Asymmetric organocatalytic conjugated addition of pyrazolin-5-ones to ortho-quinomethanes: construction of vicinal tertiary and all-carbon quaternary stereocenters

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1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. 2-(phenyl(tosyl)methyl)phenols[1] and pyrazolin-5-ones[2] were synthesized according to the known method. All reactions were carried out in glassware. Reactions were monitored by TLC on silica gel precoated on glass plates, and spots were visualized with UV light at 254nm. Flash column chromatography was performed on silica-gel.\textsuperscript{1}H and \textsuperscript{13}C NMR were recorded in CDCl\textsubscript{3} on Bruker AVANCE III (500 MHz). TMS served as internal standard (d= 0 ppm) for \textsuperscript{1}H NMR and CDCl\textsubscript{3} was used as internal standard (d= 77.0 ppm) for \textsuperscript{13}C NMR; High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source and controlled by using MassHunter software. Specific rotations were performed on a Rudolph Autopol IV automatic polarimeter. Chiral HPLC analyses were performed using Agilent 1260 chromatography. Chiralpak IA, IC, ID, and OD-H columns were purchased from Daicel Chemical Industries (Shanghai, China).


2. General procedure for the synthesis of 3

To a test tube were added catalyst \textbf{IVb} (0.05 mmol, 5 mol%), K\textsubscript{2}CO\textsubscript{3} (1.2 equiv., 0.12 mmol), the substituted 2-(phenyl(tosyl)methyl)phenol \textbf{1} or \textbf{4} (0.1 mmol) and pyrazolin-5-ones \textbf{2} (1.2 equiv., 0.12 mmol), 1.5 mL DCE and 0.5 mL H\textsubscript{2}O were then added through syringe. The resulting mixture was stirred at room temperature for 12 h. Then it was extracted with CH\textsubscript{2}Cl\textsubscript{2}, and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the product. The stereoselectivities were determined by Chiral HPLC using a Chiralpak IA, IC, ID, or AD-H column.

3. Characterization data of product 3

\textit{(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3aa)}

Compound was isolated as a white solid (93% yield) after flash column chromatography on silica-gel. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.70 (d, J = 8.1 Hz, 1H), 7.44 (dd, J = 26.6, 7.8 Hz, 4H), 7.31 (t, J = 7.9 Hz, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.15 (dq, J = 23.1, 7.6 Hz, 7H), 6.92 (t, J = 8.1 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.15 (s, 1H), 5.19 (s, 1H), 3.88 (s, 3H), 3.41 (d, J = 13.6 Hz, 1H), 3.14 (d, J = 13.6 Hz, 1H), 2.22 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 174.47, 161.62, 146.27, 143.71, 139.26, 137.50, 134.94, 129.24, 128.85, 128.56, 128.48, 128.14, 127.23, 127.09, 125.29, 124.49, 123.94, 120.14, 119.21, 109.33, 63.78, 56.00, 46.78, 40.82, 15.16. [α]D\textsuperscript{25} = 32 (c =
1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 70/30), 1.0 mL/min; Major enantiomer: $t_R = 7.56$ min, minor enantiomer: $t_R = 11.13$ min. 97:3 $dr$, 99% $ee$. HRMS (ESI) calcd for C$_{31}$H$_{28}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 499.1992, found: 499.1988.

(R)-4-benzyl-4-((S)-(2-hydroxy-4-methoxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ba)

Compound was isolated as a white solid (84% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69 – 7.65 (m, 1H), 7.46 – 7.43 (m, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.28 (dd, $J = 3.1$, 2.0 Hz, 6H), 7.14 (dd, $J = 4.3$, 2.3 Hz, 5H), 7.07 (dd, $J = 6.7$, 3.0 Hz, 3H), 6.46 (dd, $J = 8.6$, 2.6 Hz, 1H), 6.40 (s, 1H), 4.88 (s, 1H), 3.60 (s, 3H), 3.37 (d, $J = 13.7$ Hz, 3H), 3.02 (d, $J = 3.1$, 2.0 Hz, 3H), 2.29 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 175.95, 163.25, 160.16, 155.71, 138.81, 136.63, 134.22, 130.53, 129.13, 129.06, 128.66, 128.62, 128.50, 128.39, 128.23, 128.14, 127.33, 127.26, 126.10, 125.49, 120.69, 106.31, 65.36, 55.04, 46.98, 41.24, 15.16. $[\alpha]_D^{25} = 74$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH = 85/15), 1.0 mL/min; Major enantiomer: $t_R = 48.4$ min, minor enantiomer: $t_R = 12.7$ min. 56:44 $dr$, 90% $ee$. HRMS (ESI) calcd for C$_{31}$H$_{28}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 499.1992, found: 499.1992.

(R)-4-benzyl-4-((S)-(3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ca)

Compound was isolated as a colorless oil (80% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J = 8.1$, 1.3 Hz, 1H), 7.44 (ddd, $J = 25.7$, 8.4, 1.2 Hz, 4H), 7.33 – 7.29 (m, 2H), 7.22 (t, $J = 7.3$ Hz, 2H), 7.17 – 7.10 (m, 7H), 6.89 (t, $J = 8.1$ Hz, 1H), 6.79 (dd, $J = 8.1$, 1.4 Hz, 1H), 6.14 (s, 1H), 6.01 (s, 0H), 5.19 (s, 1H), 4.12 (dd, $J = 12.7$, 7.0 Hz, 2H), 3.41 (d, $J = 13.6$ Hz, 1H), 3.14 (d, $J = 13.6$ Hz, 1H), 2.22 (s, 3H), 1.46 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.46, 161.59, 145.50, 143.79, 139.29, 137.52, 134.97, 129.23, 128.87, 128.54, 128.46, 128.14, 127.20, 127.07, 125.26, 124.45, 123.77, 120.12, 119.17, 110.16, 64.56, 63.77, 46.78, 40.82, 15.16, 14.91. $[\alpha]_D^{25} = 25$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 70/30), 0.7 mL/min; Major enantiomer: $t_R = 10.68$ min, minor enantiomer: $t_R = 43.44$ min. 88:12 $dr$, 99% $ee$. HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 513.2149, found: 513.2140.

(R)-4-benzyl-4-((S)-(4-bromo-2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3da)

Compound was isolated as a colorless oil (80% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69 – 7.65 (m, 1H), 7.46 – 7.43 (m, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.28 (dd, $J = 3.1$, 2.0 Hz, 6H), 7.14 (dd, $J = 4.3$, 2.3 Hz, 5H), 7.07 (dd, $J = 6.7$, 3.0 Hz, 3H), 6.46 (dd, $J = 8.6$, 2.6 Hz, 1H), 6.40 (s, 1H), 4.88 (s, 1H), 3.60 (s, 3H), 3.37 (d, $J = 13.7$ Hz, 3H), 3.02 (d, $J = 3.1$, 2.0 Hz, 3H), 2.29 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 175.95, 163.25, 160.16, 155.71, 138.81, 136.63, 134.22, 130.53, 129.13, 129.06, 128.66, 128.62, 128.50, 128.39, 128.23, 128.14, 127.33, 127.26, 126.10, 125.49, 120.69, 106.31, 65.36, 55.04, 46.98, 41.24, 15.16. $[\alpha]_D^{25} = 25$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 70/30), 0.7 mL/min; Major enantiomer: $t_R = 10.68$ min, minor enantiomer: $t_R = 43.44$ min. 88:12 $dr$, 99% $ee$. HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 513.2149, found: 513.2140.
Compound was isolated as a white solid (96% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.94 (d, $J = 2.0$ Hz, 1H), 7.44 (d, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 7.3$ Hz, 2H), 7.32 (t, $J = 7.9$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 2H), 7.17 (dt, $J = 23.2, 7.8$ Hz, 7H), 6.92 (d, $J = 2.2$ Hz, 1H), 6.16 (s, 1H), 5.11 (s, 1H), 3.85 (s, 3H), 3.41 (d, $J = 13.5$ Hz, 1H), 3.07 (d, $J = 13.5$ Hz, 1H), 2.20 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.32, 161.22, 146.92, 142.94, 138.52, 137.33, 134.67, 132.72, 129.22, 128.76, 128.63, 128.60, 128.21, 127.50, 125.97, 125.50, 120.36, 113.00, 111.33, 63.64, 56.27, 46.64, 40.73, 15.09. $[^\alpha]D_{25}^o = 54$ (c = 1.0 in CH$_2$Cl$_2$).

The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 18.60$ min, minor enantiomer: $t_R = 34.63$ min. 98:2 dr, 97% ee. HRMS (ESI) calcd for C$_{31}$H$_{27}$N$_2$O$_3$Na m/z [M + Na]$^+$: 577.1097, found: 577.1099.

