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A simple synthesis of trifluoromethylated pyridinium azomethine ylides by three-component reaction between pyridines, phenacyl bromides, and *N*-aryltrifluoroacetimidoyl chlorides

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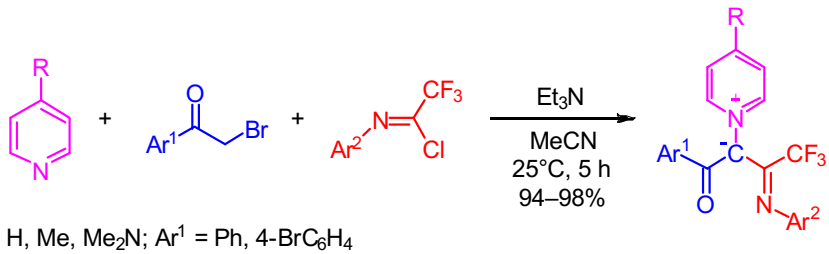


R = H, Me, Me_2N; Ar^1 = Ph, 4-BrC_6H_4
Ar^2 = 4-ClC_6H_4, 3,4-$Me_2C_6H_3$, 4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 2-ClC_6H_4, 4-FC_6H_4

A novel synthesis of trifluoromethylated pyridinium azomethine ylides by three-component reaction between pyridines, phenacyl bromides, and trifluoromethylated imidoyl chlorides in acetonitrile as solvent at room temperature without any catalyst is described. The FT-IR, ^1H, ^{13}C, ^{19}F NMR spectral and elemental analysis confirm the structures of products. The synthesized azomethine ylides are easily purified by washing with diethyl ether and are stable even at high temperature. Heating of these ylides in refluxing acetonitrile, ethanol, or DMSO did not result in the intramolecular cyclization to imidazopyridine derivatives and only starting ylides were isolated.

Keywords: imidoyl chlorides, pyridinium azomethine ylides, trifluoromethylated pyridinium azomethine ylides, phenacyl bromides, three-component reaction.

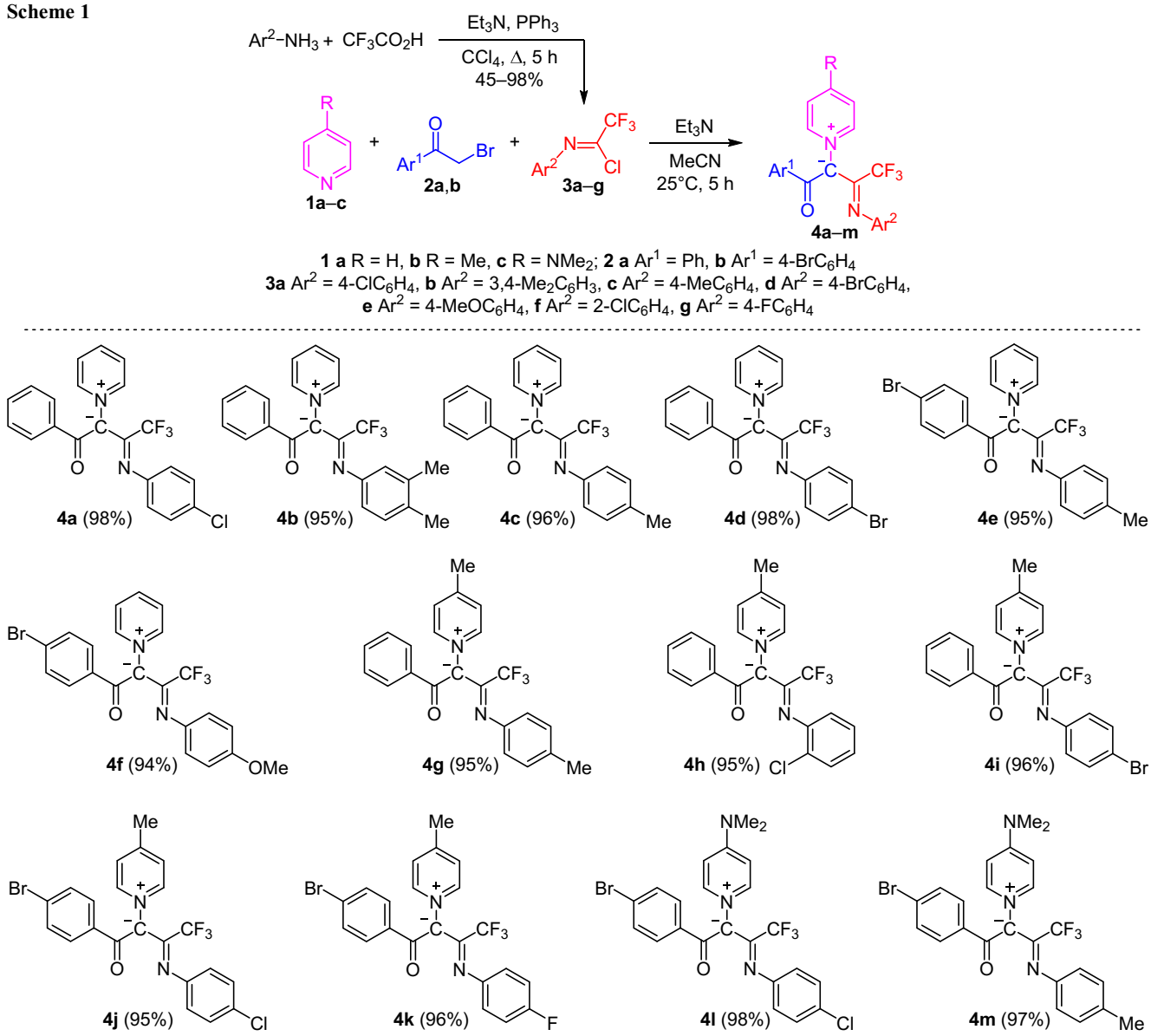
Nitrogen-containing heterocycles are key components in many biologically active compounds.[1] Pyridine and its derivatives constitute the most important family of compounds among these heterocycles, and there has been significant interest in developing efficient methods for their synthesis.[2–4]

