

## Supporting Information

# Synthesis of Allene Ferrocenes through CuI-Mediated Crabbé Homologation Reaction

Shufeng Chen, Binglong Wang, Qing Yan, Jinxiang Shi, Haiying Zhao, Baoguo Li\*

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China

E-mail address: baoguo@sohu.com

## CONTENTS

1. General Information.....	S2
2. General Procedure for the Synthesis of 1'-(1-Chloro-3-oxoprop-1-enyl)-1-acylferrocenes <b>3b-g</b> .....	S2
3. General Procedure for the Synthesis of 1'-Ethyne-1-acylferrocenes <b>1b-g</b> .....	S4
4. Synthesis of 1'-Ethyneferrocene-1-carboxylic Esters <b>1h-j</b> .....	S7
5. General Procedure for the Synthesis of Allene Ferrocenes <b>2</b> through CuI-Mediated Crabbé Homologation Reaction.....	S8
6. Synthesis and Isolation of Propargylic Amine Intermediate <b>6</b> .....	S11
7. Detailed Procedure for the Conversion of Propargylic Amine Intermediate <b>6</b> to Ferrocenyl Allene <b>2a</b> .....	S12
8. References.....	S12
9. <sup>1</sup> H and <sup>13</sup> C NMR Spectra.....	S13

**General Information.** All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled under a nitrogen atmosphere prior to use. Toluene was dried over Na with benzophenone as indicator. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 500 MHz and 125 MHz FT-NMR spectrometer. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard when  $\text{CDCl}_3$  was used as solvent. IR spectra were recorded on a FT-IR instrument. The HRMS analysis was obtained on a GCTOF mass spectrometer. Melting points were determined with melting points apparatus and are uncorrected.

#### **General Procedure for the Synthesis of**

**1'-(1-Chloro-3-oxoprop-1-enyl)-1-acylferrocenes 3b-g.**<sup>1</sup>  $\text{POCl}_3$  (22.6 mmol) was added dropwise to anhydrous DMF (5 mL) at 0 °C. After stirring for 15 min, the resulting Vilsmeier reagent was added to an ice-cold mixture of 1'-acetyl-1-acylferrocenes (7.53 mmol) and anhydrous DMF (5 mL) over a period of 15 min. The reaction mixture was warmed to room temperature and stirred for 2 h. The Vilsmeier complex was quenched with 50 mL 20% sodium acetate. Saturated aqueous  $\text{NaHCO}_3$  was added until the aqueous phase was neutralized. Extraction with  $\text{CH}_2\text{Cl}_2$ , drying ( $\text{MgSO}_4$ ), and evaporation gave the crude product, which was purified on a silica gel column to afford the desired 1'-(1-chloro-3-oxoprop-1-enyl)-1-acylferrocenes **3b-g** in moderate yields.

*1'-(1-Chloro-3-oxoprop-1-enyl)-1-benzoylferrocene (3b)*: Red solid (1.935 g, 68% yield);

mp: 147-149 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3096, 2866, 1655, 1602, 1446, 1135, 826 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.54 (t, *J* = 2.0 Hz, 2H), 4.61 (t, *J* = 2.0 Hz, 2H), 4.70 (t, *J* = 2.0 Hz, 2H), 4.95 (t, *J* = 2.0 Hz, 2H), 6.28 (d, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 4.5 Hz, 2H), 9.98 (d, *J* = 3.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.4, 73.6, 74.0, 74.8, 80.1, 81.9, 121.6, 128.2, 128.4, 132.2, 139.0, 152.7, 190.5, 197.3; HRMS calcd for C<sub>20</sub>H<sub>15</sub>ClFeO<sub>2</sub>Na [M+Na]<sup>+</sup>: 401.0008, found: 401.0010.

