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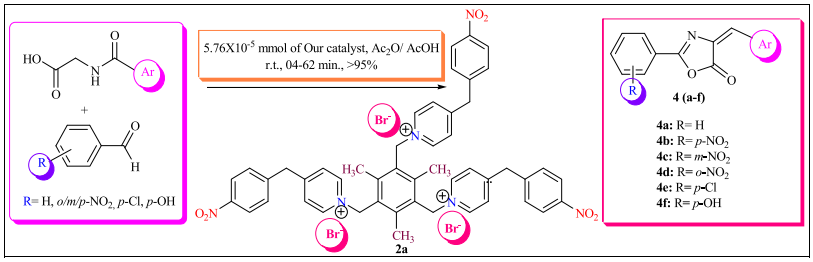

The synthesis of pyridinium salts by both conventional/silica-supported muffle furnace and microwave approaches is described. We have optimized the Erlenmeyer synthesis of azalactone with various concentrations of our synthesized pyridinium salts. Among these, bromide-containing pyridinium salts showed excellent catalytic activity than the others.

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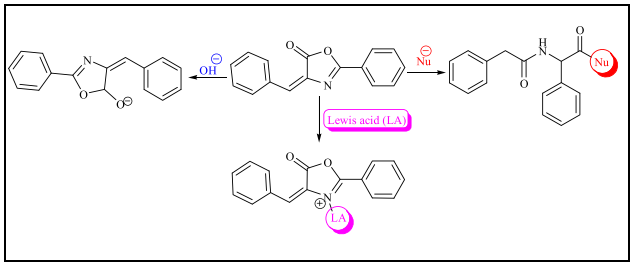
INTRODUCTION

Ionic liquids (ILs) have special behavior like tunability, which allows their physical and chemical properties to be altered as desired by changing the structure of counterions [1,2]. ILs have attracted more and more attention in recent days because of their distinct behaviors like acted as solvents [3–6], electrolyte [7,8], catalysis [3,9–11], stationary phase for chromatography [12], and lubricants [13], as well their unique behaviors of low corrosiveness, low volatility, thermal stabilities, low combustibility, and recyclability [14,15]. Nguyen Chau *et al*. reported the microwave-assisted synthesis of some imidazolium salts and its catalytic activities for condensation reactions [16]. Most of the available literatures for ILs are composed of an unsymmetrically substituted nitrogen organic cation such as imidazolium/pyridinium with an inorganic counteranion like PF_6^-, Br^-, BF_4^-, and Cl^- [17–19]. Monopyridinium salts acted as both solvent and ligand to assist for copper-catalyzed cross-coupling reactions [20]. Oxazolone and its derivatives play a very crucial role in the medicinal aspects such as anticancer, anti-microbial, antidiabetic, anti-obesity, and antidepressant [21]. Owing to the presence of several active sites are permits to produce a larger variety of biologically target molecules [22,23].



Applications of oxazolone derivatives are extended owing to the presence of an exocyclic double bond at 4-position, which gives some useful and interesting pharmaceutical drugs like immunomodulatory [24], anti-inflammatory [25], antifungal [26], and antibacterial [27] purpose. Greener approach is the construction of chemical compounds and processes that eliminate or minimize the generation and usage of environmental-polluting substances [28]. In literature, different routes were used including the use of several bases such as K_3PO_4 [29], DIPEA [30], basic ILs [31], some of transition metal catalysis [32–34], and microwave-assisted reactions [35], even though the conventional Erlenmeyer reaction that is still used to prepare oxazolone derivatives is very interesting. Herein, we wish to report the preparation of substituted pyridinium salts under conventional/silica-supported solvent-free muffle/microwave medium. We have tried Erlenmeyer reaction in the presence of optimized concentration of our substituted pyridinium salts and compared the same reaction with available literature [36].

