Supporting Information

Palladium-Catalyzed Three-Component Reaction of Ferrocenyl Allenes, Aryl Iodides and Active Methylene Compounds: Regio- and Stereoselective Synthesis of *(E)*-Alkenylferrocenes

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1. General information All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All Solvents were purified following standard literature procedures. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}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 $CDCl_3$ 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.

2. ***General procedure for the synthesis of allene ferrocenes 1***[1]

$(CH_2O)_n$ (4.3 mmol), CuI (1.9 mmol), toluene (30 mL), ferrocenylacetylene (2.4 mmol), and *i*-Pr_2NH (4.1 mmol) were added sequentially into a dried reaction tube equipped with a reflux condenser under an nitrogen atmosphere. The resulting mixture was stirred for 20 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 **1a-e.**

*Propa-1,2-dienylferrocene (**1a**):* Red oil; IR (KBr) 3094, 1944, 1460, 1105, 852 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 67.1, 68.4, 69.3, 77.5, 80.4, 90.2, 208.9; HRMS calcd for $C_{13}H_{12}Fe$: 224.0288, found: 224.0295.

*1'-(Propa-1,2-dienyl)-1-benzoylferrocene (**1b**):* Red oil; IR (KBr) 3093, 1943, 1638, 1445, 1168, 854 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 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 $C_{20}H_{16}FeO$:

328.0551, found: 328.0545.

*1'-(Propa-1,2-dienyl)-1-(2-Chlorobenzoyl)ferrocene (**1c**):* Red oil; IR (KBr) 3095, 1943, 1647, 1444, 1130, 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{40}H_{30}Cl_2Fe_2O_2Na$ $[2M+Na]^+$: 747.0229, found: 747.0222.

*1'-(Propa-1,2-dienyl)-1-(4-Chlorobenzoyl)ferrocene (**1d**):* Red oil; IR (KBr) 3094, 1944, 1630, 1444, 1165, 848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{20}H_{15}ClFeO$: 362.0161, found: 362.0163.

*1'-(Propa-1,2-dienyl)-1-(3,5-dichlorobenzoyl)ferrocene (**1e**):* Red oil; IR (KBr) 3081, 1940, 1622, 1444, 1178, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{20}H_{14}Cl_2FeO$: 395.9771, found: 395.9772.

3. General procedure for the palladium-catalyzed three-component reaction of ferrocenyl allenes, aryl iodides and active methylene compounds

To a solution of ferrocenyl allene (0.3 mmol), aryl iodide (0.36 mmol), active methylene compound (0.36 mmol) and K_2CO_3 (0.6 mmol) in 5 mL anhydrous CH_3CN under a N_2 atmosphere was added $Pd[Fc(PPh_2)_2]Cl_2 \cdot CH_2Cl_2$ (0.015 mmol, 5 mol %). The reaction mixture was then heated to reflux temperature and the progress was monitored by TLC. After completion of the reaction, solvent was removed by evaporation, and the residue was purified by column chromatography over silica gel

to give the alkenylferrocene products **4a-p**.

*Ethyl 2-acetyl-5-ferrocenyl-4-phenylpent-4-enoate (**4a**)*: Yellow oil; IR (KBr) 3110, 1739, 1715, 1639, 1400, 819, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33~7.34 (m, 4H), 7.25~7.26 (m, 1H), 6.40 (s, 1H), 4.43 (d, *J* = 1.0 Hz, 2H), 4.27 (d, *J* = 1.0 Hz, 2H), 4.16 (s, 5H), 3.98 (q, *J* = 7.5 Hz, 2H), 3.5 (t, *J* = 7.5 Hz, 1H); 3.36 (m, 2H), 2.08 (s, 3H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 203.0, 169.5, 142.5, 135.1, 128.7, 128.4, 127.1, 126.5, 81.5, 69.5, 69.1, 69.0, 61.3, 57.9, 29.4, 29.2, 13.9; HRMS calcd for $C_{25}H_{26}FeO_3$: 430.1231, found: 430.1238.

