HETEROCYCLES, Vol. 89, No. 6, 2014, pp. 1463 - 1471. © 2014 The Japan Institute of Heterocyclic Chemistry
Received, 11th March, 2014, Accepted, 22nd April, 2014, Published online, 2nd May, 2014
DOI: 10.3987/COM-14-12977

A FACILE SYNTHESIS AND RING-OPENING REACTIONS OF NOVEL 2-FERROCENYL-3,4-DIHYDROPYRANS

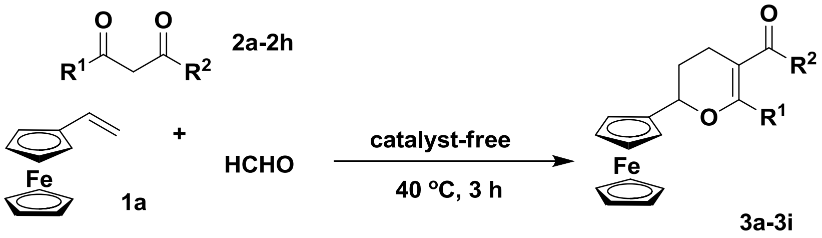
Yuying Du, Hui Qiao, Limin Han,* Ning Zhu, and Quanling Suo

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot 010051, PR China. E-mail: hhhtdyy@163.com

Abstract – A series of novel 2-ferrocenyl-3,4-dihydropyrans were synthesized in good to excellent yields through three-component reaction of vinylferrocene, 1,3-dicarbonyl compound and formaldehyde near room temperature under catalyst-free conditions. The obtained ferrocenyl dihydropyrans can also react readily with indole in the presence of alum, providing a ring-opening product in high yield, and this result opens an effective way to access a new class of complex ferrocenyl derivatives.

Recently, there has been a resurgence of interest in the synthesis and design of ferrocenyl derivatives because of their wide-spread applications in material chemistry,[1,2] asymmetric catalysis,[3] and bioorganometallic chemistry[4] and so on.[5] Of course, the design motif and synthesis strategy for ferrocenyl-based architectures play the most important roles in delivering the required properties. Although ferrocenyl derivatives are classical aromatic compounds, traditional methods for the constructing aromatic compounds may not work for ferrocene due to its specific geometric and electronic properties.[6] Furthermore, ferrocenyl fragments are sometimes sensitive to acid and high temperature.[7] Therefore, developing efficient methods for their synthesis under mild reaction conditions remains to be a challenge.

Multicomponent reactions (MCRs) have become a promising tool for synthetic organic chemists, since they allow complicated molecules to be created using one reaction in a fast, efficient, simple and energy savings manner.[8] Gu and Jérôme[9] reported a simple method for the synthesis of 2-aryl-3,4-dihydropyrans through multicomponent reaction of formaldehyde, 1,3-dicarbonyl compound and styrene. The key of this MCR is generation and the following trapping of a 2-methylene-1,3-dicarbonyl intermediate with styrene. According to a recent report of Cavaleiro,[10] *β*-vinyl-meso-tetraphenylporphyrin can also trap this type *o*-quinone methide. Because these reactions were generally performed in the absence of any catalyst under relative mild conditions, we therefore envisioned that it might be possible to use vinylferrocene, which is rather susceptible to acid and high temperature, as an alternative substrate to styrene. Herein, we will report our successful endeavor, in which a new class of ferrocenyl derivatives, 2-ferrocenyl-3,4-dihydropyrans, were synthesized through three-component reaction of vinylferrocene, 1,3-dicarbonyl compound and formaldehyde in acetonitrile near room temperature under catalyst-free conditions. Furthermore, the obtained ferrocenyl dihydropyrans can also react readily with indole in the presence of catalytic amount of alum, providing a ring-opening product in high yield **(Scheme 1)**.

