# **Supporting Information**

## A family of low molecular-weight, organic catalysts for reductive mediated C-C bond formation

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#### **1-** General methods

All glassware was oven dried at 100 °C before use. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ( $\tilde{v} = 1/\lambda$ ) are reported in cm<sup>-1</sup>. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI) All <sup>1</sup>H-NMR and <sup>13</sup>C-NMR experiments were recorded using Bruker AV-400, spectrometers at 300 K. Chemical shifts ( $\delta$ ) are quoted in ppm and coupling constants (*J*) are quoted in Hz. The 7.27 ppm resonance of residual CHCl<sub>3</sub> for proton spectra and 77.16 ppm resonance for carbon spectra were used as internal references. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with kieselgel F<sub>254</sub> with 0.2 mm thickness. Visualization was achieved by a combination of ultraviolet light (254 nm) and acidic potassium permanganate or phosphomolybdic acid. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.).

## 2- General procedure for the preparation of the diazonium salts<sup>[1]</sup>

The appropriate aniline (10 mmol) was dissolved in a mixture of 3.4 mL of hydrofluoroboric acid (50%) and 4 mL of distilled water. The reaction mixture was cooled down to 0 °C using an ice-water bath, and a solution of sodium nitrite (10 mmol) in 1.5 mL H<sub>2</sub>O was added dropwise. The resulting reaction mixture was stirred for 40 min at 0 °C and the obtained precipitate was collected by filtration, dried and re-dissolved in a minimum amount of acetone. Ice-cooled diethyl ether was then added until precipitation of diazonium tetrafluoroborate salt. The latter was filtered and washed several times with small portions of diethyl ether and was dried under vacuum.

4-nitrobenzenediazonium tetrafluoroborate 1a<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone): δppm 9.20 (d, J = 9.40 Hz, 2H), 8.87 (d, J = 9.41 Hz, 2H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone): δppm 154.2 (2C), 135.0 (2C), 126.4, 121.4.

**4-bromobenzenediazonium tetrafluoroborate 1b**<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone): δppm 8.78 (d, *J* = 9.12 Hz, 2H), 8.32 (d, *J* = 9.22 Hz, 2H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone): δppm 137.6, 135.1 (2C), 134.1 (2C), 114.6.

**3-chlorobenzenediazonium tetrafluoroborate 1c**<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  8.95 (t, J = 3.09 Hz, 2.11 Hz, 1H), 8.86 (d, J = 8.54 Hz, 1H), 8.43 (d, J = 8.56 Hz, 1H), 8.14 (t, J = 8.39 Hz, 8.34 Hz, 1H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  141.7, 136.0, 133.1, 131.7, 131.6, 117.3.

**3-trifluoromethylbenzenediazonium tetrafluoroborate 1d**<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  9.28 (s, 1H), 9.15 (d, J = 8.29 Hz, 1H), 8.73 (d, J = 8.25 Hz, 1H), 8.37 (t, J = 8.65 Hz, 8.53 Hz, 1H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  137.8, 136.5, 133.1, 130.2, 123.5, 120.8, 117.7.

4-cyanobenzenediazonium tetrafluoroborate 1e<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  9.06 (d, J = 9.1 Hz, 2H), 8.51 (d, J = 9.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  135.1 (2C), 133.5 (2C), 123.4, 120.4, 115.8.

4-carboxymethylbenzenediazonium tetrafluoroborate 1f<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone): δppm 8.98 (d, *J* = 9.04 Hz, 2H), 8.56 (d, *J* = 9.02 Hz, 2H), 4.03 (s, 3H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone): δppm 163.7, 140.6, 133.4 (2C), 131.7 (2C), 119.6, 52.9.

## Benzenediazonium tetrafluoroborate 1g<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone):  $\delta ppm 8.84$  (d, J = 8.98 Hz, 2H), 8.38 (t, J = 7.84 Hz, 7.73 Hz, 1H), 8.09 (t, J = 8.31 Hz, 8.41 Hz, 2H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone):  $\delta ppm 141.4, 132.8$  (2C), 131.6 (2C), 115.2.

# $\label{eq:2-thiomethylbenzenediazonium tetrafluoroborate 1 h^{[6]}$



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  8.76 (d, J = 8.86 Hz, 1H), 8.27 (t, J = 7.48 Hz, 7.93 Hz, 1H), 8.09 (d, J = 8.45 Hz, 1H), 7.81 (t, J = 8.02 Hz, 8.06 Hz, 1H), 2.95 (s, 3H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone):  $\delta ppm$  148.4, 141.1, 133.8, 129.7, 128.0, 112.2, 15.6.

