Supporting Information

Synthesis of Pyrazoles from Sulfonyl hydrazone and benzyl acrylate under transition-metal-free conditions

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1. General Experiment Information

All reagents were obtained from commercial sources and used as received without further purification unless otherwise stated. NMR spectra were recorded on a BrukerAvanceII 400 spectrometer and BrukerAvanceII 600 spectrometer in CDCl$_3$ with tetramethylsilane (TMS) as an internal standard; chemical shifts $\delta$ were given in ppm and coupling constants $J$ in Hz. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer.

2. General Procedures

2.1 General procedure for Synthesis of various sulfonylhydrazone.

A mixture of hydrazine (6.0 mmol), aldehyde (5.0 mmol) and anhydrous MgSO$_4$ (1.25 g) in CH$_2$Cl$_2$ (25 mL) was stirred 1 h at room temperature. After filtration of MgSO$_4$, CH$_2$Cl$_2$ was removed under reduced pressure. The hydrazone, which was usually obtained in nearly quantitative yield, was used directly for the next step without further purification.

2.2 General procedure for Synthesis of pyrazole derivatives

A mixture of substrates $p$-Toluenesulfonyl Hydrazone 1a (0.2 mmol), Benzyl acrylate 2a (0.44 mmol), DBU (2.0 equiv) in Toluene (2 mL) was charged in a round-bottom flask and stirred at 100 °C (oil bath) for 12 h. Upon completion of the reaction, water (20 mL) and DCM (10 mL) were added to the mixture, then the aqueous layer was extracted with DCM (100 mL × 3). The combined organic layer was dried over anhydrous Na$_2$SO$_4$. Finally, the solution was concentrated in vacuo to provide a crude product, which was further purified via a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 20:1 to 15:1) to supply the desired products 3a as a yellow oil.

2.3 Single crystal structure of 2b
Empirical Formula: \( C_{33}H_{28}N_{2}O_{4} \)

Formal weight: 516.57

Temperature: 200(2) K

Wavelength: 1.54178 Å

Crystal system: Monoclinic

Space group: P2\(_1\)/n

Unit cell dimensions:
- \( a = 20.6627(8) \) Å, \( \alpha = 90^\circ \)
- \( b = 5.9304(2) \) Å, \( \beta = 114.2360(10)^\circ \)
- \( c = 23.2569(9) \) Å, \( \gamma = 90^\circ \)

Volume: 2598.68(17) Å\(^3\)

Z: 4

Density (calculated): 1.320 Mg/m\(^3\)

Absorption coefficient: 0.700 mm\(^{-1}\)

\( F(000) \): 1088

Crystal size: 0.15 x 0.09 x 0.01 mm\(^3\)

Theta range for data collection: 2.414 to 68.275°

Index ranges:
- \(-24 \leq h \leq 24\)
- \(-7 \leq k \leq 5\)
- \(-28 \leq l \leq 27\)

Reflections collected: 30322

Independent reflections: 4701 [R(int) = 0.0508]

Completeness to theta = 67.679°: 99.2%

Refinement method: Full-matrix least-squares on F\(^2\)

Data / restraints / parameters: 4701 / 216 / 396

Goodness-of-fit on F\(^2\): 1.098

Final R indices [I>2sigma(I)]: R1 = 0.0370, wR2 = 0.0944

R indices (all data): R1 = 0.0463, wR2 = 0.0968

X-ray Single crystal structure of \( \text{3l} \)
Extinction coefficient 0.0220(6)
Largest diff. peak and hole 0.180 and -0.174 e Å⁻³

3. Characterization of Materials

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (3a):** Compound 3a was isolated as a yellow oil (66.1mg, 75%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.3\) Hz, 2H), 7.51 – 7.43 (m, 4H), 7.42 (d, \(J = 7.6\) Hz, 3H), 7.40 – 7.31 (m, 6H), 7.18 (s, 1H), 5.38 (s, 2H), 5.17 (s, 2H), 4.97 (t, \(J = 7.1\) Hz, 2H), 3.06 (t, \(J = 7.1\) Hz, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 170.81, 159.59, 150.35, 135.80, 135.49, 133.32, 132.51, 128.85, 128.80, 128.67, 128.48, 128.36, 128.22, 125.68, 108.52, 66.95, 66.69, 47.42, 34.93. HRMS (EI): \(m/z\) [M]+ calcd. for C\(_{27}\)H\(_{24}\)N\(_2\)O\(_4\): 440.1736. Found: 440.1739.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(p-tolyl)-1H-pyrazole-5-carboxylate (3b):** Compound 3b was isolated as a yellow oil (66.4mg, 73%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 8.1\) Hz, 2H), 7.39 – 7.27 (m, 5H), 7.26 – 7.21 (m, 5H), 7.11 (d, \(J = 7.9\) Hz, 2H), 7.03 (s, 1H), 5.25 (s, 2H), 5.04 (s, 2H), 4.85 (t, \(J = 7.2\) Hz, 2H), 2.94 (t, \(J = 7.2\) Hz, 2H), 2.29 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 170.83, 159.59, 150.35, 135.80, 135.49, 133.82, 135.51, 133.21, 129.71, 129.50, 128.84, 128.66, 128.48, 128.37, 125.59, 108.30, 66.92, 66.68, 47.37, 34.97, 21.41. HRMS (El): \(m/z\) [M]+ calcd. for C\(_{28}\)H\(_{26}\)N\(_2\)O\(_4\): 454.1893. Found: 454.1896.
**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(tert-butyl)phenyl)1H-pyrazole-5-carboxylate (3c):**

