Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Nondirected Pd-Catalyzed Aerobic C–H Alkenylation of Ruthenocene and Ferrocene

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Table of Contents

1. General Information

All chemicals used for synthesis were purchased from commercial sources and used without further purification unless otherwise noted. Thin layer chromatography (TLC) was performed on fluorescence-marked silica gel on aluminum foil (60 F254, 0.2 mm) purchased from Merck. Detection was achieved by means of an UV lamp (254 and 366 nm) or $KMnO_4$ staining. Flash column chromatography was performed on silica gel (40-63 µm) using the indicated solvent system with technical grade solvents. NMR spectra were recorded on a Bruker Avance 400 MHz, or an Agilent Varian 500 MHz NMR spectrometer. All spectra were acquired at 298 K unless stated otherwise. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26, and AcOD-d_4, δ 2.04). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$, δ 77.16). Coupling constants are reported in Hz. All obtained spectra were processed using the program MestReNova (version 14.1). Resonance multiplicities are indicated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Infrared (IR) spectra are reported as absorption wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were acquired on high-resolution mass spectrometers: Q-TOF (ionization mode: ESI). GC measurements were conducted on a Shimadzu GC-2010 Plus Series GC-FID system. To determine GC yields, calibration curves were generated using *n*-dodecane as an internal standard. Raw data processing and visualization was achieved using the programs Excel and SciDavis. Electrochemical measurements were performed using a CHI1040C (CH Instruments, Austin, TX, USA) potentiostat. Cyclic voltammetry was performed using a three-electrode chemical cell containing a glassy carbon electrode (3 mm in diameter, BASi), Ag/AgCl (BioLogic) with 0.5 M of $TBABF_4$ in DCM, and Pt wire counter electrode (99.9%, Alfa). The glassy carbon electrode was polished in air using a MicroPolish alumina suspension (0.3 µm, BUEHLER) before and after each measurement. All experiments were performed at a scan rate 100 mV/s.

2. Ligand Screening

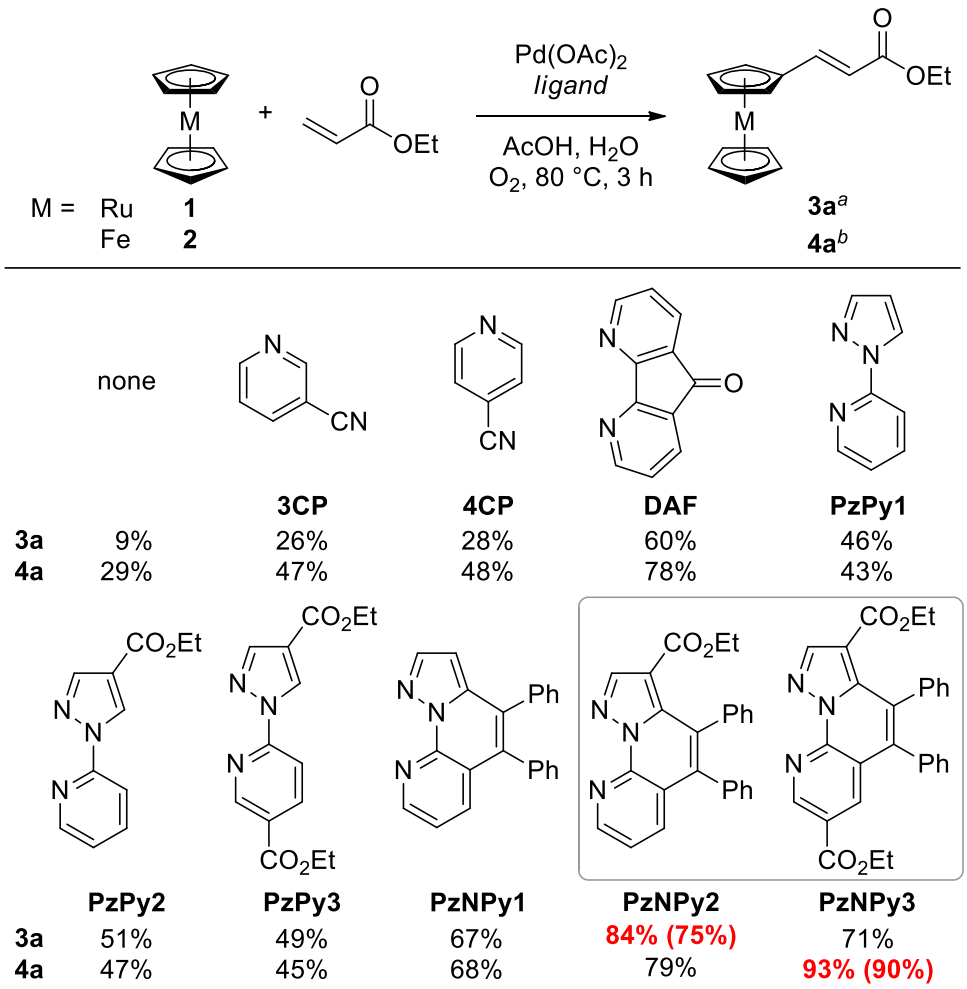
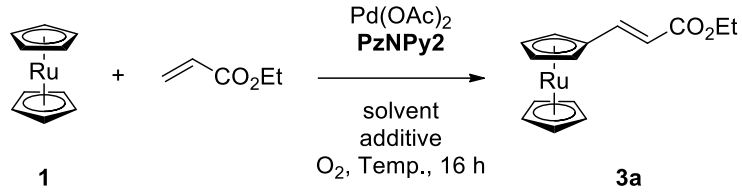


Figure S1. Ligand screening results for the model alkenylation reaction of ruthenocene and ferrocene with ethyl acrylate. [a] Reaction conditions: ruthenocene (0.25 mmol), olefin (0.50 mmol), $Pd(OAc)_2$ (2.5 mol%), ligand (2.5 mol%), O_2 (1 atm), H_2O (25 µL), AcOH (0.50 mL, 0.50 M), 80 °C, 16 h. [b] Reaction conditions: ferrocene (3.0 mmol), olefin (1.0 mmol), $Pd(OAc)_2$ (2.5 mol%), ligand (2.5 mol%), O_2 (1 atm), H_2O (50 µL), AcOH (4.00 mL, 0.25 M), 80 °C, 3 h. Yields in parentheses are isolated yields.

3. Optimization Studies

Table S1. Optimization of the reaction conditions for the alkenylation of ruthenocene with ethyl acrylate.[a]

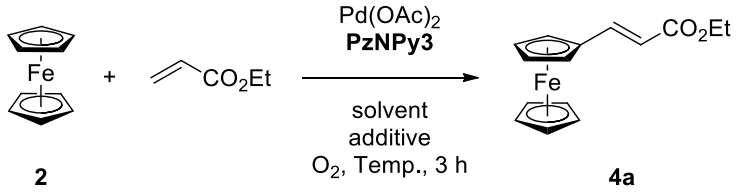


1 **3a**

Entry	RcH (mmol)	Ethyl acrylate (mmol)	$Pd(OAc)_2$ (mol%)	PzNPy2 (mol%)	Solvent (mL)	H_2O (µL)	Temp.	^1H NMR Yield	Iso Yield
1	3.00	1.00	2.5	2.5	AcOH (4.0)	50	80 °C	41%	35%
2	1.00	1.00	2.5	2.5	AcOH (4.0)	50	80 °C	59%	–
3	1.00	2.00	2.5	2.5	AcOH (4.0)	50	80 °C	64%	57%
4	0.25	0.50	2.5	2.5	AcOH (1.0)	50	80 °C	69%	–
5	0.25	0.50	1.25	1.25	AcOH (1.0)	50	80 °C	43%	–
6	0.25	0.50	5.0	5.0	AcOH (1.0)	50	80 °C	50%	–
7	0.25	0.50	2.5	2.5	AcOH (0.5)	50	80 °C	82%	–
8	0.25	0.50	1.25	1.25	AcOH (0.25)	50	80 °C	62%	–
9	0.25	0.50	2.5	2.5	AcOH (0.5)	0	80 °C	52%	–
10	0.25	0.50	2.5	2.5	AcOH (0.5)	12.5	80 °C	67%	–
11	0.25	0.50	2.5	2.5	AcOH (0.5)	25	80 °C	84%	75%
12	0.25	0.50	2.5	2.5	AcOH (0.5)	100	80 °C	78%	–
13	0.25	0.50	2.5	2.5	AcOH (0.5)	25	60 °C	47%	–
14	0.25	0.50	2.5	2.5	AcOH (0.5)	25	100 °C	64%	–
15	0.25	0.50	2.5	2.5	DMA (0.5)	25	80 °C	19%	–
16	0.25	0.50	2.5	2.5	AcOH:HFIP (9:1) (0.5)	25	80 °C	65%	–
17	0.25	0.50	2.5	2.5	HFIP (0.5)	25	80 °C	<1%	–

[a] For all experiments, after threefold air-oxygen exchange, the vial was sealed with a cap.

Table S2. Optimization of the reaction conditions for the alkenylation of ferrocene with ethyl acrylate.



Entry	FcH (mmol)	Ethyl acrylate (mmol)	$Pd(OAc)_2$ (mol%)	PzNPy3 (mol%)	Solvent (mL)	H_2O (μL)	Temp.	^1H NMR Yield	Iso Yield
1[a]	1.0	2.0	5.0	5.0	AcOH (3.0)	-	70 ℃	37%	–
2[a]	1.0	2.0	5.0	5.0	AcOH (3.0)	50	80 ℃	53% (Bis: 23%)	–
3[a]	1.0	1.0	5.0	5.0	AcOH (3.0)	50	80 ℃	69 (Bis: 9%)	–
4[a]	2.0	1.0	5.0	5.0	AcOH (3.0)	50	80 ℃	84% (Bis: 6%)	–
5[a]	3.0	1.0	5.0	5.0	AcOH (3.0)	50	80 ℃	73%	64%
6[a]	3.0	1.0	5.0	5.0	AcOH (3.0)	50	60 ℃	40%	–
7[a]	3.0	1.0	5.0	5.0	AcOH (3.0)	50	100 ℃	31%	–
8[b]	3.0	1.0	5.0	5.0	AcOH (3.0)	50	80 ℃	80%	72%
9[b]	3.0	1.0	2.5	2.5	AcOH (3.0)	50	80 ℃	88%	81%
10[b]	3.0	1.0	1.25	1.25	AcOH (3.0)	50	80 ℃	57%	–
11[b]	3.0	1.0	2.5	2.5	AcOH (2.0)	50	80 ℃	82%	75%
12[b]	3.0	1.0	2.5	2.5	AcOH (4.0)	50	80 ℃	93%	89%
13[b]	3.0	1.0	2.5	2.5	DMSO (4.0)	50	80 ℃	N.R.	–
14[b]	3.0	1.0	2.5	2.5	DMF (4.0)	50	80 ℃	<1%	–
15[b]	3.0	1.0	2.5	2.5	1,4-Dioxane (4.0)	50	80 ℃	3%	–
16[b]	3.0	1.0	2.5	2.5	PhCl (4.0)	50	80 ℃	2%	–
17[b]	3.0	1.0	2.5	2.5	Toluene (4.0)	50	80 ℃	2%	–
18[b]	3.0	1.0	2.5	2.5	DMA (4.0)	50	80 ℃	3%	–

[a] The reaction was conducted using an oxygen balloon. [b] After threefold air-oxygen exchange, the reaction vessel was sealed with a cap.

4. Experimental Procedures and Characterization Data

General Procedure A

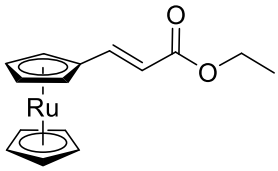
An olefin (0.50 mmol, 2.00 equiv) and ruthenocene (57.8 mg, 0.25 mmol, 1.00 equiv) were dissolved in glacial acetic acid (4.00 mL, 0.50 M) and water (25.0 μL) was added. 100 μL of a stock solution of palladium(II) acetate (1.4 mg, 6.25 μmol, 2.50 mol%) and PzNPy2 (2.5 mg, 6.25 μmol, 2.50 mol%) in glacial acetic acid was added. The vial was evacuated and subsequently flushed with oxygen. This procedure was repeated three times. The vial was sealed with a cap and the reaction mixture was then stirred in a preheated reaction block at 80 °C for 16 hours at 420 rpm. After cooling to room temperature, the residue was dissolved in DCM (10.0 mL) and adsorbed onto silica. Purification of the crude product was achieved *via* flash column chromatography to provide the desired alkenylated ruthenocene derivative.

General Procedure B

An olefin (1.00 mmol, 1.00 equiv) and ferrocene (558 mg, 3.00 mmol, 3.00 equiv) were dissolved in glacial acetic acid (4.00 mL, 0.25 M) and water (50.0 μL) was added. 100 μL of a stock solution of palladium(II) acetate (5.6 mg, 25.0 μmol, 2.50 mol%) and PzNPy3 (11.6 mg, 25.0 μmol, 2.50 mol%) in glacial acetic acid was added. The vial was evacuated and subsequently flushed with oxygen. This procedure was repeated three times. The vial was quickly sealed with a cap and the reaction mixture was stirred in a preheated reaction block at 80 °C for exactly 3 hours at 450 rpm. After cooling to room temperature, toluene (10.0 mL) was added, and the solvent removed under vacuum to afford the crude product. The residue was dissolved in DCM (15.0 mL) and adsorbed onto silica. Purification of the crude product was achieved *via* flash column chromatography to provide the desired alkenylated ferrocene derivative.

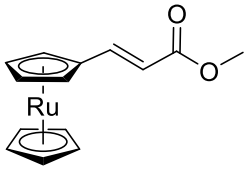
Ruthenocene Derivatives

Ethyl (*E*)-3-ruthenocenyl acrylate (3a)



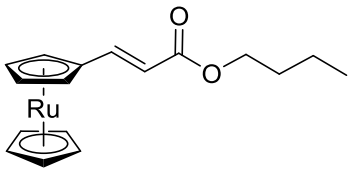
Following the general procedure A, the reaction was set up with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 20:1:1) afforded **3a** as a yellow solid (62.1 mg, 189 μmol, 75%). m.p. 87-88 °C; IR (film) 3091, 2976, 2928, 1699, 1629, 1364, 1256, 1186, 971, 804 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 15.7 Hz, 1H), 5.96 (d, *J* = 15.7 Hz, 1H), 4.85 (t, *J* = 1.8 Hz, 2H), 4.68 (t, *J* = 1.8 Hz, 2H), 4.54 (s, 5H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 144.2, 114.8, 83.1, 72.3, 71.8, 70.5, 60.3, 14.5; HRMS (ESI) calcd for $[C_{15}H_{16}O_2Ru+H]^+$ 331.0267, found: 331.0268.

Methyl (*E*)-3-ruthenocenyl acrylate (3b)



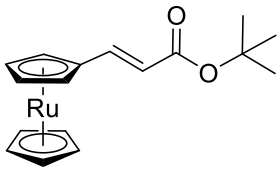
Following the general procedure A, the reaction was set up with methyl acrylate (53.0 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 9:1:1) afforded **3b** as a yellow solid (43.9 mg, 138 μmol, 55%). m.p. 119-120 °C; IR (film) 3096, 2946, 2846, 1710, 1634, 1435, 1306, 1282, 1185, 971, 799 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 15.8 Hz, 1H), 5.97 (d, *J* = 15.7 Hz, 1H), 4.85 (t, *J* = 1.8 Hz, 2H), 4.69 (t, *J* = 1.8 Hz, 2H), 4.54 (s, 5H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 144.4, 114.2, 83.0, 72.4, 71.8, 70.5, 51.5; HRMS (ESI) calcd for $[C_{14}H_{14}O_2Ru+H]^+$ 317.0116, found: 317.0131.

_n_-Butyl (_E_)-3-ruthenocenyl acrylate (3c)



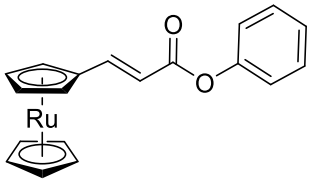
Following the general procedure A, the reaction was set up with *n*-butyl acrylate (64.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 20:1:1) afforded **3c** as a yellow solid (55.7 mg, 156 μmol, 62%). m.p. 63-66 °C; IR (film) 3090, 2956, 2927, 1631, 1459, 1246, 1188, 1158, 975, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 15.7 Hz, 1H), 5.97 (d, *J* = 15.7 Hz, 1H), 4.85 (t, *J* = 1.8 Hz, 2H), 4.69 (t, *J* = 1.8 Hz, 2H), 4.54 (s, 5H), 4.13 (t, *J* = 6.7 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.47 – 1.35 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 144.0, 114.7, 83.1, 72.3, 71.8, 70.5, 64.2, 30.9, 19.3, 13.9; HRMS (ESI) calcd for $[C_{17}H_{20}O_2Ru+H]^+$ 359.0580, found: 359.0588.

***tert*-Butyl (*E*)-3-ruthenocenyl acrylate (3d)**



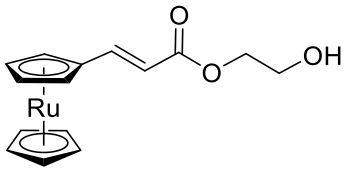
Following the general procedure A, the reaction was set up with *tert*-butyl acrylate (64.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 20:1:1) afforded **3d** as a yellow solid (49.1 mg, 137 μmol, 55%). m.p. 135-136 °C; IR (film) 3096, 2973, 2924, 1698, 1631, 1307, 1148, 977, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 15.6 Hz, 1H), 5.91 (d, *J* = 15.7 Hz, 1H), 4.85 – 4.82 (m, 2H), 4.69 – 4.65 (m, 2H), 4.54 (s, 5H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 142.9, 116.7, 83.4, 80.0, 72.1, 71.7, 70.1, 28.3; HRMS (ESI) calcd for $[C_{17}H_{20}O_2Ru+H]^+$ 359.0580, found: 359.0584.

Phenyl (*E*)-3-ruthenocenyl acrylate (3e)



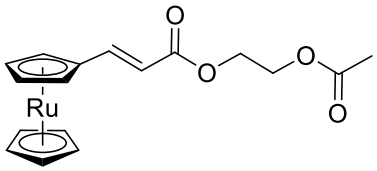
Following the general procedure A, the reaction was set up with phenyl acrylate (74.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 20:1:1) afforded **3e** as a yellow solid (53.2 mg, 141 μmol, 56%). m.p. 151-152 °C; IR (film) 3094, 2923, 2853, 1722, 1627, 1592, 1491, 1241, 1193, 1248, 969, 811 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.7 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.12 (m, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 4.92 (t, *J* = 1.8 Hz, 2H), 4.74 (t, *J* = 1.8 Hz, 2H), 4.59 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 151.1, 146.5, 129.5, 125.7, 121.8, 113.6, 82.8, 72.7, 72.0, 70.7; HRMS (ESI) calcd for $[C_{19}H_{16}O_3Ru+H]^+$ 379.0267, found: 379.0275.

2-Hydroxyethyl (*E*)-3-ruthenocenyl acrylate (3f)



Following the general procedure A, the reaction was set up with 2-hydroxylethyl acrylate (58.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 21:3:1) afforded **3f** as a yellow solid (22.6 mg, 65.4 μmol, 26%). m.p. 77-80 °C; IR (film) 3438, 3092, 2947, 1699, 1627, 1262, 1157, 1039, 972, 810, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 15.7 Hz, 1H), 6.01 (d, *J* = 15.7 Hz, 1H), 4.86 (t, *J* = 1.7 Hz, 2H), 4.70 (t, *J* = 1.8 Hz, 2H), 4.55 (s, 5H), 4.30 – 4.27 (m, 2H), 3.88 (t, *J* = 4.6 Hz, 2H), 2.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 145.2, 113.8, 82.9, 72.5, 71.9, 70.5, 66.1, 61.6; HRMS (ESI) calcd for $[C_{15}H_{16}O_3Ru+H]^+$ 347.0216, found: 347.0221.

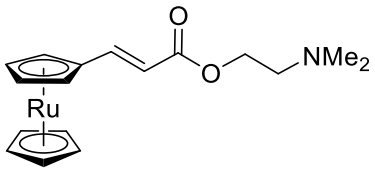
2-Acetoxyethyl (*E*)-3-ruthenocenyl acrylate (3f')



As a side product, the reaction also afforded the ester formed from the alcohol and the solvent which was isolated via flash column chromatography (hexanes/EtOAc/DCM = 21:1:1) to afford **3f'** as a yellow solid (20.7 mg, 59.9 μmol, 24%). m.p. 76-78 °C; IR (film) 3094, 2953, 1737, 1703, 1629, 1371, 1228, 1185, 1044, 975, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 15.7 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 4.87 – 4.85 (m, 2H), 4.71 – 4.69 (m, 2H), 4.55 (s, 5H), 4.34 – 4.29 (m, 4H), 2.09 (s, 3H); ^{13}C

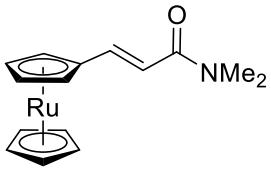
NMR (125 MHz, $CDCl_3$) δ 170.9, 167.0, 145.1, 113.8, 82.8, 72.4, 71.8, 70.5, 62.5, 62.0, 21.0; HRMS (ESI) calcd for $[C_{17}H_{18}O_4Ru+H]^+$ 389.0321, found: 389.0325.

2-Dimethylaminoethylacrylate (*E*)-3-ruthenocenyl acrylate (3g)



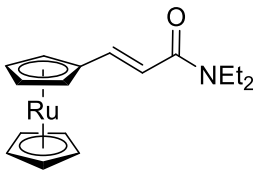
Following the general procedure A, the reaction was set up with 2-dimethylaminoethylacrylate (71.6 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 3:1) afforded **3g** as a yellow solid (30.1 mg, 80.8 μmol, 32%). m.p. 58-60 °C; IR (film) 3092, 2944, 2820, 2769, 1700, 1629, 1245, 1154, 1038, 974, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 15.8 Hz, 1H), 6.01 (d, *J* = 15.7 Hz, 1H), 4.86 – 4.83 (m, 2H), 4.71 – 4.67 (m, 2H), 4.54 (s, 5H), 4.25 (t, *J* = 5.7 Hz, 2H), 2.65 (t, *J* = 5.7 Hz, 2H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 144.6, 114.3, 83.0, 72.3, 71.8, 70.5, 61.5, 57.6, 45.4; HRMS (ESI) calcd for $[C_{17}H_{21}RuNO_2+H]^+$ 374.0694, found 374.0695.

Dimethyl (*E*)-3-ruthenocenyl acrylamide (3h)



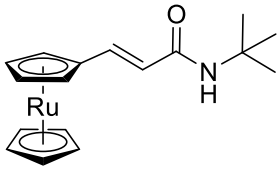
Following the general procedure A, the reaction was set up with *N*,*N*-dimethylacrylamide (49.6 mg, 0.50 mmol, 2.00 equiv) and PzNPy2 (4.92 mg, 12.5 μmol, 5.00 mol%). Purification by flash column chromatography (hexanes/EtOAc/DCM = 2:2:1) afforded **3h** as a yellow solid (33.1 mg, 101 μmol, 40%). m.p. 170-172 °C; IR (film) 3086, 2921, 2852, 1642, 1587, 1492, 1388, 1244, 1099, 977, 794 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 15.1 Hz, 1H), 6.42 (d, *J* = 15.1 Hz, 1H), 4.86 – 4.83 (m, 2H), 4.67 – 4.64 (m, 2H), 4.53 (s, 5H), 3.08 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 141.4, 113.8, 84.3, 71.8, 71.6, 70.2, 37.4. 35.9; HRMS (ESI) calcd for $[C_{15}H_{17}NORu+H]^+$ 330.0426, found: 330.0433.

Diethyl (*E*)-3-ruthenocenyl acrylamide (3i)



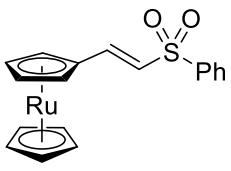
Following the general procedure A, the reaction was set up with *N*,*N*-diethylacrylamide (63.4 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 2:2:1) afforded **3i** as a yellow solid (25.6 mg, 71.8 μmol, 29%). m.p. 102-105 °C; IR (film) 2968, 2929, 2894, 1642, 1594, 1424, 1247, 1140, 976, 806 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 15.1 Hz, 1H), 6.36 (d, *J* = 15.1 Hz, 1H), 4.84 (t, *J* = 1.8 Hz, 2H), 4.65 (t, *J* = 1.8 Hz, 2H), 4.53 (s, 5H), 3.46 – 3.36 (m, 4H), 1.25 – 1.09 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 141.1, 114.4, 84.5, 71.7, 71.5, 70.2, 42.2, 41.0, 15.1, 13.3; HRMS (ESI) calcd for $[C_{17}H_{21}NORu+H]^+$ 358.0745, found: 358.0752.

***N*-*tert*-butyl (*E*)-3-ruthenocenyl acrylamide (3j)**



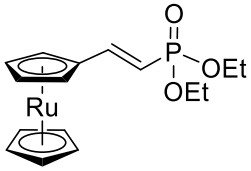
Following the general procedure A, the reaction was set up with *N*-*tert*-butylacrylamide (63.6 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 2:2:1) afforded **3j** as a yellow solid (40.6 mg, 114 μmol, 46%). m.p. 218-221 °C; IR (film) 3282, 3082, 2957, 2921, 1699, 1619, 1242, 1021, 962, 856, 799 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 15.3 Hz 1H), 5.86 (d, *J* = 15.3 Hz, 1H), 5.23 (s, 1H), 4.80 (t, *J* = 1.7 Hz, 2H), 4.64 (t, *J* = 1.7 Hz, 2H), 4.53 (s, 5H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 139.0, 118.9, 84.0, 71.7, 71.6, 70.1, 51.4, 29.0; HRMS (ESI) calcd for $[C_{17}H_{21}NORu+H]^+$ 358.0739, found: 358.0747.

Phenyl (*E*)-3-ruthenocenyl vinyl sulfone (3k)



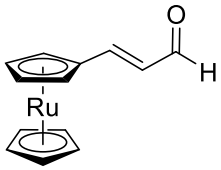
Following the general procedure A, the reaction was set up with phenyl vinyl sulfonate (84.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 21:3:1) afforded **3k** as a yellow solid (68.2 mg, 172 μmol, 69%). m.p. 194-195 °C; IR (film) 3058, 2921, 2851, 1606, 1444, 1303, 1080, 957, 813 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2, 1.8 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.51 (m, 2H), 7.48 (d, *J* = 14.6 Hz, 1H), 6.34 (d, *J* = 15.1 Hz, 1H), 4.82 (t, *J* = 1.8 Hz, 2H), 4.71 (t, *J* = 1.8 Hz, 2H), 4.52 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.5, 133.1, 129.4, 127.4, 122.3, 80.7, 73.0, 72.0, 70.6; HRMS (ESI) calcd for $[C_{18}H_{16}O_2RuS+H]^+$ 398.9993, found: 398.9999.

Diethyl (*E*)-3-ruthenocenyl vinyl phosphonate (3l)



Following the general procedure A, the reaction was set up with diethyl vinyl phosphonate (82.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 3:3:1) afforded **3l** as a yellow solid (65.9 mg, 168 μmol, 67%). m.p. 161-162 °C; IR (film) 3085, 2980, 2907, 1734, 1608, 1389, 1234, 1020, 943, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 1H), 5.81 – 5.65 (m, 1H), 4.84 (t, *J* = 1.7 Hz, 2H), 4.67 (t, *J* = 1.7 Hz, 2H), 4.53 (s, 5H), 4.12 – 4.01 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 148.1, 110.4, 108.5, 84.0, 83.7, 72.1, 71.7, 70.2, 61.62, 61.56, 16.53, 16.47; HRMS (ESI) calcd for $[C_{16}H_{21}O_3PRu+H]^+$ 395.0345, found: 395.0344.

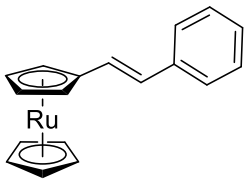
(*E*)-3-Ruthenocenyl acrolein (3m)



Following the general procedure A, the reaction was set up with acrolein (56.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 60:3:1) afforded **3m** as a yellow solid (45.2 mg, 158 μmol, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 15.6 Hz, 1H), 6.27 (dd, *J* = 15.6, 8.0 Hz, 1H), 4.91 (t, *J* = 1.8 Hz, 2H), 4.77 (t, *J* = 1.8 Hz, 2H), 4.56 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 153.4, 125.9, 82.4, 73.2, 72.2, 70.9; HRMS (ESI)

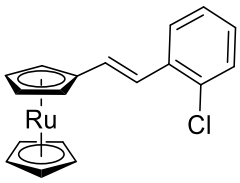
calcd for $[C_{13}H_{12}ORu+H]^+$ 287.0004, found: 287.0006. The obtained spectral data are equivalent to the ones reported in the literature.[1]

(*E*)-(2-(Ruthenocenyl)vinyl)benzene (3n)



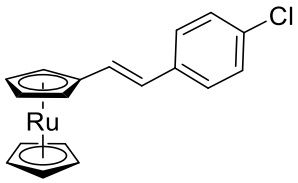
Following the general procedure A, the reaction was set up with styrene (52.1 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 200:8:2) afforded **3n** as a yellow solid (13.6 mg, 40.8 μmol, 16%). m.p. 138-141 °C; IR (film) 3082, 3023, 2921, 2851, 1099 1099, 957, 809, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.65 (d, *J* = 16.1 Hz, 1H), 4.90 – 4.81 (m, 2H), 4.64 – 4.61 (m, 2H), 4.54 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 128.7, 126.9, 125.99, 125.96, 87.6, 71.3, 70.9, 69.3; HRMS (ESI) calcd for $[C_{18}H_{16}Ru+H]^+$ 334.0296, found: 334.0295. The compound has been reported in the literature.[2]

(*E*)-1-Chloro-2-(2-(ruthenocenyl)vinyl)benzene (3o)



Following the general procedure A, the reaction was set up with 2-chlorostyrene (69.3 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 200:8:2) afforded **3o** as a yellow solid (21.4 mg, 44.3 μmol, 23%). m.p. 90-91 °C; IR (film) 3092, 3054, 3015, 2923, 2851, 1629, 1588, 1476, 1434, 1406, 1099, 1032, 996, 805, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 8.1, 2.1 Hz, 1H), 7.33 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.19 (dt, *J* = 6.6, 2.1 Hz, 1H), 7.13 (ddd, *J* = 9.3, 5.7, 1.8 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 4.91 – 4.88 (m, 2H), 4.65 – 4.62 (m, 2H), 4.55 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 132.6, 129.9, 128.8, 127.8, 126.9, 126.1, 121.9, 87.2, 71.4, 71.1, 69.6; HRMS (ESI) calcd for $[C_{18}H_{15}ClRu+H]^+$ 368.9979, found: 368.9986.

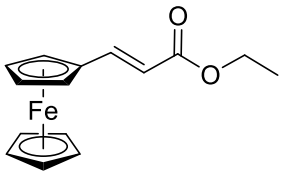
(*E*)-1-Chloro-4-(2-(ruthenocenyl)vinyl)benzene (3p)



Following the general procedure A, the reaction was set up with 4-chlorostyrene (69.3 mg, 0.50 mmol, 2.00 equiv). Purification by flash column chromatography (hexanes/EtOAc/DCM = 200:8:2) afforded **3p** as a yellow solid (21.4 mg, 44.3 μmol, 23%). m.p. 91-94 °C; IR (film) 3092, 3049, 2922, 2851, 1631, 1438, 1034, 955, 808, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 4H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.58 (d, *J* = 16.1 Hz, 1H), 4.87 – 4.84 (m, 2H), 4.64 – 4.61 (m, 2H), 4.54 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.4, 128.9, 127.1, 126.8, 124.6, 87.2, 71.3, 71.0, 69.3; HRMS (ESI) calcd for $[C_{18}H_{15}ClRu+H]^+$ 367.9906, found: 367.9907. The compound has been reported in the literature.[2]

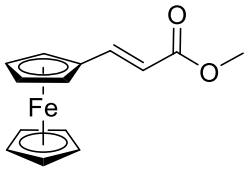
Ferrocene Derivatives

Ethyl (*E*)-3-ferrocenyl acrylate (4a)



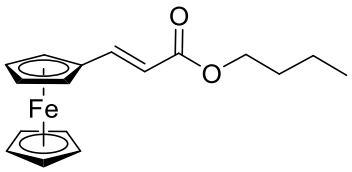
Following the general procedure B, the reaction was set up with ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4a** as an orange solid (253 mg, 895 μmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.7 Hz, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 4.50 – 4.46 (m, 2H), 4.41 – 4.36 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 5H), 1.32 (t, *J* = 7.2 Hz, 3H). The obtained spectral data are equivalent to the ones reported in the literature.[3]

Methyl (*E*)-3-ferrocenyl acrylate (4b)



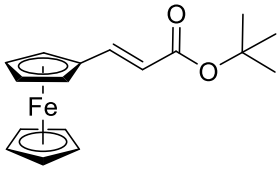
Following the general procedure B, the reaction was set up with methyl acrylate (86.1 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4b** as an orange solid (234 mg, 866 μmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.7 Hz, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 4.50 – 4.47 (m, 2H), 4.42 – 4.39 (m, 2H), 4.16 (s, 5H), 3.77 (s, 3H). The obtained spectral data are equivalent to the ones reported in the literature.[3]

***n*-Butyl (*E*)-3-ferrocenyl acrylate (4c)**



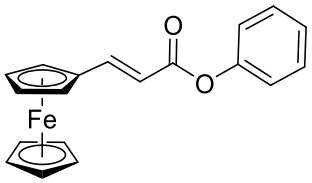
Following the general procedure B, the reaction was set up with *n*-butyl acrylate (128 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4c** as an orange solid (239 mg, 766 μmol, 77%). m.p. 63-64 °C; IR (film) 3100, 2955, 2870, 1703, 1629, 1465, 1394, 1355, 1306, 1286, 1190, 1164, 1040, 977, 863, 806, 735, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.5 Hz, 1H), 6.03 (d, *J* = 15.5 Hz, 1H), 4.50 – 4.47 (m, 2H), 4.41 – 4.38 (m, 2H), 4.19 – 4.14 (m, 7H), 1.71 – 1.65 (m, 2H), 1.48 – 1.41 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 145.6, 115.0, 78.8, 70.8, 69.7, 68.6, 64.1, 30.9, 19.3, 13.9; HRMS (ESI) calcd for $[C_{17}H_{21}FeO_2+H]^+$ 313.0885, found 313.0887. The obtained spectral data are equivalent to the ones reported in the literature.[4]

***tert*-Butyl (*E*)-3-ferrocenyl acrylate (4d)**



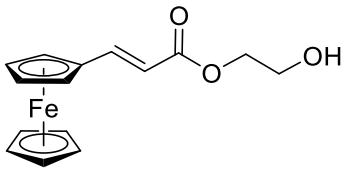
Following the general procedure B, the reaction was set up with *tert*-butyl acrylate (128 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4d** as a red solid (254 mg, 813 μmol, 81%). m.p. 72-74 °C; IR (film) 3002, 2929, 1692, 1625, 1453, 1307, 1245, 1146, 980, 834, 731, 664 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 15.5 Hz, 1H), 5.96 (d, *J* = 15.7 Hz, 1H), 4.47 – 4.44 (m, 2H), 4.38 – 4.35 (m, 2H), 4.16 (s, 5H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.5, 117.1, 80.1, 79.2, 70.7, 69.7, 68.6, 28.4; HRMS (ESI) calcd for $[C_{17}H_{20}FeO_2+H]^+$ 312.0813, found: 312.0814.

Phenyl (*E*)-3-ferrocenyl acrylate (4e)



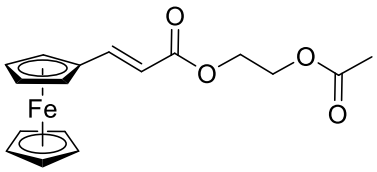
Following the general procedure B, the reaction was set up with phenyl acrylate (148 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 6:1) afforded **4e** as a red solid (217 mg, 652 μmol, 65%). m.p. 183-184 °C; IR (film) 3088, 2920, 2851, 2103, 1717, 1617, 1490, 1408, 1357, 1307, 1248, 1187, 1132, 193 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.23 – 7.16 (m, 2H), 6.25 (d, *J* = 15.7 Hz, 1H), 4.61 – 4.58 (m, 2H), 4.51 – 4.49 (m, 2H), 4.24 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 151.1, 148.2, 129.5, 125.7, 121.8, 113.9, 78.6, 71.5, 70.0, 69.1; HRMS (ESI) calcd for $[C_{19}H_{16}FeO_2+H]^+$ 333.0572, found 333.0572.

2-Hydroxyethyl (*E*)-3-ferrocenyl acrylate (4f)



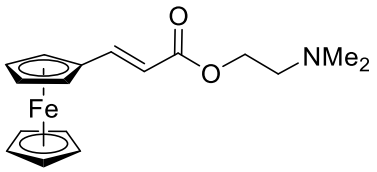
Following the general procedure B, the reaction was set up with 2-hydroxyethylacrylate (116 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 3:1) afforded **4f** as a red solid (269 mg, 895 μmol, 90%). m.p. 63-65 °C; IR (film) 3402, 3090, 2946, 2878, 2247, 1686, 1621, 1302, 1259, 1188, 1157, 1041, 908, 817, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.7 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 4.51 – 4.48 (m, 2H), 4.43 – 4.41 (m, 2H), 4.33 – 4.30 (m, 2H), 4.16 (s, 5H), 3.90 (q, *J* = 5.1 Hz, 2H), 2.07 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 146.9, 114.1, 78.5, 71.1, 69.8, 68.7, 66.0, 61.5; HRMS (ESI) calcd for $[C_{15}H_{16}FeO_3+H]^+$ 300.0449, found 300.0444.

2-Acetoxyethyl (*E*)-3-ferrocenyl acrylate (4f')



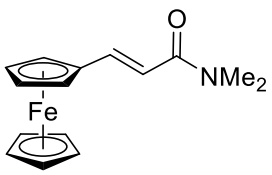
As a side product, the reaction also afforded the ester formed from the alcohol and the solvent which was isolated via flash column chromatography (hexanes/EtOAc = 6:1) to afford **4f'** as a red liquid (30.0 mg, 100 μmol, 10%). IR (film) 3092, 2954, 2922, 1740, 1706, 1628, 1243, 1188, 1157, 1046, 977, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 15.7 Hz, 1H), 6.05 (d, *J* = 15.6 Hz, 1H), 4.51 – 4.48 (m, 2H), 4.43 – 4.40 (m, 2H), 4.37 – 4.31 (m, 4H), 4.16 (s, 5H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 167.0, 146.8, 114.1, 78.5, 71.1, 69.8, 68.8, 62.5, 62.0, 21.0; HRMS (ESI) calcd for $[C_{17}H_{18}O_4Fe+H]^+$ 342.0555, found: 342.0547.

2-Dimethylamino (*E*)-3-ferrocenyl acrylate (4g)



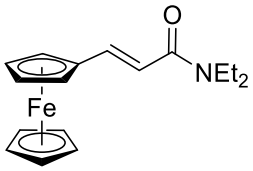
Following the general procedure B, the reaction was set up with 2-dimethylaminoethylacrylate (143.2 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 3:1) afforded **4g** as a red liquid (160 mg, 489 μmol, 49%). IR (film) 3090, 2922, 2852, 2769, 1700, 1625, 1246, 1153, 1027, 974, 818 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.7 Hz, 1H), 6.09 (d, *J* = 15.7 Hz, 1H), 4.48 (t, *J* = 1.9 Hz, 2H), 4.40 (t, *J* = 1.9 Hz, 2H), 4.27 (t, *J* = 5.7 Hz, 2H), 4.15 (s, 5H), 2.65 (t, *J* = 5.7 Hz, 2H), 2.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 145.8, 114.6, 78.5, 70.8, 69.6, 68.5, 61.8, 57.8, 45.6; HRMS (ESI) calcd for $[C_{17}H_{21}FeNO_2+H]^+$ 328.0994, found 328.1000.

***N*,*N*-Dimethyl (*E*)-3-ferrocenyl acrylamide (4h)**



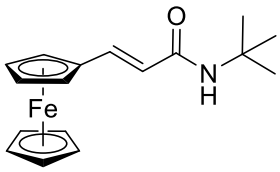
Following the general procedure B, the reaction was set up with *N*,*N*-dimethylacrylamide (99.1 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 1:1) afforded **4h** as a red solid (156 mg, 551 μmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 15.0 Hz, 1H), 6.47 (d, *J* = 15.1 Hz, 1H), 4.49 – 4.45 (m, 2H), 4.38 – 4.34 (m, 2H), 4.15 (s, 5H), 3.12 (s, 3H), 3.04 (s, 3H); HRMS (ESI) calcd for $[C_{15}H_{17}FeNO+H]^+$ 284.0732, found 284.0737. The obtained spectral data are equivalent to the ones reported in the literature.[3]

***N*,*N*-Diethyl (*E*)-3-ferrocenyl acrylamide (4i)**



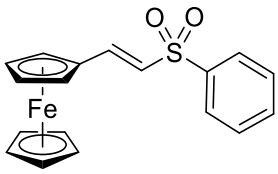
Following the general procedure B, the reaction was set up with *N*,*N*-diethylacrylamide (127 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 1:1) afforded **4i** as a red solid (181 mg, 640 μmol, 64%). m.p. 88-90 °C; IR (film) 3079, 2967, 2921, 2851, 1643, 1592, 1422, 1245, 1135, 964, 815, 783 cm^{-1}; **^{1}**H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.1 Hz, 1H), 6.41 (d, *J* = 15.1 Hz, 1H), 4.46 (t, *J* = 1.9 Hz, 2H), 4.34 (t, *J* = 1.8 Hz, 2H), 4.15 (s, 5H), 3.49 – 3.38 (m, 4H), 1.25 – 1.15 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 142.6, 114.7, 80.3, 70.3, 69.6, 68.3, 42.3, 41.1, 15.2, 13.4; HRMS (ESI) calcd for $[C_{17}H_{21}FeNO+H]^+$ 312.1045, found 312.1050.

***N*-*tert*-Butyl (*E*)-3-ferrocenyl acrylamide (4j)**



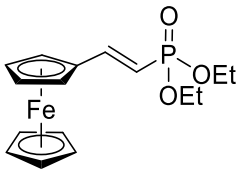
Following the general procedure B, the reaction was set up with *N*-*tert*-butylacrylamide (127 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 3:1) afforded **4j** as a red solid (246 mg, 801 μmol, 80%). m.p. 163-165 °C; IR (film) 3276, 3073, 2962, 2852, 1736, 1651, 1614, 1449, 1390, 1247, 1104, 977, 861, 738 cm^{-1}; **^{1}**H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 15.3 Hz, 1H), 5.94 (d, *J* = 15.3 Hz, 1H), 5.46 (bs, 1H), 4.41 – 4.38 (m, 2H), 4.32 – 4.29 (m, 2H), 4.12 (s, 5H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 140.2, 119.2, 79.7, 70.1, 69.5, 68.1, 51.3, 29.0; HRMS (ESI) calcd for $[C_{17}H_{21}FeNO+H]^+$ 312.1045, found 312.1044.

Phenyl (*E*)-3-ferrocenyl vinyl sulfone (4k)



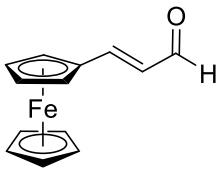
Following the general procedure B, the reaction was set up with phenyl vinylsulfonate (168 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 5:1) afforded **4k** as a red solid (213 mg, 605 μmol, 61%). m.p. 179-180 °C; IR (film) 3056, 2921, 2851, 2444, 2111, 1602, 1443, 1302, 1138, 1080, 998, 959, 817, 760, 728, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.62 – 7.57 (m, 2H), 7.56 – 7.51 (m, 2H), 6.41 (d, *J* = 15.3 Hz, 1H), 4.47 – 4.45 (m, 2H), 4.45 – 4.42 (m, 2H), 4.15 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 141.6, 133.1, 129.4, 127.4, 122.9, 76.5, 71.8, 70.0, 69.2; HRMS (ESI) calcd for $[C_{18}H_{16}FeO_2S+H]^+$ 353.0299, found 353.0297.

Diethyl (*E*)-3-ferrocenyl vinyl phosphonate (4l)



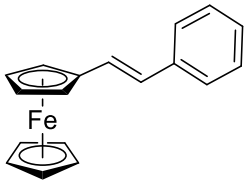
Following the general procedure B, the reaction was set up with diethyl vinyl phosphonate (164 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 1:2) afforded **4l** as an orange solid (245 mg, 704 μmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 22.0, 17.2 Hz, 1H), 5.85 – 5.70 (m, 1H), 4.51 – 4.42 (m, 2H), 4.42 – 4.34 (m, 2H), 4.14 (s, 5H), 4.13 – 4.03 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). The obtained spectral data are equivalent to the ones reported in the literature.[3]

(*E*)-3-ferrocenyl acrolein (4m)



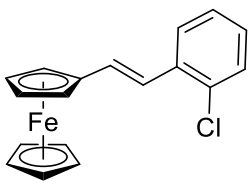
Following the general procedure B, the reaction was set up with acrolein (56.1 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 3:1) afforded **4m** as a red solid (65.6 mg, 273 μmol, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.6, 7.9 Hz, 1H), 4.58 – 4.54 (m, 2H), 4.54 – 4.48 (m, 2H), 4.18 (s, 5H); HRMS (ESI) calcd for $[C_{13}H_{12}FeO+H]^+$ 243.0310, found 243.0315. The obtained spectral data are equivalent to the ones reported in the literature.[3]

(*E*)-(2-(Ferrocenyl)vinyl)benzene (4n)



Following the general procedure B, the reaction was set up with styrene (104 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4n** as an orange solid (51.0 mg, 177 μmol, 18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 16.1 Hz, 1H), 6.65 (d, *J* = 16.1 Hz, 1H), 4.59 – 4.47 (m, 2H), 4.38 – 4.30 (m, 2H), 4.18 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 128.8, 127.0, 126.9, 126.1, 125.9, 83.4, 69.3, 69.1, 67.0; HRMS (ESI) calcd for $[C_{18}H_{16}Fe+H]^+$ 288.0601, found 288.0596. The obtained spectral data are equivalent to the ones reported in the literature.[5]

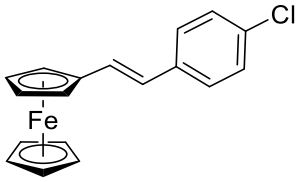
(*E*)-1-Chloro-2-(2-(ferrocenyl)vinyl)benzene (4o)



Following the general procedure B, the reaction was set up with 2-chlorostyrene (139 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4o** as an

orange liquid (62.7 mg, 194 μmol, 19%). IR (film) 3086, 2922, 2851, 2694, 1626, 1587, 1438, 1103, 1027, 953, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 16.1 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 4.43 – 4.39 (m, 2H), 4.24 – 4.20 (m, 2H), 4.06 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 132.6, 130.00, 129.95, 127.8, 127.0, 126.1, 122.1, 83.0, 69.5, 69.4; HRMS (ESI) calcd for $[C_{18}H_{15}ClFe+H]^+$ 322.0212, found 322.0209.

