# **Supporting Information**

#### **Photoinduced β-fragmentation for efficient pyridine alkylation**

#### via N-alkoxypyridinium salts

Heng Liu<sup>a</sup>, Fangrui Wu<sup>a</sup>, Zhidong Wan<sup>a</sup>, Changhai Yue<sup>b</sup>, Changsheng Wang<sup>a</sup>, Chengkou Liu<sup>a</sup>, Yuguang Li<sup>c</sup>, Zheng Fang<sup>a</sup>, d, Hong Qin<sup>a\*</sup>, Zhao Yang<sup>c\*</sup>

<sup>a</sup>College of Biotechnology and Pharmaceutical Engineering Nanjing Tech University, 30 Puzhu Rd S., Nanjing, 211816, China. E-mail: guok@njtech.edu.cn, fzcpu@163.com; Fax: +8625 5813 9935; Tel: +8625 5813 9926.

<sup>b</sup>China Construction Industrial & Energy Engineering Group Company Limited, Nanjing, 210046, Jiangsu, China. E-mail: yuechanghai@cscec.com

<sup>c</sup>Institute of Nanjing Advanced Biomaterials & Processing Equipment, Liyuguang@njibp.com

<sup>d</sup>State Key Laboratory of Materials-Oriented Chemical Engineering, 30 Puzhu Rd S., Nanjing, 211816, China

<sup>e</sup>College of Engineering, China Pharmaceutical University, 24 Tongjiaxiang, Nanjing, 210003, China. E-mail: yzcpu@163.com

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#### I. General information

Commercially available reagents were used without further purification unless otherwise stated. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (60F-254), and visualization on TLC was achieved by UV light (254 nm). Flash column chromatography was performed on silica gel (200-300 mesh). <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (101 MHz), and <sup>19</sup>F NMR (376 MHz) were measured on a 400 MHz spectrometer. Chemical shifts ( $\delta$ ) were reported in ppm, referenced to tetramethylsilane (TMS) as an internal standard. The solvent peak was used as a reference value: for <sup>1</sup>H NMR,  $CDCl_3 = 7.26$  ppm,  $(CD_3)_2CO = 3.31$  ppm; for <sup>13</sup>C NMR, CDCl<sub>3</sub> = 77.16 ppm,  $(CD_3)_2CO = 49.00$  ppm. NMR spectra use the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, dd = double doublet, tt = tripletriplet, br = broad. Coupling constants (J) are reported in hertz (Hz). NMR data were processed using the MestReNova 14.0.0 software package. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight). The Blue LEDs were made by Xuzhou Aijia Electronic Technology Co. Ltd. (wavelength of peak intensity: 30 W, 420 nm), equipped with a cooling fan for efficient temperature maintenance. The distance from the Blue LEDs to the irradiation vessel should be 5 cm. Material of the irradiation vessel: quartz tube. Do not use any filters.

#### II. Procedures for the Synthesis of N-alkoxypyridinium salts



To a solution of alkyl tosylate (1.2 equiv) in  $CH_3CN$  (0.1M) was added Pyridine-n-oxides (1.0 equiv) at room temperature. The reaction mixture was stirred at 80 °C overnight, then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (MeOH/EtOAc=1:10) to afford target product.

### **III.** Optimization of the Reaction Conditions

Table S1. Screening of solvents.<sup>a</sup>

Me , , , , , , , , , , , , ,	Ir(ppy) <sub>3</sub> (0.5 mol %), NaHCO <sub>3</sub> → Solvent (0.1M), Ar, r.t., 12h Blue LEDs (420 nm)	Me
Entry	Solvent	Yield (%) <sup>b</sup>
1	THF	NR
2	DMSO	33
3	MeOH	52
4	EtOH	46
5	DCM	69
6	H <sub>2</sub> O	NR
7	DMF	NR
8	EtOAc	NR
9	MeCN	72

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol), Ir(ppy)<sub>3</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

Me N OTs	photocat. (0.5 mol %), NaHCO <sub>3</sub> ► MeCN (0.1M), Ar, r.t., 12h Blue LEDs (420 nm)	Me
Entry	Photocatalyst	Yield (%) <sup>b</sup>
1	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	35

Table S2. Screening of photocatalysts.<sup>*a*</sup>

2	Ir[(ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	60
3	4CzIPN	68
4	5CzBN	55
5	Eosin Y	32
6	Ir(ppy) <sub>3</sub>	72
7	[Ir(dtbbpy)[dF(CF <sub>3</sub> )ppy] <sub>2</sub> ]PF <sub>6</sub>	82
8°		NR

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol) in MeCN (2.0 mL) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography. <sup>*c*</sup> Without photocatalyst.

#### Table S3. Screening of bases. <sup>a</sup>

Me N + O Ts	[Ir(dtbbpy)[dF(CF <sub>3</sub> )ppy] <sub>2</sub> ]PF <sub>6</sub> (0.5 mol %), Base MeCN (0.1 M), Ar, r.t., 12h Blue LEDs (420 nm)	→ Me N
Entry	Base	Yield (%) <sup>b</sup>
1	$CS_2CO_3$	64
2	CaCO <sub>3</sub>	52
3	Na <sub>2</sub> CO <sub>3</sub>	66
5	KH <sub>2</sub> PO <sub>4</sub>	59
6	TEA	NR
7	DABCO	NR
8	DBU	NR

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), Base (0.24 mmol), [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>]PF<sub>6</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

Table S4. Screening of the loading of the photocatalyst. <sup>a</sup>

Me N + OTs	[lr(dtbbpy)[dF(CF <sub>3</sub> )ppy] <sub>2</sub> ]PF <sub>6</sub> , NaHCO <sub>3</sub> MeCN (0.1 M), Ar, r.t., 12 h Blue LEDs (420 nm)	Me N
Entry	PC	Yield (%) <sup>b</sup>
1	0.1 mol %	67
2	1.0 mol %	74
3	1.5 mol %	66

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.3 mmol), [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>]PF<sub>6</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

Me N + O OTs	[Ir(dtbbpy)[dF(CF <sub>3</sub> )ppy] <sub>2</sub> ]PF <sub>6</sub> (0.5 mol %), Nal MeCN (0.1 M), Ar, r.t., 12 h Blue LEDs (420 nm)	HCO <sub>3</sub>
Entry	Base	Yield (%) <sup>b</sup>
1	0.1 eq	15
2	0.5 eq	53
3	1.0 eq	65
4	1.5 eq	43
5	2.0 eq	35
6	3.0 eq	46

 Table S5. Screening of the loading of the base. a

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol), [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>]PF<sub>6</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

Table S6. Screening of the the reaction time. <sup>a</sup>

Me N N O Ts	[Ir(dtbbpy)[dF(CF <sub>3</sub> )ppy] <sub>2</sub> ]PF <sub>6</sub> (0.5 mol %), Nał MeCN (0.1 M), Ar, r.t., Time Blue LEDs (420 nm)	HCO <sub>3</sub>
Entry	Time (h)	Yield (%) <sup>b</sup>
1	6	69
2	8	78
3	12	82

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol), [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>]PF<sub>6</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs. <sup>*b*</sup> Isolated yield after chromatography.

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Entry	Atmosphere	Yield (%) <sup>b</sup>
1	Ar	82
2	$N_2$	77
3	O <sub>2</sub>	24
4	$CO_2$	57
5	Air	39

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol), [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>]PF<sub>6</sub> (0.5 mol %) in a solvent (0.1 M) at room temperature under irradiation of blue LEDs for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

#### Table S8. Control experiments. <sup>a</sup>



<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), NaHCO<sub>3</sub> (0.24 mmol),  $[Ir(dtbbpy)]dF(CF_3)ppy]_2]PF_6$  (0.5 mol %) in a solvent (0.1 M) at room temperature for 12 h. <sup>*b*</sup> Isolated yield after chromatography.

## IV. Procedure for the Synthesis of Compounds 2a-z, 2aa-2ah



In an oven-dried pressure-resistant reaction tube (10 mL) equipped with a stir bar, N-alkoxypyridinium salts **1** (0.2 mmol, 1.0 equiv), NaHCO<sub>3</sub> (0.24 mmol 1.2 equiv),  $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$  (0.5 mol %) were combined and added to CH<sub>3</sub>CN (0.1 M) solvent, stirred under Ar atmosphere and irradiated by 30 W blue LEDs at RT for 12 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. The pure product 2 was obtained by flash column chromatography on silica gel (eluent:PE:EA=10:1).

#### V. Mechanistic Studies

#### **Radical Trapping Experiment Using TEMPO**



An oven-dried 10 mL vial equipped with a rubber plug and magnetic stir bar was charged with 4-methyl-substituted N-alkoxypyridinium salt (0.20 mmol, 1.0 equiv.), NaHCO<sub>3</sub> (0.24 mmol, 1.2 equiv) and CH<sub>3</sub>CN (2 mL, 0.1 M). The radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added into the reaction mixture. The reaction mixture was degassed by three cycles of freeze-pump-thaw. The reaction mixture was then stirred and irradiated with blue LEDs at temperature. After 12 hours, no desired products were observed by TLC, indicating that the reaction might involve a radical process. Then adduct was detected by HRMS. HRMS (ESI) m/z: calcd for  $C_{15}H_{29}NO [M+H]^+$ : 240.2322; found: 240.2302.



Figure S1. ESI Mass spectrum arising from TEMPO-trapping experiment

#### **Control Experiments**



The 4-methyl-substituted N-alkoxypyridinium salt and commercially available 4-Methoxycarbonylpyridine was employ as the substrate to react with N-vinylbenzamide under the Blue LEDs. After 12 h, the corresponding product of the 4-Methoxycarbonylpyridine was not detected by TLC, indicating that the reaction proceeded via the pyridine salts intermediate instead of pyridine.

#### **On/off lamp experiment**

An On/Off experiment was performed to checked the impact of light in this reaction. We carried out the experiment by following the general procedure with alternating exposure (2 hour) of light and darkness. These showed that the reaction process was completely stop in absence of light and resume in further illumination. These results demonstrate that light is an essential component for this reaction.



Figure S2. Light On/Off Experiment.

#### Cyclic voltammetry experiments

The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 2.5 V. The scan rate was 100 mVs<sup>-1</sup>. The solvent was poured into the electrochemical cell in all experiments. The electrode was used without polishing and the solvent was used without deoxygenation.



