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A General Synthetic Method for 1,1′-Bis(diacetylene-group)-Connected Ferrocene and π-Electronic System

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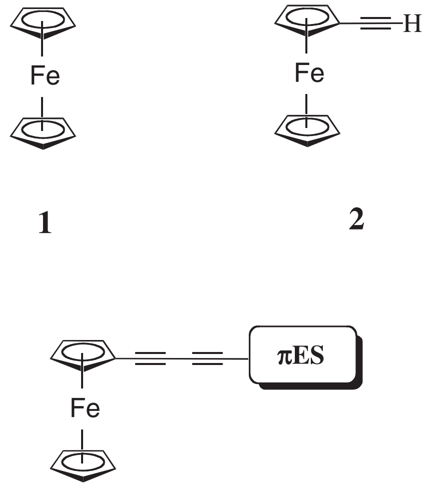
In contrast to the facile synthon ethynylferrocene for diacetylene ferrocene (Fc) derivatives, 1,1′-diethynylferrocene for the corresponding 1,1′-bis(diacetylene-group)-connected Fc derivatives is extremely difficult to handle under ordinary conditions, giving rise to spontaneous self-polymerization. Under modified Eglinton oxidative coupling conditions, it has been possible to generate 1,1′-diethynylferrocene in situ readily from a trimethylsilyl-protected precursor and to react it with other terminal acetylenes. The present tandem reactions could provide a general synthetic method for an extended π-electronic conjugation system of 1,1′-bis(diacetylene-group)-connected Fc derivatives, of which the chemistry has been scarcely developed.

Over the last two decades, a variety of extended π-electronic conjugation systems connected with the 1,3-butadiyn-1,4-diyl linkage (diacetylene) have been demonstrated for the development of new organic functional materials, due to linkage advantages such as a well-defined rigid, linear molecular structure, minimal steric hindrance, and π-conjugation.[1] Furthermore these advantageous linkage characteristics are very closely related to both functionality and processibility of the materials. In connection with development of functional materials based on diacetylene-group-connected derivatives, we have been also constructing various extended π-electronic systems (πES) by oxidative coupling reactions between curious terminal acetylene components and have been proposing structural requirements for molecular design through studies of their structure–property relationships.[2]

On one hand, in recent years, the ferrocene nucleus [**1**,[3] Fc: $Cp_2(Fe)$, Chart 1] holds a unique position as a promising candidate for functional materials, particularly by virtue of its molecular prochirality[4] and electron-donating ability.[5] Since the mean distance between faced Cp rings of Fc is ca. 4 Å, intramolecular interactions of various types could also be introduced both electronically and spherically into Fc by combination with manifold components. The Fc component itself is mostly introduced into the respective πES by connection with linkages readily derivable on Cp rings, such as vinylene,[6] phenylene,[7] and carbonyl analogs,[8] according to their material functions.



Diacetylene-group Connected Fc-πES

Chart 1.

Some diacetylene-connected derivatives composed of Fc and πES are known as well, described as Fc–πES, which are prepared by utilizing oxidative coupling reactions of ethynylferrocene (**2**,[9] Chart 1) with the corresponding terminal acetylenes.[10] Most of them however, are derivatives in which the diacetylene linkage is attached to a single Cp ring of Fc (Chart 1). In practice, strain-free 1,1′-bis(diacetylene-group)-connected Fc derivatives have not been reported, except for a few limited examples, for example, diacetylene-group-bridged Fc cyclophanes which are sterically hindered and multiply protected with bulky *tert*-butyl groups on both Cp rings.[11] Therefore, in those diacetylene-group-linked Fc compounds, even though studies of one-dimensional interaction between Fc and πES can be performed to some extent, structure–property investigations of intramolecular multidimensional interaction between two π-electronically extended Cp constituents in Fc cannot be performed comprehensively. This is simply due to synthetic issues. Actually, no general synthetic method for electronically unperturbed and strain-free 1,1′-bis(diacetylene-group)-linked Fc–πES derivatives, Fc–(πES)$_2$, has been established so far. In contrast to the high utility of ethynylferrocene (**2**), 1,1′-diethynylferrocene (**3**) which is a promising synthon is extremely difficult to handle under ordinary conditions, spontaneously giving rise to self-polymerization to form diacetylene Fc polymers **4** via oxidative coupling (Scheme 1).[11] Nevertheless, it has been previously reported

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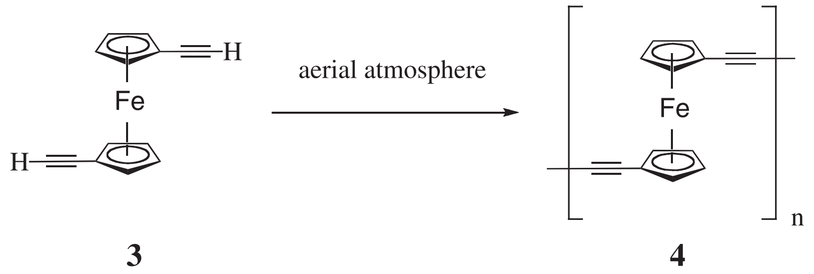
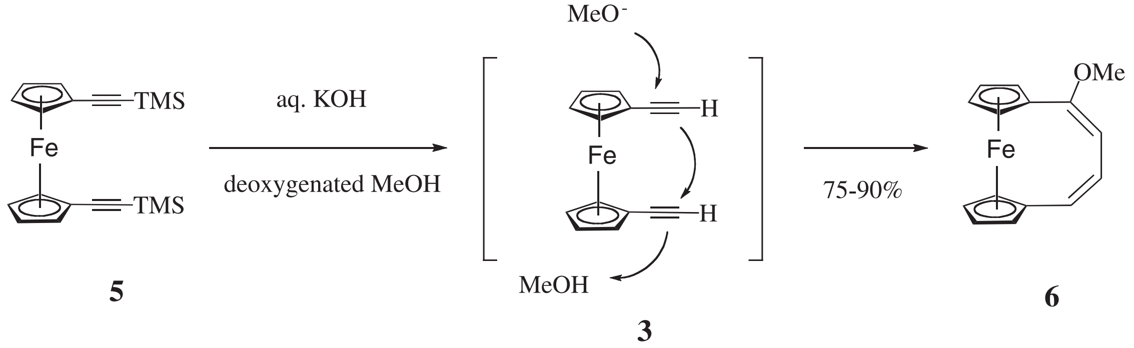
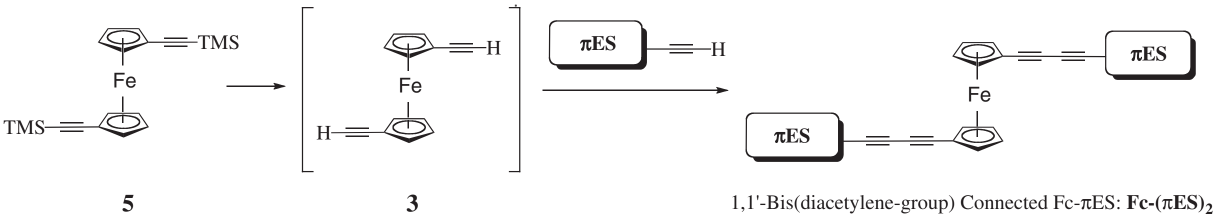


