Supporting Information

Chiral Iminophosphorane Catalyzed Asymmetric Sulfenylation of 4-Substituted Pyrazolones

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I. General Information

NMR spectra were recorded on a Bruker or Agilent 400 MHz, $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR spectra were respectively recorded at 400 MHz, 100 MHz, 376 MHz. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were equipped with an ESI source. Melting point were measured with SWG X-4. Optical rotations were reported as [α]$_D^T$ (solvent, concentration in grams/100 mL). Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns.

II. Materials

The catalysts were prepared according to the literature. All 4-substituted pyrazolones were prepared according to the literature and references therein. All substituted N-(phenylthio)-phthalimides were prepared according to the literature. All solvents were dried and/or distilled by standard methods. Unless otherwise mentioned, substrates were purchased from commercial suppliers.

III. General Procedure for the Synthesis of products

4-Substituted pyrazolones (0.1 mmol, 1.0 eq), N-(phenylthio)phthalimides (0.15 mmol, 1.5 eq) and catalyst (0.001 mmol, 1.0 mol%) were added to a Schlenk tube. Then 2 ml n-pentane was added using a syringe. The reaction was stirred at room temperature until started materials of pyrazolone derivative were disappeared in argon. After the solvent was removed in vacuo and the residue was purified by silica gel using eluent.

(R)-4-Benzyl-3-methyl-1-phenyl-4-(phenylthio) -1H-pyrazol-5(4H)-one (3a)

The crude product was purified by flash chromatography to obtain 3a (white solid, 99% yield). M. p.: 70-74 °C. [α]$_D^20$ = -197.3° (c = 0.98, DCM). Ee = 99%; HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.7 (minor) and 12.8 (major). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.46 (d, $J = 7.2$ Hz,
2H), 7.32-7.12 (m, 12H), 7.08 (t, J = 7.6 Hz, 1H), 3.56 (d, J = 14.0 Hz, 1H), 3.06 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.7, 159.0, 137.1, 135.9, 134.3, 130.3, 129.19, 129.15, 128.8, 128.6, 128.1, 127.7, 125.5, 119.7, 64.8, 38.3, 14.5. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3061, 3031, 2921, 2852, 1706, 1595, 1497, 1118, 1025, 749, 723, 689. HRMS (ESI) for C$_{23}$H$_{26}$N$_2$OS: calculated [M+H]$^+$, 373.1374. Found, 373.1360.
The crude product was purified by flash chromatography to obtain 3a’ (91% yield). \([\alpha]_{D}^{30} = 177.6^\circ\) (c=1.00, DCM). \(Ee = -99\%\); HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.1 (major) and 12.2 (minor). 1H NMR (400 MHz, CDCl3): \(\delta\) 7.46 (d, \(J = 7.2\) Hz, 2H), 7.32-7.12 (m, 12H), 7.08 (t, \(J = 7.2\) Hz, 1H), 3.56 (d, \(J = 13.6\) Hz, 1H), 3.07 (d, \(J = 13.6\) Hz, 1H), 2.26 (s, 3H); 13C NMR (100 MHz, CDCl3): \(\delta\) 171.8, 159.0, 137.2, 136.0, 134.3, 130.3, 129.22, 129.18, 128.8, 128.7, 128.2, 127.7, 125.5, 119.8, 64.8, 38.3, 14.5.
(R)-3,4-Dimethyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3b)

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\text{\begin{center}
\begin{tikzpicture}
\node[draw, rectangle, minimum width=3cm, minimum height=3cm] (myrectangle) {
\includegraphics[width=\textwidth]{image}
};
\end{tikzpicture}
\end{center}
} 
\]
The crude product was purified by flash chromatography to obtain 3b (white solid, 94% yield). M. p.: 64-68 °C. [α]_D^{28} = -546.3° (c=1.01, DCM). Ee = 98%; HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (30:1 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 16.1 (major) and 17.7 (minor). 1H NMR (400 MHz, CDCl₃): δ 7.48 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 6.8 Hz, 2H), 7.28 (t, J = 8.0 Hz, 3H), 7.19 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 2.27 (s, 3H), 1.58 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 172.7, 160.7, 137.4, 135.8, 130.3, 129.1, 128.7, 128.6, 125.3, 119.3, 59.3, 17.8, 13.5. IR ν_max (film) cm⁻¹ 3060, 2924, 2852, 1710, 1595, 1497, 1125, 1023, 750, 689. HRMS (ESI) for C₁₇H₁₆N₂O₅: calculated [M+H]^⁺, 297.1061. Found, 297.1054.
The crude product was purified by flash chromatography to obtain 3c (colorless oil, 97% yield). 
\[\alpha\]$_{D}^{28}$ = -502.3$^\circ$ (c = 1.00, DCM). $Ee$ = 99% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 6.8 (major) and 7.6 (minor). 1H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J$ = 8.4 Hz, 2H), 7.45-7.40 (m, 2H), 7.29 (t, $J$ = 8.0 Hz, 2H), 7.24 (d, $J$ = 7.2 Hz, 1H), 7.18 (t, $J$ = 7.6 Hz, 2H), 7.12 (t, $J$ = 7.6 Hz, 1H), 2.25 (s, 3H), 2.18 (td, $J$ = 14.8 Hz, 7.6 Hz, 1H), 1.88 (td, $J$ = 14.8 Hz, 7.2 Hz, 1H), 0.86 (t, $J$ = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl$_3$): $\delta$ 172.0, 159.6, 137.4, 135.8, 130.2, 129.1, 128.7, 128.4, 125.3, 119.3, 64.5, 25.8, 13.8, 9.5. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3061, 2969, 2922, 2876, 2854, 2761, 2753, 1709, 1595, 1497, 1127, 1025, 749, 689. HRMS (ESI) for C$_{18}$H$_{18}$N$_{2}$OS: calculated [M+H]$^+$, 311.1218. Found, 311.1215.
(R)-4-Allyl-3-methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3d)
The crude product was purified by flash chromatography to obtain 3d (colorless oil, 94% yield). 

\([\alpha]_{D}^{28} = -274.2^\circ\) (c = 1.00, DCM). Ee = 99% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time=7.3 (major) and 7.9 (minor) .  

