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Visible-Light-Mediated Amination of π-Nucleophiles with *N*-aminopyridinium Salts

Katarzyna Goliszewska,[a] Katarzyna Rybicka-Jasińska,[a] Jakub Szurmak[a,b] and Dorota Gryko[*a]*

[a]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[b]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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ABSTRACT

N-aminopyridinium salts generate nitrogen-centered radicals by means of photoredox catalysis. Herein, we report that they can be trapped by enol equivalents to give α-amino carbonyl compounds in excellent yields. The broad synthetic utility of this method is demonstrated by functionalization of ketones, aldehydes, esters enol equivalents, vinyl ethers and 1,3-diketones without the need for prior conversion to enol derivatives. The developed method is easily scalable, offers broad substrate scope, high chemoselectivity, and mild conditions.

INTRODUCTION

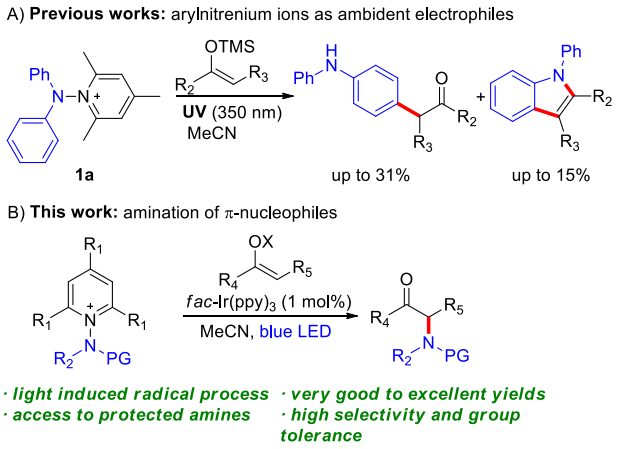
Nitrogen containing compounds not only play a crucial role in living organisms (e.g. proteins, nucleic acids, amino acids), medicine and materials science but are also extensively utilized as synthetic intermediates and coordinating ligands in organic synthesis.[1,2] Of the functional groups containing nitrogen atoms, the amine group is one of the most ubiquitous and thus selective and efficient methods leading to the formation of C-N bonds are highly desirable.

In addition to the well-established nucleophilic and electrophilic[3] direct amination reactions, recently methods utilizing nitrogen-centered radicals have attracted considerable attention.[4] Up to date developments in photoredox catalysis[5] indicate that nitrogen radicals can be generated under mild reaction conditions from stable starting materials including phtalimides,[6-7] sulfonamides,[8-10] hydrazones,[11–13] aryloxyamides[14–16] or amides.[17] Recently, Studer and coworkers added *N*-aminopyridinium salts to this list.[18] Due to the simplicity of their large-scale synthesis from commercially available pyrylium salts and hydrazine derivatives or from *N*-aminopyridinium iodide and acid chlorides, shelf life stability, and a variety of compatible protecting groups of the amine functionality they became attractive starting materials. Photochemically generated amidyl radicals easily react with electron-rich arenes, heteroarenes,[18] and styrene derivatives[19-20] enabling, among others, the facile synthesis of vicinal aminoalcohols,[21] imidazolines or oxazolines.[22]

N-aminopyridinium salts are also a source of nitrenium ions and as such they react with various nucleophiles.[23-24] In this line, Falvey and coworkers reported that under UV irradiation *N*,*N*-(diphenylamino)-2,4,6-trimethylpyridinium salt (**1a**) reacts with π-nucleophiles to give the addition products from the reaction at *para*- and *ortho*- positions on one of the phenyl rings and *N*-phenyl indole (Scheme 1A).[25] Generally amination of an electron rich double bond is not

observed, and only for silyl ketene acetals traces of α-amino acid form. But, the addition of radicals to enols represents a convenient method for the synthesis of α-substituted ketones. This approach has been adopted for practical alkylations,[26] fluoroalkylations,[27] oxyamination,[28] and azidation.[27b] Given our long standing interest in photoredox catalysis we envisioned that electrophilic N-centered radicals generated from *N*-aminopyridinium salts should be trapped by nucleophilic enol derivatives leading to the formation of the C-N bond (Scheme 1B). Such reactivity would pose a novel approach towards amination of carbonyl compounds allowing convenient access to α-amino ketones, aldehydes, unnatural amino acids etc. – compounds of significance for synthetic chemists.[29]

Scheme 1. The Reactivity of *N*-Aminopyridinium Salts Towards Enol Derivatives

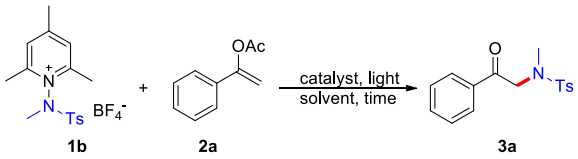


RESULTS AND DISCUSSION

To confirm our hypothesis, we initiated our studies by exploring the reactivity of *N*,*N*-(diphenylamino)pyridinium salt (**1a**) towards enol acetate **2a**. Under light irradiation the envisioned reaction catalyzed by *fac*-Ir(ppy)$_3$ did not furnish the desired product. As it is known that the diphenyl substituted iminyl radical is stabilized by the aromatic ring leading to spin-stable delocalized systems,[30] we turned our attention to less stable amidyl radicals. Replacing diphenyl

salt **1a** with *N*-Me,*N*-Ts-derivative **1b** enabled the formation of product **3a** in 51% yield (Table 1, entry 1). Background experiments proved that both the Ir-catalyst and light are essential to trigger the radical reaction (entries 2 and 3). Even though the reduction potential of salt **1b** (E_{red} = 0.7 V vs Ag/AgCl in MeCN) is accessible to other photocatalysts including $Ru(bpy)_3^{2+}$ and that the reported by Studer et al. amidation of arenes is catalyzed by the Ru-complex,[18] these were not effective in promoting our model reaction. Optimization studies indicated that MeCN may be exchanged with chlorinated solvents (DCM or $CHCl_3$) without diminishing the yield, while protic solvents are not compatible with the reaction due to plausible protonation of the amidyl radical.

Table 1. Optimization Studies[a]



Entry	Catalyst [mol%]	Light	Yield [%][b]
1	2	blue LED	67(51)[c,d]
2	none	blue LED	0
3	2	none	0
4	1	blue LED	66
5[e]	1	blue LED	93
6[e,h]	**1**	**blue LED**	**96 (95)**[c]
7[e,f]	1	blue LED	traces
8[e,g]	1	blue LED	73

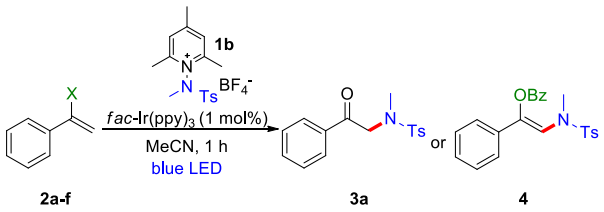
[a]Reaction conditions: enol **2a** (0.1 mmol), salt **1b** (1 equiv.), *fac*-$Ir(ppy)_3$, dry MeCN (c = 0.05 M), ambient temperature (20-22 °C), 16 h, under Ar atmosphere, light source: LED diode. [b]GC yield. [c]Isolated yield. [d]Not dry MeCN. [e]Salt **1b** (1.2 equiv.). [f]Air atmosphere. [g]With H_2O (4 equiv.). [h]1 h.

Notably, we were able to lower the catalyst loading to as low as 1 mol% with no significant changes in the reaction yield (entry 4). The highest increase in yield was observed when a small excess of salt **1b** (1.2 equiv.) was used (entry 5). In the model reaction enol **2a** was completely

consumed after just 1 h giving product **3a** in an excellent yield (95%, entry 6). The presence of oxygen, a quencher of the excited triplet state, suppresses the reaction almost completely (entry 7) while the addition of water causes only a slight drop in the reaction yield (entry 8).

Having the optimized reaction conditions, the scope and limitations of the developed amination were examined. Evaluation commenced by testing a selection of enol equivalents including esters **2a-c**, silyl ethers **2d** and **2e**, and acetamide **2f** (Table 2).

Table 2. Scope of Enol Derivatives[a]



Entry	X	Enol	Product	Yield%
1	OAc	**2a**	**3a**	95
2[b]	OBz	**2b**	**4**	45
3[b]	OTf	**2c**	**3a**	20
4	OTMS	**2d**	**3a**	83
5	OTBDMS	**2e**	**3a**	99
6[b]	NHAc	**2f**	**3a**	44[c]

[a]Reaction conditions (isolated yields): enol derivative **2** (0.25 mmol), salt **1b** (1.2 equiv.), *fac*-Ir(ppy)$_3$ (1 mol%), dry MeCN (c = 0.05 M), ambient temperature (20-22 °C), 1 h, under Ar atmosphere, light source: LED diode. [b]16 h. [c]Acidic work-up required.