Scheme 1.



Scheme 2.



Scheme 3.

that the very careful treatment of a deoxygenated solution of the trimethylsilyl (TMS)-group-protected precursor **5** for **3** in methanol (MeOH) with aqueous potassium hydroxide (KOH) gives 1,1′-(1-methoxy-1,3-butadienylene)ferrocene (**6**, a [4]-ferrocenophane) as the only detectable product in isolated yields from 75% to 90% (Scheme 2).[12] Accordingly, without rigorously controlled countermeasures, the practical use of **3** seems to be impossible. Thus, synthetic difficulty may have resulted in the paucity of systematic studies of diacetylene-group-connected Fc–(πES)$_2$ derivatives. In other words, the successful development of general synthetic methodology for 1,1′-bis(diacetylene-group) formation from the very reactive synthon **3** would further the fundamental chemistries of Fc–πES derivatives and could also open a new door of applied research, concurrently taking the advantages of molecular prochirality, electron-donating ability, and multidimensional interactions into account.

The unsettled situation of the synthesis of Fc–(πES)$_2$ derivatives strongly stimulated us to develop a methodology for practical use of **3**, on the basis of our achievements with diacetylene-group-connected πES derivatives.[2] In a previous communication, we reported the TMS-group-protected derivative **5**[13] chosen as an analogous synthon for **3** and examined its behavior in both TMS deprotection and oxidative coupling under several conditions (see below, Scheme 3). The results suggested the high potentiality of **5** as a hopeful candidate for generation of **3** and for construction of the Fc–(πES)$_2$ derivatives under basic and oxidative conditions.[14] In our continuous investigations of this methodology using **5**, it has been revealed that those reactions proceed efficiently under appropriate conditions. In this paper, a new methodology for in situ generation of **3** from **5** will be described, together with its application to the cross-coupling with some typical terminal acetylenes for the Fc–(πES)$_2$ derivatives **7**–**12** (Chart 2).

Results and Discussion

Reactivity and Behavior of TMS-Group-Protected 1,1′-Diethynylferrocene 5 under Various Conditions. As aforementioned, 1,1′-diethynylferrocene (**3**) is extremely difficult to use in synthetic reactions as is. On the other hand, the bis(TMS)-protected derivative **5** of **3** itself is easily derived from the corresponding acetylferrocene and handled in air at ambient temperature.[13] Accordingly, it is natural that the derivative **5** is employed as a useful synthon for Fc–(πES)$_2$ derivatives. However, as mentioned above, it is apparent that usual work-up after TMS removal of **5** with KOH in a deoxygenated H_2O–MeOH solution afforded the [4]ferrocenophane derivative **6** which is proposed to form via methoxide-

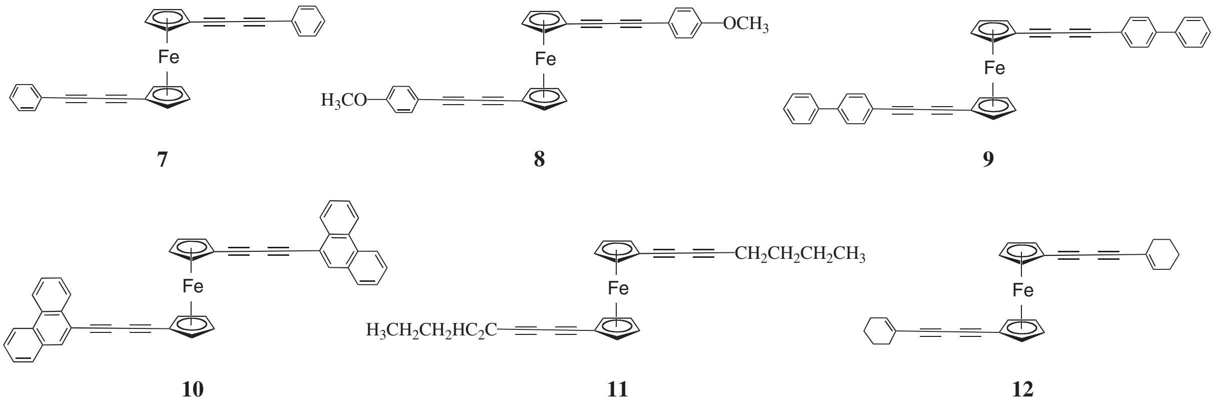
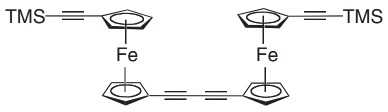


Chart 2.