(*E*)-1-Chloro-4-(2-(ferrocenyl)vinyl)benzene (4p)



Following the general procedure B, the reaction was set up with 4-chlorostyrene (139 mg, 1.00 mmol, 1.00 equiv). Purification by flash column chromatography (hexanes/EtOAc = 9:1) afforded **4p** as an orange solid (59.1 mg, 184 μmol, 18%). m.p. 147-149 °C; IR (film) 3082, 2919, 2851, 1631, 1489, 1458, 1404, 1296, 1244, 1099, 998, 962, 860, 808, 741cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 16.1 Hz, 1H), 6.65 (d, *J* = 16.1 Hz, 1H), 4.50 – 4.44 (m, 2H), 4.32 – 4.27 (m, 2H), 4.15 (s, 5H); HRMS (ESI) calcd for $[C_{18}H_{15}ClFe+H]^+$ 322.0212, found 322.0210. The obtained spectral data are equivalent to the ones reported in the literature.[6]

5. Kinetic Data

The formation of the mono-alkenylated product and the bis-alkenylated products was tracked *via* gas chromatography after prior calibration using analytically pure samples. Instead of sealing the reaction vessel, a cap with an oxygen-filled balloon and a rubber septum were used to enable the extraction of sample aliquots (~20 µL) after a particular time interval had passed. In addition, an appropriate amount of the internal standard, *n*-dodecane, was added to the reaction mixture. During our optimization studies, we observed that the use of a balloon instead of a tight seal was detrimental to the yield. However, since this effect can be seen as a uniform perturbation upon all experiments, the qualitative information obtained from them is still valid.

5.1 Ligand Binding Strength Study

Increasing quantities of pyridine (0.5, 1.0, 2.0, 4.0 equiv) were added to solutions of $Pd(OAc)_2$ (44.9 mg, 0.20 mmol) with PzNPy2 (0.20 mmol) or PzNPy3 (0.20 mmol) in $CDCl_3$ (4.0 mL, 0.50 M). After stirring for one hour at room temperature, an aliquot was taken and analyzed *via* ^1H NMR spectroscopy. Intermediate complexes were identified by comparison of the obtained spectrum with spectra of free pyridine, $Pd(py)_2(OAc)_2$, and the respective free PzNPy ligands.

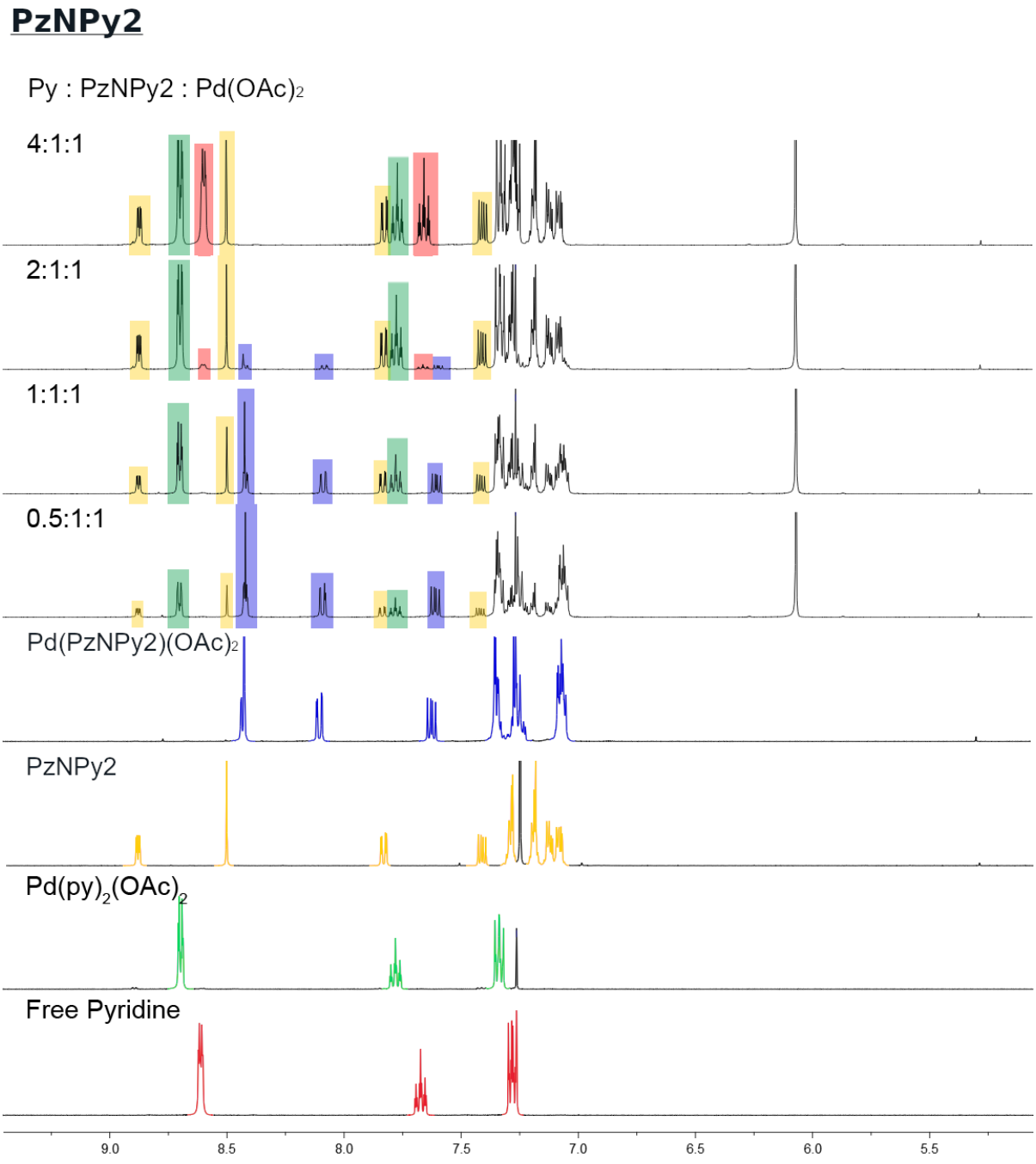


Figure S2. Titration of pyridine into solution containing $Pd(OAc)_2$, PzNPy2, and 1,3,5-trimethoxybenzene (33.6 mg, 0.20 mmol) as an internal standard in $CDCl_3$. An increase in the concentration of pyridine resulted in the dissociation of $Pd(PzNPy2)(OAc)_2$ which was accompanied by the formation of the $Pd(pyridine)_2(OAc)_2$ complex. After four equivalents of pyridine were added, PzNPy2 had dissociated almost completely and had been replaced by pyridine ligands.

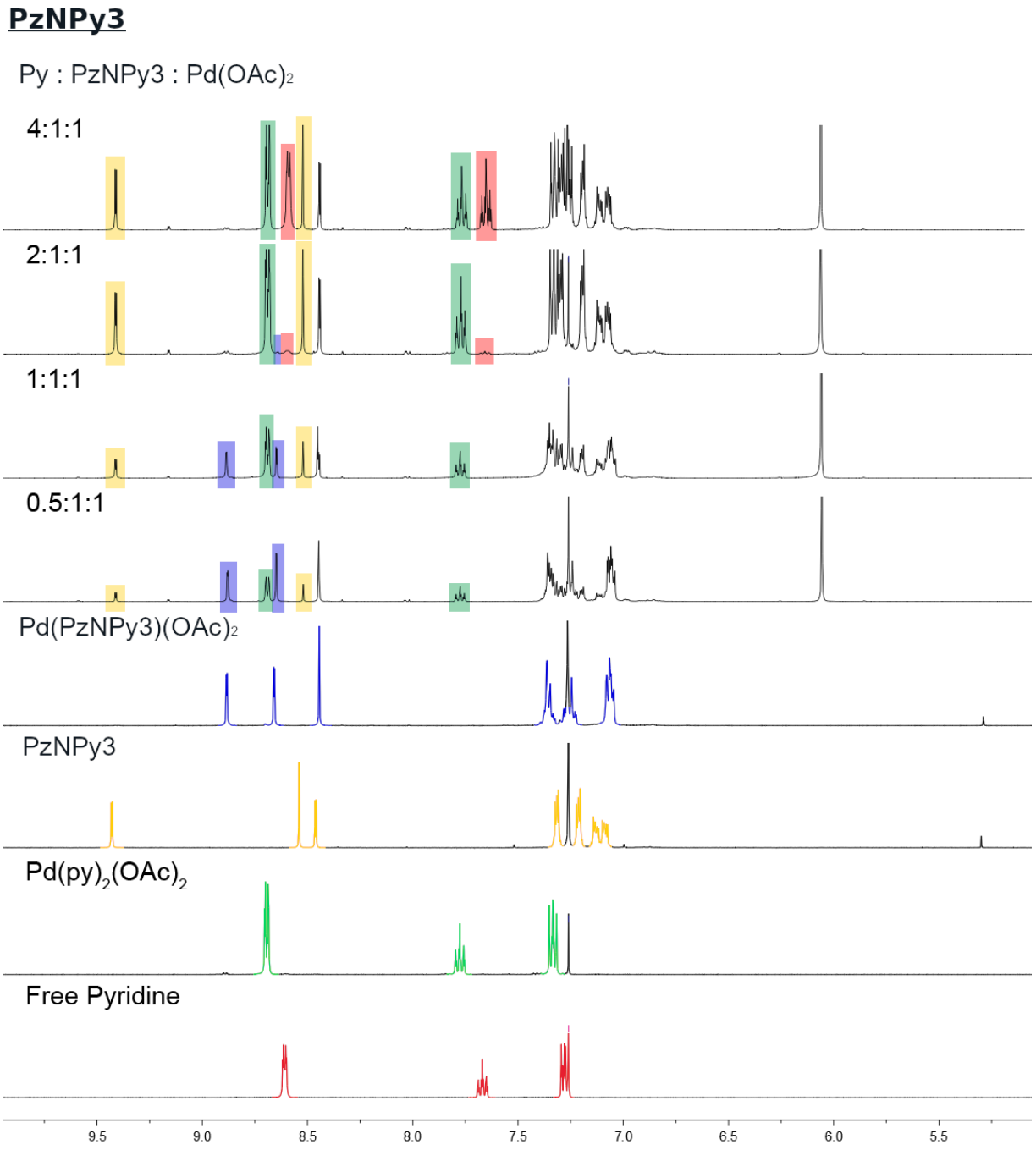
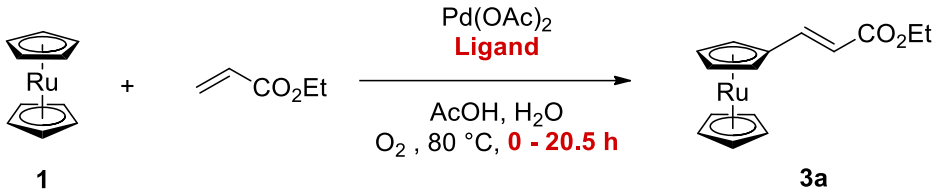


Figure S3. Titration of pyridine into solution containing $Pd(OAc)_2$, PzNPy3, and 1,3,5-trimethoxybenzene (33.6 mg, 0.20 mmol) as an internal standard in $CDCl_3$. An increase in the concentration of pyridine resulted in the dissociation of $Pd(PzNPy3)(OAc)_2$ which was accompanied by the formation of the $Pd(pyridine)_2(OAc)_2$ complex. After four equivalents of pyridine were added, PzNPy3 had dissociated almost completely and had been replaced by pyridine ligands.

5.2 Ligand Screening

Ruthenocene (Fig. 3B)



1 **3a**

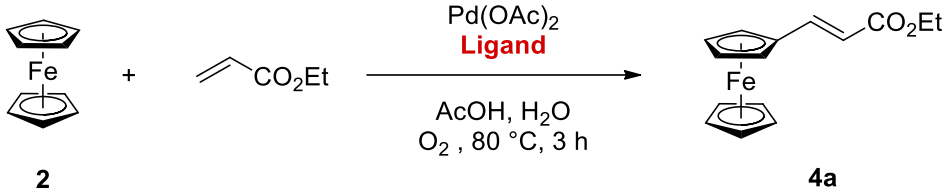
The reaction was performed as described in general procedure A with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv) as the substrate, without any ligand, or with PzNPy1 (2.0 mg, 25.0 µmol, 2.50 mol%), PzNPy2 (2.5 mg, 6.25 µmol, 2.50 mol%), PzNPy3 (2.9 mg, 25.0 µmol, 2.50 mol%), or DAF (1.1 mg, 6.25 µmol, 2.50 mol%) as the ligand.

Table S3. Alkenylation of ruthenocene with different ligands.[a]

		PzNPy1		PzNPy2		DAF		PzNPy3	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	2 h	12.98	1.62	15.42	0.60	9.70	1.93	15.73	1.01
2	4 h	18.61	2.28	21.67	0.52	17.13	3.94	20.50	1.64
3	6 h	22.34	1.91	25.05	0.54	21.71	3.97	22.44	1.40
4	8 h	24.10	1.76	26.18	0.04	24.26	3.87	23.06	1.91
5	20½ h	26.03	1.70	28.43	0.40	27.58	2.43	24.58	2.21

[a] Yields were calculated based on a ruthenocene amount of 0.25 mmol.

Ferrocene (Fig. 3C)



2 **4a**

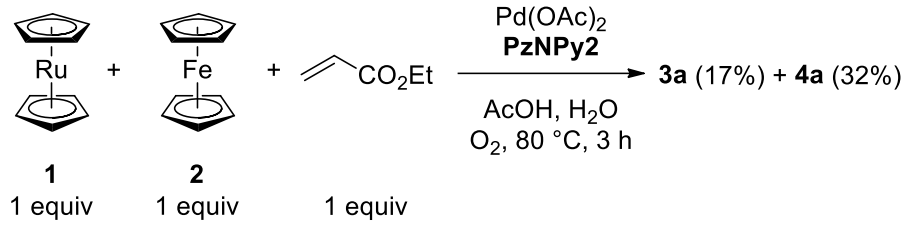
The reaction was performed as described in general procedure B with ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv) as the substrate, without any ligand, or with PzNPy1 (5.6 mg, 25.0 μmol, 2.50 mol%), PzNPy2 (9.8 mg, 25.0 μmol, 2.50 mol%), PzNPy3 (11.6 mg, 25.0 μmol, 2.50 mol%), or DAF (4.6 mg, 25.0 μmol, 2.50 mol%) as the ligand.

Table S4. Alkenylation of ferrocene with different ligands.[a]

		w/o Ligand		PzNPy1		PzNPy2		DAF		PzNPy3	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	5 min	0.80	0.22	0.92	0.09	2.03	0.60	1.81	0.27	1.73	0.05
2	10 min	3.33	0.46	3.39	0.32	4.45	0.49	5.05	0.27	5.68	0.02
3	15 min	4.44	0.61	5.37	0.64	7.10	0.25	7.56	0.22	9.18	0.31
4	20 min	5.01	0.71	6.95	0.98	9.45	0.21	39.33	41.65	11.99	0.30
5	30 min	5.59	0.74	9.84	1.71	13.03	0.31	13.80	0.57	17.12	0.67
6	40 min	6.01	0.79	11.75	2.92	16.56	1.07	18.95	1.69	22.30	0.42
7	60 min	6.99	1.02	16.63	3.57	24.90	1.47	23.08	1.49	31.14	0.76
8	80 min	8.16	1.03	20.17	4.86	29.86	0.85	30.09	2.05	39.50	0.39
9	100 min	9.35	0.98	23.81	6.15	35.51	1.17	37.63	5.66	46.51	0.87
10	120 min	10.84	1.24	26.94	6.99	40.11	1.74	42.15	5.84	55.54	0.16
11	140 min	12.83	1.77	30.17	7.93	46.36	2.01	48.04	4.50	62.23	0.78
12	160 min	14.94	1.43	32.73	8.74	49.88	2.40	56.35	7.01	69.72	0.06
13	180 min	16.25	1.78	34.77	10.24	53.68	3.36	64.36	7.60	76.04	0.09

[a] Yields were normalized for an ethyl acrylate amount of 1.00 mmol.

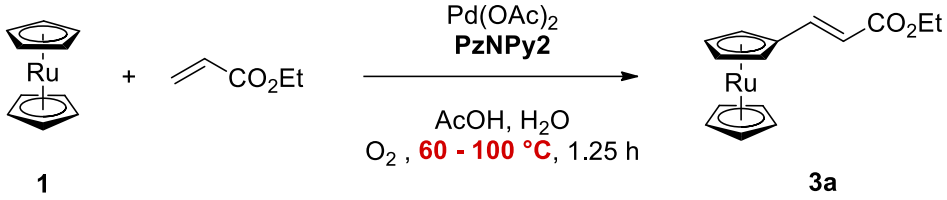
5.3 Competition Experiment



The competition experiment was set up with ferrocene (186 mg, 1.00 mmol, 1.00 equiv), ruthenocene (231 mg, 1.00 mmol, 1.00 equiv), and ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv) as substrates and PzNPy2 (9.6 mg, 25.0 μmol, 2.50 mol%) and $Pd(OAc)_2$ (5.6 mg, 25.0 μmol, 2.50 mol%) as the catalyst in glacial acetic acid (4.00 mL, 0.25 M) and water (50.0 μL). The reaction vial was sealed with a cap and stirred at 450 rpm for 3 hours at 80 °C. Then, the reaction mixture was diluted with DCM (5 mL), the internal standard was added, and an aliquot (~50 μL) was taken which was submitted to GC analysis.

5.4 Temperature-Dependence Experiments

Ruthenocene



1 **3a**

The reaction was performed as outlined in general procedure A at different temperatures with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv) as the substrate.

Table S5. Temperature-dependence experiments with ruthenocene.[a]

		60 °C		70 °C		80 °C		90 °C		100 °C	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	15 min	0.6361	0.0793	2.0980	0.3460	3.0857	0.5156	3.8922	0.5235	7.8238	0.1019
2	30min	1.3731	0.0923	4.0563	0.7052	5.1961	0.2158	7.2713	1.2724	14.2922	0.1506
3	45 min	2.1437	0.1178	5.8226	0.9886	7.3182	0.2692	11.1237	0.7849	19.0470	0.1514
4	60 min	2.8862	0.1289	7.4918	1.2435	9.2665	0.4498	12.0777	1.7389	21.8403	0.0465
5	75 min	3.4671	0.0331	9.0458	1.1984	11.0273	0.3893	14.0788	2.0694	23.5199	0.3811

[a] Yields were calculated based on a ruthenocene amount of 0.50 mmol.

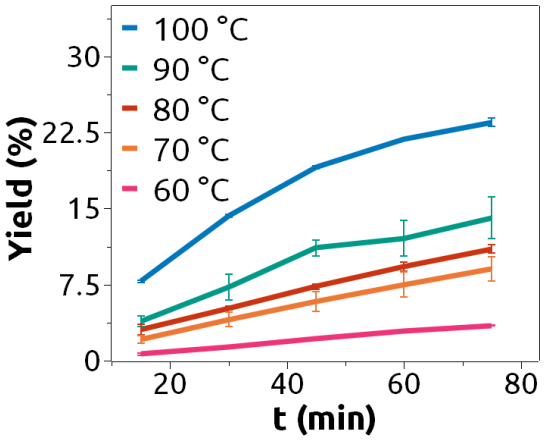


Figure S4. Plot of the yield of **3a** in a temperature range of 60-100 °C versus time.

Table S6. Data for the construction of the Eyring plot for ruthenocene.

Entry	log (k/T)	1/T (10^4 K^{-1})
1	-4.74	30.02
2	-4.36	29.14
3	-4.31	28.32
4	-4.22	27.54
5	-4.02	26.80

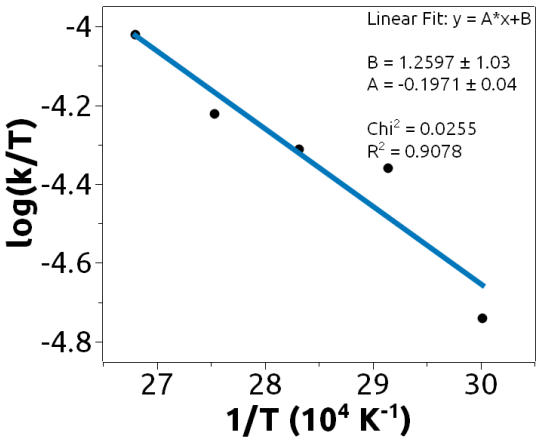
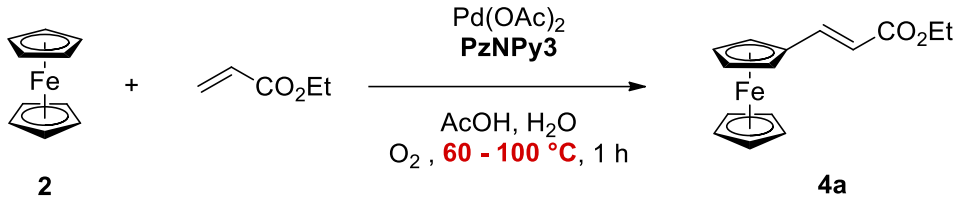


Figure S5. Eyring plot for the determination of the activation parameters of the reaction with ruthenocene.

A value of -1970.10 for the slope and a value of 1.2597 was obtained for the intercept which were subsequently used to calculate the values of the enthalpy/entropy of activation. This afforded an enthalpy of activation value of 37.7 kJ mol^{-1} and an entropy of activation value of -173.5 J K^{-1} mol^{-1}.

Ferrocene



2 **4a**

The reaction was performed as outlined in general procedure B at different temperatures with ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv) as the substrate.

Table S7. Temperature-dependence experiments with ferrocene.[a]

		60 °C		70 °C		80 °C		90 °C		100 °C	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	5 min	0.43	0.04	0.88	0.16	1.73	0.05	3.42	0.75	5.14	0.69
2	10 min	1.07	0.06	2.31	0.20	5.68	0.02	8.59	0.85	13.53	0.66
3	15 min	1.76	0.13	3.84	0.36	9.18	0.31	13.40	0.74	22.03	1.20
4	20 min	2.37	0.16	5.24	0.35	11.99	0.30	17.62	0.66	29.01	0.99
5	30 min	3.69	0.25	7.93	0.44	17.12	0.67	26.54	0.61	43.11	0.21
6	40 min	4.89	0.31	10.32	0.53	22.30	0.42	34.27	0.62	56.55	0.16
7	60 min	7.08	0.44	14.08	0.69	31.14	0.76	48.87	0.18	79.35	0.86

[a] Yields were calculated based on an ethyl acrylate amount of 1.00 mmol.

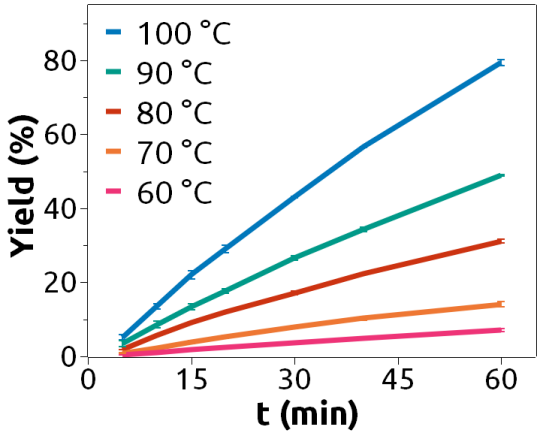


Figure S6. Plot of the yield of **4a** in a temperature range of 60-100 °C versus time.

Table S8. Data for the construction of the Eyring plot for ferrocene.

Entry	log (k/T)	1/T (10^4 K^{-1})
1	-4.72	30.02
2	-4.46	29.14
3	-4.09	28.32
4	-3.92	27.54
5	-3.72	26.80

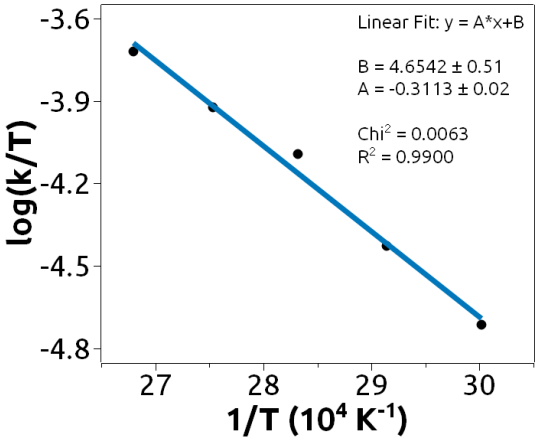
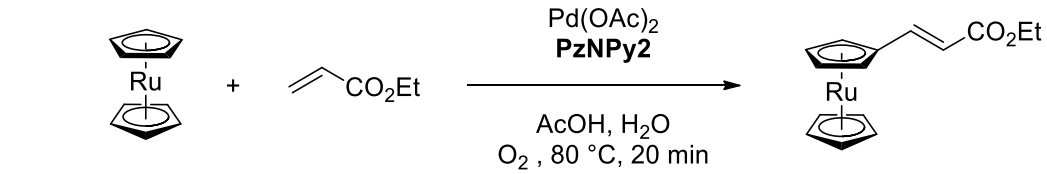


Figure S7. Eyring plot for the determination of the activation parameters of the reaction with ferrocene.

A value of -3113.17 for the slope and a value of 4.6542 was obtained for the intercept which were subsequently used to calculate the values of the enthalpy/entropy of activation. This afforded an enthalpy of activation value of 59.6 kJ mol^{-1} and an entropy of activation value of -108.6 J K^{-1} mol^{-1}.

5.5 Reaction Order

Order in Ruthenocene



1, **0.0625 - 0.375 mmol** **3a**

The reaction was performed as outlined in general procedure A at with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv) as the substrate. The amount of ruthenocene was varied.

Table S9. Alkenylation of ruthenocene with varying amounts of ruthenocene.

		0.0625 mmol		0.125 mmol		0.1875 mmol		0.25 mmol		0.375 mmol	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	4 min	0.0803	0.0229	0.1137	0.0292	0.2035	0.0010	0.3062	0.0285	0.5355	0.1037
2	8 min	0.3005	0.0709	0.3406	0.1773	0.7852	0.0209	1.0017	0.1696	1.3764	0.0642
3	12 min	0.6747	0.0219	0.6158	0.2838	1.3974	0.0044	1.7851	0.2282	2.3144	0.0562
4	16 min	0.7748	0.1405	0.9219	0.4126	1.9809	0.0042	2.5381	0.3506	3.2039	0.0768
5	20 min	0.9639	0.1133	1.1442	0.4879	2.4339	0.0000	3.0867	0.3457	3.9100	0.1026

[a] Yields were calculated based on a ruthenocene amount of 0.25 mmol.

Table S10. Initial rates obtained from performing linear fits of the individual data sets of Table S9.

Entry	n (RcH) (mmol)	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	0.0625	0.0560	0.0060
2	0.125	0.0661	0.0020
3	0.1875	0.1414	0.0042
4	0.25	0.1774	0.0058
5	0.375	0.2144	0.0056

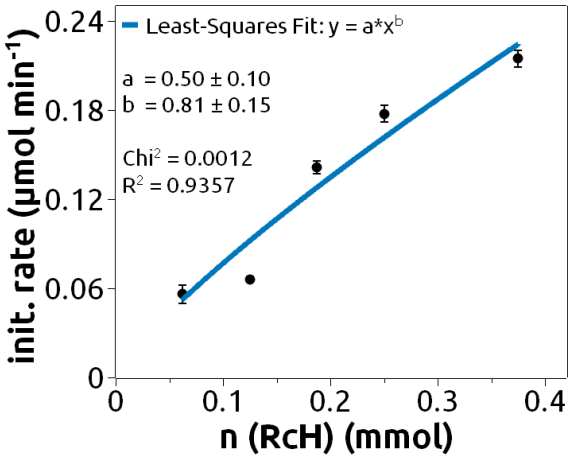
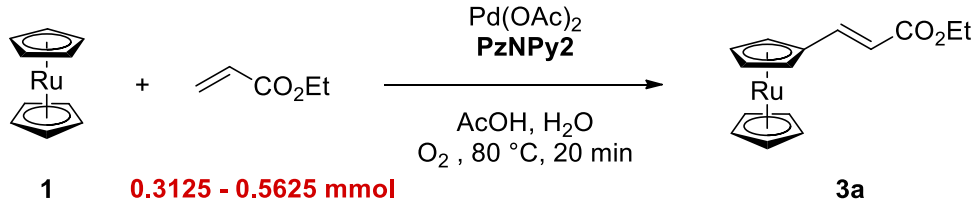


Figure S8. Plot of the initial rate versus the concentration in ruthenocene. The order in ruthenocene was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

Order in Ethyl Acrylate



The reaction was performed as outlined in general procedure A at with ruthenocene (57.8 mg, 0.25 mmol, 1.00 equiv). The amount of ethyl acrylate was varied.

Table S11. Alkenylation of ruthenocene with varying amounts of ethyl acrylate.

		0.3125 mmol		0.375 mmol		0.50 mmol		0.4375 mmol		0.5625 mmol	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	4 min	0.3416	0.1099	0.3520	0.0142	0.3062	0.0285	0.5956	0.3064	0.3885	0.1215
2	8 min	0.8267	0.0194	1.0797	0.1381	1.0017	0.1696	1.0526	0.0148	0.9807	0.0423
3	12 min	1.4097	0.0489	1.8623	0.1635	1.7851	0.2282	1.8096	0.0145	1.7635	0.0864
4	16 min	2.0146	0.0196	2.6779	0.2324	2.5381	0.3506	2.4288	0.0111	2.4840	0.1718
5	20 min	2.5534	0.0750	3.2520	0.3050	3.0867	0.3457	3.0256	0.0261	3.0835	0.2451

[a] Yields were calculated based on ruthenocene amount of 0.25 mmol.

Table S12. Initial rates obtained from performing linear fits of the individual data sets of Table S11.

Entry	n (acrylate) (mmol)	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	0.3125	0.1403	0.0028
2	0.375	0.1850	0.0056
3	0.4375	0.1559	0.0058
4	0.5	0.1774	0.0058
5	0.5625	0.1723	0.0047

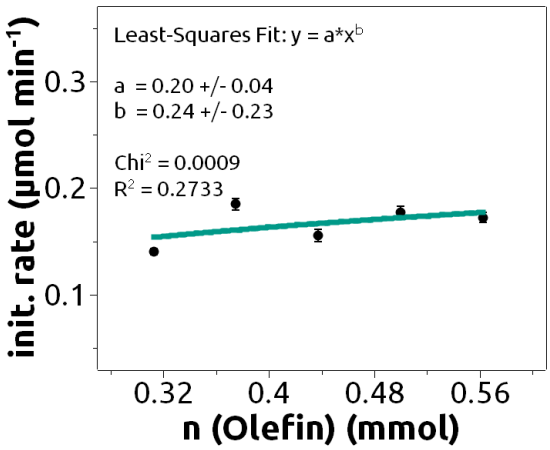
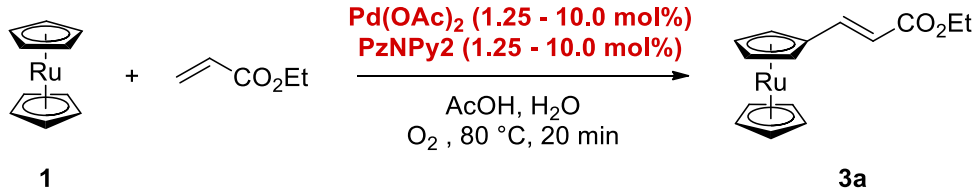


Figure S9. Plot of the initial rate versus the concentration in ethyl acrylate in the ruthenocene alkenylation. The order in ethyl acrylate was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

Order in Catalyst



1 **3a**

The reaction was performed as outlined in general procedure A with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv) as the substrates. The amount of catalyst was varied.

Table S13. Alkenylation of ruthenocene with varying amounts of the catalyst.

		1.25 mol%		2.50 mol%		3.75 mol%		5.00 mol%		10.0 mol%	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	4 min	0.3093	0.1111	0.3062	0.0285	0.5118	0.0136	0.8059	0.2180	0.7786	0.2587
2	8 min	0.4346	0.0042	1.0017	0.1696	1.4109	0.0084	1.8499	0.1792	2.7539	0.4178
3	12 min	0.7727	0.0125	1.7851	0.2282	2.4456	0.3168	3.2155	0.2885	4.7599	0.4284
4	16 min	1.0783	0.0171	2.5381	0.3506	3.4205	0.4470	4.6258	0.4952	6.7039	0.8474
5	20 min	1.4244	0.0001	3.0867	0.3457	4.5044	0.6580	5.9366	0.4989	8.7421	0.8641

[a] Yields were calculated based on ruthenocene amount of 0.25 mmol.

Table S14. Initial rates obtained from performing linear fits of the individual data sets of Table S13.

Entry	n (acrylate) (mmol)	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	1.25	0.0718	0.0058
2	2.50	0.1774	0.0058
3	3.75	0.2499	0.0043
4	5.00	0.3259	0.0093
5	10.0	0.4969	0.0018

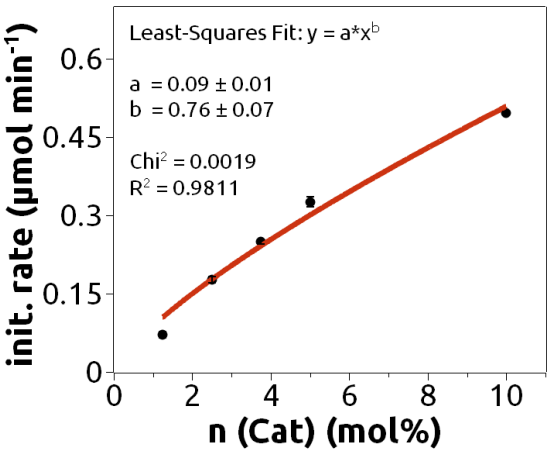
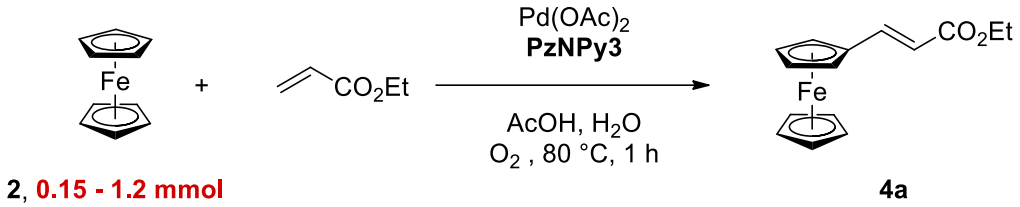


Figure S10. Plot of the initial rate versus the concentration in the catalyst, i.e. $[Pd(OAc)_2]$ and [Ligand], in the ruthenocene alkenylation. The order in ethyl acrylate was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

Order in Ferrocene



The reaction was performed as outlined in general procedure B at ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv) as the substrate. The amount of ferrocene was varied.

Table S15. Alkenylation of ferrocene with varying amounts of ferrocene.

		0.15 mmol		0.3 mmol		0.45 mmol		0.6 mmol		0.9 mmol		1.2 mmol	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	5 min	0.44	0.01	0.71	0.19	0.78	0.03	1.02	0.07	1.53	0.00	1.52	0.08
2	10 min	0.97	0.07	1.93	0.20	2.12	0.06	2.57	0.18	4.03	0.12	3.77	0.11
3	15 min	0.85	0.19	3.65	0.63	3.66	0.01	3.98	0.48	6.72	0.22	6.14	0.15
4	20 min	1.82	0.22	4.96	0.72	5.03	0.06	5.45	0.53	9.26	0.34	8.37	0.17
5	30 min	3.04	0.27	7.28	1.13	7.68	0.08	8.20	1.05	13.95	0.54	12.91	0.26
6	40 min	4.65	0.21	9.22	1.29	10.34	0.07	10.75	1.17	18.58	0.50	17.66	0.33
7	60 min	5.91	0.08	12.36	1.92	14.80	0.19	15.74	2.06	25.39	1.02	26.72	0.58

[a] Yields were calculated based on an ethyl acrylate amount of 1.00 mmol.

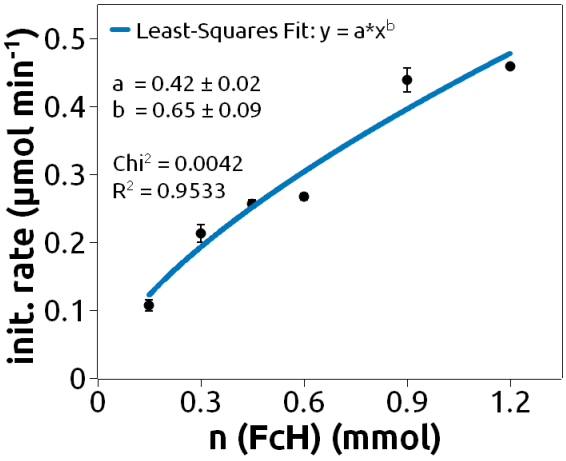
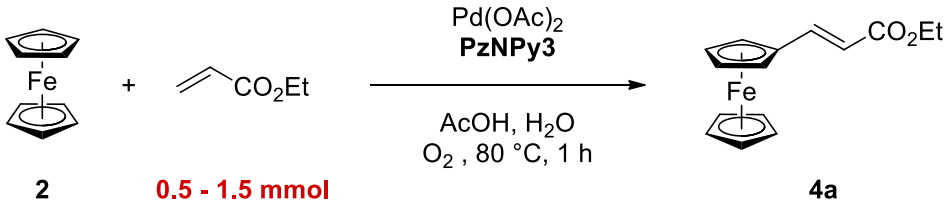


Figure S11. Plot of the initial rate versus the concentration in ferrocene. The order in ferrocene was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

Order in Ethyl Acrylate



2 **0.5 - 1.5 mmol** **4a**

The reaction was performed as outlined in general procedure B. The amount of ethyl acrylate was varied.

Table S16. Alkenylation of ferrocene with varying amounts of ethyl acrylate.[a]

		0.5 mmol		0.75 mmol		1.0 mmol		1.25 mmol		1.5 mmol	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	5 min	1.47	0.09	1.70	0.18	1.73	0.05	2.40	0.06	2.51	0.10
2	10 min	3.88	0.09	5.76	0.77	5.68	0.02	6.19	0.28	6.60	0.17
3	15 min	6.21	0.15	7.18	0.34	9.18	0.31	9.56	0.59	10.22	0.41
4	20 min	8.22	0.10	9.69	0.37	11.99	0.30	12.60	0.89	13.27	0.43
5	30 min	12.35	0.05	14.68	0.60	17.12	0.67	18.55	1.37	19.28	0.84
6	40 min	15.56	0.08	18.88	0.64	22.30	0.42	23.82	1.85	24.77	0.82
7	60 min	22.29	0.14	27.48	0.07	31.14	0.76	33.18	3.02	35.87	1.06

[a] Yields were calculated based on an ethyl acrylate amount of 1.00 mmol.

Table S17. Initial rates obtained from performing linear fits of the individual data sets of Table S16.

Entry	n (acrylate) (mmol)	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	0.5	0.3757	0.0125
2	0.75	0.4577	0.0138
3	1.0	0.5256	0.0223
4	1.25	0.5563	0.0206
5	1.5	0.5966	0.0165

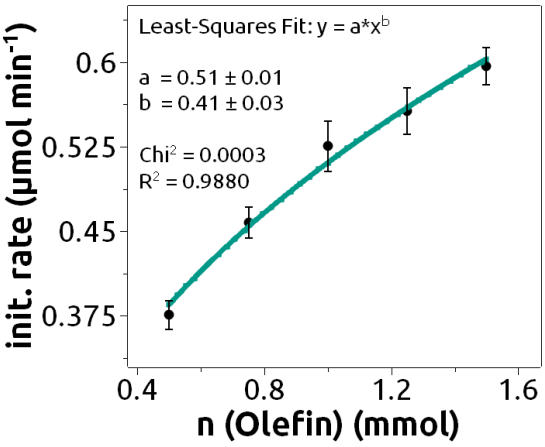
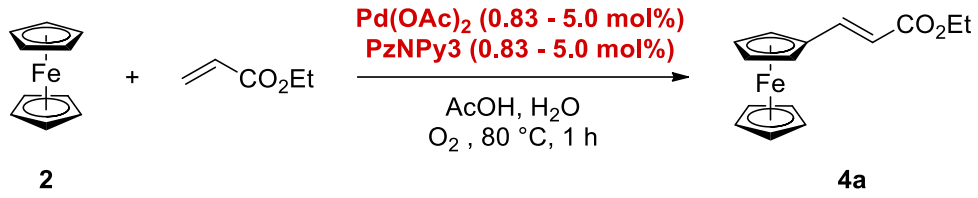


Figure S12. Plot of the initial rate versus the concentration in ethyl acrylate in the ferrocene alkenylation. The order in ethyl acrylate was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

Order in Catalyst



The reaction was performed as outlined in general procedure B with ethyl acrylate (100 mg, 1.00 mmol, 1.00 equiv) as the substrates. The amount of catalyst was varied.

Table S18. Alkenylation of ferrocene with varying amounts of the catalyst.[a]

		0.83 mol%		1.66 mol%		2.5 mol%		3.75 mol%		5.0 mol%	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	5 min	0.66	0.01	1.55	0.02	1.73	0.05	2.72	0.16	4.13	0.70
2	10 min	1.55	0.01	3.79	0.06	5.68	0.02	7.45	0.19	12.24	1.10
3	15 min	2.58	0.02	5.80	0.13	9.18	0.31	12.11	0.14	18.34	0.67
4	20 min	3.39	0.02	7.76	0.11	11.99	0.30	16.94	0.13	24.52	1.02
5	30 min	5.02	0.08	10.92	0.14	17.12	0.67	24.77	0.62	36.58	1.12
6	40 min	6.23	0.07	13.70	0.33	22.30	0.42	33.19	0.60	48.34	1.36
7	60 min	8.21	0.12	18.53	0.45	31.14	0.76	48.81	0.22	71.84	0.93

[a] Yields were calculated based on an ethyl acrylate amount of 1.00 mmol.

Table S19. Initial rates obtained from performing linear fits of the individual data sets of Table S18.

Entry	n (catalyst) (mol%)	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	0.83	0.1382	0.0087
2	1.66	0.3060	0.0163
3	2.50	0.5256	0.0223
4	3.75	0.8345	0.0144
5	5.00	1.2136	0.0190

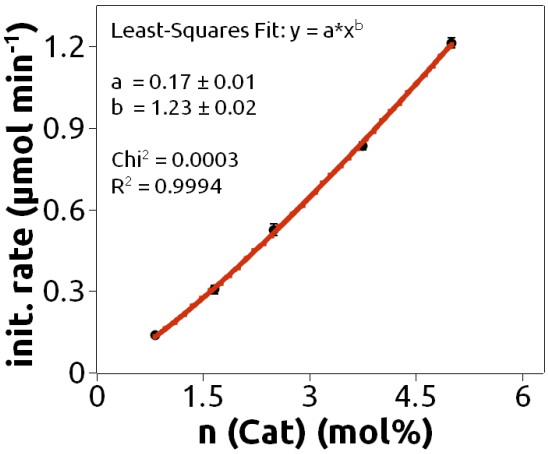
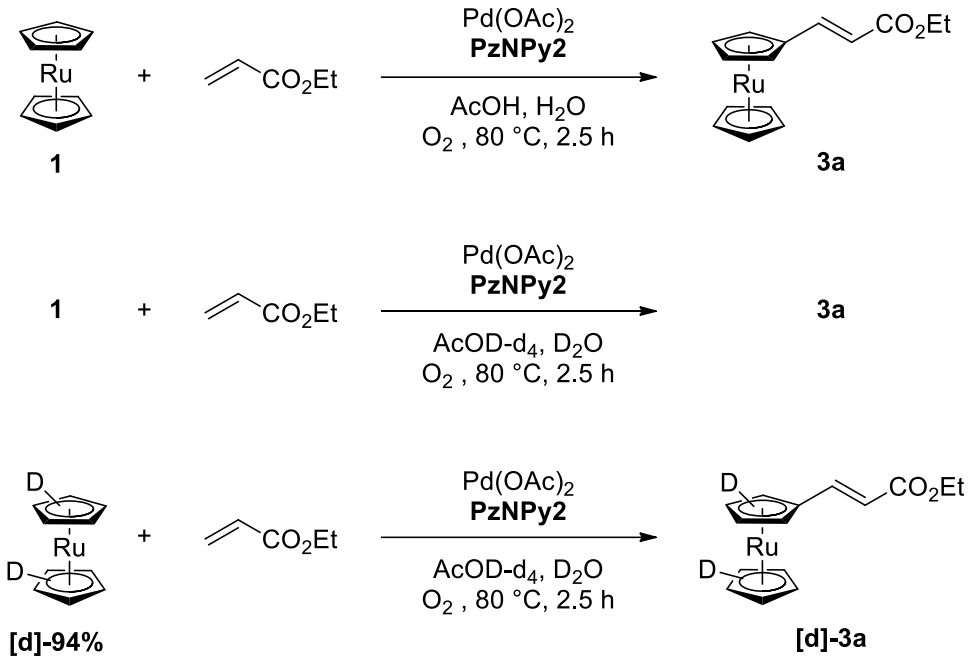


Figure S13. Plot of the initial rate versus the concentration in the catalyst, i.e. $[Pd(OAc)_2]$ and [Ligand], in the ferrocene alkenylation. The order in the catalyst was determined from a least-squares fit ($y = a*x^b$) where b equals the experimentally determined reaction order.

