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Synthesis of new 7-ferrocenyl-β-enaminone-coumarins and ferrocenyl-pyrano[3,2-g]quinolin-2-ones from coumarin and ferrocenyl-α-ketoalkynes using $Ni(CN)_2/NaOH/H_2O/CO/KCN$ aqueous catalytic system

Ivonne Arellano, Pankaj Sharma*, Laura Rubio-Perez, Armando Cabrera, Noé Rosas, A. Toscano

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Coyoacan, 04510 México D.F, Mexico

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ABSTRACT

New ferrocenyl-β-enaminone-coumarins (**1a**–**5a**) and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones (**1b**–**5b**) were obtained through a heterocyclization reaction from 7-amino-4-methyl-2*H*-chromen-2-one and several ferrocenyl-α-ketoalkynes in a nickel homogeneous aqueous catalytic system formed by $Ni(CN)_2$/CO/NaOH/KCN. In the absence of this catalytic system neither ferrocenyl substituted chromenone nor ferrocenyl-heterocycle was obtained. A possible mechanism is suggested for the synthesis of -β-enaminone-coumarins and pyrano[3,2-*g*]quinolinones. Molecular structure of 7-(1-ferrocenyl-3-(4-bromophenyl)-3-oxoprop-1-enylamino)-4-methyl-2*H*-chromen-2-one (**5a**) has been determined.

1. Introduction

Quinolinones are important compounds that are used as drugs [1–6] more specifically, pyrano-quinolinones show interesting biological activity such as immunosuppressors [7], antiallergics [8,9], antibacterials [10], androgen receptor agonists for the treatment of prostate cancer [11], and also form a part of several natural alkaloids [10,12–14].

Different methods are reported for the synthesis of quinolinones. Diels–Alder reactions of aryl amines with different dienophiles in the presence of an acid catalyst [10,14–17]; cyclocondensation of aromatic amines with malonates [18,19], intramolecular cyclizations of substituted quinolones and coumarins [20,21], are some of the reported routes to synthesize quinolinones. These kind of reactions are carried out in organic solvent, solvent free or in water but carried out generally in more than two reaction steps.

Previously our group has reported one pot catalytic synthesis of alkyl/phenyl substituted 2*H*-pyrano[3,2-*g*]quinolin-2-ones [22] (Fig. 1) from α-ketoalkynes and 7-amino-4-methyl-coumarin, using $[Ni(CN)_4]^{-4}$ as a catalytic specie, formed *in situ* in the $Ni(CN)_2/NaOH/H_2O/CO/KCN$ aqueous system [23]. Similarly enaminones are versatile reagents and have wide utility in heterocyclic synthesis. Though a variety of enaminones are reported, enaminone-coumarins are lesser known and ferrocenyl substituted enaminone-coumarins are unknown in literature.

On the other hand ferrocenyl group has been widely used in the design or redesign of drugs that can result favorable changes in their lipophilic and redox properties and biological activities [24–27]. Considering a synergistic effect between pyrano quinolinones and ferrocene on lipophilic and redox properties and biological activities, and our interest in nickel catalyzed heterocyclization reaction to synthesize different heterocycles, this work was undertaken.

In this work a facile way to obtain new ferrocenyl-β-enaminone-coumarins and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones from coupling and heterocyclization of several ferrocenyl-α-ketoalkynes and 7-amino-4-methyl-coumarin in water as a reaction medium under room temperature and atmospheric pressure using the nickel catalytic system, is reported.

2. Results and discussion

The new ferrocenyl-β-enaminone-coumarins (**1a**–**5a**) and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones (**1b**–**5b**) were obtained in mild reaction conditions at room temperature and atmospheric pressure as shown in the Scheme 1 and Table 1. α-Ketoalkynes were

* Corresponding author. Fax: +52 555 6162217.
E-mail address: pankajsh@servidor.unam.mx (P. Sharma).

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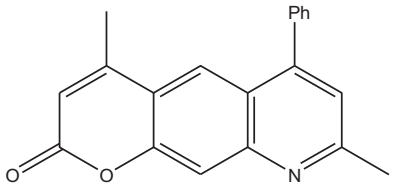


Fig. 1. 8-Ethyl-4-methyl-6-phenyl-2*H*-pyrano[3,2-*g*]quinolin-2-one.

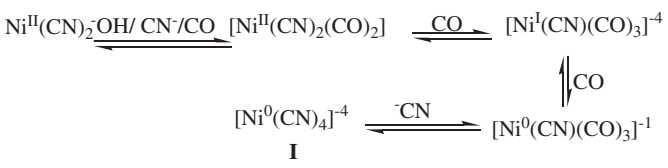
obtained from ethynylferrocene and acyl chlorides via a palladium catalyzed coupling as reported earlier by our group [28].