(R)-4-benzyl-4-((S)-(3-fluoro-2-hydroxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ea)

Compound was isolated as white solid (92% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.73 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.45 (dd, $J = 8.7, 1.2$ Hz, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.20 – 7.08 (m, 6H), 6.91 (dd, $J = 9.6, 8.2$ Hz, 3H), 6.82 (dd, $J = 8.1, 1.3$ Hz, 1H), 5.17 (s, 1H), 3.89 (s, 3H), 3.41 (d, $J = 13.6$ Hz, 1H), 3.09 (d, $J = 13.6$ Hz, 1H), 2.23 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.77, 161.84, 151.59 (d, $J = 237.5$ Hz), 142.30 (d, $J = 13.9$ Hz), 138.44, 137.06, 134.37, 129.13, 128.61, 128.59 (d, $J = 5.3$ Hz), 128.57, 128.23, 127.50, 127.49 (d, $J = 2.4$), 127.28, 127.09, 125.69, 125.67 (d, $J = 7.4$ Hz), 114.39 (d, $J = 18.3$ Hz), 64.13, 47.99, 40.80, 15.07. $[^\alpha]D_{25}^o = 65$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 15.28$ min, minor enantiomer: $t_R = 32.80$ min. 95:5 dr, 88% ee. HRMS (ESI) calcd for C$_{30}$H$_{25}$FN$_2$O$_2$Na m/z [M + Na]$^+$: 487.1792, found: 487.1791.

(R)-4-benzyl-4-((S)-(4-fluoro-2-hydroxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3fa)

Compound was isolated as white solid (93% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.08 (s, 1H), 7.51 – 7.46 (m, 1H), 7.29 – 7.22 (m, 9H), 7.16 (dd, $J = 4.0, 2.5$ Hz, 4H), 7.07 (dd, $J = 6.5, 3.0$ Hz, 2H), 6.63 (td, $J = 8.3, 2.6$ Hz, 1H), 6.56 (dd, $J = 10.1, 2.2$ Hz, 1H), 4.90 (s, 1H), 3.34 (d, $J = 13.6$ Hz, 1H), 3.01 (d, $J = 13.6$ Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 175.84, 163.07, δ 162.90 (d, $J = 246.2$ Hz), 155.97 (d, $J = 11.3$ Hz), 138.28, 136.45, 133.97, 133.35 (d, $J = 9.5$ Hz), 129.05, 128.57 (d, $J = 19.8$ Hz), 128.30, 127.49, 127.45, 126.35, 120.92, 120.48 (d, $J = 2.9$ Hz), 107.05 (d, $J = 21.1$ Hz), 65.16, 49.94, 41.09, 15.11. $[^\alpha]D_{25}^o = 102$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 85/15), 0.7 mL/min; Major
enantiomer: $t_R = 17.6$ min, minor enantiomer: $t_R = 8.2$ min. 72:28 $dr$, 94% $ee$. HRMS (ESI) calcd for C$_{30}$H$_{25}$FN$_2$O$_2$Na $m/z$ [M + Na]$^+$: 487.1792, found: 487.1792.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-(trifluoromethyl)phenyl)(phenyl)methyl)-5-methyl-2-phenyl-1,2,4-dihydro-3H-pyrazol-3-one (3ga)

Compound was isolated as a white solid (80% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 – 7.66 (m, 3H), 7.51 – 7.47 (m, 2H), 7.42 – 7.36 (m, 3H), 7.36 – 7.27 (m, 4H), 7.20 – 7.15 (m, 2H), 7.14 (q, $J = 1.3$ Hz, 2H), 7.10 – 7.07 (m, 2H), 6.90 (t, $J = 7.9$ Hz, 1H), 5.90 (s, 1H), 5.16 (s, 1H), 3.34 (d, $J = 13.4$ Hz, 1H), 3.00 (d, $J = 13.4$ Hz, 1H), 2.18 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.24, 161.56, 150.21, 137.28, 137.02, 134.26, 132.58, 129.15, 128.68, 128.24, 128.23, 127.30, $\delta$ 125.56 ($J = 4.66$ Hz), $\delta$ 124.40 ($J = 273.17$ Hz), 120.94, 119.96, $\delta$ 116.44 (q, $J = 29.23$ Hz), 62.69, 46.91, 42.01, 14.71. [$\alpha$]$D^{25}$ = 19 ($c = 1.0$ in CHCl$_3$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH = 85/15), 1.0 mL/min; Major enantiomer: $t_R = 8.0$ min, minor enantiomer: $t_R = 5.0$ min. 72:28 $dr$, 94% $ee$. HRMS (ESI) calcd for C$_{31}$H$_{25}$F$_3$N$_2$O$_2$Na $m/z$ [M + Na]$^+$: 537.1760, found: 537.1759.

(R)-4-benzyl-4-((S)-(2-hydroxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ha)

Compound was isolated as a white solid (73% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 9.82 (s, 1H), 7.67 (d, $J = 7.3$ Hz, 2H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.30 (m, 7H), 7.16 – 7.08 (m, 7H), 6.61 (t, $J = 8.0$ Hz, 1H), 5.13 (s, 1H), 3.30 (d, $J = 13.3$ Hz, 1H), 2.94 (d, $J = 13.2$ Hz, 1H), 2.15 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 174.34, 162.39, 154.11, 138.40, 137.29, 134.98, 130.92, 129.02, 128.81, 128.76, 128.26, 127.98, 127.69, 126.98, 126.76, 126.20, 125.03, 119.18, 119.06, 115.47, 62.48, 46.15, 40.81, 14.41. [$\alpha$]$D^{25}$ = 24 ($c = 1.0$ in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 31.2$ min, minor enantiomer: $t_R = 12.4$ min. 64:36 $dr$, 84% $ee$. HRMS (ESI) calcd for C$_{30}$H$_{26}$N$_2$O$_2$Na $m/z$ [M + Na]$^+$: 537.1760, found: 537.1759.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(m-tolyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ia)

Compound was isolated as a white solid (73% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 9.82 (s, 1H), 7.67 (d, $J = 7.3$ Hz, 2H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.30 (m, 7H), 7.16 – 7.08 (m, 7H), 6.61 (t, $J = 8.0$ Hz, 1H), 5.13 (s, 1H), 3.30 (d, $J = 13.3$ Hz, 1H), 2.94 (d, $J = 13.2$ Hz, 1H), 2.15 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 174.34, 162.39, 154.11, 138.40, 137.29, 134.98, 130.92, 129.02, 128.81, 128.76, 128.26, 127.98, 127.69, 126.98, 126.76, 126.20, 125.03, 119.18, 119.06, 115.47, 62.48, 46.15, 40.81, 14.41. [$\alpha$]$D^{25}$ = 24 ($c = 1.0$ in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 31.2$ min, minor enantiomer: $t_R = 12.4$ min. 64:36 $dr$, 84% $ee$. HRMS (ESI) calcd for C$_{30}$H$_{26}$N$_2$O$_2$Na $m/z$ [M + Na]$^+$: 469.1885, found: 469.1885.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(m-tolyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ia)
Compound was isolated as white solid (94% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (dd, $J = 8.2$, 1.4 Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.19 (t, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.03 – 6.96 (m, 7H), 6.86 (d, $J = 7.4$ Hz, 1H), 6.78 (t, $J = 8.1$ Hz, 1H), 6.67 (dd, $J = 8.1$, 1.3 Hz, 1H), 6.01 (s, 1H), 5.02 (s, 1H), 3.76 (s, 3H), 3.25 (d, $J = 13.6$ Hz, 1H), 3.03 (d, $J = 13.5$ Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.49, 161.70, 146.17, 143.60, 139.18, 137.98, 134.97, 129.21, 128.53, 128.34, 128.11, 127.98, 127.03, 125.80, 125.23, 124.41, 123.97, 129.09, 119.14, 109.23, 63.62, 55.96, 46.73, 40.69, 21.42, 15.11. [α]$^D_{25}$ = 4 (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 20.67$ min, minor enantiomer: $t_R = 49.90$ min. 96:4 dr, 99% ee. HRMS (ESI) calcd for C$_{30}$H$_{32}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 513.2149, found: 513.2148.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(p-tolyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ja)

Compound was isolated as colorless oil (94% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.45 (m, 4H), 7.34 – 7.30 (m, 2H), 7.18 – 7.13 (m, 3H), 7.12 (d, $J = 2.7$ Hz, 4H), 6.91 – 6.78 (m, 4H), 6.21 (s, 1H), 5.87 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.40 (d, $J = 13.6$ Hz, 1H), 3.26 (d, $J = 13.6$ Hz, 1H), 2.17 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.72, 162.30, 156.59, 146.14, 144.08, 137.59, 135.06, 129.26, 129.04, 128.50, 128.25, 128.16, 128.00, 126.93, 125.06, 124.61, 124.02, 120.69, 119.94, 118.74, 111.13, 109.14, 63.48, 55.94, 55.80, 40.85, 37.94, 14.77. [α]$^D_{25}$ = -13 (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 21.00$ min, minor enantiomer: $t_R = 25.16$ min. 96:4 dr, 99% ee. HRMS (ESI) calcd for C$_{30}$H$_{32}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 513.2149, found: 513.2141.

