

Interaction of Bis(diisopropylamino)carbene with Aroylimines Activated by Trifluoromethyl Groups

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Dedicated to Prof. Marian Mikolajczik on the occasion of his 70th birthday

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Bis(diisopropylamino)carbene deoxygenates the carbonyl group of aroylimines $\text{Ar}-\text{C}(\text{O})-\text{N}=\text{C}(\text{CF}_3)_2$ to form alkenes, which formally result from the coupling of two carbenes, $[\text{Ar}-\text{C}(\cdot)-\text{N}=\text{C}(\text{CF}_3)_2]$ and $[(i\text{Pr}_2\text{N})_2\text{C}\cdot]$.

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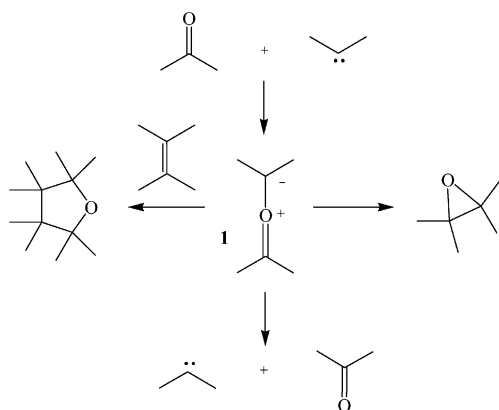
Introduction

Electrophilic singlet carbenes can react with the carbonyl group of aldehydes, ketones, esters and amides.^[1] Such reactions begin with the electrophilic attack of a carbene on the oxygen lone pair to give zwitterionic carbonyl ylides **1** (Scheme 1). These unstable intermediates may then undergo different types of transformations. They can be intercepted by other compounds (e.g. activated alkenes). In the absence of trapping agents, carbonyl ylides can cyclize to form epoxides or can react further with a second equiv. of carbonyl compound to give dioxolanes. In very rare cases, the com-

plete abstraction of the oxygen from the carbonyl group leads to the formation of a new carbene/carbonyl compound pair.^[2]

Nucleophilic singlet carbenes are known to react with aldehydes and ketones without affecting the carbonyl group.^[3] In contrast, the singlet [bis(diisopropylamino)-phosphanyl](trimethylsilyl)carbene was found to add to the carbonyl group of aldehydes giving oxiranes.^[4]

In this paper we present the reaction of stable bis(diisopropylamino)carbene **3**^[5] with the carbonyl group of aroylimines **2**, which leads to the complete cleavage of the $\text{C}=\text{O}$ bond. The choice of these aroylimines was accounted for by their strong nucleophilicity and by the absence of active hydrogens, which can readily add to nucleophilic carbenes.



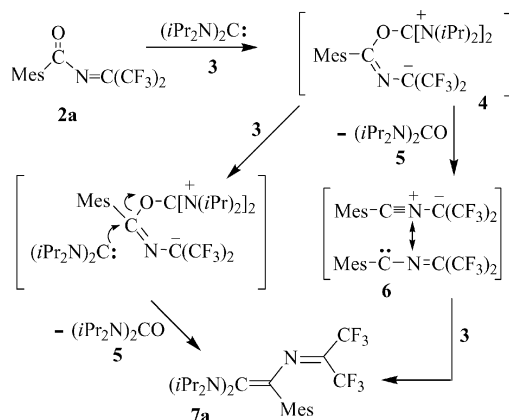
Scheme 1.

Results and Discussion

Aroylimine **2a** easily reacts with 2 equiv. of diaminocarbenes **3** in diethyl ether at room temperature to give alkene **7a** and tetraisopropylurea **5** (Scheme 2). The abstraction of the oxygen from aroylimine **2a** probably begins with the initial attack of the diaminocarbenes on the oxygen of the carbonyl group to give zwitterionic intermediate **4**. This proposal corresponds to the mechanism of the direct oxophilic attack of phosphanes, to which singlet diaminocarbenes are closely analogous, on electron-deficient carbonyl compounds such as quinones, cyclopentadienones and hexafluoroacetone. It is logical to assume that **4** undergoes decomposition with the expulsion of urea **5** to form carbene-nitrile ylide **6**, which then reacts with a second equiv. of the starting diaminocarbenes to give product **7a**. It is also possible that the decomposition of zwitterion **4** does not include the intermediate formation of free carbene **6** but is concerted, with a simultaneous attack by the second equiv.

