Supplementary Information

Regioselective addition/annulation of ferrocenyl thioamides with 1,3-diynes via a sulfur-transfer rearrangement to construct extended π-conjugated ferrocenes with luminescent property

Lipeng Yan, Jingbo Lan, * Hu Cheng, Yihang Li, Mangang Zhang, Di Wu, and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, People’s Republic of China
Table of Contents

I. General Remarks .................................................................................................................. S3
II. Synthesis of 1,3-diynes 2 ................................................................................................... S4
III. Rh catalyzed ortho-C–H activation/addition of ferroceny1 amide 1 with 1,3-diyne 2a ......................................................................................................................... S6
IV. Optimization of regioselective addition/annulation of ferrocenyl thioamide 5 with 1,3-diyne 2a ......................................................................................................................... S7
V. General procedure for regioselective addition/annulation of ferrocenyl thioamide 5 with 1,3-diynes 2 ......................................................................................................................... S9
VI. Gram-scale synthesis of 6a ................................................................................................ S9
VII. Mechanistic studies ......................................................................................................... S10
VIII. Synthesis of extended π-conjugated ferrocenes 7 ......................................................... S16
IX. Calculated molecular conformations, photophysical and electrochemical properties ................................................................................................................................. S17
X. Preparation and characterization of the described compounds ........................................ S19
XI. References ...................................................................................................................... S36
XII. Copies of 1H, 13C and 1H–1H NOESY NMR spectra ...................................................... S37
I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Ferrocenyl amide 1, ferrocenyl thioamide 5, methyl ferrocene carboxylate 8, and 2,5-diphenylthiophene 9 were prepared according to literature procedures. 1,3-Diynes 2a-2e and 2h-2j were prepared by homocouplings of the corresponding terminal alkynes. 1,3-Diynes 2f, 2g, 2k-2m and 2o-2r were prepared via the Sonogashira coupling reaction of the corresponding brominated (hetero)arenes with trimethylsilylacetylene, desilication, and homocoupling of the resulting terminal alkynes.

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. 1H NMR (400 MHz) chemical shifts were measured relative to CDCl3 or DMSO-d6 as the internal reference (CDCl3: δ = 7.26 ppm; DMSO-d6: δ = 2.50 ppm). 13C NMR (100 MHz) chemical shifts were measured relative to CDCl3 or DMSO-d6 as the internal reference (CDCl3: δ = 77.16 ppm; DMSO-d6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) spectrometer. Melting points were determined with XRC-1 with no correction. The absorption and fluorescence spectra were obtained using a HITACHI U-2910 spectrometer and a Horiba Fluorolog-3 fluorescence spectrometer, respectively.

Cyclic voltammetry (CV) measurements were carried out on a CHI660D electrochemical workstation at a scan rate of 50 mV/s in dry acetonitrile containing 0.1 M of n-Bu4NPF6 supporting electrolyte under an N2 atmosphere, using Fc/Fc+ (0.08 V) as reference. The three-electrode setup consisted of an Ag/Ag+ (0.01 M of AgNO3 in acetonitrile) reference electrode, a platinum wire counter electrode, and a platinum plate working electrode.

Spectroelectrochemical experiments were performed in a thin-layer (1 mm) quartz cell under an N2 atmosphere, employing dry acetonitrile as solvent with n-Bu4NPF6 (0.1 M) as supporting electrolyte. The three-electrode setup consisted of a platinum
network working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode (0.52 V, vs Fc/Fc⁺).

II. Synthesis of 1,3-diynes 2

2.1 Synthesis of 1,3-diyne 2s

A solution of 5-bromoindole (0.98 g, 5 mmol) in anhydrous DMF (15 mL) was added dropwise over 20 min to a stirred suspension of NaH (60% dispersion in mineral oil, 0.32 g, 8 mmol) in anhydrous DMF (15 mL) in an ice bath. A solution of n-octyl bromide (0.9 mL, 5.2 mmol) in anhydrous DMF (15 mL) was slowly added over 5 min. Then, the mixture was warmed to room temperature and stirred overnight. The reaction was quenched with ethanol (10 mL) carefully and poured into ice-water. The resulting mixture was extracted with dichloromethane twice. The combined organic layer was washed with brine, dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to give 5-bromo-1-octyl-1H-indole as a yellow oil in 87% yield (1.34 g).

A three-necked flask with a magnetic stir bar was charged with 5-bromo-1-octyl-1H-indole (1.23 g, 4 mmol), trimethylsilylacetylene (1.1 mL, 8 mmol), Pd(PPh₃)₂Cl₂ (140.4 mg, 5 mol%), CuI (76.2 mg, 10 mol%), triethylamine (3 mL) and THF (9 mL) under an N₂ atmosphere. After stirred at 80 °C for 24 h, the resulting mixture was cooled to room temperature. Then, KF (0.46 g, 8 mmol) was added along with CH₃OH (10 mL), and the mixture was stirred under air for another 4 h. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure and purified by column
chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide 5-ethyl-1-octyl-1H-indole as a yellow oil in 79% yield (0.80 g).

Cul (38.1 mg, 10 mol%) and TMEDA (0.3 mL, 2 mmol) was added to the solution of 5-ethyl-1-octyl-1H-indole (0.51 g, 2 mmol) in DMF (5 mL). The resulting mixture was then stirred at room temperature overnight. Then, the mixture was diluted in ethyl acetate (50 mL). The organic layer was washed with saline, dried over MgSO$_4$, filtered and the filtrate was concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to give 1,4-bis(1-octyl-1H-indol-5-yl)buta-1,3-diyne (2s) as a yellow oil in a yield of 81% (0.41 g).

2.2 Synthesis of 1,3-diyne 2t$^{5,7}$

Acetyl ferrocene (1.14 g, 5 mmol) was dissolved in DMF (15 mL) and then phosphorus oxychloride (3 mL) in DMF (10 mL) was added dropwise at 0 °C under N$_2$. The reaction mixture was stirred at 0 °C for 15 min and then warmed to room temperature for 2 h. The mixture was poured to 20% of NaOAc solution (100 mL) under N$_2$ and stirred for 1.5 h. The mixture was extracted with dichloromethane and washed with saline. The organic phase was dried over MgSO$_4$, filtered and the filtrate was concentrated under reduced pressure to give the crude product. To the solution of the crude product in 1,4-dioxane (8 mL) under N$_2$, 0.5 M of NaOH solution (5 mL) was added. Then the reaction mixture was refluxed for 5 min and poured into ice-water (50 mL). The mixture was subsequently neutralized by 1 N of HCl solution and extracted with ethyl acetate. The organic layer was washed with saline, dried over MgSO$_4$, filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to give ethynyl ferrocene in a yield of 61% (0.64 g).
CuI (38.1 mg, 10 mol%) and TMEDA (0.3 mL, 2 mmol) was added to the solution of ethynyl ferrocene (0.42 g, 2 mmol) in DMF (5 mL). The resulting mixture was then stirred at room temperature overnight. Then, the mixture was diluted in ethyl acetate (50 mL). The organic layer was washed with saline, dried over MgSO₄, filtered and the filtrate was concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to give 1,4-diferrocenylbuta-1,3-diyne (2t) as a red solid in a yield of 67% (0.28 g).

2.3 Synthesis of 1,3-diyne 2u and 2v

A three-necked flask with a magnetic stir bar was charged with the brominated arenes (5 mmol), trimethylsilylacetylene (10 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), CuI (10 mol%), triethylamine (3 mL) and THF (9 mL) under an N₂ atmosphere. After refluxed at 80 °C for 24 h, the resulting mixture was cooled to room temperature. Then, KF (10 mmol) was added along with CH₃OH (10 mL), and the mixture was stirred under air for another 4 h. The mixture was filtered through a celite pad and was washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel to provide the corresponding terminal alkynes.

CuI (10 mol%) and TMEDA (2 mmol) was added to the solution of the acquired terminal alkyne (2 mmol) in DMF (5 mL). The resulting mixture was then stirred at room temperature overnight. Then, the mixture was diluted in ethyl acetate (50 mL). The organic layer was washed with saline, dried over MgSO₄, filtered and the filtrate was concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel to give the final 1,3-diyne products.