Figure S3. Cyclic voltammetry experiments of substrates.

#### **VI.** References

- I. Kim, B. Park, G. Kang, J. Kim, H. Jung, H. Lee, M. H. Baik and S. Hong, Visible-Light-Induced Pyridylation of Remote C(sp<sup>3</sup>)-H Bonds by Radical Translocation of N-Alkoxypyridinium Salts, *Angew. Chem. Int. Ed.*, 2018, 57, 15517-15522.
- A. Inial, F. Morlet-Savary, J. Lalevée, A. C. Gaumont and S. Lakhdar, Visible-Light-Mediated Access to Phosphate Esters, *Org. Lett.*, 2020, 22, 4404-4407.

#### **VII.** Compound Characterizations



1-(Cyclohexylmethoxy)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (1a) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.31 – 9.24 (m, 2H), 8.05 (d, J = 6.7 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.43 (d, J = 6.1 Hz, 2H), 2.61 (s, 3H), 2.29 (s, 3H), 1.82 – 1.77 (m, 3H), 1.74 – 1.69 (m, 2H), 1.67 – 1.63 (m, 1H), 1.33 – 1.14 (m, 3H), 1.14 – 1.04 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  158.99, 146.28, 140.77, 138.07, 129.88, 128.52, 125.98, 87.59, 36.28, 29.03, 26.22, 25.40, 21.72, 21.24. HRMS (ESI): m/z calcd. For C<sub>13</sub>H<sub>20</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 206.1539, found: 206.1533.



**4-methyl-1-(2-methylbutoxy)pyridin-1-ium 4-methylbenzenesulfonate (1c)** was prepared according to the general procedure. Yellow oil. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.35 – 9.31 (m, 2H), 8.05 (d, *J* = 6.8 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.15 – 7.09 (m, 2H), 4.52 (dd, *J* = 8.2, 5.8 Hz, 1H), 4.43 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.61 (s, 3H), 2.28 (s, 3H), 1.86 (dddd, *J* = 12.4, 8.0, 6.8, 5.7 Hz, 1H), 1.56 – 1.44 (m, 1H), 1.26 (dt, *J* = 13.5, 7.5 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  158.98, 146.07, 140.78, 138.22, 129.91, 128.57, 125.98, 87.37, 33.54, 25.58, 21.71, 21.22, 16.22, 11.39. HRMS (ESI): m/z calcd. For C<sub>11</sub>H<sub>28</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 180.1383, found: 180.1372.



**1-(cyclopropylmethoxy)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (1d)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.34–9.24 (m, 2H), 8.03 (d, *J*=6.8 Hz, 2H), 7.56–7.49 (m, 2H), 7.12 (d,

*J*=7.9 Hz, 2H), 4.46 (d, *J*=7.5 Hz, 2H), 2.60 (s, 3H), 2.28 (s, 3H), 1.27–1.13 (m, 1H), 0.61–0.50 (m, 2H), 0.32–0.24 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 159.19, 146.07, 141.35, 138.27, 129.78, 128.60, 125.99, 87.39, 21.76, 21.24, 8.73, 3.63. HRMS (ESI): m/z calcd. For C<sub>10</sub>H<sub>14</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 164.1070, found: 164.1065.



**1-(cyclobutylmethoxy)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (1e)** was prepared according to the general procedure. White solid. <sup>1</sup>**H** NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.32 – 9.25 (m, 2H), 8.05 (d, *J* = 6.7 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.60 (d, *J* = 7.1 Hz, 2H), 2.79 – 2.67 (m, 1H), 2.61 (s, 3H), 2.28 (s, 3H), 2.08 – 2.01 (m, 2H), 1.96 – 1.78 (m, 4H). <sup>13</sup>**C** NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.13, 146.26, 140.93, 138.11, 129.88, 128.54, 125.98, 86.18, 32.68, 24.44, 21.74, 21.24, 18.60. HRMS (ESI): m/z calcd. For C<sub>11</sub>H<sub>16</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 178.1226, found: 178.1219.



**1-(cyclopentylmethoxy)pyridin-1-ium 4-methylbenzenesulfonate (1f)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.30 (d, *J* = 6.6 Hz, 2H), 8.03 (d, *J* = 6.5 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 4.49 (d, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.33 – 2.26 (m, 4H), 1.79 – 1.71 (m, 2H), 1.62 – 1.49 (m, 4H), 1.39 – 1.31 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.00, 146.08, 140.82, 138.22, 129.89, 128.55, 125.98, 86.72, 37.40, 29.06, 25.46, 21.73, 21.23. HRMS (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 192.1383, found: 192.1385.



#### 2,6-dimethyl-1-((tetrahydrofuran-2-yl)methoxy)pyridin-1-ium

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methylbenzenesulfonate (1g) was prepared according to the general procedure.

Yellow oil. <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.35 (t, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.55 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.42 (dd, *J* = 9.5, 7.4 Hz, 1H), 4.29 (qd, *J* = 7.3, 2.4 Hz, 1H), 3.87 – 3.72 (m, 2H), 2.84 (s, 6H), 2.29 (s, 3H), 2.10 – 2.01 (m, 1H), 1.95 – 1.78 (m, 2H), 1.63 (ddd, *J* = 12.3, 8.4, 5.9 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  154.06, 145.99, 144.30, 138.24, 128.56, 128.51, 125.97, 81.59, 75.56, 68.32, 27.48, 25.59, 21.24, 17.62. **HRMS** (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 208.1332, found: 208.1317.



**4-methyl-1-((tetrahydro-2H-pyran-4-yl)methoxy)pyridin-1-ium 4-methylbenzenesulfonate (1i)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.34 – 9.27 (m, 2H), 8.04 (d, *J* = 6.6 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.48 (d, *J* = 6.5 Hz, 2H), 3.86 (ddd, *J* = 11.5, 4.6, 1.9 Hz, 2H), 3.31 (td, *J* = 11.7, 2.1 Hz, 2H), 2.60 (s, 3H), 2.29 (s, 3H), 2.08 – 1.99 (m, *J* = 15.3, 9.4, 6.5 Hz, 1H), 1.66 (ddd, *J* = 13.0, 4.1, 2.0 Hz, 2H), 1.43 – 1.28 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.03, 146.09, 140.80, 138.24, 129.90, 128.58, 125.98, 86.70, 66.77, 33.61, 28.91, 21.72, 21.23. HRMS (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 208.1332, found: 208.1328.



#### 1-((4,4-difluorocyclohexyl)methoxy)-4-methylpyridin-1-ium

methylbenzenesulfonate (1J) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.35 – 9.27 (m, 2H), 8.06 (d, J = 6.6 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.53 (d, J = 6.4 Hz, 2H), 2.62 (s, 3H), 2.29 (s, 3H), 2.10 – 1.96 (m, 3H), 1.92 – 1.84 (m, 3H), 1.84 – 1.76 (m, 1H), 1.43 – 1.33 (m, 2H).<sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  159.14, 145.89, 140.81, 138.33, 129.89, 128.59, 125.98, 126.88 – 122.11 (m), 86.04 (d, J = 2.9 Hz), 33.83, 32.74 – 32.26 (m), 25.20 (d, J = 9.5 Hz), 21.74, 21.23. <sup>19</sup>F NMR (376 MHz,

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DMSO-*d*<sub>6</sub>)  $\delta$  -89.76 (d, *J* = 233.1 Hz), -99.43 (d, *J* = 233.9 Hz). **HRMS** (ESI): m/z calcd. For C<sub>13</sub>H<sub>18</sub>F<sub>2</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 242.1351, found: 242.1344.



**1-(cyclopentylmethoxy)pyridin-1-ium 4-methylbenzenesulfonate (1k)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.36 – 9.32 (m, 2H), 8.39 – 8.30 (m, 1H), 8.17 (dd, *J* = 8.2, 6.2 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 4.42 (d, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 2.19 (p, *J* = 7.6 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.54 – 1.41 (m, 4H), 1.24 – 1.15 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.00, 146.08, 140.82, 138.22, 129.89, 128.55, 125.98, 86.72, 37.40, 29.06, 25.46, 21.23. HRMS (ESI): m/z calcd. For C<sub>11</sub>H<sub>16</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 178.1226, found: 178.1219.



**1-(cyclopentylmethoxy)-4-methoxypyridin-1-ium 4-methylbenzenesulfonate (11)** was prepared according to the general procedure. White solid. <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.30 – 9.22 (m, 2H), 7.70 – 7.62 (m, 2H), 7.55 – 7.49 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.41 (d, *J* = 7.2 Hz, 2H), 4.09 (s, 3H), 2.34 – 2.26 (m, 4H), 1.81 – 1.68 (m, 2H), 1.66 – 1.44 (m, 4H), 1.41 – 1.33 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  170.39, 146.11, 143.38, 138.22, 128.57, 125.99, 114.53, 86.38, 58.98, 37.34, 29.06, 25.48, 21.22. **HRMS** (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 208.1332, found: 208.1325.



1-(cyclopentylmethoxy)-2-methylpyridin-1-ium 4-methylbenzenesulfonate (1m) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.47 (d, *J* = 6.6 Hz, 1H), 8.30 (t, *J* = 7.8 Hz, 1H), 8.06 – 7.94 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.45 (d, *J* = 7.1 Hz, 2H), 2.77

(s, 3H), 2.37 - 2.30 (m, 1H), 2.30 (s, 3H), 1.84 - 1.76 (m, 2H), 1.63 - 1.52 (m, 4H), 1.33 - 1.24 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  153.64, 146.24, 144.79, 141.88, 138.11, 130.79, 128.54, 127.41, 125.97, 85.78, 37.80, 29.19, 25.37, 21.24, 17.39. **HRMS** (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 192.1383, found: 192.1375.



1-(cyclopentylmethoxy)-3-fluoropyridin-1-ium 4-methylbenzenesulfonate (1n) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.55 – 9.27 (m, 2H), 8.57 – 8.22 (m, 2H), 7.68 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 4.58 (d, J = 7.3 Hz, 2H), 2.32 (s, 3H), 2.26 – 2.20 (m, 1H), 1.77 – 1.62 (m, 2H), 1.62 – 1.38 (m, 4H), 1.34 – 1.09 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 160.42 (d, J = 261.4 Hz), 143.59, 139.43, 138.82 (d, J = 4.1 Hz), 132.79 (d, J = 18.2 Hz), 131.81 (d, J = 38.3 Hz), 131.19 (d, J = 7.9 Hz), 128.66, 125.84, 88.18, 37.52, 29.03, 25.24, 21.23. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -110.40. HRMS (ESI): m/z calcd. For C<sub>11</sub>H<sub>15</sub>FNO<sup>+</sup> [M-OTs]<sup>+</sup>: 196.1332, found: 196.1326.



