Supplementary Information

Photoelectrocatalytic Arene C-H Amination

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Supplementary Methods

Devices for Photoelectrochemical Oxidation

The photoelectrochemical oxidation was performed in an undivided cell by a three-electrode configuration using VMP-3 instrument (Biologic Science Instrument). Hematite was used as a working electrode with a Ag/AgCl reference electrode and a Pt counter electrode. Blue led lamp (Kessil, A160We, 40W) was used as the light source. The distance between the lamp and the working electrode is ~5 cm (See Supplementary Figure 1).
C–N Coupling Reaction via Photoelectrocatalysis

General procedure for coupling of aromatic compounds and azoles in a photoelectrochemical cell: Under N\textsubscript{2}, LiClO\textsubscript{4} (31.9 mg, 0.1 M), arene (0.2 mmol), azole (0.4 or 0.6 mmol, 2 or 3 equiv) and solvent (HFIP/MeOH = 4:1, 3 mL) were added to a 20 mL test tube equipped with a magnetic stir bar. The photoelectrochemical oxidation were performed at a constant potential (see maintext for the specific potential for each substrate) at ambient temperature for 10~24 h in a photoreactor (Supplementary Figure 1). The resulting solution was concentrated under vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane to give the corresponding products.

1-(2-methoxyphenyl)-1H-pyrazole (3a), 1-(4-methoxyphenyl)-1H-pyrazole (3b). 3a and 3b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (26.9 mg, 77%). The ortho:para ratio of the inseparable mixture was 6:1 as determined by \textsuperscript{1}H NMR of the isolated product.

3a: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.03 (d, \(J = 2.1\) Hz, 1H, aryl-\textit{H}), 7.75-7.70 (m, 2H, aryl-\textit{H}), 7.30 (td, \(J = 7.8, 1.7\) Hz, 1H, aryl-\textit{H}), 7.09-7.02 (m, 2H, aryl-\textit{H}), 6.43 (t, \(J = 2.0\) Hz, 1H, aryl-\textit{H}), 3.87 (s, 3H, OCH\textsubscript{3}). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 151.4 (aryl-C), 140.1 (aryl-C), 131.6 (aryl-C), 129.9 (aryl-C), 128.1 (aryl-C), 125.4 (aryl-C), 121.3 (aryl-C), 112.4 (aryl-C), 106.2 (aryl-C), 56.0 (OCH\textsubscript{3}).
3b: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 2.4$ Hz, 1H, aryl-$H$), 7.69 (s, 1H, aryl-$H$), 7.59 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.97 (d, $J = 8.9$ Hz, 2H, aryl-$H$), 6.43 (t, $J = 2.0$ Hz, 1H, aryl-$H$), 3.83 (s, 3H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.3 (aryl-C), 140.7 (aryl-C), 134.1 (aryl-C), 126.9 (aryl-C), 121.0 (aryl-C), 114.6 (aryl-C), 107.3 (aryl-C), 55.7 (OCH$_3$).

These spectroscopic data correspond to reported data.$^1$

![Chemical Structure](image)

1-(2-ethoxyphenyl)-1H-pyrazole (4a). 1-(4-ethoxyphenyl)-1H-pyrazole (4b). 4a and 4b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1) to give the title compound as pale yellow oil (24.5 mg, 65%). The ortho : para ratio of the inseparable mixture was 7:1 as determined by $^1$H NMR of the isolated product.

4a: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.78 (dd, $J = 7.9$, 1.7 Hz, 1H, aryl-$H$), 7.70 (d, $J = 1.9$ Hz, 1H, aryl-$H$), 7.26 (td, $J = 8.0$, 1.7 Hz, 1H, aryl-$H$), 7.09-7.01 (m, 2H, aryl-$H$), 6.42 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 4.10 (q, $J = 7.0$ Hz, 2H, OCH$_2$CH$_3$), 1.41 (t, $J = 7.0$ Hz, 3H, OCH$_2$CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.4 (aryl-C), 140.0 (aryl-C), 131.6 (aryl-C), 130.1 (aryl-C), 127.8 (aryl-C), 125.1 (aryl-C), 121.3 (aryl-C), 113.6 (aryl-C), 106.2 (aryl-C), 64.7 (OCH$_2$CH$_3$), 14.9 (OCH$_2$CH$_3$).

4b: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.69 (s, 1H, aryl-$H$), 7.58 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.96 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.42 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 4.06 (q, $J = 6.9$ Hz, 2H, OCH$_2$CH$_3$), 1.43 (t, $J = 6.9$ Hz, 3H, OCH$_2$CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.7 (aryl-C), 140.7 (aryl-C), 134.0 (aryl-C), 126.9 (aryl-C), 121.0 (aryl-C), 115.2 (aryl-C), 107.2 (aryl-C), 63.9 (OCH$_2$CH$_3$), 14.9 (OCH$_2$CH$_3$).
HRMS-ESI (m/z): Calcd for [(C11H12N2O+H)+], 189.1022; found: 189.1025.

1-(2-(allyloxy)phenyl)-1H-pyrazole (5a). 1-(4-(allyloxy)phenyl)-1H-pyrazole (5b).

5a and 5b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (30:1~10:1) to give the title compound as pale yellow oil (22.2 mg, 55%). The ortho : para ratio of the inseparable mixture was 4:1 as determined by 1H NMR of the isolated product.

5a: 1H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 2.5 Hz, 1H, aryl-H), 7.76 (dd, J = 7.9, 1.7 Hz, 1H, aryl-H), 7.71 (d, J = 1.8 Hz, 1H, aryl-H), 7.26 (td, J = 7.7, 1.7 Hz, 1H, aryl-H), 7.10-7.01 (m, 2H, aryl-H), 6.43 (t, J = 2.1 Hz, 1H, aryl-H), 6.06-5.95 (m, 1H, CH=CH₂), 5.37 (dd, J = 17.3, 1.7 Hz, 1H, CH=CH₂), 5.27 (dd, J = 10.6, 1.7 Hz, 1H, CH=CH₂). 13C NMR (101 MHz, CDCl₃) δ 150.2 (aryl-C), 140.0 (aryl-C), 132.7 (CH=CH₂), 131.7 (aryl-C), 130.2 (aryl-C), 127.9 (aryl-C), 125.4 (aryl-C), 121.6 (aryl-C), 117.9 (CH=CH₂), 114.0 (aryl-C), 106.3 (aryl-C), 69.9 (CH₂CH=CH₂).

5b: 1H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 2.4 Hz, 1H, aryl-H), 7.69 (s, 1H, aryl-H), 7.58 (d, J = 9.0 Hz, 2H, aryl-H), 6.98 (d, J = 9.0 Hz, 2H, aryl-H), 6.43 (t, J = 2.1 Hz, 1H, aryl-H), 6.12-6.02 (m, 1H, CH=CH₂), 5.43 (dd, J = 17.2, 1.7 Hz, 1H, CH=CH₂), 5.31 (dd, J = 10.4, 1.6 Hz, 1H, CH=CH₂), 4.56 (d, J = 4.7 Hz, 2H, CH₂CH=CH₂). 13C NMR (101 MHz, CDCl₃) δ 157.3 (aryl-C), 140.7 (aryl-C), 134.2 (aryl-C), 133.1 (CH=CH₂), 126.9 (aryl-C), 121.0 (aryl-C), 118.0 (CH=CH₂), 115.5 (aryl-C), 107.3 (aryl-C), 69.2 (CH₂CH=CH₂).

HRMS-ESI (m/z): Calcd for [(C₁₁H₁₂N₂O+H)+], 201.1022; found: 201.1026.
1-(2-(benzyloxy)phenyl)-1H-pyrazole (6a). 1-(4-(benzyloxy)phenyl)-1H-pyrazole (6b). 6a and 6b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1) to give the title compound as colorless oil (33.1 mg, 66%). The ortho:para ratio of the inseparable mixture was 5:1 as determined by 1H NMR of the isolated product.

