Supporting Information

A Facile and Efficient [4 + 2] Cyclization Reaction of Sulfur Ylides: Access to N-Fused Benzimidazoles

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1. **General information**

Unless stated otherwise, all reactions for preparing compound 1a-w were carried out under an air atmosphere and all reactions for providing compound 3a-w were performed under argon atmosphere at room temperature. All reagents and solvents were of commercial quality and were used without further purification. Purification was carried out according to standard laboratory methods\(^1\). All reactions were monitored by TLC analysis with silica gel-coated plates with fluorescent indicator UV254. \(^1\)H and \(^13\)C NMR spectra were obtained on either a Bruker AV 300 at 300 MHz and 75 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are reported in Hz with TMS at 0.0 ppm (\(^1\)H and \(^13\)C) or CDCl\(_3\) referenced at 7.26 (\(^1\)H) and 77.0 ppm (\(^13\)C) and DMSO-\(d_6\) referenced at 2.50 (\(^1\)H) and 39.5 (\(^13\)C). Mass spectra were measured with an Agilent Q-TOF 6520 mass spectrometer using ESI ionization.

2. **General procedure for the synthesis of 1a-w**

\[
\begin{align*}
\text{R}^1\text{NH}_2 + \text{HOOC-R}^2 \xrightarrow{4N\text{HCl reflux}} \text{R}^1\text{NHR}^2\text{OH}
\end{align*}
\]

To a 50 mL round bottomed flask was added different substituted 1,2-phenylenediamine I (10 mmol, 1.0 equiv.), requisite acid 9 (15 mmol, 1.5 equiv.) and 4N hydrochloric acid (20 mL). The mixture was heated for 6 h under reflux. The reaction mixture was cooled to room temperature and ammonia solution was added and the mixture cooled in ice until precipitate formed. The resulting solid was recrystallised from aqueous ethanol to give compound 1a-w as a solid\(^2\).

3. **General procedure for the synthesis of 2**

A solution of 2-bromoethyl trifluoromethanesulfonate\(^3\) (4.12 g, 16.0 mmol) in anhydrous toluene (12 mL) was treated with phenyl sulfide (3.66 g, 19.2 mmol) at room temperature under argon with stirring. The reaction mixture was then heated at 100 °C under argon for 5 hours. The solution was allowed to cool to RT and diethyl ether (20 mL) was added to precipitate the product 9 which was isolated by filtration as a white to grey powder (3.22 g, 45%) after washing with Et\(_2\)O and used in the next step without further purification\(^4\).

4. **General procedure for the synthesis of 3a-w**

\[
\begin{align*}
\text{R}^1\text{NHR}^2_{\text{X}} \xrightarrow{\text{Br, PhI, KOH \text{AcN-H}_2\text{O}2:1 \text{O}^\circ \text{C to rt}}} \text{R}^1\text{NHR}^2_{\text{X}}
\end{align*}
\]
In a 25 mL round bottomed flask compound 1a-w (0.4 mmol, 1.0 equiv.) and bromoethylsulfonyl salt 2 (0.2 mmol, 2.0 equiv.) was dissolved with acetonitrile: water (ACN: H$_2$O) 2:1 and was treated with KOH (1.6 mmol, 4.0 equiv.) at 0 °C under N$_2$ for 30 minutes. Then mixture was warmed to room temperature and was stirred for 12 hours until the reaction completed. After that, reaction system was quenched with saturated ammonium chloride solution (5 mL), and was extracted with DCM (3 x 30 mL). The combined organic layer washed with H$_2$O (2 x 10 mL), dried with anhydrous sodium sulfate. After concentration, product was purified using column chromatography on silica gel with suitable eluent.

5. Characterization of products

![Structure of 1H-benzimidazol-2-methanol (1a)](image)

1H-benzimidazol-2-methanol (1a)\(^5\): White solid, 93% yield, mp 157-159 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): δ 12.34 (brs, 1H), 7.48-7.51 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.12-7.15 (dd, $J = 6.0, 3.2$ Hz, 2H), 5.76 (brs, 1H), 4.70 (s, 2H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 155.53, 138.95, 121.86, 115.26, 58.12.

HRMS (ESI-TOF) calcd for C$_8$H$_8$N$_2$O $[M+H]^+$: 149.0709; found: 149.0717.

![Structure of (5-Methoxy-1H-benzimidazol-2-yl)-methanol (1b)](image)

(5-Methoxy-1H-benzimidazol-2-yl)-methanol (1b)\(^6\): bright brown solid, 66% yield, mp 197-199 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): δ 7.38 (d, $J = 8.7$ Hz, 1H), 7.00 (d, $J = 2.3$ Hz, 1H), 6.78 (dd, $J = 8.7, 2.4$ Hz, 1H), 5.56 (brs, 1H), 4.65 (s, 2H), 3.77 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 155.71, 155.02, 111.08, 58.16, 55.84.

HRMS (ESI-TOF) calcd for C$_9$H$_{10}$N$_2$O$_2$ [M+H]$^+$: 179.0815; found: 179.0819.

![Structure of (5-Methyl-1H-benzimidazol-2-yl)-methanol (1c)](image)

(5-Methyl-1H-benzimidazol-2-yl)-methanol (1c)\(^6\): pale creamy powdery solid, 68% yield, mp 176-178 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): δ 7.38 (d, $J = 8.1$ Hz, 1H), 7.28 (s, 1H), 6.99 (dd, $J = 8.2, 1.1$ Hz, 1H), 5.94 (brs, 1H), 4.67 (s, 2H), 2.39 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 155.20, 138.59, 137.29, 131.01, 123.36, 115.16, 114.64, 58.04, 21.71.

HRMS (ESI-TOF) calcd for C$_9$H$_{10}$N$_2$O [M+H]$^+$: 163.0866; found: 163.0862.
(4-Methyl-1H-benzimidazol-2-yl)-methanol (1d): brown crystalline, 89% yield, mp 196-198 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.31 (d, $J = 7.9$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.99 (d, $J = 7.2$ Hz, 1H), 5.66 (brs, 1H), 4.69 (s, 2H), 2.50 (s, 3H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 154.81, 139.32, 137.77, 125.50, 122.18, 121.85, 112.10, 58.18, 17.23.

HRMS (ESI-TOF) calcd for C$_9$H$_{10}$N$_2$O [M+H]+: 163.0866; found: 163.0871.