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.48 (d, \(J = 7.6\) Hz, 2H), 7.43 (d, \(J = 6.8\) Hz, 2H), 7.31-7.22 (m, 3H), 7.18 (t, \(J = 7.2\) Hz, 2H), 7.11 (t, \(J = 7.2\) Hz, 1H), 5.60-5.47 (m, 1H), 5.20 (dd, \(J = 16.8\) Hz, 1.2 Hz, 1H), 5.11 (d, \(J = 10.0\) Hz, 1H), 2.89 (dd, \(J = 14.0\) Hz, 6.8 Hz, 1H), 2.58 (dd, \(J = 14.0\) Hz, 8.0 Hz, 1H), 2.25 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.7, 159.3, 137.4, 135.9, 130.3, 130.2, 129.1, 128.7, 128.1, 125.3, 120.5, 119.3, 63.1, 36.6, 14.1. IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\) 3076, 2917, 1595, 1498, 1395, 1116, 1025, 926, 748, 689. HRMS (ESI) for C\(_{19}\)H\(_{18}\)N\(_2\)O\(_2\): calculated [M+H]\(^+\), 323.1218. Found, 323.1216.
The crude product was purified by flash chromatography to obtain 3e (white solid, 99% yield). M. p.: 42-47 °C. [α]$_{D}^{29}$ = -144.8° (c=1.01, DCM). $Ee = 98\%$ HPLC condition: CHIRALPAK OJ-H. Hexane/i-PrOH eluent (90:10 ratio, 0.3 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 24.9 (major) and 29.4 (minor). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J$ = 7.2 Hz, 2H), 7.31 (d, $J$ = 7.6 Hz, 2H), 7.26-7.15 (m, 5H), 7.12-6.96 (m, 5H), 3.52(d, $J$ = 14.0 Hz, 1H), 3.02 (d, $J$ = 14.0 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.7, 159.0, 137.2, 137.1, 135.8, 131.1, 130.2, 129.3, 129.0, 128.9, 128.5, 128.1, 125.3, 119.6, 64.7, 37.8, 21.0, 14.4. IR $v_{\text{max}}$ (film) cm$^{-1}$: 3064, 3029, 2916, 2848, 1710, 1593, 1498, 1119, 1023, 744, 687. HRMS (ESI) for C$_{24}$H$_{22}$N$_2$OS: calculated [M+H]$^+$, 387.1531. Found, 387.1521.
(R)-3-Methyl-4-(3-methylbenzyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3f)
The crude product was purified by flash chromatography to obtain 3f (colorless oil, 95% yield). \( [\alpha]^{28}_D = -202.9^\circ \) (c = 1.00, DCM). \( Ee = 97\% \) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.2 (minor) and 10.1 (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.48-7.44 (m, 2H), 7.32-7.16 (m, 7H), 7.12-7.05 (m, 2H), 7.00-6.92 (m, 3H), 3.54 (d, \( J = 13.6 \) Hz, 1H), 3.02 (d, \( J = 13.6 \) Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 171.9, 159.1, 138.4, 137.2, 136.0, 134.3, 130.3, 129.9, 129.2, 128.7, 128.5, 128.3, 126.2, 125.5, 119.8, 64.8, 38.3, 21.5, 14.5. IR \( \nu_{\text{max}} \) (film) cm\(^{-1}\) 3059, 2918, 2848, 1707, 1595, 1497, 1118, 1025, 788, 750, 689. HRMS (ESI) for C\(_{24}\)H\(_{22}\)N\(_2\)OS: calculated [M+H]\(^+\), 387.1531. Found, 387.1524.
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(R)-3-Methyl-4-(2-methylbenzyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3g)

The crude product was purified by flash chromatography to obtain 3g (white solid, 95% yield). M. p.: 99-104 °C. \([\alpha]_{D}^{29} = -295.0^{\circ}\) (c = 1.01, DCM). \(Ee = 96\%\) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 8.8 (minor) and 9.8 (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.45 (d, \(J = 7.2\) Hz, 2H), 7.34 (d, \(J = 8.4\) Hz, 2H), 7.27-7.16 (m, 5H), 7.15-7.07 (m, 3H), 7.01 (t, \(J = 7.2\) Hz, 1H), 6.94 (d, \(J = 7.2\) Hz, 1H), 3.55 (d, \(J = 14.8\) Hz, 1H), 3.18 (d, \(J = 15.2\) Hz, 1H), 2.40 (s, 3H), 2.18 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 172.0, 159.2, 137.3, 136.5, 136.1, 133.3, 130.9, 130.4, 129.1, 128.6, 128.2, 128.1, 127.5, 126.4, 125.4, 119.5, 64.2, 34.0, 20.3, 14.4. IR \(\nu_{\max}\) (film) cm\(^{-1}\) 3060, 3023, 2920, 1709, 1595, 1497, 1179, 1145, 1117, 1025, 738, 688. HRMS (ESI) for C\(_{24}\)H\(_{22}\)N\(_2\)OS: calculated [M+H]\(^+\), 387.1531. Found, 387.1524.
(\(R\))-4-(4-Chlorobenzyl)-3-methyl-1-phenyl-4-(phenylthio)-1\(H\)-pyrazol-5(4\(H\))-one (3h)
The crude product was purified by flash chromatography to obtain 3h (white solid, 99% yield). M. p.: 59-62 °C. [α]D = -131.4° (c=0.99, DCM). ee=99% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80: 20 ratio, 0.5 mL/min flow rate) 254nm wave length UV. Retention time=16.8 (major) and 17.8 (minor). 1H NMR (400 MHz, CDCl3): δ 7.48-7.43 (m, 2H), 7.34-7.27 (m, 2H), 7.27-7.15 (m, 7H), 7.13-7.06 (m, 3H), 3.51(d, J = 14.0 Hz, 1H), 3.04 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 171.6, 158.7, 137.1, 136.0, 133.7, 132.8, 130.6, 130.5, 129.2, 129.0, 128.7, 127.9, 125.6, 119.6, 64.6, 37.5, 14.5. IR νmax (film) cm⁻¹ 3065, 2917, 2848, 1709, 1594, 1494, 1121, 1099, 1066, 1021, 1016, 835, 742, 687, 650. HRMS (ESI) for C23H19ClN2O5: calculated [M+H]+, 407.0985. Found, 407.0972.
(R)-4-(4-Fluorobenzyl)-3-methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3i)

The crude product was purified by flash chromatography to obtain 3i (colorless oil, 97% yield). 