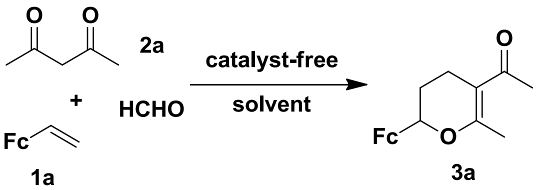


2a: R^1=Me; R^2=Me
2b: R^1=Me; R^2=OMe
2c: R^1=Me; R^2=OEt
2d: R^1=CF_3; R^2=OEt
2e: R^1=*i*-Pr; R^2=OMe
2f: R^1=*i*-Pr; R^2=OEt
2g: R^1=Ph; R^2=OEt
2h: R^1=Ph; R^2=Me

Scheme 1. Three-component reaction of vinylferrocene, acetoacetone and formaldehyde

Initially, a three-component reaction of vinylferrocene (**1a**), acetoacetone (**2a**) and formaldehyde was investigated in acetonitrile. As shown in **Table 1**, the desired product, 2-ferreenyl-3,4-dihydropran **3a**, could be obtained in 61% of yield after 3 hours of reaction at 40 °C when the ratio of **1a**/**2a**/HCHO is 1.0/1.0/1.0 (entry 1). Because vinylferrocence is the most expensive reagent among all the substrates used here, in order to increase the reaction yield, we therefore tried to increase the dosage of β-carbonyl compound and formaldehyde. As we expected, the reaction yield could be significantly improved by adding excess amount of acetoacetone and formaldehyde into the system, and finally, a maximum yield, 95%, could be obtained with the ratio of **1a**/**2a**/HCHO is 1.0/4.0/5.0 (entries 2 to 4). Because the model reaction proceeds according to a tandem Knoevenagel / *oxo* Diels-Alder reaction pathway, the only side reaction is Michael addition of the formed Knoevenagel methylene intermediate to acetoacetone,[11] the high yield obtained with large excess amount of **2a** and formaldehyde is quite reasonable. The reaction yield was significantly affected by solvent, and acetonitrile was proved to be the best solvent for the model reaction among all the solvents examined (entries 4 to 10). It should be noted that although water has been proved to be a preferable solvent for this type of reaction, only moderate yield was obtained when it was used in the model reaction (entry 6). Replacing formaldehyde aqueous solution with paraformaldehyde resulted in a significant decrease of the reaction yield (entry 11). Further investigation revealed that the model reaction was also affected by temperature and reaction time, and the optimal conditions should be 40 °C and 3 hours (entries 12 and 13).

Table 1. Three-component reaction of vinylferrocene, acetoacetone and formaldehyde[a]



entry	ratio of **1a**/**2a**/HCHO	solvent	temp. (°C)	time (h)	yield (%)
1	1.0/1.0/1.0	MeCN	40	3	61
2	1.0/1.5/2.0	MeCN	40	3	68
3	1.0/2.0/3.0	MeCN	40	3	74
4	1.0/4.0/5.0	MeCN	40	3	95
5	1.0/4.0/5.0	EtOH	40	3	65
6	1.0/4.0/5.0	H_2O	40	3	43
7	1.0/4.0/5.0	DMSO	40	3	trace
8	1.0/4.0/5.0	THF	40	3	38
9	1.0/4.0/5.0	DCE	40	3	trace
10	1.0/4.0/5.0	1,4-dioxane	40	3	24
11[b]	1.0/4.0/5.0	MeCN	40	3	27
12	1.0/4.0/5.0	MeCN	20	3	21
13	1.0/4.0/5.0	MeCN	40	2	68

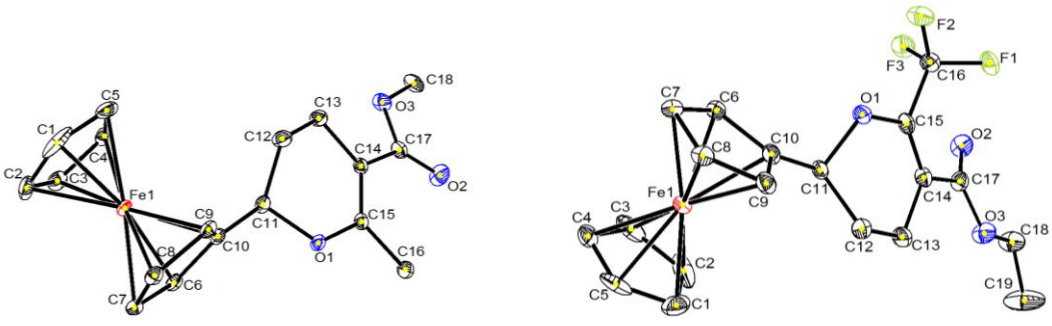
[a]: 1a: 1.0 mmol, solvent: 1 ml, aqueous formaldehyde (37 wt %) was used as HCHO source;

[b]: paraformaldehyde was used as HCHO source.