(5,6-Dimethyl-1H-benzimidazol-2-yl)-methanol (1e): brick red solid, 60% yield, mp 243-246 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.26 (s, 2H), 5.74 (brs, 1H), 4.65 (s, 2H), 2.28 (s, 6H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 154.51, 137.50, 130.08, 115.37, 58.13, 20.41.

HRMS (ESI-TOF) calcd for C$_{10}$H$_{12}$N$_2$O [M+H]+: 177.1022; found: 177.1020.

(5,6-Difluoro-1H-benzimidazol-2-yl)-methanol (1f): black solid, 74% yield, mp 198-201 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 12.56 (brs, 1H), 7.51 (t, $J_{H-F} = 9.2$ Hz, 2H), 5.76 (s, 1H), 4.67 (s, 2H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 157.08, 145.11-148.50 (dd, $J_{C-F} = 16.9, 237.3$ Hz), 102.88, 58.02.

HRMS (ESI-TOF) calcd for C$_{10}$H$_6$F$_2$N$_2$O [M+H]+: 185.0521; found: 185.0522.

(5,6-Dichloro-1H-benzimidazol-2-yl)-methanol (1g): red solid, 87% yield, mp 248-250 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.77 (s, 2H), 6.43 (brs, 1H), 4.74 (s, 2H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 158.46, 137.55, 124.95, 116.48, 57.62.

HRMS (ESI-TOF) calcd for C$_8$H$_6$Cl$_2$N$_2$O [M+H]+: 216.9930; found: 216.9928.

(5,6-Dibromo-1H-benzimidazol-2-yl)-methanol (1h): rufous crystalline, 91% yield, mp 260-262 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 12.64 (brs, 1H), 7.87 (s, 2H), 5.83 (s, 1H), 4.71 (d, $J = 4.7$ Hz, 2H).
13C NMR (75 MHz, DMSO-d6): δ 158.40, 115.90, 57.98.

(1H-Naphth[2, 3-d]imidazol-2-yl)-methanol (1i): pale brown crystalline, 57% yield, mp 257-259 °C.
1H NMR (300 MHz, DMSO-d6): δ 12.45 (brs, 1H), 7.96-8.01 (m, 4H), 7.32-7.38 (m, 2H), 5.88 (t, J = 5.9 Hz, 1H), 4.81 (d, J = 4.8 Hz, 2H).
13C NMR (75 MHz, DMSO-d6): δ 160.41, 139.34, 130.04, 128.15, 123.69, 111.17, 58.40.

(1H-benzimidazole-2-yl)-methanol (1j): white powder, 93% yield, mp 170-173 °C.
1H NMR (300 MHz, DMSO-d6): δ 7.48-7.51 (dd, J = 5.9, 3.2 Hz, 2H), 7.12-7.14 (dd, J = 5.9, 3.1 Hz, 2H), 5.81 (brs, 1H), 4.96 (q, J = 6.5 Hz, 1H), 1.52 (d, J = 6.6 Hz, 3H).
13C NMR (75 MHz, DMSO-d6): δ 159.01, 138.84, 121.82, 115.28, 64.09, 23.41.

2-(α-Hydroxyisopropyl)-benzimidazole (1k): colorless crystalline, 59% yield, mp 221-223 °C.
1H NMR (300 MHz, DMSO-d6): δ 12.13 (brs, 1H), 7.48 (m, 2H), 7.12 (dd, J = 6.0, 3.2 Hz, 2H), 5.59 (s, 1H), 1.57 (s, 6H).
13C NMR (75 MHz, DMSO-d6): δ 161.74, 121.58, 69.28, 30.47.

α-(1-Methylethyl)-1H-benzimidazol-2-methanol (II): pale brown crystalline, 25% yield, mp 225-227 °C.
1H NMR (300 MHz, DMSO-d6): δ 12.18 (brs, 1H), 7.47-7.50 (m, 2H), 7.08-7.13 (m, 2H), 5.76 (d, J = 4.7 Hz, 1H), 4.54 (t, J = 5.2 Hz, 1H), 2.15 (dq, J = 13.3, 6.7 Hz, 1H), 0.89 (dd, J = 11.5, 6.8 Hz, 6H).
13C NMR (75 MHz, DMSO-d6): δ 157.80, 121.56, 73.06, 34.08, 19.21, 18.05.
(1H-benzimidazol-2-yl)-cyclohexanol (1m): pale creamy powder, 49% yield, mp 229-232 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.49 (dd, $J = 5.9, 3.2$ Hz, 2H), 7.13 (dd, $J = 6.0, 3.2$ Hz, 2H), 5.38 (s, 1H), 4.54 (t, $J = 5.2$ Hz, 1H), 1.96-2.04 (m, 2H), 1.51-1.82 (m, 7H), 1.29-1.33 (m, 1H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 161.90, 121.69, 115.37, 70.31, 37.32, 25.62, 21.85.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{18}$N$_2$O [M+H]$^+$: 217.1335; found: 217.1340.

2-(α-Hydroxybenzyl)-benzimidazole (1n): pale creamy crystalline, 64% yield, mp 200-203 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 12.37 (brs, 1H), 7.47-7.52 (m, 4H), 7.32-7.37 (m, 2H), 7.23-7.28 (m, 1H), 7.13 (dd, $J = 5.9, 3.1$ Hz, 2H), 6.54 (d, $J = 3.4$ Hz, 1H), 5.94 (d, $J = 2.5$ Hz, 1H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 157.44, 142.87, 128.62, 127.88, 121.94, 70.43.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{12}$N$_2$O [M+H]$^+$: 225.1022; found: 225.1037.

2-(α-Hydroxy-p-fluorobenzyl)-benzimidazole (1o): pale brown solid, 58% yield, mp 160-162 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.47-7.56 (m, 4H), 7.13-7.20 (m, 4H), 6.60 (s, 1H), 5.95 (s, 1H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 160.33-163.55 (d, $J_{CF} = 241.5$ Hz), 157.22, 139.08-139.11 (d, $J_{CF} = 7.2$ Hz), 128.85-128.96 (d, $J_{CF} = 8.2$ Hz), 121.98, 115.22-115.50 (d, $J_{CF} = 41.2$ Hz), 69.71.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{13}$FN$_2$O [M+H]$^+$: 243.0928; found: 243.0942.

2-(α-Hydroxy-p-chlorobenzyl)-benzimidazole (1p): pale yellow solid, 63% yield, mp 155-158 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 12.40 (brs, 1H), 7.39-7.53 (m, 6H), 7.13 (dd, $J = 6.0, 3.2$ Hz, 2H), 6.59-6.67 (m, 1H), 5.94 (d, $J = 4.2$ Hz, 1H).

