Supporting Information for

Solvent-controlled, regio-switchable formation of 3-arylamino- or 5-aryliminopyrazole isomer in the cyclocondensation of β-aminoenones with hydrazides: intermolecular hydrogen bonding plays the role

Dexuan Xiang, Xihe Bi, Peiqiu Liao, Zikun Wang, Xiaoqing Xin and Dewen Dong

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China;
Department of Chemistry, Northeast Normal University, Changchun, 130024, China;
State Key Laboratory of Fine Chemicals, School of Chemical Engineering, University of Technology, Dalian 116012, China.

E-mail: bixh507@nenu.edu.cn; dwdong@ciac.jl.cn

Contents

Table of contents ----------------------------------------S1
I. General Information------------------------------------S2
II. Synthesis and analytical data of compounds 2----------S2-S4
III. Synthesis and analytical data of compounds 3---------S4-S6
IV. Synthesis and analytical data of compounds 4---------S6-S9
V. 1H- and 13C-NMR Spectra Copies ---------------------S9-S27

S1
I. General Information

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 MHz, 400 MHz and 100 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on a FTIR spectrophotometer in the range of 400-4000 cm$^{-1}$. Elemental analyses were conducted on a PE-2400 analyzer (Perkin-Elmer). Petroleum ether (PE) used was the fraction boiling in the range 60-90 °C.

II. Synthesis and analytical data of 2

Typical procedure (with 2a as an example): To a solution of 1-(6-(phenylamino)-3,4-dihydro-2H-pyran-5-yl)ethanone 1a (1.0 mmol, 217 mg), in DMF (10 mL) was added methylhydrazine (3.0 mmol, 0.40 mL) in one portion. The reaction mixture was stirred under at 80 °C for 5.0 hours and then poured into saturated aqueous NaCl (50 mL), which was extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 2: 1) to give 2a (208 mg, 85%).

3-(1,5-dimethyl-3-(phenylamino)-1H-pyrazol-4-yl)propan-1-ol 2a
White solid, m.p. 126-129 °C; $^1$H NMR (300 MHz, DMSO) δ = 1.44-1.53 (m, 2H), 2.09 (s, 3H), 2.31 (t, $J$ = 7.2 Hz, 2H), 3.33 (m, 2H), 3.57 (s, 3H), 4.51 (s, 1H), 6.61 (t, $J$ = 7.2 Hz, 1H), 7.08 (t, $J$ = 8.4 Hz, 2H), 7.23 (d, $J$ = 7.8 Hz, 2H), 7.51 (s, 1H); $^{13}$C NMR (100 MHz, DMSO) δ = 9.1, 18.1, 33.2, 35.6, 59.9, 106.3, 114.7, 117.5, 128.5, 135.7, 144.8, 147.7; IR (KBr) 2922, 1618, 1553, 1317, 1256, 1076, 933, 750 cm$^{-1}$; Anal. Calcd for C$_{14}$H$_{17}$N$_{3}$O: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.21; H, 7.69; N, 17.34.

CCDC deposition number: 830538
Crystal data and structure refinement of 2a.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{14}$H$</em>{17}$N$_{3}$O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>243.31</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
</tbody>
</table>
Crystal system                        orthorhombic
Space group                         P212121
Unit cell dimensions                
\[ a = 9.012(3) \text{ Å} \]
\[ b = 9.445(2) \text{ Å} \]
\[ c = 15.967(4) \text{ Å} \]
alpha = 90.00 deg.                   
beta = 90.00 deg.                    
gamma = 90.00 deg.                   
Volume                               1359.1(11) \text{ Å}^3               
Z                                      4                                       
Absorption coefficient               0.077 mm\(^{-1}\)                           
F(000)                                520                                     
Crystal size                         0.30 x 0.22 x 0.12 mm                    
Goodness-of-fit on F2                1.067                                    
Theta range for data collection      2.51 to 26.05 deg.                        

