Supplementary Information for

Redox-responsive catalysis: fine tuning of chemoselectivity in the intramolecular reaction of diazo compounds catalysed by ferrocene-functionalised dirhodium(II) complexes

Illia Ruzhylo,[a] Sandrine Vincendeau,[a] Philippe Dauban [b] Eric Manoury,[a] Rinaldo Poli,[a],[c] and Agnès Labande [a]*

[a] I. Ruzhylo, S. Vincendeau, Dr. E. Manoury, Pr R. Poli, Dr. A. Labande
LCC-CNRS, Université de Toulouse, CNRS, INPT, 205 route de Narbonne, 31077 Toulouse, France
E-mail: agnes.labande@lcc-toulouse.fr

[b] Dr. Philippe Dauban
Université Paris-Saclay, CNRS, Institut de Chimie des Substances Naturelles, UPR 2301, 91198 Gif-sur-Yvette, France.

[c] Pr R. Poli
Institut Universitaire de France, 1, rue Descartes, 75231 Paris, France.

General considerations

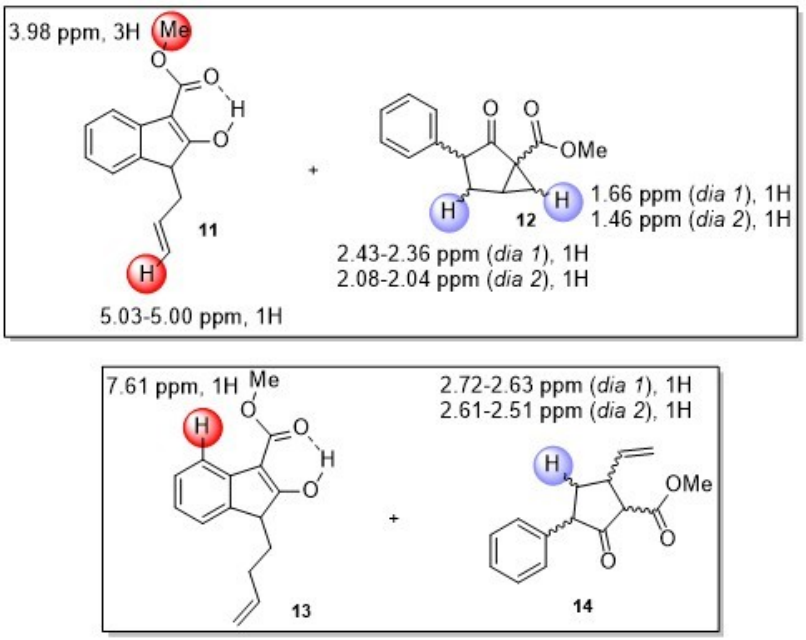
All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for all syntheses were either dried by standard methods and distilled under argon before use, or purified on an Innovative PURESOLV Solvent Purification System equipped with 4Å MS columns, unless otherwise stated. Carboxylic acids **0j** [1] and **0k** [2] were prepared according to previously reported procedures. Cp refers to the ring that possesses the CO_2H or CO_2- substituent, and Cp' to the other ring.

All catalytic tests were carried out twice to ensure the reproducibility of the results. In the ^1H NMR data given in this supplementary information, the duplicates of each reaction are noted as "a" and "b". 1D- and 2D-NMR spectra were recorded on Bruker Avance300 and Avance400 spectrometers. Chemical shifts (δ) for all nuclei are given in ppm. For ^1H and ^{13}C, the residual peak of deuterated solvents was used as reference. Peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). The proton and carbon assignments were performed by COSY, HSQC and ^1H-^{13}C HMBC experiments.

Electrospray (ES) mass spectra were recorded at the Université Paul Sabatier by the Service Commun de Spectrométrie de Masse on a MS/MS API-365 (Perkin Elmer Sciex).

Procedure for Determining Product Ratios

To measure the product ratios, the mixtures obtained were analysed by ^1H NMR. The data was processed using MestReNova software. The ratios were measured by integration of the characteristic NMR peaks resulting from the indicated hydrogens below:



Synthesis of heteroleptic dirhodium(II) complexes 1j and 1k

To a suspension of $[Rh_2(OAc)_3(tfa)]$ (1 equiv.) and carboxylic acid (1.1 equiv.) in trifluoroethanol (0.02 M solution of dirhodium precursor), *N*,*N*-diisopropylethylamine (2 equiv.) was added and the resulting mixture was stirred at 50°C for 2 h, at which time TLC analysis showed full consumption of $[Rh_2(OAc)_3(tfa)]$. Then, a spatula of Celite® was added, the solvent was removed *in vacuo* and the solid residue was purified by column chromatography (flash silica gel, hexane/AcOEt = 1:1 to 1:2).

Heteroleptic dirhodium(II) complex 1j

Starting from 50 mg of $[Rh_2(OAc)_3(tfa)]$ (0.1 mmol) and 28.6 mg of carboxylic acid **0j** (0.11 mmol), complex **1j** was obtained as a green solid (48.8 mg, 76 % yield). R_f (hexane/AcOEt = 1:2) = 0.33.

HRMS (ESI, pos.) m/z: $[M+H]^+$ calcd for $C_{19}H_{23}FeO_8Rh_2$ 640.8853, found: 640.8854; $[M+NH_4]^+$ calcd for $C_{19}H_{26}FeO_8Rh_2N$ 657.9118, found: 657.9129.

^{1}H NMR (400 MHz, acetone-d_6) δ 4.07 (s, 5H, 5 x C*H* Cp'), 3.97 (s, 4H, 4 x C*H* Cp), 2.44 (t, *J* = 7.0 Hz, 2H, $C_5H_4CH_2$), 2.29 (t, *J* = 7.0 Hz, 2H, CH_2COOH), 1.77 (s, 3H, *trans*- CH_3COO) 1.76 (s, 6H, 2 x *cis*-CH_3COO).

^{13}C NMR (101 MHz, acetone-d_6) δ 191.78 (CH_2COO), 189.57 (3 x CH_3CO_2), 88.34 (C_{quat} Cp, from HMBC), 68.37 (5 x *C*H Cp'), 67.94 (2 x *C*H Cp), 67.00 (2 x *C*H Cp), 37.97 (CH_2COO), 25.14 ($C_5H_4CH_2$), 22.46 (2 x *cis*-CH_3CO_2), 22.36 (*trans*-CH_3CO_2).

Heteroleptic dirhodium(II) complex 1k

Starting from 50 mg of $[Rh_2(OAc)_3(tfa)]$ and 30.2 mg of carboxylic acid **0k** (0.11 mmol), complex **1k** was obtained as a green solid (55.3 mg, 85 % yield). R_f (hexane/AcOEt = 1:2) = 0.42.

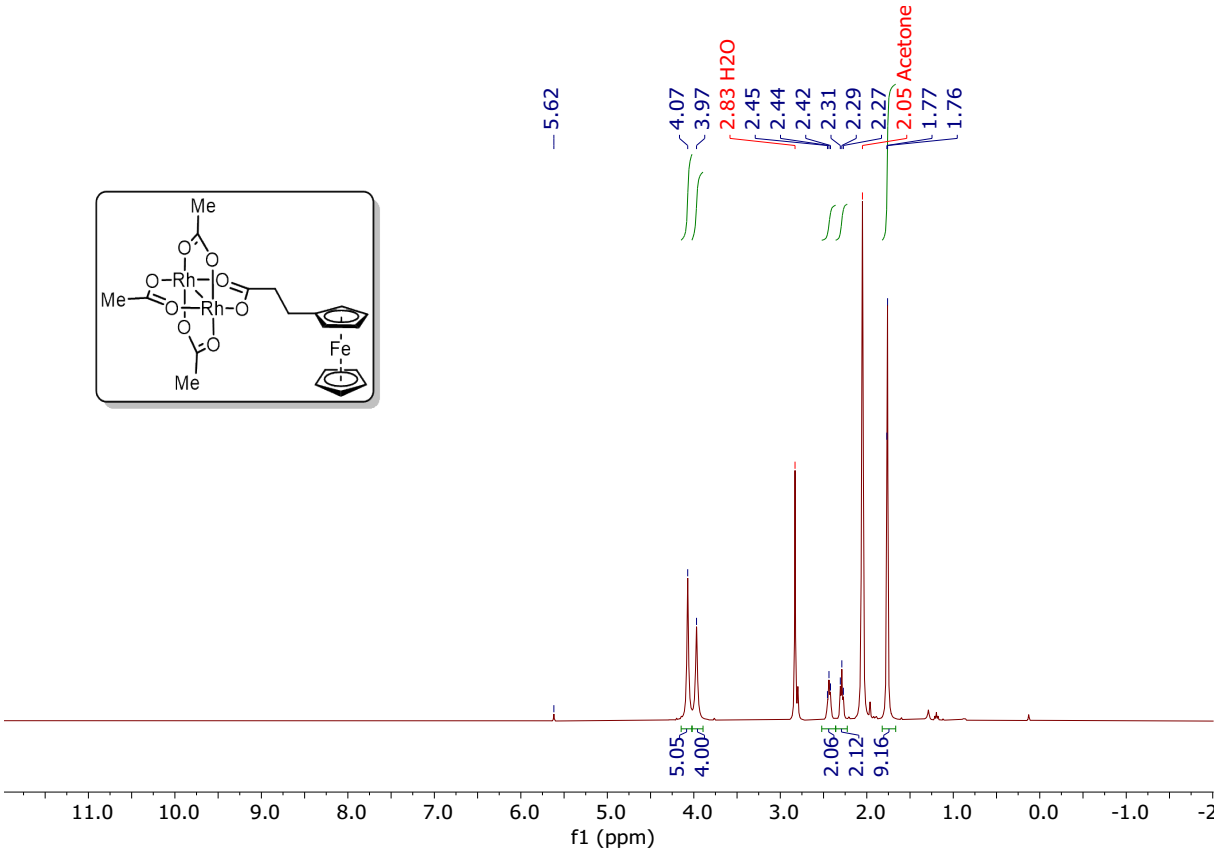
HRMS (ESI, pos.) m/z: $[M+H]^+$ calcd for $C_{20}H_{25}FeO_8Rh_2$ 654.9009, found: 654.9000; $[M+NH_4]^+$ calcd for $C_{20}H_{28}FeO_8Rh_2N$ 671.9275, found: 657.9285.

^{1}H NMR (400 MHz, acetone-d_6) δ 4.09 (s, 5H, 5 x C*H* Cp'), 4.01 (s, 4H, 4 x C*H* Cp), 2.10 (m, 4H, $C_5H_4CH_2$ and CH_2COOH), 1.82 (s, 6H, 2 x *cis*-CH_3COO), 1.78 (s, 3H, *trans*- CH_3COO), 1.66 (m, 2H, $CH_2CH_2CH_2$).

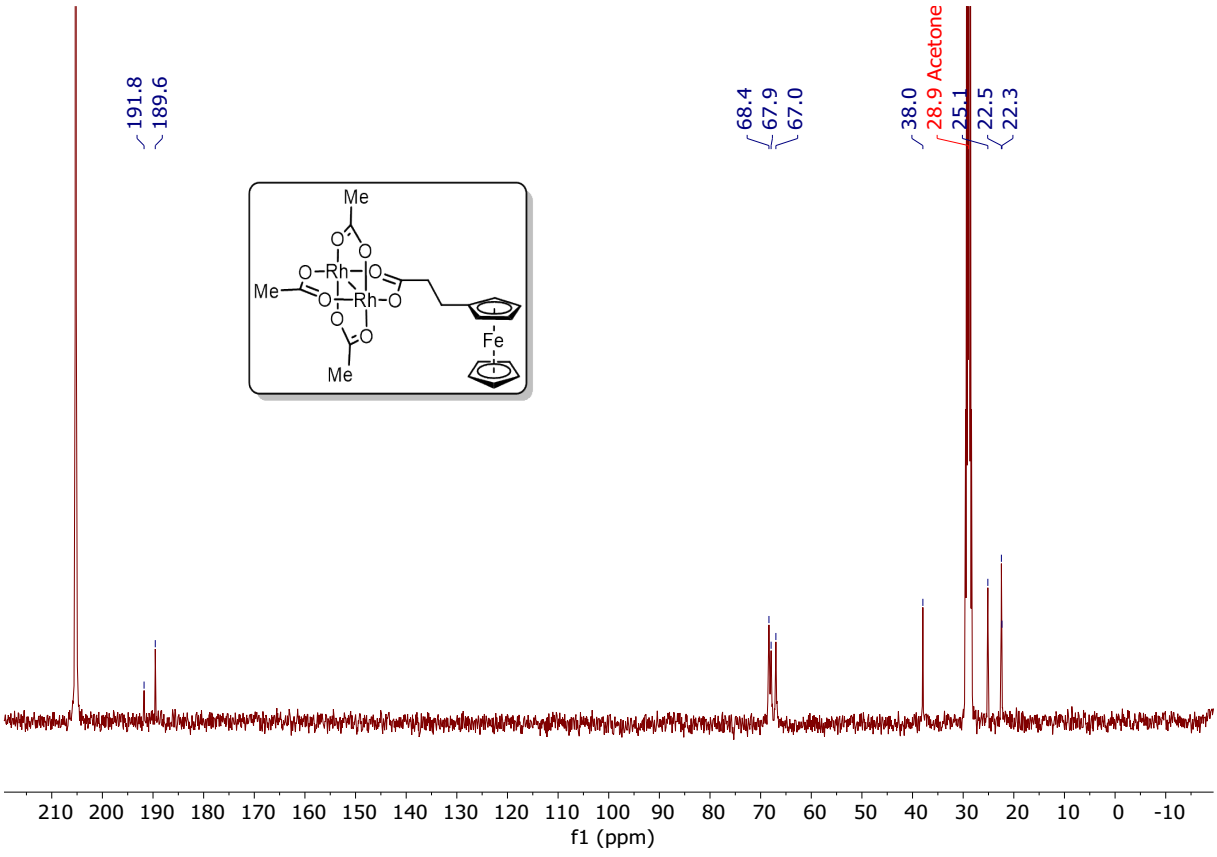
^{13}C NMR (101 MHz, acetone-d_6) δ 193.19 (CH_2COO), 190.43 (3 x CH_3CO_2), 89.34 (C_{quat} Cp), 69.23 (5 x *C*H Cp'), 68.64 (2 x *C*H Cp), 67.74 (2 x *C*H Cp), 37.11 (CH_2COOH), 28.84 ($CH_2CH_2CH_2$), 27.61 ($C_5H_4CH_2$), 23.32 (2 x *cis*-CH_3CO_2), 23.26 (*trans*-CH_3CO_2).

1. O. Galangau, C. Dumas-Verdes, E. Y. Schmidt, B. A. Trofimov and G. Clavier, *Organometallics*, 2011, **30**, 6476-6481.
2. R. Liu, G. Zhou, T. H. Hall, G. J. Clarkson, M. Wills and W. Chen, *Adv. Synth. Catal.*, 2015, **357**, 3453-3457.

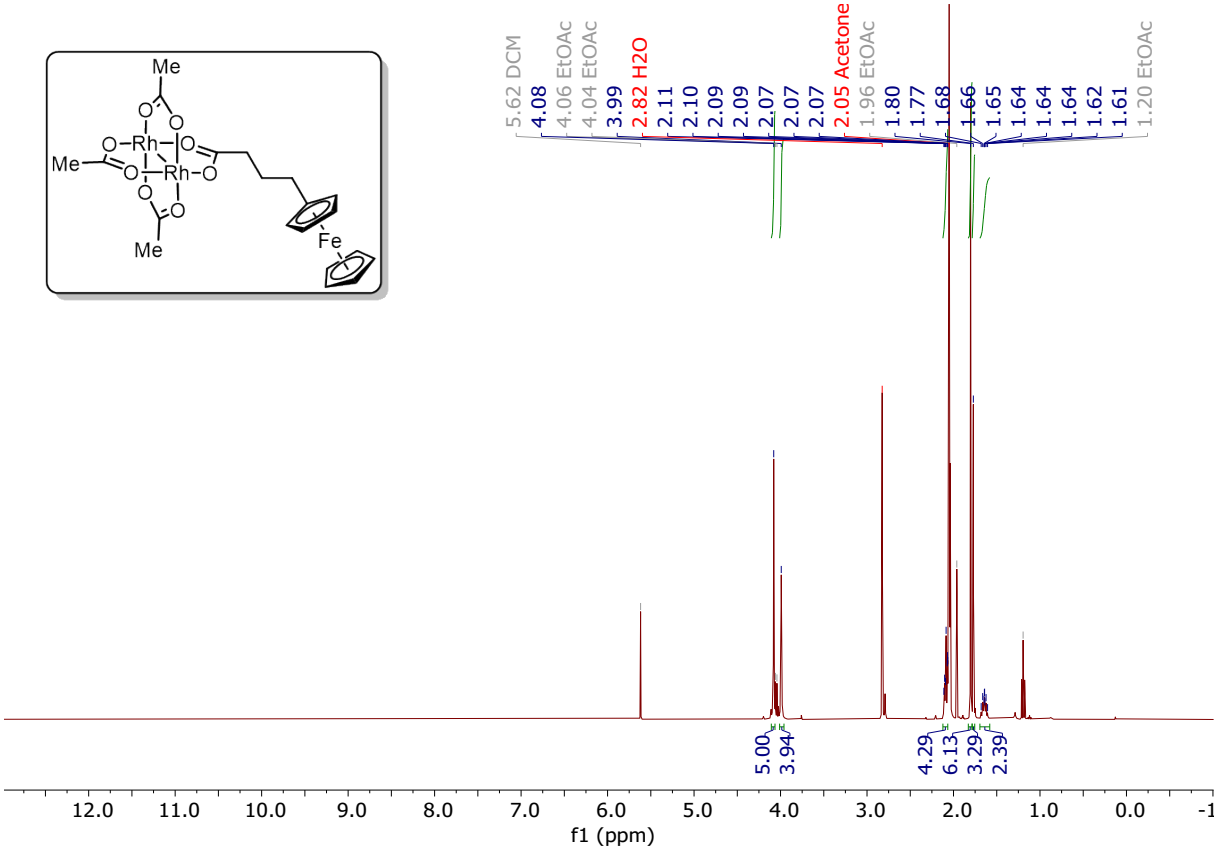
^{1}H NMR spectrum of heteroleptic dirhodium(II) complex 1j (400 MHz, acetone-d_6)



