Supporting Information

Excited-state Palladium-Catalysed Reductive Alkylation of Imines: Scope and Mechanism

Rajesh Kancherla,†a Krishnamoorthy Muralirajan†a and Magnus Rueping*\textsuperscript{a}

\textsuperscript{a}KAUST Catalysis Center, KCC, King Abdullah University of Science and Technology, KAUST, Thuwal 23955-6900, Saudi Arabia.
† These authors contributed equally to this work.
1. General information

Reagent Information. Unless otherwise stated, all reactions were carried out under argon atmosphere in screw cap reaction tubes. All the reagents and solvents were bought from Sigma Aldrich and Alfa Aesar in a sure-seal bottle and were used as received. Palladium catalysts were obtained from Sigma Aldrich and Strem chemicals. For column chromatography, silica gel (100–200 mesh) from Aldrich was used. A gradient elution using petroleum ether/ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60 F254). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Analytical Information. All isolated compounds are characterized by $^1$H NMR, $^{13}$C NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS), and high-resolution mass spectra (HRMS). Copies of the $^1$H NMR, $^{13}$C NMR can be found in the supporting information. $^1$H NMR spectra were recorded in deuterated solvents either on a Bruker Avance-II 500 (500 and 126 MHz) or 400 (400 and 101 MHz) instrument and are internally referenced to residual protic solvent signals. The $^1$H NMR spectra are reported as $\delta$/ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant $J$/Hz). All $^1$H NMR experiments are reported as follows unless otherwise stated: chemical shift ($\delta$ ppm), integration, multiplicity ($s =$ singlet, $d =$ doublet, $t =$ triplet, $q =$ quartet, $m =$ multiplet, $dd =$ doublet of doublets and $dt =$ doublet of triplets, respectively), and coupling constants (Hz). $^{13}$C NMR spectra were recorded in deuterated solvents on Bruker Avance-II spectrometers at 101 or 126 MHz, with the central peak of the deuterated solvent as the internal standard. Chemical shifts ($\delta$) are given in parts per million (ppm), and coupling constants ($J$) are given in Hertz (Hz) rounded to the nearest 0.1 Hz. The $^{13}$C NMR spectra are reported as $\delta$/ppm and were obtained with $^1$H decoupling (note: CDCl$_3$ referenced at $\delta$ 7.26 ppm for $^1$H NMR, 77.16 ppm for $^{13}$C NMR). All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple-axis detector). High-resolution mass spectra (HRMS) analysis was performed using Bruker micro Time-of-Flight (TOF)-MS equipped with an ESI source. Luminescence intensities were recorded using a fluoromax-4 spectrophotometer from Horiba Scientific. Linear absorption spectra were collected on an Agilent 8453 Spectrophotometer.

All reaction mixtures were irradiated with 34 W Kessil KSH150B blue light from a 4 cm distance. The emission maximum of the light source used is 425 nm. Regular fans are employed to maintain the temperature at room temperature ($32 \pm 2 ^\circ$C).
2. Optimization details for reductive alkylation of imines:

![Chemical diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent variation[a]</th>
<th>Yield 3f, (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>CH₂CN</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>2</td>
</tr>
</tbody>
</table>

[a]Reaction condition: Imine (0.1 mmol), bromocyclohexane (0.2 mmol), solvent (1 mL), 34 W blue LEDs, Ar, 24 h, room temperature (T = 32 ± 2 °C). [b]Yields determined by GC-FID analysis using internal standard.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base variation</th>
<th>Yield 3f, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs₂CO₃</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>CsOAc</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>K₃PO₄</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>K₂PO₄</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>Na₂CO₃</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>TEA</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>KOAc</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>K₂HPO₄</td>
<td>15</td>
</tr>
<tr>
<td>Entry</td>
<td>Miscellaneous variation</td>
<td>Yield 3f, (%)</td>
</tr>
<tr>
<td>-------</td>
<td>-------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>1</td>
<td>Cs₂CO₃ (2 equiv)</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>Cs₂CO₃ (3 equiv)</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>DMSO (0.5 mL)</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>DMSO (1 mL)</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>DMSO (1.5 mL)</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>Pd(PPh₃)₄ (5 mol%)</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Pd(PPh₃)₄ (10 mol%)</td>
<td>53</td>
</tr>
<tr>
<td>8</td>
<td>Pd(PPh₃)₄ (15 mol%)</td>
<td>81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Entry</th>
<th>PPh₃ loading</th>
<th>Yield 3f, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 mol%</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>10 mol%</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>15 mol%</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>20 mol%</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>25 mol%</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>30 mol%</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>35 mol%</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>40 mol%</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>45 mol%</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>50 mol%</td>
<td>80</td>
</tr>
</tbody>
</table>
3. General procedure for the synthesis of compounds 3a-r, and 4a-x

A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir–bar was charged with imine (0.2 mmol), Pd(OAc)$_2$ (10 mol%, 0.02 mmol, 4.5 mg), PPh$_3$ (100 mol%, 0.2 mmol, 52.5 mg), Cs$_2$CO$_3$ (2 equiv, 0.4 mmol, 130 mg, added inside glove box), and alkyl bromide (2 equiv., 0.4 mmol), capped with Teflon septum and parafilm. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate yellow color which is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography using silica gel (100-200 mesh size) and hexane or EtOAc/petether as the eluent. Note that although in case of bromocyclohexane an yield of 85% (3f) was obtained in 24 h, we still see that some amount of imine remains. In case of majority of alkyl bromides, most of
the imine were found unreacted in 24 h, and so we have chosen to extend the reaction time to 48 h for performing the scope.

*N*-adamantan-1-yl(phenyl)methyl)aniline (3a): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromoadamantane (86 mg, 0.4 mmol). Pure product was obtained as white solid in 82% (52 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

**1H NMR (400 MHz, CDCl₃)** δ 7.34 – 7.21 (m, 5H), 7.07 (t, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 7.1 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.38 (s, 1H), 3.92 (s, 1H), 2.03 (s, 3H), 1.76 (t, *J* = 11.8 Hz, 6H), 1.63 (d, *J* = 12.3 Hz, 3H), 1.54 (d, *J* = 12.1 Hz, 3H). **13C NMR (101 MHz, CDCl₃)** δ 148.01, 140.37, 129.12, 128.79, 127.71, 126.85, 116.88, 113.23, 68.08, 39.40, 37.07, 36.62, 28.57. **HRMS (ESI-TOF) m/z** calcd. for C₂₃H₂₇N (M+Na)⁺ 340.2041, found 340.2055. **GCMS (EI) m/z** calcd. for C₂₃H₂₇N [M⁺] 317.2, found 317.2, 182.1, 135.1, 104.0, 77.0.

*N*-3,5-dimethyladamantan-1-yl(phenyl)methyl)aniline (3b): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3,5-dimethyladamantane (79.5 µL, 0.4 mmol). Pure product was obtained as yellow oil in 75% (52 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

**1H NMR (500 MHz, CDCl₃)** δ 7.29 – 7.19 (m, 5H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 1H), 3.92 (s, 1H), 2.07 (p, *J* = 3.2 Hz, 1H), 1.55 – 1.52 (m, 2H), 1.37 – 1.24 (m, 6H), 1.16 – 1.04 (m, 4H), 0.81 (s, 6H). **13C NMR (101 MHz, CDCl₃)** δ 147.91, 140.41, 129.13, 128.78, 127.75, 126.84, 116.91, 113.21, 67.56, 51.17, 45.84, 45.49, 43.28, 38.51, 38.05, 31.30, 30.83, 29.56. **HRMS (ESI-TOF) m/z** calcd. for C₂₅H₃₁N (M+Na)⁺ 368.2354, found 368.2359. **GCMS (EI) m/z** calcd. for C₂₅H₃₁N [M⁺] 345.2, found 345.2, 182.1, 163.2, 121.1, 104.1, 91.1.

*N*-(cyclopropyl(phenyl)methyl)aniline (3c): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclopropane (32
µL, 0.4 mmol) for 72 h. Pure product was obtained as yellow oil in 51% (22.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

**1H NMR (400 MHz, CDCl₃)** δ 7.41 (d, J = 7.0 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.08 (t, J = 8 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.5 Hz, 2H), 4.39 (s, 1H), 3.67 (d, J = 8.3 Hz, 1H), 1.24 – 1.15 (m, 1H), 0.67 – 0.53 (m, 2H), 0.49 (dq, J = 9.9, 4.9 Hz, 1H), 0.39 (dq, J = 9.5, 4.9 Hz, 1H). **13C NMR (101 MHz, CDCl₃)** δ 147.73, 143.41, 129.15, 128.64, 127.14, 126.57, 117.35, 113.50, 63.05, 19.85, 4.31, 3.64.

**GCMS (EI) m/z** calcd. for C₁₆H₁₇N [M⁺] 223.1, found 223.1, 182.1, 131.1, 116.0, 91.0, 77.0. The analytical data correspond with those reported in the literature.

**N-(oxetan-3-yl(phenyl)methyl)aniline (3d):** The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 3-bromooxetane (33.2 µL, 0.4 mmol) for 72 h. Pure product was obtained as white solid in 70% (33.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 30% EtOAc/Pet.ether).