*Diethyl 2-(3- ferrocenyl-2-phenylallyl)malonate (**4b**)*: Yellow oil; IR (KBr) 3126, 1731, 1664, 1614, 1400, 819, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34~7.36 (m, 4H), 7.24~7.26 (m, 1H), 6.40 (s, 1H), 4.47 (s, 2H), 4.27 (s, 2H), 4.16 (s, 5H), 4.01~4.03 (m, 4H), 3.54 (t, *J* = 8.0 Hz, 1H); 3.39 (d, *J* = 8.0 Hz, 2H), 1.15 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 142.6, 135.0, 128.8, 128.3, 127.0, 126.5, 81.4, 69.3, 69.1, 69.0, 61.3, 50.6, 30.0, 14.0; HRMS calcd for $C_{26}H_{28}FeO_4$: 460.1337, found: 460.1336.

*2,2-Bis((E)-3-ferrocenyl-2-phenylallyl)malononitrile (**4d**)*: Orange solid. Mp. 198-199 ^{o}C; IR (KBr) 3132, 1659, 1651, 1614, 1401, 816, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 10H), 6.58 (s, 2H), 4.29~4.31 (m, 8H), 4.16 (s, 10H), 3.32 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 132.4, 130.9, 130.1, 128.9, 128.9, 128.3, 79.1, 70.7, 70.6, 70.5, 29.7, 27.7; HRMS calcd for $C_{41}H_{34}Fe_2N_2$: 666.1421, found: 666.1417.

*2,2-Bis((E)-2-(4-chlorophenyl)-3-ferrocenylallyl)malononitrile (**4e**)*: Orange solid. Mp. 214-215 ^{o}C; IR (KBr) 3130, 1614, 1454, 1400, 833 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.27 (m, 4H), 6.57 (s, 2H), 4.33 (m, 4H), 4.27 (m, 4H), 4.16 (s, 10H), 3.28 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 139.7, 134.5, 133.9, 130.3, 128.8, 128.5, 114.6, 80.4, 69.5, 69.4, 69.4, 38.8, 35.9; Anal. calcd for $C_{41}H_{32}Cl_2Fe_2N_2$: C, 66.97; H, 4.39; N, 3.81; Found: C, 67.15; H, 4.52; N, 3.98.

*2,2-Bis((E)-2-(4-bromophenyl)-3-ferrocenylallyl)malononitrile (**4f**)*: Orange solid. Mp. 209-210 ^{o}C; IR (KBr) 3133, 1613, 1454, 1400, 830, 729 cm^{-1}; ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.48 (m, 4H), 7.21 (m, 4H), 6.57 (s, 2H), 4.32 (m, 4H), 4.26 (m, 4H), 4.16 (s, 10H), 3.27 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 140.1, 134.5, 131.7, 130.2, 128.7, 122.0, 114.6, 80.3, 69.6, 69.4, 69.2, 38.7, 35.9; Anal. calcd for $C_{41}H_{32}Br_2Fe_2N_2$: C, 59.75; H, 3.91; N, 3.40; Found: C, 59.38; H, 4.12; N, 3.53.

2,2-Bis((E)-2-(2-chlorophenyl)-3-ferrocenylallyl)malononitrile ***(4g)***: Orange solid. Mp. 153-154 ^oC; IR (KBr) 3135, 1614, 1401, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33~7.36 (m, 4H), 7.25~7.26 (m, 4H), 6.48 (s, 2H), 4.34 (m, 8H), 4.19 (s, 10H), 3.43 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 141.3, 133.7, 131.6, 128.6, 128.0, 127.2, 114.7, 80.7, 69.4, 69.4, 38.9, 36.0; Anal. calcd for $C_{41}H_{32}Cl_2Fe_2N_2$: C, 66.97; H, 4.39; N, 3.81; Found: C, 67.22; H, 4.06; N, 3.87.