In the IR spectra, C═O and C—N vibrations were observed for all the compounds synthesized. In the IR spectra of compounds (**1a**—**5a**) a weak band at ~3370 cm^{-1} can be attributed to the stretching vibration of the hydrogen bonded enamine N—H group. This band appears at a higher frequency than the N—H frequency observed for similar ferrocenyl-β-enamino ketones [29] which may be due to the absence of N—H···O intramolecular interaction. IR spectrum of compound (**1a**) in $CHCl_3$ shows C═O vibration at 1575 cm^{-1}, suggesting the presence of α,β-unsaturated carbonyl system. In the mass spectra IE^+, the molecular ion peaks were observed for both ferrocenyl-β-enaminone-coumarins (**1a**—**5a**) and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones (**1b**—**5b**) compounds along with fragments corresponding to the loss of cyclopentadienyl ($M^+ - 65$) group, in each compound. Fragmentation pattern in all these compounds are similar. For compounds **2b**, **3b**, **5b** and **5a** high resolution mass spectra (HRMS) were also obtained, and molecular ion peaks at 486.1149 (Calc. *m*/*z* 486.1156), 532.1213 (Calc. *m*/*z* 532.1211), 550.0109 (Calc. *m*/*z* 550.0105) and 568.0204 (Calc. *m*/*z* 568.0211) respectively, were observed, confirming the molecular formulas for these compounds.

^{1}H NMR spectra of ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones (**1a**—**5a**) present similar chemical shifts pattern for ferrocenyl group between 4.09 and 5.11 ppm. In the NOESY spectra, the correlation between H-10 and the H of substituted cyclopentadienyl ring of ferrocene is observed which confirm that the ferrocene group is at the C-8, as is shown in the Fig. 2.

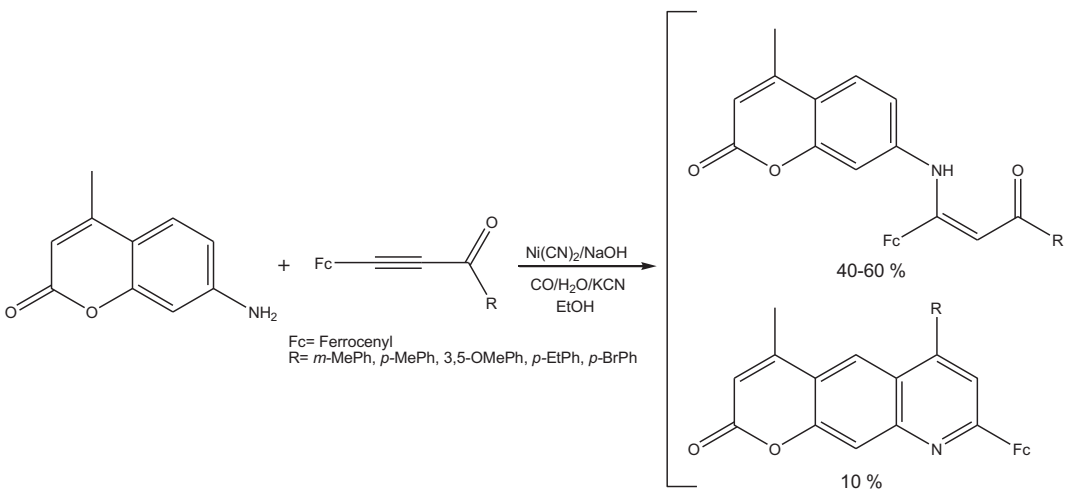
^{1}H NMR spectra of all the ferrocenyl-β-enaminone-coumarins compounds present similar chemical shifts pattern for ferrocenyl group between 4.07 and 4.42 ppm. The molecular structure of compound **5a** was unambiguously established by X-ray crystallography and is shown at the Fig. 3. Crystal data and selected bond lengths and angles are given in Tables 2 and 3, respectively. In the molecular structure of compound **5a** the unsubstituted cyclopentadienyl ring is disordered. The compound is monomeric. In the solid state this compound presents a weak intramolecular N—H···O═C hydrogen bonding, similar to the ferrocenyl-β-enamino ketones reported earlier by our group [29].

The species $[Ni(CN)_4]^{-4}$ (**I**) is obtained when an excess of KCN is added to an alkaline solution of $Ni(CN)_2$ in CO atmosphere. It is known that the presence of carbon monoxide in the media attains an equilibria which involves different carbonylic species in the solution [23]. In addition, the presence of carbon monoxide in the system results in a reductive atmosphere, which promotes low oxidation states of nickel in the reaction [23,28].



