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Nucleophilic Addition Reactions of Tricarbonyl [η^5-1-(Phenylsulfonyl)cyclohexadienyl]iron(I) Complex

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Hydride abstraction of tricarbonyl[η^4-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) complex **2** with $Ph_3C^+PF_6^-$ regiospecifically provided the title compound **3** in excellent yield. Cationic complex **3** could react with a variety of nucleophiles in good yields. Soft nucleophiles prefer to attack at the C-5 position, whereas hard nucleophiles such as methyllithium and the enolate of ethyl acetate gave the C-5 as well as the C-2 addition products. Some synthetic applications of the addition products were also studied.

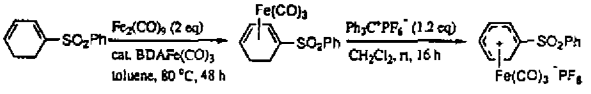
INTRODUCTION

Iron complexes of dienes are very useful in organic synthesis.[1] The iron moiety effectively decreases the electron density of the diene, thus facilitating the nucleophilic addition reactions. The nucleophiles and the reaction condition may change the regiochemistry of the reaction.[2] The substituent on the diene may also play an important role.[3] We have reported the preparation of [η^4-2-(phenylsulfonyl)-1,3-butadiene]tricarbonyliron(0) complex[4] from its 3-sulfolene precursor,[5] and have studied its reaction with various nucleophiles. All the nucleophiles added to the C-4 position of the iron complex independent of the temperatures used. Without the iron moiety, the reaction with nucleophiles proceeds at the C-1 position.[6]

The reactivity of the η^4-diene iron complexes can be further enhanced by converting it into η^5-dienylium iron complexes.[7] Thus, even weak nucleophiles such as acetone or enamines can give the addition products in good yield.[8] Although many alkyl- or alkoxy-substituted η^5-cyclohexadienyliron complexes have been reported for such reactions,[7] nucleophiles always attack at the terminal carbon. The regioselectivity is apparently dependent on the electronic and steric factors.[9] Recently we have reported the synthesis of tricarbonyl[η^5-1-(phenylthio)cyclohexadienyl]iron complex and its nucleophilic addition reactions.[10] Soft and more hindered nucleophiles added at the C-5 position of the dienylium complex, whereas hard and less hindered nucleophiles gave the C-5 as well as the C-1 addition products. Only a few electron-withdrawing groups substituted on C-1 of the dienylium system have been reported which were successful in the nucleophilic addition reactions.[8a] We now describe the first synthesis and nucleophilic addition reactions of a sulfone-substituted cyclohexadienylium iron complex **3**, and some synthetic applications of the addition products **4**.[11]

RESULTS AND DISCUSSION

Treatment of 1-(phenylsulfonyl)-1,3-cyclohexadiene **1**[12] with 2 equiv of $Fe_2(CO)_9$ in warm toluene catalyzed by (benzylideneacetone)$Fe(CO)_3$[13] gave the diene complex **2** in 76% yield. Subsequent hydride abstraction with triphenylcarbenium hexafluorophosphate regiospecifically provided the η^5-dienylium complex **3** in excellent yield (Eq. 1), which was characterized by ^1H and ^{13}C NMR spectroscopy and analytical methods.

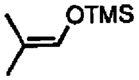
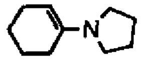


(1)

1 2 (76%) 3 (98%)

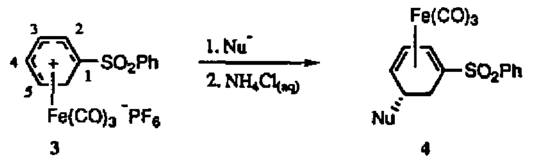
The reactions of 3 with a range of nucleophiles (Eq. 2) are shown in Table 1. It can be seen that heteroatom nucleophiles (entries 1-5), cyanide (entry 6), stabilized enolates (entries 7-9), and enol derivatives (entries 10-12) all reacted smoothly with **3** at C-5 to give the η^4-iron complexes **4**. The zinc-copper reagent (entry 13) and allylsilane (entry 14) also reacted with 3 at the C-5 position, whereas similar reaction of the phenylthio-substituted complex with the enolate of acetone, allylsilane or diethylamine gave the deprotonation/demetallation product instead.[10] Complex **3** reacted with *p*-anisidine in refluxing acetonitrile[14] to give the *C*-alkylation product **4o** in 36% yield (Eq. 3). This result is different from that of the phenylthio-substituted complex,[10] where *N*-alkylation and substitution of the phenylthio group was observed. The regiochemistry of **4** has been assigned based on the ^1H, ^{13}C NMR and DEPT experiments. For ex-

Table 1. Nucleophilic Addition Reactions of Dienylium Iron(I) Complex **3**

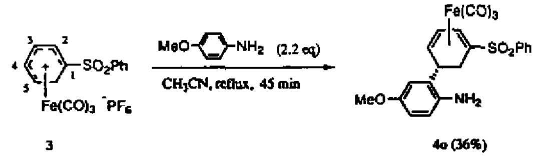
Entry	Nucleophile	Equiv	Condition	Product (%, Yield)[a]
1	MeOH		neat, 25 °C, 24 h	**4a** (88)
2	NaSPh	(1.5)	THF, -78 °C, 1 h	**4b** (91)
3	$NaSO_2Ph$	(1.5)	THF, 24 °C, 30 min	**4c** (92)
4	*i*-$PrNH_2$	(2)	THF, -78 °C, 5 min	**4d** (82)
5	$P(OEt)_3$	(1.05)	1. THF, 18 °C, 1 h 2. $NaHCO_{3(aq)}$, 1 h	**4e** (96)
6	TMSCN	(1.2)	CH_3CN, reflux, 4 h	**4f** (86)
7	$NaCH(CO_2Me)_2$	(1.35)	THF, -78 °C, 1 h, 26 °C, 1 h	**4g** (91)
8	$NaCH(CO_2Me)COMe$	(1.35)	THF, -78 °C, 1 h, 26 °C, 1 h	**4h** (98)
9	$NaCH(CO_2Me)SO_2Ph$	(1.35)	THF, -78 °C, 1 h, 26 °C, 1 h	**4i** (86)
10	CH_3COCH_3		neat, 20 °C, 26 h	**4j** (85)
11		(5)	CH_2Cl_2, 29 °C, 12 h	**4k** (66)
12		(2.5)	CH_3CN, 22 °C, 1 h	**4l** (72)
13		(2)	THF, -78 to 29 °C, 1.5 h 50 °C, 1.5 h	**4m** (82)
14		(2.5)	CH_3CN, 21 °C, 4 h	**4n** (56)

[a] Isolated yield of purified products.

ample, the compound **4a** has two protons at δ 6.17 (d, *J* = 4.6 Hz, H-2) and δ 5.42 (dd, *J* = 4.6, 5.3 Hz, H-3), and one proton at δ 3.24 (dd, *J* = 0.8, 3.2, 14.4 Hz, H-4), as well as one broad peak of the CO absorption at δ 207.2 and one quaternary carbon at δ 76.8 (C-1).

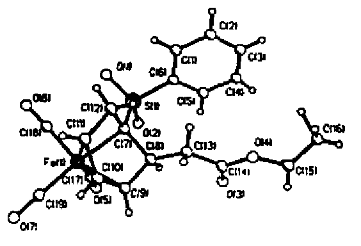


(2)



(3)

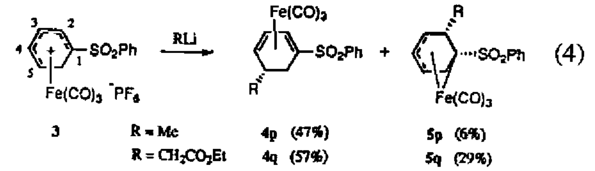
Compound **3** reacted with hard nucleophiles such as methyllithium and the enolate of ethyl acetate (Eq. 4) to give a mixture of C-5 and C-2 addition products **4** and **5**. The regiochemistry of **4p** and **5p** have been assigned based on the ^1H, ^{13}C NMR and DEPT experiments. Compound **4p** has two protons at δ 6.11 (d, *J* = 4.4 Hz, H-2) and δ 5.23 (dd, *J* = 4.4, 6.4 Hz, H-3), and one proton at δ 3.23 (dd, *J* = 2.9, 6.4 Hz, H-4), as well as one broad peak of the CO absorption at δ 208.8 and one quaternary carbon at δ 80.7 (C-1), whereas compound **5p** has absorptions at δ 4.74 (dd, *J* = 6.0, 6.2 Hz, H-3), δ 4.66 (ddd, *J* = 1.5, 6.1, 6.2 Hz, H-4) and δ 4.50 (dd, *J* = 6.0, 6.1 Hz, H-5), as well as three peaks of the CO absorptions at δ 202.4, 209.5, 209.8 and a quaternary carbon at δ 38.3 (C-1). The structure of **5q** was further confirmed by the X-ray crystallography (Fig. 1).[15] With the enolate of ethyl acetate as the nucleophile, the best condition was to use LHMDS as the base. If LDA was used as the base, then **4r** was the major product (34% yield). It can be seen from these results that the dienylium iron complex **3** is very reac-

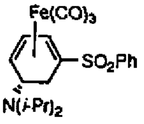


Fe (1) - C (7) 2.070 (3)
Fe (1) - C (9) 2.119 (4)
Fe (1) - C (10) 2.078 (4)
Fe (1) - C (11) 2.148 (4)
Fe (1) - C (17) 1.781 (4)
Fe (1) - C (18) 1.788 (4)
Fe (1) - C (19) 1.816 (4)

Fig. 1. Crystal structure of iron complex **5q**. Selected bond lengths are given in Å.

tive with various nucleophiles.

