An efficient copper-catalyzed formation of highly substituted pyrazoles using molecular oxygen as the oxidant

Mamta Suri, Thierry Jousseume, Julia J. Neumann and Frank Glorius

Supporting Information

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1. General Considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame dried glassware. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: MeCN (CaH$_2$ and stored over molecular sieves under argon), EtCN (CaH$_2$ and stored over molecular sieves under argon), CH$_2$Cl$_2$ (CaH$_2$), toluene (CaH$_2$), mesitylene (CaH$_2$), pyridine (CaH$_2$) and Benzonitrile (CaH$_2$ and stored over molecular sieves under argon). Anhydrous DCE, 1,4-dioxane, t-amyl alcohol, DMSO and DMF were purchased from Acros Organics and stored over molecular sieves under argon. and 3-trifluoromethylbenzonitrile was purchased in p. a. quality and used as received.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, APCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with UV light and vanillin, ninhydrine and/or KMnO$_4$ staining solutions followed by heating.

Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique or using a Biotage Isolera Flash Purification System eluting with gradients of solvents as stated for the Rf values.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts ($\delta$) for $^1$H and $^{13}$C NMR spectra are given in ppm relative to TMS, for $^{19}$F NMR spectra relative to $\delta$(CCl$_3$F) = 0 ppm. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra and the chemical shifts converted to the TMS scale (CDCl$_3$: $\delta$H = 7.26 ppm, $\delta$C = 77.16 ppm; d6-DMSO: $\delta$H = 2.50 ppm, $\delta$C = 39.52 ppm). $^{19}$F NMR spectra are not calibrated by an internal reference.
GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 µm). The major signals are quoted in m/z with the relative intensity in parentheses. The methods used start with the injection temperature T0; after holding this temperature for 3 min, the column is heated to temperature T1 (ramp) and this temperature is held for an additional time t:

Method 50_20: T0 = 50 °C, T1 = 280 °C, ramp = 20 °C/min, t = 3 min;
Method 50_40: T0 = 50 °C, T1 = 290 °C, ramp = 40 °C/min, t = 4 min;
Method 50_20_320: T0 = 50 °C, T1 = 320 °C, ramp = 20 °C/min, t = 3 min.

Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Mass Calibration was carried out directly before the measurement of the sample using clusters of sodium formate.

Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur and Shimadzu FTIR 8400S. The wave numbers (ν) of recorded IR-signals are quoted in cm⁻¹.


No attempts were made to optimize yields for substrate synthesis.
2. Screening of the Reaction Parameters

### Table S1. Effect of Lewis acids.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnCl(_2)</td>
<td>25</td>
</tr>
<tr>
<td>2(^c)</td>
<td>ZnCl(_2)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Co(acac)(_3)</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>AuCl(_2)Ph(_3)</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>BF(_3)(OEt)(_2)</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>TiCl(_4)</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 1a (0.25 mmol), Cu(OAc)\(_2\) (1.5 eq.), PhCN (2.0 eq.), additive (10 mol%), 1,2-DCB (0.6 M), air, 110 °C, 24 h; \(^b\) Determined by GC analysis with mesitylene as an internal standard; \(^c\) ZnCl\(_2\) (1.0 eq.); 1,2-DCB = 1,2-dichlorobenzene.

### Table S2: Screening Cu(I) sources.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>MX (eq.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Cu(MeCN)(_2)BF(_4)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Cu(_2)(C(_6)H(_5))(_3)SO(_3)(_2)</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 1a (0.25 mmol), MX (25 mol%), PhCN (3.0 eq.), DCE (0.5 M), 110 °C, 24 h, under an atmosphere of O\(_2\) (1 bar, closed tube); \(^b\) Determined by GC analysis with mesitylene as an internal standard; DCE = 1,2-dichloroethane.
Table S3: Effect of different additives on the catalytic reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. PhCN</th>
<th>Additive (eq.)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>--</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>Pivalic acid (0.1)</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt; (0.1)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>Water (0.11)</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>Pivalamide (0.1)</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>Pivalamide (1.0)</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>Valine (0.1)</td>
<td>39</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>Acetamide (0.1)</td>
<td>37</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>Benzamide (0.1)</td>
<td>64</td>
</tr>
<tr>
<td>10</td>
<td>1.5</td>
<td>N-Methyl pivalamide (0.1)</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>1.5</td>
<td>N-Butyl pivalamide (0.1)</td>
<td>54</td>
</tr>
<tr>
<td>12</td>
<td>1.5</td>
<td>N-Phenyl pivalamide (0.1)</td>
<td>51</td>
</tr>
<tr>
<td>13</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.1)</td>
<td>65 (60)</td>
</tr>
<tr>
<td>14</td>
<td>1.5</td>
<td>N-Pivaloyloxy pivalamide (0.1)</td>
<td>27</td>
</tr>
<tr>
<td>15</td>
<td>1.5</td>
<td>9H-4,5-Diazafluoren-9-one (0.1)</td>
<td>28</td>
</tr>
<tr>
<td>16</td>
<td>1.5</td>
<td>2-Pyrrolidinone (0.1)</td>
<td>53</td>
</tr>
<tr>
<td>17</td>
<td>1.5</td>
<td>N-Methyl-2-pyrrolidinone (0.1)</td>
<td>38</td>
</tr>
<tr>
<td>18</td>
<td>1.5</td>
<td>N-Methoxy benzamide (0.1)</td>
<td>28</td>
</tr>
<tr>
<td>19</td>
<td>1.5</td>
<td>Oxazolidin-2-one (0.1)</td>
<td>45</td>
</tr>
<tr>
<td>20</td>
<td>1.5</td>
<td>Piperidin-2-one (0.1)</td>
<td>52</td>
</tr>
<tr>
<td>21</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (1.0)</td>
<td>44</td>
</tr>
<tr>
<td>22</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.5)</td>
<td>48</td>
</tr>
<tr>
<td>23</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.25)</td>
<td>45</td>
</tr>
<tr>
<td>24</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.05)</td>
<td>67</td>
</tr>
<tr>
<td>25</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.05)</td>
<td>16</td>
</tr>
<tr>
<td>26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.5</td>
<td>N-Methoxy pivalamide (0.05)</td>
<td>32</td>
</tr>
<tr>
<td>27</td>
<td>3.0</td>
<td>N-Methoxy pivalamide (0.05)</td>
<td>69 (65)</td>
</tr>
<tr>
<td>28&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.0</td>
<td>N-Methoxy pivalamide (0.05)</td>
<td>35</td>
</tr>
<tr>
<td>29</td>
<td>3.0</td>
<td>N-Pyridin-2-yl benzamide (0.05)</td>
<td>27</td>
</tr>
<tr>
<td>30</td>
<td>3.0</td>
<td>2-Acetamido benzoic acid (0.05)</td>
<td>69 (64)</td>
</tr>
<tr>
<td>31</td>
<td>3.0</td>
<td>2-Picolinic acid (0.05)</td>
<td>84 (68)</td>
</tr>
<tr>
<td>32</td>
<td>3.0</td>
<td>Pivalic acid (0.05)</td>
<td>40</td>
</tr>
<tr>
<td>33</td>
<td>3.0</td>
<td>Thiophene-2-carboxylic acid (0.05)</td>
<td>59</td>
</tr>
<tr>
<td>34</td>
<td>3.0</td>
<td>--</td>
<td>(40)</td>
</tr>
<tr>
<td>35</td>
<td>3.0</td>
<td>Pyridine (0.05)</td>
<td>39</td>
</tr>
<tr>
<td>36</td>
<td>3.0</td>
<td>DIPEA (0.05)</td>
<td>43</td>
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<tr>
<td>37</td>
<td>3.0</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;N (0.05)</td>
<td>35</td>
</tr>
<tr>
<td>38</td>
<td>3.0</td>
<td>N-Methoxypicolinamide (0.05)</td>
<td>23</td>
</tr>
<tr>
<td>39</td>
<td>3.0</td>
<td>1H-Pyrazole-3-carboxylic acid (0.05)</td>
<td>33</td>
</tr>
<tr>
<td>40</td>
<td>3.0</td>
<td>1H-Imidazole-2-carboxylic acid (0.05)</td>
<td>20</td>
</tr>
<tr>
<td>41</td>
<td>3.0</td>
<td>DL-Proline (0.05)</td>
<td>14</td>
</tr>
<tr>
<td>42</td>
<td>3.0</td>
<td>N,N-dimethyl glycine (0.05)</td>
<td>70 (57)</td>
</tr>
<tr>
<td>43&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.0</td>
<td>2-Picolinic acid (0.05)</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.25 mmol), Cu(OAc)<sub>2</sub> (10 mol%), PhCN, additive, DCE (0.5 M), 110 °C, 24 h, under an atmosphere of O<sub>2</sub> (1 bar, closed tube). <sup>b</sup>Determined by GC analysis with mesitylene as an internal standard. Isolated yield of analytically pure product is given in parentheses. <sup>c</sup>Cu(OAc)<sub>2</sub> (5 mol%); <sup>d</sup>at 120 °C. <sup>e</sup>Without Cu(OAc)<sub>2</sub>. DIPEA = N,N-Diisopropylethylamine.
3. General Procedure for the Synthesis of Pyrazoles

**Condition A:**

Into an oven-dried screw-capped vial (approx. 7 mL in volume) with a magnetic stirring bar were weighed in air the enamine starting material 1 (1.0 mmol), Cu(OAc)$_2$ (1.5 mmol, 1.5 eq.) followed by the addition of DMF ($N,N$-dimethylformamide) (1 M) and then the nitrile 2 (3.0 eq.). (In case of liquid or oily substrates, Cu(OAc)$_2$ was added to a solution of the starting materials in DMF). The screw-capped vial was closed and the reaction mixture was stirred vigorously at room temperature to suspend the solids well. The reaction vial was placed into a preheated metal block (110 °C) and the reaction mixture was stirred at this temperature for 24 h. After cooling to room temperature, the reaction mixture was analyzed by ESI-MS, GC-MS and/or TLC. EtOAc (20 mL) was added and the mixture was shortly stirred at room temperature to suspend the metallic precipitates and filtered through a short pad of seasand (approx. 0.5 cm), silica (approx. 2 cm), seasand (approx. 0.5 cm), Celite (approx. 2 cm) and seasand (approx. 0.5 cm), prepacked with EtOAc. The solid was washed thoroughly with EtOAc (4 × 20 mL) and the combined filtrates were concentrated *in vacuo*. The crude product was solved in CH$_2$Cl$_2$, adsorbed on silica and purified by flash column chromatography (silica, gradient of pentane/EtOAc-mixtures).

**Condition B:**

Into an oven-dried Schlenk tube (approx. 10 mL in volume) with a magnetic stirring bar were weighed in air the enamine starting material (0.25 mmol), Cu(OAc)$_2$ (0.025 mmol, 10 mol%) followed by the addition of DCE (1,2-dichloroethane) (0.5 M), the nitrile (3.0 eq.) and then 2-picolinic acid (0.0125 mmol, 5 mol% eq.). The tube was stirred vigorously, evacuated and filled
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with O₂ (repeatedly 2-3 times). The reaction tube was closed and stirred in preheated oil bath at 110 °C for 24 h. After cooling to room temperature (approx. 15 min), the reaction mixture was analyzed by ESI-MS, GC-MS and/or TLC. To the reaction mixture EtOAc (10 mL) was added and shortly stirred at room temperature to suspend the metallic precipitates and filtered through a short pad of seasand (approx. 0.5 cm), Celite (approx. 1 cm) and seasand (approx. 0.5 cm) prepacked with EtOAc. The solid was washed thoroughly with EtOAc (4 × 10 mL) and the combined filtrates were concentrated in vacuo. The crude product was dissolved in CH₂Cl₂, adsorbed on silica and purified by flash column chromatography (silica, gradient of pentane/EtOAc-mixtures, unless otherwise noted).
4. Characterization of the Pyrazole Products

Methyl 5-methyl-1,3-diphenyl-1H-pyrazole-4-carboxylate (3aa)

Slightly yellowish solid.

