Diels−Alder Reactions of 1,3-Diphenylisobenzofuran with Ferrocenyl- and (η^6-Phenyl)tricarbonylchromium Analogues of Chalcone as Well as Some Other Dienophiles

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The Diels−Alder reactions of 1,3-diphenylisobenzofuran with acryloylferrocene (**1**), 4-ferrocenyl-3-buten-2-one (**2**), cinnamoylferrocene (**3**), 3-ferrocenyl-1-phenyl-2-propenone (**4**), chalcone (**5**), 1-((η^6-phenyl)tricarbonylchromio)-3-phenyl-2-propenone (**6**), 1-phenyl-3-((η^6-phenyl)tricarbonylchromio)-2-propenone (**7**), and (2-nitrovinyl)ferrocene (**8**) were examined under various conditions. The best results were achieved using SiO_2 and a very acidic montmorillonite clay, KSF, as the catalyst, and the reactions were carried out without solvent. Reasonable to good yields of the Diels−Alder (D-A) products were isolated in most cases. X-ray structural studies showed that the adducts **13b** and **13h**, derived from the (*E*)-alkenes **2** and **8**, have *exo*-acetyl or -nitro substituents and *endo*-ferrocenyl groups with respect to the bridging oxygen atom of the 7-oxabicycloheptane ring system. The product **13a** from the monosubstituted enone **1** also has an *exo*-acyl (ferrocenylcarbonyl) group. Aluminum chloride was found to be a good catalyst for the reactions of 1,3-diphenylisobenzofuran with *push-pull* alkenes like **1**, **2**, **4**, and **8**. The unexpected products were derived from α-ferrocenyl carbocation attack on the diene, followed by electrophilic 2-substitution of the cyclopentadienyl ion ring, rather than D-A addition. The X-ray structure of the 8-oxabicyclooctane **12b**, derived from **4**, revealed an *exo*-ferroceno group and *endo*-phenacyl substituent.

Introduction

A large number of papers describing the effects of various factors on the Diels−Alder (D-A) reaction have been published during recent years. In most of these studies, only very reactive dienophiles (e.g., methyl vinyl ketone, methyl ethyl ketone, maleic anhydride, etc.) were tested; however, some cyclic enones, like quinone and 2-cyclohexenone, have also been used as dienophiles.[1] Other unsaturated ketones have been sparsely examined, and a literature search of the period since 1959 reveals that chalcone (1,3-diphenyl-2-propenone) was described as a participant in D-A reactions in only 10 papers. Only six of them[2−7] describe its application as a dienophile. In the other studies,[8−10] it served as the diene. One paper[11] reported the reaction of chalcone with cyclopentadiene in the presence of pyrrolidine, and a product of a Michael addition and subsequent Knoevenagel-type cyclization was isolated.

Our goal was to study the reactivity of chalcone, and its metalloorganic and other analogues, as dienophiles in D-A reactions. We hoped to determine optimal reaction conditions for the D-A reactions of the chosen dienophiles with 1,3-diphenylisobenzofuran.

Results and Discussion

Preliminary experiments using 1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene (**9**)[12] as a diene were mostly unsuccessful. Only in the presence of $AlCl_3$ did acryloylferrocene give a D-A reaction product, and only in 35% yield. Therefore we decided to use a more reactive diene, 1,3-diphenylisobenzofuran (**10**), with $AlCl_3$ as a catalyst. $AlCl_3$ had performed well in a similar reaction of acryloylferrocene with 1-phenyl-1,3-butadiene.[13] Reaction of acryloylferrocene with 1,3-diphenylisobenzofuran resulted in a 34% yield of 1,4-diphenyl-2-(ferrocenylcarbonyl)naphthalene (**11**) (see Scheme 1). This compound could be formed *via* oxygen extrusion from the expected, but unobserved D-A adduct. This encouraging result prompted us to examine the D-A reactions of this diene with other dienophiles, but positive results were achieved only with certain *push-pull* alkenes, as summarized in Table 1.

Isolated materials **12a**−**c** had correct C, H, N microanalyses, but their broadly similar ^{1}H NMR spectra were not in accord with the proposed D-A structures. First, in the ferrocene region a disubstituted (probably

(1) Fringuelli, F.; Taticchi, A. *Org. Prep. Proc. Int.* **1990,** *22,* 131.

(2) Mayo, F. R. *Am. Chem. Soc. Div., Paint, Plastics, Printing Ink Chem. Reprints* **1959,** *19,* 326.

(3) Oida, T.; Tanimoto, S.; Ikehira, H.; Okano, M. *Bull. Inst. Chem. Res., Kyoto Univ.* **1982,** *60,* 336.

(4) Minami, T.; Chikugo, T.; Hanamoto, T. *J. Org. Chem.* **1986,** *51,* 2210.

(5) Karakasa, T.; Moriyama, S.; Motoki, S. *Chem. Lett.* **1988,** 1029.

(6) Elnagdi, M. H.; Negm, A. M.; Hassan, E. M.; El-Boreiy, A. *J. Chem. Res., Synop.* **1993,** 130.

(7) Mukaiyama T.; Watanabe K.; Shiina I. *Chem. Lett.* **1995,** 1.

(8) Kazuyoshi, S.; Satoko, T. *J. Chem. Soc., Chem. Commun.* **1991,** 89.

(9) Kazuyoshi, S.; Satoko, T. *Bull. Chem. Soc. Jpn.* **1991,** *64,* 3188.

(10) Borodaev, S. V.; Zubkova, O. V.; Shibaeva, N. V.; Pyshchev, A. I.; Lukyanov, S. M. *Khim. Geterotsikl. Soedin.* **1991,** 568; *Chem. Abstr.* **1991,** *115,* 159069u.

(11) Griesbeck, A. G. *J. Org. Chem.* **1989,** *54,* 4981.

(12) Boháč, A.; Hrnčiar, P. *Synthesis* **1991,** 881.