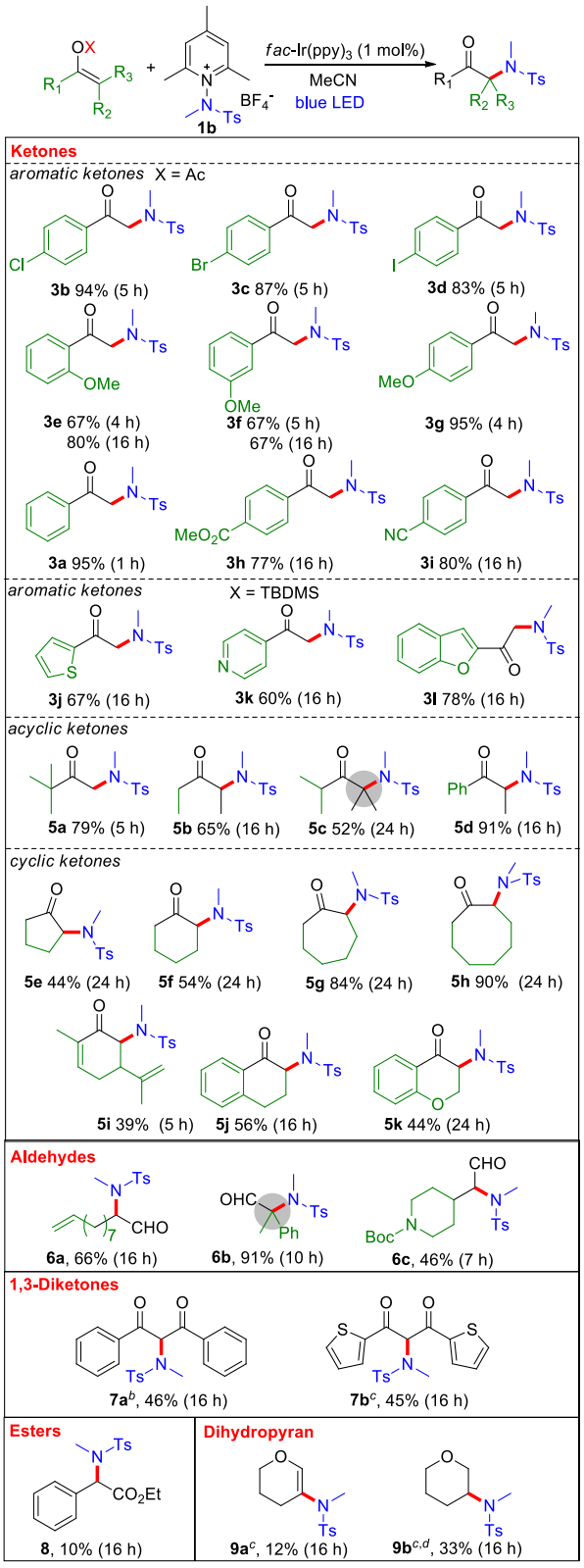
The reaction is tolerant of the most commonly used and easily accessible acyl and silyl derivatives giving the desired product **3a** in yields of up to 99%, with the highest being for TBDMS enol ether **2e** (entry 5). Notably, the use of the benzoyl group enables amination of enolate **2b** without simultaneous deprotection furnishing derivative **4** with a highly functionalized double bond with the enol reactivity retained (entry 2). Enolates **2b**, **2c** and enamide **2f** are less reactive

under the optimized reaction conditions which manifests in longer reaction times and lower yields (entries 2, 3, 6).

Following the evaluation of different enol equivalents we sought to establish the reactivity of enols derived from various carbonyl compounds. The synthesis of α-amino acetophenones (**3b-i**) tolerates a wide range of halogens (Br, Cl, I), electron-donating (OMe) and electron-withdrawing (CO_2Me, CN) groups at the phenyl ring (Scheme 2). Enols with lower electron density at the α atom need more time to reach full conversion but the corresponding α-amino ketones (**3g** and **3h**, 16 h) form with comparable yields. Importantly, the developed method may be applied to heterocyclic derivatives enabling chemoselective amination at the α-position to the carbonyl group (no amination of the ring was observed) (**3j-3l**). Enols derived from aliphatic ketones react equally well giving α-amino products **5a-5d** in good yields. It is important to note that even very challenging quaternary centers such as in **5c** can be effectively generated. For cyclic enols the yield gradually increases with the size of the ring. Having higher cyclic tension, 5- and 6-membered cyclic enol ethers gave α-aminated products **5e-f** in moderate yields while 7- and 8-membered substrates furnished α-amino ketones **5g-h** in excellent yields.

The developed method is not limited to the amination of ketones, enol equivalents derived from aldehydes or even 1,3-diketones without the need for enol derivatization are also suitable substrates providing they exist predominantly in the enol form. α-Amino aldehyde **6a** with a terminal double bond was synthesized through chemoselective functionalization at the α-position. Moreover, our preliminary results indicated that *N*-aminopyridinium salts might be applied in the synthesis of α-aminoesters **8** or selective functionalization of vinyl ethers (**9a-b**), though fine tuning of the reaction conditions is still required and will be reported in due course.

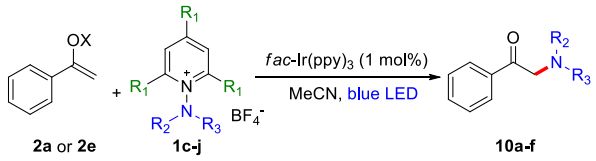
Scheme 2. Scope of Carbonyl Compounds[a]



[a]Reaction conditions (isolated yields): enol (0.25 mmol), salt **1b** (1.2 equiv.), *fac*-Ir(ppy)$_3$ (1 mol%), dry MeCN (c = 0.05 M), ambient temperature (20-22 °C), specified time, under Ar atmosphere, light source: LED diode. [b]Enolate with TMS protecting group. [c]Substrate used without prior enolate formation. [d]With CySH (2 equiv.).

The choice of protecting groups on the amine functionality is crucial as they profoundly influence the design of synthetic strategies towards complex molecules. To this end, we evaluated amino-pyridinium salts **1** with common protecting groups for the amine functionality (Table 3).

Table 3. Influence of the Salt Structure[a]



Entry	Salt			$E_{red}^{(0)}$	Time	Product	Yield
	R^1	**R^2, R^3**		[V][d,e]	[h]		[%]
1[b]	Me	Boc, Me	**1c**	-0.68	1	**10a**	89
2[b]	Me	Cbz, Me	**1d**	-1.14	1	**10b**	42
3[b]	Me	Pht	**1e**	-0.76	22	**-**	trace
4[b]	Ph	Boc, Me	**1f**	-1.17	1	**10a**	32
5[b]	H	Ts, H	**1g**	-0.77	1	**10c**	0
6[c]	H	Ts, H	**1g**	-0.77	16	**10c**	92
7[c]	H	Cbz, H	**1h**	-0.98	48	**10d**	48
8[c]	H	C_6F_5CO, H	**1i**	-0.86	16	**10e**	57
9[c]	H	CF_3CO, H	**1j**	-0.82	19	**10f**	72

[a]Reaction conditions (isolated yields): enol **2a** or **2e** (0.25 mmol), salt **1c-j** (1.2 equiv.), *fac*-Ir(ppy)$_3$ (1 mol%), dry MeCN (c = 0.05 M), ambient temperature (20-22 °C), under Ar atmosphere, light source: LED diode. [b]Enolate with TBDMS protecting group (**2e**). [c]Enolate with Ac protecting group (**2a**). [d]Cyclic voltammograms of *N*-aminopyridinium salts **1a-j** for MeCN in the presence of 100 mM N(n-Bu)$_4$ClO$_4$ recorded at a scan rate, ν = 100 mVs^{-1} (three-electrode cell equipped with a glassy carbon working electrode, a 25 mm platinum wire as the counter electrode and Ag/AgCl (3.0 M NaCl) electrode as the reference electrode). [e]V vs SCE.

Both mono- and diprotected *N*-aminopyridinium salts generate N-centered radicals, however, some differences in reactivity do exist. Among diprotected derivatives **1c-f** the most effective is salt **1c** with *N*-Me,*N*-Boc-amino functionality. The analogous Cbz-derivative **1d** affords product **10b** in 42% yield, while only traces of the desired product with *N*-phthalolyl-protection formed (entries 1-3). The character of the pyridinium salt has a strong impact on the reactivity; the replacement of methyl groups with phenyls on the pyridine moiety leads to a substantial decrease in the yield due to predominating hydrolysis of enol ether **2e** (entry 4). Monosubstituted salts **1g-j** tolerates only acyl enolates **2a** as in their presence silyl enol ether **2e** undergoes fast hydrolysis (compare entry 5 and 6).

For structurally similar mono-protected salts **1g-j**, a higher reduction potential results corresponds to a higher reaction yield (Figure 1). Such a strong correlation is not valid for diprotected *N*-aminopyridinium salts (Table 3) for which steric and electronic factors may also play a role,[30] though the trend is preserved.

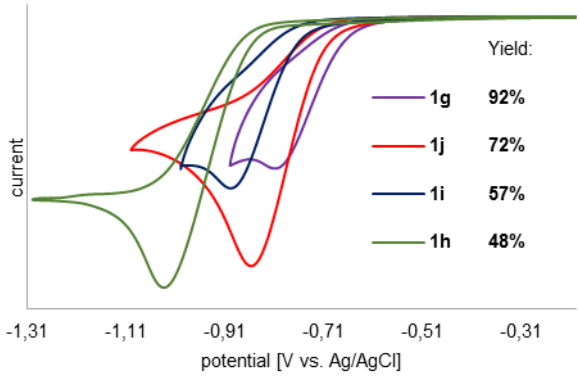
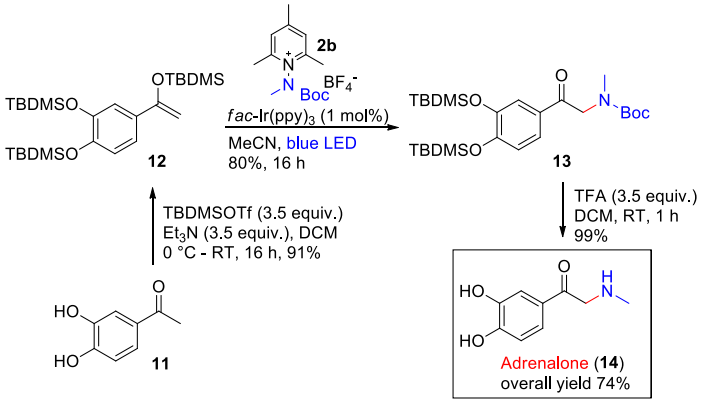


Figure 1. Comparison of reduction potentials for salts **1g-j**.