6a: 1H NMR (400 MHz, CDCl3) δ 8.11 (d, J = 2.5 Hz, 1H, aryl-H), 7.81 (dd, J = 7.9, 1.8 Hz, 1H, aryl-H), 7.73 (d, J = 1.8 Hz, 1H, aryl-H), 7.48-7.30 (m, 5H, aryl-H), 7.27 (td, J = 7.8, 1.8 Hz, 1H, aryl-H), 7.13-7.07 (m, 2H, aryl-H), 6.41 (t, J = 2.2 Hz, 1H, aryl-H), 5.13 (s, 2H, PhOCH2). 13C NMR (101 MHz, CDCl3) δ 150.3 (aryl-C), 140.1 (aryl-C), 136.5 (aryl-C), 131.7 (aryl-C), 130.4 (aryl-C), 128.7 (aryl-C), 128.2 (aryl-C), 127.9 (aryl-C), 127.3 (aryl-C), 125.3 (aryl-C), 121.8 (aryl-C), 114.3 (aryl-C), 106.4 (aryl-C), 71.2 (PhOCH2).

6b: 1H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 2.2 Hz, 1H, aryl-H), 7.70 (d, J = 2.0 Hz, aryl-H), 7.60 (d, J = 9.0 Hz, 2H, aryl-H), 7.48-7.30 (m, 5H, aryl-H), 7.05 (d, J = 9.0 Hz, 2H, aryl-H), 6.44 (t, J = 2.1 Hz, 1H, aryl-H), 5.13 (s, 2H, PhOCH2). 13C NMR (101 MHz, CDCl3) δ 157.5 (aryl-C), 140.7 (aryl-C), 136.8 (aryl-C), 134.3 (aryl-C), 128.7 (aryl-C), 128.2 (aryl-C), 127.3 (aryl-C), 126.9 (aryl-C), 121.0 (aryl-C), 115.6 (aryl-C), 107.3 (aryl-C), 70.4 (PhOCH2).

HRMS-ESI (m/z): Calcd for [(C16H14N2O+H)+], 251.1179; found: 251.1183.

Ethyl 3-(2-(1H-pyrazol-1-yl)phenoxy)propanoate (7a). Ethyl 3-(4-(1H-pyrazol-1-yl)phenoxy)propanoate (7b). 7a and 7b were synthesized following the general
procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (4:1) to give the title compound as colorless oil (44.8 mg, 86%). The ortho : para ratio of the inseparable mixture was 6:1 as determined by $^1$H NMR of the isolated product.

7a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.75 (dd, $J = 7.9$, 1.7 Hz, 1H, aryl-$H$), 7.67 (d, $J = 1.9$ Hz, 1H, aryl-$H$), 7.26 (td, $J = 7.9$, 1.7 Hz, 1H, aryl-$H$), 7.10-7.02 (m, 2H, aryl-$H$), 6.38 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 4.30 (t, $J = 6.3$ Hz, 2H, OCH$_2$CH$_2$), 4.14 (q, $J = 7.2$ Hz, 2H, OCH$_2$CH$_3$), 2.76 (t, $J = 6.2$ Hz, 2H, OCH$_2$CH$_2$), 1.24 (t, $J = 7.2$ Hz, 3H, OCH$_2$CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.9 (C=O), 149.9 (aryl-$C$), 140.0 (aryl-$C$), 131.6 (aryl-$C$), 130.1 (aryl-$C$), 127.8 (aryl-$C$), 125.2 (aryl-$C$), 121.8 (aryl-$C$), 113.6 (aryl-$C$), 106.2 (aryl-$C$), 64.7 (OCH$_2$CH$_2$), 60.9 (OCH$_2$CH$_3$), 34.6 (OCH$_2$CH$_2$), 14.2 (OCH$_2$CH$_3$).

7b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.67 (s, 1H, aryl-$H$), 7.57 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.96 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.42 (t, $J = 2.1$ Hz, 1H, aryl-$H$), 4.27 (t, $J = 6.4$ Hz, 2H, OCH$_2$CH$_2$), 4.19 (q, $J = 7.2$ Hz, 2H, OCH$_2$CH$_3$), 2.79 (t, $J = 6.5$ Hz, 2H, OCH$_2$CH$_2$), 1.27 (t, $J = 7.1$ Hz, 3H, OCH$_2$CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.0 (C=O), 157.3 (aryl-$C$), 140.7 (aryl-$C$), 134.3 (aryl-$C$), 126.8 (aryl-$C$), 120.9 (aryl-$C$), 115.4 (aryl-$C$), 107.3 (aryl-$C$), 64.0 (OCH$_2$CH$_2$), 60.9 (OCH$_2$CH$_3$), 34.7 (OCH$_2$CH$_2$), 14.3 (OCH$_2$CH$_3$).

HRMS-ESI (m/z): Calcd for [(C$_{14}$H$_{16}$N$_2$O$_3$+H)$^+$], 261.1234; found: 261.1238.

![image]

1-(2-(2-chloroethoxy)phenyl)-1H-pyrazole (8a). 1-(4-(2-chloroethoxy)phenyl)-1H-pyrazole (8b). 8a and 8b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as white solid (31.4 mg, 71%). The ortho : para ratio
of the inseparable mixture was 3:1 as determined by $^1$H NMR of the isolated product.

8a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.79 (dd, $J = 7.9$, 1.7 Hz, 1H, aryl-$H$), 7.70 (d, $J = 1.9$ Hz, 1H, aryl-$H$), 7.26 (td, $J = 7.9$, 1.7 Hz, 1H, aryl-$H$), 7.10 (td, $J = 7.7$, 1.3 Hz, 1H, aryl-$H$), 6.99 (t, $J = 8.8$ Hz, 1H, aryl-$H$), 6.43 (t, $J = 2.1$ Hz, 1H, aryl-$H$), 4.25 (t, $J = 5.6$ Hz, 2H, OCH$_2$CH$_2$Cl), 3.78 (t, $J = 5.5$ Hz, 2H, OCH$_2$CH$_2$Cl). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.6 (aryl-$C$), 140.2 (aryl-$C$), 131.9 (aryl-$C$), 130.3 (aryl-$C$), 127.9 (aryl-$C$), 125.4 (aryl-$C$), 122.3 (aryl-$C$), 113.8 (aryl-$C$), 106.5 (aryl-$C$), 69.1 (OCH$_2$CH$_2$Cl), 42.0 (OCH$_2$CH$_2$Cl).

8b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.69 (d, $J = 2.1$ Hz, 1H, aryl-$H$), 7.59 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 7.00 (d, $J = 9.0$ Hz, 2H, aryl-$H$), 6.43 (t, $J = 2.1$ Hz, 1H, aryl-$H$), 4.23 (t, $J = 5.6$ Hz, 2H, OCH$_2$CH$_2$Cl), 3.81 (t, $J = 5.6$ Hz, 2H, OCH$_2$CH$_2$Cl). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.9 (aryl-$C$), 140.8 (aryl-$C$), 134.6 (aryl-$C$), 126.9 (aryl-$C$), 121.0 (aryl-$C$), 115.5 (aryl-$C$), 107.4 (aryl-$C$), 68.5 (OCH$_2$CH$_2$Cl), 41.9 (OCH$_2$CH$_2$Cl).

HRMS-ESI (m/z): Calcd for [(C$_{11}$H$_{11}$ClN$_2$O+H)+], 223.0633; found: 223.0638.

1-[[1,1'-biphenyl]-4-yl]-1H-pyrazole (9). 9 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as white solid (21.8 mg, 50%).

