Electronic Supporting Information

New Di-cationic DABCO-based Ionic Liquids: A Scalable Metal-Free One-pot Synthesis of Bis-2-amino-5-arylidethiazol-4-ones

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**1H NMR (CDCl₃): 3a**

[Image of the NMR spectrum with chemical structure and peak assignments]
$^{13}$C NMR (CDCl$_3$): 3a
$^1$H NMR (CDCl$_3$): 3b
$^{19}\text{F NMR (CDCl}_3\text{): 3b}$
$^{13}$C NMR (CDCl$_3$): 3b
$^1$H NMR (DMSO-$d_6$): 7a
$^{13}$C NMR (DMSO-$d_6$): 7a
$^{1}H$ NMR (DMSO-$d_6$): 7b
$^1\text{H NMR (DMSO-$d_6$): 7c}$
$^1$H NMR (DMSO-$d_6$): 7d
$^1$H NMR (DMSO-$d_6$): 7e
$^{13}$C NMR (DMSO-$d_6$): 7e
$^1$H NMR (DMSO-$d_6$): 7f
$^{13}$C NMR (DMSO-$d_6$): 7f
$^1$H NMR (DMSO-$d_6$): 7g
$^{13}$C NMR (DMSO-$d_6$): 7g
$^1$H NMR (DMSO-$d_6$): 7h
$^{13}$C NMR (DMSO-$d_6$): 7h
$^1$H NMR (DMSO-$d_6$): 7i
$^{13}$C NMR (DMSO-$d_6$): 7i
$^1$H NMR (DMSO-$d_6$): 7j
$^{13}$C NMR (DMSO-$d_6$): 7j
$^1$H NMR (DMSO-$d_6$): 7k
$^{13}$C NMR (DMSO-$d_6$): 7k
$^{1}H$ NMR (DMSO-$d_6$): 71
$^{13}$C NMR (DMSO-$d_6$): 71
$^1$H NMR (DMSO-$d_6$): 7m
$^{13}$C NMR (DMSO-$d_6$): 7m
HRMS of (2-hydroxy-3-(hydroxymethyl)-5-methylphenyl)(piperidin-1-yl)methanone

Synthesis of 9a-m derivatives

(Z)-5-Benzylidene-2-(piperidin-1-yl)thiazol-4(5H)-one 9a

Yield 99%; yellow solid; mp = 215-216 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (s, 1H, =CH), 7.55 (d, 2H, J = 7.5 Hz, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.39-7.35 (m, 1H, Ar-H), 4.05-4.00 (m, 2H, Piperidine-H), 3.58-3.61 (m, 2H, Piperidine-H), 1.69-1.81 (m, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 1705 (C=O), 1612 (C=N), 1599 (C=C); HRMS: $m/z$ [M + H]$^+$ calcd: 273.1062, found 273.1054.

(Z)-5-(4-Chlorobenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9b

Yield 99%; white solid, mp = 206-208 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 7.99 (s, 1H, =CH), 7.53 (brs, 4H, Ar-H), 3.89 (brs, 4H, Piperidine-H), 1.94-1.89 (m, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 1668 (C=O), 1611 (C=N), 1587 (C=C); HRMS: $m/z$ [M]$^+$ calcd: 306.0592, found 306.0598.
**(Z)-5-(4-Methylbenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9c**

Yield 99%; yellowish solid; mp = 154-156 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (s, 1H, =CH), 7.48 (d, J = 8.1 Hz, 2H, Ar-H), 7.27 (d, J = 7.8 Hz, 2H, Ar-H), 3.88-3.84 (m, 2H, Piperidine-H), 3.59 (br, 2H, Piperidine-H), 2.31 (s, 3H, CH$_3$), 1.65 ppm (br, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{max}$ 1689 (C=O), 1621 (C=N), 1603 (C=C); HRMS: $m/z$ [M]$^+$ calcd: 286.1141, found 286.1147.

**(Z)-5-(4-Methoxybenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9d**

Yield 99%; white solid; mp = 200-201 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 7.71 (s, 1H, =CH), 7.40 (d, J = 8.8 Hz, 2H, Ar-H), 6.86 (d, J = 9 Hz, 2H, Ar-H), 3.96-3.92 (m, 2H, Piperidine-H), 3.65 (s, 3H, OCH$_3$), 3.50 (m, 2H, Piperidine-H), 1.72 (m, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{max}$ 1683 (C=O), 1608 (C=N), 1598 (C=C); HRMS: $m/z$ [M + H]$^+$ calcd: 303.1169, found 303.1184.

