Electronic Supplementary Material (ESI) for Chemical Science.

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

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I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Ferrocenyl amide **1**,[1] ferrocenyl thioamide **5**,[1] methyl ferrocene carboxylate **8**,[2] and 2,5-diphenylthiophene **9**[3] and 1-(deca-1,3-diyn-1-yl)-4-methoxybenzene **2n**[4] were prepared according to literature procedures. 1,3-Diynes **2a**-**2e** and **2h-2j** were prepared by homocouplings of the corresponding terminal alkynes.[5] 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.[5]

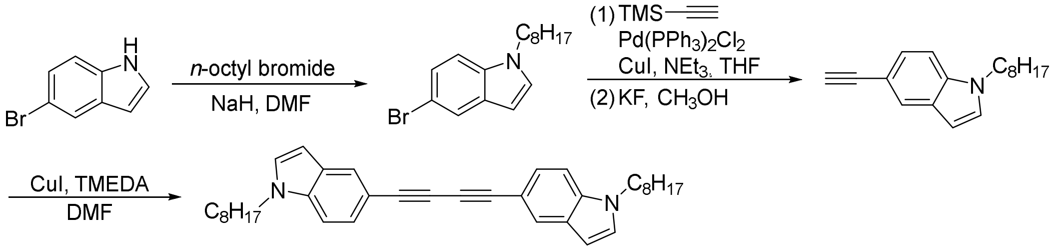
NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). ^{13}C NMR (100 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: 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-Bu_4NPF_6 supporting electrolyte under an N_2 atmosphere, using Fc/Fc$^+$ (0.08 V) as reference. The three-electrode setup consisted of an Ag/Ag$^+$ (0.01 M of $AgNO_3$ 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 N_2 atmosphere, employing dry acetonitrile as solvent with n-Bu_4NPF_6 (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[5,6]



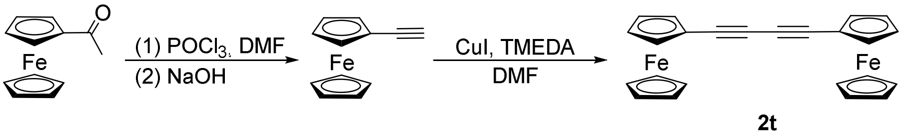
2s

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 Na_2SO_4, 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-1*H*-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-1*H*-indole (1.23 g, 4 mmol), trimethylsilylacetylene (1.1 mL, 8 mmol), $Pd(PPh_3)_2Cl_2$ (140.4 mg, 5 mol%), CuI (76.2 mg, 10 mol%), triethylamine (3 mL) and THF (9 mL) under an N_2 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 CH_3OH (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-ethynyl-1-octyl-1*H*-indole as a yellow oil in 79% yield (0.80 g).

CuI (38.1 mg, 10 mol%) and TMEDA (0.3 mL, 2 mmol) was added to the solution of 5-ethynyl-1-octyl-1*H*-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-1*H*-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]

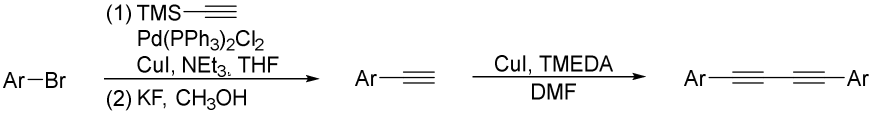


2t

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 $MgSO_4$, 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-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[5]

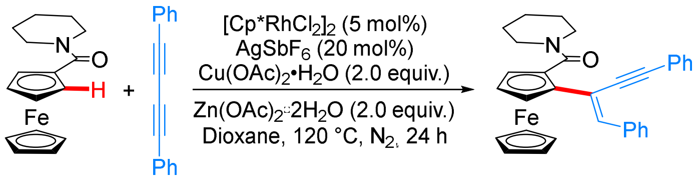


A three-necked flask with a magnetic stir bar was charged with the brominated arenes (5 mmol), trimethylsilylacetylene (10 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), triethylamine (3 mL) and THF (9 mL) under an N_2 atmosphere. After refluxed at 80 °C for 24 h, the resulting mixture was cooled to room temperature. Then, KF (10 mmol) was added along with CH_3OH (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 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 $MgSO_4$, 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

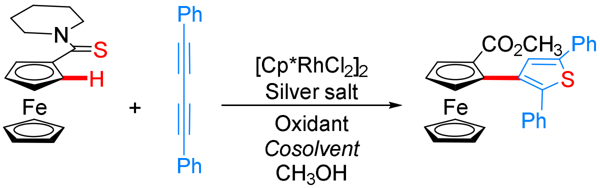
with 1,3-diyne 2a



1 **2a** **4** (14% yield)

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%), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.4 mmol, 2.0 equiv.), $Zn(OAc)_2 \cdot 2H_2O$ (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

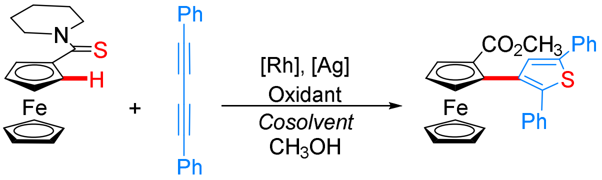


5 **2a** **6a**

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 $CDCl_3$ and analyzed by ^1H NMR with CH_2Br_2 (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 CH_2Br_2 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.[a]



5 **2a** **6a**

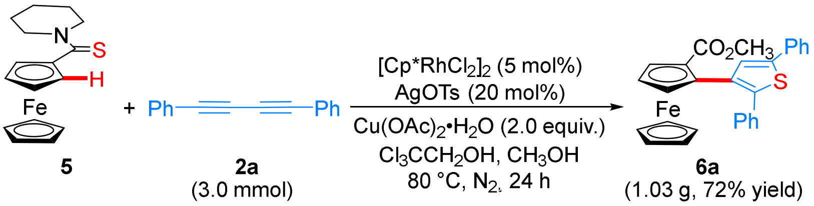
Entry	[Rh]	[Ag]	Oxidant	Solvent	Yield (%)[b]
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	46[c]
2	$[Cp^*RhCl_2]_2$	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	49
3	$[Cp^*RhCl_2]_2$	AgOTf	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	38
4	$[Cp^*RhCl_2]_2$	$AgNTf_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	55
5	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	61
6	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OPiv)_2$	CH_3OH	37
7	$[Cp^*RhCl_2]_2$	AgOTs	AgOAc	CH_3OH	trace
8	$[Cp^*RhCl_2]_2$	AgOTs	Oxygen (1 atm)	CH_3OH	N.D.
9	$[Cp^*RhCl_2]_2$	AgOTs	Benzoquinone	CH_3OH	N.D.
10[d]	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	79
11[e]	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	DCE/CH_3OH	65
12[f]	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	Cl_3CCH_2OH/CH_3OH	83 (81[c])
13[g]	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	Cl_3CCH_2OH/CH_3OH	69
14[h]	$[Cp^*RhCl_2]_2$	AgOTs	$Cu(OAc)_2{\cdot}H_2O$	Cl_3CCH_2OH/CH_3OH	47
15[i]	$[Cp^*Rh(CH_3CN)_3](OTs)_2$	–	$Cu(OAc)_2{\cdot}H_2O$	Cl_3CCH_2OH/CH_3OH	72
16[j]	$[Cp^*Rh(CH_3CN)_3](OTs)_2$	–	Air (1 atm)	Cl_3CCH_2OH/CH_3OH	N.D.

[a]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_3OH (1 mL) at 80 °C for 24 h under an N_2 atmosphere. [b]NMR yields. [c]Isolated yields. [d]CH_3OH (2 mL). [e]1,2-Dichloroethane (DCE, 0.5 mL) and CH_3OH (1.5 mL). [f]Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL). [g]Cl_3CCH_2OH (0.5 mL), CH_3OH (1.5 mL) and stirred for 16 h. [h][Cp^*RhCl_2]$_2$ (2.5 mol%), AgOTs (10 mol%), Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL). [i][$Cp^*Rh(CH_3CN)_3$]$(OTs)_2$ (10 mol%), Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL). [j][$Cp^*Rh(CH_3CN)_3$]$(OTs)_2$ (10 mol%), Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL) under air. N.D. = not detected.

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

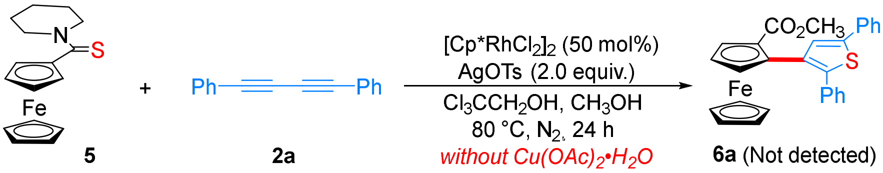
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide **5** (0.2 mmol), 1,3-diyne **2** (0.1 mmol), [Cp^*RhCl_2]$_2$ (5 mol%), AgOTs (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol), Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL) under an N_2 atmosphere. The resulting mixture 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

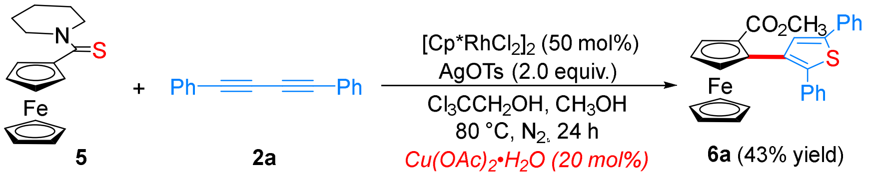


A 100 mL three-necked flask with a magnetic stir bar was charged with ferrocenyl thioamides **5** (1.88 g, 6.0 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne **2a** (0.61 g, 3.0 mmol), [Cp^*RhCl_2]$_2$ (92.7 mg, 5 mol%), AgOTs (167.4 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (1.20 g, 6.0 mmol, 2.0 equiv.), Cl_3CCH_2OH (7.5 mL) and CH_3OH (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).

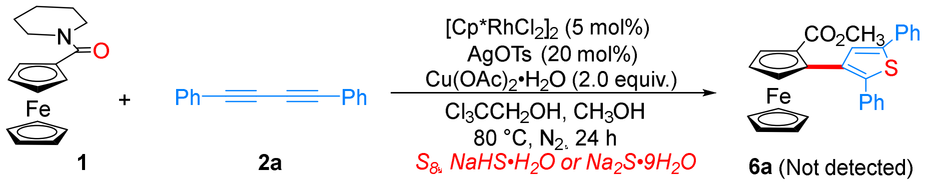
VII. Mechanistic studies



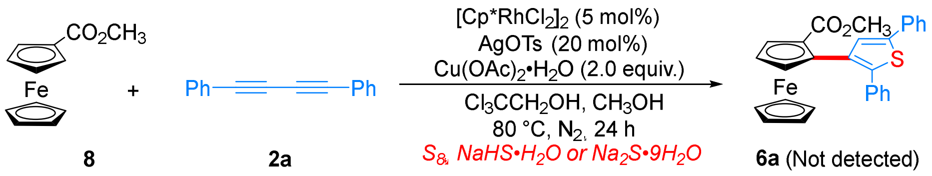
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide **5** (31.3 mg, 0.1 mmol), 1,4-diphenylbuta-1,3-diyne **2a** (20.2 mg, 0.1 mmol), [Cp*RhCl$_2$]$_2$ (30.9 mg, 0.05 mmol, 50 mol%), AgOTs (55.8 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (1.5 mL) 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 $CDCl_3$. The in-situ ^{1}H NMR spectrum of the reaction mixture showed that there was no product **6a** obtained.



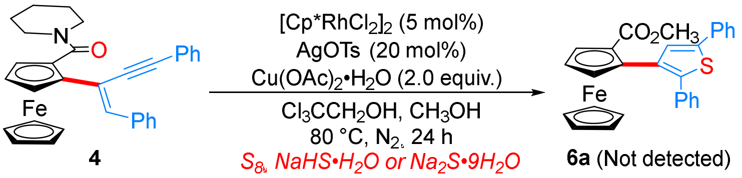
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide **5** (31.3 mg, 0.1 mmol), 1,4-diphenylbuta-1,3-diyne **2a** (20.2 mg, 0.1 mmol), [Cp*RhCl$_2$]$_2$ (30.9 mg, 0.05 mmol, 50 mol%), AgOTs (55.8 mg, 0.2 mmol, 2.0 equiv.), $Cu(OAc)_2 \cdot H_2O$ (4.0 mg, 0.02 mmol, 20 mol%), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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).



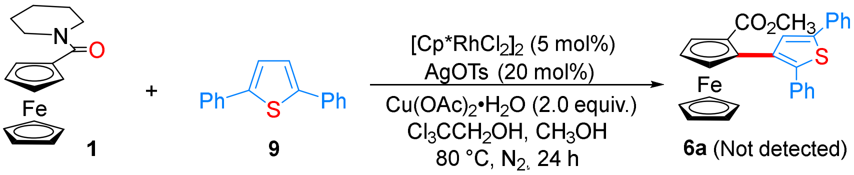
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl amide **1** (59.4 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne **2a** (20.2 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^1H NMR spectra of all the reaction mixtures showed that there was no product **6a** obtained.



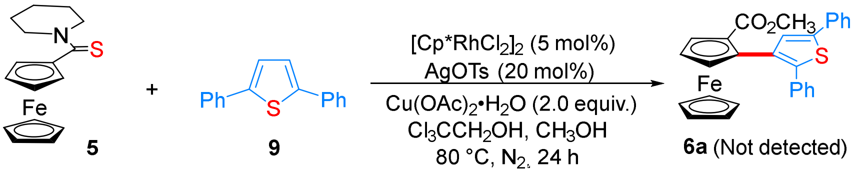
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with methyl ferrocene carboxylate **8** (48.8 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne **2a** (20.2 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^1H NMR spectra of all the reaction mixtures showed that there was no product **6a** obtained.



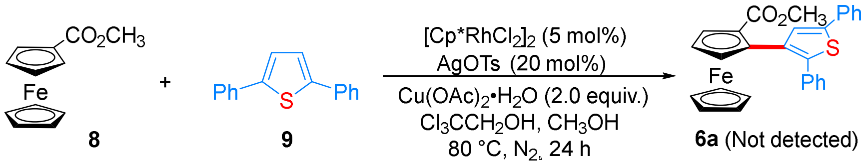
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with **4** (49.9 mg, 0.1 mmol), the corresponding external sulfur source (0.3 mmol, 3.0 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 $CDCl_3$. The in-situ ^1H NMR spectrum of the reaction mixture showed that there was no product **6a** obtained.



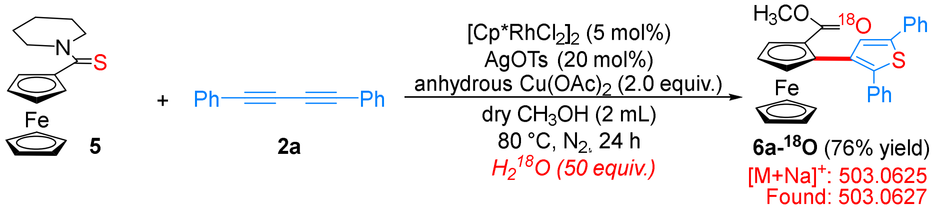
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl amide **1** (59.4 mg, 0.2 mmol, 2.0 equiv.), 2,5-diphenylthiophene **9** (23.6 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^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), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^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.), 2,5-diphenylthiophene **9** (23.6 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^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.), 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.), $[Cp^*RhCl_2]_2$ (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 CH_3OH (2 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 36.4 mg of compound **6a-^{18}O** in 76% yield. The ESI-HRMS of **6a-^{18}O** calculated for $C_{28}H_{22}Fe^{16}O^{18}OSNa$ $[M+Na]^+$ 503.0625, was found 503.0627.

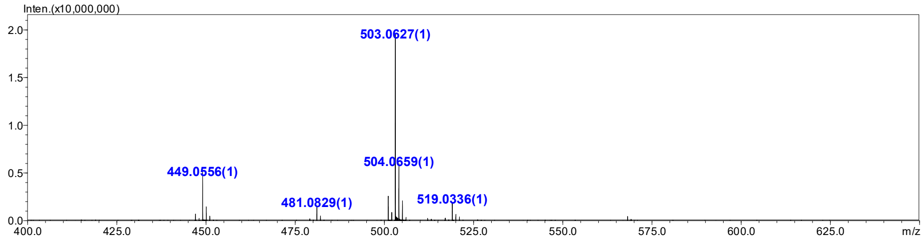
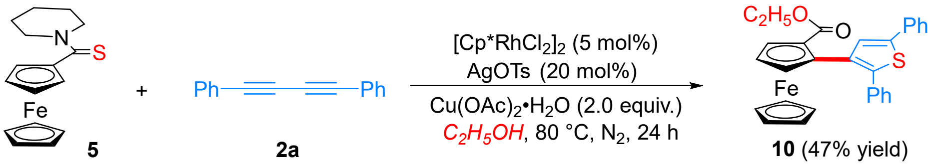
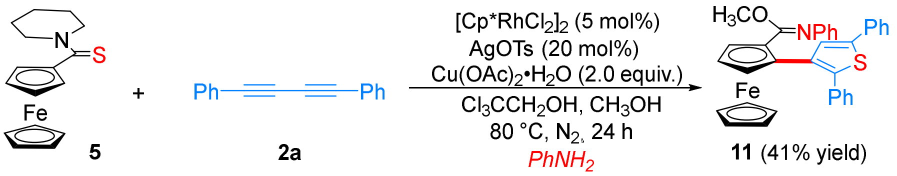


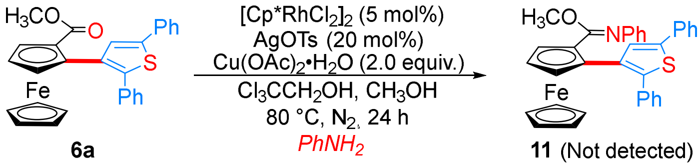
Fig. S1. ESI-HRMS spectrum of **6a-^{18}O**.



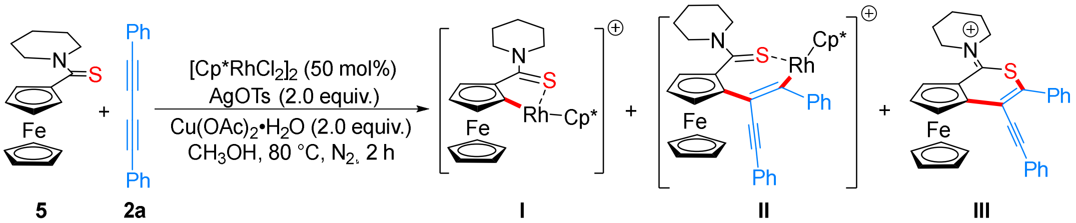
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with ferrocenyl thioamide **5** (62.6 mg, 0.2 mmol, 2.0 equiv.), 1,4-diphenylbuta-1,3-diyne **2a** (20.2 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2·H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.) and CH_3CH_2OH (2 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) to provide compound **10** as a yellow solid in a yield of 47% (23.3 mg).



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.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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) 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.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol%), AgOTs (5.6 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.), Cl_3CCH_2OH (0.5 mL) and CH_3OH (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 ^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),

$[Cp^*RhCl_2]_2$ (30.9 mg, 50 mol%), AgOTs (55.8 mg, 2.0 equiv.), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol, 2.0 equiv.) and CH_3OH (2 mL) under an N_2 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 $C_{26}H_{33}FeNRhS$ $[M]^+$ 550.0733, found 550.0731;

Intermediate **II**: calcd for $C_{42}H_{43}FeNRhS$ $[M]^+$ 752.1515, found 752.1521;

Intermediate **III**: calcd for $C_{32}H_{28}FeNS$ $[M]^+$ 514.1286, found 514.1289.

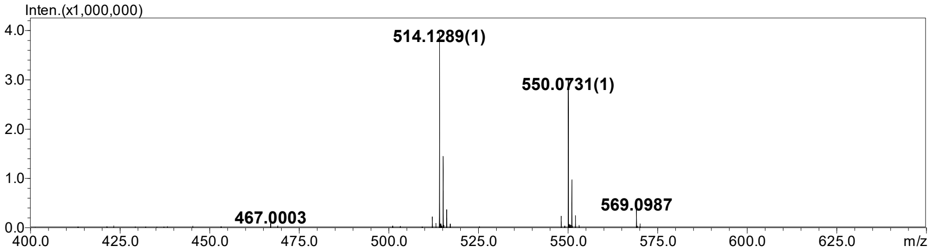


Fig. S2. ESI-HRMS spectrum of intermediates **I** and **III**.

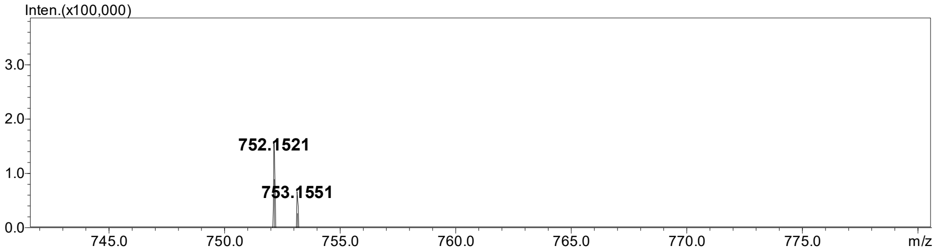
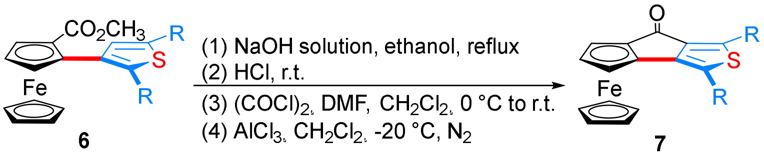


Fig. S3. ESI-HRMS spectrum of intermediate **II**.

VIII. Synthesis of extended π-conjugated ferrocenes 7



4 M of NaOH solution (15 mL) was added to the solution of thienylferrocene **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 $MgSO_4$, 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 N_2, 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 $AlCl_3$ (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 N_2 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 NH_4Cl, $NaHCO_3$ and saline solution (150 mL) successively. The organic layer was dried over $MgSO_4$, 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

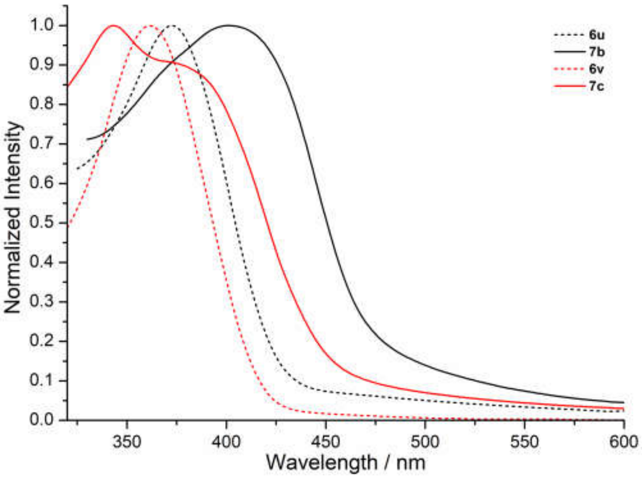


Fig. S4 UV-Vis absorption spectra of **6u**, **6v**, **7b** and **7c** in CH_3CN (1×10^{-5} M).

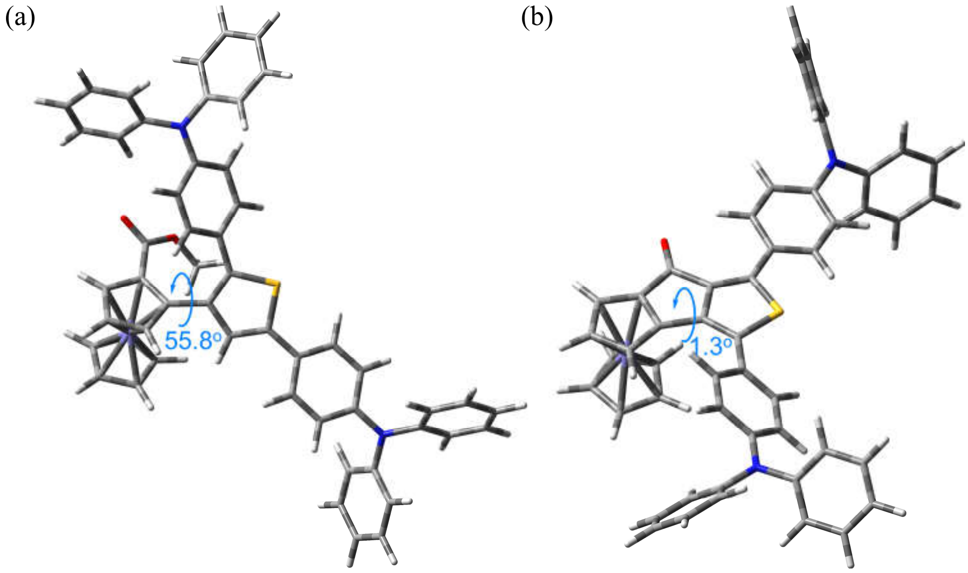


Fig. S5 Calculated molecular conformation of (a) **6u** and (b) **7b**. Molecular optimization was performed by density functional theory computation with Gaussian 09 at the B3LYP/6-31G* level.

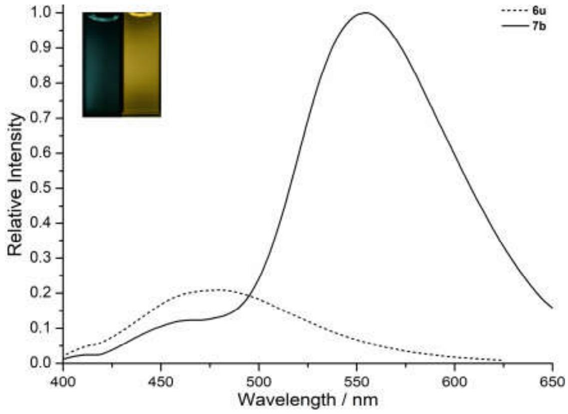


Fig. S6 Fluorescence spectra of **6u** and **7b** in CH_3CN (1×10^{-5} M). Inset: Fluorescent images of **6u** (left) and **7b** (right) in CH_3CN (1×10^{-5} M) under UV light (365 nm).

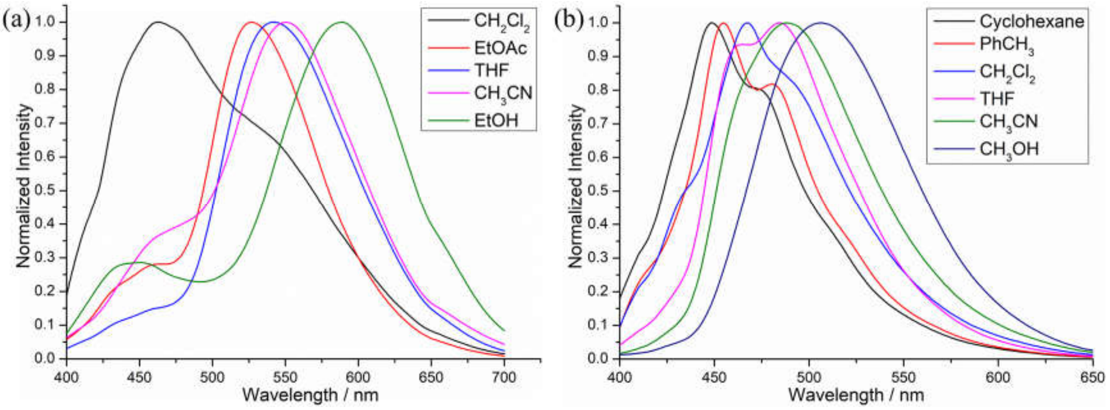


Fig. S7 Fluorescence spectra of (a) **7b** and (b) **7c** in different solvents.

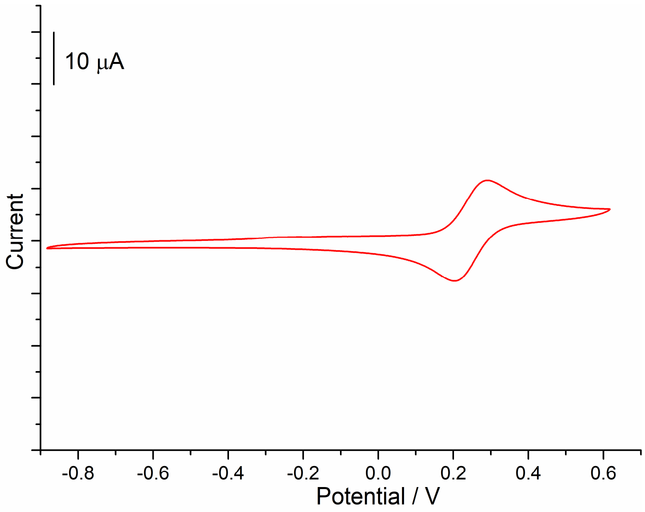


Fig. S8 Cyclic voltammograms of **6v**. Measurements were carried out at a scan rate of 50 mV/s in CH_3CN with **6v** (1×10^{-3} M) containing *n*-Bu_4NPF_6 (0.1 M), using Fc/Fc$^+$ (0.08 V) as reference. The three-electrode setup consisted of an Ag/Ag$^+$ (0.01 M of $AgNO_3$ in CH_3CN) reference electrode, a platinum wire counter electrode, and a platinum plate working electrode.

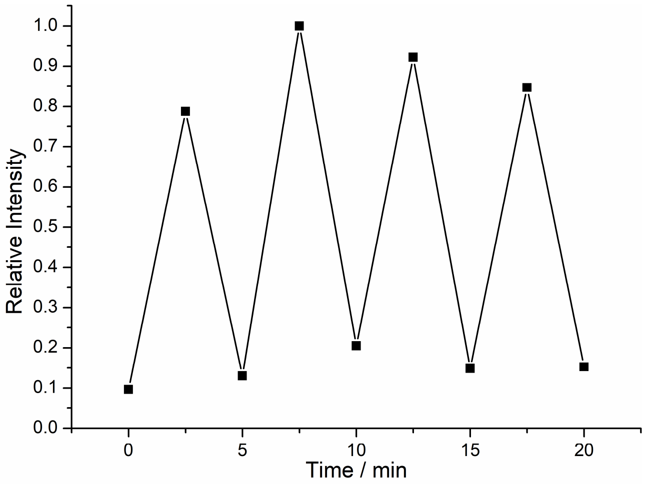
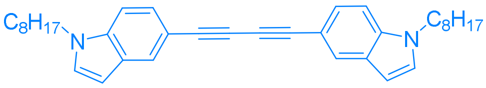


Fig. S9 Changes by the evolution of the fluorescence intensity of **6v** at 432 nm with time. Stepwise oxidation and reduction cycles carried out in CH_3CN with **6v** (5×10^{-6} M) containing *n*-Bu_4NPF_6 (0.1 M) by chronoamperometric analysis, which uses fixed potentials at + 0.48 V (for oxidation, vs Fc/Fc$^+$) and – 0.62 V (for reduction, vs Fc/Fc$^+$) changed every 150 s.

X. Preparation and characterization of the described compounds

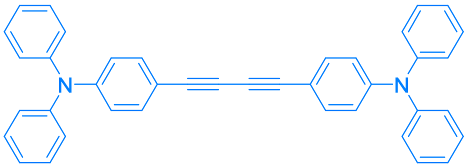


1,4-Bis(1-octyl-1*H*-indol-5-yl)buta-1,3-diyne (2s)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 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$_3$): δ = 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.

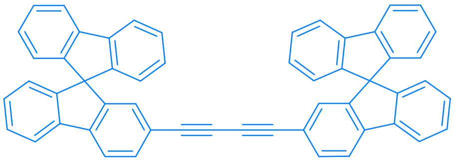
1,4-Diferrocenylbuta-1,3-diyne (**2t**)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 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$_3$): δ = 63.8, 69.4, 70.3, 71.1, 72.3, 79.2 ppm.



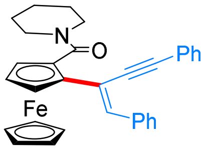
4,4'-(buta-1,3-diyne-1,4-diyl)bis(*N*,*N*-diphenylaniline) (**2u**)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 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$_3$): δ = 73.6, 82.1, 114.3, 121.7, 124.1, 125.5, 129.6, 133.5, 147.0, 148.7 ppm.



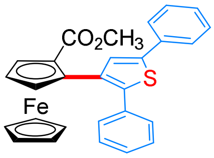
1,4-Di(9,9'-spirobifluoren-2-yl)buta-1,3-diyne (2v)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 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$_3$): δ = 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.



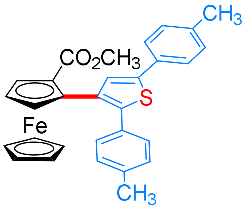
N-[2-(1,4-diphenylbut-1-en-3-yn-2-yl)ferrocenylformyl]piperidine (4)

M.p.: 84-87 °C. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* = 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$_3$): *δ* = 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.



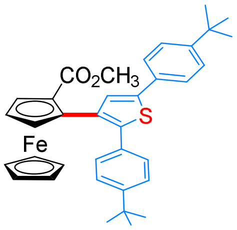
Methyl 2-(2,5-diphenylthien-3-yl)ferrocene carboxylate (6a)

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$_3$): *δ* = 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$_3$): *δ* = 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 $C_{28}H_{23}FeO_2S$ [M+H]$^+$ 479.0763, found 479.0770.



