

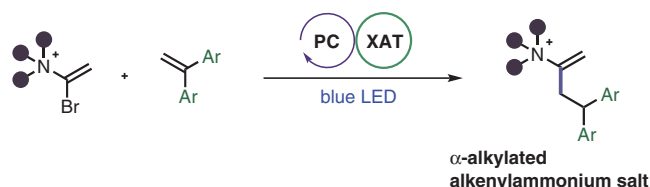
Photoredox-Enabled Synthesis of α -Alkylated Alkenylammonium Salts

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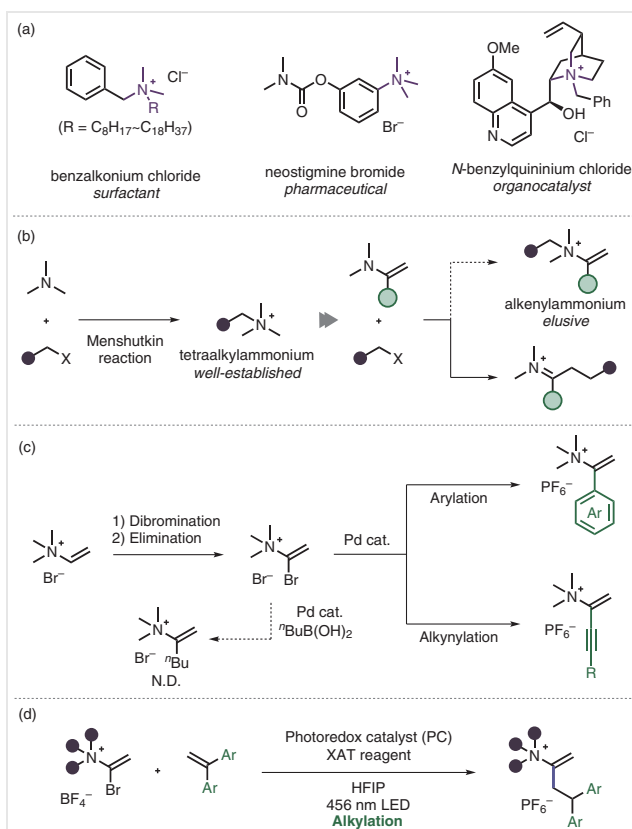
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Abstract The development of novel synthetic methods for quaternary ammonium salts is highly demanded since the current synthesis heavily relies on the conventional Menshutkin reaction. Herein, we report photoredox-catalyzed alkylation of α -brominated alkenylammonium salts. Mechanistically, the generation of a highly reactive α -ammoniovinyl radical is the key to our method. This reaction enables the synthesis of various unprecedented α -alkylated alkenylammonium salts.

Key words alkenylammonium salts, photoredox catalyst, alkylation, halogen-atom transfer, quaternary ammonium salts

Quaternary ammonium salts are important chemical compounds, which are widely used as surfactants, pharmaceuticals, and organocatalysts (Scheme 1a).¹ In most cases, these compounds are synthesized through the Menshutkin reaction: quaternarization of tertiary amines.² Although this reaction is a practical method for the synthesis of tetraalkylammonium salts, it is difficult to synthesize alkenylammonium salts. This is because the alkylation of the corresponding tertiary enamines is known to proceed on the carbon atom, not on the nitrogen atom (Scheme 1b).³ While the synthesis of trimethylvinylammonium salt, the simplest alkenylammonium salt, was attained by Kleine in 1904,⁴ a versatile synthetic method for α -substituted alkenylammonium salts has not been developed. Because of the lack of reliable synthetic methods, the chemistry of alkenylammonium salts is behind compared to that of alkenylammonium salts. Recently, we developed Suzuki–Miyaura or Sonogashira coupling of α -brominated alkenylammonium salts, which leads to structurally new α -arylated or α -alkynylated alkenylammonium salts (Scheme 1c).⁵ However, the synthesis of α -alkylated alkenylammonium salts proved to be difficult under these Pd-catalyzed conditions.

Herein, we report the photoredox-catalyzed⁶ synthesis of α -alkylated alkenylammonium salts from α -brominated alkenylammonium salts and 1,1-diarylethylenes (Scheme 1d). The halogen-atom transfer (XAT)⁷ mediated generation



Scheme 1 (a) Examples of functional quaternary ammonium salts. (b) Synthesis of quaternary ammonium salts using the Menshutkin reaction. (c) Previous work. (d) This work.

of highly reactive α -ammoniovinyl radical enables this process.

