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Solvent-free synthesis of ferrocenylchalcones

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Abstract: A series of ferrocenylmono- and dichalcone derivatives have been synthesized under solvent-free conditions via Claisen-Schmidt condensations between aryl/ferrocenyl ketones and aryl/ferrocenyl aldehydes by just grinding in an agate mortar. All the reactions occur in a short time with excellent yields (>85%) of steroselective *trans*-conformation in the chalcones. The structures of all the compounds have been characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and EI-MS and elemental analyses.
Keywords: Ferrocenylchalcones, solvent-free, agate mortar, *trans*-conformation.

Introduction

The chalcone derivatives are of considerable interest because of their useful biological and pharmacological properties such as antibacterial[1], antifungal[2], antiviral[3], antiparasitic[4], anticancer[5], antileishmanial[6] and antitubercular activities[7] as well as optical properties[8].

A classical synthesis of these compounds involves the cross aldol condensation between aromatic aldehydes with methyl ketones. This reaction is catalyzed by acids and bases under homogenous conditions in solvent systems[9]. Though quite a large number of homogeneous catalytic reactions have been reported so far, serious disadvantages are, among others, separation of reactant/product and of side reactions like decomposition, catalyst recovery and waste disposal problems.

In recent years, considerable attention has been paid to reactions done under solvent-free conditions[10, 11]. They have many advantages such as high efficiency and selectivity, easy separation and purification, along with mild reaction conditions and benefit industry as well as the environment[11, 12]. The magnitude of these advantages is clear when considering the trend to develop green and sustainable chemical processes “Green Chemistry”[13] with lesser generation of toxic and nontoxic waste. In this respect, many articles about solvent-free reactions with grinding have been reported, such as the Grignard reaction[14], Reformatsky reactions[15], Aldol condensation[16], Dieckmann condensation[17],phenol coupling reaction[18], reduction reaction[19] and others[20].

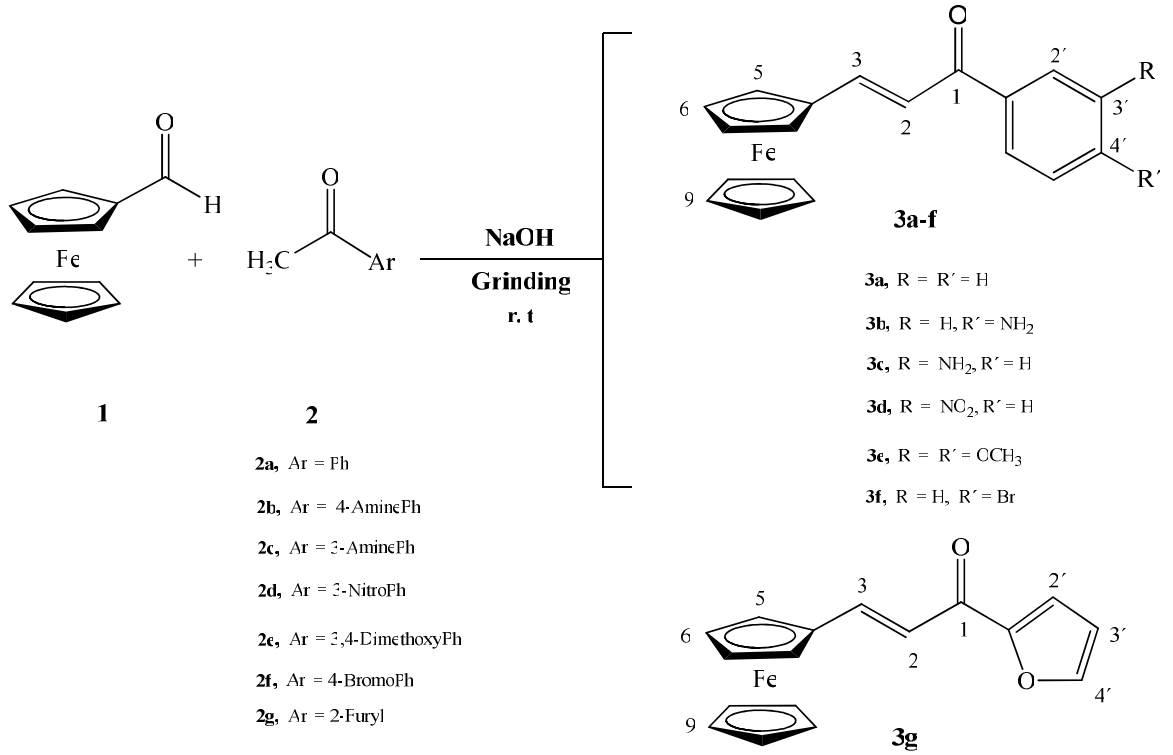
On the other hand, since the discovery of ferrocene by Kealy and Paulson[21] in 1951, an important area of organometallic chemistry is focused on ferrocene and its derivatives. It is now well established that ferrocene-functionalized organic compounds often exhibit unexpected biological activity owing to different properties, e.g., chemical and biological stable, non-toxic and able to cross cell membranes[22, 23].