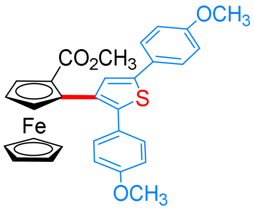
Methyl 2-[2,5-di(4-methylphenyl)thien-3-yl]ferrocene carboxylate (6b)

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. ^{1}H NMR (400 MHz, CDCl$_3$): 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. ^{13}C NMR (100 MHz, CDCl$_3$): 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 $C_{30}H_{27}FeO_2S$ [M+H]$^+$ 507.1076, found 507.1082.



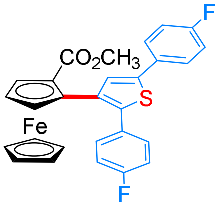
Methyl 2-[2,5-di(4-*tert*-butylphenyl)thien-3-yl]ferrocene carboxylate (6c)

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. ^{1}H NMR (400 MHz, CDCl$_3$): 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. ^{13}C NMR (100 MHz, CDCl$_3$): 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 $C_{36}H_{38}FeO_2SNa$ [M+Na]$^+$ 613.1834, found 613.1835.



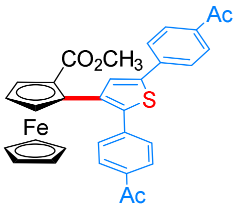
Methyl 2-[2,5-di(4-methoxylphenyl)thien-3-yl]ferrocene carboxylate (6d)

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. ^{1}H NMR (400 MHz, CDCl$_3$): 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. ^{13}C NMR (100 MHz, CDCl$_3$): 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 $C_{30}H_{27}FeO_4S$ $[M+H]^+$ 539.0974, found 539.0977.



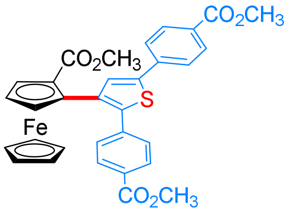
Methyl 2-[2,5-di(4-fluorophenyl)thien-3-yl]ferrocene carboxylate (6e)

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. ^{1}H NMR (400 MHz, CDCl$_3$): 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. ^{13}C NMR (100 MHz, CDCl$_3$): 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, $CDCl_3$): δ = -114.54 – -114.48 (m, 1F), -114.47 – -114.41 (m, 1F) ppm. ESI-HRMS: calcd for $C_{28}H_{20}F_2FeO_2SNa$ $[M+Na]^+$ 537.0394, found 537.0396.



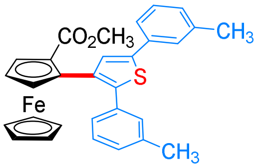
Methyl 2-[2,5-di(4-acetylphenyl)thien-3-yl]ferrocene carboxylate (6f)

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{32}H_{26}FeO_4SNa$ $[M+Na]^+$ 585.0793, found 585.0797.



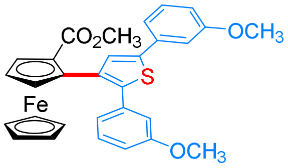
Methyl 2-[2,5-di(4-methoxycarbonylphenyl)thien-3-yl]ferrocene carboxylate (6g)

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, $CDCl_3$): δ = 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}C NMR (100 MHz, $CDCl_3$): *δ* = 51.7, 52.26, 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 $C_{32}H_{26}FeO_6SNa$ $[M+Na]^+$ 617.0692, found 617.0694.



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

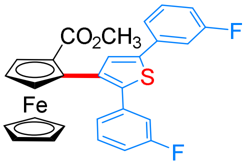
Following the general procedure for regioselective addition/annulation reaction, compound **6h** was obtained as a yellow solid (36.2 mg, 71% yield) *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.: 59-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 2.25 (s, 3H), 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}C NMR (100 MHz, $CDCl_3$): *δ* = 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 $C_{30}H_{27}FeO_2S$ $[M+H]^+$ 507.1076, found 507.1076.



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

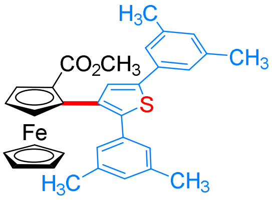
Following the general procedure for regioselective addition/annulation reaction, compound **6i** was obtained as a yellow solid (39.5 mg, 73% yield) *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v). ^{1}H NMR

(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 (s, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 8.4 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 $C_{30}H_{27}FeO_4S$ [M+H]$^+$ 539.0974, found 539.0968.



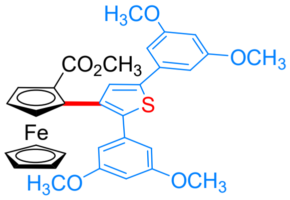
Methyl 2-[2,5-di(3-fluorophenyl)thien-3-yl]ferrocene carboxylate (6j)

Following the general procedure for regioselective 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 $C_{28}H_{21}F_2FeO_2S$ [M+H]$^+$ 515.0574, found 515.0571.



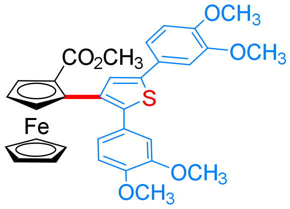
Methyl 2-[2,5-di(3,5-dimethylphenyl)thien-3-yl]ferrocene carboxylate (6k)

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{32}H_{31}FeO_2S$ $[M+H]^+$ 535.1389, found 535.1395.



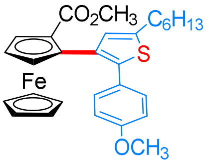
Methyl 2-[2,5-di(3,5-dimethoxylphenyl)thien-3-yl]ferrocene carboxylate (6l)

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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{32}H_{31}FeO_6S$ $[M+H]^+$ 599.1185, found 599.1181.



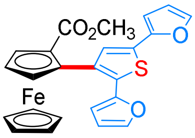
Methyl 2-[2,5-di(3,4-dimethoxylphenyl)thien-3-yl]ferrocene carboxylate (6m)

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. ^{1}H NMR (400 MHz, DMSO-d_6): 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. ^{13}C NMR (100 MHz, DMSO-d_6): 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 $C_{32}H_{31}FeO_6S$ $[M+H]^+$ 599.1185, found 599.1185.



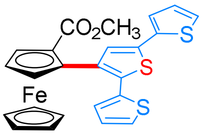
Methyl 2-[5-hexyl-2-(4-methoxylphenyl)thien-3-yl]ferrocene carboxylate (6n)

Following the general procedure for regioselective addition/annulation reaction, CH_3OH (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). ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{29}H_{32}FeO_3SNa$ $[M+Na]^+$ 539.1314, found 539.1311.



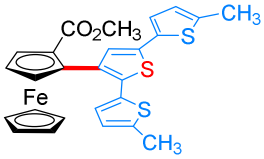
Methyl 2-[2,5-di(furan-2-yl)thien-3-yl]ferrocene carboxylate (6o)

Following the general procedure for regioselective addition/annulation reaction, CH_3OH (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). ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{24}H_{19}FeO_4S$ $[M+H]^+$ 459.0348, found 459.0353.



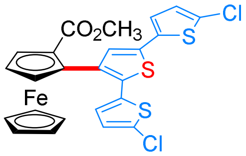
Methyl 2-[2,5-di(thien-2-yl)thien-3-yl]ferrocene carboxylate (6p)

Following the general procedure for regioselective addition/annulation reaction, CH_3OH (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. ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{24}H_{19}FeO_2S_3$ $[M+H]^+$ 490.9891, found 490.9896.



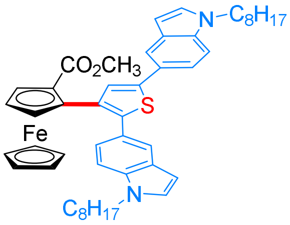
Methyl 2-[2,5-di(5-methylthien-2-yl)thien-3-yl]ferrocene carboxylate (6q)

Following the general procedure for regioselective addition/annulation reaction, CH_3OH (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, $CDCl_3$): 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), 7.39 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{26}H_{23}FeO_2S_3$ $[M+H]^+$ 519.0204, found 519.0205.



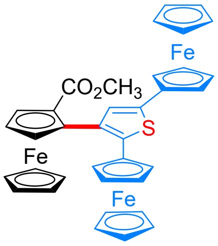
Methyl 2-[2,5-di(5-chlorothien-2-yl)thien-3-yl]ferrocene carboxylate (6r)

Following the general procedure for regioselective addition/annulation reaction, CH_3OH (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, $CDCl_3$): 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), 7.40 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{24}H_{17}{}^{35}Cl_2FeO_2S_3$ $[M+H]^+$ 558.9112, found 558.9108; $C_{24}H_{17}{}^{35}Cl^{37}ClFeO_2S_3$ $[M+H]^+$ 560.9082, found 560.9085; $C_{24}H_{17}{}^{37}Cl_2FeO_2S_3$ $[M+H]^+$ 562.9053, found 562.9049.



Methyl 2-[2,5-di(1-octyl-1*H*-indol-5-yl)thien-3-yl]ferrocene carboxylate (6s)

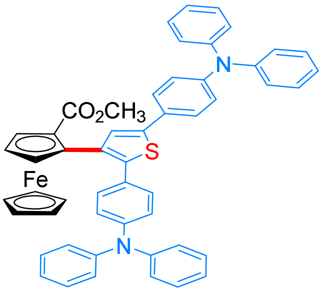
Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (1.0 mL) and CH_3OH (1.0 mL) were used as solvent, and compound **6s** was obtained as a yellow liquid (47.8 mg, 61% yield) *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{48}H_{57}FeN_2O_2S$ $[M+H]^+$ 781.3485, found 781.3481.



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

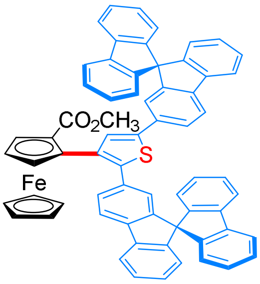
Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (1.0 mL) and CH_3OH (1.0 mL) were used as solvent, and compound **6t** was obtained as a red solid (36.3 mg, 52% yield) *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v). M.p.:

113-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{36}H_{31}Fe_3O_2S$ $[M+H]^+$ 695.0088, found 695.0091.



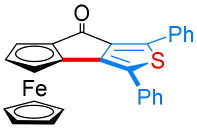
Methyl 2-[2,5-di(4-diphenylaminophenyl)thien-3-yl]ferrocene carboxylate (6u)

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (2.0 mL) and CH_3OH (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{52}H_{41}FeN_2O_2S$ $[M+H]^+$ 813.2233, found 813.2230.



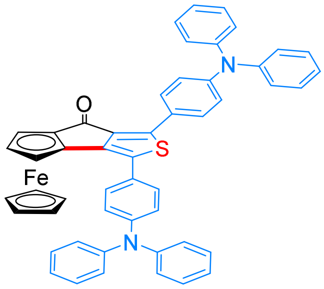
Methyl 2-[2,5-di(9,9'-spirobifluoren-2-yl)thien-3-yl]ferrocene carboxylate (6v)

Following the general procedure for regioselective addition/annulation reaction, 1,2-dichloroethane (2.0 mL) and CH_3OH (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{66}H_{42}FeO_2SNa$ $[M+Na]^+$ 977.2147, found 977.2150.



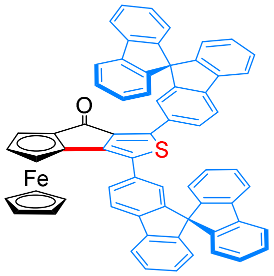
1,3-Diphenyl-7*H*-ferrocene[1',2':3,4]cyclopenta[1,2-*c*]thiophen-7-one (7a)

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 thienylferrocene **6a** (239.2 mg, 0.5 mmol) and EtOH (15 mL) in the first step. Then, oxalyl chloride (68 μL, 0.8 mmol) and $AlCl_3$ (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. ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{27}H_{18}FeOSNa$ $[M+Na]^+$ 469.0320, found 469.0318.



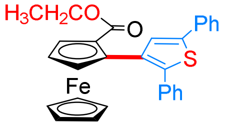
1,3-Di(4-diphenylaminophenyl)-7*H*-ferrocene[1',2':3,4]cyclopenta[1,2-*c*]thiophen-7-one (7b)

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. ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{51}H_{36}FeN_2OSNa$ $[M+Na]^+$ 803.1790, found 803.1794.



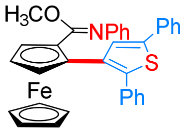
1,3-Di(9,9'-spirobifluoren-2-yl)-7*H*-ferrocene[1',2':3,4]cyclopenta[1,2-*c*]thiophen-7-one (7c)

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. ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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, 124.16, 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 $C_{65}H_{38}FeOSNa$ $[M+Na]^+$ 945.1885, found 945.1882.



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

M.p.: 45-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 60.2, 69.9, 70.5, 70.8, 71.1, 74.5, 85.6, 125.8, 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.



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

M.p.: 169-173 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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

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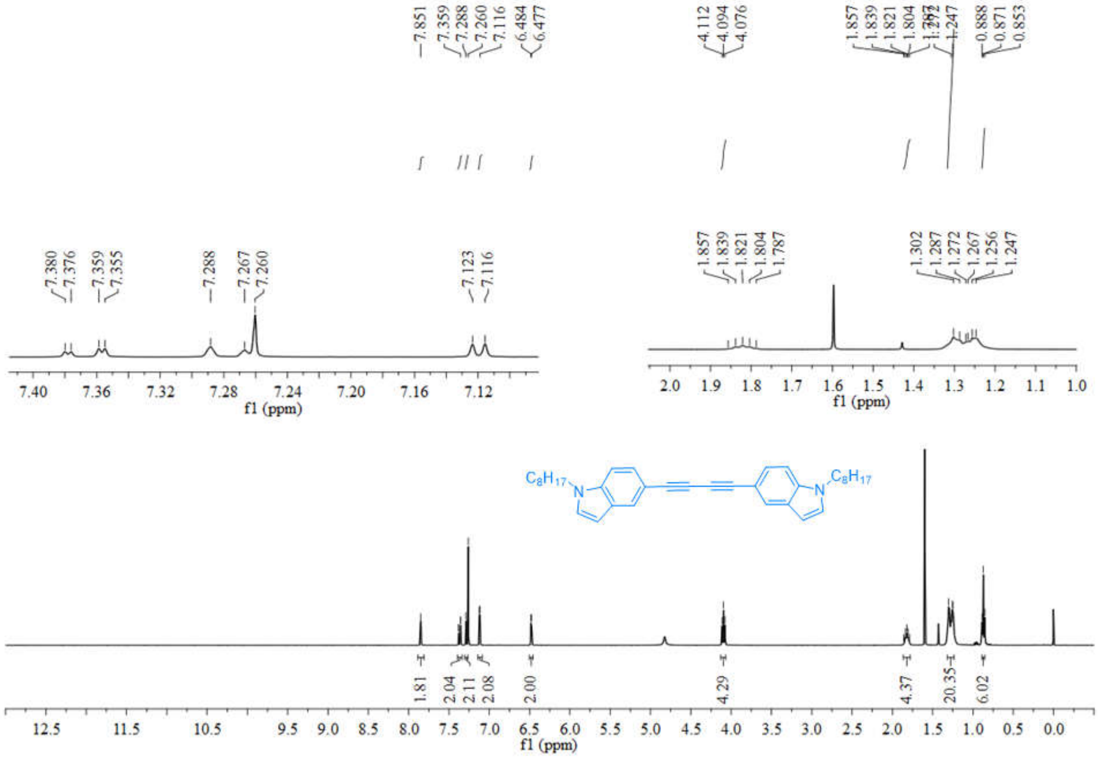
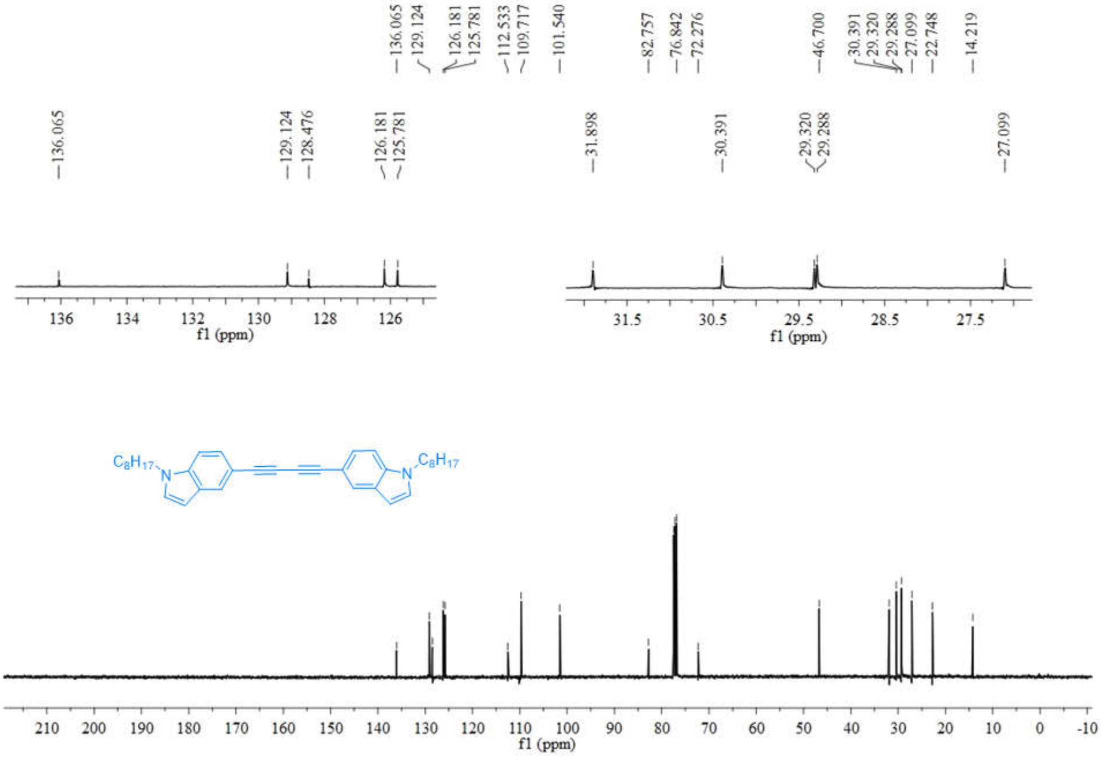
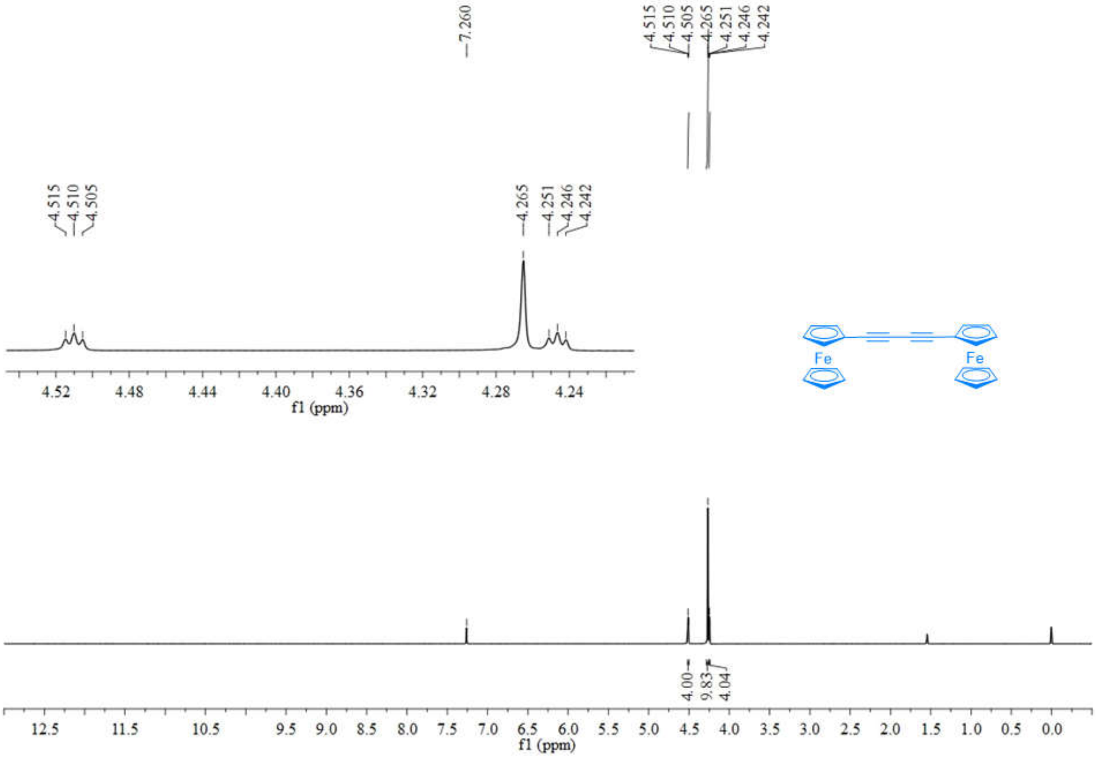
XII. Copies of ^{1}H, ^{13}C and ^{1}H-^{1}H NOESY NMR spectra



