Synthesis and dynamic NMR study of fluorinated dialkyl 2-[(*tert*-butylimino)-methylene]-3-[(2-alkoxy-2-oxoacetyl)-2-fluoroanilino]-succinates

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The 1:1 adduct produced in the reaction between *tert*-butyl isocyanide and dialkyl acetylenedicarboxylates was trapped by alkyl 2-fluoro-anilino-2-oxo-acetates or ethyl 2-oxo-2-(trifluoromethylanilino)-acetate to produce functionalised ketenimines in good yields. Dynamic NMR effects were observed in the ^{1}H NMR spectra of these compounds as a result of restricted rotation around the single bond linking the aryl group to the ketenimine system. The free energy of activation ($\Delta G^{\neq}$) for this process is 64.9–66.5 kJ mol^{-1}.

***Keywords*:** ketenimine, *tert*-butyl isocyanide, NH-acids, acetylenic esters, three-component reaction

In recent years, the synthetic applications of multifunctional heteroallenes have been widely investigated.[1,2] In spite of extensive developments in the chemistry of modified ketenes and isocyanates,[3] little attention has been paid to the synthesis of ketenimines.[4,5] In general, unsubstituted ketenimines and those with small unbranched alkyl substituents are elusive substances. Ketenimines play a role as discrete but transient intermediates in many interconversions, especially in elimination-addition processes and in the formation of heterocyclic systems.[6-9] The spectroscopic properties of ketenimines have been intensively investigated.[10,11] We wish to report a simple one-pot preparation of stable ketenimines using *tert*-butyl isocyanide, dialkyl acetylenedicarboxylates **1**, and a strong NH-acid, such as alkyl arylamino-2-oxo-acetates **2a–2c**. This three-component condensation reaction produces highly functionalised ketenimines **3** in fairly good yields (Scheme 1).

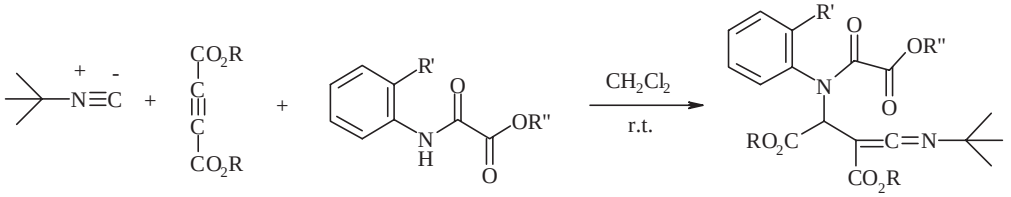
Results and discussion

The reaction of *tert*-butyl isocyanide with electron deficient acetylenic esters **1** in the presence of strong NH-acids **2** proceeded at room temperature in CH_2Cl_2, and was completed within 24 h. The IR, ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of the stable ketenimines **3** (Scheme 1). The structures of compounds **3a–3d** were deduced from their elemental analyses and their high-field ^{1}H, ^{13}C, and ^{19}F NMR spectra. The structural assignments of compounds **3a–3d** made on the basis of their NMR spectra were supported by their IR spectra. Of special interest are the strong ketenimine absorption bands at about 2050 cm^{-1} in all compounds. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values. Initial fragmentation involved the loss of *tert*-butyl moiety.

The plausible way of formation of the product is proposed in Scheme 2. On the basis of the well-established chemistry of isocyanides[12-14] it is reasonable to assume that compound **3** results from initial addition of *tert*-butyl isocyanide to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid. Then, the positively charged ion **4** is attacked by the conjugate base of the NH-acid to form ketenimine **3**.

The noteworthy feature of the ^{1}H NMR spectrum of **3a** in $CDCl_3$ solution at 25°C is the presence of several broad signals. Near 65°C the broad lines become sharper. Decreasing the temperature leads to decoalescence of the methine signals. The ^{1}H NMR spectrum at –5°C is consistent with the presence of two conformational diastereoisomers in 58:42 ratio. This dynamic NMR effect is interpreted in terms of a restricted rotation around the N-aryl bond (see Scheme 3).

