inorganics

MDPI

Article

Convenient Access to Ferrocene Fused *aza*-Heterocycles via the Intramolecular Ritter Reaction: Synthesis of Novel Racemic Planar-Chiral 3,4-Dihydroferroceno[*c*]pyridines and 1*H*-Ferroceno[*c*]pyrroles

Yuliya S. Rozhkova *, Irina V. Plekhanova, Alexey A. Gorbunov and Yurii V. Shklyaev *

Institute of Technical Chemistry UB RAS, 3 Akademik Korolev St., 614013 Perm, Russia
* Correspondence: rjs@mail.ru (Y.S.R.); yushka49@mail.ru (Y.V.S.)

Abstract: An efficient and easy approach to the synthesis of novel racemic planar-chiral 3,4-dihydroferroceno[*c*]pyridines and 1*H*-ferroceno[*c*]pyrroles via the intramolecular Ritter reaction of 2-ferrocenyl-3,3-dimethylbutan-2-ol with nitriles and thiocyanates in the presence of $MeSO_3H$ was developed. Aromatic and aliphatic nitriles, phenylacetonitriles, and *β*-oxonitriles produced exclusively 3,4-dihydroferroceno[*c*]pyridines. The condensation of 2-ferrocenyl-3,3-dimethylbutan-2-ol with various thiocyanates, including alkyl thiocyanates, benzyl thiocyanate, and ethyl 2-thiocyanatoacetate, yielded not only 3,4-dihydroferroceno[*c*]pyridines but also 1*H*-ferroceno[*c*]pyrroles. The selectivity of these reactions depended on the temperature and the order of addition. The size of substituents at the *α*-position to the sulfur atom of thiocyanates also had a significant effect on the distribution of products.

Keywords: *α*-ferrocenyl alkyl alcohol; 3,4-dihydroferroceno[*c*]pyridine; 1*H*-ferroceno[*c*]pyrrole; $MeSO_3H$; carbocation; nitrile; thiocyanate; Ritter reaction; cyclization

Citation: Rozhkova, Y.S.; Plekhanova, I.V.; Gorbunov, A.A.; Shklyaev, Y.V. Convenient Access to Ferrocene Fused *aza*-Heterocycles via the Intramolecular Ritter Reaction: Synthesis of Novel Racemic Planar-Chiral 3,4-Dihydroferroceno[*c*]pyridines and 1*H*-Ferroceno[*c*]pyrroles. *Inorganics* **2022**, *10*, 214. https://doi.org/10.3390/inorganics10110214

Academic Editor: Rainer Winter

Received: 30 October 2022
Accepted: 15 November 2022
Published: 19 November 2022

1. Introduction

One of the promising areas in the development of modern organometallic chemistry is research in the field of ferrocene. The unique properties of this compound, including specific geometry, high chemical and thermal stabilities, low toxicity, and its ability to be reversibly oxidized, result in a wide spectrum of applications for ferrocene-based compounds. Ferrocene derivatives have attracted a lot of attention in the fields of medicinal chemistry [1–9] and homogeneous catalysis [10–14]. They are widely applied in material science to create sensors [15–19], electro-optical materials [20–22], batteries [18,23], burning rate catalysts for propellants [24,25], molecular machines [26,27], and so on. Thus, the development of new approaches to the synthesis of novel functionalized ferrocene-based compounds is highly desirable.

Reactions of nucleophiles with readily available *α*-ferrocenyl substituted alcohols FcC(OH)RR′, in which R, R′ = H, Alk, Ar, constitute a synthetically useful and convenient approach to ferrocene-based compounds. A wide range of nucleophiles, including, for example, amines [28–31], aliphatic alcohols [30–32], phenols [29], thiols [28,30,31,33], enamines [34], aldehydes [35], ureas [36], 1,3-dicarbonyl [28,30,31,37,38] and electron-rich aromatic compounds [28,31,39], together with various heterocycles [28,33,37,40–47], can be employed. Reactions of FcC(OH)RR′ with nucleophiles proceeds through S_N1 mechanism via the formation of thermodynamically stable *α*-ferrocenyl carbocations FcC^+RR' to provide *α*-adducts. The generation of *α*-ferrocenyl carbocations from FcC(OH)RR′ mainly occurs under acidic conditions in the presence of Brønsted or Lewis acids. Oxidative ionization of *α*-ferrocenyl alcohols [37] and ionization of *α*-ferrocenylalkyl carbonates FcCH(R)OCOOEt formed in situ from corresponding FcCH(OH)R [29,33] are also used to obtain *α*-ferrocenyl carbocations.

Surprisingly, although a great deal of research was devoted to the investigation of the reactions of α-ferrocenyl alcohols with a variety of nucleophiles, there were no data in the literature related to investigations of the reactions of these alcohols with nitriles prior to our studies. Due to the great importance of ferrocene-based compounds, together with our established interest in the development of approaches to the synthesis of various *aza*-heterocycles via intramolecular Ritter reaction, it seemed relevant to try using α-ferrocenyl alcohols as substrates for this transformation.

In our preliminary work, we demonstrated for the first time the application of α-ferrocenyl alkyl alcohols as substrates for Ritter reaction by an example of the reaction of 1-ferrocenyl-2-methylpropan-1-ol [FcCH(OH)CH$(CH_3)_2$] with nitriles [48]. It was found that, in most cases, the nitriles were not nucleophilic enough to react with the secondary α-ferrocenyl carbocation FcCH^+CH$(CH_3)_2$ generated from FcCH(OH)CH$(CH_3)_2$ under acidic conditions. Instead, the more reactive tertiary β-ferrocenyl carbocation Fc$CH_2C^+(CH_3)_2$, formed by a 1,2-shift of the α-carbocation, readily reacted with nitriles to give the corresponding β-nitrilium cations. The latter underwent intramolecular cyclization with the formation of novel 3,4-dihydroferroceno[*c*]pyridines. These structures, being analogous of 3,4-dihydroisoquinolines, are assumed to be potentially bioactive compounds and attract sufficient interest in medicinal chemistry. It should be pointed out that the synthetic routes for the preparation of 3,4-dihydroferroceno[*c*]pyridines to date are limited, and there are only a few reports in the literature on their synthesis [49–52].

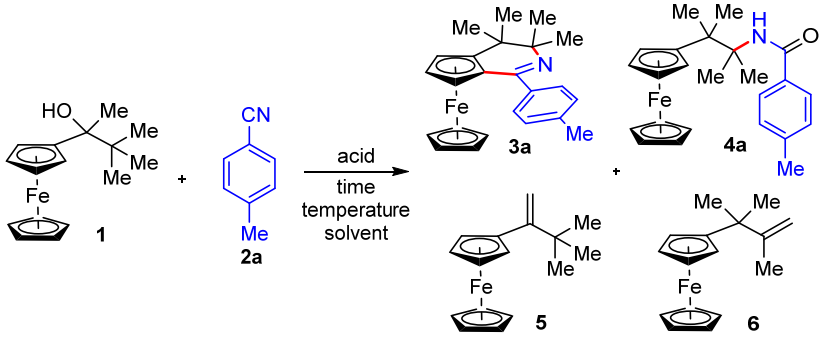
To expand the range of α-ferrocenyl alkyl alcohols suitable to be used as substrates in the intramolecular Ritter reaction, herein we studied the reaction of 2-ferrocenyl-3,3-dimethylbutan-2-ol (**1**) with nitriles under acidic conditions.

2. Results

In order to demonstrate that 2-ferrocenyl-3,3-dimethylbutan-2-ol (**1**) could serve as a substrate for the intramolecular Ritter reaction, we first examined the model reaction of alcohol **1** with 4-methylbenzonitrile (**2a**) in $MeSO_3H$ (Table 1). $MeSO_3H$ in the amount of eight equivalents was chosen since we earlier showed that it was the most effective for the synthesis of 1-R-3,3-dimethyl-3,4-dihydroferroceno[*c*]pyridines condensation of 1-ferrocenyl-2-methylpropan-1-ol with nitriles under acidic conditions [48].

The reaction of alcohol **1** with 1.2 equivalent of nitrile **2a** in the presence of $MeSO_3H$ at room temperature provided the desired ferroceno[*c*]pyridine **3a** in 59% yield within 5 h (Table 1, entry 1). In addition, amide **4a** (6%) was also isolated. The structure of compound **3a** was unambiguously confirmed by X-ray crystallography (Figure 1). Performing the reaction at higher temperatures led to the improved product yield and significantly shorter reaction times (Table 1, entries 2–5). In these cases, 60 °C was found to be the most optimal temperature both in terms of product yield and reaction time, resulting in compound **3a** in 73% yield within 15 min (Table 1, entry 3). It turned out that the use of 1.5 equivalent of nitrile **2a** did not lead to the improvement in the product yield (Table 1, entry 6). The reaction at 60 °C in DCE or toluene resulted in a longer reaction time and decreased yield of compound **3a** compared to the same reaction without solvent (Table 1, entries 7, 8 vs. entry 3). In addition to ferroceno[*c*]pyridine **3a** the inseparable mixtures of alkenes **5** and **6** were also isolated. Reactions of alcohol **1** with nitrile **2a** in H_2SO_4 or CF_3COOH at 60 °C also gave product **3a**, but in lower yields and after longer reaction times (Table 1, entries 9, 10), indicating that these acids were inferior to $MeSO_3H$ when inducing the studied reaction. No reaction occurred when CH_3COOH was used, and only starting alcohol **1** along with alkene **5** were isolated in 42% and 32% yields, respectively (Table 1, entry 11). Thus, based on the results obtained, the following reaction conditions were chosen as optimal: $MeSO_3H$, 60 °C, a ratio of **1a**/**2a** = 1:1.2, without solvent.

Table 1. Reaction of alcohol **1** with 4-methylbenzonitrile (**2a**). Optimization of the reaction conditions [1].



Entry	Acid	Temp (°C)	Solvent	Time	Yield (%) [2]		
					3a	5 + 6 [5:6] [3]	Other Products
1	$MeSO_3H$	rt	-	5 h	59	-	4a (6)
2	$MeSO_3H$	40	-	1.15 h	73	-	-
3	$MeSO_3H$	60	-	15 min	73	-	-
4	$MeSO_3H$	80	-	10 min	70	-	-
5	$MeSO_3H$	100	-	5 min	64	-	-
6 [4]	$MeSO_3H$	60	-	15 min	68	-	-
7	$MeSO_3H$	60	DCE [5]	1 h	39	15 [11:89]	-
8	$MeSO_3H$	60	toluene [5]	40 min	58	29 [10:90]	-
9	H_2SO_4	60	-	3 h	51	-	-
10	CF_3COOH	60	-	30 min	41	19 [20:80]	-
11	CH_3COOH	60	-	2.5 h	-	32 [6]	1 (42)

[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **2a** (0.42 mmol, 1.2 equiv.), acid (8 equiv.). [2] Isolated yields after silica gel column chromatography. [3] According to ^{1}H NMR analysis of the fractions of chromatography. [4] 1.5 equiv. of **2a**. [5] 0.5 mL of solvent. [6] Only alkene **5** was isolated.

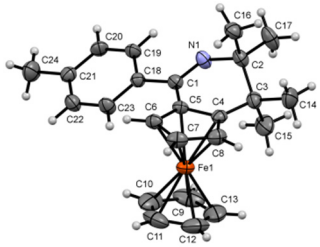
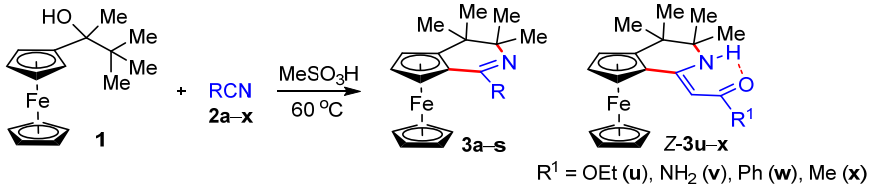


Figure 1. Molecular structure of **3a** according to XRD data in the thermal ellipsoids of the 50% probability level (only the (R_p)-enantiomer is shown).

With the optimized conditions identified, the reaction of alcohol **1** with a variety of nitriles and thiocyanates was further explored.

First, the use of aromatic and aliphatic nitriles **2b**–**t**, and *β*-oxonitriles **2u**–**x**, was investigated (Table 2). Alcohol **1** smoothly reacted with benzonitrile (**2b**) and with *ortho*-, *metha*-, and *para*-substituted benzonitriles containing electron-donating (OMe, **2c**–**e** and NH_2, **2f**) or electron-withdrawing (Br, **2h**–**j** or CF_3, **2k**–**m**) substituents within 15–50 min to provide novel ferroceno[*c*]pyridines **3b**–**f**, **h**–**m** in good to excellent yields (Table 2, entries 2–6, 8–13). In contrast to the other *ortho*-substituted benzonitriles (**2e**, **j**, **m**), 2-aminobenzonitrile (**2g**) afforded ferroceno[*c*]pyridine **3g** in a poor yield (Table 2, entry 7). The reaction of 4-nitrobenzonitrile (**2n**) with alcohol **1** led to a complex mixture of unidentified products with only trace amounts of compound **3n**, probably because of a low nucleophilicity of **2n** (Table 2, entry 14).

Table 2. Reaction of alcohol **1** with nitriles **2a–x** [1].



Entry	Nitrile 2	R	Time (min)	Product 3	Yield (%) [2]	Entry	Nitrile 2	R	Time (min)	Product 3	Yield (%) [2]
1	**2a**	4-MeC_6H_4	15	**3a**	72	13	**2m**	2-$CF_3C_6H_4$	40	**3m**	65
2	**2b**	Ph	30	**3b**	75	14	**2n**	4-$NO_2C_6H_4$	20	**3n**	trace [3,4]
3	**2c**	4-$MeOC_6H_4$	40	**3c**	77	15	**2o**	Me	15	**3o**	76
4	**2d**	3-$MeOC_6H_4$	40	**3d**	78	16	**2p**	Et	20	**3p**	80
5	**2e**	2-$MeOC_6H_4$	40	**3e**	63	17	**2q**	CH_2i-Pr	15	**3q**	75
6	**2f**	4-$NH_2C_6H_4$	50	**3f**	66	18	**2r**	CH_2Ad [5]	25	**3r**	73
7	**2g**	2-$NH_2C_6H_4$	180	**3g**	30	19	**2s**	Ad [5]	20	**3s**	71
8	**2h**	4-BrC_6H_4	30	**3h**	82	20	**2t**	CH_2CH_2OMe	15	**3t**	— [4]
9	**2i**	3-BrC_6H_4	40	**3i**	80	21	**2u**	$CH_2C(O)OEt$	20	**3u**	59
10	**2j**	2-BrC_6H_4	40	**3j**	76	22	**2v**	$CH_2C(O)NH_2$	30	**3v**	34
11	**2k**	4-$CF_3C_6H_4$	15	**3k**	76	23	**2w**	$CH_2C(O)Ph$	20	**3w**	87
12	**2l**	3-$CF_3C_6H_4$	30	**3l**	84	24	**2x**	$CH_2C(O)Me$	20	**3x**	81

[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **2a–x** (0.42 mmol, 1.2 equiv.), $MeSO_3H$ (0.18 mL, 8 equiv.), 60 °C. [2] Isolated yields after silica gel column chromatography. [3] According to GC–MS analysis of the crude residue. [4] A complex mixture of unidentified products. [5] Ad = Adamant-1-yl.

Condensation of alcohol **1** with aliphatic nitriles **2o–s**, including sterically hindered 1-adamantanecarbonitrile (**2s**), gave ferroceno[*c*]pyridines **3o–s** within 15–25 min in high yields. According to ^{1}H NMR analysis of the crude residue, 3-methoxypropionitrile (**2t**) gave a complex mixture of products, none of which could be identified and isolated (Table 2, entry 20).

Alcohol **1** reacted smoothly with *β*-oxonitriles **2u–x** to afford products **3u–x** in 34–87% yields (Table 2, entries 21–24). The NMR spectra clearly indicated that ferroceno[*c*]pyridines **3u–x** existed exclusively in the *Z*-enamine form, which was stabilized by an intramolecular hydrogen bond. That is, the ^{1}H NMR spectra of these compounds in $CDCl_3$ contained resonance signals of CH vinyl protons as singlets in the range of 4.74–5.98 ppm, together with resonance signals of NH protons as broad singlets in the range of 8.23–10.99 ppm. Cross peaks between the CH vinyl proton and H7′ proton or protons of unsubstituted Cp ring in the 2D ^{1}H–^{1}H NOESY spectra confirmed that compounds **3u–x** existed as *Z*-isomers with respect to the >C=CH– bond (Figure 2).

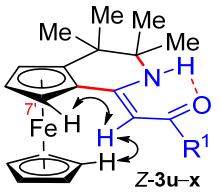
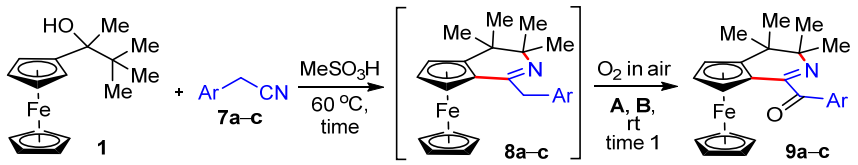


Figure 2. Key correlations in 2D ^{1}H–^{1}H NOESY spectra of compounds **3u–x**.

Phenylacetonitriles **7a–c**, like nitriles **2a–m**, **o–s**, **u–x**, readily reacted with alcohol **1** to afford the corresponding ferroceno[*c*]pyridines **8a–c**. However, products **8a–c** could not be isolated in a pure form, since they were unstable. These compounds easily oxidized in air at a benzylic position, resulting in ferroceno[*c*]pyridines **9a–c** (Table 3).

Table 3. Reaction of alcohol **1** with phenylacetonitriles **7a–c** [1].



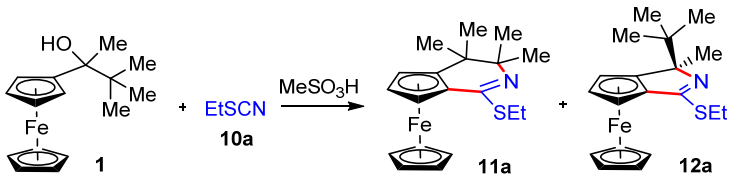
Entry	Nitrile 7	Ar	Time (min)	Time 1 (days)	Product 9	Yield (%) [2]	
						Method A	Method B
1	**7a**	3,4-$(MeO)_2C_6H_3$	10	1	**9a**	24	21
2	**7b**	Ph	15	2	**9b**	35	24
3	**7c**	4-$NO_2C_6H_4$	15	6	**9c**	16	14

[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **7a–c** (0.42 mmol, 1.2 equiv.), $MeSO_3H$ (0.18 mL, 8 equiv.), 60 °C; Method A: Storage of the mixtures of **8** and **9** obtained after purification of the crude residues by column chromatography at rt exposed to air. The ratio of **8**/**9**, according to ^{1}H NMR analysis of the fractions of chromatography performed immediately after their isolation: **8a**/**9a** = 78:22; **8b**/**9b** = 66:34; **8c**/**9c** = 65:35. Method B: Storage of the solutions of the crude residues in EtOAc at rt exposed to air. [2] Isolated yields after silica gel column chromatography.

Purification of the crude residues by silica gel column chromatography, performed immediately after the work-up of the reaction mixtures, afforded products **8a–c** as the mixtures with oxidized compounds **9a–c** in ratios of 65:35 to 78:22. Storage of these mixtures at room temperature exposed to air resulted in full conversion of **8a–c** to **9a–c** within 1–6 days and isolation of ferroceno[*c*]pyridines **9a–c** in 16–35% yields (Table 3, Method **A**). Similar results in terms of the oxidation time and yields of **9a–c** were obtained after storing the solutions of crude residues in EtOAc at room temperature exposed to air (Table 3, Method B). The rate of the conversion of compounds **8a–c** to **9a–c** strongly depends on the nature of substituents in the aromatic ring of the benzylic fragments. Thus, the oxidation of ferroceno[*c*]pyridine **8a**, containing MeO groups, proceeded much faster than that of **8c** with NO_2 groups in the aromatic ring of the benzylic fragment (Table 3, entries 1 and 3).

