Note

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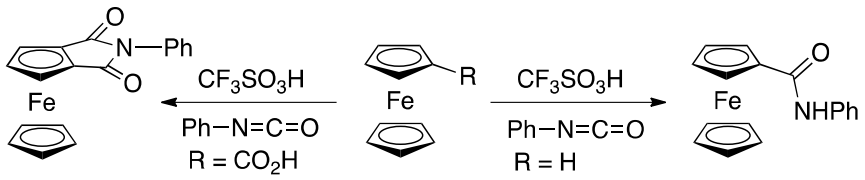
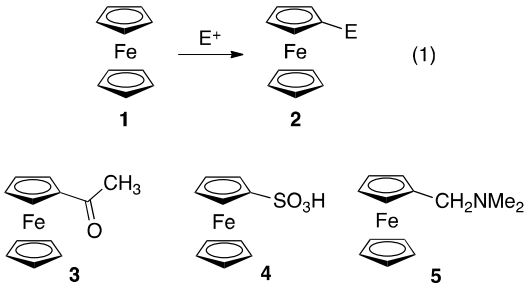


Abstract. Ferrocenes undergo one-step carboxamidation by reaction with isocyanates in CF_3SO_3H solution. The chemistry is most efficient in excess superacid and it has been accomplished with aryl and aliphatic isocyanates. In conversions with ferrocene carboxylic acids, isocyanates provide imides in good yields. A mechanism for this conversion is suggested involving carbamic acid anhydride formation and subsequent intramolecular reaction at the substituted cyclopentadienyl ring.

Shortly after the discovery of ferrocene - and related metallocene compounds - there was great interest in the development of synthetic transformations involving these compounds.[1,2] Among the synthetic routes to ferrocene derivatives,

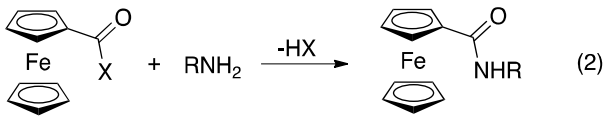
electrophilic aromatic substitution reactions provide a direct path to several types of ferrocenes (eq 1).[3] Ferrocene (**1**) itself reacts with several types of electrophiles (E^+) to give substitution products (**2**) – including products from acylation, sulfonylation, and aminomethylation (i.e., **3-5**).[4-6] As an arene nucleophile, ferrocene is considered a substance with relatively high nucleophilicity.[7] Thus,



ferrocene may be functionalized by Friedel-Crafts chemistry using even weak electrophiles. Nevertheless, several common methods of Friedel-Crafts synthesis are not compatible with ferrocene substrates. Nitration and halogenation are extremely difficult, as the electrophilic reagents (presumably) oxidize the ferrocene instead of forming bonds to the cyclopentadienyl rings. The development of new synthetic routes to ferrocene derivatives continues to be important, as ferrocenes are useful in material science, catalytic chemistry, medicinal chemistry, and in other applications.[8]

Despite decades of work in the development of electrophilic aromatic substitutions with ferrocene, there have been no reports of a one step carboxamidation. Ferrocenyl amides are useful organometallic building blocks and they have traditionally been synthesized from the carboxylic acid derivatives and an

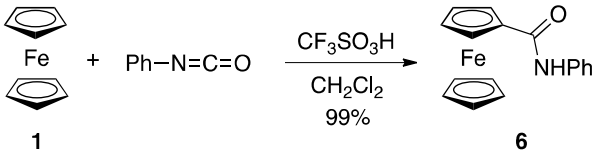
amine (eq 2).[9] However, carboxamidation of electron-rich arenes has previously been demonstrated with Friedel-Crafts reactions using isocyanates or related



(2)

species as electrophiles.[10] For example, indoles and aromatics ethers have been shown to give carboxamide products from reactions with isocyanates. In the following paper, we describe the superacid-promoted carboxamidation of ferrocene with aromatic and aliphatic isocyanates. These studies include a novel intramolecular reaction to provide ferrocenyl imides.

