Supporting Information
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Copper-Promoted Coupling of Propiophenones and Arylhydrazines for Synthesis of 1,3-Diarylpyrazoles

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General procedures

All chemicals were purchased from commercial vendors such as Aldrich or Acros and used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). Mass spectra were collected on a Shimadzu GC-MS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). Aluminium sheets 20 x 20 cm TLC Silica gel 60 F254 Merck KGaA 64271 were used for thin-layer chromatography (TLC). Silica gel 60 as the stationary phase (particle size 0.04–0.036 mm, 230-400 mesh, ASTM E.Merck) was used for column chromatography (CC). Compounds were observed using UV lamp or Dragendorff’s reagent (for detection of 3-methylphenylindole byproduct). Nuclear magnetic resonance (NMR) spectra (\(^1\)H and \(^{13}\)C) were recorded on a Bruker AV 500 spectrometer using residual solvent peaks as references. Abbreviations for multiplicites were as followed: s = singlet, d = doublet, t = triplet, m = multiplet.
Characterization of products

1,3-Diphenyl-1H-pyrazole (2aa, Scheme 2)

Propiophenone (1 mmol, 134 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (1 mmol, 181 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 167 mg (76%) of a white solid was obtained. This compound is known.$^1$

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 7.96 (d, $J = 2.5$ Hz, 1H), 7.94 – 7.90 (m, 2H), 7.80 – 7.75 (m, 2H), 7.50 – 7.40 (m, 4H), 7.37 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 6.78 (d, $J = 2.5$ Hz, 1H).

$^1$C NMR (126 MHz, CDCl$_3$, ppm) δ 153.0, 140.3, 133.2, 129.4, 128.7, 128.03, 127.99, 126.4, 125.9, 119.1, 105.0.

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3-(4-Methoxyphenyl)-1-phenyl-1H-pyrazole (2ba, Scheme 2)

4′-Methoxypropiophenone (1 mmol, 164 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (1 mmol, 181 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 163 mg (65%) of a white solid was obtained. This compound is known.$^1$

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 7.87 (d, $J$ = 2.5 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.70 (dd, $J$ = 8.5, 0.9 Hz, 2H), 7.40 (dd, $J$ = 10.8, 5.2 Hz, 2H), 7.22 (t, $J$ = 7.4 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.64 (d, $J$ = 2.5 Hz, 1H), 3.79 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 159.7, 152.8, 140.2, 129.4, 128.0, 127.2, 126.2, 125.9, 119.0, 114.1, 104.6, 55.3.
3-(3-Chlorophenyl)-1-phenyl-1H-pyrazole (2ca, Scheme 2)

3’-Chloropropiophenone (1 mmol, 169 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)₂ (0.25 mmol, 46 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 179 mg (70%) of a white solid was obtained. This compound is known.¹

¹H NMR (500 MHz, CDCl₃, ppm) δ 7.95 (d, J = 2.5 Hz, 1H), 7.92 (t, J = 1.7 Hz, 1H), 7.79 – 7.75 (m, 3H), 7.49 – 7.45 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.32 – 7.25 (m, 2H), 6.75 (d, J = 2.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃, ppm) δ 151.6, 140.1, 135.0, 134.7, 129.9, 129.5, 128.2, 127.9, 126.6, 125.9, 123.9, 119.1, 105.1.
3-(4-Chlorophenyl)-1-phenyl-1H-pyrazole (2da, Scheme 2)

4'-Chloropropiophenone (1 mmol, 169 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (1 mmol, 181 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 143 mg (56%) of a white solid was obtained. Another independent run gave 142 mg (56%) of the target compound. This compound is known.$^1$
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 7.89 (d, $J = 2.5$ Hz, 1H), 7.82 – 7.76 (m, 2H), 7.72 – 7.67 (m, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.36 – 7.31 (m, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 6.68 (d, $J = 2.5$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 151.8, 140.1, 133.8, 131.7, 129.5, 128.8, 128.2, 127.1, 126.5, 119.1, 105.0.
1-Phenyl-3-(3-(trifluoromethyl)phenyl)-1H-pyrazole (2da, Scheme 2)

3’-(Trifluoromethyl)propiophenone (1 mmol, 202 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (0.25 mmol, 46 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 170 mg (59%) of a white solid was obtained.

