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Nucleophilic substitution of ferrocenyl alcohols by cerium ammonium nitrate: C–N, C–S, and C–O bonds formation

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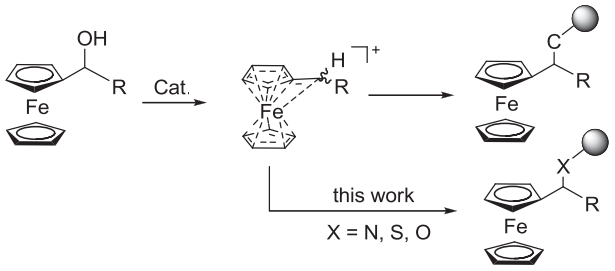
ABSTRACT

Nucleophilic substitution of ferrocenyl alcohols with N-, S-, O-centered nucleophiles promoted by a catalytic amount of cerium ammonium nitrate (CAN) was studied. By this protocol, a series of second arylamine, thioether, and ether were facilely synthesized in moderate to good yields under mild conditions.

1. Introduction

Coupling reactions between alcohols and kinds of nucleophiles have become the powerful tool for the construction of new C–C and C–X (X=O, N, S, etc.) bonds in recent years. The fact that the water was only byproduct, as the obvious advantage of this protocol, attracted more and more attention in the field of organic synthesis because it meets the demand of green chemistry. However, the poor leaving ability of hydroxyl group hindered the wide application of this method. In order to promote the reaction, a convenient catalytic system or reaction environment is strongly desirable. During the last three decades, a lot of catalytic approaches suitable for this transformation had been established. Brønsted acids, Lewis acids or other transition metal compounds are good alternatives of catalysts in such reactions.[1] Among these options, Lewis acid catalysts attracted particular attention because several advantages, for example, relatively lower catalyst loading, mild reaction conditions, and good compatibility with substrates, reagents, solvents or apparatus, were always exhibited.

Cerium ammonium nitrate (CAN), a versatile single-electron oxidant, has been widely used in organic transformations for its many advantages, such as solubility in organic solvents, high reactivity, and ease of handling.[2] The pioneering work was reported by Heiba and Dessau on CAN to prepare carbon-centered radicals in 1971.[3] Two decades later, Iranpoor and Mothaghineghad reported the first example of CAN-mediated nucleophilic substitution reaction of allylic and benzylic alcohols, in which, a radical cation mechanism was proposed.[4] Our previous work also found this catalytic mode could be adopted in the reaction of indol-3-yl alcohol and 9*H*-xanthen-9-ol with nucleophiles, such as indole.[5] Inspired by this, our group has successfully developed C–C[6a] bond formations of ferrocenyl alcohols with various nucleophiles via substitution reactions catalyzed by CAN (Scheme 1). Ferrocenyl carbocation was supposed to be the key intermediate in the reaction. In order to get more insight into this type of carbocation chemistry, we would like to study C–N,[6b] C–S, and C–O bonds formation of ferrocenyl alcohols with various nucleophiles in the presence of CAN. It was found that a series of arylamines, thioethers, and ethers containing ferrocenyl group could be facilely synthesized. Herein, we present these results.



Scheme 1.

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2. Results and discussion

Based on our successful results in C–C bond formation by CAN, we are eagerly to explore the feasibility of C–N bond formation. Initial study was focused on the optimization of solvents for this reaction. The reaction of ferroccenylphenylmethanol (**1b**) with 4-chloroaniline (**2d**) was selected as the template to achieve the goal. Among the commonly used solvents in nucleophilic substitution of alcohols, such as dichloromethane, acetonitrile, and nitromethane, etc., we found nitromethane was the best choice (Fig. 1). The desired product could be obtained in 86% yield at room temperature (entry 8, Table 1). A widely survey of reactions were performed with ferrocenyl ethanol (**1a**) as model substrate. First examination was directed toward the influence of electronic effect of arylamines on the reaction. It was found that arylamine with electron-withdrawing group at 4-position has a higher reactivity than that with electron-donating group. Stronger electron-withdrawing ability the group has, faster the reaction would proceed. For example, the reaction could complete within 1 h in 4-nitroaniline (entry 3, Table 1) case, while 3 h were needed for 4-chloroaniline. When aniline and 4-methoxyaniline were introduced, longer reaction time was required, the yields of products decreased with increasing of electron-donating ability of group at 4-position (entries 1 and 2, Table 1). The similar electronic effect was observed when the reactions performed in toluene at 80 °C.[6b]

