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Tetrahedron Letters 48 (2007) 9190–9194
Tetrahedron Letters

A facile and efficient stereoselective synthesis of highly functionalised trisubstituted alkene derivatives of ferrocenealdehyde

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Received 2 April 2007; revised 16 October 2007; accepted 19 October 2007
Available online 25 October 2007

Abstract—The reaction of the Baylis–Hillman adduct **2** of ferrocenealdehyde with various oxygen and carbon nucleophiles in the presence of montmorillonite K10 clay catalyst furnished highly functionalised trisubstituted alkene derivatives of ferrocenealdehyde in excellent yield. Synthetic use of one of products **7** has been demonstrated with the synthesis of a 1,3-diyne ether derivative of ferrocene **16** via an Eglinton coupling reaction.

The chemistry of ferrocene and its derivatives remains an important research area[1] due to its applications in novel material development,[2] asymmetric catalysis,[3] non-linear optics,[4] biological properties[5] and electrochemistry.[6] Amongst various carbon–carbon bond forming reactions, the Baylis–Hillman reaction is an important reaction giving rise to densely functionalised molecules and is considered to be atom economic.[7] Clay catalysts are eco-friendly acid catalysts which have potential for replacing conventional mineral acids and are non-polluting. The advantages of clay-catalyzed reactions are that they are generally mild, solvent-free and easy to work-up.[8] Stereoselective construction of *E*-trisubstituted alkenes appended with functional groups is a difficult task in organic synthesis and only a few methods are known.[9–11] The isomerisation of acetates of Baylis–Hillman adducts catalysed by TMSOTf,[9,10] trifluoroacetic acid,[12] benzyl trimethylammonium fluoride[13] and Montmorillonite K10 clay-microwave[14a] are reported methods.

Functionalisation of ferrocene under mild conditions is a difficult task as multi-step rigorous reaction conditions are required. To address this problem and in continuation of our research on novel synthetic applications of Baylis–Hillman adducts,[14] we have examined the reaction of the Baylis–Hillman adduct **2** of ferrocenealdehyde with various oxygen and carbon nucleophiles in the presence of Montmorillonite K10 (Mont. K10) clay catalyst. The reaction was found to afford excellent yields of highly functionalised *E*-trisubstituted alkene derivatives of ferrocenealdehyde. The preliminary results of this investigation are the subject of this Letter.

The Baylis–Hillman adduct **2** was prepared according to the literature procedure[15] (Fig. 1). Attempts to synthesise other Baylis–Hillman adducts **3–5** with activated alkenes such as methyl acrylate, vinyl sulfone and

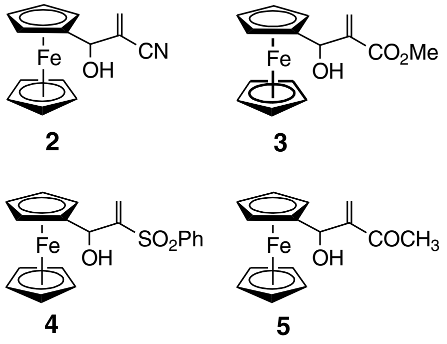

Figure 1.

Keywords: Ferrocenealdehyde; Baylis–Hillman adduct; Trisubstituted alkene; Montmorillonite K10; 1,3-Diyne ether.

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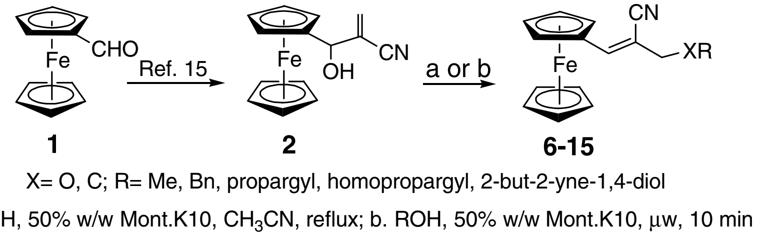
doi:10.1016/j.tetlet.2007.10.103



Scheme 1. Synthesis of highly functionalised trisubstituted alkene derivatives of ferrocenealdehyde.

methyl vinyl ketone under similar reaction conditions[15] and following other literature procedures ($TiCl_4$ and Bu_3P as catalysts)[7] failed. The reactions afforded only polymerised products of the alkenes and unreacted ferrocenealdehyde.