III. Rh catalyzed ortho-C–H activation/addition of ferrocenyl amide 1
with 1,3-diyne 2a

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl amides 1 (59.4 mg, 0.2 mmol), 1,4-diphenylbuta-1,3-diyne 2a (40.5 mg, 0.2 mmol, 1.0 equiv.), [Cp*RhCl\(_2\)]\(_2\) (6.2 mg, 5 mol%), AgSbF\(_6\) (13.7 mg, 20 mol%), Cu(OAc)\(_2\)-H\(_2\)O (79.9 mg, 0.4 mmol, 2.0 equiv.), Zn(OAc)\(_2\)-2H\(_2\)O (87.8 mg, 0.4 mmol, 2.0 equiv.) and 1,4-dioxane (2 mL) under an N\(_2\) atmosphere. The resulting mixture was stirred at 120 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) to provide compound 4 as a yellow solid in a yield of 14% (14.2 mg).

IV. Optimization of regioselective addition/annulation of ferrocenyl thioamide 5 with 1,3-diyne 2a

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (62.6 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenyl-1,3-butadiyne 2a (20.2 mg, 0.1 mmol), [Rh], [Ag], oxidant and solvent under an N\(_2\) atmosphere. The resulting mixture was stirred at 80 °C for 16-24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure.
The residue was dissolved in CDCl₃ and analyzed by ¹H NMR with CH₂Br₂ (3.5 µL, 0.05 mmol) as the internal standard. The NMR yields determined by the characteristic proton signal of 6a at 4.88 ppm relative to the internal standard signal of CH₂Br₂ at 4.93 ppm. If necessary, the residue would be purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) to give the isolated yield of 6a.

Table S1. Optimization of regioselective addition/annulation of 1,3-diyne 2a with ferrocenyl thioamide 5.

| Entry | [Rh]          | [Ag]    | Oxidant            | Solvent     | Yield (%) |
|-------|---------------|---------|--------------------|-------------|-----------|
| 1     | [Cp*RhCl₂]₂   | AgSbF₆ | Cu(OAc)₂·H₂O       | CH₃OH       | 46 c      |
| 2     | [Cp*RhCl₂]₂   | AgBF₄  | Cu(OAc)₂·H₂O       | CH₃OH       | 49        |
| 3     | [Cp*RhCl₂]₂   | AgOTf  | Cu(OAc)₂·H₂O       | CH₃OH       | 38        |
| 4     | [Cp*RhCl₂]₂   | AgNTf₂ | Cu(OAc)₂·H₂O       | CH₃OH       | 55        |
| 5     | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | CH₃OH       | 61        |
| 6     | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | CH₃OH       | 37        |
| 7     | [Cp*RhCl₂]₂   | AgOTs  | AgOAc             | CH₃OH       | trace     |
| 8     | [Cp*RhCl₂]₂   | AgOTs  | Oxygen (1 atm)     | CH₃OH       | N.D.      |
| 9     | [Cp*RhCl₂]₂   | AgOTs  | Benzoquinone       | CH₃OH       | N.D.      |
| 10    | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | CH₃OH       | 79        |
| 11    | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | Cl₂CCH₂OH/CH₃OH | 65   |
| 12    | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | Cl₂CCH₂OH/CH₃OH | 83 (81 c) |
| 13    | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | Cl₂CCH₂OH/CH₃OH | 69        |
| 14    | [Cp*RhCl₂]₂   | AgOTs  | Cu(OAc)₂·H₂O       | Cl₂CCH₂OH/CH₃OH | 47        |
| 15    | [Cp*Rh(CH₂CN)₃](OTs)₂ | - | Cu(OAc)₂·H₂O | Cl₂CCH₂OH/CH₃OH | 72        |
| 16    | [Cp*Rh(CH₂CN)₃](OTs)₂ | - | Air (1 atm) | Cl₂CCH₂OH/CH₃OH | N.D.      |
Reactions were carried out by using 5 (0.2 mmol), 2a (0.1 mmol), [Rh] (5 mol%), [Ag] (20 mol%) and oxidant (2.0 equiv.) in CH$_3$OH (1 mL) at 80 °C for 24 h under an N$_2$ atmosphere. NMR yields.

Isolated yields. 1,2-Dichloroethene (DCE, 0.5 mL) and CH$_3$OH (1.5 mL). Cl$_3$CCH$_2$OH (0.5 mL) and CH$_3$OH (1.5 mL). Cl$_3$CCH$_2$OH (0.5 mL), CH$_3$OH (1.5 mL) and stirred for 16 h. [Cp*RhCl$_2$]$_2$ (2.5 mol%), AgOTs (10 mol%), Cl$_3$CCH$_2$OH (0.5 mL) and CH$_3$OH (1.5 mL). [Cp*Rh(CH$_3$CN)$_3$](OTs)$_2$ (10 mol%), Cl$_3$CCH$_2$OH (0.5 mL) and CH$_3$OH (1.5 mL). [Cp*Rh(CH$_3$CN)$_3$](OTs)$_2$ (10 mol%), Cl$_3$CCH$_2$OH (0.5 mL) and CH$_3$OH (1.5 mL) under air. N.D. = not detected.

**V. General procedure for regioselective addition/annulation of ferrocenythioamide 5 with 1,3-diynes 2**

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (0.2 mmol), 1,3-diyn 2 (0.1 mmol), [Cp*RhCl$_2$]$_2$ (5 mol%), AgOTs (20 mol%), Cu(OAc)$_2$·H$_2$O (0.2 mmol), Cl$_3$CCH$_2$OH (0.5 mL) and CH$_3$OH (1.5 mL) under an N$_2$ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with about 20 mL of dichloromethane. Then the filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel to provide desired products 6.

**VI. Gram-scale synthesis of 6a**

A 100 mL three-necked flask with a magnetic stir bar was charged with ferrocenyl thioamides 5 (1.88 g, 6.0 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyn 2a (0.61 g, 3.0 mmol), [Cp*RhCl$_2$]$_2$ (92.7 mg, 5 mol%), AgOTs (167.4 mg, 20 mol%), Cu(OAc)$_2$·H$_2$O (1.20 g, 6.0 mmol, 2.0 equiv.), Cl$_3$CCH$_2$OH (7.5 mL) and CH$_3$OH (22.5 mL) under an N$_2$ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 20 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 30 mL of dichloromethane. Then the filtrate was concentrated under reduced
pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, v/v) to provide the desired product 6a (1.03 g, 72% yield).

**VII. Mechanistic studies**

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (31.3 mg, 0.1 mmol), 1,4-diphenylbuta-1,3-diyn 2a (20.2 mg, 0.1 mmol), \([\text{Cp}^{*}\text{RhCl}_2]\) (30.9 mg, 0.05 mmol, 50 mol%), AgOTs (55.8 mg, 0.2 mmol, 2.0 equiv.), \(\text{Cl}_3\text{CCH}_2\text{OH}\) (0.5 mL) and \(\text{CH}_3\text{OH}\) (1.5 mL) under an N\(_2\) atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, v/v), providing compound 6a with 43% yield (20.6 mg).
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl amide 1 (59.4 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyn 2a (20.2 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl₃. In-situ ¹H NMR spectra of all the reaction mixtures showed that there was no product 6a obtained.

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with methyl ferrocene carboxylate 8 (48.8 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyn 2a (20.2 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl₃. In-situ ¹H NMR spectra of all the reaction mixtures showed that there was no product 6a obtained.
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 4 (49.9 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl₃. The in-situ ¹H NMR spectrum of the reaction mixture showed that there was no product 6a obtained.

