

Synthesis of Tricarbonyl(vinylallene)iron(0) Complexes from Tricarbonyl(vinylketene)iron(0) Complexes and their Oxidation to 5,5-Disubstituted Furan-2(5*H*)-ones

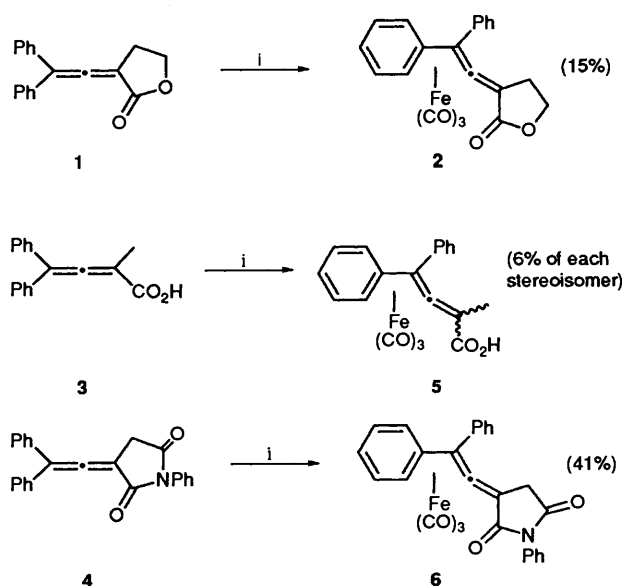
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Addition of phosphonoacetate anions to tricarbonyl(vinylketene)iron(0) complexes gave tricarbonyl(vinylallene)iron(0) complexes. Stereoselectivity as high as 98:2 was observed and the relative stereochemistry of the major stereoisomers was elucidated by X-ray crystal structure analysis of the major isomer of $[\text{Fe}^\circ\{\text{PhCH}=\text{CHC}(\text{Me})=\text{C}=\text{CHCO}_2\text{Bu}^t\}(\text{CO})_3]$ **9d**, the product obtained from the reaction between $[\text{Fe}^\circ\{\text{PhCH}=\text{CHC}(\text{Me})=\text{C}=\text{O}\}(\text{CO})_3]$ **7a** and the anion of $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Bu}^t$ **8b**. Reaction of the major isomers of the tricarbonyl(vinylallene)iron(0) complexes with FeCl_3 gave 5,5-disubstituted furan-2(5*H*)-ones.

Vinylketenes complexed to a range of transition metals including iron, vanadium, manganese, cobalt and molybdenum have been isolated and characterised over the last 30 years.¹ Although many of these complexes were found to be highly stable and easy to manipulate, very few investigations of their reactivity had been carried out probably reflecting the fact that many of the synthetic methods used to generate them were low-yielding and/or lengthy. Over the last decade transition metal complexes of vinylketenes have been proposed as key intermediates in a wide range of transition metal mediated organic reactions that lead to several important classes of organic products.² Thus the desire to understand and predict the reactivity of the proposed transient vinylketene complexes coupled with improved synthetic routes to the isolated stable vinylketene complexes has led very recently to the initiation of studies into the reactivity of the latter complexes. These investigations have shown to date that (a) iron-,³ chromium-,^{2a} and cobalt-centred⁴ vinylketene complexes react with nucleophiles at the carbon atom adjacent to the oxygen atom, (b) an iron-based vinylketene complex reacts with an electrophile through its oxygen atom,⁵ (c) cobalt-centred vinylketene complexes react with alkynes to give phenols,^{2b} whereas a chromium-based vinylketene complex reacts with an alkyne to give a cyclobutenone,^{2a} and (d) iron-centred vinylketene complexes combine with isonitriles to give metal complexes of vinylketenimines.⁶

It has been reported that uncoordinated ketenes react with phosphonate carbanions to give allenes.^{7,8} Although the allenes generated were unstable and were produced in low (32%)⁷ or unrecorded⁸ yield, it was decided to investigate whether or not readily accessible tricarbonyliron(0) complexes of vinylketenes reacted with phosphonate carbanions to give tricarbonyliron(0) complexes of vinylallenes. It was anticipated that these studies would not only provide more information about the reactivity of transition metal complexes of vinylketenes, but would also lead to a new approach to tricarbonyl(vinylallene)iron(0) compounds. It is of note in this context that the first example of a tricarbonyl(vinylallene)iron(0) complex was reported as recently as 1988 and was synthesised by irradiating the allenic lactone **1** in the presence of $\text{Fe}(\text{CO})_5$.⁹ This gave a mixture of several products including the tricarbonyl(vinylallene)iron(0) complex **2** which was characterised by X-ray crystallography. It was later reported that irradiation of allenes **3** and **4** in the presence of $\text{Fe}(\text{CO})_5$ gave tricarbonyl(vinylallene)iron(0) complexes **5** and **6**.¹⁰ Thus we considered that direct conversion of tricarbonyl(vinylketene)iron(0) complexes into tricarbonyl-



Reagent: i, $\text{Fe}(\text{CO})_5$, $h\nu$

(vinylallene)iron(0) complexes would constitute a complementary and potentially more versatile approach to this relatively new class of complex.

We wish to report herein the results of our studies which reveal that tricarbonyl(vinylketene)iron(0) complexes do react with phosphonate carbanions to give tricarbonyl(vinylallene)iron(0) complexes. Furthermore, oxidation of the vinylallene complexes with FeCl_3 leads to the release of the organic ligands as 5-alkyl-5-styrylfuran-2(5*H*)-ones. Part of this work has been the subject of a preliminary publication.¹¹

Results and Discussion

Attention initially focussed on the reaction between the methyl-substituted vinylketene complex tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) **7a** and the anion derived from commercially available trimethyl phosphonoacetate **8a**. The methyl-substituted vinylketene complex **7a** was prepared from benzylideneacetone in two steps using a published procedure.¹² This involved treating the benzylideneacetone with $\text{Fe}_2(\text{CO})_9$ to give tricarbonyl(benzylideneacetone)iron(0) which was subsequently stirred with methyl-