**1H NMR (400 MHz, CDCl₃)** δ 7.36 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 7.11 (t, J = 7.6 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8 Hz, 2H), 4.85 (t, J = 6.8 Hz, 2H), 4.71 (d, J = 8.9 Hz, 1H), 4.69 – 4.62 (m, 2H), 4.55 (t, J = 6.2 Hz, 1H), 4.24 (s, 1H), 4.23 (d, J = 8.4 Hz, 1H), 2.20 (q, J = 8.3, 7.6 Hz, 1H), 1.93 (dtd, J = 11.8, 7.5, 4.1 Hz, 1H), 1.78 – 1.41 (m, 6H), 1.40 – 1.26 (m, 1H). **13C NMR (101 MHz, CDCl₃)** δ 147.08, 141.28, 129.29, 128.95, 127.68, 126.51, 117.93, 113.74, 74.96, 74.22, 60.63, 41.95. **HRMS (ESI-TOF) m/z** calcd. for C₁₆H₁₇NO (M⁺Na)⁺ 262.1202, found 262.1179. **GCMS (EI) m/z** calcd. for C₁₆H₁₇NO [M⁺] 239.1, found 239.1, 182.1, 117.1, 104.0, 91.0, 77.0.

**N-(cyclopentyl(phenyl)methyl)aniline (3e):** The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclopentane (43 µL, 0.4 mmol). Pure product was obtained as yellow oil in 75% (37.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

**1H NMR (400 MHz, CDCl₃)** δ 7.42 – 7.30 (m, 4H), 7.24 (t, J = 7.1 Hz, 1H), 7.10 (t, J = 7.2 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.5 Hz, 2H), 4.23 (s, 1H), 4.12 (d, J = 8.4 Hz, 1H), 2.20 (q, J = 8.3, 7.6 Hz, 1H), 1.93 (dtd, J = 11.8, 7.5, 4.1 Hz, 1H), 1.78 – 1.41 (m, 6H), 1.40 – 1.26 (m, 1H). **13C NMR (101 MHz, CDCl₃)** δ 147.74, 144.04, 129.13, 128.40, 127.68, 126.51, 117.93, 113.74, 74.96, 74.22, 60.63, 41.95. **HRMS (ESI-TOF) m/z** calcd. for C₁₈H₂₁N [M⁺] 251.1, found 251.2, 182.1, 117.1, 104.0, 91.1, 77.0. The analytical data correspond with those reported in the literature.
**N-(cyclohexyl(phenyl)methyl)aniline (3f):** The title compound was prepared according to the general procedure from \(N\)-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclohexane (49.3 \(\mu\)L, 0.4 mmol). Pure product was obtained as yellow oil in 85% (45 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\delta 7.35 – 7.30 (m, 4H), 7.28 – 7.19 (m, 1H), 7.12 – 7.07 (m, 2H), 6.64 (t, \(J = 7.3\) Hz, 1H), 6.54 (d, \(J = 7.4\) Hz, 2H), 4.17 (s, 1H), 4.15 (d, \(J = 6.3\) Hz, 1H), 1.93 (d, \(J = 11.9\) Hz, 1H), 1.86 – 1.65 (m, 4H), 1.58 (m, 1H), 1.33 – 1.01 (m, 5H). \]

**\(^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}\delta 147.88, 142.76, 129.15, 128.29, 127.34, 126.84, 117.03, 113.27, 63.51, 45.02, 30.36, 29.58, 26.55, 26.51, 26.48. GCMS (EI) m/z calcd. for C\(_{19}\)H\(_{23}\)N [M\(^+\)] 265.1, found 265.1, 183.1, 181.9, 104.0, 91.0, 77.0.**

The analytical data correspond with those reported in the literature.

**N-(cycloheptyl(phenyl)methyl)aniline (3g):** The title compound was prepared according to the general procedure from \(N\)-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocycloheptane (55 \(\mu\)L, 0.4 mmol). Pure product was obtained as yellow oil in 82% (45.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\delta 7.37 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 7.09 (t, \(J = 7.7\) Hz, 2H), 6.63 (t, \(J = 7.3\) Hz, 1H), 6.51 (d, \(J = 8.0\) Hz, 2H), 4.26 (d, \(J = 5.4\) Hz, 1H), 4.12 (s, 1H), 1.96 – 1.88 (m, 1H), 1.85 – 1.65 (m, 4H), 1.65 – 1.27 (m, 8H). \]

**\(^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}\delta 147.96, 142.76, 129.15, 128.29, 127.34, 126.84, 117.03, 113.27, 63.82, 46.51, 32.37, 29.51, 28.40, 28.14, 27.11, 27.10. HRMS (ESI-TOF) m/z calcd. for C\(_{20}\)H\(_{25}\)N (M+Na\(^+\)) 302.1879, found 302.1862. GCMS (EI) m/z calcd. for C\(_{20}\)H\(_{25}\)N [M\(^+\)] 279.2, found 279.1, 182.1, 104.1, 91.1, 77.1, 55.1.**

**Tert-butyl 3-(phenyl(phenylamino)methyl)pyrrolidine-1-carboxylate (3h):** The title compound was prepared according to the general procedure from \(N\)-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-Boc-3-bromopyrrolidine (100 mg, 0.4 mmol). Pure product was obtained as yellow oil in 85% (59.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).
**Tert-butyl 4-(phenyl(phenylamino)methyl)piperidine-1-carboxylate (3i):** The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-Boc-4-bromopiperidine (105.6 mg, 0.4 mmol). Pure product was obtained as yellow solid in 82% (60 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 7.35 – 7.19 (m, 5H), 7.08 (t, J = 7.3 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.9 Hz, 2H), 4.11 – 4.17 (m, 4H), 2.75 – 2.50 (m, 2H), 1.98 – 1.70 (m, 2H), 1.46 (s, 10H), 1.35 – 1.20 (m, 2H). **13C NMR (126 MHz, CDCl3)** δ 155.25, 147.38, 141.77, 136.92, 129.21, 128.58, 128.07, 127.96, 127.29, 127.17, 117.51, 113.48, 67.14, 62.73, 44.25, 44.15, 43.26, 29.33, 28.79. **HRMS (ESI-TOF) m/z** calcd. for C23H30N2O2 (M+Na)+ 389.2205, found 389.2258. **GCMS (EI) m/z** calcd. for C23H30N2O2 [M+] 366.2, found 366.1, 266.1, 207.1, 182.1, 104.0, 77.0, 57.0.

**Benzy1 4-(phenyl(phenylamino)methyl)piperidine-1-carboxylate (3j):** The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 4-bromo-N-Z-piperidine (119.2 mg, 0.4 mmol). Pure product was obtained as yellow oil in 78% (62.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 20% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 7.48 – 7.20 (m, 10H), 7.09 (t, J = 7.7 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.9 Hz, 2H), 5.14 (s, 2H), 4.45 – 3.95 (m, 4H), 2.72 (bs, 2H), 1.99 – 1.75 (m, 2H), 1.54 – 1.18 (m, 3H). **13C NMR (126 MHz, CDCl3)** δ 155.25, 147.38, 141.77, 136.92, 129.21, 128.58, 128.07, 127.96, 127.29, 127.17, 117.51, 113.48, 67.14, 62.73, 44.25, 44.15, 43.26, 29.33, 28.79. **HRMS (ESI-TOF) m/z** calcd. for C26H28N2O2 (M+Na)+ 423.2048, found 423.2073. **GCMS (EI) m/z** calcd. for C26H28N2O2 [M+] 400.2, found 400.2, 182.1, 104.0, 91.0, 77.0, 65.0.
N-(phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (3k): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 4-bromotetrahydropyran (45 µL, 0.4 mmol). Pure product was obtained as yellow solid in 93% (49.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 12% EtOAc/Pet.ether).

\[ \text{H NMR (400 MHz, CDCl}_3\] \delta 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 7.10 (t, \text{J = 8 Hz, 2H}), 6.65 (t, \text{J = 7.3 Hz, 1H}), 6.54 (d, \text{J = 7.6 Hz, 2H}), 4.15 (d, \text{J = 6.8 Hz, 2H}), 4.04 (dd, \text{J = 11.4, 3.6 Hz, 1H}), 3.35 (dtd, \text{J = 19.8, 11.8, 2.3 Hz, 2H}), 1.95 – 1.78 (m, 2H), 1.49 (dtd, \text{J = 23.5, 11.9, 4.5 Hz, 2H}), 1.39 – 1.26 (m, 1H).

\[ \text{C NMR (101 MHz, CDCl}_3\] \delta 147.52, 141.93, 129.21, 128.53, 127.20, 117.40, 113.40, 68.11, 67.99, 63.04, 42.36, 30.38, 29.89, 28.90.

\[ \text{HRMS (ESI-TOF) m/z calcd. for C}_{18}\text{H}_{21}\text{NO} (M+Na}^+ \] 290.1521, found 290.1520.

\[ \text{GCMS (EI) m/z calcd. for C}_{18}\text{H}_{21}\text{NO [M}^+ \] 267.1, found 267.1, 182.1, 117.1, 104.0, 91.1, 77.1.

