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Reaction of unsymmetrical trifluoromethyl-containing 1,3-dicarbonyl compounds with 'push–pull' enamines

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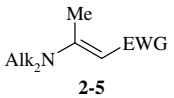
Abstract—The reaction of 'push–pull' enamines with trifluoromethyl-containing 1,3-dicarbonyl compounds was investigated. It was found that the reaction is sensitive both to the structure of the enamines and to reaction conditions. As a result, a set of various trifluoromethyldialkylanilines was obtained.

For the last few years our research group has been dealing with 'push–pull' enamines studying their reactions with various mono- and biselectrophilic fluoro-containing reagents. In particular, we are interested in reagents that react at α-methyl (methylene) groups of the linear 'push–pull' enamines. As a result, we have developed a convenient synthetic procedure for electrophilic functionalization of enamines affording trifluoromethylated building blocks.[1,2] In our previous work, we have demonstrated the possibility of using tertiary 'push–pull' enamines as 1,3-bisnucleophiles in reactions with β-trifluoroacetylvinylethers[3] and 1,1,1,5,5,5-hexafluoroacetylacetone[4] for the synthesis of trifluoromethylated functionalized dialkylanilines. At the same time, the commercially available 1,3-biselectrophilic building blocks—1,1,1,5,5,5-hexafluoroacetylacetone and 4,4,4-trifluoroacetoacetate have been widely used for the synthesis of trifluoromethylated heterocyclic compounds.[5–9] The main methods for the synthesis of trifluoromethyl-containing aromatic compounds are based on direct introduction of the trifluoromethyl group, on transformations of other functional groups into a trifluoromethyl, or chemical transformations of fluoro-containing aromatic compounds leaving the fluoro-containing substituent intact.[10]

Based on our previous experience[3,4] we continued our search for new trifluoromethyl-containing electrophilic reagents that can be used in reactions with 'push–pull' enamines with the aim to develop a new approach to trifluoromethyl-containing aromatic compounds. In this Letter we report our results on the reaction of tertiary 'push–pull' enamines having a methyl group at the α-position (Fig. 1) with unsymmetrical trifluoromethyl-1,3-dicarbonyl compounds.

Enamines **2**, derivatives of β-aminocrotonic acid, react with 4,4,4-trifluoroacetoacetate **1** on heating in dry benzene for 2–3 h affording compounds **6** as a result of addition at the methyl group of the enamines (Scheme 1).[11] In acetic acid the yields decreased markedly (according to ^{19}F NMR spectroscopy of the reaction mixture, Table 1). One can expect cyclization products to form by attack of the ester group at the β-position of the enamine. However, no such products were detected either in benzene or acetic acid.

In going from enamines **2** to enamines **3**, the reaction with 4,4,4-trifluoroacetoacetate **1** proceeded differently. In benzene, a mixture of two cyclic products **7** and **8** in ~1.5:1 molar ratio (^{19}F NMR spectroscopy of the reaction mixture) were registered. Moreover, compounds **8** were formed with participation of two



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Alk_2N = **a:** $N(CH_2)_4$, **b:** $N(CH_2CH_2)_2O$
EWG = **2:** CO_2Et; **3:** COMe; **4:** COPh; **5:** CN

Figure 1. The structures of the starting 'push–pull' enamines.

Keywords: 4,4,4-Trifluoroacetoacetate; 'Push–pull' enamines; Trifluoromethylated benzenes; Cyclocondensation.
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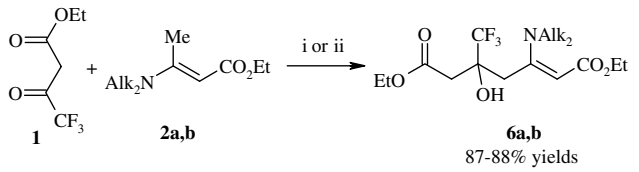


Scheme 1. Reagents and conditions: (i) benzene, reflux, 2–3 h, (ii) AcOH, reflux, several hours.