**3-chloro-1-(cyclopentylmethoxy)pyridin-1-ium 4-methylbenzenesulfonate (10)** was prepared according to the general procedure. White solid. <sup>1</sup>**H** NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.95 (t, *J* = 1.9 Hz, 1H), 9.47 (ddd, *J* = 6.6, 2.0, 1.0 Hz, 1H), 8.80 (ddd, *J* = 8.5, 1.9, 0.9 Hz, 1H), 8.27 (dd, *J* = 8.5, 6.5 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.58 (d, *J* = 7.2 Hz, 2H), 2.43 – 2.29 (m, 1H), 2.29 (s, 3H), 1.84 – 1.75 (m, 2H), 1.65 – 1.52 (m, 4H), 1.45 – 1.35 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  146.27, 145.18, 141.89, 140.91, 138.04, 135.30, 129.83, 128.51, 125.96, 87.46, 37.34, 29.03, 25.50, 21.25. **HRMS** (ESI): m/z calcd. For C<sub>11</sub>H<sub>15</sub>ClNO<sup>+</sup> [M-OTs]<sup>+</sup>: 212.0837, found: 212.0832.



**3-bromo-1-(cyclopentylmethoxy)pyridin-1-ium 4-methylbenzenesulfonate (1p)** was prepared according to the general procedure. White solid. <sup>1</sup>**H** NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.95 (t, *J* = 1.9 Hz, 1H), 9.50 (dd, *J* = 6.5, 1.9 Hz, 1H), 8.88 (d, *J* = 10.5 Hz, 1H), 8.18 (dd, *J* = 8.4, 6.5 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.76 (s, 1H), 4.57 (d, *J* = 7.2 Hz, 2H), 2.36 (p, *J* = 7.5 Hz, 1H), 2.29 (s, 3H), 1.82 – 1.73 (m, 2H), 1.66 – 1.50 (m, 4H), 1.44 – 1.34 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  147.88, 146.15, 143.42, 141.14, 138.12, 130.02, 128.53, 125.97, 122.99, 87.44, 37.36, 29.02, 25.49, 21.26. **HRMS** (ESI): m/z calcd. For C<sub>11</sub>H<sub>15</sub>BrNO<sup>+</sup> [M-OTs]<sup>+</sup>: 256.0332, found: 256.0322.



**1-(cyclopentylmethoxy)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (1q)** was prepared according to the general procedure. White solid. <sup>1</sup>**H** NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.59 (dd, J = 6.6, 1.3 Hz, 1H), 8.67 (td, J = 7.8, 1.3 Hz, 1H), 8.29 (dd, J = 8.0, 1.9 Hz, 1H), 8.24 (ddd, J = 8.1, 6.5, 1.9 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.71 – 7.63 (m, 3H), 7.53 – 7.47 (m, 2H), 7.11 (d, J = 7.9 Hz, 2H), 4.15 (d, J = 6.9 Hz, 2H), 2.28 (s, 3H), 2.09 – 2.01 (m, 1H), 1.55 – 1.43 (m, 2H), 1.40 – 1.33 (m, 4H), 0.96 – 0.87 (m, 2H). <sup>13</sup>**C** NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  151.54, 145.74, 144.25, 143.53, 138.91, 132.14, 130.93, 130.03, 129.27, 129.15, 128.49, 127.91, 126.01, 87.02, 37.52, 28.93, 24.98, 21.24. HRMS (ESI): m/z calcd. For C<sub>17</sub>H<sub>20</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 254.1539, found: 254.1531.



**1-(cyclopentylmethoxy)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (1r)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.50 – 9.33 (m, 2H), 8.50 – 8.40 (m, 1H), 8.21 – 8.08 (m, 2H), 7.78 –

7.67 (m, 2H), 7.11 (d, J = 7.9 Hz, 2H), 4.75 (dd, J = 11.4, 2.4 Hz, 1H), 4.58 (dd, J = 11.4, 8.0 Hz, 1H), 4.19 (qd, J = 7.6, 2.4 Hz, 1H), 3.73 - 3.62 (m, 2H), 2.30 (s, 3H), 2.01 – 1.88 (m, 1H), 1.87 – 1.70 (m, 2H), 1.56 – 1.47 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  144.88, 143.96, 141.93, 139.29, 129.67, 128.65, 125.91, 84.66, 75.90, 68.62, 27.41, 25.38, 21.25. **HRMS** (ESI): m/z calcd. For C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 180.1019, found: 180.1015.



2-methyl-1-((tetrahydrofuran-2-yl)methoxy)pyridin-1-ium methylbenzenesulfonate (1s) was prepared according to the general procedure. Yellow. <sup>1</sup>**H NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  9.44 (dd, J = 6.6, 1.3 Hz, 1H), 8.47 (td, J =7.7, 1.3 Hz, 1H), 8.15 (dd, J = 8.0, 1.9 Hz, 1H), 8.04 (td, J = 7.1, 1.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.12 (d, J = 7.9 Hz, 2H), 4.69 (dd, J = 10.1, 2.7 Hz, 1H), 4.56 (dd, J =10.1, 7.6 Hz, 1H), 4.25 (qd, J = 7.3, 2.7 Hz, 1H), 3.82 – 3.65 (m, 2H), 2.82 (s, 3H), 2.28 (s, 3H), 2.06 – 1.93 (m, 1H), 1.93 – 1.72 (m, 2H), 1.63 – 1.64 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 153.87, 145.93, 144.84, 141.88, 138.34, 130.75, 128.61, 127.34, 125.98, 83.62, 75.64, 68.28, 27.48, 25.53, 21.24, 17.37. HRMS (ESI): m/z calcd. For C<sub>11</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 194.1176, found: 194.1160.



2-phenyl-1-((tetrahydrofuran-2-yl)methoxy)pyridin-1-ium 4methylbenzenesulfonate (1t) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  9.64 (dd, J = 6.6, 1.3 Hz, 1H), 8.51 (td, J = 7.8, 1.3 Hz, 1H), 8.21 (ddd, J = 7.6, 6.6, 1.9 Hz, 1H), 7.92 (dd, J = 8.0, 1.51.9 Hz, 1H), 7.74 – 7.64 (m, 4H), 7.60 – 7.46 (m, 3H), 7.04 (d, J = 7.9 Hz, 2H), 4.37 -4.25 (m, 2H), 3.86 (qd, J = 7.3, 3.1 Hz, 1H), 3.52 (t, J = 6.7 Hz, 2H), 2.24 (s, 3H), 1.79 – 1.69 (m, 1H), 1.68 – 1.59 (m, 2H), 1.34 – 1.25 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  152.18, 146.16, 145.69, 142.86, 138.17, 132.21, 131.29, 130.66, 129.28,

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128.93, 128.57, 128.53, 125.99, 83.35, 75.39, 68.10, 27.38, 25.27, 21.26. **HRMS** (ESI): m/z calcd. For C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 256.1332, found: 256.1315.



**3,5-dimethyl-1-((tetrahydrofuran-2-yl)methoxy)pyridin-1-ium 4methylbenzenesulfonate (1u)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.06 (s, 2H), 7.97 (s, 1H), 7.72 (dd, J = 7.7, 3.5 Hz, 2H), 7.08 (dd, J = 7.8, 3.7 Hz, 2H), 4.87 (t, J = 10.6 Hz, 1H), 4.63 – 4.55 (m, 1H), 4.23 – 4.16 (m, 1H), 3.79 – 3.69 (m, 2H), 2.52 (d, J = 4.6 Hz, 6H), 2.29 (s, 3H), 2.01 – 1.92 (m, 1H), 1.90 – 1.72 (m, 2H), 1.60 – 1.52 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  145.82, 144.25, 140.28, 138.91, 138.33, 128.44, 125.91, 84.74, 75.77, 68.63, 27.32, 25.49, 21.24, 18.54. HRMS (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 208.1332, found: 208.1317.



**3-bromo-1-((tetrahydrofuran-2-yl)methoxy)pyridin-1-ium 4-methylbenzenesulfonate (1v)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.96 (t, J = 1.9 Hz, 1H), 9.49 (dd, J = 6.5, 2.0 Hz, 1H), 8.89 (dd, J = 8.3, 1.8 Hz, 1H), 8.18 (dd, J = 8.4, 6.5 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.75 (dd, J = 10.7, 2.9 Hz, 1H), 4.65 (dd, J = 10.7, 7.4 Hz, 1H), 4.26 (qd, J = 7.3, 2.8 Hz, 1H), 3.76 – 3.61 (m, 2H), 2.29 (s, 3H), 2.03 – 1.95 (m, 1H), 1.92 – 1.72 (m, 2H), 1.68 – 1.55 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  148.07, 146.07, 143.57, 141.32, 138.20, 129.92, 128.59, 125.97, 122.80, 84.52, 75.79, 68.29, 27.50, 25.45, 21.27. HRMS (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 258.0124, found: 258.0150.



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1-((tetrahydrofuran-2-yl)methoxy)benzo[h]quinolin-1-ium

**methylbenzenesulfonate (1w)** was prepared according to the general procedure. Yellow oil. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.92 (d, J = 6.4 Hz, 1H), 9.62 (d, J = 8.7 Hz, 1H), 9.34 (d, J = 9.5 Hz, 1H), 8.42 – 8.28 (m, 3H), 8.29 (d, J = 8.8 Hz, 1H), 8.08 (t, J = 7.5 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.51 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.7 Hz, 2H), 4.74 (dd, J = 10.0, 2.5 Hz, 1H), 4.59 (dd, J = 10.0, 8.0 Hz, 1H), 4.46 (qd, J = 7.5, 2.3 Hz, 1H), 3.84 – 3.76 (m, 2H), 2.27 (s, 3H), 2.05 (dq, J = 13.3, 7.3 Hz, 1H), 1.84 (p, J = 6.9 Hz, 2H), 1.62 (dq, J = 12.4, 7.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 146.29, 146.15, 145.19, 138.17, 136.65, 136.27, 132.81, 132.43, 132.38, 130.39, 129.95, 128.75, 128.56, 125.99, 125.68, 124.51, 121.64, 84.26, 75.69, 68.37, 27.56, 25.56, 21.23. HRMS (ESI): m/z calcd. For C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 280.1332, found: 280.1313.