(R)-4-benzyl-4-((R)-(2-hydroxy-3-methoxyphenyl)(2-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ka)
Compound was isolated as a colorless oil (91% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.48 (dd, $J = 8.5$, 1.2 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.17 – 7.09 (m, 6H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.91 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1$, 1.4 Hz, 1H), 6.14 (s, 1H), 5.16 (s, 1H), 3.88 (s, 3H), 3.39 (d, $J = 13.6$ Hz, 1H), 3.16 (d, $J = 13.6$ Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.49, 161.73, 146.20, 143.57, 137.50, 136.77, 136.22, 134.94, 129.19, 129.16, 128.65, 128.52, 128.09, 127.02, 125.21, 124.66, 123.81, 120.08, 119.15, 63.75, 55.95, 46.40, 40.83, 15.16. \[\alpha\]D$_{25}$ = 4 (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 29.36$ min, minor enantiomer: $t_R = 32.49$ min. 93:7 dr, 99% ee. HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_4$Na m/z [M + Na]$^+$: 529.2098, found: 529.2095.

(R)-4-benzyl-4-(((S)-(2-hydroxy-3-methoxyphenyl)(3-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3la)

\[\text{MeC} \quad \text{OH} \quad \text{OMe} \quad \text{Bn} \quad \text{N}^\text{Ph} \]

Compound was isolated as colorless oil (93% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.50 (d, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.9$ Hz, 2H), 7.17 – 7.08 (m, 7H), 7.01 – 6.95 (m, 2H), 6.91 (t, $J = 8.1$ Hz, 1H), 6.80 (d, $J = 7.3$ Hz, 1H), 6.72 (dd, $J = 8.1$, 1.2 Hz, 2H), 6.14 (s, 1H), 5.16 (s, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 3.37 (d, $J = 13.5$ Hz, 1H), 3.15 (d, $J = 13.5$ Hz, 1H), 2.22 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.44, 161.67, 159.51, 146.19, 143.64, 140.81, 137.52, 134.84, 129.41, 129.20, 128.52, 128.10, 127.06, 125.18, 124.27, 123.87, 121.15, 119.92, 119.17, 114.33, 112.85, 109.29, 63.61, 55.97, 55.00, 46.69, 40.83, 15.13. $[^\alpha]D_{25} = -3$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 20.28$ min, minor enantiomer: $t_R = 36.74$ min. 95:5 dr, 99% ee. HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_4$Na m/z [M + Na]$^+$: 529.2089, found: 529.2093.

(R)-4-benzyl-4-(((S)-(2-hydroxy-3-methoxyphenyl)(4-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ma)

\[\text{MeC} \quad \text{OH} \quad \text{OMe} \quad \text{Bn} \quad \text{N}^\text{Ph} \]

Compound was isolated as a colorless oil (93% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.48 (dd, $J = 8.5$, 1.2 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.17 – 7.09 (m, 6H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.91 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1$, 1.4 Hz, 1H), 6.14 (s, 1H), 5.16 (s, 1H), 3.88 (s, 3H), 3.39 (d, $J = 13.6$ Hz, 1H), 3.16 (d, $J = 13.6$ Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.51, 161.74,
158.57, 146.22, 143.52, 137.47, 134.96, 131.30, 129.87, 129.16, 128.52, 128.10, 127.02, 125.22, 124.83, 123.69, 120.05, 119.16, 113.80, 109.18, 63.94, 55.94, 55.09, 45.93, 40.76, 15.16. \([\alpha]D_{25}^2 = 4 \text{ (c = 1.0 in } CH_2Cl_2)\). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH = 80/20), 0.7 mL/min; Major enantiomer: \(t_R = 30.42 \text{ min}, \) minor enantiomer: \(t_R = 51.01 \text{ min}. 87:13 \text{ dr}, 99\% ee. HRMS (ESI) calcd for C_{32}H_{30}N_2O_4Na [M + Na]^+ : 529.2098, found: 529.2093.

\((R)-4-(((R)-benzo[d][1,3]dioxol-4-yl(2-hydroxy-3-methoxyphenyl)methyl)-4-benzyl-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3na))\)

Compound was isolated as a colorless oil (83% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.70 \text{ (dd, } J = 8.1, 1.3 \text{ Hz, 1H), 7.50 – 7.43 \text{ (m, 2H), 7.34 – 7.30 \text{ (m, 2H), 7.14 \text{ (dt, J = 7.6, 4.8 Hz, 4H)}, 7.09 \text{ (dd, J = 7.4, 2.1 Hz, 2H), 6.95 – 6.86 \text{ (m, 3H), 6.80 \text{ (dd, J = 8.1, 1.2 Hz, 1H), 6.66 \text{ (d, J = 8.1 Hz, 1H), 6.14 \text{ (s, 1H), 5.85 \text{ (dd, J = 11.3, 1.5 Hz, 2H), 5.10 \text{ (s, 1H), 3.88 \text{ (s, 3H), 3.37 \text{ (d, J = 13.5 Hz, 1H), 3.09 \text{ (d, J = 13.6 Hz, 1H), 2.24 \text{ (s, 3H). 13C NMR (126 MHz, CDCl3)}\)}} \delta 174.43, 161.65, 147.58, 146.59, 146.22, 143.51, 137.43, 134.86, 132.97, 129.16, 128.56, 128.54, 128.11, 127.05, 125.29, 124.65, 123.56, 122.04, 120.11, 119.25, 109.33, 109.28, 108.08, 100.92, 63.88, 55.95, 46.27, 40.78, 15.18. \([\alpha]D_{25}^2 = 6 \text{ (c = 1.0 in } CH_2Cl_2\). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: \(t_R = 31.82 \text{ min}, \) minor enantiomer: \(t_R = 52.97 \text{ min. 88:12 \text{ dr}, 97\% ee. HRMS (ESI) calcd for C_{32}H_{28}N_2O_5Na [M + Na]^+ : 543.1890, found: 543.1886.}\)

\((R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(3-(trifluoromethoxy)phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3oa))\)

Compound was isolated as colorless oil (81% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.74 \text{ (dd, } J = 8.2, 1.4 Hz, 1H), 7.48 – 7.40 \text{ (m, 2H), 7.36 \text{ (d, J = 7.9 Hz, 1H), 7.31 \text{ (t, J = 8.0 Hz, 2H), 7.25 \text{ (dd, J = 17.4, 9.4 Hz, 2H), 7.15 \text{ (q, J = 6.4, 4.7 Hz, 4H)}, 7.10 \text{ (dd, J = 7.3, 2.0 Hz, 2H), 7.05 \text{ (d, J = 8.2 Hz, 1H), 6.94 \text{ (t, J = 8.1 Hz, 1H), 6.83 \text{ (dd, J = 8.1, 1.3 Hz, 1H), 6.13 \text{ (s, 1H), 5.19 \text{ (s, 1H), 3.89 \text{ (s, 3H), 3.41 \text{ (d, J = 13.6 Hz, 1H), 3.08 \text{ (d, J = 13.6 Hz, 1H), 2.22 \text{ (s, 3H). 13C NMR (126 MHz, CDCl3)}\)}} \delta 174.12, 161.16, 149.10, 146.30, 143.72, 141.54, 137.29, 134.62, 129.74, 129.17, 128.53, 128.20, 127.19, 127.09, 125.39, 123.67, 123.54, 121.73, 120.37 \text{ (q, J = 257.3 Hz, 120.02, 119.53, 119.43, 109.56, 63.68, 55.97, 46.18, 40.69, 15.06. \([\alpha]D_{25}^2 = 35 \text{ (c = 1.0 in } CH_2Cl_2\). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: \(t_R =\)
13.75 min, minor enantiomer: \( t_R = 19.64 \) min. 98:2 \( dR \), 99% ee. HRMS (ESI) calcd for C\(_{32}\)H\(_{27}\)F\(_3\)N\(_2\)O\(_4\)Na \( m/z \) [M + Na\(^+\)]: 583.1815, found: 583.1809.