To show the practical utility of the developed amination of enol derivatives, we proved that the process is easily scalable by synthesizing product **3a** on a 1.0 mmol scale in 7 h 86% yield. We

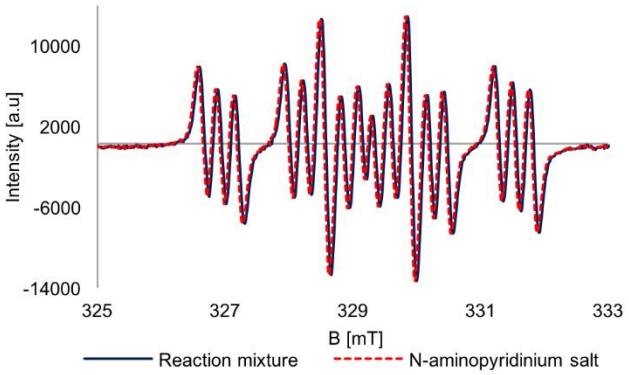
also employed our strategy for the synthesis of adrenalone (**14**), an adrenergic agonist used as a topical vasoconstrictor and hemostatic (Scheme 3). Starting from commercially available 3,4-dihydroxyacetophenone (**11**) in just two steps we were able to synthesize derivative **13** which may be quantitatively hydrolyzed to the desired adrenalone (**14**) (overall yield 74% from ketone **11**).

Scheme 3. The Synthesis of Adrenalone via Developed Amination Strategy

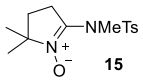


Based on previous work[18,21] we postulated that the reaction proceeds through a radical mechanism. To support this hypothesis the reaction of enol **2a** with *N*-aminopyridinium salt **1b** in the presence of TEMPO was performed, and, as expected the reaction was completely suppressed. The presence of a paramagnetic species was confirmed by EPR measurements performed for *N*-aminopyridinum salt **1b** and for the reaction mixture both after irradiation with blue LEDs and with DMPO as a spin trap (Figure 2a). The recorded signals have the same pattern suggesting the presence of the same paramagnetic species. The assumed formation of an amidyl radical is confirmed by HRMS analysis, the signal at m/z = 297.1273 $[M+H]^+$ corresponds to the adduct **15** formed with the DMPO spin trap (Figure 2b).

a)



b)



15

Figure 2. a) EPR spectra of *N*-aminopyridinium salt **1b** in the presence and of the reaction mixture in the presence of DMPO, b) the structure of adduct **15**.

As the *fac*-Ir(ppy)$_3$ catalyst is able to operate via both reductive and oxidative quenching,[31] we performed Stern-Volmer experiments for the reaction components to examine the role of the photocatalyst (Figure 3). *N*-Aminopyridinium salt **1b** quenches the luminescence of the Ir-catalyst effectively with the quenching rate constant k_q(**2a**) = 5.90 ×108 $M^{-1}s^{-1}$, while for enol **2a** quenching was not observed. Furthermore, the quantum yield of the photocatalytic model reaction was determined (see the SI). The estimated value of Φ = 9.1 ± 1.3% indicates that efficient radical chain processes are unlikely.

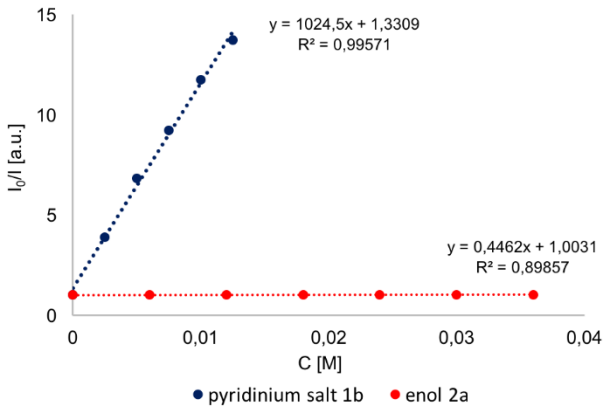
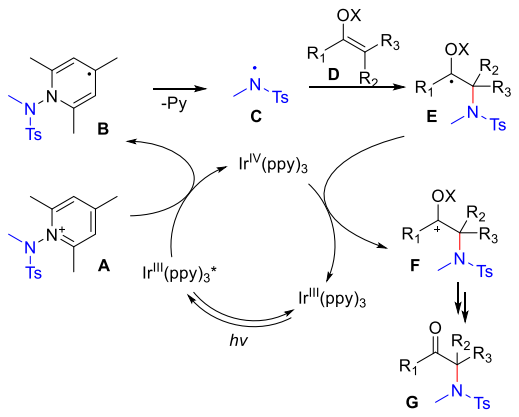


Figure 3. Stern-Volmer experiments.

On the basis of the mechanistic experiments and previous reports, we propose the plausible reaction mechanism presented in Scheme 4. Upon excitation by visible-light, the Ir-catalyst reduces *N*-aminopyridinium salt **A** via single-electron transfer to pyridyl radical **B** which undergoes fragmentation to N-centered radical **C** and a rearomatized pyridine derivative. Radical **C** adds to the π-nucleophile **D** to produce radical **E** which after oxidation to cation **F** maintains the catalytic cycle by regenerating the Ir-catalyst. Subsequent steps may involve either nucleophilic addition to cation **F**, similarly to that reported by Akita,[20] or deprotection of the ketone. Experiments with the addition of $H_2{}^{18}O$ (see SI) excluded the former possibility as no traces of the product with incorporated ^{18}O were detected, and hence, in our case the deprotection of the acyl or silyl group leading to the final α-amino ketone **G** occurs faster.

Scheme 4. Plausible Mechanism of the Amination with *N*-Aminopyridinium Salts



CONCLUSIONS

In summary, we have developed a visible-light induced amination reaction for electron-rich olefins with *N*-protected-aminopyridinium salts leading to α-amnio carbonyl compounds. The reactivity of the generated electrophilic N-centered radicals is controlled by the substitution pattern of the salt. Boc, trifluoroacetyl or pentafluorobenzoyl substituents enable effective enol functionalization while *N*-Cbz protected salts are less reactive.

Our high-yielding, widely applicable transformation occurring under mild reaction conditions can be applied for late-stage diversification of synthetic compounds and functionalization of complex molecules. The extension of the methodology for other π-nucleophiles than ketones, aldehydes, esters, vinyl ethers is currently the subject of our investigations.

Experimental Section

General Information. All solvents and commercially available reagents were purchased as reagent grade and were used without further purification. Reactions were monitored by thin layer chromatography (TLC), using 0.20 mm Merck silica plates (60F-254) or 0.20 mm Merck

aluminum oxide plates (60F-254) and visualised using UV-light or cerium molybdate stain with heat as a developing agent. Photo-induced reactions were performed in a photoreactor (6 blue LED diods, 455-475 nm, 3W) with cooling by Huber MiniChiller 300. Colum chromatography was performed using Merck silica gel 60 (230-400 mesh) or Merck Al_2O_3 neutral (50-300 mesh) deactivated with 15 wt% of H_2O. NMR spectra were recorded on Bruker 400 MHz, Varian 500 or 600 MHz and calibrated using residual undeuterated solvent or TMS as an internal reference. High-resolution mass spectra (HRMS) were recorded on a Waters AutoSpec Premier instrument using electron ionization (EI) or a Waters SYNAPT G2-S HDMS instrument using electrospray ionization (ESI) with time of flight detector (TOF). Elemental analysis (C, H, N, S) were performed using a PERKIN-ELMER 240 Elemental Analyzer. Cyclic voltammograms were recorded using Bio-Logic SP-50 potentiostat. GC-MS analyses were performed using Shimadzu GCMS-QP2010 SE gas chromatograph with FID detector and Zebron ZB 5MSi column. Fluorescence quenching experiments were performed using a Hitachi F-7000 fluorescence spectrophotometer. EPR spectrum was recorded on Magnettech MS200 spectrometer. Enol derivatives **2a-f** were prepared according to literature procedures.[32-36] *N*-aminopyridinium salts **1a-c**, **1e**, **1g**, **1i-j** were prepared according to literature procedures.[18,21,25]

General procedure A for preparation of TBDMS enol ethers. To a precooled to 0 °C solution of ketone (5.0 mmol, 1.0 equiv.) and KI (6.5 mmol, 1.3 equiv.) in anhydrous MeCN (0.5 M) under Ar atmosphere, Et_3N (6.5 mmol, 1.3 equiv) was added dropwise followed by the addition of TBDMSCl (6.5 mmol, 1.3 equiv. in one portion). The mixture was stirred for 16-24 h (determined by TLC) at room temperature. The reaction was quenched with $NaCl_{(sat.)}$ and then extracted with DCM. The organic solution was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude

product was purified by flash column chromatography on deactivated Al_2O_3 (neutral Al_2O_3 treated with 15 wt% of H_2O) using hexane as eluent.

General procedure B for preparation of *N*-aminopirydinium salts from hydrazines. 2,4,6-Trimethylpyrylium tetrafluoroborate (2.0 mmol, 1.0 equiv.) or 2,4,6-triphenylpyridinium tetrafluoroborate (2.0 mmol, 1.0 equiv.) was suspended in absolute EtOH (5 ml). Subsequently, hydrazine (2.4 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at room temperature for 16 h. After this time, Et_2O was added to the mixture. The resulting precipitate was filtered off, washed with Et_2O and dried under vacuum.

General procedure C for preparation of *N*-aminopirydinium salts from *N*-aminopyridinium iodide. To a precooled to 0 °C solution of *N*-aminopyridinium iodide (4.0 mmol, 1.0 equiv.) in anhydrous MeCN (0.2 M) was added 4-dimethylaminopyridine (DMAP, 0.04 mmol, 0.01 equiv.), K_2CO_3 (12.0 mmol, 3 equiv.) and acyl chloride (4.4 mmol, 1.1 equiv.) under Ar atmosphere. Then, the mixture was stirred for 16-24 h at room temperature (conversion determined by TLC). The resulting suspension was filtered and filtrate was concentrated in vacuo. The resulting solid was suspended in DCM and filtered to remove inorganic impurities. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on deactivated Al_2O_3 (neutral Al_2O_3 treated with 15 wt% of H_2O) using DCM/MeOH mixture as eluent. The obtained ylide was disolved in DCM (0.5 M) and tetrafluoroboric acid (4.8 mmol, 1.2 equiv., 42 wt.% in H_2O) or TfOH (4.8 mmol, 1.2 equiv.) was added to the solution at room temperature. The reaction mixture was stirred for 30 min, then the product was precipitated with Et_2O. The resulting precipitate was filtered off, washed with Et_2O and dried under vacuum.