Table 1. TMS-Group Deprotection Results of **5** under Various Conditions[a)]

Run	Reagents and media	Temperature	Products
1	K_2CO_3 (0.3 equiv) in $CHCl_3$–MeOH (1:1)[15]	RT	**4** + **5** (main)
2	K_2CO_3 (2.0 equiv) in $CHCl_3$–MeOH (1:1)	RT	**4**
3	Py–MeOH (1:1)	RT	**5**
4	$Cu(OAc)_2$ (2.0 equiv) in MeOH–Py (1:1)[19]	50 °C	**5**
5	K_2CO_3 (0.3 equiv)–$Cu(OAc)_2$ (2.0 equiv) in MeOH–Py (1:1)	50 °C	**4** (main) + **5**
6	K_2CO_3 (2.0 equiv)–$Cu(OAc)_2$ (2.0 equiv) in MeOH–Py (1:1)	RT	**4** + **5** + **13** (7%)
7	K_2CO_3 (2.0 equiv)–$Cu(OAc)_2$ (2.0 equiv) in $CHCl_3$–MeOH–Py (1:1:1)	50 °C	**4** + **5** + **13** (12%)
8	K_2CO_3 (10 equiv)–$Cu(OAc)_2$ (2.0 equiv) in $CHCl_3$–MeOH–Py (1:1:1)	50 °C	**4** + **13** (37%)
9	K_2CO_3 (10 equiv)–$Cu(OAc)_2$ (10 equiv) in $CHCl_3$–MeOH–Py (1:1:1)	50 °C	**4** + **13** (32%)

a) **5** (50 mg, 1.3×10^{-1} mmol) was admixed with reagents in 50 cm^3 of the solution and was stirred for 10 h.

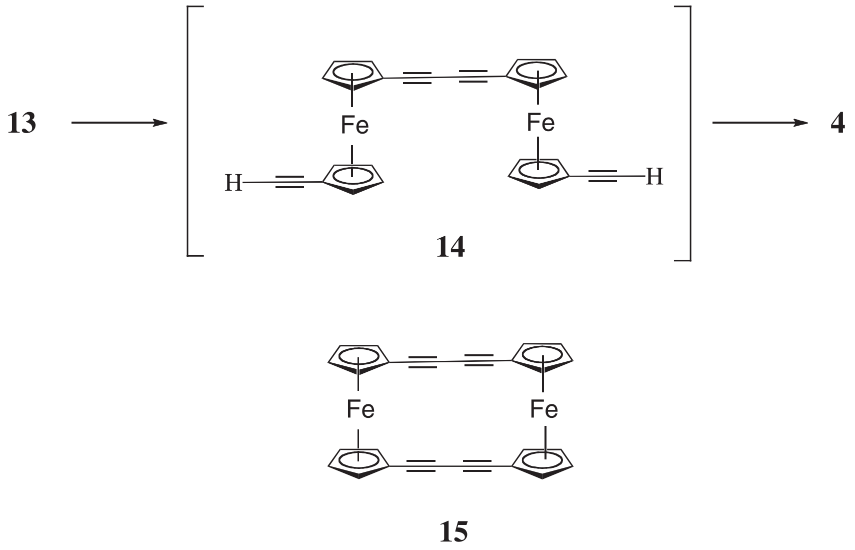


13

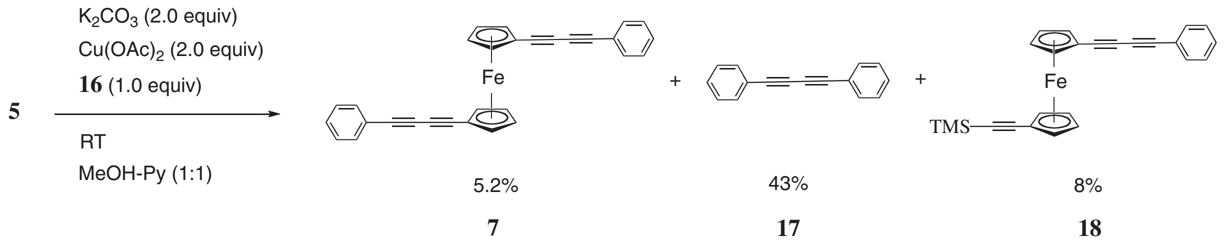
anion attack on the deprotected product **3** followed by an intramolecular cyclization (Scheme 2).[12] It is also true that treatment of **5** with potassium carbonate (K_2CO_3) in once-distilled MeOH under air for 10 h only afforded insoluble substances.[15] These substances should be a mixture of 1,1′-bis(diacetylene-group)-linked Fc polymers **4** [–(C:::C–Fc–C:::C)$_n$–], as evidenced by MS spectral measurement (Scheme 1 and also see below). In the latter case, neither the desired 1,1′-diethynyl product **3** nor any other assignable products could be isolated. The difference in product from **5** between these deprotection conditions likely arises from the content of methoxide-anion in respective reaction media, which should be further studied mechanistically. Anyway, these facts simply conclude that the TMS removal of **5** smoothly takes place even with the very weak base K_2CO_3 in MeOH to generate 1,1′-diethynylferrocene (**3**) but compound **3** is difficult to isolate.

Such highly labile behavior of **3** bearing two reaction sites led us to recall the diselenol synthon (HSe–R–SeH) with a pronounced tendency toward oxidative polymerization [–(Se–R–Se–Se–R–Se)$_n$–] under ordinary conditions.[16] In order to handle the reactive diselenol, a corresponding stable diselenocyanide derivative [(NCSe)–R–(SeCN)] was treated in a tandem system, reduction with sodium borohydride ($NaBH_4$) simultaneously with nucleophilic substitution with benzyl halides ($ArCH_2$–X). Finally, this tandem system proved to be a convenient synthetic method for bis($ArCH_2$-group)-bridged selenides ($ArCH_2$–Se–R–Se–CH_2Ar) of various types including selenacyclophanes in excellent yields.[17] Therefore, this successful methodology was similarly applied to the coupling reaction of **5** in a tandem system, TMS deprotection of **5** followed by oxidative coupling with other terminal acetylenes in one pot. Although especially in the silylated compounds, in situ TMS-deprotection is widely employed for organic reactions,[18] little attention has been paid to TMS-deprotection of **5** for organic syntheses.[11,12,14]

Preliminarily, the behavior of **5** under limited reaction conditions was examined. Each reaction was carried out for 10 h under the applied conditions. Poured into water after the deprotection, the reaction mixture was once filtered to remove the insoluble substances **4**, extracted and separated by means of successive column chromatography (see Experimental). The results are summarized in Table 1. The Eglinton media, i.e., pyridine (Py), copper(II) acetate [$Cu(OAc)_2$], and/or co-solvent MeOH in this case were found to be entirely inert to **5**, albeit a slightly basic reaction environment favorable for the TMS-group deprotection of **5** (Runs 3 and 4).[19] When a solution of **5** was added to Eglinton media in the presence of K_2CO_3, the



Scheme 4.



