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Synthesis and Structure of Ferrocenol Esters

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Abstract

N-Heterocyclic carbene-catalyzed oxidative esterification of ferroceneboronic acid by aromatic and heteroaromatic aldehydes affords the new ferrocenol hetaryl and aryl esters 1 - 4, 6 - 8 and 9 - 11. The reaction takes place under mild conditions. The X-ray crystal structure of ferrocenyl esters 3, 6, 11 was determined.

Keywords

Hydroxyferrocene, Ferroceneboronic Acid, N-Heterocyclic Carbene, Esterification, Catalysis

1. Introduction

Ferrocene is considered to be one of the most prominent molecules in modern organic and organometallic chemistry [1]-[3]. Recently, ferrocenyl-substituted compounds have found widespread application in medicinal chemistry [4]-[16], material science [17]-[21] and asymmetric catalysis [22]-[25]. Ferrocene is a source for artificial receptors [26], biosensors [27]-[29], liquid crystals [30] [31] and redox-active structures [32]-[37].

Nesmeyanov first reported hydroxyferrocene in 1959, generating it from either ferroceneboronic acid FcB$(OH)_2$ (*via* reaction with $Cu(OAc)_2$ and then potassium hydroxide) [38] or by alkaline hydrolysis of the acetate generated from FcBr and $Cu(OAc)_2$ [39]. Hydroxyferrocene is a yellow, very air-sensitive labile solid and a slightly weaker acid than phenol [40]. Due to relative instability its chemistry is not fully developed yet. Ferrocenol esters were synthesized by acylation of ferrocenol with carboxylic acid chlorides [41], but the more convenient method for their preparation is Cu-assisted reaction of haloferrocenes with carboxylic acids [39] [42]-[44]. Here we present a preparative route to ferrocenol esters from easily available ferroceneboronic acid [45]-

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[47], avoiding isolation of hydroxyferrocene. The structure of esters deduced from their X-ray diffraction analysis is also discussed. Optical properties and electrochemical behavior of ferrocenol esters were reported in our preliminary communication [48].

2. Results and Discussion

2.1. Synthesis

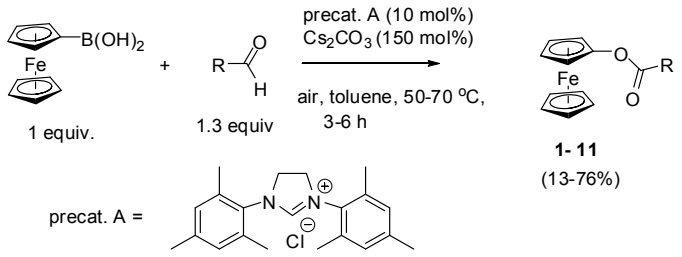
Recently oxidative esterification of aromatic (heteroaromatic) aldehydes was disclosed [49]-[54]. The reaction utilizes an organocatalytic N-heterocyclic carbene activation-airobic oxidation of aldehydes in the presence of areneboronic acids. Involving $FcB(OH)_2$ in this process gives straightforward route to ferrocenol esters (**Scheme 1**). Isolated yields of the compounds **1-11** varied within 16% - 77% (**Table 1**). The proposed reaction mechanism is discussed in literature [52] [53]. Carbene (1,3-dimesithylimidazole-2-ilidene) was generated *in situ* by the interaction of 1,3-dimethylimidazolidine chloride [55] with Cs_2CO_3.

Oxygen of the air is evidently the terminate oxidant. Therefore, we tried to bubble the air into the reaction vessel to improve the yield. However, only in the case of compound **11**, the yield increased to some extent, with other compound yields being unaffected by this improvement.

At room temperature, esters **8** and **9** decompose during storage over 3 - 4 days. Indeed, the stability of esters **1-11** has a decisive influence on the yields (**Table 1**).

2.2. The Structure of Ferrocenol Esters

Below is shown the X-ray crystal structure of compound **1** (**Figure 1**), compound **4** (**Figure 2**) and compound **10** (**Figure 3**).