*I'*-(1-Chloro-3-oxoprop-1-enyl)-1-(2-chlorobenzoyl)ferrocene (**3c**): Red oil (1.396 g, 45% yield); IR (KBr): 3104, 2850, 1663, 1597, 1445, 1131, 835 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.64 (t, *J* = 2.0 Hz, 2H), 4.61 (t, *J* = 2.0 Hz, 2H), 4.78 (t, *J* = 2.0 Hz, 2H), 4.80 (t, *J* = 2.0 Hz, 2H), 6.34 (d, *J* = 7.0 Hz, 1H), 7.36 (t, *J* = 3.5 Hz, 1H), 7.42 (t, *J* = 3.5 Hz, 1H), 7.43~ 7.47 (m, 2H), 9.99 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.1, 73.2, 74.0, 75.4, 80.1, 81.9, 121.7, 126.5, 128.8, 130.6, 131.1, 131.4, 138.5, 152.8, 190.5, 197.3; HRMS calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>FeO<sub>2</sub>Na [M+Na]<sup>+</sup>: 434.9618, found: 434.9619.

*I'*-(1-Chloro-3-oxoprop-1-enyl)-1-(4-chlorobenzoyl)ferrocene (**3d**): Red solid (2.356 g, 76% yield); mp: 118-120 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3107, 2839, 1665, 1632, 1444, 1140, 835 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.54 (s, 2H), 4.61 (s, 2H), 4.71 (s, 2H), 4.93 (s, 2H), 6.30 (d, *J* = 3.5 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.78 (d, *J* = 4.0 Hz, 2H), 10.00 (d, *J* = 4.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.3, 73.5, 74.0, 74.9, 79.8, 82.0, 121.7, 128.7, 129.6, 137.2, 138.4, 152.5, 190.4, 195.9; HRMS calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>FeO<sub>2</sub>: 411.9720, found: 411.9715.

*I'*-(1-Chloro-3-oxoprop-1-enyl)-1-(3,5-dichlorobenzoyl)ferrocene (**3e**): Red solid (2.418

g, 72% yield); mp: 101-103 °C (CH<sub>2</sub>Cl<sub>2</sub>–Petroleum ether); IR (KBr): 3086, 2848, 1659, 1601, 1449, 1133, 826 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.57 (s, 2H), 4.68 (s, 2H), 4.74 (s, 2H), 4.94 (s, 2H), 6.32 (d, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 2H), 10.04 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.4, 73.4, 74.1, 75.4, 79.0, 82.3, 122.0, 126.7, 131.9, 135.4, 141.4, 152.2, 190.4, 194.7; HRMS calcd for C<sub>20</sub>H<sub>13</sub>Cl<sub>3</sub>FeO<sub>2</sub>: 445.9331, found: 445.9329.

*1'-(1-Chloro-3-oxoprop-1-enyl)-1-(2-bromobenzoyl)ferrocene (3f)*: Red oil (2.232 g, 65% yield); IR (KBr): 3104, 2850, 1662, 1598, 1444, 1131, 834 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.63 (t, *J* = 2.0 Hz, 2H), 4.66 (t, *J* = 2.0 Hz, 2H), 4.75 (d, *J* = 2.0 Hz, 2H), 4.81 (t, *J* = 2.0 Hz, 2H), 6.36 (d, *J* = 7.0 Hz, 1H), 7.31~7.34 (m, 1H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.44~7.46 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 9.99 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.0, 73.1, 73.9, 75.3, 79.7, 81.7, 119.4, 121.6, 126.9, 128.8, 131.4, 133.6, 140.2, 152.7, 190.3, 197.9; HRMS calcd for C<sub>20</sub>H<sub>14</sub>BrClFeO<sub>2</sub>: 455.9215, found: 455.9218.

*1'-(1-Chloro-3-oxoprop-1-enyl)-1-(2-iodobenzoyl)ferrocene (3g)*: Red oil (2.656 g, 70% yield); IR (KBr): 3097, 2850, 1661, 1601, 1443, 1130, 834 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.64 (s, 2H), 4.71 (s, 2H), 4.77 (s, 2H), 4.83 (s, 2H), 6.37 (d, *J* = 7.0 Hz, 1H), 7.15~7.19 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 1H), 10.01 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 70.1, 73.4, 74.1, 75.5, 79.5, 81.9, 92.7, 121.8, 127.7, 128.6, 131.6, 140.4, 143.6, 152.9, 190.5, 199.6; HRMS calcd for C<sub>20</sub>H<sub>14</sub>ClFeIO<sub>2</sub>: 503.9076, found: 503.9072.