RESULTS AND DISCUSSION

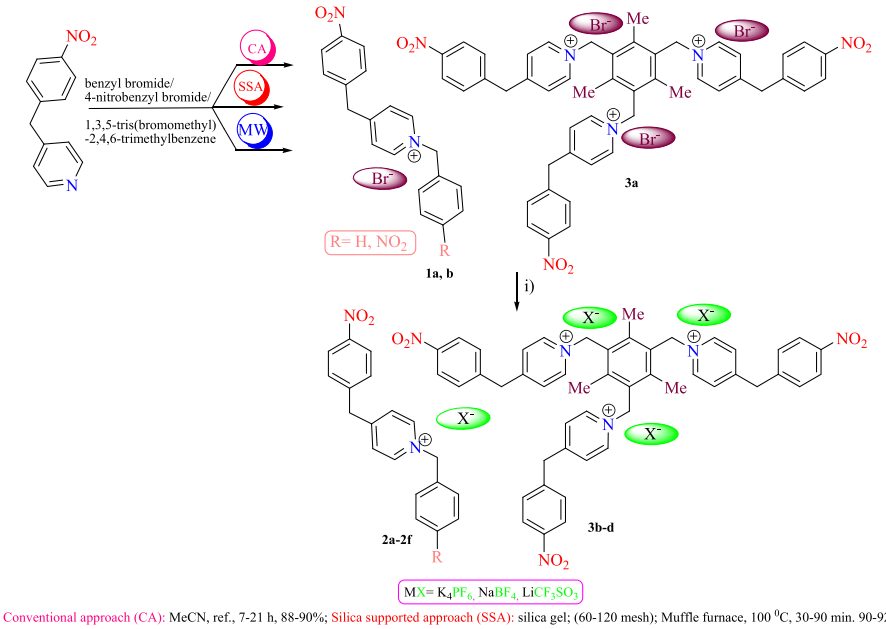
Benzylbromide/nitrobenzylbromide/1,3,5-tris(bromomethyl) tri-2,4,6-methylbenzene was treated with 4-(4-nitrobenzyl) pyridine (NBP) under conventional/silica-supported solvent-free muffle furnace/microwave approach, and benzyl/4-nitrobenzyl bromide/1,3,5-tris(bromomethyl)tri-2,4,6-methylbenzene was treated with substituted derivative of pyridine moieties in the presence of 30 mL of dry MeCN under refluxing condition for 7–21 h to

afford the *N*-alkylated pyridinium bromides **1a/1b/3a** in 95–97% yield (Scheme 1).

Quartinization reaction between substituted pyridine with benzyl/4-nitrobenzylbromide (NBB). NBB is much faster than the benzyl bromide, so we extend the quartinization with 1,3,5-tris-(bromomethyl)-2,4,6-tri-methylbenzene. These reactions are required long time for completion, so we planned to reduce the reaction period as well as nontoxic solvent-free methodology. We have examined the *n*-alkylation reaction under muffle/microwave conditions. Muffle furnace approach is nearly 15 times faster than the conventional route. Microwave route is much faster than muffle route. So quartinization reaction with previously mentioned reacting substrate under solvent-free, nontoxic routes is more suitable than the conventional Erlenmeyer synthesis of azalactone from aryl aldehyde and hippuric acid in the presence of anhydrous K_2CO_3 with 25 mL AcOH at ambient reaction condition for 5 h. There are no appreciable changes.

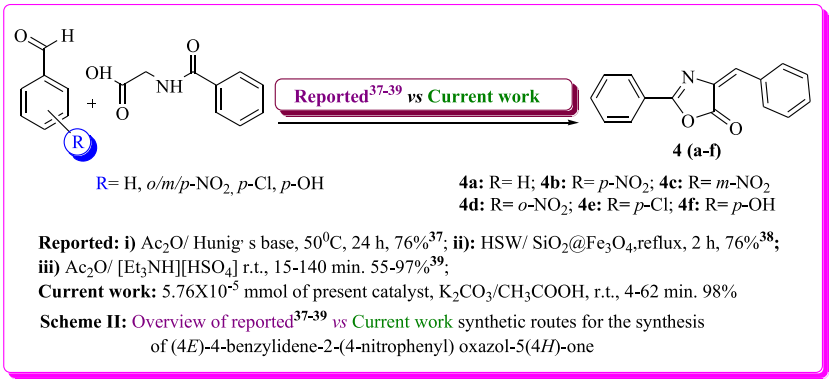
After completion of the quartinization reaction, anion exchange reaction is carried out in the presence of various counterion containing inorganic salts like K_4PF_6, $NaBF_4$, and $LiCF_3SO_3$ in the presence of water and at ambient condition with stirring for 2 h to give anion-exchanged products of compounds (**2a–f**) and (**3b–d**) in quantitative yield (Scheme 1).