Table 1. ^{19}F NMR data, yields and the reaction conditions for the compounds obtained

Enamine	Alk_2N	Solvent	Product[a]	Yield[b]	δ_F (ppm)
2a	$N(CH_2)_4$	Benzene	**6a**	87	−82.7
		AcOH		11	
2b	$N(CH_2)_4O$	Benzene	**6b**	88	−82.9
		AcOH		Traces[c]	
3a	$N(CH_2)_4$	Benzene	**7a**	40	−60.6
			8a	36	−60.2 and −82.2
3a	$N(CH_2)_4$	AcOH	**7a**	81	−60.6
3b	$N(CH_2)_4O$	Benzene	**7b**	Traces[c]	−58.7
			8b		−59.1 and −81.4
3b	$N(CH_2)_4O$	AcOH	**7b**	72	−60.8
4a	$N(CH_2)_4$	Benzene	**9a**	52	−58.9
		AcOH		57	
4b	$N(CH_2)_4O$	Benzene	—	—	—
		AcOH	**10**[d]	46	
5a	$N(CH_2)_4$	Benzene	**11**	56	—
5b	$N(CH_2)_4O$	AcOH	**11**	87	—

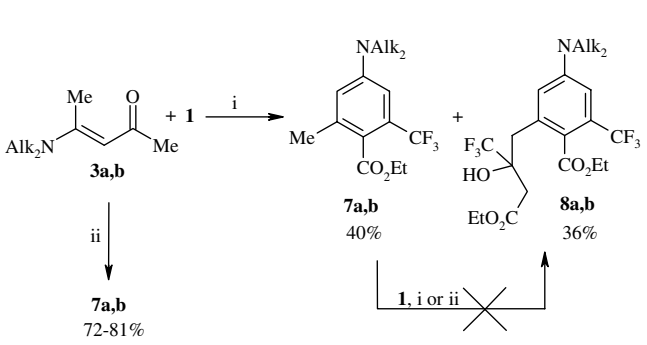
[a] Isolated products.
[b] Isolated yields.
[c] According to ^{19}F NMR spectroscopy of the reaction mixture, the content of targeted product was 5–7%.
[d] In the ^{19}F NMR spectrum of the crude product, signals of cyclic products were observed at −58.8 ppm with low intensity.

molecules of 4,4,4-trifluoroacetoacetate **1** (Scheme 2). It should be noted that under analogous reaction conditions compounds **8** were not formed from anilines **7**.

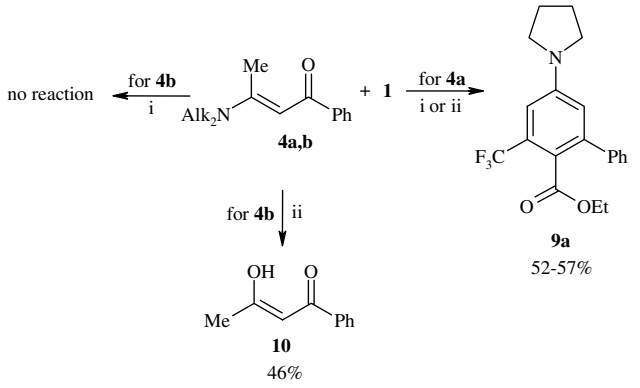
This outcome can be rationalized by the high reactivity of the acyl group of the enamines with respect to 4,4,4-trifluoroacetoacetate, as previously observed by us in the reaction of enamines **3** with methyl trifluoropyruvate.[1] To a great extent, the reaction depends on the character of the dialkylamino substituent of enamine **3**. In the case of pyrrolidine enaminone **3a**, the reaction proceeds in boiling benzene in 3 h yielding ~90% of cyclization products. In the case of the less basic morpholine enaminone **3b**, boiling the reaction mixture, even for 20 h, led to the formation of cyclic products in trace amounts only (^{19}F NMR spectroscopy of the reaction mixture ~3–5%). Running the reaction under acidic conditions, in acetic acid, gave dialkylanilines **7** as the sole cyclic products. Moreover, the basicity of the dialkylamino substituent does not play a significant role, thus on boiling for 3 h enaminones **3a** and **3b** gave trifluoromethylated dialkylaninilines **7** in good preparative yields[12] (Table 1). To the best of our knowledge this is the first example where a 'push–pull' enamine is used as a C_4-synthon in the synthesis of aromatic trifluoromethyl-containing compounds.

