

Bromination and alkylation of tricarbonyl(η^1, η^2 -but-3-en-1-yl)iron(0) anion complexes

Ming-Chang P. Yeh * and Chong-Chen Hwu

Department of Chemistry, National Taiwan Normal University 88, Sec. 5, Roosevelt road, Taipei (Taiwan)
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Abstract

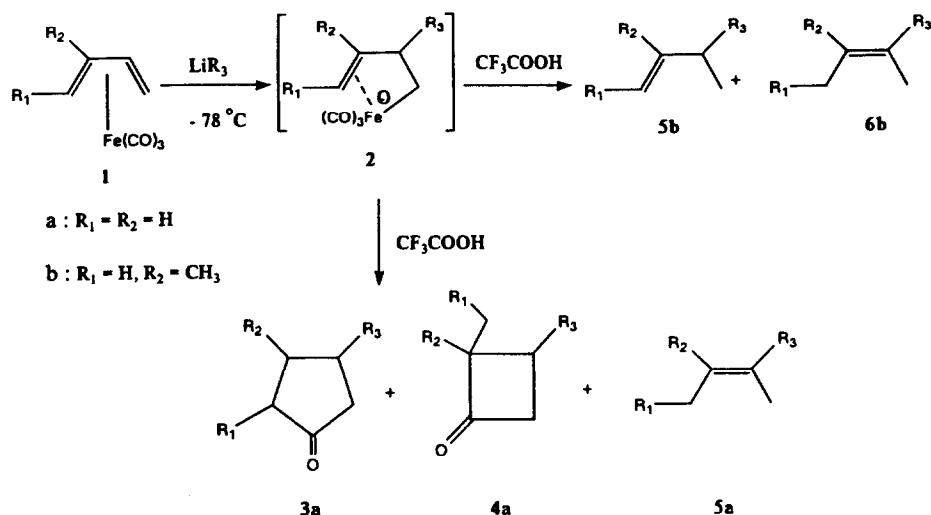
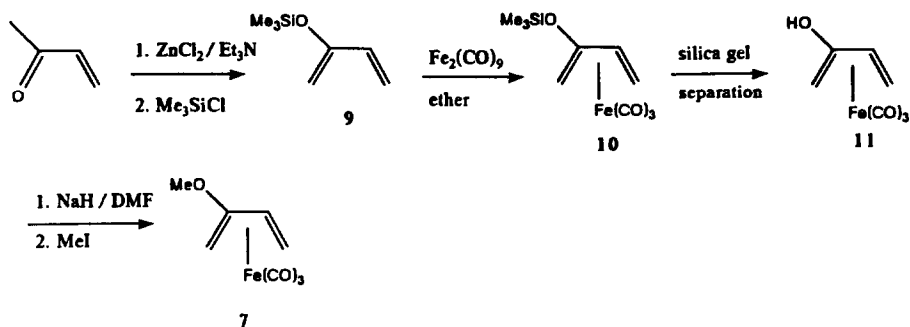
Reactive carbon nucleophiles add to tricarbonyl(η^4 -1,3-diene)iron(0) complexes at -78°C to produce putative internally coordinated tricarbonyl(η^1, η^2 -but-3-en-1-yl)iron(0) anion complexes. Treatment of the reactive intermediates with bromine, followed by an aqueous process, leads to γ, δ -unsaturated acids. Reaction of the intermediates with iodomethane or benzyl bromide gives γ, δ -unsaturated ketones after carbonyl insertions. Benzoyl chloride is also observed to react with the postulate intermediates to form γ, δ -unsaturated benzophenone derivatives.

Introduction

The metal-activated nucleophilic addition to polyene ligands opened new strategies for organic synthesis and has been an area of high activity [1]. Among them, nucleophilic addition to tricarbonyl(η^4 -1,3-diene)iron(0) complexes has been studied by the Semmelhack group [2]. Reactive carbanions added to (η^4 -1,3-diene) $\text{Fe}(\text{CO})_3$ **1** at -78°C produced intermediates that had the expected chemical properties of tricarbonyl(η^1, η^2 -but-3-en-1-yl)iron(0) anion complexes **2**. However, the products obtained from acid quenching of **2** were highly substrate dependent. For example, acid cleavage of **2a** ($\text{R}_1 = \text{R}_2 = \text{H}$) afforded a mixture of cyclopentanone **3a**, cyclobutanone **4a**, and olefin **5a**, while protonation of **2b** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}_3$) gave only olefins **5b** and **6b** [3]. We herein report on the bromination and alkylation of anion intermediate **2** to give γ, δ -unsaturated acids and ketones, respectively, through a unique reaction pathway. Furthermore, this coupling reaction furnishes two carbon–carbon bonds and certainly has important potential in organic synthesis.

Results and discussion

(η^4 -2-Methoxy-1,3-butadiene) $\text{Fe}(\text{CO})_3$ **7** [4] and (η^4 -2-methoxy-1,3-cyclohexadiene) $\text{Fe}(\text{CO})_3$ **8** [4] were prepared in a similar way starting from methyl vinyl ketone and 2-cyclohexen-1-one respectively. The synthesis of complex **7** is outlined

Scheme 1. Protonation of $(\eta^1, \eta^2\text{-but-3-en-1-yl})\text{Fe}(\text{CO})_3$ anion intermediates **2**.Scheme 2. The synthesis of complex **7**.

in Scheme 2. Treatment of methyl vinyl ketone with chlorotrimethylsilane in base gave diene **9** (80%) [5]. Complexation of **9** with $\text{Fe}_2(\text{CO})_9$ in anhydrous ethyl ether produced complex **10**. Complex **10** lost the trimethylsilyl group during separation on silica gel to form **11** in quantitative yield. Protection of **11** with sodium hydride/iodomethane in *N,N*-dimethylformamide gave complex **7** (91%). Complexes **12**–**14** were prepared by refluxing the corresponding free dienes with $\text{Fe}_2(\text{CO})_9$ in anhydrous ethyl ether for 16 h [6*]. All complexes were purified by flash column chromatography then short-path distillation under reduced pressure. The spectroscopic data of the complexes were consistent with those found in the literature.