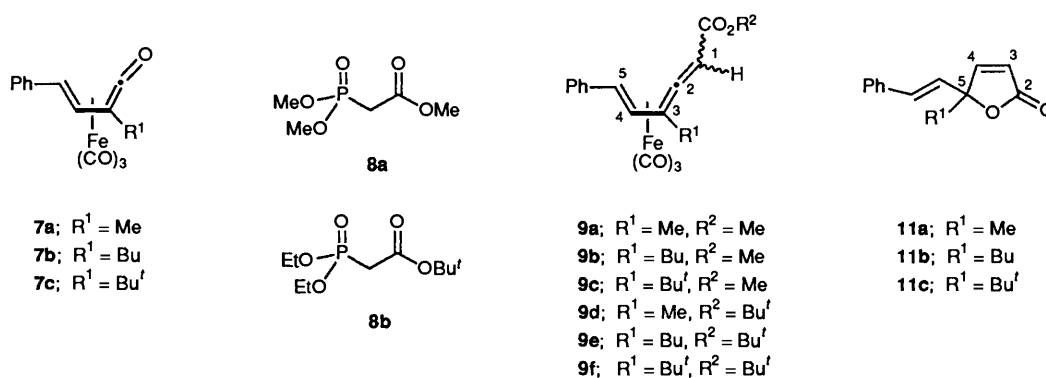


Table 1 Synthesis of tricarbonyl(vinylallene)iron(0) complexes **9** by addition of phosphonoacetate anions to tricarbonyl(vinylketene)iron(0) complexes **7**

Entry	Vinylketene complex	Phosphonoacetate	Vinylallene complex	Stereoisomeric ratio of 9 Major:Minor ^a	Yield of analytically pure major stereoisomer of 9 ^b (%)
1	7a	8a	9a	70:30	25
2	7b	8a	9b	50:50	38 ^c
3	7c	8a	9c	70:30	30
4	7a	8b	9d	98:2	71
5	7b	8b	9e	80:20	43
6	7c	8b	9f	85:15	39

^a Determined by analysis of the ¹H NMR spectrum of the crude product. ^b The major stereoisomers of **9a** and **9c-9f** were assigned the relative stereochemistry depicted for the major stereoisomer of **9d** in Fig. 1 by correlation of ¹H NMR data. ^c Yield of stereoisomeric mixture (attempts to obtain pure samples of each stereoisomer were unsuccessful for **9b**).

Table 2 Microanalytical, m.p., and IR data for tricarbonyl(vinylallene)iron(0) complexes **9**

Complex	Formula	Found (%) (Required)		M.p. ^a (°C)	IR data ^b v/cm ⁻¹		
		C	H		C≡O	C=O	C=C
9a _{maj}	C ₁₇ H ₁₄ FeO ₅	57.8 (57.7)	3.9 (4.0)	103–104	2058vs, 1998vsbr	1723m	1690m
9c _{maj}	C ₂₀ H ₂₀ FeO ₅	60.7 (60.6)	5.1 (5.1)	131–133	2055vs, 1995vsbr	1725s	1689s
9d _{maj}	C ₂₀ H ₂₀ FeO ₅	60.6 (60.6)	5.1 (5.1)	117–118	2057vs, 1996vsbr	1715m	1679m
9e _{maj}	C ₂₃ H ₂₆ FeO ₅	63.0 (63.0)	6.0 (6.0)	113–114	2056vs, 1995vsbr	1715m	1676m
9f _{maj}	C ₂₃ H ₂₆ FeO ₅	63.0 (63.0)	6.0 (6.0)	121–123	2054vs, 1994vsbr	1718m	1682m
9d _{min}	C ₂₀ H ₂₀ FeO ₅	60.6 (60.6)	5.1 (5.1)	126–128	2064vs, 2010vs, 1991vs	1716m	1697m

^a All complexes crystallised from light petroleum. ^b CCl₄ solution.

lithium under an atmosphere of carbon monoxide to give the required methyl-substituted vinylketene complex **7a** in 28% overall yield from benzylideneacetone. On addition of a THF (tetrahydrofuran) solution of the vinylketene complex **7a** to the anion of phosphonoacetate **8a** in THF, the yellow vinylketene solution instantaneously turned red. The reaction mixture was stirred at room temperature for 17 h and the resulting yellow solution was subsequently treated with water, extracted with ether, and filtered through a short plug of alumina to remove iron residues. Solvent removal gave a yellow oil which was examined by ¹H NMR spectroscopy and tentatively assigned as a 70:30 mixture of the two possible stereoisomers of the vinylallene complex **9a** (Table 1, Entry 1). Crystallisation of the yellow oil from light petroleum produced stable yellow crystals which gave spectroscopic data and microanalytical data entirely consistent with structure **9a**. The IR spectrum of the yellow crystals dissolved in CCl₄ contained two very strong ν_{C=O} absorptions at 2058 and 1998 cm⁻¹, a medium ν_{C=O} absorption at 1723 cm⁻¹, and a medium absorption at 1690 cm⁻¹ assigned to ν_{C(1)=C(2)}} (Table 2). Resonances at δ 5.82 (1 H, s), 6.05 (1 H, d, J/Hz 9) and 2.34 (1 H, d, J/Hz 9) in the

¹H NMR spectrum of the yellow product were assigned to the hydrogens attached to C(1), C(4) and C(5) respectively whilst the Ph, Me and CO₂Me substituents on the vinylallene ligand gave rise to signals at δ 7.15–7.35 (5 H, m), 2.29 (3 H, s) and 3.72 (3 H, s) (Table 3). Comparison of the ¹H NMR spectroscopic data of the crystals with the ¹H NMR spectrum of the crude product revealed that the crystals were a pure sample of the major stereoisomer **9a**_{maj}. The resonances in the spectrum of the crude product due to the minor stereoisomer **9a**_{min} were identified and assigned as indicated in Table 3. Of note is the 0.65 ppm difference in the resonances due to the hydrogen attached to C(1) (δ 5.82 in **9a**_{maj} and δ 6.47 in **9a**_{min}). The ¹³C NMR spectrum of **9a**_{maj} contained resonances at δ 110.2, 188.1, 84.5, 89.6 and 62.0 assigned to C(1)–C(5) respectively and resonances due to the Ph, Me and CO₂Me substituents (Table 4). The EI mass spectrum of **9a**_{maj} contained a small M⁺ peak (4.6%) and a fragmentation pattern corresponding to stepwise loss of the three C≡O ligands and the iron atom (Table 5). (Microanalytical and melting point data for **9a**_{maj} are given in Table 2).