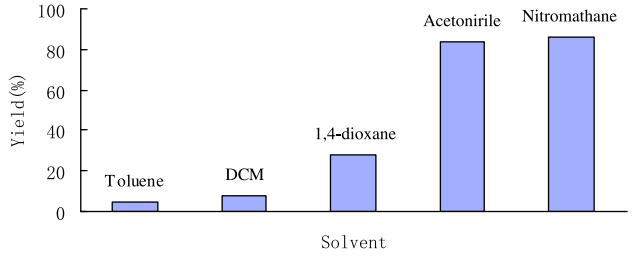
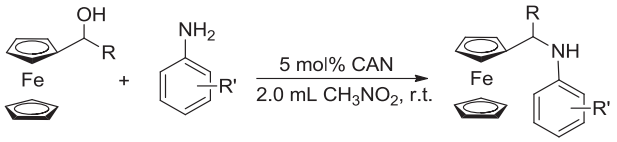


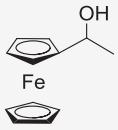
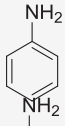
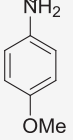
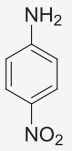
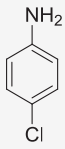
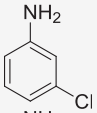
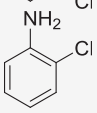
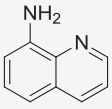
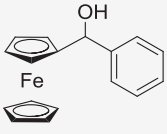
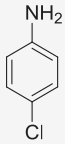
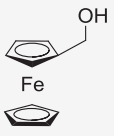
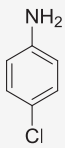
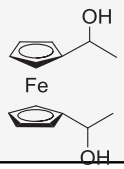
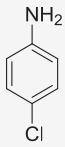
Figure. 1.

Furthermore, in order to make it clear that the influence of steric effect on the reaction, 4-chloroaniline (**2d**), 3-chloroaniline (**2e**), and 2-chloroaniline (**2f**) were compared. To our surprise, **2f** could reacted with **1a** efficiently to furnish the desired product **2af** in 89% yield within a shorter time of 0.5 h (entry 6, Table 1), meanwhile **2ad** and **2ae** could be isolated in 79% and 73%, respectively, after 3 h or 2 h at room temperature. 8-Aminoquinoline (**2g**) could also react with **1a** smoothly, and **2ag** was obtained in 63% yield (entry 7, Table 1). The reactions of other selected ferrocenyl alcohols, such as ferrocenylphenylmethanol (**1b**), ferrocenylmethanol (**1c**), and 1,1′-ferrocene diol **2d** were also performed under the same conditions, moderate to good yields of products were presented (entries 8–10, Table 1). When the similar operation was carried out on water without any catalysts, no desired product could be obtained.[7] In order to explore the generality of alcohol substrates, benzylic alcohol, allylic alcohol, and benzydrol were also introduced to this catalytic process, but none of the case was successful under the established conditions.

Followed above results, we continued our task to explore the reactivity of different thiols with ferrocenyl alcohols under the same conditions. The results were listed in Table 2. We found that CAN is an extremely efficient catalyst for C–S bond formation between ferrocenyl alcohol and aromatic thiols or heteroaromatic thiols. 1-Ferrocenyl ethanol displayed high reactivity and reacted quickly with **3a**–**d** to give the desired products in 84–96% yield within 15 min (entries 1–4, Table 2). We also observed the similar

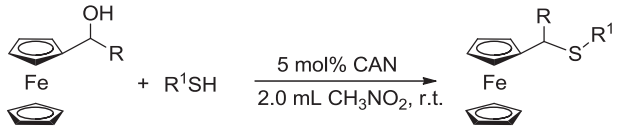
Table 1
Reaction of N-centered nucleophiles with ferrocenyl alcohols[a]

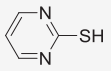
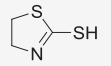
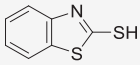
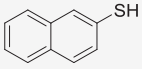
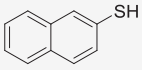
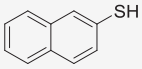
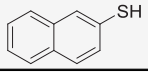


Entry	Alcohol	Ar–NH_2	Product	Time (h)	Yield (%)[b]
1		**1a**		**2a 2aa**	12	72
2				**2b 2ab**	12	62
3				**2c 2ac**	0.75	87
4				**2d 2ad**	3	80
5				**2e 2ae**	2	73
6				**2f 2af**	0.5	89
7				**2g 2ag**	12	63
8		**1b**		**2d 2bd**	9	86
9		**1c**		**2d 2cd**	12	76
10[c]		**1d**		**2d 2dd**	12	51

[a] Reaction conditions: alcohol (0.50 mmol), nucleophile (0.50 mmol), CAN (5 mol %), CH_3NO_2 (2.0 mL), room temperature.
[b] Yield of isolated product after flash chromatography.
[c] Compound **2d** (2 equiv) was added.