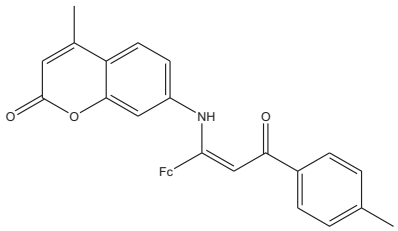
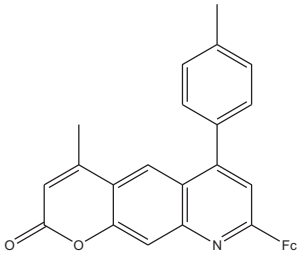
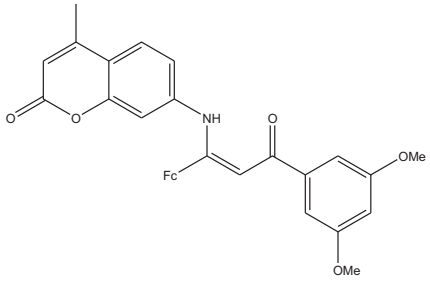
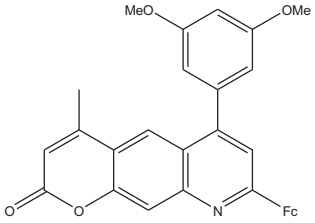
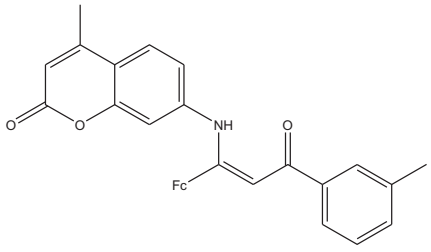
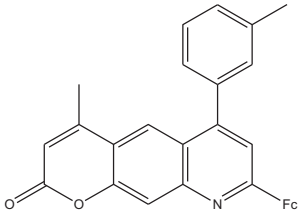
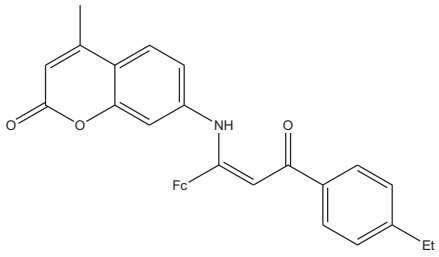
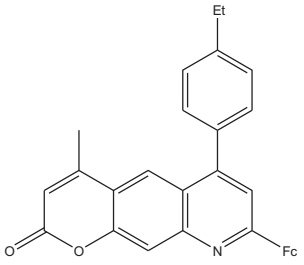
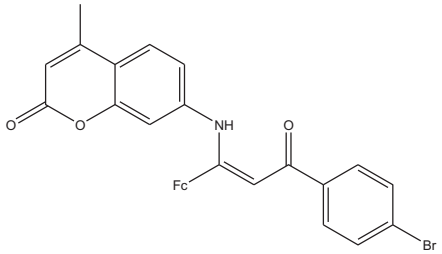
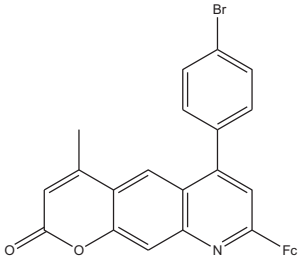
In absence of the catalyst $[Ni(CN)_4]^{-4}$, which was formed *in situ* using $Ni(CN)_2$/KCN/NaOH/H_2O/EtOH catalytic system, no reaction was observed and the product was not obtained after 20 days of reaction. But when the reaction was carried in presence of the active catalytic species $[Ni(CN)_4]^{-4}$ (**I**), corresponding β-enaminone-coumarin were obtained after 24 h of the reaction, and after 6 days the corresponding quinolinones were obtained. This indicates the utility of the active catalytic specie to activate the α-ketoalkyne and facilitates the nucleophilic attack by coumarin nucleophile to the α-ketoalkyne. The attack of $[Ni(CN)_4]^{-4}$ occurs at the carbonyl group of the ketoalkyne instead of to carbon triple bond due to stereo-electronic effect of the ferrocenyl group. A similar observation was noted previously also in the heterocyclization reaction for the formation of ferrocenyl-pyrido[2,3-*d*]pyrimidines [28].

In the Scheme 2 a proposed reaction pathway for the synthesis of the ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones and ferrocenyl-β-enaminone-coumarins is shown. First, the species $[Ni(CN)_4]^{-4}$ attacks the carbonyl group of the ferrocenyl-α-ketoalkyne, whereas an imine is generated by the basic medium from the 7-amino-4-methyl-coumarin. Then, the nucleophilic moiety (V) attacks the triple bond of the activated ketoalkyne (III) and by an addition—elimination mechanism, the catalyst is regenerated and ferrocenyl-β-enaminone-coumarin (VI) is obtained. In the basic



Scheme 1. General synthesis of ferrocenyl-β-enaminone-coumarins and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones.

Table 1
Reaction between ferrocenyl-α-ketoalkynes and 7-amino-4-methyl-coumarins.

Entry	R of ferrocenyl-α-ketoalkyne	β-Enaminone-coumarins	Yield	Pyrano[3,2-*g*]quinolinones	Yield
1	*p*-Tolyl		**1a** 58%		**1b** 6%
2	3,5-Dimethoxy-phenyl		**2a** 55%		**2b** 10%
3	*m*-Tolyl		**3a** 40%		**3b** 12%
4	*p*-Ethylphenyl		**4a** 60%		**4b** 5%
5	*p*-Bromophenyl		**5a** 57%		**5b** 8%

Reaction conditions: $Ni(CN)_2$/CO/5 N NaOH/KCN, room temperature, atmospheric pressure, yielding ferrocenyl-β-enaminone-coumarins (24 h) and ferrocenyl-pyrano[3,2-*g*] quinolinones (6 days). No reaction without $(NiCN)_2$/CO/KCN after 20 days.

medium, ketoimine (VII) anion is generated which promotes the heterocyclization and re-aromatization, affording the pyrano[3,2-*g*] quinolin-2-one (IX).

