Supporting information

for

Cu(II)-catalyzed C–H (SP³) oxidation and C–N cleavage: base-switched methylenation and formylation using tetramethylethylenediamine as carbon source

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1. General Information

All reagents and solvents were used as supplied without further purification. $^1$H NMR and $^{13}$C NMR were determined in CDCl$_3$ or DMSO-$d_6$ on a Brucker 300 or 400 MHz spectrometer at room temperature, respectively, and tetramethylsilane (TMS) served as an internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as brs (broad). Coupling constants ($J$) are given in hertz (Hz). ESI-MS were carried out on a LCMS-2020 (Shimadzu, Japan). EI-MS was taken on a QP2010 GC-MS instrument (Shimadzu, Japan). All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Qingdao Haiyang Chemical Co., Ltd).

2. General Procedure for Synthesis of Substrates and products

2.1 General procedure for the synthesis of $N$-protected indoles (1a-j) from substituted indoles with alkyl bromides (iodomethane used for methyl-protected reagent) (5 mmol scale). A 50 mL flask equipped with a stir-bar was charged with substituted indole (5 mmol) and KOH (10.0 mmol). 20 mL of DMSO was added to the flask and the solution was stirred under room temperature, then alkyl bromides (10.0 mmol) was added. The reaction mixture was stirred at room temperature and monitored by TLC. Upon finished the reaction mixture was quenched by water (20 mL) and extracted by ethyl acetate (3×30 mL). Combined organic phase were dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by $^1$H- and $^{13}$C-NMR and MS (EI or ESI).
2.2 Synthesis of 1-Tosylindole (1l) from indole with 4-methylbenzene-1-sulfonyl chloride (5 mmol scale) was according to the literature method.[1]

2.3 Synthesis of 1-Bocindole (1l) from indole with di-tert-butyl dicarbonate (5 mmol scale) was according to the literature method.[2]

2.4 General procedure for the synthesis of N-protected anilines (5b-l, 5n-p) from substituted anilines with alkyl bromides (iodomethane used for methyl-protected reagent) (5 mmol scale). A 50 mL flask equipped with a stir-bar was charged with substituted anilines (5 mmol) and KOH (10.0 mmol). 20 mL of DMSO was added to the flask and the solution was stirred under room temperature. Followed alkyl bromides (2.0 equiv for 5c-e, 5n; 4.0 equiv for 5b, 5f-l, 5o-p) was added. The reaction mixture was stirred at 50 °C and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and extracted by ethyl acetate (3×30 mL).
Combined organic phase were dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by $^1$H- and $^{13}$C-NMR and MS (EI or ESI).

2.5 General procedure for the synthesis of 3,3$'$-bisindolylmethanes (3a-j) and 4,4$'$-diaminodiphenylmethanes (6a-p). A 15 mL flask equipped with a stir-bar and condenser was charged with CuCl$_2$ (0.5 mmol, 68.0 mg) and MeCN (5.0 mL, for 6c-e DMA was use as solvent). TMEDA (1.5 mmol, 230 $\mu$L) was added to the flask while stirring at room temperature. Followed indoles or anilines (1.0 mmol) was added. The reaction mixture was stirred at refluxing (or 6c-e was heated to 140 $^\circ$C) and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and ammonia water (25%, 1.0 mL) and extracted by ethyl acetate (3×30 mL). Combined organic phase were dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure.

<table>
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<th>$R^2$</th>
<th>$R^3$</th>
<th>$R^4$</th>
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5n (88%) 5o (93%) 5p (89%)
pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by $^1$H- and $^{13}$C-NMR and MS (EI or ESI).

2.6 General procedure for the synthesis of 3-formylindoles (4a-k). A 15 mL flask equipped with a stir-bar and condenser was charged with CuCl$_2$ (0.5 mmol, 68.0 mg) and MeCN (5 mL). TMEDA (1.5 mmol, 230 μL) was added to the flask while stirring at room temperature. Followed indoles (1.0 mmol) and K$_2$CO$_3$ (2 mmol, 276 mg) was added. The reaction mixture was stirred at refluxing and monitored by TLC. Upon completion the reaction mixture was quenched by water (20 mL) and ammonia water (25%, 1.0 mL) and extracted by ethyl acetate (3×50 mL). Combined organic phase were dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether, ethyl acetate. Products were characterized by $^1$H- and $^{13}$C-NMR and MS (EI or ESI).

3. Optimization of reaction conditions and other Information
3.1 Table S1 Optimization of reaction conditions for TMEDA (2a) as methylene donor

<table>
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<tr>
<th>Entry</th>
<th>Cat. (mol%)</th>
<th>Equiv. 2a</th>
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<th>t (h)</th>
<th>Yield (%)b</th>
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<tr>
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<td>Trace</td>
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<td>Trace</td>
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a Reaction condition: 1a (1.0 mmol) was added to a mixture of catalyst, 2a, and a solvent (5 mL) heated to indicated temperature and time. b Isolated yield. c Trace amount of N-ethyl-3-formylindole (4a) were observed. d Reaction under nitrogen atmosphere.