Azomethine ylides have attracted much attention from synthetic chemists for their wide application in the synthesis of N-heterocyclic compounds. Azomethine ylides are quite unstable to be isolated and are typically generated *in situ*. In general, azomethine ylides are known to undergo [3+2] cycloaddition to π-bonds for the construction of azacyclic heterocycles.[5–8] Pyridinium azomethine ylides are very attractive for the synthetic chemists for their involvement in [3+2] and [5+2] cycloaddition reactions.[9–11] Despite the high potential of pyridinium azomethine ylides for the synthesis of new heterocyclic compounds, there are only few methods for their preparation from readily available starting materials. These ylides are usually prepared by deprotonation of the appropriate *N*-alkylpyridinium salts.[10] Pyridinium azomethine ylides have also been prepared *via* the rhodium-catalyzed reaction between pyridine and 1-sulfonyl-1,2,3-triazoles.[11]

Fluorine atoms play an important role in bioactive compounds and have been widely studied for their structural elaboration.[12–15] It has been proved that fluorine gives unique properties to the organic molecules and alters their physicochemical and biological abilities. Among the fluorinated substituents, trifluoromethyl group (CF_3) has found much attention in medicinal and agricultural chemistry and materials sciences[14] because its incorporation into the molecule provides simultaneously high lipophilicity, elevated electron density, and steric demand as, for example, isopropyl group.[16]

In continuation of our previous studies on the application of trifluoromethylated imidoyl chlorides in the synthesis of fluorinated organic compounds,[17–20] we report herein an efficient synthesis of trifluoromethylated pyridinium azomethine ylides **4a**–**m** by three-component reaction between pyridines **1a**–**c**, phenacyl bromides **2a**,**b**, and trifluoromethylated imidoyl chlorides **3a**–**g** in MeCN as solvent at room temperature without use of any catalyst

Scheme 1



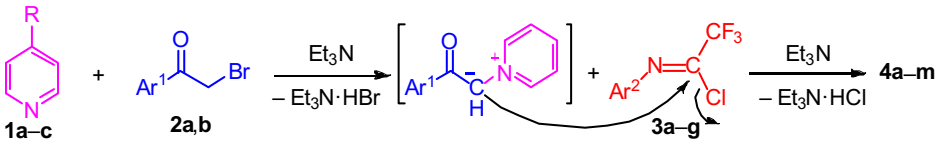
(Scheme 1). *N*-Aryltrifluoroacetimidoyl chlorides **3a**–**g** used in this work were synthesized by reaction of CF_3CO_2H, primary arylamines, and PPh_3 in CCl_4 in the presence of Et_3N. Workup and distillation of the reaction mixture gave the target imidoyl chlorides **3a**–**g** in good to excellent yields[21,22] (Scheme 1).