The reaction conditions for the synthesis of α -alkylated alkenylammonium salts were initially screened with α -brominated alkenylammonium salt **1a** and 1,1-diphenylethylene (**2a**) (Table 1). The use of (TMS)₃SiNHAd, which is reported by MacMillan and co-workers as a broadly useful XAT reagent,⁸ with 4CzIPN (PC1) in MeOH under 456 nm LED irradiation gave α -alkylated alkenylammonium salt **3a** in 54% yield along with 32% of reduced byproduct **4** (entry 1). Byproduct **4** would be generated through hydrogen atom transfer⁹ between α -ammoniovinyl radical and MeOH or (TMS)₃SiNHAd. A survey of photoredox catalysts revealed that [Ru(phen)₃]Cl₂ (PC2) and Ir(ppy)₃ (PC3) were not effective, and the conversion of **2a** decreased (entries 2 and 3). In this transformation, dramatic solvent effects were observed. With aprotic polar solvents, such as MeCN, acetone, and THF, the yield and selectivity of **3a** were not satisfactory (entries 4–6), though the exact reason for this is unclear. In addition, ^tBuOH was also not an appropriate solvent; on the other hand, the generation of byproduct **4** was almost suppressed by using HFIP as a solvent (entries 7 and 8). By increasing the amount of (TMS)₃SiNHAd and prolonging the reaction time, the yield of **3a** improved to 45% still suppressing the generation of **4** (entries 9 and 10). Another XAT reagent, (TMS)₃SiNH(^tBu), afforded product **3a** in 92% yield while triisobutylamine, which has been used for the generation of C(sp²) radical,¹⁰ failed to provide **3a** (entries 11 and 12). Finally, the conditions using 6.0 mol% of PC1 gave the best result where 93% of **3a** was obtained with good reproducibility (entry 13). Furthermore, the use of 5.0 equivalents of **2a** proved essential for achieving a high yield (entry 13 vs entries 14 and 15).

A proposed mechanism for this alkylation reaction of α -brominated alkenylammonium salts is described in Scheme 2a. Upon irradiation with blue light, the photoredox catalyst is converted into the long-lived triplet excited state PC*.^{6f} Since the excited-state photocatalyst has high oxidation ability, single-electron oxidation of (TMS)₃SiNH(^tBu) proceeds smoothly, and subsequent deprotonation gives N-centered radical **A**. Then, the electron-rich α -amino silicon-centered radical **B** is generated through the radical aza-Brook rearrangement of radical **A**.⁸ As radical **B** possesses strong halogen abstraction ability, bromine atom transfer from **1a** to radical **B** furnishes the highly reactive α -ammoniovinyl radical **D**, and the reaction of radical **D** with **2a** gives radical intermediate **E**. The resulting radical **E** is reduced to anion intermediate **F** by PC^{•-},^{6g} and protonation of **F** gives alkylated product **3a**. In the radical addition step (the reaction of radical **D** with **2a**), when MeOH is used as a solvent, the highly reactive α -ammoniovinyl radical **D** would abstract hydrogen atom from an α -C–H bond of MeOH, which competes with radical addition to **2a**. In contrast, the α -C–H bond of HFIP is less reactive for hydrogen atom abstraction than that of MeOH because of the polar

Table 1 Investigation of the reaction conditions

Entry	Photocatalyst	XAT reagent	Solvent	Yield (%) of 3a ^a	Yield (%) of 4 ^a
1	PC1	(TMS) ₃ SiNHAd	MeOH	54	32
2	PC2	(TMS) ₃ SiNHAd	MeOH	12	15
3	PC3	(TMS) ₃ SiNHAd	MeOH	9	25
4	PC1	(TMS) ₃ SiNHAd	MeCN	12	40
5	PC1	(TMS) ₃ SiNHAd	acetone	35	29
6	PC1	(TMS) ₃ SiNHAd	THF	45	48
7	PC1	(TMS) ₃ SiNHAd	^t BuOH	43	13
8	PC1	(TMS) ₃ SiNHAd	HFIP	13	3
9 ^{b,c,d}	PC1	(TMS) ₃ SiNHAd	HFIP	40	0
10 ^{b,c,e}	PC1	(TMS) ₃ SiNHAd	HFIP	45	0
11 ^{b,c,e}	PC1	(TMS) ₃ SiNH(^t Bu)	HFIP	92	0
12 ^{b,c,e}	PC1	^t Bu ₃ N	HFIP	0	0
13^{b,c,e,f}	PC1	(TMS)₃SiNH(^tBu)	HFIP	93	0
14 ^{b,c,e,f,g}	PC1	(TMS) ₃ SiNH(^t Bu)	HFIP	24	8
15 ^{b,c,e,f,h}	PC1	(TMS) ₃ SiNH(^t Bu)	HFIP	44	7

^a ¹H NMR yield using C₂H₂Cl₄ as the internal standard.

^b Reaction time of 16 h.

^c Using 1.5 mL of HFIP.