![Structural formula of 2b](image)

3-(1,5-dimethyl-3-(p-tolylamino)-1H-pyrazol-4-yl)propan-1-ol \( \text{2b} \)
White solid, m.p. 80-82 °C; \(^1\)H NMR (300 MHz, DMSO) \( \delta = 1.42-1.51 \) (m, 2H), 2.08 (s, 3H), 2.14 (s, 3H), 2.29 (t, \( J = 7.2 \) Hz, 2H), 3.28-3.33 (m, 2H), 3.56 (s, 3H), 4.50 (t, \( J = 4.8 \) Hz, 1H), 6.89 (d, \( J = 8.1 \) Hz, 2H), 7.15 (d, \( J = 8.1 \) Hz, 2H), 7.37 (s, 1H); \(^1\)H NMR (100 MHz, DMSO) \( \delta = 9.1, 18.1, 20.2, 33.1, 35.5, 59.8, 105.9, 114.8, 125.8, 128.9, 135.6, 142.3, 148.0 \); \(^1\)H NMR (100 MHz, DMSO) \( \delta = 9.1, 18.1, 20.2, 33.1, 35.5, 59.8, 105.9, 114.8, 125.8, 128.9, 135.6, 142.3, 148.0 \); IR (KBr) 2872, 1620, 1553, 1516, 1252, 932 cm\(^{-1}\); Anal. Calcd for C\(_{15}\)H\(_{21}\)N\(_3\)O: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.19; H, 8.26; N, 16.38.

![Structural formula of 2c](image)

3-(3-((4-methoxyphenyl)amino)-1,5-dimethyl-1H-pyrazol-4-yl)propan-1-ol \( \text{2c} \)
Colorless liquid, \(^1\)H NMR (300 MHz, DMSO) \( \delta = 1.43-1.52 \) (m, 2H), 2.07 (s, 3H), 2.29 (t, \( J = 7.2 \) Hz, 2H), 3.29-3.35 (m, 2H), 3.54 (s, 3H), 3.62 (s, 3H), 6.71 (d, \( J = 9.0 \) Hz, 2H), 7.22-7.25 (m, 3H); \(^1\)C NMR (100 MHz, DMSO) \( \delta = 9.1, 18.2, 33.2, 35.5, 55.3, 60.0, 105.4, 114.0, 116.2, 135.7, 138.5, 148.6, 151.8 \); Anal. Calcd for C\(_{15}\)H\(_{21}\)N\(_3\)O\(_2\): C, 69.43; H, 7.69; N, 15.26. Found: C, 69.12; H, 7.54; N, 15.07.
3-(3-((4-chlorophenyl)amino)-1,5-dimethyl-1H-pyrazol-4-yl)propan-1-ol 2d
White solid, m.p. 120-123 °C; $^1$H NMR (300 MHz, DMSO) $\delta$ = 1.43-1.52 (m, 2H), 2.09 (s, 3H), 2.31(t, $J$ = 7.2 Hz, 2H), 3.29-3.35 (m, 2H), 3.57 (s, 3H), 4.51 (t, $J$ = 4.8 Hz, 1H), 7.12 (d, $J$ = 8.7 Hz, 2H), 7.28 (d, $J$ = 8.7 Hz, 2H), 7.74 (s, 1H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ = 9.0, 18.1, 33.1, 35.5, 59.8, 106.3, 116.1, 120.7, 128.2, 135.8, 143.7, 147.3; IR (KBr) 2932, 1620, 1549, 1493, 1315, 1252, 930, 818 cm$^{-1}$; Anal. Calcd for C$_{14}$H$_{18}$ClN$_3$O: C, 60.10; H, 6.49; N, 15.02. Found: C, 60.29; H, 6.63; N, 14.87.