N-(2-methyl-1-phenylbutyl)aniline (3l): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 2-bromobutane (43.7 µL, 0.4 mmol). Pure product was obtained as yellow oil in 73% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

\[ \text{H NMR (400 MHz, CDCl}_3\] \delta 7.37 – 7.29 (m, 8H), 7.27 – 7.21 (m, 2H), 7.13 – 7.07 (m, 4H), 6.65 (tdd, \text{J = 7.3, 2.5, 1.2 Hz, 2H}), 6.53 (d, \text{J = 7.9 Hz, 4H}), 4.35 (d, \text{J = 4.8 Hz, 1H}), 4.25 (d, \text{J = 5.8 Hz, 1H}), 4.13 (s, 2H), 1.89 – 1.78 (m, 2H), 1.71 – 1.47 (m, 2H), 1.35 – 1.14 (m, 2H), 1.01 – 0.88 (m, 12H).

\[ \text{C NMR (101 MHz, CDCl}_3\] \delta 147.85, 141.93, 129.21, 128.53, 127.20, 117.40, 113.40, 68.11, 67.99, 63.04, 42.36, 30.38, 29.89, 28.90.

\[ \text{GCMS (EI) m/z calcd. for C}_{17}\text{H}_{21}\text{N [M}^+ \] 239.1, found 239.1, 182.1, 104.0, 91.0, 77.0. The analytical data correspond with those reported in the literature.\(^3\)

N-(((1R,2R,4S)-bicyclo[2.2.1]heptan-2-yl)(phenyl)methyl)aniline (3m): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol)
and exo-2-bromonorbornane (51.4 µL, 0.4 mmol). Pure product was obtained as brown oil in 83% (46 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

\[1^H \text{NMR (400 MHz, CDCl}_3\text{)} \delta 7.42 – 7.28 (m, 8H), 7.28 – 7.19 (m, 2H), 7.14 – 7.04 (m, 4H), 6.63 (m, 2H), 6.54 (m, 4H), 4.24 – 4.07 (m, 2H), 3.90 (d, J = 10.3 Hz, 1H), 3.84 (d, J = 10.1 Hz, 1H), 2.51 (d, J = 4.2 Hz, 1H), 2.34 (d, J = 4.3 Hz, 1H), 2.24 (t, J = 4.3 Hz, 1H), 1.89 (d, J = 4.2 Hz, 1H), 1.81 (td, J = 9.3, 5.5 Hz, 1H), 1.74 – 1.37 (m, 8H), 1.35 – 0.98 (m, 9H).

\[1^C \text{NMR (101 MHz, CDCl}_3\text{)} \delta 148.02, 147.73, 144.37, 142.91, 129.16, 129.11, 128.47, 128.36, 127.73, 127.30, 126.99, 126.96, 117.14, 117.05, 113.34, 113.25, 63.90, 62.47, 50.60, 49.89, 39.25, 38.60, 37.15, 36.74, 36.71, 36.14, 35.70, 35.28, 30.44, 30.22, 28.98, 28.75.

HRMS (ESI-TOF) m/z calcd. for C\text{20}H\text{23}N (M+Na)^+ 300.1723, found 300.1721.

GCMS (EI) m/z calcd. for C\text{20}H\text{23}N [M^+] 277.1, found 277.1, 182.1, 117.0, 104.0, 91.0, 77.0.

\[1^H \text{NMR (400 MHz, CDCl}_3\text{)} \delta 7.38 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 7.8 Hz, 2H), 6.66 – 6.58 (m, 3H), 4.59 (d, J = 10.7 Hz, 1H), 4.09 (s, 1H), 2.34 (s, 1H), 2.11 – 1.98 (m, 1H), 1.95 – 1.72 (m, 1H), 1.65 – 1.51 (m, 1H), 1.34 (s, 1H).

\[1^C \text{NMR (101 MHz, CDCl}_3\text{)} \delta 147.89, 143.65, 129.16, 128.48, 127.15, 126.92, 116.92, 113.18, 58.30, 51.67, 39.21, 39.19, 38.22, 32.23, 32.03, 29.17, 28.83, 28.11, 27.86. HRMS (ESI-TOF) m/z calcd. for C\text{23}H\text{27}N (M+Na)^+ 340.2041, found 340.2061.

GCMS (EI) m/z calcd. for C\text{23}H\text{27}N [M^+] 317.2, found 317.2, 182.1, 167.1, 152.1, 128.1, 104.0.

\[1^H \text{NMR (400 MHz, CDCl}_3\text{)} \delta 7.38 – 7.32 (m, 4H), 7.27 – 7.22 (m, 1H), 7.10 (t, J = 7.8 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 4.29 (td, J = 7.1, 6.6, 1.9 Hz, 1H), 4.08 (s, 1H),

\[N\text-(((1r,3r,5r,7r)adamantan-2-yl)(phenyl)methyl)aniline (3n): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 2-bromoadamantane (86 mg, 0.4 mmol). Pure product was obtained as white solid in 62% (39.3 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

\[1^H \text{NMR (400 MHz, CDCl}_3\text{)} \delta 7.38 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 7.8 Hz, 2H), 6.66 – 6.58 (m, 3H), 4.59 (d, J = 10.7 Hz, 1H), 4.09 (s, 1H), 2.34 (s, 1H), 2.11 – 1.98 (m, 1H), 1.95 – 1.72 (m, 1H), 1.65 – 1.51 (m, 1H), 1.34 (s, 1H).

\[1^C \text{NMR (101 MHz, CDCl}_3\text{)} \delta 147.89, 143.65, 129.16, 128.48, 127.15, 126.92, 116.92, 113.18, 58.30, 51.67, 39.21, 39.19, 38.22, 32.23, 32.03, 29.17, 28.83, 28.11, 27.86. HRMS (ESI-TOF) m/z calcd. for C\text{23}H\text{27}N (M+Na)^+ 340.2041, found 340.2061.

GCMS (EI) m/z calcd. for C\text{23}H\text{27}N [M^+] 317.2, found 317.2, 182.1, 167.1, 152.1, 128.1, 104.0.

\[N\text-(4,8-dimethyl-1-phenylnonyl)aniline (3o): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3,7-dimethyloctane (83 µL, 0.4 mmol). Pure product was obtained as yellow oil in 42% (27 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

\[1^H \text{NMR (400 MHz, CDCl}_3\text{)} \delta 7.38 – 7.32 (m, 4H), 7.27 – 7.22 (m, 1H), 7.10 (t, J = 7.8 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 4.29 (td, J = 7.1, 6.6, 1.9 Hz, 1H), 4.08 (s, 1H),

S11
1.90 – 1.72 (m, 2H), 1.60 – 1.07 (m, 10H), 0.87 – 0.90 (m, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.64, 144.56, 144.46, 129.21, 128.65, 126.98, 126.96, 126.53, 126.47, 117.23, 113.35, 58.78, 58.73, 39.40, 37.24, 37.13, 36.68, 36.57, 33.77, 33.69, 32.88, 32.85, 28.08, 24.84, 22.84, 22.74, 19.79, 19.73. d.r. (1:1). HRMS (ESI-TOF) m/z calcd. for C$_{23}$H$_{33}$N (M+Na)$^+$ 346.2511, found 346.2539. GCMS (EI) m/z calcd. for C$_{23}$H$_{33}$N [M$^+$] 323.2, found 323.2, 280.1, 194.1, 182.1, 167.0, 152.0, 117.0.

N-(7-chloro-1-phenyleptyl)aniline (3p): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-6-chlorohexane (59.7 μL, 0.4 mmol). Pure product was obtained as yellow oil in 35% (21 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.31 (m, 4H), 7.26 – 7.22 (m, 1H), 7.10 (t, $J = 7.7$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 2H), 4.32 (t, $J = 6.8$ Hz, 1H), 4.16 – 4.07 (m, 1H), 3.53 (t, $J = 6.7$ Hz, 2H), 1.87 – 1.72 (m, 4H), 1.48 – 1.33 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.54, 144.28, 129.21, 128.67, 126.48, 117.28, 113.34, 58.28, 45.17, 38.91, 32.61, 28.87, 26.83, 26.29. HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{24}$ClN (M+Na)$^+$ 324.1495, found 324.1520. GCMS (EI) m/z calcd. for C$_{19}$H$_{24}$ClN [M$^+$] 301.1, found 301.1, 194.1, 182.1, 167.1, 152.1, 128.1, 117.1.

Methyl 6-phenyl-6-(phenylamino)hexanoate (3q): The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and methyl 5-bromopentanoate (57.2 μL, 0.4 mmol). Pure product was obtained as yellow oil in 44% (26 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 14% EtOAc/hexane).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 7.09 (t, $J = 8.0$ Hz, 2H), 6.64 (td, $J = 7.3$, 1.2 Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 1H), 4.09 (s, 1H), 3.66 (s, 3H), 2.31 (t, $J = 7.5$ Hz, 2H), 1.88 – 1.76 (m, 2H), 1.67 (p, $J = 7.6$ Hz, 2H), 1.52 – 1.32 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.07, 147.46, 144.10, 129.20, 128.69, 127.06, 126.46, 117.31, 113.35, 58.12, 51.63, 38.61, 33.97, 25.98, 24.89. GCMS (EI) m/z calcd. for C$_{19}$H$_{24}$NO$_2$ [M$^+$] 297.1, found 297.1, 266.1, 194.1, 182.1, 167.1, 129.1, 117.1. The analytical data correspond with those reported in the literature. 4
**N-(1,4-diphenylbutyl)aniline (3r):** The title compound was prepared according to the general procedure from \( N \)-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (60.8 \( \mu \)L, 0.4 mmol). Pure product was obtained as yellow oil in 50% (30 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/hexane).