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f1 (ppm)
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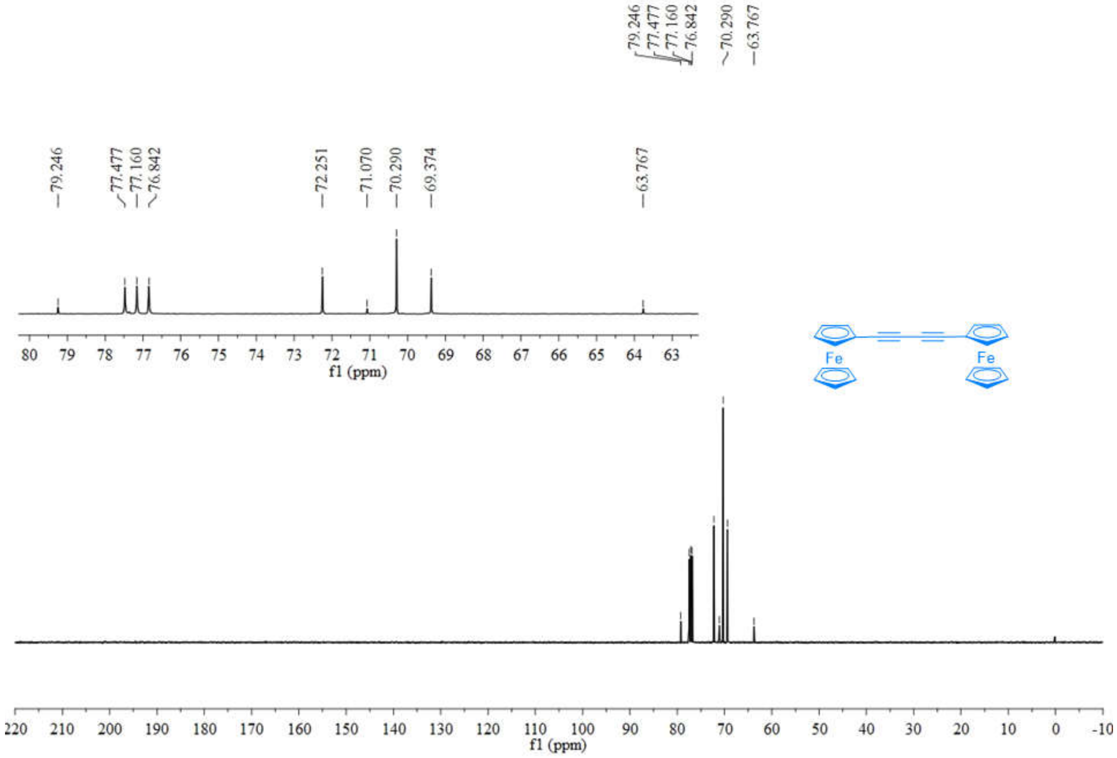
Fe
4.00
9.83
4.04
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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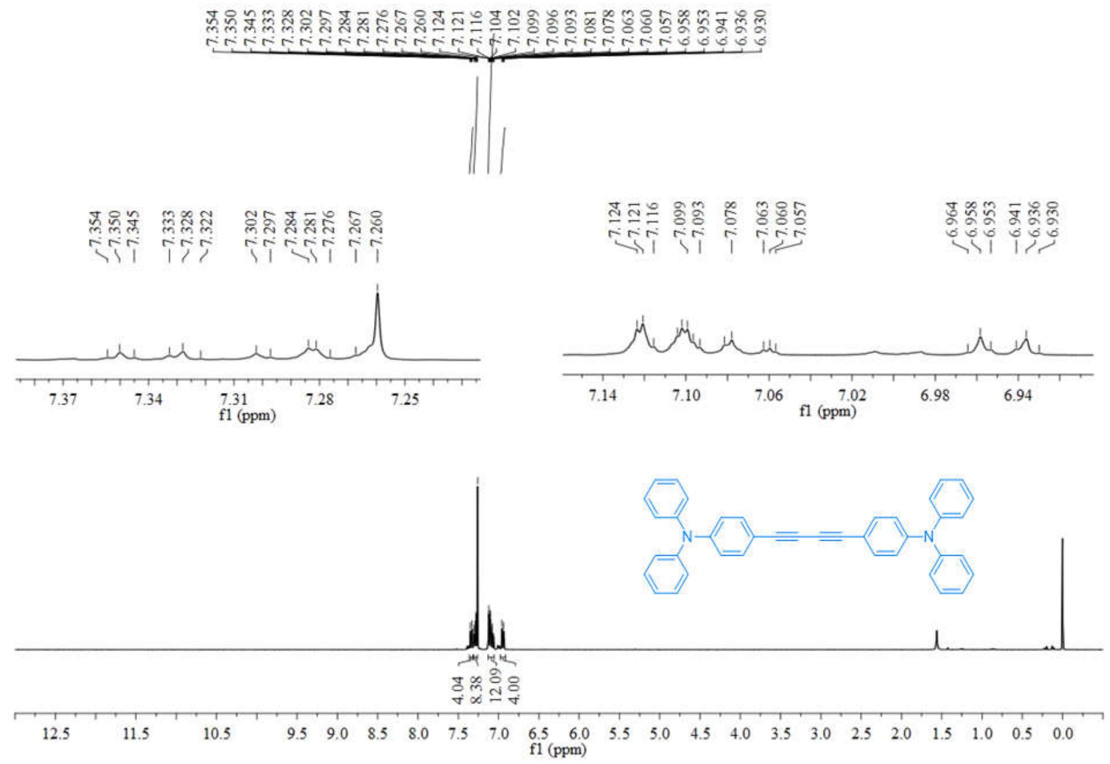
f1 (ppm)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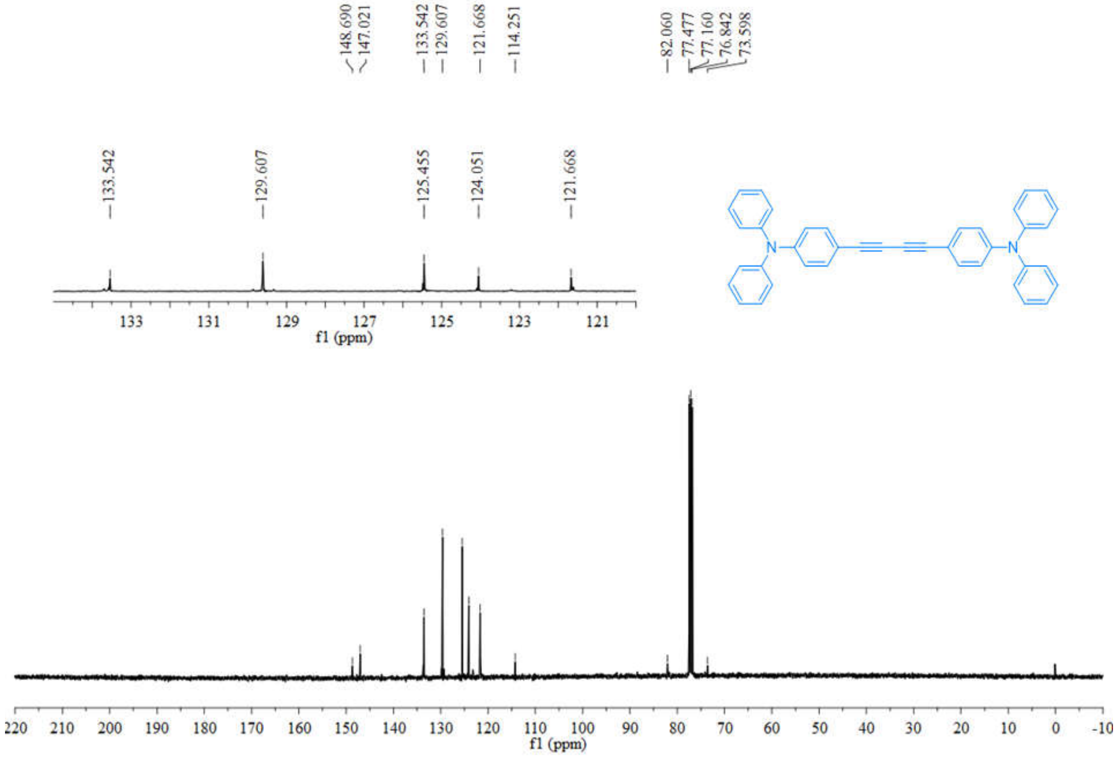
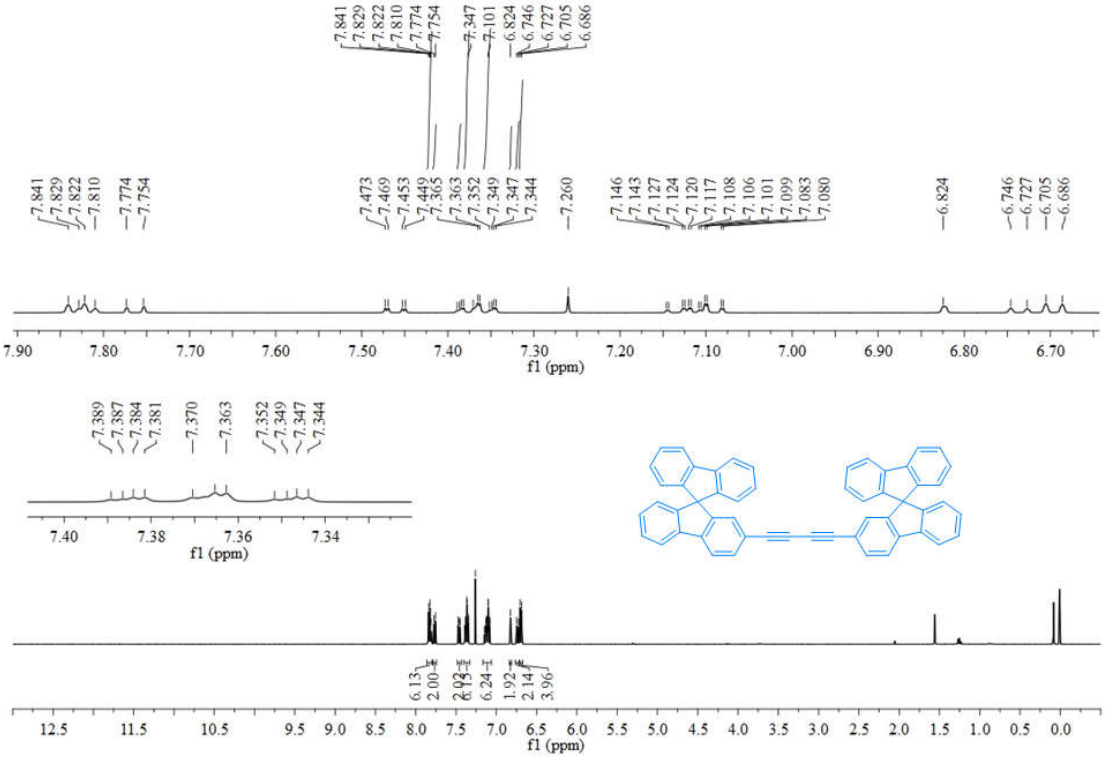
7.260
7.124
7.121
7.116
7.104
7.102
7.099
7.096
7.093
7.081
7.078
7.063
7.060
7.057
6.958
6.953
6.941
6.936
6.930
7.354
7.350
7.345
7.333
7.328
7.322
7.302
7.297
7.284
7.281
7.276
7.267
7.260
7.37
7.34
7.31
7.28
7.25
f1 (ppm)
7.124
7.121
7.116
7.099
7.093
7.078
7.063
7.060
7.057
6.964
6.958
6.953
6.941
6.936
6.930
7.14
7.10
7.06
7.02
6.98
6.94
f1 (ppm)
N
N
4.04
8.38
12.09
4.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.690
147.021
133.542
129.607
121.668
114.251
82.060
77.477
77.160
76.842
73.598
133.542
129.607
125.455
124.051
121.668
133
131
129
127
125
123
121
f1 (ppm)
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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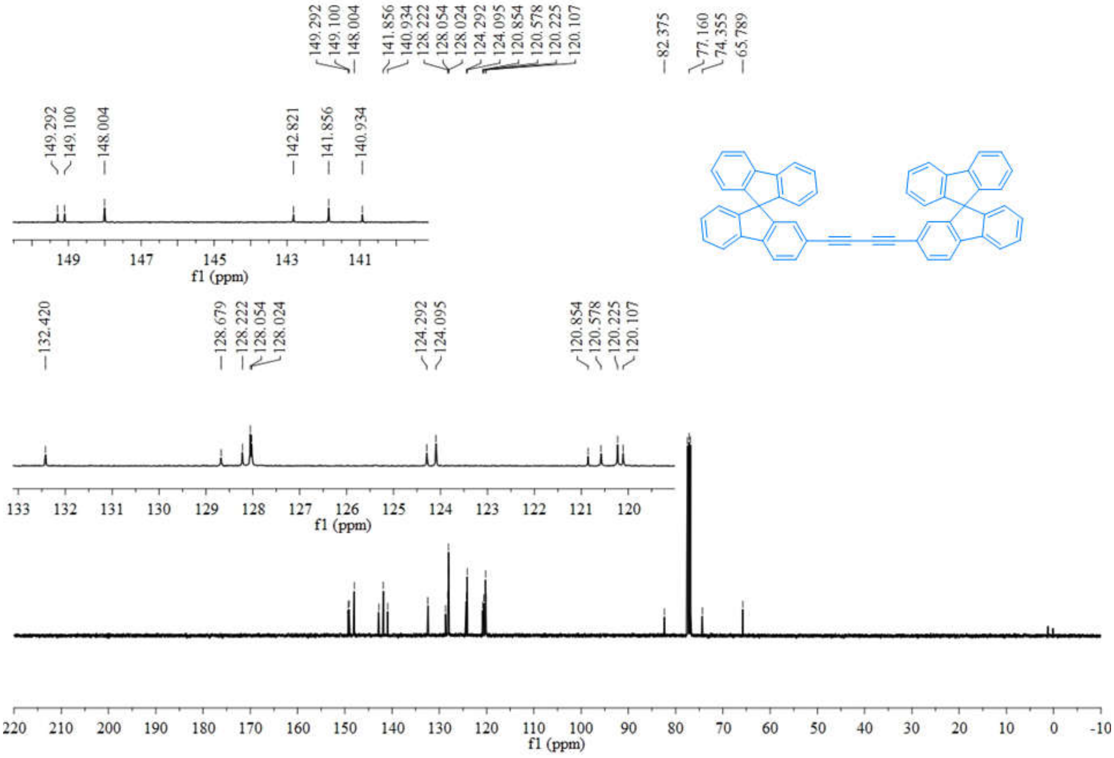
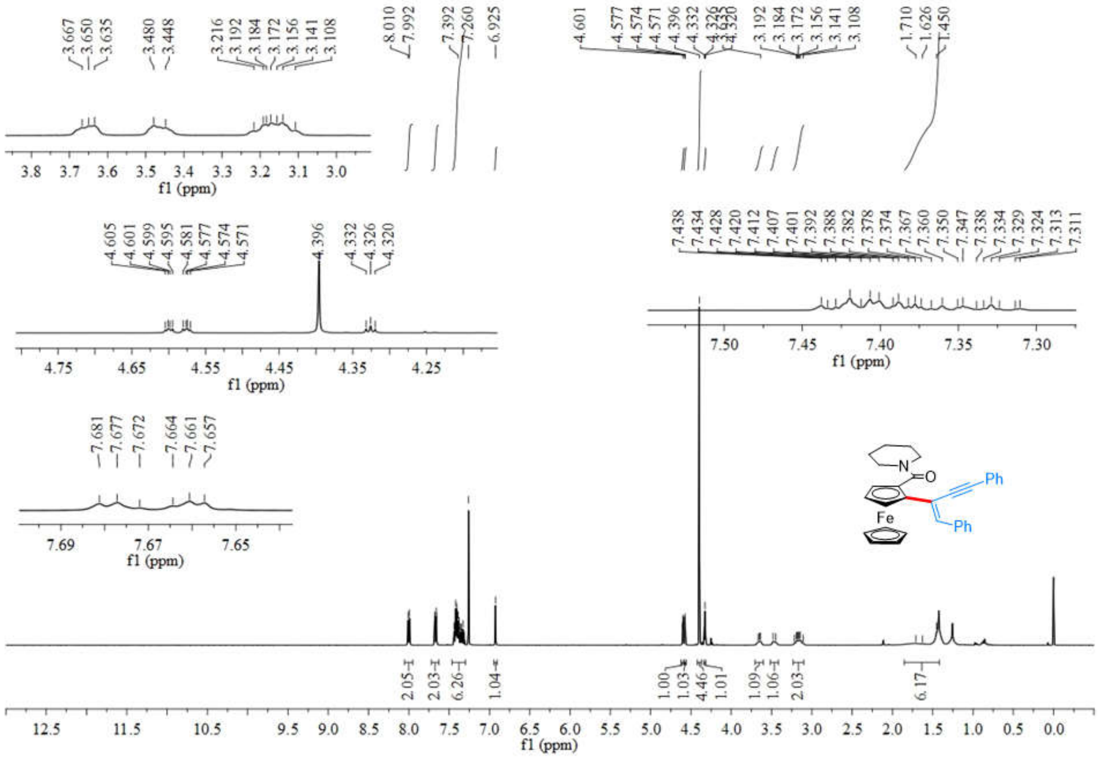
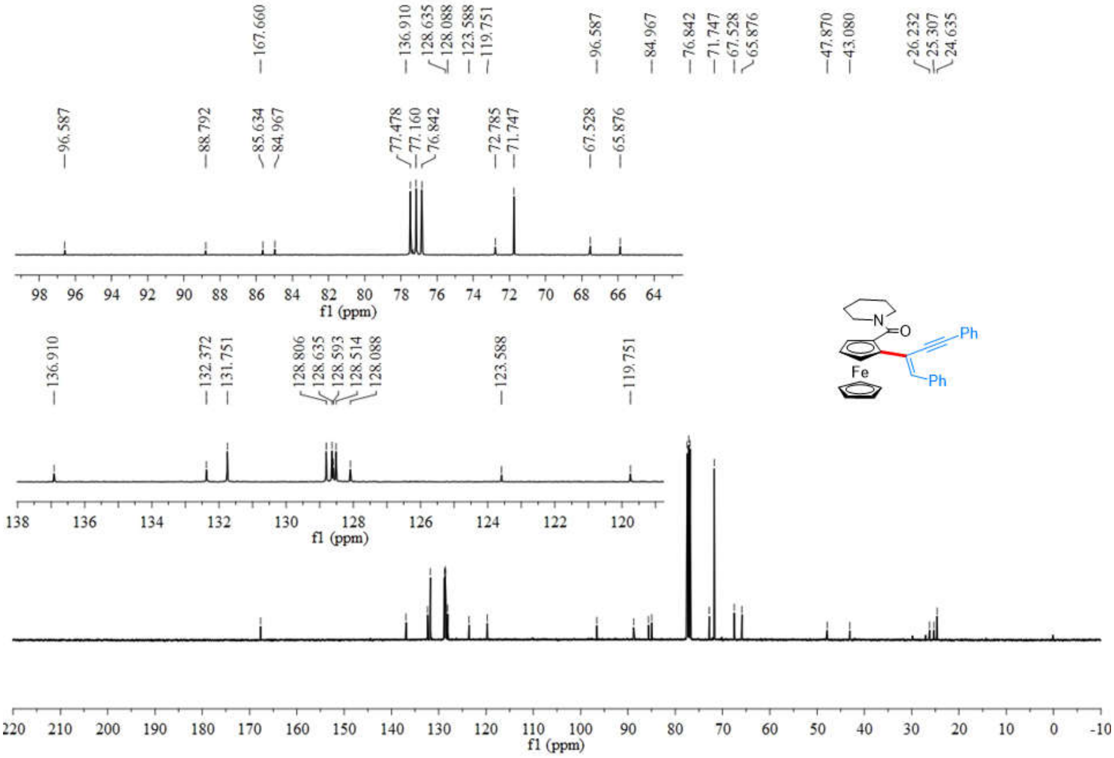
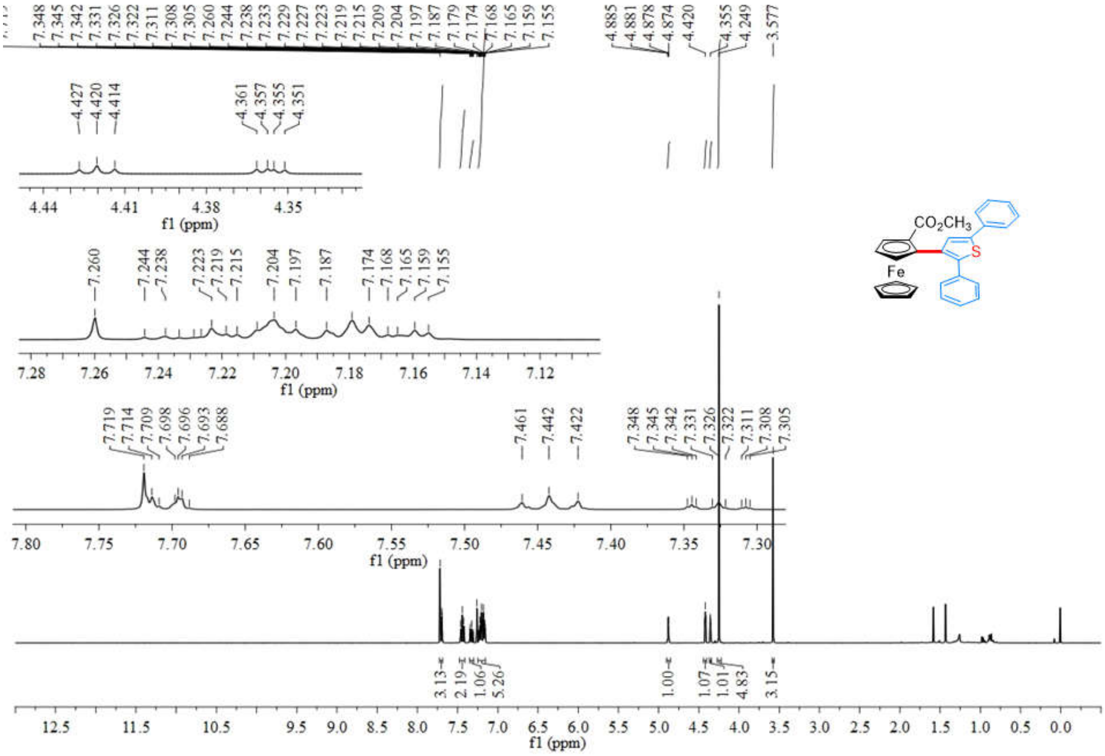
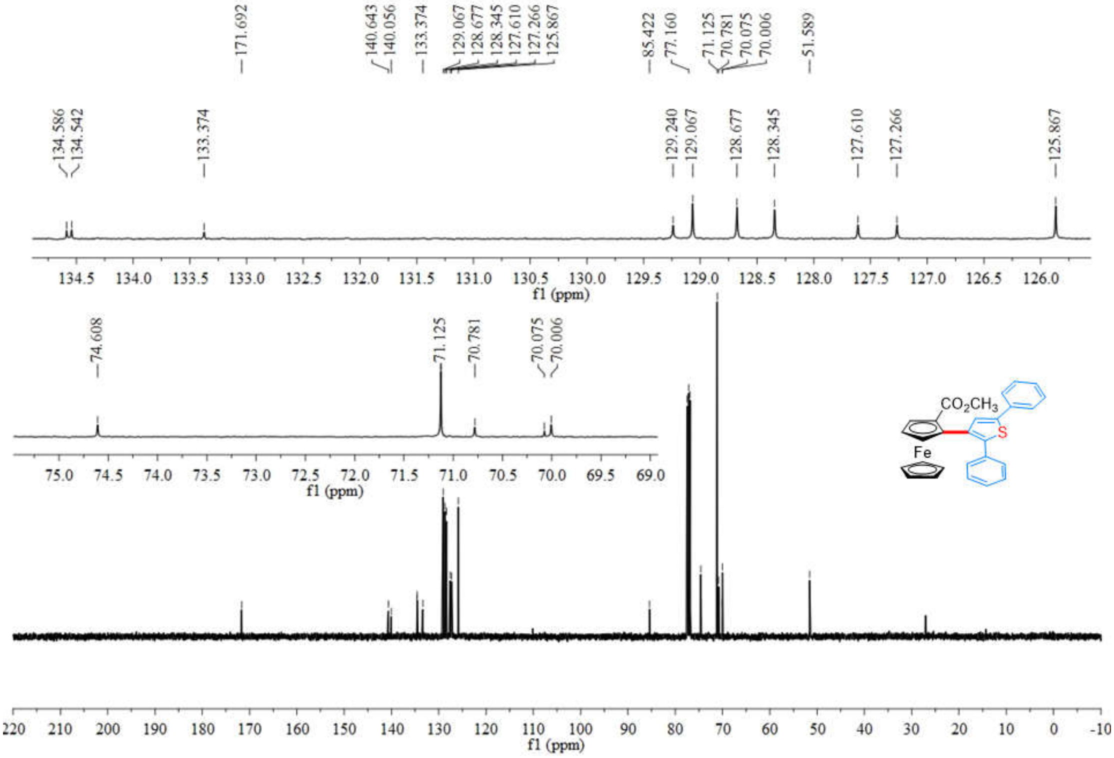
7.473, 7.469, 7.453, 7.449, 7.365, 7.363, 7.352, 7.349, 7.347, 7.344
7.260
7.146, 7.143, 7.127, 7.124, 7.120, 7.117, 7.108, 7.106, 7.101, 7.099, 7.083, 7.080
6.824
6.746, 6.727, 6.705, 6.686
7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70
f1 (ppm)
7.389, 7.387, 7.384, 7.381, 7.370, 7.363, 7.352, 7.349, 7.347, 7.344
7.40 7.38 7.36 7.34
f1 (ppm)
6.13, 2.00, 2.02, 6.13, 6.24, 1.92, 2.14, 3.96
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.292, 149.100, 148.004, 141.856, 140.934, 128.222, 128.054, 128.024, 124.292, 124.095, 120.854, 120.578, 120.225, 120.107
82.375
77.160, 74.355
65.789
149.292, 149.100, 148.004, 142.821, 141.856, 140.934
149 147 145 143 141
f1 (ppm)
132.420, 128.679, 128.222, 128.054, 128.024, 124.292, 124.095, 120.854, 120.578, 120.225, 120.107
133 132 131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.667
3.650
3.635
3.480
3.448
3.216
3.192
3.184
3.172
3.156
3.141
3.108
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f1 (ppm)
8.010
7.992
7.392
7.260
6.925
4.601
4.577
4.574
4.571
4.396
4.332
4.326
4.320
3.192
3.184
3.172
3.156
3.141
3.108
1.710
1.626
1.450
4.605
4.601
4.599
4.595
4.581
4.577
4.574
4.571
4.396
4.332
4.326
4.320
4.75 4.65 4.55 4.45 4.35 4.25
f1 (ppm)
7.438
7.434
7.428
7.420
7.412
7.407
7.401
7.392
7.388
7.382
7.378
7.374
7.367
7.360
7.350
7.347
7.338
7.334
7.329
7.324
7.313
7.311
7.50 7.45 7.40 7.35 7.30
f1 (ppm)
7.681
7.677
7.672
7.664
7.661
7.657
7.69 7.67 7.65
f1 (ppm)
N
O
Ph
Fe
Ph
2.05
2.03
6.26
1.04
1.00
1.03
4.46
1.01
1.09
1.06
2.03
6.17
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.660
136.910
128.635
128.088
123.588
119.751
96.587
84.967
76.842
71.747
67.528
65.876
47.870
43.080
26.232
25.307
24.635
96.587
88.792
85.634
84.967
77.478
77.160
76.842
72.785
71.747
67.528
65.876
98 96 94 92 90 88 86 84 82 80 78 76 74 72 70 68 66 64
f1 (ppm)
136.910
132.372
131.751
128.806
128.635
128.593
128.514
128.088
123.588
119.751
138 136 134 132 130 128 126 124 122 120
f1 (ppm)
N
O
Ph
Fe
Ph
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.348
7.345
7.342
7.331
7.326
7.322
7.311
7.308
7.305
7.260
7.244
7.238
7.233
7.229
7.227
7.223
7.219
7.215
7.209
7.204
7.197
7.187
7.179
7.174
7.168
7.165
7.159
7.155
4.885
4.881
4.878
4.874
4.420
4.355
4.249
3.577
4.427
4.420
4.414
4.361
4.357
4.355
4.351
4.44 4.41 4.38 4.35
f1 (ppm)
CO2CH3
S
Fe
7.260
7.244
7.238
7.223
7.219
7.215
7.204
7.197
7.187
7.174
7.168
7.165
7.159
7.155
7.28 7.26 7.24 7.22 7.20 7.18 7.16 7.14 7.12
f1 (ppm)
7.719
7.714
7.709
7.698
7.696
7.693
7.688
7.461
7.442
7.422
7.348
7.345
7.342
7.331
7.326
7.322
7.311
7.308
7.305
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
3.13
2.19
1.06
5.26
1.00
1.07
1.01
4.83
3.15
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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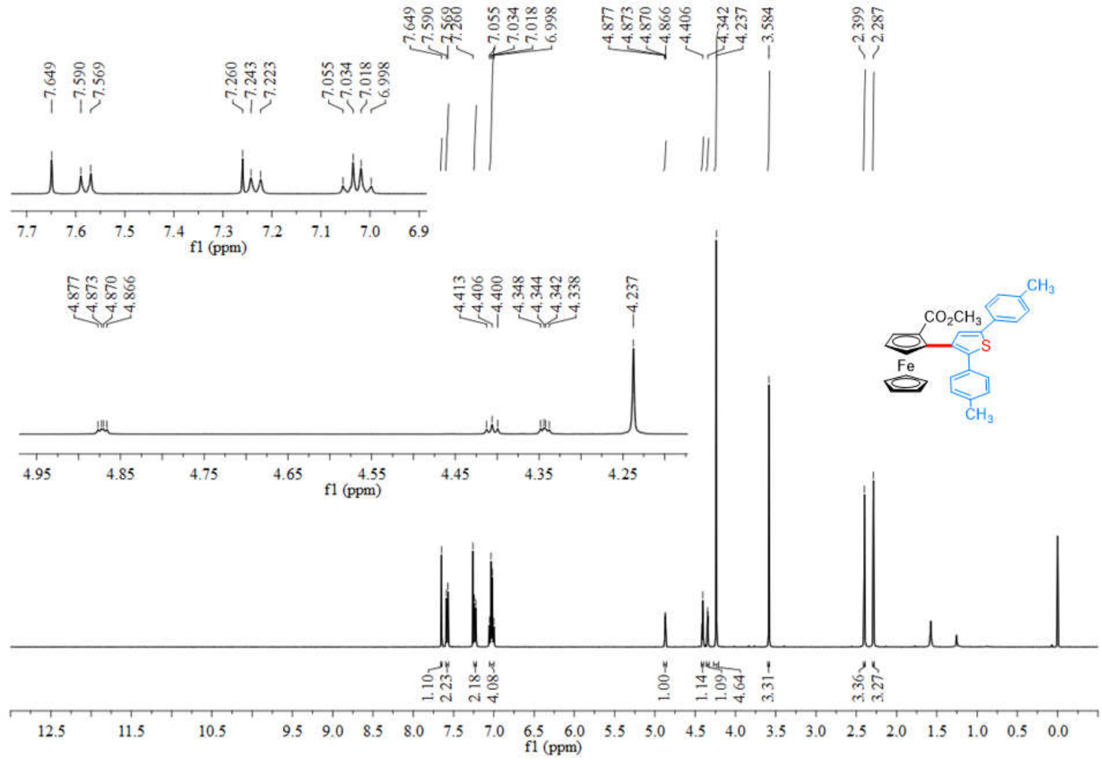
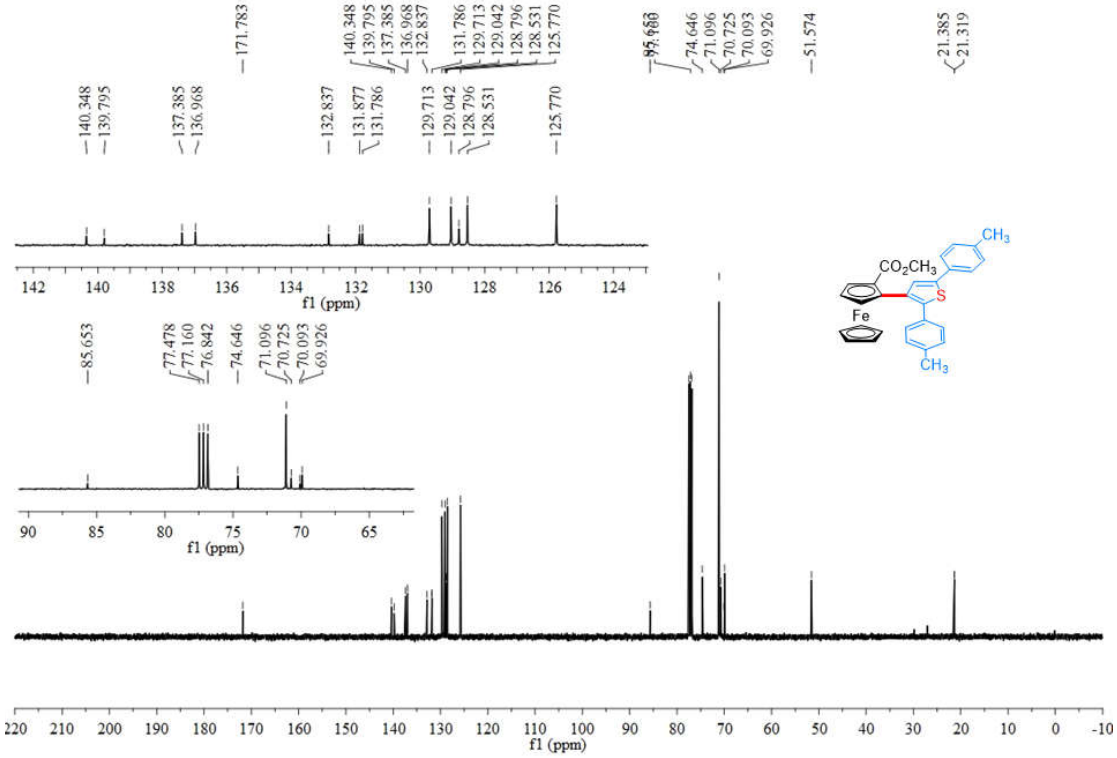
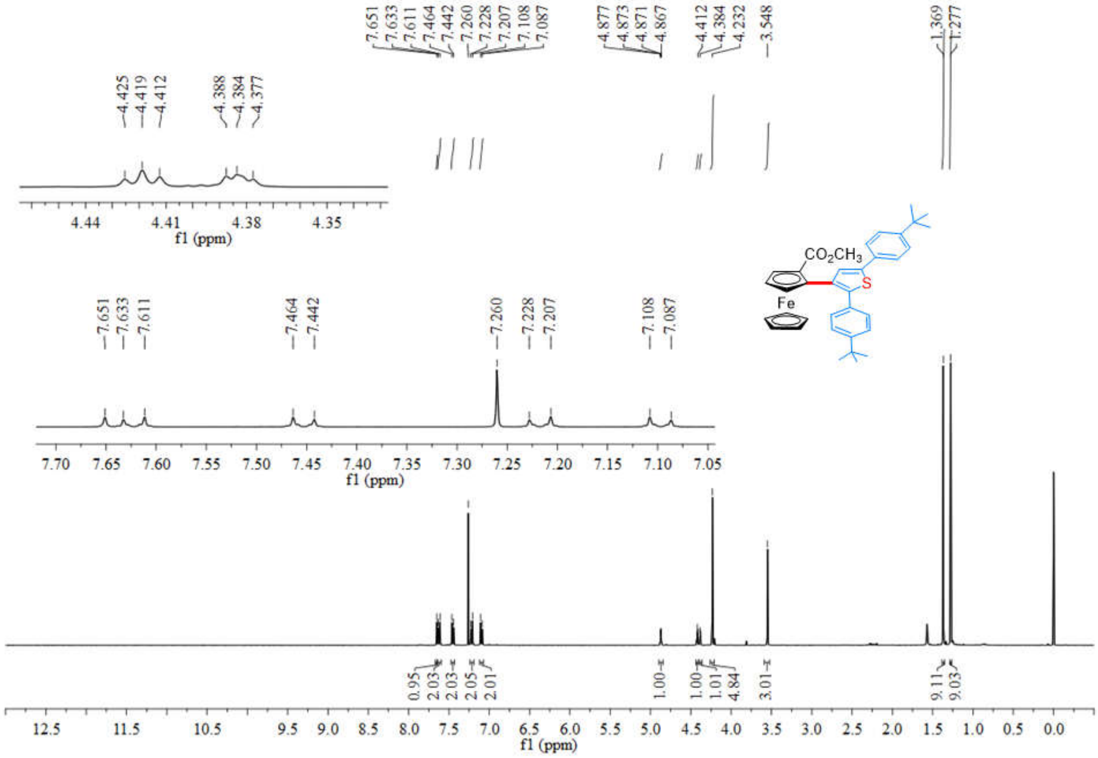
140.643
140.056
133.374
129.067
128.677
128.345
127.610
127.266
125.867
85.422
77.160
71.125
70.781
70.075
70.006
51.589
134.586
134.542
133.374
129.240
129.067
128.677
128.345
127.610
127.266
125.867
134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)
74.608
71.125
70.781
70.075
70.006
75.0 74.5 74.0 73.5 73.0 72.5 72.0 71.5 71.0 70.5 70.0 69.5 69.0
f1 (ppm)
CO2CH3
S
Fe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



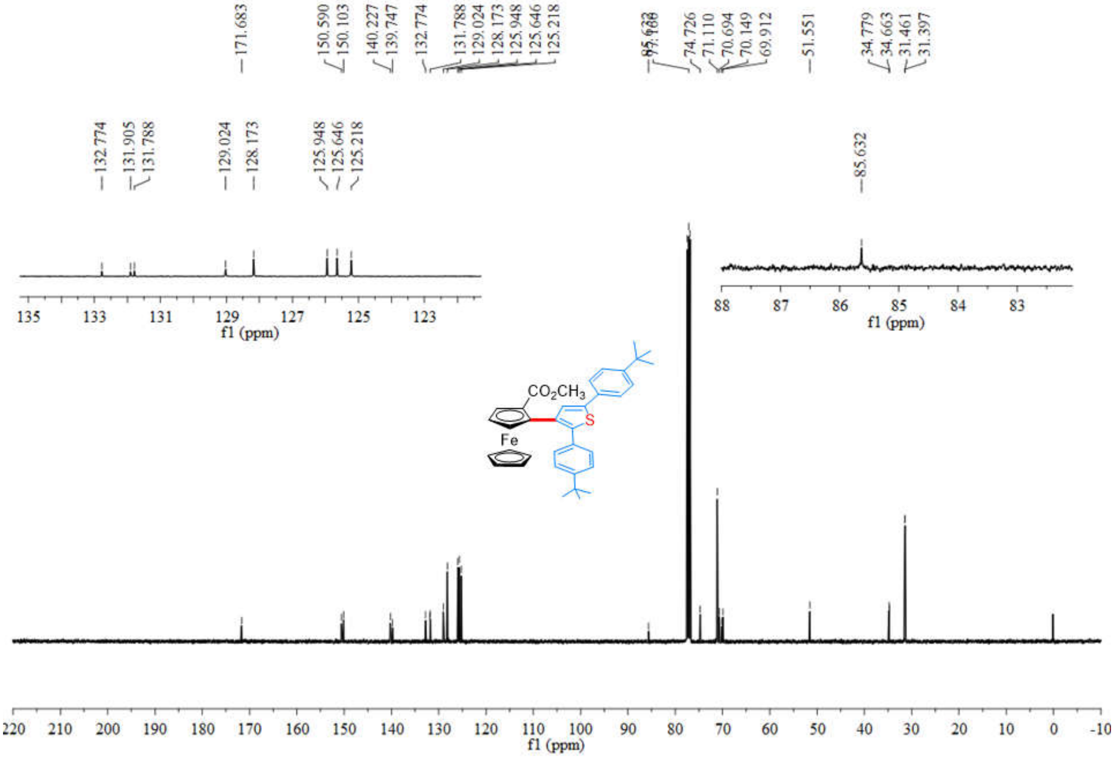
7.649
7.590
7.569
7.260
7.243
7.223
7.055
7.034
7.018
6.998
4.877
4.873
4.870
4.866
4.413
4.406
4.400
4.348
4.344
4.342
4.338
4.237
3.584
2.399
2.287
1.10
2.23
2.18
4.08
1.00
1.14
1.09
4.64
3.31
3.36
3.27
f1 (ppm)
CO2CH3
CH3
S
Fe
CH3



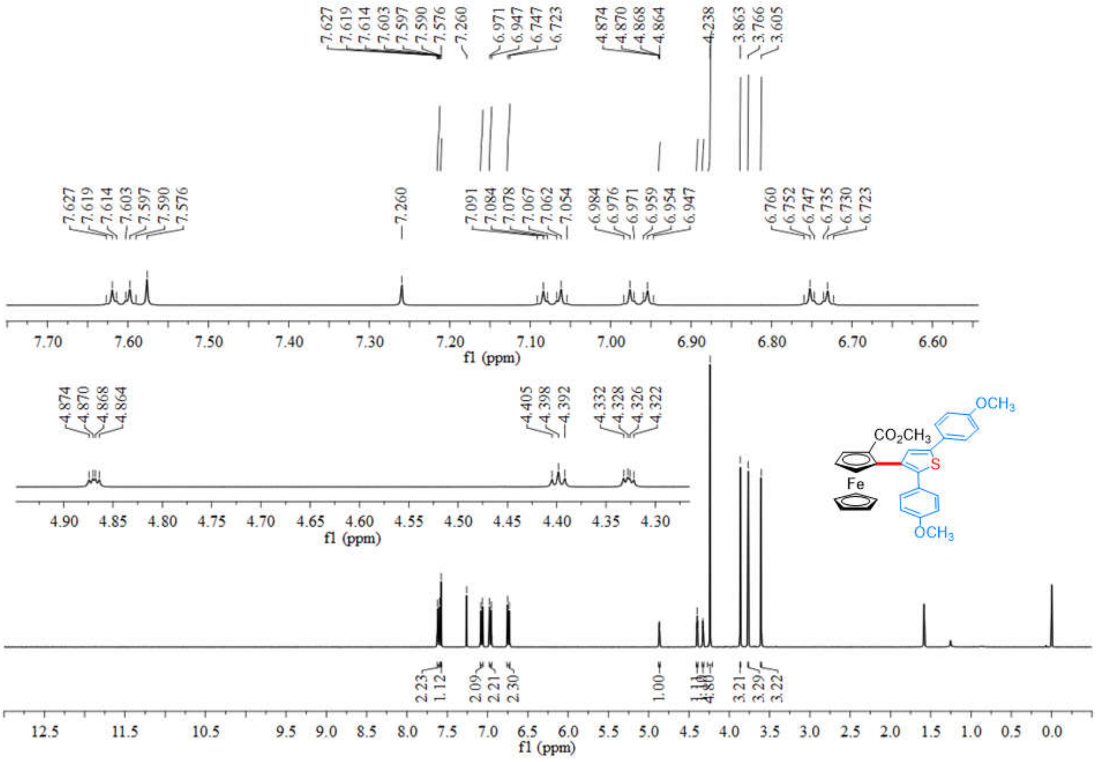
171.783
140.348
139.795
137.385
136.968
132.837
131.877
131.786
129.713
129.042
128.796
128.531
125.770
85.653
77.478
77.160
76.842
74.646
71.096
70.725
70.093
69.926
51.574
21.385
21.319
f1 (ppm)
CO2CH3
CH3
S
Fe
CH3



7.651
7.633
7.611
7.464
7.442
7.260
7.228
7.207
7.108
7.087
4.877
4.873
4.871
4.867
4.412
4.384
4.232
3.548
1.369
1.277
4.425
4.419
4.412
4.388
4.384
4.377
4.44
4.41
4.38
4.35
f1 (ppm)
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
f1 (ppm)
CO2CH3
Fe
S
0.95
2.03
2.03
2.05
2.01
1.00
1.00
1.01
4.84
3.01
9.11
9.03
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



