Cyclic (Alkyl)(amino)carbenes: Synthesis of Iminium Precursors and Structural Properties

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ABSTRACT: Using readily available pre-allylated aldehydes, we report a simple and divergent synthesis of cyclic (alkyl)(amino)carbene (CAAC) iminium precursors. Using a combination of crystallographic data and steric maps, we further elaborate on the specific steric properties of CAAC ligands with respect to state-of-the-art phosphine and carbene ligands.

INTRODUCTION

Since their discovery in 2005,[1,2] five-membered cyclic (alkyl)(amino)carbenes (CAAC-5) (Figure 1) have found numerous applications in homogeneous catalysis.[3] Better σ-donors and π-acceptors than the well-known N-heterocyclic carbenes (NHCs), these stable singlet carbenes own their growing popularity to the strong bonds they form with transition metals[4] and main group elements.[5] In parallel, we and others also demonstrated that their ambiphilic nature allows for the activation of enthalpically strong E-H bonds (E: N, P, Si, …);[6] a distinctive feature traditionally restricted to transition metals. Combined with their unique steric environment, a key factor for promoting reductive elimination at carbon,[7] these properties allowed the first non-metal catalyzed carbonylation reaction.[8] Despite these achievements,[9] a quick survey of the literature reveals that aside from recent additions to the CAAC ligand family (*i.e.* FunCAAC,[10] BiCAAC,[11] CAAC-6,[12] ChiCAAC[13], SpaceCAAC[14]), reports involving CAAC-5 ligands still largely rely on a handful of skeletons, namely ^{Me}CAAC-5, ^{Et}CAAC-5, ^{Menth}CAAC-5 and ^{Ad}CAAC-5. This is surprising, if we consider the versatility of both seminal synthetic procedures Route 1[1,2] and Route 2[15] (Scheme 1). To encourage further discoveries for CAAC-5 in catalysis, herein we report a divergent, and easily scalable route to iminium precursors of CAACs, using readily available pre-allylated aldehydes. Using crystallographic data and steric maps, we further elaborate on the distinct steric properties of CAACs with respect to popular ligand families, thus providing guidelines when considering CAACs as ligands for transition metals.

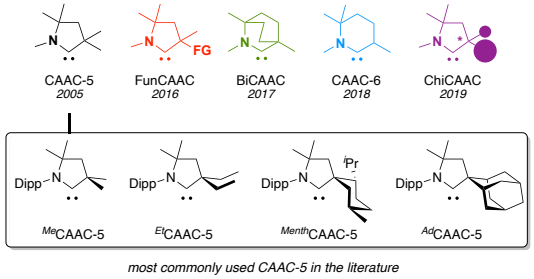
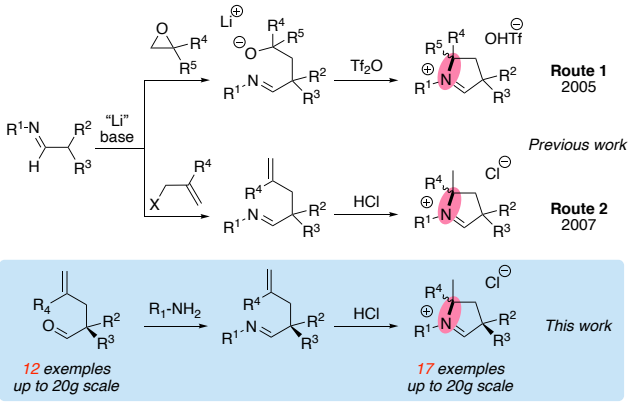


Figure 1. Known families of CAAC derivatives and most commonly used CAAC-5 motifs.

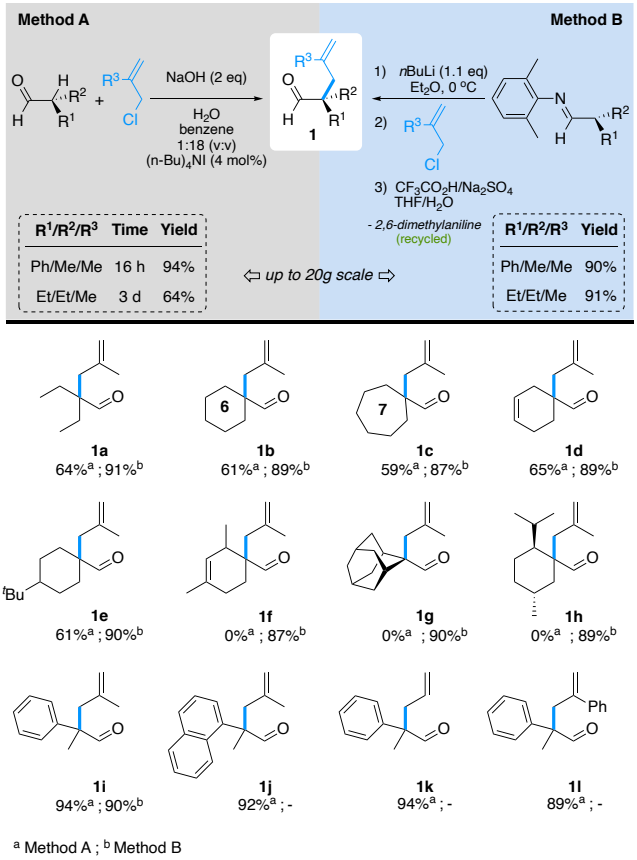


Scheme 1. Cyclic(alkyl)amino carbenes iminiums syntheses.

RESULTS AND DISCUSSION

We began our study by looking at the synthesis of pre-allylated aldehydes 1. To achieve a simplest and atom efficient strategy, we considered a phase transfer-catalyzed allylation of aldehydes (Method A) avoiding the use of *n*-BuLi (Scheme 2).[16] Rapid optimization of the reaction conditions allowed us to perform the allylation of 2-ethylbutanal and 2-phenylpropanal with 3-chloro-2-methylprop-1-ene (in 64% and 94%, respectively) in multigram quantities. The reaction was carried out in a benzene:water (18:1) mixture with sodium hydroxide as a base and tetra-butyl ammonium iodide as a phase transfer agent. Under these conditions we also obtained good to excellent yields of pre-allylated aldehydes 1a-e and 1i-l with the exception of 1f-1h which afforded inseparable mixtures of products. In this case, we considered an alternative methodology. Deprotonation of a sacrificial 2,6-dimethylaniline imine with *n*-BuLi,[17] followed by allylation with a suitable allyl electrophile and hydrolysis of the resulting pre-allylated imine under acid conditions (Method B). Note that hydrolysis using HCl (> 2M) resulted in partial to complete isomerization of the terminal olefin to the