3.2 Selection of other amines as methylene donor

Figure S1 Selection of other amines as methylene donor
3.3 To detect TMEDA (2a) transferred to 2d, an experiment using MeCN-\(d_3\) was carried under standard conditions. The signals of 2d and 2a were identified by comparing with their standard compound \(^1\)H-NMR spectra (300MHz, MeCN-\(d_3\), figure S2). It was noted that the signals of 2d or 2a appeared to be one broad peak in the presentation of CuCl\(_2\) in MeCN-\(d_3\).

![1H-NMR analysis of the reaction mixture using MeCN-\(d_3\) as the solvent](image)

Figure S2 \(^1\)H-NMR analysis of the reaction mixture using MeCN-\(d_3\) as the solvent

3.4 To exclude the possibility of 3-formylindole as an intermediate for methylenation, 4a was treated with indole 1j under standard conditions, upon isolation and GC-MS analysis, no heterobisindolylmethane 3n and 3a was detected (Fig. S3). Homobisindolylmethane 3j was isolated in 89% yield based on 1j.

![Chemical structures](image)

\[3j: R^1 = R^2 = Me, \quad (89\%, \text{ based on } 1j)\]
\[3n: R^1 = H, R^2 = Me, \quad (0\%)\]
\[3a: R^1 = R^2 = H, \quad (0\%)\]
4. Characterization data of Products and Substrates

4.1 Characterization of products

Bis(1-ethyl-1H-indol-3-yl)methane[3] (Table 1, 3a): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.29 – 7.19 (m, 2H), 7.11 (t, $J = 7.4$ Hz, 2H), 6.89 (s, 2H), 4.27 (s, 2H), 4.12 (q, $J = 7.2$ Hz, 4H), 1.43 (t, $J = 7.3$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 136.2, 128.2, 125.3, 121.2, 119.5, 118.5, 114.4, 109.2, 40.7, 21.1, 15.5; EI-MS $m/z$ (rel. int., %): 302 (100), 301 (92), 273 (26).

Bis(1-methyl-1H-indol-3-yl)methane[3] (Table 1, 3b): $^1$H NMR (300 MHz, CDCl$_3$)
δ 7.63 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 8.1 Hz, 2H), 7.09 (t, J = 7.9 Hz, 2H), 6.80 (s, 2H), 4.23 (s, 2H), 3.72 (s, 6H); 13C NMR (75 MHz, CDCl₃) δ 137.0, 127.8, 126.9, 121.3, 119.2, 118.5, 114.2, 109.0, 32.5, 20.8; EI-MS m/z (rel. int., %): 274 (100), 273 (98), 144 (20).

Bis(1-benzyl-1H-indol-3-yl)methane[4] (Table 1, 3c): ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J = 7.7 Hz, 2H), 7.34 – 7.22 (m, 8H), 7.21 – 7.15 (m, 2H), 7.14 – 7.05 (m, 6H), 6.94 (s, 2H), 5.26 (s, 4H), 4.29 (s, 2H); 13C NMR (75 MHz, CDCl₃) δ 137.8, 136.8, 128.6, 128.2, 127.4, 126.6, 126.5, 121.6, 119.4, 118.8, 114.8, 109.6, 49.8, 21.2; EI-MS m/z (rel. int., %): 426 (100), 425 (19), 335 (88).

Bis(1-(4-methoxybenzyl)-1H-indol-3-yl)methane (Table 1, 3d): ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, J = 7.9 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 7.11 – 7.00 (m, 6H), 6.90 (s, 2H), 6.84 – 6.77 (m, 4H), 5.18 (s, 4H), 4.25 (s, 2H), 3.77 (s, 6H); 13C NMR (75 MHz, CDCl₃) δ 159.0, 136.7, 129.8, 128.2, 128.0, 126.3, 121.5, 119.4, 118.7, 114.6, 114.0, 109.6, 55.2, 49.3, 21.2; MS (ESI): 487.20 [M+H]^+.

Bis(1-ethyl-5-methoxy-1H-indol-3-yl)methane (Table 1, 3e): ¹H NMR (300 MHz, CDCl₃) δ 7.25 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 1.9 Hz, 2H), 6.91 (dd, J = 8.8, 2.0 Hz,
2H), 6.87 (s, 2H), 4.20 (s, 2H), 4.09 (q, J = 7.2 Hz, 4H), 3.85 (s, 6H), 1.42 (t, J = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.5, 131.5, 128.3, 125.8, 113.6, 111.5, 109.9, 101.2, 55.9, 40.8, 21.2, 15.5; EI-MS m/z (rel. int., %): 362 (100), 361 (71), 333 (19).

