Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Rh-Catalysed Hydroacyloxylation of Cyclopropenes: Regio- and Diastereoselective Synthesis of Acyloxycyclopropanes

Ángel Manu Martínez,[1]* Gema Domínguez,[1] Inés Alonso,[2] Marta Palaín,[1] and Javier Pérez-Castells[1]*

*Correspondence to:

jpercas@ceu.es

angel.martinezgarzon@ceu.es

[1]*Department of Chemistry and Biochemistry. School of Pharmacy. Universidad San Pablo-CEU, CEU Universities. Urbanización Montepríncipe, Boadilla del Monte, 28668 Madrid, SPAIN.*

[2]*Department of Organic Chemistry. School of Science. Universidad Autónoma de Madrid. Campus de Cantoblanco. 28049 Madrid, SPAIN. Institute for Advanced Research in Chemical Sciences (IAdChem) and Center for Innovation in Advanced Chemistry (ORFEO-CINQA). Universidad Autónoma de Madrid, 28049 Madrid (Spain).*

1. Experimental procedures and data

Materials and methods. The corresponding starting materials were synthesised using oven-dried glassware under an argon atmosphere containing a Teflon-coated stirrer bar and dry septum. All reactions were performed at ambient argon pressure in oven-dried 10 mL vessels equipped with a Teflon-coated stirrer bar and sealed with a cap designed to vent and re-seal in the case of overpressure during the reaction.

Solvents were purified by standard procedures prior to use. All other commercially available compounds at Aldrich/Merck, BLDpharm, abcr, Acros, VWR and Fluorochem were used without further purification.

Thin-layer chromatography (TLC) analyses were performed on Merck silica gel 60 F254 plates using phosphomolybdic acid for detection. Column chromatography was performed using 230-400 mesh ultra-pure silica gel.

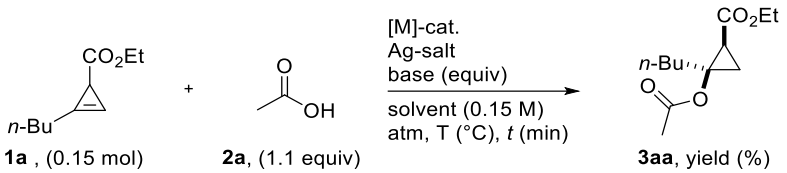
NMR spectra were obtained on a Bruker Advance III spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C and 377 MHz for ^{19}F) using acetone-d_6, chloroform-*d*, methanol-d_4 and dimethylsulfoxide-d_6 as solvents. The following abbreviations are used: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; dt, double triplet; m, multiplet.

Infrared experiments were carried out in a PerkinElmer Spectrum 100 FT-IR Spectrometer. Mass spectral data were acquired on a VG *AutoSpec* mass spectrometer.

2. Additional information

2.1. Optimisation of reaction conditions

Table S1. Optimisation of Rh-catalysed hydroacetoxylation of **1a**

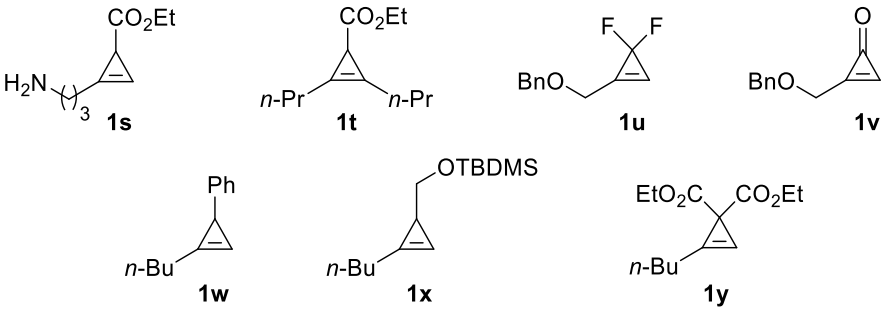


1a , (0.15 mol) **2a**, (1.1 equiv) **3aa**, yield (%)

#	[M]-cat (mol %)		Ag-salt (mol%)		base (equiv)		2a (equiv)	solvent	*T* (°C)	*t* (h)	3aa (%)[a]
1	$RuCl_3$	5.0	–	–	–	–	1.2	toluene	60	16	<2%
2	$RuCl_2(PPh_3)_2$	5.0	–	–	–	–	1.2	toluene	60	16	<2%
3[1]	$[RuCl_2(p\text{-cym})]_2$	5.0	$P(Fur)_3$	8.0	Na_2CO_3	0.2	1.2	toluene	60	16	<2%
4	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	16	73%
5	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	82%
6	–	–	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
7	$[RhCp^*Cl_2]_2$	5.0	–	–	NaOAc	1.2	1.2	DCE	60	2	<2%
8	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	–	–	1.2	DCE	60	2	<2%
9	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	–	DCE	60	2	25%
10	$[RhCl(COD)]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
11	$[Rh(OAc)_2]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
12	$Pd(OAc)_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
13	$Mn(OAc)_2{\cdot}2H_2O$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
14	$Cu(OAc)_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	1.2	DCE	60	2	<2%
15	$[RhCp^*Cl_2]_2$	5.0	AgOAc	10	NaOAc	1.2	1.2	DCE	60	2	<2%
16	$[RhCp^*Cl_2]_2$	5.0	Ag_2CO_3	10	NaOAc	1.2	1.2	DCE	60	2	<2%
17	$[RhCp^*Cl_2]_2$	5.0	Ag_2SO_4	10	NaOAc	1.2	1.2	DCE	60	2	<2%
18	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	1.2	0.6	DCE	60	2	44%
19	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	0.6	1.2	DCE	60	2	98%
20	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	0.2	1.2	DCE	60	2	98%
21	$[RhCp^*Cl_2]_2$	5.0	$AgSbF_6$	10	NaOAc	0.1	1.2	DCE	60	2	91%
22	**$[RhCp^*Cl_2]_2$**	**2.5**	**$AgSbF_6$**	**5.0**	**NaOAc**	**0.2**	**1.2**	**DCE**	**60**	**2**	**98%**
23	$[RhCp^*Cl_2]_2$	1.0	$AgSbF_6$	2.0	NaOAc	0.2	1.2	DCE	60	2	60%
24	$[RhCp^*Cl_2]_2$	0.5	$AgSbF_6$	1.0	NaOAc	0.2	1.2	DCE	60	2	23%
25[b]	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	60	2	<2%
26[c]	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	60	2	35%
27	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	80	2	40%
28	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	40	2	94%
29	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	30	2	22%
30	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	60	1.5	89%
31	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	DCE	60	1.0	67%
32	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	dioxane	60	2	<2%
33	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	acetone	60	2	<2%
34	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	EtOAc	60	2	72%
35	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	EtOH	60	2	<2%
36	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	*n*-hexane	60	2	95%
37	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	MeCN	60	2	<2%
38	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	THF	60	2	<2%
39	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	toluene	60	2	<2%
40	$[RhCp^*Cl_2]_2$	2.5	$AgSbF_6$	5.0	NaOAc	0.2	1.2	water	60	2	36%
41	**$[RhCp^*Cl_2]_2$**	**2.5**	**$AgSbF_6$**	**5.0**	**Na_2CO_3**	**0.2**	**1.2**	**DCE**	**60**	**2**	**92%**

Reaction conditions: **1a** (0.15 mmol), [M]-cat. (mol%), Ag-salt (mol%), base (equiv), AcOH (equiv), atmosphere, temperature (°C), time (min). [a] ^1H NMR yields using anisole as standard. [b] In the presence of water (10 equiv). [c] Under air.

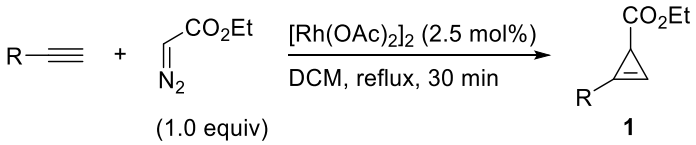
2.2. Unsuccessful substrates



Scheme S1. Unsuccessful substrates in Rh(III)-catalysed hydroacyloxylation

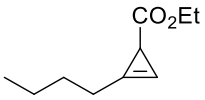
3. Synthesis of substrates

3.1. Typical procedure (A) for the synthesis of ethyl cyclopropenecarboxylates

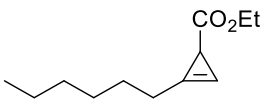


Scheme S2. Synthesis of ethyl cycloprop-2-ene-1-carboxylates from alkynes

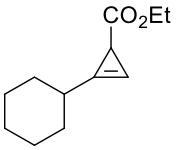
Synthesis of ethyl 2-butylcycloprop-2-ene-1-carboxylate (1a). Following a modified procedure described by Marek and Shi,[2] an oven-dried 100 mL three-necked round-bottomed flask was charged with a mixture of rhodium(II) acetate dimer (4.4 mg, 0.010 mmol, 0.025 equiv) and 1-hexyne (0.47 mL, 4.0 mmol, 1.0 equiv), in refluxing dichloromethane (15 mL). To this mixture, ethyl diazoacetate (80%) (0.53 mL, 4.0 mmol, 1.0 equiv) in 15 mL of dichloromethane was added dropwise. After addition, the resulting mixture was stirred for 30 minutes at that temperature, then cooled down and filtrated through a pad of Celite®. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 9:1) to give **1a** as a colourless oil; yield: 0.55 g (81%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.32 (q, *J* = 1.3 Hz, 1H), 4.16 – 4.08 (m, 2H), 2.49 (td, *J* = 7.4, 1.1 Hz, 2H), 2.12 (d, *J* = 1.5 Hz, 1H), 1.59 – 1.53 (m, 2H), 1.43 – 1.36 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.9, 115.7, 94.0, 60.3, 28.9, 24.8, 22.3, 19.8, 14.5, 13.9 ppm. Data consistent with the literature.[3]



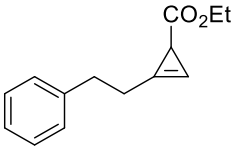
Ethyl 2-hexylcycloprop-2-ene-1-carboxylate (1b). Compound **1b** was prepared following the typical procedure A from 1-octyne (0.61 mL, 4.0 mmol, 1.0 equiv) to give **1b** as a colourless oil; yield: 0.67 g (85%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.31 (q, *J* = 1.3 Hz, 1H), 4.16 – 4.07 (m, 2H), 2.48 ((td, *J* = 7.4, 1.0 Hz, 2H), 2.11 (d, *J* = 1.5 Hz, 1H), 1.60 – 1.53 (m, 2H), 1.38 – 1.27 (m, 6H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm. Data consistent with the literature.[4]



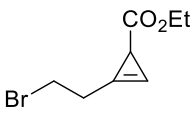
Ethyl 2-cyclohexylcycloprop-2-ene-1-carboxylate (1c). Compound **1c** was prepared following the typical procedure A from ethynylcyclohexane (0.45 g, 4.0 mmol, 1.0 equiv) to give **1c** as a colourless oil; yield: 0.65 g (83%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.24 (s, 1H), 4.19 – 4.06 (m, 2H), 2.59 – 2.55 (m, 1H), 2.13 (d, *J* = 1.4, 1H), 1.91 – 1.83 (m, 2H), 1.73 – 1.67 (m, 2H), 1.62 – 1.59 (m, 1H), 1.41 – 1.28 (m, 5H), 1.25 (t, *J* = 7.1, 3H) ppm. Data consistent with the literature.[3]



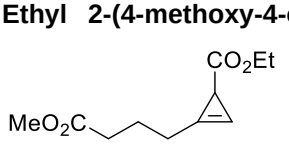
Ethyl 2-phenethylcycloprop-2-ene-1-carboxylate (1d). Compound **1d** was prepared following the typical procedure A from 4-phenyl-1-butyne (0.56 mL, 4.0 mmol, 1.0 equiv) to give **1d** as a colourless oil; yield: 0.65 g (75%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 6.39 (s, 1H), 4.20 – 4.11 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.87 – 2.83 (m, 2H), 2.18 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. Data consistent with the literature.[5]



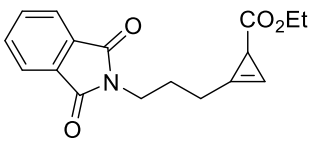
Ethyl 2-(2-bromoethyl)cycloprop-2-ene-1-carboxylate (1e). Compound **1e** was prepared following the typical procedure A from ((prop-2-yn-1-yloxy)methyl)benzene (0.38 mL, 4.0 mmol, 1.0 equiv) to give **1e** as a colourless oil; yield: 0.61 g (70%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.54 (s, 1H), 4.15 – 4.09 (m, 2H), 3.56 – 3.50 (m, 2H), 3.08 (t, *J* = 6.9 Hz, 2H), 2.21 (s, 1H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm.**^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.1, 113.1, 97.0, 60.5, 28.8, 28.2, 19.8, 14.5 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2976, 2939, 1720 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_8H_{11}BrO_2$ $[M+H]^+$ 219.0015, found 219.0017.



Ethyl 2-(4-methoxy-4-oxobutyl)cycloprop-2-ene-1-carboxylate (1f). Compound **1f** was prepared following the typical procedure A from methyl hex-5-ynoate (0.51 g, 4.0 mmol, 1.0 equiv) to give **1f** as a colourless oil; yield: 0.60 g (71%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.34 (q, *J* = 1.3 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.60 (s, 3H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.06 (t, *J* = 3.4 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.5, 173.6, 114.7, 95.3, 60.4, 51.7, 33.2, 24.5, 22.2, 19.8, 14.5 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2976, 2953, 1738 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{11}H_{16}O_4$ $[M+H]^+$ 213.1121, found 213.1122.



Ethyl 2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cycloprop-2-ene-1-carboxylate (1g). Compound **1g** was prepared following the typical procedure A from 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (0.85 g, 8.0 mmol, 1.0 equiv) to give **1g** as a colourless oil; yield: 1.0 g (84%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.86 – 7.82 (m, 2H), 7.73 – 7.70 (m, 2H), 6.41 (q, *J* = 1.2 Hz, 1H), 4.16 – 4.08 (m, 2H), 3.76 (td, *J* = 7.0, 2.1 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.15 (d, *J* = 1.3 Hz, 1H), 2.02 – 1.95 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.4, 168.4, 134.1, 132.2, 123.4, 114.6, 95.5, 60.4, 37.4, 26.0, 22.9, 20.0, 14.5 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2985, 2870, 1775, 1711, 1616 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{17}H_{17}NO_4$ $[M+H]^+$ 300.1230, found 300.1229.



Ethyl 2-((benzyloxy)methyl)cycloprop-2-ene-1-carboxylate (1i). Compound **1i** was prepared following the typical procedure A from ((prop-2-yn-1-yloxy)methyl)benzene (0.59 g, 4.0 mmol, 1.0 equiv) to give **1i** as a colourless oil; yield: 0.53 g (57%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.36 – 7.28 (m, 5H), 6.67 (q, *J* = 1.4 Hz, 1H), 4.61 (d, *J* = 1.8 Hz, 2H), 4.54 (d, *J* = 1.5 Hz, 2H), 4.18 – 4.10 (m, 2H), 2.31 (d, *J* = 1.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. Data consistent with the literature.[6]

Ethyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)cycloprop-2-ene-1-carboxylate (1j). Compound **1j** was prepared following the typical procedure A from *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (0.68 g, 4.0 mmol, 1.0 equiv) to give **1j** as a colourless oil; yield: 0.76 g (74%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.54 (q, *J* = 1.6 Hz, 1H), 4.71 – 4.61 (m, 2H), 4.15 – 4.09 (m, 2H), 2.28 (d, *J* = 1.3 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 175.8, 114.8, 96.1, 60.4, 58.2, 25.9, 20.8, 18.4, 14.5, -5.2, -5.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2953, 2851, 1734 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{13}H_{24}O_3Si$ $[M+H]^+$ 257.1567, found 257.1568.

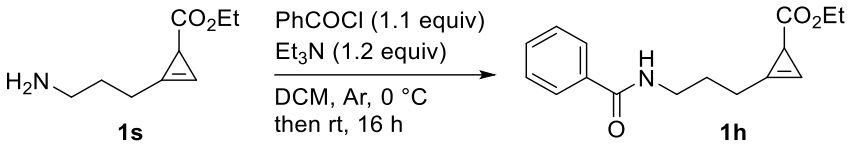
Ethyl 2-(diethoxymethyl)cycloprop-2-ene-1-carboxylate (1k). Compound **1k** was prepared following the typical procedure A from 3,3-diethoxyprop-1-yne (0.58 mL, 4.0 mmol, 1.0 equiv) to give **1k** as a colourless oil; yield: 0.40 g (47%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.79 (s, 1H), 5.50 (s, 1H), 4.17 – 4.11 (m, 2H), 3.65 – 3.58 (m, 4H), 2.36 (d, *J* = 1.1 Hz, 1H), 1.27 – 1.21 (m, 9H) ppm. Data consistent with the literature.[7]

Ethyl 2-butyl-1-phenylcycloprop-2-ene-1-carboxylate (1o). Compound **1o** was prepared following the typical procedure A from ethyl 2-diazo-2-phenylacetate (760 mg, 4.0 mmol, 1.0 equiv) to give **1o** as a colourless oil; yield: 0.46 g (47%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.31 – 7.27 (m, 4H), 7.22 – 7.18 (m, 1H), 6.66 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.41 – 1.31 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 175.4, 141.9, 128.2, 127.9, 126.0, 120.7, 96.8, 60.5, 33.0, 28.8, 24.1, 22.2, 14.3, 13.7 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2959, 2936, 2872, 1715, 1597 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{20}O_2$ $[M+H]^+$ 245.1536, found 245.1539.

Ethyl 2,3-dipropylcycloprop-2-ene-1-carboxylate (1t). Compound **1t** was prepared following the typical procedure A from oct-4-yne (0.59 mL, 4.0 mmol, 1.0 equiv) to give **1t** as a colourless oil; yield: 0.49 g (76%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.03 (q, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 4H), 1.96 (s, 1H), 1.55 – 1.46 (m, 4H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 177.0, 105.7, 59.7, 26.5, 22.2, 20.4, 14.4, 13.8 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2966, 2939, 2874, 1724 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{12}H_{20}O_2$ $[M+H]^+$ 197.1536, found 197.1534.

Diethyl 2-butylcycloprop-2-ene-1,1-dicarboxylate (1y). Compound **1y** was prepared following the typical procedure A from diethyl 2-diazomalonate (744 mg, 4.0 mmol, 1.0 equiv) to give **1y** as a colourless oil; yield: 0.61 g (64%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.34 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.40 – 1.34 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 6H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.**^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 171.7, 114.8, 93.7, 61.0, 32.8, 28.6, 23.8, 22.2, 14.3, 13.7 ppm. Data consistent with the literature.[8]

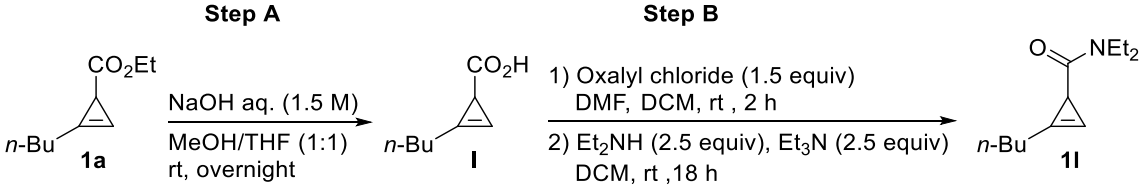
3.2. Synthesis of ethyl 2-(3-benzamidopropyl)cycloprop-2-ene-1-carboxylate (1h)



Scheme S3. Synthesis of derivative **1h** by benzoylation of **1s**

Following a procedure described by König,[9] an oven-dried flask was charged with a suspension of ethyl 2-(3-aminopropyl)cycloprop-2-ene-1-carboxylate (**1s**) (1.0 g, 6.0 mmol, 1.0 equiv) in dry dichloromethane (10 mL), to which triethylamine (1.0 mL, 7.2 mmol, 1.2 equiv) was added under argon atmosphere. The reaction mixture was then cooled to 0 °C, and benzoyl chloride (0.77 mL, 6.6 mmol, 1.1 equiv) was added dropwise. After stirring the suspension at 25 °C for a given time, the mixture was diluted with dichloromethane (10 mL) and washed with water. The aqueous phase was extracted with dichloromethane (3 × 5 mL), the combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 6:1) to give **1h** as a colourless oil; yield: 1.5 g (92%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.81 – 7.78 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 6.85 (bs, 1H), 6.36 (q, *J* = 1.2 Hz, 1H), 4.18 – 4.10 (m, 2H), 3.58 – 3.53 (m, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.16 (d, *J* = 1.3 Hz, 1H), 1.97 – 1.91 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 177.1, 167.7, 134.6, 131.4, 128.6, 127.1, 114.7, 95.3, 60.6, 39.3, 26.4, 22.9, 19.8, 14.5 ppm. **IR (NaCl)** $\tilde{\nu}$ = 3330 (broad), 2982, 2959, 2932, 2855, 1718, 1641, 1603 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{19}NO_3$ $[M+H]^+$ 274.1438, found 274.1442.

3.3. Synthesis of 2-butyl-*N*,*N*-diethylcycloprop-2-ene-1-carboxamide (1l)



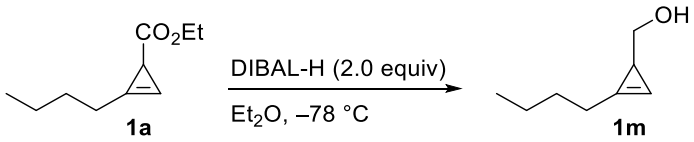
Scheme S4. Hydrolysis of **1a** towards derivative **1l**

Step A. Following a procedure described by Rubin,[10] an oven-dried 10 mL vessel was charged with a solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (0.67 g, 4.0 mmol, 1.0 equiv) in a 1:1 mixture of methanol and tetrahydrofuran (6.0 mL). At 0 °C, 3 M aqueous sodium hydroxide solution (1.7 mL, 2.3 mmol,

0.65 equiv) was added dropwise and stirred at room temperature overnight. The volatiles were removed under reduced pressure, and the remaining aqueous solution was acidified to pH = 2 by adding 1 M aqueous hydrochloric acid. The aqueous phase was extracted with dichloromethane (3 × 5 mL), the combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 2:1) to give **I** as a colourless oil; yield: 0.32 g (57%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 11.89 (bs, 1H), 6.32 (q, *J* = 1.3 Hz, 1H), 2.49 (t, *J* = 7.4 Hz, 2H), 2.10 (d, *J* = 1.5 Hz, 1H), 1.60 – 1.53 (m, 2H), 1.42 – 1.33 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 183.7, 115.3, 93.5, 28.7, 24.7, 22.3, 19.6, 13.8 ppm. Data consistent with the literature.[10]

Step B. Following the same procedure described by Rubin,[10] an oven-dried 20 mL vessel was charged with 2-butylcycloprop-2-ene-1-carboxylic acid **I** (0.28 g, 2.0 mmol, 1.0 equiv), DMF (1 drop) and dry dichloromethane (10 mL). Under an argon atmosphere, oxalyl chloride (0.26 mL, 3.0 mmol, 1.5 equiv) was added dropwise, and the mixture was stirred at room temperature for 2 hours. The solution was concentrated under reduced pressure to provide a yellow oil residue, which was re-dissolved in anhydrous dichloromethane (5.0 mL) and added dropwise to a solution of diethylamine (0.41 mL, 4.0 mmol, 2.0 equiv) and triethylamine (0.56 mL, 4.0 mmol, 2.0 equiv) in dichloromethane (8.0 mL). The reaction mixture was stirred at room temperature over the weekend. Water was added to the reaction crude (8.0 mL), and the aqueous phase was acidified to pH = 2 by adding 1 M aqueous hydrochloric acid. The organic phase was separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 4:1) to give **1l** as a colourless oil; yield: 0.14 g (36%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.31 (d, *J* = 1.2 Hz, 1H), 3.51 (q, *J* = 7.1 Hz, 2H), 3.43 – 3.33 (m, 2H), 2.58 – 2.43 (m, 2H), 2.31 (d, *J* = 1.3 Hz, 1H), 1.61 – 1.54 (m, 2H), 1.42 – 1.33 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 174.4, 115.3, 93.7, 41.4, 40.6, 28.7, 24.5, 22.0, 18.2, 14.6, 13.5, 12.9 ppm. **HRMS (ESI)** *m/z* calcd. for $C_{12}H_{21}NO$ $[M+H]^+$ 196.1696, found 196.1697.

3.4. Synthesis of (2-butylcycloprop-2-en-1-yl)methanol (1m)

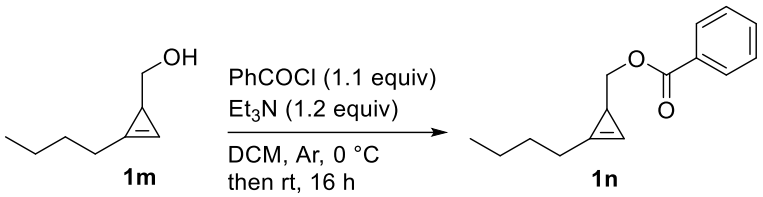


Scheme S5. Reduction **1a** towards derivative **1m**

Following a modified procedure described by Gevorgyan,[6] an oven-dried 10 mL vessel was charged with a solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (0.67 g, 4.0 mmol, 1.0 equiv) in dry ether (10 mL). A 1.2 M solution of DIBAL-H in toluene (6.7 mL, 8.0 mmol, 2.0 equiv) was added dropwise via syringe at −78 °C. The resulting mixture was stirred for 1 hour at that temperature and 1 additional hour at room

temperature. The reaction mixture was quenched with 10 mL of a saturated aqueous ammonium chloride solution, acidified with a 1.0 M aqueous hydrochloric acid solution, and extracted with diethyl ether (3 × 10 mL). The combined organics were washed with 10 mL of a saturated aqueous solution of sodium bicarbonate, dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 9:1) to give **1m** as a colourless oil; yield: 0.40 g (80%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.61 (s, 1H), 3.56 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.43 (dd, *J* = 10.6, 4.8 Hz, 1H), 2.46 (t, *J* = 7.3 Hz, 2H), 1.67 (td, *J* = 4.7, 1.4 Hz, 1H), 1.57 – 1.50 (m, *J* = 14.9 Hz, 2H), 1.41 – 1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. Data consistent with the literature.[6]

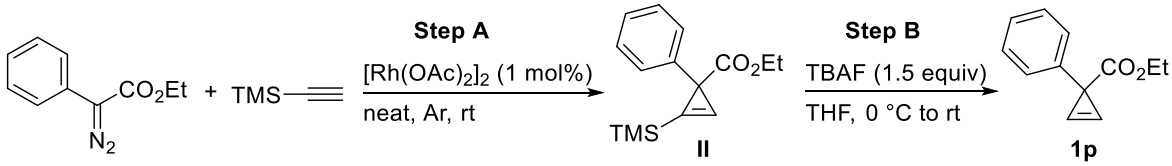
3.5. Synthesis of (2-butylcycloprop-2-en-1-yl)methyl benzoate (1n)



Scheme S6. Synthesis of derivative **1n** by benzoylation of **1m**

An oven dried flask was charged with a suspension of (2-butylcycloprop-2-en-1-yl)methanol (**1m**) (0.25 mg, 2.0 mmol, 1.0 equiv) in dry dichloromethane (10 mL) to which triethylamine (0.34 mL, 2.4 mmol, 1.2 equiv) was added under argon atmosphere. The reaction mixture was then cooled to 0 °C, and benzoyl chloride (0.26 mL, 2.2 mmol, 1.1 equiv) was added dropwise. After stirring the suspension at 25 °C for a given time, the mixture was diluted with dichloromethane (10 mL) and washed with water. The aqueous phase was extracted with dichloromethane (3 × 5 mL), the combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 20:1) to give **1n** as a colourless oil; yield: 0.39 g (85%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 8.07 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.61 (s, 1H), 4.26 (dd, *J* = 11.0, 5.0 Hz, 1H), 4.15 (dd, *J* = 11.0, 5.4 Hz, 1H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.81 (td, *J* = 5.2, 1.3 Hz, 1H), 1.60 – 1.53 (m, 2H), 1.42 – 1.33 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 166.9, 132.8, 131.0, 129.7, 128.4, 124.9, 101.7, 72.8, 29.3, 25.9, 22.5, 16.9, 14.0 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2956, 2932, 2858, 1716, 1601, 1583 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{18}O_2$ $[M+H]^+$ 231.1380, found 231.1381.

3.6. Synthesis of ethyl 1-phenylcycloprop-2-ene-1-carboxylate (1p)

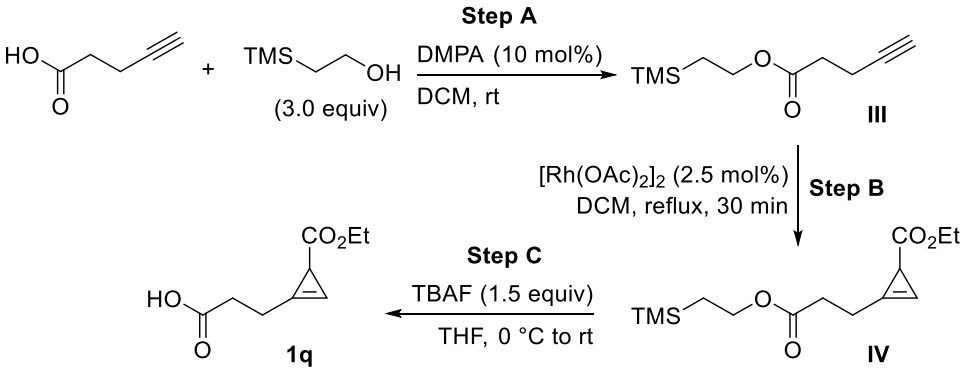


Scheme S7. Synthetic route towards derivative **1p**

Step A. Following a modified procedure described by Zhao,[11] an oven-dried 25 mL round-bottomed flask was charged with rhodium(II) acetate dimer (17 mg, 0.040 mmol, 0.010 equiv) and trimethylsilylacetylene (3.0 mL). To the resulting suspension, a solution of ethyl 2-diazo-2-phenylacetate (0.76 mg, 4.0 mmol, 1.0 equiv) in trimethylsilylacetylene (5.0 mL) was added at room temperature over 18 hours *via* syringe pump. Once the addition is complete, the volatiles were evaporated under reduced pressure, and the resulting residue was purified by silica gel column chromatography to afford **II** as a pale yellow oil; yield: 0.49 g (47%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.43 (s, 1H), 7.27 – 7.24 (m, 4H), 7.19 – 7.44 (m, 1H), 4.18 – 4.11 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.20 (s, 9H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 175.7, 142.7, 128.4, 128.0, 126.0, 119.8, 116.0, 60.7, 31.6, 14.5, −1.2 ppm.

Step B. Following a modified procedure described by Peters and Pérez-Castells,[12] an oven dried 10 mL vial was charged with ethyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**II**) (0.26 g, 1.0 mmol, 1.0 equiv) and dissolved in tetrahydrofuran (8.0 mL). To the resulting solution, a 1.0 M solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (1.5 mL, 1.5 mmol, 1.5 equiv) was added dropwise via syringe at 0 °C. The mixture was stirred for 90 minutes at room temperature. The reaction solvent was removed under reduced pressure, and the residue was re-dissolved in ethyl acetate (25 mL). The organic layer was washed with water, then dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 9:1) to give **1p** as a colourless oil; yield: 0.17 g (90%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.33 – 7.24 (m, 5H), 5.21 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. Data consistent with the literature.[11]

3.7. Synthesis of 3-(3-(ethoxycarbonyl)cycloprop-1-en-1-yl)propanoic acid (1q)



Scheme S8. Synthetic route towards derivative **1q**

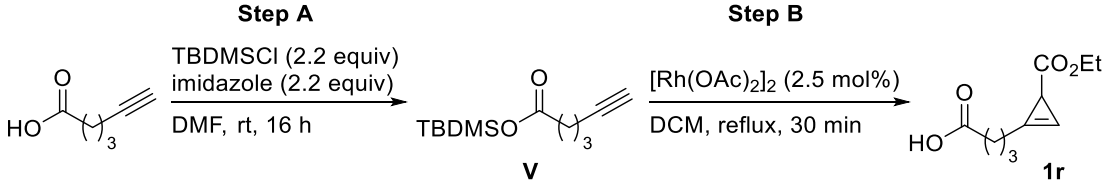
Step A. Following a modified procedure described by Bannwarth,[13] an oven-dried 25 mL round-bottomed flask was charged with a solution of 4-pentynoic acid (0.40 g, 4.0 mmol, 1.0 equiv), 2-(trimethylsilyl)ethanol (1.4 g, 12 mmol, 3.0 equiv) and 4-(*N*,*N*-dimethylamino)pyridine (41 mg, 0.40 mmol, 0.10 equiv) in dichloromethane (7.0 mL). After 30 minutes at room temperature, *N*,*N*-dicyclohexylcarbodiimide (0.83 g, 4.0 mmol, 1.0 equiv) was added at 0 °C. The reaction mixture was left stirring at room temperature for 24 hours. Then, urea was filtered through a pad of Celite®. Volatiles were removed under reduced pressure,

and the residue was purified by column chromatography on silica gel (DCM as eluent) to give 2-(trimethylsilyl)ethyl pent-4-ynoate (**III**) as a colourless oil; yield: 0.60 g (75%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.22 – 4.18 (m, 2H), 2.55 – 2.50 (m, 4H), 1.97 (t, *J* = 2.4 Hz, 1H), 1.02 – 0.97 (m, 2H), 0.04 (s, 9H) ppm. Data consistent with the literature.[14]

Step B. Compound **IV** was prepared following the typical procedure A from 2-(trimethylsilyl)ethyl pent-4-ynoate (**III**) (0.60 g, 3.0 mmol, 1.0 equiv) to give ethyl 2-(3-oxo-3-(2-(trimethylsilyl)ethoxy)propyl)cycloprop-2-ene-1-carboxylate (**IV**) as a colourless oil; yield: 0.34 g (40%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.37 (q, *J* = 1.3 Hz, 1H), 4.16 – 4.12 (m, 2H), 4.12 – 4.04 (m, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.12 (d, *J* = 1.4 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.97 – 0.93 (m, 2H), 0.00 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 176.3, 172.3, 114.3, 95.5, 63.1, 60.4, 31.7, 20.8, 20.0, 17.4, 14.5, -1.4. **IR (NaCl)** $\tilde{\nu}$ = 3141, 2955, 2901, 1805, 1731 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{24}O_4Si$ $[M+H]^+$ 285.1517, found 285.1521.