Conditions A: 210.1 mg, 0.72 mmol, 72%.
Conditions B: 49.6 mg, 0.17 mmol, 68%.

\[ \text{R}_f \text{ (pentane/EtOAc 90:10): 0.21; } \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.72\text{–}7.63 \text{ (m, 2H, } \text{H}_{\text{arom}}\text{), 7.56\text{–}7.35 \text{ (m, 8H, } \text{H}_{\text{arom}}\text{), 3.77 (s, 3H, CH}_3\text{), 2.59 (s, 3H, CH}_3\text{)}; \)

\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 164.7 \text{ (CO), 153.7 (C}_{\text{arom}}\text{), 145.0 (C}_{\text{arom}}\text{), 138.8 (C}_{\text{arom}}\text{), 133.1 (C}_{\text{arom}}\text{), 129.4 (CH}_{\text{arom}}\text{), 129.3 (CH}_{\text{arom}}\text{), 128.8 (CH}_{\text{arom}}\text{), 128.4 (CH}_{\text{arom}}\text{), 127.8 (CH}_{\text{arom}}\text{), 125.9 (CH}_{\text{arom}}\text{), 110.4 (C}_{\text{arom}}\text{), 51.2 (CH}_3\text{), 12.9 (CH}_3\text{); } \)

GC-MS: \(t_R \text{ (50}_\text{20): 15.6 min; } \)

EI-MS: \(m/z \% = 292 \text{ (100), 262 (21), 261 (100), 260 (22), 259 (20), 118 (15), 77 (52), 51 (14); } \)

Exact Mass ESI-MS: calculated \(m/z \text{ for } [C_{18}H_{16}N_{2}NaO_2]^+ : 315.1104, \text{ found: 315.1095}; \)

ATR-FTIR (cm\(^{-1}\)): 2948, 2406, 2236, 1712, 1595, 1529, 1500, 1453, 1428, 1382, 1327, 1307, 1246, 1183, 1148, 1088, 994, 770, 696, 655.

Methyl 3-(4-fluorophenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ab)

White solid

Condition A: 232.7 mg, 0.75 mmol, 75%
Condition B: 54.3 mg, 0.17 mmol, 70%

\[ \text{R}_f \text{ (pentane/EtOAc 90:10): 0.22; } \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.73 - 7.64 \text{ (m, 2H, } \text{H}_{\text{arom}}\text{), 7.52 - 7.40 \text{ (m, 5H, } \text{H}_{\text{arom}}\text{), 7.15 - } \)

\(7.05 \text{ (m, 2H, } \text{H}_{\text{arom}}\text{), 3.76 (s, 3H, CH}_3\text{), 2.57 (s, 3H, CH}_3\text{); } \)
**13C NMR (101 MHz, CDCl₃)** δ = 164.42 (CO), 162.91 (d, ¹JC₉F = 247.3 Hz, Cₐrom), 152.67 (Cₐrom), 144.98 (Cₐrom), 138.65 (Cₐrom), 131.22 (d, ³JC₉F = 8.2 Hz, CHₐrom), 129.27 (CHₐrom), 129.15 (d, ⁴JC₉F = 3.1 Hz, Cₐrom), 128.77 (CHₐrom), 125.78 (CHₐrom), 114.67 (d, ²JC₉F = 21.4 Hz, CHₐrom), 110.19 (Cₐrom), 51.06 (CH₃), 12.80 (CH₃);

**19F NMR (282 MHz, CDCl₃)**: δ = -113.71 (s, CF);

**GC-MS:** tR (50_20): 15.5 min;

**EI-MS:** m/z (%) = 310 (96), 309 (6), 295 (7), 280 (19), 280 (20), 279 (100), 277(13), 252 (6), 251 (8), 118 (14), 95 (6), 77 (38), 75 (5), 51 (10);

**Exact Mass ESI-MS:** calculated m/z for [C₁₈H₁₅FN₂O₄Na]⁺ 333.101, found 333.1002; for [(C₁₈H₁₅FN₂O₄)₂Na]⁺ 643.2127, found 643.2117;

**ATR-FTIR (cm⁻¹):** 3083, 2999, 2948, 2391, 2270, 1897, 1708, 1597, 1526, 1498, 1459, 1439, 1405, 1384, 1312, 1295, 1247, 1221, 1184, 1150, 1117, 1087, 1015, 993, 924, 837, 807, 787, 768, 700, 678, 656, 592.

**Methyl 3-(4-acetylphenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ac)**

Yellow solid

Condition A: 281.2 mg, 0.84 mmol, 84%

Condition B: 66.6 mg, 0.20 mmol, 80%

Rf (pentane/EtOAc 90:10): 0.04;

**1H NMR (300 MHz, CDCl₃):** δ = 8.05 – 7.93 (m, 2H, Hₐrom), 7.83 – 7.72 (m, 2H, Hₐrom), 7.55 – 7.38 (m, 5H, Hₐrom), 3.75 (s, 3H, CH₃), 2.60 (s, 3H, CH₃), 2.56 (s, 3H, CH₃);

**13C NMR (75 MHz, CDCl₃):** δ = 197.93 (CO), 164.29 (CO), 152.43 (Cₐrom), 145.22 (Cₐrom), 138.57 (Cₐrom), 137.85 (Cₐrom), 136.60 (Cₐrom), 129.60 (CHₐrom), 129.35 (CHₐrom), 128.94 (CHₐrom), 127.81 (CHₐrom), 125.80 (CHₐrom), 110.54 (Cₐrom), 51.20 (CH₃), 26.71 (CH₃), 12.80(CH₃);

**Exact Mass ESI-MS:** calculated m/z for [C₂₀H₁₈N₂O₃Na]⁺: 357.1210; found 357.1206;

**GC-MS:** tR (50_40): 13.0 min;
**EI-MS:** \( m/z \) (%) = 334 (53), 320 (22), 319 (100), 303 (6), 259 (7), 204 (6), 144 (8), 77 (16);

**ATR-FTIR \( (\text{cm}^{-1}) \):** 3065, 2956, 2361, 2339, 1702, 1674, 1602, 1567, 1535, 1501, 1448, 1430, 1357, 1323, 1308, 1289, 1254, 1194, 1170, 1127, 1088, 1037, 1011, 981, 957, 923, 856, 841, 798, 766, 728, 700, 683, 655, 597.

**Methyl 5-methyl-1-phenyl-3-(3-(trifluoromethyl)phenyl)-1\(H\)-pyrazole-4-carboxylate (3ad)**

Yellow solid

Condition A: 298.5 mg, 0.83 mmol, 83%

Condition B: 69.9 mg, 0.19 mmol, 78%

**R\(_f\)** (pentane/EtOAc 90:10): 0.22;

\(^1\text{H NMR}\) (300 MHz, CDCl\(_3\)): \( \delta = 7.97\) (s, 1H, H\(_{\text{arom}}\)), 7.89 (d, \( J = 7.7\) Hz, 1H, H\(_{\text{arom}}\)), 7.64 (d, \( J = 7.8\) Hz, 1H, H\(_{\text{arom}}\)), 7.58 – 7.43 (m, 6H, H\(_{\text{arom}}\)), 3.77 (s, 3H, CH\(_3\)), 2.60 (s, 3H, CH\(_3\));

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)): \( \delta = 164.24\) (CO), 152.10 (C\(_{\text{arom}}\)), 145.40 (C\(_{\text{arom}}\)), 138.53 (C\(_{\text{arom}}\)), 133.84 (C\(_{\text{arom}}\)), 132.73 (CH\(_{\text{arom}}\)), 130.06 (q, \( J = 33.1\) Hz, CH\(_{\text{arom}}\)), 129.93 (CH\(_{\text{arom}}\)), 128.93 (q, \( J = 3.7\) Hz, CH\(_{\text{arom}}\)), 126.87 (q, \( J = 271.6\) Hz, C), 125.80 (CH\(_{\text{arom}}\)), 124.91 (q, \( J = 3.8\) Hz, CH\(_{\text{arom}}\)), 110.35 (C\(_{\text{arom}}\)), 51.07 (CH\(_3\)), 12.75 (CH\(_3\));

\(^{19}\text{F NMR}\) (282 MHz, CDCl\(_3\)): \( \delta = -62.54\) (s, CF\(_3\));

**GC-MS:** \( tR \) (50 - 20): 15.1 min;

**EI-MS:** \( m/z \) (%) = 360 (77), 359 (7), 341 (6), 330 (20), 329 (100), 328 (9), 327 (10), 302 (5), 301 (7), 145 (5), 118 (11), 77 (34), 51 (8);

**Exact Mass ESI-MS:** calculated \( m/z \) for [C\(_{19}\)H\(_{15}\)F\(_3\)N\(_2\)NaO\(_2\)]\(^+\): 383.0978, found: 383.0983;

**ATR-FTIR \( (\text{cm}^{-1}) \):** 3065, 2953, 2362, 1708, 1595, 1540, 1502, 1417, 1322, 1254, 1164, 1068, 995, 808, 764, 701, 685, 663.
Methyl 3-(2-fluorophenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ae)

Yellow Solid

Condition A: 148.1 mg, 0.48 mmol, 48%
Condition B: 15.5 mg, 0.05 mmol, 20%

Rf (pentane/EtOAc 90:10): 0.19;

1H NMR (300 MHz, CDCl3): δ = 7.52 – 7.23 (m, 7H, H arom), 7.17 – 6.98 (m, 2H, H arom), 3.63 (s, 3H, CH₃), 2.50 (s, 3H, CH₃);

13C NMR (101 MHz, CDCl3): δ = 164.35 (CO), 160.6 (d, ¹JC = 248.3 Hz, C arom), 148.17 (C arom), 144.45 (C arom), 138.69 (C arom), 131.08 (d, ³JC = 3.1 Hz, CH arom), 130.27 (d, ³JC = 8.3 Hz, CH arom), 129.32 (CH arom), 128.81 (CH arom), 125.77 (CH arom), 123.83 (d, ⁴JC = 3.5 Hz, CH arom), 121.73 (d, ²JC = 14.9 Hz, C arom), 115.3 (d, ²JC = 22.3 Hz, CH arom), 112.01 (C arom), 51.17 (CH₃), 12.53 (CH₃);

19F NMR (282 MHz, CDCl3): δ = -114.47 (s, CF);

GC-MS: tR (50_20): 15.3 min;

EI-MS: m/z (%) = 310 (76), 289 (10), 281 (6), 280 (20), 279 (100), 277(9), 263(13), 261(13), 251 (6), 233 (5), 205 (9), 155 (5), 130 (5), 120 (5), 118 (18), 77 (43), 75 (5), 51 (12);

Exact Mass ESI-MS: calculated m/z for [C₁₈H₁₅F₂N₂O₂Na]⁺ 333.1010, found 333.1006; for [(C₁₈H₁₅F₂N₂O₂)₂Na]²⁺ 643.2127, found 643.2118;

ATR-FTIR (cm⁻¹): 3012, 2957, 1707, 1624, 1595, 1538, 1501, 1459, 1434, 1386, 1329, 1313, 1247, 1214, 1191, 1160, 1150, 1101, 1087, 1031, 996, 948, 913, 867, 830, 790, 760, 713, 696, 681, 658, 604.