![Image](image1.png)

**Bis(5-chloro-1-ethyl-1H-indol-3-yl)methane (Table 1, 3f):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.54 (d, J = 1.8 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.15 (dd, J = 8.7, 1.9 Hz, 2H), 6.88 (s, 2H), 4.13 – 4.05 (m, 6H), 1.41 (t, J = 7.3 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 134.5, 128.9, 126.4, 124.3, 121.5, 118.7, 113.5, 110.2, 40.9, 20.9, 15.4; EI-MS m/z (rel. int., %): 370 (100), 369 (84), 341 (18).

![Image](image2.png)

**Bis(5-cyano-1-ethyl-1H-indol-3-yl)methane (Table 1, 3g):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.86 (s, 2H), 7.43 (dd, J = 8.6, 1.4 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.02 (s, 2H), 4.21 (s, 2H), 4.16 (q, J = 7.3 Hz, 4H), 1.45 (t, J = 7.3 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.7, 127.5, 127.2, 124.9, 124.4, 120.8, 114.6, 110.1, 101.6, 41.1, 21.0, 15.4; EI-MS m/z (rel. int., %): 352 (100), 351 (89), 323 (20).

![Image](image3.png)

**Bis(1-ethyl-2-methyl-1H-indol-3-yl)methane (Table 1, 3h):** $^1$H NMR (300 MHz, MeOD) δ 7.46 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.13 (t, J = 8.1 Hz, 2H), 7.00 (t, J = 7.9 Hz, 2H), 4.20 (s, 2H), 4.14 (q, J = 7.2 Hz, 4H), 2.39 (s, 6H), 1.34 (t, J
\( \delta = 7.2 \text{ Hz, 6H}; \) \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta 135.4, 131.8, 128.3, 120.1, 118.5, 118.4, 110.4, 108.3, 37.5, 19.9, 15.3, 10.1; \) EI-MS \(m/z\) (rel. int., %): 330 (78), 315 (36), 171 (100).

Bis(1-ethyl-4-methyl-1H-indol-3-yl)methane (Table 1, 3i): \(^1\text{H NMR (300 MHz, CDCl}_3\) \(\delta 7.21 (d, J = 8.2 \text{ Hz, 2H}), 7.13 (t, J = 7.5 \text{ Hz, 2H}), 6.86 (d, J = 6.7 \text{ Hz, 2H}), 6.69 (s, 2H), 4.60 (s, 2H), 4.08 (q, J = 7.2 \text{ Hz, 4H}), 2.70 (s, 6H), 1.39 (t, J = 7.0 \text{ Hz, 6H}); \) \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta 136.7, 131.6, 126.6, 126.2, 121.4, 120.2, 116.2, 107.2, 40.8, 25.7, 20.2, 15.5; \) EI-MS \(m/z\) (rel. int., %): 330 (42), 171 (100).

Bis(1-ethyl-7-methyl-1H-indol-3-yl)methane (Table 1, 3j): \(^1\text{H NMR (300 MHz, CDCl}_3\) \(\delta 7.48 (d, J = 7.4 \text{ Hz, 2H}), 7.06 – 6.88 (m, 4H), 6.78 (s, 2H), 4.31 (q, J = 7.1 \text{ Hz, 4H}), 4.18 (s, 2H), 2.73 (s, 6H), 1.38 (t, J = 7.1 \text{ Hz, 6H}); \) \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta 135.0, 129.4, 127.2, 124.4, 120.7, 118.9, 117.6, 114.6, 43.2, 21.2, 20.0, 18.1; \) EI-MS \(m/z\) (rel. int., %): 330 (100), 329 (49), 301 (60).

1-Ethyl-3-formylindole\(^{[5]}\) (Table 1, 4a): \(^1\text{H NMR (300 MHz, CDCl}_3\) \(\delta 10.00 (s, 1H), 8.35 – 8.27 (m, 1H), 7.75 (s, 1H), 7.44 – 7.28 (m, 3H), 4.24 (q, J = 7.3 \text{ Hz, 2H}), 1.55 (t, J = 7.3 \text{ Hz, 3H}); \) \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta 184.4, 137.4, 136.9, 125.4, 123.8, 122.8, 122.0, 118.1, 109.8, 41.8, 15.0; \) MS (ESI): 174.10[M+H]\(^+\).
1-Methyl-3-formylindole[6] (Table 1, 4b): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.97 (s, 1H), 8.49 – 8.14 (m, 1H), 7.64 (s, 1H), 7.38 – 7.28 (m, 3H), 3.85 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.3, 139.2, 137.8, 125.1, 123.9, 122.8, 121.9, 117.9, 109.8, 33.6; MS (ESI): 160.10[M+H]$^+$. 