\((R)-4\)-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(4-(trifluoromethoxy)phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3pa)

![Diagram of compound 3pa]

Compound was isolated as a colorless oil (89% yield) after flash column chromatography on silica-gel. \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.78 (dd, \( J = 8.2, 1.4 \) Hz, 1H), 7.42 (t, \( J = 9.1 \) Hz, 4H), 7.31 (t, \( J = 8.0 \) Hz, 2H), 7.18 – 7.13 (m, 4H), 7.13 – 7.10 (m, 2H), 7.07 (d, \( J = 8.2 \) Hz, 2H), 6.95 (t, \( J = 8.1 \) Hz, 1H), 6.83 (dd, \( J = 8.1, 1.4 \) Hz, 1H), 6.14 (s, 1H), 5.19 (s, 1H), 3.90 (s, 3H), 3.43 (d, \( J = 13.6 \) Hz, 1H), 3.06 (d, \( J = 13.6 \) Hz, 1H), 2.24 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 174.26, 161.29, 148.24, 146.32, 143.70, 137.85, 137.26, 134.75, 130.23, 129.15, 128.60, 128.22, 127.18, 125.50, 123.97, 123.69, 120.73, 120.36 (q, \( J = 257.3 \) Hz), 120.14, 119.40, 109.50, 63.80, 55.98, 45.79, 40.52, 15.08. \([\alpha]_D^{25} = 32 \) (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: \( t_R = 22.70 \) min, minor enantiomer: \( t_R = 25.78 \) min. 96:4 \( dr \), 99% ee. HRMS (ESI) calcd for C\(_{32}\)H\(_{27}\)F\(_3\)N\(_2\)O\(_4\)Na \( m/z \) [M + Na\(^+\)]: 583.1815, found: 583.1808.

\((R)-4\)-benzyl-4-((S)-(4-fluorophenyl)(2-hydroxy-3-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3qa)

![Diagram of compound 3qa]

Compound was isolated as a white solid (95% yield) after flash column chromatography on silica-gel. \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.76 (dd, \( J = 8.0, 1.3 \) Hz, 1H), 7.45 (dd, \( J = 8.7, 1.2 \) Hz, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.20 – 7.08 (m, 6H), 6.91 (dd, \( J = 9.6, 8.2 \) Hz, 3H), 6.82 (dd, \( J = 8.1, 1.3 \) Hz, 1H), 5.17 (s, 1H), 3.89 (s, 3H), 3.41 (d, \( J = 13.6 \) Hz, 1H), 3.09 (d, \( J = 13.6 \) Hz, 1H), 2.23 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 174.34, 161.84 (d, \( J = 246.2 \) Hz), 161.45, 146.02, 143.61, 137.34, 135.01 (d, \( J = 3.4 \) Hz), 134.81, 130.40 (d, \( J = 8.0 \) Hz), 129.14, 128.59, 128.17, 127.12, 125.38, 124.30, 123.64, 120.03, 119.31, 115.27 (d, \( J = 21.2 \) Hz), 109.37, 63.87, 55.96, 45.79, 40.63, 15.09. \([\alpha]_D^{25} = 39 \) (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 70/30), 1.0 mL/min; Major enantiomer: \( t_R = 12.82 \) min, minor enantiomer: \( t_R = 50.63 \) min. 93:7 \( dr \), 99% ee. HRMS (ESI) calcd for C\(_{31}\)H\(_{27}\)F\(_3\)Na \( m/z \) [M + Na\(^+\)]: 517.1898, found: 517.1894.

\((R)-4\)-benzyl-4-((S)-(4-chlorophenyl)(2-hydroxy-3-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ra)

![Diagram of compound 3ra]
Compound was isolated as a white solid (93% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.46 (dd, $J$ = 8.6, 1.2 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.22 – 7.16 (m, 3H), 7.16 – 7.12 (m, 3H), 7.10 (dd, $J$ = 7.4, 2.1 Hz, 2H), 6.92 (t, $J$ = 8.1 Hz, 1H), 6.81 (dd, $J$ = 8.1, 1.4 Hz, 1H), 6.13 (s, 1H), 5.16 (s, 1H), 3.89 (s, 3H), 3.40 (d, $J$ = 13.6 Hz, 1H), 3.10 (d, $J$ = 13.6 Hz, 1H), 2.22 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.24, 161.36, 146.26, 143.62, 137.81, 137.32, 134.68, 133.09, 130.15, 129.15, 128.60, 128.17, 127.15, 125.41, 123.98, 123.60, 120.03, 119.34, 109.44, 63.65, 55.97, 45.95, 40.69, 15.10. $[\alpha]_D^{25}$ = 11 ($c$ = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 70/30), 1.0 mL/min; Major enantiomer: $t_R$ = 20.00 min, minor enantiomer: $t_R$ = 24.35 min. 95:5 $d_r$, 99% ee. HRMS (ESI) calcd for C$_{31}$H$_{27}$ClN$_2$O$_3$Na m/z [M + Na]$^+$: 533.1602, found: 533.1596.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(2-(trifluoromethyl)phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3sa)

Compound was isolated as a white solid (89% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J$ = 7.7 Hz, 1H), 7.56 (dd, $J$ = 11.2, 7.6 Hz, 3H), 7.41 (t, $J$ = 7.7 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.17 (t, $J$ = 7.3 Hz, 1H), 7.09 (q, $J$ = 5.8, 5.2 Hz, 5H), 6.84 (h, $J$ = 7.3 Hz, 3H), 6.17 (s, 1H), 5.72 (s, 1H), 3.93 (s, 3H), 3.55 (d, $J$ = 13.4 Hz, 1H), 3.34 (d, $J$ = 13.3 Hz, 1H), 2.07 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.89, 161.48, 146.16, 143.80, 138.81, 137.54, 134.28, 132.16, 129.47, 128.69, 128.63, 128.27 (q, $J$ = 29.5 Hz), 127.95, 127.33, 127.14, 126.83 (q, $J$ = 6.3 Hz), 125.20, 124.88, 121.42, 124.21 (q, $J$ = 274.8 Hz), 119.65, 118.21, 109.43, 63.17, 56.05, 41.96, 41.84, 14.45. $[\alpha]_D^{25}$ = -125 ($c$ = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R$ = 8.55 min, minor enantiomer: $t_R$ = 10.94 min. 99:1 $d_r$, 99% ee. HRMS (ESI) calcd for C$_{32}$H$_{27}$F$_3$N$_2$O$_3$Na m/z [M + Na]$^+$: 567.1866, found: 567.1859.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(3-(trifluoromethyl)phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ta)
Compound was isolated as white solid (92% yield) after flash column chromatography on silica-gel. ¹H NMR (500 MHz, CDCl₃) δ 7.75 (dd, J = 8.2, 1.3 Hz, 1H), 7.68 (s, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.36 – 7.29 (m, 3H), 7.16 (q, J = 6.4, 5.1 Hz, 4H), 7.11 (dd, J = 7.4, 2.0 Hz, 2H), 6.95 (t, J = 8.1 Hz, 1H), 6.83 (dd, J = 8.1, 1.4 Hz, 1H), 6.15 (s, 1H), 5.25 (s, 1H), 3.89 (s, 3H), 3.43 (d, J = 13.6 Hz, 1H), 3.10 (d, J = 13.6 Hz, 1H), 2.22 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.11, 161.15, 146.29, 143.72, 140.30, 137.23, 134.63, 132.04, 130.73 (q, J = 32.0 Hz), 129.16, 128.97, 128.56, 128.22, 127.20, 125.70 (q, J = 3.8 Hz), 125.45, 124.12 (q, J = 3.7 Hz), 123.90 (q, J = 272.5 Hz), 123.58, 123.55, 120.04, 119.47, 109.58, 63.63, 55.97, 46.32, 40.54, 15.03. [α]D²⁵ = 20 (c = 1.0 in CH₂Cl₂). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 13.37 min, minor enantiomer: t_R = 18.64 min. 97:3 dr, 99% ee. HRMS (ESI) calcd for C₃₂H₂₇F₃N₂O₃Na m/z [M + Na]+: 567.1866, found: 567.1856. (R)-4-benzyl-4-((S)-2-hydroxy-3-methoxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ua)

Compound was isolated as a colorless oil (90% yield) after flash column chromatography on silica-gel. ¹H NMR (500 MHz, CDCl₃) δ 7.72 (dd, J = 8.1, 1.4 Hz, 1H), 7.50 (q, J = 8.4 Hz, 4H), 7.46 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 7.19 – 7.13 (m, 3H), 7.11 (dd, J = 7.4, 2.0 Hz, 2H), 6.94 (t, J = 8.1 Hz, 1H), 6.83 (dd, J = 8.1, 1.4 Hz, 1H), 6.14 (s, 1H), 5.25 (s, 1H), 3.89 (s, 3H), 3.43 (d, J = 13.5 Hz, 1H), 3.10 (d, J = 13.6 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.14, 161.19, 146.31, 143.73, 143.36, 137.25, 134.57, 129.17, 129.41 (q, J = 32.6 Hz), 128.63, 128.22, 127.23, 125.41 (q, J = 3.7 Hz), 123.98 (q, J = 272.7 Hz), 123.69, 123.54, 120.07, 119.44, 109.60, 63.52, 55.99, 46.32, 40.66, 15.09. [α]D²⁵ = 21 (c = 1.0 in CH₂Cl₂). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 95/5), 1.0 mL/min; Major enantiomer: t_R = 28.40 min, minor enantiomer: t_R = 30.18 min. 97:3 dr, 98% ee. HRMS (ESI) caled for C₃₂H₂₇F₃N₂O₃Na m/z [M + Na]+: 567.1866, found: 567.1860. (R)-4-benzyl-4-((S)-3,5-bis(trifluoromethyl)phenyl)(2-hydroxy-3-methoxyphenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3va)