Further, we investigated the reaction of alcohol **1** with thiocyanates **10a–j**. It turned out that the condensation of alcohol **1** with EtSCN (**10a**) under optimal conditions gave a mixture of products in a 23:77 ratio, one of which was shown to be ferroceno[*c*]pyridine **11a** and the other one ferroceno[*c*]pyrrole **12a** (Table 4, entry 1). After silica gel column chromatography, compounds **11a** and **12a** were isolated in 18% and 65% yields, respectively. The structures of products **11a** and **12a** were unambiguously confirmed by X-ray crystallography (Figures 3 and 4). Only a single diastereomer of ferroceno[*c*]pyrrole **12a** was formed, in which the *tert*-butyl group occupied *exo*-position with respect to the iron atom, according to X-ray data. Next, we found that the selectivity of the reaction strongly depended on the temperature and the order of addition of the thiocyanate **10a**. The reaction at room temperature led to an excellent selectivity for the formation of ferroceno[*c*]pyrrole **12a** (**11a**/**12a** = 5:95), which was isolated in 87% yield (Table 4, entry 2). At the same time, addition of thiocyanate **10a** to the solution of alcohol **1** preheated to 60 °C gave a 43:57 mixture of products **11a** and **12a**, which were isolated in 33% and 53% yields, respectively (Table 4, entry 3). The reaction under similar conditions at 80 °C resulted in a predominant formation of ferroceno[*c*]pyridine **11a** (**11a**/**12a** = 74:26), isolated in 57% yield (Table 4, entry 4). Increasing the reaction temperature to 100 or 120 °C provided an even greater selectivity toward ferroceno[*c*]pyridine **11a**, resulting in products **11a** and **12a** in the ratios of 88:12 and 91:9, respectively (Table 4, entries 5, 6). However, lower yields of compound **11a** were obtained compared to the reaction at 80 °C, likely due to its partial decomposition.

Table 4. Reaction of alcohol **1** with EtSCN (**10a**) [1].



Entry	Temp. (°C)	Time (min)	11a:12a [2]	Yield (%) [3]	
				11a	12a
1	60	10	23:77	18	65
2	rt	15	5:95	4	87
3 [4]	60	10	43:57	33	53
4 [4]	80	3	74:26	57	[5]
5 [4]	100	1.5	88:12	53	[5]
6 [4,6]	120	1	91:9	23	[7]

[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **10a** (0.42 mmol, 1.2 equiv.), $MeSO_3H$ (0.18 mL, 8 equiv.). [2] According to ^1H NMR analysis of the crude residues. [3] Isolated yields after silica gel column chromatography. [4] Addition of **10a** to the solution of **1** in $MeSO_3H$ preheated to the indicated temperature. [5] Not isolated in an analytically pure form, only as a mixture with ferroceno[*c*]pyridine **11a**. [6] Considerable tar formation was observed. [7] Not isolated.

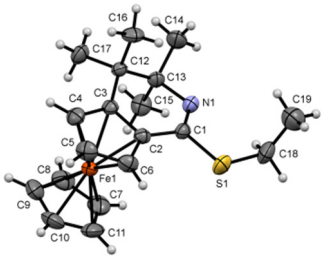


Figure 3. Molecular structure of **11a** according to XRD data in the thermal ellipsoids of the 50% probability level (only the (S_p)-enantiomer is shown).

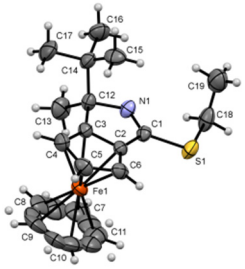
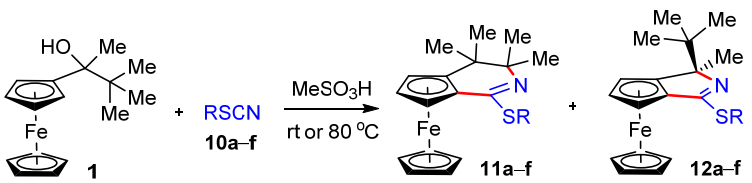


Figure 4. Molecular structure of **12a** according to XRD data in the thermal ellipsoids of the 35% probability level (only the (S_p)-enantiomer is shown).

Further, we investigated the reaction of alcohol **1** with thiocyanates **10b–f** both at room temperature and at 80 °C (Table 5). Thiocyanates **10b–f**, similar to EtSCN (**10a**), afforded ferroceno[*c*]pyrroles **12b–f** as the main products at room temperature, with **11**/**12** ratios of 16:84 to 2:98, in moderate to good yields, as single diastereomers (Table 5, entries 1, 3, 5, 7, 9 and 11). At 80 °C thiocyanates **10c–f** reacted with alcohol **1** with a predominant formation of ferroceno[*c*]pyridines **11c–f** with ratios of **11c–f** to **12c–f** in the range of 67:23 to 92:8 (Table 5, entries 6, 8, 10 and 12). In these cases, products **11c–f** were isolated in 42–61% yields. When MeSCN (**10b**) was used, the reaction proceeded with no selectivity to give a 52:48 mixture **11b** and **12b**, and ferroceno[*c*]pyridine **11b** was obtained only in 35% yield (Table 5, entry 4).

Table 5. Reaction of alcohol **1** with thiocyanates **10a–f** [1].



Entry	Thiocyanate 10	R	Temp. (°C)	Time (min)	Products 11, 12	11:12 [2]	Yield (%) [3]	
							11	12
1	**10a**	Et	rt	25	**11a**, **12a**	5:95	[4]	87
2			80	3		74:26	57	[5]
3	**10b**	Me	rt	25	**11b**, **12b**	2:98	[4]	64
4			80	3		52:48	35	[5]
5	**10c**	Pr	rt	25	**11c**, **12c**	6:94	[4]	75
6			80	3		74:26	53	[5]
7	**10d**	*i*-Pr	rt	40	**11d**, **12d**	16:84	7	53
8			80	3		92:8	61	[5]
9	**10e**	CH_2Ph	rt	25	**11e**, **12e**	5:95	[4]	37
10			80	3		67:23	42	[5]
11	**10f**	*n*-Hex	rt	40	**11f**, **12f**	4:96	[4]	65
12			80	3		79:21	55	[5]

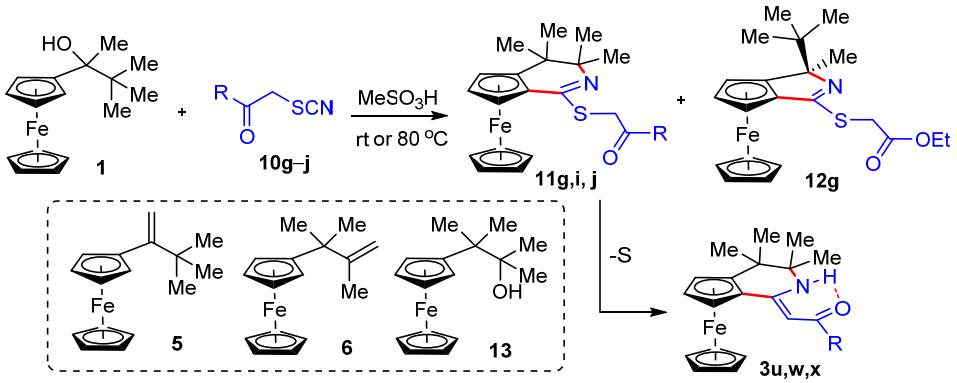
[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **10a–f** (0.42 mmol, 1.2 equiv.), $MeSO_3H$ (0.18 mL, 8 equiv.). [2] According to ^{1}H NMR analysis of the crude residues. [3] Isolated yields after silica gel column chromatography. [4] Not isolated in an analytically pure form, only as a mixture with corresponding ferroceno[*c*]pyrrole **12**. [5] Not isolated in an analytically pure form, only as a mixture with corresponding ferroceno[*c*]pyridine **11**.

The selectivity of the reaction is influenced by substituents at the *α*-position to the sulfur atom of thiocyanates **10a–f**. An increase in the substituent size results in a higher selectivity toward ferroceno[*c*]pyridines **11**, versus ferroceno[*c*]pyrroles **12**. For example, in the case of reactions at 80 °C, the most sterically hindered isopropyl thiocyanate (**10d**) afforded ferroceno[*c*]pyridine **11d** and ferroceno[*c*]pyrrole **12d** in a ratio of 92:8, whereas the reaction with a less sterically constrained MeSCN (**12b**) gave products **11b** and **12b** in a ratio of 52:48 (Table 5, entries 8 and 4). When the reaction of alcohol **1** with isopropyl thiocyanate (**10d**) was carried out at room temperature, **11d**/**12d** ratio was 16:84, while when using MeSCN (**12b**) under the same conditions, a 2:98 **11b**/**12b** ratio was observed (Table 5, entries 7 and 3).

Ethyl 2-thiocyanatoacetate (**10g**) reacted with alcohol **1** the same way as thiocyanates **10a–f** (Table 6, entries 1, 2). The use of thiocyanate **10g** at room temperature led to the formation of a 4:96 mixture of compounds **11g** and **12g**, which were isolated in 6% and 73% yields, respectively (Table 6, entry 1), whilst at 80 °C products **11g** and **12g** were formed in a ratio of 59:41, and purification by silica gel column chromatography gave 27% of ferroceno[*c*]pyridine **11g** and 26% of ferroceno[*c*]pyrrole **12g** (Table 6, entry 2). In both cases the ^{1}H NMR spectra of ferroceno[*c*]pyridine **11g** recorded immediately after its isolation indicated that this compound contained trace amounts of ferroceno[*c*]pyridine **3u** with **11g**/**3u** ratios of 99:1 and 96:4, respectively. ^{1}H NMR analyses showed that ferroceno[*c*]pyridine **11g** was very slowly converted to compound **3u** when stored at room temperature, both neat and in solution. Compound **3u** has not been isolated in a pure form in these cases. The results of the ^{1}H NMR monitoring of the transformation of thioimine **11g** to enaminone **3u** are performed in Supplementary Materials (Figure S1, Table S1). The formation of ferroceno[*c*]pyridine **3u** likely occurred due to the extrusion of sulfur from thioimine **11g**. This reaction is a typical for thioimines, containing $CH_2C(O)R$ fragment at the sulfur atom, and is the basis of such a synthetic method as Eschenmoser sulfide

contraction [53,54]. The proposed mechanism for the transformation of thioimine **11g** to enaminone **3u** is performed in Supplementary Materials (Scheme S1).

Table 6. Reaction of alcohol **1** with thiocyanates **10g–j** [1].



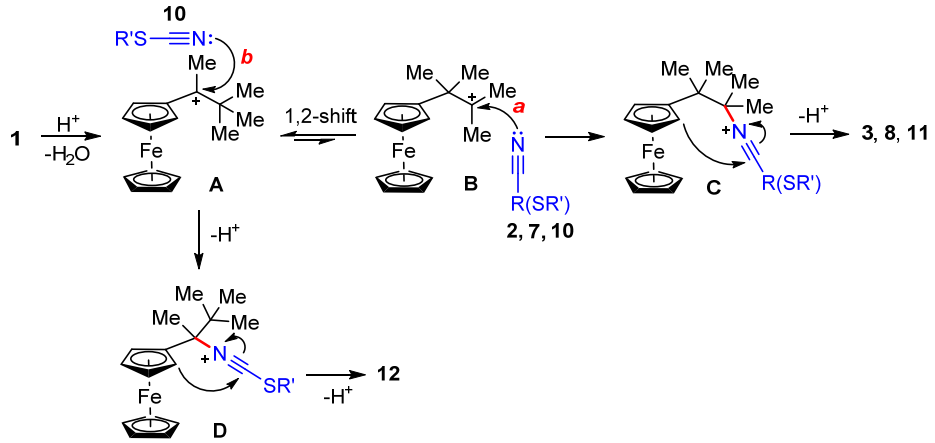
Entry	Thiocyanate 10	R	Temp. (°C)	Time	Products (Yield, %) [2]
1	**10g**	EtO	rt	1 h	**3u** (trace) [3], **11g** (6) [3], **12g** (73); [**11g**/**12g** = 4:96] [4]
2			80	15 min	**3u** (trace) 3, **11g** (27) 3, **12g** (26); [**11g**/**12g** = 59:41] [4]
3	**10h**	NH_2	rt	48 h	**1** (37), **5** + **6** (14) [**5**/**6** = 77:23] [5], **13** (13)
4			80	3 min	- [6]
5	**10i**	Ph	rt	48 h	**1** (20), **5** + **6** (18) [**5**/**6** = 55:45] [5], **10i** (38), **13** (51)
6			80	40 min	**3w** (8%), **5** + **6** (42) [**5**/**6** = 91:9] [5], **10i** (63)
7	**10j**	Me	rt	48 h	**5** + **6** (22) [**5**/**6** = 56:44] [5], **13** (48)
8			80	3 min	**3x** (trace) [4], **1** (38), **5** + **6** (20) [**5**/**6** = 96:4] [5]

[1] Reagents and conditions: **1** (0.35 mmol, 1 equiv.), **10g** (0.53 mmol, 1.5 equiv.), **10h–j** (0.42 mmol, 1.2 equiv.), $MeSO_3H$ (0.18 mL, 8 equiv.). [2] Isolated yields after silica gel column chromatography. [3] Isolated as a mixture of **11g** and **3u**. According to ^{1}H NMR analysis of the fraction of chromatography **11g**/**3u** ratios were found to be 99:1 (entry 1) and 96:4 (entry 2). [4] According to ^{1}H NMR analysis of the crude residues. [5] According to ^{1}H NMR analysis of the fraction of chromatography. [6] A complex mixture of unidentified products.

In contrast to ethyl 2-thiocyanatoacetate (**10g**), the reactions of alcohol **1** with *β*-oxothiocyanates **10h–j** at room temperature did not proceed (Table 6, entries 3, 5, and 7). In these cases the starting alcohol **1** together with alcohol **13** and inseparable mixtures of alkenes **5** and **6** were isolated. Among thiocyanates **10h–j** only **10i** was recovered in 38% yield. According to the ^{1}H NMR analysis of the crude residue, the condensation of **1** with 2-thiocyanatoacetamide (**10h**) at 80 °C resulted in the formation of a complex mixture of unidentified products, which were not isolated (Table 6, entry 4). Reaction with phenacyl thiocyanate (**10i**) at 80 °C within 40 min afforded 8% of ferroceno[*c*]pyridine **3w** (Table 6, entry 6), along with a mixture of alkenes **5** and **6** in a 42% overall yield, and 63% of recovered thiocyanate **10i**. It should be noted that the yield of the product **3w** remained at the same level upon an increase in the reaction time up to 1.5 h. According to the ^{1}H NMR spectrum of the crude residue, 2-oxopropyl thiocyanate (**10j**) at 80 °C gave trace amounts of ferroceno[*c*]pyridine **3x**, which was not isolated. Only an inseparable mixture of alkenes **5** and **6** in 20% yield together with 38% of starting alcohol **1** were isolated (Table 6, entry 8). Similar to the formation of **3u** from **11g**, products **3w** and **3x**, are assumed to be formed via sulfur extrusion from thioimines **11i** and **11j**, respectively. However, we could neither isolate nor detect ferroceno[*c*]pyridines **11i** and **11j** by ^{1}H NMR and GS-MS analysis of the crude residues.

The proposed mechanism for the formation of ferroceno[*c*]pyridines **3**, **8**, **11** and ferroceno[*c*]pyrroles **12** is shown in Scheme 1. The reaction includes initial acid-promoted ionization of starting alcohol **1** with the formation of tertiary *α*-ferrocenyl carbocation **A**, which is in an equilibrium with isomeric tertiary *β*-ferrocenyl carbocation **B**. The latter

reacts with nitriles **2**, **7**, or **10** to give nitrilium ion **C** (path a), the intramolecular cyclization of which then provides ferroceno[*c*]pyridines **3**, **8**, and **11**. Thiocyanates **10**, being more nucleophilic than nitriles **2** and **7** because of the influence of an electron-donating sulfur atom, may react not only with carbocation **B** but also with the less electrophilic *α*-ferrocenyl carbocation **A**, to form nitrilium ion **D** (path b). Subsequent intramolecular cyclization of the intermediate **D** gives ferroceno[*c*]pyrroles **12**.



Scheme 1. Proposed reaction mechanism.

The lower electrophilicity of *α*-ferrocenyl carbocation **A** compared to *β*-ferrocenyl carbocation **B** is due to the extensive delocalization of the positive charge with the participation of the ferrocenyl moiety. At room temperature an equilibrium between carbocations **A** and **B** is shifted towards the thermodynamically more stable *α*-ferrocenyl carbocation **A**, which explains the predominant formation of ferroceno[*c*]pyrroles **12** at these conditions. An increase in the reaction temperature shifts the **A**↔**B** equilibrium towards the carbocation **B**, which causes an increase in the selectivity of the formation of ferroceno[*c*]pyridines **11**.

3. Material and Methods

3.1. General Information

Thin-layer chromatography was performed on commercially available Sorbfil silica gel plates, which were visualized under UV light (254 nm). Column chromatography was performed on silica gel 60 (0.063–0.200 mm, Macherey-Nagel). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance NEO 400 spectrometer using $CDCl_3$, DMSO-d_6, or C_6D_6 as solvents. Chemical shifts are quoted on the δ scale, parts per million (ppm). The ^{1}H chemical shifts were measured relative to the internal standard HMDSO (δ_H 0.055 ppm) for $CDCl_3$ and DMSO-d_6, or residual C_6H_6 (δ_H 7.16 ppm) for C_6D_6. The ^{13}C chemical shifts were measured relative to the solvent signal (δ_C 77.16 ppm for $CDCl_3$, δ_C 39.50 ppm for DMSO-d_6, δ_C 128.06 ppm for C_6D_6). The ^{19}F chemical shifts were measured relative to the internal standard C_6F_6. The assignment of primary (CH_3), secondary (CH_2), tertiary (CH), and quaternary (C) carbon nuclei was made by using DEPT-135 spectra. The signals in the ^{1}H and ^{13}C NMR spectra of compounds **3a**, **3u**–**x**, **11a**, and **12a** were assigned based on 2D ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC and ^{1}H–^{1}H NOESY experiments. Copies of NMR spectra for all new compounds are deposited in the Supplementary Materials. Low-resolution mass spectra were obtained with an Agilent 6890N/5975B GC–MS system (column: HP-5ms, 15 or 30 m × 0.25 mm, 0.25 μm; helium as a carrier gas, 1 mL/min, electron impact ionization mode (230 °C, 70 eV)) and Agilent 7890B/5977B GC–MS system (column: HP-5ms UI, 30 m × 0.25 mm, 0.25 μm; helium as a carrier gas, 1 mL/min, electron impact ionization mode (230 °C, 70 eV)). High-resolution mass spectra were recorded with a Bruker maXis HD UHR-QTOF mass spectrometer equipped with an electrospray ionization ion source. Infrared spectra were recorded on a Bruker IFS 66 FT-IR spectrometer. Elemental analysis

was carried out on a Vario EL Cube analyzer. Melting points were determined using a PTP apparatus and are uncorrected.

2-Ferrocenyl-3,3-dimethylbutan-2-ol (**1**), ethyl 2-thiocyanatoacetate (**10g**) and 2-oxopropyl thiocyanate (**10j**) were synthesized as described below. 3-Oxo-3-phenylpropanenitrile (**2w**) [55], 3-oxobutyronitrile **2x** [56], propyl thiocyanate (**10c**) [57], hexyl thiocyanate (**10f**) [57], 2-thiocyanatoacetamide (**10h**) [58] and phenacyl thiocyanate (**10i**) [59] were prepared as previously described. All other chemicals were purchased from commercial suppliers and used without further purification.

3.2. Experimental Procedures and Characterization Data of the New Compounds

3.2.1. Synthesis of 2-Ferrocenyl-3,3-dimethylbutan-2-ol (**1**)

To a stirred solution of 1-ferrocenyl-2,2-dimethylpropan-1-one [60] (4.05 g, 10 mmol) in Et_2O (100 mL) was added dropwise a solution of MeMgI prepared from Mg (2.30 g, 96 mmol) and MeI (7.47 mL, 120 mmol) in Et_2O (70 mL). The reaction mixture was refluxed for 5 h and left overnight at room temperature. The reaction mixture was then cooled in an ice bath, and saturated aqueous NH_4Cl solution (150 mL) was slowly added dropwise with vigorous stirring. The phases were separated, and the aqueous phase was extracted with Et_2O (40 mL × 3). The combined organic phases were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography (petroleum ether/EtOAc 30:1) to afford pure alcohol **1** (3.50 g, 82%) as a yellow solid; mp 93–93.5 °C (mp 93.5–94 °C (hexane) [61]); R_f 0.43 (petroleum ether/EtOAc 30:1). IR (thin film): 3560, 3102, 3087, 2982, 2958, 2910, 2872, 1479, 1460, 1410, 1390, 1360, 1313, 1217, 1109, 1078, 1036, 1027, 1006, 897, 843, 822, 810, 543, 492, 422 cm^{-1}. NMR data are in agreement with that previously published [62]. MS (EI) *m/z* (% relative intensity): 286 $[M]^+$ (14), 269 $[M–OH]^+$ (11), 268 $[M–H_2O]^+$ (56), 229 $[M–t\text{-}C_4H_9]^+$ (32), 186 $[C_5H_5FeC_5H_5]^+$ (100), 121 $[C_5H_5Fe]^+$ (28), 56 $[Fe]^+$ (11). Analysis calculated for $C_{16}H_{22}O$: C, 67.15; H, 7.75. Found: C, 67.45; H, 7.91.