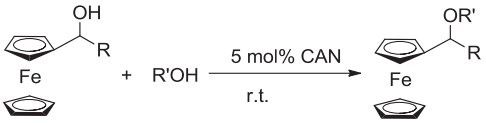
Table 2
Reaction of S-centered nucleophiles with ferrocenyl alcohols[a]



Entry	Alcohol	R-SH		Product	Time (min)	Yield (%)[b]
1			**3a**	**3aa**	15	95
2			**3b**	**3ab**	15	96
	1a					
3			**3c**	**3ac**	15	84
4			**3d**	**3ad**	10	91
5	**1b**		**3d**	**3bd**	10	95
6	**1c**		**3d**	**3cd**	20	91
7[c]	**1d**		**3d**	**3dd**	10	82

[a] Reaction conditions: alcohol (0.50 mmol), nucleophile (0.50 mmol), CAN (5 mol%), CH_3NO_2 (2.0 mL), room temperature.
[b] Yield of isolated product after flash chromatography.
[c] Compound (2 equiv) **3d** was added.

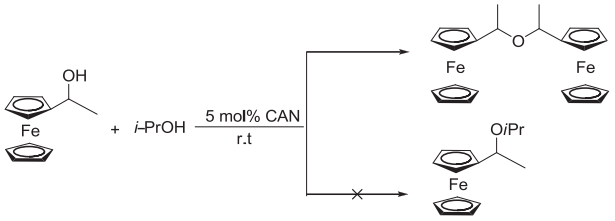
Table 3
Reaction of O-centered nucleophiles with ferrocenyl alcohols[a]



R = H, Me, Ph
R' = Me, Et, *i*-Pr, Pr

Entry	Alcohol	NuH/Solvent		Product		Time(h)	Yield(%)[b]
1	**1a**	MeOH	**6a**	R=Me	**4aa**	22	97
2	**1b**			R=Ph	**4ab**	0.25	95
3	**1c**			R=H	**4ac**	60	86
4	**1a**	EtOH	**6b**	R=Me	**4ba**	22	94
5	**1b**			R=Ph	**4bb**	0.5	94
6	**1c**			R=H	**4bc**	36	88
7	**1a**	PrOH	**6c**	R=Me	**4ca**	5	89
8	**1b**			R=Ph	**4cb**	1	87
9	**1c**			R=H	**4cc**	2	91
10	**1b**	*i*-PrOH	**6d**	R=Ph	**4db**	1.5	91
11	**1c**			R=H	**4dc**	60	69

[a] All reactions were carried out with 5 mol% CAN in 2.0 mL solvent at room temperature.
[b] Yield of isolated product after flash chromatography.



Scheme 2.

results when other ferroncenyl alcohols **1b**, **1c**, **1d**, were employed (entries 5–7, Table 2). Although Cozzi and Zoli have found some of these reactions could be performed on water without need any catalysts,[7] the far fast reaction rate and more high yields of products in our case made our protocol be more efficient.

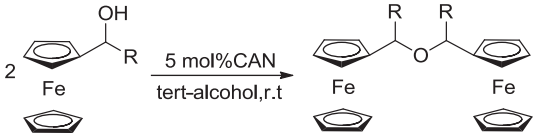
In order to explore the general application of this method, a methodology survey to C–O bond formation was carried out. It was unfortunately found that the reaction of **1a** and MeOH could hardly occur in nitromethane even two equivalent of MeOH was used. However, when **1a** was stirred in MeOH with the help of CAN, after appropriate reaction time, the desired product obtained in a satisfactory yield. The process was also suitable for other nucleophilic alcohol, for instance, EtOH, PrOH, ^{i}PrOH, etc. The details were listed in Table 3. From the results, we found ferrocenyl ethanol (**1a**) and ferrocenylmethanol (**1c**) showed less reactivity than ferrocenylphenylmethanol (**1b**), which may be up to the stability of ferrocenium intermediate. While the reaction of **1a** and ^{i}PrOH seemed a bit complex, after work-up, the intermolecular dehydrated product was obtained instead of the expected solvolytic ether (Scheme 2). Although similar observations were reported before, rare interpretation has been presented.[8] In our opinion, steric hindrance should be the critical factor, the formation of symmetrical ether may be ascribed to more bulk of alcohol reagent. As a result, *tert*-butanol and *tert*-pentanol were chosen to investigate the steric influence. As expected, when above two alcohols were used, symmetrical ethers were detected and separated at last (Table 4). At the same time, a yellow product, which was supposed to be solvolytic ether, was also detected by TLC. Attempt of separation failed because it decomposed on the silica gel column.

We have previously demonstrated a possible mechanism in C–C bond formation by CAN-catalysis.[6a] A highly delocalized carbocation was supposed be produced in the process, which would lead to maintenance of configuration at α-position.[9] In order to get more insight into this transformation, an optically active ferrocenyl ethanol (**2a′**, (*R*)-99% ee) was employed and examined (Scheme 3). To our delight, an expected result was obtained. Product **2ad′** was afforded in 98.5% ee with (*R*)-configuration.[10] It also confirmed carbocation (I), rather than carbocation (II), preferred to be formed in the reaction.