$^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 156.97, 141.87, 132.41, 128.76, 128.58, 121.93, 69.69.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{15}$ClN$_2$O [M+H]$^+$: 259.0633; found: 259.0636.

2-(α-Hydroxy-o-chlorobenzyl)-benzimidazole (1q): pale red powder, 46% yield, mp 211-214 °C.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 12.43 (brs, 1H), 7.68 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.30-7.50 (m, 5H),
7.12-7.16 (dd, \( J = 6.8, 3.6 \text{ Hz}, 2\text{H} \)), 6.62 (d, \( J = 4.9 \text{ Hz}, 1\text{H} \)), 6.24 (d, \( J = 4.7 \text{ Hz}, 1\text{H} \)).

\(^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6): }\delta 155.87, 140.24, 129.67, 129.56, 129.43, 127.69, 122.01, 67.17.\)

HRMS (ESI-TOF) calcd for \( \text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O} [\text{M+H}]^+ : 259.0633; \) found: 259.0638.

![Chemical structure](image)

2-(a-Hydroxy-p-bromobenzyl)-benzimidazole (1r): brown solid, 89\% yield, mp 249-252 °C.

\(^1\text{H NMR (300 MHz, DMSO-\text{d}_6): }\delta 7.44-7.57 (m, 6\text{H}), 7.10-7.16 (m, 2\text{H}), 6.68 (s, 1\text{H}), 5.94 (s, 1\text{H}).\)

\(^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6): }\delta 156.89, 142.25, 131.50, 129.14, 120.04, 120.98, 69.64.\)

HRMS (ESI-TOF) calcd for \( \text{C}_{14}\text{H}_{13}\text{BrN}_2\text{O} [\text{M+H}]^+ : 303.0128; \) found: 303.0133.

![Chemical structure](image)

(1H-benzimidazol-2-yl)-phenylethan (1s): pale red crystalline, 64\% yield, mp 248-250 °C.

\(^1\text{H NMR (300 MHz, DMSO-\text{d}_6): }\delta 7.50 (dd, \( J = 6.0, 3.2 \text{ Hz}, 2\text{H} \)), 7.12-7.24 (m, 7\text{H}), 5.92 (d, \( J = 3.8 \text{ Hz}, 1\text{H} \)), 5.00 (d, \( J = 3.7 \text{ Hz}, 1\text{H} \)), 3.28 (dd, \( J = 13.7, 4.9 \text{ Hz}, 1\text{H} \)), 3.07 (dd, \( J = 13.7, 8.2 \text{ Hz}, 1\text{H} \)).\)

\(^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6): }\delta 157.79, 138.88, 129.89, 128.47, 126.53, 121.84, 115.29, 69.21, 42.91.\)

HRMS (ESI-TOF) calcd for \( \text{C}_{16}\text{H}_{16}\text{N}_2\text{O} [\text{M+H}]^+ : 239.1179; \) found: 239.1194.

![Chemical structure](image)

(1H-benzimidazol-2-yl)-methanethiol (1t): white powder, 96\% yield, mp 155-157 °C.

\(^1\text{H NMR (300 MHz, DMSO-\text{d}_6): }\delta 12.40 (\text{brs}, 1\text{H}), 7.50 (dd, \( J = 6.0, 3.2 \text{ Hz}, 2\text{H} \)), 7.15 (dd, \( J = 6.0, 3.2 \text{ Hz}, 2\text{H} \)), 3.92 (s, 2\text{H}).\)

\(^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6): }\delta 154.11, 122.29, 122.07, 115.25, 21.57.\)

HRMS (ESI-TOF) calcd for \( \text{C}_{14}\text{H}_{14}\text{N}_2\text{S} [\text{M+H}]^+ : 165.0481; \) found: 165.0476.

![Chemical structure](image)

(1H-benzimidazol-2-yl)-methanamine (1u): brown solid, 79\% yield, mp 101-103 °C.

\(^1\text{H NMR (300 MHz, DMSO-\text{d}_6): }\delta 7.51 (dd, \( J = 5.9, 3.2 \text{ Hz}, 2\text{H} \)), 7.13 (dd, \( J = 6.0, 3.2 \text{ Hz}, 2\text{H} \)), 5.53 (\text{brs}, 1\text{H}), 3.97 (s, 2\text{H}).\)

\(^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6): }\delta 156.66, 139.07, 121.73, 115.11, 40.16.\)

HRMS (ESI-TOF) calcd for \( \text{C}_{12}\text{H}_{15}\text{N}_3 [\text{M+H}]^+ : 148.0869; \) found: 148.0865.
**1H-benzimidazol-2-yl)-N-methylnethanamine (1v)**: pale brown oily solid, 43% yield, mp 120-123 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.56 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.23 (dd, $J = 6.1, 3.2$ Hz, 2H), 4.15 (s, 2H), 2.53 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 151.90, 138.31, 122.59, 115.07, 48.84, 35.66. HRMS (ESI-TOF) calcd for C$_{9}$H$_{8}$N$_{3}$ [M+H]$^+$: 162.1026; found: 162.1026.

![Diagram](image)

**1H-benzimidazol-2-yl)-ethylamine (1w)**: pale yellow solid, 62% yield, mp 203-205 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.57 (dd, $J = 6.0, 3.2$ Hz, 2H), 7.23 (dd, $J = 6.0, 3.2$ Hz, 2H), 4.73 (brs, 2H), 4.46 (q, $J = 6.7$ Hz, 2H), 1.60 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 159.11, 151.62, 138.29, 122.58, 122.32, 114.98, 46.19, 23.74. HRMS (ESI-TOF) calcd for C$_{9}$H$_{8}$N$_{3}$ [M+H]$^+$: 162.1026; found: 162.1023.

![Diagram](image)

**Bromoethylsulfonium salt (2)**: grey powder, 45% yield, mp 85-87 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.06-8.12 (m, 4H), 7.71-7.77 (m, 6H), 4.92 (t, $J = 5.9$ Hz, 2H), 3.73 (t, $J = 5.9$ Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 135.3, 131.9, 131.1, 122.9, 48.2, 23.8.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{14}$BrF$_{3}$O$_{3}$S$_{2}$ [M-CF$_3$O$_{3}$S]$^+$: 292.9994; found: 293.0007.