Step C. Following a modified procedure described by Peters and Pérez-Castells,[12] an oven dried 10 mL vial was charged with ethyl 2-(3-oxo-3-(2-(trimethylsilyl)ethoxy)propyl)cycloprop-2-ene-1-carboxylate (**IV**) (0.14 g, 0.5 mmol, 1.0 equiv) and dissolved in tetrahydrofuran (4.0 mL). To the resulting solution, a 1.0 M solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (0.75 mL, 0.75 mmol, 1.5 equiv) was added dropwise via syringe at 0 °C. The mixture was stirred for 90 minutes at room temperature. The reaction solvent was removed under reduced pressure, and the residue was re-dissolved in ethyl acetate (15 mL). The organic layer was washed with water, then dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (DCM/MeOH; 20:1) to give 3-(3-(ethoxycarbonyl)cycloprop-1-en-1-yl)propanoic acid (**1q**) as a colourless oil; yield: 82 mg (89%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.44 (q, *J* = 1.2 Hz, 1H), 4.16 – 4.08 (m, 2H), 2.86 – 2.81 (m, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.17 (d, *J* = 1.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 176.6, 176.6, 113.9, 95.9, 60.6, 31.4, 20.6, 20.0, 14.4 ppm. **IR (NaCl)** $\tilde{\nu}$ = 3550 – 2900, 2982, 2863, 1790, 1716 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_9H_{12}O_4$ $[M+H]^+$ 185.0808, found 185.0810.

3.8. Synthesis of 4-(3-(ethoxycarbonyl)cycloprop-1-en-1-yl)butanoic acid (1r)



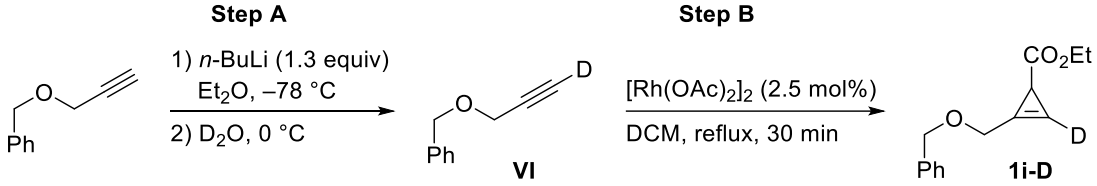
Scheme S9. Synthetic route towards derivative **1r**

Step A. Following a modified procedure described by Corey,[15] an oven-dried 100 mL round-bottomed flask was charged With a solution of *tert*-butyldimethylsilyl chloride (2.7 g, 18 mmol, 2.2 equiv) and imidazole (1.2 g, 18 mmol, 2.2 equiv) in *N*,*N*-dimethylformamide (10 mL). Then, 5-hexionic acid (0.90 mL, 8.0 mmol, 1.0 equiv) was added dropwise, and the resulting mixture was stirred at room temperature for 16 hours. After completion, acetone (50 mL) was added to the reaction crude, filtered through a pad of Celite® and

evaporated to dryness under reduced pressure. The residue was re-dissolved in ethyl acetate (50 mL), washed with water, then dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (*n*-hexane/ EtOAc; 40:1) to give *tert*-butyldimethylsilyl hex-5-ynoate (**V**) as a colourless oil; yield: 0.58 g (32%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 2.46 (t, *J* = 7.4 Hz, 2H), 2.26 (td, *J* = 7.0, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.86 – 1.78 (m, 2H), 0.93 (s, 9H), 0.26 (s, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 173.6, 83.6, 69.1, 34.7, 25.7, 23.9, 17.9, 17.7, - 4.7 ppm. **HRMS (ESI)** *m/z* calcd. for $C_{12}H_{22}O_2Si$ $[M+H]^+$ 227.1462, found 227.1462.

Step B. Compound **1r** was prepared following the typical procedure A from *tert*-butyldimethylsilyl hex-5-ynoate (**V**) (0.57 g, 2.5 mmol, 1.0 equiv) to give **1r** as a colourless oil; yield: 0.23 g (47%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.42 (s, 1H), 4.19-4.07 (m, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.15 (s, 1H), 1.98 – 1.91 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 178.7, 176.7, 114.6, 95.5, 60.5, 33.1, 24.4, 21.9, 19.8, 14.5 ppm. **IR (NaCl) $\tilde{\nu}$** = 2959, 2923, 2854, 1721, 1652, 1555 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{10}H_{14}O_4$ $[M+H]^+$ 199.0965, found 199.0967.

3.9. Synthesis of compound 1i-D



Scheme S10. Synthesis of deuterated derivative **1i-D**

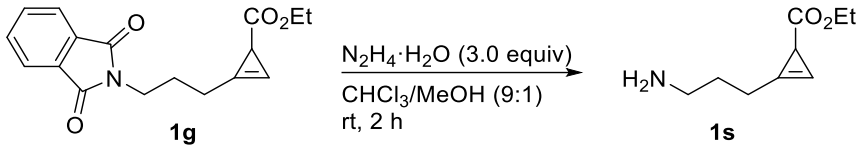
Step A. Following a modified procedure described by Tämm and Sikk,[16] an oven dried flask was charged with a solution of benzyl propargyl ether (2.9 mL, 20 mmol, 1.0 equiv) in Et_2O (12 mL), to which *n*-BuLi (19 mL, 1.4 M in *n*-hexane, 1.3 equiv) was added at −78 °C under argon atmosphere. After stirring at −78 °C for 1 hour, the mixture was warmed slowly to room temperature and stirred for 2 hours. Then, the mixture was cooled to 0 °C, and D_2O (3.0 mL) was added dropwise *via* syringe. After addition, the mixture was allowed to warm up to room temperature and stirred for 30 minutes. The mixture was separated, and the combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc; 20:1) to give 1-benzyloxy-3-deutero-2-propyne (**VI**) as a colourless oil; yield: 1.3 g (44%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.38 – 7.29 (m, 5H), 4.62 (s, 2H), 4.18 (s, 2H) ppm. Data consistent with the literature.[16]

Step B. Ethyl 2-((benzyloxy)methyl)cycloprop-2-ene-1-carboxylate-3-*d* (**1i-D**) was prepared following the typical procedure A from 1-benzyloxy-3-deutero-2-propyne (**VI**) (0.59 g, 4.0 mmol, 1.0 equiv) to give **1i-D** as a colourless oil; yield: 0.59 g (63%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.36 – 7.27 (m, 5H), 4.64 – 4.57 (m, 2H), 4.54 (s, 2H), 4.18 – 4.10 (m, 2H), 2.30 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 175.6, 137.5, 128.5, 128.01, 127.96, 112.2, 97.5 (t, *J* = 36.7 Hz) 72.6, 63.6, 60.5, 20.1, 14.4 ppm. **IR**

(NaCl) $\tilde{\nu}$ = 3063, 3032, 2982, 2928, 2859, 1834, 1726 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{15}DO_3$ $[M+H]^+$ 234.1235, found 234.1238.

3.10. Synthesis of unsuccessful substrates

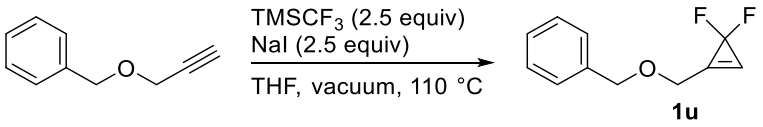
Synthesis of ethyl 2-(3-aminopropyl)cycloprop-2-ene-1-carboxylate (1s)



Scheme S11. Hydrolysis of derivative **1g** towards derivative **1s**

Following a modified procedure described by Zhou and Yi,[17] hydrazine monohydrate (0.60 mL, 12 mmol, 3.0 equiv) was added to the solution of ethyl 2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cycloprop-2-ene-1-carboxylate **1g** (1.2 g, 4.0 mmol, 1.0 equiv) in a mixture of methanol (4.0 mL) and chloroform (36 mL). The reaction was allowed to stir at room temperature overnight. Afterwards, the precipitate was filtered off and washed with dichloromethane. The filtrate was concentrated under reduced pressure to afford the desired product **1s**, as a colourless oil; yield: 0.65 g (96%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.35 (q, *J* = 1.3 Hz, 1H), 4.16 –4.08 (m, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.55 (td, *J* = 7.2, 1.0 Hz, 2H), 2.13 (d, *J* = 1.4 Hz, 1H), 1.76 – 1.69 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.7, 115.3, 94.6, 60.3, 41.6, 30.7, 22.6, 19.9, 14.5 ppm. **IR (NaCl)** $\tilde{\nu}$ = 3374, 2980, 2925, 1719 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_9H_{15}NO_2$ $[M+H]^+$ 170.1176, found 170.1180.

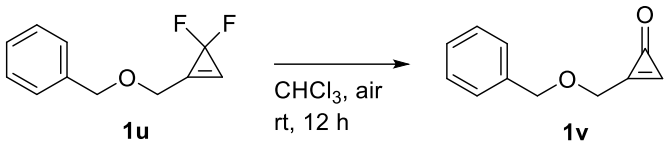
Synthesis of (((3,3-difluorocycloprop-1-en-1-yl)methoxy)methyl)benzene (1u)



Scheme S12. Difluorocyclopropenation towards derivative **1u**

Following a modified procedure described by Waser,[18] an oven-dried 20 mL vessel was charged with anhydrous NaI (1.5 g, 10 mmol, 2.5 equiv) and sealed with a Teflon-coated cap. Under vacuum, 10 mL of freshly distilled tetrahydrofuran, ((prop-2-yn-1-yloxy)methyl)benzene (0.58 mg, 4.0 mmol, 1.0 equiv) and trifluoromethyltrimethylsilane (1.6 mL, 10 mmol, 2.5 equiv) was added, in that order. The reaction was heated to 110 °C for 4 hours. The reaction was quenched with 20 mL of a saturated aqueous sodium bicarbonate solution and extracted with diethyl ether (3 × 10 mL). The combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane:Et_3N, 49:1) to give **1u** as a colourless oil; yield: 0.47 g (60%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.45 (bs, 1H), 7.40 – 7.33 (m, 5H), 4.62 (s, 2H), 4.55 – 4.53 (m, 2H) ppm. Data consistent with the literature.[19]

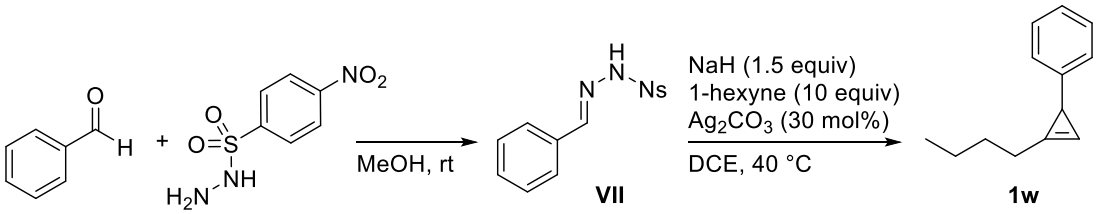
Synthesis of 2-((benzyloxy)methyl)cycloprop-2-en-1-one (1v)



Scheme S13. Hydrolysis of compound **1u** towards derivative **1v**

Following a modified procedure described by Charette,[20] an oven-dried 20 mL vessel was charged with a solution of (((3,3-difluorocycloprop-1-en-1-yl)methoxy)methyl)benzene (**1u**) (0.20 mg, 1.0 mmol, 1.0 equiv) in chloroform (5.0 mL). The reaction mixture was stirred under air for 12 hours. After that time, the volatiles were evaporated under reduced pressure at room temperature, and the resulting residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 2:3) to give **1v** as a colourless oil; yield: 0.17 g (96%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 8.48 (s, 1H), 7.38 – 7.33 (m 5H), 4.66 (s, 2H), 4.64 – 4.63 (m, 2H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 167.8, 155.2, 147.5, 136.6, 128.8, 128.5, 128.2, 73.5, 65.3.ppm. **IR (NaCl)** $\tilde{\nu}$ = 3063, 3032, 2866, 1836, 1743, 1592 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{11}H_{10}O_2$ $[M+H]^+$ 175.0754, found 175.0752.

Synthesis of (2-butylcycloprop-2-en-1-yl)benzene (1w)



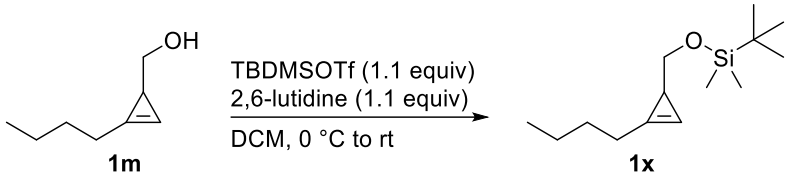
Scheme S14. Synthetic route towards derivative **1w**

Following a modified procedure described by Bi,[21] an oven-dried 20 mL vessel was charged with a solution of 4-nitrobenzenesulfonylhydrazide (0.43 g, 2.0 mmol, 1.0 equiv) in methanol (2 mL) to which benzaldehyde (0.22 mL, 2.2 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 2 hours. Then, the solid formed was filtered, washed with cold diethyl ether and dried under reduced pressure to give (*E*)-*N*'-benzylidene-4-nitrobenzenesulfonohydrazide (**VII**); yield: 0.30 g (49%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 8.41 – 8.36 (m, 2H), 8.23 – 8.18 (m, 2H), 7.85 (s, 1H), 7.77 (s, 1H), 7.59 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.44 – 7.35 (m, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 150.5, 149.1, 144.0, 132.6, 131.2, 129.5, 129.0, 127.6, 124.5, 77.2 ppm.

In a second step, an oven-dried 20 mL vessel was charged with (*E*)-*N*-benzylidene-4-nitrobenzenesulfonohydrazide (**VII**) (250 mg, 0.50 mmol, 1.0 equiv), and sodium hydride 60%w/w in mineral oil (49 mg, 1.2 mmol, 1.5 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. Under argon atmosphere, dry 1,2-dichloroethane (10 mL) was added *via* syringe. The resulting mixture was stirred at room temperature for 1 hour. Then, 1-hexyne (0.94 mL, 8.2 mmol, 10 equiv) and Ag_2CO_3 (68 mg, 0.25 mmol, 0.3 equiv) were added, and the system was stirred at 40 °C for 18 hours. The

reaction mixture was cooled to room temperature and filtered through a pad of silica gel with ethyl acetate as the only eluent, and the volatiles were removed under reduced pressure below 35 °C. The residue was purified by column chromatography on silica gel (*n*-hexane as the only eluent) to afford **1w** as a colourless oil; yield: 67 mg (48%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.06 – 7.02 (m, 2H), 6.94 – 6.88 (m, 3H), 6.35 (q, *J* = 1.0 Hz, 1H), 2.37 (d, *J* = 1.2 Hz, 1H), 2.35 – 2.22 (m, 2H), 1.41 – 1.31 (m, 2H), 1.23 – 1.13 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H) ppm. Data consistent with the literature.[21]

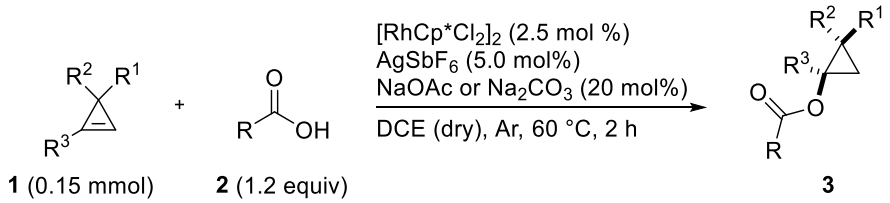
Synthesis of *tert*-butyl((2-butylcycloprop-2-en-1-yl)methoxy)dimethylsilane (1x)



Scheme S15. Protection of derivative **1m** with TBDMS

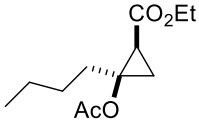
Following a modified procedure described by Didier,[22] a 50 mL flask was charged with a solution of (2-butylcycloprop-2-en-1-yl)methanol **1m** (0.50 g, 4.0 mmol, 1.0 equiv) and 2,6-lutidine (0.51 mL, 4.4 mmol, 1.1 equiv) in dichloromethane (20 mL) at 0 °C. Then, *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.0 mL, 4.4 mmol, 1.1 equiv) was added, and the reaction was stirred for 15 minutes. Then, it was quenched with 5 mL of a 1.0 M aqueous solution of hydrochloric and extracted with dichloromethane (2 × 10 mL). The combined organics were dried with brine and over sodium sulfate, and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 20:1) to afford **1x** as a colourless oil; yield: 0.66 g (69%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 6.59 (s, 1H), 3.54 – 3.45 (m, 2H), 2.46 (t, *J* = 7.3 Hz, 2H), 1.63 (td, *J* = 4.8, 1.4 Hz, 1H), 1.59 – 1.51 (m, 2H), 1.24 – 1.33 (m, 2H), 0.95 – 0.92 (m, 3H), 0,90 (m, 9H), 0.044 (s, 3H), 0.038 (s, 3H) ppm. Data consistent with the literature.[22]

4. General procedure for the Rh(III)-catalysed hydroacyloxylation of cyclopropenes



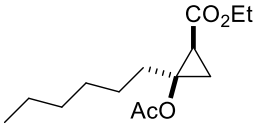
Scheme S16. Rh(III)-catalysed hydroacyloxylation of cyclopropenes

Synthesis of ethyl (1*S,2*R**)-2-acetoxy-2-butylcyclopropane-1-carboxylate (3aa).** An oven-dried argon-flushed 10 mL vessel was charged with pentamethylcyclopentadienyl rhodium dichloride dimer (2.3 mg, 0.0038 mmol, 0.025 equiv), silver hexafluoroantimonate(V) (2.6 mg, 0.0075 mmol, 0.050 equiv) and anhydrous sodium acetate (2.5 mg, 0.030 mmol,

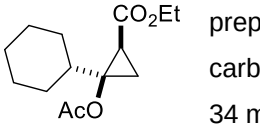


0.20 equiv) or anhydrous sodium carbonate (3.2 mg, 0.030 mmol, 0.20 equiv) [Note: If the carboxylic acid is solid, it must also be weighed at this point]. The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate (**1a**) (25 mg, 0.15 mmol, 1.0 equiv) and acetic acid (**2a**) (10 µL, 0.18 mmol, 1.2 equiv) in dry 1,2-dichloroethane (1.0 mL) was added *via* syringe. The reaction mixture was heated at 60 °C for 2 hours. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 9:1) to afford **3aa** as a yellowish oil; yield: 0.34 g (98%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.11 (q, *J* = 7.1 Hz, 2H), 2.08 – 2.02 (m, 1H), 1.99 (s, 3H), 1.87 (dd, *J* = 9.0, 7.0 Hz, 1H), 1.58 (t, *J* = 6.6 Hz, 1H), 1.53 – 1.46 (m, 1H), 1.41 – 1.30 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (dd, *J* = 9.0, 6.3 Hz, 1H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.8, 170.2, 64.2, 60.8, 35.0, 27.9, 26.0, 22.5, 21.1, 18.7, 14.4, 14.1 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2962, 2929, 2865, 1752, 1734 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{12}H_{20}O_4$ $[M+H]^+$ 229.1434, found 229.1434.

Ethyl (1*S,2*R**)-2-acetoxy-2-hexylcyclopropane-1-carboxylate (3ba).** Compound **3ba** was prepared following the general procedure from ethyl 2-hexylcycloprop-2-ene-1-carboxylate (**1b**) (29 mg, 0.15 mmol, 1.0 equiv) to give **3ba** as a colourless oil; yield: 31 mg (81%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.11 (q, *J* = 7.1 Hz, 2H), 2.08 – 2.02 (m, 1H), 2.00 (s, 3H), 1.88 (dd, *J* = 9.0, 7.0 Hz, 1H), 1.58 (t, *J* = 6.6 Hz, 1H), 1.51 – 1.36 (m, 3H), 1.33 – 1.25 (m, 6H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (dd, *J* = 9.0, 6.3 Hz, 1H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.8, 170.2, 64.2, 60.9, 35.2, 31.9, 29,1, 25.9, 25.7, 22.7, 21.1, 18.7, 14.3, 14.2 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2953, 2925, 2865, 1752, 1734 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{24}O_4$ $[M+H]^+$ 257.1747, found 257.1748.



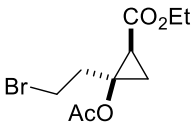
Ethyl (1*S,2*S**)-2-acetoxy-2-cyclohexylcyclopropane-1-carboxylate (3ca).** Compound **3ca** was prepared following the general procedure from ethyl 2-cyclohexylcycloprop-2-ene-1-carboxylate (**1c**) (29 mg, 0.15 mmol, 1.0 equiv) to give **3ca** as a colourless oil; yield: 34 mg (89%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.16 – 4.05 (m, 2H), 1.99 (s, 3H), 1.94 (dd, *J* = 9.1, 7.2 Hz, 1H), 1.84 – 1.81 (m, 1H), 1.75 – 1.63 (m, 5H), 1.56 (t, *J* = 6.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.26 – 0.82 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.8, 170.4, 67.7, 60.8, 41.9, 29.4, 28.9, 26.2, 26.14, 26.07, 23.6, 21.2, 16.7, 14.4 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2958, 2925, 2855, 1752, 1729 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{22}O_4$ $[M+H]^+$ 255.1591, found 255.1593.



Ethyl (1*S,2*R**)-2-acetoxy-2-phenethylcyclopropane-1-carboxylate (3da).** Compound **3da** was prepared following the general procedure from ethyl 2-phenethylcycloprop-2-ene-1-carboxylate (**1d**) (32 mg, 0.15 mmol, 1.0 equiv) to give **3da** as a colourless oil; yield: 36 mg (86%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.30 – 7.28 (m, 2H), 7.20 – 7.17 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.48 – 2.40 (m, 1H), 1.95 (s, 3H), 1.88 (dd, *J* = 9.0, 7.0 Hz, 1H), 1.79 – 1.71 (m, 1H), 1.59 – 1.56 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.08 (dd, *J* = 9.0, 6.4 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.9, 170.1, 141.2, 128.55, 128.55, 126.2, 63.7, 60.9, 37.0, 32.1, 26.0, 21.0,

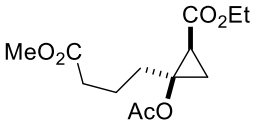
18.9, 14.4 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2920, 2851, 1752, 1729, 1645 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{20}O_4$ $[M+H]^+$ 277.1434, found 277.1435.

Ethyl (1*S,2*S**)-2-acetoxy-2-(2-bromoethyl)cyclopropane-1-carboxylate (3ea).** Compound **3ea** was



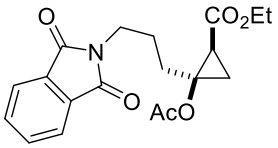
prepared following the general procedure from ethyl 2-(2-bromoethyl)cycloprop-2-ene-1-carboxylate (**1e**) (33 mg, 0.15 mmol, 1.0 equiv) to give **3ea** as a colourless oil; yield: 35 mg (83%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.12 (q, *J* = 7.1 Hz, 2H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.66 (dt, *J* = 13.9, 6.8 Hz, 1H), 2.03 – 1.93 (m, 2H), 2.02 (s, 3H), 1.67 (t, *J* = 6.8 Hz, 1H), 1.31 (dd, *J* = 9.2, 6.5 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.9, 169.7, 62.5, 61.1, 38.7, 28.0, 25.6, 21.1, 18.8, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2985, 2925, 1752, 1727 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{10}H_{15}BrO_4$ $[M+H]^+$ 279.0226, found 279.0226.

Ethyl (1*S,2*R**)-2-acetoxy-2-(4-methoxy-4-oxobutyl)cyclopropane-1-carboxylate (3fa).** Compound **3fa**



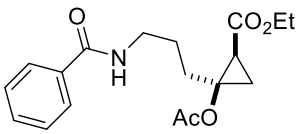
was prepared following the general procedure from ethyl 2-(4-methoxy-4-oxobutyl)cycloprop-2-ene-1-carboxylate (**1f**) (32 mg, 0.15 mmol, 1.0 equiv) to give **3fa** as a colourless oil; yield: 35 mg (85%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.10 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.04 (m, 1H), 1.99 (s, 3H), 1.88 (dd, *J* = 9.0, 7.0 Hz, 1H), 1.81 – 1.73 (m, 2H), 1.59 (t, *J* = 6.6 Hz, 1H), 1.55 – 1.47 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (dd, *J* = 9.0, 6.3 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 173.8, 170.8, 169.9, 63.5, 60.9, 51.7, 34.5, 33.3, 26.0, 21.2, 21.1, 18.7, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2957, 2940, 1752, 1729, 1646 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{13}H_{20}O_6$ $[M+H]^+$ 273.1333, found 273.1333.

Ethyl (1*S,2*R**)-2-acetoxy-2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cyclopropane-1-carboxylate (3ga).**



Compound **3ga** was prepared following the general procedure from ethyl 2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cycloprop-2-ene-1-carboxylate (**1g**) (45 mg, 0.15 mmol, 1.0 equiv) to give **3ga** as a colourless oil; yield: 47 mg (87%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.83 – 7.79 (m, 2H), 7.71 – 7.67 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.68 (t, *J* = 7.3 Hz, 2H), 2.13 – 2.05 (m, 1H), 1.97 (s, 3H), 1.89 (dd, *J* = 9.0, 7.1 Hz, 1H), 1.86 – 1.78 (m, 2H), 1.59 – 1.50 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.18 (dd, *J* = 9.0, 6.4 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.7, 169.8, 168.4, 134.1, 132.1, 123.3, 63.3, 60.9, 37.6, 32.7, 26.0, 24.9, 21.0, 18.6, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2960, 2936, 2874, 1770, 1752, 1715, 1618 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{21}NO_6$ $[M+H]^+$ 360.1442, found 360.1441.

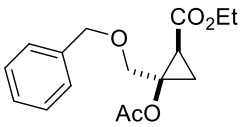
Ethyl (1*S,2*R**)-2-acetoxy-2-(3-benzamidopropyl)cyclopropane-1-carboxylate (3ha).** Compound **3ha**



was prepared following the general procedure from ethyl 2-(3-benzamidopropyl)cycloprop-2-ene-1-carboxylate (**1h**) (41 mg, 0.15 mmol, 1.0 equiv) to give **3ha** as a colourless oil; yield: 43 mg (85%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.76 – 7.74 (m, 2H), 7.51 – 7.41 (m, 3H), 6.25 (bs, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.49 (q, *J* = 6.7 Hz, 2H), 2.18 – 2.11 (m, 1H), 2.00 (s, 3H), 1.91 (dd, *J* = 9.0, 7.1 Hz, 1H), 1.83 – 1.75 (m, 2H), 1.64 – 1.58 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.21 (dd, *J* = 9.1, 6.4 Hz, 1H) ppm.

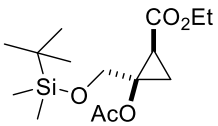
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.9, 169.9, 167.7, 134.7, 131.6, 128.7, 127.0, 63.5, 61.0, 39.8, 33.0, 26.2, 26.1, 21.1, 18.9, 14.3 ppm. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{23}NO_5$ $[M+H]^+$ 334.1649, found 334.1653.

Ethyl (1*S,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (3ia).** Compound **3ia** was



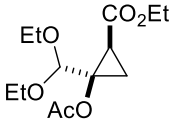
prepared following the general procedure from ethyl 2-((benzyloxy)methyl)cycloprop-2-ene-1-carboxylate (**1i**) (36 mg, 0.15 mmol, 1.0 equiv) to give **3ia** as a colourless oil; yield: 34 mg (77%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.36 – 7.29 (m, 5H), 4.56 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 10.8 Hz, 1H), 3.57 (d, *J* = 10.8 Hz, 1H), 2.06 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.02 (s, 3H), 1.65 (t, *J* = 6.7 Hz, 1H), 1.38 (dd, *J* = 9.2, 6.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.9, 169.8, 137.8, 128.6, 128.0, 127.9, 73.2, 70.9, 62.5, 61.0, 24.1, 21.1, 16.9, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2920, 2851, 1752, 1730, 1645 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{20}O_5$ $[M+H]^+$ 293.1384, found 293.1384.

Ethyl (1*S,2*R**)-2-acetoxy-2-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopropane-1-carboxylate (3ja).**



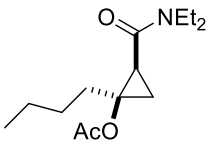
Compound **3ja** was prepared following the general procedure from ethyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)cycloprop-2-ene-1-carboxylate (**1j**) (39 mg, 0.15 mmol, 1.0 equiv) to give **3ja** as a colourless oil; yield: 31 mg (66%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.12 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 10.4 Hz, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 2.09 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.01 (s, 3H), 1.57 – 1.53 (m, 1H), 1.40 (dd, *J* = 9.2, 6.0 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.9, 170.4, 64.2, 62.3, 60.9, 25.9, 22.8, 21.1, 18.3, 15.8, 14.3, -5.27, -5.33 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2953, 2926, 2852, 1759, 1732 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{28}O_5Si$ $[M+H]^+$ 317.1779, found 317.1778.

Ethyl (1*S,2*R**)-2-acetoxy-2-(diethoxymethyl)cyclopropane-1-carboxylate (3ka).** Compound **3ka** was



prepared following the general procedure from ethyl 2-(diethoxymethyl)cycloprop-2-ene-1-carboxylate (**1k**) (32 mg, 0.15 mmol, 1.0 equiv) to give **3ka** as a colourless oil; yield: 33 mg (79%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 5.12 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.76 – 3.66 (m, 2H), 3.61 – 3.51 (m, 2H), 2.19 (dd, *J* = 9.3, 7.4 Hz, 1H), 2.04 (s, 3H), 1.59 – 1.50 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 171.0, 170.3, 97.7, 63.2, 62.8, 61.6, 61.0, 22.4, 21.0, 15.4, 15.3, 15.0, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2978, 2934, 2899, 1752, 1728 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{13}H_{22}O_6$ $[M+H]^+$ 275.1489, found 275.1490.

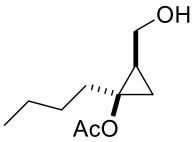
(1*R,2*S**)-1-Butyl-2-(diethylcarbamoyl)cyclopropyl acetate (3la).** Compound **3la** was prepared following



the general procedure from 2-butyl-*N*,*N*-diethylcycloprop-2-ene-1-carboxamide (**1l**) (29 mg, 0.15 mmol, 1.0 equiv) to give **3la** as a colourless oil; yield: 34 mg (89%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 3.79 – 3.70 (m, 1H), 3.62 – 3.53 (m, 1H), 3.25 – 3.16 (m, 1H), 3.09 – 3.00 (m, 1H), 2.30 – 2.20 (m, 1H), 1.92 (s, 3H), 1.89 (dd, *J* = 8.9, 6.9 Hz, 1H), 1.76 (t, *J* = 6.4 Hz, 1H), 1.44 – 1.27 (m, 5H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.97 (dd, *J* = 8.9, 6.0 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.7, 166.9, 63.9, 42.1,

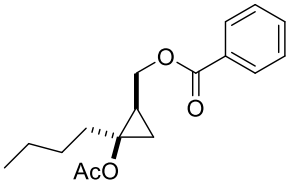
40.7, 34.9, 27.9, 25.6, 22.6, 21.1, 16.5, 14.4, 14.1, 12.6 ppm. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{25}NO_3$ $[M+H]^+$ 256.1907, found 256.1910.

(1*R,2*R**)-1-Butyl-2-(hydroxymethyl)cyclopropyl acetate (3ma).** Compound **3ma** was prepared



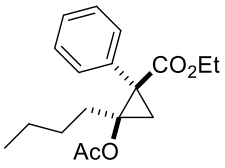
following the general procedure from (2-butylcycloprop-2-en-1-yl)methanol (**1m**) (19 mg, 0.15 mmol, 1.0 equiv) to give **3ma** as a colourless oil; yield: 12 mg (43%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 3.88 (td, *J* = 11.5, 4.1 Hz, 1H), 3.15 (dd, *J* = 11.6, 10.2 Hz, 1H), 2.28 (d, *J* = 10.3 Hz, 1H), 2.08 (s, 3H), 2.06 – 2.01 (m, 1H), 1.48 – 1.28 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.82 (dd, *J* = 9.9, 6.4 Hz, 1H), 0.57 (t, *J* = 6.8 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 172.7, 63.9, 62.2, 34.7, 28.1, 25.9, 22.6, 21.5, 14.20, 14.17 ppm. **IR (NaCl)** $\tilde{\nu}$ = 3330, 2958, 2926, 2857, 1748 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{10}H_{18}O_3$ $[M+H]^+$ 187.1329, found 187.1329.