Compound was isolated as a colorless oil (95% yield) after flash column chromatography on silica-gel. ¹H NMR (500 MHz, CDCl₃) δ 7.88 (s, 2H), 7.83 (d, J = 8.1 Hz, 1H), 7.71 (s, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.19 – 7.14 (m, 4H), 7.10 (dd, J = 7.1, 2.3 Hz, 2H), 6.99 (t, J = 8.1 Hz, 1H), 6.86 (dd, J = 8.2, 1.3 Hz, 1H), 6.14 (s, 1H), 5.30 (s, 1H), 3.91 (s, 3H),
3.46 (d, J = 13.6 Hz, 1H), 3.05 (d, J = 13.7 Hz, 1H), 2.23 (s, 3H). $^{13}$C NMR (126 MHz, CDCl<sub>3</sub>) δ 173.81, 160.71, 146.38, 143.78, 141.94, 137.00, 134.39, 131.71 (q, J = 33.4 Hz) 129.14, 129.01 (q, J = 2.65 Hz), 128.58, 128.34, 127.35, 125.64, 123.26, 123.08 (q, J = 273.42 Hz), 122.72, 121.23-121.41 (m), 119.96, 119.86, 109.93, 63.54, 56.02, 46.06, 40.33, 14.97. The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 95/5), 1.0 mL/min; Major enantiomer: $t_R = 12.09$ min, minor enantiomer: $t_R = 15.96$ min. 97:3 dr, 99% ee. HRMS (ESI) calcd for C<sub>33</sub>H<sub>26</sub>F<sub>6</sub>N<sub>2</sub>O<sub>3</sub>Na m/z [M + Na]<sup>+</sup>: 635.1740, found: 635.1729.

$^{(R)}$-4-((S)-[1,1'-biphenyl]-4-yl(2-hydroxy-3-methoxyphenyl)methyl)-4-benzyl-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3wa)

Compound was isolated as white solid (90% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 7.4 Hz, 2H), 7.48 (dd, J = 7.5, 4.3 Hz, 6H), 7.41 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.9 Hz, 3H), 7.15 (p, J = 6.3 Hz, 6H), 6.95 (t, J = 8.1 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 6.17 (s, 1H), 5.24 (s, 1H), 3.90 (s, 3H), 3.43 (d, J = 13.5 Hz, 1H), 3.17 (d, J = 13.6 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl<sub>3</sub>) δ 174.44, 161.63, 146.24, 143.67, 140.52, 139.98, 138.26, 137.45, 136.75, 134.88, 129.21, 128.65, 128.57, 128.15, 127.19, 127.09, 126.94, 125.32, 124.38, 123.87, 120.15, 119.26, 109.34, 63.76, 55.98, 46.39, 40.78, 15.20. [α]<sub>D</sub><sup>25</sup> = -51 (c = 1.0 in CH<sub>2</sub>Cl<sub>2</sub>). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 25.44$ min, minor enantiomer: $t_R = 24.17$ min. 95:5 dr, 99% ee. HRMS (ESI) calcd for C<sub>37</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Na m/z [M + Na]<sup>+</sup>: 575.2305, found: 575.2296.

$^{(R)}$-4-benzyl-4-(((S)-(2-hydroxy-3-methoxyphenyl)(naphthalen-1-yl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3xa)

Compound was isolated as white solid (91% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.42 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.52 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.22 – 7.11 (m, 7H), 6.86 – 6.75 (m, 2H), 6.37 (s, 1H), 6.08 (s, 1H), 3.91 (s, 3H), 3.54 (d, J = 13.2 Hz, 1H), 3.38 (d, J = 13.2 Hz, 1H), 1.96 (s, 3H). $^{13}$C NMR (126 MHz, CDCl<sub>3</sub>) δ 174.34, 161.93, 145.88, 143.26, 137.67, 136.43, 134.42, 134.04, 131.77, 129.42, 128.93, 128.61, 127.96, 127.95, 127.11, 126.64, 125.54, 125.37, 125.23, 125.15, 123.89, 123.01, 122.70, 119.83, 118.82, 109.31, 62.75, 55.98, 41.80, 41.47, 14.60. [α]<sub>D</sub><sup>25</sup> = -182 (c = 1.0 in CH<sub>2</sub>Cl<sub>2</sub>).
enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 20.70$ min, minor enantiomer: $t_R = 27.63$ min. 98:2 $dr$, 99% $ee$. HRMS (ESI) calecd for C$_{35}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 549.2153, found: 549.2149.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(naphthalen-2-yl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ya)

![Chemical structure of 3ya](image)

Compound was isolated as white solid (95% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (s, 1H), 7.78 – 7.74 (m, 1H), 7.73 – 7.67 (m, 2H), 7.63 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.54 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.50 (dd, $J = 8.6, 1.1$ Hz, 2H), 7.43 (dt, $J = 6.2, 3.4$ Hz, 2H), 7.36 – 7.31 (m, 2H), 7.19 – 7.13 (m, 6H), 6.91 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1, 1.4$ Hz, 1H), 6.18 (s, 1H), 5.38 (s, 1H), 3.88 (s, 3H), 3.45 (d, $J = 13.4$ Hz, 1H), 3.27 (d, $J = 13.6$ Hz, 1H), 2.22 (s, 3H). $^1$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.43, 161.68, 146.20, 143.65, 137.47, 136.97, 134.77, 134.29, 132.45, 129.26, 128.58, 128.17, 128.12, 127.92, 127.40, 127.25, 127.10, 127.09, 126.02, 125.31, 124.06, 124.04, 120.14, 119.18, 109.33, 63.50, 55.97, 46.91, 40.99, 15.18. $[\alpha]_D^{25} = -75$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 29.37$ min, minor enantiomer: $t_R = 32.88$ min. 94:6 $dr$, 99% $ee$. HRMS (ESI) calecd for C$_{35}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 549.2153, found: 549.2148.

(R)-4-benzyl-4-((S)-1-(2-hydroxy-3-methoxyphenyl)-3-phenylprop-2-yn-1-yl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3za)

![Chemical structure of 3za](image)

Compound was isolated as a colorless oil (78% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.7$ Hz, 2H), 7.40 – 7.37 (m, 2H), 7.30 – 7.27 (m, 5H), 7.23 – 7.16 (m, 7H), 6.89 (t, $J = 8.0$ Hz, 1H), 6.80 (dd, $J = 8.0, 1.4$ Hz, 1H), 6.17 (s, 1H), 5.03 (s, 1H), 3.86 (s, 3H), 3.52 (d, $J = 13.7$ Hz, 1H), 3.35 (d, $J = 13.7$ Hz, 1H), 2.51 (s, 3H). $^1$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.21, 160.71, 146.69, 143.35, 137.42, 134.90, 131.63, 129.20, 128.51, 128.28, 128.24, 128.13, 125.11, 122.82, 122.75, 121.53, 119.77, 119.53, 110.35, 86.75, 84.53, 63.96, 56.06, 39.20, 35.43, 15.88. $[\alpha]_D^{25} = -47$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 60/40), 0.7 mL/min; Major enantiomer: $t_R = 14.92$ min, minor enantiomer: $t_R = 42.04$ min. 80:20 $dr$, 86% $ee$. HRMS (ESI) calecd for C$_{37}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 573.2149, found: 573.2140.
(R)-4-benzyl-4-((S)-1-(2-hydroxy-3-methoxyphenyl)ethyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3Aa)

Compound was isolated as a colorless oil (40% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.6$ Hz, 2H), 7.35 – 7.32 (m, 3H), 7.17 – 7.13 (m, 5H), 7.06 – 7.02 (m, 2H), 6.95 (t, $J = 8.0$ Hz, 1H), 6.13 (s, 1H), 3.92 (s, 3H), 3.91 (q, $J = 8.0$ Hz 1H), 3.12 (d, $J = 13.7$ Hz, 1H), 2.98 (d, $J = 13.7$ Hz, 1H), 2.30 (s, 3H), 1.25 (d, $J = 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.36, 162.29, 146.19, 143.73, 137.65, 135.52, 128.99, 128.60, 128.14, 127.04, 126.90, 125.02, 125.02, 124.74, 119.56, 119.34, 109.27, 64.19, 56.02, 38.99, 16.07, 14.87, 14.65. $[\alpha]_D^{25} = 94$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 80/20), 1.0 mL/min; Major enantiomer: $t_R$ = 20.56 min, minor enantiomer: $t_R$ = 13.33 min. 60:40 dr, 90% ee. HRMS (ESI) calcd for C$_{26}$H$_{26}$N$_2$O$_3$Na m/z [M + Na]$^+$: 437.1836, found: 437.1828.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (3ab)

Compound was isolated as a white solid (85% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 2H), 7.19 – 7.16 (m, 1H), 7.15 – 7.08 (m, 7H), 6.90 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1$, 1.3 Hz, 1H), 5.16 (s, 1H), 3.89 (s, 3H), 3.39 (d, $J = 13.5$ Hz, 1H), 3.11 (d, $J = 13.6$ Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.29, 161.45, 146.24, 143.66, 139.26, 135.04, 135.04, 134.97, 132.24, 129.12, 128.84, 128.47, 128.13, 127.20, 127.06, 124.48, 123.96, 120.25, 119.18, 109.27, 63.65, 55.99, 46.75, 40.76, 20.98, 15.15. $[\alpha]_D^{25} = 34$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R$ = 26.31 min, minor enantiomer: $t_R$ = 52.49 min. 97:3 dr, 97% ee. HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_3$Na m/z [M + Na]$^+$: 513.2149, found: 513.2139.