## 4-methoxybenzenediazonium tetrafluoroborate $\mathbf{1I}^{[1]}$



<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-Acetone): δppm 8.76 (d, *J* = 9.49 Hz, 2H), 7.54 (d, *J* = 9.48 Hz, 2H), 4.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-Acetone): δppm 169.9, 136.3(2C), 117.6 (2C), 102.8, 57.2.

#### 3- Synthesis of α-arylated heteroarenes from diazonium salts

## *a.* Optimization of the reaction conditions<sup>[a]</sup>

Table S1: Hydrazine screen for the C-H arylation of diazonium salt 1a with thiophene



entry	Catalyst	catalyst loading (mol%)	yield of 4a	
			[%] <sup>[b]</sup>	
1	<b>3</b> a	10	30	
2	<b>3b</b>	10	5	
3	3c	10	35	
4	<b>3d</b>	10	34	
5 <sup>[c]</sup>	3d	10	34	

[a] Reactions were performed using 0.33 mmol of the diazonium salt with 5 equiv. thiophene and 10 mol% catalyst for 2 h at r.t. [b] Yields of the isolated product. [c] The reaction was performed in the dark.



In the event, addition of a catalytic amount of *N*-phenylhydrazine **3a** to the reaction mixture led to the formation of coupling product **4a** in 30% yield. Electron-poor *N*-aminophtalimide **3b** gave **4a** in only 5% yield while *N*,*N*-disubstituted hydrazines, such as *N*,*N*-dimethylhydrazine **3c** and 4-aminomorpholine **3d**, afforded 4a in 35% and 34% yield, respectively (entries 2-4). Importantly, as shown in entry 5, the yield of the reaction was unchanged when the reaction was performed in the dark, showing that light plays no appreciable role in this transformation. We chose 4-aminomorpholine **3d** to pursue our studies due to both practical considerations and its

low price. Notably, vigorous and rapid evolution of nitrogen gas was detected as soon as the hydrazine catalyst was added into the reaction mixture

 Table S2: Reaction conditions screen for the C-H arylation of diazonium salt 1a with thiophene



Entry	Solvent	Equiv. of <b>2a</b>	<b>3d</b> loading (mol%)	Reaction time (min)	Yield of <b>4a</b> (%) <sup>[b]</sup>
1	DMSO	5	10	120	34
2	DMSO	10	10	120	55
3	DMSO	20	10	10	75
4	CH <sub>3</sub> CN	20	10	120	63
5	$CH_2CI_2$	20	10	120	5<
6	Acetone	20	10	120	40
7	MeOH	20	10	120	60
8	DMF	20	10	20	57
9	DMSO	20	5	15	73
10	DMSO	20	2.5	60	73
11	DMSO	20	1	120	75
12	DMSO	20	-	15	5
13 <sup>[c]</sup>	DMSO	20	5	80	70

[a] Reaction was performed with **1a** (0.11 mmol), **2a** (20 equiv.) and catalyst **3a** in 0.6 mL of solvent in a NMR tube. [b] Yields were determined by <sup>1</sup>H NMR. [c] The reaction was performed under argon atmosphere.

b. General procedure for  $\alpha$ -arylation of heteroarenes with diazonium salts



To a solution of diazonium salt (0.316 mmol, 1 eq.) and heteroarene (6.32 mmol, 20 eq.) in DMSO (2 mL) was added a solution of hydrazine (0.1 mL, 0.16M in DMSO, 0.0158 mmol, 0.05 eq.) at once at r.t. The reaction mixture was stirred at the same temperature during the time indicated in *Scheme 2* of the manuscript. Water was then added and the mixture was extracted with ethyl acetate (2x). The organic layers were combined and washed with water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was then removed and the crude was purified by column chromatography (silica gel, 0-5% ethyl acetate/heptane) to afford the desired products (**4a-l**).

#### 2-(4-nitrophenyl)thiophene 4a<sup>[2]</sup>



Yellow solid (63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm 8.16$  (d, J = 9.0 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 7.40 (dd , J = 4.0 Hz, 1.0 Hz, 1H), 7.36 (dd , J = 4.0 Hz, 1.0 Hz, 1H), 7.07 (dd, J = 4.0 Hz, 1.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm 146.7$ , 141.6, 140.6, 128.7, 127.7, 126.0 (2C), 125.7, 124.4 (2C); HRMS (ESI<sup>+</sup>) calculated for C<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>S ([M+Na]<sup>+</sup>): 228.0095, found 228.0091.