5.6 Kinetic Isotope Effect Studies



The reaction was conducted as outlined in general procedure A with ethyl acrylate (50.1 mg, 0.50 mmol, 2.00 equiv) and ruthenocene (57.8 mg, 0.25 mmol, 1.00 equiv) or ruthenocene-d_{10} (60.3 mg, 0.25 mmol, 1.00 equiv) as the substrate with the only exception that the catalyst was added as the separate solids instead of a stock solution. Perdeuterated ruthenocene was prepared by subjecting ruthenocene to General Procedure A using AcOD-d_4 and D_2O in the absence of olefins for 7 days, which afforded a sufficient quantity over several batches with 94% deuterium content.

In total, three experiments were conducted. First, the regular reaction was run in with non-deuterated ruthenocene in non-deuterated solvents. Second, the reaction was run with non-deuterated ruthenocene in AcOD-d_4 and D_2O in order to observe a potential solvent isotope effect. Third, the reaction was run with deuterated ruthenocene in AcOD-d_4 and D_2O to subsequently determine the primary kinetic isotope effect.

Table S20. Initial rates to determine kinetic isotope effects.

		AcOH		AcOD-d_4		RcH-d_{10}	
Entry	**Reaction Time**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**	**Avg. Yield (%)**	**σ (±%)**
1	30 min	3.7001	1.0866	3.1709	0.7069	1.9626	0.1156
2	60 min	6.2042	0.8399	8.3888	1.3136	3.5555	0.3056
3	90 min	8.7227	1.2402	11.1157	1.9932	4.9142	0.5094
4	120 min	10.7875	1.7556	13.5582	2.5453	5.9468	0.6985
5	150 min	12.6356	1.9420	15.0052	2.9955	6.9169	0.6745
6	180 min	16.3145	3.3970	14.1956	2.3547	7.6874	1.0900

[a] Yields were calculated based on ruthenocene amount of 0.25 mmol.

Table S21. Initial rates obtained from performing linear fits of the individual data sets of Table 20.

Entry	Reaction	initial rate (µmol min^{-1})	σ (± µmol min^{-1})
1	RcH/AcOD-d_4	0.0838	0.0112
2	RcH/AcOH	0.0703	0.0033
3	RcH-d_{10}/AcOD-d_4	0.0378	0.0025

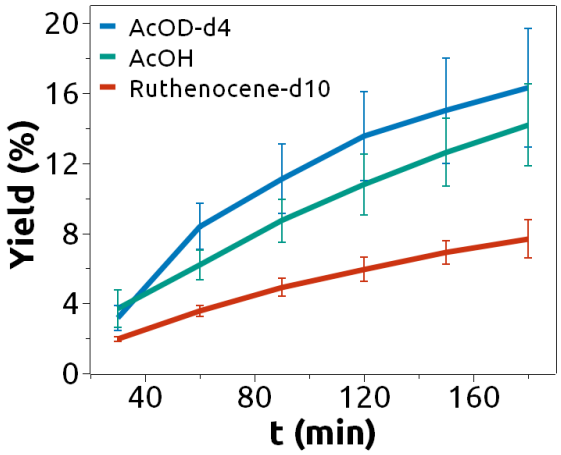
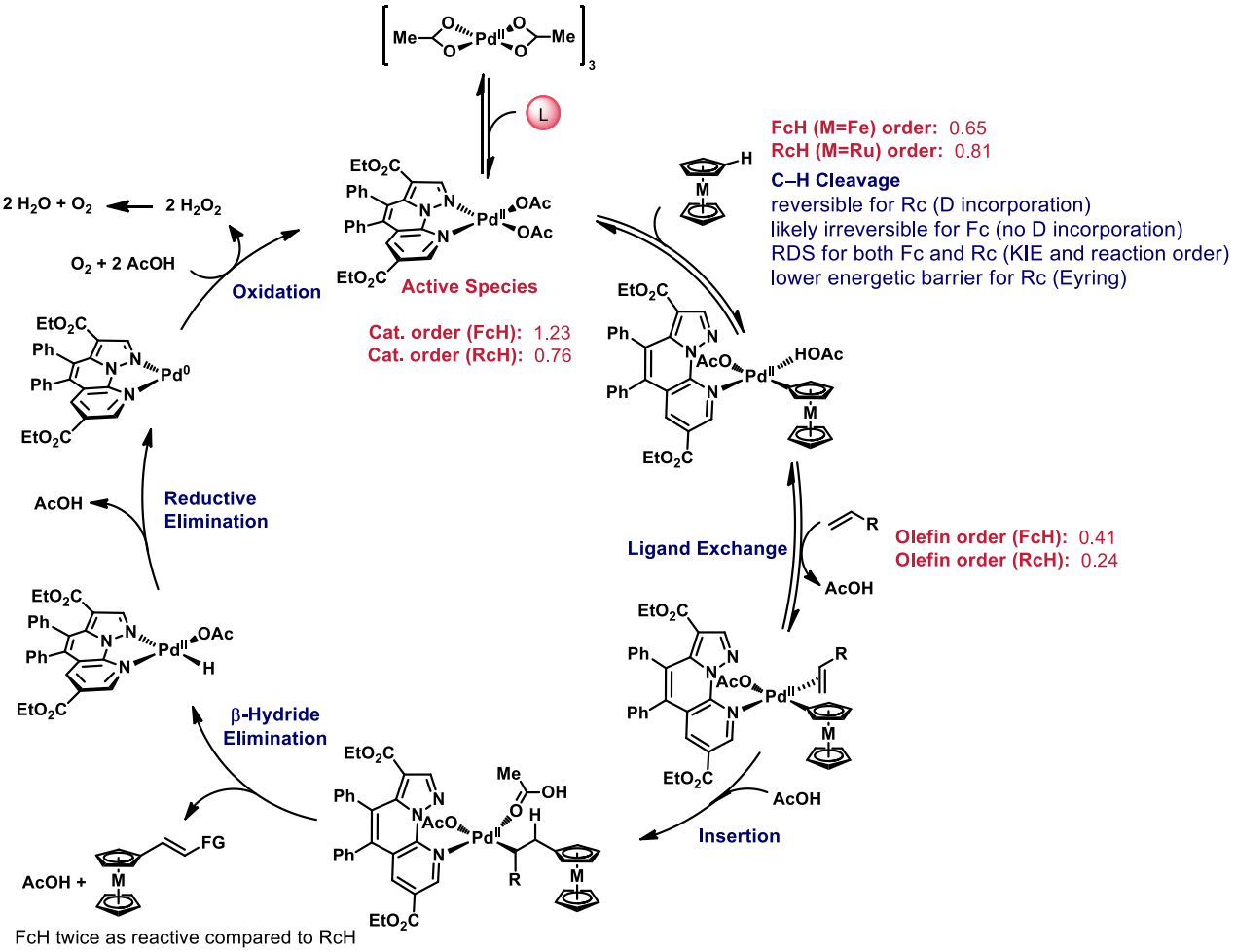


Figure S14. Plot of the yield of **3a** and deuterated **3a**. The KIE was determined by dividing the reaction rate obtained from the respective graph *via* linear regression.

5.7 Reaction Mechanism



Scheme S1. Proposed mechanism based on the kinetic data and results of the mechanistic study.

A tentative mechanism is described in Scheme S1. The exact composition and binding mode of the ligands during the C–H cleavage and migratory insertion is under investigation, which will be reported in due course. The reoxidation of Pd(0) by oxygen is based on other Pd-catalyzed aerobic oxidation reactions.[7] It is likely that hydrogen peroxide formed in this process undergoes rapid decomposition to give H_2O and O_2 in the presence of the Pd catalyst at the elevated temperature.[8]

6. Cyclic Voltammetry Experiments

Cyclic voltammetry (CV) experiments were conducted in a 20 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), an Ag/AgCl reference electrode, and a Pt wire counter electrode at a scan rate of 100 mV/s. All cyclic voltammetry studies were conducted with the CHI 1040C instrument. Measurements were performed in 0.05 M $TBABF_4$ in DCM with 0.005 M of the respective alkenylated metallocene using an undivided electrochemical cell. Unlike ferrocene derivatives that invariably exhibit high reversibility, the redox stability of Ru counterparts depends on the type of electrolytes and solvents.[9,10] The use of the weakly coordinating BF_4 anion and low-donor DCM solvent increased the redox stability of ruthenocene derivatives in our experiments. The presence of the alkenyl substituents on the ruthenocene core further increased the reversibility, presumably because of the steric effect that prevented the deposition on the electrode.

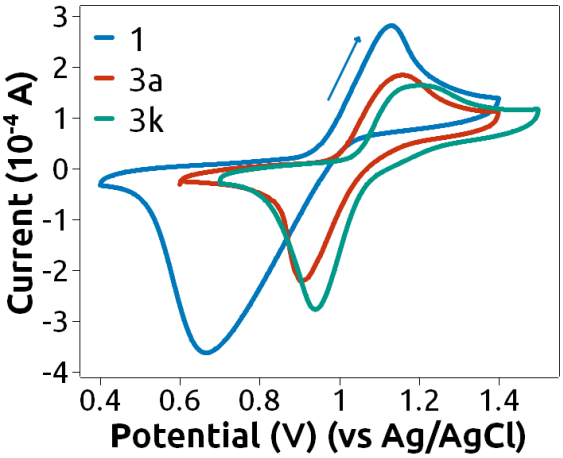


Figure S15. Cyclic voltammogram of the alkenylated ruthenocene derivatives.

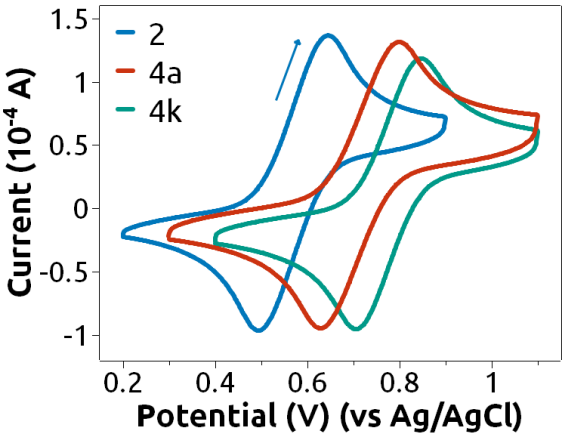
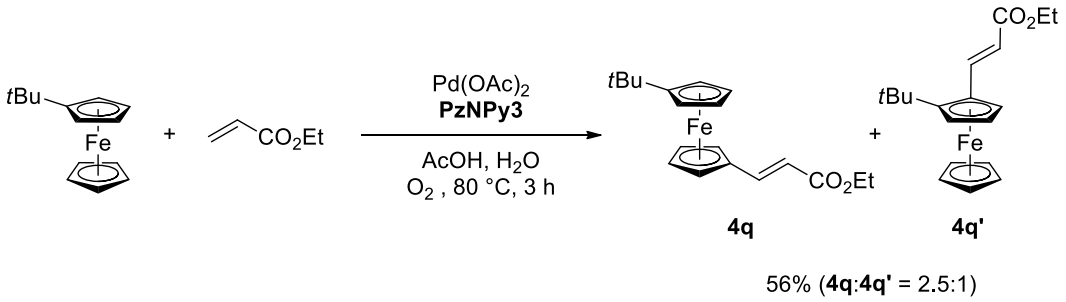


Figure S16. Cyclic voltammogram of the alkenylated ferrocene derivatives.

7. Alkenylation of Substituted Ferrocenes



Scheme S2. Alkenylation of *t*-butyl ferrocene.

Ferrocenes substituted with electron-donating groups underwent alkenylation reactions, which however gave low selectivities. For example, the reaction of *t*-butyl ferrocene afforded a mixture of inseparable regioisomers, **4q** and 4**q′** (see the spectrum in S91). In contrast to electron-rich ferrocene derivatives, ferrocenes containing electron-withdrawing groups, such as methoxycarbonyl, benzoyl, and formyl groups, did not provide the corresponding alkenylation products.

8. References

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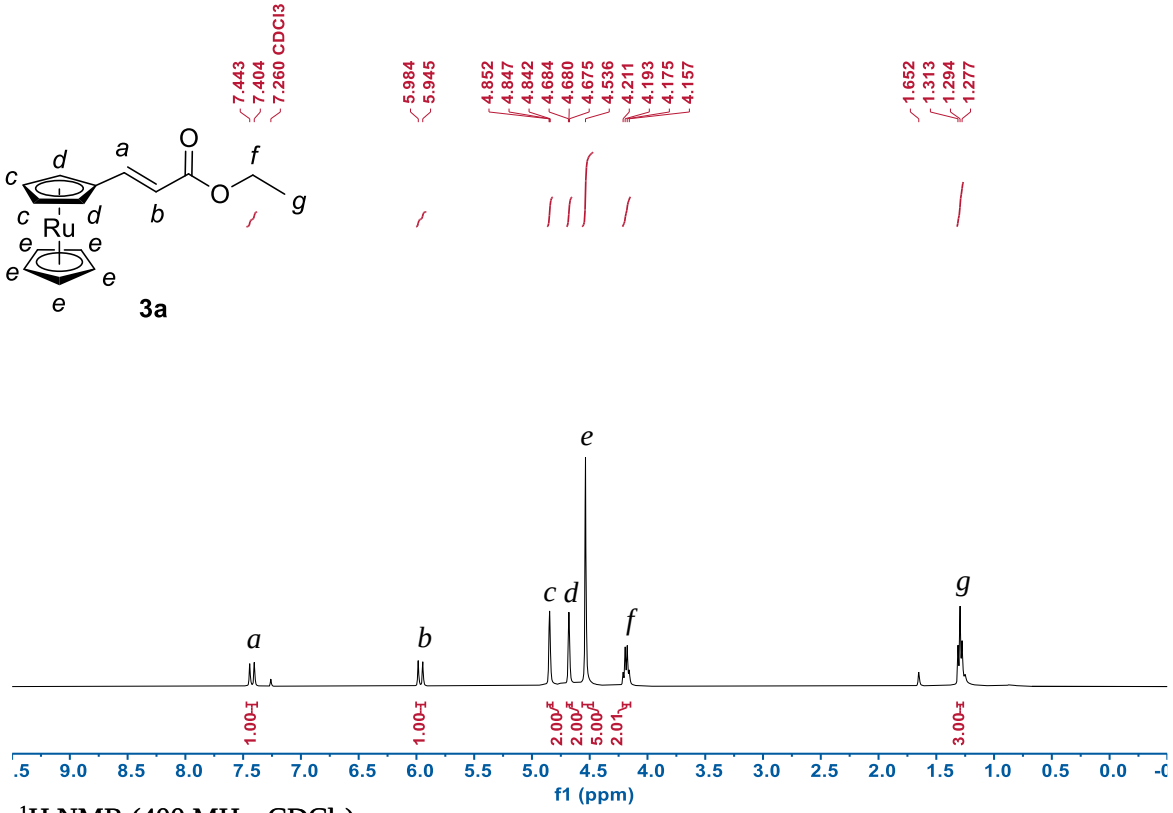
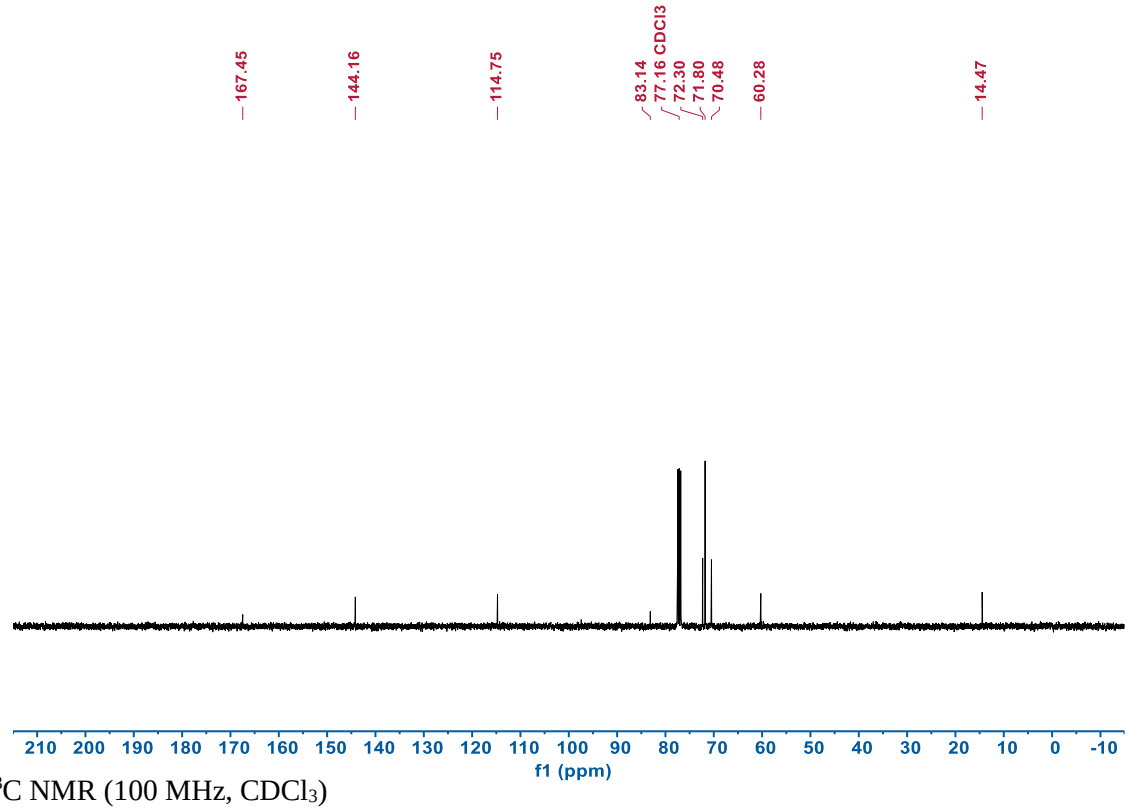
9. NMR Spectra

Ruthenocene Derivatives



^{1}H NMR (400 MHz, $CDCl_3$)



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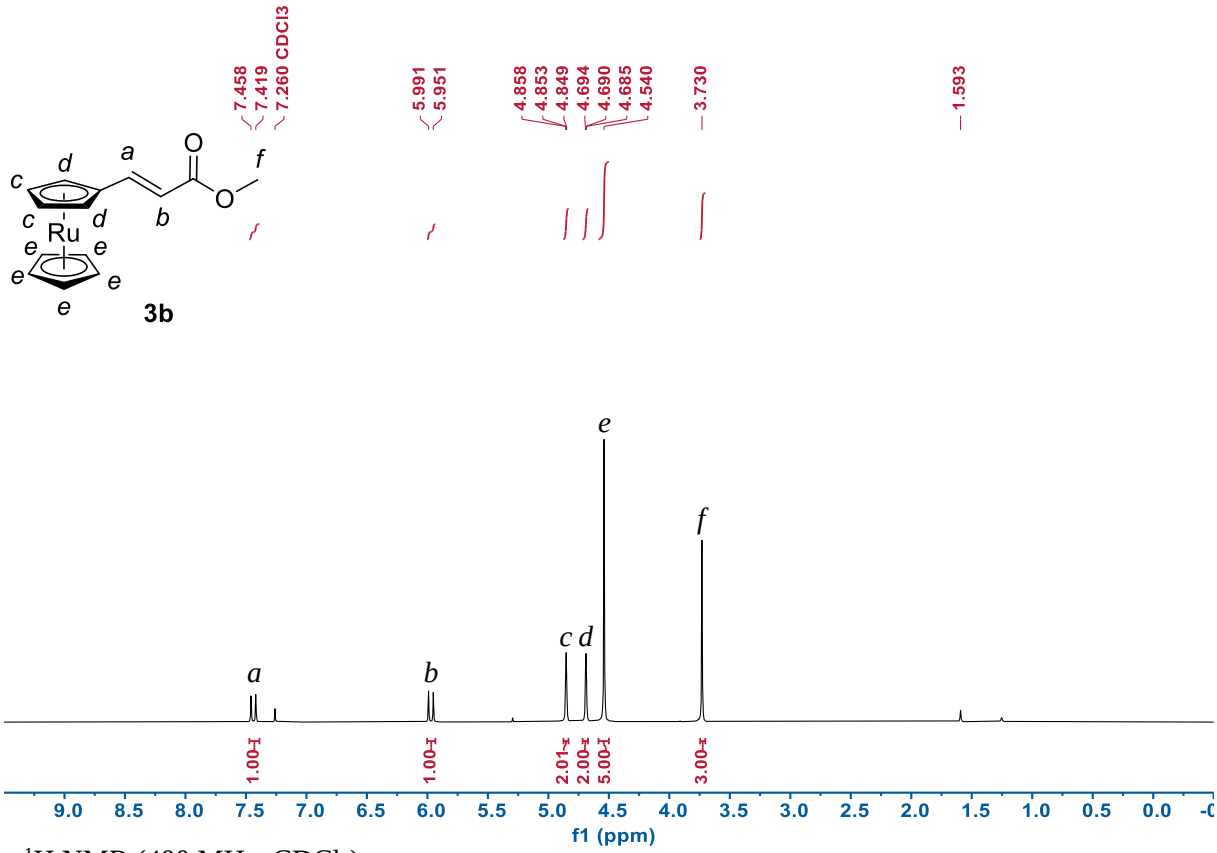

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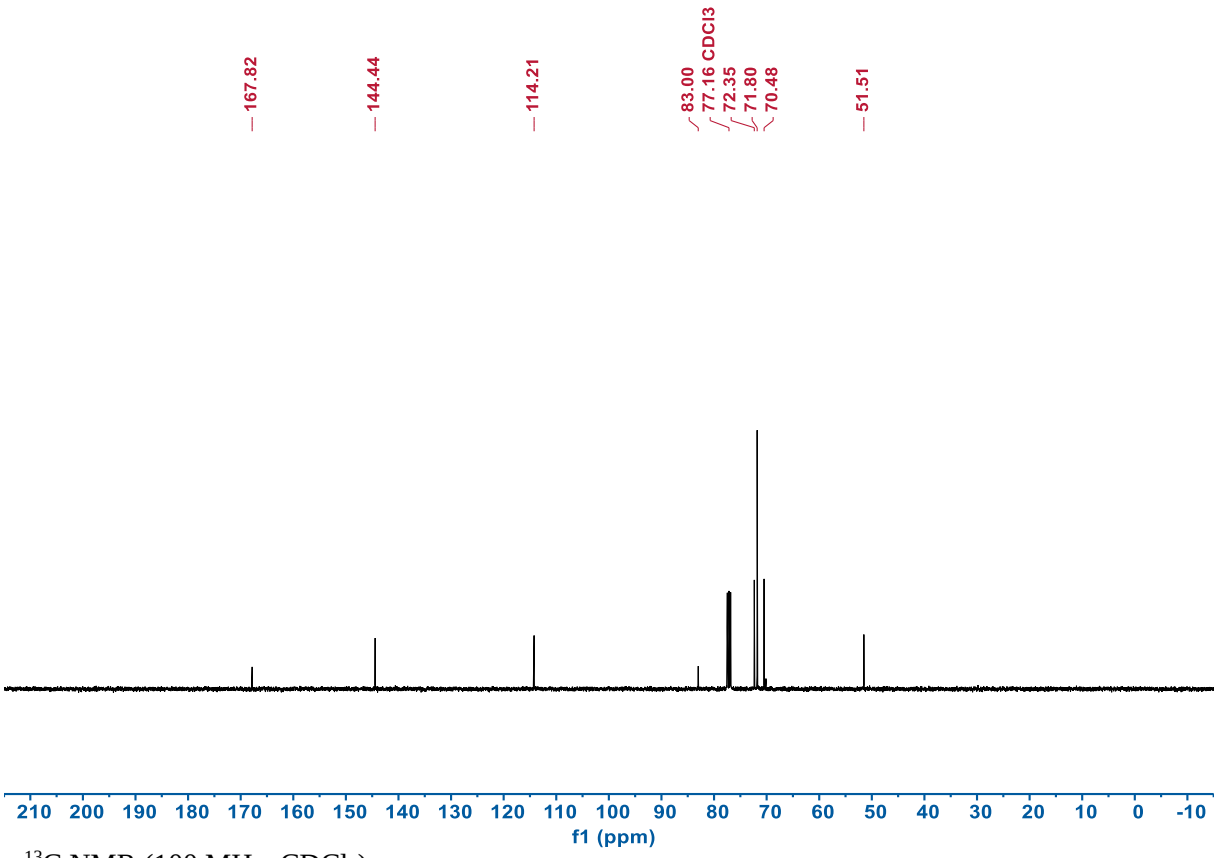

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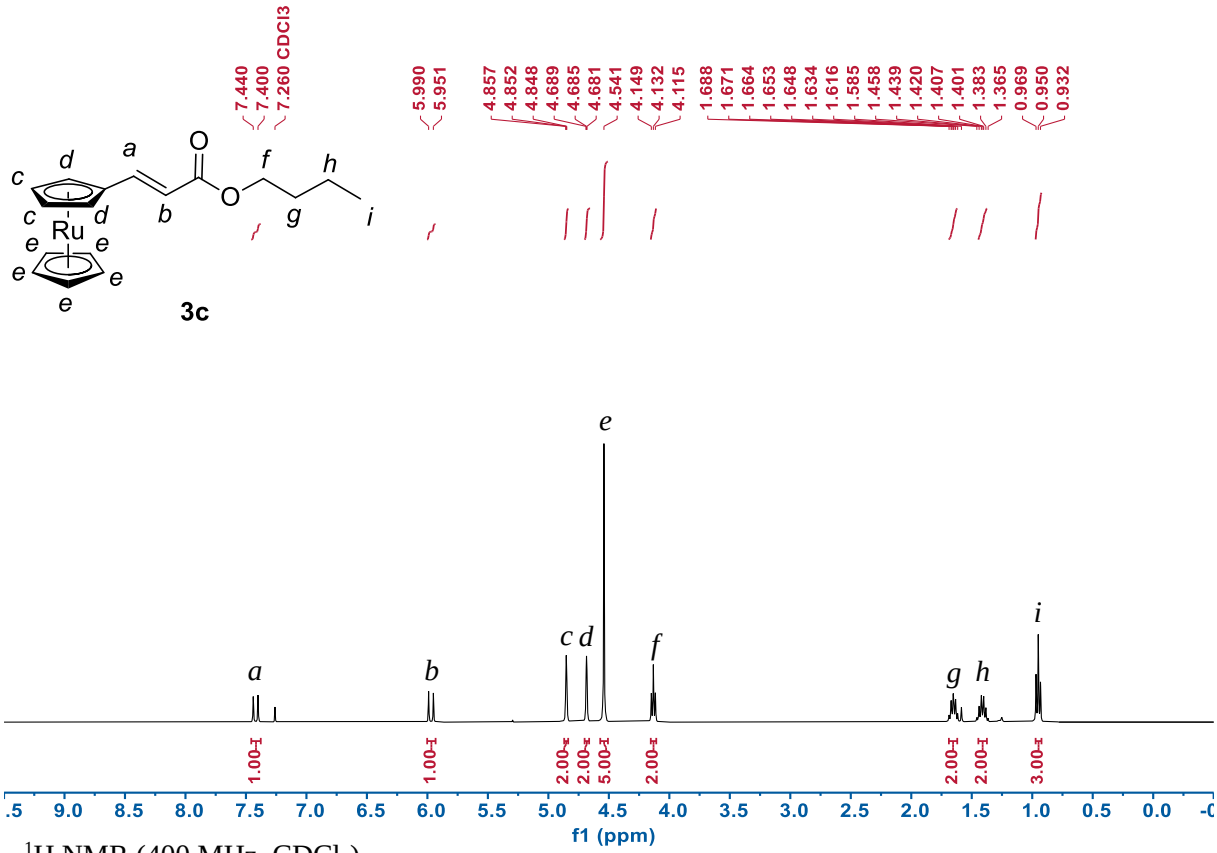
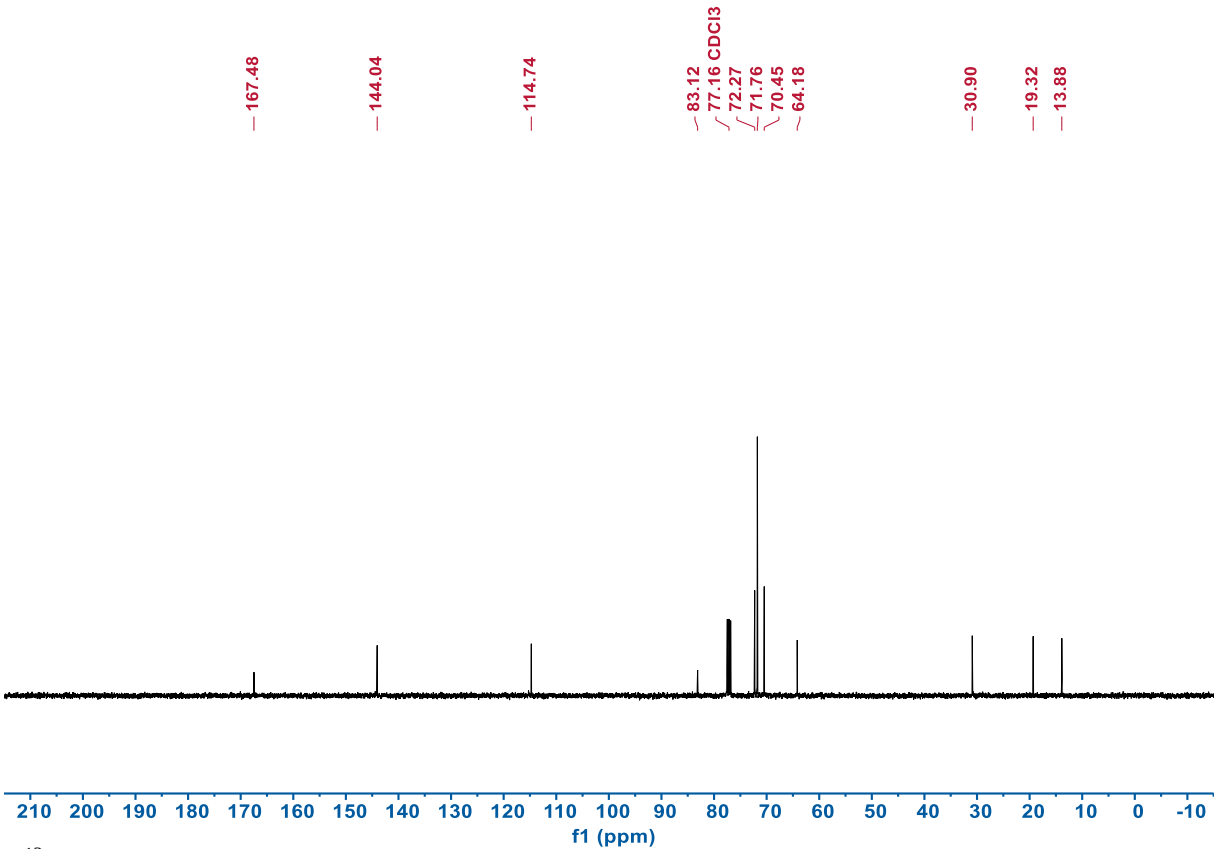


^{1}H NMR (400 MHz, $CDCl_3$)



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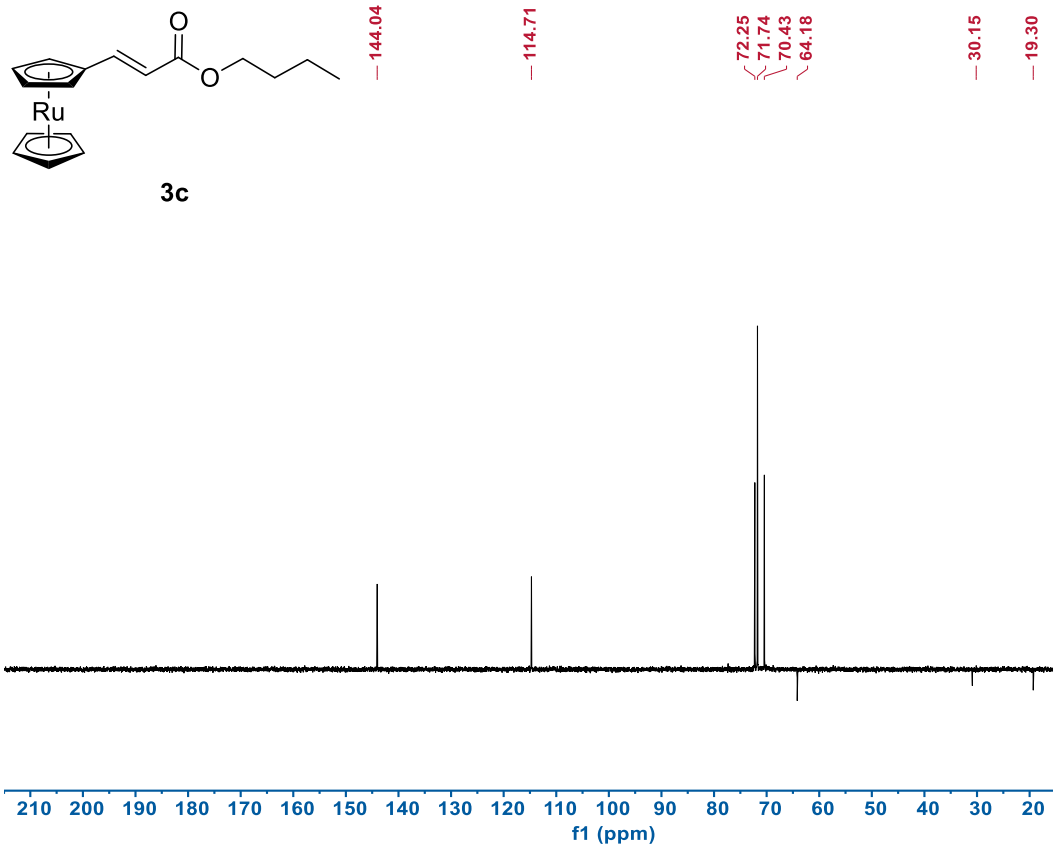
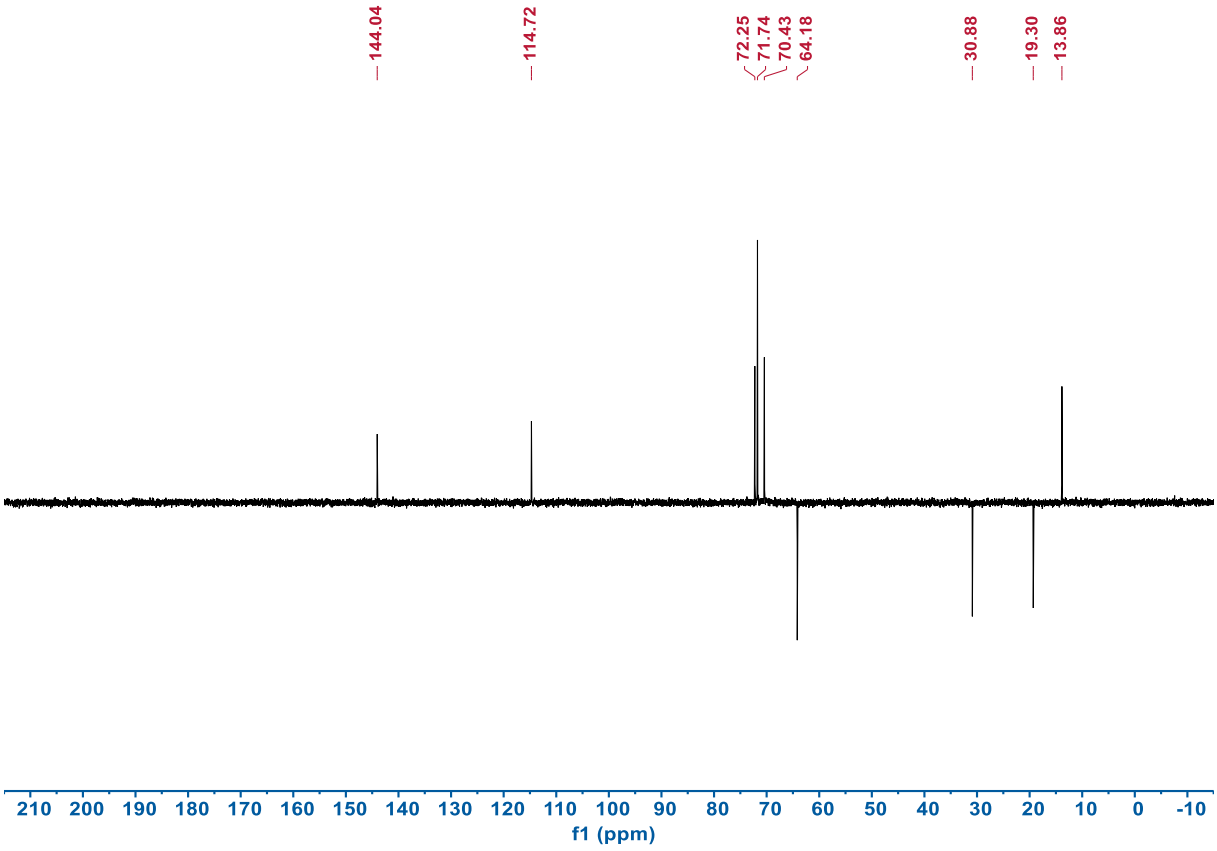
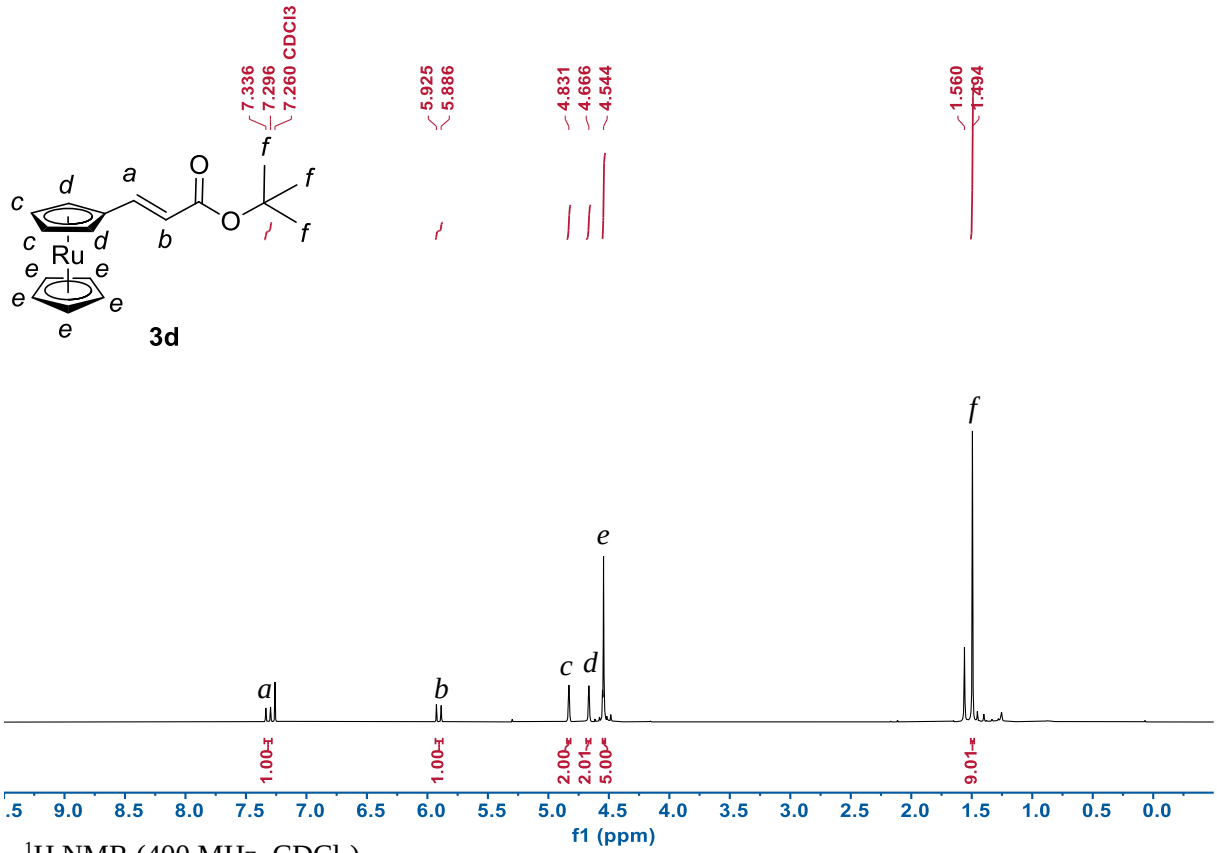


3c

^{13}C DEPT-90 NMR (100 MHz, $CDCl_3$)



^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



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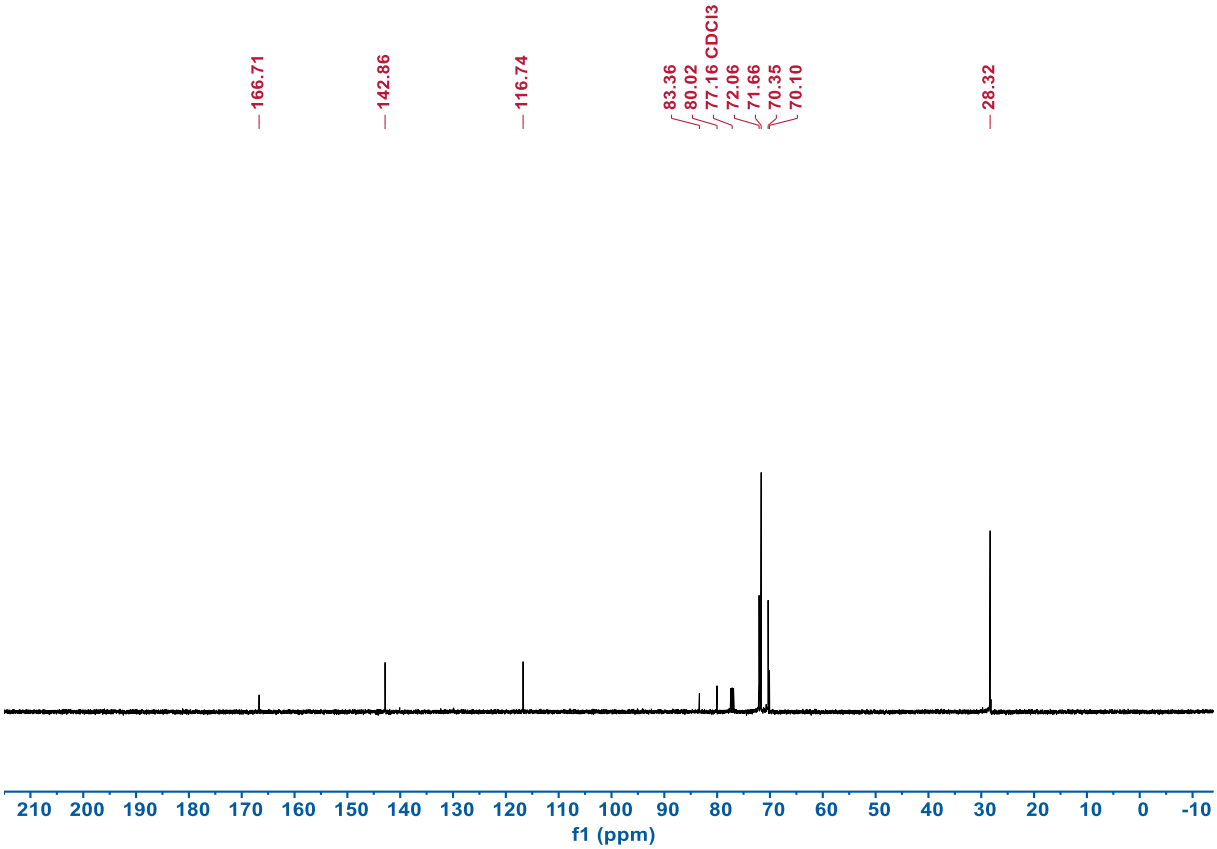