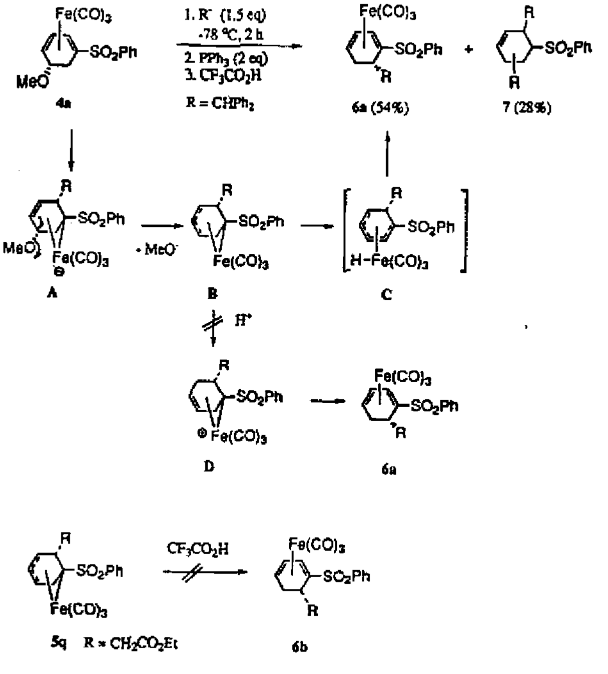




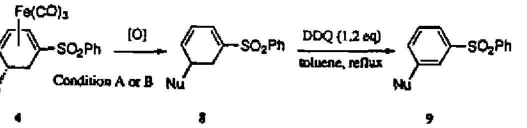
4r

Complex **4a** could be further reacted with diphenylmethane anion (Scheme I) to give a new complex **6a** in 54% yield, which can be seen as a nucleophilic addition at C-6 with concomitant removal of the methoxy group at C-5. We propose that the hard nucleophile initially adds to the C-2 of **4a** to yield a σ,η^2-anionic intermediate **A**, which then undergoes demethoxylation to give a σ,η^3-intermediate **B**. Subsequent β-hydride elimination to the intermediate **C** followed by readdition gave the final product **6a**. An alternative pathway for the formation of **6a** via protonation of **B** to give the intermediate **D** is ruled out by carrying out a protonation experiment with **5q** which did not lead to the diene product **6b**. The other product **7** is presumably obtained by a second nucleophilic addition to complex **6a** followed by demetallation.

Scheme I



The demetallation of **4** was also studied (Eq. 5 and Table 2). Treatment of the addition products **4** with anhydrous trimethylamine *N*-oxide in refluxing benzene for 1.5 h (Condition A) gave the dienes **8**. A better method is to use ceric ammonium nitrate (CAN)/acetone (Condition B). The dienes **8** containing the sulfone substituent could be used for further synthetic applications.[17] The aromatized products **9** could be obtained by treatment of the dienes **8** with DDQ. Compounds **9** bealing the sulfonyl group *meta* to the nucleophiles are rather difficult to prepare by other means.



Saponification of complex **4q** gave **4s** which could be further demetallated by treatment with CAN to give the carboxylic acid **8s** (Scheme II). The compound **8s** could undergo iodolactonation to give the bicyclic lactone **10**.[18] The stereochemistry of **10** was confirmed by the ^1H NMR, homo-decoupling and NOE experiments. Compound **10** has one vinyl proton at δ 7.20 (ddd, J = 0.9, 2.3, 5.9 Hz, H_a), an allylic proton at δ 5.09 (br d, J = 5.9 Hz, H_b), and two protons at the ring junction at δ 5.05 (ddd, J = 0.7, 1.6, 6.0 Hz, H_c), and δ 3.08-3.16 (m, H_d). We found that there was a 4.5% NOE effect between H_c and H_d, but there was no NOE effect between H_d and H_b. This means that **10** has a *cis* ring junction structure and the iodo group is substituted on the *exo*-face, in accordance with the reaction mechanism. The compound **10** could undergo further deiodination by treatment with Bu_3SnH to give a mixture of the double bond isomers **11** and **12** (10:1).

Table 2. Demetallations of η^4-Diene Iron(0) Complexes 4

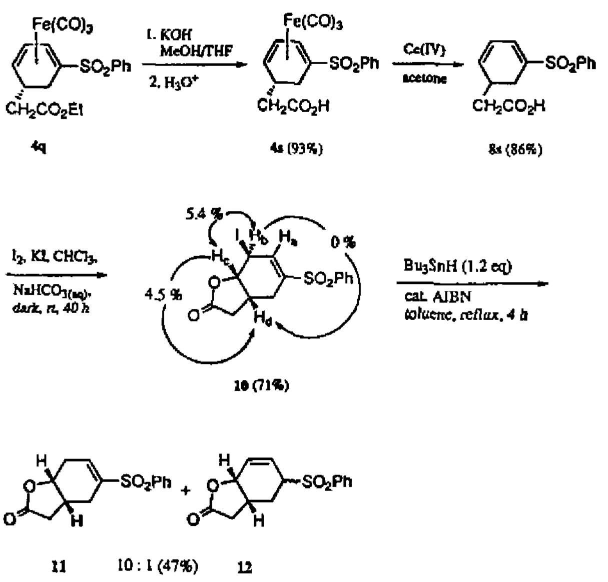
Entry	Complexes 4	Product 8 (%, Yield)[a] Condition[b] A	B	Product 9 (%, Yield)[a]
1	4a	75	77	75
2	4c	68	82	
3	4h		88	
4	4j	51[c]	74	74
5	4m	79	80	82
6	4s		86	

[a] Isolated yield of purified product.

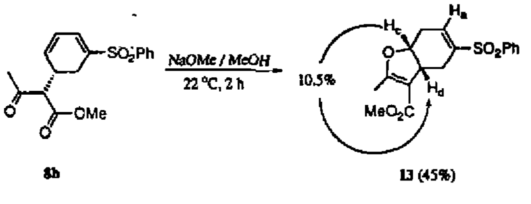
[b] Condition A: 6 equiv of anhydrous Me_3NO in refluxing benzene for 1.5 h, followed by celite filtration. Condition B: 3 equiv of $(NH_4)_2Ce(NO_3)_6$ in wet acetone at 0 °C for 2 min, and then at rt for 10 min before quenching with H_2O.

[c] 19% yield of aromatized product **9j** was also obtained.

Scheme II



The ketoester **8h** was treated with NaOMe/MeOH to give the bicyclic enol ether **13** in 45% yield (Eq. 6). The stereochemistry has been confirmed by the ^{1}H NMR, homodecoupling and NOE experiments. Compound **13** has two protons at the ring junction at δ 5.03 (ddd, J = 3.3, 3.5, 9.8 Hz, H_c) and δ 3.43-3.46 (m, H_d). We found that there was a 10.5% NOE effect between H_c and H_d, indicating that compound **13** has a *cis* ring junction structure.



(6)

In summary, the phenylsulfone-substituted dienylium iron complex **3** reacted with various nucleophiles with high regio- and stereoselectivity in good yield. The regiochemistry of the addition reaction was affected by the hardness/softness of the nucleophile. The products could be converted to substituted dienyl sulfones, *meta*-substituted aryl sulfones, or bicyclic vinyl sulfones, which are all very useful in organic synthesis.

EXPERIMENTAL SECTION

Infrared spectra were recorded with a FT-IR spectrometer Analect RFX-65. ^{1}H and ^{13}C NMR spectra were measured for samples in $CDCl_3$ with a FT-NMR spectrometer Bruker AC-300 at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. Mass spectra were recorded with a spectrometer JEOL JMS-D-100. High resolution mass spectra were measured with a mass spectrometer JEOL TMS-HX 110. Melting points were measured with an apparatus Mel-Temp and are uncorrected. High-performance liquid chromatography (HPLC) was carried out with a chromatograph Shimadzu LC-6A using LiChrosorb (Merck) as the column. The silica gel used for flash column chromatography was made by Merck (60 H). All reagents were of reagent grade and were purified prior to use.[19]

Tricarbonyl[(1-4-η^4)-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) (2)

A solution of diene **1** (6.60 g, 30 mmol), $Fe_2(CO)_9$ (22 g, 60.4 mmol) and (benzylideneacetone)$Fe(CO)_3$ (86 mg, 0.3 mmol) in toluene (120 mL) was purged with N_2 for three times, and then heated to 70-80 °C for 48 h. The brown solution was filtered through with a Celite column, and the crude product was purified by flash column chromatography using ethyl acetate/hexane (1/3) as eluent. The red band was collected, and the solvent was removed *in vacuo* to give complex **2** (8.21 g, 76% yield), recrystallized from CH_2Cl_2/hexane to give orange crystals (6.36 g, 58% yield), mp 104.5-106.3 °C; IR (KBr) 3050, 2920, 2845, 2025, 1960, 1430, 1290, 1130, 1075, 745, 710, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97-1.11 (1H, m), 1.61-1.75 (1H, m), 1.86-1.98 (2H, m), 3.32 (1H, br d), 5.27 (1H, dd, J = 4.2, 5.5 Hz), 6.02 (1H, d, J = 4.2 Hz), 7.50-7.63 (3H, m), 7.86-7.94 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.1, 25.5, 62.3, 83.1, 84.4, 85.5, 128.1, 129.0, 133.1, 139.2, 208.8; MS (rel intensity) *m/z* 360 (M^+, 3), 332 (17), 304 (100), 274 (62), 210 (66), 133 (17), 77 (15); exact mass calcd for $C_{15}H_{12}O_5SFe$ *m/z* 359.9755, found 359.9755. Anal. Calcd for $C_{15}H_{12}O_5SFe$: C, 50.02; H, 3.36. Found: C, 50.23; H, 3.36.