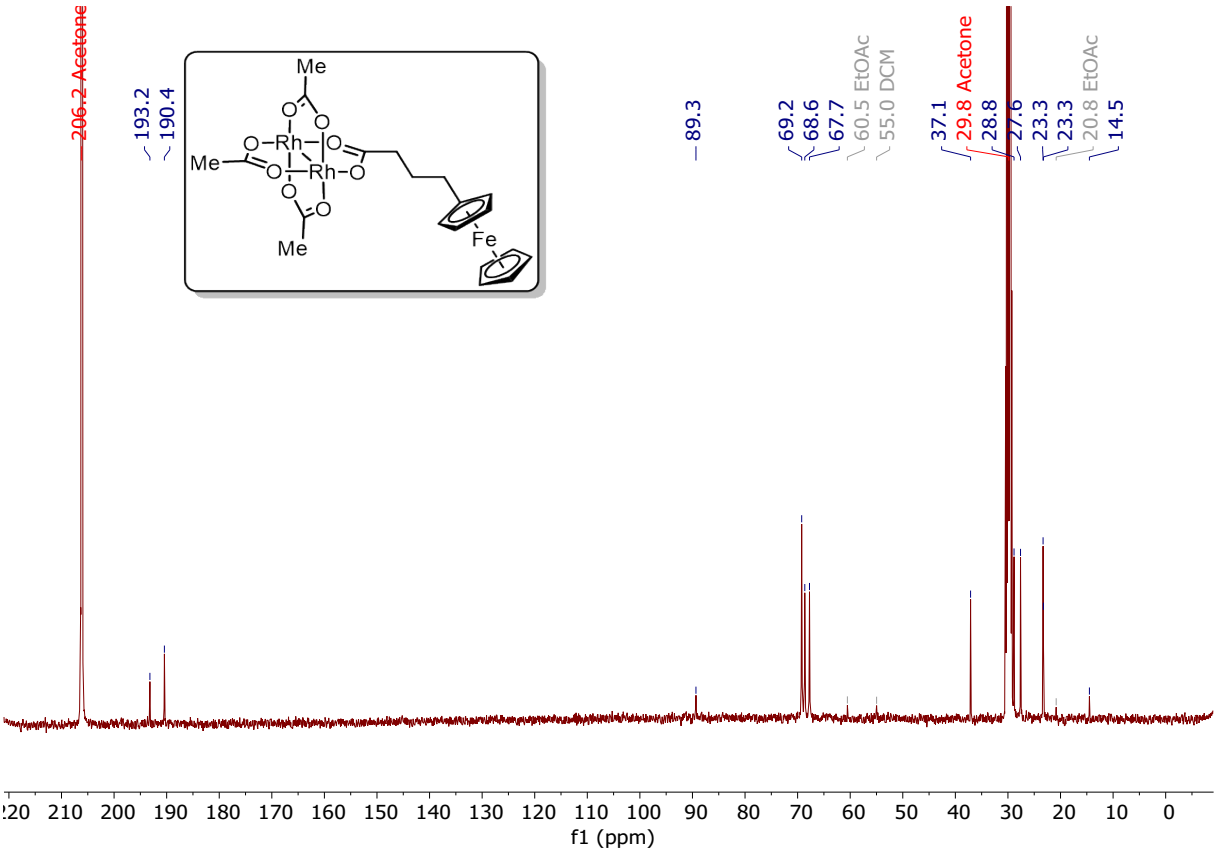
^{13}C NMR spectrum of heteroleptic dirhodium(II) complex 1j (101 MHz, acetone-d_6)



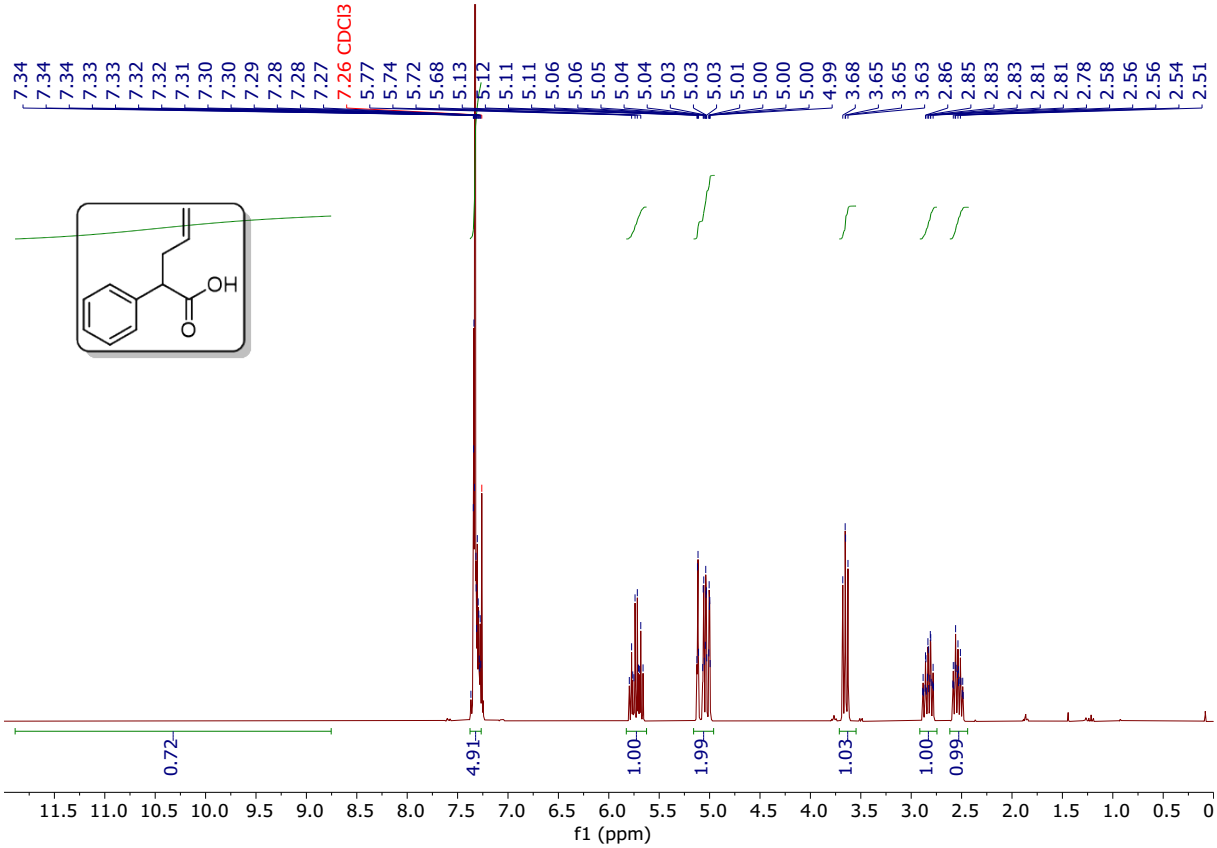
^{1}H NMR spectrum of heteroleptic dirhodium(II) complex 1k (400 MHz, acetone-d_6)



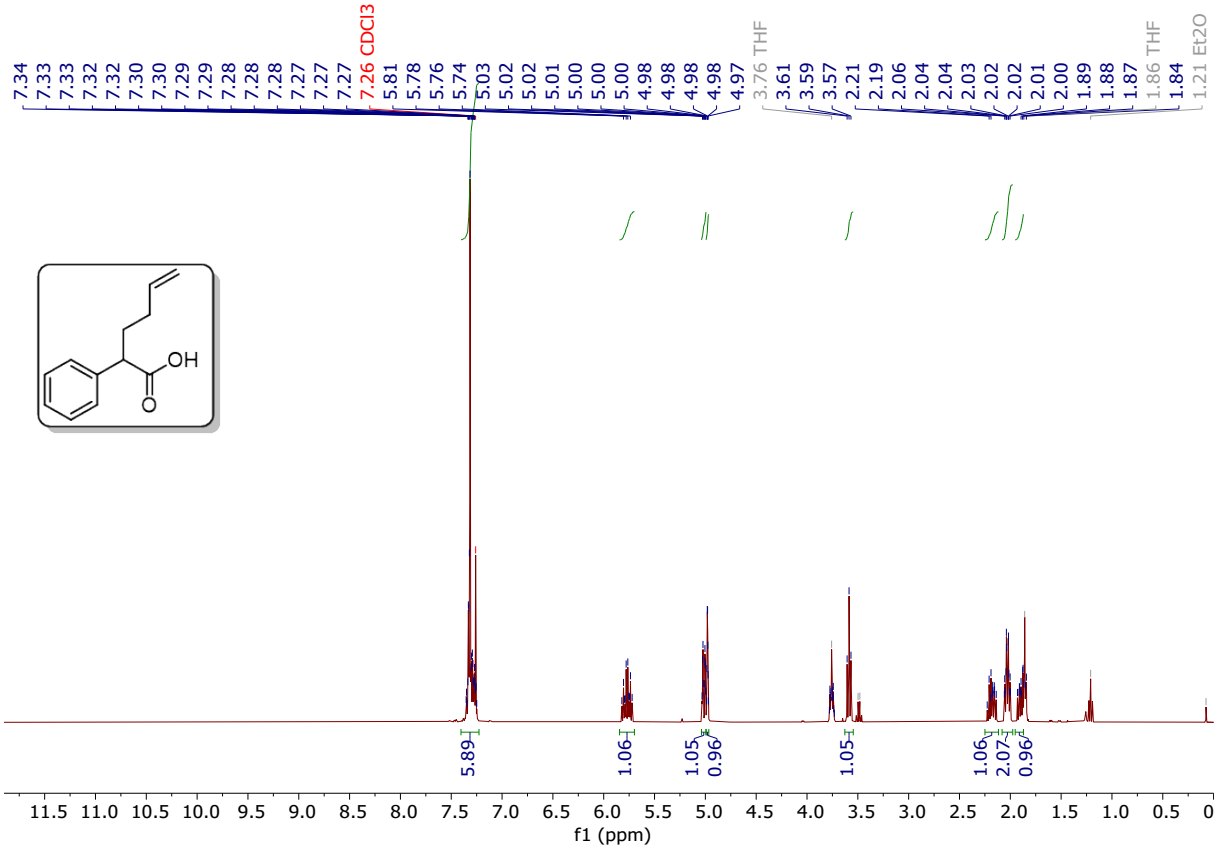
^{13}C NMR spectrum of heteroleptic dirhodium(II) complex 1k (101 MHz, acetone-d_6)



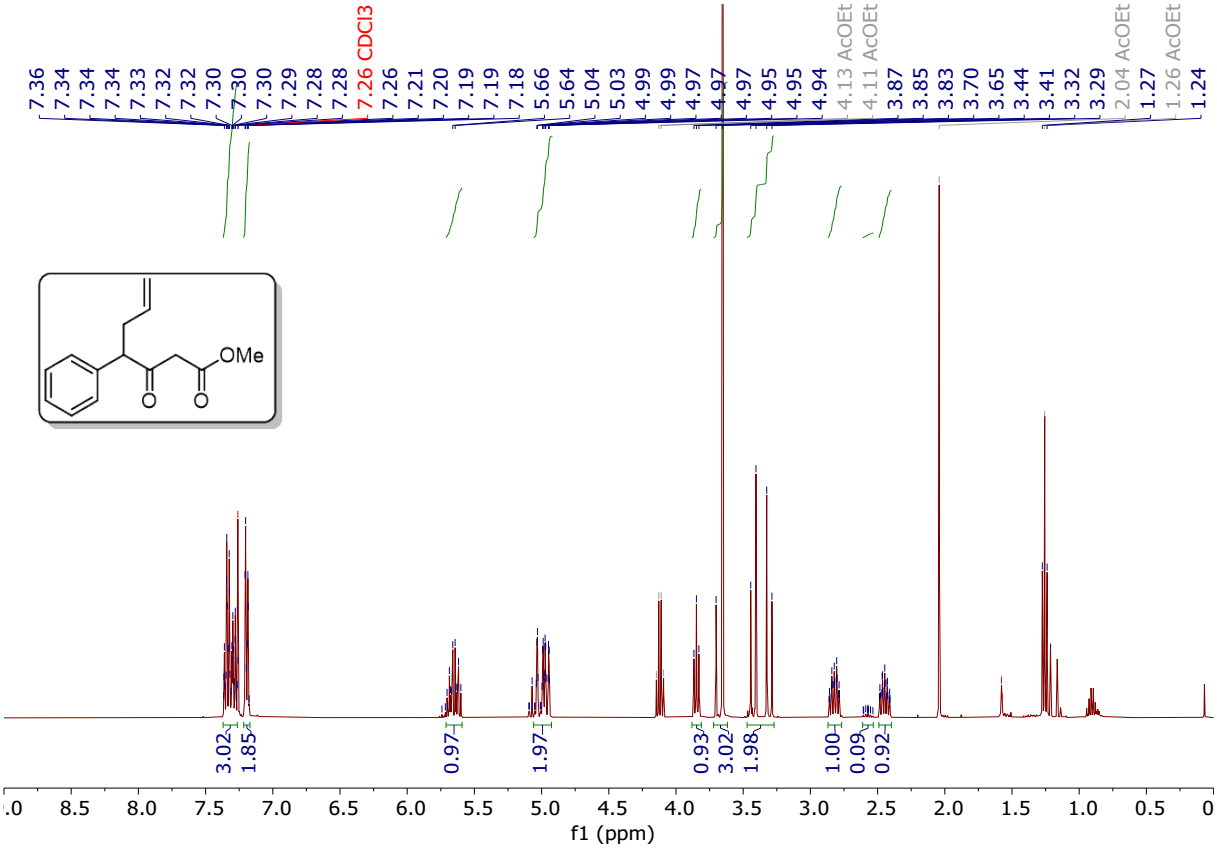
^{1}H NMR spectrum of carboxylic acid 5 (300 MHz, $CDCl_3$)



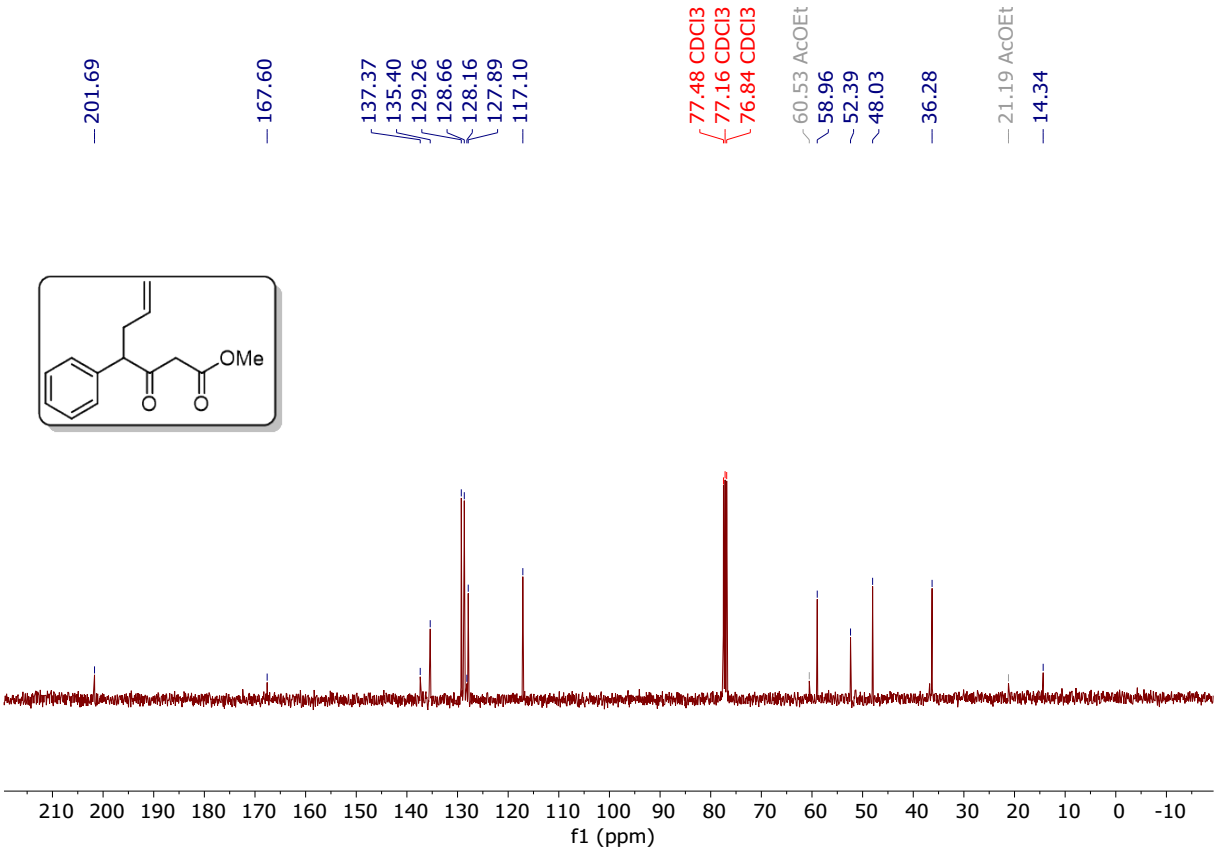
^{1}H NMR spectrum of carboxylic acid 6 (400 MHz, $CDCl_3$)



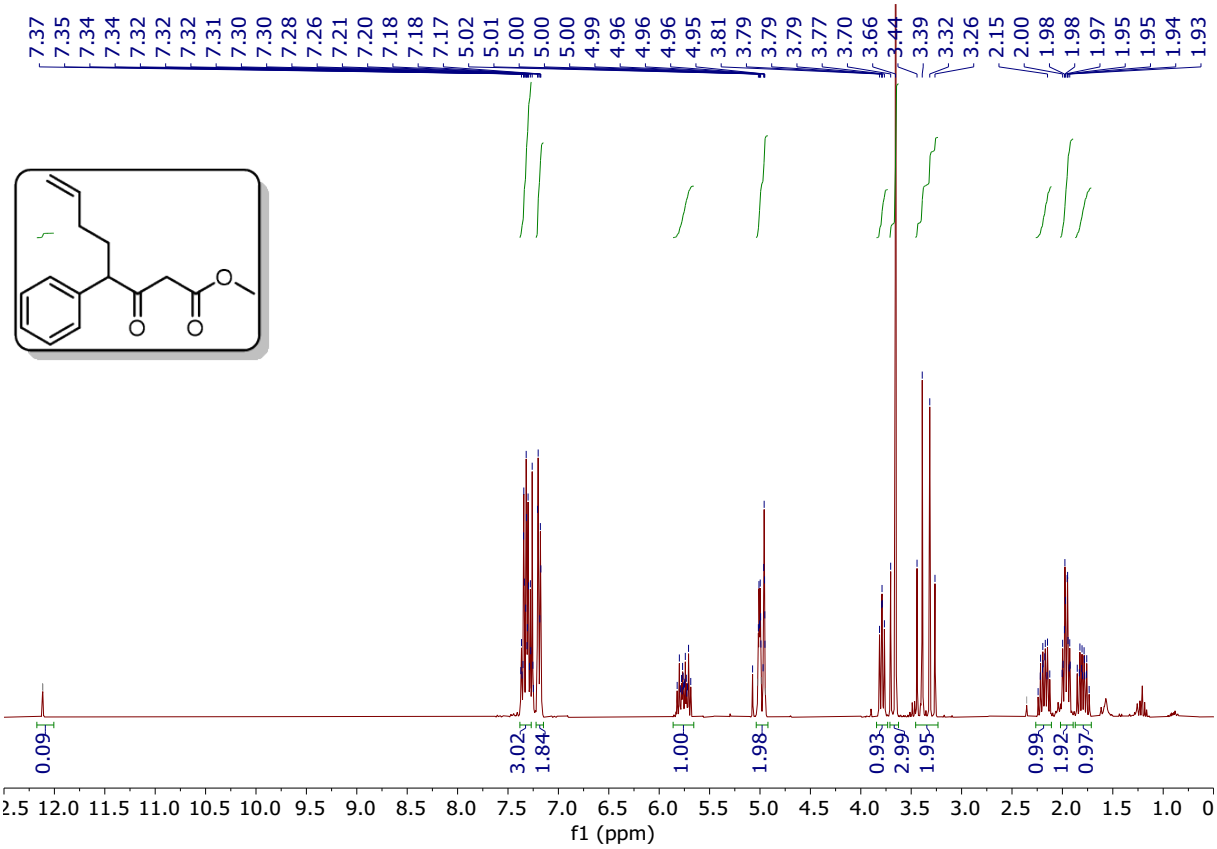
^{1}H NMR spectrum of diazo precursor 7 (400 MHz, $CDCl_3$)