Scheme 1. Synthesis of compounds **1-11**.

Table 1. Yields of compounds 1-11 and the reaction time.

Compound	R	Temperature, ˚C	Time (h)	Flash mixture, petroleum ether-ethylacetate	Yield (%)
1	3,4-$(MeO)_2C_6H_3$	50	3	5:1	76
2	3,4,5-$(MeO)_3C_6H_2$	70	6	10:1	16
3	4-$(CF3)C_6H_4$	70	3	20:1	35
4	1-naphtyl	50	6	10:1	76
5	CH=CHPh	50	3	10:1	36
6	2-furyl	50	3	10:1	34
7	2-thienyl	50	3	10:1	35
8	2-pyridyl	50	6	5:1	17
9	3-pyridyl	50	6	3:1	33
10	4-pyridyl	50	6	3:1	17
11	ferrocenyl	70	6	10:1	6
11[a]	ferrocenyl	70	6	10:1	28

[a]The air was bubbled into the reaction mixture.

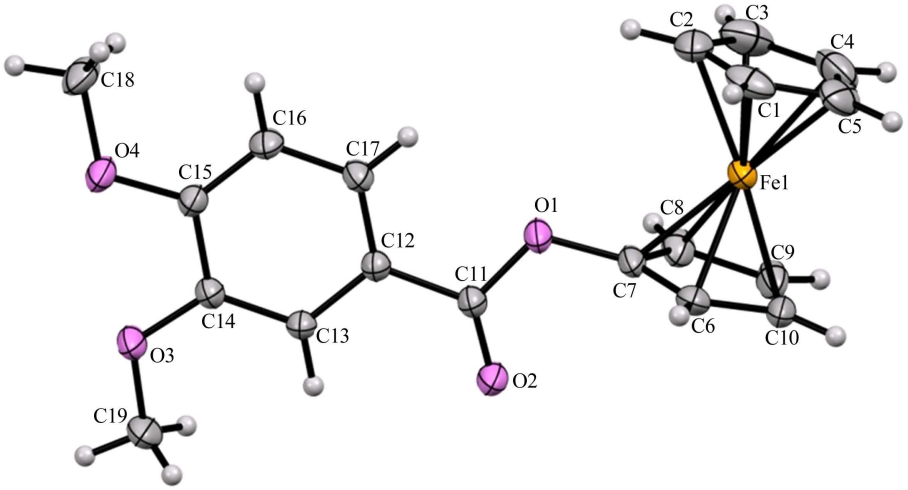


Figure 1. The X-ray structure of compound **1**.

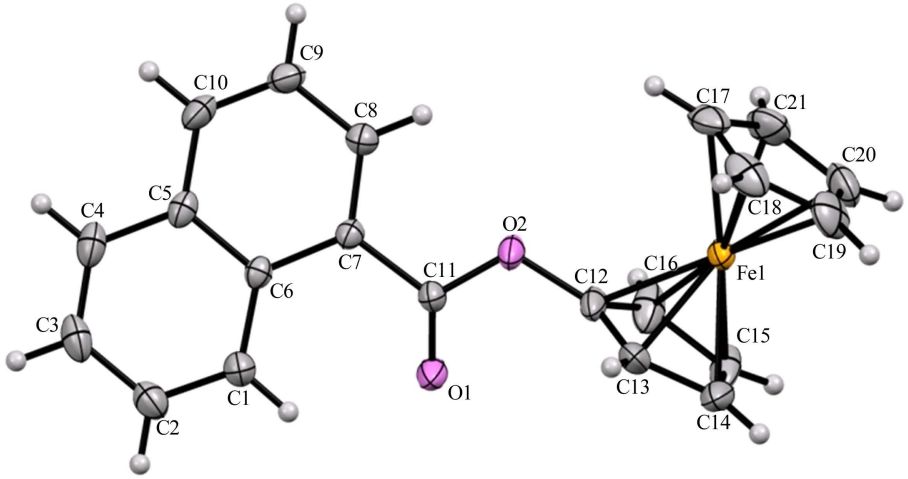


Figure 2. The X-ray structure of compound **4**.

