N- and C-Acylation in β-Enamino Ketones: Structural Effects on Regiocontrol

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Abstract: The acylation reaction of secondary (R^1 = H) β-enamino ketones [RCOCH=CHNR^1R^2, where R = CF_3, CCl_3, Ph, 4-FC_6H_4, 4-$NO_2C_6H_4$, thien-2-yl; R^1 = H, Me; R^2 = Me, Bn, Ph, 4-$NO_2C_6H_4$] with trifluoroacetic anhydride or ethyl oxalyl chloride in pyridine led regiospecifically to a series of 14 N-acylated enaminones in good yields (72–88%). On the other hand, when tertiary enaminones (R^1, R^2 = Me) were used, the acylation reaction led to a series of 12 C-acylated enaminones in good to excellent yields (75–92%).

Key words: ketones, enones, acylation, regioselectivity, substituent effects

The reactivity scope associated with the conjugated system O=C–C=C–N makes β-enaminones valuable reagents with wide applications in organic synthesis.[1,2] The versatility of β-enaminones as synthetic intermediates has been exemplified by their applications as 1,3-dielectrophilic (carbonylic carbon and β-carbon) and as nucleophilic (nitrogen and/or α-carbon) building blocks in synthetic organic chemistry.[1,2] Reactions between β-enamino compounds and electrophiles such as acyl chloride and trifluoroacetic anhydride have been reported in the literature.[3–7] These reactions are known as the acylation of β-enamino compounds and the products obtained have been utilized as precursors in the synthesis of new heterocyclic compounds, e.g., pyrimidines[4,8–10] and pyrazoles.[11] Recently, Hogenkamp et al.[12] reported the synthesis of a series of enamino esters and amides from the acylation reaction of β-enamino compounds. The new enamino esters and amides have been identified as novel positive allosteric modulators of the $GABA_A$ receptor. These compounds were orally active in mice with profound central nervous system depressant effects.[12]

Data from the literature have demonstrated that the regioselectivity of the acylation of β-enamino compounds depends on their structure, on the reactivity of the reagents and on the reaction conditions.[5,13] These data have shown that, in general, enamino esters have led exclusively to α-C-acylation.[6,12,14,15] However, when the reaction was performed with enamino ketones instead of enamino esters, the N-acylated compounds or a mixture of both N- and α-C-acylated products were observed.[5] It seems clear that the nucleophilic character of the α-carbon atom is weaker for enamino ketones than for enamino esters. This phenomenon has been explained by the fact that the partial negative charge on this carbon atom is decreased due to the higher electron-withdrawing effect of the ketonic carbonyl than that observed with an ester carbonyl group.[5] Valés et al.[5] observed the influence of the carboxylic acid chloride structure on the regiochemistry of the reaction. The authors obtained two different compounds: the N-acylated enaminones, with low to good yields (14–71%); and the α-C-acylated enaminones, with low yields (10–41%). The same report showed the effect of the amino fragment on the acylation reaction of β-enamino ketones. When the nucleophilicity of the nitrogen atom was weak, the α-C-acylation reaction occurred, leading to a mixture of α-C-acylated and N-acylated compounds.[5]

The influence of the reaction conditions on the acylation of β-enamino ketones has also been reported in the literature.[7,16,17] For instance, the acylation of β-enamino ketones with carboxylic acid chloride in the presence of Et_3N and DBU led to a mixture of α-C- and N-acylated compounds, in low yields. In some of the cases, only N-acylated products were obtained, but also only in low yields. In order to give exclusively N-acylated compounds, the classical acylation reaction in pyridine was tested, leading to the N-acylated compounds (in low yields, 26–40%), when primary enaminones were used.[16] On the other hand, Venkov et al.[7] reported the acylation reaction of β-enamino compounds in an attempt to obtain *N*-acyl derivatives. However, the acylation of enamino ketones, enamino amides, and enamino esters in the presence of bases such as Et_3N or pyridine led to α-C-acylated products. These experiments show that the structures both of β-enamino compounds and carboxylic acid chlorides did not significantly change the reactivity pattern. Besides, the nucleophilicity of the α-carbon in β-enamino compounds diminished considerably when the ketone substituent was an electron-withdrawing group, such as a trichloromethyl group, and no acylation took place under the conditions investigated. In addition, the acylation reaction of β-enamino ketones containing an activated N-benzene ring, under Friedel–Crafts-type conditions, after seven days at room temperature, led to the benzene-acylated product with good yields.[17]

Considering the importance of *N*-acyl and α-*C*-acyl enamino compounds as synthetic precursors and the difficulties in terms of regiocontrol with β-enamino ketone acylation, e.g., the limited scope and low yields of prod-

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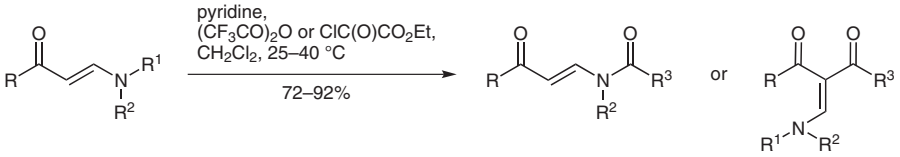
ucts, the aim of this study is to extend the reactivity scope by obtaining the α-C-acylation or N-acylation of enaminones, with regiospecific control, mild conditions, and good yields.

The enaminones used in this study were prepared according to the experimental procedures described previously.[18–21]

The acylation reactions of enaminones (entries 1–26, Table 1) were carried out in CH_2Cl_2, in the presence of pyridine, at 25–40 °C.[22] In general, the acylated enaminones were obtained in good to excellent yields (72–92%) with the exception of entry 6 (Tables 1, 52%) where 21% of starting material was recovered.

Although the reaction of trifluoroacetic anhydride with enaminone (entry 16) has been described in the literature,[3,4] it required a great excess of acylating agent and a long reaction time (3 d).