Although an extensive line shape analyses in relation to the dynamic NMR effect observed for **3a** was not undertaken in the present work, the temperature-dependent spectra allowed calculating the free energy barrier (if not the enthalpy or entropy of activation) for the dynamic NMR process in **3a**. From coalescence of the methine signal and using the expression $k = \pi \Delta\nu/\sqrt{2}$, we calculate that the first-order rate constant (k) for the dynamic NMR effect in **3a** is 62 s^{-1} at 308 K. Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation ($\Delta G^{\neq}$) of 64.9 ± 2 kJ mol^{-1} for **3a**, where all known sources of errors are estimated and included.[15] The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[16] Similar dynamic



1	R
a	Me
b	Et

2	R'	R''
a	F	Me
b	F	Et
c	CF_3	Et

3	R	R'	R''	%Yield
a	Me	F	Me	80
b	Me	F	Et	78
c	Et	F	Et	75
d	Me	CF_3	Et	80

Scheme 1

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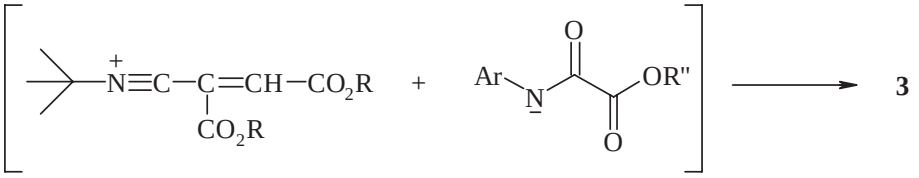
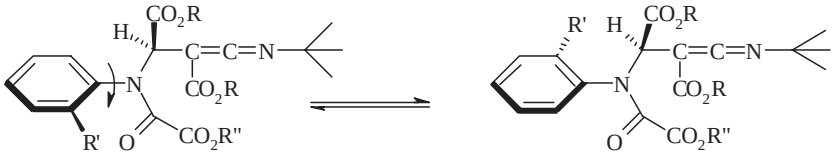


4 **3**

Scheme 2



3-I **3-II**

Scheme 3

Table 1 Equilibrium constants, standard *Gibbs* energies, and selected activation parameters for **3a**, **3b**, and **3c** in $CDCl_3$

	ΔG° / kJ mol^{-1}	$\Delta\nu$/ Hz	k / s^{-1}	T_c / K	$\Delta G^{\neq}$ / kJ mol^{-1}
3a	0.80	28	62	308	64.9 ± 2
3b	1.21	30	67	313	65.8 ± 2
3c	1.01	35	77	318	66.5 ± 2

NMR effects were observed for compounds **3b** and **3c** (see Table 1).

The NMR spectra of **3d** at room temperature are consistent with the presence of two rotamers in 57:43 ratio. No dynamic NMR effect was observed in the ^{1}H NMR of **3d** when the temperature of a solution of this compound in 1,2-dichlorobenzene was raised to 180°C.

The three-component reaction of *tert*-butyl isocyanide with electron deficient acetylenic esters in the presence of NH-acids provides a simple entry into the synthesis of polyfunctionalised ketenimines of potential synthetic interest. The present procedure carries the advantage that, not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification.

Experimental

Dialkyl acetylenedicarboxylates, *tert*-butyl isocyanide, ethyl and methyl oxalyl chloride, and arylamines were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyser. These results agreed favourably with the calculated values. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionisation potential of 70 eV. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured with a Bruker DRX-500 AVANCE instrument at 500.1, 125.7, and 470.6 MHz, respectively. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on solution in $CDCl_3$ using TMS or $CFCl_3$ as internal standard. IR spectra were measured on a Shimadzu IR-460 spectrometer.

Typical procedure for the preparation of methyl 2-(2-fluoroanilino)-2-oxo-acetate **(2a):** To a stirred solution of 1.11 g 2-fluoro-aniline (10 mmol) in 20 ml CH_2Cl_2 was added, drop wise a mixture of 1.22 g methyl oxalyl chloride (10 mmol) in 10 ml CH_2Cl_2 and a solution of 0.40 g NaOH (10 mmol) in 10 ml water at 0 °C over 10 min. The reaction mixture was then allowed to warm-up to room temperature and stirred for 24 h. The product was extracted three times with 20 ml of CH_2Cl_2. The organic phase was treated with anhydrous $MgSO_4$ and evaporated. The product was recrystalised from methanol to yield **2a** as colourless crystals; yield 1.77 g (90%), m.p. 85–87°C.