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of **3** and the expulsion of urea **5** (Scheme 2). The latter possibility is in keeping with the cleavage of the C–O bond of anhydrides by dimethoxycarbene.^[6]



Scheme 2.

Alkene **7a** was isolated as a yellow crystalline product in good yield. The single-crystal X-ray analysis of **7a** (Figure 1) showed a certain amount of averaging of the C1–C2, C2–N1 and N1–C13 distances, caused by the presence of electron-donating and electron-withdrawing groups on opposite ends of the azadiene chain. Thus, the hexafluoroisopropyl and bis(diisopropylamino)carbene fragments contain partial negative and positive charges, respectively, and the structure of the compound can be represented by two mesomeric forms, as shown in Scheme 3. However, the N1–C13 bond of **7a** still has partial double-bond character, which is confirmed by the inequivalence of the CF₃ groups displaying two characteristic quartets in the ¹⁹F NMR spectrum at room temperature. This compound is stable and displays no tendency either to a migration of the fluorines or to the dissociation of the C=C double bond.

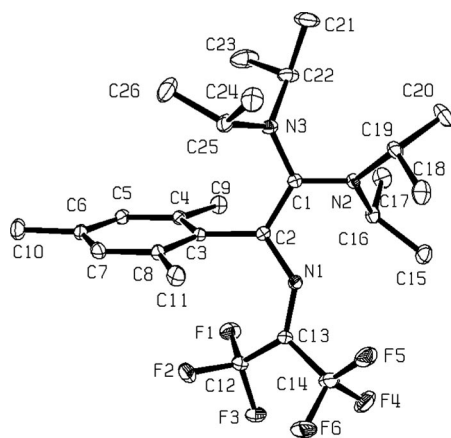
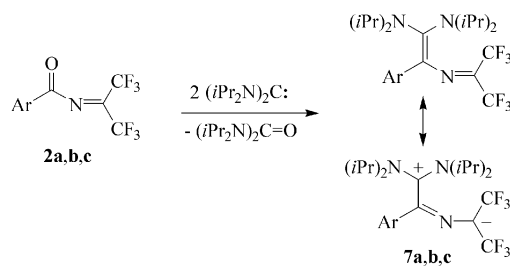


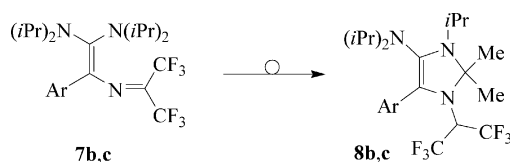
Figure 1. Crystal structure of **7a**. Selected bond lengths [Å] and angles [°]: N2–C1 1.377(4), C1–C2 1.405(4), C2–N1 1.362(4), N1–C13 1.296(4), C1–C2–N1 114.3(3), N2–C1–N3 117.3(3), C1–C2–C3–C4 66.95, C1–C2–N1–C13 165.93.



Scheme 3. Ar = Mes (**7a**, **8a**), Ph (**7b**, **8b**), *p*-NO₂C₆H₄ (**7c**, **8c**).

Taking into account that aroylimine **2a** contains the sterically demanding mesityl group, one would expect that less bulky and/or more electronegative substituents on the carbonyl group could give additional information about the reaction of aroylimines with diaminocarbene **3**. For this reason, aroylimines **2b** and **2c**, containing phenyl and *p*-nitrophenyl groups, respectively, were used. Bis(diisopropylamino)carbene **3** smoothly deoxygenated the carbonyl groups of these compounds to give alkenes **7b** and **7c** (Scheme 3). These compounds were isolated as yellow and red crystalline products, respectively, in good yields by crystallization from hexane at –15 °C. Unlike in alkene **7a**, the CF₃ and *i*Pr groups in **7b** and **7c** are equivalent and display common broad signals in the ¹H, ¹³C and ¹⁹F NMR spectra at room temperature. The structures of **7b** and **7c** are closer to the zwitterionic form than is that of **7a**, probably due to less steric hindrance. The hexafluoroisopropyl and amidinium units can rotate around the N1–C13 and C1–C2 bonds, respectively. It is only at –30 °C that this rotation stops (on the NMR time scale), and the CF₃ groups display two clear quartets in the ¹⁹F NMR spectra.