Further, we also studied enamine **4a**, which is a derivative of benzoylacetone, its reaction with 4,4,4-trifluoroacetoacetate **1** gave trifluoromethylated aniline **9a**.[13] Changing the reaction conditions had little influence on the product yields and rate of the reaction (Scheme 3, Table 1). The nature of the dialkylamino substituents crucially influences the reaction. Reaction of morpholine enamine **4b** in acetic acid resulted only in the hydrolysis product of the enamine, that is, benzoylacetone **10**. According to ^{19}F NMR spectroscopy of the reaction mixture, no reaction was observed between enamine **4b** and 4,4,4-trifluoroacetoacetate **1** in dry benzene.

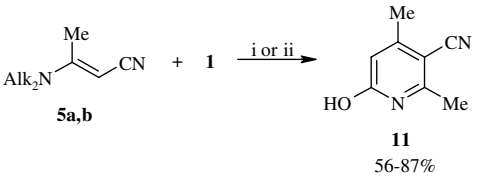
Unfortunately, all our attempts to run the reaction with derivatives of β-aminocrotonitrile failed. Thus, boiling a reaction mixture of enamines **5** with 4,4,4-trifluoroacetoacetate **1** in benzene for 5 h did not give any reaction products. In the ^{19}F NMR spectrum of the reaction mixture, only the signal of the starting 4,4,4-trifluoroacetoacetate **1** of the same intensity was observed. After cooling the reaction mixture, pyridone **11**, that is, the self-condensation product of the enamine, precipitated (Scheme 4).



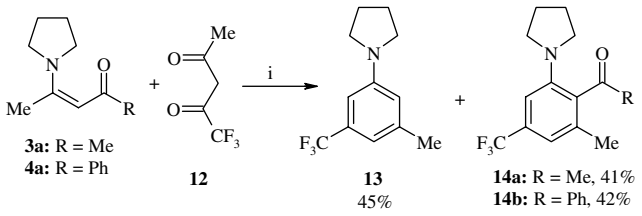
Scheme 2. Reagents and conditions: (i) benzene, reflux, 2–3 h, (ii) AcOH, reflux, 3 h.



Scheme 3. Reagents and conditions: (i) benzene, reflux, 2–3 h, (ii) AcOH, reflux, 2 h.



Scheme 4. Reagents and conditions: (i) benzene, reflux, 2–3 h, (ii) AcOH, reflux, 2 h.



Scheme 5. Reagents and conditions: (i) 70 °C, 4 h, neat.

As this approach leads to polyfunctional aromatic compounds, we embarked on extending its scope. Thus, we investigated other unsymmetrical trifluoromethyl-containing 1,3-diketones. The reaction should be run under more drastic conditions, but unfortunately, in many cases this resulted in the destruction of either the enamine or the 1,3-dicarbonyl compounds. Thus, on prolonged boiling of enamine **2a** with 1,1,1-trifluoroacetylacetone **12** in benzene, the ^{19}F NMR spectrum of the reaction mixture exhibited numerous signals in the region −60 to −80 ppm. Our attempts to optimize the reaction conditions failed. Enamine **5a** behaved likewise. The only product we managed to separate from the reaction with 1,1,1-trifluoroacetylacetone was pyridone **11**. In contrast to enamines **2a** and **5a**, enamines **3a** and **4a** did react with 1,1,1-trifluoroacetylacetone in a pressure tube on heating at 70 °C for 4 h affording trifluoromethylated dialkylanilines **13** and **14** (∼1:1).