**1-(cyclohexylmethoxy)pyridin-1-ium 4-methylbenzenesulfonate (1x)** was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.57 – 9.33 (m, 2H), 8.72 – 8.53 (m, 1H), 8.31 – 8.17 (m, 2H), 7.58 – 7.40 (m, 2H), 7.11 (d, J = 7.9 Hz, 2H), 4.49 (d, J = 6.1 Hz, 2H), 2.29 (s, 3H), 1.89 – 1.76 (m, 3H), 1.72 (dt, J = 12.2, 3.2 Hz, 2H), 1.68 – 1.61 (m, 1H), 1.35 – 1.15 (m, 3H), 1.14 – 1.04 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  146.23, 145.46, 141.90, 138.09, 129.83, 128.54, 125.96, 87.79, 36.32, 29.02, 26.22, 25.40, 21.26. HRMS (ESI): m/z calcd. For C<sub>12</sub>H<sub>18</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 192.1383, found: 192.1379.



**1-(cyclohexylmethoxy)-[2,2'-bipyridin]-1-ium 4-methylbenzenesulfonate** (1y) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.67 (d, *J* = 6.6 Hz, 1H), 8.88 (d, *J* = 5.0 Hz, 1H), 8.75 (t, *J* = 7.8 Hz, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.34 (t, *J* = 7.3 Hz, 1H), 8.15 (t, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 4.29 (d, *J* = 6.2 Hz, 2H), 2.28 (s, 3H), 1.68 – 1.50 (m, 4H), 1.45 (d, *J* = 12.7 Hz, 2H), 1.16 – 0.99 (m, 3H), 0.78 (q, *J* = 11.0, 10.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  153.84, 146.22, 144.31, 138.14, 136.65, 132.02, 131.74, 128.56, 128.53, 125.99, 120.45, 79.52, 33.14, 21.27, 17.50. HRMS (ESI): m/z calcd. For C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sup>+</sup> [M-OTs]<sup>+</sup>: 269.1648, found: 269.1634.



**1-phenethoxypyridin-1-ium 4-methylbenzenesulfonate** (1z) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.50 – 9.43 (m, 2H), 8.62 (t, J = 7.7 Hz, 1H), 8.26 – 8.18 (m, 2H), 7.61 – 7.55 (m, 2H), 7.38 – 7.28 (m, 4H), 7.28 – 7.20 (m, 1H), 7.13 (d, J = 7.9 Hz, 2H), 4.93 (t, J = 7.0 Hz, 2H), 3.14 (t, J = 7.0 Hz, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  145.92, 145.62, 141.94, 138.42, 136.64, 129.84, 129.42, 129.00, 128.68, 127.22, 126.04, 82.92, 33.68, 21.26. HRMS (ESI): m/z calcd. For C<sub>13</sub>H<sub>14</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 200.1070, found: 200.1055.



4-(methoxycarbonyl)-1-phenethoxypyridin-1-ium 4-methylbenzenesulfonate (1aa) was prepared according to the general procedure. White solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.26 – 9.14 (m, 2H), 7.75 – 7.62 (m, 2H), 7.56 – 7.45 (m, 2H), 7.34 (d, J = 4.4 Hz, 4H), 7.30 – 7.23 (m, 1H), 7.11 (d, J = 7.9 Hz, 2H), 4.79 (t, J = 7.0 Hz, 2H), 4.10 (s, 3H), 3.11 (t, J = 7.1 Hz, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 162.73, 146.19, 143.46, 143.31, 138.12, 136.58, 129.44, 129.05, 128.55, 127.31, 125.97, 83.29, 54.44, 33.61, 21.26. **HRMS** (ESI): m/z calcd. For C<sub>15</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 258.1225, found: 258.1224.



**4-methyl-1-phenethoxypyridin-1-ium 4-methylbenzenesulfonate** (1ab) was prepared according to the general procedure. Yellow oil. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.32 – 9.24 (m, 2H), 7.99 (d, J = 6.7 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.38 – 7.33 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 7.14 (d, J = 7.8 Hz, 2H), 4.87 (t, J = 7.1 Hz, 2H), 3.12 (t, J = 7.0 Hz, 2H), 2.56 (s, 3H), 2.27 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  159.10, 145.73, 140.73, 138.56, 136.63, 129.90, 129.41, 128.98, 128.72, 127.17, 126.06, 82.71, 33.65, 21.75, 21.23. HRMS (ESI): m/z calcd. For C<sub>14</sub>H<sub>16</sub>NO<sup>+</sup> [M-OTs]<sup>+</sup>: 214.1226, found: 214.1210.



6-methoxy-1-(4-methylphenethoxy)quinolin-1-ium 4-methylbenzenesulfonate (1af) was prepared according to the general procedure. Yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.82 (dd, J = 6.3, 1.2 Hz, 1H), 9.12 (d, J = 8.5 Hz, 1H), 8.15 (dd, J= 8.5, 6.2 Hz, 1H), 8.09 (d, J = 9.5 Hz, 1H), 7.97 (d, J = 2.7 Hz, 1H), 7.77 (dd, J = 9.6, 2.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.31 – 7.25 (m, 2H), 7.15 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.94 (t, J = 6.9 Hz, 2H), 3.99 (s, 3H), 3.25 (t, J = 6.8 Hz, 2H), 2.30 (s, 3H), 2.27 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  160.35, 146.06, 144.68, 142.03, 138.26, 136.37, 133.77, 133.17, 131.99, 129.58, 129.42, 129.00, 128.59, 126.03, 123.23, 118.30, 108.25, 83.35, 56.94, 33.51, 21.23, 21.13. HRMS (ESI): m/z calcd. For C<sub>19</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 298.1484, found: 298.1470.



**1-(4-bromophenethoxy)-6-methoxyquinolin-1-ium 4-methylbenzenesulfonate** (1ag) was prepared according to the general procedure. Yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.84 (dd, *J* = 6.3, 1.1 Hz, 1H), 9.13 (d, *J* = 8.4 Hz, 1H), 8.21 – 8.11 (m, 2H), 7.96 (d, *J* = 2.7 Hz, 1H), 7.79 (dd, *J* = 9.6, 2.7 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.53 – 7.49 (m, 2H), 7.43 – 7.37 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.98 (t, *J* = 6.8 Hz, 2H), 3.99 (s, 3H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  160.34, 145.83, 144.73, 142.00, 138.42, 136.41, 131.90, 133.13, 131.84, 131.82, 129.05, 128.65, 126.04, 123.20, 120.44, 118.28, 108.23, 82.81, 56.93, 33.23, 21.24. HRMS (ESI): m/z calcd. For C<sub>18</sub>H<sub>17</sub>BrNO<sub>2</sub><sup>+</sup> [M-OTs]<sup>+</sup>: 358.0437, found: 358.0414.



**2-cyclohexyl-4-methylpyridine (2a)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1a** (0.2 mmol), compound **2a** (28.75 mg, 82%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.27 (d, *J* = 5.1 Hz, 1H), 6.86 (s, 1H), 6.79 (dd, *J* = 5.2, 1.7 Hz, 1H), 2.55 (tt, *J* = 11.9, 3.4 Hz, 1H), 2.20 (s, 3H), 1.87 – 1.80 (m, 2H), 1.75 (dt, *J* = 12.6, 3.2 Hz, 2H), 1.67 – 1.61 (m, 1H), 1.43 (qd, *J* = 12.3, 2.8 Hz, 2H), 1.30 (qt, *J* = 12.3, 3.0 Hz, 2H), 1.19 (tt, *J* = 12.5, 3.2 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  166.24, 148.73, 147.25, 122.01, 121.85, 46.43, 32.91, 26.59, 26.08, 21.03. **HRMS** (ESI) m/z calcd. For C<sub>12</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 176.1434, found: 176.1422.



**methyl 2-isopropylisonicotinate (2b)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1b** (0.2 mmol), compound **2b** (25.81 mg, 72%) was

obtained. Yellow oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.66 (d, J = 5.1 Hz, 1H), 7.72 (s, 1H), 7.63 (dd, J = 5.1, 1.6 Hz, 1H), 3.93 (s, 3H), 3.13 (hept, J = 6.9 Hz, 1H), 1.31 (d, J = 7.0 Hz, 6H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  168.49, 165.96, 149.69, 137.86, 120.29, 120.05, 52.61, 36.33, 22.43. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 180.1019, found: 180.1023.



**2-(sec-butyl)-4-methylpyridine (2c)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1c** (0.2 mmol), compound **2c** (22.98 mg, 77%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.28 (dd, *J* = 5.0, 0.8 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.79 – 6.77 (m, 1H), 2.64 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.19 (s, 3H), 1.71 – 1.60 (m, 1H), 1.56 – 1.45 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.73 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  166.10, 148.74, 146.98, 122.31, 121.90, 43.41, 29.84, 20.86, 20.28, 12.01. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 150.1277, found: 150.1268.



**2-cyclopropyl-4-methylpyridine (2d)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1d** (0.2 mmol), compound **2d** (14.65 mg, 55%) was obtained. Yellow oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.51 (d, *J* = 4.9 Hz, 1H), 7.78 (dt, *J* = 1.7, 0.8 Hz, 1H), 7.23 – 7.21 (m, 1H), 3.41 (tt, *J* = 8.0, 4.7 Hz, 1H), 2.35 (s, 3H), 1.20 – 1.14 (m, 2H), 1.05 – 1.01 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  152.59, 147.77, 147.22, 126.75, 121.55, 20.08, 14.85, 11.69. **HRMS** (ESI) m/z calcd. For C<sub>9</sub>H<sub>11</sub>N [M+H]<sup>+</sup>: 134.0964, found: 134.0959.



**2-cyclobutyl-4-methylpyridine (2e)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1e** (0.2 mmol), compound **2e** (14.72 mg, 50%) was obtained. Yellow oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.51 (d, *J* = 4.9 Hz, 1H), 7.96 – 7.81 (m, 1H), 7.34 – 7.15 (m, 1H), 4.48 (pd, *J* = 8.5, 1.1 Hz, 1H), 2.42 (s, 3H), 2.38 – 2.22 (m, 4H), 2.14 – 2.05 (m, 1H), 1.95 – 1.83 (m, 1H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  152.71, 148.81, 148.16, 127.72, 123.17, 41.29, 25.04, 21.09, 18.26. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 148.1121, found: 148.1113.