(13) Toma, Š.; Elečko, P.; Gažová, J.; Solčániová, E. *Collect. Czech. Chem. Commun.* **1987,** *52,* 391.
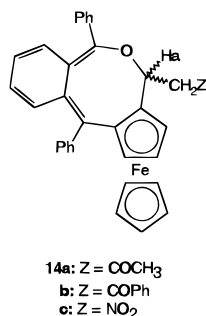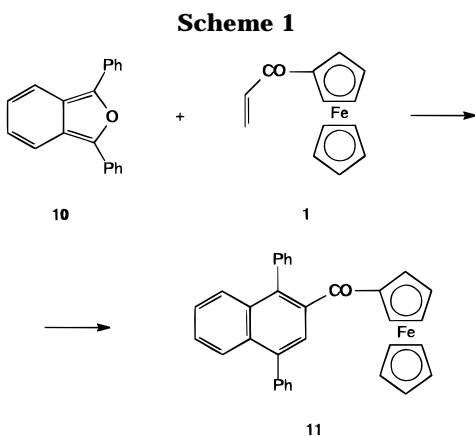
14a: Z = COCH₃
b: Z = COPh
c: Z = NO₂

Figure 1.

Scheme 1

Table 1: Reaction Conditions and Results of AlCl₃-Mediated Reactions of 1,3-Diphenylisobenzofuran with Some Alkenes

starting material				
entry	compd	reactin time, h	product	yield, %
1	**1**	20.5	**11**	33.7
2	**2**	24.3	**12a**	61.3
3	**4**	29.0	**12b**	31.8
4	**8**	30.0	**12c**	20.4

1,2-) cyclopentadienyl ring was suggested by a one-proton multiplet and a two-proton multiplet, together with a C₅H₅ singlet. Second, instead of the expected two signals derived from the ene protons, three groups of signals corresponding to an AMX system were observed. Two protons appearing as doublets at δ 2.81−3.21 (*J* = 17.5−18.0 Hz) and δ 2.23−2.89 (*J* = 10.5−10.6 Hz) were clearly adjacent to a carbonyl group, but individually coupled to another proton appearing as a double doublet near δ 5.00−5.20. Although this later signal is out from the "normal" region for -OCH protons, it was presumed that in a structure such as **14** (Figure 1) the chemical shift of Ha would be governed by a *syn* or *anti* orientation of the adjacent fused ferrocenyl group. Although intuitively unattractive, **14** could arise from Lewis acid-catalyzed ring opening of the isobenzofuran, α-Friedel−Crafts alkylation of the C₅H₄Fe ring, and subsequent Michael addition of an O-nucleophile. In fact an X-ray analysis of **12b** showed that it possessed an 8-oxabicyclo[3.2.1]-octane structure (Figure 2). On the basis of the same reaction conditions and similar ¹H NMR spectra, we assign analogous structures to products **12a** and **12c**. No product was formed either with chalcone or with its tricarbonylchromium analogues **6** and **7**. A control experiment (without the diene) proved that AlCl₃ caused decomplexation of **6** and **7** back to chalcone itself. If we accept that the reaction proceeds *via* a stable carbocation, then enones **5**, **6**, and **7** cannot form the structure **12**.
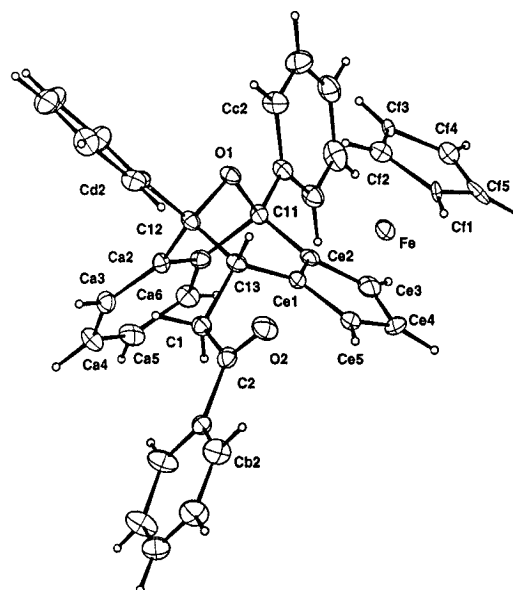

Figure 2. View of one of the two crystallographically independent molecules of C₃₄H₂₈O₂Fe (**12b**). The same atom numbering scheme has been used for each molecule. Phenyl ring atoms are numbered in sequence C*n*1−C*n*6, starting with the ipso carbon atom, and only the label of C*n*2 is shown for each ring; for clarity parentheses have been removed from atom labels. 20% probability ellipsoids are displayed, except for hydrogen atoms which are represented by spheres of arbitrary radius.

The ferrocenyl group is absent in the alkenes **5**, **6**, and **7**. Examination of structure **12b** (Figure 2) confirms the ¹H NMR predictions of a 1,2-disubstituted ferrocene linked to an AMX system [C(1)−C(13)]. It also reveals the unique magnetic environment of Ha attached to C(13). Conceivably, **12b** could exist in four different stereoisomeric forms depending upon (i) the orientation of the ferrocene residue relative to the oxygen bridge and (ii) the *endo* or *exo* orientation of the phenacyl substituent at C(13). However, there was no experimental evidence for the existence of any other isomers. A surprising feature of the crystal structure of **12b** is that it belongs to a chiral space group. Our results do not indicate that the crystal of **12b** used was a racemic twin but, instead, suggest that spontaneous resolution occurred on crystallization. In the crystal studied all molecules have absolute configuration *R*,*S*, and *R* at C(11), C(12), and C(13), respectively. The formation of compound **12b** is easily understood if it is assumed that a trace of water in the AlCl₃ caused protonation of the enone (e.g., **4**) to generate a stabilized α-ferrocenyl carbocation. This could then undergo the usual electrophilic 2,5-addition across the isobenzofuran, followed by an intramolecular Friedel−Crafts alkylation of the C₅H₄Fe ring (Scheme 2). Precedent for such a reaction was found in the observation by Turbitt and Watts[14] that α-ferrocenyl carbocations alkylated 1,3-cyclopentadiene and then suffered intramolecular substitution (Scheme 3).