![Diagram](image)

**3, 4-Dihydro-1H- [1, 4] oxazino[4,3-a] benzimidazole (3a)**: pale yellow solid, 61 mg, 88% yield, mp 125-127 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.73-7.76 (m, 1H), 7.28-7.36 (m, 3H), 5.07 (s, 2H), 4.18-4.22 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 147.86, 142.55, 134.00, 122.69, 122.41, 119.45, 108.78, 65.49, 63.97, 42.02.

HRMS (ESI-TOF) calcd for C$_{10}$H$_{10}$N$_{2}$O [M+H]$^+$: 175.0866; found: 175.0866.

![Diagram](image)

**3, 4-Dihydro-8-methoxy-1H-[1, 4] oxazino[4,3-a] benzimidazole (3b)**: white solid, 34 mg, 41% yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.19-7.22 (m, 2H), 6.90 (m, 1H), 5.01 (s, 2H), 4.16-4.20 (m, 2H), 4.08-4.13 (m, 2H), 3.87 (s, 3H).
13C NMR (75 MHz, CDCl3): δ 156.43, 148.04, 143.08, 128.49, 119.77, 112.30, 101.78, 65.28, 63.88, 55.86, 41.97.

3, 4-Dihydro-7-methoxy-1H-[1, 4]oxazino[4,3-a]benzimidazole (3b): white solid, 39 mg, 46% yield.
1H NMR (300 MHz, CDCl3): δ 7.61 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.09-7.13 (m, 1H), 5.03 (s, 2H), 4.18-4.21 (m, 2H), 4.12-4.15 (m, 2H), 2.50 (s, 3H).
13C NMR (75 MHz, CDCl3): δ 147.41, 142.59, 134.18, 123.88, 119.17, 108.30, 65.39, 63.95, 41.99, 21.60.

3, 4-Dihydro-8-methyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3c1): white solid, 27 mg, 33% yield.
1H NMR (300 MHz, CDCl3): δ 7.52 (m, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.09-7.13 (m, 1H), 5.03 (s, 2H), 4.18-4.21 (m, 2H), 4.12-4.15 (m, 2H), 2.50 (s, 3H).
13C NMR (75 MHz, CDCl3): δ 147.41, 142.59, 134.18, 123.88, 119.17, 108.30, 65.39, 63.95, 41.99, 21.60.

3, 4-Dihydro-7-methyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3c2): white solid, 43 mg, 51% yield.
1H NMR (300 MHz, CDCl3): δ 7.63 (d, J = 8.8 Hz, 1H), 7.09-7.13 (m, 2H), 5.03 (s, 2H), 4.18-4.21 (m, 2H), 4.12-4.15 (m, 2H), 2.51 (s, 3H).
13C NMR (75 MHz, CDCl3): δ 147.31, 140.41, 132.47, 124.25, 118.84, 108.78, 65.45, 63.99, 41.96, 21.74.

3, 4-Dihydro-9-methyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3d): pale yellow solid, 58 mg, 70%

S9
yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.15-7.21 (m, 2H), 7.08-7.11 (m, 1H), 5.07 (s, 2H), 4.17-4.21 (m, 2H), 4.12-4.15 (m, 2H), 2.66 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 147.04, 141.77, 133.62, 129.41, 123.11, 122.32, 106.29, 65.59, 63.98, 42.08, 16.68.

HRMS (ESI-TOF) calcd for C$_{11}$H$_{12}$N$_2$O [M+H]$^+$: 189.1022; found: 189.1020.

3, 4-Dihydro-6-methyl-1H-[1, 4]oxazino[4,3-α]benzimidazole (3d): pale yellow solid, 6 mg, 7% yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J = 8.2$ Hz, 1H), 7.14 (d, $J = 3.5$ Hz, 1H), 6.97 (d, $J = 7.3$ Hz, 1H), 5.03 (s, 2H), 4.17-4.21 (m, 2H), 4.12-4.15 (m, 2H), 2.69 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 147.66, 140.74, 131.34, 122.50, 117.35, 65.72, 64.25, 44.85, 18.16.

HRMS (ESI-TOF) calcd for C$_{11}$H$_{12}$N$_2$O [M+H]$^+$: 189.1022; found: 189.1018.

3, 4-Dihydro-7, 8-dimethyl-1H-[1, 4]oxazino[4,3-α]benzimidazole (3e): pale yellow solid, 59 mg, 73% yield, mp 185-187 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.47 (s, 1H), 7.08 (s, 1H), 4.99 (s, 2H), 4.14-4.18 (m, 2H), 4.07-4.10 (m, 2H), 2.38 (d, $J = 3.9$ Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 131.45, 131.40, 119.53, 109.06, 65.56, 64.03, 42.01, 20.49, 20.33.

HRMS (ESI-TOF) calcd for C$_{15}$H$_{14}$N$_2$O [M+H]$^+$: 203.1179; found: 203.1176.

3, 4-Dihydro-7, 8-difluoro-1H-[1, 4]oxazino[4,3-α]benzimidazole (3f): pale red crystalline, 73 mg, 85% yield, mp 155-158 °C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.49 (dd, $J_{HF} = 10.5, 7.2$ Hz, 1H), 7.12 (dd, $J_{HF} = 9.5, 6.9$ Hz, 1H), 5.01 (s, 2H), 4.19-4.23 (m, 2H), 4.10-4.13 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 149.40-149.66 (dd, $J_{CF} = 1.1, 14.3$ Hz), 146.24-146.48 (dd, $J_{CF} = 2.6, 14.5$ Hz), 137.64-137.79 (d, $J_{CF} = 11.2$ Hz), 129.30-129.35 (d, $J_{CF} = 3.3$ Hz), 106.78-107.06 (dd, $J_{CF} = 0.9, 20.0$ Hz), 96.79-97.10 (dd, $J_{CF} = 0.8, 22.7$ Hz), 65.37, 63.79, 42.22.

HRMS (ESI-TOF) calcd for C$_{10}$H$_{6}$F$_2$N$_2$O [M+H]$^+$: 211.0677; found: 211.0678.
3, 4-Dihydro-7, 8-dichloro-1H-[1, 4]oxazino[4,3-a]benzimidazole (3g): pale yellow solid, 77 mg, 78% yield, mp 190-193 °C.

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.78 (s, 1H), 7.42 (s, 1H), 5.00 (s, 2H), 4.18-4.22 (m, 2H), 4.10-4.13 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.92, 142.00, 133.31, 126.63, 126.43, 120.68, 110.26, 65.32, 63.75, 42.22.