Reactive carbanions (1.2 eq) added to tricarbonyl(η^4 -1,3-diene)iron(0) complexes at -78°C for 2 h, followed by trapping the anion intermediates with

* Reference number with asterisk indicates a note in the list of references.

bromine (0.9 eq), produce mainly the γ,δ -unsaturated acids in moderate yields. With the exception of complexes **7** and **8** (entries 1 and 2, Table 1), intramolecular cyclization occurred to generate lactones **15** and **16** respectively. A possible mechanism for the formation of the acids and lactones is shown in Scheme 3. The initial addition of the nucleophile (diphenylmethyl anion) at the internal position of complex **7** would give the homoallyl intermediate **20**, which after bromination generates **21**. The postulated intermediate **21** could undergo carbonyl insertion and then reductive elimination to form acyl bromide **22**. Reaction of **22** with H_2O would produce acid **23**. This reaction pathway has also been proposed for the alkylation, and bromination of tetracarbonyliron dianion [7]. With the pendant vinyl ether at the γ -position of the acid, protonation of the double bond (**23**) followed by cyclization (**24**) gave γ -lactone **15**. The spectroscopic evidence for lactones **15** and **16** was based upon the frequencies of the CO stretching bands. The infrared spectra exhibited absorptions at 1788 (lactone **15**) and 1772 (lactone **16**) cm^{-1} for the stretching vibration of CO in the γ -lactone rings. These absorptions were consistent with those found in most γ -lactone derivatives (1795–1760 cm^{-1}) [8*]. The carbon-13 NMR spectra exhibited signals for carbonyl at 175.0 (lactone **15**) and 175.6 (lactone **16**) ppm. These figures were also close to the chemical shift of carbonyl of most γ -lactone derivatives (178 ppm) [9*]. Moreover, peaks at 109.4 (lactone **15**) and 111.8 (lactone **16**) ppm strongly suggest that the molecules contain ketal carbon centers [10*]. The *syn* stereochemistry for the diphenylmethyl and methoxy units was assigned on the basis of their 2D NOESY NMR spectra. The spectra clearly showed the correlation between the aromatic and methoxy protons. The stereochemistry of compound **17** was assigned as the *trans* isomer based upon the coupling constant (9.8 Hz) between the Hs at C-3, 4 and similar compounds obtained via different routes [1e].

We also examined the possibility of trapping homoallyl anion intermediates **2** with carbon electrophiles. Treatment of **7** with diphenylmethyl anion (1.2 eq) followed by addition of benzyl bromide (excess) gave the γ,δ -unsaturated ketone **26** in 40% yield. The reaction proceeded smoothly for several combinations of carbon nucleophiles and carbon electrophiles. Table 1 summarizes the results of the addition/trapping sequence. In general, γ,δ -unsaturated ketones were obtained in moderate yields (20–40%). However, the yields of ketones increased when reactions were performed under an atmosphere of CO. For example, γ,δ -unsaturated ketone **26** was isolated in 78% yield by introducing CO (approx. 14 psi) right after quenching the reaction mixture with benzyl bromide. A possible explanation for the increased yield is shown in Scheme 4. Treatment of the putative intermediate **20** with benzyl bromide would produce **32**. Carbonyl insertion to the carbon–iron bond generated the acyliron intermediate **33**. Reductive elimination of **33** gave the γ,δ -unsaturated ketone **26**. Therefore, an atmosphere of CO might drive the reaction toward completion.

The enol ether of the resulting γ,δ -unsaturated ketones could easily be hydrolyzed to 1,4-diones (**29**, **30**, entries 10, 11) under acid conditions. It should be noted that this method reverses the regular conjugate addition/trapping sequence elaborated on α,β -unsaturated ketones. In most cases, organocuprates add at the β -position of conjugated enones (1,4-addition). Electrophilic trapping of the resulting enolates led to α (electrophiles), β (nucleophiles) disubstituted ketones. However, addition/trapping of complex **7** produced α (nucleophiles), β (electro-

Table 1

Reaction of $(\eta^1, \eta^2\text{-but-3-en-1-yl})\text{Fe}(\text{CO})_3$ anion complexes with electrophiles ^a

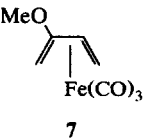
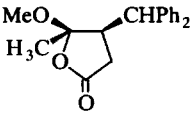
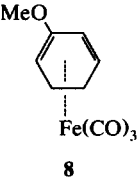
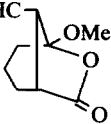
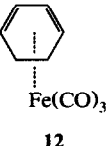
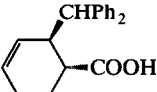
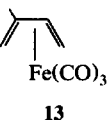
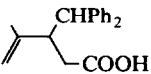
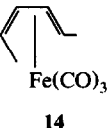
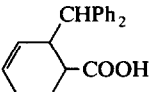
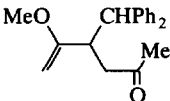
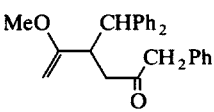
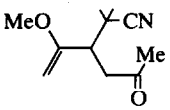
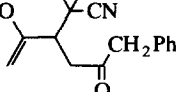
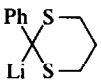
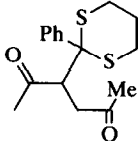
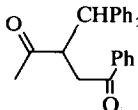
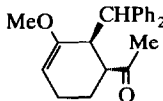
Entry	Complexes	Nucleophiles	Electrophiles	Products ^b
1	 7	LiCHPh ₂	Br ₂ / CO / H ₂ O	 15 (42%)
2	 8	LiCHPh ₂	Br ₂ / CO / H ₂ O	 16 (39%)
3	 12	LiCHPh ₂	Br ₂ / CO / H ₂ O	 17 (58%)
4	 13	LiCHPh ₂	Br ₂ / CO / H ₂ O	 18 (48%)
5	 14	LiCHPh ₂	Br ₂ / CO / H ₂ O	 19 (33%)
6	7	LiCHPh ₂	MeI / CO	 25 (63%)
7	7	LiCHPh ₂	PhCH ₂ Br / CO	 26 (78%)
8	7	Li(CH ₃) ₂ CN	MeI / CO	 27 (46%)

Table 1 (continued)

Entry	Complexes	Nucleophiles	Electrophiles	Products ^b
9	7	LiC(CH ₃) ₂ CN	PhCH ₂ Br/CO	 28 (56%)
10	7		MeI/CO	 29 (17%) ^c
11	7	LiCHPh ₂	PhCOCl	 30 (18%) ^c
12	8	LiCHPh ₂	MeI/CO	 31 (40%)