In summary, it was found that the reaction between 7-amino-4-methyl-coumarin and several ferrocenyl-α-ketoalkynes in the presence of a nickel catalytic system affords ferrocenyl-β-enaminone-coumarins and ferrocenyl-pyrano[3,2-*g*]quinolin-2-ones. It is to be noted that the substitution at C-8 depends on the nature of the α-ketoalkyne used. When ketoalkyne with a weak electron donating group e.g. alkyl or phenyl group, the substitution of this

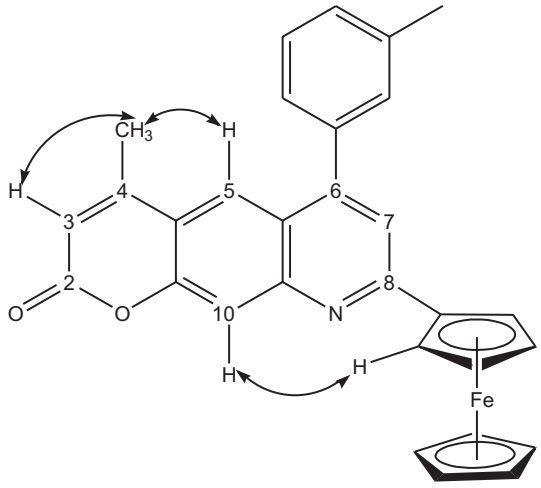


Fig. 2. NOESY correlations for compound **1b**.

group will be occurred at C-6 of the pyrano[3,2-*g*]quinolinone, as reported earlier [22], and with ferrocenyl group with higher electron donating capacity, the substitution will be at the C-8 of the heterocycle as observed in this report.

3. Experimental

Ferrocenyl-ketoalkynes were prepared according to previous report [28, 29]. 7-Amino-4-methyl-coumarin was purchased from Aldrich. ^{1}H and ^{13}C spectra were recorded on a JEOL GX3 00 instrument, 300 MHz for ^{1}H and 75 MHz for ^{13}C using $CDCl_3$ as solvent. IR spectra were recorded in film on a Nicolet FT 5SX spectrophotometer. MS spectra were obtained using a JEOL JMS-AX505HA spectrometer.

3.1. General procedure

A 5 N NaOH solution (10 mL) was degassed and saturated with CO under atmospheric pressure for 30 min, 0.2 mmol of $Ni(CN)_2 \cdot 4H_2O$ was added to the solution, the mixture was kept at room temperature overnight, with stirring and slow bubbling of CO (2–3 mL/min), until a pale yellow solution was obtained. Addition of 1.5 mmol of KCN resulted in a color change to orange. The species (1) is obtained when an excess of KCN is added to an alkaline solution of $Ni(CN)_2$ in CO atmosphere. It is known that the presence of carbon monoxide in the media attains an equilibria which involves different carbonylic species in the solution [23]. In addition, the presence of carbon monoxide in the system results in a reductive atmosphere, which promotes low oxidation states of nickel in the reaction [23,28]. After stirring for 0.5 h the corresponding ferrocenyl-α-ketoalkyne (1 mmol), 7-amino-4-methyl-coumarin (2 mmol) and 2 mL of ethanol were added. The evolution of the reaction was following by TLC. At the end of the reaction, ethyl acetate was used to extract the product. After evaporation of the solvent followed by drying over $MgSO_4$, the crude product was purified by flash chromatography using ethyl acetate:hexane (80:20) as eluent.

3.2. X-ray crystallography

The X-ray intensity data were measured at 298 K on a Bruker Smart APEX CCD 01-670 diffractometer. The detector was placed at a distance of 4.837 cm from the crystal. Analysis of the data showed negligible decays during data collections. A semi-empirical method based on equivalents absorption correction was applied. Crystal structure was refined by full-matrix least squares method. SMART software (data collection and data reduction) and SHELXTL were used for solution and refinement of the structure.