HRMS (ESI-TOF) calcd for C$_{10}$H$_8$Cl$_2$N$_2$O [M+H]$^+$: 243.0086; found: 243.0081.

3, 4-Dihydro-7, 8-dibromo-1H-[1, 4]oxazino[4,3-a]benzimidazole (3g): pale brown crystalline, 98 mg, 73% yield, mp 202-205 °C.

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.99 (s, 1H), 7.63 (s, 1H), 5.02 (s, 2H), 4.20-4.23 (m, 2H), 4.12-4.15 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.78, 142.81, 134.18, 123.90, 117.95, 117.68, 113.48, 65.26, 63.73, 42.23.


1H-naphth[2', 3': 4, 5]imidazo[2,1-c][1,4]oxazine (3i): sliver crystalline, 83 mg, 90% yield, mp 227-229 °C.

$^1$H NMR (300 MHz, CDCl$_3$): δ 8.19 (s, 1H), 7.98-8.08 (m, 1H), 7.88-7.97 (m, 1H), 7.63 (s, 1H), 7.38-7.51 (M, 2H), 5.06 (s, 2H), 4.17-4.20 (m, 2H), 4.10-4.14 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 152.06, 142.54, 134.76, 130.56, 130.16, 128.51, 127.45, 124.45, 123.68, 116.22, 104.58, 65.57, 63.97, 42.05.

HRMS (ESI-TOF) calcd for C$_{14}$H$_{12}$N$_2$O [M+H]$^+$: 225.1022; found: 225.1016.

3, 4-Dihydro-1-methyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3j): pale yellow oily solid, 73 mg, 88% yield.

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.70-7.80 (m, 1H), 7.22-7.35 (m, 3H), 5.00 (q, J = 6.5 Hz, 1H), 4.38 (ddd, J = 11.6, 4.5, 1.8 Hz, 1H), 4.14-4.27 (m, 1H), 3.99-4.09 ((m, 2H), 1.76 (d, J = 6.6 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 151.93, 142.45, 134.15, 122.60, 122.47, 119.51, 108.93, 71.79, 63.06, 42.24, 19.22.

HRMS (ESI-TOF) calcd for C$_{11}$H$_{12}$N$_2$O [M+H]$^+$: 189.1022; found: 189.1025.
3, 4-Dihydro-1-dimethyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3k): colorless oil, 49 mg, 60% yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.75-7.78 (m, 1H), 7.24-7.41 (m, 3H), 4.11-4.27 (m, 4H), 1.75 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 154.94, 142.50, 133.96, 122.58, 122.28, 119.49, 108.99, 74.69, 58.39, 42.46, 27.46

HRMS (ESI-TOF) calcd for C$_{12}$H$_{14}$N$_2$O [M+H]$^+$: 203.1179; found: 203.1195.

3, 4-Dihydro-1-isopropyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3l): pale yellow oil, 64 mg, 74% yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.75-7.78 (m, 1H), 7.24-7.41 (m, 3H), 4.11-4.27 (m, 4H), 1.75 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.91, 142.75, 134.18, 122.46, 122.22, 119.59, 108.78, 79.81, 63.17, 42.27, 31.85, 19.04, 16.05.

HRMS (ESI-TOF) calcd for C$_{13}$H$_{16}$N$_2$O [M+H]$^+$: 217.1335; found: 217.1349.

3, 4-Dihydro-1-spirocyclohexyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3m): red oil, 55 mg, 56% yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.72-7.84 (m, 1H), 7.22-7.41 (m, 3H), 4.04-4.26 (m, 4H), 2.08-2.13 (m, 4H), 1.63-1.84 (m, 5H), 1.40-1.52 m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 155.37, 142.49, 134.02, 122.47, 122.16, 119.48, 108.92, 75.49, 57.70, 42.41, 34.72, 25.12, 21.02.

HRMS (ESI-TOF) calcd for C$_{15}$H$_{18}$N$_2$O [M+H]$^+$: 243.1492; found: 243.1516.

3, 4-Dihydro-1-phenyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3n): pale yellow solid, 86 mg, 86% yield, mp 156-158 °C.
\[ \text{HRMS (ESI-TOF) calcd for C}_{16}\text{H}_{13}\text{N}_2\text{O} [\text{M+H}]^+: 251.1179; \text{found: 251.1186.} \]

3, 4-Dihydro-1-(4-fluorophenyl)-1H-[1, 4]oxazino[4,3-a]benzimidazole (3o): grey solid, 93 mg, 86% yield, mp 144-147 °C.

\[ \text{HRMS (ESI-TOF) calcd for C}_{16}\text{H}_{13}\text{FN}_2\text{O} [\text{M+H}]^+: 269.1085; \text{found: 269.1093.} \]

3, 4-Dihydro-1-(4-chlorophenyl)-1H-[1, 4]oxazino[4,3-a]benzimidazole (3p): colorless crystal, 104 mg, 92% yield, mp 108-111 °C.

\[ \text{HRMS (ESI-TOF) calcd for C}_{16}\text{H}_{13}\text{ClN}_2\text{O} [\text{M+H}]^+: 285.0789; \text{found: 285.0790.} \]

3, 4-Dihydro-1-(2-chlorophenyl)-1H-[1, 4]oxazino[4,3-a]benzimidazole (3q): pale yellow oil, 106 mg, 94% yield.

\[ \text{HRMS (ESI-TOF) calcd for C}_{16}\text{H}_{13}\text{ClN}_2\text{O} [\text{M+H}]^+: 285.0789; \text{found: 285.0790.} \]
127.02, 122.73, 122.67, 120.05, 108.93, 75.06, 62.66, 42.27.
HRMS (ESI-TOF) calcd for C_{16}H_{13}ClN_{2}O [M+H] \^\ast: 285.0789; found: 285.0799.

3, 4-Dihydro-1-(4-bromophenyl)-1H-[1, 4]oxazino[4,3-a]benzimidazole (3r): pale brown solid, 110 mg, 82% yield, mp 113-116 °C.
^1H NMR (300 MHz, CDCl\_3): \( \delta \) 7.75-7.80 (m, 1H), 7.52-7.55 (m, 2H), 7.30-7.45 (m, 5H), 6.00 (s, 1H), 4.15-4.44 (m, 4H).
^{13}C NMR (75 MHz, CDCl\_3): \( \delta \) 149.08, 142.64, 136.66, 134.03, 134.02, 131.82, 129.87, 123.03, 122.81, 122.78, 120.02, 108.99, 76.60, 62.15, 42.31.
HRMS (ESI-TOF) calcd for C_{16}H_{13}BrN_{2}O [M+H] \^\ast: 329.0284; found: 329.0292.