Methyl 5-methyl-1-phenyl-3-(m-tolyl)-1H-pyrazole-4-carboxylate (3af)

Yellowish solid.

Conditions A: 205.0 mg, 0.67 mmol, 67%.
Conditions B: 30.6 mg, 0.10 mmol, 40%.
Methyl 3-(4-(dimethylamino)phenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ag)

Yellow solid.

Conditions A: 167.4 mg, 0.50 mmol, 50%.

Conditions B: 16.8 mg, 0.05 mmol, 20%.

$R_F$ (pentane/EtOAc 90:10): 0.13;

$^1H$ NMR (300 MHz, CDCl$_3$) $\delta = 7.60$ (d, $J = 8.9$ Hz, 2H), 7.51 – 7.38 (m, 5H), 6.77 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 3H), 2.99 (s, 6H), 2.56 (s, 3H); 

$^{13}C$ NMR (75 MHz, CDCl$_3$) $\delta = 165.07$ (CO), 153.85 ($C_{arom}$), 150.59 ($C_{arom}$), 144.75 ($C_{arom}$), 139.08 ($C_{arom}$), 133.69 ($C_{arom}$), 130.23 ($CH_{arom}$), 129.27 ($CH_{arom}$), 128.58 ($CH_{arom}$), 125.96 ($CH_{arom}$), 111.87 ($CH_{arom}$), 110.02 ($CH_{arom}$), 51.10 (CH$_3$), 40.62 (CH$_3$), 12.93 (CH$_3$); 

Exact Mass ESI-MS: calculated [C$_{20}$H$_{21}$N$_3$O$_2$H]$^+$ 336.1707, found 336.1707;
[C$_{20}$H$_{21}$N$_3$O$_2$Na]$^+$ 358.1526, found 358.1523; for [(C$_{20}$H$_{21}$N$_3$O$_2$Na)$_2$]$^+$ 693.3160, found 693.3162;

**ATR-FTIR (cm$^{-1}$):** 2955, 2886, 2400, 2212, 1713, 1611, 1503, 1456, 1432, 1343, 1312, 1254, 1199, 1148, 1118, 1090, 1053, 1015, 940, 821, 786, 765, 734, 697, 660, 645, 588.

**Methyl 3-(4-ethoxyphenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ah)**

Yellowish solid.

Conditions A: 105.5 mg, 0.63 mmol, 63%.

Conditions B: 29.4 mg, 0.09 mmol, 35%.

R$_f$ (pentane/EtOAc 90:10): 0.13;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.67 – 7.58 (m, 2H, H$_{arom}$), 7.54 – 7.38 (m, 5H, H$_{arom}$), 6.98 – 6.89 (m, 2H, H$_{arom}$), 4.07 (q, $J$ = 7.0 Hz, 2H, CH$_2$), 3.77 (s, 3H, CH$_3$), 2.57 (s, 3H, CH$_3$), 1.42 (t, $J$ = 7.0 Hz, 3H, CH$_3$);

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 164.81 (CO), 159.21 (C$_{arom}$), 153.43 (C$_{arom}$), 144.90 (C$_{arom}$), 138.90 (C$_{arom}$), 130.68 (C$_{arom}$), 129.31 (C$_{arom}$), 128.72 (C$_{arom}$), 125.94 (C$_{arom}$), 125.40 (C$_{arom}$), 113.86 (C$_{arom}$), 110.16 (C$_{arom}$), 63.48 (CH$_2$), 51.13 (CH$_3$), 14.94 (CH$_3$), 12.91 (CH$_3$);

GC-MS: $t_R$ (50_20): 18.1 min;

EI-MS: m/z (%): 336 (100), 308 (12), 307 (13), 305 (12), 304 (5), 278 (7), 277 (31), 276 (9), 275 (10), 247 (5), 118 (13), 115 (5), 77 (23);

**Exact Mass ESI-MS:** calculated [C$_{20}$H$_{20}$N$_2$O$_3$Na]$^+$ 359.1366, found 359.1361; for [(C$_{20}$H$_{20}$N$_2$O$_3$Na)$_2$]$^+$ 695.2840, found 695.2839;

**ATR-FTIR (cm$^{-1}$):** 3068, 2982, 2949, 2885, 1983, 1703, 1614, 1596, 1580, 1523, 1498, 1453, 1436, 1412, 1389, 1311, 1290, 1243, 1185, 1145, 1116, 1088, 1049, 1018, 995, 923, 837, 805, 788, 771, 701, 680, 659, 642, 620.
Methyl 3-(furan-2-yl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ai)

Yellow solid
Condition A: 218.0 mg, 0.77 mmol, 77%
Condition B: 46.2 mg, 0.16 mmol, 66%

Rf (pentane/EtOAc 90:10): 0.15;

1H NMR (300 MHz, CDCl3): δ = 7.46 – 7.33 (m, 6H, H-arom), 7.20 – 7.16 (m, 1H, H-arom), 6.42 (dd, J = 3.4, 1.8 Hz, 1H, CH3), 3.81 (s, 3H, CH3), 2.45 (s, 3H, CH3);

13C NMR (75 MHz, CDCl3): δ = 164.14 (CO), 146.78 (C-arom), 144.94 (C-arom), 144.13 (C-arom), 142.72 (CH-arom), 138.66 (C-arom), 129.32 (CH-arom), 129.02 (CH-arom), 126.18 (CH-arom), 111.96 (CH-arom), 111.24 (CH-arom), 51.35 (CH3), 12.99 (CH3);

GC-MS: tR (50_20): 15.0 min;

EI-MS: m/z (%) = 282 (100), 253 (22), 252 (9), 251 (44), 250 (14), 249 (20), 239 (13), 224(5), 223 (5), 221(6), 193 (9), 118 (17), 90 (5), 89 (9), 77 (40), 64 (6), 63 (8), 51 (12), 39 (6);

Exact Mass ESI-MS: calculated m/z for [C16H14N2O3H]+ 283.1077, found 283.1069; for [C16H14N2O3Na]+ 305.0897, found 305.0888; for [(C16H14N2O3)2Na]+ 587.1901, found 587.1889;

ATR-FTIR (cm⁻¹): 3112, 2944, 2836, 2362, 2339, 1760, 1710, 1595, 1529, 1495, 1475, 1450, 1412, 1384, 1367, 1325, 1306, 1294, 1252, 1222, 1191, 1173, 1140, 1122, 1090, 1048, 1019, 995, 953, 917, 886, 844, 809, 765, 699, 680, 656, 603.

Methyl 5-methyl-3-(3-methylpyridin-2-yl)-1-phenyl-1H-pyrazole-4-carboxylate (3aj)

Yellow Solid
Condition A: 198.5 mg, 0.65 mmol, 65%

Rf (pentane/EtOAc 75:25): 0.10;

1H NMR (300 MHz, CDCl3): δ = 8.50 (d, J = 3.6 Hz, 1H, H-arom), 7.57 (d, J = 7.7 Hz, 1H, H-arom), 7.53 – 7.37 (m, 5H, H-arom), 7.22 (dd, J = 7.6, 4.8 Hz, 1H, H-arom), 3.63 (s, 3H, CH3), 2.62 (s, 3H, CH3), 2.27 (s, 3H, CH3);
\[ ^{13}\text{C NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 164.09 \text{ (CO)}, 152.74 \text{ (C}_{\text{arom}}), 152.37 \text{ (C}_{\text{arom}}), 146.48 \text{ (CH}_{\text{arom}}), 144.29 \text{ (C}_{\text{arom}}), 138.78 \text{ (C}_{\text{arom}}), 137.56 \text{ (CH}_{\text{arom}}), 133.22 \text{ (C}_{\text{arom}}), 129.28 \text{ (CH}_{\text{arom}}), 128.78 \text{ (CH}_{\text{arom}}), 125.85 \text{ (CH}_{\text{arom}}), 123.18 \text{ (CH}_{\text{arom}}), 111.55 \text{ (C}_{\text{arom}}), 51.20 \text{ (CH}_3, 19.01 \text{ (CH}_3), 12.66 \text{ (CH}_3); \]

**Exact Mass ESI-MS:** calculated \( m/z \) for \([\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2\text{H}]^+\) 308.1394, found 308.1401.

**Methyl 3,5-dimethyl-1-phenyl-1H-pyrazole-4-carboxylate (3ak)**

![Methyl 3,5-dimethyl-1-phenyl-1H-pyrazole-4-carboxylate (3ak)](image)

Yellowish solid

Condition A: 126.1 mg, 0.55 mmol, 55%

Condition B: 17.4 mg, 0.08 mmol, 30%

\( R_f \) (pentane/EtOAc 90:10): 0.17;

\[^1\text{H NMR} \ (300 \text{ MHz, CDCl}_3): \delta = 7.50-7.34 \text{ (m, 5H, H}_{\text{arom}}), 3.83 \text{ (s, 3H, H}_{\text{arom}}), 2.49 \text{ (s, 3H, CH}_3), 2.47 \text{ (s, 3H, CH}_3); \]

\[^{13}\text{C NMR} \ (75 \text{ MHz, CDCl}_3): \delta = 165.1 \text{ (CO)}, 151.5 \text{ (C}_{\text{arom}}), 144.6 \text{ (C}_{\text{arom}}), 138.8 \text{ (C}_{\text{arom}}), 129.3 \text{ (CH}_{\text{arom}}), 128.5 \text{ (CH}_{\text{arom}}), 125.7 \text{ (CH}_{\text{arom}}), 110.7 \text{ C}_{\text{arom}}, 51.0 \text{ (CH}_3), 14.4 \text{ (CH}_3), 12.7 \text{ (CH}_3); \]

**GC-MS:** \( t_R \) (50_20): 12.9 min;

**EI-MS:** \( m/z \) (%): 230 (68), 215 (3), 199 (100), 172 (13), 130 (5), 118 (8), 103 (4), 77 (41), 65 (5), 51 (13), 39 (7);

**Exact Mass ESI-MS:** calculated \( m/z \) for \([\text{C}_{13}\text{H}_{14}\text{N}_2\text{NaO}_2]^+\): 253.0947, found: 253.0933;

**ATR-FTIR (cm\(^{-1}\)):** 2993, 2951, 2839, 1708, 1598, 1550, 1507, 1483, 1457, 1434, 1393, 1324, 1307, 1289, 1251, 1189, 1128, 1102, 1074, 1054, 1041, 1023, 987, 962, 915, 900, 840, 783, 764, 698, 684, 654, 633.
Methyl 3-ethyl-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3a)\textsuperscript{3}

Yellow solid

Condition A: 126.4 mg, 0.52 mmol, 52%
Condition B: 19.5 mg, 0.08 mmol, 32%

R\textsubscript{f} (pentane/EtOAc 90:10): 0.26;

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.51-7.36\) (m, 5H, H\textsubscript{arom}), 3.85 (s, 3H, CH\textsubscript{3}), 2.92 (q, \(J = 7.5\) Hz, 2H, CH\textsubscript{2}), 2.50 (s, 3H, CH\textsubscript{3}), 1.27 (t, \(J = 7.5\) Hz, 3H, CH\textsubscript{3});

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta = 165.0\) (CO), 156.8 (C\textsubscript{arom}), 144.7 (C\textsubscript{arom}), 139.0 (C\textsubscript{arom}), 129.3 (CH\textsubscript{arom}), 128.5 (CH\textsubscript{arom}), 125.8 (CH\textsubscript{arom}), 110.0 (C\textsubscript{arom}), 51.0 (CH\textsubscript{3}), 21.8 (CH\textsubscript{2}), 13.6 (CH\textsubscript{3}), 12.8 (CH\textsubscript{3});

GC-MS: tR (50-20): 13.1 min;

EI-MS: m/z (%) = 244 (100), 243 (24), 230 (5), 229 (32), 214 (8), 213 (58), 212 (27), 211 (33), 199 (13), 186 (18), 185 (16), 130 (5), 118 (14), 105 (7), 78 (5), 77 (46), 51 (11);

Exact Mass ESI-MS: calculated m/z for [C\textsubscript{14}H\textsubscript{16}N\textsubscript{2}NaO\textsubscript{2}]\textsuperscript{+}: 267.1104, found: 267.1115;

ATR-FTIR (cm\textsuperscript{-1}): 3059, 2980, 2951, 2362, 1914, 1689, 1600, 1548, 1509, 1430, 1329, 1281, 1257, 1187, 1096, 1057, 970, 795, 768, 698, 656.

