Ultrasound assisted synthesis of 1-amino-3-ferrocenyl-3-oxoprop-1-enes

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ABSTRACT
A clean and efficient, mediated in water and assisted by ultrasound method for the synthesis of a series of N-substituted 1-amino-3-ferrocenyl-3-oxoprop-1-enes starting from acetyl ferrocene was developed. Our approach offers shortening of the reaction time under the mild reaction conditions and easy work up procedure.

1. Introduction

Studies on the chemistry of ferrocene\textsuperscript{1-3} have attracted the interest of many scientists and research groups due to its applications in material science,\textsuperscript{4} asymmetric synthesis\textsuperscript{4} and biology.\textsuperscript{5,6} The ferrocene derivatives exhibit also an antiparasitic,\textsuperscript{7-9} antitumor,\textsuperscript{10} and DNA cleaving\textsuperscript{12} activities, have an antiproliferative effects on the MCF7 cell lines,\textsuperscript{11} activity and have chemotherapeutic action on drug-resistant cancer.\textsuperscript{4,13}

On the other hand, enaminones are important building blocks in the synthesis of many heterocyclic compounds\textsuperscript{14} and many therapeutic: antitumor,\textsuperscript{15} antimicrobial,\textsuperscript{15-17} anticonvulsant,\textsuperscript{18} anti-inflammatory,\textsuperscript{19} analgesic,\textsuperscript{19} ulcerogenic agents.\textsuperscript{20} Keeping in view the biological importance of enaminones,\textsuperscript{18,21} we have recently reported\textsuperscript{22} the synthesis of (Z)-3-adamantyl-1-aryl-prop/but-2-en-1-ones which were tested for anti-inflammatory and anticancer properties. Also, not much work has been done on the synthesis of enaminones containing the ferrocenyl moiety except for an isolated report on the synthesis of 1-benzylamino-3-ferrocenyl-3-oxoprop-1-ene by Moskalenko et al.\textsuperscript{25} In continuation with our ongoing studies on enaminones\textsuperscript{22-24} and with the interest in exploring the chemistry of ferrocene due to its unique properties, we decided to develop synthetic strategy for enaminones containing the ferrocenyl moiety.
Ultrasound irradiation offers remarkable effect for the improvement of classical organic reactions.\textsuperscript{26} Ultrasound reactions work by cavitation process producing localised hot spots with transient high temperature and pressure.\textsuperscript{27} It offers an alternative source of energy and may reduce the reaction times and enhance the reaction yields under milder conditions.\textsuperscript{26-27}

Prompted by these, herein we report the synthesis of 1-amino-3-ferrocenyl-3-oxoprop-1-enes 3(a-j) under ultrasound irradiation activation in aqueous medium assisted by KHSO\textsubscript{4}.

2. Results and Discussion

In order to synthesize the target enaminones 3(a-j), we first formylated 1-acetylferrocene (1)\textsuperscript{25} by reacting with N,N-dimethylformamide dimethylectal (DMF-DMA) to give 1-dimethylamino-3-ferrocenyl-3-oxoprop-1-ene (2). The ferrocenyl enaminone 2 was then underwent the reaction with aniline in ethanol: water mixture (1:1) containing KHSO\textsubscript{4} under the ultrasound irradiation at 25 °C to give a precipitated product in 88 % yield. The reaction conditions could easily be extrapolated for the synthesis of 3b–3h in 75–95 % overall yields (Scheme 1). However, the synthesis of 3i and 3j could not be achieved under these conditions. They could be synthesised following the conventional method of refluxing in ethanol for 22 hours in 70 and 73 % yields respectively.