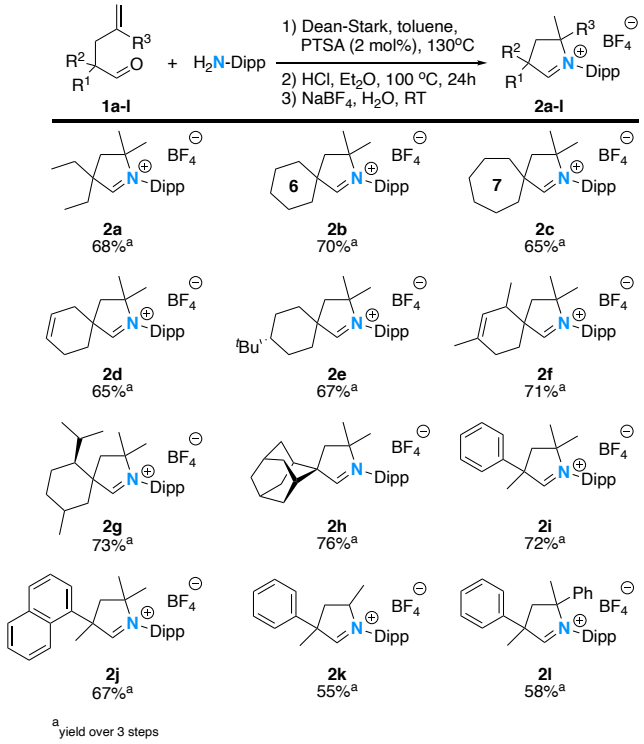
internal olefin. However milder conditions using trifluoroacetic acid in the presence of sodium sulfate gave the desired pre-allylated aldehydes 1f-1h in excellent yields.[18] More importantly, recycling of 2,6-dimethylaniline was achieved through a simple acid/base workup, thus increasing significantly the overall atom economy of the method. Method B is also amenable to multiple designs and large-scale synthesis.



[a] Method A ; [b] Method B

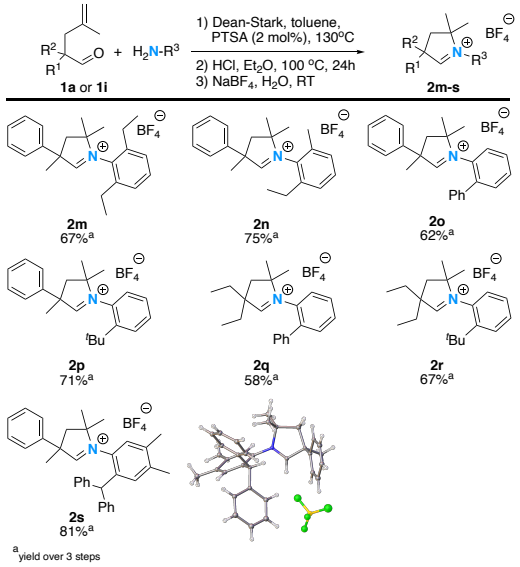
Scheme 2. Proposed strategies and scope for the preparation of pre-allylated aldehydes.

Having obtained a range of pre-allylated aldehydes, we next evaluated their use as precursors for CAAC iminiums. The condensation of aldehydes featuring a tertiary carbon in α-position can be challenging when using bulky or deactivated anilines.[19] However, upon screening a number of conditions, we achieved consistent conversions in a reasonable time when performing the condensation in a Dean-Stark apparatus using PTSA (2 mol%) at reflux (Scheme 3). Under these conditions the corresponding imines were isolated in quantitative yields, but they can also be engaged in the next step without further purification. The intramolecular hydro-iminiumation step was achieved by treating the resulting aldimine with two equivalents of dry hydrochloric acid (2M in Et_2O) and heating the resulting mixture at 100 °C for 24 h. Subsequent anion exchange with $NaBF_4$ in water to replace HCl_2^- afforded the corresponding CAAC.BF_4 conjugate acids 2a-2l in good to excellent yields (over 3 steps). As expected, the availability of the pre-allylated aldehydes allows for a divergent access to N-aryl substituted iminiums as seen with compounds 2m-2r (Scheme 4). More importantly, it provides a mean to access iminiums which are difficult to obtain otherwise. This is the case with compound 2s which cannot be synthesized via either Route 1 or 2 (Figure 1) due to the presence of an *o*-trityl group on the aniline fragment which conflicts with the deprotonation of the aldimine using *n*-BuLi.



[a] yield over 3 steps

Scheme 3. Scope for the synthesis of various Dipp-substituted CAAC ligands



[a] yield over 3 steps

Scheme 4. Scope for various substituents on the nitrogen

Then, we examined this library of CAAC precursors, using SambaVca 2.1,[20] a convenient tool for evaluating the steric map of ligands.[21,22,23] For comparison, we also considered classical and non-classical phosphines and NHCs, meanwhile highlighting steric contributions at a main group element (ca. 0 Å), and a putative transition metal (ca. 2 Å). As shown in Figure 2, there are distinct steric map profiles between all three ligand families. With phosphines, at the exception of tailored motifs, such as Buchwald type ligands (e.g. JohnPhos),[24] the volume sits preferentially above the coordination sphere. On the contrary with NHCs, it largely occupies confined hemispheres flanking the carbene center on both sides. This is in marked contrast with CAACs which appear to provide a rather even distribution bellow the coordination plane. This singularity is well evidenced

in the ^{Menth}CAAC 2g which is comparatively the bulkiest motif at carbon, despite being deprived of "bulk-by-design" as in P(*t*Bu)$_3$, P(Ad)$_3$[25], IPr*[26] and IPr**[27]. Consequently, we believe that the steric environment around the CAACs is better described as inverted with respect to that of phosphines, whereas popular aryl substituted NHCs behave more as a double wall flanking the carbene center. Interestingly, the presence of a quaternary carbon in α-position of the carbene center allows for non-linear modulations of the steric environment. This is well evidenced with ^{Triv}CAAC 2f and *tert*-butylcyclohexyl CAAC 2e which are comparatively less sterically demanding than ^{Menth}CAAC 2g at carbon (V_{Bur} = 81.6 and 79.0 respectively), yet more demanding at a putative metal center (V_{Bur} = 51.4 and 53.3). Interestingly, this specificity was recently exploited by Hong and co-workers in designing a reversibly photoswitchable catalysts for olefin metathesis reactions.[28]

In conclusion, we report a divergent synthetic route to CAAC ligand precursors which relies on readily available pre-allylated aldehydes. This methodology allows for accessing CAAC precursors which were not available with the previously described routes 1 and 2. We highlight marked differences in the steric profiles of CAACs compared to other popular ligand families. We expect that these results will foster new designs of CAAC ligands, including a range of chiral CAACs variants (ChiCAACs) providing the use of pre-allylated enantiopure aldehydes.