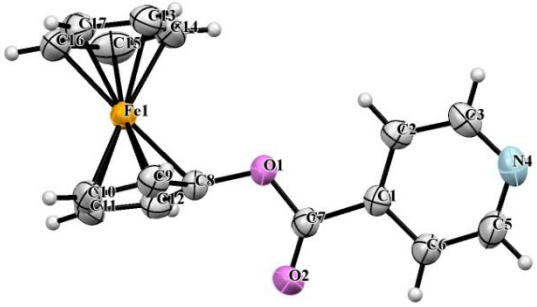


Figure 3. Compound **10** in the thermal ellipsoids of the 50% probability (one independent molecule).

In accord with XRD data, two independent molecules of ferrocenyl isonicotinate **10** are crystallized in the unit cell (**Figure 4**). The plane of the pyridine ring in molecules is approximately perpendicular towards the plane of the cyclopentadienyl ring; planes of the independent molecules in the unit cell are also approximately perpendicular. These structural features are similar to esters **1** and **4**. No any deviations from standard bonds lengths or angles in the molecules are observed and no any shortened contacts are presented in the molecular packing.

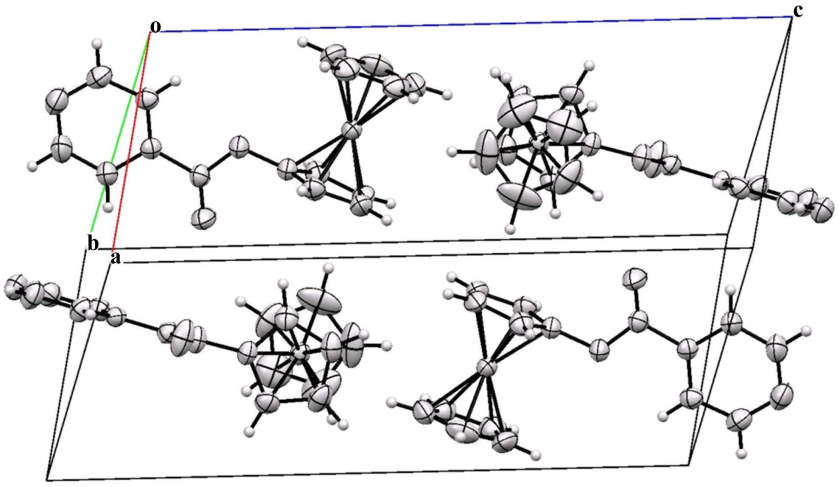


Figure 4. Two independent molecules in the unit cell of the compound **10**.

3. Experimental

3.1. General

The melting points were determined on the PTP apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ using a Varian Mercury Plus 300 at 300 MHz (^1H) and 75 (^{13}C) MHz. Chemical shifts were referenced to solvent signals (^{13}C) and GMDS (^1H). The IR spectra were recorded in Nujol on Bruker IFS 66 ps. Elemental analysis was carried out on CHNS Leco 9321P analyzer. The reaction mixture was qualitatively analyzed by GC-MS Agilent Technologies 6890N/5975B system with HP-5 ms, 30,000 × 0.25 mm column. The column was heated up to 260˚C. The same device was used for recording mass-spectra (EI, 70 eV). The crude product was purified by column chromatography on Silica gel 60 (AlfaAesar, 0.032 - 0.070 mm).

3.2. General Method of Oxidative Esterification

A mixture of ferroceneboronic acid (0.105 g, 0.5 mmol), corresponding aldehyde (0.65 mmol), $CsCO_3$ (0.244 g, 0.75 mmol) and 1,3-bis(2,4,6-trimethyphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (0.017 g, 0.05 mmol) was suspended in toluene (10 ml), and stirred in air at 50˚C or at 70˚C for 3 or 6 h (**Table 1**). The solvent was removed under a vacuum, products were purified by flash chromatography on silica gel (petroleum ether- ethyl acetate), from 10:1 to 3:1 (**Table 1**).