^d Using 2.0 equivalents of XAT reagent.

^e Using 2.5 equivalents of XAT reagent.

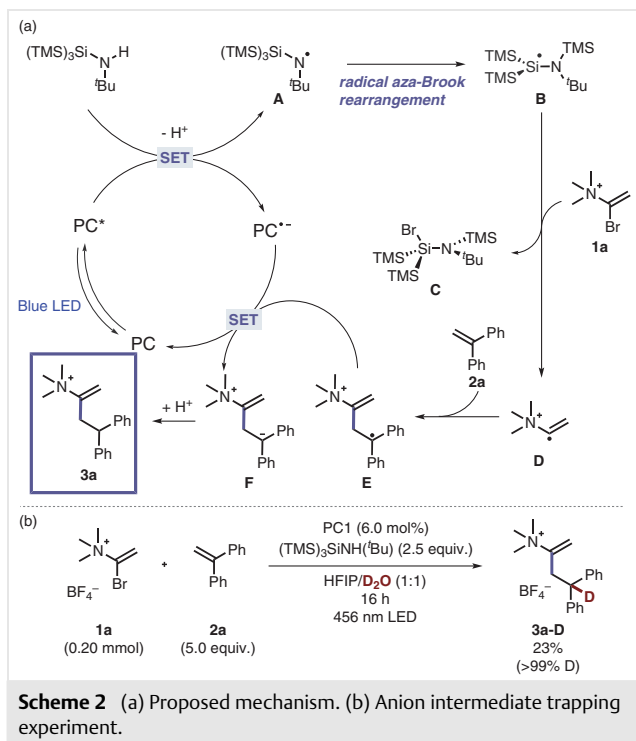
^f Using 6.0 mol% of PC1.

^g Using 1.0 equivalents of **2a**.

^h Using 3.0 equivalents of **2a**.

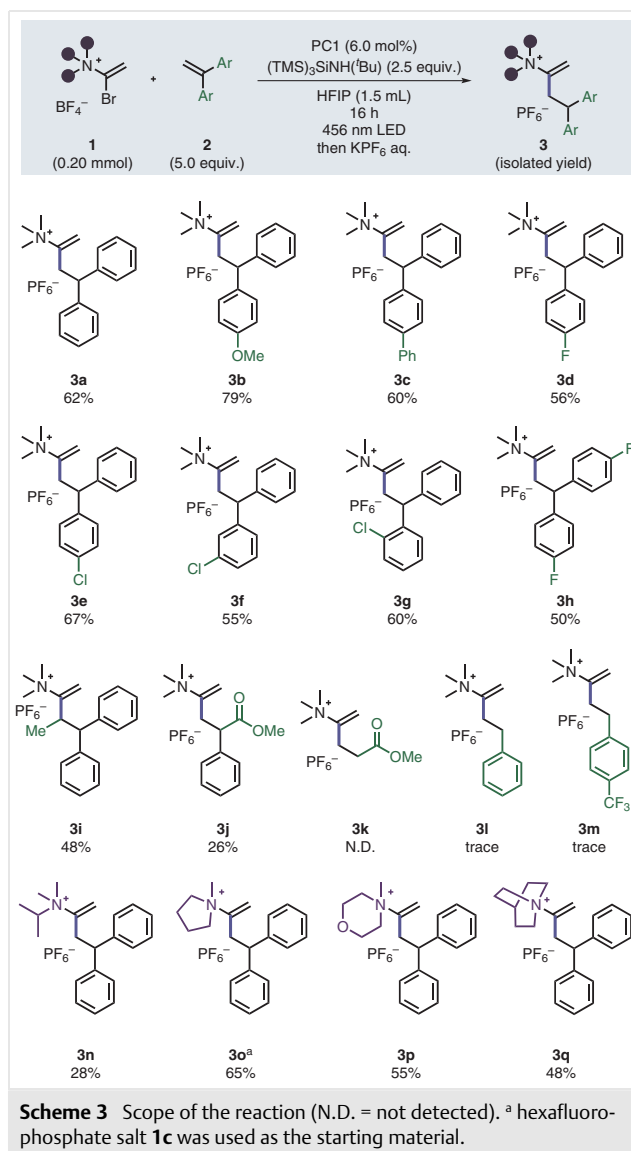
and electrostatic influence of fluorine substituents.¹¹ The undesired reduction pathway, therefore, is suppressed by using HFIP as the solvent. To confirm the generation of anion intermediate **F**, this reaction was performed in HFIP/D₂O (Scheme 2b). As a result, deuterated product **3a-D**

was obtained in 23% (^1H NMR yield), along with 40% recovery of **1a**. The result indicates that PC^- reduces radical **E** to anion intermediate **F**, which is then quenched with D_2O .