Methyl 5-methyl-1-phenyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate (3a)

White solid

Condition A: 92.4 mg, 0.33 mmol, 65%

R\textsubscript{f} (pentane/EtOAc 90:10): 0.29;

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.58-7.47\) (m, 3H, H\textsubscript{arom}), 7.44 – 7.36 (m, 2H, H\textsubscript{arom}), 3.90 (s, 3H, CH\textsubscript{3}), 2.55 (s, 3H, CH\textsubscript{3});

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 162.54\) (CO), 146.63 (C\textsubscript{arom}), 142.37 (q, \(\textsuperscript{2}J_{CF3} = 38.0\) Hz, C\textsubscript{arom}), 137.95 (C\textsubscript{arom}), 129.67 (CH\textsubscript{arom}), 129.59 (CH\textsubscript{arom}), 125.95 (CH\textsubscript{arom}), 120.76 (q, \(\textsuperscript{1}J_{CF3} = 268.8\) Hz, CF\textsubscript{3}), 110.42 (C\textsubscript{arom}), 51.81 (CH\textsubscript{3}), 12.44 (CH\textsubscript{3}).
$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -62.40$ (s, CF$_3$);

**GC-MS:** $t_R$ (50:20): 12.2 min;

**EI-MS:** $m/z$ (%) = 284 (38), 265 (13), 264 (36), 263 (27), 254 (14), 253 (100), 249 (30), 229 (13), 184 (5), 118 (7), 77 (41), 51 (14);

**Exact Mass ESI-MS:** calculated $m/z$ for $[C_{13}H_{11}F_3N_2O_2Na]^+$ 307.0665, found 307.0669; for $[[C_{13}H_{11}F_3N_2O_2Na]^+] 591.1437$, found 591.1435;

**ATR-FTIR (cm$^{-1}$):** 3066, 3003, 2957, 2848, 2154, 1720, 1597, 1548, 1495, 1472, 1444, 1397, 1329, 1226, 1168, 1133, 1096, 1038, 1013, 951, 923, 881, 817, 768, 700, 665, 630, 533.

Methyl 5-methyl-1-phenyl-3-styryl-1H-pyrazole-4-carboxylate (3an)

Yellow oil

Condition A: 60.3 mg, 0.19 mmol, 19%

$R_f$ (pentane/EtOAc 90:10): 0.21;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.61 (d, $J = 16.4$ Hz, 1H, H$_{arom}$), 7.53 – 7.45 (m, 3H, H$_{arom}$), 7.45 – 7.36 (m, 5H, H$_{arom}$), 7.26 (t, $J = 7.4$ Hz, 2H, H$_{arom}$), 7.19 (d, $J = 7.4$ Hz, 1H, H$_{arom}$), 3.84 (s, 3H, CH$_3$), 2.45 (s, 3H, CH$_3$);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 164.84 (CO), 150.67 (C$_{arom}$), 144.90 (C$_{arom}$), 138.92 (C$_{arom}$), 137.31 (C$_{arom}$), 131.92 (CH$_{arom}$), 129.43 (CH$_{arom}$), 128.92 (CH$_{arom}$), 128.68 (CH$_{arom}$), 128.01 (CH), 127.06 (CH$_{arom}$), 126.03 (CH$_{arom}$), 118.86 (CH), 110.51 (C$_{arom}$), 51.34 (CH$_3$), 12.85 (CH$_3$);

**GC-MS:** $t_R$ (50:40): 12.5 min;

**EI-MS:** $m/z$ (%) = 318 (66), 317 (100), 287 (6), 285 (11), 259 (8), 258 (7), 257 (16), 152 (5), 128 (6), 118 (8), 77 (24);

**Exact Mass ESI-MS:** calculated $m/z$ for $[C_{20}H_{18}N_2O_2Na]^+$ 319.1441, found 319.1438; for $[C_{20}H_{18}N_2O_2Na]^+$ 341.1260, found 341.1255; for $[[C_{20}H_{18}N_2O_2Na]^+] 659.2629$, found 659.2619;

**ATR-FTIR (cm$^{-1}$):** 3720, 3663, 3062, 2950, 2361, 1703, 1637, 1597, 1540, 1501, 1471, 1440, 1391, 1355, 1290, 1254, 1189, 1141, 1100, 1028, 971, 916, 876, 837, 786, 754, 695, 654, 607.
Methyl 3-(4-fluorophenyl)-5-methyl-1-(o-tolyl)-1H-pyrazole-4-carboxylate (3bb)

Yellowish solid

Condition A: 225.7 mg, 0.70 mmol, 70%
Condition B: 54.3 mg, 0.17 mmol, 67%

Rf (pentane/EtOAc 90:10): 0.23;

1H NMR (300 MHz, CDCl3) δ = 7.69 – 7.53 (m, 2H, H_arom), 7.34 – 7.15 (m, 4H, H_arom), 7.06 – 6.93 (m, 2H, H_arom), 3.70 (s, 3H, CH3), 2.29 (s, 3H, CH3), 2.02 (s, 3H, CH3);

13C NMR (75 MHz, CDCl3) δ = 164.60 (CO), 162.97 (d, 1JCF = 246.6 Hz, C_arom), 152.64 (C_arom), 145.97 (C_arom), 137.59 (C_arom), 136.02 (C_arom), 131.29 (d, 3JCF = 8.2 Hz, CH_arom), 131.24 (CH_arom), 129.92 (CH_arom), 129.19 (d, 4JCF = 3.3 Hz, C_arom), 127.77 (CH_arom), 126.89 (CH_arom), 114.73 (d, 2JCF = 21.6 Hz, CH_arom), 109.13 (C_arom), 51.16 (CH3), 17.35 (CH3), 12.23 (CH3);

19F NMR (282 MHz, CDCl3): δ = -113.83 (s, CF);

GC-MS: tR (50_20): 15.3 min;

EI-MS: m/z (%) = 324 (85), 323 (6), 310 (20), 309 (100), 293 (23), 278 (7), 277 (35), 251 (7), 250 (6), 146 (7), 144 (6), 132 (6), 95 (6), 91 (21), 65 (12);

Exact Mass ESI-MS: calculated m/z for [C19H17F2N2O2Na]+ 347.1166, found 347.1165; for [C19H17F2N2O2H]+ 325.1347, found 325.1344; for [(C19H17F2N2O2)2Na]+ 671.2440, found 671.2444;

ATR-FTIR (cm⁻¹): 3062, 2951, 1708, 1524, 1502, 1456, 1410, 1383, 1313, 1290, 1257, 1222, 1192, 1155, 1127, 1085, 1001, 984, 946, 913, 841, 771, 669, 628, 593, 535.

Methyl 3-(4-fluorophenyl)-5-methyl-1-(m-tolyl)-1H-pyrazole-4-carboxylate (3cb)

Yellow solid

Condition A: 212.0 mg, 0.65 mmol, 65%
Condition B: 50.3 mg, 0.16 mmol, 62%
**Supporting Information**

\[ R_f (\text{pentane/EtOAc} 90:10): 0.23; \]

\[ \text{H NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta = 7.70 - 7.62 \ (m, 2H, H_{arom}), 7.38 \ (t, J = 7.7 \text{ Hz}, 1H, H_{arom}), 7.31 - 7.21 \ (m, 3H, H_{arom}), 7.13 - 7.04 \ (m, 2H, H_{arom}), 3.77 \ (s, 3H, CH_3), 2.57 \ (s, 3H, CH_3), 2.42 \ (s, 3H, CH_3); \]

\[ \text{C NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta = 164.40 \ (CO), 163.02 \ (d, ^1J_{CF} = 246.5 \text{ Hz}, C_{arom}), 152.71 \ (C_{arom}), 145.08 \ (C_{arom}), 139.66 \ (C_{arom}), 138.63 \ (C_{arom}), 131.32 \ (d, ^2J_{CF} = 8.3 \text{ Hz}, C\text{arom}), 129.69 \ (CH_{arom}), 129.23 \ (d, ^4J_{CF} = 3.2 \text{ Hz}, C\text{arom}), 126.62 \ (CH_{arom}), 122.88 \ (CH_{arom}), 114.79 \ (d, ^2J_{CF} = 21.5 \text{ Hz}, CH_{arom}), 110.13 \ (C_{arom}), 51.20 \ (CH_3), 21.41 \ (CH_3), 12.95 \ (CH_3); \]

\[ \text{F NMR} \ (282 \text{ MHz, CDCl}_3): \ \delta = -113.85 \ (s, CF); \]

**Exact Mass ESI-MS:** calculated \( m/z \) for \([\text{C}_{19}\text{H}_{17}\text{FN}_2\text{O}_2\text{Na}]^+\) 347.1166, found 347.1167; for \([\text{C}_{19}\text{H}_{17}\text{FN}_2\text{O}_2\text{Na}]^+\) 671.2440, found 671.2442;

**ATR-FTIR (cm\(^{-1}\):** 3063, 2957, 2849, 2361, 2340, 1945, 1893, 1706, 1609, 1593, 1521, 1495, 1459, 1433, 1402, 1372, 1318, 1285, 1257, 1223, 1196, 1146, 1117, 1090, 1039, 1000, 946, 913, 886, 864, 838, 806, 780, 702, 674, 645, 592.