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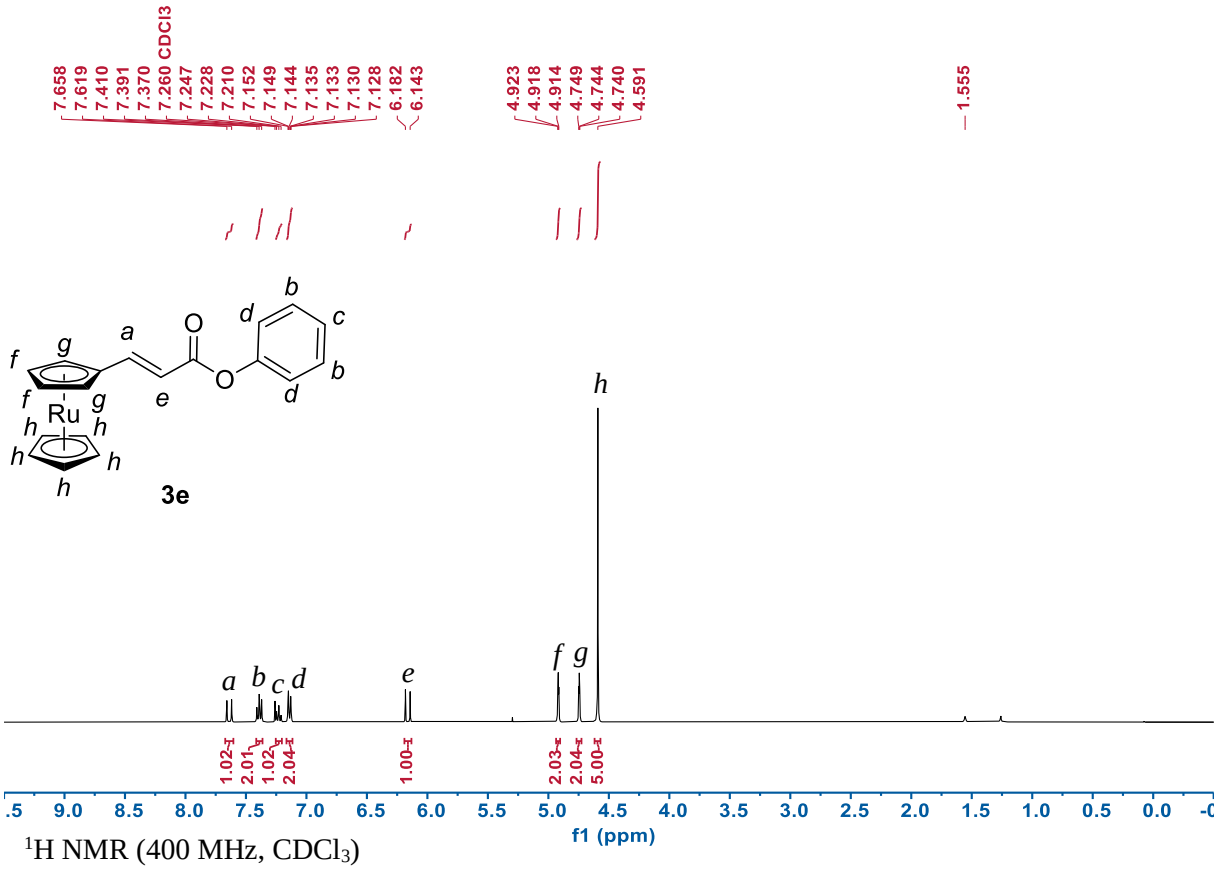

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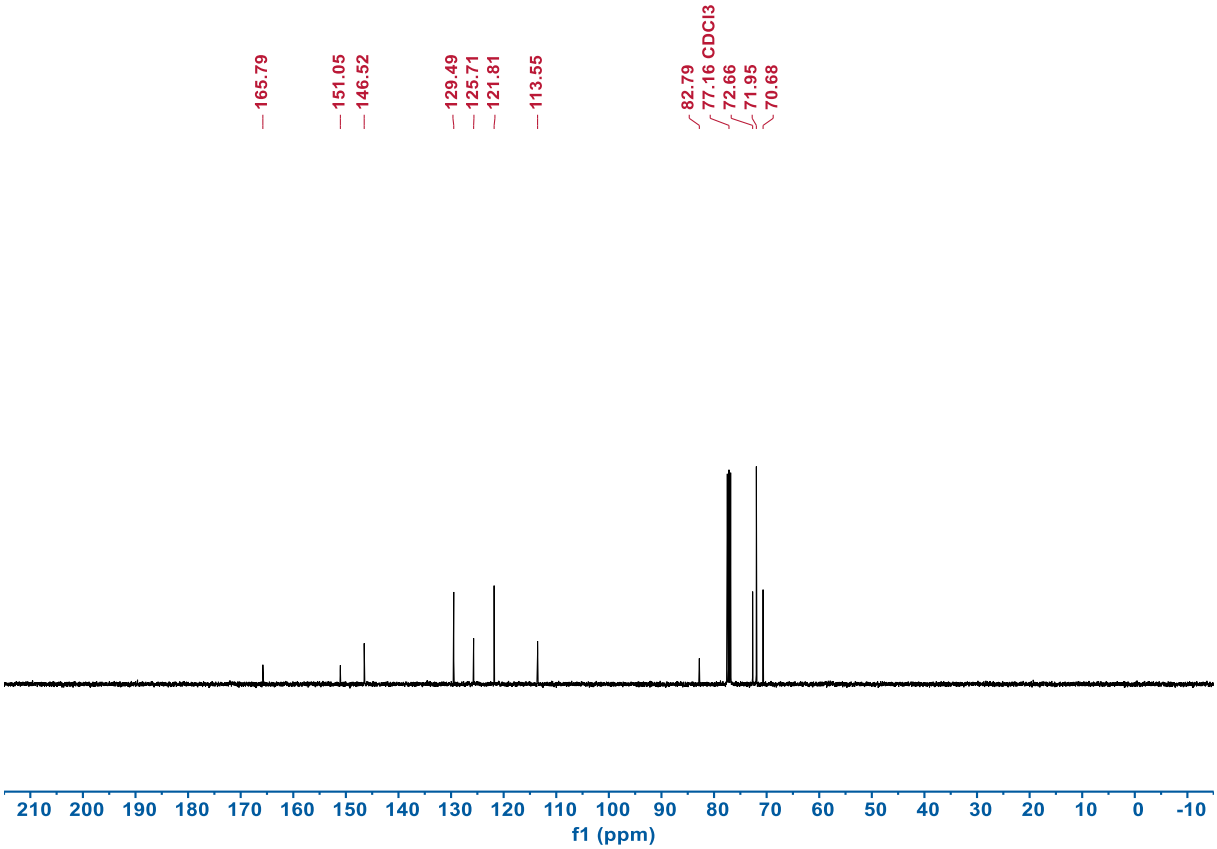

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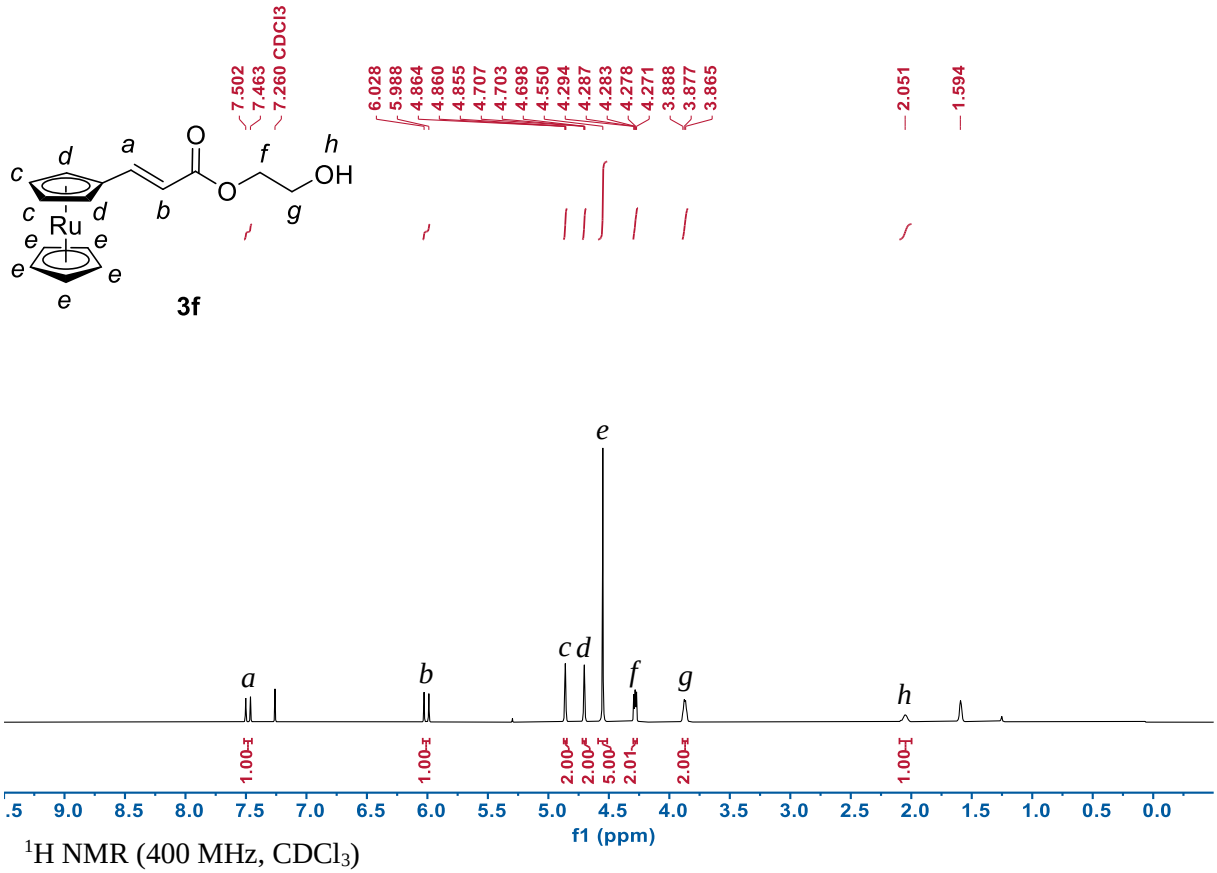
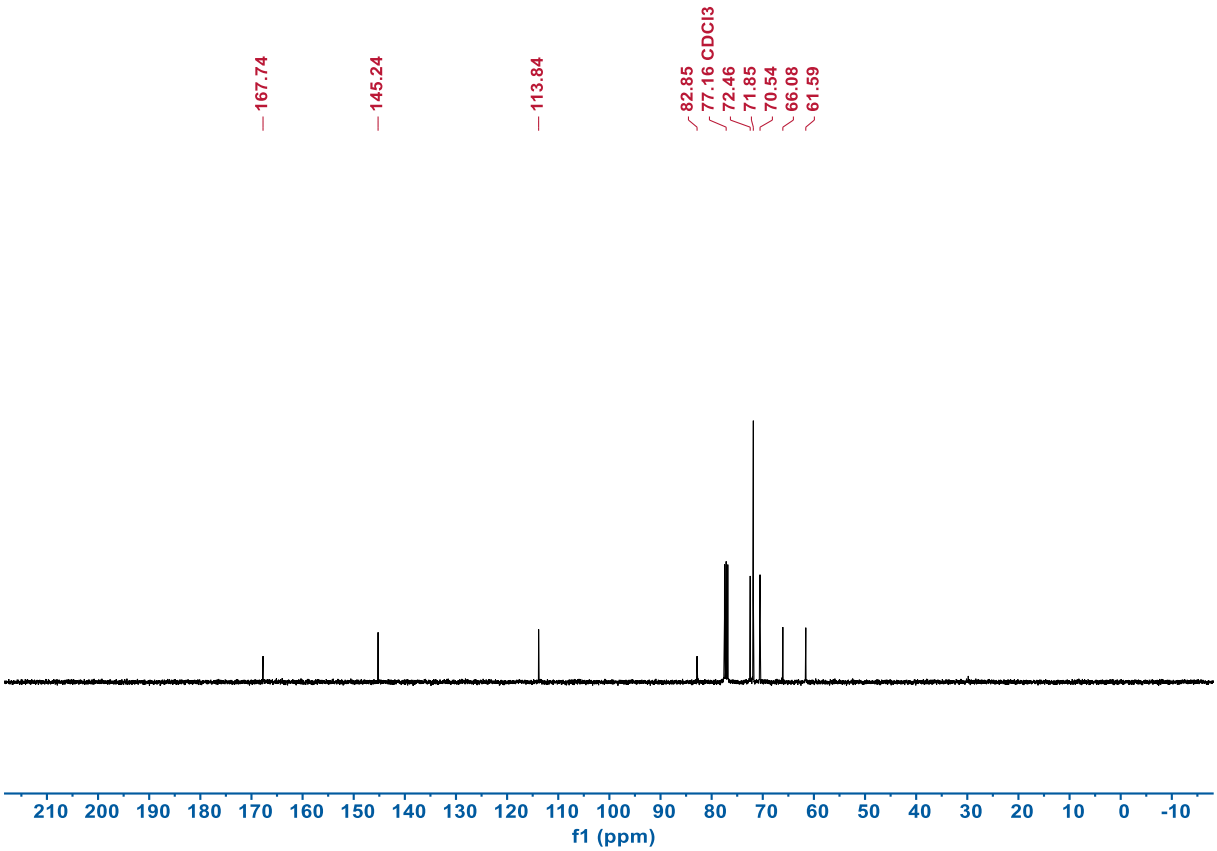


3f

^{1}H NMR (400 MHz, $CDCl_3$)



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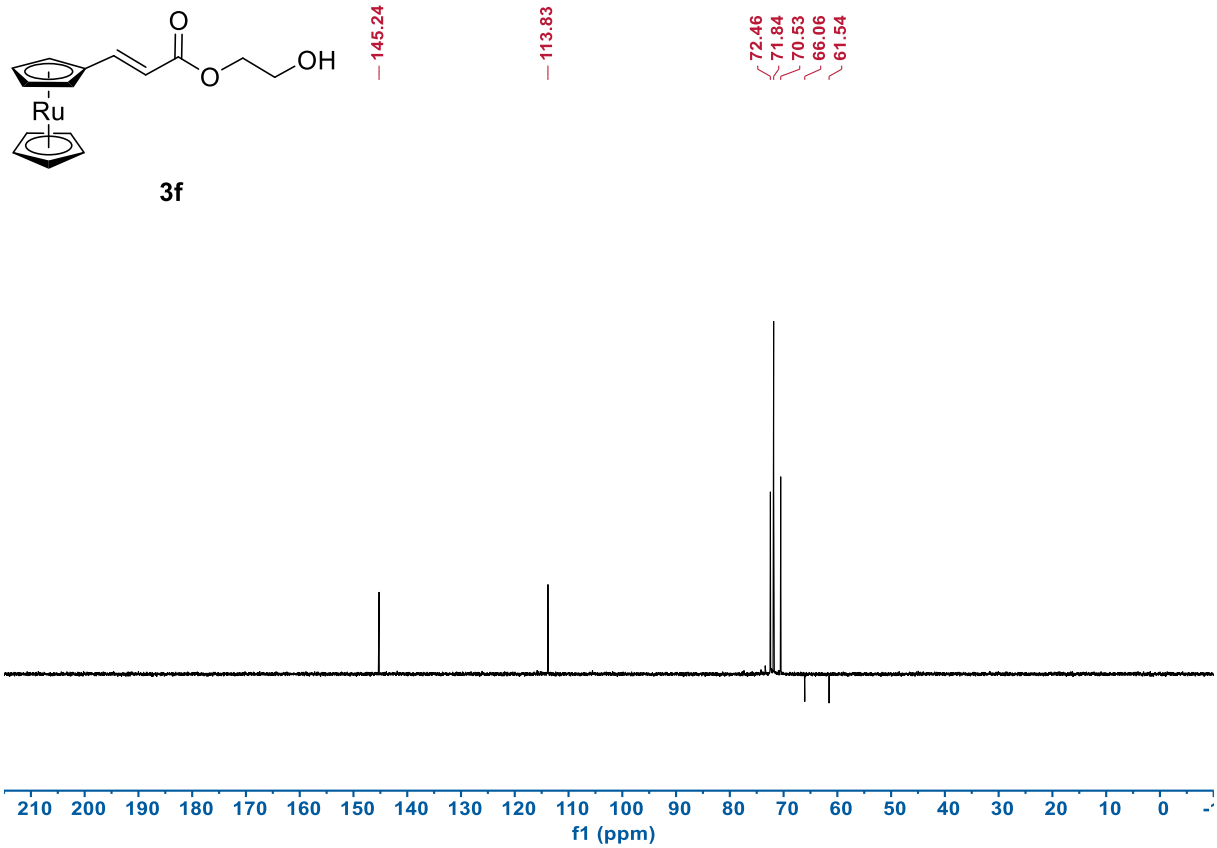

3f

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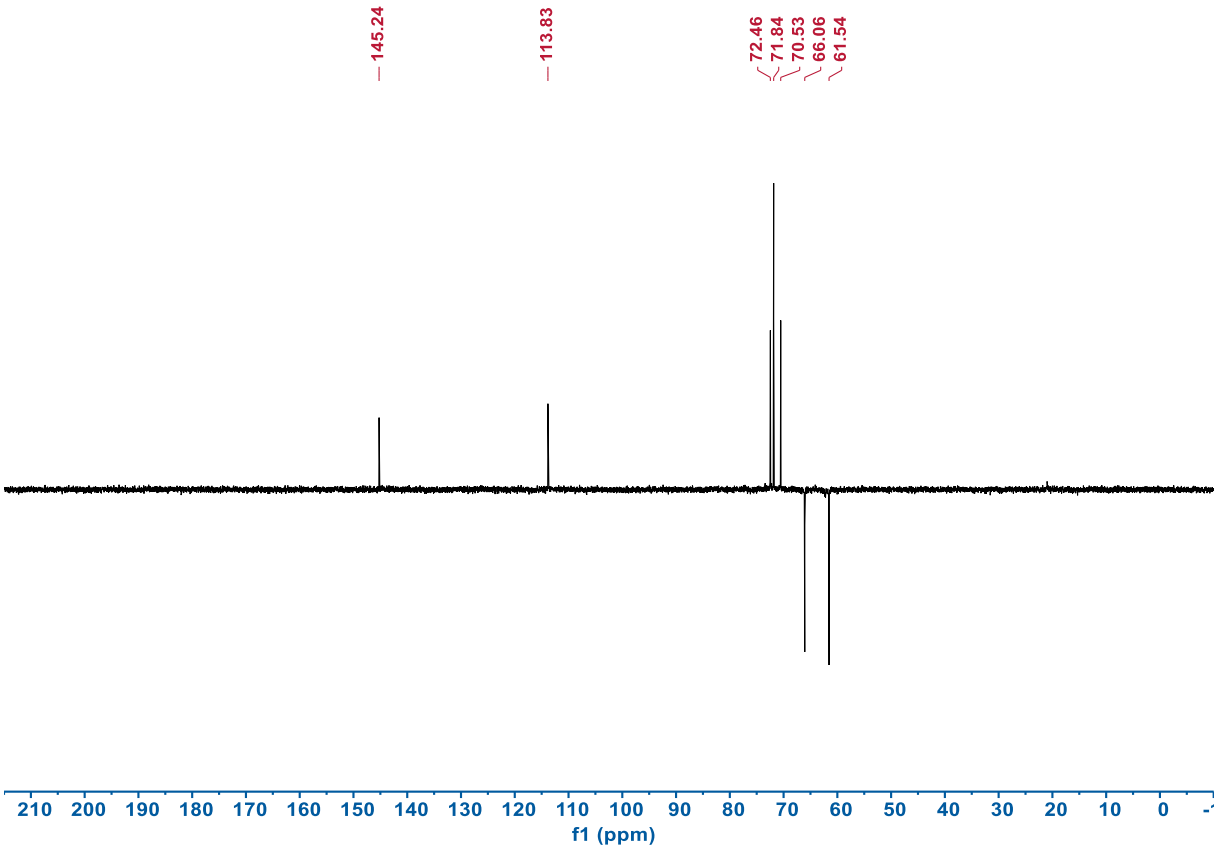

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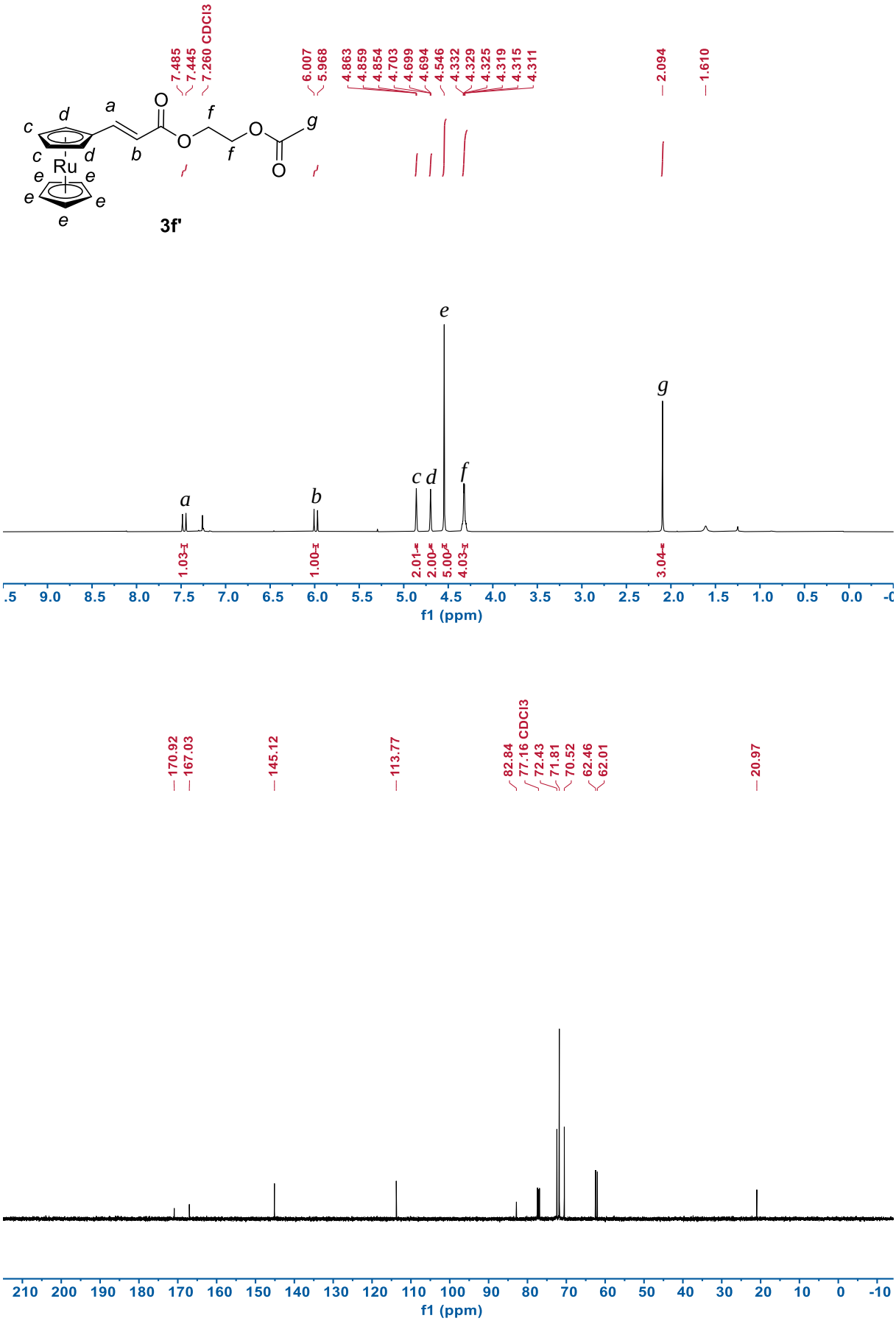

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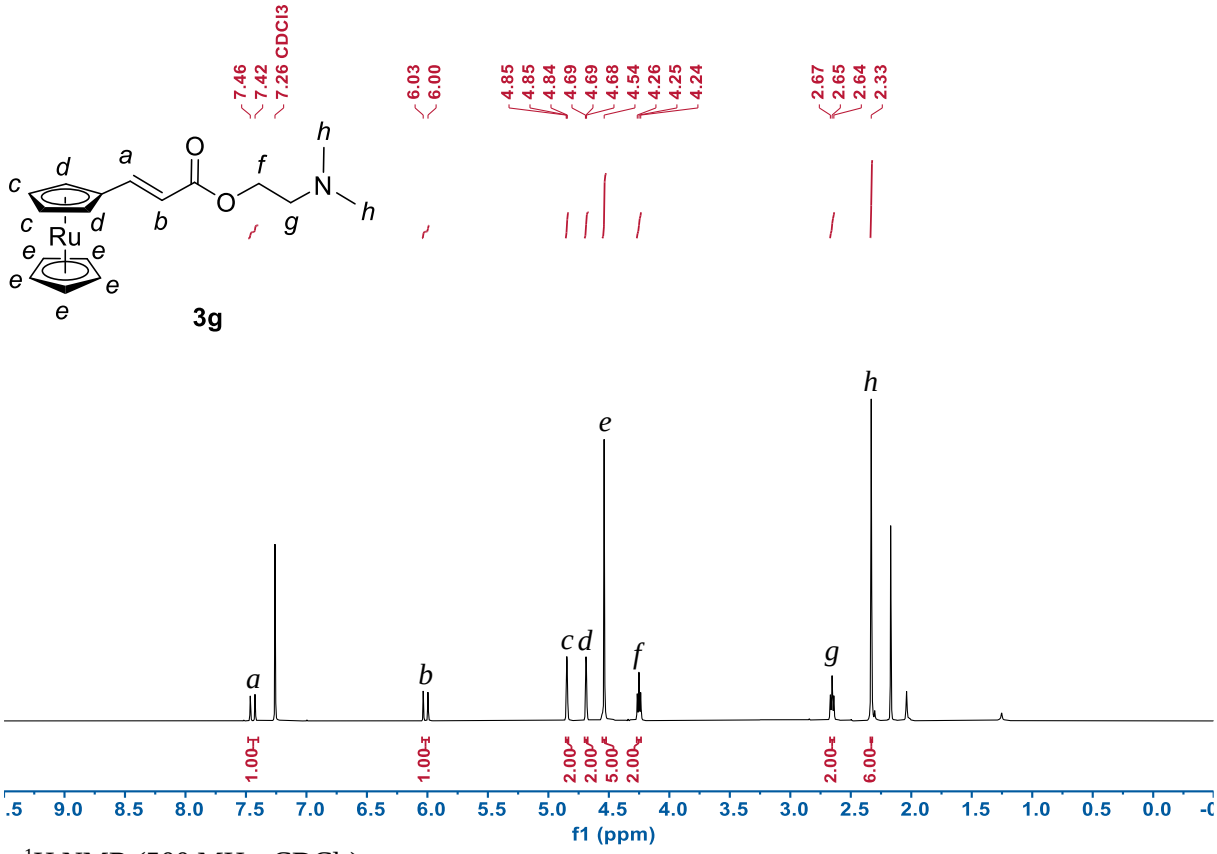

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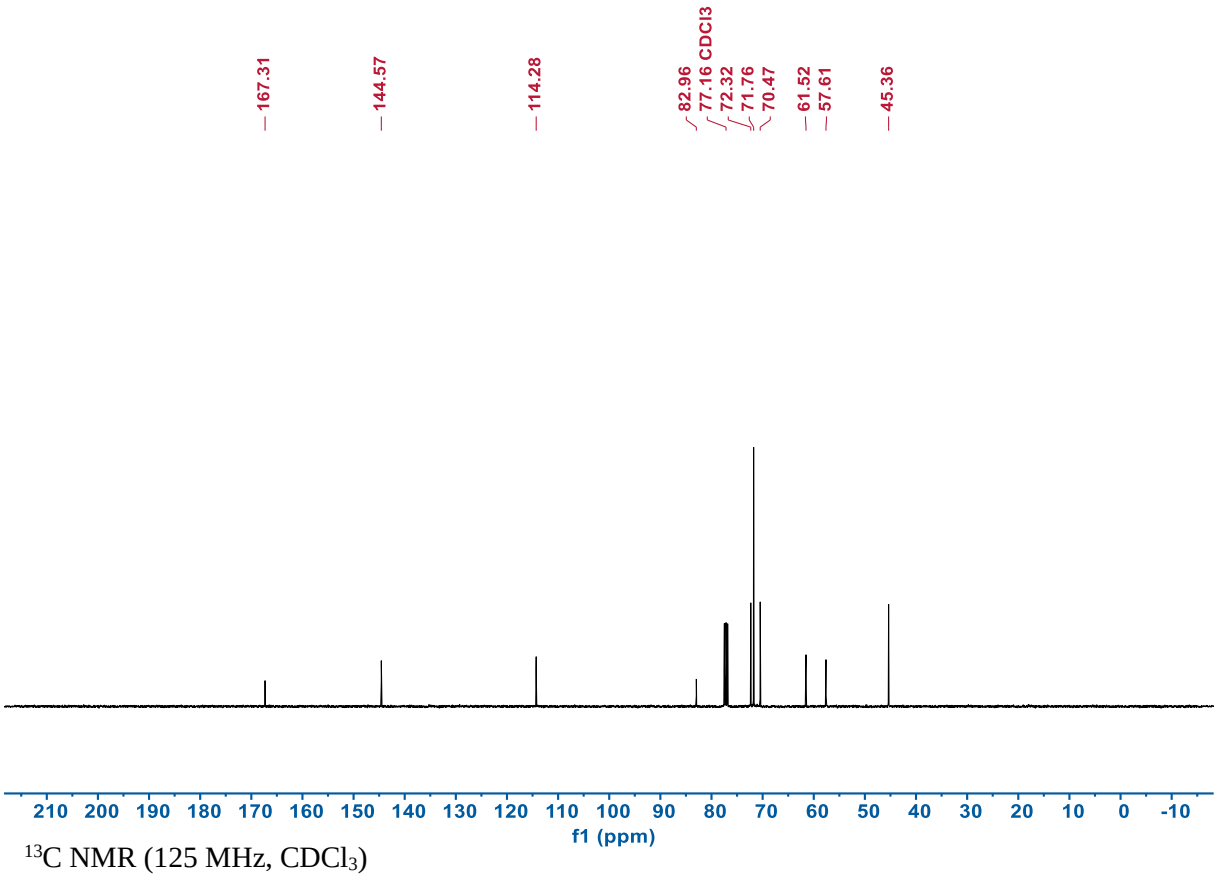

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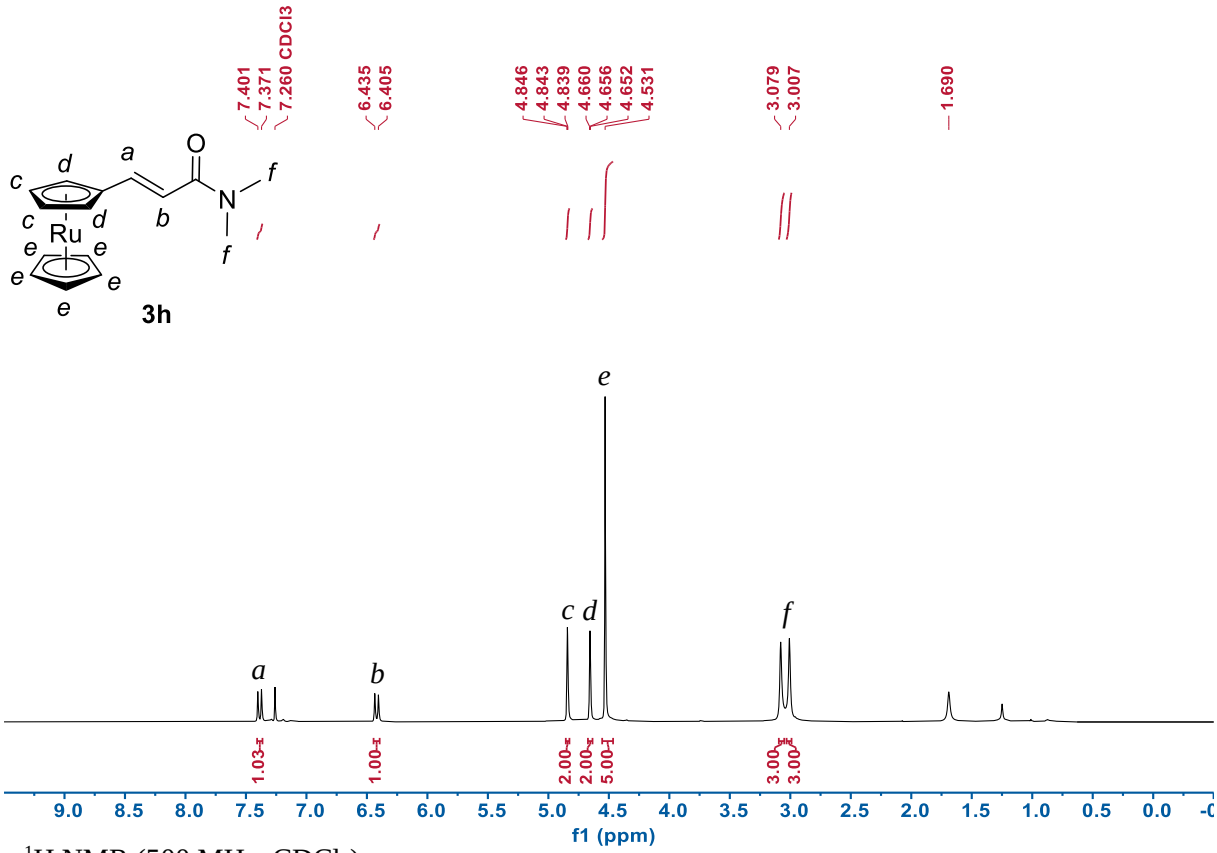

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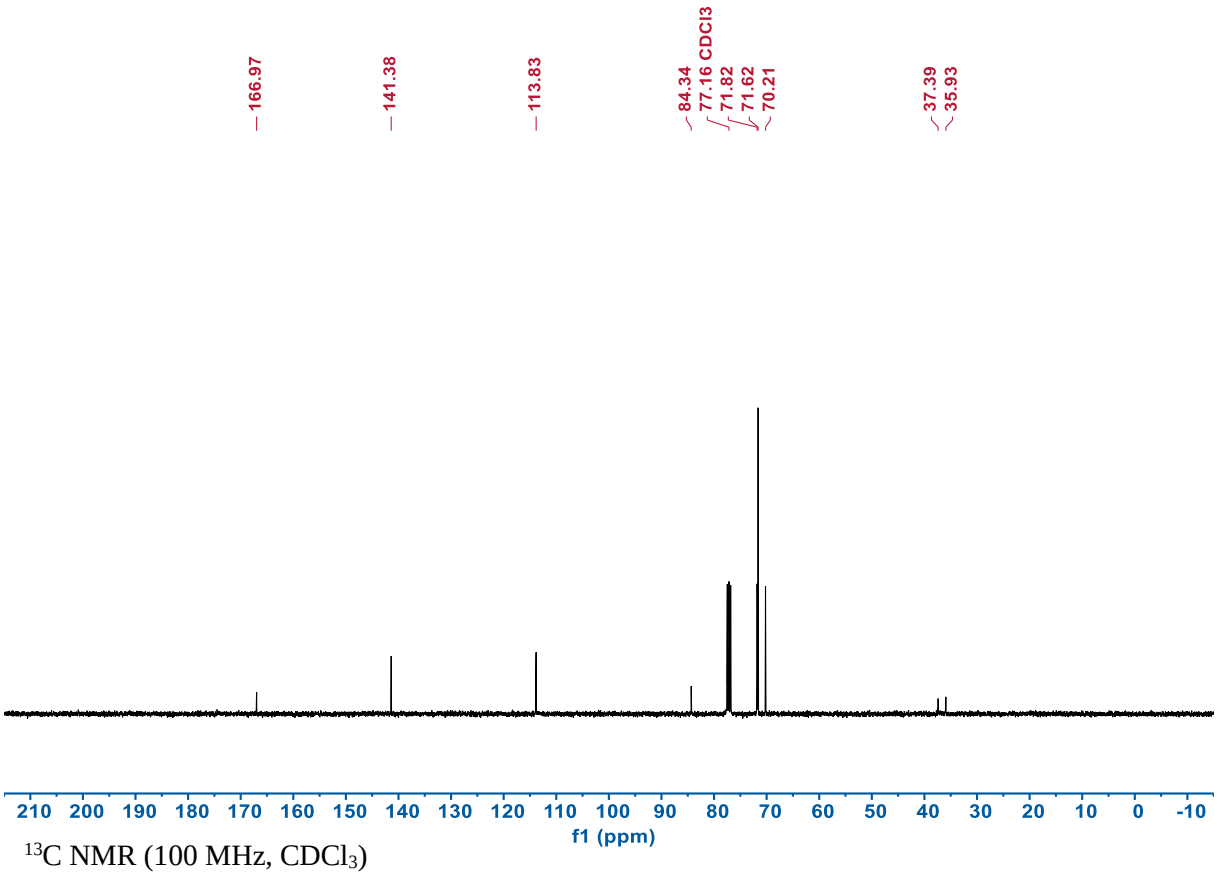

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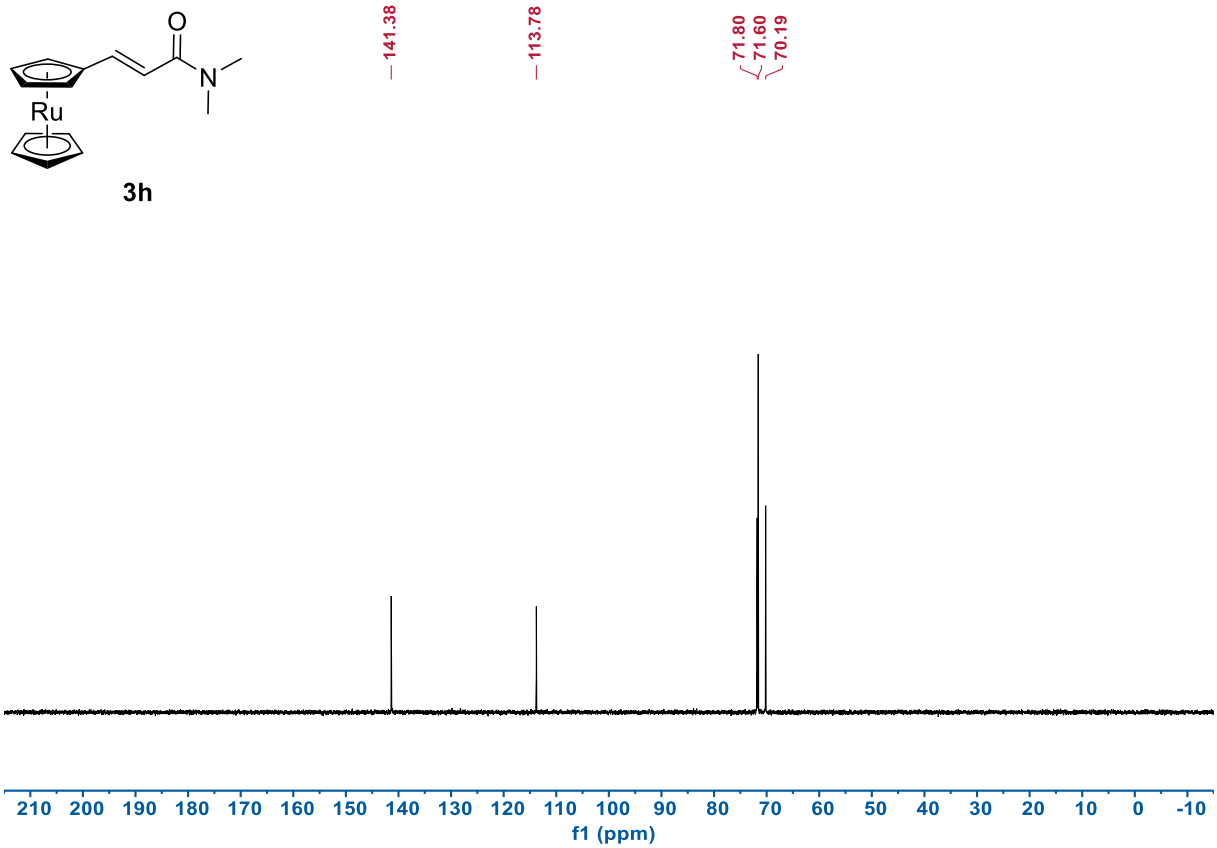

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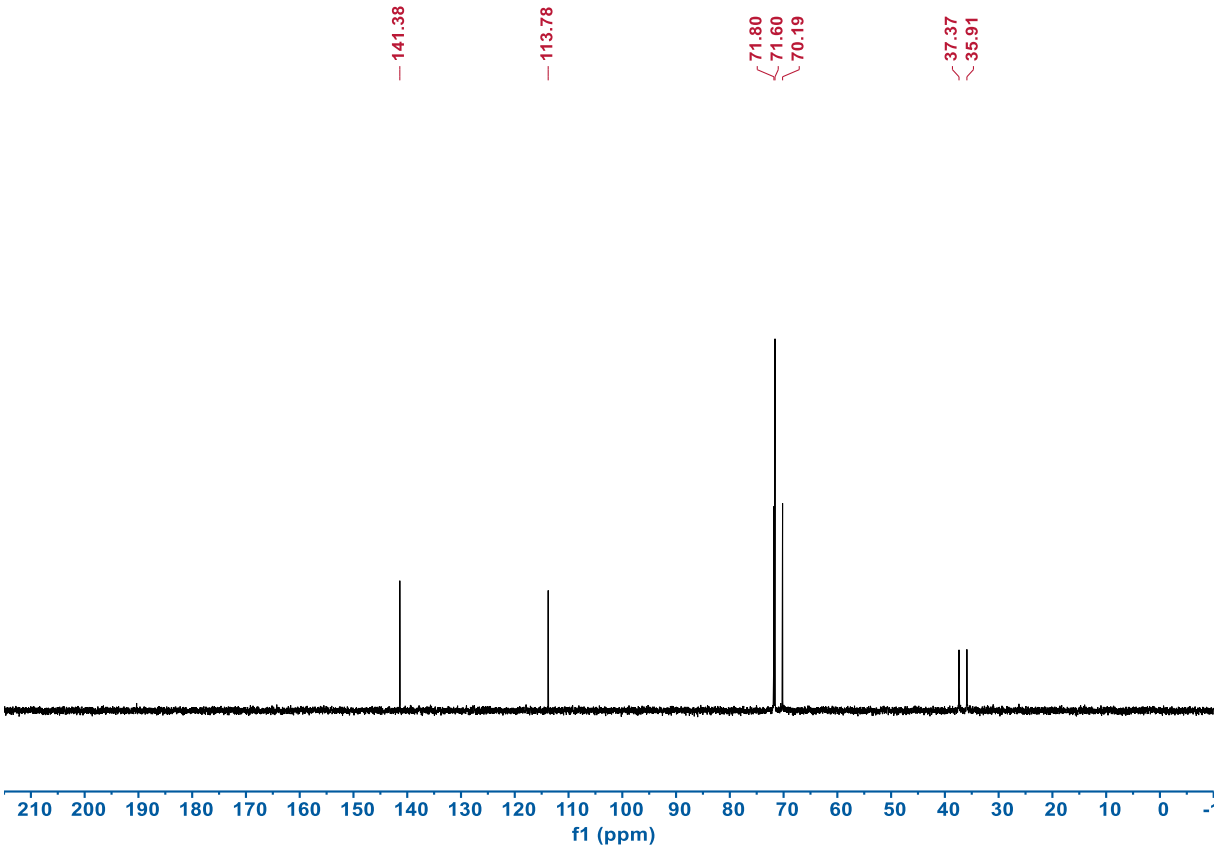

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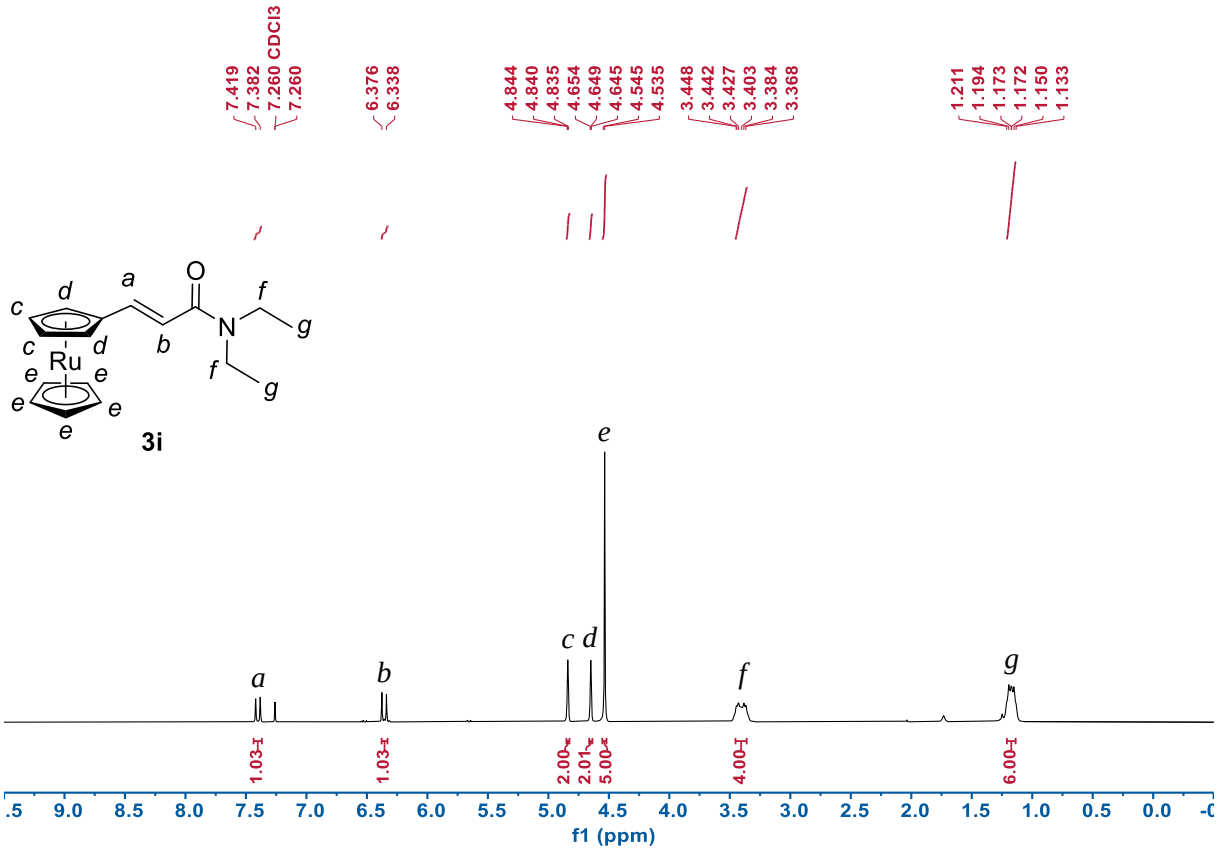