$[\alpha]_{D}^{29} = -179.8^\circ$ (c = 1.01, DCM). $Ee = 99\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 10.5 (major) and 11.5 (minor). $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J = 7.2$ Hz, 2H), 7.32-7.16 (m, 7H), 7.16-7.06 (m, 3H), 6.89 (t, $J = 8.8$ Hz, 2H), 3.51(d, $J = 13.6$ Hz, 1H), 3.06 (d, $J = 14.0$ Hz, 1H), 2.26 (s, 3H); $^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta$ 171.5, 162.1 (d, $J = 245.1$ Hz), 158.7, 136.9, 135.8, 130.8 (d, $J = 8.0$ Hz), 130.3, 130.0 (d, $J = 3.3$ Hz), 129.1, 128.6, 127.9, 125.5, 119.5, 115.6 (d, $J = 21.3$ Hz), 64.6, 37.3, 14.3. IR $\nu_{\text{max}}$ (film) cm$^{-1}$: 3061, 2921, 2849, 1706, 1596, 1499, 1222, 1098, 1067, 1024, 992, 879, 749, 689. HRMS (ESI) for C$_{23}$H$_{19}$FN$_2$OS: calculated [M+H]$^+$ 391.1280. Found, 391.1271.
(R)-4-(4-Bromobenzyl)-3-methyl-1-phenyl-4-(phenylthio) -1H-pyrazol-5(4H)-one (3)
The crude product was purified by flash chromatography to obtain 3j (colorless oil, 98% yield).

\([\alpha]_{D}^{28} = -117.6^\circ\) (c = 1.02, DCM). \(Ee = 98\%\) HPLC condition: CHIRALPAK AD-H. Hexane/i-
PrOH eluent (90:10 ratio, 0.5 mL/min flow rate) with 254 nm wave length UV. Retention time =
25.9 (major) and 27.4 (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.45 (d, J = 7.2 Hz, 2H), 7.32 (t, J =
8.8 Hz, 4H), 7.28-7.16 (m, 5H), 7.10 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 3.50(d, J = 14.0
Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 171.6, 158.7,
137.1, 136.0, 133.4, 131.9, 130.9, 130.5, 129.2, 128.7, 127.9, 125.6, 121.9, 119.7, 64.5, 37.6, 14.5.
IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\) 3060, 2920, 2849, 1706, 1594, 1488, 1362, 1144, 1071, 1011, 992, 832, 798,
(R)-3-Methyl-1-phenyl-4-(phenylthio)-4-(4-(trifluoromethyl) benzyl)-1H-pyrazol-5(4H)-one (3k)

The crude product was purified by flash chromatography to obtain 3k (colorless oil, 99% yield).

$[\alpha]^{28}_D = -46.8^\circ$ (c = 1.00, DCM). $Ee = 96\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =10.6 (major) and 11.5 (minor). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.43 (m, 4H), 7.30-7.16 (m, 9H), 7.09 (tt, $J$ = 7.2 Hz,1.6 Hz, 1H), 3.59(d, $J$ = 13.6 Hz, 1H), 3.12(d, $J$ = 13.6 Hz, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.3, 158.4, 137.6 (d, $J$ = 146.1 Hz), 135.9, 130.4, 130.0 (d, $J$ = 32.2 Hz), 129.5, 129.1, 128.6, 127.6, 125.69, 125.6 (d, $J$ = 3.8 Hz), 125.56, 125.2 (q, $J$ = 270.5 Hz), 119.5, 64.3, 37.7, 14.3; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.7 (m). IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3062, 2922, 2850, 1707, 1595, 1499, 1321, 1164, 1110, 1067, 1018, 846, 747, 689. HRMS (ESI) for C$_{24}$H$_{19}$F$_3$N$_2$OS: calculated [M+H]$^+$, 441.1248. Found, 441.1239.
(R)-3-Methyl-4-(4-nitrobenzyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one  (3l)
The crude product was purified by flash chromatography to obtain 31 (white solid, 99% yield). M. p.: 120-122 °C. [α]^{29}_D = -120.9° (c = 1.01, DCM). Ee = 90% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 17.2 (major) and 22.4 (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.07 (d, \(J = 8.4\) Hz, 2H), 7.45 (d, \(J = 7.6\) Hz, 2H), 7.39-7.16 (m, 9H), 7.10 (t, \(J = 6.8\) Hz, 1H), 3.61 (d, \(J = 14.0\) Hz, 1H), 3.18 (d, \(J = 14.0\) Hz, 1H), 2.27 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): δ 171.1, 158.2, 147.4, 141.7, 136.7, 135.9, 130.5, 130.2, 129.2, 128.7, 127.4, 125.7, 123.9, 119.3, 64.1, 37.6, 14.3. \(\text{IR}\ \nu_{\text{max}}\) (film) cm\(^{-1}\) 3185, 3074, 2920, 2849, 1707, 1597, 1515, 1499, 1343, 1118, 1106, 1067, 753, 729, 692. HRMS (ESI) for C\(_{23}\)H\(_{19}\)N\(_3\)O\(_3\)S: calculated [M+H]\(^+\), 418.1225. Found, 418.1215.
(R)-4-(4-Methoxybenzyl)-3-methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3m)

The crude product was purified by flash chromatography to obtain 3m (pale yellow solid, 99% yield).

M. p.: 78-82 °C. [α]$_D^{28}$ = -148.6° (c=1.01, DCM). Ee = 98% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (90:10 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 22.2 (major) and 23.5 (minor). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.28-7.14 (m, 5H), 7.12-7.03 (m, 3H), 6.72 (d, J = 7.6 Hz, 2H), 3.70 (s, 3H), 3.50 (d, J = 13.6 Hz, 1H), 3.02 (d, J = 13.6 Hz, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.9, 159.1, 159.0, 137.2, 135.9, 130.33, 130.26, 129.1, 128.6, 128.3, 126.3, 125.4, 119.7, 114.1, 64.9, 55.2, 37.5, 14.5. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 2961, 2920, 2836, 1707, 1595, 1511, 1253, 1085, 1068, 1027, 799, 750, 689. HRMS (ESI) for C$_{24}$H$_{22}$N$_2$O$_2$S: calculated [M+H]$^+$, 403.1480. Found, 403.1472.
(R)-3-Methyl-4-(naphthalen-2-ylmethyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (3n)
The crude product was purified by flash chromatography to obtain \(3n\) (white solid, 98% yield).

M. p.: 148-153 °C. \([\alpha]^{28}\D = -36.8^\circ\) (c = 0.98, DCM). \(Ee = 86\%\) HPLC condition: CHIRALPAK IF-3. Hexane/i-PrOH eluent (60:40 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV. Retention time (min) =10.5 (major) and 11.9 (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.77-7.65\) (m, 3H), 7.63 (s, 1H), 7.48 (d, \(J = 7.2\) Hz, 2H), 7.44-7.38 (m, 2H), 7.31-7.24 (m, 4H), 7.24-7.17 (m, 4H), 7.07 (t, \(J = 7.2\) Hz, 1H), 3.75 (d, \(J = 14.0\) Hz, 1H), 3.23 (d, \(J = 13.6\) Hz, 1H), 2.27 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 171.9, 159.1, 137.2, 136.1, 133.4, 132.7, 132.0, 130.4, 129.2, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 127.0, 126.4, 126.2, 125.5, 119.8, 64.7, 38.5, 14.6. IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\) 3056, 3028, 3011, 2920, 1701, 1592, 1488, 1118, 1087, 1064, 1025, 858, 816, 747, 687. HRMS (ESI) for C\(_{27}\)H\(_{22}\)N\(_2\)OS: calculated [M+H]\(^+\), 423.1531. Found, 423.1524.
The crude product was purified by flash chromatography to obtain 3o (white solid, 84% yield).