Tricarbonyl[(1-5-η^5)-1-(phenylsulfonyl)-1,3-cyclohexadienyl]iron(I) Hexafluorophosphate (3)

To a solution of **2** (7.20 g, 20 mmol) in dried CH_2Cl_2 (40 mL) at 0 °C was added triphenylcarbenium hexafluorophosphate (9.18 g, 24 mmol), and then warmed to room temperature. The mixture was stirred for another 16 h. To the brown solution was added diethyl ether (60 mL). A large amount of yellow salt was precipitated which was filtered by suction, and then washed with diethyl ether (20 mL × 3). The pale yellow powder was collected and dried *in vacuo* to give complex **3** (9.88 g, 98% yield), mp 165.4-166.6 °C (decomp); IR (KBr) 3070, 3040, 2100, 2060, 1970, 1425, 1295, 1135, 1080, 820, 745, 715, 690 cm^{-1}; ^{1}H NMR (acetone-d_6)

δ 1.92 (1H, d, *J* = 14.5 Hz), 2.03-2.05 (1H, m), 3.52 (1H, dd, *J* = 6.9, 14.5 Hz), 5.21 (1H, dd, *J* = 6.9, 7.0 Hz), 6.32 (1H, dd, *J* = 5.8, 7.0 Hz), 7.04 (1H, d, *J* = 5.8 Hz), 7.69-7.74 (3H, m), 7.81-7.86 (2H, m); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 31.6, 65.7, 67.7, 76.2, 84.8, 86.6, 127.6, 129.3, 133.1, 138.4, 208.6. Anal. Calcd for $C_{15}H_{11}F_6O_5PSFe$: C, 35.7; H, 2.20. Found: C, 35.4; H, 2.38.

General Procedure for Nucleophilic Addition Reactions of Tricarbonyl[(1-5-η^5)-1-(phenylsulfonyl)-1,3-cyclohexadienyl]iron(I) Hexafluorophosphate (3) (Table 1)

To a solution of **3** (0.5 mmol) in dried THF (4 mL) at suitable temperatures (Table 1) was added a solution of nucleophile/solvent. The mixture was stirred until the solution became clear, and was then quenched with saturated ammonium chloride solution. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (20 mL × 2), washed with water, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (3/1 to 1/1) as eluent to give **4** and **5**.

Tricarbonyl[(1-4-η^4)-5-*exo*-methoxy-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4a)

Yellow crystal; mp 116.7-137.7 °C (decomp); IR (neat) 3080, 2930, 2070, 1980, 1440, 1300, 1140, 1070, 975, 725, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79 (1H, dd, *J* = 3.2, 14.4 Hz), 2.50 (1H, ddd, *J* = 0.8, 10.4, 14.4 Hz), 3.16 (3H, s), 3.24 (1H, ddd, *J* = 0.8, 3.2, 6.4 Hz), 3.94 (1H, ddd, *J* = 5.3, 6.4, 10.4 Hz), 5.42 (1H, dd, *J* = 4.6, 5.3 Hz), 6.17 (1H, d, *J* = 4.6 Hz), 7.51-7.64 (3H, m), 7.84-7.87 (2H, m); ^{13}C NMR ($CDCl_3$) δ 30.1, 56.4, 59.3, 76.8, 78.2, 84.2, 87.2, 128.1, 129.2, 133.3, 138.7, 207.2; MS (rel intensity) *m/z* 390 (M$^+$, 0.35), 334 (19), 306 (36), 291 (84), 275 (28), 274 (39), 218 (40), 210 (68), 125 (100), 77 (51); exact mass calcd for $C_{16}H_{14}O_6SFe$ *m/z* 389.9861, found 389.9865. Anal. Calcd for $C_{16}H_{14}O_6SFe$: C, 49.25; H, 3.62. Found: C, 49.23; H, 3.61.

Tricarbonyl[(1-4-η^4)-5-*exo*-phenylthio-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4b)

Yellow liquid; IR (neat) 3060, 2920, 2060, 2000, 1295, 1140, 1080, 750, 725, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (1H, dd, *J* = 4.2, 14.4 Hz), 2.53 (1H, dd, *J* = 11.0, 14.4 Hz), 3.31 (1H, dd, *J* = 3.8, 4.2 Hz), 3.70 (1H, ddd, *J* = 3.8, 5.1, 11.0 Hz), 5.22 (1H, dd, *J* = 4.6, 5.1 Hz), 5.94 (1H, d, *J* = 4.6 Hz), 7.19-7.28 (5H, m), 7.51-7.65 (3H, m), 7.81-7.84 (2H, m); ^{13}C NMR ($CDCl_3$) δ 30.9, 46.6, 63.2, 79.5, 83.4, 86.0, 128.4 (×2), 129.0, 129.1, 133.2, 133.5 (×2), 138.7, 208.0; MS (rel intensity) *m/z* 384 (M$^+$ - 3CO, 3), 359 (21), 306 (21), 275 (14), 218 (61), 125 (100), 77 (65); exact mass calcd for $C_{18}H_{16}O_2S_2Fe$ *m/z* 383.9942, found 383.9944.

Tricarbonyl[(1-4-η^4)-1,5-*exo*-bis(phenylsulfonyl)-1,3-cyclohexadiene]iron (4c)

Yellow crystal; mp 163.3-165.4 °C; IR (neat) 3050, 2935, 2080, 2005, 1315, 1155, 1140, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (1H, dd, *J* = 3.9, 14.8 Hz), 2.33 (1H, ddd, *J* = 1.1, 11.5, 14.8 Hz), 3.03 (1H, ddd, *J* = 1.1, 3.6, 6.0 Hz), 3.65 (1H, ddd, *J* = 3.6, 3.9, 11.5 Hz), 5.44 (1H, dd, *J* = 4.6, 6.0 Hz), 5.94 (1H, dd, *J* = 4.6 Hz), 7.45-7.82 (10H, m); ^{13}C NMR ($CDCl_3$) δ 26.0, 51.6, 64.4, 79.6, 84.2, 86.7, 128.0, 128.9, 129.2, 129.4, 133.6, 134.0, 136.7, 138.2, 206.8; MS (rel intensity) *m/z* 500 (M$^+$, 0.04), 434 (10), 359 (75), 291 (93), 275 (50), 218 (73), 210 (20), 125 (100), 77 (91). Anal. Calcd for $C_{21}H_{16}O_7S_2Fe$: C, 50.41; H, 3.22. Found: C, 50.30; H, 3.20.

Tricarbonyl[(1-4-η^4)-5-*exo*-(isopropylamino)-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4d)

Yellow liquid; IR (neat) 3636, 3214, 3073, 2988, 2076, 2004, 1730, 1704, 1448, 1304, 1289, 1147, 1087, 841, 730, 690 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.10-1.17 (7H, m), 2.05-2.10 (2H, m), 2.62 (1H, ddd, *J* = 0.9, 10.6, 14.2 Hz), 3.30 (1H, heptet, *J* = 6.4 Hz), 3.97 (1H, ddd, *J* = 3.5, 3.6, 10.6 Hz), 5.74 (1H, dd, *J* = 4.6, 5.8 Hz), 6.38 (1H, d, *J* = 4.6 Hz), 7.65-7.70 (2H, m), 7.73-7.80 (1H, m), 7.92-7.95 (2H, m); ^{13}C NMR (acetone-d_6) δ 20.6, 21.0, 29.7, 49.1, 55.4, 59.4, 78.6, 85.4, 88.4, 128.7, 130.0, 134.1, 139.7, 209.2.

Tricarbonyl[1-*exo*-diethyl [(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]phosphite]iron (4e)

Yellow crystal; mp 117.8-119.6 °C; IR (neat) 3059, 2939, 2857, 2064, 1993, 1447, 1369, 1306, 1244, 1110, 1050, 1028, 965, 761, 729, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (3H, br t), 1.19 (3H, br t), 1.27-1.43 (1H, m), 2.23 (1H, br t), 2.55 (1H, br s), 3.28 (1H, br s), 3.95 (4H, br q), 5.40 (1H, br s), 6.10 (1H, br d), 7.53-7.58 (2H, m), 7.61-7.66 (1H, m), 7.88-7.90 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.3 (×2), 25.1 (×2), 57.0, 62.3 (×2), 82.3, 84.0, 86.1, 128.2, 129.2, 133.4, 138.8, 207.8; MS (rel intensity) *m/z* 496 (M$^+$, 3), 440 (12), 414 (17), 412 (100), 354 (10), 302 (14), 287 (29), 275 (48), 241 (66), 214 (47), 210 (36), 158 (77), 141 (77), 138 (82), 123 (46), 110 (71), 109 (66), 78 (73), 77 (91); exact mass calcd for $C_{19}H_{21}O_8PSFe$ *m/z* 496.0045, found 496.0054.

Tricarbonyl[(1-4-η^4)-5-*exo*-cyano-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4f)

Yellow crystal; mp 158.5-159.5 °C (decomp); IR (neat) 3070, 2935, 2240, 2080, 2030, 1990, 1305, 1150, 730, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.31 (1H, dd, *J* = 4.2, 13.9 Hz), 2.45 (1H, dd, *J* = 12.0, 13.9 Hz), 3.11-3.22 (2H, m), 5.43 (1H, dd, *J* = 4.6, 6.0 Hz), 5.94 (1H, d, *J* = 4.6 Hz), 7.55-7.68 (3H, m), 7.84-7.87 (2H, m); ^{13}C NMR (CDCl$_3$) δ 27.4, 28.5, 55.7, 81.1, 83.0, 88.0, 120.1, 128.1, 129.5, 133.8, 138.1, 206.5; MS (rel intensity) *m/z* 385 (M$^+$, 2), 429 (40), 301 (100), 274 (50), 210 (93), 133 (26), 77 (39); exact mass calcd for $C_{16}H_{11}NO_5SFe$: *m/z* 384.9707, found 384.9708. Anal. Calcd for $C_{16}H_{11}NO_5SFe$: C, 49.89; H, 2.88; N, 3.64. Found: C, 49.89; H, 2.97; N, 3.75.