As shown in Scheme 1, we initiated our studies by treating the Baylis–Hillman adduct **2** with the unsaturated alcohol, but-2-yne-1,4-diol, and 50% w/w Mont. K10 clay in refluxing acetonitrile for 15 min to afford an excellent yield (95%) of the *E*-trisubstituted olefin **6** after silica gel column purification. The crude proton NMR spectrum of **6** revealed only the formation of the *E*-isomer. In the alkene region of the spectrum, the vinylic proton was observed at δ 7.01. To compare this reaction (conventional vs. microwave heating), the reaction mixture, without any solvent, was irradiated in a microwave oven (60% power level, SAMSUNG, Model: CE 118KF) for 10 min to afford a slightly better yield (97%) of compound **6** (Table 1, entry 1).

To show the generality of the method, reactions with a number of saturated and unsaturated alcohols, benzylamine, *p*-methylthiophenol and salicylaldehyde were studied with adduct **2** under optimised reaction conditions and conventional heating. All the reactions proceeded cleanly and smoothly to afford the corresponding trisubstituted olefins **7**–**15** in excellent yields (85–98%). In some cases, the alcohols acted as the solvent in place of acetonitrile (Table 1, entries 1, 8–10). We noticed the formation of *E*-trisubstituted olefins in most cases (Table 1). To prove this, the crude proton NMR spectra of compounds **7**–**11**, **13**, and **15** revealed the formation of the *E*-isomer only; in the alkene region of the spectra only a singlet due to the presence of one isomer was observed. The *E*-olefin proton was observed as a singlet in the range of δ 6.51–7.03 for all the reported compounds. Conclusive evidence for the structure, regio and stereochemistry of the reported compounds, was obtained by a single crystal X-ray analysis of compound **13**, Figure 2.[16]

The geometries of the *E*-isomers were further established based on NOE-irradiation studies (Fig. 3). Thus, the *E*-isomer **7** showed positive enhancement of the methylene protons at δ 4.24 (5.2%) upon irradiation of the vinyl proton at δ 7.03, similarly the *E*-isomer **9** upon irradiation of the vinyl proton at δ 6.96 showed positive enhancement (2.9%) of the methylene protons at δ 4.03, confirming that the compounds possessed *E*-geometry. The assignment of geometry of the products was also compared with previous reports.[10,14a,b]

The formation of unusual arylation product **12** was probably due to a Mont. K10 clay catalysed Friedel–Crafts arylation reaction. The regio and stereochemistry of compound **12** was determined based on ^1H NMR chemical shifts and couplings in the aromatic and olefinic region as shown in Figure 4. The olefinic H_a proton appeared as a singlet at δ 6.89. Amongst the aromatic protons H_b, H_c and H_d, the H_b proton appeared as a triplet at 7.05 ($J = 7.5$ Hz) whilst H_c and H_d occurred as a doublet at δ 7.53 ($J = 7.8$ Hz). The aldehyde and hydroxyl protons appeared as singlets at δ 9.91 (H_e) and δ 11.42 (H_f), respectively. The *Z*-geometries of compounds **12** and **14** were assigned based on NOE-irradiation experiment as shown in Figure 3.

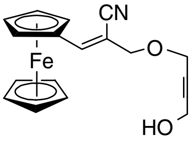
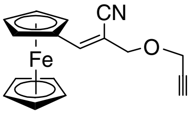
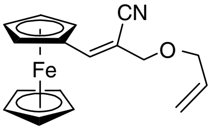
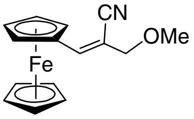
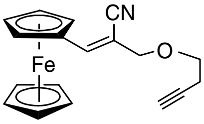
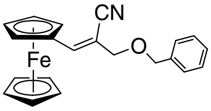
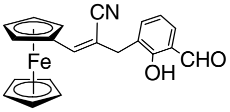
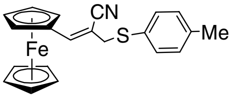
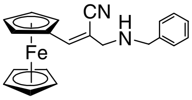
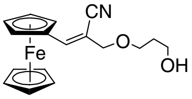
In a comparative study, the experiments reported herein were examined under microwave irradiation conditions. The reactions under microwave irradiation also provided excellent yields of the desired products being slightly higher than those from conventional heating. All new compounds were characterised from spectroscopic (IR, ^1H and ^{13}C NMR) and HRMS data (see typical procedure and spectral data). The results are summarised in Table 1.

To demonstrate the synthetic use of the products obtained, an Eglinton coupling reaction of ferrocene propargyl derivative **7** afforded the corresponding highly functionalised novel diyne ether derivative of ferrocene **16** in 41% yield, (Scheme 2). The structure of **16** was assigned based on spectroscopic and analytical data. The compounds obtained here are highly functionalised and can be used for further manipulations.