Having the optimized condition in hand, we then examined the substrate scope with respect to 1,3-dicarbonyl compounds. As shown in **Table 2**, various 1,3-diketones and *β*-ketoesters could be successfully used in the title reaction, providing 2-ferrocenyl-3,4-dihydropyrans in good to excellent yields. When benzoylacetone was used, two regioisomers could be obtained in a ratio in favor of the cycloadduct with the benzoyl group (entry 8, **3h** and **3i**). All the obtained compounds were characterized by ^{1}H, and ^{13}C NMR, IR and elemental analysis. Crystals of compounds **3b** and **3d** suitable for x-ray analysis were recrystallized from a solution of hexane and dichloromethane (50:1 v/v). Supplementary material crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 931129, 931130).

Table 2. Three-component reaction of **1a**, formaldehyde and different 1,3-dicarbonyl compounds

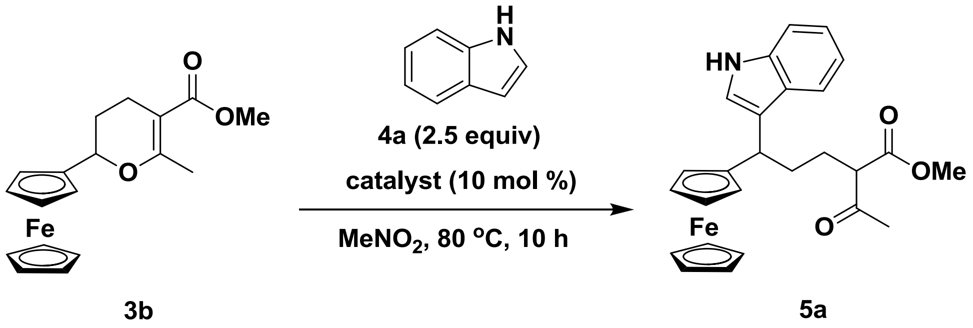
entry	1,3-dicarbonyl compound	product	yield (%)
1	**2a**	**3a**	95
2	**2b**	**3b**	68
3	**2c**	**3c**	66
4	**2d**	**3d**	89
5	**2e**	**3e**	86
6	**2f**	**3f**	60
7	**2g**	**3g**	67
8	**2h**	**3h**	56
		3i	30



3b **3d**

Figure 1. X-Ray structures of compounds **3b** and **3d**

It is well known that 2-aryl-3,4-dihydropyrans could be used as an electrophile to react with some nucleophiles, such as Grignard reagent,[12] indole and thiophenols,[13] in the presence of an appropriate acid catalyst. With this in mind, we then investigated the possibility of using the obtained 2-ferrocenyl-3,4-dihydropyran as a substrate in this type of Friedel-Crafts type ring-opening reaction. As shown in **Scheme 2**, when indole was used as a nucleophile, the desired product, **5a**, was obtained only in 5% of yield in the presence of $MnCl_2$ that has been proved to be an efficient catalyst for this type of ring-opening reaction.[14] The reaction yields could be improved, to some extent, by using strong acids, such as $In(OTf)_3$ and PTSA, as catalysts, however, the yields are still far from satisfactory. Interestingly, a good yield, 83%, was obtained with alum catalyst under the identical conditions. Because alum is a cheap and largely available chemical, this result opens thus an effective way to access a new class of ferrocenyl derivatives.



catalyst	yield (%)
$MnCl_2 \cdot 4H_2O$	5
$In(OTf)_3$	21
p-TSA$\cdot H_2O$	52
$KAl(SO_4)_2 \cdot 12H_2O$	83

Scheme 2. Friedel-Crafts ring-opening reaction of **3b** with indole

In summary, a three-component reaction of vinylferrocene, 1,3-dicarbonyl compound and formaldehyde was developed by using acetonitrile as solvent, which offers an effective way to access various novel 2-ferrocenyl-3,4-dihydropyrans. In the presence of alum catalyst, the obtained dihydropyran reacted readily with indole, providing a hitherto unpresented ferrocenyl derivative in excellent yield.

