Synthesis and Reactivity of Cross-Conjugated Polyenones with a Planar Chirality

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The complexes **6** are the first examples of a novel class of cross conjugated polyenones bearing a planar chirality introduced by an organometallic moiety. Their synthesis is described using, as a key intermediate, the easily accessible new phosphorane **9**. The free double bond of the selectively protected polyenes **6** reacts efficiently, although with low diastereoselectivities, in Diels−Alder or 1,3 dipolar cycloaddition reactions or with nucleophiles. Cyclopentyl radical also adds to **6**, and this is the first example of a radical reaction in the presence of carbonyliron complexes. Decomplexation of the various adducts leads, in good yields, to the corresponding polyfunctionalized free dienes, which can be of further synthetic use.

Cross-conjugated polyenones are very interesting derivatives from several viewpoints. Some of them have been isolated as bioactive compounds: clavuridenone (**1**)[1] and ptilodene (**2**),[2] for instance, are marine polyunsaturated fatty acid metabolites with antiinflammatory activity; melodienone (**3**) shows significant toxicity against human tumor cell lines.[3] Others, like damascenone (**4**) and *β*-damascone (**5**) are odoriferous compounds isolated from Bulgarian rose oil,[4] and they are very useful in perfumery (Figure 1). In addition, cross-conjugated polyenones are found in the framework of some synthetic dyes[5] and in photopolymerization initiator compositions[6] and are key structural fragments of annulenones.[7] Furthermore, they are versatile intermediates in organic synthesis, for instance, in the Nazarov cyclization,[8] in the synthesis of heterocycles,[9] or in tandem reactions.[10]

A number of methods are available for the synthesis of cross-conjugated polyenones. Aldol-type condensations are generally efficient for the preparation of annulenone's fragments.[11] Another route can be found in acylation reactions: the direct Friedel−Crafts acylation of alkenes

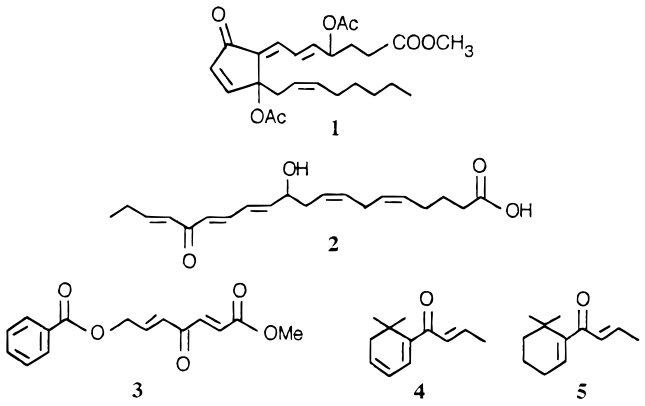

Figure 1.

with α,*β*-unsaturated acid halides in the presence of aluminum chloride usually leads to mixtures of products,[12] while the reaction of α,*β*-unsaturated acid chlorides with vinylic organometallic derivatives (Hg, Cu, Sn)[13] in the presence of Lewis acids is cleaner and gives moderate to excellent yields of products. Other possibilities are carbonylations,[14] Horner−Wittig−Emmons reactions,[15] or isomerizations of triple bonds.[16]

In order to extend the synthetic potential of such derivatives, it appears interesting to first provide selec-

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(1) Kobayashi, M.; Yasuzawa, T.; Yoshihara, M.; Akutsu, H.; Kyogoku, Y.; Kitawaga, I. *Tetrahedron Lett.* **1982**, *23*(50), 5331−5334. Kikuchi, H.; Tsukitani, Y. *Tetrahedron Lett.* **1982**, *23*(49), 5171−5174.

(2) Lopez, A; Gerwick W. H. *Tetrahedron Lett.* **1988**, *29*(13), 1505−1506.

(3) Jung, J. H.; Pummangura, S.; Chaichantipyuth, C.; Patarapanich, C.; Fanwick, P. E.; Chang, C.-J.; Mc Laughlin, J. L. *Tetrahedron* **1990**, *46*, 5043−5054.

(4) Demole, E.; Enggist, P.; Saüberli, U.; Stoll, M. *Helv. Chim. Acta* **1977**, *53*(3), 541−551.

(5) Venkataraman, K., Ed. *The Chemistry of Synthetic Dyes*; Academic Press: New York, 1971; Vol. 4.

(6) Goto, Y.; Nakayama, M. Nippon Oils and Fats Co, Ltd. Japan Kokai Tokkyo Koho JP62,174,203[87,174,203] (C1008F2/50), 1987; App 86/14,740, 1986.

(7) See, for instance: Higuchi, H.; Kondo, S.; Watanabe, Y.; Ojima, J.; Yamamoto, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, *14*, 1957−1968 and references cited therein.

(8) Habermas, K. L.; Denmark, S. E.; Jones, T. K. *Org. React. (New York)* **1994**, *45*, 1−158.

(9) (a) Hermann, K.; Dreiding, A. S. *Helv. Chim. Acta* **1976**, *59*, 626−642. (b) Jakubcová, M.; Végh, D.; Kozisek, J.; Dvorsky, A. *Synth. Commun.* **1994**, *24*, 1333−1338.

(10) (a) Winkler, J. D.; Kim, S.; Condroski, K. R.; Asensio, A.; Houk, K. N. *J. Org. Chem.* **1994**, *59*, 6879−6881. (b) Winkler, J. D.; Kim, H. S.; Kim, S. *Tetrahedron Lett.* **1995**, *36*, 687−690.

(11) See, for instance: Nakatsuji, S.; Akiyama, S.; Nakagawa, M. *Tetrahedron Lett.* **1977**, *42*, 3723−3726. Higuchi, H.; Asano, K.; Hiraiwa, N.; Kondo, S.; Ojima, J.; Yamamoto, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1579−1587.

(12) Hacini, S.; Pardo, R.; Santelli, M. *Tetrahedron Lett.* **1979**, *47*, 4553−4556.

(13) (a) Larock, R. C.; Bernhardt, J. C. *Tetrahedron Lett.* **1976**, *36*, 3097−3100. (b) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696−3702. Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1986**, *42*(5), 1369−1380. (c) Parrain, J. L.; Beaudet, I.; Duchêne, A.; Watrelot, S.; Quintard, J. P. **1993**, *34*(34), 5445−5448.

(14) (a) Larock, R. C.; Hershberger, S. S. *J. Org. Chem.* **1980**, *45*, 3840−3846. (b) Goure, W. F.; Wright, M. E.; Davis, P. D.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417−6422.

(15) Motoyoshiya, J.; Miyajima, M.; Hirakawa, K.; Kakurai, T. *J. Org. Chem.* **1985**, *50*, 1326−1327.

(16) Guo, C.; Lu, X. *Tetrahedron Lett.* **1991**, *32*(51), 7549−7552. Guo, C.; Lu, X. *Synlett* **1992**, 405−406.

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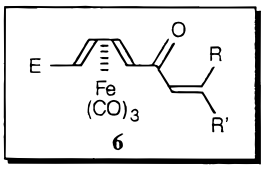
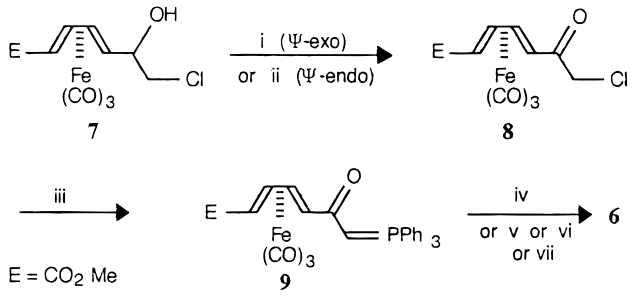


E = -CO_2Me a: R = R'= CO_2Et; b: R = H, R'= COPh;
c: R= D, R'= COPh; d: R= H, R'= CO_2Me

Figure 2.

Scheme 1[a]



6a: R= R'= CO_2Et; **6b**: R= H, R'= COPh;
6c: R= D, R'= COPh; **6d**: R= H, R'= CO_2Me

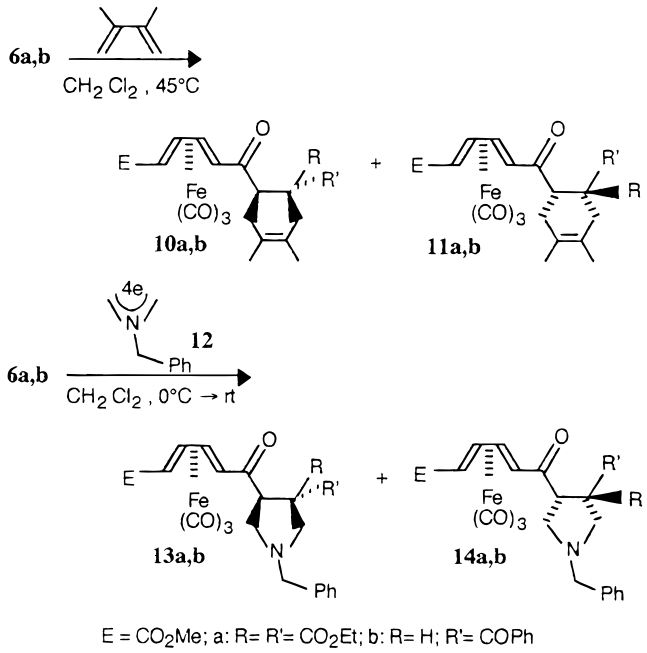
[a] Reagents and conditions: (i) Swern, (66%); (ii) MnO_2, CH_2Cl_2, rt, 2 h (89%); (iii) PPh_3, $CHCl_3$, 75 °C, 72 h and then Et_3N (50%); (iv) $(EtO_2C)_2CO$, toluene, 75 °C, 3 h (98%); (v) PhCOCHO, H_2O, toluene, molecular sieves, 75 °C, 2 h (83%); (vi) PhCOCDO, toluene, 75 °C, 1 h (90%); (vi) MeO_2C−CHO, toluene, 75 °C, 3 h (54%).

tive and temporary protection for one of the two polyenic chains and second introduce chirality in the molecule. Both aspects can be solved by the use of organometallic complexes. In this paper, we want to describe the synthesis and studies on the reactivity of new complexes of type **6** (Figure 2); to the best of our knowledge, *these are the first examples of cross conjugated polyenones bearing a planar chirality*.[17] The versatile key intermediate for the preparation of **6** is the organometallic phosphorane **9**.

Complexes **6** were prepared by a three-step sequence starting from the readily available chlorhydrins **7** (Scheme 1).[18] In agreement with previous results,[19] oxidation is compatible with the organometallic moiety, but it is interesting to note that, for the synthesis of **8**, the best yields were obtained using Swern oxidation in the case of the more polar Ψ-exo[20] complex, while MnO_2 proved to be more efficient for the Ψ-endo derivative.

Reaction of chloro ketone **8** with PPh_3 followed by basic treatment yielded the stable, crystalline, phosphorane **9** (50% yield). Wittig reactions with diethyl mesoxalate, or with phenylglyoxal monohydrate, gave the desired model compounds **6a** and **6b** in high yields. The deuterated complex **6c** was necessary to study the regioselectivity of the additions; it was obtained by reaction of **9** with deuterated phenylglyoxal, the latter being prepared from acetophenone-d_3 by oxidation with SeO_2. **6d** was prepared similarly from methyl glyoxylate.

Scheme 2



E = CO_2Me; a: R= R'= CO_2Et; b: R= H; R'= COPh

Reactivity in cycloaddition reactions was studied first (Scheme 2). Diels−Alder reactions with an excess of 2,3-dimethylbutadiene at 45 °C gave good yields of a mixture of the two adducts, which could be easily separated by silica gel chromatography. The diastereoselectivity of these reactions (**10a**/**11a** = 55/45 and **10b**/**11b** = 64/36) was determined by high-field NMR studies on the crude reaction mixtures, and the stereochemistry of the cycloadducts was unambiguously established by X-ray crystallography[21] of **10a** and **11b** (Figure 3). In each case the major diastereoisomer corresponds to a reaction of the diene on the face anti to the bulky $Fe(CO)_3$ group on the conformer represented for **6**.

In the same manner, 1,3-dipolar addition with azomethine ylide **12** generated by the method of Achiwa[22] led to a mixture of two diastereoisomers. While the adducts **13b** and **14b** were easily separated by chromatography, pyrrolidines **13a** and **14a** from **6a** obtained as a 70/30 mixture could not be separated. The stereochemistry of these cycloadducts was tentatively assigned as indicated by analogy with the preceding Diels−Alder reactions; it is also in agreement with the other types of addition, *vide infra*.