3.3. Ferrocenyl 3,4-Dimethoxybenzoate (1)

Yield 76%, yellow prisms from methanol. Mp.: 131˚C - 134˚C. FT-IR (Nujol, cm^{-1}): 3078, 1727, 1596, 1517, 1417, 1349, 1289, 1273, 1250, 1233, 1214, 1193, 1172, 1142, 1105, 1084, 1025, 1001, 931, 905, 893, 810, 768, 758, 609, 513, 501, 489. ^1H NMR (300 MHz, $CDCl_3$): δ 3.94 (3H, s, MeO), 3.95 (3H, s, MeO), 4.00 (2H, s, Fc), 4.26 (5H, s, Fc), 4.56 (2H, s, Fc), 6.76 (1H, d, J = 8.4 Hz, H-5'), 7.58 (1H, s, H-2'), 7.75 (1H, d, J = 8.4 Hz, H-6'). ^{13}C NHC (75 MHz, $CDCl_3$): δ 55.99, 60.87, 63.28, 69.35, 110.23, 112.08, 116.23, 122.05, 123.93, 148.64, 153.25, 164.64. EI-MS (rel. int.%): 367 (5) $[M+1]^+$, 336 (24) $[M]^+$. Anal. Calc. for $C_{16}H_{13}FeNO_2$: C, 62.3; H, 4.9%. Found: C, 62.0; H, 4.9%.

3.4. Ferrocenyl 3,4,5-Trimethoxybenzoate (2)

Yield 16%, brown solid. Mp.: 123˚C - 127˚C. FT-IR (Nujol, cm^{-1}): 1731, 1587, 1503, 1331, 1234, 1212, 1181, 1170, 1130, 1104, 1097, 1033, 994, 940, 865, 824, 803, 779, 757, 647, 512, 499. ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (3H, s, 4-MeO), 3.93 (6H, s, 3,5-MeO), 4.10 (2H, s, Fc), 4.35 (5H, s, Fc), 4.67 (2H, s, Fc), 7.33 (2H, s, Ar-2,6). ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.42, 56.34, 60.94, 61.27, 63.99, 70.25, 107.16, 152.95, 161.38, 164.32. EI-MS (rel. int.%): 397 (8) $[M+1]^+$, 396 (25) $[M]^+$. Anal. Calc. for $C_{20}H_{20}FeO_5$: C, 60.6; H, 5.1. Found: C, 60.7; H, 5.5%.

3.5. Ferrocenyl 4-(Trifluromethyl)-Benzoate (3)

Yield 35%, red powder, Mp.: 106˚C - 107˚C. FT-IR (Nujol, cm^{-1}): 3117, 1735, 1695, 1412, 1334, 1307, 1281, 1238, 1161, 1115, 1107, 1095, 1069, 1019, 1001, 927, 859, 814, 768, 698, 662, 592, 513, 484. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.01 (2H, t, J = 1.8 Hz, Fc), 4.25 (5H, s, Fc), 4.57 (2H, t, J = 1.8 Hz, Fc), 7.74 (2H, d, J = 8.1 Hz, H-3', 5'), 8.72 (2H, d, J = 8.1 Hz, H-2', 6'). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.84, 63.46, 69.42, 99, 95, 125.45, 125.55, 130.22. EI-MS (rel. int.%): 375 (12) $[M+1]^+$, 374 (49) $[M]^+$. Anal. Calc. for $C_{18}H_{13}FeO_2$: C, 57.78; H, 3.50. Found: C 57.76; H 3.49%.

