

Supporting Information for:

**Gold-Catalyzed C-H Bond Functionalization of Metallocenes: Synthesis of Densely
Functionalized Ferrocene Derivatives**

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1. General Considerations.

All reactions were carried out under nitrogen using standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 . The solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial supplier and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ^1H NMR (300, 400 MHz) and ^{13}C NMR (75.5 and 100 MHz) spectra were recorded at room temperature in CDCl_3 on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts are given in ppm relative to TMS (^1H , 0.0 ppm) or CDCl_3 (^{13}C , 77.0 ppm). Carbon multiplicities were assigned by DEPT techniques. 2D NMR experiments were recorded on a Bruker AVANCE-400 MHz. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. This study was carried out using vinyl diazoacetates **1a-f** and metallocenes **2** and **4** (Figure S1). Vinyl diazoacetates **1a-f** were prepared according to well-known procedures previously described in the literature. $[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ and deuterated ferrocene were prepared according to literature procedures. All other reagents used in this work were of the best commercial grade available and used without further purification.

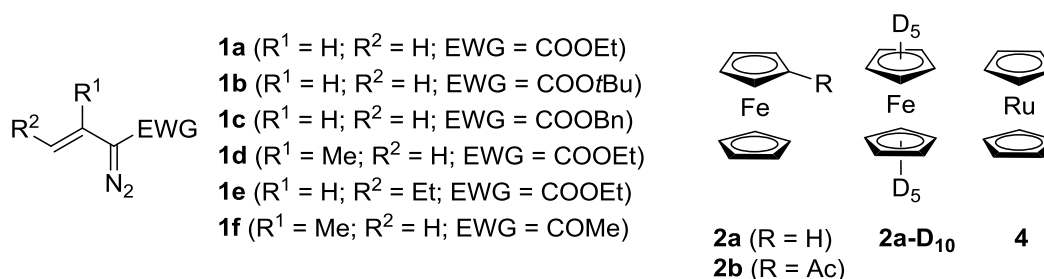
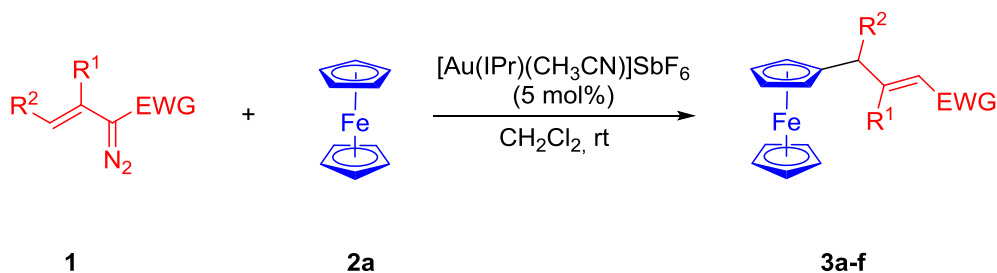


Figure S1. Starting materials used in this work

2. General Procedure for the Synthesis of Compounds 3a-f



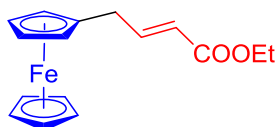
[Au(IPr)(CH₃CN)]SbF₆ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyl diazo compound **1** (0.5 mmol) and ferrocene (**2a**) (370 mg, 2 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography. Elution with hexanes/ethyl acetate (10:1) produced 2 major fractions. The first fraction was unreacted ferrocene and the second fraction was found to be pure functionalized ferrocene derivatives **3**. In some cases a third purple fraction was observed and found to correspond to the oxidation product **6** (see Section 6 of this Supporting Information).

In the case of vinyl diazo compound **1e** (EWG = COOEt, R¹ = H, R² = Et) the reaction was conducted in DCE (5 mL) at 50 °C.

3. Characterization Data of Compounds 3a-f.

Ethyl (*E*)-4-ferrocenylbut-2-enoate (**3a**)

The general procedure was followed using vinyl diazoacetate **1a** (70.1 mg). Final chromatographic purification afforded compound **3a** (112 mg, 75%).

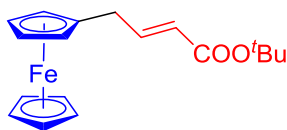


3a

¹H-NMR (300 MHz): 1.31 (t, *J* = 7.2 Hz, 3H), 3.23 (dd, *J* = 6.9 and 1.5 Hz, 2H), 4.08-4.09 (m, 2H), 4.12-4.13 (m, 2H), 4.16 (s, 5H), 4.22 (q, *J* = 7.2 Hz, 2H), 5.82 (dt, *J* = 15.6 and 1.5 Hz, 1H), 7.12 (dt, *J* = 15.6 and 6.9 Hz, 1H); ¹³C-NMR (75 MHz): 14.7 (CH₃), 32.5 (CH₂), 60.6 (CH₂), 68.1 (CH), 68.6 (CH), 69.0 (CH), 85.1 (C), 122.0 (CH), 147.8 (CH), 167.0 (C); Anal. Calc. for C₁₆H₁₈FeO₂: C 64.45, H 6.09. Found: C 64.81, H 6.13.

***tert*-Butyl (*E*)-4-ferrocenylbut-2-enoate (**3b**)**

The general procedure was followed using vinyl diazoacetate **1b** (84.1 mg). Final chromatographic purification afforded compound **3b** (76.7 mg, 47%).

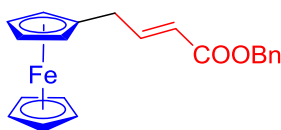


3b

¹H-NMR (300 MHz): 1.51 (s, 9H), 3.20 (dd, *J* = 6.6 and 1.5 Hz, 2H), 4.09-4.10 (m, 2H), 4.12-4.13 (m, 2H), 4.16 (s, 5H), 5.74 (dt, *J* = 15.6 and 1.5 Hz, 1H), 7.02 (dt, *J* = 15.6 and 6.6 Hz, 1H); ¹³C-NMR (75 MHz): 28.2 (CH₃), 32.0 (CH₂), 67.7 (CH), 68.3 (CH), 68.6 (CH), 80.2 (C), 85.1 (C), 123.3 (CH), 146.2 (CH), 166.0 (C); Anal. Calc. for C₁₈H₂₂FeO₂: C 66.27, H 6.80. Found: C 66.04, H 6.82.

Benzyl (*E*)-4-ferrocenylbut-2-enoate (3c**)**

The general procedure was followed using vinyl diazoacetate **1c** (101.1 mg). Final chromatographic purification afforded compound **3c** (108.1 mg, 60%).

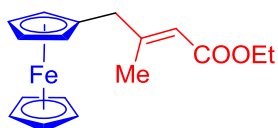


3c

¹H-NMR (300 MHz): 3.27 (dd, *J* = 6.9 and 1.5 Hz, 2H), 4.10-4.12 (m, 2H), 4.15-4.16 (m, 2H), 4.18 (s, 5H), 5.24 (s, 2H), 5.91 (dt, *J* = 15.3 and 1.5 Hz, 1H), 7.22 (dt, *J* = 15.3 and 6.9 Hz, 1H), 7.35-7.43 (m, 5H); ¹³C-NMR (75 MHz): 32.2 (CH₂), 66.2 (CH₂), 67.8 (CH), 68.3 (CH), 68.7 (CH), 84.6 (C), 121.3 (CH), 128.3 (CH), 128.6 (CH), 136.1 (C), 148.2 (CH), 166.4 (C); Anal. Calc. for C₂₁H₂₀FeO₂: C 70.02, H 5.60. Found: C 70.27, H 5.44.

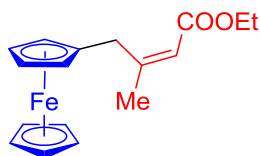
Ethyl 4-ferrocenyl-3-methylbut-2-enoate (3d**)**

The general procedure was followed using vinyl diazoacetate **1d** (77.1 mg). Final chromatographic purification afforded compounds (*E*)-**3d** (65.5 mg, 42%) and (*Z*)-**3d** (32.8 mg, 21%).



(*E*)-**3d**

$^1\text{H-NMR}$ (400 MHz): 1.25 (t, $J = 7.2$ Hz, 3H), 2.12 (s, 3H), 3.19 (s, 2H), 4.09-4.14 (m, 11H), 5.55 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz): 14.3 (CH_3), 18.8 (CH_3), 41.3 (CH_2), 59.5 (CH_2), 67.8 (CH), 68.7 (CH), 69.1 (CH), 84.4 (C), 115.9 (CH), 159.0 (C), 166.9 (C); Anal. Calc. for $\text{C}_{17}\text{H}_{20}\text{FeO}_2$: C 65.40, H 6.46. Found: C 65.12, H 6.37.

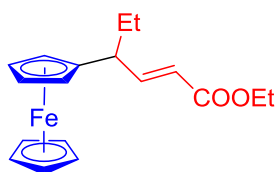


(Z)-3d

$^1\text{H-NMR}$ (400 MHz): 1.31 (t, $J = 7.2$ Hz, 3H), 1.78 (s, 3H), 3.74 (s, 2H), 4.057-4.061 (m, 2H), 4.14-4.20 (m, 9H), 5.60 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz): 14.4 (CH_3), 24.7 (CH_3), 33.0 (CH_2), 59.5 (CH_2), 67.4 (CH), 68.7 (CH), 69.0 (CH), 86.0 (C), 115.7 (CH), 158.6 (C), 166.4 (C); Anal. Calc. for $\text{C}_{17}\text{H}_{20}\text{FeO}_2$: C 65.40, H 6.46. Found: C 65.23, H 6.45.

Ethyl (*E*)-4-ferrocenylhex-2-enoate (3e)

The general procedure was followed using vinyl diazoacetate **1e** (84.1 mg). Final chromatographic purification afforded compound **3e** (19.6 mg, 12%).

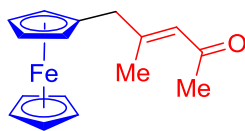


3e

$^1\text{H-NMR}$ (300 MHz): 0.92 (t, $J = 7.2$ Hz, 3H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.50-1.82 (m, 2H), 2.98-3.06 (m, 1H), 4.04-4.07 (m, 2H), 4.12-4.13 (m, 2H), 4.14 (s, 5H), 4.20 (q, $J = 7.2$ Hz, 2H), 5.85 (d, $J = 15.6$ Hz, 1H), 7.05 (dd, $J = 15.6$ and 9.0 Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz): 12.2 (CH_3), 14.3 (CH_3), 28.6 (CH_2), 43.8 (CH), 60.3 (CH_2), 66.4 (CH), 67.2 (CH), 67.3 (CH), 67.6 (CH), 68.6 (CH), 90.5 (C), 120.5 (CH), 151.5 (CH), 166.8 (C); Anal. Calc. for $\text{C}_{18}\text{H}_{22}\text{FeO}_2$: C 66.27, H 6.80. Found: C 66.65, H 7.12.

(*E*)-5-Ferrocenyl-4-methyl-3-penten-2-one (3f)

The general procedure was followed using vinyl diazoacetate **1f** (62.1 mg). Final chromatographic purification afforded compound **3f** (70.5 mg, 50%).



(*E*)-**3f**

¹H-NMR (300 MHz): 2.10 (s, 3H), 2.14 (s, 3H), 3.20 (s, 2H), 4.10 (br s, 2H), 4.14 (br s, 7H), 5.94 (s, 1H); ¹³C-NMR (75 MHz): 19.4 (CH₃), 31.8 (CH₃), 41.5 (CH₂), 67.8 (CH), 68.7 (CH), 69.1 (CH), 84.4 (C), 123.6 (CH), 157.5 (C), 199.1 (C); Anal. Calc. for C₁₆H₁₈FeO: C 68.11, H 6.43. Found: C 68.22, H 6.46.