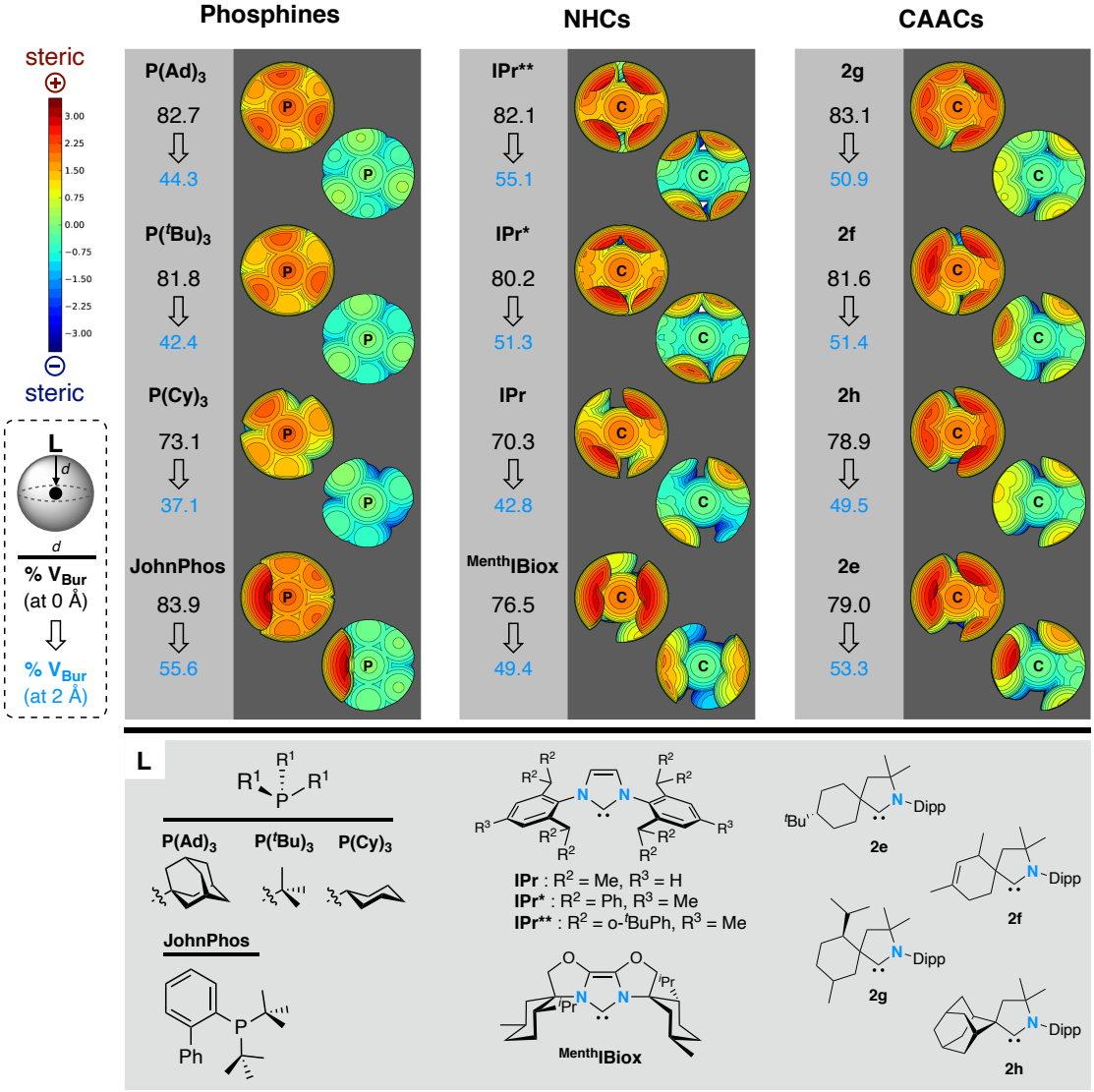


Figure 2. Comparison of percent buried volume and steric maps in phosphines, NHCs and CAACs.

EXPERIMENTAL SECTION

General Methods. All reactions involving chemicals sensitive to water and/or oxygen were carried out under dry argon using standard glovebox and Schlenk techniques. Unless otherwise stated, the organic solvents were dried and purified according to standard procedures and stored under argon. Flash chromatography (pressure, 1.5 bar) was carried out using silica gel as the stationary phase (35–70 µm, Merck). The silica gel was treated with 25% aqueous ammonia solution (7% by weight related to the silica gel), and the resulting mixture was shaken until a homogeneous powder was obtained. Imines derived from 2,6-dimethylaniline were obtained according to standard literature procedures.[29] NMR Characterization: Deuterium-labeled solvents were purchased from Cambridge Isotope Laboratories. NMR: Multinuclear NMR data were recorded on a Varian INOVA 500 MHz and a Bruker Avance 300 MHz at UCSD. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual solvent signals (^{1}H, ^{13}C). Coupling constants J are given in Hertz (Hz). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q =

quartet, sext = sextet, sept = septet, m = multiplet, br = broad. All spectra were recorded at 298 K unless otherwise noted.

General Method A for the synthesis of pre-allylated aldehydes. A mixture of aldehyde (22.4 mmol) and chloro-alkene (22.4 mmol) was added dropwise at 60 °C within 3 h to a vigorously stirred mixture of powdered sodium hydroxide (1.34 g, 33.5 mmol), tetra-n-butylammonium iodide (82.7 mg, 224 µmol), water (2.69 mL), and benzene (50 mL). After the addition was complete, the mixture was stirred at 60 °C for 16 h (if R^2 = alkyl and R^3 = aryl) or 72h (if R^2 and R^3 = alkyls) and was then cooled to 20 °C, followed by sequential addition of water (25 mL) and Et_2O (25 mL). The organic layer was separated, the aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate (99:1 v/v)) or distillated to afford the desired products as colorless liquids. Special note: When "R^2 and R^3 = alkyls", the concentration of the reaction becomes a critical component to prevent side reactions. In this case, a higher dilution of the regents is most desirable. In contrary, when "R^2 = alkyl and R^3 = aryl", the reaction may be performed at a higher concentration and a shorter time than the standard conditions described herewith.

General Method B for the synthesis of pre-allylated aldehydes. Step 1: To a solution of 2,6-dimethylaniline imine (22.4 mmol) in Et_2O (50 ml) cooled to -78 °C was added *n*-butyllithium (2.5 M in hexanes, 1.1 eq.) and the mixture was allowed to warm up to room temperature. Step 2: After 2h the mixture was cooled to -78 °C and the corresponding alkyl halide (1.2 eq.) was added. The reaction was slowly warmed up and stirred overnight at room temperature. The crude mixture was washed with water (2x 50 ml) and the organic phase was evaporated under reduced pressure to afford a crude oily residue. Step 3:[18] To this residue were added trifluoroacetic acid (7 eq.), Na_2SO_4 (65 eq.), THF/H_2O (10:1, 200 ml) and the mixture was stirred at room temperature for 36h. The mixture was diluted with Et_2O (200mL), and then washed with 10% HCl to recover the 2,6-dimethylaniline salt (Note! higher concentration of HCl will trigger an isomerization of the olefin moiety). Washing of the organic phase with a saturated solution of $NaHCO_3$ and brine, drying over $MgSO_4$ and concentration under vacuum afforded a crude residue which was further purified on silica gel (n-hexane/ethyl acetate (99:1 v/v)).