**2-cyclopentyl-4-methylpyridine (2f)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1f** (0.2 mmol), compound **2f** (25.80 mg, 80%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.26 (d, *J* = 5.1 Hz, 1H), 6.85 (s, 1H), 6.74 (dd, *J* = 5.2, 1.7 Hz, 1H), 3.00 (p, *J* = 8.4 Hz, 1H), 2.16 (s, 3H), 2.01 – 1.86 (m, 2H), 1.76 – 1.61 (m, 4H), 1.59 – 1.54 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  165.14, 148.68, 146.73, 122.32, 121.69, 47.64, 33.27, 25.66, 20.72. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 162.1277, found: 162.1280.



2,6-dimethyl-4-(tetrahydrofuran-2-yl)pyridine (2g) was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to IV. From N-alkoxyheteroarenium salt 1g (0.2 mmol), compound 2g (31.91 mg, 90%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$ 

6.79 (s, 2H), 4.66 (t, J = 7.2 Hz, 1H), 3.92 (dt, J = 8.3, 6.8 Hz, 1H), 3.78 (dt, J = 8.3, 6.9 Hz, 1H), 2.37 (s, 6H), 2.18 (dq, J = 12.0, 6.7 Hz, 1H), 1.82 (dt, J = 13.6, 6.9 Hz, 2H), 1.58 (dq, J = 12.2, 7.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  157.09, 153.01, 116.62, 78.76, 68.31, 33.81, 25.43, 23.84. HRMS (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 178.1226, found: 178.1226.



**2-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-methylpyridine (2h)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1h** (0.2 mmol), compound **2h** (34.01 mg, 88%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.26 (d, *J* = 5.1 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.92 – 6.86 (m, 1H), 5.07 (t, *J* = 6.9 Hz, 1H), 4.34 (dd, *J* = 8.3, 6.8 Hz, 1H), 3.82 (dd, *J* = 8.3, 6.9 Hz, 1H), 2.24 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  159.67, 148.60, 147.76, 123.32, 120.64, 109.90, 77.96, 70.10, 26.33, 25.49, 20.95. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 194.1176, found: 194.1174.



**4-methyl-2-(tetrahydro-2H-pyran-4-yl)pyridine (2i)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1i** (0.2 mmol), compound **2i** (31.55 mg, 89%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.27 – 8.25 (m, 1H), 6.88 (s, 1H), 6.83 – 6.81 (m, 1H), 4.00 – 3.91 (m, 2H), 3.40 (tt, *J* = 11.4, 2.9 Hz, 2H), 2.83 – 2.74 (m, 1H), 2.23 – 2.18 (m, 3H), 1.83 – 1.68 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  163.72, 148.46, 147.19, 122.08, 121.40, 67.60, 42.80, 32.05, 20.57. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 178.1226, found: 178.1222.



**2-(4,4-difluorocyclohexyl)-4-methylpyridine (2j)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1j** (0.2 mmol), compound **2j** (32.98 mg, 78%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.31 (d, *J* = 5.1 Hz, 1H), 6.92 (s, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 2.77 – 2.66 (m, 1H), 2.25 (s, 3H), 2.17 – 2.09 (m, 2H), 1.95 – 1.91 (m, 2H), 1.85 – 1.80 (m, 2H), 1.80 – 1.72 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  163.51 (d, *J* = 2.2 Hz), 148.65, 148.01, 123.14 (dd, *J* = 242.3, 239.5 Hz), 122.69, 121.79, 43.93, 33.75 (dd, *J* = 25.5, 22.6 Hz), 28.78 (d, *J* = 9.9 Hz), 21.07. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.68 (d, *J* = 235.7 Hz), -101.73 (d, *J* = 235.7 Hz). HRMS (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>F<sub>2</sub>N [M+H]<sup>+</sup>: 242.1351, found: 242.1344.



**2-cyclopentylpyridine (2k)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1k** (1.0 mmol), compound **2k** (66.25 mg, 45%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.41 – 8.39 (m, 1H), 7.40 (td, *J* = 7.6, 1.9 Hz, 1H), 7.02 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.91 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 3.12 – 2.93 (m, 1H), 1.98 – 1.90 (m, 2H), 1.76 – 1.63 (m, 4H), 1.60 – 1.52 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  165.46, 148.96, 135.94, 121.51, 120.71, 47.82, 33.36, 25.69. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 148.1121, found: 148.1113.



**4-cyclopentylpyridine (2k')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1k** (1.0 mmol), compound **2k'** (38.28 mg, 26%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.40 – 8.35 (m, 2H), 7.08 – 7.02 (m, 2H), 2.94 – 2.81 (m, 1H), 2.03 – 1.94 (m, 2H), 1.78 – 1.64 (m, 2H), 1.60 – 1.55 (m, 2H), 1.54 – 1.43 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  149.48, 122.58, 45.06, 33.86, 25.46. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 148.1121, found: 148.1113.



**2-cyclopentyl-4-methoxypyridine (21)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **11** (0.2 mmol), compound **21** (26.23 mg, 74%) was obtained. Yellow oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.35 (d, *J* = 5.8 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 5.7, 2.5 Hz, 1H), 3.82 (s, 3H), 3.18 – 3.05 (m, 1H), 2.12 – 2.01 (m, 2H), 1.86 – 1.73 (m, 4H), 1.73 – 1.65 (m, 2H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  167.36, 165.93, 150.33, 107.54, 107.05, 54.92, 48.04, 33.36, 25.74. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 178.1226, found: 178.1216.



**2-cyclopentyl-6-methylpyridine (2m)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1m** (0.2 mmol), compound **2m** (11.13 mg, 35%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.46 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.52 (s, 3H), 2.12 – 2.05 (m, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.65 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  165.19, 157.41, 136.38, 120.34, 117.83, 48.28, 33.68, 25.66, 24.59. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 162.1277, found: 162.1280.



**4-cyclopentyl-2-methylpyridine** (2m') was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1m** (0.2 mmol), compound **2m'** (10.76 mg, 33%) was obtained. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.36 (d, *J* = 5.2 Hz, 1H), 7.02 (d, *J* = 1.7 Hz, 1H), 6.96 (dd, *J* = 5.3, 1.7 Hz, 1H), 2.93 (tt, *J* = 9.2, 7.5 Hz, 1H), 2.53 (s, 3H), 2.11 – 2.02 (m, 2H), 1.86 – 1.77 (m, 2H), 1.75 – 1.65 (m, 2H), 1.63 – 1.52 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  158.01, 156.04, 148.80, 122.20, 119.77, 45.12, 33.90, 25.53. HRMS (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 162.1277, found: 162.1280.



**2-cyclopentyl-3-fluoropyridine (2n)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1n** (1.0 mmol), compound **2n** (66.08 mg, 40%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.25 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.00 (dt, *J* = 8.4, 4.3 Hz, 1H), 3.45 – 3.33 (m, 1H), 1.99 – 1.88 (m, 2H), 1.83 – 1.72 (m, 4H), 1.65 – 1.55 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  157.51 (d, *J* = 255.7 Hz), 153.60 (d, *J* = 14.0 Hz), 144.67 (d, *J* = 5.6 Hz), 122.17 (d, *J* = 19.8 Hz), 121.89 (d, *J* = 3.6 Hz), 40.34 (d, *J* = 2.2 Hz), 31.96, 25.94. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -125.74. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>FN [M+H]<sup>+</sup>: 166.1027, found: 166.1031.



**4-cyclopentyl-3-fluoropyridine (2n')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1n** (1.0 mmol), compound **2n'** (23.45 mg, 14%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, J = 2.1 Hz, 1H), 8.23 (d, J = 5.0 Hz, 1H), 3.23 – 3.10 (m, 1H), 2.06 – 1.94 (m, 2H), 1.80 – 1.71 m, 2H), 1.68 – 1.59 (m, 2H), 1.59 – 1.46 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.36 (d, J = 253.7 Hz), 145.59 (d, J = 5.0 Hz), 142.01 (d, J = 12.4 Hz), 137.55 (d, J= 25.5 Hz), 122.48 (d, J = 2.7 Hz), 38.17, 32.72, 25.45. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -132.14. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>FN [M+H]<sup>+</sup>: 166.1027, found: 166.1031.



**5-chloro-2-cyclopentylpyridine (20)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **10** (1.0 mmol) compound **20** (63.43 mg, 35%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.38 (d, *J* = 5.1 Hz, 1H), 7.20 (d, *J* = 5.1 Hz, 1H), 3.65 – 3.18 (m, 1H), 2.17 – 2.06 (m, 2H), 1.86 – 1.78 (m, 2H), 1.78 – 1.70 (m, 2H), 1.63 – 1.51 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 152.69, 149.20, 147.79, 132.20, 121.80, 41.60, 32.63, 25.50. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>ClN [M+H]<sup>+</sup>: 182.0713, found: 182.0726.



**3-chloro-2-cyclopentylpyridine, 3-chloro-4-cyclopentylpyridine (20', 20'')** were purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **10** (1.0 mmol), compound **20', 20''** (41.54 mg, 23%) were obtained. Yellow oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.48 (d, *J* = 2.5 Hz, 1H, **20'**), 8.45 (dd, *J* = 4.7, 1.6 Hz,

1H, 2o<sup>''</sup>), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H, 2o<sup>''</sup>), 7.55 (dd, *J* = 8.3, 2.6 Hz, 1H, 2o<sup>'</sup>), 7.13 (d, *J* = 8.4 Hz, 1H, 2o<sup>'</sup>), 7.05 (dd, *J* = 8.0, 4.6 Hz, 1H, 2o<sup>''</sup>), 3.77 – 3.58 (m, 1H, 2o<sup>'</sup>), 3.22 – 3.05 (m, 1H, 2o<sup>''</sup>), 2.11 – 1.99 (m, 4H, 2o<sup>'</sup>, 2o<sup>''</sup>), 1.93 – 1.78 (m, 8H, 2o<sup>'</sup>, 2o<sup>''</sup>), 1.77 – 1.63 (m, 4H, 2o<sup>'</sup>, 2o<sup>''</sup>). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 163.94 (2o<sup>''</sup>), 162.22 (2o<sup>'</sup>), 147.94 (2o<sup>''</sup>), 147.16 (2o<sup>'</sup>), 136.62 (2o<sup>'</sup>), 135.86 (2o<sup>''</sup>), 131.17 (2o<sup>'</sup>), 129.06 (2o<sup>''</sup>), 122.49 (2o<sup>''</sup>), 121.79 (2o<sup>'</sup>), 47.33 (2o<sup>''</sup>), 43.36 (2o<sup>'</sup>), 33.55 (2o<sup>''</sup>), 32.08 (2o<sup>'</sup>), 25.99 (2o<sup>'</sup>), 25.77 (2o<sup>''</sup>). HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>CIN [M+H]<sup>+</sup>: 182.0713, found: 182.0726.