Addition of the anion derived from phosphonoacetate **8a** to

Table 3 ^1H NMR (δ)^a data for tricarbonyl (vinylallene)iron(0) complexes **9**

Complex	δ_{H}					
	C(1)H ^b	C(4)H	C(5)H	Ph	C(3) substituent (R ¹)	CO ₂ R ²
9a _{maj} ^c	5.82 (1 H, s)	6.05 (1 H, d, J 9)	2.34 (1 H, d, J 9)	7.15–7.35 (5 H, m)	2.29 (3 H, s)	3.72 (3 H, s)
9b _{maj} ^{d,e}	5.73 (1 H, s)	5.94 (1 H, d, J 9)	2.29 (1 H, d, J 9)	7.15–7.35 (5 H, m)	— ^f	3.64 (3 H, s)
9c _{maj} ^c	5.87 (1 H, s)	6.02 (1 H, d, J 9)	2.25 (1 H, d, J 9)	7.15–7.35 (5 H, m)	1.39 (9 H, s)	3.71 (3 H, s)
9d _{maj} ^c	5.72 (1 H, s)	6.02 (1 H, d, J 9)	2.32 (1 H, d, J 9)	7.15–7.35 (5 H, m)	2.29 (3 H, s)	1.48 (9 H, s)
9e _{maj} ^c	5.71 (1 H, s)	5.98 (1 H, d, J 9)	2.36 (1 H, d, J 9)	7.15–7.35 (5 H, m)	0.98 (3 H, t, J 7), 1.72 (2 H, m), 2.37 (2 H, m), 2.82, (2 H, m)	1.48 (9 H, s)
9f _{maj} ^c	5.79 (1 H, s)	6.00 (1 H, d, J 9)	2.26 (1 H, d, J 9)	7.15–7.35 (5 H, m)	1.39 (9 H, s)	1.49 (9 H, s)
9a _{min} ^d	6.47 (1 H, s)	6.12 (1 H, d, J 9)	2.48 (1 H, d, J 9)	7.15–7.35 (5 H, m)	2.16 (3 H, s)	3.83 (3 H, s)
9b _{min} ^{d,e}	6.41 (1 H, s)	5.97 (1 H, d, J 9)	2.43 (1 H, d, J 9)	7.15–7.35 (5 H, m)	— ^f	3.78 (3 H, s)
9c _{min} ^d	6.44 (1 H, s)	6.08 (1 H, d, J 9)	2.44 (1 H, d, J 9)	7.15–7.40 (5 H, m)	1.28 (9 H, s)	3.86 (3 H, s)
9d _{min} ^c	6.41 (1 H, s)	6.08 (1 H, d, J 9)	2.43 (1 H, d, J 9)	7.15–7.35 (5 H, m)	2.16 (3 H, s)	1.59 (3 H, s)
9e _{min} ^d	6.42 (1 H, s)	6.04 (1 H, d, J 9)	2.45 (1 H, d, J 9)	7.15–7.35 (5 H, m)	— ^f	1.60 (3 H, s)
9f _{min} ^d	6.37 (1 H, s)	6.06 (1 H, d, J 9)	2.38 (1 H, d, J 9)	7.15–7.35 (5 H, m)	1.30 (9 H, s)	1.60 (3 H, s)

^a CDCl₃, 300 K, 270 MHz. ^b See Fig. 1 for numbering. ^c Data measured from analytically pure material. ^d Data measured from crude reaction product containing major and minor stereoisomers. ^e The two stereoisomers of **9b** were produced in a 1:1 ratio and thus assignment of this spectrum was carried out by comparison with values measured for major and minor stereoisomers of **9a** and **9c–9f**. ^f Not assigned due to complex overlapping multiplets in this area of spectrum.

Table 4 $^{13}\text{C}\{^1\text{H}\}$ NMR (δ)^a data for tricarbonyl(vinylallene)iron(0) complexes **9**

Complex	δ											
	C(1) ^b	C(2)	C(3)	C(4)	C(5)	C(6)	Ph (other than C(6))		C(3) substituent	CO ₂ R ²	CO ₂ R ²	
9a _{maj}	110.2	188.1	84.5	89.6	62.0	138.7	126.4	127.2	128.9	19.0	163.4	51.5
9c _{maj}	111.0	186.2	98.8	85.3	63.8	138.5	126.5	127.3	128.9	30.6, 33.0	163.3	51.4
9d _{maj}	112.4	185.6	84.6	89.3	61.6	138.9	126.4	127.0	128.9	19.0	162.3	28.3, 80.3
9e _{maj}	112.3	185.1	90.0	87.1	61.9	138.9	126.4	127.0	128.8	14.0, 22.7, 29.9, 30.7	162.3	28.3, 80.1
9f _{maj}	113.0	183.2	99.1	85.2	63.4	138.7	126.5	127.1	128.8	30.6, 33.1	162.7	28.3, 80.1
9d _{min}	113.3	185.1	81.8	91.5	61.0	138.6	126.4	127.1	128.9	19.5	166.6	28.2, 80.4

^a CDCl₃, 297 K, 125.8 MHz. ^b See Fig. 1 for numbering.

