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Cerium ammonium nitrate: an efficient catalyst for carbon–carbon bond formation from ferrocenyl alcohol substrate

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ABSTRACT

The substitution reaction of ferrocenyl alcohol with various nucleophiles catalyzed by cerium ammonium nitrate (CAN) was investigated. This CAN-mediated direct carbon–carbon bond formation provides the corresponding products in moderate to high yields with relatively lower catalyst loading (5 mol %) at room temperature. It demonstrated a convenient synthetic protocol for the ferrocene functionalities.

1. Introduction

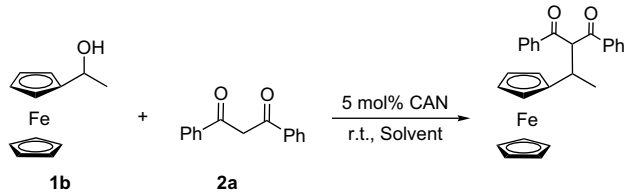
Coupling reactions between reactive nucleophiles such as organometallic compounds (R′M) and halide or a related species (RX) are well developed to prepare R–R′ via carbon–carbon bond formation. In this type of reaction, substrates and reagents are often prepared from the corresponding alcohols (ROH) and active methylenes (R′H), what's more, the salt wastes are inevitably produced. Compared to this, the direct reaction of ROH and R′H would be an ideal alternative because the raw materials are easily available and water would be the only byproduct, which would simplify the separation process. So, a water-tolerant catalyst is required to activate either ROH or R′H in the reaction.

Cerium ammonium nitrate (CAN), a versatile single-electron oxidant, has been widely used in organic transformations due to its many advantages such as solubility in organic solvents, high reactivity, and ease of handling. The pioneering work was reported by Heiba and Dessau on CAN to prepare carbon-centered radicals in 1971.[1] Subsequently, Nair et al. developed a facile CAN-mediated protocol for the thiocyanation and selenocyanation of olefins.[2] In recent years, several synthetic transformations have been reported involving both C–C as well as and C–X (X=hetero atom) bond-forming reactions facilitated by catalytic amounts of CAN.[3] But in these reactions, rare examples were accomplished by the approach of activating the alcohol.

We have been interested in the carbon–carbon formation from the alcohol precursor for years. In our previous work, we established the synthetic protocol of bis(indole) derivatives from indol-3-yl alcohol.[4] Since then, we also found that xanthene derivatives could be promoted by CAN and react with indole or pyrrole to afford the corresponding alkylation products.[5] As a continuation of our on-going investigations in CAN-mediated new C–C bond formation, we would like to introduce the ferrocenyl to the alcohol substrate to synthesize some novel functionalized molecules. Herein, these results are reported.

2. Results and discussion

In view of our previous findings,[5] 5 mol % CAN as the catalyst was examined in the model reaction of **1b** with **2a** at first (Scheme 1). The reaction proceeded at room temperature smoothly, within 0.5 h, to afford a 97% yield of the desired product. Another set of experiments showed that less catalyst loading (2 mol % CAN) decreased the yield of product and more catalyst loading (10 mol % CAN) was not favorable either. The same model reaction was performed to select the best solvent for this reaction, and the details are listed in Table 1. The solvent had great influence on the yield of final product. Acetonitrile, rather than THF, diethyl ether, or methanol, turned out to be the best solvent suitable for the reaction although the similar result was obtained in dichloromethane.



1b **2a**

Scheme 1.

The scope of the substrates was studied subsequently (Scheme 2). Different α-substituted ferrocenyl alcohol, such as

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Table 1
The reaction of **1b** with **2a** in different solvents[a]

Entry	Solvent	Time/h	Yield[b]/%
1	CH_3OH	13	71
2	CH_3CN	0.5	97
3	CH_2Cl_2	0.5	92
4	THF	0.5	58
5	Et_2O	0.5	0

