Primary vs. Secondary Alkylpyridinium Salts: A Comparison under Electrochemical and Chemical Reduction Conditions

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Supporting Information

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General Information

Unless otherwise indicated, all Ni-catalyzed reactions were set up inside a nitrogen-purged glovebox and performed under an inert atmosphere of nitrogen, using Sure-seal (Sigma-Aldrich or Thermo Fisher) anhydrous solvents. $NiBr_2$(DME) was purchased from Strem Chemicals Inc. (catalog number 28-1145). Pyridine-2,6-dicarboxamidine dihydrochloride was purchased from Sigma-Aldrich (catalog number 902047) and PharmaBlock (catalog number PBT3949-1). 4,4'-Di-*tert*-butyl-2,2'-bipyridine was purchased from Oakwood Chemical (catalog number 212480). All other commercial reagents were purchased from Sigma-Aldrich, Fisher, TCI, Combi-Blocks, Alfa Aeser and Ambeed and used as received.

The electrochemical mediator $[Ni(terpy)_2]\cdot 2PF_6$ was prepared according to literature procedure.[1]

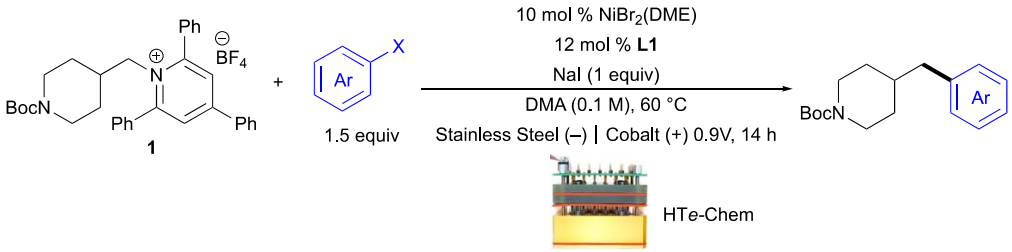
High-throughput electrochemical experimentation (HT*e*-Chem) optimizations and scope evaluation were conducted using a 24-well electrochemical parallel reactor from Analytical Sales and Services. Procedures for the assembly of HT*e*-Chem can be found at *ACS Cent. Sci.* **2021**, *7*, 1347. Cobalt electrodes were purchased from Surepure Chemicals L.L.C. (Product #10054, 1.60 mm diameter x 31.2 mm long), and stainless-steel electrodes were purchased from Analytical Sales (SKU: 700700, 1.63 mm diameter x 31.2 mm long). Within the undivided cells of the reactor, the cobalt sacrificial anode is 2 mm away from the stainless-steel cathode with a surface area of 34 mm^2. Non-electrochemical HTE experiments were performed in 1-mL glass vials secured in either a 96-well or 24-well aluminum block purchased from Analytical Sales and Services. For HT*e*-Chem experiments, electrodes and other consumables were purchased from Surepure Chemetals (Florham Park, New Jersey, USA) or Analytical Sales and Services (Flanders, New Jersey, USA). Electrodes were sonicated briefly in 0.1 M HCl solution then hexanes/acetone (1:1 v:v) mixture prior to use.

Analysis of all high throughput experimentation experiments was completed on a Waters Acquity Arc UHPLC-MS equipped with PDA and QDa detectors. A Waters 4.6 x 50 mm CORTECS column was used. The 5-minute analysis method used was 0 min, 10% B, 1.2 mL/min; 0.5 min, 10% B, 1.2 mL/min; 3.5 min, 100% B, 1.2 mL/min; 4.5 min, 100% B, 1.2 mL/min; 4.6 min, 10% B, 1.2 mL/min, where A = 0.1% formic acid in water and B = 0.1% formic acid in acetonitrile. Liquid chromatography area percentages (LCAPs) were determined from UV-Vis data collected from 210–400 nm and processed using PEAKSEL integration software. For more information visit https://elsci.io/peaksel/index.html.

Proton nuclear magnetic resonance spectra (^{1}H NMR), carbon nuclear magnetic resonance spectra (^{13}C NMR), and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded on a 400, 500, or 600 NMR spectrometer. Chemical shifts for protons are recorded in parts per million and referenced to residual $CHCl_3$ ($CHCl_3$ = δ 7.26) in deuterated chloroform. Chemical shifts for carbon are recorded in parts per million and referenced to carbon resonances of deuterated chloroform ($CDCl_3$ = δ 77.2). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, etc.), coupling constants (Hz), integration.

High-Throughput Electrochemical (HTe-Chem) Procedures

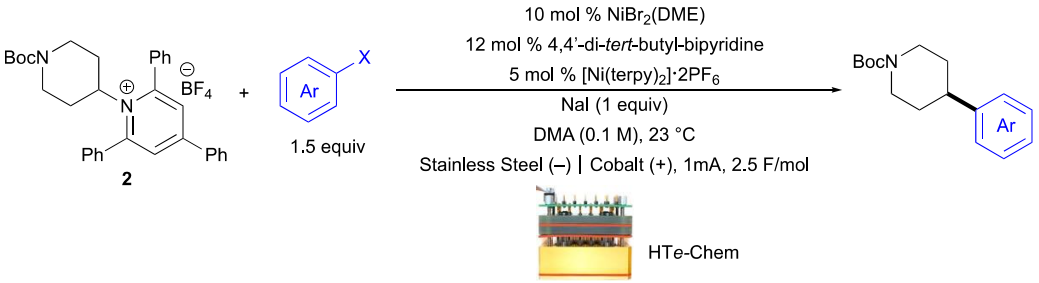
Constant Voltage Procedure with Primary Alkylpyridinium Salt