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl amide 1 (59.4 mg, 0.2 mmol, 2.0 equiv.), 2,5-diphenylthiophene 9 (23.6 mg, 0.1 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl₃. In-situ ¹H NMR spectra of all the reaction mixtures showed that there was no product 6a obtained.
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (62.6 mg, 0.2 mmol, 2.0 equiv.), 2,5-diphenylthiophene 9 (23.6 mg, 0.1 mmol), \([\text{Cp}^*\text{RhCl}_2]_2\) (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)\(_2\)·H\(_2\)O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl\(_3\)CCH\(_2\)OH (0.5 mL) and CH\(_3\)OH (1.5 mL) under an N\(_2\) atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl\(_3\). In-situ \(^1\)H NMR spectra of all the reaction mixtures showed that there was no product 6a obtained.

\[
\begin{array}{c}
\text{Fe} \quad \text{CO}_2\text{CH}_3 \quad + \quad \begin{array}{c} \text{Ph} \\ \text{S} \end{array} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad \begin{array}{c} \text{[Cp}^*\text{RhCl}_2]_2 \quad \text{(5 mol\%)} \\ \text{AgOTs (20 mol\%)} \end{array} \quad \begin{array}{c} \text{Cu(OAc)}_2\cdot\text{H}_2\text{O (2.0 equiv.)} \\ \text{Cl}_3\text{CCH}_2\text{OH, CH}_3\text{OH} \\ 80^\circ\text{C, N}_2, 24\text{ h} \end{array} \quad \begin{array}{c} \text{Fe} \\ \text{CO}_2\text{CH}_3 \end{array} \quad \text{S} \\ \text{Ph} \end{array}
\]

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with methyl ferrocene carboxylate 8 (48.8 mg, 0.2 mmol, 2.0 equiv.), 2,5-diphenylthiophene 9 (23.6 mg, 0.1 mmol), \([\text{Cp}^*\text{RhCl}_2]_2\) (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)\(_2\)·H\(_2\)O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl\(_3\)CCH\(_2\)OH (0.5 mL) and CH\(_3\)OH (1.5 mL) under an N\(_2\) atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl\(_3\). In-situ \(^1\)H NMR spectra of all the reaction mixtures showed that there was no product 6a obtained.

\[
\begin{array}{c}
\text{Fe} \quad \text{CO}_2\text{CH}_3 \quad + \quad \begin{array}{c} \text{Ph} \\ \text{S} \end{array} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad \begin{array}{c} \text{[Cp}^*\text{RhCl}_2]_2 \quad \text{(5 mol\%)} \\ \text{AgOTs (20 mol\%)} \end{array} \quad \begin{array}{c} \text{anhydrous Cu(OAc)}_2 \quad \text{(2.0 equiv.)} \\ \text{dry CH}_3\text{OH (2 mL)} \\ 80^\circ\text{C, N}_2, 24\text{ h} \end{array} \quad \begin{array}{c} \text{Fe} \\ \text{CO}_2\text{CH}_3 \end{array} \quad \text{S} \\ \text{Ph} \end{array}
\]

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (62.6 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne 2a (20.2 mg, 0.1 mmol), heavy-oxygen water (H\(_2\)\(^{18}\)O, 90 µL, 5.0 mmol, 50 equiv.), \([\text{Cp}^*\text{RhCl}_2]_2\) (3.1
mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), anhydrous Cu(OAc)₂ (36.3 mg, 0.2 mmol, 2.0 equiv.) and dry CH₃OH (2 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, v/v), providing 36.4 mg of compound 6a-¹⁸O in 76% yield. The ESI-HRMS of 6a-¹⁸O calculated for C₂₈H₂₂Fe¹⁸O₂Na [M+Na]+ 503.0625, was found 503.0627.

![Fig. S1. ESI-HRMS spectrum of 6a-¹⁸O.](image)

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (62.6 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyn 2a (20.2 mg, 0.1 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.) and CH₂CH₂OH (2 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, v/v) to provide compound 10 as a yellow solid in a yield of 47% (23.3 mg).

![reaction_diagram](image)
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (62.6 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne 2a (20.2 mg, 0.1 mmol), aniline (27 µL, 0.3 mmol, 3.0 equiv.), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1, v/v) to provide compound 11 as a yellow solid in 41% yield (22.7 mg).

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with thienylferrocene 6a (47.8 mg, 0.1 mmol), aniline (27 µL, 0.3 mmol, 3.0 equiv.), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl₃CCH₂OH (0.5 mL) and CH₃OH (1.5 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 24 h and then diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated under reduced pressure, followed by dissolved in CDCl₃. In-situ ¹H NMR spectra of the reaction mixture showed that there was no product 11 obtained.

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide 5 (31.3 mg, 0.1 mmol), 1,4-diphenylbuta-1,3-diyne 2a (20.2 mg, 0.1 mmol),
[Cp*RhCl₂]₂ (30.9 mg, 50 mol%), AgOTs (55.8 mg, 2.0 equiv.), Cu(OAc)₂·H₂O (39.9 mg, 0.2 mmol, 2.0 equiv.) and CH₃OH (2 mL) under an N₂ atmosphere. The resulting mixture was stirred at 80 °C for 2 h, and then cooled to room temperature for ESI-HRMS detection.

Intermediate I: calcd for C₂₆H₃₃FeNRhS [M]⁺ 550.0733, found 550.0731;
Intermediate II: calcd for C₄₂H₄₃FeNRhS [M]⁺ 752.1515, found 752.1521;
Intermediate III: calcd for C₃₂H₂₈FeNS [M]⁺ 514.1286, found 514.1289.

Fig. S2. ESI-HRMS spectrum of intermediates I and III.

Fig. S3. ESI-HRMS spectrum of intermediate II.

VIII. Synthesis of extended π-conjugated ferrocenes 7

4 M of NaOH solution (15 mL) was added to the solution of thiencylferrocene 6 (0.3 mmol) and EtOH (45 mL). Monitored by thin-layer chromatography, the mixture was refluxed until hydrolyzed completely. Then, 2 N of HCl solution was added carefully at room temperature until the mixture was weakly acidic. After evaporated under reduced pressure, the residue was diluted with 150 mL of ethyl acetate and washed
with saline solution (200 mL) three times. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was re-dissolved in 50 mL of dichloromethane and filtered out the insoluble. Finally, the filtrate was concentrated under reduced pressure to give the hydrolysate.

Then, oxalyl chloride (45 µL, 0.53 mmol) was added to the solution of the hydrolysate in dry dichloromethane (20 mL) at 0 °C under N₂, followed by two drops of DMF. The mixture was stirred for 6 h at room temperature and evaporated under reduced pressure. To a mixture of AlCl₃ (160.0 mg, 1.2 mmol) in dry dichloromethane (20 mL) cooled to −20 °C, the solution of the prepared acyl chloride re-dissolved in dry dichloromethane (20 mL), which had also been cooled to −20 °C, was added via a double-ended needle under an N₂ atmosphere. The resulting mixture was stirred for overnight at −20 °C. Then 2 mL water was poured into the reaction flask at −20 °C, stirring for 5 min. The mixture was diluted with 100 mL of dichloromethane and washed with NH₄Cl, NaHCO₃ and saline solution (150 mL) successively. The organic layer was dried over MgSO₄, filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel to provide extended π-conjugated ferrocenes 7.

IX. Calculated molecular conformations, photophysical and electrochemical properties

![Fig. S4 UV-Vis absorption spectra of 6u, 6v, 7b and 7c in CH₃CN (1 × 10⁻⁵ M).]
Fig. S5 Calculated molecular conformation of (a) 6u and (b) 7b. Molecular optimization was performed by density functional theory computation with Gaussian 09 at the B3LYP/6-31G* level.

Fig. S6 Fluorescence spectra of 6u and 7b in CH$_3$CN (1 × 10$^{-5}$ M). Inset: Fluorescent images of 6u (left) and 7b (right) in CH$_3$CN (1 × 10$^{-5}$ M) under UV light (365 nm).

Fig. S7 Fluorescence spectra of (a) 7b and (b) 7c in different solvents.
**Fig. S8** Cyclic voltammograms of 6v. Measurements were carried out at a scan rate of 50 mV/s in CH$_3$CN with 6v (1 × 10$^{-3}$ M) containing n-Bu$_4$NPF$_6$ (0.1 M), using Fc/Fc$^+$ (0.08 V) as reference. The three-electrode setup consisted of an Ag/Ag$^+$ (0.01 M of AgNO$_3$ in CH$_3$CN) reference electrode, a platinum wire counter electrode, and a platinum plate working electrode.

**Fig. S9** Changes by the evolution of the fluorescence intensity of 6v at 432 nm with time. Stepwise oxidation and reduction cycles carried out in CH$_3$CN with 6v (5 × 10$^{-6}$ M) containing n-Bu$_4$NPF$_6$ (0.1 M) by chronoamperometric analysis, which uses fixed potentials at + 0.48 V (for oxidation, vs Fc/Fc$^+$) and −0.62 V (for reduction, vs Fc/Fc$^+$) changed every 150 s.