3. Conclusion

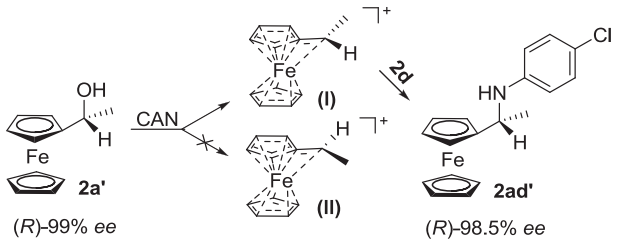
In summary, a CAN-catalyzed direct nucleophilic substitution of ferrocenyl alcohols was extensively studied. By this way, new C–N,

Table 4
Formation of symmetric ethers by CAN[a]



Entry	Substrate	Solvent		Product	Yield (%)[b]
1	**1b**	*t*-BuOH	**6e**	**5bb**	43
2		*t*-PeOH	**6f**		52
3	**1a**	*t*-BuOH	**6e**	**5aa**	49
4		*t*-PeOH	**6f**		55
5	**1c**	*t*-BuOH	**6e**	**5cc**	44
6		*t*-PeOH	**6f**		58

[a] All reactions were carried out with 5 mol% CAN in 2.0 mL solvent at room temperature.
[b] Isolated yield after 48 h.



Scheme 3.

C–S, and C–O bonds formation was realized. Various ferrocene derivatives were facilely and economically synthesized, which paved a good basis for the functionalization of ferrocene.

4. Experimental section

4.1. General

Ferrocenyl alcohols were prepared by the similar method according to the literature.[11] Other chemicals were commercially available. Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. ^{1}H NMR (300 MHz or 400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian INOVA MHz spectrometer using $CDCl_3$ (DMSO-d_6) as solvent and TMS as internal standard. High resolution mass spectra were obtained using Micromа GCT-TOF instrument. Optical rotation was measured at 589 nm (Na D line) on a Autopol IV automatic polarimeter. The enantiomeric excesses of the product was determined by HPLC analysis on a Chiralpak AD-H column using 2-propanol/hexane as the eluent.

4.2. Typical experimental procedure of C–N and C–S bonds formation

To a mixture of ferrocenyl alcohol (0.5 mmol), nucleophiles (0.5 mmol), catalyst (5 mol %), 2.0 mL solvent was added, the system was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford the product.

4.3. Typical experimental procedure of C–O bond formation

To a mixture of ferrocenyl alcohol (0.5 mmol) and solvent (2.0 mL), catalyst (5 mol %) was added, the system was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford the product.

*4.3.1. N-(1-Ferrocenylethyl)benzenamine (**2aa**).* Orange oil; IR (KBr): ν 3409, 3092, 2971, 1602, 1504, 1313, 1105, 1000, 819, 748, 692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53(d, J=6.6 Hz, 3H, CH_3), 4.16–4.22(m, 10H, FcH, NH), 4.31–4.38(m, 1H, CH), 6.66–6.75(m, 3H, ArH), 7.19–7.27(m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 129.8, 117.6, 113.7, 94.0, 68.9, 68.2, 68.0, 67.5, 66.6, 47.5, 21.2. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{19}FeN$: 305.0867, found: 305.0876.

*4.3.2. N-(1-Ferrocenylethyl)-4-methoxybenzenamine (**2ab**).* Orange oil; IR (KBr): ν 3405, 3089, 2980, 1597, 1510, 1308, 1100, 819 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, J=6.3 Hz, 3H, CH_3), 3.76–4.27 (m, 10H, FcH, CH), 6.23 (s, 3H, OCH_3), 6.23 (d, J=8.7 Hz, 2H, ArH), 6.80 (d, J=8.7 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 142.0, 115.4, 115.3, 93.9, 68.8, 68.1, 67.9, 67.5, 66.5, 56.2, 48.8, 21.5. HRMS (m/z): $[M]^+$, calcd for $C_{19}H_{21}FeNO$: 335.0973, found: 335.0981.

*4.3.3. N-(1-Ferrocenylethyl)-4-nitrobenzenamine (**2ac**).* Orange solid; mp: 110–112 °C. IR (KBr): ν 3400, 3084, 2986, 1593, 1509, 1455, 1307, 1101, 821 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (d, J=6.6 Hz, 3H, CH_3), 4.06–4.19 (m, 9H, FcH), 4.40–4.44 (m, 1H, CH), 6.54 (d, J=6.0 Hz, 2H, ArH), 8.07 (d, J=6.0 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 137.7, 126.9, 111.5, 91.8, 68.9, 68.5, 68.2, 67.4, 66.3, 47.3, 20.7. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}FeN_2O_2$: 350.0718, found: 350.0715.