1-Benzyl-3-formylindole[5] (Table 1, 4c): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.99 (s, 1H), 8.47 – 8.22 (m, 1H), 7.70 (s, 1H), 7.40 – 7.27 (m, 6H), 7.22 – 7.14 (m, 2H), 5.35 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.5, 138.4, 137.4, 135.2, 129.0, 128.3, 127.1, 125.4, 124.1, 123.0, 122.1, 118.4, 110.3, 50.8; MS (ESI): 236.10[M+H]$^+$. 

1-(4-Methoxybenzyl)-3-formylindole[7] (Table 1, 4d): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.97 (s, 1H), 8.48 – 8.21 (m, 1H), 7.67 (s, 1H), 7.41 – 7.28 (m, 3H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.93 – 6.85 (m, 2H), 5.28 (s, 2H), 3.80 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.6, 159.5, 138.4, 137.3, 128.8, 127.0, 125.4, 124.0, 123.0 (s), 122.0, 118.2, 114.4, 110.3, 55.2, 50.3; MS (ESI): 266.10[M+H]$^+$. 

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1-Ethyl-3-formyl-5-methoxyindole\textsuperscript{[8]} (Table 1, 4e): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.93 (s, 1H), 7.79 (d, $J = 2.4$ Hz, 1H), 7.67 (s, 1H), 7.25 (d, $J = 8.9$ Hz, 1H), 6.96 (dd, $J = 8.9$, 2.5 Hz, 1H), 4.17 (q, $J = 7.3$ Hz, 2H), 3.89 (s, 3H), 1.52 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.3, 156.5, 137.5, 131.8, 126.1, 117.8, 114.3, 110.7, 103.3, 55.7, 41.9, 15.0; MS (ESI): 204.10[M+H]$^+$. 

5-Chloro-1-ethyl-3-formylindole (Table 1, 4f): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.95 (s, 1H), 8.29 (s, 1H), 7.75 (s, 1H), 7.29 (s, 2H), 4.21 (q, $J = 7.3$ Hz, 2H), 1.55 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.1, 138.0, 135.2, 128.8, 126.3, 124.2, 121.7, 117.5, 110.9, 42.0, 14.9; MS (ESI): 208.05[M+H]$^+$. 

5-Cyano-1-ethyl-3-formylindole (Table 1, 4g): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.01 (s, 1H), 8.65 (d, $J = 0.8$ Hz, 1H), 7.87 (s, 1H), 7.56 (dd, $J = 8.6$, 1.5 Hz, 1H), 7.46 (d, $J = 8.5$ Hz, 1H), 4.28 (q, $J = 7.3$ Hz, 2H), 1.58 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 184.1, 138.9, 138.4, 127.5, 126.8, 125.0, 119.7, 118.2, 110.9, 106.1, 42.2, 15.0; MS (ESI): 199.10[M+H]$^+$. 

S13
1-Ethyl-3-formyl-2-methylindole (Table 1, 4h): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.14 (s, 1H), 8.43 – 8.10 (m, 1H), 7.46 – 7.15 (m, 3H), 4.14 (q, \(J = 7.3\) Hz, 2H), 2.66 (s, 3H), 1.38 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 184.0, 146.8, 135.8, 125.9, 123.0, 122.6, 120.8, 114.2, 109.2, 38.0, 14.6, 10.2; MS (ESI): 188.10[M+H]\(^+\).

1-Ethyl-3-formyl-4-methylindole (Table 1, 4i): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.15 (s, 1H), 7.89 (s, 1H), 7.25 – 7.21 (m, 2H), 7.10 – 7.08 (m, 1H), 4.22 (q, \(J = 7.3\) Hz, 2H), 2.84 (s, 3H), 1.54 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 184.7, 137.2, 136.3, 132.3, 125.2, 124.1, 123.3, 119.5, 107.8, 41.8, 22.5, 14.8; MS (ESI): 188.10[M+H]\(^+\).

1-Ethyl-3-formyl-7-methylindole (Table 1, 4j): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.99 (s, 1H), 8.20 (d, \(J = 7.9\) Hz, 1H), 7.69 (s, 1H), 7.19 (t, \(J = 7.6\) Hz, 1H), 7.06 (d, \(J = 7.2\) Hz, 1H), 4.46 (q, \(J = 7.2\) Hz, 2H), 2.74 (s, 3H), 1.54 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 184.4, 139.0, 135.7, 126.9, 126.5, 122.9, 121.2, 119.9, 117.9, 44.4, 19.5, 17.2; MS (ESI): 188.10[M+H]\(^+\).
3-Formylindole[9] (Table 1, 4k): $^1$H NMR (300 MHz, DMSO) $\delta$ 12.13 (s, 1H), 9.93 (s, 1H), 8.28 (d, $J = 3.1$ Hz, 1H), 8.09 (d, $J = 8.3$ Hz, 1H), 7.50 (d, $J = 7.1$ Hz, 1H), 7.27 – 7.18 (m, $J = 7.1$, 1.3 Hz, 2H); $^{13}$C NMR (75 MHz, DMSO) $\delta$ 185.3, 138.8, 137.4, 124.5, 123.8, 122.5, 121.2, 118.5, 112.8; MS (ESI): 146.05[M+H]$^+$. 