A detailed analysis (Table 4, supporting information) of the structure **12b** shows that bond lengths are normal.[15] The six-membered ring O(1)−C(11)−C(e2)−C(e1)−C(13)−C(12) adopts an envelope conformation with O(1)

(14) Turbitt, T. D.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 631; *J. Chem. Soc., Perkin Trans. 2* **1974**, 195.
(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. In *International Tables for Crystallography*, Volume C; International Union of Crystallography: 1992.

Scheme 2
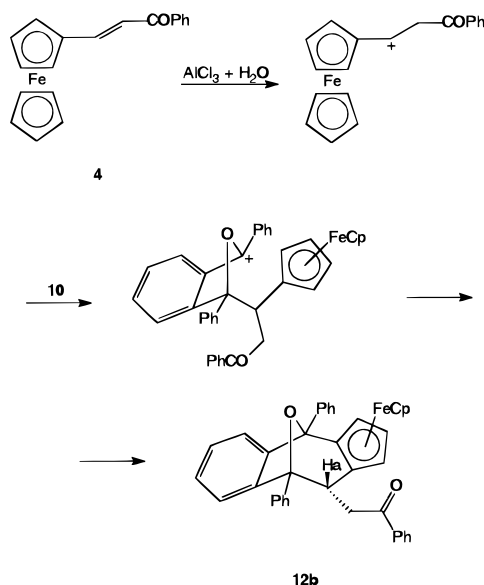
Scheme 3
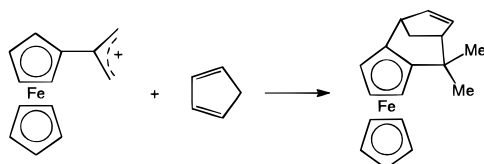
Table 2: Reaction Conditions and Yields of SiO₂-Mediated D-A Reactions of Dienophiles 1−8 with 1,3-Diphenylisobenzofuran

| entry	compd	reactn time, h	product	yield, %
1	**1**	26.0	**13a**	48.0
2	**2**	20.3−44.0	**13b**	51.0−58.0
3	3	29.25	**13c**	68.2
4	**4**	29.25	**13d**	24.7
5	**5**	44.5	**13e**	41.3
6	**6**	32.0	**13f**	46.6
7	**7**	41.0	**13g**	51.8
8	**8**	25.5	**13h**	78.0

at the flap and near-zero endocyclic torsion angles across C(13)−C(e1) and C(e1)−C(e2) (Table 4); the ring-puckering parameters [$Q = 0.614(7)$ Å, $\theta = 53.7(7)°$, $\varphi = 358-(1)°$] are also quite typical.[16] Cyclopentadienyl ring f is disordered and was modeled on the assumption that it adopts two orientations with equal probability.

Being unsuccessful in AlCl₃-catalyzed D-A reactions of 1,3-diphenylisobenzofuran with our chosen dienophiles, we turned our attention to solid supports. D-A reactions on SiO₂ under solvent-free conditions have been reported.[17] Following suit, easily accessible **2** was the first dienophile examined and reaction with diene **10** resulted in a 51−58% yield of the adduct, which was characterized by microanalysis and ¹H NMR. Encouraged by such a good result, we examined the other dienophiles under the same conditions (20.3−44.5 h, rt). Table 2 shows that moderate to good yields of the desired adducts were isolated with all dienophiles. It seems possible that even higher yields could be obtained after some optimization

(16) (a) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354. (b) Boeyens, J. C. A. *J. Cryst. Mol. Strust.* **1978**, *8*, 317.

(17) Veselovsky, V. V.; Gybin, A. S.; Lozanova, A. V.; Moiseenkov, A. M.; Smit, W. A.; Caple, R. *Tetrahedron Lett.* **1988**, *29*, 175.

Table 3: Reaction Conditions and Yields of KSF-Mediated D-A Reactions of Dienophiles 1−8 with 1,3-Diphenylisobenzofuran

entry	compd	reactn time, h	product	yield, %
1	**1**	24.5	**13a**	99.7[a]
2	**2**	24.0	**13b**	61.5
3	**3**	27.0	**13c**	18.5
4	**4**	24.6	**13d**	5.7
5	**5**	26.5	**13e**	49.6
6	**6**	28.0	**13f**	18.6
7	**7**	41.0	**13g**	25.8
8	**8**	25.5	**13h**	48.8

[a] Yields of stereoisomers of **13a** (48.9% CO−Fc oriented *endo* and 50.8% CO−Fc oriented *exo* with respect to bridging oxygen atom).

Scheme 4
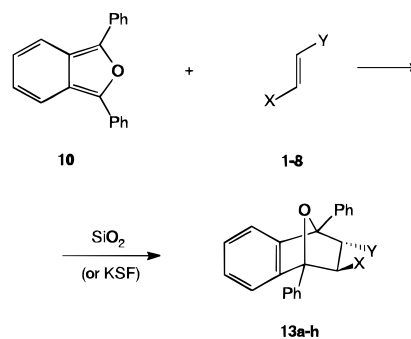
1, 13a: X = COFc, Y = H
2, 13b: X = COCH₃, Y = Fc
3, 13c: X = COFc, Y = Ph
4, 13d: X = COPh, Y = Fc

5, 13e: X = COPh, Y = Ph
6, 13f: X = COPhCr(CO)₃, Y = Ph
7, 13g: X = COPh, Y = PhCr(CO)₃
8, 13h: X = NO₂, Y = Fc

Fc = C₅H₄Fe(C₅H₅)

of the experimental conditions (reaction time, SiO₂/reagents ratio or diene/dienophile ratio). It is known that the very acidic montmorillonite clay KSF can be used as the inorganic support for some D-A reactions.[18] We therefore explored its application as the catalyst for our reactions. The results are shown in Table 3. KSF is a very good catalyst for reactions of **1**, **2**, and **5** (compared with SiO₂), but D-A adducts of **3**, **4**, **6**, **7**, and **8** were obtained in much lower yield. In the case of acryloyl-ferrocene as dienophile and KSF as catalyst, both possible *endo* and *exo* isomers of the adduct were isolated in reasonable yields (see note *a* in Table 3). In all other cases, the same single isomer of the adduct was obtained (both for SiO₂ and KSF).