*4.3.4. 4-Chloro-N-(1-ferrocenylethyl)benzenamine (**2ad**).* Orange solid; mp: 96–97 °C. IR (KBr): ν 3403, 3086, 2972, 2870, 1595, 1500, 1398, 1308, 1132, 1028, 998, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (d, J=6.0 Hz, 3H, CH_3), 3.90 (br s, 1H, NH), 4.18–4.23 (m, 10H, FcH, CH), 6.56 (d, J=8.4 Hz, 2H, ArH), 7.13 (d, J=8.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 129.6, 122.0, 114.7, 93.6, 69.1, 68.9, 68.3, 68.1, 67.5, 66.5, 47.8, 21.2. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}ClFeN$: 339.0477, found: 339.0478.

*4.3.5. 3-Chloro-N-(1-ferrocenylethyl)benzenamine (**2ae**).* Orange oil; IR (KBr): ν 3400, 3078, 2965, 1595, 1497, 1035 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (d, J=13.5 Hz, 3H, CH_3), 4.01 (s, 1H, NH), 4.20–4.21 (m, 10H, FcH, CH), 6.49–6.67 (m, 3H, ArH), 7.06–7.11 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.8, 117.3, 113.1, 111.9, 93.4, 68.9, 68.4, 68.1, 67.5, 66.5, 47.5, 21.2. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}ClFeN$: 339.0477, found: 339.0478.

*4.3.6. 2-Chloro-N-(1-ferrocenylethyl)benzenamine (**2af**).* Orange solid; mp: 97–99 °C. IR (KBr): ν 3396, 3094, 2968, 1595, 1500, 1031, 742 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (d, J=6.3 Hz, 3H, CH_3), 4.18–4.28 (m, 10H, FcH, CH), 4.83 (br s, 1H, NH), 6.62 (t, J=7.2 Hz, 1H, ArH), 6.72 (d, J=8.1 Hz, 1H, ArH), 7.15 (t, J=7.2 Hz, 1H, ArH), 7.28 (m, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 129.8, 128.3, 119.4, 117.2, 112.0, 93.7, 68.9, 68.3, 68.2, 67.3, 66.6, 46.6, 20.9. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}ClFeN$: 339.0477, found: 339.0476.

*4.3.7. N-(1-Ferrocenylethyl)quinolin-8-amine (**2ag**).* Orange solid; mp: 111–112 °C. IR (KBr): ν 3356, 2970, 2870, 1574, 1510, 1475, 1371, 1137, 1102, 818, 794, 492 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59–1.70 (m, 3H, CH_3), 4.03–4.33 (m, 9H, FcH), 4.46–4.52 (m, 1H, CH), 6.75 (d, J=7.5 Hz, 1H, ArH), 7.03 (d, J=8.1 Hz, 1H, ArH), 7.35–7.48 (m, 2H, ArH), 8.06 (d, J=8.1 Hz, 1H, ArH), 8.75 (d, J=3.6 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 136.3, 128.3, 121.8, 113.7, 109.0, 94.2, 69.1, 68.1, 68.0, 67.4, 67.1, 46.5, 20.9. HRMS (m/z): $[M]^+$, calcd for $C_{21}H_{20}FeN_2$: 356.0976, found: 356.0973.

*4.3.8. N-((Ferrocenyl)(phenyl)methyl)-4-chlorobenzenamine (**2bd**).* Orange solid, mp: 85–86 °C. IR (KBr): ν 3411, 3025, 1597 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.07–4.28 (m, 9H, FcH), 4.74 (s, 1H), 4.98 (s, 1H), 6.46 (d, J=8.0 Hz, 2H, ArH), 7.04 (d, J=8.0 Hz, 2H, ArH), 7.24–7.42 (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3, 142.8, 129.4, 128.9, 127.6, 127.1, 122.4, 114.8, 94.1, 69.1, 68.5, 68.3, 67.7, 67.1, 57.9. HRMS (m/z): $[M]^+$, calcd for $C_{23}H_{20}ClFeN$: 401.0634, found: 401.0634.

*4.3.9. 4-Chloro-N-(1-ferrocenyl methyl)benzenamine (**2cd**).* Orange solid; mp: 116–117 °C. IR (KBr): ν 3421, 3086, 2901, 2856, 1595, 1499, 1463, 1400, 1320, 1247, 1102, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (br s, 3H, CH_2, NH), 4.15–4.23 (m, 9H, FcH), 6.57 (d, J=7.5 Hz, 2H, ArH), 7.13 (d, J=7.2 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 129.5, 129.2, 122.3, 114.3, 86.4, 69.1, 69.1, 68.9, 68.6, 68.4, 68.2, 43.9. HRMS (m/z): $[M]^+$, calcd for $C_{17}H_{16}ClFeN$: 325.0321, found: 325.0322.