Me$_2$N

$^6$a

4,4'-Methylenebis(N,N-dimethylaniline)[10] (Table 2, 6a): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J = 8.6$ Hz, 4H), 6.70 (d, $J = 8.6$ Hz, 4H), 3.82 (s, 2H), 2.91 (s, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.0, 130.3, 129.4, 113.0, 40.9, 39.8; MS (ESI): 255.15[M+H]$^+$. 

Et$_2$N

$^6$b

4,4'-Methylenebis(N,N-diethylaniline)[11] (Table 2, 6b): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.03 (d, $J = 8.6$ Hz, 4H), 6.61 (d, $J = 8.6$ Hz, 4H), 3.77 (s, 2H), 3.30 (q, $J = 7.0$ Hz, 8H), 1.12 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.0, 129.5, 129.0, 112.1, 44.4, 39.7, 12.6; MS (ESI): 311.20[M+H]$^+$. 

4,4'-Methylenebis(N-benzyl-N-methylaniline) (Table 2, 6c): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.30 (m, 4H), 7.28 – 7.22 (m, 6H), 7.06 (d, $J = 8.5$ Hz, 4H), 6.71 (d, $J = 8.0$ Hz, 4H), 4.50 (s, 4H), 3.81 (s, 2H), 2.99 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 148.0, 139.2, 130.1, 129.5, 128.5, 126.8, 112.6, 56.9, 39.8, 38.6; MS (ESI):
407.20 [M+H]^+. 

4,4'-Methylenebis(N-(4-methoxybenzyl)-N-methylaniline) (Table 2, 6d): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.15 (d, $J = 8.5$ Hz, 4H), 7.04 (d, $J = 8.5$ Hz, 4H), 6.84 (d, $J = 8.6$ Hz, 4H), 6.69 (d, $J = 8.6$ Hz, 4H), 4.41 (s, 4H), 3.79 (s, 8H), 2.93 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.5, 148.0, 131.0, 130.0, 129.4, 128.0, 113.8, 112.6, 56.3, 55.2, 39.8, 38.4; MS (ESI): 467.25 [M+H]^+. 

4,4'-Methylenebis(N-allyl-N-methylaniline) (Table 2, 6e): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.04 (d, $J = 8.6$ Hz, 4H), 6.66 (d, $J = 8.4$ Hz, 4H), 5.88 – 5.79 (m, 2H), 5.29 – 4.99 (m, 4H), 3.94 – 3.83 (m, 4H), 3.79 (s, 2H), 2.89 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.7, 134.0, 130.0, 129.3, 116.1, 112.6, 55.5, 39.7, 38.0; MS (ESI): 307.20 [M+H]^+. 

4,4'-Methylenebis(N,N-diethyl-3,5-dimethoxyaniline) (Table 2, 6f): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.91 (s, 4H), 3.80 (s, 2H), 3.71 (s, 12H), 3.30 (q, $J = 7.1$ Hz, 8H), 1.14 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.5, 146.9, 108.8, 91.0, 56.2, 44.6, 16.2, 12.6; MS (ESI): 431.25 [M+H]^+. 

S16
4,4'-Methylenebis(N,N-diethyl-3,5-dimethylaniline) (Table 2, 6g): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.35 (s, 4H), 3.89 (s, 2H), 3.30 (q, $J = 7.0$ Hz, 8H), 2.11 (s, 12H), 1.13 (d, $J = 7.1$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.5, 137.5, 126.1, 112.8, 44.1, 29.8, 21.4, 12.6; MS (ESI): 367.30[M+H]$^+$. 

4,4'-Methylenebis(N,N-diethyl-3-methoxyaniline) (Table 2, 6h): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.88 (d, $J = 8.3$ Hz, 2H), 6.42 – 6.06 (m, 4H), 3.83 (s, 6H), 3.77 (s, 2H), 3.34 (q, $J = 7.0$ Hz, 8H), 1.17 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.4, 147.4, 130.6, 117.4, 104.4, 96.0, 55.3, 44.6, 27.8, 12.6; MS (ESI): 371.25[M+H]$^+$. 

4,4'-Methylenebis(N,N-diethyl-3-methylaniline) (Table 2, 6i): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.77 (d, $J = 8.3$ Hz, 2H), 6.56 (s, 2H), 6.47 (d, $J = 7.5$ Hz, 2H), 3.73 (s, 2H), 3.33 (q, $J = 7.0$ Hz, 8H), 2.25 (s, 6H), 1.16 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.2, 137.2, 130.1, 126.5, 114.0, 109.9, 44.4, 34.7, 20.3, 12.7; MS (ESI): 339.25 [M+H]$^+$. 

