Metal-, Photocatalyst-, and Light-Free Late-Stage C–H Alkylation of N-Heteroarenes with Organotrimethylsilanes using Persulfate as a Stoichiometric Oxidant

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1. General Information

Reagents were purchased from commercial sources and were used as received. $^1$H and $^{13}$C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts ($\delta$) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).
Many alkyl-trimethyl-silanes (except for commercially available benzyltrimethylsilane 2) were synthesized using procedures reported in the literature. Scheme S1 depicts the silanes that have been prepared and the corresponding literature references.

Scheme S1. The alkyl-trimethyl-silanes synthesized according to procedure reported in the literature.

3. Investigation of the key reaction parameters.
Table S1: Screening of different solvents

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN:H&lt;sub&gt;2&lt;/sub&gt;O=1:1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>HCl</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$O</td>
<td>NR</td>
</tr>
</tbody>
</table>

*General conditions: 1 (0.3 mmol), 2 (0.6 mmol), K$_2$S$_2$O$_8$ (0.6 mmol) and solvent (1.5 mL) under Ar atmosphere. *NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard; NR, no reaction.

**Table S2: Screening of oxidants.**

<table>
<thead>
<tr>
<th>entry</th>
<th>oxidant</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K$_2$S$_2$O$_8$</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>t-BPA</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>t-BHP</td>
<td>5</td>
</tr>
</tbody>
</table>

*General conditions: 1 (0.3 mmol), 2 (0.6 mmol), oxidant (0.6 mmol) and DMSO (1.5 mL) under Ar atmosphere. *NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard.

**Table S3: Screening of different temperature.**

<table>
<thead>
<tr>
<th>entry</th>
<th>temperature/$^o$C</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>85</td>
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<tr>
<td>4</td>
<td>50</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>86</td>
</tr>
</tbody>
</table>

*General conditions: 1 (0.3 mmol), 2 (0.6 mmol), (NH$_4$)$_2$S$_2$O$_8$ (0.6 mmol) and DMSO (1.5 mL) under Ar atmosphere. *NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard;

**Table S4: Screening of the amount of benzyltrimethylsilane and oxidant.**

<table>
<thead>
<tr>
<th>entry</th>
<th>y equiv</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>2 x</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>85</td>
</tr>
</tbody>
</table>

*General conditions: 1 (0.3 mmol), 2 (0.6 mmol), (NH$_4$)$_2$S$_2$O$_8$ (0.6 mmol) and DMSO (1.5 mL) under Ar atmosphere. *NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard;
<table>
<thead>
<tr>
<th>Entry</th>
<th>x eq. 2</th>
<th>y eq. ((\text{NH}_4)_2\text{S}_2\text{O}_8)</th>
<th>Yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>2.0</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>2.0</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>2.0</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>1.5</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>3.0</td>
<td>93 (91%)(^c)</td>
</tr>
</tbody>
</table>

\(^a\)General conditions: 1 (0.3 mmol), 2 (0.3x mmol), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (0.3y mmol) and DMSO (1.5 mL) under Ar atmosphere. \(^b\)NMR yield determined with 1,1,2,2-tetrachloroethane (0.3 mmol) as an internal standard; \(^c\)Isolated yield.

**Table S5 Control experiments**

![Scheme S2](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>control conditions</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>w/o ((\text{NH}_4)_2\text{S}_2\text{O}_8)</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>w/o TFA</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>standard conditions, w/all</td>
<td>93</td>
</tr>
</tbody>
</table>

The yield was determined by \(^1\)H NMR spectroscopy using dibromomethane as the internal standard.

4. Investigation of the mechanism.

4.1 TEMPO was used as radical scavengers.

![Scheme S2](image)

4.2 1,1-diphenylethylene was used as radical scavengers.
To a 8 mL glass vial was added 1 (40 μL, 0.3 mmol, 1.0 equiv), 2 (114 μL, 0.6 mmol, 2.0 equiv), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (205 mg, 0.9 mmol, 2.0 equiv), 1,1-diphenylethylene (117 mg, 0.75 mmol, 2.5 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The product 3 was obtained in less than 5% yield; and instead a 6% yield of compound 51, was isolated from the reaction.

4.3 Detection of by-product 53

To a 8 mL glass vial was added 1 (40 μL, 0.3 mmol, 1.0 equiv), 46 (128.4 mg, 0.6 mmol, 2.0 equiv), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The byproduct of radical coupling 53 was isolated from the reaction in 15% yield.

5. Experimental procedures and product characterization

5.1 General procedure A for the alkylation of N-heteroarenes.

To a 8 mL glass vial was added heteroarene (0.3 mmol, 1.0 equiv), alkyl-trimethyl-silanes (0.6 mmol, 2.0 equiv), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 30 °C for 24 h. The mixture was diluted with 20 mL of aqueous 1 M NaHCO₃ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.2 General procedure B for the alkylation of N-heteroarenes.

To a 8 mL glass vial was added heteroarene (0.3 mmol, 1.0 equiv), alkyl-trimethyl-silanes (0.6 mmol, 2.0 equiv), \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (205 mg, 0.9 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 1.5 mL of DMSO. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly at 60 °C for 24 h. The mixture was diluted with 20 mL of aqueous 1 M NaHCO₃ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried
over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.3. Product characterization

2-benzyl-4-methylquinoline (3).

According to the general procedure A. The spectral data is consistent with the literature data.$^6$ Brown solid (63.9 mg, 91%). M.p. = 64 – 65 °C. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 7.69 (t, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 7.6 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 7.06 (s, 1H), 4.29 (s, 2H), 2.60 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 147.8, 144.7, 139.5, 129.7, 129.4, 129.3, 128.7, 127.0, 126.6, 125.9, 123.8, 122.3, 45.7, 18.8.

HRMS (ESI) calcd for C$_{17}$H$_{16}$N [M + H]$^+$ 234.1277, found 234.1279.

2-benzyl-4-chloroquinoline (4).

According to the general procedure A. Yellow oil (30.4 mg, 40%). R$_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H), 7.76 (t, $J$ = 7.6 Hz, 1H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.26 (s, 1H), 4.31 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.3, 148.8, 143.0, 138.6, 130.6, 129.5, 129.4, 128.9, 129.1, 128.9, 127.1, 126.9, 125.2, 124.1, 121.6, 45.5.

HRMS (ESI) calcd for C$_{16}$H$_{13}$ClN [M + H]$^+$ 254.0731, found 254.0731.

2-benzyl-4-methoxyquinoline (5).