At the beginning of our investigation, we carried out the reaction between pyridine (**1a**), phenacyl bromide (**2a**), and 4-(chlorophenyl)-2,2,2-trifluoroacetimidoyl chloride (**3a**) in the presence of Et_3N in MeCN as a solvent. After stirring for 5 h at room temperature, the analysis of the reaction mixture by TLC showed the presence of only one product. Evaporation of solvent under reduced pressure and simple washing of the product with Et_2O afforded trifluoromethylated pyridinium azomethine ylide **4a** in nearly quantitative yield. The structure of the product was proved by the IR, NMR spectral data and elemental analysis.

IR spectrum of compound **4a** displayed characteristic C=O and C=N vibrations at 1592 and 1581 cm^{-1}, respectively. ^1H NMR spectrum of compound **4a** showed two doublet signals at 6.59 and 6.99 ppm ($^3J_{HH}$ = 8.0 Hz) for chlorophenyl ring. The protons of phenyl ring were observed as a doublet at 7.17 ($^3J_{HH}$= 8.0 Hz, *ortho* protons) and two triplets at 7.24 ($^3J_{HH}$ = 8.0 Hz, *meta* protons), and 7.32 ppm ($^3J_{HH}$ = 8.0 Hz, *para* protons). Three broad signals were observed at 7.85, 8.29, and 8.76 ppm for protons of pyridinium ring. Delocalization of the carbon electron pair (negative charge) toward the pyridinium ring gives a partial double bond character to the C–N bond and results in the restricted rotation of pyridine ring around this bond and broadening of the resonance signals related to the protons of pyridine ring. Fifteen distinct resonances were observed in the ^{13}C NMR spectrum of compound **4a** in agreement with the proposed structure. The ^{19}F NMR spectrum of compound **4a** in DMSO-d_6 showed a signal at −64.05 ppm for the CF_3 group.

To define the scope and generality of the reaction, a series of substituted *N*-aryltrifluoroacetimidoyl chlorides

Scheme 2

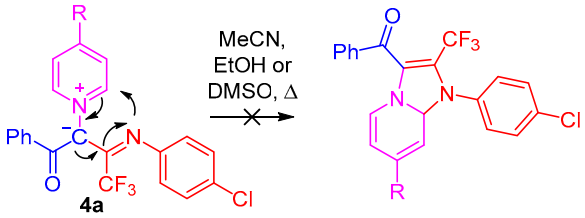


3a–**g**, phenacyl bromides **2a**,**b**, and pyridines **1a**–**c** were examined. To our delight, in each case, the desired pyridinium azomethine ylide was obtained in excellent yield (Scheme 1).

A plausible mechanism for the formation of compounds **4a**–**m** is shown in Scheme 2. Substitution of the bromine atom of phenacyl bromide **2a**,**b** by pyridine derivative **1a**–**c** followed by deprotonation with Et_3N afforded pyridinium ylide, which attacks imidoyl chloride **3a**–**g** to produce products **4a**–**m** after deprotonation with Et_3N.

To examine the possibility of intramolecular ring closure of ylide **4a** to produce imidazopyridine derivatives, we heated compound **4a** in different solvents, such as MeCN, EtOH, and DMSO, but in each case, the starting ylide **4a** was isolated (Scheme 3).

Scheme 3



In conclusion, we have synthesized a series of pyridinium azomethine ylides by a three-component reaction between readily accessible starting materials in excellent yields. The reactions are carried out at room temperature without any catalyst, and the products are purified by simple washing with diethyl ether.

Experimental

IR spectra (KBr) were obtained on a Thermo Scientific Nicolet IS10 Fourier transform IR spectrometer (Thermo Fisher Scientific, Waltham, MA). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer (400, 100, and 376 MHz, respectively) in DMSO-d_6. TMS was used as internal standard for ^{1}H and ^{13}C NMR spectra, $CFCl_3$ for ^{19}F NMR spectra. Melting points were determined on a Melt-Temp II melting point apparatus and are uncorrected. TLC was performed on Merck 60 F_{254} silica gel plates, visualization by a UV lamp (254 nm).

All chemicals and solvents were purchased from commercial sources and used without further purification, unless otherwise stated.