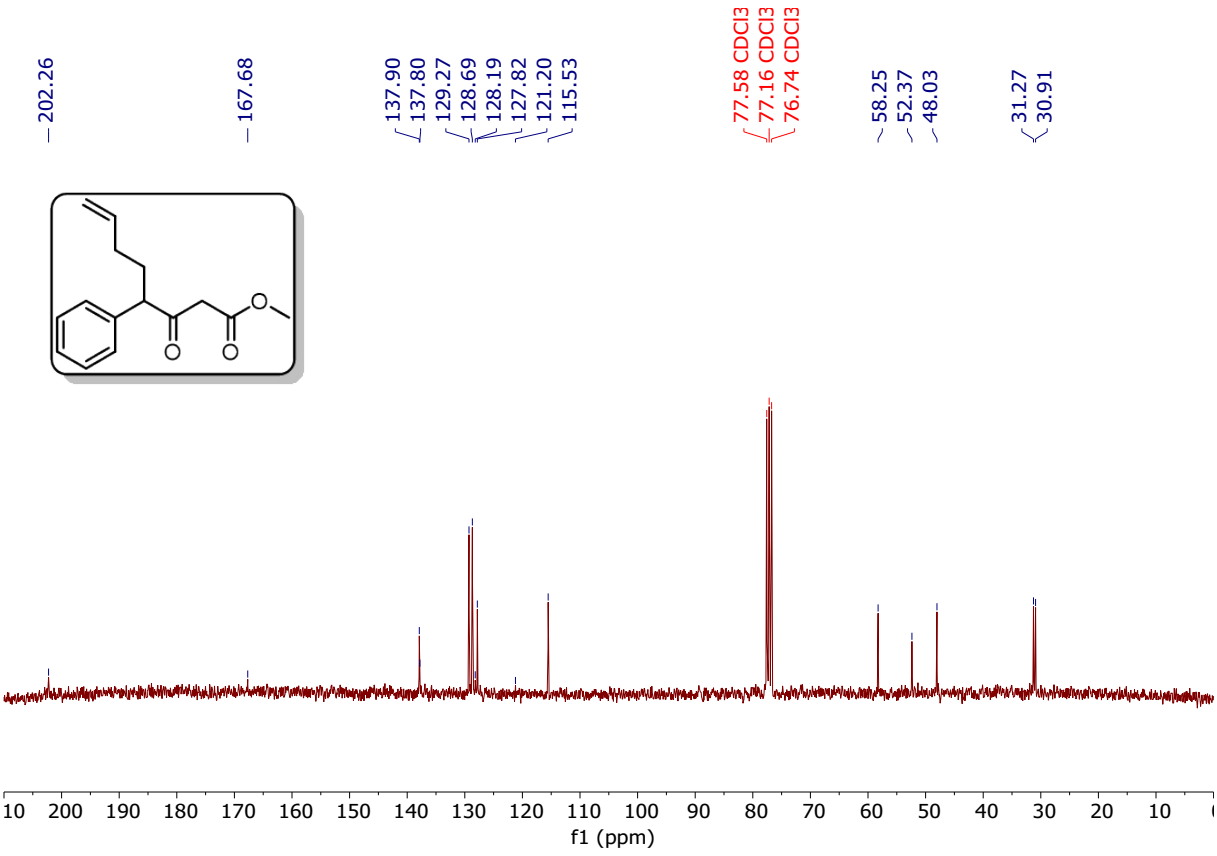
^{13}C NMR spectrum of diazo precursor 7 (101 MHz, $CDCl_3$)



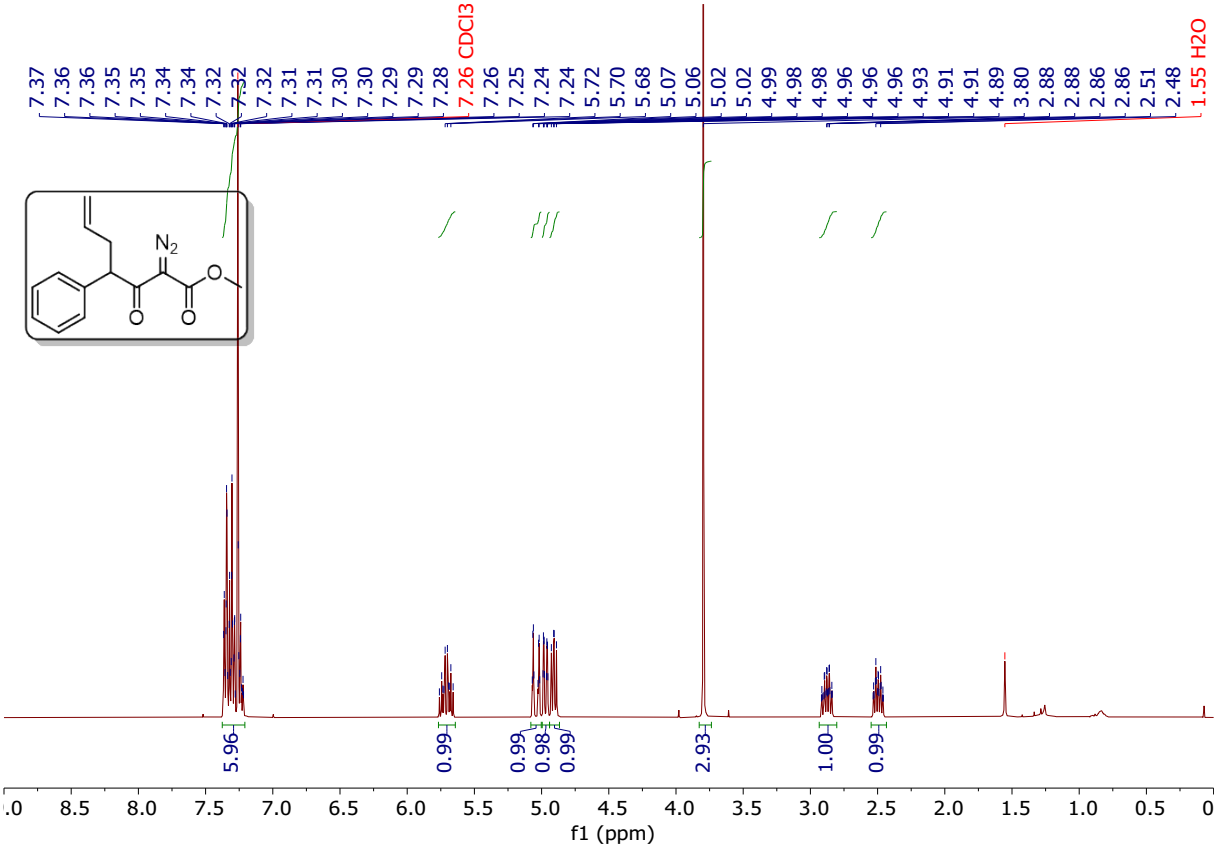
^{1}H NMR spectrum of diazo precursor 8 (300 MHz, $CDCl_3$)



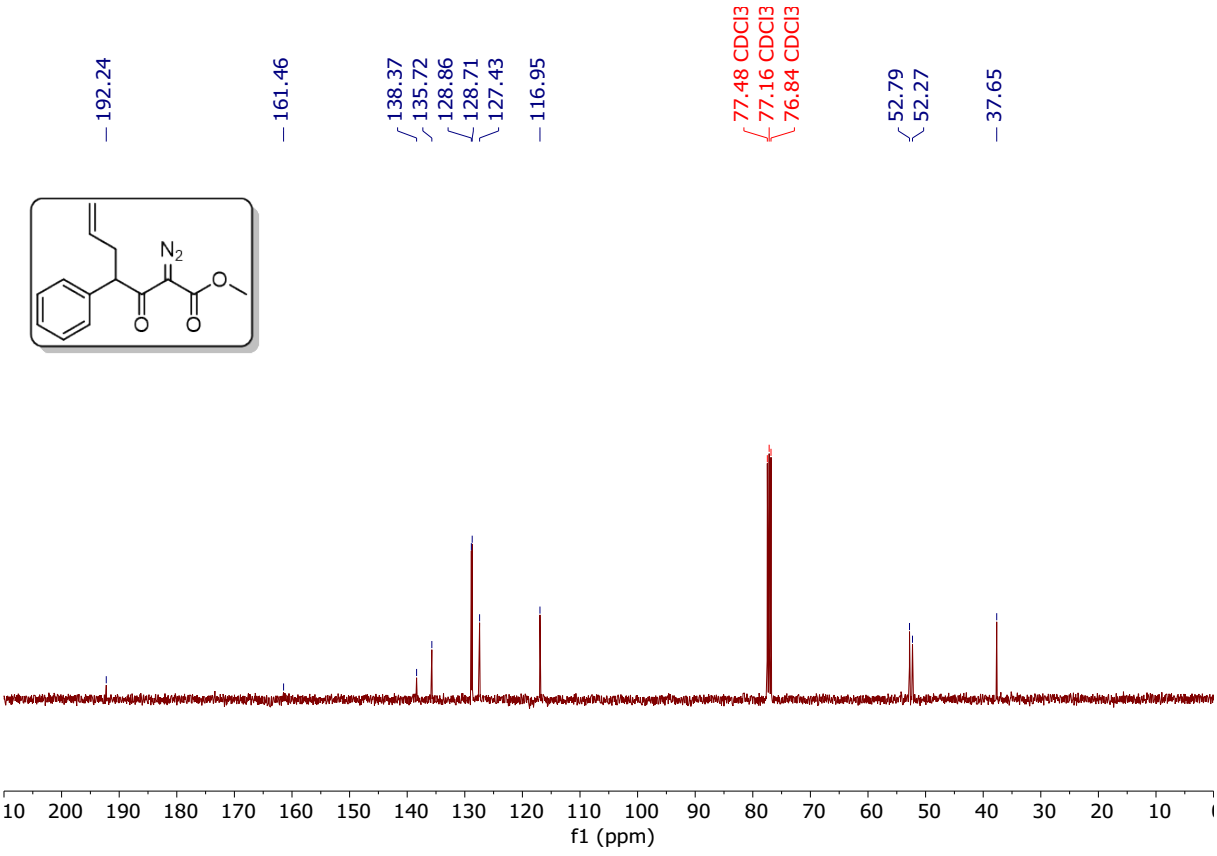
^{13}C NMR spectrum of diazo precursor 8 (75.5 MHz, $CDCl_3$)



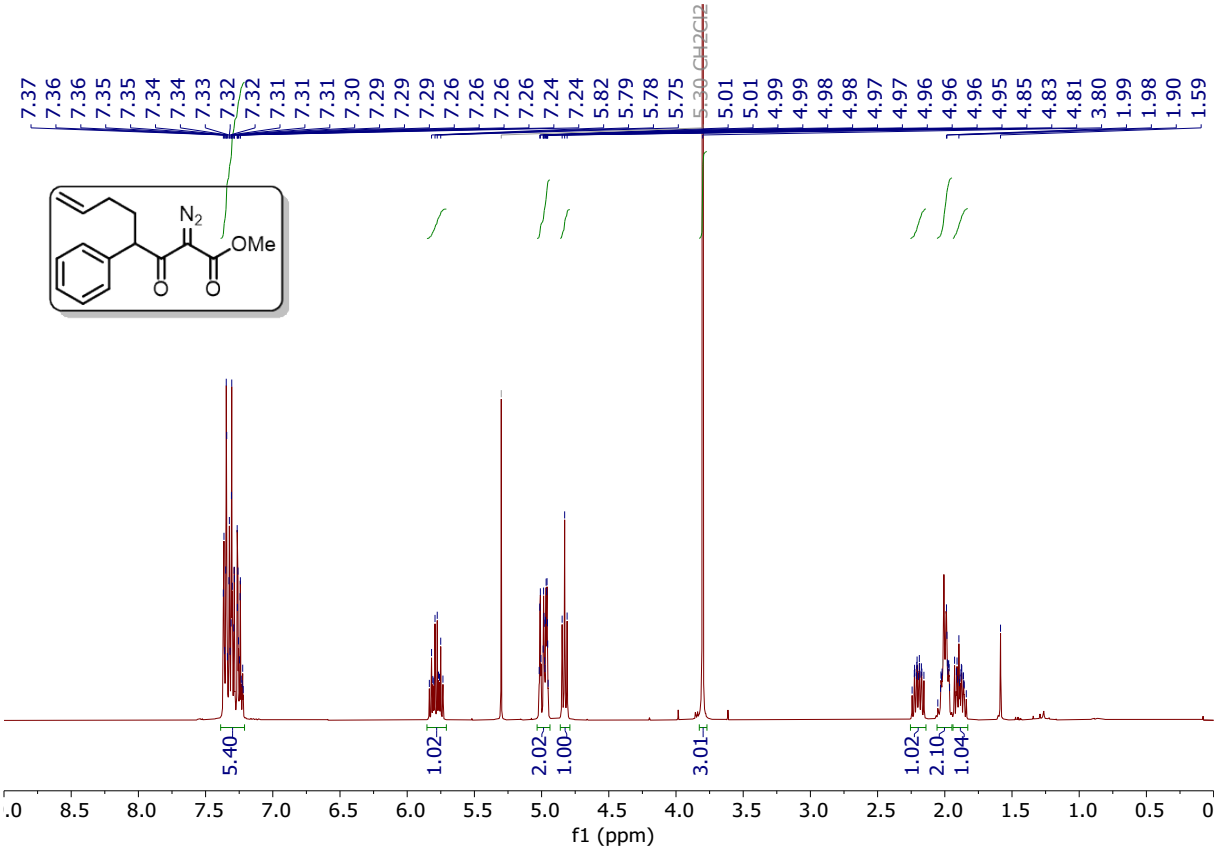
^{1}H NMR spectrum of diazo substrate 9 (400 MHz, $CDCl_3$)



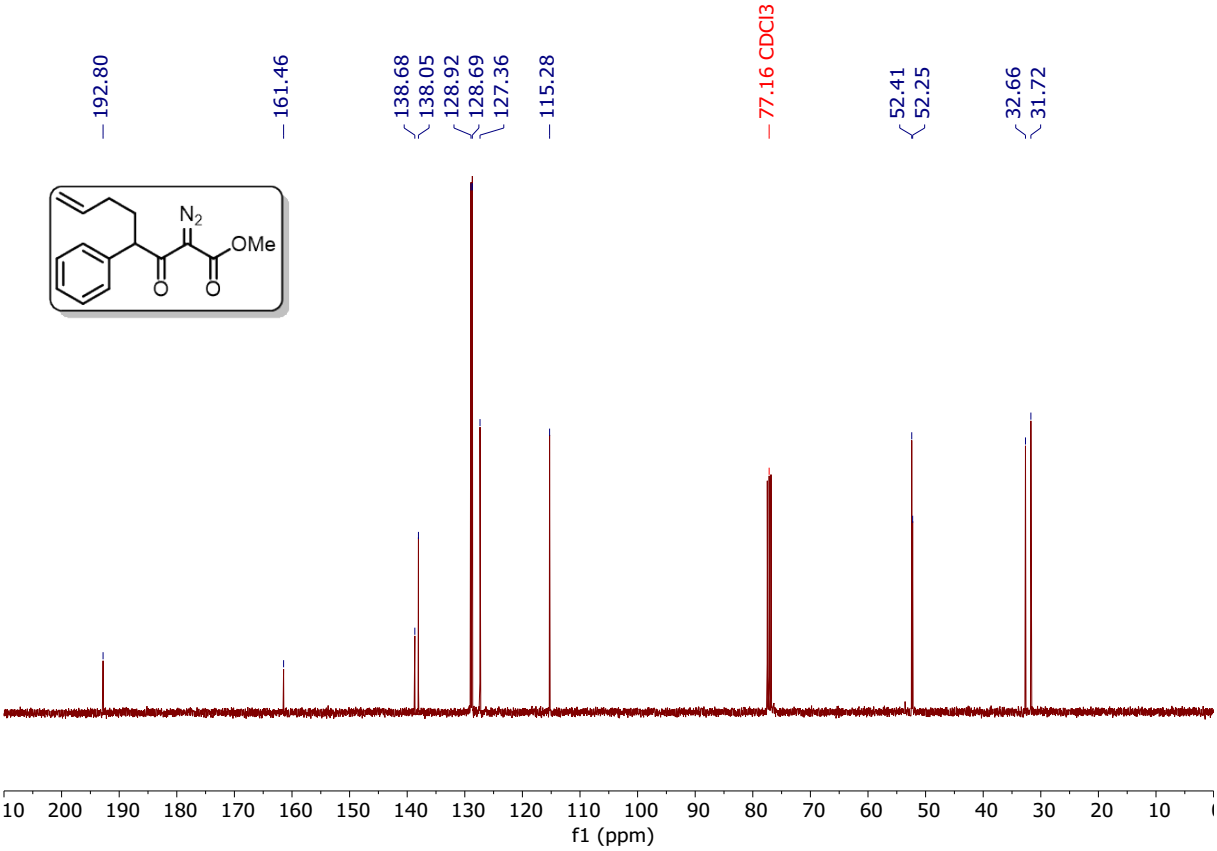
^{13}C NMR spectrum of diazo substrate 9 (101 MHz, $CDCl_3$)



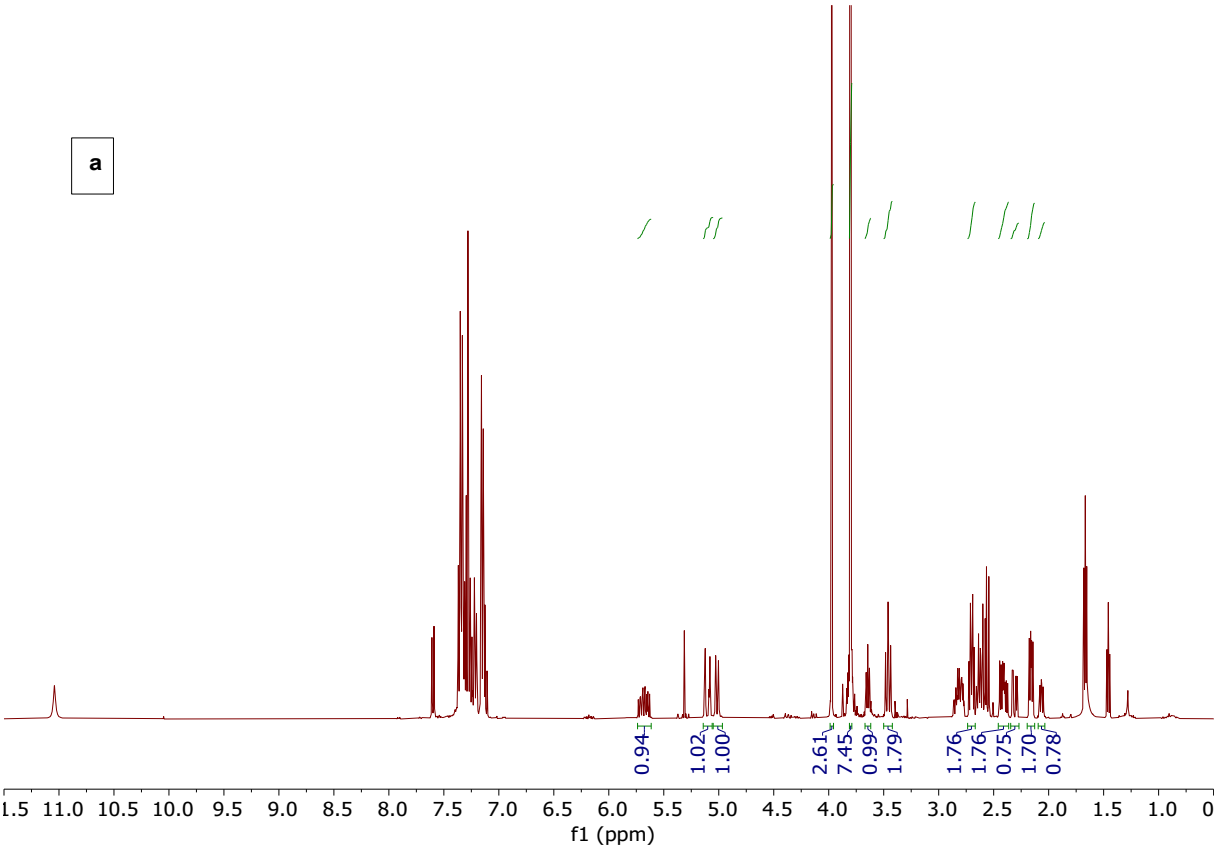
^{1}H NMR spectrum of diazo substrate 10 (400 MHz, $CDCl_3$)