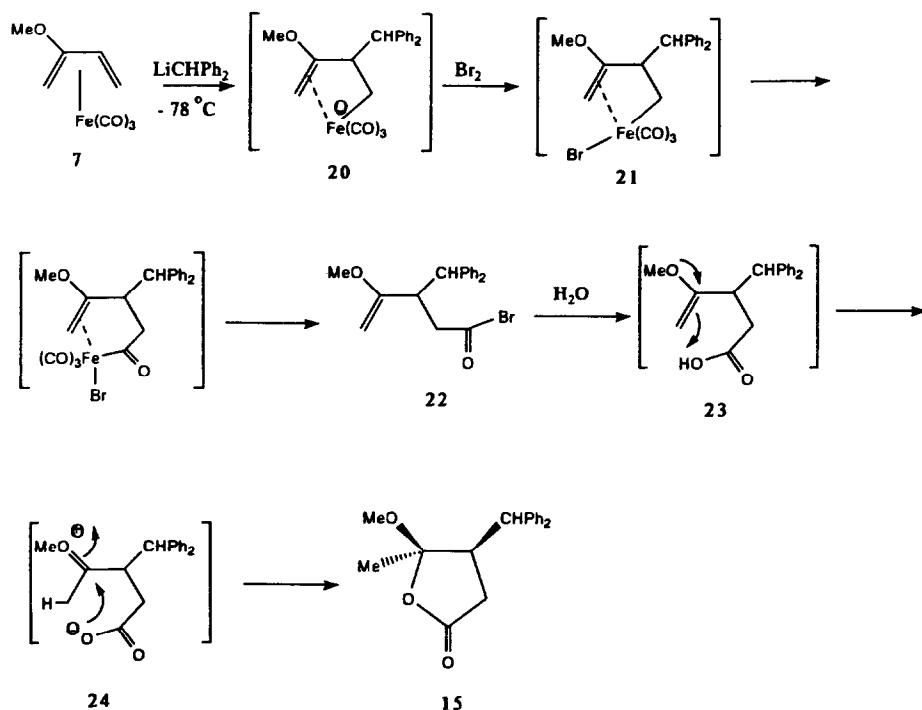
^a All reactions were performed under an atmosphere of CO. ^b All indicated yields are isolated yields of analytically pure compounds. Satisfactory spectral data (IR, ¹H and ¹³C NMR, high resolution mass spectra) were obtained for all compounds. ^c Yields were obtained after acid hydrolysis of the corresponding vinyl ether.

philes) disubstituted ketones. Thus, complex **7** showed the umpolung reactivity of methyl vinyl ketone [11*].

In conclusion, we have shown that upon reaction with bromine, tricarbonyl(η^1, η^2 -but-3-en-1-yl)iron(0) anion complexes give γ, δ -unsaturated acids after an aqueous process. The same reaction intermediates also reacted with iodomethane, benzyl bromide and benzoyl chloride to give γ, δ -unsaturated ketones as the major products. The addition/trapping reaction of tricarbonyl(η^4 -2-methoxy-1,3-dienes)iron(0) complexes represents a polarity inverted synthon of α, β -unsaturated enones.

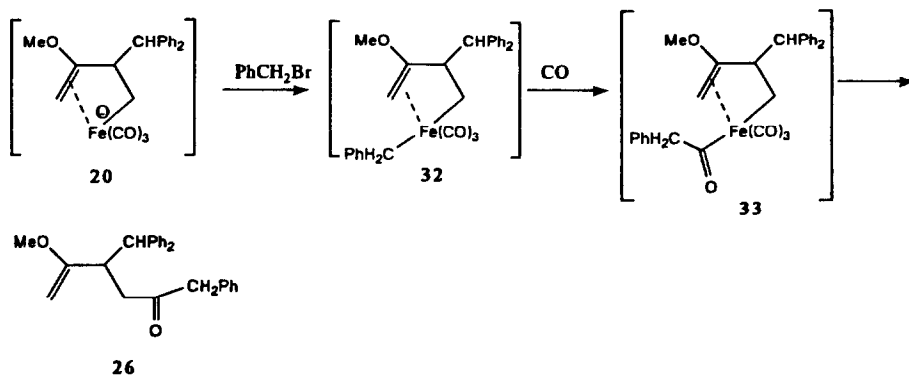
Experimental

¹H NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 200 MHz and are quoted in ppm down-field from TMS. ¹³C NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 50.5 MHz and are quoted relative to chloroform-*d* (77.00). Infrared spectra (4000–800 cm⁻¹) were recorded on a Perkin-Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film (1602 cm⁻¹). All spectra were recorded as original liquid between KBr plates or as dichloromethane solution in KBr cells. Peaks intensities were

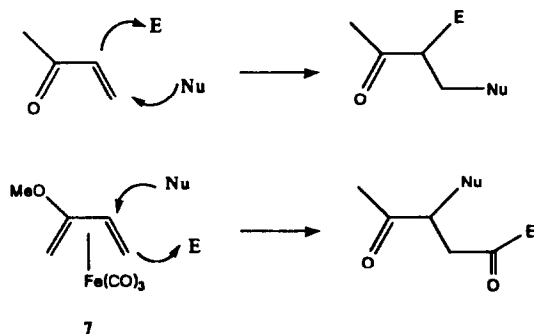


Scheme 3. The proposed reaction pathway for the formation of γ -lactone **15**.

recorded as strong (s), medium (m), or weak (w). Mass spectra were recorded on the AEI MS-902 instrument and the Kratos MS-50 at the Department of Chemistry, Academia Sinica, Taipei. Only the parent ion in the mass spectra is generally reported to establish molecular weight. The data are expressed with the nominal fragment weight followed in parentheses by the percent intensity (taking the biggest peak as 100%). High resolution mass spectra (HRMS) data were obtained on an AEI MS-9 double focusing mass spectrometer in the Department of Chemistry, Academia Sinica, Taipei.



Scheme 4. The proposed reaction pathway for the formation of the γ/δ -unsaturated ketone **28**.



Scheme 5. Complex 7 shows the umpolung reactivity of methyl vinyl ketone.

Standard Schlenk techniques were used for all manipulations involving oxygen or moisture sensitive experiments. Diethyl ether and THF were dried over sodium and redistill under nitrogen from sodium benzophenone ketyl.

Generation of lithio diphenylmethane

To a solution of diphenylmethane (0.25 mL, 1.50 mmol) in THF (3 mL), in a Schlenk flask equipped with a rubber septum and a magnetic stirrer, under argon at -78°C , was added rapidly via syringe a solution of *n*-butyllithium (0.9 mL, 1.35 mmol, 1.50 *M* in hexane), followed by addition of 1 mL of hexamethylphosphoramide (HMPA). The resulting orange-red solution was stirred at 0°C for 1.5 h. This solution was used immediately in reaction with iron complexes (1 mmol in 1 mL THF, see below).