Synthesis of trifluoromethylated pyridinium azomethine ylides 4a–m (General method). Dry, one-necked, 50-ml round bottomed flask was charged with dry MeCN (5 ml), pyridine derivative **1a**–**c** (1.0 mmol), 2-bromo-1-phenylethan-1-one derivative **2a**,**b** (1.0 mmol), and Et_3N (121 mg, 1.2 mmol). The solution was stirred at room temperature for 10 min, then a solution of 2,2,2-trifluoroacetimidoyl chloride derivative **3a**–**g** (1.0 mmol in 2 ml of dry MeCN) was added dropwise over a period of 10 min. The mixture was stirred at room temperature for 5 h. The reaction was monitored by TLC. After completion, EtOAc (10 ml) was added. Then the organic layer was separated and aqueous layer was extracted with EtOAc (2×10 ml). After combination of organic layers, organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give the crude product, which was purified by washing with Et_2O (2×15 ml) and *n*-hexane (2×15 ml).

3-[(4-Chlorophenyl)imino]-4,4,4-trifluoro-1-oxo-1-phenyl-2-(pyridinium-1-yl)butan-2-ide (4a) was synthesized from pyridine **1a**, phenacyl bromide **2a**, and imidoyl chloride **3a**. Yield 394 mg (98%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1592 (C=O), 1581 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.59 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 6.99 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.17 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.24 (2H, t, $^3J_{HH}$ = 8.0, H Ar); 7.32 (1H, t, $^3J_{HH}$ = 8.0, H Ar); 7.85 (2H, br. s, H Py); 8.29 (1H, t, $^3J_{HH}$ = 8.0, H Py); 8.76 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 121.6 (q, $^1J_{CF}$ = 280.1, CF_3); 121.7; 127.1; 127.7; 127.8; 128.2; 128.8; 129.9; 131.5; 141.9; 143.2; 148.8; 149.0; 152.6 (q, $^2J_{CF}$ = 28.1, C–CF_3); 180.1 (C=O). ^{19}F NMR spectrum, δ, ppm: −64.05. Found, %: C 62.12; H 3.38; N 7.11. $C_{21}H_{14}ClF_3N_2O$. Calculated, %: C 62.62; H 3.50; N 6.95.

3-[(3,4-Dimethylphenyl)imino]-4,4,4-trifluoro-1-oxo-1-phenyl-2-(pyridinium-1-yl)butan-2-ide (4b) was synthesized from pyridine **1a**, phenacyl bromide **2a**, and imidoyl chloride **3b**. Yield 376 mg (95%), orange solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1689 (C=O), 1625 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.96 (3H, s, CH_3); 2.06 (3H, s, CH_3); 6.17 (1H, s, H Ar); 6.47 (1H, d, $^3J_{HH}$ = 8.1, H Ar); 6.77 (1H, d, $^3J_{HH}$ = 8.1, H Ar); 7.23−7.33 (5H, m, H Ar); 7.67–7.78 (2H, m, H Py); 8.15–8.25 (1H, m, H Py); 8.58–8.69 (2H, m, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 19.2 (CH_3); 19.8 (CH_3); 116.8; 121.5 (q, $^1J_{CF}$ = 267.1, CF_3); 121.7; 127.4; 127.9; 128.2; 128.4; 128.7; 129.7; 130.7; 131.4; 136.7; 142.4; 144.2; 148.3; 154.5 (q, $^2J_{CF}$ = 28.1, C–CF_3); 183.1 (C=O). ^{19}F NMR spectrum, δ, ppm: −60.76. Found, %: C 69.71; H 4.86; N 7.04. $C_{23}H_{19}F_3N_2O$. Calculated, %: C 69.69; H 4.83; N 7.07.

4,4,4-Trifluoro-3-[(4-methylphenyl)imino]-1-oxo-1-phenyl-2-(pyridinium-1-yl)butan-2-ide (4c) was synthesized from pyridine **1a**, phenacyl bromide **2a**, and imidoyl chloride **3c**. Yield 367 mg (96%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1689 (C=O), 1580 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15 (3H, s, CH_3); 6.50 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 6.79 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.21−7.32 (5H, m, H Ar); 7.75 (2H, br. s, H Py); 8.18 (1H, br. s, H Py); 8.61 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 20.9 (CH_3); 120.1; 121.5 (q, $^1J_{CF}$ = 284.1, CF_3); 127.6; 127.9; 128.2; 128.8; 129.4; 129.7; 129.9; 132.8; 142.0; 142.7; 148.3; 152.6 (q, $^2J_{CF}$ = 28.0, C–CF_3); 179.8 (C=O). ^{19}F NMR spectrum, δ, ppm:

−63.94. Found, %: C 69.13; H 4.42; N 7.30. $C_{22}H_{17}F_3N_2O$. Calculated, %: C 69.10; H 4.48; N 7.33.