We also tested the reactions of **2** with other compounds. However, negative results were obtained using cyclohexadiene as well as sorbic acid as the dienes, whether the reaction was catalyzed (AlCl₃, SiO₂) or not. In all cases, the starting **2** was recovered (44−81%).

The ¹H NMR spectra of all adducts isolated from the SiO₂- or KSF-catalyzed D-A reactions are in accordance with structures **13a−h** (see Scheme 4). This assignment is based on the observation that the two-proton signal of the phenyl or (η⁶-phenyl)tricarbonylchromium group (ortho protons) was found at very high field (δ 6.48−6.49 in compounds **13c**, **13e**, and **13f** and at 4.30 and 5.44 ppm for the (η⁶-phenyl)tricarbonylchromium group in

(18) (a) Laszlo, P.; Luchetti, J. *Tetrahedron Lett.* **1984**, *25*, 2147. (b) Laszlo, P.; Luchetti, J. *Tetrahedron Lett.* **1984**, *25*, 4387. (c) Laszlo, P.; Moison, H. *Chem. Lett.* **1989**, 1031. (d) Cativiela, C.; Figueras, F.; Fraile, J. M.; Garcia, J. I.; Mayoral, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 953.
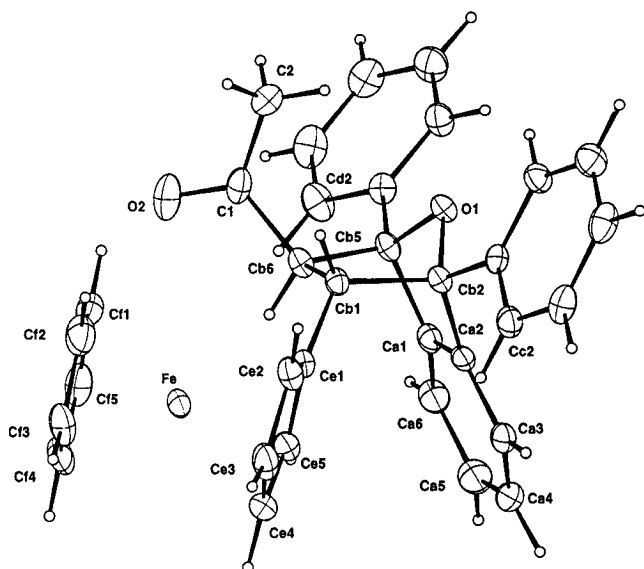
Figure 3. View of a molecule of $C_{39}H_{30}O_2Fe$ (**13b**) showing the atom numbering scheme. 20% probability ellipsoids are displayed, except for hydrogen atoms which are represented by spheres of arbitrary radius. Only one orientation of disordered ring f is shown for clarity.

13g). This is due to the shielding effect of the residual adjacent α-phenyl group from the 1,3-diphenylisobenzo-furan. When the aryl group was ferrocenyl, only the one-proton signal of one cyclopentadienyl α-H was shielded by the phenyl moiety, resonating at δ 2.63–2.96 (**13b**, **13d**, **13h**). Molecular models revealed that, in this case, no rotation about the Fc–C bond is possible, due to the bulkiness of the ferrocenyl group. Structures assigned for **13a**, **13b**, and **13h** in which the electron-withdrawing group (X) is *exo* and the aryl group is *endo* oriented with respect to the bridging oxygen were proved by X-ray analyses of these compounds. In this respect the orienta-tion of the acyl group is opposite to that found for **12a**–**c** but is in keeping with the known preference for furan to give the thermodynamic *exo* isomer.

A single-crystal diffraction analysis of **13b** reveals that it contained two independent molecules which are struc-turally and conformationally nearly identical (Figure 3, Table 5, supporting information). **13b** is the product expected from addition of (*E*)-MeC(O)CH=CHC$_5$H$_4$Fe-(C$_5$H$_5$) to 1,3-diphenylisobenzofuran. From Figure 3 it is apparent that the acetyl group is *exo* and the ferrocenyl substituent *endo* with respect to the bridging O(1) oxygen atom. **13a** (Figure 4) and **13h** (Figure 5) resemble **13b** in that substituent X, which carries C=O or N=O α to the bicyclic ring system, is again found to be *exo* with respect to the bridging oxygen atom.[19]

Bonds lengths in **13b** (Table 5, supporting information) in general agree well with accepted values.[15] However, the newly formed C(b1)–C(b2) and C(b5)–C(b6) bonds [1.580(6)–1.594(6) Å] are rather longer than, for example, the typical C_3C–CHC_2 mean distance of 1.556 Å.[15] In each independent molecule of **13b** the ferrocenyl unit is ordered and the Fe atom is virtually equidistant from rings e and f; the average values of Fe–C bond lengths for the four cyclopentadienyl rings fall in a narrow range [2.036(5)–2.042(9) Å] and are appreciably shorter than the accepted mean for such distances (2.080 Å),[15] but are
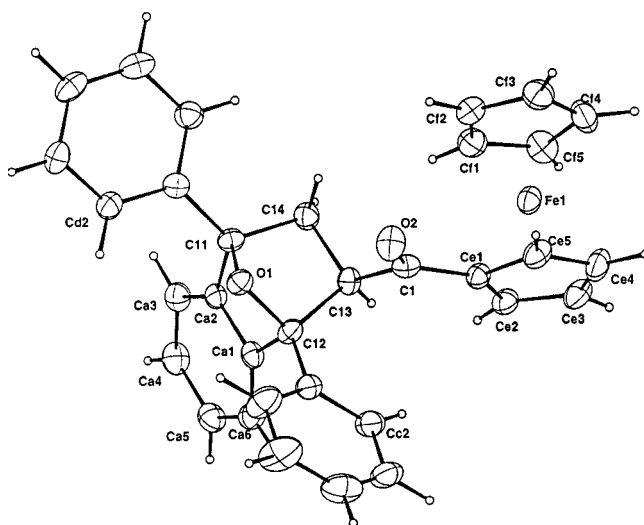

