



Original Research Article

Synthesis and Theoretical Studies of [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl] Ferrocene Derivatives

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ABSTRACT

In this study, syntheses of [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene derivatives from reaction of ferrocenecarboxaldehyde, ethyl cyanoacetate, aniline, and acetylenic esters in the presence of piperidine were reported in good yields. The reaction proceeded smoothly and cleanly under mild reaction conditions and no side reactions were observed. The structures of the products were confirmed by IR, ¹H NMR, ¹³C NMR, mass spectroscopy, and elemental analysis. Then, structure, electronic and spectroscopic properties of the synthesized molecules were computed at the CAM-B3LYP/jorge-DZP (H,C,N,O) and Def2-TZVPPD (Fe) level of theory. First hyperpolarizability value were calculated to describe the nonlinear optical (NLO) properties of these molecules. The HOMO-LUMO study to find the band gap of the prepared molecules was extended to calculate global hardness, chemical potential and global electrophilicity for the investigation of the chemical behavior of the compounds. The energies of iron *d*-orbitals and formal electron configurations of iron atom were calculated by natural bond orbital (NBO) analysis.

Keywords: Frontier orbitals; hyperpolarizability; ferrocenecarboxaldehyde; NBO analysis.

Introduction

The four-component reaction of amines, acetylenic esters, aromatic aldehydes, and ethyl cyanoacetate that causes the synthesis of 1,4-dihydropyridine derivatives under variate conditions has been reported in the literature [1-4]. Many methods and catalysts have been used for the synthesis of 1,4-dihydropyridines such as Sm/ZrO₂ [5], NEt₃ [6], KF/Al₂O₃ [7], NaOH [8], piperidine [9], *L*-proline,[10] cellulose-sulfuric acid [11], triphenylphosphine [12], iron (III) trifluoroacetate,[13] aluminium phosphate,[14] etc. which include the use of microwaves, ionic liquids, reflux at high temperature. 1,4-Dihydropyridines are a main group of compounds that have biological activities such as antiviral,[15] antioxidant,[16] anti-tumor [17], anti-inflammatory [18], antimicrobial,[19] antitubercular [20], antihistaminic [21], and anticancer activities [22]. In connection with our interest in the synthesis of ferrocene compounds,[23-25], the synthesis of [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene derivatives **5** by a four-component reaction of ferrocenecarboxaldehyde (**1**), ethyl cyanoacetate (**2**), aniline (**3**), and acetylenic esters **4** in the presence of piperidine, in high yields and fairly mild reaction conditions, is reported herein (Figure 1). For theoretical studying, we replaced substituents of 1,4-dihydropyridine with hydrogen atoms, and electronic parameters, vibrations, and hyperpolarizability of [1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene were explored.

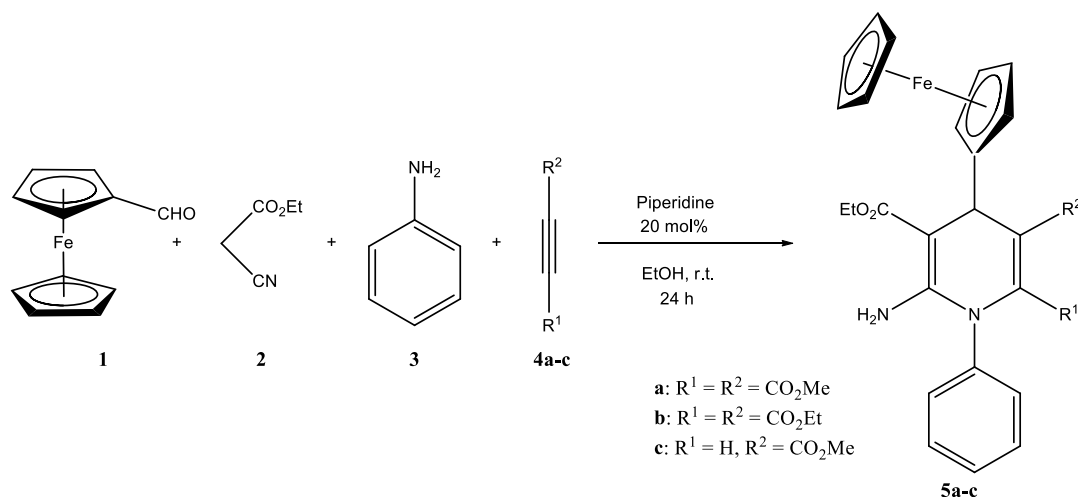


Figure 1. Four-component reaction of ferrocenecarboxaldehyde (**1**), ethyl cyanoacetate (**2**), aniline (**3**), and acetylenic esters **4a-c**.