EXPERIMENTAL

Vinylferrocene was prepared according to a known method.[15] Other chemicals were commercially available. Melting points were recorded on an Electro-thermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet Nexus 670 FT spectrometer in KBr with absorptions in cm^{-1}. NMR spectra were measured using a Bruker AV-500 Avance spectrometer at 500.13 MHz (^{1}H) and 125.75 MHz (^{13}C), respectively. Chemical shifts were reported in ppm relative to TMS in $CDCl_3$. Mass spectra were obtained using Finnigan Polaris QMS or LCMS-2020 instrument. Elemental analysis was recorded on an Elementar Vario EL III elemental analyzer. X-ray diffraction data were recorded on a Bruker-Smart Apex CCD area detector with graphite monochromated Mo Kα radiation.

General procedure

Typical experimental procedure for three component reaction of vinylferrocene (1a), 2,4-pentanedione (2a) and formaldehyde: All reactions were conducted in a 10 mL U-type tube equipped with magnetic stirring. In a typical reaction, vinylferrocene **(1a)** (106.0 mg, 0.5 mmol) and 2,4-pentanedione **(2a)** (200.2 mg, 2.0 mmol) were mixed with formalin (202.7 mg, 2.5 mmol, 37 wt %)

and MeCN (1.0 mL) under air. The mixture was then heated at 40 °C for 3 h. After the reaction, the mixture was cooled to room temperature, and then extracted with CH_2Cl_2 (10.0 mL × 3). The obtained organic phase was then combined together and dried with anhydrous Mg_2SO_4. After concentration of the organic phases, the crude compounds were purified by chromatography over silica gel using CH_2Cl_2 as eluent. The desired product **3a** was obtained in 95% of yield (158.5 mg). Substrate scope for the three-component reaction was performed according to an analogous procedure.

Vinylferrocene (1a)[15]: Orange solid; mp 50-51 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.10-4.35 (m, 9H), 5.01-5.35 (m, 2H), 6.42-6.48, (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 134.7, 111.1, 83.6, 69.2, 68.7, 66.7; IR (KBr) *v*: 3132, 3008, 1626, 1400, 1100, 999, 894, 813 cm$^{-1;}$. EIMS *m/z* (M^+): 212.05. Anal. Calcd for $C_{12}H_{12}Fe$: C 67.96, H 5.70. Found: C 67.64, H 5.68.

3-Acyl-6-ferrocenyl-2-methyl-5,6-dihydropyran (3a): Yield 95%. Orange solid; mp 105-108 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.80-1.87 (m, 1H), 2.17 (s, 1H), 2.23-2.26 (q, 6H), 2.44-2.48 (m, 2H), 4.17-4.25 (m, 9H), 4.67 (dd, J_a = 2.0 Hz, J_b = 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 199.0, 164.7, 109.8, 87.6, 74.9, 68.8, 68.2, 68.0, 67.2, 66.3, 29.7, 28.1, 23.2, 21.2; IR (KBr) *v*: 3097, 2918, 2852, 1661, 1283, 1241, 1104, 918, 816 cm^{-1}; EIMS *m/z* (M^+): 324.17. Anal. Calcd for $C_{18}H_{20}FeO_2$: C 66.69, H 6.22. Found: C 66.34, H 6.40.

Methyl 3,4-dihydro-2-ferrocenyl-6-methyl-*2H*-pyran-5-carboxylate (3b): Yield 68%. Orange solid; mp 122-124 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.77-1.83 (m, 1H), 2.17-2.22 (m, 1H), 2.28 (s, 3H) 2.32-2.37 (m, 1H), 2.45-2.48 (m, 1H), 3.71 (s, 3H), 4.17-4.25 (t, 9H), 4.66 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 169.1, 165.2, 100.8, 87.7, 75.0, 68.8, 68.2, 68.0, 67.3, 66.3, 51.0, 27.9, 21.9, 20.4; IR (KBr) *v*: 3097, 2949, 2852, 1704, 1268, 1085, 922, 809 cm^{-1}; EIMS *m/z* (M^+): 340.05. Anal. Calcd for $C_{18}H_{20}FeO_3$: C 63.55, H 5.93. Found: C 63.41, H 5.80.