According to the general procedure A. Yellow solid (35.9 mg, 48%). M.p. = 71 – 72 °C. R$_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (dd, $J$ = 8.4, 0.8 Hz, 1H), 8.02 (d, $J$ = 8.4 Hz, 1H), 7.68 (ddd, $J$ = 8.4, 7.2, 1.2 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.54 (s, 1H), 4.29 (s, 2H), 3.91 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 162.5, 148.8, 139.5, 129.9, 129.3, 128.7, 128.6, 126.6, 125.2, 121.8, 120.3, 100.2, 55.6, 46.2.
HRMS (ESI) calcd for C_{17}H_{16}NO [M + H]^+ 250.1226, found 250.1231.

2-benzyl-4-chloro-6-fluoroquinoline (6).

According to the general procedure A.
Yellow solid (34.1 mg, 42%). M.p. = 72 – 73 °C.
$R_l$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (dd, $J = 9.1, 5.2$ Hz, 1H), 7.78 (d, $J = 9.2$ Hz, 1H), 7.51 (t, $J = 8.4$ Hz, 1H), 7.37 – 7.28 (m, 5H), 7.28 – 7.22 (m, 1H), 4.29 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0 (d, $J = 247.2$ Hz), 160.7 (d, $J = 2.9$ Hz), 145.8, 142.2 (d, $J = 5.5$ Hz), 138.5, 132.1 (d, $J = 9.0$ Hz), 129.3, 128.9, 126.1 (d, $J = 10.3$ Hz), 126.0, 122.2, 120.7 (d, $J = 25.8$ Hz), 107.9 (d, $J = 24.3$ Hz), 45.3.
HRMS (ESI) calcd for C$_{16}$H$_{12}$ClFN [M + H]$^+$ 272.0637, found 272.0637.

4-benzyl-2-methylquinoline (7).

According to the general procedure A.
Yellow oil (60.1 mg, 86%).
$R_l$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.22 (d, $J = 6.8$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 6.99 (s, 1H), 4.34 (s, 2H), 2.67 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.8, 148.1, 146.4, 138.7, 129.4, 129.2, 128.9, 128.7, 126.6, 125.9, 125.7, 123.7, 122.7, 38.1, 25.4.
HRMS (ESI) calcd for C$_{17}$H$_{16}$N [M + H]$^+$ 234.1277, found 234.1280.

4-benzyl-2-phenylquinoline (8).

According to the general procedure A.
Yellow oil (81.4 mg, 92%).
$R_l$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.4$ Hz, 1H), 8.12 – 8.05 (m, 2H), 7.98 – 7.90 (m, 1H), 7.64 (ddd, $J = 8.4, 6.8, 1.2$ Hz, 1H), 7.59 (s, 1H), 7.49 – 7.36 (m, 4H), 7.30 – 7.22 (m, 2H), 7.22 – 7.14 (m, 3H), 4.40 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 148.7, 147.1, 139.8, 138.9, 130.6, 129.5, 129.4, 129.0, 128.9, 128.8, 127.6, 126.7, 126.4, 123.9, 119.9, 38.6.
HRMS (ESI) calcd for C_{22}H_{18}N [M + H]^+ 296.1434, found 296.1436.

1-benzylisoquinoline (9).

According to the general procedure A.
Yellow oil (57.3 mg, 96%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J$ = 5.6 Hz, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 1H), 7.57 (t, $J$ = 7.6 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.30 – 7.19 (m, 4H), 7.13 (t, $J$ = 7.2 Hz, 1H), 4.65 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.2, 142.1, 139.5, 136.6, 129.9, 128.6, 128.55, 127.4, 127.2, 126.3, 125.8, 119.8, 42.1.
HRMS (ESI) calcd for C_{16}H_{14}N [M + H]^+ 200.1121, found 200.1123.

1-benzyl-4-methoxyisoquinoline (10).

According to the general procedure A.
Yellow solid (61.3 mg, 82%). M.p. = 67 – 68 °C.
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J$ = 8.4 Hz, 1H), 8.02 (d, $J$ = 8.8 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.43 (m, 1H), 7.28 – 7.18 (m, 4H), 7.16 – 7.09 (m, 1H), 4.57 (s, 2H), 4.00 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 149.7, 139.9, 129.0, 128.9, 128.6, 128.5, 127.4, 127.2, 126.3, 125.5, 121.8, 121.7, 55.9, 41.7.
HRMS (ESI) calcd for C_{17}H_{26}NO [M + H]^+ 250.1226, found 250.1223.

1-benzyl-6-methylisoquinoline (11).

According to the general procedure A.
Gray oil (66.4 mg, 95%).
R_f 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 5.6 Hz, 1H), 8.02 (d, $J$ = 8.4 Hz, 1H), 7.55 (s, 1H), 7.45 (d, $J$ = 5.6 Hz, 1H), 7.33 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.18 – 7.11 (m, 1H), 4.63 (s, 2H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9, 142.2, 140.2, 139.7, 137.0, 129.5, 128.69, 128.6, 128.5, 127.4, 126.2, 125.5, 121.8, 121.7, 55.9, 41.7.
**HRMS** (ESI) calcd for C$_{17}$H$_{16}$N [M + H]$^+$ 234.1277, found 234.1281.

**methyl 1-benzylisoquinoline-3-carboxylate (12).**

According to the general procedure A.

Yellow solid (70.6 mg, 85%). M.p. = 110 – 111 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 8.13 (d, $J$ = 8.3 Hz, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.60 – 7.53 (m, 1H), 7.30 – 7.17 (m, 4H), 7.13 (t, $J$ = 7.0 Hz, 1H), 4.76 (s, 2H), 4.05 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.51, 160.69, 140.57, 139.04, 136.14, 130.52, 129.46, 128.77, 128.58, 128.49, 126.31, 126.13, 123.55, 52.83, 42.41.

**HRMS** (ESI) calcd for C$_{18}$H$_{16}$NO$_2$ [M + H]$^+$ 278.1176, found 278.1181.

**methyl 1-benzylisoquinoline-4-carboxylate (13).**

According to the general procedure A.

Yellow solid (56.5 mg, 68%). M.p. = 77 – 78 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.14 (s, 1H), 8.95 (d, $J$ = 8.8 Hz, 1H), 8.21 (d, $J$ = 8.4 Hz, 1H), 7.74 (t, $J$ = 7.6 Hz, 1H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.25 (d, $J$ = 4.4 Hz, 4H), 7.17 (dd, $J$ = 8.4, 4.4 Hz, 1H), 4.71 (s, 2H), 4.01 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 165.2, 145.9, 138.8, 134.6, 131.6, 128.7, 128.7, 127.6, 126.9, 126.6, 126.3, 125.8, 119.7, 52.4, 42.6.