Table 1. Conditions and yields for the synthesis of amide **6**.



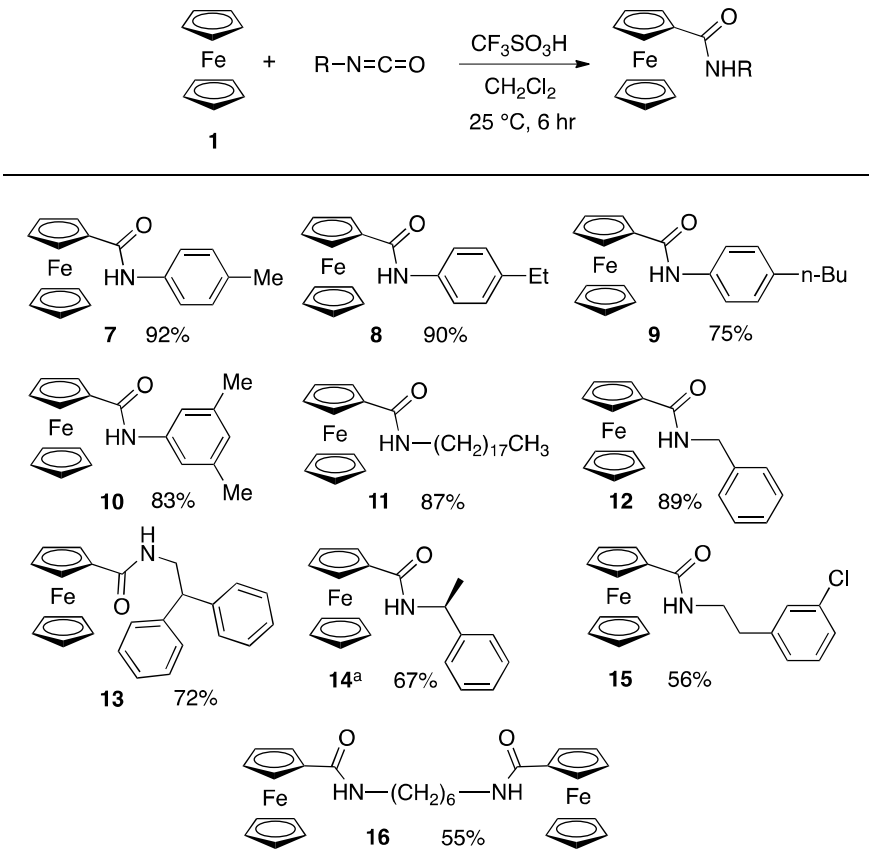
1 **6**

acid/equiv.	**temp/time**	**yield**
CF_3SO_3H/10	25 °C/8 hr	99%
CF_3SO_3H/5.0	-30 °C/3 hr	73%
CF_3SO_3H/0.2	25 °C/24 hr	31%
CF_3SO_3H-CF_3CO_2H (1:1)/5.0	25 °C/8 hr	81%
CF_3CO_2H/10	25 °C/24 hr	0%
p-TsOH/5.0	25 °C/24 hr	0%
H_2SO_4/6.0	25 °C/24 hr	0%

Our initial experiments utilized phenyl isocyanate in reactions with ferrocene (Table 1). Using an excess of triflic acid, the corresponding ferrocenyl amide is formed quantitatively. Other Brønsted and Lewis acids were examined as catalysts for the conversion, however the triflic acid was found to be the best acid promoter for carboxamidation.[11] Using triflic acid, diminished yields were obtained with decreasing amounts of triflic acid. Weaker Brønsted acids such as H_2SO_4 and CF_3CO_2H were also used, but no amide was obtained.