IR (KBr) (ν_{max}/cm^{-1}): 3370 (NH), 1720, 1710 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, Me), 7.23–7.36 (m, 3 H, Ar), 8.10 (m, 1 H, Ar), 9.20 (br, 1 H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.0 (OMe), 115.4 (d, $^2J_{CF}$ = 18 Hz, CH), 124.9 (d, $^2J_{CF}$ = 17 Hz, C-N), 123.1 (CH), 124.6 (d, $^4J_{CF}$ = 4 Hz, CH), 126.4 (d, $^3J_{CF}$ = 8 Hz, CH), 156.3 (d, $^1J_{CF}$ = 247 Hz, CF), 154.5 (C=O), 160.8 (C=O). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –128.91 (CF).

Ethyl 2-(2-fluoroanilino)-2-oxo-acetate (**2b**): Colourless oil; yield: 1.9 g (90%). IR (KBr) (ν_{max}/cm^{-1}): 3375 (NH), 1704, 1705 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.48 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 4.50 (q, 2 H, $^3J_{HH}$ = 7 Hz, CH_2), 7.01–7.38 (m, 3 H, Ar), 8.25–8.40 (m, 1 H, Ar), 9.20 (br, 1 H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4 (Me), 63.4 (OCH_2), 115.0 (d, $^2J_{CF}$ = 18 Hz, C–N), 125.2 (d, $^2J_{CF}$ = 17 Hz, C–N), 121.4 and 124.8 (2 CH), 125.8 (d, $^3J_{CF}$ = 8 Hz, CH), 152.7 (d, $^1J_{CF}$ = 246 Hz, C-F), 154.1 (C=O), 160.5 (C=O). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –130.65 (CF).

Ethyl 2-oxo-2-[2-(trifluoromethyl)-anilino]-acetate (**2c**): Colourless oil; yield: 2.4 g (92 %). IR (KBr) (ν_{max}/cm^{-1}): 3380 (NH), 1757, 1715 (C=O). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.48 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 4.50 (q, 2 H, $^3J_{HH}$ = 7 Hz, CH_2), 7.30–8.40 (m, 4 H, Ar), 9.35 (br, 1 H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 64.1 (OCH_2), 120.6 (q, $^2J_{CF}$ = 30 Hz, C), 123.5 and 125.8 (2 CH), 124.2 (q, $^1J_{CF}$ = 276 Hz, CF_3), 126.7 (q, $^3J_{CF}$ = 6 Hz, CH), 133.6 (CH), 134.3 (C–N), 154.7 (C=O), 160.9 (C=O). ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –61.41 (CF_3).

Typical procedure for the preparation of dimethyl 2[(tert-butylimino)-methylene]-3-[(2-fluoro-(2-methoxy-2-oxoacetyl)-anilino]-succinate **(3a):** To a stirred solution of 0.39 g methyl 2-(fluoro-anilino)-2-oxo-acetate (2 mmol) and 0.28 g dimethyl acetylendicarboxylate (2 mmol) in 6 ml CH_2Cl_2, was added, drop wise at 0 °C over 10 min 0.45 g tert-butyl isocyanide (2 mmol) in 2 ml CH_2Cl_2. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h. The solvent was removed under reduced pressure. The oily residue was separated by silica (Merck 230–400 mesh) column chromatography using *n*-hexane-EtOAc mixture as eluent, to yield **3a** as colourless oil; yield 0.67 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 2040 (C=C=N–R), 1740, 1680 (C=O).

MS: *m/z* (%) = 423 (M^++1, 8), 422 (M^+, 5), 366 (50), 226 (60), 197 (90), 138 (75), 57 (100). Anal. Calcd for $C_{20}H_{23}FN_2O_7$: C, 56.87; H, 5.49; N, 6.63%. Found: C, 56.9; H, 5.5; N, 6.6%.

3a–I (58%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.27 (s, 9 H, C*Me*$_3$), 3.51, 3.60, and 3.93 (3s, 9 H, 3 OMe), 5.74 (s, 1 H, CH), 7.04–7.68 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (C*Me*$_3$), 51.7, 52.4, and 52.9 (3 OMe), 58.3 (CH), 59.9 (*C*=C=N), 62.2 (N-*C*Me$_3$), 115.1 (d, $^2J_{CF}$ = 19 Hz, CH), 124.8, 125.9, 131.1, and 132.0 (Ph), 152.7 (d, $^1J_{CF}$ = 239 Hz, CF), 160.8, 161.4, 161.8, 168.1, and 169.1 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –118.41 (CF) ppm.