**HRMS** (ESI) calcd for C$_{18}$H$_{16}$NO$_2$ [M + H]$^+$ 278.1176, found 278.1181.

**2-benzylquinoxaline (14).**

According to the general procedure A.

Red oil (30.4 mg, 46%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (s, 1H), 8.07 (ddd, $J$ = 7.6, 6.0, 1.6 Hz, 2H), 7.81 – 7.67 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 4.38 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.9, 146.1, 142.2, 141.3, 138.0, 130.2, 129.4, 129.3, 129.2, 129.2, 129.0, 127.0, 43.1.

**HRMS** (ESI) calcd for C$_{15}$H$_{13}$N$_2$ [M + H]$^+$ 221.1073, found 221.1076.

**2-benzyl-4-phenylpyridine (15).**
According to the general procedure B.

Yellow oil (33.1 mg, 45%).

\( R_f 0.30 \) (Petroleum ether/EtOAc, 5/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.59 (d, J = 4.8 \text{ Hz}, 1H), 7.57 (d, J = 7.2 \text{ Hz}, 2H), 7.44 (dd, J = 16.0, 8.4 \text{ Hz}, 3H), 7.35 – 7.27 (m, 6H), 7.23 – 7.15 (m, 1H), 4.22 (s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 161.6, 149.9, 149.1, 139.6, 138.5, 129.2, 129.0, 128.8, 127.2, 126.6, 121.2, 119.5, 44.9.

HRMS (ESI) calcd for C\(_{18}\)H\(_{16}\)N \([\text{M} + \text{H}]^+\) 246.1277, found 246.1280.

4-benzyl-3,6-dichloropyridazine (16).

According to the general procedure B.

Yellow oil (30.7 mg, 43%).

\( R_f 0.30 \) (Petroleum ether/EtOAc, 5/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.47 – 7.31 (m, 3H), 7.19 (d, J = 7.2 \text{ Hz}, 2H), 7.08 (s, 1H), 4.06 (s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 156.9, 156.3, 143.7, 134.6, 129.6, 129.5, 127.9, 38.4.

HRMS (ESI) calcd for C\(_{11}\)H\(_9\)Cl\(_2\)N\(_2\) \([\text{M} + \text{H}]^+\) 239.0137, found 239.0135.

9-benzylacridine (17).

According to the general procedure A.

Brown solid (50.8 mg, 63%). M.p. = 163 – 164 °C.

\( R_f 0.30 \) (Petroleum ether/EtOAc, 5/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.25 (d, J = 8.8 \text{ Hz}, 2H), 8.18 (d, J = 8.8 \text{ Hz}, 2H), 7.78 – 7.67 (m, 2H), 7.47 (dddd, J = 8.8, 6.4, 1.0 \text{ Hz}, 2H), 7.22 – 7.10 (m, 3H), 7.07 (d, J = 7.2 \text{ Hz}, 2H), 4.95 (s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 148.9, 143.5, 139.4, 130.4, 129.9, 128.8, 128.2, 126.5, 126.1, 125.7, 124.8, 33.2.

HRMS (ESI) calcd for C\(_{20}\)H\(_{16}\)N \([\text{M} + \text{H}]^+\) 270.1277, found 270.1281.

6-benzylphenanthridine (18).
According to the *general procedure A*.
Yellow solid (76.7 mg, 95%). M.p. = 103 – 104 °C.
\( R_t \) 0.30 (Petroleum ether/EtOAc, 5/1).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 8.50 (d, \( J = 8.4 \) Hz, 1H), 8.45 (d, \( J = 7.6 \) Hz, 1H), 8.19 (dd, \( J = 8.0, 0.7 \) Hz, 1H), 8.12 (d, \( J = 8.4 \) Hz, 1H), 7.74 – 7.61 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.29 (d, \( J = 7.6 \) Hz, 2H), 7.20 (t, \( J = 7.6 \) Hz, 2H), 7.12 (t, \( J = 7.2 \) Hz, 1H), 4.72 (s, 2H).

**\(^13\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 160.1, 143.8, 139.2, 133.2, 130.3, 129.9, 128.7, 128.6, 127.3, 127.0, 126.7, 125.4, 123.9, 122.4, 122.0, 43.1.

**HRMS (ESI)** calcd for \( \text{C}_{20}\text{H}_{16}\text{N} \) \([M + H]^+\) 270.1277, found 270.1282.

2-benzyl-4,6-dimethylpyrimidine (19).

\[
\text{\begin{tikzpicture}[baseline={([yshift=-.5ex]current bounding box.center)}]
\node (A) at (0,0) {N};
\node (B) at (0.5,0) {N};
\node (C) at (0.5,-0.5) {Ph};
\draw (A) -- (B) -- (C);
\end{tikzpicture}}
\]

According to the *general procedure B*.
Yellow solid (30.9 mg, 52%). M.p. = 68 – 69 °C.
\( R_t \) 0.30 (Petroleum ether/EtOAc, 5/1).

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 (d, \( J = 7.6 \) Hz, 2H), 7.27 (d, \( J = 6.8 \) Hz, 2H), 7.19 (t, \( J = 7.2 \) Hz, 1H), 6.85 (s, 1H), 4.21 (s, 2H), 2.44 (s, 6H).

**\(^13\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 169.1, 166.9, 138.8, 129.2, 128.4, 126.4, 117.7, 46.1, 24.2.

**HRMS (ESI)** calcd for \( \text{C}_{13}\text{H}_{15}\text{N}_2 \) \([M + H]^+\) 199.1230, found 199.1233.

2-benzylquinazolin-4(3\(H\))-one (20).

\[
\text{\begin{tikzpicture}[baseline={([yshift=-.5ex]current bounding box.center)}]
\node (A) at (0,0) {N};
\node (B) at (0.5,0) {N};
\node (C) at (0.5,-0.5) {NH};
\node (D) at (1,0) {O};
\node (E) at (1.25,0) {Ph};
\node (F) at (1,1.5) {O};
\node (G) at (0.25,1.5) {O};
\draw (A) -- (B) -- (C) -- (D) -- (E);
\draw (F) .. controls (0.25,1) .. (A);
\draw (G) .. controls (0.25,2) .. (A);
\end{tikzpicture}}
\]

According to the *general procedure B*.
White solid (38.9 mg, 55%). M.p. = 249 – 250 °C.
\( R_t \) 0.30 (Petroleum ether/EtOAc, 5/1).