![Scheme 1. Synthesis of ferrocenyl enaminone 3(a-j) from 1-acetylferrocene (1)](image)

The structures of the products were established by means of spectroscopic and analytical data. Also, X-ray crystallography for a selected compound 3b was studied for the final confirmation of the structure. Thus, the IR spectra of 3a–3j showed characteristic absorption bands due to stretching vibrations of C-H bond of the cyclopentadienyl rings at 2889–3097 cm\textsuperscript{-1}. The carbonyl stretching appeared in the vicinity of 1634 cm\textsuperscript{-1}, while N-H stretching was located in the range of 3263–3442 cm\textsuperscript{-1}. In the proton NMR spectra of 3(a–j), the three sets of protons of ferrocenyl group resonated as three distinct singlets around 4.15, 4.38 and 4.71 ppm except in compound 3d where a set of proton gets merged with the –CH\textsubscript{2} group protons of benzyl and appeared as multiplet in the range 4.37–4.40 ppm. The proton at α-position appeared as doublet (J=8 Hz) at about 5.31 ppm due to its coupling with the proton at β-position which itself resonated as multiplet at about 7.26–7.35 ppm for compounds (3a–3d) with the aryl group and 6.64–6.96 ppm for compounds (3e–3i) with alkyl substituents. In the case of compound 3j, the β-proton clearly appeared as doublet of doublets (J= 6, 12 Hz) due to its coupling with the α-proton as well as its additional coupling with N-H proton. While, aromatic protons appeared in their usual range, the NH signal was recognized as broad doublet close to 9.85 ppm for compounds 3e–3i and as doublet with coupling constant 12 Hz at 11.78 ppm for compounds 3a–3d, 3j. Further, the structures of the compounds were well supported by mass spectrometry.
In the $^{13}$C NMR spectra of these products, the most significant signals were due to carbonyl carbon at 192.5–195.7 ppm. The ferrocenyl carbon atoms resonated at 68.8, 70.1, 71.2, 81.5, 96.1 ppm in compound 3a-3e, 3h and at around 68.5–68.7, 69.8–69.9, 70.2–70.9, 71.0–71.1 and 82.3–91.4 ppm in compounds 3f, 3g, 3i, 3j. In compound 3j the signals due to adamantyl group carbon atoms appeared as expected at 29.4, 36.2, 43.5 and 52.1 ppm. The synthesised ferrocenyl enamiones are presented in Table 1.

**Table 1. Synthesis of N-substituted 1-amino-3-ferrocenyl-3-oxoprop-1-enes 3a–3j**

| Entry | Compound | Reaction time, min | $^\circ$C | Yield, % |
|-------|----------|--------------------|---------|---------|
| 1     | ![3a](image) | 1                  | 152     | 88      |
| 2     | ![3b](image) | 1                  | 178-180 | 95      |
| 3     | ![3c](image) | 1.5                | 183-185 | 80      |
| 4     | ![3d](image) | 2                  | >240    | 78      |
Crystal structure of 1-p-tolylamino-3-ferrocenyl-3-oxoprop-1-ene (3b)

Crystals suitable for X-ray crystallographic study were obtained by the slow crystallisation of 3b from ethylacetate. The CCDC reference number for the crystallographic data of the structure is 1401880. The crystal belongs to monoclinic, space group P2(1)/c with a = 19.8419 (5) Å, b = 7.5584 (2) Å, c = 11.3131 (3) Å, β = 105.362 (2)°, V = 1636.04 (7) Å³ and Z = 4. The molecular graphic was performed using ORTEP-3 and displacement ellipsoids are drawn at 30 % probability level (Fig. 1).
Fig. 1. ORTEP structure of 3b (a) top view and (b) side view. Ellipsoids are drawn for 30% probability.