#### 2-(4-nitrophenyl) furan 4b<sup>[2]</sup>



Yellow solid (95% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 8.23 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 3.4 Hz, 1H), 6.54 (dd, J = 3.4 Hz, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 151.7, 146.4, 144.1, 136.4, 124.3 (2C), 123.9 (2C), 112.4, 108.9; HRMS (ESI) calculated for C<sub>10</sub>H<sub>7</sub>NO<sub>3</sub> ([M+Na]<sup>+</sup>): 212.0324, found 212.0322.

## Tert-butyl 2-(4-nitrophenyl)-1H-pyrrole-1-carboxylate 4c<sup>[2]</sup>



Yellow solid (81% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm 8.22$  (d, J = 8.9 Hz, 2H), 7.51 (d, J = 8.9 Hz, 2H), 7.41 (dd, J = 3.3 Hz, 1.8 Hz, 1H), 6.33 (dd, J = 3.4, 1.8 Hz, 1H), 6.27 (t, J = 3.3 Hz, 1H), 1.43 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm 148.8$ , 146.5, 140.6, 132.7, 129.5 (2C), 124.3, 122.9 (2C), 116.4, 111.1, 84.5, 27.7 (3C); HRMS (ESI) calculated for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> ([M+Na]<sup>+</sup>): 311.1008, found 311.1008.

#### 4-(furan-2-yl)benzonitrile 4d<sup>[2]</sup>



Beige solid (81% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.73 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.53 (dd, J = 1.8Hz, 0.5 Hz, 1H), 6.81 (dd, J = 3.4 Hz, 0.5 Hz, 1H), 6.52 (dd, J = 3.4 Hz, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  152.0, 143.7, 134.7, 132.6 (2C),

124.0 (2C), 118.9, 112.24, 110.3, 108.2; **HRMS (ESI)** calculated for  $C_{11}H_7NO$  ([M+Na]<sup>+</sup>): 192.0426, found 192.0421.

#### 4-(thiophen-2-yl)benzonitrile 4e<sup>[2]</sup>



White solid (66% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.69 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.43–7.38 (m, 2H); 7.13 (dd, J = 5.1 Hz, 3.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  142.1, 138.7, 132.7 (2C), 128.5, 127.4, 126.1 (2C), 125.1, 118.8, 110.6; HRMS (ESI) calculated for C<sub>11</sub>H<sub>7</sub>NS ([M+Na]<sup>+</sup>): 208.0197, found 208.0192.

methyl-4-(furan-2-yl)benzoate 4f<sup>[2]</sup>



White solid (66% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 1.2 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 6.51 (dd, J = 3.4 Hz, 1.8 Hz, 1H), 3.84 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.9, 153.0, 143.1, 134.8, 130.1 (2C), 128.6, 123.4 (2C), 112.0, 107.2, 52.1; HRMS (ESI) calculated for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub> ([M+Na]<sup>+</sup>): 225.0528, found 225.0522.

## **2-(4-bromophenyl) furan 4g**<sup>[2]</sup>



White solid (75% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.55–7.48 (m, 4H), 7.47 (dd, J = 1.8 Hz, 0.6 Hz, 1H), 6.65 (dd, J = 3.4 Hz, 0.6 Hz, 1H), 6.47 (dd, J = 3.4 Hz, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 152.9, 142.4, 131.9 (2C), 129.8, 125.6 (2C), 121.1, 111.8, 105.5; HRMS (ESI) calculated for C<sub>10</sub>H<sub>7</sub>BrO ([M+Na]<sup>+</sup>): 221.9675, found 221.9674.

#### 2-(3-(trifluoromethyl)phenyl)furan 4h



Colorless oil (55% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.92 (s, 1H), 7.86–7.80 (m, 1H), 7.54–7.48 (m, 3H), 6.74 (dd, J = 3.4 Hz, 0.4 Hz, 1H), 6.50 (dd, J = 3.4 Hz, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  152.5, 142.8, 131.6, 131.1 (t, J = 32.3 Hz), 129.2, 126.8, 124.1 (q, J = 270.7 Hz), 123.8 (t, J = 3.6 Hz), 120.5 (t, J = 3.8 Hz), 111.9, 106.3; **IR (neat, cm<sup>-1</sup>)** 3057, 1503, 1262, 1164, 119, 1075, 1013, 794, 734, 696, 593; **HRMS (EI)** calculated for C<sub>11</sub>H<sub>7</sub>F<sub>3</sub>O: 212.0444, found 212.0442.