M. p.: 174-178 °C. [α]$_{29}$$^{0}$ = -244.0° (c = 0.99, DCM). Ee = 88% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 14.9 (major) and 17.2 (minor). $^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, $J$ = 7.2 Hz, 2H), 7.38 (t, $J$ = 7.2 Hz, 1H), 7.29 (d, $J$ = 7.6 Hz, 2H), 7.24-7.05 (m, 8H), 6.81 (d, $J$ = 8.0 Hz, 1H, 1.2 Hz, 2H), 3.47 (d, $J$ = 13.6 Hz, 1H), 3.09 (d, $J$ = 13.6 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 175.9, 160.3, 136.1, 136.0, 133.9, 130.7, 129.4, 129.1, 128.9, 127.83, 127.80, 127.7, 127.2, 62.9, 38.3, 14.6. IR $\nu_{max}$ (film) cm$^{-1}$: 2919, 2849, 1719, 1597, 1438, 1244, 1220, 1052, 756, 721, 692. HRMS (ESI) for C$_{23}$H$_{20}$N$_{2}$O$_{2}$S$_{2}$: calculated [M+H]$^{+}$, 405.1095. Found, 405.1084.
(R)-4-Benzyl-3-methyl-4-(phenylthio) -1-(p-tolyl)-1H-pyrazol-5(4H)-one    (3p)
The crude product was purified by flash chromatography to obtain 3p (white solid, 97% yield).

M. p.: 87-92 °C. [α]$_D^{29}$ = -175.2° (c = 0.98, DCM). $Ee$ = 98% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 17.4 (minor) and 21.3 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J = 7.6$ Hz, 2H), 7.28-7.10 (m, 10H), 7.03 (d, $J = 8.4$ Hz, 2H), 3.56 (d, $J = 14.0$ Hz, 1H), 3.06 (d, $J = 14.4$ Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.6, 158.8, 135.9, 135.3, 134.7, 134.4, 130.3, 129.23, 129.20, 129.17, 128.8, 128.3, 127.7, 119.9, 64.7, 38.3, 21.1, 14.5. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3057, 2920, 2849, 1700, 1613, 1508, 1127, 1079, 1026, 822, 751, 723, 691. HRMS (ESI) for C$_{24}$H$_{22}$N$_2$OS: calculated [M+H]$^+$, 387.1531. Found, 387.1522.
(R)-4-Benzyl-1-(4-iodophenyl)-3-methyl-4-(phenylthio)-1H-pyrazol-5(4H)-one  (3q)

The crude product was purified by flash chromatography to obtain 3q (pale yellow solid, 99% yield). M. p.: 75-79 °C. [α]$_{29}^{D}$ = -144.5° ($c=1.00$, DCM). Ee = 98% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 12.8 (minor) and 17.8 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.22-7.07 (m, 9H), 3.54 (d, $J = 14.0$ Hz, 1H), 3.06 (d, $J = 13.6$ Hz, 1H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.7, 159.4, 137.6, 137.0, 135.9, 134.2, 130.4, 129.2, 129.1, 128.8, 128.0, 127.8, 121.0, 89.2, 64.9, 38.2, 14.5. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3058, 3029, 2919, 2849, 1709, 1582, 1486, 1218, 1125, 1025, 1002, 747, 725, 692. HRMS (ESI) for C$_{23}$H$_{19}$IN$_2$OS: calculated [M+H]$^+$, 499.0341. Found, 499.0335.
(R)-4-Benzyl-3-methyl-4-(phenylthio)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5(4H)-one (3r)
The crude product was purified by flash chromatography to obtain 3r (white solid, 88% yield).

M. p.: 116-120 °C. [α]29D = -134.5° (c = 0.99, DCM). Ee = 93% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 7.9 (minor) and 11.3 (major). 1H NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.27-7.10 (m, 8H), 3.57 (d, J = 14.0 Hz, 1H), 3.09 (d, J = 13.6 Hz, 1H), 2.28 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 172.2, 159.7, 140.0, 136.0, 134.2, 130.5, 129.2 (d, J = 6.7 Hz), 128.9, 127.89, 127.86, 126.7 (d, J = 32.7 Hz), 125.9 (d, J = 3.8 Hz), 125.89 (d, J = 11.2 Hz), 125.5 (q, J = 270.0 Hz), 118.6, 65.0, 38.2, 14.5; 19F NMR (376 MHz, CDCl₃): δ -62.2 (s). IR νmax (film) cm⁻¹ 3058, 3031, 2921, 2848, 1713, 1610, 1584, 1316, 1120, 1062, 1012, 849, 748, 695, 664. HRMS (ESI) for C₂₄H₁₉F₃N₂OS: calculated [M+H]⁺, 441.1248. Found, 441.1232.
(R)-4-Benzyl-3-methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5(4H)-one (3s)

The crude product was purified by flash chromatography to obtain 3s (white solid, 80% yield). M. p.: 69-73 °C. [α]$_{27}^D$ = -167.4° (c = 1.02, DCM). Ee = 84% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 10.1 (minor) and 13.1 (major). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.33 (d, $J$ = 8.0 Hz, 2H), 7.30 (dd, $J$ = 8.8 Hz, 1.2 Hz, 2H), 7.23 (t, $J$ = 8.0 Hz, 2H), 7.20-7.12 (m, 5H), 7.08 (t, $J$ = 7.2 Hz, 1H), 6.99 (d, $J$ = 8.0 Hz, 2H), 3.55 (d, $J$ = 14.0 Hz, 1H), 3.05 (d, $J$ = 14.0 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.9, 159.0, 140.7, 137.3, 135.9, 134.5, 129.9, 129.2, 128.8, 128.6, 127.7, 125.4, 124.7, 119.8, 64.8, 38.2, 21.3, 14.5. IR $v_{max}$ (film) cm$^{-1}$ 3062, 3031, 2920, 2851, 1707, 1595, 1496, 1454, 1119, 1030, 811, 754, 723, 692. HRMS (ESI) for C$_{24}$H$_{22}$N$_2$OS: calculated [M+H]$^+$, 387.1531. Found, 387.1523.
(R)-4-Benzyl-3-methyl-1-phenyl-4-((o-tolylthio)-1H-pyrazol-5(4H)-one (3t)
The crude product was purified by flash chromatography to obtain 3t (white solid, 93% yield).