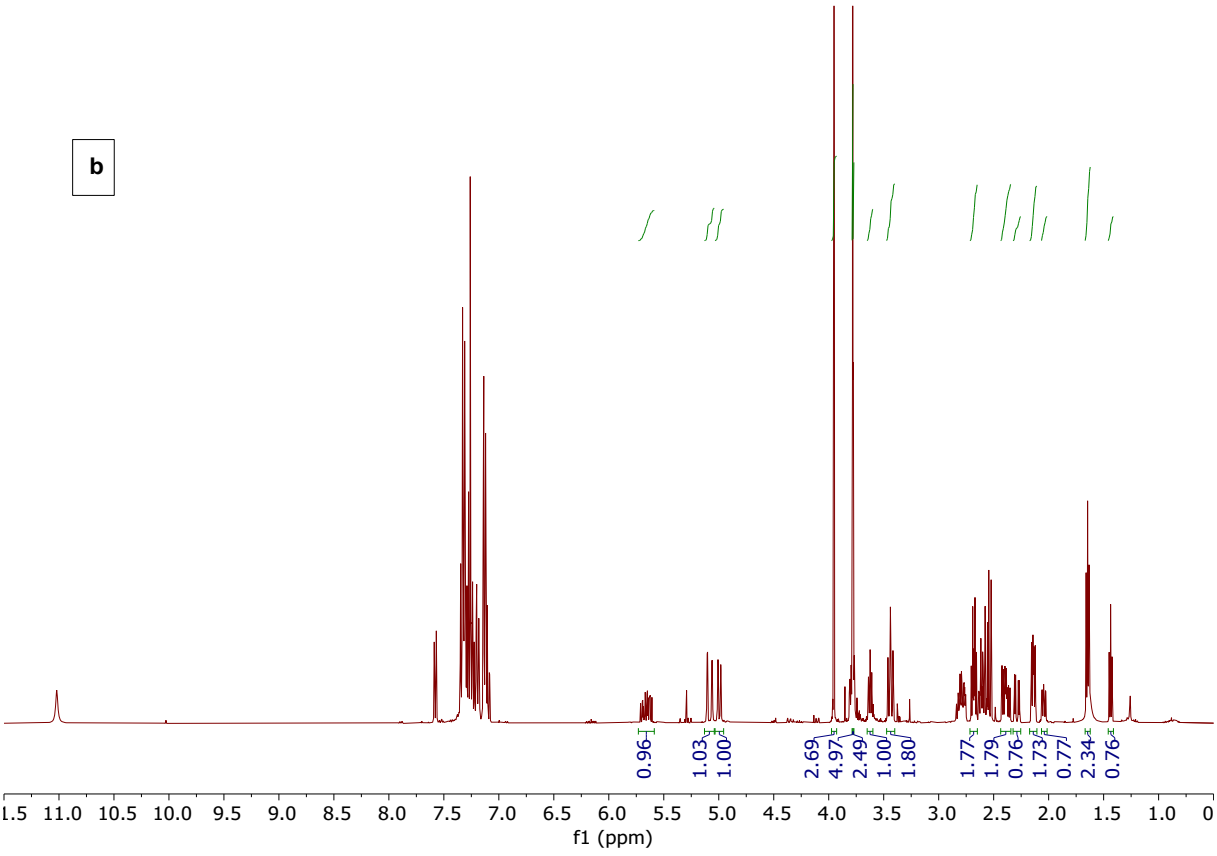


^{13}C NMR spectrum of diazo substrate 10 (101 MHz, $CDCl_3$)

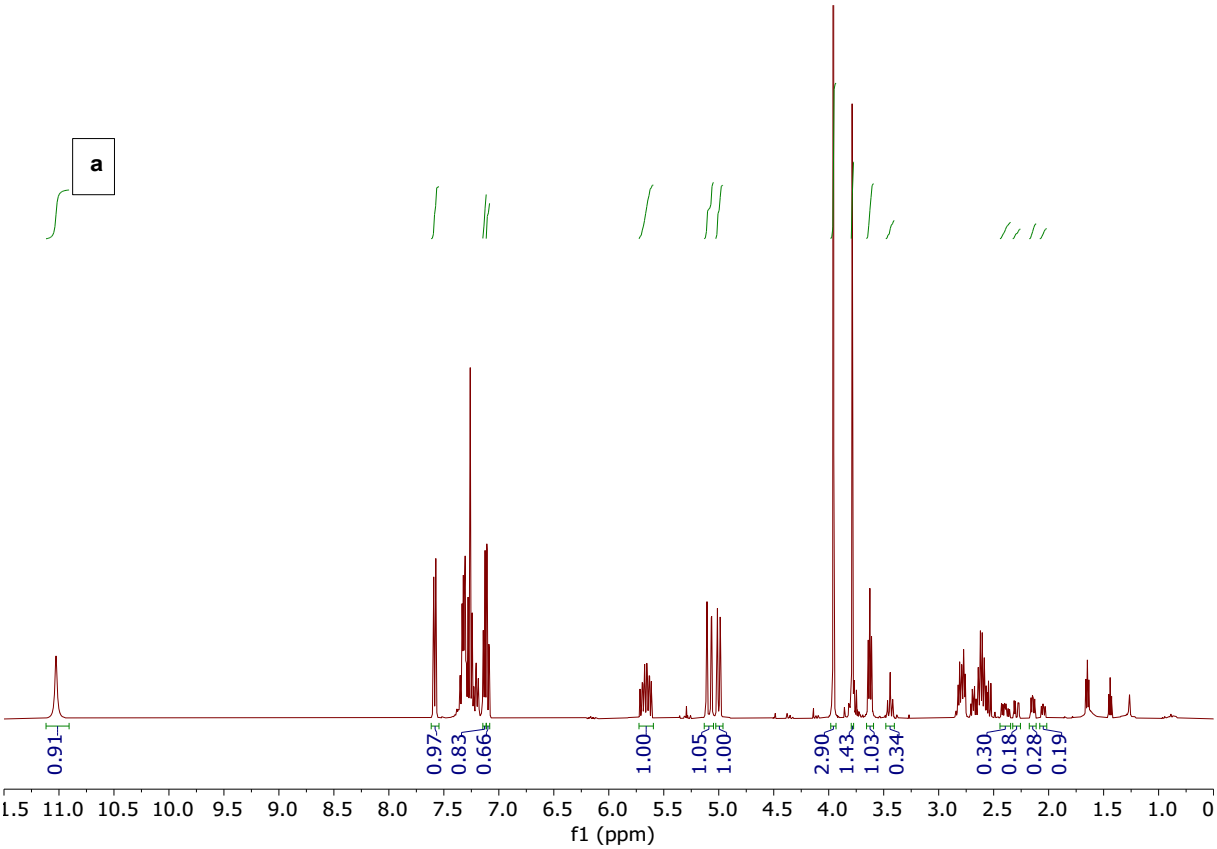


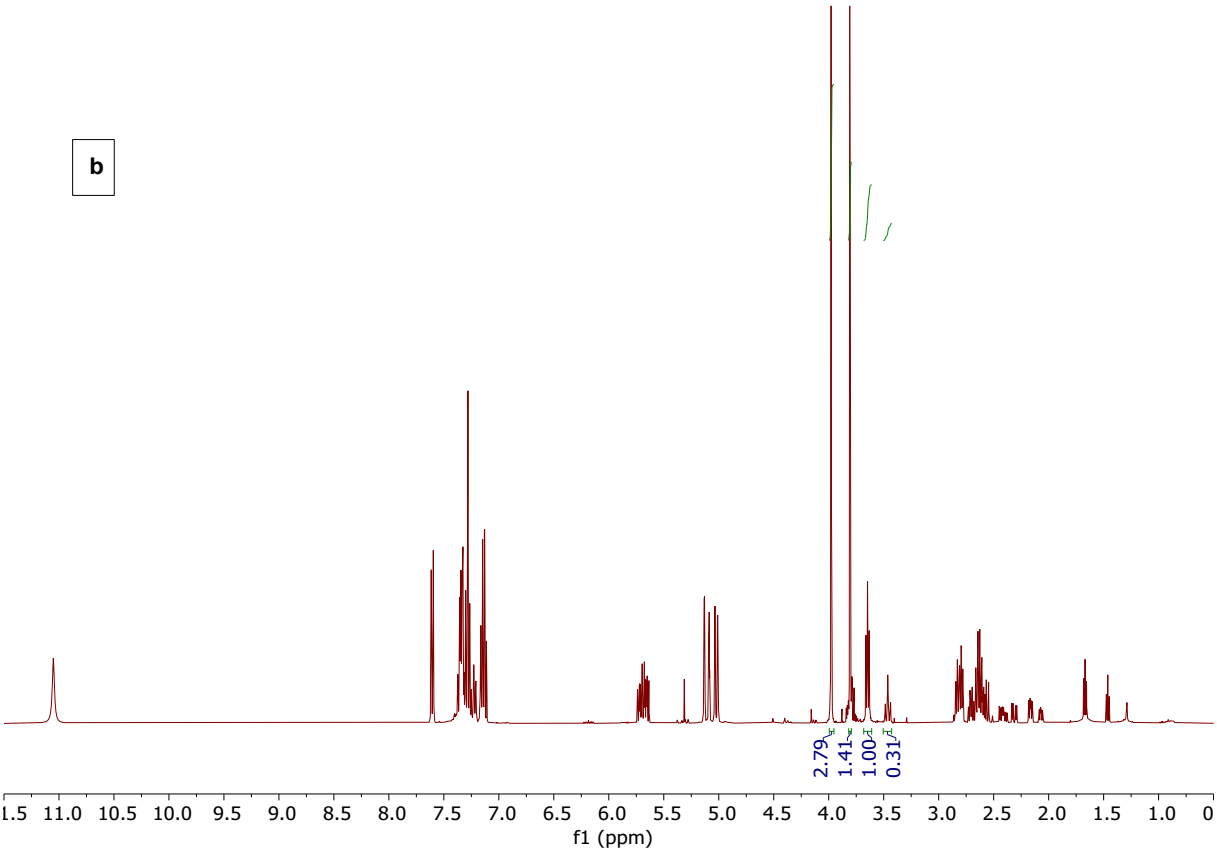
^{1}H NMR spectra of products 11+12 from the decomposition of 9 with $Rh_2(OAc)_4$ (400 MHz, $CDCl_3$)



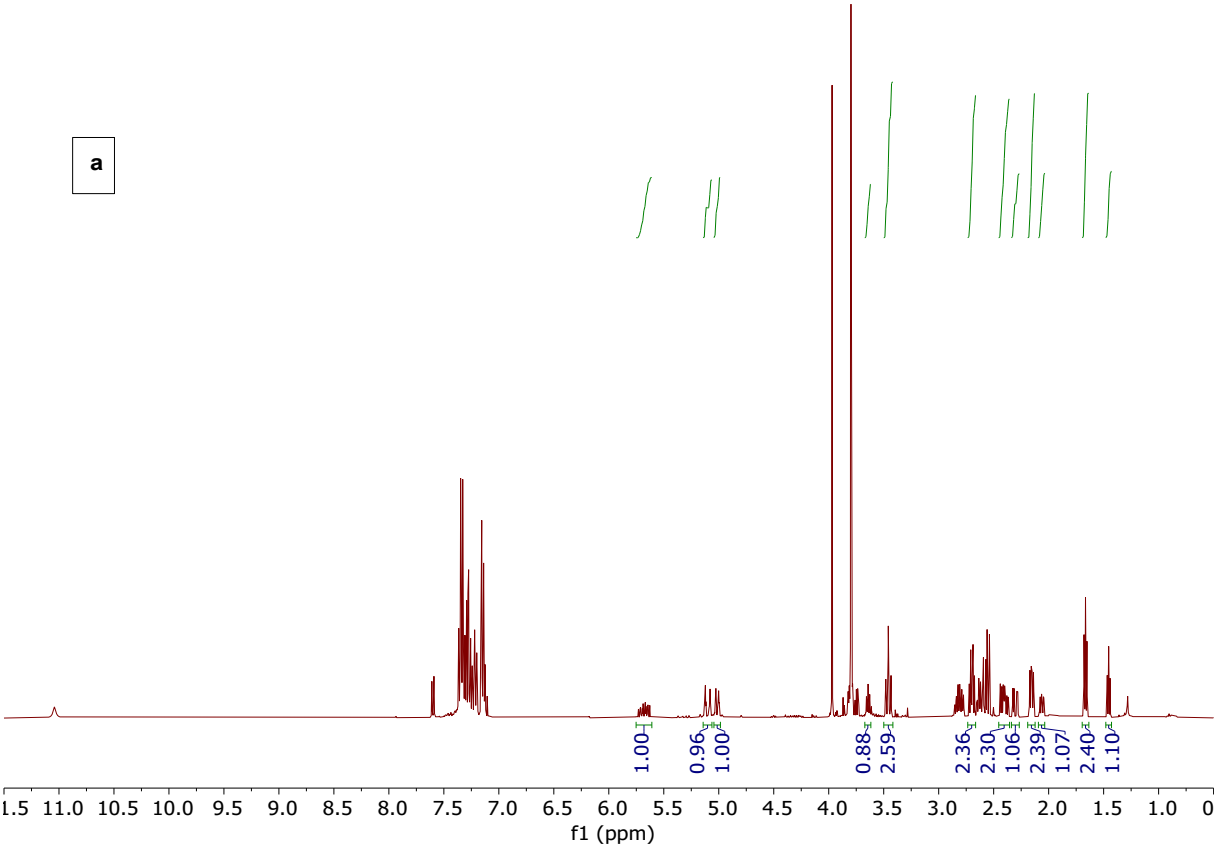


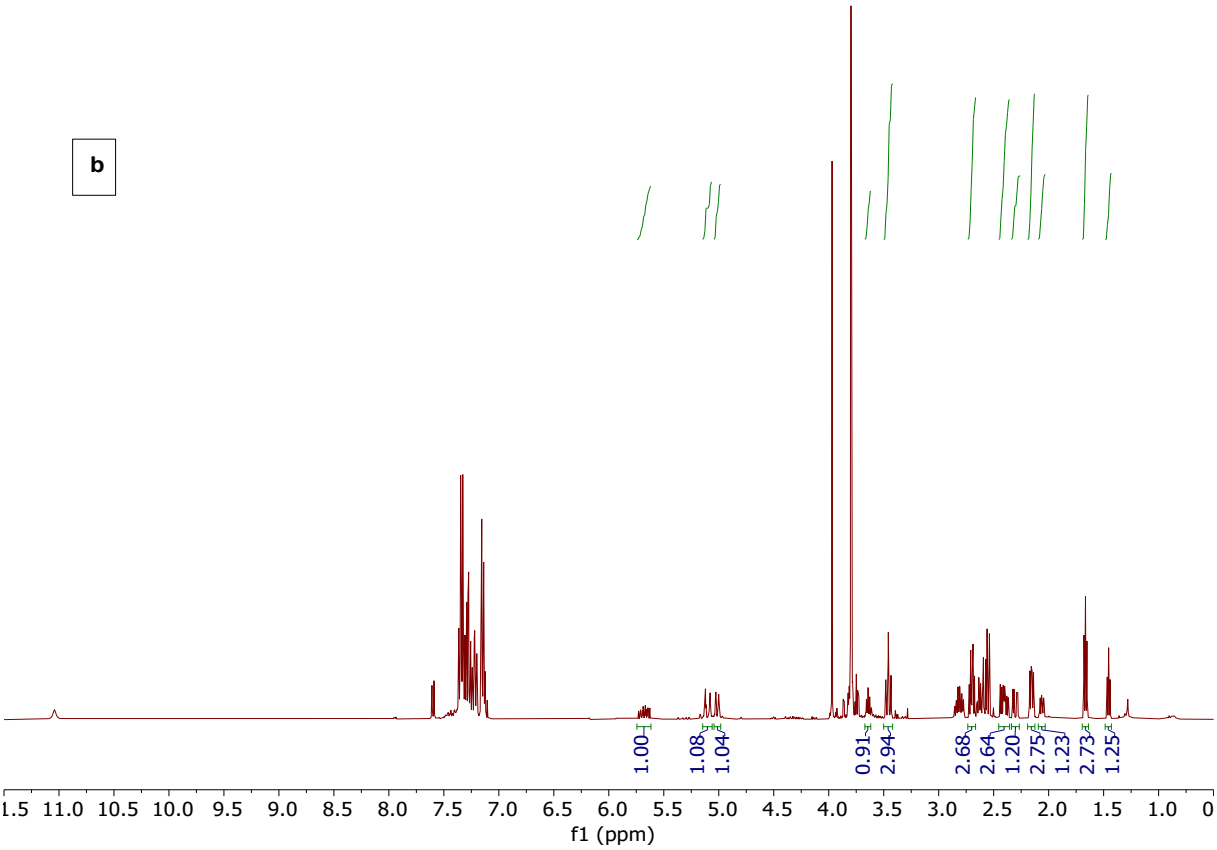
^{1}H NMR spectra of products 11+12 from the decomposition of 9 with $Rh_2(OAc)_{3(}tfa)$ (400 MHz, $CDCl_3$)