Tricarbonyl[1-*exo*-dimethyl [(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]malonate]iron (4g)

Yellow crystal; mp 177.6-179.4 °C (decomp), IR (neat) 3060, 2970, 2080, 1990, 1730, 1315, 1155, 735, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (1H, dd, *J* = 4.1, 14.0 Hz), 2.28 (1H, dd, *J* = 10.3, 14.0 Hz), 2.97-2.98 (1H, m), 2.98 (1H, d, *J* = 8.0 Hz), 3.14 (1H, ddd, *J* = 1.3, 3.0, 6.3 Hz), 3.57 (3H, s), 3.65 (3H, s), 5.27 (1H, dd, *J* = 4.4, 6.3 Hz), 6.07 (1H, d, *J* = 4.4 Hz), 7.51-7.65 (3H, m), 7.84-7.87 (2H, m); ^{13}C NMR (CDCl$_3$) δ 27.9, 38.6, 52.4, 52.5, 58.3, 61.2, 80.6, 83.8, 86.2, 128.2, 129.1, 133.3, 138.9, 167.8, 167.9, 208.5; MS (rel intensity) *m/z* 490 (M$^+$, 0.38), 406 (51), 336 (100), 305 (46), 275 (49), 133 (17), 77 (21); exact mass calcd for $C_{20}H_{18}O_9SFe$ *m/z* 490.0021, found 490.0022. Anal. Calcd for $C_{20}H_{18}O_9SFe$: C, 48.98; H, 3.70. Found: C, 48.91; H, 3.73.

Tricarbonyl[1-*exo*-methyl [(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]acetoacetate]iron (4h)

Yellow liquid; a separable diastereomeric mixture (43/57); IR (neat) 3080, 2965, 2080, 1980, 1725, 1710, 1440, 1430, 1300, 1145, 1085, 725, 688 cm^{-1}. MS (rel intensity) *m/z* 474 (M$^+$, 0.36), 390 (100), 357 (44), 332 (58), 305 (58), 275 (80), 248 (18), 125 (39), 91 (22), 77 (53); exact mass calcd for $C_{20}H_{18}O_8SFe$ *m/z* 474.0072, found 474.0075. Anal. Calcd for $C_{20}H_{18}O_8SFe$: C, 50.65; H, 3.82. Found: C, 49.25; H, 3.87. These two diastereomeric isomers could be separated by recrystallation from CH_2Cl_2/hexane to give the major isomer in 84% purity and the pure minor isomer. The major isomer: ^{1}H NMR (CDCl$_3$) δ 0.76 (1H, dd, *J* = 4.2, 14.0 Hz), 2.03 (3H, s), 2.26 (1H, dd, *J* = 11.3, 13.6 Hz), 2.89-2.98 (1H, m), 3.01 (1H, d, *J* = 9.2 Hz), 3.09-3.14 (1H, m), 3.69 (3H, s), 5.25 (1H, dd, *J* = 4.1, 6.3 Hz), 6.08 (1H, d, *J* = 4.1 Hz), 7.51-7.65 (3H, m), 7.83-7.86 (2H, m); ^{13}C NMR (CDCl$_3$) δ 28.3, 29.1, 37.8, 52.2, 61.6, 66.3, 80.6, 83.8, 86.1, 128.0, 129.1, 133.3, 138.7, 168.1, 201.4, 208.1. The minor isomer: Yellow crystal; mp 139.0-141.8 °C (decomp); ^{1}H NMR (CDCl$_3$) δ 0.95 (1H, dd, *J* = 4.1, 14.2 Hz), 2.14 (3H, s), 2.28 (1H, dd, *J* = 11.3, 13.6 Hz), 2.92-3.00 (1H, m), 3.05-3.07 (1H, m), 3.08 (1H, d, *J* = 8.6 Hz), 3.59 (3H, s), 5.24 (1H, dd, *J* = 4.4, 6.2 Hz), 6.09 (1H, d, *J* = 4.4 Hz), 7.53-7.65 (3H, m), 7.86-7.88 (2H, m); ^{13}C NMR (CDCl$_3$) δ 27.7, 29.6, 38.1, 52.4, 61.5, 66.6, 80.9, 83.5, 86.3, 128.2, 129.1, 133.3, 138.9, 168.1, 201.1, 208.4.

Tricarbonyl[1-*exo*-methyl [(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl](phenylsulfonyl)acetate]iron (4i)

Yellow crystal; mp 139-141 °C (decomp); an inseparable diastereomeric mixture (45/55); IR (neat) 3080, 2965, 2070, 1980, 1725, 1605, 1440, 1430, 1295, 1140, 1085, 755, 745, 735, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13 (dd), 1.30 (dd), 2.11 (dd), 2.34 (dd), 2.90-3.10 (m), 3.04-3.09 (m), 3.28 (s), 3.34 (dd), 3.45 (s), 3.42-3.46 (m), 3.64-3.67 (m), 5.22 (dd), 5.26 (dd), 6.02 (dd), 7.46-7.63 (m), 7.65-7.78 (m), 7.83-7.92 (m); ^{13}C NMR (CDCl$_3$) δ 26.9, 28.0, 37.1, 37.2, 52.6, 52.8, 59.3, 60.4, 76.0, 76.4, 80.7, 80.8, 83.3, 83.7, 86.7 (×2), 128.1, 128.2, 128.9 (×2), 129.0 (×2), 129.1 (×2), 129.3, 133.3, 133.4 (×2), 134.4, 137.4, 137.5, 138.6, 164.8, 165.3, 207.6; MS (rel intensity) *m/z* 516 (M$^+$-2CO, 17), 488 (62), 446 (58), 415 (32), 351(100), 275 (34), 149 (51), 91 (66); exact mass calcd for $C_{22}H_{20}O_7S_2Fe$ *m/z* 516.0001, found 515.9995. These two isomers have some distinct ^{1}H and ^{13}C NMR absorptions. The major isomer: ^{1}H NMR δ 1.13 (1H, dd, *J* = 4.1, 14.3 Hz), 2.11 (1H, dd, *J* = 11.2, 14.3 Hz), 5.26 (1H, dd, *J* = 5.0, 5.8 Hz); ^{13}C NMR (CDCl$_3$) δ 26.9, 37.1, 52.6, 59.3, 76.4, 80.7, 83.3, 128.1, 133.3, 137.5, 165.3. The minor isomer: ^{1}H NMR δ 1.30 (1H, dd, *J* = 3.9, 14.4 Hz), 2.34 (1H, dd, *J* = 11.5, 14.4 Hz), 5.22 (1H, dd, *J* = 4.7, 6.1 Hz); ^{13}C NMR (CDCl$_3$) δ 28.0, 37.2, 52.8, 60.4, 76.0, 80.8, 83.7, 128.2, 133.4, 137.4, 164.8.

Tricarbonyl[[1-*exo*-(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]propane-2-one]iron (4j)

Yellow crystal; mp 97.8-99.2 °C; IR (neat) 3110, 2980, 2075, 1985, 1710, 1300, 1145, 1095, 735, 685 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.70 (1H, dd, *J* = 4.2, 14.0 Hz), 2.00 (3H, s), 2.17-2.36 (3H, m), 2.69 (1H, ddd, *J* = 3.1, 6.5, 14.0 Hz), 3.22 (1H, dd, *J* = 3.3, 5.2 Hz), 5.22 (1H, dd, *J* = 4.5, 6.3 Hz), 6.11 (1H, d, *J* = 4.3 Hz), 7.52-7.65 (3H, m), 7.86-7.89 (2H, m); ^{13}C NMR (CDCl$_3$) δ 29.8, 30.0, 52.7, 81.0, 83.4, 86.0, 128.3, 129.2, 133.3, 139.1, 206.2, 208.5; MS (rel intensity) *m/z* 416 (M$^+$, 0.43), 360 (27), 332 (100), 274 (46), 255 (26), 210 (73), 191 (46), 133 (33), 91 (28), 77 (26); exact mass calcd for $C_{18}H_{16}O_6SFe$ *m/z* 416.0017, found 416.0014. Anal. Calcd for $C_{18}H_{16}O_6SFe$: C, 51.94; H, 3.87. Found: C, 51.91; H, 4.00.

Tricarbonyl[[1-*exo*-2,2-dimethyl-2-(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]acetaldehyde]iron (4k)

Yellow liquid; IR (neat) 3066, 2970, 2930, 2062, 1989, 1715, 1584, 1446, 1304, 1149, 1088, 759, 729, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.74-0.80 (1H, m), 0.76 (3H, s), 0.84 (3H, s), 2.08 (1H, dd, J = 11.2, 13.8 Hz), 2.54 (1H, ddd, J = 3.4, 4.7, 11.2 Hz), 3.05 (1H, dd, J = 3.4, 6.3 Hz), 5.38 (1H, dd, J = 4.3, 6.3 Hz), 6.07 (1H, d, J = 4.3 Hz), 7.52-7.63 (3H, m), 7.84-7.87 (2H, m), 9.27 (1H, s); ^{13}C NMR (CDCl$_3$) δ 18.9, 19.1, 25.1, 44.9, 49.9, 60.3, 80.8, 84.9, 85.1, 127.9, 129.1, 133.3, 138.9, 204.3, 208.4; MS (rel intensity) *m/z* 430 (M$^+$, 2.4), 374 (39), 346 (100), 274 (74), 218 (76), 210 (89), 133 (50), 125 (98), 91 (29), 77 (98); exact mass calcd for $C_{19}H_{18}O_6SFe$ *m/z* 430.0174, found 430.0181.