171.683
150.590
150.103
140.227
139.747
132.774
131.788
129.024
128.173
125.948
125.646
125.218
85.632
74.726
71.110
70.694
70.149
69.912
51.551
34.779
34.663
31.461
31.397
132.774
131.905
131.788
129.024
128.173
125.948
125.646
125.218
135
133
131
129
127
125
123
f1 (ppm)
85.632
88
87
86
85
84
83
f1 (ppm)
CO2CH3
Fe
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.627
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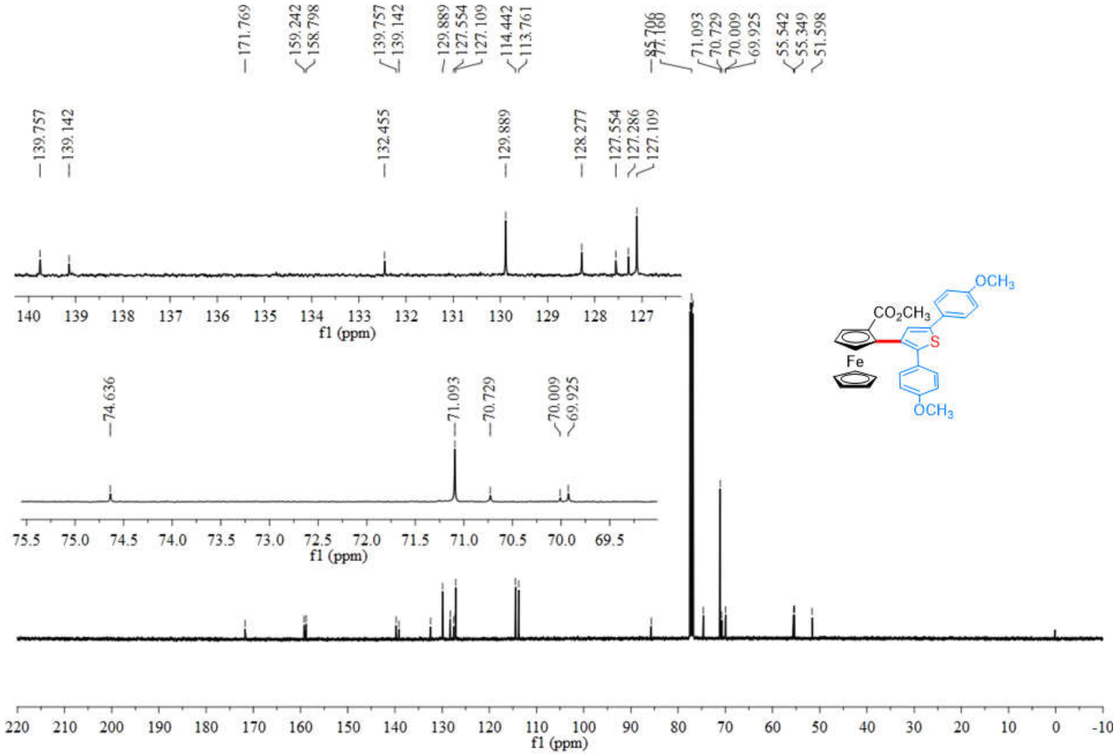
7.614
7.603
7.597
7.590
7.576
7.260
6.971
6.947
6.747
6.723
4.874
4.870
4.868
4.864
4.238
3.863
3.766
3.605
7.627
7.619
7.614
7.603
7.597
7.590
7.576
7.260
7.091
7.084
7.078
7.067
7.062
7.054
6.984
6.976
6.971
6.959
6.954
6.947
6.760
6.752
6.747
6.735
6.730
6.723
7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70 6.60
f1 (ppm)
4.874
4.870
4.868
4.864
4.405
4.398
4.392
4.332
4.328
4.326
4.322
4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30
f1 (ppm)
CO2CH3
OCH3
Fe
S
OCH3
2.23
1.12
2.09
2.21
2.30
1.00
1.11
1.11
4.80
3.21
3.29
3.22
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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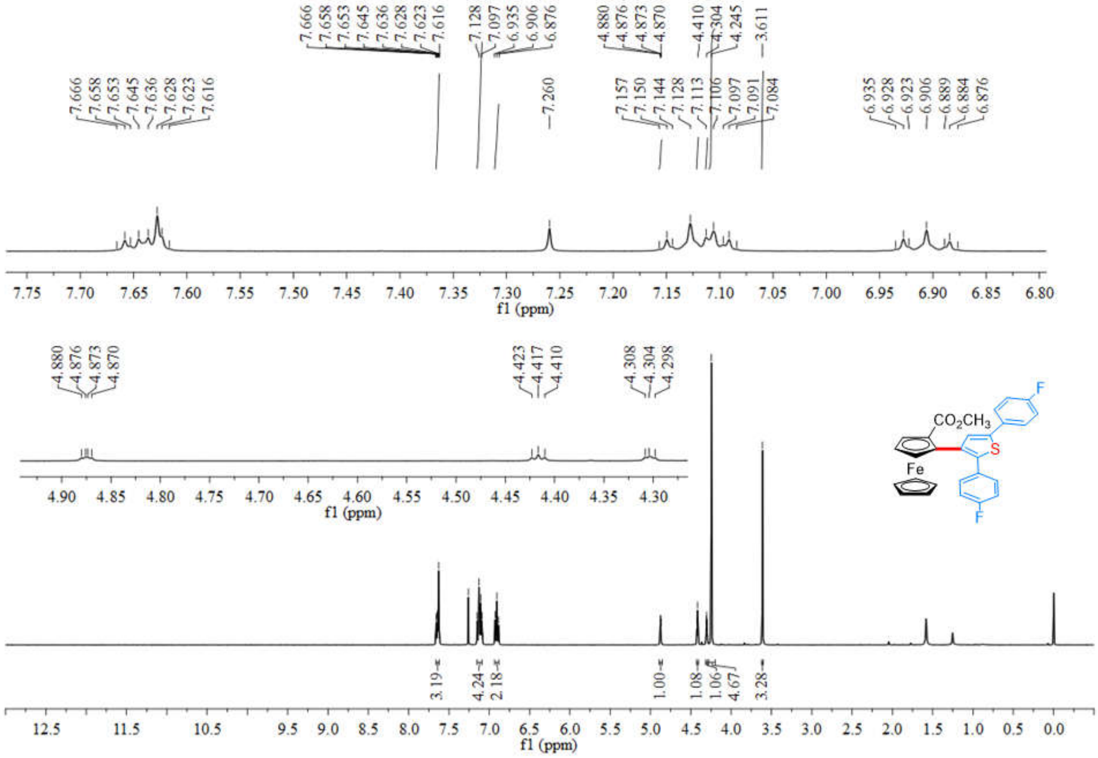
139.142
129.889
127.554
127.109
114.442
113.761
85.706
77.160
71.093
70.729
70.009
69.925
55.542
55.349
51.598
139.757
139.142
132.455
129.889
128.277
127.554
127.286
127.109
140 139 138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
74.636
71.093
70.729
70.009
69.925
75.5 75.0 74.5 74.0 73.5 73.0 72.5 72.0 71.5 71.0 70.5 70.0 69.5
f1 (ppm)
CO2CH3
OCH3
Fe
S
OCH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.628
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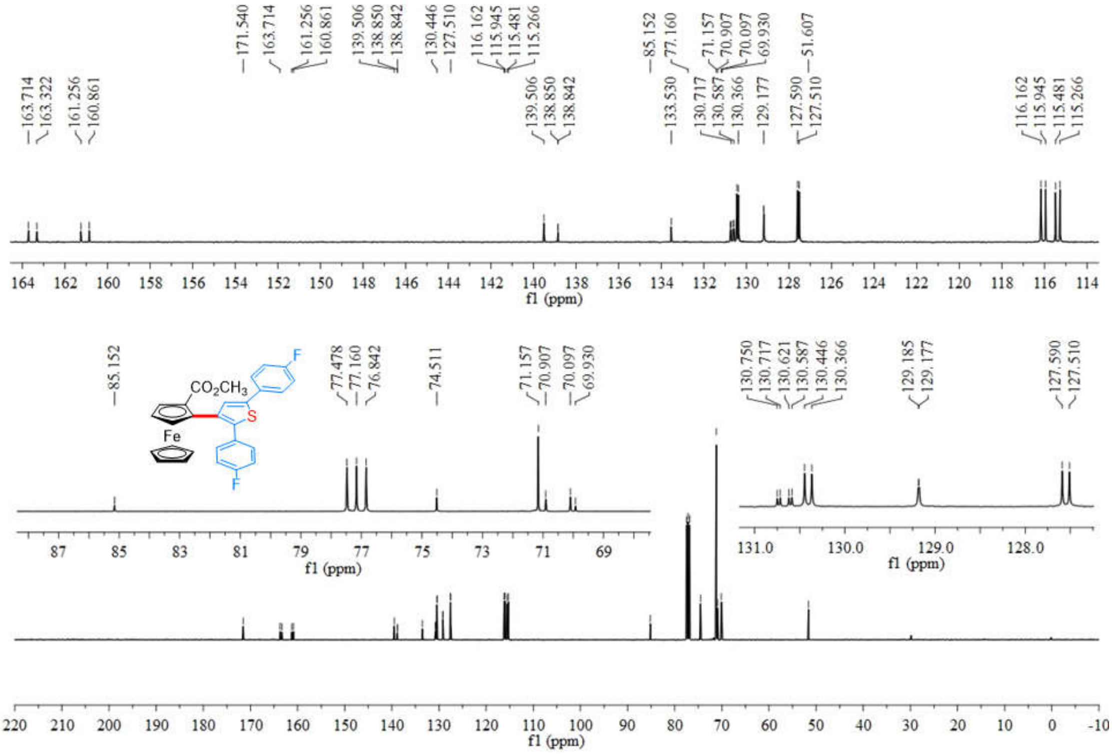
7.616
7.128
7.097
6.935
6.906
6.876
4.880
4.876
4.873
4.870
4.410
4.304
4.245
3.611
7.260
7.157
7.150
7.144
7.128
7.113
7.106
7.097
7.091
7.084
6.935
6.928
6.923
6.906
6.889
6.884
6.876
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
4.880
4.876
4.873
4.870
4.423
4.417
4.410
4.308
4.304
4.298
4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30
f1 (ppm)
CO_2CH_3
F
S
Fe
F
3.19
4.24
2.18
1.00
1.08
1.06
4.67
3.28
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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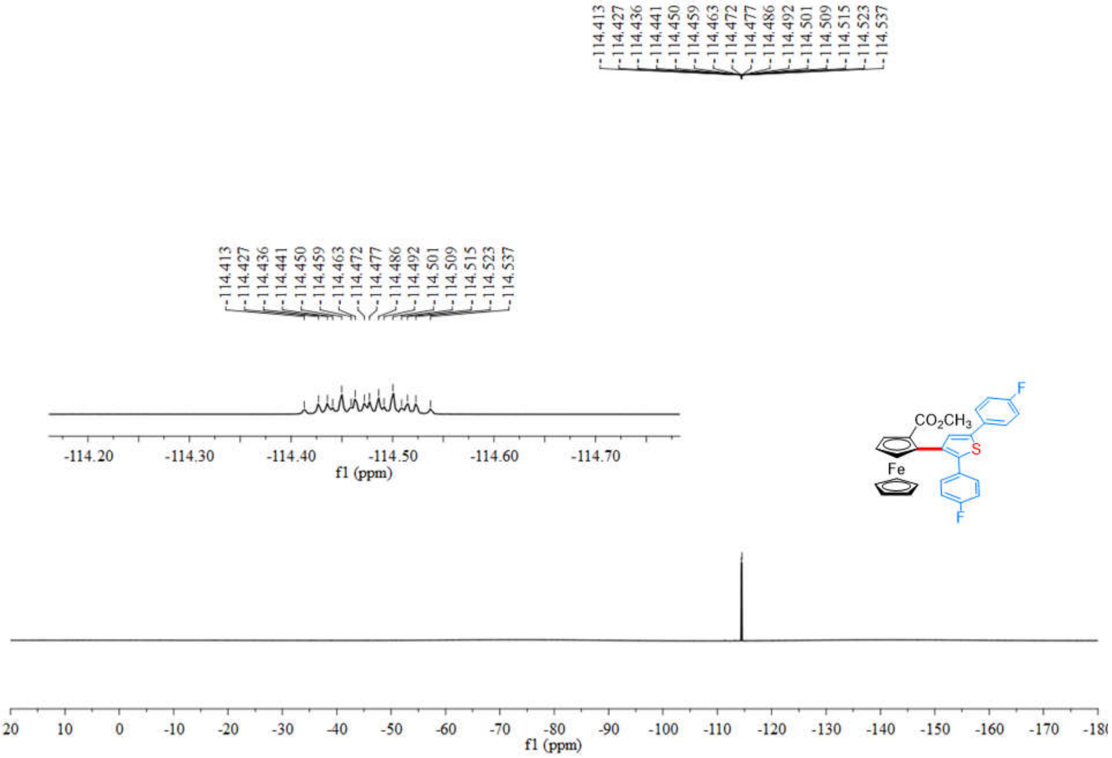
160.861
139.506
138.850
138.842
130.446
127.510
116.162
115.945
115.481
115.266
85.152
77.160
71.157
70.907
70.097
69.930
51.607
163.714
163.322
161.256
160.861
139.506
138.850
138.842
133.530
130.717
130.587
130.366
129.177
127.590
127.510
116.162
115.945
115.481
115.266
164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
85.152
CO_2CH_3
F
S
Fe
F
77.478
77.160
76.842
74.511
71.157
70.907
70.097
69.930
87 85 83 81 79 77 75 73 71 69
f1 (ppm)
130.750
130.717
130.621
130.587
130.446
130.366
129.185
129.177
127.590
127.510
131.0 130.0 129.0 128.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.413
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-114.441
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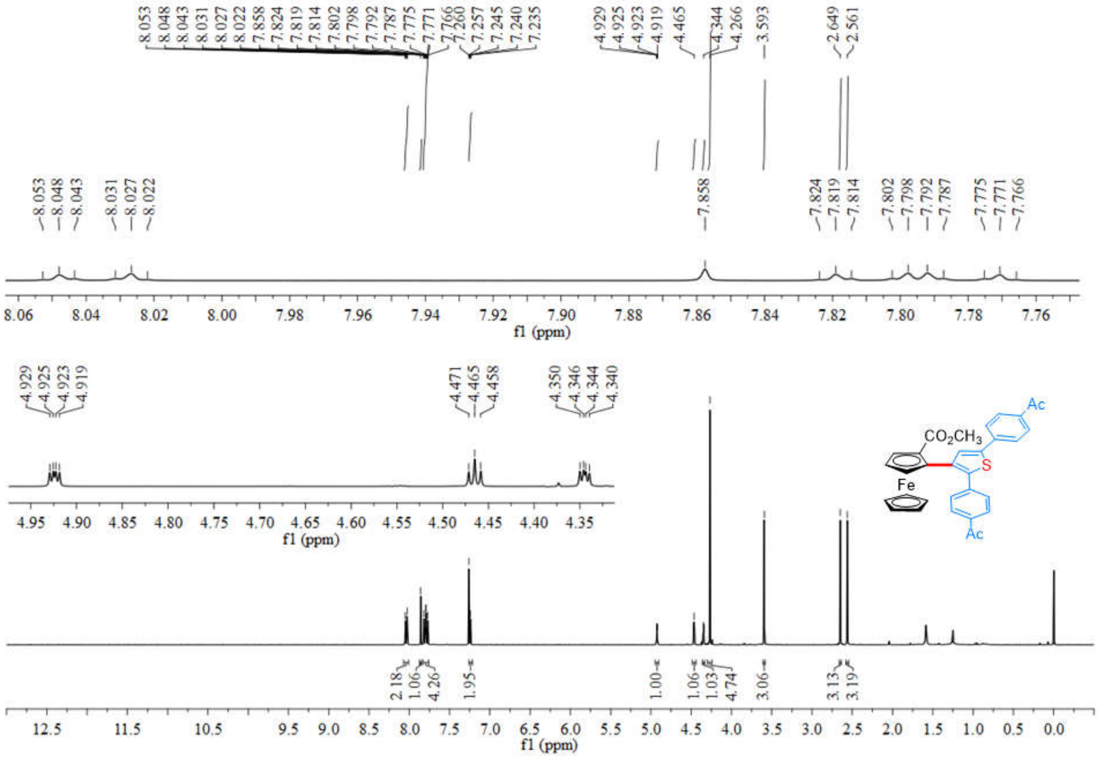
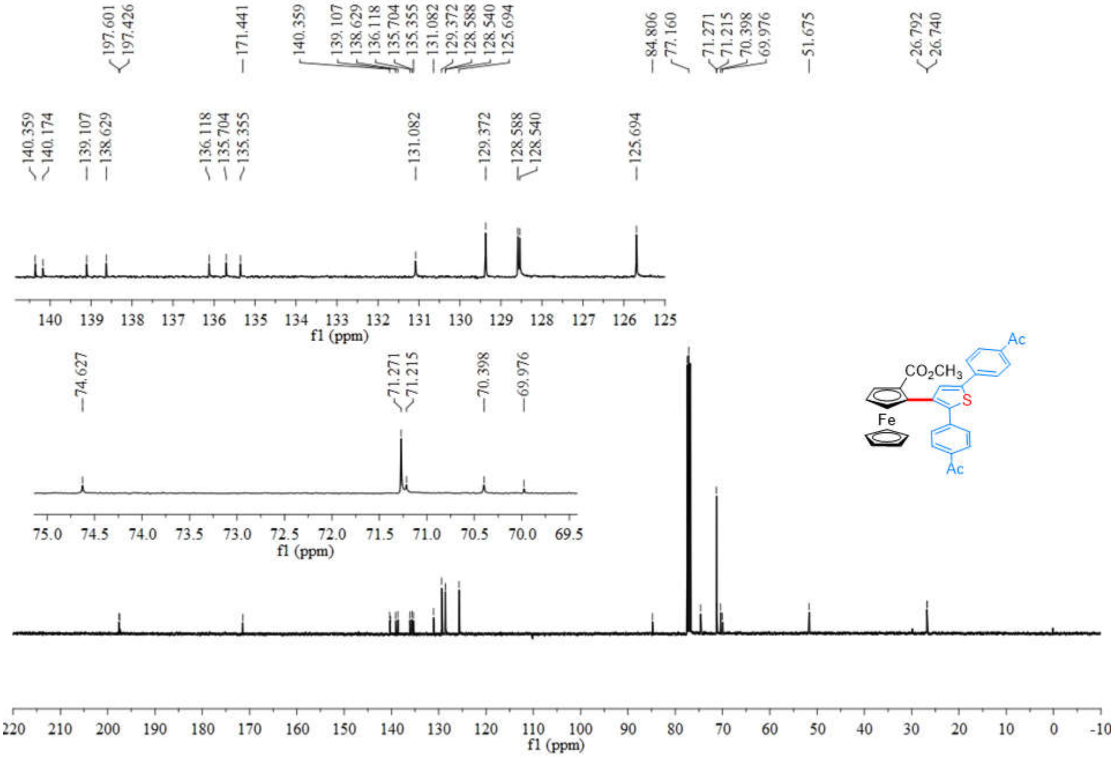
-114.459
-114.463
-114.472
-114.477
-114.486
-114.492
-114.501
-114.509
-114.515
-114.523
-114.537
-114.20
-114.30
-114.40
-114.50
-114.60
-114.70
f1 (ppm)
CO2CH3
S
F
F
Fe
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


8.053
8.048
8.043
8.031
8.027
8.022
7.858
7.824
7.819
7.814
7.802
7.798
7.792
7.787
7.775
7.771
7.766
7.260
7.257
7.245
7.240
7.235
4.929
4.925
4.923
4.919
4.465
4.344
4.266
3.593
2.649
2.561
4.471
4.465
4.458
4.350
4.346
4.344
4.340
2.18
1.06
4.26
1.95
1.00
1.06
1.03
4.74
3.06
3.13
3.19
f1 (ppm)
CO_2CH_3
Ac
Fe
S
Ac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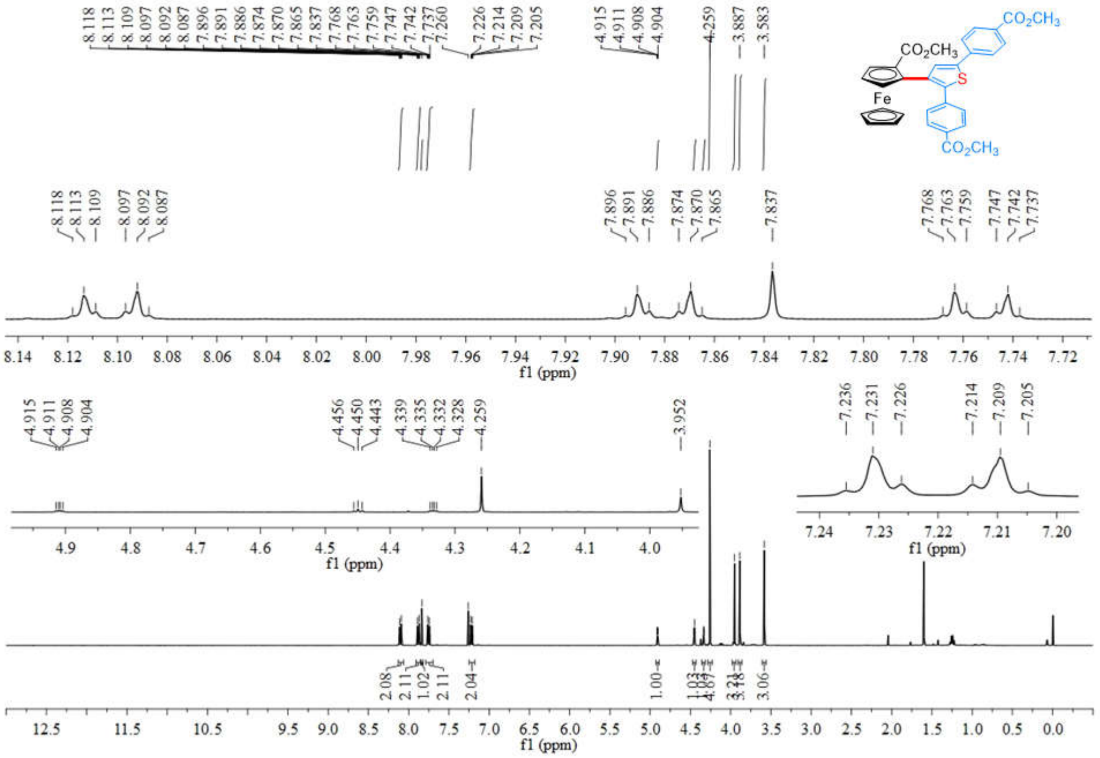
197.426
171.441
140.359
139.107
138.629
136.118
135.704
135.355
131.082
129.372
128.588
128.540
125.694
84.806
77.160
71.271
71.215
70.398
69.976
51.675
26.792
26.740
140.359
140.174
139.107
138.629
136.118
135.704
135.355
131.082
129.372
128.588
128.540
125.694
74.627
71.271
71.215
70.398
69.976
f1 (ppm)
CO_2CH_3
Ac
Fe
S
Ac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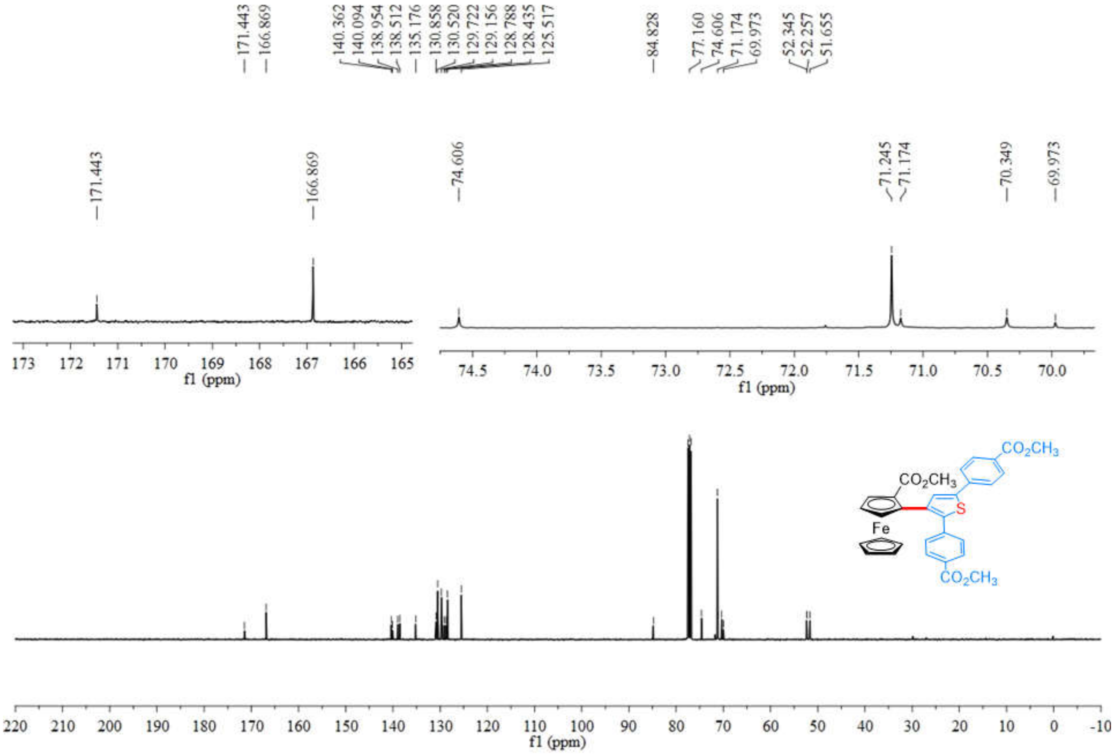
8.109
8.097
8.092
8.087
7.896
7.891
7.886
7.874
7.870
7.865
7.837
7.768
7.763
7.759
7.747
7.742
7.737
7.260
7.226
7.214
7.209
7.205
4.915
4.911
4.908
4.904
4.259
3.887
3.583
CO$_2$CH$_3$
CO$_2$CH$_3$
Fe
S
CO$_2$CH$_3$
f1 (ppm)
4.456
4.450
4.443
4.339
4.335
4.332
4.328
3.952
7.236
7.231
7.226
7.214
7.209
7.205
f1 (ppm)
f1 (ppm)
2.08
2.11
1.02
2.11
2.04
1.00
1.03
1.03
4.97
3.21
3.18
3.06
f1 (ppm)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140.362
140.094
138.954
138.512
135.176
130.858
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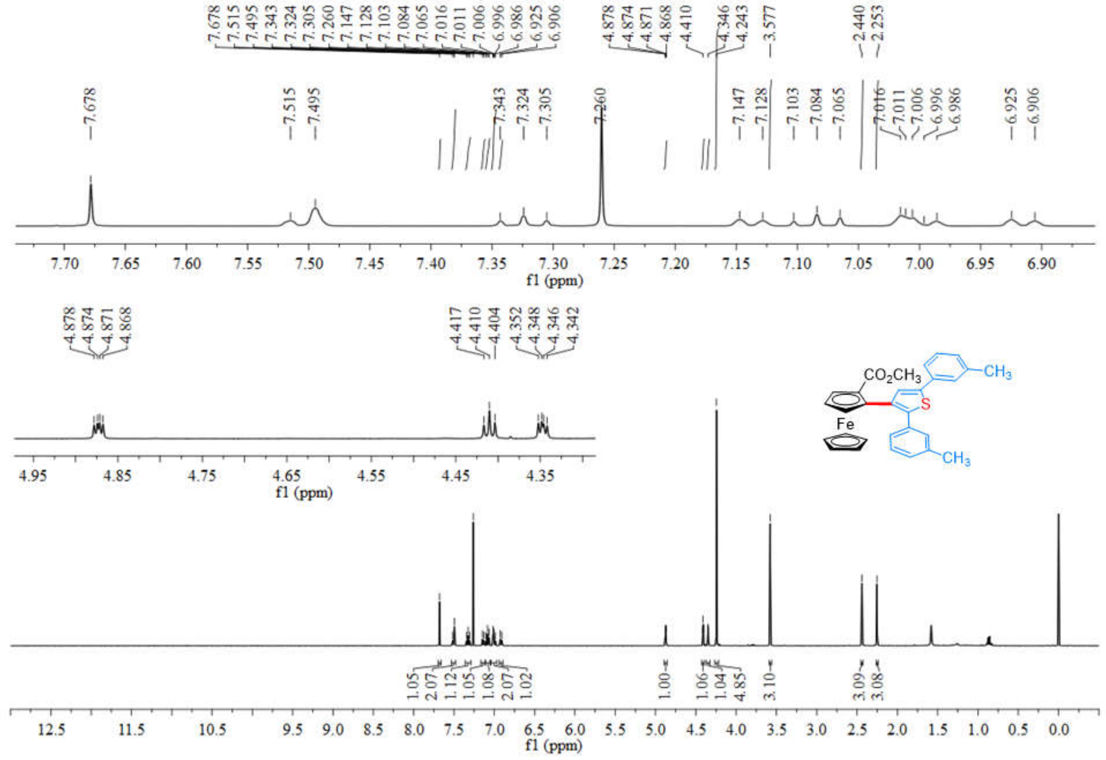
129.722
129.156
128.788
128.435
125.517
84.828
77.160
74.606
71.174
69.973
52.345
52.257
51.655
171.443
166.869
f1 (ppm)
74.606
71.245
71.174
70.349
69.973
f1 (ppm)
CO$_2$CH$_3$
CO$_2$CH$_3$
Fe
S
CO$_2$CH$_3$
f1 (ppm)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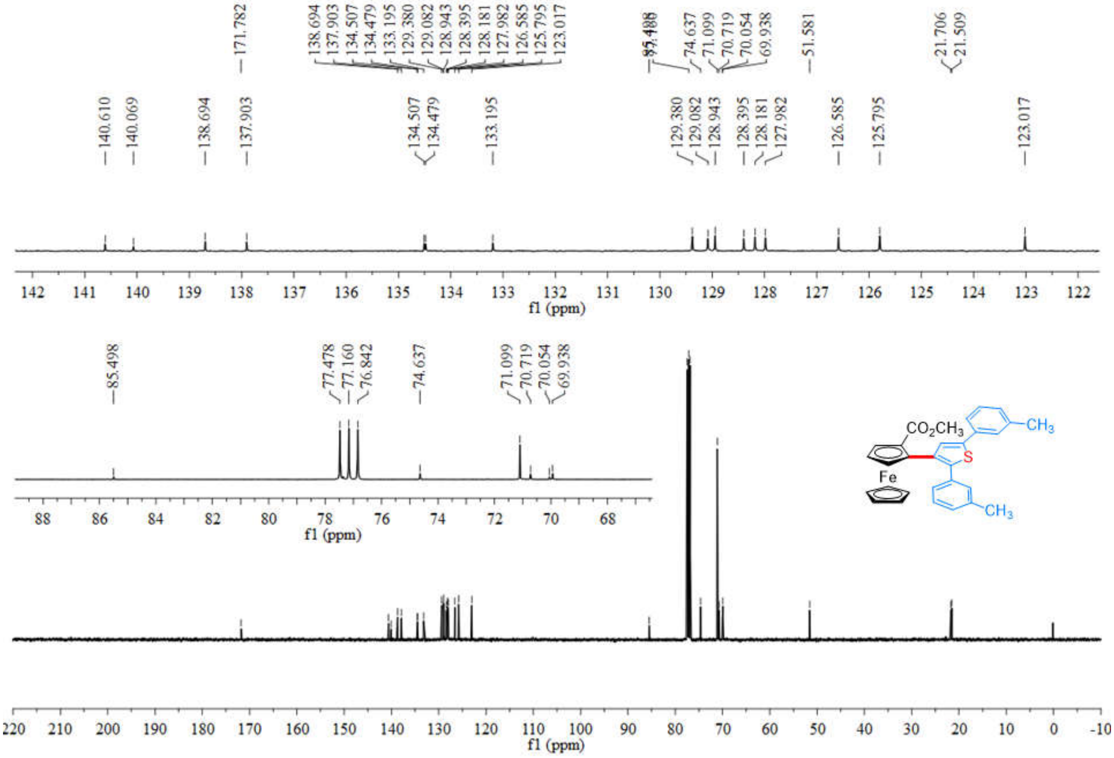
7.515
7.495
7.343
7.324
7.305
7.260
7.147
7.128
7.103
7.084
7.065
7.016
7.011
7.006
6.996
6.986
6.925
6.906
4.878
4.874
4.871
4.868
4.410
4.346
4.243
3.577
2.440
2.253
4.417
4.404
4.352
4.348
4.342
1.05
2.07
1.12
1.05
1.08
2.07
1.02
1.00
1.06
1.04
4.85
3.10
3.09
3.08
f1 (ppm)
CO_2CH_3
CH_3
Fe
S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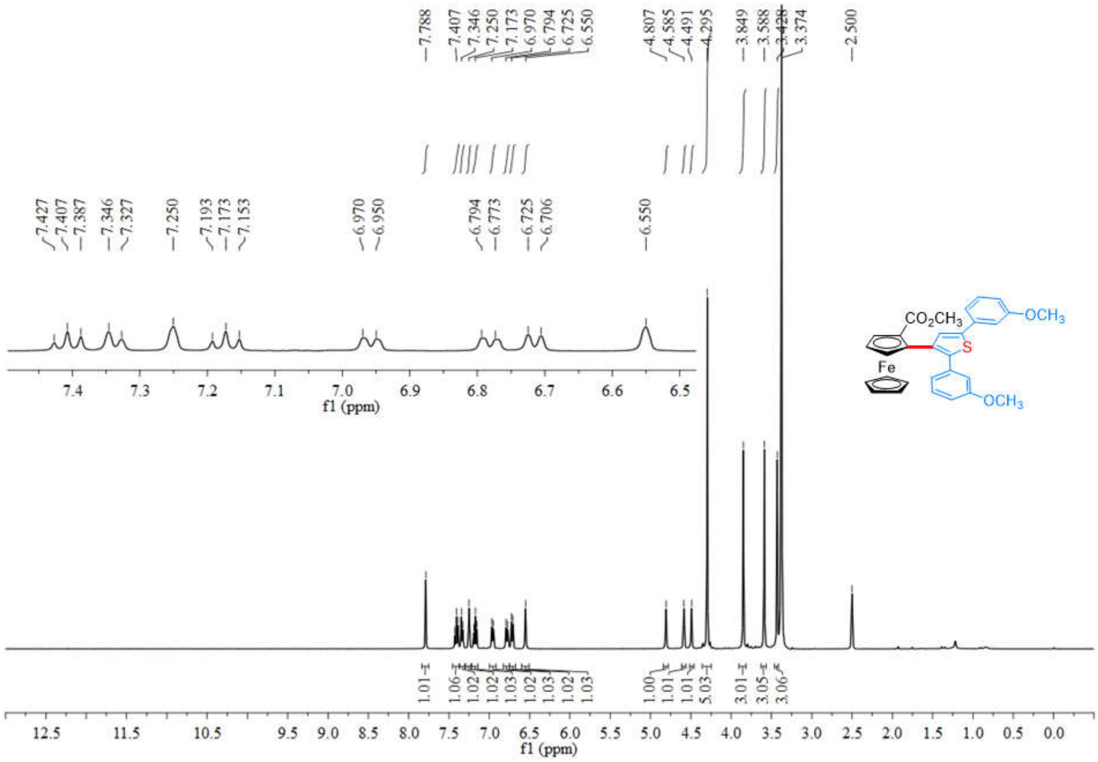
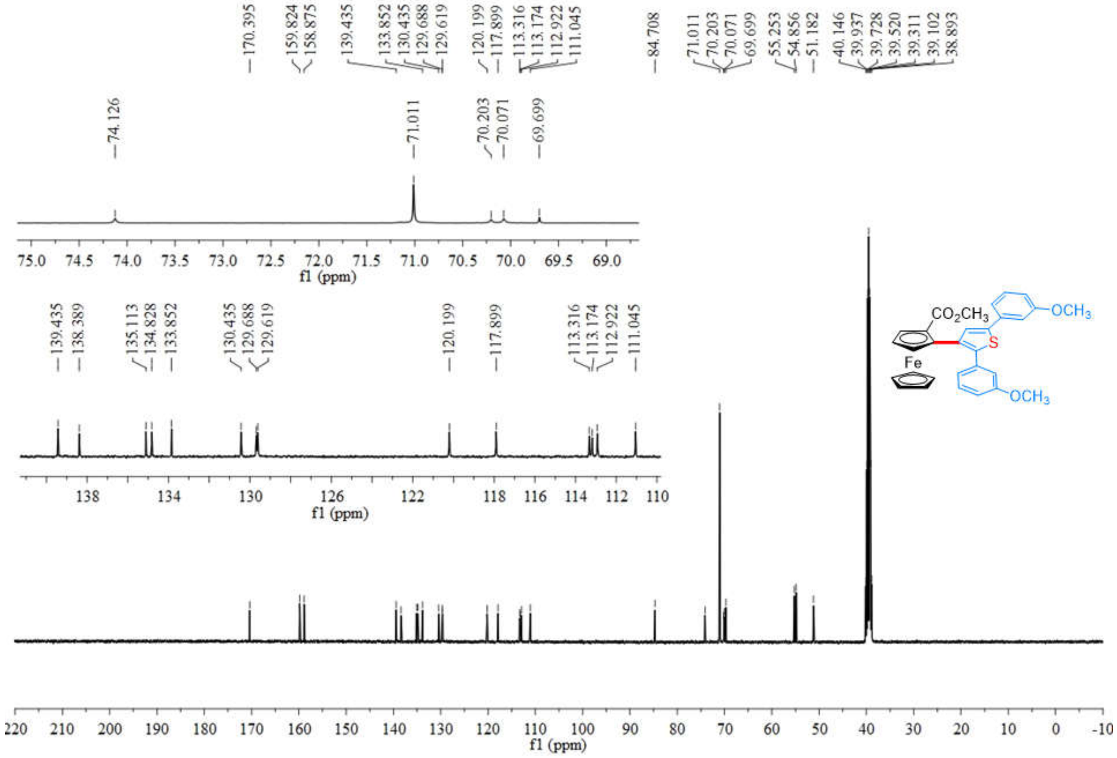
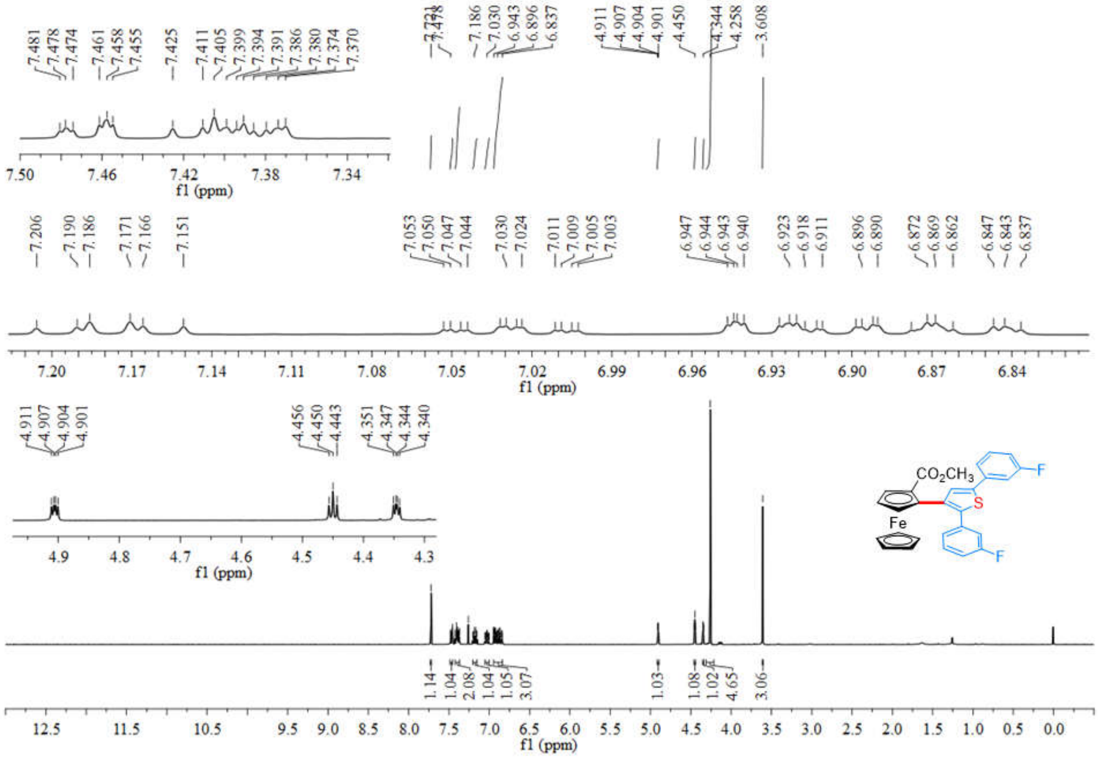
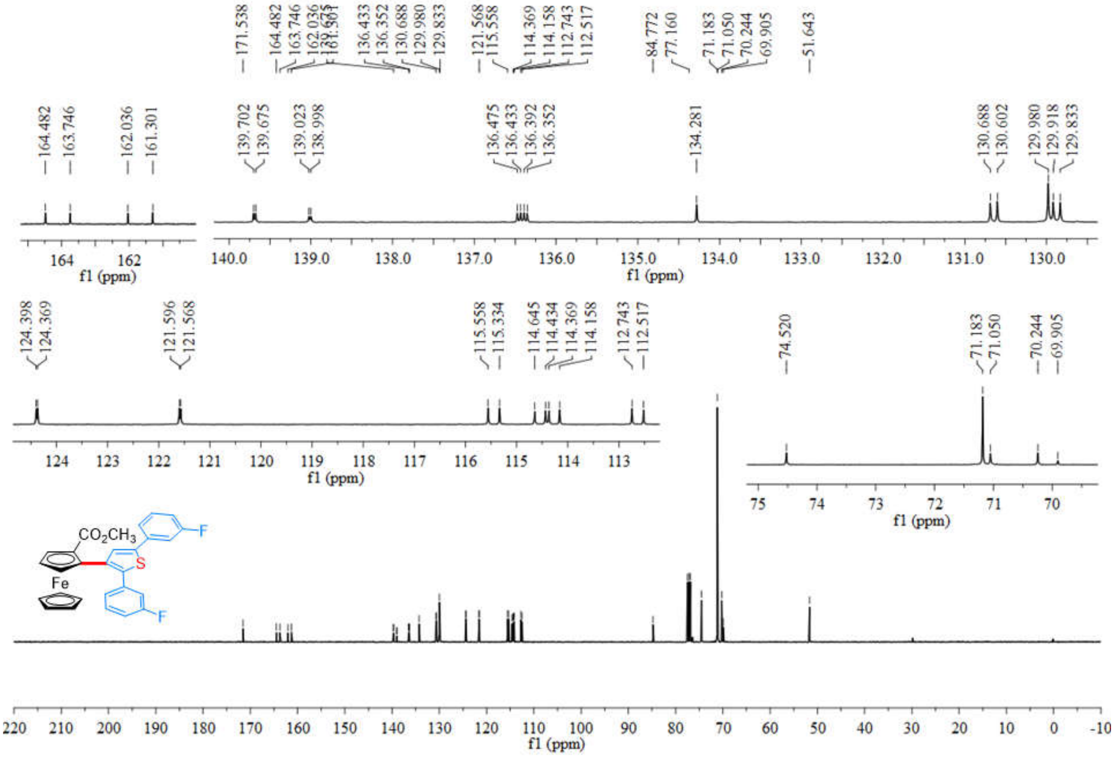
140.610
140.069
138.694
137.903
134.507
134.479
133.195
129.380
129.082
128.943
128.395
128.181
127.982
126.585
125.795
123.017
85.498
77.478
77.160
76.842
74.637
71.099
70.719
70.054
69.938
51.581
21.706
21.509
f1 (ppm)
CO_2CH_3
CH_3
Fe
S