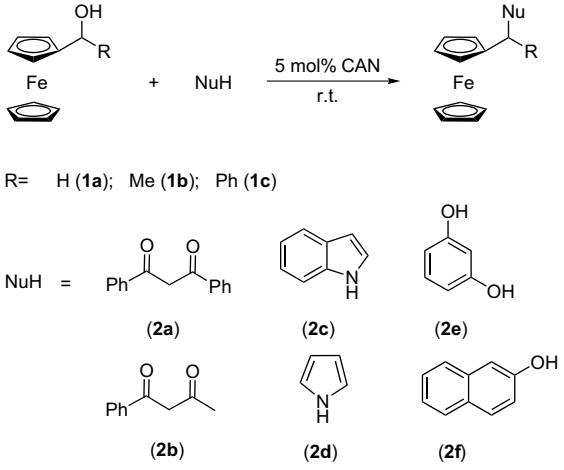
[a] The reactions were performed at room temperature, entry 1 was carried out at 50 °C.
[b] Isolated yield.

ferrocenyl methanol (**1a**) and (ferrocenyl)(phenyl)methanol (**1c**) were used as substrates. After the reactions proceeded for a prolonged time, **3a** (crystal structure was shown in Fig. 1) and **3c** were obtained in high yields (entries 1 and 3, Table 2). It is noteworthy that no excessive nucleophile was required in the reaction. In addition, a similar result as Cozzi's[7] was observed, that is, no reaction occurred between **1c** and **2a** in the absence of catalyst (entry 4, Table 2). As an analogous active methylene compound, **2b** also showed good reactivity in this reaction (entries 5–7, Table 2).

The modification of indoles is an attractive field because of their significance in organic and medicinal chemistry. In this area, transition metal catalysts or catalytic systems play an important role.[8] Application of our present strategy to indoles gave 3-alkylated products in relatively good yields (entries 8–10, Table 2), and no regioisomers through N- or 2-alkylation were observed. The structure of typical compound **3i** was confirmed by X-ray crystal structure (Fig. 2). Compared with indole, pyrrole is more electron rich in heterocyclic aromatics. The reaction of pyrrole seemed to be a bit complicated, **1b** and **1c** reacted well with pyrrole to produce the desired products, while no product was observed when **1a** was used.

Benzene or naphthalene system, being activated by hydroxyl group, can also act as good nucleophiles for the reaction. More the substrate is activated, better the yields of the desired products are, for example, resorcinol reacted with all of the three alcohols successfully in a short time to provide the products in excellent yields (entries 14–16, Table 2). Moderate results, however, were obtained in the reactions with 2-naphthol. A reaction mixture of **1a** and **2o** was stirred at room temperature for 120 h, only 23% yield of the product was obtained (entry 17, Table 2), which maybe ascribed to the less reactive substrate and reagent. But a 72% yield of the product can be obtained within 0.5 h when the reaction was carried out at 50 °C (entry 18, Table 2).

A possible mechanism of the reaction is illustrated in Scheme 3, which might involve first the oxidation of the alcohol (I) to a radical cation (II) and then the heterolytic cleavage of the C–O bond to



Scheme 2.

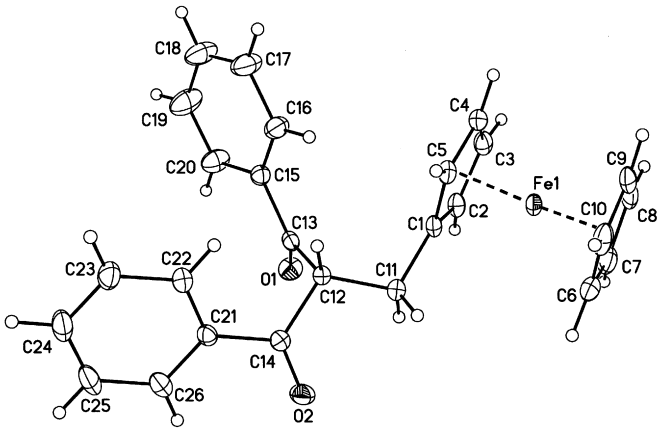


Figure 1. Crystal structure of **3a**.

a cabocation (III)[9] (or (III′)[10]). A hydroxyl radical could be reduced by Ce^{3+} with the regeneration of Ce^{4+}, and the cabocation could subsequently react with the nucleophile, after deprotonation, to give the desired product. Meanwhile, the hydroxyl anion and proton combined to produce water as the only byproduct.

3. Conclusion

In summary, we have described an efficient and direct C–C bond formation from alcohols and nucleophiles in the presence of a cerium(IV) catalyst. The advantages of this reaction are: (1) inexpensive, water-tolerant, and less loading catalyst; (2) no excessive nucleophiles were needed; and (3) simple operation. Furthermore, ferrocene is facilely introduced into the products, which may have potential applications.