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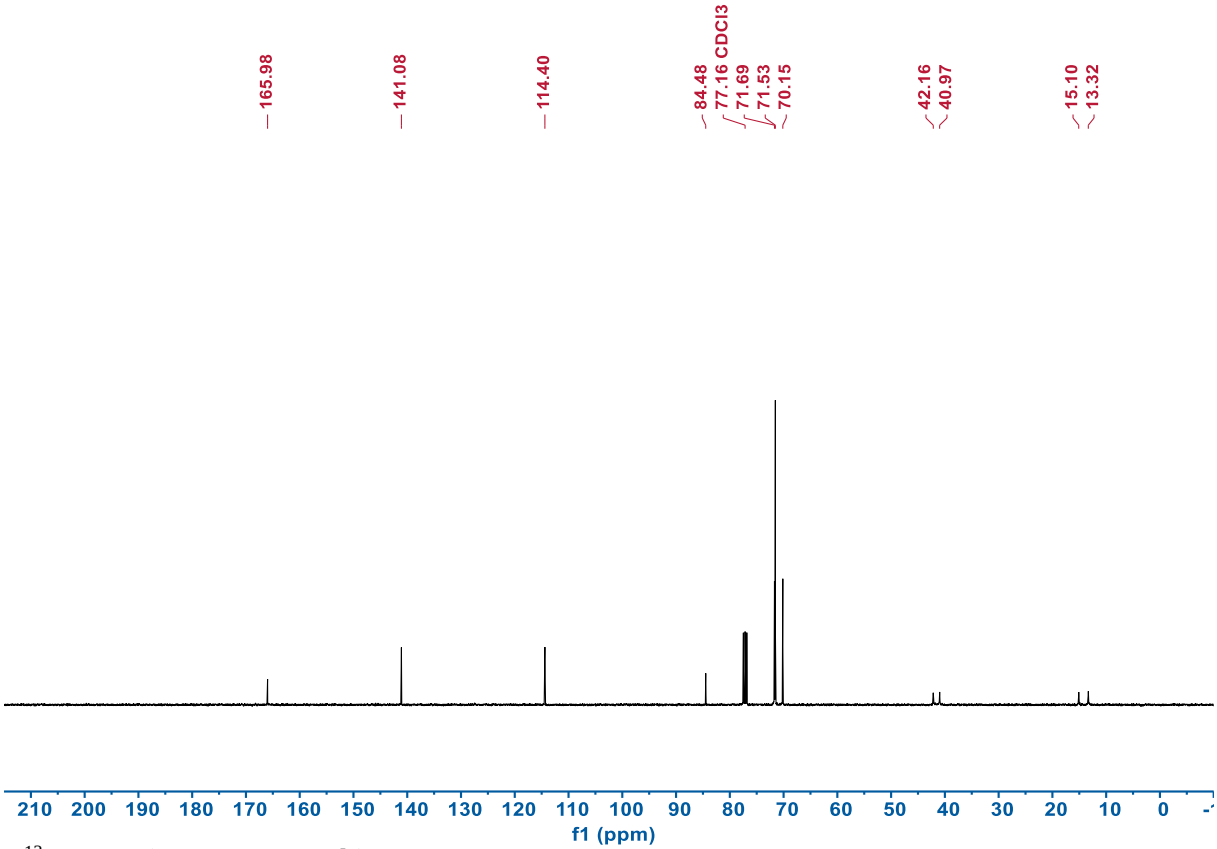

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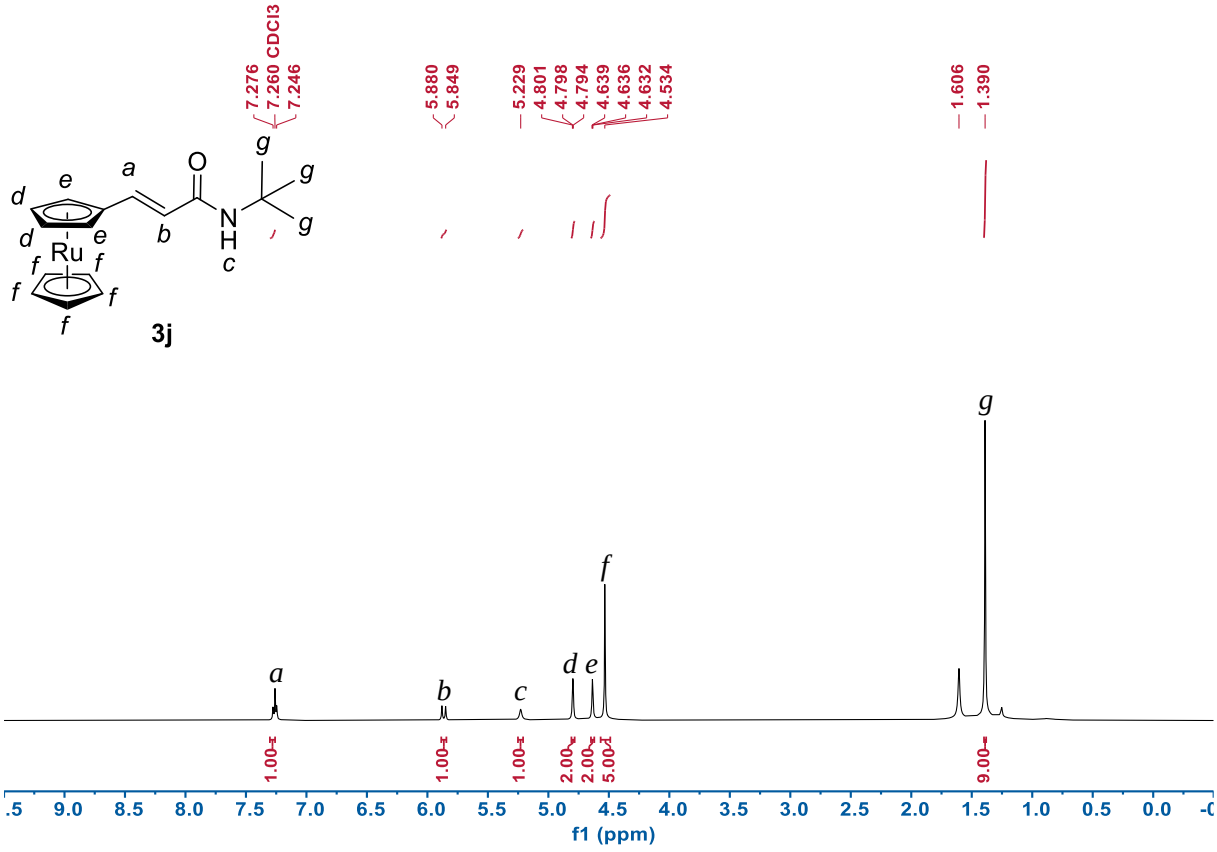

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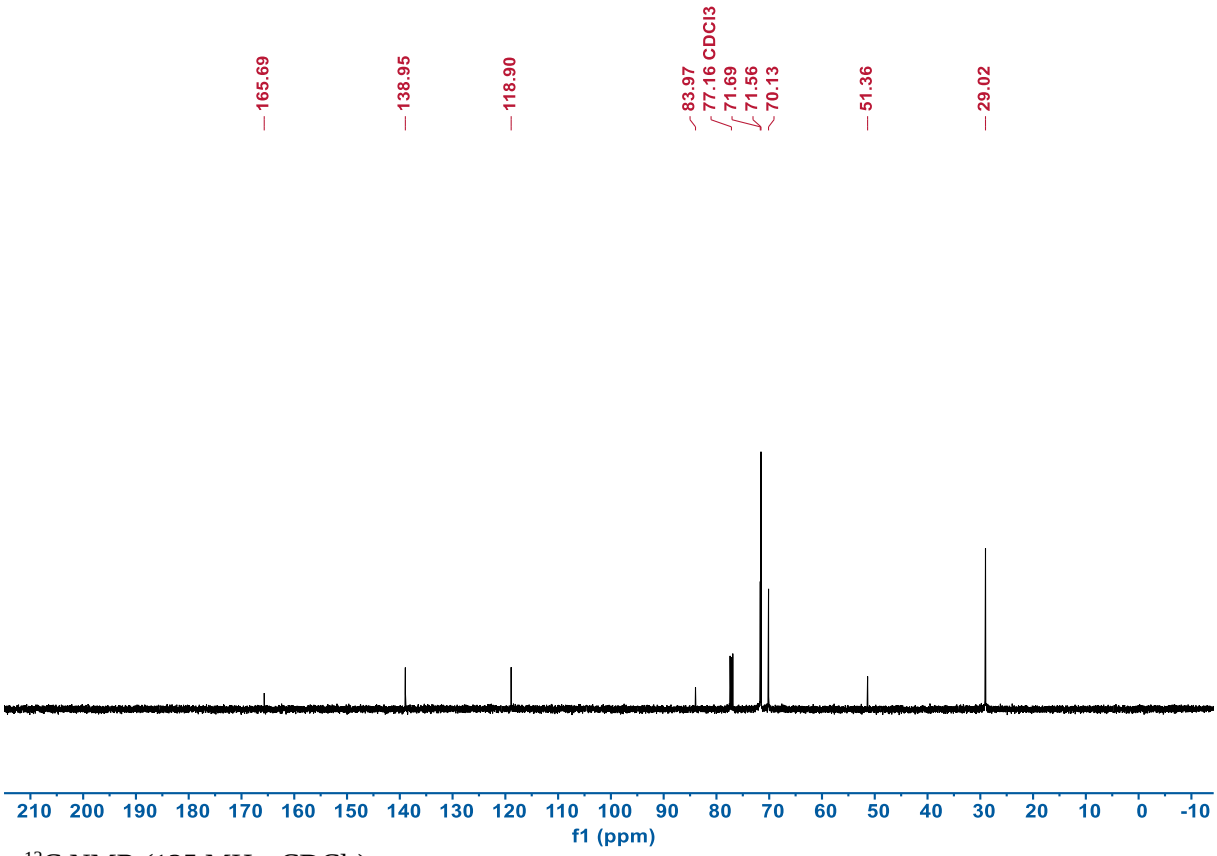

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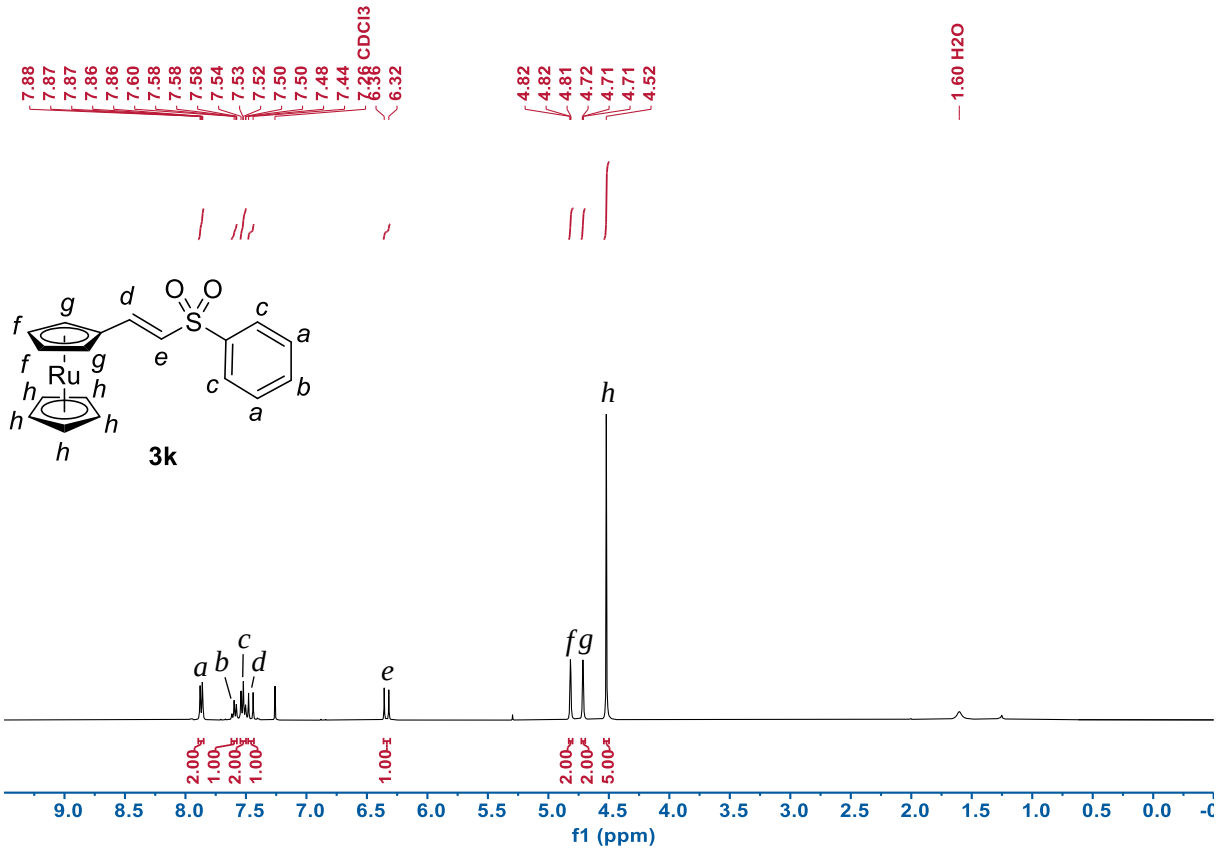

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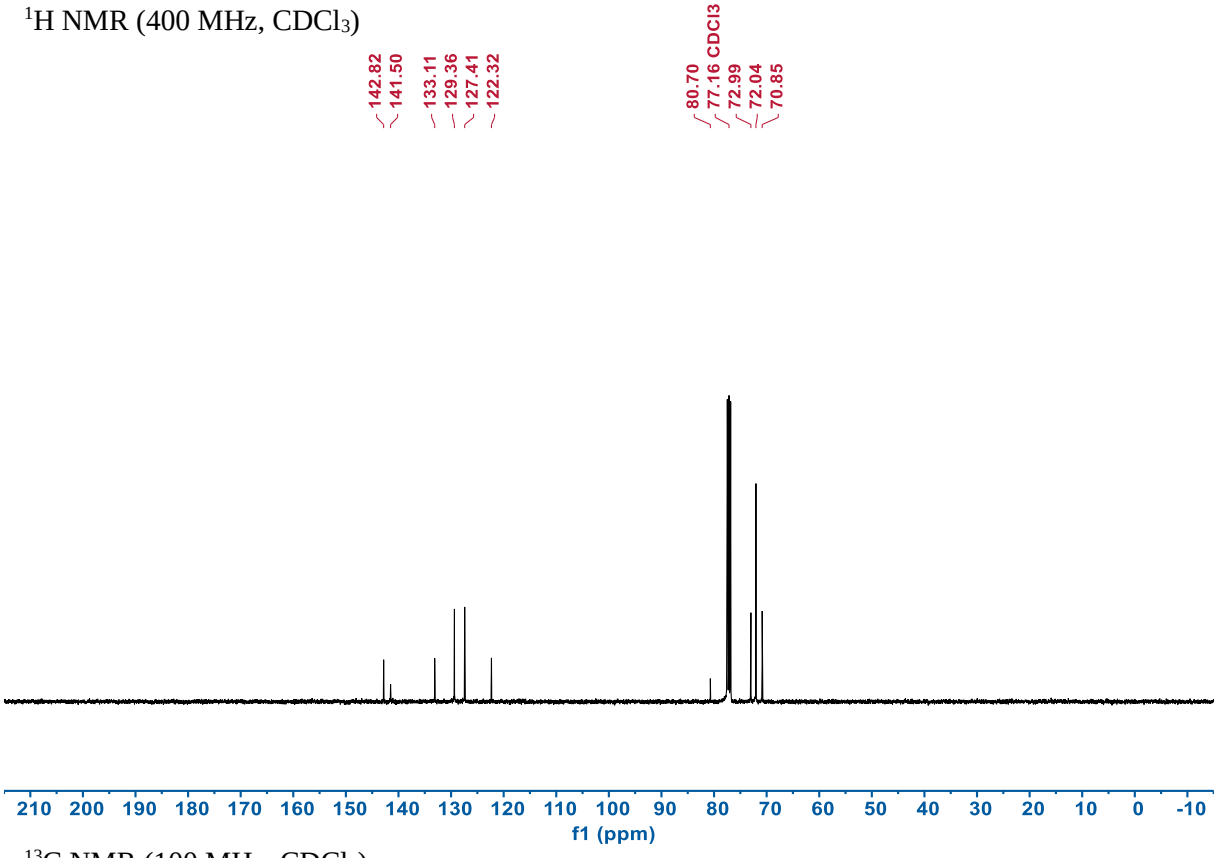

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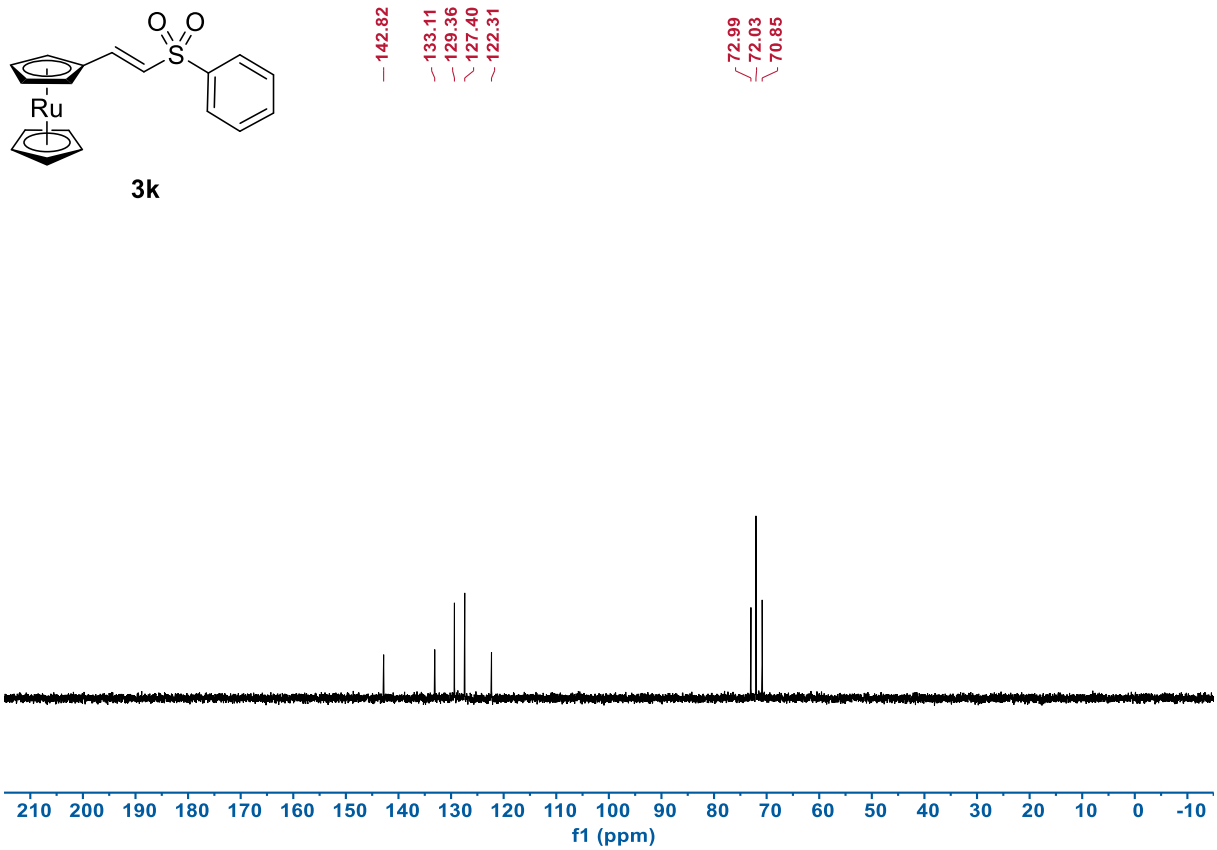

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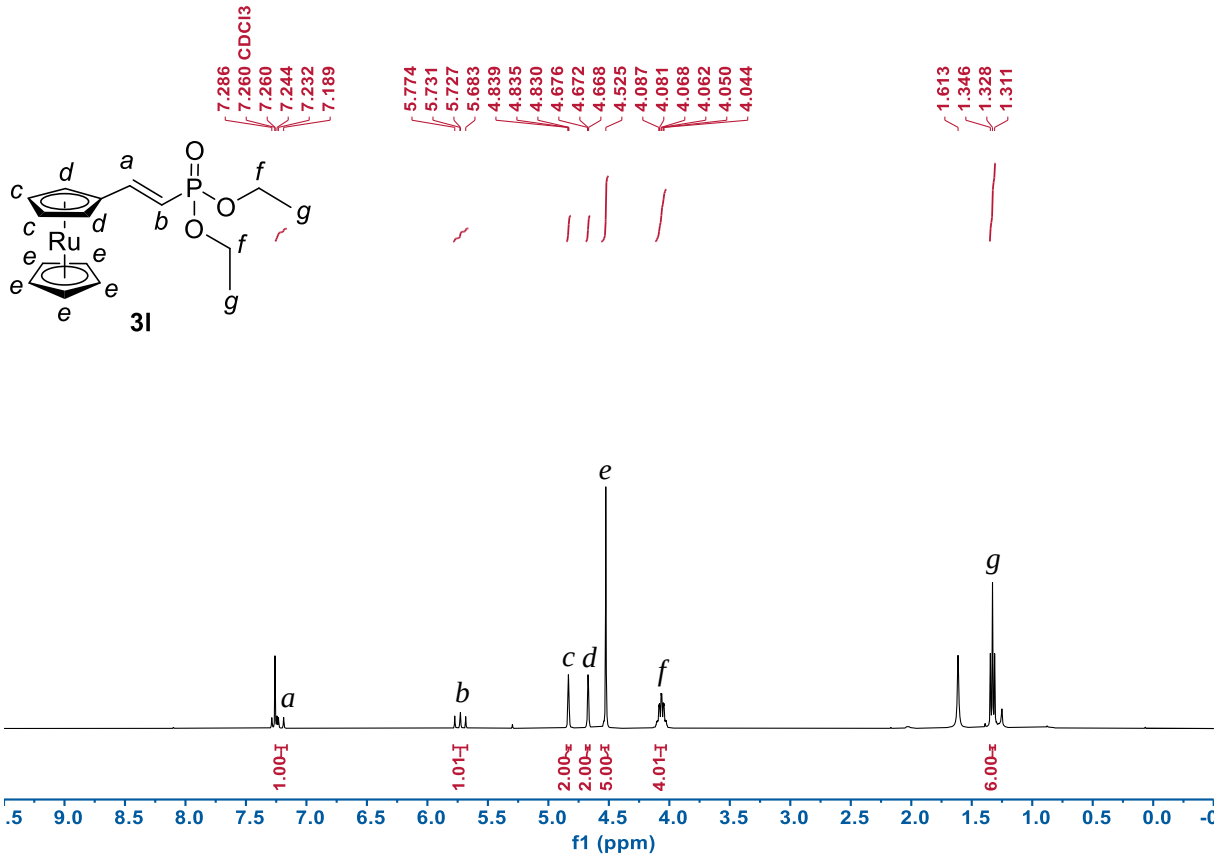

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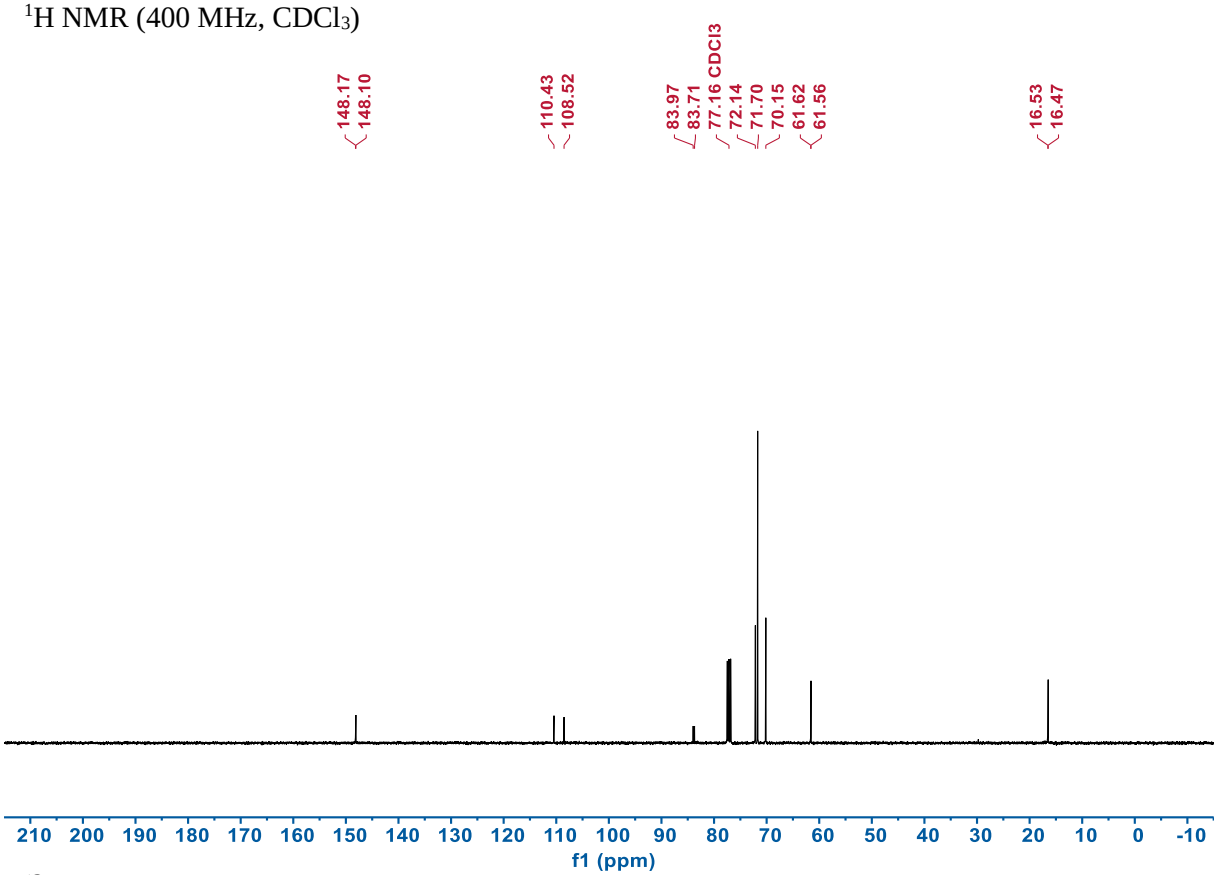

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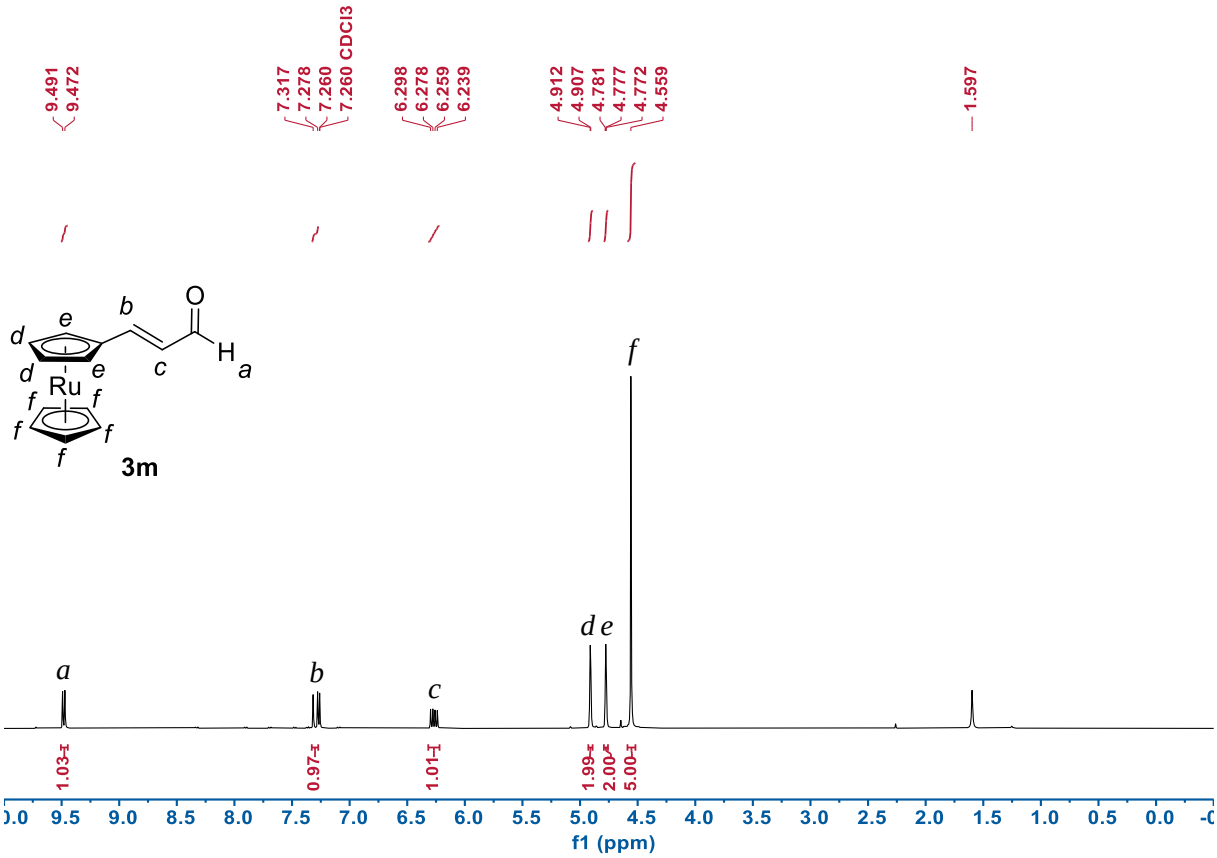

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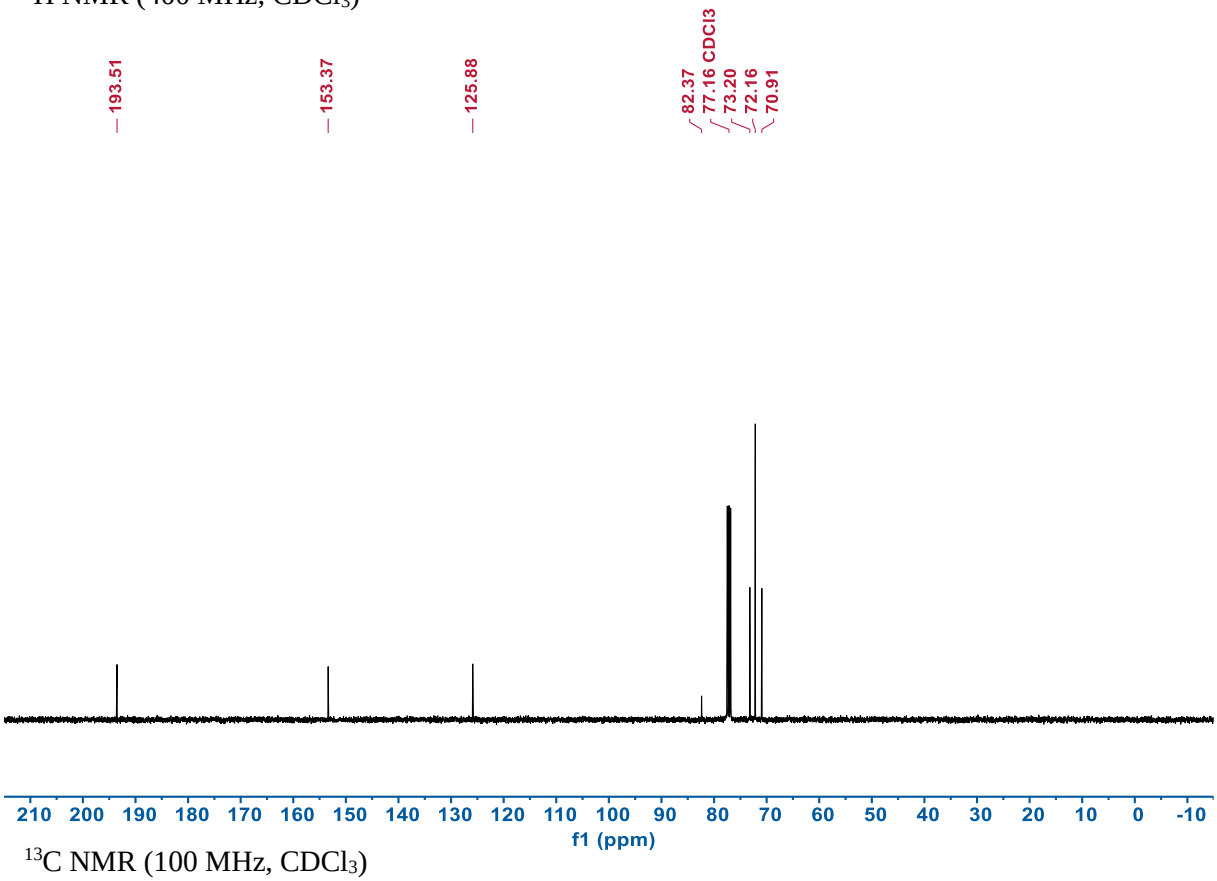

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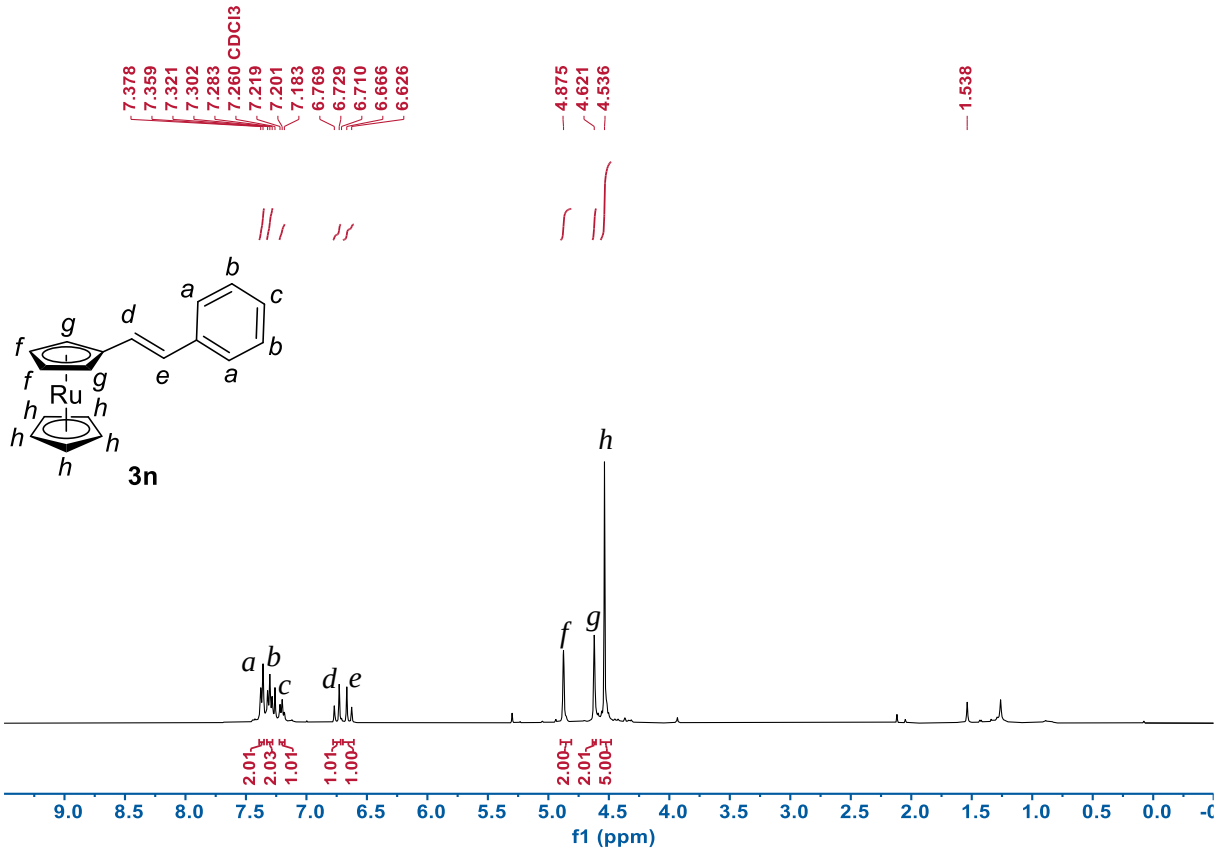

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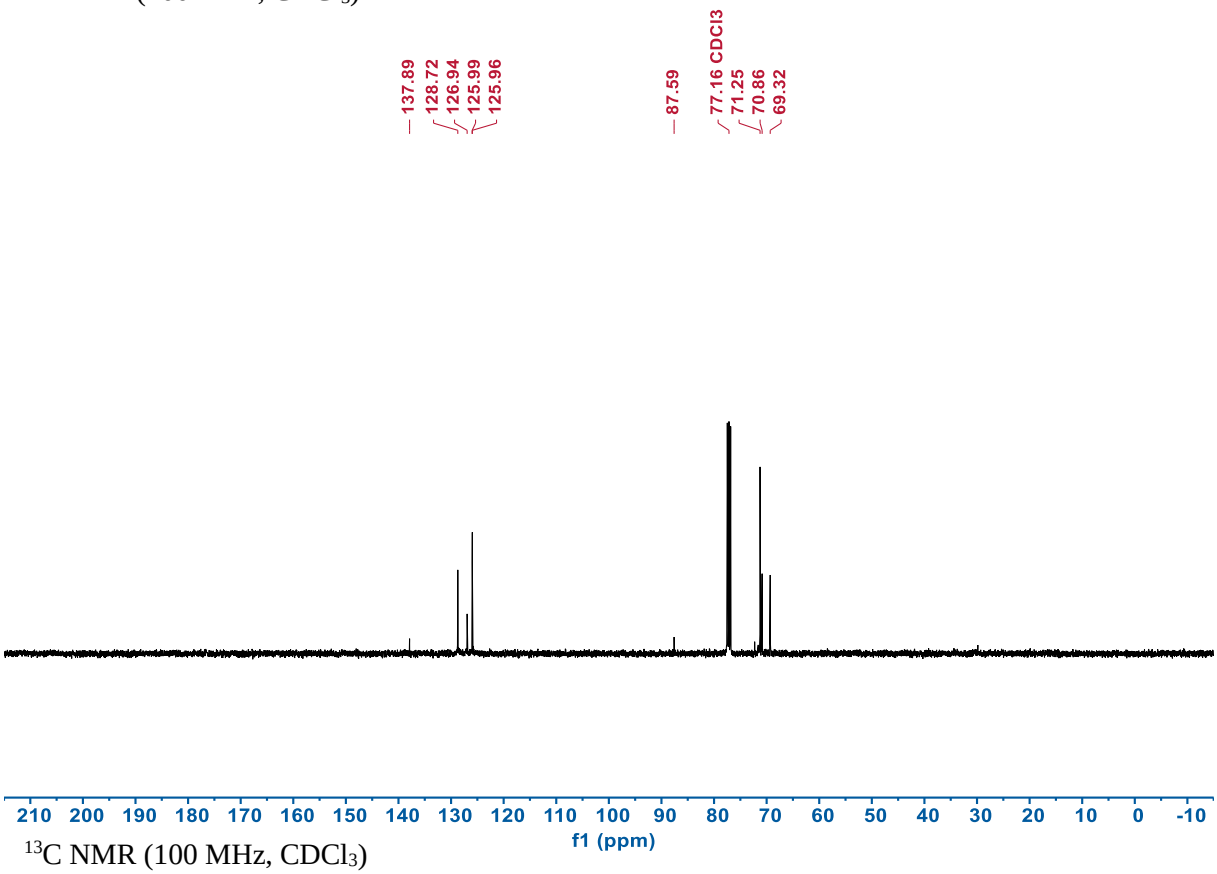

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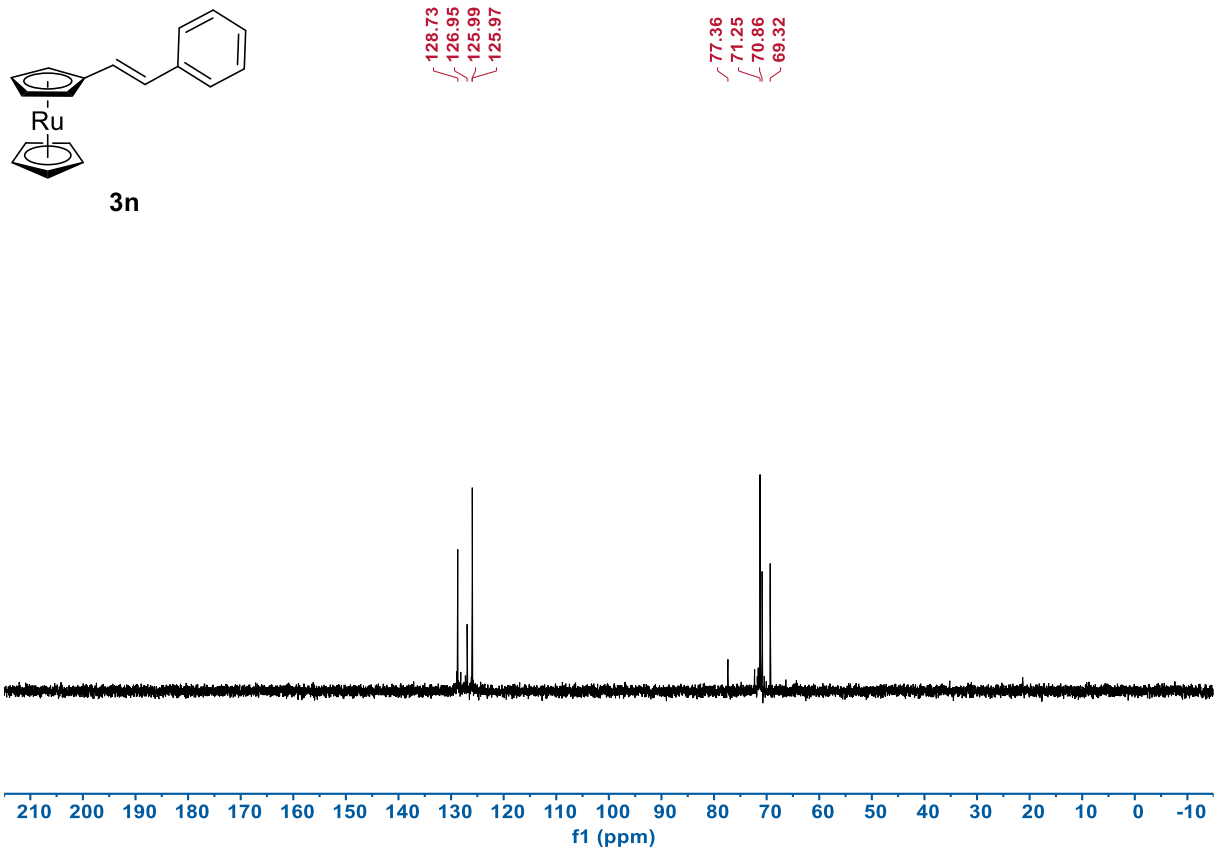