Compound 3c was isolated as a white solid (67.5mg, 68%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 93.5–94.2 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.4\) Hz, 2H), 7.49 (d, \(J = 7.4\) Hz, 2H), 7.47 – 7.40 (m, 5H), 7.39 – 7.32 (m, 5H), 7.17 (s, 1H), 5.38 (s, 2H), 5.17 (s, 2H), 4.97 (t, \(J = 7.2\) Hz, 2H), 3.06 (t, \(J = 7.2\) Hz, 2H), 1.39 (s, 9H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 170.83, 159.63, 151.28, 150.36, 135.82, 135.51, 133.19, 129.72, 128.83, 128.65, 128.47, 128.36, 128.33, 125.70, 125.42, 108.33, 66.90, 66.65, 47.36, 34.94, 34.75, 31.42. HRMS (EI): \(m/z\) [M]\(^+\) calcd. for C\(_{31}\)H\(_{32}\)N\(_2\)O\(_4\): 496.2362. Found: 496.2363.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-methoxyphenyl)1H-pyrazole-5-carboxylate (3d):**

Compound 3d was isolated as a yellow oil (62.1mg, 66%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 – 7.60 (m, 2H), 7.46 – 7.33 (m, 5H), 7.34 – 7.27 (m, 5H), 7.06 (s, 1H), 7.00 – 6.86 (m, 2H), 5.33 (s, 2H), 5.12 (s, 2H), 4.91 (t, \(J = 7.2\) Hz, 2H), 3.83 (s, 3H), 3.00 (t, \(J = 7.2\) Hz, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 170.85, 159.75, 159.64, 150.23, 135.83, 135.53, 133.21, 128.84, 128.67, 128.47, 128.37, 126.97, 125.34, 114.20, 107.97, 66.91, 66.67, 55.45, 47.32, 34.98. HRMS (EI): \(m/z\) [M]\(^+\) calcd. for C\(_{28}\)H\(_{26}\)N\(_2\)O\(_5\): 470.1842. Found: 470.1840.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-fluorophenyl)-1H-pyrazole-5-carboxylate (3e): Compound 3e was isolated as a yellow oil (58.7mg, 64%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (dd, $J =$ 8.7, 5.4 Hz, 2H), 7.41 (dt, $J =$ 15.9, 8.0 Hz, 5H), 7.36 – 7.27 (m, 5H), 7.11 – 7.03 (m, 3H), 5.33 (s, 2H), 5.12 (s, 2H), 4.92 (t, $J =$ 7.1 Hz, 2H), 3.01 (t, $J =$ 7.1 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.81, 163.67 (d, $J =$ 224.5 Hz), 162.04 (d, $J =$ 224.5 Hz), 159.52, 149.45, 135.76, 135.42 (d, $J =$ 51 Hz), 133.43 (d, $J =$ 51 Hz), 128.85, 128.71, 128.67, 128.49, 128.40, 128.36, 127.41 (d, $J =$ 9 Hz), 127.35 (d, $J =$ 9 Hz), 115.81 (d, $J =$ 22.5 Hz), 115.66 (d, $J =$ 22.5 Hz), 108.27, 67.00, 66.70, 47.40, 34.89. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{27}$H$_{23}$FN$_2$O$_4$: 458.1642. Found: 458.1645.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chlorophenyl)-1H-pyrazole-5-carboxylate (3f): Compound 3f was isolated as a yellow oil (61.7mg, 65%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 63.0 – 63.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, $J =$ 8.5 Hz, 2H), 7.52 – 7.40 (m, 6H), 7.40 – 7.33 (m, 6H), 7.16 (s, 1H), 5.39 (s, 2H), 5.17 (s, 2H), 4.98 (t, $J =$ 7.1 Hz, 2H), 3.07 (t, $J =$ 7.1 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.71, 159.39, 149.14, 135.71, 135.35, 133.91, 133.44, 130.98, 128.92, 128.81, 128.67, 128.62, 128.46, 128.35, 128.30, 126.86, 108.39, 66.98, 66.65, 47.41, 34.79. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{27}$H$_{23}$ClN$_2$O$_4$: 474.1346. Found: 474.1347.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-bromophenyl)-1H-pyrazole-5-carboxylate (3g):

Compound 3g was isolated as a white solid (72.7mg, 70%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 73.0–73.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.46 – 7.34 (m, 5H), 7.35 – 7.27 (m, 5H), 7.10 (s, 1H), 5.33 (s, 2H), 5.11 (s, 2H), 4.91 (t, $J = 7.1$ Hz, 2H), 3.00 (t, $J = 7.1$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.78, 159.47, 149.25, 135.75, 135.39, 133.53, 131.94, 131.49, 128.87, 128.74, 128.74, 128.68, 128.53, 128.43, 128.38, 127.22, 122.18, 108.46, 67.06, 66.73, 47.49, 34.87. HRMS (El): $m/z$ [M]$^+$ calcd. for C$_{27}$H$_{23}$BrN$_2$O$_4$: 518.0841. Found: 518.0843.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3h):

Compound 3h was isolated as a white solid (71.2mg, 70%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 80.9–81.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.57 – 7.43 (m, 5H), 7.43–7.35 (m, 5H), 7.27 (s, 1H), 5.44 (s, 2H), 5.21 (s, 2H), 5.03 (t, $J = 7.0$ Hz, 2H), 3.12 (t, $J = 7.0$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.72, 159.39, 148.83, 135.90, 135.74, 135.35, 133.71, 130.33 (q, $J = 33$ Hz), 130.11 (q, $J = 33$ Hz), 129.90 (q, $J = 33$ Hz), 129.68 (q, $J = 33$ Hz), 128.88, 128.77, 128.67, 128.56, 128.42, 128.38, 127.01 (q, $J = 270$ Hz), 125.79, 125.21 (q, $J = 270$ Hz), 125.41 (q, $J = 270$ Hz), 121.61 (q, $J = 270$ Hz), 108.91, 67.13, 66.73, 47.59, 34.81. HRMS (El): $m/z$ [M]$^+$ calcd. for C$_{28}$H$_{23}$F$_3$N$_2$O$_4$: 508.1610. Found: 508.1614.
Benzyl 1-(3-(benzylxylo)-3-oxopropyl)-3-(4-cyanophenyl)-1H-pyrazole-5-carboxylate (3i):

Compound 3i was isolated as a white solid (37.2mg, 40%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 112.5−113.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J =$ 8.2 Hz, 2H), 7.70 (d, $J =$ 8.2 Hz, 2H), 7.53 − 7.38 (m, 5H), 7.40 − 7.31 (m, 5H), 7.23 (s, 1H), 5.39 (s, 2H), 5.16 (s, 2H), 4.98 (t, $J =$ 7.0 Hz, 2H), 3.07 (t, $J =$ 7.0 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.67, 159.28, 148.29, 136.82, 135.71, 135.26, 133.93, 132.68, 128.89, 128.81, 128.68, 128.57, 128.45, 128.36, 126.03, 111.49, 109.13, 67.21, 66.76, 47.68, 34.73. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{28}$H$_{23}$N$_3$O$_4$: 465.1689. Found: 465.1686.