Table 5 MS data^a for tricarbonyl(vinylallene)iron(0) complexes **9**

Complex	Mass spectrum
9a _{maj}	354 (M ⁺ , 4.6%), 326 (2.5, M – CO), 323 (0.9, M – OMe), 298 (8.1, M – 2CO), 270 (100, M – 3CO) and 214 (13.4, M – 3CO – Fe).
9c _{maj}	396 (M ⁺ , 5.2%), 368 (2.3, M – CO), 365 (1.1, M – OMe), 340 (4.6, M – 2CO), 312 (100, M – 3CO), 256 (2.9, M – 3CO – Fe).
9d _{maj}	396 (M ⁺ , 3.5%), 368 (0.2, M – CO), 340 (3.0, M – 2CO), 323 (3.1, M – OMe), 312 (30.8, M – 3CO), 256 (100, M – 3CO – Fe).
9e _{maj}	438 (M ⁺ , 1.5%), 410 (0.4, M – CO), 382 (3.1, M – 2CO), 365 (2.5, M – OMe), 354 (32, M – 3CO), 298 (100, M – 3CO – Fe).
9f _{maj}	438 (M ⁺ , 1.8%), 410 (0.2, M – CO), 382 (1.0, M – 2CO), 365 (2.6, M – OMe), 354 (31.9, M – 3CO), 298 (100, M – 3CO – Fe).
9d _{min}	396 (M ⁺ , 1.6%), 368 (10.9, M – CO), 340 (5.2, M – 2CO), 323 (3.4, M – OMe), 312 (28.3, M – 3CO) and 256 (100, M – 3CO – Fe).

^a EI, 70 eV, 70–220 °C.

the butyl-substituted vinylketene complex **7b** (prepared in 39% overall yield from benzylidenemethyl butyl ketone¹²) and to the *tert*-butyl-substituted vinylketene complex **7c** (prepared in 74% overall yield from benzylidenemethyl *tert*-butyl ketone¹²), using the procedure described above, gave in each case a yellow oil containing two stereoisomers. These were assigned as vinylallene complexes **9b** (stereoisomeric ratio, 50:50) and **9c** (stereoisomeric ratio, 70:30) respectively (Table 1, Entries 2 and 3). Attempts to separate the two stereoisomers of **9b** either by column chromatography or by crystallisation were unsuccessful but crystallisation of the oil containing the two stereoisomers of **9c** gave pure crystals of the major stereoisomer **9c**_{maj}. Complex **9c**_{maj} was fully characterised (Tables 2–5), and the ^1H NMR resonances for **9b**_{maj}, **9b**_{min} and **9c**_{min} were identified in the spectra obtained from the crude products (Table 2).

The results obtained using trimethyl phosphonoacetate **8a** and the vinylketene complexes **7a–c** clearly demonstrate that the carbon–oxygen double bond of tricarbonyl(vinylketene)iron(0) complexes may be replaced by a carbon–carbon double bond to give stable tricarbonyl(vinylallene)iron(0) complexes. The production of two stereoisomers in approximately equal amounts, however, is synthetically unattractive and so a method for improving the selectivity of vinylallene complex formation was sought. We proposed that an increase in the steric demands of the phosphonoacetate may lead to improved stereoselectivity in the reaction and so *tert*-butyl diethyl phosphonoacetate **8b** was synthesised from diethylchlorophosphate and *tert*-butyl acetate,¹³ and its anion reacted with vinylketene complexes **7a–c** (Table 1, Entries 4–6). The results obtained revealed that the butoxycarbonyl-substituted vinylallene products **9d–f**, were all formed more selectively than the

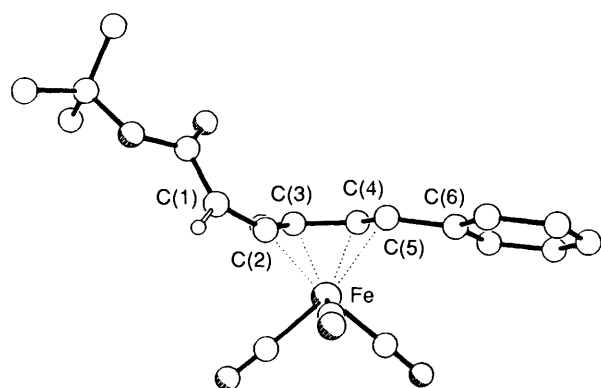


Fig. 1 Molecular structure of the major stereoisomer of $\text{Fe}^0\text{-}\{\text{PhCH}=\text{CHC}(\text{Me})=\text{C}=\text{CHCO}_2\text{Bu}^+\}\text{(CO)}_3$ **9d**_{major}. Selected bond lengths (Å), bond angles, and torsion angles (°): C(1)–C(2) 1.331(8), C(2)–C(3) 1.417(8), C(3)–C(4) 1.424(8), C(4)–C(5) 1.401(8), C(5)–C(6) 1.483(8), Fe–C(2) 1.953(6), Fe–C(3) 2.096(5), Fe–C(4) 2.089(5), Fe–C(5) 2.152(6); C(1)–C(2)–C(3) 137.8(5), C(2)–C(3)–C(4) 112.4(5), C(3)–C(4)–C(5) 118.4(5), C(4)–C(5)–C(6) 123.7(6); C(1)–C(2)–C(3)–C(4) 133.4(8), C(2)–C(3)–C(4)–C(5) –8.0(8), C(3)–C(4)–C(5)–C(6) 170.3(5).

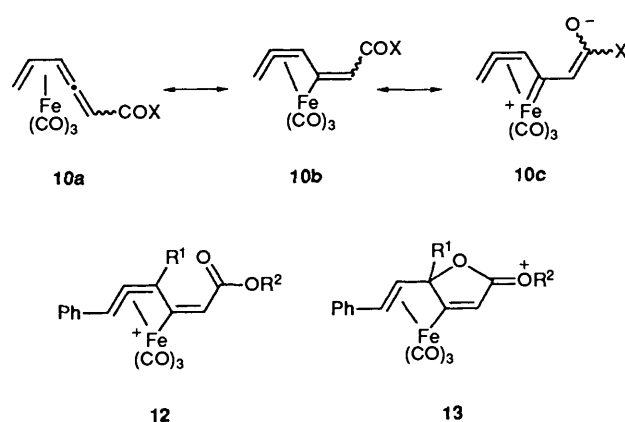
Table 6 FeCl_3 mediated oxidation of tricarbonyl(vinylallene)iron(0) complexes **9** to 5-alkyl-5-styrylfuran-2(5*H*)-ones **11**