Generation of 2-lithio-2-methylpropionitrile

To a solution of diisopropylamine (0.21 mL, 1.50 mmol) in THF (3 mL), in a Schlenk flask equipped with a rubber septum and a magnetic stirrer, under argon at -78°C , was added rapidly via syringe a solution of *n*-butyllithium in hexane (0.9 mL, 1.35 mmol, 1.50 *M* in hexane). The mixture was stirred at -78°C for 20 min. To the solution prepared above 2-methylpropionitrile (0.13 mL, 1.40 mmol), was added rapidly neat via syringe, followed by addition of 1.00 mL of hexamethylphosphoramide (HMPA). The resultant light yellow solution was stirred at -78°C for 20 min, and was used immediately in reaction with iron complexes (1.00 mmol in 1.00 mL THF, see below).

Generation of 2-lithio-2-phenyl-1,3-dithiane

2-Phenyl-1,3-dithiane (0.49 g, 2.50 mmol) was placed in a 100 mL Schlenk flask under argon. The reaction was cooled to -78°C and 3 mL of THF added. A solution of *n*-butyllithium (1.50 mL, 2.25 mmol, 1.5 *M* in hexane) was then added to the mixture followed by 1 mL of HMPA. The resulting orange-red solution was stirred at 0°C for 2 h and used immediately in reaction with iron complexes (1.00 mmol in 1.00 mL of THF, see below).

General procedure for addition of anions to $(\eta^4\text{-1,3-butadienes})\text{Fe}(\text{CO})_3$ complexes

Formation of tricarbonyl(η^1, η^2 -but-3-en-1-yl)iron(0) anion intermediates. To a solution of an anion (1.5 mmol, see above) at -78°C under argon was added

rapidly via syringe a $(\eta^4\text{-1,3-diene})\text{Fe}(\text{CO})_3$ complex (1.00 mmol) in 1.00 mL of THF. The temperature was maintained at -78°C for 2 h.

Synthesis of $(\eta^4\text{-2-methoxy-1,3-butadiene})\text{Fe}(\text{CO})_3$ 7 [12]. To a solution of 35 mL of triethylamine was added via spatula 3.6 g of zinc chloride [13*]. The reaction mixture was stirred at 23°C until a suspension formed (approx. 1 h). With the solution at 23°C , a solution of 10 mL (0.12 mol) of methyl vinyl ketone in 40 mL of benzene was added via syringe followed by addition of 25 mL of chlorotrimethylsilane. The reaction mixture was diluted with 200 mL of anhydrous ethyl ether after stirring at 70°C for 19 h. The solid suspension was filtered through Celite and the Celite was fully washed with 100 mL of ether. The solvent was concentrated on a rotary evaporator. Flash distillation under vacuum gave 7.6 g of the desired diene **9**. ^1H NMR (CDCl_3 , 200 MHz): δ 6.20 (dd, J 17.0, 10.5 Hz, 1H), 5.47 (dd, J 17.0, 2.1 Hz, 1H), 5.09 (dd, J 10.5, 2.1 Hz, 1H), 4.36 (brs, 2H), 0.238 (s, 9H). Diene **9** was used immediately for the complexation with $\text{Fe}_2(\text{CO})_9$ without further purification. To a solution of 7.6 g (53.5 mmol) of diene **9** in 65 mL of anhydrous ethyl ether was added 17 g of $\text{Fe}_2\text{C}(\text{CO})_9$ slowly via spatula. The reaction was stirred under reflux for 12 h. The reaction mixture was then filtered through a bed of Celite and the Celite was washed with 50 mL of ether. The solvent was concentrated on a rotary evaporator.

Flash column chromatography of the residue on silica gel with hexane/ethyl acetate (30:1) as eluent afforded crude complex **11**. The crude complex **11** was used in the next step without purification. ^1H NMR (CDCl_3 , 200 MHz): δ 5.27 (br t, 1H), 2.08 (dd, 1H), 1.45 (dd, 1H), 0.25 (d, 1H), -0.36 (dd, 1H). To a solution of 0.82 g (27 mmol) of sodium hydride in 50 mL of *N,N*-dimethylformamide [14*] at 0°C under argon was added slowly via syringe a solution of 4.4 g (20.9 mmol) of complex **11** in 30 mL of *N,N*-dimethylformamide. The reaction mixture was allowed to stir at 0°C for 30 min. Iodomethane (1.7 mL, 27 mmol) was added to the solution via syringe. The reaction mixture was then diluted with 300 mL of hexane after being stirred at 23°C for 4 h. The hexane was washed three 200 mL portions of water, three 200 mL portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate and finally concentrated on a rotary evaporator. Flash column chromatography on silica gel with hexane/ethyl acetate (3:1) as eluent followed by short-path distillation ($50\text{--}60^\circ\text{C}$, 0.08 mmHg) produced 2.82 g (12.5 mmol, 91%) of complex **7**. ^1H NMR (CDCl_3 , 200 MHz): δ 5.13 (brt, J 6.9 Hz, 1H), 3.65 (s, 3H), 2.13 (dd, J 4.4, 2.0 Hz, 1H), 1.44 (dd, J 7.0, 2.5 Hz, 1H), 0.22 (d, J 4.4 Hz, 1H), -0.31 (dd, J 8.0, 2.5 Hz, 1H).