#### 2-(3-chlorophenyl)furan 4i<sup>[3]</sup>



Colorless oil (63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.66 (t, *J* = 1.8 Hz, 1H), 7.54 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.48 (dd, *J* = 1.8 Hz, 0.7 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.22 (ddd, *J* = 2.1 Hz, 7.8 Hz, 1.2 Hz, 1H), 6.67 (dd, *J* = 3.4 Hz, 0.6 Hz, 1H), 6.48 (dd, *J* = 3.4 Hz, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 152.6, 142.6, 134.7, 132.5, 129.9, 127.2, 123.8, 121.8, 111.8, 106.1; HRMS (EI) calculated for C<sub>10</sub>H<sub>7</sub>ClO: 178.0180, found 178.0183.

tert-butyl 2-(4-cyanophenyl)-1H-pyrrole-1-carboxylate 4j<sup>[2]</sup>



Pink oil (89% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.63 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.39 (dd, J = 3.1 Hz, 1.9 Hz, 1H), 6.26 (m, 2H), 1.41 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  148.9, 138.7, 133.0, 131.3 (2C), 129.5 (2C), 123.9, 118.9, 116.0, 111.0, 110.4, 84.3, 27.6 (3C); HRMS (ESI) calculated for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> ([M+Na]<sup>+</sup>): 291.1109, found 291.1109.

*tert*-butyl 2-(4-(methoxycarbonyl)phenyl)-1H-pyrrole-1-carboxylate 4k<sup>[2]</sup>



Orange oil (69% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 8.03 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.38 (dd, J = 3.0 Hz, 2.1 Hz, 1H), 6.25–6.23 (m, 2H), 3.84 (s, 3H), 1.38 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 166.4 (2C), 149.1, 138.7, 134.0, 128.9 (2C), 128.8 (2C), 123.4, 115.3, 110.8, 84.0, 52.1, 27.6 (3C); HRMS (ESI) calculated for C<sub>17</sub>H<sub>19</sub>NO<sub>4</sub> ([M+Na]<sup>+</sup>): 324.1212, found 324.1212.

methyl-4-(furan-2-yl)benzoate 4l<sup>[2]</sup>



Red solid (55% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, J = 8.9 Hz, 2H), 7.33 (dd, J = 0.76 Hz, J = 0.71 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 6.42 (d, J = 3.5 Hz, 1H), 6.35 (dd, J = 1.8 Hz, 1.9 Hz, 1H), 3.73 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 154.1, 141.8, 125.3

(2C), 124.7, 114.8 (2C), 111.5, 103.4, 55.3; **HRMS (EI)** calculated for  $C_{11}H_{10}O_2$ : 174.0675, found 174.0673.

c. Procedure for the scale-up of the  $\alpha$ -arylation of heteroarenes with diazonium salts



To a solution of diazonium salt **1a** (3 g, 12.7 mmol, 1 eq.) and furan **2b** (18.3 mL, 252 mmol, 20 eq.) in dry DMSO (70 mL) was added hydrazine **3c** (10  $\mu$ L, 0.13 mmol, 0.01 eq.) at once at r.t. The reaction mixture was stirred at the same temperature for 2 h. Water was then added and the mixture was extracted with ethyl acetate (2x). The organic layers were combined and washed with water (3x), brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was then removed and the crude was purified by short pad column chromatography (silica gel, 30% ethyl acetate/heptane) to afford product **4b** (2.0 g, 85% yield).

## 4- Synthesis of α-arylated ketones from diazonium salts

#### a. Optimization conditions for the synthesis of $\alpha$ -arylated ketones



Entry	Equiv. of <b>5</b>	Equiv. catalyst <b>3d</b>	Solvent	Time (h)	Yield of <b>6a</b> (%) <sup>[a]</sup>
1	5	0.2	DMF	2	38 <sup>[b]</sup>
2	10	0.1	DMF	2	70
3	10	0.1	DMF	0.25	52
4	20	0.1	DMF	0.25	48
5	10	0.1	DMF	16	40
6	10	0.1	CH <sub>3</sub> CN	16	30
7	10	0.1	DMSO	2	42
8	10	0.1	DMF+H <sub>2</sub> O (1 equiv.)	2	50

[a] Yields were determined by <sup>1</sup>H NMR; [b] Yields were of isolated product **6a**.