4. Experimental

4.1. General

Ferrocenyl alcohols were prepared by the similar method according to the literature.[6] 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. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. High resolution mass spectra were obtained using Microma GCT-TOF instrument. X-ray diffraction data were recorded on a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation.

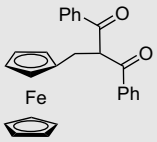
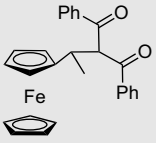
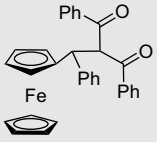
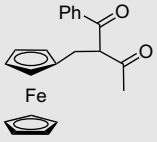
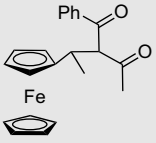
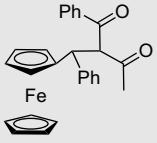
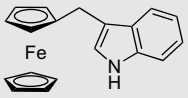
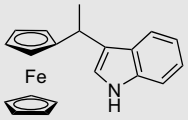
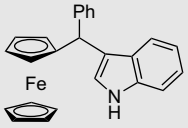
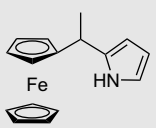
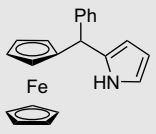
4.2. Typical experimental procedure

A mixture of ferrocenyl alcohol (**1b**) (0.5 mmol), 1,3-diphenylpropane-1,3-dione (**2a**) (0.5 mmol) and CAN (5 mol %) in acetonitrile (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford product **3b**. This procedure was followed for the synthesis of other ferrocenyl derivatives (**3a**, **3c**–**3q**).

4.3. 2-Ferrocenylmethyl-1,3-diphenylpropane-dione (3a)

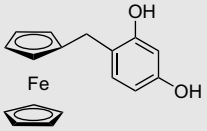
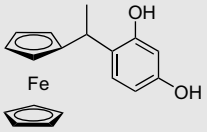
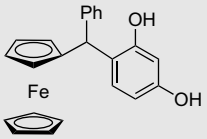
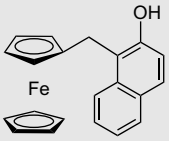
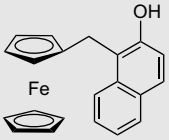
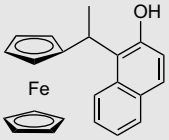
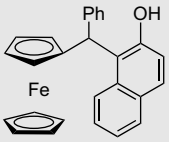
Orange solid; mp: 130.2–131.0 °C; IR (KBr): ν 3062, 2932, 1699, 1596, 1303 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.15 (d, J=6.4 Hz, 2H, CH_2), 4.01–4.13 (m, 9H, Fc–H), 5.31 (t, J=6.4 Hz, 1H), 7.31–7.39 (m,

Table 2
The reactions of **1a–c** with **2a–f** catalyzed by CAN[a]

Entry	Alcohol	NuH	Product		Time/h	Yield[b]/%
1	**1a**	**2a**		**3a**	3	98
2	**1b**	**2a**		**3b**	0.5	97
3	**1c**	**2a**		**3c**	1	87
4[c]	**1c**	**2a**			8	N.R.[d]
5	**1a**	**2b**		**3d**	4.5	96
6	**1b**	**2b**		**3e**	5	99
7	**1c**	**2b**		**3f**	13.5	89
8	**1a**	**2c**		**3g**	0.5	66
9	**1b**	**2c**		**3h**	1	64
10	**1c**	**2c**		**3i**	1.25	80
11	**1a**	**2d**	—	—	3.5	N.R.[d]
12	**1b**	**2d**		**3j**	1.0	52
13	**1c**	**2d**		**3k**	0.25	88

(*continued on next page*)

Table 2 (*continued*)

Entry	Alcohol	NuH	Product		Time/h	Yield[b]/%
14	**1a**	**2e**		**3l**	1.5	96
15	**1b**	**2e**		**3m**	1.5	95
16	**1c**	**2e**		**3n**	2	91
17	**1a**	**2f**		**3o**	120	23
18[e]	**1a**	**2f**		**3o**	0.5	72
19	**1b**	**2f**		**3p**	24	64
20	**1c**	**2f**		**3q**	2	56

[a] All reactions were carried out with 5 mol % CAN in 2 mL acetonitrile at room temperature.
[b] Isolated yield.
[c] In the absence of catalyst.
[d] N.R.=no reaction.
[e] The reaction was performed at 50 °C.