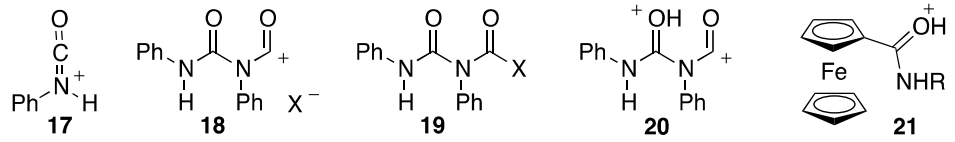
Using an excess of triflic acid as the acid promoter, a series of ferrocene amides were prepared (Table 2). As above, aromatic isocyanates provide good yields of ferrocene amides (**7-10**). The aliphatic isocyanate provides amide **11** while a benzylic isocyanates lead to **12** and a reasonable good yield of the optically active ferrocene (**14**). A bis(isocyanate) also react with ferrocene, and this chemistry provides diamide **16**. In the case of phenyl isocyanate, efforts were made to form a diamide from electrophilic attack at both cyclopentadienyl rings by utilizing excess isocyanate. However, only amide **6** could be isolated. Efforts were also made to extend the carboxamidation chemistry to both ruthenicene and osmocene, as both of these metallocenes are known to give products from Friedel-Crafts reactions.[12] Despite a variety of conditions and acids being used in the attempted transformations, no amide products could be obtained from reactions with ruthenicene and osmocene.

Table 2. Products and isolated yields from the reactions of ferrocene **1** with isocyanates.



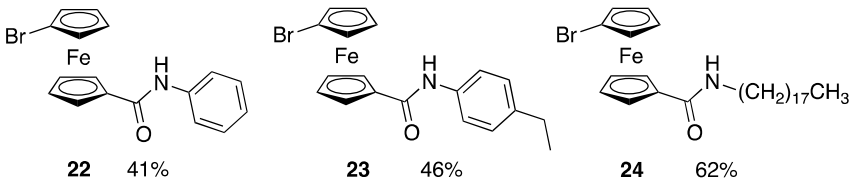
[a]Reaction done with 1:1 mixture of CF_3SO_3H:CF_3CO_2H

An obvious question arises from these results: why does the reaction work best in excess superacid? It is conceivable that the superacidic CF_3SO_3H generates the electrophilic *N*-protonated isocyanate (i.e., **17**). Recent work by Ohwada and others have suggested *N*-protonated isocyanates are intermediates in some carboxamidation of arenes.[13] However, a previous study by Olah and coworkers demonstrated that isocyanates exist as allophanyl cations (dimers of isocyanates) in



superacid media at low temperature.[14] In the case of phenyl isocyanate, the allophanyl cation **18** was observed by NMR from solutions of FSO_3H-SO_3.[14] While it is possible carboxamidation of ferrocene could occur directly via cation **18**, the triflic acid likely has some other role in the chemistry besides simply generating **18**. NMR experiments were done with phenyl isocyanate in triflic acid – the conditions of carboxamidation – and the ^{1}H and ^{13}C NMR spectra are complex. ^{13}C NMR spectra shows peaks indicating no less than three types of phenyl groups and carbonyl-type resonances (see Supporting Information). These results are consistent with an equilibrium involving several species, such as the *N*-protonated isocyanate (**17**), the allophanyl cation (**18**)**,** the allophanate (**19**), and others. The excess superacid may be important in suppressing formation of less reactive species (i.e., **19**) or in providing a low concentration of the *N*-protonated isocyanate (**17**). Alternatively, this type of superacidic reaction conditions may lead to protosolvation of the electrophile.[15] In the present case, superelectrophile **20** may be a reactive intermediate in the transformation. A potential driving force in the reaction may also be the acidic solvation of the product amide. This may explain why carboxamidation of the second cyclopentadienyl ring (functionalization of both rings) does not occur, as the acid-protonated carboxamide (i.e., **21**) would be expected to unreactive toward further electrophilic attack.