**\(^1\)H NMR** (400 MHz, DMSO) \( \delta \) 12.43 (s, 1H), 8.08 (d, \( J = 8.0 \) Hz, 1H), 7.78 (t, \( J = 7.6 \) Hz, 1H), 7.61 (d, \( J = 8.0 \) Hz, 1H), 7.47 (t, \( J = 7.6 \) Hz, 1H), 7.39 (d, \( J = 7.2 \) Hz, 2H), 7.33 (t, \( J = 7.6 \) Hz, 2H), 7.24 (t, \( J = 7.2 \) Hz, 1H), 3.94 (s, 2H).

**\(^13\)C NMR** (100 MHz, DMSO) \( \delta \) 162.3, 156.4, 149.4, 137.04, 134.9, 129.4, 129.0, 127.4, 127.3, 126.7, 126.2, 121.2, 41.2.

**HRMS (ESI)** calcd for \( \text{C}_{15}\text{H}_{13}\text{N}_2\text{O} \) \([M + H]^+\) 237.1022, found 237.1022.

2-benzyl-6,7-dimethoxyquinazolin-4(3\(H\))-one (21).

\[
\text{\begin{tikzpicture}[baseline={([yshift=-.5ex]current bounding box.center)}]
\node (A) at (0,0) {N};
\node (B) at (0.5,0) {N};
\node (C) at (0.5,-0.5) {NH};
\node (D) at (1,0) {O};
\node (E) at (1.25,0) {Ph};
\node (F) at (1,1.5) {O};
\node (G) at (0.25,1.5) {O};
\draw (A) -- (B) -- (C) -- (D) -- (E);
\draw (F) .. controls (0.25,1) .. (A);
\draw (G) .. controls (0.25,2) .. (A);
\end{tikzpicture}}
\]

According to the *general procedure B*.
White solid (42.6 mg, 48%). M.p. = 66 – 67 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, DMSO) $\delta$ 12.34 (s, 1H), 7.48 – 7.36 (m, 5H), 7.30 (t, $J$ = 7.2 Hz, 1H), 7.14 (s, 1H), 3.96 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H).

$^1$H NMR (400 MHz, DMSO) $\delta$ 161.2, 154.5, 154.4, 148.2, 145.0, 136.8, 128.8, 128.4, 126.7, 113.5, 107.8, 104.8, 55.9, 55.6, 40.6.

HRMS (ESI) calcd for C_{17}H_{17}N_{2}O_{3} $[M + H]^+$ 297.1234, found 297.1236.

2-benzylbenzo[d]thiazole (22).

According to the general procedure B.

Yellow oil (54.7 mg, 81%).

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J$ = 8.0 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.40 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 4.44 (s, 2H).

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.3, 153.4, 137.3, 135.8, 129.3, 129.0, 127.5, 126.1, 124.9, 122.9, 121.7, 40.8.

HRMS (ESI) calcd for C_{14}H_{12}NS $[M + H]^+$ 226.0685, found 226.0685.

7-benzyl-3-bromo-6-chloroimidazo[1,2-b]pyridazine (23).

According to the general procedure B.

Yellow solid (39.5 mg, 41%). M.p. = 60 – 61 °C.

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (s, 1H), 7.41 – 7.27 (m, 5H), 6.72 (s, 1H), 4.37 (s, 2H).

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.4, 142.5, 139.0, 136.2, 134.2, 129.6, 129.0, 127.5, 117.62, 101.7, 35.7.

HRMS (ESI) calcd for C_{13}H_{10}BrClN$_3$ $[M + H]^+$ 321.9741, found 321.9739.

7-benzyl-3-bromoimidazo[1,2-b]pyridazine (24).

According to the general procedure B.

Yellow solid (42.2 mg, 49%). M.p. = 70 – 71 °C.

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 4.4 Hz, 1H), 7.79 (s, 1H), 7.39 – 7.27 (m, 5H), 6.71 (d, $J$ = 4.4 Hz, 1H), 4.41 (s, 2H).

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.1, 140.8, 140.4, 136.9, 133.6, 129.6, 129.0, 127.3, 115.6, 101.0, 35.6.

HRMS (ESI) calcd for C_{13}H_{11}BrN$_3$ $[M + H]^+$ 288.0131, found 288.0132.
2-(4-\((\text{tert}-\text{butyl})\)benzyl)-4-methylquinoline (25).

According to the general procedure A.
Yellow solid (72.8 mg, 84%). M.p. = 63 – 64 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.71 – 7.60 (m, 1H), 7.54 – 7.43 (m, 1H), 7.32 (dd, $J = 8.4$, 2.0 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.06 (s, 1H), 4.25 (s, 2H), 2.56 (s, 3H), 1.28 (s, 9H).
$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 161.1, 149.2, 147.7, 144.5, 136.3, 129.6, 129.2, 128.9, 126.9, 125.7, 125.6, 123.7, 122.3, 45.1, 34.5, 31.4, 18.8.
HRMS (ESI) calcd for C$_{21}$H$_{24}$N $[\text{M} + \text{H}]^+$ 290.1903, found 290.1909.

4-methyl-2-(2-methylbenzyl)quinolone (26).

According to the general procedure A.
Yellow solid (47.4 mg, 64%). M.p. = 55 – 56 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 7.91 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.56 – 7.46 (m, 1H), 7.22 – 7.12 (m, 4H), 6.93 (s, 1H), 4.31 (s, 2H), 2.56 (s, 3H), 2.29 (s, 3H).
$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 160.7, 147.7, 144.6, 137.6, 137.2, 130.5, 130.3, 129.5, 129.2, 126.9, 126.8, 125.8, 125.7, 121.7, 43.3, 20.0, 18.8.
HRMS (ESI) calcd for C$_{18}$H$_{18}$N $[\text{M} + \text{H}]^+$ 248.1434, found 248.1437.

2-(3,4-dimethoxybenzyl)-4-methylquinoline (27).

According to the general procedure A.
Yellow oil (80.9 mg, 92%).
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.4$, 0.8 Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.05 (s, 1H), 6.90 – 6.83 (m, 2H), 6.82 – 6.75 (m, 1H), 4.22 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 2.58 (s, 3H).
$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 161.1, 149.0, 147.5, 147.6, 144.6, 131.9, 129.4, 129.1, 126.8, 125.7, 123.6, 122.0, 121.2, 112.4, 111.2, 55.8, 45.1, 18.7.
HRMS (ESI) calcd for C$_{19}$H$_{20}$O$_2$ [M + H]$^+$ 294.1489, found 294.1489.