3-[(4-Bromophenyl)imino]-4,4,4-trifluoro-1-oxo-1-phenyl-2-(pyridinium-1-yl)butan-2-ide (4d) was synthesized from pyridine **1a**, phenacyl bromide **2a**, and imidoyl chloride **3d**. Yield 438 mg (98%), orange solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1632 (C=O), 1585 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 6.51 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.11 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.16−7.20 (2H, m, H Ar); 7.24 (2H, t, $^3J_{HH}$ = 8.0, H Ar); 7.30−7.34 (1H, m, H Ar); 7.84 (2H, br. s, H Py); 8.29 (1H, m, H Py); 8.75 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 115.1; 121.6 (q, $^1J_{CF}$ = 289.1, CF_3); 122.1; 127.7; 127.8; 128.2; 129.9; 131.7; 141.9; 143.2; 148.9; 149.5; 152.5 (q, $^2J_{CF}$ = 32.0, C–CF_3); 180.1 (C=O). ^{19}F NMR spectrum, δ, ppm: −68.10. Found, %: C 56.43; H 3.12; N 6.20. $C_{21}H_{14}BrF_3N_2O$. Calculated, %: C 56.39; H 3.16; N 6.26.

1-(4-Bromophenyl)-4,4,4-trifluoro-3-[(4-methylphenyl)-imino]-1-oxo-2-(pyridinium-1-yl)butan-2-ide (4e) was synthesized from pyridine **1a**, phenacyl bromide **2b**, and imidoyl chloride **3c**. Yield 438 mg (95%), orange solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1686 (C=O), 1587 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3); 6.47 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 6.77 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.06 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.40 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.79 (2H, br. s, H Py); 8.24 (1H, br. s, H Py); 8.67 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 20.9 (CH_3); 110.0; 119.8; 121.5 (q, $^1J_{CF}$ = 278.7, CF_3); 122.9; 127.5; 129.4; 129.7; 131.1; 132.7; 142.6; 146.8; 147.2; 148.2; 152.5 (q, $^2J_{CF}$ = 30.0, C–CF_3); 177.3 (C=O). ^{19}F NMR spectrum, δ, ppm: −61.19. Found, %: C 57.31; H 3.55; N 6.01. $C_{22}H_{16}BrF_3N_2O$. Calculated, %: C 57.28; H 3.50; N 6.07.

1-(4-Bromophenyl)-4,4,4-trifluoro-3-[(4-methoxyphenyl)-imino]-1-oxo-2-(pyridinium-1-yl)butan-2-ide (4f) was synthesized from pyridine **1a**, phenacyl bromide **2b**, and imidoyl chloride **3e**. Yield 448 mg (94%), red solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1687 (C=O), 1628 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.67 (3H, s, OCH_3); 6.55−6.62 (4H, m, H Ar); 7.10 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.43 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.84 (2H, br. s, H Py); 8.26 (1H, br. s, H Py); 8.74 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 55.7 (OCH_3); 121.4; 121.6 (q, $^1J_{CF}$= 280.1, CF_3); 122.9; 127.6; 128.4; 129.7; 130.7; 131.1; 132.8; 142.7; 144.4; 147.9; 151.7 (q, $^2J_{CF}$ = 31.0, C–CF_3); 156.2; 177.3 (C=O). ^{19}F NMR spectrum, δ, ppm: −73.91. Found, %: C 55.32; H 3.40; N 5.85. $C_{22}H_{16}BrF_3N_2O_2$. Calculated, %: C 55.36; H 3.38; N 5.87.

