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N-ferrocenoyl benzotriazole: A convenient tool for the synthesis of ferrocenoyl esters

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ABSTRACT

A new synthesis methodology has been presented for the preparation of the ferrocenoyl esters. Ferrocene carboxylic acid was derivatized using direct 1*H*-benzotriazole/$SOCl_2$ methodology to prepare *N*-ferrocenoyl benzotriazole as a convenient tool for the functionalization of ferrocene ring. *N*-ferrocenoyl benzotriazole was reacted with alcohols in mild conditions to prepare ferrocenoyl esters in high purity and in good yield. The solid state structure of benzyl-1-ferrocenoate, **2f**, has also been determined by X-ray crystallography. In the crystal structure, intermolecular C–H···O hydrogen bonds link the molecules into a two-dimensional network. The π···π contacts between the cyclopentadiene rings and cyclopentadiene and phenyl rings, [centroid–centroid distances = 3.296(1) and 3.750(1) Å] may further stabilize the structure. Two weak C–H···π interactions are also found.

1. Introduction

Ferrocene chemistry and its applications have been studied to a considerable degree since it was first prepared unintentionally and characterized. Current areas of concern in ferrocene chemistry contain the preparation of ferrocene based catalyst [1], sensors [2] and immunoassay reagents [3–10].

Ferrocene has a rich chemistry by virtue of capability for the preparation of a large number of derivatives. Ferrocenoyl esters have extensive applications. Ferrocenoyl esters were synthesized as a ferrocenyl carbohydrate conjugates and their biological activities have been investigated [11]. Additionally, ferrocenoyl esters have been obtained as a product in the reactions of ferrocene with solvent radicals under arylation conditions [12]. Ferrocenoyl esters are used as a substrate in photochemical rearrangement [13], as a Cp donor in the double ligand-transfer reaction [14]. A general intermediate for the synthesis of these kind of systems is ferrocenoylchloride. It is known that to obtain chlorocarbonyl ferrocene is fairly hard. Formation of this compound from the corresponding acids is capricious and can result in low yields [15].

In our previous literature we have used 1*H*-benzotriazole/$SOCl_2$ methodology for the preparation of novel *N*-ferrocenyl benzotriazole **1** as starting material for the derivatisation of ferrocenoyl group [16] following the Katritzky's methodology [17] (Scheme 1).

2. Results and discussion

All spectroscopic data collected for the starting material **1** was in agreement with literature [16]. Starting material **1** was treated with an equimolar amount of alcohol in THF at room temperature for 15 min. to give the corresponding ferrocenoyl esters **2a–l**. The ^{1}H NMR spectra of the products show no signals corresponding to these assigned to the *N*-substituted benzotriazole groups of starting material **1** (between 7.5 and 8.5 ppm two doublet and two triplet.). The ^{13}C NMR spectra of these compounds also no longer show signals for a *N*-substituted benzotriazole group (chemical shifts around 120 and 146 ppm). Ferrocenoyl ester products show characteristic mono substituted ferrocene peaks around 4.0–5.0 ppm in ^{1}H NMR and 69–75 ppm in ^{13}C NMR. No significant shift was observed for the carbonyl carbon (around 170 ppm) during the transformation from starting material **1** to products **2a–l**. The products list was given in Table 1 with overall yields.

2.1. X-ray structure of *2f*

The X-ray structural determination of compound **2f** confirms the assignment of its structure from spectroscopic data. The molecular structure of compound **2f** along with the atom-numbering scheme is depicted in Fig. 1, in which the bond lengths and angles are within normal ranges.

Rings A (C1–C5), B (C6–C10) and C (C13–C18) are, of course, planar. The dihedral angles between the rings are A/B = 1.90(7)°, A/C = 88.07(5)° and B/C = 88.48(6)°. The (O1/O2/C9/C11/C12) moiety is nearly planar [with a maximum deviation of 0.1113(17) Å for

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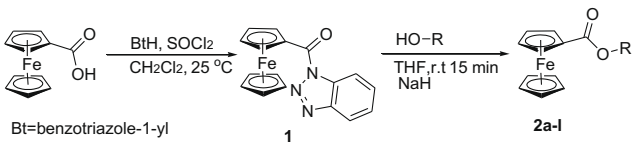


Scheme 1. Preparation of ferrocenoyl esters.

atom C12] and it is oriented with respect to rings A, B and C at dihedral angles of 20.05(7)°, 18.34(7)° and 79.97(5)°, respectively.