These products could be easily separated by column chromatography on SiO_2 using EtOAc–cyclohexane = 1:9 as eluent[14,15] (Scheme 5).

In conclusion, the reactions of 1,3-dicarbonyl compounds with 'push–pull' enamines having a methyl group at the α-position was investigated. It was found that the reaction was very sensitive to both the structure of the starting enamines and to the reaction conditions. As a result, a series of trifluoromethylated dialkylanilines bearing functional groups at the benzene ring were obtained. Readily available starting materials and simple synthetic procedures make this method very attractive and convenient for the synthesis of various trifluoromethyl benzene derivatives, which are useful building blocks for organic and medicinal chemistry.

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11. *General procedure for the preparation of compounds* **6a** *and* **6b**:
A mixture of enamine **2** (5.46 mmol) and 4,4,4-trifluoroacetoacetate **1** (1 g, 5.46 mmol) in dry benzene (15 mL) was refluxed for 4 h. The solvent was evaporated and the residue was purified by column chromatography using EtOAc–*n*-hexane = 1:1 as eluent to afford the target product.
Diethyl 5-hydroxy-3-pyrrolidin-1-yl-5-(trifluoromethyl)-hept-2-enedioate (**6a**):
Yellow oil (1.74 g, 87%). ^1H NMR (300 MHz, C_6D_6): 0.84 (3H, t, $^3J_{HH} = 7.2$, CH_3), 1.13 (3H, t, $^3J_{HH} = 7.2$, CH_3), 1.21 (4H, m, CH_2), 2.66–2.86 (4H, m, NCH_2), 3.18 and 3.26 (2H, AB-syst., $^2J_{HH} = 15.3$, CH_2), 3.79 (3H, m), 4.13 (2H, m, CH_2), 4.57 (1H, br m), 4.79 (1H, s, CH), 6.75 (1H, br s, OH). ^{13}C NMR (75 MHz, C_6D_6): 13.7, 14.8, 24.9, 33.1, 35.7, 48.8, 58.7, 61.3, 76.3 (CCF_3, $^2J_{CF} = 27.7$), 87.6, 126.5 (CF_3, $^1J_{CF} = 286.1$), 155.9, 169.8, 173.2. MS (EI, 70 eV): *m/z* (%) = 367 (16) [M^+], 322 (35), 183 (100), 111 (58), 110 (32), 70 (82). Anal. Calcd for $C_{16}H_{24}F_3NO_5$: C, 52.31; H, 6.59; N, 3.81. Found C, 52.27; H, 6.62; N, 3.84.
Diethyl 5-hydroxy-3-morpholin-4-yl-5-(trifluoromethyl)-hept-2-enedioate (**6b**):

Yellow oil (1.84 g, 88%) ^{1}H NMR (300 MHz, C_6D_6): 0.84 (3H, t, $^3J_{HH} = 7.2$, CH_3), 1.08 (3H, t, $^3J_{HH} = 7.2$, CH_3), 2.59–2.82 (4H, m, NCH_2), 2.93 and 3.11 (2H, AB-syst., $^2J_{HH} = 16.2$, CH_2), 3.29 (5H, m), 3.77 (2H, q, $^3J_{HH} = 7.2$, CH_2), 4.07 (2H, q, $^3J_{HH} = 7.2$, CH_2), 4.34 (1H, br m), 4.89 (1H, s, CH), 6.42 (1H, br s, OH). ^{13}C NMR (100 MHz, C_6D_6): 13.4, 14.3, 28.9, 35.3, 45.5, 59.1, 60.9, 65.9, 75.3 (CCF_3, $^2J_{CF} = 27.6$), 93.1, 125.4 (CF_3, $^1J_{CF} = 284.4$), 158.3, 169.1, 172.3. MS (EI, 70 eV): m/z (%) = 383 (10) [M^+], 338 (37), 199 (77), 198 (100), 170 (23), 126 (93), 69 (36). Anal. Calcd for $C_{16}H_{24}F_3NO_6$: C, 50.13; H, 6.31; N, 3.65. Found C, 50.09; H, 6.33; N, 3.66.