General Method for the synthesis of CAAC.HBF$_4$ salts. A pre-allylated aldehyde (22.4 mmol), an aniline (22.4 mmol), *p*TSOH (cat.) and toluene (40 mL) were combined in a round-bottom flask fitted with a Dean-Stark apparatus. The mixture was set to reflux for 16h. After this time, the reaction vessel was cooled to room temperature and the formation of the corresponding imine was confirmed by NMR. The mixture was transferred to a heavy wall pressure schlenk of 100 mL with help of 2x 10 mL of dry toluene under argon atmosphere. The toluene was then removed under high vacuum, before adding 2.5 equivalents (with respect to the aldehyde) of hydrogen chloride (2M in Et_2O) at 0 °C. Immediate precipitation of the intermediate aldiminium was observed. The mixture was sealed and stirred under argon atmosphere at 100 °C for 24h. After this time the pressure schlenk was brought back to room temperature and left stirring for 2h to enforce precipitation of the product before being carefully opened to argon line. Removal of the supernatant via canula, and further washing with dry Et_2O (3x 50 mL) afforded an off-white powder. The latter was dissolved in DCM (50 mL), to which was added an aqueous solution of sodium tetrafluoroborate (2 eq./imine). After stirring the biphasic mixture for 1h at room temperature, the organic phase was separated, washed with water (3 x 25 mL) and dried over $MgSO_4$. Following evaporation of the DCM under vacuum, a white powder was obtained. After dissolution in Et_2O, precipitation with pentane and filtration, the iminium was obtained as a white crystalline solid.

2,2-diethyl-4-methylpent-4-enal (**1a**): The reaction was performed using 200 mmol of 2-ethylbutyraldehyde. Yields provided hereafter result from an average of 3 runs. Method A: colorless oil (64% yield). Method B: light pink oil (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 4.81 (d, 1H, J=1.5Hz), 4.68 (d, 1H, J=1.5Hz), 2.25 (s, 2H), 1.63 (s, 3H), 1.59 (dq, 2H, J=1.0Hz, J=7.5Hz), 1.48 (dq, 2H, J=1.0Hz, J=7.5Hz), 0.79 (t, 3H, J=7.5Hz), 0.79 (t, 3H, J=7.5Hz) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 207.5, 141.7, 115.0, 52.8, 41.3, 24.3, 23.5, 7.8 HRMS: m/z calculated for $[C_{10}H_{19}O]^+$ $[M+H]^+$ 155.1430, found 155.1429.

1-(2-methylallyl)cyclohexane-1-carbaldehyde (**1b**). Method A: Colorless oil (61% yield). Method B: Light pink oil (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.51 (s, 1H), 4.82 (d, 1H, J=2.0Hz), 4.66 (d, 1H, J=2.0Hz), 2.20 (s, 2H), 1.85-1.88 (m, 2H), 1.63 (s, 3H), 1.55-1.59 (m, 2H), 1.23-1.37 (m, 6H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 207.5, 141.1, 115.2, 49.8, 45.3, 31.4, 25.8, 24.5, 22.6 HRMS: m/z calculated for $[C_{11}H_{19}O]^+$ $[M+H]^+$ 167.1430, found 167.1432.

1-(2-methylallyl)cycloheptane-1-carbaldehyde **(1c).** Method A: Colorless oil (59% yield). Method B: Colorless oil (87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 4.82 (d, 1H, J=2.0Hz), 4.66 (d, 1H, J=2.0Hz), 2.25 (s, 2H), 1.62 (s, 3H), 1.44-1.52 (m, 8H), 1.19-1.26 (m, 4H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 206.6, 141.7, 115.3, 52.9, 45.9, 32.5, 30.8, 24.3, 22.8 HRMS: m/z calculated for $[C_{12}H_{21}O]^+$ $[M+H]^+$ 181.1587, found 181.1585.

1-(2-methylallyl)cyclohex-2-ene-1-carbaldehyde **(1d).** Method A: Colorless oil (65% yield). Method B: Light pink oil (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 5.67 (m, 2H), 4.83 (d, 1H, J=1.5Hz), 4.67 (d, 1H, J=1.5Hz), 2.34 (d, 1H, J=14.0Hz), 2.19 (d, 1H, J=14.0Hz), 2.04-2.12 (m, 2H), 1.92-2.01 (m, 2H), 1.85-1.90 (m, 1H), 1.64 (s, 3H), 1.52-1.58 (m, 1H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 206.2, 141.1, 126.8, 124.6, 115.3, 48.2, 44.5, 29.7, 28.0, 24.4, 22.4 HRMS: m/z calculated for $[C_{11}H_{17}O]^+$ $[M+H]^+$ 165.1275, found 165.1275.

4-(tert-butyl)-1-(2-methylallyl)cyclohexane-1-carbaldehyde **(1e).** Method A: Colorless oil (61% yield). Method B: Colorless oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 4.81 (d, 1H, J=1.5Hz), 4.63 (d, 1H, J=1.5Hz), 2.10 (s, 2H), 1.64 (s, 3H), 1.25 (m, 1H), 1.19-1.21 (m, 2H), 1.12-1.15 (m, 2H), 0.89-0.94 (m, 2H), 0.82-0.85 (m, 2H), 0.78 (s, 9H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 208.3, 141.3, 115.6, 49.8, 47.6, 47.1, 32.4, 32.2, 27.3, 24.4, 23.9 HRMS: m/z calculated for $[C_{15}H_{27}O]^+$ $[M+H]^+$ 223.2056, found 223.2056.

(1S)-2,4-dimethyl-1-(2-methylallyl)cyclohex-3-ene-1-carbaldehyde **(1f)**. Method A: Inseparable mixture of products. Method B: Colorless oil (87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.68 (s, 1H), 5.28 (m, 1H), 4.83 (d, 1H, J=1.5Hz), 4.69 (d, 1H, J=1.5Hz), 2.40 (d, 1H, J=14.0Hz), 2.35 (d, 1H, J=14.0Hz), 1.93-1.96 (m, 2H), 1.72-1.74 (m, 1H), 1.65 (s, 3H), 1.64 (s, 3H), 1.00-1.05 (m, 2H), 0.90 (d, 3H, J=7.0Hz) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 207.8, 141.9, 133.0, 124.9, 115.3, 50.6, 41.8, 35.8, 26.9, 24.4, 23.4, 21.9, 17.7 HRMS: m/z calculated for $[C_{13}H_{21}O]^+$ $[M+H]^+$ 193.1587, found 193.1587.

(1R,3S,5r,7r)-2-(2-methylallyl)adamantane-2-carbaldehyde **(1g)**. Method A: Inseparable mixture of products. Method B: Colorless oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 4.84 (d, 1H, J=1.5Hz), 4.68 (d, 1H, J=1.5Hz), 2.42 (s, 2H), 2.04-2.07 (m, 4H), 1.84-1.90 (m, 2H), 1.78-1.84 (m, 2H), 1.67 (s, 3H), 1.62-1.72 (m, 3H), 1.23-1.27 (m, 2H), 1.12-1.15 (m, 1H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 209.7, 141.4, 115.9, 54.2, 41.6, 38.0, 34.4, 32.0, 31.2, 27.5, 27.3, 24.7 HRMS: m/z calculated for $[C_{15}H_{23}O]^+$ $[M+H]^+$ 219.1743, found 219.1744.

