A Novel Synthesis of Trifluoromethyl Enones and Enediones

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Abstract: Reactions of trifluoromethyl enamino ketones, (E)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one (**2**) and 3-(dimethylaminomethylene)-1,1,1,5,5,5-hexafluoropentane-2,4-dione (**3**), with various types of lithium derivatives of aromatic or heteroaromatic compounds proceed with the formation of the corresponding aryl- or hetaryl-substituted trifluoromethyl enones and enediones in good yields. The reactions of enamino ketone **2** proceed stereospecifically, only (*E*)-isomers of the enones being formed.

Key words: trifluoroacetylation, trifluoromethyl α,β -unsaturated ketones, enones, enediones

 α,β -Unsaturated ketones with a trifluoromethyl substituent represent interesting building blocks for the synthesis of trifluoromethyl-containing compounds, especially heterocyclic systems, which often show high biological activities.^{1, 2} However, the conventional procedures for the synthesis of simple unsaturated ketones have proven to be not applicable to the preparation of their trifluorinated analogs. Although a number of methods for the synthesis of trifluoromethyl enones have been reported,^{3, 4} elaboration of new, more direct and general methods remains an actual goal.

The utilization of organometallic reagents has been found to be an efficient route to the preparation of some trifluoromethyl enones. The 1,4-addition of organocuprates to the acetylenic ketones obtained by acylation of acetylides with ethyl trifluoroacetate has been studied.^{5, 6} The ethylenic ketones were prepared with high regioselectivity, however, stereoselectivity is variable and yields were moderate. Recently the reaction of β -(trifluoroacetyl)vinyl tellurides (prepared by direct trifluoroacetylation of vinyl tellurides) with different zinc cuprates has been investigated.⁷ Although the corresponding trifluoromethyl enones were obtained in good yields, utilization of organotellurium compounds is a major disadvantage of this method.

It is known that organolithium compounds react quite smoothly with enamino ketones with substitution of the amino group by an alkyl group to give alkyl-substituted enones in moderate to high yields.^{8, 9} This method could be especially useful for the preparation of trifluoromethyl enones. However, only one example of such an approach has been described so far. The reaction of phenylmagnesium bromide with (*E*)-Et₂NCH=CHCOCF₃ provides (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one in 55% yield, whereas the reaction with (*E*)-EtOCH=CHCOCF₃ (1) led to a mixture of the phenyl enone and allyl alcohol formed by its reduction.¹⁰

Herein we report on a simple synthesis of aryl- or hetarylsubstituted trifluoromethyl enones and enediones from the readily available trifluoromethyl enamino ketones 2 and 3.

It was found that (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one (**2**) can be easily prepared in high yield from dimethylamine and enone $\mathbf{1}$,¹¹ obtained by trifluoroacetylation of ethyl vinyl ether.^{12–14} We have prepared enamino ketone **2** from ethyl vinyl ether in a one-pot technique without isolation of enone **1** (Scheme 1).

It is known that the reaction of tertiary amines with trifluoroacetic anhydride results in the formation of bistrifluoroacetylated enamines,¹⁵ and the trifluoroacetylation of 1-amino-4-(trifluoroacetyl)buta-1,3-dienes leads to the corresponding bistrifluoroacetyl derivatives.¹⁶ We found that trifluoroacetylation of enamino ketone **2** with trifluoroacetic anhydride in the presence of pyridine gives 3-(dimethylaminomethylene)-1,1,1,5,5,5-hexafluoropentane-2,4-dione (**3**) in almost quantitative yield (Scheme 1).



Our attempts to perform the acylation of enamino ketone **2** with acetyl or benzoyl chloride or trifluoroacetylation of (E)-Me₂NCH=CHCO₂Et were unsuccessful, only the starting materials were recovered. We believe such diacylation is the unique property of trifluoromethyl enamino ketones like **2**.