We previously observed the dissociation of the fluorines from an analogous hexafluoroisopropyl fragment followed by an unusual rearrangement.^[7] One could expect that the more pronounced zwitterionic structures of alkenes **7b** and **7c** could lead to the reduction of their stability. Indeed, in dichloromethane or chloroform, alkenes **7b** and **7c** were unstable and underwent a quantitative and irreversible rearrangement at room temperature. However, this decomposition was not caused by the migration of the fluorines but by an intramolecular cyclization into structural isomers **8b** and **8c**, respectively (Scheme 4). The rearrangement is slow and requires a few days at 20 °C. The activation of the Me₂C–H bond of the *i*Pr groups is obviously accounted for by the influence of the adjacent, positively charged, iminium center.



Scheme 4. Ar = Ph (**7b**, **8b**), *p*-NO₂C₆H₄ (**7c**, **8c**).

The single-crystal X-ray analysis of *p*-nitrophenyl-substituted product **8c** displayed an envelope conformation of the five-membered ring, with C1, C2, N1 and N2 lying in the

same plane and C3 deviating from it. The configurations N1 and N2 are different. The conjugation of the C1=C2 double bond with the electron pair of N1 makes this nitrogen almost ideally flat (sum of angles: 359.88°). The N2 atom has a more pronounced tetrahedral geometry (sum of angles = 343.37°). Owing to the absence of inversion at N2 in the crystalline form, **8c** is represented by two stable N2(*R*) and N2(*S*) enantiomers, one of which is shown in Figure 2. In solution, the chirality disappears because of fast interconversion of the enantiomers. The ¹H and ¹³C NMR spectra display common signals of magnetically equivalent methyl groups at C3. However, another type of isomerism appears for these compounds in solution. According to the NMR spectra, the restriction of free rotation of the sterically demanding isopropyl and hexafluoroisopropyl groups leads to the formation of stable rotamers. Two major rotamers are well observed in the NMR spectra, with the ratio between them being dependent on the solvent. This dependence is particularly noticeable in **8b**. For example, in hexane and in benzene, the rotamer ratio is 112:100 and 47:100, respectively.

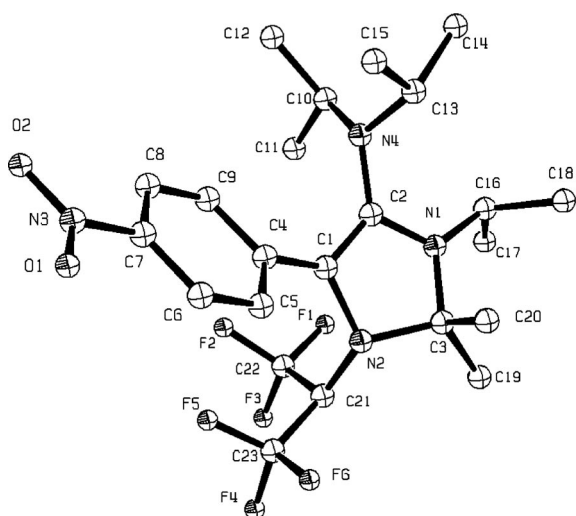
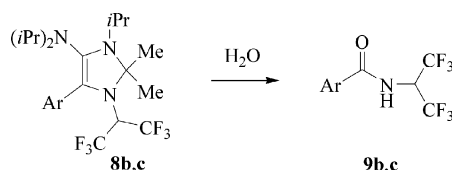


Figure 2. Crystal structure of **8c**. Selected bond lengths [Å] and angles [°]: C1–C2 1.359(4), C2–N1 1.377(4), N1–C3 1.476(4), C1–N2 1.446(4), C2–N4 1.416(4), C2–N1–C3 107.0(2), N1–C2–C1–N2 3.32, C2–C1–N2–C3 19.64, C2–C1–C4–C9 48.23.