**General Procedure for the Synthesis of 1'-Ethynyl-1-acylferrocenes 1b-g.**<sup>1</sup> A solution

of **3b-g** (3.96 mmol) in anhydrous dioxane (30 mL) was heated at reflux temperature for 5 min and subsequently treated with a boiling solution of 0.5 M NaOH (50 mL). The reaction mixture was refluxed for 25 min and subsequently cooled by addition of ice water. Neutralization with diluted HCl was followed by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed by reduced pressure. The residue was purified on a silica gel column to give the desired 1'-ethynyl-1-acylferrocenes **1b-g** in moderate yields.

*1'-Ethynyl-1-benzoylferrocene (1b)*: Red solid (907 mg, 73% yield); mp: 93-96 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3206, 3093, 1633, 1446, 1174, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.73 (s, 1H), 4.24 (s, 2H), 4.46 (s, 2H), 4.61 (s, 2H), 4.93 (s, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 66.1, 71.0, 73.1, 73.5, 74.8, 75.2, 79.4, 80.7, 128.3, 128.3, 131.7, 139.6, 198.3; HRMS calcd for C<sub>19</sub>H<sub>14</sub>FeO: 314.0394. Found: 314.0392.

*1'-Ethynyl-1-(2-chlorobenzoyl)ferrocene (1c)*: Red solid (1.061 g, 77% yield); mp: 64-66 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3301, 3096, 1656, 1445, 1129, 827 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.73 (s, 1H), 4.33 (t, *J* = 2.0 Hz, 2H), 4.51 (t, *J* = 2.0 Hz, 2H), 4.61 (t, *J* = 2.0 Hz, 2H), 4.75 (t, *J* = 2.0 Hz, 2H), 7.32~7.35 (m, 1H), 7.37~7.40 (m, 1H), 7.43~7.45 (m, 1H), 7.53~7.55 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 66.1, 71.0, 72.7, 73.4, 75.4, 75.4, 79.5, 80.6, 126.4, 128.8, 130.3, 131.0, 131.0, 139.2, 198.0; HRMS calcd for C<sub>19</sub>H<sub>13</sub>ClFeOK [M+K]<sup>+</sup>: 386.9641, found: 386.9643.

*1'-Ethynyl-1-(4-chlorobenzoyl)ferrocene (1d)*: Red oil (1.088 g, 79% yield); IR (KBr): 3311, 3096, 1627, 1444, 1161, 848 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.75 (s, 1H), 4.24

(s, 2H), 4.45 (s, 2H), 4.63 (s, 2H), 4.89 (s, 2H), 7.44 (d,  $J = 4.5$  Hz, 2H), 7.89 (d,  $J = 4.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  66.2, 70.9, 73.0, 73.5, 74.7, 75.3, 79.1, 80.5, 128.5, 129.7, 137.7, 137.9, 196.9; HRMS calcd for  $\text{C}_{19}\text{H}_{13}\text{ClFeO}$ : 348.0004, found: 348.0001.

*1'-Ethynyl-1-(3,5-dichlorobenzoyl)ferrocene (1e)*: Red oil (1.074 g, 71% yield); IR (KBr): 3287, 3090, 1635, 1446, 1180, 802  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.77 (s, 1H), 4.25 (s, 2H), 4.47 (s, 2H), 4.66 (s, 2H), 4.89 (s, 2H), 7.52 (s, 1H), 7.78 (d,  $J = 2.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  66.6, 71.0, 73.0, 73.7, 75.2, 75.8, 78.4, 80.3, 126.7, 131.4, 135.1, 142.0, 195.3; HRMS calcd for  $\text{C}_{19}\text{H}_{12}\text{Cl}_2\text{FeO}$ : 381.9615, found: 381.9619.

*1'-Ethynyl-1-(2-bromobenzoyl)ferrocene (1f)*: Red oil (977 mg, 63% yield); IR (KBr): 3294, 3113, 1639, 1444, 1132, 826  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.75 (s, 1H), 4.34 (s, 2H), 4.51 (s, 2H), 4.61 (s, 2H), 4.73 (s, 2H), 7.29~7.32 (m, 1H), 7.38 (t,  $J = 7.5$  Hz, 1H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.61 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  66.1, 71.0, 72.7, 73.4, 75.4, 75.5, 79.3, 80.6, 119.5, 126.9, 128.9, 131.1, 133.4, 141.1, 198.8; HRMS calcd for  $\text{C}_{19}\text{H}_{13}\text{BrFeO}$ : 391.9499, found: 391.9494.