4. General Procedure for the Synthesis of Ruthenocene Derivatives 5a,b

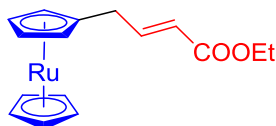


$[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyl diazo compound **1** (0.5 mmol) and ruthenocene (**4**) (460 mg, 2 mmol) in DCE (5 mL). The mixture was stirred at 50 °C until the disappearance of the starting diazo compound (monitored by TLC: 10 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2 , hexane/ethyl acetate 20:1) to yield functionalized ruthenocene derivatives **5a, b**.

5. Characterization Data of Compounds 5a, b

Ethyl (*E*)-4-ruthenocenylobut-2-enoate (**5a**)

The general procedure was followed using vinyl diazoacetate **1a** (70.1 mg). Final chromatographic purification afforded compound **5a** (42.9 mg, 25%).

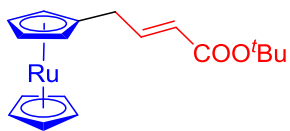


5a

$^1\text{H-NMR}$ (300 MHz): 1.32 (t, $J = 7.2$ Hz, 3H), 3.09 (dd, $J = 7.2$ and 1.5 Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.50 (s, 4H), 4.57 (s, 5H), 5.80 (dt, $J = 15.6$ and 1.5 Hz, 1H), 6.95 (dt, $J = 15.6$ and 6.9 Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz): 14.3 (CH_3), 31.6 (CH_2), 60.2 (CH_2), 69.9 (CH), 70.7 (CH), 71.0 (CH), 88.2 (C), 121.1 (CH), 148.0 (CH), 166.7 (C); Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Ru}$: C 55.96, H 5.28. Found: C 56.13, H 5.27.

tert-Butyl (*E*)-4-ruthenocenylobut-2-enoate (**5b**)

The general procedure was followed using vinyl diazoacetate **1b** (84.1 mg). Final chromatographic purification afforded compound **5b** (81.7 mg, 44%).



5b

^1H -NMR (300 MHz): 1.51 (s, 9H), 3.05 (dd, J = 6.9 and 1.8 Hz, 2H), 4.49-4.51 (m, 4H), 4.57 (s, 5H), 5.72 (dt, J = 15.6 and 1.5 Hz, 1H), 6.84 (dt, J = 15.6 and 6.9 Hz, 1H); ^{13}C -NMR (75 MHz): 28.2 (CH_3), 31.4 (CH_2), 69.8 (CH), 70.7 (CH), 71.0 (CH), 80.1 (C), 88.5 (C), 122.8 (CH), 146.8 (CH), 166.0 (C); Anal. Calc. for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Ru}$: C 58.21, H 5.97. Found: C 58.33, H 5.80.

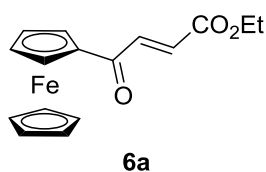
6. General Procedure for the Synthesis of Ferrocene Derivatives 6a-c

To a solution of the corresponding ferrocene derivative **3** (0.1 mmol) in a few mL of CH₂Cl₂ was added silica gel (1.8 g). The resulting suspension was stirred at room temperature for a while and then the solvent was evaporated under reduced pressure to dryness. The schlenk flask was then charged with oxygen and allow to stand at room temperature. After 3 days CH₂Cl₂ was added (10 mL) and the silica gel was removed by filtration and the crude product was purified by flash chromatography (SiO₂, hexane/ethyl acetate 5:1) to afford ferrocene derivatives **6**.

7. Characterization Data of Compounds 6a-c

Ethyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (**6a**)

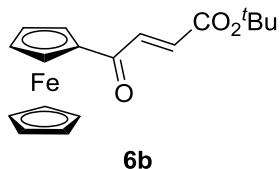
The general procedure was followed using ferrocene derivative **3a** (29.8 mg). Final chromatographic purification afforded compound **6a** (15.9 mg, 51%).



¹H-NMR (300 MHz): 1.38 (t, *J* = 7.2 Hz, 3H), 4.25 (s, 5H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.68-4.69 (m, 2H), 4.90-4.91 (m, 2H), 6.93 (d, *J* = 15.6, 1H), 7.50 (d, *J* = 15.6 Hz, 1H); ¹³C-NMR (75 MHz): 14.2 (CH₃), 61.2 (CH₂), 70.0 (CH), 70.4 (CH), 73.7 (CH), 79.7 (C), 129.2 (CH), 137.3 (CH), 166.2 (C), 191.8 (C); Anal. Calc. for C₁₆H₁₆FeO₃: C 61.57, H 5.17. Found: C 61.19, H 5.14.

tert-Butyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (**6b**)

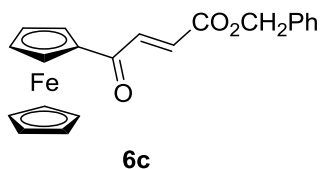
The general procedure was followed using ferrocene derivative **3b** (32.6 mg). Final chromatographic purification afforded compound **6b** (12.2 mg, 36%).



¹H-NMR (300 MHz): 1.57 (s, 9H), 4.24 (s, 5H), 4.66-4.68 (m, 2H), 4.89-4.90 (m, 2H), 6.86 (d, *J* = 15.3 Hz, 1H), 7.43 (d, *J* = 15.3 Hz, 1H); ¹³C-NMR (75 MHz): 28.1 (CH₃), 70.0 (CH), 70.3 (CH), 73.6 (CH), 79.7 (C), 81.7 (C), 131.3 (CH), 136.5 (CH), 165.4 (C), 192.1 (C); Anal. Calc. for C₁₈H₂₀FeO₃: C 63.55, H 5.93. Found: C 63.84, H 5.87.

Benzyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (6c**)**

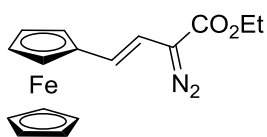
The general procedure was followed using ferrocene derivative **3c** (36.0 mg). Final chromatographic purification afforded compound **6c** (8.6 mg, 23%).



$^1\text{H-NMR}$ (300 MHz): 4.24 (s, 5H), 4.68-4.70 (m, 2H), 4.89-4.90 (m, 2H), 5.31 (s, 2H), 6.98 (d, J = 15.0 Hz, 1H), 7.38-7.46 (m, 5H), 7.53 (d, J = 15.0 Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz): 67.0 (CH_2), 70.0 (CH), 70.4 (CH), 73.8 (CH), 79.6 (C), 128.3 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 135.5 (C), 137.8 (CH), 166.0 (C), 191.7 (C); Anal. Calc. for $\text{C}_{21}\text{H}_{18}\text{FeO}_3$: C 67.40, H 4.85. Found: C 67.21, H 4.99.

8. Synthesis of ethyl (*E*)-2-diazo-4-ferrocenylbut-3-enoate (**7a**)

To a solution of ethyl (*E*)-4-ferrocenylbut-2-enoate (**3a**, 149 mg, 0.5 mmol) and 4-acetylbenzenesulfonyl azide (151 mg, 0.63 mmol) in acetonitrile (5 mL) at 0 °C was added dropwise DBU (90 μ L, 0.63 mmol). The resulting solution was stirred for 30 min at 0 °C and allowed to warm to room temperature. The reaction mixture was hydrolyzed and extracted with ether. The organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was subjected to flash chromatography (SiO₂, hexane/ethyl acetate 10:1) to afford the diazo compound **7a** as a orange oil (100.5 mg, 62%).

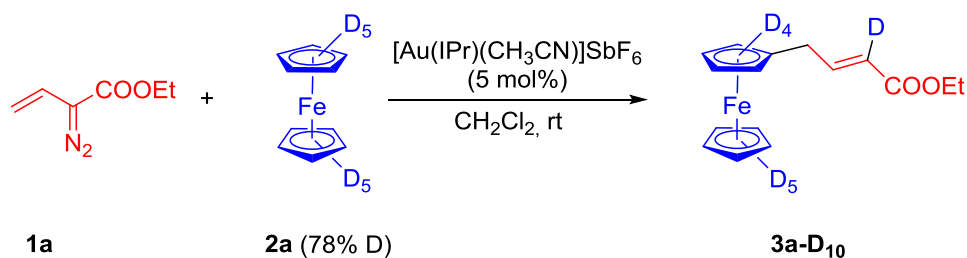


7a

¹H-NMR (300 MHz): 1.34 (t, *J* = 7.2 Hz, 3H), 4.13 (s, 5H), 4.24-4.25 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.36-4.37 (m, 2H), 5.96 (d, *J* = 16.2 Hz, 1H), 6.03 (d, *J* = 16.2 Hz, 1H); ¹³C-NMR (75 MHz): 14.5 (CH₃), 61.2 (CH₂), 66.3 (CH), 68.8 (CH), 69.3 (CH), 83.5 (C), 107.6 (CH), 121.4 (CH), 165.5 (C).

9. Some additional mechanistic experimental data

A) Gold(I)-catalyzed reaction of vinyldiazo compound **1a** with deuterated ferrocene



$[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyldiazo compound **1a** (70.1 mg, 0.5 mmol) and partially deuterated ferrocene (78% deuterium content) (392.2 mg, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography. The ^1H -NMR spectrum (Figures S2 and S3) is consistent with a 63% deuterium incorporation at the α -position of the resulting ferrocene derivative.

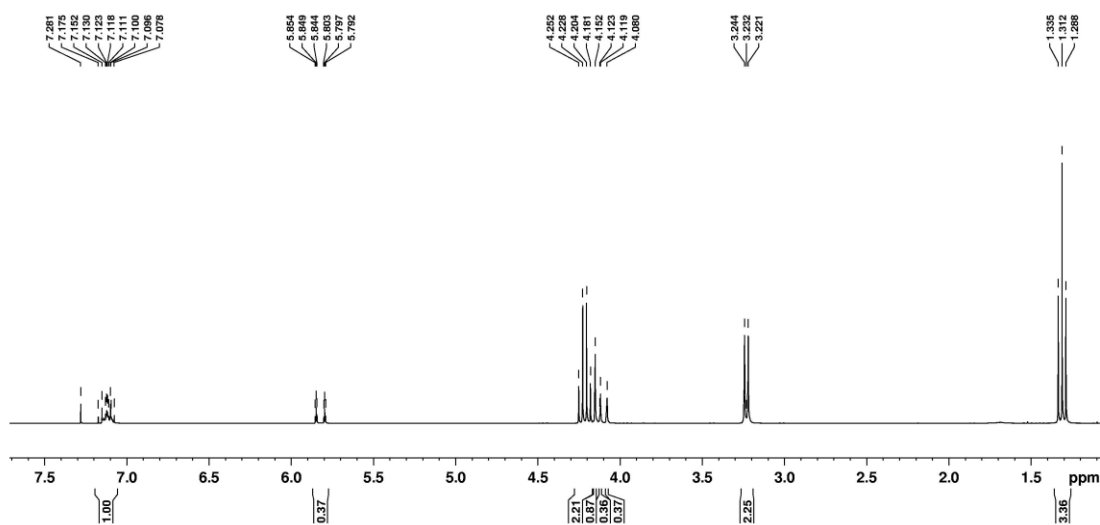


Figure S2. ^1H -NMR (300 MHz) spectrum of the ferrocene derivative resulting from the reaction of vinyldiazo compound **1a** and deuterated ferrocene.