Results and Discussion

A one-pot four-component reaction of ferrocenecarboxaldehyde (**1**), ethyl cyanoacetate (**2**), aniline (**3**), and acetylenic esters **4** in the presence of piperidine led to [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene derivatives **5** in high yields, under fairly mild reaction conditions (Figure 1 and Table 1). A mechanistic rationalization for this reaction is provided in Figure 2. The structures of the products **5** were deduced from their ^1H NMR, ^{13}C NMR, mass, IR spectra, and elemental analysis.

Table 1. Synthesis of [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene derivatives **5**.

Entry	R ¹	R ²	Product	Yield%
1	CO ₂ Me	CO ₂ Me	5a	87
2	CO ₂ Et	CO ₂ Et	5b	83
3	H	CO ₂ Me	5c	75

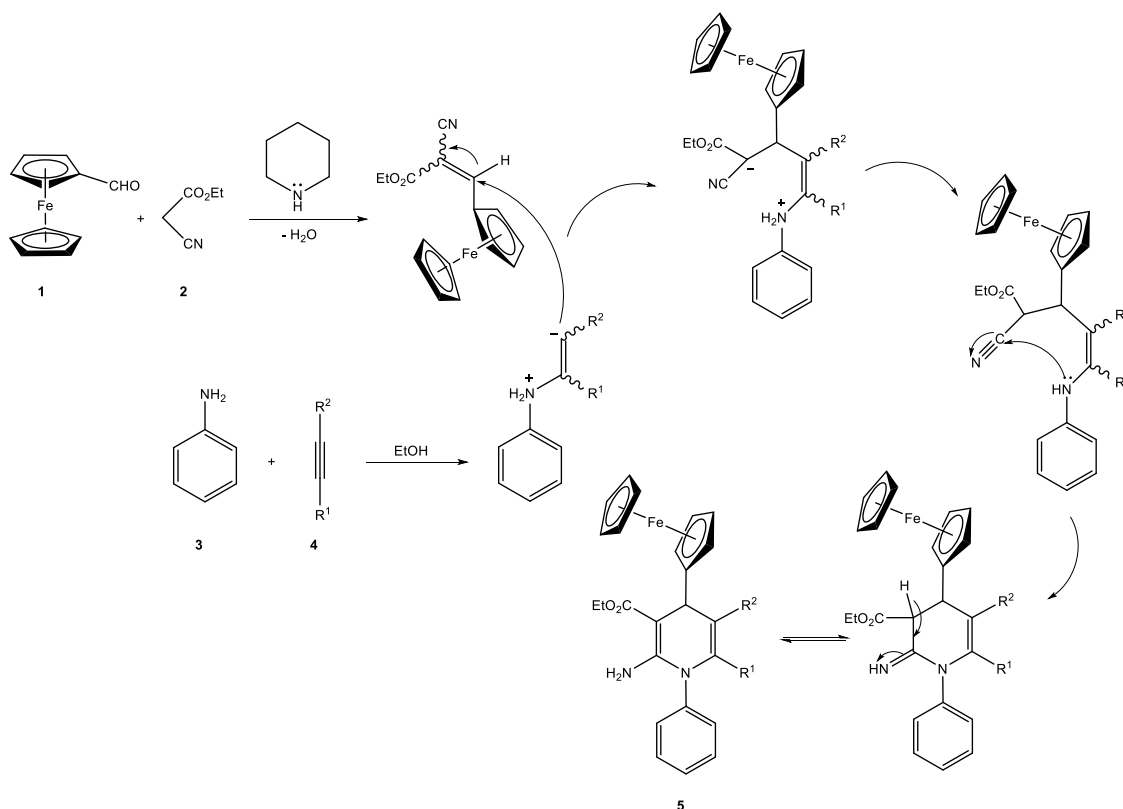


Figure 2. A proposed mechanism for the formation of **5a-c**.