9: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.78 (d, $J = 8.8$ Hz, 2H, aryl-$H$), 7.76 (s, 1H, aryl-$H$), 7.69 (d, $J = 8.6$ Hz, 2H, aryl-$H$), 7.63 (d, $J = 7.3$ Hz, 2H, aryl-$H$), 7.47 (t, $J = 7.7$ Hz, 2H, aryl-$H$), 7.37 (t, $J = 7.4$ Hz, 1H, aryl-$H$), 6.50 (t, $J = 2.2$ Hz, 1H, aryl-$H$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.3 (aryl-$C$), 140.2 (aryl-$C$), 139.5 (aryl-$C$), 139.5 (aryl-$C$), 129.0 (aryl-$C$), 128.2 (aryl-$C$), 127.6 (aryl-$C$), 127.1
These spectroscopic data correspond to reported data.\(^1\)

1-(5-(tert-butyl)-2-methoxyphenyl)-1H-pyrazole (10). 10 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (35.8 mg, 77%).

10: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 2.4\) Hz, 1H, aryl-\(H\)), 7.72 (d, \(J = 1.4\) Hz, 2H, aryl-\(H\)), 7.32 (dd, \(J = 8.6, 1.8\) Hz, 2H, aryl-\(H\)), 6.98 (d, \(J = 8.7\) Hz, 1H, aryl-\(H\)), 6.44 (t, \(J = 1.6\) Hz, 1H, aryl-\(H\)), 3.85 (s, 3H, OCH\(_3\)), 1.35 (s, 9H, C(CH\(_3\))\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 149.3 (aryl-\(C\)), 144.4 (aryl-\(C\)), 140.0 (aryl-\(C\)), 131.8 (aryl-\(C\)), 129.2 (aryl-\(C\)), 125.0 (aryl-\(C\)), 122.7 (aryl-\(C\)), 112.1 (aryl-\(C\)), 106.2 (aryl-\(C\)), 56.1 (OCH\(_3\)), 34.4 (C(CH\(_3\))\(_3\)), 31.5 (C(CH\(_3\))\(_3\)).

HRMS-ESI (m/z): Calcd for \([\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}+\text{H}]^+\), 231.1492; found: 231.1496.

Methyl 4-methoxy-3-(1H-pyrazol-1-yl)benzoate (11). 11 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1~5:1) to give the title compound as white solid (17.0 mg, 37%).

11: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.39 (d, \(J = 2.2\) Hz, 1H, aryl-\(H\)), 8.01 (d, \(J = 2.5\) Hz, 1H, aryl-\(H\)), 7.99 (dd, \(J = 8.7, 2.2\) Hz, 2H, aryl-\(H\)), 7.71 (d, \(J = 1.8\) Hz, 1H, aryl-\(H\)), 7.05 (d, \(J = 8.7\) Hz, 1H, aryl-\(H\)), 6.42 (t, \(J = 2.2\) Hz, 1H, aryl-\(H\)), 3.92 (s, 3H, COOCH\(_3\)).
3.87 (s, 3H, ArOCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 166.2 (COOCH₃), 154.8 (aryl-C), 140.5 (aryl-C), 131.6 (aryl-C), 129.9 (aryl-C), 129.5 (aryl-C), 126.7 (aryl-C), 123.3 (aryl-C), 111.8 (aryl-C), 106.6 (aryl-C), 56.3 (OCH₃), 52.1 (COOCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₂H₁₂N₂O₃+H)+], 233.0921; found: 233.0923.

4-methoxy-3-(1H-pyrazol-1-yl)phenyl 4-methylbenzenesulfonate (12). 12 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as yellow oil (37.1 mg, 54%).

12: ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 2.5 Hz, 1H, aryl-H), 7.72 (d, J = 8.4 Hz, 2H, aryl-H), 7.64 (d, J = 1.6 Hz, 1H, aryl-H), 7.47 (t, J = 1.6 Hz, 1H, aryl-H), 7.30 (d, J = 8.0 Hz, 2H, aryl-H), 6.91 (d, J = 1.7 Hz, 2H, aryl-H), 6.38 (t, J = 2.2 Hz, 1H, aryl-H), 3.84 (s, 3H, ArOCH₃), 2.42 (s, 3H, ArCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 149.6 (aryl-C), 145.6 (aryl-C), 143.0 (aryl-C), 140.4 (aryl-C), 132.3 (aryl-C), 131.5 (aryl-C), 130.0 (aryl-C), 129.9 (aryl-C), 128.6 (aryl-C), 121.1 (aryl-C), 119.0 (aryl-C), 112.7 (aryl-C), 106.7 (aryl-C), 56.4 (ArOCH₃), 21.8 (ArCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₇H₁₆N₂O₄S+H)+], 345.0904; found: 345.0909.

1-(5-chloro-2-methoxyphenyl)-1H-pyrazole (13). 13 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (23.2 mg, 56%).
13: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.81 (d, $J = 2.6$ Hz, 1H, aryl-$H$), 7.70 (d, $J = 1.8$ Hz, 1H, aryl-$H$), 7.23 (dd, $J = 8.8, 2.6$ Hz, 1H, aryl-$H$), 6.96 (d, $J = 8.8$ Hz, 1H, aryl-$H$), 6.43 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 3.87 (s, 3H, ArOCH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.7 (aryl-C), 140.5 (aryl-C), 131.7 (aryl-C), 130.5 (aryl-C), 127.4 (aryl-C), 126.3 (aryl-C), 125.0 (aryl-C), 113.5 (aryl-C), 106.8 (aryl-C), 56.4 (OCH$_3$).

These spectroscopic data correspond to reported data.$^2$

![Structure](attachment:structure.png)

1-(5-bromo-2-methoxyphenyl)-1H-pyrazole (14). 14 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (25.6 mg, 51%).

14: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.94 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.70 (d, $J = 1.8$ Hz, 1H, aryl-$H$), 7.37 (dd, $J = 8.8, 2.5$ Hz, 1H, aryl-$H$), 6.90 (d, $J = 8.8$ Hz, 1H, aryl-$H$), 6.42 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 3.87 (s, 3H, ArOCH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.2 (aryl-C), 140.5 (aryl-C), 131.7 (aryl-C), 130.7 (aryl-C), 130.4 (aryl-C), 127.7 (aryl-C), 113.9 (aryl-C), 113.3 (aryl-C), 106.8 (aryl-C), 56.3 (OCH$_3$).

HRMS-ESI (m/z): Calcd for [(C$_{10}$H$_9$BrN$_2$O+H)+], 252.9971; found: 252.9978.

![Structure](attachment:structure.png)

4'-(pentyloxy)-3'-(1H-pyrazol-1-yl)-[1,1'-biphenyl]-4-carbonitrile (15). 15 was synthesized following the general procedure. The residue was purified by
chromatography on silica gel, eluting with hexane/ethyl acetate (8:1) to give the title compound as white solid (34.2 mg, 52%).