3, 4-Dihydro-1-benzyl-1H-[1, 4]oxazino[4,3-a]benzimidazole (3s): bright white solid, 88 mg, 84% yield, mp 115-117 °C.
^1H NMR (300 MHz, CDCl\_3): \( \delta \) 7.80-7.85 (m, 1H), 7.26-7.44 (m, 8H), 5.17 (dd, \( J = 9.6, 2.7 \) Hz, 1H), 4.34-4.44 (m, 1H), 4.15-4.27 (m, 1H), 4.06-4.13 (m, 1H), 3.93-4.05 (m, 1H), 3.79 (dd, \( J = 14.6, 2.7 \) Hz, 1H), 3.22 (dd, \( J = 14.6, 9.7 \) Hz, 1H).
^{13}C NMR (75 MHz, CDCl\_3): \( \delta \) 150.62, 142.58, 137.71, 134.30, 129.62, 128.34, 126.47, 122.68, 122.53, 119.64, 108.96, 76.28, 63.07, 42.23, 39.75.
HRMS (ESI-TOF) calcd for C_{17}H_{16}N_{2}O [M+H] \^\ast: 265.1335; found: 265.1359.

3, 4-Dihydro-1H-[1, 4]thiazino[4,3-a]benzimidazole (3t): yellow solid, 25 mg, 33% yield, mp 146-148 °C.
^1H NMR (300 MHz, CDCl\_3): \( \delta \) 7.59-7.64 (m, 1H), 7.15-7.22 (m, 3H), 4.14-4.24 (m, 2H), 3.99 (s, 2H), 2.99-3.08 (m, 2H).
^{13}C NMR (75 MHz, CDCl\_3): \( \delta \) 146.76, 141.53, 134.84, 122.76, 122.46, 119.25, 108.81, 44.77, 26.66, 26.05.
HRMS (ESI-TOF) calcd for C_{10}H_{10}N_{2}S [M+H] \^\ast: 191.0637; found: 191.0632.
1, 2, 3, 4-Tetrahydropyrazino[1,2-α]benzimidazole (3a): pale yellow solid, 14 mg, 20% yield, mp 129-132 °C.

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): δ 7.53-7.58 (m, 1H), 7.42-7.50 (m, 1H), 7.15-7.21 (m, 2H), 3.97-4.08 (m, 4H), 3.19 (t, \(J = 5.6\) Hz, 2H), 1.67 (s, 1H).

\(^13\)C NMR (75 MHz, DMSO-\(d_6\)): δ 150.58, 142.60, 134.80, 122.10, 121.71, 118.70, 109.86, 44.89, 43.16, 42.59.

HRMS (ESI-TOF) calcd for C\(_{10}\)H\(_{11}\)N\(_3\) [M+H]: 174.1026; found: 174.1018.

1, 2, 3, 4-Tetrahydro-2-methyl-pyrazino[1,2-α]benzimidazole (3v): white solid, 21 mg, 28% yield, mp 144-146 °C.

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): δ 7.53-7.62 (m, 1H), 7.45-7.51 (m, 1H), 7.14-7.27 (m, 2H), 4.13 (t, \(J = 5.6\) Hz, 2H), 3.76 (s, 2H), 2.93 (t, \(J = 5.6\) Hz, 2H), 2.45 (s, 3H).

\(^13\)C NMR (75 MHz, DMSO-\(d_6\)): δ 149.64, 142.94, 134.47, 122.19, 121.92, 118.87, 110.09, 53.77, 51.26, 45.36, 41.92.

HRMS (ESI-TOF) calcd for C\(_{11}\)H\(_{13}\)N\(_3\) [M+H]: 188.1182; found: 188.1173.

1, 2, 3, 4-Tetrahydro-1-methyl-pyrazino[1,2-α]benzimidazole (3v): white solid, 27 mg, 36% yield, mp 153-155 °C.

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): δ 7.55-7.60 (m, 1H), 7.38-7.49 (m, 1H), 7.12-7.26 (m, 2H), 4.07-4.19 (m, 2H), 3.89-4.05 (m, 1H), 3.30-3.40 (m, 1H), 3.04-3.20 (m, 1H), 1.50 (d, \(J = 6.7\) Hz, 3H), 1.29-1.38 (m, 1H).

\(^13\)C NMR (75 MHz, DMSO-\(d_6\)): δ 154.28, 142.63, 134.91, 122.05, 121.83, 118.90, 110.02, 50.54, 43.27, 41.81, 19.80.

HRMS (ESI-TOF) calcd for C\(_{11}\)H\(_{13}\)N\(_3\) [M+H]: 188.1182; found: 188.1176.

1-Ethenyl-1H-benzimidazole-2-methanol (4a): pale white solid, 32 mg, 45% yield, mp 110-112 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.64-7.76 (m, 1H), 7.47-7.60 (m, 1H), 7.26-7.37 (m, 2H), 7.12-7.26 (m, 1H), 6.12 (s, 1H), 5.66 (d, \(J = 15.8\) Hz, 1H), 5.33 (d, \(J = 8.9\) Hz, 1H), 4.92 (s, 2H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)): δ 153.30, 141.58, 133.81, 128.34, 123.87, 123.19, 119.52, 111.25,
HRMS (ESI-TOF) calc for C_{10}H_{10}N_{2}O [M+H]^+ : 175.0866; found: 175.0869.

6. Reference

7. Copies of $^1$H NMR and $^{13}$C NMR Spectra

Figure S1. The $^1$H NMR Spectrum of Compound 1a in DMSO-$d_6$

Figure S2. The $^{13}$C NMR Spectrum of Compound 1a in DMSO-$d_6$
Figure S3. The HR-ESI-MS Spectrum of Compound 1a

Figure S4. The $^1$H NMR Spectrum of Compound 1b in DMSO-$_d_6$
Figure S5. The $^{13}$C NMR Spectrum of Compound 1b in DMSO-$d_6$. 

Figure S6. The HR-ESI-MS Spectrum of Compound 1b.
Figure S7. The $^1$H NMR Spectrum of Compound 1c in DMSO-$d_6$.