Scheme 1. Synthesis of pyridinium salts under conventional, solid-supported, and microwave approaches. [Color figure can be viewed at wileyonlinelibrary.com]



Conventional approach (CA): MeCN, ref., 7-21 h, 88-90%; Silica supported approach (SSA): silica gel; (60-120 mesh); Muffle furnace, 100 ^{0}C, 30-90 min. 90-92%; Microwave reaction condition (MW): 08-27 min. 95-97%; i) MX/ H_2O r.t., 2 h, 85-92%

Scheme 2. Overview of reported [37–39] versus this work synthetic routes (A, B, and C vs. D) for the synthesis of (4*E*)-4-benzylidene-2-(4-nitrophenyl) oxazol-5(4*H*)-one. [Color figure can be viewed at wileyonlinelibrary.com]



We have to separate the pyridinium salt from metal bromide, which is not easy because the usual organic solvent extraction is not feasible owing to the water-soluble nature of both metallic bromide and pyridinium salt. Under this circumstance, we carried out the Soxhlet extraction in the presence of dry tetrahydrofuron for 2 h under refluxing condition to give metallic bromide-free pyridinium salt with excellent yield. After completion of Soxhlet extraction, we have checked with aqueous $AgNO_3$ solution; fortunately, we did not obtain any pale yellow precipitate, so we can further conformed that our pyridinium salt is metal bromide free. The synthesized compounds (**2a–f**) and (**3b–d**) are confirmed with spectral and analytical data.

CATALYTIC ACTIVITY

Flavio *et al*. reported the modified Erlenmeyer reaction between electron donating and withdrawing aryl aldehyde

Table 1

1.92×10^{-5} mmol concentration of substituted pyridinium salts for Erlenmeyer reaction.

	Substituted aryl aldehyde											
	p-NO_2		*m*-NO_2		*O*-NO_2		H		*p*-Cl		*p*-OH	
Catalyst	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1a	16	84	17	78	21	74	21	71	24	66	20	83
1b	19	78	19	75	21	76	33	68	25	60	45	58
2a	19	83	21	77	22	72	28	63	38	56	52	72
2b	24	80	24	74	27	72	28	54	46	62	40	74
2c	24	80	26	74	28	70	34	64	47	61	52	71
2d	33	73	32	68	36	64	28	50	41	58	55	61
2e	30	73	35	62	35	62	39	47	43	60	58	59
2f	38	66	33	68	33	62	38	48	48	56	58	60
3a	14	82	15	76	18	84	22	72	23	66	39	74
3b	19	85	18	71	20	74	24	66	35	69	51	70
3c	23	80	25	68	27	69	26	64	42	54	55	66
3d	26	73	27	65	29	69	31	52	48	65	57	66

Reaction condition: *p*-nitrobenzaldehyde (6.173×10^{-3} mmol; 1.0 equiv), hippuric acid (6.749×10^{-3} mmol; 1.02 equiv), AcOH (25 mL), and our catalyst (1.92×10^{-5} mmol). Absence of pyridinium salt: no appreciable change even after 5 h; yield of isolated product.

Table 2

3.84×10^{-5} mmol concentration of substituted pyridinium salts for Erlenmeyer reactions.