Entry	Vinylallene complex	Furanone	Yield (%)
1	9a	11a	82
2	9c	11c	18
3	9d	11a	96
4	9e	11b	54

corresponding methoxycarbonyl-substituted allene complexes **9a–c**. Crystallisation of the crude vinylallene complexes **9e** and **9f** led to the isolation of pure samples of the major stereoisomers **9e**_{major} and **9f**_{major} and these complexes were fully characterised (Tables 2–5). Crystallisation of crude **9d**, however, gave lemon-yellow crystals together with a relatively small number of easily distinguishable orange–yellow crystals which were readily separated by hand. Comparison of the ^1H NMR spectra of the two types of crystal with the ^1H NMR spectrum of crude **9d** revealed that the lemon–yellow crystals were pure major stereoisomer **9d**_{major} and that the orange–yellow crystals were pure minor stereoisomer **9d**_{minor}. Thus, in this case, both stereoisomers produced in the reaction were fully characterised (Tables 2–5).

The relative stereochemistry of the major and minor stereoisomers of the vinylallene complexes was determined by an X-ray crystal structure analysis of the major stereoisomer of vinylallene complex **9d**_{major} and correlation of ^1H NMR data. The X-ray analysis (Fig. 1) revealed that in the major stereoisomer of **9d**, the bulky butoxycarbonyl group is directed away from the tricarbonyliron(0) unit. Comparison of the ^1H NMR δ values for the proton attached to C(1) in the major and minor stereoisomers of complexes **9d**, **9a**, **9c**, **9e** and **9f** (δ for major stereoisomers = 5.71–5.87, δ for minor stereoisomers = 6.37–6.47; see Table 3) indicated that all the major stereoisomers had the same relative stereochemistry as the major stereoisomers of **9d**.

Finally, the feasibility of using unstabilised phosphorus ylides in this new approach to tricarbonyl(vinylallene)iron(0) complexes was investigated. Reaction of the vinylketene complex **7a** with the ylide $\text{Ph}_3\text{P}=\text{CH}_2$, however, repeatedly gave a highly complex mixture of products. It is of note, in this context, that all tricarbonyl(vinylallene)iron(0) complexes synthesised to date *i.e.* complexes **2**, **5**, **6** and **9** have carried carbonyl



substituents on C(1) of the allene unit and so it may be postulated that (a) the resonance structure **10c** plays a small but significant role in the stabilisation of these complexes, and that (b) addition of $\text{Ph}_3\text{P}=\text{CH}_2$ to vinylketene complex **7a** resulted in the formation of a highly unstable vinylallene complex which subsequently decomposed.

The reactivity patterns of tricarbonyl(vinylallene)iron(0) complexes are essentially unknown. [Their single reported reaction to date involved stirring the tricarbonyl(vinylallene)iron(0) complex **2** with tetracyanoethylene. This led to decomplexation and isolation of the free allene in 62% yield.⁹] Our attention focussed on the outcome of oxidising the tricarbonyl(vinylallene)iron(0) complexes **9**. Thus the major isomer of tricarbonyl-1-*tert*-butoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0) **9d**_{major} was stirred with FeCl_3 and a few drops of water in industrial methylated spirit (IMS) for 17 h at room temperature. TLC analysis of the reaction mixture after 17 h revealed that some of the vinylallene complex was still present and so the reaction mixture was heated at 60 °C for a further 4 h. Subsequent work-up and chromatography of the product mixture gave a colourless oil which was identified as the new compound 5-methyl-5-styrylfuran-2(5*H*)-one **11a** on the basis of its IR, ^1H NMR, ^{13}C NMR, and MS data. The IR spectrum of the colourless oil dissolved in CCl_4 contained a strong $\nu_{\text{C}=\text{O}}$ absorption at 1777 cm^{-1} consistent with the proposed furan-2(5*H*)-one structure.^{8–14} Resonances observed at δ 6.06 (1 H, d, J/Hz 5.6) and 7.46 (1 H, d, J/Hz 5.6) in the ^1H NMR spectrum of the product are consistent with signals expected for hydrogens attached to C(3) and C(4) respectively of structure **11a** [the corresponding hydrogen atoms in the parent unsubstituted furan-2(5*H*)-one resonate at δ 6.08 and 7.60 respectively (J/Hz 5.8)¹⁵] whilst signals at δ 6.18 (1 H, d, J/Hz 16.1), 6.65 (1 H, d, J/Hz 16.1) and 7.25–7.40 (5 H, m) were assigned to the 5-styryl substituent of structure **11a** and the three-proton singlet at δ 1.66 was assigned to the 5-methyl substituent. The ^{13}C NMR spectrum of **11a** contained resonances at δ 172.3 and 159.3 which are consistent with values recorded for C(2) and C(4) of 3,5-dimethylfuran-2(5*H*)-one (δ 173.8 and 150.8 respectively¹⁶), and resonances at δ 87.9 and 126.9 which were assigned to C(5) and C(3) respectively of structure **11a**. The spectrum also contained resonances consistent with the presence of methyl and styryl substituents and the latter were assigned by analogy with the reported spectrum of styrene.¹⁷ The EI mass spectrum of **11a** contained a molecular ion (68%) and a fragmentation pattern corresponding to loss of Me and MeCO which is consistent with fragmentation patterns observed previously for 5,5-disubstituted furan-2(5*H*)-ones.¹⁸

Thus the 5-methyl-5-styrylfuran-2(5*H*)-one **11a** was obtained in good yield (96%, Table 6) from the 3-methyl substituted vinylallene complex **9d**_{major}. Using essentially the same

procedure, the other 3-methyl substituted vinylallene complex available **9a_{maj}** was also converted into the same furan-2(5*H*)-one in good yield (82%). Similar treatment of the 3-butyl and 3-*tert*-butyl vinylallene complexes, **9c_{maj}** and **9c_{min}**, however, led to significantly lower yields of the corresponding new compounds 5-butyl-5-styrylfuran-2(5*H*)-one **11b** and 5-*tert*-butyl-5-styrylfuran-2(5*H*)-one **11c** (54 and 18% respectively, Table 6).