3-(1,5-dimethyl-3-((4-(trifluoromethyl)phenyl)amino)-1H-pyrazol-4-yl)propan-1-ol 2e
White solid, m.p. 104-106 °C; $^1$H NMR (300 MHz, DMSO) $\delta$ = 1.43-1.52 (m, 2H), 2.11 (s, 3H), 2.31(t, $J$ = 7.2 Hz, 2H), 3.28-3.34 (m, 2H), 3.60 (s, 3H), 4.50 (t, $J$ = 4.8 Hz, 1H), 7.31 (d, $J$ = 8.7 Hz, 2H), 7.41 (d, $J$ = 8.7 Hz, 2H), 8.13 (s, 1H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ = 9.1, 18.2, 33.2, 35.7, 59.9, 107.4, 114.0, 116.8, 117.1, 117.4, 117.7, 123.2, 123.8, 125.8, 125.9, 126.5, 136.2, 146.4, 148.3; IR (KBr) 2939, 1624, 1553, 1481, 1325, 1109, 930, 824 cm$^{-1}$; Anal. Calcd for C$_{15}$H$_{18}$F$_3$N$_3$O: C, 57.50; H, 5.79; N, 13.41. Found: C, 57.11; H, 5.96; N, 13.64.

3-(3-((2,4-dimethylphenyl)amino)-1,5-dimethyl-1H-pyrazol-4-yl)propan-1-ol 2f
Colorless liquid, $^1$H NMR (300 MHz, DMSO) $\delta$ = 1.42-1.51 (m, 2H), 2.09 (s, 3H), 2.12 (s, 3H), 2.28 (t, $J$ = 7.2 Hz, 2H), 3.25-3.29 (m, 2H), 3.57 (s, 3H), 4.57 (s, 1H), 6.47 (s, 1H), 6.75 (d, $J$ = 8.1 Hz, 1H), 6.80 (s, 1H), 7.18 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ = 9.2, 17.8, 18.2, 20.2, 32.5, 35.5, 59.4, 107.3, 114.7, 123.3, 126.5, 126.6, 130.7, 135.9, 140.8, 148.4; Anal. Calcd for C$_{15}$H$_{18}$F$_3$N$_3$O: C, 57.50; H, 5.79; N, 13.41. Found: C, 57.11; H, 5.96; N, 13.64.

III. Synthesis and analytical data of 3

Typical procedure (with 3a as an example): To a solution of 1-(6-(phenylamino)-3,4-dihydro-2H-pyran-5-y1)ethanone 1a (1.0 mmol, 217 mg) and
TBAB (0.1 mmol, 32 mg) in water (10 mL) was added methylhydrazine (3.0 mmol, 0.40 mL) in one portion. The reaction mixture was stirred under reflux for 6.0 hours, and then poured into saturated aqueous NaCl (50 mL), which was extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 2: 1) to give 3a (230 mg, 94%).

3-((1,3-dimethyl-5-(phenylamino)-1H-pyrazol-4-yl)propan-1-ol 3a
White solid, m.p. 80-82 °C; ¹H NMR (300 MHz, DMSO) δ = 1.41-1.50 (m, 2H), 2.07 (s, 3H), 2.18 (t, J = 7.5, 2H), 3.24-3.30 (m, 2H), 3.4 (s, 3H), 4.37 (t, J = 5.1 Hz, 1H), 6.45 (d, J = 8.1 Hz, 2H), 6.65 (t, J = 7.2 Hz 1H), 7.10 (t, J = 7.8 Hz, 2H), 7.56 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ = 12.3, 19.2, 33.0, 34.3, 60.4, 112.0, 112.9, 117.9, 129.1, 137.2, 144.4, 146.5; IR (KBr) 2926, 1609, 1501, 1439, 1298, 1038, 746 cm⁻¹; Anal. Calcd for C₁₄H₁₉N₃O: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.20; H, 7.95; N, 17.31.