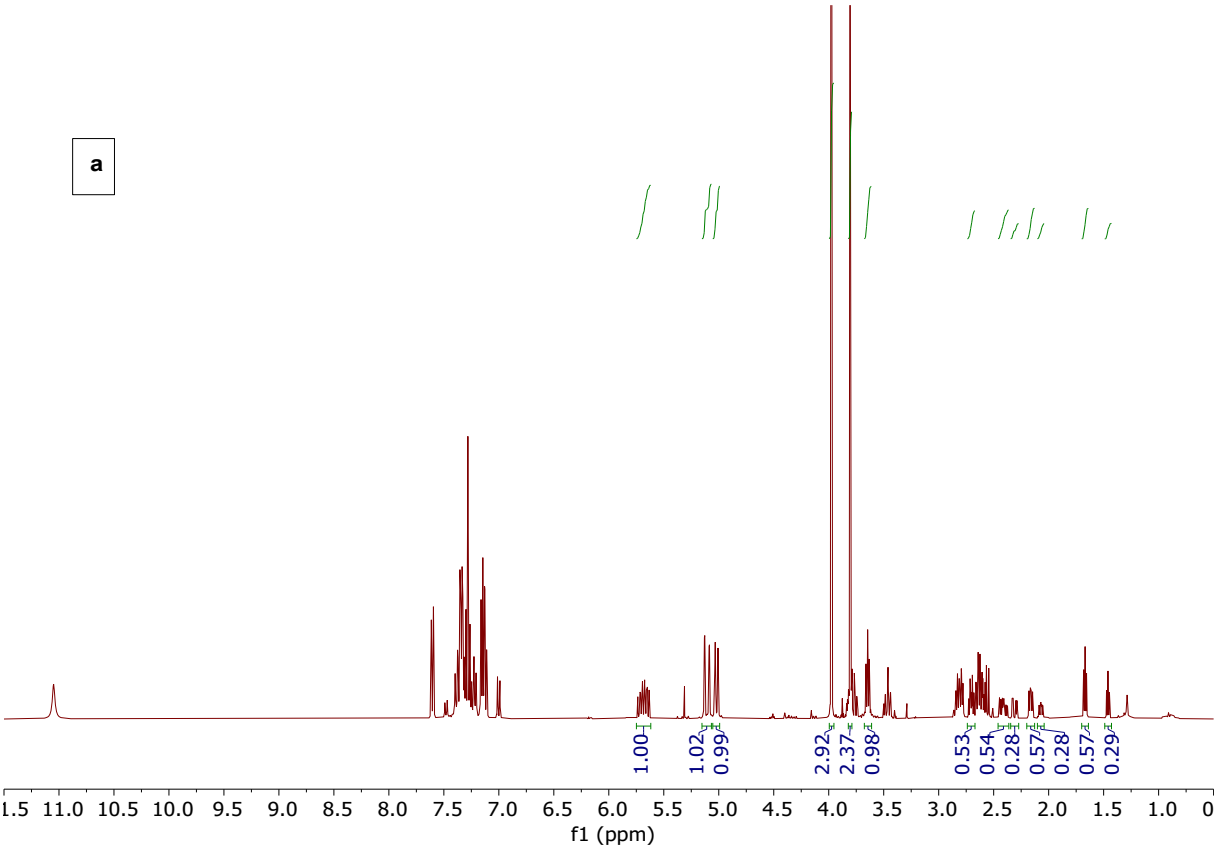


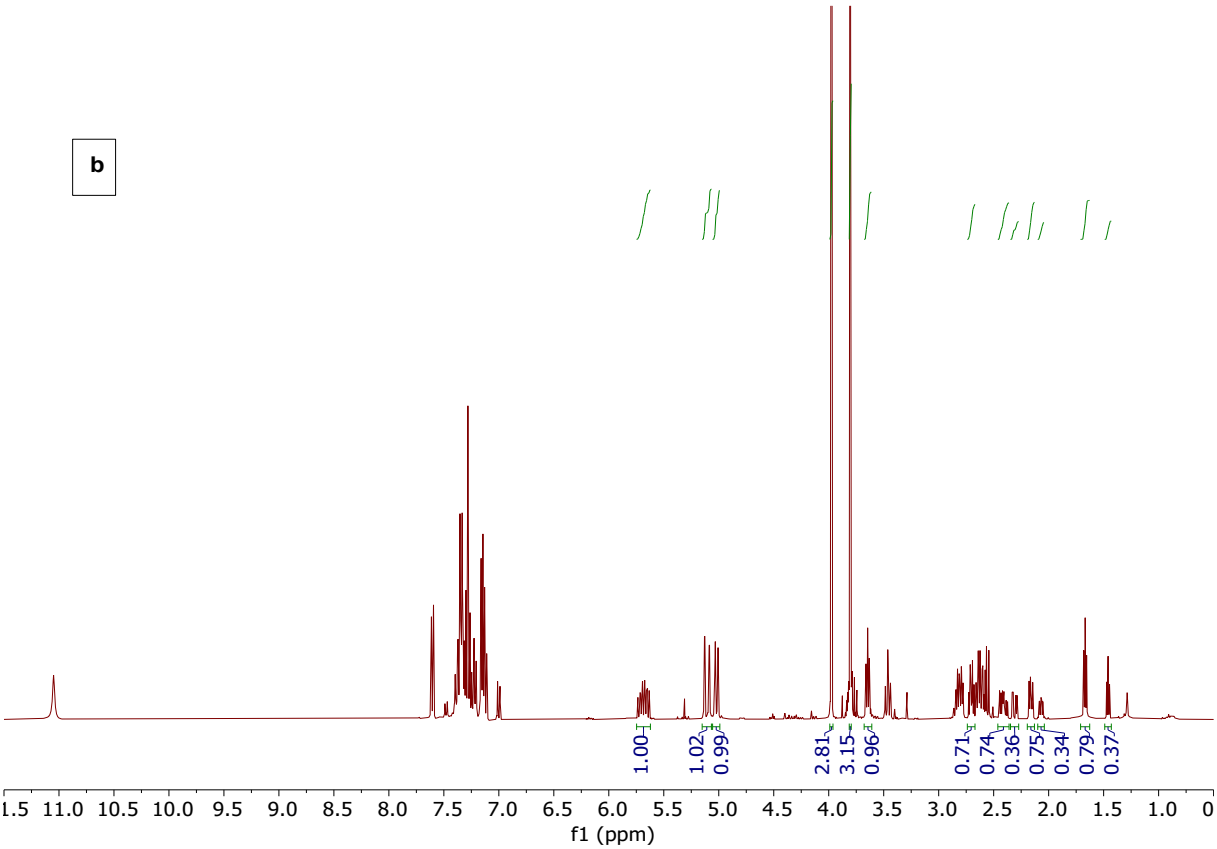
^{1}H NMR spectra of products 11+12 from the decomposition of 9 with 1a (400 MHz, $CDCl_3$)



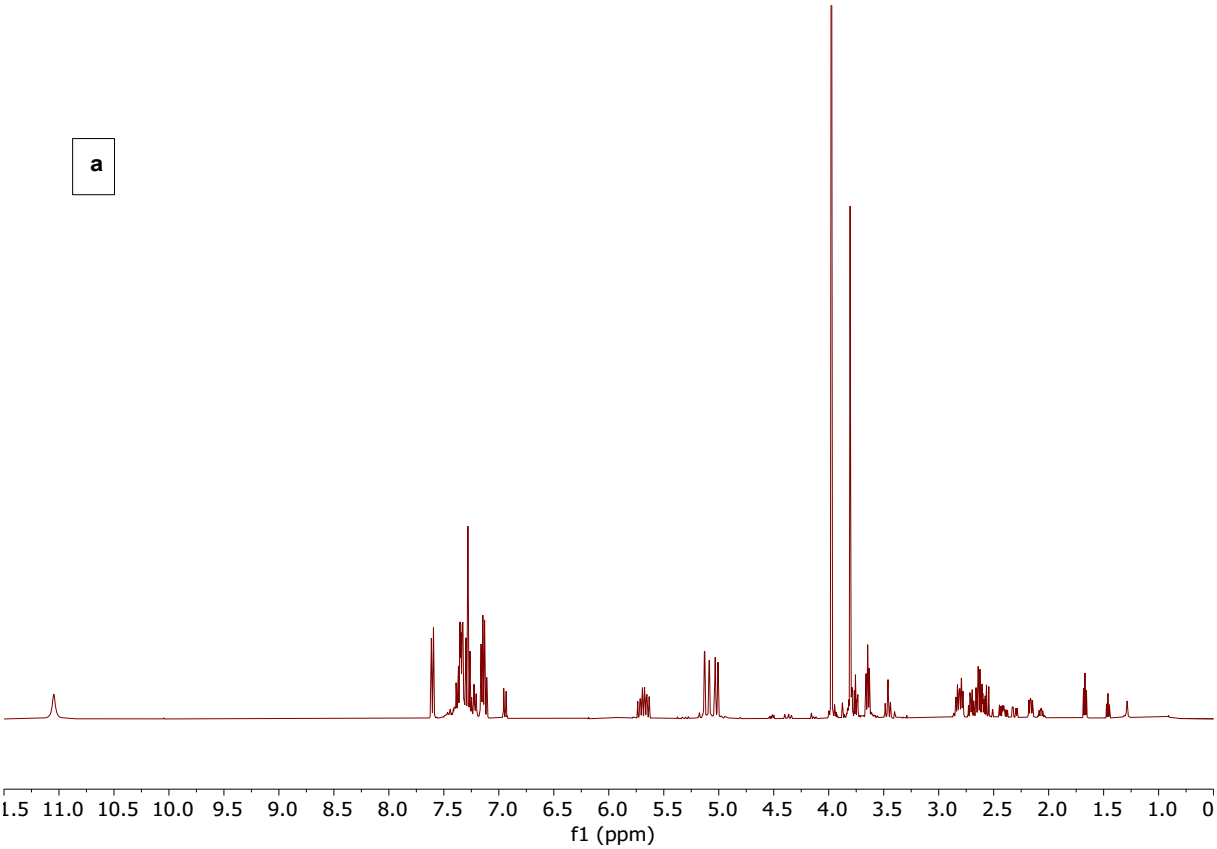


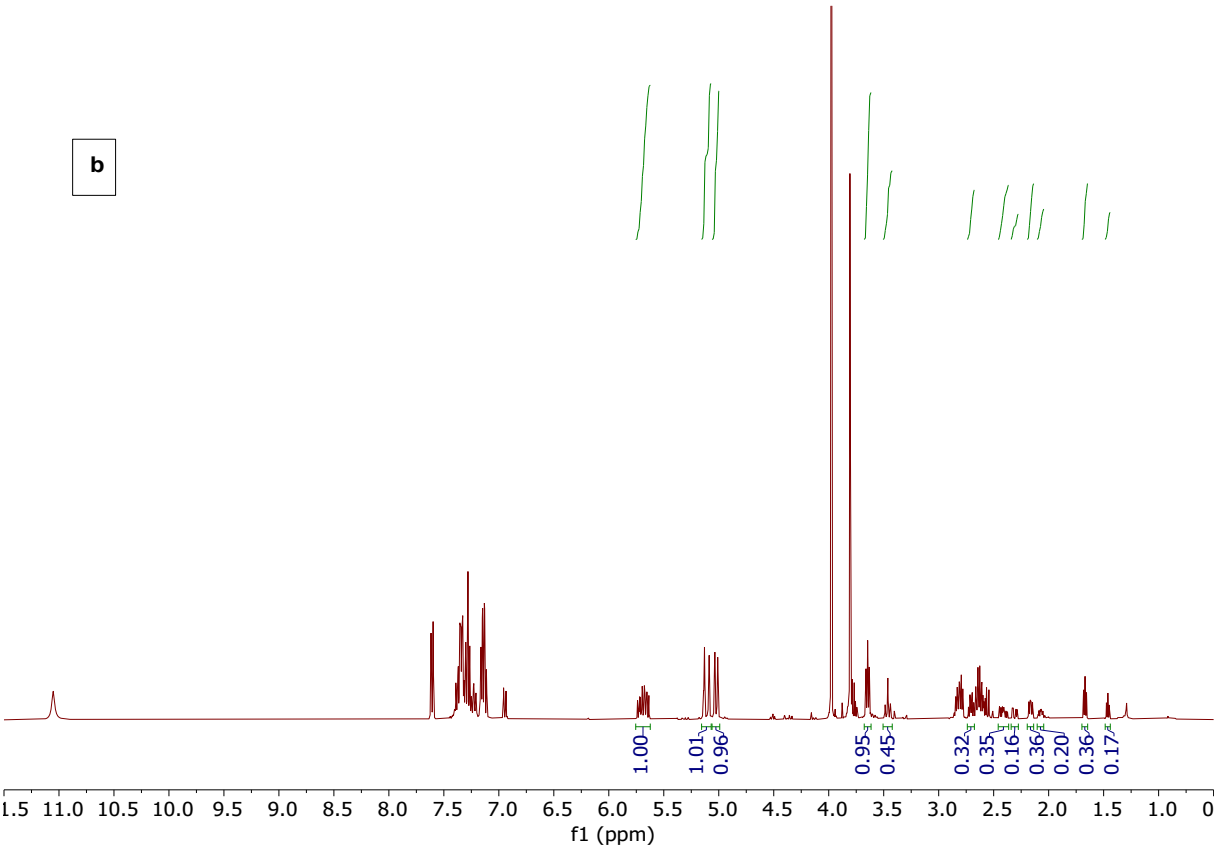
^{1}H NMR spectra of products 11+12 from the decomposition of 9 with $1a^+BF_4^-$ (400 MHz, $CDCl_3$)



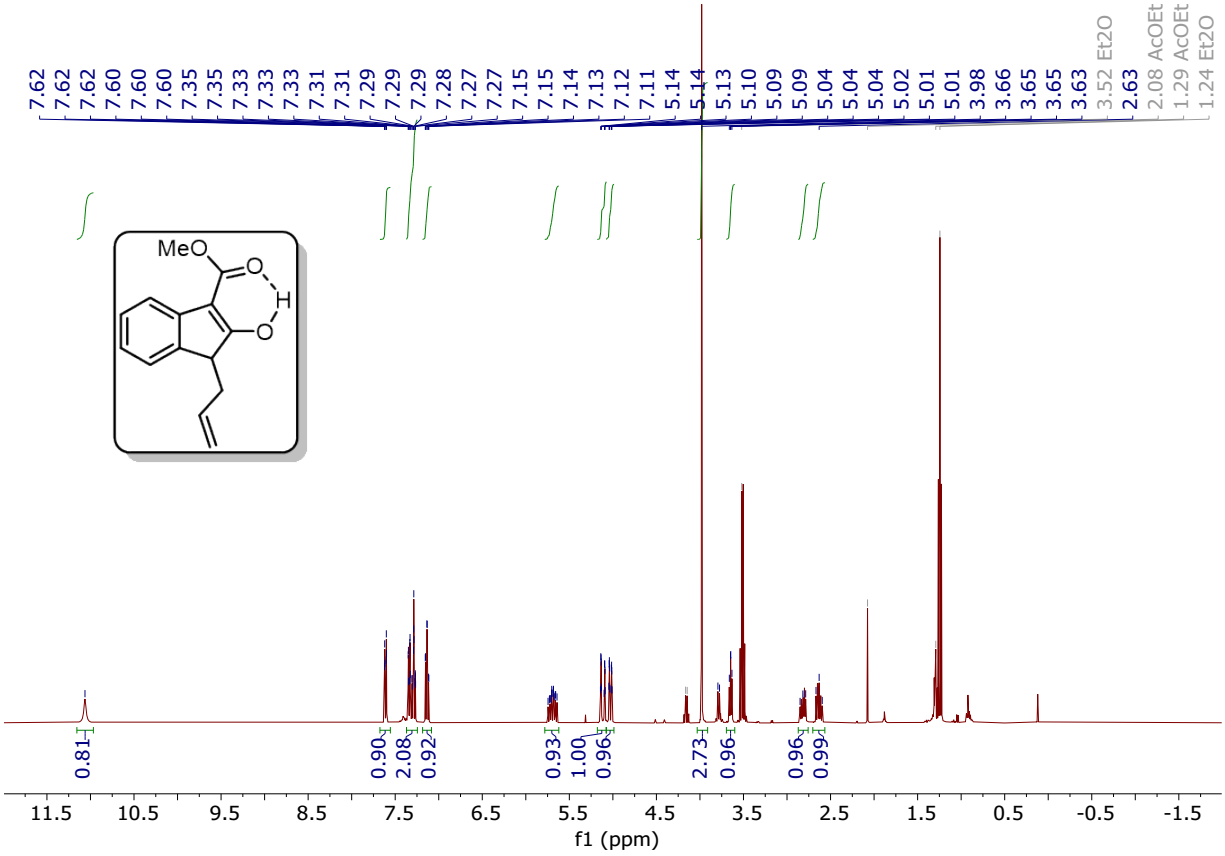


^{1}H NMR spectra of products 11+12 from the decomposition of 9 with $1a^+SbF_6^-$ (400 MHz, $CDCl_3$)