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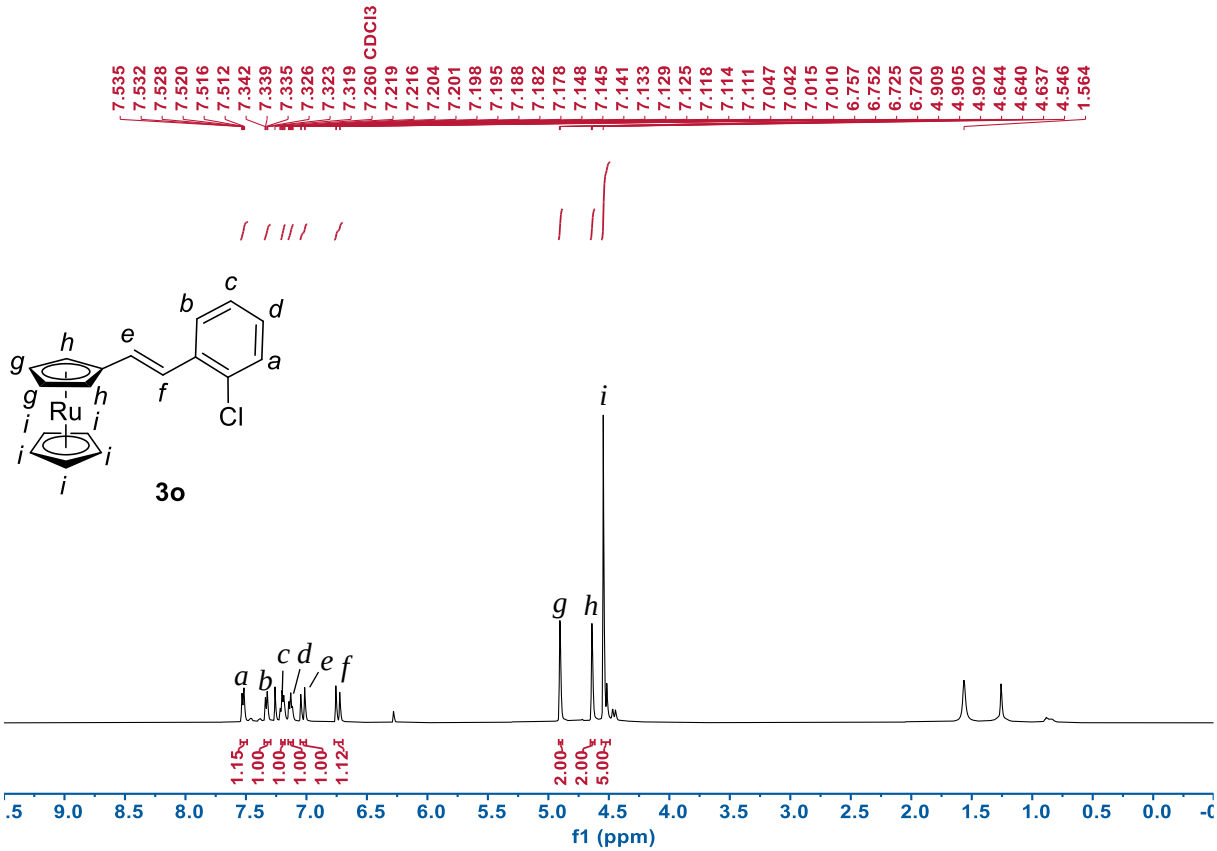
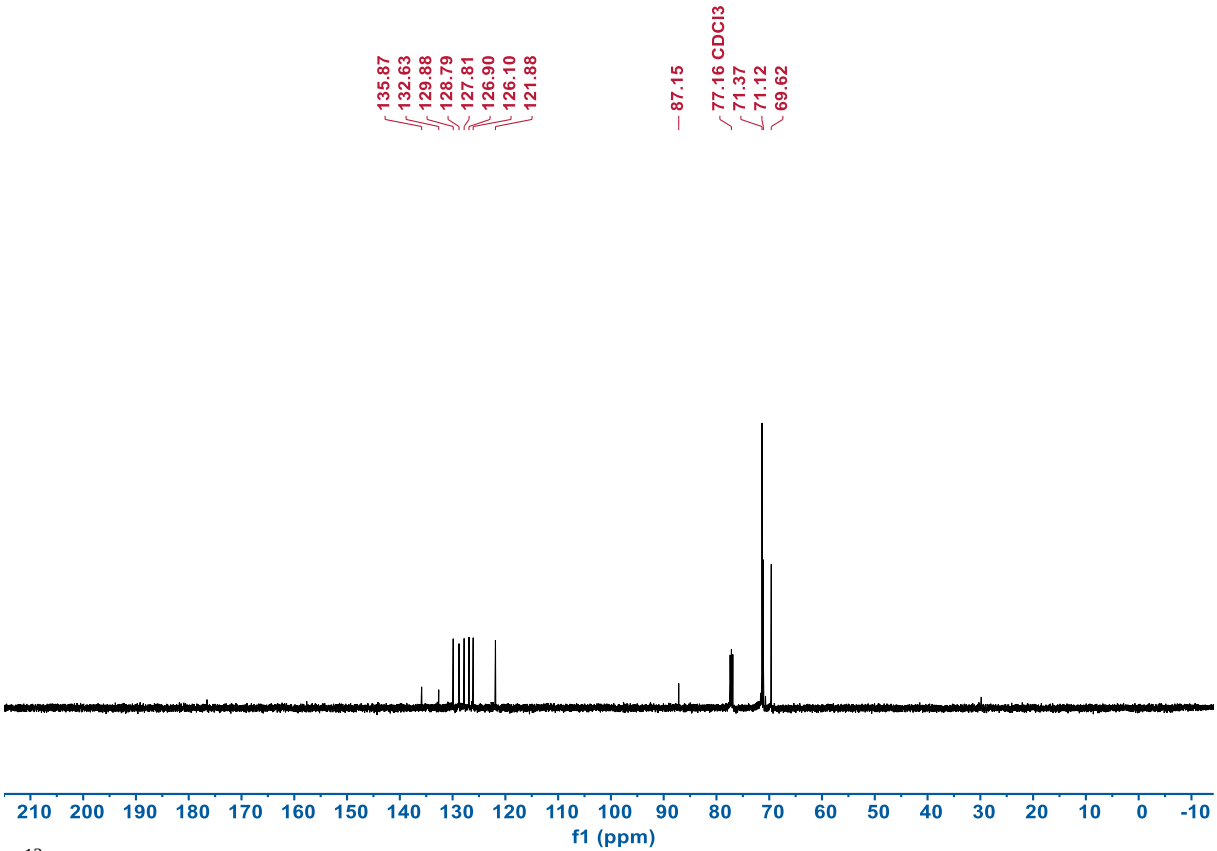


^{1}H NMR (500 MHz, $CDCl_3$)



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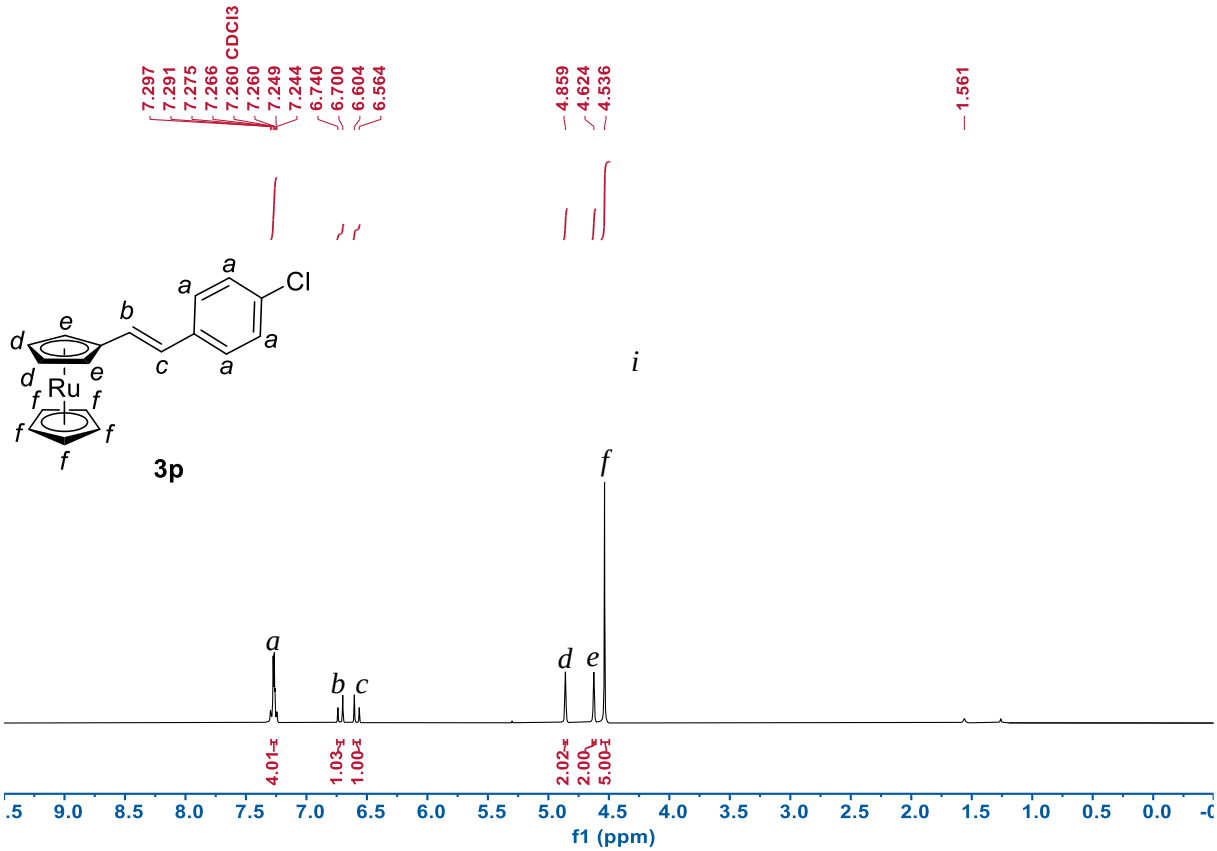
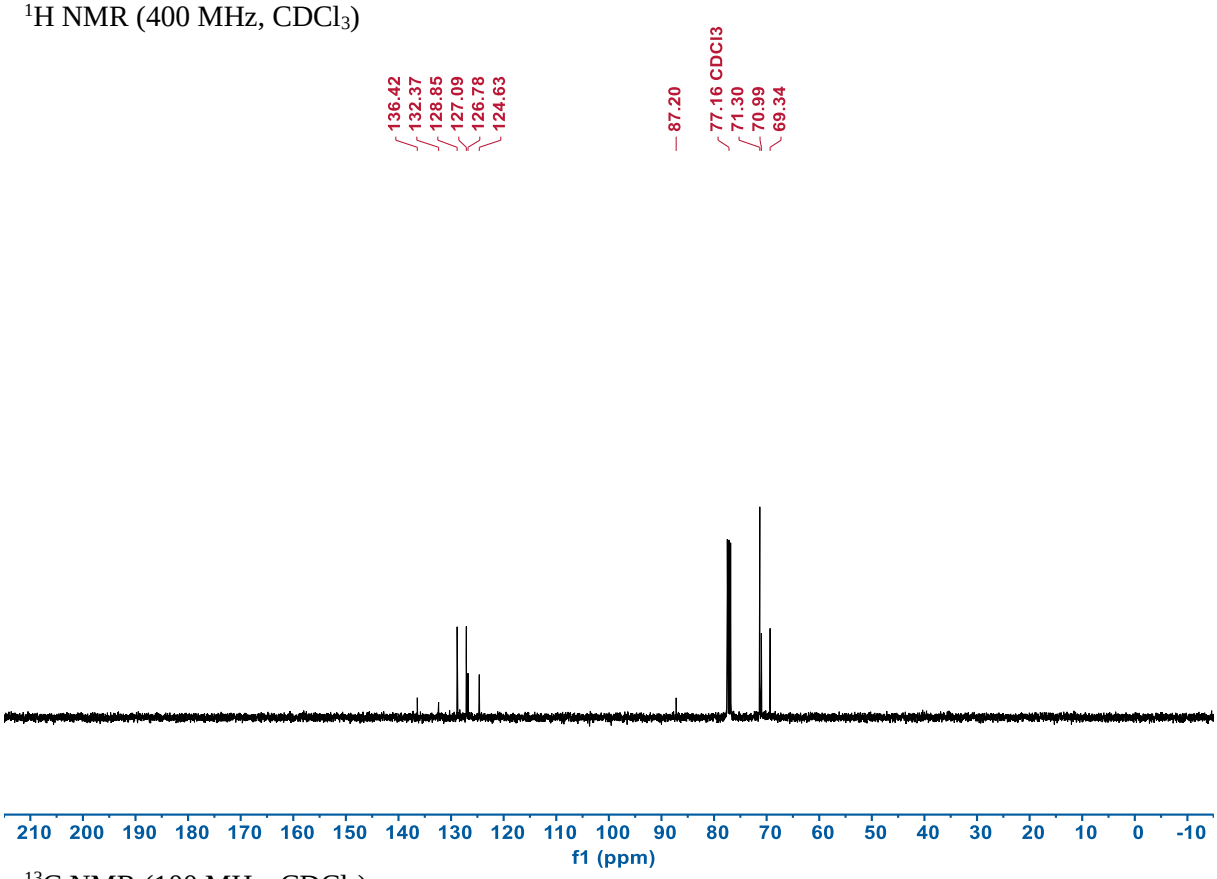
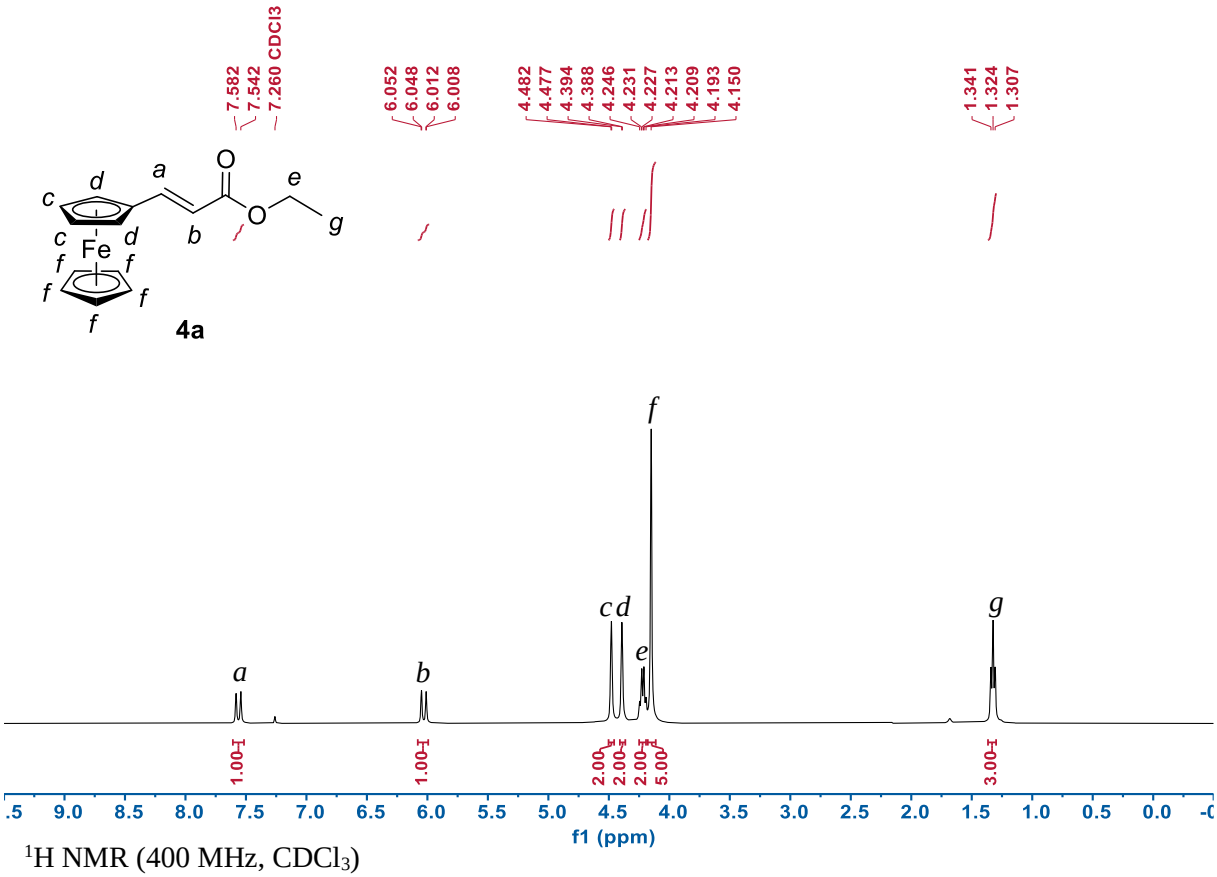


^{1}H NMR (400 MHz, $CDCl_3$)



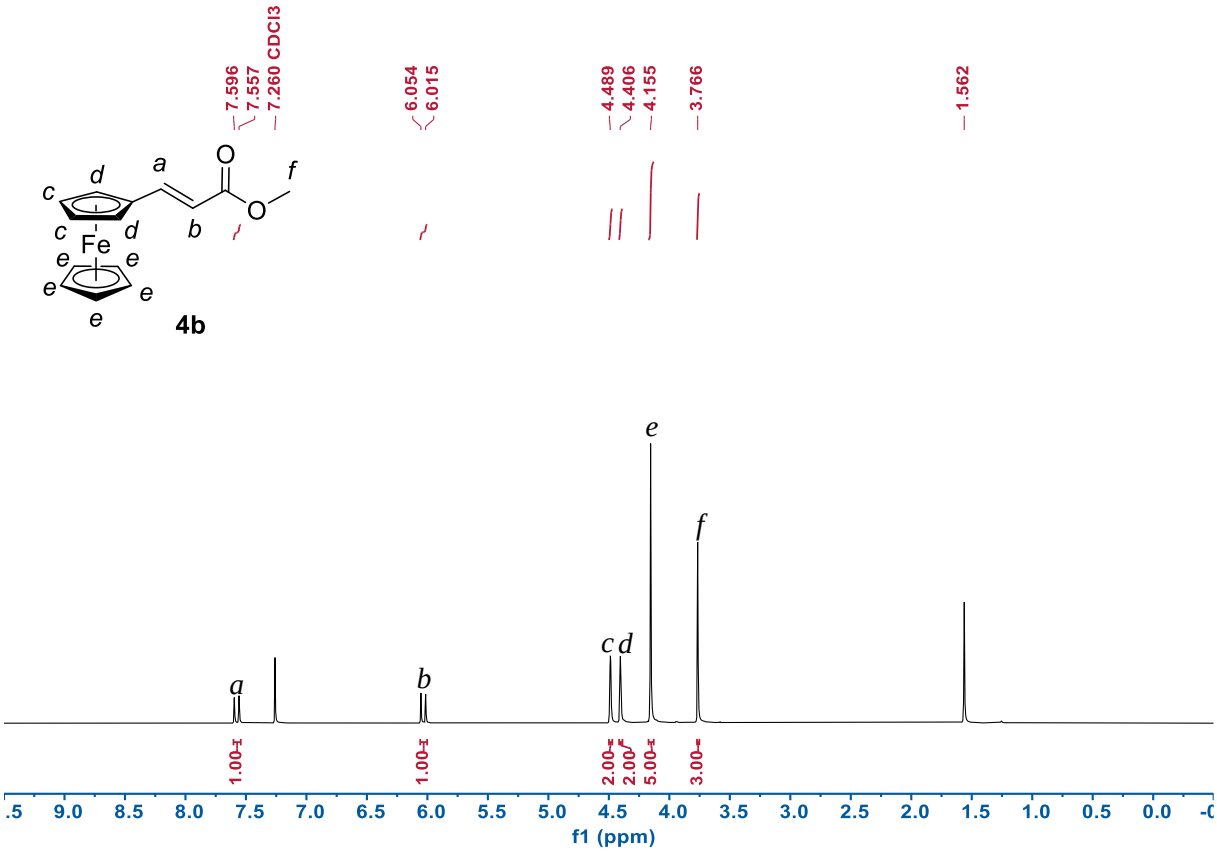
^{13}C NMR (100 MHz, $CDCl_3$)

Ferrocene Derivatives

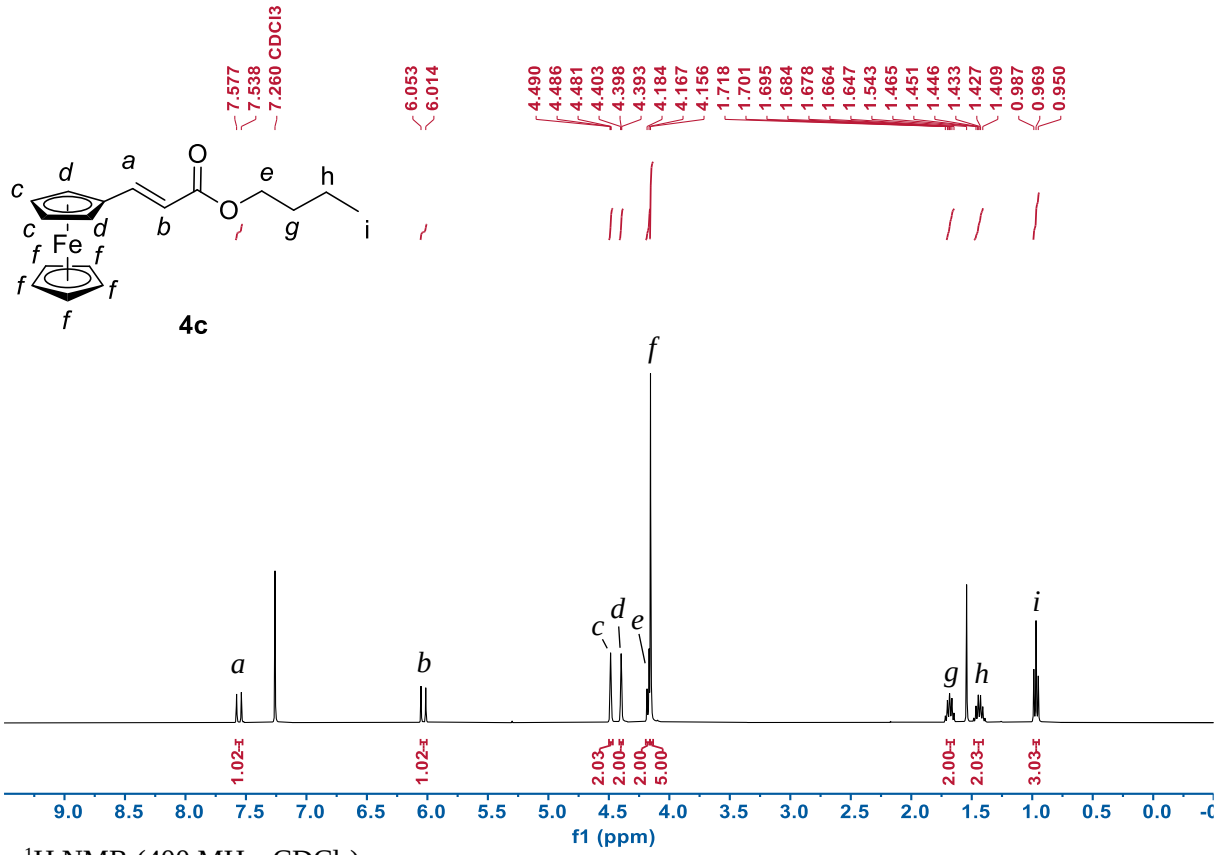


4a

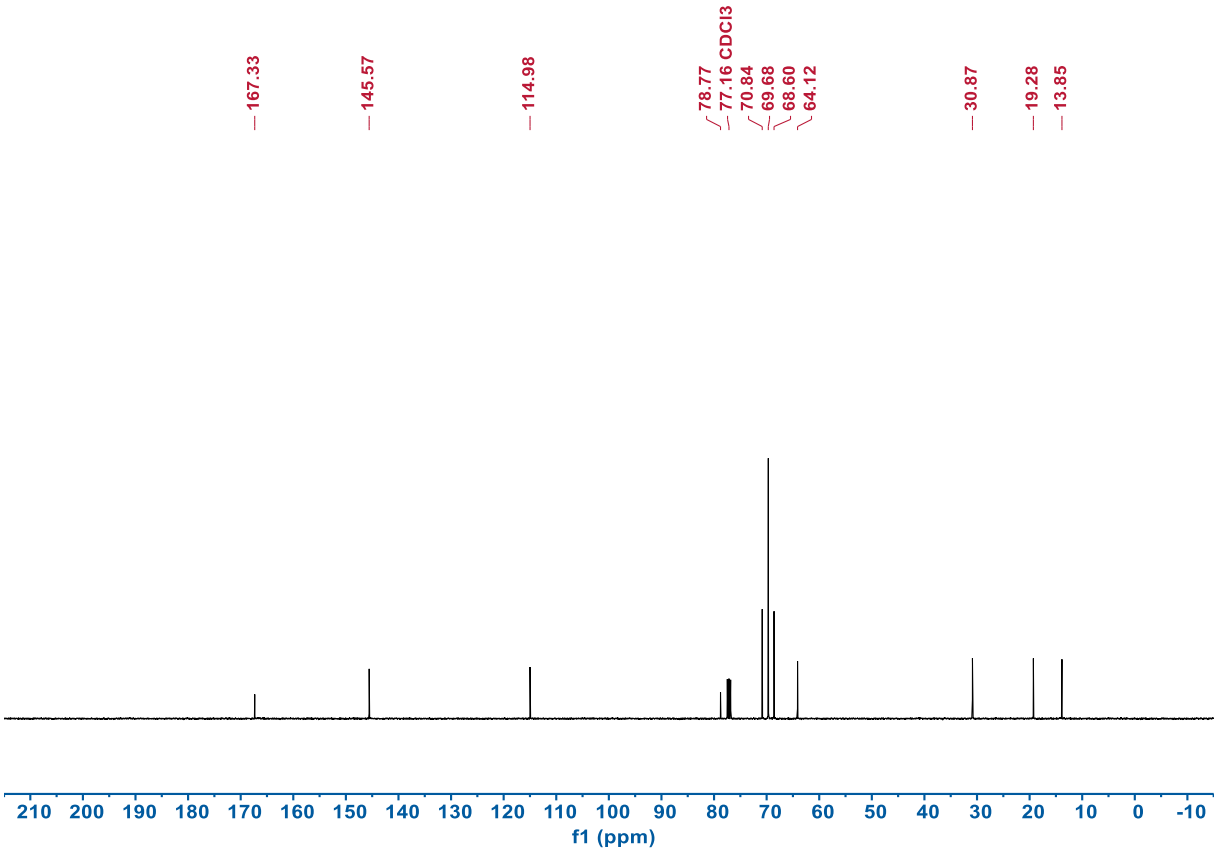
^{1}H NMR (400 MHz, $CDCl_3$)



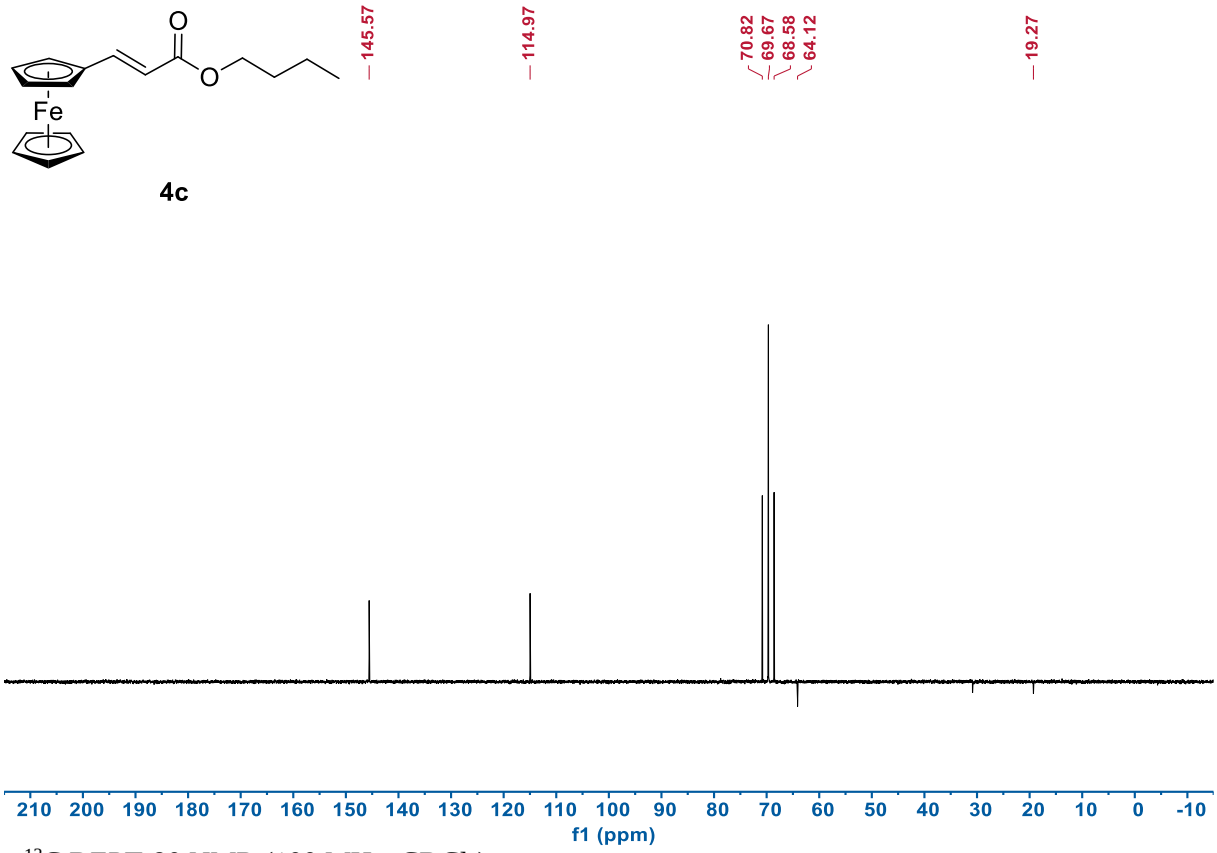
^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

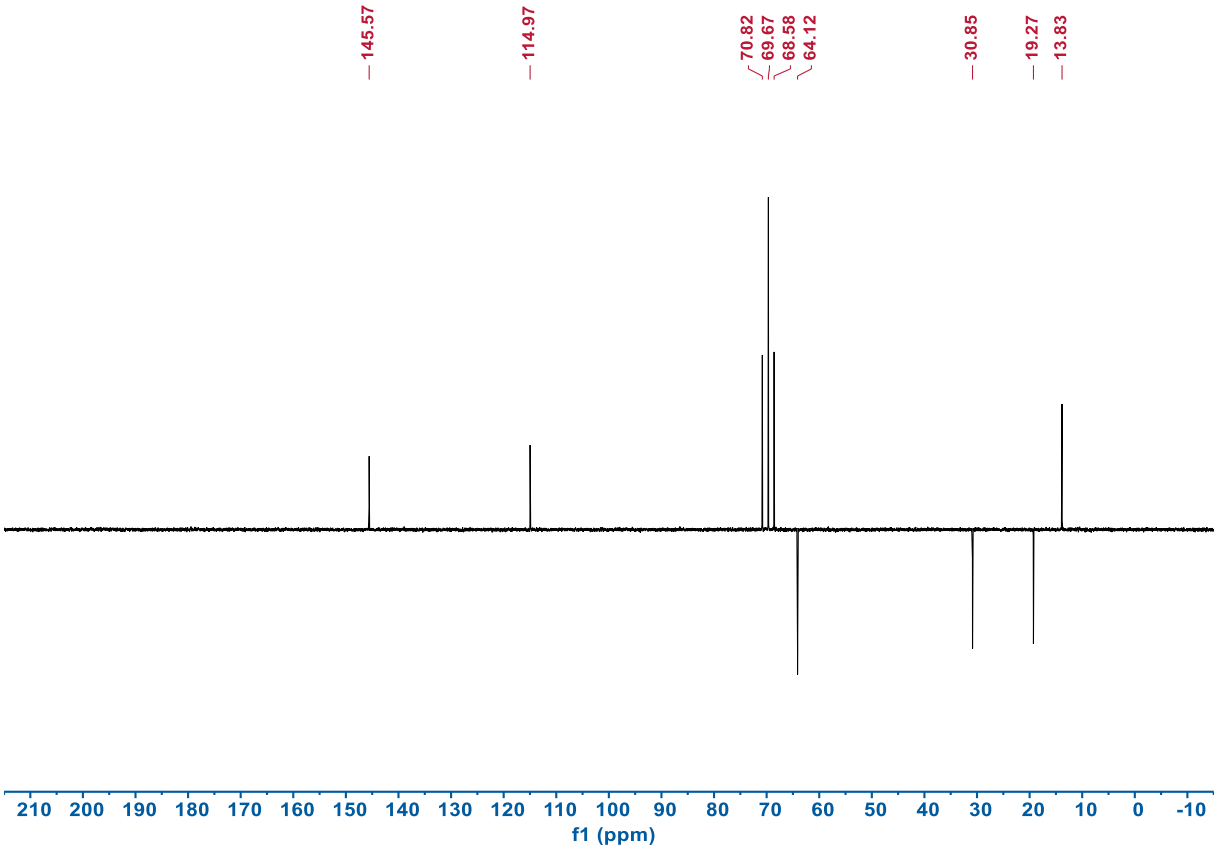


^{13}C NMR (100 MHz, $CDCl_3$)

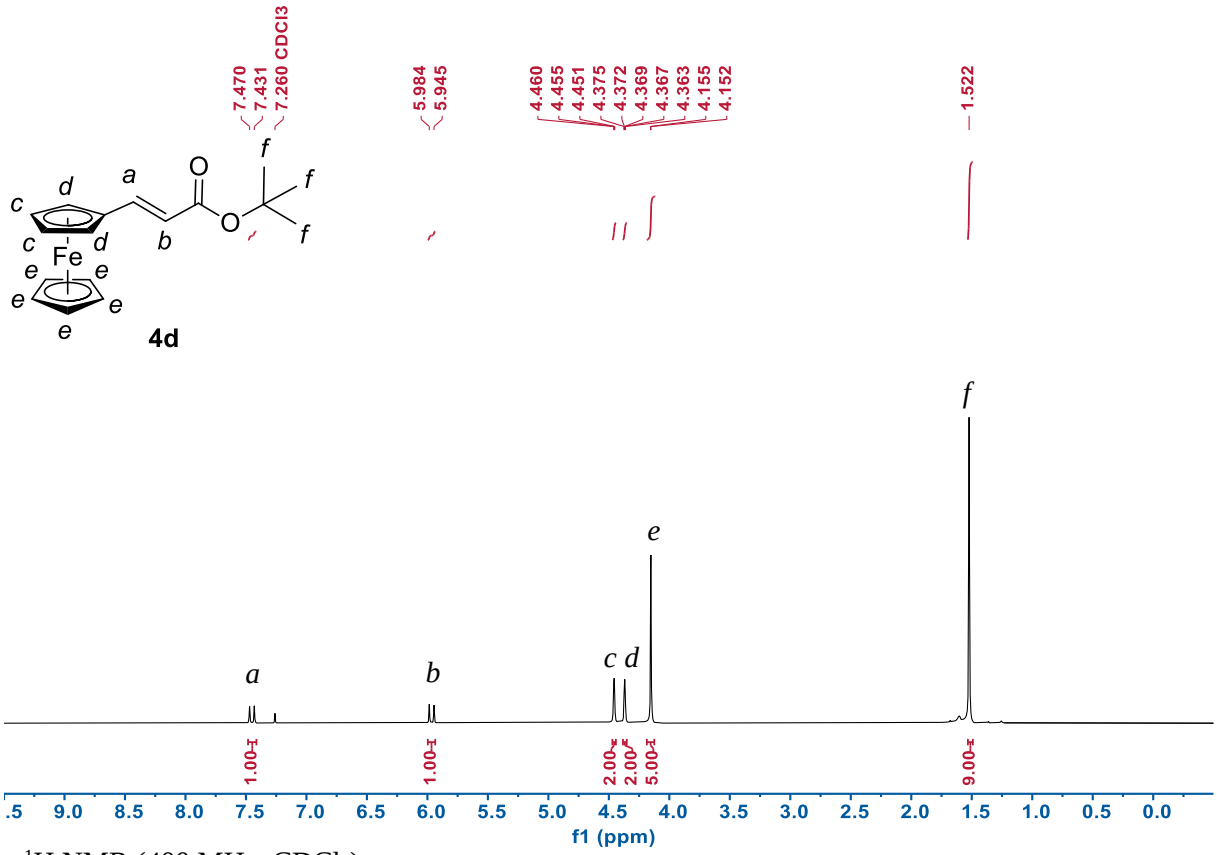


4c

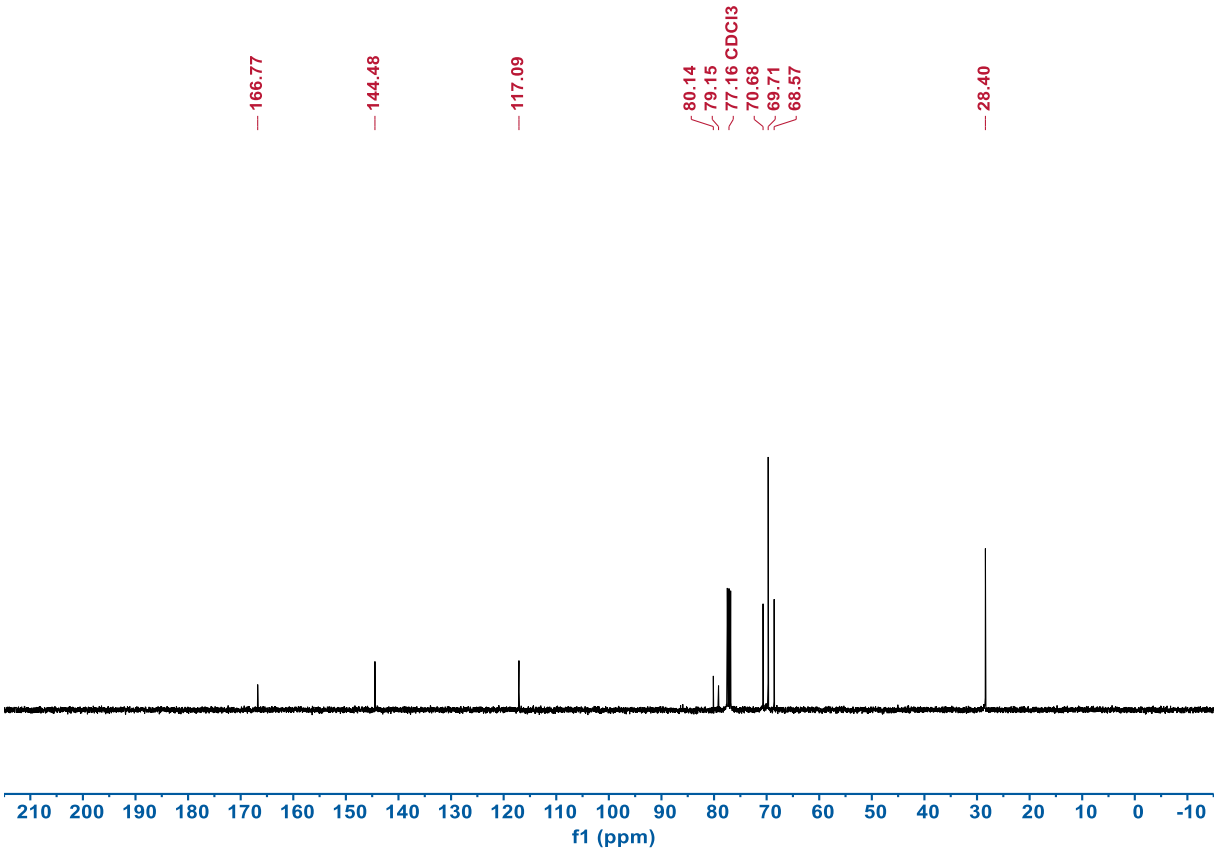
^{13}C DEPT-90 NMR (100 MHz, $CDCl_3$)



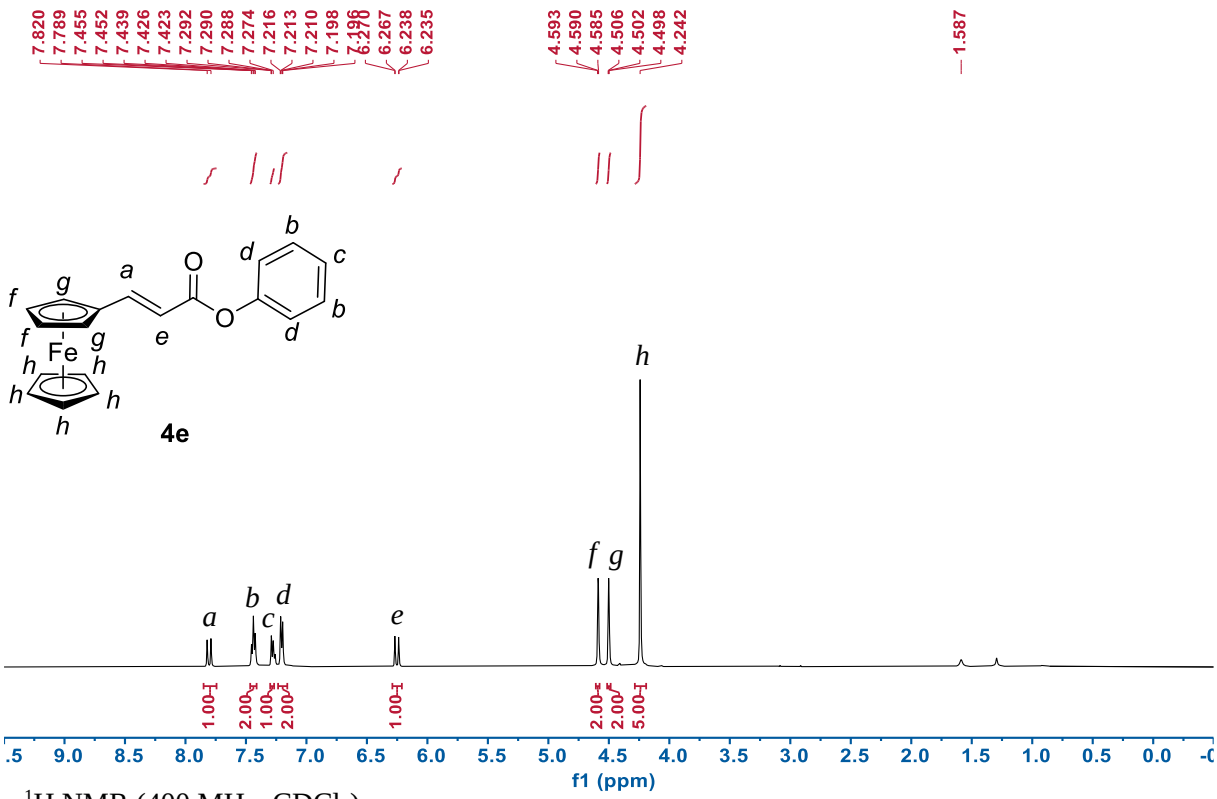
^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



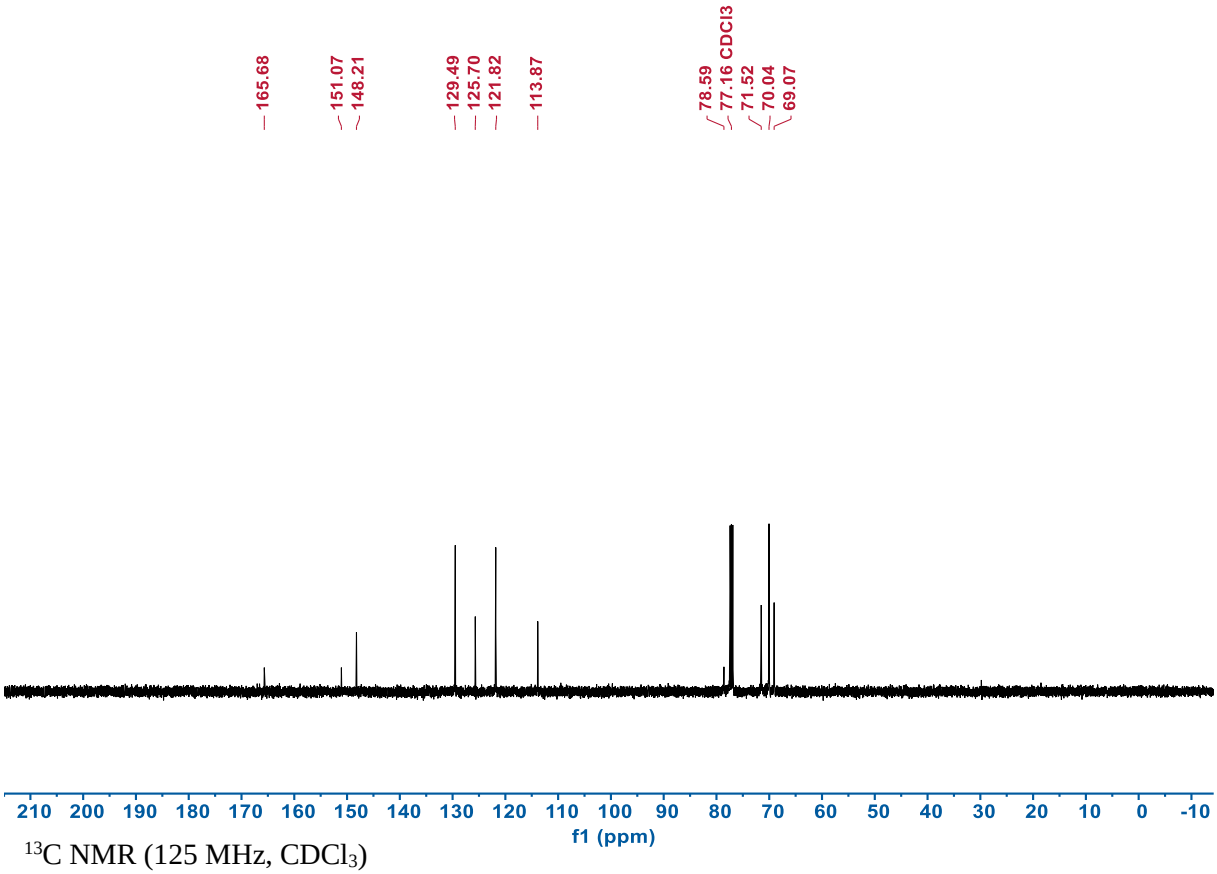
^{1}H NMR (400 MHz, $CDCl_3$)



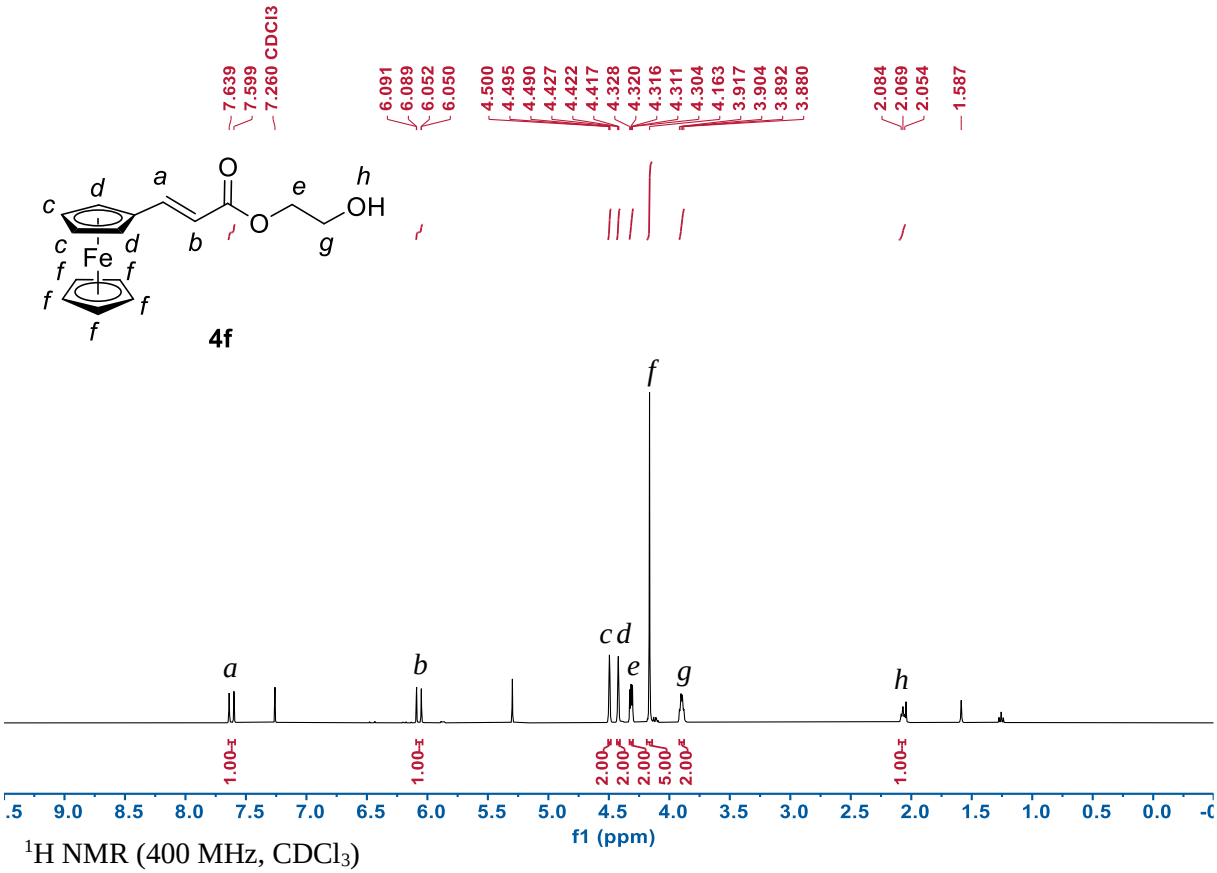
^{13}C NMR (100 MHz, $CDCl_3$)