3.2.2. Synthesis of Ethyl 2-Thiocyanatoacetate (**10g**) and 2-Oxopropyl Thiocyanate (**10j**)

The title compounds were synthesized according to the literature procedure [59] with slight modifications.

Compound **10g**. Well-ground NH_4SCN (2.09 g, 27.5 mmol) was added portionwise to a stirred solution of ethyl 2-bromoacetate (2.8 mL, 25 mmol) in *i*-PrOH (3 mL), and the resulting mixture was heated under reflux with stirring for 5 h. The reaction mixture was then cooled to room temperature, diluted with water (10 mL) until the complete dissolution of the precipitate, and extracted with EtOAc (10 mL × 3). The combined organic phases were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was dissolved in EtOH (20 mL), and charcoal (2 g) was added. The resulting mixture was stirred at room temperature for 30 min, and the charcoal was removed by filtration and washed with EtOH (5 mL). The combined filtrates were concentrated in vacuo to afford pure product **10g** (3.25 g, 90%) as a colorless liquid; R_f 0.30 (hexane/EtOAc 5:1). IR (thin film): 2987, 2943, 2161, 1739, 1369, 1306, 1272, 1188, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 4.28 (q, 2H, *J* = 7.1 Hz), 3.76 (s, 2H), 1.32 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.3 (C), 110.7 (C), 63.0 (CH_2), 35.1 (CH_2), 14.1 (CH_3). MS (EI) *m/z* (% relative intensity): 145 $[M]^+$ (11), 100 $[M–OC_2H_5]^+$ (12), 72 $[M–CH_2SCN]^+$ (13), 29 $[M–C_2H_5]^+$ (14). Analysis calculated for $C_5H_7NO_2S$: C, 41.37; H, 4.86; N, 9.65; S, 22.08. Found: C, 41.62; H, 5.03; N, 9.62, S, 22.22.

Compound **10j**. Well-ground NH_4SCN (2.09 g, 27.5 mmol) was added portionwise to a stirred solution of chloroacetone (2 mL, 25 mmol) in *i*-PrOH (3 mL), and the resulting mixture was stirred at room temperature for 20 h. The reaction mixture was then worked up as described for the preparation of compound **10g** to afford pure product **10j** (2.03 g, 71%) as a light yellow liquid; R_f 0.20 (hexane/EtOAc 5:1). IR (thin film): 2973, 2847, 2159, 2110, 2057, 1718, 1360, 190, 1157, 575, 563 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 4.02 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 198.7 (C), 111.3 (C), 44.4

(CH_2), 28.5 (CH_3). MS (EI) *m/z* (% relative intensity): 115 $[M]^+$ (11), 72 $[M–CH_3CO]^+$ (7), 43 $[M–CH_2SCN]^+$ (57). Analysis calculated for C_4H_5NOS: C, 41.72; H, 4.38; N, 12.16; S, 27.84. Found: C, 41.86; H, 4.27; N, 12.23, S, 28.06.

3.2.3. Synthesis of Ferroceno[*c*]pyridines **3a**–**m**, **o**–**s**, **u**–**x** (Table 2)

General Procedure (GP). Nitrile **2a**–**m, o**–**s, u**–**x** (0.42 mmol) was added to a stirred solution of alcohol **1** (100 mg, 0.35 mmol) in $MeSO_3H$ (0.18 mL) at room temperature, and the resulting mixture was heated at 60 °C in an oil bath with vigorous stirring for the indicated time (monitored by TLC). The reaction mixture was then cooled to room temperature, neutralized with 10% aq. Na_2CO_3 solution (3 mL) and extracted with EtOAc (10 mL × 4). The combined organic phases were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography.

rac-3,3,4,4-Tetramethyl-1-(4-methylphenyl)-3,4-dihydroferroceno[c]pyridine (**3a**). The title compound was prepared according to GP using 4-methylbenzonitrile (**2a**) (0.05 mL, 0.42 mmol); reaction time = 15 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3a** (98 mg, 73%) as an orange solid; mp 123.5–125 °C (hexane); R_f 0.08 (petroleum ether/EtOAc 25:1); R_f 0.30 (petroleum ether/TEA 100:1). IR (thin film): 3094, 2973, 2928, 2868, 1588, 1560, 1453, 1372, 1361, 1314, 1301, 1175, 1156, 1108, 1141, 1108, 1002, 933, 899, 822, 755, 745, 495, 467 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.96 (br d, 2H, *J* = 8.2 Hz, H2′, H6′), 7.31 (br d, 2H, *J* = 7.9 Hz, H3′, H5′), 4.45 (d, 2H, *J* = 1.9 Hz, H5, H6), 4.37 (t, 1H, *J* = 1.8 Hz, H7), 4.27 (s, 5H, H Cp), 2.41 (s, 3H, 4′-CH_3), 1.45 (s, 3H, 4-CH_3), 1.44 (s, 3H, 3-CH_3), 1.11 (s, 3H, 4-CH_3), 0.74 (s, 3H, 3-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 162.3 (C1), 138.5 (C4′), 135.7 (C1′), 128.3 (C3′, C5′), 127.1 (C2′, C6′), 98.3 (C4a), 71.4 (C7a), 69.4 (5 CH Cp), 66.9 (C5 or C6), 65.7 (C7), 65.4 (C5 or C6), 61.7 (C3), 33.9 (C4), 28.0 (4-CH_3), 24.4 (4-CH_3), 23.7 (3-CH_3), 23.1 (3-CH_3), 20.6 (4′-CH_3). MS (EI) *m/z* (% relative intensity): 385 $[M]^+$ (35), 370 $[M–CH_3]^+$ (100), 342 $[M–i\text{-}C_3H_7]^+$ (5), 329 $[M–C_4H_8]^+$ (18), 314 $[M–C_4H_8–CH_3]^+$ (11), 121 $[C_5H_5Fe]^+$ (15), 56 $[Fe]^+$ (5). Analysis calculated for $C_{24}H_{27}FeN$: C, 74.81; H, 7.06; N, 3.64. Found: C, 75.01; H, 7.19; N, 3.56.

rac-3,3,4,4-Tetramethyl-1-phenyl-3,4-dihydroferroceno[c]pyridine (**3b**). The title compound was prepared according to GP using benzonitrile (**2b**) (0.043 mL, 0.42 mmol); reaction time = 30 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3b** (97 mg, 75%) as a red solid; mp 103–105 °C (hexane); R_f 0.10 (petroleum ether/EtOAc 25:1); R_f 0.35 (petroleum ether/TEA 100:1). IR (thin film): 3093, 2973, 2930, 2868, 1592, 1565, 1452, 1372, 1361, 1317, 1302, 1174, 1156, 1108, 1002, 935, 897, 823, 780, 754, 725, 697, 473, 453 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 30 °C): δ 8.06–8.03 (m, 2H), 7.55–7.49 (m, 3H), 4.49 (d, 2H, *J* = 1.8 Hz), 4.40 (t, 1H, *J* = 1.8 Hz), 4.30 (s, 5H), 1.46 (s, 3H), 1.45 (s, 3H), 1.11 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 162.7 (C), 138.4 (C), 129.2 (CH), 127.9 (2 CH), 127.3 (2 CH), 98.3 (C), 71.3 (C), 69.6 (5 CH), 67.1 (CH), 65.8 (CH), 65.6 (CH), 61.9 (C), 33.9 (C), 28.1 (CH_3), 24.7 (CH_3), 23.8 (CH_3), 23.2 (CH_3). MS (EI) *m/z* (% relative intensity): 371 $[M]^+$ (47), 356 $[M–CH_3]^+$ (100), 328 $[M–i\text{-}C_3H_7]^+$ (6), 315 $[M–C_4H_8]^+$ (22), 300 $[M–C_4H_8–CH_3]^+$ (13), 121 $[C_5H_5Fe]^+$ (9), 56 $[Fe]^+$ (3). Analysis calculated for $C_{23}H_{25}FeN$: C, 74.40; H, 6.79; N, 3.77. Found: C, 74.70; H, 7.06; N, 3.77.

rac-1-(4-Methoxyphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3c**). The title compound was prepared according to GP using 4-methoxybenzonitrile (**2c**) (0.056 mg, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3c** (108 mg, 77%) as an orange solid; mp 140.5–142 °C (hexane); R_f 0.02 (petroleum ether/EtOAc 25:1); R_f 0.15 (petroleum ether/TEA 100:1). IR (thin film): 3091, 2973, 2933, 2868, 2836, 1608, 1589, 1562, 1513, 1453, 1441, 1372, 1361, 1309, 1251, 1168, 1155, 1108, 1033, 1002, 933, 899, 836, 825, 751, 660, 544, 518, 478, 461 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 60 °C): δ 8.07–8.03 (m, 2H), 7.07–7.03 (m, 2H), 4.45 (d, 2H, *J* = 1.9 Hz), 4.38 (t, 1H, *J* = 1.8 Hz),

4.27 (s, 5H), 3.86 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.12 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 161.9 (C), 160.3 (C), 130.8 (C), 128.8 (2 CH), 113.3 (2 CH), 98.3 (C), 71.4 (C), 69.5 (5 CH), 67.0 (CH), 66.0 (CH), 65.7 (CH), 61.7 (C), 55.1 (CH_3), 33.9 (C), 28.5 (CH_3), 24.2 (CH_3), 24.1 (CH_3), 23.0 (CH_3). MS (EI) *m/z* (% relative intensity): 401 $[M]^+$ (38), 386 $[M–CH_3]^+$ (100), 371 $[M–CH_2O]^+$ (7), 358 [M–*i*-C_3H_7 and/or M–CH_3–CO]$^+$ (6), 345 $[M–C_4H_8]^+$ (23), 330 $[M–C_4H_8–CH_3]^+$ (15), 165 (11), 134 (11), 121 $[C_5H_5Fe]^+$ (28), 56 $[Fe]^+$ (8). Analysis calculated for $C_{24}H_{27}FeNO$: C, 71.83; H, 6.78; N, 3.49. Found: C, 71.64; H, 7.13; N, 3.44.

rac-1-(3-Methoxyphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3d**). The title compound was prepared according to GP using 3-methoxybenzonitrile (**2d**) (0.051 mL, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3d** (110 mg, 78%) as an orange solid; mp 100–102 °C (hexane); R_f 0.03 (petroleum ether/EtOAc 25:1); R_f 0.20 (petroleum ether/TEA 100:1). IR (thin film): 3094, 2973, 2937, 2869, 2834, 1599, 1568, 1487, 1462, 1435, 1372, 1361, 1305, 1285, 1274, 1238, 1168, 1152, 1108, 1049, 1039, 1002, 948, 882, 824, 802, 791, 755, 742, 697, 663, 534, 516, 473, 449 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C): δ 7.61 (dt, 1H, *J* = 7.6, 1.3 Hz), 7.56 (dd, 1H, *J* = 2.7, 1.5 Hz), 7.41 (t, 1H, *J* = 7.9 Hz), 7.06 (ddd, 1H, *J* = 8.2, 2.7, 1.0 Hz), 4.47 (d, 2H, *J* = 1.8 Hz), 4.39 (t, 1H, *J* = 1.8 Hz), 4.27 (s, 5H), 3.88 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H), 1.11 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 162.5 (C), 158.9 (C), 139.8 (C), 129.0 (CH), 119.9 (CH), 114.9 (CH), 112.7 (CH), 98.3 (C), 71.3 (C), 69.6 (5 CH), 67.1 (CH), 65.8 (CH), 65.6 (CH), 62.0 (C), 55.1 (CH_3), 33.9 (C), 28.1 (CH_3), 24.6 (CH_3), 23.8 (CH_3), 23.2 (CH_3). MS (EI) *m/z* (% relative intensity): 401 $[M]^+$ (51), 386 $[M–CH_3]^+$ (100), 371 $[M–CH_2O]^+$ (6), 358 [M–*i*-C_3H_7 and/or M–CH_3–CO]$^+$ (6), 345 $[M–C_4H_8]^+$ (22), 330 $[M–C_4H_8–CH_3]^+$ (12), 121 $[C_5H_5Fe]^+$ (10), 56 $[Fe]^+$ (3). Analysis calculated for $C_{24}H_{27}FeNO$: C, 71.83; H, 6.78; N, 3.49. Found: C, 72.05; H, H 7.20; N, 3.49.

rac-1-(2-Methoxyphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3e**). The title compound was prepared according to GP using 2-methoxybenzonitrile (**2e**) (0.051 mL, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3e** (88 mg, 63%) as a brown solid; mp 100–101 °C (hexane); R_f 0.05 (petroleum ether/EtOAc 25:1); R_f 0.25 (petroleum ether/TEA 100:1). IR (thin film): 3096, 2972, 2933, 2869, 2834, 1597, 1494, 1463, 1435, 1372, 1361, 1312, 1267, 1243, 1153, 1117, 1108, 1049, 1027, 1003, 939, 922, 900, 821, 751, 659, 512, 476, 455 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.42–7.38 (m, 1H), 7.28 (dd, 1H, *J* = 7.4, 1.7 Hz), 7.11 (br d, 1H, *J* = 8.3 Hz), 7.05 (td, 1H, *J* = 7.4, 1.0 Hz), 4.32 (dd, 1H, *J* = 2.2, 1.2 Hz), 4.29 (t, 1H, *J* = 2.4 Hz), 4.12 (s, 5H), 4.02 (dd, 1H, *J* = 2.4, 1.2 Hz), 3.79 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 1.01 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 162.9 (C), 156.3 (C), 129.6 (C), 129.0 (CH), 128.9 (CH), 119.9 (CH), 111.6 (CH), 97.7 (C), 73.3 (C), 69.2 (5 CH), 66.6 (CH), 64.3 (CH), 64.0 (CH), 61.4 (C), 55.5 (CH_3), 34.1 (C), 26.2 (CH_3), 26.2 (CH_3), 24.4 (CH_3), 22.7 (CH_3). MS (EI) *m/z* (% relative intensity): 401 $[M]^+$ (100), 386 $[M–CH_3]^+$ (61), 371 $[M–CH_2O]^+$ (11), 358 [M–*i*-C_3H_7 and/or M–CH_3–CO]$^+$ (15), 345 $[M–C_4H_8]^+$ (50), 330 $[M–C_4H_8–CH_3]^+$ (11), 263 (10), 121 $[C_5H_5Fe]^+$ (9), 56 $[Fe]^+$ (3). Analysis calculated for $C_{24}H_{27}FeNO{\cdot}0.15C_6H_{14}$: C, 72.20; H, 7.08; N, 3.38. Found: C, 72.43; H, 7.10; N, 3.05.

rac-4-(3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridin-1-yl)aniline (**3f**). The title compound was prepared according to GP using 4-aminobenzonitrile (**2f**) (49 mg, 0.42 mmol); reaction time = 50 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 5:1–petroleum ether/TEA 100:1) gave pure compound **3f** (89 mg, 66%) as an orange solid; mp 167.5–169 °C (hexane); R_f 0.02 (petroleum ether/EtOAc 5:1); R_f 0.30 (petroleum ether/TEA 100:1). IR (thin film): 3464, 3433, 3378, 3321, 3204, 3094, 2973, 2931, 2868, 1621, 1609, 1584, 1556, 1518, 1454, 1372, 1361, 1315, 1296, 1171, 1155, 1107, 1002, 834, 754, 660, 504, 470 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.88–7.85 (m, 2H), 6.68–6.65 (m, 2H), 5.31 (br s, 2H), 4.44–4.42 (m, 2H), 4.37 (t, 1H, *J* = 1.8 Hz), 4.26 (s, 5H), 1.44 (s, 3H), 1.39 (s, 3H), 1.12 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C):

δ 161.8 (C), 150.1 (C), 128.6 (2 CH), 126.0 (C), 112.8 (2 CH), 98.4 (C), 71.9 (C), 69.4 (5 CH), 66.6 (CH), 66.3 (CH), 65.4 (CH), 61.4 (C), 33.9 (C), 28.7 (CH_3), 24.4 (CH_3), 24.0 (CH_3), 23.0 (CH_3). MS (EI) *m/z* (% relative intensity): 386 $[M]^+$ (44), 371 $[M–CH_3]^+$ (100), 330 $[M–C_4H_8]^+$ (19), 315 $[M–C_4H_8–CH_3]^+$ (12), 121 $[C_5H_5Fe]^+$ (10), 56 $[Fe]^+$ (4). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{23}H_{27}FeN_2$, 387.1518; found, 387.1523.

rac-2-(3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridin-1-yl)aniline (**3g**). The title compound was prepared according to GP using 2-aminobenzonitrile (**2g**) (49 mg, 0.42 mmol); reaction time = 180 min. Purification by silica gel column chromatography (petroleum ether/acetone 15:1) gave pure compound **3g** (40 mg, 30%) as an orange oil; R_f 0.20 (petroleum ether/acetone 15:1). IR (thin film): 3452, 3202, 3093, 2973, 2929, 2868, 1613, 1580, 1540, 1450, 1372, 1361, 1308, 1264, 1159, 1108, 1002, 936, 818, 750, 659, 493, 472, 453 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 8.25 (dd, 1H, *J* = 7.9, 1.6 Hz), 7.14–7.10 (m, 1H), 6.87 (br s, 2H), 6.75 (dd, 1H, *J* = 8.2, 1.3 Hz), 6.70–6.65 (m, 1H), 4.47 (t, 1H, *J* = 2.4 Hz), 4.44 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.33 (dd, 1H, *J* = 2.5, 1.2 Hz), 4.29 (s, 5H), 1.46 (s, 3H), 1.43 (s, 3H), 1.13 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 165.3 (C), 148.5 (C), 130.1 (CH), 129.6 (CH), 118.0 (C), 116.0 (CH), 114.0 (CH), 98.1 (C), 71.9 (C), 69.6 (5 CH), 67.3 (CH), 67.1 (CH), 65.5 (CH), 61.6 (C), 33.2 (C), 28.2 (CH_3), 24.2 (CH_3), 23.8 (CH_3), 23.75 (CH_3). MS (EI) *m/z* (% relative intensity): 386 $[M]^+$ (100), 371 $[M–CH_3]^+$ (96), 330 $[M–C_4H_8]^+$ (27), 303 (10), 265 $[M–C_5H_5Fe]^+$ (11), 121 $[C_5H_5Fe]^+$ (16), 56 $[Fe]^+$ (7). Analysis calculated for $C_{23}H_{26}FeN_2$: C, 71.51; H, 6.78; N, 7.25. Found: C, 71.56; H, 7.17; N, 7.04.

rac-1-(4-Bromphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3h**). The title compound was prepared according to GP using 4-bromobenzonitrile (**2h**) (76 mg, 0.42 mmol); reaction time = 30 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3h** (129 mg, 82%) as a brown solid; mp 85–86.5 °C (hexane); R_f 0.12 (petroleum ether/EtOAc 25:1); R_f 0.40 (petroleum ether/TEA 100:1). IR (thin film): 3094, 2974, 2931, 2869, 1588, 1556, 1488, 1452, 1391, 1372, 1361, 1310, 1155, 1108, 1070, 1011, 934, 898, 824, 754, 697, 518, 506, 475, 440 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 8.00–7.99 (m, 2H), 7.68–7.65 (m, 2H), 4.43 (d, 2H, *J* = 1.8 Hz), 4.34 (t, 1H, *J* = 1.9 Hz), 4.24 (s, 5H), 1.40 (s, 6H), 1.07 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 161.6 (C), 137.4 (C), 130.8 (2 CH), 129.2 (2 CH), 122.6 (C), 98.2 (C), 70.9 (C), 69.4 (5 CH), 67.1 (CH), 65.6 (CH), 65.5 (CH), 62.0 (C), 33.8 (C), 28.0 (CH_3), 24.3 (CH_3), 23.6 (CH_3), 22.9 (CH_3). MS (EI) *m/z* (% relative intensity): 449 $[M]^+$ (64), 434 $[M–CH_3]^+$ (100), 406 $[M–i\text{-}C_3H_7]^+$ (4), 393 $[M–C_4H_8]^+$ (23), 378 $[M–C_4H_8–CH_3]^+$ (3), 369 $[M–HBr]^+$ (3), 314 (43), 299 (57), 191 (13), 121 $[C_5H_5Fe]^+$ (14), 56 $[Fe]^+$ (5). Analysis calculated for $C_{23}H_{24}BrFeN·0.1C_6H_{14}$: C, 61.78; H, 5.58; N, 3.05. Found: C, 61.61; H, 5.92; N, 3.05.