In a nitrogen-filled glovebox, to 1-mL vials (secured in a 24-well aluminum block) equipped with PTFE-covered 5 x 2 mm magnetic stir bars was added pyridinium **1** (175 µL, 0.2 M solution in DMA, 35 µmol, 1 equiv), aryl halide (105 µL, 0.5 M solution in DMA, 52.5 µmol, 1.5 equiv), NaI (50 µL, 0.7 M solution in DMA, 35 µmol, 1 equiv), and pre-complexed $NiBr_2$(DME) catalyst/ligand **L1** mixture (23.3 µL, 0.15 M solution in DMA, 3.5 µmol, 10 mol %) sequentially. The electrodes were inserted, and the HT*e*-Chem reaction block was assembled inside the glovebox. The reactor was then connected to the external power supply inside the glovebox and heated to the appropriate temperature with 1000 RPM stirring on an IKA stir plate. Upon reaching the desired temperature, the reactions were electrolyzed under constant voltage mode (V = 0.9 V) for 14 h (overnight). After electrolysis, the HT*e*-Chem reactor was allowed to cool to room temperature, taken outside of the glovebox, and disassembled. Samples for analysis were prepared by transferring a 5 µL aliquot of the crude reaction mixture into a polypropylene analysis plate and diluting with 395 µL DMSO for LC-MS analysis.

Preparation of 0.15 M stock mixture of $NiBr_2$(DME)/**L1** mixture: In a nitrogen-filled glovebox, a 4-mL vial (equipped with a stir bar) was charged with $NiBr_2$(DME) catalyst (239 µmol, 73.6 mg) and **L1** (287 µmol, 61.5 mg, 1.2 equiv with regard to Ni) and DMA (1340 µL) was added to prepare the final 0.15 M stock mixture. The mixtures were stirred for ~20 minutes (resulting in a slurry) before dosing into the reaction vials. The slurry was continually stirred at 1000 rpm while dosing.

Constant Current Procedure with Secondary Alkylpyridinium Salt



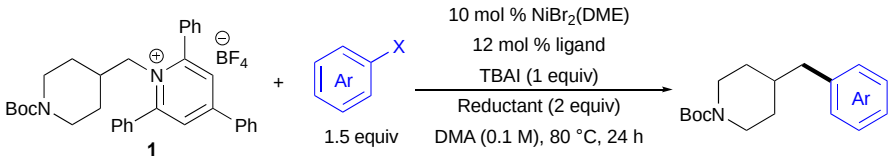
In a nitrogen-filled glovebox, to 1-mL vials (secured in a 24-well aluminum block) equipped with PTFE-covered 5 x 2 mm magnetic stir bars was added pyridinium **2** (175 µL, 0.2 M solution in DMA, 35 µmol, 1 equiv), aryl halide (105 µL, 0.5 M solution in DMA, 52.5 µmol, 1.5 equiv), NaI (50 µL, 0.7 M solution in DMA, 35 µmol, 1 equiv), and pre-complexed $NiBr_2$(DME) catalyst/ligand (4,4'-di-*tert*-butyl-bipyridine)/mediator $[Ni(terpy)_2]\cdot 2PF_6$ mixture (23.3 µL, 0.15 M solution in DMA, 3.5 µmol $NiBr_2$(DME), 10 mol % $NiBr_2$(DME) and 5 mol % $[Ni(terpy)_2]\cdot 2PF_6$) sequentially.

The electrodes were inserted, and the HT*e*-Chem reaction block was assembled inside the glovebox. The reactor was then connected to the external power supply inside the glovebox and heated to the appropriate temperature on an IKA stir plate. Upon reaching the desired temperature, the reactions were electrolyzed under constant current mode (I = 1 mA, 2.5 F/mol). After electrolysis, the HT*e*-Chem reactor was taken outside of the glovebox, and disassembled. Samples for analysis were prepared by transferring 5 µL aliquots of the crude reaction mixture into a polypropylene analysis plate and diluting with 395 µL of DMSO for LC-MS analysis.

Preparation of 0.15 M stock mixture of $NiBr_2$(DME)/ligand mixture: In a nitrogen-filled glovebox, a 4-mL vial (equipped with a stir bar) was charged with $NiBr_2$(DME) catalyst (239 µmol, 73.6 mg), 4,4'-di-*tert*-butyl-2,2'-bipyridine (287 µmol, 76.8 mg, 1.2 equiv with regard to $NiBr_2$(DME)), $[Ni(terpy)_2]\cdot 2PF_6$ (544 µmol, 97.9 mg, 0.5 equiv with regard to $NiBr_2$(DME)), and DMA (1340 µL) to prepare the final 0.15 M stock mixture. The mixture was stirred for ~20 minutes (resulting in a slurry) before dosing into the reaction vials. The slurry was continually stirred at 1000 rpm while dosing.