Scheme 5.

reaction gradually proceeded to form a linear Fc dimer **13** as a homocoupling product, together with a considerable quantity of **4** (Runs 5 and 6). The reaction temperature of around 50 °C is applicable to the present reaction, as is generally the case for Eglinton coupling.[2,19] Chloroform ($CHCl_3$) was also effective for the reaction (Run 7), probably due to good solubility of **13**. Furthermore, it shows that 10 molar equivalents of K_2CO_3 to **5** works adequately, while 2 molar equivalents of $Cu(OAc)_2$ to **5** is satisfactory (Runs 8 and 9). At this stage, it may be concluded that the TMS removal of **5** followed by oxidative coupling to **13** takes place rather efficiently under the conditions of Run 8.

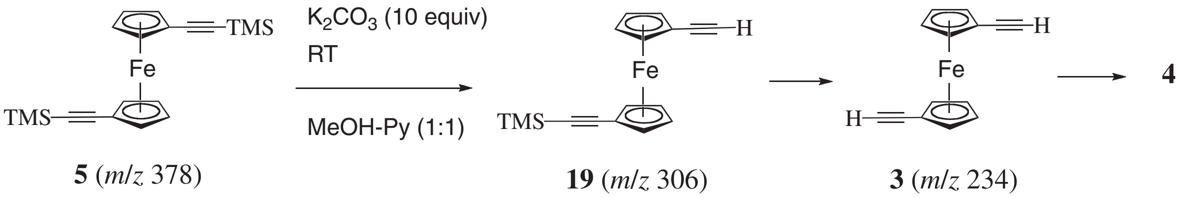
In this reaction, the cyclic Fc dimer **15**, diacetylene-group-bridged Fc cyclophane, was not isolated at all (Scheme 4). This indicates that two terminal acetylene sites in **14** exist opposite from each other in the present reaction media, apparently suffering a steric disadvantage from the entropy-controlled coupling reaction.[11]

As a result, it is suggested that 1,1′-diethynylferrocene (**3**) possibly is generated from the TMS-protected precursor **5** and is potentially oxidatively coupled with other terminal acetylenes to the corresponding diacetylene Fc derivatives, somewhere in the Eglinton oxidative coupling media containing K_2CO_3. In fact, this expectation proved to be correct by the following observations (see below).

Rate of Deprotection of 5 under the Applied Conditions. According to the preliminary and aforementioned results,[14] an oxidative heterocoupling of TMS-protected derivative **5** with phenylacetylene (**16**) was examined in a mixture of MeOH–Py (1:1) containing $Cu(OAc)_2$ and K_2CO_3 (Scheme 5). As expected, the desired 1,1′-bis(4-phenyl-1,3-butadiynyl) Fc derivative **7** could be obtained, though not in good yield (ca. 5% yield under the conditions of Run 6 in Table 1, see Scheme 5). To our best knowledge however, the present low-yielded product **7** is the first example of Fc–(πES)$_2$ derivatives with no additional substituents on the Cp rings.

In this reaction, it is apparently convenient for phenylacetylene (**16**) to exist in the same media to react immediately with the deprotected products from **5**, because product **3** is extremely liable toward self-polymerization. But, it would not be necessarily profitable for **16** to exist in the same media from the beginning of deprotection of **5**. The TMS removal reaction of **5** should compete with the oxidative homocoupling of **16** to **17**, since both reactions proceed in one pot under basic and oxidative coupling conditions (Schemes 3 and 5, also see Table 1). During the progress of the deprotection, the terminal acetylene **16** is also consumed to some extent to form **17**, resulting in a collapse of molar ratio between **5** and **16** (lowering yield of **7**). Yet, needless to say, the reactivity of the respective terminal acetylenes under the oxidative conditions is different, though it may be lower than that of **3**.

Therefore, deprotection of **5** (1.0 equiv) with K_2CO_3 (10 equiv) in a mixture of MeOH–Py (1:1) in the absence of $Cu(OAc)_2$ was followed and observed by means of MS, because the first stage product **19** could be hardly separated with column chromatography but could be eventually detected



Scheme 6.