Synthesis of $(\eta^4\text{-2-methoxy-1,3-cyclohexadiene})\text{Fe}(\text{CO})_3$ 8 [12]. To a solution of 16 mL of triethylamine was added via spatula 1.5 g of zinc chloride [13*]. The reaction mixture was stirred at 23°C until a suspension formed (approx. 1 h). With the solution at 23°C , a solution of 5 mL (0.05 mol) of 2-cyclohexen-1-one in 16 mL of benzene was added via syringe followed by addition of 13 mL of chlorotrimethylsilane. The reaction mixture was diluted with 200 mL of anhydrous ethyl ether after stirring at 70°C for 19 h. The solid suspension was filtered through Celite and the Celite was fully washed with 100 mL of ether. The solvent was concentrated on a rotary evaporator. Flash distillation under vacuum gave 7.6 g of the desired diene. ^1H NMR (CDCl_3 , 200 MHz): δ 5.78 (m, 1H), 5.57 (m, 1H), 4.75 (m, 1H), 1.95–2.05 (m, 4H), 0.07 (s, 9H). The crude diene was used without further purification. To a solution of 7.4 g (44 mmol) of the diene obtained above in 60 mL

of anhydrous ethyl ether was added 19 g of $\text{Fe}_2(\text{CO})_9$, slowly via spatula. The reaction was stirred under reflux for 16 h. The reaction mixture was then filtered through a bed of Celite and the Celite was washed with 50 mL of ether. The solvent was concentrated on a rotary evaporator. Flash column chromatography of the residue on silica gel with hexane/ethyl acetate (20:1) afforded a crude oil. The crude oil was used in the next step without purification. To a solution of 1.0 g (33 mmol) of sodium hydride in 5 mL of *N,N*-dimethylformamide [14*] at 0 °C under argon was added slowly via syringe a solution of 6.0 g (25 mmol) of the crude complex in 30 mL of *N,N*-dimethylformamide. The reaction was stirred at 0 °C for 40 min. Iodomethane (3.0 mL, 48 mmol) was added to the solution via syringe. The reaction mixture was then diluted with 300 mL of hexane/ethyl acetate (1:1) after being stirred at 23 °C for 5 h. The solution was washed three 200 mL portions of water, three 200 mL portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate and finally concentrated on a rotary evaporator. Flash column chromatography of the residue on silica gel with hexane/ethyl acetate (10:1) as eluent followed by short-path distillation (50–60 °C, 0.08 mmHg) produced 4.8 g (19 mmol, 77%) of complex **8**. ^1H NMR (CDCl_3 , 200 MHz): δ 5.09 (dd, *J* 6.6, 2.3 Hz, 1H), 3.61 (s, 3H), 3.45 (m, 1H), 2.76 (m, 1H), 1.72 (m, 2H), 1.52 (m, 2H).

General method for the synthesis of complexes 12–14

Complexes **12–14** were generated by refluxing 1 mol-eq of the corresponding free dienes with 4 mol-eq of $\text{Fe}_2(\text{CO})_9$ in anhydrous ethyl ether for 14 h. The resulting solution was filtered through a bed of Celite and solvent was concentrated on a rotary evaporator. Flash column chromatography of the residue on silica gel with hexane as eluent followed by vacuum distillation generated complexes **12–14**. Complex **12** (51%) [2]: ^1H NMR (CDCl_3 , 200 MHz): δ 5.3 (d, *J* 5.2 Hz, 2H), 3.3 (m, 2H), 1.7 (s, 4H). Complex **13** (60%) [15]: ^1H NMR (CDCl_3 , 200 MHz): δ 5.3 (dd, *J* 9.1, 7.0 Hz, 1H), 2.2 (s, 3H), 1.8 (d, *J* 2.0 Hz, 1H), 1.6 (dd, *J* 7.0, 2.1 Hz, 1H), 0.3 (d, *J* 2.0 Hz, 1H), 0.02 (dd, *J* 9.1, 2.0 Hz, 1H). Complex **14** (55%) [16]: ^1H NMR (CDCl_3 , 200 MHz): δ 5.25 (dd, *J* 8.6, 5.0 Hz, 1H), 5.06 (dd, *J* 8.6, 3.3 Hz, 1H), 2.64 (m, 1H), 2.36 (m, 1H), 1.45 (d, *J* 6.1 Hz, 3H), 1.09 (d, *J* 6.1 Hz, 3H).

Reaction of complex 7 with lithio diphenylmethane followed by bromination

To a solution of complex **7** (1.00 mmol) and lithio diphenylmethane (1.50 mmol, see above) at –78 °C was added bromine (0.04 mL, 0.80 mmol). The reaction was pressed by an atmosphere of CO and stirred at –78 °C for 1 h. The resultant reaction mixture was diluted with water (10 mL) and stirred at 25 °C for 40 min. The solution was extracted with ethyl acetate (2 × 100 mL). The combined extracts were washed with three 100 mL portions of water, three 100 mL portions of saturated sodium chloride solution, dried over magnesium sulfate, filtered through Celite, and finally concentrated on a rotary evaporator. Flash column chromatography of the residue (0.52 g) on silica gel with hexane/ethyl acetate (20:1) as eluent afforded a fraction containing γ -lactone **15** (0.10 g, 0.34 mmol, 42%). Recrystallization of the solid from hexane/ethyl acetate produced a white crystalline compound. γ -Lactone **15**: m.p. 110–112 °C. ^1H NMR (CDCl_3 , 200 MHz): δ 7.28–7.08 (m, 10H), 4.14 (d, *J* 11.5 Hz, 1H), 3.25 (s, 3H), 3.17 (td, *J* 11.3, 2.1 Hz, 1H), 2.39 (brs, 1H), 2.34 (d, *J* 2.1 Hz, 1H), 0.86 (s, 3H). The *syn* relationship

between the methoxy and the diphenyl methyl groups was assigned on the basis of its 2D-NOESY experiment. The spectrum clearly showed the correlation between the methoxy and aromatic protons. None of the correlation between the methyl and the aromatic protons was found. ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 175.0, 142.9, 142.6, 128.8, 128.5, 128.3, 127.7, 120.7, 109.4, 51.5, 50.9, 50.2, 35.0, 20.9. IR (CH_2Cl_2): 3087 (s), 2995 (s), 1788 (s, CO), 1664 (s) cm^{-1} . Mass spec. (m/e): 296 (M^+ , 2), 264 (23), 246 (15), 221 (100), 193 (20), 180 (23), 167 (82), 251 (8), 129 (5), 115 (8), 91 (5), 83 (35), 81 (8), 69 (10). HRMS: $\text{C}_{19}\text{H}_{20}\text{O}_3$ calc.: 296.1412. Found: 296.1428.