7.788
7.407
7.346
7.250
7.173
6.970
6.794
6.725
6.550
4.807
4.585
4.491
4.295
3.849
3.588
3.428
3.374
2.500
7.427
7.407
7.387
7.346
7.327
7.250
7.193
7.173
7.153
6.970
6.950
6.794
6.773
6.725
6.706
6.550
CO2CH3
OCH3
S
Fe
OCH3
f1 (ppm)
1.01
1.06
1.02
1.02
1.03
1.02
1.03
1.02
1.03
1.00
1.01
1.01
5.03
3.01
3.05
3.06
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

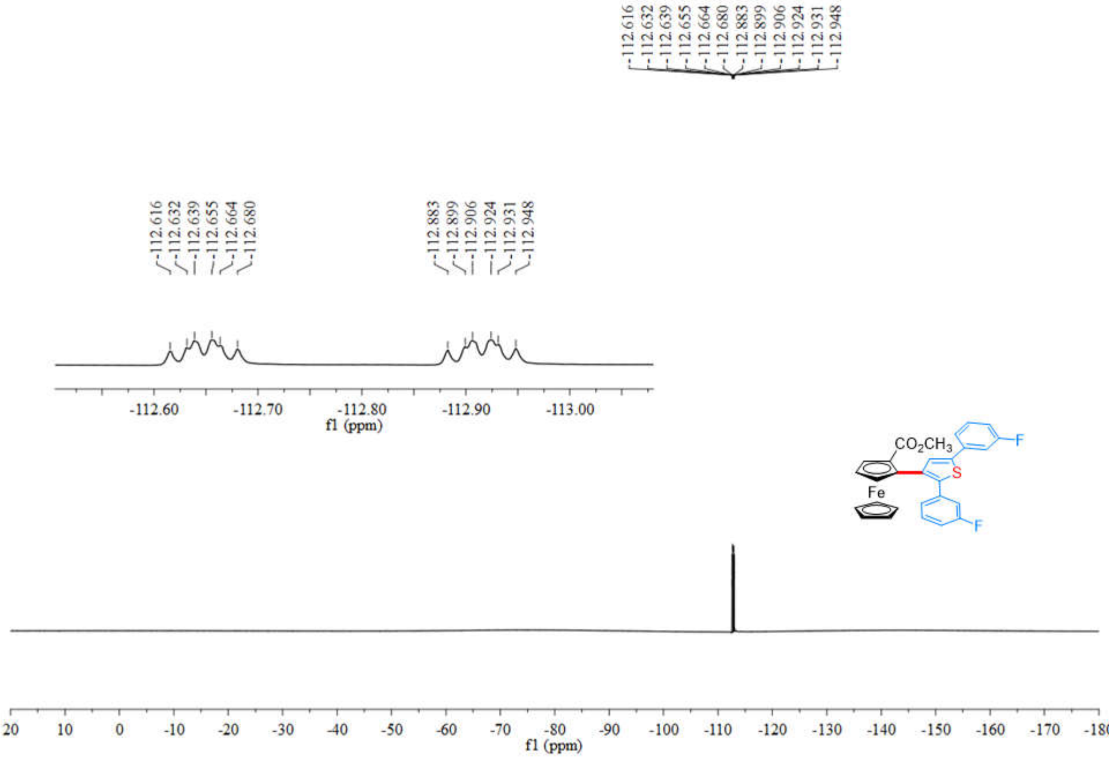

170.395
159.824
158.875
139.435
133.852
130.435
129.688
129.619
120.199
117.899
113.316
113.174
112.922
111.045
84.708
71.011
70.203
70.071
69.699
55.253
54.856
51.182
40.146
39.937
39.728
39.520
39.311
39.102
38.893
74.126
71.011
70.203
70.071
69.699
f1 (ppm)
139.435
138.389
135.113
134.828
133.852
130.435
129.688
129.619
120.199
117.899
113.316
113.174
112.922
111.045
f1 (ppm)
CO2CH3
OCH3
S
Fe
OCH3
f1 (ppm)

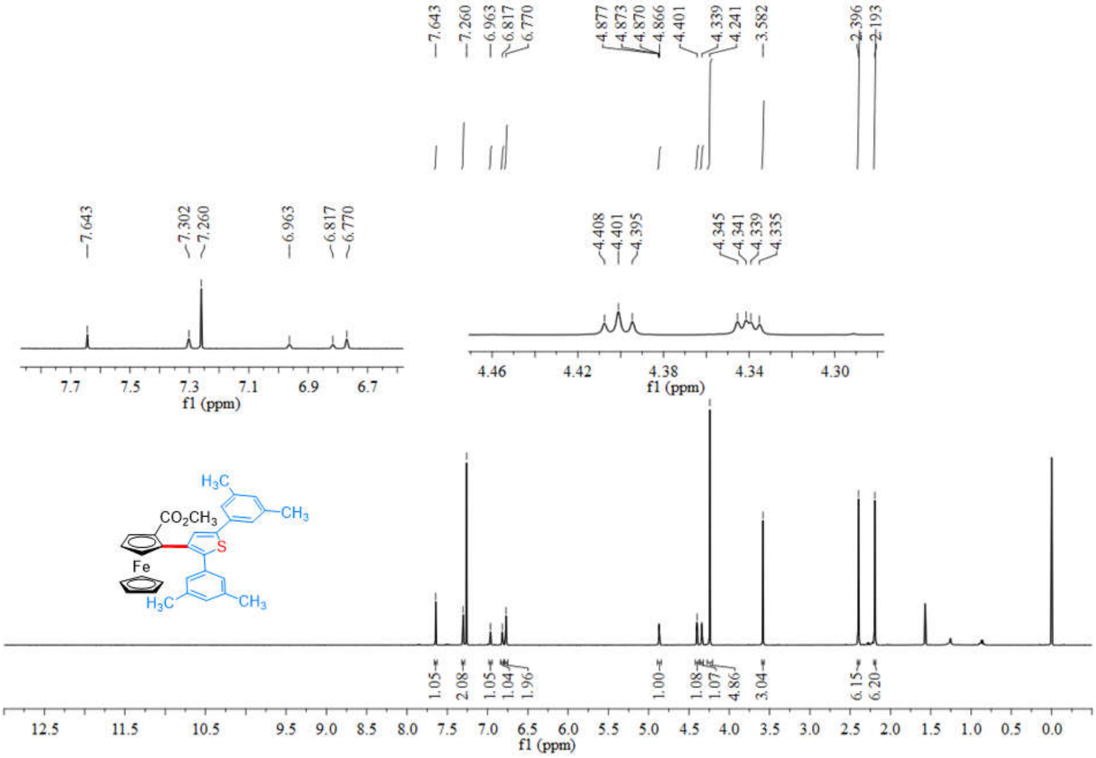


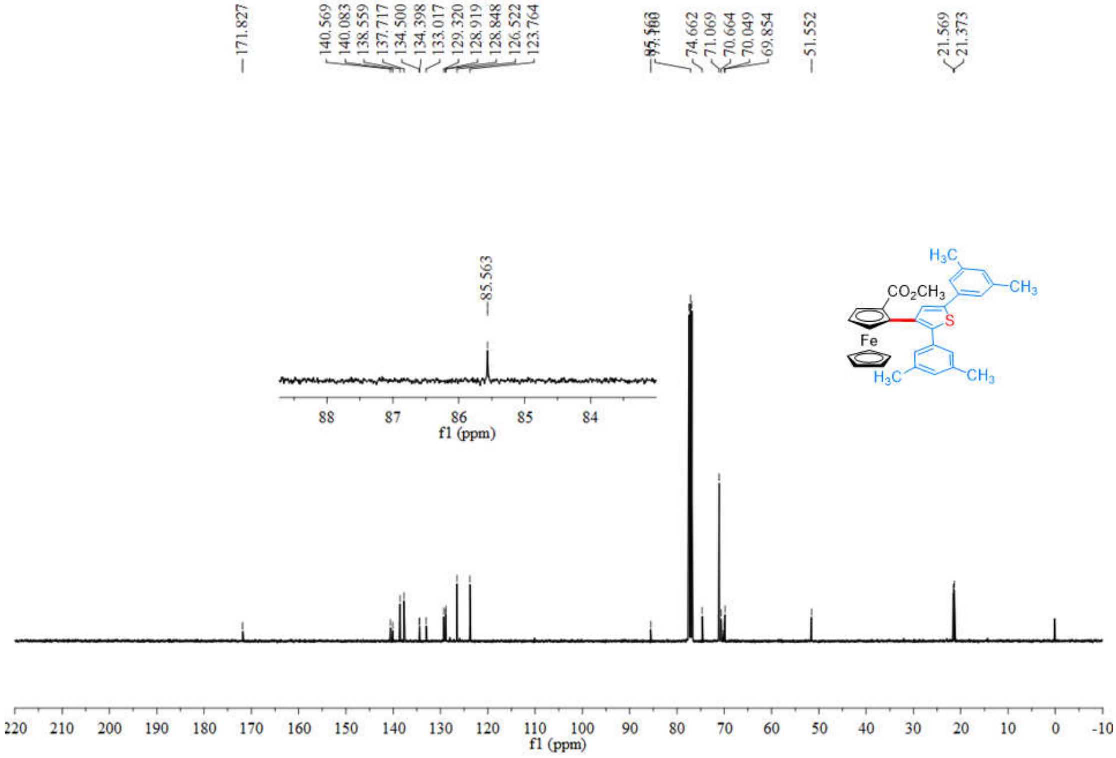
7.481 7.478 7.474 7.461 7.458 7.455 7.425 7.411 7.405 7.399 7.394 7.391 7.386 7.380 7.374 7.370
7.50 7.46 7.42 7.38 7.34
f1 (ppm)
7.721 7.478 7.186 7.030 6.943 6.896 6.837
4.911 4.907 4.904 4.901 4.450 4.344 4.258 3.608
7.206 7.190 7.186 7.171 7.166 7.151
7.053 7.050 7.047 7.044 7.030 7.024 7.011 7.009 7.005 7.003
6.947 6.944 6.943 6.940 6.923 6.918 6.911 6.896 6.890 6.872 6.869 6.862 6.847 6.843 6.837
7.20 7.17 7.14 7.11 7.08 7.05 7.02 6.99 6.96 6.93 6.90 6.87 6.84
f1 (ppm)
4.911 4.907 4.904 4.901 4.456 4.450 4.443 4.351 4.347 4.344 4.340
4.9 4.8 4.7 4.6 4.5 4.4 4.3
f1 (ppm)
CO2CH3
S
F
Fe
F
1.14 1.04 2.08 1.04 1.05 3.07 1.03 1.08 1.02 4.65 3.06
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



