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Friedel–Crafts acylation of ferrocene with alkynoic acids

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ABSTRACT

Ferrocene reacts with alkynoic acids (conjugated or nonconjugated terminal), trifluoroacetic anhydride and triflic acid (or boron trifluoride etherate) to afford the corresponding ferrocenyl ynones in good yields. Only in the case of propynoic- and 3-butynoic acid complex, untreatable reaction mixtures were obtained. However, propynoilferrocene was obtained by desilylation of (trimethylsilyl)propynoilferrocene with KF/18-crown-6. Reaction with nonconjugated terminal alkynoic acids, carried out in the presence of a large excess of triflic acid (4 equiv.) results in formation of complex mixtures of products (in the reaction with 4-pentynoic acid enol triflate of ferrocenyl 1,4-diketone and 2-ferrocenyl-5-methylfuran were isolated). Ferrocenyl ynones obtained in this work can be used for synthesis of more complex ferrocenyl systems by "click" chemistry.

1. Introduction

Friedel–Crafts acylation of arenes is one of the most important C–C bond forming reactions of electron-rich aromatic compounds [1,2]. It also plays a very important role in the ferrocene chemistry enabling an easy access to monoacyl- and 1,1′-diacylferrocenes, transformable into *plethora* of other derivatives via classical functional group transformations [3–8]. Numerous ferrocene derivatives prepared in this way found applications as ligands in homogenous catalysis, in material science (e.g. in nonlinear optics) and in bioorganometallic chemistry as redox-active probes or candidates for drugs [9,10].

In most cases saturated aliphatic or aromatic acid halides or anhydrides in the presence of a Lewis or Brønsted acid have been used as acylating agents. There are also a few reports on the use of alkenoic acids halides to obtain alkenoyl ferrocenes [11–14]. Generally, these reactions are more difficult to perform because of side reactions (e.g. cyclization to ferrocenophanones). To the best of our knowledge, there is only one example of the Friedel–Crafts reaction of ferrocene with an *alkynoic* acid derivative. Crawford and Watts reported that reaction of ferrocene with phenylpropiolic acid chloride and $AlCl_3$ yields the corresponding ynone in 41% yield [15].

Recently, we developed a mild and efficient method of acylation of ferrocene with saturated aliphatic and aromatic carboxylic acids and trifluoroacetic anhydride (TFAA) in the presence of trifluoromethanesulfonic acid (TfOH) [16]. A similar system (carboxylic acid/TFAA/H_3PO_4) has been employed for acylation of purely organic substrates [17,18] but it failed in the case of ferrocene [17].

We thought that it would be interesting to look whether our system can be applied for acylation of ferrocene with unsaturated acids, especially with alkynoic acids. This reaction would open a direct route to practically unexplored class of ferrocenyl ynones, which are expected to be versatile starting materials, e.g. in syntheses of ferrocenyl-substituted heterocycles [19] or for the azide–alkyne "click" chemistry [20] (numerous synthetic applications of organic ynones have been reported [21–25]).

Herein, we report that ferrocene can be efficiently acylated, under mild conditions, with alkynoic acids and TFAA in the presence of a strong Brønstedt (TfOH) or Lewis (BF_3) acid.

In our first attempts, we added ferrocene (1 mmol) and TfOH (1.1 mmol or 4 mmol) or $BF_3 \cdot Et_2O$ (4 mmol) to solutions of conjugated acetylenic acids **1a–e** (1.1 mmol) and TFAA (1.1 mmol) in dichloromethane stirred previously for 1 min at rt and continued the stirring for 2 h. Pleasingly, the workup afforded the corresponding ferrocenyl ynones **2a–e** in good yields (Scheme 1 and Table 1).

Compounds **2a–c,e** were characterized by spectroscopic methods and gave correct elemental analyses. Compound **2d** displayed spectroscopic data identical with those reported in the literature [15].

It is seen from Table 1 that acylating systems based on TfOH are more efficient than that using $BF_3 \cdot Et_2O$. The yields of **2a–e** are satisfactory for reactions carried out in the presence of 1.1 equiv. of TfOH and the increase of amount of this acid to 4 equiv. only leads to a slight increase of the yields.