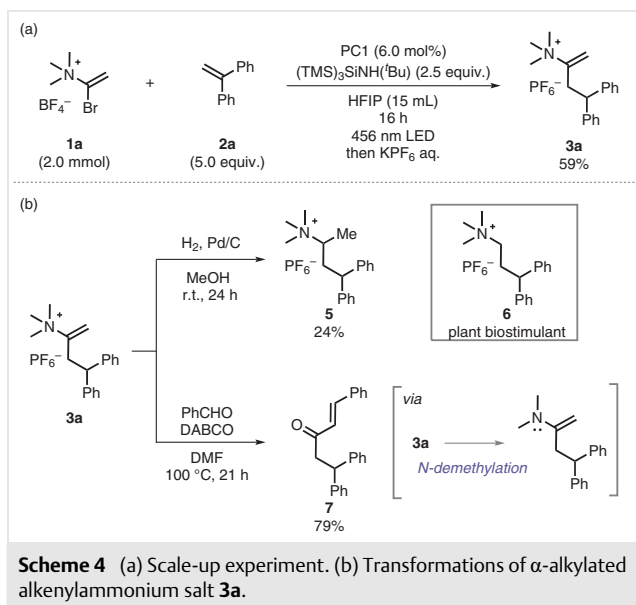
With the optimal reaction conditions in hand, we investigated the substrate scope of the synthesis of α -alkylated alkenylammonium salts (Scheme 3). For ease of isolation, the product α -alkylated alkenylammonium salts were collected as the PF_6^- salts. In addition to 1,1-diphenylethylene (**2a**), 1,1-diarylethylenes having various substituents, such as a methoxy, phenyl, fluoro, or chloro group, at the *para* position were applicable for this transformation, and the corresponding products **3b–3e** were obtained in moderate to good yields (56–79%). Both *meta*- and *ortho*-chlorinated olefins (**2f** and **2g**) were smoothly converted into α -alkylated alkenylammonium salts (**3f** and **3g**). Not only unsymmetrical olefins, but also a symmetrical olefin provided the alkylated product **3h** in 50% yield. Notably, trisubstituted olefin and methyl atropate were compatible with our procedure (**3i** and **3j**), while methyl acrylate and styrene derivatives did not give the corresponding products (**3k–3m**). Next, we explored alternative α -brominated alkenylammonium salts in conjunction with 1,1-diphenylethylene (**2a**) as a model olefin. The reaction of the bulkier isopropyl-dimethylammonium salt gave **3n** in 28% yield. Heterocyclic ammonium salts were also tolerated by this reaction, and **3o–3q** were obtained in 48–65% yield.

Considering that there had been no prior examples for the preparation of α -alkylated alkenylammonium salts, we then demonstrated synthetic applications using **3a**. First, a



scale-up synthesis was accomplished, where 59% of **3a** was obtained on a 2.0-mmol scale (Scheme 4a). Then, derivatizations of obtained **3a** were conducted (Scheme 4b). Hydrogenation of **3a** using Pd/C gave **5** in 24% yield, which is a methylated analogue of plant biostimulant **6** discovered by our group.^{12,13} Moreover, selective *N*-demethylation of **3a** occurred in the presence of DABCO, and the corresponding enamine reacted with benzaldehyde to give the condensation product **7** in 79% yield. This result highlights the utility of α -alkylated alkenylammonium salts as a new stable precursor of enamines.

In summary, we have developed a new synthetic method for α -alkylated alkenylammonium salts. Our photocatalytic conditions enable access to various α -alkylated alkenylammonium salts from α -brominated alkenylammonium salts and 1,1-diarylethylenes under mild conditions. Addi-



tionally, the scale-up synthesis and derivatizations of product **3a** further enhance the synthetic potential of our method. Further investigation of the physical properties and bioactivity of the obtained products is ongoing in our lab.

General experimental details are given in the Supporting Information.

α -Alkylated Alkenylammonium Salt **3a**; Typical Procedure

A dried reaction tube with a stirring bar was charged with 1-bromo-*N,N,N*-trimethylethenammonium tetrafluoroborate (**1a**, 50 mg, 0.20 mmol, 1.0 equiv.), 4*Cz*IPN (9.6 mg, 0.012 mmol, 6.0 mol%), and (TMS)₃SiNHAd(^tBu) (160 mg, 0.50 mmol, 2.5 equiv.). The tube was filled with nitrogen by employing the usual Schlenk technique (evacuate–refill cycle). HFIP (1.5 mL) and 1,1-diphenylethylene (**2a**, 180 mg, 1.0 mmol, 5.0 equiv.) were added to the tube and the mixture was stirred under blue light irradiation with a cooling fan (a 40 W Kessil PR160 blue LED was placed 1 cm below the reaction vial) for 16 h. The crude mixture was concentrated in vacuo and purified by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH = 80:20) to provide the product. To exchange the counter anion, the obtained product was dissolved in CH₂Cl₂ and washed with saturated aqueous KPF₆ solution three times. The organic layer was dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was recrystallized (CH₂Cl₂/Et₂O) to give **3a** (52.1 mg) as a white solid, which contained 0.25 mg of acetone, 0.28 mg of MeOH, and 0.94 mg of CH₂Cl₂. The yield of **3a** was calculated as 62%. Note: the ratio of **3a**, acetone, MeOH, and CH₂Cl₂ was determined by ¹H NMR since acetone, MeOH, and CH₂Cl₂ were not completely removed after drying in vacuo for 24 h.