Reaction of complex 8 with lithio diphenylmethane followed by bromination

To a solution of complex **8** (0.5 g, 2.00 mmol) and lithio diphenylmethane (2.40 mmol, see above) at -78°C was added bromine (0.08 mL, 1.60 mmol). The reaction mixture was pressed by an atmosphere of CO and stirred at -78°C for 1 h. After the regular aqueous process (see above), the solution was concentrated. Flash column chromatography of the residue (0.90 g) on silica gel with hexane/ethyl acetate (20:1) as eluent produced a fraction containing lactone **16** (0.20 g, 0.62 mmol, 39%). Recrystallization of the solid from hexane gave a white crystalline compound. Lactone **16**: m.p. $192\text{--}194^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 7.35–7.16 (m, 10H), 4.16 (d, J 11.9 Hz, 1H), 3.48 (dd, J 11.9, 4.4 Hz, 1H), 2.90 (s, 3H), 2.77 (m, 1H), 2.20 (m, 1H), 1.97 (m, 1H), 1.72 (m, 4H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 175.5, 142.1, 141.6, 129.5, 128.9, 128.4, 128.3, 127.5, 127.3, 111.9, 50.0, 48.8, 48.0, 45.4, 27.7, 18.9, 18.8. IR (CH_2Cl_2): 3054 (m), 2954 (m), 2882 (m), 1772 (s), 1601 (m), 1495 (m), 1450 (m), 1425 (m), 1359 (m), 1289 (m), 1225 (m), 1118 (m), 1062 (m) cm^{-1} . Mass spec. (m/e): 320 (M^+ , 27), 294 (54), 262 (14), 239 (15), 180 (100), 167 (20), 155 (27), 111 (70). HRMS: $\text{C}_{21}\text{H}_{22}\text{O}_2$ calc.: 322.1568. Found: 322.1571.

Reaction of complex 12 with lithio diphenylmethane followed by bromination

To a solution of complex **12** (0.22 g, 1.00 mmol) and lithio diphenylmethane (1.44 mmol, see above) at -78°C was added bromine (0.04 mL, 0.80 mmol). The reaction mixture was pressed by an atmosphere of CO and stirred at -78°C for 1 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (0.60 g) on silica gel with hexane/ethyl acetate (5:1) as eluent produced a fraction containing γ,δ -unsaturated acid **17** (0.14 g, 0.46 mmol, 58%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline compound. γ,δ -Unsaturated acid **17**: m.p. $152\text{--}154^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 7.19 (m, 10H), 5.62 (d, J 10.3 Hz, 1H), 5.42 (dt, J 10.3, 1.5 Hz, 1H), 3.79 (d, J 10.4 Hz, 1H), 3.47 (m, 1H), 2.47 (dd, J 9.8, 4.6 Hz, 1H), 1.98 (m, 2H), 1.84 (m, 2H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 182.1, 142.9, 142.6, 128.5, 128.4, 128.2, 127.9, 127.6, 127.3, 126.5, 126.4, 56.5, 42.0, 39.8, 22.9, 22.6. IR (CH_2Cl_2): 3028 (s), 2928 (s), 1702 (s), 1599 (m), 1492 (m), 1055 (m), 908 (s), 849 (m), 731 (s) cm^{-1} . Mass spec. (m/e): 292 (M^+ , 20), 279 (37), 267 (16), 256 (60), 241 (41), 228 (39), 213 (38), 205 (55), 193 (48), 179 (100). HRMS: $\text{C}_{18}\text{H}_{20}\text{O}_2$ calc.: 292.1460. Found: 292.1460.

Reaction of complex 13 with lithio diphenylmethane followed by bromination

To a solution of complex **13** (0.42 g, 2.00 mmol) and lithio diphenylmethane (3.00 mmol, see above) at -78°C was added bromine (0.1 mL, 2.00 mmol). The

reaction mixture was pressed by an atmosphere of CO and stirred at -78°C for 1 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (1.12 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing γ,δ -unsaturated acid **18** (0.27 g, 0.96 mmol, 48%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline compound. γ,δ -Unsaturated acid **18**: m.p. $179\text{--}180^{\circ}\text{C}$ (decomposed). ^1H NMR (CDCl_3 , 200 MHz): δ 7.03–7.07 (m, 10H), 4.84 (s, 1H), 4.73 (d, J 1.2 Hz, 1H), 3.80 (d, J 11.9 Hz, 1H), 3.55 (m, 1H), 2.35 (m, 2H), 1.553 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 177.4, 144.9, 142.9, 142.8, 128.5, 128.2, 128.1, 128.0, 126.7, 126.3, 115.06, 55.4, 47.6, 37.49, 18.9. IR (CH_2Cl_2): 3512 (w), 3065 (m), 3026 (m), 2973 (m), 2920 (m), 2803 (m), 1734 (m), 1707 (s), 1596 (m), 1487 (m), 1446 (m), 1441 (m), 1285 (m), 826 (m), 649 (s) cm^{-1} . Mass spec. (m/e): 280 (M^+ , 3), 256 (2), 220 (3), 203 (30), 167 (100), 152 (9), 139 (10), 115 (9). HRMS: $\text{C}_{19}\text{H}_{20}\text{O}_2$ calc.: 280.1463. Found: 280.1458.

Reaction of complex 14 with lithio diphenylmethane followed by bromination

To a solution of complex **14** (0.88 g, 4.00 mmol) and lithio diphenylmethane (6.00 mmol, see above) at -78°C was added bromine (0.2 mL, 4.00 mmol). The reaction mixture was pressed by an atmosphere of CO and stirred at -78°C for 1 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (1.69 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing γ,δ -unsaturated acid **19** (0.36 g, 1.26 mmol, 33%) as a clean oil. γ,δ -Unsaturated acid **19**: ^1H NMR (CDCl_3 , 200 MHz): δ 7.16 (m, 10H), 5.45 (m, 1H), 5.16 (m, 1H), 4.23 (d, J 10.4 Hz, 1H), 3.40 (m, 1H), 2.57 (m, 1H), 1.52 (d, J 6.3 Hz, 3H), 1.05 (d, J 6.2 Hz, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 180.9, 143.6, 143.4, 129.5, 128.9, 128.5, 128.2, 128.0, 127.6, 126.9, 126.3, 125.9, 54.5, 44.6, 18.9, 15.7, 13.4. IR (CH_2Cl_2): 3491 (m), 3024 (s), 2960 (s), 1701 (s), 1594 (s), 1429 (s), 1701 (s), 1594 (s), 1429 (s), 1338 (m), 1291 (m), 1214 (m), 1075 (m), 1023 (m), 903 (s) cm^{-1} . Mass spec. (m/e): 294 (M^+ , 4), 220 (5), 205 (4), 180 (12), 167 (100), 152 (4), 118 (16), 91 (4). HRMS: $\text{C}_{19}\text{H}_{22}\text{O}_2$ calc.: 294.1621. Found: 294.1613.