Complexes **6a,b** also reacted with nucleophiles, and parathiocresol, for instance, added readily to **6a** at room temperature to give a (63:37) mixture of two adducts (Scheme 3); they were separated by chromatography, and the stereochemistry of the major isomer **15a** was unambiguously established by X-ray crystallography analysis (Figure 4). The free double bond in the selectively protected polyenone **6a** also reacted with the cyclopentyl radical generated by the method of Chatgiglialoglu[23] to

(17) An interesting type of biscomplexed polyene has been reported very recently: Nakanishi, S.; Kumeta, K.; Terada, K. *Synthesis* **1995**, 33−35.

(18) Lellouche, J. P.; Bulot, E.; Beaucourt, J. P.; Martelli, J.; Grée, R. *J. Organomet. Chem.* **1988**, *342*, C21−C25.

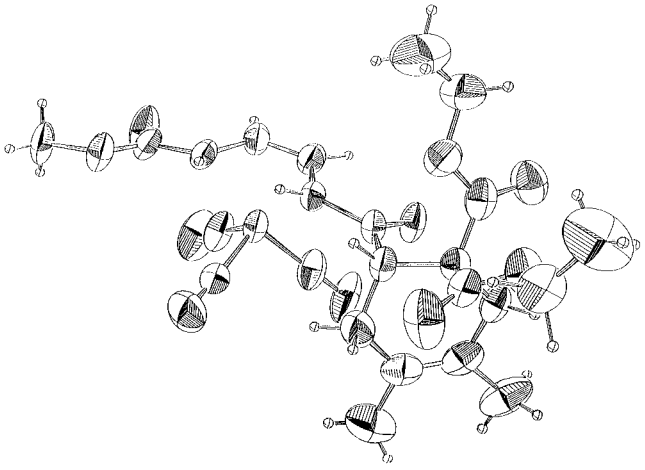
(19) (a) Grée, R. *Synthesis* **1989**, 341−355. (b) Grée, R.; Lellouche, J. P. *Advances in Metal Organic Chemistry*, Liebeskind, L. S., Ed.; JAI Press Ltd.: Greenwich, Vol. 4, in press.

(20) For an explanation of the Ψ_{exo}/Ψ_{endo} nomenclature see: Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058−3064.

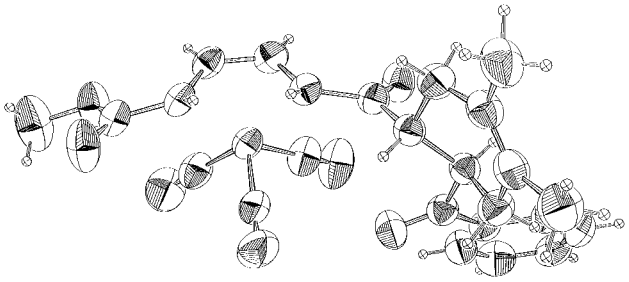
(21) The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(22) Terao, Y.; Kotaki, H.; Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1985**, *33(7)*, 2762−2766.

(23) (a) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641−3642. (b) Ballestri, M.; Chatgilialoglu, C. *J. Org. Chem.* **1991**, *56*, 678−683.



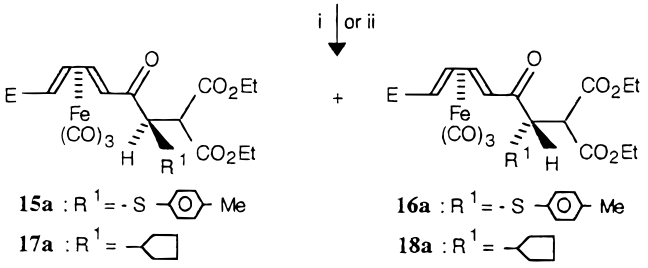
10a



11b

Figure 3.

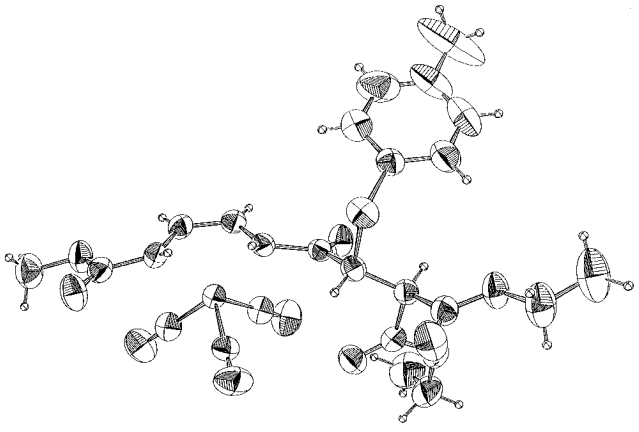
Scheme 3[a]



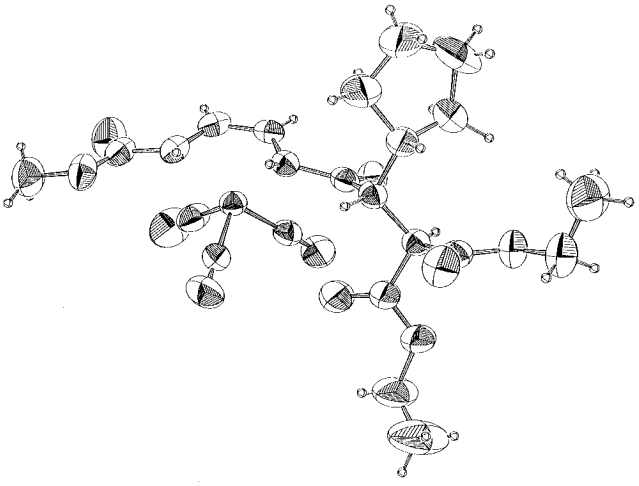
[a] Reagents and conditions: (i) *p*-thiocresol, THF, 0 °C → rt, 4 h, **15a** (44%) and **16a** (25%); (ii) cyclopentyl bromide, AIBN, toluene, 90 °C and then $(Me_3Si)_3SiH$ in toluene via syringe pump over 3 h, **17a** (52%) and **18a** (20%).

give a mixture of diastereoisomeric adducts **17a, 18a** readily separated by chromatography (Scheme 3). The stereochemistry of the major isomer **17a** was also established by X-ray crystallography (Figure 4). It is important to note that both adducts are again in agreement with an addition anti to the bulky $Fe(CO)_3$ group, in the conformation indicated for **6a** (Figure 2).

The same reactions carried out in parallel for **6b** led to four adducts reflecting the two possible sites of addition (Scheme 4). Derivatives corresponding to an addition close to the organometallic complex are the major adducts (70% for nucleophilic addition and 56% for the radical type reaction), and they were isolated in stereoisomerically pure form. The adducts corresponding to the addition vicinal to the benzoyl group were isolated as a 1:1 mixture of epimers. The attribution was particularly difficult, using NMR data, because both types of structures were almost identical: in the



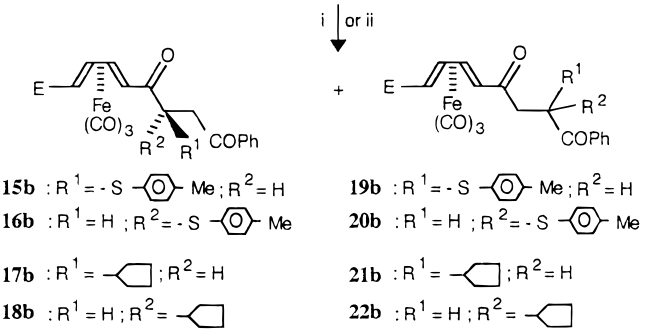
15a



17a

Figure 4.

Scheme 4[a]

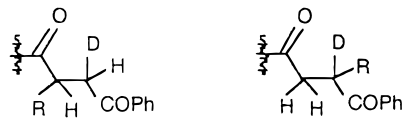


[a] Reagents and conditions: (i) *p*-thiocresol, THF, 0 °C → rt, 4 h, **15b** (31%), **16b** (28%), **19b** (12.5%), and **20b** (12.5%); (ii) cyclopentyl bromide, AIBN, toluene, 90 °C and then $(Me_3Si)_3SiH$ in toluene via syringe pump over 5 h, **17b** (19%), **18b** (14%), **21b** (13%), and **22b** (13%).

case of the addition close to the organometallic complex, the skeleton was $-COCHRCH_2CO-$, while it became $-COCH_2CHRCO-$ in the case of the addition vicinal to the benzoyl group.

In order to unambiguously solve this problem, deuterated analogs were synthetized from **6c**. The attribution of the structures was achieved using ^{13}C NMR experiments and especially DEPT spectra: in the case of type **A** structures, the DEPT spectrum showed one CH and one CHD signal, while it showed one CH_2 and one CD

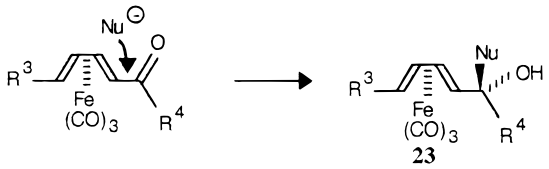
Scheme 5



Structure A Structure B

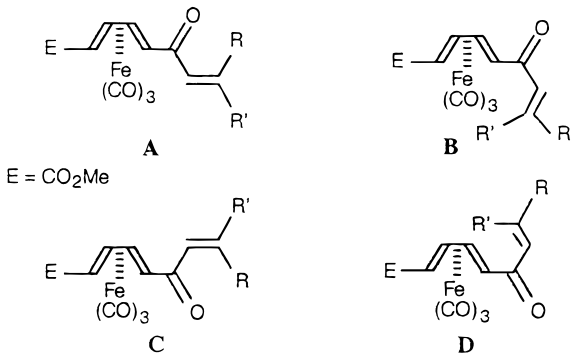
15c, 16c, 17c, 18c **19c, 20c, 21c, 22c**

Scheme 6



23

Scheme 7



A **B**

E = CO_2Me

C **D**

signal for type **B** structures (Scheme 5). These ^{13}C NMR experiments, done for each of the isolated deuterated adducts, permitted the attribution of their structures and thus also for corresponding products derived from **6b**. The stereochemistry of the major isomers was tentatively assigned in analogy with preceding results.

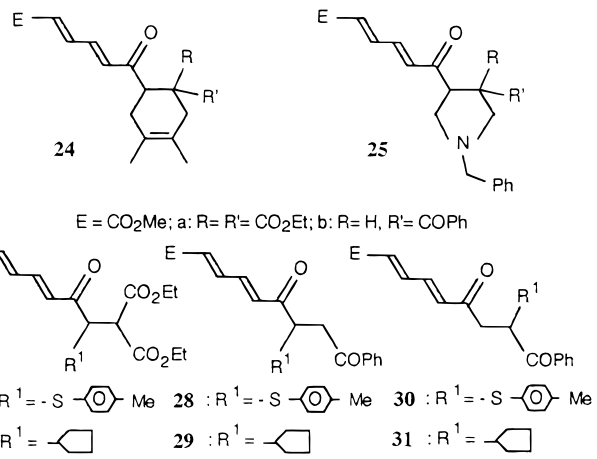
It is well recognized that addition reactions on a ketone vicinal to a diene−tricarbonyliron complex lead exclusively to the Ψ-endo derivative *via* an addition (anti to the bulky iron carbonyl unit) on the cisoid conformer (Scheme 6).[19]

This is indeed the case with these new type **6** derivatives since the reduction of **6d**, used as a model, gives exclusively the Ψ-endo derivative **23d** ($R^3 = CO_2Me$; Nu = H; R^4 = CH=$CHCO_2Me$). Thus, from the four conformers **A** to **D** theoretically possible for **6** (Scheme 7), only conformations **A** and **B** should probably be considered. Then, the low diastereoselectivities may reflect the relatively low energy difference between the cisoid conformation **A** and the transoid **B**. The approach of the reagent would again occur exclusively from the face opposite the metal in both conformations to give the previously described mixtures of diastereoisomers. The major adducts come from addition on type **A** conformers.

The decomplexation of all these adducts under usual conditions (Ce^{4+}, MeOH, −15 °C) gave the corresponding racemic derivatives in good yields (Scheme 8). The diene units of these new compounds can be further utilized in synthesis as already demonstrated in a related system.[19]

In conclusion, it is possible using this strategy to build a novel class of cross-conjugated polyenones bearing an organometallic protective group. Since the starting complex is easily resolved,[24] these derivatives should be accessible in optically pure form. Various types of

Scheme 8



24 **25**

E = CO_2Me; a: R= R'= CO_2Et; b: R= H, R'= COPh

26 : R^1 = -S-Ph-Me **28** : R^1 = -S-Ph-Me **30** : R^1 = -S-Ph-Me

27 : R^1 = **29** : R^1 = **31** : R^1 =

reactions are possible, leading to polyfunctionalized molecules of interest, for instance, in the total synthesis of complex natural products and structural analogs. *Furthermore, to the best of our knowledge, we have described here the first examples of radical type reactions in the presence of carbonyliron complexes.* It indicates that it should be possible to combine the synthetic potentialities of both the organometallic complexes and the recently developped organic chemistry of radicals.[25]

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Nicolet 205. ^1H NMR spectra were recorded at 300 and 400 MHz and ^{13}C NMR at 100.6 and 22.5 MHz. Elemental analyses were performed by the "Service de microanalyses" (IdRS Suresnes and ICSN Gif sur Yvette). All separations were carried out under flash chromatographic conditions on Merck silica gel Geduran Si60 (230−240 mesh) using, as eluent, mixtures of ether and low-boiling (≤60 °C) petroleum ether. CH_2Cl_2 was distilled on P_2O_5, toluene on $CaCl_2$, and THF on natrium/benzophenone complex.