*1'-Ethynyl-1-(2-iodobenzoyl)ferrocene (1g)*: Red oil (992 mg, 57% yield); IR (KBr): 3253, 3104, 1636, 1445, 1152, 835  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.76 (s, 1H), 4.37 (t,  $J = 2.0$  Hz, 2H), 4.53 (t,  $J = 2.0$  Hz, 2H), 4.62 (t,  $J = 2.0$  Hz, 2H), 4.73 (t,  $J = 2.0$  Hz, 2H), 7.12~7.15 (m, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.52~7.54 (m, 1H), 7.89 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  66.1, 71.0, 72.9, 73.3, 75.4, 75.6, 78.8, 80.7, 92.6, 127.6, 128.5, 131.2, 140.0, 144.5, 200.3; HRMS calcd for  $\text{C}_{19}\text{H}_{13}\text{FeIO}$ : 439.9361, found: 439.9368.

### General Procedure for the Synthesis of 1'-Ethynylferrocene-1-carboxylic Esters **1h-j**.<sup>2</sup>

To a solution of 1'-ethynylferrocene-1-carboxylic acid (1.5 mmol) and PhOH (3.0 mmol) in 10 mL anhydrous benzene (for methyl 1'-ethynylferrocene-1-carboxylate: 10 mL methanol was used directly as solvent) was added DCC (1.5 mmol) and DMAP (0.15 mmol) and then the mixture was heated at reflux temperature for 6 h. The mixture was cooled to room temperature and filtered. The organic layer was washed with saturated NaHCO<sub>3</sub>, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed by reduced pressure. The residue was purified by flash chromatography to give **1h-j** as an orange solid.

*Phenyl 1'-ethynylferrocene-1-carboxylate (1h)*: Orange solid (227 mg, 46% yield); mp: 70-72 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3229, 3107, 1731, 1452, 1106, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.76 (s, 1H), 4.32 (s, 2H), 4.53 (s, 2H), 4.55 (s, 2H), 4.98 (s, 2H), 7.23 (t, *J* = 9.0 Hz, 3H), 7.41 (t, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 66.3, 70.6, 71.9, 72.4, 73.4, 73.9, 75.3, 80.7, 121.8, 125.7, 129.4, 150.9, 169.2; HRMS calcd for C<sub>38</sub>H<sub>28</sub>Fe<sub>2</sub>O<sub>4</sub>Na [2M+Na]<sup>+</sup>: 683.0584, found: 683.0597.

*Methyl 1'-ethynylferrocene-1-carboxylate (1i)*: Orange solid (133 mg, 33% yield); mp: 70-73 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3234, 3105, 1718, 1465, 1149, 825 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.76 (s, 1H), 3.83 (s, 3H), 4.23 (s, 2H), 4.43 (s, 2H), 4.48 (s, 2H), 4.85 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 51.6, 66.0, 70.3, 71.7, 73.1, 73.2, 74.7, 80.8, 170.9; HRMS calcd for C<sub>14</sub>H<sub>12</sub>FeO<sub>2</sub>Na [M+Na]<sup>+</sup>: 291.0084, found: 291.0087.

*N,N'-Dicyclohexylcarbamidoyl 1'-ethynylferrocene-1-carboxylate (1j)*: Orange solid (309 mg, 45% yield); mp: 136-139 °C (CH<sub>2</sub>Cl<sub>2</sub>-Petroleum ether); IR (KBr): 3271, 3048, 1704, 1447, 1131, 824 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.06~1.35 (m, 8H), 1.63~1.96

(m, 12H), 2.76 (s, 1H), 3.58 (t,  $J = 3.5$  Hz, 1H), 4.20 (t,  $J = 6.0$  Hz, 1H), 4.24 (s, 2H), 4.37 (s, 2H), 4.45 (s, 2H), 4.73 (s, 2H), 6.29 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  24.7, 25.3, 25.4, 26.2, 30.9, 32.4, 49.9, 55.9, 65.6, 71.4, 71.9, 72.7, 73.5, 74.7, 78.8, 81.3, 154.6, 170.1; HRMS calcd for  $\text{C}_{26}\text{H}_{32}\text{FeN}_2\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 483.1711, found: 483.1716.