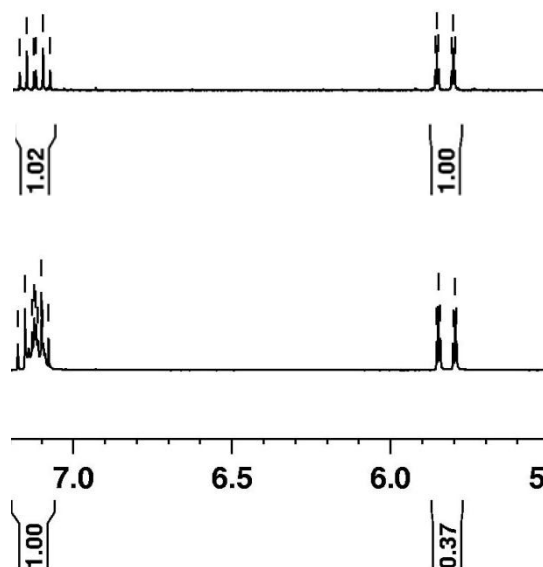
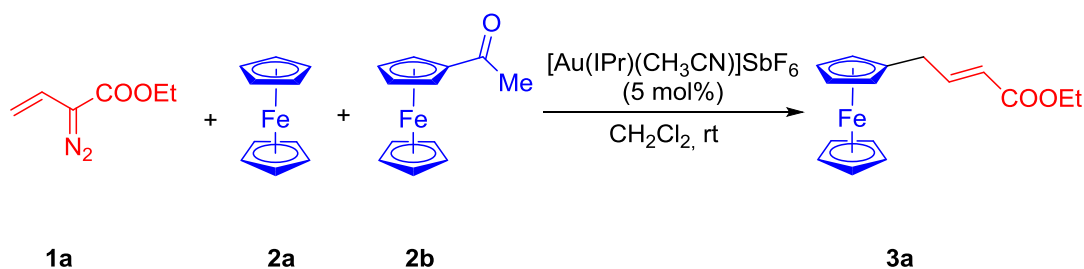


Figure S3. ^1H -NMR spectra (olefinic region) of the functionalized ferrocene derivatives resulting from the reaction of vinyl diazo compound **1a** and ferrocene (top) and partially deuterated ferrocene (bottom).

*B) Competition experiment between ferrocene (**2a**) and acetylferrocene (**2b**)*



$[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyl diazo compound **1a** (70.1 mg, 0.5 mmol), ferrocene (**2a**) (370 mg, 2 mmol), and acetylferrocene (**2b**) (456.1 mg, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4 h). The solvent was removed under reduced pressure. The ^1H -NMR of the crude mixture revealed the presence of unreacted ferrocene, unreacted acetylferrocene and ferrocene derivative **3a** (Figure S4). The crude mixture was purified by flash chromatography (SiO_2 , hexane/ethyl acetate 10:1) to afford ferrocene derivative **3a** (83.5 mg, 56 %).

and some olefinic signals overlapped with that corresponding to compound **3g**). Although the structure of this byproduct remains uncertain, complexation of the gold catalyst to ferrocene derivative **3g** can be tentatively proposed.]

10. Electrochemical measurements

Cyclic voltammetric studies were performed using a μ -AutoLab type II equipped with a GPES 4.9 software (EcoChemie, The Netherlands). All measurements were carried out using a conventional three electrode system in phosphate saline buffer (pH 7.4). A modified carbon paste acted as the working electrode and a Pt wire as a counter electrode. All potentials were referred to a $\text{Ag}|\text{AgCl}|\text{KCl}_{(\text{sat})}$ reference electrode.

Preparation of the modified electrode

Unmodified carbon paste was prepared by thorough mixing 1 g of spectroscopy grade graphite powder (Ultra Carbon, Dicoex, Spain) and 0.323 g of silicone high vacuum grease. The ferrocene derivative **3a** was solubilized in the minimum volume of dichloromethane and transferred to a mortar where the solvent was evaporated before adding the carbon paste to avoid the deleterious effect of organic solvents on the quality of the electrode material. After thorough mixing the resulting modified carbon paste containing a 3% of the compound was packed into the well of the working electrode ($d=3\text{ mm}$) made of a Teflon body and a stainless steel contact. Finally, the electrode surface was smoothed against a filter paper.

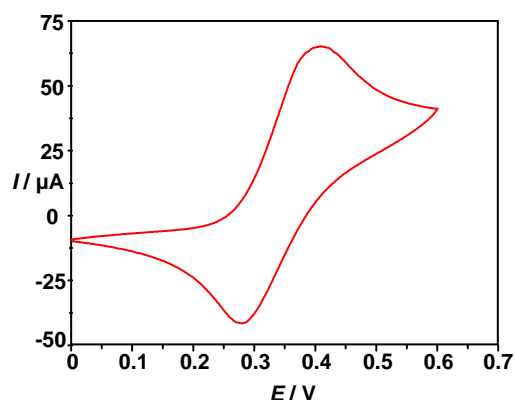


Figure S5. Cyclic voltammogram obtained with the carbon paste modified with ferrocene derivative **3a** in PBS at a scan rate of 100 mV/s.

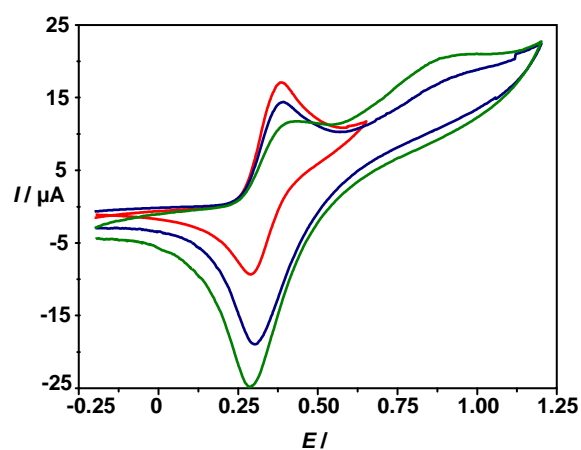
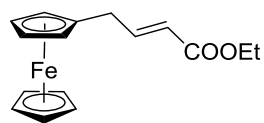
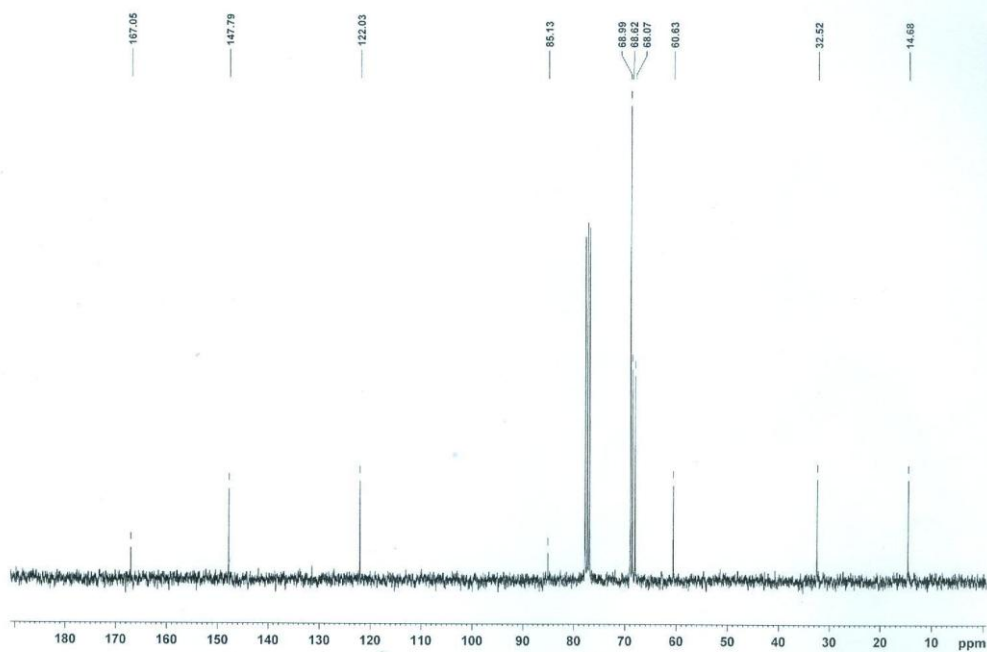
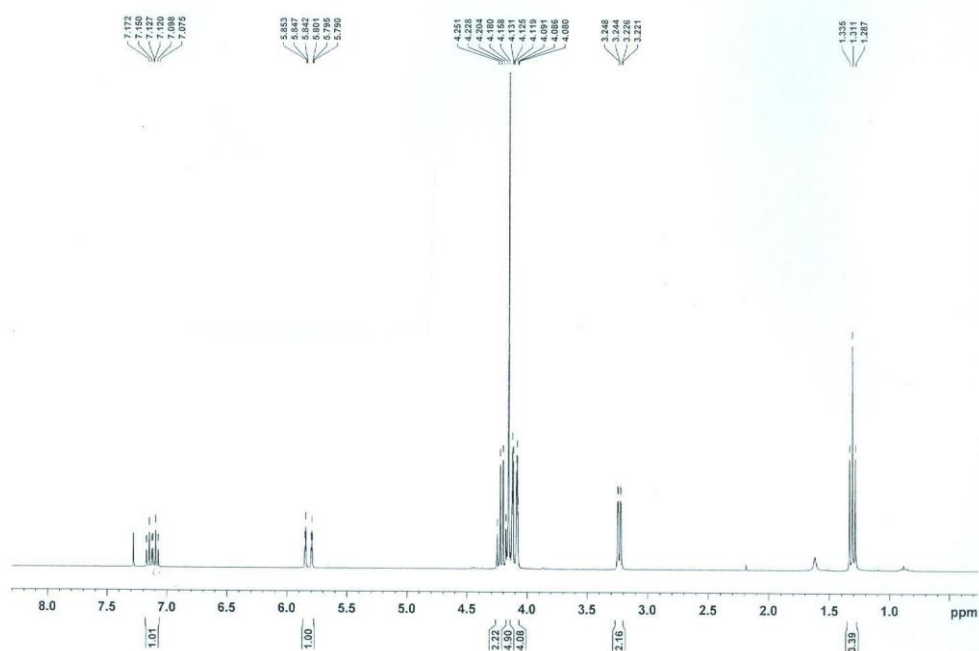


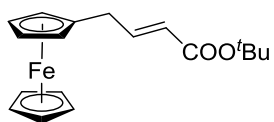
Figure S6. Cyclic voltammogram obtained with the modified carbon paste electrode in PBS at a scan rate of 10 mV/s, before oxidation at high potentials (red), first cycle of oxidation up to 1.2 V (blue) and second cycle (green).