Thus, survey of the literature shows that ferrocenylenones, known as ferrocenylchalcones, could be synthesized by Claisen-Schmidt condensation between the corresponding ketones with aldehydes in a basic alcohol solution under conventional[24-27] and non-conventional techniques, such as ultrasound waves[28] or by solvent-free conditions[29, 30].

In this regard, the present work describes the green synthesis of two seriesferrocenylchalcone derivatives wherein the carbonyl group is attached to the phenyl ring **3a-g**, and wherein the carbonyl group is directly attached to the ferrocenyl ring **6a-d** by Claisen-Schmidt condensation under solvent-free conditions simply by grinding the mixture of substrates in the presence of NaOH. To the best of my knowledge, the preparation of compounds **3b-g** has not been reported in the literature using solvent-free conditions in agate mortar. Furthermore, compounds **3b,3c**, **3d** and **3f** are considered as new compounds. This solvent freesynthesis method is eco-friendly, high yielding, requires no special apparatus, non-hazardous, simple and convenient.

Results and Discussion

The general synthetic plan employed to synthesize the ferrocenylchalcone derivatives **3a-g** used the Claisen-Schmidt condensation between suitable aldehydes and ketones under solvent-free conditions at room temperature (Scheme 1). At first, an equal molar amount of acetophenone derivatives and NaOH was ground in an agate mortar with a pestle resulting in the formation of the enolate intermediary as a black viscous liquid mixture; then the ferrocencarboxaldehyde is subsequently added and viscosity rapidly increases to form a sticky darkened red liquid of constant mixing (Tacky darkened red solid for compounds **6a-d**). During the reaction between two solid reactants, the reaction mixture undergoes a phase transition into a eutectic melt. We note that, by grinding together the solid aldehydes or ketones without addition of catalyst, this eutectic phase can be reproduced; however, there is no observedconversion to the aldol product upon workup. More importantly, upon addition of the catalyst a rise in temperature was recorded. After completion, the reaction mixture was diluted with CH_2Cl_2, and was washed with brine. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure. Finally, the crude residue was purified by column chromatography with silica gel to give the corresponding pure aldol product as a red solid.This procedure afforded ferrocenyl chalcones in good to excellent yields (88–95%). The chemical structures of the synthesized compounds were established by spectroscopic data (FT-IR, ^{1}H-NMR, ^{13}C-NMR, EI-MS) and elemental analyses. The results are listed in table 1 and in experimental section.



Scheme 1. Synthesis of (2*E*)-3-Ferrocenyl-1-(aryl)prop-2-en-1-ones (**3a-g**) under solvent-free conditions.

Table 1. Yields, melting points and elemental analysis of compounds **3a-g** and **6a-d**.