Tricarbonyl[2-*exo*-[(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]cyclohexanone]iron (4l)

Pale yellow crystal; mp 139.0-142.4 °C; an inseparable diastereomeric mixture (34/66); IR (neat) 2940, 2865, 2055, 1965, 1695, 1445, 740, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.74-0.80 (m), 1.53-1.63 (m), 1.40-1.60 (m), 1.72-1.85 (m), 1.85-2.04 (m), 2.12-2.30 (m), 2.66-2.89 (m), 3.15 (dd), 3.17 (dd), 5.26-5.31 (m), 6.07-6.08 (m), 7.51-7.65 (m), 7.85-7.89 (m); ^{13}C NMR (CDCl$_3$) δ 24.5, 24.8, 26.3, 26.9, 27.3, 27.7, 29.3, 30.0, 30.3, 38.3, 39.0, 41.8, 42.1 (×2), 56.8, 56.9, 62.8, 64.9, 81.2, 84.1, 84.3, 85.1, 85.4, 128.1, 128.9, 133.1, 139.0, 139.1, 208.7, 211.1, 211.2; MS (rel intensity) *m/z* 456 (M$^+$, 0.06), 400 (10), 372 (100), 291 (19), 275 (19), 247 (21), 231 (42), 210 (18); exact mass calcd for $C_{19}H_{20}O_4SFe$ *m/z* 400.0433, found 400.0428. Anal. Calcd for $C_{21}H_{20}O_6SFe$: C, 55.28; H, 4.42. Found: C, 55.50; H, 4.51. These two isomers have some distinct ^{1}H and ^{13}C NMR absorptions. The major isomer: ^{1}H NMR (CDCl$_3$) δ 3.15 (1H, dd, J = 1.3, 3.1 Hz); ^{13}C NMR (CDCl$_3$) δ 24.8, 26.9, 27.7, 30.4, 38.3, 56.9, 62.8, 84.1, 85.4, 211.2. The minor isomer: ^{1}H NMR (CDCl$_3$) δ 3.17 (1H, dd, J = 1.3, 3.2 Hz); ^{13}C NMR (CDCl$_3$) δ 24.5, 26.3, 27.3, 30.0, 39.0, 56.8, 64.4, 84.4, 85.1, 211.1.

Tricarbonyl[(1-4-η^4)-5-*exo*-(3-cyanopropyl)-1-(phenylsulfonyl)-1,3-cyclohexadienyl]iron (4m)

Yellow crystal; mp 86.2-87.5 °C; IR (neat) 3075, 2930, 2260, 2070, 1975, 1440, 1295, 1190, 720, 685 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.65 (1H, dd, J = 3.5, 12.8 Hz), 1.11-1.32 (2H, m), 1.36-1.54 (2H, m), 2.12-2.34 (4H, m), 3.19 (1H, ddd, J = 2.0, 3.0, 5.4 Hz), 5.25 (1H, dd, J = 4.4, 6.4 Hz), 6.08 (1H, d, J = 4.4 Hz), 7.51-7.65 (3H, m), 7.83-7.86 (2H, m); ^{13}C NMR (CDCl$_3$) δ 17.0, 23.5, 29.5, 38.2, 39.4, 65.5, 80.6, 83.7, 85.7, 119.0, 128.1, 129.1, 133.3, 139.0, 208.7; MS (rel intensity) *m/z* 327 (M$^+$, 0.47), 371 (38), 343 (100), 279 (21), 218 (61), 201 (17), 133 (37), 91 (47), 77 (36); exact mass calcd for $C_{19}H_{17}NO_5SFe$ *m/z* 427.0178, found 427.0180. Anal. Calcd for $C_{19}H_{17}NO_5SFe$: C, 53.41; H, 4.01. Found: C, 53.50; H, 4.04.

Tricarbonyl[(1-4-η^4)-5-*exo*-(2-propenyl)-1-(phenylsulfonyl)-1,3-cyclohexadienyl]iron (4n)

Yellow crystal; mp 98.4-100.9 °C; IR (neat) 3075, 2930, 2070, 1975, 1440, 1300, 1145, 725, 680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.75 (1H, dd, J = 4.2, 13.5 Hz), 1.75-1.92 (2H, m), 2.13 (1H, dd, J = 11.1, 13.5 Hz), 2.32-2.37 (1H, m), 3.23 (1H, dd, J = 2.8, 5.9 Hz), 4.83 (1H, d, J = 17.2), 4.91 (1H, d, J = 10.0 Hz), 5.27 (1H, dd, J = 4.5, 6.0 Hz), 5.46-5.60 (1H, m), 6.08 (1H, d, J = 4.5 Hz), 7.51-7.64 (3H, m), 7.86-7.88 (2H, m); ^{13}C NMR (CDCl$_3$) δ 29.1, 39.6, 43.2, 66.4, 80.8, 83.8, 88.5, 116.8, 128.1, 129.0, 133.1, 135.5, 139.2, 209.1; MS (rel intensity) *m/z* 400 (M$^+$, 1.8), 344 (15), 316 (100), 274 (51), 210 (79); exact mass calcd for $C_{18}H_{16}O_5SFe$ *m/z* 400.0068, found 400.0075. Anal. Calcd for $C_{18}H_{16}O_5SFe$: C, 54.02; H, 4.03. Found: C, 53.89; H, 4.08.

Tricarbonyl[(1-4-η^4)-5-*exo*-(2-amino-5-methoxyphenyl)-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4o)

Yellow crystal; mp 142.2-143.6 °C (decomp); IR (neat) 3435, 3360, 3060, 2940, 2055, 1990, 1495, 1295, 1140, 730, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.00 (1H, dd, J = 4.8, 13.7 Hz), 1.27 (1H, d, J = 3.0 Hz), 2.57 (1H, dd, J = 11.5, 13.7 Hz), 3.25-3.29 (2H, m), 3.57-3.69 (1H, m), 3.65 (3H, s), 5.49 (1H, dd, J = 4.4, 6.4 Hz), 6.19 (1H, d, J = 4.4 Hz), 6.42 (1H, br s), 6.54 (2H, br s), 7.47-7.60 (3H, m), 7.85-7.87 (2H, m); ^{13}C NMR (CDCl$_3$) δ 30.1, 40.6, 55.6, 64.8, 81.3, 84.1, 85.7, 112.2, 112.8, 117.6, 128.1, 129.2, 131.0, 133.2, 136.9, 139.1, 153.0, 208.6; MS (rel intensity) *m/z* 481 (M$^+$, 9), 397 (100), 254 (16), 199 (65), 184 (77); exact mass calcd for $C_{22}H_{19}NO_6SFe$ *m/z* 481.0283, found 481.0286. Anal. Calcd for $C_{22}H_{19}NO_6SFe$: C, 54.90; H, 3.98; N, 2.91. Found: C, 54.71; H, 4.22; N, 2.72.

Tricarbonyl[(1-4-η^4)-5-*exo*-methyl-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4p)

Yellow crystal; mp 124.6-126.8 °C; IR (neat) 3067, 2958, 2922, 2864, 2059, 1988, 1712, 1446, 1303, 1147, 1091, 726, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.63 (1H, dd, J = 4.2, 13.4 Hz), 0.83 (3H, s), 2.20 (1H, dd, J = 11.2, 13.4 Hz), 2.40 (1H, m), 3.23 (1H, dd, J = 2.9, 5.7 Hz), 5.23 (1H, dd, J = 4.4, 6.4 Hz), 6.11 (1H, d, J = 4.4 Hz), 7.49-7.64 (3H, m), 7.86-7.89 (2H, m); ^{13}C NMR (CDCl$_3$) δ 24.8, 31.1, 35.0, 69.3, 80.7, 83.5, 85.6, 128.1, 129.1, 133.1, 139.2, 208.8; MS (rel intensity) *m/z* 374 (M$^+$, 0.52), 346 (8), 318 (97), 288

(85), 224 (100), 133 (33), 91 (26), 77 (25). Anal. Calcd for $C_{16}H_{14}O_5SFe$: C, 51.36; H, 3.77. Found: C, 51.28; H, 3.84.

Tricarbonyl[(3-5-η^3)-2-*exo*-methyl-1-(phenylsulfonyl)cyclohexenediyl]iron (5p)

Yellow crystal; mp 149.5-151.3 °C (decomp); IR (neat) 3060, 2976, 2931, 2825, 2062, 2005, 1447, 1289, 1144, 1126, 1080, 857, 758, 734, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.29 (3H, d, J = 6.5 Hz), 2.62 (1H, d, J = 12.9 Hz), 3.06 (1H, dd, J = 7.2, 13.4 Hz), 3.09 (1H, m), 4.50 (1H, dd, J = 6.0, 6.0 Hz), 4.65 (1H, ddd, J = 1.5, 6.0, 6.1 Hz), 4.74 (1H, dd, J = 6.2, 6.2 Hz), 7.38-7.43 (2H, m), 7.48-7.53 (1H, m), 7.61-7.64 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.6, 30.7, 38.3, 38.9, 56.8, 61.9, 101.0, 127.8, 129.0, 132.4, 140.1, 202.4, 209.5, 209.8; MS (rel intensity) *m/z* 374 (M^+, 0.1), 346 (7), 318 (45), 290 (34), 205 (40), 176 (22), 148 (100), 133 (25), 91 (47), 77 (31). Anal. Calcd for $C_{16}H_{14}O_5SFe$: C, 51.36; H, 3.77. Found: C, 51.00; H, 3.83.

Tricarbonyl[1-*exo*-ethyl [(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]acetate]iron (4q)

Yellow crystal; mp 97.8-99.5 °C; IR (neat) 3080, 3000, 2070, 1980, 1715, 1300, 1150, 1085, 725, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (1H, dd, J = 4.3, 13.8 Hz), 1.16 (3H, t, J = 7.2 Hz), 2.04 (1H, dd, J = 7.8, 15.3 Hz), 2.14 (1H, dd, J = 6.5, 15.3 Hz), 2.27 (1H, dd, J = 11.1, 13.8 Hz), 2.63-2.74 (1H, m), 3.23 (1H, dd, J = 3.1, 6.2 Hz), 4.04 (2H, q, J = 7.2 Hz), 5.27 (1H, dd, J = 4.5, 6.2 Hz), 6.11 (1H, d, J = 4.5 Hz), 7.52-7.66 (3H, m), 7.86-7.89 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 29.4, 36.1, 43.2, 60.4, 65.0, 80.7, 83.6, 86.0, 128.2 (×2), 129.1 (×2), 133.2, 139.0, 171.1, 208.8; MS (rel intensity) *m/z* 418 (M^+-CO, 4.2), 390 (39), 362 (78), 302 (25), 275 (28), 237 (94), 221 (30), 218 (26), 133 (51), 91 (100), 77 (40). Anal. Calcd for $C_{19}H_{18}O_7SFe$: C, 51.14; H, 4.07. Found: C, 51.17; H, 4.08.