High-Throughput Experimentation (HTE) Procedures with Chemical Reductants

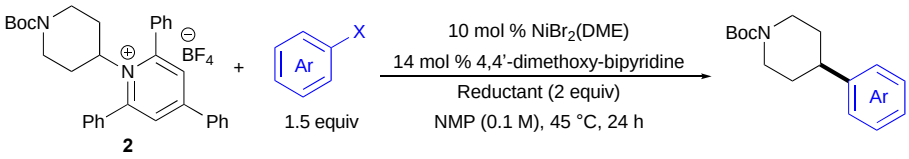
General Procedure A for Primary Alkylpyridinium Salt 1



In a nitrogen-filled glovebox, to 1-mL vials (secured in a 24-well aluminum block) equipped with PTFE-covered 5 x 2 mm magnetic stir bars was added pyridinium (25 µL, 0.4 M solution in DMA, 10 µmol, 1 equiv), aryl halide (30 µL, 0.5 M solution in solvent, 15 µmol, 1.5 equiv), TBAI (14.3 µL, 0.7 M solution in solvent, 10 µmol, 1 equiv), pre-complexed $NiBr_2$(DME) catalyst/ligand mixture (10 µL, 0.1 M solution in solvent, 3.5 µmol, 10 mol %), and appropriate reductant (33.3 µL, 0.6 M in solvent, 20 µmol, 2 equiv) sequentially. For Mn^0 the mixture was added as a slurry stirred at 1000 rpm. The reaction block was sealed and placed on an IKA magnetic stir plate pre-heated at the appropriate temperature and stirred at 500 RPM for 24 h. The reaction block was allowed to cool to room temperature and taken out of the glovebox. Samples for analysis were prepared by transferring 5 µL aliquots of the crude reaction mixture into a polypropylene analysis plate and diluting with 395 µL DMSO for LC-MS analysis.

Preparation of 0.1 M stock mixture of $NiBr_2$(DME)/ligand mixture: In a nitrogen-filled glovebox, a 4-mL vial (equipped with a stir bar) was charged with $NiBr_2$(DME) catalyst (253 µmol, 78.1 mg) and appropriate ligand (304 µmol, 1.2 equiv regarding Ni) and solvent (2340 µL) to prepare the final 0.1 M stock solution. The mixtures were stirred for ~20 minutes (resulting in a slurry) before dosing into the reaction vials. The slurry was continually stirred at 1000 rpm while dosing.

General Procedure B using Mn^0 with Secondary Alkylpyridinium Salt 2



In a nitrogen-filled glovebox, to 1-mL vials (secured in a 24-well aluminum block) equipped with PTFE-covered 5 x 2 mm magnetic stir bars was added pyridinium (25 µL, 0.4 M solution in NMP, 10 µmol, 1 equiv), aryl halide (30 µL, 0.5 M solution in NMP, 15 µmol, 1.5 equiv), pre-complexed $NiBr_2$(DME) catalyst/ligand mixture (10 µL, 0.1 M solution in NMP, 3.5 µmol, 10 mol %), and Mn^0 (47.6 µL, 0.42 M in NMP, 20 µmol, 2 equiv) sequentially. For Mn^0 the mixture was added as a slurry stirred at 1000 rpm. The reaction block was sealed and placed on an IKA magnetic stir plate pre-heated at the appropriate temperature and stirred at 500 RPM for 24 h. The reaction block was allowed to cool to room temperature and taken out of the glovebox. Samples for analysis were prepared by transferring 5 µL aliquots of the crude reaction mixture into a polypropylene analysis plate and diluting with 395 µL DMSO for LC-MS analysis.

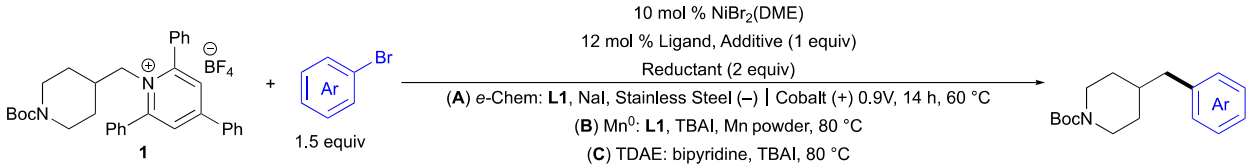
Preparation of 0.1 M stock mixture of $NiBr_2$(DME)/ligand mixture: In a nitrogen-filled glovebox, a 4-mL vial (equipped with a stir bar) was charged with $NiBr_2$(DME) catalyst (253 µmol, 78.1 mg) and 4,4'-dimethoxy-bipyridine (354 µmol, 76.6 mg, 1.4 equiv regarding Ni), and NMP (2340 µL) to prepare the final 0.1 M stock solution. The mixtures were stirred for ~20 minutes (resulting in a slurry) before dosing into the reaction vials. The slurry was continually stirred at 1000 rpm while dosing.

Reproducibility Data for Aryl Bromide Scope

Percentages reflect product LCAPs. Formation of triphenylpyridine was not considered for LCAP determinations. For chemical reduction coniditions with both substrates, experiments for runs 2 and 3 were conducted at the same time.