M. p.: 60-64 °C. [α]_{D}^{28} = -123.9° (c = 1.00, DCM). Ee = 86% HPLC condition: CHIRALPAK IF-3. Hexane/i-PrOH eluent (70:30 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV.

Retention time (min) = 7.7 (major) and 8.2 (minor). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.36 (d, $J$ = 7.6 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 2H), 7.26-7.11 (m, 9H), 7.08 (t, $J$ = 7.6 Hz, 1H), 6.98 (d, $J$ = 7.2 Hz, 1H), 3.60 (d, $J$ = 13.6 Hz, 1H), 3.09 (d, $J$ = 13.6 Hz, 1H), 2.55 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.6, 159.2, 143.3, 137.3, 136.7, 134.4, 130.8, 130.2, 129.2, 128.8, 128.7, 128.0, 127.7, 126.4, 125.4, 119.7, 64.3, 38.8, 21.4, 14.7. IR $\nu$$_{max}$ (film) cm$^{-1}$ 3059, 3031, 2920, 2850, 1704, 1594, 1492, 1081, 1060, 1030, 757, 725, 692. HRMS (ESI) for C$_{24}$H$_{22}$N$_{2}$OS: calculated [M+H]$^{+}$, 387.1531. Found, 387.1523.
The crude product was purified by flash chromatography to obtain 3u (colorless oil, 97% yield).

\([\alpha]^{25}_D = -177.5^\circ\) (c = 1.00, DCM). \(Ee = 83\%\) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.5 (minor) and 15.5 (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.38 (d, \(J = 8.4\) Hz, 2H), 7.33 (d, \(J = 7.6\) Hz, 2H), 7.27-7.10 (m, 7H), 7.08 (t, \(J = 7.2\) Hz, 1H), 6.69 (d, \(J = 8.8\) Hz, 2H), 3.65 (s, 3H), 3.54 (d, \(J = 14.0\) Hz, 1H), 3.03 (d, \(J = 14.0\) Hz, 1H), 2.25 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.9, 161.4, 159.1, 137.7, 137.3, 134.6, 129.2, 128.8, 128.6, 127.6, 125.4, 119.7, 118.7, 114.7, 65.0, 55.4, 37.9, 14.5. IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\): 3062, 3031, 3007, 2920, 2837, 1706, 1590.
1492, 1248, 1120, 1105, 1093, 1081, 1027, 829, 755, 723, 692. HRMS (ESI) for C_{24}H_{22}N_{2}O_{2}S: calculated [M+H]^+, 403.1480. Found, 403.1471.

(R)-4-Benzyl-4-((4-fluorophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3v)
The crude product was purified by flash chromatography to obtain 3v (white solid, 99% yield). M. p.: 107-111 °C. [a]^{28}_D = -160.4° (c = 1.00, DCM). Ee = 95% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.7 (minor) and 10.9 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.42 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.22 (m, 2H), 7.21-7.12 (m, 5H), 7.10 (t, $J$ = 7.6 Hz, 1H), 6.89 (t, $J$ = 8.4 Hz, 2H), 3.55 (d, $J$ = 14.0 Hz, 1H), 3.05 (d, $J$ = 14.0 Hz, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.6, 164.1 (d, $J$ = 250.4 Hz), 158.8, 138.2 (d, $J$ = 8.8 Hz), 137.1, 134.2, 129.2, 128.8, 128.7, 127.8, 125.6, 123.5 (d, $J$ = 3.3 Hz), 119.5, 116.4 (d, $J$ = 21.8 Hz), 64.9, 38.1, 14.4; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -109.5 (m). IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3060, 3035, 3012, 2919, 1700, 1589, 1489, 1227, 1118, 1081, 1030, 835, 759, 725, 691. HRMS (ESI) for C$_{23}$H$_{19}$FN$_2$OS: calculated [M+H]$^+$ 391.1280. Found, 391.1272.
The crude product was purified by flash chromatography to obtain 3w (colorless oil, 95% yield).

$[\alpha]^{28}_{D} = -165.6^\circ$ (c = 1.01, DCM). $Ee = 92\%$ HPLC condition: CHIRALPAK AD-H.

Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 10.3 (minor) and 13.1 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.35 (m, 2H), 7.30-7.22 (m, 4H), 7.22-7.08 (m, 8H), 3.54 (d, $J = 13.6$ Hz, 1H), 3.05 (d, $J = 14.0$ Hz, 1H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.5, 158.8, 137.2, 137.04, 136.97, 134.1, 129.4, 129.2, 128.8, 128.7, 127.8, 126.6, 125.7, 119.6, 64.8, 38.2, 14.5. IR $\nu_{max}$ (film) cm$^{-1}$: 3062, 3031, 2920, 2849, 1706, 1594, 1497, 1093, 1030, 1013, 823, 754, 722, 692. HRMS (ESI) for C$_{23}$H$_{16}$ClN$_2$OS: calculated [M+H]$^+$, 407.0985. Found, 407.0976.
(R)-4-Benzyl-4-((2-bromophenyl)thio)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one  (3x)
The crude product was purified by flash chromatography to obtain 3x (colorless oil, 92% yield).

$[\alpha]^{28}_D = -149.3^\circ$ (c = 1.01, DCM). $Ee = 69\%$ HPLC condition: CHIRALPAK IF-3. Hexane/i-
PrOH eluent (97:3 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV. Retention time (min)
= 18.2 (major) and 20.5 (minor). $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta$ 7.62-7.57 (m, 1H), 7.53-7.48 (m,
1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.23-7.05 (m, 8H), 3.57 (d, $J = 13.6$ Hz, 1H),
3.16 (d, $J = 13.6$ Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.5, 159.2, 141.6, 137.3,
137.1, 133.9, 133.7, 131.2, 130.4, 129.9, 129.3, 128.8, 128.0, 127.9, 125.6, 119.6, 64.3, 39.0, 15.0.
IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3061, 3032, 2920, 2850, 1706, 1595, 1498, 1362, 1159,
1117, 1019, 991, 752, 722, 692. HRMS (ESI) for C$_{23}$H$_{19}$BrN$_2$OS: calculated [M+H]$^+$,
The crude product was purified by flash chromatography to obtain 3y (colorless oil, 96% yield). 