More work is required to delineate a detailed mechanism for the oxidation of the tricarbonyl(vinylallene)iron(0) complexes **9** to the furan-2(5*H*)-ones **11**. It may be postulated, however, that the first step is an FeCl₃-mediated one-electron oxidation of the vinylallene complex to give the cationic species **12**. Subsequent intramolecular nucleophilic attack of the η³-allyl ligand by the alkoxy carbonyl group leads to the intermediate **13** which under the acidic reaction conditions will give rise to the product furan-2(5*H*)-one by (a) protonation of the iron centre followed by reductive elimination, and (b) hydrolysis of the C=O⁺R group. An alternative mechanism in which oxidation by the FeCl₃ leads to complete decomplexation of the vinylallene ligand cannot be discounted, however, as uncomplexed 1-ethoxycarbonylallenes have been reported to cyclise to furan-2(5*H*)-ones under acidic conditions.⁸ Investigations to distinguish between the two types of mechanism using optically pure vinylallene complexes are in hand.

Experimental

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.¹⁹ Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Light petroleum refers to the fraction boiling in the range 60–80 °C. Industrial methylated spirit (IMS) contained min. 94% EtOH, max. 3.5% MeOH and max. 1.43% H₂O. Enneacarbonyldiiron(0),²⁰ tricarbonyl(vinylketene)iron(0) complexes **7a–c**,¹² and *tert*-butyl diethyl phosphonoacetate¹³ were prepared using published procedures. All other reagents were used as obtained from commercial sources. M.p.s were obtained on a Reichert 7905 microscope hot stage and are uncorrected. Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department and Imperial College Microanalytical Service. IR spectra were obtained on a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded in CDCl₃ on Jeol GSX 270 (270 MHz ¹H) and Bruker AM 500 (125.8 MHz ¹³C) spectrometers; *J* values are given in Hz. Mass spectra were recorded on VG Mass Lab 12/250 and VG Analytical ZAB/E instruments at the SERC Mass Spectrometry Service Centre, Swansea, and on a VG Micromass 7070E instrument at Imperial College using EI and CI techniques. The X-ray crystal structure analysis of the tricarbonyl(vinylallene)iron(0) complex **9d_{maj}** has been reported previously.¹¹ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Reaction of Tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7a with Trimethyl Phosphonoacetate 8a.—To stirring THF (20 cm³) under nitrogen was added 60% NaH dispersion (0.056 g, 1.40 mmol) rapidly followed by trimethyl phosphonoacetate **8a** (0.24 g, 0.21 cm³, 1.31 mmol). After 0.5 h, the vinylketene complex **7a** (0.130 g, 0.436 mmol) in THF (5 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17 h. The resultant yellow solution was transferred *via* a cannula into vigorously stirring water (30 cm³) and the mixture was extracted with diethyl ether (3 × 20 cm³). The combined organic extracts were dried (Na₂SO₄) and the solvent removed under reduced pressure to give a yellow oil which was shown by ¹H NMR spectroscopy to contain **9a_{maj}** and **9a_{min}**

in a ratio of 69:31 (see Table 1). Crystallisation of the yellow oil from light petroleum gave *tricarbonyl(1-methoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0) 9a_{maj}* (0.039 g, 25%) as yellow crystals. The microanalytical, m.p., IR, ¹H NMR, ¹³C NMR and MS data for **9a_{maj}** are recorded in Tables 2–5.

Reaction of Tricarbonyl(3-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7b with Trimethyl Phosphonoacetate 8a.—To stirring THF (20 cm³) under nitrogen was added 60% NaH dispersion (0.062 g, 1.54 mmol) rapidly followed by trimethyl phosphonoacetate **8a** (0.28 g, 0.25 cm³, 1.54 mmol). After 0.5 h, the vinylketene complex **7a** (0.21 g, 0.617 mmol) in THF (6 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17 h. The resultant yellow solution was transferred *via* a cannula into vigorously stirring water (20 cm³) and the mixture was extracted with diethyl ether (3 × 15 cm³). The combined organic extracts were dried over Na₂SO₄. After filtering through a plug of alumina (Brockmann 1, basic; diethyl ether), the solvent was removed under reduced pressure to give a yellow oil (0.244 g, 38%) which was shown by ¹H NMR spectroscopy to contain **9b_{maj}** and **9b_{min}** in a ratio of 50:50 (see Table 1). Repeated attempts to separate **9b_{maj}** and **9b_{min}** by column chromatography and crystallisation were unsuccessful. The ¹H NMR data for **9b_{maj}** and **9b_{min}** are recorded in Table 3.

Reaction of Tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7c with Trimethyl Phosphonoacetate 8a.—To stirring THF (20 cm³) under nitrogen was added 40% NaH dispersion (0.116 g, 1.93 mmol) rapidly followed by trimethyl phosphonoacetate **8a** (0.35 g, 0.31 cm³, 1.93 mmol). After 0.5 h, the vinylketene complex **7a** (0.220 g, 0.647 mmol) in THF (7 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17 h. The resultant yellow solution was transferred *via* a cannula into vigorously stirring water (20 cm³) and the mixture was extracted with diethyl ether (3 × 20 cm³). The combined organic extracts were dried (Na₂SO₄), filtered through alumina (Brockmann 1, basic; diethyl ether), and the solvent removed under reduced pressure to give a yellow oil which was shown by ¹H NMR spectroscopy to contain **9c_{maj}** and **9c_{min}** in a ratio of 70:30 (see Table 1). Crystallisation of the yellow oil from light petroleum gave *tricarbonyl-(3-*tert*-butyl-1-methoxycarbonyl-5-phenylpenta-1,2,4-triene)iron(0) 9c_{maj}* (0.076 g, 30%) as yellow crystals. The microanalytical, m.p., IR, ¹H NMR, ¹³C NMR, and MS data for **9c_{maj}** are recorded in Tables 2–5.