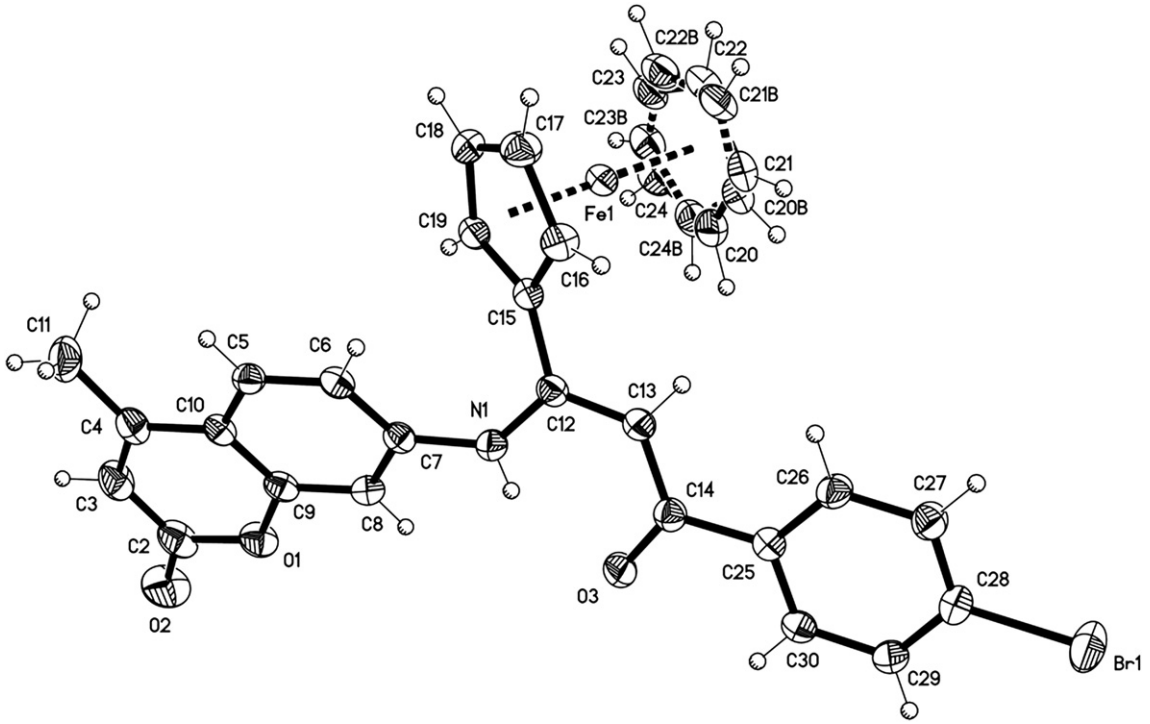


Fig. 3. ORTEP diagram of 7-(1-ferrocenyl-3-(4-bromophenyl)-3-oxoprop-1-enylamino)-4-methyl-2*H*-chromen-2-one.

Table 2
Crystallographic data for compound (**5a**).

Parameter	Compound (**5a**)	Parameter	Compound (**5a**)
Empirical formula	$C_{29}H_{22}BrFeNO_3$	Z	4
Formula weight	568.24	D_{Calc} (Mg/m^3)	1.561
Crystal color	Red prism	λ (mm^{-1})	2.309
Crystal system	Monoclinic	2Θ (°)	1.76–25.41
Space group	$P2/c$	Reflections collected	19,635
Crystal size (mm)	0.408 × 0.158 × 0.112	Independent reflections	4435
a (Å)	12.415(2)	R_{int}	0.0521
b (Å)	13.191(2)	R_1 [$I > 2\sigma(I)$]	0.0401
c (Å)	15.82(3)	wR_2	0.0857
α (°)	90	GOF	1.025
β (°)	9111.646(3)	Max/min $\Delta\rho$ (e Å^{-3})	0.692/−0.584
γ (°)	90		
Volume (Å^3)	2417.5(7)		

Table 3
Selected bond angles (°) and selected bond length (Å) for the compound (**5a**).

Bond angles (°)		Bond length (Å)	
O(3)–C(14)–C(13)	122.4(3)	O(3)–C(14)	1.254(4)
N(1)–C(12)–C(13)	119.4(3)	C(12)–C(13)	1.372(4)
C(12)–C(13)–C(14)	125.1(3)	C(13)–C(14)	1.418(4)
C(13)–C(12)–C(15)	119.9(3)	C(12)–N(1)	1.359(4)
		C(14)-C(25)	1.498(4)
		C(12)–C(15)	1.468(4)

*3.2.1. 7-(1-Ferrocenyl-3-(p-tolyl)-3-oxoprop-1-enylamino)-4-methyl-2H-chromen-2-one (**1a**)*

The product was obtained as described in the general procedure as a red-orange solid (58%); Empirical formula: $C_{30}H_{25}NO_3Fe$; mp. 185 °C; IR (KBr, selected, cm^{-1}) 1588, 1718, 2923, 3327; Mass spectrum EI: m/z (%) = 503 (83) M$^+$, 438 (68) [M − cp]$^+$, 273 (100) [M − Fc-C-CHC(=O)tolyl]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.35 (s, 3H, C*H*$_3$C4), 2.43 (s, 3H, C*H*$_3$Ph), 4.17 (s, 5H, C_5H_5), 4.36 (t, 2H, J = 1.8 Hz, C_5H_4), 4.42 (t, 2H, J = 1.8 Hz, C_5H_4), 6.14 (s, 1H, C3-*H*), 6.68 (s, 1H, C=C*H*–CO), 6.69 (s, 1H, C8-*H*), 6.80 (dd, 1H, J = 2.1 Hz, C6-*H*), 7.29 (d, 2H, J = 7.9 Hz, 3,5-Ph), 7.37 (d, 1H, J = 8.5 Hz, C5-*H*), 7.89 (d, 2H, J = 8.1 Hz, 2,6-Ph), 13.02 (s, 1H, N*H*).