Ethyl 2-ferrocenyl-6-methyl-3,4-dihydro-*2H*-pyran-5-carboxylate (3c): Yield 66%. Orange solid; mp 83-85 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.28 (t, 3H), 1.77-1.83 (m, 1H), 2.17-2.22 (m, 1H), 2.28 (s, 3H), 2.31-2.38 (m, 1H), 2.46-2.49 (t, 1H), 4.17-4.20 (t, 9H), 4.23 (s, 1H), 4.26 (s, 1H), 4.66 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 168.7, 164.9, 101.1, 87.8, 74.9, 68.8, 68.1, 67.93, 67.3, 66.3, 59.6, 27.9, 22.0, 20.4, 14.5; IR (KBr) *v*: 3097, 2969, 2922, 2856, 1700, 1268, 1077, 929, 816 cm^{-1}; EIMS *m/z* (M^+): 354.05. Anal. Calcd for $C_{19}H_{22}FeO_3$: C 64.42, H 6.26. Found: C 64.61, H 6.35.

Ethyl 2-ferrocenyl-6-(trifluoromethyl)-3,4-dihydro-*2H*-pyran-5-carboxylate (3d): Yield 89%. Yellow solid; mp 90-91 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 1.30-1.33 (t, *J* = 7.0 Hz, 3H), 1.83-1.90 (m, 1H), 2.18-2.23 (m, 1H), 2.43-2.49 (m, 1H), 2.56-2.60 (m, 1H), 4.19-4.25 (m, 11H), 4.73 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 167.0, 145.9, 145.6, 120.6, 118.4, 109.8, 86.6, 75.8, 68.9, 68.3, 68.0, 66.6, 61.4, 27.6, 23.1, 13.9; IR (KBr) *v*: 3097, 2984, 2934, 1723, 1280, 1190, 1093, 929, 824 cm^{-1}; EIMS *m/z* (M$^+$): 408.05. Anal. Calcd for $C_{19}H_{19}F_3FeO_3$: C 55.91, H 4.69. Found: C 55.44, H 4.81.

Methyl 2-ferrocenyl-6-isopropyl-3,4-dihydro-*2H*-pyran-5-carboxylate (3e): Yield 86%. Orange solid; mp 61-62 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 1.17-1.25 (m, 6H), 1.67-1.71(m, 1H), 2.07-2.10 (m, 1H), 2.28-2.35 (m, 1H), 2.43-2.47 (m, 1H), 3.71 (s, 3H), 3.90-3.93 (m, 1H), 4.16-4.22 (m, 9H), 4.61 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 172.1, 168.9, 99.15, 88.8, 74.5, 68.7, 67.8, 67.6, 66.1, 65.9, 51.0, 30.3, 29.0, 22.1, 20.3, 20.0; IR (KBr) *v*: 3089, 2953, 2864, 1704, 1264, 1093, 929, 809 cm^{-1}; EIMS *m/z* (M$^+$): 368.10. Anal. Calcd for $C_{20}H_{24}FeO_3$: C 65.23, H 6.57. Found: C 65.39, H 6.73.

Ethyl 2-ferrocenyl-6-isopropyl-3,4-dihydro-*2H*-pyran-5-carboxylate (3f): Yield 60%. Orange solid; mp 62-63 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 1.17-1.19 (m, 6H), 1.29 (t, J = 7.5 Hz, 3H), 1.68-1.71 (m, 1H), 2.06-2.10 (m, 1H), 2.32-2.35 (m, 1H), 2.44-2.48 (m, 1H), 3.88-3.91(m, 1H), 4.15-4.19 (m, 9H), 4.21-4.22 (m, 2H), 4.61 (dd, J_a = 2.5 Hz, J_b = 10.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 171.7, 168.6, 99.5, 74.5, 68.7, 67.7, 67.6, 66.1, 65.9, 59.6, 30.3, 29.1, 22.2, 20.3, 20.0, 14.4; IR (KBr) *v*: 3093, 2969, 2914, 2867, 1677, 1287, 1101, 813 cm^{-1}; EIMS *m/z* (M$^+$): 382.10. Anal. Calcd for $C_{21}H_{26}FeO_3$: C 65.98, H 6.86. Found: C 66.23, H 7.07.