Compound	Formula	M_r	Time[a]	w_i(calc.)/% w_i(found)/%		Yield[b]	M.p.
			min	C	H	%	°C
3a	$C_{19}H_{16}FeO$	316.06	14	72.18 72.13	5.10 5.24	94	141-143
3b	$C_{19}H_{17}FeNO$	331.07	19	68.90 68.81	5.17 5.03	93	83-85
3c	$C_{19}H_{17}FeNO$	331.07	14	68.90 68.78	5.17 5.09	88	58-60
3d	$C_{19}H_{15}FeNO_3$	361.04	21	63.18 63.07	4.19 4.23	90	105-107
3e	$C_{21}H_{20}FeO_3$	376.08	11	67.04 67.15	5.36 5.28	91	92-93
3f	$C_{19}H_{15}BrFeO$	393.97	18	57.76 55.83	3.83 3.95	95	125-127
3g	$C_{17}H_{14}FeO_2$	306.03	15	66.70 67.03	4.61 4.47	89	108-110
6a	$C_{19}H_{16}FeO$	316.06	13	72.18 73.11	5.10 4.97	92	138-139
6b	$C_{17}H_{14}FeO_2$	306.03	12	66.70 66.55	4.61 4.58	94	154-155
6c	$C_{28}H_{22}FeO_2$	446.10	16	75.35 75.29	4.97 4.88	87	179-180
6d	$C_{24}H_{18}FeO_4$	426.06	19	67.63 67.59	4.26 4.17	85	159-161

[a]Exothermic reaction (5–12°C).
[b]Isolated yields.

Thesynthesized products were recrystallized and melting point was taken which are compatible with the reported melting points. The percent yield obtained by solvent free method was found to be more tan that of conventional method. Both the method gives the desired products, but by applying the solvent free synthesis method, we can able to avoid the use of ethanol and diluted acid neutralizer.

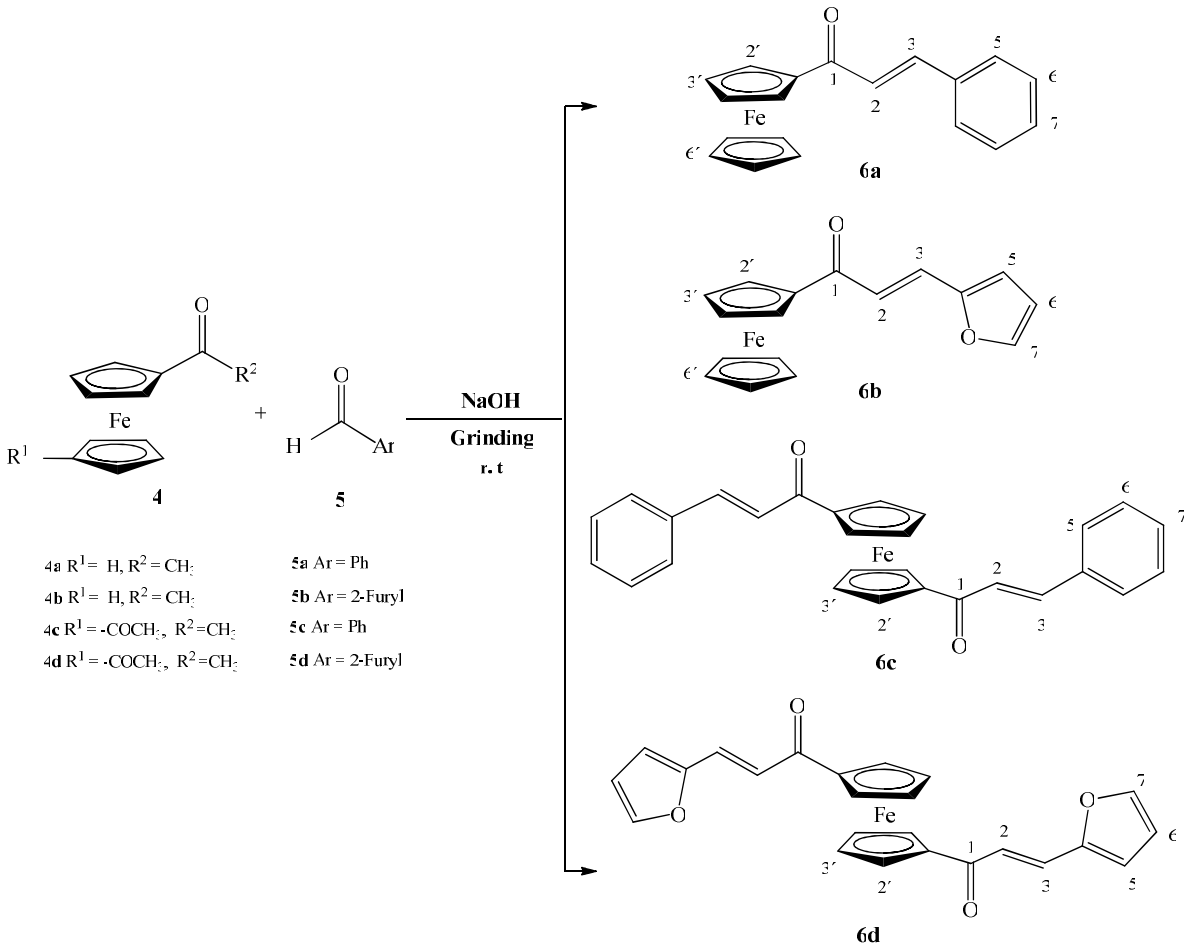
The FT-IR spectra of the compounds **3a-g**showed two strong bands at stretching frequencies in the range of 1660–1630 cm^{-1} and 1596–1572 cm^{-1}, which are characteristic of C=O and C=C group respectively.