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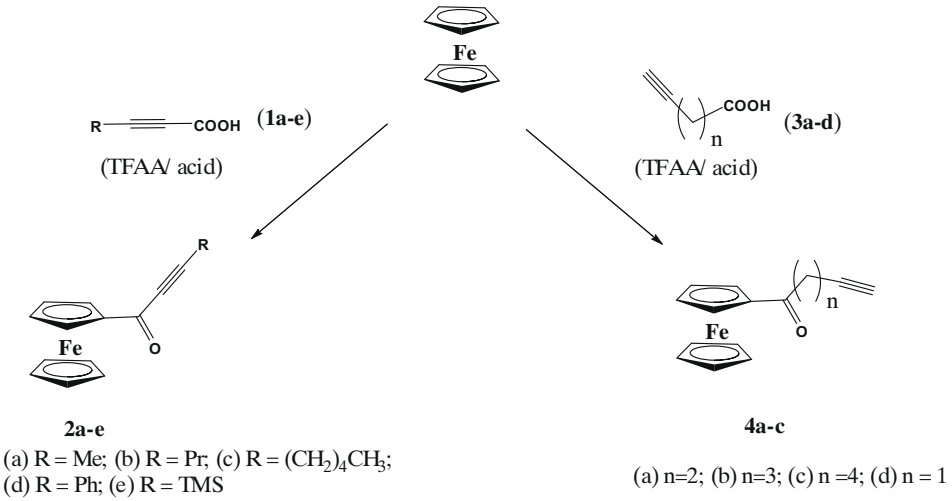
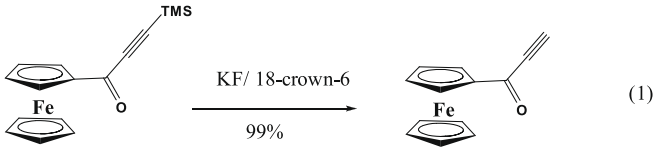


Scheme 1. Acylation of ferrocene with alkynoic acids (acid = TfOH or $BF_3 \cdot Et_2O$).

Attempted reaction of ferrocene with propynoic acid (**1**, R = H) gave, under the same conditions, an untreatable mixture of products. However, we obtained propynoilferrocene **2f** in nearly quantitative yield by desilylation of the trimethylsilyl compound **2e** using potassium fluoride in the presence of 18-crown-6 in THF

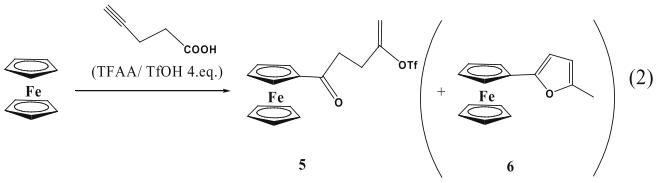


2e **2f**

Compound **2f** was already prepared by a less direct way – reaction of ferrocenecarbaldehyde with ethynylmagnesium bromide and subsequent oxidation of the alcohol formed [26].

Prompted by the above results we decided to look whether nonconjugated alkynoic acids having a terminal acetylenic bond, **3a–d** (Scheme 1), react similarly with ferrocene to afford corresponding ferrocenyl ynones. However, in this case we found that the amount of TfOH and workup are of critical importance. Treatment of ferrocene with acids **3a–c** and TFAA in the presence of 1.1 equiv. of TfOH or 4 equiv. of $BF_3 \cdot Et_2O$ afforded expected ynones **4a–c** in high yields (Scheme 1 and Table 2).

In contrast, reactions carried out in the presence of 4 equiv. of TfOH had completely different outcome and the products **4a–c** were not formed. In the case of reaction with 4-pentynoic acid the triflate **5** was the sole isolable product (37% yield, Eq. (2)). However, a slight change of workup (extraction after 2 h of stirring of the reaction mixture poured onto water at rt instead of immediate extraction) afforded a mixture of **5** (49%) and 2-ferrocenyl-5-methylfuran **6** (23%)



Ccompounds **5** and **6** were separated by column chromatography and fully characterized. Control experiments showed that neither ynone **4a** nor triflate **5** yields **6** under reaction conditions tested. We believe that **5** and **6** might be formed on workup from diketone **7**, but we failed to detect this compound in the reaction mixture

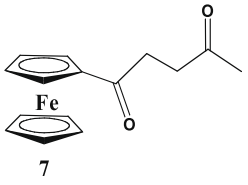


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Table 2
Acylation of ferrocene with terminal alkynoic acids.