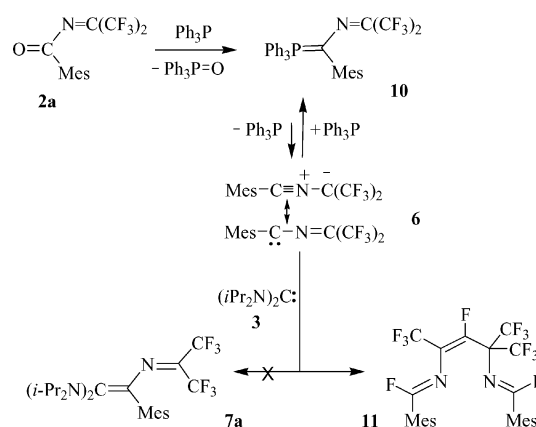
Dihydroimidazoles **8b** and **8c** can hydrolyze, with the cleavage of the C–N bond and C=C double bond to give substituted amides **9b,c** (Scheme 5). The reaction is slow at room temperature and requires several hours for **8b** and about two weeks for nitro-substituted derivative **8c**.



Scheme 5. Ar = Ph (**8b**, **9b**), *p*-NO₂C₆H₄ (**8c**, **9c**).

Taking into account the close analogy of singlet diaminocarbenes to trivalent phosphorus compounds, it is interesting to compare the interaction of aroylimine **2** and diaminocarbene **3** with the recently reported deoxygenation of **2** by triphenylphosphane.^[8] Similarly to other examples of this kind,^[9,10] the reaction probably included the intermediate formation of carbene-nitrile ylide **6** and its further reaction with a second equiv. of triphenylphosphane to give ylide **10** quantitatively. This conclusion is supported by the fact that the P=C ylide bond of **10** is capable of dissociation to form triphenylphosphane and carbene-nitrile ylide **6**. Compound **6** can also be trapped by cyclohexene or phenylisocyanate to give the appropriate 1,3-addition products.^[8] In these reactions, **6** displays properties of the mesomeric nitrile ylide.

One would expect **6** to display carbene-like properties if its generation is conducted in the presence of diaminocarbene **3**. In this case, the coupling of these two carbenes would give alkene **7a**. However, heating ylide **10** with 1 equiv. of diisopropylaminocarbene **3** unexpectedly resulted in the almost quantitative asymmetrical dimerization of **6** into **11**, and no traces of alkene **7a** were found (Scheme 6).^[11] Bis(diisopropylamino)carbene **3** acted as a catalyst in this reaction, remaining unchanged. It is quite interesting that carbene-nitrile ylide **6** can be easily trapped by cyclohexene but does not react with the highly active carbene **3**.



Scheme 6.

Although alkene **7a** is stable, we could not exclude its participation in the formation of dimer **10** as an intermediate capable of undergoing rearrangement with migration of a fluoride anion and expulsion of free carbene **3**. However, this assumption was not confirmed experimentally. The generation of carbene **6** in the presence of **7a** resulted in no reaction. The subsequent addition of diaminocarbene **3** to this mixture led to the quantitative asymmetrical dimerization of nitrile ylide **6**, whereas alkene **7a** remained unchanged.

Thus, we conclude that the formation of alkene **7a** from aroylimine **2a** and bis(diisopropylaminocarbene) **3** does not include the intermediate formation of carbene **6**. The alter-

native is that diaminocarbene **3** adds to carbene **6** in this reaction but catalyses the asymmetrical dimerization of **6** obtained from the dissociation of ylide **10**.

