# An efficient synthesis of triazolium ion based NHC precursor using diaryliodonium salts and their photophysical properties

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# **Supporting Information**

## **Table of Contents**

1.	General Information	S 2
2.	General experimental procedure for the synthesis of triazolium salts (3a-t)	S 2
3.	Benzoin condensation: Synthesis of $\alpha$ -hydroxyketones (5)	S 3
4.	Characterization data of synthesized triazolium salts	S 3
5.	References	S 11
6.	Copies of <sup>1</sup> H, <sup>13</sup> C NMR and HRMS data of triazolium salts	S 12

#### **1. General Information**

Laboratory reagents were obtained commercially. Progress of the reaction was monitored by thin layer chromatography (TLC), which was performed on Merck pre-coated plates (silica gel 60, F  $_{254}$ , 0.25mm) and it was visualized by fluorescence quenching under hand-UV lamp (254 nm). The column chromatography was performed using 60-120 mesh silica gel. All the reactions were performed in a CEM focused microwave oven at 100 Watt power. The solvents were evaporated using Buchi rotary evaporator. Melting points were determined using *E*-Z melting point apparatus and are uncorrected. NMR (<sup>1</sup>H and <sup>13</sup>C) spectra were recorded using Bruker-Avance II (400 MHz). In <sup>1</sup>H NMR the coupling constants (*J*) were given in Hz, chemical shift ( $\delta$ ) in ppm. TMS was used as an internal standard. The proton multiplicities were described as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet and m = multiplet. IR spectra are recorded on Shimadzu FT-IR spectrophotometer and are reported in wave numbers (cm<sup>-1</sup>). Starting material fused triazoles<sup>1</sup> (**1a-e**) and diaryliodonium salts<sup>2</sup> (**2a-n**) were prepared using literature reported methods.

#### 2. General experimental procedure for the synthesis of triazolium salts (3a-t)



A dried round bottom flask was charged with triazolopyridine 1 (0.42 mmol), 5% of  $Cu(OTf)_2$  and diaryliodonium salt (0.42 mmol) in DCE (2 mL). The reaction mixture was stirred at 110 °C for 3 h in an oil bath. Progress of the reaction was monitored by checking TLC. After completion, reaction mixture was cool down to room temperature and DCE was removed under reduced pressure. The residue so obtained was passed through a column chromatography using dichloromethane/methanol (8:2) as an eluent to afford pure triazolium salt **3** in 78-95% yields.

#### **3.** Benzoin condensation: Synthesis of α-hydroxyketones

A 10 mL dried round-bottomed flask was charged with the triazolium salt **3a** (6.5 mg, 0.0188 mmol) in 2 mL of dry THF at room temperature followed by the addition of *t*-BuOK (2.6 mg, 0.0188 mmol). The traction mixture was stirred for 15 min, then benzaldehyde **4** (100 mg, 0.943 mmol) was added. The stirring was continued at room temperature for another 8 h. Thereafter, reaction mixture was poured into water and extracted with ethylacetate. The organic layer was evaporated, and crude product so obtained was passed through a column chromatography using hexane/ethylacetate (9:1) as an eluent to afford pure  $\alpha$ -hydroxy ketone **5** in 60% yield; mp 133-134 °C (lit. mp 132°C).

#### 4. Characterization data of synthesized triazolium salts



#### 2-Phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3a)

Brown thick liquid (137 mg, 95%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.00 (s, 1H), 9.12 (d, J = 6.8 Hz, 1H), 8.44 – 8.14 (m, 2H), 7.85 (d, J = 7.9 Hz, 2H), 7.81 – 7.60 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  142.5, 139.9, 137.9, 135.3, 130.9, 130.8, 128.9, 124.7, 119.6, 111.6; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>10</sub>N<sub>3</sub>, 196.0869; found, 196.0857.



#### 2-Phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium hexafluorophosphate (3b)

Off white solid (111 mg, 78%); mp 204-205 °C, lit.<sup>[3]</sup> mp 203-205 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.00 (s, 1H), 9.12 (d, J = 6.7 Hz, 1H), 8.33-8.26 (m, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.81–7.68 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 142.5, 139.9, 138.0, 135.3, 131.0, 130.8,

129.0, 124.7, 119.6, 111.6; HRMS  $[M - PF_6]^+$  calcd for  $C_{12}H_{10}N_3$ , 196.0869; found, 196.0870.



2-Phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium tetrafluoroborate (3c)

Brown Solid (125 mg, 86%); <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  9.99 (s, 1H), 9.11 (d, *J* = 6.0 Hz, 1H), 8.30-8.21 (m, 2H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.75-7.70 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  142.5, 140.0, 138.0, 135.3, 130.9, 130.8, 128.9, 124.7, 119.6, 111.6; HRMS [M – BF<sub>4</sub>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>10</sub>N<sub>3</sub>, 196.0869; found, 196.0869.