((1*R,2*R**)-2-acetoxy-2-butylcyclopropyl)methyl benzoate (3na).** Compound **3na** was prepared



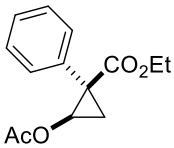
following the general procedure from (2-butylcycloprop-2-en-1-yl)methyl benzoate (**1n**) (35 mg, 0.15 mmol, 1.0 equiv) to give **3na** as a colourless oil; yield: 30 mg (69%); **^{1}H NMR ($CDCl_3$, 400 MHz)**: 8.09 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.47 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.15 (dd, *J* = 11.9, 8.5 Hz, 1H), 2.00 (s, 3H), 1.95 – 1.88 (m, 1H), 1.78 – 1.70 (m, 1H), 1.65 – 1.60 (m, 1H), 1.48 – 1.44 (m, 2H), 1.36 – 1.31 (m, 2H), 1.15 (dd, *J* = 10.4, 6.6 Hz, 1H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.65 (t, *J* = 6.8 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.6, 166.8, 133.1, 130.4, 129.8, 128.5, 64.8, 62.7, 30.5, 28.3, 22.8, 22.6, 21.5, 16.8, 14.2 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2955, 2932, 2858, 1744, 1721 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{17}H_{22}O_4$ $[M+H]^+$ 291.1591, found 291.1592.

Ethyl (1*R,2*R**)-2-acetoxy-2-butyl-1-phenylcyclopropane-1-carboxylate (3oa).** Compound **3oa** was



prepared following the general procedure from ethyl 2-butyl-1-phenylcycloprop-2-ene-1-carboxylate (**1o**) (37 mg, 0.15 mmol, 1.0 equiv) to give **3oa** as a colourless oil; yield: 30 mg (65%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.47 (d, *J* = 7.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 4.14 – 4.06 (m 1H), 3.99 – 3.91 (m, 1H), 2.20 (dd, *J* = 6.3, 1.3 Hz, 1H), 2.06 (s, 3H), 2.04 – 1.99 (m, 1H), 1.43 (d, *J* = 6.3 Hz, 1H), 1.41 – 1.26 (m, 2H), 1.23 – 1.16 (m, 2H),1.13 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.69 – 0.61 (m, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.8, 170.3, 136.5, 131.0, 128.0, 127.4, 67.8, 61.5, 39.9, 33.0, 28.1, 23.9, 22.5, 21.3, 14.16, 14.15 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2959, 2932, 2867, 1748, 1721,1638 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{24}O_4$ $[M+H]^+$ 305.1747, found 305.1751.

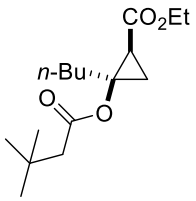
Ethyl (1*R,2*R**)-2-acetoxy-1-phenylcyclopropane-1-carboxylate (3pa).** Compound **3pa** was prepared



following the general procedure from ethyl 1-phenylcycloprop-2-ene-1-carboxylate (**1p**) (28 mg, 0.15 mmol, 1.0 equiv) to give **3pa** as a colourless oil; yield: 27 mg (73%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.51 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.27 (m, 3H), 4.35 (dd, *J* = 7.0, 4.9 Hz, 1H), 4.18 – 4.02 (m, 2H), 2.17 – 2.15 (m, 1H), 2.11 (s, 3H), 1.58 – 1.55 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 171.6, 169.7, 137.9, 130.4, 128.5, 127.8, 61.5,

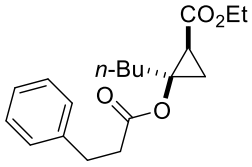
59.1, 35.8, 20.9, 19.0, 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2964, 2918, 2849, 1753, 1721 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{16}O_4$ $[M+H]^+$ 249.1121, found 249.1119.

Ethyl (1*S,2*R**)-2-butyl-2-((3,3-dimethylbutanoyl)oxy)cyclopropane-1-carboxylate (3ab).** Compound



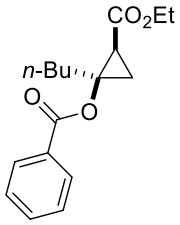
3ab was prepared following the general procedure from 3,3-dimethylbutanoic acid (**2b**) (21 mg, 0.18 mmol, 1.2 equiv) to give **3ab** as a colourless oil; yield: 35 mg (83%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.10 (q, *J* = 7.1 Hz, 2H), 2.19 – 2.10 (m, 2H), 2.02 – 1.95 (m, 1H), 1.89 – 1.85 (m, 1H), 1.59 – 1.50 (m, 2H), 1.44 – 1.29 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (dd, *J* = 8.7, 6.4 Hz, 1H), 1.01 (s, 9H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 172.0, 170.1, 64.0, 60.8, 47.7, 35.1, 30.7, 29.6, 27.9, 26.0, 22.5, 18.6, 14.4, 14.1 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2957, 2929, 2865, 1738 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{28}O_4$ $[M+H]^+$ 285.2060, found 285.2060.

Ethyl (1*S,2*R**)-2-butyl-2-((3-phenylpropanoyl)oxy)cyclopropane-1-carboxylate (3ac).** Compound **3ac**



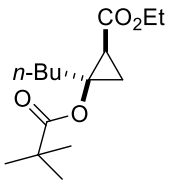
was prepared following the general procedure from 3-phenylpropanoic acid **(2c)** (27 mg, 0.18 mmol, 1.2 equiv) to give **3ac** as a colourless oil; yield: 36 mg (75%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.29 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.89 (m, 2H), 2.61 – 2.57 (m, 2H), 2.02 – 1.95 (m, 1H), 1.88 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.59 (t, *J* = 6.6 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.33 – 1.27 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (dd, *J* = 9.0, 6.3 Hz, 1H), 0.86 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 172.6, 170.1, 140.6, 128.5, 128.4, 126.3, 64.1, 60.8, 35.7, 35.0, 30.8, 27.8, 26.0, 22.5, 18.7, 14.4, 14.1 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2962, 2934, 2874, 1748, 1729, 1609 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{26}O_4$ $[M+H]^+$ 319.1904, found 319.1903.

(1*R,2*S**)-1-Butyl-2-(ethoxycarbonyl)cyclopropyl benzoate (3ad).** Compound **3ad** was prepared



following the general procedure from benzoic acid (**2d**) (22 mg, 0.18 mmol, 1.2 equiv) to give **3ad** as a colourless oil; yield: 31 mg (71%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.99 – 7.97 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 4.14 – 4.01 (m, 2H), 2.13 – 2.06 (m, 1H), 1.98 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.77 (t, *J* = 6.5 Hz, 1H), 1.73 – 1.68 (m, 1H), 1.50 – 1.43 (m, 2H), 1.39 – 1.31 (m, 2H), 1.29 (dd, *J* = 9.0, 6.3 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 169.9, 166.2, 133.1, 130.3, 129.8, 128.5, 64.6, 60.9, 35.2, 27.9, 26.2, 22.5, 18.9, 14.3, 14.1 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2957, 2925, 2865, 1734, 1604, 1581 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{17}H_{22}O_4$ $[M+H]^+$ 291.1591, found 291.1589.

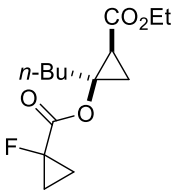
Ethyl (1*S,2*R**)-2-butyl-2-(pivaloyloxy)cyclopropane-1-carboxylate (3ae).** Compound **3ae** was



prepared following the general procedure from pivalic acid (**2e**) (18 mg, 0.18 mmol, 1.2 equiv) to give **3ae** as a colourless oil; yield: 34 mg (84%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.18 – 4.02 (m, 2H), 1.95 – 1.88 (m, 1H), 1.85 (dd, *J* = 8.8, 7.0 Hz, 1H), 1.62 – 1.54 (m, 2H), 1.43 – 1.30 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.17 – 1.14 (m, 1H), 1.16 (s, 9H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 178.0, 169.8, 63.6, 60.7, 38.8, 34.9, 27.9, 27.2, 26.1,

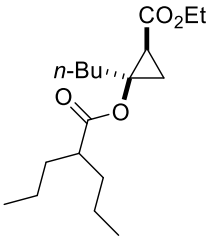
22.5, 18.5, 14.4, 14.1 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2963, 2932, 2871, 1737 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{26}O_4$ $[M+H]^+$ 271.1904, found 271.1909.

Ethyl (1*S,2*R**)-2-butyl-2-((1-fluorocyclopropane-1-carbonyl)oxy)cyclopropane-1-carboxylate (3af).**



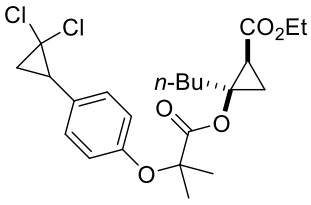
Compound **3af** was prepared following the general procedure from 1-fluorocyclopropane-1-carboxylic acid (**2f**) (19 mg, 0.18 mmol, 1.2 equiv) to give **3af** as a colourless oil; yield: 35 mg (86%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.15 – 4.07 (m, 2H), 2.03 – 1.96 (m, 1H), 1.89 (dd, *J* = 9.0, 7.1 Hz, 1H), 1.64 – 1.59 (m, 2H), 1.41 – 1.32 (m, 8H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.20 (dd, *J* = 9.1, 6.5 Hz, 1H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 170.0 (d, *J* = 25.1 Hz), 169.7, 74.6 (d, *J* = 225.3 Hz), 64.8, 61.0, 34.9, 27.8, 25.9, 22.4, 18.7, 14.7 (d, *J* = 8.1 Hz), 14.6 (d, *J* = 8.0 Hz), 14.3, 14.1 ppm. **^{19}F NMR ($CDCl_3$, 337 MHz)** δ: -200.83 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2959, 2932, 2875, 2867, 1764, 1730 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{21}FO_4$ $[M+H]^+$ 273.1497, found 273.1497.

Ethyl (1*S,2*R**)-2-butyl-2-((2-propylpentanoyl)oxy)cyclopropane-1-carboxylate (3ag).** Compound **3ag**



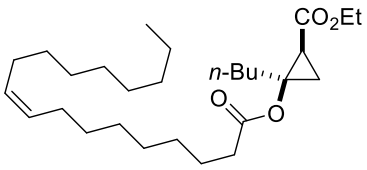
was prepared following the general procedure from 2-propylpentanoic acid (**2g**) (26 mg, 0.18 mmol, 1.2 equiv) to give **3ag** as a colourless oil; yield: 30 mg (64%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.17 – 4.05 (m, 2H), 2.32 – 2.25 (m, 1H), 1.89 – 1.81 (m, 2H), 1.67 – 1.54 (m, 4H), 1.44 – 1.29 (m, 10H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (dd, *J* = 8.8, 6.3 Hz, 1H), 0.90 – 0.87 (td, *J* = 7.1, 1.8 Hz, 9H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.0, 169.7, 63.8, 60.7, 45.1, 35.1, 34.4, 34.0, 27.8, 26.0, 22.5, 20.6, 20.5, 18.5, 14.4, 14.19, 14.15, 14.14. **IR (NaCl)** $\tilde{\nu}$ = 2959, 2932, 2877, 1739 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{32}O_4$ $[M+H]^+$ 313.2373, found 313.2370.

Ethyl (1*S,2*R**)-2-butyl-2-((2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl)oxy)cyclo-**

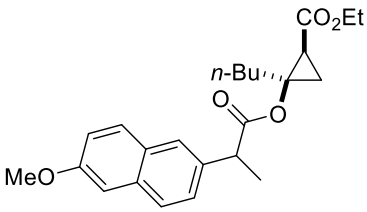


propane-1-carboxylate (3ah). Compound **3ah** was prepared following the general procedure from 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoic acid (**2h**) (52 mg, 0.18 mmol, 1.2 equiv) to give **3ah** as a mixture of isomers, colourless oil; yield: 47 mg (69%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.10 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.13 – 4.07 (m, 2H), 2.81 (dd, *J* = 10.2, 8.9 Hz, 1H), 1.95 – 1.85 (m, 3H), 1.76 (t, *J* = 7.9 Hz, 1H), 1.65 – 1.59 (m, 2H), 1.57 (s, 3H), 1.56 (s, 3H), 1.27 – 1.19 (m, 8H), 0.82 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 173.4, 169.6, 154.9, 129.5, 128.0, 118.9, 79.0, 64.7, 60.9, 60.8, 34.83, 34.80, 34.79, 27.6, 25.85, 25.84, 25.83, 25.81, 25.67, 25.64, 25.19, 25.16, 22.4, 18.26, 18.25, 14.3, 14.0 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2990, 2953, 2935, 2871, 1731, 1612 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{30}Cl_2O_5$ $[M+H]^+$ 457.1543, found 457.1546.

Ethyl (1*S,2*R**)-2-butyl-2-(oleoyloxy)cyclopropane-1-carboxylate (3ai).** Compound **3ai** was prepared following the general procedure from oleic acid (**2i**) (51 mg, 0.18 mmol, 1.2 equiv) and a reaction time of 6 hours to give **3ai** as a colourless oil; yield: 50 mg (74%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 5.37 – 5.29 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 2.06 – 1.97 (m, 5H), 1.87 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.59 – 1.54 (m, 3H), 1.53 – 1.46 (m, 1H), 1.43 – 1.23 (m, 27H), 1.15 (dd, *J* = 8.9, 6.3 Hz, 1H), 0.90 – 0.85 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 173.5, 170.1, 130.1, 129.9, 63.9, 60.8, 35.0, 34.3, 32.0, 29.9, 29.8, 29.7, 29.5, 29.5, 29.32, 29.28, 29.2, 27.9, 27.34, 27.31, 26.0, 24.9, 22.8, 22.5, 18.6, 14.4, 14.3, 14.2 ppm. **IR (NaCl)** $\tilde{\nu}$ = 3004, 2956, 2925, 2860, 1748, 1730 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{28}H_{50}O_4$ $[M+H]^+$ 451.3782, found 451.3782.

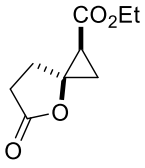


Ethyl (1*S,2*R**)-2-butyl-2-((-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)cyclopropane-1-carboxylate (3aj).** Compounds **3aj** were prepared following the general procedure from 2-(6-methoxynaphthalen-2-yl)propanoic acid (**2j**) (41 mg, 0.18 mmol, 1.2 equiv) to give **3aj** as a mixture of isomers. ***Major isomer***: colourless oil; yield: 22 mg (37%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.70 – 7.66 (m, 3H), 7.41 – 7.39 (m, 1H), 7.14 – 7.11 (m, 2H), 4.11 – 4.00 (m, 2H), 3.91 (s, 3H), 3.78 (q, *J* = 7.2 Hz, 1H), 1.80 (dd, *J* = 8.7, 7.1 Hz, 1H), 1.75 – 1.70 (m, 1H), 1.65 (t, *J* = 6.7 Hz, 1H), 1.60 – 1.56 (m, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.14 – 1.11 (m, 5H), 0.68 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 174.3, 169.7, 157.7, 135.5, 133.8, 129.4, 129.0, 127.0, 126.7, 126.2, 119.0, 105.6, 64.2, 60.8, 55.4, 45.6, 34.9, 27.6, 25.8, 22.3, 18.8, 18.4, 14.5, 14.0 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2957, 2934, 2865, 1734, 1632, 1609 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{30}O_5$ $[M+H]^+$ 399.2166, found 399.2167.



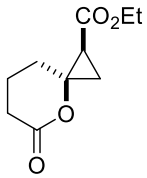
Minor isomer: colourless oil; yield: 20 mg (34%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.70 – 7.65 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.11 (m, 2H), 4.17 – 4.00 (m, 2H), 3.91 (s, 3H), 3.81 (q, *J* = 7.1 Hz, 1H), 2.04 – 1.98 (m, 1H), 1.90 (dd, *J* = 8.8, 7.1 Hz, 1H), 1.56 (t, *J* = 6.3 Hz, 1H), 1.49 (d, *J* = 7.1 Hz, 3H), 1. 24 (t, *J* = 7.1 Hz, 3H), 1.21 – 1.16 (m, 1H), 1.09 – 0.94 (m, 5H), 0.58 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 174.3, 170.2, 157.7, 135.7, 133.8, 129.4, 129.1, 127.2, 126.4, 126.2, 119.0, 105.6, 64.1, 60.8, 55.4, 45.3, 34.7, 27.5, 26.2, 22.3, 18.4, 18.2, 14.4, 13.9 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2962, 2934, 2874, 1743, 1729,1636, 1609 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{30}O_5$ $[M+H]^+$ 399.2166, found 399.2166.

Ethyl (1*S,3*R**)-5-oxo-4-oxaspiro[2.4]heptane-1-carboxylate (3q).** Compound **3q** was prepared following the general procedure from 3-(2-(ethoxycarbonyl)cyclopropyl)propanoic acid (**1q**) (28 mg, 0.15 mmol, 1.0 equiv) to give **3q** as a colourless oil; yield: 15 mg (54%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.21 – 4.15 (m, 2H), 2.82 – 2.67 (m, 2H), 2.48 – 2.40 (m, 1H), 2.34 – 2.26 (m, 1H), 2.04 (t, *J* = 6.9 Hz, 1H), 1.89 (dd, *J* = 9.0, 7.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (dd, *J* = 9.1, 6.9 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 175.6, 168.2, 68.7, 61.4, 29.7, 29.0,



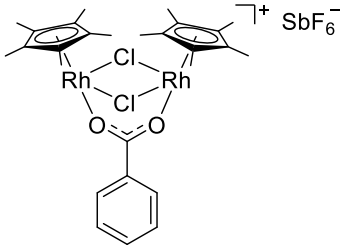
26.6, 16.4, 14.4. ppm. **IR (NaCl)** $\tilde{\nu}$ = 2978, 2873, 2901, 1786, 1728 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_9H_{12}O_4$ $[M+H]^+$ 185.0808, found 185.0811.

Ethyl (1*S,3*R**)-5-oxo-4-oxaspiro[2.5]octane-1-carboxylate (3r).** Compound **3r** was prepared following the general procedure from 4-(2-(ethoxycarbonyl)cyclopropyl)butanoic acid (**1r**) (30 mg, 0.15 mmol, 1.0 equiv) to give **3r** as a colourless oil; yield: 18 mg (62%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 4.18 (q, *J* = 7.1 Hz, 2H), 2.72 – 2.55 (m, 2H), 2.17 – 2.05 (m, 2H), 2.03 – 1.96 (m, 1H), 1.91 – 1.83 (m, 2H), 1.68 (dd, *J* = 13.0, 6.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (dd, *J* = 8.3, 5.9 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 171.6, 168.1, 66.1, 61.4, 29.6, 29.4, 27.6, 18.0, 17.5, 14.4 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2973, 2946, 2863, 1771, 1712 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{10}H_{14}O_4$ $[M+H]^+$ 199.0965, found 199.0962.



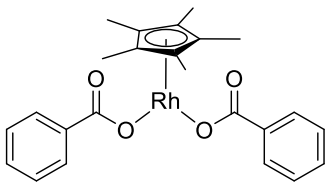
5. Synthesis of complex Rh-A

An oven-dried 10 mL vessel was charged with pentamethylcyclopentadienylrhodium(III) chloride dimer (25 mg, 0.040 mmol, 1.0 equiv), $AgSbF_6$ (28 mg, 0.080 mmol, 2.0 equiv) and sodium benzoate (23 mg, 0.16 mmol, 4.0 equiv), and sealed with a Teflon lined cap, then evacuated and flushed with argon three times. Under argon atmosphere, 2.0 mL of dry 1,2-dichloroethane were added via syringe. The resulting solution was stirred at room temperature overnight. Then, the reaction mixture was cooled down and filtered through a pad of Celite®. The resulting solid was dried under a vacuum until a dark reddish oil was obtained. The residue was recrystallised using dichloromethane and *n*-hexane to afford μ-(benzoato-κ^2*O*:*O*′)-di-μ-chloro-bis[(pentamethyl-η^5-cyclopentadienyl)rhodium(III)] hexafluoroantimonate(V) (**Rh-A**) as an orange solid; yield: 23 mg (64%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 8.00 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 1.64 (s, 30H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 176.4, 135.1, 131.9, 129.2, 128.3, 95.2, 95.1, 8.9 ppm. **HRMS (ESI)** *m/z* calcd. for $C_{27}H_{35}Cl_2O_2Rh_2$ $[M]^+$ 667.0124, found 667.0122.



6. Synthesis of Cp*Rh(OBz)$_2$

Following a modified procedure described by Merola,[23] an oven dried 10 mL vessel was charged with pentamethylcyclopentadienylrhodium(III) chloride dimer (25 mg, 0.040 mmol, 1.0 equiv), silver benzoate (37 mg, 0.16 mmol, 4.0 equiv), and sealed with a Teflon lined cap, then evacuated and flushed with argon three times. Under argon atmosphere, 2.0 mL of dry dichloromethane were added via syringe, and the resulting solution was stirred at room temperature overnight. The resulting mixture was filtered through a pad of Celite®, and the volatiles were partially removed under reduced pressure. Addition of *n*-hexane and gentle sonication promote the precipitation of bis(benzoato-κ*O*)[(pentamethyl-η^5-cyclopentadienyl)rhodium(III)] (**Cp*Rh(OBz)$_2$**) as an orange solid; yield: 10 mg (52%);



^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.98 (d, *J* = 7.1 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 1.78 (s, 15H) ppm. Data consistent with the literature.[23]

7. X-Ray structure and crystal data

The single crystal of complex **Rh-A** was obtained by diffusion of dichloromethane and *n*-hexane, and the vessel was kept under refrigeration for 12 hours. The obtained crystals were suitable for characterisation by X-ray diffraction. Ellipsoid contour was set at 100% probability levels in the caption for the Oak Ridge thermal ellipsoid plot (ORTEP). The crystal data of **Rh-A** have been obtained in a four-circle Bruker Kappa Apex II diffractometer with sealed tube molybdenum source and deposited in CCDC with number 2378540.

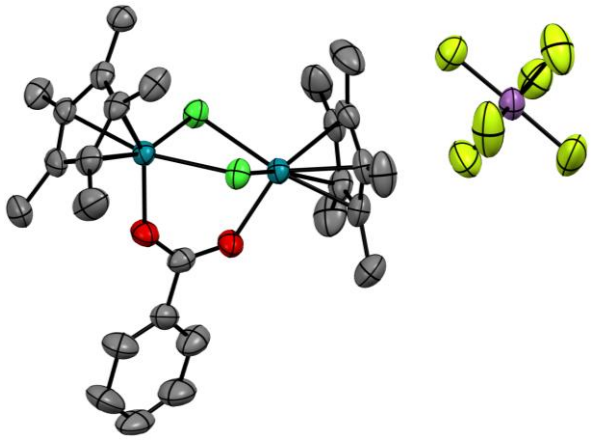


Figure S1. ORTEP view of **Rh-A**, hydrogen atoms have been removed for simplicity

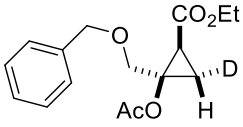
Table S2. Sample and crystal data for **Rh-II**

Compound	**04092**		
Formula	$C_{55.25}H_{72.5}Cl_{6.5}F_{12}O_4Rh_4Sb_2$	*Z'*	1
$D_{calc.}$/ g cm^{-3}	1.817	Wavelength/Å	1.54184
μ/mm^{-1}	16.405	Radiation type	Cu K_α
Formula Weight	1914.19	Θ_{min}/°	2.703
Colour	clear intense orange	Θ_{max}/°	68.520
Shape	ribbon	Measured Refl.	65451
Size/mm^3	0.15 × 0.02 × 0.01	Independent Refl.	12667
T/K	200.00(10)	Reflections with I > 2(I)	10548
Crystal System	triclinic	R_{int}	0.0656
Space group	*P*-1	Parameters	809
a/Å	8.1103(2)	Restraints	508
b/Å	19.9704(2)	Largest Peak	2.345
c/Å	22.1424(2)	Deepest Hole	−1.227
α/°	77.4221(9)	GooF	1.046
β/°	88.9106(17)	wR_2 (all data)	0.1639
γ/°	88.3440(17)	wR_2	0.1570
V/Å^3	3498.48(11)	R_1 (all data)	0.0651
Z	2	R_1	0.0553

8. Mechanistic experiments

8.1. Stereoselectivity determination

8.1.1. Deuteration labelling studies

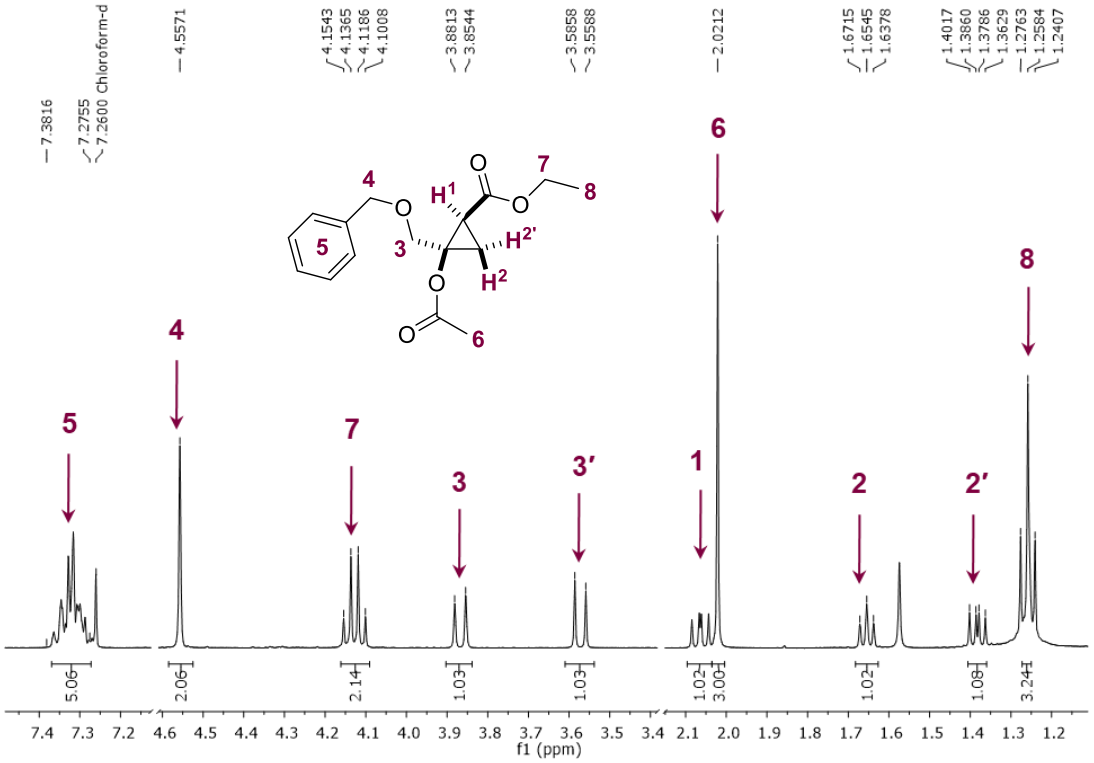
Synthesis of ethyl (1*S,2*R**,3*S**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate-3-*d* (3ia-D).** 

An oven-dried argon-flushed 10 mL vessel was charged with pentamethylcyclopentadienyl rhodium dichloride dimer (2.3 mg, 0.0038 mmol, 0.025 equiv), silver hexafluoroantimonate(V) (2.6 mg, 0.0075 mmol, 0.050 equiv) and anhydrous sodium acetate (2.5 mg, 0.030 mmol, 0.20 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-((benzyloxy)methyl)cycloprop-2-ene-1-carboxylate-3-*d* **1i-D** (35 mg, 0.15 mmol, 1.0 equiv) in dry 1,2-dichloroethane (1.0 mL) and acetic acid (10 µL, 1.8 mmol, 1.2 equiv) were subsequently added *via* syringe. The reaction mixture was heated at 60 °C for 2 hours. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc) to afford ethyl (1*S**,2*R**,3*S**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate-3-*d* (**3ia-D**) as a yellowish oil; yield: 34 mg (77%); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ: 7.37 – 7.29 (m, 5H), 4.56 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 10.8 Hz, 1H), 3.56 (d, *J* = 10.8 Hz, 1H), 2.06 (d, *J* = 8.0 Hz, 1H), 2.02 (s, 3H), 1.64 (d, *J* = 7.1 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 101 MHz)** δ: 171.0, 169.8, 137.8, 128.6, 128.0, 127.9, 73.2, 70.9, 62.4, 61.0, 24.0, 21.1, 16.6 (t, *J* = 25.0 Hz), 14.3 ppm. **IR (NaCl)** $\tilde{\nu}$ = 2981, 2956, 2924, 2855, 1751, 1730 cm^{-1}. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{19}DO_5$ $[M+H]^+$ 294.1446, found 294.1447.

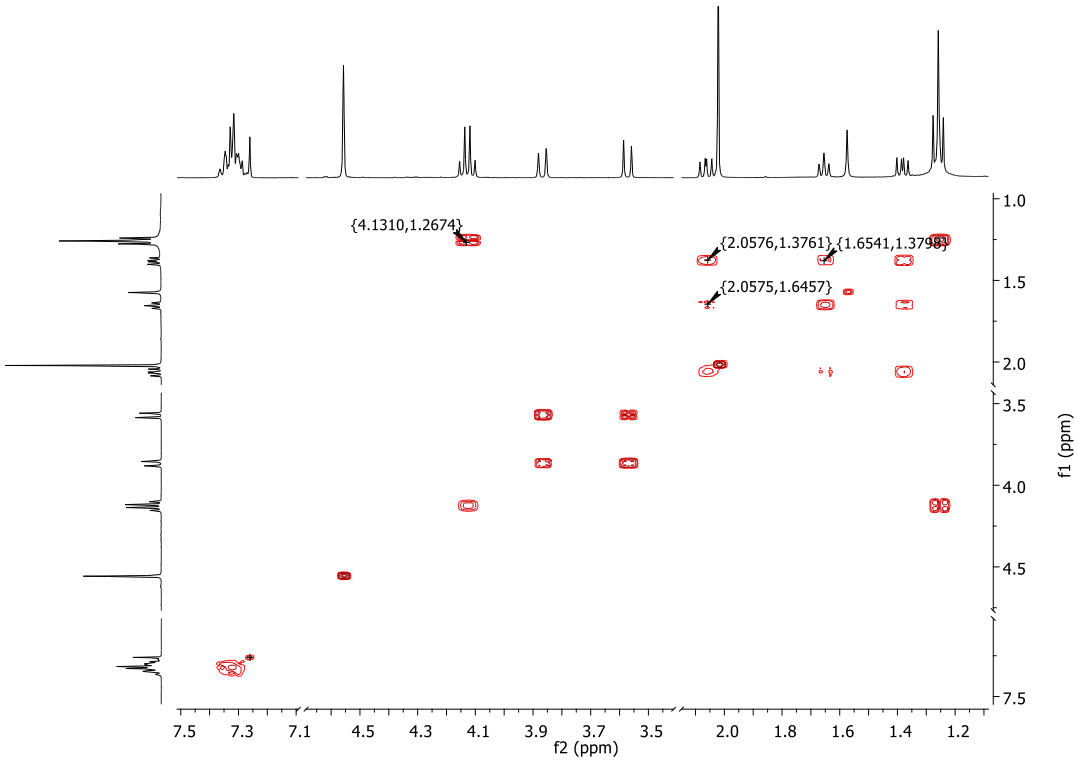
The diastereo- and *syn*-selectivity of the hydroacyloxylation reaction was determined by characterising ethyl (1*S**,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (**3ia**) by the two-dimensional NMR (COSY, HMQC and NOESY) experiments detailed below. The signal assignment was further confirmed by comparison with the previously described deuterated derivative **3ia-D** (*vide infra*).