15: \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 8.19 (d, \(J = 1.6\) Hz, 1H, aryl-\(H\)), 8.09 (d, \(J = 2.4\) Hz, 1H, aryl-\(H\)), 7.73 (d, \(J = 1.8\) Hz, 1H, aryl-\(H\)), 7.72-7.65 (m, 4H, aryl-\(H\)), 7.49 (dd, \(J = 8.6, 2.4\) Hz, 1H, aryl-\(H\)), 7.12 (d, \(J = 8.6\) Hz, 1H, aryl-\(H\)), 6.46 (t, \(J = 2.1\) Hz, 1H, aryl-\(H\)), 4.10 (t, \(J = 6.5\) Hz, 1H, OCH\(_2\)), 1.88-1.78 (m, 2H, OCH\(_2\)CH\(_2\)), 1.47-1.32 (m, 4H, CH\(_2\)CH\(_2\)CH\(_3\)), 0.92 (t, \(J = 7.0\) Hz, 3H, CH\(_2\)CH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 150.8 (aryl-\(C\)), 144.5 (aryl-\(C\)), 140.3 (aryl-\(C\)), 132.7 (aryl-\(C\)), 132.1 (aryl-\(C\)), 131.7 (aryl-\(C\)), 130.4 (aryl-\(C\)), 127.4 (aryl-\(C\)), 126.2 (aryl-\(C\)), 123.6 (aryl-\(C\)), 119.1 (CN), 113.9 (aryl-\(C\)), 110.7 (aryl-\(C\)), 106.6 (aryl-\(C\)), 69.5 (OCH\(_2\)), 28.9 (OCH\(_2\)CH\(_2\)), 28.3 (OCH\(_2\)CH\(_2\)CH\(_2\)), 22.4 (CH\(_2\)CH\(_3\)), 14.1 (CH\(_2\)CH\(_3\)).

HRMS-ESI (m/z): Calcd for [(C\(_{21}\)H\(_{21}\)N\(_3\)O+H)+], 332.1757; found: 332.1761.

\[
\text{MeO} \quad \text{O} \\
\text{N} \quad \text{N}
\]

1-(5-methoxy-2-(1H-pyrazol-1-yl)phenyl)ethan-1-one (16a). 16a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (14.6 mg, 34%).

16a: \(^1\)H NMR (400 MHz, CDCl\(_3\))  δ 7.69 (d, \(J = 1.9\) Hz, 1H, aryl-\(H\)), 7.64 (d, \(J = 2.4\) Hz, 1H, aryl-\(H\)), 7.34 (d, \(J = 8.5\) Hz, 1H, aryl-\(H\)), 7.07 (d, \(J = 2.8\) Hz, 1H, aryl-\(H\)), 7.04 (dd, \(J = 8.5, 2.9\) Hz, 1H, aryl-\(H\)), 6.46 (t, \(J = 2.2\) Hz, 1H, aryl-\(H\)), 3.85 (s, 3H, ArOCH\(_3\)), 1.90 (s, 3H, C=OCH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\))  δ 201.1 (C=O), 159.3 (aryl-\(C\)), 141.2 (aryl-\(C\)), 137.5 (aryl-\(C\)), 131.8 (aryl-\(C\)), 130.3 (aryl-\(C\)), 126.4 (aryl-\(C\)), 117.6 (aryl-\(C\)), 113.0 (aryl-\(C\)), 107.8 (aryl-\(C\)), 55.9 (ArOCH\(_3\)), 28.8 (C=OCH\(_3\)).
1-(3-methoxy-2-(1H-pyrazol-1-yl)phenyl)ethan-1-one (16b). 16b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as white solid (6.0 mg, 14%).

16b: ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 2.4 Hz, 1H, aryl-H), 7.71 (d, J = 1.9 Hz, 1H, aryl-H), 7.41 (t, J = 8.0 Hz, 1H, aryl-H), 7.18 (d, J = 7.7 Hz, 1H, aryl-H), 7.14 (d, J = 8.3 Hz, 1H, aryl-H), 6.49 (t, J = 2.2 Hz, 1H, aryl-H), 3.84 (s, 3H, ArOCH₃), 1.85 (s, 3H, COOC₃H₅).

¹³C NMR (101 MHz, CDCl₃) δ 200.9 (C=O), 153.5 (aryl-C), 140.8 (aryl-C), 139.4 (aryl-C), 129.4 (aryl-C), 127.5 (aryl-C), 120.2 (aryl-C), 114.4 (aryl-C), 107.2 (aryl-C), 56.5 (ArOCH₃), 28.7 (C=OCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₂H₁₂N₂O₂+H)+], 217.0972; found: 217.0975.

Methyl 5-methoxy-2-(1H-pyrazol-1-yl)benzoate (17a). 17a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (31.0 mg, 67%).

17a: ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 1.2 Hz, 1H, aryl-H), 7.60 (d, J = 2.3 Hz, 1H, aryl-H), 7.37 (d, J = 8.8 Hz, 1H, aryl-H), 7.33 (d, J = 3.0 Hz, 1H, aryl-H), 7.07 (dd, J = 8.7, 3.0 Hz, 1H, aryl-H), 6.40 (t, J = 2.0 Hz, 1H, aryl-H), 3.86 (s, 3H, ArOCH₃), 3.69 (s, 3H, COOCH₃).

¹³C NMR (101 MHz, CDCl₃) δ 166.8 (COOCH₃), 159.0 (aryl-
C), 140.6 (aryl-C), 133.0 (aryl-C), 130.4 (aryl-C), 128.8 (aryl-C), 127.4 (aryl-C), 117.9 (aryl-C), 115.0 (aryl-C), 106.6 (aryl-C), 55.9 (ArOCH₃), 52.5 (COOCH₃).

These spectroscopic data correspond to reported data.³

Methyl 3-methoxy-2-(1H-pyrazol-1-yl)benzoate (17b). 17b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (10.2 mg, 22%).

17b: ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 2H, aryl-H), 7.45-7.39 (m, 2H, aryl-H), 7.17 (dd, J = 5.7, 4.0 Hz, 1H, aryl-H), 6.44 (t, J = 2.2 Hz, 1H, aryl-H), 3.83 (s, 3H, ArOC₃H₃), 3.69 (s, 3H, COOCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 166.9 (COOCH₃), 154.3 (aryl-C), 140.3 (aryl-C), 132.4 (aryl-C), 131.1 (aryl-C), 129.3 (aryl-C), 128.8 (aryl-C), 122.0 (aryl-C), 115.1 (aryl-C), 106.2 (aryl-C), 56.5 (ArOCH₃), 52.5 (COOCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₂H₁₂N₂O₃+H)+], 233.0921; found: 233.0925.

1-(2-bromo-4-methoxyphenyl)-1H-pyrazole (18a). 18a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (25.2 mg, 50%).

18a: ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H, aryl-H), 7.69 (d, J = 2.5 Hz, 1H, aryl-H), 7.38 (d, J = 9.0 Hz, 1H, aryl-H), 7.20 (d, J = 2.8 Hz, 1H, aryl-H), 6.92 (dd, J = 8.8,
2.6 Hz, 1H, aryl-\(H\)), 6.43 (t, \(J = 2.2\) Hz, 1H, aryl-\(H\)), 3.84 (s, 3H, ArOCH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.9 (aryl-C), 140.5 (aryl-C), 133.2 (aryl-C), 131.5 (aryl-C), 129.0 (aryl-C), 119.9 (aryl-C), 118.4 (aryl-C), 113.9 (aryl-C), 106.2 (aryl-C), 55.9 (ArOCH\(_3\)).

HRMS-ESI (m/z): Calcd for [(C\(_{10}\)H\(_9\)BrN\(_2\)O+H)+], 252.9971; found: 252.9981.

1-(4-bromo-2-methoxyphenyl)-1\(H\)-pyrazole (18b). 18b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (16.2 mg, 32%).

\(\textbf{18b}: \) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 2.5\) Hz, 1H, aryl-\(H\)), 7.70 (d, \(J = 1.8\) Hz, 1H, aryl-\(H\)), 7.63 (d, \(J = 8.3\) Hz, 1H, aryl-\(H\)), 7.23-7.16 (m, 2H, aryl-\(H\)), 6.43 (t, \(J = 2.2\) Hz, 1H, aryl-\(H\)), 3.89 (s, 3H, ArOCH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.6 (aryl-C), 140.3 (aryl-C), 131.5 (aryl-C), 128.9 (aryl-C), 126.2 (aryl-C), 124.3 (aryl-C), 120.8 (aryl-C), 115.8 (aryl-C), 106.5 (aryl-C), 56.3 (ArOCH\(_3\)).