We have investigated the reactions of trifluoromethyl enamino ketones 2 and 3 with some organolithium compounds 4 prepared by lithiation of aromatics, heteroaromatics¹⁷ and aromatic organometallics (cymantrene¹⁸ and ferrocene¹⁹) or the metal-halogen exchange reaction of the corresponding bromo compounds with butyllithium. We have found that the enamino ketones 2 and 3 react with a number of organolithium compounds in THF at low temperature to give the corresponding trifluoromethyl enones 5 and enediones 6 in moderate to high yields (Scheme 2, Table 1).

Reactions of enamino ketone 2 proceed stereospecifically; according to the ¹H NMR data, in all cases only (*E*)-isomers of the corresponding enones are formed. We believe





Table 1. Reaction of Enamino Ketones ${\bf 2}$ and ${\bf 3}$ with Organometallic Compounds

Substrate	Enamino Ketone	Product	Yield (%)	mp (°C) (hexane)
4a	2	5a	51	37–38
4b	2	5b	70	14–15 ^a
4c	2	5c	30	21-22
4d	2	5d	46	35-36
4e	2	5e	95	117–118 ^b
4f	2	5f	97	111-112
4g	2	5g	57	66–67
4h	2	5h	74	53-54
4i + 4j	2	5i	38	62-63
4i + 4j	2	5j	8	118–119
4a	3	6a	62	27-28
4b	3	6b	41	29-30
4c	3	7	7	132-133
4e	3	6e	69	117-118
4f	3	8	63	209–211 ^c
4g	3	6g	51	91-92
4h	3	6h	83	56-57
4i + 4j	3	6i	35	90-91
PhMgBr	3	9	18	oil ^d

 a n_{D}^{20} 1.4350.

^b Solvent = hexane/Et₂O 5:1.

^c Solvent = hexane/Et₂O 1:1.

^d bp 150–153 °C/6.6 mbar.

Exceptions were the reactions with 3-thienyl- and 3-furyllithium (**4c** and **4d** respectively); in these cases a complicated mixture of products was formed. In the case of the reaction with 3-thienyllithium the cyclopenta[*b*]thiophene derivative **7** was isolated in very low yield. According to the NMR data one diastereomer was formed, but the configuration was not determined (Scheme 3).



Scheme 3

Side reactions such as cyclization processes and further transformations apparently take place because of the high activity of position 2 in thiophene and furan. To check this proposal we studied the reaction of enamino ketone **3** with 1-methyl-1*H*-indol-2-yllithium (**4f**) since position 3 in indoles is known to be very active. Fortunately, we found that this reaction proceeds smoothly with spontaneous cyclization of originally formed enedione **6f** to give the cyclopenta[*b*]indole derivative **8** in good yield (Scheme 4).



Scheme 4

We found that the reaction of enamino ketone **2** with the mixture of mono- and dilithioferrocenes (**4i** and **4j**) obtained from butyllithium and ferrocene in THF^{19–21} leads to the enones **5i** and **5j** in 38 and 8% yield, respectively, based on original enamino ketone (using butyllithium, ferrocene and enamino ketone in a ratio 2.6:2:1). In the case of enamino ketone **3** the monosubstituted product **6i** was obtained in 35% yield; disubstituted product was not isolated apparently due to side reactions (Scheme 5).

that the reactions of enamino ketones with organolithium compounds proceed as an addition–elimination process with the formation of the thermodynamically favorable product having (E)-configuration.

Unexpectedly, enamino ketone 3 reacted with most of the organolithium compounds with substitution of the amino group to give the corresponding enediones in good yields, in spite of the presence of two trifluoroacetyl moieties.