Benzyl 1-(3-(benzylxylo)-3-oxopropyl)-3-(3-nitrophenyl)-1H-pyrazole-5-carboxylate (3j):

Compound 3j was isolated as a yellow solid (58.3mg, 60%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 143.1−143.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J =$ 8.8 Hz, 2H), 7.94 (d, $J =$ 8.8 Hz, 2H), 7.53 − 7.39 (m, 5H), 7.39 − 7.32 (m, 5H), 7.27 (s, 1H), 5.40 (s, 2H), 5.17 (s, 2H), 5.00 (t, $J =$ 7.0 Hz, 2H), 3.08 (t, $J =$ 7.0 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.61, 159.19, 147.87, 147.39, 138.64, 135.67, 135.21, 134.01, 128.86, 128.79, 128.65, 128.55, 128.42, 128.34, 126.05, 124.20, 109.38, 67.21, 66.72, 47.70, 34.66. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{27}$H$_{23}$N$_3$O$_6$: 485.1587. Found: 485.1591.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-isopropylphenyl)-1H-pyrazole-5-carboxylate (3k):

Compound 3k was isolated as a yellow oil (66.6mg, 69%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.52 – 7.38 (m, 5H), 7.39 – 7.32 (m, 5H), 7.29 (d, $J = 7.3$ Hz, 2H), 7.15 (s, 1H), 5.38 (s, 2H), 5.16 (s, 2H), 4.97 (t, $J = 7.2$ Hz, 2H), 3.05 (t, $J = 7.2$ Hz, 2H), 2.97 (dt, $J = 13.8$, 6.9 Hz, 1H), 1.31 (d, $J = 6.9$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.84, 159.64, 150.46, 149.06, 135.81, 135.52, 133.19, 130.11, 128.84, 128.65, 128.48, 128.36, 126.86, 125.69, 108.32, 66.91, 66.67, 47.36, 34.96, 34.05, 24.06. HRMS (EI): $m/z$ [M$^+$] calcd. for C$_{30}$H$_{30}$N$_2$O$_4$: 482.2206. Found: 482.2205.

Benzyl 3-(1,1'-biphenyl)-4-yl)-1-(3-(benzyloxy)-3-oxopropyl)-1H-pyrazole-5-carboxylate (3l):

Compound 3l was isolated as a white solid (62.0mg, 60%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 129.9–130.5 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 8.3$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 4H), 7.54 – 7.45 (m, 6H), 7.43 (dd, $J = 11.2$, 4.8 Hz, 2H), 7.40 – 7.33 (m, 5H), 7.24 (s, 1H), 5.41 (s, 2H), 5.19 (s, 2H), 5.01 (t, $J = 7.1$ Hz, 2H), 3.10 (t, $J = 7.1$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.79, 159.55, 149.97, 140.92, 140.77, 135.78, 135.46, 133.35, 131.47, 128.91, 128.83, 128.66, 128.65, 128.48, 128.35, 127.47, 127.09, 126.05, 108.53, 66.95, 66.67, 47.43, 34.91. HRMS (EI): $m/z$ [M$^+$] calcd. for C$_{33}$H$_{28}$N$_2$O$_4$: 516.2049. Found: 516.2053.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(o-tolyl)-1H-pyrazole-5-carboxylate (3m): Compound 3m was isolated as a yellow oil (38.2mg, 42%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 6.6$ Hz, 1H), 7.43 (ddd, $J = 10.0$, 6.9 Hz, 5H), 7.33 (d, $J = 12.1$ Hz, 5H), 7.25 (dt, $J = 8.9$, 4.0 Hz, 3H), 7.04 (s, 1H), 5.37 (s, 2H), 5.15 (s, 2H), 4.97 (t, $J = 7.1$ Hz, 2H), 3.05 (t, $J = 7.1$ Hz, 2H), 2.48 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.83, 159.72, 150.79, 136.19, 135.80, 135.54, 132.54, 132.19, 131.03, 129.25, 128.84, 128.66, 128.47, 128.37, 128.16, 126.00, 111.52, 66.90, 66.69, 47.29, 34.88, 21.35. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{28}$H$_{26}$N$_2$O$_4$: 454.1893. Found: 454.1896.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-methoxyphenyl)-1H-pyrazole-5-carboxylate (3n): Compound 3n was isolated as a yellow oil (35.8mg, 38%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 7.3$ Hz, 2H), 7.46 – 7.38 (m, 4H), 7.38 – 7.31 (m, 6H), 7.02 (dd, $J = 15.4$, 7.9 Hz, 2H), 5.39 (s, 2H), 5.16 (s, 2H), 4.98 (t, $J = 7.2$ Hz, 2H), 3.94 (s, 3H), 3.05 (t, $J = 7.2$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.85, 159.86, 156.87, 147.18, 135.84, 135.69, 129.39, 128.80, 128.70, 128.67, 128.57, 128.44, 128.37, 121.26, 120.96, 112.75, 111.34, 66.80, 66.67, 55.64, 47.41, 35.01. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{28}$H$_{26}$N$_2$O$_5$: 470.1842. Found: 470.1844.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-chlorophenyl)-1H-pyrazole-5-carboxylate (3o):