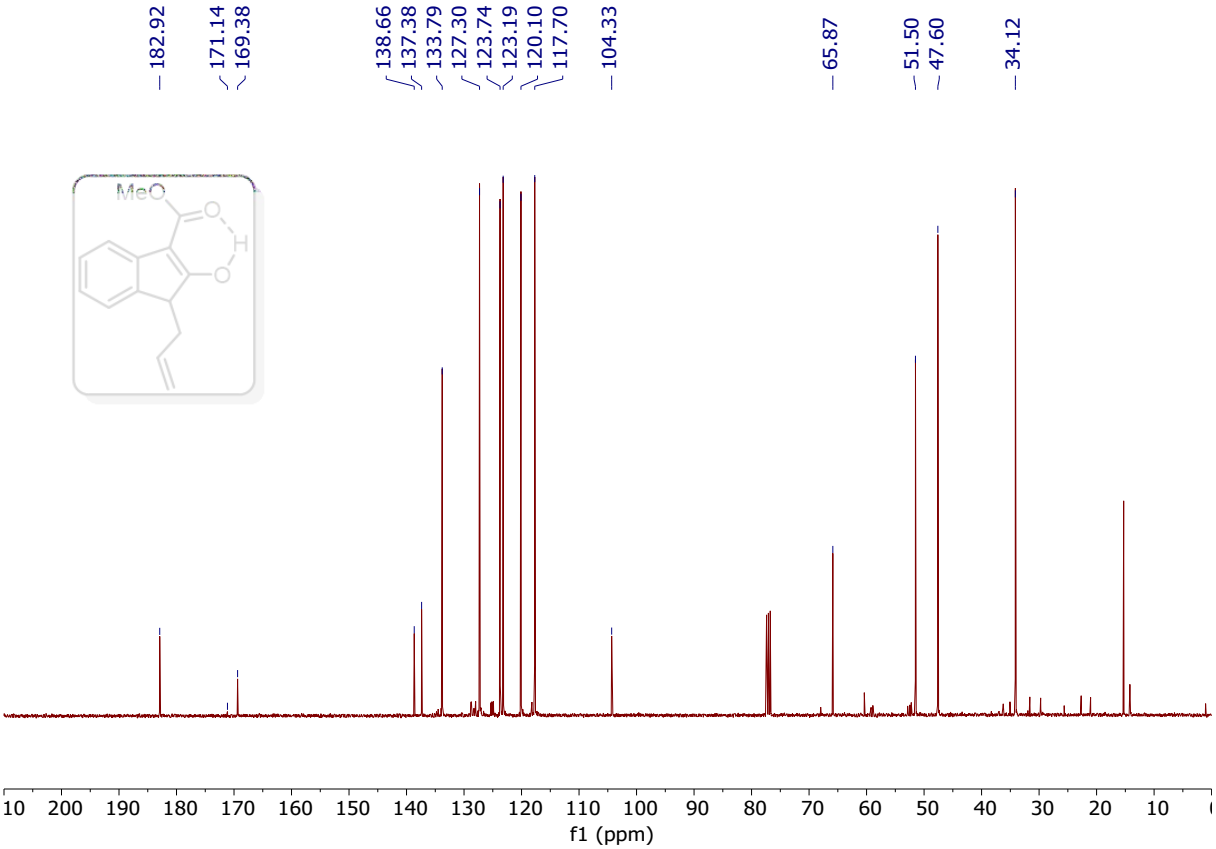




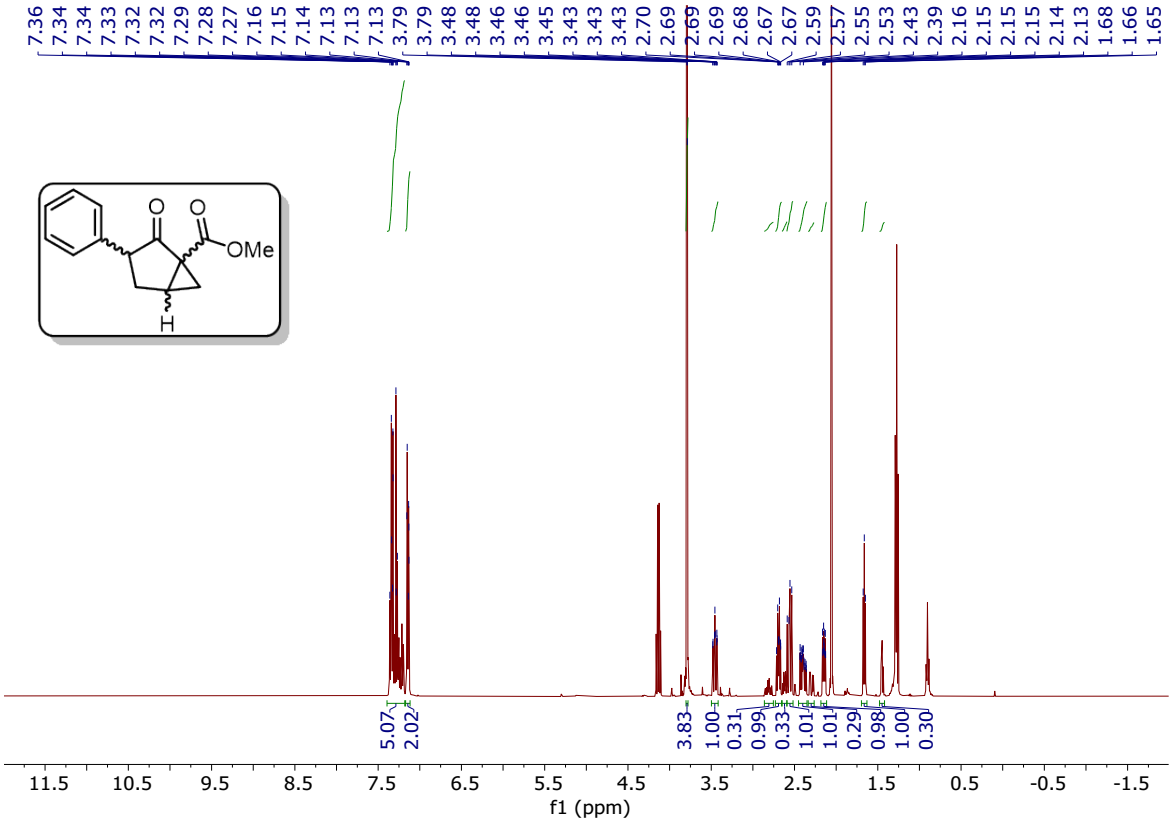
^{1}H NMR spectrum of product 11 from the decomposition of 9 (400 MHz, $CDCl_3$)



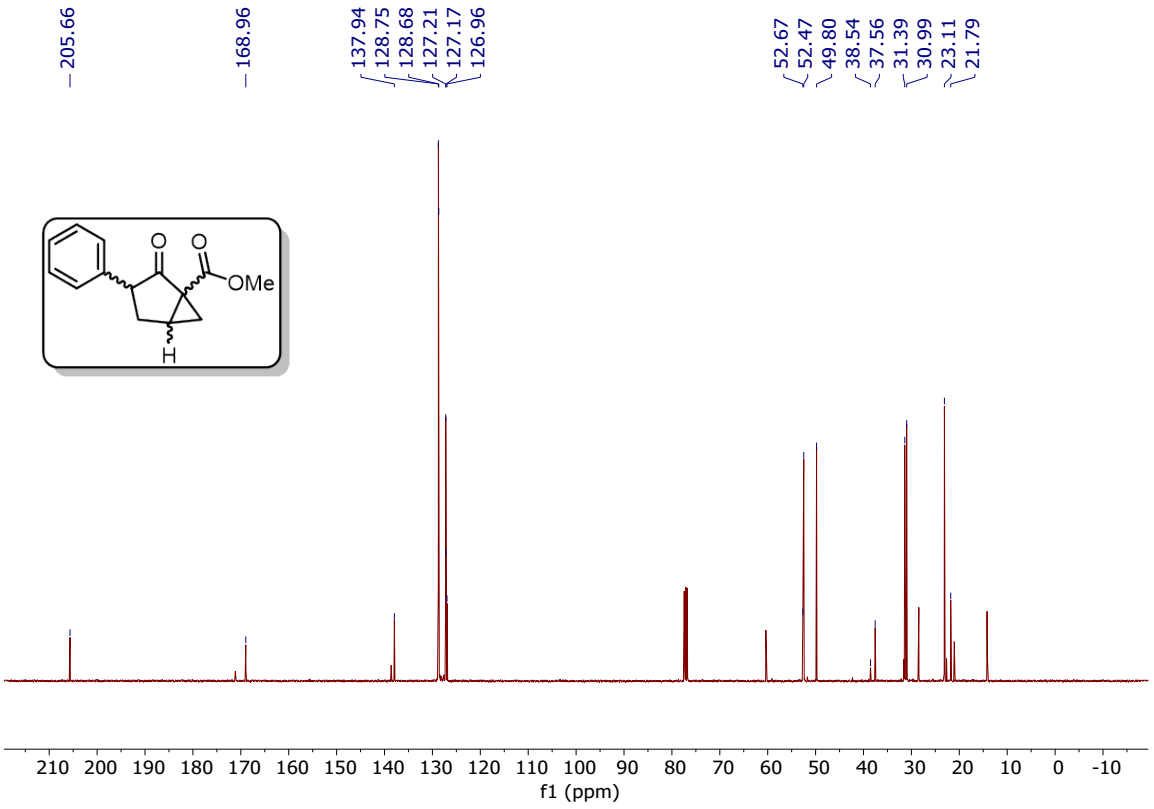
^{13}C NMR spectrum of product 11 from the decomposition of 9 (101 MHz, $CDCl_3$)


182.92
171.14
169.38
138.66
137.38
133.79
127.30
123.74
123.19
120.10
117.70
104.33
65.87
51.50
47.60
34.12
MeO
O
H
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

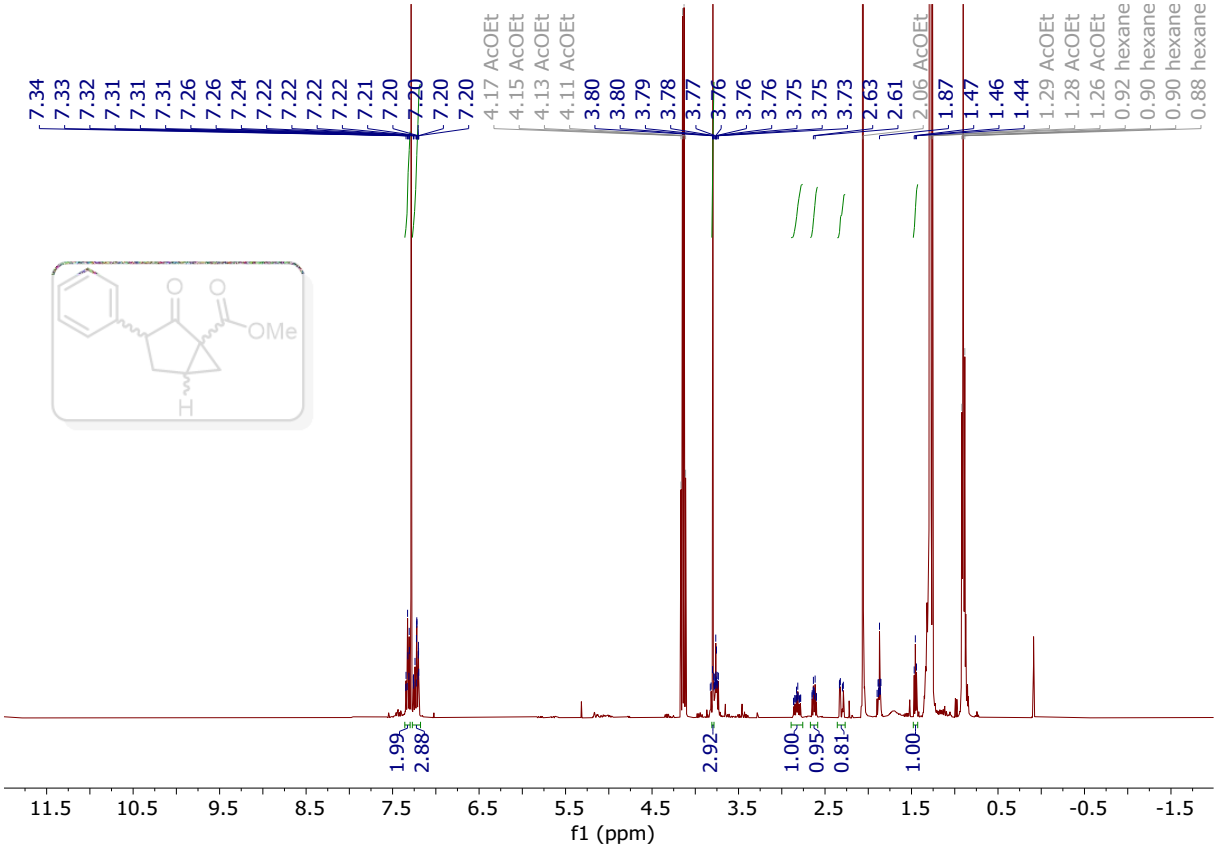
^{1}H NMR spectrum of product 12-dia1 (+ traces of 12-dia2) from the decomposition of 9 (400 MHz, $CDCl_3$)



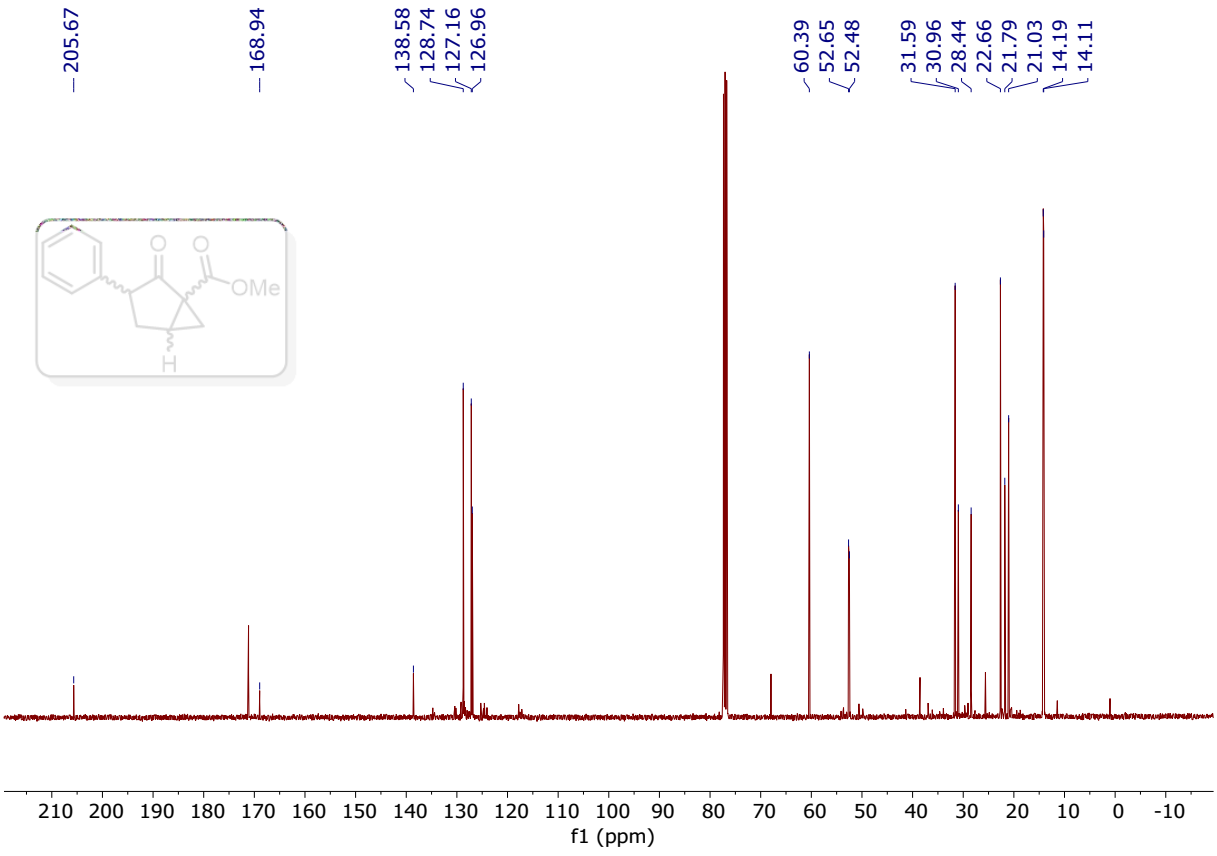
^{13}C NMR spectrum of product 12-dia1 (+ traces of 12-dia2) from the decomposition of 9 (101 MHz, $CDCl_3$)



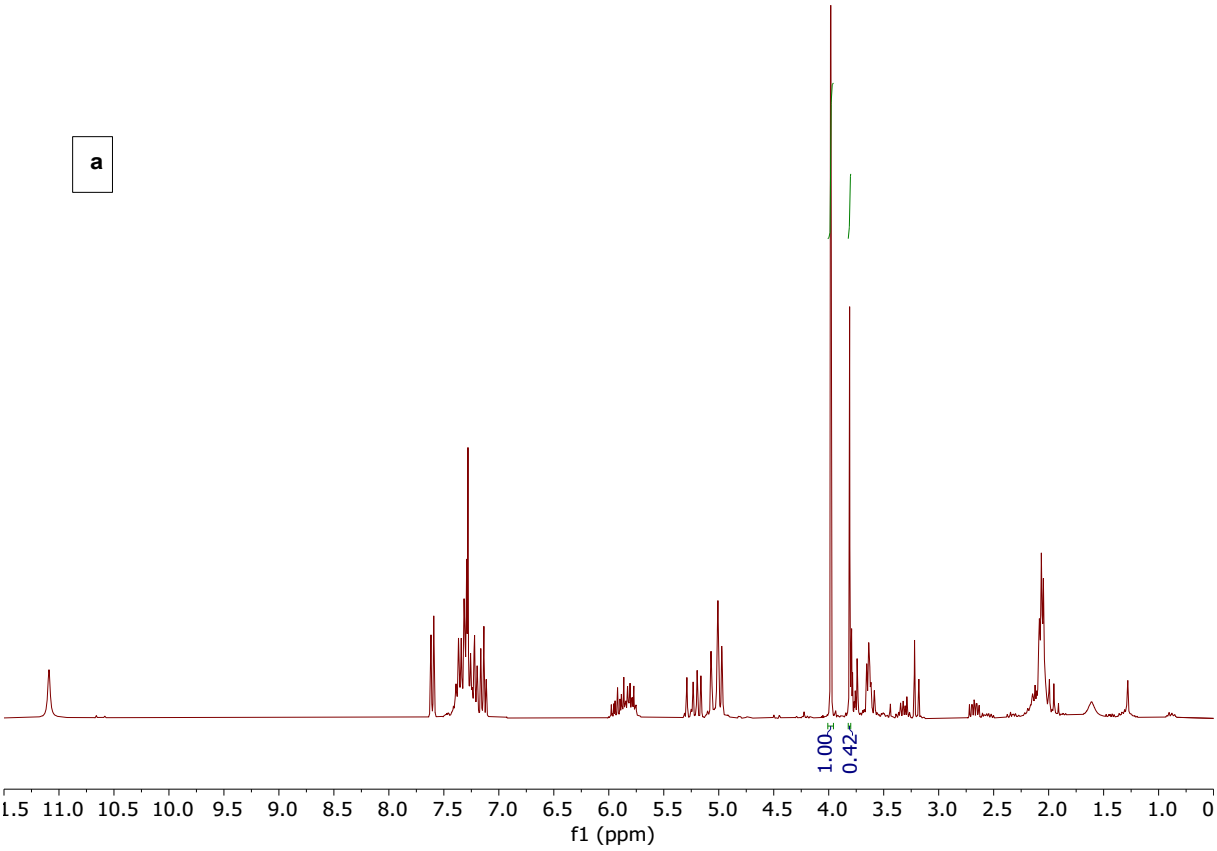
^{1}H NMR spectrum of product 12-dia2 from the decomposition of 9 (400 MHz, $CDCl_3$)

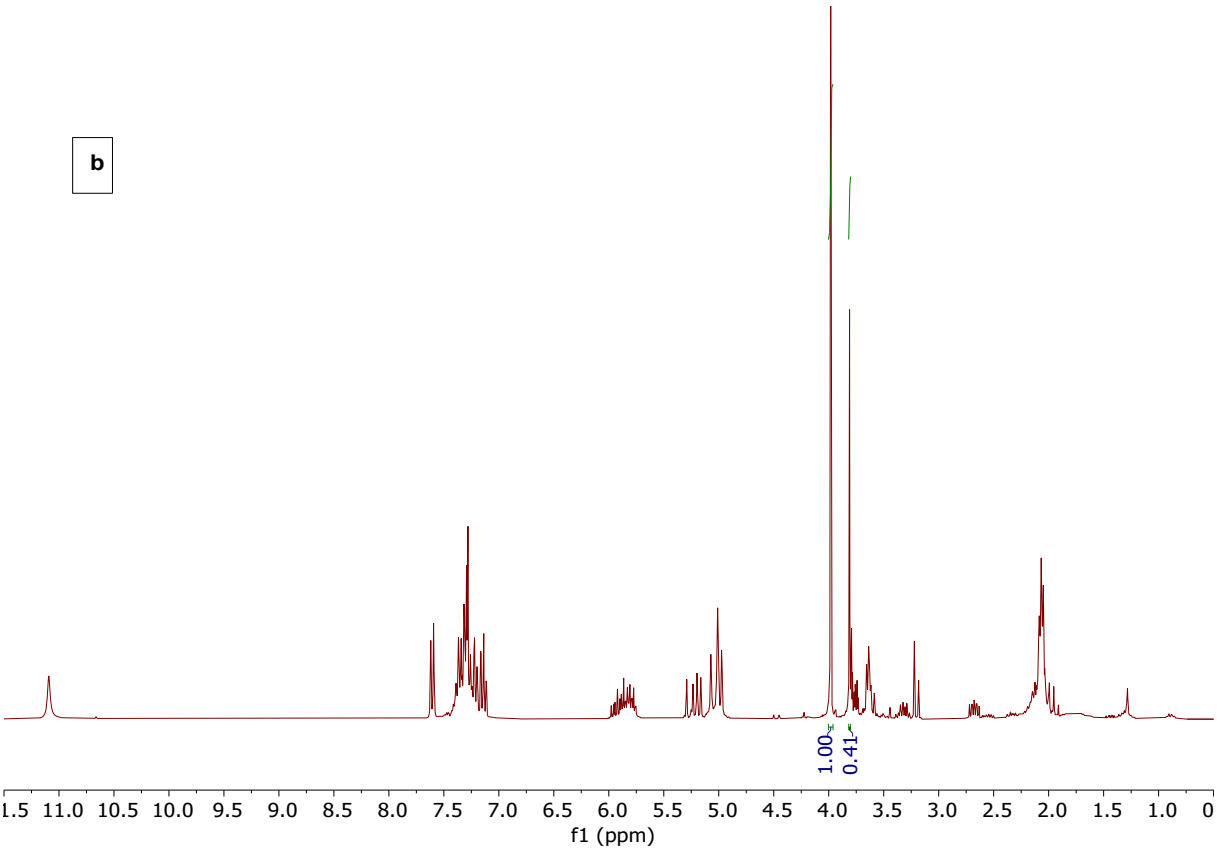


^{13}C NMR spectrum of product 12-dia2 from the decomposition of 9 (101 MHz, $CDCl_3$)