Lowest LCAP — Highest LCAP

Primary Alkylpyridinium Salt (Scheme 2A)



Electrochemical Conditions (A)

ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 1	0	2	2	4	6	10	4	25	18	22	24	22	18	15	34	19	28	35	40	29	32	54	35	38	22
Run 2	0	2	2	4	11	11	12	12	16	20	20	20	20	21	24	25	21	28	31	32	39	40	41	44	21
Run Average	0	2	2	4	9	11	8	19	17	21	22	21	19	18	29	22	25	32	36	31	36	47	38	41	

Mn^0 Conditions (B)

ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 1	9	4	3	7	13	38	4	19	18	12	8	19	29	32	25	11	14	22	48	18	22	54	40	20	20
Run 2	21	3	4	25	10	19	6	27	17	20	3	16	10	26	28	18	27	18	40	23	36	24	43	40	21
Run 3	17	5	3	11	4	25	8	27	14	18	2	18	8	23	33	19	24	20	46	24	35	23	29	48	20
Run Average	16	4	3	14	9	27	6	24	16	17	4	18	16	27	29	16	22	20	45	22	31	34	37	36	

TDAE Conditions (C)

ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 1	2	3	20	25	46	6	6	7	23	16	2	43	24	34	38	37	44	47	22	36	20	67	6	13	24
Run 2	2	3	20	21	48	26	11	12	30	12	0	34	22	32	48	38	41	45	24	38	17	56	16	17	26
Run 3	2	2	19	26	46	12	6	11	24	13	0	34	20	34	47	36	48	42	22	33	19	61	17	17	25
Run Average	2	3	20	24	47	15	8	10	26	14	1	37	22	33	44	37	44	45	23	36	19	61	13	16	

Secondary Alkylpyridinium Salt (Scheme 2B)

Electrochemical Conditions (A)

ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 1	4	0	23	5	30	7	21	10	3	11	2	12	22	4	24	17	26	29	4	28	13	13	28	23	15
Run 2	1	0	16	5	20	10	16	9	5	7	7	8	17	5	25	16	16	30	1	10	18	12	25	18	12
Run Average	3	0	20	5	25	9	19	10	4	9	5	10	20	5	25	17	21	30	3	19	16	13	27	21	

Mn^0 Conditions (B)

ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 1	3	0	16	3	16	7	1	1	1	2	1	13	4	4	27	21	23	15	11	31	4	2	2	3	9
Run 2	4	0	13	3	15	8	3	2	1	2	1	12	3	2	22	12	24	15	12	28	3	1	1	7	8
Run 3	2	0	11	3	15	8	4	2	0	2	1	11	5	2	23	17	22	17	17	22	4	1	1	10	8
Run Average	3	0	13	3	15	8	3	2	1	2	1	12	4	3	24	17	23	16	13	27	4	1	1	7	

Reproducibility Data for Informer Halide Scope

Percentages reflect product LCAPs. Formation of triphenylpyridine was not considered for LCAP determinations.

Lowest LCAP Highest LCAP

Primary Alkylpyridinium Salt (Scheme 3A)

Electrochemical Conditions (A)

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	LCAP Average
Run 1	36	19	0	2	32	26	0	4	1	0	0	15	21	12
Run 2	34	20	0	2	33	31	0	4	1	0	0	8	21	12
Run Average	35	20	0	2	33	29	0	4	1	0	0	12	21	

Mn^0 Conditions (B)

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	LCAP Average
Run 1	23	28	10	3	19	34	0	6	0	1	1	9	5	11
Run 2	30	27	9	2	18	26	0	6	0	0	1	3	4	10
Run Average	27	28	10	3	19	30	0	6	0	1	1	6	5	

TDAE Conditions (C)

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	LCAP Average
Run 1	0	61	15	16	3	55	0	21	0	0	0	23	2	15
Run 2	0	72	15	7	2	56	0	8	0	0	0	26	2	14
Run Average	0	67	15	12	3	56	0	15	0	0	0	25	2	

Secondary Alkylpyridinium Salt (Scheme 3B)

Electrochemical Conditions (A)

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	LCAP Average
Run 1	13	22	4	6	23	19	0	8	25	0	0	20	12	12
Run 2	10	24	4	5	17	17	0	7	29	0	0	17	17	11
Run Average	12	23	4	6	20	18	0	8	27	0	0	19	15	

Mn^0 Conditions (B)

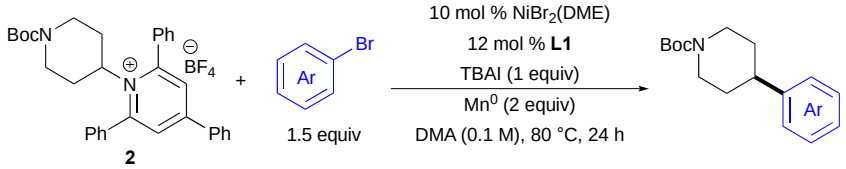
Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	LCAP Average
Run 1	3	14	5	0	1	22	0	3	30	0	0	5	8	7
Run 2	3	12	5	0	1	12	0	2	0	1	5	0	0	3
Run Average	3	13	5	0	1	17	0	3	15	1	3	3	4	

Evaluation of Alternative Conditions with Mn^0 and TDAE for Secondary Katritzky Pyridinium Salt 2

Percentages reflect product LCAPs. Formation of triphenylpyridine was not considered for LCAP determinations.