Table 1 Reaction Conditions and Yields of *N*-Acyl and α-*C*-Acyl Enaminones



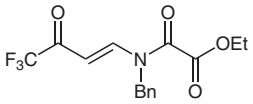
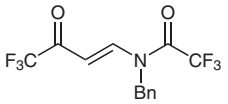
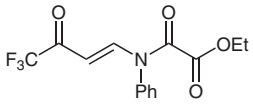
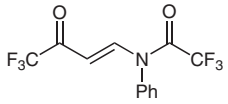
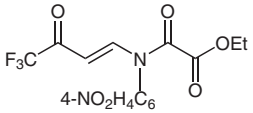
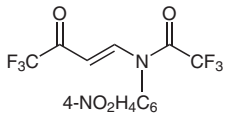
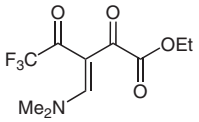
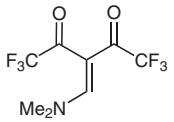
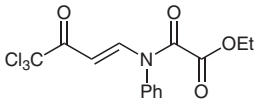
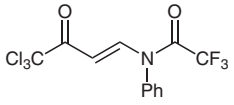
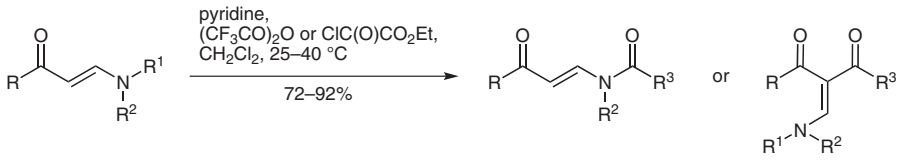
Entry	R	R^1	R^2	R^3	Product	Temp (°C)	Time (h)	Isolated yield (%)
1	CF_3	H	Bn	CO_2Et		40	15	78
2	CF_3	H	Bn	CF_3		40	15	78
3	CF_3	H	Ph	CO_2Et		40	15	82
4	CF_3	H	Ph	CF_3		40	15	77
5	CF_3	H	4-$NO_2C_6H_4$	CO_2Et		40	24	79
6	CF_3	H	4-$NO_2C_6H_4$	CF_3		40	48	52[a]
7	CF_3	Me	Me	CO_2Et		40	15	81
8	CF_3	Me	Me	CF_3		40	15	76
9	CCl_3	H	Ph	CO_2Et		40	24	72
10	CCl_3	H	Ph	CF_3		40	15	77

Table 1 Reaction Conditions and Yields of *N*-Acyl and α-*C*-Acyl Enaminones (continued)



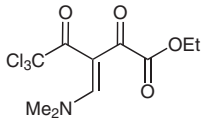
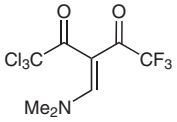
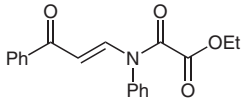
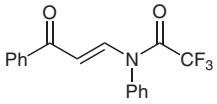
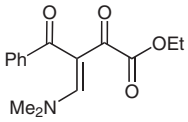
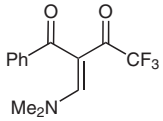
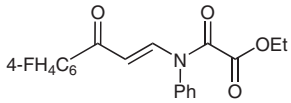
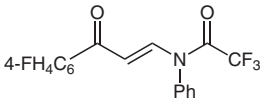
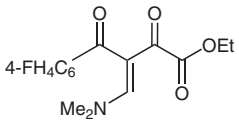
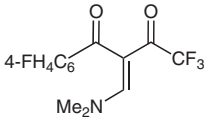
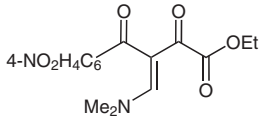
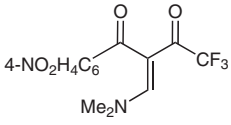
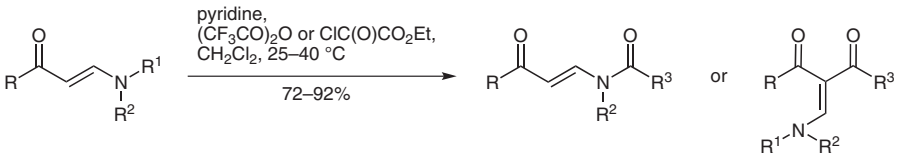
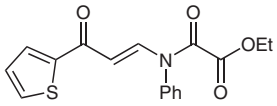
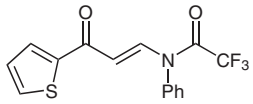
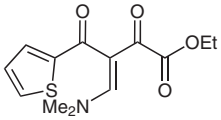
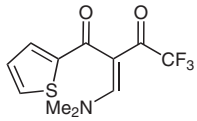
Entry	R	R^1	R^2	R^3	Product	Temp (°C)	Time (h)	Isolated yield (%)
11	CCl_3	Me	Me	CO_2Et		40	24	80
12	CCl_3	Me	Me	CF_3		40	15	75
13	Ph	H	Ph	CO_2Et		25	5	80
14	Ph	H	Ph	CF_3		40	15	85
15	Ph	Me	Me	CO_2Et		40	15	84
16	Ph	Me	Me	CF_3		40	15	85
17	4-FC_6H_4	H	Ph	CO_2Et		25	5	84
18	4-FC_6H_4	H	Ph	CF_3		40	15	83
19	4-FC_6H_4	Me	Me	CO_2Et		40	15	76
20	4-FC_6H_4	Me	Me	CF_3		40	15	80
21	4-$NO_2C_6H_4$	Me	Me	CO_2Et		40	15	92
22	4-$NO_2C_6H_4$	Me	Me	CF_3		40	15	79

Table 1 Reaction Conditions and Yields of *N*-Acyl and α-*C*-Acyl Enaminones (continued)



Entry	R	R^1	R^2	R^3	Product	Temp (°C)	Time (h)	Isolated yield (%)
23	thien-2-yl	H	Ph	CO_2Et		25	5	75
24	thien-2-yl	H	Ph	CF_3		40	15	88
25	thien-2-yl	Me	Me	CO_2Et		40	15	80
26	thien-2-yl	Me	Me	CF_3		40	15	80

[a] 21% starting material was recovered.