Table 2. General and crystal data and summary of intensity data collection and structure refinement for compounds 3b

| Compound No. | 3b                      | Compound No. | 3b                      |
|--------------|-------------------------|--------------|-------------------------|
| Formulae     | C_{20}H_{20}FeNO        | F(000)       | 723.9                   |
| Mol. wt.     | 346.22                  |              |                         |
| Crystal system | Monoclinic             | Total no. of reflections | 24578               |
| Space group  | P2_1/c                  | Observed reflections | 2580                 |
| a /Å         | 19.8419 (5)             | Independent reflections | 4070            |
| b /Å         | 7.5584 (2)              | 0 range      | 2.9–23.7°               |
| c /Å         | 11.3131 (3)             | Ranges (h, k, l) | -26≤ h ≤ 26           |
| α/°          | 90.00                   |              |                         |
| β/°          | 105.362 (2)             | Restraints/Parameters | 0/ 256           |
| γ/°          | 90.00                   | R(F^2 > 2σ(F^2)) | 0.040                  |
| V/Å^3        | 1636.04 (7)             | Δρ (max;min), e. Å^3 | 0.32, -0.24   |
| Z            | 4                       | Goodness-of-fit = S | 1.07                 |
| Density/Mgm^-3 | 1.41                    | R indices (all data) | 0.044              |
| Abs. Coeff. /mm^-1 | 0.925                  | wR(F^2)     | 0.110                  |

A summary of the crystal data and experimental detail are given in Table 2. Selected bond lengths and bond angles are given in Table 3 and Table 4.

Table 3. Selected bond lengths 3b (Å)

| Bonds | Distance | Bonds | Distance |
|-------|----------|-------|----------|
| H5-C5 | 0.96(3)  | Fe-C3 | 2.038(2) |
| H-N   | 0.88(3)  | Fe-C1 | 2.059(4) |
| H12-C12 | 1.02(3) | Fe-C6 | 2.035(4) |
| C9-C10 | 1.427(7) | Fe-C7 | 2.030(4) |
| N-C14 | 1.421(4) | C12-C13 | 1.362(5) |
| N-C13 | 1.333(4) | C20-H20A | 0.960(4) |
| C2-C3 | 1.429(4) | C9-C8 | 1.391(7) |
| C2-C1 | 1.415(4) | C17-C18 | 1.390(3) |
| O-C11 | 1.248(3) | C17-C20 | 1.512(4) |
| C11-C3 | 1.486(4) | C16-H16 | 0.929(2) |
| C11-C12 | 1.424(4) | C14-C19 | 1.386(3) |

Compound 3b displays hydrogen bonding between N-H·O (Fig. 2) with a bond distance of 2.056 Å and thus attains the Z configuration. The bond angles of C2–Fe–C3, C14–N–C13, O–C11–C3, C2–
C3–C11 and N–C14–C19 are 40.9, 126.5, 118.8, 124.6 and 123.3 respectively. The molecule as a whole adopts a planar configuration with the torsion angles C2–C3–C11–C12, C13–N–C14–C15, C11–C12–C13–N as 166.1, -170.9 and -1.5 respectively. It can be seen that there is no puckering of the rings, or departure from planarity of any atoms of the cyclopentadienyl rings. The C–C bonds of the cyclopentadienyl ring are almost of the same lengths, approximately 1.42 Å and the C–C–C bond angles almost approximately 108.0° which are not significantly different from the tetrahedral angle 109.5°. The average Fe–C bond was found to be 2.03 Å which is similar to those ferrocene derivatives reported. The C–C bond length of the aryl group was found to be approximately 1.38 Å as expected due to the delocalisation of electrons. The bond lengths of O–C11, C11–C12, C12–C13 and C13–N are 1.24, 1.42, 1.36, 1.33 Å respectively.