*4.3.10. 1,1′-Bis(1-(4-chlorobenzamino)ethyl)ferrocene (**2dd**).* Orange solid; mp: 92–93 °C. IR (KBr): ν 3398, 3088, 2973, 1593, 1496, 1393,

1309, 1237, 816 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.48 (d, J=6.3 Hz, 6H, $2CH_3$), 3.88 (br s, 2H, 2NH), 4.16–4.30 (m, 10H, FcH, 2CH), 6.53 (d, J=8.4 Hz, 4H, ArH), 7.12 (d, J=8.7 Hz, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3, 129.6, 122.2, 122.1, 114.9, 114.8, 93.9, 93.8, 68.8, 68.5, 67.9, 67.6, 67.2, 66.9, 47.8, 21.5, 21.3. HRMS (m/z): $[M]^+$, calcd for $C_{26}H_{26}Cl_2FeN_2$: 492.0822, found: 492.0828.

*4.3.11. 2-(1-Ferrocenylethylthio)pyrimidine (**3aa**).* Orange solid; mp: 137–138 °C. IR (KBr): ν 3097, 2979, 2928, 1564, 1545, 1378, 1184, 1104, 1023, 815, 774, 500 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (d, J=5.1 Hz, 3H, CH_3), 4.19–4.31 (m, 9H, FcH), 4.85–4.87 (m, 1H, CH), 6.96 (s, 1H, ArH), 8.54 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 157.6, 116.7, 90.2, 69.2, 68.2, 68.1, 67.2, 40.1, 22.0. HRMS (m/z): $[M]^+$, calcd for $C_{16}H_{16}FeN_2S$: 324.0384, found: 324.0388.

*4.3.12. 2-(1-Ferrocenylethylthio)-4,5-dihydrothiazole (**3ab**).* Orange solid; mp: 137–138 °C. IR (KBr): ν 3093, 2983, 2928, 2869, 1473, 1442, 1423, 1306, 1294, 1156, 997, 819, 500 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, J=6.6 Hz, 3H, CH_3), 3.06–3.13 (m, 2H), 3.57–3.63 (m, 1H), 3.76–3.85 (m, 1H), 4.20–4.49 (m, 9H, FcH), 6.02–6.09 (m, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.8, 69.3, 68.9, 68.0, 66.3, 53.3, 51.7, 27.7, 16.2. HRMS (m/z): $[M]^+$, calcd for $C_{15}H_{17}FeNS_2$: 331.0152, found: 331.0153.

*4.3.13. 2-(1-Ferrocenylethylthio)-benzo[d]thiazole (**3ac**).* Orange solid; mp: 112–113 °C. IR (KBr): ν 3080, 2926, 1458, 1379, 1312, 1262, 1123, 1000, 749 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.82 (d, J=7.2 Hz, 3H, CH_3), 4.06–4.51 (m, 10H, FcH, CH), 7.11–7.26 (m, 3H, ArH), 7.40 (d, J=7.2 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 127.6, 126.4, 124.5, 121.5, 114.6, 86.3, 69.8, 69.6, 68.9, 68.7, 67.8, 67.2, 53.9. HRMS (m/z): $[M]^+$, calcd for $C_{19}H_{17}FeNS_2$: 379.0152, found: 379.0170.

*4.3.14. 2-(1-Ferrocenylethylthio)-naphthalene (**3ad**).* Orange oil; IR (KBr): ν 3087, 2971, 1656, 1581, 1364, 1221, 1002, 813 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.67 (d, J=6.9 Hz, 3H, CH_3), 4.06–4.29 (m, 10H, FcH, CH), 7.42–7.48 (m, 3H, ArH), 7.73–7.83 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0, 133.2, 132.8, 132.1, 130.9, 128.6, 128.1, 127.9, 126.8, 126.5, 91.2, 69.1, 68.4, 68.2, 68.1, 66.6, 44.0, 21.6. HRMS (m/z): $[M]^+$, calcd for $C_{22}H_{20}FeS$: 372.0635, found: 372.0635.

*4.3.15. 2-((Ferrocenyl)(phenzyl)methylthio)-naphthalene (**3bd**).* Orange solid; mp: 140–141 °C. IR (KBr): ν 3051, 2922, 1581, 1494, 1194, 1028, 815, 742 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.11–4.19 (m, 9H, FcH), 5.25 (s, 1H, CH), 7.18–7.23 (m, 2H, ArH), 7.28–7.32 (m, 2H, ArH), 7.40–7.43 (m, 4H, ArH), 7.63–7.68 (m, 3H, ArH), 7.72–7.76 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4, 133.9, 133.6, 132.6, 131.5, 130.2, 128.8, 128.6, 128.4, 128.0, 127.9, 127.7, 126.7, 126.4, 90.0, 69.4, 69.0, 68.6, 68.2, 68.1, 54.7. HRMS (m/z): $[M]^+$, calcd for $C_{27}H_{22}FeS$: 434.0792, found: 434.0792.