Ethyl (1*S,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (3ia)**

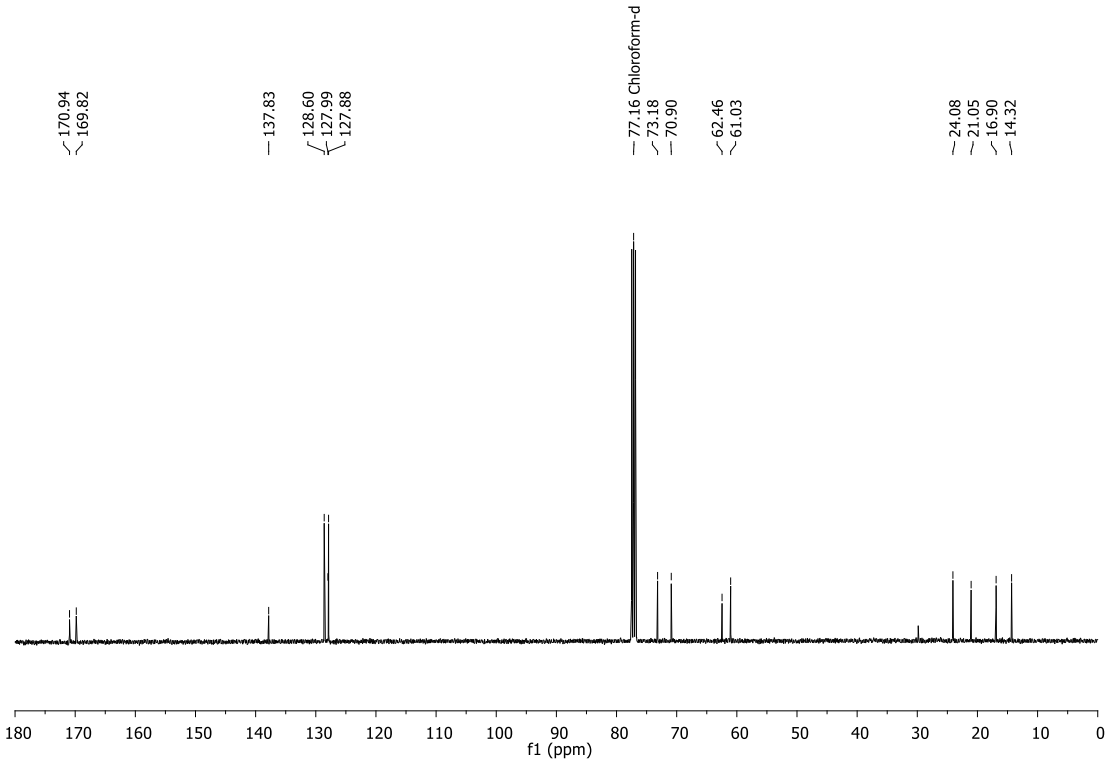
^{1}H NMR ($CDCl_3$, 400 MHz) – Signal assignment by COSY, HMQC and NOESY



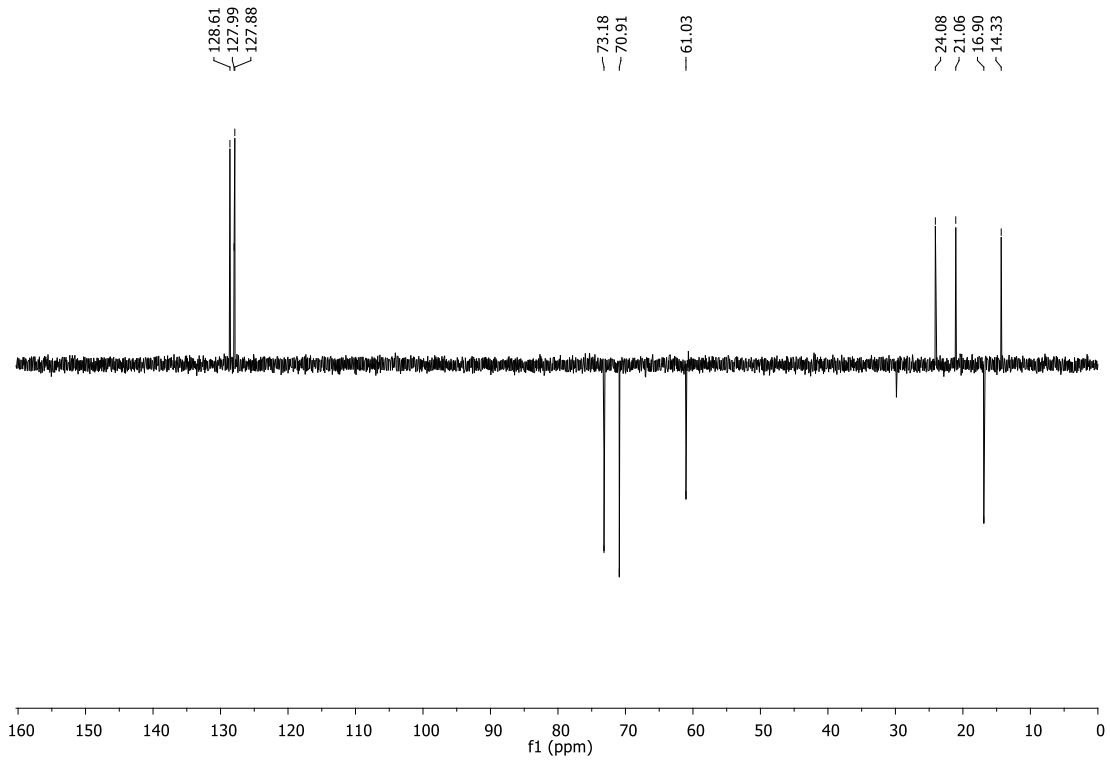
COSY ($CDCl_3$, 400 MHz)



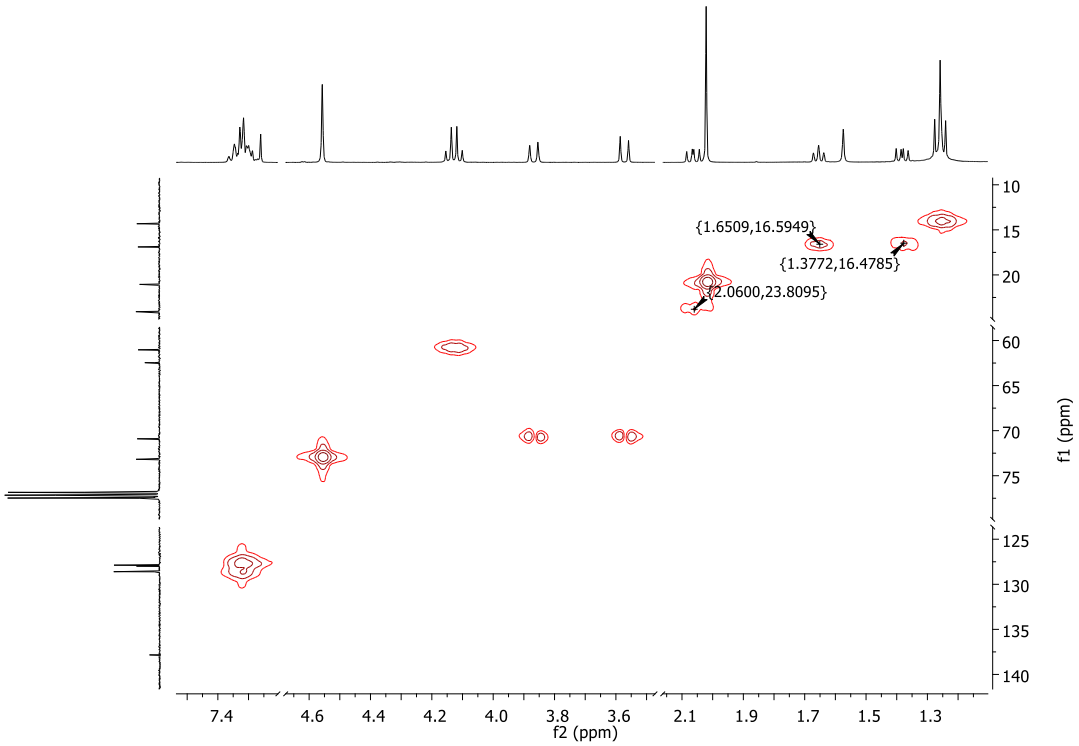
^{13}C NMR ($CDCl_3$, 101 MHz)



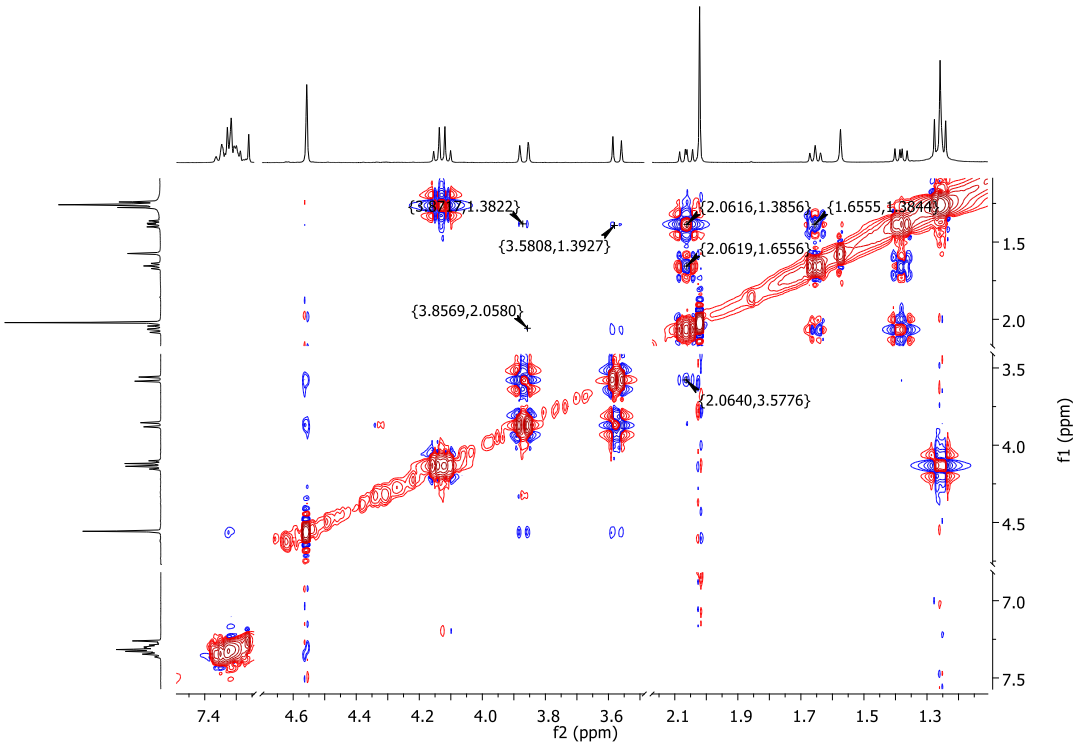
^{13}C NMR-DEPT-135 ($CDCl_3$, 101 MHz)



HMQC ($CDCl_3$, 400/101 MHz)

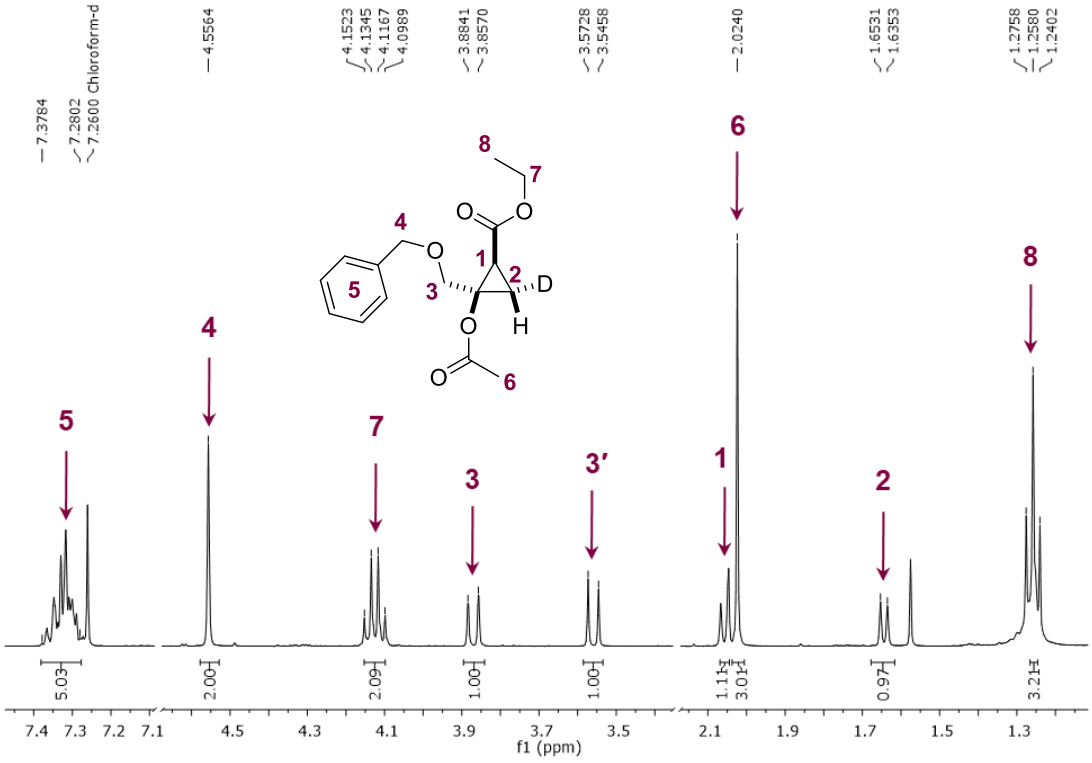


NOESY ($CDCl_3$, 400 MHz)

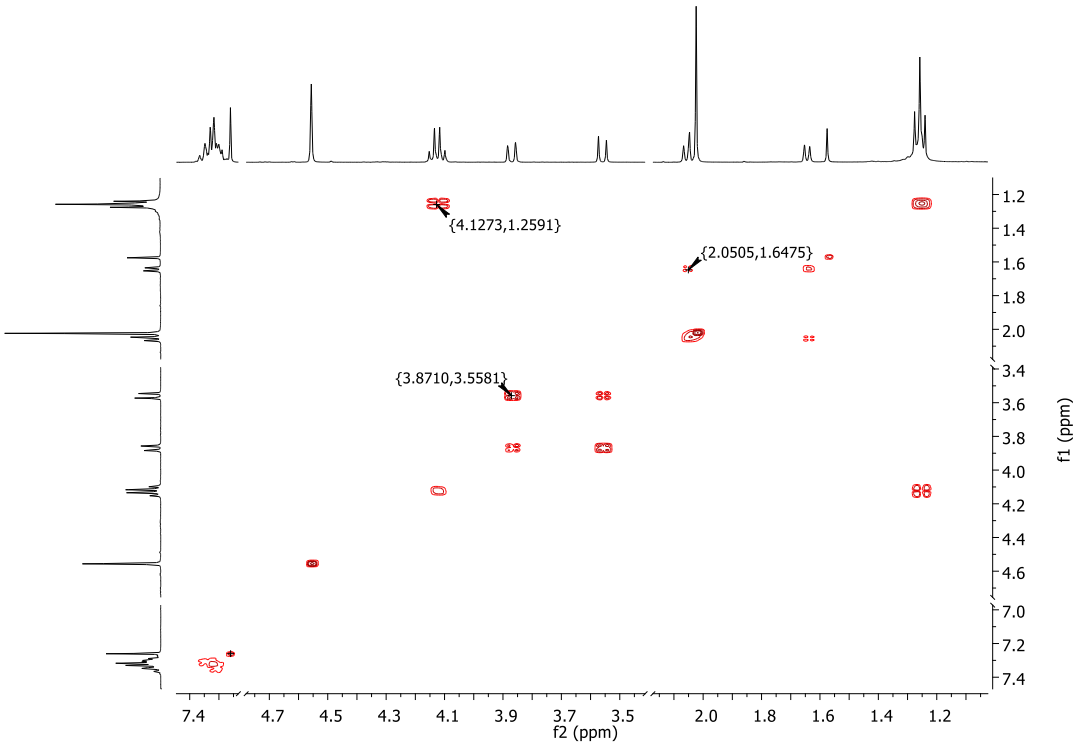


Ethyl (1*S,2*R**,3*S**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate-3-*d* (3ia-D)**

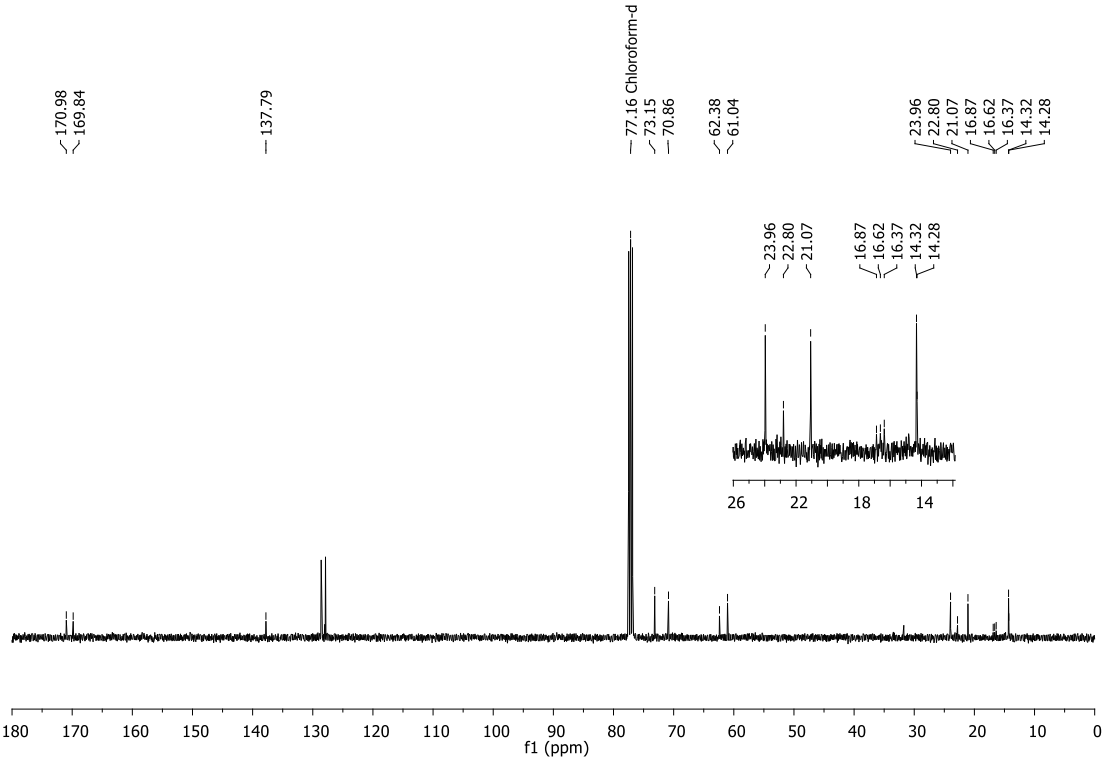
^{1}H NMR ($CDCl_3$, 400 MHz) – Signal assignment by COSY, HMQC and NOESY



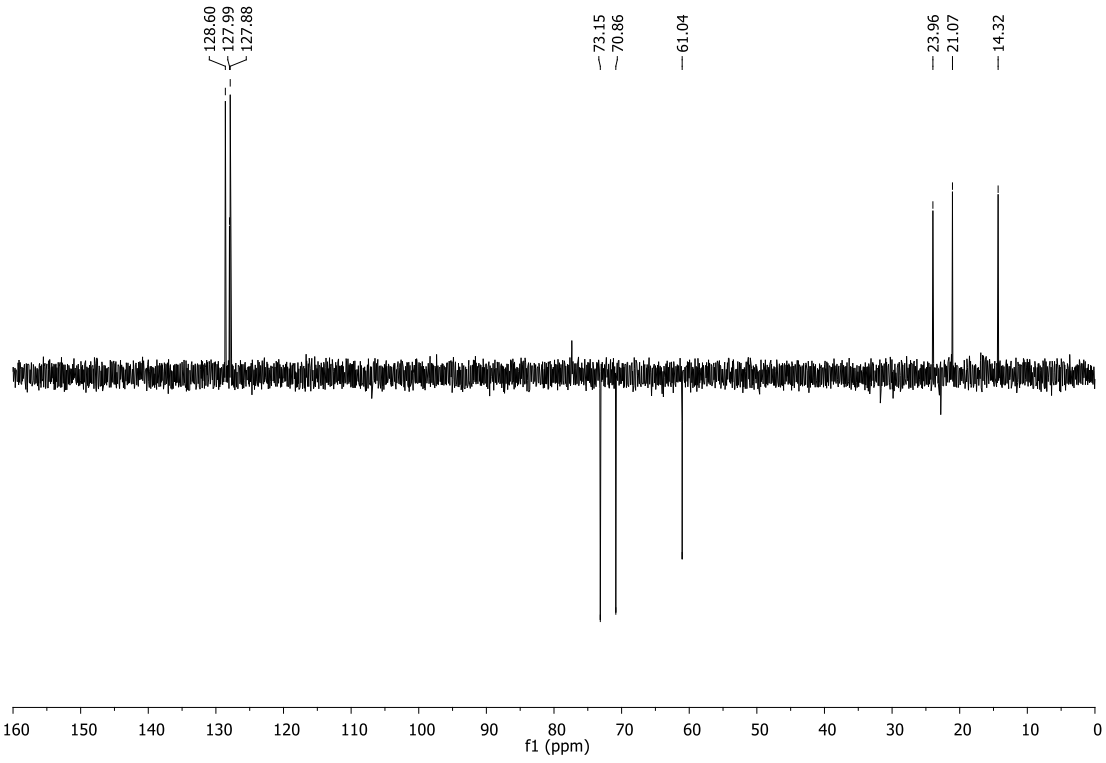
COSY ($CDCl_3$, 400 MHz)



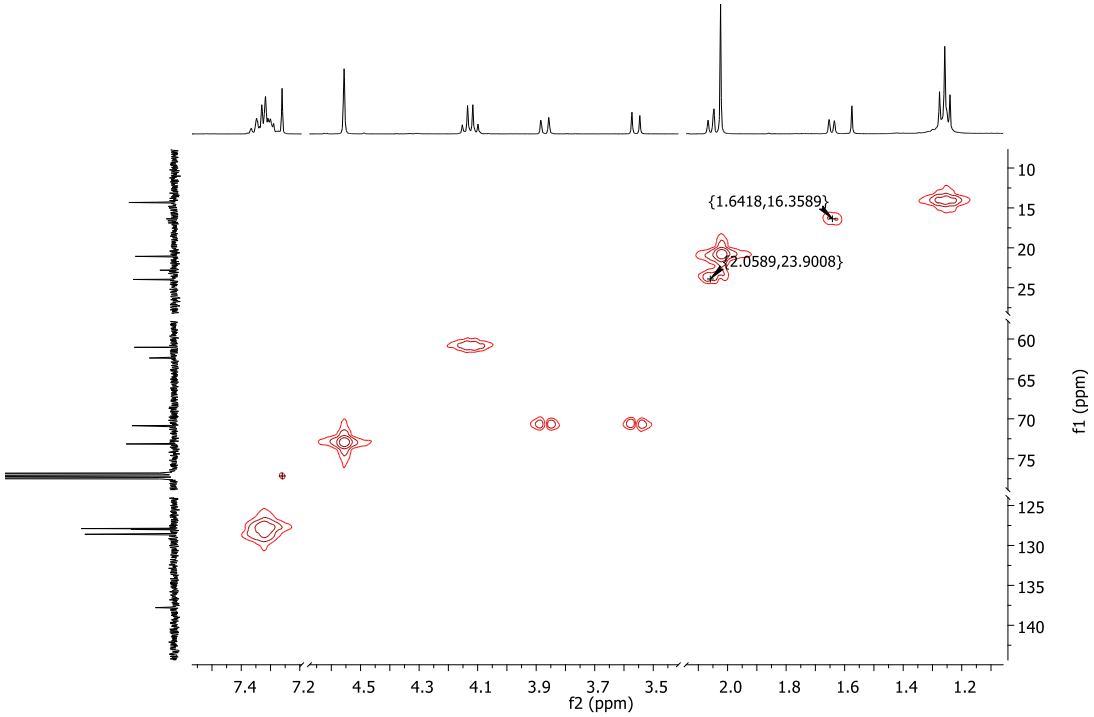
^{13}C NMR ($CDCl_3$, 101 MHz)



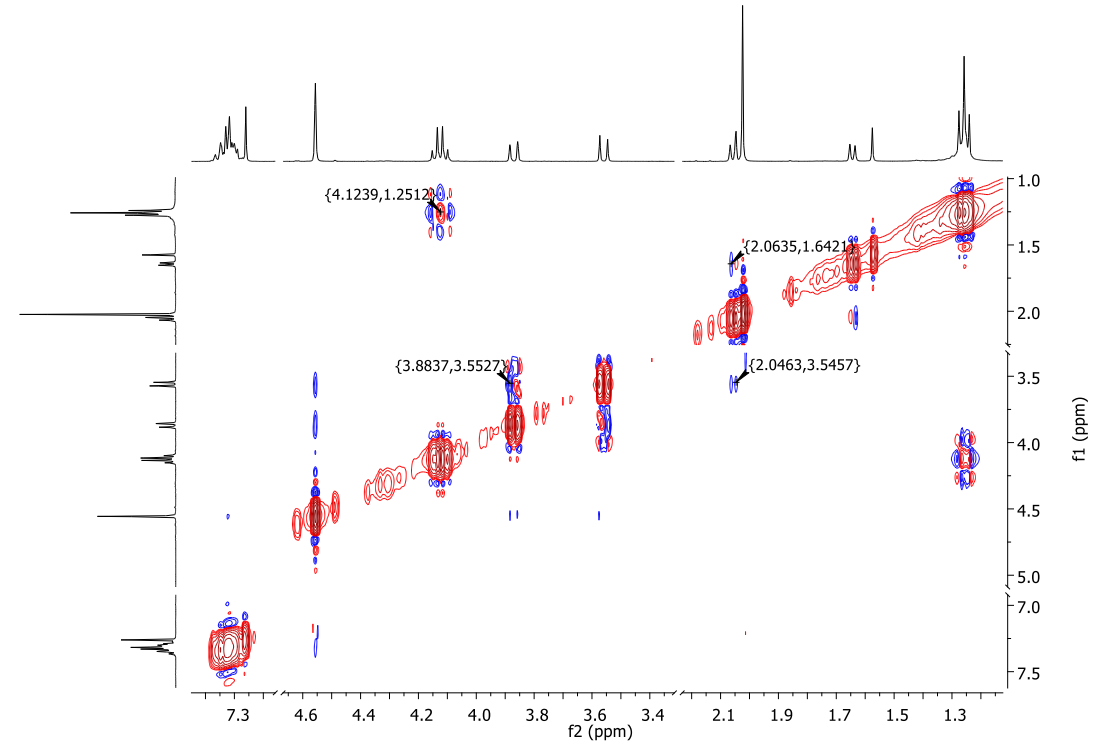
^{13}C NMR-DEPT-135 ($CDCl_3$, 101 MHz)



HMQC ($CDCl_3$, 400/101 MHz)



NOESY ($CDCl_3$, 400 MHz)



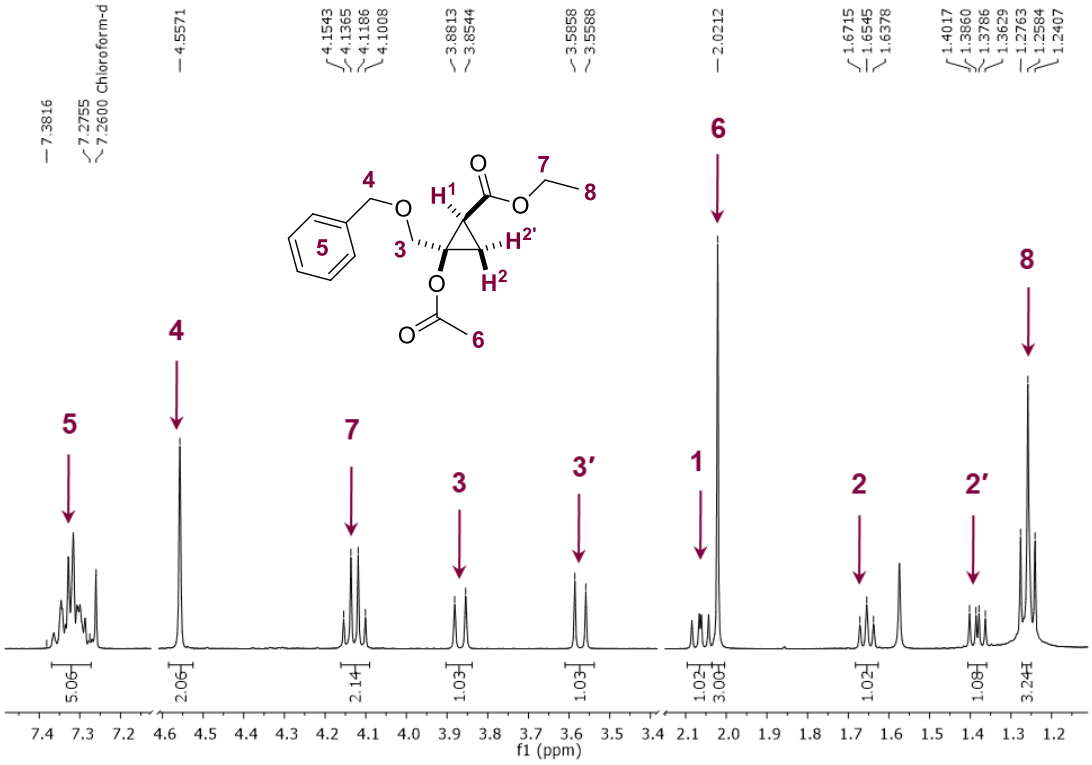
8.1.2. 1D Nuclear Overhauser Effect (nOe) experiments

The diastereo- and *syn*-selectivity of the hydroacyloxylation reaction was further confirmed by 1D nOe difference (NOEDIFF) experiments of ethyl (1*S**,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (**3ia**). The signal assignment of compound **3ia** is detailed below, as described in the previous section.

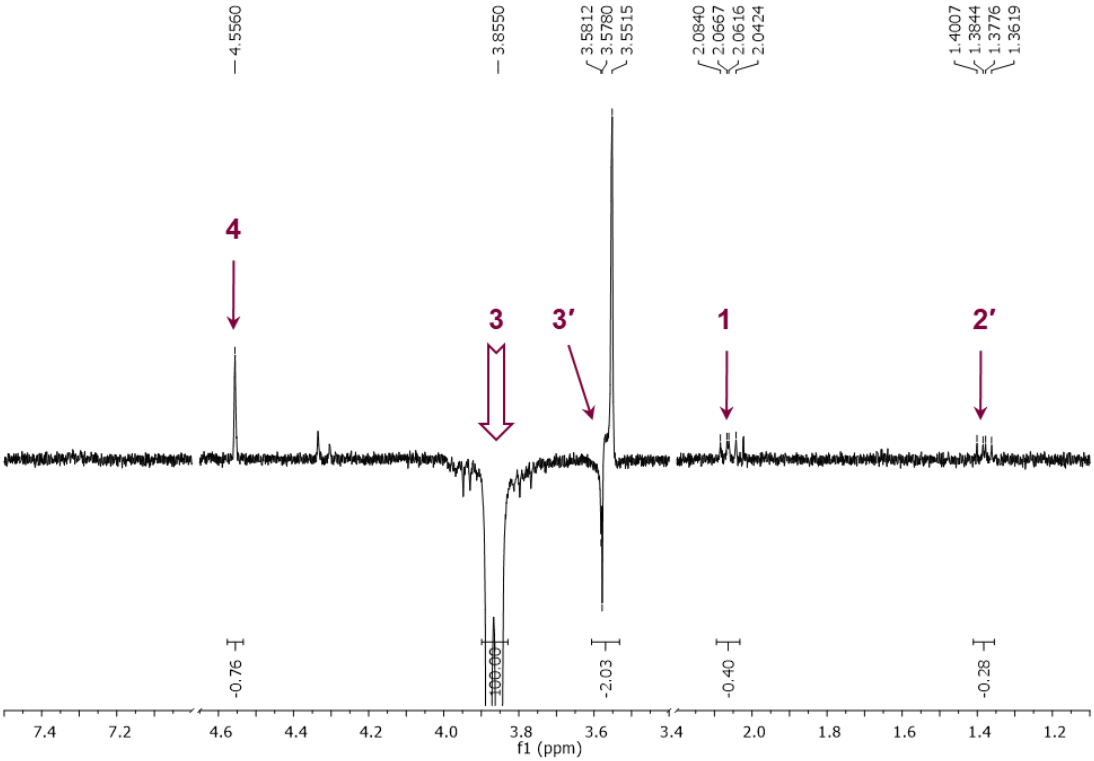
Two parallel nOe spectra were recorded irradiating signals at 3.86 and 3.58 ppm (see below). The calculated nOe confirmed that benzyl moiety (protons 3 and 3') is located on the same face of the cyclopropane as the protons labelled 1 and 2'.