**X. Preparation and characterization of the described compounds**

\[
\text{C}_{6}H_{17}\begin{array}{c}
\equiv \\
\equiv \\
\equiv \\
\equiv
\end{array}\text{C}_{6}H_{17}
\]

1,4-Bis(1-octyl-1H-indol-5-yl)buta-1,3-diyne (2s)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.87$ (t, $J = 7.2$ Hz, 6H), 1.25-1.30 (m, 20H), 1.79-1.86 (m, 4H), 4.09 (t, $J = 7.2$ Hz, 4H), 6.48 (d, $J = 2.8$ Hz, 2H), 7.12 (d, $J = 2.8$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.36 (dd, $J = 8.4$ Hz, 1.6 Hz, 2H), 7.85 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 14.2$, 22.7, 27.1, 29.29, 29.32, 30.4, 31.9, 46.7, 72.3, 82.8, 101.5, 109.7, 112.5, 125.8, 126.2, 128.5, 129.1, 136.1 ppm.

![1,4-Diferrocenylbuta-1,3-diyn]](image)

1,4-Diferrocenylbuta-1,3-diyn (2t)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.25$ (t, $J = 2.0$ Hz, 4H), 4.26 (s, 10H), 4.51 (t, $J = 2.0$ Hz, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 63.8$, 69.4, 70.3, 71.1, 72.3, 79.2 ppm.

![4,4'-(buta-1,3-diyn-1,4-diyl)bis(N,N-diphenylaniline)](image)

4,4'-{(buta-1,3-diyn-1,4-diyl)bis(N,N-diphenylaniline)} (2u)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.95$ (dt, $J = 8.8$ Hz, 2.0 Hz, 4H), 7.06-7.12 (m, 12H), 7.27-7.30 (m, 8H), 7.34 (dt, $J = 8.8$ Hz, 2.0 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 73.6$, 82.1, 114.3, 121.7, 124.1, 125.5, 129.6, 133.5, 147.0, 148.7 ppm.

![1,4-Di(9,9'-spirobifluoren-2-yl)buta-1,3-diyn](image)

1,4-Di(9,9'-spirobifluoren-2-yl)buta-1,3-diyn (2v)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.70$ (d, $J = 7.6$ Hz, 4H), 6.74 (d, $J = 7.6$ Hz, 2H), 6.82 (s, 2H), 7.08-7.15 (m, 6H), 7.34-7.39 (m, 6H), 7.46 (dd, $J = 8.0$ Hz, 1.6 Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.81-7.84 (m, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 65.8$, 74.4, 82.4, 120.1, 120.2, 120.6, 120.9, 124.1, 124.3, 128.0, 128.1, 128.2, 128.7, 132.4, 140.9, 141.9, 142.8, 148.0, 149.1, 149.3 ppm.
**N-[2-(1,4-diphenylbut-1-en-3-yn-2-yl)ferrocenylformyl]piperidine (4)**

M.p.: 84-87 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.45-1.71 (m, 6H), 3.11-3.22 (m, 2H), 3.45-3.48 (m, 1H), 3.64-3.67 (m, 1H), 4.33 (t, $J$ = 2.4 Hz, 1H), 4.40 (s, 5H), 4.57 (dd, $J$ = 2.4 Hz, 1.6 Hz, 1H), 4.60 (dd, $J$ = 2.4 Hz, 1.6 Hz, 1H), 6.93 (s, 1H), 7.31-7.44 (m, 6H), 7.67 (dt, $J$ = 6.4 Hz, 1.6 Hz, 2H), 8.00 (d, $J$ = 7.2 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 24.6, 25.3, 26.2, 43.1, 47.9, 65.9, 67.5, 71.7, 72.8, 85.0, 85.6, 88.8, 96.6, 119.8, 123.6, 128.1, 128.5, 128.59, 128.64, 128.8, 131.8, 132.4, 136.9, 167.7 ppm. ESI-HRMS: calcd for C$_{32}$H$_{29}$FeNONa $[M+Na]^+$ 522.1491, found 522.1487.

**Methyl 2-(2,5-diphenylthien-3-yl)ferrocene carboxylate (6a)**

Following the general procedure for regioselective addition/annulation reaction, compound 6a was obtained as a yellow solid (38.8 mg, 81% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 155-156 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.58 (s, 3H), 4.25 (s, 5H), 4.36 (dd, $J$ = 2.4 Hz, 1.6 Hz, 1H), 4.42 (t, $J$ = 2.4 Hz, 1H), 4.88 (dd, $J$ = 2.8 Hz, 1.6 Hz, 1H), 7.16-7.24 (m, 5H), 7.31-7.35 (m, 1H), 7.44 (t, $J$ = 8.0 Hz, 2H), 7.69-7.72 (m, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.6, 70.0, 70.1, 70.8, 71.1, 74.6, 85.4, 125.9, 127.3, 127.6, 128.3, 128.7, 129.1, 129.2, 133.4, 134.5, 134.6, 140.1, 140.6, 171.7 ppm. ESI-HRMS: calcd for C$_{28}$H$_{23}$FeO$_2$S [M+H]$^+$ 479.0763, found 479.0770.
Methyl 2-[2,5-di(4-methylphenyl)thien-3-yl]ferrocene carboxylate (6b)

Following the general procedure for regioselective addition/annulation reaction, compound 6b was obtained as a yellow solid (38.2 mg, 75% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 93-95 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.29 (s, 3H), 2.40 (s, 3H), 3.58 (s, 3H), 4.24 (s, 5H), 4.34 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 4.41 (t, J = 2.4 Hz, 1H), 4.87 (dd, J = 2.8 Hz, 1.6 Hz, 1H), 7.00-7.06 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.65 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.3, 21.4, 51.6, 69.9, 70.1, 70.7, 71.1, 74.6, 85.7, 125.8, 128.5, 128.8, 129.0, 129.7, 131.8, 131.9, 132.8, 137.0, 137.4, 139.8, 140.3, 171.8 ppm. ESI-HRMS: calcd for C₃₀H₂₂FeO₂S [M+H]⁺ 507.1076, found 507.1082.

![Methyl 2-[2,5-di(4-methylphenyl)thien-3-yl]ferrocene carboxylate (6b)](image)

Methyl 2-[2,5-di(4-tert-butylphenyl)thien-3-yl]ferrocene carboxylate (6c)

Following the general procedure for regioselective addition/annulation reaction, compound 6c was obtained as a yellow solid (40.9 mg, 69% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 92-94 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (s, 9H), 1.37 (s, 9H), 3.55 (s, 3H), 4.23 (s, 5H), 4.38-4.39 (m, 1H), 4.42 (t, J = 2.4 Hz, 1H), 4.87 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.65 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 31.4, 31.5, 34.7, 34.8, 51.6, 69.9, 70.1, 70.7, 71.1, 74.7, 85.6, 125.2, 125.6, 125.9, 128.2, 129.0, 131.8, 131.9, 132.8, 139.7, 140.2, 150.1, 150.6, 171.7 ppm. ESI-HRMS: calcd for C₃₆H₃₈FeO₂SNa [M+Na]⁺ 613.1834, found 613.1835.

522
Methyl 2-[2,5-di(4-methoxyphenyl)thien-3-yl]ferrocene carboxylate (6d)

Following the general procedure for regioselective addition/annulation reaction, compound 6d was obtained as a yellow solid (39.6 mg, 74% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v). M.p.: 164-167 °C. 1H NMR (400 MHz, CDCl₃): δ = 3.60 (s, 3H), 3.77 (s, 3H), 3.86 (s, 3H), 4.24 (s, 5H), 4.33 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 4.40 (t, J = 2.4 Hz, 1H), 4.87 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 6.74 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 6.96 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 7.07 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 7.58 (s, 1H), 7.61 (dt, J = 8.8 Hz, 2.0 Hz, 2H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 51.6, 55.3, 55.5, 69.9, 70.0, 70.7, 71.1, 74.6, 85.7, 113.8, 114.4, 127.1, 127.3, 127.6, 128.3, 129.9, 132.5, 139.1, 139.8, 158.8, 159.2, 171.8 ppm. ESI-HRMS: calcd for C₃₀H₂₇FeO₄S [M+H]+ 539.0974, found 539.0977.