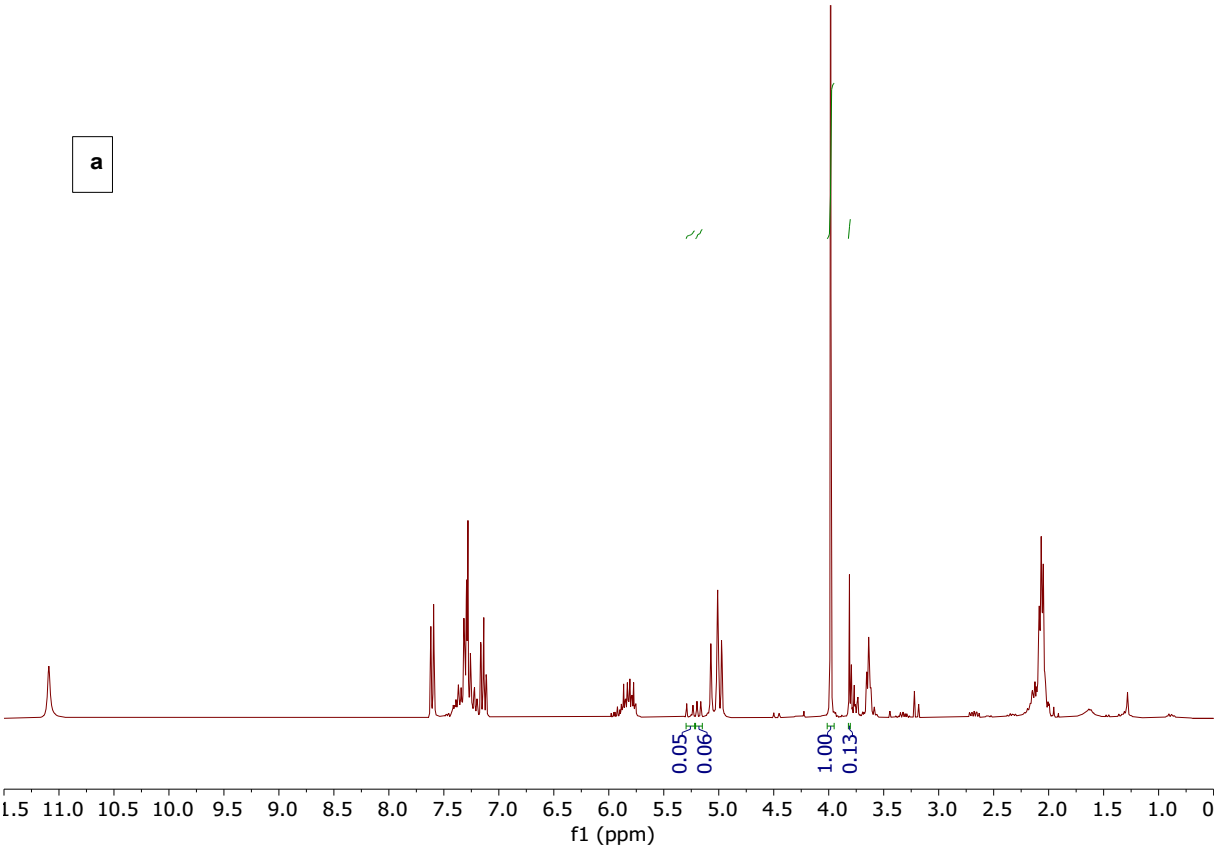


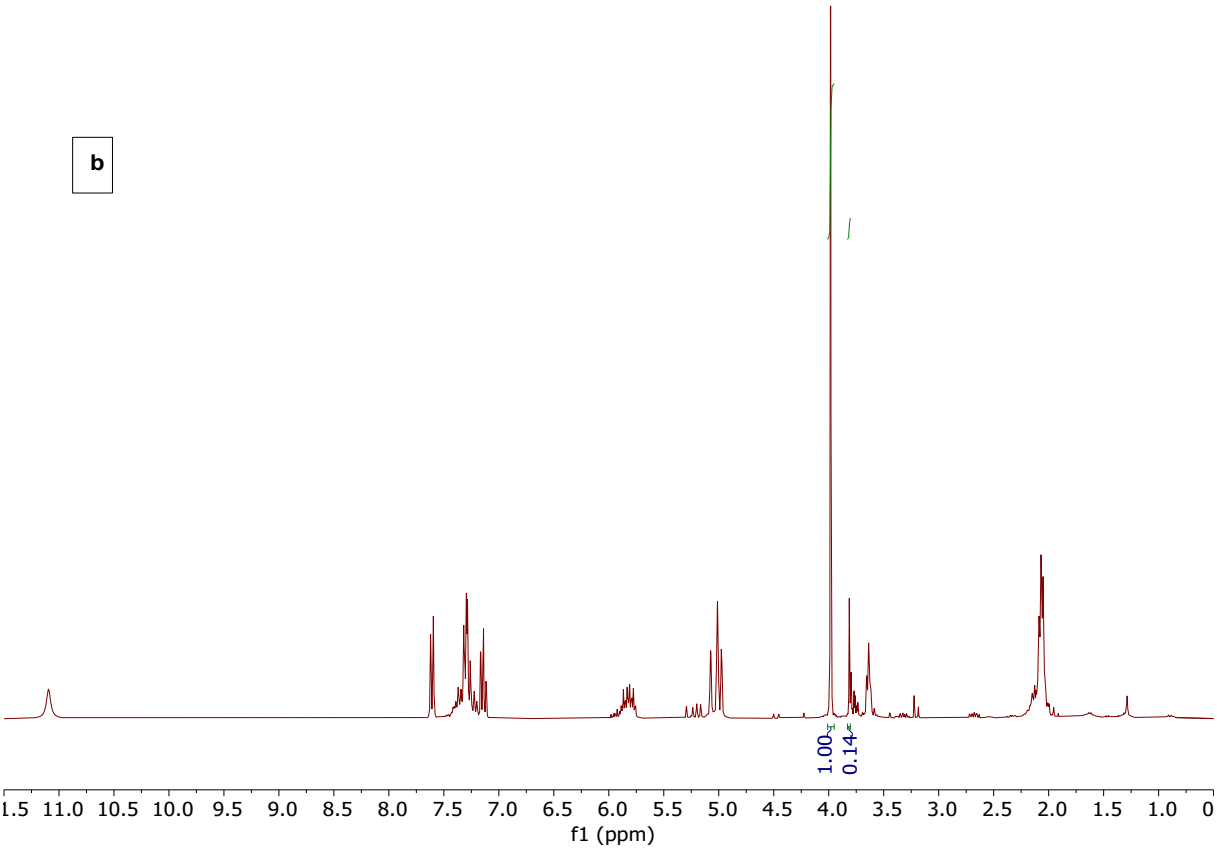
^{1}H NMR spectra of products 13+14 from the decomposition of 10 with $Rh_2(OAc)_4$ (400 MHz, $CDCl_3$)



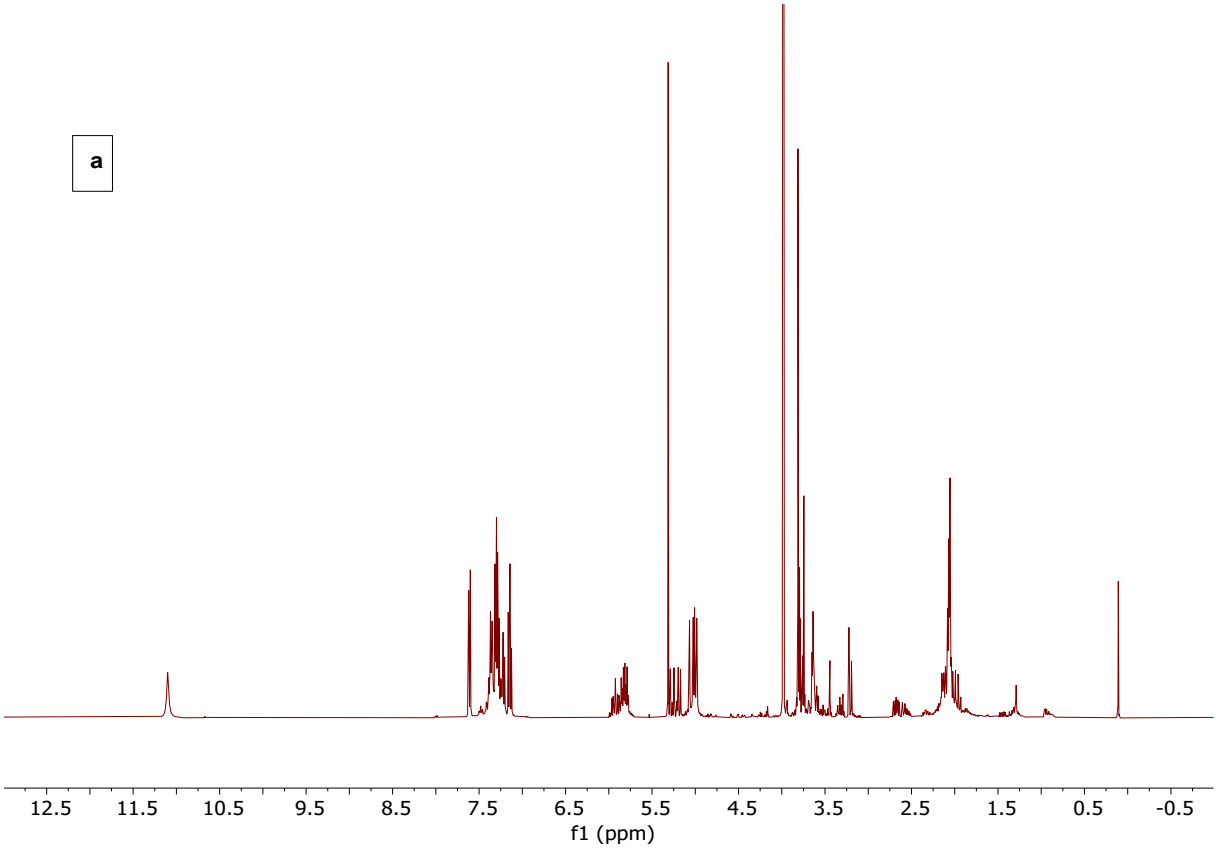


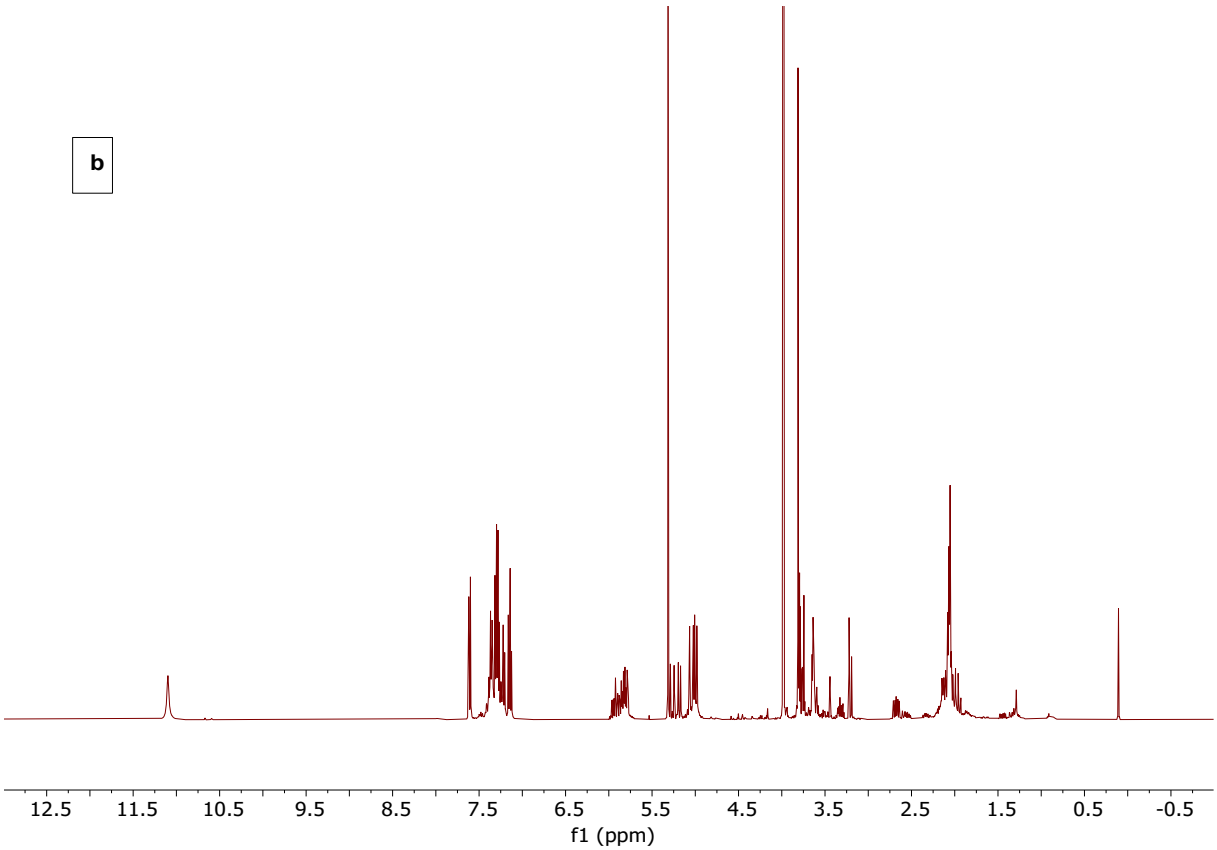
^{1}H NMR spectra of products 13+14 from the decomposition of 10 with $Rh_2(OAc)_3(tfa)$ (400 MHz, $CDCl_3$)



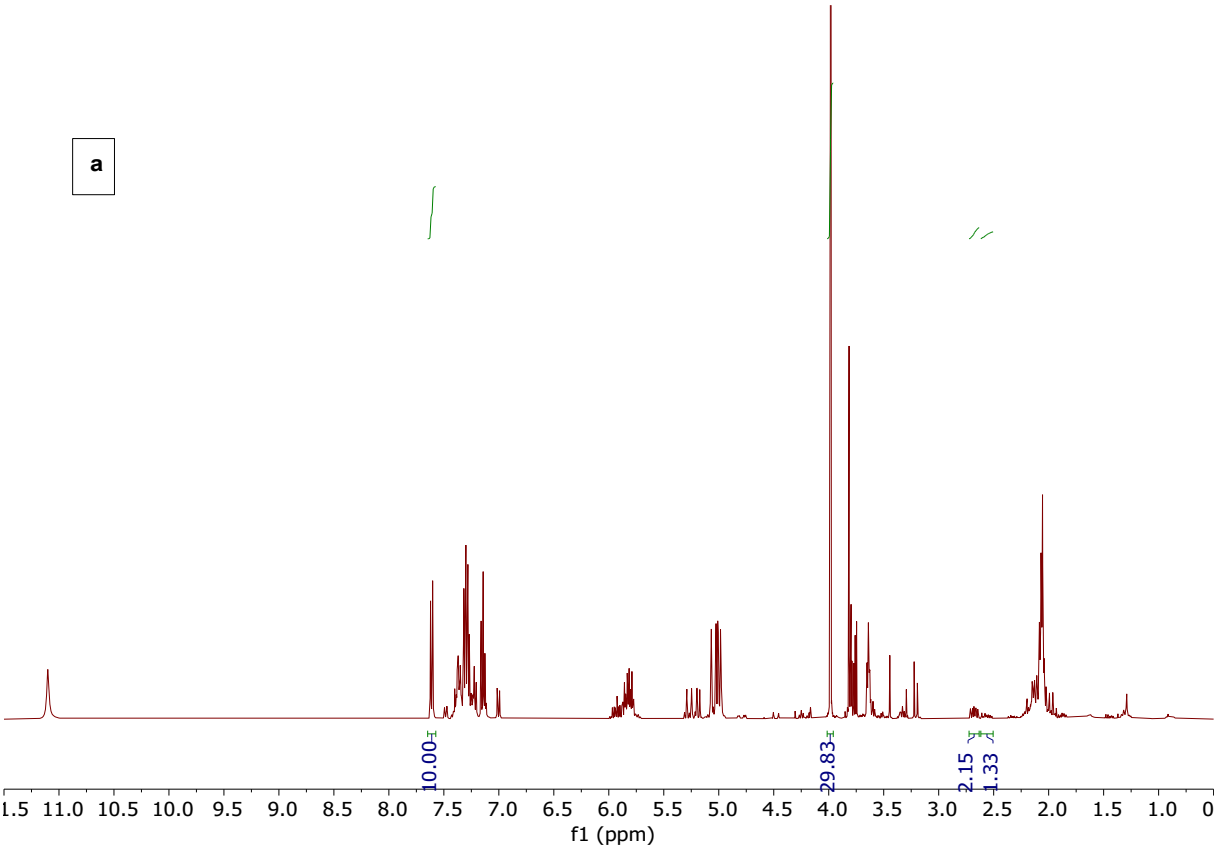


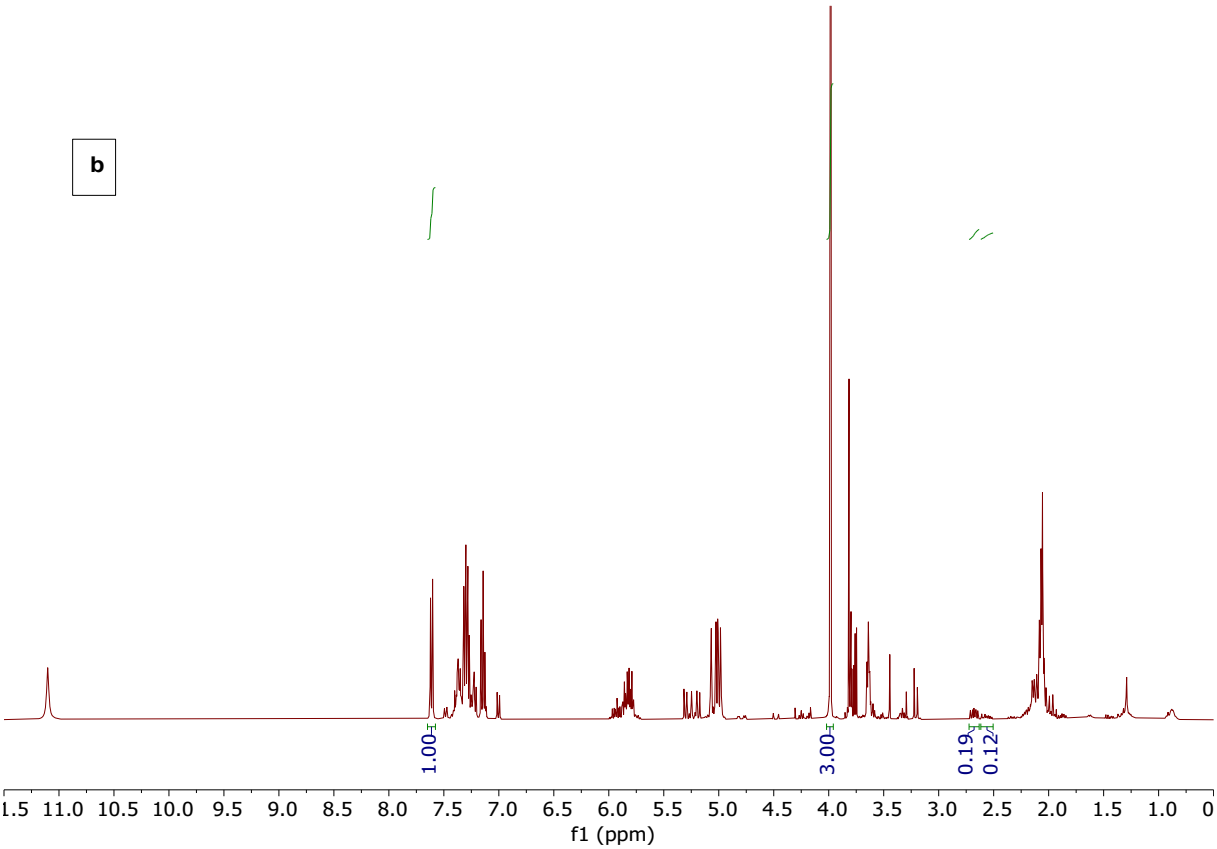
^{1}H NMR spectra of products 13+14 from the decomposition of 10 with 1a (400 MHz, $CDCl_3$)