Lowest LCAP — Highest LCAP

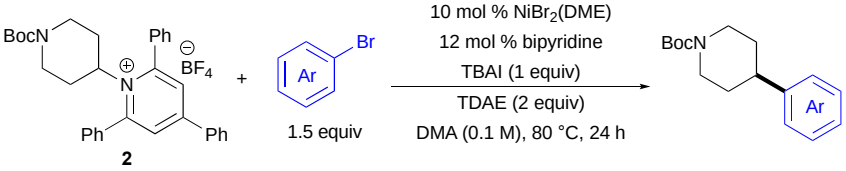
Evaluation of Mn^0 Conditions Optimal for 1° Alkylpyridinium



ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Average
LCAP	4	11	7	0	2	3	3	10	3	3	6	4	2	1	2	9	9	4	8	6	4	5	22	6	6

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	Average
LCAP	5	3	3	1	5	7	0	1	42	1	0	4	1	6

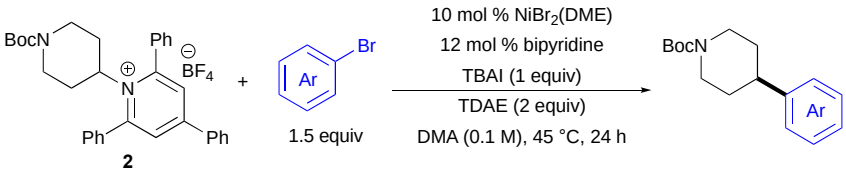
Evaluation of TDAE Conditions Optimal for 1° Alkylpyridinium



ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Average
LCAP	2	3	3	0	1	3	0	1	8	0	2	2	0	1	1	9	6	1	4	3	0	3	4	2	2

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	Average
LCAP	0	3	2	0	1	3	0	0	0	0	0	2	0	1

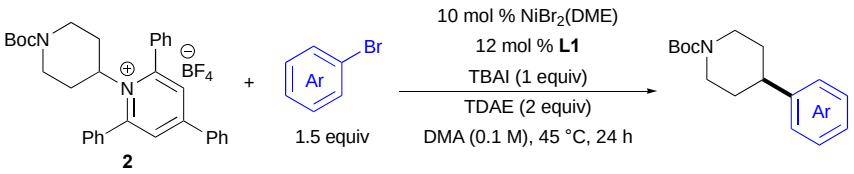
Evaluation of TDAE Conditions at 45°C



ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	LCAP Average
Run 2	5	0	7	1	4	1	1	1	0	1	2	2	1	1	12	7	5	8	2	10	1	2	1	5	3
Run 3	6	0	7	1	5	1	1	1	0	1	2	2	1	1	11	6	2	8	2	9	1	2	1	5	3
Run Average	6	0	7	1	5	1	1	1	0	1	2	2	1	1	12	7	4	8	2	10	1	2	1	5	

Informer	1	2	3	4	5	6	7	8	9	10	11	12	13	Average
LCAP	0	3	2	0	1	3	0	0	0	0	0	2	0	1

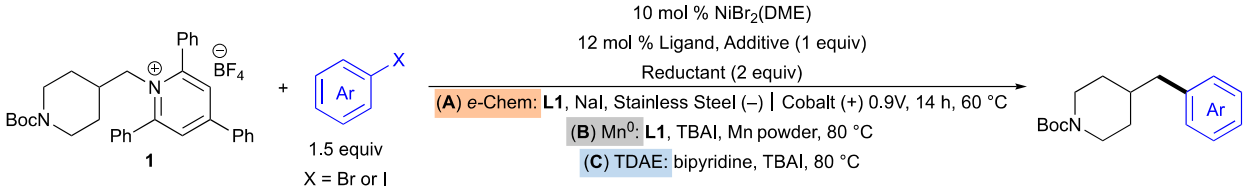
Evaluation of TDAE Conditions with Ligand L1

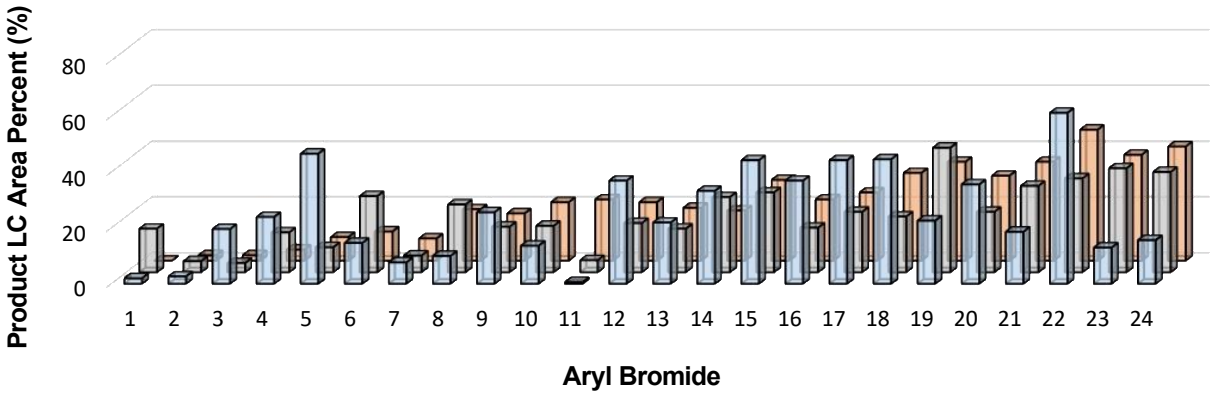


ArBr	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Average
LCAP	0	4	6	0	0	0	2	0	0	0	1	0	0	0	0	3	5	0	4	5	1	3	2	0	2