Methyl 2-[2,5-di(4-fluorophenyl)thien-3-yl]ferrocene carboxylate (6e)

Following the general procedure for regioselective addition/annulation reaction, compound 6e was obtained as a yellow solid (37.2 mg, 72% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 141-143 °C. 1H NMR (400 MHz, CDCl₃): δ = 3.61 (s, 3H), 4.24 (s, 5H), 4.30-4.31 (m, 1H), 4.42 (t, J = 2.4 Hz, 1H), 4.87 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 6.88-6.94 (m, 2H), 7.08-7.16 (m, 4H), 7.62-7.67 (m, 3H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 51.6, 69.9, 70.1, 70.9, 71.2, 74.5, 85.2, 115.4 (d, J = 21.5 Hz), 116.1 (d, J = 21.7 Hz), 127.6 (d, J = 8.0 Hz), 129.2 (d, J = 0.8 Hz), 130.4 (d, J = 8.0 Hz), 130.6 (d, J = 3.4 Hz), 130.7 (d, J = 3.3 Hz), 133.5, 138.8 (d, J = 0.8 Hz), 139.5, 162.1 (d, J = 246.1 Hz), 162.5 (d, J = 245.8 Hz),
171.5 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -114.54 - 114.48$ (m, 1F), -114.47 - -114.41 (m, 1F) ppm. ESI-HRMS: calcd for C$_{28}$H$_{20}$F$_2$FeO$_2$SNa [M+Na]$^+$ 537.0394, found 537.0396.

Methyl 2-[2,5-di(4-acetylphenyl)thien-3-yl]ferrocene carboxylate (6f)

Following the general procedure for regioselective addition/annulation reaction, compound 6f was obtained as a yellow solid (38.5 mg, 68% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v). M.p.: 169-172 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.56$ (s, 3H), 2.65 (s, 3H), 3.59 (s, 3H), 4.27 (s, 5H), 4.35 (dd, $J = 2.4$ Hz, 1.6 Hz, 1H), 4.47 (t, $J = 2.4$ Hz, 1H), 4.92 (dd, $J = 2.4$ Hz, 1.6 Hz, 1H), 7.24-7.26 (m, 2H), 7.77-7.82 (m, 4H), 7.86 (s, 1H), 8.04 (dt, $J = 8.4$ Hz, 2.0 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 26.7$, 26.8, 51.7, 70.0, 70.4, 71.2, 71.3, 74.6, 84.8, 125.7, 128.5, 128.6, 129.4, 131.1, 135.4, 135.7, 136.1, 138.6, 139.1, 140.2, 140.4, 171.4, 197.4, 197.6 ppm. ESI-HRMS: calcd for C$_{32}$H$_{26}$FeO$_4$SNa [M+Na]$^+$ 585.0793, found 585.0797.

Methyl 2-[2,5-di(4-methoxycarbonylphenyl)thien-3-yl]ferrocene carboxylate (6g)

Following the general procedure for regioselective addition/annulation reaction, compound 6g was obtained as a yellow solid (39.0 mg, 66% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v). M.p.: 189-191 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.58$ (s, 3H), 3.89 (s, 3H), 3.95 (s, 3H), 4.26 (s, 5H), 4.33 (dd, $J = 2.8$ Hz, 1.6 Hz, 1H), 4.45 (t, $J = 2.8$ Hz, 1H), 4.91 (dd, $J = 2.8$ Hz,
1.6 Hz, 1H), 7.22 (dt, J = 8.4 Hz, 2.0 Hz, 2H), 7.75 (dt, J = 8.4 Hz, 2.0 Hz, 2H), 7.84 (s, 1H), 7.88 (dt, J = 8.4 Hz, 2.0 Hz, 2H), 8.10 (dt, J = 8.4 Hz, 2.0 Hz, 2H) ppm. \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 51.7, 52.6, 52.34, 70.0, 70.3, 71.17, 71.24, 74.6, 84.8, 125.5, 128.4, 128.8, 129.2, 129.7, 130.5, 130.9, 135.2, 138.5, 139.0, 140.1, 140.4, 166.9, 171.4\) ppm. ESI-HRMS: calcd for C\(_{32}\)H\(_{26}\)FeO\(_6\)SNa [M+Na]\(^+\) 617.0692, found 617.0694.

**Methyl 2-[2,5-di(3-methylphenyl)thien-3-yl]ferrocene carboxylate (6h)**

Following the general procedure for regioselective addition/annulation reaction, compound 6h was obtained as a yellow solid (36.2 mg, 71% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 59-63 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.25\) (s, 3H), 2.44 (s, 3H), 3.58 (s, 3H), 4.24 (s, 5H), 4.35 (dd, \(J = 2.4\) Hz, 1.6 Hz, 1H), 4.41 (t, \(J = 2.4\) Hz, 1H), 4.87 (dd, \(J = 2.4\) Hz, 1.6 Hz, 1H), 6.92 (d, \(J = 7.6\) Hz, 1H), 6.99-7.02 (m, 2H), 7.08 (t, \(J = 7.6\) Hz, 1H), 7.14 (d, \(J = 7.6\) Hz, 1H), 7.32 (t, \(J = 7.6\) Hz, 1H), 7.50-7.52 (m, 2H), 7.68 (s, 1H) ppm. \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 21.5, 21.7, 51.6, 69.9, 70.1, 70.7, 71.1, 74.6, 85.5, 123.0, 125.8, 126.6, 128.0, 128.2, 128.4, 128.9, 129.1, 129.4, 133.2, 134.48, 134.51, 137.9, 138.7, 140.1, 140.6, 171.8\) ppm. ESI-HRMS: calcd for C\(_{30}\)H\(_{27}\)FeO\(_2\)S [M+H]\(^+\) 507.1076, found 507.1076.

**Methyl 2-[2,5-di(3-methoxylphenyl)thien-3-yl]ferrocene carboxylate (6i)**

Following the general procedure for regioselective addition/annulation reaction, compound 6i was obtained as a yellow solid (39.5 mg, 73% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v). \(^1\text{H}\) NMR
(400 MHz, DMSO-d$_6$): δ = 3.43 (s, 3H), 3.59 (s, 3H), 3.85 (s, 3H), 4.30 (s, 5H), 4.49 (br, 1H), 4.59 (br, 1H), 4.81 (br, 1H), 6.55 (d, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 7.17 (t, $J = 8.0$ Hz, 1H), 7.25 (s, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.79 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ = 51.2, 54.9, 55.3, 69.7, 70.1, 70.2, 71.0, 74.1, 84.7, 111.0, 112.9, 113.2, 113.3, 117.9, 120.2, 129.6, 129.7, 130.4, 133.9, 134.8, 135.1, 138.4, 139.4, 158.9, 159.8, 170.4 ppm.

ESI-HRMS: calcd for C$_{30}$H$_{27}$FeO$_4$S [M+H]$^+$ 539.0974, found 539.0968.

Methyl 2-[2,5-di(3-fluorophenyl)thien-3-yl]ferrocene carboxylate (6j)

Following the general procedure for regioslective addition/annulation reaction, compound 6j was obtained as a yellow solid (33.3 mg, 65% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.61 (s, 3H), 4.26 (s, 5H), 4.35 (dd, $J = 2.8$ Hz, 1.6 Hz, 1H), 4.45 (t, $J = 2.8$ Hz, 1H), 4.91 (dd, $J = 2.8$ Hz, 1.6 Hz, 1H), 6.84-6.95 (m, 3H), 7.00-7.05 (m, 1H), 7.15-7.21 (m, 1H), 7.37-7.43 (m, 2H), 7.47 (dt, $J = 8.0$ Hz, 1.2 Hz, 1H), 7.72 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 51.6, 69.9, 70.2, 71.1, 71.2, 74.5, 84.8, 112.6 (d, $J = 22.6$ Hz), 114.3 (d, $J = 21.1$ Hz), 114.5 (d, $J = 21.1$ Hz), 115.4 (d, $J = 22.4$ Hz), 121.6 (d, $J = 2.8$ Hz), 124.4 (d, $J = 2.9$ Hz), 129.9 (d, $J = 8.5$ Hz), 130.0, 130.6 (d, $J = 8.6$ Hz), 134.3, 136.39 (d, $J = 8.1$ Hz), 136.43 (d, $J = 8.3$ Hz), 139.0 (d, $J = 2.5$ Hz), 139.7 (d, $J = 2.7$ Hz), 162.5 (d, $J = 244.5$ Hz), 163.3 (d, $J = 244.6$ Hz), 171.5 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ = -112.95 – -112.88 (m, 1F), -112.68 – -112.62 (m, 1F) ppm. ESI-HRMS: calcd for C$_{28}$H$_{21}$F$_2$FeO$_2$S [M+H]$^+$ 515.0574, found 515.0571.