**Methyl 3-(4-fluorophenyl)-5-methyl-1-(p-tolyl)-1H-pyrazole-4-carboxylate (3db)**

Yellow solid

Condition A: 241.4 mg, 0.74 mmol, 74%

Condition B: 55.8 mg, 0.17 mmol, 69%

\[ R_f (\text{pentane/EtOAc} 90:10): 0.20; \]

\[ \text{H NMR} \ (300 \text{ MHz, CDCl}_3) \ \delta = 7.73 - 7.58 \ (m, 2H, H_{arom}), 7.38 - 7.27 \ (m, 4H, H_{arom}), 7.13 - 7.04 \ (m, 2H, H_{arom}), 3.77 \ (s, 3H, CH_3), 2.55 \ (s, 3H, CH_3), 2.43 \ (s, 3H, CH_3); \]

\[ \text{C NMR} \ (75 \text{ MHz, CDCl}_3) \ \delta = 164.62 \ (CO), 163.01 \ (d, ^1J_{CF} = 246.8 \text{ Hz}, C_{arom}), 152.64 \ (C_{arom}), 145.10 \ (C_{arom}), 139.01 \ (C_{arom}), 136.25 \ (C_{arom}), 131.31 \ (d, ^2J_{CF} = 8.3 \text{ Hz}, C\text{arom}), 129.94 \ (CH_{arom}), 129.26 \ (d, ^4J_{CF} = 3.3 \text{ Hz}, C\text{arom}), 125.75 \ (CH_{arom}), 114.79 \ (d, ^2J_{CF} = 21.8 \text{ Hz}, CH_{arom}), 110.06 \ (C_{arom}), 51.19 \ (CH_3), 21.29 \ (CH_3), 12.91 \ (CH_3); \]

\[ \text{F NMR} \ (282 \text{ MHz, CDCl}_3): \ \delta = -113.89 \ (s, CF); \]
**GC-MS:** \( t_R \) (50_20): 16.1 min;

**EI-MS:** \( m/z \) (%) = 324 (100), 323 (11), 309 (5), 294 (18), 293 (90), 292 (8), 291 (12), 266 (6), 265 (8), 132 (10), 95 (5), 91 (23), 65 (11);

**Exact Mass ESI-MS:** calculated \( m/z \) for \([C_{19}H_{17}FN_2O_2]^{+}\) 347.1166, found 347.1162; for \([C_{19}H_{17}FN_2O_2)_2Na]^{+}\) 671.2440, found 671.2445;

**ATR-FTIR (cm\(^{-1}\)):** 3082, 3024, 2952, 2922, 2348, 1712, 1612, 1515, 1460, 1438, 1408, 1385, 1323, 1308, 1293, 1253, 1222, 1189, 1147, 1108, 1087, 999, 949, 910, 828, 807, 784, 731, 715, 668, 615, 587.

### Methyl 1-(4-ethoxyphenyl)-3-(4-fluorophenyl)-5-methyl-1\(H\)-pyrazole-4-carboxylate (3eb)

![Methyl 1-(4-ethoxyphenyl)-3-(4-fluorophenyl)-5-methyl-1\(H\)-pyrazole-4-carboxylate](image)

**Yellow solid**

**Condition A:** 281.7 mg, 0.80 mmol, 80%

**Condition B:** 65.5 mg, 0.18 mmol, 74%

**\( R_f \)** (pentane/EtOAc 90:10): 0.17;

**\( ^1H \) NMR** (400 MHz, CDCl\(_3\)) \( \delta = 7.71 - 7.62 \) (m, 2H, \( H_{arom} \)), 7.39 – 7.31 (m, 2H, \( H_{arom} \)), 7.13 – 7.04 (m, 2H, \( H_{arom} \)), 7.01 – 6.95 (m, 2H, \( H_{arom} \)), 4.07 (q, \( J = 7.0 \) Hz, 2H, CH\(_2\)), 3.76 (s, 3H, CH\(_3\)), 2.52 (s, 3H, CH\(_3\)), 1.43 (t, \( J = 7.0 \) Hz, 3H, CH\(_3\));

**\( ^{13}C \) NMR** (101 MHz, CDCl\(_3\)) \( \delta = 164.58 \) (CO), 162.97 (d, \( J_{CF} = 246.7 \) Hz, \( C_{arom} \)), 159.25 (\( C_{arom} \)), 152.47 (\( C_{arom} \)), 145.20 (\( C_{arom} \)), 131.51 (\( C_{arom} \)), 131.29 (d, \( J_{CF} = 8.1 \) Hz, CH\(_{arom} \)), 129.29 (d, \( J_{CF} = 3.3 \) Hz, \( C_{arom} \)), 127.24 (CH\(_{arom} \)), 114.96 (CH\(_{arom} \)), 114.73 (d, \( J_{CF} = 21.8 \) Hz, CH\(_{arom} \)), 109.83 (\( C_{arom} \)), 63.92 (CH\(_2\)), 51.12 (CH\(_3\)), 14.79 (CH\(_3\)), 12.81 (CH\(_3\));

**\( ^{19}F \) NMR** (282 MHz, CDCl\(_3\)): \( \delta = -113.91 \) (s, CF);

**GC-MS:** \( t_R \) (50_20): 17.8 min;

**EI-MS:** \( m/z \) (%) = 354 (100), 353 (9), 326 (7), 325 (18), 324 (5), 323 (22), 296 (6), 295 (25), 294 (5), 293 (9), 218 (5), 134 (5), 65 (5);

**Exact Mass ESI-MS:** calculated \( m/z \) for \([C_{20}H_{19}FN_2O_3]^{+}\) 377.1272, found 377.1267; for \([C_{20}H_{19}FN_2O_3)_2Na]^{+}\) 731.2652, found 731.2650;
Supporting Information

**ATR-FTIR (cm\(^{-1}\))**: 2973, 2936, 2893, 2392, 2281, 1897, 1712, 1514, 1474, 1450, 1393, 1372, 1299, 1245, 1219, 1189, 1173, 1148, 1119, 1086, 1046, 998, 945, 920, 839, 805, 786, 751, 729, 695, 655, 589, 522.

**Methyl 1-(4-(dimethylamino)phenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3fb)**

Yellow oil

Condition A: 97.2 mg, 0.28 mmol, 28%

Condition B: 13.2 mg, 0.04 mmol, 15%

\(R_f\) (pentane/EtOAc 90:10): 0.11;

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.63 - 7.53\) (m, 2H, H\(_{arom}\)), 7.22 - 7.16 (m, 2H, H\(_{arom}\)), 7.04 - 6.96 (m, 2H, H\(_{arom}\)), 6.68 (d, \(J = 9.0\) Hz, 2H, H\(_{arom}\)), 3.68 (s, 3H, CH\(_3\)), 2.93 (s, 6H, CH\(_3\)), 2.44 (s, 3H, CH\(_3\));

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 164.76\) (CO), 162.95 (d, \(^1J_{CF} = 246.7\) Hz, C\(_{arom}\)), 152.26 (C\(_{arom}\)), 150.60 (C\(_{arom}\)), 145.24 (C\(_{arom}\)), 131.33 (d, \(^3J_{CF} = 8.3\) Hz, CH\(_{arom}\)), 129.50 (d, \(^4J_{CF} = 3.3\) Hz, C\(_{arom}\)), 127.73 (C\(_{arom}\)), 126.83 (CH\(_{arom}\)), 114.72 (d, \(^5J_{CF} = 21.5\) Hz, CH\(_{arom}\)), 112.19 (CH\(_{arom}\)), 109.49 (C\(_{arom}\)), 51.10 (CH\(_3\)), 40.61 (CH\(_3\)), 12.87 (CH\(_3\));

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -114.17\) (s, CF);

**GC-MS:** \(tR\) (50 _20_ 320): 17.6 min;

**EI-MS:** \(m/z\) (%) = 335 (100), 334 (23), 304 (6), 223 (5), 152 (6), 77 (8);

**Exact Mass ESI-MS:** calculated \(m/z\) for \([C_{20}H_{20}F_{2}N_{3}O_{2}Na]^+\) 376.1432, found 376.1420; for \([[(C_{20}H_{20}F_{2}N_{3}O_{2})_{2}Na]^+]\) 729.2971, found 729.2957;

**ATR-FTIR (cm\(^{-1}\))**: 3061, 2991, 2949, 2896, 2860, 2809, 2389, 2348, 2295, 2253, 2226, 2175, 2132, 2030, 1892, 1706, 1610, 1518, 1447, 1383, 1356, 1299, 1259, 1222, 1189, 1154, 1115, 1087, 1065, 1017, 998, 946, 911, 841, 820, 789, 731, 706, 645, 611, 584, 557, 523.
Methyl 1,3-bis(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3gb)

White solid

Condition A: 211.8 mg, 0.65 mmol, 65%
Condition B: 48.5 mg, 0.15 mmol, 59%

$R_f$ (pentane/EtOAc 90:10): 0.22;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.70 – 7.60 (m, 2H, H$_{arom}$), 7.48 – 7.41 (m, 2H, H$_{arom}$), 7.24 – 7.17 (m, 2H, H$_{arom}$), 7.14 – 7.06 (m, 2H, H$_{arom}$), 3.77 (s, 3H, CH$_3$), 2.55 (s, 3H, CH$_3$);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 164.49 (CO), 163.10 (d, $^1$J$\text{C-F} = 247.2$ Hz, C$_{arom}$), 162.58 (d, $^1$J$\text{C-F} = 249.3$ Hz, C$_{arom}$), 152.92 (C$_{arom}$), 145.24 (C$_{arom}$), 134.88 (d, $^4$J$\text{C-F} = 3.2$ Hz, $^4$J$\text{C-F}$), 131.30 (d, $^3$J$\text{C-F} = 8.3$ Hz, CH$_{arom}$), 129.07 (d, $^4$J$\text{C-F} = 3.3$ Hz, C$_{arom}$), 127.88 (d, $^3$J$\text{C-F} = 8.8$ Hz, CH$_{arom}$), 116.44 (d, $^2$J$\text{C-F} = 23.3$ Hz, CH$_{arom}$), 114.88 (d, $^2$J$\text{C-F} = 21.6$ Hz, CH$_{arom}$), 110.40 (C$_{arom}$), 51.28 (CH$_3$), 12.88 (CH$_3$);

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ = -111.80 (s, CF), -113.62 (s, CF);

GC-MS: $t_R$ (50_20): 15.2 min;

EI-MS: $m/z$ (%) = 328 (95), 313 (7), 298 (18), 297 (100), 296 (11), 295 (13), 270 (5), 269 (6), 136 (18), 95 (24), 75 (8);

Exact Mass ESI-MS: calculated $m/z$ for [C$_{18}$H$_{14}$F$_2$N$_2$O$_2$Na]$^+$ 351.0916, found 351.0915; for [(C$_{18}$H$_{14}$F$_2$N$_2$O$_2$)$_2$Na]$^+$ 679.1939, found 679.1937;

ATR-FTIR (cm$^{-1}$): 3398, 3124, 3069, 3009, 2962, 2848, 2348, 2166, 2103, 1709, 1601, 1510, 1456, 1441, 1408, 1382, 1320, 1298, 1256, 1219, 1194, 1150, 1119, 1085, 1015, 999, 951, 832, 807, 785, 730, 698, 664, 639, 617, 587, 515.