Conclusions

Bis(diisopropylamino)carbene deoxygenates the carbonyl group of aroylimines to form alkenes. This reaction may have a more general character, and other alkenes can be obtained from singlet nucleophilic diaminocarbenes and ketones that are properly activated and do not contain acidic hydrogens.

Experimental Section

General: All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. The NMR spectra were recorded with Varian Gemini 400 MHz and JEOL FX-90Q spectrometers. The ^1H and ^{13}C chemical shifts are referenced to tetramethylsilane (TMS) and the ^{19}F chemical shifts are referenced to CFCl_3 . The ^{31}P chemical shifts were measured with 85% aqueous H_3PO_4 as an external standard.

Compound 7a: To a solution of **3** (100 mg, 0.47 mmol) in diethyl ether (1.5 mL), **2a** (70 mg, 0.23 mmol) was added at room temperature. The resulting solution turned yellow and slightly turbid. After 15 min, the solvent was evaporated in vacuo. The residue was dissolved in hexane (0.6 mL) and stored at -15°C overnight to form yellow crystals. Yield 60 mg (52%), m.p. $158\text{--}160^\circ\text{C}$. ^1H NMR (400.07 MHz, CDCl_3): δ = 0.78 [d, $^3J_{\text{H,H}} = 6.84$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.27 [d, $^3J_{\text{H,H}} = 6.84$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.39 [d, $^3J_{\text{H,H}} = 6.84$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.47 [d, $^3J_{\text{H,H}} = 6.84$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 2.08 (s, 6 H, *o*- CH_3), 2.26 (s, 3 H, *p*- CH_3), 3.54 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.02 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$], 4.19 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 6.83 (s, 2 H, Ar) ppm. ^{13}C NMR (100.61 MHz, CDCl_3): δ = 20.94 (s, 2 C, CH_3), 21.86 (s, 1 C, CH_3), 22.82 (s, 2 C, CH_3), 23.85 (s, 4 C, CH_3), 24.43 (s, 2 C, CH_3), 53.17 (s, 1 C, CH_3), 53.30 (s, 1 C, CH_3), 55.56 (s, 2 C, CH_3), 112.44 [sept, $^1J_{\text{C,F}} = 36.62$ Hz, $\text{C}(\text{CF}_3)_2$], 113.55 (s, 1 C, ArCN), 118.72 (q, $^1J_{\text{C,F}} = 280.76$ Hz, 1 C, CF_3), 122.4 (q, $^1J_{\text{C,F}} = 276.18$ Hz, 1 C CF_3), 128.61 (s, 2 C, Ar), 135.46 (s, 1 C, Ar), 136.59 (s, 1 C, Ar), 137.71 (s, 2 C, Ar), 172.60 (s, 1 C, NCN) ppm. ^{19}F NMR (84.26 MHz, CDCl_3): δ = -62.30 (q, $^4J_{\text{F,F}} = 7.32$ Hz, 3 F, CF_3), -59.99 (q, $^4J_{\text{F,F}} = 7.32$ Hz, 3 F, CF_3) ppm.

Crystal Data for 7a: Data were collected on a Enraf–Nonius CAD4 diffractometer. $\text{C}_{26}\text{H}_{39}\text{F}_6\text{N}_3$, $M = 507.60$, monoclinic, $a = 12.239(4)$, $b = 16.483(5)$, $c = 13.875(4)$ Å, $\beta = 92.20(2)^\circ$, $V = 2797(2)$ Å 3 , $T = 293$ K, space group $P 2_1/n$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.099$ mm $^{-1}$, $\lambda = 0.71069$ Å, 5380 reflections measured, 4928 unique ($R_{\text{int}} = 0.0011$). Final R indices $R_1 = 0.0580$, $wR(F^2) = 0.1252$ [for 2551 reflections with $\|I/I\| > 3.0$].