Figure S8. The $^{13}$C NMR Spectrum of Compound 1c in DMSO-$d_6$. 
Figure S9. The HR-ESI-MS Spectrum of Compound 1c

Figure S10. The $^1$H NMR Spectrum of Compound 1d in DMSO-$d_6$
Figure S11. The $^{13}$C NMR Spectrum of Compound 1d in DMSO-$d_6$

Figure S12. The HR-ESI-MS Spectrum of Compound 1d
Figure S13. The $^1\text{H}$ NMR Spectrum of Compound 1e in DMSO-$d_6$

Figure S14. The $^{13}\text{C}$ NMR Spectrum of Compound 1e in DMSO-$d_6$
Figure S15. The HR-ESI-MS Spectrum of Compound 1e

Figure S16. The $^1$H NMR Spectrum of Compound 1f in DMSO-$d_6$
Figure S17. The $^{13}$C NMR Spectrum of Compound 1f in DMSO-$d_6$.

Figure S18. The HR-ESI-MS Spectrum of Compound 1f.
**Figure S19.** The $^1$H NMR Spectrum of Compound 1g in DMSO-$d_6$.

**Figure S20.** The $^{13}$C NMR Spectrum of Compound 1g in DMSO-$d_6$. 
Figure S21. The HR-ESI-MS Spectrum of Compound 1g

Figure S22. The $^1$H NMR Spectrum of Compound 1h in DMSO-$d_6$
Figure S23. The $^{13}$C NMR Spectrum of Compound 1h in DMSO-$d_6$

Figure S24. The HR-ESI-MS Spectrum of Compound 1h
Figure S25. The $^1$H NMR Spectrum of Compound 1i in DMSO-$d_6$

Figure S26. The $^{13}$C NMR Spectrum of Compound 1i in DMSO-$d_6$
Figure S27. The HR-ESI-MS Spectrum of Compound 1i

Figure S28. The $^1$H NMR Spectrum of Compound 1j in DMSO-$d_6$
Figure S29. The $^{13}$C NMR Spectrum of Compound 1j in DMSO-$d_6$.

Figure S30. The HR-ESI-MS Spectrum of Compound 1j.
Figure S31. The $^1$H NMR Spectrum of Compound 1k in DMSO-$d_6$.

Figure S32. The $^{13}$C NMR Spectrum of Compound 1k in DMSO-$d_6$.
Figure S33. The HR-ESI-MS Spectrum of Compound 1k

Figure S34. The $^1$H NMR Spectrum of Compound 1l in DMSO-$d_6$
Figure S35. The $^{13}$C NMR Spectrum of Compound 11 in DMSO-$d_6$.

Figure S36. The HR-ESI-MS Spectrum of Compound 11.
Figure S37. The $^1$H NMR Spectrum of Compound 1m in DMSO-$d_6$

Figure S38. The $^{13}$C NMR Spectrum of Compound 1m in DMSO-$d_6$
Figure S39. The HR-ESI-MS Spectrum of Compound 1m

Figure S40. The $^1$H NMR Spectrum of Compound 1n in DMSO-$d_6$
Figure S41. The $^{13}$C NMR Spectrum of Compound 1n in DMSO-$d_6$

Figure S42. The HR-ESI-MS Spectrum of Compound 1n
Figure S43. The $^1$H NMR Spectrum of Compound 1 in DMSO-$d_6$

Figure S44. The $^{13}$C NMR Spectrum of Compound 1 in DMSO-$d_6$
**Figure S45.** The HR-ESI-MS Spectrum of Compound 1o

**Figure S46.** The $^1$H NMR Spectrum of Compound 1p in DMSO-$d_6$
Figure S47. The $^{13}$C NMR Spectrum of Compound 1p in DMSO-$d_6$

Figure S48. The HR-ESI-MS Spectrum of Compound 1p
Figure S49. The $^1$H NMR Spectrum of Compound 1q in DMSO-$d_6$.

Figure S50. The $^{13}$C NMR Spectrum of Compound 1q in DMSO-$d_6$. 

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Figure S51. The HR-ESI-MS Spectrum of Compound 1q

Figure S52. The $^1$H NMR Spectrum of Compound 1r in DMSO-$d_6$
Figure S53. The $^{13}$C NMR Spectrum of Compound 1r in DMSO-$d_6$.

Figure S54. The HR-ESI-MS Spectrum of Compound 1r.
Figure S55. The $^1$H NMR Spectrum of Compound 1s in DMSO-$d_6$

Figure S56. The $^{13}$C NMR Spectrum of Compound 1s in DMSO-$d_6$
Figure S57. The HR-ESI-MS Spectrum of Compound 1s

Figure S58. The $^1$H NMR Spectrum of Compound 1t in DMSO-$d_6$
Figure S59. The $^{13}$C NMR Spectrum of Compound 1t in DMSO-$d_6$.

Figure S60. The HR-ESI-MS Spectrum of Compound 1t.
Figure S61. The $^1$H NMR Spectrum of Compound 1u in DMSO-d$_6$

Figure S62. The $^{13}$C NMR Spectrum of Compound 1u in DMSO-d$_6$
**Figure S63.** The HR-ESI-MS Spectrum of Compound 1u

**Figure S64.** The $^1$H NMR Spectrum of Compound 1v in CDCl$_3$
Figure S65. The $^{13}$C NMR Spectrum of Compound 1v in CDCl$_3$

Figure S66. The HR-ESI-MS Spectrum of Compound 1v
Figure S67. The $^1$H NMR Spectrum of Compound 1w in CDCl$_3$

Figure S68. The $^{13}$C NMR Spectrum of Compound 1w in CDCl$_3$
Figure S69. The HR-ESI-MS Spectrum of Compound 1w

Figure S70. The $^1$H NMR Spectrum of Compound 2 in CDCl$_3$
Figure S71. The $^{13}$C NMR Spectrum of Compound 2 in CDCl$_3$

Figure S72. The HR-ESI-MS Spectrum of Compound 2
Figure S73. The $^1$H NMR Spectrum of Compound 3a in CDCl$_3$

Figure S74. The $^{13}$C NMR Spectrum of Compound 3a in CDCl$_3$
Figure S75. The HR-ESI-MS Spectrum of Compound 3a

Figure S76. The $^1$H NMR Spectrum of Compound 3b$_1$ in CDCl$_3$
**Figure S77.** The $^{13}$C NMR Spectrum of Compound 3b₁ in CDCl₃

**Figure S78.** The HR-ESI-MS Spectrum of Compound 3b₁
Figure S79. The $^1$H NMR Spectrum of Compound 3b$_2$ in CDCl$_3$

Figure S80. The $^{13}$C NMR Spectrum of Compound 3b$_2$ in CDCl$_3$
Figure S81. The HR-ESI-MS Spectrum of Compound 3b2

Figure S82. The ¹H NMR Spectrum of Compound 3c1 in CDCl₃
Figure S83. The $^{13}$C NMR Spectrum of Compound 3c₁ in CDCl₃

Figure S84. The HR-ESI-MS Spectrum of Compound 3c₁
Figure S85. The $^1$H NMR Spectrum of Compound 3e$_2$ in CDCl$_3$

Figure S86. The $^{13}$C NMR Spectrum of Compound 3e$_2$ in CDCl$_3$
Figure S87. The HR-ESI-MS Spectrum of Compound 3c.