(1S,2S,5R)-2-isopropyl-5-methyl-1-(2-methylallyl)cyclohexane-1-carbaldehyde **(1h)**. Method A: Inseparable mixture of products. Method B: Colorless oil (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.0 (s, 1H), 4.83 (d, 1H, J=1.5Hz), 4.66 (d, 1H, J=1.5Hz), 2.87 (d, 1H, J=13.5), 2.34 (m, 1H), 2.02 (d, 1H, J=13.5Hz), 1.87-1.92 (m, 1H), 1.74-1.79 (m, 2H), 1.63 (s, 3H), 1.54-1.59 (m, 2H), 1.28 (m, 1H), 1.17-1.23 (m, 2H), 0.95 (d, 3H, J=7.0Hz), 0.85 (d, 3H, J=7.0Hz), 0.75 (d, 3H, J=7.0Hz) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 209.2, 142.3, 115.7, 53.3, 52.5, 44.5, 41.2, 35.1, 28.5, 24.9, 24.3, 24.1, 22.9, 22.9, 18.7 HRMS: m/z calculated for $[C_{15}H_{27}O]^+$ $[M+H]^+$ 223.2056, found 223.2054.

2,4-dimethyl-2-phenylpent-4-enal (**1i**). The reaction was performed using 150 mmol of 2-phenylpropanal. Yields provided hereafter result from an average of 3 runs. Method A: Colorless viscous oil (94% yield). Method B: Colorless viscous oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 7.34 (t, 2H, J=7.5Hz), 7.23-7.26 (m, 3H), 4.77 (d, 1H, J=1.5Hz), 4.59 (d, 1H, J=1.5Hz), 2.69 (d, 1H, J=14.0Hz), 2.62 (d, 1H, J=14.0Hz), 1.43 (s, 3H), 1.36 (s, 3H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 202.1, 141.6, 139.9, 128.9, 128.7, 127.4, 115.5, 53.6, 44.3, 24.2, 18.6 HRMS: m/z calculated for $[C_{13}H_{17}O]^+$ $[M+H]^+$ 189.1274, found 189.1274.

2,4-dimethyl-2-(naphthalen-1-yl)pent-4-enal **(1j)**. Method A: Colorless viscous oil (92% yield). Method B: Not performed. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.60 (s, 1H), 7.83-7.87 (m, 3H), 7.75 (m, 1H), 7.49-7.52 (m, 2H), 7.41 (dd, 1H, J=2.0Hz, J=8.5Hz), 4.81 (d, 1H, J=1.5Hz), 4.65 (d, 1H, J=1.5Hz), 2.82 (d, 1H, J=14.0Hz), 2.78 (d, 1H, J=14.0Hz), 1.58 (s, 3H), 1.40 (s, 3H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 202.1, 141.6, 137.3, 133.5, 132.5, 128.6, 128.2, 127.7, 126.5, 126.5, 126.4, 125.4, 115.6, 53.8, 44.2, 24.4, 18.8 HRMS: m/z calculated for $[C_{17}H_{19}O]^+$ [M+H]$^+$ 239.1430, found 239.1431.

2-methyl-2-phenylpent-4-enal **(1k)**. Method A: Colorless viscous oil (94% yield). Method B: Not performed. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.52 (s, 1H), 7.39 (t, 2H, J=7.5Hz), 7.30-7.34 (m, 1H), 7.26 (d, 2H, J=7.5Hz), 5.50-5.58 (m, 1H), 5.06 (dd, 1H, J=1.5Hz, J=17.0Hz), 5.03 (dd, 1H, J=1.5Hz, J=11.0Hz), 2.69 (dd, 1H, J=7.0Hz, J=14.0Hz), 2.62 (dd, J=7.0Hz, J=14.0Hz), 1.44 (s, 3H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 202.1, 139.5, 133.3, 129.0, 127.5, 127.3, 118.7, 53.7, 40.7, 18.9 HRMS: m/z calculated for $[C_{12}H_{15}O]^+$ [M+H]$^+$ 175.1117, found 175.1114 HRMS: m/z calculated for $[C_{12}H_{15}O]^+$ [M+H]$^+$ 175.1117, found 175.1114.

2-methyl-2,4-diphenylpent-4-enal (**1l**). Method A: Colorless viscous oil (89% yield). Method B: Not performed. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.42 (s, 1H), 7.31-7.34 (m, 2H), 7.22-7.26 (m, 7H), 5.19 (d, 1H, J=1.5Hz), 4.94 (d, 1H, J=1.5Hz), 3.32 (d, 1H, J=14.0Hz), 3.11 (d, 1H, J=14.0Hz), 1.31 (s, 3H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 200.7, 144.5, 141.4, 138.9, 128.0, 127.5, 126.7, 126.6, 126.5, 125.9, 116.9, 53.5, 40.8, 18.1 HRMS: m/z calculated for $[C_{18}H_{19}O]^+$ [M+H]$^+$ 251.1430, found 251.1429.

Cyclic Iminium **2a.** White powder (68% yield). ^{1}H NMR (300 MHz, CD_3CN) δ = 8.86 (s, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 2H), 2.69 (sept, J = 6.6 Hz, 2H), 2.38 (s, 2H), 1.95 (q, J = 7.5 Hz, 4H), 1.52 (s, 6H), 1.33 (d, J = 6.6 Hz, 6H), 1.08 (d, J = 6.6 Hz, 6H), 1.05 (t, J = 7.5 Hz, 6H) ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ = 193.0, 145.4, 132.9, 130.1, 126.5, 85.0, 57.2, 44.1, 30.4, 29.7, 28.6, 26.2, 22.1, 9.2 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{22}H_{36}N]$+ [M]+ 314.2842, found 314.2842.

Cyclic Iminium **2b.** White powder (70% yield). ^{1}H NMR (300 MHz, CD_3CN) δ = 8.80 (s, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.47 (d, J = 7.9 Hz, 2H), 2.71 (sept, J = 6.7 Hz, 2H), 2.46 (s, 2H), 1.90-2.05 (m, 8H), 1.56-1.85 (m, 6H), 1.52 (s, 6H), 1.34 (d, J = 6.7 Hz, 6H), 1.08 (d, J = 6.7 Hz, 6H) ^{13}C NMR (126 MHz, CD_3CN) δ = 190.9, 145.4, 132.9, 130.0, 126.3, 84.9, 53.5, 45.9, 34.6, 30.2, 28.7, 26.0, 25.2, 22.1, 22.0 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{23}H_{36}N]$+ [M]+ 326.2842, found 326.2842.

Cyclic Iminium **2c.** White powder (65% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 8.81 (s, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.47 (d, J = 7.9 Hz, 2H), 2.71 (sept, J = 6.7 Hz, 2H), 2.46 (s, 2H), 1.91-2.01 (m, 6H), 1.58-1.82 (m, 6H), 1.52 (s, 6H), 1.34 (d, J = 6.7 Hz, 6H), 1.08 (d, J = 6.7 Hz, 6H) ^{13}C NMR (126 MHz, CD_3CN) δ = 190.6, 145.5, 132.9, 129.9, 126.4, 84.9, 55.6, 47.1, 37.6, 30.2, 29.5, 28.4, 26.1, 24.4, 22.1 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{24}H_{38}N]$+ [M]+ 340.2999, found 340.2996.