3-((1,3-dimethyl-5-(p-tolylamino)-1H-pyrazol-4-yl)propan-1-ol 3b
White solid, m.p. 70-72 °C; ¹H NMR (400 MHz, DMSO) δ = 1.44-1.48 (m, 2H), 2.08 (s, 3H), 2.16 (s, 3H), 2.19 (t, J = 8.0 Hz, 2H), 3.28-3.29 (m, 2H), 3.34 (s, 3H), 3.42 (s, 3H), 4.34 (s, 1H), 6.37 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 7.37 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ = 12.3, 19.1, 20.0, 33.0, 34.3, 60.4, 111.8, 113.0, 126.3, 129.5, 137.6, 144.1, 144.3; IR (KBr) 2920, 1616, 1516, 1447, 1379, 1296, 1040, 810 cm⁻¹; Anal. Calcd for C₁₅H₂₁N₃O: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.70; H, 8.05; N, 16.48.

3-((5-((4-methoxyphenyl)amino)-1,3-dimethyl-1H-pyrazol-4-yl)propan-1-ol 3c
White solid, m.p. 129-131 °C; ¹H NMR (400 MHz, DMSO) δ = 1.45-1.50 (m, 2H), 2.07 (s, 3H), 2.19 (t, J = 8.0 Hz, 2H), 3.29 (t, J = 6.4 Hz, 2H), 3.42 (s, 3H), 3.64 (s, 3H), 4.34 (s, 1H), 6.42 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 7.23 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ = 12.3, 19.2, 33.1, 34.3, 55.2, 60.5, 111.5, 114.1, 114.7, 138.2, 140.3, 144.3, 152.0; IR (KBr) 2926, 1595, 1510, 1296, 1246, 1034, 947, 814 cm⁻¹; Anal. Calcd for C₁₅H₂₁N₃O₂: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.72; H,
7.54; N, 15.09.

3-(5-((4-chlorophenyl)amino)-1,3-dimethyl-1H-pyrazol-4-yl)propan-1-ol 3d
White solid, m.p. 101-105 °C; ¹H NMR (400 MHz, DMSO) δ = 1.50-1.55 (m, 2H), 2.12 (s, 3H), 2.34 (t, J = 7.2 Hz, 2H), 3.35 (t, J = 6.4 Hz, 2H), 3.61 (s, 3H), 4.49 (s, 1H), 7.14 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.73 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ = 9.1, 18.1, 33.2, 35.6, 59.8, 106.3, 116.0, 120.6, 128.2, 135.9, 143.7, 147.2; IR (KBr) 2932, 1620, 1553, 1491, 1315, 1252, 930, 818 cm⁻¹; Anal. Calcd for C₁₄H₁₈ClN₃O: C, 60.10; H, 6.49; N, 15.02. Found: C, 60.33; H, 6.62; N, 14.87.

3-(1,3-dimethyl-5-((4-(trifluoromethyl)phenyl)amino)-1H-pyrazol-4-yl)propan-1-ol 3e
White solid, m.p. 127-129 °C; ¹H NMR (300 MHz, DMSO) δ = 1.41-1.50 (m, 2H), 2.10 (s, 3H), 2.19 (t, J = 4.8 Hz, 2H), 3.24-3.31 (m, 2H), 3.43 (s, 3H), 4.38 (t, J = 6.8 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 8.21 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ = 12.3, 19.2, 33.0, 34.3, 60.4, 112.6, 117.8, 118.1, 126.3, 126.6, 135.8, 144.6, 149.8; IR (KBr) 2937, 1622, 1514, 1330, 1188, 1068, 947, 847 cm⁻¹; Anal. Calcd for C₁₅H₁₈F₃N₃O: C, 57.50; H, 5.79; N, 13.41. Found: C, 57.26; H, 5.87; N, 13.62.

3-(5-((2,4-dimethylphenyl)amino)-1,3-dimethyl-1H-pyrazol-4-yl)propan-1-ol 3f
White solid, m.p. 125-127 °C; ¹H NMR (300 MHz, DMSO) δ = 1.38-1.48 (m, 2H), 2.05 (s, 3H), 2.10 (s, 3H), 2.15 (d, J = 7.8 Hz, 2H), 2.17 (s, 3H), 3.24-3.25 (m, 2H), 3.36 (s, 3H), 4.39 (s, 1H), 5.90 (d, J = 8.1 Hz, 1H), 6.66 (s, 1H), 6.69 (d, J = 8.1 Hz, 1H), 6.83 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ = 12.3, 17.6, 19.0, 20.0, 32.7, 34.2, 60.3, 111.7, 112.0, 122.7, 126.6, 126.9, 131.0, 138.1, 141.9, 144.2; Anal. Calcd for C₁₆H₂₃N₃O: C, 70.30; H, 8.48; N, 15.37. Found: C, 70.63; H, 8.36; N, 15.21.