*3.2.2. 7-(1-Ferrocenyl-3-(3,5-dimethoxyphenyl)-3-oxoprop-1-enylamino)-4-methyl-2H-chromen-2-one (**2a**)*

The product was obtained as described in the general procedure as a red-orange solid (55%); Empirical formula: $C_{31}H_{27}NO_5Fe$; mp. 130 °C; IR (film, selected, cm^{-1}) 1590, 1722, 2924, 3356; Mass spectrum EI: m/z (%) = 549 (100) M$^+$, 484 (94) [M − cp]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.35 (s, 3H, C*H*$_3$C4), 3.88 (s, 6H, OC*H*$_3$), 4.07 (s, 5H, C_5H_5), 4.37 (t, 2H, J = 1.8 Hz, C_5H_4), 4.42 (t, 2H, J = 1.8 Hz, C_5H_4), 6.16 (s, 1H, C3-*H*), 6.60 (s, 1H, C=C*H*–CO), 6.63 (s, 1H, 4-Ph), 6.72 (s, 1H, C8-*H*), 6.81 (dd, 1H, J = 2.4 Hz, C6-*H*), 7.13 (d, 2H, J = 2.1 Hz, 2,6-Ph), 7.39 (d, 1H, J = 8.4 Hz, C5-*H*), 13.07 (s, 1H, N*H*).

*3.2.3. 7-(1-Ferrocenyl-3-(m-tolyl)-3-oxoprop-1-enylamino)-4-methyl-2H-chromen-2-one (**3a**)*

The product was obtained as described in the general procedure as a red-orange solid (40%); Empirical formula: $C_{30}H_{25}NO_3Fe$; mp. 149 °C, decomposition; IR (Film, selected, cm^{-1}) 1575, 1712, 3003, 3391; Mass spectrum EI: m/z (%) = 503 (91) M$^+$, 438 (100) [M − cp]$^+$, 28 (44) [CO]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 2.36 (s, 3H, C*H*$_3$C4), 2.43 (s, 3H, C*H*$_3$Ph), 4.17 (s, 5H, C_5H_5), 4.37 (t, 2H, J = 1.9 Hz, C_5H_4), 4.42 (t, 2H, J = 1.9 Hz, C_5H_4), 6.15 (s, 1H, C3-*H*), 6.68 (s, 1H, C=C*H*–CO), 6.69 (d, 1H, J = 2.0 Hz, C8-*H*), 6.80 (dd, 1H, J = 2.1 Hz, C6-*H*), 7.30 (d, 2H, J = 8.3 Hz, 3,5-Ph), 7.38 (d, 1H, J = 8.5 Hz, C5-*H*), 7.89 (d, 2H, J = 8.1 Hz, 2,6-Ph).

*3.2.4. 7-(1-Ferrocenyl-3-(4-ethylphenyl)-3-oxoprop-1-enylamino)-4-methyl-2H-chromen-2-one (**4a**)*

The product was obtained as described in the general procedure as a red-orange solid (60%); Empirical formula: $C_{31}H_{27}NO_3Fe$; mp. 165 °C; IR (film, selected, cm^{-1}) 1587, 1726, 2923, 3088; Mass spectrum EI: m/z (%) = 517 (97) M$^+$, 452 (100) [M − cp]$^+$, ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 1.30 (t, 3H, C*H*$_3$CH$_2$Ph), 2.37 (s, 3H, C*H*$_3$C4), 2.73 (*q*, 2H, C*H*$_2$Ph), 4.19 (s, 5H, C_5H_5), 4.38 (t, 2H, J = 1.8 Hz, C_5H_4), 4.44 (t, 2H, J = 1.8 Hz, C_5H_4), 6.16(s, 1H, C3-*H*), 6.71(s, 1H, C8-*H*), 6.83 (dd, 1H, J = 2.1 Hz, C6-*H*), 7.26(s, 1H, C=C*H*–CO), 7.29 (d, 2H, J = 7.9 Hz, 3,5-Ph), 7.39 (d, 1H, J = 8.5 Hz, C5-*H*), 7.93 (d, 2H, J = 8.1 Hz, 2,6-Ph), 13.04 (s, 1H, N*H*).

*3.2.5. 7-(1-Ferrocenyl-3-(4-bromophenyl)-3-oxoprop-1-enylamino)-4-methyl-2H-chromen-2-one (**5a**)*

The product was obtained as described in the general procedure as a red-orange solid (57%); Empirical formula: $C_{29}H_{22}NO_3BrFe$; mp. 190 °C, decomposition; IR (Film, selected, cm^{-1}) 1583, 1723, 2923, 3416; Mass spectrum EI: m/z (%) = 567 (100) M$^+$, 549 (14) [M − 18]$^+$, 502 (98) [M − cp]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 2.32 (s, 3H, C**H**$_3$C4), 4.12 (s, 5H, C_5H_5), 4.33 (t, 2H, J = 1.9 Hz, C_5H_4), 4.38 (t, 2H, J = 1.9 Hz, C_5H_4), 6.11 (s, 1H, C3-*H*), 6.56 (s, 1H, C=C*H*–CO), 6.68 (d, 1H, J = 2.0 Hz, C8-*H*), 6.77 (dd, 1H, J = 2.1 Hz, C6-*H*), 7.36 (d, 1H, J = 8.5 Hz, C5-*H*), 7.57 (d, 2H, J = 8.7 Hz, 3,5-Ph), 7.80 (d, 2H, J = 8.5 Hz, 2,6-Ph), 13.04 (s, 1H, N*H*).