\textbf{\( ^1H \text{ NMR (500 MHz, CDCl}_3 \)} \( \delta \) 7.40 – 7.30 (m, 6H), 7.28 – 7.17 (m, 4H), 7.12 (t, \( J = 7.7 \) Hz, 2H), 6.67 (t, \( J = 7.3 \) Hz, 1H), 6.54 (d, \( J = 8.0 \) Hz, 2H), 4.36 (t, \( J = 6.6 \) Hz, 1H), 4.06 (s, 1H), 2.67 (td, \( J = 7.4, 2.8 \) Hz, 2H), 1.93 – 1.66 (m, 4H). \( ^{13}C \text{ NMR (126 MHz, CDCl}_3 \)} \( \delta \) 147.49, 144.13, 142.06, 129.20, 128.68, 128.52, 128.47, 127.04, 126.50, 125.98, 117.29, 113.34, 58.23, 38.41, 35.76, 28.13. \textbf{GCMS (EI)} \( m/\text{z} \) calcd. for C\(_{22}\)H\(_{23}\)N [M\(^+\)] 301.1, found 301.1, 208.1, 194.1, 182.1, 167.1, 152.1, 131.1. The analytical data correspond with those reported in the literature.\(^2\)

**N-(cyclohexyl(o-tolyl)methyl)aniline (4a):** The title compound was prepared according to the general procedure from \( N \)-phenyl-1-(o-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 \( \mu \)L, 0.4 mmol). Pure product was obtained as white solid in 70% (39 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

\textbf{\( ^1H \text{ NMR (500 MHz, CDCl}_3 \)} \( \delta \) 7.29 (d, \( J = 6.7 \) Hz, 1H), 7.17 – 7.05 (m, 5H), 6.61 (t, \( J = 7.0 \) Hz, 1H), 6.46 (d, \( J = 8.0 \) Hz, 2H), 4.39 (d, \( J = 6.1 \) Hz, 1H), 4.13 (s, 1H), 2.46 (s, 3H), 1.93 (d, \( J = 12.1 \) Hz, 1H), 1.81 – 1.54 (m, 5H), 1.29 – 1.08 (m, 5H). \( ^{13}C \text{ NMR (126 MHz, CDCl}_3 \)} \( \delta \) 148.02, 141.05, 135.33, 130.61, 129.22, 126.48, 126.45, 126.15, 116.97, 113.02, 59.30, 44.40, 30.81, 28.85, 26.73, 26.62, 26.61, 19.72. \textbf{HRMS (ESI-TOF)} \( m/\text{z} \) calcd. for C\(_{20}\)H\(_{25}\)N [M\(^+\)+Na\(^+\)] 302.1885, found 302.1908. \textbf{GCMS (EI)} \( m/\text{z} \) calcd. for C\(_{20}\)H\(_{25}\)N [M\(^+\)] 279.2, found 279.2, 196.2, 180.1, 104.1, 91.1, 77.1.

**N-(cyclohexyl(2-methoxyphenyl)methyl)aniline (4b):** The title compound was prepared according to the general procedure from 1-(2-methoxyphenyl)-\( N \)-phenylmethanimine (42.2 mg, 0.2 mmol) and bromocyclohexane (49.3 \( \mu \)L, 0.4 mmol). Pure product was obtained as white solid...
in 72% (42.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl₃)** δ 7.22 – 7.16 (m, 2H), 7.06 (t, J = 8 Hz, 2H), 6.89 – 6.86 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 7.4 Hz, 2H), 4.53 (d, J = 7.3 Hz, 1H), 4.29 (s, 1H), 3.89 (s, 3H), 2.00 (d, J = 12.6 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.46 (d, J = 12.0 Hz, 1H), 1.27 – 1.03 (m, 5H). **13C NMR (126 MHz, CDCl₃)** δ 157.43, 148.22, 130.87, 129.14, 128.25, 127.64, 120.56, 116.70, 113.12, 110.60, 57.83, 55.50, 43.45, 30.49, 29.84, 26.68, 26.56, 26.51. **HRMS (ESI-TOF) m/z** calcd. for C₂₀H₂₅NO (M+Na)⁺ 318.1834, found 318.1861. **GCMS (EI) m/z** calcd. for C₂₀H₂₅NO [M⁺] 295.1, found 295.2, 212.1, 196.1, 180.1, 121.1, 115.1, 104.1, 91.1, 77.1.

**N-(cyclohexyl(2-fluorophenyl)methyl)aniline (4c):** The title compound was prepared according to the general procedure from 1-(2-fluorophenyl)-N-phenylmethanimine (39.8 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as white solid in 77% (43.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl₃)** δ 7.29 – 7.24 (m, 1H), 7.10 – 7.06 (m, 3H), 7.02 (d, J = 10.0 Hz, 1H), 6.91 (td, J = 8.4, 2.6 Hz, 1H), 6.64 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 8.0 Hz, 2H), 4.14 (s, 1H), 4.12 (d, J = 6.1 Hz, 1H), 1.88 (d, J = 12.8 Hz, 1H), 1.81 – 1.72 (m, 2H), 1.68 – 1.61 (m, 2H), 1.55 (d, J = 13.0 Hz, 1H), 1.29 – 1.02 (m, 5H). **13C NMR (126 MHz, CDCl₃)** δ 163.16 (d, J = 245.6 Hz), 147.60, 145.87 (d, J = 6.1 Hz), 129.73 (d, J = 8.2 Hz), 129.23, 123.05 (d, J = 2.8 Hz), 117.35, 114.10 (d, J = 21.3 Hz), 113.80 (d, J = 21.3 Hz), 113.27, 63.21, 44.94, 30.32, 29.47, 26.49, 26.45, 26.43. **19F NMR (471 MHz, CDCl₃)** δ -113.43. **HRMS (ESI-TOF) m/z** calcd. for C₁₉H₂₃FN (M+Na)⁺ 306.1628, found 306.1608. **GCMS (EI) m/z** calcd. for C₁₉H₂₃FN [M⁺] 283.1, found 283.1, 200.2, 185.1, 180.1, 170.1, 152.1, 146.1, 133.1.

**N-(cyclohexyl(3-methoxyphenyl)methyl)aniline (4d):** The title compound was prepared according to the general procedure from 1-(3-methoxyphenyl)-N-phenylmethanimine (42.2 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 78% (46 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl₃)** δ 7.22 (t, J = 7.9 Hz, 1H), 7.07 (t, J = 7.9 Hz, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.76 (dd, J = 8.2, 2.6 Hz, 1H), 6.61 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.4 Hz,
N-(cyclohexyl(p-tolyl)methyl)aniline (4e): The title compound was prepared according to the general procedure from N-phenyl-1-(p-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 μL, 0.4 mmol). Pure product was obtained as yellow oil in 69% (38.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.19 (d, $J = 7.9$ Hz, 2H), 7.09 (dd, $J = 20.0, 7.8$ Hz, 4H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.15 (s, 1H), 4.11 (d, $J = 6.3$ Hz, 1H), 2.33 (s, 3H), 1.94 – 1.89 (m, 1H), 1.80 – 1.55 (m, 5H), 1.29 – 1.01 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.98, 139.69, 136.29, 129.15, 129.01, 127.23, 116.94, 113.27, 63.21, 45.04, 30.35, 29.62, 26.57, 26.53, 26.49, 21.21. GCMS (EI) m/z calcd. for C$_{20}$H$_{25}$N [M$^+$] 279.2, found 279.1, 196.1, 180.1, 165.1, 152.1, 128.1. The analytical data correspond with those reported in the literature.\(^5\)

N-(cyclohexyl(4-fluorophenyl)methyl)aniline (4f): The title compound was prepared according to the general procedure from 1-(4-fluorophenyl)-N-phenylmethanimine (39.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μL, 0.4 mmol). Pure product was obtained as yellow oil in 67% (38 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.23 (m, 2H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.99 (t, $J = 8.7$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.13 (s, 1H), 4.11 (d, $J = 6.2$ Hz, 1H), 1.88 (d, $J = 12.5$ Hz, 1H), 1.81 – 1.59 (m, 4H), 1.54 (d, $J = 13.4$ Hz, 1H), 1.26 – 0.99 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.86 (d, $J = 244.3$ Hz), 147.68, 138.37 (d, $J = 3.2$ Hz), 129.20, 128.71 (d, $J = 7.9$ Hz), 117.25, 115.15 (d, $J = 21.3$ Hz), 113.30, 62.91, 45.08, 30.23, 29.56, 26.52, 26.47, 26.43. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -116.41. GCMS (EI) m/z calcd. for C$_{19}$H$_{22}$FN [M$^+$] 283.1, found 283.1, 200.2, 185.1, 170.1, 152.1, 146.1, 133.1. The analytical data correspond with those reported in the literature.\(^6\)
Methyl 4-(cyclohexyl(phenylamino)methyl)benzoate (4g): The title compound was prepared according to the general procedure from methyl-4-((phenylimino)methyl)benzoate (47.8 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow solid in 94% (60.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.07 (t, $J = 7.9$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 8.7$ Hz, 2H), 4.20 (s, 1H), 4.18 (s, 1H), 3.90 (s, 3H), 1.87 (d, $J = 11.8$ Hz, 1H), 1.79 – 1.64 (m, 4H), 1.54 (d, $J = 13.9$ Hz, 1H), 1.26 – 1.02 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.14, 148.47, 147.49, 129.70, 129.19, 128.90, 127.38, 117.37, 113.26, 63.40, 52.10, 44.88, 30.28, 29.44, 26.44, 26.42, 26.39. GCMS (EI) m/z calcd. for C$_{21}$H$_{25}$NO$_2$ [M$^+$] 323.1, found 323.2, 292.1, 240.2, 209.1, 181.1, 149.1, 141.1. The analytical data correspond with those reported in the literature.