Reaction of Tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7a with *tert*-Butyl Diethyl Phosphonoacetate 8b.—To stirring THF (25 cm³) under nitrogen was added 60% NaH dispersion (0.35 g, 8.66 mmol) rapidly followed by *tert*-butyl diethyl phosphonoacetate **8b** (2.18 g, 2.03 cm³, 8.66 mmol). After 0.5 h, the vinylketene complex **7a** (1.29 g, 4.33 mmol) in THF (15 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17 h. The resultant yellow solution was transferred *via* a cannula into vigorously stirring water (20 cm³) and the mixture was extracted with diethyl ether (3 × 20 cm³). The combined organic extracts were dried (Na₂SO₄), filtered through alumina (Brockmann 1, basic; diethyl ether), and the solvent removed under reduced pressure to give a yellow oil which was shown by ¹H NMR spectroscopy to contain **9d_{maj}** and **9d_{min}** in a ratio of 98:2 (see Table 1). Crystallisation of the

yellow oil from light petroleum gave lemon yellow crystals of the major stereoisomer of *tricarbonyl(1-tert-butoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0)* **9d_{maj}** (1.22 g, 71%) and orange-yellow crystals of the minor stereoisomer of *tricarbonyl(1-tert-butoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0)* **9d_{min}** (0.008 g, 0.47%) which were readily distinguishable and easily separated by hand. The microanalytical, m.p., IR, ¹H NMR, ¹³C NMR, and MS data for **9d_{maj}** and **9d_{min}** are recorded in Tables 2–5.

Reaction of Tricarbonyl(3-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7b with tert-Butyl Diethyl Phosphonoacetate 8b.—To stirring THF (10 cm³) under nitrogen was added 60% NaH dispersion (0.07 g, 1.84 mmol) rapidly followed by *tert*-butyl diethyl phosphonoacetate **8b** (0.46 g, 0.43 cm³, 1.84 mmol). After 0.5 h, the vinylketene complex **7b** (0.25 g, 0.735 mmol) in THF (6 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17 h. The resultant yellow solution was transferred *via* a cannula into vigorously stirring water (20 cm³) and the mixture was extracted with diethyl ether (3 × 15 cm³). The combined organic extracts were dried (Na₂SO₄), filtered through alumina (Brockmann 1, basic; diethyl ether), and the solvent removed under reduced pressure to give a yellow oil which was shown by ¹H NMR spectroscopy to contain **9e_{maj}** and **9e_{min}** in a ratio of 82:18 (see Table 1). Crystallisation of the yellow oil from light petroleum gave yellow crystals of the major stereoisomer of *tricarbonyl(1-tert-butoxycarbonyl-3-butyl-5-phenylpenta-1,2,4-triene)iron(0)* **9e_{maj}** (0.139 g, 43%). The microanalytical, m.p., IR, ¹H NMR, ¹³C NMR and MS data for **9e_{maj}** are recorded in Tables 2–5.

Reaction of Tricarbonyl(3-tert-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) 7c with tert-Butyl Diethyl Phosphonoacetate 8b.—To stirring THF (6 cm³) under nitrogen was added 60% NaH dispersion (0.042 g, 1.05 mmol) rapidly followed by *tert*-butyl diethyl phosphonoacetate **8b** (0.26 g, 0.24 cm³, 1.02 mmol). After 0.5 h, the vinylketene complex **7c** (0.35 g, 1.02 mmol) in THF (6 cm³) was added to the clear stirring solution of the anion. The yellow vinylketene complex solution turned wine-red on contact with the anion solution and the reaction mixture was stirred for 17.5 h. A further equivalent of the phosphonoacetate anion solution in THF (6 cm³) was then added and the reaction mixture stirred for a further 4 h. The resultant yellow solution was filtered through a plug of alumina (Brockmann 1, neutral; diethyl ether) and the solvent removed under reduced pressure to give a yellow oil which was shown by ¹H NMR spectroscopy to contain **9f_{maj}** and **9f_{min}** in a ratio of 86:14 (see Table 1). Crystallisation of the yellow oil from light petroleum gave yellow crystals of the major stereoisomer of *tricarbonyl(1-tert-butoxycarbonyl-3-tert-butyl-5-phenylpenta-1,2,4-triene)iron(0)* **9f_{maj}** (0.17 g, 39%). The microanalytical, m.p., IR, ¹H NMR, ¹³C NMR, and MS data for **9f_{maj}** are recorded in Tables 2–5.

Oxidation of the Major Stereoisomer of Tricarbonyl(1-methoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0) 9a_{maj} with FeCl₃.—Complex **9a_{maj}** (0.013 g, 0.0367 mmol) and anhydrous FeCl₃ (0.9 g, 5.5 mmol) were dissolved in IMS (20 cm³) causing effervescence. After addition of water (4 drops) the reaction mixture was stirred for 20 h at 70 °C. The resulting brown mixture was diluted with water (50 cm³) and extracted with diethyl ether (3 × 10 cm³). The combined ether extracts were dried (Na₂SO₄) and the solvent removed under reduced pressure to give a brown-yellow oil which was filtered through alumina (Brockmann 1, neutral; Et₂O). Removal of solvent under reduced pressure gave a colourless oil which was

homogeneous by TLC (*R_f* 0.07; 0.2 mm Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4) and was identified as *5-methyl-5-styrylfuran-2(5H)-one 11a* (0.006 g, 82%) by comparison of its TLC, IR, ¹H NMR and MS data with the data obtained from the material formed by oxidising **9d_{maj}** with FeCl₃ in IMS (see two experiments below).