Chloro Ketone 8. Method A. To a solution of the endo chlorohydrin **7** (2.1g; 6.35 mmol) in CH_2Cl_2 (50 mL) was added freshly prepared MnO_2 (5.5 g; 10 equiv). The reaction mixture was stirred at room temperature for 2 h. The dark solution was filtered on celite and the solvent removed *in vacuo*, giving a crude oil that was purified by chromatography on silica gel (elution with ether/petroleum ether 1/1). Pure product **8** was obtained as a yellow oil (1.85 g; 89%).

Method B. To a well-stirred solution of $(COCl)_2$ (3.5 mL) in anhydrous CH_2Cl_2 (17 mL) was added slowly at −70 °C a solution of DMSO (4.6 mL) in anhydrous CH_2Cl_2 (12 mL). The reaction mixture was stirred at −70 °C for 20 min, and then a solution of the exo chlorohydrin **7** (2.9 g; 8.77 mmol) in anhydrous CH_2Cl_2 (17 mL) was added dropwise at −70 °C. The resulting mixture was stirred for 30 min at −70 °C before Et_3N (5.7 mL) was slowly added. The solution was stirred for 30 min at −70 °C and then allowed to warm to −30 °C, quenched with saturated aqueous NH_4Cl, and extracted with two portions of ether. The combined organic extracts were washed with water, dried ($MgSO_4$), and concentrated *in vacuo* to give a crude oil that was purified by chromatography on silica gel (elution with ether/petroleum ether 3/7). Pure product **8** was obtained as a yellow solid (1.9 g; 66%).

8. Mp: 48 °C (from ether). ^1H NMR (400 MHz; C_6D_6): δ 1.15 (d, J = 8.1 Hz, 1H, H_2 or H_5); 1.18 (d, J = 8.1 Hz, 1H, H_2 or H_5); 3.39 (s, 3H, CO_2Me); 3.41 (s, 2H, CH_2Cl); 5.50 (dd, J = 7.9, 5.2 Hz, 1H, H_3 or H_4); 5.55 (dd, J = 7.9, 5.2 Hz, 1H, H_3 or

(24) Monpert, A.; Martelli, J.; Grée, R.; Carrié, R. *Tetrahedron Lett.* **1981**, *22*, 1961−1964.

(25) Giese, B. *Radicals in Organic Synthesis*; Pergamon Press: New York, 1986.

H_4). ^{13}C NMR (100 MHz; $CDCl_3$): δ 47.3 and 49.6 (C_2 and C_5); 47.4 (CH_2Cl); 52.1 (CO_2Me); 85.3 and 87.9 (C_3 and C_4); 171.7 (C_1); 198.4 (C_6). IR (Nujol): 1675 (ketone); 1712 (ester); 2006 and 2075 ($Fe(CO)_3$). Anal. Calcd for $C_{11}H_9ClFeO_6$: C, 46.37; H, 3.24. Found: C, 46.18; H, 3.32.

Keto Phosphorane 9. In a dry three-necked round-bottom flask fitted with a reflux condenser were placed chloro ketone **8** (1.79 g; 5.45 mmol), freshly distilled chloroform (140 mL), and anhydrous potassium carbonate (1.4 g). Argon was bubbled in the mixture for 20 min, then anhydrous triphenylphosphine (1.37 g; 0.96 equiv) was added and the reaction mixture was refluxed for 3 days under argon. After removal of chloroform *in vacuo*, the crude oil was rapidly filtered through silica gel (elution with ether + 833 μL (1.1 equiv) of Et_3N). The solvents were removed *in vacuo*, and the crude product was purified by chromatography on silica gel (elution with ether/petroleum ether 1/1) to yield pure keto phosphorane as an orange solid (1.55 g; 51%) and chloro ketone **8** (300 mg), which can be recycled. **9**. Mp: 166−168 °C (from ether). ^1H NMR (400 MHz; $CDCl_3$): δ 1.15 (d, J = 8.3 Hz, 1H, H_2 or H_5); 1.98 (d, J = 8.5 Hz, 1H, H_2 or H_5); 3.66 (s, 3H, CO_2Me); 3.91 (d, J_{HP} = 24.5 Hz, 1H, H_7); 5.85 (dd, J = 8.0, 5.4 Hz, 1H, H_3 or H_4); 6.00 (dd, J = 8.4, 5.2 Hz, 1H, H_3 or H_4); 7.45 (6H, arom); 7.55 (3H, arom); 7.60−7.65 (6H, arom). ^{13}C NMR (100 MHz; $CDCl_3$): δ 45.4 (C_2); 51.6 (CO_2Me); 53.4 (d, J_{CP} = 110.9 Hz, C_7); 62.5 (d, J_{CP} = 20.3 Hz, C_5); 83.7 (C_3); 85.6 (d, J_{CP} = 3 Hz, C_4); 126.8 (d, J_{CP} = 90.5 Hz, C_{ipso}); 128.8 (d, J_{CP} = 12.2 Hz, C_{ortho}); 132.1 (d, J_{CP} = 3.1 Hz, C_{para}); 133.0 (d, J_{CP} = 10.2 Hz, C_{meta}); 173.0 (C_1); 185.0 (d, J_{CP} = 3.0 Hz, C_6). ^{31}P NMR (162 MHz; $CDCl_3$): δ 15.16. IR (Nujol): 1627 (ketone); 1708 (ester); 1970, 2001, and 2057 ($Fe(CO)_3$). Anal. Calcd for $C_{29}H_{23}FeO_6P$: C, 62.84; H, 4.18. Found: C, 62.59; H, 4.39.

Olefin 6a. A solution of keto phosphorane **9** (750 mg; 1.37 mmol) and diethyl ketomalonate (206 μL; 1 equiv) in toluene (40 mL) was stirred under N_2 at 75 °C for 3 h. The reaction mixture was filtered, and toluene was removed *in vacuo*. Chromatography of the crude oil (elution with ether/petroleum ether 4/6) yielded **6a** (605 mg; 98%) as an orange solid. **6a**. Mp: 93 °C (from ether). R_f = 0.36 (E/PE 1/1). ^1H NMR (400 MHz, C_6D_6): δ 0.69 (d, J = 8.1 Hz, 1H, H_2 or H_5); 0.86 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.04 (d, J = 8.6 Hz, 1H, H_2 or H_5); 1.12 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 3.29 (s, 3H, CO_2Me); 3.91 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 4.30 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 5.38 (dd, J = 8.1, 5.6 Hz, 1H, H_3 or H_4); 5.44 (dd, J = 8.1, 5.6 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, C_6D_6): δ 14.5 and 14.6 ($CO_2CH_2CH_3$); 48.3 and 55.9 (C_2 and C_5); 51.2 (CO_2Me); 62.5 and 62.9 ($CO_2CH_2CH_3$); 85.5 and 88.5 (C_3 and C_4); 135.7 (C_7); 137.8 (C_8); 163.8, 165.3, and 172.1 (CO_2-Et and C_1); 192.3 (C_6). IR (Nujol): 1622 (alkene); 1670 (ketone); 1718 and 1742 (ester); 2013 and 2073 ($Fe(CO)_3$). Anal. Calcd for $C_{18}H_{18}FeO_{10}$: C, 48.02, H, 4.03. Found: C, 48.10, H, 4.08.

Olefin 6b. A solution of keto phosphorane **9** (500 mg; 0.90 mmol) and phenylglyoxal monohydrate (165 mg; 1.2 equiv) in toluene (20 mL) was stirred in the presence of molecular sieves (4 Å) under N_2 at 75 °C for 2 h. The reaction mixture was filtered, and toluene was removed *in vacuo*. Chromatography of the crude oil (elution with ether/petroleum ether 4/6) allowed the separation of **6b** from a small amount of its *Z*-isomer. **6b** (305 mg; 83%) is a yellow solid. Mp: 136−137 °C (from ether). R_f = 0.42 (E/PE 1/1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, J = 8.2 Hz, 1H, H_2 or H_5); 1.73 (d, J = 8.1 Hz, 1H, H_2 or H_5); 3.73 (s, 3H, CO_2Me); 6.11 (dd, J = 8.2, 5.2 Hz, 1H, H_3 or H_4); 6.17 (dd, J = 8.1, 5.8 Hz, 1H, H_3 or H_4); 7.16 (d, J = 15.3 Hz, 1H, H_7); 7.83 (d, J = 15.3 Hz, 1H, H_8); 7.52 (2H, arom); 7.63 (1H, arom); 8.02 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.5 and 54.7 (C_2 and C_5); 52.0 (CO_2Me); 85.2 and 88.0 (C_3 and C_4); 128.8, 128.9, 133.9, and 137.8 (*C*H arom and C_7); 133.1 (C_8); 136.8 (*C* arom); 171.7 (C_1); 189.9 and 193.7 (C_6 and C_9). IR (Nujol): 1608 (arom and alkene); 1641 and 1661 (ketone); 1713 (ester); 1991 and 2072 ($Fe(CO)_3$). Anal. Calcd for $C_{19}H_{14}FeO_7$: C, 55.64, H, 3.44. Found: C, 55.75, H, 3.61.

Z-Isomer (8%). R_f = 0.24 (E/PE 1/1). ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (d, J = 7.1 Hz, 1H, H_2 or H_5); 1.53 (d, J = 7.1 Hz, 1H, H_2 or H_5); 3.70 (s, 3H, CO_2Me); 5.96−6.02 (m, 2H, H_3 and H_4); 6.56 (d, J = 11.7 Hz, 1H, H_7 or H_8); 6.82 (d, J = 11.7 Hz, 1H, H_7 or H_8); 7.45 (2H, arom); 7.55 (1H, arom); 7.91 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.2 and 54.4 (C_2 and C_5); 52.0 (CO_2Me); 85.0 and 87.5 (C_3 and C_4); 128.5, 128.7, 133.5, 133.6, 135.7, and 138.5 (C_7 and C_8 and arom); 171.8 (C_1); 194.1 and 194.3 (C_6 and C_9). IR (Nujol): 1582, 1602, and 1610 (arom and alkene); 1663 (ketone); 1714 (ester); 2001 and 2068 ($Fe(CO)_3$).

Deuterated Phenylglyoxal. In a two-necked round-bottom flask fitted with a reflux condenser were introduced dioxane (50 mL), water (1 mL), and SeO_2 (1.82 g; 2.7 equiv). The reaction mixture was heated at 65 °C until complete dissolution of SeO_2, and then acetophenone-d_3 (700 μL; 5.99 mmol) was added and the mixture refluxed for 48 h. After rapid filtration on silica gel and removal of the solvents, the crude product was purified by chromatography on silica gel (elution with ether/petroleum ether 3/7), yielding deuterated phenylglyoxal as a white solid (800 mg; quant). The NMR spectra were similar to those of commercial phenylglyoxal monohydrate, except for the disappearance of the singlet at 9.67 ppm (*CH*O → *CD*O) for the ^1H NMR spectrum and the weakness of the signal at 87.1 ppm (*C*HO,H_2O → *C*DO) for the ^{13}C NMR spectrum.

Olefin 6c. A solution of keto phosphorane **9** (150 mg; 0.27 mmol) and deuterated phenylglyoxal (42 mg; 1 equiv) in toluene (8 mL) was stirred under N_2 at 75 °C for 1 h. Toluene was removed *in vacuo*, and chromatography of the crude oil (elution with ether/petroleum ether 4/6) yielded **6c** (65 mg; 90%) as a yellow solid. NMR spectra were similar to those of **6b**, except for the ^1H NMR spectrum, where the doublet at 7.16 ppm was simplified into a singlet (H_7) and the doublet at 7.83 ppm (H_8 → D) disappeared, and for the ^{13}C NMR spectrum, where a triplet appeared at 133.1 ppm instead of a singlet (C_8).