171.538 164.482 163.746 162.036 161.301 136.433 136.352 130.688 129.980 129.833 121.568 115.558 114.369 114.158 112.743 112.517 84.772 77.160 71.183 71.050 70.244 69.905 51.643
164.482 163.746 162.036 161.301
164 162
f1 (ppm)
139.702 139.675 139.023 138.998 136.475 136.433 136.392 136.352 134.281 130.688 130.602 129.980 129.918 129.833
140.0 139.0 138.0 137.0 136.0 135.0 134.0 133.0 132.0 131.0 130.0
f1 (ppm)
124.398 124.369 121.596 121.568 115.558 115.334 114.645 114.434 114.369 114.158 112.743 112.517
124 123 122 121 120 119 118 117 116 115 114 113
f1 (ppm)
74.520 71.183 71.050 70.244 69.905
75 74 73 72 71 70
f1 (ppm)
CO2CH3
S
F
Fe
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-112.616
-112.632
-112.639
-112.655
-112.664
-112.680
-112.883
-112.899
-112.906
-112.924
-112.931
-112.948
-112.60
-112.70
-112.80
-112.90
-113.00
f1 (ppm)
CO$_2$CH$_3$
Fe
S
F
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.643
7.260
6.963
6.817
6.770
4.877
4.873
4.870
4.866
4.401
4.339
4.241
3.582
2.396
2.193
7.643
7.302
7.260
6.963
6.817
6.770
7.7
7.5
7.3
7.1
6.9
6.7
f1 (ppm)
4.408
4.401
4.395
4.345
4.341
4.339
4.335
4.46
4.42
4.38
4.34
4.30
f1 (ppm)
H_3C
CO_2CH_3
CH_3
S
Fe
H_3C
CH_3
1.05
2.08
1.05
1.04
1.96
1.00
1.08
1.07
4.86
3.04
6.15
6.20
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.827
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134.398
133.017
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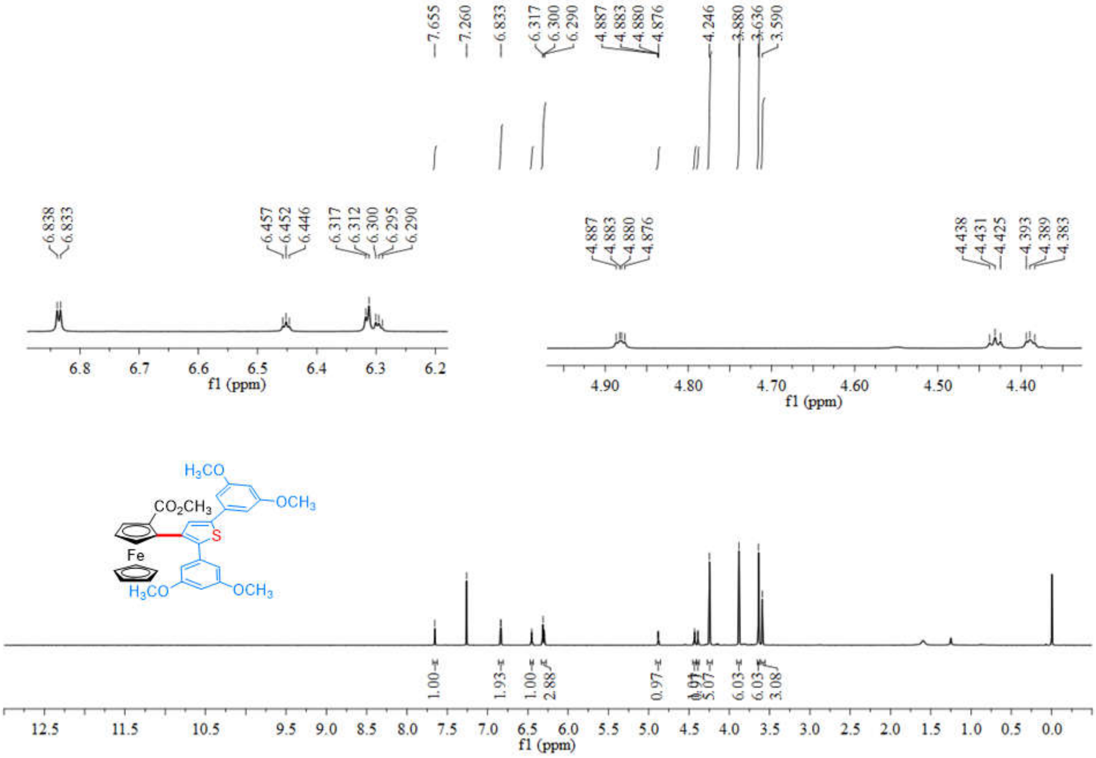
128.919
128.848
126.522
123.764
85.563
77.160
74.662
71.069
70.664
70.049
69.854
51.552
21.569
21.373
85.563
88
87
86
85
84
f1 (ppm)
H_3C
CO_2CH_3
CH_3
S
Fe
H_3C
CH_3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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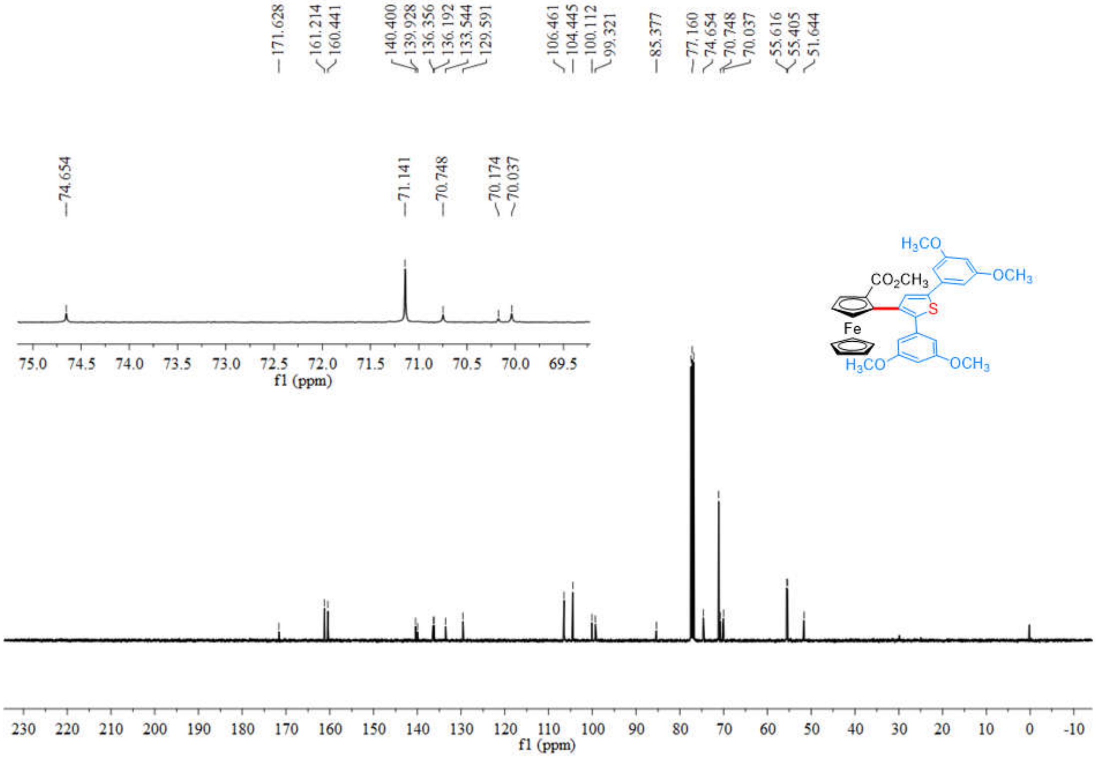
6.833
6.317
6.300
6.290
4.887
4.883
4.880
4.876
4.246
3.880
3.636
3.590
6.838
6.833
6.457
6.452
6.446
6.317
6.312
6.300
6.295
6.290
f1 (ppm)
4.887
4.883
4.880
4.876
4.438
4.431
4.425
4.393
4.389
4.383
f1 (ppm)
H_3CO
CO_2CH_3
OCH_3
S
Fe
H_3CO
OCH_3
1.00
1.93
1.00
2.88
0.97
5.07
6.03
6.03
3.08
f1 (ppm)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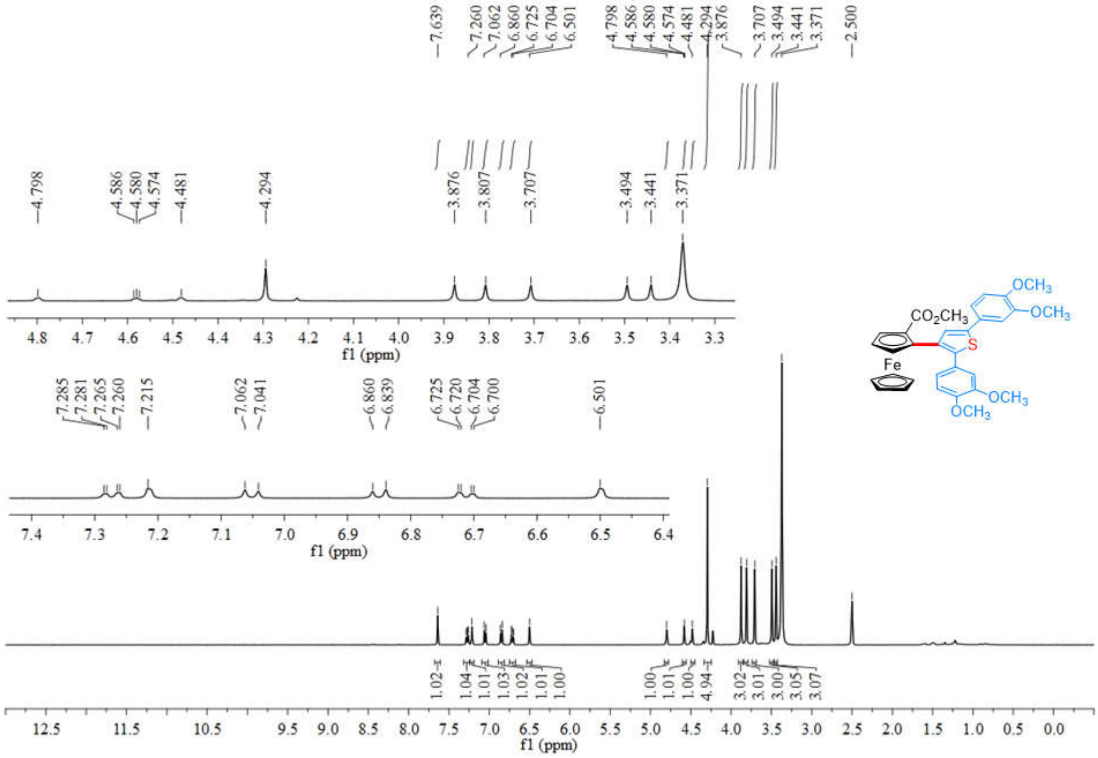
160.441
140.400
139.928
136.356
136.192
133.544
129.591
106.461
104.445
100.112
99.321
85.377
77.160
74.654
70.748
70.037
55.616
55.405
51.644
74.654
71.141
70.748
70.174
70.037
f1 (ppm)
H_3CO
CO_2CH_3
OCH_3
S
Fe
H_3CO
OCH_3
f1 (ppm)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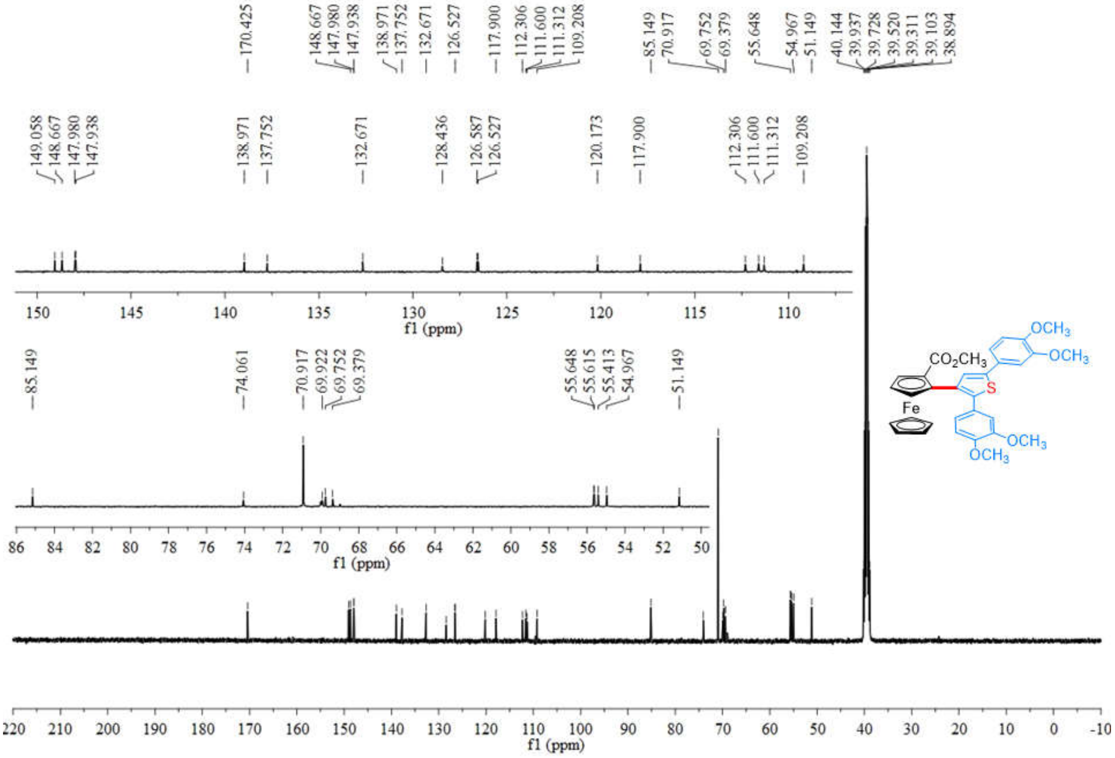
6.725
6.704
6.501
4.798
4.586
4.580
4.574
4.481
4.294
3.876
3.707
3.494
3.441
3.371
2.500
4.798
4.586
4.580
4.574
4.481
4.294
3.876
3.807
3.707
3.494
3.441
3.371
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
f1 (ppm)
7.285
7.281
7.265
7.260
7.215
7.062
7.041
6.860
6.839
6.725
6.720
6.704
6.700
6.501
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)
CO$_2$CH$_3$
OCH$_3$
OCH$_3$
S
Fe
OCH$_3$
OCH$_3$
1.02
1.04
1.01
1.01
1.03
1.02
1.01
1.00
1.00
1.01
1.00
4.94
3.02
3.01
3.00
3.05
3.07
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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147.980
147.938
138.971
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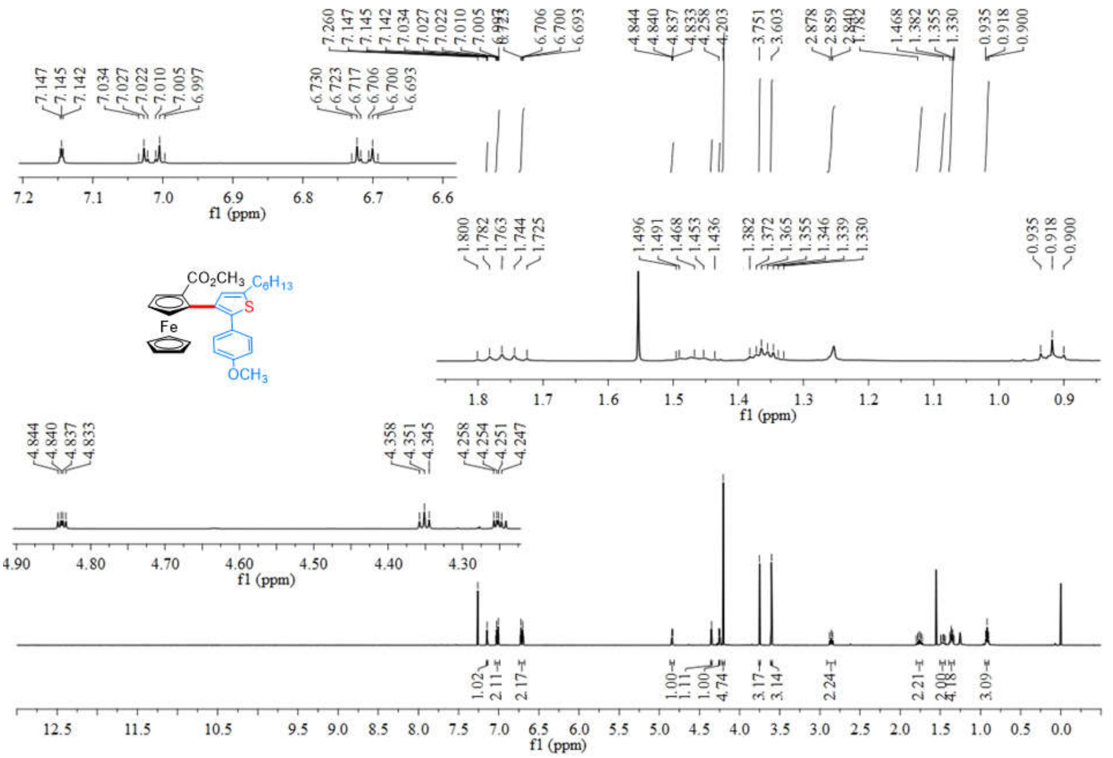
132.671
126.527
117.900
112.306
111.600
111.312
109.208
85.149
70.917
69.752
69.379
55.648
54.967
51.149
40.144
39.937
39.728
39.520
39.311
39.103
38.894
149.058
148.667
147.980
147.938
138.971
137.752
132.671
128.436
126.587
126.527
120.173
117.900
112.306
111.600
111.312
109.208
150 145 140 135 130 125 120 115 110
f1 (ppm)
85.149
74.061
70.917
69.922
69.752
69.379
55.648
55.615
55.413
54.967
51.149
86 84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50
f1 (ppm)
CO$_2$CH$_3$
OCH$_3$
OCH$_3$
S
Fe
OCH$_3$
OCH$_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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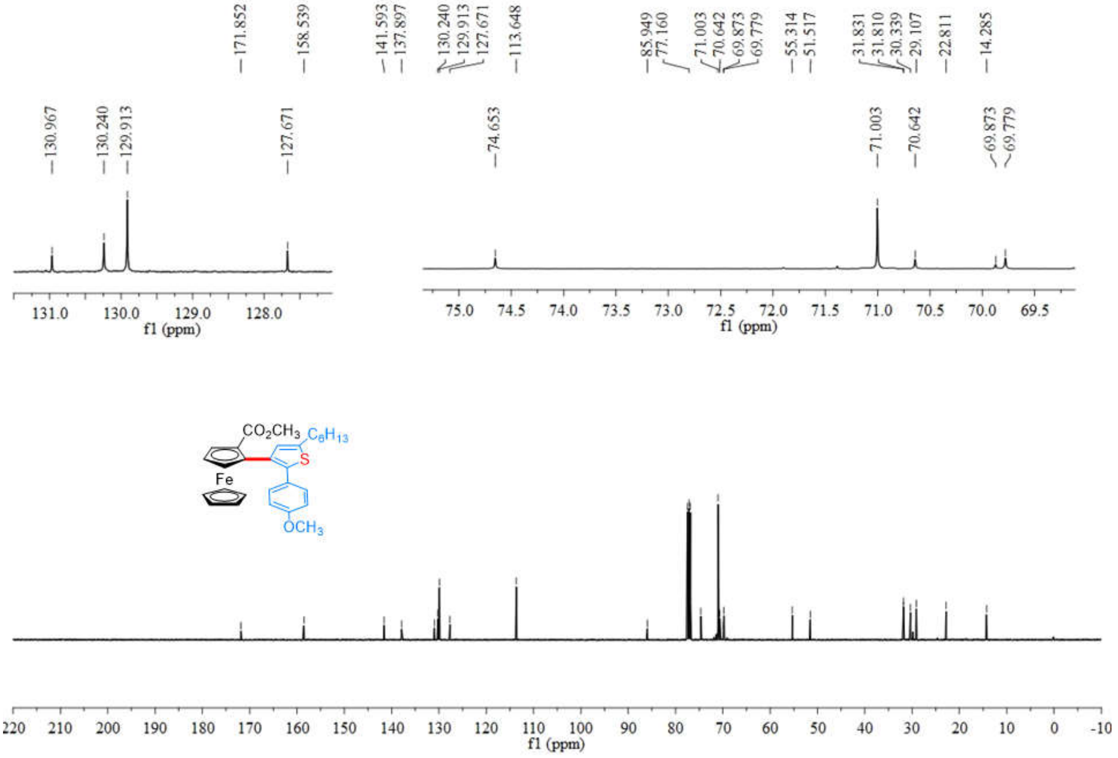
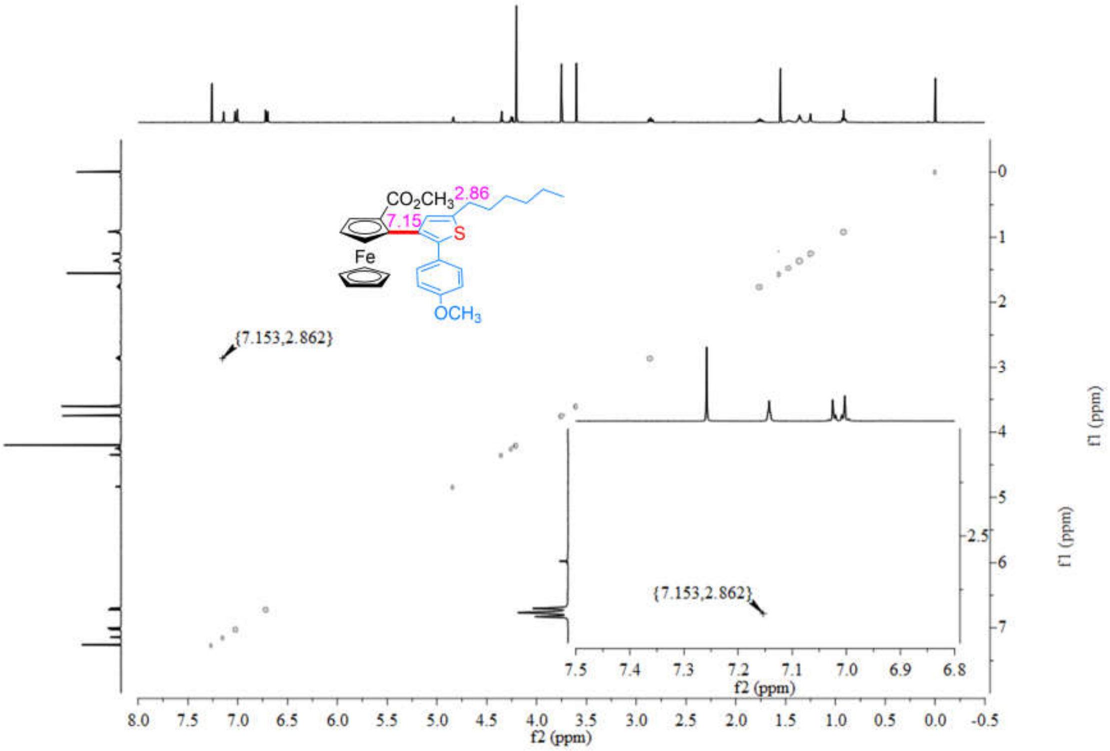
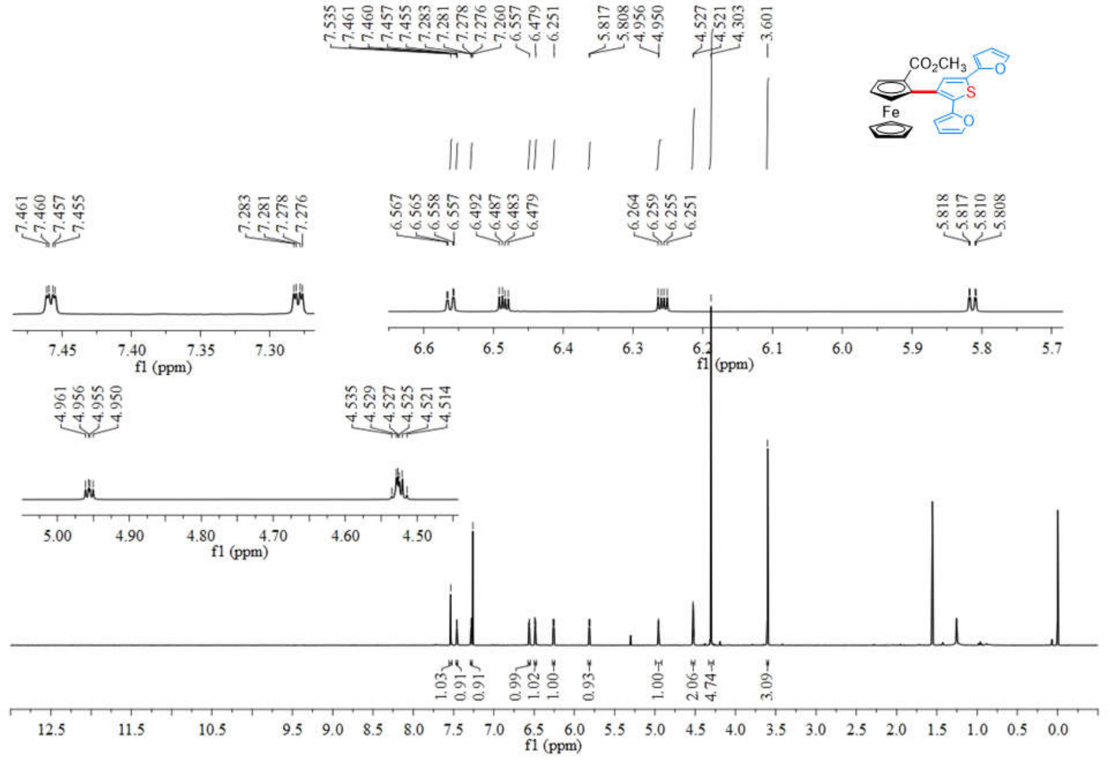
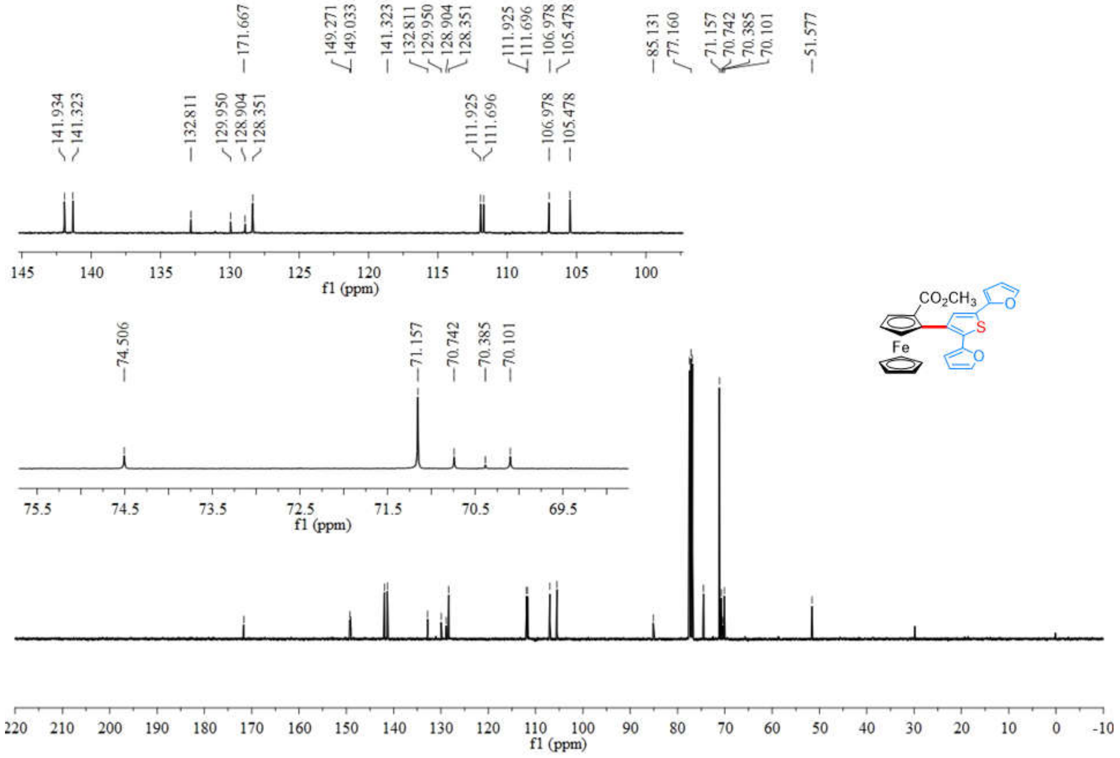
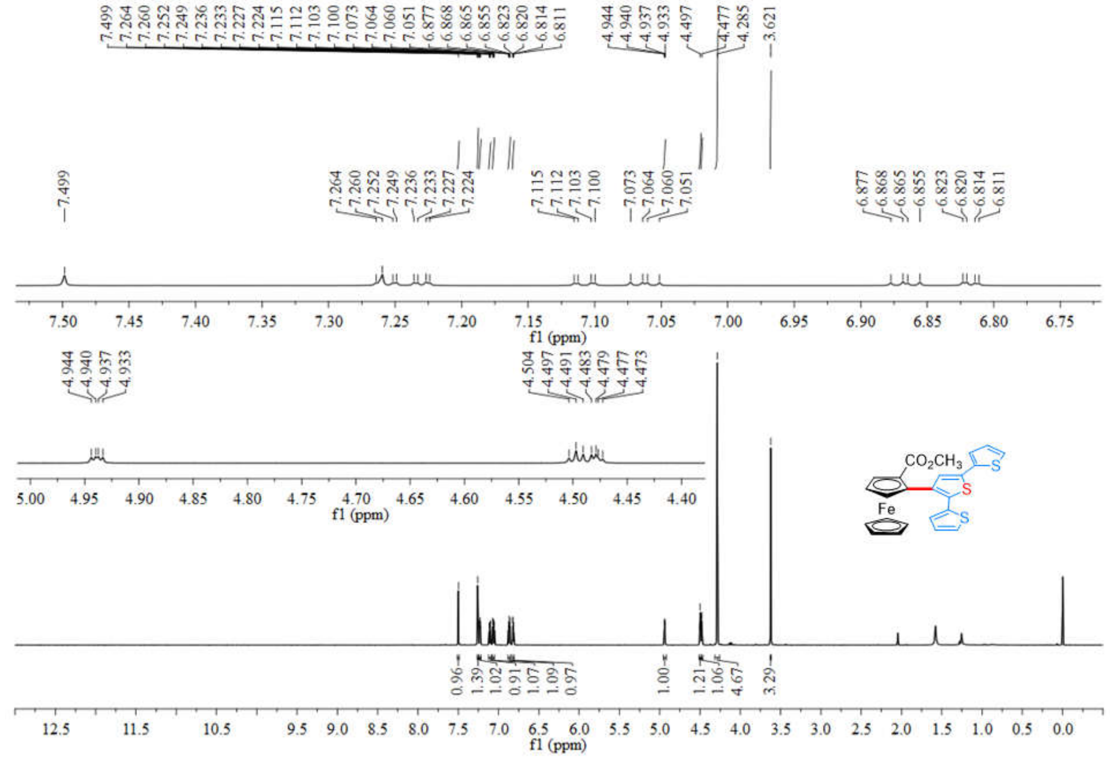
7.145
7.142
7.034
7.027
7.022
7.010
7.005
6.997
6.723
6.706
6.700
6.693
4.844
4.840
4.837
4.833
4.258
4.203
3.751
3.603
2.878
2.859
2.840
1.782
1.468
1.382
1.355
1.330
0.935
0.918
0.900
6.730
6.717
1.800
1.763
1.744
1.725
1.496
1.491
1.453
1.436
1.372
1.365
1.346
1.339
4.358
4.351
4.345
4.254
4.251
4.247
CO2CH3
C6H13
S
Fe
OCH3
1.02
2.11
2.17
1.00
1.11
1.00
4.74
3.17
3.14
2.24
2.21
2.00
4.18
3.09
f1 (ppm)

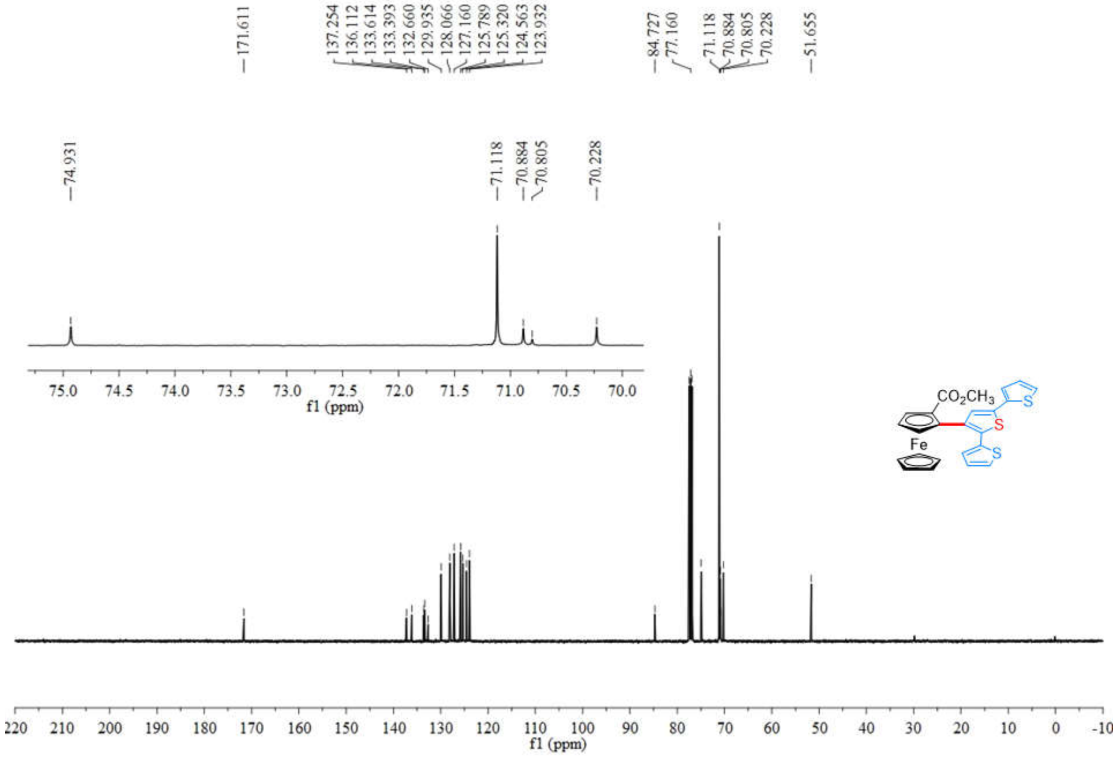

171.852
158.539
141.593
137.897
130.240
129.913
127.671
113.648
85.949
77.160
71.003
70.642
69.873
69.779
55.314
51.517
31.831
31.810
30.339
29.107
22.811
14.285
130.967
74.653
CO2CH3
C6H13
S
Fe
OCH3
f1 (ppm)

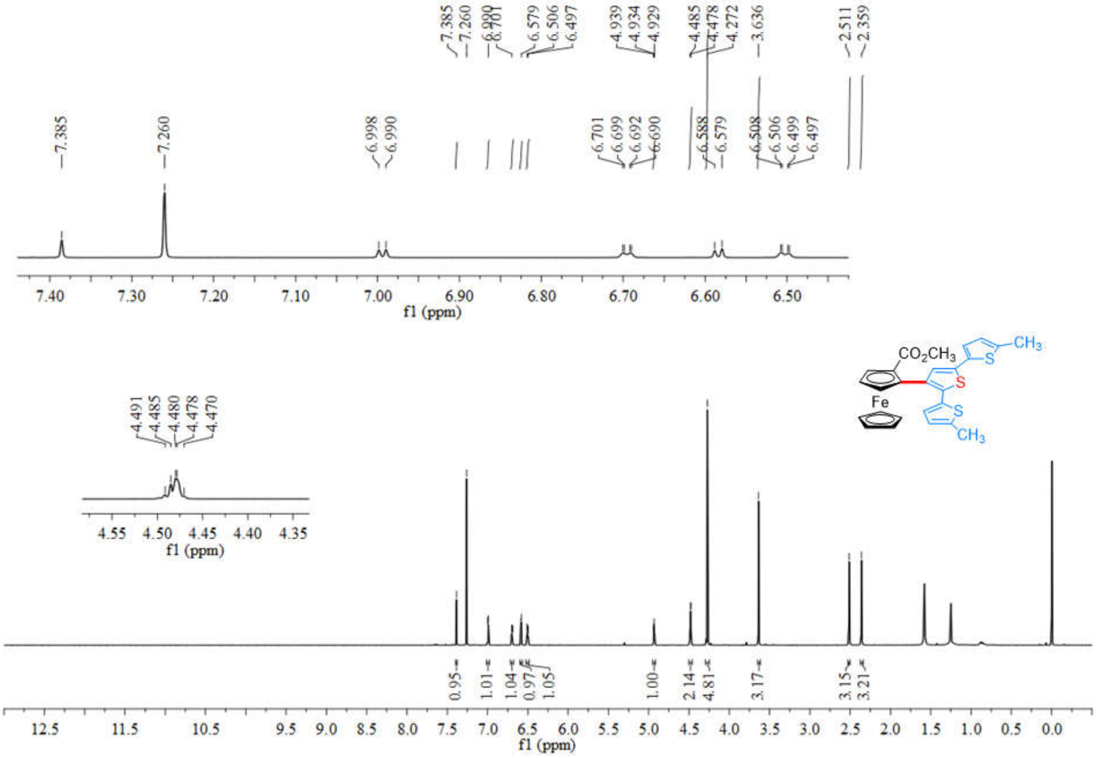

CO$_2$CH$_3$
2.86
7.15
S
Fe
OCH$_3$
{7.153,2.862}
{7.153,2.862}
f2 (ppm)
f1 (ppm)
f2 (ppm)
f1 (ppm)
2.5
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 1 2 3 4 5 6 7
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8

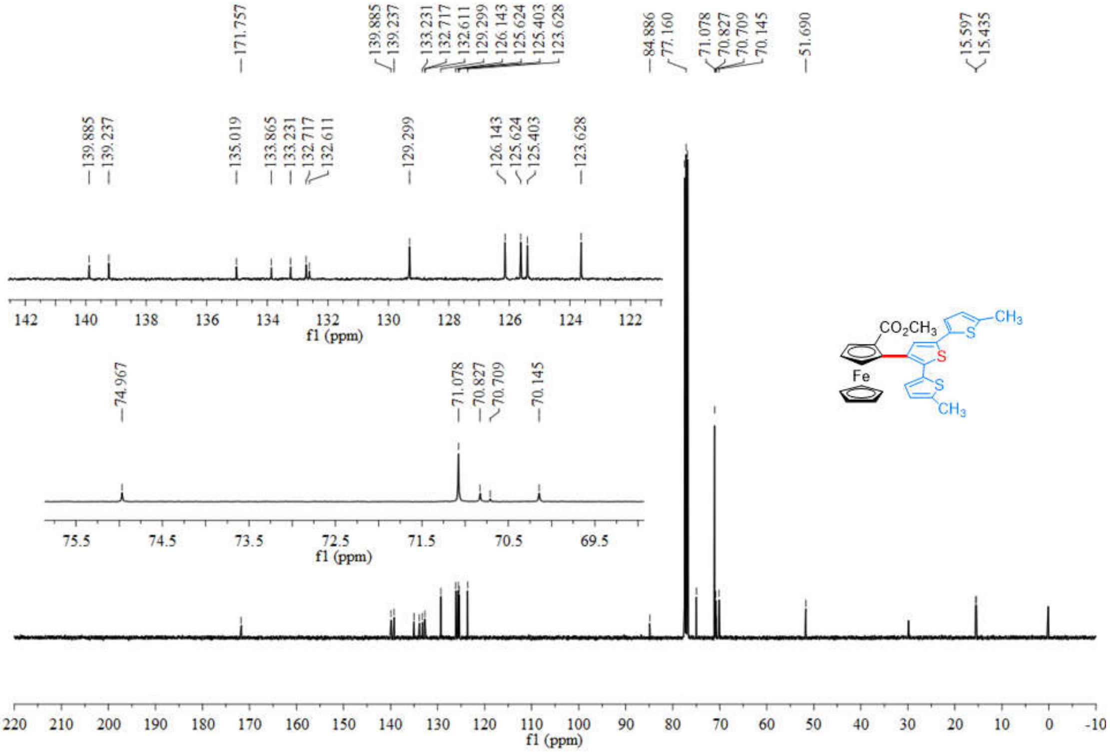

7.535
7.461
7.460
7.457
7.455
7.283
7.281
7.278
7.276
7.260
6.557
6.479
6.251
5.817
5.808
4.956
4.950
4.527
4.521
4.303
3.601
CO2CH3
Fe
S
O
O
1.03
0.91
0.91
0.99
1.02
1.00
0.93
1.00
2.06
4.74
3.09
6.567
6.565
6.558
6.557
6.492
6.487
6.483
6.479
6.264
6.259
6.255
6.251
5.818
5.817
5.810
5.808
4.961
4.956
4.955
4.950
4.535
4.529
4.527
4.525
4.521
4.514
f1 (ppm)

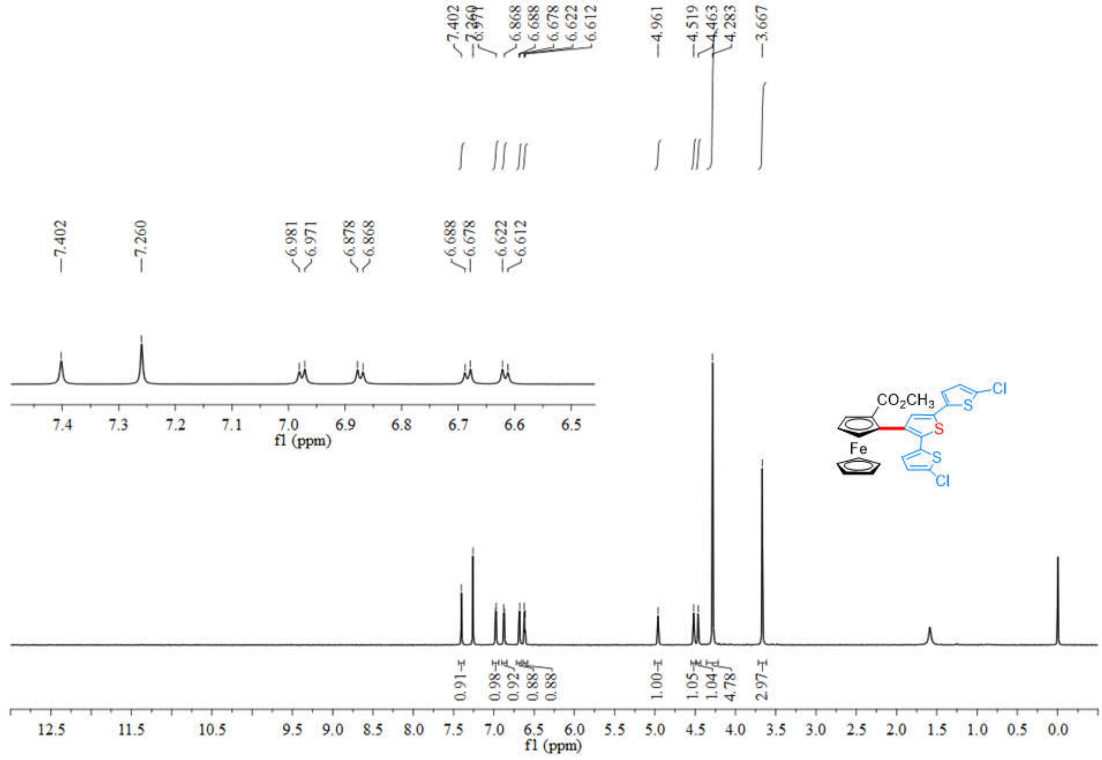

171.667
149.271
149.033
141.323
132.811
129.950
128.904
128.351
111.925
111.696
106.978
105.478
85.131
77.160
71.157
70.742
70.385
70.101
51.577
141.934
141.323
132.811
129.950
128.904
128.351
111.925
111.696
106.978
105.478
74.506
71.157
70.742
70.385
70.101
CO2CH3
Fe
S
O
O
f1 (ppm)