In the crystal structure, intermolecular C–H···O hydrogen bonds (Table 4) link the molecules into a two-dimensional network, in which they may be effective in the stabilization of the structure. The π···π contacts between the cyclopentadiene rings and cyclopentadiene and phenyl rings, Cg1···Cg2 and Cg1···Cg3^{i} [symmetry code: (i) 1−*x*, −*y*, 1−*z*, where Cg1, Cg2 and Cg3 are centroids of the rings A (C1–C5), B (C6–C10) and C (C13–C18), respectively] may further stabilize the structure, with centroid–centroid distances of 3.296(1) and 3.750(1) Å, respectively. Two weak C–H···π interactions (Table 4) are also found.

3. Experimental

3.1. General

THF was used freshly after distillation with sodium in presence of benzophenone. Column chromatography was conducted with silica gel 200–425 mesh. Melting points were determined on a hot-stage apparatus and were uncorrected. NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard for ^{1}H (500 MHz) or a solvent as the internal standard for ^{13}C (125 MHz) using Bruker NMR equipment.

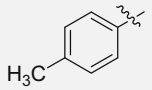
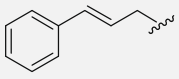
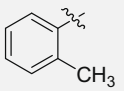
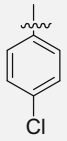
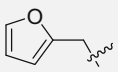
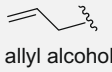
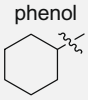
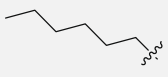
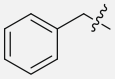
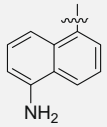
3.2. X-ray crystallography

Orange crystals of compound **2f** were crystallized from ethyl acetate/hexane mixture at room temperature. The selected bond lengths and angles are given in Table 2, crystallographic data are listed in Table 3 and the hydrogen bond data are given in Table 4. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at $T = 100(2)$ K. Absorption correction by multi-scan [18] was applied. Structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data [19]. All non-H atoms were refined anisotropically. H atom positions were calculated geometrically at distances of 0.93 Å (CH) and 0.97 Å (CH_2) from parent C atoms; a riding model was used during the refinement process and the U_{iso}(H) values were constrained to be 1.2 U_{eq} (carrier atom).

3.3. General procedure for the preparation of ferrocenoyl esters

To a solution of an appropriate alcohol (1 eq) in freshly distilled THF in the presence of NaH in a round bottom flask, solution of FcCOBt, **1**, (1 eq), solved in THF, was added dropwise under nitrogen atmosphere and the reaction mixture was stirred at 25 °C for 30 min. After the solvent was evaporated under vacuum, the reaction mixture was added ethylacetate, washed with 20% water solution of Na_2CO_3 to remove free 1*H*-benzotriazole (Bt-H). The collected organic layers were dried over $MgSO_4$. After evaporation of the solvent, crude product purified via column chromatography using ethyl acetate:hexanes (1:5) mixture as eluent. Solvent was evaporated under vacuum to obtain ferrocenoyl esters in good yields. Only compound **2f** was recrystallized in ethyl acetate:hexanes (1:5) mixture for X-ray analysis.