	Substituted aryl aldehyde											
	p-NO_2		*m*-NO_2		*O*-NO_2		H		*p*-Cl		*p*-OH	
Catalyst	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1a	11	86	11	81	11	76	11	83	10	84	14	84
1b	15	90	17	80	19	78	17	80	10	82	33	60
2a	11	87	12	82	14	80	18	77	23	75	31	70
2b	15	80	17	73	18	76	20	75	30	70	19	74
2c	17	86	17	81	19	74	21	71	37	64	19	76
2d	28	78	25	72	25	69	23	70	28	66	40	58
2e	26	78	30	60	32	70	29	68	30	55	39	62
2f	30	80	30	60	32	70	32	68	40	59	40	58
3a	09	90	09	85	11	82	08	85	09	84	25	76
3b	11	89	11	84	13	85	14	83	20	74	39	65
3c	16	82	17	77	19	76	14	83	28	78	57	58
3d	16	89	16	84	18	80	16	75	34	66	62	68

Reaction condition: *p*-nitrobenzaldehyde (6.173×10^{-3} mmol; 1.0 equiv), hippuric acid (6.749×10^{-3} mmol; 1.02 equiv), AcOH (25 mL), and our catalyst (3.84×10^{-5} mmol). Absence of pyridinium salt: no appreciable change even after 5 h; yield of isolated product.

Table 3

5.76×10^{-5} mmol concentration of substituted pyridinium salts for Erlenmeyer reactions.

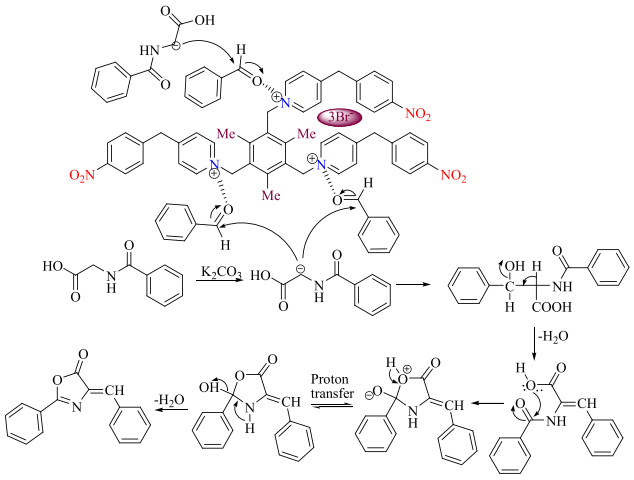
	Substituted aryl aldehyde											
	p-NO_2		*m*-NO_2		*O*-NO_2		H		*p*-Cl		*p*-OH	
Catalyst	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1a	04	95	05	90	06	88	05	83	07	89	08	89
1b	10	96	12	84	16	86	14	78	06	86	25	76
2a	07	90	08	85	09	85	08	83	09	83	12	82
2b	11	85	12	80	14	76	14	77	10	83	10	86
2c	12	89	12	84	13	78	15	78	13	84	11	80
2d	14	98	16	90	14	80	16	74	14	78	38	68
2e	14	90	14	81	16	82	16	74	12	70	31	74
2f	15	90	14	78	15	74	18	68	12	82	28	74
3a	04	98	04	93	05	92	04	87	06	90	14	84
3b	07	90	06	85	10	85	09	85	07	84	19	85
3c	09	92	11	87	13	85	10	79	08	79	28	82
3d	12	95	13	90	14	84	10	75	11	80	35	78

Reaction condition: *p*-nitrobenzaldehyde (6.173×10^{-3} mmol; 1.0 equiv), hippuric acid (6.749×10^{-3} mmol; 1.02 equiv), AcOH (25 mL), and our catalyst (5.76×10^{-5} mmol). Absence of pyridinium salt: no appreciable change even after 5 h; yield of isolated product.

with various substituted hippuric acids in the presence of Hunig's base to afford the quantitative yield but need for long period nearly 24 h for completion [37]. Parveen *et al*. reported the preparation of azalactone and its derivatives from various aryl aldehydes and hippuric acid in the presence of higher concentration (20% mol) of ILs at 100°C to give quantitative yield [38]. Azalactone and its derivatives were derived from required reactants in the presence of $[Et_3NH][HSO_4]$ for 15–140 min to afford from moderate to quantitative yield. Parveen *et al*. employed to prepare their target molecules and used special reaction setup; unfortunately, they received only moderate yield [38].