rac-1-(3-Bromphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3i**). The title compound was prepared according to GP using 3-bromobenzonitrile (**2i**) (76 mg, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3i** (125 mg, 80%) as a brown solid; mp 131–132 °C (hexane); R_f 0.03 (petroleum ether/EtOAc 25:1); R_f 0.35 (petroleum ether/TEA 100:1). IR (thin film): 3094, 2974, 2930, 2869, 1591, 1555, 1451, 1372, 1361, 1302, 1186, 1155, 1108, 1070, 999, 937, 902, 870, 824, 791, 756, 738, 709, 692, 518, 474, 453 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.23 (t, 1H, *J* = 1.8 Hz), 7.92 (dt, 1H, *J* = 7.8, 1.2 Hz), 7.53 (ddd, 1H, *J* = 7.9, 2.1, 1.1 Hz), 7.29 (t, 1H, *J* = 7.8 Hz), 4.35–4.33 (m, 2H), 4.27 (dd, 1H, *J* = 2.3, 1.4 Hz), 4.23 (s, 5H), 1.49 (s, 3H), 1.46 (s, 3H), 1.10 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): 163.5 (C), 141.4 (C), 132.3 (CH), 131.1 (CH), 129.9 (CH), 126.3 (CH), 122.4 (C), 99.2 (C), 71.9 (C), 70.0 (5 CH), 67.4 (CH), 66.2 (CH), 66.0 (CH), 62.9 (C), 34.7 (C), 28.7 (CH_3), 25.2 (CH_3), 24.0 (CH_3), 23.6 (CH_3). MS (EI) *m/z* (% relative intensity): 449 $[M]^+$ (90), 434 $[M–CH_3]^+$ (100), 406 $[M–i\text{-}C_3H_7]^+$ (10), 393 $[M–C_4H_8]^+$ (48), 378 $[M–C_4H_8–CH_3]^+$ (7), 314 (32), 299 (16), 249 (12), 234 (12), 218 (14), 191 (22), 121 $[C_5H_5Fe]^+$ (25), 56 $[Fe]^+$ (10). Analysis calculated for $C_{23}H_{24}BrFeN$: C, 61.36; H, 5.37; N, 3.11. Found: C, 61.60; H, 5.39; N, 3.04.

rac-1-(2-Bromphenyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3j**). The title compound was prepared according to GP using 2-bromobenzonitrile (**2j**) (76 mg, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3j** (120 mg, 76%) as an orange solid; mp 110–111 °C (hexane); R_f 0.02 (petroleum ether/EtOAc 25:1); R_f 0.20 (petroleum ether/TEA 100:1). IR (thin film): 3095, 2973, 2930, 2868, 1604, 1476, 1452, 1432, 1342, 1372, 1361, 1312, 1193, 1154, 1108, 1086, 1049, 1029, 1021, 1003, 923, 861, 822, 767, 751, 742, 693, 546, 486, 468, 447 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.65 (dd, 1H, *J* = 8.0, 1.1 Hz), 7.51–7.43 (m, 2H), 7.36–7.31 (m, 1H), 4.36 (dd, 2H, *J* = 2.4, 1.2Hz), 4.32 (t, 1H, *J* = 2.4 Hz), 4.17 (s, 5H), 3.90 (dd, 1H, *J* = 2.4, 1.1 Hz), 1.47 (s, 3H), 1.46 (s, 3H), 1.03 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): 163.4 (C), 140.1 (C), 132.3 (CH), 129.51 (C), 129.46 (C), 127.1 (CH), 120.2 (C), 97.8 (C), 71.8 (C), 69.4 (5 CH), 67.0 (CH), 64.4 (CH), 64.1 (CH), 61.8 (C), 34.1 (C), 26.6 (CH_3), 25.8 (CH_3), 24.4 (CH_3), 22.2 (CH_3). MS (EI) *m/z* (% relative intensity): 449 $[M]^+$ (100), 406 $[M–i\text{-}C_3H_7]^+$ (5), 393 $[M–C_4H_8]^+$ (28), 384 (13), 370 $[M–Br]^+$ (20), 355 $[M–CH_3–Br]^+$ (22), 354 $[M–CH_3–HBr]^+$ (22), 326 (19), 312 (18), 262 (11), 248 (59), 234 (62), 218 (22), 192 (29), 178 (31), 165 (15), 152 (10), 121 $[C_5H_5Fe]^+$ (18), 56 $[Fe]^+$ (8). Analysis calculated for $C_{23}H_{24}BrFeN·0.2C_6H_{14}$: C, 62.18; H, 5.78; N, 3.00. Found: C, 62.44; H, 5.63; N, 3.02.

rac-3,3,4,4-Tetramethyl-1-(4-(trifluoromethyl)phenyl)-3,4-dihydroferroceno[c]pyridine (**3k**). The title compound was prepared according to GP using 4-(trifluoromethyl)benzonitrile (**2k**) (71 mg, 0.42 mmol); reaction time = 15 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave pure compound **3k** (117 mg, 76%) as an orange solid; mp 121.5–123 °C (hexane); R_f 0.16 (petroleum ether/EtOAc 50:1); R_f 0.30 (petroleum ether/TEA 100:1). IR (thin film): 3095, 2976, 2934, 2871, 1620, 1594, 1564, 1453, 1373, 1362, 1327, 1313, 1165, 1127, 1107, 1081, 1067, 1018, 1003, 849, 824, 758, 474, 444 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 8.24 (br d, 2H, *J* = 7.9 Hz), 7.87 (br d, 2H, *J* = 7.9 Hz), 4.50 (d, 2H, *J* = 1.8 Hz), 4.41 (t, 1H, *J* = 1.8 Hz), 4.31 (s, 5H), 1.464 (s, 3H), 1.456 (s, 3H), 1.11 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): 161.8 (C), 141.9 (C), 129.3 (q, $^2J_{C,F}$ = 31.8 Hz, C), 127.9 (s, 2 CH), 124.8 (q, $^3J_{C,F}$ = 3.8 Hz, 2 CH), 124.1 (q, $^1J_{C,F}$ = 271.0 Hz, CF_3), 98.2 (C), 70.8 (C), 69.5 (5 CH), 67.2 (CH), 65.6 (CH), 65.4 (CH), 62.2 (C), 33.9 (C), 27.9 (CH_3), 24.5 (CH_3), 23.5 (CH_3), 23.0 (CH_3). ^{19}F NMR (377 MHz, DMSO-d_6, 50 °C): δ 101.5 (s, CF_3). MS (EI) *m/z* (% relative intensity): 439 $[M]^+$ (88), 424 $[M–CH_3]^+$ (60), 396 $[M–i\text{-}C_3H_7]^+$ (8), 383 $[M–C_4H_8]^+$ (55), 368 (16), 284 (100), 243 (11), 227 (13), 121 $[C_5H_5Fe]^+$ (13), 56 $[Fe]^+$ (3). Analysis calculated for $C_{24}H_{24}F_3FeN$: C, 65.62; H, 5.51; N, 3.19. Found: C, 65.92; H, 5.78; N, 3.11.

rac-3,3,4,4-Tetramethyl-1-(3-(trifluoromethyl)phenyl)-3,4-dihydroferroceno[c]pyridine (**3l**). The title compound was prepared according to GP using 3-(trifluoromethyl)benzonitrile (**2l**) (0.056 mL, 0.42 mmol); reaction time = 30 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave pure compound **3l** (129 mg, 84%) as a brown oil; R_f 0.15 (petroleum ether/EtOAc 50:1); R_f 0.30 (petroleum ether/TEA 100:1). IR (thin film): 3093, 2976, 2931, 2870, 1599, 1574, 1454, 1433, 1373, 1362, 1336, 1296, 1266, 1185, 1166, 1127, 1109, 1095, 1072, 1002, 825, 808, 702, 690, 473, 448 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 8.40–8.39 (m, 1H), 8.33–8.30 (m, 1H), 7.84–7.81 (m, 1H), 7.75–7.71 (m, 1H), 4.49–4.47 (m, 2H), 4.34 (dd, 1H, *J* = 2.4, 1.3 Hz), 4.27 (s, 5H), 1.419 (s, 3H), 1.415 (s, 3H), 1.10 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 161.5 (C), 138.9 (C), 131.0 (CH), 129.1 (CH), 128.8 (q, $^2J_{C,F}$ = 31.6 Hz, C), 125.6 (q, $^3J_{C,F}$ = 3.7 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 123.5 (q, $^3J_{C,F}$ = 4.2, CH), 98.3 (C), 70.8 (C), 69.4 (5 CH), 67.2 (CH), 65.8 (CH), 65.4 (CH), 62.2 (C), 33.9 (C), 28.2 (CH_3), 24.1 (CH_3), 23.6 (CH_3), 22.7 (CH_3). ^{19}F NMR (377 MHz, DMSO-d_6, 50 °C): δ 101.6 (s, CF_3). MS (EI) *m/z* (% relative intensity): 439 $[M]^+$ (100), 424 $[M–CH_3]^+$ (44), 396 $[M–i\text{-}C_3H_7]^+$ (17), 383 $[M–C_4H_8]^+$ (74), 368 $[M–C_4H_8–CH_3]^+$ (11), 284 (59), 121 $[C_5H_5Fe]^+$ (10), 56 $[Fe]^+$ (2). Analysis calculated for $C_{24}H_{24}F_3FeN$: C, 65.62; H, 5.51; N, 3.19. Found: C, 65.99; H, 5.63; N, 3.21.

rac-3,3,4,4-Tetramethyl-1-(2-(trifluoromethyl)phenyl)-3,4-dihydroferroceno[c]pyridine (**3m**). The title compound was prepared according to GP using 2-(trifluoromethyl)benzonitrile (**2m**) (0.056 mL, 0.42 mmol); reaction time = 40 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave pure compound **3m** (100 mg, 65%) as brown oil; R_f 0.04 (petroleum ether/EtOAc 50:1); R_f 0.20 (petroleum ether/TEA 100:1). IR (thin film): 3095, 2977, 2932, 2870, 1603, 1580, 1456, 1447, 1373, 1362, 1315, 1264, 1163, 1136, 1109, 1059, 1034, 1003, 823, 768, 683, 545, 449 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 30 °C): δ 7.80–7.76 (m, 2H), 7.65–7.61 (m, 2H), 4.36 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.33 (t, 1H, *J* = 2.5 Hz), 4.22 (s, 5H), 3.81 (dd, 1H, *J* = 2.5, 1.2 Hz), 1.46 (s, 3H), 1.45 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 162.1 (C), 138.1 (C, broad), 131.7 (CH), 129.8 (CH), 128.0 (CH), 126.3 (q, $^2J_{C,F}$ = 30.6 Hz, C), 126.0 (q, $^3J_{C,F}$ = 4.9 Hz, CH), 123.8 (q, $^1J_{C,F}$ = 274.3 Hz, CF_3), 97.8 (C), 72.2 (C), 69.5 (5 CH), 67.2 (CH), 64.1 (CH), 63.7 (CH), 61.7 (C), 34.2 (C), 26.8 (CH_3), 25.3 (CH_3), 24.5 (CH_3), 21.9 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6, 50 °C): δ 106.7 (s, CF_3). MS (EI) *m/z* (% relative intensity): 439 $[M]^+$ (100), 424 $[M–CH_3]^+$ (10), 396 $[M–i\text{-}C_3H_7]^+$ (19), 383 $[M–C_4H_8]^+$ (19), 368 $[M–C_4H_8–CH_3]^+$ (2), 284 (22), 121 $[C_5H_5Fe]^+$ (5), 56 $[Fe]^+$ (1). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{25}F_3FeN$, 440.1283; found, 440.1291.

rac-1,3,3,4,4-Pentamethyl-3,4-dihydroferroceno[c]pyridine (**3o**). The title compound was prepared according to GP using acetonitrile (**2o**) (0.02 mL, 0.42 mmol); reaction time = 15 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3o** (82 mg, 76%) as a red oil; R_f 0.07 (petroleum ether/EtOAc 25:1); R_f 0.25 (petroleum ether/TEA 100:1). IR (thin film): 3094, 2972, 2868, 1619, 1465, 1438, 1387, 1373, 1361, 1301, 1164, 1135, 1108, 1027, 1001, 854, 821, 658, 511, 487, 475, 458 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 30 °C): δ 4.46 (t, 1H, *J* = 1.8 Hz), 4.32 (d, 2H, *J* = 1.8 Hz), 4.23 (s, 5H), 2.18 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.00 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 162.5 (C), 97.8 (C), 73.5 (C), 69.2 (5 CH), 66.3 (CH), 65.1 (CH), 63.5 (CH), 61.2 (C), 33.9 (C), 28.2 (CH_3), 25.1 (CH_3), 23.8 (CH_3), 23.6 (CH_3), 22.7 (CH_3). MS (EI) *m/z* (% relative intensity): 309 $[M]^+$ (100), 294 $[M–CH_3]^+$ (24), 266 $[M–i\text{-}C_3H_7]^+$ (52), 251 $[M–i\text{-}C_3H_7–CH_3]^+$ (11), 226 (12), 186 $[C_5H_5FeC_5H_5]^+$ (13), 162 (14), 146 (11), 129 (10), 121 $[C_5H_5Fe]^+$ (44), 115 (20), 91 (10), 56 $[Fe]^+$ (19), 42 (12). Analysis calculated for $C_{18}H_{23}FeN$: C, 69.91; H, 7.88; N, 4.53. Found: C, 69.55; H, 7.89; N, 4.49.

rac-1-Ethyl-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3p**). The title compound was prepared according to GP using propiononitrile (**2p**) (0.03 mL, 0.42 mmol); reaction time = 20 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave pure compound **3p** (90 mg, 80%) as a red oil; R_f 0.05 (petroleum ether/EtOAc 50:1); R_f 0.10 (petroleum ether/TEA 100:1). IR (thin film): 3095, 2972, 2932, 2870, 1615, 1465, 1442, 1387, 1360, 1287, 1248, 1194, 1158, 1128, 1108, 1028, 1002, 922, 870, 821, 511, 482 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 4.33 (dd, 1H, *J* = 2.4, 1.1 Hz), 4.25 (t, 1H, *J* = 2.4 Hz), 4.20 (dd, 1H, *J* = 2.4, 1.1 Hz), 4.15 (s, 5H), 2.50 (qt, 2H, *J* = 7.6, 3.6 Hz), 1.40 (s, 6H), 1.25 (t, 3H, *J* = 7.6 Hz), 0.97 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 168.0 (C), 99.0 (C), 73.1 (C), 69.7 (5 CH), 66.9 (CH), 65.0 (CH), 63.7 (CH), 61.4 (C), 34.7 (C), 30.6 (CH_2), 27.7 (CH_3), 26.3 (CH_3), 24.5 (CH_3), 23.6 (CH_3), 13.1 (CH_3). MS (EI) *m/z* (% relative intensity): 323 $[M]^+$ (100), 308 $[M–CH_3]^+$ (18), 280 $[M–i\text{-}C_3H_7]^+$ (34), 267 $[M–C_4H_8]^+$ (18), 265 $[M–i\text{-}C_3H_7–CH_3]^+$ (13), 121 $[C_5H_5Fe]^+$ (20), 56 $[Fe]^+$ (9). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{26}FeN$, 324.1409; found, 324.1411.

rac-1-Isobutyl-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3q**). The title compound was prepared according to GP using isovaleronitrile (**2q**) (0.044 mL, 0.42 mmol); reaction time = 15 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave pure compound **3q** (92 mg, 75%) as a red oil; R_f 0.07 (petroleum ether/EtOAc 25:1); R_f 0.30 (petroleum ether/TEA 100:1). IR (thin film): 3097, 2969, 2930, 2868, 1613, 1464, 1386, 1372, 1361, 1304, 1259, 1245, 1224, 1194, 1159, 1144, 1135, 1108, 1028, 1002, 862, 821, 754, 510, 447 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 50 °C): δ 4.06 (dd, 1H, *J* = 2.5, 1.1 Hz), 4.00 (s, 6H), 3.96 (t, 1H, *J* = 2.4 Hz), 2.49–2.32 (m, 3H), 1.52 (s, 3H), 1.37 (s, 3H), 1.09 (d, 3H, *J* = 6.2 Hz), 1.06 (d, 3H, *J* = 6.3 Hz,), 1.01 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, C_6D_6, 50 °C): δ 164.3 (C), 99.2 (C), 74.8 (C), 69.8 (5 CH), 66.8 (CH), 65.0 (CH), 63.6 (CH), 61.9 (C), 46.0 (CH_2), 34.9 (C), 28.0 (CH_3), 26.8 (CH), 26.3 (CH_3), 24.8 (CH_3), 24.0 (CH_3), 23.2 (CH_3), 23.0 (CH_3). MS (EI) *m/z* (% relative intensity): 351 $[M]^+$ (100), 336 $[M–CH_3]^+$ (45), 308 $[M–i\text{-}C_3H_7]^+$ (40), 251 (19), 121 $[C_5H_5Fe]^+$ (47), 56 $[Fe]^+$ (12). Analysis calculated for $C_{21}H_{29}FeN$: C, 71.80; H, 8.32; N, 3.99. Found: C, 71.82; H, 8.73; N, 3.80.

rac-1-(Adamantan-1-yl)methyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3r**). The title compound was prepared according to GP using 1-adamantaneacetonitrile (**2r**) (61 mg, 0.42 mmol); reaction time = 25 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave pure compound **3r** (113 mg, 73%) as a red solid; mp 137–139.5 °C (MeOH); R_f 0.10 (petroleum ether/EtOAc 50:1); R_f 0.40 (petroleum ether/TEA 100:1). IR (thin film): 3096, 2970, 2902, 2846, 1460, 1387, 1372, 1360, 1314, 1293, 1262, 1208, 1150, 1121, 1108, 1029, 1002, 821, 753, 660, 508, 448 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 4.11 (dd, 1H, *J* = 2.5, 1.2 Hz), 4.01 (s, 5H), 3.99 (dd, 1H, *J* = 2.4, 1.1 Hz), 3.96 (t, 1H, *J* = 2.4 Hz), 2.41 (d, 1H, *J* = 13.0 Hz), 2.35 (d, 1H, *J* = 13.0 Hz), 2.00–1.90 (m, 6H), 1.76–1.70 (m, 9H), 1.55 (s, 3H), 1.36 (s, 3H), 1.11 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 163.5 (C), 99.3 (C), 76.0 (C), 69.9 (5 CH), 66.9 (CH), 64.70 (CH), 64.68 (CH), 61.9 (C), 50.5 (CH_2), 43.8 (3 CH_2), 37.6 (3 CH_2), 34.7 (C), 34.4 (C), 29.5 (3 CH), 27.6 (CH_3), 26.8 (CH_3), 25.5 (CH_3), 23.8 (CH_3). MS (EI) *m/z* (% relative intensity): 443 $[M]^+$ (100), 428 $[M–CH_3]^+$ (11), 400 $[M–i\text{-}C_3H_7]^+$ (33), 385 $[M–i\text{-}C_3H_7–CH_3]^+$ (12), 359 (44), 308 $[M–Ad]^+$ (12), 251 (19), 135 $[Ad]^+$ (14), 121 $[C_5H_5Fe]^+$ (33), 56 $[Fe]^+$ (6). Analysis calculated for $C_{28}H_{37}FeN{\cdot}0.55MeOH$: C, 74.37; H, 8.57; N, 3.04. Found: C, 74.73; H, 8.95; N, 3.00.

rac-1-(Adamantan-1-yl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**3s**). The title compound was prepared according to GP using adamantane-1-carbonitrile (**2s**) (68 mg, 0.42 mmol); reaction time = 20 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 75:1–petroleum ether/TEA 100:1) gave pure compound **3s** (107 mg, 71%) as an orange oil; R_f 0.10 (petroleum ether/EtOAc 75:1); R_f 0.40 (petroleum ether/TEA 100:1). IR (thin film): 3096, 2970, 2927, 2903, 2848, 1597, 1450, 1370, 1359, 1292, 1250, 1162, 1108, 1002, 820, 758, 475, 456 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 50 °C): δ 4.34 (dd, 1H, *J* = 2.5, 1.1 Hz), 4.04 (t, 1H, *J* = 2.5 Hz), 4.02 (s, 5H), 4.00 (dd, 1H, *J* = 2.5, 1.1 Hz), 2.22–2.11 (m, 6H), 2.09–2.06 (m, 3H), 1.79 (br t, 6H, *J* = 3.2 Hz), 1.51 (s, 3H), 1.34 (s, 3H), 1.05 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 50 °C): δ 169.3 (C), 100.2 (C), 70.8 (C), 70.1 (5 CH), 67.2 (CH), 66.4 (CH), 63.9 (CH), 60.9 (C), 42.2 (C), 41.8 (3 CH_2), 37.7 (3 CH_2), 34.6 (C), 29.6 (3 CH), 26.7 (CH_3), 26.4 (CH_3), 25.1 (CH_3), 23.6 (CH_3). MS (EI) *m/z* (% relative intensity): 429 $[M]^+$ (100), 414 $[M–CH_3]^+$ (14), 386 $[M–C_3H_7]^+$ (17), 373 $[M–C_4H_8]^+$ (37), 294 $[M–Ad]^+$ (11), 121 $[C_5H_5Fe]^+$ (11), 56 $[Fe]^+$ (2). Analysis calculated for $C_{27}H_{35}FeN$: C, 75.52; H, 8.22; N, 3.26. Found: C, 74.98; H, 8.49; N, 3.04.