The compound structures were determined by ^{1}H NMR and ^{13}C NMR spectroscopy, MS spectrometry, and elemental analysis.[22] Moreover, X-ray crystallography data have confirmed the structure of entries 10 and 22 (Figure 1 and Figure 2, respectively).[23] It was possible to completely modify the direction of the reaction in order to obtain α-C-acylated or N-acylated enaminones in accordance with the structure of the amino fragment present in the enamino ketones. Thus, for substrates containing a secondary amino fragment, N-acylated compounds were obtained exclusively (Table 1, entries 1–6, 9, 10, 13, 14, 17, 18, 23, and 24). However, the regiochemistry of the reaction was not modified for enaminones containing a secondary amino fragment attached to phenyl or nitro-4-phenyl substituents, and N-acylated compounds were obtained. Furthermore, for the reaction shown in entry 6, Table 1, (R = CF_3, R^1 = H, R^3 = 4-$NO_2C_6H_4$, R^4 = CF_3), it was observed that 48 hours were necessary for partial conversion into the product (52% of product and 21% of starting material). On the other hand, for substrates containing a tertiary amino fragment, C-acylated compounds were obtained exclusively (Table 1, entries 7, 8, 11, 12, 15, 16, 19–22, 25, and 26). The structure of the acylating reagent seemed not to interfere in the regiochemistry of the reaction, rather only in the reaction time. When ethyl oxalyl chloride was used as the acylating reagent (Table 1, entries 13, 17, and 23), the reaction time was shorter than when anhydride trifluoroacetic was used (Table 1, entries 14, 18, and 24). In addition, even when the nucleophilicity of the α-carbon in enaminones was diminished considerably for electron-withdrawing groups [Table 1, entries 7 and 8 (CF_3) and entries 11, 12 (CCl_3)], it was observed that α-C-acylation nevertheless occurred for entries 21 and 22 (4-$NO_2C_6H_4$). The wide scope of the reaction demonstrates that diacylation is possible for a variety of β-enamino ketones and not only for trifluoromethyl enamino ketones as has been described up to now in the literature.[3]

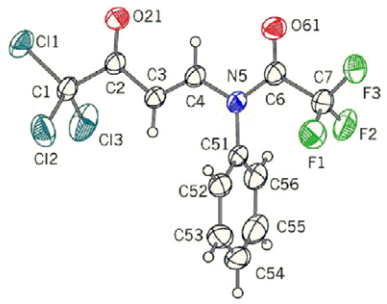


Figure 1 The ORTEP diagram of entry 10, N-acylated enaminone

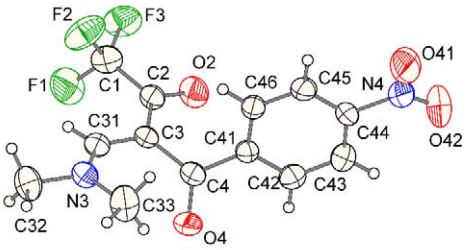


Figure 2 The ORTEP diagram of entry 22, α-C-acylated enaminone

In summary, the methods proposed in this study allow for the preparation of a wide scope of regiospecific N-acylated and α-C-acylated enaminones. The simplicity, wide scope, and good yields of this method and the possible application of the *N*-acyl and α-*C*-acyl enaminones in the synthesis of new heterocyclic compounds make this reaction highly attractive. We have already investigated the use of these compounds in the construction of heterocyclic molecules and the preliminary results have shown that *N*-acyl enaminones could be used in the synthesis of substituted pyrroles, while α-*C*-acyl enaminones could lead to different heterocycles, such as isoxazoles and pyrazoles. These data will be communicated hereafter.

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(22) **Typical Procedure for Synthesis of *N*-Acyl and α-*C*-Acyl Enaminones**

A solution of β-enamino ketones (2 mmol), anhyd CH_2Cl_2 (6 mL), and pyridine (1.7 ml, 2 mmol) was added dropwise to a stirred solution of ethyl oxalyl chloride (0.22 mL, 2 mmol) or TFAA (0.28 mL, 2 mmol) in CH_2Cl_2 (8 mL) at 0 °C under nitrogen atmosphere. After warming to r.t. the solution was stirred at the temperature and time showed in Table 1. The organic layer was then washed with a solution of H_2O–HCl (10:1; 1 × 20 mL) and with distilled H_2O (3 × 20 mL). Finally, the organic layer was dried over Na_2SO_4 and evaporated under vacuum to afford the *N*-acyl or α-*C*-acyl enaminones. When necessary, the products were recrystallized from hexane.

_N_-Benzyl-_N_-(4,4,4-trifluoro-3-oxobut-1-enyl)oxalamic Acid Ethyl Ester (Entry 1)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (br, 3 H, $OCCH_3$), 4.48 (br, 2 H, OCH_2), 4.96 (s, 2 H, CH_2Ph), 6.01 (d, 1 H, *J* = 14 Hz, H2), 7.21–7.36 (m, 5 H, Ph), 8.15 (br, 1 H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7 ($OCCH_3$), 47.1 (CH_2Ph), 63.7 (OCH_2), 102.0 (C2), 116.0 (q, $^1J_{C-F}$ = 290 Hz, CF_3), 126.6, 128.3, 129.1, 133.1 (Ph), 145.0 (C3), 160.2 (C4), 161.8 (C5), 179.1 (q, $^2J_{C-F}$ = 36 Hz, C1). MS: *m/z* (%) = 329 (10) [M^+], 260 (9) [M – CF_3], 228 (85) [M – C(O)CO_2Et], 91 (100) [CH_2Ph], 69 (5) [CF_3]. Anal. Calcd for $C_{15}H_{14}F_3NO_4$: C, 54.72; H, 4.29; N, 4.25. Found: C, 54.86; H, 4.53, N, 4.49.