2-(3-fluorobenzyl)-4-methylquinoline (28).
According to the general procedure A.
Brown solid (27.1 mg, 36%). M.p. = 50 – 51 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 8.4 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 7.70 (t, $J$ = 7.6 Hz, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.32 – 7.21 (m, 1H), 7.13 – 6.97 (m, 3H), 6.91 (t, $J$ = 8.4 Hz, 1H), 4.28 (s, 2H), 2.62 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.1 (d, $J$ = 245.8 Hz), 160.1, 147.8, 145.0, 141.9 (d, $J$ = 7.3 Hz), 130.1 (d, $J$ = 8.4 Hz), 129.5 (d, $J$ = 25.5 Hz), 127.0, 126.0, 125.0, 124.9, 123.8, 122.2, 116.2 (d, $J$ = 21.2 Hz), 113.5 (d, $J$ = 21.0 Hz), 45.2 (d, $J$ = 1.5 Hz), 18.8.

HRMS (ESI) calcd for C$_{17}$H$_{15}$FN [M + H]$^+$ 252.1183, found 252.1187.

2-(4-chlorobenzyl)-4-methylquinoline (29).

According to the general procedure A.
Yellow solid (36.8 mg, 46%). M.p. = 41 – 42 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.69 (t, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 7.6 Hz, 1H), 7.30 – 7.19 (m, 4H), 7.02 (s, 1H), 4.24 (s, 2H), 2.60 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.3, 147.8, 144.9, 137.9, 132.4, 130.6, 129.6, 129.3, 128.8, 127.0, 126.0, 123.8, 122.1, 44.9, 18.8.

HRMS (ESI) calcd for C$_{17}$H$_{15}$ClN [M + H]$^+$ 268.0888, found 268.0891.

4-methyl-2-(naphthalen-2-ylmethyl)quinolone (30).

According to the general procedure A.
Yellow solid (53.3 mg, 64%). M.p. = 48 – 49 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J$ = 8.4 Hz, 1H), 7.86 (d, $J$ = 8.4 Hz, 1H), 7.75 (dd, $J$ = 11.6, 4.8 Hz, 4H), 7.70 – 7.62 (m, 1H), 7.46 (dd, $J$ = 11.2, 4.0 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.03 (s, 1H), 4.43 (s, 2H), 2.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8, 147.7, 144.7, 137.0, 133.7, 132.3, 129.6, 129.2, 128.3, 127.8, 127.7, 127.6, 127.5, 126.9, 126.1, 125.8, 125.6, 123.7, 122.3, 45.7, 18.7.

HRMS (ESI) calcd for C$_{21}$H$_{18}$N [M + H]$^+$ 284.1434, found 284.1438.
(R)-4-methyl-2-(1-phenylethyl)quinolone (31).

According to the general procedure A.
Red solid (38.5 mg, 52%). M.p. = 63 – 64 °C.
Rf 0.30 (Petroleum ether/EtOAc, 5/1).
1H NMR (400 MHz, CDCl3) δ 8.11 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.51 (dd, J = 11.2, 4.0 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.02 (s, 1H), 4.45 (q, J = 7.2 Hz, 1H), 2.59 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H).
13C NMR (100 MHz, CDCl3) δ 164.9, 147.6, 144.9, 144.5, 129.9, 129.1, 128.6, 127.9, 127.1, 126.5, 125.8, 123.7, 121.4, 48.1, 20.5, 18.9.

2-(benzo[b]thiophen-3-ylmethyl)-4-methylquinoline (32).

According to the general procedure A.
Yellow solid (63.3 mg, 73%). M.p. = 77 – 78 °C.
Rf 0.50 (Petroleum ether/EtOAc, 10/1).
1H NMR (400 MHz, CDCl3) δ 8.12 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.19 (s, 1H), 6.51 (s, 2H), 2.56 (s, 3H).
13C NMR (100 MHz, CDCl3) δ 159.6, 147.8, 144.9, 144.5, 129.9, 129.1, 128.6, 127.9, 127.1, 125.9, 124.4, 124.2, 123.8, 123.7, 122.9, 122.4, 121.9, 38.9, 18.8.
HRMS (ESI) calcd for C19H16NS [M + H]+ 290.0998, found 290.0998.

methyl 1-((4-methylquinolin-2-yl)methyl)-1H-indole-3-carboxylate (33).

According to the general procedure A.
Yellow solid (68.5 mg, 84%). M.p. = 145 – 146 °C.
Rf 0.30 (Petroleum ether/EtOAc, 5/1).
1H NMR (400 MHz, CDCl3) δ 8.21 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.31 – 7.16 (m, 2H), 6.75 (s, 1H), 5.56 (s, 2H), 3.92 (s, 3H), 2.50 (s, 3H).
13C NMR (100 MHz, CDCl3) δ 165.5, 155.9, 147.5, 146.2, 136.9, 134.9, 129.8, 129.7, 127.5, 126.9, 126.7, 123.9, 123.2, 122.2, 121.8, 119.1, 110.6, 108.0, 53.5, 51.1, 18.9.
HRMS (ESI) calcd for C21H19N2O2 [M + H]+ 331.1441, found 331.1442.
4-methyl-2-(phenoxy)methyl)quinolone (34).

![Chemical Structure]

According to the general procedure A.
Yellow oil (47.1 mg, 63%).
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 8.4 Hz, 1H), 7.99 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.72 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.56 (ddd, $J$ = 8.4, 7.2, 1.2 Hz, 1H), 7.52 (s, 1H), 7.36 – 7.25 (m, 2H), 7.03 (dd, $J$ = 8.8, 0.8 Hz, 2H), 6.96 (t, $J$ = 7.2 Hz, 1H), 5.34 (s, 2H), 2.71 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.6, 157.7, 147.5, 145.5, 129.7, 129.6, 127.8, 126.4, 123.9, 121.3, 119.9, 115.0, 71.4, 19.1.
HRMS (ESI) calcd for C$_{17}$H$_{16}$NO $[M + H]^+$ 250.1226, found 250.1226.

4-methyl-2-((p-tolyloxy)methyl)quinolone (35).

![Chemical Structure]

According to the general procedure A.
Yellow oil (40.2 mg, 51%).
$R_f$ 0.50 (Petroleum ether/EtOAc, 10/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 1H), 7.96 (dd, $J$ = 8.4, 0.4 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.60 – 7.45 (m, 2H), 7.07 (d, $J$ = 8.4 Hz, 2H), 6.93 (d, $J$ = 8.4 Hz, 2H), 5.30 (s, 2H), 2.68 (s, 3H), 2.27 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.9, 156.5, 147.5, 145.5, 130.4, 130.1, 129.6, 129.5, 126.3, 123.9, 119.8, 114.8, 71.5, 20.6, 19.0.
HRMS (ESI) calcd for C$_{18}$H$_{18}$NO $[M + H]^+$ 264.1383, found 264.1386.

2-((4-((tert-butyl)phenoxy)methyl)-4-methylquinoline (36).