11. ^1H - and ^{13}C -NMR spectra for new compounds

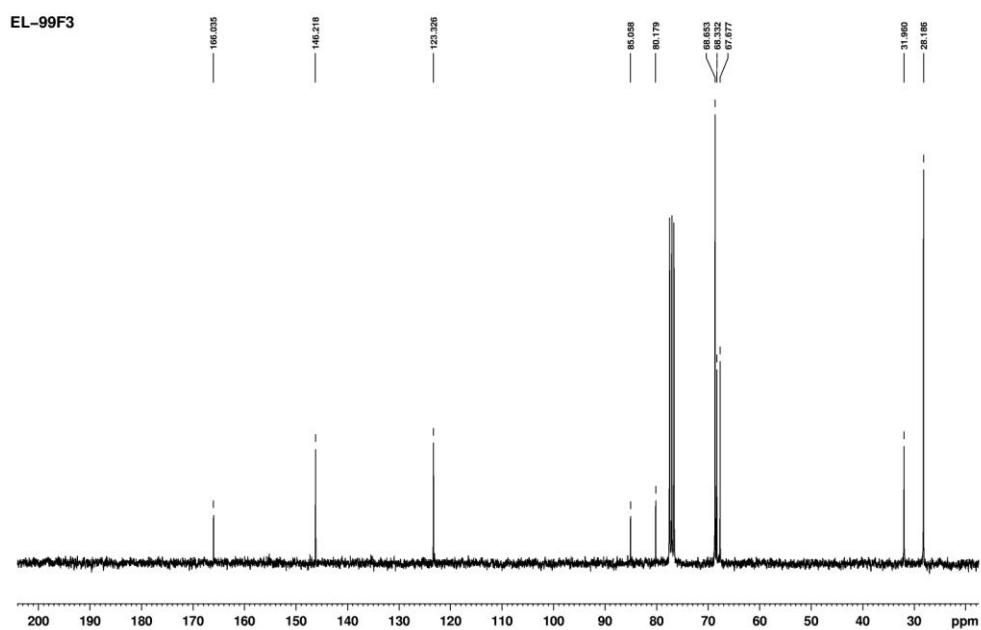
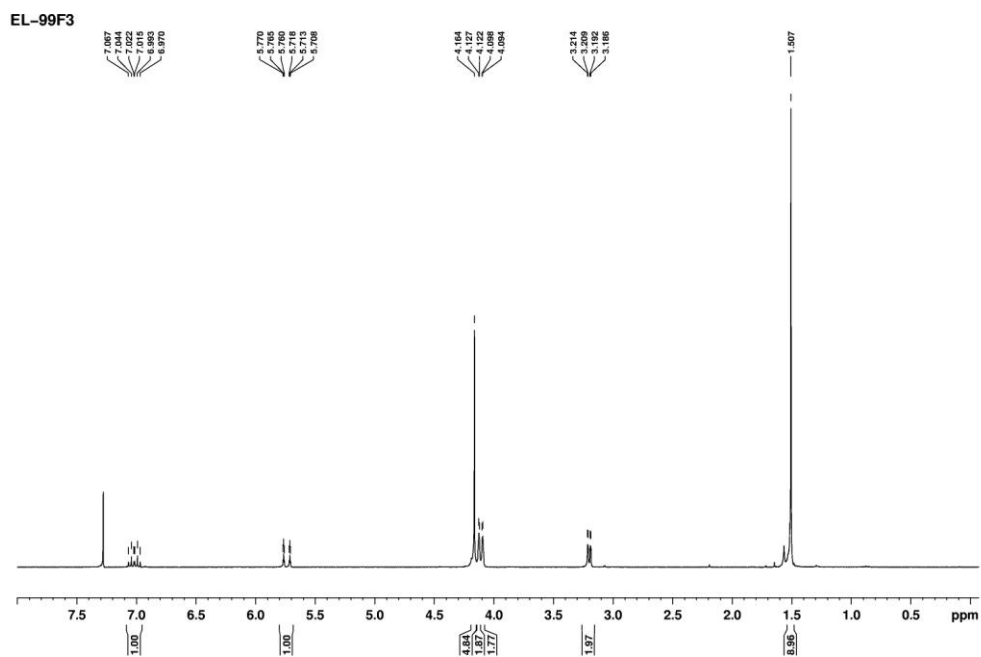


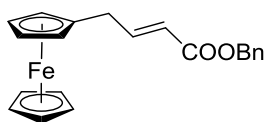
Ethyl (*E*)-4-ferrocenylbut-2-enoate (**3a**)



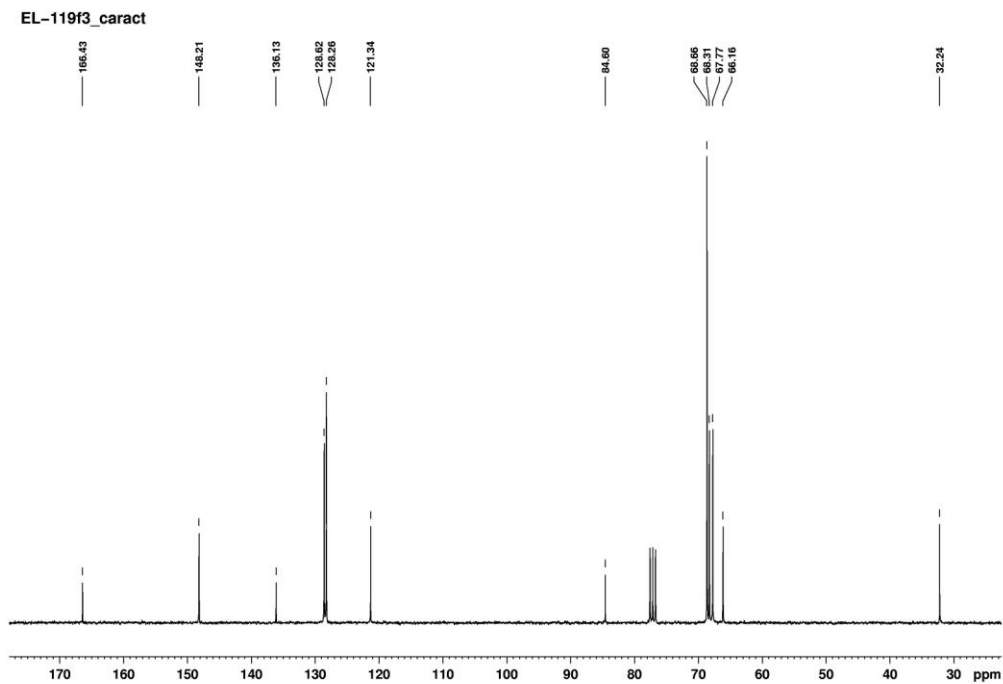
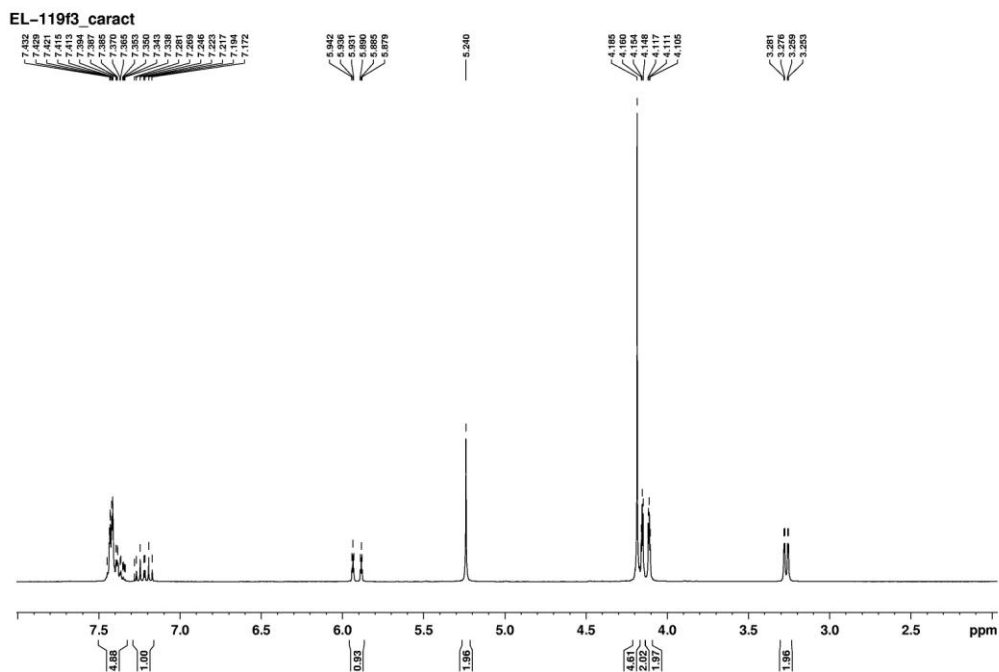


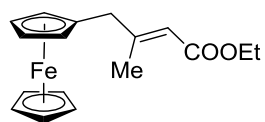
tert-Butyl (*E*)-4-ferrocenylbut-2-enoate (**3b**)





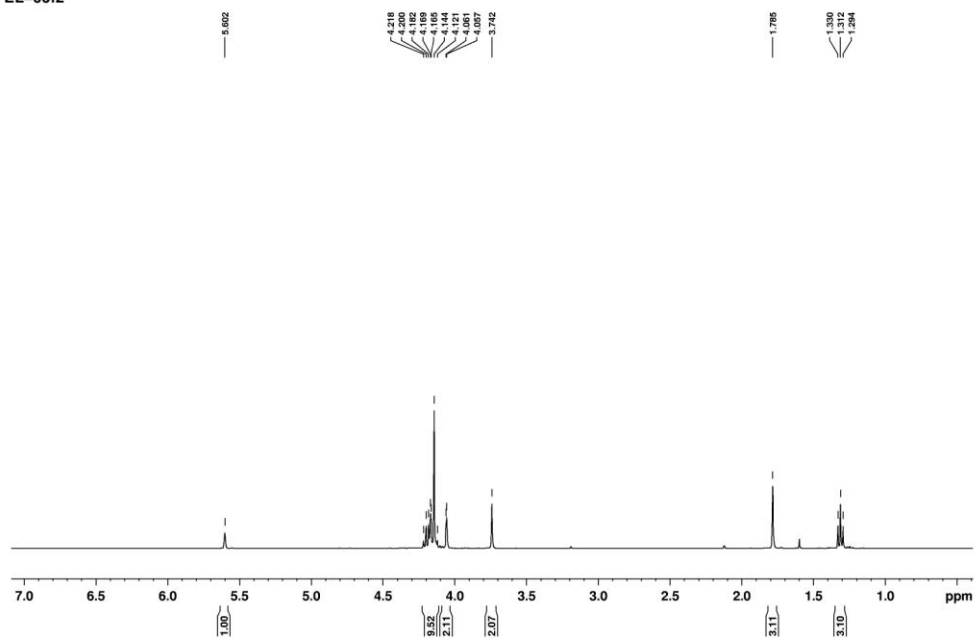
Benzyl (*E*)-4-ferrocenylbut-2-enoate (**3c**)



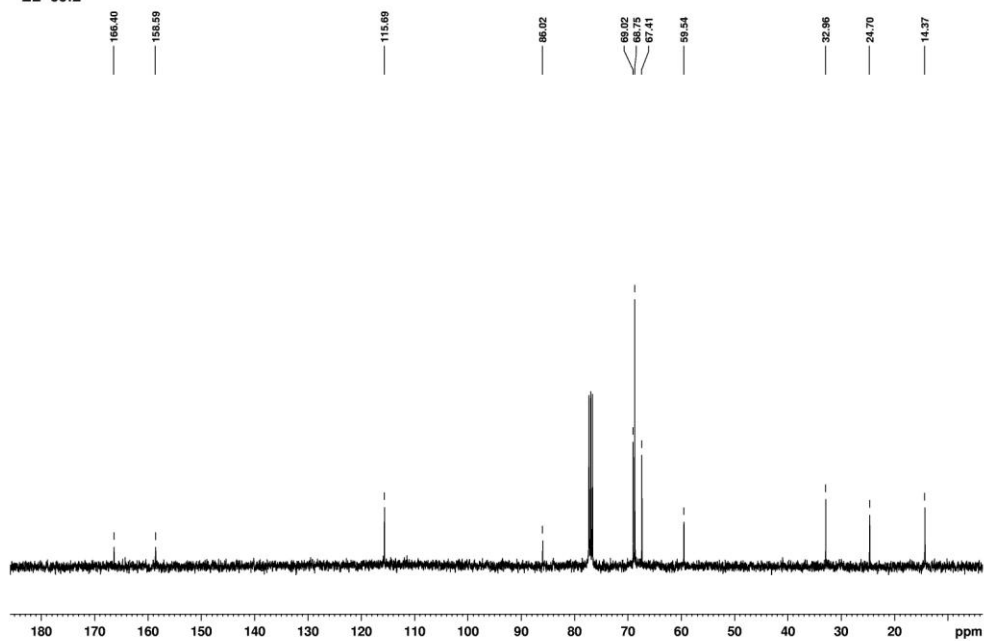


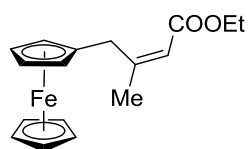
Ethyl (*E*)-4-ferrocenyl-3-methylbut-2-enoate (**3d**)