Mp 190 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.16–3.18 (m, 11 H), 4.36 (t, *J* = 8.0 Hz, 1 H), 5.26 (brs, 1 H), 5.59 (d, *J* = 5.5 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 2 H), 7.33 (t, *J* = 7.5 Hz, 4 H), 7.37 (d, *J* = 7.5 Hz, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.8, 49.6, 54.9, 111.8, 127.7, 128.6, 129.7, 144.1, 152.1.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 705 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₄N: 266.1909 [M]⁺; found: 266.1919.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9644.

3b

Synthesized according to the typical procedure from **1a** (51 mg, 0.20 mmol) using 1-(4-methoxyphenyl)-1-phenylethene (**2b**, 220 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (160 mg, 0.50 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3b** (69.9 mg) as a pale yellow solid, which contained 0.27 mg of Et₂O. The yield of **3b** was calculated as 79%. Note: the ratio of **3b** and Et₂O was determined by ¹H NMR since Et₂O was not completely removed after drying in vacuo for 24 h.

Mp 119 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.13 (d, *J* = 8.0 Hz, 2 H), 3.16 (s, 9 H), 3.74 (s, 3 H), 4.30 (t, *J* = 8.0 Hz, 1 H), 5.25 (brs, 1 H), 5.59 (d, *J* = 4.0 Hz, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 7.22 (t, *J* = 7.0 Hz, 1 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 7.31–7.36 (m, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 34.0, 48.9, 54.9, 55.8, 111.7, 114.9, 127.6, 128.5, 129.6, 129.7, 136.0, 144.5, 152.2, 159.4.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 707 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₀H₂₆NO: 296.2014 [M]⁺; found: 296.2014.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9636.

3c

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using 4-(1-phenylethenyl)-1,1'-biphenyl (**2c**, 260 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (180 mg, 0.55 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 95:5 to 90:10) and recrystallization (CH₂Cl₂/Et₂O) afforded **3c** (62.8 mg) as a yellow solid, which contained 1.6 mg of Et₂O, 1.1 mg of acetone, and 0.33 mg of MeOH. The yield of **3c** was calculated as 60%. Note: the ratio of **3c**, Et₂O, acetone, and MeOH was determined by ¹H NMR since Et₂O, acetone, and MeOH were not completely removed after drying in vacuo for 24 h.

Mp 134 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.19 (s, 9 H), 3.22 (d, *J* = 7.5 Hz, 2 H), 4.41 (t, *J* = 7.5 Hz, 1 H), 5.30 (brs, 1 H), 5.62 (d, *J* = 4.5 Hz, 1 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.34–7.37 (m, 3 H), 7.40–7.47 (m, 6 H), 7.61 (d, *J* = 8.0 Hz, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.8, 49.3, 55.0, 111.8, 127.7, 127.8, 128.2, 128.4, 128.6, 129.1, 129.79, 129.83, 140.3, 141.1, 143.4, 144.0, 152.1.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 707 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₅H₂₈N: 342.2222 [M]⁺; found: 342.2205.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9637.

3d

Synthesized according to the typical procedure from **1a** (51 mg, 0.20 mmol) using 1-(4-fluorophenyl)-1-phenylethene (**2d**, 210 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (190 mg, 0.58 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3d** (48.8 mg) as a pale yellow solid, which contained 0.24 mg of acetone and 0.85 mg of CH₂Cl₂. The yield of **3d** was calculated as 56%. Note: the ratio of **3d**, acetone, and CH₂Cl₂ was determined by ¹H NMR since acetone and CH₂Cl₂ were not completely removed after drying in vacuo for 24 h.

Mp 152 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.13–3.18 (m, 11 H), 4.37 (t, *J* = 8.0 Hz, 1 H), 5.25 (brs, 1 H), 5.60 (d, *J* = 5.0 Hz, 1 H), 7.07 (t, *J* = 8.5 Hz, 2 H), 7.23 (t, *J* = 6.5 Hz, 1 H), 7.32–7.39 (m, 6 H).