Compound 3o was isolated as a yellow oil (47.5mg, 50%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.69 (m, 1H), 7.46 – 7.37 (m, 4H), 7.31 (dd, J = 7.1, 3.1 Hz, 2H), 5.38 (s, 2H), 5.16 (s, 2H), 5.00 (t, J = 7.1 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 170.76, 159.63, 147.89, 135.78, 135.50, 132.64, 132.30, 131.39, 130.56, 130.46, 129.29, 128.83, 128.67, 128.65, 128.47, 128.39, 128.37, 127.03, 112.57, 66.96, 66.71, 47.47, 34.90. HRMS (EI): m/z [M]+ calcd. for C₂₇H₂₃ClN₂O₄: 474.1346. Found: 474.1342.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-fluorophenyl)-1H-pyrazole-5-carboxylate (3p):

Compound 3p was isolated as a yellow solid (53.2mg, 58%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 61.8 – 62.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (td, J = 7.7, 1.2 Hz, 1H), 7.53 – 7.38 (m, 5H), 7.39 – 7.29 (m, 7H), 7.18 (dt, J = 10.9, 8.0 Hz, 2H), 5.39 (s, 2H), 5.16 (s, 2H), 5.00 (t, J = 7.1 Hz, 2H), 3.07 (t, J = 7.1 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 170.77, 160.98 (d, J = 249 Hz), 159.62, 159.32 (d, J = 249 Hz), 144.89, 135.77, 135.48, 133.11, 129.59 (d, J = 7.5 Hz), 129.54 (d, J = 7.5 Hz), 128.82, 128.65, 128.45, 128.35, 124.43 (d, J = 3 Hz), 124.41 (d, J = 3 Hz), 120.42 (d, J = 12 Hz), 120.34 (d, J = 12 Hz), 116.25 (d, J = 22.5 Hz), 116.10 (d, J = 22.5 Hz), 112.06 (d, J = 9 Hz), 112.00 (d, J = 9 Hz), 66.93, 66.70, 47.49, 34.88. HRMS (EI): m/z [M]+ calcd. for C₂₇H₂₃FN₂O₄: 458.1642. Found: 458.1647.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(m-tolyl)-1H-pyrazole-5-carboxylate (3q): Compound 3q was isolated as a white solid (61.8mg, 68%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 67.2–68.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 – 7.39 (m, 5H), 7.35 (d, J = 8.0 Hz, 5H), 7.31 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 15.4 Hz, 2H), 5.38 (s, 2H), 5.17 (s, 2H), 4.98 (t, J = 7.0 Hz, 2H), 4.07 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.79, 159.59, 150.49, 138.42, 135.78, 135.48, 133.23, 132.37, 129.00, 128.82, 128.70, 128.65, 128.47, 128.34, 126.31, 122.84, 108.55, 66.92, 66.66, 47.39, 34.96, 21.56. HRMS (EI): m/z [M]+ calcld. for C₂₈H₂₆N₂O₄: 454.1893. Found: 454.1896.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-methoxyphenyl)-1H-pyrazole-5-carboxylate (3r): Compound 3r was isolated as a yellow oil (61.2mg, 65%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dt, J = 9.7, 4.8 Hz, 4H), 7.41 – 7.31 (m, 8H), 7.30 (s, 1H), 7.17 (s, 1H), 6.96 – 6.83 (m, 1H), 5.38 (s, 2H), 5.16 (s, 2H), 4.97 (t, J = 7.2 Hz, 2H), 3.88 (s, 3H), 3.06 (t, J = 7.2 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 170.79, 160.09, 159.54, 150.19, 135.79, 135.45, 133.72, 133.39, 129.87, 128.86, 128.71, 128.68, 128.51, 128.39, 128.37, 118.27, 114.36, 110.84, 108.68, 67.01, 66.72, 55.48, 47.43, 34.97. HRMS (EI): m/z [M]+ calcld. for C₂₈H₂₆N₂O₅: 470.1842. Found: 470.1845.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-fluorophenyl)-1H-pyrazole-5-carboxylate (3s):

Compound 3s was isolated as a white solid (59.6mg, 65%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 88.4–89.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.8$ Hz, 1H), 7.53 (dd, $J = 9.8$, 1.9 Hz, 1H), 7.51 – 7.37 (m, 6H), 7.38 – 7.33 (m, 5H), 7.17 (s, 1H), 7.05 (td, $J = 8.4$, 2.1 Hz, 1H), 5.39 (s, 2H), 5.18 (s, 2H), 4.98 (t, $J = 7.1$ Hz, 2H), 3.07 (t, $J = 7.1$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.73, 164.07 (d, $J = 243$ Hz), 162.45 (d, $J = 243$ Hz), 159.42, 149.14, 135.73, 135.38, 134.74 (d, $J = 9$ Hz), 134.68 (d, $J = 9$ Hz), 133.50, 130.34 (d, $J = 9$ Hz), 130.28 (d, $J = 9$ Hz), 128.84, 128.70, 128.48, 128.37, 128.35, 121.27 (d, $J = 1.5$ Hz), 121.26 (d, $J = 1.5$ Hz), 115.04 (d, $J = 21$ Hz), 114.90 (d, $J = 21$ Hz), 112.61 (d, $J = 22.5$ Hz), 112.46 (d, $J = 22.5$ Hz), 108.65, 67.01, 66.70, 47.47, 34.80. HRMS (EI): m/z [M]$^+$ calcd. for C$_{27}$H$_{23}$FN$_2$O$_4$: 458.1642. Found: 458.1644.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-chlorophenyl)-1H-pyrazole-5-carboxylate (3t):

Compound 3t was isolated as a yellow oil (59.8mg, 63%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (s, 1H), 7.62 (dd, $J = 8.2$, 6.4 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.36 – 7.22 (m, 7H), 7.12 (s, 1H), 5.33 (s, 2H), 5.12 (s, 2H), 4.92 (t, $J = 7.1$ Hz, 2H), 3.01 (t, $J = 7.1$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.76, 159.43, 148.97, 135.73, 135.37, 134.82, 134.29, 133.54, 130.08, 128.87, 128.73, 128.68, 128.52, 128.41, 128.38, 128.18, 125.75, 123.74, 108.66, 67.06, 66.75, 47.50, 34.84. HRMS (EI): m/z [M]$^+$ calcd. for C$_{27}$H$_{23}$ClN$_2$O$_4$: 460.1261. Found: 460.1259.
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-cyanophenyl)-1H-pyrazole-5-carboxylate (3u):