**Table 4. Selected bond angles for 3b (°)**

| Bond Angles | Distance | Bond Angles | Distance |
|-------------|----------|-------------|----------|
| C2-Fe-C3    | 40.9(1)  | C14-N-C13   | 126.5(2) |
| C2-Fe-C9    | 123.9(2) | H4-C4-C3    | 126(2)   |
| H-N-C14     | 117(2)   | H6-C6-C8    | 124(2)   |
| H-N-C13     | 116(2)   | C14-C19-H19 | 120.1(2) |
| O-C11-C12   | 122.7(2) | H13-C13-N   | 113(2)   |
| C3-C11-C12  | 118.5(2) | H13-C13-C12 | 122(2)   |
| N-C14-C19   | 123.3(2) | N-C13-C12   | 125.1(3) |
| C16-C17-C20 | 121.6(2) | H12-C12-C13 | 115(2)   |
| C19-C14-C15 | 118.5(2) | H5-C5-C4    | 125(2)   |
| C2-C3-C4    | 107.4(2) | H20A-C20-H20B | 109.5(3) |
| C2-C1-C5    | 108.3(3) | C17-C20-H20A | 109.4(3) |
| O-C11-C3    | 118.8(2) | C2-C3-C11   | 124.6(2) |

*Fig. 2. Packing diagram of compound 3b. Intramolecular hydrogen bonding shown by the broken lines*

3. **Conclusions**

We have developed a facile synthetic route to enaminones containing the ferrocenyl moiety. The synthetic protocol involving ultrasound irradiation offers several advantages like short reaction time, high yield, mild reaction conditions, easy work-up with high degree of purity. Also, water being used as solvent make this method very convenient and efficient.

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4. Experimental

4.1. Materials and Methods

Melting points were recorded by open capillary method and are uncorrected. The IR spectra were recorded on a fourier transform infrared spectroscopy (FTIR), Perkin Elmer spectrometer in KBr. $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) were measured on a DRX-400 Varian spectrometer and $^1$H NMR (600 MHz), $^{13}$C NMR (150 MHz) were recorded using a Bruker spectrometer. The chemical shifts (δ ppm) and the coupling constants (Hz) are reported in the standard fashion with reference to TMS as internal reference and CDCl$_3$ as solvent. The crystallographic data for the structure were deposited to the Cambridge Crystallographic Data Center (CCDC no.1401880). The X-ray diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART APEX II CCD diffractometer equipped with a graphite monochromator. The structures were solved by direct methods (SHELXS97) and refined by full-matrix least-squares based on F square. All calculations were carried out using WinGX system version 1.80.05. All the non-H atoms were refined in the anisotropic approximation: H-atoms were located at calculated positions. The electron spray mass spectra were recorded on a THERMO Finnigan LCQ Advantage max ion trap mass spectrometer. High resolution mass spectra (HRMS) were recorded on Agilent Q-TOF 6500 instrument (ESI +ve mode). In spectral data dd, bs, s, d, m, Fc stands for double-double, broad singlet, singlet, doublet, multiplet and ferrocene, respectively. Ultrasound irradiation was carried out in an EQUITRON Digital Ultrasonic Cleaner- 2.5 litre, model 8425.025.424 at 170 watt and 50 Hz.

4.2.1 Synthesis of compound 2

Formylation of 1-acetyl ferrocene was carried out following the method as reported by Moskalenko et al.$^{25}$

4.2.2 General procedure of synthesis of 1-amino-3-ferrocenyl-3-oxoprop-1-enes (3a-3j)

To a mixture of ferrocenyl enaminone 2 (1 mmol) and primary amine (1 mmol) in 5 cm$^3$ ethanol: water mixture (1:1), KH$_2$SO$_4$ (2 mmol) was added and the resulting mixture was subjected to ultrasound irradiation at 60 °C for 1–30 minutes (Scheme 1). After the completion of the reaction (monitored by TLC), the reaction mixture was allowed to cool and the precipitated product (3a–3h) was collected by filtration, washed with ethanol: water mixture (1:1) and dried over anhydrous CaCl$_2$.

For compounds 3i, 3j the reaction did not go to completion under similar conditions and therefore was refluxed in ethanol for 22 hours, whereby the desired products were obtained. On completion of the reaction, ethanol was removed and triturated with hexane to give the crude products. Purification of the products was achieved by column chromatography (silica gel, 5 % EtOAc-Hexane).