Cyclic Iminium **2d.** White powder (65% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 8.82 (s, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 5.88 (m, 1H), 5.76 (m, 1H), 2.72 (sept, *J* = 6.7 Hz, 2H), 2.58-2.65 (m, 1H), 2.43-2.52 (m, 2H), 2.39 (m, 1H), 2.20-2.29 (m, 3H), 2.03-2.11 (m, 1H), 1.54 (s, 6H), 1.34 (d, *J* = 6.7 Hz, 6H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H) ^{13}C NMR (126 MHz, CD_3CN) δ = 190.5, 145.3, 132.9, 130.0, 128.2, 126.4, 123.1, 85.0, 51.3, 46.3, 34.2, 31.3, 30.2, 28.7, 28.4, 26.0, 22.2 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{23}H_{34}N]$+ [M]+ 324.2686, found 324.2682.

Cyclic Iminium **2e**. White powder (67% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 9.14 (s, 1H), 7.61 (t, *J* = 6.9 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 2H), 2.72 (sept, *J* = 6.7 Hz, 2H), 2.38 (s, 2H), 2.30-2.34 (m, 1H), 1.88-1.98 (m, 4H), 1.36-1.41 (m, 2H), 2.25-1.29 (m, 2H), 1.53 (s, 6H), 1.13 (d, *J* = 6.7 Hz, 6H), 0.89 (s, 9H) ^{13}C NMR (126 MHz, CD_3CN) δ = 192.0, 145.5, 132.9, 130.3, 126.3, 83.8, 52.7, 48.8, 47.7, 37.7, 32.4, 29.7, 27.9, 27.1, 25.3, 24.6, 21.6 ^{19}F NMR (282 MHz, CD_3CN) δ = -152.3 HRMS: m/z calculated for $[C_{27}H_{44}N]$+ [M]+ 382.3468, found 382.3470.

Cyclic Iminium **2f.** White powder (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.07 (s, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 5.25 (s, 1H), 2.53 (sept, *J* = 6.6 Hz, 2H), 2.46-2.49 (m, 1H), 2.36 (s, 2H), 2.01 (t, J = 6.2 Hz, 2H), 1.80-1.89 (m, 2H), 1.62 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H), 1.24 (d, *J* = 6.6 Hz, 6H), 1.13-1.18 (m, 6H), 1.09 (d, *J* = 6.6 Hz, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.3, 144.6, 144.0, 134.0, 131.9, 129.1, 125.4, 125.3, 123.9, 83.0, 55.1, 46.1, 39.7, 30.4, 30.0, 29.9, 29.2, 28.3, 26.8, 26.7, 26.3, 23.4, 22.2, 18.8 HRMS: m/z calculated for $[C_{25}H_{38}N]$+ [M]+ 352.3004, found 352.3000.

Cyclic Iminium **2g**. White powder (73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = δ = 9.23 (s, 1H), 7.40 (t, 1H, J=7.5Hz), 7.21 (d, 1H, J=7.5Hz), 7.20 (d, 1H, J=7.5Hz), 2.55 (m, 1H), 2.51 (sept, 2H, J=7.0Hz), 2.13 (m, 1H), 2.08 (m, 1H), 1.94 (sept, 1H, J=7.0Hz), 1.87-1.91 (m, 1H), 1.61-1.72 (m, 4H), 1.46 (s, 3H), 1.42 (s, 3H), 1.23 (d, 3H, J=7.0Hz), 1.22 (d, 3H, J=7.0Hz), 1.06 (d, 3H, J=7.0Hz), 1.02 (d, 3H, J=7.0Hz), 0.93 (d, 3H, J=7.0Hz), 0.87-0.93 (m, 2H), 0.81 (d, 3H, J=7.0Hz), 0.68 (d, 3H, J=7.0Hz) ^{13}C NMR (126 MHz, $CDCl_3$) δ = 192.5, 145.2, 145.1, 132.3, 129.4, 126.1, 125.6, 81.9, 58.5, 52.2, 51.1, 45.5, 34.6, 29.9, 29.4, 29.1, 28.1, 27.0, 26.7, 25.5, 22.7, 22.6, 22.1, 22.1, 22.1, 18.5 ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.7 HRMS: m/z calculated for $[C_{27}H_{44}N]$+ [M]+ 382.3468, found 382.3466.

Cyclic Iminium **2h.** White powder (76% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 9.23 (s, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 2.70 (sept, *J* = 6.5 Hz, 2H), 2.58 (s, 2H), 2.23 (m, 2H), 2.11-2.14 (m, 2H), 1.92-2.03 (m, 6H), 1.85-1.88 (m, 4H), 1.52 (s, 6H), 1.33 (d, *J* = 6.5 Hz, 6H), 1.10 (d, *J* = 6.5 Hz, 6H) ^{13}C NMR (126 MHz, CD_3CN) δ = 191.5, 145.3, 144.0, 132.8, 130.3, 126.3, 126.3, 84.1, 59.4, 46.4, 37.8, 37.3, 34.2, 33.3, 30.2, 28.7, 28.0, 27.0, 28.8, 22.1 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{27}H_{40}N]$+ [M]+ 378.3155, found 378.3152.

Cyclic Iminium **2i.** White powder (72% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 9.26 (s, 1H), 7.64 (t, 1H, J=7.5Hz), 7.55 (t, 2H, J=7.5Hz), 7.52 (d, 1H, J=7.5Hz), 7.48 (d, 2H, J=7.5Hz), 7.45 (d, 2H, J=7.5Hz), 3.10 (d, 1H, J=14.0Hz), 2.82 (d, 1H, J=14.0Hz), 2.79 (sept, 1H, J=7.0Hz), 2.55 (sept, 1H, J=7.0Hz), 1.93 (s, 3H), 1.58 (s, 3H), 1.40 (s, 3H), 1.39 (d, 3H, J=7.0Hz), 1.25 (d, 3H, J=7.0Hz), 1.15 (d, 3H, J=7.0Hz), 1.08 (d, 3H, J=7.0Hz) ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ = 189.8, 145.7, 145.4, 142.0, 133.2, 130.8, 130.0, 129.6, 126.7, 126.6, 126.6, 85.3, 55.7, 48.6, 29.9, 29.7, 27.2, 26.8, 26.8, 25.6, 25.5, 21.5, 21.4 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{25}H_{34}N]$+ [M]+ 348.2686, found 348.2687.

Cyclic Iminium **2j.** White powder (67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.89 (s, 1H), 8.03 (d, 1H, J=8.0Hz), 7.91 (d, 1H, J=8.0Hz), 7.80 (d, 1H, J=8.0Hz), 7.61 (t, 1H, J=7.5Hz), 7.52-7.55 (m, 2H), 7.33-7.38 (m, 4H), 3.30 (d, 1H, J=14.0Hz), 3.19 (d, 1H, J=14.0Hz), 2.70 (sept, 1H, J=6.5Hz), 2.69 (sept, 1H, J=6.5Hz), 2.15 (s, 3H), 1.54 (s, 3H), 1.37 (d, 3H, J=6.5Hz), 1.31 (d, 3H, J=6.5Hz), 1.25 (s, 3H), 1.23 (d, 3H, J=6.5Hz), 1.20 (d, 3H, J=6.5Hz) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 191.6, 145.3, 144.3, 138.3, 135.8, 132.6, 130.5, 130.1, 129.3, 129.3, 127.2, 126.6, 126.0, 126.0, 125.6, 124.8, 123.5, 84.0, 55.8, 50.0, 30.0, 29.4, 28.1, 26.9, 26.9, 25.9, 25.6, 22.3, 22.0 ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.7 HRMS: m/z calculated for $[C_{29}H_{36}N]$+ [M]+ 398.2842, found 398.2835.