Table 1
Alcohols for the preparation of ferrocenylesters

Entry	Product	R	Yield (%)	Entry	Product	R	Yield (%)
1	**2a**	 *p*-cresol	82	7	**2g**	 cinnamyl alcohol	38
2	**2b**	 *o*-cresol	70	8	**2h**	 4-chlorophenol	83
3	**2c**	 furfuryl alcohol	79	9	**2i**	 allyl alcohol	55
4	**2d**	 phenol	75	10	**2j**	 propargyl alcohol	80
5	**2e**	 cyclohexanol	87	11	**2k**	 hexan-1-ol	43
6	**2f**	 benzyl alcohol	85	12	**2l**	 5-amino,1-naphthol	30

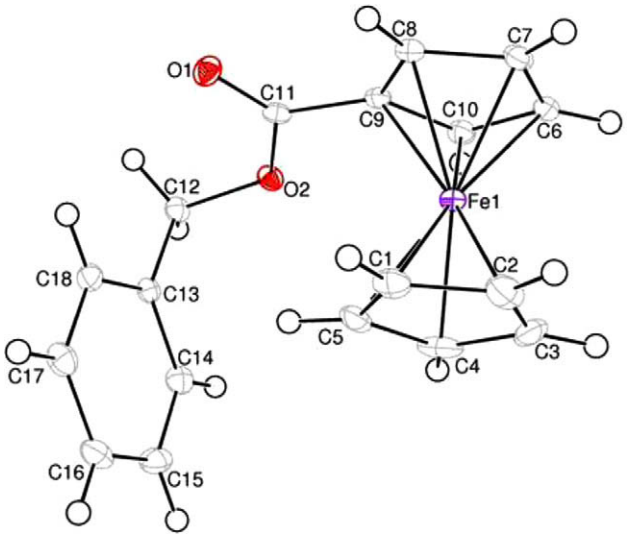


Fig. 1. The molecular structure of **2f**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 3
Crystallographic data for **2f**.

Empirical formula	$C_{18}H_{16}FeO_2$
Formula weight	320.17
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	5.8534(1)
b (Å)	26.2786(5)
c (Å)	8.9849(2)
α (°)	90.00
β (°)	91.845(1)
γ (°)	90.00
V (Å^3)	1381.33(5)
Z	4
μ (cm^{-1})	1.092
ρ (calcd) (g cm^{-1})	1.54
Number of reflections collected	12 704
Number of reflections total	3381
Number of reflections unique	2762
R_{int}	0.035
$2\theta_{max}$ (°)	56.62
T_{min}/T_{max}	0.617/0.853
Number of parameters	190
R [$F^2 > 2\sigma(F^2)$]	0.0314
wR	0.0666

1-(Ferrocenylcarbonyl)-1H-benzotriazole, ***1***, (dark-red needles, 79%), m.p. 152–154 °C. ^{1}HNMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.42 (d, $^3J_{H,H}$ = 8.36 Hz, 1H, *Bt-ring*), 8.18 (d, $^3J_{H,H}$ = 8.22 Hz, 1H, *Bt-ring*), 7.70 (t, $^3J_{H,H}$ = 7.67 Hz, 1H, *Bt-ring*), 7.55 (t, $^3J_{H,H}$ = 7.67 Hz, 1H, *Bt-ring*), 5.60 (t, $^{3,4}J_{H,H}$ = 1.57 Hz, 2H, *subst. Cp ring*), 4.78 (t, $^3J_{H,H}$ = 1.57 Hz, 2H, *subst. Cp ring*), 4.26 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.4, 145.5, 132.2, 130.1, 125.9, 120.0, 115.0, 73.5, 73.1, 71.0, 70.5 ppm.

Elemental Anal. Calc. for $C_{17}H_{13}FeN_3O$: C, 61.66; H, 3.96; N, 12.69. Found: C, 61.43; H, 3.87; N, 12.72%.

(4-Methylphenyl)-1-ferrocenoate, ***2a***, (brown microcrystals, 82%). m.p. 90–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.24 (d, $^3J_{H,H}$ = 8.20 Hz, 2H, *Ph ring*), 7.09 (d, $^3J_{H,H}$ = 8.51 Hz, 2H, *Ph ring*), 4.99 (t,$^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.52 (t,,$^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.33 (s, 5H, *Cp ring*), 2.40 (s, 3H, Ph-C*H*$_3$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.5, 148.7, 135.2, 129.9, 121.4, 71.9, 70.6, 70.3, 69.9, 21.0 ppm.