**General Procedure for the Synthesis of Allene Ferrocenes **2** through CuI-Mediated Crabbé Homologation Reaction.**  $(\text{CH}_2\text{O})_n$  (0.43 mmol), CuI (0.19 mmol), toluene (3 mL), ferrocenylacetylene (0.24 mmol), and *i*-Pr<sub>2</sub>NH (0.41 mmol) were added sequentially into a dried reaction tube equipped with a reflux condenser under an nitrogen atmosphere. The resulting mixture was stirred for 10 min at room temperature and then heated at 130 °C for the indicated time. The mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (eluent: petroleum ether) to provide the desired ferrocenyl allene product **2**.

*Propa-1,2-dienylferrocene (2a)*: Red oil (48.4 mg, 90% yield); IR (KBr) 3094, 1944, 1460, 1105, 852  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.13 (s, 5H), 4.16 (s, 2H), 4.25 (s, 2H), 4.85 (d,  $J = 7.0$  Hz, 2H), 5.84 (t,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  67.1, 68.4, 69.3, 77.5, 80.4, 90.2, 208.9; HRMS calcd for  $\text{C}_{13}\text{H}_{12}\text{Fe}$ : 224.0288, found: 224.0295.

*1'-(Propa-1,2-dienyl)-1-benzoylferrocene (2b)*: Red oil (58.3 mg, 74% yield); IR (KBr) 3093, 1943, 1638, 1445, 1168, 854  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.20 (t,  $J = 2.0$  Hz, 2H), 4.26 (d,  $J = 1.5$  Hz, 2H), 4.53 (t,  $J = 2.0$  Hz, 2H), 4.77 (d,  $J = 7.0$  Hz, 2H), 4.87 (t,  $J = 2.0$  Hz, 2H), 5.67 (t,  $J = 7.0$  Hz, 1H), 7.45 (t,  $J = 7.5$  Hz, 2H), 7.53 (t,  $J = 7.5$  Hz, 1H), 7.87 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.7, 70.4, 72.5, 73.7, 77.9, 79.0, 82.6,

88.4, 128.2, 128.3, 131.5, 139.9, 198.5, 209.0; HRMS calcd for C<sub>20</sub>H<sub>16</sub>FeO: 328.0551, found: 328.0545.

*1'-(Propa-1,2-dienyl)-1-(2-Chlorobenzoyl)ferrocene (2c)*: Red oil (64.3 mg, 74% yield); IR (KBr) 3095, 1943, 1647, 1444, 1130, 854 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.32 (d, *J* = 12.5 Hz, 4H), 4.55 (s, 2H), 4.68 (s, 2H), 4.83 (s, 2H), 5.72 (s, 1H), 7.34~7.52 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 68.7, 70.6, 72.1, 74.5, 78.0, 79.0, 82.5, 88.7, 126.3, 128.8, 130.4, 130.9, 131.1, 139.4, 198.4, 209.0; HRMS calcd for C<sub>40</sub>H<sub>30</sub>Cl<sub>2</sub>Fe<sub>2</sub>O<sub>2</sub>Na [2M+Na]<sup>+</sup>: 747.0229, found: 747.0222.

*1'-(Propa-1,2-dienyl)-1-(4-Chlorobenzoyl)ferrocene (2d)*: Red oil (74.7 mg, 86% yield); IR (KBr) 3094, 1944, 1630, 1444, 1165, 848 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.20 (s, 2H), 4.27 (s, 2H), 4.56 (s, 2H), 4.79 (d, *J* = 7.0 Hz, 2H), 4.85 (s, 2H), 5.67 (t, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 68.7, 70.4, 72.3, 73.8, 78.0, 78.6, 82.6, 88.3, 128.4, 129.7, 137.7, 138.1, 197.1, 209.0; HRMS calcd for C<sub>20</sub>H<sub>15</sub>ClFeO: 362.0161, found: 362.0163.