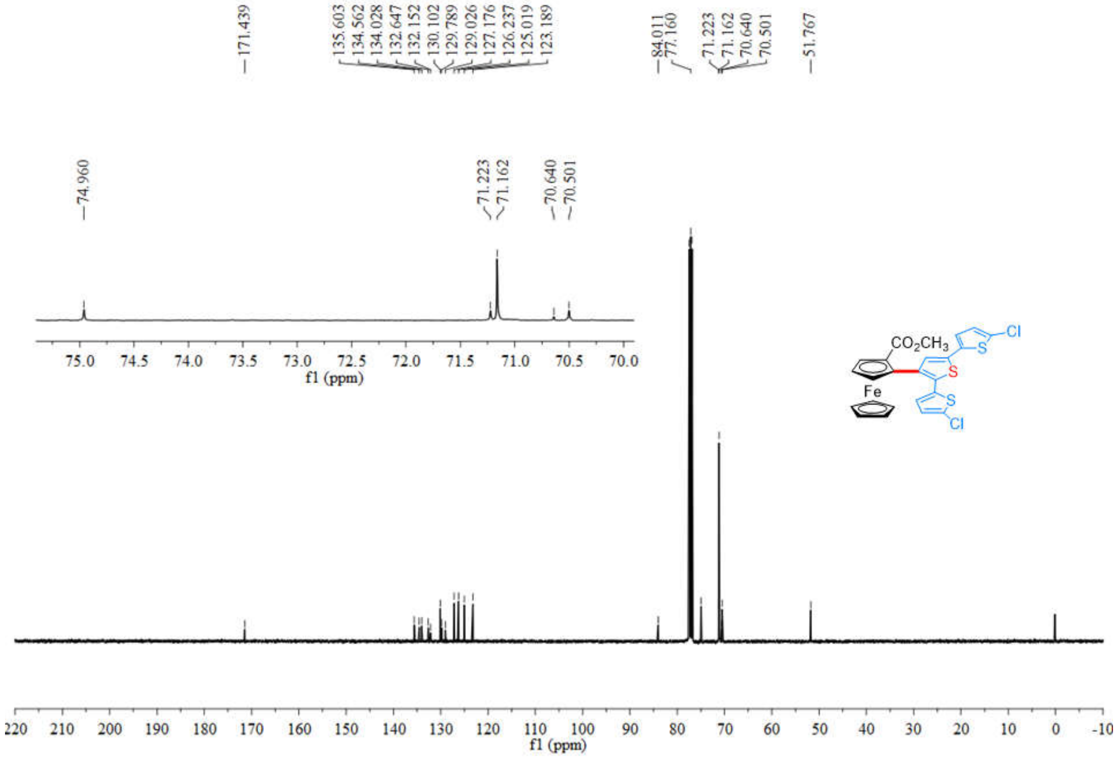

7.499
7.264
7.260
7.252
7.249
7.236
7.233
7.227
7.224
7.115
7.112
7.103
7.100
7.073
7.064
7.060
7.051
6.877
6.868
6.865
6.855
6.823
6.820
6.814
6.811
4.944
4.940
4.937
4.933
4.497
4.477
4.285
3.621
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)
4.504
4.497
4.491
4.483
4.479
4.477
4.473
5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40
f1 (ppm)
CO_2CH_3
S
S
S
Fe
0.96
1.39
1.02
0.91
1.07
1.09
0.97
1.00
1.21
1.06
4.67
3.29
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

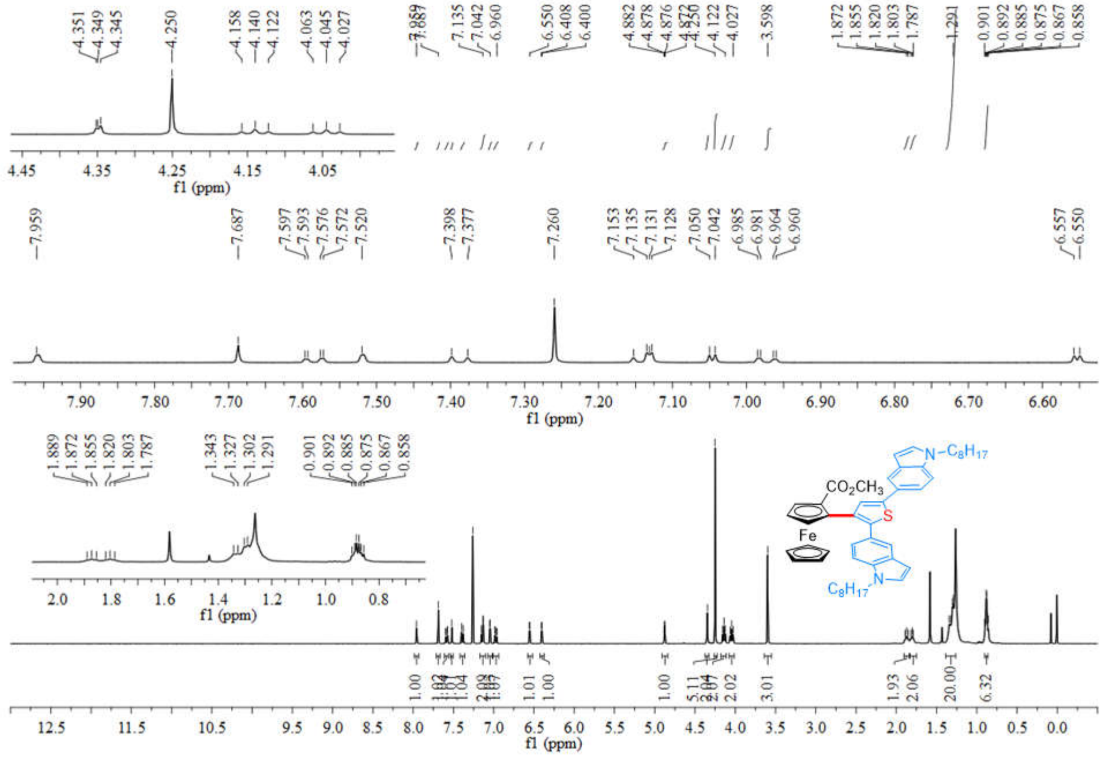

171.611
137.254
136.112
133.614
133.393
132.660
129.935
128.066
127.160
125.789
125.320
124.563
123.932
84.727
77.160
71.118
70.884
70.805
70.228
51.655
74.931
71.118
70.884
70.805
70.228
75.0 74.5 74.0 73.5 73.0 72.5 72.0 71.5 71.0 70.5 70.0
f1 (ppm)
CO_2CH_3
S
S
S
Fe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.385
7.260
6.990
6.701
6.579
6.506
6.497
4.939
4.934
4.929
4.485
4.478
4.272
3.636
2.511
2.359
7.385
7.260
6.998
6.990
6.701
6.699
6.692
6.690
6.588
6.579
6.508
6.506
6.499
6.497
7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70 6.60 6.50
f1 (ppm)
4.491
4.485
4.480
4.478
4.470
4.55 4.50 4.45 4.40 4.35
f1 (ppm)
CO2CH3
CH3
S
Fe
S
S
CH3
0.95
1.01
1.04
0.97
1.05
1.00
2.14
4.81
3.17
3.15
3.21
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

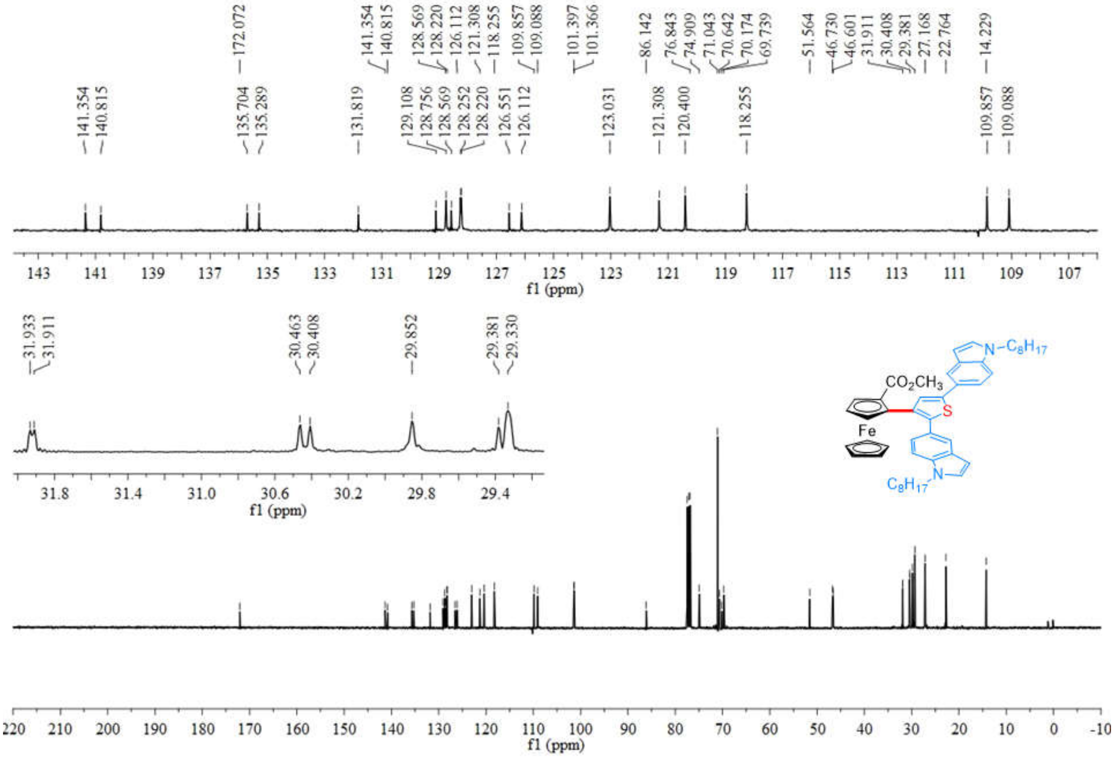

171.757
139.885
139.237
133.231
132.717
132.611
129.299
126.143
125.624
125.403
123.628
84.886
77.160
71.078
70.827
70.709
70.145
51.690
15.597
15.435
139.885
139.237
135.019
133.865
133.231
132.717
132.611
129.299
126.143
125.624
125.403
123.628
142 140 138 136 134 132 130 128 126 124 122
f1 (ppm)
74.967
71.078
70.827
70.709
70.145
75.5 74.5 73.5 72.5 71.5 70.5 69.5
f1 (ppm)
CO2CH3
CH3
S
Fe
S
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.402
7.260
6.971
6.868
6.688
6.678
6.622
6.612
4.961
4.519
4.463
4.283
3.667
7.402
7.260
6.981
6.971
6.878
6.868
6.688
6.678
6.622
6.612
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f1 (ppm)
CO_2CH_3
Cl
S
Fe
S
Cl
0.91
0.98
0.92
0.88
0.88
1.00
1.05
1.04
4.78
2.97
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

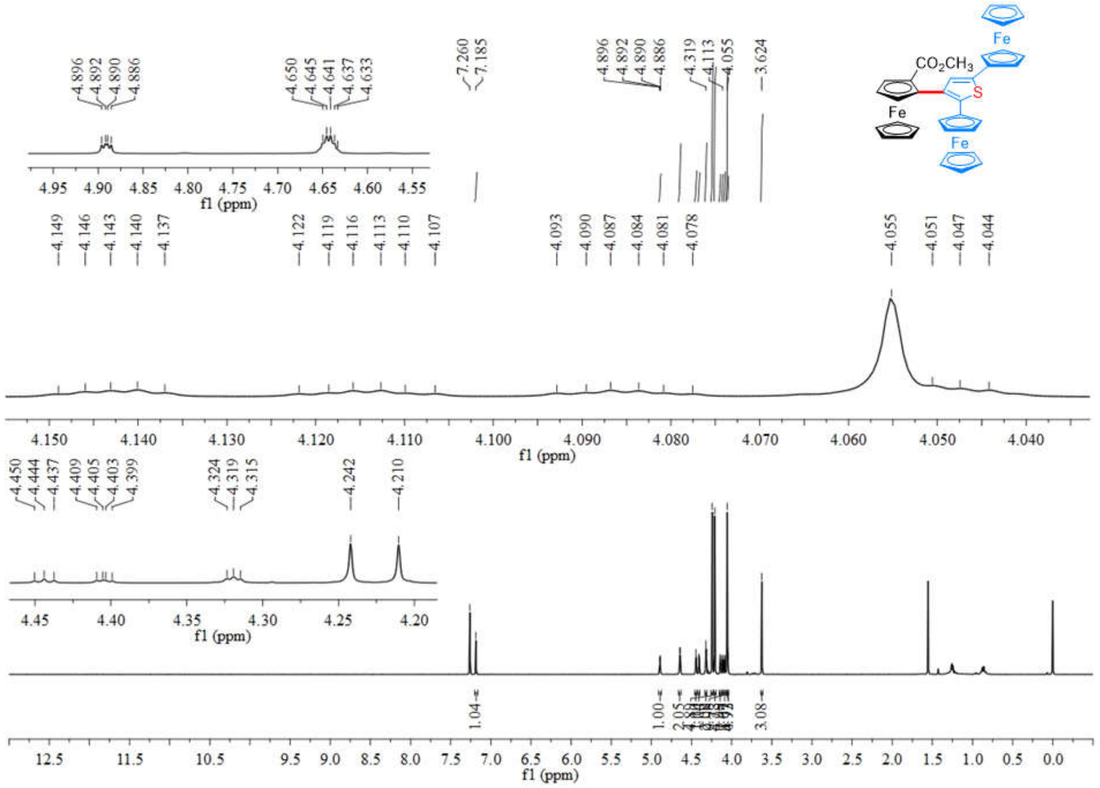

171.439
135.603
134.562
134.028
132.647
132.152
130.102
129.789
129.026
127.176
126.237
125.019
123.189
84.011
77.160
71.223
71.162
70.640
70.501
51.767
74.960
71.223
71.162
70.640
70.501
75.0
74.5
74.0
73.5
73.0
72.5
72.0
71.5
71.0
70.5
70.0
f1 (ppm)
CO_2CH_3
Cl
S
Fe
S
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4.351
4.349
4.345
4.250
4.158
4.140
4.122
4.063
4.045
4.027
4.45
4.35
4.25
4.15
4.05
f1 (ppm)
7.959
7.687
7.135
7.042
6.960
6.550
6.408
6.400
4.882
4.878
4.876
4.872
4.250
4.122
4.027
3.598
1.872
1.855
1.820
1.803
1.787
1.291
0.901
0.892
0.885
0.875
0.867
0.858
7.959
7.687
7.597
7.593
7.576
7.572
7.520
7.398
7.377
7.260
7.153
7.135
7.131
7.128
7.050
7.042
6.985
6.981
6.964
6.960
6.557
6.550
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
6.60
f1 (ppm)
1.889
1.872
1.855
1.820
1.803
1.787
1.343
1.327
1.302
1.291
0.901
0.892
0.885
0.875
0.867
0.858
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f1 (ppm)
CO2CH3
Fe
S
N–C8H17
C8H17–N
1.00
1.02
1.04
1.04
2.08
1.05
1.01
1.00
1.00
5.11
2.04
2.07
2.02
3.01
1.93
2.06
20.00
6.32
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



172.072
141.354
140.815
128.569
128.220
126.112
121.308
118.255
109.857
109.088
101.397
101.366
86.142
76.843
74.909
71.043
70.642
70.174
69.739
51.564
46.730
46.601
31.911
30.408
29.381
27.168
22.764
14.229
141.354
140.815
135.704
135.289
131.819
129.108
128.756
128.569
128.252
128.220
126.551
126.112
123.031
121.308
120.400
118.255
109.857
109.088
143
141
139
137
135
133
131
129
127
125
123
121
119
117
115
113
111
109
107
f1 (ppm)
31.933
31.911
30.463
30.408
29.852
29.381
29.330
31.8
31.4
31.0
30.6
30.2
29.8
29.4
f1 (ppm)
CO2CH3
Fe
S
N–C8H17
C8H17–N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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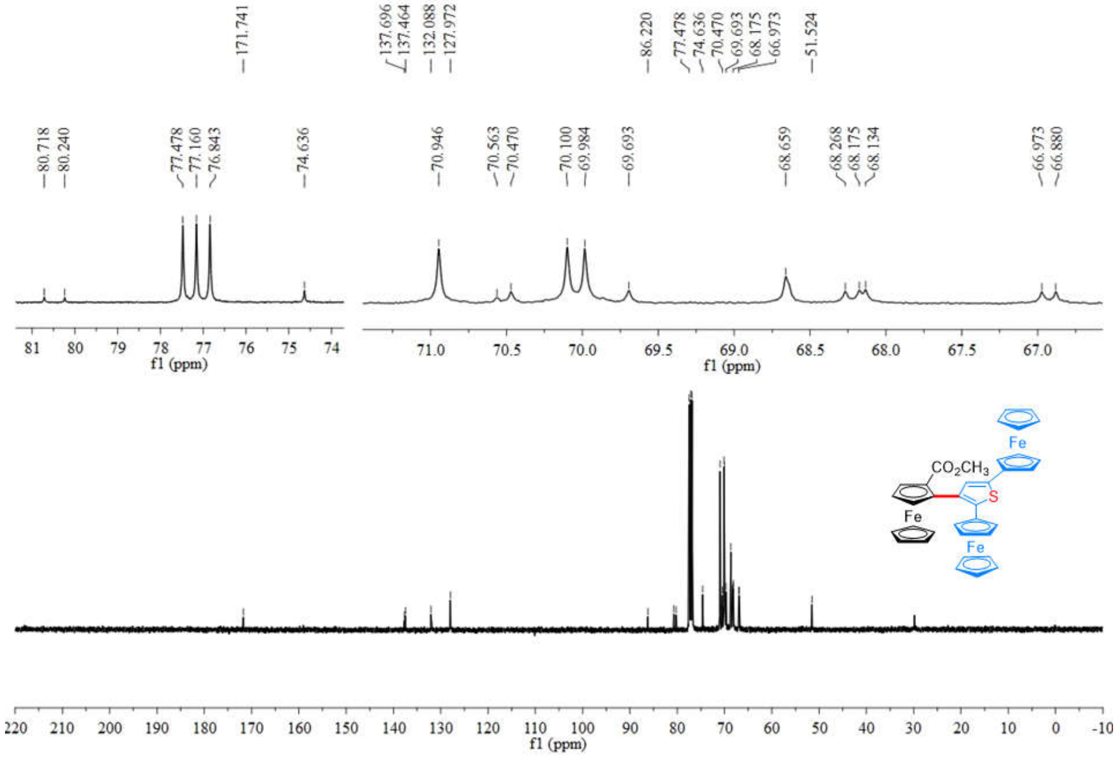
4.892
4.890
4.886
4.650
4.645
4.641
4.637
4.633
4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55
f1 (ppm)
7.260
7.185
4.896
4.892
4.890
4.886
4.319
4.113
4.055
3.624
CO$_2$CH$_3$
Fe
Fe
Fe
S
4.149
4.146
4.143
4.140
4.137
4.122
4.119
4.116
4.113
4.110
4.107
4.093
4.090
4.087
4.084
4.081
4.078
4.055
4.051
4.047
4.044
4.150 4.140 4.130 4.120 4.110 4.100 4.090 4.080 4.070 4.060 4.050 4.040
f1 (ppm)
4.450
4.444
4.437
4.409
4.405
4.403
4.399
4.324
4.319
4.315
4.242
4.210
4.45 4.40 4.35 4.30 4.25 4.20
f1 (ppm)
1.04
1.00
2.05
3.08
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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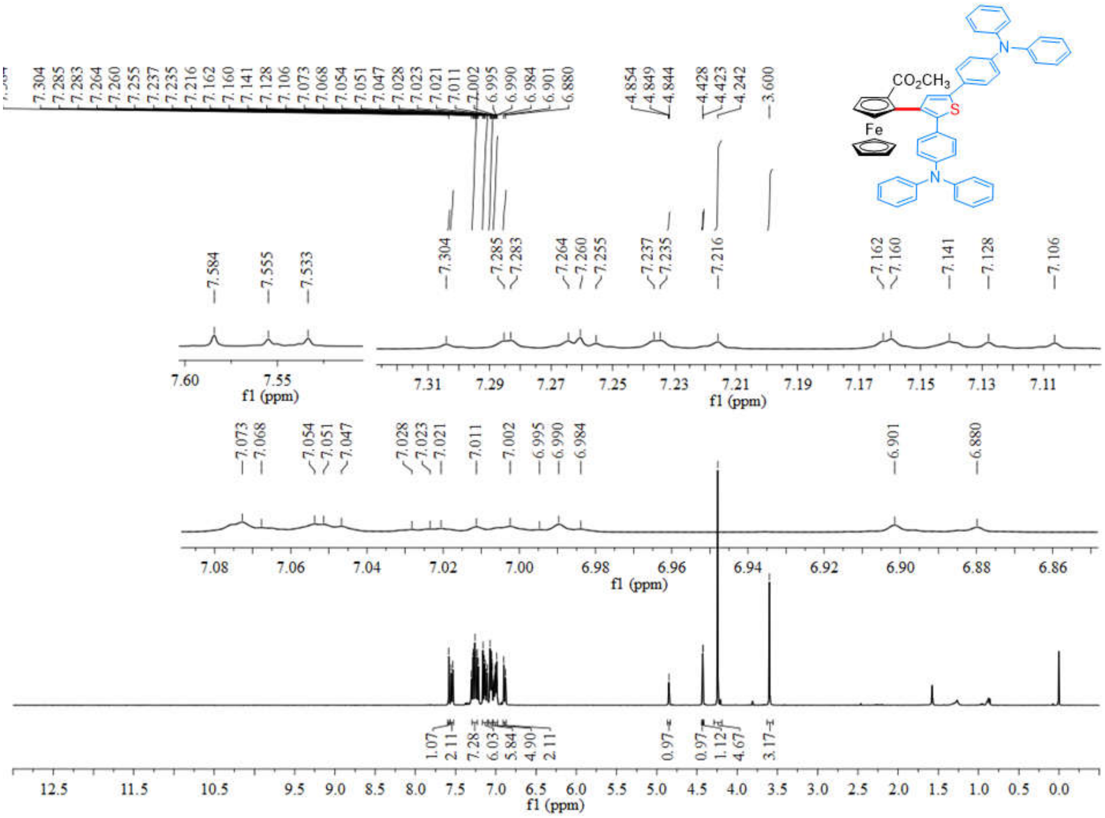
137.696
137.464
132.088
127.972
86.220
77.478
74.636
70.470
69.693
68.175
66.973
51.524
80.718
80.240
77.478
77.160
76.843
74.636
81 80 79 78 77 76 75 74
f1 (ppm)
70.946
70.563
70.470
70.100
69.984
69.693
68.659
68.268
68.175
68.134
66.973
66.880
71.0 70.5 70.0 69.5 69.0 68.5 68.0 67.5 67.0
f1 (ppm)
CO$_2$CH$_3$
Fe
Fe
Fe
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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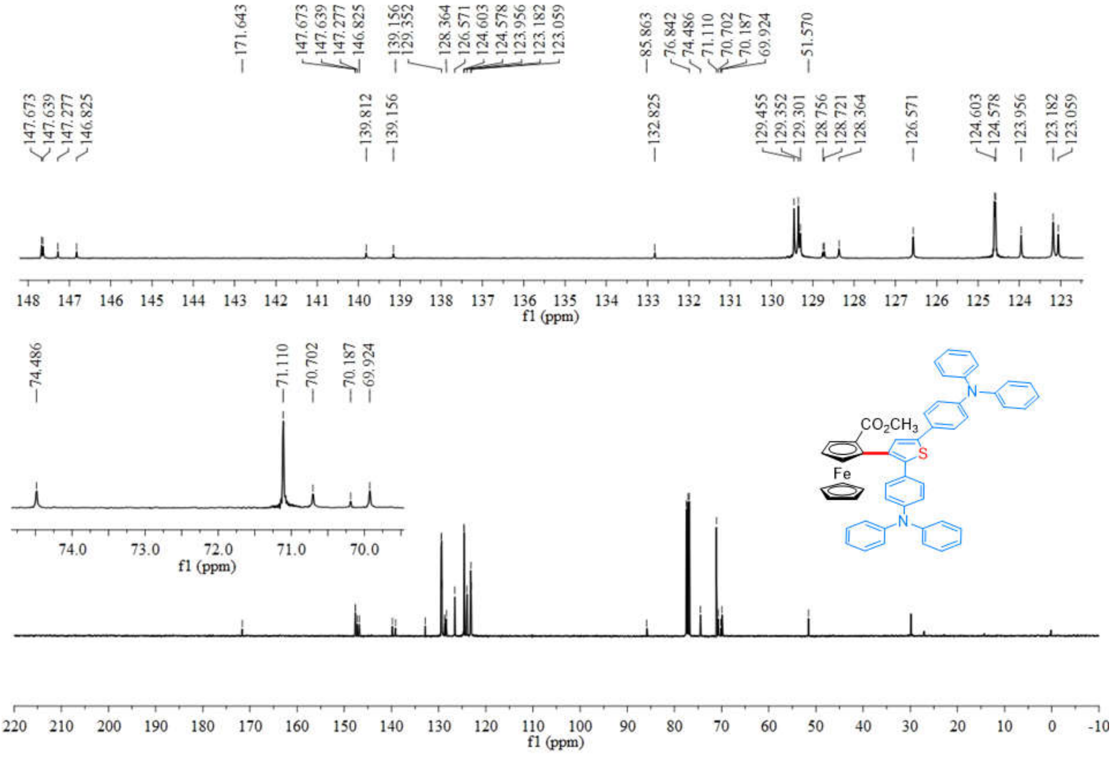
7.283
7.264
7.260
7.255
7.237
7.235
7.216
7.162
7.160
7.141
7.128
7.106
7.073
7.068
7.054
7.051
7.047
7.028
7.023
7.021
7.011
7.002
6.995
6.990
6.984
6.901
6.880
4.854
4.849
4.844
4.428
4.423
4.242
3.600
CO₂CH₃
Fe
S
N
N
7.584
7.555
7.533
7.60
7.55
f1 (ppm)
7.31
7.29
7.27
7.25
7.23
7.21
7.19
7.17
7.15
7.13
7.11
f1 (ppm)
7.08
7.06
7.04
7.02
7.00
6.98
6.96
6.94
6.92
6.90
6.88
6.86
f1 (ppm)
1.07
2.11
7.28
6.03
5.84
4.90
2.11
0.97
0.97
1.12
4.67
3.17
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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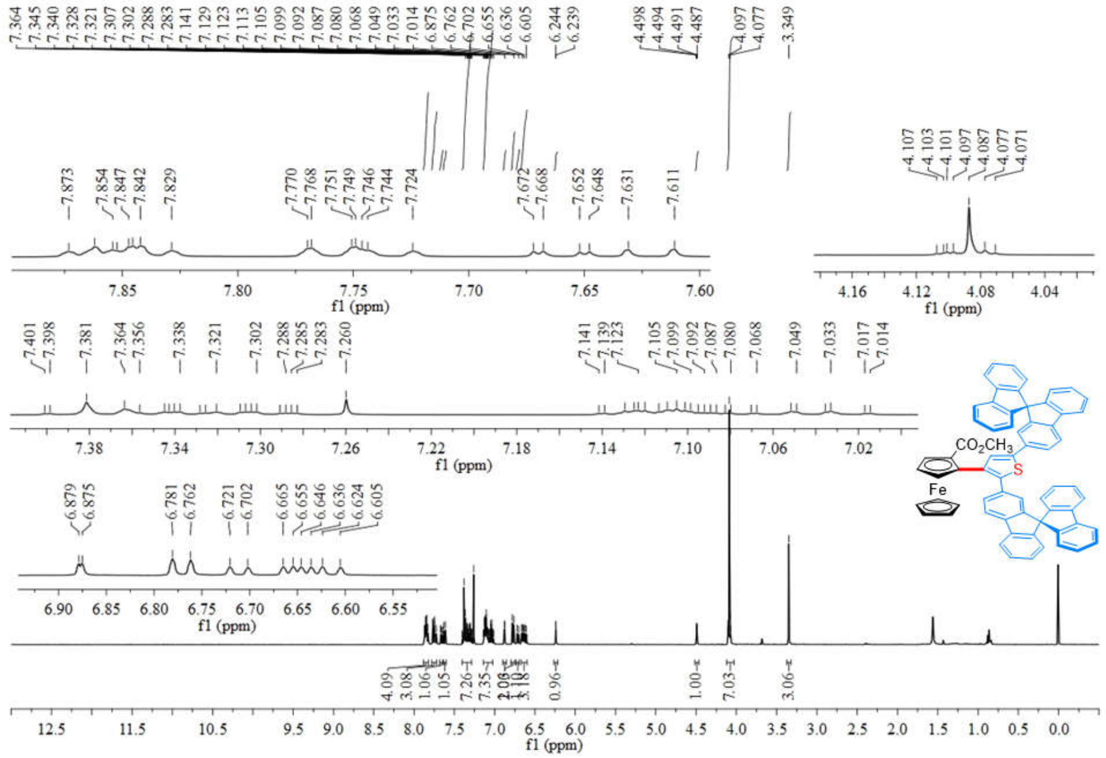
146.825
139.156
129.352
128.364
126.571
124.603
124.578
123.956
123.182
123.059
85.863
76.842
74.486
71.110
70.702
70.187
69.924
51.570
147.673
147.639
147.277
146.825
139.812
139.156
132.825
129.455
129.352
129.301
128.756
128.721
128.364
126.571
124.603
124.578
123.956
123.182
123.059
148
147
146
145
144
143
142
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
f1 (ppm)
74.486
71.110
70.702
70.187
69.924
74.0
73.0
72.0
71.0
70.0
f1 (ppm)
CO₂CH₃
Fe
S
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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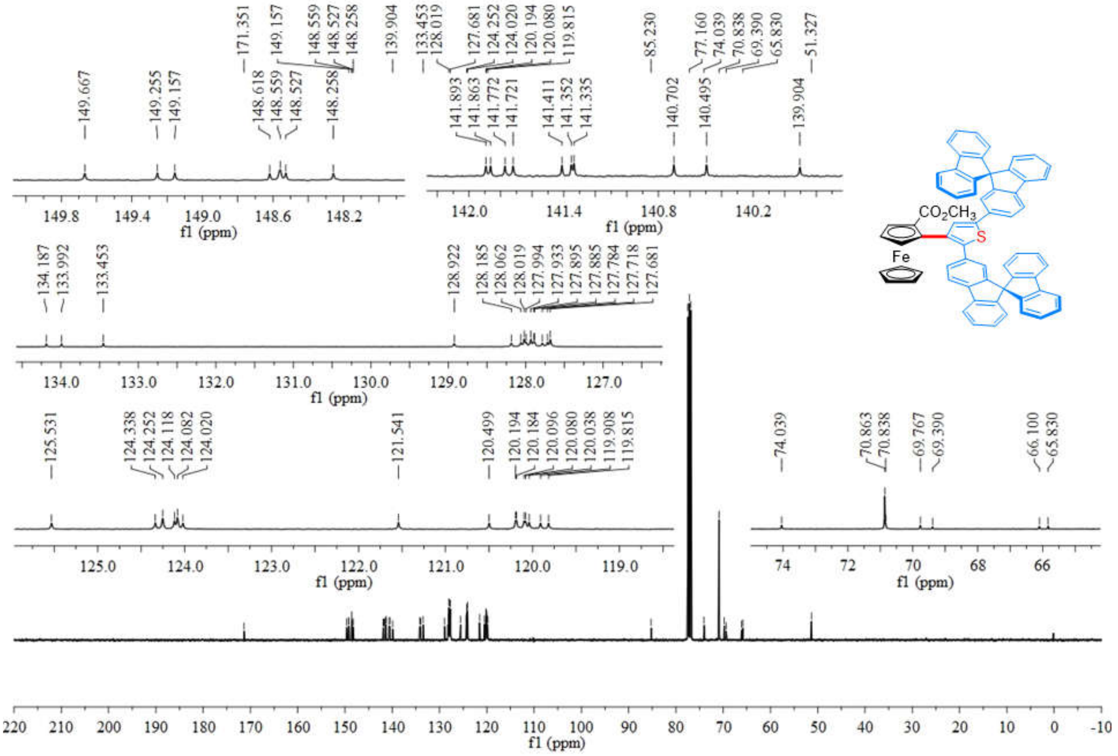
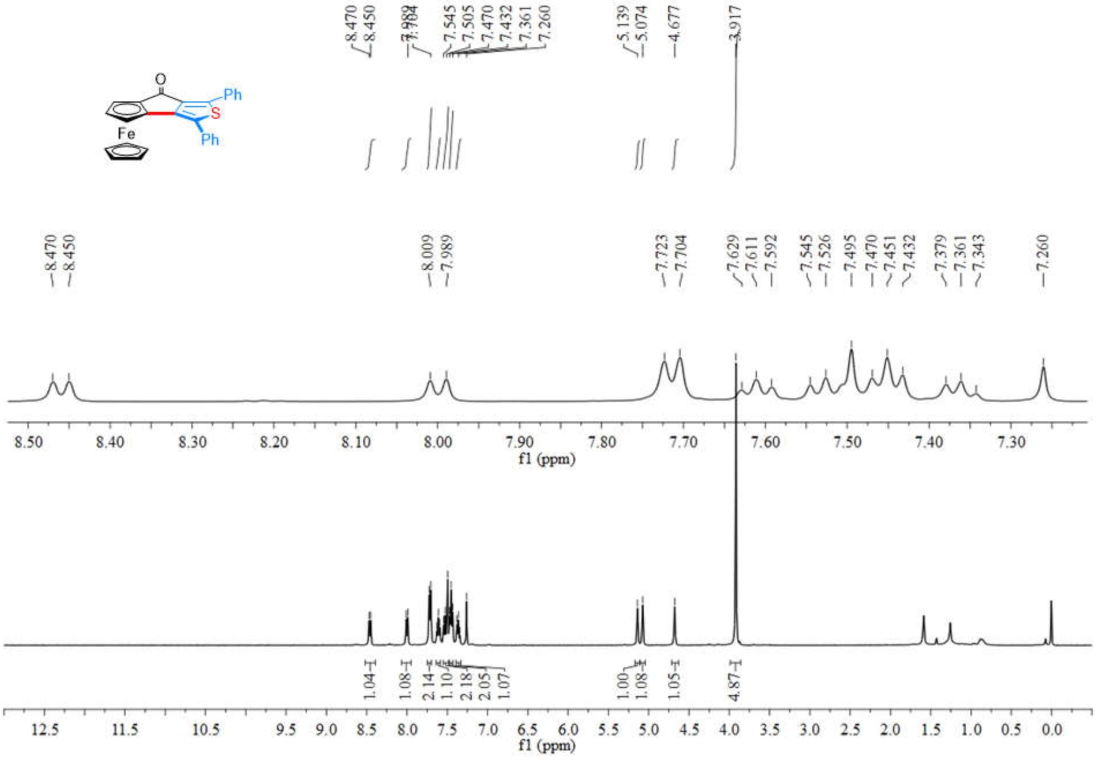
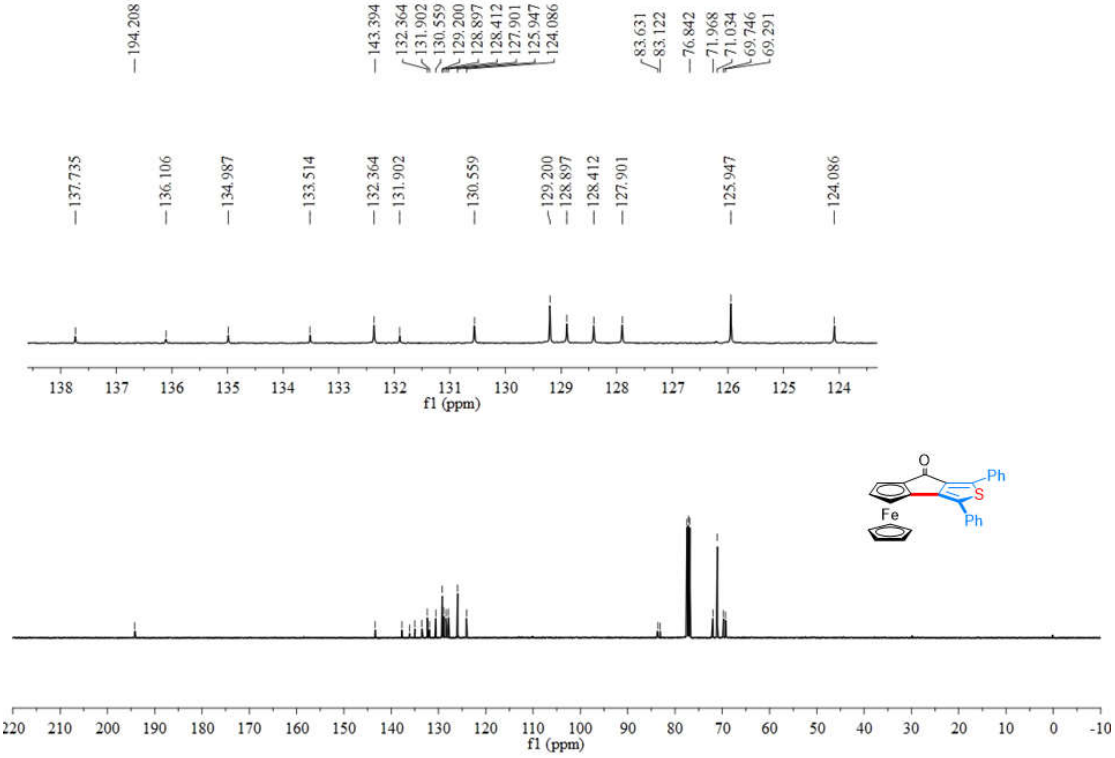
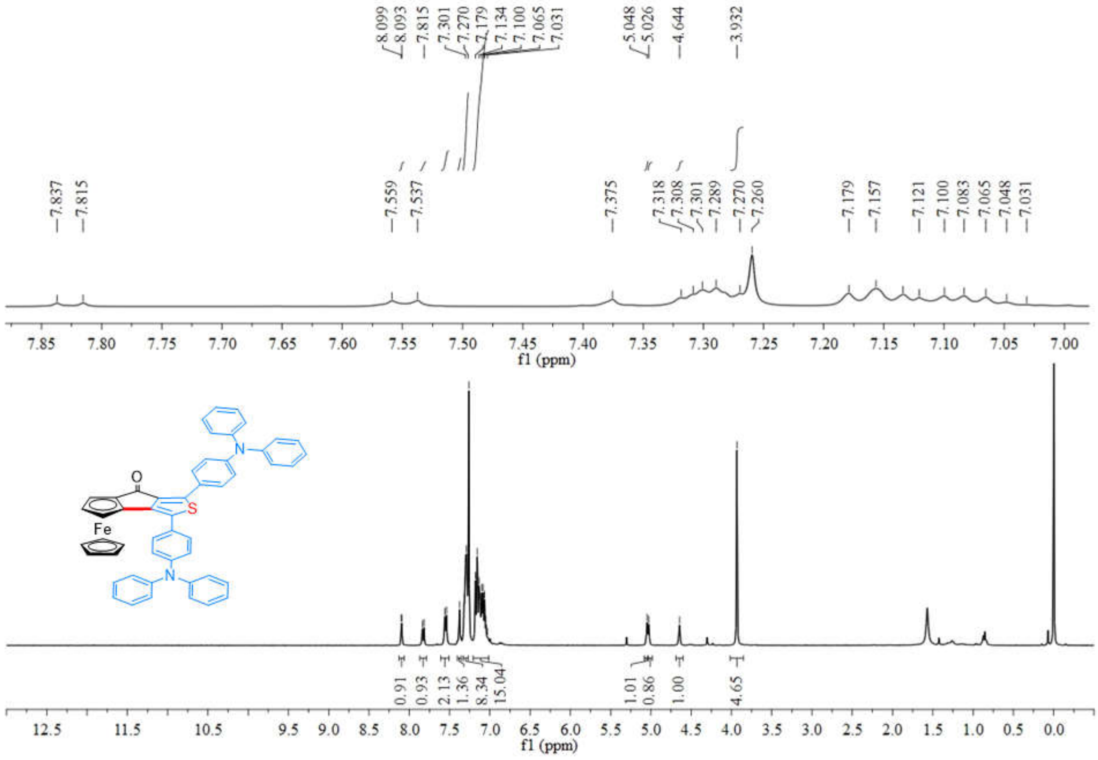
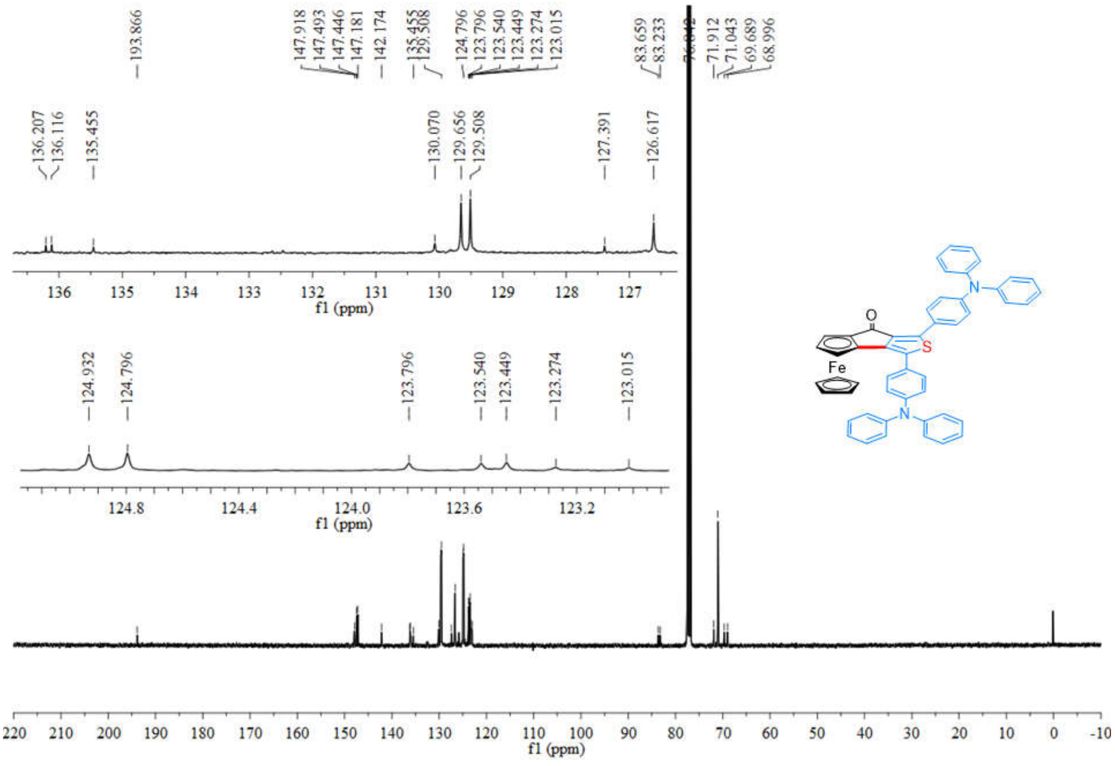
7.340
7.328
7.321
7.307
7.302
7.288
7.283
7.141
7.129
7.123
7.113
7.105
7.099
7.092
7.087
7.080
7.068
7.049
7.033
7.014
6.875
6.762
6.702
6.655
6.636
6.605
6.244
6.239
4.498
4.494
4.491
4.487
4.097
4.077
3.349
7.873
7.854
7.847
7.842
7.829
7.770
7.768
7.751
7.749
7.746
7.744
7.724
7.672
7.668
7.652
7.648
7.631
7.611
7.85
7.80
7.75
7.70
7.65
7.60
f1 (ppm)
4.107
4.103
4.101
4.097
4.087
4.077
4.071
4.16
4.12
4.08
4.04
f1 (ppm)
7.401
7.398
7.381
7.364
7.356
7.338
7.321
7.302
7.288
7.285
7.283
7.260
7.141
7.139
7.123
7.105
7.099
7.092
7.087
7.080
7.068
7.049
7.033
7.017
7.014
7.38
7.34
7.30
7.26
7.22
7.18
7.14
7.10
7.06
7.02
f1 (ppm)
6.879
6.875
6.781
6.762
6.721
6.702
6.665
6.655
6.646
6.636
6.624
6.605
6.90
6.85
6.80
6.75
6.70
6.65
6.60
6.55
f1 (ppm)
CO$_2$CH$_3$
S
Fe
4.09
3.08
1.06
1.05
7.26
7.35
2.08
3.10
3.18
0.96
1.00
7.03
3.06
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