Ethyl (1*S,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (3ia)**

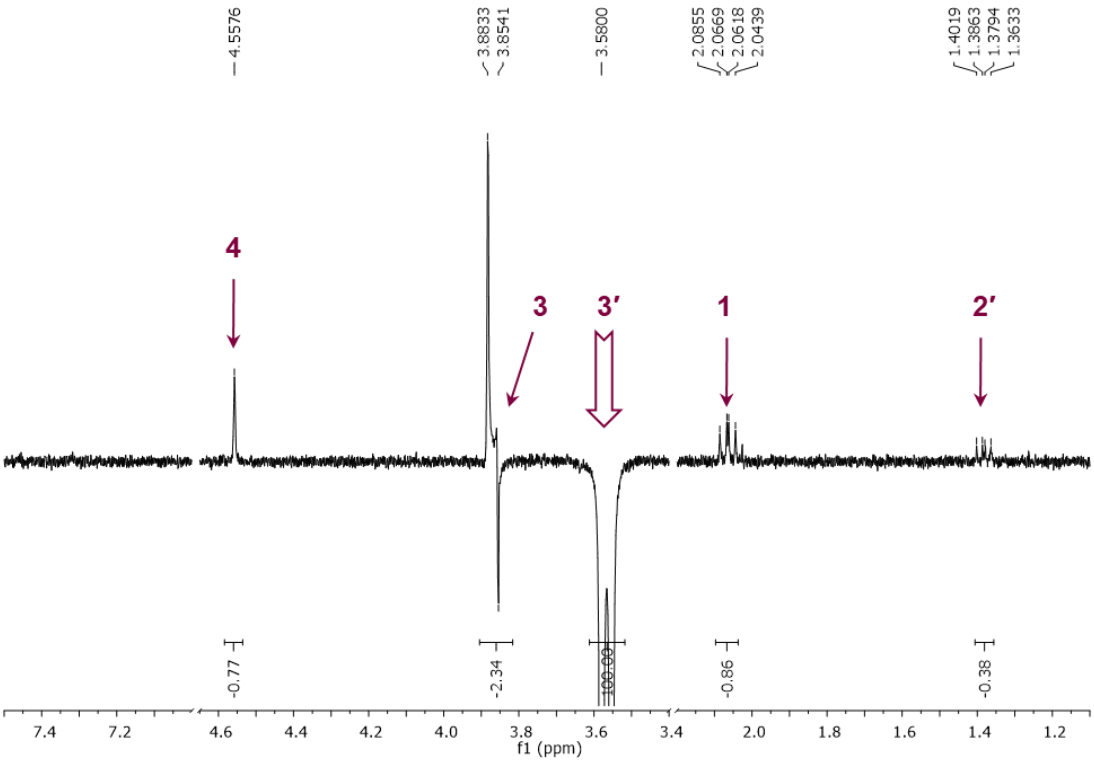
^{1}H NMR ($CDCl_3$, 400 MHz) – Signal assignment by COSY, HMQC and NOESY



1D Selective Gradient NOESY ($CDCl_3$, 400 MHz) – Irradiating signal at 3.86 ppm

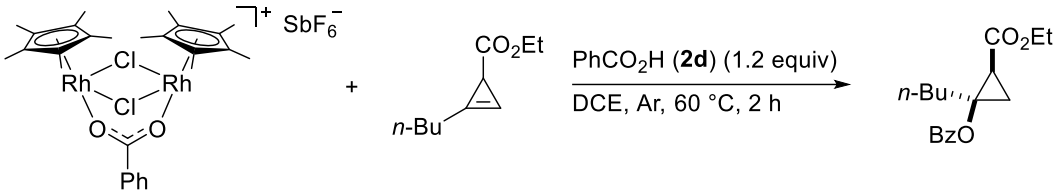


1D Selective Gradient NOESY ($CDCl_3$, 400 MHz) – Irradiating signal at 3.58 ppm



8.2. Stoichiometric studies with isolated Rh-complexes

8.2.1. Using complex Rh-A

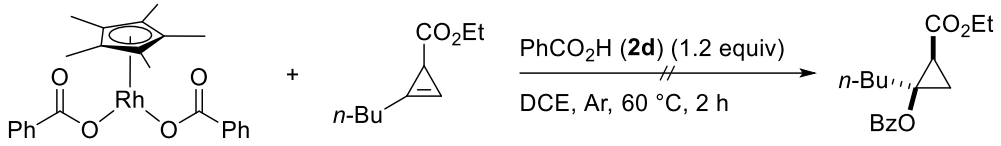


Rh-A (0.10 mmol) **1a** (1.0 equiv) **3ad**, 92% yield

Scheme S17. Hydrobenzoyloxylation of **1a** using **Rh-A** in stoichiometric amounts

An oven-dried argon-flushed 10 mL vessel was charged with **Rh-A** (90 mg, 0.10 mmol, 1.0 equiv) and benzoic acid (15 mg, 0.12 mmol, 1.2 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (17 mg, 0.10 mmol, 1.0 equiv) in dry 1,2-dichloroethane (1.0 mL) was added *via* syringe, and the resulting mixture was heated at 60 °C for 2 hours. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 9:1) to afford **3ad** as a yellowish oil; yield: 27 mg (92%). The analytical data (NMR) matched those obtained previously for compound **3ad**, which suggested **Rh-A** has a key role during the hydroacyloxylation reaction.

8.2.2. Using Cp*Rh(OBz)$_2$



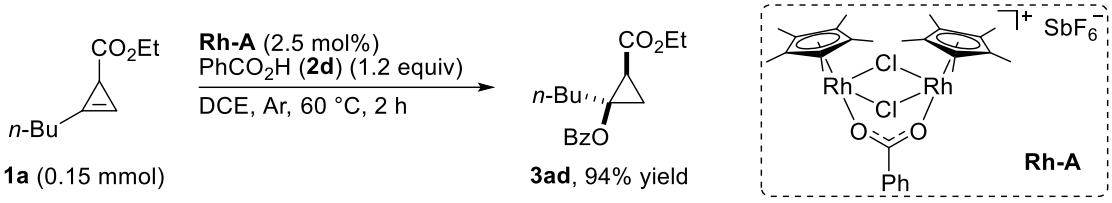
Cp*Rh(OBz)$_2$ (0.10 mmol) **1a** (1.0 equiv) **3ad**, <2% yield

Scheme S18. Hydrobenzoyloxylation of **1a** using **Cp*Rh(OBz)$_2$** in stoichiometric amounts

An oven-dried argon-flushed 10 mL vessel was charged with **Cp*Rh(OBz)$_2$** (48 mg, 0.1 mmol, 1.0 equiv) and benzoic acid (15 mg, 0.12 mmol, 1.2 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (17 mg, 0.10 mmol, 1.0 equiv) in dry 1,2-dichloroethane (1.0 mL) was added *via* syringe, and the resulting mixture was heated at 60 °C for 2 hours. Volatiles were then removed under reduced pressure and the residue was analysed by ^{1}H NMR. Complete recovery of unaltered starting material **1a** ruled out **Cp*Rh(OBz)$_2$** as a feasible reaction intermediate.

8.3. Catalytic studies with isolated Rh-complexes

8.3.1. Using complex Rh-A

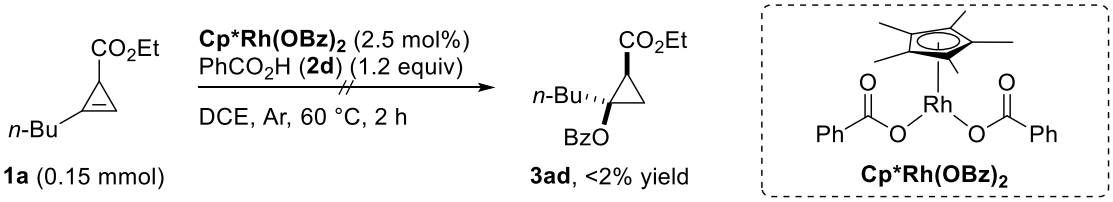


1a (0.15 mmol) **3ad**, 94% yield

Scheme S19. Hydrobenzoyloxylation of **1a** using **Rh-A** in catalytic amounts

An oven-dried argon-flushed 10 mL vessel was charged with **Rh-A** (3.4 mg, 0.0038 mmol, 0.025 equiv) and benzoic acid (22 mg, 1.8 mmol, 1.2 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (25 mg, 0.15 mmol, 1.0 equiv) in dry 1,2-dichloroethane (1.0 mL) was added *via* syringe, and the resulting mixture was heated at 60 °C for 2 hours. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 9:1) to afford **1e** as a yellowish oil; yield: 41 mg (94%). The analytical data (NMR) matched those obtained previously for compound **2a**, which suggested that **Rh-A** is a plausible catalytically active species.

8.3.2. Using Cp*Rh(OBz)$_2$



1a (0.15 mmol) **3ad**, <2% yield

Scheme S20. Hydrobenzoyloxylation of **1a** using **Cp*Rh(OBz)$_2$** in catalytic amounts

An oven-dried argon-flushed 10 mL vessel was charged with **Cp*Rh(OBz)$_2$** (3.4 mg, 0.0038 mmol, 0.025 equiv) and benzoic acid (22 mg, 1.8 mmol, 1.2 equiv). The reaction vessel was sealed, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (25 mg, 0.15 mmol, 1.0 equiv) in dry 1,2-dichloroethane (1.0 mL) was added *via* syringe, and the resulting mixture was heated at 60 °C for 2 hours. Volatiles were then removed under reduced pressure and the residue was analysed by ^{1}H NMR. Complete recovery of unaltered starting material **1a** ruled out the generation of **Cp*Rh(OBz)$_2$** during the course of the reaction.

8.4. NMR Monitoring experiments

For clarity, ^{1}H NMR spectra of the most relevant compounds of this section are shown below (**Figure S2** to **Figure S5**). In this section, all spectra were recorded in 1,2-dichloroethane-d_4.

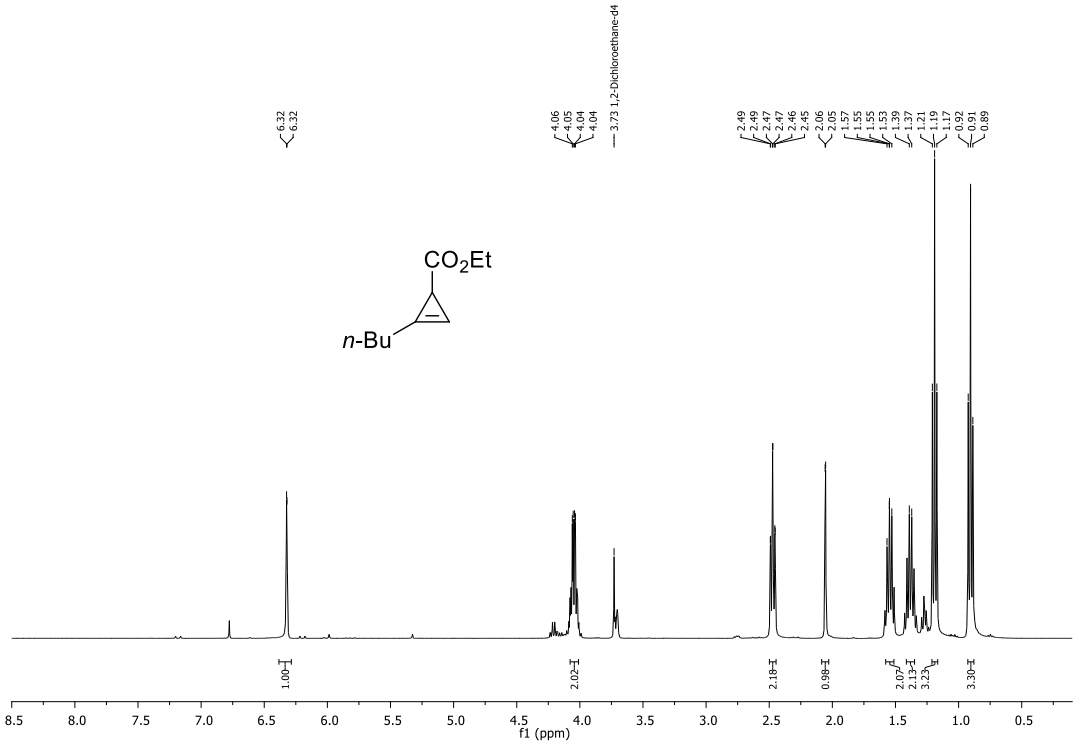


Figure S2. NMR Spectrum of **1a** in 1,2-dichloroethane-d_4

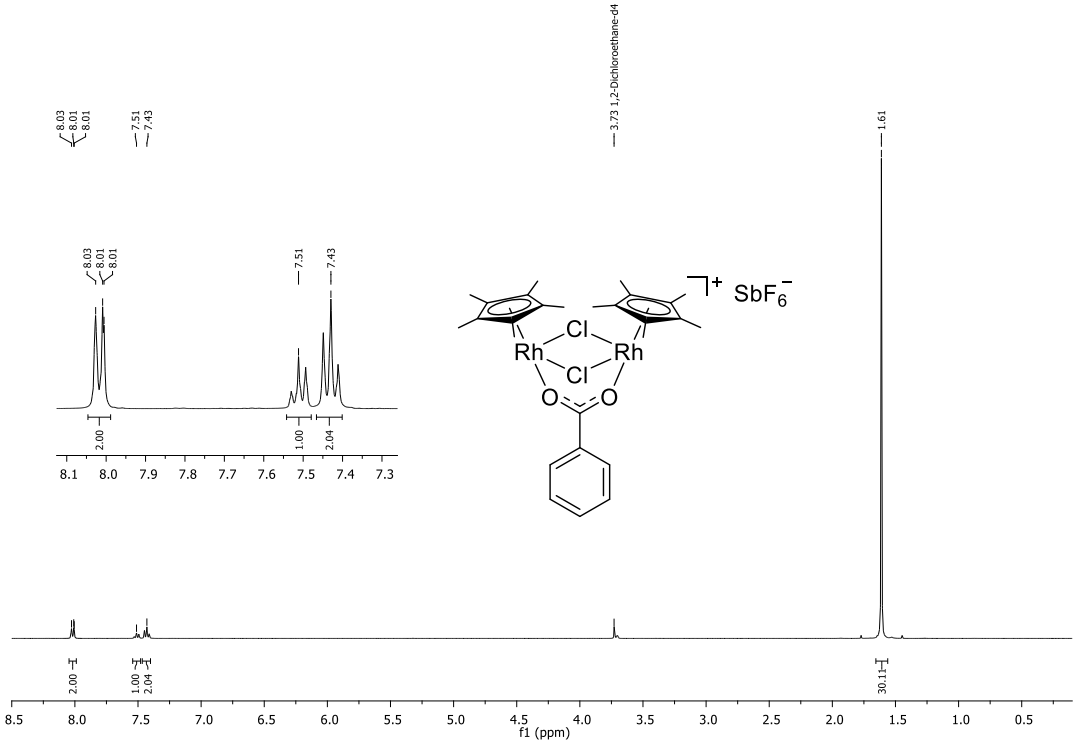


Figure S3. NMR Spectrum of **Rh-A** in 1,2-dichloroethane-d_4

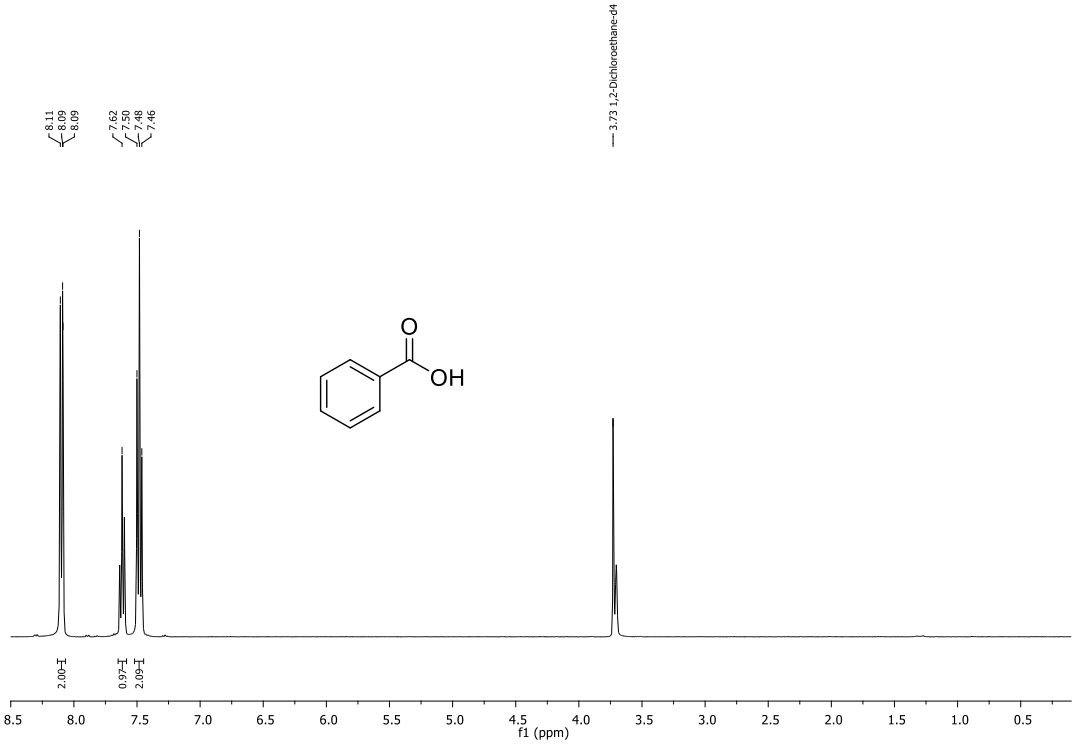


Figure S4. NMR Spectrum of **2d** in 1,2-dichloroethane-d_4

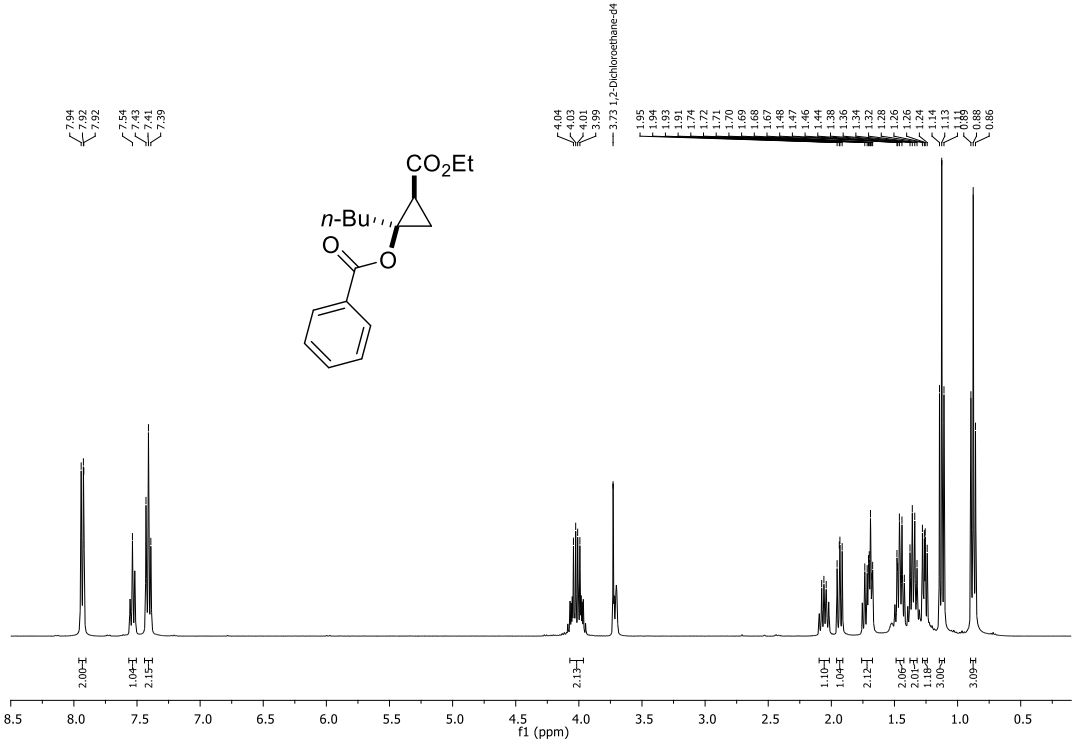


Figure S5. NMR Spectrum of **3ad** in 1,2-dichloroethane-d_4

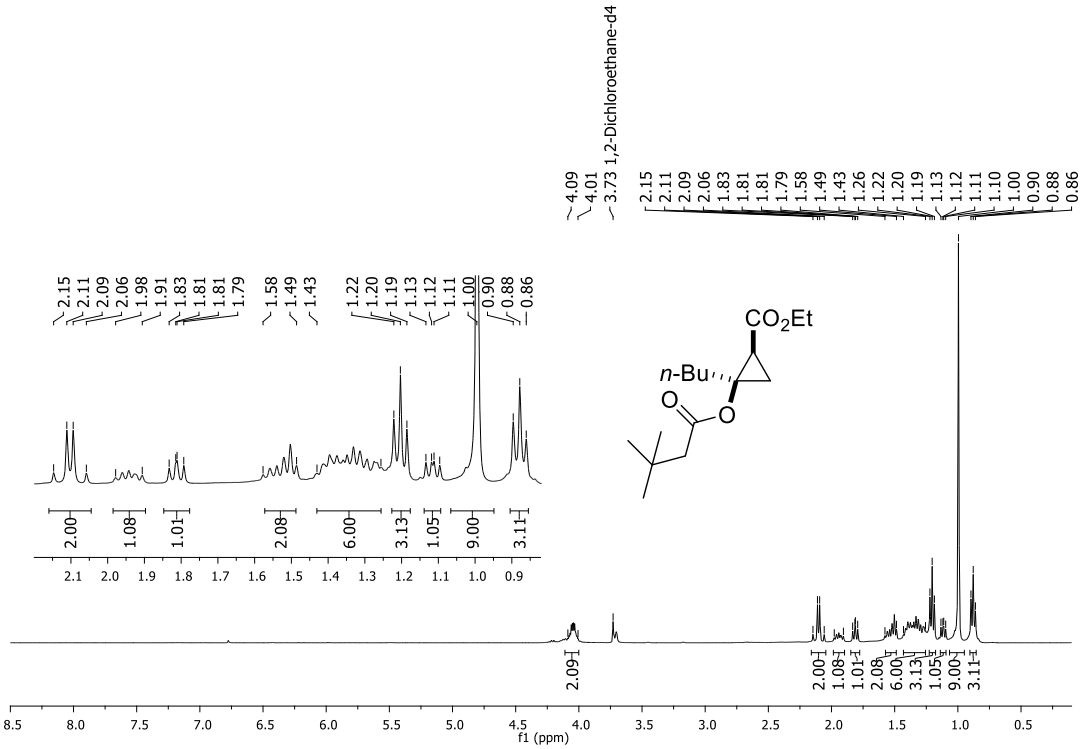
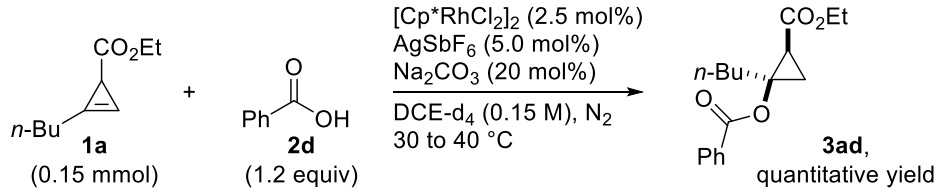


Figure S6. NMR Spectrum of **1a** in 1,2-dichloroethane-d_4

8.4.1. Model reaction



Scheme S21. NMR-monitored Rh(III)-catalysed hydroacyloxylation of cyclopropenes

To monitor the reaction, an oven-dried NMR tube was charged with pentamethylcyclopentadienyl rhodium dichloride dimer (4.6 mg, 0.0075 mmol, 0.10 equiv), silver hexafluoroantimonate(V) (5.2 mg, 0.015 mmol, 0.20 equiv) and anhydrous sodium carbonate (3.2 mg, 0.030 mmol, 0.40 equiv) and benzoic acid (**2d**) (11 mg, 0.090 mmol, 1.20 equiv). The tube was sealed with a Teflon septum, then evacuated and flushed with nitrogen three times. Under a nitrogen atmosphere, a solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (13 mg, 0.075 mmol, 1.0 equiv) in 1,2-dichloroethane-d_4 (0.5 mL) was added via syringe. A first ^{1}H NMR spectrum was recorded at 30 °C to establish the starting point (**Figure S7**), using diethyl malonate as the internal standard (6.78 ppm).

Then, the temperature was increased to 40 °C (**Figure S8**), and a relevant conversion of **1a** to the final product **3ad** was observed. At this point, it was possible to assign characteristic signals for the compounds

of interest: **1a** = 6.32 ppm (d, *J* = 1.4 Hz, 1H); **3ad** = 7.93 ppm (d, *J* = 7.1 Hz, 2H); and **Rh-A** = 8.02 ppm (d, *J* = 7.0 Hz, 2H). Once the NMR tube reached 40 °C, ^{1}H NMR spectra were recorded periodically (15-minute period) for 105 minutes (from **Figure S8** to **Figure S14**) until complete consumption of **1a**. The collection of spectra in stacked form is depicted in **Figure S15**.

This experiment demonstrates that the dimeric species is formed during the reaction, with a characteristic signal in the aromatic region (**Figure S8**). Noteworthy, along the whole experiment (from **Figure S8** to **Figure S14**), the appearance of an additional signal at *ca*. 8.05 ppm (overlapped doublet, *J* = 7.3 Hz, 2H) suggests that **Rh-A** is rather a resting state which acts as a reservoir for the actual catalytically active species. The non-variation of the value of the integral of both species during the reaction also supports this hypothesis. Accordingly, when the reaction ends, since such elusive active species is no longer required, its concentration decreases (signal at 8.05 ppm), allowing the concentration of **Rh-A** to be restored (**Figure S14**). Furthermore, characteristic singlets at 1.60 ppm and 1.64 ppm, corresponding to the Cp*-methyl groups of **Rh-A** and the catalytically active species, also point in that direction. **Figure S16** shows the superimposed spectra view of the model reaction after 115 minutes and complex **Rh-A**.

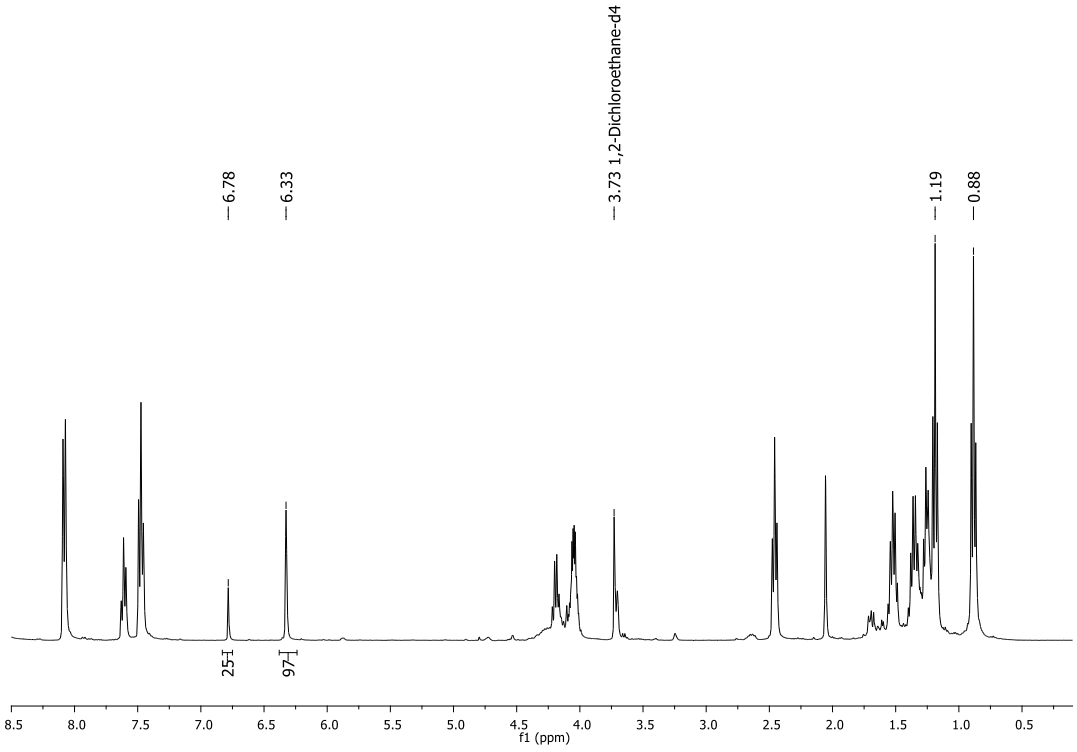


Figure S7. Reaction mixture at 30 °C (*t* = 0 min)

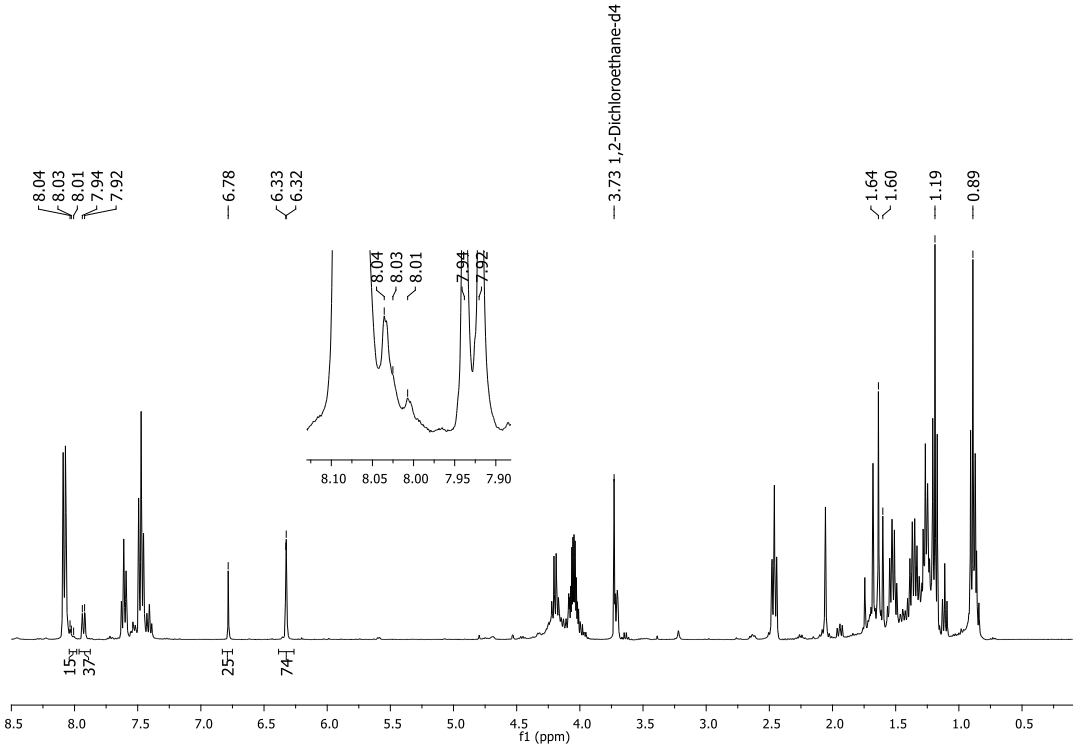


Figure S8. Reaction mixture at 40 °C (*t* = 15 min)

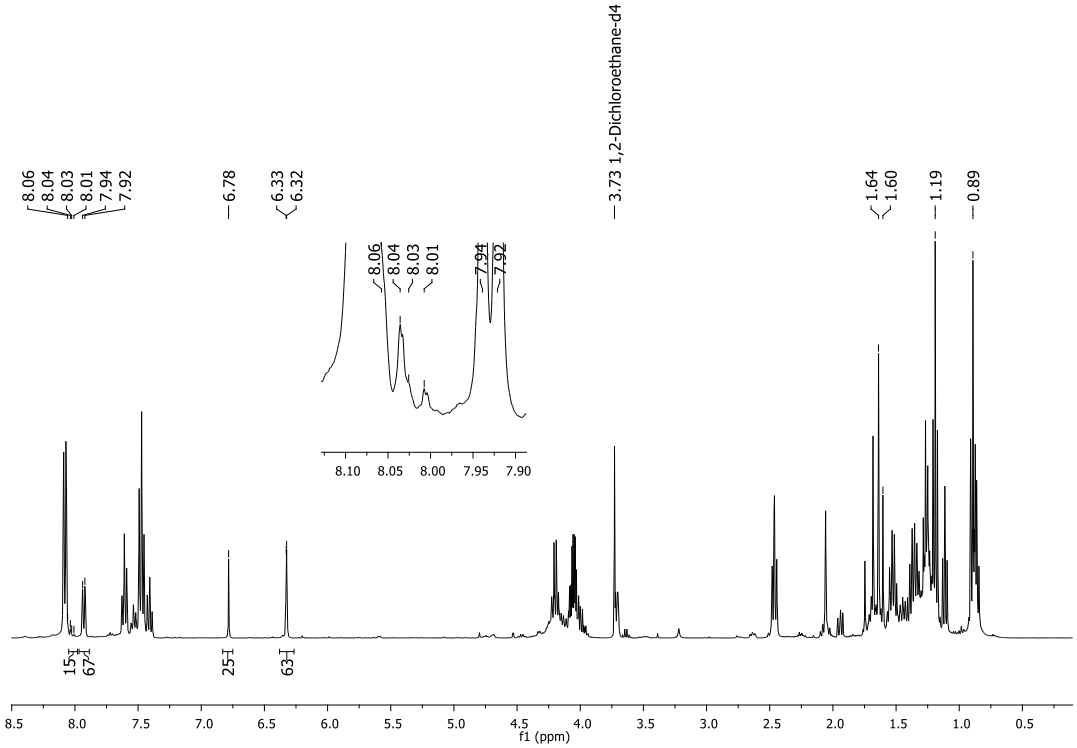


Figure S9. Reaction mixture at 40 °C (*t* = 30 min)