$\alpha^{27}_{D} = -84.2^\circ \text{ (c = 0.98, DCM).}$  

$Ee = 98\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.0 (minor) and 14.8 (major). $^1\text{H NMR (400 MHz, CDCl}_3$: δ 7.67 (dd, $J = 8.8$ Hz, 1.2 Hz, 2H), 7.37-7.30 (m, 2H), 7.24-7.07 (m, 11H), 3.71 (d, $J = 12.4$ Hz, 1H), 3.58 (d, $J = 12.4$ Hz, 1H), 3.46 (d, $J = 14.0$ Hz, 1H), 2.99 (d, $J = 13.6$ Hz, 1H), 2.13 (s, 3H); $^{13}\text{C NMR (100 MHz, CDCl}_3$: δ 171.8, 159.3, 137.5, 135.7, 134.0, 129.3, 129.2, 128.9, 128.7, 128.6, 127.8, 127.7, 125.4, 119.3, 61.3, 39.5, 34.3, 14.2. IR $\nu_{\text{max}}$ (film) cm$^{-1}$: 3061, 3030, 2912, 2848, 1705, 1594, 1495, 1081, 1030, 755, 722, 692. HRMS (ESI) for C$_{24}$H$_{22}$N$_2$OS: calculated [M+H]$^+$, 387.1531. Found, 387.1522.
(R)-4-Benzyl-1,3-diphenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (5a)
The crude product was purified by flash chromatography to obtain 5a (white solid, 98% yield).

M. p.: 106-110 °C. [α]^{28}_D = 10.8° (c = 1.00, DCM). Ee = 93% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80: 20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 11.7 (minor) and 13.7 (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.25-8.20 (m, 2H), 7.54-7.48 (m, 3H), 7.39-7.30 (m, 4H), 7.27-7.16 (m, 3H), 7.13-6.97 (m, 6H), 6.85 (d, \(J = 7.2\) Hz, 2H), 3.65 (d, \(J = 13.2\) Hz, 1H), 3.50 (d, \(J = 13.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 172.4, 156.2, 137.2, 136.2, 134.0, 131.2, 130.7, 130.4, 129.6, 129.0, 128.9, 128.7, 128.4, 128.1, 127.5, 127.1, 125.8, 120.1, 63.8, 39.6. IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\) 3060, 3028, 2918, 2849, 1711, 1593, 1491, 1182, 1136, 1022, 751, 689, 645. HRMS (ESI) for C\(_{28}\)H\(_{22}\)N\(_2\)O\(_5\): calculated [M+H]\(^+\), 435.1531. Found, 435.1527.
The crude product was purified by flash chromatography to obtain 5b (colorless oil, 96% yield). $\left[\alpha\right]_{D}^{28} = -53.7^\circ$ (c=0.99, DCM). $Ee = 97\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.6 (minor) and 10.6 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (td, $J = 3.6$ Hz, 1.2 Hz, 2H), 7.60 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.54-7.47 (m, 3H), 7.36-7.28 (m, 4H), 7.22-7.12 (m, 2H), 7.08 (t, $J = 7.6$ Hz, 2H), 2.44-2.21 (m, 2H), 0.78 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.8, 156.6, 137.4, 136.1, 130.7, 130.6, 130.3, 128.94, 128.93, 128.8, 128.2, 126.9, 125.6, 119.5, 63.7, 27.6, 9.8. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3059, 2967, 2932, 1712, 1594, 1492, 1384, 1152, 748, 688. HRMS (ESI) for C$_{23}$H$_{20}$N$_{2}$OS: calculated [M+H]$^+$, 373.1375. Found, 373.1368.
(R)-4-(2-Methylbenzyl)-1, 3-diphenyl-4-(phenylthio) -1H-pyrazol-5(4H)-one  (5c)
The crude product was purified by flash chromatography to obtain 5c (colorless oil, 97% yield). \([\alpha]^{28}_D = -7.9^\circ\) (c = 1.01, DCM). \(Ee = 62\%\) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.0 (minor) and 13.0 (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.21 (dd, \(J = 7.6\) Hz, 2.0 Hz, 2H), 7.51-7.42 (m, 3H), 7.37 (d, \(J = 8.0\) Hz, 4H), 7.29-7.16 (m,3H), 7.10 (q, \(J = 8.0\) Hz, 3H), 7.01-6.92 (m, 2H), 6.86 (d, \(J = 2.8\) Hz, 2H), 3.70 (d, \(J = 14.4\) Hz, 1H), 3.53 (d, \(J = 14.4\) Hz, 1H), 2.10 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 172.5, 156.6, 137.2, 137.0, 136.2, 132.9, 131.2, 130.67, 130.65, 130.4, 129.01, 128.96, 128.9, 128.7, 128.0, 127.4, 127.3, 125.9, 125.7, 119.9, 63.7, 35.2, 19.9. IR \(\nu_{\text{max}}\) (film) cm\(^{-1}\) 3062, 2917, 1708, 1593, 1489, 1129, 747, 690. HRMS (ESI) for C\(_{29}\)H\(_{24}\)N\(_2\)OS: calculated [M+H]\(^+\), 449.1688. Found, 449.1680.
(R)-4-(4-Nitrobenzyl)-1,3-diphenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one \( (5d) \)

The crude product was purified by flash chromatography to obtain \( 5d \) (white solid, 96% yield). M. p.: 48-52 °C. \( [\alpha]_{28}^D = 2.0^\circ \) (c = 1.00, DCM). \( Ee = 83\% \) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 21.2 (major) and 28.3 (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 8.23 \) (dd, \( J = 7.6 \) Hz, 2.0 Hz, 2H), 7.89 (d, \( J = 8.8 \) Hz, 2H), 7.61-7.51 (m, 3H), 7.37 (dd, \( J = 8.8 \) Hz, 8.0 Hz, 4H), 7.30-7.20 (m,3H), 7.13 (q, \( J = 7.6 \) Hz, 3H), 7.00 (d, \( J = 8.4 \) Hz, 2H), 3.73 (d, \( J = 13.2 \) Hz, 1H), 3.59 (d, \( J = 13.2 \) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 171.9, 155.6, 147.3, 141.6, 136.8, 136.3, 131.1, 130.73, 130.71, 130.6, 129.20, 129.17, 128.8, 127.4, 127.0, 126.0, 123.6, 119.7, 63.2, 38.9. IR \( \nu_{max} \) (film) \( \text{cm}^{-1} \) 3060, 2925, 1710, 1597, 1520, 1492, 1386, 1131, 1025, 855, 750, 726,
689. HRMS (ESI) for C_{28}H_{21}N_{3}O_{3}S: calculated [M+H]^+, 480.1382. Found, 480.1374.