4,4,4-Trifluoro-3-[(4-methylphenyl)imino]-2-(4-methyl-pyridinium-1-yl)-1-oxo-1-phenylbutan-2-ide (4g) was synthesized from pyridine **1b**, phenacyl bromide **2a**, and imidoyl chloride **3c**. Yield 377 mg (95%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1632 (C=O), 1577 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.16 (3H, s, CH_3); 2.49 (3H, s, CH_3); 6.45 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 6.77 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.17−7.29 (5H, m, H Ar); 7.56 (2H, br. s, H Py); 8.45 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 20.9 (CH_3); 21.5 (CH_3); 119.9; 121.4 (q, $^1J_{CF}$ = 280.1, CF_3); 127.8; 128.1; 129.3; 129.4; 129.5; 129.9; 132.2; 141.9; 142.6; 147.8; 148.3; 150.6 (q, $^2J_{CF}$ = 31.0, C–CF_3); 180.0 (C=O). ^{19}F NMR spectrum, δ, ppm: −68.63. Found, %: C 69.70; H 4.80; N 7.02. $C_{23}H_{19}F_3N_2O$. Calculated, %: C 69.69; H 4.83; N 7.07.

3-[(2-Chlorophenyl)imino]-4,4,4-trifluoro-2-(4-methyl-pyridinium-1-yl)-1-oxo-1-phenylbutan-2-ide (4h) was synthesized from pyridine **1b**, phenacyl bromide **2a**, and imidoyl chloride **3f**. Yield 396 mg (95%), red solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1627 (C=O), 1592 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, CH_3); 6.78–6.90 (1H, m, H Ar); 6.97−7.03 (3H, m, H Ar); 7.25−7.30 (5H, m, H Ar); 7.55 (2H, br. s, H Py); 8.47 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 21.5 (CH_3); 120.5; 121.3 (q, $^1J_{CF}$ = 280.2, CF_3); 124.1; 125.7; 127.5; 127.7; 127.8; 128.3; 129.7; 129.8; 142.4; 147.1; 148.6; 152.7 (q, $^2J_{CF}$ = 29.0, C–CF_3); 156.9; 181.0 (C=O). ^{19}F NMR spectrum, δ, ppm: −68.53. Found, %: C 63.35; H 3.89; N 6.70. $C_{22}H_{16}ClF_3N_2O$. Calculated, %: C 63.39; H 3.87; N 6.72.

3-[(4-Bromophenyl)imino]-4,4,4-trifluoro-2-(4-methyl-pyridinium-1-yl)-1-oxo-1-phenylbutan-2-ide (4i) was synthesized from pyridine **1b**, phenacyl bromide **2a**, and imidoyl chloride **3d**. Yield 442 mg (96%), orange solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1603 (C=O), 1580 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, CH_3); 6.49 (2H, d, $^3J_{HH}$ = 8.0, H Ar); 7.09−7.13 (4H, m, H Ar); 7.17−7.25 (2H, m, H Ar); 7.28−7.32 (1H, m, H Ar); 7.70 (2H, br. s, H Py); 8.62 (2H, d, ^3J = 8.0, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 21.6 (CH_3); 114.8; 121.7 (q, $^1J_{CF}$ = 281.0, CF_3); 122.1; 127.7; 128.0; 128.2; 129.7; 131.6; 142.0; 148.4; 149.8; 152.0 (q, $^2J_{CF}$ = 35.0, C–CF_3); 156.9; 180.2 (C=O). ^{19}F NMR spectrum, δ, ppm: −61.00. Found, %: C 57.23; H 3.54; N 6.02. $C_{22}H_{16}BrF_3N_2O$. Calculated, %: C 57.28; H 3.50; N 6.07.

1-(4-Bromophenyl)-3-[(4-chlorophenyl)imino]-4,4,4-trifluoro-2-(4-methylpyridinium-1-yl)-1-oxobutan-2-ide (4j) was synthesized from pyridine **1b**, phenacyl bromide **2b**, and imidoyl chloride **3a**. Yield 471 mg (95%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1637 (C=O), 1500 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.56 (3H, s, CH_3); 6.58 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 6.99−7.04 (4H, m, H Ar); 7.42 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 7.74 (2H, br. s, H Py); 8.66 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 21.7 (CH_3); 115.6 (q, $^1J_{CF}$ = 279.0, CF_3); 121.7; 123.0; 127.0; 128.1; 128.8; 129.7; 131.2; 141.1; 148.4; 149.3; 152.0 (q, $^2J_{CF}$ = 29.0, C–CF_3); 157.3; 178.7 (C=O). ^{19}F NMR spectrum, δ, ppm: −68.53. Found, %: C 53.28; H 3.01; N 5.61. $C_{22}H_{15}BrClF_3N_2O$. Calculated, %: C 53.30; H 3.05; N 5.65.