Cyclic Iminium **2k.** White powder (55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.33 (s, 1H), 9.27 (s, 0.8H), 7.61 (d, 1.8H, J=8.0Hz), 7.50 (t, 1H, J=8.0Hz), 7.42-7.46 (m, 6.2H), 7.30-7.39 (m, 2.8H,), 7.28 (d, 1.8H, J=8.0Hz), 7.14 (d, 0.8H, J=8.0Hz), 5.10 (m, 1H), 4.72 (m, 0.8H), 3.51 (dd, 0.8H, J=6.0Hz, J=14.0Hz), 3.17 (dd, 1H, J=6.0Hz, J=14.0Hz), 2.64-2.71 (m, 1.8H), 2.57-2.62 (m, 1.8H), 2.30-2.40 (m, 1.8H), 1.94 (s, 2.4H), 1.89 (s, 3H), 1.42 (d, 2.4H, J=6.5Hz), 1.29-1.33 (m, 8.4H), 1.25 (d, 3H, J=6.5Hz), 1.24 (d, 2.4H, J=6.5Hz), 1.21 (d, 3H, J=6.5Hz), 1.11 (d, 3H, J=6.5Hz), 1.01 (d, 2.4H, J=6.5Hz), 0.70 (d, 2.4H, J=6.5Hz) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 189.4, 188.7, 144.4, 143.8, 143.6, 143.6, 140.7, 136.8, 132.4, 132.4, 130.6, 130.4, 130.2, 129.7, 128.9, 127.0, 125.9, 125.5, 125.4, 72.8, 72.6, 56.5, 56.0, 43.4, 42.0, 29.2, 29.0, 29.0, 28.2, 26.1, 25.2, 25.1, 24.8, 24.0, 24.0 23.3, 22.6, 22.4, 17.1, 17.1 ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.2 HRMS: m/z calculated for $[C_{24}H_{32}N]$+ [M]+ 334.2529, found 334.2530.

Cyclic Iminium **2l**. White powder (75% yield). Mixture of two atropisomers (ratio of 3.2:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.96 (s, 1H), 9.71 (s, 0.3H), 7.60 (d, 2H, J=8.8Hz), 7.49-7.54 (m, 4.9H), 7.39-7.45 (m, 2.9H), 7.32-7.37 (m, 1.6H), 7.29 (t, 2H, J=8.8Hz), 7.21 (t, 0.6H, J=8.8Hz), 7.02-7.06 (m, 2.3H), 6.91 (d, 2H, J=8.8Hz), 3.87 (d, 0.3H, J=14.4Hz), 3.55 (d, 1H, J=13.6Hz), 3.39 (d, 1H, J=13.6Hz), 3.03

(d, 0.3H, J=14.4Hz), 2.93 (sept, 0.3H, J=6.8Hz), 2.70 (sept, 1H, J=6.8Hz), 2.21 (s, 0.9H), 2.11 (s, 0.9H), 2.05 (s, 3H), 1.75 (sept, 1H, J=6.8Hz), 1.60 (s, 3H), 1.60 (m, 0.3H), 1.52 (d, 0.9H, J=6.8Hz), 1.36 (d, 3H, J=6.8Hz), 1.35 (d, 0.9H, J=6.8Hz), 1.34 (d, 3H, J=6.8Hz), 0.98 (d, 3H, J=6.8Hz), 0.86 (d, 0.9H, J=6.8Hz), 0.21 (d, 3H, J=6.8Hz), 0.18 (d, 0.9H, J=6.8Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 190.7, 145.1, 144.8, 141.1, 135.6, 132.5, 130.4, 130.2, 129.4, 129.1, 128.9, 127.5, 126.7, 125.7, 124.8, 87.0, 55.6, 45.9, 30.9, 30.5, 29.3, 29.1, 25.9, 25.4, 23.4, 20.1 ^{19}F NMR (282 MHz, $CDCl_3$) δ = -151.7 HRMS: m/z calculated for $[C_{30}H_{36}N]+$ [M+H]+ 410.2842, found 410.2841.

Cyclic Iminium **2m**. White powder (67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 7.47 (t, 2H, J=7.5Hz), 7.44 (d, 2H, J=7.5Hz), 7.42 (d, 1H, J=7.5Hz), 7.33 (t, 1H, J=7.5Hz), 7.31 (d, 1H, J=7.5Hz), 7.24 (d, 1H, J=7.5Hz), 3.16 (d, 1H, J=14.0Hz), 2.67 (d, 1H, J=14.0Hz), 2.55 (q, 2H, J=7.5Hz), 2.33 (dt, 1H, J=7.5Hz), 2.16 (dt, 1H, J=7.5Hz), 1.91 (s, 3H), 1.52 (s, 3H), 1.31 (s, 3H), 1.26 (t, 3H, J=7.5Hz), 1.09 (t, 3H, J=7.5Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 190.5, 141.0, 140.2, 139.7, 131.8, 131.0, 130.3, 128.9, 128.3, 128.1, 126.0, 83.8, 55.5, 48.3, 28.9, 26.9, 26.6, 24.8, 24.6, 15.3, 14.5 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.6 HRMS: m/z calculated for $[C_{23}H_{30}N]+$ [M]+ 320.2373, found 320.2369.

Cyclic Iminium **2n**. White powder (75% yield). Mixture of two atropisomers (ratio of 1:1): ^{1}H NMR (500 MHz, CD_3CN) δ = 9.18 (s, 1H), 9.15 (s, 1H), 7.38-7.44 (m, 6H), 7.45-7.52 (m, 8H), 7.34 (d, 1H, J=8.0Hz), 7.30 (d, 1H, J=8.0Hz), 3.04 (d, 1H, J=14.0Hz), 3.01 (d, 1H, J=14.0Hz), 2.76 (d, 1H, J=14.0Hz), 2.75 (d, 1H, J=14.0Hz), 2.66 (dq, 1H, J=7.5Hz, J=15Hz), 2.51 (dq, 1H, J=7.5Hz, J=15Hz), 2.51 (dq, 1H, J=7.5Hz, J=15Hz), 2.33 (s, 3H), 2.31 (dq, 1H, J=7.5Hz, J=15Hz), 2.15 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H), 1.39 (s, 3H) 1.38 (s, 3H), 1.22 (t, 3H, J=7.5Hz), 1.11 (t, 3H, J=7.5Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 189.6, 189.5, 141.9, 141.9, 141.0, 140.9, 134.7, 134.6, 132.8, 132.7, 132.1, 132.1, 130.8, 130.7, 130.6, 130.6, 129.4, 129.4, 128.9, 128.8, 126.7, 126.7, 85.8, 85.7, 56.1, 56.1, 49.3, 49.2, 28.4, 27.9, 27.9, 27.8, 27.4, 27.1, 25.5, 25.5, 19.8, 19.7, 15.5, 15.4 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{22}H_{28}N]+$ [M]+ 306.2216, found 306.2220.