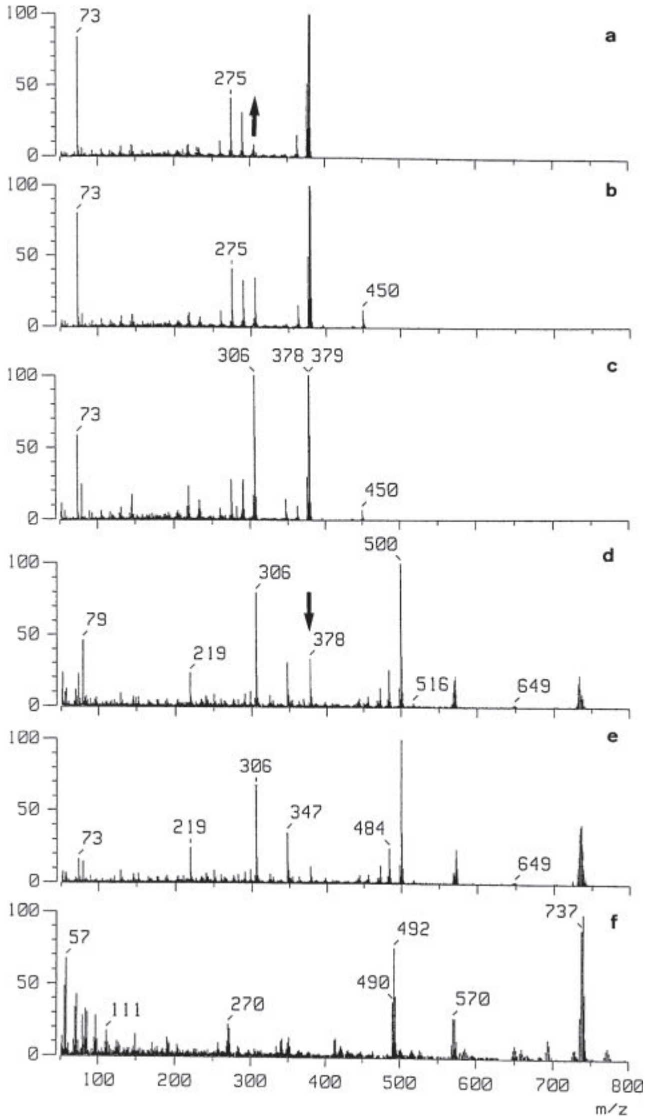


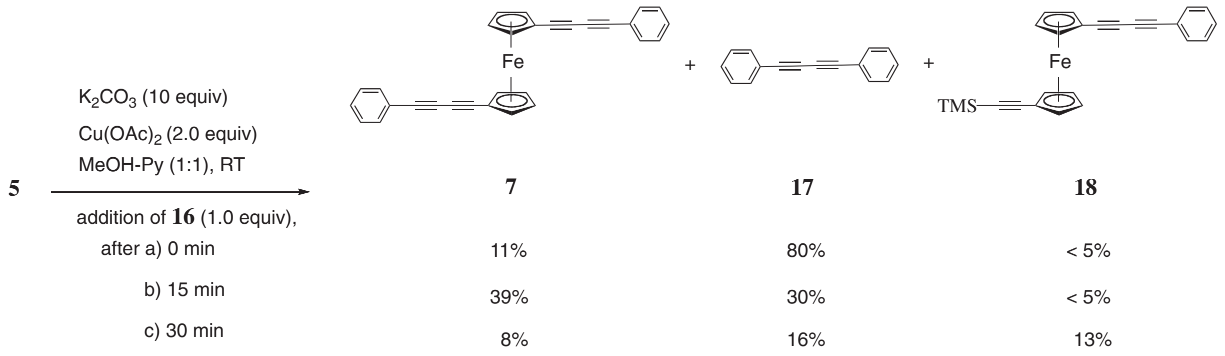
Figure 1. TMS removal of **5** (50 mg, 1.3×10^{-1} mmol) with K_2CO_3 (1.3 mmol) in a mixture of MeOH and Py (1:1, 50 cm^3) was followed by MS measurements in a region of *m*/*z* 50–800. Each reaction mixture was quenched and treated similarly to the general reaction before measurement (see Experimental). MS spectra (a) after 15 min, (b) after 20 min, (c) after 30 min, (d) after 1 h, (e) after 2 h, and (f) the insoluble substances **4**.

with MS (Figure 1 and Scheme 6). The *m*/*z* value of 234 corresponding to 1,1′-diethynylferrocene (**3**) was not observed at all, indicating that immediately after the second TMS removal, the oxidative self-coupling of **3** spontaneously and dominantly takes place to form diacetylene Fc polymers **4**. Under the applied conditions, the mono-deprotected product **19** (*m*/*z* 306, marked by an arrow in Figure 1a) was negligibly observed for 15 min since the deprotection of **5** started. Additionally, compound **19** gradually began forming at around 20 min, as well as polymers **4** (Figures 1b and 1c). After around 1 h, the intensities of **19** and **5** (*m*/*z* 378, marked by an arrow in Figure 1d) were reversed. The deprotection of **5** was largely complete within about 10 h, and the first-stage product **19** disappeared completely and was replaced with Fc polymers **4** entirely (Figures 1e and 1f).

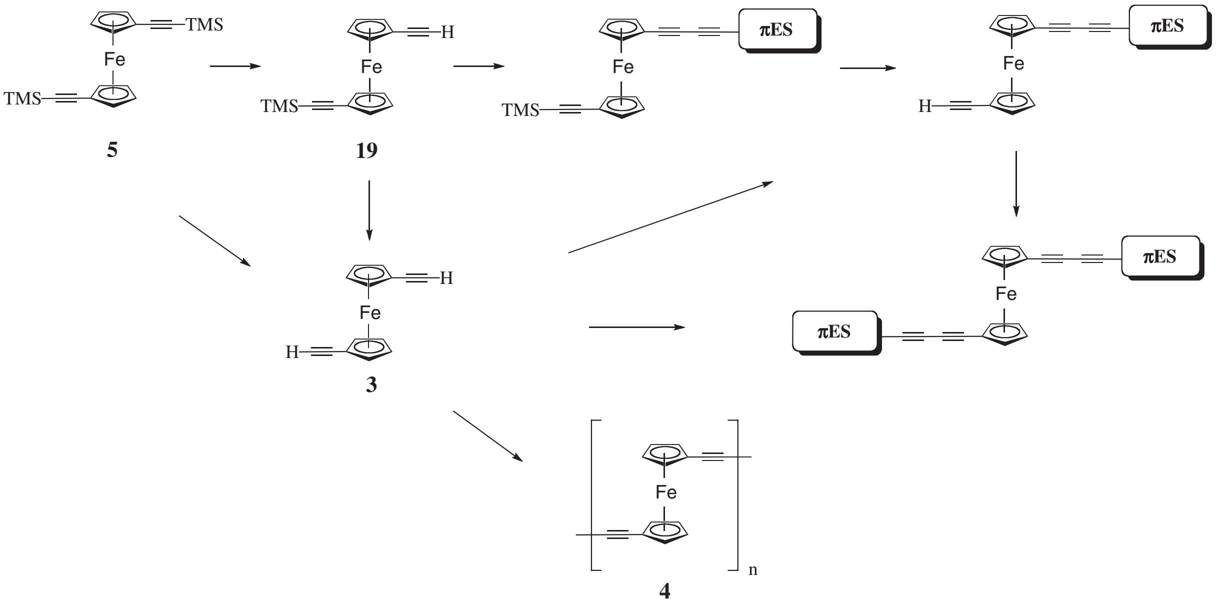
These results indicate the existence of a time zone for addition of the terminal acetylene into the prepared solution, i.e., between 15 and 20 min after the admixed point of **5** and K_2CO_3. In practice, when phenylacetylene (**16**, 1.0 equiv) existed in the same media from the beginning of the deprotection of **5** (1.0 equiv) with K_2CO_3 (10 equiv) under the Eglinton conditions [Cu(OAc)$_2$, 2.0 equiv], 1,4-diphenyl-1,3-butadiyne (**17**) was the main product (ca. 80% yield) and 1,1′-bis(diacetylene) Fc derivative **7** was a very minor product (Scheme 7). Similarly, when **16** was added 30 min later into an admixed solution of **5** and K_2CO_3, the yield of **7** was only 8%. In both cases, insoluble Fc polymers **4** formed in quantity. In contrast, when **16** was added 15 min later into the admixed solution of **5** and K_2CO_3 under the same conditions, the yield of **7** significantly increased to ca. 40% (Scheme 7). As a consequence, though it has not been optimized yet, the respective terminal acetylenes should be added continuously into the basic and Eglinton media containing **5** ca. 15 min later, taking the reactivity of **3** and the terminal acetylenes into consideration (see general procedure in Experimental).