Methyl 2-[2,5-di(3,5-dimethylphenyl)thien-3-yl]ferrocene carboxylate (6k)
Following the general procedure for regioselective addition/annulation reaction, compound 6k was obtained as a yellow solid (38.5 mg, 72% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 88-91 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.19\) (s, 6H), 2.40 (s, 6H), 3.58 (s, 3H), 4.24 (s, 5H), 4.34 (dd, \(J = 2.4\) Hz, 1.6 Hz, 1H), 4.40 (t, \(J = 2.4\) Hz, 1H), 4.87 (dd, \(J = 2.8\) Hz, 1.6 Hz, 1H), 6.77 (s, 2H), 6.82 (s, 1H), 6.96 (s, 1H), 7.30 (s, 2H), 7.64 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 21.4, 21.6, 51.6, 69.9, 70.0, 70.7, 71.1, 74.7, 85.6, 123.8, 126.5, 128.8, 128.9, 129.3, 133.0, 134.4, 134.5, 137.7, 138.6, 140.1, 140.6, 171.8\) ppm. ESI-HRMS: calcd for C\(_{32}\)H\(_{31}\)FeO\(_2\)S [M+H]\(^+\) 535.1389, found 535.1395.

Methyl 2-[2,5-di(3,5-dimethoxyphenyl)thien-3-yl]ferrocene carboxylate (6l)

Following the general procedure for regioselective addition/annulation reaction, compound 6l was obtained as a yellow solid (39.9 mg, 67% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v/v). M.p.: 125-129 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.59\) (s, 3H), 3.64 (s, 6H), 3.88 (s, 6H), 4.25 (s, 5H), 4.38-4.39 (m, 1H), 4.43 (t, \(J = 2.8\) Hz, 1H), 4.88 (dd, \(J = 2.8\) Hz, 1.6 Hz, 1H), 6.29-6.32 (m, 3H), 6.45 (t, \(J = 2.0\) Hz, 1H), 6.84 (d, \(J = 2.0\) Hz, 2H), 7.66 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 51.6, 55.4, 55.6, 70.0, 70.2, 70.7, 71.1, 74.7, 85.4, 99.3, 100.1, 104.4, 106.5, 129.6, 133.5, 136.2, 136.4, 139.9, 140.4, 160.4, 161.2, 171.6\) ppm. ESI-HRMS: calcd for C\(_{32}\)H\(_{31}\)FeO\(_2\)S [M+H]\(^+\) 599.1185, found 599.1181.

Methyl 2-[2,5-di(3,4-dimethoxyphenyl)thien-3-yl]ferrocene carboxylate (6m)
Following the general procedure for regioselective addition/annulation reaction, compound **6m** was obtained as a yellow solid (41.5 mg, 69% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v). M.p.: 153-156 °C. ¹H NMR (400 MHz, DMSO-<d>6</d>): δ = 3.44 (s, 3H), 3.49 (s, 3H), 3.71 (s, 3H), 3.81 (s, 3H), 3.88 (s, 3H), 4.29 (s, 5H), 4.48 (br, 1H), 4.58 (t, J = 2.4 Hz, 1H), 4.80 (br, 1H), 6.50 (s, 1H), 6.71 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 7.22 (s, 1H), 7.27 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.64 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-<d>6</d>): δ = 51.1, 55.0, 55.4, 55.62, 55.65, 69.4, 69.8, 69.9, 70.9, 74.1, 85.1, 109.2, 111.3, 111.6, 112.3, 117.9, 120.2, 126.5, 126.6, 128.4, 132.7, 137.8, 139.0, 147.9, 148.0, 148.7, 149.1, 170.4 ppm. ESI-HRMS: calcd for C₃₂H₃₁FeO₆S [M+H]⁺ 599.1185, found 599.1185.

**Methyl 2-[5-hexyl-2-(4-methoxyphenyl)thien-3-yl]ferrocene carboxylate (6n)**

Following the general procedure for regioselective addition/annulation reaction, CH₃OH (2.0 mL) was used as solvent, and compound **6n** was obtained as a yellow liquid (13.8 mg, 27% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). ¹H NMR (400 MHz, CDCl₃): δ = 0.92 (t, J = 7.2 Hz, 3H), 1.33-1.38 (m, 4H), 1.44-1.50 (m, 2H), 1.73-1.80 (m, 2H), 2.86 (t, J = 7.6 Hz, 2H), 3.60 (s, 3H), 3.75 (s, 3H), 4.20 (s, 5H), 4.25 (dd, J = 2.8 Hz, 1.6 Hz, 1H), 4.35 (t, J = 2.8 Hz, 1H), 4.84 (dd, J = 2.8 Hz, 1.6 Hz, 1H), 6.71 (dt, J = 9.2 Hz, 2.8 Hz, 2H), 7.02 (dt, J = 8.8 Hz, 2.8 Hz, 2H), 7.15 (t, J = 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.3, 22.8, 29.1, 30.3, 31.81, 31.83, 51.5, 55.3, 69.8, 69.9, 70.6, 71.0, 74.7, 85.9, 113.6, 127.7, 129.9, 130.2, 131.0, 137.9, 141.6, 158.5, 171.9 ppm. ESI-HRMS: calcd for C₂₉H₃₂FeO₅SNa [M+Na]⁺ 539.1314, found 539.1311.
Methyl 2-[2,5-di(furan-2-yl)thien-3-yl]ferrocene carboxylate (6o)

Following the general procedure for regioselective addition/annulation reaction, CH$_3$OH (2.0 mL) was used as solvent, and compound 6o was obtained as a yellow solid (20.7 mg, 45% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.60 (s, 3H), 4.30 (s, 5H), 4.51-4.54 (m, 2H), 4.96 (dd, $J$ = 2.4 Hz, 2.0 Hz, 1H), 5.81 (dd, $J$ = 3.6 Hz, 0.8 Hz, 1H), 6.26 (dd, $J$ = 3.6 Hz, 2.0 Hz, 1H), 6.49 (dd, $J$ = 3.6 Hz, 2.0 Hz, 1H), 6.56 (dd, $J$ = 3.6 Hz, 0.8 Hz, 1H), 7.28 (dd, $J$ = 2.0 Hz, 0.8 Hz, 1H), 7.46 (dd, $J$ = 2.0 Hz, 0.8 Hz, 1H), 7.54 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.6, 70.1, 70.4, 70.7, 71.2, 74.5, 85.1, 105.5, 107.0, 111.7, 111.9, 128.4, 128.9, 130.0, 132.8, 141.3, 141.9, 149.0, 149.3, 171.7 ppm. ESI-HRMS: calcd for C$_{24}$H$_{19}$FeO$_4$S [M+H]$^+$ 459.0348, found 459.0353.

Methyl 2-[2,5-di(thien-2-yl)thien-3-yl]ferrocene carboxylate (6p)

Following the general procedure for regioselective addition/annulation reaction, CH$_3$OH (2.0 mL) was used as solvent, and compound 6p was obtained as a yellow solid (25.8 mg, 53% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v). M.p.: 160-162 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.62 (s, 3H), 4.28 (s, 5H), 4.47-4.48 (m, 1H), 4.50 (t, $J$ = 2.8 Hz, 1H), 4.94 (dd, $J$ = 2.8 Hz, 1.6 Hz, 1H), 6.82 (dd, $J$ = 3.6 Hz, 1.2 Hz, 1H), 6.87 (dd, $J$ = 5.2 Hz, 3.6 Hz, 1H), 7.06 (dd, $J$ = 5.2 Hz, 3.6 Hz, 1H), 7.11 (dd, $J$ = 4.8 Hz, 1.2 Hz, 1H), 7.23 (dd, $J$ = 3.6 Hz, 1.2 Hz, 1H), 7.25-7.26 (m, 1H), 7.50 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.7, 70.2, 70.8, 70.9, 71.1, 74.9, 84.7, 123.9, 124.6, 125.3, 125.8, 127.2, 128.1, 129.9, 132.7, 133.4, 133.6, 136.1, 137.3, 171.6 ppm. ESI-HRMS: calcd for C$_{24}$H$_{19}$FeO$_2$S$_3$ [M+H]$^+$ 490.9891, found 490.9896.
Methyl 2-[2,5-di(5-methylthien-2-yl)thien-3-yl]ferrocene carboxylate (6q)

Following the general procedure for regioselective addition/annulation reaction, CH₃OH (2.0 mL) was used as solvent, and compound 6q was obtained as a yellow solid (35.4 mg, 68% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v). M.p.: 153-157 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3H), 2.51 (s, 3H), 3.64 (s, 3H), 4.27 (s, 5H), 4.47-4.49 (m, 2H), 4.93 (t, J = 2.0 Hz, 1H), 6.50 (dd, J = 3.6 Hz, 0.8 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 6.70 (dd, J = 3.6 Hz, 0.8 Hz, 1H), 6.99 (d, J = 3.2 Hz, 1H), ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.4, 15.6, 51.7, 70.1, 70.7, 70.8, 71.1, 75.0, 84.9, 123.6, 125.4, 125.6, 126.1, 129.3, 132.6, 132.7, 133.2, 133.9, 135.0, 139.2, 139.9, 171.8 ppm. ESI-HRMS: calcd for C₂₆H₂₃FeO₂S₃ [M+H]+ 519.0204, found 519.0205.