S17
4,4'-Methylenebis(N,N-diethyl-2,5-dimethoxyaniline) (Table 2, 6k): $^1$H NMR (300 MHz, CDCl$_3$) δ 6.61 (s, 2H), 6.58 (s, 2H), 3.86 (s, 2H), 3.79 (s, 6H), 3.71 (s, 6H), 3.13 (q, $J = 6.8$ Hz, 8H), 1.02 (t, $J = 7.0$ Hz, 12H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 151.2, 148.0, 137.3, 123.3, 114.2, 106.4, 56.4, 55.7, 46.4, 29.0, 12.0; MS (ESI): 431.25[M+H]$^+$. 

Bis(4-(pyrrolidin-1-yl)phenyl)methane (Table 2, 6m): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.04 (d, $J = 7.8$ Hz, 4H), 6.50 (d, $J = 7.8$ Hz, 4H), 3.80 (s, 2H), 3.25 (s, 8H), 1.98 (s, 8H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 146.2, 129.5, 129.0, 111.6, 47.7, 39.9, 25.4; MS (ESI): 307.20[M+H]$^+$. 

Bis(1-ethyl-1,2,3,4-tetrahydroquinolin-6-yl)methane (Table 2, 6n): $^1$H NMR (300 MHz, CDCl$_3$) δ 6.87 (d, $J = 8.3$ Hz, 2H), 6.78 (s, 2H), 6.52 (d, $J = 8.3$ Hz, 2H), 3.68 (s, 2H), 3.31 (q, $J = 7.0$ Hz, 4H), 3.25 – 3.17 (m, 4H), 2.70 (t, $J = 6.4$ Hz, 4H), 2.04 – 1.82 (m, 4H), 1.11 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.0, 129.6, 129.0, 127.2, 122.4, 110.6, 48.3, 45.3, 39.9, 28.1, 22.4, 10.7; MS (ESI): 335.20[M+H]$^+$. 

S18
4,4'-Methylenebis(N,N-dimethylnaphthalen-1-amine)[10] (Table 2, 6o): 1H NMR (300 MHz, CDCl3) δ 8.34 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.60 – 7.41 (m, 4H), 7.01 – 6.94 (m, 4H), 4.76 (s, 2H), 2.89 (s, 12H); 13C NMR (75 MHz, CDCl3) δ 149.6, 133.3, 130.9, 129.0, 126.9, 125.8, 124.9, 124.7, 124.5, 113.8, 45.3, 35.2; MS (ESI): 355.20[M+H]+.

4.2 Characterization of substrates

1-Ethylindole (1a): 1H NMR (300 MHz, CDCl3) δ 7.66 (dd, J = 7.8, 0.9 Hz, 1H), 7.38 (dd, J = 8.2, 0.7 Hz, 1H), 7.24 (dt, J = 8.2, 1.2 Hz, 1H), 7.15 – 7.10 (m, 2H), 6.52 (dd, J = 3.1, 0.8 Hz, 1H), 4.20 (q, J = 7.3 Hz, 2H), 1.49 (t, J = 7.3 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 135.7, 128.6, 127.0, 121.3, 121.0, 119.2, 109.3, 101.0, 40.9, 15.4; EI-MS m/z (rel. int., %): 145 (65), 130 (100).

1-Methylindole (1b): 1H NMR (300 MHz, CDCl3) δ 7.64 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.15 – 7.09 (m, 1H), 7.06 (d, J = 3.0 Hz, 1H), 6.50 (d, J = 2.7 Hz, 1H), 3.81 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 136.6, 128.7, 128.4, 121.4, 120.8, 119.2, 109.1, 100.8, 32.7; MS (ESI): 132.10[M+H]+.
1-Benzylinole (1c): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 (dd, $J = 7.1$, 1.1 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.23 – 7.07 (m, 5H), 6.58 (d, $J = 2.7$ Hz, 1H), 5.34 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.5, 136.3, 128.7, 128.2, 127.6, 126.8, 124.6, 121.7, 121.0, 119.5, 109.7, 101.7, 50.0; MS (ESI): 208.10[M+H]$^+$.  

1-(4-Methoxybenzyl)indole (1d): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.69 (d, $J = 7.7$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.25 – 7.18 (m, 2H), 7.12 – 7.06 (m, 2H), 6.90 – 6.82 (m, 1H), 6.58 (d, $J = 3.1$ Hz, 1H), 5.28 (s, 2H), 3.79 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.0, 136.2, 129.4, 128.2, 128.1, 121.6, 120.9, 119.5, 114.1, 113.8, 109.7, 101.5, 55.2, 49.5; MS (ESI): 238.15[M+H]$^+$.  