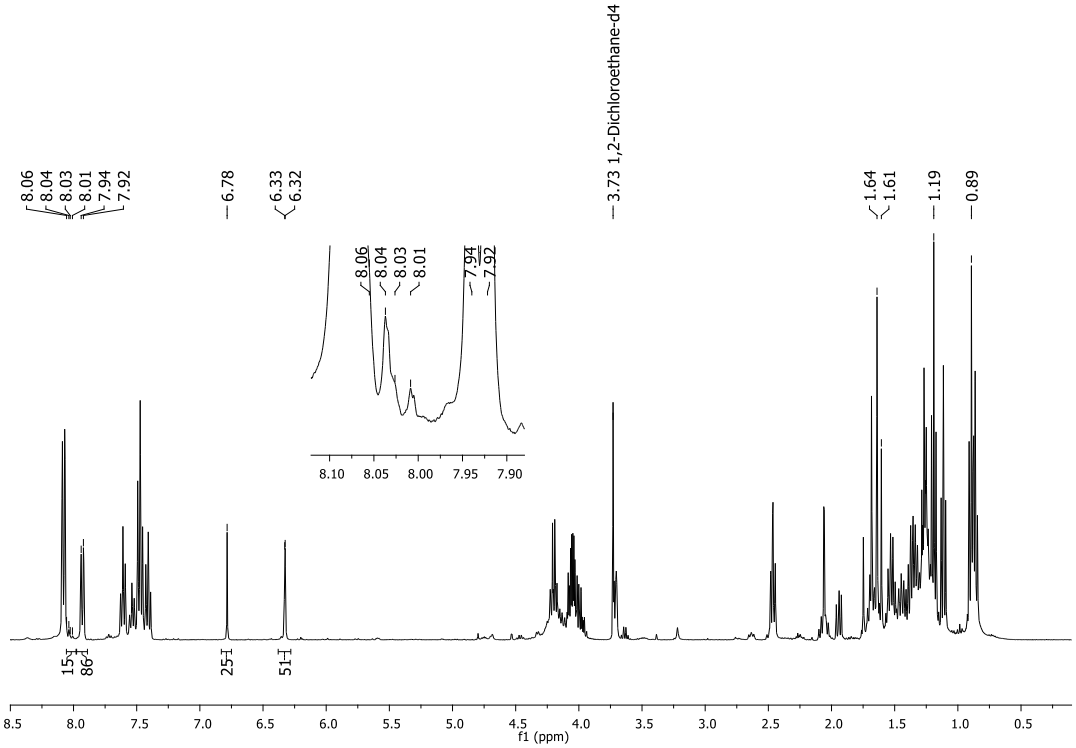


Figure S10. Reaction mixture at 40 °C (*t* = 45 min)

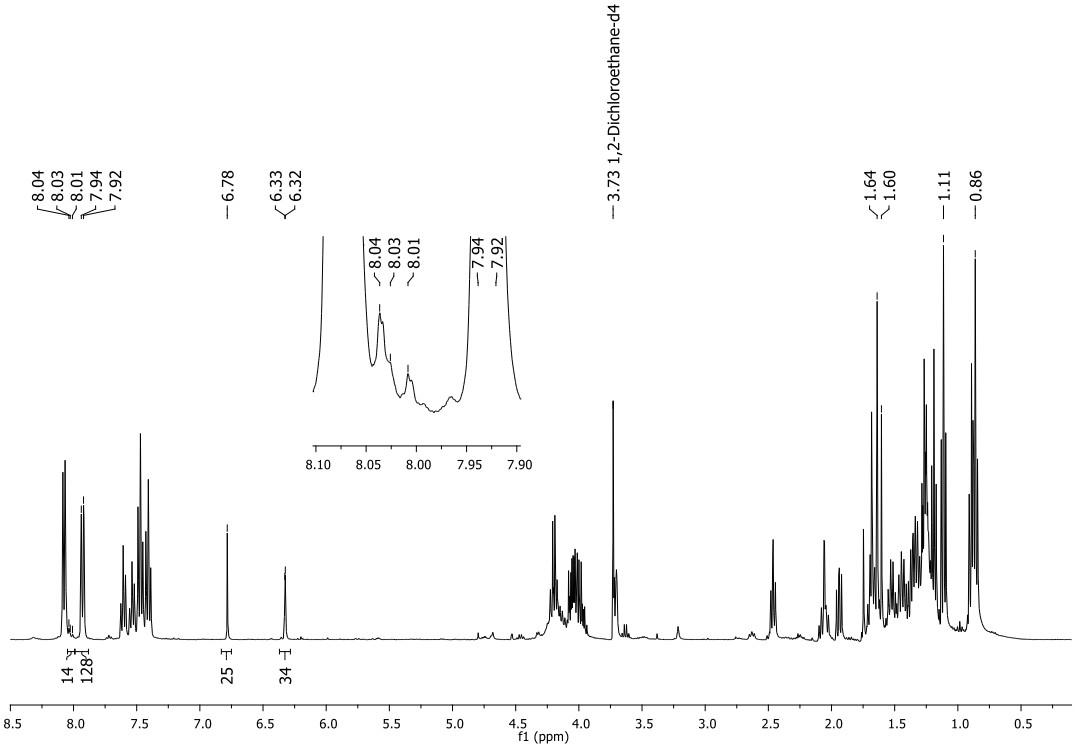


Figure S11. Reaction mixture at 40 °C (*t* = 60 min)

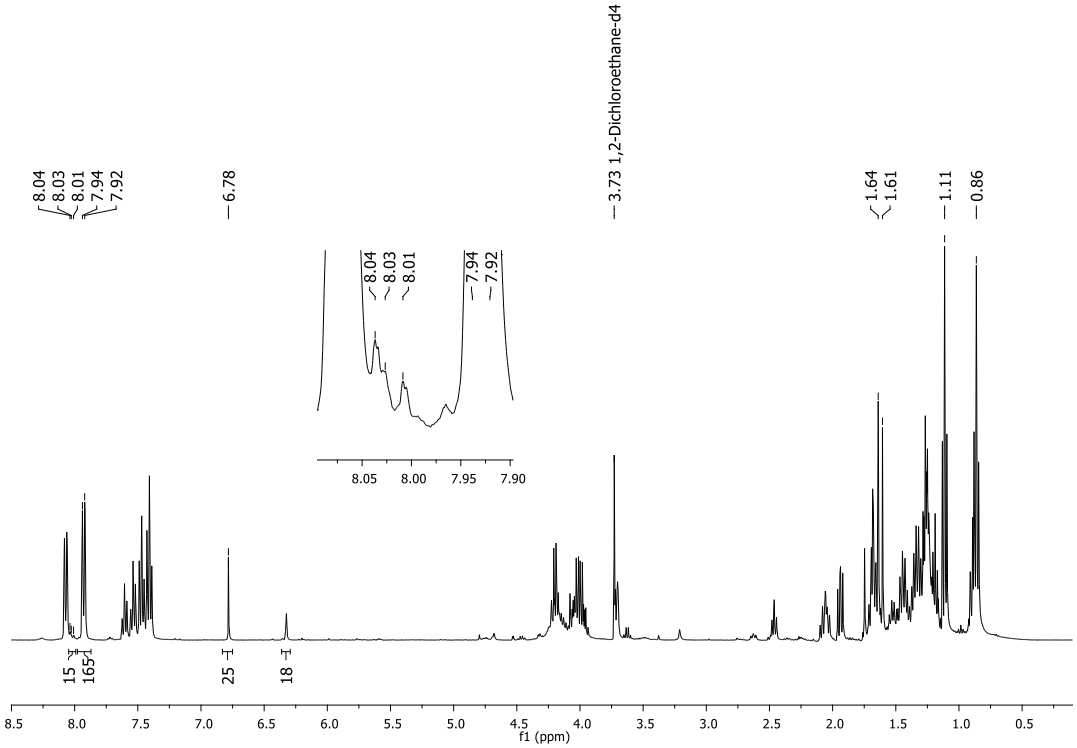


Figure S12. Reaction mixture at 40 °C (*t* = 75 min)

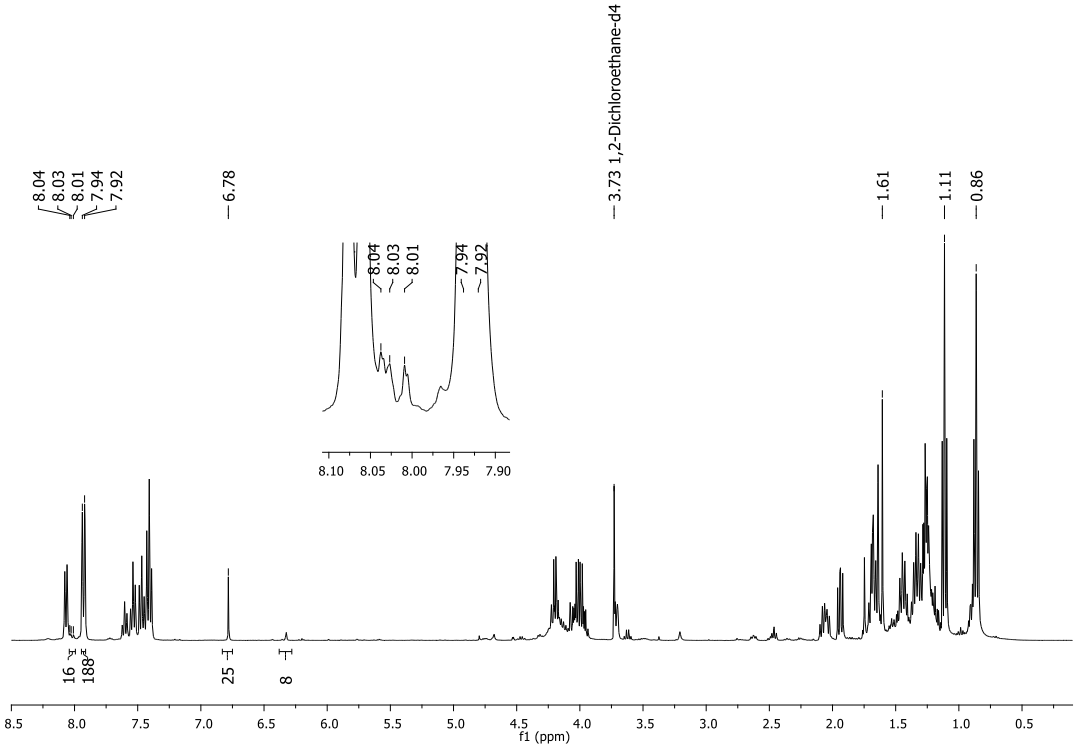


Figure S13. Reaction mixture at 40 °C (*t* = 90 min)

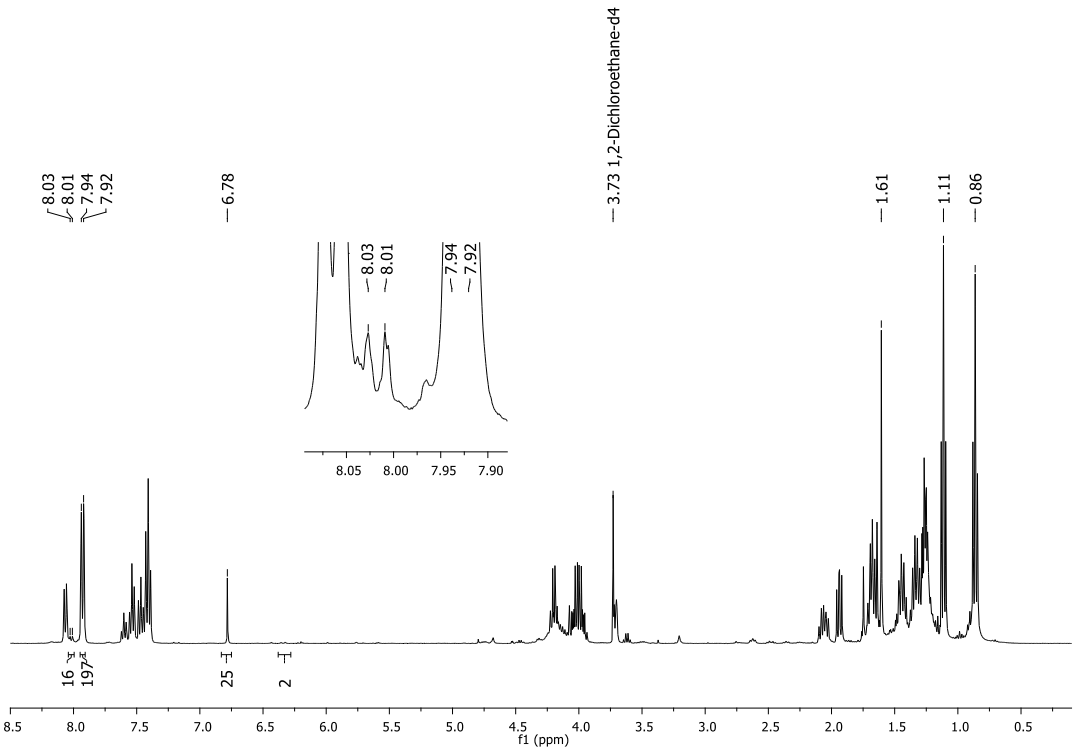


Figure S14. Reaction mixture at 40 °C (*t* > 115 min)

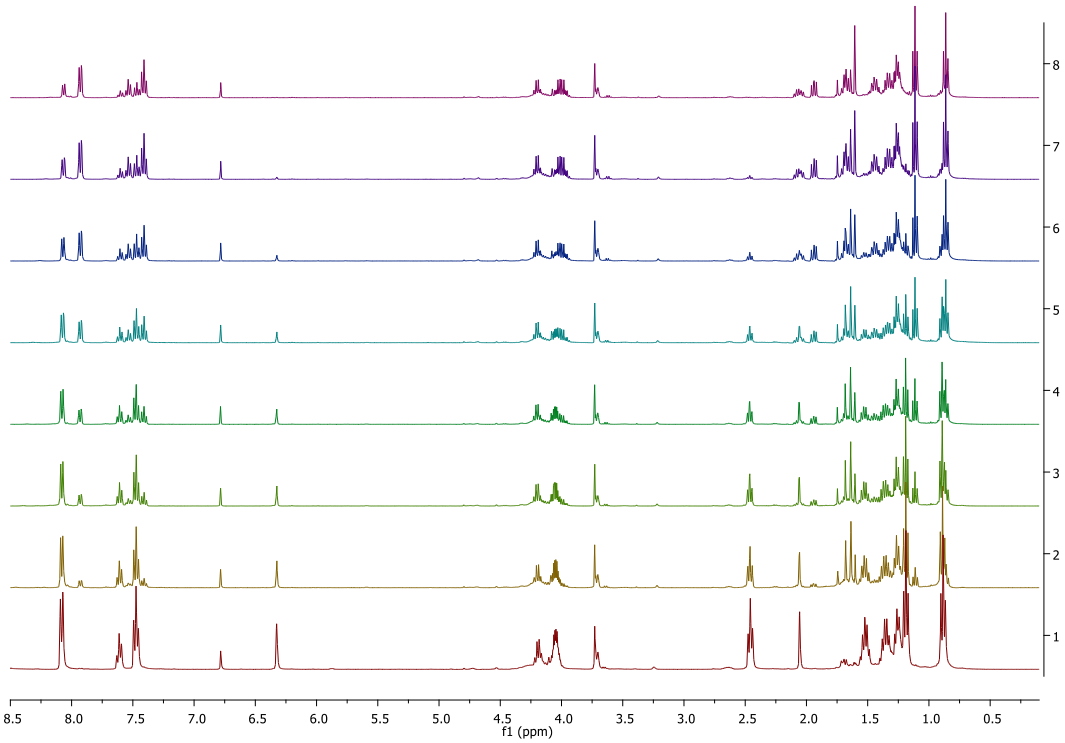


Figure S15. Stacked view of spectra 1 (*t* = 0 min) to 8 (*t* > 115 min)

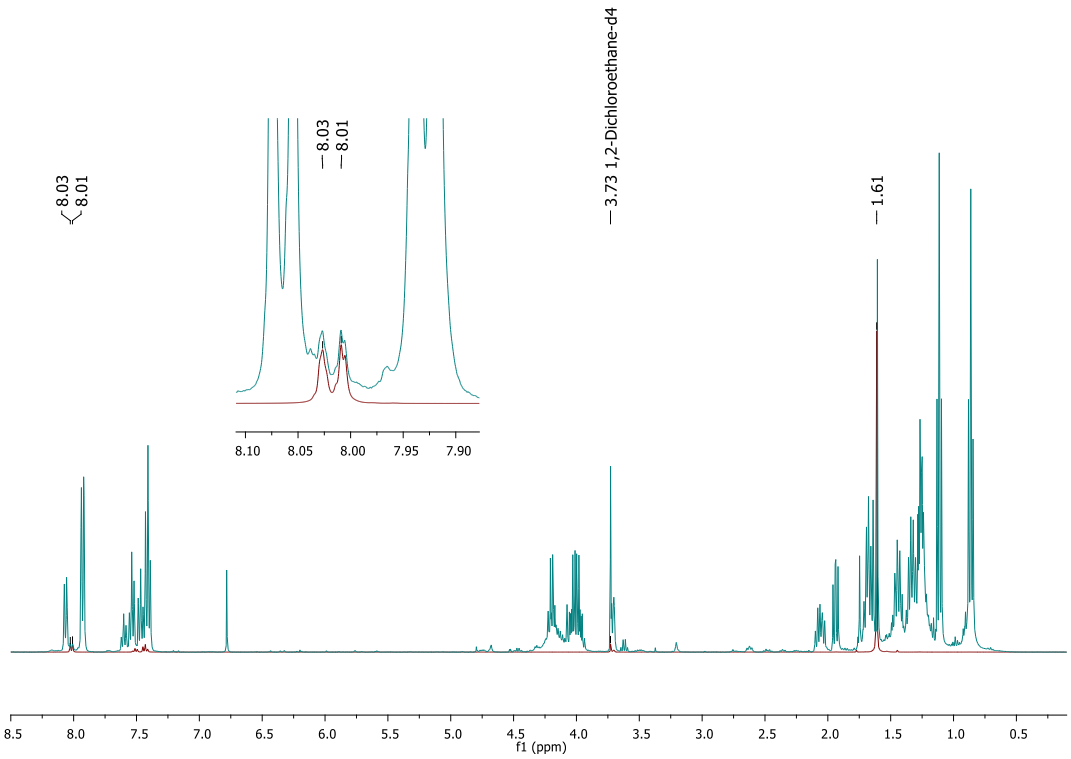
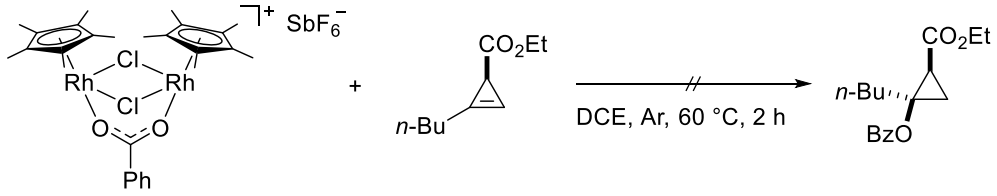


Figure S16. Superimposed view of model reaction after 115 minutes (blue) and **Rh-A** (garnet)

8.4.2. Stoichiometric experiment in the absence of an acid



Rh-A (0.075 mmol) **1a** (1.0 equiv) **3ad**, traces

Scheme S22. Mixture of **1a** and stoichiometric amounts of **Rh-A** in the absence of an acid

To monitor the reaction, an oven-dried NMR tube was charged with complex **Rh-A** (68 mg, 0.075 mmol, 1.0 equiv) and sealed with a Teflon septum, then evacuated and flushed with nitrogen three times. Under a nitrogen atmosphere, a solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (13 mg, 0.075 mmol, 1.0 equiv) in 1,2-dichloroethane-d_4 (0.5 mL) was added via syringe. A first ^{1}H NMR spectrum was recorded at 60 °C to establish the starting point (**Figure S17**), using diethyl malonate as the internal standard (6.78 ppm). Although some traces of the final product (**3ad**) were detected at 7.93 ppm (d, J = 7.1 Hz, 2H), not a significant conversion of **1a** was observed over the next 30 minutes (**Figure S18**), suggesting the reaction requires an additional amount of carboxylic acid to proceed.

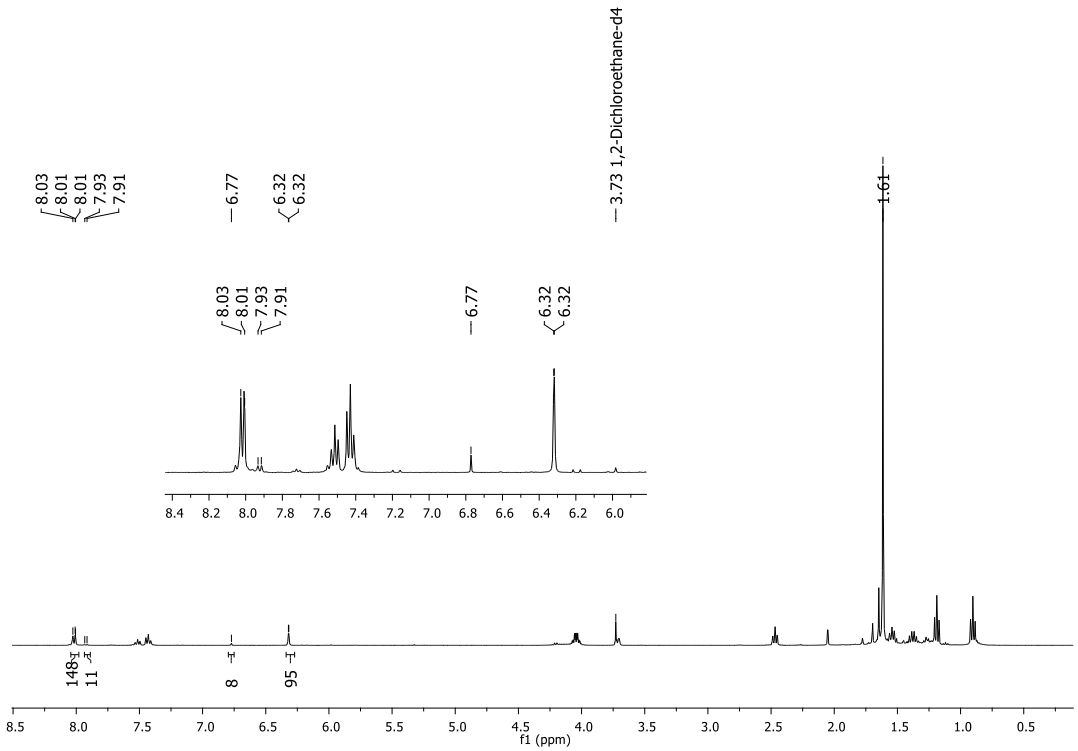


Figure S17. Reaction mixture at 40 °C (*t* = 0 min)

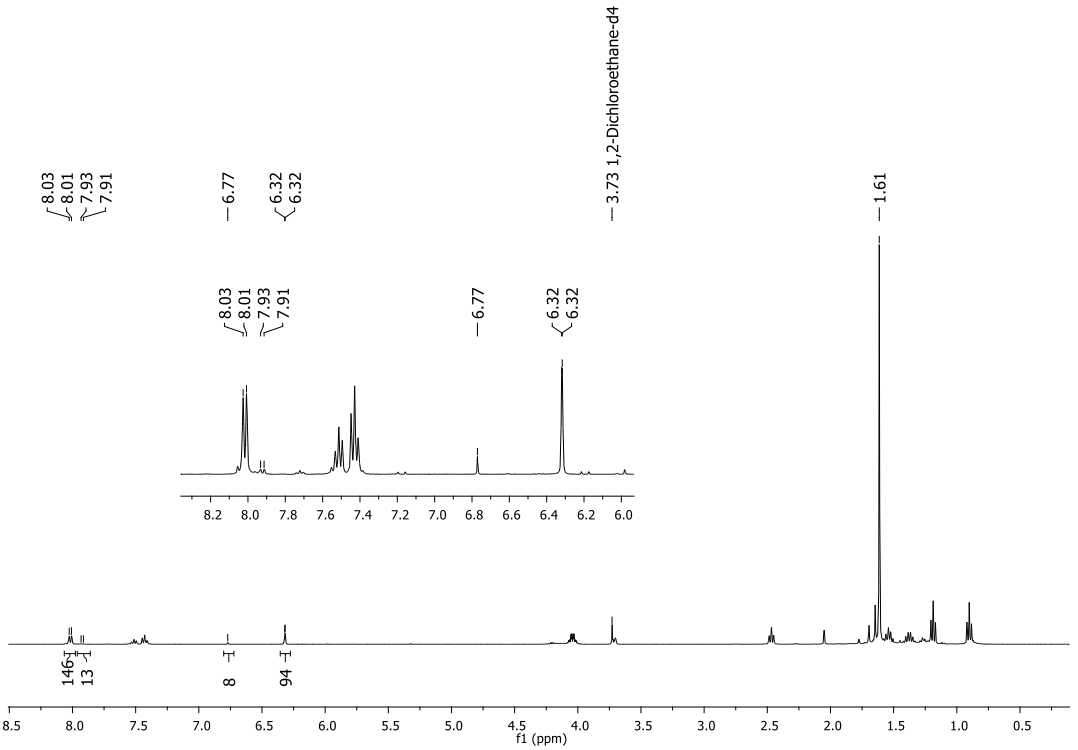
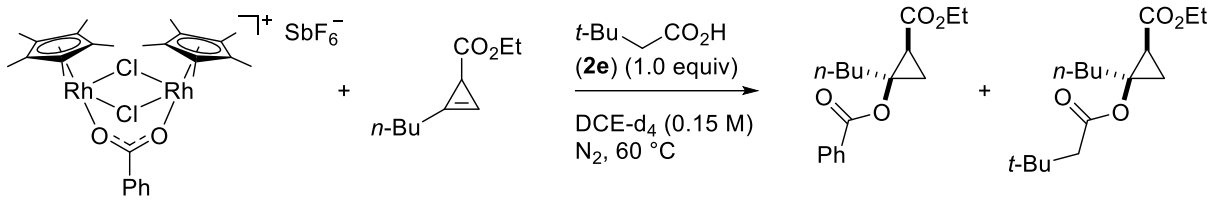


Figure S18. Reaction mixture at 40 °C (*t* = 30 min)

8.4.3. Stoichiometric experiment in the presence of an additional acid



Rh-A (0.075 mmol) **1a** (1.0 equiv) **3ad** (2:3) **3ae**

Scheme S23. Monitored reaction among **1a** and **Rh-A** in the presence of 3,3-dimethylbutyric acid (**2e**)

To the unreacted mixture from the previous experiment, 3,3-dimethylbutyric acid **2e** (10 µL, 0.0075 mmol, 1.0 equiv) was added *via* syringe to observe the formation of the elusive catalytically active species without overlap by excess of benzoic acid. A first ^{1}H NMR spectrum was then recorded at 60 °C to establish the starting point (**Figure S19**), showing that the presence of a proton source prompted the formation of product **3ad**. Superimposed spectra of **Rh-A** (blue), the model reaction (garnet) and the stoichiometric experiment (green) evidence that complex **Rh-A** partially evolved to the elusive species at 8.05 ppm (d, *J* = 7.2 Hz, 1H) detected in the model reaction. ^{1}H NMR spectra were recorded periodically for 180 minutes (from **Figure S21** to **Figure S25**) until complete consumption of **1a**, providing products **3ad** and **3ae**. The collection of spectra in stacked form is depicted in **Figure S26** and **Figure S27**.

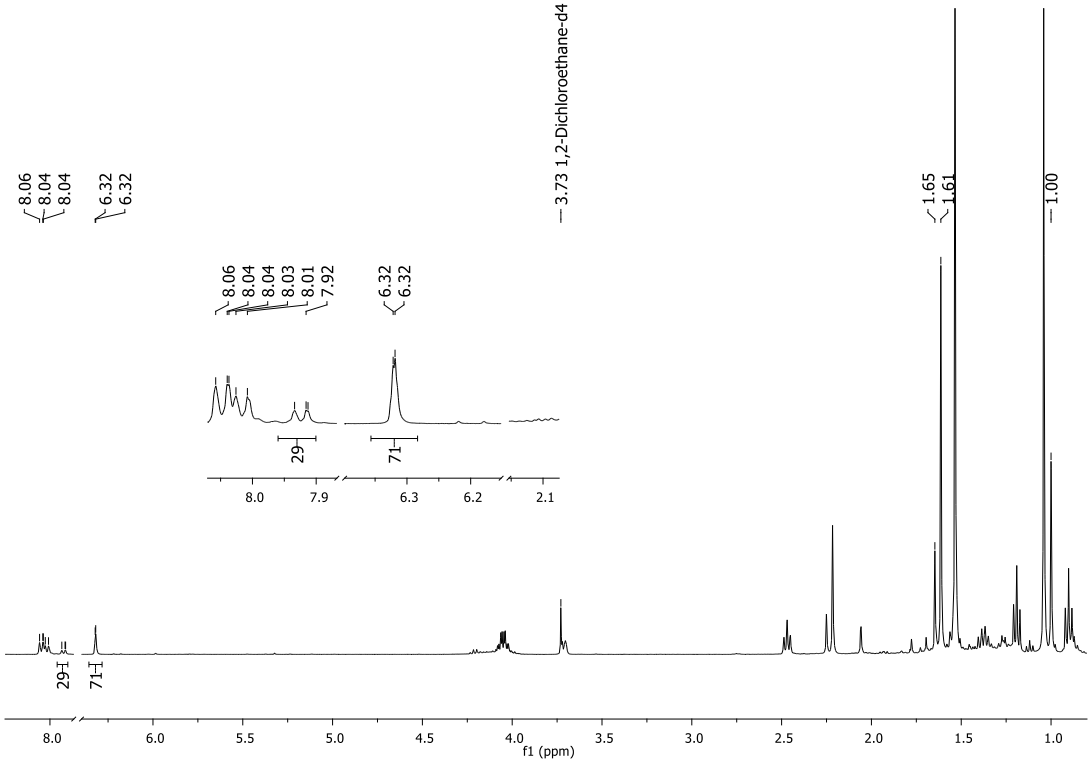


Figure S19. Reaction mixture at 40 °C (*t* = 30 min)

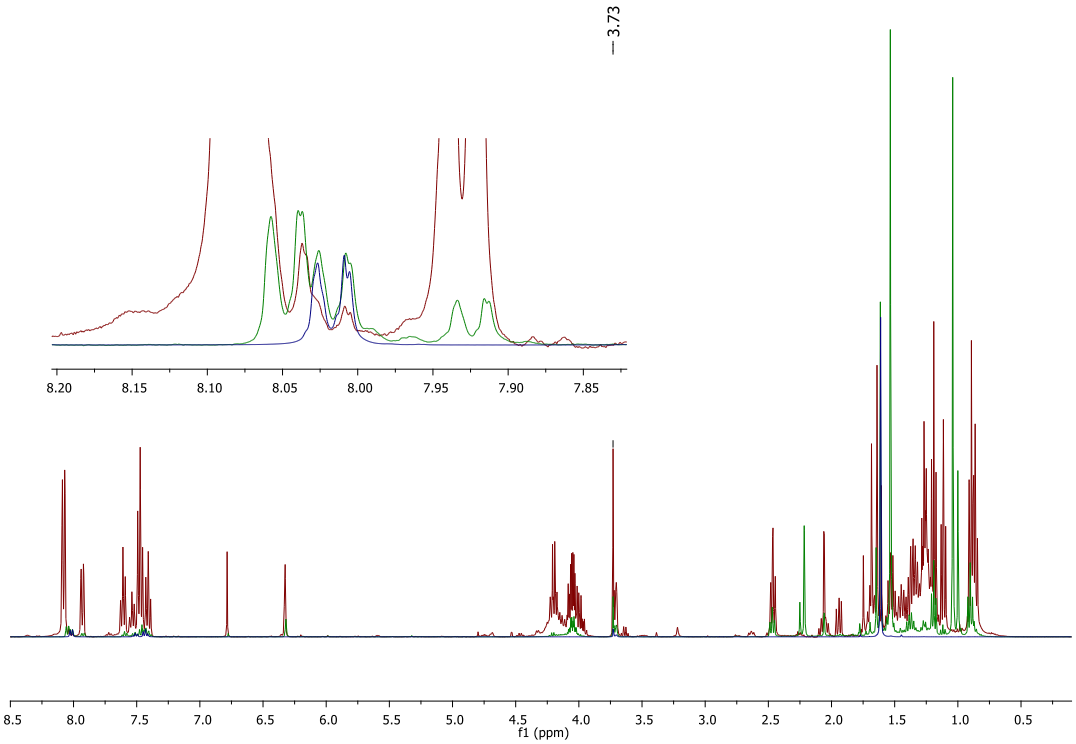


Figure S20. Superimposed view of **Rh-A** (blue), model reaction (garnet) and stoichiometric experiment (green)