Scheme 5

We also attempted to carry out reactions with 2- and 3-pyridyllithium and quinolin-3-yllithium, prepared from the corresponding bromopyridines and bromoquinoline by the exchange reaction with butyllithium.¹⁷ These organolithium compounds are much less stable and we found that the reactions do not proceed in a temperature range from -100 to -70 °C. Raising of the reaction temperature leads only to decomposition of the organolithium compounds. We believe that the reactivity of enamino ketones is insufficient for reactions with these organolithium compounds. The reactions of enamino ketones 2 and 3 with butyllithium and enamino ketone 3 with phenyllithium were also studied. These reactions resulted only in complicated product mixtures; trifluoromethyl enones (enediones) could not be isolated. In our opinion, this is apparently due to the high nucleophilicity and basicity of butyl- and phenyllithium. Strong basicity can lead to the deprotonation of enamino ketones and further transformations.²² Hence, we have used phenylmagnesium bromide instead of phenyllithium in the reaction with enamino ketone 3; however, the expected enedione was not formed. The product of a double addition of organometallic compound to the enamino ketone as a 1:1 mixture of (E)- and (Z)-isomers 9 was isolated in low yield (Scheme 6).



Scheme 6

Thus, the reactions of enamino ketones 2 and 3 with lithium derivatives of electron-rich aromatic and heteroaromatic compounds result in the corresponding aryl- and hetaryl-substituted trifluoromethyl enones (enediones) in good yields. The aryl- and hetaryl-substituted enediones with two trifluoroacetyl moieties were obtained for the first time. The reactions investigated provide a convenient route to the preparation of these compounds.

Mps were determined in sealed capillaries and are uncorrected. TLC was performed on Silufol UV 254 plates visualizing by UV and by aq KMnO₄. NMR spectra were recorded on Varian VXR-400 and Bruker AMX 400 spectrometers with TMS as an internal standard. The IR spectra were obtained with a UR-20 spectrometer. Column chromatography was performed on silica gel (63–200 mesh, Merck). All solvents used were dried and distilled according to standard procedures. Organolithium compounds were prepared according to the literature techniques.^{17–19} Cymantrenyllithium was prepared according to the literature procedure.¹⁸ A mixture of mono- and dilithiated ferrocenes (**4i** and **4j**) for the reaction with 10 mmol of enamino ketone **2** or **3** was prepared using excess BuLi (26 mmol) and ferrocene (3.72 g, 20 mmol) according to the literature protocol.¹⁹

(E)-4-(Dimethylamino)-1,1,1-trifluorobut-3-en-2-one (2):

Liquid Me₂NH (27.0 g, 0.60 mol) was added dropwise to a stirred and cooled (below 0 °C) solution of (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (**1**) in CH₂Cl₂, prepared from ethyl vinyl ether (18.0 g, 0.25 mol) and trifluoroacetic anhydride (63.0 g, 0.30 mol) according to the literature protocol.¹² The resulting mixture was allowed to

warm to r.t. and then concentrated in vacuo. The residue was chromatographed (silica gel, 150 g; CHCl₃, ~500 mL). After evaporation of most of the solvent in vacuo, hexane (100 mL) was added and the crystalline product was filtered. Yield 31.0 g (74%) of colorless solid; mp 57–58 °C (Lit.²³ mp 58 °C).

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

Trifluoroacetic anhydride (13.7 g, 65 mmol) was added to a stirred solution of enamino ketone **2** (8.35 g, 50 mmol) and pyridine (5.14 g, 65 mmol) in CH₂Cl₂ (50 mL) at -10° C. The mixture was allowed to warm to r.t. and then washed with ice-water (2 × 25 mL). The resulting solution was dried (CaCl₂) and passed through a short column of silica gel (~10 g), eluent CH₂Cl₂ (30 mL). The combined solutions were concentrated in vacuo, and the product was crystallized by addition of hexane (30 mL). Yield 12.5 g (95%) of colorless solid; mp 50–51 °C.

¹H NMR (400 MHz, CDCl₃): δ = 2.76 (s, 3H, CH₃), 3.41 (s, 3H, CH₃), 7.72 (s, 1H, H methylene).