Elemental Anal. Calc. for $C_{18}H_{16}FeO_2$: C, 67.53; H, 5.04. Found: C, 67.91; H, 5.17%.

(2-Methylphenyl)-1-ferrocenoate, ***2b***, (orange microcrystals, 70%). m.p. 106–109 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.29 (t, $^3J_{H,H}$ = 7.88 Hz, 1H, *Ph ring*), 7.27 (d, $^3J_{H,H}$ = 7.57 Hz, 1H, *Ph ring*), 7.19 (t, $^3J_{H,H}$ = 7.25 Hz, 1H, *Ph ring*), 7.14 (d, $^3J_{H,H}$ = 7.88 Hz, 1H, *Ph ring*), 5.01 (t,$^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.53 (t,,$^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.34 (s, 5H, *Cp ring*), 2.32 (s, 3H, Ph-C*H*$_3$) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.0, 149.6, 131.1, 130.2, 126.9, 125.7, 122.1, 71.8, 70.6, 70.5, 69.8, 16.3 ppm.

Elemental Anal. Calc. for $C_{18}H_{16}FeO_2$: C, 67.53; H, 5.04. Found: C, 67.73; H, 5.34%.

Furfuryl-1-ferrocenoate, ***2c***, (orange microcrystals, 79%). m.p. 87–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, $^3J_{H,H}$ = 1.37 Hz, 1H, *furan ring*), 6.52 (d, $^3J_{H,H}$ = 3.15 Hz, 1H, *furan ring*), 6.42 (dd, $^3J_{H,H}$ = 3.15 Hz, 1.89 Hz, 1H, *furan ring*), 5.25 (s, 2H, –C*H*$_2$–O–), 4.84 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.41 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.13 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 171.2, 150.0, 143.1, 110.7, 71.6, 70.3, 69.8, 69.7, 57.5, 29.7 ppm.

Elemental Anal. Calc. for $C_{16}H_{14}FeO_3$: C, 61.97; H, 4.55. Found: C, 61.74; H, 4.27%.

Phenyl-1-ferrocenoate, ***2d***, (red microcrystals, 75%). m.p. 119–122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.46 (t, $^3J_{H,H}$ = 7.57 Hz, 2H, *Ph ring*), 7.29 (t, $^3J_{H,H}$ = 7.57 Hz, 1H, *Ph ring*), 7.21 (d, $^3J_{H,H}$ = 7.57 Hz, 1H, *Ph ring*), 5.00 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.53 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.34 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.4, 160.0, 129.5, 125.7, 121.9, 72.0, 70.7, 70.2, 70.0 ppm.

Elemental Anal. Calc. for $C_{17}H_{14}FeO_2$: C, 66.70; H, 4.61. Found: C, 66.38; H, 4.96%.

Cyclohexyl-1-ferrocenoate, ***2e***, (brown microcrystals, 87%). m.p. 67–70 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.97 (m, 1H, –C*H*–O–), 4.84 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*),4.40 (d, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.22 (s, 5H, *Cp ring*), 1.94 (m, 2H, *cyclohexyl ring*), 1.81 (m, 2H, *cyclohexyl ring*), 1.58 (m, 2H, *cyclohexyl ring*), 1.47 (m, 2H, *cyclohexyl ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 171.0, 128.6, 71.9, 71.1, 70.1, 69.7, 31.9, 29.7, 25.6, 23.7 ppm.

Elemental Anal. Calc for $C_{17}H_{20}FeO_2$: C, 65.40; H, 6.46. Found: C, 65.18; H, 6.85%.

Benzyl-1-ferrocenoate, ***2f***, (orange microcrystals, 85%). m.p. 88–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.50 (d, $^3J_{H,H}$ = 7.12 Hz, 2H, *Ph ring*), 7.44–7.39 (m, 3H, *Ph ring*), 4.87 (s, 2H, PhC*H*$_2$–), 4.73(s, 2H, *subst. Cp ring*), 4.43 (s, 2H, *subst. Cp ring*), 4.14 (s, 5H, *Cp ring*) ppm.