(R)-4-benzyl-2-(2-ethylphenyl)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2,4-dihydro-3H-pyrazol-3-one (3ac)

Compound was isolated as a colorless oil (77% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.1$ Hz, 1H), 7.54 – 7.48 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.16 (m, 4H), 7.03 (td, $J = 7.5$, 1.9 Hz, 1H), 6.94 (t, $J = 8.1$ Hz, 1H), 6.82 (dd, $J = 8.1$, 1.3 Hz, 1H), 6.29 (dd, $J = 7.9$, 1.2 Hz, 1H), 6.26 (s, 1H), 5.18 (s, 1H), 3.89 (s, 3H), 3.44 (d, $J = 13.5$ Hz, 1H), 3.03 (d, $J = 13.5$ Hz, 1H), 2.38 (s, 3H), 1.87 (qd, $J =
7.6, 4.4 Hz, 2H), 0.94 (t, J = 7.6 Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 174.82, 160.90, 146.50, 143.85, 141.09, 138.87, 135.13, 135.08, 129.85, 129.49, 128.46, 128.37, 128.35, 128.34, 127.24, 127.14, 126.55, 124.90, 124.89, 119.35, 119.34, 63.58, 63.00, 46.75, 40.40, 23.27, 15.51, 14.07. [\(\alpha\)]\(_{D}\)\(^{25}\) = 55 (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: \(t_R\) = 16.39 min, minor enantiomer: \(t_R\) = 21.40 min. 97:3 \(dr\), 99% ee. HRMS (ESI) calcd for C\(_{33}\)H\(_{32}\)N\(_2\)O\(_3\)Na m/z [M + Na]\(^+\): 527.2305, found: 527.2297.

**(R)**-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-2-(4-methoxyphenyl)-5-methyl-2,4-dihydro-3H-pyrazol-3-one (3ad)

Compound was isolated as a white solid (93% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.71 (d, \(J = 8.1\) Hz, 1H), 7.44 – 7.39 (m, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.10 (m, 6H), 6.91 (t, \(J = 8.1\) Hz, 1H), 6.85 – 6.82 (m, 2H), 6.80 (dd, \(J = 8.1, 1.2\) Hz, 1H), 5.17 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.11 (d, \(J = 13.5\) Hz, 1H), 2.21 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 174.22, 161.41, 157.36, 146.28, 143.69, 139.27, 135.01, 130.71, 129.29, 128.88, 128.46, 128.14, 127.22, 127.08, 124.51, 123.94, 122.28, 119.19, 113.84, 109.29, 63.59, 55.99, 55.43, 46.71, 40.69, 15.15. [\(\alpha\)]\(_{D}\)\(^{25}\) = 36 (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: \(t_R\) = 25.55 min, minor enantiomer: \(t_R\) = 41.21. 97:3 \(dr\), 99% ee. HRMS (ESI) calcd for C\(_{32}\)H\(_{30}\)N\(_2\)O\(_4\)Na m/z [M + Na]\(^+\): 529.2098, found: 529.2091.

**(R)**-4-benzyl-2-(3-bromophenyl)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2,4-dihydro-3H-pyrazol-3-one (3ae)

Compound was isolated as a colorless oil (78% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.70 (t, \(J = 1.9\) Hz, 1H), 7.60 (d, \(J = 8.1\) Hz, 1H), 7.52 (ddd, \(J = 8.2, 2.1, 1.0\) Hz, 1H), 7.38 – 7.34 (m, 2H), 7.27 – 7.15 (m, 5H), 7.14 – 7.11 (m, 3H), 7.06 (dd, \(J = 7.2, 2.3\) Hz, 2H), 6.91 (t, \(J = 8.1\) Hz, 1H), 6.81 (ddd, \(J = 8.1, 1.3\) Hz, 1H), 6.08 (s, 1H), 5.17 (s, 1H), 3.89 (s, 3H), 3.37 (d, \(J = 13.6\) Hz, 1H), 3.14 (d, \(J = 13.6\) Hz, 1H), 2.21 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 174.53, 162.10, 146.21, 143.61, 139.06, 138.60, 134.65, 129.86, 129.12, 128.72, 128.53, 128.17, 127.95, 127.30, 127.18, 124.18, 123.72, 122.30, 122.20, 119.19, 117.85, 109.30, 63.94, 55.99, 46.64, 40.86, 15.15. [\(\alpha\)]\(_{D}\)\(^{25}\) = 27 (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: \(t_R\) = 21.93 min, minor enantiomer: \(t_R\) = 75.67 min. 96:4 \(dr\), 99% ee. HRMS (ESI) calcd for C\(_{31}\)H\(_{27}\)BrN\(_2\)O\(_3\)Na m/z [M + Na]\(^+\): 577.1097, found: 577.1090.

**(R)**-4-benzyl-2-(4-bromophenyl)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2,4-dihydro-3H-pyrazol-3-one (3af)
Compound was isolated as a white solid (85% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.1$ Hz, 1H), 7.41 (s, 4H), 7.07 – 7.04 (m, 2H), 6.90 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1$, 1.4 Hz, 1H), 6.08 (s, 1H), 5.16 (s, 1H), 3.89 (s, 3H), 3.37 (d, $J = 13.5$ Hz, 1H), 3.13 (d, $J = 13.6$ Hz, 1H), 2.20 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.44, 162.05, 146.23, 143.64, 139.09, 136.54, 134.73, 131.57, 129.14, 128.76, 128.52, 128.16, 127.30, 127.16, 124.23, 123.73, 121.08, 119.20, 118.03, 109.31, 63.92, 56.00, 46.66, 40.82, 15.19. $[\alpha]_D^{25} = 40$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: $t_R = 10.36$ min, minor enantiomer: $t_R = 9.70$ min. 89:11 $dr$, 98% ee. HRMS (ESI) calcd for C$_{31}$H$_{27}$BrN$_2$O$_3$Na $m/z$ [M + Na]$^+$: 577.1097, found: 577.1094.

(R)-4-benzyl-4-(S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-(perfluorophenyl)-2,4-dihydro-3H-pyrazol-3-one (3ag)

Compound was isolated as white solid (95% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.42 – 7.16 (m, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 2H), 7.19 – 7.16 (m, 1H), 7.15 – 7.08 (m, 7H), 6.90 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.1$, 1.3 Hz, 1H), 5.16 (s, 1H), 3.89 (s, 3H), 3.39 (d, $J = 13.5$ Hz, 1H), 3.11 (d, $J = 13.6$ Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.74, 163.37, 146.23, 144.64 – 144.43 (m), 143.63, 142.54 – 142.34 (m), 140.27 – 140.00 (m), 138.80 – 138.56 (m), 138.59, 136.88 – 136.45 (m), 134.13, 129.36, 128.84, 128.62, 128.38, 124.08, 123.54, 119.39, 111.91 – 111.53 (m), 109.37, 62.74, 55.97, 46.66, 40.78, 15.35. $[\alpha]_D^{25} = 1$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 10.46$ min, minor enantiomer: $t_R = 9.70$ min. 89:11 $dr$, 99% ee. HRMS (ESI) calcd for C$_{31}$H$_{23}$F$_5$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 589.1521, found: 589.1511.