Application to One-Pot Synthesis of Fc–(πES)$_2$ Derivatives. Based on a well-thought-out deprotection of **5**, heterocoupling reactions of TMS-protected derivative **5** (1.0 equiv) with typical terminal acetylenes were performed in a mixture of MeOH–Py–CHCl$_3$ (1:1:1) containing Cu(OAc)$_2$ (2.0 equiv) and K_2CO_3 (10 equiv) at 50 °C (see Table 1, Run 8). The solution of **5** was stirred punctually for 15 min and then a solution of the terminal acetylene (2.0 equiv) was added to the resultant mixture continuously over 30 min. The reaction mixture was stirred until the reactants **5** and terminal acetylene disappeared completely, mostly within around 10 h. After usual work-up, the mixture was separated by column chromatography on silica gel (SiO$_2$). The corresponding Fc–(πES)$_2$ derivatives **7**–**12** were successfully obtained in acceptable yields, together with respective homocoupling products of the terminal acetylenes (Chart 2).

In the case of the reaction with phenylacetylene (**16**), the Fc–πES derivative **18** bearing one diacetylene linkage could also be isolated as a by-product (Scheme 5). In addition to the MS



Scheme 7.



Scheme 8.

detection of compound **19**, the isolation of compounds **13** and **18** suggests that both TMS deprotection of **5** and diacetylene-linkage formation leading to Fc–(πES)$_2$ proceed rather stepwise under the present conditions, prior to other one-step courses (Scheme 8). All the Fc–πES derivatives including **13** and **18** are bright orange microcrystallines and are stable enough to be stored in a refrigerator for more than 1 year.

Conclusion

A synthetic methodology for 1,1′-bis(diacetylene-group)-connected Fc–(πES)$_2$ derivatives has been successfully developed by employing a tandem system, TMS-group deprotection of **5** and oxidative coupling of the in situ generated synthon **3** (probably via **19**) with other terminal acetylenes in one pot. At present, this synthetic methodology for Fc–(πES)$_2$ seems to be applicable to terminal acetylenes of several types bearing not only alkenyl and aromatic but also alkyl structures, though not in excellent yields. Therefore, the present results would expand the research area of diacetylene Fc–πES derivatives in material science, since each Cp ring of Fc carries no substituents and thus inherently is less perturbed both sterically and electronically.[11] Further investigations of the TMS-group-protected derivative **5** as a useful synthon for Fc–(πES)$_2$ are under way, in terms of optimization and mechanism for the present coupling reaction, as well as limitation of application to other terminal acetylenes such as heterocyclic nucleic compounds like pyridine and thiophene.[20]

Experimental

The melting points (Mp) were determined on a hot-stage apparatus and are uncorrected. EI and FAB mass spectra were recorded with a JEOL JMS-700 spectrometer. IR spectra were measured on a Jasco FT/IR 7300 spectrophotometer as KBr disk or neat sample; only significant absorptions are recorded in ν values (cm^{-1}). ^{1}H NMR spectra were measured in CDCl$_3$ solution on a JEOL ECX-300A (300 MHz) or a JEOL JMN-EPC 600 (600 MHz) spectrometer and were recorded in δ values (ppm) with TMS as an internal standard. The coupling constants (J) are given in Hz. Electronic absorption spectra were measured in CHCl$_3$ solution on a Shimadzu UV-2200A spectrophotometer and absorption maxima of respective bands are reported in $\lambda_{\max}$ values (nm) with their extinction coefficient (ε) (sh: shoulder). SiO$_2$ (Fujisilysia BW 820MH or BW 127ZH) was used for column chromatography. Reactions were followed by TLC on aluminum sheets precoated with Merck SiO$_2$ F$_{254}$ or with Merck Al$_2$O$_3$ GF$_{254}$.

Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4) or magnesium sulfate ($MgSO_4$) prior to removal of the solvents.

TMS Deprotection of 5 under the Reaction Conditions of Run 8 in Table 1. A solution of **5** (49 mg, 0.13 mmol), $Cu(OAc)_2$ (48 mg, 0.26 mmol), and K_2CO_3 (179 mg, 1.3 mmol) in a mixture of $CHCl_3$, MeOH, and Py (50 cm^3, 1:1:1) was stirred at 50 °C for 10 h. The resultant solution was concentrated to ca. 10 cm^3 under reduced pressure at ambient temperature. Poured into water and filtered once, the reaction mixture was extracted with $CHCl_3$. The extracts were washed with 1 M HCl, with brine, and then dried. The residue obtained after removal of the solvents was chromatographed ($\phi 3 \times$ 10 cm) with hexane–$CHCl_3$ (3:1) to afford compound **13** (16 mg, 37%) as yellow solid. **13**: Orange powder (hexane–$CHCl_3$); mp: 175–180 °C (dec); EI-MS: m/z 610 and 611 (M^+ and $M^+ + 1$) for $C_{34}H_{34}Si_2Fe_2$ as ^{56}Fe; IR (KBr): $\nu = 2220$, 2150, 1495, and 1435; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.50–4.48 (8H, m, Fc-H), 4.29 and 4.27 (4H each, tm, $J = 2.4$ Hz, Fc-H), 0.25 (18H, s, $SiCH_3$); UV–vis (ε): broad absorption curve with a shoulder band of $\lambda_{max} = 303$ nm (38000, sh) tailing up to around 700 nm. Anal. Calcd for $C_{34}H_{34}Si_2Fe_2$: C, 66.89; H, 5.61%. Found: C, 66.85; H, 5.73%.