In conclusion, we have demonstrated a short and efficient stereoselective synthesis of highly functionalised trisubstituted alkene derivatives of ferrocenealdehyde. Further work using these compounds for the synthesis of novel ferrocene based materials is in progress in our laboratory.

General experimental procedure: Conventional heating: A mixture of Baylis–Hillman adduct **2** (1 mmol), 50% w/w Mont. K-10 clay and alcohols/aldehyde/thiophenol/benzylamine in acetonitrile was allowed to reflux for 15–30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the crude mixture was purified by silica gel column chromatography using gradient elution with hexane and hexane/EtOAc to afford pure compounds. *Microwave irradiation*: A mixture as above, without any solvent was irradiated (60% power level) in a microwave oven

Table 1. Synthesis of highly functionalised *E*-trisubstituted alkene derivatives of ferrocenealdehyde (**6**–**15**) from adduct **2**

Entry	Conditions		Product[c]	Yield[d] (%)	
	Conventional heating (A)[a]	Microwave irradiation (B)[b]		A	B
1	But-2-yne-1,4-diol, 50% w/w Mont. K10, CH_3CN, 15 min	But-2-yne-1,4-diol, 50% w/w Mont. K10, μw, 10 min	 **6**	95	97
2	Propargyl alcohol, 50% w/w Mont. K10, 15 min	Propargyl alcohol, 50% w/w Mont. K10, μw, 10 min	 **7**	98	98
3	Allyl alcohol, 50% w/w Mont. K10, reflux, 20 min	Allyl alcohol, 50% w/w Mont. K10, μw, 10 min	 **8**	90	92
4	Trimethyl orthoformate 50% w/w Mont. K10, reflux, 30 min	Trimethyl orthoformate 50% w/w Mont. K10, μw, 10 min	 **9**	92	94
5	Homopropargyl alcohol, 50% w/w Mont. K10, 20 min	Homopropargyl alcohol, 50% w/w Mont. K10, μw, 10 min	 **10**	90	96
6	Benzyl alcohol, 50% w/w Mont. K10, 20 min	Benzyl alcohol, 50% w/w Mont. K10, μw, 10 min	 **11**	94	97
7	Salicylaldehyde 50% w/w Mont. K10, 20 min	Salicylaldehyde 50% w/w Mont. K10, μw, 10 min	 **12**	90	92
8	4-Methylthiophenol 50% w/w Mont. K10, CH_3CN, 20 min	4-Methylthiophenol 50% w/w Mont. K10, μw, 10 min	 **13**	93	95
9	Benzylamine 50% w/w Mont. K10, CH_3CN, 20 min	Benzylamine 50% w/w Mont. K10, μw, 10 min	 **14**	85	92
10	Propane-1,3-diol 50% w/w Mont. K10, CH_3CN, 20 min	Propane-1,3-diol 50% w/w Mont. K10, μw, 10 min	 **15**	90	96

[a] Reflux.

[b] Irradiated at 60% power level, SAMSUNG, Model: CE 118KF.

[c] Stereochemistry of vinylic protons assigned based on ^1H NMR studies.

[d] After purification.

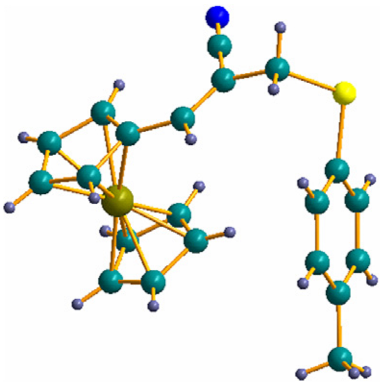
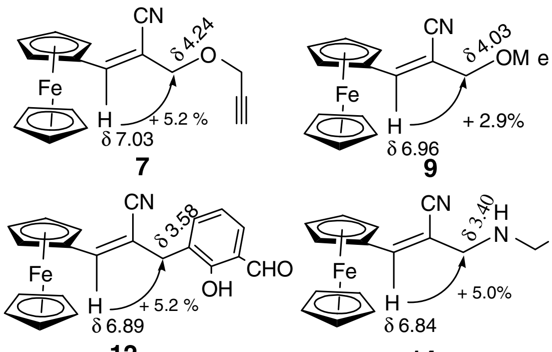


Figure 2. X-ray crystal structure of compound **13**.



7 **9** **12** **14**

Figure 3. NOE correlations of compounds **7**, **9**, **12** and **14**.