3.6. Ferrocenyl Naphthalene-1-Carboxylate (4)

Yield 76%, red crystals, Mp.: 95˚C - 101˚C. FT-IR (Nujol, cm^{-1}): 1732, 1690, 1593, 1575, 1510, 1411, 1348, 1276, 1231, 1189, 1121, 1106, 1069, 1032, 1024, 1001, 987, 923, 869, 810, 779, 648, 610, 559, 509, 489. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (2H, t, J = 1.8 Hz, Fc), 4.29 (5H, s, Fc), 4.62 (2H, J = 2.0 Hz, Fc), 7.50 - 7.70 (3H, m, H-7',6',3'), 7.89 (1H, d, J = 8.1 Hz, H-5'), 8.05 (1H, d, J = 8.1 Hz, H-4'), 8.28 (1H, dd, J = 7.4 Hz, J = 1.1 Hz, H-2'), 8.96 (1H, d, J = 8.7 Hz, H-8'). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.13, 63.42, 69.39, 124.49, 125.65, 126.34, 128.01, 128.62, 130.66, 133.86, 133.87. EI-MS (rel. int.%): 357 (12) $[M+1]^+$, 356 (48) $[M]^+$. Anal. Calc. for $C_{18}H_{13}FeO_2$: C 70.81; H 4.53. Found: C, 70.61; H, 4.20%.

3.7. Ferrocenyl Cinnamate (5)

Yield 36%, yellow crystals. Mp.: 82˚C - 83.5˚C. (lit.: 88.5˚C - 90˚C [44]). FT-IR (Nujol, cm^{-1}): 3108, 1732, 1642, 1331, 1310, 1234, 1157, 1105, 979, 804, 764, 516, 491. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17 (2H, s, Fc), 4.43 (5H, s, Fc), 4.70 (2H, s, Fc), 6.46 (1H, d, J = 15.6 Hz, CO-CH=), 7.40 (3H, m, H-2',4',6'), 7.54 (2H, m, H-3',5'), 7.71 (1H, d, J = 15.6 Hz, Ar-CH=). EI-MS (rel. int.%): 332 (18) $[M]^+$.

3.8. Ferrocenyl Furan-2-Carboxylate (6)

Yield 34%, orange powder, Mp.: 94˚C - 95˚C. FT-IR (Nujol, cm^{-1}): 1741, 1578, 1568, 1552, 1410, 1393, 1293, 1236, 1173, 1105, 1097, 1074, 1013, 935, 917, 884, 826, 809, 595, 492. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.01 (2H, t, J = 2.0 Hz, Fc), 4.28 (5H, s, Fc), 4.60 (2H, t, J = 2.0 Hz, Fc), 6.58 (1H, dd, J = 3.5 Hz, J = 1.7 Гц, H-4′), 7.30 (1H, dd, J = 3.5 Hz, J = 0.8 Hz, H-3') 7.66 (1H, dd, J = 1.7 Hz, J = 0.8 Hz, H-5'). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.26, 62.78, 68.95, 111.51, 115.46, 118.19, 143.76, 146.28, 156.14. EI-MS (rel. int.%): 297 (19) $[M+1]^+$, 296 (100) $[M]^+$. Anal. Calc. for $C_{15}H_{12}FeO_3$: C, 60.84; H, 4.08. Found: C, 60.06; H, 4.00%.

3.9. Ferrocenyl Thiophene-2-Carboxylate (7)

Yield 35%, yellow solid. Mp.: 108˚C - 109˚C. FT-IR (Nujol, cm^{-1}): 1734, 1522, 1355, 1266, 1245, 1233, 1213, 1103, 1076, 1061, 1018, 1009, 924, 859, 849, 838, 827, 807, 742, 614, 499, 486. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.04 (2H, s, Fc), 4.31 (5H, s, Fc), 4.61 (2H, s, Fc), 7.13 (1H, dd, J = 4.8 Hz, J = 2.7 Hz, H-4'), 7.60 (1H, d, J = 4.8 Hz, H-3'), 7.86 (1H, d, J = 2.7 Hz, H-5'). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.21, 63.81, 69.97, 127.89, 133.05, 134.04, 160.25. EI-MS (rel. int.%): 314 (6) $[M+2]^{+\cdot}$, 313 (18) $[M+1]^+$, 312 (87) $[M]^+$. Anal. Calc. for $C_{16}H_{13}FeNO_2$: C, 57.7; H, 3.9; S, 10.3%. Found: C, 57.5; H, 4.0; S, 10.1%.