(R)-4-(Naphthalen-2-ylmethyl)-1, 3-diphenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one  (5e)
The crude product was purified by flash chromatography to obtain 5e (colorless oil, 99% yield). 

\[ \alpha \] _{28D}^0 = 36.0° (c=1.01, DCM). Ee = 97% HPLC condition: CHIRALPAK AD-H. Hexane/i-
PrOH eluent (80:20 ratio, 0.5 mL/min flow rate) with 254 nm wave length UV. Retention time 
(min) = 23.2 (major) and 24.4 (minor). ^1H NMR (400 MHz, CDCl₃): \( \delta \) 8.22 (d, \( J = 8.0 \) Hz, 2H), 
7.69-7.61 (m, 1H), 7.60-7.26 (m, 11H), 7.24-7.17 (m, 4H), 7.16-7.04 (m, 3H), 6.99 (dd, \( J = 8.4 \) Hz, 
1.2 Hz, 1H), 3.81 (d, \( J = 13.6 \) Hz, 1H), 3.64 (d, \( J = 13.2 \) Hz, 1H); ^13C NMR (100 MHz, CDCl₃): \( \delta \) 
172.4, 156.3, 137.1, 136.3, 133.1, 132.5, 131.6, 131.3, 130.7, 130.4, 129.1, 128.9, 128.8, 128.6, 
128.0, 127.8, 127.6, 127.4, 127.3, 126.0, 125.9, 125.7, 120.0, 108.7, 63.8, 39.5. IR \( \nu_{max} \) (film) cm\(^{-1}\) 
3056, 2921, 1710, 1594, 1492, 1126, 734, 690. HRMS (ESI) for C₃₂H₂₄N₂O₅S: calculated [M+H]^+,
(R)-4-(4-Methoxybenzyl)-1, 3-diphenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one  (5f)

The crude product was purified by flash chromatography to obtain 5f (colorless oil, 99% yield).

[α]$^27_D = 6.9^\circ$ (c = 0.99, DCM). Ee = 97% HPLC condition: CHIRALPAK OD. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 7.3 (minor) and 8.8 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (q, $J = 3.2$ Hz, 2H), 7.56-7.48 (m, 3H), 7.39-7.32 (m, 4H), 7.29-7.17 (m, 3H), 7.11 (q, $J = 8.0$ Hz, 3H), 6.76 (d, $J = 8.8$ Hz, 2H), 6.54 (d, $J = 8.8$ Hz, 2H), 3.64 (s, 3H), 3.59 (d, $J = 13.6$ Hz, 1H), 3.46 (d, $J = 13.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.5, 158.8, 156.3, 137.2, 136.2, 131.2, 130.69, 130.64, 130.3, 129.0, 128.9, 128.7, 128.1, 127.1, 126.0, 125.7, 120.0, 113.7, 63.9, 55.1, 38.7. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3059, 2960, 1711, 1595, 1510, 1492, 1250, 1026, 749, 688. HRMS (ESI) for C$_{29}$H$_{24}$N$_2$O$_2$S: calculated [M+H]$^+$, 465.1637. Found, 465.1629.
(R)-4-benzyl-1, 3-diphenyl-4-((4-chlorophenyl)thio) -1H-pyrazol-5(4H)-one  (5g)
The crude product was purified by flash chromatography to obtain 5g (colorless oil, 94% yield). 
\([\alpha]^{27}_D = 25.6^\circ \) (c=1.00, DCM). 
\( Ee = 97\% \) HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.1 (minor) and 14.9 (major). 

\( ^1\)H NMR (400 MHz, CDCl$_3$): \( \delta \) 8.24-8.17 (m, 2H), 7.58-7.48 (m, 3H), 7.35 (dd, \( J = 8.4 \) Hz, 1.2 Hz, 2H), 7.29 (t, \( J = 8.4 \) Hz, 4H), 7.15 (t, \( J = 7.2 \) Hz, 1H), 7.07 (d, \( J = 8.4 \) Hz, 3H), 7.02 (t, \( J = 7.2 \) Hz, 2H), 6.84 (d, \( J = 7.2 \) Hz, 2H), 3.63 (d, \( J = 13.2 \) Hz, 1H), 3.50 (d, \( J = 13.2 \) Hz, 1H); 

\( ^{13}\)C NMR (100 MHz, CDCl$_3$): \( \delta \) 172.2, 155.9, 137.4, 136.99, 136.97, 133.8, 130.93, 130.81, 129.5, 129.3, 129.0, 128.8, 128.4, 127.6, 127.0, 126.5, 125.9, 119.9, 63.8, 39.4. 

IR \( \nu_{\text{max}} \) (film) cm$^{-1}$ 3061, 2921, 1711, 1595, 1493, 1311, 1013, 822, 756, 723, 689. 

HRMS (ESI) for C$_{28}$H$_{21}$ClN$_2$O$_5$: calculated [M+H]$^+$, 469.1141. Found, 469.1134.
(R)-4-Benzyl-1, 3-diphenyl-4-(benzylthio)-1H-pyrazol-5(4H)-one (5h)

The crude product was purified by flash chromatography to obtain 5h (colorless oil, 91% yield). 

$[\alpha]_{D}^{27} = 48.2^\circ$ (c=0.99, DCM). $Ee = 99\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 15.2 (minor) and 17.6 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (dd, $J = 8.0$ Hz, 1.6 Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.55-7.45 (m, 3H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.22-6.97 (m, 9H), 6.82 (d, $J = 6.8$ Hz, 2H), 3.76 (q, $J = 12.4$ Hz, 2H), 3.54 (d, $J = 13.6$ Hz, 1H), 3.43 (d, $J = 13.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.6, 155.9, 137.5, 135.4, 133.7, 130.9, 130.8, 129.5, 129.3, 128.9, 128.8, 128.6, 128.3, 127.59, 127.56, 126.9, 125.6, 119.5, 60.2, 40.8, 34.6. IR $\nu$$_{max}$ (film) cm$^{-1}$ 3060, 3029, 2962, 1709, 1595, 1492, 1383, 1127, 1025, 755, 689. HRMS (ESI) for C$_{29}$H$_{24}$N$_{2}$OS: calculated [M+H]$^+$, 449.1688. Found, 449.1680.
(R)-4-Benzyl-3-(4-fluorophenyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one  (5i)
The crude product was purified by flash chromatography to obtain 5\textbf{i} (white solid, 88% yield).

M. p.: 118-123 °C. $[\alpha]^{28}_D = 17.2$° (c = 0.99, DCM). $Ee = 94\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV.