4.3 Physical and Spectral Data

1-Anilino-3-ferrocenyl-3-oxoprop-1-ene (3a, C$_{19}$H$_{16}$FeNO)

Brown solid (291 mg, 88 %); m.p.: 152 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 4.19 (s, 5H, C$_5$H$_5$); 4.46 (s, 2H, C$_5$H$_3$); 4.79 (s, 2H, C$_5$H$_2$); 5.59 (d, 1H–αH, J = 8 Hz); 7.01–7.06 (m, 3H, phenyl); 7.26–7.36 (m, 3H; 2H-phenyl, 1H–βH); 11.78 (d, 1H, NH, J = 12 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 68.9, 70.1, 71.7, 81.5 (ferrocene-CH), 95.5 (ferrocene-C), 110.2 (α–C), 115.8, 123.1, 129.8 (aromatic–CH), 140.7 (aromatic–C), 142.1 (β–C), 195.4 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3423 (NH), 2900 (Fc), 1631 (CO), 1600 (C=–C) cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{17}$FeNO [MH]$^+$: 332.0733. Found: 332.0796.

1-p-Tolylamino-3-ferrocenyl-3-oxoprop-1-ene (3b, C$_{28}$H$_{19}$FeNO)

Orange solid (327 mg, 95 %); m.p.: 178–180 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 22.30 (s, 3H–CH$_3$); 4.18 (s, 5H, C$_5$H$_5$); 4.44 (s, 2H, C$_5$H$_3$); 4.78 (s, 2H, C$_5$H$_2$); 5.56 (d, 1H–αH, J = 8 Hz); 6.96 (s,
2H–phenyl); 7.11 (s, 2H–phenyl); 7.26–7.31 (m, 1H–βH); 11.76 (d, 1H, NH, J = 12 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 20.9 (methyl–C), 68.8, 70.1, 71.6, 81.9 (ferrocene–CH), 95.0 (ferrocene–C), 110.0 (α–C), 115.9, 130.4 (aromatic–CH), 132.8, 138.3 (aromatic–C), 142.6 (β–C), 195.7 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3442 (NH), 2889 (Fe), 1634 (CO), 1550 (C=C) cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{20}$H$_{19}$FeNO [MH]$^+$: 346.0889. Found: 346.0949.

1-(4-Chlorophenyl)amino-3-ferrocenyl-3-oxoprop-1-ene (3c, C$_{19}$H$_{15}$ClFeNO)

Brown solid (292 mg, 80%); mp 183–185 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 419 (s, 5H, C$_3$H$_2$); 4.54 (s, 2H, C$_2$H$_2$); 4.80 (s, 2H, C$_3$H$_2$); 5.62 (d, 1H–αH, J = 8 Hz); 7.00 (d, 2H–phenyl, J = 8 Hz); 7.34–7.35 (m, 3H, 1H–βH, 2H–phenyl); 11.79 (d, 1H, NH, J = 12 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 68.9, 70.1, 71.8, 81.3 (ferrocene–CH), 96.1 (ferrocene-C), 112.0 (α–C), 116.9 (aromatic–CH), 127.9 (aromatic–C), 129.8 (aromatic–CH), 139.4 (aromatic–C), 141.7 (β–C), 195.7 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3441 (NH), 2900 (Fe), 1635 (CO), 1596 (C=C) cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{15}$ClFeNO [MH]$^+$: 366.0343. Found: 366.0414.

1-(4-Nitrophenyl)amino-3-ferrocenyl-3-oxoprop-1-ene (3d, C$_{19}$H$_{15}$Fe$_2$O$_3$)

Brown solid (308 mg, 78%); m.p. >240 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 4.20 (s, 5H, C$_3$H$_2$); 4.54 (s, 2H, C$_2$H$_2$); 4.81 (s, 2H, C$_3$H$_2$); 5.74 (d, 1H–αH, J = 8 Hz); 7.07 (d, 2H-phenyl, J = 8 Hz); 7.33–7.35 (m, 1H–βH); 8.22 (d, 2H–phenyl, J = 8 Hz); 11.99 (d, 1H, NH, J = 12 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 69.2, 70.3, 72.5, 81.5 (ferrocene–CH), 99.1 (ferrocene-C), 110.8 (α–C), 114.8, 126.3, (aromatic–CH), 133.5, 139.4 (aromatic–C), 142.7 (β–C), 194.1 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3437 (NH), 3050 (Fe), 1638 (CO), 1603 (C=C) cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{15}$Fe$_2$O$_3$ [MH]$^+$: 377.0584. Found: 377.0541.