¹³C NMR (100 MHz, CDCl₃): δ = 43.09 (CH₃), 48.83 (CH₃), 101.16 (3-C), 116.23 (q, ¹J_{C-F} = 289 Hz, 2CF₃), 159.48 (C methylene), 179.41 (q, ²J_{C-F} = 35.2 Hz, 2CO).

Reaction of Enamino Ketones 2 and 3 with Organolithium Compounds:

A solution of organolithium compound 4 (10 mmol) in THF^{17-19} was cooled to -70 °C and a solution of the enamino ketone 2 (1.67 g, 10 mmol) or 3 (2.63 g, 10 mmol) in THF (10 mL) was added dropwise while maintaining the temperature between -70 and -60 °C. The mixture was then allowed to warm slowly (over ~ 1 h) to 0 °C. In the case of (2,6-dimethoxyphenyl)lithium (4g) the temperature was kept between -40 and -30 °C during the addition of the enamino ketone and then allowed to warm to r.t. The resulting mixture was hydrolyzed with 10% aq HCl (10 mL, 27 mmol) or sat. aq NH₄Cl (10 mL) (in the case of furan derivatives 5b, 5d and 6b) with cooling below 0°C. The organic layer was separated, and the aqueous layer was extracted with CHCl₃ (2 \times 10 mL). The combined solutions were dried (CaCl₂) and concentrated in vacuo. The residue was chromatographed (short silica gel column, 15-20 g; hexane/benzene 1:1, ~50 mL); the target products had $R_f 0.2-0.5$ (hexane/EtOAc 9:1). After evaporation of the solvents in vacuo, hexane (15 mL) was added and the products were crystallized with cooling to -30 to -10 °C, then the cold suspension was filtered. The ketone 5e was crystallized from hexane/Et₂O 5:1 (~30 mL) without purification by chromatography because of its low solubility. The product 7 was separated by chromatography (silica gel column, 20-30 g; benzene) (Rf 0.55, CHCl₃/MeOH 9:1) and crystallized from hexane. The indole derivatives 5f and 8 were chromatographed using CH2Cl2/acetone 9:1 or 1:1 (~50 mL) as eluent, respectively; compound 8 was then crystallized from hexane/Et₂O 1:1 (~20 mL). The mixture in the case of lithiated ferrocenes (4i and 4j) was hydrolyzed with concd aq HCl (5.0 mL, ~50 mmol) and concentrated in vacuo without separation. The residue was shaken with benzene (30 mL) and the mixture was passed through a silica gel column (~30 g); the insoluble residue and the silica gel column were then additionally washed with benzene (~100 mL). The solvent was removed in vacuo and the mixture of the products was chromatographed on a silica gel column (~50 g). Excess ferrocene was removed by elution with hexane (150-200 mL); the ketones 5i and 6i were eluted with hexane/benzene 1:1 (~150 mL), the ketone 5j (in the case of the reaction with enamino ketone 2) was then eluted with benzene (~150 mL).

Reaction of Enamino Ketone 3 with Phenylmagnesium Bromide: The reaction was carried out under a similar manner to that described above using a solution of PhMgBr (10 mmol) in THF.¹⁷ The residue after hydrolysis and evaporation of the solvents was chromatographed (silica gel column, 20–30 g; benzene). The product **9** (R_f 0.84, CHCl₃/MeOH 9:1) was separated and distilled in vacuo.