The FT-IR spectra of **3b** and **3c**showed thepresence of a NH_2 stretch at υ 3332–3363 and 3349–3467 cm^{-1}.

A characteristic feature of the ^1H NMR spectra in $CDCl_3$ for **3a-g** is the pair of AB doublets at 7.88–7.08 ppm consistent with olefinic protons of the chalcone moieties with large coupling constants ($^3J_{HH}$= 15.2–15.6 Hz) indicating that the ethylene moiety in the enone linkage is in a *trans*-conformation[31] in the chalcone system. The aromatic protons of the ferrocenyl chalcones appeared downfield between 7.28 and 8.79 ppm in the aromatic region of the spectrum,along with three peaks from the ferrocenyl moieties between 4.65–4.17 ppm. No trace of *Z* isomer was found in the proton spectrum. The ^{13}C NMR spectrum of **3a-g** displayed characteristic carbonyl signal between 187.0–193.4 ppm, i.e. about 6.0 ppm lower than those of the acetophenones. This means that the influence of the substituent is small, but the average π-electron density on C1 is considerably higher than in the acetophenones. This is obviously caused by a rather strong conjugation in the side chain.

Mass spectra for **3a-g** displayed the molecular ion peaks at *m/z* 316, 331, 331, 361, 376, 394 and 306 respectively, matching the expected molecular weights in each case.

Compounds **6a-d** were prepared according to the procedure already mentioned. For compounds **6c** and **6d** themole ratio of the aromatic aldehyde to 1,1´-diacetylferrocene was 3:1. The synthetic route to the compounds is outlined in Scheme 2.



Scheme 2. Synthesis of (2*E*)-1-Ferrocenyl-3-(aryl)prop-2-en-1-ones (**6a**, **6b**), (2*E*)-1,1´-Dicinnamoylferrocene **6c** and (2*E*)-1,1´-bis[*β*-(2-Furyl)acryloyl]ferrocene **6d**under solvent-free conditions.

The FT-IR spectra of compounds **6a-d** showed absorption bands in the range of 1657-1649 cm^{-1} for carbonyl groups (C=O) and 1598-1590 cm^{-1} for olefinic double bonds (C=C). The ^{1}H-NMR spectrum of compounds **6a-d** showed two doublets around 7.82–7.51 ppm and 7.11–6.92 ppm with the magnitude of the coupling constant (^{3}J = 15.2–15.6Hz) being in the expected range. The chemical shift differences Δδ (H-*α*, H-*β*) (their average being 0.65 ppm for compounds **6a-d**) are no significantly greater than those of compounds **3a-g** (Δδ ~ 0.15 ppm). Characteristic ferrocene peaks of compounds **6a-d** appeared around 4.93–4.21 ppm which are shifted downfield approximately at 0.3 ppm with respect to compounds **3a-g**. The ^{13}C NMR spectrum displayed ferrocene peaks around 81.8–70.0 ppm. No significant shift was observed for the carbonyl carbon (around 192 ppm) of compounds **6a-d**.

Mass spectra for **6a-d** displayed the molecular ion peaks at *m/z* 316, 306, 446 and 426 respectively, matching the expected molecular weights in each case.