3a–II (42%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.25 (s, C*Me*$_3$), 3.51, 3.60, and 3.94 (3s, 3 H, 3 OMe), 5.45 (s, 1 H, CH), 7.04–7.68 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (C*Me*$_3$), 51.9, 52.1, and 52.6 (3 OMe), 58.3 (CH), 58.5 (*C*=C=N), 62.2 (N–*C*Me$_3$), 116.3 (d, $^2J_{CF}$ = 20 Hz, CH), 124.3, 125.9, 131.1, and 132.0 (Ph), 152.8 (d, $^1J_{CF}$ = 251 Hz, CF), 160.8, 161.4, 161.8, 168.2, and 169.1 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –119.38 (CF) ppm.

Dimethyl 2-[(tert-butylimino)-methylene]-3-[(2-ethoxy-2-oxoacetyl)-2-fluoroanilino]-succinate **(3b):** Colourless oil, yield 0.68 g (78%). IR (KBr) (ν_{max}/cm^{-1}): 2050 (C=C=N–R), 1737, 1677(C=O) cm^{-1}. MS: *m/z* (%) = 437 (M^++1, 20), 436 (M^+, 8), 380 (70), 244 (50), 226 (100), 57 (75). Anal. Calcd for $C_{21}H_{25}FN_2O_7$: C, 57.79; H, 5.77; N, 6.42%. Found: C, 57.8; H, 5.7; N, 6.5%.

3b–I (62%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.94 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.24 (s, 9 H, CMe_3), 3.58 and 3.74 (2s, 6 H, 2 OMe), 3.95 (q, 2 H, $^3J_{HH}$ = 7 Hz, CH_2), 5.77 (s, 1 H, CH), 7.05–7.58 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (Me), 29.99 (C*Me*$_3$), 51.7 and 52.8 (2 OMe), 58.1 (CH), 59.9 (*C*=C=N), 61.8 (OCH_2), 62.2 (N–*C*Me$_3$), 116.2 (d, $^2J_{CF}$ = 20 Hz, CH), 124.5, 125.8, 131.2, and 132.4 (Ph), 159.3 (d, $^1J_{CF}$ = 252 Hz, CF), 161.0, 161.6, 162.1, 168.1, and 169.0 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –118.02 (CF) ppm.

3b–II (38%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.94 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.34 (s, 9 H, CMe_3), 3.61 and 3.75 (2s, 6 H, 2 OMe), 3.95 (q, 2 H, $^3J_{HH}$ = 7 Hz, CH_2), 5.43 (s, 1 H, CH), 7.05–7.58 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (Me), 30.0 (C*Me*$_3$), 51.7 and 52.8 (2 OMe), 58.1 (CH), 59.9 (*C*=C=N), 61.8 (OCH_2), 62.2 (N–*C*Me$_3$), 116.2 (d, $^2J_{CF}$ = 20 Hz, CH), 124.5, 125.8, 131.2, and 132.4 (Ph), 159.3 (d, $^1J_{CF}$ = 252 Hz, CF), 161.0, 161.6, 162.1, 168.1, and 169.0 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –118.98 (CF) ppm.

Diethyl 2-[(tert-butylimino)-methylene]-3-[(2-ethoxy-2-oxoacetyl)-2-fluoroanilino]-succinate **(3c):** Colourless oil, yield 0.70 g (75%). IR (KBr) (ν_{max}/cm^{-1}): 2020 (C=C=N–R), 1730, 1672 (C=O) cm^{-1}. MS: *m/z* (%) = 465 (M^++1, 25), 464 (M^+, 10), 409 (50), 379 (50), 254 (80), 211 (90), 57 (100). Anal. Calcd for $C_{23}H_{29}FN_2O_7$: C, 59.47; H, 6.29; N, 6.03%. Found: C, 59.5; H, 6.3; N, 6.0%.