Compound 3u was isolated as a white solid (49.3mg, 53%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 123.5−124.2 °C. 1H NMR (400 MHz, CDCl3) δ 8.08 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.56 – 7.38 (m, 6H), 7.33 (d, J = 17.6 Hz, 5H), 7.20 (s, 1H), 5.39 (s, 2H), 5.17 (s, 2H), 4.98 (t, J = 6.9 Hz, 2H), 3.07 (t, J = 6.9 Hz, 2H). 13C NMR (150 MHz, CDCl3) δ 170.63, 159.26, 148.02, 135.68, 135.26, 133.80, 131.43, 129.70, 129.61, 129.10, 128.86, 128.77, 128.65, 128.53, 128.41, 128.35, 118.76, 113.02, 108.61, 67.15, 66.73, 47.58, 34.73. HRMS (EI): m/z [M]+ calcd. for C28H23N3O4: 465.1689. Found: 465.1692.

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3v):

Compound 3v was isolated as a white solid (66.1mg, 65%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 76.9−77.5 °C. 1H NMR (400 MHz, CDCl3) δ 8.08 (s, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.53 – 7.41 (m, 5H), 7.39 – 7.33 (m, 5H), 7.23 (s, 1H), 5.40 (s, 2H), 5.18 (s, 2H), 5.00 (t, J = 7.1 Hz, 2H), 3.09 (t, J = 7.1 Hz, 2H). 13C NMR (150 MHz, CDCl3) δ 170.71, 159.39, 148.86, 135.72, 135.34, 133.68, 133.33, 131.53 (q, J = 33 Hz), 131.32 (q, J = 33 Hz), 131.10 (q, J = 33 Hz), 130.89 (q, J = 33 Hz), 129.27, 128.86, 128.78, 128.74, 128.64, 128.54, 128.39, 128.35, 126.93 (q, J = 270 Hz), 125.12 (q, J = 270 Hz), 124.76 (q, J = 4.5 Hz), 124.74 (q, J = 4.5 Hz), 124.71 (q, J = 4.5 Hz), 124.68 (q, J = 4.5 Hz), 123.32 (q, J = 270 Hz).
Hz), 122.44 (q, \( J = 3 \) Hz), 122.42 (q, \( J = 3 \) Hz), 122.40 (q, \( J = 3 \) Hz), 122.37 (q, \( J = 3 \) Hz), 121.51 (q, \( J = 270 \) Hz), 108.62, 67.09, 66.72, 47.52, 34.83; HRMS (EI): \( m/z \) [M]\(^+\) calcd. for \( C_{28}H_{23}F_3N_2O_4 \): 508.1610. Found: 508.1607.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-nitrophenyl)-1\( H \)-pyrazole-5-carboxylate (3w):**

Compound 3w was isolated as a yellow solid (61.2mg, 63%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 100.1–100.6 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.63 (s, 1H), 8.19 (dd, \( J = 8.2, 1.3 \) Hz, 1H), 8.12 (d, \( J = 7.8 \) Hz, 1H), 7.58 (t, \( J = 8.0 \) Hz, 1H), 7.52 – 7.38 (m, 5H), 7.39 – 7.31 (m, 5H), 7.25 (s, 1H), 5.39 (s, 2H), 5.17 (s, 2H), 4.99 (t, \( J = 7.0 \) Hz, 2H), 3.08 (t, \( J = 7.0 \) Hz, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 170.68, 159.28, 148.78, 147.93, 135.71, 135.26, 134.30, 133.94, 131.32, 129.77, 128.89, 128.79, 128.66, 128.56, 128.41, 128.38, 122.74, 120.46, 108.79, 67.19, 66.76, 47.61, 34.75. HRMS (EI): \( m/z \) [M]\(^+\) calcd. for \( C_{27}H_{22}N_3O_6 \): 485.1587. Found: 485.1581.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chloro-3-fluorophenyl)-1\( H \)-pyrazole-5-carboxylate (3x):**

Compound 3x was isolated as a white solid (67.0mg, 68%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 45.6–46.2 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.85 (dd, \( J = 7.0, 1.8 \) Hz, 1H), 7.64 (ddd, \( J = 8.4, 4.4, 1.9 \) Hz, 1H), 7.52 – 7.39 (m, 5H), 7.39 – 7.30 (m, 5H), 7.18 (t, \( J = 8.7 \) Hz, 1H), 7.12 (s, 1H), 5.38 (s, 2H), 5.17 (s, 2H), 4.96 (t, \( J = 7.1 \) Hz, 2H), 3.05 (t, \( J = 7.1 \) Hz, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 170.71, 159.36, 158.84 (d, \( J = 247.5 \) Hz), 157.19 (d, \( J = 247.5 \) Hz), 148.22, 135.72 (d, \( J = 58.5 \) Hz), 135.33 (d, \( J = 58.5 \) Hz), 133.65, 129.88 (d, \( J = 4.5 \) Hz),
129.85 (d, J = 4.5 Hz), 128.86, 128.75, 128.66, 128.53, 128.41, 128.36, 127.83, 125.37 (d, J = 6 Hz),
125.33 (d, J = 6 Hz), 121.55 (d, J = 18 Hz), 121.43 (d, J = 18 Hz), 116.98 (d, J = 22.5 Hz), 116.83 (d, J = 22.5 Hz), 108.37, 67.08, 66.73, 47.48, 34.81. HRMS (EI): m/z [M]+ calcd. for C_{27}H_{22}ClF_{2}N_{2}O_{4}: 492.1252. Found: 492.1249.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(naphthalen-2-yl)-1H-pyrazole-5-carboxylate (3y):**

Compound 3y was isolated as a yellow oil (54.0mg, 55%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). ^1H NMR (400 MHz, CDCl₃) δ 8.48 (dd, J = 6.1, 3.4 Hz, 1H), 7.93 (dd, J = 11.1, 5.6 Hz, 2H), 7.68 (d, J = 7.1 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.50 (d, J = 6.9 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.39 – 7.31 (m, 5H), 7.22 (s, 1H), 5.42 (s, 2H), 5.18 (s, 2H), 5.08 (t, J = 7.1 Hz, 2H), 3.13 (t, J = 7.1 Hz, 2H). ^13C NMR (150 MHz, CDCl₃) δ 170.80, 159.67, 150.34, 135.76, 135.48, 134.05, 132.81, 131.27, 130.41, 128.88, 128.84, 128.67, 128.65, 128.48, 128.38, 128.36, 127.31, 126.64, 126.01, 125.40, 112.33, 66.99, 66.72, 47.45, 35.02. HRMS (EI): m/z [M]+ calcd. for C_{31}H_{26}N_{2}O_{4}: 490.1893. Found: 490.1895.

**Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(thiophen-2-yl)-1H-pyrazole-5-carboxylate (3z):**

Compound 3z was isolated as a yellow solid (52.7mg, 59%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 87.6 – 88.2 °C. ^1H NMR (400 MHz, CDCl₃) δ 7.45 (dt, J = 16.2, 8.2 Hz, 5H), 7.38 (d, J = 9.8 Hz, 5H), 7.35 – 7.33 (m, 1H), 7.29 (d, J = 4.3 Hz, 1H), 7.08 (dd, J = 6.1, 4.9 Hz, 2H), 5.37 (s, 2H), 5.17 (s, 2H), 4.95 (t, J = 7.2 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H). ^13C
NMR (150 MHz, CDCl$_3$) $\delta$ 170.69, 159.38, 145.80, 135.77, 135.37, 133.28, 128.84, 128.69, 128.65, 128.48, 128.36, 127.62, 125.10, 124.23, 108.30, 67.01, 66.70, 47.31, 34.92. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{25}$H$_{22}$N$_2$O$_4$S: 446.1300. Found: 446.1304.

Methyl 1-(3-methoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4a): Compound 4a was isolated as a yellow oil (44.4mg, 77%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$ = 7.4 Hz, 2H), 7.40 (t, $J$ = 7.5 Hz, 2H), 7.32 (t, $J$ = 7.3 Hz, 1H), 7.12 (s, 1H), 4.90 (t, $J$ = 7.3 Hz, 2H), 3.91 (s, 3H), 3.69 (s, 3H), 2.96 (t, $J$ = 7.3 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.37, 160.22, 150.32, 133.29, 132.52, 128.80, 128.21, 125.63, 108.28, 52.17, 51.96, 47.37, 34.77. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{25}$H$_{16}$N$_2$O$_4$: 288.1110. Found: 288.1107.

Ethyl 1-(3-ethoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4b): Compound 4b was isolated as a yellow oil (44.3mg, 70%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J$ = 7.3 Hz, 2H), 7.40 (t, $J$ = 7.5 Hz, 2H), 7.31 (t, $J$ = 7.3 Hz, 1H), 7.13 (s, 1H), 4.90 (t, $J$ = 7.3 Hz, 2H), 4.38 (q, $J$ = 7.1 Hz, 2H), 4.15 (q, $J$ = 7.1 Hz, 2H), 2.95 (t, $J$ = 7.3 Hz, 2H), 1.41 (t, $J$ = 7.1 Hz, 3H), 1.24 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.96, 159.79, 150.22, 133.65, 132.59, 128.79, 128.17, 125.64, 108.23, 61.30, 60.84, 47.46, 35.06, 14.36. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{17}$H$_{20}$N$_2$O$_4$: 316.1423. Found: 316.1425.
Butyl 1-(3-butoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4c): Compound 4c was isolated as a yellow oil (54.4mg, 73%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.11 (s, 1H), 4.90 (t, J = 7.3 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 4.09 (t, J = 6.7 Hz, 2H), 2.96 (t, J = 7.3 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.39 – 1.28 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 171.03, 159.87, 150.23, 133.63, 132.61, 128.77, 128.15, 125.65, 108.19, 65.14, 47.48, 35.03, 30.76, 19.19, 13.83. HRMS (EI): m/z [M]+ calcd. for C₂₁H₂₈N₂O₄: 372.2049. Found: 372.2046.

Allyl 1-(3-(allyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4d): Compound 4d was isolated as a yellow oil (34.0mg, 50%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.15 (s, 1H), 6.09 – 5.98 (m, 1H), 5.95 – 5.84 (m, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.31 (t, J = 13.5 Hz, 2H), 5.21 (d, J = 10.4 Hz, 1H), 4.92 (t, J = 7.2 Hz, 2H), 4.82 (d, J = 5.7 Hz, 2H), 4.60 (d, J = 5.8 Hz, 2H), 3.00 (t, J = 7.2 Hz, 2H). ¹³C NMR (150 MHz, DMSO) δ 170.22, 158.69, 149.12, 133.19, 132.46, 132.14, 131.98, 128.73, 128.10, 125.21, 118.39, 117.78, 108.05, 65.26, 64.64, 46.94, 34.04. HRMS (EI): m/z [M]+ calcd. for C₁₉H₂₀N₂O₄: 340.1423. Found: 340.1425.
Cyclohexyl 1-(3-(cyclohexyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4e): Compound 4e was isolated as a white solid (58.6mg, 69%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 65.9–66.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 7.2 Hz, 2H), 7.39 (t, $J$ = 7.5 Hz, 2H), 7.31 (t, $J$ = 7.3 Hz, 1H), 7.12 (s, 1H), 5.06 – 4.97 (m, 1H), 4.89 (t, $J$ = 7.3 Hz, 2H), 4.83 – 4.73 (m, 1H), 2.94 (t, $J$ = 7.3 Hz, 2H), 2.00 – 1.28 (m, 20H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.39, 159.24, 150.15, 134.09, 132.67, 128.76, 128.12, 125.68, 108.24, 73.87, 73.14, 47.65, 35.44, 31.66, 25.47, 23.80. HRMS (EI): m/z [M]+ calcld. for C$_{25}$H$_{32}$N$_2$O$_4$: 424.2365. Found: 424.2365.