**(Z)-5-(2-Bromobenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9e**

Yield 97%; yellow solid, mp = 165-168°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.02 (s, 1H, =CH), 7.66 (d, J = 7.7 Hz, 1H, Ar-H), 7.56 (d, J = 7.7 Hz, 1H, Ar-H), 7.38 (t, J = 7.4 Hz, 1H, Ar-H), 7.22 (t, J = 7.7 Hz, 1H, Ar-H), 4.01 (s, 2H, Piperidine-H), 3.57 (s, 2H, Piperidine-H), 1.76 (br, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{max}$ 1698 (C=O), 1611 (C=N), 1599 (C=C); HRMS: $m/z$ [M]$^+$ calcd: 350.0089, found 350.0084.
(Z)-4-((4-Oxo-2-(piperidin-1-yl)thiazol-5(4H)-ylidene)methyl)benzonitrile 9f

Yield 98%; yellow solid; mp = 193-195; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.97 (d, J = 8.7 Hz, 2H, Ar-H), 7.80 (d, J = 8.7 Hz, 2H, Ar-H), 7.67 (s, 1H, =CH), 3.96–3.90 (m, 2H, Piperidine-H), 3.65-3.66 (m, 2H, br s, Piperidine-H), 1.66-1.67 (m, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 2223 (C≡N), 1689 (C=O), 1617 (C=N), 1610 (C=C); HRMS: $m/z$ [M + H]$^+$ calcd: 298.1015, found 298.1019.

(Z)-5-(Benzo[d][1,3]dioxol-4-ylmethylene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9g

Yield 98%; white solid; mp = 185-186 °C; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 7.69 (s, 1H, =C-H), 7.01 (d, J = 8.8 Hz, 1H, Ar-H), 6.97 (m, 1H, Ar-H); 6.80 (d, J = 8.8 Hz, 1H, Ar-H); 6.03 (s, 2H, CH$_2$), 3.99-3.96 (m, 2H, Piperidine-H), 3.49 (m, 2H, Piperidine-H), 1.79-1.73 (m, 6H, Piperidine-H); IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 1699 (C=O), 1605 (C=N), 1585 (C=C); HRMS: $m/z$ [M + H]$^+$ calcd: 317.0960, found 317.0957.

(Z)-5-(3,4-Dimethoxybenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9h

Yield 97%; yellowish solid; mp = 198-199°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.72 (s, 1H, =CH), 7.13-7.14 (dd, J = 8.7, 1.7 Hz, 1H, Ar-H), 7.01 (d, J = 1.7 Hz, 1H, Ar-H), 6.93 (d, J = 8.7 Hz, 1H, Ar-H),
3.99-4.01 (t, J = 5.9 Hz, 2H, Piperidine-H), 3.90 (d, 6H, -OCH3), 3.56 (br, 2H, piperidine-H), 1.78 (br, 6H, piperidine-H); IR (KBr, cm⁻¹): νmax 1655 (C=O), 1614 (C=N), 1601 (C=C); HRMS: m/z [M + H]⁺ calcd: 333.1271, found 333.1274.

(Z)-5-(4-Aminobenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9i

Yield 96%; yellow solid, mp = 213-215 °C; ¹H NMR (400 MHz, DMSO-d6) δ: 7.43 (s, 1H, =CH), 7.25 (d, J = 8.7 Hz, 2H, Ar-H), 6.69 (d, J = 8.8 Hz, 2H, Ar-H), 5.90 (br, 2H, NH2), 3.92 (br, 2H, Piperidine-H), 3.55 (br, 2H, Piperidine-H), 1.60 (br, 6H, Piperidine-H); IR (KBr): 1688 (C=O), 1609 (C=N), 1597 (C=C); HRMS: m/z [M + Na]⁺ calcd: 310.0991, found 310.0987.