Methyl 2-[2,5-di(5-chlorothien-2-yl)thien-3-yl]ferrocene carboxylate (6r)

Following the general procedure for regioselective addition/annulation reaction, CH₃OH (2.0 mL) was used as solvent, and compound 6r was obtained as a yellow solid (26.3 mg, 47% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v). M.p.: 152-155 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.67 (s, 3H), 4.28 (s, 5H), 4.46 (br, 1H), 4.52 (br, 1H), 4.96 (br, 1H), 6.62 (d, J = 4.0 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.87 (d, J = 4.0 Hz, 1H), 6.98 (d, J = 4.0 Hz, 1H), ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 51.8, 70.5, 70.6, 71.16, 71.22, 75.0, 84.0, 123.2, 125.0, 126.2, 127.2, 129.0, 129.8, 130.1, 132.2, 132.6, 134.0, 134.6, 135.6, 171.4 ppm. ESI-HRMS: calcd for C₂₄H₁₇Cl₂FeO₂S₃ [M+H]+ 558.9112, found 558.9108; C₂₄H₁₇Cl₂ClFeO₂S₃ [M+H]+ 560.9082, found 560.9085; C₂₄H₁₇Cl₂FeO₂S₃ [M+H]+ 562.9053, found 562.9049.
**Methyl 2-[2,5-di(1-octyl-1H-indol-5-yl)thien-3-yl]ferrocene carboxylate (6s)**

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (1.0 mL) and CH$_3$OH (1.0 mL) were used as solvent, and compound 6s was obtained as a yellow liquid (47.8 mg, 61% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.86$-$0.90$ (m, 6H), 1.29-1.34 (m, 20H), 1.80 (t, $J = 6.8$ Hz, 2H), 1.87 (t, $J = 6.8$ Hz, 2H), 3.60 (s, 3H), 4.05 (t, $J = 7.2$ Hz, 2H), 4.14 (t, $J = 7.2$ Hz, 2H), 4.25 (s, 5H), 4.34-4.35 (m, 2H), 4.88 (dd, $J = 2.4$ Hz, 1.6 Hz, 1H), 6.40 (d, $J = 3.2$ Hz, 1H), 6.55 (d, $J = 2.8$ Hz, 1H), 6.97 (dd, $J = 8.4$ Hz, 1.6 Hz, 1H), 7.05 (d, $J = 3.2$ Hz, 1H), 7.13-7.15 (m, 2H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.52 (s, 1H), 7.58 (dd, $J = 8.4$ Hz, 1.6 Hz, 1H), 7.69 (s, 1H), 7.96 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 14.2$, 22.8, 27.2, 29.3, 29.4, 29.9, 30.4, 30.5, 31.91, 31.93, 46.6, 46.7, 51.6, 69.7, 70.2, 70.6, 71.0, 74.9, 86.1, 101.37, 101.40, 109.1, 109.9, 118.3, 120.4, 121.3, 123.0, 126.1, 126.6, 128.2, 128.3, 128.6, 128.8, 129.1, 131.8, 135.3, 135.7, 140.8, 141.4, 172.1 ppm. ESI-HRMS: calcd for C$_{48}$H$_{57}$FeN$_2$O$_2$S $[M+H]^+$ 781.3485, found 781.3481.

**Methyl 2-(2,5-diferrocenylthien-3-yl)ferrocene carboxylate (6t)**

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (1.0 mL) and CH$_3$OH (1.0 mL) were used as solvent, and compound 6t was obtained as a red solid (36.3 mg, 52% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.:
113-117 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.62 (s, 3H), 4.04-4.05 (m, 1H), 4.06 (s, 5H), 4.08-4.09 (m, 1H), 4.11-4.12 (m, 1H), 4.14-4.15 (m, 1H), 4.21 (s, 5H), 4.24 (s, 5H), 4.32 (t, $J$ = 1.6 Hz, 2H), 4.40 (dd, $J$ = 2.4 Hz, 1.6 Hz, 1H), 4.44 (t, $J$ = 2.4 Hz, 1H), 4.63-4.65 (m, 2H), 4.89 (dd, $J$ = 2.4 Hz, 1.6 Hz, 1H), 7.19 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.5, 66.9, 67.0, 68.1, 68.2, 68.3, 68.7, 69.7, 70.0, 70.1, 70.5, 70.6, 70.9, 74.6, 80.2, 80.7, 86.2, 128.0, 132.1, 137.5, 137.7, 171.7 ppm. ESI-HRMS: calcd for C$_{36}$H$_{31}$Fe$_3$O$_2$S [M+H]$^+$ 695.0088, found 695.0091.

Methyl 2-[2,5-di(4-diphenylaminophenyl)thien-3-yl]ferrocene carboxylate (6u)

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (2.0 mL) and CH$_3$OH (2.0 mL) were used as solvent, and the reaction mixture was stirred at 120 °C for 24 h under an N$_2$ atmosphere. Then, compound 6u was obtained as a yellow solid (23.8 mg, 29% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/2, v/v/v). M.p.: 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.60 (s, 3H), 4.24 (s, 5H), 4.42 (br, 1H), 4.43 (br, 1H), 4.85 (t, $J$ = 2.0 Hz, 1H), 6.89 (d, $J$ = 8.4 Hz, 2H), 6.98-7.03 (m, 5H), 7.05-7.07 (m, 6H), 7.11-7.16 (m, 6H), 7.22-7.30 (m, 7H), 7.54 (d, $J$ = 8.8 Hz, 2H), 7.58 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.6, 69.9, 70.2, 70.7, 71.1, 74.5, 85.9, 123.1, 123.2, 124.0, 124.58, 124.60, 126.6, 128.4, 128.7, 128.8, 129.3, 129.4, 129.5, 132.8, 139.2, 139.8, 146.8, 147.3, 147.6, 147.7, 171.6 ppm. ESI-HRMS: calcd for C$_{52}$H$_{41}$FeN$_2$O$_2$S [M+H]$^+$ 813.2233, found 813.2230.
Methyl 2-[2,5-di[9,9'-spirobifluoren-2-yl]thien-3-yl]ferrocene carboxylate (6v)

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (2.0 mL) and CH$_3$OH (2.0 mL) were used as solvent, and the reaction mixture was stirred at 120 °C for 24 h under an N$_2$ atmosphere. Then, compound 6v was obtained as a yellow solid (34.2 mg, 36% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/2, v/v/v). M.p.: 204-206 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.35 (s, 3H), 4.07-4.11 (m, 7H), 4.49 (dd, $J$ = 2.8 Hz, 1.6 Hz, 1H), 6.24 (d, $J$ = 2.0 Hz, 1H), 6.61-6.67 (m, 3H), 6.71 (d, $J$ = 7.6 Hz, 1H), 6.77 (d, $J$ = 7.6 Hz, 2H), 6.88 (d, $J$ = 1.6 Hz, 1H), 7.01-7.14 (m, 7H), 7.28-7.40 (m, 7H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.66 (dd, $J$ = 8.0 Hz, 1.6 Hz, 1H), 7.72-7.77 (m, 3H), 7.83-7.87 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 51.3, 65.8, 66.1, 69.4, 69.8, 70.8, 70.9, 74.0, 85.2, 119.8, 119.9, 120.0, 120.08, 120.10, 120.18, 120.19, 120.5, 121.5, 124.0, 124.08, 124.12, 124.25, 124.34, 125.5, 127.68, 127.72, 127.8, 127.89, 127.90, 127.93, 127.99, 128.02, 128.1, 128.2, 128.9, 133.5, 134.0, 134.2, 139.9, 140.5, 140.7, 141.3, 141.35, 141.41, 141.7, 141.8, 141.86, 141.89, 148.3, 148.5, 148.56, 148.62, 149.2, 149.3, 149.7, 171.4 ppm. ESI-HRMS: calcd for C$_{66}$H$_{42}$FeO$_2$SNa [M+Na]$^+$ 977.2147, found 977.2150.