Tert-butyl 1-(3-(tert-butoxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4f): Compound 4f was isolated as a white solid (55.9mg, 75%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1), m.p. 57.6–58.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 7.2 Hz, 2H), 7.39 (t, $J$ = 7.5 Hz, 2H), 7.30 (t, $J$ = 7.3 Hz, 1H), 7.04 (s, 1H), 4.82 (t, $J$ = 7.4 Hz, 2H), 2.87 (t, $J$ = 7.4 Hz, 2H), 1.61 (s, 9H), 1.43 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.21, 158.99, 149.87, 134.96, 132.79, 128.75, 128.04, 125.66, 108.19, 82.53, 81.00, 47.73, 36.27, 28.36. HRMS (EI): m/z [M]+ calcld. for C$_{21}$H$_{32}$N$_2$O$_4$: 372.2049. Found: 372.2047.
Benzyl (E)-3-(2-benzylidene-1-tosylhydrazinyl)propanoate (5): Compound 5 was isolated as a yellow oil (52.4 mg, 60%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 15:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.65 (d, $J = 6.8$ Hz, 2H), 7.45 – 7.29 (m, 10H), 5.12 (s, 2H), 3.85 (t, $J = 7.2$ Hz, 2H), 2.67 (t, $J = 7.2$ Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.95, 155.15, 144.38, 135.62, 133.71, 133.63, 131.08, 129.69, 128.84, 128.68, 128.48, 128.46, 128.44, 128.11, 66.77, 45.46, 33.19, 21.69. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{24}$H$_{24}$N$_2$O$_4$S: 436.1457. Found: 436.1460.

The mixture of compound 6 and 7: Compound 6 and 7 was isolated as a white solid (32.8mg, 45%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 13:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 7.4$ Hz, 3H), 7.48 (d, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.2$ Hz, 4H), 7.39–7.31 (m, 6.55H), 7.19 (s, 0.43H), 7.15 (s, 1H), 5.39 (s, 0.89H), 5.17 (s, 2H), 4.95 (q, $J = 7.3$ Hz, 3H), 3.93 (s, 3H), 3.72 (s, 1.38H), 3.06 (t, $J = 7.1$ Hz, 2H), 2.99 (t, $J = 7.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.28, 170.74, 160.13, 159.49, 150.27, 150.23, 135.68, 135.37, 133.22, 133.20, 132.44, 132.40, 128.74, 128.72, 128.58, 128.55, 128.39, 128.26, 128.12, 125.56, 108.40, 108.23, 66.86, 66.60, 52.07, 51.87, 47.33, 47.26, 34.83, 34.69. HRMS (EI): $m/z$ [M]$^+$ calcd. for C$_{21}$H$_{20}$N$_2$O$_4$: 364.1423. Found: 364.1426.
4. Copies of NMR Spectra

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (3a): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (3a): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(p-tolyl)-1H-pyrazole-5-carboxylate (3b): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(p-tolyl)-1H-pyrazole-5-carboxylate (3b): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(tert-butyl)phenyl)-1H-pyrazole-5-carboxylate (3c): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(tert-butyl)phenyl)-1H-pyrazole-5-carboxylate (3c): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-methoxyphenyl)-1H-pyrazole-5-carboxylate (3d): $^1$H NMR

$^1$C NMR (400 MHz, CDCl$_3$)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-methoxyphenyl)-1H-pyrazole-5-carboxylate (3d): $^{13}$C NMR

$^{13}$C NMR (150 MHz, CDCl$_3$)
Benzyl 1-(3-(benzyl oxy)-3-oxopropyl)-3-(4-fluorophenyl)-1H-pyrazole-5-carboxylate (3e): $^1$H NMR

Benzyl 1-(3-(benzyl oxy)-3-oxopropyl)-3-(4-fluorophenyl)-1H-pyrazole-5-carboxylate (3e): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chlorophenyl)-1H-pyrazole-5-carboxylate (3f): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chlorophenyl)-1H-pyrazole-5-carboxylate (3f): $^{13}$C NMR
Benzyl 1-(3-(benzyl oxy)-3-oxopropyl)-3-(4-bromophenyl)-1H-pyrazole-5-carboxylate (3g): $^1$H NMR

Benzyl 1-(3-(benzyl oxy)-3-oxopropyl)-3-(4-bromophenyl)-1H-pyrazole-5-carboxylate (3g): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3h): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3h): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-cyanophenyl)-1H-pyrazole-5-carboxylate (3i): $^1$H NMR

\[
\text{\includegraphics[width=\textwidth]{3i_HNMR.png}}
\]

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-cyanophenyl)-1H-pyrazole-5-carboxylate (3i): $^{13}$C NMR

\[
\text{\includegraphics[width=\textwidth]{3i_CNMR.png}}
\]
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-nitrophenyl)-1H-pyrazole-5-carboxylate (3j): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-nitrophenyl)-1H-pyrazole-5-carboxylate (3j): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-isopropylphenyl)-1H-pyrazole-5-carboxylate (3k): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-isopropylphenyl)-1H-pyrazole-5-carboxylate (3k): $^{13}$C NMR
Benzyl 3-((1,1'-biphenyl)-4-yl)-1-(3-(benzyloxy)-3-oxopropyl)-1H-pyrazole-5-carboxylate (3l): ¹H NMR

Benzyl 3-((1,1'-biphenyl)-4-yl)-1-(3-(benzyloxy)-3-oxopropyl)-1H-pyrazole-5-carboxylate (3l): ¹³C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(o-tolyl)-1H-pyrazole-5-carboxylate (3m): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(o-tolyl)-1H-pyrazole-5-carboxylate (3m): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-methoxyphenyl)-1H-pyrazole-5-carboxylate (3n): $^1$H NMR

$^1$H NMR (400 MHz, CDCl$_3$)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-methoxyphenyl)-1H-pyrazole-5-carboxylate (3n): $^{13}$C NMR