2,2-Bis((E)-3-ferrocenyl-2-p-tolylallyl)malononitrile ***(4h)***: Orange solid. Mp. 198-199 ^oC; IR (KBr) 3133, 1614, 1401, 820, 585 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23~7.25 (m, 4H), 7.15~7.17 (m, 4H), 6.54 (s, 2H), 4.27~4.28 (m, 8H), 4.15 (s, 10H), 3.30 (s, 4H), 2.34 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.4, 137.8, 133.0, 131.7, 129.2, 127.1, 114.8, 80.9, 69.4, 69.3, 69.2, 38.9, 36.0, 21.2; Anal. calcd for $C_{43}H_{38}Fe_2N_2$: C, 74.37; H, 5.52; N, 4.03; Found: C, 74.69; H, 5.41; N, 4.12.

2,2-Bis((E)-3-ferrocenyl-2-(4-methoxyphenyl)allyl)malononitrile ***(4i)***: Orange solid. Mp. 141-142 ^oC; IR (KBr) 3135, 1609, 1401, 1242, 836, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27~7.28 (m, 4H), 6.88~6.89 (m, 4H), 6.51 (s, 2H), 4.28 (m, 4H), 4.27 (m, 4H), 4.15 (s, 10H), 3.80 (s, 6H), 3.29 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 159.5, 133.7, 132.4, 131.4, 128.4, 114.9, 113.9, 81.0, 69.4, 69.3, 55.2, 39.0, 36.0; Anal. calcd for $C_{43}H_{38}Fe_2N_2O_2$: C, 71.09; H, 5.27; N, 3.86; Found: C, 69.85; H, 5.49; N, 3.97.

2,2-Bis((E)-2-(3,5-dichlorophenyl)-3-ferrocenylallyl)malononitrile ***(4j)***: Orange solid. Mp. 146-147 ^oC; IR (KBr) 3134, 1613, 1401, 796, 676 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.26 (m, 2H), 7.21 (m, 2H), 6.65 (s, 2H), 4.38 (m, 4H), 4.34 (m, 4H), 4.21 (s, 10H), 3.27 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 144.5, 135.3, 135.3, 128.3, 127.7, 125.6, 114.4, 79.7, 70.0, 69.6, 69.3, 47.7, 29.7; Anal. calcd for $C_{41}H_{30}Cl_4Fe_2N_2$: C, 61.23; H, 3.76; N, 3.48; Found: C, 61.49; H, 3.99; N, 4.27.

2,2-Bis((E)-3-ferrocenyl-2-(4-nitrophenyl)allyl)malononitrile ***(4k)***: Orange solid.

Mp. 194-195 °C; IR (KBr) 3134, 1614, 1401, 855, 587 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22~8.23 (m, 4H), 7.50~7.52 (m, 4H), 6.74 (s, 2H), 4.41 (m, 4H), 4.33 (m, 4H), 4.20 (s, 10H), 3.38 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 147.7, 147.3, 137.5, 129.1, 127.8, 124.1, 114.4, 79.7, 70.1, 69.7, 69.6, 38.5, 35.9; Anal. calcd for $C_{41}H_{32}Fe_2N_4O_4$: C, 65.10; H, 4.26; N, 7.41; Found: C, 65.39; H, 4.35; N, 7.64.

2,2-Bis((E)-2-(4-acetylphenyl)-3-ferrocenylallyl)malononitrile ***(4l)***: Orange solid. Mp. 119-120 °C; IR (KBr) 3129, 1680, 1602, 1402, 1270, 826, 731, 584 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94~7.95 (m, 4H), 7.44~7.46 (m, 4H), 6.68 (s, 2H), 4.36 (m, 4H), 4.31 (m, 4H), 4.17 (s, 10H), 3.37 (s, 4H), 2.58 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 197.3, 146.0, 136.3, 135.8, 130.2, 128.7, 127.2, 114.5, 80.1, 69.8, 69.6, 69.5, 38.4, 36.0, 26.6; Anal. calcd for $C_{45}H_{38}Fe_2N_2O_2$: C, 72.02; H, 5.10; N, 3.73; Found: C, 71.83; H, 5.21; N, 3.79.