_N_-Benzyl-2,2,2-trifluoro-_N_-(4,4,4-trifluoro-3-oxobut-1-enyl)acetamide (Entry 2)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.05 (s, 2 H, CH_2Ph), 6.09 (d, 1 H, *J* = 14 Hz, H2), 7.18–7.38 (m, 5 H, Ph), 8.32 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.8 (CH_2Ph), 103.9 (C2), 115.6 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 115.9 (q, $^1J_{C-F}$ = 290 Hz, CF_3), 126.3, 128.5, 129.3, 132.7 (Ph), 143.5 (C3), 157.2 (q, $^1J_{C-F}$ = 38 Hz, C4), 179.0 (q, $^1J_{C-F}$ = 36 Hz, C1). MS: *m/z* (%) = 325 (28) [M], 256 (29) [M – CF_3], 228 (76) [M – C(O)CF_3], 91 (100) [CH_2Ph], 69 (53) [CF_3]. Anal. Calcd for $C_{13}H_9F_6NO_2$: C, 48.01; H, 2.79; N, 4.31. Found: C, 48.20; H, 2.98, N, 4.58.

_N_-Phenyl-_N_-(4,4,4-trifluoro-3-oxobut-1-enyl)oxalamic Acid Ethyl Ester (Entry 3)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.02 (br, 3 H, $OCCH_3$), 4.06 (br, 2 H, OCH_2), 5.59 (d, 1 H, *J* = 14 Hz, H2), 7.30–7.56 (m, 5 H, Ph), 8.77 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 ($OCCH_3$), 62.6 (OCH_2), 103.9 (C2), 116.0 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 128.2, 130.3, 130.7, 134.6 (Ph), 144.5 (C3), 159.9 (C4), 160.4 (C5), 179.5 (q, $^2J_{C-F}$ = 35 Hz, C1). MS: *m/z* (%) = 315 (6) [M^+], 242 (8) [M – CO_2Et], 218 (29) [M – C(O)CF_3], 146 (100), 104 (49), 77 (81) [Ph], 69 (13) [CF_3]. Anal. Calcd for $C_{14}H_{12}F_3NO_4$: C, 53.34; H, 3.84; N, 4.44. Found: C, 53.35; H, 4.10; N, 4.70.

2,2,2-Trifluoro-_N_-phenyl-_N_-(4,4,4-trifluoro-3-oxobut-1-enyl)acetamide (Entry 4)

Mp 30–32 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.44 (d, 1 H, *J* = 14 Hz, H2), 7.27–7.60 (m, 5 H, Ph), 8.79 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.6 (C2), 115.4 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 115.9 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 128.3, 130.2, 130.9, 133.8 (Ph), 145.8 (C3), 156.2 (q, $^1J_{C-F}$ = 38 Hz, C4), 179.5 (q, $^1J_{C-F}$ = 36 Hz, C1). MS: *m/z* (%) = 311 (39) [M^+], 242 (85) [M – CF_3], 214 (47) [M – C(O)CF_3], 172 (42), 145 (44), 117 (37), 77 (100) [Ph], 69 (43) [CF_3]. Anal. Calcd for $C_{12}H_7F_6NO_2$: C, 46.32; H, 2.27; N, 4.50. Found: C, 46.44; H, 2.36; N, 4.67.

_N_-(4-Nitrophenyl)-_N_-(4,4,4-trifluoro-3-oxobut-1-enyl)oxalamic Acid Ethyl Ester (Entry 5)

Mp 93–95 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, 3 H, $OCCH_3$), 4.19 (q, 2 H, OCH_2), 5.56 (d, 1 H, *J* = 14 Hz, H2), 7.53–8.44 (m, 4 H, C_6H_4), 8.71 (br, 1 H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 ($OCCH_3$), 63.4 (OCH_2), 104.1 (C2), 115.8 (q, $^1J_{C-F}$ = 290 Hz, CF_3), 125.6, 129.5, 144.1, 148.7

(C_6H_4), 140.3 (C3), 159.2 (C4), 159.2 (C5), 179.1 (q, $^2J_{C-F}$ = 36 Hz, C1). MS: *m/z* (%) = 360 (3) [M^+], 291 (17) [M – CF_3], 287 (12) [M – CO_2Et], 263 (50) [M – $C(O)CF_3$], 191 (100), 145 (49), 116 (51), 76 (51), 69 (40) [CF_3]. Anal. Calcd for $C_{14}H_{11}F_3N_2O_6$: C, 46.68; H, 3.08; N, 7.78. Found: C, 46.66; H, 3.28; N, 7.87.

2,2,2-Trifluoro-*N*-(4-nitrophenyl)-*N*-(4,4,4-trifluoro-3-oxobut-1-enyl)acetamide (Entry 6)

Mp 112–114 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.44 (d, 1 H, *J* = 14 Hz, H2), 7.54–8.49 (m, 4 H, C_6H_4), 8.75 (d, 1 H, *J* = 14 Hz, H2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.9 (C2), 115.2 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 115.7 (q, $^1J_{C-F}$ = 290 Hz, CF_3), 125.8, 130.0, 144.8, 149.1 (C_6H_4), 139.2 (C3), 155.5 (q, $^1J_{C-F}$ = 39 Hz, C4), 180.7 (q, $^1J_{C-F}$ = 35 Hz, C1). MS: *m/z* (%) = 356 (13) [M^+], 287 (72) [M – CF_3], 259 (47) [M – $C(O)CF_3$], 217 (100), 116 (38), 69 (62) [CF_3]. Anal. Calcd for $C_{12}H_6F_6N_2O_4$: C, 40.47; H, 1.70; N, 7.86. Found: C, 40.64; H, 1.98; N, 8.02.