![Chemical Structure]

According to the general procedure A.
Brown solid (60.4 mg, 66%). M.p. = 35 – 36 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 8.4 Hz, 1H), 7.97 (d, $J$ = 8.4 Hz, 1H), 7.71 (t, $J$ = 7.6 Hz, 1H), 7.60 – 7.45 (m, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 5.32 (s, 2H), 2.69 (s, 3H),
1.29 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.9, 156.4, 147.5, 145.4, 143.9, 129.6, 129.5, 127.7, 126.4, 126.3, 123.9, 119.9, 114.4, 71.5, 34.2, 31.6, 19.0.

HRMS (ESI) calcd for C$_{21}$H$_{24}$NO [M + H]$^+$ 306.1852, found 306.1856.

2-((4-fluorophenoxy)methyl)-4-methylquinoline (37).

![Chemical structure of 2-((4-fluorophenoxy)methyl)-4-methylquinoline (37).]

According to the general procedure A.
Yellow solid (50.5 mg, 63%). M.p. = 54 – 55 °C.
$R_f$ 0.50 (Petroleum ether/EtOAc, 10/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.4$ Hz, 1H), 7.97 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.71 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.55 (ddd, $J = 8.4$, 7.2, 1.2 Hz, 1H), 7.48 (s, 1H), 6.96 (d, $J = 6.4$ Hz, 4H), 5.28 (s, 2H), 2.69 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6 (d, $J = 240$ Hz), 157.4, 154.7, 147.5, 145.5, 129.6 (d, $J = 2.5$ Hz), 127.7, 126.4, 123.9, 119.8, 116.1, 116.0, 115.9, 72.0, 19.0.

HRMS (ESI) calcd for C$_{17}$H$_{15}$FNO [M + H]$^+$ 268.1132, found 268.1136.

2-((4-chlorophenoxy)methyl)-4-methylquinoline (38).

![Chemical structure of 2-((4-chlorophenoxy)methyl)-4-methylquinoline (38).]

According to the general procedure A.
Yellow solid (54.3 mg, 64%). M.p. = 77 – 78 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.49 (s, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 2H), 5.32 (s, 2H), 2.72 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 157.1, 147.5, 145.6, 129.6, 126.5, 126.1, 123.9, 119.8, 116.3, 71.7, 19.0.

HRMS (ESI) calcd for C$_{17}$H$_{15}$ClNO [M + H]$^+$ 284.0837, found 284.0839.

2-((4-bromophenoxy)methyl)-4-methylquinoline (39).

![Chemical structure of 2-((4-bromophenoxy)methyl)-4-methylquinoline (39).]

According to the general procedure A.
Yellow solid (54.0 mg, 55%). M.p. = 72 – 73 °C.
$R_f$ 0.50 (Petroleum ether/EtOAc, 10/1).
**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, J = 8.4 Hz, 1H), 7.97 (dd, J = 8.4, 0.8 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.45 (s, 1H), 7.41 – 7.32 (m, 2H), 6.94 – 6.85 (m, 2H), 5.28 (s, 2H), 2.69 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.7, 157.0, 147.5, 145.6, 132.5, 129.6, 129.6, 127.7, 126.5, 123.9, 119.8, 116.8, 113.5, 71.6, 19.0.

**HRMS** (ESI) calcd for C<sub>17</sub>H<sub>15</sub>BrNO [M + H]<sup>+</sup> 328.0332, found 328.0334.

2-((3-chlorophenoxy)methyl)-4-methylquinoline (40).

![2-((3-chlorophenoxy)methyl)-4-methylquinoline (40)](image)

According to the general procedure A.

Yellow oil (34.8 mg, 41%).

R<sub>f</sub> 0.50 (Petroleum ether/EtOAc, 10/1).

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 6.8 Hz, 1H), 7.56 (t, J = 6.8 Hz, 1H), 7.46 (s, 1H), 7.19 (td, J = 8.0, 2.4 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 7.00 – 6.83 (m, 2H), 5.30 (d, J = 2.4 Hz, 2H), 2.71 (d, J = 2.0 Hz, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.3, 156.9, 147.4, 145.6, 135.1, 130.4, 129.7, 129.6, 127.8, 126.5, 123.9, 121.5, 119.8, 115.7, 113.2, 71.6, 19.0.

**HRMS** (ESI) calcd for C<sub>17</sub>H<sub>15</sub>ClNO [M + H]<sup>+</sup> 284.0837, found 284.0838.

4-methyl-2-((p-tolylthio)methyl)quinolone (41).

![4-methyl-2-((p-tolylthio)methyl)quinolone (41)](image)

According to the general procedure A.

Brown oil (31.8 mg, 38%).

R<sub>f</sub> 0.50 (Petroleum ether/EtOAc, 10/1).

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.59 – 7.47 (m, 1H), 7.34 (s, 1H), 7.26 (t, J = 5.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 4.35 (s, 2H), 2.64 (s, 3H), 2.27 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.0, 147.5, 145.6, 135.1, 130.4, 129.7, 129.6, 127.8, 126.5, 123.9, 121.5, 119.8, 115.7, 113.2, 116.0.

**HRMS** (ESI) calcd for C<sub>18</sub>H<sub>18</sub>NS [M + H]<sup>+</sup> 280.1154, found 280.1156.

2-(((4-(tert-butyl)phenyl)thio)methyl)-4-methylquinoline (42).

![2-(((4-(tert-butyl)phenyl)thio)methyl)-4-methylquinoline (42)](image)

According to the general procedure A.
Yellow solid (34.7 mg, 36%). M.p. = 40 – 41 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.37 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 4.36 (s, 2H), 2.64 (s, 3H), 1.26 (s, 9H). $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.0, 149.7, 147.6, 145.0, 132.5, 129.8, 129.7, 129.3, 127.3, 126.2, 126.0, 123.7, 121.8, 41.7, 34.6, 31.4, 18.9.
HRMS (ESI) calcd for C$_{21}$H$_{24}$N$_2$S [M + H]$^+$ 322.1624, found 322.1620.

2-(((4-fluorophenyl)thio)methyl)-4-methylquinoline (43).

According to the general procedure A.
Yellow oil (28.0 mg, 33%).
$R_f$ 0.50 (Petroleum ether/EtOAc, 10/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 8.4$ Hz, 1H), 7.94 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.68 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.53 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.33 (ddd, $J = 12.4$, 7.2, 4.4 Hz, 3H), 6.98 – 6.87 (m, 2H), 4.31 (s, 2H), 2.66 (s, 3H). $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1 (d, $J = 248$ Hz), 157.7, 147.5, 145.1, 132.8 (d, $J = 8.0$ Hz), 130.6 (d, $J = 3.2$ Hz), 129.7, 129.5, 127.3, 126.3, 123.7, 121.7, 116.0 (d, $J = 22.0$ Hz), 42.4, 18.9.
HRMS (ESI) calcd for C$_{17}$H$_{15}$FNS [M + H]$^+$ 284.0904, found 284.0906.