Table 2. Spectral Data of Compounds 5-9

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Prod- uct ^a	IR (Nujol) v (cm ⁻¹)	¹ H NMR (CDCl ₃ /TMS), δ , J (Hz)	¹³ C NMR (CDCl ₃ /TMS), δ , J (Hz)
5a	1550 (C=C), 1680 (C=O)	6.70 (d, 1H, ${}^{3}J$ = 15.6, 3-H), 7.07 (dd, 1H, ${}^{3}J$ = 3.7, ${}^{3}J$ = 5.0, 4-H thienyl), 7.40 (d, 1H, ${}^{3}J$ = 3.7), 7.50 (d, 1H, ${}^{3}J$ = 5.0), 7.99 (d, 1H, ${}^{3}J$ = 15.6, 4-H)	114.92 (3-C), 116.33 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 128.89, 132.01, 134.76, 138.92 (2-C thienyl), 142.14 (4-C), 179.63 (q, ${}^{2}J_{C-F} = 35.0$, CO)
5b	1610 (C=C), 1710 (C=O) ^b	6.50 (dd, 1H, ${}^{3}J$ = 3.4, ${}^{3}J$ = 1.8, 4-H furyl), 6.81 (d, 1H, ${}^{3}J$ = 15.5, 3-H), 6.83 (d, 1H, ${}^{3}J$ = 3.4), 7.53 (d, 1H, ${}^{3}J$ = 1.8), 7.60 (d, 1H, ${}^{3}J$ = 15.5, 4-H)	113.79, 113.40, 116.41 (q, ${}^{1}J_{C-F} = 291$, CF ₃), 119.92, 134.70, 146.96 (4-C), 150.51 (2-C furyl), 179.74 (q, ${}^{2}J_{C-F} = 35.3$, CO)
5c	1560 (C=C), 1690 (C=O)	6.82 (d, 1H, ${}^{3}J$ = 15.8, 3-H), 7.38 (s, 2H, 4-H and 5-H thienyl), 7.73 (s, 1H, 2-H thienyl), 7.93 (d, 1H, ${}^{3}J$ = 15.8, 4-H)	116.11 (3-C), 116.35 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 125.00, 127.61, 132.60, 136.94 (3-C thienyl), 142.93 (4-C), 180.10 (q, ${}^{2}J_{C-F} = 35.8$, CO)
5d	1590 (C=C), 1690 (C=O)	6.69 (m, 1H), 6.72 (dt, 1H, ${}^{3}J = 15.6$, ${}^{5}J = 0.6$, 3-H), 7.50 (m, 1H), 7.84 (q, 1H, $J = 0.9$, 2-H furyl), 7.89 (d, 1H, ${}^{3}J = 15.6$, 4-H)	107.14, 116.37 (q, ${}^{1}J_{C-F}$ = 291, CF ₃), 116.54, 122.72 (3-C furyl), 140.07, 145.16, 147.68, 179.82 (q, ${}^{2}J_{C-F}$ = 35.4, CO)
5e	1550 (C=C), 1680 (C=O)	6.98 (d, 1H, ${}^{3}J$ = 15.6, 3-H), 7.46 (t, 1H, ${}^{3}J$ = 7.4), 7.52 (t, 1H, ${}^{3}J$ = 7.4), 7.96 (d, 1H, ${}^{3}J$ = 8.2), 7.99 (d, 1H, ${}^{3}J$ = 8.2), 8.07 (s, 1H, 3-H benzo[<i>b</i>]thiophene), 8.31 (d, 1H, ${}^{3}J$ = 15.6, 4-H)	117.67 (q, ${}^{1}J_{C-F}$ = 288, CF ₃), 118.24, 123.98, 126.67 (2C), 128.99, 135.25, 139.96, 140.86, 142.48, 144.12, 178.68 (q, ${}^{2}J_{C-F}$ = 36.0, CO)