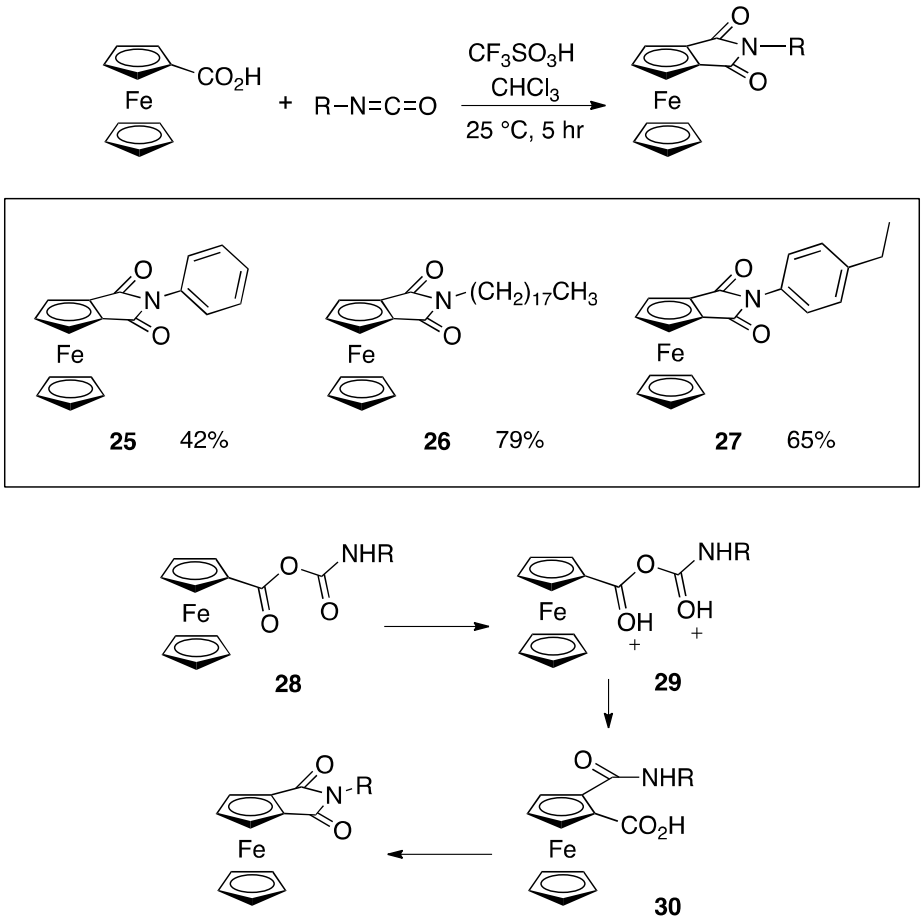
We also sought to use substituted ferrocenes in the carboxamidation chemistry, although mixed results were obtained. In the case of acetyl ferrocene (**3**), no product from carboxamidation could be obtained. With bromoferrocene, carboxamidation occurs at the unsubstituted cyclopentadienyl ring, providing compounds **22-24** in fair yields. When ferrocenecarboxylic acid is treated with



22 41% **23** 46% **24** 62%

isocyanates and triflic acid, the ferrocene imides are formed (Scheme 1). Thus, reaction of ferrocenecarboxylic acid gives compound **25** from the superacid-promoted reaction with phenyl isocyanate. Likewise, products **26** and **27** are prepared from the respective isocyanates. These are striking transformations, especially since no products were obtained from reactions with acetylferrocene and electrophilic attack occurs at the ring carbon adjacent to the acid group. In order to explain this conversion, we suggest the formation of adduct **28** upon mixing the ferrocenecarboxylic acid with isocyanate (prior to the addition of triflic acid). Upon solvation in superacid, an intramolecular electrophilic reaction occurs – possibly through the diprotonated species **29**. Formation of the intermediate **30** is then followed by dehydration to the observed imide product. The proposed mechanism is supported by an earlier literature precedent, that isocyanates are known to form

Scheme 1. Reactions of ferrocenecarboxylic acid with isocyanates and a proposed mechanism for the conversions.