4-methyl-2-(((o-tolylthio)methyl)quinolone (44).

According to the general procedure A.
Brown solid (48.5 mg, 58%). M.p. = 58 – 59 °C.
$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.69 (dd, $J = 11.2$, 4.0 Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.41 – 7.36 (m, 1H), 7.34 (s, 1H), 7.17 – 7.02 (m, 3H), 4.37 (s, 2H), 2.65 (s, 3H), 2.36 (s, 3H). $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.7, 147.6, 145.1, 137.6, 135.5, 130.1, 129.7, 129.4, 128.6, 127.3, 126.6, 126.2, 126.0, 123.7, 121.7, 40.5, 20.4, 18.9.
HRMS (ESI) calcd for C$_{18}$H$_{18}$NS [M + H]$^+$ 280.1154, found 280.1156.

2-benzyl-5,7-dichloro-4-(4-fluorophenoxy)quinolone (45).
According to the *general procedure A*.

Yellow solid (35.7 mg, 30%). M.p. = 112 – 113 °C. 

R<sub>f</sub> 0.30 (Petroleum ether/EtOAc, 5/1).

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 7.12 – 7.05 (m, 2H), 7.04 – 6.98 (m, 2H), 6.46 (s, 1H), 4.12 (s, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 164.0, 162.6, 160.0 (d, J = 244.3 Hz), 151.5, 150.1 (d, J = 2.7 Hz), 138.4, 135.2, 130.2, 129.0, 128.8, 127.7, 126.8, 122.1, 122.0, 117.1 (d, J = 23.4 Hz), 117.0, 107.4, 45.3.

**HRMS** (ESI) calcd for C<sub>22</sub>H<sub>15</sub>Cl<sub>2</sub>FNO [M + H]<sup>+</sup> 398.0509, found 398.0504.

1-(4-((1-benzylisoquinolin-5-yl)sulfonyl)-1,4-diazepan-1-yl)ethan-1-one (46).

According to the *general procedure A*.

Yellow oil (103.6 mg, 82%). 

R<sub>f</sub> 0.30 (Petroleum ether/EtOAc, 5/1).

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.65 (dd, J = 6.4, 2.8 Hz, 1H), 8.41 (dd, J = 8.4, 4.4 Hz, 1H), 8.31 (d, J = 6.4 Hz, 1H), 8.28 – 8.20 (m, 1H), 7.65 – 7.52 (m, 1H), 7.29 – 7.22 (m, 4H), 4.71 (s, 2H), 4.37 – 3.69 (m, 1H), 3.62 (ddd, J = 13.2, 11.2, 6.4 Hz, 3H), 3.52 – 3.47 (m, 3H), 3.43 (dd, J = 11.6, 6.4 Hz, 2H), 3.37 (t, J = 6.0 Hz, 1H), 2.05 (s, 3H), 2.01 – 1.92 (m, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.3, 170.1, 161.3, 161.2, 144.2, 144.1, 138.9, 134.8, 132.6, 132.4, 131.7, 128.8, 128.6, 127.9, 126.6, 125.7, 116.4, 116.3, 50.8, 50.1, 49.2, 48.4, 48.0, 47.7, 46.9, 44.5, 42.7, 29.0, 27.7, 21.6, 21.1.

**HRMS** (ESI) calcd for C<sub>23</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>S [M + H]<sup>+</sup> 424.1689, found 424.1693.

**ethyl 4-(2-benzyl-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (47).**

According to the *general procedure A*.

Red solid (48.1 mg, 34%). M.p. = 119 – 120 °C. 

R<sub>f</sub> 0.30 (Petroleum ether/EtOAc, 5/1).

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.14 (m, 9H), 6.88 (d, J = 7.6 Hz, 1H), 4.23 – 4.02 (m, 11H), 3.79 (s, 2H), 3.41 – 3.21 (m, 2H), 3.19 – 3.03 (m, 2H), 2.87 – 2.70 (m, 2H), 2.53 – 2.21 (m, 2H), 1.26 (t, J =
7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.1, 156.3, 155.6, 139.9, 138.3, 138.0, 137.6, 134.4, 132.9, 130.7, 129.2, 129.0, 128.6, 126.4, 126.2, 121.7, 61.4, 44.9, 44.4, 31.8, 31.4, 31.0, 30.7, 29.8, 14.8.

HRMS (ESI) calcd for C$_{29}$H$_{30}$ClN$_2$O$_2$ [M + H]$^+$ 473.1990, found 473.1993.

1-(6-benzylpyridin-3-yl)-2-methyl-2-(pyridin-3-yl)propan-1-one (48).

According to the general procedure A.

Yellow oil (31.3 mg, 33%).

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 – 8.47 (m, 3H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 7.2$ Hz, 3H), 7.24 – 7.16 (m, 3H), 7.03 (d, $J = 8.4$ Hz, 1H), 4.10 (s, 2H), 1.65 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.9, 164.6, 150.9, 148.6, 147.5, 140.2, 138.4, 137.8, 133.5, 129.2, 128.8, 128.7, 126.8, 124.0, 122.7, 50.3, 44.7, 27.5.

HRMS (ESI) calcd for C$_{21}$H$_{21}$N$_2$O [M + H]$^+$ 317.1648, found 317.1650.

1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinoline (49).

According to the general procedure A.

Yellow solid (89.5 mg, 88%). M.p. = 138 – 139 °C.

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 5.6$ Hz, 1H), 7.42 (d, $J = 5.6$ Hz, 1H), 7.33 (s, 1H), 7.03 (s, 1H), 6.82 (d, $J = 7.2$ Hz, 2H), 6.76 (d, $J = 8.4$ Hz, 1H), 4.53 (s, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.7, 152.3, 149.7, 148.9, 147.4, 140.9, 133.4, 132.2, 128.8, 120.4, 118.7, 111.8, 111.1, 105.2, 104.1, 55.9, 55.8, 55.7, 42.2.

HRMS (ESI) calcd for C$_{20}$H$_{22}$NO$_4$ [M + H]$^+$ 340.1543, found 340.1545.

prop-1-ene-1,1,3-triyltribenzene (51).

The spectral data is consistent with the literature data.\(^7\)

Yellow oil.

$R_f$ 0.30 (Petroleum ether/EtOAc, 5/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (t, $J = 7.2$ Hz, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.23 (m, 8H), 7.20 (d, $J = 5.6$ Hz, 3H), 6.27 (t, $J = 7.6$ Hz, 1H), 3.47 (d, $J = 7.6$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
1,2-di(naphthalen-2-yl)ethane (53).