Figure 4. View of a molecule of $C_{33}H_{26}O_2Fe$ (**13a**) showing the *exo* relationship of the C(O)C$_5$H$_4$Fe(C$_5$H$_5$) substituent to O(1). Atom numbering conventions are explained in the caption to Figure 2. 20% probability ellipsoids are displayed, except for hydrogen atoms which are represented by spheres of arbitrary radius.

comparable with the value of 2.045 Å found in the ordered low-temperature form of ferrocene itself.[19] The C(e1)–Cp(e)–Cp(f)–C(f1) torsion angles, where Cp(e) and Cp(f) are the centroids of rings e and f, of −9.2 and −6.9° indicate an eclipsed ferrocene conformation and are close to the value of 9° for the ordered low-temperature form of ferrocene. The diphenylisobenzofuran units in **13b** and **12b** are closely comparable except for the orientations of the phenyl rings: in **13b** O(1) lies close to the planes of both phenyl rings [O(1)–C–C_{ar}–C_{ar} = 7.2(4)–12.6(4)°] whereas in **12b** O(1) is close to the plane of ring c but not to that of ring d [respective O(1)–C–C_{ar}–C_{ar} torsion angles −1.9(7) and 56.9(8)°].

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz with CDCl$_3$ or CD$_3$COCD$_3$ as solvents. 1,3-Diphenylisobenzofuran (Aldrich) was used without puri-fication. KSF (Süd Chemie AG München). Solid supports were not dried. Solvents were purified as usual.

Acryloylferrocene was synthesized in two steps. After Friedel–Crafts acylation of ferrocene with 2-chloropropionyl chloride, elimination of HCl was effected by KF/Al$_2$O$_3$. The *push-pull* alkene **2** was prepared by aldol-type condensation of ferrocenecarboxaldehyde with acetone.[20] The methods of synthesis of the other compounds used by us as the dienophiles in studied D-A reactions are described in the literature: cinnamoylferrocene (**3**) and 3-ferrocenyl-1-phenyl-2-propenone (**4**),[21] 1-((η^6-phenyl)tricarbonylchromio)-3-phenyl-2-propenone (**6**) and 1-phenyl-3-((η^6-phenyl)tricarbonylchromio)-2-prope-none (**7**),[22] and 2-nitrovinylferrocene (**8**).[23]

General Procedure for AlCl$_3$-Catalyzed D-A Reactions. 1,3-Diphenylisobenzofuran (**10**) (0.110 g, 0.0004 mol) and alkenes **1**–**8** (0.0004 mol) were dissolved in 20 mL of dry CH$_2$-Cl$_2$, and AlCl$_3$ (0.0004 mol) was added to the stirred reaction

(19) (a) Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1979**, B35, 1068, 2020. (b) Muir, K. W.; Torabi, A. A. Unpublished results.

(20) Furdík, M.; Dzurilla, M.; Toma, Š.; Suchy, J. *Acta. Fac. Rer. Natur., Univ. Com., Chimia* **1964**, *8*, 569. *Chem. Abstr.* **1964**, *61*, 14710b.

(21) Boichard, J.; Morin, J. P.; Tirouflet, J. *Bull. Soc. Chim. Fr.* **1963**, 851.

(22) Federič, J.; Toma, Š.; Gautheron, B. *J. Organomet. Chem.* **1988**, *338*, 211.

(23) Shiga, M.; Kono, H.; Motoyama, I.; Hata, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1897.
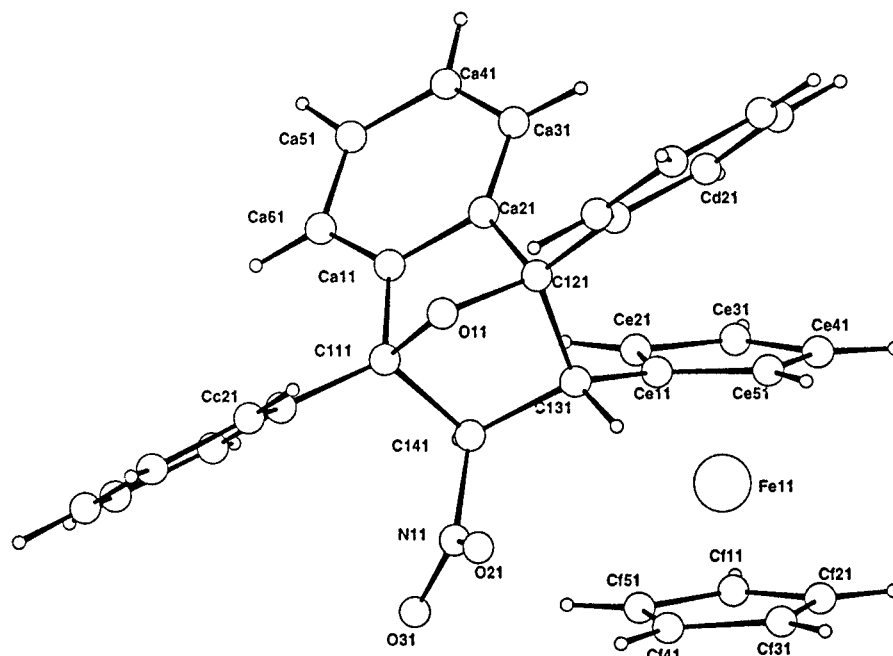
Figure 5. View of one of the two crystallographically independent molecules of $C_{33}H_{25}O_3NFe$ (**13h**). In both molecules the NO_2 group is exo and the $C_5H_4Fe(C_5H_5)$ group endo with respect to O(11). Atom numbering conventions are those of Figure 2, and all atoms are represented by spheres of arbitrary radius.

mixture at rt. The course of the reaction was followed by TLC. At the end of the reaction the contents of the flask were poured into ice water and extracted into CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4. The product of the D-A reaction was purified by chromatography on SiO_2 (elution with gradient from isohexane to the mixture isohexane/ethyl acetate = 1/1) and crystallized (isohexane/ethyl acetate).