3c–I (60%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.90 and 0.91 (2t, 6 H, $^3J_{HH}$ = 7 Hz, 2 Me), 1.11 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.21 (s, 9 H, CMe_3), 3.92, 4.02, and 4.18 (3 m, 6 H, 3 OCH_2), 5.73 (s, 1 H, CH), 7.02–7.59 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 13.9, and 14.1 (3 Me), 29.8 (C*Me*$_3$), 59.0 (CH), 59.1 (*C*=C=N), 60.2, 61.5, and 61.8 (3 OCH_2), 61.9 (N–*C*Me$_3$), 116.1, 124.4, 125.6, 131.1, and 132.5 (Ph), 159.3 (d, $^1J_{CF}$ = 253 Hz, CF), 161.0, 161.5, 163.0, 167.4, and 168.3 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = -117.86 (CF) ppm.

3c–II (40%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.90 and 0.91 (2t, 6 H, $^3J_{HH}$ = 7 Hz, 2 Me), 1.11 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.32 (s, 9 H, CMe_3), 3.92, 4.02, and 4.18 (3m, 6 H, 3 OCH_2), 5.35 (s, 1 H, CH), 7.02–7.59 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 14.0, and 14.1 (3 Me), 29.8 (C*Me*$_3$), 59.0 (CH), 59.1 (*C*=C=N), 60.2, 61.5, and 61.8 (3 OCH_2), 62.0 (N–*C*Me$_3$), 116.1, 124.4, 127.3, 131.1, and 132.5 (Ph), 159.2 (d, $^1J_{CF}$ = 250 Hz, CF), 161.0, 161.7, 163.1, 168.3, and 169.3 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –118.75 (CF) ppm.

Dimethyl 2-[(tert-butylimino)- methylene]-3-[(2-ethoxy-2-oxoacetyl)-2-(trifluoromethyl)-anilino]-succinate **(3d):** Colourless oil, yield 0.78 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 2050 (C=C=N–R), 1736, 1686 (C=O) cm^{-1}. MS: *m/z* (%) = 486 (M^+, 8), 430 (50), 261 (52), 226 (100), 168 (50), 57 (90). Anal. Calcd for $C_{22}H_{25}F_3N_2O_7$: C, 54.32; H, 5.18; N, 5.76%. Found: C, 54.3; H, 5.2; N, 5.7%.

3d–I (57%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.01 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.34 (s, 9 H, CMe_3), 3.59 and 3.81 (2s, 6 H, 2 OMe), 4.04 (q, 2 H, $^3J_{HH}$ = 7 Hz, OCH_2), 5.63 (s, 1 H, CH), 7.47–7.83 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (Me), 30.1 (C*Me*$_3$), 51.7 and 52.8 (2 OMe), 58.9 (CH), 61.9 (OCH_2), 62.3 and 63.4 (N–*C*Me$_3$ and *C*=C=N), 125.2 (q, $^1J_{CF}$ = 274 Hz, CF), 127.7 (q, $^3J_{CF}$ = 5 Hz, CH), 129.6 (q, $^2J_{CF}$ = 23 Hz, *C*–CF_3), 129.8, 130.9, 133.3, and 135.3 (Ph), 160.4, 160.8, 162.2, 168.8, and 169.4 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –58.77 (CF_3) ppm.

3d–II (43%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.05 (t, 3 H, $^3J_{HH}$ = 7 Hz, Me), 1.47 (s, 9 H, CMe_3), 3.66 and 3.84 (2s, 6 H, 2 OMe), 3.99 (q, 2 H, $^3J_{HH}$ = 7 Hz, OCH_2), 5.19 (s, 1 H, CH), 7.47–7.83 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (Me), 30.0 (C*Me*$_3$), 51.7 and 53.2 (2 OMe), 58.8 (CH), 60.9 and 62.5 (N–*C*Me$_3$ and *C*=C=N), 62.0 (OCH_2), 125.1 (q, $^1J_{CF}$ = 274 Hz, CF), 127.4 (q, $^3J_{CF}$ = 5 Hz, CH), 129.1 (q, $^2J_{CF}$ = 22 Hz, *C*–CF_3), 129.2, 132.3, 133.2, and 139.2 (Ph), 160.0, 160.2, 162.8, 168.4, and 170.9 (N=*C*=C, 4 C=O) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –59.65 (CF_3) ppm.

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