The **5a-5c** structures are optimized at the CAM-B3LYP/jorge-DZP (H,C,N,O) and Def2-TZVPPD (Fe) level of theory. Absolute energy, zero point vibration energy, absolute thermodynamics parameters, molar capacity at constant volume, dipole moment of these complexes are gathered in Table 2.

Table 2. Absolute energy (a.u), dipole moment (μ , Debye), frontier orbital energies (HOMO and LUMO, eV), hardness (η , eV), chemical potential (μ , eV), electrophilicity (ω , eV) of the **5a**, **5b**, **5c** (ferrocene derivatives), **5a'**, **5b'** and **5c'** (non-ferrocene derivatives) molecules.

	E	μ	E(HOMO)	E(LUMO)	η	μ	ω
5a	-2907.9040804	7.9096	-6.92	-0.06	3.43	-3.49	1.78
5b	-2986.4953258	7.9261	-6.90	-0.03	3.43	-3.46	1.75
5c	-2680.0839727	8.0113	-6.91	0.03	3.47	-3.44	1.71
5a'	-1258.3986559	7.7358	-6.88	-0.19	3.35	-3.54	1.87
5b'	-1336.9903971	7.7151	-6.85	-0.16	3.34	-3.51	1.84
5c'	-1030.5772841	7.7914	-6.94	0.07	3.50	-3.43	1.68

The calculated dipole moment values of the synthesized molecules are tabulated in Table 2. These values show the **5c** complex has the most polarity in compared to **5a** and **5b** complexes. On the other hand, it can be seen the more polarity in ferrocene derivatives (**5a-5c**) in compared to non-ferrocene derivatives (**5a'-5c'**).

The calculated frontier orbital (FMO) energies (E(HOMO) and E(LUMO)), hardness (η), electrophilicity (ω), and chemical potential (μ) of the synthesized molecules are tabulated in Table 2 [26-28]. These values show the most stability of frontier orbitals and electrophilicity for **5a** molecule. Also, the most hardness and chemical potential values are belong to **5c** molecule. On the other hand, it can be observed the more stability of HOMO in ferrocene derivatives (**5a** and **5b**) in compared to non-ferrocene derivatives (**5a'** and **5b'**). In contrast, the stability of HOMO in **5c'** non-ferrocene derivative is more than **5c** ferrocene derivative.

Table 3. Isotropic and anisotropic polarizability values of the **5a**, **5b**, **5c** (ferrocene derivatives), **5a'**, **5b'** and **5c'** (non-ferrocene derivatives) molecules.

	α_{xx}	α_{yy}	α_{zz}	α_{iso}	α_{aniso}
5a	409.389	309.619	310.737	343.25	99.22

5b	430.942	339.074	330.976	367.00	96.17
5c	390.314	283.464	282.168	318.65	107.50
5a'	250.759	257.327	177.650	228.58	76.60
5b'	271.449	287.612	197.647	252.24	83.07
5c'	269.326	207.502	142.165	206.33	110.14

Polarizability defines the reply of a structure in an applied electric field. The polarizability values describe the strength of molecular interactions (like the long range intermolecular induction, dispersion forces, etc.), the cross sections of different scattering and collision processes, and the NLO properties of the system.

The isotropic polarizability $\langle\alpha\rangle$ is evaluated as the mean value as the subsequent equation:

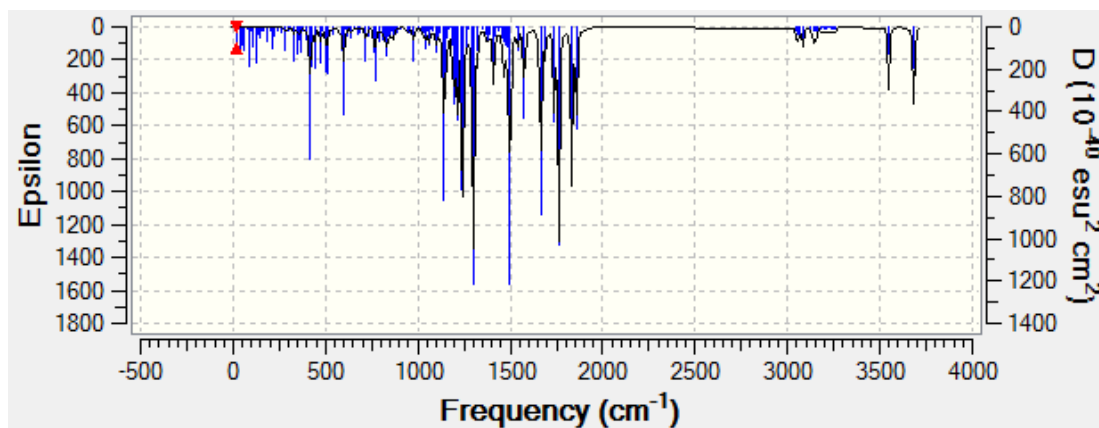
$$\langle\alpha\rangle = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3}$$

and the polarizability anisotropy is:

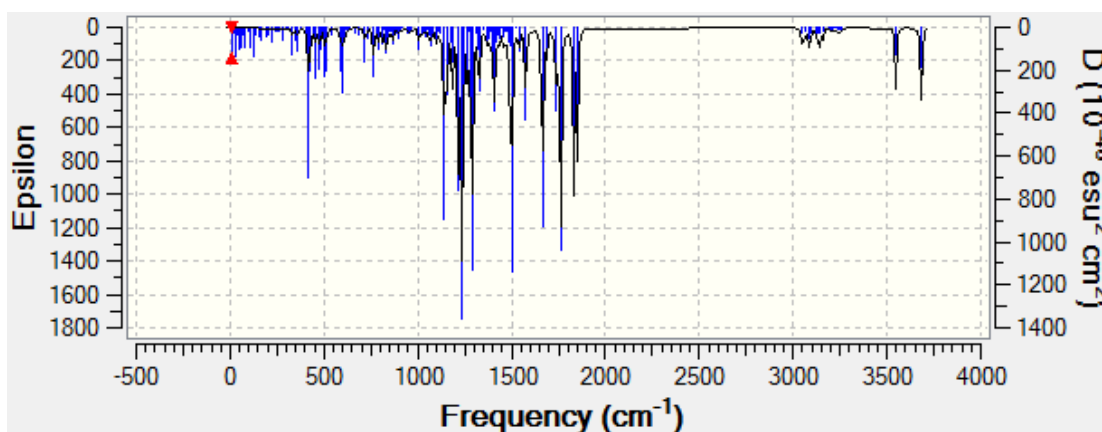
$$\Delta\alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2} \right]^{\frac{1}{2}}$$

The evaluated isotropic and anisotropic polarizability values of the synthesized complexes are listed in Table 3. The largest isotropic and anisotropic polarizability values are observed for **5b** and **5c**, respectively. It can be seen the larger isotropic polarizability values in ferrocene derivatives (**5a-5c**) in compared to non-ferrocene derivatives (**5a'-5c'**). On the other hand, the anisotropic polarizability values in ferrocene derivatives (**5b** and **5c**) are larger than non-ferrocene derivatives (**5b'** and **5c'**). The anisotropic polarizability value in **5a** ferrocene derivatives (**5b** and **5c**) are smaller than **5a'** non-ferrocene derivatives.

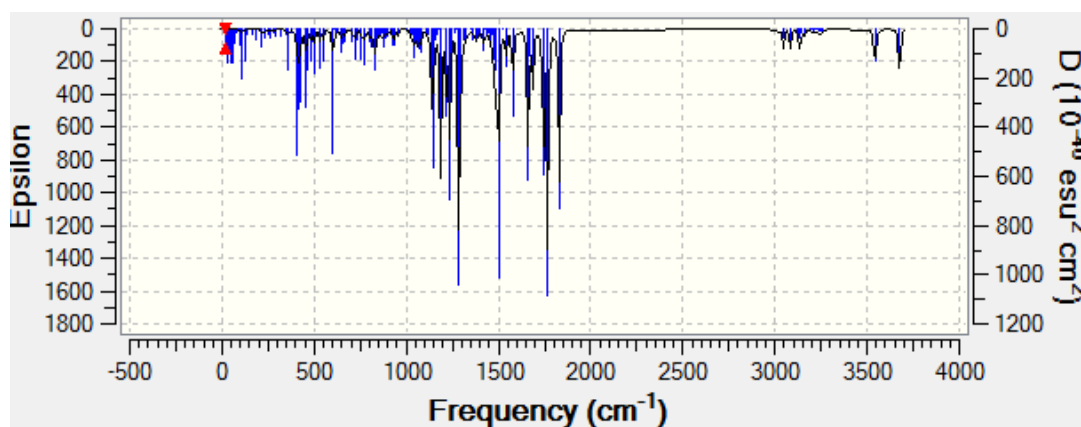
The calculated IR-spectrum of the synthesized complexes are presented in Figure 2. Vibrational analysis reveal that the most intensity vibrational of these complexes are 1499, 1762 and 1766 cm^{-1} for **5a**, **5b** and **5c** complexes, respectively. It can be observed, C=O stretching frequencies of COOEt group place at 1762 and 1766 cm^{-1} . H-N-C bending frequency of amino group places at 1499 cm^{-1} .