5f	1550 (C=C), 1680 (C=O)	3.82 (s, 3H, CH ₃), 7.03 (dq, 1H, ${}^{3}J$ = 15.6, ${}^{4}J_{C-F}$ = 0.8, 3-H), 7.13 (ddd, 1H, ${}^{3}J$ = 8.1, J = 5.8, J = 2.2), 7.22 (s, 1H, 3-H indole), 7.34–7.31 (m, 2H indole), 7.63 (dt, 1H, ${}^{3}J$ = 8.1, J = 1.0), 8.06 (d, 1H, ${}^{3}J$ = 15.6, 4-H)	29.99 (CH ₃), 107.65, 109.99, 115.07, 116.55 (q, ${}^{1}J_{C-F}$ = 294, CF ₃), 121.16, 122.22, 125.58, 127.33, 134.17, 137.16, 140.32, 179.45 (q, ${}^{2}J_{C-F}$ = 35.2, CO)
5g	1560 (C=C), 1690 (C=O)	3.90 (s, 6H, 2CH ₃), 6.56 (d, 2H, ${}^{3}J$ = 8.4, 3-H and 5-H phenyl), 7.35 (t, 1H, ${}^{3}J$ = 8.4, 4-H phenyl), 7.48 (d, 1H, ${}^{3}J$ = 16.0, 3-H), 8.48 (d, 1H, ${}^{3}J$ = 16.0, 4-H)	55.80 (2CH ₃), 103.63 (2C, 3-C and 5-C phenyl), 111.73 (1-C phenyl), 116.76 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 118.37 (3-C), 133.77 (4-C phenyl), 141.08 (4-C), 161.19 (2C, 2-C and 6-C phenyl), 181.43 (q, ${}^{2}J_{C-F} =$ 33.8, CO)
5h	1610 (C=C), 1720 (C=O), 1950, 2030 (Mn-C=O)	4.87 (br s, 2H cymantrene), 5.21 (br s, 2H cyman- trene), 6.58 (br s, 1H, 3-H), 7.51 (br s, 1H, 4-H)	83.98 (2C cymantrene), 86.00 (2C cymantrene), 90.34 (1-C cymantrene), 116.16 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 116.18 (3-C), 144.44 (4-C), 179.15 (q, ${}^{2}J_{C-F} = 36.0$, CO), 222.97 (Mn-CO)
5i	1600 (C=C), 1700 (C=O)	4.21 (s, 5H, unsubst. ferrocene ring), 4.63 (s, 4H, sub- stituted ferrocene ring), 6.57 (d, 1H, ${}^{3}J = 15.4$, 3-H), 7.97 (d, 1H, ${}^{3}J = 15.4$, 4-H)	69.89 (2C substituted ferrocene ring), 70.28 (4C unsubst. ferrocene ring), 73.12 (2C substituted ferrocene ring), 77.31 (1-C ferrocene), 113.12 (3-C), 116.71 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 153.60 (4-C), 178.86 (q, ${}^{2}J_{C-F} = 35.1$, CO)