Alkynoic acid	Product	Yield,%	
		TfOH (1.1 equiv.)	$BF_3 \cdot Et_2O$ (4 equiv.)
3a	**4a**	70	73
3b	**4b**	91	83
3c	**4c**	74	98
3d	[a]	–	–

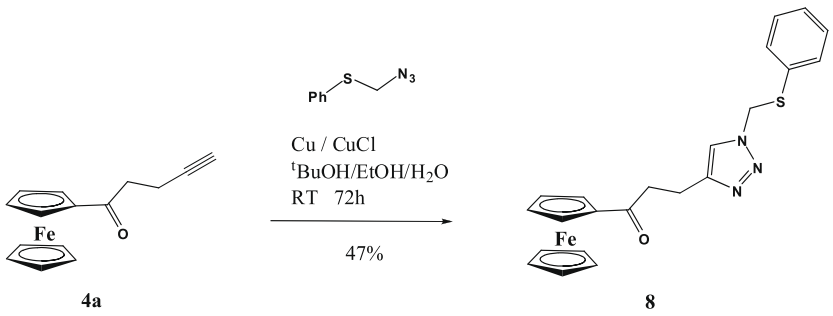
[a] Complex, inseparable mixture of products was obtained, containing, according to ^1H NMR, $FcCOCH_2COCH_3$ and its BF_2-complex [27] (when $BF_3 \cdot Et_2O$ was used).

Table 1
Acylation of ferrocene with conjugated alkynoic acids.

Alkynoic acid	Product	Yield (%)		
		TfOH (1.1 equiv.)	TfOH (4 equiv.)	$BF_3 \cdot Et_2O$ (4 equiv.)
1a	**2a**	66	74	44
1b	**2b**	70	78	61
1c	**2c**	74	80	47
1d	**2d**	73	82	52
1e	**2e**	80	73	39

Under the same conditions reaction of ferrocene with 5-hexynoic and 6-heptynoic acids, afforded, regardless workup employed, complex inseparable mixtures.

Ynones **4a–c** are potential starting materials for syntheses of ferrocene-based molecular materials using the copper (I) catalyzed azide-alkyne "click" chemistry [20]. To prove this possibility we carried out a copper-catalysed reaction of **4a** with (phenylthio)methyl azide. We isolated the corresponding triazole **8** in 47% yield (the conditions of this reaction were not optimized).



(3)

In conclusion, we have elaborated a simple and efficient one-step route to both conjugated of non-conjugated terminal ferrocenyl alkynones starting from ferrocene and corresponding alkynoic acids. It is worthy noting that compounds prepared by our method are isomers of ferrocenylethynyl ketones (FcC≡CCOR), which can be obtained from ethynylferrocene and acyl chlorides or aryl iodides and CO in palladium-catalyzed reactions [28–31].

2. Experimental

All reactions were carried out under argon. All reagents used in this work are commercially available (Aldrich) and were used without further purifications. Solvents were dried over appropriate drying agents and distilled before use. Chromatographic separations were carried out using Silica gel 60 (Merck, 230–400 mesh ASTM). The NMR spectra were run on Varian Gemini 200 BB (200 MHz for ^{1}H) and Bruker Advance 250 (250 MHz for ^{1}H) spectrometers and IR spectra on a FT-IR Nexus spectrometer. Mass spectra were measured on a Finnigan MAT 95 spectrometer. Elemental analyses were performed by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