Reaction of complex 7 with lithio diphenylmethane followed by methylation

To a solution of complex **7** (0.22 g, 1.00 mmol) and lithio diphenylmethane (1.35 mmol, see above) at -78°C was added iodomethane (1.0 mL, 10.0 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 16 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (0.55 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing γ,δ -unsaturated ketone **25** (0.19 g, 0.63 mmol, 63%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline compound. γ,δ -Unsaturated ketone **25**: m.p. $64\text{--}66^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 7.29–7.03 (m, 10H), 3.96 (d, J 11.9 Hz, 1H), 3.77 (d, J 2.2 Hz, 1H), 3.65 (d, J 2.2 Hz, 1H), 3.53 (td, J 10.0, 3.4 Hz, 1H), 3.27 (s, 3H), 2.67 (dd, J 16.1, 9.9 Hz, 1H), 2.25 (dd, J 16.0, 3.4 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 207.8, 161.9, 143.2, 142.7, 128.7, 128.2, 127.9, 126.5, 125.9, 84.3, 54.6, 54.3, 45.8, 45.4, 30.6. IR (CH_2Cl_2): 3084 (m), 3060 (m), 3026 (m), 3001 (m), 2995 (m), 2920 (m), 2916 (m), 1712 (s), 1657 (m), 1622 (m), 1599 (m), 1583 (m),

1540 (m), 1490 (s), 1464 (s) cm^{-1} . Mass spec. (m/e): 294 (M^+ , 13), 276 (4), 262 (20), 251 (12), 236 (9), 219 (15), 204 (8), 185 (11), 167 (100), 152 (12), 129 (10), 69 (9). HRMS: $\text{C}_{20}\text{H}_{22}\text{O}_2$ calc.: 294.1620. Found: 294.1628. Found: 294.1628. γ,δ -Unsaturated ketone **25** was hydrolyzed under acidic condition (2 *N* HCl in MeOH) to give the corresponding dione, m.p. 106–108 °C. ^1H NMR (CDCl_3 , 200 MHz): δ 7.33–7.06 (m, 10H), 3.84 (m, 2H), 2.91 (dd, J 19.1, 8.9 Hz, 1H), 2.44 (dd, J 18.9, 2.1 Hz, 1H), 1.92 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 212.8, 207.4, 141.9, 141.6, 128.7, 128.0, 127.9, 126.9, 54.3, 50.8, 46.5, 32.6, 29.5. IR (CH_2Cl_2): 3061 (m), 3029 (m), 3003 (m), 2934 (m), 1707 (s), 1597 (m), 1490 (m) cm^{-1} . Mass spec. (m/e): 280 (M^+ , 2), 262 (30), 237 (4), 223 (75), 207 (30), 193 (5), 179 (10), 167 (100), 152 (18), 115 (5), 91 (5). HRMS: $\text{C}_{19}\text{H}_{20}\text{O}_2$ calc.: 280.1463. Found: 280.1459.

Reaction of complex 7 with lithio diphenylmethane followed by trapping with benzyl bromide

To a solution of complex **7** (0.22 g, 1.00 mmol) and lithio diphenylmethane (1.50 mmol, see above) at -78°C was added benzyl bromide (1.0 mL, 8.00 mmol). The reaction was pressed immediately by an atmosphere of CO and stirred at 23°C for 12 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (1.60 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing γ,δ -unsaturated ketone **26** (0.29 g, 0.78 mmol, 78%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline compound. γ,δ -Unsaturated ketone **26**, m.p. 58–60 °C. ^1H NMR (CDCl_3 , 200 MHz): δ 7.24–6.95 (m, 15H), 3.93 (d, J 11.9 Hz, 1H), 3.72 (d, J 2.2 Hz, 1H), 3.63 (s, 1H), 3.59 (d, J 2.2 Hz, 1H), 3.52 (m, 1H), 3.42 (s, 1H), 3.17 (s, 3H), 2.69 (dd, J 16.0, 9.8 Hz, 1H), 2.25 (dd, J 16.0, 3.4 Hz, 1H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 207.1, 161.7, 143.2, 142.6, 133.9, 129.4, 128.7, 128.5, 128.3, 127.9, 127.0, 126.8, 126.5, 126.0, 84.4, 54.5, 54.2, 50.6, 49.0, 45.5, 43.8. IR (CH_2Cl_2): 3084 (m), 3028 (m), 2949 (m), 2908 (m), 2840 (m), 1713 (s), 1661 (m), 1603 (m), 1495 (m) cm^{-1} . Mass spec. (m/e): 370 (M^+ , 13), 352 (4), 338 (10), 279 (7), 251 (6), 236 (4), 212 (7), 203 (9), 185 (6), 167 (100), 91 (11). HRMS: $\text{C}_{20}\text{H}_{28}\text{O}_2$ calc.: 370.1933. Found: 370.1934.

Reaction of complex 7 with 2-lithio-2-methylpropionitrile followed by methylation

To a solution complex **7** (0.22 g, 1.00 mmol) and 2-lithio-2-methylpropionitrile (1.35 mmol, see above) at -78°C was added iodomethane (1.0 mL, 16.00 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 16 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue on silica gel with hexane/ethyl acetate (20:1) as eluent (0.30 g) produced a fraction containing γ,δ -unsaturated ketone **27**, as a yellow oil (0.09 g, 0.46 mmol, 46%). ^1H NMR (CDCl_3 , 200 MHz): δ 4.00 (d, J 3.7 Hz, 2H), 3.48 (s, 3H), 2.99 (dd, J 15.7, 9.0 Hz, 1H), 2.63 (m, 2H), 2.11 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 205.9, 160.3, 124.1, 85.1, 54.7, 47.8, 42.9, 34.6, 30.5, 26.4, 24.7. IR (CH_2Cl_2): 2989 (s), 2938 (s), 2878 (w), 2838 (w), 2239 (s), 1718 (s), 1658 (m), 1621 (m) cm^{-1} . Mass spec. (m/e): 195 (M^+ , 100), 175 (8), 73 (8). HRMS: $\text{C}_{11}\text{H}_{17}\text{NO}_2$ calc.: 195.1258. Found: 195.1248.