(10 min, SAMSUNG, Model: CE 118KF). The crude was purified by silica gel column chromatography. *Eglinton coupling of* **7**: A mixture of **7** (1 mmol) and 2 equiv of Cu(OAc)$_2$·H$_2$O (2 mmol) in pyridine-CH$_3$OH (1:1, 5 mL) was refluxed at 70 °C for 12 h. After completion of the reaction, the solvent was removed under reduced pressure. The crude reaction mixture was diluted with ethyl acetate (50 mL) and washed successively with 2N HCl, water, aqueous NaHCO$_3$ solution and brine. The organic layer was separated, dried (anhyd Na$_2$SO$_4$) and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography by elution with hexane/EtOAc mixture to afford pure 1, 3-diyne **16**.

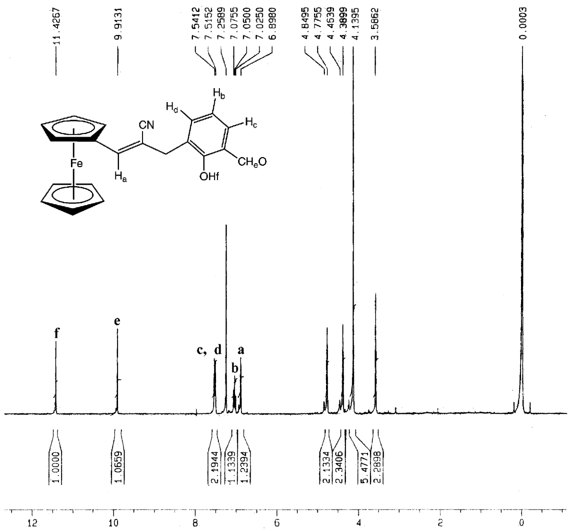
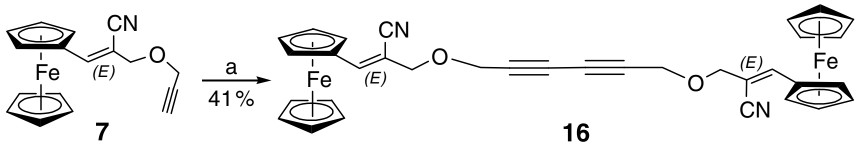


Figure 4. ^{1}H NMR (300.1 MHz, CDCl$_3$/TMS) spectrum of compound**12**.

Spectral data for selected compounds: *Compound* **6**: Red solid, mp 110–113 °C (decomposed); R_f: 0.5 in hexane/EtOAc (90:10); IR (CH$_2$Cl$_2$): $\nu_{\max}$ 3346, 2230, 2208, 1613, 1446, 1057 cm^{-1}; ^{1}H NMR (CDCl$_3$/TMS, 300.1 MHz): δ 1.95 (bs, 1H), 4.17–4.34 (m, 11H), 4.46 (s, 2H), 4.83 (s, 2H), 7.01 (s, 1H); ^{13}C NMR (CDCl$_3$/TMS, 75.3 MHz): δ 51.04, 57.40, 69.85, 69.91, 70.56, 70.83, 71.38, 71.81, 76.26, 80.98, 102.46, 118.21, 147.73; HRMS: Calcd for C$_{18}$H$_{17}$FeNO$_2$: 335.0609; found 335.0600. *Compound* **7**: Red solid, mp 95–98 °C (decomposed); R_f: 0.4 in hexane/EtOAc (90:10); IR (CH$_2$Cl$_2$): $\nu_{\max}$ 3236, 2917, 2208, 2115, 1613, 1445, 1058 cm^{-1}; ^{1}H NMR (CDCl$_3$/TMS, 300.1 MHz): δ 2.51 (t, $J = 2.2$ Hz, 1H), 4.20–4.42 (m, 9H), 4.48 (s, 2H), 4.85 (s, 2H), 7.03 (s, 1H); ^{13}C NMR (CDCl$_3$/TMS, 75.3 MHz): δ 59.91, 69.81, 69.89, 70.36, 71.37, 75.41, 76.24, 102.17, 118.85, 147.78.; HRMS: Calcd for C$_{17}$H$_{15}$FeNO: 305.0503; found: 305.0496. *Compound* **9**: Red solid, mp 90–93 °C, R_f: 0.4 in hexane/EtOAc (90:10); IR (CH$_2$Cl$_2$): $\nu_{\max}$ 2917, 2215, 2115, 1613, 1445, 1058 cm^{-1}; ^{1}H NMR (CDCl$_3$/TMS, 300.1 MHz): δ 3.41 (s, 3H), 4.02 (s, 2H), 4.19 (s, 5H), 4.45 (s, 2H), 4.82 (s, 2H), 6.96 (s, 1H); ^{13}C NMR (CDCl$_3$/TMS, 75.3 MHz): δ 57.91, 69.68, 69.72, 71.07, 73.42, 103.18, 118.71, 146.32; HRMS: Calcd for C$_{15}$H$_{15}$FeNO: 281.0503; found 281.0500. *Compound* **11**: Red solid, mp 115–119 °C (decomposed), R_f: 0.4 in hexane/EtOAc (90:10); IR (CH$_2$Cl$_2$): $\gamma_{\max}$: 2917, 2218, 2113, 1613, 1445, 1058 cm^{-1}; ^{1}H NMR (CDCl$_3$/TMS, 300.1 MHz): δ 4.09 (s, 2H), 4.18 (s, 5H), 4.44 (s, 2H), 4.58 (s, 2H), 4.82 (s, 2H), 6.96 (s, 1H), 7.36 (s, 5H); ^{13}C NMR (CDCl$_3$/TMS, 75.3 MHz): δ 69.64, 69.69, 70.82, 71.05, 72.04, 103.25, 118.75, 127.66, 127.81, 128.40, 137.26, 146.40; HRMS: Calcd for C$_{21}$H$_{19}$FeNO: 357.0816; found 357.0810. *Compound* **12**: Red solid, mp 130–133 °C (decomposed), R_f: 0.4 in hexane/EtOAc (90:10); IR (CH$_2$Cl$_2$): $\nu_{\max}$ 3236, 2917, 2208, 1640, 1613 cm^{-1}; ^{1}H