HRMS-ESI (m/z): Calcd for [(C\(_{10}\)H\(_9\)BrN\(_2\)O+H)+], 252.9971; found: 252.9981.

1-mesityl-1\(H\)-pyrazole (19). 19 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (8:1) to give the title compound as colorless oil (18.5 mg, 50%).

\(\textbf{19}: \) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 1.9\) Hz, 1H, aryl-\(H\)), 7.43 (d, \(J = 2.3\) Hz, 1H, aryl-\(H\)), 6.94 (s, 2H, aryl-\(H\)), 6.43 (t, \(J = 2.1\) Hz, 1H, aryl-\(H\)), 2.33 (s, 3H, ArCH\(_3\)),
1.97 (s, 6H, ArCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 140.0 (aryl-C), 138.8 (aryl-C), 137.0 (aryl-C), 136.0 (aryl-C), 130.9 (aryl-C), 128.8 (aryl-C), 105.8 (aryl-C), 21.2 (ArCH₃), 17.3 (ArCH₃).

These spectroscopic data correspond to reported data.¹

1-(2-methoxy-4,6-dimethylphenyl)-1H-pyrazole (20a). 20a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (23.2 mg, 57%).

20a: ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 1.9 Hz, 1H, aryl-H), 7.47 (d, J = 2.3 Hz, 1H, aryl-H), 6.71 (s, 1H, aryl-H), 6.66 (s, 1H, aryl-H), 6.42 (t, J = 2.2 Hz, 1H, aryl-H), 3.72 (s, 3H, ArOCH₃), 2.37 (s, 6H, ArCH₃), 2.00 (s, 3H, ArCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 155.3 (aryl-C), 140.1 (aryl-C), 139.9 (aryl-C), 137.5 (aryl-C), 132.0 (aryl-C), 126.8 (aryl-C), 123.2 (aryl-C), 110.2 (aryl-C), 105.6 (aryl-C), 56.1 (ArOCH₃), 21.8 (ArCH₃), 17.3 (ArCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₂H₁₄N₂O+H)+], 203.1179; found: 203.1183.

1-(4-methoxy-2,6-dimethylphenyl)-1H-pyrazole (20b). 20b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (8.3 mg, 21%).
2r**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 1.9$ Hz, 1H, aryl-H), 7.42 (d, $J = 2.3$ Hz, 1H, aryl-H), 6.65 (s, 2H, aryl-H), 6.42 (t, $J = 2.1$ Hz, 1H, aryl-H), 3.81 (s, 3H, ArOCH$_3$), 1.97 (s, 6H, ArCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.5 (aryl-C), 140.1 (aryl-C), 137.7 (aryl-C), 132.8 (aryl-C), 131.2 (aryl-C), 113.2 (aryl-C), 105.9 (aryl-C), 55.5 (ArOCH$_3$), 17.7 (ArCH$_3$).

HRMS-ESI (m/z): Calcd for [(C$_{12}$H$_{14}$N$_2$O+H)$^+$], 203.1179; found: 203.1183.

![Image](image.png)

1-(naphthalen-1-yl)-1H-pyrazole (21). 21 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (24.2 mg, 62%).

2s**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96-7.90 (m, 2H, aryl-H), 7.86 (d, $J = 1.9$ Hz, 1H, aryl-H), 7.85-7.81 (m, 1H, aryl-H), 7.80 (d, $J = 2.4$ Hz, 1H, aryl-H), 7.58-7.48 (m, 4H, aryl-H), 6.55 (t, $J = 2.1$ Hz, 1H, aryl-H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.9 (aryl-C), 137.5 (aryl-C), 134.4 (aryl-C), 131.7 (aryl-C), 129.3 (aryl-C), 129.0 (aryl-C), 128.2 (aryl-C), 127.3 (aryl-C), 126.7 (aryl-C), 125.2 (aryl-C), 123.3 (aryl-C), 106.6 (aryl-C).

These spectroscopic data correspond to reported data.$^4$

![Image](image.png)

1-(9,9-dimethyl-9H-fluoren-3-yl)-1H-pyrazole (22). 22 was synthesized following the general procedure. The residue was purified by chromatography on silica gel,
eluting with hexane/ethyl acetate (10:1) to give the title compound as pale yellow oil (31.1 mg, 60%).

**2t**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 2.0$ Hz, 1H, aryl-$H$), 7.84 (s, 1H, aryl-$H$), 7.79-7.75 (m, 2H, aryl-$H$), 7.73 (d, $J = 6.9$ Hz, 1H, aryl-$H$), 7.62 (dd, $J = 8.2$, 2.1 Hz, 1H, aryl-$H$), 7.46 (d, $J = 6.8$ Hz, 1H, aryl-$H$), 7.40-7.31 (m, 2H, aryl-$H$), 6.50 (t, $J = 2.2$ Hz, 1H, aryl-$H$), 1.55 (s, 6H, C(CH$_3$)$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.3 (aryl-$C$), 153.9 (aryl-$C$), 141.1 (aryl-$C$), 139.6 (aryl-$C$), 138.4 (aryl-$C$), 137.8 (aryl-$C$), 127.5 (aryl-$C$), 127.3 (aryl-$C$), 127.1 (aryl-$C$), 122.8 (aryl-$C$), 120.8 (aryl-$C$), 120.1 (aryl-$C$), 118.2 (aryl-$C$), 114.4 (aryl-$C$), 107.7 (aryl-$C$), 47.3 (C(CH$_3$)$_2$), 27.2 (C(CH$_3$)$_2$).

These spectroscopic data correspond to reported data.$^5$

![Image of 4-chloro-1-(2-methoxyphenyl)-1H-pyrazole and 4-chloro-1-(4-methoxyphenyl)-1H-pyrazole](image_url)

**4-chloro-1-(2-methoxyphenyl)-1H-pyrazole (23a). 4-chloro-1-(4-methoxyphenyl)-1H-pyrazole (23b).** 23a and 23b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (15.6 mg, 41%). The ortho : para ratio of the inseparable mixture was 7:1 as determined by $^1$H NMR of the isolated product.

**23a**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H, aryl-$H$), 7.68 (dd, $J = 7.8$, 1.7 Hz, 1H, aryl-$H$), 7.51 (s, 1H, aryl-$H$), 7.27 (td, $J = 7.9$, 1.6 Hz, 1H, aryl-$H$), 7.07-7.00 (m, 2H, aryl-$H$), 3.88 (s, 3H, OCH$_3$), 2.16 (s, 3H, ArCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.3 (aryl-$C$), 140.9 (aryl-$C$), 130.3 (aryl-$C$), 130.0 (aryl-$C$), 127.8 (aryl-$C$), 125.1 (aryl-$C$), 121.3 (aryl-$C$), 116.7 (aryl-$C$), 112.3 (aryl-$C$), 56.0 (OCH$_3$), 9.1 (ArCH$_3$).

**23b**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (s, 1H, aryl-$H$), 7.54 (d, $J = 9.1$ Hz, 2H, aryl-
$H), 7.49$ (s, 1H, aryl-$H$), $6.95$ (d, $J = 9.0$ Hz, 2H, aryl-$H$), $3.83$ (s, 3H, OCH$_3$), $2.15$ (s, 3H, ArCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ $158.0$ (aryl-C), $141.3$ (aryl-C), $134.3$ (aryl-C), $125.6$ (aryl-C), $120.5$ (aryl-C), $117.9$ (aryl-C), $114.6$ (aryl-C), $55.6$ (OCH$_3$), $9.0$ (ArCH$_3$).

These spectroscopic data correspond to reported data.$^1$

4-chloro-1-(2-methoxyphenyl)-1H-pyrazole (24a). 4-chloro-1-(4-methoxyphenyl)-1H-pyrazole (24b). 24a and 24b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (24.4 mg, 58%). The ortho : para ratio of the inseparable mixture was 14:1 as determined by $^1$H NMR of the isolated product.