Conclusions

In summary, a simple, convenient and general method has been developed for the preparation of ferrocenylmono- and dichalcones derivatives under solvent-free conditions by just grinding. Thereactions occurs under mild conditions and requires easier workup procedures andsimpler equipment, compared to similar reactions carried out in solution. Additionally, the compounds **3b**, **3c**, **3d** and **3f** were obtained in high yields and are considered as new compounds.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL 400S spectrometer, using $CDCl_3$ as solvent. Signals were assigned using 1D ^{1}H and ^{13}C experiments. Chemical shift values (δ) are expressed in ppm and are relative to that of TMS as the internal standard. The multiplicity of each NMR signal is defined as one of the following: s (singlet), d (doublet), t (triplet) or m (multiplet).IR spectra were performed on a Nicolet-Magna 750 FT-IR spectrometer. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA Mass spectrometer operated in the positive ion mode. The acquisition conditions were ion source temperature 230 °C, ionization energy 70 eV, emission current 0.14 ・A and ionization current 100 ・A. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Elemental analyses (C and H only) were recorded froma Euro EA elemental analyzer. All reagents were obtained fromcommercial suppliers and used as received.Solvents were purified by standard methods and were freshly distilled prior to use.

General procedure for preparation of compounds 3a-g.

A mixture of **1** (2.19 mmol), **2** (2.19 mmol) and 2.19 mmol of solid NaOH pellet was ground together in an agate mortar with a pestle at room temperature for 11–28 min (See table 1). The reaction proceeds exothermically (Indicated by a rise in temperature of 5–12^{o}C). The progress of reaction was monitored by TLC.After the completion of reaction, the reaction mixture was diluted with CH_2Cl_2 and washed with brine. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure.The crude product was purified by column chromatography using Silica-gel (grade 60, 70–230 mesh) and 4:1 hexanes–ethyl acetate as eluent to give compounds **3a-g**as red solids. The compounds **3a**, **3e** and **3g** exhibit melting points corresponding to the literature.

(2E)-3-Ferrocenyl-1-(phenyl)prop-2-en-1-one (3a).

M.p. 141-143 ^{o}C (Lit. M.p. 142-145^{o}C) [26, 29].–IR (KBr): ν = 3060 (H-Ar),1652 (C=O), 1590 (C=C), 484 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.18 (s, 5H, 9-H), 4.49 (t, 2H, *J* = 1.6 Hz, 6-H), 4.60 (t, 2H, *J* = 1.6 Hz, 5-H), 7.15 (d, 1H, *J* = 15.6 Hz, 2-H), 7.58–7.46 (m, 3H, H-Ar), 7.77 (d, 1H, *J* = 15.6 Hz, 3-H), 8.00–7.96 (m, 2H, H-Ar). – ^{13}C RMN ($CDCl_3$/TMS): δ = 69.0 (C-6), 69.8 (C-9),71.3 (C-5), 77.3 (Fc_{ipso}), 119.1 (C_{α}), 128.3 (C-2'),128.5 (C-4´), 130.4 (C-3'), 132.3 (C_{ipso}), 146.0 (C_{β}), 193.4 (C=O).– MS (EI, 70 Ev): *m/z* (%) = 316 (100) $[M]^{+}$. –Anal. calcd. C 72.18, H 5.10; Found C 72.13, H 5.24.

(2E)-3-Ferrocenyl-1-(4-aminophenyl)prop-2-en-1-one (3b).

M.p. 83-85 ^{o}C.– IR (KBr): ν = 3449 and 3332 (HN-Ar), 3085 (H-Ar), 1630 (C=O), 1596 (C=C), 488 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 2H, NH_2), 4.17 (s, 5H, 9-H), 4.44 (t, 2H, *J* = 1.6 Hz, 6-H), 4.58 (t, 2H, *J* = 1.6 Hz, 5-H), 6.71 (d, 2H, H-Ar), 7.16 (d, 1H, *J* = 15.2 Hz, 2-H), 7.72 (d, 1H, *J* = 15.2 Hz, 3-H), 7.90 (d, 2H, H-Ar). – ^{13}C RMN ($CDCl_3$/TMS): δ = 68.7 (C-6), 69.6 (C-9), 70.9 (C-5), 80.1 (Fc_{ipso}),118.8 (C_α), 126.9 (C-2'),127.5 (C-3'),129.3 (C_{ipso}),138.1 (C_{ipso}),145.8 (C_β), 193.1 (C=O). –MS (EI, 70 Ev): *m/z* (%) =331 (80) $[M]^+$. –Anal. calcd. C 68.90, H 5.17;Found C 68.81, H 5.03.