Reaction of 10 with acryloylferrocene (1) gave a red crystalline solid **(11)**, mp 242–244 °C; ^{1}H NMR (CDCl₃) δ 4.10 (s, 5H), 4.39 (t, J = 1.5 Hz, 2H), 4.57 (t, J = 1.5 Hz, 2H), 7.35–7.60 (m, 10H), 7.72 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H); IR (CHCl₃, 0.1 mm) ν 1640 cm⁻¹. Anal. Calcd for $C_{33}H_{24}OFe$: C, 80.50; H, 4.91. Found: C, 80.20, H, 5.08.

Reaction of 10 with 4-ferrocenyl-3-buten-2-one (2) gave a yellow crystalline solid **(12a)**, mp 166–168 °C; ^{1}H NMR (CDCl₃) δ 2.19 (s, 3H), 2.23 (dd, J_1 = 10.6 Hz, J_2 = 18.0 Hz, 1H), 2.81 (d, J = 18.0 Hz, 1H), 3.92 (m, 1H), 3.99 (m, 1H), 4.12 (s, 5H), 4.22 (m, 1H), 5.00 (d, J = 10.6 Hz, 1H), 6.90 (m, 1H), 7.14 (m, 3H), 7.51 (m, 8H), 8.05 (d, J = 7.7 Hz, 2H); IR (CHCl₃, 0.1 mm) ν 1715 cm⁻¹; MS (EI) m/z 524 (M⁺), 467 (M⁺ − CH₂COCH₃), 121 ($C_5H_5Fe^+$). Anal. Calcd for $C_{34}H_{28}O_2Fe$: C, 77.87; H, 5.38. Found: C, 78.17; H, 5.56.

Reaction of 10 with 3-ferrocenyl-1-phenyl-2-propenone (4) gave a yellow crystalline solid **(12b)**, mp 252.5–255 °C; ^{1}H NMR (CDCl₃) δ 2.89 (dd, J_1 = 10.4 Hz, J_2 = 18.0 Hz, 1H), 3.21 (d, J = 17.5 Hz, 1H), 3.91 (m, 2H), 4.14 (s, 5H), 4.19 (m, 1H), 5.20 (d, J = 10.5 Hz, 1H), 6.99 (m, 1H), 7.16 (m, 3H), 7.40–7.63 (m, 11H), 7.92 (d, 2H), 8.08 (d, 2H); IR (CHCl₃, 0.1 mm) ν 1685 cm⁻¹. Anal. Calcd for $C_{39}H_{30}O_2Fe$: C, 79.87; H, 5.16. Found: C, 79.59; H, 5.07.

Reaction of 10 with (2-nitrovinyl)ferrocene (8) gave an orange crystalline solid **(12c)**, mp 209–211 °C; ^{1}H NMR (CDCl₃) δ 4.01 (br s, 1H), 4.20 (s, 5H), 4.15–4.40 (m, 3H), 4.71 (d, J = 14.8 Hz, 1H), 4.95 (br s, 1H), 6.86 (m, 1H), 7.20 (m, 3H), 7.38–7.48 (m, 6H), 7.67 (d, J = 6.6 Hz, 2H), 7.93 (d, J = 5.5 Hz, 2H); IR (CHCl₃, 0.1 mm) ν 1555 cm⁻¹, 1380. Anal. Calcd for $C_{32}H_{25}NO_3Fe$: C, 72.88; H, 4.78; N, 2.65. Found: C, 72.43; H, 4.81; N, 2.39.

General Procedure for D-A Reactions on Solid Supports. 1,3-Diphenylisobenzofuran **(10)** (0.100 g, 3.6 mmol) and dienophiles **1**–**8** (3.6 mmol) were dissolved in about 20 mL of CH_2Cl_2, and then 2.0 g of SiO_2 (100/250 mesh) or KSF was added into this solution. Solvent was evaporated *in vacuo* (rotatory evaporator), and the dry reaction mixture was

allowed to stand. Reaction times are given in Tables 2 and 3. The product was isolated by column chromatography on SiO_2 (elution with gradient from isohexane to the mixture isohexane/ethyl acetate = 1/1) and crystallized (isohexane/ethyl acetate).

2,3-Benzo-1,4-diphenyl-6-ferrocenoyl-7-oxa[2.2.1]-bicycloheptane (13a) (product of SiO_2-mediated reaction, CO–Fc *endo* oriented): pale orange crystalline solid, mp 186–188.5 °C; ^{1}H NMR (CDCl₃) δ 2.47 (dd, J_1 = 10.9 Hz, J_2 = 5.4 Hz, 1H), 3.01 (t, J = 10.9 Hz, 1H) 4.08 (s, 5H), 4.14 (dd, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H), 4.43 (dt, J_1 = 3.9 Hz, J_2 = 1.3 Hz, 1H), 4.50 (dq, J_1 = 5.0 Hz, J_2 = 1.3 Hz, 2H), 4.74 (m, J_1 = 3.9 Hz, 1H), 6.95–6.98 (m, 1H), 7.18 (dt, J_1 = 4.2 Hz, J_2 = 1.5 Hz, 2H), 7.31–7.52 (m, 7H), 7.65 (t, J = 1.5 Hz, 1H), 7.68 (t, J = 1.5 Hz, 1H), 7.72 (t, J = 1.5 Hz, 1H), 7.74 (t, J = 1.5 Hz, 1H). Anal. Calcd for $C_{33}H_{26}O_2Fe$: C, 77.65; H, 5.13. Found: C, 77.65; H, 5.09.