(R)-4-benzyl-4-(S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-(naphthalen-2-yl)-2,4-dihydro-3H-pyrazol-3-one (3ah)

Compound was isolated as white solid (94% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 2.0$ Hz, 1H), 7.84 – 7.78 (m, 3H), 7.73 – 7.67 (m, 2H), 7.45 (dd, $J = 7.9$, 1.5 Hz, 4H), 7.24 – 7.21 (m, 2H), 7.20 – 7.16 (m, 1H), 7.16 – 7.11 (m, 5H), 6.95 (t, $J = 8.1$ Hz, 1H), 6.82 (dd, $J = 8.0$, 1.3 Hz, 1H), 6.17 (s, 1H), 5.24 (s, 1H), 3.89 (s, 3H),
3.19 (d, J = 13.6 Hz, 1H), 2.27 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.69, 161.92, 146.27, 143.70, 139.27, 133.41, 131.15, 129.24, 128.85, 128.56, 128.38, 128.21, 127.99, 127.55, 127.29, 127.15, 126.25, 125.31, 124.42, 123.92, 119.25, 117.02, 109.33, 63.93, 56.01, 46.81, 40.94, 15.25. $\text{[\alpha]}_2^{D} = 53$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 9.75$ min, minor enantiomer: $t_R = 17.67$ min. 95:5 dr, 99% ee.

### HRMS (ESI) calcd for C$_{35}$H$_{30}$N$_2$O$_3$Na m/z [M + Na]$^+$: 549.2149, found: 549.2135.

(R)-4-benzyl-5-ethyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ai)

Compound was isolated as a colorless oil (89% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.24 – 7.19 (m, 2H), 7.19 – 7.11 (m, 5H), 7.08 (dd, $J = 7.4$, 2.1 Hz, 2H), 6.91 (t, $J = 8.1$ Hz, 1H), 6.80 (dd, $J = 8.0$, 1.4 Hz, 1H), 6.15 (s, 1H), 5.20 (s, 1H), 5.89 (s, 3H), 3.38 (d, $J = 13.6$ Hz, 1H), 3.16 (d, $J = 13.6$ Hz, 1H), 2.60 (q, $J = 7.3$ Hz, 2H), 1.10 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.77, 165.33, 146.19, 143.64, 139.48, 137.70, 135.00, 129.20, 128.74, 128.51, 128.43, 128.06, 127.11, 127.01, 125.15, 124.55, 124.05, 120.09, 119.13, 109.22, 63.70, 55.96, 46.78, 41.12, 22.04, 8.60. $\text{[\alpha]}_2^{D} = 32$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 9.16$ min, minor enantiomer: $t_R = 15.1$ min. 98:2 dr, 99% ee.

### HRMS (ESI) calcd for C$_{32}$H$_{30}$N$_2$O$_3$Na m/z [M + Na]$^+$: 513.2149, found: 513.2135.

(R)-4-benzyl-5-isopropyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3aj)

Compound was isolated as a colorless oil (85% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 7.8$ Hz, 2H), 7.40 – 7.34 (m, 3H), 7.28 (d, $J = 7.2$ Hz, 2H), 7.22 – 7.14 (m, 4H), 7.15 – 7.07 (m, 5H), 6.80 (dd, $J = 8.0$, 1.4 Hz, 1H), 6.29 (s, 1H), 5.89 (s, 1H), 3.34 (d, $J = 14.0$ Hz, 1H), 3.30 (d, $J = 14.0$ Hz, 1H), 2.93 (hept, $J = 6.9$ Hz, 1H), 1.15 (d, $J = 6.8$ Hz, 3H), 1.06 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.77, 169.16, 146.09, 143.59, 140.61, 137.83, 135.17, 129.37, 128.61, 128.46, 128.28, 127.95, 126.95, 126.82, 125.34, 125.13, 124.99, 119.92, 119.07, 109.11, 62.94, 56.00, 46.36, 41.33, 28.43, 21.90, 21.26. $\text{[\alpha]}_2^{D} = -44$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 25.58$ min, minor enantiomer: $t_R = 54.29$ min. 97:3 dr, 99% ee.

### HRMS (ESI) calcd for C$_{33}$H$_{30}$N$_2$O$_3$Na m/z [M + Na]$^+$: 527.2305, found: 527.2293.
Compound was isolated as a colorless oil (82% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13 (dd, $J = 6.6$, 3.2 Hz, 2H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.52 (dd, $J = 5.0$, 1.9 Hz, 3H), 7.49 (dt, $J = 8.6$, 1.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.22 – 7.18 (m, 3H), 7.07 (dd, $J = 5.1$, 1.9 Hz, 3H), 7.03 – 6.97 (m, 6H), 6.86 (dd, $J = 8.1$, 1.2 Hz, 1H), 6.33 (s, 1H), 5.79 (s, 1H), 3.92 (s, 3H), 3.69 (d, $J = 13.7$ Hz, 1H), 3.53 (d, $J = 13.7$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 175.11, 159.13, 146.32, 144.04, 138.72, 137.36, 134.94, 131.69, 129.98, 129.42, 129.06, 128.67, 128.54, 128.05, 127.88, 127.04, 127.03, 126.88, 125.59, 124.59, 124.30, 120.49, 119.20, 109.40, 64.06, 56.00, 46.58, 41.29. $[\alpha]_D^{25} = -44$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 12.82$ min, minor enantiomer: $t_R = 50.62$ min. 93:7 dr, 99% ee. HRMS (ESI) calcd for C$_{36}$H$_{30}$N$_2$O$_3$Na $m/z$ [M + Na]$^+$: 561.2149, found: 561.2141.

(R)-4-benzyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3al)

Compound was isolated as a colorless oil (82% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10 – 8.07 (m, 2H), 7.97 – 7.91 (m, 1H), 7.51 – 7.46 (m, 2H), 7.35 – 7.31 (m, 2H), 7.23 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 7.08 (dt, $J = 4.8$, 1.7 Hz, 3H), 7.06 – 7.03 (m, 3H), 7.03 – 6.96 (m, 6H), 6.85 (dd, $J = 8.1$, 1.3 Hz, 1H), 6.37 (s, 1H), 5.76 (s, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.63 (d, $J = 13.7$ Hz, 1H), 3.51 (d, $J = 13.7$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.96, 160.91, 158.93, 146.33, 144.04, 138.76, 137.43, 135.04, 129.43, 129.10, 128.69, 128.62, 128.50, 128.03, 127.85, 127.00, 126.83, 125.45, 124.63, 124.39, 124.36, 120.44, 114.08, 109.39, 64.01, 56.02, 55.32, 46.72, 41.21. $[\alpha]_D^{25} = -52$ (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R = 19.96$ min, minor enantiomer: $t_R = 35.47$ min. 95:5 dr, 99% ee. HRMS (ESI) calcd for C$_{37}$H$_{32}$N$_2$O$_4$Na $m/z$ [M + Na]$^+$: 591.2254, found: 591.2250.

(R)-4-benzyl-5-(4-fluorophenyl)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3am)
Compound was isolated as a colorless oil (79% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13 – 8.09 (m, 2H), 7.88 (d, $J$ = 8.1 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.18 (m, 5H), 7.09 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.06 – 6.98 (m, 6H), 6.86 (dd, $J$ = 8.1, 1.3 Hz, 1H), 6.28 (s, 1H), 5.72 (s, 1H), 3.92 (s, 3H), 3.64 (d, $J$ = 13.7 Hz, 1H), 3.52 (d, $J$ = 13.7 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.90, $\delta$ 163.65 (d, $J$ = 251.4 Hz), 158.21, 146.11, 143.66, 139.00, 137.45, 136.52, 133.75, 130.48, 128.79, 128.58, 128.56, 128.39, 127.20, 126.88, 125.68, 125.27, 124.58, 123.88, 120.13, 119.19, 109.22, 63.26, 55.96, 46.86, 35.66, 20.04, 15.08. $[\alpha]_D^{25}$ = -45 (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: $t_R$ = 22.50 min, minor enantiomer: $t_R$ = 29.53 min. 97:3 dr, 99% ee. HRMS (ESI) calcd for C$_{36}$H$_{29}$FN$_2$O$_3$Na $m/z$ [M+Na]$^+$: 579.2054, found: 579.2044. 

(R)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-4-(2-methylbenzyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3an)

Compound was isolated as a colorless oil (84% yield) after flash column chromatography on silica-gel. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J$ = 8.0 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.34 – 7.29 (m, 2H), 7.21 (dd, $J$ = 8.2, 6.4 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.07 (d, $J$ = 7.5 Hz, 1H), 7.03 (td, $J$ = 7.5, 6.8, 2.5 Hz, 1H), 6.98 – 6.90 (m, 3H), 6.81 (dd, $J$ = 8.0, 1.4 Hz, 1H), 6.13 (s, 1H), 5.18 (s, 1H), 3.89 (s, 3H), 3.45 (d, $J$ = 14.5 Hz, 1H), 3.21 (d, $J$ = 14.5 Hz, 1H), 2.29 (s, 3H), 2.19 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.78, 161.84, 146.11, 143.66, 139.00, 137.45, 136.52, 133.75, 130.48, 128.79, 128.58, 128.56, 128.39, 127.20, 126.88, 125.68, 125.27, 124.58, 123.88, 120.13, 119.19, 109.22, 63.26, 55.96, 46.86, 35.66, 20.04, 15.08. $[\alpha]_D^{25}$ = -4 (c = 1.0 in CH$_2$Cl$_2$). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: $t_R$ = 19.70 min, minor enantiomer: $t_R$ = 43.00 min. 90:10 dr, 99% ee. HRMS (ESI) calcd for C$_{36}$H$_{29}$FN$_2$O$_3$Na $m/z$ [M+Na]$^+$: 513.2149, found: 513.2151. 