Olefin 6d. A solution of keto phosphorane **9** (740 mg; 1.33 mmol) and freshly distilled methyl glyoxylate (400 mg; 1.3 equiv) in toluene (20 mL) was stirred under N_2 at 75 °C for 3 h. The reaction mixture was filtered, and toluene was removed *in vacuo*. Chromatography of the crude oil (elution with ether/petroleum ether 4/6) allowed the separation of **6d** from its *Z*-isomer. **6d** (260 mg; 54%) is an orange solid. Mp: 151 °C (from ether). R_f = 0.38 (E/PE 1/1). ^1H NMR (400 MHz, C_6D_6): δ 0.86 (d, J = 7.9 Hz, 1H, H_2 or H_5); 0.90 (d, J = 8.1 Hz, 1H, H_2 or H_5); 3.30 (s, 3H, CO_2Me); 3.31 (s, 3H, CO_2Me); 5.46 (dd, J = 7.8, 5.1 Hz, 1H, H_3 or H_4); 5.54 (dd, J = 7.8, 5.6 Hz, 1H, H_3 or H_4); 6.78 (d, J = 15.8 Hz, 1H, H_7 or H_8); 7.02 (d, J = 15.8 Hz, 1H, H_7 or H_8). ^{13}C NMR (100 MHz, C_6D_6): δ 48.3 and 55.1 (C_2 and C_5); 52.2 and 52.3 (CO_2Me); 85.8 and 88.5 (C_3 and C_4); 130.7 and 130.1 (C_7 and C_8); 166.4 and 172.1 (C_1 and C_9); 193.0 (C_6). IR (Nujol): 1627 (alkene); 1671 (ketone); 1702 and 1721 (ester); 2006, 2018, and 2075 (Fe-$(CO)_3$). Anal. Calcd for $C_{14}H_{12}FeO_8$: C, 46.18, H, 3.32. Found: C, 46.37, H, 3.24.

Z-isomer (21%). Mp: 76 °C (from ether). R_f = 0.21 (E/PE 1/1). ^1H NMR (400 MHz, C_6D_6): δ 1.08 (d, J = 8.1 Hz, 2H, H_2 and H_5); 3.31 (s, 3H, CO_2Me); 3.35 (s, 3H, CO_2Me); 5.49 (dd, J = 8.1, 5.1 Hz, 1H, H_3 or H_4); 5.62 (dd, J = 8.1, 5.6 Hz, 1H, H_3 or H_4); 5.66 (d, J = 12.0 Hz, 1H, H_7 or H_8); 5.82 (d, J = 12.0 Hz, 1H, H_7 or H_8). ^{13}C NMR (100 MHz, C_6D_6): δ 48.0 and 55.2 (C_2 and C_5); 52.1 and 52.2 (CO_2Me); 85.8 and 88.0 (C_3 and C_4); 127.1 and 139.9 (C_7 and C_8); 166.4 and 172.2 (C_1 and C_9); 196.0 (C_6); 205.6, 206.1, and 206.6 ($Fe(CO)_3$). IR (Nujol): 1618 (alkene); 1668 (ketone); 1704 and 1724 (ester); 2003 and 2072 ($Fe(CO)_3$).

Cycloaddition with 2,3-Dimethyl-1,3-butadiene: from 6a. A solution of olefin **6a** (140 mg; 0.31 mmol) and dimethylbutadiene (1 mL) in CH_2Cl_2 (2 mL) was heated at 45 °C for 40 h. The reaction mixture was evaporated, and chromatography of the residual oil (elution with ether/petroleum ether 2/8) allowed the separation of the two isomers **10a** and **11a** (93%; **10a**/**11a** = 55/45).

Isomer 10a. Mp: 108 °C (from ether). R_f = 0.57 (E/PE 1/1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.23 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.34 (d, J = 7.3 Hz, 1H, H_2 or H_5); 1.56 (d, J = 7.4 Hz, 1H, H_2 or H_5); 1.57 (s, 3H, *Me*); 1.63 (s, 3H, *Me*); 2.18 (m, 1H, H_{12}); 2.49 (m, 1H, H_{12}); 2.63 (d, J = 16.9 Hz, 1H, H_9); 2.89 (d, J = 17.3 Hz,

1H, H_9); 3.49 (dd, J = 7.7, 4.4 Hz, 1H, H_7) 3.70 (s, 3H, CO_2Me); 4.07−4.23 (m, 4H, $CO_2CH_2CH_3$); 5.93−6.01 (m, 2H, H_3 and H_4). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9 ($CO_2CH_2CH_3$); 18.7 and 18.9 (Me); 31.8 and 35.1 (CH_2); 46.5 and 53.2 (C_2 and C_5); 48.6 (C_7); 51.8 (CO_2Me); 55.5 (C_8); 61.4 and 62.6 ($CO_2CH_2CH_3$); 85.9 and 86.5 (C_3 and C_4); 121.4 and 124.6 (Me*C*=*C*Me); 169.8, 170.6, and 172.0 (C_1 and CO_2Et); 203.8 (C_6). IR (Nujol): 1668 (alkene), 1719 (broad, ketone and ester), 2001, 2022 and 2075 ($Fe(CO)_3$). Anal. Calcd for $C_{24}H_{28}FeO_{10}$: C, 54.15; H, 5.30. Found: C, 54.08; H, 5.30.

Isomer 11a. Mp: 114 °C (from ether). R_f = 0.41 (E/PE 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.23 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.33 (d, J = 8.4 Hz, 1H, H_2 or H_5); 1.56 (d, J = 8.1 Hz, 1H, H_2 or H_5); 1.63 (s, 3H, *Me*); 1.66 (s, 3H, *Me*); 2.40 (broad dd, J = 17.5, 14.0 Hz, 1H, H_{12}); 2.52 (broad dd, J = 17.8, 7.2 Hz, 1H, H_{12}); 2.58 (d, J = 16.9 Hz, 1H, H_9); 2.75 (d, J = 17.3 Hz, 1H, H_9); 3.48 (dd, J = 14.0, 7.0 Hz, 1H, H_7); 3.71 (s, 3H, CO_2Me); 4.11−4.21 (m, 4H, $CO_2CH_2CH_3$); 5.93−6.06 (m, 2H, H_3 and H_4). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0 ($CO_2CH_2CH_3$); 18.6 and 18.9 (Me); 32.7 and 35.6 (CH_2); 46.7 and 52.9 (C_2 and C_5); 49.6 (C_7); 51.9 (CO_2Me); 55.9 (C_8); 61.3 and 61.7 ($CO_2CH_2CH_3$); 86.2 and 87.3 (C_3 and C_4); 121.6 and 124.7 (Me*C*=*C*Me); 170.0, 170.9, and 171.9 (C_1 and CO_2Et); 204.8 (C_6). IR (Nujol): 1663 (alkene), 1719 (ketone), 1756 (ester), 1997 and 2065 ($Fe(CO)_3$). Anal. Calcd for $C_{24}H_{28}FeO_{10}$: C, 54.15; H, 5.30. Found: C, 53.82; H, 5.35.

From 6b. A solution of olefin **6b** (200 mg; 0.49 mmol) and dimethylbutadiene (2 mL) in CH_2Cl_2 (4 mL) was heated at 45 °C for 4 h. The reaction mixture was evaporated, and chromatography of the residual oil (elution with ether/petroleum ether 2/8) allowed the separation of the two isomers **10b** and **11b** (quant; **10b**/**11b** = 64/36).

Isomer 10b. Mp: 132 °C (from ether). R_f = 0.56 (E/PE 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (d, J = 7.5 Hz, 1H, H_2 or H_5); 1.60 (d, J = 8.0 Hz, 1H, H_2 or H_5); 1.62 (s, 3H, *Me*); 1.66 (s, 3H, *Me*); 2.06 (m, 2H, CH_2); 2.29 (broad dd, J = 15.9, 5.2 Hz, 2H, CH_2); 3.22 (td, J = 11.4, 5.2 Hz, 1H, H_7); 3.70 (s, 3H, CO_2Me); 3.86 (td, J = 11.3, 5.5 Hz, 1H, H_8); 5.90 (ddd, J = 8.1, 5.5, 0.7 Hz, 1H, H_4); 5.96 (dd, J = 8.1, 5.2 Hz, 1H, H_3); 7.43 (2H, arom); 7.53 (1H, arom); 7.98 (2H, arom). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 18.6 (Me); 34.7 and 37.5 (CH_2); 43.8 (C_8); 46.2 and 54.0 (C_2 and C_5); 49.2 (C_7); 51.7 (CO_2Me); 84.9 and 86.6 (C_3 and C_4); 124.0 and 124.7 (Me*C*=*C*Me); 128.2, 128.4, and 132.7 (*C*H arom); 136.4 (*C* arom); 172.1 (C_1); 202.6 and 206.8 (C_6 and C_9). IR (Nujol): 1672 (arom and alkene), 1719 (ketone), 1743 (ester), 1989, 2006 and 2063 ($Fe(CO)_3$). Anal. Calcd for $C_{25}H_{24}FeO_7$: C, 60.99; H, 4.91. Found: C, 60.79; H, 5.02.

Isomer 11b. Mp: 90 °C (from ether). R_f = 0.50 (E/PE 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (d, J = 8.5 Hz, 1H, H_2 or H_5); 1.62 (s, 3H, *Me*); 1.71 (s, 3H, *Me*); 1.73 (d, J = 8.3 Hz, 1H, H_2 or H_5); 2.00 (m, 1H, H_{10}); 2.13−2.30 (broad, 2H, H_{10} and H_{13}); 2.43 (broad dd, J = 16.6, 4.9 Hz, 1H, H_{13}); 3.25 (td, J = 11.2, 5.4 Hz, 1H, H_7); 3.71 (s, 3H, CO_2Me); 3.86 (td, J = 11.5, 5.4 Hz, 1H, H_8); 5.91 (ddd, J = 8.3, 5.2, 1.2 Hz, 1H, H_4); 6.02 (dd, J = 8.4, 5.2 Hz, 1H, H_3); 7.45 (2H, arom); 7.55 (1H, arom); 7.94 (2H, arom). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 18.7 (Me); 35.8 and 36.2 (CH_2); 45.8 (C_8); 47.2 and 54.3 (C_2 and C_5); 49.3 (C_7); 51.9 (CO_2Me); 85.7 and 87.3 (C_3 and C_4); 124.5 (Me*C*=*C*Me); 128.5, 128.6 and 133.1 (*C*H arom); 136.2 (*C* arom); 171.9 (C_1); 203.3 and 208.7 (C_6 and C_9). IR (Nujol): 1666 (arom and alkene), 1720 (ketone), 1755 (ester), 2004 and 2070 ($Fe(CO)_3$). Anal. Calcd for $C_{25}H_{24}FeO_7$: C, 60.99; H, 4.91. Found: C, 61.25; H, 4.91.

Cycloaddition with Azomethine Ylide: from 6a. To the solution of olefin **6a** (240 mg; 0.43 mmol) and amino ether (240 μL) in CH_2Cl_2 (25 mL) was added under N_2 at 0 °C a 0.1 M solution of trifluoroacetic acid in CH_2Cl_2 (3.4 mL; 0.8 equiv). The reaction mixture was stirred for 24 h and then hydrolyzed with saturated aqueous Na_2CO_3 and extracted with ether. The organic layer was washed with water until neutral pH, dried ($MgSO_4$), and evaporated. Chromatography of the residual oil (elution with ether/petroleum ether 2/8) yielded a 70/30 unseparable mixture of **13a** and **14a** (240 mg; 96%). R_f = 0.52 (E/PE 7/3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, J = 7.1 Hz, $CO_2CH_2CH_3$ **14a**); 1.22 (t, J = 7.1 Hz, $CO_2CH_2CH_3$ **13a**); 1.24 (t, J = 7.1 Hz, $CO_2CH_2CH_3$ **14a**); 1.25 (t, J = 7.1 Hz, $CO_2CH_2CH_3$ **13a**); 1.33 (d, J = 8.1 Hz, H_5 **13a**); 1.39 (d, J = 8.1 Hz, H_5 **14a** and H_2 **13a**); 1.72 (d, J = 8.1 Hz, H_2 **14a**); 2.56 (dd, J = 9.4, 6.4 Hz, H_{10} **13a** and **14a**); 2.70 (t, J = 8.7 Hz, H_{10} **13a**); 3.07 (d, J = 9.7 Hz, H_9 **13a**); 3.23 (s, NCH_2Ph **14a**); 3.25 (s, NCH_2Ph **13a**); 3.28 (d, J = 10.7 Hz, H_9 **14a**); 3.36 (d, J = 9.7 Hz, H_9 **13a**); 3.58−3.65 (m, H_7 **13a** and **14a**); 3.66 (s, CO_2Me **13a**); 3.70 (s, CO_2Me **14a**); 3.96−4.11 (m, $CO_2CH_2CH_3$ **13a** and **14a**); 4.19 and 4.27 (m, $CO_2CH_2CH_3$ **13a** and **14a**); 5.90−6.03 (m, H_3 and H_4 **13a** and **14a**); 7.23−7.31 (5H, arom **13a** and **14a**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8 ($CO_2CH_2CH_3$ **13a**); 13.9 ($CO_2CH_2CH_3$ **14a**); 46.7 and 55.1 (C_2 and C_5, **13a**); 47.1 and 54.8 (C_2 and C_5, **14a**); 51.9 (CO_2Me, **13a**); 52.0 (CO_2Me, **14a**); 54.1 (C_7, **13a** and **14a**); 56.4 and 59.1 (CH_2, **13a**); 56.6 and 59.1 (CH_2, **14a**); 59.6 (NCH_2Ph **13a**); 60.3 (NCH_2Ph **14a**); 61.6 and 62.1 ($CO_2CH_2CH_3$, **13a**); 61.8 and 62.3 ($CO_2CH_2CH_3$, **14a**); 62.0 (C_8 **13a**); 63.1 (C_8 **14a**); 85.0 and 87.3 (C_3 and C_4, **13a**); 85.9 and 86.7 (C_3 and C_4, **14a**); 127.1, 128.3, 128.4, 128.5, and 138.4 (*C* arom, **13a** and **14a**); 168.7, 170.4, and 171.9 (C_1 and CO_2Et, **14a**); 169.0, 170.2, and 172.0 (C_1 and CO_2Et, **13a**); 203.2 (C_6 **13a**); 203.5 (C_6 **14a**). IR (Nujol): 1590 (arom and alkene), 1679 (ketone), 1725 (broad, ester), 1998 and 2072 ($Fe(CO)_3$). Anal. Calcd for $C_{27}H_{29}FeNO_{10}$: C, 55.59; H, 5.01. Found: C, 55.63; H, 5.16.