5a



5b



5c

Figure 3. Theoretical IR spectrum of the 5a, 5b and 5c complexes.

The calculated non-zero μ values display that the investigated complex might have microscopic first static hyperpolarizabilities with non-zero values found by the numerical second derivative of the electric dipole moment according to the applied field strength. A good relationship can be found between the calculated μ and β_{tot} values. Consequently, in our study, the μ values may be accountable for decreasing and enhancing the β_{tot} value. The molecular hyperpolarizability magnitude, existence of the chromophores number and the noncentrosymmetry grade for the second order susceptibility values would be the determining criteria in a NLO system.

The responses of NLO characteristics can be understood by investigation of the FMO calculations [29].

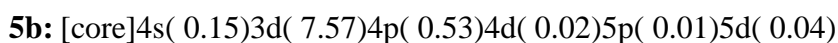
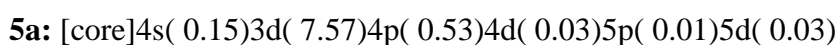
The calculated hyperpolarizability components, β , of complex are presented in Table 4.

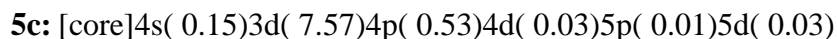
Table 4. hyperpolarizability components of the 5a, 5b, 5c (ferrocene derivatives), 5a', 5b' and 5c' (non-ferrocene derivatives) molecules.

	5a-H	5b-H	5c-H	5a	5b	5c
β_{xxx}	-704.46	-629.71	-122.87	204.79	206.22	584.40
β_{xxy}	57.67	-106.70	-645.85	294.45	236.49	162.82
β_{xyy}	308.49	266.66	202.25	-171.95	14.21	-385.49
β_{yyy}	42.16	111.24	482.98	-197.67	-349.24	59.12
β_{xxz}	41.60	13.54	149.16	19.37	124.37	-172.87
β_{xyz}	-4.75	37.35	-25.55	-147.24	-130.57	-31.02
β_{yyz}	73.51	51.23	21.40	190.49	18.39	257.83
β_{xzz}	15.65	21.04	20.25	-34.41	-167.74	12.51
β_{vzz}	6.17	39.25	-4.17	23.08	133.77	-73.51
β_{zzz}	64.66	119.01	22.49	20.25	92.51	8.78
$10^{30}\beta_{\text{tot}}$	3.748	3.376	2.368	2.242	2.091	2.374

One can see that β_{tot} values decrease in the ferrocene derivatives in compared to non-ferrocene derivatives. On the other hand, these value increase as 5b < 5a < 5c.

The formal electron configuration of Fe atom is [Ar]4s²3d⁶. However, the natural electron configuration of the atom in title complex is:





Comparing the formal and natural electron configurations showed that the 4s population decreased and 3d populations increased. Considering the donor–acceptor interactions, the lone-pair electrons of ligands must have been responsible for the larger population in the formal configuration.

The energies of iron *d*-orbitals in the studied complex are calculated from NBO (natural bond orbital) analysis. The energies of these orbitals are:

5a: $d_{xy} = -0.20587$; $d_{xz} = -0.20136$; $d_{yz} = -0.22931$; $d_{x^2-y^2} = -0.25192$; $d_{z^2} = -0.23677$ a.u

5b: $d_{xy} = -0.17536$; $d_{xz} = -0.22687$; $d_{yz} = -0.22656$; $d_{x^2-y^2} = -0.27401$; $d_{z^2} = -0.21894$

5c: $d_{xy} = -0.27474$; $d_{xz} = -0.18728$; $d_{yz} = -0.21819$; $d_{x^2-y^2} = -0.19042$; $d_{z^2} = -0.25498$;