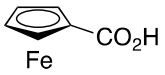
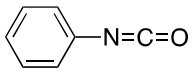


carbamic acid anhydrides – such as **28** – from carboxylic acids.[16] In previous studies, carbamic acid anhydrides have been shown to undergo decarboxylation to provide amides in good yields.[16,17] Intramolecular reactions involving carbamic acid anhydrides have not been previously described.

In order to gain further evidence for the involvement of **28**, we conducted NMR experiments (Table 3). Solutions of phenyl isocyanate and ferrocene carboxylic acid were combined and allowed to react for several hours. Following this period, the mixture was subjected to ^{1}H and ^{13}C NMR analysis in d_6-DMSO

solution. The ^{13}C NMR of the phenyl isocyanate/ferrocene carboxylic acid mixture reveals a new peak at δ 153, consistent with the formation of the carbamyl group.

Table 3. NMR analysis of ferrocenecarboxylic acid, phenylisocyanate, and the mixture of these substances in d_6-DMSO.[a]

	^{13}C NMR (d_6-DMSO)
	δ: 70.0 (Cp), 70.4, 71.5, 72.3, 172.6 (CO)
	δ: 124.6 (CO), 125.1 (Ph), 126.2 (Ph), 129.9 (Ph), 133.3 (Ph)
Major Product: (3 hrs, 25 °C)	δ: 70.0 (Cp), 71.0, 73.2, 118.7 (Ph), 122.2 (Ph), 129.2 (Ph), 140.3 (Ph), 153.0 (CO), 172.8 (CO)

[a]Product mixture also contains minor and trace components

DEPT experiments confirmed this to be a quaternary carbon, so it is assumed to be the new carbonyl group. There is also a considerable shift of the phenyl group *ortho* and *meta* ^{13}C resonances upon mixing phenyl isocyanate with ferrocenecarboxylic acid. These resonances are observed at δ 125.1 and 129.9 for the isocyanate, while δ 118.7 and 129.2 for the product mixture. While it might be argued that simple proton transfer might account for the changes in the NMR spectrum, the observed signals are more consistent with formation of structure **28** rather than the formation of a carboxylate salt. Typically, carboxylate anions exhibit ^{13}C resonances around δ 180 – significantly different than the newly observed carbonyl resonance at δ 153.0.

In summary, we have found that ferrocene undergoes one-step carboxamidation with isocyanates in superacid. The exact nature of the reacting electrophile is not known, as NMR experiments indicate a complex equililbria of isocyanate products in triflic acid. Bromoferrocene and ferrocenecarboxylic acid also react with isocyanates. In the later case, ferrocenyl imides were produced. It is proposed that these products are the result of carbamic acid anhydride formation and subsequent reaction at the ferrocenyl ring.

EXPERIMENTAL SECTION

General Information. All reactions were performed using oven dried glassware under an argon atmosphere. Trifluoromethanesulfonic acid (triflic acid) was freshly distilled prior to use. All commercially available compounds and solvents were used as received. ^{1}H and ^{13}C NMR were done using either 300 MHz or 500 MHz spectrometer. Chemical shifts were made in reference to NMR solvent signals. Low-resolution mass spectra were obtained from a gas chromatography instrument equipped with a mass selective detector utilizing electron impact ionization. High-resolution mass spectra were obtained from a commercial analytical laboratory; time-of-flight (TOF) mass analyzer was used the samples. NOTE: Triflic and trifluoroacetic acids are highly corrosive and isocyanates are very toxic. These substances should only be handled within an efficient fume hood and using appropriate personal safety equipment.

General Procedure A. Ferrocene (1 mmol) is added to a solution of the isocyanate (1.2 mmol) in dry chloroform (5 mL) at room temperature and then triflic acid (1 mL, 11 mmol) is added slowly to the reaction mixture and it is stirred for 6 hours at 25 °C. The solution is then poured over about 10 g of ice, and the mixture is extracted twice with chloroform. The combined organic extracts are washed with DI water followed by brine solution. The organic solution is isolated, dried with anhydrous sodium sulfate, and filtered. Removal of the solvent provides the crude product, which itself may be purified by column chromatography (SiO_2, 2:1 hexanes:ethyl acetate). In the case of (bis)isocyanates, 2 mmol of ferrocene and 1 mmol of the (bis)isocyanate is used.