2.1. Friedel–Crafts reaction of ferrocene with alkynoic acids

A solution of an alkynoic acid (1.1 mmol) and TFAA (153 μl, 1.1 mmol) in dichloromethane (5 ml) was stirred 1 min at rt and ferrocene (186 mg, 1 mmol) and TfOH (97 μl, 1.1 mmol or 337 μl, 4 mmol) or $BF_3 \cdot Et_2O$ (0.5 ml, 4 mmol) were added. The resulting solution was stirred for 2 h. Water (15 ml) was added, the organic layer was separated and aqueous layer extracted with dichloromethane. The combined organic extracts were washed with water, dried ($MgSO_4$) and the solvent evaporated. Column chromatography (silica gel/dichloromethane) afforded corresponding ferrocenyl ynones. Yields are given in Tables 1 and 2. Spectroscopic and analytical data:

2.2. FcCOC≡CMe (**2a**)

Orange crystals. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.92 (t, J = 1.9 Hz, 2H, Cp), 4.57 (t, J = 1.9 Hz, 2H, Cp), 4.26 (s, 5H, Cp), 2.10 (s, 3H, CH_3). ^{13}C NMR (62.90 MHz, $CDCl_3$, δ): 181.57, 92.30, 88.37, 80.35, 79.79, 72.95, 70.36, 4.17. IR (KBr, cm^{-1}): 2966, 2931, 2279, 2213, 1617, 1447, 1280. MS (EI, m/z): 252 (M^+). Anal. Calcd for $C_{14}H_{12}FeO$: C, 66.70; H, 4.80. Found: C, 66.49; H, 4.67.

2.3. FcCOC≡C$CH_2CH_2CH_3$ (**2b**)

Red solid. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.92 (t, J = 2.0 Hz, 2H, Cp), 4.58 (t, J = 2.0 Hz, 2H, Cp), 4.26 (s, 5H, Cp), 2.44 (t, J = 6.9 Hz, 2H, CH_2), 1.70 (sextet, J = 7.4 Hz, 2H, CH_2), 1.11 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (62.90 MHz, $CDCl_3$, δ): 181.47, 92.57, 80.60, 80.45, 72.91, 70.43, 70.34, 21.47, 20.97, 13.53. IR (neat, cm^{-1}): 3108, 3085, 2996, 2931, 2874, 2213, 1618, 1447, 1280. MS (EI, m/z): 280 (M^+). Anal. Calcd for $C_{16}H_{16}FeO$: C, 68.60; H, 5.76. Found: C, 68.65; H, 5.61.

2.4. FcCOC≡C$CH_2CH_2CH_2CH_2CH_3$ (**2c**)

Red oil. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.91 (t, J = 2.0 Hz, 2H, Cp), 4.57 (t, J = 2.0 Hz, 2H, Cp), 4.26 (s, 5H, Cp), 2.45 (t, J = 6.8 Hz, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.46 (m, 4H, CH_2), 0.95 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 181.42, 92.64, 80.33, 80.28, 72.79, 70.23, 70.17, 30.75, 27.35, 21.82, 18.70, 13.67. IR (neat, cm^{-1}): 3099, 3081, 2953, 2925, 2872, 2857, 2211, 1614, 1448, 1280. MS (EI, m/z): 308 (M^+). Anal. Calcd for $C_{18}H_{20}FeO$: C, 70.15; H, 6.54. Found: C, 70.11; H, 6.41.

2.5. FcCOC≡CPh (**2d**)

Dark red-violet. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.67 (m, 2H, Ph), 7.46 (m, 3H, Ph), 5.02 (t, J = 2.2 Hz, 2H, Cp), 4.64 (t, J = 2.1 Hz, 2H, Cp), 4.31 (s, 5H, Cp). ^{13}C NMR (62.90 MHz, $CDCl_3$, δ): 181.19, 132.78, 130.36, 128.66, 120.64, 89.53, 87.75, 80.62, 73.28, 70.57. IR (KBr, cm^{-1}): 3099, 3087, 3067, 2205, 1608, 1489, 1449, 1375, 1296, 1703, 1030, 757, 689, 501; identical with those reported in the literature [15].