Methyl 1-(4-(ethoxycarbonyl)phenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3hb)

White solid

Condition A: 258.7 mg, 0.68 mmol, 68%
Supporting Information

Condition B: 59.2 mg, 0.15 mmol, 62%

Rf (pentane/EtOAc 90:10): 0.13;

1H NMR (400 MHz, CDCl3) δ = 8.23 – 8.14 (m, 2H, H_aron), 7.68 – 7.61 (m, 2H, H_aron), 7.60 – 7.54 (m, 2H, H_aron), 7.10 (ddd, J = 10.8, 5.9, 2.5 Hz, 2H, H_aron), 4.41 (q, J = 7.1 Hz, 2H, CH2), 3.77 (s, 3H, CH3), 2.62 (s, 3H, CH3), 1.41 (t, J = 7.1 Hz, 3H, CH3);

13C NMR (101 MHz, CDCl3) δ = 165.66 (s), 164.36 (CO), 163.12 (d, J = 247.7 Hz, C_aron), 153.32 (C_aron), 145.13 (C_aron), 142.25 (C_aron), 131.27 (d, 3J_CF = 8.3 Hz, CH_aron), 130.75 (CH_aron), 130.59 (C_aron), 128.95 (d, 4J_CF = 3.3 Hz, C_aron), 125.39 (CH_aron), 114.8 8 (d, 2J_CF = 21.7 Hz, CH_aron), 111.10 (C_aron), 61.51 (CH2), 51.30 (CH3), 14.40 (CH3), 13.09 (CH3);

19F NMR (282 MHz, CDCl3): δ = -113.45 (s, CF);

Exact Mass ESI-MS: calculated m/z for [C21H19FN2O4H]+ 383.1402, found 383.1406; for [(C21H19FN2O4)2Na]+ 787.2550, found 787.2548;

ATR-FTIR (cm\(^{-1}\)): 2988, 2361, 2339, 1714, 1610, 1516, 1464, 1440, 1362, 1322, 1285, 1255, 1230, 1197, 1153, 1136, 1102, 1084, 1014, 993, 941, 884, 855, 830, 807, 787, 769, 727, 697, 660, 597.

Methyl 3-(4-fluorophenyl)-5-methyl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3ib)

![Methyl 3-(4-fluorophenyl)-5-methyl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3ib)](image)

Yellow oil

Condition A: 227.0 mg, 0.60 mmol, 60%

Condition B: 46.5 mg, 0.12 mmol, 49%

Rf (pentane/EtOAc 90:10): 0.19;

1H NMR (300 MHz, CDCl3) δ = 7.91 – 7.81 (m, 1H, H_aron), 7.77 – 7.60 (m, 4H, H_aron), 7.44 (d, J = 7.3 Hz, 1H, H_aron), 7.17 – 6.99 (m, 2H, H_aron), 3.78 (s, 3H, CH3), 2.37 (s, 3H, CH3);

13C NMR (75 MHz, CDCl3) δ = 164.37 (CO), 163.1 (d, 1J_CF = 246.0 Hz, C_aron), 152.90 (C_aron), 147.18 (C_aron), 136.34 (C_aron), 133.08 (CH_aron), 131.39 (d, 3J_CF = 8.3 Hz, CH_aron), 130.50 (CH_aron), 130.42 (CH_aron), 129.00 (d, 4J_CF = 3.3 Hz, C_aron), 128.59 (q, 2J_CF3 = 31.5 Hz, C_aron),
Methyl 3-(3-fluorophenyl)-5-methyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3jb)

![Structure](image)

White solid

**Condition A**: 257.3 mg, 0.68 mmol, 68%

**Condition B**: 56.8 mg, 0.15 mmol, 60%

**Rf** (pentane/EtOAc 90:10): 0.20;

**1H NMR** (300 MHz, CDCl₃) δ = 7.79 (s, 1H, H_arom), 7.75 – 7.60 (m, 5H, H_arom), 7.17 – 7.04 (m, 2H, H_arom), 3.78 (s, 3H, CH₃), 2.61 (s, 3H, CH₃);

**13C NMR** (75 MHz, CDCl₃) δ = 164.33 (CO), 163.15 (d, 1J_CF = 248.2 Hz, C_arom), 153.39 (C_arom), 145.23 (C_arom), 139.23 (C_arom), 132.11 (q, 2J_CF = 32.0 Hz, C_arom), 131.29 (d, 3J_CF = 8.1 Hz, CH_arom), 130.09 (CH_arom), 128.98 (CH_arom), 128.86 (d, 4J_CF = 3.3 Hz, C_arom), 125.59 (q, 3J_CF = 3.8 Hz, C_arom), 123.48 (q, 1J_CF = 272.3 Hz, CF₃), 122.93 (q, 3J_CF = 3.8 Hz, C_arom), 114.93 (d, 2J_CF = 22.2Hz, CH_arom), 111.00 (C_arom), 51.34 (CH₃), 12.96 (CH₃);

**19F NMR** (282 MHz, CDCl₃): δ = -62.72 (s, CF₃), -113.38 (s, CF);

**GC-MS**: t_R (50_20): 14.9 min;

**EI-MS**: m/z (%) = 378 (84), 348 (20), 347 (100), 343 (6), 320 (5), 277 (14), 186 (25), 146 (7), 145 (31), 125 (6), 95 (9), 75 (6);

**Exact Mass ESI-MS**: calculated m/z for [C₁₉H₁₄F₄N₂O₂Na]<sup>+</sup> 401.0884, found 401.0881; for [(C₁₉H₁₄F₄N₂O₂)<sub>2</sub>Na]<sup>+</sup> 779.1875, found 779.1869;

**ATR-FTIR** (cm<sup>-1</sup>): 3121, 3077, 3001, 2953, 2388, 2349, 2299, 2155, 1711, 1608, 1525, 1507, 1458, 1385, 1314, 1278, 1223, 1174, 1118, 1090, 1063, 1036, 999, 946, 841, 807, 772, 732, 689, 641, 593, 533.
**EI-MS:** $m/z$ (%) = 378 (87), 363 (6), 359 (6), 348 (21), 347 (100), 346 (12), 345 (15), 320 (5), 319 (18), 146 (6), 145 (31), 125 (6), 95 (8), 75 (5);

**Exact Mass ESI-MS:** calculated $m/z$ for $[\text{C}_{19}\text{H}_{14}\text{F}_{4}\text{N}_{2}\text{O}_{2}\text{Na}]^+$ 401.0884, found 401.0880; for $[(\text{C}_{19}\text{H}_{14}\text{F}_{4}\text{N}_{2}\text{O}_{2})_{2}\text{Na}]^+$ 779.1875, found 779.1876;

**ATR-FTIR (cm$^{-1}$):** 3077, 2953, 2361, 2339, 1893, 1711, 1600, 1525, 1500, 1446, 1377, 1330, 1308, 1288, 1225, 1159, 1122, 1091, 1072, 1030, 999, 985, 898, 842, 808, 789, 699, 662, 642, 620, 593.

### Methyl 3-(4-fluorophenyl)-5-methyl-1-(4-(trifluoromethyl)phenyl)-1$H$-pyrazole-4-carboxylate (3kb)

Yellowish solid

**Condition A:** 238.4 mg, 0.63 mmol, 63%  
**Condition B:** 53.9 mg, 0.14 mmol, 57%

**$R_f$** (pentane/EtOAc 90:10): 0.19;

**$^1$H NMR** (300 MHz, CDCl$_3$) $\delta$ = 7.80 (d, $J = 8.4$ Hz, 2H, H$_{arom}$), 7.71 – 7.58 (m, 4H, H$_{arom}$), 7.16 – 7.05 (m, 2H, H$_{arom}$), 3.78 (s, 3H, CH$_3$), 2.63 (s, 3H, CH$_3$);

**$^{13}$C NMR** (75 MHz, CDCl$_3$) $\delta$ = 164.34 (CO), 163.16 (d, $^1J_{CF} = 247.6$ Hz, C$_{arom}$), 153.43 (C$_{arom}$), 145.17 (C$_{arom}$), 141.61 (C$_{arom}$), 131.28 (d, $^3J_{CF} = 8.2$ Hz, CH$_{arom}$), 130.78 (q, $^2J_{CF3} = 33.1$ Hz, C$_{arom}$), 128.85 (d, $^4J_{CF} = 3.3$ Hz, C$_{arom}$), 126.63 (q, $^3J_{CF3} = 3.7$ Hz, CH$_{arom}$), 125.98 (CH$_{arom}$), 123.74 (q, $^1J_{CF3} = 272.5$ Hz, CF$_3$), 114.94 (d, $^2J_{CF} = 21.8$ Hz, CH$_{arom}$), 111.18 (C$_{arom}$), 51.35 (CH$_3$), 13.05 (CH$_3$);

**$^{19}$F NMR** (282 MHz, CDCl$_3$): $\delta$ = -62.60 (s, CF$_3$), -113.32 (s, CF);

**GC-MS:** tR (50.20): 15.3 min;

**EI-MS:** $m/z$ (%) = 378 (89), 377 (3), 363 (6), 359 (6), 348 (20), 347 (100), 346 (12), 345 (15), 320 (4), 319 (5), 189 (3), 186 (17), 146 (6), 145 (32), 126 (3), 125 (6), 120 (4), 95 (9), 75 (5);

**Exact Mass ESI-MS:** calculated $m/z$ for $[\text{C}_{19}\text{H}_{14}\text{F}_{4}\text{N}_{2}\text{O}_{2}\text{Na}]^+$ 401.0884, found 401.0878; for $[(\text{C}_{19}\text{H}_{14}\text{F}_{4}\text{N}_{2}\text{O}_{2})_{2}\text{Na}]^+$ 779.1875, found 779.1859;
ATR-FTIR (cm\(^{-1}\)): 3082, 2957, 1703, 1616, 1539, 1520, 1439, 1406, 1323, 1304, 1261, 1230, 1169, 1158, 1102, 1069, 1009, 982, 955, 837, 813, 787, 729, 694, 642, 594.

Ethyl 3-(4-fluorophenyl)-1-mesityl-5-methyl-1\(H\)-pyrazole-4-carboxylate (3lb)

Yellowish solid

Condition A: 290.2 mg, y.y mmol, 79%

Condition B: 66.1 mg, 0.18 mmol, 72%

\(R_f\) (pentane/EtOAc 90:10): 0.46;

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.75 - 7.64\) (m, 2H, \(H_{arom}\)), \(7.14 - 7.02\) (m, 2H, \(H_{arom}\)), 6.98 (s, 2H, \(H_{arom}\)), 4.27 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 2.34 (s, 3H, CH\(_3\)), 2.30 (s, 3H, CH\(_3\)), 1.98 (s, 6H, CH\(_3\)), 1.27 (t, \(J = 7.1\) Hz, 3H, CH\(_3\));

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 164.33\) (CO), 162.98 (d, \(^1\)J\(_{CF} = 247.0\) Hz, \(C_{arom}\)), 152.94 (\(C_{arom}\)), 145.99 (\(C_{arom}\)), 139.66 (\(C_{arom}\)), 136.02 (\(C_{arom}\)), 134.31 (\(C_{arom}\)), 131.46 (d, \(^3\)J\(_{CF} = 8.5\) Hz, CH\(_{arom}\)), 129.44 (d, \(^4\)J\(_{CF} = 3.2\) Hz, \(C_{arom}\)), 129.17 (CH\(_{arom}\)) 114.63 (d, \(^2\)J\(_{CF} = 21.5\) Hz, CH\(_{arom}\)), 109.05 (\(C_{arom}\)), 60.14 (CH\(_2\)), 21.26 (CH\(_3\)), 17.40 (CH\(_3\)), 14.28 (CH\(_3\)), 11.75 (CH\(_3\)).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -114.05\) (s, CF);

GC-MS: \(t_R\) (50,40,320): 10.5 min;

EI-MS: \(m/z\) (%) = 366 (70), 352 (25), 351 (100), 337 (7), 323 (7), 322 (5), 321 (16), 305 (12), 279 (9), 278 (5), 157 (5), 156 (5), 145 (5), 123 (5), 122 (5), 119 (7), 117 (5), 115 (6), 91 (12), 77 (7);