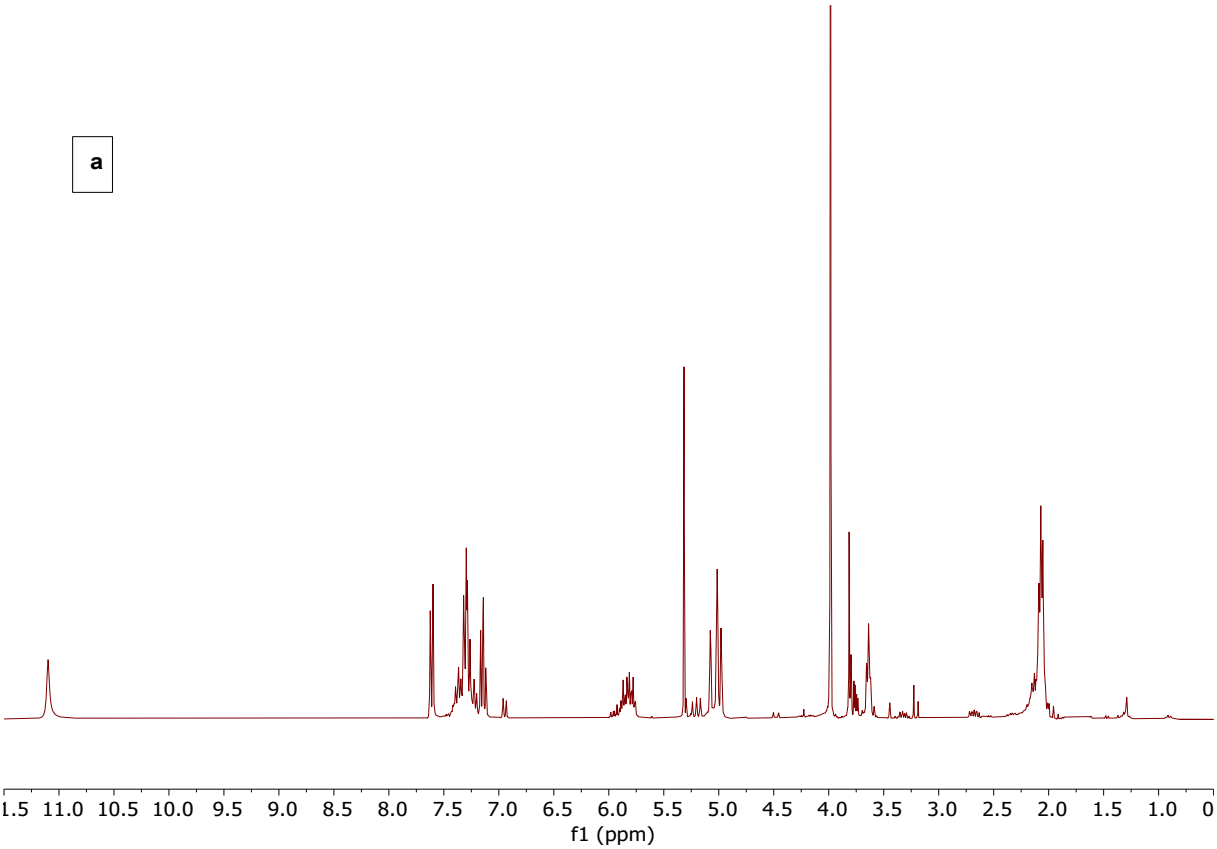


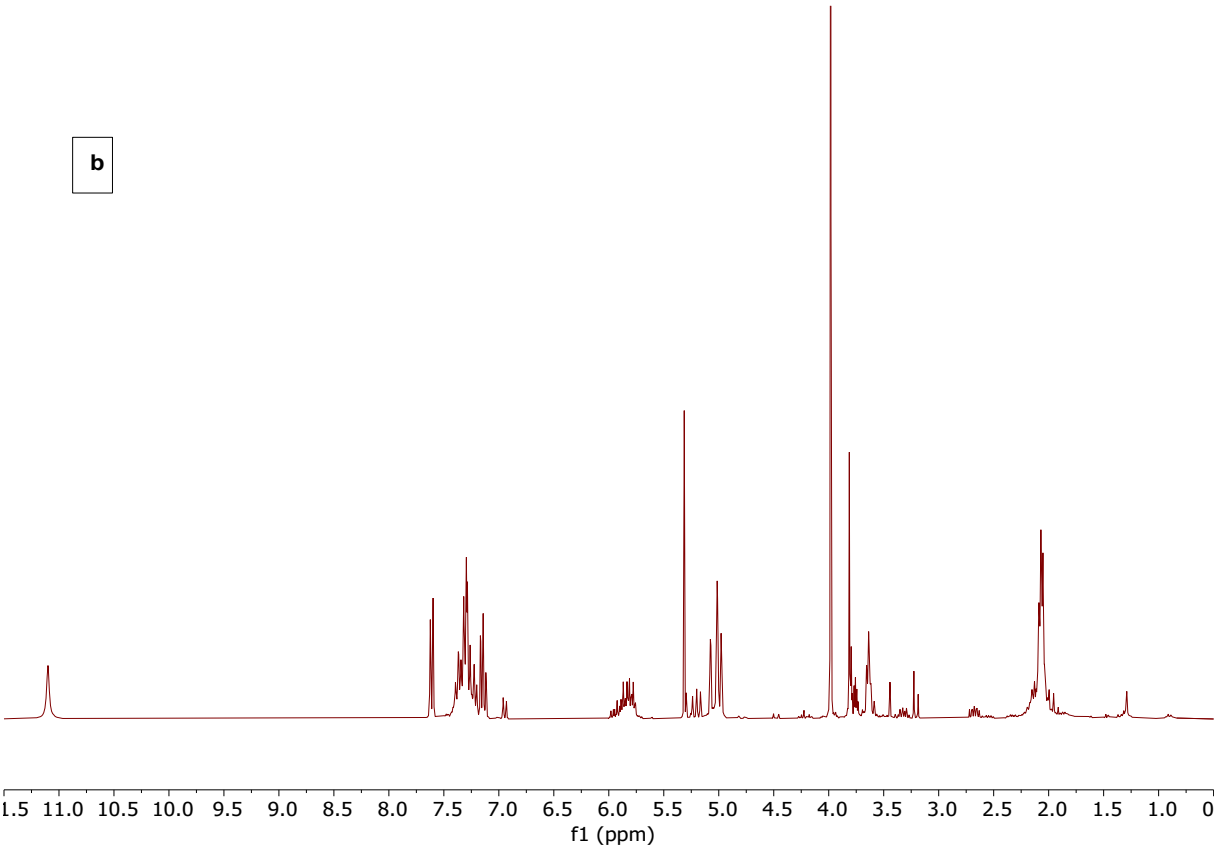
^{1}H NMR spectra of products 13+14 from the decomposition of 10 with $1a^+BF_4^-$ (400 MHz, $CDCl_3$)



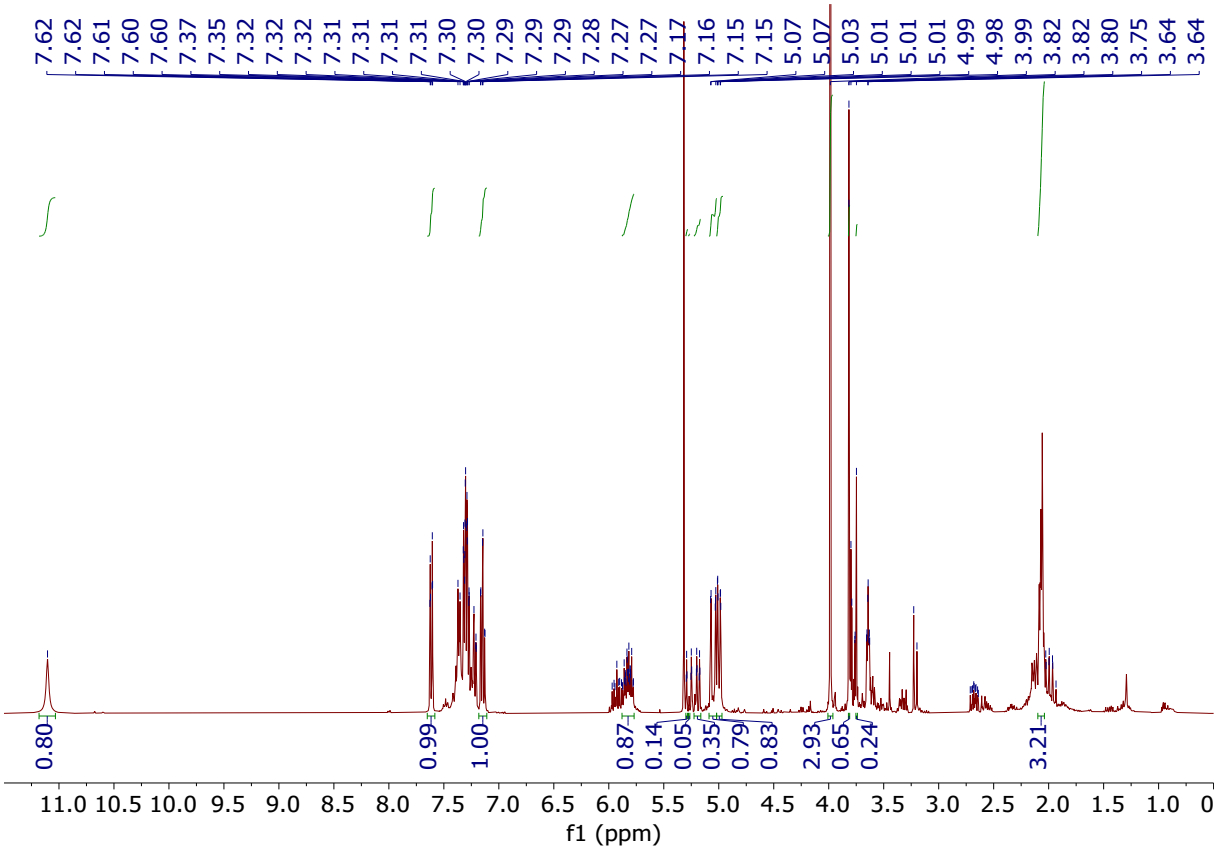


^{1}H NMR spectra of products 13+14 from the decomposition of 10 with $1a^+SbF_6^-$ (300 MHz, $CDCl_3$)

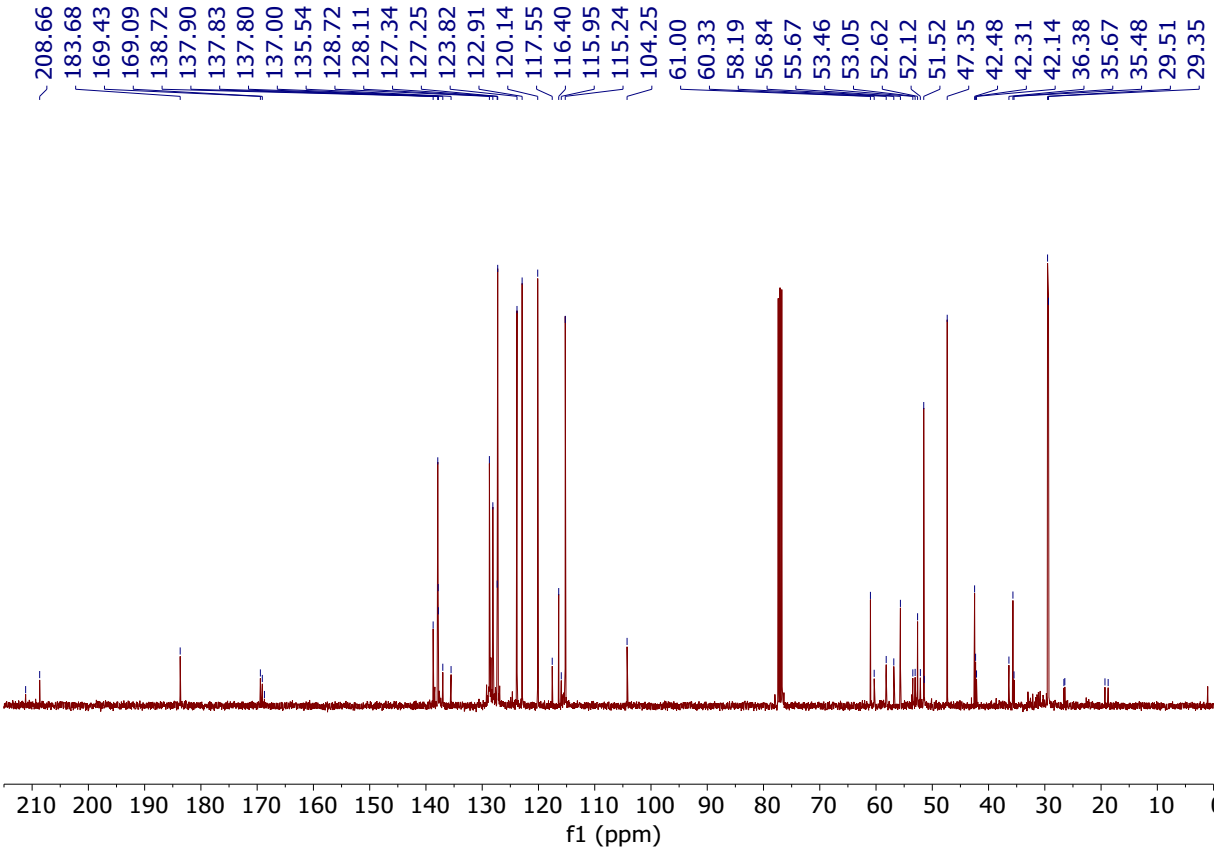




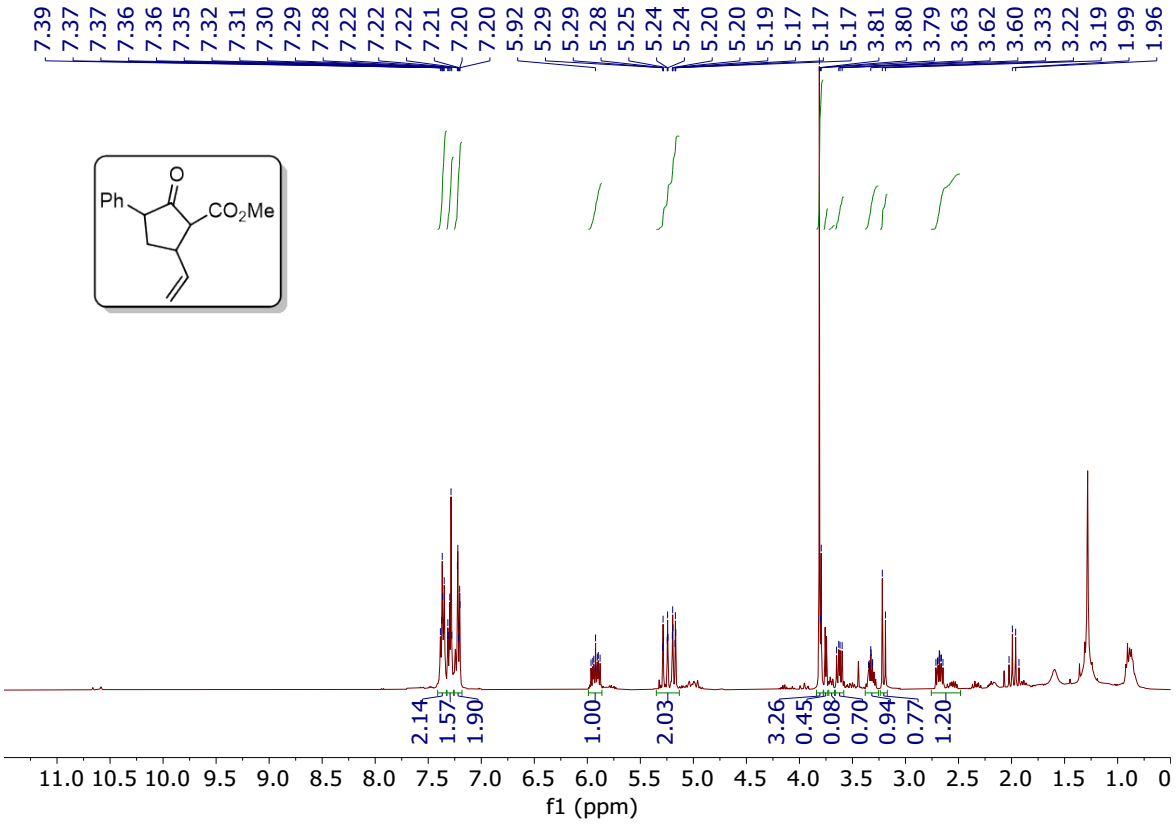
^{1}H NMR spectra of products 13+14 from the decomposition of 10 (400 MHz, $CDCl_3$)



^{13}C NMR spectra of products 13+14 from the decomposition of 10 (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of product 14 (+traces of 13) from the decomposition of 10 (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product 14 (+traces of 13) from the decomposition of 10 (101 MHz, $CDCl_3$)