EL-66f2



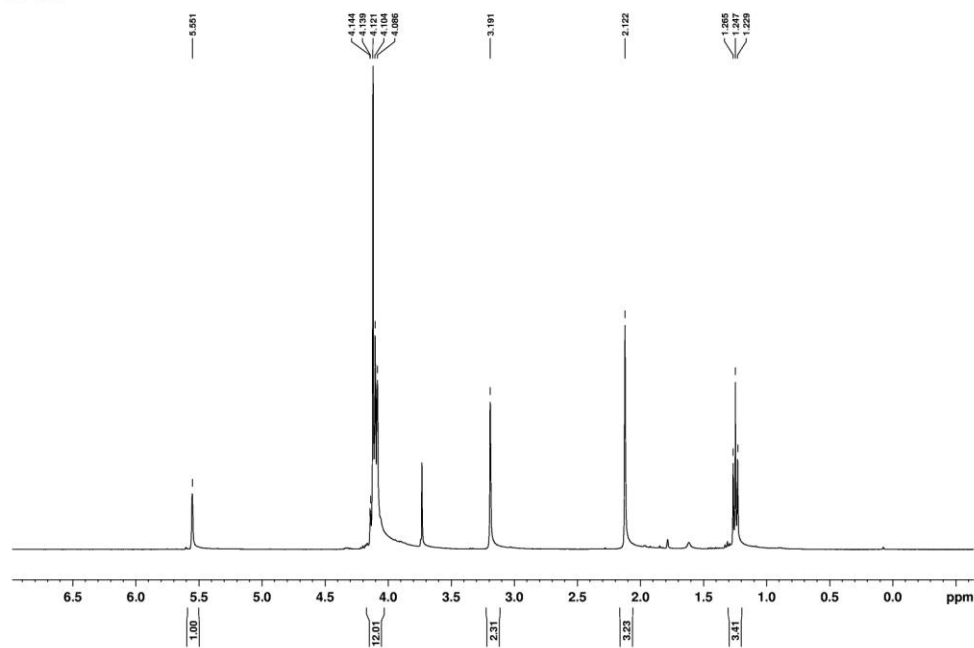
EL-66f2



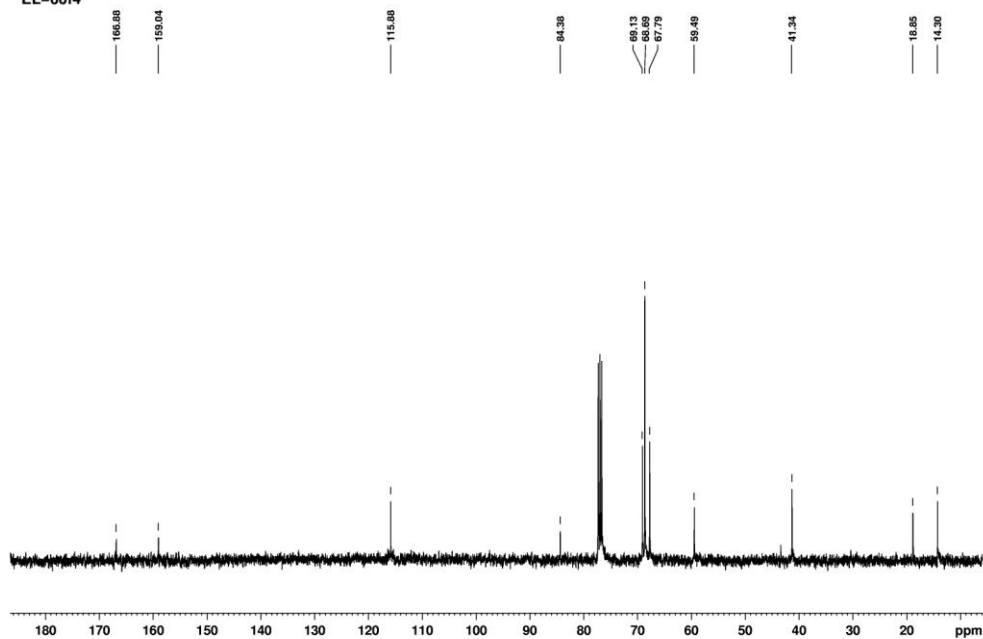


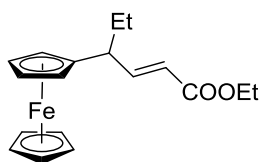
Ethyl (*Z*)-4-ferrocenyl-3-methylbut-2-enoate (**3d**)

EL-6614



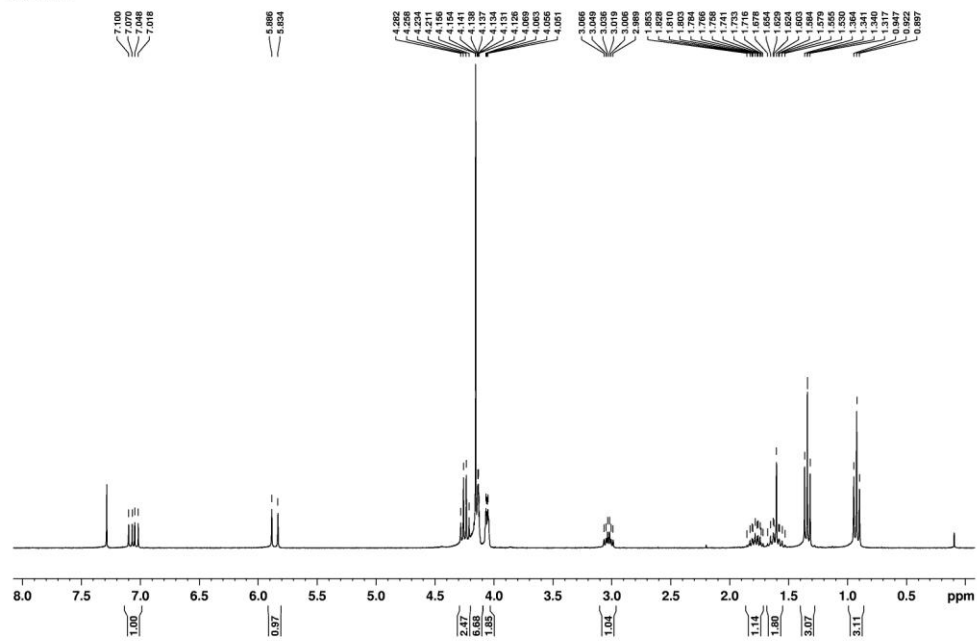
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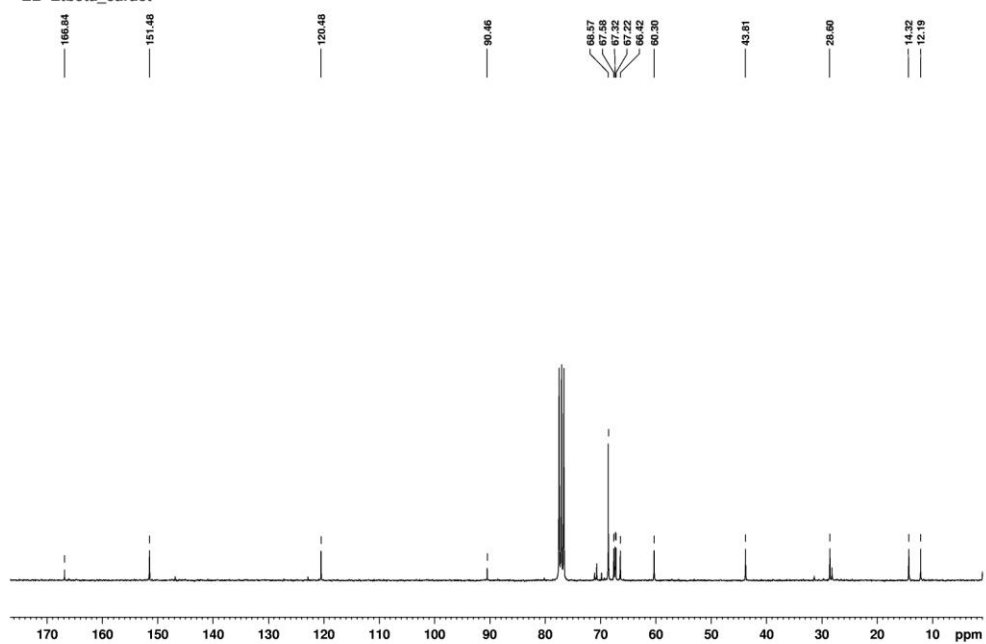


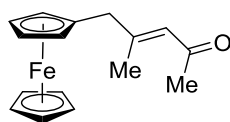
Ethyl (*E*)-4-ferrocenylhex-2-enoate (**3e**)