24a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ $8.04$ (s, 1H, aryl-$H$), $7.70$ (d, $J = 7.9$ Hz, 1H, aryl-$H$), $7.62$ (s, 1H, aryl-$H$), $7.31$ (t, $J = 7.8$ Hz, 1H, aryl-$H$), $7.09$-$7.01$ (m, 2H, aryl-$H$), $3.89$ (s, 3H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ $151.0$ (aryl-C), $138.5$ (aryl-C), $129.6$ (aryl-C), $129.3$ (aryl-C), $128.5$ (aryl-C), $124.7$ (aryl-C), $121.2$ (aryl-C), $112.3$ (aryl-C), $110.7$ (aryl-C), $55.9$ (OCH$_3$).

24b: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ $7.80$ (s, 1H, aryl-$H$), $7.62$ (s, 1H, aryl-$H$), $7.52$ (d, $J = 8.6$ Hz, 2H, aryl-$H$), $6.96$ (d, $J = 8.7$ Hz, 2H, aryl-$H$), $3.83$ (s, 3H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ $158.6$ (aryl-C), $139.0$ (aryl-C), $133.5$ (aryl-C), $131.6$ (aryl-C), $124.9$ (aryl-C), $120.7$ (aryl-C), $114.6$ (aryl-C), $55.6$ (OCH$_3$).

These spectroscopic data correspond to reported data.$^6$
4-bromo-1-(2-methoxyphenyl)-1H-pyrazole (25). 25 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (22.3 mg, 44%).

25: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H, aryl-H), 7.70 (d, $J = 7.9$ Hz, 1H, aryl-H), 7.65 (s, 1H, aryl-H), 7.31 (t, $J = 7.8$ Hz, 1H, aryl-H), 7.09-7.01 (m, 2H, aryl-H), 3.89 (s, 3H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.1 (aryl-C), 140.6 (aryl-C), 131.7 (aryl-C), 129.3 (aryl-C), 128.6 (aryl-C), 124.8 (aryl-C), 121.3 (aryl-C), 112.3 (aryl-C), 94.1 (aryl-C), 56.0 (OCH$_3$).

These spectroscopic data correspond to reported data.$^6$

1-(2-methoxyphenyl)-3-methyl-1H-pyrazole (26a). 1-(4-methoxyphenyl)-3-methyl-1H-pyrazole (26b). 26a and 26b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (14.2 mg, 38%).

The ortho : para ratio of the inseparable mixture was 7:1 as determined by $^1$H NMR of the isolated product.

26a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 2.4$ Hz, 1H, aryl-H), 7.70 (d, $J = 7.7$ Hz, 1H, aryl-H), 7.30-7.22 (m, 1H, aryl-H), 7.08-6.99 (m, 2H, aryl-H), 6.21 (d, $J = 2.4$ Hz, 1H, aryl-H), 3.86 (s, 3H, OCH$_3$), 2.38 (s, 3H, ArCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.3 (aryl-C), 149.5 (aryl-C), 132.4 (aryl-C), 129.9 (aryl-C), 137.7 (aryl-C).
125.2 (aryl-C), 121.3 (aryl-C), 112.3 (aryl-C), 106.2 (aryl-C), 56.0 (OCH₃), 13.8 (ArCH₃).

**26b**: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.70 (s, 1H, aryl-\(H\)), 7.54 (d, \(J = 9.0\) Hz, 2H, aryl-\(H\)), 6.94 (d, \(J = 9.0\) Hz, 2H, aryl-\(H\)), 6.21 (d, \(J = 2.4\) Hz, 1H, aryl-\(H\)), 3.83 (s, 3H, OCH₃), 2.38 (s, 3H, ArCH₃). \(^1\)C NMR (101 MHz, CDCl₃) \(\delta\) 158.0 (aryl-C), 150.1 (aryl-C), 134.2 (aryl-C), 127.6 (aryl-C), 120.7 (aryl-C), 114.6 (aryl-C), 107.1 (aryl-C), 55.7 (OCH₃), 13.8 (ArCH₃).

These spectroscopic data correspond to reported data.\(^1\)

![Chemical structure](image)

**1-(2-methoxyphenyl)-5-methyl-1H-pyrazole (26c).** 1-(4-methoxyphenyl)-5-methyl-1H-pyrazole (26d).** 26c and 26d were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (10.0 mg, 27%). The *ortho : para* ratio of the inseparable mixture was 1:1 as determined by \(^1\)H NMR of the isolated product.

**26c**: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.60 (s, 1H, aryl-\(H\)), 7.41 (td, \(J = 8.0, 1.8\) Hz, 1H, aryl-\(H\)), 7.33 (d, \(J = 4.1\) Hz, 1H, aryl-\(H\)), 7.08-7.00 (m, 2H, aryl-\(H\)), 6.17 (s, 1H, aryl-\(H\)), 3.79 (s, 3H, OCH₃), 2.15 (s, 3H, ArCH₃). \(^1\)C NMR (101 MHz, CDCl₃) \(\delta\) 154.8 (aryl-C), 140.8 (aryl-C), 139.9 (aryl-C), 130.3 (aryl-C), 129.2 (aryl-C), 128.7 (aryl-C), 120.9 (aryl-C), 112.2 (aryl-C), 105.3 (aryl-C), 55.9 (OCH₃), 11.4 (ArCH₃).

**26d**: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.55 (s, 1H, aryl-\(H\)), 7.34 (d, \(J = 8.8\) Hz, 2H, aryl-\(H\)), 6.97 (d, \(J = 8.9\) Hz, 2H, aryl-\(H\)), 6.17 (s, 1H, aryl-\(H\)), 3.85 (s, 3H, ArCH₃), 2.29 (s, 3H, ArCH₃). \(^1\)C NMR (101 MHz, CDCl₃) \(\delta\) 159.1 (aryl-C), 139.6 (aryl-C), 138.9
(aryl-C), 133.1 (aryl-C), 126.5 (aryl-C), 114.3 (aryl-C), 106.4 (aryl-C), 55.7 (OCH₃), 12.3 (ArCH₃).

These spectroscopic data correspond to reported data.¹

![Structure](image)

1-(2-methoxyphenyl)-1H-1,2,4-triazole (27a). 1-(4-methoxyphenyl)-1H-1,2,4-triazole (27b). 27a and 27b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as pale yellow oil (15.2 mg, 43%). The ortho : para ratio of the inseparable mixture was 2:1 as determined by ¹H NMR of the isolated product.

**27a:** ¹H NMR (400 MHz, CDCl₃) δ 8.73 (s, 1H, aryl-H), 8.06 (d, J = 2.0 Hz, 1H, aryl-H), 7.35 (t, J = 7.8 Hz, 1H, aryl-H), 7.08 (t, J = 8.2 Hz, 2H, aryl-H), 6.99 (d, J = 8.5 Hz, 1H, aryl-H), 3.90 (s, 2H, OCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 151.3 (aryl-C), 129.1 (aryl-C), 126.4 (aryl-C), 124.5 (aryl-C), 121.3 (aryl-C), 112.2 (aryl-C), 56.0 (OCH₃).

**27b:** ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H, aryl-H), 8.06 (d, J = 2.0 Hz, 1H, aryl-H), 7.76 (d, J = 7.9 Hz, 2H, aryl-H), 7.55 (d, J = 8.7 Hz, 2H, aryl-H), 3.84 (s, 3H, OCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.5 (aryl-C), 152.4 (aryl-C), 140.8 (aryl-C), 130.5 (aryl-C), 121.9 (aryl-C), 114.8 (aryl-C), 55.6 (OCH₃).