Tricarbonyl[(3-5-η^3)-2-*exo*-(ethoxycarbonylmethyl)-1-(phenylsulfonyl)cyclohexenediyl]iron (5q)

Yellow crystal; mp 134.2-136.0 °C (decomp); IR (neat) 3040, 2960, 2810, 2045, 1975, 1700, 1280, 1240, 1165, 1130, 720, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (1H, dd, J = 2.7, 15.2 Hz), 1.25 (3H, t, J = 7.1 Hz), 1.72 (1H, dd, J = 10.9, 15.2 Hz), 2.49 (1H, d, J = 13.1 Hz), 3.08 (1H, dd, J = 5.9, 13.1 Hz), 3.43 (1H, br d), 4.11 (2H, q, J = 7.1 Hz), 4.56 (1H, dd, J = 5.4, 7.8 Hz) 4.81-4.83 (2H, m), 7.42-7.47 (2H, m), 7.52-7.57 (1H, m), 7.64-7.66 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.2, 31.2, 36.7, 40.0, 41.5, 57.2, 59.6, 60.6, 101.2, 127.8, 129.2, 132.8, 149.5, 170.7, 202.1, 208.9, 209.3; MS (rel intensity) *m/z* 418 (M^+-CO, 5.8), 390 (50), 237 (45), 290 (97), 219 (60), 133 (78), 91 (100), 77 (84). Anal. Calcd for $C_{19}H_{18}O_7SFe$: C, 51.14; H, 4.07. Found: C, 51.16; H, 4.21.

Tricarbonyl[(1-4-η^4)-5-*exo*-(diisopropylamino)-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (4r)

Yellow crystal; mp 116.9-125.7 °C (decomp); IR (neat) 3070, 2970, 2060, 1980, 1390, 1360, 1300, 1145, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.71 (6H, d, J = 6.5 Hz), 0.79 (6H, d, J = 6.4 Hz), 2.12 (1H, br t), 2.70-2.74 (2H, m), 2.96 (1H, br d), 3.59 (1H, br d), 5.35 (1H, br t), 6.05 (1H, br d), 7.52-7.59 (3H, m), 7.85-7.88 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.4 (×2), 22.8 (×2), 27.7, 44.2 (×2), 55.1, 66.3, 77.9, 84.3, 85.1, 128.0 (×2), 129.0 (×2), 133.0, 139.3, 209.1; MS (rel intensity) *m/z* 459 (M^+, 17), 403 (41), 359 (31), 298 (50), 275 (88), 250 (45), 234 (100), 178 (61), 133 (46), 77 (50); exact mass calcd for $C_{21}H_{25}NO_5SFe$ *m/z* 459.0796, found 459.0804. Anal. Calcd for $C_{21}H_{25}NO_5SFe$: C, 54.91; H, 5.49; N, 3.05. Found: C, 54.98; H, 5.43; N, 3.29.

Tricarbonyl[1-*exo*-[(2-5-η^4)-5-(phenylsulfonyl)-2,4-cyclohexadienyl]acetic acid]iron (4s)

To a solution of 3 N potassium hydroxide (0.94 mmol) in methanol (2 mL) at 0 °C was added a solution of **4q** (210 mg, 0.47 mmol) in THF (2 mL). The mixture was stirred at 0 °C for 5 min, and then at room temperature for 8 h. To the yellow reaction mixture was added water (10 mL). After removal of the solvent, the residue was rinsed with CH_2Cl_2 (10 mL × 2). The aqueous solution was acidified with aqueous 5% HCl, and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried ($MgSO_4$) and evaporated. The crude product was recrystallized from ethyl acetate/hexane to give a yellow crystal (183 mg, 93% yield). mp 177.2-178.5 °C (decomp); IR (neat) 3484, 3068, 2062, 1992, 1708, 1446, 1303, 1146, 1087, 729, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (1H, dd, J = 4.2, 13.7 Hz), 2.14 (2H, br d), 2.30 (1H, dd, J = 11.3, 13.7 Hz), 2.67-2.71 (1H, m), 3.24 (1H, dd, J = 2.7, 6.4 Hz), 5.27 (1H, dd, J = 4.4, 6.4 Hz), 6.13 (1H, d, J = 4.4 Hz), 7.34-7.66 (3H, m), 7.86-7.89 (2H, m); ^{13}C NMR ($CDCl_3$) δ 29.5, 35.8, 42.9, 64.5, 80.6, 83.5, 86.2, 128.2 (×2), 129.2 (×2), 133.3, 139.0, 176.6, 208.9; MS (rel intensity) *m/z* 362 (M^+-2CO, 2.4), 334 (10), 278 (12), 219 (53), 153 (14), 130 (33), 125 (30), 91 (100), 77 (88); exact mass calcd for $C_{15}H_{14}O_5SFe$ *m/z* 361.9912, found 361.9910. Anal. Calcd for $C_{17}H_{14}O_7SFe$: C, 48.83; H, 3.37. Found: C, 48.75; H, 3.36.

Tricarbonyl[(1-4-η^4)-6-*exo*-diphenylmethyl-1-(phenylsulfonyl)-1,3-cyclohexadiene]iron (6a)

To a solution of diphenylmethane (0.11 mL, 0.65 mmol) in THF/HMPA = (4:1, 2 mL) was added butyllithium

(1.6 M in hexane, 0.78 mL, 0.6 mmol) at -78 °C under nitrogen. The mixture was allowed to stir at 0 °C for 1.5 h. A solution of **4a** (167 mg, 0.43 mmol) in THF (1 mL) was added at -78 °C, and then stirred for 2 h before quenching with trifluoroacetic acid (0.5 mL). After stirring at 25 °C for 2 h, the reaction mixture was diluted with water and then concentrated by a rotary evaporator. The residue was passed through a flash column of silica gel using hexane/ethyl acetate (3:1) as eluent to give a pale yellow crystal **6a** (122 mg) in 54% yield. mp 209.0 °C (decomp); IR (neat) 3067, 2956, 2925, 2852, 1689, 1643, 1446, 1384, 1304, 1238, 1153, 1092, 1004, 770, 733, 712, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82-0.87 (1H, m), 2.03-2.13 (1H, m), 3.01 (1H, d, $J = 6.5$ Hz), 3.07-3.10 (2H, m), 5.21 (1H, dd, $J = 4.5$, 6.3 Hz), 6.05 (1H, d, $J = 4.5$ Hz), 6.93-6.96 (2H, m), 7.08-7.19 (6H, m), 7.22-7.29 (2H, m), 7.42-7.47 (2H, m), 7.54-7.57 (1H, m), 7.72-7.75 (2H, m); ^{13}C NMR ($CDCl^3$) δ 29.9, 43.3, 61.6, 65.0, 80.9, 83.7, 86.0, 126.5, 126.6, 127.3 (×2), 128.0 (×2), 128.1 (×2), 128.5 (×2), 128.8 (×2), 129.0 (×2), 133.1, 139.1, 142.7, 143.4, 208.7; MS (rel intensity) *m/z* 526 (M^{+}, 0.13), 442 (30), 384 (4), 359 (6), 275 (6), 224 (24), 167 (100), 165 (34), 152 (15), 91 (5), 77 (14); exact mass calcd for $C_{25}H_{22}O_2SFe$ *m/z* 442.0690, found 442.0691.

General Procedure for the Demetallation of Diene Iron Complexes 4 (Table 2)

Condition A: To a solution of anhydrous trimethylamine *N*-oxide (90 mg, 1.2 mmol) in dry benzene (5 mL) was added a solution of complex **4** (0.2 mmol) in benzene (1 mL) at 0 °C in 1 min. The reaction mixture was warmed to room temperature for another 20 min. To the brown solution was added water (10 mL) and was then extracted with diethyl ether (20 mL × 2). Condition B: To a solution of iron complex **4** (2 mmol) in wet acetone (5 mL) at 0 °C was added ceric ammonium nitrate (329 mg, 6 mmol) in 2 min, and then the mixture was warmed to room temperature for another 10 min. To the mixture was added water (10 mL). After removal of the solvent, the mixture was extracted with diethyl ether (20 mL × 2). The organic layer was dried ($MgSO_4$) and evaporated. The residue was passed through a flash column of silica gel using hexane/ethyl acetate (3/1 to 10/1) as eulent to give **8**.

5-Methoxy-1-(phenylsulfonyl)-1,3-cyclohexadiene (8a)

Yellow liquid; IR (neat) 3067, 2925, 2856, 1447, 1306, 1152, 1086, 727, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.53 (1H, ddd, $J = 2.0$, 7.8, 18.1 Hz), 2.66 (1H, ddd, $J = 0.9$, 5.2, 18.1 Hz), 3.09 (3H, s), 4.00-4.07 (1H, m), 6.15 (1H, dd, $J = 4.4$, 9.6 Hz), 6.29 (1H, dd, $J = 5.5$, 9.6 Hz), 7.11 (1H, dd, $J = 0.9$, 5.5 Hz), 7.51-7.57 (2H, m), 7.60-7.65 (1H, m), 7.87-7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ 26.5, 55.0, 71.1, 124.4, 128.0, 129.2, 130.2, 131.2, 133.3, 136.8, 139.3; MS (rel intensity) *m/z* 248 (M^{+}-2H, 97), 218 (25), 155 (28), 125 (100), 97 (18), 91 (22), 77 (81); exact mass calcd for $C_{13}H_{12}O_3S$ *m/z* 248.0508, found 248.0500.

1,5-Bis(phenylsulfonyl)-1,3-cyclohexadiene (8c)

Yellow liquid; IR (neat) 3065, 2925, 2854, 1732, 1447, 1307, 1152, 1083, 725, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.72 (1H, ddd, $J = 2.4$, 11.1, 19.4 Hz), 3.16 (1H, dd, $J = 4.0$, 19.4 Hz), 3.93-4.00 (1H, m), 6.09 (1H, dd, $J = 5.4$, 9.6 Hz), 6.31 (1H, ddd, $J = 1.3$, 5.7, 9.6 Hz), 6.70 (1H, dd, $J = 2.4$, 5.7 Hz), 7.43-7.48 (2H, m), 7.56-7.71 (6H, m), 7.83-7.86 (2H, m); ^{13}C NMR ($CDCl_3$) δ 29.6, 60.1, 123.6, 127.9, 128.3, 128.9, 129.3, 129.4, 129.5, 133.1, 134.5, 135.6, 138.4, 141.6; MS (rel intensity) *m/z* 358 (M^{+}-2H, 0.7), 284 (29), 256 (17), 218 (89), 152 (18), 125 (100), 97 (41), 77 (92); exact mass calcd for $C_{18}H_{14}O_4S_2$ *m/z* 358.0334, found 358.0330.