1-Benzylamino-3-ferrocenyl-3-oxoprop-1-ene (3e)

Orange solid (313 mg, 91%); m.p.: 132–135 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 4.14 (s, 5H, C$_3$H$_2$); 4.37–4.40 (m, 4H, C$_2$H$_2$ 2H–CH$_2$); 4.71 (s, 2H, C$_2$H$_2$); 5.34–5.35 (m, 1H-αH); 6.78–6.81 (m, 1H–βH); 7.28–7.33 (m, 5H-phenyl); 10.11 (bs, 1H, NH); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 52.6 (methylene–C), 68.6, 69.9, 71.2, 82.1 (ferrocene–CH), 92.4 (ferrocene–C), 127.3 (α–C), 127.8, 128.9, 129.0 (aromatic–CH), 138.3 (aromatic–C), 151.8 (β–C), 194.4 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3424 (NH), 3000 (Fe), 1631 (CO), 1550 (C=C) cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{19}$H$_{15}$FeNO [MH]$^+$: 346.0889. Found: 346.0489.

1-Methylamino-3-ferrocenyl-3-oxoprop-1-ene (3f, C$_{14}$H$_{15}$FeNO)

Brown flakes (201 mg, 75%); m.p.: 130–132 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = .98 (s, 3H–CH$_3$); 4.11 (s, 5H, C$_3$H$_2$); 4.33 (s, 2H, C$_2$H$_2$); 4.68 (s, 2H, C$_3$H$_2$); 5.25 (d, 1H–αH, J = 8 Hz); 6.64–6.69 (m, 1H–βH); 9.66 (bs, 1H, NH); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 35.3 (methyl–C), 68.6, 69.9, 70.9, 71.1 (ferrocene–CH), 82.3 (ferrocene–C), 91.7 (α–C), 153.2 (β–C), 194.0 (carbonyl–C); HRMS (ESI) m/z calcd for C$_{14}$H$_{15}$FeNO [MH]$^+$: 270.0576. Found: 270.0538.

1-Ethylamino-3-ferrocenyl-3-oxoprop-1-ene (3g, C$_{15}$H$_{16}$FeNO)

Brown flakes (198 mg, 70%); m.p.: 123–126 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ = 1.21–1.22 (m, 3H–CH$_3$); 3.24 (s, 2H–CH$_2$); 4.14 (s, 5H, C$_3$H$_2$); 4.35 (s, 2H, C$_2$H$_2$); 4.71 (s, 2H, C$_3$H$_2$); 5.26 (d, 1H–αH, J = 8 Hz); 6.72–6.76 (m, 1H–βH); 9.84 (bs, 1H, NH); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm: 16.8 (methylene–C), 43.7 (methyl–C), 68.5, 69.9, 70.9, 71.1 (ferrocene–CH), 82.3 (ferrocene–C), 91.4 (α–C), 151.6 (β–C), 193.9 (carbonyl–C); IR (KBr) $\nu_{\text{max}}$ = 3263 (NH), 3097 (Fe), 1635 (CO), 1546 (C=C) cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{15}$H$_{16}$FeNO [MH]$^+$: 284.0733. Found: 284.0695.