Retention time (min) = 12.9 (minor) and 14.5 (major). $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 (dd, $J$ = 8.8 Hz, 5.6 Hz, 2H), 7.38-7.29 (m, 4H), 7.29-7.17 (m, 5H), 7.16-7.00 (m, 6H), 6.84 (d, $J$ = 7.2 Hz, 2H), 3.66 (d, $J$ = 13.2 Hz, 1H), 3.44 (d, $J$ = 13.6 Hz, 1H); $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $\delta$ 172.3, 165.3, 162.8, 155.2, 137.0, 136.1, 133.9, 130.5, 129.5, 129.2 ($J$ = 8.3 Hz), 129.1, 128.7, 128.4, 127.9, 127.4 ($J$ = 3.4 Hz), 126.7 ($J$ = 176 Hz), 120.0, 116.1 ($J$ = 21.6 Hz), 63.7, 39.5; $^{19}\text{F}$ NMR (376 MHz, CDCl$_3$): $\delta$ -108.8 (m). IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3068, 3030, 2922, 1704, 1595, 1494, 1226, 1099, 1067, 1027, 1007, 879, 749, 687. HRMS (ESI) for C$_{28}$H$_{21}$FN$_2$OS: calculated [M+H]$^+$, 453.1437. Found, 453.1434.
(R)-4-Benzyl-3-(3-fluorophenyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5(4H)-one (5j)

The crude product was purified by flash chromatography to obtain 5j (colorless oil, 95% yield).

$[\alpha]^{28}_D = 16.5^\circ$ (c = 1.00, DCM). $Ee = 96\%$ HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.2 (minor) and 14.1 (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 10.0$ Hz, 1H), 7.51 (q, $J = 8.0$ Hz, 1H), 7.38-7.18 (m, 8H), 7.16-7.00 (m, 6H), 6.85 (d, $J = 7.2$ Hz, 2H), 3.66 (d, $J = 13.6$ Hz, 1H), 3.47 (d, $J = 13.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.4, 164.2, 161.8, 155.1 ($J = 3.0$ Hz), 137.0, 136.2, 133.8, 133.2 ($J = 8.0$ Hz), 130.52 ($J = 8.0$ Hz), 130.51, 129.5, 129.1, 128.7, 128.5, 127.9, 126.8 ($J = 169.2$ Hz), 122.9 ($J = 2.9$ Hz), 120.1, 117.7 ($J = 21.3$ Hz), 113.8 ($J = 23.5$ Hz), 63.7, 39.5; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -111.4 (m). IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3062, 2916, 1714, 1589, 1487, 1228, 1083, 1069, 1025, 976, 875, 752, 690. HRMS (ESI) for C$_{28}$H$_{21}$FN$_2$OS: calculated [M+H]$^+$, 453.1437. Found, 453.1428.
*(R)*-4-Benzyl-3-(4-bromophenyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one  (5k)
The crude product was purified by flash chromatography to obtain 5k (white solid, 95% yield).

M. p.: 147-151 °C. [α]²⁸D = 41.6° (c = 1.01, DCM). Ee = 95% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.5 (minor) and 17.5 (major). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.36-7.19 (m, 7H), 7.16-7.00 (m, 6H), 6.85 (d, J = 6.8 Hz, 2H), 3.66 (d, J = 13.2 Hz, 1H), 3.45 (d, J = 13.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 172.3, 155.2, 136.9, 136.1, 133.8, 132.2, 130.5, 130.0, 129.5, 129.1, 128.7, 128.48, 128.46, 127.8, 127.6, 125.9, 125.1, 120.1, 63.6, 39.5. IR νmax (film) cm⁻¹: 3060, 2921, 2850, 1706, 1589, 1491, 1378, 1181, 1127, 1023, 955, 748, 727, 687. HRMS (ESI) for C₂₈H₂₁BrN₂OS: calculated [M+H]⁺, 513.0636. Found, 513.0630.
The crude product was purified by flash chromatography to obtain 5l (white solid, 99% yield).

M. p.: 148-152 °C. [α]26D = 54.2° (c = 1.00, DCM). Ee = 92% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 16.0 (minor) and 26.8 (major). $^1$H NMR (400 MHz, CDCl₃): δ 8.18 (d, $J = 8.8$ Hz, 2H), 7.39-7.30 (m, 4H), 7.25-7.17 (m, 3H), 7.14-6.99 (m, 8H), 6.87 (d, $J = 6.8$ Hz, 2H), 3.94 (s, 3H), 3.63 (d, $J = 13.2$ Hz, 1H), 3.48 (d, $J = 13.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃): δ 172.2, 161.4, 155.9, 137.2, 136.2, 134.1, 130.3, 129.6, 129.0, 128.7, 128.6, 128.3, 128.2, 127.5, 125.6, 123.8, 120.0, 114.2, 63.8, 55.5, 39.7. IR $\nu_{\text{max}}$ (film) cm$^{-1}$ 3061, 2963, 2927, 1703, 1598, 1254, 1126, 1025, 837, 748, 689. HRMS (ESI) for C$_{29}$H$_{32}$N$_{2}$O$_{2}$S: calculated [M+H]$^+$, 465.1637. Found, 465.1634.
IV. Crystallographic information

Structure Refinement and Crystal Data for 3g
**Table 1. Crystal data and structure refinement for mo_d8v17287_0m.**

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Data / restraints / parameters 3804 / 1 / 256
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Absolute structure parameter 0.00(2)
Extinction coefficient 0.022(7)
Largest diff. peak and hole 0.128 and -0.123 e.Å$^{-3}$

Crystal Data and Structure Refinement for 5l

Figure S2. (a) Crystal structure of 5l (left); (b) Packing model (right). (carbon atoms in this view are depicted with ellipsoids at the 30% probability level)

Table 2. Crystal data and structure refinement for mo_d8v17770_0m.

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Theta range for data collection 1.991 to 25.999°.
Index ranges -12<=h<=12, -9<=k<=10, -34<=l<=34
Reflections collected 38624
Independent reflections 9155 [R(int) = 0.0559]
Completeness to theta = 25.242° 99.5%
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7456 and 0.5383
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 9155 / 1 / 615
Goodness-of-fit on F² 1.037
Final R indices [I>2sigma(I)] R1 = 0.0370, wR2 = 0.0945
R indices (all data) R1 = 0.0415, wR2 = 0.0986
Absolute structure parameter 0.05(3)
Extinction coefficient n/a
Largest diff. peak and hole 0.271 and -0.304 e.Å⁻³

V. References

1. X. Gao, J. Han, L. Wang. Organic Letters. 2015, 17, 4596.


VI. NMR spectra
$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{1}H$ NMR (CDCl$_3$)

$^{13}C$ NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
\(^{19}\text{F NMR (CDCl}_3\)}

\(^{1}\text{H NMR (CDCl}_3\)}
$^{13}$C NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)
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$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)
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