Ethyl 2-ferrocenyl-6-phenyl-3,4-dihydro-*2H*-pyran-5-carboxylate (3g): Yield 67%. Orange solid; mp 109-111 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 0.91-0.94 (t, *J* = 7.0 Hz, 3H), 1.90-1.94 (m, 1H), 2.28-2.32 (m, 1H), 2.44-2.51 (m, 1H), 2.68-2.73 (m, 1H), 3.92-3.97(q, *J* = 7.0 Hz, 2H), 4.17-4.30 (t, 9H), 4.86 (d, *J* = 9.0 Hz, 1H), 7.34-7.41 (m, 5H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 169.0, 163.1, 137.0, 128.9, 128.7, 127.6, 103.6, 87.6, 75.9, 68.8, 68.2, 68.0, 67.2, 66.4, 59.8, 28.3, 23.0, 13.7; IR (KBr) *v*: 3082, 2984, 2922, 2844, 1684, 1486, 1443, 1291, 1093, 836 cm^{-1}; EIMS *m/z* (M$^+$): 416.10. Anal. Calcd for $C_{24}H_{24}FeO_3$: C 69.24, H 5.81. Found: C 68.93, H 5.69.

1-(2-Ferrocenyl-6-phenyl-3,4-dihydro-*2H*-pyran-5-yl)ethanone (3h): Yield 56%. Orange solid; mp 71-72 °C. ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 1.79 (s, 3H), 1.87-1.89 (t, 1H), 2.27-2.30 (m, 1H), 2.41 (s, 1H), 2.61 (d, *J* = 7.0 Hz, 1H), 4.19-4.31 (m, 9H), 4.79 (dd, J_a = 2.0 Hz, J_b = 10.0 Hz, 1H), 7.41-7.71 (m, 5H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 198.5, 161.8, 140.8, 131.5, 128.5, 128.4, 110.2, 87.7, 75.1, 68.8, 68.2, 68.0, 67.4, 66.3, 27.8, 23.4, 20.8; IR (KBr) *v*: 3085, 2926, 2852, 1603, 1435, 1291, 1019, 816 cm^{-1}; EIMS *m/z* (M$^+$): 386.10. Anal. Calcd for $C_{23}H_{22}FeO_2$: C 71.52, H 5.74. Found: C 71.32, H 5.62.

(2-Ferrocenyl-6-methyl-3,4-dihydro-*2H*-pyran-5-yl)(phenyl)methanone (3i): Yield 30%. Orange solid; mp 143-145 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 1.73 (s, 3H), 1.84-1.91 (m, 1H), 2.29-2.24 (m, 2H), 2.78-2.83 (m, 1H), 4.17-4.30 (m, 9H), 4.84 (d, *J* = 9.5 Hz, 1H), 7.38-7.44 (m, 5H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 198.5, 164.7, 136.7, 131.5, 130.1, 129.5, 128.9, 128.8, 110.2, 87.7, 75.1, 68.8, 68.2, 68.0, 67.4, 67.3, 66.4, 66.3, 28.4, 22.8, 20.8; IR (KBr) *v*: 3085, 2926, 2848, 1634, 1595, 1482, 1435, 1283, 1077, 824 cm^{-1}; EIMS *m/z* (M$^+$): 386.10. Anal. Calcd for $C_{23}H_{22}FeO_2$: C 71.52, H 5.74. Found: C 71.38, H 5.60.

Procedure for electrophilic ring-opening reaction of dihydropyran 3b with indole: The reactions were conducted in a 10 mL U-type flask equipped with magnetic stirring. In a typical reaction, $MeNO_2$ (1.0 mL) was mixed with **3b** (42.5 mg, 0.125 mmol), indole **4a** (36.6 mg, 0.3125 mmol) and $KAl(SO_4)_2 \cdot 12H_2O$ (6 mg, 0.0125 mmol, 10 mol %) under air. The mixture was stirred at 80 °C for 10 h. After the reaction, the mixture was cooled to room temperature and the desired product, **5a**, was obtained by chromatography over silica gel using EtOAc/ hexane (1:6) as eluent.