III. Synthesis and analytical data of 4

Typical procedure (with 4a as an example): To a solution of
1-(6-(phenylamino)-3,4-dihydro-2H-pyran-5-yl)ethanone 1a (1.0 mmol, 217 mg) and TBAB (0.1 mmol, 32 mg) in water (10 mL) was added hydrazine hydrate (5.0 mmol, 0.24 mL) in one portion. The reaction mixture was stirred under reflux for 5.0 hours, and then poured into saturated aqueous NaCl (50 mL), which was extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 2: 1) to give 4a (213 mg, 92%).

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

3-(5-methyl-3-(phenylamino)-1H-pyrazol-4-yl)propan-1-ol 4a

White solid, m.p. 80-83 °C; \(^1\)H NMR (300 MHz, DMSO) \(\delta = 1.48-1.54 \text{ (m, 2H), 2.28 (s, 3H), 2.31 (t, } J = 7.2 \text{ Hz, 2H), 3.29-3.34 (m, 2H), 4.49 (t, } J = 4.5 \text{ Hz, 1H), 6.60 (t, } J = 7.2 \text{ Hz, 1H), 7.07 (t, } J = 7.5 \text{ Hz, 2H), 7.25 (d, } J = 7.8 \text{ Hz, 2H), 7.50 (s, 1H), 11.56 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO) \(\delta = 9.4, 17.7, 33.0, 59.9, 105.5, 114.6, 117.3, 128.4, 135.5, 145.0, 149.3; \text{ IR (KBr) 2928, 1604, 1560, 1499, 1308, 1250, 920, 744 cm}^{-1}; \text{ Anal. Calcd for } \text{C}_{13}\text{H}_{17}\text{N}_{3}\text{O: C, 67.51; H, 7.41; N, 18.17. Found: C, 67.86; H, 7.27; N, 18.17.}

3-(5-methyl-3-(p-tolylamino)-1H-pyrazol-4-yl)propan-1-ol 4b

White solid, m.p. 108-112 °C; \(^1\)H NMR (300 MHz, DMSO) \(\delta = 1.45-1.54 \text{ (m, 2H), 2.07 (s, 3H), 2.14 (s, 3H), 2.31 (t, } J = 6.9 \text{ Hz, 2H), 3.31-3.33 (m, 2H), 4.47 (t, } J = 4.5 \text{ Hz, 1H), 6.89 (d, } J = 8.1 \text{ Hz, 2H), 7.14 (d, } J = 8.1 \text{ Hz, 2H), 7.34 (s, 1H), 11.48 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO) \(\delta = 9.6, 17.9, 20.2, 33.1, 60.1, 105.5, 114.8, 125.9, 129.0, 135.9, 142.7, 149.4; \text{ IR (KBr) 2928, 1618, 1549, 1425, 1250, 1180, 1078, 920, 808 cm}^{-1}; \text{ Anal. Calcd for } \text{C}_{14}\text{H}_{19}\text{N}_{3}\text{O: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.27; H, 7.93; N, 17.32.}