CCDC-651200 contains the supplementary crystallographic data for **7a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 7b: To a frozen (in liquid nitrogen) solution of **3** (84 mg, 0.4 mmol) in Et_2O (1 mL) a solution of **2b** (52 mg, 0.19 mmol) in Et_2O (0.4 mL) was slowly added so that the mixture remained solid. Then the mixture was slowly warmed to room temperature over 20 min whilst stirring. Diethyl ether was evaporated, and hexane (1 mL) was added to the residue. The hexane solution was sepa-

rated and stored overnight at -15°C to yield yellow crystals. Yield 45 mg (50%), m.p. 110°C . ^1H NMR (400.07 MHz, C_6D_6): δ = 0.81 [br., 12 H, $\text{CH}(\text{CH}_3)_2$], 1.23 [br., 12 H, $\text{CH}(\text{CH}_3)_2$], 3.86 [sept, $^3J_{\text{H,H}} = 7.03$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$], 7.17–7.30 (m, 5 H, Ph) ppm. ^{13}C NMR (100.61 MHz, C_6D_6): δ = 22.72 (br.), 54.68 (br.), 112.28 [sept, $^2J_{\text{C,F}} = 36.00$ Hz, $\text{C}(\text{CF}_3)_2$], 115.65 (PhCN), 123.48 (q, $^1J_{\text{C,F}} = 285.34$ Hz, 1 C, CF_3), 123.78 (q, $^1J_{\text{C,F}} = 285.34$ Hz, 1 C, CF_3), 127.02 (s, 1 C, Ph), 128.28 (s, 2 C, Ph), 131.33 (s, 2 C, Ph), 140.22 (s, 1 C, Ph), 171.25 (NCN) ppm. ^{19}F NMR (84.26 MHz, CDCl_3 , 20°C): δ = -58.64 (br., 3 F, CF_3), -61.64 (br., 3 F, CF_3) ppm. ^{19}F NMR (84 MHz, CDCl_3 , -30°C): δ = -62.23 (q, $^4J_{\text{F,F}} = 6.84$ Hz, 3 F, CF_3), -58.80 (q, $^4J_{\text{F,F}} = 6.84$ Hz, 3 F, CF_3) ppm.

Compound 7c: To a solution of **3** (210 mg, 1 mmol) in hexane (3 mL), solid **2c** (157 mg, 0.5 mmol) was slowly added. The mixture was stirred for 5 min, and the solution was separated and stored overnight at -15°C to give red crystals. Yield 116 mg (46%), m.p. $120\text{--}122^\circ\text{C}$. ^1H NMR (400.07 MHz, C_6D_6): δ = 1.35 [br., 24 H, $\text{CH}(\text{CH}_3)_2$], 3.95 [sept, $^3J_{\text{H,H}} = 7.32$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$], 7.31 (d, $^3J_{\text{H,H}} = 8.79$ Hz, 2 H, Ar), 8.16 (d, $^3J_{\text{H,H}} = 8.79$ Hz, 2 H, Ar) ppm. ^{13}C NMR (100.61 MHz, CDCl_3): δ = 23.35 (br.), 54.72 (br.), 112.00 (PhCN), 113.30 [sept, $^2J_{\text{C,F}} = 35.01$ Hz, $\text{C}(\text{CF}_3)_2$], 120.28 (q, $^1J_{\text{C,F}} = 277.71$ Hz, CF_3), 123.53 (s, 1 C, Ar), 126.62 (s, 2 C, Ar), 131.35 (s, 2 C, Ar), 147.47 (s, 1 C, Ar), 171.06 (NCN) ppm. ^{19}F NMR (84.26 MHz, CDCl_3 , 20°C): δ = -61.86 (br., 6 F, CF_3) ppm. ^{19}F NMR (84 MHz, CDCl_3 , -30°C): δ = -61.86 (br., 6 F, CF_3) ppm.