N-(cyclohexyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)aniline (4h): The title compound was prepared according to the general procedure from N-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanimine (61.4 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow solid in 74% (58 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 8% EtOAc/Pet.ether).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 7.7$ Hz, 2H), 7.03 (t, $J = 7.1$ Hz, 2H), 6.59 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.17 (s, 1H), 4.13 (d, $J = 6.2$ Hz, 1H), 1.87 (d, $J = 11.6$ Hz, 1H), 1.80 – 1.47 (m, 5H), 1.33 (s, 12H), 1.24 – 0.98 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.80, 146.24, 134.83, 129.16, 126.83, 117.10, 113.31, 83.81, 63.64, 44.98, 30.35, 29.54, 26.52, 26.47, 25.06, 24.99. The carbon directly attached to boron atoms is not detected due to quadrupolar broadening. HRMS (ESI-TOF) m/z calcd. for C$_{25}$H$_{34}$BNO$_2$ (M+Na)$^+$ 414.2580, found 414.2588. GCMS (EI) m/z calcd. for C$_{25}$H$_{34}$BNO$_2$ [M$^+$] 391.2, found 391.3, 308.2, 208.1, 146.6, 104.1, 77.1.
N-(cyclohexyl(pyridin-3-yl)methyl)aniline (4i): The title compound was prepared according to the general procedure from N-phenyl-1-(pyridin-3-yl)methanimine (37.6 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as white solid in 42% (22.3 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 37% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58 (s, 1H), 8.48 (d, $J = 6.4$ Hz, 1H), 7.61 (dt, $J = 7.9$, 2.0 Hz, 1H), 7.21 (dd, $J = 7.8$, 4.8 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.64 (t, $J = 7.4$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.18 (bs, 2H), 1.89 (d, $J = 12.7$ Hz, 1H), 1.80 – 1.65 (m, 4H), 1.56 (d, $J = 12.8$ Hz, 1H), 1.27 – 1.00 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 149.46, 148.46, 147.26, 138.08, 134.75, 129.25, 123.43, 117.54, 113.28, 61.28, 44.79, 30.06, 29.45, 26.38, 26.32, 26.28. HRMS (ESI-TOF) m/z calcd. for C$_{18}$H$_{22}$N$_2$ (M+Na)$^+$ 289.1675, found 289.1667. GCMS (EI) m/z calcd. for C$_{18}$H$_{22}$N$_2$ [M$^+$] 266.1, found 266.1, 207.1, 183.2, 174.1, 166.1, 154.1, 130.1.

N-(cyclohexyl(thiophen-3-yl)methyl)aniline (4j): The title compound was prepared according to the general procedure from N-phenyl-1-(thiophen-3-yl)methanimine (37.4 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow solid in 69% (37.4 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.16 (d, $J = 5.1$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 2H), 6.95 – 6.93 (m, 2H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 2H), 4.45 (d, $J = 6.2$ Hz, 1H), 4.08 (s, 1H), 1.97 – 1.93 (m, 1H), 1.87 – 1.64 (m, 5H), 1.32 – 1.07 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 148.12, 147.72, 129.24, 126.62, 124.31, 123.64, 117.64, 113.43, 59.57, 45.40, 30.14, 29.60, 26.50, 26.41, 26.36. HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{21}$NS (M+Na)$^+$ 294.1292, found 294.1295. GCMS (EI) m/z calcd. for C$_{17}$H$_{21}$NS [M$^+$] 271.1, found 271.1, 188.1, 179.1, 154.1, 135.0, 128.1.
N-(cyclohexyl(phenyl)methyl)-4-methylaniline (4k): The title compound was prepared according to the general procedure from 1-phenyl-N-(p-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow solid in 63% (35.2 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 – 7.31 (m, 4H), 7.23 (h, $J = 4.1$ Hz, 1H), 6.90 (d, $J = 8.1$ Hz, 2H), 6.45 (d, $J = 8.4$ Hz, 2H), 4.12 (d, $J = 6.2$ Hz, 1H), 4.06 (s, 1H), 2.19 (s, 3H), 1.91 (d, $J = 12.9$ Hz, 1H), 1.81 – 1.63 (m, 4H), 1.57 (d, $J = 12.7$ Hz, 1H) 1.28 – 1.03 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 145.65, 142.98, 129.67, 128.27, 127.35, 126.77, 126.12, 113.36, 63.76, 45.05, 30.37, 29.54, 26.57, 26.53, 26.50, 20.43. GCMS (EI) m/z calcd. for C$_{20}$H$_{25}$N [M$^+$] 279.2, found 279.1, 196.1, 180.1, 165.1, 152.1, 141.1. The analytical data correspond with those reported in the literature.

N-(cyclohexyl(phenyl)methyl)-4-methoxyaniline (4l): The title compound was prepared according to the general procedure from N-(4-methoxyphenyl)-1-phenylmethanimine (42.3 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as brown oil in 66% (39 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 6.70 (d, $J = 8.9$ Hz, 2H), 6.48 (d, $J = 8.9$ Hz, 2H), 4.08 (d, $J = 6.2$ Hz, 1H), 3.94 (s, 1H), 3.70 (s, 3H), 1.93 (d, $J = 11.9$ Hz, 1H), 1.82 – 1.63 (m, 4H), 1.57 (d, $J = 12.3$ Hz, 1H), 1.30 – 1.00 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.75, 142.99, 142.21, 128.24, 127.38, 126.77, 114.84, 114.41, 64.39, 55.84, 45.05, 30.31, 29.62, 26.55, 26.52, 26.48. GCMS (EI) m/z calcd. for C$_{20}$H$_{25}$NO [M$^+$] 295.1, found 295.1, 212.2, 197.1, 168.1, 134.1, 122.1, 108.1. The analytical data correspond with those reported in the literature.
4-Bromo-N-(cyclohexyl(phenyl)methyl)aniline (4m): The title compound was prepared according to the general procedure from N-(4-bromophenyl)-1-phenylmethanimine (52 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 54% (37.1 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.20 (m, 5H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.37 (d, $J = 8.8$ Hz, 2H), 4.19 (s, 1H), 4.06 (d, $J = 6.3$ Hz, 1H), 1.88 (d, $J = 11.9$ Hz, 1H), 1.79 – 1.60 (m, 4H), 1.55 – 1.50 (m, 1H), 1.30 – 0.96 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.78, 142.13, 131.83, 128.39, 127.27, 127.05, 114.87, 108.62, 63.56, 44.91, 30.29, 29.59, 26.50, 26.45, 26.42. GCMS (EI) m/z calcd. for C$_{19}$H$_{22}$BrN [M$^+$] 343.0, found 345.1, 343.1, 262.1, 260.1, 182.0, 180.1, 171.1, 155.0, 115.1, 104.1. The analytical data correspond with those reported in the literature.$^9$

N-(cyclohexyl(phenyl)methyl)-4-(trifluoromethyl)aniline (4n): The title compound was prepared according to the general procedure from 1-phenyl-N-(4-(trifluoromethyl)phenyl)methanimine (49.8 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 70% (46.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 – 7.23 (m, 7H), 6.52 (d, $J = 8.5$ Hz, 2H), 4.50 (s, 1H), 4.16 (d, $J = 6.4$ Hz, 1H), 1.91 (d, $J = 12.3$ Hz, 1H), 1.81 – 1.64 (m, 4H), 1.54 (d, $J = 14.4$ Hz, 1H), 1.30 – 1.02 (m, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.24, 141.79, 128.50, 127.23, 127.21, 126.55 (q, $J_{C-F} = 370.9$ Hz), 118.57 (q, $J = 32.76$ Hz), 112.44, 63.23, 44.83, 30.29, 29.60, 26.46, 26.41, 26.38. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -61.03. HRMS (ESI-TOF) m/z calcd. for C$_{20}$H$_{22}$F$_3$N (M$^+$Na)$^+$ 356.1602, found 356.1625. GCMS (EI) m/z calcd. for C$_{20}$H$_{22}$F$_3$N [M$^+$] 333.1, found 333.2, 314.2, 250.0, 231.1, 180.1, 172.0.
Methyl 4-((cyclohexyl(phenyl)methyl)amino)benzoate (4o): The title compound was prepared according to the general procedure from methyl-4-(benzylideneamino)benzoate (47.8 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as white solid in 83% (53.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 7.76 (d, J = 8.8 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.47 (d, J = 8.8 Hz, 2H), 4.64 (s, 1H), 4.18 (t, J = 6.0 Hz, 1H), 3.81 (s, 3H), 1.90 (d, J = 12.8 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.53 (d, J = 12.8 Hz, 1H), 1.27 – 0.99 (m, 5H). **13C NMR (126 MHz, CDCl3)** δ 167.40, 151.55, 141.72, 131.47, 128.46, 127.20, 127.17, 118.23, 112.18, 63.06, 51.57, 44.75, 30.25, 29.59, 26.43, 26.37, 26.34. **HRMS (ESI-TOF)** m/z calcd. for C21H25NO2 (M+Na)+ 346.1783, found 346.1832. **GCMS (EI)** m/z calcd. for C21H25NO2 [M+] 323.1, found 323.2, 292.2, 240.1, 181.1, 135.1, 91.1, 77.1.