3-(3-((4-methoxyphenyl)amino)-5-methyl-1H-pyrazol-4-yl)propan-1-ol 4c

White solid, m.p. 72-74 °C; \(^1\)H NMR (300 MHz, DMSO) \(\delta = 1.44-1.53 \text{ (m, 2H), 2.06 (s, 3H), 2.29 (t, } J = 7.2 \text{ Hz, 2H), 3.28-3.33 (m, 2H), 3.62 (s, 3H), 4.48 (t, } J = 4.8 \text{ Hz, 1H), 6.70 (d, } J = 9.0 \text{ Hz, 2H), 7.22-7.26 (m, 3H), 11.41 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO) \(\delta = 9.5, 17.8, 33.1, 55.2, 60.0, 104.7, 114.0, 116.0, 135.5, 138.7, 150.0, 151.6; \text{ IR (KBr) 2928, 1556, 1512, 1234, 1036, 820 cm}^{-1}; \text{ Anal. Calcd for } \text{C}_{14}\text{H}_{16}\text{N}_{3}\text{O}_2: C,
64.35; H, 7.33; N, 16.08. Found: C, 64.24; H, 7.20; N, 16.35.

3-(3-((4-chlorophenyl)amino)-5-methyl-1H-pyrazol-4-yl)propan-1-ol 4d
White solid, m.p. 101-103 °C; $^1$H NMR (400 MHz, DMSO) δ = 1.50-1.57 (m, 2H), 2.12 (s, 3H), 2.34 (t, $J = 7.2$ Hz, 2H), 3.36 (t, $J = 4.8$ Hz, 2H), 4.48 (s, 1H), 7.13-7.15 (m, 2H), 7.27 (s, 2H), 7.72 (s, 1H) 11.64 (s, 1H); $^{13}$C NMR (100 MHz, DMSO) δ = 9.4, 17.8, 33.0, 60.0, 105.5, 116.0, 120.6, 128.2, 135.7, 143.9, 148.9; IR (KBr) 2932, 1591, 1555, 1493, 1312, 1246, 1177, 822 cm$^{-1}$; Anal. Calcd for C$_{13}$H$_{16}$ClN$_3$O: C, 58.76; H, 6.07; Cl, 13.34; N, 15.81. Found: C, 58.98; H, 5.93; N, 15.52.

CCDC deposition number: 819257

<table>
<thead>
<tr>
<th>Crystal data and structure refinement of 4d.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
</tr>
<tr>
<td><strong>alpha = 92.490(2) deg.</strong></td>
</tr>
<tr>
<td><strong>beta = 91.719(2) deg.</strong></td>
</tr>
<tr>
<td><strong>gamma = 107.966(2) deg.</strong></td>
</tr>
<tr>
<td><strong>Volume</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F2</strong></td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
</tr>
</tbody>
</table>

3-(5-methyl-3-((4-(trifluoromethyl)phenyl)amino)-1H-pyrazol-4-yl)propan-1-ol 4e
White solid, m.p. 132-135 °C; $^1$H NMR (300 MHz, DMSO) δ = 1.46-1.55 (m, 2H), 2.10 (s, 3H), 2.32 (t, $J = 7.2$ Hz, 1H), 3.29-3.35 (m, 2H), 4.49 (t, $J = 4.8$ Hz, 1H), 7.32
3-(3-((2,4-dimethylphenyl)amino)-5-methyl-1H-pyrazol-4-yl)propan-1-ol 4f

White solid, m.p. 117-120 °C; $^1$H NMR (300 MHz, DMSO) $\delta = 1.44-1.53$ (m, 2H), 2.08 (s, 3H), 2.12 (s, 3H), 2.14 (s, 3H), 2.27 (t, $J = 6.6$ Hz, 2H), 3.24-3.30 (m, 2H), 4.55 (s, 1H), 6.47 (s, 1H), 6.73 (d, $J = 8.1$ Hz, 1H), 6.80 (s, 1H), 7.18 (s, 1H), 11.62 (s, 1H); $^{13}$C NMR (100 MHz, DMSO) $\delta = 9.8, 17.7, 17.9, 20.2, 32.4, 59.5, 106.6, 114.2, 123.0, 126.2, 126.6, 130.6, 136.4, 141.1, 149.3; IR (KBr) 2918, 1506, 1300, 1161, 1082, 922, 814 cm$^{-1}$; Anal. Calcd for C$_{15}$H$_{21}$N$_3$O: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.20; H, 8.32; N, 16.45.
IV. $^1$H- and $^{13}$C-NMR Spectra Copies

2a