From 6b. To the solution of olefin **6b** (300 mg; 0.73 mmol) and amino ether (610 μL) in CH_2Cl_2 (30 mL) was added under N_2 at 0 °C a 0.1 M solution of trifluoroacetic acid in CH_2Cl_2 (3.6 mL; 0.5 equiv). The reaction mixture was stirred for 4 h and then hydrolyzed with saturated aqueous Na_2CO_3 and extracted with ether. The organic layer was washed with water until neutral pH, dried ($MgSO_4$), and evaporated. Chromatography of the residual oil (elution with ether/petroleum ether 2/8) allowed the separation of the two isomers **13b** and **14b** (78%; **13b**/**14b** = 70/30).

Isomer 13b. Mp: 110 °C (from ether). R_f = 0.35 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (d, J = 7.2 Hz, 1H, H_2 or H_5); 1.47 (d, J = 7.2 Hz, 1H, H_2 or H_5); 2.68 (dd, J = 9.0, 6.7 Hz, 1H, H_{10}); 2.88 (dd, J = 9.2, 6.2 Hz, 1H, H_{11}); 2.97 (t, J = 8.9 Hz, 1H, H_{10}); 3.03 (t, J = 9.2 Hz, 1H, H_{11}); 3.61 (s, 2H, NCH_2Ph); 3.68 (s, 3H, CO_2Me); 3.71 (q, J = 6.2 Hz, 1H, H_7); 4.40 (m, 1H, H_8); 5.98−6.03 (m, 2H, H_3 and H_4); 7.24−7.30 (5H, arom); 7.43 (2H, arom); 7.55 (1H, arom); 7.92 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.2 and 52.0 (C_2 and C_5); 47.1 (C_8); 52.0 (CO_2Me); 53.5 (C_7); 56.9 and 56.9 (CH_2); 59.4 (NCH_2Ph); 85.5 and 87.1 (C_3 and C_4); 127.2, 128.4, 128.6, 128.6, 128.7, and 133.3 (*C*H arom); 136.1 and 138.3 (*C* arom); 171.9 (C_1); 199.1 and 204.1 (C_6 and C_9). IR (Nujol): 1596 (arom and alkene), 1656 and 1693 (ketone), 1713 (ester), 2004 and 2060 ($Fe(CO)_3$). Anal. Calcd for $C_{28}H_{25}FeNO_7$: C, 61.89; H, 4.64. Found: C, 61.69; H, 4.82.

Isomer 14b. Yellow oil. R_f = 0.40 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (d, J = 8.1 Hz, 1H, H_2 or H_5); 1.47 (d, J = 8.1 Hz, 1H, H_2 or H_5); 2.72 (dd, J = 9.7, 6.3 Hz, 1H, H_{10}); 2.85 (dd, J = 8.7, 6.4 Hz, 1H, H_{11}); 3.06 (t, J = 8.6 Hz, 1H, H_{10}); 3.10 (t, J = 9.2 Hz, 1H, H_{11}); 3.64 (s, 2H, NCH_2Ph); 3.69 (s, 3H, CO_2Me); 3.83 (dt, J = 7.6, 6.1 Hz, 1H, H_7); 4.39 (dt, J = 9.2, 6.1 Hz, 1H, H_8); 5.97 (dd, J = 8.1, 5.5 Hz, 1H, H_3 or H_4); 6.01 (dd, J = 7.9, 5.5 Hz, 1H, H_3 or H_4); 7.22−7.34 (5H, arom); 7.44 (2H, arom); 7.55 (1H, arom); 7.92 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.0 and 53.1 (C_2 and C_5); 47.5 (C_8); 51.9 (C_7); 52.0 (CO_2Me); 57.2 and 57.5 (CH_2); 59.4 (NCH_2Ph); 86.0 and 87.3 (C_3 and C_4); 127.2, 128.3, 128.6, 128.7, 128.7, and 133.3 (*C*H arom); 136 and 138.3 (*C* arom); 171.8 (C_1); 199.1 and 205.0 (C_6 and C_9). IR (Nujol): 1581 and 1598 (arom and alkene), 1675 (ketone), 1723 (ester), 2006 and 2071 ($Fe(CO)_3$). Anal. Calcd for $C_{28}H_{25}FeNO_7$: C, 61.89; H, 4.64. Found: C, 61.86; H, 4.75.

Nucleophilic Addition with *p*-Thiocresol: from 6a. To a stirred solution of olefin **6a** (250 mg; 0.55 mmol) in dry THF (10 mL) was added, under N_2 at 0 °C, *p*-thiocresol (140 mg; 2 equiv). The mixture was stirred for 10 min at 0 °C and then 4 h at room temperature, hydrolyzed with saturated aqueous Na_2CO_3, and extracted with ether. The separated organic layer was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residual oil (elution with ether/

petroleum ether 2/8) allowed the separation of the two isomers **15a** and **16a** (69%; **15a**/**16a** = 63/37).

Isomer 15a. Mp: 109 °C (from ether). R_f = 0.6 (E/PE 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.36 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.35 (d, J = 7.3 Hz, 1H, H_2 or H_5); 1.85 (d, J = 8.1 Hz, 1H, H_2 or H_5); 2.34 (s, 3H, *Me*); 3.71 (s, 3H, CO_2Me); 3.83 (d, J = 11.6 Hz, 1H, H_7 or H_8); 4.13 (d, J = 11.6 Hz, 1H, H_8 or H_7); 4.09 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 4.34 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$); 5.93 (ddd, J = 7.9, 5.2, 0.8 Hz, 1H, H_3 or H_4); 6.02 (ddd, J = 8.4, 5.2, 0.8 Hz, 1H, H_3 or H_4); 7.13 (2H, arom); 7.30 (2H, arom). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9 and 14.1 ($CO_2CH_2CH_3$); 21.2 (Me); 46.5 and 52.5 (C_2 and C_5); 51.8 (CO_2Me); 53.9 and 54.2 (C_7 and C_8); 61.8 ($CO_2CH_2CH_3$); 85.2 and 86.9 (C_3 and C_4); 125.3 (*C* arom); 130.0 and 135.8 (*C*H arom); 140.1 (*C* arom); 167.1 and 172.1 (C_1 and CO_2Et); 196.7 (C_6). IR (Nujol): 1668 (arom and alkene), 1706 (ketone), 1733 and 1754 (ester), 1998, 2023, and 2078 ($Fe(CO)_3$). Anal. Calcd for $C_{25}H_{26}FeO_{10}S$: C, 52.28; H, 4.56; S, 5.58. Found: C, 52.17; H, 4.58; S, 5.39.

Isomer 16a. Mp: 92 °C (from ether). R_f = 0.44 (E/PE 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.26 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.36 (dd, J = 8.1, 0.9 Hz, 1H, H_2 or H_5); 1.69 (dd, J = 7.9, 0.8 Hz, 1H, H_2 or H_5); 2.33 (s, 3H, *Me*); 3.71 (s, 3H, CO_2Me); 3.97 (d, J = 10.5 Hz, 1H, H_7 or H_8); 4.23 (d, J = 10.5 Hz, 1H, H_7 or H_8); 4.06−4.25 (m, 4H, $CO_2CH_2CH_3$); 5.88 (ddd, J = 8.0, 5.1, 0.9 Hz, 1H, H_3 or H_4); 5.99 (ddd, J = 8.1, 5.1, 0.8 Hz, 1H, H_3 or H_4); 7.13 (2H, arom); 7.39 (2H, arom). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9 and 14.0 ($CO_2CH_2CH_3$); 21.2 (Me); 46.7 and 55.3 (C_2 and C_5); 51.9 (CO_2Me); 53.8 and 53.9 (C_7 and C_8); 61.9 and 62.0 ($CO_2CH_2CH_3$); 86.6 and 87.5 (C_3 and C_4); 127.7 (*C* arom); 130.0 and 133.4 (*C*H arom); 139.0 (*C* arom); 167.0 and 167.6 (CO_2Et); 171.9 (C_1); 201.0 (C_6). IR (Nujol): 1680 (arom and alkene), 1705 (ketone), 1726 and 1747 (ester), 1994, 2025, and 2071 ($Fe(CO)_3$). Anal. Calcd for $C_{25}H_{26}FeO_{10}S$: C, 52.28; H, 4.56; S, 5.58. Found: C, 52.19; H, 4.62; S, 5.75.

From 6b. To the stirred solution of olefin **6b** (250 mg; 0.61 mmol) in dry THF (20 mL) was added under N_2 at 0 °C *p*-thiocresol (150 mg; 2 equiv). The reaction mixture was stirred for 4 h and then hydrolyzed with saturated aqueous Na_2CO_3 and extracted with ether. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residual oil (elution with ether/petroleum ether 2/8) allowed the separation of three fractions: **15b**, **16b**, and a 50/50 unseparable mixture of **19b** and **20b** (84%; **15b**/**16b**/**19b**/**20b** = 37/33/15/15).

Isomer 15b. Mp: 195 °C (from ethyl acetate). R_f = 0.72 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, J = 7.1 Hz, 1H, H_2 or H_5); 1.88 (d, J = 7.1 Hz, 1H, H_2 or H_5); 2.35 (s, 3H, *Me*); 3.21 (dd, J = 17.8, 3.5 Hz, 1H, H_8); 3.69 (dd, J = 17.8, 10.7 Hz, 1H, H_8); 3.72 (s, 3H, CO_2Me); 4.19 (dd, J = 10.7, 3.1 Hz, 1H, H_7); 5.98−6.03 (m, 2H, H_3 and H_4); 7.15 (2H, arom); 7.32 (2H, arom); 7.42 (2H, arom); 7.53 (1H, arom); 7.87 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (Me); 39.8 (C_8); 46.4 and 54.1 (C_2 and C_5); 50.7 (C_7); 51.9 (CO_2Me); 85.1 and 86.9 (C_3 and C_4); 127.2, 136.5, and 139.6 (*C* arom); 128.0, 128.5, 130.1, 133.2, and 134.9 (*C*H arom); 172.2 (C_1); 197.1 and 198.5 (C_6 and C_9). IR (Nujol): 1582 and 1594 (arom and alkene), 1670 (ketone), 1714 (ester), 2005, 2021 and 2062 ($Fe(CO)_3$). Anal. Calcd for $C_{26}H_{22}FeO_7S$: C, 58.44; H, 4.15; S, 6.00. Found: C, 58.23; H, 4.22; S, 5.80.

Isomer 16b. Mp: 165 °C (from ethyl acetate/hexane). R_f = 0.63 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (d, J = 8.1 Hz, 1H, H_2 or H_5); 1.87 (d, J = 8.1 Hz, 1H, H_2 or H_5); 2.34 (s, 3H, *Me*); 3.28 (dd, J = 18.0, 3.0 Hz, 1H, H_8); 3.72 (s, 3H, CO_2Me); 3.77 (dd, J = 18.0, 10.0 Hz, 1H, H_8); 4.30 (dd, J = 9.9, 3.5 Hz, 1H, H_7); 5.96 (ddd, J = 7.9, 5.6, 1.0 Hz, 1H, H_3 or H_4); 6.03 (ddd, J = 8.4, 5.6, 1.0 Hz, 1H, H_3 or H_4); 7.15 (2H, arom); 7.38 (2H, arom); 7.42 (2H, arom); 7.55 (1H, arom); 7.87 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (Me); 41.3 (C_8); 46.4 and 53.6 (C_2 and C_5); 51.2 (C_7); 52.0 (CO_2Me); 86.9 and 86.9 (C_3 and C_4); 128.1, 128.6, 130.1, 133.0, and 133.5 (*C*H arom); 128.9, 136.0, and 138.6 (*C* arom); 172.0 (C_1); 197.6 and 202.4 (C_6 and C_9); 205.2, 205.5, and 212.0 ($Fe(CO)_3$). IR (Nujol): 1581 and 1600 (arom and alkene), 1665 (ketone), 1708 (ester), 1989, 2011, and 2063 ($Fe(CO)_3$). Anal. Calcd for $C_{26}H_{22}FeO_7S$: C, 58.44; H, 4.15; S, 6.00. Found: C, 58.59; H, 4.26; S, 5.95.