¹³C NMR (126 MHz, CD₃CN): δ = 34.1, 48.9, 55.0, 112.0, 116.3 (d, *J* = 21.6 Hz), 127.9, 128.6, 129.8, 130.4 (d, *J* = 8.4 Hz), 140.2 (d, *J* = 3.6 Hz), 143.9, 152.0, 162.5 (d, *J* = 244 Hz).

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 707 Hz, 6 F), –116.2 (m, 1 F).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₃FN: 284.1815 [M]⁺; found: 284.1825.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9648.

3e

Synthesized according to the typical procedure from **1a** (51 mg, 0.20 mmol) using 1-(4-chlorophenyl)-1-phenylethene (**2e**, 220 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (210 mg, 0.67 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3e** (66.0 mg) as a yellow solid, which contained 3.7 mg of Et₂O and 2.8 mg of CH₂Cl₂. The yield of **3e** was calculated as 67%. Note: the ratio of **3e**, Et₂O, and CH₂Cl₂ was determined by ¹H NMR since Et₂O and CH₂Cl₂ were not completely removed after drying in vacuo for 24 h.

Mp 129.4–134.2 °C.

¹H NMR (500 MHz, CD₃CN): δ = 3.14–3.16 (m, 11 H), 4.36 (t, *J* = 8.0 Hz, 1 H), 5.24 (brs, 1 H), 5.60 (d, *J* = 4.5 Hz, 1 H), 7.22–7.26 (m, 1 H), 7.32–7.37 (m, 8 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.8, 49.0, 55.0, 112.0, 128.0, 128.6, 129.7, 129.8, 130.3, 133.0, 143.0, 143.6, 151.9.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 705 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₃ClN: 300.1519 [M]⁺; found: 300.1504.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9644.

3f

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using 1-(3-chlorophenyl)-1-phenylethene (**2f**, 220 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (160 mg, 0.52 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 90:10) and recrystallization (CH₂Cl₂/*n*-hexane) afforded **3f** (49.0 mg, 0.110 mmol, 55%) as a pale yellow solid.

Mp 144 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.15–3.17 (m, 11 H), 4.37 (t, *J* = 8.0 Hz, 1 H), 5.24 (brs, 1 H), 5.60 (d, *J* = 5.0 Hz, 1 H), 7.23–7.26 (m, 2 H), 7.31–7.38 (m, 6 H), 7.43 (s, 1 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.5, 49.2, 54.9, 111.9, 127.2, 127.8, 128.0, 128.5, 128.6, 129.8, 131.3, 134.9, 143.2, 146.5, 151.8.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 707 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₃ClN: 300.1519 [M]⁺; found: 300.1516.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9639.

3g

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using 1-(2-chlorophenyl)-1-phenylethene (**2g**, 220 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (210 mg, 0.67 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3g** (54.5 mg, 0.122 mmol, 60%) as a pale yellow solid.

Mp 134 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.15–3.18 (m, 11 H), 4.84 (t, *J* = 8.0 Hz, 1 H), 5.19 (brs, 1 H), 5.60 (d, *J* = 5.5 Hz, 1 H), 7.26 (t, *J* = 7.5 Hz, 2 H), 7.33–7.38 (m, 5 H), 7.43 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.50 (dd, *J* = 7.5, 1.5 Hz, 1 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.8, 45.5, 55.0, 111.8, 128.0, 128.6, 129.1, 129.3, 129.4, 129.7, 130.8, 134.4, 140.8, 142.3, 151.8.

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 704 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₃ClN: 300.1519 [M]⁺; found: 300.1519.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9643.

3h

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using 1,1-bis(4-fluorophenyl)ethene (**2h**, 220 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (180 mg, 0.55 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 95:5 to 86:14) and recrystallization (CH₂Cl₂/Et₂O) afforded **3h** (46.0 mg) as a white solid, which contained 0.32 mg of Et₂O, 0.51 mg of acetone, and 0.35 mg of CH₂Cl₂. The yield of **3h** was calculated as 50%. Note: the ratio of **3h**, Et₂O, acetone, and CH₂Cl₂ was determined by ¹H NMR since Et₂O, acetone, and CH₂Cl₂ were not completely removed after drying in vacuo for 24 h.

Mp 150 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.11 (d, *J* = 7.5 Hz, 2 H), 3.15 (s, 9 H), 4.38 (t, *J* = 8.0 Hz, 1 H), 5.24 (brs, 1 H), 5.61 (d, *J* = 4.5 Hz, 1 H), 7.06–7.11 (m, 4 H), 7.35–7.38 (m, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 34.2, 48.0, 54.9, 112.0, 116.3 (d, *J* = 21.6 Hz), 130.4 (d, *J* = 8.4 Hz), 139.9 (d, *J* = 3.6 Hz), 151.7, 162.5 (d, *J* = 244 Hz).