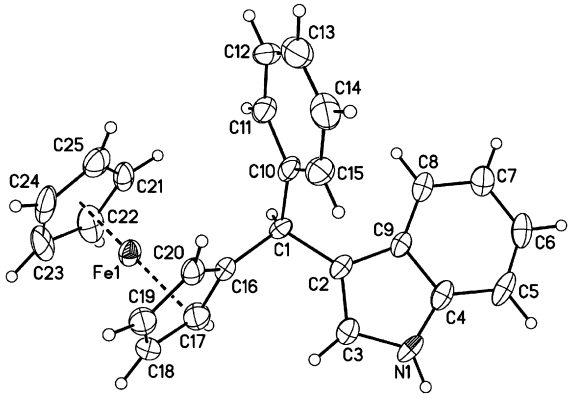


Figure 2. Crystal structure of **3i**.

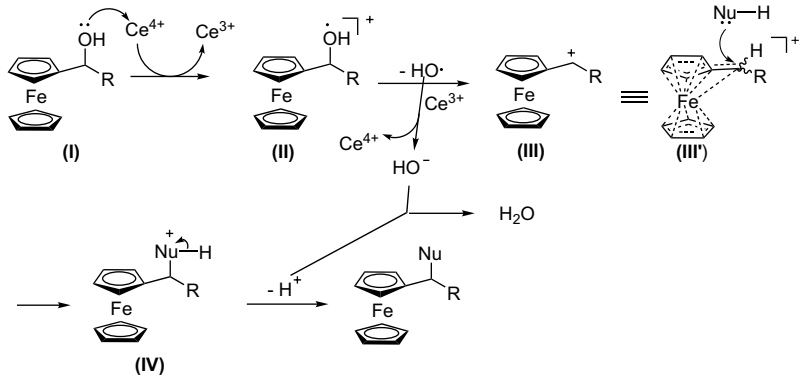
10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 136.3, 133.6, 129.0, 128.9, 86.0, 69.2, 69.0, 68.0, 60.0, 30.4. HRMS (m/z): $[M]^+$, calcd for $C_{26}H_{22}O_2Fe$: 422.0969. Found: 422.0974.

4.4. 2-(1-Ferrocenylethyl)-1,3-diphenylpropane-dione (3b)

Orange solid; mp: 155.5–156.6 °C; IR (KBr): ν 3058, 1689, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (d, J=6.8 Hz, 3H, CH_3), 3.78–3.84 (m, 1H, Fc–CH), 3.87–4.13 (m, 9H, Fc–H), 5.29 (d, J=10.2 Hz, 1H, COCH), 7.29–7.85 (m, 10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 194.7, 137.3, 137.1, 133.6, 133.2, 128.9, 128.8, 128.7, 128.6, 92.3, 69.4, 68.9, 67.7, 67.6, 66.0, 65.1, 35.5, 18.8. HRMS (m/z): $[M]^+$, calcd for $C_{27}H_{24}O_2Fe$: 436.1126. Found: 436.1143.

4.5. 1,3-Diphenyl-2-[phenyl(ferrocenyl)methyl]propane-1,3-dione (3c)

Orange solid; mp: 215.0–216.2 °C (200 °C[11]); IR (KBr): ν 3058, 1689, 1595, 1447, 1263 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82–4.01 (m, 9H, Fc–H), 4.95 (d, J=10.2 Hz, 1H, COCH), 6.03 (d,



Scheme 3.

J=10.2 Hz, 1H, Fc–CH), 7.16–7.84 (m, 15H, Ar–H). HRMS (m/z): $[M]^+$, calcd for $C_{32}H_{26}O_2Fe$: 498.1282. Found: 498.1289.