1-Ethyl-5-methoxyindole (1e): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.23 (s, 1H), 7.10 (d, $J = 2.2$ Hz, 2H), 6.88 (dd, $J = 8.9$, 2.4 Hz, 1H), 6.41 (d, $J = 2.4$ Hz, 1H), 4.15 (q, $J = 7.3$ Hz, 2H), 3.86 (s, 3H), 1.46 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.9, 131.1, 128.9, 127.4, 111.7, 109.9, 102.6, 100.5, 55.8, 41.0, 15.4; MS (ESI): 176.10[M+H]$^+$.  

S20
5-Chloro-1-ethylindole (1f): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 1.7$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.18 – 7.12 (m, 2H), 6.43 (dd, $J = 3.1$, 0.7 Hz, 1H), 4.16 (q, $J = 7.3$ Hz, 2H), 1.46 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.1, 129.6, 128.3, 124.9, 121.6, 120.2, 110.2, 100.7, 41.1, 15.3; MS (ESI): 180.10[M+H]$^+$. 

1-Ethyl-2-methylindole (1h): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 8.3$ Hz, 1H), 7.19 – 7.10 (m, 1H), 7.07 (dd, $J = 10.7$, 4.1 Hz, 1H), 6.24 (s, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.44 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 136.3, 136.0, 128.3, 120.5, 119.8, 119.2, 108.9, 99.9, 37.7, 15.3, 12.6; MS (ESI): 160.15[M+H]$^+$. 

5-Cyano-1-ethylindole (1g): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (s, 1H), 7.43 (dd, $J = 8.6$, 1.4 Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 1H), 7.24 (d, $J = 3.2$ Hz, 1H), 6.58 (d, $J = 3.2$ Hz, 1H), 4.21 (q, $J = 7.3$ Hz, 2H), 1.48 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 137.1, 129.2, 128.2, 126.5, 124.2, 120.8, 110.0, 102.2, 60.3, 41.2, 15.3; MS (ESI): 171.10[M+H]$^+$. 

1-Ethyl-4-methylindole (1i): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 8.2$ Hz, 1H), 7.19 – 7.11 (m, 2H), 6.93 (d, $J = 6.9$ Hz, 1H), 6.53 (dd, $J = 3.1$, 0.7 Hz, 1H), 4.19 (q, $J = 7.3$ Hz, 2H), 2.59 (s, 3H), 1.48 (dd, $J = 9.2$, 5.4 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.5, 130.5, 128.6, 126.5, 121.6, 119.5, 107.0, 99.6, 41.1, 18.9, 15.6; MS (ESI): 180.10[M+H]$^+$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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160.10[M+H]+.

1-Ethyl-7-methylindole (1j): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 7.7$ Hz, 1H), 7.08 (d, $J = 3.1$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 6.9$ Hz, 1H), 6.52 (d, $J = 3.1$ Hz, 1H), 4.42 (q, $J = 7.2$ Hz, 2H), 2.77 (s, 3H), 1.46 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.5, 129.9, 128.7, 124.5, 120.8, 119.6, 119.2, 101.7, 43.5, 19.9, 18.0; MS (ESI): 160.15[M+H]+.

1-Tosylindole (1l): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.3$ Hz, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 3.7$ Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.24 – 7.20 (m, 3H), 6.65 (d, $J = 3.6$ Hz, 1H), 2.33 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.9, 135.2, 134.7, 130.7, 129.8, 126.7, 126.2, 124.5, 123.2, 121.3, 113.4, 109.0, 21.5; MS (ESI): 272.05[M+H]+.

1-tert-Butoxycarbonylindole (1m): $^1$H NMR (300 MHz, DMSO) $\delta$ 8.14 (d, $J = 8.0$ Hz, 1H), 7.59 – 7.54 (m,2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.35 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 1.68 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.7, 135.1, 130.5, 125.8, 124.1, 122.6, 120.8, 115.1, 107.2, 28.1, 27.8; MS (ESI): 218.10[M+H]+.
N,N-Diethylaniline (5b): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J = 8.1$ Hz, 2H), 6.72 – 6.64 (m,3H), 3.37 (q, $J = 7.1$ Hz, 4H), 1.18 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.7, 129.2, 115.2, 111.7, 44.2, 12.5; MS (ESI): 150.15[M+H]$^+$.  

![5c](image)

N-Benzyl-N-methylaniline (5c): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 – 7.30 (m, 2H), 7.27 – 7.22 (m,5H), 6.79 – 7.72 (m, 3H), 4.56 (s, 2H), 3.04 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.7, 139.0, 129.2, 128.6, 126.8, 126.7, 116.5, 112.3, 56.6, 38.5; MS (ESI): 198.15[M+H]$^+$.  

![5d](image)

N-(4-Methoxybenzyl)-N-methylaniline (5d): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26 (t, $J = 7.7$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 8.3$ Hz, 2H), 6.82 – 6.73 (m,3H), 4.51 (s, 2H), 3.82 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.5, 149.7, 130.8, 129.1, 127.9, 116.4, 113.9, 112.4, 56.0, 55.2, 38.3; MS (ESI): 228.15[M+H]$^+$.  