**5-bromo-2-cyclopentylpyridine (2p)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1p** (1.0 mmol), compound **2p** (66.75 mg, 30%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.64 (s, 1H), 8.41 (d, *J* = 5.1 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 3.42 – 3.30 (m, 1H), 2.19 – 2.06 (m, 2H), 1.90 – 1.66 (m, 4H), 1.65 – 1.49 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$ 154.47, 151.79, 148.38, 123.58, 122.21, 44.20, 32.85, 25.53. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 226.0226, found: 226.0235.



**3-bromo-2-cyclopentylpyridine, 3-bromo-4-cyclopentylpyridine (2p', 2p'')** were purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1p** (1.0 mmol), compound **2p', 2p''** (65.01 mg, 30%) were obtained. Yellow oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.49 (d, *J* = 2.3 Hz, 1H), 8.40 (dd, *J* = 4.6, 1.6 Hz, 1H, **2p'**), 7.70 (dd, *J* = 8.1, 1.6 Hz, 1H, **2p'**), 7.60 (dd, *J* = 8.4, 2.5 Hz, 1H, **2p''**), 6.99 (d, *J* = 8.4 Hz, 1H, **2p''**), 6.88 (dd, *J* = 8.0, 4.6 Hz, 1H, **2p'**), 3.65 – 3.50 (m, 1H, **2p'**), 3.09 – 2.99 (m, 1H, **2p**''), 2.02 – 1.93 (m, 4H, **2p**', **2p**''), 1.84 – 1.70 (m, 8H, **2p**', **2p**''), 1.70 – 1.54 (m, 4H, **2p**', **2p**''). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 163.27 (**2p**''), 162.32 (**2p**'), 149.07 (**2p**''), 146.72 (**2p**'), 138.92 (**2p**'), 137.62 (**2p**''), 122.04 (**2p**''), 121.07 (**2p**'), 120.73 (**2p**'), 116.58 (**2p**''), 46.31 (**2p**''), 44.42 (**2p**'), 32.47 (**2p**''), 31.25 (**2p**'), 24.97 (**2p**'), 24.73 (**2p**''). HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 226.0226, found: 226.0235.



**2-cyclopentyl-6-phenylpyridine (2q)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1q** (0.2 mmol), compound **2q** (14.29 mg, 32%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.21 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.17 – 3.09 (m, 1H), 2.02 – 1.95 (m, 2H), 1.82 – 1.70 (m, 4H), 1.64 – 1.54 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 164.47, 155.17, 138.81, 135.58, 127.53, 127.50, 125.81, 118.88, 116.28, 46.95, 32.48, 24.83. **HRMS** (ESI) m/z calcd. For C<sub>16</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 224.1434, found: 224.1436.



**4-cyclopentyl-2-phenylpyridine (2q')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1q** (0.2 mmol), compound **2q'** (13.22 mg, 30%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.57 (dd, *J* = 5.1, 0.8 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.58 – 7.57 (m, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.10 (dd, *J* = 5.1, 1.7 Hz, 1H), 3.10 – 2.98 (m, 1H), 2.16 – 2.08 (m, 2H), 1.90 – 1.78 (m, 2H), 1.78 – 1.59 (m, 4H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.49, 156.38, 149.56, 139.85, 128.77, 128.70, 127.02, 121.15, 119.71, 45.43, 34.04, 25.59. HRMS (ESI) m/z calcd. For C<sub>16</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 224.1434, found: 224.1436.



**2-(tetrahydrofuran-2-yl)pyridine** (**2r**) was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1r** (0.2 mmol), compound **2r** (12.53 mg, 42%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.47 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.60 (td, *J* = 7.8, 1.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.95 (t, *J* = 6.4 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.98 – 3.86 (m, 1H), 2.43 – 2.27 (m, 1H), 1.99 – 1.84 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  162.97, 149.00, 136.60, 122.03, 119.81, 81.31, 69.06, 33.07, 25.77. HRMS (ESI) m/z calcd. For C<sub>9</sub>H<sub>11</sub>NO [M+H]<sup>+</sup>: 150.0913, found: 150.0903.



**4-(tetrahydrofuran-2-yl)pyridine** (2r') was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1r** (0.2 mmol), compound **2r'** (12.02 mg, 40%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.55 – 8.37 (m, 2H), 7.22 – 7.12 (m, 2H), 4.81 (t, *J* = 7.2 Hz, 1H), 4.00 (dt, *J* = 8.3, 6.8 Hz, 1H), 3.87 (dt, *J* = 8.2, 6.9 Hz, 1H), 2.37 – 2.24 (m, 1H), 1.97 – 1.85 (m, 2H), 1.67 (dq, *J* = 12.2, 7.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  149.55, 120.52, 79.04, 68.95, 34.30, 25.80. HRMS (ESI) m/z calcd. For C<sub>9</sub>H<sub>11</sub>NO [M+H]<sup>+</sup>: 150.0913, found: 150.0903.



**2-methyl-6-(tetrahydrofuran-2-yl)pyridine (2s)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1s** (0.2 mmol), compound **2s** 

(11.59 mg, 36%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$ 7.46 (t, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 4.97 – 4.87 (m, 1H), 4.07 – 3.97 (m, 1H), 3.92 – 3.83 (m, 1H), 2.45 (s, 3H), 2.41 – 2.25 (m, 1H), 1.96 – 1.79 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  162.49, 157.52, 136.75, 121.54, 116.47, 81.47, 68.98, 33.22, 25.64, 24.41. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>NO [M+H]<sup>+</sup>: 164.1070, found: 164.1071.



**2-methyl-4-(tetrahydrofuran-2-yl)pyridine (2s')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1s** (0.2 mmol), compound **2s'** (11.12 mg, 34%) was obtained. Colorless oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.42 (d, *J* = 5.2 Hz, 1H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.03 (dd, *J* = 5.3, 1.6 Hz, 1H), 4.83 (t, *J* = 7.2 Hz, 1H), 4.06 (dt, *J* = 8.4, 6.7 Hz, 1H), 3.93 (dt, *J* = 8.3, 6.9 Hz, 1H), 2.54 (s, 3H), 2.34 (dq, *J* = 12.1, 6.8 Hz, 1H), 2.02 – 1.90 (m, 2H), 1.73 (dq, *J* = 12.2, 7.7 Hz, 1H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  158.19, 152.86, 148.90, 119.72, 117.53, 79.01, 68.71, 34.11, 25.70, 24.31. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>13</sub>NO [M+H]<sup>+</sup>: 164.1070, found: 164.1071.



**2-phenyl-6-(tetrahydrofuran-2-yl)pyridine (2t)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1t** (0.2 mmol), compound **2t** (15.73 mg, 34%) was obtained. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 – 7.98 (m, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.46 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 5.12 (t, *J* = 7.2 Hz, 1H), 4.13 (dt, *J* = 8.1, 6.6 Hz, 1H), 4.00 (dt, *J* = 8.2, 7.0 Hz, 1H), 2.46 (dq, *J* = 12.2, 7.2 Hz, 1H), 2.15 – 2.11 (m, 1H), 2.06 – 1.95 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  163.04, 156.58, 139.57, 137.23,

128.84, 128.70, 127.00, 118.81, 118.21, 81.60, 69.10, 32.96, 25.76. **HRMS** (ESI) m/z calcd. For C<sub>15</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 226.1226, found: 226.1225.



**2-phenyl-4-(tetrahydrofuran-2-yl)pyridine (2t')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1t** (0.2 mmol), compound **2t'** (18.25 mg, 40%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.60 (dd, J = 5.1, 0.9 Hz, 1H), 8.08 – 7.93 (m, 2H), 7.68 (dd, J = 1.6, 0.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.13 (dd, J = 5.4, 1.7 Hz, 1H), 4.88 (t, J = 7.2 Hz, 1H), 4.05 (dt, J = 8.4, 6.8 Hz, 1H), 3.91 (dt, J = 8.3, 6.9 Hz, 1H), 2.32 (dq, J = 12.2, 6.9 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.73 (dq, J = 12.2, 7.6 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  157.47, 153.59, 149.58, 139.50, 128.90, 128.68, 126.98, 119.05, 117.22, 79.23, 68.90, 34.31, 25.83. **HRMS** (ESI) m/z calcd. For C<sub>15</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 226.1226, found: 226.1225.



**3,5-dimethyl-2-(tetrahydrofuran-2-yl)pyridine (2u)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1u** (0.2 mmol), compound **2u** (25.88 mg, 73%) was obtained. Colorless oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.47 – 8.04 (m, 1H), 7.26 – 7.23 (m, 1H), 5.11 (t, *J* = 7.2 Hz, 1H), 4.12 (dt, *J* = 8.0, 6.7 Hz, 1H), 3.91 (dt, *J* = 7.9, 5.7 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 2.25 – 2.18 (m, 2H), 2.17 – 2.09 (m, 1H), 2.05 – 1.99 (m, 1H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  155.56, 147.06, 138.91, 131.71, 130.62, 78.50, 68.70, 30.51, 26.26, 18.24, 17.90. **HRMS** (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 178.1226, found: 178.1225.



**5-bromo-2-(tetrahydrofuran-2-yl)pyridine (2v)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1v** (1.0 mmol), compound **2v** (93.74 mg, 41%) was obtained. Colorless oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.63 (s, 1H), 8.48 (d, *J* = 4.9 Hz, 1H), 7.44 (d, *J* = 4.9 Hz, 1H), 5.08 (t, *J* = 7.1 Hz, 1H), 4.19 – 4.14 (m, 1H), 4.02 – 3.96 (m, 1H), 2.63 – 2.55 (m, 1H), 2.10 – 1.89 (m, 2H), 1.72 – 1.63 (m, 1H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  161.68, 149.95, 139.20, 121.31, 118.81, 80.75, 69.12, 33.04, 25.73. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 226.0226, found: 226.0228.