Table 2
Selected bond lengths (Å) and angles (°) for **2f**.

Fe1–C1	2.0546(18)	Fe1–C6	2.0500(17)	C9–C11	1.468(2)
Fe1–C2	2.0488(19)	Fe1–C7	2.0489(17)	C11–O1	1.211(2)
Fe1–C3	2.0383(19)	Fe1–C8	2.0436(17)	C11–O2	1.349(2)
Fe1–C4	2.0330(18)	Fe1–C9	2.0327(17)	C12–O2	1.471(2)
Fe1–C5	2.0471(17)	Fe1–C10	2.0371(17)	C12–C13	1.503(2)
O1–C11–O2	123.80(16)	C9–C11–O2	112.34(14)	O2–C12–C13	109.02(14)
C9–C11–O1	123.85(16)	C11–O2–C12	115.97(13)		

Table 4
Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
C12–H12A···O1^{i}	0.97	2.49	3.333(2)	145
C14–H14···O1^{i}	0.93	2.56	3.362(2)	145
C3–H3···Cg2^{ii}	0.93	2.82	3.717(2)	164
C5–H5···Cg3	0.93	2.63	3.536(2)	166

Symmetry codes: (i) $x-1, y, z$ (ii) $x-3/2, -y-1/2, z-3/2$.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 171.6, 141.0, 136.7, 128.7, 128.4, 127.0, 71.5, 70.3, 69.8, 65.9 ppm.

Elemental Anal. Calc. for $C_{18}H_{16}FeO_2$: C, 67.53; H, 5.04. Found: C, 67.83; H, 5.36%.

Cinnamyl-1-ferrocenoate, ***2g***, (orange microcrystals, 38%). m.p. 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $^3J_{H,H}$ = 7.57 Hz, 2H, *Ph ring*), 7.37 (t, $^3J_{H,H}$ = 7.25 Hz, 1H, *Ph ring*), 7.29 (t, $^3J_{H,H}$ = 7.25 Hz, 2H, *Ph ring*), 6.77 (d, $^3J_{H,H}$ = 15.76 Hz, 1H, Ph–C*H*=CH–), 6.42 (dt, $^3J_{H,H}$ = 6.31 Hz, 15.76 Hz, 2H, Ph–CH=C*H*–), 4.92 (d, $^3J_{H,H}$ = 6,32 Hz, 2H, CH=CH–CH_2–O–), 4.88 (t, $^3J_{H,H}$ = 1.58 Hz, 2H, *subst. Cp ring*), 4.44 (t, $^3J_{H,H}$ = 1.58 Hz, 2H, *subst. Cp ring*), 4,24 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ = 171.5, 136.4, 133.9, 128.7, 128.0, 126.6, 123.8, 71.4, 71.1, 70.2, 69.8, 64.7 ppm.

Elemental Anal. Calc. for $C_{20}H_{18}FeO_2$: C, 69.39; H, 5.24. Found: C, 69.21; H, 5.57%.

(4-Chlorophenyl)-1-ferrocenoate, ***2h***, (brown microcrystals, 83%). m.p. 98.3–101.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.41 (d, $^3J_{H,H}$ = 8.83 Hz, 2H, *Ph ring*), 7.15 (d, $^3J_{H,H}$ = 8.83 Hz, 2H, *Ph ring*), 4.98 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.54 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.33 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.2, 149.4, 131.1, 129.4, 123.2, 72.2, 70.7, 70.0, 69.8 ppm.

Elemental Anal. Calc. for $C_{17}H_{13}ClFeO_2$: C, 59.95; H, 3.85. Found: C, 61.21; H, 3.67%.

Allyl-1-ferrocenoate, ***2i***, (red microcrystals, 55%). m.p. 36–38 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.05 (m, 1H, CH_2=C*H*–CH_2–), 5.44 (d, $^3J_{H,H}$ = 17.34 Hz, 1H, CH_2=CH–CH_2–), 5.31 (d, $^3J_{H,H}$ = 10.40 Hz, 1H, CH_2=CH–CH_2–), 4.86 (s, 2H, *subst. Cp ring*), 4.75 (d, $^3J_{H,H}$ = 5.67 Hz, 2H, CH_2=CH–CH_2–O–), 4.43 (s, 2H, *subst. Cp ring*), 4.23 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 171.5, 132.9, 118.0, 117.8, 71.5, 71.1, 70.0, 65.0 ppm.