(R)-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-4-(4-methylbenzyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ao)
Compound was isolated as a colorless oil (95% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.67\) (dd, \(J = 8.1, 1.4\) Hz, 1H), 7.47 (dd, \(J = 8.6, 1.2\) Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 6.99 (d, \(J = 8.1\) Hz, 2H), 7.00 – 6.89 (m, 3H), 6.80 (dd, \(J = 8.0, 1.4\) Hz, 1H), 6.15 (s, 1H), 5.17 (s, 1H), 3.88 (s, 3H), 3.37 (d, \(J = 13.6\) Hz, 1H), 3.10 (d, \(J = 13.6\) Hz, 1H), 2.21 (s, 3H), 2.21 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 174.54, 161.78, 146.17, 143.59, 139.20, 136.53, 131.72, 128.99, 128.82, 128.77, 128.52, 128.43, 127.16, 125.23, 124.38, 123.82, 120.10, 119.12, 109.19, 63.75, 55.92, 46.71, 40.36, 20.93, 15.15. \([\alpha]_D^{25} = 39\) (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: \(t_R = 19.16\) min, minor enantiomer: \(t_R = 37.45\) min. 98:2 \(d_r\), 99% ee. HRMS (ESI) calcd for C\(_{32}\)H\(_{30}\)N\(_2\)O\(_3\)Na \(m/z\) [M+Na]+: 513.2149, found: 513.2148.

(\(R\))-4-(2-fluorobenzyl)-4-(\((S)\)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ap)

Compound was isolated as a colorless oil (94% yield) after flash column chromatography on silica-gel. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.64\) (dd, \(J = 8.2, 1.4\) Hz, 1H), 7.50 (dd, \(J = 8.6, 1.2\) Hz, 2H), 7.42 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.22 (t, \(J = 7.3\) Hz, 2H), 7.20 – 7.14 (m, 3H), 7.12 – 7.05 (m, 1H), 6.99 – 6.84 (m, 3H), 6.80 (dd, \(J = 8.1, 1.4\) Hz, 1H), 6.17 (s, 1H), 5.22 (s, 1H), 3.89 (s, 3H), 3.54 (d, \(J = 13.8\) Hz, 1H), 3.21 – 3.14 (m, 1H), 2.21 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 174.34, 160.78\) (d, \(J = 244.7\) Hz), 162.27, 146.17, 143.63, 139.18, 137.38, 131.64 (d, \(J = 3.9\) Hz), 128.83 (d, \(J = 8.6\) Hz), 128.66, 128.57, 128.51, 127.22, 124.02, 124.00 (d, \(J = 36.1\) Hz), 123.83, 121.92 (d, \(J = 15.4\) Hz), 119.95, 119.11, 115.09 (d, \(J = 23.1\) Hz), 109.22, 63.17, 55.94, 46.56, 32.70, 14.47. \([\alpha]_D^{25} = 9.0\) (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 95/5), 0.7 mL/min; Major enantiomer: \(t_R = 18.42\) min, minor enantiomer: \(t_R = 45.23\) min. 98:2 \(d_r\), 99% ee. HRMS (ESI) calcd for C\(_{31}\)H\(_{27}\)FN\(_2\)O\(_2\)Na \(m/z\) [M+Na]+: 517.1890, found:517.1895.

(\(R\))-4-(\((S)\)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-4,5-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3aq)
Compound was isolated as a colorless oil (81% yield) after flash column chromatography on silica-gel.\(^1\)\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.76 (dd, \(J = 8.7, 1.2\) Hz, 2H), 7.54 (dd, \(J = 8.0, 1.4\) Hz, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 7.23 – 7.15 (m, 4H), 6.86 (t, \(J = 8.0\) Hz, 1H), 6.77 (dd, \(J = 8.1, 1.4\) Hz, 1H), 6.03 (s, 1H), 4.99 (s, 1H), 3.87 (s, 3H), 2.17 (s, 3H), 1.44 (s, 3H).\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 175.57, 164.04, 146.18, 143.58, 139.08, 137.91, 128.70, 128.35, 127.14, 125.01, 124.50, 123.27, 119.37, 119.05, 109.17, 57.40, 55.92, 46.73, 20.81, 14.23. \([\alpha]\r{D}\)\(_{25}^2\) = -100 (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: \(t_R = 21.43\) min, minor enantiomer: \(t_R = 23.25\) min. 92:8 \(dR\), 97% ee. HRMS (ESI) calcd for C\(_{25}\)H\(_{24}\)N\(_2\)O\(_3\)Na m/z \([M+Na]^+\): 423.1679, found: 423.1677.

\((R)-4\)-ethyl-4-((S)-(2-hydroxy-3-methoxyphenyl)(phenyl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (3ar)

Compound was isolated as a colorless oil (85% yield) after flash column chromatography on silica-gel.\(^1\)\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.79 – 7.72 (m, 2H), 7.58 (dd, \(J = 8.1, 1.3\) Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.21 – 7.17 (m, 3H), 7.15 (dd, \(J = 8.4, 6.0\) Hz, 1H), 6.86 (t, \(J = 8.1\) Hz, 1H), 6.76 (dd, \(J = 8.0, 1.4\) Hz, 1H), 6.03 (s, 1H), 5.00 (s, 1H), 3.87 (s, 3H), 2.15 (s, 3H), 2.09 – 2.04 (dd, \(J = 14.0, 7.3\) Hz, 1H), 1.87 (dd, \(J = 14.0, 7.3\) Hz, 1H), 0.70 (s, \(J = 7.5\) Hz, 3H).\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 174.85, 162.46, 146.13, 143.56, 139.24, 137.74, 128.71, 128.69, 128.37, 127.12, 125.09, 124.58, 123.50, 119.50, 119.02, 109.10, 63.08, 55.92, 46.70, 27.51, 14.41, 8.44. \([\alpha]\r{D}\)\(_{25}^2\) = -70 (c = 1.0 in CH\(_2\)Cl\(_2\)). The enantiomers were analyzed by HPLC using Daicel Chiralpak IE column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: \(t_R = 29.62\) min, minor enantiomer: \(t_R = 72.78\) min. 95:5 \(dR\), 99% ee. HRMS (ESI) calcd for C\(_{26}\)H\(_{26}\)N\(_2\)O\(_3\)Na m/z [M+Na]\(^+\): 437.1836, found: 437.1838.

4. HPLC spectra of products 3
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### 图片 1
![图片 1](image1.png)

### 图片 2
![图片 2](image2.png)

### 表格 3

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34
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### 第三张图

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- ![Graph](image1.png)
- ![Graph](image2.png)
- ![Graph](image3.png)
- ![Graph](image4.png)
- ![Graph](image5.png)
- ![Graph](image6.png)
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![化学结构式](image1)

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![分子结构图](attachment:image.png)

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5. NMR spectra of products 3

![NMR Spectra of Products 3](image-url)
Crystals of enantiopure 3ra suitable for X-ray analysis were obtained from crystallization in a solution of ethyl acetate and n-hexan
CCDC deposition number                      1875350
Empirical formula  C_{31} H_{27} Cl N_{2} O_{3}  
Formula weight  529.01
Temperature  296(2) K
Wavelength  0.71073 Å
Crystal system  Orthorhombic
Space group  P 21 21 21
Unit cell dimensions  
\begin{align*}
a &= 9.0064(3) \text{ Å} & \alpha &= 90^\circ. \\
b &= 9.7885(3) \text{ Å} & \beta &= 90^\circ. \\
c &= 30.9078(11) \text{ Å} & \gamma &= 90^\circ. \\
\end{align*}
Volume  2724.80(16) Å³
Z  4
Density (calculated)  1.290 Mg/m³
Absorption coefficient  0.179 mm⁻¹
F(000)  1112
Crystal size  0.200 x 0.170 x 0.140 mm³
Theta range for data collection  2.182 to 25.996°.
Index ranges  \(-11\leq h\leq10, -12\leq k\leq10, -34\leq l\leq38\)
Reflections collected  13582
Independent reflections  5302 \([R\text{int} = 0.0320]\)
Completeness to theta = 25.242°  99.0 %
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.7456 and 0.6367
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  5302 / 0 / 347
Goodness-of-fit on F²  1.083
Final R indices [I>2sigma(I)]  R1 = 0.0448, wR2 = 0.1069
R indices (all data)  R1 = 0.0615, wR2 = 0.1185
Absolute structure parameter  0.02(3)
Extinction coefficient  0.030(5)
Largest diff. peak and hole  0.202 and -0.242 e.Å⁻³