We wanted to conduct the Erlenmeyer synthesis of azalactone from aryl aldehyde and hippuric acid under the absence of catalyst and anhydrous K_2CO_3 with 25 mL of CH_3COOH at ambient reaction condition for 5 h. There are no appreciable changes. Same reacting substrates along with optimized very low concentration of our pyridinium salts at ambient reaction condition stirring from 4 to 62 min to afford the target molecules **4** (**a–f**) in excellent yields (Scheme 2). We have examined the catalytic activities of our pyridinium cation with different anions. We found that trimeric pyridinium bromide showed excellent catalytic response than the others. We have examined the Erlenmeyer reaction with various concentrations of TPB like (1.92×10^{-5} mmol/ 3.84×10^{-5} mmol/5.76×10^{-5} mmol) among these concentrations; 5.76×10^{-5} mmol showed effective response. While increasing the catalyst concentration, there are no appreciable changes made, and results are summarized (shown in Tables 1–3).

Proposed reaction mechanism for Erlenmeyer synthesis of azalactone for trimeric pyridinium salts



CONCLUSIONS

We have synthesized trimeric pyridinium cation with different counterions under conventional refluxing condition as well as solid supported neat reaction condition. We have observed that the solid-supported solvent-free approach reached the target molecule method. We have studied the Erlenmeyer synthesis of azalactone reaction in the presence of trimeric pyridinium salts. We examined the catalytic concentration of our trimeric pyridinium salt from 1.92×10^{-5} to 3.84×10^{-5} mmol and higher concentrations and found that 5.76×10^{-5} mmol concentrations give higher

yield with shorter reaction time. So 5.76×10^{-5} mmol is the optimum concentration for Erlenmeyer synthesis of azalactone reaction.

EXPERIMENTAL

Preparation of substituted pyridinium bromide under conventional route. Required equivalent of NBP is treated with BB/NBB/TBMTMB in the presence of 20 mL of dry MeCN under refluxing condition for 7–21 h to afford the substituted pyridinium bromides **1a/1b/3a** in 88–90% yield.

Preparation of substituted pyridinium bromide under silica-supported solvent-free routes. Required equivalence, which is used in conventional route but without solvent, is transferred into mortar and pestle followed by fine grinding with silica gel (60–120) mesh. The silica-supported reactant is divided into two portions and kept in muffle/microwave reactor and monitors the reaction using thin-layer chromatography.

1-Benzyl-4-(4-nitrobenzyl) pyridine-1-ium bromide 1a. Yield: 1.0 g, 98%; mp 135–140°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 2H), 4.49 (s, 2H), 7.65–8.02 (m, 5H), 8.04–8.25 (m, 4H), 8.41–8.93 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.6, 59.0, 122.0, 124.4, 128.6, 129.1, 131.1, 135.1, 140.0, 144.3, 145.8, 147.0, 160.6. MS: *m/z*: 385.25; *anal.* calcd for $C_{19}H_{17}BrN_2O_2$: C, 59.18; H, 4.41; N, 7.26; found: C, 59.10; H, 4.33; N, 7.18.

1,4-Bis(4-nitrobenzyl)pyridine-1-ium bromide 1b. Yield: 1.0 g, 98%; mp 115–120°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.26 (s, 2H), 4.49 (s, 2H), 7.65–8.04 (m, 4H), 8.41–8.92 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.6, 65.0, 121.0, 124.4, 128.6, 129.1, 131.1, 135.3, 144.3, 145.8, 147.0, 150.0, 160.6. MS: *m/z*: 430.25; *anal.* calcd for $C_{19}H_{16}BrN_3O_4$: C, 52.99; H, 3.71; N, 9.76; found: C, 52.91; H, 3.63; N, 9.68.