Methyl [1-(phenylsulfonyl)-1,3-cyclohexadien-5-yl]acetoacetate (8h)

Yellow liquid; an inseparable diastereomeric mixture (43/57); IR (neat) 3068, 2954, 1741, 1714, 1447, 1306, 1152, 1091, 1000, 729, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.12 (s), 2.18 (s), 2.20-2.56 (m), 3.17-3.25 (m), 3.48 (d), 3.50 (s), 3.55 (d), 3.70 (s), 5.95 (dd), 6.07 (dd), 6.15-6.22 (m), 7.05-7.09 (m), 7.52-7.58 (m), 7.60-7.64 (m), 7.84-7.88 (m); ^{13}C NMR ($CDCl_3$) δ 24.3, 30.2, 30.3, 31.7, 32.2, 52.3, 52.6, 60.0, 60.9, 123.9, 124.0, 127.9, 128.0, 129.2, 129.3, 130.8, 131.0, 133.3, 133.4, 133.8, 134.2, 135.7, 136.2, 139.2, 139.3, 167.7, 200.9; MS (rel intensity) *m/z* 332 (M^{+}-2H, 20), 300 (33), 290 (41), 258 (96), 219 (80), 141 (51), 125 (44), 116 (35), 77 (100); exact mass calcd for $C_{17}H_{16}O_5S$ *m/z* 332.0718, found 332.0721. These two isomers have some distinct ^{1}H and ^{13}C NMR absorptions. The major isomer: ^{1}H NMR ($CDCl_3$) δ 2.12 (3H, s), 3.55 (1H, d, $J = 10.1$ Hz), 6.07 (1H, dd, $J = 5.0$, 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 30.2, 31.7, 52.3, 60.0, 124.0, 128.0, 129.3, 131.0, 133.4, 134.2, 135.7, 139.2. The minor isomer: ^{1}H NMR ($CDCl_3$) δ 2.18 (3H, s), 3.48 (1H, d, $J = 9.9$ Hz), 5.95 (1H, dd, $J = 4.9$, 9.4 Hz); ^{13}C NMR ($CDCl_3$) δ 30.3, 32.2, 52.6, 60.9, 123.9, 127.9, 129.2, 131.8, 133.3, 133.8, 136.2, 139.3.

1-[5-(Phenylsulfonyl)-2,4-cyclohexadien-1-yl]propan-2-one (8j)

Yellow liquid; IR (neat) 3067, 2922, 2856, 1712, 1447, 1361, 1150, 1083, 756, 724, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (3H, s), 2.20 (1H, dd, $J = 7.1$, 17.2 Hz), 2.35 (2H, d, $J = 7.1$ Hz), 2.45 (1H, dd, $J = 8.6$, 17.2 Hz), 2.87-2.98 (1H, m), 6.03 (1H, dd, $J = 4.4$, 9.7 Hz), 6.11 (1H, dd, $J = 5.3$, 9.7

Hz), 7.05 (1H, dd, *J* = 0.9, 5.3 Hz), 7.51-7.68 (3H, m), 7.86-7.90 (2H, m); ^{13}C NMR ($CDCl_3$) δ 26.0, 28.6, 30.2, 45.8, 122.5, 128.0, 129.2, 131.0, 133.3, 135.6, 136.9, 139.4, 206.1; MS (rel intensity) *m/z* 276 (M^+, 3), 274 (16), 232 (100), 219 (23), 210 (9), 165 (13), 151 (29), 125 (21), 109 (16), 91 (57), 77 (73); exact mass calcd for $C_{15}H_{14}O_3S$ *m/z* 274.0665, found 274.0659.

5-(3-Cyanopropyl)-1-(phenylsulfonyl)-1,3-cyclohexadiene (8m)

Yellow liquid; IR (neat) 3040, 2920, 2240, 1435, 1295, 1135, 1085, 750, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26-1.52 (4H, m), 2.12-2.23 (3H, m), 2.35-2.58 (2H, m), 5.99 (1H, dd, *J* = 3.9, 9.5 Hz), 6.13 (1H, dd, *J* = 5.6, 9.5 Hz), 7.03 (1H, d, *J* = 5.6 Hz), 7.53-7.67 (3H, m), 7.87-7.90 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.1, 22.2, 25.7, 32.0, 32.7, 119.1, 122.6, 127.9 (×2), 129.2 (×2), 131.1, 133.2, 135.7, 136.7, 139.3; MS (rel intensity) *m/z* 287 (M^+, 20), 286 (31), 219 (85), 141 (43), 125 (21), 91 (39), 77 (100); exact mass calcd for $C_{16}H_{17}NO_2S$ *m/z* 287.0982, found 287.0978.

[5-(Phenylsulfonyl)-2,4-cyclohexadien-1-yl]acetic Acid (8s)

Colorless liquid; IR (neat) 3467, 3067, 2954, 2923, 1723, 1447, 1304, 1150, 1092, 727, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17-2.36 (3H, m), 2.55 (1H, dd, *J* = 8.5, 17.0 Hz), 2.75-2.97 (1H, m), 6.06 (1H, dd, *J* = 4.2, 8.8 Hz), 6.16 (1H, dd, *J* = 1.2, 5.2, 8.8, Hz), 7.06 (1H, d, *J* = 5.2 Hz), 6.13 (1H, d, *J* = 4.4 Hz), 7.56-7.70 (3H, m), 7.86-7.89 (2H, m); ^{13}C NMR ($CDCl_3$) δ 26.0, 29.9, 36.8, 123.1, 128.0 (×2), 129.3 (×2), 131.0, 133.4, 135.9, 139.2 (×2), 176.0; MS (rel intensity) *m/z* 276 (M^+-2H, 57), 219 (17), 183 (43), 165 (17), 125 (77), 91 (30), 77 (100); exact mass calcd for $C_{14}H_{12}O_4S$ *m/z* 276.0456, found 276.0457.

General Procedure for the Aromatization of Diene 8 with DDQ (Table 2)

To a solution of diene **8** (0.5 mmol) in toluene (5 mL) was added DDQ (0.6 mmol) at room temperature, and then the reaction mixture was heated to reflux for 4 h. To the yellow solution was added 10% $Na_2S_2O_{3(aq)}$ (5 mL), and the mixture was extracted with diethyl ether (10 mL × 2), dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (3/1 to 10/1) as eluent to give **9**.

1-Methoxy-3-(phenylsulfonyl)benzene (9a)[20]

Yellow liquid; IR (neat) 3066, 2922, 2856, 1596, 1446, 1305, 1151, 1100, 1067, 724, 683, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (1H, br s), 3.84 (3H, s), 7.07 (1H, dd, *J* = 0.7, 7.8 Hz), 7.40 (1H, dd, *J* = 7.8, 8.0 Hz), 7.44-7.59 (4H, m), 7.94-7.98 (3H, m); ^{13}C NMR ($CDCl_3$) δ 55.6, 112.3, 119.5, 119.9, 127.6, 128.2, 129.0, 129.2, 133.8, 133.9, 139.2; MS (rel intensity) *m/z* 248 (M^+, 62), 218 (39), 155 (20), 125 (100), 97 (16), 92 (14), 77 (63); exact mass calcd for $C_{13}H_{12}O_3S$ *m/z* 248.0508, found 248.0515.

1-(2-Oxopropyl)-3-(phenylsulfonyl)benzene (9j)

Yellow liquid; IR (neat) 3067, 2956, 2925, 2856, 1721, 1447, 1322, 1304, 1153, 1103, 730, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3H, s), 3.79 (2H, s), 7.40 (1H, br d), 7.45-7.60 (4H, m), 2.79 (1H, br s), 7.84 (1H, br d), 7.93-7.96 (2H, m); ^{13}C NMR ($CDCl_3$) δ 29.7, 50.0, 126.4, 127.7 (×2), 128.5, 129.3 (×2), 129.6, 133.2, 134.4, 135.7, 141.6, 142.0, 204.4. MS (rel intensity) *m/z* 274 (M^+, 21), 232 (100), 219 (25), 165 (13), 125 (21), 109 (19), 91 (56), 77 (74); exact mass calcd for $C_{15}H_{14}O_3S$ *m/z* 274.0665, found 274.0667.

1-(3-Cyanopropyl)-3-(phenylsulfonyl)benzene (9m)

Yellow liquid; IR (neat) 3056, 2933, 2862, 2266, 1580, 1472, 1441, 1421, 1082, 1026, 785, 744, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.99 (2H, tt, *J* = 7.0, 7.4 Hz), 2.34 (2H, t, *J* = 7.0 Hz), 2.84 (2H, t, *J* = 7.4 Hz), 7.41-7.49 (2H, m), 7.52-7.61 (3H, m), 7.78-7.82 (2H, m), 7.93-7.97 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.5, 26.6, 34.2, 118.9, 126.0, 127.2, 127.7 (×2), 129.3 (×3), 129.7, 133.2, 133.3, 141.4, 141.5; MS (rel intensity) *m/z* 285 (M^+, 37), 245 (25), 231 (22), 220 (31), 192 (54), 165 (16), 152 (15), 141 (14), 125 (100), 91 (24), 77 (78); exact mass calcd for $C_{16}H_{17}NO_2S$ *m/z* 285.0824, found 285.0822.