N-(cyclohexyl(4-methoxyphenyl)methyl)-4-fluoroaniline (4p): The title compound was prepared according to the general procedure from N-(4-fluorophenyl)-1-(4-methoxyphenyl)methanimine (45.8 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 51% (32 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 7.17 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.76 (t, J = 8.8 Hz, 2H), 6.43 – 6.39 (m, 2H), 4.00 – 3.98 (m, 2H), 3.78 (s, 3H), 1.91 – 1.86 (m, 1H), 1.79 – 1.69 (m, 2H), 1.68 – 1.51 (m, 3H), 1.28 – 0.96 (m, 5H). **13C NMR (126 MHz, CDCl3)** δ 158.56, 155.59 (d, J = 234.3 Hz), 144.32, 134.48, 128.30, 115.53 (d, J = 22.1 Hz), 114.03 (d, J = 7.4 Hz), 113.73, 63.61, 55.31, 45.13, 30.19, 29.77, 26.56, 26.50, 26.46. **19F NMR (471 MHz, CDCl3)** δ -128.86. **GCMS (EI)** m/z calcd. for C20H24FNO [M+] 313.1, found 313.2, 230.1, 202.2, 186.1, 134.1, 121.1, 111.1, 95.1, 77.1. The analytical data correspond with those reported in the literature.10
**N-(cyclohexyl(4-fluorophenyl)methyl)-4-fluoroaniline (4q):** The title compound was prepared according to the general procedure from N-1-bis(4-fluorophenyl)methanimine (43.4 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 58% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.25 – 7.22 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.80 – 6.75 (t, J = 8.7 Hz, 2H), 6.42 – 6.37 (m, 2H), 4.04 (s, 1H), 4.03 (s, 1H), 1.89 – 1.86 (m, 1H), 1.81 – 1.71 (m, 2H), 1.69 – 1.57 (m, 2H), 1.53 (m, 1H), 1.28 – 0.97 (m, 5H). ^13C NMR (126 MHz, CDCl\textsubscript{3}) δ 161.89 (d, J = 244.6 Hz), 155.71 (d, J = 234.6 Hz), 144.04 (d, J = 2.0 Hz), 138.14 (d, J = 3.1 Hz), 128.72 (d, J = 7.8 Hz), 115.60 (d, J = 22.1 Hz), 115.21 (d, J = 21.3 Hz), 114.04 (d, J = 7.3 Hz), 63.58, 45.06, 30.16, 29.61, 26.49, 26.44, 26.40. HRMS (ESI-TOF) m/z calcd. for C\textsubscript{19}H\textsubscript{21}F\textsubscript{2}N (M+Na)^+ 324.1540, found 324.1563. GCMS (EI) m/z calcd. for C\textsubscript{19}H\textsubscript{21}F\textsubscript{2}N [M+] 301.1, found 301.1, 218.1, 170.0, 146.1, 133.0, 122.0, 109.0.

**4-Butyl-N-(cyclohexyl(4-methoxyphenyl)methyl)aniline (4r):** The title compound was prepared according to the general procedure from N-(4-butylphenyl)-1-(4-methoxyphenyl)methanimine (53.4 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 50% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.22 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.4 Hz, 2H), 4.06 (d, J = 6.1 Hz, 1H), 4.03 (s, 1H), 3.80 (s, 3H), 2.45 (t, J = 8 Hz, 2H), 1.90 (d, J = 12.5 Hz, 1H), 1.80 – 1.48 (m, 7H), 1.33 (h, J = 7.3 Hz, 2H), 1.27 – 0.99 (m, 5H), 0.91 (t, J = 7.3 Hz, 3H). ^13C NMR (101 MHz, CDCl\textsubscript{3}) δ 158.40, 145.90, 135.00, 131.31, 129.00, 128.29, 113.63, 113.25, 63.17, 55.28, 45.17, 34.79, 34.09, 30.25, 29.69, 26.58, 26.54, 26.50, 22.48, 14.12. HRMS (ESI-TOF) m/z calcd. for C\textsubscript{24}H\textsubscript{33}NO (M+Na)^+ 374.2460, found 374.2489. GCMS (EI) m/z calcd. for C\textsubscript{24}H\textsubscript{33}NO [M+] 351.2, found 351.3, 268.1, 238.2, 225.1, 210.1, 160.1, 121.1, 106.1.
**N-(cyclohexyl(4-(methylthio)phenyl)methyl)-4-methoxyaniline (4s):** The title compound was prepared according to the general procedure from N-(4-methoxyphenyl)-1-(4-(methylthio)phenyl)methanimine (51.4 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as brown oil in 54% (36.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 13% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 7.23 – 7.18 (m, 4H), 6.68 (d, J = 8.9 Hz, 2H), 6.45 (d, J = 8.9 Hz, 2H), 4.02 (d, J = 6.1 Hz, 1H), 3.89 (s, 1H), 3.69 (s, 3H), 2.47 (s, 3H), 1.88 (d, J = 12.8 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.68 – 1.54 (m, 3H), 1.27 – 0.99 (m, 5H).

**13C NMR (126 MHz, CDCl3)** δ 151.82, 142.10, 140.06, 136.32, 127.92, 126.62, 114.85, 114.43, 63.94, 55.85, 45.03, 30.20, 29.60, 26.53, 26.49, 26.45, 16.02.

**GCMS (EI) m/z** calcld. for C21H27NOS [M+] 341.1, found 341.2, 258.1, 243.1, 218.1, 137.1, 122.0, 108.1, 77.1. The analytical data correspond with those reported in the literature.

**N-(benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)-4-methoxyaniline (4t):** The title compound was prepared according to the general procedure from 1-(benzo[d][1,3]dioxol-5-yl)-N-(4-methoxyphenyl)methanimine (51 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as brown oil in 51% (34.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% EtOAc/Pet.ether).

**1H NMR (500 MHz, CDCl3)** δ 6.79 (s, 1H), 6.74 (s, 2H), 6.69 (d, J = 8.9 Hz, 2H), 6.46 (d, J = 8.9 Hz, 2H), 5.92 (dd, J = 9.1, 1.5 Hz, 2H), 3.95 (d, J = 6.2 Hz, 1H), 3.85 (s, 1H), 3.69 (s, 3H), 1.90 (d, J = 12.3 Hz, 1H), 1.79 – 1.71 (m, 2H), 1.68 – 1.64 (m, 1H), 1.61 – 1.51 (m, 2H), 1.28 – 0.97 (m, 5H).

**13C NMR (126 MHz, CDCl3)** δ 151.83, 147.77, 146.34, 142.16, 137.17, 120.60, 114.86, 114.44, 107.96, 107.53, 100.94, 64.20, 55.88, 45.16, 30.26, 29.81, 26.56, 26.51, 26.47.

**GCMS (EI) m/z** calcld. for C21H25NO3 [M+] 339.1, found 339.2, 256.1, 216.1, 135.1, 108.1, 77.1. The analytical data correspond with those reported in the literature.
**N-((2-chlorophenyl)(cyclohexyl)methyl)-4-fluoroaniline (4u):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-N-(4-fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and bromocyclohexane (49.3 µL, 0.4 mmol). Pure product was obtained as brown oil in 93% (59 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

**1H NMR (400 MHz, CDCl3)** δ 7.37 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 7.26 – 7.14 (m, 2H), 6.81 (t, J = 8.7 Hz, 2H), 6.46 – 6.41 (m, 2H), 4.62 (d, J = 6.4 Hz, 1H), 4.12 (s, 1H), 1.94 (d, J = 12.3 Hz, 1H), 1.83 – 1.69 (m, 4H), 1.57 – 1.53 (m, 1H), 1.31 – 1.07 (m, 5H).

**13C NMR (101 MHz, CDCl3)** δ 155.70 (d, J = 234.6 Hz), 143.77, 140.03, 133.69, 129.71, 128.35, 128.05, 126.97, 115.64 (d, J = 22.3 Hz), 113.83 (d, J = 7.3 Hz), 59.99, 43.85, 30.29, 28.93, 26.55, 26.50, 26.44.

**HRMS (ESI-TOF) m/z** calcd. for C_{19}H_{21}ClFN (M+Na)^+ 340.1244, found 340.1262.

**GCMS (EI) m/z** calcd. for C_{19}H_{21}ClFN [M+](1+ 317.1, found 317.1, 234.1, 198.1, 170.1, 151.1, 122.1, 95.1.

**N-(1-(2-chlorophenyl)-2-methylpropyl)-4-fluoroaniline (4v):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-N-(4-fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and 2-bromopropane (18.7 µL, 0.4 mmol). Pure product was obtained as brown oil in 76% (42.2 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

**1H NMR (400 MHz, CDCl3)** δ 7.36 (dd, J = 7.4, 1.9 Hz, 1H), 7.31 (dd, J = 7.3, 2.2 Hz, 1H), 7.17 (pd, J = 7.3, 1.8 Hz, 2H), 6.79 (t, J = 8.7 Hz, 2H), 6.41 (dd, J = 8.9, 4.3 Hz, 2H), 4.59 (d, J = 5.9 Hz, 1H), 4.07 (s, 1H), 2.18 – 2.06 (m, 1H), 1.01 (d, J = 6.9 Hz, 6H).