Figure S88. The $^1$H NMR Spectrum of Compound 3d, in CDCl$_3$. 
Figure S89. The $^{13}$C NMR Spectrum of Compound 3d₁ in CDCl₃

Figure S90. The HR-ESI-MS Spectrum of Compound 3d₁
Figure S91. The $^1$H NMR Spectrum of Compound 3d$_2$ in CDCl$_3$

Figure S92. The $^{13}$C NMR Spectrum of Compound 3d$_2$ in CDCl$_3$
Figure S93. The HR-ESI-MS Spectrum of Compound 3d:

Figure S94. The $^1$H NMR Spectrum of Compound 3e in CDCl$_3$
Figure S95. The $^{13}$C NMR Spectrum of Compound 3e in CDCl$_3$

Figure S96. The HR-ESI-MS Spectrum of Compound 3e
Figure S97. The $^1$H NMR Spectrum of Compound 3f in CDCl$_3$

Figure S98. The $^{13}$C NMR Spectrum of Compound 3f in CDCl$_3$
Figure S99. The HR-ESI-MS Spectrum of Compound 3f

Figure S100. The $^1$H NMR Spectrum of Compound 3g in CDCl₃
Figure S101. The $^{13}$C NMR Spectrum of Compound 3g in CDCl$_3$

Figure S102. The HR-ESI-MS Spectrum of Compound 3g
Figure S103. The $^1$H NMR Spectrum of Compound 3h in CDCl$_3$

Figure S104. The $^{13}$C NMR Spectrum of Compound 3h in CDCl$_3$
Figure S105. The HR-ESI-MS Spectrum of Compound 3h

Figure S106. The $^1$H NMR Spectrum of Compound 3i in CDCl$_3$
**Figure S107.** The $^{13}$C NMR Spectrum of Compound 3i in CDCl$_3$

**Figure S108.** The HR-ESI-MS Spectrum of Compound 3i
Figure S109. The $^1$H NMR Spectrum of Compound 3j in CDCl$_3$

Figure S110. The $^{13}$C NMR Spectrum of Compound 3j in CDCl$_3$
Figure S111. The HR-ESI-MS Spectrum of Compound 3j

Figure S112. The $^1$H NMR Spectrum of Compound 3k in CDCl$_3$
Figure S113. The $^{13}$C NMR Spectrum of Compound 3k in CDCl$_3$

Figure S114. The HR-ESI-MS Spectrum of Compound 3k
Figure S115. The $^1$H NMR Spectrum of Compound 3l in CDCl$_3$

Figure S116. The $^{13}$C NMR Spectrum of Compound 3l in CDCl$_3$
Figure S117. The HR-ESI-MS Spectrum of Compound 3l

Figure S118. The $^1$H NMR Spectrum of Compound 3m in CDCl$_3$
Figure S119. The $^{13}$C NMR Spectrum of Compound 3m in CDCl$_3$

Figure S120. The HR-ESI-MS Spectrum of Compound 3m
Figure S121. The $^1$H NMR Spectrum of Compound 3n in CDCl$_3$

Figure S122. The $^{13}$C NMR Spectrum of Compound 3n in CDCl$_3$
Figure S123. The HR-ESI-MS Spectrum of Compound 3n.

Figure S124. The 1H NMR Spectrum of Compound 3o in CDCl3.
Figure S125. The $^{13}$C NMR Spectrum of Compound 3o in CDCl$_3$

Figure S126. The HR-ESI-MS Spectrum of Compound 3o
Figure S127. The $^1$H NMR Spectrum of Compound 3p in CDCl$_3$

Figure S128. The $^{13}$C NMR Spectrum of Compound 3p in CDCl$_3$
Figure S129. The HR-ESI-MS Spectrum of Compound 3p

Figure S130. The \(^1\)H NMR Spectrum of Compound 3q in CDCl\(_3\)
Figure S131. The $^{13}$C NMR Spectrum of Compound 3q in CDCl$_3$

Figure S132. The HR-ESI-MS Spectrum of Compound 3q
Figure S133. The $^1$H NMR Spectrum of Compound 3r in CDCl$_3$

Figure S134. The $^{13}$C NMR Spectrum of Compound 3r in CDCl$_3$
Figure S135. The HR-ESI-MS Spectrum of Compound 3r

Figure S136. The $^1$H NMR Spectrum of Compound 3s in CDCl$_3$
Figure S137. The $^{13}$C NMR Spectrum of Compound 3s in CDCl$_3$

Figure S138. The HR-ESI-MS Spectrum of Compound 3s
Figure S139. The $^1$H NMR Spectrum of Compound 3t in CDCl$_3$

Figure S140. The $^{13}$C NMR Spectrum of Compound 3t in CDCl$_3$
**Figure S141.** The HR-ESI-MS Spectrum of Compound 3t

**Figure S142.** The $^1$H NMR Spectrum of Compound 3u in DMSO-$d_6$
Figure S143. The $^{13}$C NMR Spectrum of Compound 3u in DMSO-$d_6$

Figure S144. The HR-ESI-MS Spectrum of Compound 3u
Figure S145. The $^1$H NMR Spectrum of Compound 3v in DMSO-$d_6$

Figure S146. The $^{13}$C NMR Spectrum of Compound 3v in DMSO-$d_6$
Figure S147. The HR-ESI-MS Spectrum of Compound 3v

Figure S148. The $^1$H NMR Spectrum of Compound 3w in DMSO-$d_6$
Figure S149. The $^{13}$C NMR Spectrum of Compound 3w in DMSO-$d_6$

Figure S150. The HR-ESI-MS Spectrum of Compound 3w
Figure S151. The $^1$H NMR Spectrum of Compound 4a in CDCl$_3$

Figure S152. The $^{13}$C NMR Spectrum of Compound 4a in CDCl$_3$
Figure S153. The HR-ESI-MS Spectrum of Compound 4a