According to the reaction conditions of Run 8 in Table 1, all Fc–(πES)$_2$ derivatives **7–12** in this study were synthesized. General experimental procedures are described, with **7** as an example: A solution of **5** (200 mg, 0.53 mmol), $Cu(OAc)_2$ (200 mg, 1.10 mmol), and K_2CO_3 (760 mg, 5.50 mmol) in a mixture of Py, MeOH and $CHCl_3$ (200 cm^3, 1:1:1) was stirred for 15 min at 50 °C. To the resulting mixture, phenylacetylene (**16**, 120 mg, 1.17 mmol) in the same mixed solution (30 cm^3) was added continuously within 30 min and kept with vigorous stirring for 10 h. The reaction mixture was concentrated to ca. one-third in volume under reduced pressure, poured into water, filtered once to remove insoluble substances **4** and extracted with $CHCl_3$. The extracts were shaken with 1 M HCl, washed with brine thoroughly and then dried. The residue obtained after removal of the solvent under reduced pressure was chromatographed ($\phi 3 \times 20$ cm) with hexane–$CHCl_3$ (2:1) to afford compound **7** (115 mg, 50%) and compound **18** (18 mg, 8% based on **5**), together with homocoupling product **17** (35 mg, 17% based on **16**).

Compound 7: Orange microcrystalline (hexane–$CHCl_3$); mp: gradual decomp. above 165 °C; EI-MS: m/z 434 and 435 (M^+ and $M^+ + 1$) for $C_{30}H_{18}Fe$ as ^{56}Fe; IR (KBr): $\nu = 2218$, 2144, 1492, and 1441; ^{1}H NMR: δ 7.45 (4H, dm, $J = 6.6$ Hz, phenyl-H), 7.32 (2H, tm, $J = 7.2$ Hz, phenyl-H), 7.25 (4H, dm, $J = 7.2$ Hz, phenyl-H), 4.58 and 4.37 (4H each, tm, $J = 2.4$ Hz, Fc-H); UV–vis (ε): $\lambda_{max} = 265$ (14700), 277 (15800), 295 (14900), 316 (15200), 345 (12500, sh), and 463 (800). Anal. Calcd for $C_{30}H_{18}Fe$: C, 82.96; H, 4.18%. Found: C, 82.68; H, 4.41%.

1,4-Diphenyl-1,3-butadiyne (17):[21] Colorless fine needles (hexane–$CHCl_3$); EI-MS: m/z 202 and 203 (M^+ and $M^+ + 1$) for $C_{16}H_{10}$; IR (KBr): $\nu = 3050$, 2148, 1484, 915, and 755; ^{1}H NMR: δ 7.54–7.52 (4H, m, phenyl-H) and 7.39–7.32 (6H, m, phenyl-H); UV–vis (ε): $\lambda_{max} = 261$ (26200), 290 (15800), 308 (31800), and 330 (29500). Anal. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98%. Found: C, 94.91; H, 5.23%.

Compound 18: Yellow-orange microcrystalline (hexane–$CHCl_3$); mp: gradual decomp. above 160 °C; EI-MS: m/z 406 and 407 (M^+ and $M^+ + 1$) for $C_{25}H_{22}SiFe$ as ^{56}Fe; IR (KBr): $\nu = 2218$, 2148, 1495, and 1430; ^{1}H NMR: δ 7.51 (2H, dm, $J = 7.8$ Hz, phenyl-H), 7.37–7.28 (3H, m, phenyl-H), 4.52 and 4.50 (2H each, tm, $J = 2.0$ Hz, Fc-H), 4.29 (4H, broad s, Fc-H), 0.24 (9H, s, $SiCH_3$); UV–vis (ε): 274 (38100), 289 (34400), 311 (30700), 331 (21500, sh), 378 (4800, sh), and 453 (1850). Anal. Calcd for $C_{25}H_{22}SiFe$: C, 73.89; H, 5.46%. Found: C, 73.77; H, 5.98%. Attempts to improve the elemental analysis failed.

Other 1,1′-bis(diacetylene-group)-connected Fc–πES derivatives **8–12** were synthesized in a way similar to the general procedures described above. Basically characteristic properties of the respective Fc–(πES)$_2$ derivatives only are shown, together with those of the corresponding homocoupling products between terminal acetylenes.

Compound 8: 36% yield. Orange fine needles (hexane–$CHCl_3$); mp: 177–183 °C (dec); EI-MS: m/z 495 and 496 ($M^+ + 1$ and $M^+ + 2$) for $C_{32}H_{22}O_2Fe$ as ^{56}Fe; IR (KBr): $\nu = 3006$, 2219, 2144, 1602, 1510, 1251, and 831; ^{1}H NMR: δ 7.39 (4H, d, $J = 8.8$ Hz, phenyl-H), 6.77 (4H, d, $J = 8.8$ Hz, phenyl-H), 4.57 and 4.35 (4H each, t, $J = 2.0$ Hz, Fc-H), 3.80 (6H, s, OCH_3); UV–vis (ε): $\lambda_{max} = 283$ (30700), 302 (30100), 319 (29300), 343 (26200, sh), and 451 (1200). Anal. Calcd for $C_{32}H_{22}O_2Fe$: C, 77.75; H, 4.49%. Found: C, 77.52; H, 4.65%.

1,4-Bis(*p*-methoxyphenyl)-1,3-butadiyne: 55% yield. Pale yellow needles (hexane–$CHCl_3$); mp: gradual decomp. above 175 °C; EI-MS: m/z 262 and 263 (M^+ and $M^+ + 1$) for $C_{18}H_{14}O_2$; IR (KBr): $\nu = 3002$, 2840, 2138, 1599, 1504, 1294, 1254, 1167, and 842; ^{1}H NMR: δ 7.46 and 6.85 (4H each, d, $J = 9.2$ Hz, phenyl-H), 3.81 (6H, s, OCH_3). UV–vis (ε): $\lambda_{max} = 270$ (26800), 283 (25100), 300 (28200), 320 (35100), and 343 (29100). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%. Found: C, 82.33; H, 5.63%.

Compound 9: 46% yield. Orange fine needles (hexane–$CHCl_3$); mp: gradual decomp. above 170 °C; FAB-MS: m/z 587 and 588 ($M^+ + 1$ and $M^+ + 2$) for $C_{42}H_{26}Fe$ as ^{56}Fe; IR (KBr): $\nu = 2923$, 2851, 2218, 2148, 1487, 1282, 993, and 841; ^{1}H NMR: δ 7.50–7.48 (8H, m, biphenyl-H), 7.44 (4H, d, $J = 5.6$ Hz, biphenyl-H), 7.40–7.37 (4H, m, biphenyl-H), 7.36–7.34 (2H, m, biphenyl-H), 4.60 and 4.37 (4H each, t, $J = 2.0$ Hz, Fc-H); UV–vis (ε): $\lambda_{max} = 285$ (47500, sh), 325 (49500), 355 (31300), and 454 (1800). Anal. Calcd for $C_{42}H_{26}Fe$: C, 86.01; H, 4.47%. Found: C, 85.86; H, 4.66%.