Oxidation of the Major Stereoisomer of Tricarbonyl(3-tert-butyl-1-methoxycarbonyl-5-phenylpenta-1,2,4-triene)iron(0) 9c_{maj} with FeCl₃.—Complex **9c_{maj}** (0.052 g, 0.131 mmol) and anhydrous FeCl₃ (3 g, 18.5 mmol) were dissolved in IMS (30 cm³). After addition of water (4 drops) the reaction mixture was stirred and monitored by TLC (Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4). After 4 days at room temperature, no reaction was evident and so the reaction mixture was heated at 70 °C for 4 h. The brown product mixture was diluted with water (20 cm³) and extracted with diethyl ether (3 × 10 cm³). The combined organic extracts were dried (Na₂SO₄) and concentrated under reduced pressure to give a yellow oil. Preparative thin-layer chromatography of the yellow oil (Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:3) gave a colourless oil which was homogeneous by TLC (*R_f* 0.21; 0.2 mm Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4) and was identified as *5-tert-butyl-5-styrylfuran-2(5H)one 11c* (0.007 g, 18%) (Found: *m/z* 243.1385. C₁₆H₁₉O₂ (MH) requires 243.1385); *v*_{max}(CCl₄)/cm⁻¹ 1770s (C=O); *δ*_H(CDCl₃) 0.99 (9 H, s, Bu^t), 6.02 [1 H, d, *J* 5.9, H(3)], 6.34 (1 H, d, *J* 16.1, PhCH=CH), 6.61 (1 H, d, *J* 16.1, PhCH=CH), 7.2–7.3 (5 H, m, Ph) and 7.54 [1 H, d, *J* 5.9, H(4)]; *δ*_C{¹H} (CDCl₃) 25.4 (CH₃), 38.2 (CMe₃), 95.3 [C(5)], 120.6 (PhCH=CH), 123.9 [C(3)], 126.6 (C_{ortho}), 128.2 (C_{para}), 128.7 (C_{meta}), 131.5 (PhCH=CH), 136.0 (C_{ipso}), 157.0 [C(4)] and 172.7 [C(2)]; *m/z* (CI) 243 (MH⁺, 43%), 186 (100, MH – Bu^t) and 157 (5, M – Bu^t – CO).

Oxidation of the Major Stereoisomer of Tricarbonyl(1-tert-butoxycarbonyl-3-methyl-5-phenylpenta-1,2,4-triene)iron(0) 9d_{maj} with FeCl₃.—Complex **9d_{maj}** (0.100 g, 0.26 mmol) and anhydrous FeCl₃ (4.00 g, 24.6 mmol) were dissolved in IMS (15 cm³) causing effervescence. After addition of water (0.01 cm³), the reaction mixture was stirred for 17 h at room temperature. TLC analysis (Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4) revealed that some **9d_{maj}** remained in the reaction mixture and so the brown mixture was heated at 60 °C for a further 4 h after which water (50 cm³) was added. This mixture was extracted with diethyl ether (3 × 20 cm³) and the combined organic extracts were dried (Na₂SO₄) and evaporated to dryness under reduced pressure. The resulting pale yellow oil was chromatographed (Kieselgel 60; CCl₄) to yield a colourless oil which was homogeneous by TLC (*R_f* 0.07; 0.2 mm Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4) and was identified as *5-methyl-5-styrylfuran-2(5H)-one 11a* (0.050 g, 96%) (Found: *m/z* 200.0837. C₁₃H₁₂O₂ requires *M*, 200.0837); *v*_{max}(CCl₄)/cm⁻¹ 1777s (C=O); *δ*_H(CDCl₃) 1.66 (3 H, s, Me), 6.06 [1 H, d, *J* 5.6, H(3)], 6.18 (1 H, d, *J* 16.1, PhCH=CH), 6.65 (1 H, d, *J* 16.1, PhCH=CH), 7.25–7.40 (5 H, m, Ph) and 7.46 [1 H, d, *J* 5.6, H(4)]; *δ*_C{¹H} (CDCl₃) 24.2 (CH₃), 87.9 [C(5)], 119.9 (PhCH=CH), 126.7 (C_{ortho}), 126.9 [C(3)], 128.4 (C_{para}), 128.7 (C_{meta}), 131.0 (PhCH=CH), 135.6 (C_{ipso}), 159.3 [C(4)] and 172.3 [C(2)]; *m/z* (EI) 200 (M⁺, 68%), 185 (88, M – Me) and 157 (100, M – CH₃ – CO).

Oxidation of the Major Stereoisomer of Tricarbonyl(1-tert-butoxycarbonyl-3-butyl-5-phenylpenta-1,2,4-triene)iron(0) 9e_{maj} with FeCl₃.—Complex **9e_{maj}** (0.074 g, 0.169 mmol) and anhydrous FeCl₃ (3 g, 18.5 mmol) were dissolved in IMS (20 cm³) and water (4 drops) was added. The reaction mixture was heated at 70 °C for 5 h and then diluted with water (50 cm³) and

extracted with diethyl ether ($3 \times 15 \text{ cm}^3$). The combined organic extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure. The resultant pale yellow oil was passed through alumina (Brockmann 1, neutral; diethyl ether). Subsequent solvent removal yielded a colourless oil which was homogeneous by TLC (R_f 0.13; 0.2 mm Kieselgel 60 GF₂₅₄; diethyl ether–light petroleum, 1:4) and was identified as 5-butyl-5-styrylfuran-2(5H)-one **11b** (0.022 g, 54%) (Found: m/z 242.1307. $\text{C}_{16}\text{H}_{18}\text{O}_2$ requires M , 242.1307; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1774s (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.70–0.90 [3 H, m, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$], 1.20–1.35 [4 H, m, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$], 1.70–2.00 [2 H, m, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$], 5.97 [1 H, d, J 6, H(3)], 6.11 (1 H, d, J 16.1, PhCH=CH), 6.54 (1 H, d, J 16.1, PhCH=CH), 7.2–7.3 (5 H, m, Ph) and 7.36 [1 H, d, J 6, H(4)]; $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl₃) 13.8 [$\text{CH}_3(\text{CH}_2)_3$], 22.7 [$\text{MeCH}_2(\text{CH}_2)_2$], 25.65 ($\text{MeCH}_2\text{CH}_2\text{CH}_2$), 37.58 [$\text{Me}(\text{CH}_2)_2\text{CH}_2$], 90.6 [C(5)], 120.1 (PhCH=CH), 126.2 [C(3)], 126.6 (C_{ortho}), 128.3 (C_{para}), 128.7 (C_{meta}), 130.9 (PhCH=CH), 135.7 (C_{ipso}), 158.4 [C(4)] and 172.5 [C(2)]; m/z (EI) 242 (M^+ , 5%), 185 (100, $M - \text{Bu}$) and 157 (21, $M - \text{Bu} - \text{CO}$).

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