rac-Ethyl (Z)-2-(3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridin-1(2H)-ylidene)acetate (**3u**). The title compound was prepared according to GP using ethyl cyanoacetate **2u** (0.045 mL, 0.42 mmol); reaction time = 20 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1) gave pure product **3u** (79 mg, 59%) as an orange oil; R_f 0.30 (petroleum ether/EtOAc 25:1). IR (thin film): 3288, 3096, 2975, 2930, 2870, 1646, 1602, 1499, 1465, 1442, 1366, 1295, 1187, 1154, 1108, 1072, 1044, 1002, 822, 784, 756, 629, 470 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.23 (br d, 1H, NH), 4.84 (s, 1H, H2), 4.53 (dd, 1H, *J* = 2.5, 1.2 Hz, H7′), 4.27 (t, 1H, *J* = 2.5 Hz, H6′), 4.21 (dd, 1H, *J* = 2.5, 1.2 Hz, H5′), 4.18–4.09 (m, 2H, $OC\underline{H}_2CH_3$, partially overlapped), 4.14 (s, 5H, H Cp), 1.55 (s, 3H, 4′-CH_3), 1.37 (s, 3H, 3′-CH_3), 1.30 (t, 3H, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$), 1.06 (s, 3H, 4′-CH_3), 0.95 (s, 3H, 3′-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 170.9 (C1), 160.7 (C1′), 98.3 (C4a′), 78.6 (C2), 74.1 (C7a′), 70.5 (5 CH, Cp), 67.3 (C6′), 66.0 (C5′), 64.2 (C7′), 58.4 ($O\underline{C}H_2CH_3$), 57.5 (C3′), 36.4 (C4′), 28.9 (4′-CH_3), 25.8 (3′-CH_3), 25.1 (4′-CH_3), 23.8 (3′-CH_3), 14.9 ($OCH_2\underline{C}H_3$). GC–MS analyses of product **3u** indicated the presence of a peak in the chromatogram that, based on its MS spectra, belonged to compound **3o**. The latter was likely produced by the thermolysis of the parent compound in the GC instrument injector. HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{28}FeNO_2$, 382.1464; found, 382.1458.

rac-(Z)-2-(3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridin-1(2H)-ylidene)acetamide (**3v**). The title compound was prepared according to GP using cyanoacetamide **2v** (35 mg, 0.42 mmol); reaction time = 30 min. Purification by silica gel column chromatography (petroleum ether/acetone 3:1) followed by recrystallization from hexane gave pure product **3v** (42 mg, 34%) as an orange solid, m.p. 147–149 °C (hexane); R_f 0.30 (petroleum ether/acetone 3:1). IR (thin film): 3440, 3326, 3213, 3098, 2972, 2927, 2870, 2856, 1684, 1621, 1572, 1457, 1364, 1337, 1151, 1108, 1002, 823, 756, 666, 507, 471 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$,30 °C): δ 8.80 (br s, 1H, NH), 4.74 (s, 1H, H2), 4.67 (br s, 2H, NH_2), 4.47 (dd, 1H, *J* = 2.5, 1.2 Hz, H7′), 4.24 (t, 1H, *J* = 2.5 Hz, H6′), 4.20 (dd, 1H, *J* = 2.5, 1.2 Hz, H5′), 4.14 (s, 5H, H Cp), 1.55 (s, 3H, 4′-CH_3), 1.36 (s, 3H, 3′-CH_3), 1.05 (s, 3H, 4′-CH_3), 0.94 (s, 3H, 3′-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 172.9 (C1), 158.9 (C1′), 98.5 (C4a′), 80.0 (C2), 74.4 (C7a′), 70.4 (5 CH, Cp), 66.9 (C6′), 65.9 (C5′), 63.6 (C7′), 57.1 (C3′), 36.3 (C4′), 28.8 (4′-CH_3), 25.8 (3′-CH_3), 25.1 (4′-CH_3), 23.8 (3′-CH_3). GC–MS analyses of product **3v** indicated the presence of a peak in the chromatogram that, based on its MS spectra, belonged to compound **3o**. The latter was likely produced by the thermolysis of the parent compound in the GC instrument injector. HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{25}FeN_2O$, 353.1311; found, 353.1307.

rac-(Z)-1-Phenyl-2-(3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridin-1(2H)-ylidene)ethan-1-one (**3w**). The title compound was prepared according to GP using 3-oxo-3-phenylpropanenitrile **2w** (61 mg, 0.42 mmol); reaction time = 20 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 10:1) gave pure compound **3w** (126 mg, 87%) as a red oil; R_f 0.30 (petroleum ether/EtOAc 10:1). IR (thin film): 2975, 2929, 1594, 1580, 1543, 1451, 1438, 1366, 1324, 1304, 1265, 1229, 1153, 1108, 1055, 1026, 1002, 824, 755, 732, 711, 620, 512, 487, 461 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 10.99 (br d, 1H, NH), 7.95–7.91 (m, 2H, H2″, H6″), 7.44–7.41 (m, 3H, H3″, H4″, H5″), 5.98 (s, 1H, H2), 4.69 (dd, 1H, *J* = 2.6, 1.2 Hz, H7′), 4.38 (t, 1H, *J* = 2.5 Hz, H6′), 4.31 (dd, 1H, *J* = 2.5, 1.2 Hz, H5′), 4.18 (s, 5H, H Cp), 1.57 (s, 3H, 4′-CH_3), 1.46 (s, 3H, 3′-CH_3), 1.10 (s, 3H, 4′-CH_3), 1.03 (s, 3H, 3′-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 187.2 (C1), 163.2 (C1′), 141.2 (C1″), 130.4 (C4″), 128.3 (C3″, C5″), 127.0 (C2″, C6″), 98.3 (C4a′), 88.0 (C2), 73.5 (C7a′), 70.7 (5 CH, Cp), 67.9 (C6′), 66.6 (C5′), 64.8 (C7′), 57.9 (C3′), 36.3 (C4′), 28.8 (4′-CH_3), 25.7 (3′-CH_3), 25.0 (4′-CH_3), 23.5 (3′-CH_3). MS (EI) *m/z* (% relative intensity): 413 $[M]^+$ (100), 370 $[M–i\text{-}C_3H_7]^+$ (19), 348 (42), 308 $[M–C(O)C_6H_5]^+$ (12), 121 $[C_5H_5Fe]^+$ (9), 56 $[Fe]^+$ (2). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{25}H_{28}FeNO$, 414.1420; found, 414.1515.

rac-(Z)-1-(3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridin-1(2H)-ylidene)propan-2-one (**3x**). The title compound was prepared according to GP using 3-oxobutyronitrile **2x** (0.036 mL, 0.42 mmol); reaction time = 20 min. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1) gave pure compound **3x** (99 mg, 81%) as a red oil, which solidified on long-term standing; mp 158.5–162 °C; R_f 0.20 (petroleum ether/EtOAc 25:1). IR (thin film): 3094, 2974, 2927, 2870, 1603, 1566, 1509, 1449, 1365, 1354, 1317, 1262, 1201, 1153, 1108, 1005, 961, 823, 757, 715, 508, 469 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 10.43 (br s, 1H, NH), 5.28 (s, 1H, H2), 4.55 (dd, 1H, *J* = 2.5, 1.2 Hz, H7′), 4.32 (t, 1H, *J* = 2.5 Hz, H6′), 4.25 (dd, 1H, *J* = 2.4, 1.1 Hz, H5′), 4.15 (s, 5H, H Cp), 2.07 (s, 3H, 1-CH_3), 1.53 (s, 3H, 4′-CH_3), 1.39 (s, 3H, 3′-CH_3), 1.06 (s, 3H, 4′-CH_3), 0.97 (s, 3H, 3′-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 194.3 (C1), 161.2 (C1′), 98.4 (C4a′), 91.1(C2), 73.2 (C7a′), 70.6 (5 CH, Cp), 67.6 (C6′), 66.4 (C5′), 64.5 (C7′), 57.5 (C3′), 36.2 (C4′), 29.2 (1-CH_3), 28.7 (4′-CH_3), 25.6 (3′-CH_3), 25.1 (4′-CH_3), 23.6 (3′-CH_3). MS (EI) *m/z* (% relative intensity): 351 $[M]^+$ (100), 308 $[M–C(O)CH_3)$ or/and $i\text{-}C_3H_7]^+$ (27), 286 (61), 242 (10), 228 (10), 121 $[C_5H_5Fe]^+$ (9), 56 $[Fe]^+$ (2). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{20}H_{26}FeNO$, 352.1358; found, 352.1354.

3.2.4. Synthesis of Ferroceno[*c*]pyridines **8a–c** and **9a–c** (Table 3)

General Procedure 1 (GP1). Phenylacetonitrile **7a–c** (0.42 mmol) was added to the stirred solution of alcohol **1** (100 mg, 0.35 mmol) in $MeSO_3H$ (0.18 mL) at room temperature, and the resulting mixture was heated at 60 °C in an oil bath with vigorous stirring for the indicated time (monitored by TLC). The reaction mixture was then cooled to room temperature, neutralized with 10% aq. Na_2CO_3 solution (3 mL), and extracted with EtOAc

(10 mL × 4). The combined organic phases were washed with water, dried over anhydrous Na_2SO_4, and filtered. *Method A*: Dried organic extract was concentrated in vacuo, and the crude residue was purified by silica gel column chromatography to obtain a mixture of compounds **8a–c** and **9a–c**; the ratios of **8a–c** and **9a–c** were determined by NMR ^{1}H immediately after the isolation of the mixed fraction. Storage of this mixture at room temperature exposed to air until full conversion of **8a–c** to **9a–c** (monitored by TLC, reaction time 1), followed by purification by silica gel column chromatography, afforded pure compound **9a–c**. *Method B:* Dried organic extract was stored at room temperature exposed to air until full conversion of **8a–c** to **9a–c** (monitored by TLC, reaction time 1) and then concentrated in vacuo. The crude residue was purified by silica gel column chromatography to afford pure compound **9a–c**.

rac-1-(3,4-Dimethoxybenzyl)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**8a**) *and rac-(3,4-Dimethoxyphenyl)(3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine)methanone* (**9a**). The title compounds were prepared according to GP1 using 3,4-dimethoxyphenylacetonitrile (**7a**) (74 mg, 0.42 mmol); reaction time = 10 min; reaction time 1 = 1 day. *Method A*: Purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 3:1–petroleum ether/EtOAc/Et_3N 100:5:3) gave an inseparable mixture of **7a**, **8a** and **9a** (108 mg, **7a**/**8a**/**9a** = 31:54:15; **8a**/**9a** = 78:22). Storage of the mixture of **7a**, **8a** and **9a** at room temperature exposed to air until full conversion of **8a** to **9a**, followed by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 25:1), afforded pure compound **9a** (39 mg, 24%). *Method B*: Purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 25:1) gave pure **9a** (33 mg, 21%). Data for **8a** [spectroscopic data for **8a** were obtained only from the mixture of **7a**, **8a** and **9a**]: R_f 0.15 (petroleum ether/EtOAc 5:1). ^{1}H NMR (DMSO-d_6, 400 MHz, 30 °C): δ 7.04 (d, 1H, J = 1.8 Hz), 7.01–6.94 (m, 2H, overlapped), 4.32–4.24 (m, 3H), 4.00 (s, 5H), 3.78 (s, 3H, overlapped), 3.76 (s, 3H), 3.71 (d, 1H, J = 13.5 Hz), 3.66 (d, 1H, J = 13.5 Hz), 1.42 (s, 3H), 1.40 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): 148.5 (C), 147.4 (C), 131.2 (C), 120.7 (CH), 112.2 (CH), 111.9 (CH), 98.0 (C), 72.0 (C, broad), 69.3 (5 CH), 66.8 (CH, broad), 64.2 (CH, broad), 63.8 (CH, broad), 61.2 (C), 55.5 (CH_3O), 55.3 (CH_3O), 42.5 (CH_2), 34.0 (C), 26.5 (CH_3), 26.3 (CH_3), 24.6 (CH_3), 22.9 (CH_3); one quaternary carbon peak is missing, probably due to the broadening of the signal. MS (EI) *m/z* (% relative intensity): 445 $[M]^+$ (100), 402 $[M–i\text{-}C_3H_7]^+$ (13), 364 (10), 294 $[M–(CH_3O)_2C_6H_3CH_2]^+$ (17), 266 (15), 121 $[C_5H_5Fe]^+$ (9), 56 (2). Data for **9a**: red oil; R_f 0.27 (petroleum ether/EtOAc 5:1). IR (thin film): 3085, 2975, 2936, 1658, 1593, 1514, 1463, 1417, 1321, 1274, 1260, 1242, 1209, 1175, 1138, 1117, 1025, 1003, 823, 757, 666, 448 cm^{-1}. ^{1}H NMR(DMSO-d_6, 400 MHz, 30 °C): δ 7.82 (dd, 1H, J = 8.4, 2.0 Hz), 7.70 (d, 1H, J = 1.9 Hz), 7.22 (d, 1H, J = 8.5 Hz), 4.51–4.50 (m, 2H), 4.45 (t, 1H, J = 2.4 Hz), 4.17 (s, 5H), 3.92 (s, 3H), 3.88 (s, 3H), 1.54 (s, 3H), 1.47 (s, 3H), 1.10 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C): δ 189.9 (C), 163.4 (C), 153.7 (C), 148.5 (C), 127.5 (C), 125.5 (CH), 111.8 (CH), 111.0 (CH), 98.0 (C), 69.5 (5 CH), 67.8 (CH), 65.9 (CH), 64.6 (CH), 62.3 (C), 55.8 (CH_3O), 55.4 (CH_3O), 34.3 (C), 28.3 (CH_3), 25.4 (CH_3), 23.2 (CH_3). MS (EI) *m/z* (% relative intensity): 459 $[M]^+$ (100), 444 $[M–CH_3]^+$ (13), 403 $[M–C_4H_8]^+$ (40), 321 $[M–(CH_3O)_2C_6H_4]^+$ (13), 306 $[M–(CH_3O)_2C_6H_4–CH_3]^+$ (19), 294 $[M–(CH_3O)_2C_6H_3C(O)]^+$ (21), 237 (17), 165 $[(CH_3O)_2C_6H_3C(O)]^+$ (22), 121 $[C_5H_5Fe]^+$ (16), 56 $[Fe]^+$ (3). Analysis calculated for $C_{26}H_{29}FeNO_3$: C, 67.98; H, 6.36; N, 3.05. Found: C, 68.20; H, 6.80; N, 3.15.

rac-1-Benzyl-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**8b**) *and rac-Phenyl(3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine)methanone* (**9b**). The title compounds were prepared according to GP1 using phenylacetonitrile (**7b**) (0.48 mL, 0.42 mmol); reaction time = 15 min; reaction time 1 = 2 days. *Method A:* Purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, **9b** (20 mg, 14%) and an inseparable mixture of **8b** and **9b** (56 mg, **8b**/**9b** = 89:11); calculated **8b**/**9b** = 66:34. Storage of the mixture of **8b** and **9b** at room temperature exposed to air until full conversion of **8b** to **9b**, followed by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 25:1), afforded pure compound **9b** (29 mg, 21%). Overall yield of **9b**: 49 mg, 35%. *Method B:* Purification by silica gel column

chromatography (petroleum ether–petroleum ether/EtOAc 25:1) gave pure **9b** (33 mg, 24%). Data for **8b** [spectroscopic data for **8b** were obtained only from the mixture of **8b** and **9b**]: R_f 0.10 (petroleum ether/EtOAc 25:1). ^{1}H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.47–7.43 (m, 2H), 7.40–7.36 (m, 2H), 7.27–7.24 (m, 1H), 4.27–4.25 (m, 3H), 3.97 (s, 5H), 3.79 (d, 1H, *J* = 13.8 Hz), 3.75 (d, 1H, *J* = 13.8 Hz), 1.42 (s, 3H), 1.41 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H). The ^{13}C spectrum of mixture **8b** and **9b** was complex, including broadening and overlapping of some signals, and it was impossible to clearly assign the peaks corresponding to **8b**. MS (EI) *m/z* (% relative intensity): 385 $[M]^+$ (100), 342 $[M–i\text{-}C_3H_7]^+$ (14), 329 $[M–C_4H_8]^+$ (10), 304 (11), 121 $[C_5H_5Fe]^+$ (16), 56 $[Fe]^+$ (5). Data for **9b**: red solid; mp 120.5–122 °C (hexane); R_f 0.20 (petroleum ether/EtOAc 25:1). IR (thin film): 3086, 2975, 2930, 2868, 1669, 1595, 1458, 1448, 1374, 1362, 1324, 1274, 1225, 1154, 1122, 1108, 1002, 876, 830, 737, 692, 493, 451 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 50 °C): δ 8.14–8.12 (m, 2H), 7.75–7.71 (m, 1H), 7.65–7.61 (m, 2H), 4.55 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.49 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.46 (t, 1H, *J* = 2.4 Hz), 4.18 (s, 5H), 1.55 (s, 3H), 1.48 (s, 3H), 1.09 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 191.2 (C), 163.1 (C), 135.0 (C), 133.3 (CH), 129.8 (2 CH), 128.3 (2 CH), 97.9 (C), 69.3 (5 CH), 67.7 (CH), 65.7 (CH), 64.5 (CH), 62.4 (C), 34.2 (C), 28.0 (CH_3), 25.3 (CH_3), 23.1 (CH_3), 22.9 (CH_3). MS (EI) *m/z* (% relative intensity): 399 $[M]^+$ (100), 384 $[M–CH_3]^+$ (13), 343 $[M–C_4H_8]^+$ (33), 294 $[M–CH_2C_6H_5]^+$ (11), 246 (18), 237 (13), 121 $[C_5H_5Fe]^+$ (19), 56 $[Fe]^+$ (6). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{26}FeNO$, 400.1358; found, 400.1363.

rac-3,3,4,4-Tetramethyl-1-(4-nitrobenzyl)-3,4-dihydroferroceno[c]pyridine (**8c**) *and rac-(4-Nitrophenyl)(3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine)methanone* (**9c**). The title compounds were prepared according to GP1 using 2-(4-nitrophenyl)acetonitrile (**7c**) (68 mg, 0.42 mmol); reaction time = 15 min; reaction time 1 = 6 days. *Method A*: Purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave an inseparable mixture of **8c** and **9c** (41 mg, **8c**/**9c** = 65:35; contaminated with unidentified compounds). Storage of the mixture of **8c** and **9c** at room temperature exposed to air until full conversion of **8c** to **9c**, followed by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1), afforded pure compound **9c** (25 mg, 16%). *Method B*: Purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1) gave pure compound **9c** (21 mg, 14%). Data for **8c** [spectroscopic data for **8c** were obtained only from the mixture of **8c** and **9c**, contaminated with identified compounds]: R_f 0.13 (petroleum ether/EtOAc 25:1). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): 7.90–7.88 (m, 2H), 7.14–7.11 (m, 2H), 3.93 (dd, 1H, *J* = 2.5, 1.1 Hz), 3.89 (t, 1H, *J* = 2.4 Hz), 3.79 (dd, 1H, *J* = 2.5, 1.1 Hz), 3.77 (s, 5H), 3.63 (d, 1H, *J* = 14 Hz), 3.57 (d, 1H, *J* = 14.1 Hz). A great signal overlapping was observed in the region of 0.73–1.16 ppm, and it was impossible to clearly assign the peaks of methyl groups corresponding to **8c**. ^{13}C spectrum of mixture **8c** and **9c** was complex, including overlapping of the some signals, and it was impossible to clearly assign the peaks corresponding to **8c**. MS (EI) *m/z* (% relative intensity): 430 $[M]^+$ (100), 400 $[M–C_2H_6]^+$ (13), 387 $[M–i\text{-}C_3H_7]^+$ (11), 374 $[M–C_4H_8]^+$ (10), 294 (14), 263 (10), 237 (10), 121 $[C_5H_5Fe]^+$ (10), 56 $[Fe]^+$ (3). Data for **9c**: brown oil; R_f 0.25 (petroleum ether/EtOAc 25:1). IR (thin film): 3105, 3047, 2978, 2926, 2867, 2850, 1677, 1601, 1588, 1527, 1457, 1374, 1362, 1347, 1318, 1273, 1217, 1155, 1122, 1108, 1002, 989, 882, 857, 824, 737, 711, 697, 507, 483, 447 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 8.04–8.01 (m, 2H), 7.77–7.74 (m, 2H), 4.92 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.08 (t, 1H, *J* = 2.4 Hz), 4.05 (dd, 1H, *J* = 2.5, 1.2 Hz), 4.00 (s, 5H), 1.44 (s, 3H), 1.35 (s, 3H), 0.95 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 189.9 (C), 163.7 (C), 150.4 (C), 141.1 (C), 131.6 (2 CH), 123.2 (2 CH), 98.7 (C), 70.2 (5 CH), 68.6 (CH), 66.6 (CH), 66.2 (CH), 63.9 (C), 35.0 (C), 29.0 (CH_3), 25.7 (CH_3), 23.4 (CH_3), 23.4 (CH_3). MS (EI) *m/z* (% relative intensity): 444 $[M]^+$ (100), 429 $[M–CH_3]^+$ (14), 414 $[M–C_2H_6]^+$ (10), 388 $[M–C_4H_8]^+$ (41), 306 (10), 294 (15), 277 (13), 237 (17), 121 $[C_5H_5Fe]^+$ (19), 56 $[Fe]^+$ (4). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{25}FeN_2O_3$, 445.1209; found, 445.1208.