![5e](image)

N-Allyl-N-methylaniline (5e): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.17 (m, 2H), 6.77 – 6.71 (m,3H), 5.92 – 5.83 (m, 1H), 5.23 – 5.15 (m, 2H), 3.96 – 3.94 (m,2H), 2.97 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.4, 133.8, 129.1, 116.4, 116.1, 112.4, 55.2, 38.0; MS (ESI): 148.15[M+H]$^+$.  

![5f](image)
**N,N-Diethyl-3,5-dimethoxyaniline (5f):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.87 (brs, 3H), 3.78 (s, 6H), 3.32 (q, $J = 7.0$ Hz, 4H), 1.16 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.7, 149.5, 91.0, 87.3, 55.0, 44.4, 12.6; MS (ESI): 210.15 [M+H]$^+$.  

![Image of 5f](image)

**N,N-Diethyl-3,5-dimethylaniline (5g):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.33 (brs, 3H), 3.31 (q, $J = 7.1$, 4H), 2.27 (s, 6H), 1.15 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.7, 117.5, 112.0, 109.8, 44.3, 24.3, 12.5; MS (ESI): 178.15[M+H]$^+$.  

![Image of 5g](image)

**N,N-Diethyl-3-methoxyaniline (5h):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.13 (t, $J = 8.5$ Hz, 1H), 6.32 (d, $J = 8.6$ Hz, 1H), 6.24 – 6.20 (m, 2H), 3.80 (s, 3H), 3.34 (q, $J = 7.1$ Hz, 4H), 1.16 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.9, 149.10, 129.8, 105.0, 99.9, 98.3, 55.0, 44.4, 12.6; MS (ESI): 180.15[M+H]$^+$.  

![Image of 5h](image)

**N,N-Diethyl-3-methylaniline (5i):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12 (dd, $J = 9.1$, 7.3 Hz, 1H), 6.53 – 6.47 (m, 3H), 3.35 (q, $J = 7.0$ Hz, 4H), 2.32 (s, 3H), 1.16 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.8, 138.8, 129.1, 116.3, 112.5, 109.0, 44.2, 22.0, 12.6; MS (ESI): 164.15[M+H]$^+$.  

![Image of 5i](image)

**3-Chloro-N,N-diethylaniline (5j):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.10 (t, $J = 8.0$ Hz, 1H),
1H), 6.64 – 6.49 (m, 3H), 3.33 (q, J = 7.1 Hz, 4H), 1.16 (t, J = 7.1 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 148.7, 135.1, 130.1, 114.9, 111.3, 109.7, 44.3, 12.4; MS (ESI): 184.10[M+H]+.

N,N-Diethyl-2,5-dimethoxyaniline (5k): 1H NMR (300 MHz, CDCl3) δ 6.76 (d, J = 8.7 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 6.47 (dd, J = 8.7, 2.9 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.16 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 153.6, 148.0, 140.1, 111.8, 109.0, 105.0, 55.8, 55.4, 45.9, 11.8; MS (ESI): 210.10[M+H]+.

N,N-Diethyl-2-methylaniline (5l): 1H NMR (300 MHz, CDCl3) δ 7.20 – 7.13 (m, 2H), 7.10 – 6.94 (m, 2H), 2.99 (q, J = 7.1 Hz, 4H), 2.31 (s, 3H), 0.99 (t, J = 7.1 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 149.8, 135.3, 130.8, 125.9, 123.1, 122.1, 47.5, 18.3, 12.5; MS (ESI): 164.15[M+H]+.

1-Ethyl-1,2,3,4-tetrahydroquinoline (5n): 1H NMR (300 MHz, CDCl3) δ 7.10 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 6.67 – 6.58 (m, 2H), 3.40 (q, J = 7.0 Hz, 2H), 3.35 – 3.26 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.24 – 1.14 (m, 3H); 13C NMR (75 MHz, CDCl3) δ 144.9, 129.1, 127.0, 122.4, 115.3, 110.4, 48.3, 45.2, 28.2, 22.2, 10.7; MS (ESI): 162.15[M+H]+.
N,N-Dimethylnaphthalen-1-amine (5p): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.29 – 8.22 (m, 1H), 7.83 (dd, $J = 6.6$, 2.8 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 7.3$ Hz, 1H), 2.92 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 150.8, 134.8, 128.8, 128.4, 125.8, 125.7, 125.2, 124.2, 122.9, 113.9, 45.2; MS (ESI): 172.10[M+H]$^+$. 

N,N-Diethyl-4-methylaniline (5p): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.04 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 8.5$ Hz, 2H), 3.32 (q, $J = 7.0$ Hz, 4H), 2.25 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.7, 129.7, 124.7, 112.4, 44.5, 20.1, 12.5; MS (ESI): 164.15[M+H]$^+$. 

References
5. NMR Spectra of unknown Products