Therefore, the splitting patterns of metal *d*-orbitals in the complexes are

5a: $d_{xz} > d_{xy} > d_{yz} > d_{z^2} > d_{x^2-y^2}$

5b: $d_{xy} > d_{z^2} > d_{yz} > d_{xz} > d_{x^2-y^2}$

5c: $d_{xz} > d_{x^2-y^2} > d_{yz} > d_{z^2} > d_{xy}$

Experimental

The starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The IR spectra were recorded on a Jasco FT-IR 6300 spectrometer. The ^1H NMR and ^{13}C NMR spectra were measured (CDCl_3 solution) with a Bruker DRX-400 Avance spectrometer at 400 and 100 MHz, respectively. The elemental analyses were realized using a Heraeus CHN-O-rapid analyzer. Mass spectra were recorded with an Agilent Technologies 5975C VL MSD mass spectrometer.

General Procedure for the Synthesis of 5a-c

A mixture of ferrocenecarboxaldehyde (**1**) (1.0 mmol), ethyl cyanoacetate (**2**) (1.0 mmol) and piperidine (20 mol%) was taken in a 50 mL RB flask containing 5 mL of ethanol. The resulting mixture was stirred at room temperature for about 10-15 min. To this, a 3 mL ethanolic solution of acetylenic ester **4** (1.0 mmol) and aniline (**3**) (1.0 mmol) was added slowly. Then the reaction mixture was allowed to stir at room temperature for 24 h. After the completion of the

reaction as monitored by TLC, the solvent was removed under reduced pressure and the viscous residue was purified by preparative TLC (silica gel, petroleum ether / ethyl acetate 8:2) to obtain product **5**. The characterization data of the compounds **5a-c** are given below.

[2-Amino-3-(ethoxycarbonyl)-1,4-dihydro-5,6-bis(methoxycarbonyl)-1-phenyl-4-pyridinyl]ferrocene (5a)

Purple solid; mp > 250 °C; yield: 87%; anal. calcd. for C₂₈H₂₈FeN₂O₆ (544.38): C, 61.78; H, 5.18; N, 5.15%; found: C, 61.86; H, 5.13; N, 5.08; IR (KBr, cm⁻¹): 3421 (NH), 2927, 1739 (C=O), 1707 (C=O), 1667 (C=O), 1599, 1440, 1370, 1279, 1249, 1090, 1024, 757; ¹H NMR (CDCl₃, 400.2 MHz): δ_H 1.32-1.41 (3H, m, CH₂CH₃), 3.67 and 3.72 (6H, two s, 2 x OCH₃), 4.26 (5H, s, ferrocene C₅H₅), 4.27-4.36 (2H, m, OCH₂), 4.72-5.02 (4H, two m, ferrocene C₅H₄), 5.39 (1H, s, H-4), 6.88-8.19 (5H, m, C₆H₅), 9.69 (2H, s, NH₂); ¹³C NMR (CDCl₃, 100.6 MHz): δ_C 14.2 (CH₂CH₃), 51.2 and 52.8 (2 x OCH₃), 62.1 (OCH₂), 62.9 (C-4), 70.6, 71.8, 74.2, and 93.5 (ferrocene), 97.2, 116.9, 120.6, 124.2, 129.2, 140.2, 148.0, and 158.7 (C-2,3,5,6 and C₆H₅), 163.2, 164.8, and 169.8 (3 x C=O); MS: *m/z* (%) (EI) 544 (M⁺, 1), 510 (8), 460 (10), 389 (100), 330 (20), 286 (7), 241 (10), 169 (9), 118 (8), and 77 (30).

[2-Amino-3,5,6-tris(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene(5b)