3.2.5. Synthesis of Ferroceno[*c*]pyridines **11a**–**g** and Ferroceno[*c*]pyrroles **12a**–**g** (Tables 5 and 6)

General Procedure 2 (GP2). Thiocyanate **10a**–**g** (0.42 mmol) was added to the stirred solution of alcohol **1** (100 mg, 0.35 mmol) in $MeSO_3H$ (0.18 mL) at room temperature, and the resulting mixture was stirred at this temperature for the indicated time (monitored by TLC). The reaction mixture was then worked up as described in GP.

General Procedure 3 (GP3). Thiocyanate **10a**–**g** (0.42 mmol) was added to the solution of **1** in $MeSO_3H$, and preheated to 80 °C with stirring. The resulting mixture was then stirred at this temperature for 3 min, cooled to room temperature, and worked up as described in GP.

rac-1-(Ethylthio)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**11a**) *and (1R*,S_p*)-1-(tert-Butyl)-3-(ethylthio)-1-methyl-1H-ferroceno[c]pyrrole* (**12a**). The title compounds were prepared according to GP2 (reaction time = 25 min) and GP3 using ethyl thiocyanate (**10a**) (0.037 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of **11a** and **12a** (6 mg, 5%, **11a**/**12a** = 19:81) and **12a** (108 mg, 87%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, **11a** (70 mg, 57%) and a mixture of **11a** and **12a** (36 mg, 29%, **11a**/**12a** = 22:78). Data for **11a**: brown solid; mp 81–83 °C (hexane); R_f 0.61 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2971, 2927, 2868, 1580, 1448, 1372, 1361, 1287, 1239, 1151, 1141, 1108, 1097, 1002, 932, 899, 822, 512, 478 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.41 (dd, 1H, *J* = 2.4, 1.1 Hz, H7), 4.10 (s, 5H, H Cp), 3.99 (dd, 1H, *J* = 2.4, 1.1 Hz, H5), 3.92 (t, 1H, *J* = 2.4 Hz, H6), 3.22–3.12 (m, 1H, $SC\underline{H}_2CH_3$), 3.11–3.02 (m, 1H, $SC\underline{H}_2CH_3$), 1.50 (s, 3H, 3-CH_3), 1.40 (s, 3H, 4-CH_3), 1.28 (t, 3H, *J* = 7.3 Hz, $SCH_2C\underline{H}_3$), 0.98 (s, 3H, 4-CH_3), 0.88 (s, 3H, 3-CH_3). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.3 (C1), 99.1 (C4a), 75.0 (C7a), 70.5 (5 CH Cp), 66.5 (C6), 65.7 (C5), 64.3 (C3), 63.9 (C7), 35.7 (C4), 29.2 (4-CH_3), 25.2 (4-CH_3), 24.8 (3-CH_3), 24.2 (3-CH_3), 22.9 ($S\underline{C}H_2CH_3$), 15.1 ($SCH_2\underline{C}H_3$). MS (EI) *m/z* (% relative intensity): 355 $[M]^+$ (100), 340 $[M–CH_3]^+$ (1), 326 $[M–C_2H_5]^+$ (34), 293 (17), 269 (75), 172 (11), 121 $[C_5H_5Fe]^+$ (12), 117 (22), 56 $[Fe]^+$ (4). Analysis calculated for $C_{19}H_{25}FeNS$: C, 64.23; H, 7.09; N, 3.94; S, 9.02. Found: C, 64.04; H, 7.36; N, 3.83; S, 8.74. Data for **12a**: brown solid; mp 79.5–81.5 °C (hexane); R_f 0.47 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2969, 2936, 2908, 2871, 1522, 1451, 1391, 1366, 1299, 1149, 1141, 1106, 1003, 887, 821, 648, 508, 488 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 50 °C): δ 4.08 (dd, 1H, *J* = 2.3, 0.6 Hz, H4), 4.05 (dd, 1H, *J* = 2.1, 0.6 Hz, H6), 4.04 (s, 5H, H Cp), 3.87 (t, 1H, *J* = 2.3 Hz, H5), 3.25–3.16 (m, 1H, $SC\underline{H}_2CH_3$), 3.07–2.98 (m, 1H, $SC\underline{H}_2CH_3$), 1.76 (s, 3H, 1-CH_3), 1.30 (t, 3H, *J* = 7.3 Hz, $SCH_2C\underline{H}_3$), 0.90 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, C_6D_6, 50 °C): δ 165.8 (C3), 110.1 (C6a), 90.8 (C3a), 78.5 (C1), 71.0 (C5), 69.8 (5 CH Cp), 62.8 (C6), 57.0 (C4), 37.8 ($\underline{C}(CH_3)_3$), 26.1 ($C(\underline{C}H_3)_3$), 24.5 ($S\underline{C}H_2CH_3$), 23.1 (1-CH_3), 15.2 ($SCH_2\underline{C}H_3$). MS (EI) *m/z* (% relative intensity): 355 $[M]^+$ (23), 298 $[M–t\text{-}C_4H_9]^+$ (100), 270 (18), 121 $[C_5H_5Fe]^+$ (6), 56 $[Fe]^+$ (2). Analysis calculated for $C_{19}H_{25}FeNS$: C, 64.23; H, 7.09; N, 3.94; S, 9.02. Found: C, 63.94; H, 7.32; N, 3.86; S, 8.80.

rac-3,3,4,4-Tetramethyl-1-(methylthio)-3,4-dihydroferroceno[c]pyridine (**11b**) *and (1R*,S_p*)-1-(tert-Butyl)-1-methyl-3-(methylthio)-1H-ferroceno[c]pyrrole* (**12b**). The title compounds were prepared according to GP2 (reaction time = 25 min) and GP3 using methyl thiocyanate (**10b**) (0.028 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of **11b** and **12b** (33 mg, 28%, **11b**/**12b** = 9:91) and **12b** (76 mg, 64%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, **11b** (41 mg, 35%) and a mixture of **11b** and **12b** (54 mg, 45%, **11b**/**12b** = 14:86). Data for **11b**: brown solid; mp 70–74 °C (hexane); R_f 0.61 (petroleum ether/EtOAc 25:1). IR (thin film): 2973, 2924, 1581, 1449, 1372, 1361, 1286, 1241, 1151, 1108, 1097, 1002, 899, 822, 626, 512, 478 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.41 (dd, 1H, *J* = 2.5, 1.1 Hz), 4.09 (s, 5H), 3.99 (dd, 1H, *J* = 2.4, 1.2 Hz), 3.92 (t, 1H, *J* = 2.4 Hz), 2.40 (s, 3H), 1.52 (s, 3H), 1.40 (s,

3H), 0.98 (s, 3H, CH_3), 0.88 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.9 (C), 99.1 (C), 74.9 (C), 70.5 (5 CH), 66.6 (CH), 65.7 (CH), 64.4 (C), 63.8 (CH), 35.8 (C), 29.2 (CH_3), 27.3 (C), 25.2 (CH_3), 24.7 (CH_3), 24.3 (CH_3), 11.4 (CH_3). MS (EI) *m/z* (% relative intensity): 341 $[M]^+$ (100), 326 $[M–CH_3]^+$ (16), 293 (22), 269 (32), 252 (15), 237 (11), 173 (11), 121 $[C_5H_5Fe]^+$ (10), 117 (21), 89 (10), 56 $[Fe]^+$ (4). Analysis calculated for $C_{18}H_{23}FeNS$: C, 63.35; H, 6.79; N, 4.10; S, 9.39. Found: C, 63.34; H, 6.66; N, 4.04; S, 9.60. Data for **12b**: brown solid; mp 97–106.5 °C (hexane); R_f 0.38 (petroleum ether/EtOAc 25:1). IR (thin film): 3079, 2981, 2970, 2953, 2939, 2907, 2871, 1525, 1453, 1364, 1297, 1286, 1144, 1103, 1004, 926, 812, 653, 508, 482 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 50 °C): δ 4.07 (dd, 1H, *J* = 2.3, 0.7 Hz), 4.05 (dd, 1H, *J* = 2.2, 0.7 Hz), 4.03 (s, 5H), 3.87 (t, 1H, *J* = 2.3 Hz), 2.42 (s, 3H), 1.76 (s, 3H), 0.89 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, 50 °C): δ 166.5 (C), 110.4 (C), 90.5 (C), 78.5 (C), 71.0 (CH), 69.8 (5 CH), 62.9 (CH), 56.9 (CH), 37.7 (C), 26.0 (3 CH_3), 23.2 (CH_3), 12.7 (CH_3). MS (EI) *m/z* (% relative intensity): 341 $[M]^+$ (23), 284 $[M–t\text{-}C_4H_9]^+$ (100), 269 (10), 218 (14), 121 $[C_5H_5Fe]^+$ (12), 56 $[Fe]^+$ (3). Analysis calculated for $C_{18}H_{23}FeNS$: C, 63.35; H, 6.79; N, 4.10; S, 9.39. Found: C, 63.13; H, 6.99; N, 4.06; S, 9.05.

rac-3,3,4,4-Tetramethyl-1-(propylthio)-3,4-dihydroferroceno[c]pyridine (**11c**) *and (1R*,S_p*)-1-(tert-Butyl)-1-methyl-3-(propylthio)-1H-ferroceno[c]pyrrole* (**12c**). The title compounds were prepared according to GP2 (reaction time = 25 min) and GP3 using propyl thiocyanate (**10c**) (0.043 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of **11c** and **12c** (29 mg, 23%, **11c**/**12c** = 24:76) and **12c** (97 mg, 75%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, **11c** (68 mg, 53%) and a mixture of **11c** and **12c** (37 mg, 29%, **11c**/**12c** = 14:86). Data for **11c**: brown oil; R_f 0.67 (petroleum ether/EtOAc 25:1). IR (thin film): 3097, 2969, 2930, 2870, 1580, 1449, 1372, 1361, 1286, 1238, 1151, 1141, 1108, 1097, 1002, 932, 899, 822, 512, 478 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 4.43 (dd, 1H, *J* = 2.4, 1.1 Hz), 4.11 (s, 5H), 3.99 (dd, 1H, *J* = 2.4, 1.1 Hz), 3.93 (t, 1H, *J* = 2.4 Hz), 3.24–3.09 (m, 2H), 1.70 (h, 2H, *J* = 7.3 Hz), 1.49 (s, 3H), 1.40 (s, 3H), 0.98 (s, 3H), 0.96 (t, 3H, *J* = 7.3 Hz), 0.88 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.4 (C), 99.1 (C), 75.0 (C), 70.5 (5 CH), 66.6 (CH), 65.7 (CH), 64.4 (C), 63.9 (CH), 35.7 (C), 30.4 (CH_2), 29.2 (CH_3), 25.2 (CH_3), 24.7 (CH_3), 24.2 (CH_3), 23.5 (CH_2), 13.7 (CH_3). MS (EI) *m/z* (% relative intensity): 369 $[M]^+$ (100), 326 $[M–C_3H_7]^+$ (38), 293 (20), 269 (70), 252 (7), 172 (11), 121 $[C_5H_5Fe]^+$ (12), 117 (27), 56 $[Fe]^+$ (3). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{20}H_{28}FeNS$, 370.1286; found, 370.1288. Data for **12c**: brown oil; R_f 0.51 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2966, 2935, 2871, 1521, 1453, 1366, 1288, 1149, 1108, 1003, 933, 887, 820, 648, 508, 488 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 4.09 (dd, 1H, *J* = 2.3, 0.7 Hz), 4.04 (s, 5H), 4.03 (dd, 1H, *J* = 2.3, 0.7 Hz), 3.85 (t, 1H, *J* = 2.3 Hz), 3.32–3.26 (m, 1H), 3.07–3.00 (m, 1H), 1.76 (s, 3H), 1.79–1.65 (m, 2H), 0.94–0.90 (m, 12H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 165.9 (C), 110.0 (C), 90.7 (C), 78.4 (C), 71.1 (CH), 69.8 (5 CH), 62.8 (CH), 57.0 (CH), 37.7 (C), 32.0 (CH_2), 26.0 (3 CH_3), 23.5 (CH_2), 23.2 (CH_3), 13.5 (CH_3). MS (EI) *m/z* (% relative intensity): 369 $[M]^+$ (19), 312 $[M–t\text{-}C_4H_9]^+$ (100), 270 (24), 204 (5), 121 $[C_5H_5Fe]^+$ (7), 56 $[Fe]^+$ (2). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{20}H_{28}FeNS$, 370.1286; found, 370.1287.

rac-1-(Isopropylthio)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**11d**) *and (1R*,S_p*)-1-(tert-Butyl)-3-(isopropylthio)-1-methyl-1H-ferroceno[c]pyrrole* (**12d**). The title compounds were prepared according to GP2 (reaction time = 40 min) and GP3 using isopropyl thiocyanate (**10d**) (0.044 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, **11d** (9 mg, 7%), a mixture of **11d** and **12d** (30 mg, 23%, **11d**/**12d** = 18:82) and **12d** (68 mg, 53%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, **11d** (79 mg, 61%) and a mixture of **11d** and **12d** (25 mg, 19%, **11d**/**12d** = 70:30). Data for **11d**: brown oil; R_f 0.47 (petroleum ether/EtOAc 100:1). IR (thin film): 3097, 2971, 2927, 2866, 1578, 1463, 1449, 1415, 1388, 1372, 1286, 1234, 1151, 1141, 1116, 1108, 1095, 1057,

1035, 1023, 1002, 932, 899, 822, 651, 512, 478 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.40 (dd, 1H, *J* = 2.4, 1.1 Hz), 4.19 (hept, 1H, *J* = 6.8 Hz), 4.10 (s, 5H), 3.99 (dd, 1H, *J* = 2.5, 1.2 Hz), 3.91 (t, 1H, *J* = 2.4 Hz), 1.51 (s, 3H), 1.41 (s, 3H), 1.40 (d, 3H, *J* = 6.6 Hz), 1.35 (d, 3H, *J* = 6.8 Hz), 0.98 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.8 (C), 99.0 (C), 75.0 (C), 70.5 (5 CH), 66.5 (CH), 65.7 (CH), 64.3 (C), 63.9 (CH), 35.6 (C), 33.5 (CH), 29.3 (CH_3), 25.1 (CH_3), 24.8 (CH_3), 24.2 (CH_3), 23.4 (CH_3), 23.2 (CH_3). MS (EI) *m/z* (% relative intensity): 369 $[M]^+$ (52), 326 $[M–i\text{-}C_3H_7]^+$ (38), 269 (100), 172 (10), 121 $[C_5H_5Fe]^+$ (17), 117 (25), 56 $[Fe]^+$ (5). Analysis calculated for $C_{20}H_{27}FeNS$: C, 65.04; H, 7.37; N, 3.79; S, 8.68. Found: C, 65.44; H, 7.45; N, 3.57; S, 8.66. HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{20}H_{28}FeNS$, 370.1286; found, 370.1284. Data for **12d**: brown oil; R_f 0.50 (petroleum ether/EtOAc 25:1). IR (thin film): 3097, 2966, 2934, 2911, 2868, 1519, 1478, 1451, 1424, 1392, 1382, 1366, 1294, 1241, 1226, 1148, 1108, 1102, 1004, 934, 886, 820, 660, 513, 487 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.14 (hept, 1H, *J* = 6.8 Hz), 4.07 (dd, 1H, *J* = 2.3, 0.7 Hz), 4.04 (s, 5H), 4.03 (dd, 1H, *J* = 2.2, 0.8 Hz), 3.85 (t, 1H, *J* = 2.2 Hz), 1.76 (s, 3H), 1.39 (d, 3H, *J* = 6.8 Hz), 1.35 (d, 3H, *J* = 6.9 Hz), 0.91 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 165.9 (C), 109.7 (C), 90.9 (C), 78.6 (C), 71.1 (CH), 69.8 (5 CH), 62.8 (CH), 57.0 (CH), 37.8 (C), 35.3 (CH), 26.1 (3 CH_3), 23.6 (CH_3), 23.2 (CH_3), 23.1 (CH_3). MS (EI) *m/z* (% relative intensity): 369 $[M]^+$ (18), 312 $[M–t\text{-}C_4H_9]^+$ (61), 270 (100), 204 (15), 121 $[C_5H_5Fe]^+$ (14), 56 $[Fe]^+$ (6). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{20}H_{28}FeNS$, 370.1286; found, 370.1288.

rac-1-(Benzylthio)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**11e**) *and (1R*,S_p*)-3-(Benzylthio)-1-(tert-butyl)-1-methyl-1H-ferroceno[c]pyrrole* (**12e**). The title compounds were prepared according to GP2 (reaction time = 25 min) and GP3 using benzyl thiocyanate (**10e**) (62.6 mg, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of **11e** and **12e** (80 mg, 55%, **11e**/**12e** = 22:78) and **12e** (54 mg, 37%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of starting thiocyanate **10e** and **11e** (70 mg, **10e**/**11e** = 16:84) and a mixture of **11e** and **12e** (57 mg, 39%, **11e**/**12e** = 27:73). The mixture of **10e** and **11e** was additionally chromatographed on silica gel (benzene–benzene/TEA 100:1) to yield pure compound **11e** (61 mg, 42%). Data for **11e**: brown solid; mp 62.5–67.5 °C; R_f 0.79 (petroleum ether/EtOAc 25:1). IR (thin film): 3086, 3062, 3028, 2972, 2926, 2867, 2855, 1581, 1495, 1450, 1372, 1361, 1287, 1236, 1151, 1108, 1096, 1035, 1002, 932, 898, 823, 759, 700, 512, 477 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.42–7.40 (m, 2H), 7.16–7.11 (m, 3H), 7.05–7.01 (m, 1H), 4.44 (dd, 1H, *J* = 13.6 Hz), 4.40 (d, 1H, *J* = 13.6 Hz), 4.36 (dd, 1H, *J* = 2.4, 1.1 Hz), 4.05 (s, 5H), 3.97 (dd, 1H, *J* = 2.5, 1.1 Hz), 3.90 (t, 1H, *J* = 2.4 Hz), 1.52 (s, 3H), 1.38 (s, 3H), 0.97 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.1 (C), 139.9 (C), 129.6 (2 C), 128.5 (2 C), 127.0 (C), 99.1 (C), 74.6 (C), 70.5 (5 CH), 66.7 (CH), 65.8 (CH), 64.6 (C), 63.8 (CH), 35.7 (C), 32.8 (CH_2), 29.2 (CH_3), 25.2 (CH_3), 24.6 (CH_3), 24.3 (CH_3). MS (EI) *m/z* (% relative intensity): 417 $[M]^+$ (69), 402 $[M–CH_3]^+$ (2), 326 $[M–CH_2C_6H_5]^+$ (40), 269 (100), 132 (9), 121 $[C_5H_5Fe]^+$ (9), 56 $[Fe]^+$ (2). Analysis calculated for $C_{24}H_{27}FeNS$: C, 69.06; H, 6.52; N, 3.36; S, 7.68. Found: C, 69.13; H, 6.75; N, 3.05; S, 7.83. Data for **12e**: brown oil, R_f 0.65 (petroleum ether/EtOAc 25:1). IR (thin film): 3088, 3063, 3029, 2969, 2952, 2909, 2870, 1521, 1495, 1478, 1453, 1392, 1366, 1299, 1225, 1194, 1149, 1103, 1003, 929, 886, 821, 767, 699, 649, 508, 488, 472, 439 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 50 °C): δ 7.50–7.47 (m, 2H), 7.36–7.31 (m, 2H), 7.29–7.24 (m, 1H), 4.46 (d, 1H, *J* = 13.6 Hz), 4.41 (dd, 1H, *J* = 2.2, 0.7 Hz), 4.41 (d, 1H, *J* = 13.6 Hz), 4.31 (dd, 1H, *J* = 2.3, 0.7 Hz), 4.26 (t, 1H, *J* = 2.2 Hz), 4.14 (s, 5H), 1.71 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 50 °C): δ 164.3 (C), 138.4 (C), 128.6 (2 CH), 127.9 (2 CH), 126.7 (CH), 108.9 (C), 89.0 (C), 77.5 (C), 70.7 (CH), 69.0 (5 CH), 62.4 (CH), 56.2 (CH), 32.8 (CH_2), 25.2 (3 CH_3), 22.4 (CH_3). MS (EI) *m/z* (% relative intensity): 417 $[M]^+$ (23), 360 $[M–t\text{-}C_4H_9]^+$ (100), 269 (37), 121 $[C_5H_5Fe]^+$ (7), 56 $[Fe]^+$ (2). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{28}FeNS$, 418.1286; found, 418.1294.