EL-104f3



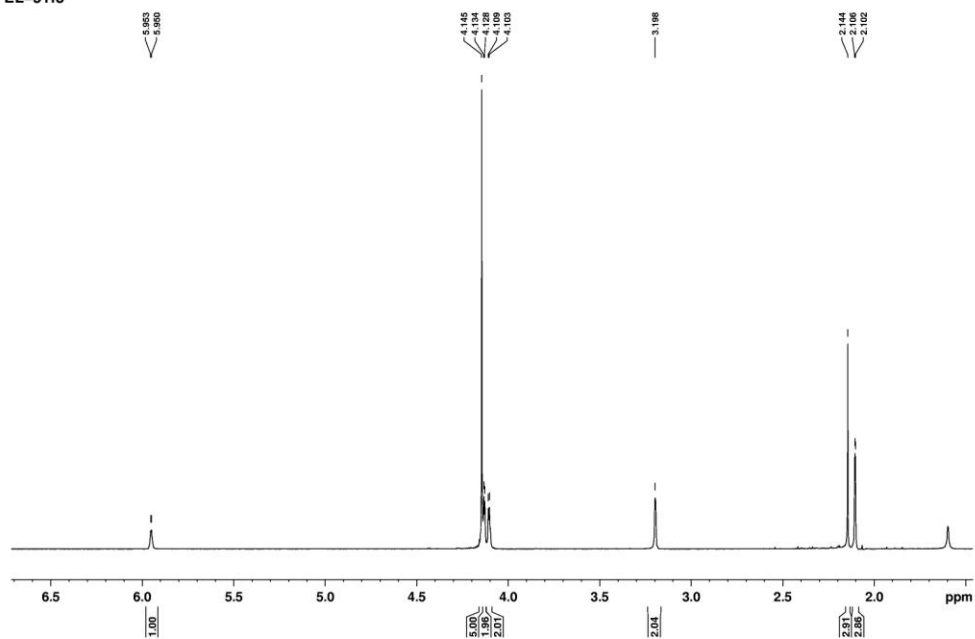
EL-Etbeta_caract



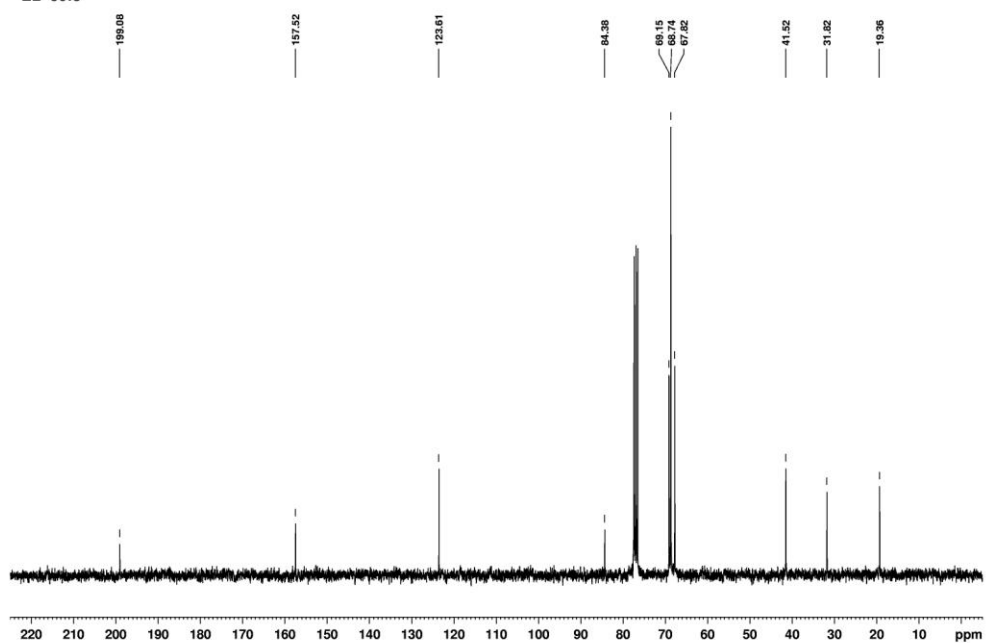


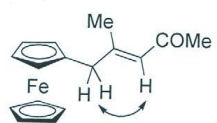
(*E*)-5-Ferrocenyl-4-methyl-3-penten-2-one (**3f**)

EL-51f3

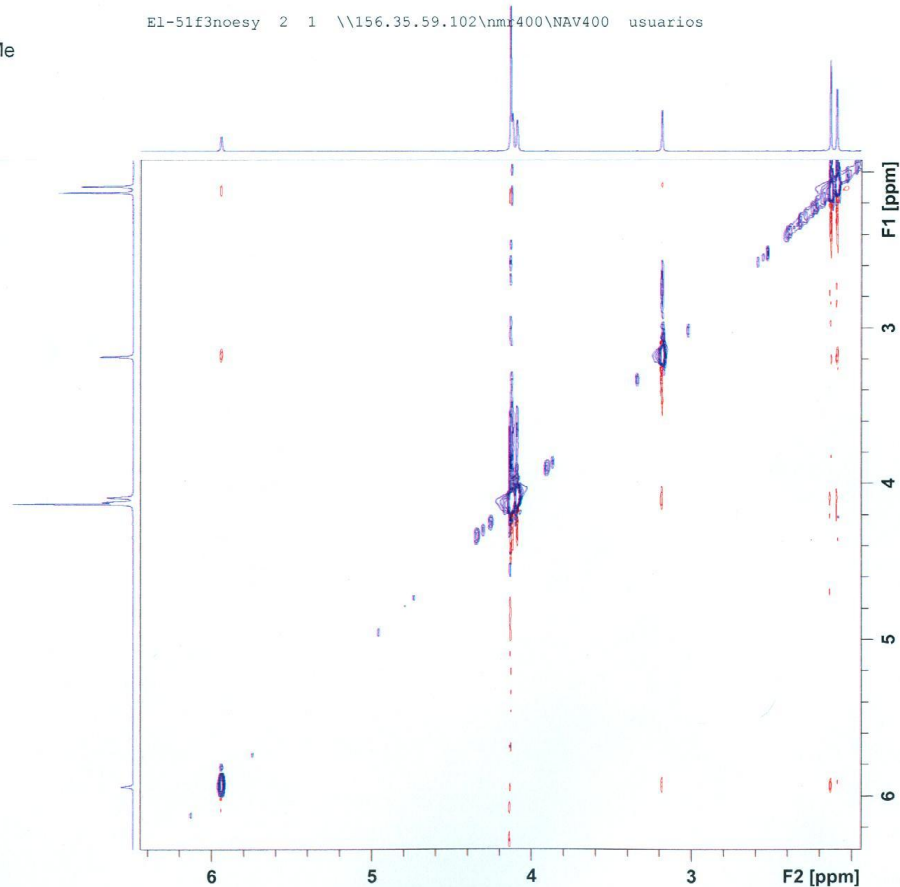


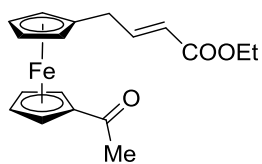
EL-50f3



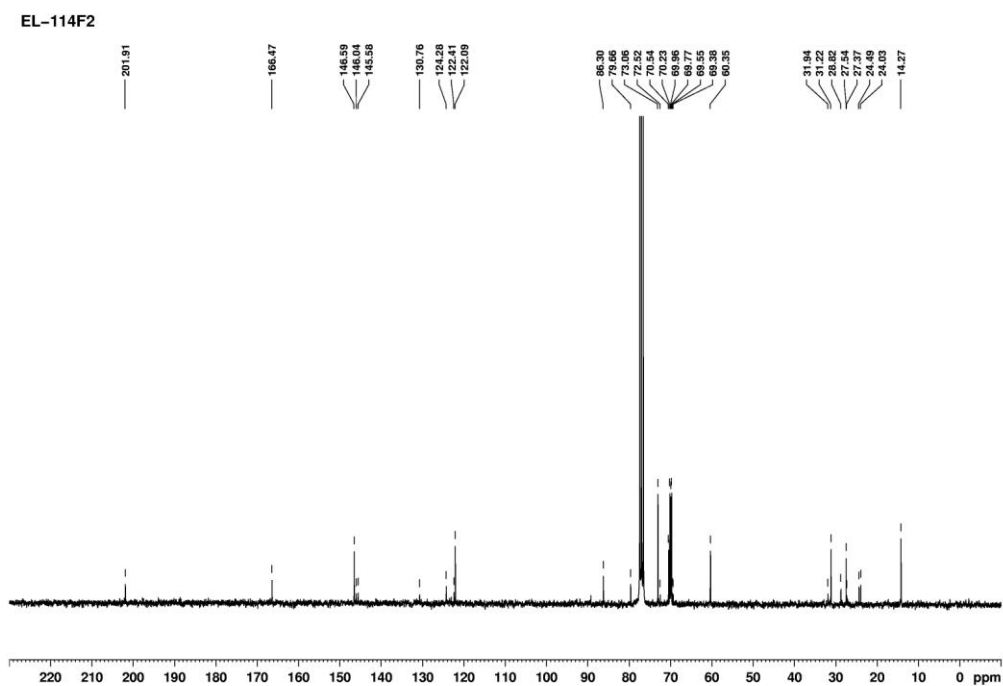
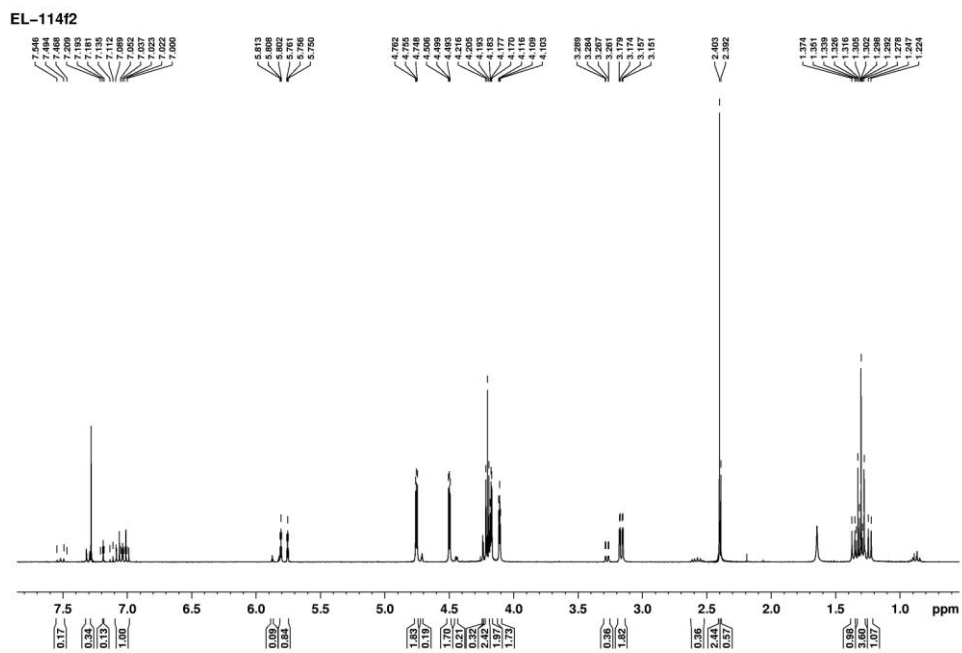


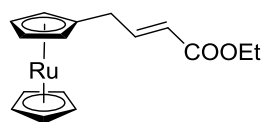
El-51f3noesy 2 1 \\156.35.59.102\nmr400\NAV400 usuarios