Elemental Anal. Calc. for $C_{14}H_{14}FeO_2$: C, 62.25; H, 5.22. Found: C, 62.20; H, 5.37%.

2-Propynyl-1-ferrocenoate, ***2j***, (red microcrystals, 80%). m.p. 86–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.88 (s, 2H, –CH_2–O–), 4.84 (s, 2H, *subst. Cp ring*), 4.45 (s, 2H, *subst. Cp ring*), 4.27 (s, 5H, *Cp ring*), 2.53 (s, 1H, *H*C≡C–) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ = 171.1, 78.8, 74.5, 71.8, 71.3, 70.3, 69.8, 51.7 ppm.

Elemental Anal. Calc. for $C_{14}H_{12}FeO_2$: C, 62.72; H, 4.51. Found: C, 62.54; H, 4.27%.

Hexyl-1-ferrocenoate, ***2k***, (orange microcrystals, 43%). m.p. 82–84 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.83 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.41 (t, $^3J_{H,H}$ = 1.89 Hz, 2H, *subst. Cp ring*), 4.24 (t, $^3J_{H,H}$ = 6.62 Hz, 2H, CH_3–$(CH_2)_4$–CH_2–O–), 4.20 (s, 5H, *Cp ring*), 1.75 (p, $^3J_{H,H}$ = 6.63, 7.45 Hz, 2H, (–CH_2–CH_2–O–), 1.47 (m, 2H), 1.39 (m, 2H), 1.28 (m, 2H), 0.95 (t, $^3J_{H,H}$ = 6.94 Hz, 3H, CH_3–$(CH_2)_4$–) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ = 171.8, 71.6, 71.2, 70.1, 69.7, 64.3, 31.5, 28.9, 25.8, 22.6, 14.0 ppm.

Elemental Anal. Calc. for $C_{17}H_{22}FeO_2$: C, 64.98; H, 7.06. Found: C, 70.24; H, 7.41%.

(5-Amino,1-nafthyl)-1-ferrocenoate, ***2l***, (orange microcrystals, 30%). m.p. 153–155 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.76 (d, $^3J_{H,H}$ = 8.51 Hz, 1H, *Ph ring*), 7.66 (d, $^3J_{H,H}$ = 8.51 Hz, 1H, *Ph ring*), 7.58 (d, $^3J_{H,H}$ = 8.51 Hz, 1H, *Ph ring*), 7.50 (t, $^3J_{H,H}$ = 7.88 Hz, 1H, *Ph ring*), 7.41 (d, $^3J_{H,H}$ = 8.51 Hz, 1H, *Ph ring*), 7.38 (d, $^3J_{H,H}$ = 7.88 Hz, 1H, *Ph ring*), 6.84 (s, 2H, –NH_2), 5.11 (s, 2H, *subst. Cp ring*), 4.58 (s, 2H, *subst. Cp ring*), 4.39 (s, 5H, *Cp ring*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 170.4, 142.4, 142.2, 126.9, 124.2, 118.7, 118.3, 112.0, 110.2, 113.5, 109.0, 72.0, 70.7, 70.3, 70.0 ppm.

Elemental Anal. Calc. for $C_{21}H_{17}NFeO_2$: C, 67.95; H, 4.62; N, 3.77. Found: C, 67.73; H, 4.37; N, 3.84%.

4. Conclusion

In this work, we prepared ferrocene esters by using *N*-ferrocenoyl benzotriazole which was reacted with alcohols under mild conditions and obtained ferrocenoyl esters in high purity and in good yields. In addition, it is easy to monitor the progress of the reaction and the reaction time is quite short.

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Appendix A. Supplementary material

CCDC 749578 contains the supplementary crystallographic data for compound **2f**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.015.

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