General procedure D for visible-light mediated amination of electron-rich olefins. A glass vial equipped with a stirring bar and sealed with septum was charged with enol (if solid, 0.25 mmol, 1.0 equiv.), *fac*-Ir(ppy)$_3$ (0.04 mmol, 1.0 mol%) and *N*-aminopyridinium salt (0.3 mmol, 1.2 equiv.). Anhydrous MeCN (5 ml) was added and the resulting mixture was degassed by argon bubbling for 20 minutes. Subsequently, (enol if liquid, 0.25 mmol, 1.0 equiv. was added) the reaction mixture was placed in a photoreactor and irradiated with blue LED for the specified time. After the removal of solvent, a crude product was purified flash column chromatography using hexane/Et$_2$O mixture (100% hexane to 50% Et$_2$O in hexane) as eluent.

((2H-chromen-4-yl)oxy)(tert-butyl)dimethylsilane. Following the general procedure **A** the title compound was obtained from 4-chromanone (5.0 mmol). The crude product was purified by column chromatography to afford 1.1 g of a colorless oil (Yield = 87%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H), 7.13 (td, *J* = 8.1 Hz, 1.7 Hz, 1H), 6.90 (td, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 6.78 (dd, *J* = 8.1 Hz, *J* = 1.1 Hz, 1H), 4.89-4.87 (m, 1H), 4.84 (d, *J* = 3.6 Hz, 2H), 1.02 (s, 9H), 0.23 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.7, 146.0, 129.5, 122.5, 122.4, 120.9, 115.4, 97.9, 65.8, 25.8, 18.3, -4.6. HRMS (ESI, *m/z*) calcd for $C_{15}H_{23}O_2Si$ $(M + H)^+$ 263.1103, found 263.1102.

tert-butyldimethyl(undeca-1,10-dien-1-yloxy)silane (Z/E mixture). Following the general procedure **A** the title compound was obtained from 10-undecenal (5.0 mmol). The crude product was purified by column chromatography to afford 1.2 g of a colorless oil (Yield = 90%, 16 h, *Z/E* ratio: 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (dt, *J* = 5.9 Hz, *J* = 1.6 Hz, 1H), 5.86-5.75 (m, 1H), 5.02-4.95 (m, 1H), 4.94-4.91 (m, 1H), 4.46-4.41 (m, 1H), 2.06-2.03 (m, 4H), 1.37-1.30 (m, 10H), 0.92 (s, 9H), 0.11 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.2, 138.3, 114.0, 110.8, 33.8, 29.7, 29.3, 29.2, 29.1, 28.9, 25.6, 23.6, 18.3, -5.4. HRMS (ESI, *m/z*) calcd for $C_{17}H_{35}OSi$ $(M + H)^+$ 283.2457, found 283.2447.

tert-butyl 4-(2-((2-(trimethylsilyl)propan-2-yl)oxy)vinyl)piperidine-1-carboxylate (E/Z mixture). Following the general procedure **A** the title compound was obtained from *N*-Boc-4-piperidineacetaldehyde (5.0 mmol). The crude product was purified by column chromatography to afford 1.2 g of a colorless oil (Yield = 83%, 16 h, *E/Z* ratio: 9/1). ^{1}H NMR (400 MHz, $CDCl_3$):

δ *6.25 (dd, J =0.8 Hz, J = 12.0 Hz, 1H)*, 6.12 (dd, *J* = 5.9 Hz, *J* = 1.7 Hz, 1H), *5.24-5.22 (m, 1H), 4.95-4.91 (m, 1H)*, 4.28 (dd, *J* = 8.5 Hz, *J* = 5.9 Hz, 1H), 4.07-3.93 (m, 2H + *m, 2H*), 2.82-2.72 (m, 2H + *m, 2H*), *2.03-1.94 (m, 1H)*, 1.69-1.56 (m, 2H), 1.45 (s, 9H + *s, 9H*), 1.29-1.18 (m, 3H + *m, 3H*), 0.90 (s, 9H), *0.87 (s, 9H)*, 0.11 (s, 6H), *0.06 (s, 6H)*. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.9, 138.1, 114.3, 32.0, 31.4, 28.5, 25.7, 25.6, 18.3, *17.9*, *-3.4*, -5.4. HRMS (ESI, *m/z*) calcd for $C_{18}H_{35}NO_3SiNa$ $(M + Na)^+$ 364.2284, found 364.2271.

*1-(((benzyloxy)carbonyl)(methyl)amino)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate (**1d**)*. Following the general procedure **B** compound **1d** was obtained from 2,4,6-trimethylpyridinium tetrafluoroborate (2.0 mmol) and benzyl 1-methylhydrazinecarboxylate (1.2 equiv.) as a white solid (0.68 g, Yield = 92%). ^{1}H NMR (400 MHz, $CDCl_3$): mixture of rotamers, δ 7.59 (s, 1H, first rotamer), *7.56 (s, 1H, second rotamer)*, 7.41 (s, 3H + *second rotamer 3H*), 7.37-7.33 (m, 1H + *second rotamer 1H*), 7.25 (m, 1H + *second rotamer 1H*), 7.23-7.18 (m, 1H + *second rotamer 1H*), 5.31 (s, 2H, first rotamer), *5.16 (s, 2H, second rotamer)*, 3.59 (s, 3H, first rotamer), *3.52 (s, 3H, second rotamer)*, 2.59 (s, 9H, first rotamer), *2.50 (s, 9H, second rotamer)*. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): mixture of rotamers, δ 162.2, 161.8, 156.7, 156.4, 153.0, 151.7, 134.5, 134.3, 129.3, 129.1, 129.0, 128.94, 128.88, 128.85, 128.5, 123.6, 70.1, 69.8, 37.5, 36.5, 22.1, 21.1, 18.7, 18.6. ^{19}F NMR (375 MHz, $CDCl_3$): δ -152.80 ($^{11}BF_4$), -152.86 ($^{10}BF_4$). HRMS (ESI, *m/z*) calcd for $C_{17}H_{21}N_2O_2^+$ $(M\text{-}BF_4)^+$ 285.1603, found 285.1602.

*1-((tert-butoxycarbonyl)(methyl)amino)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1f**)*. Following the general procedure **B** compound **1f** was obtained from 2,4,6-triphenylpyridinium tetrafluoroborate (2.0 mmol) and *tert*-butyl 1-methylhydrazinecarboxylate (1.2 equiv.) as a white solid (0.91 g, Yield = 91%). ^{1}H NMR (400 MHz, CD_3CN) mixture of rotamers, δ 8.38 (s, 1H, first rotamer), *8.36 (s, 1H, second rotamer)*, 8.10-8.03 (m, 1H + *second rotamer 1H*), 7.74-7.59 (m, 15H + *second rotamer 15H*), 2.90 (s, 3H, first rotamer), *2.81 (s, 3H, second rotamer)*, 1.29 (s, 9H, first rotamer), *1.27 (s, 9H, second rotamer)*. ^{13}C {^{1}H} NMR (100 MHz, CD_3CN): mixture of rotamers, δ 158.5, 158.3, 158.1, 158.0, 152.7, 150.0, 133.5, 133.4, 133.2, 133.1, 131.7, 131.6, 130.8, 130.6, 129.9, 129.8, 129.1, 129.0, 128.9, 128.8, 128.5, 127.0, 126.9, 85.5, 84.6, 39.2, 39.0, 27.0, 26.9. ^{19}F NMR (375 MHz, CD_3CN): δ -151.85 ($^{11}BF_4$), -151.91 ($^{10}BF_4$). HRMS (ESI, *m/z*) calcd for $C_{29}H_{29}N_2O_2^+$ $(M\text{-}BF_4)^+$ 437.2229, found 437.2231.

*1-(((benzyloxy)carbonyl)amino)pyridin-1-ium tetrafluoroborate (**1h**)*. Following the general procedure **C** compound **1h** was obtained from *N*-aminopyridinium iodide (4.0 mmol) and benzyl

chloroformate (1.2 equiv.) as a white solid (0.77 g, Yield = 61%). ^{1}H NMR (400 MHz, CD_3CN): δ 10.42 (brs, 1H), 8.78 (d, *J* = 5.6 Hz, 2H), 8.66 (t, *J* = 7.9 Hz, 1H), 8.17-8.13 (m, 2H), 7.44-7.38 (m, 5H), 5.29 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ 154.0, 147.9, 146.6, 135.0, 129.0, 128.8, 128.7, 128.4, 69.2. ^{19}F NMR (375 MHz, CD_3CN): δ -151.7 ($^{11}BF_4$), -151.8 ($^{10}BF_4$). HRMS (ESI, *m/z*) calcd for $C_{13}H_{13}N_2O_2^+$ $(M\text{-}BF_4)^+$ 229.0977, found 229.0977.