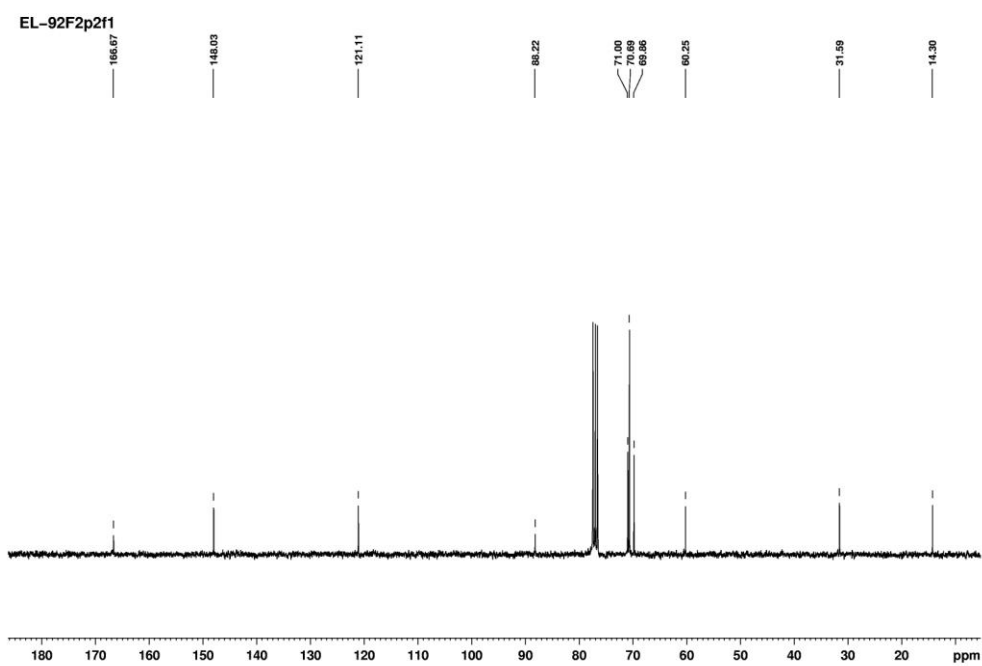
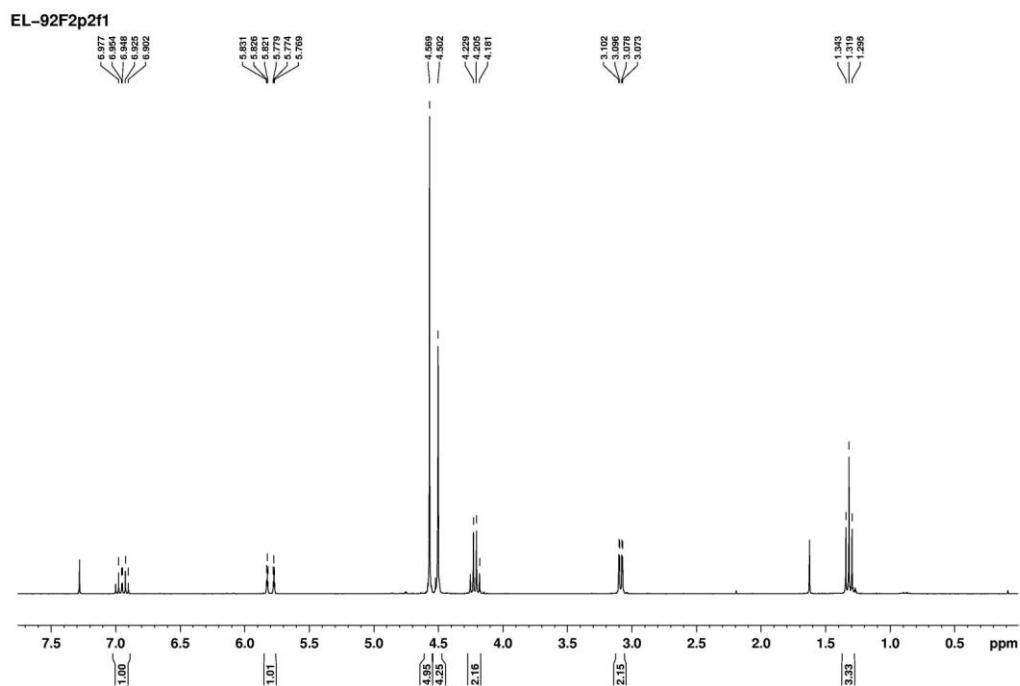


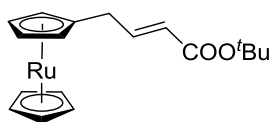
Ethyl (*E*)-4-(1'-acetylferrocen-1-yl)but-2-enoate (**3g**)



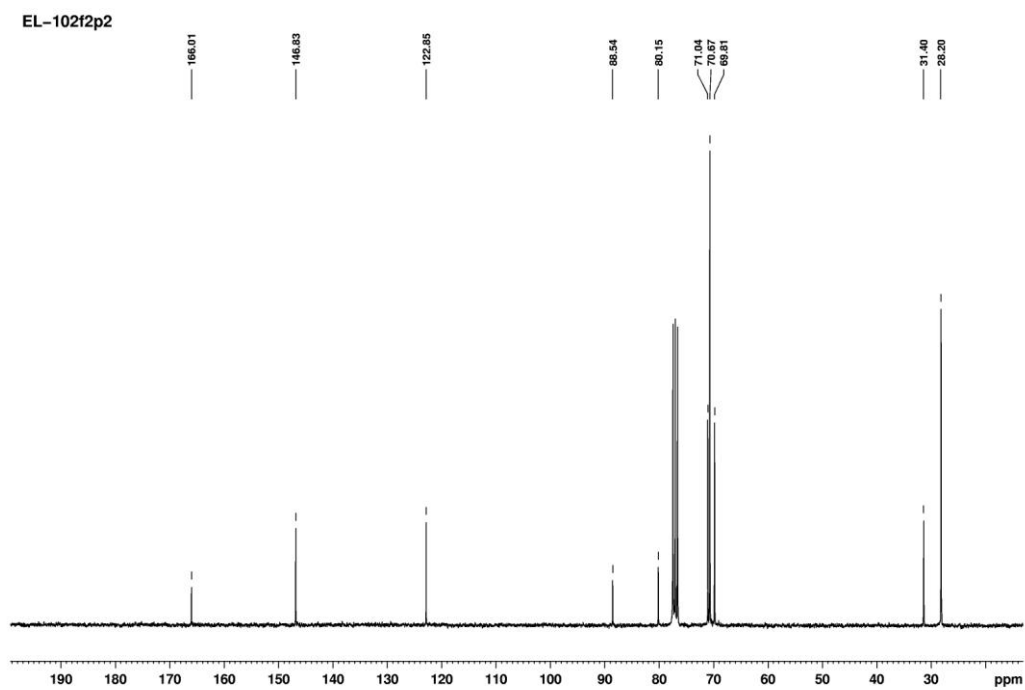
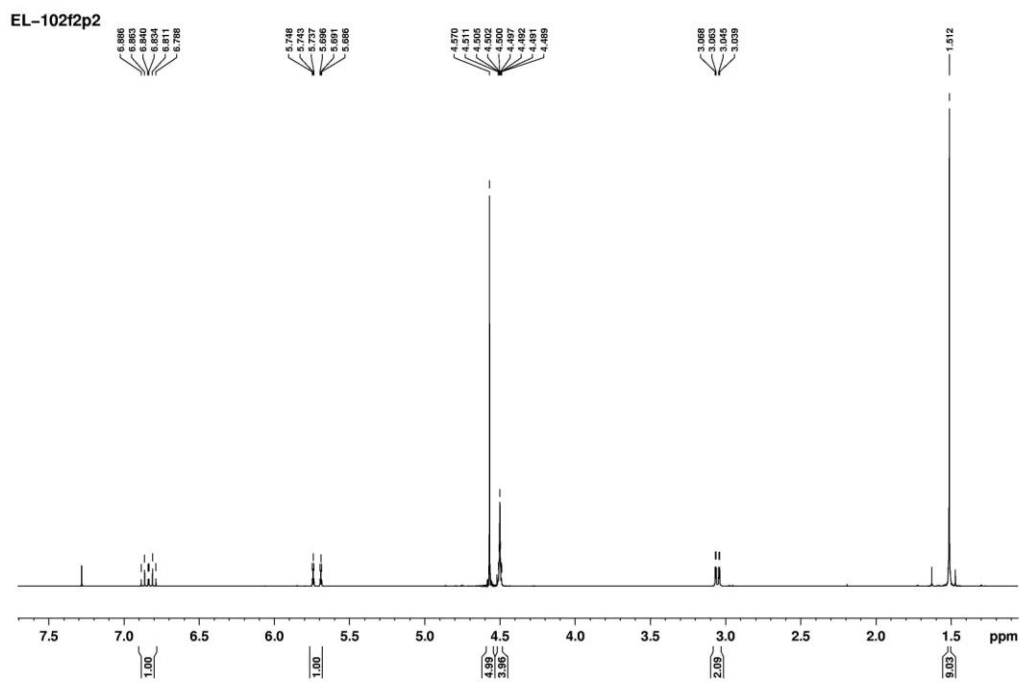


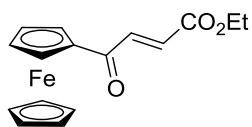
Ethyl (*E*)-4-ruthenocenylbut-2-enoate (**5a**)





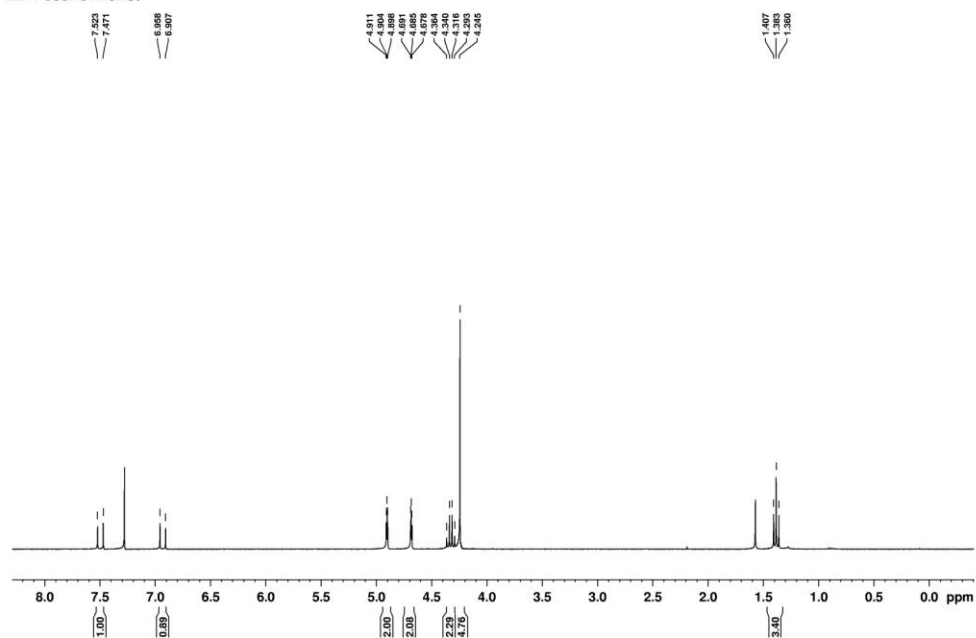
tert-Butyl (*E*)-4-ruthenocenylobut-2-enoate (**5b**)



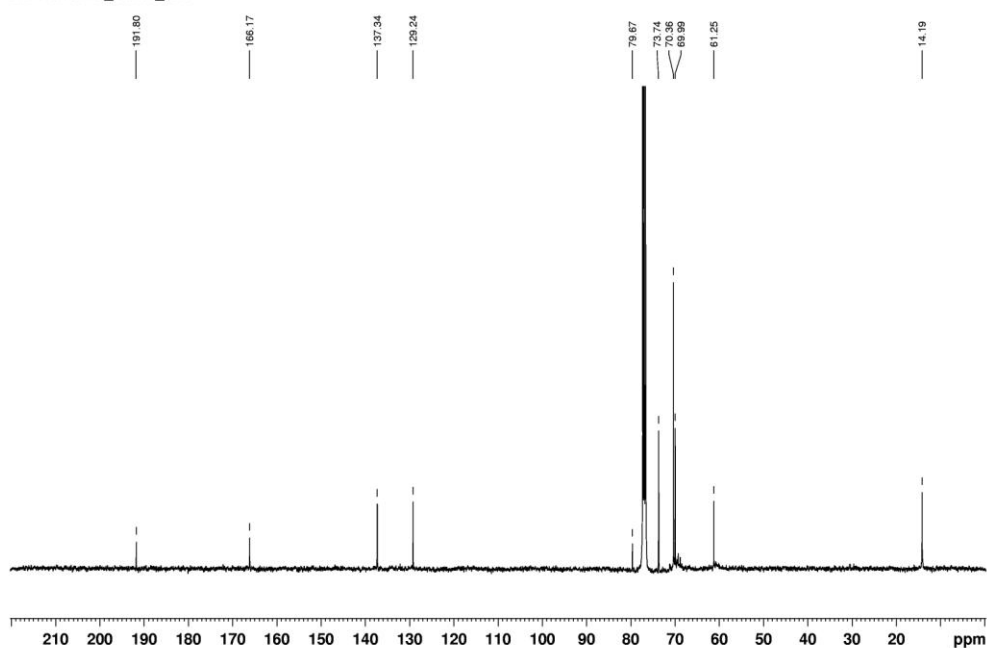


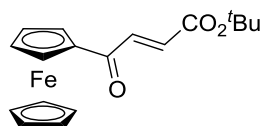
Ethyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (**6a**)