Compound 8b: A solution of alkene **7b** (0.1 mmol, 46 mg) in CHCl_3 (0.7 mL) was stored for 24 h at 30°C . The solvent was evaporated in vacuo, yielding a yellow-brown oil (46 mg, 100%). ^1H NMR (400.07 MHz, C_6D_6), 2:1 rotamer ratio: δ = 0.93 [br., $\text{CH}(\text{CH}_3)_2$], 1.06 [d, $^3J_{\text{H,H}} = 7.81$ Hz, $\text{CH}(\text{CH}_3)_2$], 1.21 [d, $^3J_{\text{H,H}} = 7.83$ Hz, $\text{CH}(\text{CH}_3)_2$], 1.24 [br. s, $\text{C}(\text{CH}_3)_2$], 1.63 [br. s, $\text{C}(\text{CH}_3)_2$], 3.15 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, $\text{CH}(\text{CH}_3)_2$], 3.27 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, $\text{CH}(\text{CH}_3)_2$], 3.94 [sept, $^3J_{\text{H,H}} = 7.81$ Hz, $\text{CH}(\text{CH}_3)_2$], 4.05 [sept, $^3J_{\text{F,H}} = 8.78$ Hz, $\text{CHC}(\text{CF}_3)_2$], 4.30 [sept, $^3J_{\text{F,H}} = 8.78$ Hz, $\text{CHC}(\text{CF}_3)_2$], 6.98–7.27 (m, Ph), 7.42–7.51 (m, Ph) ppm. ^{13}C NMR (100.61 MHz, C_6D_6), 2:1 rotamer ratio: δ = 21.70 [$\text{CH}(\text{CH}_3)_2$], 22.05 [$\text{CH}(\text{CH}_3)_2$], 23.11 [$\text{CH}(\text{CH}_3)_2$], 23.43 [$\text{CH}(\text{CH}_3)_2$], 27.30 [$\text{C}(\text{CH}_3)_2$], 27.57 [$\text{C}(\text{CH}_3)_2$], 43.82 [$\text{CH}(\text{CH}_3)_2$], 45.38 [$\text{CH}(\text{CH}_3)_2$], 51.13 [$\text{CH}(\text{CH}_3)_2$], 51.35 [$\text{CH}(\text{CH}_3)_2$], 61.06 [sept, $^2J_{\text{C,F}} = 31.28$ Hz, $\text{CH}(\text{CF}_3)_2$], 61.26 [sept, $^2J_{\text{C,F}} = 29.76$ Hz, $\text{CH}(\text{CF}_3)_2$], 80.16 [$\text{C}(\text{CH}_3)_2$], 80.47 [$\text{C}(\text{CH}_3)_2$], 111.81, 118.76, 123.45 (q, $^1J_{\text{C,F}} = 286.86$ Hz, CF_3), 123.79 (q, $^1J_{\text{C,F}} = 288.39$ Hz, CF_3), 126.49 (Ph), 127.32 (Ph), 128.07 (Ph), 128.74 (Ph), 130.57 (Ph), 131.65 (Ph), 133.41 (Ph), 135.06 (Ph), 135.55 (NCN), 142.11 (NCN) ppm. ^{19}F NMR (84.26 MHz, C_6D_6), 2:1 rotamer ratio: δ = -66.03 (d, $^3J_{\text{F,H}} = 8.55$ Hz, CF_3 , major rotamer), -65.22 (d, $^3J_{\text{F,H}} = 8.55$ Hz, CF_3 , minor rotamer) ppm.