General Procedure B. Bromoferrocene (1 mmol) is added to a solution of the isocyanate (1.2 mmol) in dry chloroform (5 mL) at room temperature and then triflic acid (1 mL, 11 mmol) is added slowly to the reaction mixture and it is stirred for 4 hours at 25 °C. The solution is then poured over about 10 g of ice, and the mixture is extracted twice with chloroform. The combined organic extracts are washed with DI water followed by brine solution. The organic solution is isolated, dried with anhydrous sodium sulfate, and filtered. Removal of the solvent provides the crude product, which itself may be purified by column chromatography (SiO_2, hexanes:ethyl acetate).

General Procedure C. Ferrocenecarboxylic acid (1 mmol) is added to a solution of the isocyanate (1.2 mmol) in dry chloroform (5 mL) at room temperature and then triflic acid (1 mL, 11 mmol) is added slowly to the reaction mixture and it is stirred for 4 hours at 25

°C. The solution is then poured over about 10 g of ice, and the mixture is extracted twice with chloroform. The combined organic extracts are washed with DI water followed by brine solution. The organic solution is isolated, dried with anhydrous sodium sulfate, and filtered. Removal of the solvent provides the crude product, which itself may be purified by column chromatography (SiO_2, 2:1 hexanes:ethyl acetate).

***N*-phenylferrocenamide (6).** Using general procedure A, the title compound is isolated (0.302 g, 1.0 mmol, 100%). Spectral data are consistent with previously published data.[18]

***N*-(4-methylphenyl)ferrocenamide (7).** Using general procedure A, the title compound is isolated (0.293 g, 0.92 mmol, 92%). Spectral data are consistent with previously published data.[19]

***N*-(4-ethylphenyl)ferrocenamide (8).** Using general procedure A, the title compound is isolated (0.300 g, 0.90 mmol, 90%). Spectral data are consistent with previously published data.[20]

***N*-(4-butylphenyl)ferrocenamide (9).** Using general procedure A, the title compound (0.271 g, 0.75 mmol, 75%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 150-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J= 3.45 Hz, 3H), 1.36-1.41 (m, 2H), 1.59-1.63 (m, 2H), 2.62 (t, J= 7.8 Hz, 2H), 4.26 (s, 5H), 4.40-4.41 (m, 2H), 4.85-4.86 (m, 2H), 7.18 (d, J= 8.2 Hz, 2H), 7.56 (d, J= 8.35 Hz, 2H), 7.75 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.3, 33.7, 35.1, 68.4, 69.9, 70.9, 76.3, 120.2, 128.9, 135.8, 138.8, 168.8.

Low-resolution mass spectrum (EI), 361 [M+], 226, 213, 185, 159, 129. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{21}H_{23}ONFe$ 361.11291; Found 361.11296.

***N*-(3,5-dimethylphenyl)ferrocenamide (10).** Using general procedure A, the title compound (0.274 g, 0.83 mmol, 83%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 215-220 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 6H), 4.28 (s, 5H), 4.44 (s, 2H), 4.80 (s, 2H), 6.80 (s, 1H), 7.28-7.30 (m, 2H), 7.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 68.6, 69.8, 71.2, 117.8, 125.9, 138.0, 138.9, 168.6. Low-resolution mass spectrum (EI), 333 [M+], 268, 241, 213, 185, 129. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{19}H_{19}ONFe$ 333.08161, found 333.08134.