**3-bromo-2-(tetrahydrofuran-2-yl)pyridine (2v')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1v** (1.0 mmol), compound **2v** (13.93 mg, 6%) was obtained. Colorless oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.57 (dd, J = 4.6, 1.5 Hz, 1H), 7.84 (dd, J = 8.0, 1.5 Hz, 1H), 7.08 (dd, J = 8.0, 4.6 Hz, 1H), 5.45 – 5.33 (m, 1H), 4.31 – 4.17 (m, 1H), 4.03 – 3.97 (m, 1H), 2.50 – 2.32 (m, 1H), 2.22 – 1.96 (m, 3H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  159.24, 148.12, 140.49, 123.63, 119.98, 79.36, 69.39, 31.41, 26.10. **HRMS** (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 226.0226, found: 226.0228.



**3-bromo-4-(tetrahydrofuran-2-yl)pyridine (2v'')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1v** (1.0 mmol), compound **2v**
(34.89 mg, 15%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$ 8.60 (d, J = 2.4 Hz, 1H), 7.79 (dd, J = 8.4, 2.3 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 5.02 – 4.94 (m, 1H), 4.14 – 4.04 (m, 1H), 4.03 – 3.93 (m, 1H), 2.49 – 2.36 (m, 1H), 2.08 – 1.85 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  161.73, 150.05, 139.15, 121.29, 118.81, 80.79, 69.14, 33.05, 25.73. HRMS (ESI) m/z calcd. For C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 226.0226, found: 226.0228.



**2-(tetrahydrofuran-2-yl)benzo[h]quinoline (2w)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1w** (0.2 mmol), compound **2w** (22.44 mg, 45%) was obtained. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  9.32 – 9.18 (m, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.77 (m, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.57 (m, 4H), 5.24 (t, *J* = 7.2 Hz, 1H), 4.11 (dt, *J* = 8.3, 6.7 Hz, 1H), 3.99 (dt, *J* = 8.2, 6.9 Hz, 1H), 2.47 (dq, *J* = 12.4, 7.3 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.06 – 1.92 (m, 2H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  162.06, 145.70, 136.32, 133.73, 131.53, 128.02, 127.73, 127.14, 126.79, 125.28, 125.22, 124.54, 118.68, 82.09, 69.17, 33.04, 25.92. **HRMS** (ESI) m/z calcd. For C<sub>17</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 250.1226, found: 250.1229.



**4-(tetrahydrofuran-2-yl)benzo[h]quinoline (2w)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1w** (0.2 mmol), compound **2w**' (14.57 mg, 29%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.32 (d, *J* = 8.1, 1H), 8.96 (d, *J* = 4.6 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.76 (d, *J* = 4.2 Hz, 2H), 7.74 –7.70 (m, 1H), 7.69 – 7.63 (m, 2H), 5.61 (t, *J* = 7.1 Hz, 1H), 4.21 (dt, *J* = 8.3, 6.9 Hz, 1H), 4.02 (dt, *J* = 8.4, 7.1 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.07

- 1.93 (m, 2H), 1.87 – 1.77 (m, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 149.39, 148.86, 146.32, 133.05, 131.91, 128.13, 127.69, 127.54, 127.18, 124.82, 123.21, 120.70, 117.33, 76.98, 69.08, 34.08, 26.00. HRMS (ESI) m/z calcd. For C<sub>17</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 250.1226, found: 250.1229.



**2-cyclohexylpyridine (2x)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1x (1.0 mmol)** compound **2x** (40.85 mg, 25%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.52 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.14 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.07 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 2.69 (tt, *J* = 11.9, 3.4 Hz, 1H), 1.98 – 1.92 (m, 2H), 1.89 – 1.82 (m, 2H), 1.78 –1.72 (m, 1H), 1.53 (qd, *J* = 12.3, 2.7 Hz, 2H), 1.41 (qt, *J* = 12.5, 3.0 Hz, 2H), 1.30 (tt, *J* = 12.2, 3.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  166.46, 148.99, 136.29, 120.95, 46.55, 32.89, 26.57, 26.06. HRMS (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 162.1277, found: 162.1280.



**4-cyclohexylpyridine (2x')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1a (1.0 mmol)** compound **2x'** (59.66 mg, 37%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.48 – 8.36 (m, 2H), 7.12 – 6.97 (m, 2H), 2.49 – 2.36 (m, 1H), 1.82 – 1.76 (m, 4H), 1.72 – 1.67 (m, 1H), 1.36 – 1.30 (m, 4H), 1.26 – 1.12 (m, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  155.58, 148.67, 121.35, 42.79, 32.47, 25.49, 24.90. HRMS (ESI) m/z calcd. For C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 162.1277, found: 162.1280.



**6-cyclohexyl-2,2'-bipyridine (2y)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1y** (0.2 mmol), compound **2y** (22.88 mg, 48%) was obtained. Colorless oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.55 – 8.48 (m, 1H), 8.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.61 (td, *J* = 7.7, 1.9 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.09 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 6.99 (d, *J* = 7.7, 1H), 2.64 (tt, *J* = 11.8, 3.5 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.77 – 1.70 (m, 2H), 1.66 – 1.60 (m, 1H), 1.48 (qd, *J* = 12.4, 3.2 Hz, 2H), 1.30 (qt, *J* = 12.5, 3.2 Hz, 2H), 1.19 (tt, *J* = 12.6, 3.3 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  165.77, 156.78, 155.12, 148.97, 137.01, 136.66, 123.36, 121.18, 121.01, 118.17, 46.45 32.95, 26.61, 26.20. **HRMS** (ESI) m/z calcd. For C<sub>16</sub>H<sub>18</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 239.1543, found: 239.1535.



**2-benzylpyridine (2z)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1z** (1.0 mmol), compound **2z** (44.85 mg, 27%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.39 (dd, *J* = 4.9, 2.2 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.18 – 7.09 (m, 4H), 7.07 – 7.02 (m, 1H), 6.93 – 6.86 (m, 2H), 4.01 (d, *J* = 1.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  161.02, 149.37, 139.57, 136.53, 129.16, 128.63, 126.43, 123.13, 121.26, 44.77. HRMS (ESI) m/z calcd. For C<sub>12</sub>H<sub>11</sub>N [M+H]<sup>+</sup>: 170.0964, found: 170.0964.



**4-benzylpyridine (2z')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From

N-alkoxyheteroarenium salt **1z** (1.0 mmol), compound **2z'** (13.59 mg, 8%) was obtained. Colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.47 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.18 – 7.16 (m, 2H), 7.11 – 7.08 (m, 2H), 3.96 (s, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 150.03, 149.89, 138.90, 129.08, 128.77, 126.72, 124.22, 41.25. HRMS (ESI) m/z calcd. For C<sub>12</sub>H<sub>11</sub>N [M+H]<sup>+</sup>: 170.0964, found: 170.0964.



methyl 2-benzylisonicotinate (2aa) was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to IV. From N-alkoxyheteroarenium salt 1aa (0.2 mmol), compound 2aa (24.09 mg, 53%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.49 – 8.47 (m, 1H), 7.52 (s, 1H), 7.45 – 7.43 (m, 1H), 7.09 – 7.07 (m, 4H), 7.02 – 6.89 (m, 1H), 4.02 (d, J = 2.6 Hz, 2H), 3.65 (dd, J = 3.0, 1.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 165.54, 162.15, 150.13, 138.99, 137.86, 129.04, 128.64, 126.53, 122.24, 120.43, 52.47, 44.57. HRMS (ESI) m/z calcd. For C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 228.1019, found: 228.1016.



**2-benzyl-4-methylpyridine (2ab)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ab** (0.2 mmol), compound **2ab** (23.83 mg, 65%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.38 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 6.91 (d, *J* = 4.7 Hz, 2H), 4.10 (s, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  160.73, 149.08, 147.64, 139.69, 129.12, 128.58, 126.34, 124.00, 122.33, 44.60, 21.00. HRMS (ESI) m/z calcd. For C<sub>13</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 184.1211, found: 184.1123.



**2-benzylquinoline (2ac)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ac** (0.2 mmol), compound **2ac** (18.16 mg, 41%) was obtained. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.10 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.36 – 7.34 (m, 1H), 7.30 – 7.18 (m, 4H), 7.18 – 7.11 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 4.29 (s, 2H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  161.26, 147.90, 139.32, 136.55, 129.57, 129.32, 129.07, 128.74, 127.62, 126.84, 126.61, 126.06, 121.61, 45.62. **HRMS** (ESI) m/z calcd. For C<sub>16</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 220.1121, found: 220.1122.



**2-benzylquinoline (2ac')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ac** (0.2 mmol), compound **2ac'** (12.35 mg, 28%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.82 (d, *J* = 4.4 Hz, 1H), 8.13 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.54 – 7.50 (m, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.21 – 7.18 (m, 2H), 7.13 (d, *J* = 4.4 Hz, 1H), 4.44 (s, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  150.35, 148.38, 146.64, 138.63, 130.21, 129.20, 128.97, 128.77, 127.65, 126.69, 126.62, 123.91, 121.90, 38.19. HRMS (ESI) m/z calcd. For C<sub>16</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 220.1121, found: 220.1122.



**1-benzylisoquinoline (2ad)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to IV. From

N-alkoxyheteroarenium salt **1ad** (0.2 mmol), compound **2ad** (31.58 mg, 72%) was obtained. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.48 (d, J = 5.8 Hz, 1H), 8.11 (d, J = 8.6, 1H), 7.74 (d, J = 8.2, 1.2 Hz, 1H), 7.58 – 7.54 (m, J = 8.2, 6.9, 1.2 Hz, 1H), 7.50 (d, J = 5.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.28 – 7.20 (m, 4H), 7.16 – 7.10 (m, 1H), 4.65 (s, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  160.19, 142.07, 139.52, 136.62, 129.89, 128.68, 128.57, 127.39, 127.26, 126.32, 125.85, 119.87, 42.10. HRMS (ESI) m/z calcd. For C<sub>16</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 220.1121, found: 220.1127.