(2E)-3-Ferrocenyl-1-(3-aminophenyl)prop-2-en-1-one (3c).

M.p. 58-60 ^{o}C. – IR (KBr): ν = 3467 and 3363 (HN-Ar), 3087 (H-Ar), 1660 cm^{-1}ν(C=O), 1572 (C=C), 488 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 2H, NH_2), 4.17 (s, 5H, 9-H), 4.47 (t, 2H, *J* = 1.6 Hz, 6-H), 4.59 (t, 2H, *J* = 1.6 Hz, 5-H), 6.88-6.86 (m, 1H, H-Ar), 7.25 (d, 1H, *J* = 15.6 Hz, 2-H), 7.35-7.26 (m, 3H, H-Ar), 7.74 (d, 1H, *J* = 15.6 Hz, 3-H). – ^{13}C RMN ($CDCl_3$/TMS): δ= 68.9 (C-6), 69.7 (C-9), 71.3 (C-5), 79.2 (Fc_{ipso}), 118.9 (C_α), 114.3 (C-4'), 118.6 (C-2'), 119.3 (C-5'), 119.6 (C-6'), 129.4 (C_{ipso}), 139.7 (C_{ipso}), 146.7 (C_β), 190.0 (C=O).–MS (EI, 70 Ev): *m/z* (%) =331 (100) $[M]^+$. –Anal. calcd.C 68.90, H 5.17;Found C 68.78, H 5.09.

(2E)-3-Ferrocenyl-1-(3-nitrophenyl)prop-2-en-1-one (3d).

M.p. 105-107 ^{o}C. – IR (KBr): ν = 3090 (H-Ar), 1658 (C=O), 1593 (C=C), 1526 and 1349 (NO_2), 486 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.21 (s, 5H, 9-H), 4.56 (t, 2H, *J* = 1.6 Hz, 6-H), 4.65 (t, 2H, *J* = 1.6 Hz, 5-H), 7.26 (d, 1H, *J* = 15.2 Hz, 2-H), 7.72–7.68 (m, 1H, H-Ar), 7.88 (d, 1H, *J* = 15.2 Hz, 3-H), 8.79–8.28 (m, 3H, H-Ar). – ^{13}C RMN ($CDCl_3$/TMS): δ= 69.3 (C-6), 69.9 (C-9), 72.0 (C-5), 78.5 (Fc_{ipso}), 117.4 (C_α), 123.1 (C-4'), 126.6 (C-2'), 129.7 (C-5'), 129.8 (C-6'), 134.0 (C_{ipso}), 139.9 (C_{ipso}), 149.3 (C_β), 187.0 (C=O).–MS (EI, 70 Ev): *m/z* (%) =361 (82) $[M]^+$. –Anal. calcd.C 63.18, H 4.19;Found C 63.07, H 4.23.

(2E)-3-Ferrocenyl-1-(3,4-dimethoxyphenyl)prop-2-en-1-one (3e).

M.p. 91-93 ^{o}C (Lit. M.p. 93-95^{o}C) [27]. –IR (KBr): ν = 484 (Cp-Fe), 1579 (C=C), 1647 ν(C=O), 3060 (Ar-H) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3H, OMe), 3.97(s, 3H, OMe), 4.18 (s, 5H, 9-H), 4.47 (t, 2H, *J* = 1.6 Hz, 6-H), 4.60 (t, 2H, *J* = 1.6 Hz, 5-H), 6.93-6.88(m, 1H, H-Ar), 7.18 (d, 1H, *J* = 15.2 Hz, 2-H), 7.64-7.53 (m, 2H, H-Ar), 7.77 (d, 1H, *J* = 15.2 Hz, 3-H). – ^{13}C RMN ($CDCl_3$/TMS): δ = 55.9, 55.8 (-OMe), 68.9 (C-6), 69.6 (C-9), 71.1 (C-5), 79.8 (Fc_{ipso}),109.8, 109.9, 110.6 (H-Ar), 118.5 (C_α),122.5 (C_{ipso}),123.2 (C_{ipso}),145.7 (C_β),192.7 (C=O). –MS (EI, 70 Ev): *m/z* (%) = 376(100) $[M]^+$. –Anal. calcd. C 67.04, H 5.36;Found C 67.15, H, 5.28.