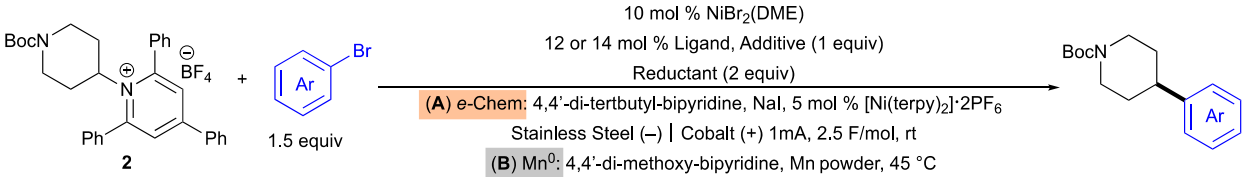
Comparison of Electrochemical vs. Chemical Conditions for Aryl Bromide Scope

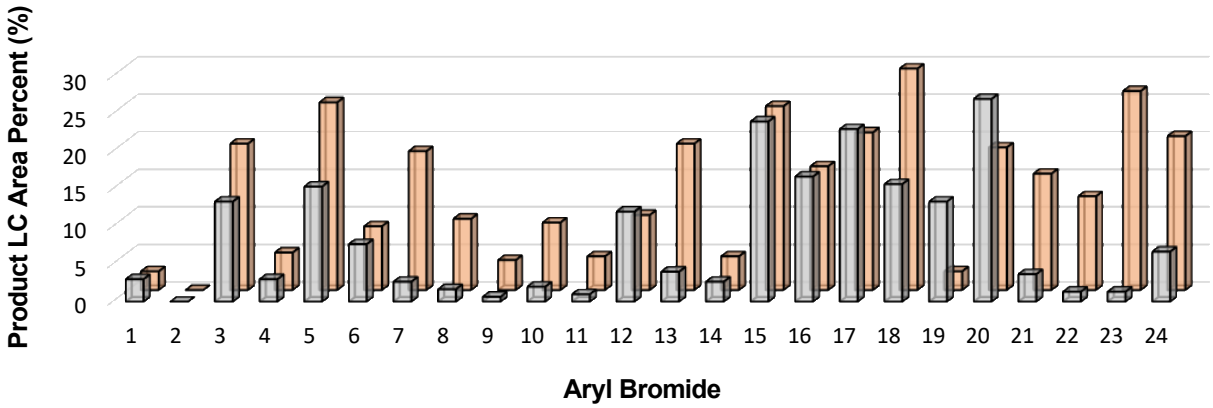
Primary Alkylpyridinium Salt (Scheme 2A)





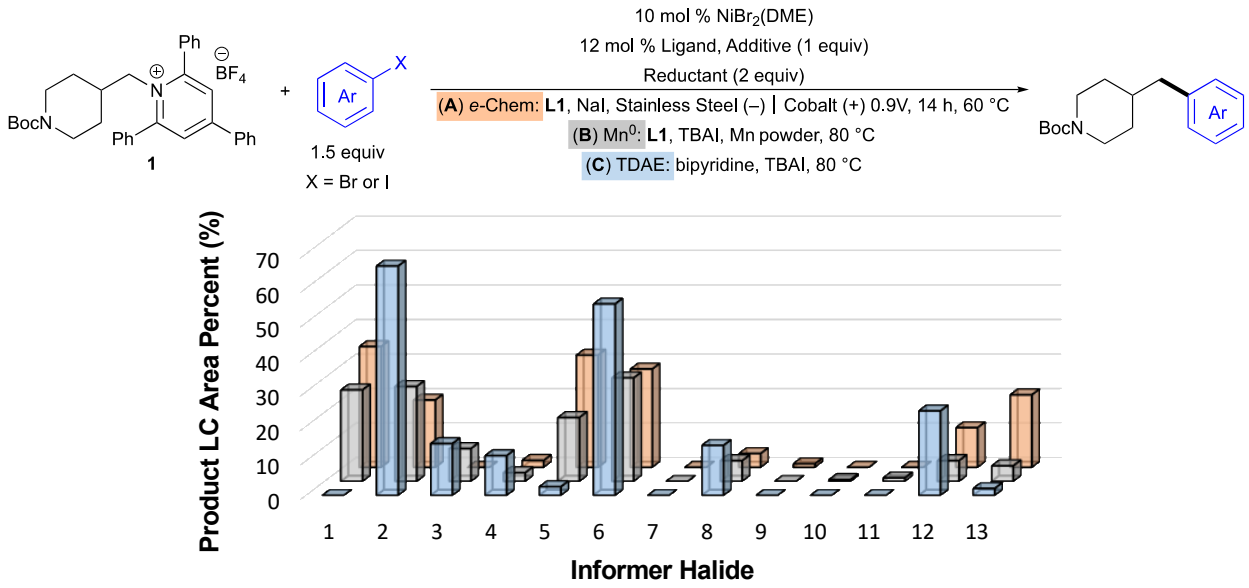
Secondary Alkylpyridinium Salt (Scheme 2B)