2,2-Bis((E)-3-(1'-benzoylferrocenyl)-2-phenylallyl)malononitrile ***(4m)***: Yellow oil; IR (KBr) 3126, 1638, 1450, 1400, 1285, 854, 729, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78~7.79 (m, 4H), 7.48~7.50 (m, 2H), 7.38~7.40 (m, 4H), 7.19-7.30 (m, 10H), 6.33 (s, 2H), 4.87 (m, 4H), 4.54 (m, 4H), 4.30 (m, 4H), 4.22 (m, 4H), 3.18 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 198.3, 140.8, 139.5, 133.3, 131.7, 131.6, 128.6, 128.2, 128.2, 128.1, 127.1, 114.5, 82.4, 78.9, 73.9, 72.7, 71.3, 71.3, 65.8, 38.6, 35.9; Anal. calcd for $C_{55}H_{42}Fe_2N_2O_2$: C, 75.53; H, 4.84; N, 3.20; Found: C, 75.91; H, 4.73; N, 3.12.

2,2-Bis((E)-3-(1'-o-chlorobenzoylferrocenyl)-2-phenylallyl)malononitrile ***(4n)***: Orange solid. Mp. 97-98 °C; IR (KBr) 3128, 1640, 1614, 1453, 1400, 1291, 854, 753, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22~7.44 (m, 18H), 6.40 (s, 2H), 4.69 (m, 4H), 4.56 (m, 4H), 4.41 (m, 4H), 4.33 (m, 4H), 3.20 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 198.0, 140.8, 138.9, 133.3, 131.6, 131.0, 131.0, 130.4, 128.8, 128.6, 128.3, 127.1, 126.3, 114.4, 82.4, 79.1, 74.5, 72.3, 71.4, 71.0, 38.7, 35.9; Anal. calcd for $C_{55}H_{40}Cl_2Fe_2N_2O_2$: C, 70.01; H, 4.27; N, 2.97; Found: C, 70.30; H, 4.15; N, 2.69.

2,2-Bis((E)-3-(1'-p-chlorobenzoylferrocenyl)-2-phenylallyl)malononitrile ***(4o)***: Orange solid. Mp. 179-180 °C; IR (KBr) 3134, 1641, 1616, 1442, 1399, 1286, 839, 759, 698, 470 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70~7.72 (m, 4H), 7.29~7.36 (m,

10H), 7.19~7.21 (m, 4H), 6.30 (s, 2H), 4.84 (m, 4H), 4.56 (m, 4H), 4.29 (m, 4H), 4.21 (m, 4H), 3.18 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 196.9, 140.7, 137.9, 137.6, 133.4, 131.4, 129.6, 128.6, 128.5, 128.4, 128.3, 127.0, 114.4, 82.4, 78.6, 74.0, 72.6, 71.3, 65.7, 38.6, 35.9; Anal. calcd for $C_{55}H_{40}Cl_2Fe_2N_2O_2$: C, 70.01; H, 4.27; N, 2.97; Found: C, 70.42; H, 4.12; N, 2.78.

*2,2-Bis((E)-3-(1'-(3,5-dichlorobenzoyl)ferrocenyl)-2-phenylallyl)malononitrile (**4p**)*: Yellow oil; IR (KBr) 3118, 1639, 1563, 1446, 1398, 1282, 908, 805, 762, 738 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65~7.66 (m, 4H), 7.46 (m, 2H), 7.25~7.34 (m, 10H), 6.32 (s, 2H), 4.84 (m, 4H), 4.61 (m, 4H), 4.32 (m, 4H), 4.25 (m, 4H), 3.20 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 195.4, 141.8, 140.7, 135.1, 133.8, 131.1, 128.7, 128.4, 127.0, 126.6, 114.4, 82.7, 77.9, 74.6, 72.6, 71.5, 71.4, 38.7, 36.0; Anal. calcd for $C_{55}H_{38}Cl_4Fe_2N_2O_2$: C, 65.25; H, 3.78; N, 2.77; Found: C, 65.53; H, 3.61; N, 2.70.

References.

1. S. Chen, B. Wang, Q. Yan, J. Shi, H. Zhao and B. Li, *RSC Adv.,* 2013, **3**, 1758.