*4.3.16. 2-(Ferrocenylmethylthio)-naphthalene (**3cd**).* Orange solid; mp: 104–105 °C. IR (KBr): ν 3083, 2939, 1735, 1584, 1496, 1459, 1260, 1131, 810 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.99–4.14 (m, 11H, FcH, CH_2), 7.39–7.47 (m, 3H, ArH), 7.70–7.78 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.0, 134.1, 132.2, 128.7, 128.2, 128.1, 127.5, 126.9, 126.1, 84.7, 69.3, 69.2, 68.5, 35.1. HRMS (m/z): $[M]^+$, calcd for $C_{21}H_{18}FeS$: 358.0479, found: 358.0477.

*4.3.17. 1,1′-Bis((naphthalene-2-ylthio)ethyl)ferrocene (**3dd**).* Orange oil; IR (KBr): ν 3080, 2967, 1673, 1581, 1219, 1017, 813 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.64 (d, J=6.9 Hz, 6H, $2CH_3$), 4.04–4.22 (m, 8H, FcH), 4.24–4.31 (m, 2H, 2CH), 7.40–7.48 (m, 6H, ArH), 7.71–7.81 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0, 133.0, 132.8, 132.2, 132.1, 130.9, 128.6, 128.1, 127.9, 126.8, 126.5, 105.2, 91.7, 69.4, 69.3, 69.2, 69.1, 69.0, 67.3, 67.1, 43.8, 21.7. HRMS (m/z): $[M]^+$, calcd for $C_{34}H_{30}FeS_2$: 558.1138, found: 558.1133.

*4.3.18. 1-Methoxyethyl ferrocene (**4aa**)[12a].* Orange liquid; IR (KBr): ν 3095, 2926, 2935, 2816, 1456, 1404, 1237, 1106, 817 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.55 (d, J=0.8 Hz, 3H, CH_3), 3.26 (s, 3H, OCH_3), 4.14–4.21 (m, 10H, FcH, CH). HRMS (m/z): $[M]^+$, calcd for $C_{13}H_{16}FeO$: 244.0551, found 244.0549.

*4.3.19. Ferrocenyl (phenyl) (methoxyl)methane (**4ab**)[12b].* Orange solid; mp: 112–113 °C. IR (KBr): ν 3091, 2981, 2870, 1494, 1453, 1397, 1194 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.28 (s, 3H, CH_3), 3.98–4.30 (m, 9H, FcH), 4.98 (s, 1H, CH), 7.30–7.42 (m, 5H, ArH). HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}FeO$: 306.0707, found 306.0707.

*4.3.20. Methoxyl methyl ferrocene (**4ac**).* Orange solid; mp: 70–71 °C. IR (KBr): ν 3230, 2957, 2925, 1236, 1104, 988 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.31 (s, 3H, CH_3), 4.14–4.24 (m, 11H, FcH, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 94.0, 89.4, 74.7, 73.9, 73.8, 73.7, 73.6, 73.0, 64.8. HRMS (m/z): $[M]^+$, calcd for $C_{12}H_{14}FeO$: 230.0394, found 230.0390.

*4.3.21. 1-Ethoxyethyl ferrocene (**4ba**)[12c].* Orange liquid; IR (KBr): ν 3095, 2974, 2927, 2866, 1367, 1306, 1105, 816, 482 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, J=0.4 Hz, 3H, CH_3), 1.54 (d, J=0.8 Hz, 3H, CH_3), 3.43–3.44 (m, 2H, CH_2), 4.13 (s, 10H, FcH, CH). HRMS (m/z): $[M]^+$, calcd for $C_{14}H_{18}FeO$: 258.0707, found 258.0708.

*4.3.22. Ferrocenyl (phenyl) (ethoxyl)methane (**4bb**).* Orange solid; mp: 54–55 °C. IR (KBr): ν 3085, 3027, 2869, 2840, 1491, 1452, 1104 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.19 (s, 3H, CH_3), 3.42 (d, J=3.6 Hz, 2H, CH_2), 4.00–4.32 (m, 9H, FcH), 5.08 (s, 1H, CH), 7.29–7.41 (m, 5H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.0, 133.7, 132.9, 132.5, 96.3, 85.2, 74.2, 73.0, 73.0, 72.8, 72.4, 69.2, 21.0. HRMS (m/z): $[M]^+$, calcd for $C_{19}H_{20}FeO$: 320.0864, found 320.0864.

*4.3.23. Ethoxyl methyl ferrocene (**4bc**)[12d].* Orange solid; mp: 50–52 °C. IR (KBr): ν 3095, 2974, 2929, 2876, 1635, 1236, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, J=7.2 Hz, 3H, CH_3), 3.48 (q, J=7.2 Hz, 2H, OCH_2), 4.13–4.27 (m, 11H, FcH, CH_2). HRMS (m/z): $[M]^+$, calcd for $C_{13}H_{16}FeO$: 244.0551, found 244.0550.