2-(*p*-Tolyl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3e)

Brown thick liquid (134 mg, 89%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.98 (s, 1H), 9.11 (d, J = 6.8 Hz, 1H), 8.26 (d, J = 2.2 Hz, 2H), 7.72 (dd, J = 8.7, 2.2 Hz, 3H), 7.55 (d, J = 5.9 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ))  $\delta$  142.4, 140.9, 139.8, 137.8, 132.9, 131.1, 128.9, 124.6, 119.5, 111.5, 21.4; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>, 210.1026; found, 210.1030.



**2-(4-Chlorophenyl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3f)** Brown thick liquid (124 mg, 78%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.01 (s, 1H), 9.13 (d, J = 6.8 Hz, 1H), 8.55 – 8.15 (m, 2H), 7.92 – 7.81 (m, 4H), 7.79-7.75 (m, 1H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  142.6, 140.1, 138.0, 135.5, 134.1, 130.8, 129.0, 126.7, 119.7, 111.6; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>9</sub>ClN<sub>3</sub>, 230.0480; found, 230.0466.



2-(3-(Methoxycarbonyl)phenyl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3g)

Yellow liquid (135 mg, 80%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.03 (s, 1H), 9.15 (d, J = 6.8 Hz, 1H), 8.41 – 8.30 (m, 3H), 8.29 – 8.22 (m, 1H), 8.16-8.13 (m, 1H), 7.98 – 7.88 (m, 1H), 7.85 – 7.74 (m, 1H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  165.5, 142.8, 140.3, 138.1, 135.7, 132.0, 131.5, 131.3, 129.5, 129.0, 125.5, 119.7, 111.6, 53.3; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub>, 254.0924; found, 254.0937.



### 2-Mesityl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3g')

Yellow liquid (145 mg, 75%); <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  10.27 (s, 1H), 9.28 (d, *J* = 6.8 Hz, 1H), 8.28 (dd, *J* = 9.0, 7.9 Hz, 1H), 7.93 – 7.66 (m, 2H), 7.22 (s, 2H), 1.95 (s, 6H), 1.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  143.0, 141.9, 140.7, 138.7, 136.6, 130.2, 129.8, 119.4, 110.2, 21.2, 17.3; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>, 238.1339; found, 238.1338.



#### 2,3-Diphenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3h)

Brown solid (102 mg, 95%); mp 138-139 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.07 (d, J = 7.0 Hz, 1H), 8.38-8.29 (m, 2H), 8.01 – 7.99 (m, 2H), 7.89 (d, J = 7.4 Hz, 2H), 7.81-7.75 (m, 5H), 7.73 – 7.69 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  146.9, 143.4, 139.9, 135.2,

133.0, 131.1, 130.9, 130.2, 130.0, 127.8, 124.8, 122.7, 120.0, 111.8; HRMS  $[M - OTf^{-}]^{+}$  calcd for  $C_{18}H_{14}N_3$ , 272.1182; found, 272.1166.



# 2-(4-Chlorophenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane Sulfonate (3i)

Brown liquid (99 mg, 85%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.12 (d, J = 6.9 Hz, 1H), 8.46 – 8.31 (m, 2H), 8.03 (d, J = 6.9 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.7 Hz, 2H), 7.79-7.75 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  147.0, 143.6, 140.1, 135.6, 134.1, 133.0, 130.9, 130.3, 130.0, 127.9, 126.8, 122.5, 120.1, 111.7; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>ClN<sub>3</sub>, 306.0793; found, 306.0768.



# 2-(4-Bromophenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane Sulfonate (3j)

Brown liquid (108 mg, 85%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.11 (d, J = 6.6 Hz, 1H), 8.62 – 8.26 (m, 2H), 8.01 (t, J = 6.7 Hz, 4H), 7.88 (d, J = 8.4 Hz, 2H), 7.84-7.74 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  143.5, 140.1, 134.5, 133.9, 133.1, 130.3, 130.0, 127.8, 126.8, 124.2, 122.5, 120.1, 111.7; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>BrN<sub>3</sub>, 350.0287; found, 350.0266.



**3-Phenyl-2-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3k)** Off-white solid (100 mg, 90%); mp 203-204 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.08 (d, *J* = 6.9 Hz, 1H), 8.36-8.30 (m, 2H), 8.02 (d, *J* = 6.9 Hz, 2H), 7.88 – 7.69 (m, 6H), 7.59 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  146.7, 143.3, 141.1, 139.8, 133.0, 132.8, 131.2, 130.2, 130.1, 127.8, 124.7, 122.7, 119.9, 111.7, 21.3; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>, 286.1339; found, 286.1325.