(2E)-3-Ferrocenyl-1-(4-bromophenyl)prop-2-en-1-one (3f).

M.p. 125-127 ^{o}C. –IR (KBr): ν = 3089 (H-Ar), 1654 (C=O), 1588 (C=C), 483 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.18 (s, 5H, 9-H), 4.51 (t, 2H, *J* = 1.6 Hz, 6-H), 4.60 (t, 2H, *J* = 1.6 Hz, 5-H), 7.08 (d, 1H, *J* = 15.2 Hz, 2-H), 7.64–7.62 (d, 2H, *J* = 8.4 Hz, 3´-H), 7.78 (d, 1H, *J* = 15.2 Hz, H-3),7.86-7.83 (d, 2H, *J* = 8.4 Hz, H-2'). – ^{13}C RMN ($CDCl_3$/TMS): δ = 69.0 (C-6), 69.8 (C-9), 71.5 (C-5), 79.2 (Fc_{ipso}),118.3 (C_α),122.4 (C-2'),129.8 (C-3´), 131.7(C_{ipso}), 134.2(C_{ipso}),147.5 (C_β), 192.9 (C=O). –MS (EI, 70 Ev): *m/z* (%) =394(100) $[M]^+$. –Anal. calcd.C 57.76, H, 3.83;Found C 55.83, H, 3.95.

(2E)-3-Ferrocenyl-1-(2-furyl)prop-2-en-1-ones (3g).

M.p. 107-109 ^{o}C (Lit. M.p. 107-108^{o}C) [27]. –IR (KBr): ν = 3060 (H-furyl), 1647 (C=O), 1579 (C=C), 484 (Cp-Fe)cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ =4.18 (s, 5H, 9-H), 4.49 (t, 2H, *J* = 1.6 Hz, 6-H),4.60 (t, 2H, *J* = 1.6 Hz, 5-H),7.01 (d, 1H, *J* = 15.6 Hz, 2-H),7.28-7.26 (m, 2H, furyl, 2´-H, 3´-H),7.64 (s, 1H, furyl, 4´-H),7.80 (d, 1H, *J* = 15.6 Hz, 3-H).– ^{13}C RMN ($CDCl_3$/TMS): δ = 69.7 (C-9),71.4 (C-6),73.1 (C-5),78.9 (Fc_{ipso}),116.7 (C-3´),117.3 (C-4´),118.1 (C-2´),135.8. (C_α),146.0 (C_β),153.8 (C_{ipso}),193.4 (C=O). –MS (EI, 70 Ev): *m/z* (%) = 306(100) $[M]^+$. –Anal. calcd.C 66.70, H 4.61;Found C 67.03, H, 4.47.

General procedure for preparation of compounds 6a-d.

A mixture of **4**(2.19 mmol), **5** (2.19 mmol) and 2.19 mmol of solid NaOH pellet was ground together in an agate mortar with a pestle at room temperature for 12–19 min (See table 1). For compounds **6c** and **6d** the ratio of 4/5 was 1:3. The progress of reaction was monitored by TLC.After the completion of reaction, the reaction mixture was washed with brine. All crude products were purified by column chromatography (silica gel, 4:1 hexanes–ethyl acetate as eluent) to give compounds **6a-d**as red solids. All Compoundsexhibit melting points corresponding to the literature.

(2E)-1-Ferrocenyl-3-(phenyl)prop-2-en-1-one (6a).

M.p. 138-139 ^{o}C (Lit. M.p. 141-142^{o}C) [28, 29]. –IR (KBr): ν = 3086 (Ar-H), 1649 (C=O), 1595 (C=C), 482 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ =4.22 (s, 5H, 6´-H), 4.60 (s, 2H, 3´-H),4.92 (s, 2H, 2´-H),7.11 (d, 1H, *J* = 15.2 Hz, 2-H),7.42 (m, 3H, Ar, 6-H, 7-H),7.65 (s, 2H, Ar, 5-H),7.82 (d, 1H, *J* = 15.2 Hz, 3-H). – ^{13}C RMN ($CDCl_3$/TMS): δ =69.8 (C-2´), 70.0 (C-6´), 72.7 (C-3´),80.7 (Fc_{ipso}),128.24 (C-7),128.9 (C-6, C-8),130.0 (C-5, C-9),135.3 (C_{ipso}),123.1 (C_α),140.8 (C_β), 192.6 (C=O). – MS (EI, 70 Ev): *m/z* (%) =316 (100) $[M]^+$. – Anal. calcd.C 72.18, H 5.10;Found C 73.11, H, 4.97.