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 8.12 (s, 1H), 8.02 (d, $J = 7.6$ Hz, 1H), 7.92 (d, $J = 2.5$ Hz, 1H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 1H), 6.75 (d, $J = 2.4$ Hz, 1H).
$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 151.5, 140.1, 134.0, 132.5, 131.1 (q, $J$ = 32.4 Hz), 129.5, 129.1, 129.0, 128.3, 126.7, 124.5 (q, $J$ = 3.8 Hz), 124.2 (q, $J$ = 273.0 Hz), 122.6 (q, $J$ = 3.8 Hz), 119.2, 105.1.

HRMS (ESI+) m/z calcd. for C$_{16}$H$_{12}$N$_2$F$_3^+$ (M+H)$^+$: 289.0947, found: 289.0949.
3-(4-Bromophenyl)-1-phenyl-1\textit{H}\textsuperscript{-}pyrazole (2fa, Scheme 2)

4'-Bromopropiophenone (1 mmol, 213 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)\textsubscript{2} (1.3 mmol, 235 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 200 mg (67\%) of a white solid was obtained. This compound is known\textsuperscript{1}. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, ppm) δ 7.89 (d, \(J = 2.5\) Hz, 1H), 7.75 – 7.65 (m, 4H), 7.48 (d, \(J = 8.5\) Hz, 2H), 7.40 (dd, \(J = 11.8, 4.1\) Hz, 2H), 7.27 – 7.21 (m, 1H), 6.68 (d, \(J = 2.5\) Hz, 1H).
$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 151.8, 140.1, 132.1, 131.8, 129.5, 128.2, 127.4, 126.5, 121.9, 119.1, 105.0.
3-(4-Methylphenyl)-1-phenyl-1H-pyrazole (2ga, Scheme 2)

4'-Methylpropiophenone (1 mmol, 148 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (1.3 mmol, 235 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 183 mg (78%) of a white solid was obtained. Another independent run gave 186 mg (79%) of the target compound. This compound is known.$^1$
\(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta\) 7.88 (d, \(J = 2.5\) Hz, 1H), 7.75 (d, \(J = 8.1\) Hz, 2H), 7.72 – 7.69 (m, 2H), 7.40 (dd, \(J = 10.8, 5.2\) Hz, 2H), 7.22 (t, \(J = 7.4\) Hz, 1H), 7.18 (d, \(J = 7.9\) Hz, 2H), 6.68 (d, \(J = 2.5\) Hz, 1H), 2.33 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), ppm) \(\delta\) 153.0, 140.3, 137.8, 130.4, 129.4, 129.4, 127.9, 126.2, 125.8, 119.0, 104.9, 21.3.
5-Methyl-1,3-diphenyl-1H-pyrazole (2ha, Scheme 2)

Butyrophenone (1 mmol, 148 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (0.25 mmol, 46 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 141 mg (60%) of a yellow oil was obtained. Another independent run gave 144 mg (61%) of the target compound. This compound is known.$^2$

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$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 7.84 – 7.76 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 (dd, $J$ = 10.4, 5.2 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.25 (t, $J$ = 7.4 Hz, 1H), 6.47 (s, 1H), 2.32 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 151.5, 140.2, 140.0, 133.4, 129.1, 128.6, 127.8, 127.6, 125.7, 125.0, 104.4, 12.6.
3-Methyl-1,5-diphenyl-1H-pyrazole (2ia, Scheme 2)

Benzylacetone (1 mmol, 148 mg), phenylhydrazine (4 mmol, 432 mg), CuBr₂ (0.25 mmol, 36 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 129 mg (55%) of a colorless oil was obtained. This compound is known.³

$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 7.25 – 7.14 (m, 10H, overlapping with CHCl$_3$ signal), 6.25 (s, 1H), 2.33 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 149.5, 143.7, 140.2, 130.8, 128.9, 128.7, 128.4, 128.1, 127.1, 125.2, 107.8, 13.6.
3-Ethyl-5-nitro-1-phenyl-1\textit{H}-indazole (4a, Scheme 3)

3’-Nitropropiophenone (1 mmol, 179 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (0.25 mmol, 46 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 136 mg (51%) of a yellow solid was obtained.