2,3-Benzo-1,4-diphenyl-6-ferrocenoyl-7-oxa[2.2.1]-bicycloheptane (13a) (product of SiO_2-mediated reaction, CO–Fc *exo* oriented): orange-red crystalline solid, mp 177–178.5 °C; ^{1}H NMR (CDCl₃) δ 2.65 (br s, 1H), 4.07 (s, 5H), 4.13–3.99 (m, 3H), 4.14 (dd, J = 1.9 Hz, J = 1.3 Hz, 1H), 4.32 (d, J = 2.0 Hz, 1H), 5.37 (d, J = 2.0 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.0 Hz, 1H), 7.26 (m, 1H), 7.36–7.54 (m, 7H), 7.64 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 7.3 Hz, 2H). Anal. Calcd for $C_{33}H_{26}O_2Fe$: C, 77.65; H, 5.13. Found: C, 77.53; H, 5.14.

2,3-Benzo-1,4-diphenyl-6-acetyl-5-ferrocenyl-7-oxa[2.2.1]-bicycloheptane (13b): orange crystalline solid, mp = 153–156 °C; ^{1}H NMR (CDCl₃) δ 2.07 (s, 3H), 2.68 (br s, 1H), 3.37 (d, J = 4.1 Hz, 1H), 3.83 (d, J = 4.2 Hz, 1H), 3.91 (br s, 1H), 4.07 (s, 5H), 4.07 (br s, 2H), 6.95 (d, J = 7.4 Hz, 1H), 7.07 (t, J = 7.0 Hz, 1H), 7.17 (m, 2H), 7.38–7.51 (m, 6H), 7.67 (d, J = 7.6 Hz, 4H); IR (CHCl₃, 0.1 mm) ν 1690 cm⁻¹. Anal. Calcd for $C_{34}H_{28}O_2Fe$: C, 77.87; H, 5.38; Fe, 10.65. Found: C, 77.60; H, 5.61; Fe, 10.32.

2,3-Benzo-1,4-diphenyl-5-ferrocenoyl-6-phenyl-7-oxa-[2.2.1]bicycloheptane (13c): orange crystalline solid, mp 145–147 °C; ^{1}H NMR (CDCl₃) δ 3.71 (s, 5H), 3.90 (d, J = 5.3 Hz, 1H), 4.11 (m, 1H), 4.18 (d, J = 5.5 Hz, 1H), 4.24 (m, 1H), 4.39 (br s, 1H), 4.54 (br s, 1H), 6.49 (d, J = 7.1 Hz, 2H), 7.00–7.50 (m, 13H), 7.65 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.84 (dd, J_1 = 7.1 Hz, J_2 = 2.8 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H); IR (CHCl₃, 0.1 mm) ν 1657 cm⁻¹. Anal. Calcd for

$C_{39}H_{30}O_2Fe$: C, 79.87; H, 5.16; Fe, 9.52. Found: C, 79.86; H, 5.31; Fe, 9.55.

2,3-Benzo-1,4-diphenyl-6-benzoyl-5-ferrocenyl-7-oxa-[2.2.1]bicyclo-heptane (13d): orange-red crystalline solid, mp 147–149.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.96 (br s, 1H), 3.85 (s, 5H), 4.09 (br s, 1H), 4.12 (m, 1H), 4.38 (br s, 1H), 4.49 (t, $J = 1.9$ Hz, 1H), 4.60 (t, $J = 1.9$ Hz, 1H), 7.03–7.15 (m, 5H), 7.25 (m, 1H), 7.33 (m, 2H), 7.47 (m, 7H), 7.76 (m, 4H). Anal. Calcd for $C_{39}H_{30}O_2Fe$: C, 79.87; H, 5.16; Fe, 9.52. Found: C, 79.67; H, 5.22; Fe, 9.14.

2,3-Benzo-1,4-diphenyl-6-benzoyl-5-phenyl-7-oxa[2.2.1]-bicycloheptane (13e): white crystalline solid, mp 142–143 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 4.14 (d, $J = 5.5$ Hz, 1H), 4.66 (d, $J = 5.5$ Hz, 1H), 6.49 (dd, $J = 7.1$ Hz, $J = 1.4$ Hz, 2H), 7.07–7.68 (m, 22H). Anal. Calcd for $C_{35}H_{26}O_2$: C, 87.84; H, 5.48. Found: C, 87.78; H, 5.46.

2,3-Benzo-1,4-diphenyl-5-phenyl-6-[1-((η^6-phenyl)tri-carbonylchromio)-1-oxo]-7-oxa[2.2.1]bicycloheptane (13f): orange crystalline solid, mp 162–165 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 4.14 (d, $J = 5.5$ Hz, 1H), 4.24 (d, $J = 5.5$ Hz, 1H), 5.34 (t, $J = 6.0$ Hz, 1H), 5.42 (t, $J = 6.6$ Hz, 1H), 5.76 (d, $J = 6.0$ Hz, 1H), 5.87 (t, $J = 6.2$ Hz, 1H), 6.36 (d, $J = 6.2$ Hz, 1H), 6.48 (d, $J = 7.4$ Hz, 2H), 7.06–7.86 (m, 17H). Anal. Calcd for $C_{38}H_{26}O_5Cr$: C, 74.26; H, 4.26. Found: C, 73.92; H, 4.39.

2,3-Benzo-1,4-diphenyl-6-benzoyl-5-((η^6-phenyl)tricar-bonylchromio)-7-oxa[2.2.1]bicycloheptane (13g): yellow crystalline solid, mp 139–142 °C; ^{1}H NMR (CD$_3$COCD$_3$) δ 4.30 (d, $J = 7.2$ Hz, 1H), 4.36 (d, $J = 4.5$ Hz, 1H), 4.52 (d, $J = 4.5$ Hz, 1H), 5.33 (t, $J = 6.5$ Hz, 1H), 5.44 (d, $J = 7.2$ Hz, 1H), 5.53 (t, $J = 6.2$ Hz, 1H), 5.61 (t, $J = 6.1$ Hz, 1H), 7.14–7.62 (m, 15H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H). Anal. Calcd for $C_{38}H_{26}O_5Cr$: C, 74.26; H, 4.26. Found: C, 74.23; H, 4.29.