1-(4-Bromophenyl)-4,4,4-trifluoro-3-[(4-fluorophenyl)-imino]-2-(4-methylpyridinium-1-yl)-1-oxobutan-2-ide (4k) was synthesized from pyridine **1b**, phenacyl bromide **2b**, and imidoyl chloride **3g**. Yield 460 mg (96%), red solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1635 (C=O), 1589 (C=N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.56 (3H, s, CH_3); 6.58−6.61 (2H, m, H Ar); 6.79−6.83 (2H, m, H Ar); 7.05 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 7.42 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 7.73 (2H, br. s, H Py); 8.65 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 21.6 (CH_3); 115.5 (d, $^2J_{CF}$ = 22.0, C–CF); 121.5 (d, $^3J_{CF}$ = 8, C–C–CF); 121.7 (d, $^1J_{CF}$ = 280.0, CF_3); 123.0; 128.1; 129.7; 131.1; 141.2; 145.6;

146.6; 148.1; 152.3 (q, $^2J_{CF}$ = 30.0, C–CF_3); 157.5; 158.2 (q, $^1J_{CF}$ = 292.0, C–F); 178.1 (C=O). ^{19}F NMR spectrum, δ, ppm: −68.16; −113.60. Found, %: C 55.10; H 3.19; N 5.80. $C_{22}H_{15}BrF_4N_2O$. Calculated, %: C 55.13; H 3.15; N 5.85.

1-(4-Bromophenyl)-3-[(4-chlorophenyl)imino]-2-[4-(dimethylamino)pyridinium-1-yl]-4,4,4-trifluoro-1-oxobutan-2-ide (4l) was synthesized from pyridine **1c**, phenacyl bromide **2b**, and imidoyl chloride **3a**. Yield 514 mg (98%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 1563 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.18 (6H, s, $2CH_3$); 6.53−6.57 (2H, m, H Ar); 6.80 (2H, br. s, H Py); 6.96−7.00 (4H, m, H Ar); 7.36 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 7.97 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 40.6 (CH_3); 107.5; 115.7; 121.9 (q, $^1J_{CF}$ = 276.1, CF_3); 121.7; 122.2; 128.6; 129.0; 129.7; 130.9; 141.8; 147.7; 150.2; 152.0 (q, $^2J_{CF}$ = 35.0, C–CF_3); 155.6; 179.2 (C=O). ^{19}F NMR spectrum, δ, ppm: −64.39. Found, %: C 52.60; H 3.43; N 8.06. $C_{23}H_{18}BrClF_3N_3O$. Calculated, %: C 52.64; H 3.46; N 8.01.

1-(4-Bromophenyl)-2-[4-(dimethylamino)pyridinium-1-yl]-4,4,4-trifluoro-3-[(4-methylphenyl)imino]-1-oxobutan-2-ide (4m) was synthesized from pyridine **1c**, phenacyl bromide **2b**, and imidoyl chloride **3c**. Yield 489 mg (97%), yellow solid, mp >300°C. IR spectrum, ν, cm^{-1}: 1646 (C=O), 1562 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.16 (3H, s, CH_3); 3.16 (6H, s, $2CH_3$); 6.42 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 6.76–6.78(4H, m, H Ar); 7.00 (2H, br. s, H Py); 7.35 (2H, d, $^3J_{HH}$ = 8.1, H Ar); 7.87 (2H, br. s, H Py). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 20.9 (CH_3); 40.6 ($2CH_3$); 107.5; 131.1 (q, $^1J_{CF}$ = 318.1, CF_3); 119.8; 122.3; 129.3; 129.7; 130.9; 131.4; 140.8; 141.9; 147.3; 148.6; 155.5; 156.1 (q, $^2J_{CF}$ = 38.0, C–CF_3); 178.4 (C=O). ^{19}F NMR spectrum, δ, ppm: −65.02. Found, %: C 57.19; H 4.23; N 8.30. $C_{24}H_{21}BrF_3N_3O$. Calculated, %: C 57.15; H 4.20; N 8.33.

Supplementary information file containing ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds **4a**–**m** is available at the journal website at http://link.springer.com/journal/10593.

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