*1'-(Propa-1,2-dienyl)-1-(3,5-dichlorobenzoyl)ferrocene (2e)*: Red oil (80.0 mg, 82% yield); IR (KBr) 3081, 1940, 1622, 1444, 1178, 850 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.21 (s, 2H), 4.30 (s, 2H), 4.60 (s, 2H), 4.82 (d, *J* = 6.5 Hz, 2H), 4.84 (s, 2H), 5.67 (t, *J* = 6.5 Hz, 1H), 7.52 (s, 1H), 7.76 (d, *J* = 1.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 68.8, 70.5, 72.3, 74.2, 78.0, 78.1, 83.0, 88.1, 126.7, 131.2, 135.0, 142.2, 195.7, 209.0; HRMS calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>FeO: 395.9771, found: 395.9772.

*1'-(Propa-1,2-dienyl)-1-(2-bromobenzoyl)ferrocene (2f)*: Red oil (68.2 mg, 70% yield); IR (KBr) 3093, 1943, 1647, 1443, 1180, 853 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.32 (t, *J*

= 1.5 Hz, 2H), 4.35 (t,  $J = 1.5$  Hz, 2H), 4.55 (t,  $J = 2.0$  Hz, 2H), 4.67 (t,  $J = 2.0$  Hz, 2H), 4.83 (d,  $J = 7.0$  Hz, 2H), 5.73 (t,  $J = 7.0$  Hz, 1H), 7.30~7.33 (m, 1H), 7.37~7.41 (m, 1H), 7.51~7.52 (m, 1H), 7.62~7.64 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.7, 70.6, 72.1, 74.5, 78.0, 78.8, 82.5, 88.7, 119.6, 126.8, 128.9, 131.0, 133.5, 141.3, 199.2, 209.0; HRMS calcd for  $\text{C}_{20}\text{H}_{15}\text{BrFeO}$ : 405.9656, found: 405.9656.

*1'-(Propa-1,2-dienyl)-1-(2-iodobenzoyl)ferrocene (2g)*: Red oil (79.5 mg, 73% yield); IR (KBr) 3089, 1942, 1647, 1442, 1179, 852  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.35~4.37 (m, 4H), 4.56 (s, 2H), 4.67 (s, 2H), 4.84 (d,  $J = 6.5$  Hz, 2H), 5.74 (t,  $J = 6.5$  Hz, 1H), 7.13~7.16 (m, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.50~7.52 (m, 1H), 7.91 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.6, 70.6, 72.3, 74.5, 78.0, 78.3, 82.5, 88.7, 92.7, 127.5, 128.5, 131.0, 140.1, 144.6, 200.7, 209.0; HRMS calcd for  $\text{C}_{20}\text{H}_{15}\text{FeIO}$ : 453.9517, found: 453.9518.

*Phenyl 1'-(propa-1,2-dienyl)ferrocene-1-carboxylate (2h)*: Orange solid (68.5 mg, 83% yield); mp 63-66  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ -Petroleum ether); IR (KBr) 3101, 1944, 1718, 1454, 1110, 831  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.30 (t,  $J = 1.5$  Hz, 2H), 4.37 (d,  $J = 1.5$  Hz, 2H), 4.46 (t,  $J = 1.5$  Hz, 2H), 4.85 (d,  $J = 7.0$  Hz, 2H), 4.92 (t,  $J = 2.0$  Hz, 2H), 5.83 (t,  $J = 7.0$  Hz, 1H), 7.21 (t,  $J = 4.5$  Hz, 2H), 7.24 (t,  $J = 3.5$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.5, 70.1, 71.3, 71.6, 72.9, 78.1, 82.5, 88.6, 121.8, 125.6, 129.4, 151.0, 169.7, 209.2; HRMS calcd for  $\text{C}_{40}\text{H}_{32}\text{Fe}_2\text{O}_4\text{Na}$  [ $2\text{M}+\text{Na}$ ] $^+$ : 711.0897, found: 711.0917.