Isomers 19b and 20b. R_f = 0.55 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, J = 7.6 Hz, 1H, H_5 **19b**); 1.33 (d, J = 8.1 Hz, 1H, H_5 **20b**); 1.44 (d, J = 8.1 Hz, 1H, H_2 **19b**); 1.49 (d, J = 7.6 Hz, 1H, H_2 **20b**); 2.33 (s, 3H, *Me* **20b**); 2.34 (s, 3H, *Me* **19b**); 2.86 (dd, J = 17.3, 4.1 Hz, 1H, H_7 **19b**); 2.93 (dd, J = 17.8, 4.5 Hz, 1H, H_7 **20b**); 3.25 (dd, J = 17.8, 9.2 Hz, 1H, H_7 **20b**); 3.28 (dd, J = 17.8, 11.7 Hz, 1H, H_7 **19b**); 3.69 (s, 3H, CO_2Me **19b**); 3.70 (s, 3H, CO_2Me **20b**); 4.90 (dd, J = 9.2, 4.6 Hz, 1H, H_8 **19b**); 4.90 (dd, J = 10.2, 4.6 Hz, 1H, H_8 **20b**); 5.88−5.99 (m, 4H, H_3 and H_4 **19b** and **20b**); 7.09 (2H, arom **20b**); 7.10 (2H, arom **19b**); 7.19 (2H, arom **20b**); 7.21 (2H, arom **19b**); 7.43 (4H, arom **19b** and **20b**); 7.52−7.56 (2H, arom **19b** and **20b**); 7.94 (2H, arom **20b**); 7.97 (2H, arom **19b**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 and 21.2 (*Me* **19b** and **20b**); 44.1 (C_7 **20b**); 44.5 (C_7 **19b**); 45.5 (C_8 **19b**); 47.2 (C_8 **20b**); 46.6 and 53.8 (C_2 and C_5 **19b**); 47.2 and 54.1 (C_2 and C_5 **20b**); 51.9 and 52.0 (CO_2Me **19b** and **20b**); 84.2 and 86.9 (C_3 and C_4 **19b**); 85.0 and 87.1 (C_3 and C_4 **20b**); 126.9, 135.7, and 139.6 (*C* arom **19b**); 126.9, 135.8, and 139.5 (*C* arom **20b**); 128.5, 128.8, 129.9, 132.9, and 135.3 (*C*H arom **20b**); 128.5, 128.8, 129.9, 133.1, and 135.5 (*C*H arom **19b**); 171.8 (C_1 **19b**); 172.0 (C_1 **20b**); 194.4 and 202.3 (C_6 and C_9 **20b**); 194.8 and 202.3 (C_6 and C_9 **19b**). IR (Nujol): 1574 and 1598 (arom and alkene), 1674 (ketone), 1712 (ester), 2002 and 2073 ($Fe(CO)_3$). Anal. Calcd for $C_{26}H_{22}FeO_7S$: C, 58.44; H, 4.15; S, 6.00. Found: C, 58.42; H, 4.48.

From 6c. The reaction yielded, as from **6b**, four adducts. Chromatography allowed the separation of three fractions: **15c**, **16c**, and a 50/50 unseparable mixture of **19c** and **20c**. **15c**. ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no CH_2 at 39.8 ppm (C_8 → *C*HD) and one *C*H at 50.7 ppm (C_7). ^{13}C NMR (100 MHz, $CDCl_3$): modification of the signal at 39.8 ppm into a triplet (C_8 → *C*HD). ^{1}H NMR (400 MHz, $CDCl_3$): disappearance of the dd at 3.21 ppm (H_8 → D); simplification of the dd at 3.69 ppm into a d (J = 10.7 Hz, 1H, H_8); simplification of the dd at 4.19 ppm into a d (J = 10.7 Hz, H_7). **16c**. ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no CH_2 at 41.3 ppm (C_8 → *C*HD) and one *C*H at 51.2 ppm (C_7). ^{13}C NMR (100 MHz, $CDCl_3$): modification of the signal at 41.3 ppm into a triplet (C_8 → *C*HD). ^{1}H NMR (400 MHz, $CDCl_3$): disappearance of the dd at 3.28 ppm (H_8 → D); simplification of the dd at 3.77 ppm into a d (J = 10.0 Hz, 1H, H_8); simplification of the dd at 4.30 ppm into a d (J = 10.0 Hz, H_7). **19c** and **20c**. ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no modification of the CH_2 at 44.1 and 44.5 ppm (C_7). ^{1}H NMR (400 MHz, $CDCl_3$): simplification of the dd at 2.86 and 2.93 ppm into d (J = 17.3 Hz, H_7); simplification of the dd at 3.25 and 3.28 ppm into d (J = 17.8 Hz, H_7); disappearance of the dd at 4.90 and 4.90 ppm (H_8 → D).

Radical-Type Addition. from 6a. To a solution of olefin **6a** (195 mg; 0.43 mmol), cyclopentyl bromide (1 equiv; 46 μL), and a crystal of AIBN in dry toluene (7 mL) at 90 °C was added via syringe pump a solution of cyclopentyl bromide (185 μL; 4 equiv) and tris(trimethylsilyl)silane (145 μL; 1.1 equiv) in dry toluene (15 mL) over a 3 h period. After 1 h 30 min of stirring, a second portion of cyclopentyl bromide (185 μL; 4 equiv) and tris(trimethylsilyl)silane (145 μL; 1.1 equiv) in toluene (15 mL) was added dropwise over a 3 h period. The reaction mixture was stirred again at 90 °C for 1 h 30 min, and then toluene was removed *in vacuo* and the crude product purified by chromatography on silica gel. Elution with ether/petroleum ether 2/8 allowed the separation of the two isomers **17a** and **18a** (72%; **17a**/**18a** = 72/28).

Isomer 17a. Mp: 120 °C (from ether). R_f = 0.55 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.28 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.30 (d, J = 8.2 Hz, 1H, H_2 or H_5); 1.53 (d, J = 8.1 Hz, 1H, H_2 or H_5); 1.40−1.48, 1.53−1.61, 1.65−1.75, and 1.83−1.93 (series of m, 9H, Hcyclopentyl); 3.39 (dd, J = 10.6, 6.2 Hz, 1H, H_7); 3.70 (s, 3H, CO_2Me); 3.86 (d, J = 10.6 Hz, 1H, H_8); 4.06−4.17 (m, 2H, $CO_2CH_2CH_3$); 4.21 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 5.88 (dd, J = 8.0, 5.3 Hz, 1H, H_3 or H_4); 5.96 (dd, J = 8.0, 5.3 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 and 14.0 ($CO_2CH_2CH_3$); 24.1, 24.5, 28.6, and 31.0 (CH_2 cyclopentyl); 41.5 (*C*H

cyclopentyl); 46.0 and 56.9 (C_2 and C_5); 51.9 (CO_2Me); 53.5 and 53.9 (C_7 and C_8); 61.5 and 61.6 ($CO_2CH_2CH_3$); 85.9 and 86.4 (C_3 and C_4); 168.0 and 168.7 (CO_2Et); 172.3 (C_1); 204.8, 206.0, and 211.4 ($Fe(CO)_3$); 205.9 (C_6). IR (Nujol): 1656 (ketone), 1703 and 1756 (ester), 2001, 2015, and 2079 ($Fe(CO)_3$). Anal. Calcd for $C_{23}H_{28}FeO_{10}$: C, 53.09; H, 5.42. Found: C, 53.59; H, 5.54.

Isomer 18a. Yellow oil. $R_f = 0.43$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$); 1.27 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$); 1.35 (d, $J = 8.3$ Hz, 1H, H_2 or H_5); 1.54−1.56, 1.60−1.70, 1.72−1.75, and 2.03−2.10 (series of m, 9H, Hcyclopentyl); 1.68 (d, $J = 8.0$ Hz, 1H, H_2 or H_5); 3.34 (dd, $J = 8.5$, 7.7 Hz, 1H, H_7); 3.71 (s, 3H, CO_2Me); 3.78 (d, $J = 8.9$ Hz, 1H, H_8); 4.06 to 4.15 (m, 2H, $CO_2CH_2CH_3$); 4.19 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$); 5.87 (dd, $J = 8.0$, 5.2 Hz, 1H, H_3 or H_4); 5.96 (dd, $J = 8.2$, 5.2 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0 and 14.2 ($CO_2CH_2CH_3$); 24.6, 24.7, 30.1 and 30.2 (CH_2 cyclopentyl); 41.2 (*C*H cyclopentyl); 46.7 and 57.5 (C_2 and C_5); 52.0 (CO_2Me); 54.5 and 54.6 (C_7 and C_8); 61.7 and 61.8 ($CO_2CH_2CH_3$); 86.6 and 87.8 (C_3 and C_4); 168.3 and 168.7 (CO_2Et); 172.0 (C_1); 205.5, 205.6, and 211.4 ($Fe(CO)_3$); 207.0 (C_6). IR (Nujol): 1663 (ketone), 1705 and 1733 (ester), 1998, 2012 and 2070 ($Fe(CO)_3$). Anal. Calcd for $C_{23}H_{28}FeO_{10}$: C, 53.09; H, 5.42. Found: C, 53.15; H, 5.89.

from 6b. To a solution of olefin **6b** (300 mg; 0.73 mmol), cyclopentyl bromide (1.2 equiv; 120 μL), and a crystal of AIBN in dry toluene (25 mL) at 75 °C was added via syringe pump a solution of cyclopentyl bromide (275 μL; 3.5 equiv), tris(trimethylsilyl)silane (270 μL; 1.2 equiv), and a crystal of AIBN in dry toluene (35 mL) over a 5 h period. After 1 h 30 min of stirring, toluene was removed *in vacuo*. Chromatography of the residual oil (elution with ether/petroleum ether 2/8) allowed the separation of three fractions: **17b**, **18b**, and a 50/50 unseparable mixture of **21b** and **22b** (59%; **17b**/**18b**/**21b**/**22b** = 19/14/13/13).

Isomer 17b. Mp: 131 °C (from ether). $R_f = 0.58$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16−1.31 (m, 4H, CH_2 cyclopentyl); 1.34 (d, $J = 7.6$ Hz, 1H, H_2 or H_5); 1.44−1.60 (m, 2H, CH_2 cyclopentyl); 1.67 (d, $J = 7.6$ Hz, 1H, H_2 or H_5); 1.70−1.83 (m, 2H, CH_2 cyclopentyl); 1.88−1.98 (m, 1H, C*H* cyclopentyl); 2.95 (dd, $J = 17.8$, 2.5 Hz, 1H, H_8); 3.11 (ddd, $J = 10.7$, 8.1, 2.5 Hz, 1H, H_7); 3.64 (dd, $J = 18.1$, 10.6 Hz, 1H, H_8); 3.71 (s, 3H, CO_2Me); 5.94 (dd, $J = 7.4$, 5.1 Hz, 1H, H_3 or H_4); 5.98 (dd, $J = 7.9$, 5.1 Hz, 1H, H_3 or H_4); 7.43 (2H, arom); 7.53 (1H, arom); 7.95 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 25.2, 30.5, 31.4 (CH_2 cyclopentyl); 39.2 (C_8); 42.7 (*C*H cyclopentyl); 46.0 and 55.9 (C_2 and C_5); 51.2 and 51.9 (C_7 and CO_2Me); 85.6 and 86.4 (C_3 and C_4); 128.0, 128.4, and 132.9 (*C*H arom); 136.9 (*C* arom); 172.3 (C_1); 198.4 and 207.5 (C_6 and C_9); 204.6, 206.0, and 212.0 ($Fe(CO)_3$). IR (Nujol): 1563 and 1599 (low, arom and alkene), 1665 and 1689 (ketone), 1721 (ester), 1987, 2014, and 2068 ($Fe(CO)_3$). Anal. Calcd for $C_{24}H_{24}FeO_7$: C, 60.02; H, 5.04. Found: C, 60.13; H, 5.25.