rac-1-(Hexylthio)-3,3,4,4-tetramethyl-3,4-dihydroferroceno[c]pyridine (**11f**) *and (1R*,S_p*)-1-(tert-Butyl)-3-(hexylthio)-1-methyl-1H-ferroceno[c]pyrrole* (**12f**). The title compounds were

prepared according to GP2 (reaction time = 40 min) and GP3 using hexyl thiocyanate (**10f**) (0.065 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/EtOAc 100:1–petroleum ether/TEA 100:1) gave, in order of elution, a mixture of **11f** and **12f** (38 mg, 26%, **11f**/**12f** = 22:78) and **12f** (94 mg, 65%). GP3: purification by silica gel column chromatography (petroleum ether–petroleum ether/EtOAc 200:1–petroleum ether/EtOAc 50:1–petroleum ether/TEA 100:1) gave, in order of elution, **11f** (79 mg, 55%) and a mixture of **11f** and **12f** (45 mg, 31%, **11f**/**12f** = 42:58). Data for **11f**: brown oil; R_f 0.83 (petroleum ether/EtOAc 25:1). IR (thin film): 3097, 2970, 2927, 2857, 1580, 1449, 1372, 1361, 1286, 1240, 1151, 1141, 1108, 1097, 1035, 1002, 932, 899, 822, 512, 478, 453 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.44 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.12 (s, 5H), 3.99 (dd, 1H, *J* = 2.4, 1.1 Hz), 3.93 (t, 1H, *J* = 2.4 Hz), 3.30–3.15 (m, 2H), 1.76–1.69 (m, 2H), 1.52 (s, 3H), 1.45–1.36 (m, 2H, partially overlapped), 1.41 (s, 3H), 1.28–1.22 (m, 4H), 0.99 (s, 3H), 0.90 (s, 3H), 0.88–0.85 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 161.5 (C), 99.1 (C), 75.1 (C), 70.5 (5 CH), 66.6 (CH), 65.7 (CH), 64.4 (C), 63.9 (CH), 35.7 (C), 31.8 (CH_2), 30.1 (CH_2), 29.2 (CH_3), 29.0 (CH_2), 28.4 (CH_2), 25.2 (CH_3), 24.8 (CH_3), 24.3 (CH_3), 22.9 (CH_2), 14.2 (CH_3). MS (EI) *m/z* (% relative intensity): 411 $[M]^+$ (100), 326 $[M–C_6H_{13}]^+$ (58), 293 (28), 269 (84), 172 (13), 132 (11), 121 $[C_5H_5Fe]^+$ (15), 117 (29), 56 $[Fe]^+$ (3). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{23}H_{34}FeNS$, 412.1756; found, 412.1760. Data for **12f**: brown oil; R_f 0.56 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2955, 2930, 2871, 2858, 1521, 1478, 1453, 1425, 1391, 1366, 1298, 1286, 1225, 1193, 1149, 1108, 1035, 1003, 933, 887, 820, 648, 508, 487, 472, 439 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.11 (dd, 1H, *J* = 2.4, 0.7 Hz), 4.06 (s, 5H), 4.04 (dd, 1H, *J* = 2.3, 0.5 Hz), 3.86 (t, 1H, *J* = 2.2 Hz), 3.37–3.31 (m, 1H), 3.16–3.09 (m, 1H), 1.81–1.69 (m, 2H, partially overlapped), 1.77 (s, 3H), 1.41–1.33 (m, 2H), 1.27–1.18 (m, 4H), 0.92 (s, 9H), 0.87–0.83 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6, 50 °C): 166.1 (C), 110.1 (C), 90.8 (C), 78.5 (C), 71.1 (CH), 69.9 (5 CH), 62.9 (CH), 57.0 (CH), 37.8 (C), 31.8 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 26.1 (3 CH_3), 23.2 (CH_3), 22.9 (CH_2), 14.1 (CH_3). MS (EI) *m/z* (% relative intensity): 411 $[M]^+$ (17), 354 $[M–t\text{-}C_4H_9]^+$ (100), 270 (21), 121 $[C_5H_5Fe]^+$ (3), 56 $[Fe]^+$ (1). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{23}H_{34}FeNS$, 412.1756; found, 412.1762.

rac-Ethyl 2-((3,3,4,4-Tetramethyl-3,4-dihydroferroceno[c]pyridine)thio)acetate (**11g**) *and (1R*,S_p*)-Ethyl 2-((1-(tert-Butyl)-1-methyl-1H-ferroceno[c]pyrrole)thio)acetate* (**12g**). The title compounds were prepared according to GP2 (reaction time = 1 h) and GP3 (reaction time = 15 min) using ethyl 2-thiocyanatoacetate (**10g**) (0.064 mL, 0.53 mmol). GP2: purification by silica gel column chromatography (petroleum ether/EtOAc 25:1) gave, in order of elution, **11g** (8 mg, 6%; according to ^1H NMR analysis contained ~1% of **3u**; **11g**/**3u** = 99:1) and **12g** (106 mg, 73%). GP3: purification by silica gel column chromatography (petroleum ether/EtOAc 25:1) gave, in order of elution, **11g** (41 mg, according to ^1H NMR analysis contained 4% of **3u**; **11g**/**3u** = 96:4; calculated yield of **11g**: 27%) and **12g** (38 mg, 26%). Data for **11g**: brown oil; R_f 0.25 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2975, 2927, 2869, 2856, 1739, 1647, 1587, 1463, 1448, 1389, 1372, 1363, 1289, 1261, 1242, 1151, 1108, 1097, 1034, 1002, 933, 899, 823, 744, 712, 627, 583, 512, 479, 453 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 4.36 (dd, 1H, *J* = 2.5, 1.1 Hz), 4.13 (s, 5H), 4.02–3.97 (m, 4H), 3.91 (t, 1H, *J* = 2.4 Hz), 3.77 (d, 1H, *J* = 15.8 Hz), 1.44 (s, 3H), 1.37 (s, 3H), 0.99 (t, 3H, *J* = 7.1 Hz), 0.95 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 169.2 (C), 160.2 (C), 99.2 (C), 74.2 (C), 70.6 (5 CH), 66.8 (CH), 65.8 (CH), 64.6 (C), 63.6 (CH), 61.0 (CH_2), 35.8 (C), 31.2 (CH_2), 29.1 (CH_3), 25.2 (CH_3), 24.5 (CH_3), 24.1 (CH_3), 14.3 (CH_3). GC–MS analyses of product **11g** indicated the presence in the chromatogram of a peak that, based on corresponding MS spectra, belonged to compound **3o**. The latter was likely produced by the thermolysis of the parent compound in the GC instrument injector. HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{28}FeNO_2S$, 414.1185; found, 414.1186. Data for **12g**: orange oil, which solidified on long-term standing; mp 51–52.5 °C; R_f 0.32 (petroleum ether/EtOAc 25:1). IR (thin film): 3096, 2973, 2954, 2908, 2871, 1740, 1527, 1478, 1452, 1392, 1367, 1294, 1262, 1226, 1153, 1104, 1032, 1004, 934, 887, 822, 650, 488 cm^{-1}. ^1H NMR (400 MHz, C_6D_6, 50 °C): δ 4.07 (s, 5 CH), 4.05 (dd, 1H, *J* = 2.4, 0.6 Hz), 4.04 (dd, 1H, *J* = 2.2, 0.7 Hz), 4.00–3.95 (m, 2H), 3.93 (d, 1H, *J* = 15.7 Hz, partially overlapped), 3.85 (d, 1H, *J* = 15.8 Hz), 3.86 (t, 1H, *J* = 2.3 Hz), 1.71 (s,

3H), 0.98 (t, 3H, *J* = 7.1 Hz), 0.86 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, 50 °C): 168.6 (C), 164.8 (C), 110.4 (C), 89.6 (C), 78.7 (C), 71.2 (CH), 70.0 (5 CH), 63.1 (CH), 61.2 (CH_2), 57.0 (CH), 37.7 (C), 32.5 (CH_2), 25.9 (3 CH_3), 23.0 (CH_3), 14.2 (CH_3). GC–MS analysis of compound **12g** indicated the presence of a peak of substance with a molecular mass of 309. MS (EI) *m/z* (% relative intensity): 309 $[M]^+$ (31), 253 $[M–C_4H_8]^+$ (60), 252 $[M–t\text{-}C_4H_9]^+$ (100), 211 (8), 121 $[C_5H_5Fe]^+$ (11), 56 $[Fe]^+$ (3). Apparently, this is a 1-(*tert*-butyl)-1,3-dimethyl-1*H*-ferroceno[*c*]pyrrole yielded by the thermolysis of **12g** in the GC injector. The proposed mechanism for the thermolysis of ferroceno[*c*]pyrrole **12g** is performed in Supplementary Materials (Scheme S2). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{28}FeNO_2S$, 414.1185; found, 414.1191.

3.2.6. Reaction of Alcohol **1** with 2-Thiocyanatoacetamide (**10h**) (Table 6, Entries 3, 4)

According to GP2 (reaction time = 48 h) and GP3 using **10h** (48 mg, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/EtOAc 25:1) gave, in order of elution, an inseparable mixture of alkenes **5** and **6** (13 mg, 14%, **5**/**6** = 77:23), recovered alcohol **1** (37 mg, 37%) and alcohol **13** (13 mg, 13%). GP3: complex mixture of unidentified products was formed. *3-Ferrocenyl-2,3-dimethylbutan-2-ol* (**13**): yellow solid; mp 61.5–63 °C (hexane); R_f 0.25 (petroleum ether/EtOAc 25:1). IR (thin film): 3348, 2958, 2924, 2871, 2853, 1737, 1710, 1652, 1547, 1462, 1457, 1380, 1138, 1105, 1081, 1026, 1003, 879, 818, 529, 486 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 4.15 (s, 5H), 4.13–4.12 (m, 2H), 4.09–4.08 (m, 2H), 1.37 (s, 6H), 1.21 (br s, 1H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 97.4 (C), 74.4 (C), 68.7 (5 CH), 67.9 (2 CH), 67.3 (2 CH), 41.5 (C), 25.6 (2 CH_3), 24.0 (2 CH_3). MS (EI) *m/z* (% relative intensity): 286 $[M]^+$ (27), 229 (51), 186 $[C_5H_5FeC_5H_5]^+$ (100), 149 (13), 121 $[C_5H_5Fe]^+$ (8), 56 $[Fe]^+$ (2). HRMS-ESI (*m/z*): $[M]^+$ calculated for $C_{16}H_{22}FeO$, 286.1015; found, 286.1011.

Data for alkenes **5** and **6** see below.

3.2.7. Reaction of Alcohol **1** with Phenacyl Thiocyanate (**10i**) (Table 6, Entries 5, 6)

According to GP2 (reaction time = 48 h) and GP3 (reaction time = 40 min) using **10i** (74 mg, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/CH_2Cl_2 1:1–petroleum ether/acetone 5:1) gave, in order of elution, an inseparable mixture of alkenes **5** and **6** (17 mg, 18%, **5**/**6** = 55:45), recovered alcohol **1** (20 mg, 20%), thiocyanate **10i** (28 mg, 38%) and alcohol **13** (51 mg, 51%). GP3: purification by silica gel column chromatography (benzene–benzene/TEA 100:1) gave, in order of elution, an inseparable mixture of alkenes **5** and **6** (39 mg, 42%, **5**/**6** = 91:9), recovered thiocyanate **10i** (29 mg, 39%) and a mixture of compound **3w** and thiocyanate **10i** (31 mg, **3w/10i =** 33:67). The mixture of **3w** and **10i** was additionally chromatographed (benzene–benzene/TEA 100:1) to yield thiocyanate **10i** (18 mg, 24%) and pure compound **3w** (11 mg, 8%).

3.2.8. Reaction of Alcohol **1** with 2-Oxopropyl Thiocyanate (**10j**) (Table 6, Entries 7, 8)

According to GP2 (reaction time = 48 h) and GP3 using **10j** (0.04 mL, 0.42 mmol). GP2: purification by silica gel column chromatography (petroleum ether/EtOAc 10:1, 5:1) gave, in order of elution, an inseparable mixture of alkenes **5** and **6** (21 mg, 22%, **5**/**6** = 56:44) and alcohol **13** (48 mg, 48%). GP3: purification by silica gel column chromatography (petroleum ether/EtOAc 10:1, 5:1) gave, in order of elution, an inseparable mixture of alkenes **5** and **6** (19 mg, 20%, **5**/**6** = 94:6), recovered alcohol **1** (38 mg, 38%) and 15 mg of a mixture of unidentified products containing trace amounts of compound **3x** according to NMR ^{1}H analysis.

3.2.9. Optimization of the Reaction of Alcohol **1** with 4-Methylbenzonitrile (**2a**). Representative Examples (Table 1, Entries 1, 10 and 11)

Table 1, *entry 1.* Nitrile **2a** (0.05 mL, 0.42 mmol) was added to a stirred solution of alcohol **1** (100 mg, 0.35 mmol) in $MeSO_3H$ (0.18 mL) at room temperature, and the resulting mixture was stirred at this temperature for 5 h. The reaction mixture was then worked up as described in GP. Purification by silica gel column chromatography (petroleum ether/EtOAc

25:1–petroleum ether/TEA 100:1) gave, in order of elution, amide **4a** (9 mg, 6%) and ferroceno[*c*]pyridine **3a** (79 mg, 59%).

Table 1, *entry 10.* Nitrile **2a** (0.05 mL, 0.42 mmol) was added to a stirred solution of alcohol **1** (100 mg, 0.35 mmol) in CF_3COOH (0.21 mL) at room temperature, and the resulting mixture was heated at 60 °C in an oil bath with vigorous stirring for 30 min. The reaction mixture was then worked up as described in GP. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, inseparable mixture of alkenes **5** and **6** (18 mg, 19%, **5**/**6** = 20:80) and ferroceno[*c*]pyridine **3a** (55 mg, 41%).

Table 1, *entry 11.* Nitrile **2a** (0.05 mL, 0.42 mmol) was added to a stirred solution of alcohol **1** (100 mg, 0.35 mmol) in CH_3COOH (0.16 mL) at room temperature, and the resulting mixture was heated at 60 °C in an oil bath with vigorous stirring for 2.5 h. The reaction mixture was then worked up as described in GP. Purification by silica gel column chromatography (petroleum ether/EtOAc 25:1–petroleum ether/TEA 100:1) gave, in order of elution, alkene **5** (30 mg, 32%) and recovered alcohol **1** (42 mg, 42%).

N-(2,3-Dimethyl-3-ferrocenylbutan-2-yl)-4-methylbenzamide (**4a**): yellow solid; mp 115.5–117 °C (hexane); R_f 0.39 (petroleum ether/EtOAc 25:1). IR (thin film): 3419, 3095, 2955, 2925, 2870, 2854, 1667, 1612, 1525, 1496, 1457, 1393, 1374, 1299, 1284, 1261, 1190, 1154, 1143, 1116, 1107, 1039, 1034, 1001, 890, 878, 822, 750, 514, 495, 447 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.47–7.44 (m, 2H), 7.15–7.13 (m, 2H), 6.06 (br s, NH), 4.20 (t, 2H, *J* = 1.8 Hz), 4.18 (s, 5H), 4.15 (t, 2H, *J* = 1.9 Hz), 2.34 (s, 3H), 1.44 (s, 6H), 1.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 166.7 (C), 141.2 (C), 133.8 (C), 129.2 (CH), 126.7 (2 CH), 97.1 (C), 68.9 (5 CH), 67.8 (CH), 67.7 (CH), 59.1 (C), 41.6 (C), 24.1 (2 CH_3), 22.7 (2 CH_3), 21.5 (CH_3). MS (EI) *m/z* (% relative intensity): 403 $[M]^+$ (6), 227 (65), 176 (21), 121 $[C_5H_5Fe]^+$ (16), 119 $[CH_3C_6H_4CO]^+$ (100), 91 $[CH_3C_6H_4]^+$ (15), 56 $[Fe]^+$ (3). Analysis calculated for $C_{24}H_{29}FeNO$: C, 71.47; H, 7.25; N, 3.47. Found: C, 71.13; H, 7.66; N, 3.25.

(3,3-Dimethylbut-1-en-2-yl)ferrocene (**5**): Orange oil. R_f 0.90 (petroleum ether/EtOAc 25:1). NMR data are in agreement with that previously published [60]. MS (EI) *m/z* (% relative intensity): 268 $[M]^+$ (100), 238 $[M–C_2H_6]^+$ (10), 211 $[M–t\text{-}C_4H_9]^+$ (14), 121 $[C_5H_5Fe]^+$ (19), 56 $[Fe]^+$ (8). Analysis calculated for $C_{16}H_{20}$: C, 71.66; H, 7.52. Found: C, 71.93; H, 7.58.

(2,3-Dimethylbut-3-en-2-yl)ferrocene (**6**) [spectroscopic data for **6** were obtained only from the mixture of **5** and **6**]: R_f 0.90 (petroleum ether/EtOAc 25:1). ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 4.58–4.57 (m, 2H), 4.16 (s, 5H), 4.11–4.10 (m, 2H), 4.03 (t, 2H, *J* = 1.9 Hz), 1.61 (t, 3H, *J* = 1.1 Hz), 1.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 154.0 (C), 108.6 (CH_2), 99.9 (C), 68.5 (5 CH), 66.9 (2 CH), 66.7 (2 CH), 38.8 (C), 27.8 (2 CH_3), 20.2 (CH_3). MS (EI) *m/z* (% relative intensity): 268 $[M]^+$ (100), 253 $[M–CH_3]^+$ (34), 238 $[M–C_2H_6]^+$ (26), 227 $[M–C_3H_5]^+$ (26), 186 $[C_5H_5FeC_5H_5]^+$ (10), 121 $[C_5H_5Fe]^+$ (22), 56 $[Fe]^+$ (7).

3.3. X-ray Diffraction Analysis

Single crystals of compounds **3a**, **11a**, and **12a** suitable for X-ray diffraction analysis were obtained by slow crystallization from hexane. X-ray data for **3a**, **11a** and **12a** were collected on an Xcalibur Ruby diffractometer equipped with the CCD detector using the standard procedure (MoK-irradiation, graphite monochromator, ω-scans with 1° step at T = 295(2) K). The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm [63]. Using OLEX2 [64], the structures were solved with the SHELXS program [65] and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms with the SHELXL program [66]. Hydrogen atoms were included in the refinement using a rider model with dependent isotropic thermal parameters. Crystallographic data for compounds **3a**, **11a**, and **12a** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 2210002, 2210003, 2210004). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Compound **3a** (CCDC No. 2210002). $C_{24}H_{27}FeN$, orange crystal, M = 385.31; crystal data: monoclinic, space group $P2_1/n$, a = 10.2339(17) Å, b = 17.372(3) Å, c = 10.952(2) Å, β = 103.462(19)°, V = 1893.59 Å^3, Z = 4, d_{calc} = 1.352 g/cm^3, μ(Mo Kα) = 0.803 mm^{-1}; 9378 reflections measured, 4464 unique (R_{int} = 0.0312) which were used in all calculations. The final wR_2 was 0.1299 (all data) and R_1 was 0.0473 ($I > 2\sigma(I)$).

Compound **11a** (CCDC No. 2210003). $C_{19}H_{25}FeNS$, red crystal, M = 355.31; crystal data: monoclinic, space group $P2_1/c$, a = 8.8836(13) Å, b = 15.552(2) Å, c = 13.226(2) Å, β = 108.990(17)°, V = 1727.83 Å^3, Z = 4, d_{calc} = 1.366 g/cm^3, μ(Mo Kα) = 0.990 mm^{-1}; 12,014 reflections measured, 3989 unique (R_{int} = 0.0315) which were used in all calculations. The final wR_2 was 0.0927 (all data) and R_1 was 0.0366 ($I > 2\sigma(I)$).