**13C NMR (101 MHz, CDCl3)** δ 155.77 (d, J = 234.7 Hz), 143.72, 140.17, 133.62, 129.80, 128.23, 128.14, 127.00, 115.68 (d, J = 22.3 Hz), 113.91 (d, J = 7.3 Hz), 60.37, 33.68, 20.11, 17.92.

**HRMS (ESI-TOF) m/z** calcd. for C_{16}H_{17}ClFN (M+Na)^+ 300.0931, found 300.0942.

**GCMS (EI) m/z** calcd. for C_{16}H_{17}ClFN [M^+] 277.1, found 277.1, 199.0, 183.0, 171.0, 152.0, 139.0, 133.0.

**N-(bicyclo[2.2.1]heptan-7-yl(2-chlorophenyl)methyl)-4-fluoroaniline (4w):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-N-(4-
fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and 7-bromobicyclo[2.2.1]heptane (50.8 μL, 0.4 mmol) for 72 h. Pure product was obtained as yellow oil in 71% (46.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

**1H NMR (400 MHz, CDCl3)** δ 7.39 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.6, 1.8 Hz, 1H), 6.78 (t, J = 8.7 Hz, 2H), 6.49 – 6.44 (m, 2H), 4.57 (d, J = 10.1 Hz, 1H), 4.18 (s, 1H), 2.37 (t, J = 4.3 Hz, 1H), 2.18 – 2.04 (m, 1H), 1.89 – 1.77 (m, 2H), 1.71 – 1.59 (m, 2H), 1.52 – 1.43 (m, 1H), 1.37 – 1.13 (m, 4H). **13C NMR (101 MHz, CDCl3)** δ 155.81 (d, J = 234.7 Hz), 143.57, 141.82, 133.17, 129.73, 128.63, 128.16, 127.47, 115.65 (d, J = 22.3 Hz), 114.05 (d, J = 7.3 Hz), 58.68, 38.43, 37.82, 30.77, 29.85, 28.24, 27.59. **HRMS (ESI-TOF) m/z** calcd. for C20H21ClFN (M+Na)+ 352.1244, found 352.1263. **GCMS (EI) m/z** calcd. for C20H21ClFN [M+] 329.1, found 329.1, 234.1, 219.1, 198.0, 177.0, 151.0, 122.0.

**Ethyl 2-cyclohexyl-2-(p-tolylamino)acetate (4x):** The title compound was prepared according to the general procedure from ethyl-2-(p-tolylimino)acetate (38.2 mg, 0.2 mmol) and bromocyclohexane (49.3 μL, 0.4 mmol). Pure product was obtained as yellow oil in 30% (16.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% EtOAc/Pet.ether).

**1H NMR (400 MHz, CDCl3)** δ 6.97 (d, J = 8.1 Hz, 2H), 6.56 (d, J = 8.3 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.82 (d, J = 6.0 Hz, 1H), 2.22 (s, 3H), 1.87 – 1.65 (m, 6H), 1.28 – 1.09 (m, 9H). **13C NMR (101 MHz, CDCl3)** δ 173.94, 145.19, 129.89, 127.58, 113.96, 62.67, 60.89, 41.43, 29.75, 29.36, 26.35, 26.25, 26.21, 20.53, 14.46. **GCMS (EI) m/z** calcd. for C17H23NO2 [M+] 275.1, found 275, 202, 106. The analytical data correspond with those reported in the literature.11

**Three-component reaction**

\[
\text{R}^1\text{CHO} + \text{R}^2\text{NH}_2 + \text{CyBr} \xrightarrow{\text{Pd(OAc)}_2 (10 \text{ mol}%), \text{PPh}_3 (100 \text{ mol}%), \text{Cs}_2\text{CO}_3 (2 \text{ equiv.}), \text{DMSO} (0.1 \text{ M}), \text{Ar, blue LEDs, RT}} \text{HN}\text{R}^2
\]

R1, R2 = Ph; 3f, 65%  
R1 = 4-COO2MePh, R2 = Ph; 4g, 78%  
R1 = Ph, R2 = 4-COO2MePh; 4o, 59%
A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir–bar was charged with aldehyde (0.2 mmol), aniline (0.2 mmol), Pd(OAc)$_2$ (10 mol%, 0.02 mmol, 4.5 mg), PPh$_3$ (100 mol%, 0.2 mmol, 52.5 mg), Cs$_2$CO$_3$ (2 equiv, 0.4 mmol, 130 mg), and alkyl bromide (2 equiv., 0.4 mmol), capped with Teflon septum and parafilmed. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate a yellow color. The reaction is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography using silica gel (100-200 mesh size) and EtOAc/petether as the eluent.

**Radical clock experiment**

Following the general procedure, radical clock experiment with 6-bromohex-1-ene were carried out which showed the formation of radical rearranged products 5 exclusively, confirming the radical reactivity of metal alkyl species.

![Radical clock experiment diagram](image)

**N-(2-cyclopentyl-1-phenylethyl)aniline (5):** The title compound was prepared according to the general procedure from N-benzylideneaniline (36.2 mg, 0.2 mmol) and 6-bromo-1-hexene (53.3 µL, 0.4 mmol). Pure product was obtained as yellow oil in 28% (14.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

**$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.37 – 7.30 (m, 4H), 7.24 (q, $J = 7.1$, 6.5 Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 7.9$ Hz, 2H), 4.34 (t, $J = 6.7$ Hz, 1H), 4.10 (s, 1H), 1.88 – 1.76 (m, 5H), 1.69 – 1.48 (m, 4H), 1.24 – 1.12 (m, 2H).

**$^{13}$C NMR (101 MHz, CDCl$_3$)** δ 147.62, 144.75, 129.22, 128.68, 126.96, 126.46, 117.18, 113.31, 57.76, 45.87, 37.18, 33.01, 25.32, 25.10.

**HRMS (ESI-TOF)** m/z calcd. for C$_{19}$H$_{23}$N (M+Na)$^+$ 288.1728, found 288.1730. **GCMS (EI)** m/z calcd. for C$_{19}$H$_{23}$N [M$^+$] 265.1, found 265.1, 182.1, 167.1, 152.0, 128.0, 115.0, 104.0.

**TEMPO trapping experiment**
TEMPO radical trapping experiment was conducted to support the proposed light-mediated inner shear electron transfer oxidative addition mechanism. A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir–bar was charged with \( N \)-benzylideneaniline (36.2 mg, 0.2 mmol), bromocyclohexane (49.3 \( \mu \)L, 0.4 mmol), \( \text{Pd(OAc)}_2 \) (10 mol%, 0.02 mmol, 4.5 mg), \( \text{PPh}_3 \) (100 mol%, 0.2 mmol, 52.5 mg), TEMPO (46.8 mg, 0.3 mmol), and \( \text{Cs}_2\text{CO}_3 \) (2 equiv, 0.4 mmol, 130 mg), capped with Teflon septum and parafilm. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate yellow color which is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, and then subjected to GCMS. The GC-MS of the crude reaction mixture did not show the formation of product 3f, while a TEMPO-alkyl adduct was observed.

**Steady-state Stern-Volmer quenching experiments**

Emission spectra were collected on a fluoromax-4 Spectrophotometer with excitation and emission slit widths of 5 nm. Quenching experiments were carried out using a 0.4 mM solution of \( \text{Pd(PPh}_3)_4 \) in DMF and variable concentrations of bromocyclohexane dispensed in DMF (4, 8, 12, 16, 20 mM). The samples were prepared in 2 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside a nitrogen-filled glove box, removed from the glove box and an emission spectrum was collected. Samples were excited at 380 nm and the intensity of emission was monitored at 630 nm expressed as the ratio \( I_0/I \), where \( I_0 \) is the emission intensity of [Pd] at 630 nm in the absence of a quencher and \( I \) is the observed intensity, as a function of the quencher concentration was measured. Fluorescence emission spectra and Stern-Volmer plot are given in the Figures below.
Figure S1. Emission spectra of Pd(PPh$_3$)$_4$ (0.4 mM) at different concentrations of bromocyclohexane ($\lambda_{ex}$ = 380 nm).

Figure S2. The Stern-Volmer plot of Pd(PPh$_3$)$_4$ (0.4 mM) at different concentrations of bromocyclohexane.
Photoluminescence lifetime (Time-resolved Stern-Volmer quenching) experiments

Time-resolved Stern-Volmer quenching experiments were carried out using a 0.4 mM solution of Pd(PPh₃)₄ in DMF and variable concentrations of bromocyclohexane dispensed in DMF (4, 8, 12, 16, 20 mM). The samples were prepared in 2 mL quartz cuvettes, equipped with screw cap PTFE stoppers, and sealed with parafilm inside the argon-filled glove-box. The intensity of the emission peak at 630 nm is expressed as the ratio $k_{\text{obs}}/k_0$, where $k_0$ is the decay of Pd(PPh₃)₄ at 630 nm in the absence of bromocyclohexane and $k_{\text{obs}}$ is the observed decay, as a function of the bromocyclohexane concentration was measured. An Argon saturated 0.4 mM solution in DMF was used for the determination of the photoluminescence lifetimes of the Pd(PPh₃)₄. Photoluminescence decay traces were acquired based on time-correlated single-photon-counting (TCSPC) techniques using a fluoromax-4 spectrophotometer from Horiba Scientific. A 372 nm diode laser was used as the excitation source. The photoluminescence signals were obtained using an automated motorized monochromator. Time-resolved emission data were fit to a single exponential decay to extract the observed rate constant ($k_{\text{obs}}$). Phosphorescence emission spectra and Stern-Volmer plots for each component are given in below.