*2-(Me,Ts-amino)-1-phenylethanone (**3a**)*. Following the general procedure **D** compound **3a** was obtained from enol **2a** (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 72 mg of compound **3a** as beige solid (Yield = 95%, 1 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.56 (s, 2H), 2.82 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.7, 143.6, 134.9, 134.8, 133.8, 129.7, 128.8, 128.3, 127.6, 56.1, 35.6, 21.5. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[37]

*2-(Me,Ts-amino)-1-(4-chlorophenyl)ethanone (**3b**)*. Following the general procedure **D** compound **3b** was obtained from 1-(4-chlorophenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[38]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 79 mg of compound **3b** as white solid (Yield = 94%, 5 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.93 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.48-7.43 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.48 (s, 2H), 2.79 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.8, 143.8, 140.4, 134.5, 133.1, 129.8, 129.7, 129.2, 127.6, 56.1, 35.6, 21.5. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[37]

*2-(Me,Ts-amino)-1-(4-bromophenyl)ethanone (**3c**)*. Following the general procedure **D** compound **3c** was obtained from 1-(4-bromophenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[32]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 80 mg of compound **3c** as white solid (Yield = 87%, 5 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.47 (s, 2H), 2.79 (s, 3H), 2.45 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.0, 143.8, 134.5, 133.5, 132.2, 129.9, 129.8, 129.1, 127.6, 56.1, 35.6, 21.5. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[37]

*2-(Me,Ts-amino)-1-(4-iodophenyl)ethanone (**3d**).* Following the general procedure **D** compound **3d** was obtained from 1-(4-iodophenyl)vinyl acetate (0.25 mmol, prepared according to literature

procedure[39]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 89 mg of compound **3d** as white solid (Yield = 83%, 5 h).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.76-7.58 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.46 (s, 2H), 2.79 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.3, 143.8, 138.2, 134.5, 134.0, 129.7, 129.7, 127.6, 102.0, 56.1, 35.6, 21.6. HRMS (ESI, *m/z*) calcd for $C_{16}H_{17}INO_3S$ $(M + H)^+$ 429.9974, found 429.9973. Anal. Calcd for $C_{16}H_{16}INO_3S$: C, 44.77; H, 3.76; N, 3.26; S, 7.47; found: C, 44.94; H, 3.73; N, 3.25; S, 7.42.

*2-(Me,Ts-amino)-1-(2-methoxyphenyl)ethanone (**3e**)*. Following the general procedure **D** compound **3e** was obtained from 1-(2-methoxyphenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[40]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 67 mg of compound **3e** as white solid (Yield = 80%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.69 (m, 3H), 7.53-7.46 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 16.5, 8.1 Hz, 2H), 4.63 (s, 2H), 3.93 (s, 3H), 2.87 (s, 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.1, 159.1, 143.2, 135.9, 134.6, 130.8, 129.5, 127.6, 125.5, 120.9, 111.5, 60.1, 55.6, 35.7, 21.5. HRMS (ESI, *m/z*) calcd for $C_{17}H_{19}NO_4SNa$ $(M + Na)^+$ 356.0932, found 356.0923. Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20; S, 9.62; found: C, 61.25; H, 5.89; N, 4.08; S, 9.68.

*2-(Me,Ts-amino)-1-(3-methoxyphenyl)ethanone (**3f**)*. Following the general procedure **D** compound **3f** was obtained from 1-(3-methoxyphenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[39]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 56 mg of compound **3f** as white solid (Yield = 67%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.57-7.52 (m, 1H), 7.50 (dd, *J* = 2.6, 1.3 Hz, 1H), 7.41-7.29 (m, 3H), 7.16-7.10 (m, 1H), 4.53 (s, 2H), 3.85 (s, 3H), 2.82 (s, 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.6, 159.9, 143.6, 136.1, 134.9, 129.8, 129.7, 127.6, 120.8, 120.5, 112.5, 56.2, 55.5, 35.6, 21.5. HRMS (ESI, *m/z*) calcd for $C_{17}H_{19}NO_4SNa$ $(M + Na)^+$ 356.0932, found 356.0929. Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20; S, 9.62; found: C, 61.09; H, 5.64; N, 4.10; S, 9.48.

*2-(Me,Ts-amino)-1-(4-methoxyphenyl)ethanone (**3g**)* Following the general procedure **D** compound **3g** was obtained from 1-(4-methoxyphenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[32]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 79 mg of compound **3g** as white solid (Yield =

95%, 4 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.95-6.92 (m, 2H), 4.46 (s, 2H), 3.86 (s, 3H), 2.79 (s, 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.2, 164.1, 143.6, 134.7, 130.7, 129.7, 127.8, 127.6, 114.0, 55.9, 55.5, 35.6, 21.5. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[37]

*Methyl 4-(2-(Me,Ts-amino)acetyl)benzoate (**3h**)*. Following the general procedure **D** compound **3h** was obtained from methyl 4-(1-acetoxyvinyl)benzoate (0.25 mmol, prepared according to literature procedure[32]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 70 mg of compound **3h** as white solid (Yield = 77%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.56 (s, 2H), 3.95 (s, 3H), 2.82 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.7, 166.2, 143.9, 138.1, 134.9, 134.7, 130.1, 129.9, 128.4, 127.7, 56.5, 52.7, 35.8, 21.7. HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NO_5SNa$ $(M + Na)^+$ 384.0882, found 384.0869. Anal. Calcd for $C_{18}H_{19}NO_5S$: C, 59.82; H, 5.30; N, 3.88; S, 8.87; found: C, 59.65; H, 5.43; N, 3.81; S, 8.88.

*2-(Me,Ts-amino)-1-(4-cyanophenyl)ethanone (**3i**)*. Following the general procedure **D** compound **3i** was obtained from 1-(4-cyanophenyl)vinyl acetate (0.25 mmol, prepared according to literature procedure[38]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 66 mg of compound **3i** as white solid (Yield = 80%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.09 (m, 2H), 7.79-7.77 (m, 2H), 7.71-7.69 (m, 2H), 7.35-7.33 (m, 2H), 4.48 (s, 2H), 2.78 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.0, 144.0, 137.7, 134.2, 132.6, 129.8, 128.9, 127.6, 117.7, 117.1, 56.5, 35.7, 21.6. HRMS (ESI, *m/z*) calcd for $C_{17}H_{16}N_2O_3SNa$ $(M + Na)^+$ 351.0779, found 351.0770. Anal. Calcd for $C_{17}H_{16}N_2O_3S$: C, 62.18; H, 4.91; N, 8.53; S, 9.76; found: C, 61.90; H, 4.75; N, 8.63; S, 9.86.

*2-(Me,Ts-amino)-1-(thiophen-2-yl)ethanone (**3j**)*. Following the general procedure **D** compound **3j** was obtained from *tert*-butyldimethyl((1-(thiophen-2-yl)vinyl)oxy)silane (0.25 mmol, prepared according to literature procedure[33]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product ,67%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 3.8 Hz, *J* = 1.1 Hz, 1H), 7.72-7.68 (m, 3H), 7.34-7.31 (m, 2H), 7.17-7.15 (m, 1H), 4.41 (s, 2H), 2.83 (s. 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.8, 143.7, 141.0, 134.5, 134.4, 133.2, 129.7, 128.4, 127.5, 56.3, 35.7, 21.5. HRMS (ESI, *m/z*) calcd for $C_{14}H_{15}NO_3S_2Na$ $(M + Na)^+$ 332.0391, found 332.0388. Anal.

Calcd for $C_{14}H_{15}NO_3S_2$: C, 54.35; H, 4.89; N, 4.53; S, 20.72; found: C, 54.55; H, 4.86; N, 4.55; S, 20.67.

*2-(Me,Ts-amino)-1-(pyridin-4-yl)ethanone (**3k**)*. Following the general procedure **D** compound **3k** was obtained from 4-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine (0.25 mmol, prepared according to literature procedure[41]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 46 mg of compound **3k** as white solid (Yield = 60%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.78-7.76 (m, 2H), 7.72-7.70 (m, 2H), 7.36-7.34 (m, 2H), 4.51 (s, 2H), 2.81 (s, 3H), 2.45 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.7, 151.1, 143.9, 140.5, 134.4, 129.8, 127.5, 121.1, 56.4, 35.7, 21.5. HRMS (ESI, *m/z*) calcd for $C_{15}H_{17}N_2O_3S$ $(M + H)^+$ 305.0960, found 305.0961. Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20; S, 10.53; found: C, 59.20; H, 5.32; N, 9.05; S, 10.62.

*1-(benzofuran-2-yl)-2-(Me,Ts-amino)ethanone (**3l**)*. Following the general procedure **D** compound **3l** was obtained from ((1-(benzofuran-2-yl)vinyl)oxy)(*tert*-butyl)dimethylsilane (0.25 mmol, prepared according to literature procedure[33]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 67 mg of compound **3l** as white solid (Yield = 78%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 4H), 7.58-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.35-7.31 (m, 3H), 4.53 (s, 2H), 2.89 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.8, 155.7, 150.5, 143.7, 134.8, 129.7, 128.8, 127.5, 126.8, 124.2, 123.6, 114.6, 112.4, 56.0, 35.8, 21.5; HRMS (ESI, *m/z*) calcd for $C_{18}H_{18}NO_4S$ $(M + H)^+$ 344.0957, found 344.0954. Anal. Calcd for $C_{18}H_{17}NO_4S$: C, 62.96; H, 4.99; N, 4.08; S, 9.34; found: C, 62.85; H, 4.89; N, 3.93; S, 9.15.

*2-(N,4-Dimethylphenylsulfonamido)-1-phenylvinyl benzoate (**4**)*. Following the general procedure **D** compound **4** was obtained from enol **2b** (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 46 mg of compound **4** as beige solid (Yield = 45%, 16 h). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-7.98 (m, 4H), 7.64-7.59 (m, 4H), 7.49 (t, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.20 (s, 1H), 2.96 (s, 3H), 2.41 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.6, 143.8, 135.3, 134.9, 134.4, 129.6, 129.1, 128.6, 127.6, 65.2, 32.4, 21.6. HRMS (ESI, *m/z*) calcd for $C_{23}H_{21}NO_4SNa$ $(M + Na)^+$ 430.1089, found 430.1094. Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79; H, 5.19; N, 3.44; S, 7.87; found: C, 67.62; H, 5.20; N, 3.26; S, 8.01.