According to the *general procedure A*. The spectral data is consistent with the literature data.\(^8\)

Yellow solid. M.p. = 164 – 165 °C.

\(R_f 0.30\) (Petroleum ether/EtOAc, 5/1).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 7.77\) (dd, \(J = 15.4, 8.0\) Hz, 6H), 7.63 (s, 2H), 7.47 – 7.37 (m, 4H), 7.33 (d, \(J = 8.4\) Hz, 2H), 3.15 (s, 4H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 139.4, 133.8, 132.2, 128.0, 127.8, 127.6, 126.5, 126.0, 125.3, 38.1\).

6. Gram-scale Reaction

\[
\begin{align*}
\text{N} & \quad \text{TFA} \\
\text{1} & \quad (0.8 \text{ mL, 6 mmol, 1.0 equiv}) \\
\text{2} & \quad (2.0 \text{ g, 12 mmol, 2.0 equiv}) \\
\text{3} & \quad (1.16 \text{ g, 83%})
\end{align*}
\]

To a 250 mL glass vial was added lepidine 1 (0.8 mL, 6 mmol, 1.0 equiv), benzyltrimethylsilane 2 (2.0 g, 12 mmol, 2.0 equiv), (NH\(_4\))\(_2\)S\(_2\)O\(_8\) (4.0 g, 18 mmol, 3.0 equiv), TFA (0.9 mL, 12 mmol, 2.0 equiv) and 30 mL of DMSO. The reaction mixture was stirred rapidly at 30 °C for 24 h. The mixture was diluted with 100 mL of aqueous 1 M NaHCO\(_3\) solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na\(_2\)SO\(_4\), and concentrated in vacuo. After purification by flash column chromatography on silica gel, the product was obtained in 83% yield.

References

NMR Spectra

$^1$H NMR spectrum of compound 3
$^{13}$C NMR spectrum of compound 3

$^1$H NMR spectrum of compound 4
\begin{center}
\textbf{C NMR spectrum of compound 4}
\end{center}

\begin{center}
\textbf{H NMR spectrum of compound 5}
\end{center}
$^{13}$C NMR spectrum of compound 5

$^1$H NMR spectrum of compound 6
\(^{13}\)C NMR spectrum of compound 6

\(^{1}\)H NMR spectrum of compound 7
$^{13}$C NMR spectrum of compound 7

$^1$H NMR spectrum of compound 8
$^{13}$C NMR spectrum of compound 8

$^1$H NMR spectrum of compound 9
$\text{\(^1\)H NMR spectrum of compound 10}$

$\text{\(^{13}\)C NMR spectrum of compound 9}$
$^{13}$C NMR spectrum of compound 11

$^{1}$H NMR spectrum of compound 12
$^{13}$C NMR spectrum of compound 12

$^1$H NMR spectrum of compound 13
$^{13}$C NMR spectrum of compound 13

$^1$H NMR spectrum of compound 14
$^{13}$C NMR spectrum of compound 14

$^1$H NMR spectrum of compound 15
$^{13}$C NMR spectrum of compound 15

$^1$H NMR spectrum of compound 16
$^{13}$C NMR spectrum of compound 16

$^1$H NMR spectrum of compound 17
\(^{13}\)C NMR spectrum of compound 17

\(^1\)H NMR spectrum of compound 18
$^{13}$C NMR spectrum of compound 18

$^1$H NMR spectrum of compound 19
$^{13}$C NMR spectrum of compound 19

$^1$H NMR spectrum of compound 20
$^{13}$C NMR spectrum of compound 21

$^1$H NMR spectrum of compound 22
$^{13}$C NMR spectrum of compound 22

$^1$H NMR spectrum of compound 23
$^{13}$C NMR spectrum of compound 23

$^1$H NMR spectrum of compound 24
\(^{13}\text{C}\) NMR spectrum of compound 24

\(^1\text{H}\) NMR spectrum of compound 25
$^{13}$C NMR spectrum of compound \textbf{25}

$^1$H NMR spectrum of compound \textbf{26}
$^{13}$C NMR spectrum of compound 26

$^1$H NMR spectrum of compound 27
$^{13}$C NMR spectrum of compound 27

$^1$H NMR spectrum of compound 28
$^{13}$C NMR spectrum of compound 28

$^1$H NMR spectrum of compound 29
\textbf{\textsuperscript{13}C NMR spectrum of compound 29}

\textbf{\textsuperscript{1}H NMR spectrum of compound 30}
$^{13}$C NMR spectrum of compound 30

$^1$H NMR spectrum of compound 31
$^{13}$C NMR spectrum of compound 31

$^1$H NMR spectrum of compound 32
$^{13}$C NMR spectrum of compound 32

$^1$H NMR spectrum of compound 33
$^{13}$C NMR spectrum of compound 33

$^1$H NMR spectrum of compound 34
$^{13}$C NMR spectrum of compound 34

$^1$H NMR spectrum of compound 35
$^{13}$C NMR spectrum of compound 35

$^1$H NMR spectrum of compound 36
$^1$H NMR spectrum of compound 37

$^{13}$C NMR spectrum of compound 36
$^{13}$C NMR spectrum of compound 37

$^1$H NMR spectrum of compound 38
$^{13}$C NMR spectrum of compound 38

$^1$H NMR spectrum of compound 39
$^{13}$C NMR spectrum of compound 39

$^1$H NMR spectrum of compound 40
C NMR spectrum of compound 40

\(^1\)H NMR spectrum of compound 41
$^{13}$C NMR spectrum of compound 41

$^1$H NMR spectrum of compound 42
$^{13}$C NMR spectrum of compound 42

$^1$H NMR spectrum of compound 43
\[\text{\(^1\)H NMR spectrum of compound 44}\]

\[\text{\(^{13}\)C NMR spectrum of compound 43}\]
$^{13}$C NMR spectrum of compound 44

$^1$H NMR spectrum of compound 45
$^{13}$C NMR spectrum of compound 45

$^1$H NMR spectrum of compound 46
$^{13}$C NMR spectrum of compound 46

$^1$H NMR spectrum of compound 47
$^{13}$C NMR spectrum of compound 47

$^1$H NMR spectrum of compound 48
$^{13}$C NMR spectrum of compound 48

$^1$H NMR spectrum of compound 49
$^{13}$C NMR spectrum of compound 49

$^1$H NMR spectrum of compound 51
$^{13}$C NMR spectrum of compound 51

$^1$H NMR spectrum of compound 53
$^{13}$C NMR spectrum of compound 53