4.6. 1-Phenyl-2-ferrocenylbutane-1,3-dione (3d)

Orange solid; mp: 80.2–80.8 °C (82–84 °C[12]); IR (KBr): ν 3085, 1714, 1661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, CH_3), 3.00–3.11 (m, 2H, Fc–CH_2), 4.00–4.10 (m, 9H, Fc–H), 4.59 (t, J=6.8 Hz, 1H, COCH), 7.43–7.92 (m, 5H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.7, 196.2, 136.9, 134.0, 129.3, 129.1, 85.6, 69.2, 69.1, 69.0, 68.2, 68.1, 65.9, 30.0, 29.0. HRMS (m/z): $[M]^+$, calcd for $C_{21}H_{20}O_2Fe$: 360.0813. Found: 360.0811.

4.7. 1-Phenyl-2-(1-ferrocenylethyl)butane-1,3-dione (3e)

Orange solid; mp: 199.4–200.6 °C; IR (KBr): ν 3083, 1711, 1669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, J=6.8 Hz, 3H, CH_3), 1.94 (s, 3H, $COCH_3$), 3.57–3.61 (m, 1H, COCH), 3.89–4.16 (m, 9H, Fc–H), 4.41–4.47 (m, 1H, Fc–CH), 7.33–7.91 (m, 5H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.7, 195.3, 137.6, 137.4, 133.8, 133.5, 129.0, 128.8, 92.0, 72.5, 71.3, 68.9, 68.0, 67.9, 67.7, 65.9, 65.6, 34.9, 34.8, 30.5, 28.4, 19.1, 18.4. HRMS (m/z): $[M]^+$, calcd for $C_{22}H_{22}O_2Fe$: 374.0969. Found: 374.0971.

4.8. 1-Phenyl-2-[phenyl(ferrocenyl)methyl]butane-1,3-dione (3f)

Orange solid; mp: 193.5–194.8 °C; IR (KBr): ν 3083, 1711, 1669, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.91 (s, 3H), 3.91–3.99 (m, 9H, Fc–H), 4.77 (d, J=10.8 Hz, 1H), 5.25 (d, J=10.8 Hz, 1H), 7.28–7.95 (m, 10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 193.8, 142.0, 137.2, 133.6, 128.9, 128.8, 128.6, 128.4, 127.0, 90.0, 71.2, 69.8, 69.0, 68.8, 67.4, 67.1, 48.9, 30.2. HRMS (m/z): $[M]^+$, calcd for $C_{27}H_{24}O_2Fe$: 436.1126. Found: 436.1138.

4.9. (1*H*-Indol-3-yl)ferrocenylmethane (3g)

Orange solid; mp: 120.8–121.8 °C (146–147 °C[13]); IR (KBr): ν 3397, 3057, 1454, 1420, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 2H, CH_2), 4.06–4.17 (m, 9H, Fc–H), 6.57–7.42 (m, 4H, In–H), 7.64 (d, J=8.4 Hz, 1H, In–H), 7.89 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO): δ 141.6, 132.4, 127.9, 126.2, 123.9, 123.6, 120.4, 116.7, 94.3, 73.8, 72.3, 30.6 HRMS (m/z): $[M]^+$, calcd for $C_{19}H_{17}NFe$: 315.0710. Found: 315.0703.

4.10. (1*H*-Indol-3-yl)ferrocenylmethylmethane (3h)

Orange solid; mp: 127.3–129.1 °C (112–113 °C[14]); IR (KBr): ν 3406, 3057, 1457, 1420, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.72 (d, J=7.2 Hz, 3H, CH_3), 4.09–4.17 (m, 9H, Fc–H), 4.27 (s, 1H, Fc–CH), 6.76 (s, 1H, CH), 7.12–7.34 (m, 3H, In–H), 7.68 (d, J=6.9 Hz, 1H, In–H), 7.82 (s, 1H, NH); HRMS (m/z): $[M]^+$, calcd for $C_{20}H_{19}NFe$: 329.0867. Found: 329.0881.

4.11. (1*H*-Indol-3-yl)ferrocenylphenylmethane (3i)

Orange solid; mp: 157.9–159.7 °C (152–153 °C[14]); IR (KBr): ν 3411, 3056, 1620 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.09–4.31 (m, 9H, Fc–H), 5.28 (s, 1H, Fc–CH), 6.84 (s, 1H, CH), 6.95 (t, J=7.5 Hz, 1H, In–H), 7.11 (t, J=7.5 Hz, 1H, In–H), 7.13–7.35 (m, 7H, In–H), 7.90 (s, 1H, In–NH). HRMS (m/z): $[M]^+$, calcd for $C_{25}H_{21}NFe$: 391.1023. Found: 391.1021.