*1-(Me,Ts-amino)-3,3-dimethylbutan-2-one (**5a**).* Following the general procedure **D** compound **5a** was obtained from ((3,3-dimethylbut-1-en-2-yl)oxy)trimethylsilane (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 56 mg of compound **5a** as colorless oil (Yield = 79%, 5 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.20 (s, 2H), 2.80 (s, 3H), 2.42 (s, 3H), 1.14 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 209.1, 143.3, 135.7, 129.5, 127.4, 77.3, 77.0, 76.7, 53.7, 43.3, 35.4, 26.2, 21.5. HRMS (ESI, *m/z*) calcd for $C_{14}H_{21}NO_3SNa$ $(M + Na)^+$ 306.1140, found 306.1129. Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94; S, 11.31; found: C, 59.56; H, 7.43; N, 4.78; S, 11.28.

*2-(Me,Ts-amino)pentan-3-one (**5b**).* Following the general procedure **D** compound **5b** was obtained from *tert*-butyldimethyl(pent-2-en-3-yloxy)silane (0.25 mmol, *E*/*Z* mixture, prepared according to literature procedure[42]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 44 mg of compound **5b** as colorless oil (Yield = 65%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.57 (q, *J* = 7 Hz, 1H), 2.69-2.61 (m, 4H), 2.58-2.52 (m, 1H), 2.40 (s, 3H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.95 (d, *J* = 7.0 Hz 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 209.1, 143.6, 136.0, 129.8, 127.1, 59.9, 32.4, 30.0, 21.5, 11.4, 7.7. HRMS (ESI, *m/z*) calcd for $C_{13}H_{19}NO_3SNa$ $(M + Na)^+$ 292.0983, found 292.0979. Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.90; found: C, 57.83; H, 6.97; N, 5.04; S, 12.06.

*2-(Me,Ts-amino)-2,4-dimethylpentan-3-one (**5c**).* Following the general procedure **D** compound **5c** was obtained from *tert*-butyl((2,4-dimethylpent-2-en-3-yl)oxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[33]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 38 mg of compound **5c** as colorless oil (Yield = 52%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.42-3.32 (m, 1H), 2.75 (s, 3H), 2.42 (s, 3H), 1.40 (s, 6H), 1.17 (d, *J* = 6.7 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 215.0, 143.4, 137.2, 129.5, 127.8, 68.0, 34.3, 32.0, 23.7, 21.5, 20.9. HRMS (ESI, *m/z*) calcd for $C_{15}H_{23}NO_3SNa$ $(M + Na)^+$ 320.1289, found 320.1296. Anal. Calcd for $C_{15}H_{23}NO_3S$: C, 60.58; H, 7.80; N, 4.71; S, 10.78; found: C, 60.48; H, 7.68; N, 4.76; S, 10.81.

*2-(Me,Ts-amino)-1-phenylpropan-1-one (**5d**).* Following the general procedure **D** compound **5d** was obtained from *tert*-butyldimethyl((1-phenylprop-1-en-1-yl)oxy)silane (0.25 mmol, *E*/Z

mixture, prepared according to literature procedure[43]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 72 mg of compound **5d** as beige solid (Yield = 91%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.07 (m, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.62-7.55 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 5.66 (q, *J* = 6.9 Hz, 1H), 2.70 (s, 3H), 2.41 (s, 3H), 1.16 (d, *J* = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.5, 143.6, 136.0, 135.1, 133.5, 129.7, 129.0, 128.71, 127.4, 55.3, 29.8, 21.5, 12.4. HRMS (ESI, *m/z*) calcd for $C_{17}H_{20}NO_3S$ $(M + H)^+$ 318.1164, found 318.1161. Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41; S, 10.10; found: C, 64.08; H, 5.99; N, 4.31; S, 10.21.

*2-(Me,Ts-amino)cyclopentanone (**5e**)*. Following the general procedure **D** compound **5e** was obtained from *tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[44]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 29 mg of compound **5e** as colorless oil (Yield = 44%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.46-4.41 (m, 1H), 2.64 (s, 3H), 2.41 (s, 3H), 2.33-2.25 (m, 1H), 2.20-2.14 (m, 1H), 2.06-1.99 (m, 2H), 1.87-1.78 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 212.8, 143.3, 136.4, 129.5, 127.4, 64.8, 35.4, 30.4, 25.7, 21.4, 17.8. HRMS (ESI, *m/z*) calcd for $C_{13}H_{18}NO_3S$ $(M + H)^+$ 268.1007, found 268.1002. Anal. Calcd for $C_{13}H_{17}NO_3S$: C, 58.41; H, 6.41; N, 5.24; S, 11.99; found: C, 58.66; H, 6.28; N, 5.15; S, 11.82.

*2-(Me,Ts-amino)cyclohexanone (**5f**)*. Following the general procedure **D** compound **5f** was obtained from *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[45]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 38 mg of compound **5f** as colorless oil (Yield = 54%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.65 (dd, *J* = 11.7 Hz, *J* = 6.1 Hz, 1H), 2.80 (s, 3H), 2.45-2.42 (m, 1H), 2.40 (s, 3H), 2.33-2.25 (m, 1H), 2.15-2.02 (m, 2H), 1.99-1.93 (m, 1H), 1.87-1.75 (m, 2H), 1.62-1.53 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 205.6, 143.1, 136.7, 129.5, 127.2, 64.6, 41.8, 32.2, 30.5, 26.6, 24.7, 21.5. HRMS (ESI, *m/z*) calcd for $C_{14}H_{20}NO_3S$ $(M + H)^+$ 282.1164, found 282.1155. Anal. Calcd for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98; S, 11.39; found: C, 59.75; H, 6.79; N, 4.90; S, 11.46.

*2-(Me,Ts-amino)cycloheptanone (**5g**)*. Following the general procedure **D** compound **5g** was obtained from *tert*-butyl(cyclohept-1-en-1-yloxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[46]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was

purified by column chromatography to afford 62 mg of compound **5g** as colorless oil (Yield = 84%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3Hz, 2H), 4.74 (dd, *J* = 9.5 Hz, *J* = 2.9 Hz, 1H), 2.82 (s, 3H), 2.54 (ddd, *J* = 16.4 Hz, *J* = 5.9 Hz, *J* = 2.3 Hz, 1H), 2.42 (s, 3H), 2.35-2.27 (m, 1H), 1.95-1.76 (m, 4H,), 1.73-1.60 (m, 3H), 1.36-1.26 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 209.0, 143.1, 136.6, 129.5, 127.2, 65.4, 42.0, 30.8, 30.3, 29.5, 28.3, 23.3, 21.5. HRMS (ESI, *m/z*) calcd for $C_{15}H_{21}NO_3SNa$ $(M + Na)^+$ 318.1140, found 318.1133. Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74; S, 10.85; found: C, 60.93; H, 7.21; N, 4.55; S, 10.69.

*2-(Me,Ts-amino)cyclooctanone (**5h**)*. Following the general procedure **D** compound **5h** was obtained from *tert*-butyl(cyclohept-1-en-1-yloxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[44]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 70 mg of compound **5h** as colorless oil (Yield = 90%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.76 (dd, *J* = 10.1 Hz, *J* = 4.1 Hz, 1H), 3.00 (s, 3H), 2.50 (ddd, *J* = 8.0 Hz, *J* = 3.2 Hz, 1H), 2.40 (s, 3H), 2.22-2.15 (m, 1H), 2.06-1.94 (m, 1H), 1.85-1.62 (m, 5H), 1.56-1.43 (m, 3H), 1.13-1.07 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 213.9, 143.3, 136.5, 129.6, 127.0, 60.2, 42.6, 31.5, 31.2, 27.8, 24.9, 23.6, 23.6, 21.5. HRMS (ESI, *m/z*) calcd for $C_{16}H_{23}NO_3SNa$ $(M + Na)^+$ 332.1296, found 332.1286. Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53; S, 10.36; found: C, 62.26; H, 7.40; N, 4.36; S, 10.47.

*6-(Me,Ts-amino)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (**5i**)*. Following the general procedure **D** compound **5i** was obtained from *tert*-butyldimethyl((6-methyl-3-(prop-1-en-2-yl)cyclohexa-1,5-dien-1-yl)oxy)silane (0.25 mmol, prepared according to literature procedure[47]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 33 mg of compound **5i** as colorless oil (Yield = 39%, 5 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.72-6.70 (m, 1H), 4.93-4.90 (m, 2H), 4.86 (d, *J* = 13.0 Hz, 1H), 3.01-2.94 (m, 1H), 2.72-2.65 (m, 1H), 2.63 (s, 3H), 2.41 (s, 3H), 2.40-2.37 (m, 1H), 1.91 (s, 3H), 1.73 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.4, 144.0, 143.9, 142.9, 136.6, 135.4, 129.1, 128.0, 114.8, 65.3, 48.4, 31.6, 29.6, 21.5, 17.7, 15.7. HRMS (ESI, *m/z*) calcd for $C_{18}H_{24}NO_3S$ $(M + H)^+$ 334.1477, found 334.1468. Anal. Calcd for $C_{18}H_{23}NO_3S$: C, 64.84; H, 6.95; N, 4.20; S, 9.61; found: C, 64.62; H, 6.93; N, 4.25; S, 9.44.

*2-(Me,Ts-amino)-3,4-dihydronaphthalen-1(2H)-one (**5j**)*. Following the general procedure **D** compound **5j** was obtained from *tert*-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane (0.25 mmol, prepared according to literature procedure[41]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 47 mg of compound **5j** as beige solid (Yield = 57%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32-7.30 (m, 2H), 7.29-7.23 (m, 2H*)*, 4.93 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.26 (ddd, *J* = 17.3, 12.2, 5.3 Hz, 1H), 3.10-3.02 (m, 1H), 2.80 (s, 3H), 2.44 (s, 3H), 2.40-2.29 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.4, 143.3, 143.2, 136.8, 133.9, 132.3, 129.5, 128.7, 127.8, 127.5, 126.9, 63.5, 30.3, 29.3, 29.2, 21.6. HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NO_3SNa$ $(M + Na)^+$ 352.0983, found 352.0978. Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25; S, 9.73; found: C, 65.52; H, 5.85, N, 4.25; S, 9.73.