Methyl 2-acetyl-5-ferrocenyl-5-(1*H*-indol-3-yl)pentanoate (5a): Yield 83%. Orange solid; mp 34-36 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.76-2.10 (m, 7H), 3.37-3.44 (m, 1H), 3.65-3.69 (m, 3H), 3.86-4.04 (m, 9H), 4.22-4.27 (m, 1H), 6.94 (s, 1H), 7.05-7.58 (m, 4H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 203.4, 170.4, 170.3, 136.4, 126.7, 121.9, 121.8, 121.6, 119.5, 119.4, 119.2, 111.3, 68.7, 68.6, 68.0, 67.9, 67.5, 67.3, 66.9, 66.7, 59.9, 59.4, 52.9, 52.5, 52.4, 38.2, 37.2, 36.7, 36.1, 34.1, 33.7, 29.5, 28.9, 28.6, 27.3, 26.9; IR (KBr) v: 3405, 3085, 2945, 2864, 1735, 1712, 1451, 1222, 1100, 813 cm^{-1}; EIMS *m/z* (M^+): 457.20. Anal. Calcd for $C_{26}H_{27}FeNO_3$: C 68.28, H 5.95. Found: C 68.01, H 5. 82.

ACKNOWLEDGEMENTS

The authors are thankful to the Fund of National Natural Science Foundation of China (No. 21062011) for the financial support. Inner Mongolia Natural Science Foundation (No. 2010MS0211) is highly acknowledged.

REFERENCES

1. A. Togni and T. Hayashi, Ferrocenes, VCH, New York, 1995.
2. S. Barlow and S. R. Marderin, in Functional Organic Materials, ed. by T. J. J. Muller and U. H. F. Bunz, Wiley-VCH, Weinheim, 2007, 393.
3. R. G. Arrayas, J. Adrido, and J. C. Carretero, *Angew. Chem. Int. Ed.*, 2006, **45**, 7674.
4. D. Hamels, P. M. Dansette, E. A. Hillard, S. Top, A. Vessières, P. Herson, G. Jaouen, and D. Mansuy, *Angew. Chem. Int. Ed.*, 2009, **48**, 9124.
5. R. C. J. Atkinson, V. C. Gibson, and N. J. Long, *Chem. Soc. Rev.*, 2004, **33**, 313.
6. V. H. Purecha, N. S. Nandurkar, B. M. Bhanage, and J. M. Nagarkar, *Tetrahedron Lett.*, 2008, **49**, 1384.
7. S. Chen, B. Wang, Q. Yan, J. Shi, H. Zhao, and B. Li, *RSC Adv.*, 2013, **3**, 1758.
8. J. Zhu and H. Bienaymé, Multicomponent Reactions; Wiley-VCH: New York, 2005, 944.
9. Y. Gu, R. De Sousa, G. Frapper, C. Bachmann, J. Barrault, and F. Jerome, *Green Chem.*, 2009, **11**, 1968.

10. J. C. J. M. D. S. Menezes, A. T. P. C. Gomes, A. M. S. Silva, M. A. F. Faustino, M. G. P. M. S. Neves, A. C. Tomé, F. de C. da Silva, V. F. Ferreira, and J. A. S. Cavaleiro, *Synlett*, 2011, 1841.
11. J. N. Tan, H. Li, and Y. Gu, *Green Chem.*, 2010, **12**, 1772.
12. P. T. Franke, B. Richter, and K. A. Jørgensen, *Chem. Eur. J.*, 2008, **14**, 6317.
13. M. Li, C. Tang, J. Yang, and Y. Gu, *Chem. Commun.*, 2011, **47**, 4529; M. Li, H. Li, T. Li, and Y. Gu, *Org. Lett.*, 2011, **13**, 1064.
14. M. Li, J. Yang, and Y. Gu, *Adv. Synth. Catal.*, 2011, **353**, 1551.
15. M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, 1957, **22**, 903; K. R. Berger, E. R. Biehl, and P. C. Reeves, *J. Org. Chem.*, 1974, **39**, 477.