Exact Mass ESI-MS: calculated \(m/z\) for \([C_{22}H_{23}FN_2O_2H]^+\) 367.1816, found 367.1816; for \([C_{22}H_{23}FN_2O_2Na]^+\) 389.1636, found 389.1634; for \([[(C_{22}H_{23}FN_2O_2)_2Na]^+]\) 755.3379, found 755.3380;

ATR-FTIR (cm\(^{-1}\)): 2980, 2914, 2360, 2341, 1897, 1709, 1524, 1492, 1453, 1379, 1258, 1233, 1214, 1173, 1144, 1124, 1087, 1026, 981, 945, 863, 841, 816, 789, 751, 727, 706, 587.
**Supporting Information**

**Ethyl 1-(2,6-diisopropylphenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3mb)**

Yellowish solid

Condition A: 178.0 mg, 0.44 mmol, 44%

Condition B: 25.4 mg, 0.06 mmol, 25%

R<sub>f</sub> (pentane/EtOAc 90:10): 0.53;

**<sup>1</sup>H** NMR (300 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.54 (m, 2H, H<sub>arom</sub>), 7.44 – 7.33 (m, 1H, H<sub>arom</sub>), 7.20 (d, J = 8.7 Hz, 2H, H<sub>arom</sub>), 7.00 (dd, J = 12.2, 5.4 Hz, 2H, H<sub>arom</sub>), 4.20 (q, J = 7.1 Hz, 2H, CH<sub>2</sub>), 2.36 – 2.18 (m, 5H, CH, CH, CH<sub>3</sub>), 1.21 (t, J = 7.1 Hz, 3H, CH<sub>3</sub>), 1.09 (d, J = 6.9 Hz, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 1.08 (d, J = 6.9 Hz, 6H, C(CH<sub>3</sub>)<sub>2</sub>);

**<sup>13</sup>C** NMR (101 MHz, CDCl<sub>3</sub>) δ = 164.36 (CO), 162.99 (d, <sup>1</sup>J<sub>CF</sub> = 246.8 Hz, C<sub>arom</sub>), 152.44 (C<sub>arom</sub>), 146.82 (C<sub>arom</sub>), 146.57 (C<sub>arom</sub>), 134.27 (C<sub>arom</sub>), 131.50 (d, <sup>2</sup>J<sub>CF</sub> = 8.2 Hz, CH<sub>arom</sub>), 130.51 (CH<sub>arom</sub>), 129.47 (d, <sup>3</sup>J<sub>CF</sub> = 3.3 Hz, C<sub>arom</sub>), 124.09 (CH<sub>arom</sub>), 114.64 (d, <sup>3</sup>J<sub>CF</sub> = 21.5 Hz, CH<sub>arom</sub>), 109.08 (C<sub>arom</sub>), 60.19 (CH<sub>2</sub>), 28.57 (CH), 24.69 (CH<sub>3</sub>), 23.43 (CH<sub>3</sub>), 14.29 (CH<sub>3</sub>), 12.51 (CH<sub>3</sub>);

**<sup>19</sup>F** NMR (282 MHz, CDCl<sub>3</sub>): δ = -114.11 (s, CF);

**GC-MS:** r<sub>R</sub> (50_40_320): 10.4 min;

**EI-MS:** m/z (%) = 408 (38), 407 (5), 394 (27), 393 (100), 379 (5), 365 (10), 363 (7);

**Exact Mass ESI-MS:** calculated m/z for [C<sub>25</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup> 431.2105, found 431.2107; for [C<sub>25</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>2</sub>H]<sup>+</sup> 409.2286, found 4409.2288; for [(C<sub>25</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Na]<sup>+</sup> 839.4318, found 839.4328;

Methyl 3-(4-fluorophenyl)-1,5-dimethyl-1\textit{H}-pyrazole-4-carboxylate (3nb)

White solid

*Condition C: 184.7 mg, 0.74 mmol, 74%

Condition B: 26.1 mg, 0.11 mmol, 42%

*Condition A, with nitrile (7.0 eq.) and \(N,N\)-Dimethylacetamide (1 M)

\(R_f\) (pentane/EtOAc 90:10): 0.03;

\(^1\text{H} \text{NMR}\) (300 MHz, CDCl\(_3\)) \(\delta = 7.64 - 7.47\) (m, 2H, \(H_{\text{arom}}\)), 7.11 - 6.99 (m, 2H, \(H_{\text{arom}}\)), 3.81 (s, 3H, \(CH_3\)), 3.70 (s, 3H, \(CH_3\)), 2.53 (s, 3H, \(CH_3\));

\(^{13}\text{C} \text{NMR}\) (75 MHz, CDCl\(_3\)) \(\delta = 164.46\) (CO), 162.82 (d, \(^1J_{CF} = 248.9\) Hz, \(C_{\text{arom}}\)), 151.65 (\(C_{\text{arom}}\)), 144.50 (\(C_{\text{arom}}\)), 131.09 (d, \(^3J_{CF} = 8.2\) Hz, \(CH_{\text{arom}}\)), 129.45 (d, \(^4J_{CF} = 3.3\) Hz, \(C_{\text{arom}}\)), 114.69 (d, \(^2J_{CF} = 21.5\) Hz, \(CH_{\text{arom}}\)), 109.00 (\(C_{\text{arom}}\)), 50.97 (\(CH_3\)), 36.44 (\(CH_3\)), 11.50 (\(CH_3\)).

\(^{19}\text{F} \text{NMR}\) (282 MHz, CDCl\(_3\)) \(\delta = -114.15\) (s, CF);

\textbf{GC-MS}: \(t_R\) (50-20): 13.0 min;

\textbf{EI-MS}: \(m/z\) (%) =248 (65), 233 (5), 218 (14), 217 (100), 216 (8), 190 (5), 146 (8), 145 (5), 120 (5), 56 (12);

\textbf{Exact Mass ESI-MS}: calculated \(m/z\) for \([C_{13}H_{13}F_N_2O_2Na]^+\) 271.0853, found 271.0860, for \([((C_{13}H_{13}F_N_2O_2)Na]^+\) 519.1814, found 519.1815;

\textbf{ATR-FTIR (cm\(^{-1}\))}: 3810, 3790, 3663, 3640, 3000, 2949, 2843, 2361, 2336, 1097, 1780, 1706, 1603, 1525, 1456, 1379, 1313, 1299, 1273, 1218, 1190, 1159, 1140, 1098, 1073, 1017, 995, 945, 842, 806, 790, 775, 731, 707, 668, 644, 632, 606, 585, 522.

Methyl 1-butyl-3-(4-fluorophenyl)-5-methyl-1\textit{H}-pyrazole-4-carboxylate (3ob)

Yellow oil

*Condition C: 202.9 mg, 0.70 mmol, 70%

Condition B: 25.4 mg, 0.09 mmol, 35%

*Condition A, with nitrile (7.0 eq.) and \(N,N\)-Dimethylacetamide (1 M)
**Supporting Information**

**R**<sub>f</sub> (pentane/EtOAc 90:10): 0.19;

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 7.65 – 7.50 (m, 2H, H<sub>arom</sub>), 7.15 – 6.98 (m, 2H, H<sub>arom</sub>), 4.09 (t, J = 7.4 Hz, 2H, CH₂), 3.71 (s, 3H, CH₃), 2.55 (s, 3H, CH₃), 1.90 – 1.75 (m, 2H, CH₂), 1.46 – 1.29 (m, 2H, CH₂), 0.95 (t, J = 7.3 Hz, 3H, CH₃);

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 164.64 (CO), 162.85 (d, <sup>1</sup>J<sub>CF</sub> = 246.4 Hz, C<sub>arom</sub>), 151.72 (C<sub>arom</sub>), 143.93 (C<sub>arom</sub>), 131.16 (d, <sup>3</sup>J<sub>CF</sub> = 8.2 Hz, CH<sub>arom</sub>), 129.67 (d, <sup>4</sup>J<sub>CF</sub> = 3.3 Hz, C<sub>arom</sub>), 114.71 (d, <sup>2</sup>J<sub>CF</sub> = 21.6 Hz, CH<sub>arom</sub>), 108.87 (C<sub>arom</sub>), 50.98 (CH₂), 49.25 (CH₂), 32.12 (CH₂), 19.97 (CH₂), 13.77 (CH₃), 11.46 (CH₃);

**<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>): δ = -114.30 (s, CF);

**GC-MS:** t<sub>R</sub> (50_20): 13.8 min;

**EI-MS:** m/z (%) = 290 (18), 275 (9), 248 (29), 247 (100), 234 (14), 215 (9), 203 (28), 146 (6);

**Exact Mass ESI-MS:** calculated m/z for [C₁₆H₁₉FN₂O₂Na]<sup>+</sup> 313.1323, found 313.1329; for [(C₁₆H₁₉FN₂O₂)₂Na]- 603.2753, found 603.2754;

**ATR-FTIR (cm⁻¹):** 3064, 2957, 2874, 2682, 2390, 2349, 2277, 2213, 2184, 2155, 2131, 2093, 1893, 1705, 1608, 1524, 1484, 1453, 1381, 1306, 1221, 1191, 1157, 1138, 1074, 1015, 998, 986, 947, 888, 841, 807, 788, 731, 653, 624, 603, 587, 525.

**Methyl 3-(4-fluorophenyl)-1-isopropyl-5-methyl-1H-pyrazole-4-carboxylate (3pb)**

Yellow oil

*Condition C: 96.5 mg, 0.35 mmol, 35%

*Condition A, with nitrile (7.0 eq.) and N,N-Dimethylacetamide (1 M)

**R**<sub>f</sub> (pentane/EtOAc 90:10): 0.24;

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 7.66 – 7.52 (m, 2H, H<sub>arom</sub>), 7.06 (t, J = 8.8 Hz, 2H, H<sub>arom</sub>), 4.51 (hept, J = 6.6 Hz, 1H, CH), 3.71 (s, 3H, CH₃), 2.57 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 1.50 (s, 3H, CH₃);
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 164.89\) (CO), 162.89 (d, \(\text{J}_{\text{CF}} = 246.0\) Hz, \(\text{C}_{\text{arom}}\)), 151.52 (\(\text{C}_{\text{arom}}\)), 143.00 (\(\text{C}_{\text{arom}}\)), 131.27 (d, \(\text{J}_{\text{CF}} = 8.2\) Hz, \(\text{C}_{\text{arom}}\)), 130.10 (d, \(\text{J}_{\text{CF}} = 3.3\) Hz, \(\text{C}_{\text{arom}}\)), 114.70 (d, \(\text{J}_{\text{CF}} = 21.2\) Hz, \(\text{C}_{\text{arom}}\)), 108.84 (\(\text{C}_{\text{arom}}\)), 50.94 (CH), 50.23 (CH\(_3\)), 22.31 (CH\(_3\)), 11.08 (CH\(_3\));

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -114.58\) (s, CF);

GC-MS: \(t_R\) 50.20: 13.1 min;

EI-MS: \(m/z\) (%) = 276 (78), 261 (32), 245 (14), 234 (26), 229 (17), 204 (13), 203 (100), 202 (12), 147 (6), 146 (14), 145 (7), 134 (6), 120 (6), 95 (6), 42 (7);

Exact Mass ESI-MS: calculated \(m/z\) for [C\(_{15}\)H\(_{17}\)FN\(_2\)O\(_2\)Na\(^+\)] 299.1166, found 299.1177; for [C\(_{15}\)H\(_{17}\)FN\(_2\)O\(_2\)H\(^+\)] 277.1347, found 277.1355; for [(C\(_{15}\)H\(_{17}\)FN\(_2\)O\(_2\)Na\(^2+\)] 575.2441, found 575.2440;