# 2-(2-Nitrophenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane Sulfonate (3l)

Off-white solid (106 mg, 89%); 209-210 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.21 (d, J = 6.9 Hz, 1H), 8.53 (d, J = 7.8 Hz, 1H), 8.49 – 8.42 (m, 1H), 8.37 (d, J = 7.8 Hz, 1H), 8.19 (t, J = 7.3 Hz, 1H), 8.11-8.08 (m, 2H), 8.05 (d, J = 7.0 Hz, 2H), 7.85-7.77 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  147.5, 144.7, 141.1, 136.4, 133.9, 133.3, 130.4, 130.3, 130.1, 128.6, 127.4, 127.3, 122.2, 120.4, 111.4; HRMS [M – OTf <sup>–</sup>]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>, 317.1013; found, 317.1017.



# 2-(2-(Methoxycarbonyl)phenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3m)

White solid (110 mg, 90%); mp 140-141 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.19 (d, J = 6.9 Hz, 1H), 8.38 – 8.32 (m, 1H), 8.29 (d, J = 7.7 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.09 – 8.04 (m, 3H), 7.97-7.94 (m, 2H), 7.84-7.77 (m, 4H), 3.67 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  164.6, 146.7, 144.6, 140.3, 135.2, 133.4, 133.2, 132.6, 130.3, 130.0, 129.6, 128.1, 127.5, 122.4, 120.1, 111.4, 53.5; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>, 330.1237; found, 330.1220.



**3-Phenyl-2-(m-tolyl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3n)** White solid (105 mg, 90%); mp 130-131 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.10 (d, J = 6.9 Hz, 1H), 8.43 (d, J = 9.3 Hz, 1H), 8.36-8.32 (m, 1H), 8.04 (d, J = 6.6 Hz, 2H), 7.87 – 7.77 (m, 3H), 7.75-7.66 (m, 4H), 7.55 (d, J = 7.3 Hz, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  146.8, 143.3, 140.8, 139.9, 135.2, 133.0, 131.7, 130.6, 130.2, 130.0, 127.8, 124.9, 122.7, 121.8, 120.0, 111.8, 21.3; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>, 286.1339; found, 286.1319.



# 2-(3,4-Dimethylphenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane Sulfonate (30)

Light brown solid (103 mg, 90%); mp 138-139 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.08 (d, J = 6.9 Hz, 1H), 8.40 – 8.27 (m, 2H), 8.02 (d, J = 6.5 Hz, 2H), 7.84 – 7.76 (m, 3H), 7.76 – 7.70 (m, 1H), 7.68 (s, 1H), 7.64-7.62 (m, 1H), 7.54 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H), 2.39 (s,

3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  146.7, 143.2, 139.9, 139.7, 139.5, 133.0, 131.5, 130.2, 130.0, 127.7, 125.3, 122.7, 121.9, 119.9, 111.8, 19.9, 19.7; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>N<sub>3</sub>, 300.1495; found, 300.1481.



# 2-(3,4-Difluorophenyl)-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane sulfonate (3p)

Brown liquid (93 mg, 80%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ))  $\delta$  9.13 (d, J = 6.9 Hz, 1H), 8.47 (d, J = 9.2 Hz, 1H), 8.44 – 8.36 (m, 1H), 8.17 – 8.10 (m, 1H), 8.04 (d, J = 7.0 Hz, 2H), 7.91 (d, J = 9.2 Hz, 1H), 7.87 – 7.76 (m, 5H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  146.9, 143.8, 140.3, 136.7, 133.1, 130.2, 130.0, 127.8, 122.7, 122.5, 120.3, 119.9, 119.6, 115.6, 115.4, 111.7; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>18</sub>H<sub>12</sub>F<sub>2</sub>N<sub>3</sub>, 308.0994; found, 308.0975.



**2-Mesityl-3-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3q)** Brown liquid (99 mg, 84%); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.16 (s, 1H), 8.39 – 8.24 (m, 1H), 8.08 (d, J = 6.4 Hz, 2H), 7.88 (d, J = 8.2 Hz, 1H), 7.85 – 7.73 (m, 4H), 7.25 (s, 2H), 2.41 (s, 3H), 2.08 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  147.5, 144.0, 141.9, 140.4, 136.7, 132.9, 130.2, 130.0, 129.8, 128.6, 123.0, 119.7, 110.6, 21.4, 17.5; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>20</sub>N<sub>3</sub>, 314.1652; found, 314.1667.