***N*-octadecylferrocenamide (11).** Using general procedure A, the title compound (0.419 g, 0.87 mmol, 87%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 112-118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J= 6.30 Hz, 3H), 1.27 (s, 30 H), 1.55-1.61 (m, 2H), 3.35-3.39 (m, 2H), 4.21 (s, 5H), 4.34 (s, 2H), 4.69 (s, 2H), 5.83 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 27.0, 29.4, 29.4, 29.6, 29.7, 29.7, 30.0, 31.9, 39.6, 68.1, 69.7, 70.7, 170.1. Low-resolution mass spectrum (EI), 481 [M+], 229, 213, 187, 121. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{29}H_{47}ONFe$ 481.30071, found 481.30107.

***N*-benzylferrocenamide (12).** Using general procedure A, the title compound is isolated (0.284 g, 0.89 mmol, 89%).[21] Spectral data are consistent with previously published data.

***N*-(2,2-diphenylethyl)ferrocenamide (13).** Using general procedure A, the title compound (0.295 g, 0.72 mmol, 72%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). 192-196 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94-3.98 (m, 5H), 4.00-4.15 (m, 2H), 4.27-4.29 (m, 2H), 4.34-4.39 (m, 1H), 4.51-4.52 (m, 2H), 5.71 (s, 1H), 7.20-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.8, 50.8, 68.0, 69.6, 70.3, 127.0, 128.1, 128.8, 141.9, 170.2. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{25}H_{23}ONFe$ 409.11291, found 409.11332.

(S)-*N*-(α-methylbenzyl)ferrocenamide (14). Ferrocene (0.4 mmol) is added to a solution of the (*S*)-(-)-α-methylbenzyl isocyanate (0.5 mmol) in dry chloroform (5 mL) at room temperature and then a mixture of trifluoroacetic acid/triflic acid (1:1 v:v, 5 equiv.) is added slowly to the reaction mixture and it is stirred for 4 hours at 25 °C. The solution is then poured over about 10 g of ice, and the mixture is extracted twice with chloroform. The combined organic extracts are washed with water, followed by brine solution. The organic solution is isolated, dried with anhydrous sodium sulfate, and filtered. Removal of the solvent provides the crude product, is purified by column chromatography (SiO_2, 2:1 hexanes:ethyl acetate) to give compound **14** (0.090 g, 0.27 mmol, 67%). Spectral data are consistent with previously published data.[22]

***N*-(3-chlorophenethyl)ferrocenamide (15).** Using general procedure A, the title compound (0.206 g, 0.56 mmol, 56%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 129-135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (t, J= 6.78 Hz, 2H), 3.65 (t, J= 6.57, 2H), 4.15 (s, 5H), 4.34 (s, 2H), 4.61 (s, 2H), 5.75 (s, 1H), 7.16-7.32 (m, 4H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 35.6, 40.3, 68.0, 69.7, 70.4, 76.1, 126.8, 127.0, 128.9, 134.5, 141.1, 170.3. Low-resolution mass spectrum (EI), 367/369 [M+], 229, 213, 185, 129. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{19}H_{18}ONFeCl$ 367.04263, found 367.04283.

***N*-hexamethylene-bis(ferrocenamide) (16).** Using general procedure A, the title compound (0.300 g, 0.55 mmol, 55%) is isolated as a gray solid (2:1 hexane: ethyl acetate). Spectral results are consistent with previously published data.[20]

1-Bromo-1′-*N*-phenylferrocenamide (22). Using general procedure B, the title compound (0.157 g, 0.41 mmol, 41%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 132-137 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.38 (s, 1H), 4.23 (s, 2H), 4.50-4.53 (m, 3H), 5.07 (s, 2H), 7.07 (s, 1H), 7.33 (s, 2H), 7.73 (s, 2H), 9.49 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 69.3, 71.2, 71.7, 73.4, 78.8, 79.2, 120.9, 123.7, 128.97, 139.6, 167.2. Low-resolution mass spectrum (EI), 383/385 [M+], 291/293, 263/265, 240. 156, 128. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{17}H_{14}ONFeBr$ 382.96081, found 382.96163.