**2-benzyl-6-methoxyquinoline (2ae)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ae** (0.2 mmol), compound **2ae** (25.93 mg, 52%) was obtained. Yellow oil. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.05 (d, *J* = 9.2 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.35 – 7.24 (m, 5H), 7.22 – 7.12 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 2.9 Hz, 1H), 4.29 (s, 2H), 3.72 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, Chloroform-*d*)  $\delta$  158.57, 157.35, 143.80, 139.58, 135.32, 130.30, 129.20, 128.63, 127.67, 126.45, 122.01, 121.74, 105.22, 55.25, 45.21. **HRMS** (ESI) m/z calcd. For C<sub>17</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 250.1226, found: 250.1211.



**4-benzyl-6-methoxyquinoline (2ae')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ae** (0.2 mmol), compound **2ae'** (13.37 mg, 27%) was obtained. Yellow oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.68 (d, *J* = 4.4 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.26 (s, 1H), 7.23 – 7.20 (m, 3H), 7.15 – 7.08 (m, 1H), 4.38 (s, 2H), 3.84 (s, 3H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$ 157.71, 147.82, 145.08, 144.46, 138.64, 131.61, 128.95, 128.77, 128.54, 126.67, 122.14, 121.49, 102.13, 55.46, 38.63. **HRMS** (ESI) m/z calcd. For C<sub>17</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 250.1226, found: 250.1211.



**6-methoxy-2-(4-methylbenzyl)quinoline (2af)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1af** (0.2 mmol), compound **2af**' (27.51 mg, 52%) was obtained. Yellow oil. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.90 (d, J = 9.2 Hz, 1H), 7.81 (dd, J = 8.6, 0.8 Hz, 1H), 7.26 (dd, J = 9.2, 2.8 Hz, 1H), 7.13 – 7.04 (m, 3H), 7.01 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 2.8 Hz, 1H), 4.18 (s, 2H), 3.80 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  158.99, 157.43, 143.72, 136.43, 135.99, 135.46, 130.31, 129.34, 129.11, 127.69, 122.02, 121.80, 105.24, 55.52, 44.81, 21.05. **HRMS** (ESI) m/z calcd. For C<sub>18</sub>H<sub>17</sub>NO [M+H]<sup>+</sup>: 264.1383, found: 264.1374.



6-methoxy-4-(4-methylbenzyl)quinoline (2af') was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1af** (0.2 mmol), compound **2af'** (11.08 mg, 21%) was obtained. Yellow oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, J = 4.4 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 7.34 (dd, J = 9.1, 2.8 Hz, 1H), 7.24 (d, J = 2.7 Hz, 2H), 7.16 – 7.07 (m, 5H), 4.34 (s, 2H), 3.86 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.67, 147.82, 145.41, 144.42, 136.24, 135.51, 131.58, 129.44, 128.84, 128.55, 122.04, 121.45, 102.13, 55.46, 38.19, 21.05. HRMS (ESI) m/z calcd. For C<sub>18</sub>H<sub>17</sub>NO [M+H]<sup>+</sup>: 264.1383, found: 264.1374.



**2-(4-bromobenzyl)-6-methoxyquinoline (2ag)** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ag** (0.2 mmol), compound **2ag** (27.57 mg, 42%) was obtained. Yellow solid. <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.87 (dd, *J* = 16.1, 8.9 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.28 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.12 – 7.03 (m, 3H), 6.95 (d, *J* = 2.9 Hz, 1H), 4.17 (s, 2H), 3.82 (s, 3H). <sup>13</sup>C **NMR** (101 MHz, Chloroform-*d*)  $\delta$  157.90, 157.58, 143.75, 138.48, 135.66, 131.68, 130.91, 130.29, 127.76, 122.27, 121.67, 120.40, 105.21, 55.55, 44.50. **HRMS** (ESI) m/z calcd. For C<sub>17</sub>H<sub>14</sub>BrNO [M+H]<sup>+</sup>: 329.0332, found: 329.0338.



**4-(4-bromobenzyl)-6-methoxyquinoline (2ag')** was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to **IV**. From N-alkoxyheteroarenium salt **1ag** (0.2 mmol), compound **2ag'** (10.47 mg, 16%) was obtained. Yellow solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.58 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.26 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 7.00 – 6.95 (m, 3H), 4.21 (s, 2H), 3.74 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  156.74, 146.71, 143.37, 143.24, 136.54, 130.78, 130.62, 129.56, 127.27, 121.02, 120.48, 119.48, 100.90, 54.40, 36.90. HRMS (ESI) m/z calcd. For C<sub>17</sub>H<sub>14</sub>BrNO [M+H]<sup>+</sup>: 329.0332, found: 329.0338.



6-methoxy-2-(thiophen-2-ylmethyl)quinoline (2ah) was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1), prepared according to IV. From N-alkoxyheteroarenium salt 1ah (0.2 mmol), compound 2ah (27.58 mg, 54%) was obtained. Black oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.88 (d, *J* = 9.2 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.23 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.05 – 7.03 (m, 1H), 6.89 – 6.87 (m, 1H), 6.83 – 6.78 (m, 2H), 4.36 (s, 2H),

3.75 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.60, 157.56, 143.55, 141.62, 135.78, 130.22, 127.88, 127.01, 125.94, 124.51, 122.29, 121.38, 105.22, 55.53, 39.19. HRMS (ESI) m/z calcd. For C<sub>15</sub>H<sub>13</sub>NOS [M+H]<sup>+</sup>: 256.0719, found: 256.0796.

# Appendix I

# Spectral Copies of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR Data Obtained in this Study





# <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **1c**

9.9.33 (9.9.33) (9.9.





# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of **1d** $\begin{pmatrix} 8.04 \\ 28.03 \\ 7.54 \\ 7.53 \\ 7.51 \\ 7.13 \\ 7.12 \\ 7.12 \end{pmatrix}$ 4.47 4.45 9.31 9.31 9.29 9.29 9.28 2.602.2381.1231.1241.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.1211.12221.12221Me ŌTs Image: state 3.26-F00 15-1 -0. 2.0 1.6 1.2 0.8 0.0 0.4 $^{13}$ C NMR (101 MHz, DMSO- $d_6$ ) of 1d ~146.07 ~141.35 ~138.27 ~129.78 ~125.99 -159.19 -87.39 21.76 -8.73 -3.63 Me ŌTs





00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)



# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of **1g**



# <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **1i**



# <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **1**j 8.07 8.05 8.05 8.05 7.51 7.51 7.49 7.13 7.13 9.32 9.32 9.31 9.30 ŌTs 20 × 08 12 4 054 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 fl (ppm) <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **1**j -159.14-145.89 -140.81 -140.81 -138.33 -138.33 -128.59 -126.88 -126.88 -126.88 -126.88 -126.88 86.05 86.02 33.83 32.74 32.50 32.50 32.26 25.15 25.15 25.15 25.15 21.74 21.74 21.74 ŌTs

00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

# <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) of **1**j

-89.46
-90.07
-99.12
-99.74





# $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of 1k

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# <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **1**k



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **1**I









# $^{19}\mathrm{F}$ NMR (376 MHz, CDCl<sub>3</sub>) of 1n





--110.40

# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of **10**



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of **1**p



# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of 1q

(a) 200 (a) 200 (b) 200 (b) 200 (c) 200 (c)



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

# $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of 1r

 0
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100 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

# <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **1s**

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# $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of 1t





# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of 1v



# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of **1w**



# <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) of 1x














195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2a

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#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2b**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2c**



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ( fl (ppm)

#### $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of **2d**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2e



#### $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of **2f**

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200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### $^1\text{H}$ NMR (400 MHz, CDCl<sub>3</sub>) of 2g



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2h**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2i



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2**j



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

## $^{19}F$ NMR (376 MHz, CDCl<sub>3</sub>) of 2j

~91.37
~92.00
~101.41
~102.04







#### $^{13}\text{C}$ NMR (101 MHz, CDCl<sub>3</sub>) of 2k



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2k'**



#### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2k'**



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2l**



#### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2**l



#### $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>) of **2m**

7.7.7.48 (6.97) (7.4.6.97) (6.97)



#### $^{13}\text{C}$ NMR (101 MHz, CDCl<sub>3</sub>) of 2m



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2m'**



## <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2m**'



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2n**



#### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2n**



-100 fl (ppm) 5 -10 -20 -200 -30 -40 -50 -60 -70 -80 -90 -110 -120 -130 -140 -150 -160 -170 -180 -190

COSY



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2n'







#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **20**



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 6 fl (ppm)

COSY



HSQC



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **20', 20''**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2p**



COSY

Π.

.



99

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 f2 (ppm)

-130 -140

-150

# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2p', 2p''**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2q

 $\begin{array}{c} 7.59\\ 7.794\\ 7.794\\ 7.792\\ 7.792\\ 7.792\\ 7.792\\ 7.792\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.732\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.7222\\ 7.$ 3.17 3.15 3.15 3.15 3.15 3.17 3.11 3.315 3





#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2q'**



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2r





20 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2r'**



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2s

7.7.48 7.7.146 7.7.146 7.7.146 7.7.146 7.7.146 7.7.146 7.7.147 7.7.146 7.7.147 7.7.146 7.7.147 7.7.146 7.7.





195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2t



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2t'


## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2u

(8.82) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17725) (1.17775) (1.177



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2v



COSY



HSQC



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2v'



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2v**"

 $\begin{array}{c} 8.8 \\ 8.8 \\ 8.8 \\ 6.8 \\ 7.7 \\ 7.8 \\ 8.8 \\ 7.7 \\ 7.8 \\ 7.7 \\ 7.8 \\ 8.8 \\ 7.7 \\ 7.7 \\ 7.8 \\ 8.8 \\ 7.7 \\ 7.7 \\ 7.8 \\ 8.8 \\ 7.8$ 1.96 1.96 1.95 1.95 1.94 1.93 1.93



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2w



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2w'



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2**x



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2x**'



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2y

8.8.53 8.8.55 7.7.55 8.8.55 7.7.55 8.8.55 7.7.55 8.8.55 7.7.55 8.8.55 7.7.55 8.8.55 7.7.55 8.8.55 7.7.55 7.



COSY



#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2z











## <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2ab**



00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 c fl (ppm)

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2ac



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00 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)

## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2ac'



# <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 2ac'



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)

## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2ad

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## <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2ad**



COSY



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2ae

8.06 8.00 7.75 









195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 fl (ppm)







#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2ah**