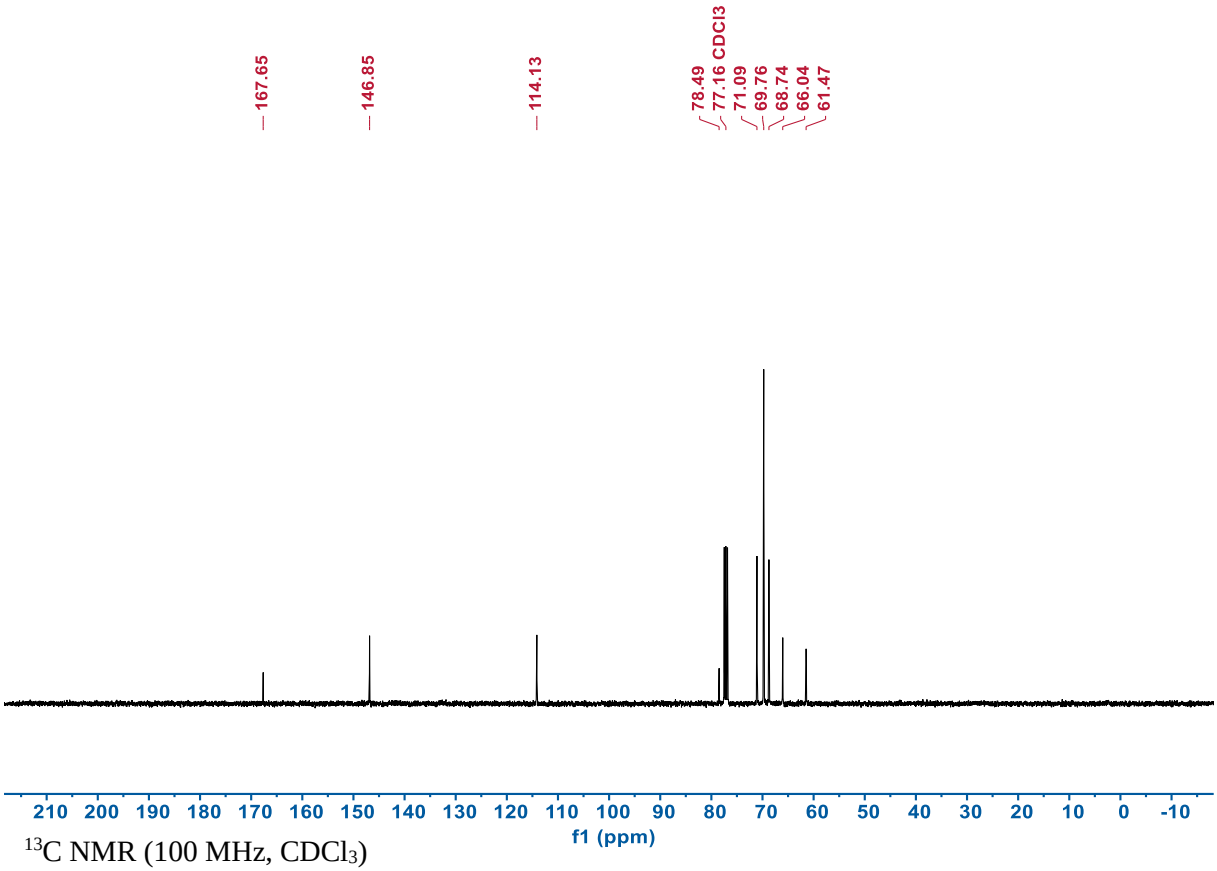
^{1}H NMR (400 MHz, $CDCl_3$)



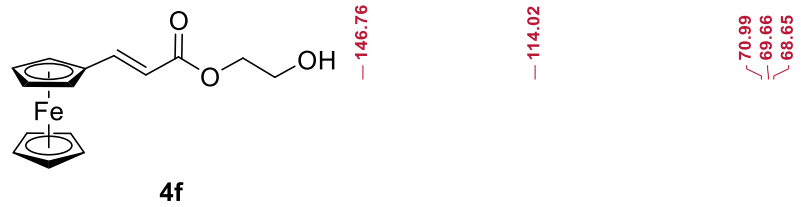
^{13}C NMR (125 MHz, $CDCl_3$)



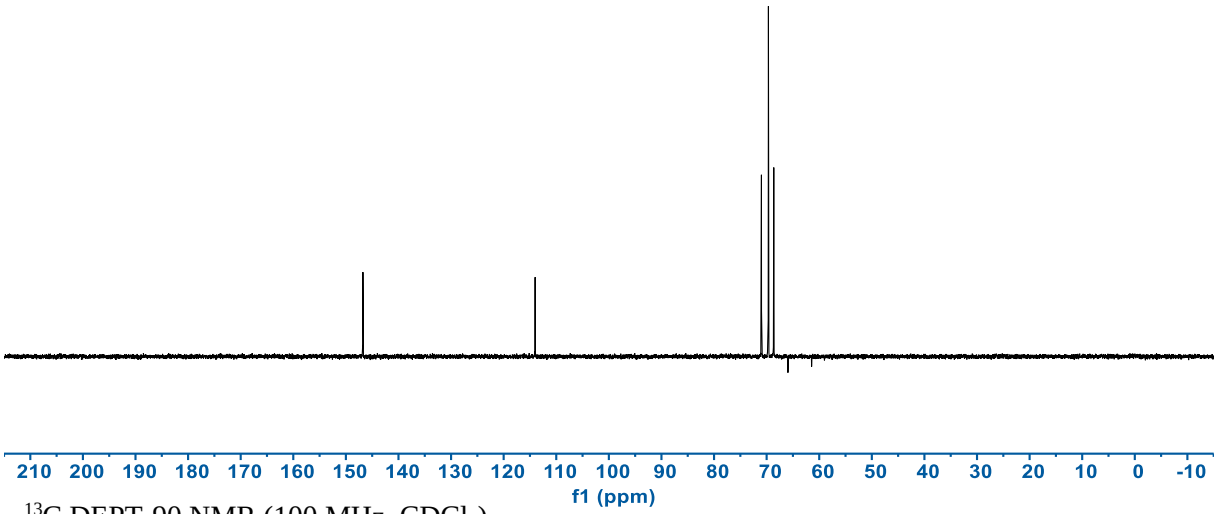
^{1}H NMR (400 MHz, $CDCl_3$)



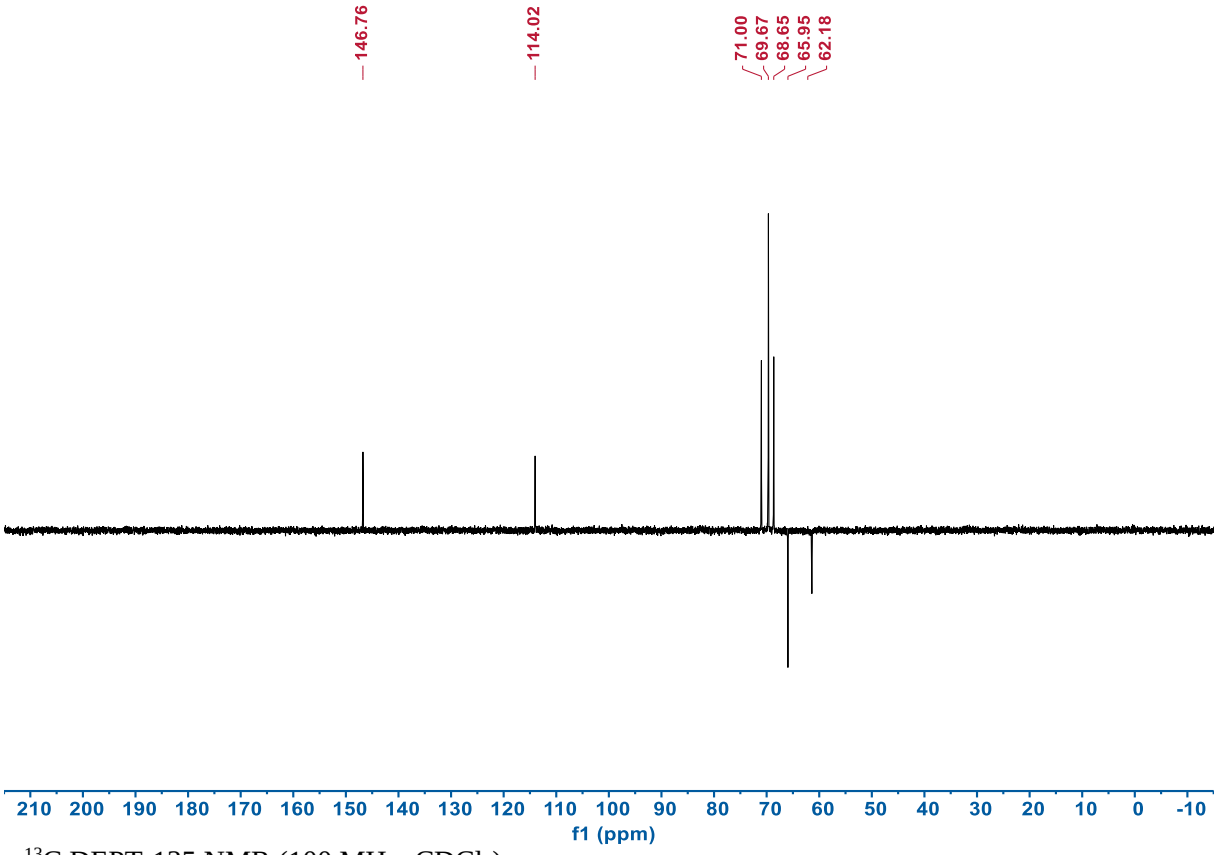
^{13}C NMR (100 MHz, $CDCl_3$)



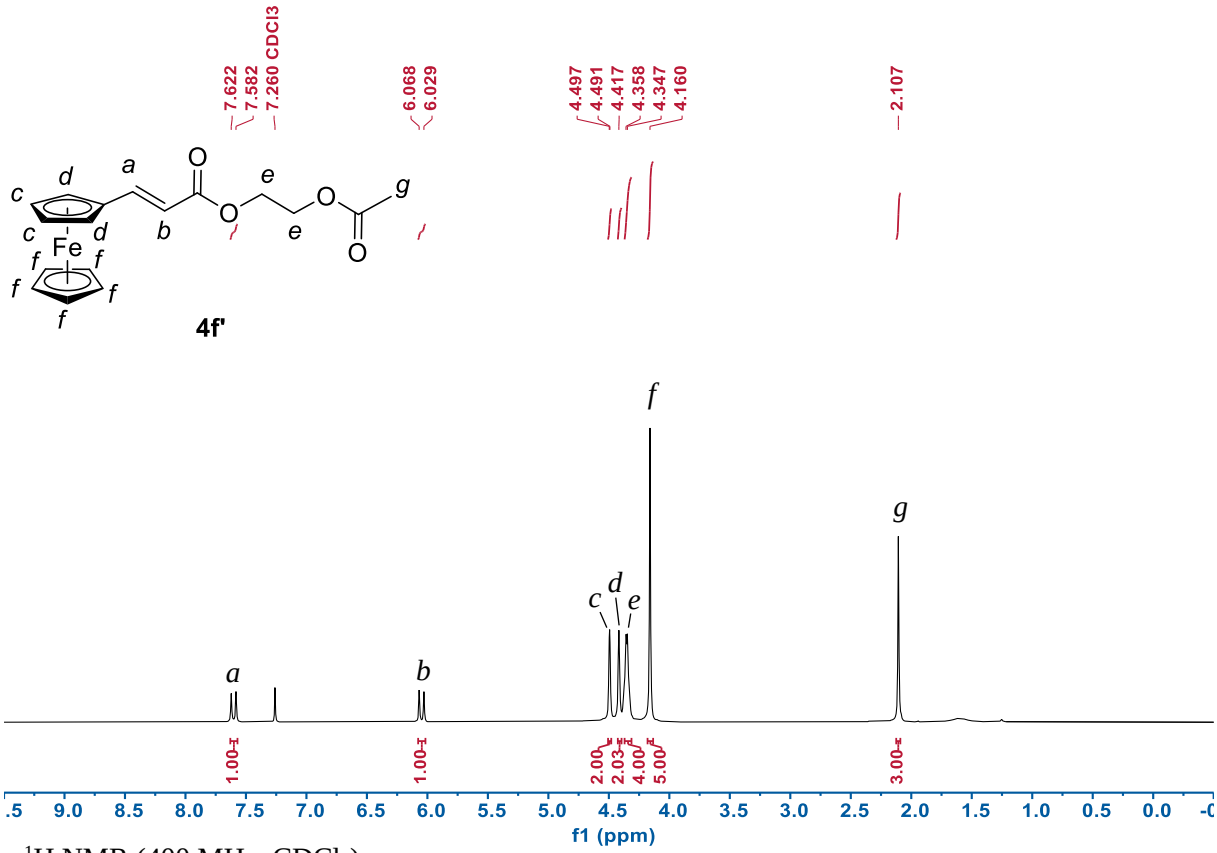
4f



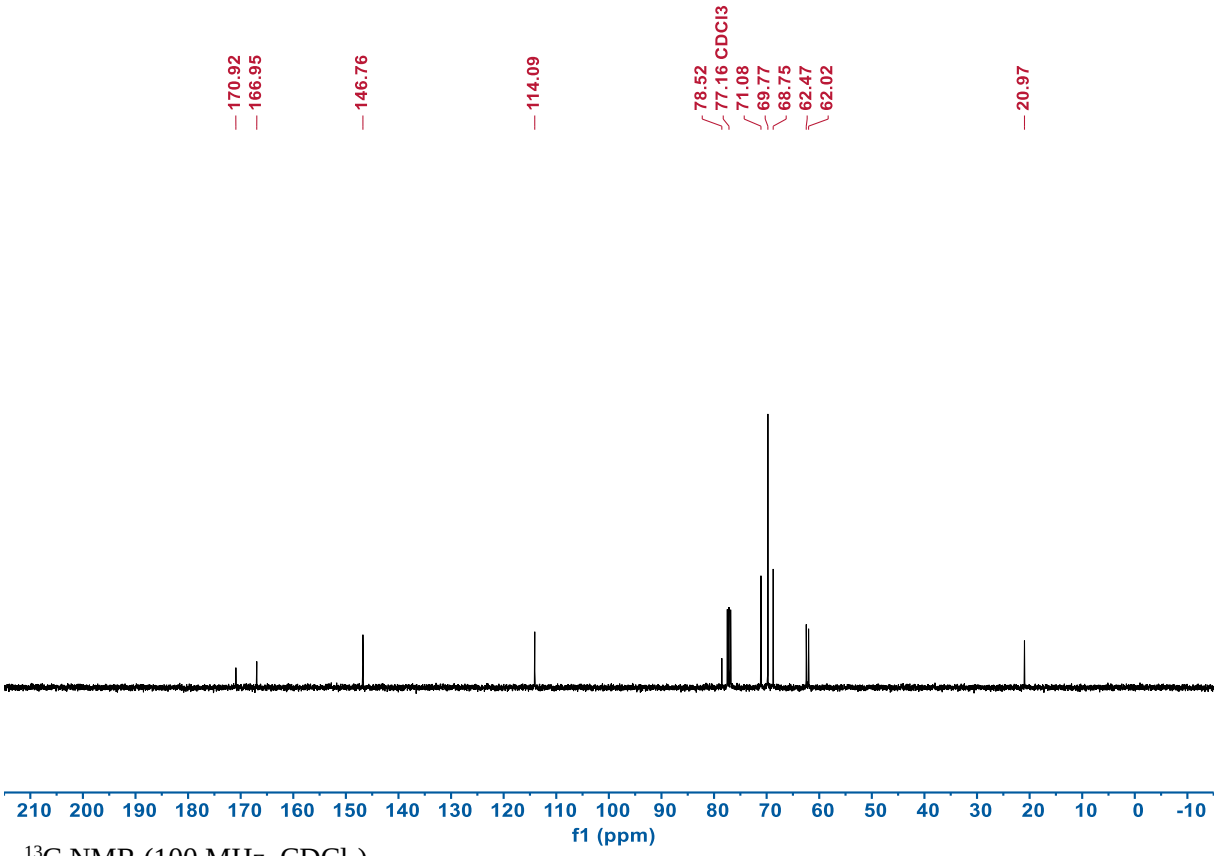
^{13}C DEPT-90 NMR (100 MHz, $CDCl_3$)



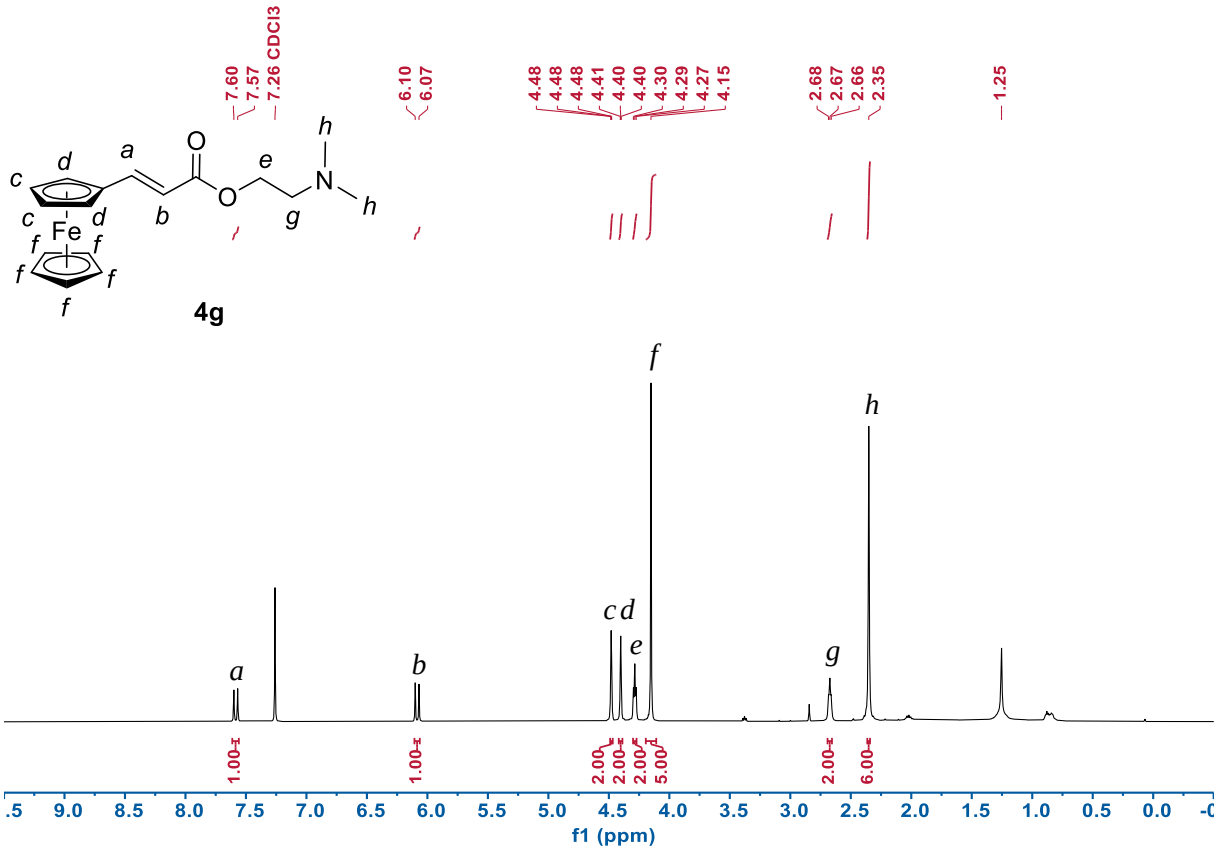
^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



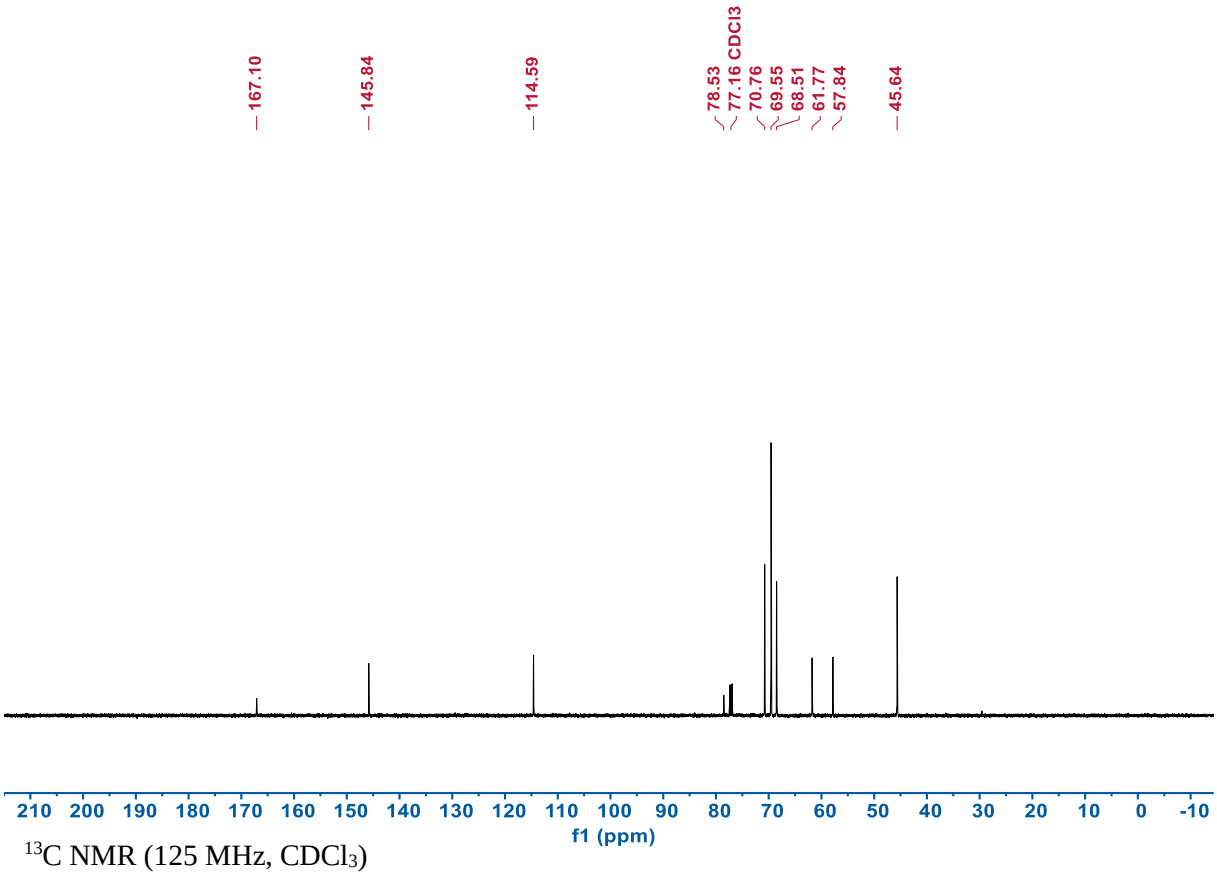
^{1}H NMR (400 MHz, $CDCl_3$)



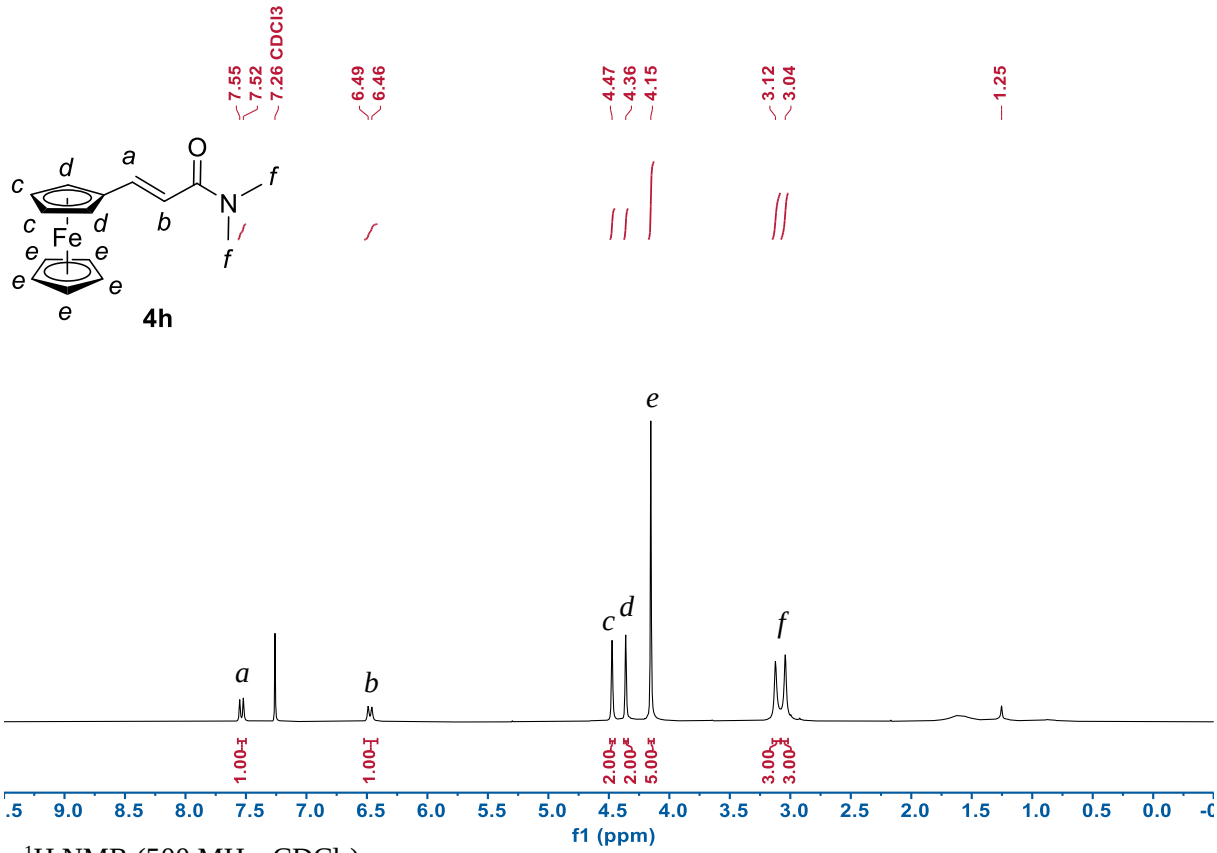
^{13}C NMR (100 MHz, $CDCl_3$)



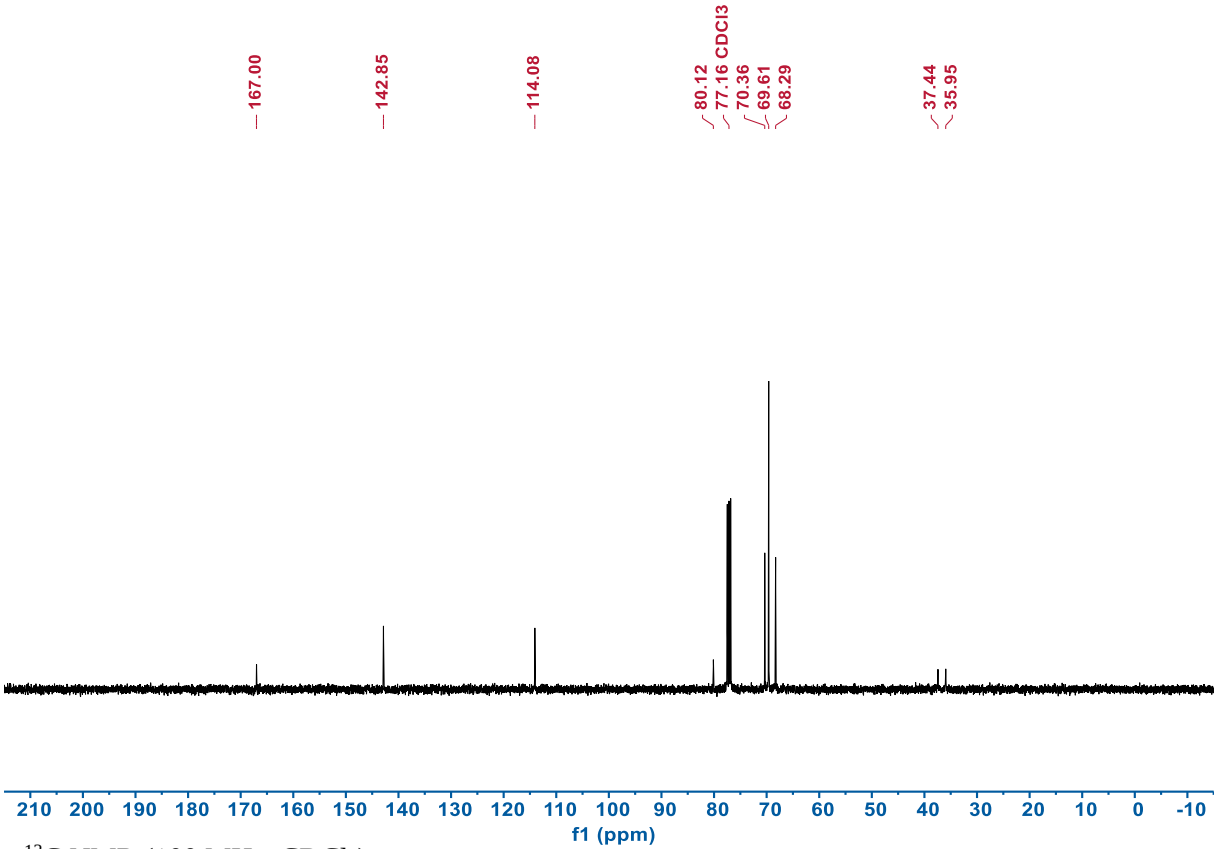
^{1}H NMR (500 MHz, $CDCl_3$)



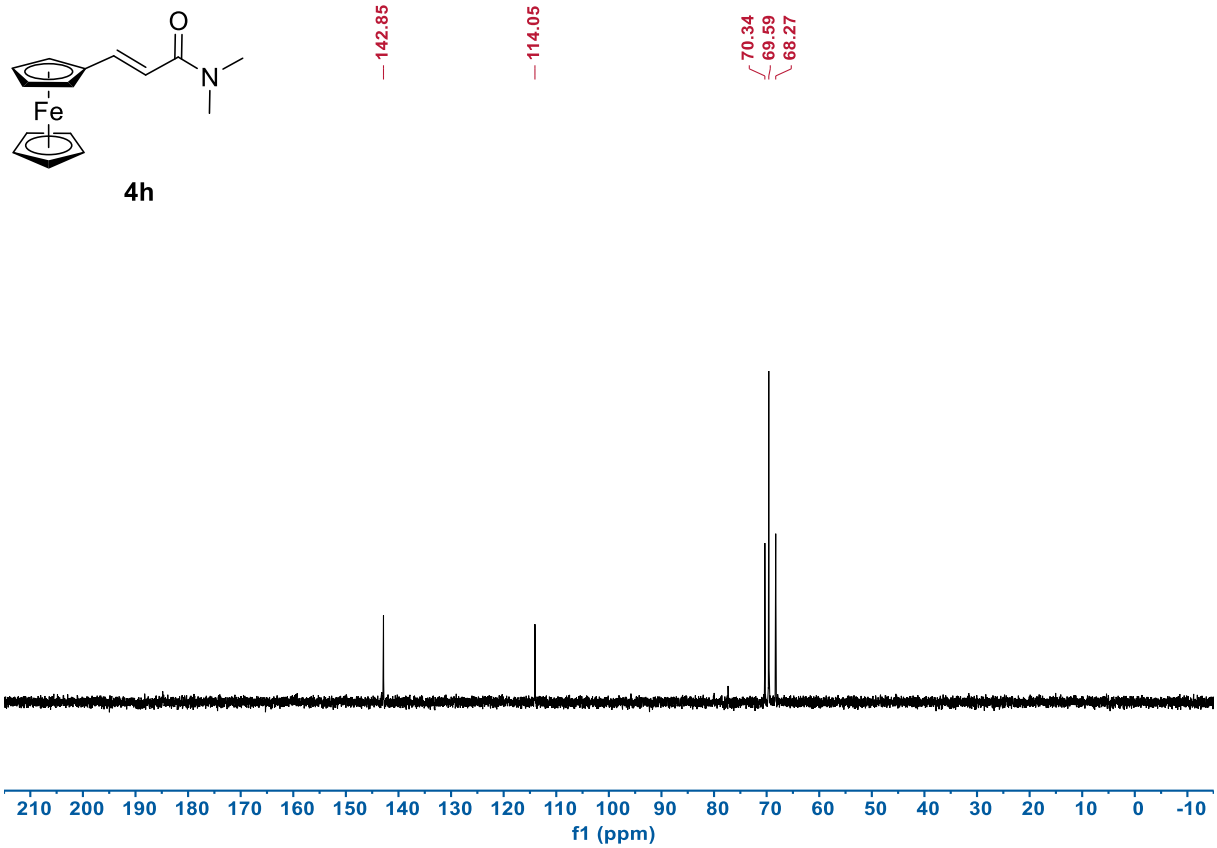
^{13}C NMR (125 MHz, $CDCl_3$)



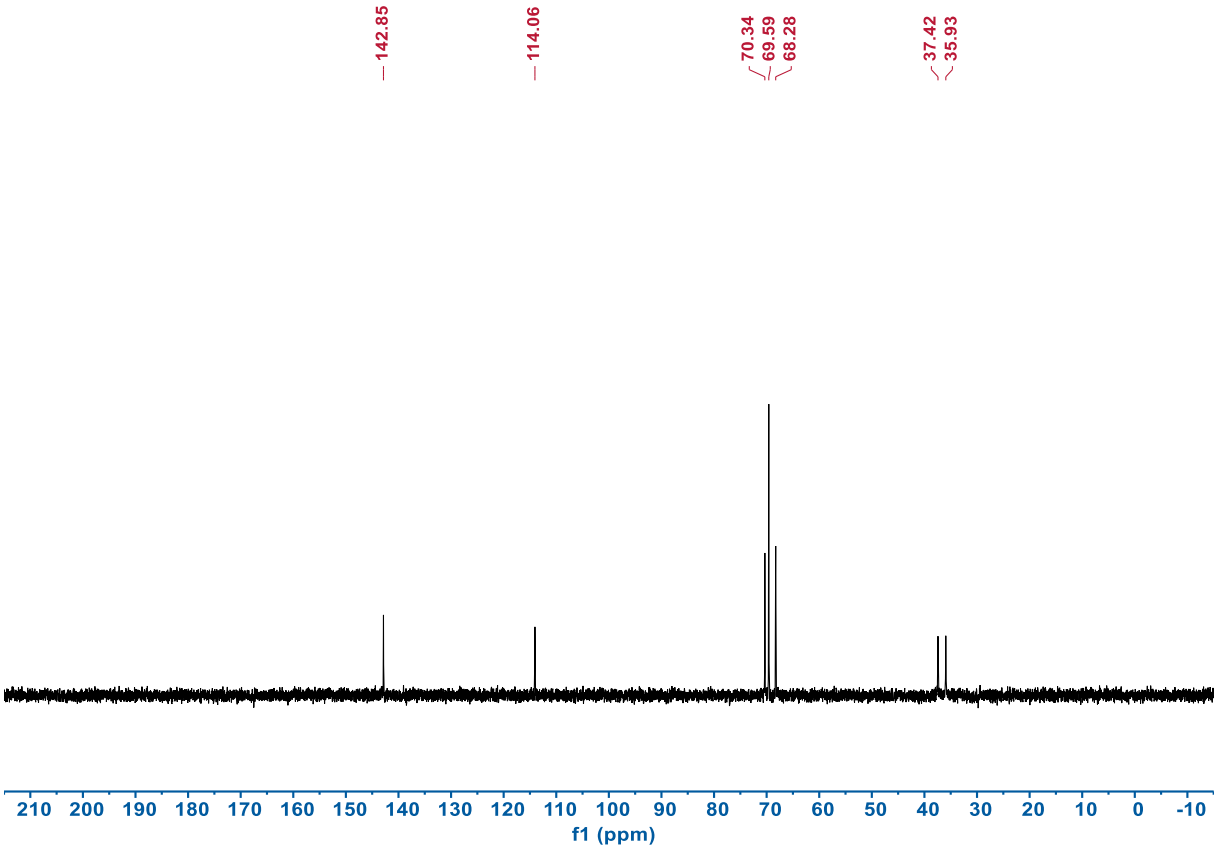
^{1}H NMR (500 MHz, $CDCl_3$)



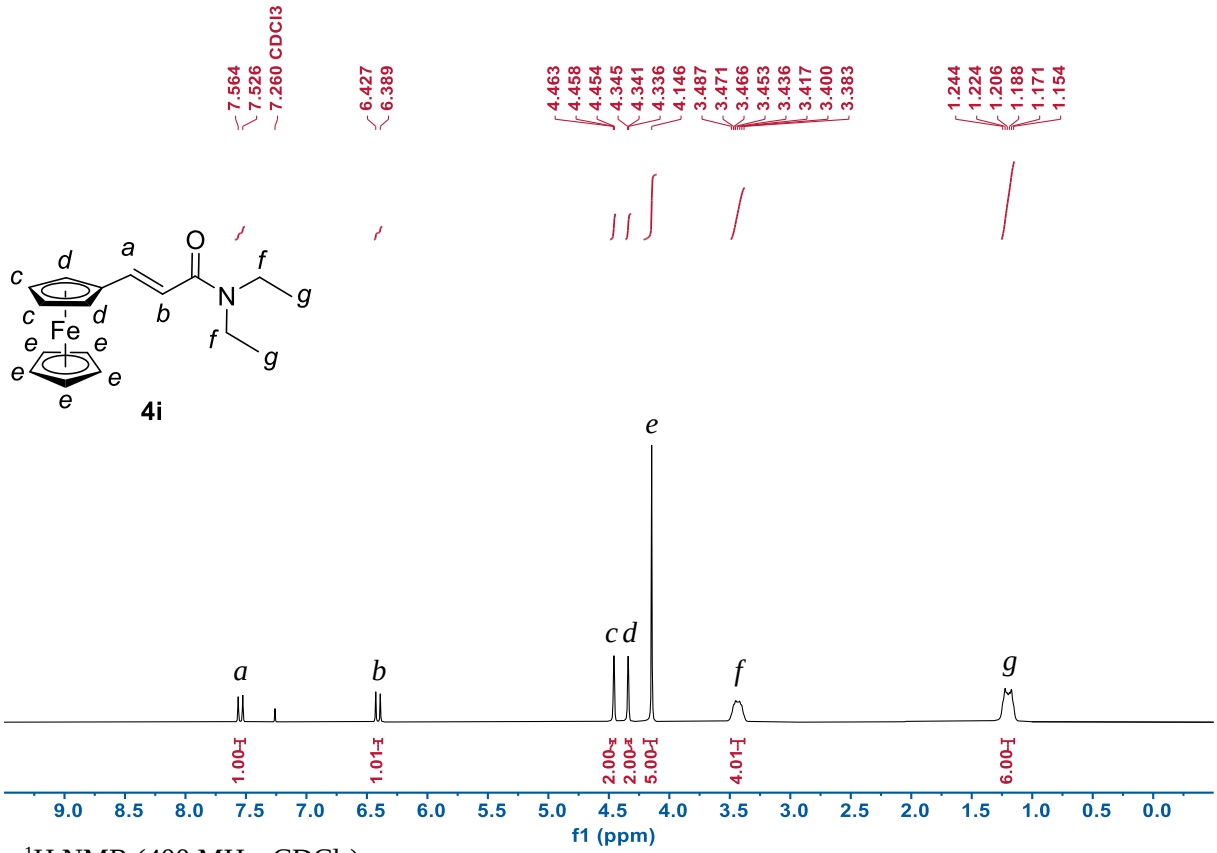
^{13}C NMR (100 MHz, $CDCl_3$)



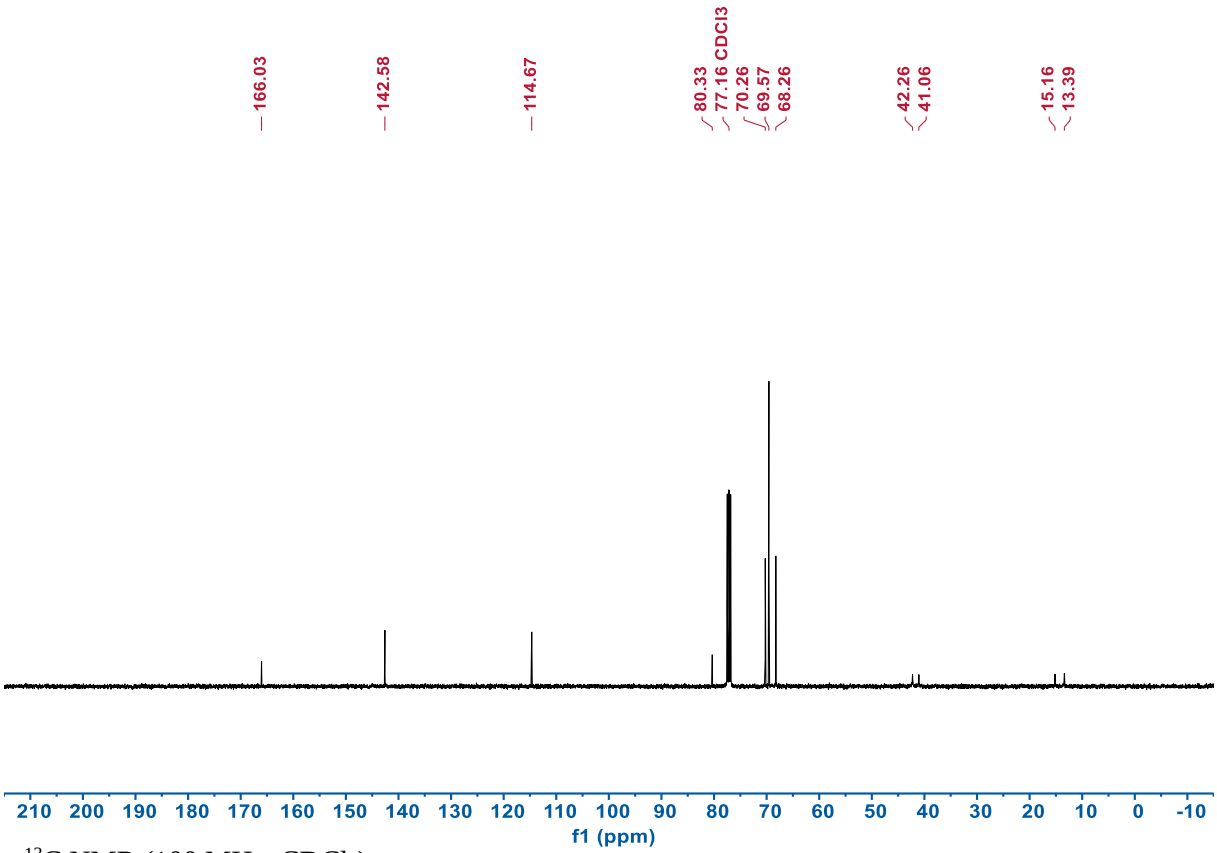
^{13}C DEPT-90 NMR (100 MHz, $CDCl_3$)