1,4-Bis(*p*-biphenyl)-1,3-butadiyne: 33% yield. Pale yellow needles (hexane–$CHCl_3$); mp: gradual decomp. above 160 °C; EI-MS: m/z 355 and 356 ($M^+ + 1$ and $M^+ + 2$) for $C_{28}H_{18}$; IR (KBr): $\nu = 3031$, 2923, 2852, 2146, 1598, 1482, 1006, 841, and 766; ^{1}H NMR: δ 7.62–7.58 (12H, m, biphenyl-H), 7.47–7.45 (4H, m, biphenyl-H), 7.39–7.36 (2H, m, biphenyl-H); UV–vis (ε): $\lambda_{max} = 303$ (27800, sh), 312 (43800), 333 (50100), and 355 (30000). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%. Found: C, 94.82; H, 5.38%.

Compound 10: 12% yield. Orange needles (hexane–$CHCl_3$); mp: gradual decomp. above 175 °C; FAB-MS: m/z 634 and 635 (M^+ and $M^+ + 1$) for $C_{46}H_{26}Fe$; IR (KBr):

$\nu = 2925$, 2850, 2220, 2150, 1485, 1285, and 841; ^{1}H NMR: δ 8.35–8.28 (6H, m, phenanthryl-H), 7.72 (2H, s, phenanthryl-H), 7.61–7.38 (10H, m, phenanthryl-H), 4.67 and 4.41 (4H each, t, $J = 1.8$ Hz, Fc-H); UV–vis (ε): $\lambda_{\max} = 317$ (44600, sh), 337 (61500), 359 (47600), 379 (20700, sh), and 468 (2800). Anal. Calcd for $C_{46}H_{26}Fe$: C, 87.07; H, 4.13%. Found: C, 86.95; H, 4.28%.

1,4-Di-9-phenanthryl-1,3-butadiyne: 58% yield. Yellow fine needles (hexane–$CHCl_3$); mp: gradual decomp. above 160 °C; EI-MS: *m/z* 402 and 403 (M^+ and $M^+ + 1$) for $C_{32}H_{18}$; IR (KBr): $\nu = 3028$, 2925, 2850, 2146, 1598, 1482, 840, and 760; ^{1}H NMR: δ 8.74–8.68 (4H, m, phenanthryl-H), 8.56–8.53 (2H, m, phenanthryl-H), 8.20 (2H, s, phenanthryl-H), 7.91 (2H, d, $J = 7.9$ Hz, phenanthryl-H), 7.76–7.64 (8H, m, phenanthryl-H); UV–vis (ε): $\lambda_{\max} = 321$ (35600, sh), 334 (55500), 353 (66900), and 381 (62600). Anal. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51%. Found: C, 95.33; H, 4.75%.

Compound 11: 38% yield. Bright orange needles (hexane–$CHCl_3$); mp: gradual decomp. above 155 °C; EI-MS: *m/z* 394 and 395 (M^+ and $M^+ + 1$) for $C_{26}H_{26}Fe$ as ^{56}Fe; IR (KBr): $\nu = 3103$, 2960, 2931, 2860, 2233, 2151, and 824; ^{1}H NMR: δ 4.48 and 4.28 (4H each, t, $J = 1.8$ Hz, Fc-H), 2.32 (4H, t, $J = 7.0$ Hz, CH_2), 1.58–1.41 (8H, m, CH_2), 0.93 (6H, t, $J = 7.3$ Hz, CH_3); UV–vis (ε): $\lambda_{\max} = 275$ (13500, sh), 299 (15400), and 451 (970). Anal. Calcd for $C_{26}H_{26}Fe$: C, 79.19; H, 6.65%. Found: C, 78.90; H, 6.83%.

1,4-Dibutyl-1,3-butadiyne (=5,7-dodecadiyne):[22] 45% yield. Colorless solid (hexane); EI-MS: *m/z* 162 and 163 (M^+ and $M^+ + 1$) for $C_{12}H_{18}$; ^{1}H NMR: δ 2.54 (4H, t, $J = 7.2$ Hz, CH_2), 1.56–1.44 (8H, m, CH_2), 0.91 (6H, t, $J = 7.8$ Hz, CH_3). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18%. Found: C, 88.61; H, 11.25%.

Compound 12: 53% yield. Orange powder (hexane–$CHCl_3$); mp: gradual decomp. above 165 °C; EI-MS: *m/z* 443 and 444 ($M^+ + 1$ and $M^+ + 2$) for $C_{30}H_{26}Fe$ as ^{56}Fe; IR (KBr): $\nu = 3102$, 2930, 2860, 2211, 2138, 1346, 1239, 990, and 827; ^{1}H NMR: δ 6.30–6.28 (2H, m, olefinic-H), 4.51 and 4.31 (4H each, t, $J = 2.0$ Hz, Fc-H), 2.17–2.15 (4H, m, CH_2), 2.13–2.10 (4H, m, CH_2), 1.65–1.62 (4H, m, CH_2), 1.61–1.55 (4H, m, CH_2); UV–vis (ε): $\lambda_{\max} = 315$ (17100) and 457 (950). Anal. Calcd for $C_{30}H_{26}Fe$: C, 81.45; H, 5.92%. Found: C, 81.43; H, 6.10%.

1,4-Dicyclohexenyl-1,3-butadiyne: 32% yield. Pale yellow needles (hexane); mp: 140–145 °C (dec); EI-MS: *m/z* 210 and 211 (M^+ and $M^+ + 1$) for $C_{16}H_{18}$; IR (KBr): $\nu = 3026$, 2931, 2860, 2199, 2129, 1616, 1434, 1346, 917, and 841; ^{1}H NMR: δ 6.25–6.23 (2H, m, olefinic-H), 2.13–2.09 (8H, m, CH_2), 1.64–1.61 (4H, m, CH_2), and 1.59–1.56 (4H, m, CH_2); UV–vis (ε): $\lambda_{\max} = 263$ (8200), 278 (13600), 295 (18800), and 313 (14800). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63%. Found: C, 91.22; H, 8.75%.

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