5j	1580, 1600 (C=C), 1710 (C=O)	4.55 (t, $J = 1.8$, 4H ferrocene), 4.58 (t, $J = 1.8$, 4H ferrocene), 6.46 (d, 2H, ${}^{3}J = 15.6$, 3-H and 3'-H), 7.69 (d, 2H, ${}^{3}J = 15.6$, 4-H and 4'-H)	71.34 (4C ferrocene), 74.43 (4C ferrocene), 79.08 (1-C and 1'-C ferrocene), 115.02 (3-C and 3'-C), 116.42 (q, ${}^{1}J_{C-F} = 288$, 2CF ₃), 150.86 (4-C and 4'-C), 178.85 (q, ${}^{2}J_{C-F} = 35.3$, 2CO)
6a	1580 (C=C), 1690, 1750 (C=O)	7.19 (dd, 1H, ${}^{3}J = 3.7$, ${}^{3}J = 5.0$, 4-H thienyl), 7.57 (d, 1H, ${}^{3}J = 3.7$), 7.81 (d, 1H, ${}^{3}J = 5.0$), 8.05 (s, 1H, H methylene)	115.02 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 115.90 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 123.13 (3-C), 129.24 (C thienyl), 134.32 (2-C thienyl), 138.03, 140.62, 143.82, 178.54 (q, ${}^{2}J_{C-F} = 36.1$, CO), 185.27 (q, ${}^{2}J_{C-F} = 39.0$, CO)
6b	1590 (C=C), 1700, 1750, (C=O)	6.61 (dd, 1H, ${}^{3}J = 1.8$, ${}^{3}J = 3.7$, 4-H furyl), 7.10 (d, 1H, ${}^{3}J = 3.7$), 7.62 (s, 1H, H methylene), 7.63 (d, 1H, ${}^{3}J = 1.8$)	114.60, 115.03 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 115.92 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 122.88 (3-C), 125.15, 134.62 (q, ${}^{4}J_{C-F} = 3.2$, C methylene), 147.44 (2-C furyl), 149.97, 177.41 (q, ${}^{2}J_{C-F} = 36.3$, CO), 184.21 (q, ${}^{2}J_{C-F} = 39.3$, CO)
6e	1580 (C=C), 1690, 1750 (C=O)	7.44 (ddd, 1H, ${}^{3}J = 8.1$, ${}^{3}J = 7.1$, $J = 1.0$), 7.52 (ddd, 1H, ${}^{3}J = 8.1$, ${}^{3}J = 7.1$, $J = 1.1$), 7.83 (dq, 1H, ${}^{3}J = 8.1$, $J = 0.8$), 7.87 (s, 1H, 3-H benzo[<i>b</i>]thiophene), 7.88 (d, 1H, ${}^{3}J = 8.1$), 8.17 (s, 1H, H methylene)	115.05 (q, ${}^{1}J_{C-F} = 292$, CF ₃), 115.91 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 122.69, 125.52 (3-C), 125.90 (2C), 129.09, 133.98, 138.16, 138.71, 143.98, 144.24 (q, ${}^{4}J_{C-F} = 3.3$, C methylene), 178.37 (q, ${}^{2}J_{C-F} = 36.6$, CO), 185.17 (q, ${}^{2}J_{C-F} = 37.1$, CO)