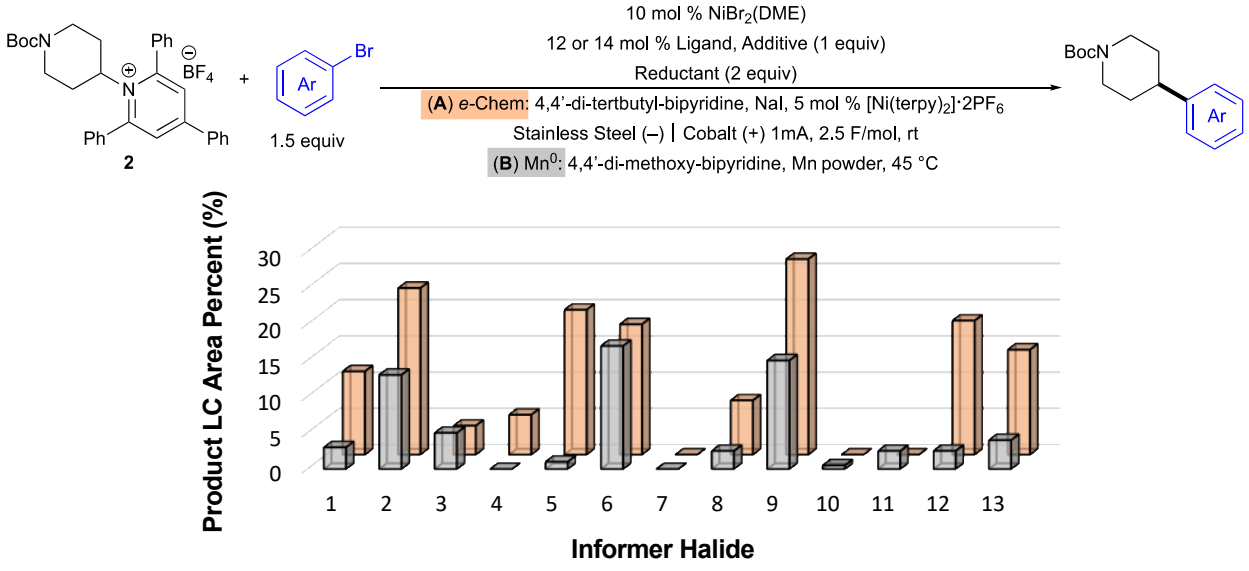


Comparison of Electrochemical vs. Chemical Conditions for Informer Halide Scope

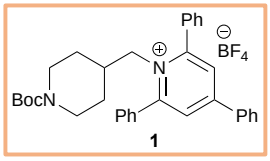
Primary Alkylpyridinium Salt (Scheme 3A)



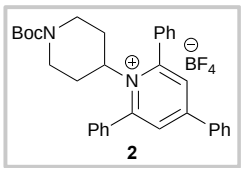
Secondary Alkylpyridinium Salt (Scheme 3B)



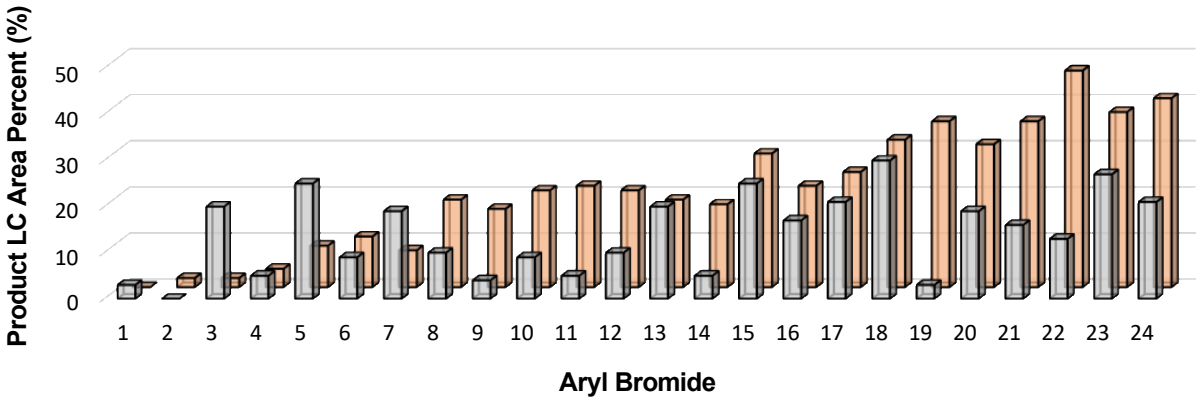
Comparison of ArBr Scope for 1° vs. 2° Alkylpyridiniums under Electrochemical Conditions

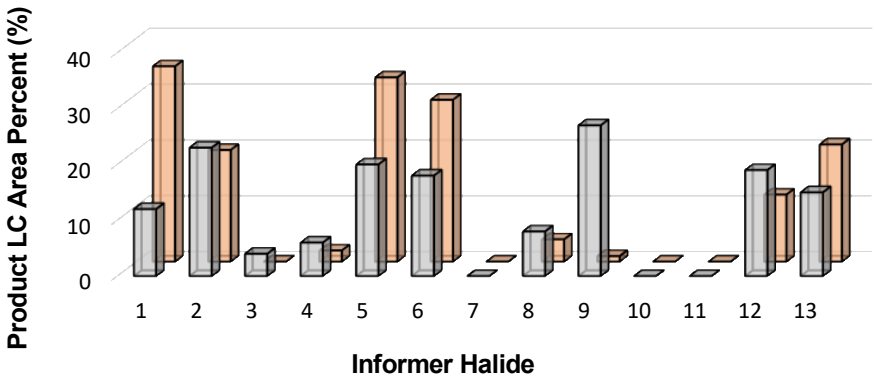


1



2

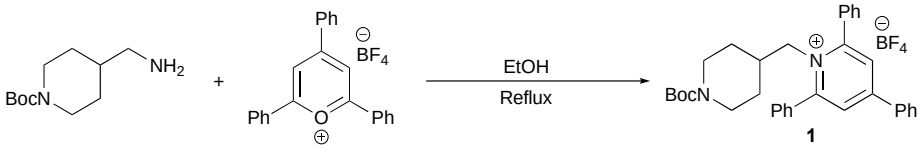




Preparation and Characterization of Katritzky Alkylpyridinium Salts

Synthesis of Primary Alkylpyridinium Salt 1

Primary pyridinium **1** was prepared as previously described.[2]