*3-(Me,Ts-amino)chroman-4-one (**5k**)*. Following the general procedure **D** compound **5k** was obtained from ((2H-chromen-4-yl)oxy)(*tert*-butyl)dimethylsilane (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 36 mg of compound **5k** as white solid (Yield = 44%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 8.3Hz, 2H), 7.51-7.46 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.04-6.97 (m, 2H), 5.11 (dd, *J* = 12.6 Hz, *J* = 5.9 Hz, 1H), 4.61 (dd, *J* = 10.8 Hz, *J* = 5.9 Hz, 1H), 4.46 (dd, *J* = 12.6 Hz, *J* = 10.9 Hz, 1H), 2.83 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.6, 161.4, 143.6, 136.5, 135.9, 129.6, 127.5, 127.5, 122.0, 120.8, 118.0, 69.3, 59.6, 31.3, 21.6. HRMS (ESI, *m/z*) calcd for $C_{17}H_{18}NO_4S$ $(M + H)^+$ 332.0957, found 332.0941. Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.62; H, 5.17; N, 4.23; S, 9.67; found: C, 61.71; H, 5.12; N, 4.12; S, 9.86.

*2-(Me,Ts-amino)undec-10-enal (**6a**)*. Following the general procedure **D** compound **6a** was obtained from *tert*-butyldimethyl(penta-1,4-dien-1-yloxy)silane (0.25 mmol, *E*/*Z* mixture) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 59 mg of compound **6a** as colorless oil (Yield = 67%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.86-5.75 (m, 1H), 5.02-4.96 (m, 1H), 4.95-4.91 (m, 1H), 4.41 (dd, *J* = 9.3 Hz, *J* = 5.5 Hz, 1H), 2.77 (s, 3H), 2.43 (s, 3H), 2.06-2.01 (m, 2H), 1.87-1.78 (m, 1H), 1.44-1.24 (m, 11H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.3, 143.6, 139.0, 136.6, 129.7, 127.2, 114.2, 65.6, 33.7, 30.4, 29.1, 29.0, 28.9, 28.8, 25.9, 25.6, 21.5.

HRMS (ESI, *m/z*) calcd for $C_{19}H_{29}NO_3SNa$ $(M + Na)^+$ 374.1766, found 374.1761. Anal. Calcd for $C_{19}H_{29}NO_3S$: C, 64.92; H, 8.32; N, 3.98; S, 9.12; found: C, 65.03; H, 8.34; N, 3.96; S, 9.19.

*2-(Me,Ts-amino)-2-phenylpropanal (**6b**)*. Following the general procedure **D** compound **6b** was obtained from *tert*-butyldimethyl((2-phenylprop-1-en-1-yl)oxy)silane (0.25 mmol, *E*/*Z* mixture prepared according to literature procedure[48]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 72 mg of compound **6b** as colourless oil (Yield = 91%, 10 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.42-7.32 (m, 7H), 2.48 (s, 3H), 2.46 (s, 3H), 1.71 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.9, 144.1, 135.9, 135.7, 129.8, 129.4, 128.8, 128.1, 127.5, 72.7, 31.7, 21.6, 14.6. HRMS (ESI, *m/z*) calcd for $C_{17}H_{19}NO_3SNa$ $(M + Na)^+$ 340.0983, found 340.0973. Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41; S, 10.10; found: C, 64.07; H, 5.93; N, 4.38; S, 9.94.

*tert-Butyl 4-(1-(Me,Ts-amino)-2-oxoethyl)piperidine-1-carboxylate (**6c**)*. Following the general procedure **D** compound **6c** was obtained from *tert*-butyl 4-(2-((tert-butyldimethylsilyl)oxy)vinyl)piperidine-1-carboxylate (0.25 mmol, *E*/*Z* mixture) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 48 mg of compound **6c** as colorless oil (Yield = 47%, 7 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.25 (d, *J* = 7.9 Hz, 1H), 4.13-4.08 (m, 2H), 2.76 (s, 3H), 2.72-2.65 (m, 1H), 2.43 (s, 3H), 2.01-1.93 (m, 1H), 1.85-1.80 (m, 1H), 1.59-1.52 (m, 1H), 1.45 (s, 9H), 1.33-1.17 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.6, 154.6, 143.9, 136.4, 129.8, 127.2, 79.6, 68.7, 33.8, 30.9, 29.5, 28.7, 28.4, 21.5. HRMS (ESI, *m/z*) calcd for $C_{20}H_{30}N_2O_5SNa$ $(M + Na)^+$ 433.1773, found 433.1773. Anal. Calcd for $C_{20}H_{30}N_2O_5S$: C, 58.51; H, 7.37; N, 6.82; S, 7.81; found: C, 58.40; H, 7.34; N, 6.79; S, 7.94.

*2-(Me,Ts-amino)-1,3-diphenylpropane-1,3-dione (**7a**)*. Following the general procedure **D** compound **7a** was obtained from 1,3-diphenylpropane-1,3-dione (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 47 mg of compound **7a** as beige solid (Yield = 46%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.65-7.59 (m, 4H), 7.49 (t, *J* = 7.7 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 1H), 2.96 (s, 3H), 2.41 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.6, 143.8, 135.3, 134.9, 134.2, 129.6, 129.1, 128.6, 127.6, 65.2, 32.4, 21.6. HRMS (ESI, *m/z*) calcd for $C_{23}H_{21}NO_4SNa$ $(M + Na)^+$ 430.1089, found 430.1081. Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79; H, 5.19; N, 3.44; S, 7.87; found: C, 67.72; H, 5.30; N, 3.36; S, 7.86.

*2-(Me,Ts-amino)-1,3-di(thiophen-2-yl)propane-1,3-dione (**7b**)*. Following the general procedure **D** compound **7b** was obtained from 1,3-di(thiophen-2-yl)propane-1,3-dione (0.25 mmol, prepared according to literature procedure[49]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 47 mg of compound **7b** as yellow solid (Yield = 45%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.95 (m, 2H), 7.73 (dd, *J* = 4.9, 0.7 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 4.8, 4.1 Hz, 2H), 6.86 (s, 1H), 3.03 (s, 3H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.6, 144.0, 141.6, 135.5, 135.1, 133.9, 129.6, 128.8, 127.5, 66.6, 32.7, 21.6. HRMS (ESI, *m/z*) calcd for $C_{19}H_{17}NO_4S_3Na$ $(M + Na)^+$ 442.0217, found 442.0210. Anal. Calcd for $C_{19}H_{17}NO_4S_3$: C, 54.39; H, 4.08; N, 3.34; S, 22.93; found: C, 54.43; H, 3.96; N, 3.42; S, 22.87.

*ethyl 2-(Me,Ts-amino)-2-phenylacetate (**8**)*. Following the general procedure **D** compound **8** was obtained from *tert*-butyl((1-ethoxy-2-phenylvinyl)oxy)dimethylsilane (0.25 mmol, *E*/*Z* mixture prepared according to literature procedure[50]) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 9 mg of compound **8** as colorless oil (Yield = 10%, 24 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.35-7.22 (m, 7H), 5.85 (s, 1H), 4.08-4.02 (m, 2H), 2.75 (s, 3H), 2.43 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.6, 143.4, 136.3, 133.8, 129.5, 128.8, 128.6, 128.6, 127.3, 62.4, 61.2, 30.8, 21.5, 14.0. HRMS (ESI, *m/z*) calcd for $C_{18}H_{21}NO_4SNa$ $(M + Na)^+$ 370.1089, found 370.1073.

*N-Me-N-Ts-3,4-dihydro-2H-pyran-5-amine (**9a**)*. Following the general procedure **D** compound **9a** was obtained from 3,4-dihydro-2H-pyran (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol). The crude product was purified by column chromatography to afford 8 mg of compound **9a** as colorless oil (Yield = 12%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.31-7.26 (m, 2H), 6.28 (s, 1H), 3.91-3.85 (m, 2H), 2.97 (s, 3H), 2.42 (s, 3H), 2.02 (td, *J* = 6.2, 1.2 Hz, 2H), 1.87-1.78 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.9, 143.3, 135.6, 129.4, 127.6, 117.6, 65.6, 37.5, 22.8, 22.0, 21.5. HRMS (ESI, *m/z*) calcd for $C_{13}H_{17}NO_3SNa$ $(M + Na)^+$ 290.0827, found 290.0831.

*N-Me-N-Ts-tetrahydro-2H-pyran-3-amine (**9b**)*. Following the general procedure **D** compound **9b** was obtained from 3,4-dihydro-2H-pyran (0.25 mmol) and *N*-aminopyridinium salt **1b** (0.3 mmol) with addition of cyclohexanethiol (2 equiv.). The crude product was purified by column chromatography to afford 22 mg of compound **9b** as colorless oil (Yield = 33%, 16 h). ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.94-3.85 (m, 1H), 3.85-3.78 (m, 1H), 3.69-3.62 (m, 1H), 3.24-3.15 (m, 2H), 2.78 (s, 3H), 2.42 (s, 3H), 1.69-1.59 (m, 3H), 1.58-1.55 (m, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 143.3, 137.0, 129.8, 127.0, 69.3, 67.6, 53.1, 29.7, 27.2, 25.8, 21.5. HRMS (ESI, *m/z*) calcd for $C_{13}H_{19}NO_3SNa$ $(M + Na)^+$: 292.0983, found 292.0978.