3-Dimethylaminomethylene-5,5,5-trifluoro-2,4-dioxopentanoic Acid Ethyl Ester (Entry 7)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.37 (t, 3 H, $OCCH_3$), 2.98 (s, 3 H, NMe_2), 3.47 (s, 3 H, NMe_2), 4.35 (q, 2 H, OCH_2), 7.82 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 ($OCCH_3$), 43.5 (NMe_2), 48.7 (NMe_2), 61.9 (OCH_2), 102.4 (C3), 116.7 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 160.8 (q, $^4J_{C-F}$ = 3 Hz, C4), 164.1 (C1), 177.6 (q, $^2J_{C-F}$ = 34 Hz, C3′), 182.3 (C2). MS: *m/z* (%) = 267 (2) [M^+], 194 (100) [M – CO_2Et], 144 (78), 69 (10) [CF_3]. Anal. Calcd for $C_{10}H_{12}F_3NO_4$: C, 44.95; H, 4.53; N, 5.24. Found: C, 45.28; H, 4.85; N, 5.48.

3-Dimethylaminomethylene-1,1,1,5,5,5-hexafluoropentane-2,4-dione (Entry 8)

Mp 54–56 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.81 (s, 3 H, NMe_2), 3.45 (s, 3 H, NMe_2), 7.74 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.1 (NMe_2), 48.9 (NMe_2), 100.3 (C3), 116.2 (q, $^1J_{C-F}$ = 291 Hz, 2 CF_3), 159.4 (C4), 179.5 (q, $^2J_{C-F}$ = 34 Hz, C2, C3′). MS: *m/z* (%) = 263 (19) [M^+], 194 (86) [M – CF_3], 144 (100), 69 (31) [CF_3]. Anal. Calcd for $C_8H_7F_6NO_2$: C, 36.52; H, 2.68; N, 5.32. Found: C, 36.80; H, 3.01; N, 5.62.

***N*-Phenyl-*N*-(4,4,4-trichloro-3-oxobut-1-enyl)oxalamic Acid Ethyl Ester (Entry 9)**

Mp 82–84 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.04 (t, 3 H, $OCCH_3$), 4.07 (q, 2 H, OCH_2), 5.92 (d, 1 H, *J* = 14 Hz, H2), 7.32–7.55 (m, 5 H, Ph), 8.76 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 ($OCCH_3$), 62.5 (OCH_2), 96.0 (CCl_3), 103.1 (C2), 128.2, 130.2, 130.5, 135.0 (Ph), 144.1 (C3), 160.1 (C4), 160.3 (C5), 180.0 (C1). MS: *m/z* (%) = 246 (51) [M^+ – CCl_3], 218 (6) [M – $C(O)CCl_3$], 146 (100), 117 (55) [CCl_3], 104 (66), 77 (77) [Ph]. Anal. Calcd for $C_{14}H_{12}Cl_3NO_4$: C, 46.12; H, 3.32; N, 3.84. Found: C, 46.11; H, 3.67; N, 4.09.

2,2,2-Trifluoro-*N*-phenyl-*N*-(4,4,4-trichloro-3-oxobut-1-enyl)acetamide (Entry 10)

Mp 85–87 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.77 (d, 1 H, *J* = 14 Hz, H2), 7.30–7.59 (m, 5 H, Ph), 8.79 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 95.8 (CCl_3), 105.1 (C2), 115.4 (q, $^1J_{C-F}$ = 287 Hz, CF_3), 128.3, 130.2, 130.8, 134.2 (Ph), 145.3 (C3), 156.0 (q, $^2J_{C-F}$ = 38 Hz, C4), 179.7 (C1). MS: *m/z* (%) = 359 (1) [M^+], 242 (100) [M – CCl_3], 214 (4) [M – $C(O)CCl_3$], 172 (23), 145 (21) [$C(O)CCl_3$], 117 (19) [CCl_3], 77 (53) [Ph], 69 (12) [CF_3]. Anal. Calcd for $C_{12}H_7Cl_3F_3NO_2$: C, 39.98; H, 1.96; N, 3.88. Found: C, 40.04; H, 2.12; N, 3.99.

5,5,5-Trichloro-3-dimethylaminomethylene-2,4-dioxopentanoic Acid Ethyl Ester (Entry 11)

Mp 93–95 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.38 (t, 3 H, $OCCH_3$), 3.05 (s, 3 H, NMe_2), 3.46 (s, 3 H, NMe_2), 4.35 (q, 2 H, OCH_2), 8.31 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 ($OCCH_3$), 43.3 (NMe_2), 48.5 (NMe_2), 61.5 (OCH_2), 96.3 (C3), 98.0 (CCl_3), 161.7 (C4), 164.5 (C1), 179.5 (C2), 182.5 (C3′). MS: *m/z* (%) = 315 (1) [M^+], 280 (3) [M – Cl], 242 (85) [M – CO_2Et], 214 (12) [M – $C(O)CO_2Et$], 198 (6) [M – CCl_3], 170 (97) [M – $C(O)CCl_3$], 92 (100). Anal. Calcd for $C_{10}H_{12}Cl_3NO_4$: C, 37.94; H, 3.82; N, 4.42. Found: C, 38.23; H, 4.16; N, 4.61.

1,1,1-Trichloro-3-dimethylaminomethylene-5,5,5-trifluoropentane-2,4-dione (Entry 12)

Mp 94–96 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.87 (s, 3 H, NMe_2), 3.42 (s, 3 H, NMe_2), 7.93 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.3 (NMe_2), 48.9 (NMe_2), 95.5 (CCl_3), 100.1 (C3), 116.5 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 157.9 (C4), 178.6 (q, $^2J_{C-F}$ = 34 Hz, C2), 184.2 (C3′). MS: *m/z* (%) = 312 (4) [M + 2], 276 (7) [M – Cl], 242 (5) [M – CF_3], 194 (100) [M – CCl_3], 166 (6) [M – $C(O)CCl_3$], 144 (92), 116 (13), 69 (24) [CF_3]. Anal. Calcd for $C_8H_7Cl_3F_3NO_2$: C, 30.75; H, 2.26; N, 4.48. Found: C, 30.77; H, 2.48; N, 4.57.