¹⁹F NMR (471 MHz, CD₃CN): δ = –71.4 (d, *J* = 705 Hz, 6 F), –116.1 (m, 2 F).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₉H₂₂F₂N: 302.1720 [M]⁺; found: 302.1721.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆[–]: 144.9642 [M][–]; found: 144.9637.

3i

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using 1,1-diphenylpropene (**2i**, 190 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (170 mg, 0.54 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3i** (41.5 mg) as a pale yellow solid, which contained 0.75 mg of Et₂O. The yield of **3i** was calculated as 48%. Note: the ratio of **3i** and Et₂O was determined by ¹H NMR since Et₂O was not completely removed after drying in vacuo for 24 h.

Mp 134 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 1.21 (d, *J* = 7.0 Hz, 3 H), 2.90 (s, 9 H), 3.36–3.40 (m, 1 H), 4.10 (d, *J* = 11.5 Hz, 1 H), 5.76–5.79 (m, 2 H), 7.16 (t, *J* = 7.5 Hz, 1 H), 7.22–7.31 (m, 5 H), 7.39 (t, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H).

¹³C NMR (126 MHz, CD₃CN): δ = 24.3, 38.7, 54.6, 59.6, 111.9, 127.77, 127.82, 129.3, 129.4, 129.7, 130.0, 143.0, 143.4, 158.0.

¹⁹F NMR (471 MHz, CD₃CN): δ = -71.4 (d, *J* = 705 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₀H₂₆N: 280.2065 [*M*]⁺; found: 280.2068.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆⁻: 144.9642 [*M*]⁻; found: 144.9639.

3j

Synthesized according to the typical procedure from **1a** (50 mg, 0.20 mmol) using methyl atropate (**2j**, 98 mg, 0.60 mmol, 3.0 equiv.) and (TMS)₃SiNH(^tBu) (170 mg, 0.54 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 25:75) and recrystallization (MeOH/Et₂O) afforded **3j** (20.8 mg, 0.0529 mmol, 26%) as a white solid.

Mp 169.1–169.9 °C.

¹H NMR (500 MHz, CD₃CN): δ = 2.76 (dd, *J* = 17.5, 6.0 Hz, 1 H), 3.15 (dd, *J* = 17.5, 9.5 Hz, 1 H), 3.21 (s, 9 H), 3.63 (s, 3 H), 4.06 (dd, *J* = 9.5, 6.0 Hz, 1 H), 5.33 (brs, 1 H), 5.64 (d, *J* = 5.0 Hz, 1 H), 7.33–7.41 (m, 5 H).

¹³C NMR (126 MHz, CD₃CN): δ = 32.3, 50.0, 53.0, 54.9, 110.7, 128.8, 129.0, 129.9, 138.2, 151.7, 173.5.

¹⁹F NMR (471 MHz, CD₃CN): δ = -71.4 (d, *J* = 707 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₁₅H₂₂NO₂: 248.1651 [*M*]⁺; found: 248.1652.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆⁻: 144.9642 [*M*]⁻; found: 144.9636.

3n

Synthesized according to the typical procedure from 1-bromo-*N*-(2-propyl)-*N,N*-dimethylethanammonium tetrafluoroborate (**1b**, 56 mg, 0.20 mmol) using 1,1-diphenylethylene (**2a**, 180 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (170 mg, 0.52 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 95:5) and recrystallization (CH₂Cl₂/Et₂O) afforded **3n** (24.8 mg, 0.0566 mmol, 28%) as a white solid.

Mp 137 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 1.17 (d, *J* = 6.5 Hz, 6 H), 2.99 (s, 6 H), 3.13 (d, *J* = 7.5 Hz, 2 H), 3.95–4.00 (m, 1 H), 4.39 (t, *J* = 7.5 Hz, 1 H), 5.44 (brs, 1 H), 5.55 (d, *J* = 5.0 Hz, 1 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 7.33 (t, *J* = 7.5 Hz, 4 H), 7.39 (d, *J* = 7.5 Hz, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 16.3, 34.0, 48.1, 49.6, 65.7, 113.4, 127.8, 128.5, 129.7, 144.2, 150.9.

¹⁹F NMR (471 MHz, CD₃CN): δ = -71.4 (d, *J* = 705 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₁H₂₈N: 294.2222 [*M*]⁺; found: 294.2231.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆⁻: 144.9642 [*M*]⁻; found: 144.9639.

3o

Synthesized according to the typical procedure from *N*-(1-bromoethenyl)-*N*-methylpyrrolidinium hexafluorophosphate (**1c**, 68 mg, 0.20 mmol) using 1,1-diphenylethylene (**2a**, 180 mg, 0.98 mmol) and (TMS)₃SiNH(^tBu) (160 mg, 0.51 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3o** (56.9 mg, 0.130 mmol, 65%) as a pale yellow solid.