1,3-Diphenyl-7H-ferrocene[1',2':3,4]cyclopenta[1,2-c]thiophen-7-one (7a)

Following the general procedure for synthesis of extended π-conjugated ferrocenes, 4 M of NaOH solution (5 mL) was added to the solution of the thiienylferrocene 6a (239.2 mg, 0.5 mmol) and EtOH (15 mL) in the first step. Then, oxalyl chloride (68 µL,
0.8 mmol) and AlCl₃ (266.7 mg, 2.0 mmol) was used respectively in the next steps. Compound 7a was obtained as an orange solid (141.8 mg, 64% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v). M.p.: 181-184 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.92 (s, 5H), 4.68 (br, 1H), 5.07 (br, 1H), 5.14 (br, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.50-7.55 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 8.0 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 69.3, 69.7, 71.0, 72.0, 83.1, 83.6, 124.1, 125.9, 127.9, 128.4, 128.9, 129.2, 130.6, 131.9, 132.4, 133.5, 135.0, 136.1, 137.7, 143.4, 194.2 ppm. ESI-HRMS: calcd for C₂₇H₁₈FeOSNa [M+Na]⁺ 469.0320, found 469.0318.

1,3-Di(4-diphenylaminophenyl)-7H-ferrocene[1',2':3,4]cyclopenta[1,2-c]thiophen-7-one (7b)

Following the general procedure for synthesis of extended π-conjugated ferrocenes, compound 7b was obtained as a yellow solid (79.4 mg, 34% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/2, v/v/v). M.p.: 99-102 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.93 (s, 5H), 4.64 (br, 1H), 5.02 (br, 1H), 5.05 (br, 1H), 7.03-7.18 (m, 15H), 7.27-7.32 (m, 8H), 7.38 (br, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 69.0, 69.7, 71.0, 71.9, 83.2, 83.7, 123.0, 123.3, 123.4, 123.5, 123.8, 124.8, 124.9, 126.6, 127.4, 129.5, 129.7, 130.1, 135.5, 136.1, 136.2, 142.2, 147.2, 147.4, 147.5, 147.9, 193.9 ppm. ESI-HRMS: calcd for C₅₁H₃₆FeN₂OSNa [M+Na]⁺ 803.1790, found 803.1794.
1,3-Di(9,9'-spirobifluoren-2-yl)-7H-ferrocene[1',2':3,4]cyclopenta[1,2-c]thiophen-7-one (7c)

Following the general procedure for synthesis of extended π-conjugated ferrocenes, compound 7c was obtained as a yellow solid (146.6 mg, 53% yield) via column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/2, v/v/v). M.p.: > 250 °C. 1H NMR (400 MHz, CDCl3): δ = 3.85 (s, 5H), 4.61 (br, 1H), 4.95 (br, 1H), 5.08 (br, 1H), 6.66-6.82 (m, 6H), 6.95 (d, J = 1.2 Hz, 1H), 7.06-7.18 (m, 7H), 7.23 (s, 1H), 7.34-7.43 (m, 6H), 7.57 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.81 (t, J = 8.0 Hz, 2H), 7.87-7.94 (m, 4H), 7.99 (d, J = 7.6 Hz, 1H), 8.86 (s, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 66.1, 66.2, 68.6, 69.8, 71.0, 71.9, 83.5, 83.8, 120.2, 120.3, 120.4, 120.6, 121.0, 121.1, 121.6, 123.97, 124.03, 124.1, 124.14, 124.20, 124.27, 124.31, 124.4, 126.3, 127.9, 127.99, 128.03, 128.13, 128.15, 128.20, 128.25, 128.3, 128.8, 131.6, 133.0, 135.9, 136.1, 137.2, 140.5, 140.9, 141.77, 141.83, 141.9, 142.0, 142.2, 143.0, 148.1, 148.3, 148.4, 148.5, 149.40, 149.41, 149.6, 152.9, 194.8 ppm. ESI-HRMS: calcd for C65H38FeOSNa [M+Na]+ 945.1885, found 945.1882.

**Ethyl 2-(2,5-diphenylthien-3-yl)ferrocene carboxylate (10)**

M.p.: 45-46 °C. 1H NMR (400 MHz, CDCl3): δ = 1.19 (t, J = 7.2 Hz, 3H), 3.94-4.16 (m, 2H), 4.25 (s, 5H), 4.33 (dd, J = 2.8 Hz, 1.6 Hz, 1H), 4.41 (t, J = 2.8 Hz, 1H), 4.90 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 7.16-7.24 (m, 5H), 7.30-7.35 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.69-7.72 (m, 2H), 7.73 (s, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 14.5, 60.2, 69.9, 70.5, 70.8, 71.1, 74.5, 85.6, 125.8, 127.7, 127.2, 127.6, 128.3, 128.7, 129.1, 129.5, 133.5,
134.51, 134.55, 140.0, 140.4, 171.1 ppm. ESI-HRMS: calcd for C_{29}H_{25}FeO_2S [M+H]^+ 493.0919, found 493.0921.

![N-phenyl-2-(2,5-diphenylthien-3-yl)ferrocene carbimdate (11)](image)

**Methyl N-phenyl-2-(2,5-diphenylthien-3-yl)ferrocene carbimdate (11)**

M.p.: 169-173 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.88$ (s, 3H), 4.02 (dd, $J = 2.4$ Hz, 1.6 Hz, 1H), 4.09 (t, $J = 2.4$ Hz, 1H), 4.18 (s, 5H), 4.18-4.19 (m, 1H), 6.38 (d, $J = 7.2$ Hz, 2H), 6.80 (t, $J = 7.6$ Hz, 1H), 6.87-6.90 (m, 2H), 7.03 (t, $J = 7.6$ Hz, 2H), 7.18-7.20 (m, 3H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 2H), 7.57 (s, 1H), 7.70 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 54.1$, 68.2, 70.7, 70.9, 71.2, 76.1, 82.7, 121.4, 122.6, 125.7, 127.3, 127.7, 128.1, 128.2, 128.5, 129.17, 129.18, 134.1, 134.2, 134.6, 138.6, 140.9, 148.6, 160.7 ppm. ESI-HRMS: calcd for C$_{34}$H$_{28}$FeNOS [M+H]$^+$ 554.1236, found 554.1232.

**XI. References**

1. Y.-H. Liu, P.-X. Li, Q.-J. Yao, Z.-Z. Zhang, D.-Y. Huang, M. D. Le, H. Song, L. Liu and B.-F. Shi, *Org. Lett.*, 2019, **21**, 1895–1899.

2. T. Wang, J. Du, S. Ye, L. Tan and J. Fu, *ACS Appl. Mater. Interfaces*, 2019, **11**, 4425–4438.

3. G. Zhang, H. Yi, H. Chen, C. Bian, C. Liu and A. Lei, *Org. Lett.*, 2014, **16**, 6156–6159.

4. X. Li, X. Liu, H. Chen, W. Wu, C. Qi and H. Jiang, *Angew. Chem., Int. Ed.*, 2014, **53**, 14485–14489.

5. R. S. Jordan, Y. L. Li, C.-W. Lin, R. D. McCurdy, J. B. Lin, J. L. Brosmer, K. L. Marsh, S. I. Khan, K. N. Houk, R. B. Kaner and Y. Rubin, *J. Am. Chem. Soc.*, 2017, **139**, 15878–15890.

6. T. Yang, W. Moreira, S. A. Nyantakyi, H. Chen, D. Aziz, M.-L. Go and T. Dick, *J. Med. Chem.*, 2017, **60**, 2745–2763.

7. P. Chen, C. Liu, J. Hu, H. Zhang and R. Sun, *J. Organomet. Chem.*, 2018, **854**, 113–121.
XII. Copies of $^1$H, $^{13}$C and $^1$H-$^1$H NOESY NMR spectra