***N*-(3-Oxo-3-phenylpropenyl)-*N*-phenyloxalamic Acid Ethyl Ester (Entry 13)**

Mp 56–58 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (br, 3 H, $OCCH_3$), 4.02 (br, 2 H, OCH_2), 6.13 (d, 1 H, *J* = 14 Hz, H2), 7.34–7.73 (m, 10 H, 2 Ph), 8.62 (br, 1 H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3 ($OCCH_3$), 62.1 (OCH_2), 109.6 (C2), 127.8, 128.3, 128.4, 129.9, 130.0, 132.5, 135.4, 137.6 (2 Ph), 140.3 (C3), 160.4 (C4), 160.5 (C5), 189.5 (C1). MS: *m/z* (%) = 323 (10) [M^+], 322 (26), 250 (30) [M – CO_2Et), 222 (53) [M – $C(O)CO_2Et$], 218 (41) [M – C(O)Ph], 105 (94) [C(O)Ph], 77 (100) [Ph]. Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.76; H, 5.53; N, 4.13.

2,2,2-Trifluoro-*N*-(3-oxo-3-phenylpropenyl)-*N*-phenylacetamide (Entry 14)

Mp 110–112 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.99 (d, 1 H, *J* = 14 Hz, H2), 7.33–7.70 (m, 10 H, 2 Ph), 8.65 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.3 (C2), 115.6 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 128.0, 128.4, 128.5, 130.0, 130.4, 132.8, 134.8, 137.5 (2 Ph), 141.9 (C3), 155.8 (q, $^2J_{C-F}$ = 38, C4), 189.3 (C1). MS: *m/z* (%) = 319 (52) [M^+], 318 (100), 222 (8) [M – $C(O)CF_3$], 214 (23) [M – C(O)Ph], 105 (21) [C(O)Ph], 77 (50) [Ph], 69 (9) [CF_3]. Anal. Calcd for $C_{17}H_{12}F_3NO_2$: C, 63.95; H, 3.97; N, 4.39. Found: C, 63.74; H, 4.14; N, 4.58.

3-Benzoyl-4-dimethylamino-2-oxobut-3-enoic Acid Ethyl Ester (Entry 15)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.09 (t, 3 H, $OCCH_3$), 2.81 (s, 3 H, NMe_2), 3.35 (s, 3 H, NMe_2), 3.89 (q, 2 H, OCH_2), 7.42–7.75 (m, 5 H, Ph), 7.87 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0 ($OCCH_3$), 42.1 (NMe_2), 47.4 (NMe_2), 60.7 (OCH_2), 106.9 (C3), 127.8, 128.4, 131.6, 139.4 (Ph), 159.0 (C4), 164.3 (C1), 182.9 (C2), 192.9 (C3′). MS: *m/z* (%) = 275 (4) [M^+], 202 (36) [M – CO_2Et], 174 (2) [M – $C(O)CO_2Et$], 105 (100) [C(O)Ph], 77 (60) [Ph]. Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.45; H, 6.37; N, 5.18.

2-Dimethylaminomethylene-4,4,4-trifluoro-1-phenylbutane-1,3-dione (Entry 16)

Oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.71 (s, 3 H, NMe_2), 3.31 (s, 3 H, NMe_2), 7.50–7.85 (m, 5 H, Ph), 7.76 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.1 (NMe_2), 47.6 (NMe_2), 105.3 (C3), 117.1 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 128.3, 128.8, 132.7, 138.6 (Ph), 157.0 (C4), 176.6 (q, $^2J_{C-F}$ = 33 Hz, C2), 194.0 (C3′). MS: *m/z* (%) = 271 (9) [M^+], 202 (32) [M – CF_3], 174 (7) [M – $C(O)CF_3$], 105 (100) [C(O)Ph], 77 (63) [Ph], 69 (4) [CF_3]. Anal. Calcd for $C_{13}H_{12}F_3NO_2$: C, 57.57; H, 4.46; N, 5.16. Found: C, 57.69; H, 4.79; N, 5.27.

***N*-[3-(4-Fluorophenyl)-3-oxopropenyl]-*N*-phenyloxalamic Acid Ethyl Ester (Entry 17)**

Mp 87–89 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.01 (br, 3

H, $OCCH_3$), 4.03 (br, 2 H, OCH_2), 6.08 (d, 1 H, *J* = 14 Hz, H2), 7.07–7.76 (m, 4 H, C_6H_4), 7.34–7.55 (m, 5 H, Ph); 8.60 (br, 1 H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 ($OCCH_3$), 62.3 (OCH_2), 109.3 (C2), 115.5 (d, $^2J_{C-F}$ = 22 Hz, C_6H_4), 128.5, 130.1, 130.2, 135.6 (Ph), 130.6 (d, $^3J_{C-F}$ = 9 Hz, C_6H_4), 134.2 (d, $^4J_{C-F}$ = 3 Hz, C_6H_4), 140.9 (C3), 160.5 (C4), 160.6 (C5), 165.4 (d, $^1J_{C-F}$ = 254 Hz, C_6H_4), 188.1 (C1). MS: *m/z* (%) = 341 (6) [M^+], 340 (27), 268 (49) [M – CO_2Et), 240 (49) [M – $C(O)CO_2Et$], 218 (55) [M – $C(O)C_6H_4$ (4-F)], 123 (100) [$C(O)C_6H_4$ (4-F)], 95 (49) [C_6H_4 (4-F)], 77 (30) [Ph]. Anal. Calcd for $C_{19}H_{16}FNO_4$: C, 66.86; H, 4.72; N, 4.10. Found: C, 66.46; H, 4.90; N, 4.12.