$^{13}$C NMR (150 MHz, CDCl$_3$)
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-chlorophenyl)-1H-pyrazole-5-carboxylate (3o): ¹H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-chlorophenyl)-1H-pyrazole-5-carboxylate (3o): ¹³C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-fluorophenyl)-1H-pyrazole-5-carboxylate (3p): \(^1\)H NMR

\[\text{\[1H NMR (400 MHz, CDCl}_3\\]}\]

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(2-fluorophenyl)-1H-pyrazole-5-carboxylate (3p): \(^{13}\)C NMR

\[\text{\[^{13}C NMR (150 MHz, CDCl}_3\\]}\]
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(m-tolyl)-1H-pyrazole-5-carboxylate (3q): $^1$H NMR

![H NMR (400 MHz, CDCl$_3$)](image)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(m-tolyl)-1H-pyrazole-5-carboxylate (3q): $^{13}$C NMR

![C NMR (150 MHz, CDCl$_3$)](image)
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-methoxyphenyl)-1H-pyrazole-5-carboxylate (3r): \(^1\)H NMR

\[ \text{\(3\r\)} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\))

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-methoxyphenyl)-1H-pyrazole-5-carboxylate (3r): \(^13\)C NMR

\[ \text{\(3\r\)} \]

\(^13\)C NMR (150 MHz, CDCl\(_3\))
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-fluorophenyl)-1H-pyrazole-5-carboxylate (3s): $^{1}$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-fluorophenyl)-1H-pyrazole-5-carboxylate (3s): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-chlorophenyl)-1H-pyrazole-5-carboxylate (3t): $^1$H NMR

$^1$H NMR (400 MHz, CDCl$_3$)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-chlorophenyl)-1H-pyrazole-5-carboxylate (3t): $^{13}$C NMR

$^{13}$C NMR (150 MHz, CDCl$_3$)
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-cyanophenyl)-1\textit{H}-pyrazole-5-carboxylate (3u): \textit{\textsuperscript{1}H} NMR

\[\text{\textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3})}\]

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-cyanophenyl)-1\textit{H}-pyrazole-5-carboxylate (3u): \textit{\textsuperscript{13}C} NMR

\[\text{\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3})}\]
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3v): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-5-carboxylate (3v): $^{13}$C NMR
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-nitrophenyl)-1H-pyrazole-5-carboxylate (3w): $^1$H NMR

![1H NMR spectrum of 3w](image)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-nitrophenyl)-1H-pyrazole-5-carboxylate (3w): $^{13}$C NMR

![$^{13}$C NMR spectrum of 3w](image)
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chloro-3-fluorophenyl)-1H-pyrazole-5-carboxylate (3x): \(^1\)H NMR

\[ \text{Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(4-chloro-3-fluorophenyl)-1H-pyrazole-5-carboxylate (3x): } ^{13}\text{C NMR} \]
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(naphthalen-2-yl)-1H-pyrazole-5-carboxylate (3y): $^1$H NMR

![1H NMR (400 MHz, CDCl₃)](image)

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(naphthalen-2-yl)-1H-pyrazole-5-carboxylate (3y): $^{13}$C NMR

![13C NMR (150 MHz, CDCl₃)](image)
Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(thiophen-2-yl)-1H-pyrazole-5-carboxylate (3z): $^1$H NMR

Benzyl 1-(3-(benzyloxy)-3-oxopropyl)-3-(thiophen-2-yl)-1H-pyrazole-5-carboxylate (3z): $^{13}$C NMR
Methyl 1-(3-methoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4a): $^1$H NMR

Methyl 1-(3-methoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4a): $^{13}$C NMR
Ethyl 1-(3-ethoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4b): $^1$H NMR

![1H NMR (400 MHz, CDCl₃)](image)

Ethyl 1-(3-ethoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4b): $^{13}$C NMR

![$^{13}$C NMR (150 MHz, CDCl₃)](image)
Butyl 1-(3-butoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4c): $^1$H NMR

Butyl 1-(3-butoxy-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4c): $^{13}$C NMR
Allyl 1-(3-(allyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4d): $^1$H NMR

![$^1$H NMR (400 MHz, CDCl$_3$)](image)

Allyl 1-(3-(allyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4d): $^{13}$C NMR

![$^{13}$C NMR (150 MHz, DMSO)](image)
Cyclohexyl 1-(3-(cyclohexyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4e): $^1$H NMR

Cyclohexyl 1-(3-(cyclohexyloxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4e): $^{13}$C NMR
Tert-butyl 1-(3-(tert-butoxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4f): \(^1\)H NMR

\[
\text{\includegraphics[width=0.5\textwidth]{nmr1h.png}}
\]

Tert-butyl 1-(3-(tert-butoxy)-3-oxopropyl)-3-phenyl-1H-pyrazole-5-carboxylate (4f): \(^1\)C NMR

\[
\text{\includegraphics[width=0.5\textwidth]{nmr13c.png}}
\]
Benzyl \((E)-3\)-(2-benzylidene-1-tosylhydrazinyl)propanoate (5): $^1$H NMR

\[ \text{Benzyl} \ (E) -3\)-(2-benzylidene-1-tosylhydrazinyl)propanoate (5): $^1$H NMR \]

\[ \text{Benzyl} \ (E) -3\)-(2-benzylidene-1-tosylhydrazinyl)propanoate (5): $^{13}$C NMR \]

\[ \text{Benzyl} \ (E) -3\)-(2-benzylidene-1-tosylhydrazinyl)propanoate (5): $^{13}$C NMR \]
The mixture of compound 6 and 7: $^1$H NMR

\[
\begin{align*}
\text{6} & \quad \text{O-Bn} \\
\text{N} & \quad \text{O} \\
\text{6} & \quad \text{O-Bn}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$)

The mixture of compound 6 and 7: $^{13}$C NMR

\[
\begin{align*}
\text{6} & \quad \text{O-Bn} \\
\text{N} & \quad \text{O} \\
\text{6} & \quad \text{O-Bn}
\end{align*}
\]

$^{13}$C NMR (151 MHz, CDCl$_3$)