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Prod- uct ^a	IR (Nujol) v (cm ⁻¹)	¹ H NMR (CDCl ₃ /TMS), δ , <i>J</i> (Hz)	¹³ C NMR (CDCl ₃ /TMS), δ , J (Hz)
6g	1560 (C=C), 1690, 1750 (C=O)	3.83 (s, 6H, 2CH ₃), 6.59 (d, 2H, ${}^{3}J$ = 8.4, 3-H and 5-H phenyl), 7.45 (t, 1H, ${}^{3}J$ = 8.4, 4-H phenyl), 8.36 (s, 1H, H methylene)	55.76 (2CH ₃), 103.98 (2C, 3-C and 5-C phenyl), 110.71 (1-C phenyl), 115.48 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 116.13 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 127.57 (3-C), 135.68 (4- C phenyl), 144.65 (q, ${}^{4}J_{C-F} = 3.2$, C methylene), 158.95 (2C, 2-C and 6-C phenyl), 179.15 (q, ${}^{2}J_{C-F} = 35.6$, CO), 182.41 (q, ${}^{2}J_{C-F} = 38.4$, CO)
6h	1600 (C=C), 1700, 1750 (C=O), 1950, 2030 (Mn- C=O)	5.03 (br s, 2H cymantrene), 5.17 (br s, 2H cyman- trene), 7.51 (s, 1H, H methylene)	85.60 (2C cymantrene), 88.61 (2C cymantrene), 91.46 (1-C cymantrene), 114.89 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 115.78 (q, ${}^{1}J_{C-F} = 288$, CF ₃), 125.19 (3-C), 147.02 (C methylene), 177.60 (q, ${}^{2}J_{C-F} = 35.5$, CO), 185.34 (q, ${}^{2}J_{C-F} = 39.5$, CO), 221.66 (Mn-CO)
6i	1600 (C=C), 1700, 1750 (C=O)	4.32 (s, 5H, unsubst. ferrocene ring), 4.52 (s, 2H, sub- stituted ferrocene ring), 4.89 (s, 2H, substituted ferro- cene ring), 7.93 (s, 1H, H methylene)	71.41 (4C unsubst. ferrocene ring), 72.66 (2C substituted ferrocene ring), 76.24 (2C substituted ferrocene ring), 77.12 (1-C ferrocene), 115.03 (q, ${}^{1}J_{C-F} = 290$, CF ₃), 116.32 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 121.32 (3-C), 155.16 (C methylene), 177.38 (q, ${}^{2}J_{C-F} = 35.3$, CO), 186.57 (q, ${}^{2}J_{C-F} = 37.8$, CO)
7	2900–3400 (OH)	6.69 (s 1H, OH), 7.02 (s, 1H, OH), 7.12 (d, ${}^{4}J$ = 4.8, H- 4 cyclopenta[<i>b</i>]thiophene), 7.31 (s, 2H, 4-H and 5-H thienyl), 7.47 (dd, 1H, ${}^{3}J$ = 3.1, ${}^{4}J$ = 4.8, 3-H cyclopen- ta[<i>b</i>]thiophene), 7.65 (s, 1H, 2-H thienyl), 7.66 (d, 1H, ${}^{3}J$ = 3.1, 2-H cyclopenta[<i>b</i>]thiophene)	79.26 (q, ${}^{2}J_{C-F} = 29.9$), 85.71 (q, ${}^{2}J_{C-F} = 32.5$), 125.29 (q, ${}^{1}J_{C-F} = 283$, CF ₃), 126.05 (q, ${}^{1}J_{C-F} = 284$, CF ₃), 121.54, 126.09, 126.94, 127.84, 131.88, 133.35, 139.23, 141.29, 143.23, 149.19
8	1750 (C=O), 2900–3400 (OH)	4.01 (s, 3H, CH ₃), 5.91 (br s, 1H, OH), 7.23 (t, 1H, ³ J = 8.0), 7.36 (t, 1H, ³ J = 8.4), 7.55 (d, 1H, ³ J = 8.8), 7.71 (d, 1H, ³ J = 8.0), 8.47 (q, 1H, ⁵ J _{C-F} = 2.0, 3-H)	31.36 (CH ₃), 82.50 (q, ${}^{2}J_{C-F} = 35.0$, 1-C), 112.45, 117.59 (q, ${}^{1}J_{C-F} = 289$, CF ₃), 121.58, 122.86, 123.49 (2-C), 125.80 (q, ${}^{1}J_{C-F} = 284$, CF ₃), 125.96, 126.63, 138.69, 144.60, 144.64, 144.95 (3-C), 173.90 (q, ${}^{2}J_{C-F} = 35.2$, CO)
9 ^c	1620 (C=C), 1740 (C=O), 2900-3400 (OH)	3.74 (1H, OH of one isomer), 3.86 (1H, OH of another isomer), 7.45–7.03 (m, 22H, 10H Ph and H methylene of two isomers)	80.02 (q, ${}^{2}J_{C-F} = 29.6$, 4-C of one isomer), 80.09 (q, ${}^{2}J_{C-F} = 29.7$, 4-C of another isomer), 114.61 (q, ${}^{1}J_{C-F} = 290$, CF ₃ of two isomers), 115.92 (q, ${}^{1}J_{C-F} = 290$, CF ₃ of two isomers), 126.96, 127.17, 127.78, 128.08, 128.19, 128.32, 128.68, 128.78, 128.81, 128.97, 129.49, 130.10, 133.29, 135.90, 136.77, 140.59 (C methylene of one isomer), 146.93 (C methylene of another isomer), 189.91 (q, ${}^{2}J_{C-F} = 37.6$, CO of one isomer), 183.87 (q, ${}^{2}J_{C-F} = 35.2$, CO of another isomer)

 a Satisfactory microanalysis were obtained for all new compounds: C \pm 0.46, H \pm 0.21.

^b Film.

^c 1:1 mixture of (E)- and (Z)-isomers.

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