Isomer 18b. $R_f = 0.53$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16−1.28 (m, 1H, CH_2 cyclopentyl); 1.29−1.42 (m, 1H, CH_2 cyclopentyl); 1.39 (d, $J = 7.9$ Hz, 1H, H_2 or H_5); 1.46−1.66 and 1.67−1.78 (m, 5H, CH_2 cyclopentyl); 1.74 (d, $J = 7.3$ Hz, 1H, H_2 or H_5); 1.79−1.91 (m, 1H, CH_2 cyclopentyl); 2.19−2.31 (m, 1H, C*H* cyclopentyl); 3.08 (dd, $J = 18.0$, 3.0 Hz, 1H, H_8); 3.20 (ddd, $J = 9.9$, 7.4, 2.7 Hz, 1H, H_7); 3.51 (dd, $J = 18.0$, 10.1 Hz, 1H, H_8); 3.71 (s, 3H, CO_2Me); 5.90 (dd, $J = 8.1$, 5.6 Hz, 1H, H_3 or H_4); 6.02 (dd, $J = 8.2$, 5.2 Hz, 1H, H_3 or H_4); 7.45 (2H, arom); 7.56 (1H, arom); 7.92 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 25.3, 29.5, 31.3 (CH_2 cyclopentyl); 39.7 (C_8); 41.9 (*C*H cyclopentyl); 46.8 and 56.2 (C_2 and C_5); 51.5 and 52.0 (C_7 and CO_2Me); 86.7 and 87.3 (C_3 and C_4); 128.1, 128.6, and 133.3 (*C*H arom); 136.5 (*C* arom); 172.0 (C_1); 198.8 and 208.8 (C_6 and C_9). IR (Nujol): 1598 (low, arom and alkene), 1675 (ketone), 1707 (ester), 2001 and 2069 ($Fe(CO)_3$).

Isomers 21b and 22b. $R_f = 0.45$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 to 1.30 (m, CH_2 cyclopentyl); 1.35 (d, $J = 8.1$ Hz, 1H, H_5 **22b**); 1.38 (d, $J = 8.1$ Hz, 1H, H_5 **21b**); 1.43−1.65 (m, 4H, CH_2 cyclopentyl); 1.52 (d, $J = 8.0$ Hz, 2H, H_2 **21b** and H_2 **22b**); 1.67−1.80 (m, 1H, C*H* cyclopentyl **21b**); 1.93−2.08 (m, 1H, C*H* cyclopentyl **22b**); 2.64 (dd, $J = 17.8$, 3.6 Hz, 1H, H_7 **22b**); 2.68 (dd, $J = 17.8$, 3.6 Hz, 1H, H_7 **21b**); 3.24 (dd, $J = 17.6$, 10.0 Hz, 1H, H_7 **21b**); 3.25 (dd, $J = 17.5$, 10.6 Hz, 1H, H_7 **22b**); 3.69 (s, 3H, CO_2Me **21b**); 3.69 (s, 3H, CO_2Me **22b**); 3.88 (td, $J = 10.1$, 3.6 Hz, 1H, H_8 **21b**); 3.91 (td, $J = 11$, 3.1 Hz, 1H, H_8 **22b**); 5.86−5.99 (m, H_3 and H_4 **21b** and **22b**); 7.44 (2H, arom **21b** and **22b**); 7.51 (1H, arom **22b**); 7.54 (1H, arom **21b**); 7.99 (2H, arom **21b** and **22b**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 25.1, 30.2, 31.1 (CH_2 cyclopentyl **22b**); 24.5, 25.1, 30.1 and 31.0 (CH_2 **21b**); 42.8 (*C*H **22b**); 43.0 (*C*H **21b**); 43.7 (C_7 **21b**); 44.0 (C_7 **22b**); 45.4 (C_8 **22b**); 45.7 (C_8 **21b**); 46.5 and 54.3 (C_2 and C_5 **22b**); 47.2 and 54.2 (C_2 and C_5 **21b**); 51.9 (CO_2Me **22b**); 51.9 (CO_2Me **21b**); 84.4 and 86.9 (C_3 and C_4 **22b**); 85.0 and 87.0 (C_3 and C_4 **21b**); 128.4, 128.4, and 132.6 (*C*H arom **22b**); 128.5, 128.5 and 132.8 (*C*H arom **21b**); 137.9 (*C* arom **21b**); 138.1 (*C* arom **22b**); 171.9 (C_1 **21b**); 172.1 (C_1 **22b**); 203.6, 203.7, 203.7, and 203.9 (C_6 and C_9 **21b** and **22b**); 202.0, 203.2, and 203.3 ($Fe(CO)_3$). IR (Nujol): 1583 and 1603 (arom and alkene), 1673 (ketone), 1717 (ester), 2005 and 2070 ($Fe(CO)_3$). Anal. Calcd for $C_{24}H_{24}FeO_7$: C, 60.02; H, 5.04. Found: C, 60.65; H, 5.34.

From 6c. The reaction yielded, as for **6b**, four adducts. Chromatography allowed the separation of three fractions: **17c**, **18c**, and a 50/50 unseparable mixture of **21c** and **22c**. **17c**: ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no CH_2 at 39.2 ppm ($C_8 \rightarrow$ *C*HD) and one *C*H at 51.2 ppm (C_7). ^{13}C NMR (100 MHz, $CDCl_3$): modification of the signal at 39.2 ppm into a triplet ($C_8 \rightarrow$ *C*HD). ^{1}H NMR (400 MHz, $CDCl_3$): disappearance of the dd at 2.95 ppm ($H_8 \rightarrow$ D); simplification of the ddd at 3.11 ppm into a dd ($J = 7.9$ and 2.0 Hz, H_7); simplification of the dd at 3.64 ppm into a d ($J = 11.2$ Hz, H_8). **18c**: ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no CH_2 at 39.7 ppm ($C_8 \rightarrow$ *C*HD) and one *C*H at 51.5 ppm (C_7). ^{13}C NMR (100 MHz, $CDCl_3$): modification of the signal at 39.7 ppm into a triplet ($C_8 \rightarrow$ *C*HD). ^{1}H NMR (400 MHz, $CDCl_3$): disappearance of the dd at 3.08 ppm ($H_8 \rightarrow$ D); simplification of the ddd at 3.20 ppm into a dd ($J = 10.1$ and 7.8 Hz, H_7); simplification of the dd at 3.48 ppm into a d ($J = 9.8$ Hz, H_8). **19c** and **20c**: ^{13}C NMR−DEPT (100 MHz, $CDCl_3$): no modification of the CH_2 at 43.7 and 44.0 ppm (C_7). ^{13}C NMR (100 MHz, $CDCl_3$): modification of the signals at 45.4 and 45.7 ppm into triplets ($C_8 \rightarrow$ *C*HD). ^{1}H NMR (400 MHz, $CDCl_3$): simplification of the dd at 2.64 and 2.68 ppm into d ($J = 17.8$ Hz, H_7); simplification of the dd at 3.24 and 3.25 ppm into d ($J = 17.7$ Hz, H_7); disappearance of the dd at 3.88 and 3.91 ppm ($H_8 \rightarrow$ D).

Hydride Reduction of 6d. To a stirred solution of **6d** (150 mg; 0.41 mmol) in $MeOH/CH_2Cl_2$ (10 mL/5 mL) at −30 °C was added $NaBH_4$ (15 mg; 1 equiv) in one portion. The reaction mixture was allowed to warm to 0 °C in 30 min and then hydrolyzed and extracted with ether. The separated organic layer was washed with water, dried ($MgSO_4$), and evaporated. Purification of the crude product yielded **23d** (130 mg; 86%) as a yellow solid. **23d**: Mp: 112 °C (from ether). $R_f = 0.18$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, $J = 8.2$ Hz, 1H, H_2); 1.23 (t, $J = 7.6$ Hz, 1H, H_5); 2.34 (d, $J = 3.6$ Hz, 1H, O*H*); 3.67 (s, 3H, CO_2Me); 3.77 (s, 3H, CO_2Me); 4.33 (m, 1H, H_6); 5.45 (dd, $J = 8.4$, 5.1 Hz, 1H, H_3); 5.85 (dd, $J = 7.8$, 5.3 Hz, 1H, H_4); 6.04 (d, $J = 15.9$ Hz, 1H, H_8); 6.96 (dd, $J = 15.6$, 5.0 Hz, 1H, H_7). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.0 and 65.1 (C_2 and C_5); 51.8 and 51.9 (CO_2Me); 72.1 (C_6); 83.5 and 83.8 (C_3 and C_4); 118.6 (C_8) and 148.8 (C_7); 166.7 and 172.5 (C_1 and C_9). IR (Nujol): 1660 (alkene); 1691 (ketone); 1708 (ester); 1972, 1997, and 2048 ($Fe(CO)_3$). Anal. Calcd for $C_{14}H_{14}FeO_8$: C, 45.93, H, 3.85. Found: C, 45.96, H, 3.85.

General Procedure for the Decomplexation of Adducts 24a, 25a,b, and 26−31. To a stirred solution of the corresponding complex in a mixture of $MeOH/CH_2Cl_2$ was added, under N_2 at −15 °C, ammonium cerium nitrate (10 equiv). The reaction mixture was stirred for 45 min and allowed to rise up to room temperature, before addition of water and extraction with ether. The separated organic layer was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residual oil (elution with ether/petroleum ether 4/6) yielded the desired dienes **24** (except **24b**) to **31**.

Diene 24a. 69% yield from **10a** or **11a**. **24a**. $R_f = 0.33$ (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, $J = 7.2$ Hz, 3H, $CO_2CH_2CH_3$); 1.25 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$); 1.58

(s, 3H, *Me*); 1.65 (s, 3H, *Me*); 2.20 (broad d, J = 18.5 Hz, 1H, H_{12}); 2.49 (dd, J = 18.3, 7.7 Hz, 1H, H_{12}); 2.65 (d, J = 17.3 Hz, 1H, H_9); 2.80 (d, J = 17.3 Hz, 1H, H_9); 3.68 (m, 1H, H_7); 3.78 (s, 3H, CO_2Me); 4.15 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 4.20 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 6.23 (d, J = 15.0 Hz, 1H, H_2 or H_5); 6.62 (d, J = 14.9 Hz, 1H, H_2 or H_5); 7.23 (dd, J = 15.1, 11.5 Hz, 1H, H_3 or H_4); 7.34 (dd, J = 14.9, 11.5 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 and 14.0 ($CO_2CH_2CH_3$); 18.7 and 19.0 (Me); 34.2 and 35.0 (CH_2); 48.2 (C_7); 51.9 (CO_2Me); 55.6 (C_8); 61.5 and 61.8 ($CO_2CH_2CH_3$); 121.4 and 124.5 (MeC=CMe); 128.6, 133.8, 138.8, and 141.5 (C_2 to C_5); 166.4 (C_1); 170.1 and 170.7 (CO_2Et); 198.6 (C_6). IR (film): 1597 (alkene), 1692 (ketone), 1729 (ester). Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.24; H, 7.19. Found: C, 64.24; H, 7.34.

Diene 25a. 65% yield from **13a** or **14a**. **25a**. R_f = 0.38 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.25 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 2.67 (dd, J = 9.2, 7.6 Hz, 1H, H_{10}); 3.17 (broad t, J = 8.7 Hz, 1H, H_{10}); 3.20 (d, J = 9.8 Hz, 1H, H_9); 3.31 (d, J = 9.8 Hz, 1H, H_9); 3.65 (s, 2H, NCH_2Ph); 3.78 (s, 3H, CO_2Me); 4.00−4.12 (m, 2H, $CO_2CH_2CH_3$); 4.25 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 4.33 (t, J = 7.7 Hz, H_7); 6.25 (d, J = 14.7 Hz, 1H, H_2 or H_5); 6.55 (d, J = 14.8 Hz, 1H, H_2 or H_5); 7.22−7.34 (m, 7H, H_3 and H_4 and arom).^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8 and 14.0 ($CO_2CH_2CH_3$); 52.0 (CO_2Me); 53.2 (C_7); 55.9, 59.0, and 60.1 (CH_2); 61.7 and 62.3 ($CO_2CH_2CH_3$); 62.8 (C_8); 127.1, 128.3, 128.4, 129.0, 135.2, 139.2, and 141.4 (C_2 to C_5 and *C*H arom); 138.4 (*C* arom); 166.2, 168.5, and 170.4 (C_1 and CO_2Et); 197.7 (C_6). IR (film): 1597 (arom and alkene), 1670 (ketone), 1697 and 1729 (ester). Anal. Calcd for $C_{24}H_{29}NO_7$: C, 65.00; H, 6.59. Found: C, 65.04; H, 6.78.