2,2,2-Trifluoro-*N*-[3-(4-fluorophenyl)-3-oxopropenyl]-*N*-phenylacetamide (Entry 18)

Mp 99–101 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.96 (d, 1 H, *J* = 14 Hz, H2), 7.06–7.73 (m, 4 H, C_6H_4), 7.34–7.60 (m, 5 H, Ph), 8.65 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.8 (C2), 115.6 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 115.6 (d, $^2J_{C-F}$ = 22 Hz, C_6H_4), 128.6, 130.1, 130.5, 134.8 (Ph), 130.7 (d, $^3J_{C-F}$ = 9 Hz, C_6H_4), 133.9 (d, $^4J_{C-F}$ = 3 Hz, C_6H_4), 142.1 (C3), 155.9 (q, $^2J_{C-F}$ = 38 Hz, C4), 165.5 (d, $^1J_{C-F}$ = 255 Hz, C_6H_4), 187.6 (C1). MS: *m/z* (%) = 337 (13) [M^+], 336 (50), 268 (10) [M – CF_3], 240 (7) [M – $C(O)CF_3$], 123 (100) [$C(O)C_6H_4$ (4-F)], 95 (58) [C_6H_4 (4-F)], 77 (22) [Ph], 69 (5) [CF_3]. Anal. Calcd for $C_{17}H_{11}F_4NO_2$: C, 60.54; H, 3.29; N, 4.15. Found: C, 60.60; H, 3.90; N, 4.46.

4-Dimethylamino-3-(4-fluorobenzoyl)-2-oxobut-3-enoic Acid Ethyl Ester (Entry 19)

Oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.12 (t, 3 H, $OCCH_3$), 2.81 (s, 3 H, NMe_2), 3.36 (s, 3 H, NMe_2), 3.94 (q, 2 H, OCH_2), 7.10–7.78 (m, 4 H, C_6H_4), 7.86 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 ($OCCH_3$), 42.5 (NMe_2), 47.8 (NMe_2), 61.3 (OCH_2), 107.5 (C3), 115.3 (d, $^2J_{C-F}$ = 22 Hz, C_6H_4), 131.4 (d, $^3J_{C-F}$ = 9 Hz, C_6H_4), 136.3 (d, $^4J_{C-F}$ = 3 Hz, C_6H_4), 159.1 (C4), 164.4 (C1), 164.9 (d, $^1J_{C-F}$ = 253, C_6H_4), 183.0 (C2), 191.8 (C3′). MS: *m/z* (%) = 293 (6) [M^+], 220 (68) [M – CO_2Et], 192 (4) [M – $C(O)CO_2Et$], 123 (100) [$C(O)C_6H_4$ (4-F)], 95 (40) [C_6H_4 (4-F)]. Anal. Calcd for $C_{15}H_{16}FNO_4$: C, 61.43; H, 5.50; N, 4.78. Found: C, 61.58; H, 5.78; N, 4.94.

2-Dimethylaminomethylene-4,4,4-trifluoro-1-(4-fluorophenyl)butane-1,3-dione (Entry 20)

Mp 56–58 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.71 (s, 3 H, NMe_2), 3.32 (s, 3 H, NMe_2), 7.12–7.87 (m, 4 H, C_6H_4), 7.76 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.3 (NMe_2), 47.9 (NMe_2), 105.4 (C3), 115.5 (d, $^2J_{C-F}$ = 21 Hz, C_6H_4), 117.2 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 131.6 (d, $^3J_{C-F}$ = 9 Hz, C_6H_4), 135.2 (d, $^4J_{C-F}$ = 3 Hz, C_6H_4), 157.2 (C4), 165.4 (d, $^1J_{C-F}$ = 254 Hz, C_6H_4), 176.6 (q, $^2J_{C-F}$ = 33 Hz, C2), 192.5 (C3′). MS: *m/z* (%) = 289 (9) [M^+], 220 (32) [M – CF_3], 192 (7) [M – $C(O)CF_3$], 123 (100) [$C(O)C_6H_4$ (4-F)], 95 (49) [C_6H_4 (4-F)], 69 (6) [CF_3]. Anal. Calcd for $C_{13}H_{11}F_4NO_2$: C, 53.99; H, 3.83; N, 4.84. Found: C, 54.07; H, 3.89; N, 4.83.

4-Dimethylamino-3-(4-nitrobenzoyl)-2-oxobut-3-enoic Acid Ethyl Ester (Entry 21)

Oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.16 (t, 3 H, $OCCH_3$), 2.87 (s, 3 H, NMe_2), 3.42 (s, 3 H, NMe_2), 4.00 (q, 2 H, OCH_2), 7.87 (s, 1 H, H4), 7.89–8.26 (m, 4 H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 ($OCCH_3$), 43.0 (NMe_2), 48.2 (NMe_2), 61.6 (OCH_2), 107.2 (C3), 123.4, 129.6, 144.9, 149.2 (C_6H_4), 160.3 (C4), 164.2 (C1), 182.8 (C2), 191.1 (C3′). MS: *m/z* (%) = 320 (7) [M^+], 247 (100) [M – CO_2Et], 219 (4) [M – $C(O)CO_2Et$], 150 (69) [$C(O)C_6H_4$ (4-NO_2)], 104 (47). Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.03; N, 8.75. Found: C, 56.50; H, 5.22; N, 8.63.

2-Dimethylaminomethylene-4,4,4-trifluoro-1-(4-nitrophenyl)butane-1,3-dione (Entry 22)

Mp 100–102 °C. ^1H NMR (200 MHz, $CDCl_3$): d = 2.76 (s, 3 H, NMe_2), 3.40 (s, 3 H, NMe_2), 7.81 (s, 1 H, H4), 7.94–8.28 (m, 4 H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): d = 42.5 (NMe_2), 48.4 (NMe_2), 105.2 (C3), 117.1 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 123.7, 129.7, 143.9, 149.8 (C_6H_4), 158.5 (q, $^4J_{C-F}$ = 3 Hz, C4), 177.2 (q, $^2J_{C-F}$ = 33 Hz, C2), 192.0 (C3¢). MS: *m/z* (%) = 316 (17) [M^+], 247 (75) [M – CF_3], 219 (13) [M – $C(O)CF_3$], 150 (100) [$C(O)C_6H_4$ (4-NO_2)], 104 (49), 76 (43), 69 (6) [CF_3]. Anal. Calcd for $C_{13}H_{11}F_3N_2O_4$: C, 49.38; H, 3.51; N, 8.86. Found: C, 49.39; H, 3.67; N, 8.95.