1,1′,1″-(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene) tris(4-(4-nitrobenzyl)pyridine-1-ium)bromide 3a. Yield: 1.63 g, 98%; mp 105–110°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.35 (s, 9H), 3.15 (s, 6H), 5.99 (s, 6H), 7.65–7.79 (d, 12H), 8.10–8.22 (d, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.9, 28.9, 62.0, 124.4, 128.3, 130.6, 131.1, 132.1, 141.6, 145.4, 148.4, 160.7. MS: *m/z*: 1041.62; *anal.* calcd for $C_{48}H_{45}Br_3N_6O_6$: C, 55.29; H, 4.32; N, 8.06; found: C, 55.21; H, 4.24; N, 7.98.

General procedure for anion exchange reaction. Substituted pyridinium bromide **1a/1b/3a** (1.038×10^{-3} mmol; 1.0 equiv) mixed with required equivalent of inorganic salts such as $NaBF_4$, K_4PF_6, $LiCF_3SO_3$ (1.038×10^{-3} mmol; 1.0 equiv) in the presence of 10 mL of deionized water at ambient reaction condition for stirring 2 h to afford the anion-exchanged products of compounds (**2a–f**) and (**3b–d**) along with metal bromide. After completing the anion exchange reaction with the assistance of Soxhlet extraction by using dry tetrahydrofuron for extraction, we have separated metallic bromide-free pyridinium salts in quantitative yield.

1-Benzyl-4-(4-nitrobenzyl) pyridine-1-ium hexafluorophosphate 2a. Yield: 0.40 g, 92%; mp 143–145°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 2H), 4.54 (s, 2H), 7.70–8.06 (m, 5H), 8.07–8.30 (m, 4H), 8.46–8.98 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.8, 60.0, 121.2, 124.6, 128.8, 129.3, 131.3, 135.7, 140.9, 144.5, 145.9, 147.2, 160.8. MS: *m/z*: 450.31; anal. calcd for $C_{19}H_{17}F_6N_2O_2P$: C, 50.63; H, 3.77; N, 6.21; found: C, 50.55; H, 3.69; N, 6.13.

1-Benzyl-4-(4-nitrobenzyl) pyridine-1-ium tetrafluoroborate 2b. Yield: 0.40 g, 93%; mp 155–160°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 2H), 4.52 (s, 2H), 7.68–8.05 (m, 5H), 8.05–8.28 (m, 4H), 8.44–8.96 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.9, 63.8, 121.3, 124.7, 128.9, 129.4, 131.4, 135.9, 140.5, 144.6, 145.1, 147.3, 160.9. MS: *m/z*: 392.16; *anal.* calcd for $C_{19}H_{17}BF_4N_2O_2$: C, 58.13; H, 4.33; N, 7.13; found: C, 58.05; H, 4.25; N, 7.05.

1-Benzyl-4-(4-nitrobenzyl) pyridine-1-ium trifluoromethanesulfonate 2c. Yield: 0.40 g, 93%; mp 160–165°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.26 (s, 2H), 4.55 (s, 2H), 7.71–8.08 (m, 5H), 8.08–8.31 (m, 4H), 8.47–8.99 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.1, 62.0, 121.4, 124.8, 128.1, 129.5, 131.6, 135.3, 140.1, 144.7, 145.9, 147.4, 160.1. MS: *m/z*: 454.42; *anal.* calcd for $C_{20}H_{17}F_3N_2O_5S$: C, 52.81; H, 3.74; N, 6.16; found: C, 52.73; H, 3.66; N, 6.08.