7 **16**

^{a} Cu(OAc)$_2$.H$_2$O (2 equiv.), Py:MeOH (1:1), 70 ^{o}C, 12 h

Scheme 2. Synthesis of the 1, 3-diyne ether derivative **16** of ferrocene from alkynyl ether **7**.

NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.58 (s, 2H), 4.13 (s, 5H), 4.38 (s, 2H), 4.77 (s, 2H), 6.89 (s, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 2H), 9.91(s, 1H), 11.42 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 34.92, 69.53, 69.65, 70.02, 70.83, 71.24, 103.68, 119.75, 120.56, 125.95, 132.89, 137.50, 145.58, 159.85, 196.58; HRMS: Calcd for $C_{21}H_{17}FeNO_2$: 371.0609; found 371.0600. *Compound* **13**: Red solid, mp 120–122 °C (decomposed); R_f: 0.4 in hexane/EtOAc (90:10); IR (CH_2Cl_2): ν_{max} 2650, 2208, 1613 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.33 (s, 3H), 3.55 (s, 2H), 4.25–4.97 (m, 9H), 6.51 (s, 1H), 6.98–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 21.23, 40.54, 70.05, 71.61, 72.07, 73.31, 102.95, 119.13, 130.05, 132.35, 137.87, 146.43; HRMS: Calcd for $C_{21}H_{19}FeNS$: 373.0588; found 373.0581. *Compound* **14**: Red solid, mp 130–133 °C (decomposed), R_f: 0.4 in hexane/EtOAc (90:10); IR (CH_2Cl_2): ν_{max} 3536, 2209, 1613 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.40 (s, 2H), 3.81 (s, 2H), 4.11–4.42 (m, 5H), 4.41 (s, 3H), 4.79 (s, 2H), 6.84 (s, 1H), 7.32–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 51.90, 52.22, 64.22, 69.50, 69.59, 69.69, 70.51, 70.78, 71.49, 105.41, 119.27, 127.14, 128.07, 128.25, 128.44, 139.29, 145.05; HRMS: Calcd for $C_{21}H_{20}FeN_2$: 356.0976; found 356.0971. *Compound* **16**: Red solid, mp 150–155 °C (decomposed), R_f: 0.4 in hexane/EtOAc (90:10); IR (CH_2Cl_2) ν_{max}: 2239, 2208, 1613, 1443, 1075 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 4.21 (s, 14H), 4.33 (s, 4H), 4.48 (s, 4H), 4.85 (s, 4H), 7.04 (s, 2H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 29.69, 57.45, 69.86, 69.95, 70.83, 71.06, 71.47, 74.91, 76.57, 101.73, 118.81, 148.18; HRMS: Calcd for $C_{34}H_{28}Fe_2N_2O_2$: 608.0850; found: 608.0850.

Acknowledgements

The authors thank Prof. Dr. T. K. Chandrashekar, Director, for providing infrastructure facilities. Financial support (SR/S1/OC-38/2005) from the DST (New Delhi) is gratefully acknowledged. P.S. thanks the reviewer of this manuscript for constructive suggestions. V.V. and B.V. thank CSIR (New Delhi) for the award of a Senior Research Fellowship.

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16. CCDC file number. 659838 contains the supplementary crystallographic data for compound **13**.