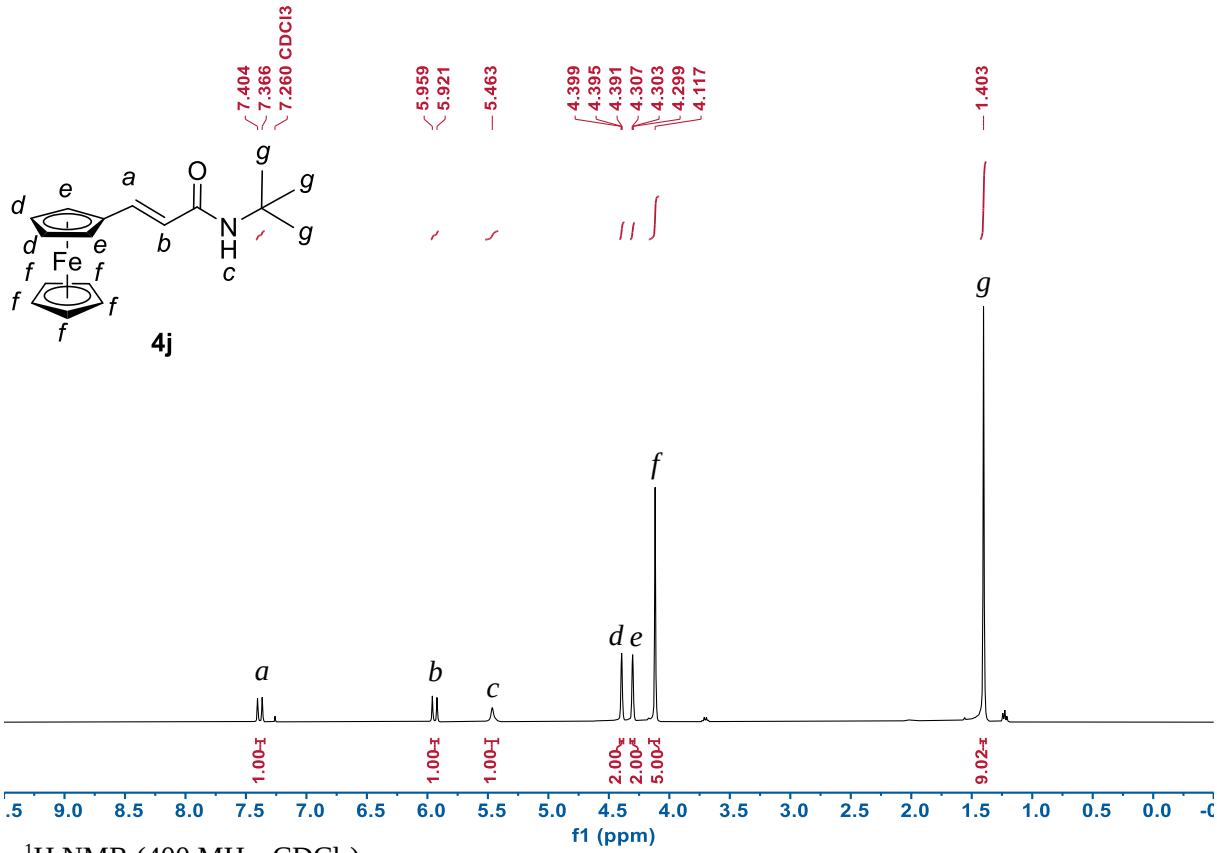
^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



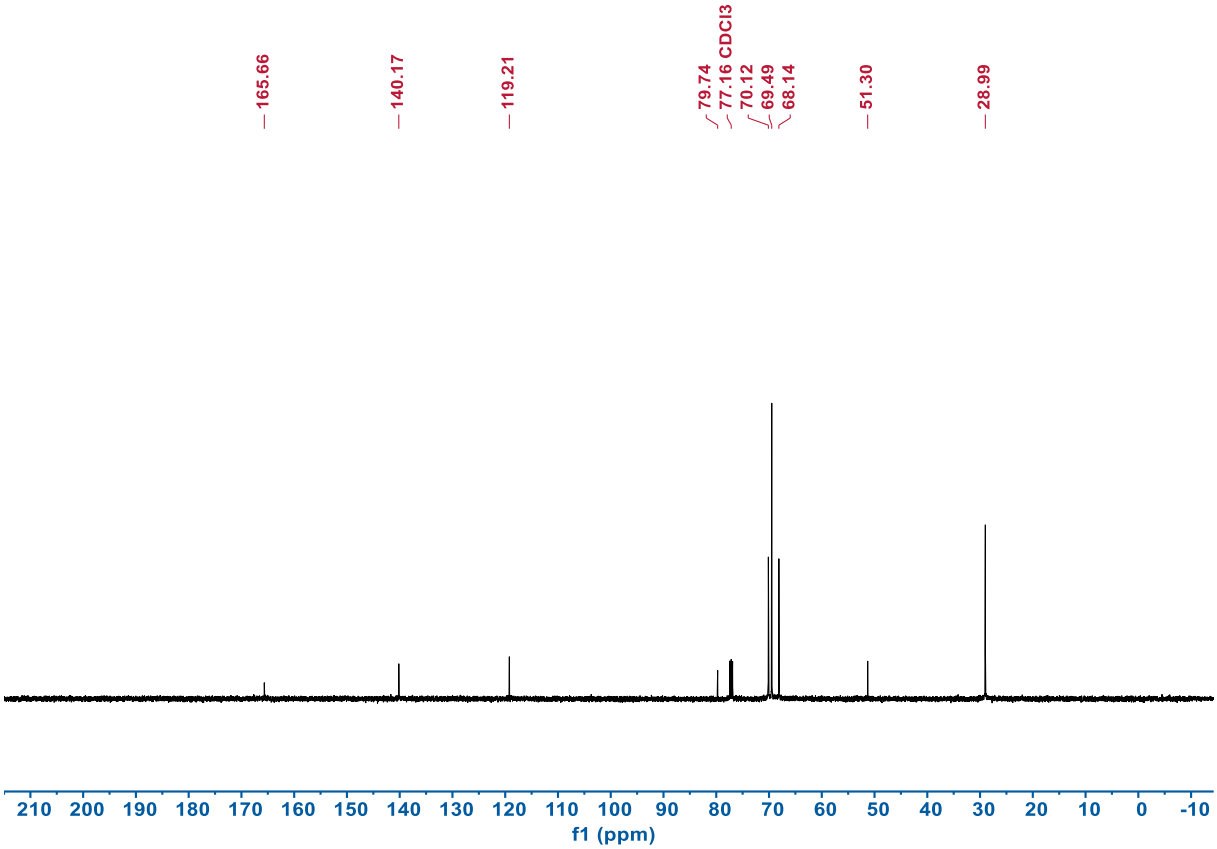
^{1}H NMR (400 MHz, $CDCl_3$)



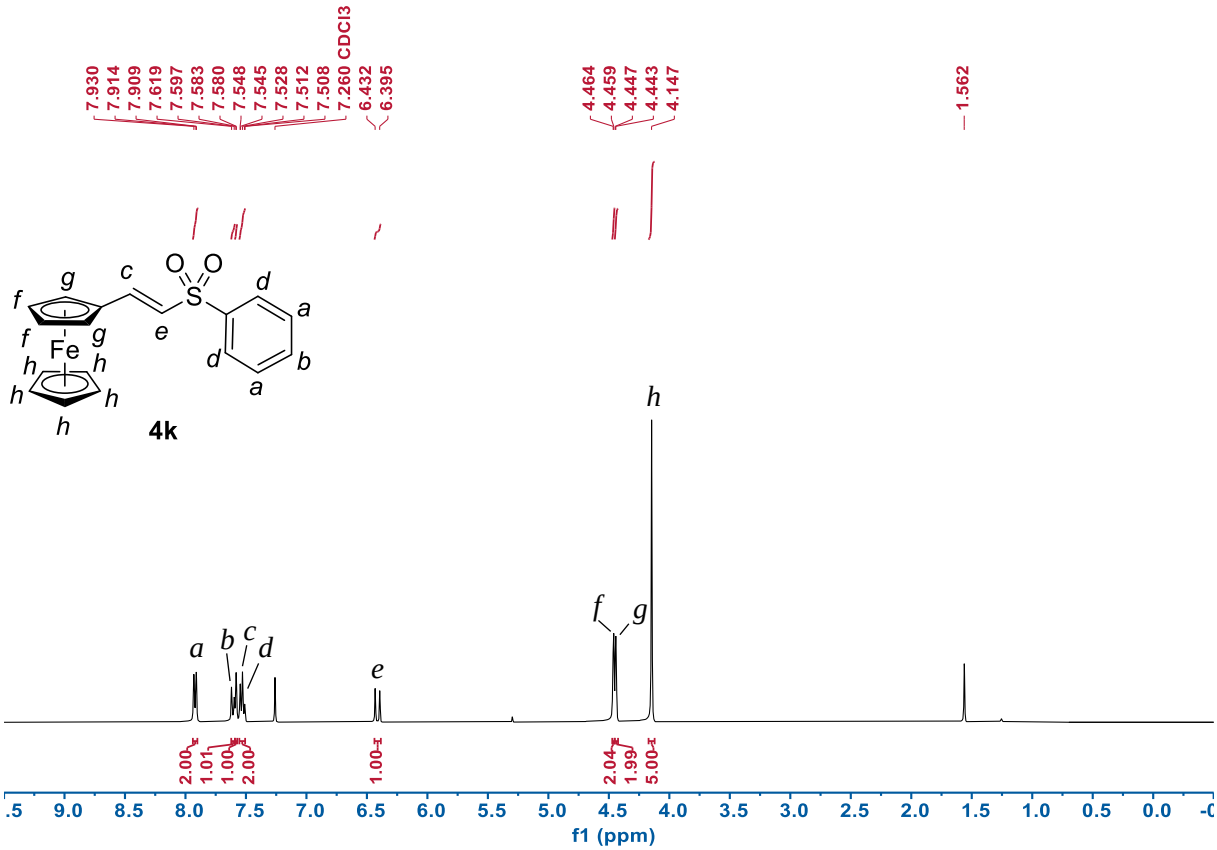
^{13}C NMR (100 MHz, $CDCl_3$)



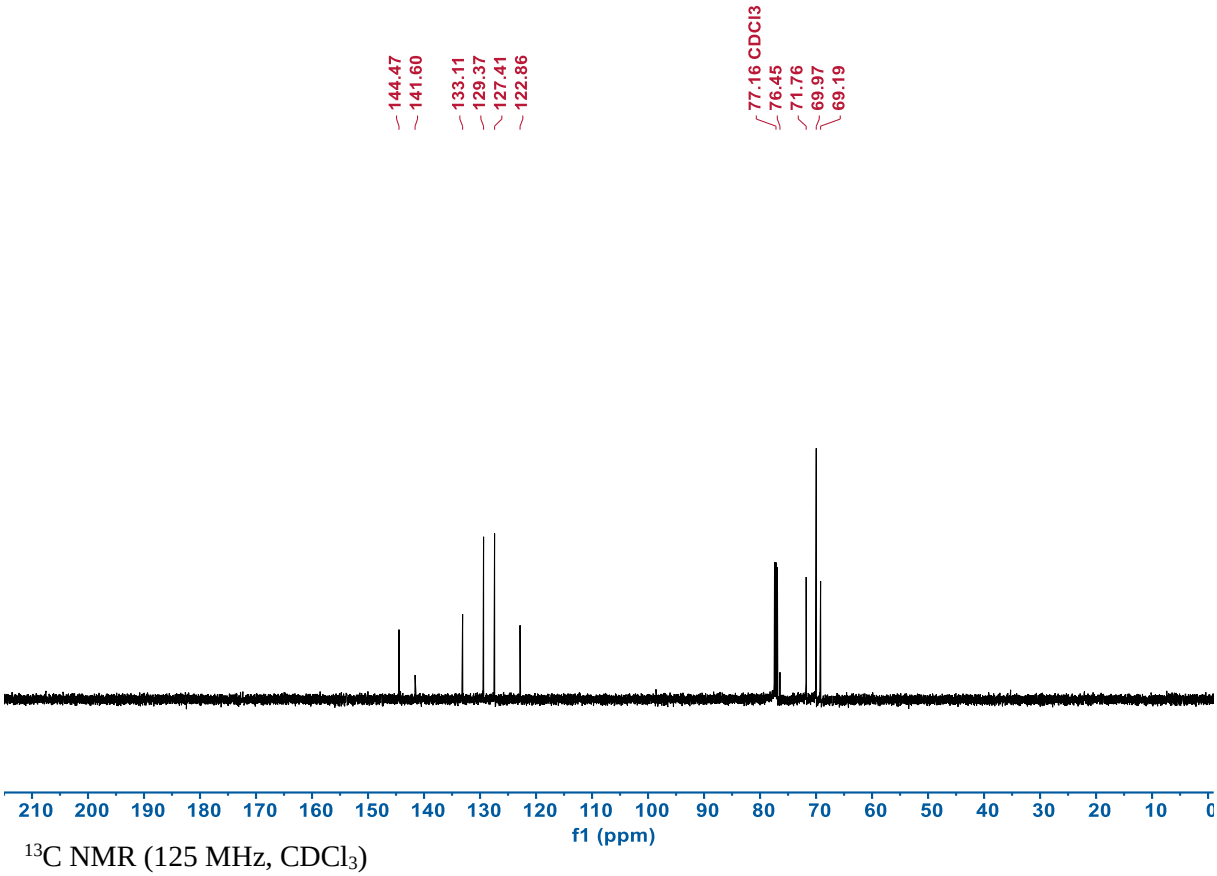
^{1}H NMR (400 MHz, $CDCl_3$)



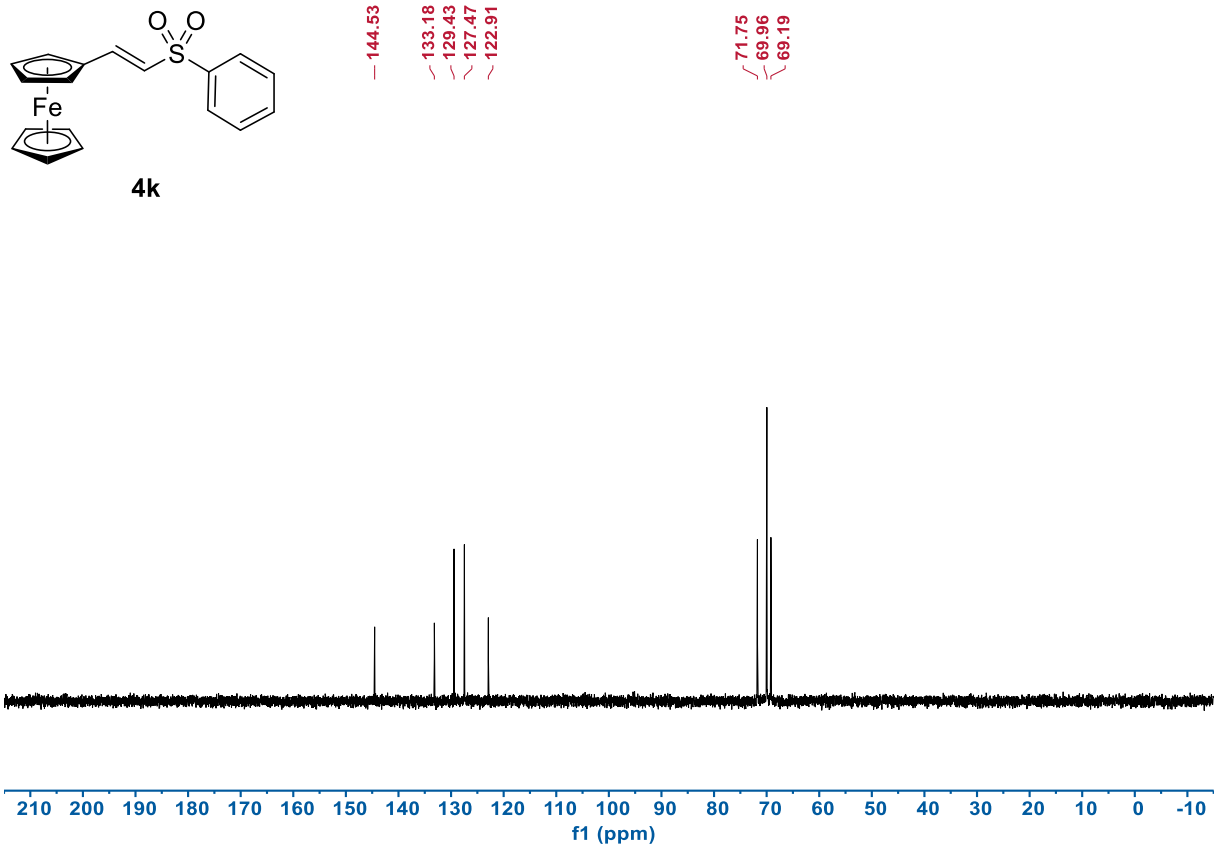
^{13}C NMR (100 MHz, $CDCl_3$)



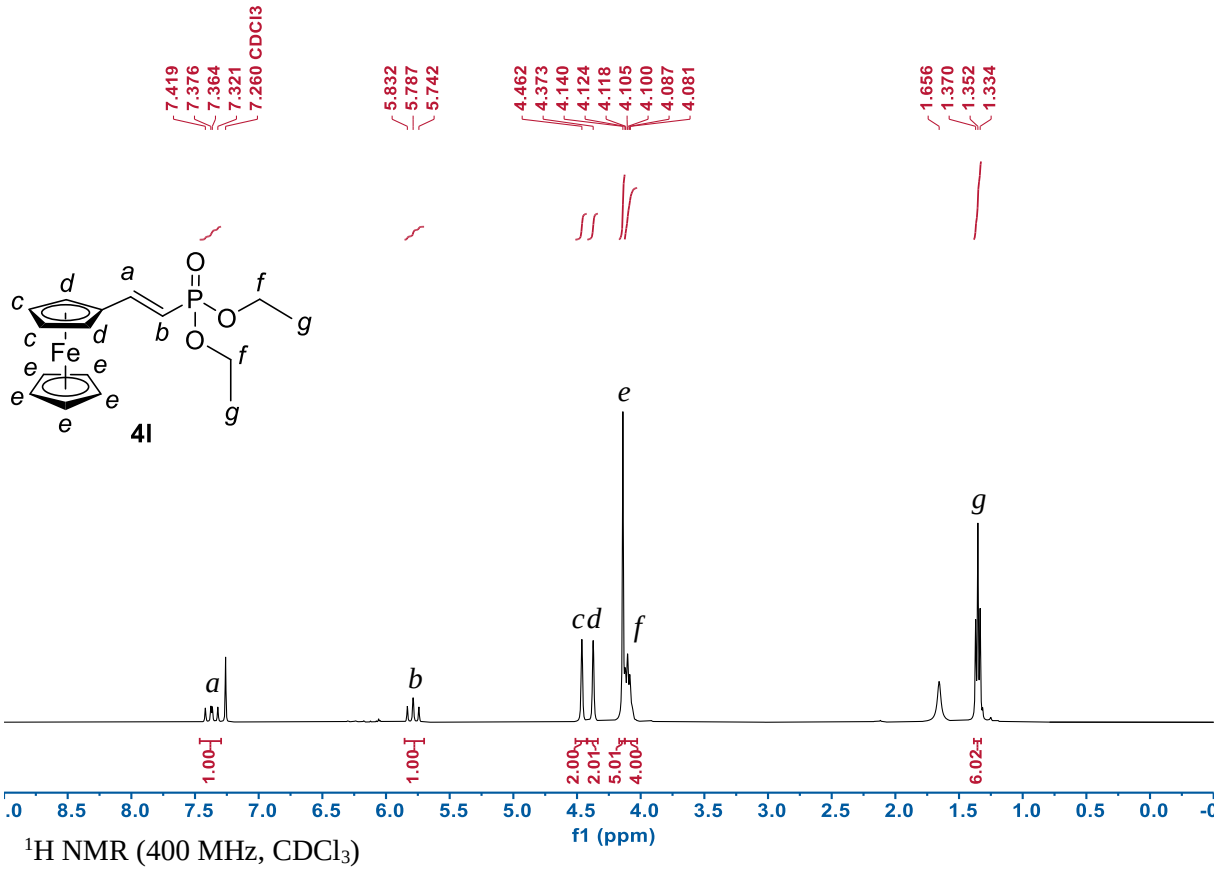
^{1}H NMR (400 MHz, $CDCl_3$)



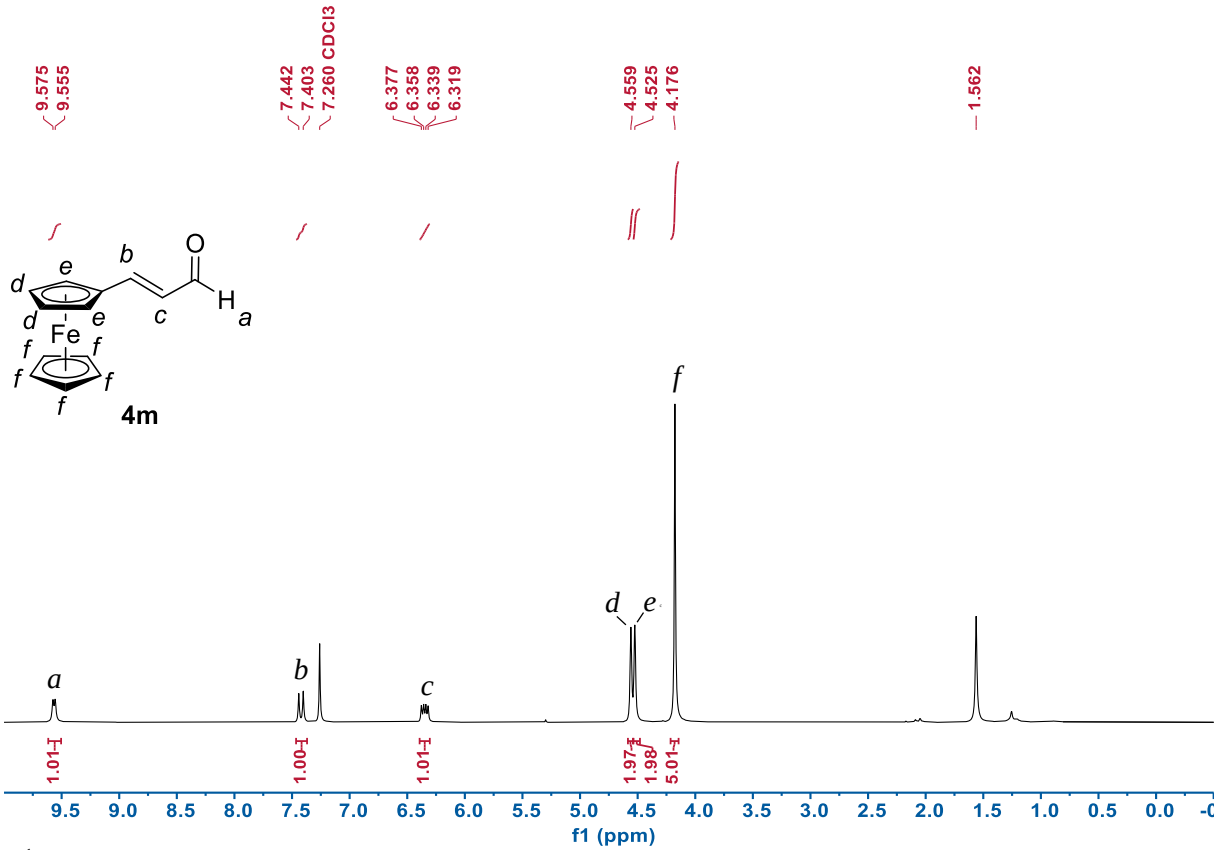
^{13}C NMR (125 MHz, $CDCl_3$)



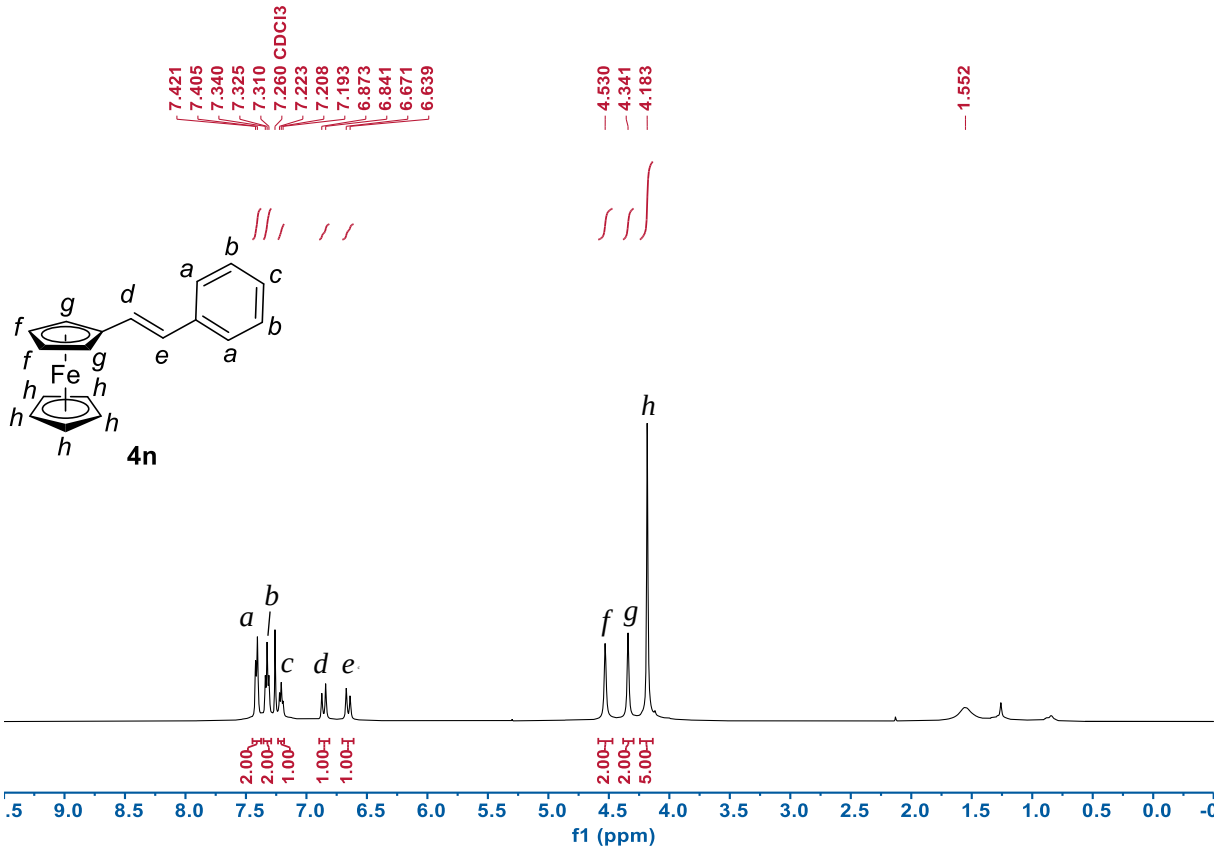
^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



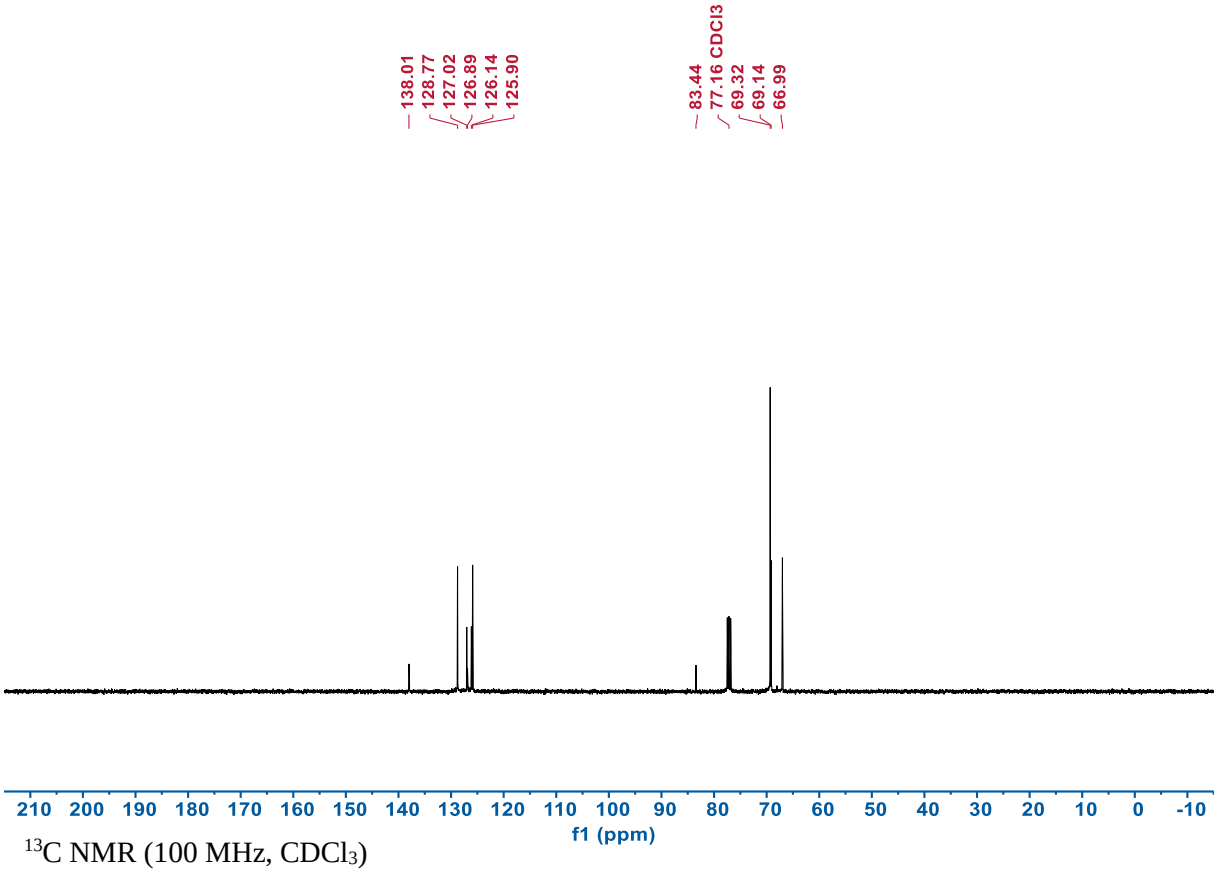
^{1}H NMR (400 MHz, $CDCl_3$)



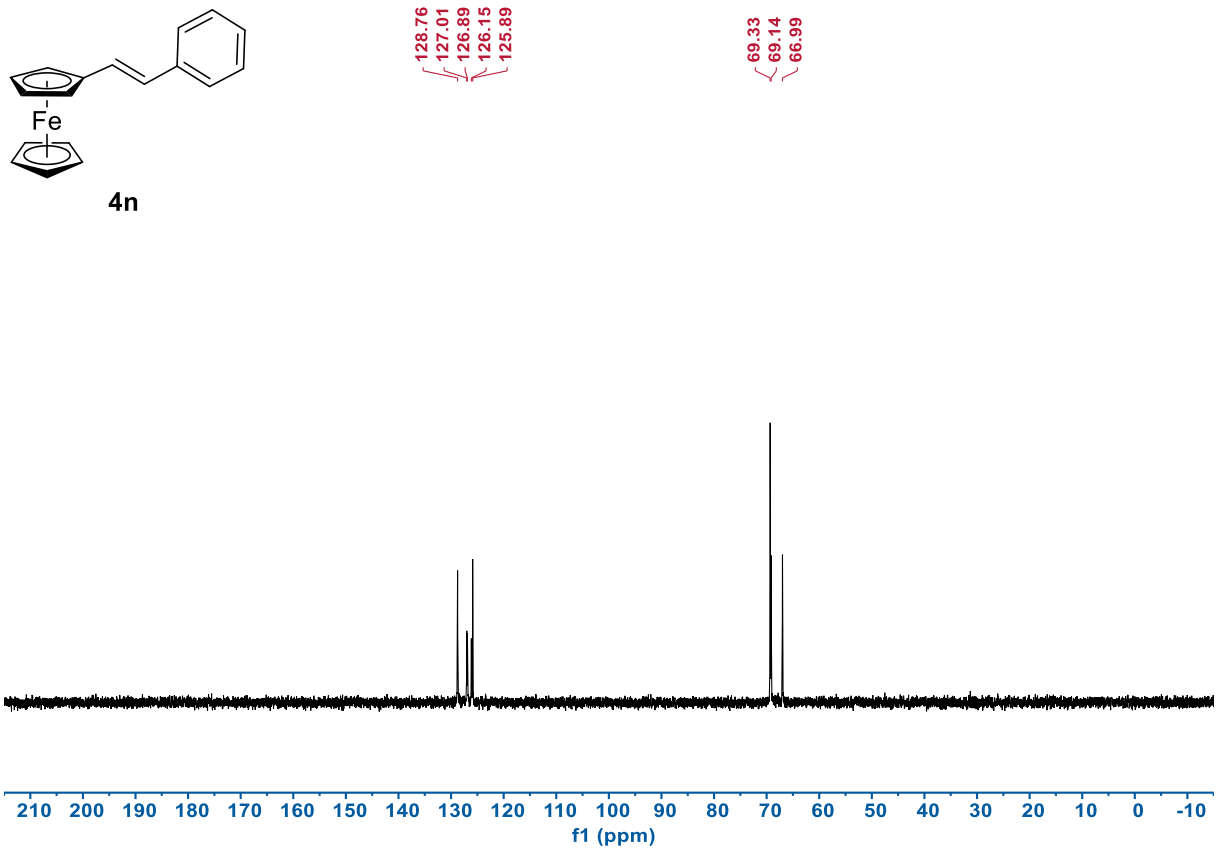
^{1}H NMR (400 MHz, $CDCl_3$)



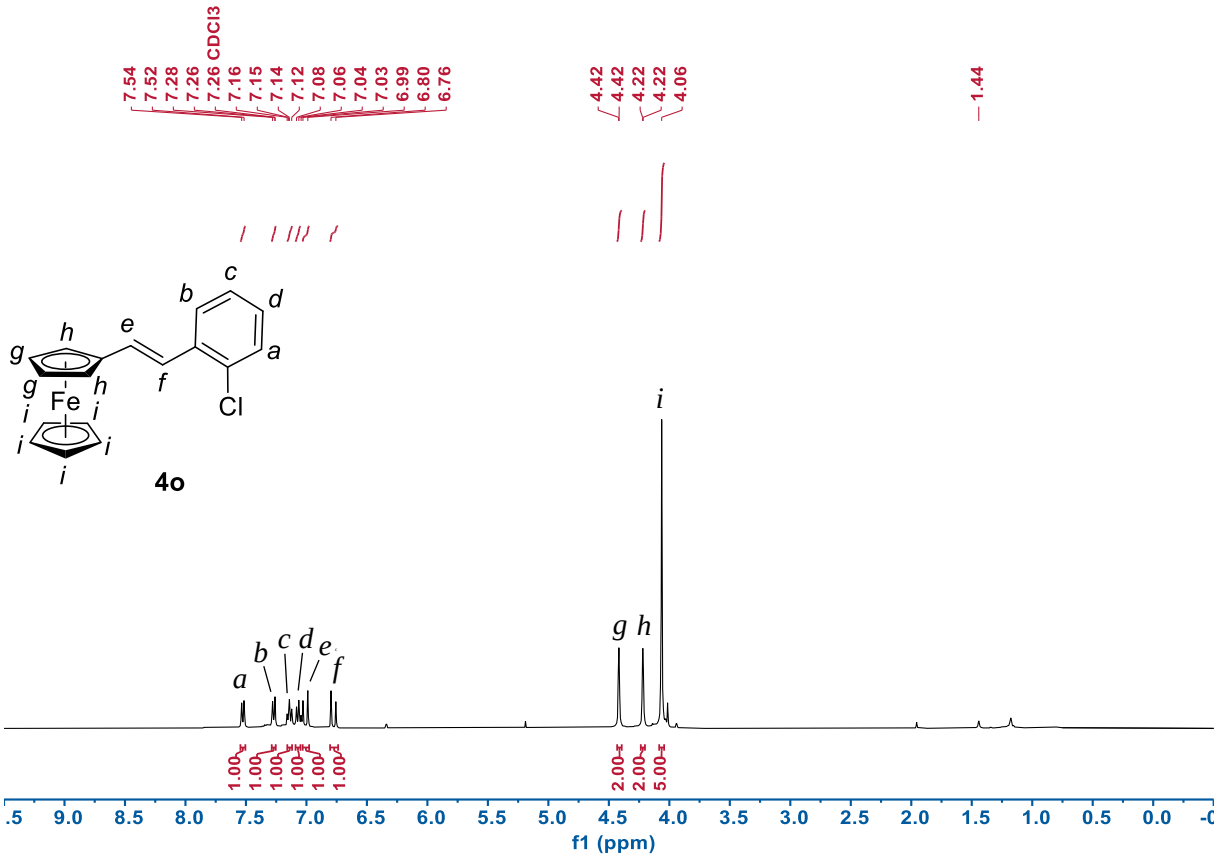
^{1}H NMR (400 MHz, $CDCl_3$)



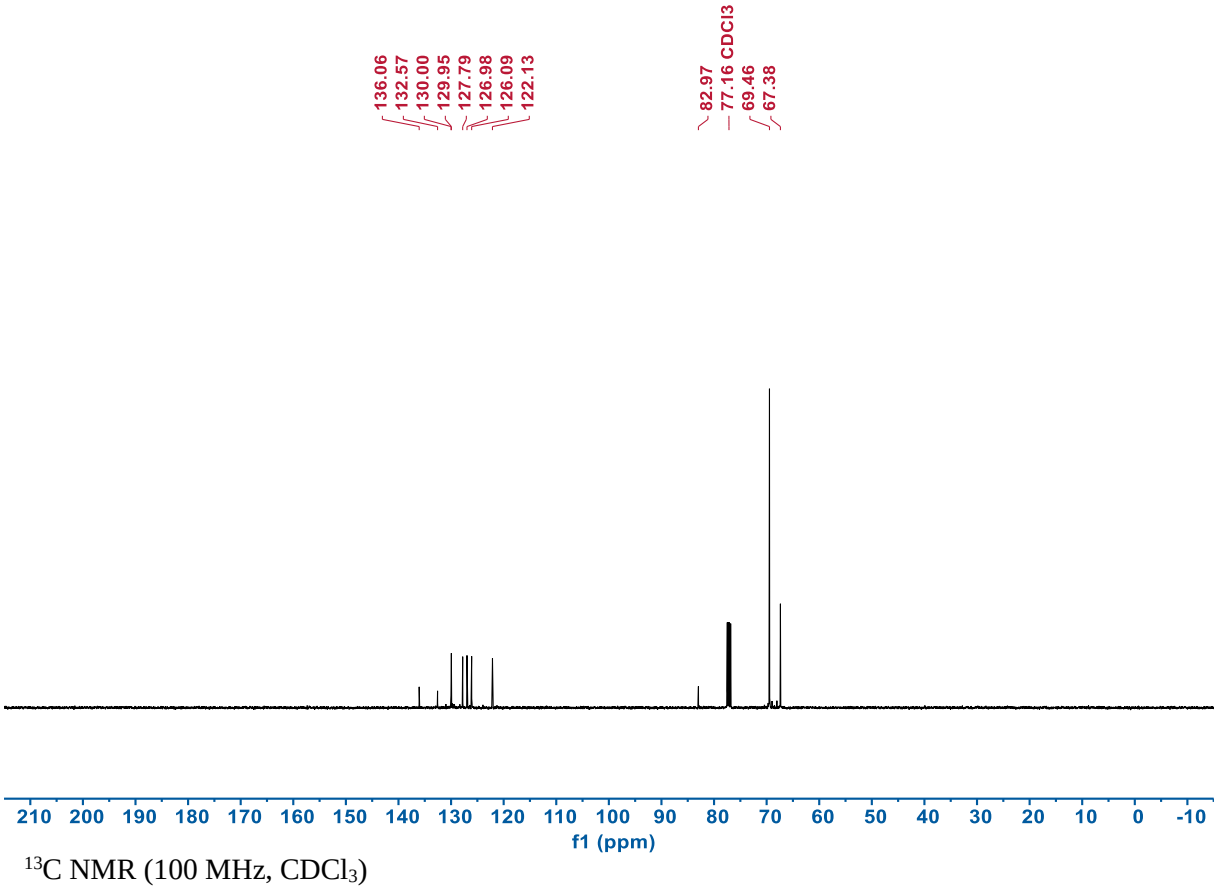
^{13}C NMR (100 MHz, $CDCl_3$)



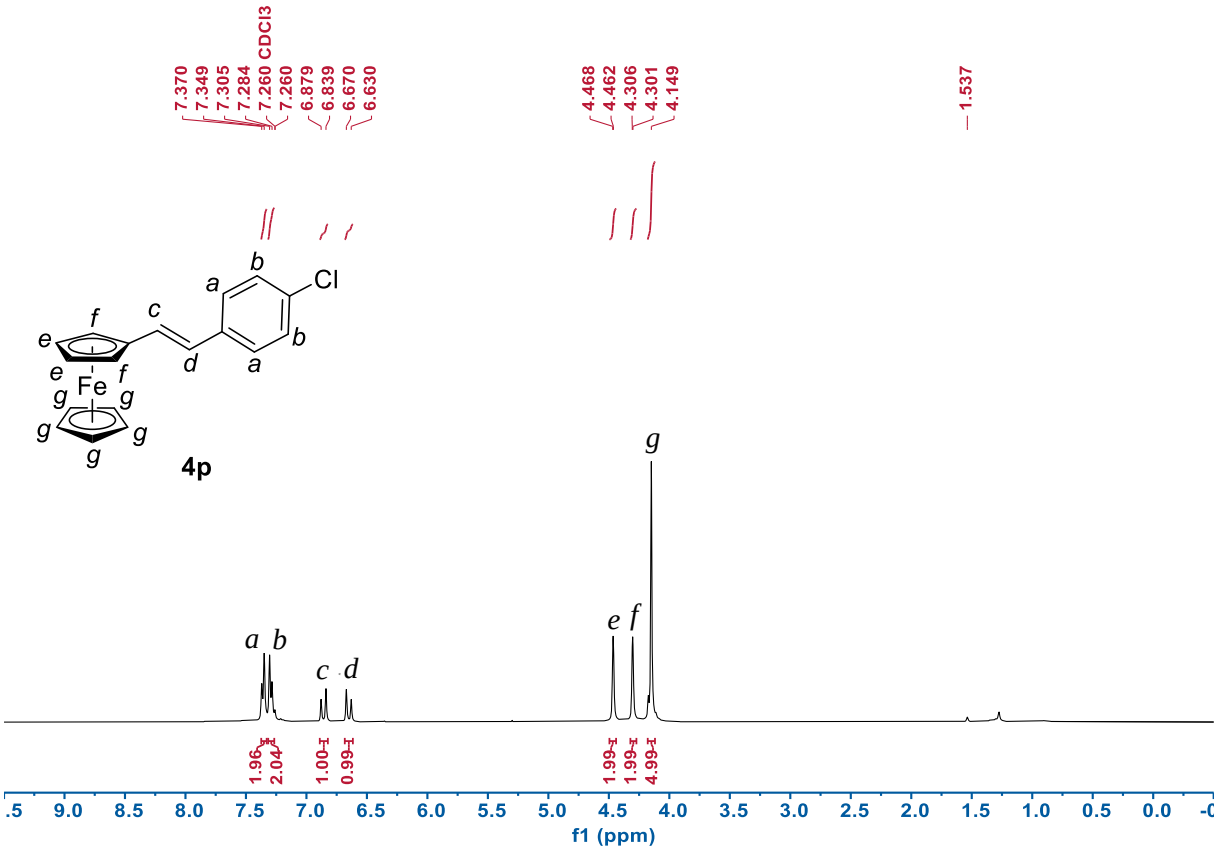
^{13}C DEPT-135 NMR (100 MHz, $CDCl_3$)



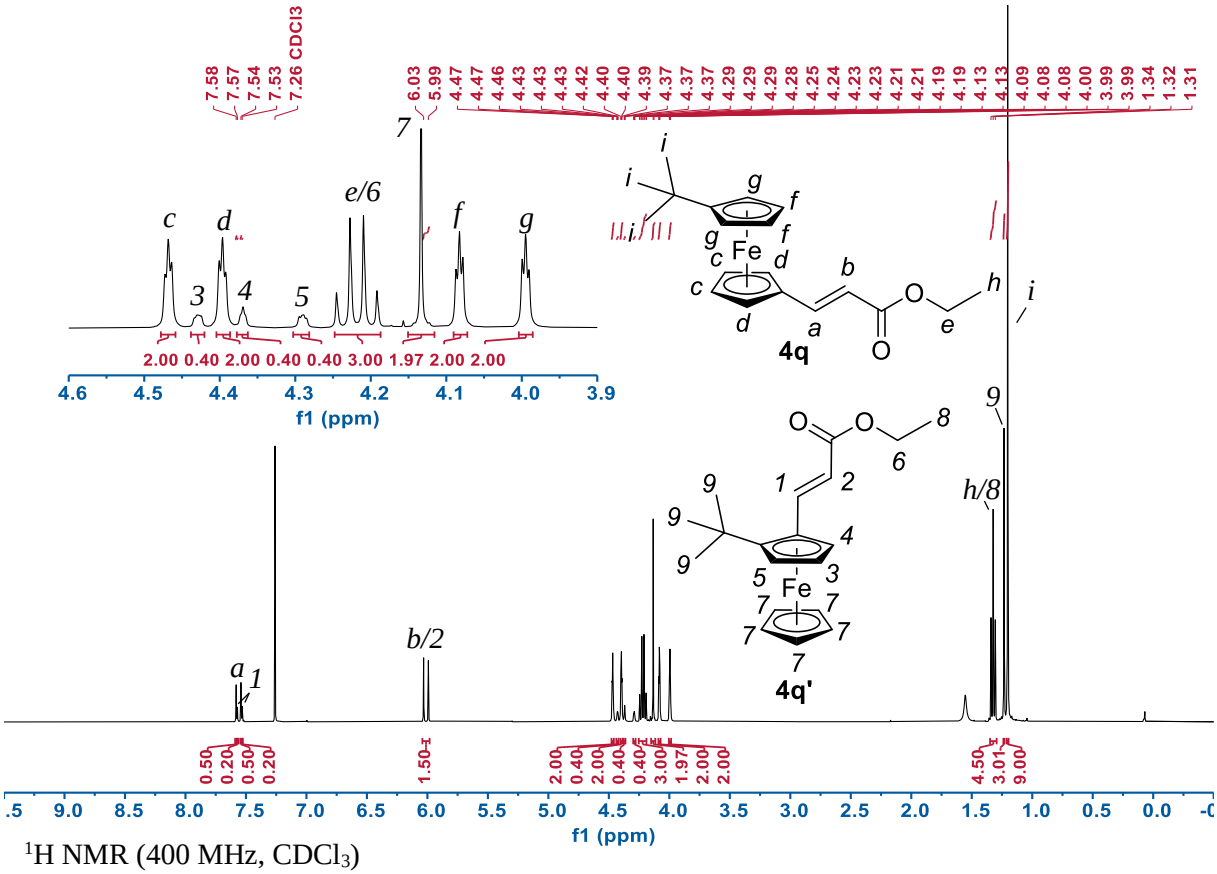
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)