*2-(Me,Boc-amino)-1-phenylethanone (**10a**)*. Following the general procedure **D** compound **10a** was obtained from enol **2e** (0.25 mmol) and *N*-aminopyridinium salt **1c** (0.3 mmol). The crude product was purified by column chromatography to afford 55 mg of compound **10a** as colourless oil (Yield = 89%, 1 h). ^1H NMR (400 MHz, $CDCl_3$): mixture of rotamers, δ 7.92 (t, *J* = 7.4 Hz, 2H + *second rotamer 2H*), 7.60 – 7.54 (m, 1H + *second rotamer 1H*), 7.49-7.42 (m, 2H + *second rotamer 2H*), 4.66 (s, 2H, first rotamer), *4.57 (s, 2H, second rotamer)*, *2.96 (s, 3H, second rotamer)*, 2.93 (s, 3H, first rotamer), 1.48 (s, 9H, first rotamer), *1.37 (s, 9H, second rotamer)*. ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): mixture of rotamers, δ 195.2, 194.8, 156.2, 155.7, 135.3, 133.4, 128.8, 128.7, 127.9, 127.7, 80.00, 55.7, 55.1, 35.7, 35.6, 28.4, 28.2. The observed characterization data (^1H and ^{13}C) were consistent with those previously reported.[51]

*2-(Me,Cbz-amino)-1-phenylethanone (**10b**)*. Following the general procedure **D** compound **10b** was obtained from enol **2e** (0.25 mmol) and *N*-aminopyridinium salt **1d** (0.3 mmol). The crude product was purified by column chromatography to afford 30 mg of compound **10b** as colorless oil (Yield = 42%, 1 h). ^1H NMR (400 MHz, $CDCl_3$): mixture of rotamers, δ 7.97 – 7.86 (m, 2H + *second rotamer 2H*), 7.62 – 7.55 (m, 1H + *second rotamer 1H*), 7.50-7.20 (m, 7H + *second rotamer 7H*), 5.19 (s, 2H, first rotamer), *5.11 (s, 2H, second rotamer)*, 4.74 (s, 2H, first rotamer), *4.68 (s, 2H, second rotamer)*, 3.04 (s, 3H), *3.03 (s, 3H, second rotamer)*. ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): mixture of rotamers, δ 194.6, 194.2, 156.9, 156.4, 136.7, 136.6, 135.2, 135.1, 133.63, 133.60, 128.81, 128.76, 128.5, 128.4, 128.0, 127.91, 127.89, 127.80, 127.78, 67.5, 67.3, 55.6, 55.3, 36.2, 35.5. HRMS (ESI, *m/z*) calcd for $C_{17}H_{17}NO_3Na$ $(M + Na)^+$ 306.1106, found 306.1092. Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94; found: C, 72.35; H, 5.99; N, 4.74.

*2-(Ts-amino)-1-phenylethanone (**10c**)*. Following the general procedure **D** compound **10c** was obtained from enol **2a** (0.25 mmol) and *N*-aminopyridinium salt **1g** (0.3 mmol). The crude product was purified by column chromatography to afford 67 mg of compound **10c** as white solid (Yield = 92%, 16 h). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.68 (s, 1H), 4.45 (d, *J*

= 4.5 Hz, 2H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.6, 143.7, 136.2, 134.4, 133.8, 129.8, 129.0, 127.9, 127.2, 48.7, 21.5. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[20]

*2-(Cbz-amino)-1-phenylethanone (**10d**)*. Following the general procedure **D** compound **10d** was obtained from enol **2a** (0.25 mmol) and *N*-aminopyridinium salt **1h** (0.3 mmol). The crude product was purified by column chromatography to afford 32 mg of compound **10d** as colorless oil (Yield = 48%, 48 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.41-7.29 (m, 5H), 5.80 (brs, 1H), 5.16 (s, 2H), 4.72 (d, *J* = 4.4 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.0, 156.3, 136.4, 134.4, 134.0, 128.9, 128.5, 128.2, 128.1, 127.9, 67.0, 47.9. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[52]

*2,3,4,5,6-pentafluoro-N-(2-oxo-2-phenylethyl)benzamide (**10e**)*. Following the general procedure **D** compound **10e** was obtained from enol **2a** (0.25 mmol) and *N*-aminopyridinium salt **1i** (0.3 mmol). The crude product was purified by column chromatography to afford 47 mg of compound **10e** as white solid (Yield = 57%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 -7.60 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.25 (brs, 1H), 4.96 (d, *J* = 4.3 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.0, 157.4, 145.4 (m), 143.4 (m), 141.4 (m), 138.7 (m), 136.7 (m), 134.5, 133.9, 129.0, 128.0, 111.0 (t, *J* = 18.5 Hz), 46.9. ^{19}F NMR (375 MHz, $CDCl_3$): δ -139.92-140.18 (m, 2F), -150.30 (tt, *J* = 20.7, 3.2 Hz, 1F), -159.82-160.18 (m, 2F). HRMS (ESI, *m/z*) calcd for $C_{15}H_8NO_2F_5Na$ $(M + Na)^+$ 352.0373, found 352.0365. Anal. Calcd for $C_{15}H_8F_5NO_2$: C, 54.72; H, 2.45; N, 4.25; found: C, 54.66; H, 2.39; N, 4.44.

*2,2,2-trifluoro-N-(2-oxo-2-phenylethyl)acetamide (**10f**)*. Following the general procedure **D** compound **10f** was obtained from enol **2a** (0.25 mmol) and *N*-aminopyridinium salt **1j** (0.3 mmol). The crude product was purified by column chromatography to afford 42 mg of compound **10f** as white solid (Yield = 72%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.48 (brs, 1H), 4.82 (d, *J* = 4.3 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.0, 157.2 (q, *J* = 37.8 Hz), 134.7, 133.7, 129.1, 128.0, 115.7 (q, *J* = 287.3 Hz), 46.2. ^{19}F NMR (375 MHz, $CDCl_3$): δ -75.7. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[53]

*((4-(1-((tert-butyldimethylsilyl)oxy)vinyl)-1,2-phenylene)bis(oxy))bis(tert-butyldimethylsilane) (**12**)*. Commercially available ketone **11** (0.5 mmol, 1.0 equiv) was placed in an oven-dried flask

sealed with a septum under Ar atmosphere and dissolved in anhydrous DCM (0.1 M). The solution was cooled to 0 °C, and then Et_3N (1.75 mmol, 3.5 equiv.) was added dropwise followed by the addition of TBDMSOTf (1.75 mmol, 3.5 equiv.). The mixture was stirred at room temperature for 16 h. The reaction was quenched by the addition of $NaCl_{(sat.)}$, extracted with DCM, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography on deactivated Al_2O_3 (neutral Al_2O_3 treated with 15 wt% of H_2O) using hexene as eluent to give 226 mg of product **12** as colorless oil (yield = 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 2.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 1.6 Hz, 1H), 4.29 (d, *J* = 1.6 Hz, 1H), 1.03-0.98 (m, 27H), 0.21 (d, *J* = 3.7 Hz, 18H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.7, 147.1, 146.3, 131.4, 120.4, 118.6, 118.4, 89.0, 25.9, 25.9, 18.5, 18.4, 18.3, -4.08, -4.12, -4.6. HRMS (ESI, *m/z*) calcd for $C_{26}H_{51}O_3Si_3$ $(M + H)^+$ 495.3146, found 495.3138.

*tert-butyl (2-(3,4-bis((tert-butyldimethylsilyl)oxy)phenyl)-2-oxoethyl)(methyl)carbamate (**13**)*. Following the general procedure **D** compound **13** was obtained from substrate **12** (0.46 mmol) and *N*-aminopyridinium salt **1b** (0.55 mmol). The crude product was purified by column chromatography to afford 188 mg of compound **13** as colorless oil (Yield = 80%, 16 h). ^{1}H NMR (400 MHz, $CDCl_3$): mixture of rotamers, δ 7.46-7.41 (m, 2H + *second rotamer 2H*), 6.85 (t, *J* = 7.5 Hz, 1H + *second rotamer 1H*), 4.59 (s, 2H, first rotamer), *4.48 (s, 2H, second rotamer)*, 2.95 (s, 3H, first rotamer), *2.92 (s, 3H, second rotamer)*, 1.48 (s, 9H, first rotamer), *1.36 (s, 9H, second rotamer)*, 0.98 (s, 18H + *second rotamer 18H*), 0.21-0.21 (m, 12H + *second rotamer 12H*). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) mixture of rotamers, δ 192.1, 152.7, 147.2, 143.5, 134.8, 129.6, 128.6, 127.6, 122.8, 120.7, 120.5, 55.8, 35.6, 25.9, 25.8, 21.5, 18.5, 18.4. HRMS (ESI, *m/z*) calcd for $C_{26}H_{47}NO_5Si_2Na$ $(M+Na)^+$ 532.2890, found 532.2879. Anal. Calcd for $C_{26}H_{47}NO_5Si_2$: C, 61.25; H, 9.29; N, 2.75; found: C, 61.13; H, 9.16; N, 2.65.

*adrenalone (**14**)*. Compound **13** (188 mg, 0.37 mmol) was dissolved in DCM (10 ml) and TFA (1.3 mmol, 3.5 quiv.) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. Then, the mixture was basified with $NaHCO_{3(sat)}$ to pH ~ 8 and extracted with DCM (3x30 ml). The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo to give 67 mg of adrenalone (**30**) as a yellow oil (yield = quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82-9.70 (m, 2H), 7.40-7.39 (m, 2H), 6.86-6.84 (m, 1H), 4.56-4.54 (m, 2H), 2.90 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1, 152.7, 147.2, 128.6, 127.6, 120.7, 120.5, 55.8,

35.6. The observed characterization data (^{1}H and ^{13}C) were consistent with those previously reported.[54]

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C NMR spectra and HPLC analyses are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Dorota Gryko, e-mail: dorota.gryko@icho.edu.pl

Present Addresses

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Notes

The authors declare no competing financial interests.

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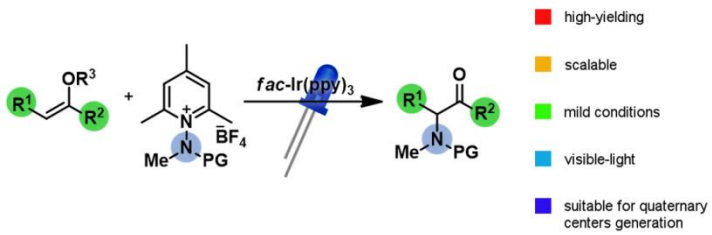
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