2-Phenyl-3-(thiophen-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethane

## Sulfonate (3r)

Brown solid (98 mg, 90%); mp 155-56 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.30 (d, J = 6.9 Hz, 1H), 8.39-8.82 (m, 2H), 8.24-8.19 (m, 2H), 7.89 (d, J = 7.4 Hz, 2H), 7.83-7.74 (m, 4H), 7.53 – 7.51 (m, 1H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  143.5, 142.4, 140.0, 135.1, 133.3, 132.6, 131.2, 130.9, 129.6, 128.0, 124.9, 122.6, 120.2, 111.9; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>N<sub>3</sub>S, 278.0746.; found, 278.0728.



# 3-(Furan-2-yl)-2-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3s)

Brown solid (94 mg, 90%); mp 127-128 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.39 (d, J = 6.4 Hz, 1H), 8.39-8.31 (m, 3H), 7.89-7.75 (m, 7H), 7.03 (d, J = 0.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  148.2, 143.3, 140.0, 139.9, 138.3, 135.1, 131.3, 130.9, 128.4, 125.0, 120.3, 116.7, 113.5, 112.0; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>N<sub>3</sub>O, 262.0975; found, 262.0959.



# 2-Phenyl-3-(pyridin-2-yl)-[1,2,4]triazolo[4,3-a]pyridin-2-ium trifluoromethanesulfonate (3t)

Dark brown solid (98 mg, 91%); mp 146-147 °C (decomposed); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.23 (d, J = 7.0 Hz, 1H), 8.99 (d, J = 4.3 Hz, 1H), 8.48 (d, J = 7.9 Hz, 1H),

8.44 – 8.35 (m, 2H), 8.24 (t, J = 7.8 Hz, 1H), 7.94 (d, J = 7.4 Hz, 2H), 7.91 – 7.85 (m, 1H), 7.85 – 7.75 (m, 4H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  150.3, 144.8, 144.1, 143.3, 140.0, 139.3, 135.2, 131.4, 130.9, 130.2, 127.3, 125.1, 124.4, 120.3, 111.8; HRMS [M – OTf<sup>-</sup>]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>N<sub>4</sub>, 273.1135; found, 273.1116.



*a*-hydroxy ketone; Benzoin (5)<sup>3</sup>: Yellow solid (60%); mp 133-134 °C (lit. mp 132°C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 – 7.86 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.27 (m, 5H), 5.98 (s, 1H), 4.58 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 139.0, 133.9, 133.5, 129.1, 129.1, 128.7, 128.6, 127.8, 76.2; HRMS [(M+H)-H<sub>2</sub>O]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>O, 195.0804; found, 195.0808.

#### 5. References

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- 3 Y. Ma, S. Wei, J. Lan, J. Wang, R. Xie, J. You, J. Org. Chem. 2008, 73, 8256.

# 6. Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of triazolium salts

## <sup>1</sup>H NMR spectrum of **3a**







Mass spectrum of 3a



<sup>1</sup>H NMR spectrum of **3b** 



<sup>13</sup>C NMR spectrum of **3b** 



Mass spectrum of 3b



 $^1\mathrm{H}$  NMR spectrum of 3c



<sup>13</sup>C NMR spectrum of **3**c



Mass spectrum of 3c



<sup>1</sup>H NMR spectrum of **3e** 





Mass spectrum of 3e



# $^1\mathrm{H}$ NMR spectrum of $\mathbf{3f}$







# <sup>13</sup>C NMR spectrum of **3f**



Mass spectrum of  $\mathbf{3f}$ 



<sup>1</sup>H NMR spectrum of **3g** 



<sup>13</sup>C NMR spectrum of **3**g



Mass spectrum of 3g



## <sup>1</sup>H NMR spectrum of **3g**'



## Mass spectrum of 3g'



<sup>1</sup>H NMR spectrum of **3h** 



## <sup>13</sup>C NMR spectrum of **3h**



Mass Spectrum of 3h





f1 (ppm) 

## Mass Spectrum of 3i



<sup>1</sup>H NMR spectrum of **3**j





Mass Spectrum of 3j





<sup>13</sup>C NMR spectrum of **3**k



Mass Spectrum of 3k



<sup>1</sup>H NMR spectrum of **3**l





Mass Spectrum of 31







# <sup>13</sup>C NMR spectrum of **3m**



Mass Spectrum of 3m





Mass Spectrum of 3n









Mass Spectrum of 30



<sup>&</sup>lt;sup>1</sup>H NMR spectrum of **3p** 





Mass Spectrum of 3p



<sup>1</sup>H NMR spectrum of **3**q



<sup>13</sup>C NMR spectrum of **3q** 



Mass Spectrum of 3q







# <sup>13</sup>C NMR spectrum of **3r**



Mass Spectrum of 3r









Mass Spectrum of 3s



<sup>1</sup>H NMR spectrum of **3t** 





Mass Spectrum of 3t







Mass Spectrum of 5