4.12. 2-(Ferrocenylethyl)-1*H*-pyrrole (3j)[7]

Orange oil; IR (KBr): ν 3438, 3090, 2870, 1618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.61 (d, J=6.8 Hz, 3H, CH_3), 3.87 (m, 1H, Fc–CH), 4.09–4.16 (m, 9H, Fc–H), 5.93 (s, 1H), 6.11 (s, 1H), 6.61 (s, 1H), 7.96 (s, 1H, NH). HRMS (m/z): $[M]^+$, calcd for $C_{16}H_{17}NFe$: 279.0710. Found: 279.0706.

4.13. 2-[Phenyl(1-ferrocenyl)methyl]-1*H*-pyrrole (3k)[7]

Orange oil; IR (KBr): ν 3432, 3093, 2866, 1490, 1451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.94–4.12 (m, 9+1H, Fc–H and CH), 5.07 (s, 1H), 5.62 (s, 1H), 7.19–7.32 (m, 5H, Ar–H), 8.08 (s, 1H, NH). HRMS (m/z): $[M]^+$, calcd for $C_{21}H_{19}NFe$: 341.0867. Found: 341.0870.

4.14. 4-Ferrocenylmethylbenzene-1,3-diol (3l)[15]

Orange oil; IR (KBr): ν 3362, 3289, 1608, 1489, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.59 (d, J=16.0 Hz, 2H, CH_2), 4.12–4.16 (m, 9H, Fc–H), 5.16 (m, 2H, OH), 6.31–6.40 (m, 2H, Ar–H), 6.70–7.10 (m, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 154.9, 154.3, 152.4, 148.9, 148.8, 140.6, 133.6, 131.7, 131.0, 130.7, 120.2, 108.4, 108.2, 108.2, 107.8, 103.5, 103.2, 88.3, 69.7, 69.6, 69.5, 69.4, 69.1, 68.0, 61.3. HRMS (m/z): $[M]^+$, calcd for $C_{17}H_{16}O_2Fe$: 308.0500. Found: 308.0493.

4.15. 4-(Ferrocenylethyl)benzene-1,3-diol (3m)

Orange oil; IR (KBr): ν 3504, 3389, 2966, 2870, 1617, 1430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.68 (d, J=6.8 Hz, 3H, CH_3), 3.97–3.99 (m, 1H, CH), 4.06–4.26 (m, 9H, Fc–H), 5.26–5.29 (m, 1H, OH), 5.50–5.54 (m, 1H, OH), 6.31–6.40 (m, 2H, Ar–H), 6.81–7.00 (m, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 157.0, 154.6, 153.7, 151.6, 130.6, 69.1, 68.5, 68.3, 68.2, 67.3, 66.9, 61.3, 33.1, 21.3. HRMS (m/z): $[M]^+$, calcd for $C_{18}H_{18}O_2Fe$: 322.0656. Found: 322.0653.

4.16. 4-[Ferrocenyl(phenyl)methyl]benzene-1,3-diol (3n)

Orange oil; IR (KBr): ν 3028, 2930; 1709, 1600, 1514 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (t, J=8.4 Hz, 1H, CH), 4.00–4.20 (m, 9H, Fc–H), 5.20–5.21 (d, J=6.0 Hz, 1H, OH), 5.28 (s, 1H, OH), 6.20–6.38 (m, 2H, Ar–H), 6.68–7.04 (m, 1H, Ar–H), 7.20–7.27 (m, 5H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 152.7, 133.2, 129.5, 129.0, 128.9, 128.8, 127.0, 126.8, 123.3, 121.4, 120.1, 90.9, 69.7, 69.5, 68.9, 68.0. HRMS (m/z): $[M]^+$, calcd for $C_{23}H_{20}O_2Fe$: 384.0813. Found: 384.0825.