These spectroscopic data correspond to reported data.¹
1-(2-methoxyphenyl)-1H-1,2,3-triazole (28a). 28a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as colorless oil (20.5 mg, 59%).

28a: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H, aryl-H), 7.81 (s, 1H, aryl-H), 7.78 (dd, $J = 7.9, 1.6$ Hz, 1H, aryl-H), 7.42 (td, $J = 7.9, 1.6$ Hz, 1H, aryl-H), 7.14-7.05 (m, 2H, aryl-H), 3.88 (s, 2H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.3 (aryl-C), 133.3 (aryl-C), 130.2 (aryl-C), 126.4 (aryl-C), 125.8 (aryl-C), 125.7 (aryl-C), 121.3 (aryl-C), 112.4 (aryl-C), 56.1 (OCH$_3$).

1-(4-methoxyphenyl)-1H-1,2,3-triazole (28b). 28b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as white solid (5.2 mg, 15%).

28b: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (s, 1H, aryl-H), 7.84 (s, 1H, aryl-H), 7.64 (d, $J = 8.5$ Hz, 2H, aryl-H), 7.03 (d, $J = 8.5$ Hz, 2H, aryl-H), 3.87 (s, 3H, OCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.0 (aryl-C), 134.4 (aryl-C), 130.7 (aryl-C), 122.5 (aryl-C), 122.0 (aryl-C), 114.9 (aryl-C), 55.8 (OCH$_3$).

These spectroscopic data correspond to reported data.$^1$

1-(2-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (29a). 1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (29b). 29a and 29b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with
hexane/ethyl acetate (2:1) to give the title compound as pale yellow oil (26.5 mg, 59%).
The ortho : para ratio of the inseparable mixture was 4:1 as determined by $^1$H NMR of
the isolated product.

**29a:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.2$ Hz, 1H, aryl-$H$), 7.54-7.41 (m, 3H,
aryl-$H$), 7.37 (t, $J = 8.6$ Hz, 2H, aryl-$H$), 7.16-7.11 (m, 2H, aryl-$H$), 3.77 (s, 3H, OCH$_3$).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.7 (aryl-$C$), 145.7 (aryl-$C$), 134.1 (aryl-$C$), 131.1
(aryl-$C$), 128.2 (aryl-$C$), 127.6 (aryl-$C$), 125.3 (aryl-$C$), 123.9 (aryl-$C$), 121.1 (aryl-$C$),
119.9 (aryl-$C$), 112.5 (aryl-$C$), 111.3 (aryl-$C$), 56.0 (OCH$_3$).

**29b:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.2$ Hz, 1H, aryl-$H$), 7.61-7.67 (m, 3H,
aryl-$H$), 7.54-7.41 (m, 2H, aryl-$H$), 7.09 (d, $J = 8.9$ Hz, 2H, aryl-$H$), 3.88 (s, 3H, OCH$_3$).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.9 (aryl-$C$), 146.3 (aryl-$C$), 132.7 (aryl-$C$), 130.0
(aryl-$C$), 128.1 (aryl-$C$), 124.6 (aryl-$C$), 124.3 (aryl-$C$), 120.2 (aryl-$C$), 115.0 (aryl-$C$),
110.3 (aryl-$C$), 55.7 (OCH$_3$).

These spectroscopic data correspond to reported data.$^1$
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Ethyl 2-(4-chloro-2-(1H-pyrazol-1-yl)phenoxy)-2-methylpropanoate (32). 32 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (38.2 mg, 62%).

32: ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 2.5 Hz, 1H, aryl-H), 7.78 (d, J = 2.7 Hz, 1H, aryl-H), 7.69 (d, J = 1.9 Hz, 1H, aryl-H), 7.15 (d, J = 8.8, 2.7 Hz, 1H, aryl-H), 6.95 (d, J = 8.9 Hz, 1H, aryl-H), 6.41 (t, J = 2.2 Hz, 1H, aryl-H), 4.22 (q, J = 7.1 Hz, 2H, CH₂CH₃), 1.42 (s, 6H, C(CH₃)₂), 1.26 (t, J = 7.1 Hz, 3H, CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 173.5 (C=O), 145.5 (aryl-C), 140.7 (aryl-C), 134.2 (aryl-C), 131.9 (aryl-C), 128.7 (aryl-C), 127.2 (aryl-C), 125.5 (aryl-C), 121.6 (aryl-C), 106.8 (aryl-C), 81.7 (OC(CH₃)₂), 61.8(OCH₂CH₃), 24.9 (OC(CH₃)₂), 14.2 (OCH₂CH₃).

HRMS-ESI (m/z): Calcd for [(C₁₅H₁₇ClN₂O₃+H)+], 309.1000; found: 309.1007.

5-((3,5-dimethyl-2-(1H-pyrazol-1-yl)phenoxy)methyl)oxazolidin-2-one (34a). 34a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate to give the title compound as white solid (28.3 mg, 49%).

34a: ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 1.9 Hz, 1H, aryl-H), 7.48 (d, J = 2.3
Hz, 1H, aryl-H), 6.78 (s, 1H, aryl-H), 6.67 (s, 1H, aryl-H), 6.42 (s, 1H, aryl-H), 5.79 (s, 1H, NH), 4.73 (m, 1H, COOCH), 4.08 (dd, J = 10.3, 4.6 Hz, 1H, ArOCH₂), 3.98 (dd, J = 8.9 Hz, 1H, CH₂NH), 3.26 (dd, J = 8.6, 6.1 Hz, 1H, CH₂NH), 2.36 (s, 3H, ArC), 2.05 (s, 3H, ArC). ¹³C NMR (101 MHz, CDCl₃) δ 159.4 (C=O), 153.8 (aryl-C), 140.1 (aryl-C), 140.0 (aryl-C), 137.6 (aryl-C), 132.2 (aryl-C), 127.5 (aryl-C), 124.5 (aryl-C), 112.2 (aryl-C), 105.8 (aryl-C), 74.0 (COOCH), 69.1 (ArOCH₂), 42.1 (CH₂NH), 21.7 (ArC), 17.3 (ArC).

HRMS-ESI (m/z): Calcd for [(C₁₅H₁₇N₃O₃+H)+], 288.1343; found: 288.1348.

5-((3,5-dimethyl-4-(1H-pyrazol-1-yl)phenoxy)methyl)oxazolidin-2-one (34b). 34b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, hexane/ethyl acetate (5:1) to give the title compound as white solid (13.7 mg, 24%).

34b: ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H, aryl-H), 7.42 (s, 1H, aryl-H), 6.67 (s, 2H, aryl-H, aryl-H), 6.43 (s, 1H, aryl-H), 5.62 (s, 1H, NH), 4.97 (m, 1H, COOCH), 4.16 (d, J = 4.8 Hz, 2H, ArOCH₂), 3.78 (t, J = 8.8 Hz, 1H, CH₂NH), 3.61 (t, J = 7.4 Hz, 1H, CH₂NH), 1.96 (s, 6H, ArCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.2 (C=O), 157.9 (aryl-C), 140.1 (aryl-C), 137.9 (aryl-C), 133.5 (aryl-C), 131.1 (aryl-C), 113.9 (aryl-C), 105.9 (aryl-C), 74.1 (COOCH), 68.1 (ArOCH₂), 42.6 (CH₂NH), 16.4 (ArCH₃).

HRMS-ESI (m/z): Calcd for [(C₁₅H₁₇N₃O₃+H)+], 288.1343; found: 288.1346.

Ethyl 2-(4-chloro-2-(1H-pyrazol-1-yl)phenoxy)-2-methylpropanoate (36). 36 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with DCM/MeOH (10:1) to give the title
compound as pale yellow oil (89.8 mg, 87%).