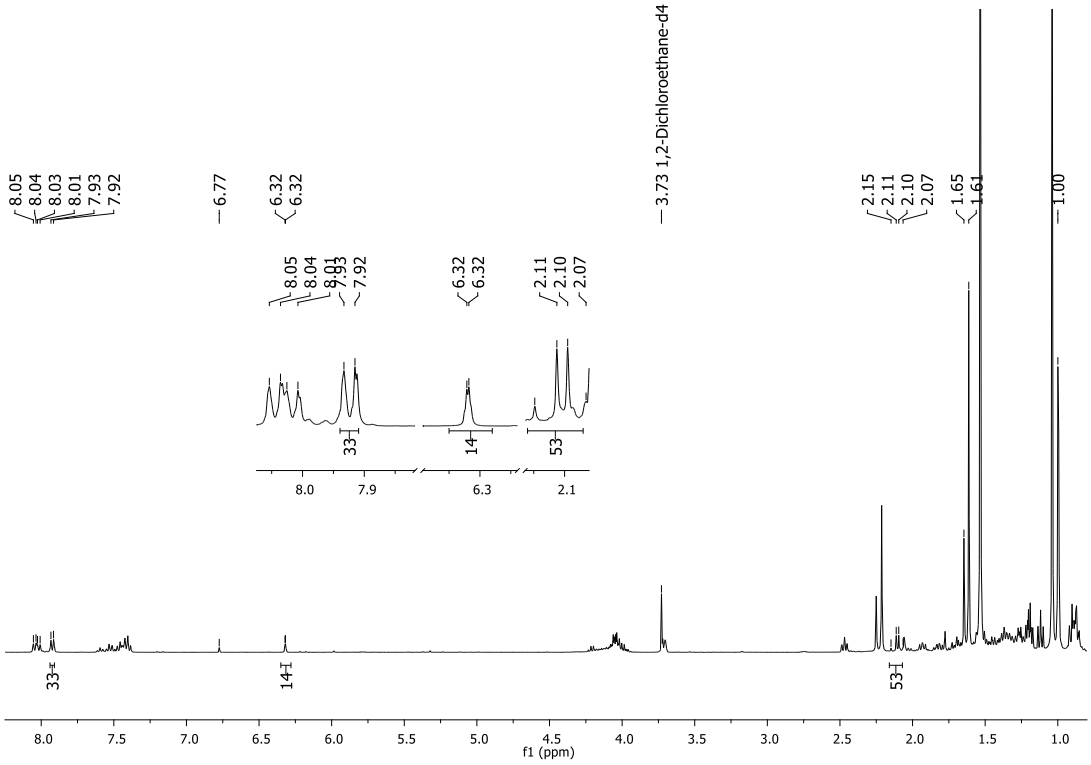


Figure S21. Reaction mixture at 60 °C (*t* = 30 min)

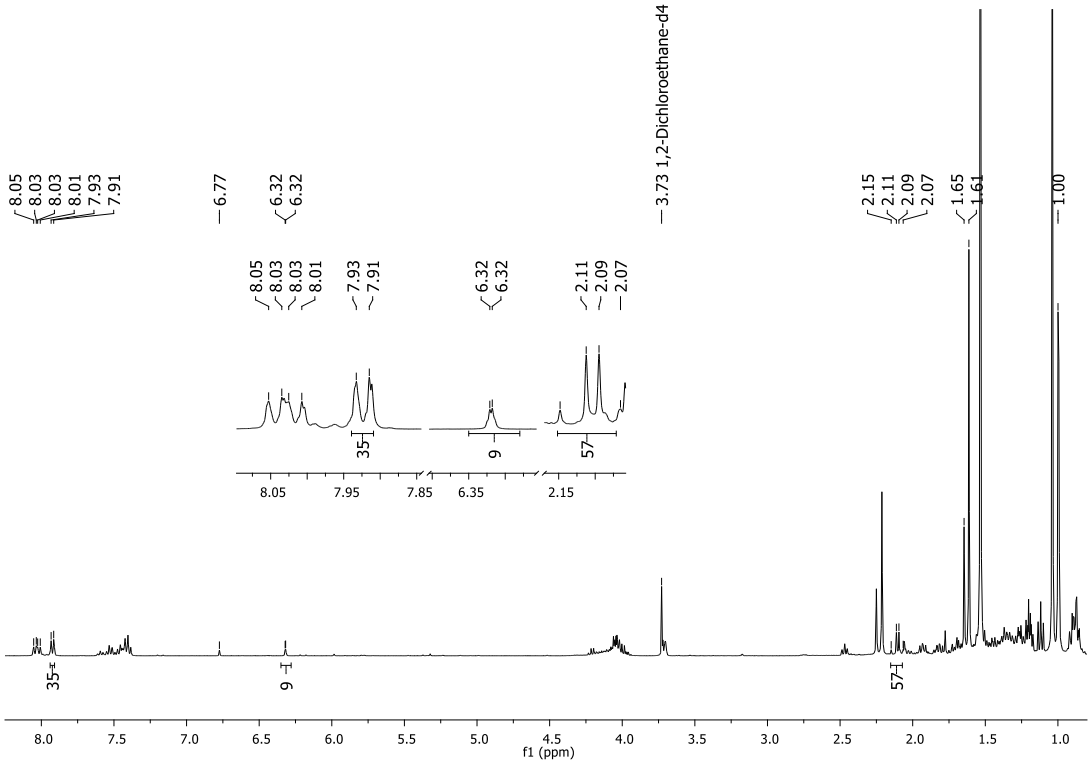


Figure S22. Reaction mixture at 60 °C (*t* = 60 min)

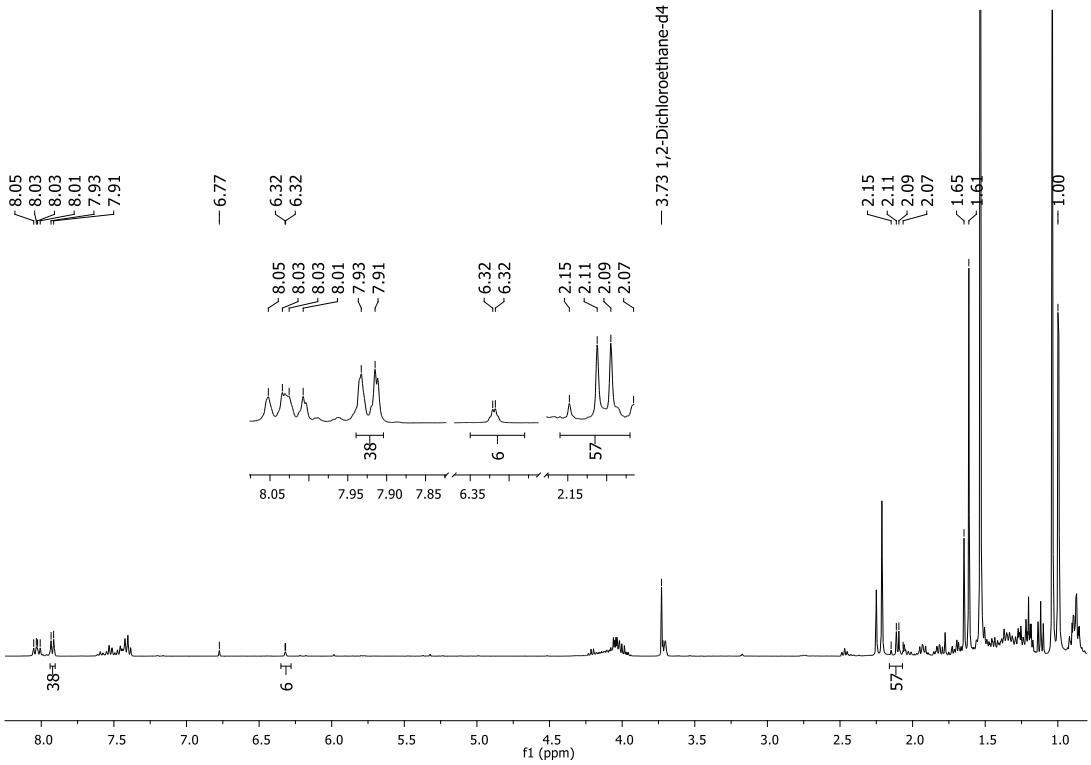


Figure S23. Reaction mixture at 60 °C (*t* = 90 min)

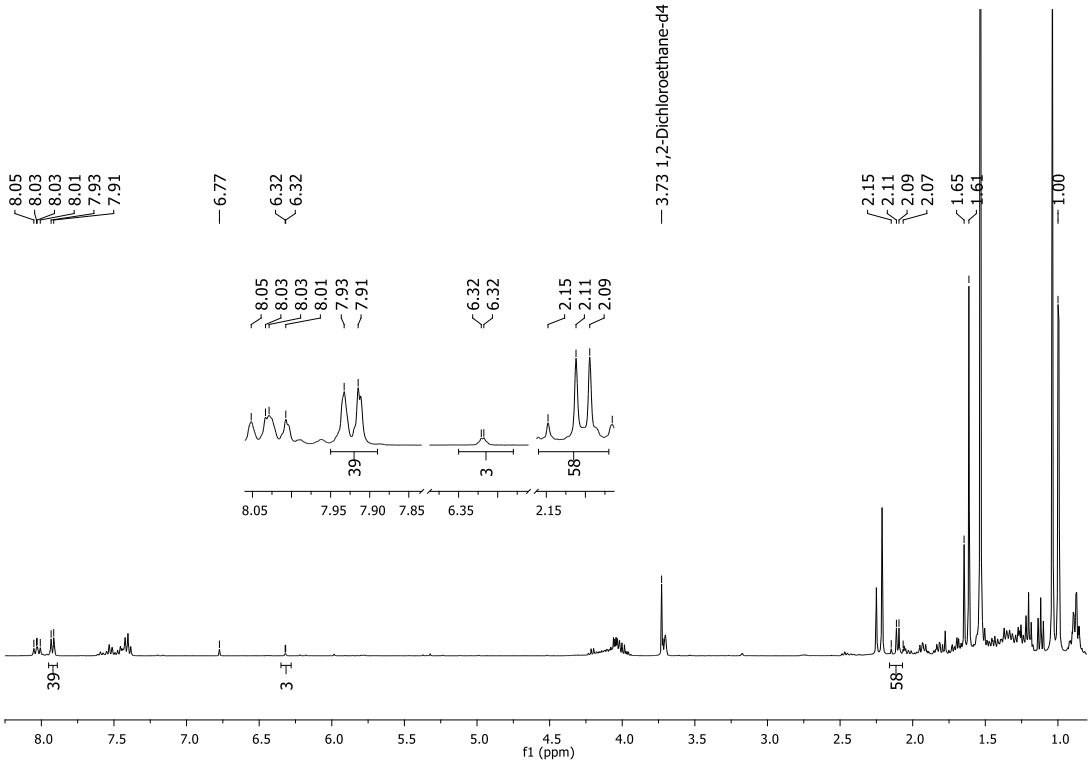


Figure S24. Reaction mixture at 60 °C (*t* = 120 min)

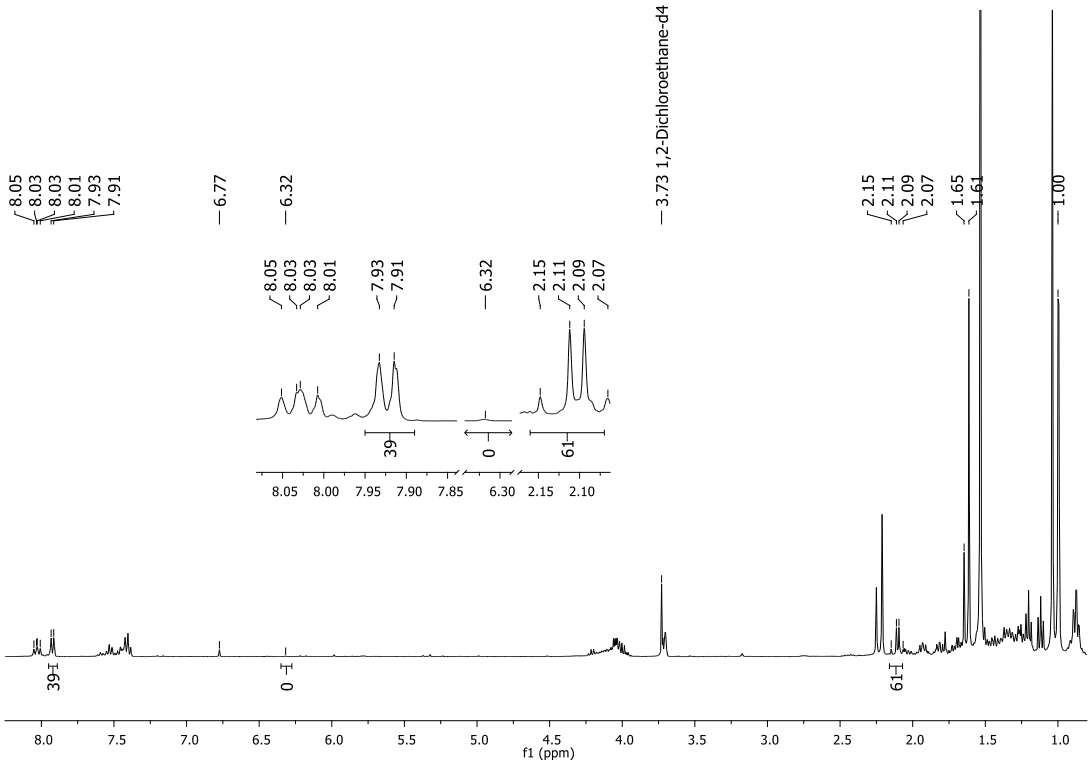


Figure S25. Reaction mixture at 60 °C (*t* = 180 min)

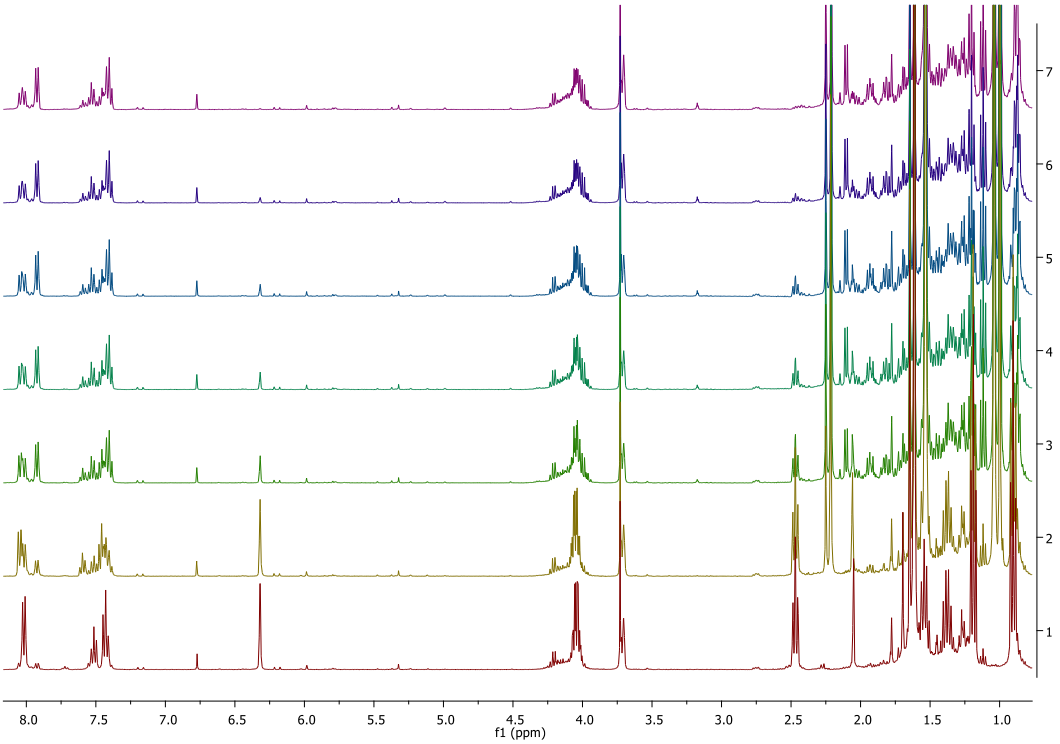


Figure S26. Stacked view of spectra 1 (*t* = 0 min) to 7 (*t* = 180 min)

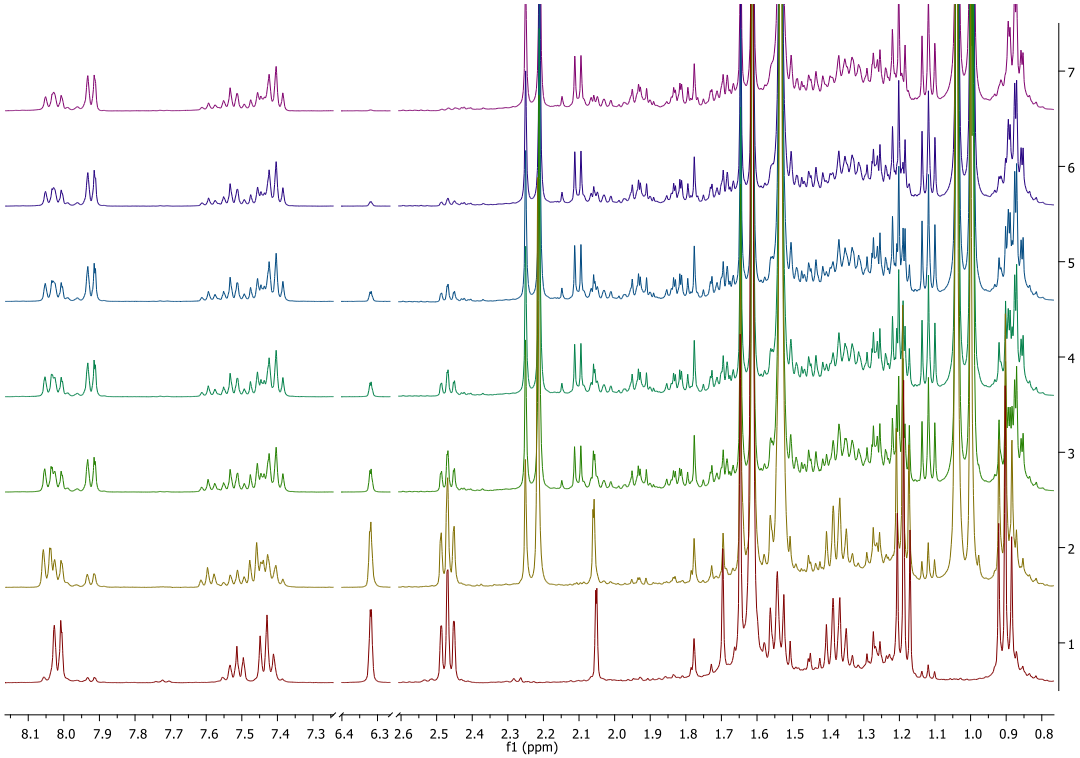


Figure S27. Zoom of superimposed spectra 1 (*t* = 0 min) to 7 (*t* = 180 min)

8.5. Reaction analysis by *in situ* HRMS

To determine potential reaction intermediates, the model reaction between ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (25 mg, 0.15 mmol, 1.0 equiv), benzoic acid **2d** (22 mg, 1.8 mmol, 1.2 equiv) in the presence of pentamethylcyclopentadienyl rhodium dichloride dimer (2.3 mg, 0.0038 mmol, 0.025 equiv), silver hexafluoroantimonate(V) (2.6 mg, 0.0075 mmol, 0.050 equiv) and anhydrous sodium carbonate (3.2 mg, 0.030 mmol, 0.20 equiv) in dry 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere was run for 10 minutes and then analysed by time-of-flight mass spectrometry (TOF-MS) using the electrospray ionisation (ESI) technique.

Figure S28 highlights peaks with *m/z* values of 291.1589 u and 667.0122 u, which correspond to the final product (**3ad**) and the isolated dimeric complex **Rh-A**, respectively. The value *m/z* = 359.0517 u was assigned to the proposed catalytically active species **Rh-B**, a cationic Cp*Rh-based monomer bearing a benzoate with a theoretical *m/z* = 359.0518 u. Additionally, a peak at *m/z* = 527.1671 u was also observed, whose mass corresponds to a cationic complex **Rh-C**, presumably formed from **Rh-B** upon coordination with an additional unit of **1a** (consistent with the theoretical value *m/z* = 527.1663 u).

Likewise, we also detected what appear to be intermediates based on rhodium hydroxycomplexes (**Rh-D** and **Rh-E**), presumably originating from the use of sodium carbonate.

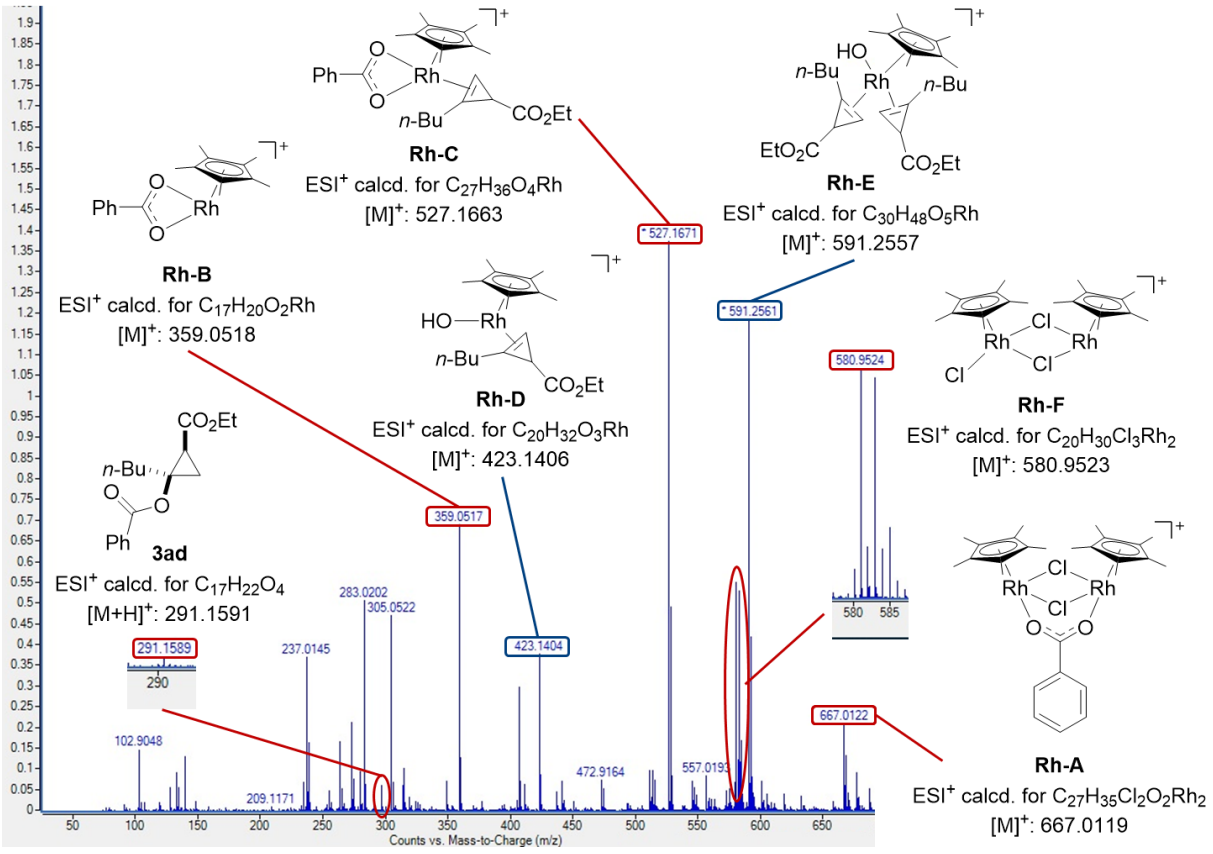


Figure S28. ESI-HRMS spectrum of the reaction crude between **1a** and **2d**.

9. Scale-up

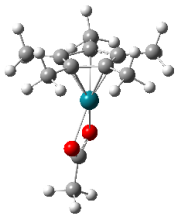
Synthesis of ethyl (1*S**,2*R**)-2-acetoxy-2-butylcyclopropane-1-carboxylate (**3aa**). An oven-dried 100 mL round-bottomed flask was charged with pentamethylcyclopentadienyl rhodium dichloride dimer (68 mg, 0.11 mmol, 0.025 equiv), silver hexafluoroantimonate(V) (75 mg, 0.22 mmol, 0.050 equiv) and anhydrous sodium acetate (72 mg, 0.88 mmol, 0.20 equiv). The reaction flask was sealed with a PTFE-septum, then evacuated and flushed with argon three times. A solution of ethyl 2-butylcycloprop-2-ene-1-carboxylate **1a** (0.74 g, 4.4 mmol, 1.0 equiv) in dry 1,2-dichloroethane (45 mL) and the acetic acid **2a** (0.30 mL, 5.3 mmol, 1.2 equiv) were subsequently added *via* syringe. The reaction mixture was heated at 60 °C overnight. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (*n*-hexane:EtOAc, 9:1) to afford **3aa** as a yellowish oil; yield: 0.92 g (92%). The analytical data (NMR and HRMS analysis) matched those obtained previously for compound **3aa**.

10. Theoretical studies

10.1. Computational details

DFT calculations were performed with Gaussian 16.[24] Geometries were optimized using the B97-D3 functional[25] in the gas phase without symmetry restrictions. A mixed basis set of LANL2DZ(f) for Rh with 6-31G(d) for all other atoms was used in geometry optimisations (BS1). The LANL2DZ basis set was supplemented with an f-type polarisation function (exponent 1.350) for Rh.[26] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). All potential energies were corrected by single-point calculations with the same functional and a mixed basis set of LANL2TZ(f) for Rh[27] with 6-311++G(d,p) for all other atoms (BS2). Solvation was introduced implicitly in all cases through the SMD model,[28] with dichloroethane as the solvent (ε = 10.125). The reported free energies include zero-point energies and thermal corrections calculated at 298 K with B97-D3/BS1

10.2. Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures



[RhCp*OAc]$^+$

E(B97-D3/BS1) = -727.760792977

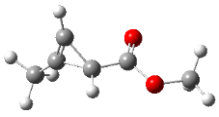
G(correction)= 0.219245

$E(B97\text{-}D3/BS2)_{DCE}$ = -728.03176459

Imaginary frequencies: 0

45	0	0.33542	0.00004	-0.17534
8	0	2.14705	1.10058	-0.17071
6	0	2.8259	0.0008	-0.2191
8	0	2.14684	-1.09918	-0.16968
6	0	4.31666	-0.00025	-0.29952
1	0	4.66814	-0.88676	-0.84056

1	0	4.72384	-0.04166	0.72311
1	0	4.67458	0.92018	-0.77498
6	0	-1.10572	0.00082	1.37967
6	0	-1.34058	1.18761	0.55685
6	0	-1.33984	-1.18733	0.55853
6	0	-0.77978	0.00209	2.83291
6	0	-1.63757	0.7355	-0.76691
6	0	-1.24409	2.60134	1.03075
6	0	-1.63717	-0.73723	-0.76586
6	0	-1.24288	-2.60041	1.03425
1	0	-1.72177	0.00213	3.4086
1	0	-0.21365	0.89512	3.12176
1	0	-0.21283	-0.88995	3.12322
6	0	-1.90902	1.58721	-1.96198
1	0	-1.06577	3.29527	0.20209
1	0	-0.434	2.72529	1.75996
1	0	-2.18644	2.89199	1.52245
6	0	-1.90845	-1.59072	-1.95969
1	0	-0.43564	-2.7223	1.76693
1	0	-1.05993	-3.29486	0.20701
1	0	-2.18681	-2.89219	1.52225
1	0	-2.99855	1.68765	-2.09999
1	0	-1.50315	1.1399	-2.87803
1	0	-1.48889	2.59281	-1.84979
1	0	-2.99798	-1.6898	-2.09874
1	0	-1.48989	-2.59671	-1.84524
1	0	-1.50095	-1.14562	-2.8761



mod1

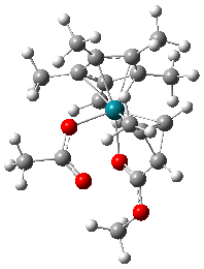
E(B97-D3/BS1) = -383.588035428

G(correction)= 0.091163

$E(B97\text{-}D3/BS2)_{DCE}$ = -383.71290636

Imaginary frequencies: 0

6	0	0.54359	0.70974	-0.46817
6	0	1.6191	1.26292	0.43652
6	0	1.8943	0.11754	-0.10739
6	0	-0.6749	0.08758	0.15112
1	0	0.37193	1.14312	-1.46175
1	0	1.84951	2.08327	1.10557
6	0	2.71211	-1.09353	-0.32524
8	0	-0.71065	-0.49185	1.22557
8	0	-1.76131	0.24059	-0.66501
1	0	2.91869	-1.23975	-1.39689
1	0	3.66638	-1.03679	0.21622
1	0	2.15893	-1.97866	0.02509
6	0	-2.98178	-0.33889	-0.15966
1	0	-3.25897	0.119	0.79899
1	0	-3.74079	-0.13134	-0.92104
1	0	-2.86459	-1.42091	-0.01387



IM1

E(B97-D3/BS1) = -1111.39026807

G(correction)= 0.341202

$E(B97\text{-}D3/BS2)_{DCE}$ = -1111.76770361

Imaginary frequencies: 0

45	0	-0.33627	-0.09237	-0.07296
6	0	-1.92236	0.91203	1.22989
6	0	-2.21626	1.0108	-0.19746
6	0	-1.88174	-0.47486	1.57861
6	0	-1.64877	2.08806	2.1019
6	0	-2.42941	-0.3266	-0.69806
6	0	-2.36472	2.29588	-0.94436

6	0	-2.17283	-1.25674	0.39024
6	0	-1.55191	-1.05801	2.91376
1	0	-2.48464	2.80124	2.05019
1	0	-0.7442	2.6003	1.7365
1	0	-1.49732	1.80267	3.14823
6	0	-2.91494	-0.66258	-2.07287
1	0	-2.4093	2.1331	-2.0272
1	0	-1.52082	2.96201	-0.72205
1	0	-3.29197	2.80652	-0.639
6	0	-2.34714	-2.74307	0.3692
1	0	-1.13204	-0.30927	3.59341
1	0	-0.82738	-1.87699	2.81378
1	0	-2.46157	-1.47364	3.3757
1	0	-3.98539	-0.41442	-2.14718
1	0	-2.80602	-1.72788	-2.30276
1	0	-2.38846	-0.08382	-2.84233
1	0	-3.33826	-3.01087	0.76929
1	0	-1.5919	-3.24031	0.99067
1	0	-2.2792	-3.15203	-0.64535
1	0	2.25339	3.37983	1.73313
6	0	2.34413	3.34972	0.63711
6	0	1.98718	1.94635	0.14128
1	0	1.65867	4.10122	0.22464
1	0	3.37684	3.584	0.35749
8	0	2.84846	1.1493	-0.23698
8	0	0.68204	1.73723	0.18554
1	0	1.72957	1.54974	-2.57367
6	0	1.03029	0.7944	-2.94466
6	0	0.86335	-0.30131	-1.95755
1	0	1.44645	0.36905	-3.87309
1	0	0.06695	1.26541	-3.17994
6	0	1.72678	-1.44164	-1.44299
6	0	0.22758	-1.47169	-1.66368
6	0	2.1734	-1.38131	-0.03301
1	0	2.39836	-1.93156	-2.15356
1	0	-0.48042	-2.1869	-2.06744
8	0	1.37405	-1.02749	0.87548
8	0	3.40007	-1.77797	0.20688
6	0	3.91075	-1.58241	1.56286
1	0	3.3102	-2.1596	2.27457
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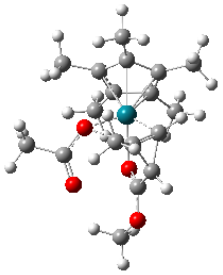


TS1

E(B97-D3/BS1) = -1111.37534783

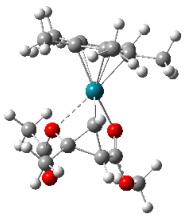
G(correction)= 0.340652

$E(B97\text{-}D3/BS2)_{DCE}$ = -1111.7492925

Imaginary frequencies: 1 (-219.5113 cm^{-1})

45	0	0.45644	0.09329	-0.13526
6	0	2.4116	-0.7569	-0.40534
6	0	2.11118	-0.85286	1.01752
6	0	2.46476	0.65456	-0.75696
6	0	2.748	-1.91404	-1.29163
6	0	1.87083	0.46734	1.51256
6	0	1.95959	-2.1448	1.75043
6	0	2.07827	1.41005	0.40606
6	0	2.87792	1.21479	-2.08063
1	0	2.55464	-1.68474	-2.3466
1	0	2.1615	-2.79987	-1.01836
1	0	3.81525	-2.17162	-1.19395
6	0	1.4777	0.86001	2.90096
1	0	2.90093	-2.71352	1.71713
1	0	1.17916	-2.75627	1.27372
1	0	1.68697	-1.9915	2.8
6	0	1.98318	2.89769	0.52096
1	0	3.96388	1.4005	-2.07506
1	0	2.37827	2.1671	-2.29463

1	0	2.66877	0.51749	-2.90092
1	0	1.07413	0.01094	3.46407
1	0	0.7173	1.65112	2.88552
1	0	2.35272	1.24783	3.44695
1	0	2.89866	3.29713	0.98657
1	0	1.13281	3.1913	1.14877
1	0	1.86696	3.3732	-0.4597
6	0	-0.5156	0.34958	-2.06872
6	0	-1.44379	-0.64974	-1.91437
6	0	-1.95152	0.74422	-1.71505
1	0	0.12195	0.6261	-2.90553
6	0	-1.98459	-1.91233	-2.4468
6	0	-2.15579	1.30293	-0.34915
1	0	-2.6767	1.08331	-2.46286
1	0	-2.8145	-2.28044	-1.83379
1	0	-2.37602	-1.69395	-3.45725
1	0	-1.20277	-2.67529	-2.53499
8	0	-1.23447	1.32273	0.49941
8	0	-3.34146	1.83316	-0.14798
6	0	-3.64949	2.26952	1.21176
1	0	-2.94121	3.0455	1.52326
1	0	-4.666	2.66421	1.15214
1	0	-3.59595	1.3994	1.87366
8	0	-0.87089	-1.65796	0.0464
6	0	-1.95084	-1.72228	0.8318
6	0	-1.86593	-2.85405	1.8519
8	0	-2.93247	-0.98665	0.74243
1	0	-1.12927	-2.59075	2.62582
1	0	-1.52669	-3.78355	1.37603
1	0	-2.84323	-3.00446	2.32269