*3.2.6. 8-Ferrocenyl-4-methyl-6-p-tolyl-2H-pyrano[3,2-g]quinolin-2-one (**1b**)*

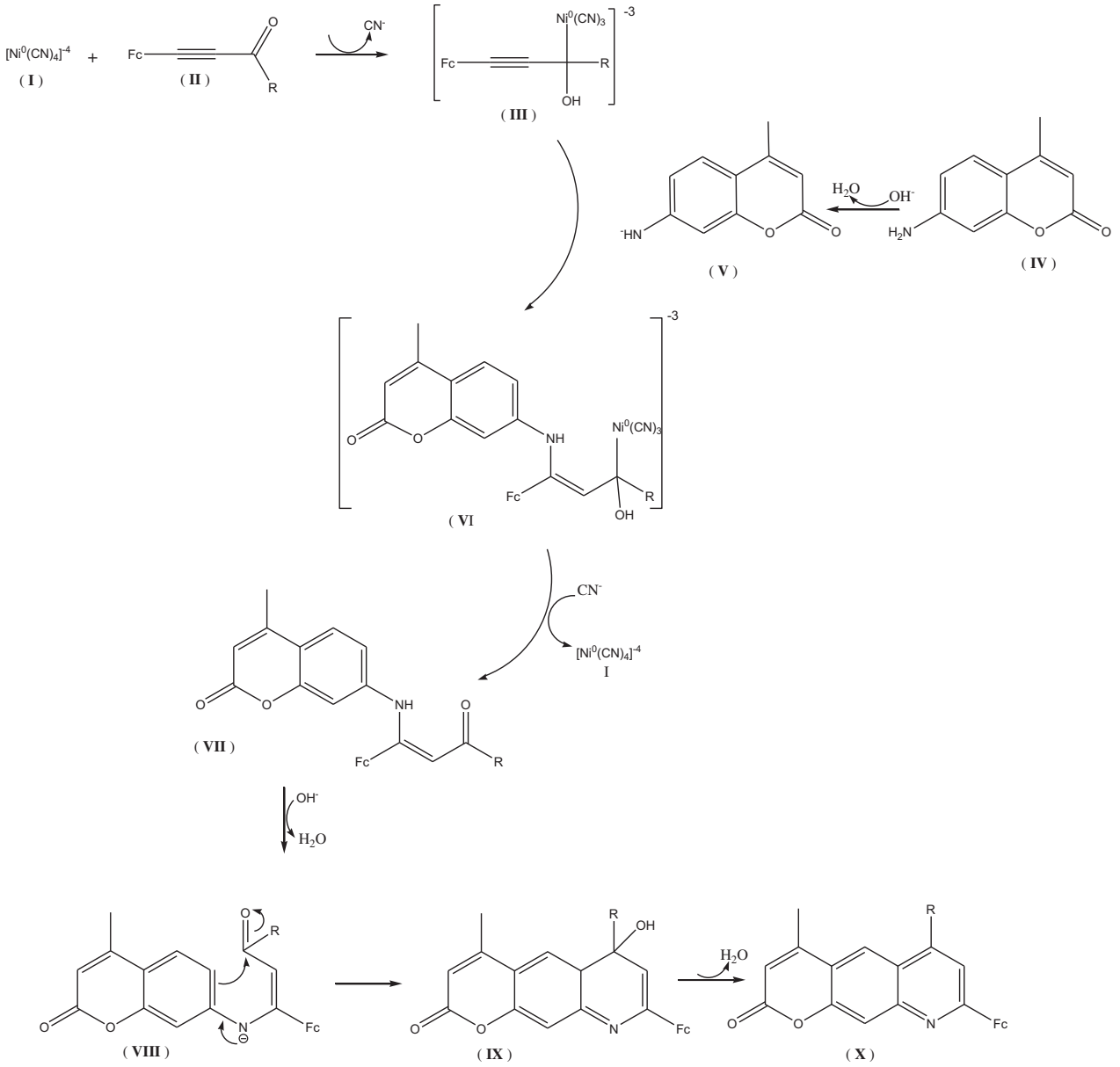
The product was obtained as described in the general procedure as a pink-red solid (6%); Empirical formula: $C_{30}H_{23}NO_2Fe$; mp. > 430 °C decomposition; IR (KBr, selected, cm^{-1}) 3417, 2924, 2854, 1731, 1622, 1588; Mass spectrum EI: m/z (%) = 485 (100) M$^+$, 420 (19) [M − cp]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.39 (s, 3H, C*H*$_3$C=C), 2.52 (s,3H, C*H*$_3$Ph), 4.09 (s, 5H, C_5H_5), 4.54 (t, 2H, C_5H_4, J = 1.9 Hz), 5.11 (t, 2H, C_5H_4, J = 1.9), 6.32 (s, 1H, C=C*H*–C=O–O), 7.42 (d, 2H, J = 7.9 Hz, 3,5-Ph), 7.45 (s, 1H, C=C*H*–C), 7.49 (d, 2H, J = 8.1 Hz, 2,6-Ph), 7.95 (s, 1H, OC=C*H*–CN), 8.09 (s, 1H, CH$_3$C–C=C*H*–C).