12. *General procedure for the preparation of compounds* **7** *and* **8a**:

Method A. To a solution of enamine **3** (5.46 mmol) in benzene (15 mL) was added 4,4,4-trifluoroacetoacetate **1** (1.0 g, 5.46 mmol). The reaction mixture was refluxed for 5 h. The solvent was evaporated in vacuo and the residue was subjected to flash column chromatography using EtOAc as eluent. After evaporation of the eluent, the resulting crude mixture of products was dissolved in *n*-hexane (10 mL). The solution was left for 1 h at 4 °C during which time **8a** precipitated as a white solid (953 mg, 36%). Evaporation of the mother liquor afforded **7a** as colorless oil (640 mg, 40%). *Method B*. A mixture of enamine **3** (5.46 mmol) and 4,4,4-trifluoroacetoacetate **1** (1.11 g, 6 mmol) was refluxed in AcOH (15 mL) for 3 h. The solvent was evaporated in vacuo, water (10 mL) was added and the pH of the reaction mixture was adjusted to ~8 with aqueous ammonia. The aqueous layer was extracted with ether (2 × 10 mL). The combined organic layer was dried over sodium sulfate, evaporated and the crude product was purified by column chromatography using EtOAc as eluent ($R_f = 0.85$) to give compound **7** as an orange oil.

Ethyl 2-methyl-4-pyrrolidin-1-yl-6-(trifluoromethyl)benzoate (**7a**):

^{1}H NMR (300 MHz, $CDCl_3$): 1.35 (3H, t, $^3J_{HH} = 7.2$, CH_3), 2.03 (4H, t, $^3J_{HH} = 6.9$, CH_2), 2.34 (3H, s, CH_3), 3.30 (4H, t, $^3J_{HH} = 6.9$, NCH_2), 4.34 (2H, t, $^3J_{HH} = 7.2$, CH_2), 6.46 (1H, s, CH), 6.61 (1H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 13.9, 20.2, 25.4, 47.5, 61.3, 106.5, 115.4, 118.5, 123.4 (CF_3, $^1J_{CF} = 272.5$), 128.8 (CCF_3, $^2J_{CF} = 31.2$), 137.9, 147.8, 168.6. MS (EI, 70 eV): m/z (%) = 301 (100) [M^+], 300 (48) [M^+-1], 272 (22), 256 (61), 228 (19). Anal. Calcd for $C_{15}H_{18}F_3NO_2$: C, 59.79; H, 6.02; N, 4.65. Found C, 59.81; H, 6.03; N, 4.63.

Ethyl 2-[4-ethoxy-2-hydroxy-4-oxo-2-(trifluoromethyl)-butyl]-4-pyrrolidin-1-yl- 6-(trifluoromethyl)benzoate (**8a**):

Mp = 49 °C. 1.26 (3H, t, $^3J_{HH} = 7.2$, CH_3), 1.36 (3H, t, $^3J_{HH} = 7.2$, CH_3), 2.05 (4H, t, $^3J_{HH} = 6.3$, CH_2), 2.49 and 2.71 (2H, AB-syst., $^2J_{HH} = 15.3$, CH_2), 3.09 and 3.16 (2H, AB-syst., $^2J_{HH} = 14.1$, CH_2), 3.33 (4H, t, $^3J_{HH} = 6.3$, NCH_2), 4.15 (2H, t, $^3J_{HH} = 7.2$, CH_2), 4.34 (2H, t, $^3J_{HH} = 7.2$, CH_2), 6.16 (1H, s, OH), 6.73 (1H, d, $^4J_{HH} = 2.1$, CH), 6.97 (1H, d, $^4J_{HH} = 2.1$, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 13.7, 13.8, 25.4, 35.7, 36.3, 47.6, 61.3, 62.2, 74.6 (CCF_3, $^2J_{CF} = 26.4$), 108.5, 117.6, 118.7, 123.7 (CF_3, $^1J_{CF} = 246.5$), 126.1 (CF_3, $^1J_{CF} = 259.1$), 129.8 (CCF_3, $^2J_{CF} = 30.2$), 134.8, 148.0, 169.5, 171.4. MS (EI, 70 eV): m/z (%) = 486 (20) [M^++1], 485 (100) [M^+], 440 (16), 352 (12), 301 (15), 252 (13), 228 (11). Anal. Calcd for $C_{20}H_{23}F_6NO_5$: C, 50.96; H, 4.92; N, 2.97. Found C, 50.93; H, 4.95; N, 3.01.