Reaction of complex 7 with 2-lithio-2-methylpropionitrile followed by trapping with benzyl bromide

To a solution of complex **7** (0.22 g, 1.00 mmol) and 2-lithio-2-methylpropionitrile (2.80 mmol, see above) at -78°C was added benzyl bromide (0.8 mL, 6.70 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 12 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (1.20 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing γ,δ -unsaturated ketone **28** as a yellow oil (0.15 g, 0.56 mmol, 56%). ^1H NMR (CDCl_3 , 200 MHz): δ 3.99 (d, J 2.6 Hz, 2H), 3.70 (s, 2H), 3.4 (s, 3H), 3.1 (dd, J 15.8, 9.2 Hz, 1H), 2.68 (m, 2H), 1.30 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 205.4, 160.1, 133.5, 129.4, 128.6, 127.0, 124.0, 85.4, 54.7, 50.6, 47.9, 41.3, 34.6, 26.4, 24.8. IR (CH_2Cl_2): 3084 (s), 3026 (s), 2986 (m), 2942 (m), 2232 (s), 1720 (s), 1661 (m), 1627 (w), 1496 (m), 1466 (w), 1452 (m) cm^{-1} . Mass spec. (m/e): 271 (M^+ , 24), 256 (9), 219 (6), 180 (100), 152 (18), 138 (15), 125 (15), 112 (39), 91 (62). HRMS: $\text{C}_{17}\text{H}_{21}\text{NO}_2$ calc.: 271.1556. Found: 271.1526.

Reaction of complex 7 with 2-lithio-2-phenyl-1,3-dithiane followed by methylation

To a solution of complex **7** (0.22 g, 1.00 mmol) and 2-lithio-2-phenyl-1,3-dithiane (2.25 mmol, see above) at -78°C was added iodomethane (1.0 mL, 16.00 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 12 h. After the regular aqueous process, the solution was concentrated. Treatment of the residue with 2 N HCl in MeOH followed by the regular aqueous process. Flash column chromatograph of the residue (0.70 g) on silica gel with hexane/ethyl acetate (20:1) as eluent produced a fraction containing the 1,4-dione **29** as a yellow oil (0.05 g, 0.17 mmol, 17%). ^1H NMR (CDCl_3 , 200 MHz): δ 8.02–7.31 (m, 5H), 3.42 (m, 2H), 3.21 (dd, J 11.3, 8.5 Hz, 1H), 2.70 (m, 4H), 2.33 (s, 3H), 1.95 (m, 2H), 1.74 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 207.6, 207.1, 139.5, 129.6, 128.9, 127.7, 60.4, 57.8, 44.4, 32.8, 29.5, 27.5, 27.1, 24.6. IR (CH_2Cl_2): 3086 (s), 2915 (w), 2852 (w), 1707 (s), 1650 (m), 1528 (s), 1479 (m) cm^{-1} . Mass spec. (m/e): 308 (M^+ , 19), 265 (34), 223 (8), 202 (95), 195 (75), 174 (22), 159 (100), 174 (22), 159 (100), 149 (29), 117 (17), 91 (7), 75 (7). HRMS: $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}_2$ calc.: 308.0904. Found: 308.0898.

Reaction of complex 7 with lithio diphenylmethane followed by addition of benzoyl chloride

To a solution of complex **7** (0.22 g, 1.00 mmol) and lithio diphenylmethane (1.35 mmol, see above) at -78°C was added benzoyl chloride (1.0 mL, 8.60 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 18 h. After the regular aqueous process, the solution was concentrated. Treatment of the residue with 2 N HCl in MeOH was followed by the regular aqueous process. Flash column chromatography of the residue (1.50 g) on silica gel with hexane/ethyl acetate (30:1) as eluent produced a fraction containing the 1,4-dione **30** (0.06 g, 0.18 mmol, 18%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline γ,δ -unsaturated ketone **30**, m.p. $146\text{--}148^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 7.74–7.10 (m, 15H), 3.97 (m, 2H), 3.49 (dd, J 18.3, 10.1 Hz, 1H), 2.98 (dd, J 18.3, 1.8 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 212.9, 198.8, 142., 141.7, 133.2, 128.9, 128.8, 128.4, 128.1, 127.9, 120.9, 54.6, 52.0, 42.1, 32.7. IR (CH_2Cl_2): 3080 (s), 3030 (m), 2992 (w), 2906 (w), 1709 (s),

1683 (m), 1600 (m), 1582 (m), 1494 (w), 1453 (w) cm^{-1} . Mass spec. (m/e): 342 (M^+ , 2), 324 (20), 298 (1), 281 (8), 223 (100), 207 (20), 205 (11), 180 (20), 167 (74), 105 (30). HRMS: $\text{C}_{24}\text{H}_{22}\text{O}_2$ calc.: 342.1619. Found: 342.1620.

Reaction of complex 8 with lithio diphenylmethane followed by methylation

To a solution of complex 7 (0.44 g, 2.00 mmol) and lithio diphenylmethane (2.40 mmol), see above) at -78°C was added iodomethane (1.0 mL, 16.00 mmol). The reaction mixture was pressed immediately by an atmosphere of CO and stirred at 23°C for 14 h. After the regular aqueous process, the solution was concentrated. Flash column chromatography of the residue (1.10 g) on silica gel with hexane-ethyl acetate (30:1) as eluent produced a fraction containing, γ,δ -unsaturated ketone **31** (0.26 g, 0.80 mmol, 40%). Recrystallization of the solid from hexane/ethyl acetate gave a white crystalline compound. γ,δ -Unsaturated ketone **31**: m.p. $70\text{--}72^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 7.29–7.12 (m, 10 H), 4.53 (t, J 3.8 Hz, 1H), 4.13 (d, 9.0 Hz, 1H), 3.53 (br d, J 8.9 Hz, 1H), 3.04 (s, 3H), 2.63 (m, 1H), 2.06 (s, 3H), 2.02 (m, 1H), 1.86 (m, 1H), 1.63 (m, 2H). ^{13}C NMR (CDCl_3 , 50.5 MHz): δ 209.7, 155.5, 143.1, 142.8, 128.7, 128.5, 128.2, 127.7, 126.3, 125.9, 94.2, 55.1, 53.3, 50.0, 41.7, 27.6, 20.8. IR (CH_2Cl_2): 3058 (m), 3028 (m), 2998 (m), 2944 (m), 2840 (m), 1708 (s), 1667 (m), 1602 (m), 1494 (m), 1424 (w), 1368 (w), 1282 (M), 1210 (w), 1162 (m), 1053 (w), 989 (w) cm^{-1} . Mass spec. (m/e): 320 (M^+ , 9), 277 (100), 167 (70). HRMS: $\text{C}_{22}\text{H}_{24}\text{O}_2$ calc.: 320.1776. Found: 320.1765.

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