## b. General Procedure for Preparation of Enol Acetates<sup>[4]</sup>

To a mixture of the corresponding acetophenone (13.3 mmol, 1 eq.) and isopropenyl acetate (66.6 mmol, 5 eq.) was added *p*-toluenesulfonic acid (1.2 mmol, 0.09 eq.). The resulting mixture was refluxed at 110 °C for 16 h. The reaction was cooled to r.t. and the solvent was removed under vacuum. The crude was diluted with 50 ml diethyl ether and washed with H<sub>2</sub>O (3x25ml), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude was purified by column chromatography (silica gel, 5% ethyl acetate/heptane) to afford the desired products **5c** and **5e**.

**1-phenylvinyl acetate 5c**<sup>[4]</sup>



Yellow oil (75% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δppm 7.38 (d, *J* = 9.4 Hz, 2H), 7.26 (m, 3H), 5.39 (d, *J* = 2.1 Hz, 1H), 4.94 (d, *J* = 2.2 Hz, 1H), 2.19 (s, 3H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δppm 169.1, 153.0, 134.3, 129.0, 128.6 (2C), 124.9 (2C), 102.2, 21.0.

## 1-phenylvinyl acetate 5e<sup>[4]</sup>



White solid (37% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δppm 7.40 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.35 (d, *J* = 2.1 Hz, 1H), 4.91 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δppm 169.1, 160.2, 152.7, 126.9, 126.3 (2C), 113.9 (2C), 100.3, 55.3, 21.0.

#### *c. General Procedure for the preparation of* $\alpha$ *-arylated ketones:*



To a solution of diazonium salt (0.316 mmol, 1 eq.) and alkenyl acetate (3.16 mmol, 10 eq.) in DMF (2 mL) was added a solution of hydrazine (0.2 mL, 0.16M in DMSO, 0.0316 mmol, 0.1 eq.) at once at r.t. The reaction mixture was stirred at the same temperature during the time indicated in *Scheme 3* of the manuscript. The solvent was removed under vacuo and the

crude was purified by column chromatography (silica gel, 0-30% ethyl acetate/heptane) to afford the desired product **6a–h**.

## **1-(4-nitrophenyl)propan-2-one 6a**<sup>[5]</sup>



Yellow oil (58% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm 8.12$  (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 3.78 (s, 2H), 2.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm 204.3$ , 147.2, 141.8, 130.5 (2C), 123.8 (2C), 50.1, 29.8; HRMS (ESI) calculated for C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub> ([M+Na]<sup>+</sup>): 202.0480, found 202.0476.

methyl-4-(2-oxopropyl)benzoate 6b<sup>[5]</sup>



Pink oil (77% yield) <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δppm 8.11–7.94 (m, 2H), 7.31–7.17 (m, 2H), 3.84 (s, 3H), 3.75 (s, 2H), 2.16 (s, 3H); <sup>13</sup>**C NMR (100 MHz, CDCl<sub>3</sub>)** δppm 205.3, 166.4,139.2, 129.9 (2C), 129.5 (2C), 129.0, 52.1, 50.7, 29.5; **HRMS (ESI)** calculated for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub> ([M+Na]<sup>+</sup>): 215.0684, found 215.0685.

## 4-(2-oxo-2-phenylethyl)benzonitrile 6c



White solid (61% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm 8.00$  (d, J = 7.2 Hz, 2H), 7.67–7.58 (m, 3H), 7.49 (t, J = 7.9 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 4.36 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm 196.1$ , 140.0, 136.2, 133.7, 132.4 (2C), 130.5 (2C), 128.9 (2C), 128.5 (2C), 118.8, 111.0, 45.2; **IR (neat, cm<sup>-1</sup>)** 3059, 2895, 2222, 1686, 1593, 1506, 1446, 1338, 1317, 1205, 990, 868, 792, 749, 682; **HRMS (ESI)** calculated for C<sub>15</sub>H<sub>11</sub>NO ([M+Na]<sup>+</sup>): 244.0739, found 244.0736.