2,3-Benzo-1,4-diphenyl-5-ferrocenyl-6-nitro-7-oxa[2.2.1]-bicycloheptane (13h): brown crystalline solid, mp 175–177 °C; ^{1}H NMR (CDCl$_3$) δ 2.63 (br s, 1H), 4.06 (s, 5H), 3.98–4.13 (m, 3H), 4.34 (d, $J = 3.2$ Hz, 1H), 5.41 (d, $J = 3.4$ Hz, 1H), 6.98 (d, $J = 7.1$ Hz, 1H), 7.15 (t, $J = 6.5$ Hz, 1H), 7.25 (m, 1H), 7.38–7.55 (m, 7H), 7.64 (d, $J = 7.4$ Hz, 2H), 7.76 (d, $J = 7.4$ Hz, 2H). Anal. Calcd for $C_{32}H_{25}NO_3Fe$: C, 72.88; H, 4.78; N, 2.65; Fe, 10.59. Found: C, 72.85; H, 4.93; N, 2.46; Fe, 10.83.

Crystal Structure Analysis of $C_{39}H_{30}O_2Fe$ (12b). All measurements were made at 19 °C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å, and the crystal was a small yellow plate $0.28 \times 0.18 \times 0.02$ mm.

Crystal data: $C_{39}H_{30}Fe$, $M = 586.48$, orthorhombic, space group $P2_12_12_1$, $a = 10.150(2)$, $b = 14.508(2)$, and $c = 19.742(3)$ Å, $V = 2907.2(8)$ Å^3, $Z = 4$, $D_{calc} = 1.340$ g cm^{-3}, $\mu = 0.55$ mm^{-1}.

Measurements. Cell dimensions are based on the setting angles of 15 reflections with $3.6 \leq \theta$(Mo Kα) $\leq 15.4°$. Measurements for 3159 reflections with θ(Mo Kα) $\leq 23°$, $-1 \leq h \leq 12$, $-2 \leq k \leq 17$, $-2 \leq l \leq 23$ yielded 2919 unique intensities (R_{int} 0.045) of which 1744 had $I > 2\sigma(I)$.

Structure Analysis. The structure was refined using 2875 unique reflections with $I > -3\sigma(I)$ by full-matrix least-squares on F^2 with $w = 1/[\sigma^2(F^2) + a^2P^2]$ [$a = 0.041$, $P = (F_{obs} + 2F_{calc})/3$]. Refinement of 377 parameters (Table 6, supporting information), including an extinction coefficient of 0.0017(4), converged ($\Delta/\sigma < 0.42$) at $R[F, 2\sigma(I)] = 0.048$, $R_w(F^2,\text{all data}) = 0.119$, $S = 1.04$ with $|\Delta\rho| < 0.34$ e Å^{-3}. Calculations were performed on a DCS486 computer using SHELXL-93 and local programs.[24,25] Disordered ring f was modeled as two rigid pentagonal groups of carbon atoms with C site occupancies =

0.5 and C–C = 1.42 Å; five pairs of these disordered carbon atoms were each constrained to have similar U_{ij} parameters, and for one such pair a restraint to near isotropic behavior was necessary. The absolute configuration was confirmed by refinement of the Flack parameter[26] to $x = 0.03(4)$.

Crystal Structure Analysis of $C_{34}H_{28}O_2Fe$ (13b). Unless stated otherwise, techniques similar to those used for **12b** were employed. Measurements were made at 22 °C. The crystal was an orange prism $0.20 \times 0.20 \times 0.10$ mm.

Crystal data: $C_{34}H_{28}O_2Fe$, $M = 1048.89$, triclinic, space group $P1$, $a = 11.728(1)$, $b = 13.421(1)$, and $c = 17.619(1)$ Å, $\alpha = 78.183(5)$, $\beta = 70.709(5)$, and $\gamma = 86.780(6)°$, $V = 2561.9(3)$ Å^3, $Z = 4$, $D_{calc} = 1.359$ g cm^{-3}, $\mu = 0.62$ mm^{-1}.

Measurements. Cell dimensions are based on the setting angles of 25 reflections with $17.5 \leq \theta$(Mo Kα) $\leq 20.8°$. The intensities of 9450 reflections with θ(Mo K α) $\leq 25°$, $0 \leq h \leq 13$, $-15 \leq k \leq 15$, $-19 \leq l \leq 20$ were measured from $\omega/2\theta$ scans. Merging yielded 8974 unique intensities (R_{int} 0.026), and further calculations proceeded with 4915 unique reflections for which $I > 3\sigma(I)$.

Structure Analysis. The structure was solved by the heavy atom method and refined by full-matrix least-squares on F with $w = 1/\sigma^2(F)$. Anisotropic U_{ij} values were used for all non-H atoms. H atoms rode on parent C atoms with the constraints C–H = 0.96 Å and U(H) = $1.2U_{eq}$(C). The orientations of the methyl groups were obtained from a difference synthesis. Refinement of 667 parameters (Table 7, supporting information) converged ($\Delta/\sigma < 0.01$) at $R = 0.041$, $R_w = 0.041$, $S = 1.46$ with $|\Delta\rho| < 0.31$ e Å^{-3}. Calculations were performed on a VAX 4000/60 computer using the GX package.[24] Scattering factors and anomalous dispersion corrections were taken from ref 27.

Tables of atomic parameters and a complete geometry listing for **12b** and **13b** have been deposited with the Cambridge Crystallographic Data Centre.

Supporting Information Available: Tables of selected X-ray data for **12b** and **13b** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.

(25) Sheldrick, G. M. SHELXL-93. A program for refining crystal structures. University of Gottingen, Germany, 1993.

(26) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876. Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1985**, *A41*, 500.

(27) International Tables for X-ray Crystallography, Vol. IV; International Union of Crystallography: Kynoch, Birmingham, 1974; Tables 2.1B and 2.3.1.

(28) These coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.