1-(2-Hydroxyethyl)amino-3-ferrocenyl-3-oxoprop-1-ene (3h, C$_{15}$H$_{17}$FeNO$_2$)

Brown flakes (221 mg, 74%); m.p.: 120–122 °C; $^1$H NMR (CDCl$_3$, 600 MHz) δ ppm: 3.36 (s, 2H–CH$_2$–NH); 3.75 (s, 2H–CH$_2$–OH); 4.15 (s, 5H, C$_3$H$_2$); 4.38 (s, 2H, C$_3$H$_2$); 4.79 (s, 2H, C$_2$H$_2$); 5.31
(d, 1H-αH, J = 6 Hz); 6.78–6.79 (m, 1H-βH); 9.86 (bs, 1H, NH); 13C NMR (CDCl3, 150 MHz) δ ppm: 51.5 (–CH3NH–), 62.6 (–CH2OH), 68.7, 70.0, 71.1, 82.0 (ferrocene–CH), 92.3 (ferrocene–C), 96.9 (α-C), 152.6 (β–C), 194.6 (carbonyl–C); IR (KBr) vmax = 3383 (NH), 2924 (Fcc), 1634 (CO), 1553 (C=C) cm⁻¹; HRMS (ESI) m/z calcd for C15H17FeNO2 [MH]+: 300.0682. Found: 300.0742.

1-(Phenylethyl)amino-3-ferrocenyl-3-oxoprop-1-ene (3i, C21H19FeNO)

Brown solid (280 mg, 78 %); m.p.: 123–125 °C; 1H NMR (CDCl3, 600 MHz) δ ppm: 3.36 (s, 2H–CH2–NH); 3.75 (s, 2H–CH2–OH); 4.14 (s, 5H, C2H5); 4.36 (s, 2H, C3H2); 4.71 (s, 2H, C2H5); 5.23 (s, 1H-αH); 6.55–6.58 (m, 1H-βH); 7.19–7.20 (m, 1H-phenyl); 7.21–7.24 (m, 2H–phenyl); 7.29–7.32 (m, 2H–phenyl); 9.91 (bs, 1H, NH); 13C NMR (CDCl3, 150 MHz) δ ppm: 38.1 (–CH2–aromatic), 50.9 (–CH2NH–), 68.6, 69.9, 70.2, 71.0 (ferrocene–CH), 91.9 (ferrocene–C), 114.0 (α-C), 126.7, 128.8, 129.1 (aromatic–CH), 138.5 (aromatic–C), 151.9 (β–C), 192.5 (carbonyl–C); IR (KBr) vmax = 3437 (NH), 2900 (Fcc), 1623 (CO), 1540 (C=C) cm⁻¹; HRMS (ESI) m/z calcd for C21H20FeNO [MH]+: 360.1046. Found: 360.1364.

1-(Adamantan-1-yl)amino-3-ferrocenyl-3-oxoprop-1-ene (3j, C23H26FeNO)

Orange solid (283 mg, 73 %); m.p.: 207–208 °C; 1H NMR (CDCl3, 600 MHz) δ ppm: 1.64–1.70 (m, 6H–adamantane); 1.82–1.83 (m, 6H–adamantane); 2.14 (s, 3H–adamantane) 4.15 (s, 5H, C2H5); 4.34 (s, 2H, C3H2); 4.71 (s, 2H, C3H2); 5.28 (d, 1H-αH, J = 6 Hz); 6.93–6.96 (dd, 1H-βH, J = 6 Hz, 12 Hz); 10.17 (d, 1H, NH, J = 12 Hz); 13C NMR (CDCl3, 150 MHz) δ ppm: 29.4 (3, CH–adamantane), 36.2 (3, CH2–adamantane), 43.5 (3, CH2–adamantane), 52.1 (C–adamantane), 68.5, 69.8, 70.8, 71.0 (ferrocene–CH), 91.2 (ferrocene–C), 111.1 (α-C), 146.6 (β–C), 193.5 (carbonyl–C); IR (KBr) vmax = 3440 (NH), 2925 (Fcc), 1628 (CO), 1556 (C=C) cm⁻¹; HRMS (ESI) m/z calcd for C23H27FeNO [MH]+: 390.1515. Found: 390.1583.

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