(2E)-1-Ferrocenyl-3-(2-furyl)prop-2-en-1-one (6b).

M.p. 154-155^{o}C (Lit. M.p. 157^{o}C) [29]. –IR (KBr): ν = 3085 (H-furyl), 1650 (C=O), 1591 (C=C), 483 (Cp-Fe)cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.21 (s, 5H, H-6´), 4.58 (s, 2H, 3´-H),4.91 (s, 2H, 2´-H),6.52 (s, 1H, furyl, 6-H),6.68 (s, 1H, furyl, 5-H),6.97 (d, 1H, *J* = 15.6 Hz, 2-H),7.51 (d, 1H, *J* = 15.6 Hz, 3-H),7.53 (s, 1H, furyl, 7-H). – ^{13}C RMN ($CDCl_3$/TMS): δ =69.9 (C-6´), 70.3 (C-2´), 72.9 (C-3´),80.9 (Fc_{ipso}),112.8 (C-6),115.6 (C-7),120.9 (C-5),127.3 (C_α),144.5 (C_β), 152.1 (C-4),192.9 (C=O). – MS (EI, 70 Ev): *m/z* (%) = 306 (100) $[M]^+$. –Anal. calcd.C 66.70, H 4.61;Found C 66.55, H, 4.58.

(2E)-1,1´-Dicinnamoylferrocene (6c).

M.p. 179-180 ^{o}C (Lit. M.p. 181-183^{o}C) [30]. –IR (KBr): ν = 3088 (Ar-H), 1656 (C=O), 1598 (C=C), 475 (Cp-Fe) cm^{-1}. – ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.60 (s, 2H, 3´-H), 4.93 (s, 2H, 2´-H),7.08 (d, 1H, *J* = 15.2 Hz, 2-H),7.60–7.36 (m, 5H, H-Ar), 7.79 (d, 1H, *J* = 15.2 Hz, H-3). – ^{13}C RMN ($CDCl_3$/TMS): δ =71.2 (C_5H_4),74.1 (C_5H_4),81.8 (Fc_{ipso}),122.2 (C_α),130.2, 128.8, 128.3 (Ar),134.6 (C_{ipso}),142.0 (C_β), 192.0 (C=O). – MS (EI, 70 Ev): *m/z* (%) = 446(67) $[M]^+$. –Anal. calcd.C 75.35, H 4.97;Found C 75.29, H 4.88.

(2E)-1,1´-bis[β-(2-Furyl)acryloyl]ferrocene(6d).

M.p. 159-161^{o}C (Lit. M.p. 160^{o}C) [30]. –IR (KBr): ν = 3094 (furyl-H), 1657(C=O), 1590 (C=C), 483 (Cp-Fe)cm^{-1}.– ^{1}HNMR (400 MHz, $CDCl_3$):δ = 4.57 (s, 4H, H-3´), 4.93 (s, 4H, H-2´),6.47 (s, 2H, furyl, H-6),6.66 (s, 2H, furyl, H-5),6.95 (d, 2H, *J* = 15.2 Hz, H-2),7.46 (s, 2H, furyl, H-7),7.53 (d, 2H, *J* = 15.2 Hz, H-3). – ^{13}C

RMN ($CDCl_3$/TMS): δ =71.2 (C_5H_4), 74.4 (C_5H_4),82.0 (Fc_{ipso}),112.5 (C-6, furyl),115.9 (C-7, furyl),120.0 (C-5, furyl),128.0 (C_α),144.6 (C_β),151.9 (C-4, furyl),δ 192.1 (C=O). – MS (EI, 70 Ev): *m/z* (%) = 426(100) $[M]^+$. – Anal. calcd.C, 67.63; H, 4.26;Found C 67.59; H, 4.17.

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