EL-Fcsenc1Hcris1

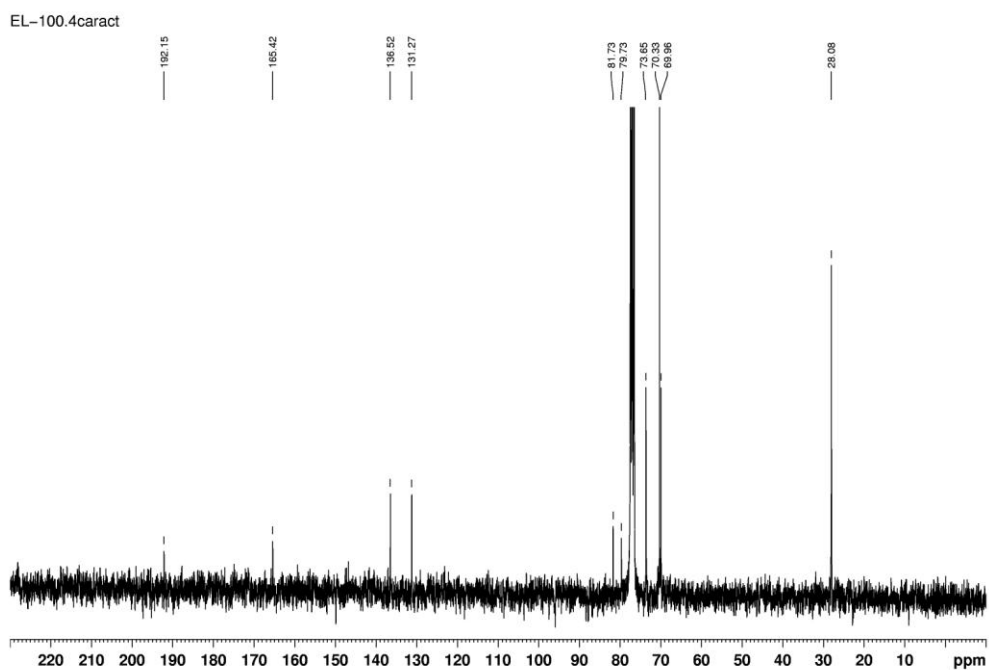
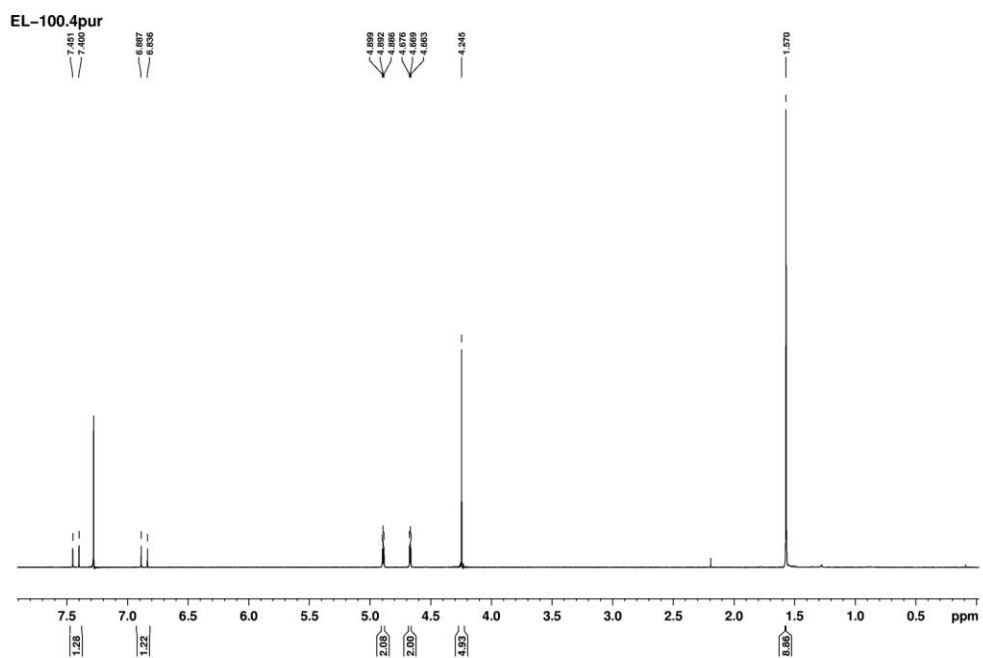


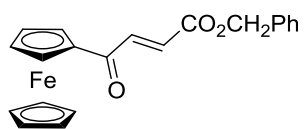
EL-Fcoxsenc_caract_400





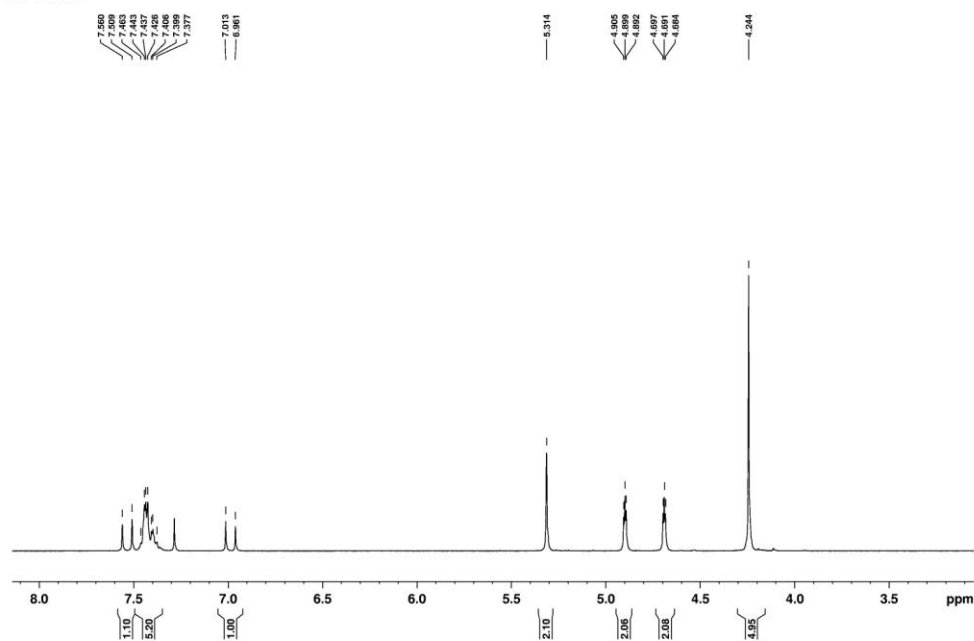
tert-Butyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (**6b**)



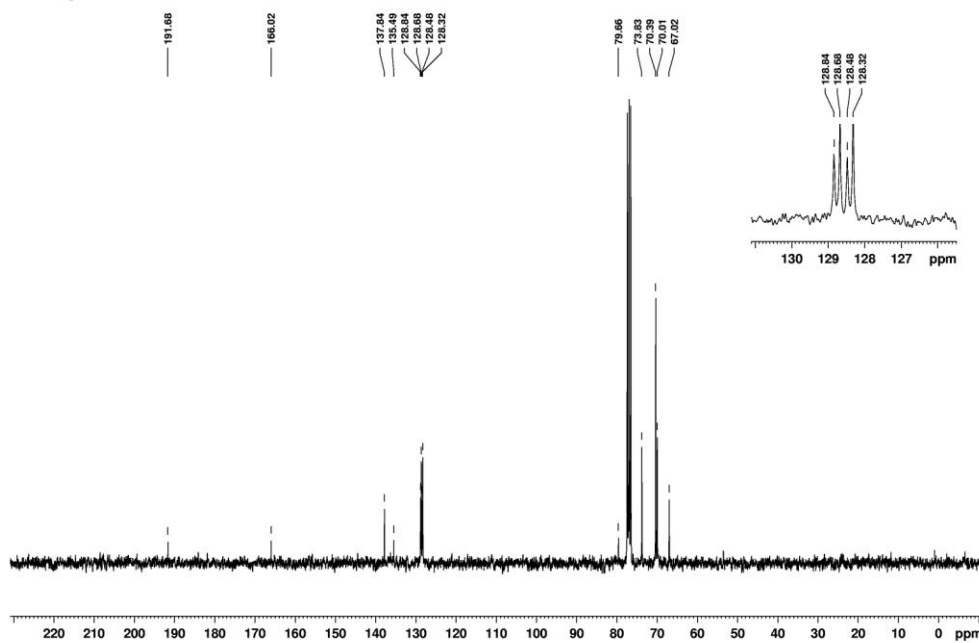


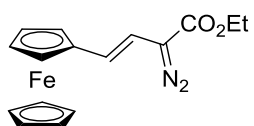
Benzyl (*E*)-4-oxo-4-ferrocenylbut-2-enoate (**6c**)

EL-120.112



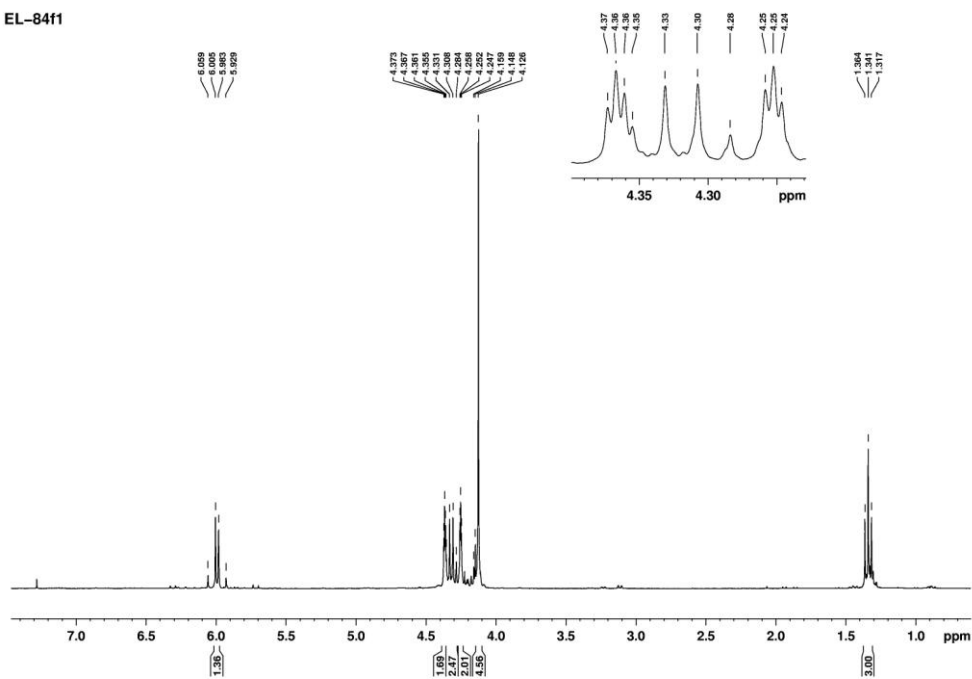
EL-120.112





Ethyl (*E*)-2-diazo-4-ferrocenylbut-3-enoate (**7a**)

EL-8411



EL-8411.13C