Compound **12a** (CCDC No. 2210004). $C_{19}H_{25}FeNS$, red crystal, M = 355.31; crystal data: monoclinic, space group $P2_1/c$, a = 7.5335(12) Å, b = 17.276(3) Å, c = 13.931(3) Å, β = 96.182(15)°, V = 1802.56 Å^3, Z = 4, d_{calc} = 1.309 g/cm^3, μ(Mo Kα) = 0.949 mm^{-1}; 9501 reflections measured, 4197 unique (R_{int} = 0.0257) which were used in all calculations. The final wR_2 was 0.0987 (all data) and R_1 was 0.0380 ($I > 2\sigma(I)$).

4. Conclusions

In summary, we demonstrated that 2-ferrocenyl-3,3-dimethylbutan-2-ol was a suitable substrate in the intramolecular Ritter reaction. Condensation of starting alcohol with a variety of nitriles in the presence of $MeSO_3H$ yielded novel 3,4-dihydroferroceno[*c*]pyridines. The reaction of 2-ferrocenyl-3,3-dimethylbutan-2-ol with thiocyanates gave not only 3,4-dihydroferroceno[*c*]pyridines but also 1*H*-ferroceno[*c*]pyrroles. The selectivity of this reaction depended on the temperature, the order of addition, and the size of substituents at the α-position to the sulfur atom of thiocyanates. The simplicity of the procedure and the availability of starting materials make the reaction of 2-ferrocenyl-3,3-dimethylbutan-2-ol with nitriles and thiocyanates very convenient and attractive to the synthesis of variously functionalized ferrocene-fused *aza*-heterocycles.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10110214/s1, Figure S1: ^{1}H NMR (400 MHz) monitoring of the conversion of thioimine **11g** to enaminone **3u** at rt; Table S1: ^{1}H NMR (400 MHz) monitoring of the conversion of thioimine **11g** to enaminone **3u**; Scheme S1: Proposed mechanism for the transformation of thioimine **11g** to enaminone **3u**; Scheme S2: Proposed mechanism for the thermolysis of ferroceno[*c*]pyrrole **12g**; Figures S2–S27, S29, S30, S32, S33 and S35−S97: Copies of ^{1}H and ^{13}C NMR spectra for compounds **3a–m**, **o–s, u–x**, **4**, **6**, **8a–c**, **9a–c**, **10g**, **j**, **11a–g**, **12a–g**, **13**; Figures S28, S31 and S34: Copies of ^{19}F spectra for compounds **3k–m**; **Figures S98–S118**: Copies of 2D NMR spectra for compounds **3a**,**u-x**, **11a**, **12a**.

Author Contributions: Conceptualization, Y.V.S. and Y.S.R.; methodology, Y.S.R.; validation, Y.S.R.; formal analysis, Y.S.R.; investigation, I.V.P. and A.A.G.; resources, Y.V.S. and Y.S.R.; data curation, Y.S.R.; writing—original draft preparation, Y.S.R.; writing—review and editing, Y.S.R., I.V.P., A.A.G. and Y.V.S.; supervision, Y.V.S. and Y.S.R.; funding acquisition, Y.V.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Russian Foundation for Basic Research (No. 17-03-00546) and Ministry of Science and Higher Education of the Russian Federation (No. 122012500098-4).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Top, S.; Tang, J.; Vessières, A.; Carrez, D.; Provote, C.; Jaouen, G. Ferrocenyl hydroxytamoxifen: A prototype for a new range of oestradiol receptor site-directed cytotoxics. *Chem. Commun.* **1996**, 955–956. [CrossRef]
2. Biot, C.; Glorian, G.; Maciejewski, L.A.; Brocard, J.S. Synthesis and antimalarial activity in vitro and in vivo of a new ferrocene-chloroquine analogue. *J. Med. Chem.* **1997**, *40*, 3715–3718. [CrossRef] [PubMed]
3. Wang, R.; Chen, H.; Yan, W.; Zheng, M.; Zhang, T.; Zhang, Y. Ferrocene-containing hybrids as potential anticancer agents: Current developments, mechanisms of action and structure-activity relationships. *Eur. J. Med. Chem.* **2020**, *190*, 112109. [CrossRef]

4. Jaouen, G.; Vessières, A.; Top, S. Ferrocifen type anti cancer drugs. *Chem. Soc. Rev.* **2015**, *44*, 8802–8817. [CrossRef] [PubMed]
5. Sijongesonke, P.; Blessing, A.A. Ferrocene-based compounds with antimalaria/anticancer activity. *Molecules* **2019**, *24*, 3604. [CrossRef]
6. Wani, W.A.; Jameel, E.; Baig, U.; Mumtazuddin, S.; Hun, L.T. Ferroquine and its derivatives: New generation of antimalarial agents. *Eur. J. Med. Chem.* **2015**, *101*, 534–551. [CrossRef]
7. Raičević, V.; Radulović, N.; Sakač, M. Toward selective anticancer agents: Ferrocene-steroid conjugates. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202100951. [CrossRef]
8. Sharma, B.; Kumar, V. Has ferrocene really delivered its role in accentuating the bioactivity of organic scaffolds? *J. Med. Chem.* **2021**, *64*, 16865–16921. [CrossRef]
9. Chellan, P.; Sadler, P.J. Enhancing the activity of drugs by conjugation to organometallic fragments. *Chem. Eur. J.* **2020**, *26*, 8676–8688. [CrossRef]
10. Xu, D.; Zhang, J.; Dai, L. Chiral oxazolinyl hydroxyl ferrocene catalysts: Synthesis and applications in asymmetric reactions. *ChemistrySelect* **2020**, *5*, 9443–9456. [CrossRef]
11. Zhu, J.-C.; Cui, D.-X.; Li, Y.-D.; Jiang, R.; Chen, W.-P.; Wang, P.-A. Ferrocene as a privileged framework for chiral organocatalysts. *ChemCatChem* **2018**, *10*, 907–919. [CrossRef]
12. Perez-Sanchez, J.C.; Raquel, P.; Herrera, R.P.; Gimeno, M.C. Ferrocenyl gold complexes as efficient catalysts. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202101067. [CrossRef]
13. Drusan, M.; Sebesta, R. Enantioselective C-C and C-heteroatom bond forming reactions using chiral ferrocene catalysts. *Tetrahedron* **2014**, *70*, 759–786. [CrossRef]
14. Toma., Š.; Csizmadiová, J.; Mečiarová, M.; Šebesta, R. Ferrocene phosphane-heteroatom/carbon bidentate ligands in asymmetric catalysis. *Dalt Trans.* **2014**, *43*, 16557–16579. [CrossRef] [PubMed]
15. Beitollahi, H.; Khalilzadeh, M.A.; Tajik, S.; Safaei, M.; Zhang, K.; Jang, H.W.; Shokouhimehr, M. Recent advances in applications of voltammetric sensors modified with ferrocene and its derivatives. *ACS Omega* **2020**, *5*, 2049–2059. [CrossRef]
16. Rabti, A.; Raouafi, N.; Merkoçi, A. Bio(sensing) devices based on ferrocene-functionalized graphene and carbon nanotubes. *Carbon* **2016**, *108*, 481–514. [CrossRef]
17. Sun, R.; Wang, L.; Yu, H.; Abdin, Z.; Chen, Y.; Huang, J.; Tong, R. Molecular recognition and sensing based on ferrocene derivatives and ferrocene-based polymers. *Organometallics* **2014**, *33*, 4560–4573. [CrossRef]
18. Hu, M.-L.; Abbasi-Azad, M.; Habibi, B.; Rouhani, F.; Moghanni-Bavil-Olyaei, H.; Liu, K.-G.; Morsali, A. Electrochemical applications of ferrocene-based coordination polymers. *ChemPlusChem.* **2020**, *85*, 2397–2418. [CrossRef]
19. Pal, A.; Bhatta, S.R.; Thakur, A. Recent advances in the development of ferrocene based electroactive small molecules for cation recognition: A comprehensive review of the years 2010–2020. *Coord. Chem. Rev.* **2021**, *431*, 213685. [CrossRef]
20. Kaur, S.; Kaur, M.; Kaur, P.; Clays, K.; Singh, K. Ferrocene chromophores continue to inspire. Fine-tuning and switching of the second-order nonlinear optical response. *Coord. Chem. Rev.* **2017**, *343*, 185–219. [CrossRef]
21. Gallei, M.; Rüttiger, C. Recent trends in metallopolymer design: Redox-controlled surfaces, porous membranes, and switchable optical materials using ferrocene-containing polymers. *Chem. Eur. J.* **2018**, *24*, 10006–10021. [CrossRef] [PubMed]
22. Heck, J.; Dede, M. Ferrocene-based electro-optical materials. In *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; John Wiley & Sons, Ltd.: Chichester, UK, 2008; Chapter 9; pp. 319–392.
23. Jha, B.N.; Singh, N.; Sahay, A.N.; Raghuvanshi, A. Scope of ferrocene in cathodic materials of lithium-ion batteries (LIBs): A review. *J. Electron. Mater.* **2021**, *50*, 6073–6086. [CrossRef]
24. Amin, B.U.; Yu, H.; Wang, L.; Nazir, A.; Fahad, S.; Haq, F.; Mahmood, S.; Liang, R.; Uddin, M.A.; Lin, T. Recent advances on ferrocene-based compounds and polymers as a burning rate catalysts for propellants. *J. Organomet. Chem.* **2020**, *921*, 121368. [CrossRef]
25. Usman, M.; Wang, L.; Yu, H.; Haq, F.; Haroon, M.; Ullah, R.S.; Khan, A.; Fahad, S.; Nazir, A.; Elshaarani, T. Recent progress on ferrocene-based burning rate catalysts for propellant applications. *J. Organomet. Chem.* **2018**, *872*, 40–53. [CrossRef]
26. Sivaev, I.B. Ferrocene and transition metal bis(dicarbollides) as platform for design of rotatory molecular switches. *Molecules* **2017**, *22*, 2201. [CrossRef]
27. Baroncini, M.; Silvi, S.; Credi, A. Photo- and redox-driven artificial molecular motors. *Chem. Rev.* **2020**, *120*, 200–268. [CrossRef]
28. Boev, V.I.; Snegur, L.V.; Babin, V.N.; Nekrasov, Y.S. α-Metallocenylalkylation. *Russ. Chem. Rev.* **1997**, *66*, 613–636. [CrossRef]
29. Shevaldina, E.V.; Shagina, A.D.; Ponomaryov, A.B.; Moiseev, S.K. One-pot α-ferrocenylalkylation of amines and alcohols with α-ferrocenyl substituted alcohols under acid-free conditions. *J. Organomet. Chem.* **2019**, *880*, 29–38. [CrossRef]
30. Allali, N.; Mamane, V. $Al(OTf)_3$ as a new efficient catalyst for the direct nucleophilic substitution of ferrocenyl alcohol substrates. Convenient preparation of ferrocenyl-PEG compounds. *Tetrahedron Lett.* **2012**, *53*, 2604–2607. [CrossRef]
31. Jiang, R.; Chu, X.-Q.; Xu, X.-P.; Wu, B.; Ji, S.-J. Direct C−O bond activation mediated by AcOH: A new metal-free way for α-functionalization of ferrocene alcohols. *Aust. J. Chem.* **2011**, *64*, 1530–1537. [CrossRef]
32. Jiang, R.; Shen, Y.; Zhang, Y.; Xu, X.; Shao, J.; Ji, S. Etherification of ferrocenyl alcohol by highly-efficient ytterbium triflate. *Chin. J. Chem.* **2011**, *29*, 1887–1893. [CrossRef]
33. Shevaldina, E.V.; Opredelennova, K.A.; Chichvarina, O.A.; Spiridonov, Y.Y.; Smol'yakov, A.F.; Dorovatovskii, P.V.; Moiseev, S.K. One-pot acid-free ferrocenylalkylation of azoles with α-ferrocenyl alcohols: Ferrocene-based plant growth regulators and herbicide safeners. *Appl. Organomet. Chem.* **2019**, *33*, e5228. [CrossRef]

34. Xiao, M.; Ren, D.; Xu, L.; Li, S.-S.; Yu, L.; Xiao, J. S_N1-type alkylation of *N*-heteroaromatics with alcohols. *Org. Lett.* **2017**, *19*, 5724–5727. [CrossRef]
35. Xiao, J.; Zhao, K.; Loh, T.-P. The acid free asymmetric intermolecular α-alkylation of aldehydes in fluorinated alcohols. *Chem. Commun.* **2012**, *48*, 3548–3550. [CrossRef] [PubMed]
36. Minić, A.; Novaković, S.B.; Bogdanović, G.A.; Bugarinović, J.P.; Pešić, M.S.; Todosijević, A.; Komatina, D.I.; Damljanović, I.; Stevanović, D. Synthesis and structural characterizations of novel atropoisomeric ferrocene-containing six-membered cyclic ureas. *Polyhedron* **2020**, *177*, 114316. [CrossRef]
37. Xu, X.; Jiang, R.; Zhou, X.; Liu, Y.; Ji, S.; Zhang, Y. Cerium ammonium nitrate: An efficient catalyst for carbon–carbon bond formation from ferrocenyl alcohol substrate. *Tetrahedron* **2009**, *65*, 877–882. [CrossRef]
38. Noji, M.; Konno, Y.; Ishii, K. Metal triflate-catalyzed cationic benzylation and allylation of 1,3-dicarbonyl compounds. *J. Org. Chem.* **2007**, *72*, 5161–5167. [CrossRef]
39. Minić, A.; Stevanović, D.; Vukićević, M.; Bogdanović, G.A.; D'hooghe, M.; Radulović, N.S.; Vukićević, R.D. Synthesis of novel 4-ferrocenyl-1,2,3,4-tetrahydroquinolines and 4-ferrocenylquinolines via α-ferrocenyl carbenium ions as key intermediates. *Tetrahedron* **2017**, *73*, 6268–6274. [CrossRef]
40. Snegur, L.V.; Simenel, A.A.; Rodionov, A.N.; Boev, V.I. Ferrocene modification of organic compounds for medicinal applications. *Russ. Chem. Bull.* **2014**, *63*, 26–36. [CrossRef]
41. Rodionov, A.N.; Korlyukov, A.A.; Simenel, A.A. Synthesis, structure of 5,7-dimethyl-3-ferrocenyl-2,3-dihydro-1*H*-pyrazolo-[1,2-*a*]-pyrazol-4-ium tetrafluoroborate. DFTB calculations of interaction with DNA. *J. Mol. Struct.* **2022**, *1251*, 132070. [CrossRef]
42. Rodionov, A.N.; Snegur, L.V.; Belousov, Y.A.; Korlyukov, A.A.; Simenel, A.A. The nature of ferrocenylalkylating agent in the acid-catalyzed reactions with ferrocenyl(phenyl)methanol. *Russ. Chem. Bull.* **2021**, *70*, 1900–1907. [CrossRef]
43. Garbicz, M.; Latos-Grażyński, L. *meso*-Tetraaryl-21-carbaporphyrin—incorporation of a cyclopentadiene unit into a porphyrin architecture. *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 6089–6093. [CrossRef] [PubMed]
44. Iurlo, M.; Mengozzi, L.; Rapino, S.; Marcaccio, M.; Perone, R.C.; Masiero, S.; Cozzi, P.; Paolucci, F. New approaches toward ferrocene−guanine conjugates: Synthesis and electrochemical behavior. *Organometallics* **2014**, *33*, 4986–4993. [CrossRef]
45. Ren, D.; Xu, L.; Wang, L.; Li, S.-S. Catalytic Formal Benzylic C−H Bond Functionalization of 2,5-Dialkylfuran Derivatives with Ferrocenyl Alcohols as Alkylation Reagents. *Org. Lett.* **2019**, *21*, 627–631. [CrossRef] [PubMed]
46. Snegur, L.V.; Borisov, Y.A.; Kuzmenko, Y.V.; Davankov, V.A.; Ilyin, M.M.; Ilyin Jr., M.M.; Arhipov, D.E.; Korlyukov, A.A.; Kiselev, S.S.; Simenel, A.A. Enantiomeric-enriched ferrocenes: Synthesis, chiral resolution, and mathematic evaluation of CD-chiral selector energies with ferrocene-conjugates. *Molecules* **2017**, *22*, 1410. [CrossRef] [PubMed]
47. Osipova, E.Y.; Ivanova, A.S.; Rodionov, A.N.; Korlyukov, A.A.; Arkhipov, D.E.; Simenel, A.A. Ferrocenylalkylation of 2-mercaptobenzoxazoles. *Russ. Chem. Bull.* **2016**, *65*, 2868–2872. [CrossRef]
48. Rozhkova, Y.S.; Plekhanova, I.V.; Gorbunov, A.A.; Stryapunina, O.G.; Chulakov, E.N.; Krasnov, V.P.; Ezhikova, M.A.; Kodess, M.I.; Slepukhin, P.A.; Shklyaev, Y.V. Synthesis of novel racemic 3,4-dihydroferroceno[*c*]pyridines via the Ritter reaction. *Tetrahedron Lett.* **2019**, *60*, 768–772. [CrossRef]
49. Osgerby, J.M.; Pauson, P.L. Ferrocene Derivatives. Part VIII. Tetrahydropyridoferrocenes. *J. Chem Soc.* **1961**, 4600–4604. [CrossRef]
50. Popp, F.D.; Moynahan, E.B. Ferrocene Sutdies. VIII. Pyridoferrocenes. *J. Heterocycl Chem.* **1974**, *11*, 267–269. [CrossRef]
51. Khand, I.U.; Lanez, T.; Pauson, P.L. Ferrocene derivatives. Part 24. Synthesis of dihydro-2-pyrindines and dihydro-3*H*-2-cyclopent[*c*]azepines by photolysis of their cyclopentadienyliron derivatives. *J. Chem. Soc. Perkin Trans.* **1989**, *402*, 2075–2078. [CrossRef]
52. Yasue, R.; Miyauchi, M.; Yoshida, K.A. Planar chiral six-membered cyclic (amino)(ferrocenyl)carbene and its sulfur adduct. *Tetrahedron Asymmetry* **2017**, *28*, 824–829. [CrossRef]
53. Braverman, S.; Cherkinsky, M. The Ramberg–Bäcklund rearrangement and the Eschenmoser coupling reaction. In *Comprehensive Organic Synthesis II*, 2nd ed.; Knochel, P., Molander, G.A., Eds.; Elsiver: Amsterdam, The Netherlands, 2014; Volume 3, pp. 887–943. [CrossRef]
54. Hussaini, S.R.; Chamala, R.R.; Wang, Z. The Eschenmoser sulfide contraction method and its application in the synthesis of natural products. *Tetrahedron* **2015**, *71*, 6017–6086. [CrossRef]
55. Zheng, C.; Zhang, X.; Hussain, M.I.; Huang, M.; Liu, Q.; Xiong, Y.; Zhu, X. One-pot dichlorinative deamidation of primary β-ketoamides. *Tetrahedron Lett.* **2017**, *58*, 574–577. [CrossRef]
56. Tanaka, Y.; Saito, T.; Ihara, H. Amidite compound and method for producing polynucleotide using said compound. *Eur. Pat. Appl.* **2021**, 3786173.
57. Benfodda, Z.; Guillen, F.; Arnion, H.; Dahmani, A.; Blancou, H. A new synthesis of alkane and polyfluoroalkanesulfonyl chlorides. *Heteroat. Chem.* **2009**, *20*, 355–361. [CrossRef]
58. Shiryaev, A.K.; Moiseev, I.K. Adamantylation of thiocyanatoacetamide and thiocyanatoacetylurea. *Rus. J. Org. Chem.* **2001**, *37*, 746–747. [CrossRef]
59. Bisogno, F.R.; Cuetos, A.; Lavandera, I.; Gotor, V. Simple and quick preparation of α-thiocyanate ketones in hydroalcoholic media. Access to 5-aryl-2-imino-1,3-oxathiolanes. *Green Chem.* **2009**, *11*, 452–454. [CrossRef]
60. Wang, R.; Hong, X.; Shan, Z. A novel, convenient access to acylferrocenes: Acylation of ferrocene with acyl chlorides in the presence of zinc oxide. *Tetrahedron Lett.* **2008**, *49*, 636–639. [CrossRef]
61. Rausch, M.D.; Pryde, C.A. Studies on some ferrocenyl ketones and pinacols. *J. Organomet. Chem.* **1971**, *26*, 141–146. [CrossRef]

62. Korb, M.; Mahrholdt, J.; Lang, H. (Planar-Chiral) Ferrocenylmethanols: From anionic homo phospho-Fries rearrangements to α-ferrocenyl carbenium ions. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4028–4048. [CrossRef]
63. CrysAlisPro, Agilent Technologies. Version 1.171.37.33. Available online: https://www.agilent.com/cs/library/usermanuals/Public/CrysAlis_Pro_User_Manual.pdf (accessed on 13 November 2022).
64. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [CrossRef]
65. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. A Found. Adv.* **2008**, *A64*, 112–122. [CrossRef] [PubMed]
66. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *C71*, 3–8. [CrossRef] [PubMed]