3.10. Ferrocenyl Pyridine-2-Carboxylate (8)

Yield 17%, black solid. Compound is unstable in air (decomposes in 2 - 3 days at room temperature). FT-IR (Nujol, cm^{-1}): 3231, 1777, 1705, 1666, 1625, 1593, 1567, 1259, 1047, 858, 765, 663. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (2H, s, Fc), 4.26 (5H, s, Fc), 4.66 (2H, s, Fc), 7.53 (1H, m, H-5'), 7.89 (1H, m, H-3'), 8.19 (1H, m, H-4'), 8.82 (1H, m, H-6'). NMR ^{13}C, δ 60.32, 62.85, 69.01, 124.94, 126.59, 126.60, 136.59, 140.87, 149.64, 162.74. EI-MS (rel. int.%): 308 (20) $[M+1]^+$, 307 (100) $[M]^+$. $C_{16}H_{13}FeNO_2$. No correct elemental analysis could be obtained for this compound, despite several attempts.

3.11. Ferrocenyl Pyridine-3-Carboxylate (9)

Yield 33%, brown solid. Compound is unstable in air. Mp.: 69˚C - 76˚C. FT-IR (Nujol, cm^{-1}): 1730, 1679,

1279, 1235, 1103, 1086, 1038, 1027, 835, 809, 700, 516, 506, 492. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (2H, s, Fc), 4.27 (5H, s, Fc), 4.58 (2H, s, Fc), 7.48 (1H, m, H-5'), 8.37 (1H, d, J = 6.9 Hz, H-4'), 8.88 (1H, m, H-6'), 9.36 (1H, s, H-2'). NMR ^{13}C (75 MHz, $CDCl_3$): δ 60.42, 63.01, 68.98, 115.52, 123.12, 129.21 136.77, 150.69, 153.26, 163.18. EI-MS (rel. int.%): 308 (17) $[M+1]^+$, 307 (86) $[M]^+$. $C_{16}H_{13}FeNO_2$. We failed to obtain correct elemental analysis for this compound.

3.12. Ferrocenyl Pyridine-4-Carboxylate (10)

Yield 17%, brown prisms from hexanes-AcOEt. Mp.: 82˚C - 85˚C. FT-IR (Nujol, cm^{-1}): 1748, 1712, 1675, 1351, 1324, 1272, 1234, 1104, 1064, 923, 818, 753, 701, 490. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (2H, s, Fc), 4.26 (5H, s, Fc), 4.58 (2H, s, Fc), 7.93 (2H, m, H-3',5'), 8.87 (2H, m, H-2',6'). ^{13}C NHC (75 MHz, $CDCl_3$): δ 60.74, 63.48, 69.42, 122.90, 129.38, 129.61, 150.71, 163.42. EI-MS (rel. int.%): 308 (21) $[M+1]^+$, 307 (100) $[M]^+$. Anal. Calc. for $C_{16}H_{13}FeNO_2$: C, 62.6; H, 4.3; N, 4.6%. Found: C, 62.9; H, 4.7; N, 3.9%.

3.13. Ferrocenyl Ferrocenate (11)

This compound is already known [41]. Yield 28%, brown crystals from methanol. Mp.: 148˚C - 149˚C. FT-IR (Nujol, cm^{-1}): 1717, 1411, 1351, 1274, 1230, 1114, 1105, 1055, 1047, 1035, 1018, 1003, 927, 836, 827, 814, 761, 533, 501, 487, 463. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.98 (2H, t, J = 2.0 Hz, Fc), 4.25 (5H, s, Fc), 4.26 (5H, s, Fc), 4.45 (2H, t, J = 2.0 Hz, Fc), 4.51 (2H, t, J = 2.0 Hz, Fc), 4.88 (2H, t, J = 2.0 Hz, Fc). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.79, 63.15, 69.30, 69.88, 70.38, 71.70. EI-MS (rel. int.%): 415 (18) $[M+1]^+$, 414 (55) $[M]^+$. Anal. Calc. for $C_{21}H_{18}Fe_2O_2$: C, 60.9; H, 4.4. Found: C, 60.1; H, 4.6%.