2.6. FcCOC≡CTMS (**2e**)

Dark red powder. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.92 (t, J = 2.0 Hz, 2H, Cp), 4.61 (t, J = 2.0 Hz, 2H, Cp), 4.26 (s, 5H, Cp), 0.32 (s, 9H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 180.80, 102.03, 96.24, 80.10, 73.33, 70.57, 0.59. IR (KBr, cm^{-1}): 3104, 3086, 2958, 2149, 1611, 1275, 847. MS (EI, m/z): 310 (M^+). Anal. Calcd for $C_{16}H_{18}FeOSi$: C, 61.94; H, 5.85. Found: C, 62.24; H, 6.10.

2.7. FcCOCH$_2$CH$_2$C≡CH (**4a**)

Orange crystals. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.80 (t, J = 1.9 Hz, 2H, Cp), 4.51 (t, J = 1.9 Hz, 2H, Cp), 2.97 (t, J = 6.6 Hz, 2H, CH_2), 2.59 (dt, J = 6.6 Hz, 2.0 Hz, 2H, CH_2), 2.00 (t, J = 2.0 Hz, 1H, CH). ^{13}C NMR (62.90 MHz, $CDCl_3$, δ): 201.58, 83.88, 78.34, 72.29, 69.76, 69.18, 68.65, 38.34, 13.08. IR (KBr, cm^{-1}): 1655, 3250. MS (EI, m/z): 266 (M^+). Anal. Calcd for $C_{14}H_{15}FeO$: C, 67.70; H, 5.30. Found: C, 67.50; H, 5.26.

2.8. FcCOCH$_2$CH$_2$CH$_2$C≡CH (**4b**)

Red oil. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.81 (t, J = 1.9 Hz, 2H, Cp), 4.51 (t, J = 1.9 Hz, 2H, Cp), 4.22 (s, 5H, Cp), 2.89 (t, J = 7.1 Hz, 2H, CH_2), 2.35 (dt, J = 6.8 Hz, 2.8 Hz, 2H, CH_2), 2.02 (t, J = 2.6 Hz, 1H, CH), 1.94 (m, 2H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 203.62, 83.93, 78.98, 72.13, 69.76, 69.21, 69.05, 37.68, 22.70, 17.87. IR (neat, cm^{-1}): 3297, 3256, 3096, 2938, 2116, 1667. MS (EI, m/z): 280 (M^+). Anal. Calcd for $C_{16}H_{16}FeO$: C, 68.60; H, 5.76. Found: C, 68.59; H, 5.93.

2.9. FcCOCH$_2$CH$_2$CH$_2$CH$_2$C≡CH (**4c**)

Red liquid. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.79 (t, J = 1.9 Hz, 2H, Cp), 4.50 (t, J = 1.9 Hz, 2H, Cp), 4.20 (s, 5H, Cp), 2.74 (t, J = 7.0 Hz, 2H, CH_2), 2.27 (dt, J = 2.6 Hz, 7.0 Hz, 2H, CH_2), 1.98 (t, J = 2.7 Hz, 1H, CH), 1.85 (m, 2H, CH_2), 1.64 (m, 2H, CH_2). ^{13}C NMR (62.90 MHz, $CDCl_3$, δ): 204.02, 84.09, 79.01, 72.10, 69.70, 69.25, 68.54, 38.98, 28.11, 23.54, 18.27. IR (neat, cm^{-1}): 3301, 3252, 3096, 2938, 2865, 2116, 1557. MS (EI, m/z): 294 (M^+). Anal. Calcd for $C_{17}H_{18}FeO$: C, 69.41; H, 6.17. Found: C, 69.25; H, 6.03.