Figure S3. Phosphorescence lifetime of Pd(PPh₃)₄ in DMF (0.4 mM). Spectroscopic experiments were performed one single time. The excited-state $^3$Pd(PPh₃)₄ exhibits a long lived triplet state with a life time of $\tau_0 = 494.85\pm1.62$ ns.
Figure S4. Phosphorescence lifetimes of Pd(PPh₃)₄ (0.4 mM) at different concentrations of bromocyclohexane. Spectroscopic experiments were performed one single time.

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>kₜₐₜ</th>
<th>kₜₐₜ/k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.229465011</td>
<td>1</td>
</tr>
<tr>
<td>0.004</td>
<td>2.989996608</td>
<td>1.341127397</td>
</tr>
<tr>
<td>0.008</td>
<td>3.774240627</td>
<td>1.69289072</td>
</tr>
<tr>
<td>0.012</td>
<td>4.462542534</td>
<td>2.001620349</td>
</tr>
<tr>
<td>0.016</td>
<td>5.210638498</td>
<td>2.337169892</td>
</tr>
<tr>
<td>0.02</td>
<td>5.998940947</td>
<td>2.690753574</td>
</tr>
</tbody>
</table>

Figure S5. Time-resolved Stern-Volmer quenching plot of Pd(PPh₃)₄ in DMF (0.4 mM) at different concentrations of bromocyclohexane.¹²
Figure S6. Combined steady-state and time-resolved Stern-Volmer quenching plot of Pd(PPh$_3)_4$ in DMF (0.4 mM) at different concentrations of bromocyclohexane.$^{12}$

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>$k_{obs}$</th>
<th>$k = 1/t_1$</th>
<th>$k_0 = 1/t_0$</th>
<th>$k_{ET}$</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>2.229465</td>
<td>0.760531597</td>
<td>760531.597</td>
<td>760531.597</td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td>3.77424</td>
<td>1.544775616</td>
<td>1544775.616</td>
<td>1544775.616</td>
<td></td>
</tr>
<tr>
<td>0.012</td>
<td>4.46254</td>
<td>2.233077523</td>
<td>2233077.523</td>
<td>2233077.523</td>
<td></td>
</tr>
<tr>
<td>0.016</td>
<td>5.21064</td>
<td>2.981173487</td>
<td>2981173.487</td>
<td>2981173.487</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>5.99894</td>
<td>3.769475936</td>
<td>3769475.936</td>
<td>3769475.936</td>
<td></td>
</tr>
</tbody>
</table>

Figure S7. A Plot of the observed rate constant ($k_{obs}$) of *Pd(PPh$_3)_4$ (0.4 mM) corrected by its intrinsic ground state recovery rate ($k_0$) vs. different concentrations of bromocyclohexane to determine the electron transfer rate constant ($k_{ET}$) between Pd and bromocyclohexane. Data were collected by the use of phosphorescence lifetime measurements.$^{12}$
Mechanistic discussion:

A plausible reaction mechanism proceeding via the inner-sphere ET pathway is proposed (Figure 2f, and S8). The in situ generated Pd(PPh₃)₄ complex undergoes excitation in the presence of visible light resulting in the triplet state *Pd⁰L₃ (7) that provides open coordination site for the alkyl bromide association. This results in the inner sphere electron transfer furnishing hybrid alkyl radical Pd⁺ intermediate. The alkyl radical then adds to the imine resulting in an N-centered radical intermediate 9 which undergoes radical recombination with Pd⁰ forming a PdⅡ intermediate 10 with the release of PPh₃. To realize the product formation and the regeneration of Pd⁰ from intermediate 10, hydrogen and oxygen are required which made us investigate their source. We initially tested the reaction using DMSO-d₆ as a solvent which did not result in any deuterium incorporated alkylation product 3f which confirmed that the DMSO is not acting as a source of...
hydrogen. Besides, the formation of triphenylphosphine oxide is observed even in solvents without oxygen (CH$_3$CN, Toluene), making us conclude that the DMSO being used in the reaction is acting as the source of neither hydrogen nor oxygen. This helped us to identify the CsHCO$_3$ being generated in the reaction as the source of hydrogen and oxygen, which facilitates the release of hydroalkylation product 3 and Pd$^0$ from intermediate 10 along with the generation of triphenylphosphine oxide which is observed in comparable yields to the amine 3 formed (Figure 2f, S8 and S9).

Besides, hybrid alkyl radical Pd$^I$ intermediate 8 also can undergo radical recombination to give Pd$^{II}$ intermediate 11 followed by the β-hydride elimination resulting in the release of olefination intermediate 13 and Pd$^0$. Intermediate 10 in the presence of Cs$_2$CO$_3$ could also release the hydroalkylation product 3 along with the reduction of Pd$^{II}$ to Pd$^0$ via Pd$^{II}$-mediated allylic C–H bond activation followed by β-hydride elimination from intermediate 13 to give oxidized substrate 14. Both compounds 13 and 14 have been identified under the standard reaction conditions. Alongside, it is conceivable that a hydrogen atom transfer (HAT) mechanism might also be operative, where the N-centered radical intermediate 9 can undergo intermolecular HAT with olefination intermediate 13 resulting in the formation of hydroalkylation product 3 along with the release of Pd$^{II}$-intermediate 15 that undergoes β-hydride elimination to release 14 and reduced Pd$^0$.

The reduction of Pd$^{II}$ by dehydrogenation to produce 14 is not a representative process for this reaction. However, we included this as an alternate pathway, which will be applicable for the alkyl bromides that can undergo a series of β-hydride elimination events. Since we use 100 mol% of PPh$_3$, we believe that the catalysis and the reduction of Pd$^{II}$ to Pd$^0$ are facilitated mainly by the excess phosphine used. Alongside, examples where the alkyl bromides can undergo a series of β-hydride elimination events, this alternate pathway proposed can also be considered. We could see the diene in case of 3h, and 3j which is easy to analyze. In the case of 3i we could not identify the diene due to the fragmentation. However in the case of bromocyclohexane, we could see the formation of cyclohexene, but identifying the diene/triene in this particular case is difficult due to the solvent interference.
References

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

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3a
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3b

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3b
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3c

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3c
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3d

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3d
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3e

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3e
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3f

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3f
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3g

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3g
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \] of compound 3h

\[ \text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3\text{)} \] of compound 3h
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3i

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 3i
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3j

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 3j
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3k

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3k
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3l

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3l
H NMR (400 MHz, CDCl₃) of compound 3m

¹³C NMR (101 MHz, CDCl₃) of compound 3m
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3n

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3n
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3o

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3o
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3p

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 3p
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3q

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 3q
H NMR (500 MHz, CDCl$_3$) of compound 3r

$^1$H NMR (500 MHz, CDCl$_3$) of compound 3r

C NMR (126 MHz, CDCl$_3$) of compound 3r

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 3r

S51
$^{1}$H NMR (500 MHz, CDCl$_3$) of compound 4a

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4a
\[ \text{\[^1\text{H NMR (500 MHz, CDCl}_3\text{) of compound 4b}} \]

\[ \text{\[^{13}\text{C NMR (126 MHz, CDCl}_3\text{) of compound 4b}} \]\n
S53
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4c

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4c
$^{19}$F NMR (471 MHz, CDCl$_3$) of compound 4c

$^1$H NMR (500 MHz, CDCl$_3$) of compound 4d
$^{13}$C NMR (261 MHz, CDCl$_3$) of compound 4d

$^1$H NMR (400 MHz, CDCl$_3$) of compound 4e
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4e

$^1$H NMR (500 MHz, CDCl$_3$) of compound 4f
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4f

$^{19}$F NMR (471 MHz, CDCl$_3$) of compound 4f
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4g

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4g
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4h

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4h
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4i

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4i
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4j

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4j
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4k

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4k
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4l

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4l
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4m

$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4m
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4n

$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4n
$^{19}\text{F NMR (471 MHz, CDCl}_3\text{)}$ of compound 4n

$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$ of compound 4o
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4o

$^1$H NMR (500 MHz, CDCl$_3$) of compound 4p
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4p

$^{19}$F NMR (471 MHz, CDCl$_3$) of compound 4p
$\text{H NMR (500 MHz, CDCl}_3\text{) of compound 4q}$

$\text{C NMR (126 MHz, CDCl}_3\text{) of compound 4q}$
\[19^F \text{NMR (471 MHz, CDCl}_3\text{) of compound 4q}\]

\[1^H \text{NMR (400 MHz, CDCl}_3\text{) of compound 4r}\]
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) of compound 4r

\(^1\)H NMR (500 MHz, CDCl\(_3\)) of compound 4s
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4s

$^1$H NMR (500 MHz, CDCl$_3$) of compound 4t
$^{13}$C NMR (126 MHz, CDCl$_3$) of compound 4t

$^1$H NMR (400 MHz, CDCl$_3$) of compound 4u
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4u

$^1$H NMR (400 MHz, CDCl$_3$) of compound 4v
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4w

$^1$C NMR (101 MHz, CDCl$_3$) of compound 4v
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 4w

$^1$H NMR (400 MHz, CDCl$_3$) of compound 4x
$^1$H NMR (400 MHz, CDCl$_3$) of compound 5

$^1$C NMR (101 MHz, CDCl$_3$) of compound 4

S78
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 5