Ethyl 2-methyl-4-(4-morpholinyl)-6-(trifluoromethyl)benzoate (**7b**):

Method B was applied. Brown oil (1.35 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.37 (3H, t, $^3J_{HH} = 7.2$, CH_3), 2.34 (3H, s, CH_3), 3.22 (4H, t, $^3J_{HH} = 4.5$, NCH_2), 3.86 (4H, t, $^3J_{HH} = 4.5$, OCH_2), 4.36 (2H, q, $^3J_{HH} = 7.2$, CH_2), 6.85 (1H, s, CH), 6.97 (1H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 13.9, 20.0, 48.3, 61.6, 66.5, 110.1 ($CCCF_3$, $^3J_{CF} = 3.8$), 119.1, 122.7, 123.7 (CF_3, $^1J_{CF} = 265.4$), 128.7 (CCF_3, $^2J_{CF} = 31.4$), 137.9, 151.4, 168.0. MS (EI, 70 eV): m/z (%) = 318 (17) [M^++1], 317 (100) [M^+], 272 (52), 259 (55), 214 (37). Anal. Calcd for $C_{15}H_{18}F_3NO_3$: C, 56.78; H, 5.72; N, 4.41. Found C, 56.80; H, 5.74; N, 4.39.

13. *Ethyl 5-(pyrrolidin-1-yl)-3-(trifluoromethyl)-[1,1′-biphenyl]-2-carboxylate* (**9a**).

A mixture of enamine **4a** (1 g, 4.65 mmol) and 4,4,4-trifluoroacetoacetate **1** (0.86 g, 4.65 mmol) in 15 mL of acetic acid was refluxed for 2 h. The solvent was evaporated in vacuo, water (10 mL) was added and the pH of the reaction mixture was adjusted to ~7 with sodium bicarbonate. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layer was dried over sodium sulfate, evaporated and the crude product was purified by column chromatography using EtOAc–*n*-hexane = 2:1 as eluent ($R_f = 0.8$) to give compound **9a** as a pale yellow solid (0.96 g, 57%). Mp = 53 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 0.97 (3H, t, $^3J_{HH} = 7.2$, CH_3), 2.04 (4H, m, CH_2), 3.34 (4H, t, $^3J_{HH} = 4.3$, NCH_2), 4.02 (2H, q, $^3J_{HH} = 7.2$, CH_3), 6.57 (1H, d, $^4J_{HH} = 2.4$, CH), 6.77 (1H, d, $^4J_{HH} = 2.4$, CH), 7.37 (5H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): 13.6, 25.6, 47.8, 62.3, 108.2 ($CCCF_3$, $^3J_{CF} = 6.5$), 119.8, 120.2, 123.5 (CF_3, $^1J_{CF} = 271$), 123.8, 125.3, 128.7, 129.4 (CCF_3, $^2J_{CF} = 31.5$), 131.9, 137.9, 150.2, 162.9. MS (EI, 70 eV): m/z (%) = 364 (23) [M^++1], 363 (100) [M^+], 334 (13), 318 (44). Anal. Calcd for $C_{20}H_{20}F_3NO_2$: C, 66.11; H, 5.55; N, 3.85. Found C, 66.14; H, 5.54; N, 3.87.