(1S*,2S*,6S*)-1,2,5,6,7,8-Hexahydro-2-iodo-8-oxo-4-(phenylsulfonyl)benzofuran (10)

To a solution of potassium iodide (623 mg, 3.75 mmol) in saturated sodium bicarbonate (4 mL) was added iodine (159 mg, 0.63 mmol), and then the mixture was stirred at room temperature for 10 min. A solution of diene **8s** (87 mg, 0.313 mmol) in chloroform (4 mL) was added at room temperature (22 °C), and stirred for 4 days in dark. To the brown solution was added water (10 mL), and the mixture was extracted with dichloromethane (10 mL × 3). The combined organic solution was washed with 10% sodium bisulfite (25 mL), dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (3/1) as eluent to give a yellow to brown liquid **10** (89 mg) in 71% yield. IR (neat) 3067, 2958, 2922, 2867, 1769, 1304, 1147, 1088, 721, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (1H, dd, *J* = 3.1, 17.7 Hz), 2.15 (1H, dd, *J* = 4.5, 17.7 Hz), 2.58 (1H, ddd, *J* = 2.3, 7.7, 17.7 Hz), 2.72 (1H, dd, *J* = 8.6, 17.7 Hz), 3.08-3.16 (1H, m), 5.05

(1H, ddd, $J = 0.9, 1.7, 6.0$ Hz), 5.09 (1H, br d, $J = 5.9$ Hz), 7.20 (1H, ddd, $J = 0.9, 2.3, 5.9$ Hz), 7.56-7.61 (2H, m), 7.65-7.70 (1H, m), 7.82-7.86 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.3, 24.7, 30.5, 36.6, 81.3, 128.2 (≥2), 129.6 (×2), 134.1, 135.2, 137.7, 140.6, 174.0; MS (rel intensity) *m/z* 404 (M^+, 0.11), 277 (32), 219 (37), 153 (53), 151 (63), 125 (100), 91 (46), 77 (86); exact mass calcd for $C_{14}H_{13}O_4S$ (M^+-127) *m/z* 277.0535, found 277.0531.

(1S*,6S*)-1,2,5,6,7,8-Hexahydro-8-oxo-4-(phenylsulfonyl)benzofuran (11) and (1S*,6S*)-1,4,5,6,7,8-Hexahydro-8-oxo-4-(phenylsulfonyl)benzofuran (12)

To a solution of **10** (40 mg, 0.1 mmol) in dried benzene (5 mL) was added AIBN (5 mg) and tributyltin hydride (32 µL, 0.12 mmol), and then the mixture was heated at reflux for 4 h under N_2. The mixture was evaporated and the yellow crude product was purified by flash column chromatography using hexane/ethyl acetate (3/2) as eluent to give an inseparable mixture of **11** and **12** (13 mg, 10:1, 47% yield) as a light yellow liquid; IR (neat) 3063, 2926, 2922, 1790, 1694, 1447, 1308, 1152, 1086, 1036, 966, 759, 720, 688 cm^{-1}; MS (rel intensity) *m/z* 278 (M^+, 13), 235 (39), 231 (29), 219 (27), 208 (31), 151 (56), 125 (42), 122 (36), 109 (46), 91 (16), 77 (100); exact mass calcd for $C_{14}H_{14}O_4S$ *m/z* 278.0614, found 278.0622. These two isomers have some distinct ^{1}H and ^{13}C NMR absorptions. The compound **11**: ^{1}H NMR ($CDCl_3$) δ 2.28 (1H, dd, $J = 8.2, 17.3$ Hz), 2.56 (1H, ddd, $J = 1.5, 4.9, 18.9$ Hz), 2.67 (1H, dd, $J = 7.7, 17.3$ Hz), 2.55-2.75 (1H, m), 2.91 (1H, ddd, $J = 1.7, 5.9, 18.9$ Hz), 3.26-3.33 (1H, m), 4.75 (1H, d, $J = 7.0$ Hz), 6.86 (1H, br s), 7.60-7.68 (2H, m), 7.72-7.79 (1H, m), 7.89-7.95 (2H, m); ^{13}C NMR ($CDCl_3$) δ 24.1, 33.3 (×2), 34.4, 77.2, 128.1, 128.9 (×2), 129.1, 130.0 (×2), 135.1, 136.3, 172.9. The compound **12**: ^{1}H NMR ($CDCl_3$) δ 4.64 (1H, dd, $J = 3.5, 5.5$ Hz), 5.18-5.20 (1H, m), 6.22 (1H, br d, $J = 11.1$ Hz), 6.79 (1H, dd, $J = 3.5, 11.1$ Hz).

(1S*,6S*)-1,2,5,6-Tetrahydro-7-(methoxycarbonyl)-8-methyl-4-(phenylsulfonyl)benzofuran (13)

To a solution of **8h** (34 mg, 0.1 mmol) in dried methanol (5 mL) was added a sodium methoxide solution (0.1 M in MeOH, 0.7 mL, 0.1 mmol). The mixture was then stirred at room temperature (22 °C) for 2 h under N_2, and was then quenched with saturated ammonium chloride solution. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (10 mL × 2), washed with water, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (3/1) as eluent to give a colorless liquid **13** (15 mg, 45% yield) which was crystallized with CH_2Cl_2/hexane, mp 112.6-113.8 °C; IR (neat) 3062, 2924, 2853, 1687, 1646, 1446, 1304, 1152, 1092, 1002, 731, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.90 (3H, d, $J = 1.3$ Hz), 2.23-2.35 (2H, m), 2.66 (1H, ddd, $J = 2.3, 16.2$ Hz), 2.88 (1H, ddd, $J = 2.8, 3.2, 6.1$ Hz), 3.43-3.46 (1H, m), 3.51 (3H, s), 5.03 (1H, ddd, $J = 3.3, 3.5, 9.8$ Hz), 7.17 (1H, ddd, $J = 2.8, 3.2, 6.1$ Hz), 7.46-7.52 (2H, m), 7.58-7.64 (1H, m), 7.78-7.79 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 25.2, 29.3, 41.2, 50.5, 80.5, 104.4, 128.1 (×2), 129.0 (×2), 133.2, 135.9, 138.7, 142.5, 165.0, 169.4; MS (rel intensity) *m/z* 334 (M^+, 27), 322 (14), 302 (26), 219 (22), 149 (34), 141 (21), 140 (100), 125 (25), 109 (34), 91 (13), 77 (42); exact mass calcd for $C_{17}H_{18}O_5S$ *m/z* 334.0876, found 334.0884.

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Key Words

Iron complexes; Dienes; Nucleophilic addition reactions; Sulfone.

REFERENCES

1. Grée, R. *Synthesis* **1989**, 341.
2. (a) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (b) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497.
3. (a) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2751. (b) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1985**, *107*, 1455. (c) Yeh, M. C. P.; Chu, C. H.; Sun, M. L.; Kang, K. P. *J. Chin. Chem. Soc.* **1990**, *37*, 547.
4. Chou, S. S. P.; Hsu, C. H.; Yeh, M. C. P. *Tetrahedron Lett.* **1992**, *33*, 643.
5. Yeh, M. C. P.; Chou, T. S.; Tso, H. H.; Tsai, C. Y. *J. Chem. Soc., Chem. Commun.* **1990**, 897.
6. (a) Bäckvall, J. E.; Plobeck, N. A. *J. Org. Chem.* **1990**, *55*, 4528. (b) Bäckvall, J. E.; Juntunen, S. K. *J. Org. Chem.* **1988**, *53*, 2389. (c) Sellen, M.; Bäckvall, J. E.; Helquist, P. *J. Org. Chem.* **1991**, *56*, 835.
7. Pearson, A. J. *Synlett* **1990**, 10 and references cited therein.

8. (a) Birch, A. J.; Chamberlain, K. B.; Hass, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1882. (b) Ireland, R. E.; Brown, Jr. G. G. *J. Org. Chem.* **1974**, *39*, 51.
9. (a) Pearson, A. J.; Ham, P.; Ong, C. W.; Perrior, T. R.; Rees, D. C. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1527. (b) Pearson, A. J. *Science*, **1984**, *223*, 895.
10. Chou, S. S. P.; Hsu, C. H. *J. Chin. Chem. Soc.* **1996**, *43*, 355.
11. Preliminary results have been reported: Chou, S. S. P.; Hsu, C. H. *Tetrahedron Lett.* **1996**, *37*, 5373.
12. Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208.
13. Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 821.
14. (a) Birch, A. J.; Liepa, A. J.; Stephenson, G. R. *Tetrahedron Lett.* **1979**, 3565. (b) Knolker, H.-J.; Bauermeister, M.; Boese, R.; Pannek, J.-B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 223. (c) Knolker, H.-J.; Bauermeister, M. *J. Chem. Soc., Chem. Commun.* **1990**, 664. (d) Knolker, H.-J.; Bauermeister, M.; Boese, R.; Pannek, J.-B. *Tetrahedron* **1993**, *49*, 841. (e) Knolker, H.-J.; Bauermeister, M. *Tetrahedron* **1993**, *49*, 11221.
15. Crystal data for **5q**: $C_{19}H_{18}FeO_7S$, Mr = 446.2, monoclinic, $P2_1/n$, a = 7.9910(10) Å, b = 11.984(4) Å, c = 20.568(2) Å, β = 90.790(0), V = 1969.5(7) $Å^3$, Z = 4, Dx = 1.505 Mg/m^3, λ(MoKα) = 0.71073 Å, μ = 0.910 mm^{-1}, F(000) = 920, T = 298 K. Sample was studied on an automatic diffractometer Siemens P4. Structure was solved with a Patterson map and refined by full-matrix least-square techniques with the resulting R = 3.58%, Rω = 3.14% and Sω = 1.97 (residual $\Delta\rho < 0.21$ e$Å^{-3}$).
16. Yeh, M. C. P.; Sheu, B. A.; Fu, H. W.; Tau, S. I.; Chuang, L. W. *J. Am. Chem. Soc.* **1993**, *115*, 5941.
17. (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903.
18. Marino, J. P.; Ferro, M. P. *J. Org. Chem.* **1981**, *46*, 1828.
19. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.
20. Marziano, N.; Montaudo, G.; Passerini, R. *Ann. Chim. (Rome)*, **1962**, *52*, 143.