Purple solid; mp > 250 °C; yield: 83%; anal. calcd. for C₃₀H₃₂FeN₂O₆ (572.44): C, 62.95; H, 5.63; N, 4.89%; found: C, 62.90; H, 5.71; N, 4.82; IR (KBr, cm⁻¹): 3401 (NH), 2925, 1735 (C=O), 1703 (C=O), 1670 (C=O), 1601, 1444, 1372, 1276, 1245, 1088, 1021, 756; ¹H NMR (CDCl₃, 400.2 MHz): δ_H 1.05-1.55 (9H, m, 3 x CH₃), 4.05-5.51 (16H, m, 3 x OCH₂, H-4, and ferrocene 9 x CH), 6.96-8.23 (5H, m, C₆H₅), 9.72 (2H, s, NH₂); ¹³C NMR (CDCl₃, 100.6 MHz): δ_C 13.7, 14.2, and 14.4 (3 x CH₃), 60.0, 62.07, and 62.11 (3 x OCH₂), 63.2 (C-4), 70.6, 71.8, 74.1, and 93.8 (ferrocene), 97.2, 116.9, 121.0, 124.2, 129.1, 140.4, 148.4, and 158.8 (C-2,3,5,6 and C₆H₅), 163.3, 164.4, and 169.6 (3 x C=O).

[2-Amino-3-(ethoxycarbonyl)-1,4-dihydro-5-(methoxycarbonyl)-1-phenyl-4-pyridinyl]ferrocene (5c)

Purple solid; mp > 250 °C; yield: 75%; anal. calcd. for C₂₆H₂₆FeN₂O₄ (486.35): C, 64.21; H, 5.39; N, 5.76%; found: C, 64.12; H, 5.45; N, 5.70; IR (KBr, cm⁻¹): 3411 (NH), 2922, 1734 (C=O), 1706 (C=O), 1665 (C=O), 1596, 1438, 1369, 1278, 1247, 1087, 1020, 756; ¹H NMR

(CDCl₃, 400.2 MHz): δ_{H} 1.31-1.49 (3H, m, CH₂CH₃), 3.79 (3H, s, OCH₃), 4.18-5.18 (12H, m, OCH₂, H-4, and ferrocene 9 x CH), 7.15-8.21 (6H, m, C₆H₅ and H-6), 9.62 (2H, s, NH₂); ¹³C NMR (CDCl₃, 100.6 MHz): δ_{C} 14.2 (CH₂CH₃), 52.9 (OCH₃), 62.1 (OCH₂), 63.0 (C-4), 70.6, 71.9, 74.2, and 93.8 (ferrocene), 97.0, 113.2, 114.9, 116.8, 131.8, 142.2, 147.2, and 158.8 (C-2,3,5,6 and C₆H₅), 163.3 and 169.8 (2 x C=O).

Computational Methods

The quantum mechanics calculations were performed using the Gaussian 09 program [30]. While the main group elements were described by jorge-DZP basis set [31-34], the Fe element was considered using the standard Def2-TZVPPD basis set [31]. The geometries of the compound were optimized by the CAM-B3LYP functional. This functional is Handy and coworkers' long range corrected version of B3LYP using the Coulomb-attenuating method [35]. This functional has not been designed for this class of compounds, but it has been widely used these last years for several purposes, and it looks interesting to assess its efficiency in our context. The NLO (nonlinear optical) responses of the studied structure were realized by studying their frontier molecular orbitals (FMOs) [29]. Their total β_{tot} values were calculated using:

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$$

where

$$\beta_i = \frac{1}{3} \sum_{k=x,y,z} (\beta_{ikk} + \beta_{kik} + \beta_{kki}); i = x, y, z$$

The components of β are defined as the term coefficients appearing in the Taylor series expansion of the energy affected by an external electric field. The Taylor expansion holds through as the following equation, provided that the applied electric field is weak and homogeneous:

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2 \sum_{ij} \alpha_{ij} F^i F^j} - \frac{1}{6 \sum_{ijk} \beta_{ijk} F^i F^j F^k}$$

Here, E_0 represents energy of the unperturbed molecules, F^i is the field magnitude at the origin, and μ_i , α_{ij} and β_{ijk} refer to the dipole moment, polarizability and first hyperpolarizability components, respectively.

Conclusion

The reported method offers a mild, simple, and efficient route for the preparation of [2-amino-3-(ethoxycarbonyl)-1,4-dihydro-1-phenyl-4-pyridinyl]ferrocene derivatives **5** in high yields and fairly mild reaction conditions. [1,4-Dihydro-1-phenyl-4-pyridinyl]ferrocene was selected in theoretical studies, and structural geometrical parameters, vibrational, FMOs, hyperpolarizability of the molecule were performed on the basis of M062X method. NBO analysis revealed the splitting pattern of metal d-orbitals in the complex as: $dx^2-y^2 > dyz > dxz > dxy > dz^2$.

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