14. *General procedure for the preparation of compounds* **13** *and* **14a**:

Enamine **3a** (1 g, 6.54 mmol) and 1,1,1-trifluoroacetylacetone **12b** (1.06 g, 6.54 mmol) were mixed without solvent in a pressure tube and heated for 4 h. The resulting oil was separated by column chromatography on SiO_2 using EtOAc–cyclohexane = 1:9 as eluent giving targeted compounds **13** ($R_f = 0.62$) and **14a** ($R_f = 0.38$).

1-[3-Methyl-5-(trifluoromethyl)phenyl]pyrrolidine (**13**):

Brown oil (0.67 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): 2.04 (4H, m, CH_2), 2.38 (3H, s, CH_3), 3.32 (4H, m, NCH_2), 6.54 (1H, s, CH), 6.61, (1H, s, CH), 6.75 (1H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 21.7, 25.5, 47.7, 105.3, 112.6, 115.2, 124.7 (CF_3, $^1J_{CF} = 271.6$), 131.2 (CCF_3, $^2J_{CF} = 31.4$), 139.5, 147.9. Anal. Calcd for $C_{12}H_{14}F_3N$: C, 62.87; H, 6.16; N, 6.11. Found C, 62.85; H, 6.15; N, 6.13.

1-[2-Methyl-6-pyrrolidin-1-yl-4-(trifluoromethyl)phenyl]ethanone (**14a**):

Orange oil (0.73 g, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.94 (4H, m, CH_2), 2.25 (3H, s, CH_3), 2.46 (3H, s, CH_3), 3.23 (4H, m, NCH_2), 6.87 (2H, s, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 19.8, 25.5, 31.7, 51.4, 108.9 ($CCCF_3$, $^3J_{CF} = 3.77$), 116.7 ($CCCF_3$, $^3J_{CF} = 3.77$), 124.1 (CF_3, $^1J_{CF} = 272.9$), 131.2 (CCF_3, $^2J_{CF} = 32.7$), 133.1, 147.0, 206.7. Anal. Calcd for $C_{14}H_{16}F_3NO$: C, 61.99; H, 5.94; N, 5.16. Found C, 62.01; H, 5.95; N, 5.17.

15. *[2-Methyl-6-pyrrolidin-1-yl-4-(trifluoromethyl)phenyl]-(phenyl)methanone* (**14b**).

Enamine **4a** (1 g, 4.65 mmol) and 1,1,1-trifluoroacetylacetone **12b** (0.72 g, 4.65 mmol) were mixed without solvent in a pressure tube and heated for 4 h. The resulting oil was purified by column chromatography using EtOAc–*n*-hexane = 1:2 as eluent ($R_f = 0.7$) to give compound **14b** as a yellow oil (0.65 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.79 (4H, m, CH_2), 2.08 (3H, s, CH_3), 3.18 (4H, br s,

NCH_2), 6.83 (2H, d, $^4J_{HH} = 7.5$, CH), 7.46 (2H, t, $^3J_{HH} = 7.2$, CH), 7.58 (1H, t, $^3J_{HH} = 7.2$, CH), 7.86 (2H, d, $^3J_{HH} = 7.2$, CH). ^{13}C NMR (125 MHz, $CDCl_3$): 20.3, 25.6, 50.6, 108.5, 115.3, 124.2 (CF_3, $^1J_{CF} = 272.9$), 128.8, 129.4, 131.5 (CCF_3, $^2J_{CF} = 31.4$), 133.4, 137.1, 138.1, 146.8, 199.5. MS (EI, 70 eV): m/z (%) = 334 (21) [M^++1], 333 (100) [M^+], 332 (25) [M^+−1], 316 (10), 304 (14), 256 (10), 201 (17), 91 (21), 77 (12), 70 (18). Anal. Calcd for $C_{19}H_{18}F_3NO$: C, 68.46; H, 5.44; N, 4.20. Found C, 68.45; H, 5.42; N, 4.18.