1,4-Bis(4-nitrobenzyl)pyridine-1-ium hexafluorophosphate 2d. Yield: 0.50 g, 91%; mp 135–140°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 2H), 4.57 (s, 2H), 7.72–8.04 (m, 4H), 8.47–8.98 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.9, 63.6, 121.9, 124.8, 128.5, 129.3, 131.4, 135.7, 144.0, 145.3, 147.7, 150.9, 160.8. MS: *m/z*: 495.31; *anal.* calcd for $C_{19}H_{16}F_6N_3O_4P$: C, 46.03; H, 3.23; N, 8.48; found: C, 45.95; H, 3.15; N, 8.40.

1,4-Bis(4-nitrobenzyl)pyridine-1-ium tetrafluoroborate 2e. Yield: 0.50 g, 90%; mp 130–135°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.29 (s, 2H), 4.53 (s, 2H), 7.67–8.08 (m, 4H), 8.49–8.95 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.8, 62.9, 121.1, 124.8, 128.8, 129.0, 131.7, 135.5, 144.7, 145.9, 147.1, 150.3, 160.8. MS: *m/z*: 437.15; *anal.* calcd for $C_{19}H_{16}BF_4N_3O_2$: C, 52.05; H, 3.66; N, 9.60; found: C, 51.97; H, 3.58; N, 9.52.

1,4-Bis(4-nitrobenzyl)pyridine-1-ium trifluoromethanesulfonate 2f. Yield: 0.50 g, 88%; mp 150–155°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 2H), 4.58 (s, 2H), 7.71–8.05 (m, 4H), 8.51–8.96 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 39.8, 63.2, 121.1, 124.7, 128.9, 129.5, 131.3, 135.9, 144.5, 145.9, 147.1, 150.9, 160.2. MS: *m/z*: 499.42; *anal.* calcd for $C_{20}H_{16}F_3N_3O_2S$: C, 48.05; H, 3.20; N, 8.40; found: C, 47.97; H, 3.12; N, 8.32.

1,1′,1″-(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene) tris(4-(4-nitrobenzyl)pyridine-1-ium) hexafluorophosphate 3b. Yield: 0.50 g, 87%; mp 198–200°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 9H), 3.05 (s, 6H), 6.14 (s, 6H), 7.67–7.81 (d, 12H), 8.12–8.24 (d, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.7, 28.8, 62.1, 124.6, 128.1, 130.8, 131.3, 133.3, 141.9, 145.6, 148.6, 160.9. MS: *m/z*: 1236.08; *anal.* calcd for $C_{48}H_{45}F_{18}N_6O_6P_3$: C, 46.61; H, 3.67; N, 6.79; found: C, 46.53; H, 3.59; N, 6.71.

1,1′,1″-(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene) tris(4-(4-nitrobenzyl)pyridine-1-ium)tetrafluoroborate 3c. Yield: 0.50 g, 75%; mp 205–208°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 9H), 3.07 (s, 6H), 6.11 (s, 6H), 7.70–7.84 (d, 12H), 8.15–8.27 (d, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.5, 28.5, 62.5, 124.9, 128.1, 130.3, 131.4, 133.1, 141.8, 145.9, 148.7, 160.8. MS: *m/z*: 1062.32; *anal.* calcd for $C_{48}H_{45}B_3F_{12}N_6O_6$: C, 54.22; H, 4.23; N, 7.90; found: C, 54.14; H, 4.15; N, 7.82.

1,1′,1''-(2,4,6-Trimethylbenzene-1,3,5-triyl)tris(methylene) tris(4-(4-nitrobenzyl)pyridine-1-ium) trifluoromethanesulfonate 3d. Yield: 0.50 g, 76%; mp 170–175°C.^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 9H), 3.25 (s, 6H), 6.16 (s, 6H), 7.74–7.87 (d, 12H), 8.19–8.31 (d, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.3, 28.4, 62.7, 124.3, 128.7, 130.9, 131.7, 133.4, 141.6, 145.2, 148.5, 160.8. MS: *m/z*: 1249.11; *anal.* calcd for $C_{51}H_{45}F_9N_6O_{15}S_3$: C, 48.99; H, 3.63; N, 6.73; found: C, 48.91; H, 3.55; N, 6.65.

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