36: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J = 2.5$ Hz, 1H, aryl-$H$), 7.61 (dd, $J = 6.1$, 2.1 Hz, 2H, aryl-$H$), 7.47-7.35 (m, 5H, aryl-$H$), 7.30-7.25 (m, 1H, aryl-$H$), 6.93 (d, $J = 8.7$ Hz, 1H, aryl-$H$), 6.40 (t, $J = 2.1$ Hz, 1H, aryl-$H$), 4.47 (s, 2H, ArCH$_2$N), 4.16 (t, $J = 4.2$ Hz, 2H), 3.90 (t, $J = 4.6$ Hz, 2H), 3.83 (t, $J = 4.2$ Hz, 2H), 3.53 (t, $J = 4.6$ Hz, 2H), 2.91 (s, 6H, N(CH$_3$)$_2$), 1.71 (s, 2H, CH$_2$C(CH$_3$)$_3$), 1.35 (s, 6H, ArC(CH$_3$)$_2$), 0.72 (s, 9H, CH$_2$C(CH$_3$)$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.0 (aryl-C), 144.0 (aryl-C), 140.0 (aryl-C), 133.3 (aryl-C), 131.9 (aryl-C), 130.9 (aryl-C), 129.3 (aryl-C), 129.2 (aryl-C), 126.9 (aryl-C), 126.0 (aryl-C), 123.6 (aryl-C), 113.0 (aryl-C), 106.5 (aryl-C), 69.8, 69.6, 68.3, 65.0, 63.1, 56.8, 50.3, 38.2, 32.4, 31.9, 31.6.

HRMS-ESI (m/z): Calcd for [(C$_{30}$H$_{44}$ClN$_3$O$_2$-Cl$^+$)], 478.3428; found: 478.3426.
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Supplementary Figures

Supplementary Figure 1. Undivided cell for photoelectrochemical oxidation
Supplementary Figure 2. Time-dependent concentration profile of reactants and products. Reaction conditions: Anisole (0.2 mmol), Pyrazole (0.4 mmol) in HFIP/MeOH (4:1, 3 mL) containing LiClO$_4$ (0.1 M). Applied potential: $E = 0.73$ V vs Fc/Fc$^+$. 

Supplementary Figure 3. CV curve of ferrocene in HFIP/MeOH (3:1) containing LiClO$_4$ (0.1 M). Glassy carbon electrode was used as a working electrode with a Ag/AgCl reference electrode and a Pt counter electrode. Scan rate: 30 mV/s.
Supplementary Figure 4. Electrochemical impedance spectroscopy (EIS) investigation. a. Electronic equivalent circuit representing the photoanode/electrolyte system used for EIS data modeling. $R_s$ represents a circuit series resistance. $R_{SC}$ represent the charge transfer resistance and $C_{CS}$ represent the capacitance of space charge region. $R_{CT}$ represent the semiconductor-electrolyte charge transfer resistance and $C_H$ represent the Helmholtz capacitance. b. Mott-Schottky curve of hematite in HFIP/MeOH (4:1) derived from EIS data. Electrochemical impedance spectroscopy (EIS) was conducted on two different hematite samples, and the results are similar.
Supplementary Figure 5. LSV curves of PEC oxidation under LED illumination. The electrolyte is 0.3 mmol LiClO4. Photocurrent profiles correspond to the organic solvent alone (HFIP: MeOH = 4:1, 3 mL) (red) and the solvent plus substrates (0.2 mmol anisole and 0.4 mmol pyrazole) (green). Scan rate: 30 mV/s. The oxidation of MeOH appears to occur as a background reaction.

Supplementary Figure 6. LSV curves of PEC oxidation under LED illumination. The electrolyte is 0.3 mmol TBAPF6. Photocurrent profiles correspond to 0.2 mmol anisole in 3 mL HFIP (red) and 0.4 mmol pyrazole in 3 mL HFIP (black). Scan rate: 30 mV/s.
NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) of 3a and 3b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3a and 3b
$\text{^1H NMR (400 MHz, CDCl}_3\text{) of 4a and 4b}$

$\text{^{13}C NMR (101 MHz, CDCl}_3\text{) of 4a and 4b}$
$^1$H NMR (400 MHz, CDCl$_3$) of 5a and 5b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 5a and 5b
$^1$H NMR (400 MHz, CDCl$_3$) of $6a$ and $6b$

$^{13}$C NMR (101 MHz, CDCl$_3$) of $6a$ and $6b$
$^1$H NMR (400 MHz, CDCl$_3$) of 7a and 7b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 7a and 7b
$^1$H NMR (400 MHz, CDCl$_3$) of 8a and 8b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 8a and 8b
\textbf{H NMR (400 MHz, CDCl$_3$) of 9}

\textbf{\textsuperscript{13}C NMR (101 MHz, CDCl$_3$) of 9}
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 10

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 10
$^1$H NMR (400 MHz, CDCl$_3$) of 11

$^{13}$C NMR (101 MHz, CDCl$_3$) of 11
$^1$H NMR (400 MHz, CDCl$_3$) of 12

$^{13}$C NMR (101 MHz, CDCl$_3$) of 12
$^1$H NMR (400 MHz, CDCl$_3$) of 13

$^{13}$C NMR (101 MHz, CDCl$_3$) of 13
$^1$H NMR (400 MHz, CDCl$_3$) of 14

$^{13}$C NMR (101 MHz, CDCl$_3$) of 14
$^1$H NMR (400 MHz, CDCl$_3$) of 15

$^{13}$C NMR (101 MHz, CDCl$_3$) of 15
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 16a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 16a
$^1$H NMR (400 MHz, CDCl$_3$) of 16b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 16b
$^1$H NMR (400 MHz, CDCl$_3$) of 17a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 17a
$^1$H NMR (400 MHz, CDCl$_3$) of 17b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 17b
$^1$H NMR (400 MHz, CDCl$_3$) of 18a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 18a
$^{1}$H NMR (400 MHz, CDCl$_3$) of 18b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 18b
$^1$H NMR (400 MHz, CDCl$_3$) of 19

$^{13}$C NMR (101 MHz, CDCl$_3$) of 19
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 20a

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 20a
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 20b

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 20b
$^1$H NMR (400 MHz, CDCl$_3$) of 21

$^{13}$C NMR (101 MHz, CDCl$_3$) of 21
$^1$H NMR (400 MHz, CDCl$_3$) of 22

$^{13}$C NMR (101 MHz, CDCl$_3$) of 22
$^1$H NMR (400 MHz, CDCl$_3$) of 23a and 23b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 23a and 23b
$\text{H NMR (400 MHz, CDCl}_3$ of 24a and 24b

$\text{C NMR (101 MHz, CDCl}_3$ of 24a and 24b

$\text{H NMR (400 MHz, CDCl}_3$ of 24a and 24b

$\text{C NMR (101 MHz, CDCl}_3$ of 24a and 24b
$^1$H NMR (400 MHz, CDCl$_3$) of 25

$^{13}$C NMR (101 MHz, CDCl$_3$) of 25
$^{1}$H NMR (400 MHz, CDCl$_3$) of 26a and 26b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 26a and 26b
$^1$H NMR (400 MHz, CDCl$_3$) of 26c and 26d

$^{13}$C NMR (101 MHz, CDCl$_3$) of 26c and 26d
$^1$H NMR (400 MHz, CDCl$_3$) of 27a and 27b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 27a and 27b
$^1$H NMR (400 MHz, CDCl$_3$) of 28a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 28a
$^1$H NMR (400 MHz, CDCl$_3$) of 28b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 28b
$^1$H NMR (400 MHz, CDCl$_3$) of 29a and 29b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 29a and 29b
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 32

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 32
$^{1}$H NMR (400 MHz, CDCl$_3$) of 34a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 34a
$^1$H NMR (400 MHz, CDCl$_3$) of 34b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 34b
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 36

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 36