2.10. FcCOCH$_2$CH$_2$C(OTf)=CH$_2$ (**5a**)

Orange crystals. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 5.17 (d, J = 3.6 Hz, 1H, CH), 5.09 (dt, J = 3.6 Hz, 1.0 Hz, 1H, CH), 4.80 (t, J = 1.8 Hz, 2H, Cp), 4.54 (t, J = 2.0 Hz, 2H, Cp), 4.21 (s, 5H, Cp), 2.99 (dt, J = 7.2 Hz, 1.5 Hz, 2H, CH_2), 2.79 (dt, J = 6.6 Hz, 0.9 Hz, 2H). ^{13}C NMR (176.15 MHz, $CDCl_3$, δ): 201.20, 155.82, 118.49 (q, J_{C-F} = 320.5 Hz, CF_3), 105.42, 78.24, 72.50, 69.84, 69.21, 35.57, 28.39. IR (KBr, cm^{-1}): 1655, 1417, 1251, 1210, 1150, 1124, 960, 915, 617. MS (EI, m/z): 416 (M^+). Anal. Calcd for $C_{16}H_{15}F_3FeO_4S$: C, 46.17; H, 3.63. Found: C, 46.37; H, 3.80.

2.11. 2-Ferrocenyl-5-methylfuran (**6**)

Yellow crystals. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 6.13 (d, J = 3.0 Hz, 1H, CH), 5.92 (dq, J = 1.0 Hz, 3.0 Hz, 1H, CH), 4.55 (t, J = 1.9 Hz, 2H, Cp), 4.23 (t, J = 1.8 Hz, 2H, Cp), 4.10 (s, 5H, Cp), 2.32 (d, J = 1.0 Hz, 3H, CH_3). ^{13}C NMR (50.0 MHz, $CDCl_3$, δ): 151.60, 150.53, 124.9, 107.00, 104.39, 69.33, 68.13, 13.72. IR (KBr, cm^{-1}): 3114, 3096, 3086, 2955, 2921,1578, 1443, 1106, 821, 792. MS (EI, m/z): 266 (M^+). Anal. Calcd for $C_{15}H_{14}FeO$: C, 67.70; H, 5.30. Found: C, 67.65; H, 5.41.

2.12. Desilylation of **2e**

To a solution of **2e** (86.5 mg, 0.279 mmol), 18-crown-6 (2.5 mg) in THF, powdered anhydrous KF (350 mg, 6.0 mmol) was added at rt and the resulting mixture was stirred 30 min. After addition of water (30 ml) the product was extracted with dichloromethane (3 × 25 ml). Flash chromatography (silica gel/dichloromethane) afforded **FcCOC≡CH** (**2f**) as dark red crystals. Yield 59.4 mg (99%) ^{1}H NMR (200 MHz, $CDCl_3$,) δ 4.95 (m, 2H, Cp), 4.64 (m, 2H, Cp), 4.28 (s, 5H, Cp), 3.27 (s, 1H, CH); IR (KBr, cm^{-1})1620 (C=O), 1449, 1274; identical with those reported in the literature [26].

2.13. "Click" reaction of **4a** with (phenylthio)methyl azide

To a solution of **4a** (288 mg, 1.08 mmol) in the mixture of *tert*-butanol (10 ml), ethanol (10 ml) and water (5 ml) were added (phenylthio)methyl azide (288 mg, 1.75 mmol), CuCl (2 mg) and Cu (50 mg as a thin wire). After 72 h stirring at ambient temperature water (40 ml) was added and the product was extracted with dichloromethane. Flash chromatography (eluent chloroform–ethyl acetate) and crystallization (chloroform–hexane) afforded **8** as orange solid. Yield 221 mg (47%). ^{1}H NMR $CDCl_3$, δ): 7.42 (s, 1H, CH), 7.30 (m, 5H, Ph), 5.58 (s, 2H, CH_2), 4.77 (t, J = 1.7 Hz, 2H, Cp), 4.49 (t, J = 1.8 Hz, 2H, Cp), 4.11 (s, 5H, Cp), 3.11 (m, 4H, CH_2CH_2). ^{13}C NMR (DMSO-d_6, δ): 202.07, 146.67, 132.73, 130.45, 129.24, 127.58, 122.01, 78.82, 72.02, 69.51, 68.99, 51.46, 38.04, 19.47. IR (KBr, cm^{-1}): 3119, 3082, 2963, 2925, 2857, 1729, 1649, 1455. MS (EI, m/z): 431 (M^+). Anal. Calcd for $C_{23}H_{23}FeN_3O$: C, 61.26; H, 4.91; N, 9.74. Found: C, 61.23; H, 4.95; N, 9.81.

Acknowledgments

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