R$_f$ = 0.4 (hexanes/EtOAc 10:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 8.66 (d, $J = 1.5$ Hz, 1H), 8.20 (dd, $J = 9.2$, 1.7 Hz, 1H), 7.64 – 7.61 (m, 3H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 3.05 (q, $J = 7.6$ Hz, 2H), 1.42 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 151.9, 142.2, 141.4, 139.2, 129.7, 127.5, 123.5, 123.0, 122.2, 118.4, 110.6, 20.4, 13.3.

HRMS (ESI+) m/z calcd. for C$_{15}$H$_{14}$N$_3$O$_2$$(\text{M+H})^+$: 268.1081, found: 268.1085.
3-Methyl-5-nitro-1-phenyl-1H-indazole (4b, Scheme 3)

3’-Nitroacetophenone (1 mmol, 165 mg), phenylhydrazine (4 mmol, 432 mg), Cu(OAc)$_2$ (0.25 mmol, 46 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (gradient hexanes/ethyl acetate from 10:1 to 6:1), 146 mg (57%) of a yellow solid was obtained. This compound is known.$^4$

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$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.65 (d, $J = 1.6$ Hz, 1H), 8.22 (dd, $J = 9.2$, 1.8 Hz, 1H), 7.64 (d, $J = 9.0$ Hz, 1H), 6.61 (d, $J = 8$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 2.65 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 146.7, 142.3, 141.3, 139.1, 129.7, 127.5, 124.3, 122.9, 122.3, 118.4, 110.6, 11.9.
1-(2-Chlorophenyl)-3-phenyl-1H-pyrazole (2ab, Scheme 3)

Propiophenone (1 mmol, 134 mg), 2-chlorophenylhydrazine hydrochloride (4 mmol, 716 mg), Cu(OAc)$_2$ (1.3 mmol, 235 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 120 mg (47%) of a white solid was obtained. This compound is known.$^5$

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$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 7.86 (d, $J = 2.5$ Hz, 1H), 7.85 – 7.82 (m, 2H), 7.64 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.47 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.27 (dddd, $J = 7.6$, 5.8, 3.3, 1.5 Hz, 2H), 6.72 (d, $J = 2.5$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 152.9, 138.3, 133.0, 132.8, 130.7, 128.9, 128.7, 128.12, 128.09, 127.9, 127.8, 125.9, 104.2.
3-Phenyl-1-(3-(trifluoromethyl)phenyl)-1H-pyrazole (2ac, Scheme 3)

Propiophenone (1 mmol, 134 mg), 3-trifluoromethylphenylhydrazine (4 mmol, 783 mg), Cu(OAc)₂ (1.3 mmol, 235 mg), TEMPO (4 mmol, 624 mg), acetic acid (1 mmol, 60 mg), DMF (5 mL), 140 °C, 48 h. After column chromatography (hexanes/ethyl acetate 10:1), 205 mg (71%) of a beige solid was obtained. This compound is known.⁶

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$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 8.18 (s, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 2.4$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.49 (t, $J = 7.9$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 2.4$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 151.5, 140.1, 131.1 (q, $J = 32.2$ Hz), 134.0, 129.5, 129.1, 129.0, 128.3, 126.7, 124.5 (q, $J = 3.8$ Hz), 124.2 (q, $J = 272.3$ Hz), 122.6 (q, $J = 3.8$ Hz), 119.2, 105.1.

Zac, Scheme 3