1-Bromo-1′-(*N*-4-ethylphenyl)ferrocenamide (23). Using general procedure B, the title compound (0.189 g, 0.46 mmol, 46%) is isolated as a yellow solid (2:1 hexane: ethyl acetate). Mp 120-124 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.18 (br, s, 3H), 3.35 (br, s, 2H), 4.23 (br, s, 2H), 4.49-4.51 (m, 4H), 5.05 (br, s, 2H), 7.15-7.17 (m, 2H), 7.61-7.63 (m, 2H), 9.42 (s, 1H); ^{13}C NMR (500 MHz, DMSO-d_6) δ 16.2, 28.1, 69.3, 71.2, 71.7, 73.4, 78.7, 79.3, 121.0, 128.2, 137.3, 139.1, 167.0. Low-resolution mass spectrum (EI),

411/413 [M+)] 291/293, 263/265, 128. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{19}H_{18}ONFeBr$ 410.99211, found 410.99146.

1-Bromo-1′-*N*-octadecylferrocenamide (24). Using general procedure B, the title compound (0.347 g, 0.62 mmol, 62%) is isolated as an orange solid (2:1 hexane: ethyl acetate). 63-65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (br, s, 3H), 1.28 (br, s, 32H), 1.64-1.69 (m, 2H), 4.19 (br, s, 2H), 4.43 (br, s, 4H), 4.64 (br, s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 27.1, 29.4, 29.7, 29.9, 31.9, 39.8, 68.9, 70.9, 71.9, 72.7, 74.6, 74.8, 78.0, 169.1. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{29}H_{46}ONFeBr$ 559.21121, found 559.21121.

***N*-Phenylferrocene imide (25).** Using general procedure C, the title compound (0.139 g, 0.42 mmol, 42%) is isolated as an orange solid (2:1 hexane: ethyl acetate). Mp 202-206 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 (br, s, 5H), 4.85 (br, s, 1H), 5.15-5.16 (m, 2H), 7.34-7.42 (m, 3H), 7.49-7.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 68.2, 72.8, 75.0, 126.9, 127.9, 129.1, 169.5. Low-resolution mass spectrum (EI), 331 [M+], 287, 209, 184, 128. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{18}H_{13}O_2NFe$ 331.02957, found 331.02862.

***N*-Octadecylferrocene imide (26).** Using general procedure C, the title compound (0.401 g, 0.79 mmol, 79%) is isolated as a brown solid (2:1 hexane: ethyl acetate). Mp 76-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85-0.89 (m, 3H), 1.24-1.34 (m, 28H), 1.58-1.63 (m, 2H), 3.48 (t, J= 7.26, 2H), 4.31-4.34 (m, 4H), 4.72-4.73 (m, 1H), 4.98-4.99 (m,

2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 27.0, 28.8, 29.4, 29.6, 29.7, 31.9, 38.4, 67.5, 72.6, 75.4, 75.8, 170.4. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{30}H_{45}O_2NFe$ 507.27997, found 507.27948.

***N*-(4-Ethylphenyl)ferrocene imide (27).** Using general procedure C, the title compound (0.233 g, 0.65 mmol, 65%) is isolated as an orange solid (2:1 hexane: ethyl acetate). Mp 194-196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26-1.31 (m, 3H), 2.68-2.75 (m, 2H), 4.21-4.38 (m, 2H), 4.45-4.58 (m, 3H), 4.83 (br, s, 1H), 5.14 (br, s, 1H), 5.31 (br, s, 1H), 7.23-7.35 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 28.6, 53.4, 68.2, 72.3, 72.8, 75.0, 126.8, 128.6, 130.1, 144.2, 169.7. Low-resolution mass spectrum (EI), 359 [M+], 315, 300, 286, 209, 128. HRMS (EI-TOF) m/z: [M+] Calcd for $C_{20}H_{17}O_2NFe$ 359.06087, found 359.06060.

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Supporting Information Available:

NMR spectra for compounds **6-16** and **22-27** and the product/intermediate from the reaction of phenyl isocyanate with ferrocene carboxylic acid. This material is available free of charge via the Internet at http:///www.pubs.acs.org.

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