*Methyl 1'-(propa-1,2-dienyl)ferrocene-1-carboxylate (2i)*: Orange solid (41.3 mg, 61% yield); mp 77-79  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ -Petroleum ether); IR (KBr) 3105, 1942, 1709, 1463, 1139,

820  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.79 (s, 3H), 4.19 (d,  $J = 2.0$  Hz, 2H), 4.29 (s, 2H), 4.35 (t,  $J = 2.0$  Hz, 2H), 4.78 (t,  $J = 2.0$  Hz, 2H), 4.87 (d,  $J = 3.5$  Hz, 2H), 5.73 (t,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  51.4, 68.2, 69.8, 71.0, 72.1, 72.5, 77.8, 82.0, 88.3, 171.3, 209.1; HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{FeO}_2$ : 282.0343, found: 282.0347.

*1'-(propa-1,2-dienyl)-1-(N-cyclohexyl)ferrocenecarboxamide (2j)*: Orange solid (39.5 mg, 47% yield); mp 127-129  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ -Petroleum ether); IR (KBr) 3289, 3081, 1944, 1622, 1536, 1448, 1147, 832  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15~1.25(m, 4H), 1.38~1.46 (m, 2H), 1.76 (t,  $J = 7.0$  Hz, 2H), 2.01 (d,  $J = 9.5$  Hz, 2H), 3.87~3.95 (m, 1H), 4.20 (d,  $J = 1.5$  Hz, 2H), 4.24 (d,  $J = 1.5$  Hz, 2H), 4.29 (t,  $J = 1.5$  Hz, 2H), 4.58 (d,  $J = 1.5$  Hz, 2H), 4.87 (d,  $J = 3.5$  Hz, 2H), 5.59 (d,  $J = 3.5$  Hz, 1H), 5.82 (t,  $J = 6.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  25.0, 25.6, 33.5, 48.2, 68.5, 69.2, 70.1, 71.4, 77.4, 77.8, 81.6, 89.1, 168.6, 208.9; HRMS calcd for  $\text{C}_{20}\text{H}_{23}\text{FeNONa}$   $[\text{M}+\text{Na}]^+$ : 372.1027, found: 372.1031.

**Synthesis and Isolation of Propargylic Amine Intermediate 6.**  $(\text{CH}_2\text{O})_n$  (0.86 mmol), CuI (0.38 mmol), toluene (5 mL), ferrocenylacetylene (0.48 mmol), and *i*-Pr<sub>2</sub>NH (0.82 mmol) were added sequentially into a dried reaction tube equipped with a reflux condenser under an nitrogen atmosphere. The resulting mixture was stirred for 5 min at room temperature and then heated at 130  $^\circ\text{C}$  for 15 min (the TLC indicated that propargylic amine intermediate **6** as well as minor allene product were formed). The mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (eluent: petroleum ether-ethyl acetate = 10:1~5:1) to provide the desired propargylic amine intermediate **6** as a red oil.

*N,N*-Diisopropyl-3-ferrocenylprop-2-yn-1-amine (**6**): Red oil (146.0 mg, 95% yield); IR (KBr) 3098, 2966, 2927, 2231, 1463, 1381, 1175, 818 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.14 (d, *J* = 7.0 Hz, 12H), 3.25 (m, 2H), 3.53 (s, 2H), 4.12 (t, *J* = 2.0 Hz, 2H), 4.17 (s, 5H), 4.35 (t, *J* = 2.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 20.8, 34.9, 48.4, 66.3, 68.2, 69.7, 71.1, 81.5, 85.1; HRMS calcd for C<sub>19</sub>H<sub>25</sub>FeNNa [M+Na]<sup>+</sup>: 346.1234, found: 346.1241.

**Detailed Procedure for the Conversion of Propargylic Amine Intermediate 6 to Ferrocenyl Allene 2a.** Propargylic amine intermediate **6** (0.15 mmol), copper catalyst (0.12 mmol), toluene (2 mL) were added sequentially into a dried reaction tube equipped with a reflux condenser under an nitrogen atmosphere. The resulting mixture was heated at reflux temperature for 4 h. The mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (eluent: petroleum ether) to provide the desired ferrocenyl allene as a red oil.

## References.

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## $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



















