#### 1-(4-bromophenyl)propan-2-one 6d<sup>[5]</sup>



Yellow oil (55% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.46 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 3.70 (s, 2H), 2.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 205.4, 133.1, 131.8 (2C), 131.1 (2C), 121.1, 50.2, 29.4; HRMS (ESI+) calculated for C<sub>9</sub>H<sub>9</sub>BrO ([M+Na]+): 234.9735, found 234.9726.

## 1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one 6e<sup>[5]</sup>



Yellow solid (94% yield) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm 8.09$  (d, J = 8.6 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.27 (s, 2H), 3.79 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm 194.5$ , 164.1, 147.1, 142.7, 130.8 (2C), 130.5 (2C), 129.3, 123.7 (2C), 114.1 (2C), 55.5, 44.6; HRMS (ESI) calculated for C<sub>15</sub>H<sub>13</sub>NO<sub>4</sub> ([M+Na]<sup>+</sup>): 294.0742, found 294.0743.

#### 4-(2-oxopropyl)benzonitrile 6f<sup>[5]</sup>



White solid (67% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.62 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.79 (s, 2H), 2.21 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  204.3, 139.4, 132.4 (2C), 130.4 (2C), 118.7, 111.1, 50.4, 29.8; HRMS (ESI) calculated for C<sub>10</sub>H<sub>9</sub>NO ([M+Na]<sup>+</sup>): 182.0582, found 182.0574.

#### 1-(3-chlorophenyl)propan-2-one 6g



Yellow oil (45% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δppm 7.30–7.23 (m, 2H), 7.20 (s, 1H), 7.17–7.04 (m, 1H), 3.68 (s, 2H), 2.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δppm 205.3, 136.0, 134.5, 129.9, 129.6, 127.6, 127.3, 50.3, 29.4; **IR (neat, cm<sup>-1</sup>)** 3063, 3003, 2923, 1717, 1597, 1573, 1476, 1431, 1358, 1323, 1121, 1096, 1080, 881, 772, 704, 683; **HRMS (ESI)** calculated for C<sub>9</sub>H<sub>9</sub>ClO ([M+Na]<sup>+</sup>): 191.0240, found 191.0234.

#### 1-(3-(trifluoromethyl)phenyl)propan-2-one 6h



Yellow oil (61% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.53 (d, J = 7.7 Hz, 1H), 7.50–7.42 (m, 2H), 7.38 (d, J = 7.7 Hz, 1H), 3.78 (s, 2H), 2.20 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 204.9, 135.0, 132.9, 131.1 (t, J = 32.0 Hz), 129.1, 126.2 (q, J = 3.7 Hz), 124.0 (q, J = 270 Hz), 123.9 (q, J = 3.7 Hz), 50.2, 29.6; IR (neat, cm<sup>-1</sup>) 2922, 1718, 1451, 1328, 1159, 1117, 1073,

902, 786, 702, 668, 651; **HRMS (ESI)** calculated for  $C_{10}H_9F_3O$  ([M+Na]<sup>+</sup>): 225.0503, found 225.0497.

#### 5- General procedure for the synthesis of 2-substituted benzothiophenes



Diazonium salt **1h** (0.2 mmol, 1eq.) was dissolved in 1ml DMSO (0.2M). Alkyne **7** (1.05 mmol, 5 eq.) was added to the solution followed by 4-aminomorpholine (0.01 mmol, 0.05 eq.). The reaction was stirred at r.t. for 14 h. Water was then added and the mixture was extracted with ether (3x). The organic layers were combined and washed with water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude material was purified by column chromatography (silica gel, 0-5% ethyl acetate/heptane) to afford the desired products **8a–e**.

#### methyl benzo[b]thiophene-2-carboxylate 8a<sup>[6]</sup>



Red oil (68% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.99 (s, 1H), 7.82–7.77 (m, 2H), 7.41–7.31 (m, 2H), 3.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  163.3, 142.4, 138.6, 133.7, 130.6, 127.0, 125.6, 124.9, 122.7, 52.5; HRMS (ESI) calculated for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>S ([M+Na]<sup>+</sup>): 215.0143, found 215.0139.

ethyl benzo[b]thiophene-2-carboxylate 8b<sup>[6]</sup>



Red solid (54% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.98 (s, 1H), 7.81–7.77 (m, 2H), 7.40–7.31 (m, 2H), 4.37–4.30 (q, J = 7.2 Hz, 7.2 Hz, 7.1 Hz, 2H), 1.34–1.32 (t, J = 7.2 Hz, 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 162.8, 142.2, 138.7, 133.9, 130.4, 126.9, 125.4, 124.9, 122.8, 61.6, 14.3; HRMS (ESI) calculated for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>S ([M+Na]<sup>+</sup>): 229.0299, found 229.0296.