Cyclic Iminium **2o** White powder (62% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 9.16 (s, 1H), 7.76 (t, 1H, J=7.5Hz), 7.67 (t, 1H, J=7.5Hz), 7.62 (d, 1H, J=7.5Hz), 7.59 (d, 1H, J=7.5Hz), 7.44-7.47 (m, 3H), 7.39-7.42 (m, 3H), 7.31 (d, 2H, J=7.0Hz), 7.26 (d, 2H, J=7.0Hz), 2.68 (d, 1H, J=14.0Hz), 2.44 (d, 1H, J=14.0Hz), 1.66 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 188.3, 139.1, 137.5, 133.2, 133.0, 132.6, 131.0, 130.9, 130.4, 129.8, 129.8, 129.3, 127.7, 126.9, 83.7, 55.5, 49.4, 27.8,27.7,27.5 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{25}H_{26}N]+$ [M]+ 340.2060, found 340.2059.

Cyclic Iminium **2p**. White powder (71% yield). Mixture of two atropisomers (ratio of 1.5:1): ^{1}H NMR (500 MHz, CD_3CN) δ = 9.44 (s, 1H), 9.34 (s, 0.5H), 7.90 (dd, 1H, J=1.5Hz, J=8.0Hz), 7.84 (dd, 0.5H, J=1.5Hz, J=8.0Hz), 7.61-7.65 (m, 1.5H), 7.47-7.52 (m, 4.5H), 7.42-7.44 (m, 3H), 7.37-7.41 (m, 1.5H), 7.33 (dd, 0.5H, J=1.5Hz, J=8.0Hz), 3.16 (d, 1H, J=14.0Hz), 3.08 (d, 0.5H, J=14.0Hz), 2.87 (d, 0.5H, J=14.0Hz), 2.66 (d, 1H, J=14.0Hz), 1.90 (s, 1.5H), 1.82 (s, 1.5H), 1.80 (s, 3H), 1.51 (s, 1.5H), 1.50 (s, 3H), 1.46 (s, 9H), 1.36 (s, 3H), 1.19 (s, 4.5H) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 188.6, 187.6, 145.8, 145.6, 142.4, 141.5, 133.1, 132.9, 132.3, 132.2, 130.7, 130.4, 129.3, 129.0, 128.5, 128.3, 128.0, 127.8, 126.6, 126.6, 84.4, 83.5, 55.9, 55.8, 49.1, 47.2, 38.5, 38.2, 33.9, 33.6, 30.3, 29.8, 28.7, 28.0, 27.2, 26.1 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{23}H_{30}N]+$ [M]+ 320.2373, found 320.2376.

Cyclic Iminium **2q**. White powder (58% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 8.90 (s, 1H), 7.77 (dt, 1H, J=7.5Hz, J=1.5Hz), 7.68 (dt, 1H, J=7.5Hz, J=1.5Hz), 7.61 (dd, 1H, J=7.5Hz, J=1.5Hz), 7.58 (dd, 1H, J=7.5Hz, J=1.5Hz), 7.51-7.54 (m, 3H), 7.34-7.36 (m, 2H), 2.30 (br, 2H), 1.74 (br, 2H), 1.64 (br, 2H), 1.24 (br, 6H), 0.96 (t, 6H, J=7.5Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 191.3, 139.1, 137.6, 133.1, 133.0, 132.4, 130.8, 129.7, 129.6, 127.8, 83.1, 56.3, 44.7, 28.9, 28.5, 8.7 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{22}H_{28}N]+$ [M]+ 306.2216, found 306.2215.

Cyclic Iminium **2r.** White powder (67% yield). ^{1}H NMR (500 MHz, CD_3CN) δ = 8.90 (s, 1H), 7.85 (dd, 1H, J=7.5Hz, J=1.5Hz), 7.60 (dt, 1H, J=7.5Hz, J=1.5Hz), 7.39 (dt, 1H, J=7.5Hz, J=1.5Hz), 7.21 (dd, 1H, J=7.5Hz, J=1.5Hz), 2.41 (d, 1H, J=14.0Hz), 2.27 (d, 1H, J=14.0Hz), 1.99 (q, 1H, J=7.5Hz), 1.92 (q, 1H, J=7.5Hz), 1.91 (q, 1H, J=7.5Hz), 1.74 (q, 1H, J=7.5Hz), 1.65 (s, 3H), 1.48 (s, 3H), 1.39 (s, 9H), 1.04 (t, 3H, J=7.5Hz), 1.01 (t, 3H, J=7.5Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 190.3, 145.6, 132.8, 132.3, 132.0, 129.1, 127.6, 83.5, 56.0, 45.9, 38.4, 33.8, 31.0, 27.5, 27.4, 8.7, 7.9 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{20}H_{32}N]+$ [M]+ 286.2529, found 286.2527.

Cyclic Iminium **2s.** White powder (81% yield). Mixture of two atropisomers (ratio of 1.25:1): ^{1}H NMR (500 MHz, CD_3CN) δ = 8.35 (s, 0.8H), 8.09 (s, 1H), 7.36-7.42 (m, 7.2H), 7.16-7.35 (m, 12.6H), 6.98-7.16 (m, 5.4H), 6.69-6.95 (m, 5.4H), 5.53 (s, 1H), 5.32 (s, 0.8H), 2.94-2.97 (m, 1.8H), 2.74 (d, 1.8H, J=13.8Hz), 2.34 (s, 5.4H), 2.24 (s, 5.4H), 1.72-1.86 (m, 7.8H), 1.47-1.65 (m, 8.4H) $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ = 188.6, 187.8, 143.2, 143.0, 142.5, 142.5, 142.0, 140.9, 140.9, 138.5, 136.4, 136.3, 133.6, 131.5, 130.4 130.1, 130.1, 130.0, 129.8, 129.5, 129.5, 129.2, 128.5, 128.2, 128.1, 126.7, 83.9, 83.3, 55.8, 55.4, 51.6, 51.1, 49.8, 48.1, 28.9, 28.2, 28.1, 28.1, 27.7, 27.0, 19.8, 19.2 ^{19}F NMR (282 MHz, CD_3CN) δ = -151.7 HRMS: m/z calculated for $[C_{34}H_{36}N]+$ [M]+ 458.2842, found 458.2838.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.xxxxx. General methods and materials, experimental procedures and characterization data, X-ray crystal structure determination (CIF: **2e**, **2f**, **2j**, **2q**, **2r**, **2s**), and NMR spectra (PDF).

Accession Codes

Crystallographic data for **2e** (CCDC 2127093), **2f** (CCDC 2127097), **2j** (CCDC 2127095), **2q** (CCDC 2127096), **2r** (CCDC 2127094), and **2s** (CCDC 2127092). The supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Catalysis Science Program, under Award # DE-SC0009376, and the Agence Nationale de la Recherche (ANR-20-CE07-0000-cResolu).

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