Compound 8c: A solution of alkene **7c** (0.1 mmol, 51 mg) in CHCl_3 (0.7 mL) was stored for 78 h at 20°C and then heated at 50°C for 30 min. The solvent was evaporated in vacuo, yielding red-black crystals (51 mg, 100%). Crystals, suitable for X-ray analysis, were grown from hexane at -15°C . M.p. $106\text{--}108^\circ\text{C}$. ^1H NMR (400.07 MHz, CDCl_3): 7:1 rotamer ratio, major rotamer: δ = 1.02–1.10 {br., 12 H, $\text{N}[\text{CH}(\text{CH}_3)_2]_2$ }, 1.28 [d, $^3J_{\text{H,H}} = 6.84$ Hz, 6 H, $=\text{NCH}(\text{CH}_3)_2$], 1.54 [d, 6 H, $\text{C}(\text{CH}_3)_2$], 3.45 {sept, $^3J_{\text{H,H}} = 6.84$ Hz, 2 H, $\text{N}[\text{CH}(\text{CH}_3)_2]_2$ }, 4.02 [sept, $^3J_{\text{H,H}} = 6.84$ Hz, 1 H, $=\text{NCH}(\text{CH}_3)_2$], 4.20 [sept, $^3J_{\text{F,H}} = 7.81$ Hz, 1 H, $\text{CHC}(\text{CF}_3)_2$], 7.39 (d, $^3J_{\text{H,H}} = 7.81$ Hz, 2 H, Ar), 8.06 (d, $^3J_{\text{H,H}} = 7.81$ Hz, 2 H, Ar) ppm. ^{13}C NMR (100.61 MHz, CDCl_3): 7:1 rotamer ratio, major rotamer: δ = 23.32 [$\text{N}[\text{CH}(\text{CH}_3)_2]_2$], 23.59 [$=\text{NCH}(\text{CH}_3)_2$], 27.54 [$\text{C}(\text{CH}_3)_2$], 44.40 [$=\text{NCH}(\text{CH}_3)_2$], 51.33 [$\text{N}[\text{CH}(\text{CH}_3)_2]_2$], 61.04 [sept, $^2J_{\text{C,F}} = 28.99$ Hz, $\text{NCH}(\text{CF}_3)_2$], 81.56 [$\text{C}(\text{CH}_3)_2$], 109.90

(ArCN), 122.76 (q, $^1J_{C,F}$ = 285.34 Hz, CF₃), 122.86 (Ar), 126.65 (Ar), 143.21 (Ar), 144.00 (NCN), 148.19 (Ar) ppm. ^{19}F NMR (84.26 MHz, CDCl₃): 7:1 rotamer ratio: δ = -66.12 (d, $^3J_{F,H}$ = 7.81 Hz, CF₃, major rotamer), -63.43 (d, $^3J_{F,H}$ = 7.81 Hz, CF₃, minor rotamer).

Crystal Data for 8c: Data were collected on Bruker Smart Apex II diffractometer. C₂₆H₃₉F₆N₃, M = 510.24, orthorhombic, a = 38.6167(7), b = 7.68240(10), c = 17.6309(3) Å, V = 5230.54(15) Å³, T = 273(2) K, space group $Pna2_1$, Z = 8, $\mu(\text{Mo-K}\alpha)$ = 0.113 mm⁻¹, λ = 0.71073 Å, 31489 reflections measured, 7046 unique (R_{int} = 0.031). Final R indices R_1 = 0.0416, $wR(F^2)$ = 0.0976 [for reflections with $I/\sigma(I)$ > 2.0].

CCDC-637869 contains the supplementary crystallographic data for **8c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 9b: A solution of **8b** (0.1 mmol, 46 mg) in THF (0.7 mL) containing water (0.05 mL) was stored for 24 h at 30 °C at stirring. The solvent was evaporated in vacuo, and the residue was crystallized twice from CHCl₃ to give white crystals. Yield 10 mg, 37%. M.p. 143 °C. ^1H NMR (400.07 MHz, [D₆]DMSO): δ = 6.11 [br. s, 1 H, CH(CF₃)₂], 7.52 (m, 2 H, Ar), 7.61 (m, 1 H, Ar), 7.94 (m, 2 H, Ar), 9.75 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.61 MHz, [D₆]DMSO) δ = 52.11 [sept, $^2J_{C,F}$ = 32.04 Hz, CH(CF₃)₂], 122.13 (q, $^1J_{C,F}$ = 282.90, CF₃), 128.18 (s, 2 C, Ar), 128.50 (s, 2 C, Ar), 132.26 (s, 1 C, Ar), 132.54 (s, 1 C, Ar), 167.73 (C=O) ppm. ^{19}F NMR (84.26 MHz, [D₆]DMSO): δ = -65.35 (d, $^3J_{F,H}$ = 6.84 Hz, CF₃) ppm. ^{19}F NMR (84.26 MHz, CDCl₃): δ = -72.07 (d, $^3J_{F,H}$ = 6.84 Hz, CF₃) ppm.

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