#### **2-phenylbenzo[b]thiophene 8c**<sup>[6]</sup>



White solid (45% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.74 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H) 7.45 (s, 1H), 7.36–7.31 (t, J = 7.4 Hz, 7.8 Hz, 2H), 7.28–7.19 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  144.3, 140.7, 139.5, 134.6, 128.9, 128.3, 126.6 (2C), 124.5 (2C), 124.3 (2C), 123.6, 122.3; HRMS (EI) calculated for C<sub>14</sub>H<sub>10</sub>S: 210.0503, found 210.0506.

2-(p-tolyl)benzo[b]thiophene 8d<sup>[7]</sup>



White solid (73% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.75 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H) 7.42 (s, 1H), 7.28-7.21 (m, 2H), 7.17–7.13 (d, J = 8.3 Hz, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  144.4, 140.8, 139.4, 138.3, 131.2, 129.6 (2C), 126.4 (2C), 124.4, 124.1, 123.4, 122.2, 118.8, 21.3; HRMS (EI) calculated for C<sub>15</sub>H<sub>12</sub>S: 224.0660, found 224.0660.

2-(4-methoxyphenyl)benzo[b]thiophene 8e<sup>[6]</sup>



Red solid (71% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.72 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.56 (d, J = 8.7 Hz, 2H) 7.34 (s, 1H), 7.28–7.18 (m, 2H), 6.89–6.86 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  159.9, 144.1, 140.9, 139.2, 127.8 (2C), 127.1, 124.6, 123.9, 123.3, 122.2, 118.2, 114.8 (2C), 55.4; HRMS (EI) calculated for C<sub>15</sub>H<sub>12</sub>OS: 240.0609, found 240.0609.

#### 6- General procedure for the synthesis of aryl-benzoquinone compounds



To a solution of diazonium salt 1 (0.316 mmol, 1 eq.) and benzoquinone 9 (1.58 mmol, 5 eq.) in DMSO (2 mL, 0.18M) was added a solution of 4-ainomorpholine 3d (0.1 mL, 0.16M in DMSO, 0.0158 mmol, 0.05 eq.) at once at r.t. The reaction mixture was stirred at the same temperature during the time indicated in *Scheme 5* of the manuscript. Water was then added and the mixture was extracted with ethyl acetate (2x). The organic layers were combined and washed with water, brine and dried over  $Na_2SO_4$ . Evaporation and column chromatography (silica gel, 5% ethyl acetate/heptane) afforded the desired products 10a-c.

4'-nitro-[1,1'-biphenyl]-2,5-dione 10a<sup>[8]</sup>



Yellow solid (67% yield); <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta ppm 8.30$  (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.9 Hz, 2H), 6.94–6.93 (m, 1H), 6.92–6.90 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  186.8, 185.6, 148.7, 143.9, 138.8, 137.0, 136.6, 134.1, 130.3 (2C), 123.6 (2C); Product is unstable under HRMS conditions.

## 4'-bromo-[1,1'-biphenyl]-2,5-dione 10b<sup>[8]</sup>



Yellow solid (60% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 7.59 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 6.88–6.84 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm 187.3, 186.2, 144.9, 137.0, 136.4, 132.7, 131.9 (2C), 131.5, 130.8 (2C), 125.0; Product is unstable under HRMS conditions.

methyl 2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-4-carboxylate 10c<sup>[8]</sup>



Yellow solid (63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δppm 8.11 (d, *J* = 8.5 Hz, 2H), 7,55 (d, *J* = 8.5 Hz, 2H), 6.92–6.83 (m, 3H), 6, 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δppm 187.2, 186.1, 166.4, 145.1, 137.1, 136.9, 133.4, 131.5, 129.7 (2C), 129.3 (2C), 52.3; Product is unstable under HRMS conditions.