3.14. Crystal Structure Determination

The unit cell parameters and the X-ray diffraction intensities of compounds **1**, **4** were measured on a Xcalibur R diffractometer. The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm [56]. The structures were solved by direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms using the SHELX-97 program package [57]. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined using a riding model.

A suitable crystal of compound **10** was selected and XRD analysis was accomplished on a Xcalibur, Eos diffractometer on standard procedure (MoK-irradiation, graphite monochromator, T = 295(2) K, ω-scanning with 1˚ step). Empirical absorption correction was applied [58]. Using Olex2 [59], the structure was solved with the Superflip [60] structure solution program using Charge Flipping and refined with the ShelXL [57] refinement package using Least Squares minimization.

Crystal Data of **1**. $C_{19}H_{18}FeO_4$, M = 366.18, triclinic, a = 7.8682(9) Å, b = 10.2613(10) Å, c = 11.2587(13) Å, α = 110.514(10)˚, β = 104.022(10)˚, γ = 104.022(10)˚, V = 816.95(15) Å^3, T = 295(2), space group P-1, Z = 2, μ (Mo Kα) = 0.942 mm^{-1}. The final refinement parameters: R_1 = 0.0407, wR_2 = 0.0924 (for all independent 3766 reflections, R_{int} = 0.0259); R_1 = 0.0349, wR_2 = 0.0879 [for observed 3347 reflections with $I > 2\sigma(I)$], S = 1.059. Largest diff. peak and hole 0.256 and −0.421 ēÅ^{-3}.

Crystal Data of **4**. $C_{21}H_{16}FeO_2$, M = 356.19, monoclinic, a = 12.2242(18) Å, b = 7.6261(13) Å, c = 17.941(3) Å, β = 108.440(17)˚, V = 1586.7(5) Å^3, T = 295(2), space group $P2_1/n$, Z = 4, μ (Mo Kα) = 0.960 mm^{-1}. The final refinement parameters: R_1 = 0.0457, wR_2 = 0.1043 (for all independent 3686 reflections, R_{int} = 0.0347); R_1 = 0.0385, wR_2 = 0.0999 [for observed 3165 reflections with $I > 2\sigma(I)$], S = 1.064. Largest diff. peak and hole 0.427 and −0.473 ēÅ^{-3}.

Crystal Data of **10**. $C_{16}H_{13}FeNO_2$, M = 306.13, triclinic, a = 7.5025(2) Å, b = 10.7990(4) Å, c = 16.9885(7) Å, α = 98.444(3)˚, β = 100.017(3)˚, γ = 90.630(3)˚, V = 1339.78(9) Å^3, T = 295(2), space group P-1, Z = 4, μ (Mo Kα) = 1.125 mm^{-1}. On the angles 1.91 < θ < 30.80˚ 12392 reflections measured, 7233 unique (5201 with I > 2σ(I), R_{int} = 0.0287) which were used in all calculations. Completeness for θ < 26.0˚ 100%. The final wR_2 was 0.1495 (all data) and R_1 was 0.0426 (I > 2σ(I)). Largest diff. peak and hole 0.564 and −0.431 ēÅ^{-3}.

4. Conclusion

Herein, we disclose the simple straightforward method for synthesis of ferrocenol esters, beginning with easily

accessible ferrocenol boronic acid and aryl-(hetaryl)-aldehydes. The reaction is catalyzed by N-heterocyclic carbene (IMes) and is suitable for synthesis of substituted benzoic acid, as well as for heterocyclic acids; however, 2- and 3-pyridylcarboxylic acid ferrocenol esters are rather unstable. Limitation and scope of the method are currently under investigation in our laboratory.

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Supplementary Material

CCDC 1034705 (compound **10**), 1453993 (compound **1**) and 1453994 (compound **4**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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