(Z)-5-(4-Hydroxy-3-methoxybenzylidene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9j

Yield 98%; yellow solid; mp = 193-195°C; ¹H NMR (400 MHz, CDCl3) δ: 7.70 (s, 1H, =CH), 7.10-7.12 (dd, J = 8.5, 1.7 Hz, 1H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 4.00-4.02 (t, J = 5.9 Hz, 2H, Piperidine-H), 3.96 (s, 3H, OCH3), 3.59 (br, 2H, Piperidine-H), 1.76 (br, 6H, Piperidine-H); IR (KBr, cm⁻¹): νmax 1672 (C=O), 1598 (C=N, C=C); HRMS: m/z [M]⁺ calcd: 318.1036, found 318.1038.
(Z)-2-(Piperidin-1-yl)-5-(pyridin-4-ylmethylene)thiazol-4(5H)-one 9k

Yield 98%; yellow solid; mp = 171-173 °C; \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.67 (d, \( J = 5.0 \) Hz, 2H, Ar-H), 7.56-7.52 (m, 3H, Ar-H + =CH), 3.89 (br, 2H, Piperidine-H), 3.63 (br, 2H, Piperidine-H), 1.65 (br, 6H, Piperidine-H); IR (KBr, cm\(^{-1}\)): \( \nu_{\text{max}} \) 1691 (C=O), 1624 (C=N), 1611 (C=C); HRMS: \( m/z \) [M + Na]\(^+\) calcd: 296.0832, found 296.0837.

(Z)-2-(Piperidin-1-yl)-5-(thiophen-2-ylmethylene)thiazol-4(5H)-one 9l

Yield 96%; greenish solid; mp = 203-205 °C; \( ^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \): 7.93 (d, \( 1H, J = 5.4 \) Hz, Ar-H), 7.87 (s, \( 1H, =CH \)), 7.59 (d, \( 1H, J = 3.5 \) Hz, Ar-H), 7.26-7.24 (dd, \( 1H, J = 1.4, 4.1 \) Hz, Ar-H), 3.96–3.88 (m, 2H, Piperidine-H), 3.66–3.63 (m, 2H, Piperidine-H), 1.62-1.65 ppm (m, 6H, Piperidine-H); IR (KBr, cm\(^{-1}\)): \( \nu_{\text{max}} \) 1701 (C=O), 1609 (C=N), 1591 (C=C); HRMS: \( m/z \) [M]\(^+\) calcd: 278.0548, found 278.0529.

(Z)-5-((1H-Indol-3-yl)methylene)-2-(piperidin-1-yl)thiazol-4(5H)-one 9m

Yield 98%; yellow solid; mp = 244-246 °C; \( ^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \): 11.99 (s, \( 1H, NH \)), 7.89 (s, \( 1H, =CH \)), 7.85 (d, \( J = 8.7 \) Hz, 1H, Ar-H), 7.74 (s, \( 1H, Ar-H \)), 7.49 (d, \( J = 7.5 \) Hz, Ar-H), 7.46 (d, \( J = 8.1 \) Hz, Ar-H), 7.14–7.01 ppm (m, 2H, Indole-H).
1H, Ar-H), 7.19-7.11 (m, 2H, Ar-H), 3.88-3.78 (m, 4H, Piperidine-H), 1.78–1.70 ppm (m, 6H, Piperidine-H); IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 1691 (C=O), 1612 (C=N), 1598 (C=C); HRMS: \(m/z\) [M + H]\(^{+}\) calcd: 312.1167, found 312.1172.

**SEM of TiO\(_2\)**

![SEM of TiO\(_2\)](image)
TEM of TiO$_2$
SEM of ZnO
TEM of ZnO
Green Metrics Calculations$^{1,2}$

\[
\% \text{ Atomic Efficiency (AE)} = \frac{\text{Mol Wt. of desired product}}{\text{Mol Wt. of all reagents}} \times 100
\]

\[
\% \text{ Carbon Efficiency (CE)} = \frac{\text{Mass of carbon in product}}{\text{Totall mass of carbon in the reactants}} \times 100
\]

\[
\text{Reaction Mass Efficiency (RME)} = \frac{\text{Mass of the isolated product}}{\text{Total mass of reactants used in the reaction}} \times 100
\]

\[
\% \text{ Yield Economy (YE)} = \frac{\text{Reaction percent}}{\text{Time in min}} \times 100
\]

\[
\text{E-Factor (EF)} = \frac{\text{Mass of the total waste}}{\text{Mass of the crude product}}
\]

\[
\text{Process Mass Intensity (PMI)} = \frac{\text{Total mass used in process}}{\text{Mass of product}}
\]

References

1. D. Curzons, D. J. C. Constable, D. N. Mortimer and V. L. Cunningham, *Green Chem.*, 2001, 3, 1-6.
2. C. Jimenez-Gonzalez, D. J. C. Constable and C. S. Ponder, *Chem. Soc. Rev.*, 2012, 41, 1485-1498.