*3.2.7. 8-Ferrocenyl-6-(3,5-dimethoxyphenyl)-4-methyl-2H-pyrano[3,2-g]quinolin-2-one (**2b**)*

The product was obtained as described in the general procedure as a pink-red solid (10%); Empirical formula: $C_{31}H_{25}NO_4Fe$; mp. > 430 °C decomposition; IR (KBr, selected, cm^{-1}) 3346, 2923, 2854, 1724, 1587; Mass spectrum EI: m/z (%) = 532 (18), 531 (<5) M$^+$, 466 (<5) [M − cp]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.39 (s, 3H, C*H*$_3$C=C), 3.89 (s, 6H, OMe), 4.09 (s, 5H, C_5H_5), 4.55 (t, 2H, C_5H_4, J = 1.9 Hz), 5.11 (t, 2H, C_5H_4, J = 1.9 Hz), 6.32 (s, 1H, C=C*H*–C=O–O), 6.65 (t, 1H, 4-Ph), 6.69 (d, 2H, J = 2.3 Hz, 2,6-Ph), 7.47 (s, 1H, C=C*H*–C), 7.94 (s, 1H, OC=C*H*–CN), 8.12 (s, 1H, CH$_3$C–C=C*H*–C).

*3.2.8. 8-Ferrocenyl-4-methyl-6-m-tolyl-2H-pyrano[3,2-g]quinolin-2-one (**3b**)*

The product was obtained as described in the general procedure as a pink-red solid (12%); Empirical formula: $C_{30}H_{23}NO_2Fe$; mp. > 430 °C decomposition; IR (KBr, selected, cm^{-1}) 3417, 2924, 2854, 1731, 1622, 1588; Mass spectrum EI: m/z (%) = 485 (100) M$^+$, 420 (19) [M-cp]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.37 (s, 3H,



Scheme 2. Possible reaction pathway for ferrocenyl-heterocycles and ferrocenyl-β-enaminone-coumarins.

$CH_3C{=}C$), 2.51 (s,3H, CH_3Ph), 4.10 (s, 5H, C_5H_5), 4.54 (t, 2H, C_5H_4, $J = 1.9$ Hz), 5.12 (t, 2H, C_5H_4, $J = 1.9$), 6.32 (s, 1H, C═C*H*–C═O–O), 7.39 (s br, 2H, Ph), 7.46 (s, 1H, C═C*H*–C), 7.91 (s br, 2H, Ph), 7.95 (s, 1H, O–C═C*H*–CN), 8.06 (s, 1H, $CH_3C{-}C{=}CH{-}C$).

3.2.9. 8-Ferrocenyl-6-(4-ethylphenyl)-4-methyl-2H-pyrano[3,2-g] quinolin-2-one (**4b**)

The product was obtained as described in the general procedure as a pink-red solid (5%); Empirical formula: $C_{35}H_{25}NO_2Fe$; mp. > 430 °C decomposition; IR (KBr, selected, cm^{-1}) 3417, 2923, 2854, 1729, 1624, 1588; Mass spectrum EI: m/z (%) = 499 (100) $[M]^+$, 434(15) $[M - cp]^+$; ^1H NMR (300 MHz, $CDCl_3$, δ in ppm) 1.37 (t, 3H, $J = 7.6$ Hz, CH_3CH_2), 2.82 (*c*, 2H, $J = 7.6$ Hz, CH_3CH_2), 4.09 (s, 5H, C_5H_5), 4.54 (t, 2H, $J = 1.9$ Hz, C_5H_4), 5.11 (t, 2H, $J = 1.9$ Hz, C_5H_4), 6.31 (s, 1H, C═C**H**–C═O–O), 7.43 (s, 1H, C═C**H**–C), 7.46 (d, 2H, $J = 2.2$ Hz, 3,5-Ph), 7.50 (d, 2H, $J = 8.3$ Hz, 2,6-Ph), 7.95 (s,1H, OC═C**H**–CN), 8.10 (s, 1H, $CH_3C{-}C{=}CH{-}C$).

3.2.10. 8-Ferrocenyl-6-(4-bromophenyl)-4-methyl-2H-pyrano[3,2-g]quinolin-2-one (**5b**)

The product was obtained as described in the general procedure as a pink-red solid (8%); Empirical formula: $C_{29}H_{20}NO_2Fe$; mp. > 430 °C decomposition; IR (KBr, selected, cm^{-1}) 3417, 2923, 2854, 1729, 1624, 1588; Mass spectrum EI: m/z (%) = 551 (62) $[M+2]^+$, 549 (63) M^+, 484 (12) $[M - cp]^+$; ^1H NMR (300 MHz, $CDCl_3$, δ in ppm) 2.38 (s, 3H, $CH_3C{=}C$), 4.09 (s, 5H, C_5H_5), 4.55 (t, 2H, C_5H_4, $J = 1.9$ Hz), 5.11 (t, 2H, C_5H_4, $J = 1.9$ Hz), 6.33 (s, 1H, C═C*H*–C═O–O), 7.41 (s, 1H, C═C*H*–C), 7.46 (d, 2H, $J = 8.2$ Hz, Ph), 7.75 (d, 2H, $J = 8.4$ Hz, Ph), 7.95 (s,1H, OC═C*H*–CN), 7.97 (s, 1H, $CH_3C{-}C{=}CH{-}C$).

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Appendix A. Supplementary material

CCDC No. 846488 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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