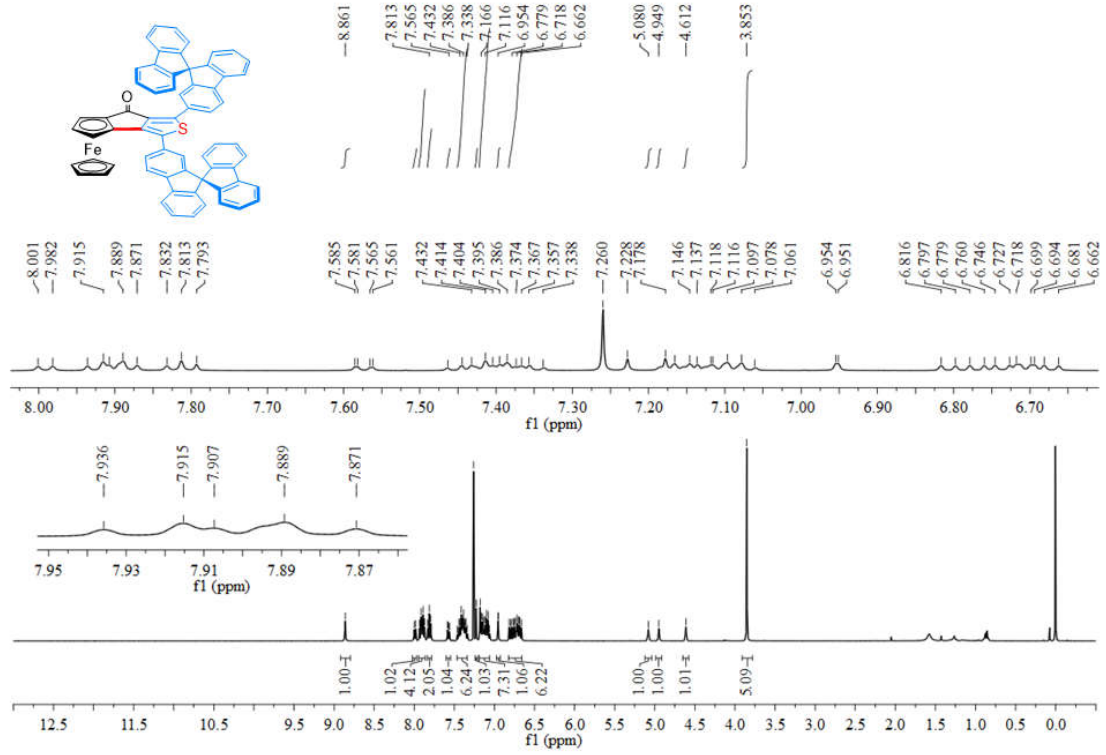

171.351
149.157
148.559
148.527
148.258
139.904
133.453
128.019
127.681
124.252
124.020
120.194
120.080
119.815
85.230
77.160
74.039
70.838
69.390
65.830
51.327
149.667
149.255
149.157
148.618
148.559
148.527
148.258
149.8
149.4
149.0
148.6
148.2
f1 (ppm)
141.893
141.863
141.772
141.721
141.411
141.352
141.335
140.702
140.495
139.904
142.0
141.4
140.8
140.2
f1 (ppm)
CO$_2$CH$_3$
S
Fe
134.187
133.992
133.453
128.922
128.185
128.062
128.019
127.994
127.933
127.895
127.885
127.784
127.718
127.681
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
125.531
124.338
124.252
124.118
124.082
124.020
121.541
120.499
120.194
120.184
120.096
120.080
120.038
119.908
119.815
125.0
124.0
123.0
122.0
121.0
120.0
119.0
f1 (ppm)
74.039
70.863
70.838
69.767
69.390
66.100
65.830
74
72
70
68
66
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Ph
S
Ph
Fe
8.470
8.450
7.989
7.704
7.545
7.505
7.470
7.432
7.361
7.260
5.139
5.074
4.677
3.917
8.470
8.450
8.009
7.989
7.723
7.704
7.629
7.611
7.592
7.545
7.526
7.495
7.470
7.451
7.432
7.379
7.361
7.343
7.260
8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30
f1 (ppm)
1.04
1.08
2.14
1.10
2.18
2.05
1.07
1.00
1.08
1.05
4.87
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

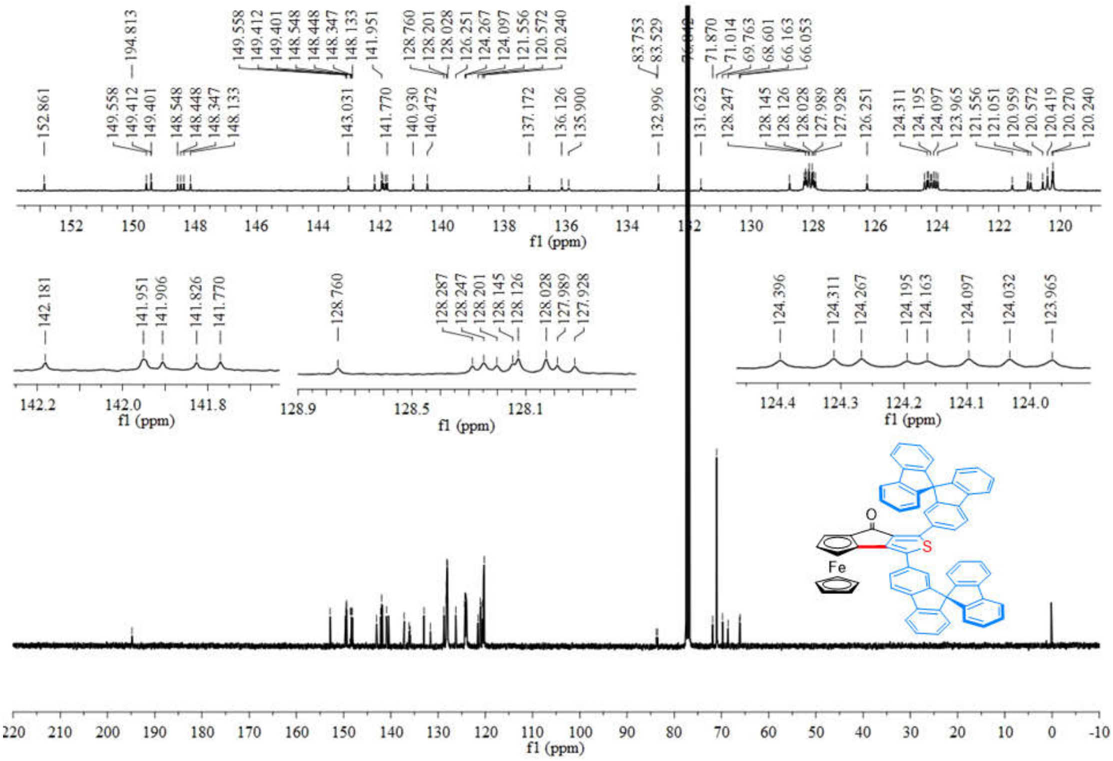

194.208
143.394
132.364
131.902
130.559
129.200
128.897
128.412
127.901
125.947
124.086
83.631
83.122
76.842
71.968
71.034
69.746
69.291
137.735
136.106
134.987
133.514
132.364
131.902
130.559
129.200
128.897
128.412
127.901
125.947
124.086
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
O
Ph
S
Ph
Fe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.099
8.093
7.815
7.301
7.270
7.179
7.134
7.100
7.065
7.031
5.048
5.026
4.644
3.932
7.837
7.815
7.559
7.537
7.375
7.318
7.308
7.301
7.289
7.270
7.260
7.179
7.157
7.121
7.100
7.083
7.065
7.048
7.031
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
O
Fe
S
N
0.91
0.93
2.13
1.36
8.34
15.04
1.01
0.86
1.00
4.65
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

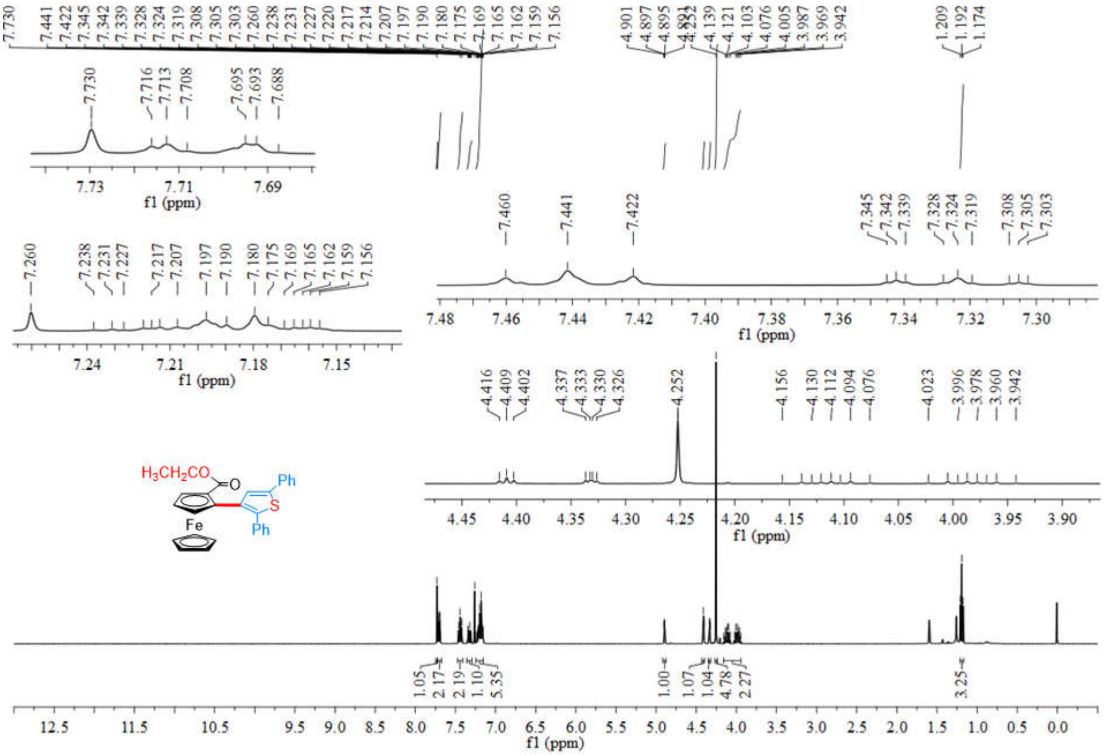

193.866
147.918
147.493
147.446
147.181
142.174
135.455
129.508
124.796
123.796
123.540
123.449
123.274
123.015
83.659
83.233
76.842
71.912
71.043
69.689
68.996
136.207
136.116
135.455
130.070
129.656
129.508
127.391
126.617
136 135 134 133 132 131 130 129 128 127
f1 (ppm)
124.932
124.796
123.796
123.540
123.449
123.274
123.015
124.8 124.4 124.0 123.6 123.2
f1 (ppm)
O
Fe
S
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

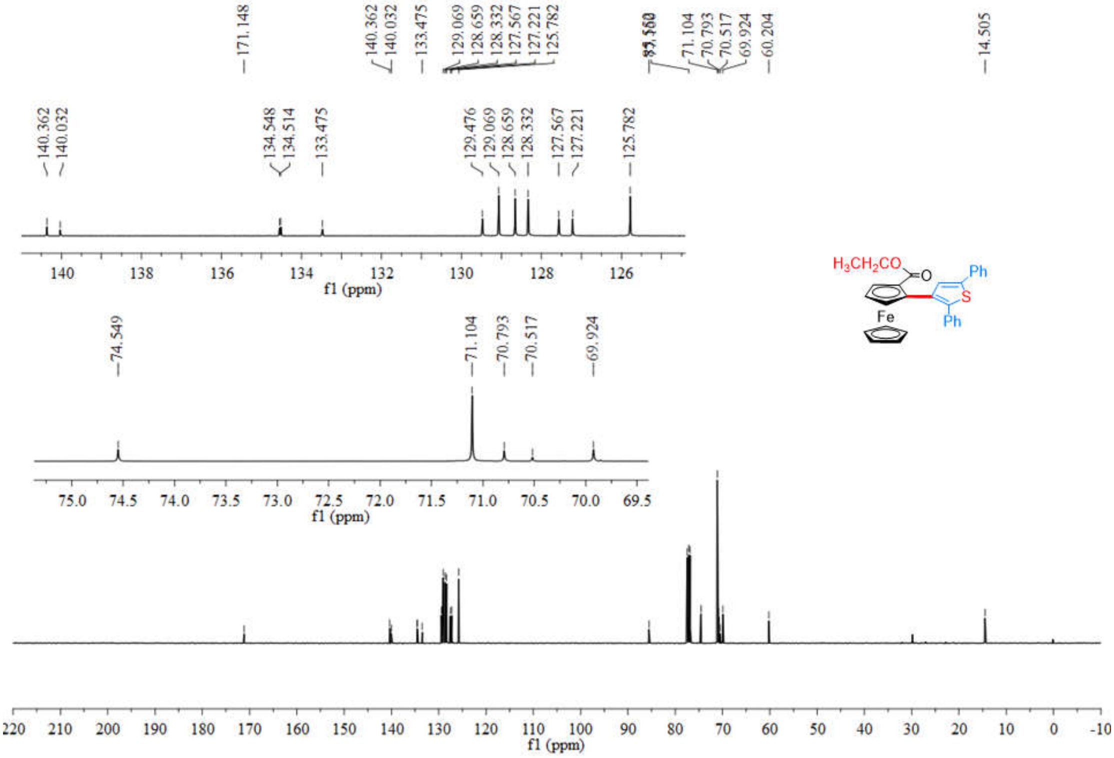


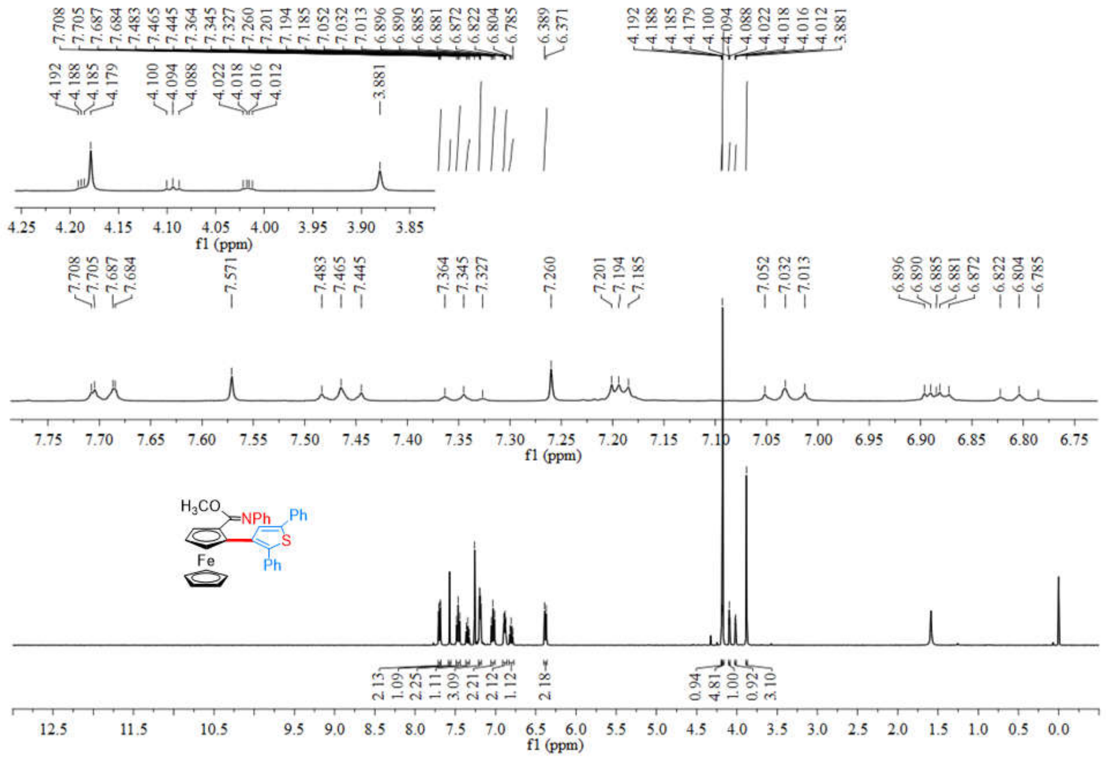
O
Fe
S
8.861
7.813
7.565
7.432
7.386
7.338
7.166
7.116
6.954
6.779
6.718
6.662
5.080
4.949
4.612
3.853
8.001
7.982
7.915
7.889
7.871
7.832
7.813
7.793
7.585
7.581
7.565
7.561
7.432
7.414
7.404
7.395
7.386
7.374
7.367
7.357
7.338
7.260
7.228
7.178
7.146
7.137
7.118
7.116
7.097
7.078
7.061
6.954
6.951
6.816
6.797
6.779
6.760
6.746
6.727
6.718
6.699
6.694
6.681
6.662
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
f1 (ppm)
7.936
7.915
7.907
7.889
7.871
7.95
7.93
7.91
7.89
7.87
f1 (ppm)
1.00
1.02
4.12
2.05
1.04
6.24
1.03
7.31
1.06
6.22
1.00
1.00
1.01
5.09
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

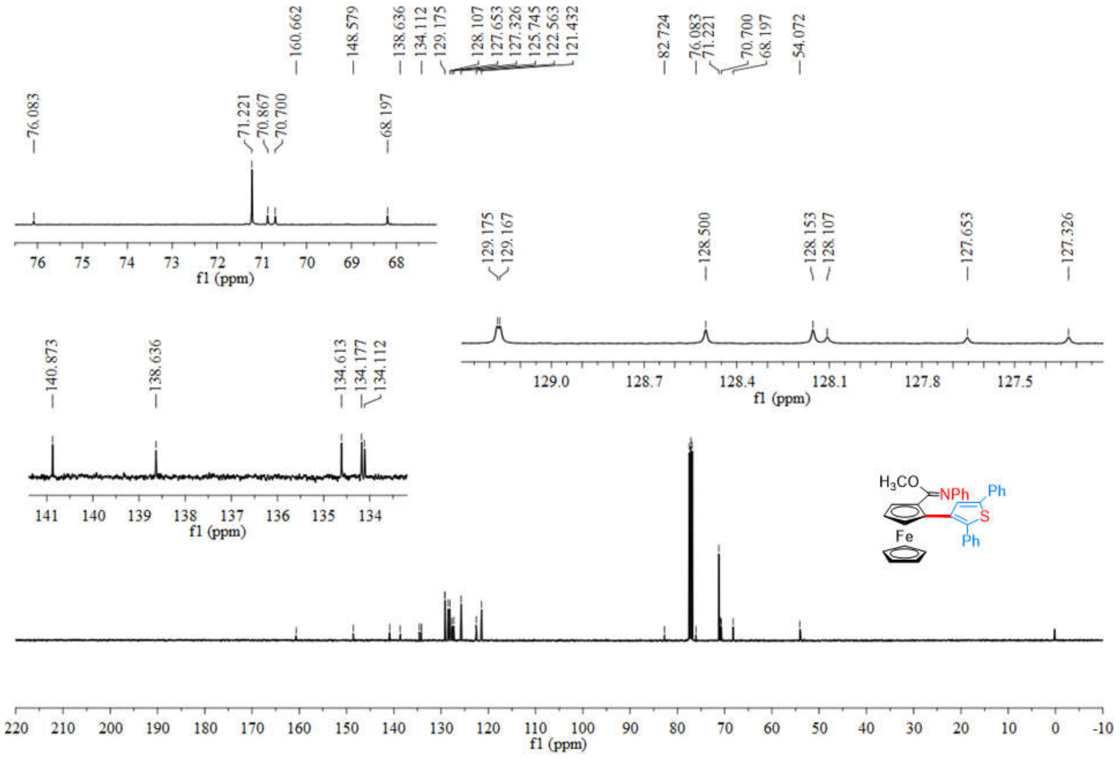


194.813
149.558
149.412
149.401
148.548
148.448
148.347
148.133
141.951
128.760
128.201
128.028
126.251
124.267
124.097
121.556
120.572
120.240
83.753
83.529
76.812
71.870
71.014
69.763
68.601
66.163
66.053
152.861
149.558
149.412
149.401
148.548
148.448
148.347
148.133
143.031
141.770
140.930
140.472
137.172
136.126
135.900
132.996
131.623
128.247
128.145
128.126
128.028
127.989
127.928
126.251
124.311
124.195
124.097
123.965
121.556
121.051
120.959
120.572
120.419
120.270
120.240
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
f1 (ppm)
142.181
141.951
141.906
141.826
141.770
142.2
142.0
141.8
f1 (ppm)
128.760
128.287
128.247
128.201
128.145
128.126
128.028
127.989
127.928
128.9
128.5
128.1
f1 (ppm)
124.396
124.311
124.267
124.195
124.163
124.097
124.032
123.965
124.4
124.3
124.2
124.1
124.0
f1 (ppm)
O
Fe
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.730
7.441
7.422
7.345
7.342
7.339
7.328
7.324
7.319
7.308
7.305
7.303
7.260
7.238
7.231
7.227
7.220
7.217
7.214
7.207
7.197
7.190
7.180
7.175
7.169
7.165
7.162
7.159
7.156
4.901
4.897
4.895
4.891
4.252
4.139
4.121
4.103
4.076
4.005
3.987
3.969
3.942
1.209
1.192
1.174
7.716
7.713
7.708
7.695
7.693
7.688
7.460
4.416
4.409
4.402
4.337
4.333
4.330
4.326
4.156
4.130
4.112
4.094
4.023
3.996
3.978
3.960
1.05
2.17
2.19
1.10
5.35
1.00
1.07
1.04
4.78
2.27
3.25
H_3CH_2CO
O
Ph
S
Ph
Fe
f1 (ppm)


171.148
140.362
140.032
134.548
134.514
133.475
129.476
129.069
128.659
128.332
127.567
127.221
125.782
85.160
74.549
71.104
70.793
70.517
69.924
60.204
14.505
H_3CH_2CO
O
Ph
S
Ph
Fe
f1 (ppm)


7.708
7.705
7.687
7.684
7.483
7.465
7.445
7.364
7.345
7.327
7.260
7.201
7.194
7.185
7.052
7.032
7.013
6.896
6.890
6.885
6.881
6.872
6.822
6.804
6.785
6.389
6.371
4.192
4.188
4.185
4.179
4.100
4.094
4.088
4.022
4.018
4.016
4.012
3.881
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85
f1 (ppm)
7.571
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)
H3CO
NPh
Ph
S
Ph
Fe
2.13
1.09
2.25
1.11
3.09
2.21
2.12
1.12
2.18
0.94
4.81
1.00
0.92
3.10
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.662
148.579
138.636
134.112
129.175
128.107
127.653
127.326
125.745
122.563
121.432
82.724
76.083
71.221
70.700
68.197
54.072
76.083
71.221
70.867
70.700
68.197
76 75 74 73 72 71 70 69 68
f1 (ppm)
129.175
129.167
128.500
128.153
128.107
127.653
127.326
129.0 128.7 128.4 128.1 127.8 127.5
f1 (ppm)
140.873
138.636
134.613
134.177
134.112
141 140 139 138 137 136 135 134
f1 (ppm)
H3CO
NPh
Ph
S
Ph
Fe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)