Mp 148 °C (dec).

¹H NMR (500 MHz, CD₂Cl₂): δ = 2.21–2.28 (m, 4 H), 3.08 (s, 3 H), 3.16 (d, *J* = 7.5 Hz, 2 H), 3.53–3.58 (m, 2 H), 3.68–3.72 (m, 2 H), 4.27 (t, *J* = 7.5 Hz, 1 H), 5.35 (brs, 1 H), 5.55 (d, *J* = 5.0 Hz, 1 H), 7.24 (t, *J* = 7.0 Hz, 2 H), 7.30–7.36 (m, 8 H).

¹³C NMR (126 MHz, CD₂Cl₂): δ = 20.9, 35.4, 49.8, 50.9, 64.5, 112.7, 127.6, 127.9, 129.4, 142.6, 150.6.

¹⁹F NMR (471 MHz, CD₂Cl₂): δ = -73.0 (d, *J* = 711 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₁H₂₆N: 292.2065 [*M*]⁺; found: 292.2074.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆⁻: 144.9642 [*M*]⁻; found: 144.9642.

3p

Synthesized according to the typical procedure from *N*-(1-bromoethenyl)-*N*-methylmorpholinium tetrafluoroborate (**1d**, 59 mg, 0.20 mmol) using 1,1-diphenylethylene (**2a**, 180 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (160 mg, 0.51 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3p** (49.8 mg, 0.110 mmol, 55%) as a pale yellow solid.

Mp 160 °C (dec).

¹H NMR (500 MHz, CD₃CN): δ = 3.10 (d, *J* = 7.5 Hz, 2 H), 3.12 (s, 3 H), 3.48–3.53 (m, 2 H), 3.71–3.76 (m, 2 H), 3.79–3.82 (m, 2 H), 3.89–3.92 (m, 2 H), 4.40 (t, *J* = 7.5 Hz, 1 H), 5.51 (brs, 1 H), 5.60 (d, *J* = 5.0 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 2 H), 7.33 (t, *J* = 7.5 Hz, 4 H), 7.39 (d, *J* = 7.5 Hz, 4 H).

¹³C NMR (126 MHz, CD₃CN): δ = 33.8, 49.4, 53.4, 60.7, 62.1, 114.8, 127.8, 128.5, 129.8, 144.0, 148.8.

¹⁹F NMR (471 MHz, CD₃CN): δ = -71.4 (d, *J* = 705 Hz).

HRMS (ESI-MS, positive): *m/z* calcd for C₂₁H₂₆NO: 308.2014 [*M*]⁺; found: 308.2007.

HRMS (ESI-MS, negative): *m/z* calcd for PF₆⁻: 144.9642 [*M*]⁻; found: 144.9640.

3q

Synthesized according to the typical procedure from *N*-(1-bromoethenyl)quinuclidium tetrafluoroborate (**1e**, 60 mg, 0.20 mmol) using 1,1-diphenylethylene (**2a**, 180 mg, 1.0 mmol) and (TMS)₃SiNH(^tBu) (160 mg, 0.51 mmol). Purification by flash column chromatography on NaBr-treated silica gel (CH₂Cl₂/MeOH, 80:20) and recrystallization (CH₂Cl₂/Et₂O) afforded **3q** (44.2 mg, 0.0954 mmol, 48%) as a white solid.

Mp 194 °C (dec).

^1H NMR (500 MHz, CD_3OD): δ = 2.02–2.05 (m, 6 H), 2.19–2.20 (m, 1 H), 3.25 (d, J = 8.0 Hz, 2 H), 3.62 (t, J = 8.0 Hz, 6 H), 4.37 (t, J = 7.5 Hz, 1 H), 5.34 (brs, 1 H), 5.65 (d, J = 4.5 Hz, 1 H), 7.20 (t, J = 7.5 Hz, 2 H), 7.30 (t, J = 7.5 Hz, 4 H), 7.38 (d, J = 7.5 Hz, 4 H).

^{13}C NMR (126 MHz, CD_3OD): δ = 20.6, 25.1, 35.4, 50.7, 56.5, 113.3, 127.9, 129.0, 129.8, 144.5, 152.7.

^{19}F NMR (471 MHz, CD_3OD): δ = -72.5 (d, J = 708 Hz).

HRMS (ESI-MS, positive): m/z calcd for $\text{C}_{23}\text{H}_{28}\text{N}$: 318.2222 [M]⁺; found: 318.2236.

HRMS (ESI-MS, negative): m/z calcd for PF_6^- : 144.9642 [M]⁻; found: 144.9639.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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