*4.3.24. 1-Propoxyethyl ferrocene (**4ca**).* Orange liquid; IR (KBr): ν 3095, 2960, 2854, 1464, 1339, 1105, 1091, 817 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=7.2 Hz, 3H, CH_3), 1.51–1.58 (m, 5H, CH_2, CH_3), 3.30–3.36 (m, 2H, OCH_2), 4.15–4.24 (m, 10H, FcH, CH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 115.0, 95.4, 78.3, 74.6, 74.1, 74.0, 73.1, 72.9, 71.2, 28.5, 26.0, 16.3. HRMS (m/z): $[M]^+$, calcd for $C_{15}H_{20}FeO$: 272.0864, found 272.0870.

*4.3.25. Ferrocenyl (phenyl) (propoxyl)methane(**4cb**).* Orange solid; mp: 43–46 °C. IR (KBr): ν 3080, 3024, 2960, 2932, 2874, 1636, 1550, 1450, 1090, 816, 728, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J=7.2 Hz, 3H, CH_3), 1.57–1.63 (m, 2H, CH_2), 3.33 (t, J=6.8 Hz, 2H, OCH_2), 3.98–4.28 (m, 9H, FcH), 5.06 (s, 1H, CH), 7.28–7.41 (m, 5H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 133.7, 132.9, 132.5, 96.5, 85.3, 75.6, 74.2, 73.0, 72.9, 72.7, 72.3, 28.4, 16.4. HRMS (m/z): $[M]^+$, calcd for $C_{20}H_{22}FeO$: 334.1020, found 334.1017.

*4.3.26. Propoxyl methyl ferrocen(**4cc**)[12e].* Orange liquid; IR (KBr): ν 3095, 2960, 2934, 2852, 1464, 1379, 1105, 1091,818, 482 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J=7.2 Hz, 3H, CH_3), 1.52–1.62 (m, 2H, CH_2), 3.37 (t, J=6.8 Hz, 2H, OCH_2), 4.13–4.26 (m, 11H, FcH, CH_2). HRMS (m/z): $[M]^+$, calcd for $C_{14}H_{18}FeO$: 258.0707, found 258.0707.

*4.3.27. Ferrocenyl (phenyl) (isopropoxyl)mathan(**4db**).* Orange solid; mp: 67–68 °C. IR (KBr): ν 3084, 2965, 2925, 2872, 1490, 1453,

1103, 1062, 809, 726, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J=6.0 Hz, 3H, CH_3), 1.21 (d, J=6.0 Hz, 3H, CH_3), 3.51–3.60 (m, 1H, OCH), 3.94–4.25 (m, 9H, FcH), 5.22 (s, 1H, Fc–CH), 7.27–7.44 (m, 5H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.7, 133.6, 132.6, 97.0, 82.1, 74.2, 73.8, 72.9, 72.8, 72.7, 72.3, 28.8, 27.1. HRMS (m/z): $[M]^+$, calcd for $C_{20}H_{22}FeO$: 334.1020, found 334.1018.

*4.3.28. Isopropoxyl methyl ferrocene(**4dc**)*[12f]. Orange solid; mp: 103–105 °C. IR (KBr): ν 3090, 2919, 1104, 1033, 999, 819 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, J=6.8 Hz, 6H, CH_3), 3.61–3.67 (m, 1H, CH), 4.12–4.26 (m, 11H, FcH, CH_2). HRMS (m/z): $[M]^+$, calcd for $C_{14}H_{18}FeO$: 258.0707, found 258.0708.

*4.3.29. Bis(ferrocenyl ethyl) ether(**5aa**)*[12g]. Orange liquid; IR (KBr): ν 3095, 2972, 2868, 1456, 1367, 1097, 1000, 816 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.42 (d, J=6.0 Hz, 3H, CH_3), 1.48 (d, J=6.4 Hz, 3H, CH_3) 4.10–4.23 (m, 18H, FcH), 4.38–4.42 (m, 2H, CH). HRMS (m/z): $[M]^+$, calcd for $C_{24}H_{26}Fe_2O$: 442.0682, found 442.0682.

*4.3.30. Bis(phenyl ferrocenyl methyl) ether(**5bb**)*[12h]. Orange solid; mp: 115–116 °C. IR (KBr): ν 3085, 3024, 2889, 1491, 1453, 1105, 1045, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.90–4.22 (m, 18H, FcH), 5.02 (s, 2H, CH), 7.29–7.44 (m, 10H, ArH). HRMS (m/z): $[M]^+$, calcd for $C_{34}H_{30}Fe_2O$: 566.0995, found 566.1002.

*4.3.31. Bis(ferrocenyl methyl) ether(**5cc**)*[12i]. Orange solid; mp: 128–129 °C. IR (KBr): ν 3029, 2959, 2920, 2865, 1236, 1104 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.14–4.24 (m, 22H, FcH, CH_2). HRMS (m/z): $[M]^+$, calcd for $C_{22}H_{22}Fe_2O$: 414.0369, found 414.0365.

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Supplementary data

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References and notes

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