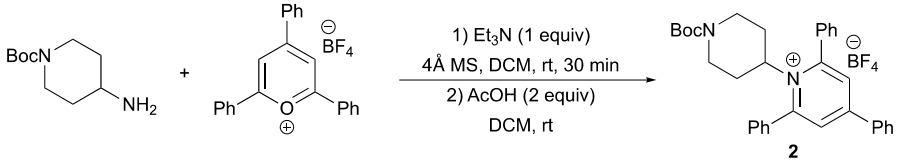


To a mixture of 2,4,6-triphenylpyrylium tetrafluoroborate (14.5 mmol, 5.8 g, 1.0 equiv) and 4-aminomethyl-1-Boc-piperidine (14.5 mmol, 3.1g, 1.0 equiv) was added EtOH (1.0 M) in a round-bottomed flask under air. The flask was fitted with a reflux condenser. The mixture was stirred and heated at reflux in an oil bath overnight. The mixture was then allowed to cool to room temperature. The mixture was diluted with Et_2O (2–3x volume of EtOH used) and vigorously stirred for 1 h. The resulting solid pyridinium salt was filtered and washed with Et_2O (3 x 25 mL).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.71 (m, 8H), 7.68 – 7.44 (m, 9H), 4.64 (d, *J* = 6.9 Hz, 2H), 3.81 (d, *J* = 13.5 Hz, 2H), 2.30 (t, *J* = 11.6 Hz, 2H), 1.69 – 1.51 (m, 1H), 1.35 (s, 9H), 1.00 (d, *J* = 11.7 Hz, 2H), 0.60 (qd, *J* = 12.2, 4.3 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 156.3, 154.6, 133.9, 133.3, 132.5, 131.5, 129.9, 129.72, 129.68, 128.3, 126.9, 79.9, 59.5, 43.1, 36.9, 29.3, 28.5
^{19}F NMR (565 MHz, $CDCl_3$) δ –153.0, –153.1.
The spectral data of **1** is consistent with that previously reported in the literature.[2]

Synthesis of Secondary Alkylpyridinium Salt 2

Secondary pyridinium **2** was prepared as previously described.[3]



Under air, 2,4,6-triphenylpyrylium tetrafluoroborate (25 mmol, 9.9 g, 1.0 equiv), crushed activated 4Å molecular sieves (500 mg/mmol), and CH_2Cl_2 (0.5 M) were added to a round-bottomed flask with a stir bar. 4-Amino-1-Boc-piperdine (25 mmol, 5 g, 1.0 equiv) was added, and the flask was fitted with a septum. A vent needle was inserted, and Et_3N (25 mmol, 3.5 mL, 1.0 equiv) was added via syringe. The vent needle was removed, and the mixture was stirred at room temperature for 30 min. The vent needle was inserted again, and AcOH (50 mmol, 2.9 mL, 2.0 equiv) was added via syringe. The vent needle was removed, and the mixture was stirred at room temperature overnight. The mixture was filtered through a short pad of Celite, rinsing with CH_2Cl_2. The filtrate was then washed with aq. HCl (1.0 M, 2 x 30 mL), aq. $NaHCO_3$ (sat., 2 x 30 mL) and aq. NaCl (sat., 2 x 30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Et_2O was added to the residue to precipitate the alkylpyridinium salt, which was collected by filtration and washed with Et_2O.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.84 – 7.71 (m, 6H), 7.64 – 7.47 (m, 9H), 4.81 (dd, *J* = 13.7, 10.8 Hz, 1H), 3.93 (d, *J* = 55.6 Hz, 2H), 2.43 – 1.65 (m, 6H), 1.31 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.35, 155.70, 154.36, 134.06, 133.88, 132.23, 131.25, 129.79, 129.47, 129.17, 128.45, 80.29, 70.10, 43.8 (br), 32.8 (br), 28.38. Note: one aromatic resonance is not observed due to coincidental overlap.
^{19}F NMR (565 MHz, $CDCl_3$) δ –153.04, –153.09.
The spectral data of **2** is consistent with that previously reported in the literature.[3]

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2. Sandfort, F.; Strieth-Kalthoff, F.; Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Borylation of Aliphatic Amines Enabled by Visible Light Excitation of an Electron Donor–Acceptor Complex. *Chem. Eur. J.* **2018**, *24* (65), 17210-17214. DOI: https://doi.org/10.1002/chem.201804246.
3. Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P. Harnessing Alkyl Amines as Electrophiles for Nickel-Catalyzed Cross Couplings via C-N Bond Activation. *J. Am. Chem. Soc.* **2017**, *139* (15), 5313-5316. DOI: 10.1021/jacs.7b02389.