4.17. 1-(Ferrocenylmethyl)-naphthalen-2-ol (3o)

Orange solid; mp: 111.0–112.0 °C; IR (KBr): ν 3410, 3031, 1620, 1600, 1465, 1196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.05 (s, 2H, CH_2), 4.14–4.20 (m, 9H, Fc–H), 5.25 (s, 1H, OH), 7.08 (d, J=8.8 Hz, 1H, Ar–H), 7.33 (t, J=7.2 Hz, 1H, Ar–H), 7.49 (t, J=7.2 Hz, 1H, Ar–H), 7.65 (d, J=8.8 Hz, 1H, Ar–H), 7.77 (d, J=8.0 Hz, 1H, Ar–H), 7.99 (d, J=8.8 Hz, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.5, 129.6, 128.8, 128.4, 126.7, 126.6, 123.6, 123.3, 119.4, 118.2, 69.6, 69.2, 68.8, 67.9, 25.0. HRMS (m/z): $[M]^+$, calcd for $C_{21}H_{18}OFe$: 342.0707. Found: 342.0708.

4.18. 1-([1-Ferrocenyl]ethyl)-naphthalen-2-ol (3p)

Orange solid; mp: 145.7–146.1 °C; IR (KBr): ν 3420, 3036, 1617, 1598, 1468, 1201 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.73 (d, J=7.6 Hz, 3H, CH_3), 4.28 (s, 8H, Fc–H), 4.56 (s, 1H, Fc–H), 5.08 (s, 1H, OH), 5.71 (s, 1H, CH), 6.99 (d, J=8.8 Hz, 1H, Ar–H), 7.38–8.10 (m, 5H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 132.5, 129.8, 129.1, 128.7, 126.8, 123.1, 120.2, 70.0, 69.9, 69.8, 69.5, 69.4, 66.5, 31.9, 18.5. HRMS (m/z): $[M]^+$, calcd for $C_{22}H_{20}OFe$: 356.0864. Found: 356.0863.

4.19. 1-[Phenyl(ferrocenyl)methyl]-naphthalen-2-ol (3q)

Orange solid; mp: 159.2–163.1 °C. IR (KBr): ν 3443, 3031, 1620, 1602, 1468, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.98–4.30 (m, 9H, Fc–H), 5.48 (s, 1H, OH), 6.18 (s, 1H, CH_3), 7.06 (d, J=8.4 Hz, 1H, Ar–H), 7.22 (m, 1H, Ar–H), 7.29–7.34 (m, 3H, Ar–H), 7.39–7.41 (m, 2H, Ar–H), 7.43–7.48 (m, 1H, Ar–H), 7.70 (d, J=8.8 Hz, 1H, Ar–H), 7.77 (d, J=8.0 Hz, 1H, Ar–H), 8.08 (d, J=8.0 Hz, 1H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 164.5, 157.0, 155.2, 154.0, 152.4, 144.3, 132.2, 132.1, 131.0, 130.7, 129.0, 128.8, 128.5, 126.5, 91.5, 69.2, 68.8, 68.4, 68.0, 61.3. HRMS (m/z): $[M]^+$, calcd for $C_{27}H_{22}OFe$: 418.1020. Found: 418.1026.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.11.048.

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15. Pennie, J. T.; Bieber, T. I. *Tetrahedron Lett.* **1972**, *13*, 3535; Notes: crystallographic data for the structures of **3a** and **3i** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with Nos. CCDC 697351 and 697350, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: linstead@ccdc.cam.ac.uk or deposit@ccdc.cam.ac.uk; fax: +44 01223 336033). Structural parameters for **3a**: data collection: Rigaku Mercury CCD area detector; crystal size: 0.70×0.24×0.20 mm^3; $C_{26}H_{22}FeO_2$, Mr=422.29, monoclinic, space group $P21/c$, a=13.860(3), b=14.844(3), c=9.937(2) Å, α=90.00, β=96.720(5), γ=90.00, V=2030.3(8) $Å^3$, Z=4, D_{calcd}=1.382 g cm^{-3}, $R_{[I>2\sigma(I)]}$=0.0519, $wR[I>2\sigma(I)]$=0.1093. Structural parameters for **3i**: data collection: Rigaku Mercury CCD area detector; crystal size: 0.34×0.26×0.10 mm^3; $C_{25}H_{21}FeN$, Mr=391.28, monoclinic, space group $P2/c$, a=10.582(5), b=9.433(4), c=19.280(7) Å, α=90.00, β=99.607(12), γ=90.00, V=1897.6(13) $Å^3$, Z=4, D_{calcd}=1.370 g cm^{-3}, $R_{[I>2\sigma(I)]}$=0.0865, $wR_{[I>2\sigma(I)]}$=0.1582.