***N*-(3-Oxo-3-thiophen-2-yl-propenyl)-*N*-phenyloxalamic Acid Ethyl Ester (Entry 23)**

Mp 83–85 °C. ^1H NMR (200 MHz, $CDCl_3$): d = 1.02 (br, 3 H, $OCCH_3$), 4.05 (br, 2 H, OCH_2), 6.02 (d, 1 H, *J* = 14 Hz, H2), 7.05, 7.44, 7.60 (m, 3 H, thien-2-yl), 7.34–7.54 (m, 5 H, Ph), 8.64 (br, 1 H, H3). ^{13}C NMR (100 MHz, $CDCl_3$): d = 13.4 ($OCCH_3$), 62.3 (OCH_2), 109.4 (C2), 128.5, 130.0, 130.1, 135.6 (Ph), 128.0, 131.3, 133.6, 145.0 (thien-2-yl), 139.8 (C3), 160.4 (C4), 160.6 (C5), 181.4 (C1). MS: *m/z* (%) = 329 (1) [M^+], 328 (4), 256 (9) [M – CO_2Et], 228 (24) [M – $C(O)CO_2Et$], 212 (100), 111 (80) [C(O)thien-2-yl], 77 (31) [Ph]. Anal. Calcd for $C_{17}H_{15}NO_4S$: C, 61.99; H, 4.59; N, 4.25. Found: C, 61.63; H, 4.86; N, 4.28.

2,2,2-Trifluoro-*N*-(3-oxo-3-thiophen-2-ylpropenyl)-*N*-phenylacetamide (Entry 24)

Mp 81–83 °C. ^1H NMR (200 MHz, $CDCl_3$): d = 5.87 (d, 1 H, *J* = 14 Hz, H2), 7.05, 7.40, 7.59 (m, 3 H, thien-2-yl), 7.33–7.59 (m, 5 H, Ph), 8.66 (d, 1 H, *J* = 14 Hz, H3). ^{13}C NMR (100 MHz, $CDCl_3$): d = 111.1 (C2), 115.6 (q, $^1J_{C-F}$ = 288 Hz, CF_3), 128.6, 130.0, 130.1, 131.6 (Ph), 128.1, 130.4, 134.0, 144.8 (thien-2-yl), 141.2 (C3), 155.9 (q, $^2J_{C-F}$ = 38 Hz, C4), 181.2 (C1). MS: *m/z* (%) = 325 (2) [M^+], 324 (13), 212 (100), 111 (41) [C(O)thien-2-yl], 83 (7) [thien-2-yl], 69 (16) [CF_3]. Anal. Calcd for $C_{15}H_{10}F_3NO_2S$: C, 55.38; H, 3.10; N, 4.31. Found: C, 55.41; H, 3.47; N, 4.70.

4-Dimethylamino-2-oxo-3-(thiophene-2-carbonyl)but-3-enoic Acid Ethyl Ester (Entry 25)

Oil. ^1H NMR (200 MHz, $CDCl_3$): d = 1.14 (t, 3 H, $OCCH_3$), 2.87 (s, 3 H, NMe_2), 3.35 (s, 3 H, NMe_2), 3.99 (q, 2 H, OCH_2), 7.06, 7.45, 7.62 (m, 3 H, thien-2-yl), 7.84 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): d = 13.5 ($OCCH_3$), 42.3 (NMe_2), 48.0 (NMe_2), 61.6 (OCH_2), 108.0 (C3), 127.6, 133.1, 133.6, 146.9 (thien-2-yl), 158.2 (C4), 164.3 (C1), 182.6 (C2), 184.9 (C3¢). MS: *m/z* (%) = 281 (7) [M^+], 208 (65) [M – CO_2Et], 180 (4) [M – $C(O)CO_2Et$], 111 (100) [C(O)thien-2-yl], 83 (9) [thien-2-yl]. Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.61; H, 5.65; N, 5.27.

2-Dimethylaminomethylene-4,4,4-trifluoro-1-thiophen-2-ylbutane-1,3-dione (Entry 26)

Oil. ^1H NMR (200 MHz, $CDCl_3$): d = 2.80 (s, 3 H, NMe_2), 3.30 (s, 3 H, NMe_2), 7.12, 7.56, 7.69 (m, 3 H, thien-2-yl), 7.73 (s, 1 H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): d = 40.4 (NMe_2), 47.5 (NMe_2), 105.2 (C3), 117.0 (q, $^1J_{C-F}$ = 291 Hz, CF_3), 127.9, 133.7, 134.3, 145.7 (thien-2-yl), 156.2 (C4), 175.8 (q, $^2J_{C-F}$ = 33 Hz, C2), 185.7 (C3¢). MS: *m/z* (%) = 277 (5) [M^+], 208 (7) [M – CF_3], 180 (1) [M – $C(O)CF_3$], 111 (100) [C(O)thien-2-yl], 83 (8) [thien-2-yl], 69 (6) [CF_3]. Anal. Calcd for $C_{11}H_{10}F_3NO_2S$: C, 47.65; H, 3.64; N, 5.05. Found: C, 47.67; H, 3.87; N, 5.26.

(23) Crystallographic data for entries 10 and 22, reported in this paper, have been deposited with the Cambridge Crystallographic Data Center (CCDC 654351 and CCDC 654350, respectively). Copies of the data can be obtained, free of charge, on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (1223)336033 or e-mail: deposit@ccdc.cam.ac.uk].