**Ethyl 3-(4-fluorophenyl)-1,5-diphenyl-1\(H\)-pyrazole-4-carboxylate (3qb)**

Yellowish solid

Condition A: 282.2 mg, 0.73 mmol, 73%

Condition B: 64.5 mg, 0.17 mmol, 67%

\(R_t\) (pentane/EtOAc 90:10): 0.34;

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.77 – 7.62\) (m, 2H, \(\text{H}_{\text{arom}}\)), 7.33 – 7.21 (m, 5H, \(\text{H}_{\text{arom}}\)), 7.20 – 7.12 (m, 5H, \(\text{H}_{\text{arom}}\)), 7.09 – 6.99 (m, 2H, \(\text{H}_{\text{arom}}\)), 3.99 (q, \(J = 7.1\) Hz, 2H, CH\(_2\)), 0.89 (t, \(J = 7.1\) Hz, 3H, CH\(_3\));

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 163.69\) (CO), 163.13 (d, \(\text{J}_{\text{CF}} = 246.2\) Hz, \(\text{C}_{\text{arom}}\)), 152.56 (\(\text{C}_{\text{arom}}\)), 146.60 (\(\text{C}_{\text{arom}}\)), 139.16 (\(\text{C}_{\text{arom}}\)), 131.21 (d, \(\text{J}_{\text{CF}} = 8.3\) Hz, \(\text{C}_{\text{arom}}\)), 130.47 (\(\text{C}_{\text{arom}}\)), 129.15 (\(\text{C}_{\text{arom}}\)), 128.93 (\(\text{C}_{\text{arom}}\)), 128.89 (d, \(\text{J}_{\text{CF}} = 3.3\) Hz, \(\text{C}_{\text{arom}}\)), 128.15 (\(\text{C}_{\text{arom}}\)), 128.03 (\(\text{C}_{\text{arom}}\)), 125.48 (\(\text{C}_{\text{arom}}\)), 114.96 (d, \(\text{J}_{\text{CF}} = 21.8\) Hz, \(\text{C}_{\text{arom}}\)), 112.04 (\(\text{C}_{\text{arom}}\)), 60.34 (CH\(_2\)), 13.75 (CH\(_3\));
\(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -113.50\) (s, CF);

**Exact Mass ESI-MS:** calculated \(m/z\) for \([C_{24}H_{19}FN_2O_2Na]^+\) 409.1323, found 409.1319; for \([[(C_{24}H_{19}FN_2O_2)_2Na]^+\) 795.2753, found 795.2746;

**ATR-FTIR (\text{cm}^{-1}):** 3059, 2986, 2905, 2685, 2388, 2348, 2210, 2144, m 1976, 1957, 1902, 1810, 1705, 1596, 1524, 1495, 1450, 1373, 1310, 1296, 1252, 1225, 1187, 1146, 1099, 1075, 1034, 1021, 974, 947, 918, 876, 841, 816, 793, 766, 741, 695, 660, 611, 566, 540, 522.

(3-(4-fluorophenyl)-5-methyl-1-phenyl-1\(H\)-pyrazol-4-yl)(phenyl)methanone (3rb)

White solid

Condition A: 108.0 mg, 0.30 mmol, 30%

Condition B: 16.1 mg, 0.05 mmol, 18%

\(R_f\) (pentane/EtOAc 90:10): 0.16;

**\(^1\)H NMR (400 MHz, CDCl\(_3\)):** \(\delta = 7.68 - 7.60\) (m, 2H, \(H_{arom}\)), 7.51 - 7.44 (m, 4H, \(H_{arom}\)), 7.42 - 7.38 (m, 1H, \(H_{arom}\)), 7.36 - 7.30 (m, 3H, \(H_{arom}\)), 7.21 - 7.17 (m, 2H, \(H_{arom}\)), 6.82 - 6.74 (m, 2H, \(H_{arom}\)), 2.35 (s, 3H, CH\(_3\)).

**\(^{13}\)C NMR (101 MHz, CDCl\(_3\)):** \(\delta = 192.73\) (CO), 162.69 (d, \(^1J_{CF} = 247.6\) Hz, \(C_{arom}\)), 151.66 (\(C_{arom}\)), 143.59 (\(C_{arom}\)), 138.90 (\(C_{arom}\)), 138.48 (\(C_{arom}\)), 132.81 (\(CH_{arom}\)), 130.54 (d, \(^3J_{CF} = 8.3\) Hz, \(CH_{arom}\)), 129.84 (\(CH_{arom}\)), 129.48 (\(CH_{arom}\)), 128.85 (\(CH_{arom}\)) - 128.75 (d, \(^4J_{CF} = 3.2\) Hz, \(C_{arom}\)), 128.28 (\(CH_{arom}\)), 125.71 (\(CH_{arom}\)), 118.89 (\(C_{arom}\)), 115.14 (d, \(^2J_{CF} = 21.7\) Hz, \(CH_{arom}\)), 12.43 (CH\(_3\)).

**\(^{19}\)F NMR (282 MHz, CDCl\(_3\)):** \(\delta = -113.80\) (s, CF);

**GC-MS:** \(t_R\) (50-40-320): 11.5 min;

**EI-MS:** \(m/z\) (%) = 356 (76), 355 (100), 339 (6), 280 (9), 279 (46), 118 (10), 105 (5), 77 (38), 51 (8);

**Exact Mass ESI-MS:** calculated \(m/z\) for \([C_{23}H_{17}FN_2ONa]^+\) 379.1217, found 379.1219; for \([[(C_{23}H_{17}FN_2O)_2Na]^+\) 735.2542; found 735.2531;
ATR-FTIR (cm$^{-1}$): 3063, 2928, 2390, 2348, 2246, 1744, 1642, 1597, 1580, 1523, 1501, 1447, 1434, 1407, 1371, 1320, 1292, 1254, 1223, 1194, 1173, 1158, 1136, 1098, 1074, 1014, 984, 910, 840, 820, 767, 744, 724, 696, 641, 587, 542, 524.
5. Kinetic Study of the Additive

\[
\begin{align*}
&\begin{array}{c}
\text{Me} \\
\text{Ph}
\end{array} \\
&\begin{array}{c}
\text{CO}_2\text{Me}
\end{array}
\end{align*}
\]

\[
1a \quad (1 \text{ eq}) + 2a \quad (3 \text{ eq}) \xrightarrow{\text{Cu(OAc)}_2 (10 \text{ mol\%})} \quad \begin{array}{c}
\text{Me} \\
\text{Ph}
\end{array} \\
\begin{array}{c}
\text{CO}_2\text{Me}
\end{array}
\]

Into two oven-dried Schlenk tubes (A and B) (approx. 10 mL in volume) with a magnetic stirring bar in each tube, were weighed in air the enamine starting material 1a (0.25 mmol), Cu(OAc)\(_2\) (0.025 mmol, 10 mol\%) followed by the addition of DCE (1,2-dichloroethane) (0.5 M) and benzonitrile 2a (3.0 eq.). In tube A, 2-picolinic acid (0.0125 mmol, 5 mol\% eq.) was added. The tubes were fitted with septas and stirred vigorously, evacuated and filled with molecular oxygen with a balloon at 1 bar (repeatedly 2-3 times). Through the septas, 25 µL mesitylene was added as internal standard to each tube. The reaction tubes were closed and stirred vigorously. Through the septas, small aliquot (approx. 10 µL) were taken from each tube for zero time readings. The tubes were then kept stirring in preheated oil bath at 110 °C for 24 h. At regular interval of time, small aliquots (approx. 10 µL) were taken out from the tubes through the septas. The aliquots were diluted with EtOAc to suspend the metallic precipitates and filtered through a short pad of silica and were analyzed by pre-calibrated GC. The GC yield (%) of product 3aa was plotted against the time.

![Graph](image)

**Fig. 2** Kinetic study of the effect of 2-picolinic acid on the the formation of 3aa; data points (*) with and (△) without the additive.
<table>
<thead>
<tr>
<th>Time (h.)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>B</th>
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<tr>
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<td>83</td>
<td>45</td>
<td>0</td>
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</table>

Reaction conditions: as mentioned above. Tube A – with and tube B – without the additive. "Determined by GC analysis with mesitylene as an internal standard."
6. Spectra of the Pyrazole Products

Methyl 5-methyl-1,3-diphenyl-1H-pyrazole-4-carboxylate (3aa)
Methyl 3-(4-fluorophenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ab)
$^{19}$F NMR
decoupled
Methyl 3-(4-acetylphenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ac)
Methyl 5-methyl-1-phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3ad)
Methyl 3-(2-fluorophenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ae)
Methyl 5-methyl-1-phenyl-3-\((m\)-tolyl\)-1H-pyrazole-4-carboxylate (3af)
Methyl 3-(4-(dimethylamino)phenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ag)
Methyl 3-(4-ethoxyphenyl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ah)
Methyl 3-(furan-2-yl)-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3ai)
Methyl 5-methyl-3-(3-methylpyridin-2-yl)-1-phenyl-1H-pyrazole-4-carboxylate (3aj)
Methyl 3,5-dimethyl-1-phenyl-1H-pyrazole-4-carboxylate (3ak)
Methyl 3-ethyl-5-methyl-1-phenyl-1H-pyrazole-4-carboxylate (3al)
Methyl 5-methyl-1-phenyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate (3am)
Methyl 5-methyl-1-phenyl-3-styryl-1H-pyrazole-4-carboxylate (3an)
Methyl 3-(4-fluorophenyl)-5-methyl-1-(o-tolyl)-1H-pyrazole-4-carboxylate (3bb)
Methyl 3-(4-fluorophenyl)-5-methyl-1-(m-tolyl)-1H-pyrazole-4-carboxylate (3cb)
$^{19}$F nmr decoupled
Methyl 3-(4-fluorophenyl)-5-methyl-1-(p-tolyl)-1H-pyrazole-4-carboxylate (3db)
Methyl 1-(4-ethoxyphenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3eb)
$^{19}$F-nmr decoupled
Methyl 1-(4-(dimethylamino)phenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3fb)
Methyl 1,3-bis(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3gb)
$^{19}{\text{F}}$-nmr decoupled
Methyl 1-(4-(ethoxycarbonyl)phenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3hb)
Methyl 3-(4-fluorophenyl)-5-methyl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3ib)
Methyl 3-(4-fluorophenyl)-5-methyl-1-(3-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3jb)
Methyl 3-(4-fluorophenyl)-5-methyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole-4-carboxylate (3kb)
Ethyl 3-(4-fluorophenyl)-1-mesityl-5-methyl-1H-pyrazole-4-carboxylate (3lb)
Ethyl 1-(2,6-diisopropylphenyl)-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3mb)
Methyl 3-(4-fluorophenyl)-1,5-dimethyl-1H-pyrazole-4-carboxylate (3nb)
Methyl 1-butyl-3-(4-fluorophenyl)-5-methyl-1H-pyrazole-4-carboxylate (3om)
Methyl 3-(4-fluorophenyl)-1-isopropyl-5-methyl-1H-pyrazole-4-carboxylate (3pb)
Ethyl 3-(4-fluorophenyl)-1,5-diphenyl-1\textit{H}-pyrazole-4-carboxylate (3qb)
(3-(4-fluorophenyl)-5-methyl-1-phenyl-1H-pyrazol-4-yl)(phenyl)methanone (3rb)
7. References


3 See ref. 1(a).