Diene 26. 97% yield from **15a** or **16a**. **26**. Mp: 142 °C (from ethyl acetate). R_f = 0.35 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.37 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 2.33 (s, 3H, *Me*); 3.80 (s, 3H, CO_2Me); 3.91 (d, J = 11.7 Hz, 1H, H_7 or H_8); 4.12 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 4.31−4.39 (m, 2H, $CO_2CH_2CH_3$); 4.33 (d, J = 11.7 Hz, 1H, H_7 or H_8); 6.21 (d, J = 15.2 Hz, 1H, H_2 or H_5); 6.76 (d, J = 15.2 Hz, 1H, H_2 or H_5); 7.12 (2H, arom); 7.22 (dd, J = 15.1, 11.5 Hz, 1H, H_3 or H_4); 7.29 (2H, arom); 7.37 (dd, J = 15.2, 11.5 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 and 14.2 ($CO_2CH_2CH_3$); 21.3 (Me); 52.0 (CO_2Me); 52.7 and 53.9 (C_7 and C_8); 62.1 and 62.1 ($CO_2CH_2CH_3$); 125.2 and 140.2 (*C* arom); 128.8, 133.9, 139.5, and 141.4 (C_2 to C_5); 130.2 and 135.9 (*C*H arom); 166.1 (C_1); 167.3 and 167.3 (CO_2Et); 191.0 (C_6). IR (Nujol): 1597 (alkene and arom); 1682 (ketone); 1708 and 1730 (ester). Anal. Calcd for $C_{22}H_{26}O_7S$: C, 60.81; H, 6.03. Found: C, 60.76; H, 6.18.

Diene 27. 78% yield from **17a** or **18a**. **27**. Mp: 108 °C (from ether). R_f = 0.37 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.29 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$); 1.14−1.24, 1.36−1.50, 1.52−1.61, and 1.62−1.80 (m, 8H, CH_2 cyclopentyl); 1.86−2.02 (m, 1H, C*H* cyclopentyl); 3.58 (dd, J = 10.2, 7.1 Hz, 1H, H_7); 3.79 (s, 3H, CO_2Me); 3.93 (d, J = 10.2 Hz, 1H, H_8); 4.05−4.16 (m, 2H, $CO_2CH_2CH_3$); 4.23 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$); 6.26 (d, J = 15.3 Hz, 1H, H_2 or H_5); 6.60 (d, J = 15.3 Hz, 1H, H_2 or H_5); 7.22 (dd, J = 15.3, 11.4 Hz, 1H, H_3 or H_4); 7.35 (dd, J= 15.3, 11.4 Hz, 1H, H_3 or H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 and 14.0 ($CO_2CH_2CH_3$); 24.2, 24.5, 28.8, and 30.8 (CH_2 cyclopentyl); 41.7 (*C*H cyclopentyl); 52.0 (CO_2Me); 51.9 and 54.7 (C_7 and C_8); 61.5 and 61.8 ($CO_2CH_2CH_3$); 128.7, 136.8, 138.1, and 141.7 (C_2−C_5); 166.3 (C_1); 168.4 and 168.8 (CO_2Et); 200.7 (C_6). IR (Nujol): 1591 (alkene); 1684 (ketone); 1728 (ester). Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.01; H, 7.32.

Diene 25b. 64% yield from **13b** or **14b**. **25b**. Mp: 110 °C (from ethyl acetate). R_f = 0.21 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73 (dd, J = 9.2, 6.6 Hz, 1H, CH_2); 2.83 (dd, J = 9.7, 5.7 Hz, 1H, CH_2); 2.98 (t, J = 9.2 Hz, 1H, CH_2); 3.13 (t, J = 9.2 Hz, 1H, CH_2); 3.62 (s, 2H, NCH_2Ph); 3.77 (s, 3H, CO_2Me); 4.07 (dt, J = 8.6, 5.6 Hz, 1H, H_7 or H_8); 4.45 (dt, J = 8.6, 6.1 Hz, 1H, H_7 or H_8); 6.18−6.28 (m, 1H, H_2 or H_3); 6.43−6.51 (m, 1H, H_2 or H_5); 7.22−7.31 (m, 7H, H_3 and H_4 and arom); 7.45 (2H, arom); 7.56 (1H, arom); 7.95 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.0 and 50.0 (C_7 and C_8); 52.0 (CO_2Me); 56.3, 57.6, and 59.3 (CH_2); 127.2, 128.3, 128.6, 128.7, 128.7, and 129.0 (*C*H arom); 133.4, 134.4, 139.6, and 141.3 (C_2 to C_5); 135.9 and 138.1 (*C* arom); 166.2 (C_1); 198.6 and 199.1 (C_6 and C_9). IR (Nujol): 1596 (arom and alkene), 1682 (ketone), 1713 (ester). Anal. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.24; N, 3.47. Found: C, 74.06; H, 6.15; N, 3.36.

Diene 28. 89% yield from **15b** or **16b**. **28**. Mp: 110 °C (from hexane/ethyl acetate). R_f = 0.41 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, *Me*); 3.38 (dd, J = 17.8, 4.6 Hz, 1H, H_8); 3.70 (dd, J = 17.8, 9.1 Hz, 1H, H_8); 3.79 (s, 3H, CO_2Me); 4.37 (dd, J = 9.4, 4.6 Hz, 1H, H_7); 6.21 (d, J = 15.3 Hz, 1H, H_2 or H_5); 6.80 (d, J = 14.8 Hz, 1H, H_2 or H_5); 7.13 (2H, arom); 7.25 (dd, J = 14.7, 11.2 Hz, 1H, H_3 or H_4); 7.30 (2H, arom); 7.37 (dd, J = 15.2, 11.2 Hz, 1H, H_3 or H_4); 7.45 (2H, arom); 7.56 (1H, arom); 7.92 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (*Me*); 39.7 (C_8); 50.4 and 51.9 (C_7 and CO_2Me); 126.9, 133.5, and 139.7 (*C* arom); 128.1, 128.5, 128.6, 130.1, 133.5, 134.3, 135.1, 139.1, and 141.6 (C_2 to C_5 and *C*H arom); 166.4 (C_1); 193.0 and 197.2 (C_6 and C_9). IR (Nujol): 1594 (alkene and arom); 1677 and 1690 (ketone); 1708 (ester). Anal. Calcd for $C_{23}H_{22}O_4S$: C, 70.03; H, 5.62. Found: C, 69.55; H, 5.62.

Diene 30. 85% yield from **19b** and **20b**. **30**. R_f = 0.51 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, *Me*); 3.09 (dd, J = 17.8, 4.6 Hz, 1H, H_7); 3.77 (s, 3H, CO_2Me); 3.81 (m, 1H, H_7); 4.96 (dd, J = 9.1, 4.6 Hz, 1H, H_8); 6.11 (d, J = 14.7 Hz, 1H, H_2 or H_5); 6.65 (d, J = 14.2 Hz, 1H, H_2 or H_5); 7.13 (2H, arom); 7.25 (dd, J = 14.7, 11.2 Hz, 1H, H_3 or H_4); 7.30 (2H, arom); 7.37 (dd, J = 15.2, 11.2 Hz, 1H, H_3 or H_4); 7.45 (2H, arom); 7.56 (1H, arom); 7.92 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (Me); 42.1 (C_8); 51.0 and 51.8 (C_7 and CO_2Me); 127.8, 135.5, and 140.0 (*C* arom); 128.1, 128.5, 128.6, 130.1, 133.5, 134.3, 135.1, 139.1, and 141.6 (C_2−C_5 and *C*H arom); 166.6 (C_1); 193.5 and 195.0 (C_6 and C_9). IR (film): 1592 (alkene and arom); 1682 and 1702 (ketone); 1714 (ester). High-resolution mass spectrum for $C_{23}H_{22}O_4S$: calcd 394.1239, found 394.1261.

Diene 29. 64% yield from **17b** or **18b**. **29**: R_f = 0.51 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17−1.29, 1.49−1.59, 1.63−1.72, 1.79−1.90, and 1.93−2.03 (series of m, 9H, H cyclopentyl); 3.18 (dd, J = 18.1, 3.0 Hz, 1H, H_8); 3.30 (td, J = 10.7, 3.0 Hz, 1H, H_7); 3.68 (dd, J = 18.1, 10.4 Hz, 1H, H_8); 3.81 (s, 3H, CO_2Me); 6.25 (d, J = 15.1 Hz, 1H, H_2 or H_5); 6.69 (d, J = 15.1 Hz, 1H, H_2 or H_5); 7.27 (dd, J = 15.1, 11.7 Hz, 1H, H_3 or H_4); 7.39 (dd, J = 15.0, 11.7 Hz, 1H, H_3 or H_4); 7.45 (2H, arom); 7.56 (1H, arom); 7.94 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 25.2, 30.8, and 31.1 (CH_2 cyclopentyl); 40.9 (C_8); 42.7 (*C*H cyclopentyl); 49.8 (C_7); 51.9 (CO_2Me); 128.1, 128.3, and 128.6 (*C*H arom); 133.3, 136.6, 137.9, and 142.0 (C_2−C_5); 136.3 (*C* arom); 166.4 (C_1); 198.8 and 202.9 (C_6 and C_9). IR (film): 1582 and 1598 (alkene and arom), 1682 (ketone), 1722 (ester). High-resolution mass spectrum for ion $C_{19}H_{21}O_2$: calcd 281.1541, found 281.1438.

Diene 31. 90% yield from **21b** and **22b**. **30**: R_f = 0.39 (E/PE 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06−1.15, 1.21−1.30, 1.41−1.59, 1.63−1.82, and 1.94−2.07 (series of m, 9H, H cyclopentyl); 2.84 (dd, J = 17.8, 3.1 Hz, 1H, H_7); 3.43 (dd, J = 17.8, 10.2 Hz, 1H, H_7); 3.77 (s, 3H, CO_2Me); 3.93 (td, J = 10.7, 3.0 Hz, 1H, H_8); 6.22 (d, J = 15.3 Hz, 1H, H_2 or H_5); 6.43 (d, J = 15.3 Hz, 1H, H_2 or H_5); 7.17 (dd, J = 15.3, 11.2 Hz, 1H, H_3 or H_4); 7.28 (dd, J = 15.3, 11.2 Hz, 1H, H_3 or H_4); 7.47 (2H, arom); 7.56 (1H, arom); 8.04 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 25.1, 30.4, and 31.1 (CH_2 cyclopentyl); 42.7 (C_8); 43.0 (*C*H cyclopentyl); 45.3 (C_7); 51.9 (CO_2Me); 128.5 and 128.7 (*C*H arom); 132.8, 135.1, 138.6, and 141.5 (C_2 to C_5); 138.0 (*C* arom); 166.2 (C_1); 198.6 and 203.9 (C_6 and C_9). IR (film): 1598 (alkene and arom), 1679 (ketone), 1728 (ester). High-resolution mass spectrum for $C_{21}H_{24}O_4$: calcd 340.1674, found 340.1672.

Diene 24b. A solution of trimethylamine *N*-oxide dihydrate (300 mg; 15 equiv) in CH_2Cl_2 (20 mL) was refluxed in the presence of molecular sieves (4 Å). After 30 min, 10 mL of this solution was added under N_2 at room temperature to a stirred solution of **10b** or **11b** (110 mg; 0.22 mmol) in CH_2Cl_2

(20 mL). The reaction mixture was refluxed in the presence of molecular sieves (4 Å) for 1 h 30 min and then allowed to cool to room temperature, quenched with water, and extracted with dichloromethane. The separated organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. Chromatography of the residual oil (elution with ether/petroleum ether 3/7) yielded **24b** (62 mg; 80%) as an oil. **24b**. $R_f = 0.33$ (E/PE 3/7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 3H, *Me*); 1.68 (s, 3H, *Me*); 1.98−2.15 (m, 2H, CH_2); 2.32 (broad d, $J = 16.5$ Hz, 2H, CH_2); 3.45 to 3.52 (m, 1H, H_7); 3.78 (s, 3H, CO_2*Me*); 3.93 (td, $J = 11.2$, 5.6 Hz, 1H, H_8); 6.23 (d, $J = 14.8$ Hz, 1H, H_2 or H_5); 6.58 (d, $J = 15.3$ Hz, 1H, H_2 or H_5); 7.24 (dd, $J = 15.0$, 10.8 Hz, 1H, H_3 or H_4); 7.35 (dd, $J = 15.2$, 11.2 Hz, 1H, H_3 or H_4); 7.46 (2H, arom); 7.56 (1H, arom); 7.98 (2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7 and 19.0 (Me); 34.6 and 35.8 (*C*H_2); 44.3 (C_8); 47.4 (C_7); 51.9 (CO_2*Me*); 124.3 and 124.7 (Me*C*═*C*Me); 128.5, 128.6, and 128.6 (*C*H arom); 133.1, 134.9, 138.8, and 141.8 (C_2 to C_5); 136.2 (*C* arom); 166.3 (C_1); 202.4 and 203.2 (C_6 and C_9). IR (film): 1596 (arom and alkene), 1682 (ketone), 1713 (ester). Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.05; H, 7.25.

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