#### 7- General procedure for trapping of benzene radical with TEMPO



Diazonium salt **1g** (0.52 mmol, 1 eq.) was dissolved in 2 ml DMSO (0.25M). Tempo **11** (1.04 mmol, 2eq.) was added under argon at 20 °C. 4-aminomorpholine (0.026 mmol, 0.05 eq.) was added and the mixture was stirred at the dark for 2 h. Water was then added and the mixture was extracted with diethyl ether (3x). The organic layers were combined and washed with water, brine and dried over  $Na_2SO_4$ . The crude material was then purified by column chromatography (silica gel, 5% ethyl acetate/heptane) to afford product **12** in 44% yield.

#### 2,2,6,6-tetramethyl-1-phenoxypiperidine 12



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta ppm$  7.16–7.07 (m, 4H), 6.78–6.73 (m, 1H), 1.61–1.45 (m, 5H) 1.36–1.31 (m, 1H), 1.15 (s, 6H), 0.93 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta ppm$  163.8, 128.8 (2C), 119.8, 114.0 (2C), 60.5 (2C), 40.0 (2C), 32.8 (2C), 20.8 (2C), 17.3; HRMS (ESI) calculated for C<sub>15</sub>H<sub>24</sub>NO ([M+H]<sup>+</sup>): 234.1858, found 234.1858.

## 8- Catalytic behavior of 4-aminomorpholine



a) For LC-MS studies:

To a solution of diazonium salt (0.26 mmol, 1 eq.) and furan (5.2 mmol, 20 eq.) in CH<sub>3</sub>CN (1 mL) was added 4-aminomorpholine (6  $\mu$ L, 0.065 mmol, 0.25 eq.) at once in a vial at r.t. The reaction mixture was stirred at the same temperature for 30 min. A LC-MS trace of the reaction mixture was recorded.





b) For NMR studies:

To a solution of diazonium salt (0.26 mmol, 1 eq.) and furan (5.2 mmol, 20 eq.) in DMSO- $d_6$  (1 mL) was added 4-aminomorpholine (6  $\mu$ L, 0.065 mmol, 0.25 eq.) at once in a vial at r.t. The reaction mixture was stirred at the same temperature for 30 min. A NMR of the reaction mixture was then recorded. An extra 0.25 eq. of 4-aminomorpholine was then added to the reaction mixture and a second NMR was recorded (See spectra on the next page).



**Conclusion**: 4-aminomorpholine (**3d**) is present by LC-MS in the reaction mixture after reaction completion. The presence of 4-aminomorpholine was also confirmed by <sup>1</sup>H NMR by two peak enhancements at 2.97 and 3.71 ppm after addition of an extra 0.25 eq. of **3d**. The amount of **3d** in the reaction mixture (before addition of extra **3d**) was estimated at 0.25 eq. after integration of the NMR signals, allowing us to conclude that all **3d** was present in the mixture at the end of the reaction.

## 9- Discussion about the evolution of gas

The evolution of gas was observed in all the reported examples. It is important to note that this phenomenon is particularly vigorous at the beginning of the reaction and dramatically slows down in a few seconds after addition of the catalyst to the reaction solution.

The evolution of gas also depends on the nature of the substituent on the diazonium salts. Therefore, the intensity of the gas evolution increases with the electro-withdrawing property of the substituent:  $CO_2Me < Br \approx CN < NO_2$ .

A control experiment was run as followed: HBF<sub>4</sub> solution (0.05 eq) was added to a solution of 4-aminomorpholine (0.05 eq.) in DMSO at r.t. The mixture was stirred at r.t. for 15 min. To the solution was added furan (20 eq.) followed by *p*-nitrodiazonium salt **1a** (1 eq.). Strong evolution of gas was observed within a few second after the addition of the diazo compound. Usual work-up and purification led to the desired product in 92% yield.

The same experiment was run with 0.5 eq. of HBF<sub>4</sub> (ratio of 4-aminomorpholine to HBF<sub>4</sub> 1/10). The evolution of gas was less intense as described in the previous experiment and the yield dropped to 57% due to the presence of the by-product **A** (structure confirmed by NMR and MS). Mixing only HBF<sub>4</sub> (0.5 eq.), furan (20 eq.) and diazo **1a** led to **A** only.



To summarize the mechanism: The hydrazine adds to the diazo moiety of the diazonium salt to generate the tetrazene intermediate. The latter decomposes to form the aryl radical intermediate. The rate of this activation step depends on the nature of the substituent on the aryl group: The more electron-withdrawing group, the faster the formation of the aryl radical, the stronger the evolution of gas at the beginning of the reaction; overall reaction times are usually dependent on the nature of the substituents on **13**.

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11- Spectra