IM2

E(B97-D3/BS1) = -1111.41163565

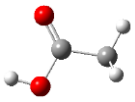
G(correction)= 0.343037

$E(B97\text{-}D3/BS2)_{DCE}$ = -1111.78083628

Imaginary frequencies: 0

45	0	0.51072	0.02282	-0.14723
6	0	-0.6696	-0.53109	-1.74363
6	0	-1.72613	-1.32105	-1.0787
6	0	-2.04783	0.10375	-1.57431
1	0	-0.30817	-0.78374	-2.74101
6	0	-2.47262	-2.50834	-1.62336
6	0	-2.10991	1.18805	-0.58683
1	0	-2.76918	0.15002	-2.3905
1	0	-3.44931	-2.61666	-1.13489
1	0	-2.63359	-2.38269	-2.70221
1	0	-1.88635	-3.4245	-1.46489
8	0	-1.15654	1.40536	0.20964
8	0	-3.21762	1.90427	-0.58233
6	0	-3.34444	2.93704	0.43987
1	0	-2.50808	3.64132	0.36788
1	0	-4.29516	3.42799	0.22148
1	0	-3.36411	2.46469	1.42846
8	0	-1.35371	-1.46095	0.33308
6	0	-2.34242	-1.23506	1.30391
6	0	-1.7583	-1.40095	2.68379
8	0	-3.47583	-0.93501	1.01206
1	0	-1.04193	-0.58882	2.87521
1	0	-1.21724	-2.35289	2.7633
1	0	-2.56212	-1.36062	3.42495
6	0	2.36183	-1.06214	0.07126
6	0	2.28287	-0.25614	1.30675
6	0	2.44617	-0.16657	-1.05209
6	0	2.49856	-2.55146	0.03721
6	0	2.21412	1.10181	0.94266
6	0	2.23443	-0.84261	2.6824
6	0	2.23491	1.17619	-0.53161
6	0	2.71987	-0.53275	-2.47702

1	0	2.23617	-2.95854	-0.94624
1	0	1.85713	-3.02858	0.7892
1	0	3.53965	-2.8397	0.25705
6	0	2.06215	2.29373	1.83469
1	0	3.23119	-1.21109	2.97316
1	0	1.54881	-1.69983	2.72617
1	0	1.91566	-0.10802	3.43069
6	0	2.25612	2.44617	-1.3196
1	0	3.80537	-0.50837	-2.66308
1	0	2.24551	0.16999	-3.17246
1	0	2.36252	-1.5426	-2.71135
1	0	1.87116	2.0048	2.87433
1	0	1.23302	2.93215	1.49944
1	0	2.97811	2.90482	1.8139
1	0	3.27958	2.85647	-1.33922
1	0	1.60193	3.20344	-0.87004
1	0	1.93785	2.28326	-2.356



HOAc

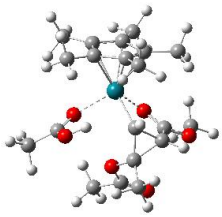
E(B97-D3/BS1) = -228.947702172

G(correction)= 0.033414

$E(B97\text{-}D3/BS2)_{DCE}$ = -229.03851184

Imaginary frequencies: 0

6	0	-0.09283	0.12844	0.00001
8	0	-0.65326	1.20841	-0.00005
8	0	-0.77619	-1.05869	-0.00001
1	0	-1.72362	-0.80834	-0.00006
6	0	1.4019	-0.10615	0.00005
1	0	1.69143	-0.68966	0.88512
1	0	1.69147	-0.68972	-0.88497
1	0	1.922	0.8562	0.00003



IM3

E(B97-D3/BS1) = -1340.38522684

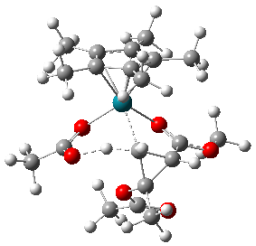
G(correction)= 0.400164

$E(B97\text{-}D3/BS2)_{DCE}$ = -1340.83394274

Imaginary frequencies: 0

45	0	-0.76656	-0.03335	0.00971
6	0	0.6049	-0.06909	-1.57376
6	0	-2.19453	-1.57138	-0.38365
6	0	2.05345	0.28187	-1.43379
6	0	1.62689	-1.19051	-1.3566
1	0	0.20444	-0.00013	-2.58871
6	0	-2.46718	-0.45336	-1.25631
6	0	-2.49669	-1.15275	1.00116
6	0	-1.86739	-2.97135	-0.79841
6	0	2.8876	0.71337	-2.6205
8	0	2.42119	0.97384	-0.24141
6	0	1.56237	-1.81134	-0.02516
1	0	1.9856	-1.82722	-2.16505
6	0	-2.75804	0.68377	-0.40984
6	0	-2.49487	-0.47728	-2.75167
6	0	-2.84918	0.21222	0.98216
6	0	-2.35557	-2.05547	2.1852
1	0	-2.79011	-3.56651	-0.89343
1	0	-1.22983	-3.46494	-0.05429
1	0	-1.3505	-2.99452	-1.76534
1	0	3.942	0.45394	-2.45631
1	0	2.54583	0.21872	-3.53904
1	0	2.80487	1.80109	-2.75651
6	0	3.49767	0.51362	0.49168
8	0	0.82868	-1.35141	0.88613
8	0	2.31706	-2.88446	0.13854

6	0	-3.15599	2.05286	-0.8671
1	0	-3.51224	-0.72418	-3.09421
1	0	-1.81459	-1.23459	-3.15945
1	0	-2.22831	0.49642	-3.18106
6	0	-3.17836	1.0982	2.1421
1	0	-2.50211	-1.51917	3.12901
1	0	-1.35625	-2.51289	2.20478
1	0	-3.09341	-2.87119	2.13304
6	0	3.72339	1.41648	1.68162
8	0	4.13059	-0.48095	0.20415
6	0	2.37847	-3.46014	1.47404
1	0	-2.72251	2.30157	-1.84302
1	0	-2.84857	2.82117	-0.14722
1	0	-4.2528	2.10981	-0.96286
1	0	-4.21563	1.45936	2.06594
1	0	-2.52129	1.979	2.16054
1	0	-3.06779	0.57601	3.09869
1	0	2.79892	1.49473	2.26987
1	0	3.99282	2.42686	1.34205
1	0	4.53244	1.01273	2.29744
1	0	1.37195	-3.71654	1.82468
1	0	2.99803	-4.35295	1.36479
1	0	2.84659	-2.73929	2.15356
1	0	0.01093	2.00471	-1.16759
8	0	0.20825	2.91775	-0.82275
6	0	0.31169	2.794	0.49844
8	0	0.05772	1.73425	1.09926
6	0	0.76699	4.03863	1.20242
1	0	1.8318	4.19771	0.97821
1	0	0.21917	4.91311	0.82848
1	0	0.63431	3.93167	2.28281



TS2

E(B97-D3/BS1) = -1340.36383995

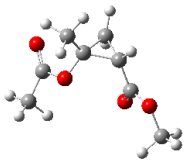
G(correction)= 0.394296

$E(B97\text{-}D3/BS2)_{DCE}$ = -1340.81449800

Imaginary frequencies: 1 (-761.1203 cm^{-1})

45	0	0.83128	-0.00292	-0.06585
6	0	2.77864	0.66383	0.50962
6	0	2.45486	-0.52043	1.2955
6	0	2.85513	0.26225	-0.89057
6	0	3.12972	2.0124	1.05283
6	0	2.22599	-1.60973	0.38898
6	0	2.38915	-0.57442	2.78733
6	0	2.47808	-1.11907	-0.97143
6	0	3.19773	1.17847	-2.02028
1	0	2.51499	2.26817	1.92355
1	0	2.98552	2.79352	0.29787
1	0	4.18764	2.02959	1.36162
6	0	1.87045	-3.01841	0.74663
1	0	3.38799	-0.81607	3.18508
1	0	1.69515	-1.34684	3.13932
1	0	2.08922	0.39034	3.21348
6	0	2.3539	-1.9527	-2.20558
1	0	4.26383	1.44931	-1.97091
1	0	2.60944	2.10327	-1.96363
1	0	3.00571	0.71525	-2.99374
1	0	2.78073	-3.63438	0.82406
1	0	1.22873	-3.47302	-0.01848
1	0	1.34841	-3.07083	1.70983
1	0	2.33159	-1.33826	-3.11192
1	0	1.43657	-2.55477	-2.18002
1	0	3.20838	-2.64443	-2.27791

8	0	0.05373	1.65999	-1.15411
6	0	-0.2458	2.68121	-0.43143
8	0	-0.2793	2.66174	0.8394
6	0	-0.59754	3.96594	-1.15054
1	0	-1.67758	4.13998	-1.04163
1	0	-0.0815	4.80985	-0.67513
1	0	-0.34327	3.9102	-2.21383
1	0	-0.36869	1.30498	1.12839
6	0	-0.73006	0.1677	1.62731
6	0	-2.24662	0.30393	1.45929
6	0	-1.6125	-1.0564	1.31012
1	0	-0.36864	0.17222	2.65735
6	0	-3.16112	0.59373	2.62413
8	0	-2.58398	1.02911	0.28719
6	0	-1.52093	-1.71343	-0.01246
1	0	-1.82699	-1.73747	2.1338
1	0	-4.17832	0.24954	2.39239
1	0	-2.81519	0.08128	3.53107
1	0	-3.18233	1.67505	2.81514
6	0	-3.53098	0.50834	-0.57545
8	0	-0.81067	-1.26741	-0.94063
8	0	-2.2395	-2.81725	-0.11439
6	0	-3.70546	1.43845	-1.74964
8	0	-4.09089	-0.55255	-0.38936
6	0	-2.33451	-3.43203	-1.4324
1	0	-2.74556	1.53914	-2.27565
1	0	-4.00181	2.43795	-1.40284
1	0	-4.46738	1.03784	-2.42462
1	0	-1.33394	-3.65011	-1.82302
1	0	-2.90611	-4.34854	-1.27175
1	0	-2.86794	-2.74829	-2.10148



mod3

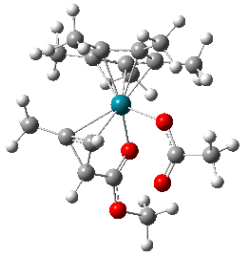
E(B97-D3/BS1) = -612.59729778

G(correction)= 0.150732

$E(B97\text{-}D3/BS2)_{DCE}$ = -612.79406646

Imaginary frequencies: 0

6	0	0.3488	1.28796	1.26794
1	0	0.59947	2.25827	1.6956
6	0	-0.79271	1.21048	0.26482
6	0	0.66623	1.04771	-0.16586
1	0	0.42557	0.43812	1.9433
6	0	-1.66541	0.00097	0.31199
1	0	-1.28304	2.12652	-0.06095
6	0	1.31628	2.10513	-1.02719
8	0	1.00152	-0.28026	-0.57025
8	0	-1.4061	-1.05095	0.87322
8	0	-2.81839	0.22758	-0.3827
1	0	0.9577	3.1053	-0.74813
1	0	2.4053	2.07435	-0.88777
1	0	1.08588	1.9344	-2.08832
6	0	2.14859	-0.8221	-0.04217
6	0	-3.73118	-0.89109	-0.41434
8	0	2.9399	-0.21195	0.64882
6	0	2.24334	-2.27812	-0.44376
1	0	-4.0271	-1.1759	0.60358
1	0	-4.59643	-0.54236	-0.98689
1	0	-3.26325	-1.75466	-0.90449
1	0	2.16924	-2.38164	-1.53494
1	0	1.39791	-2.82645	-0.00444
1	0	3.18961	-2.69691	-0.0879



IM1'

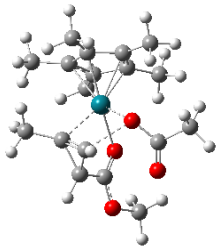
E(B97-D3/BS1) = -1111.38351017

G(correction)= 0.340212

$E(B97\text{-}D3/BS2)_{DCE}$ = -1111.76105022

Imaginary frequencies: 0

45	0	0.30546	0.01348	-0.09466
8	0	-0.81058	1.73147	-0.63133
6	0	-2.12208	1.85182	-0.76008
6	0	-2.52126	3.31685	-0.96329
8	0	-2.96149	0.95052	-0.7207
1	0	-2.40847	3.86027	-0.01347
1	0	-3.5676	3.36647	-1.28294
1	0	-1.87485	3.80304	-1.70537
6	0	-0.74714	-0.82327	-1.86692
6	0	-0.2352	-1.9568	-1.33947
6	0	-1.7253	-1.72072	-1.14069
1	0	-0.77232	-0.18515	-2.74321
6	0	0.60756	-3.15807	-1.55168
6	0	-2.18769	-1.29041	0.19834
1	0	-2.43426	-2.31253	-1.72672
1	0	0.81411	-3.69299	-0.61665
1	0	0.03758	-3.84538	-2.19928
1	0	1.54944	-2.92016	-2.05967
8	0	-1.41276	-0.68943	0.99194
8	0	-3.39915	-1.66518	0.53536
6	0	-3.93877	-1.12851	1.78221
1	0	-3.94513	-0.03586	1.7132
1	0	-4.95261	-1.53008	1.84026
1	0	-3.33087	-1.4657	2.62916
1	0	2.18667	-2.85208	1.24115
6	0	2.86804	-2.18146	0.70275
6	0	2.31711	-0.79579	0.58653
1	0	3.09234	-2.62145	-0.27325
1	0	3.8106	-2.1463	1.27256
6	0	1.71514	-0.05374	1.65908
6	0	2.46968	0.10997	-0.55031
6	0	1.49549	1.30405	1.20882
6	0	1.34512	-0.58786	3.0038
6	0	2.02317	1.41537	-0.14378
6	0	3.12214	-0.21338	-1.85714
6	0	0.9187	2.43539	1.99518
1	0	2.10235	-0.28491	3.74476
1	0	1.28765	-1.68199	3.00427
1	0	0.37737	-0.18985	3.33318
6	0	2.03295	2.67203	-0.94395
1	0	4.19413	0.03706	-1.80866
1	0	2.68006	0.36323	-2.67838
1	0	3.04297	-1.27782	-2.10257
1	0	0.36579	2.07814	2.87133
1	0	0.23701	3.02146	1.36604
1	0	1.7221	3.1027	2.3456
1	0	2.60549	3.44699	-0.41212
1	0	1.00132	3.03641	-1.06428
1	0	2.47939	2.52783	-1.9337



TS1'

E(B97-D3/BS1) = -1111.36479573

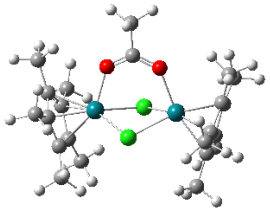
G(correction)= 0.340910

$E(B97\text{-}D3/BS2)_{DCE}$ = -1111.73914738

Imaginary frequencies: 1 (-236.9114 cm^{-1})

45	0	0.38046	-0.07606	-0.05954
6	0	1.76025	-0.55013	1.53746
6	0	2.41696	-0.844	0.29126
6	0	1.48198	-1.51018	2.64842
6	0	1.47087	0.88552	1.57573
6	0	3.04899	-2.14495	-0.08067
6	0	2.45288	0.3839	-0.48827
1	0	0.5147	-1.29827	3.11995

1	0	1.47275	-2.54734	2.29427
1	0	2.26112	-1.42055	3.42262
6	0	1.93859	1.45735	0.34678
6	0	0.81551	1.60049	2.71451
1	0	3.14035	-2.26507	-1.16492
1	0	2.49829	-3.00239	0.32401
1	0	4.06641	-2.17726	0.34239
6	0	3.06694	0.56672	-1.84002
6	0	1.80938	2.87629	-0.09769
1	0	1.55318	1.81633	3.50415
1	0	0.0202	0.98839	3.15765
1	0	0.37305	2.55074	2.39388
1	0	4.12944	0.84315	-1.74062
1	0	2.56242	1.36569	-2.39706
1	0	3.01688	-0.35311	-2.43485
1	0	1.46195	3.52741	0.71152
1	0	1.09099	2.94188	-0.92956
1	0	2.77808	3.25369	-0.45588
6	0	-0.43028	-1.56245	-1.55478
6	0	-1.9208	-1.54558	-1.19118
6	0	-1.21517	-0.56872	-2.06985
6	0	0.42236	-2.64674	-2.14339
6	0	-2.2717	-1.18112	0.20678
1	0	-2.64067	-2.20277	-1.69232
1	0	-1.4546	-0.01431	-2.96841
1	0	0.82313	-3.31301	-1.37097
1	0	-0.18739	-3.25646	-2.82903
1	0	1.25556	-2.22304	-2.7197
8	0	-1.42796	-0.68274	0.98871
8	0	-3.49778	-1.48899	0.56623
6	0	-3.93798	-1.03037	1.88108
1	0	-3.88202	0.06269	1.90337
1	0	-4.96962	-1.37864	1.9648
1	0	-3.30696	-1.4722	2.66056
8	0	-0.82949	1.39002	-1.21717
6	0	-1.98267	1.92761	-0.78567
6	0	-1.94936	3.4528	-0.8362
8	0	-2.96509	1.29637	-0.41097
1	0	-1.29237	3.8298	-0.03804
1	0	-2.96009	3.8464	-0.6853
1	0	-1.54318	3.80491	-1.79326



[(RhClCp*)$_2$OAc]$^+$

E(B97-D3/BS1) = -2147.95327264

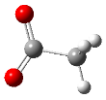
G(correction)= 0.420679

E(B97-D3/BS2)$_{DCE}$ = -2148.39940884

Imaginary frequencies: 0

45	0	-1.77256	0.0323	0.00038
17	0	0.00822	-0.49825	-1.6844
6	0	-3.85476	0.65127	-0.25938
8	0	-1.14819	2.07695	-0.02035
45	0	1.77238	0.03153	-0.00569
6	0	-3.50436	-0.35629	-1.2304
6	0	-3.63482	0.09868	1.06509
6	0	-4.27134	2.05938	-0.53303
6	0	0.00018	2.62887	-0.04013
6	0	3.85851	0.66268	0.20427
6	0	-3.13396	-1.57328	-0.50449
6	0	-3.56308	-0.21812	-2.71764
6	0	-3.23597	-1.2954	0.90323
6	0	-3.8749	0.81223	2.35673
1	0	-4.4242	2.23662	-1.60294
1	0	-3.49857	2.7551	-0.17421
1	0	-5.20859	2.28534	-0.00386
8	0	1.14803	2.07486	-0.05585
6	0	0.00419	4.15214	-0.00638
6	0	3.51234	-0.28874	1.23218
6	0	3.62675	0.03883	-1.08563

6	0	4.27733	2.08343	0.39812
6	0	-2.7613	-2.87725	-1.13353
1	0	-4.55052	-0.54079	-3.08604
1	0	-2.801	-0.83889	-3.20263
1	0	-3.40317	0.82035	-3.02987
6	0	-2.97247	-2.25763	2.01527
1	0	-4.91133	0.65121	2.696
1	0	-3.71802	1.89145	2.24172
1	0	-3.20085	0.45074	3.14246
1	0	0.87833	4.54537	-0.53804
1	0	0.06364	4.47906	1.04269
1	0	-0.91888	4.55066	-0.44199
6	0	3.13764	-1.54402	0.57692
6	0	3.58065	-0.06763	2.70903
6	0	3.2285	-1.34439	-0.84442
6	0	3.85493	0.67944	-2.41704
1	0	4.48045	2.30591	1.45116
1	0	3.48161	2.75867	0.04953
1	0	5.1854	2.29323	-0.1852
1	0	-3.67083	-3.43114	-1.4171
1	0	-2.18335	-3.50282	-0.44382
1	0	-2.1607	-2.7228	-2.03773
1	0	-2.62265	-1.7423	2.91653
1	0	-2.21812	-3.00078	1.73352
1	0	-3.90421	-2.79074	2.26505
6	0	2.76898	-2.81159	1.27839
1	0	4.56781	-0.37549	3.09061
1	0	2.81704	-0.65483	3.23212
1	0	3.42877	0.98791	2.96259
6	0	2.95875	-2.36676	-1.89988
1	0	4.88554	0.49218	-2.76056
1	0	3.70654	1.7644	-2.35924
1	0	3.16768	0.28074	-3.17278
1	0	3.68054	-3.35738	1.57107
1	0	2.17304	-3.46638	0.6324
1	0	2.18786	-2.60777	2.18539
1	0	2.5963	-1.90283	-2.82382
1	0	2.21216	-3.0979	-1.57002
1	0	3.89088	-2.90763	-2.13084
17	0	-0.0088	-0.43648	1.69693



AcO$^-$

E(B97-D3/BS1) = -228.360761621

G(correction)= 0.019464

E(B97-D3/BS2)$_{DCE}$ = -228.55126813

Imaginary frequencies: 0

6	0	0.22374	0.00218	0.00011
8	0	0.81826	-1.11307	-0.00007
8	0	0.69462	1.17604	-0.0001
6	0	-1.36221	-0.05988	0.00008
1	0	-1.76323	0.46842	0.88424
1	0	-1.7632	0.46855	-0.88402
1	0	-1.74588	-1.09446	-0.00001

Cl$^-$

E(B97-D3/BS1) = -460.260339951

G(correction)= -0.015023

E(B97-D3/BS2)$_{DCE}$ = -460.40853924

17	0	-0.26798	-0.00924	0.

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11. References

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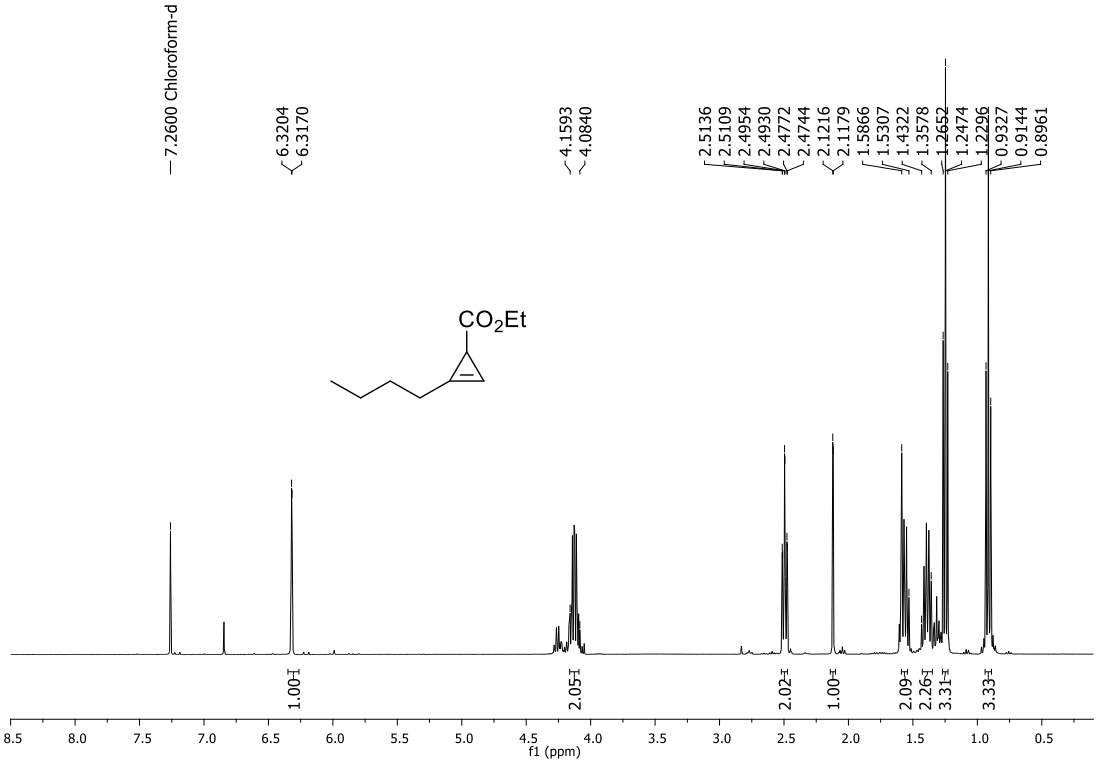
12. NMR Spectra

The chemical shifts of the used solvent signals observed for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are listed in the following chart. The multiplicity is shown as "*s*" for a singlet, "*d*" for a doublet, and so on.

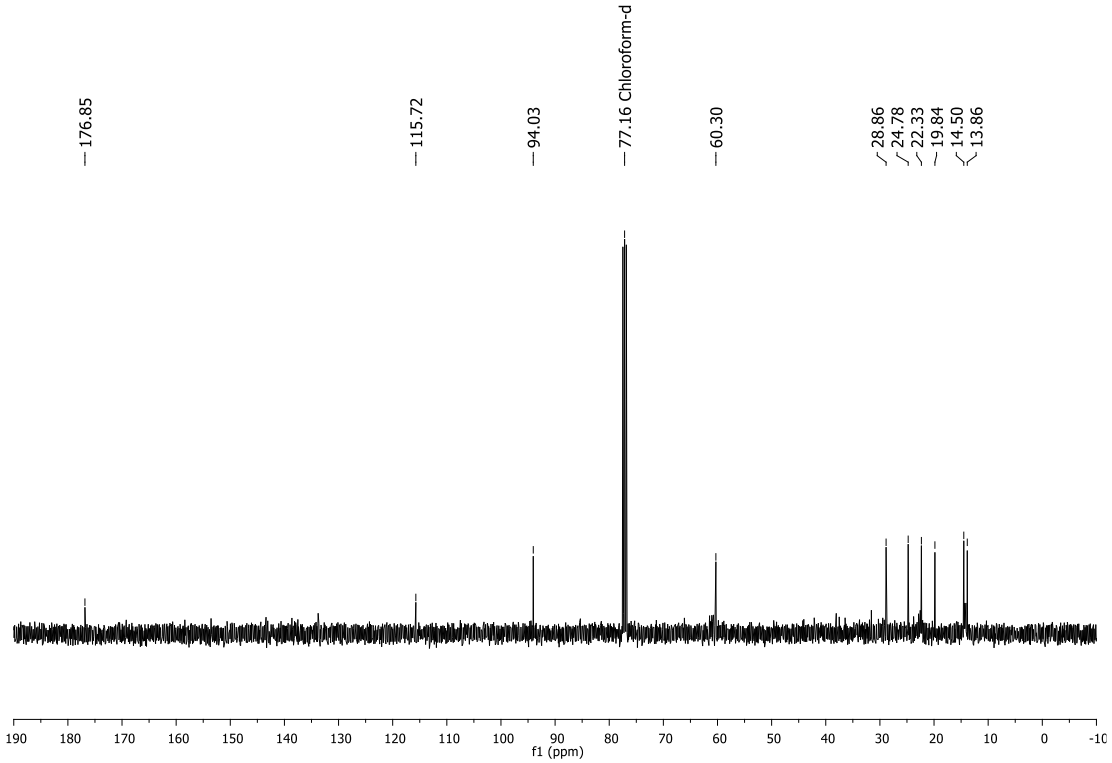
Solvent	**^{1}H NMR (ppm)**	**^{13}C NMR (ppm)**	**^{19}F NMR (ppm)**
Chloroform-*d*	7.26 (s)	77.2 (t)	–
Dimethylsulfoxide-d_6	2.5 (quint)	39.5 (sept)	–
Methanol-d_4	4.87 (s), 3.31(quint)	49.1 (sept)	–
Hexafluorobenzene	–	–	−164.9 (s)

Ethyl 2-butylcycloprop-2-ene-1-carboxylate (1a)

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

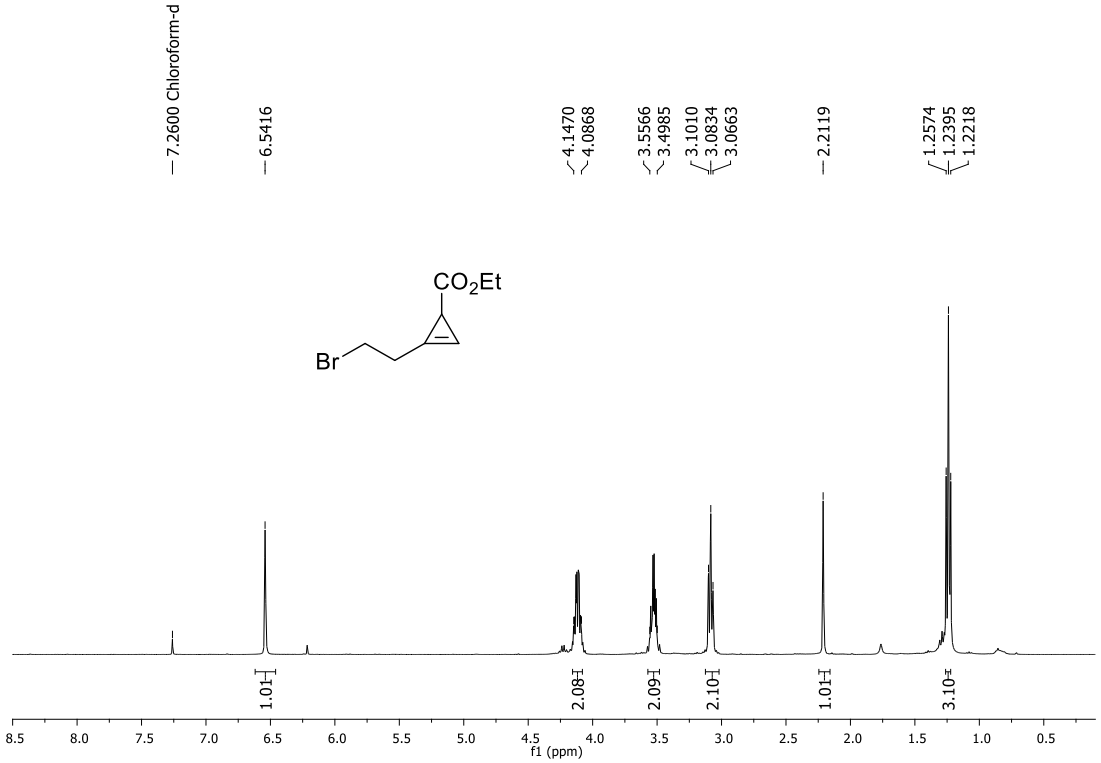


^{13}C NMR ($CDCl_3$, 101 MHz)

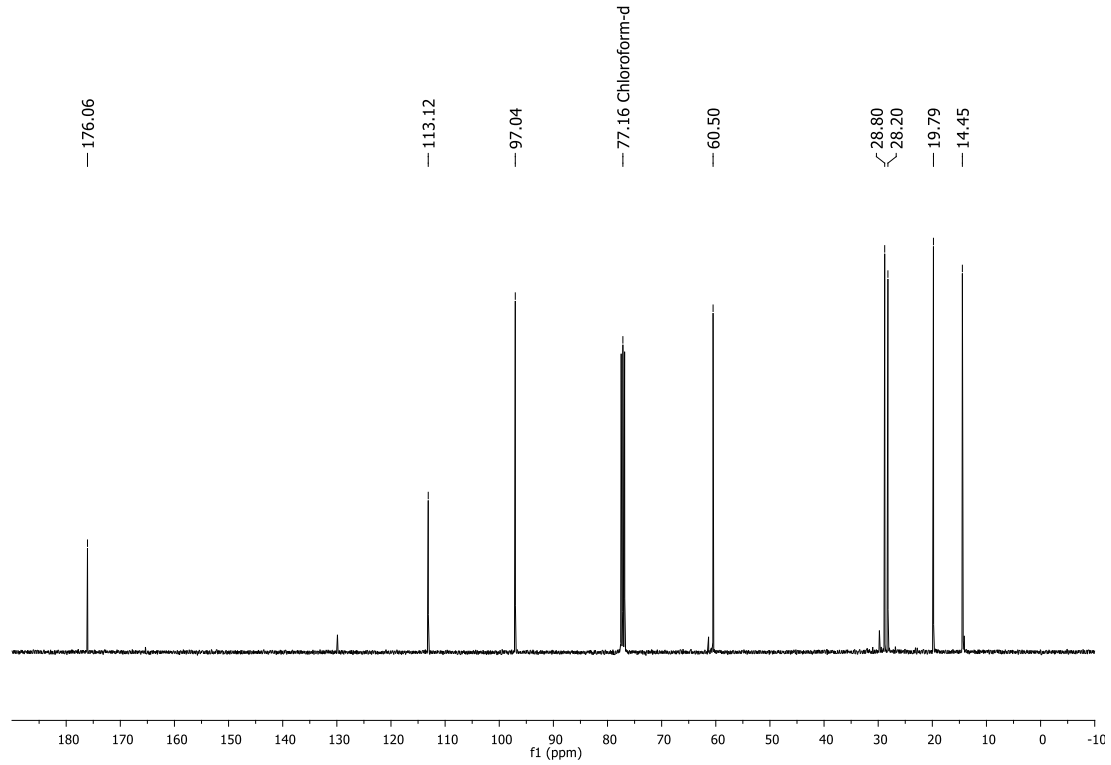


Ethyl 2-(2-bromoethyl)cycloprop-2-ene-1-carboxylate (1e)

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

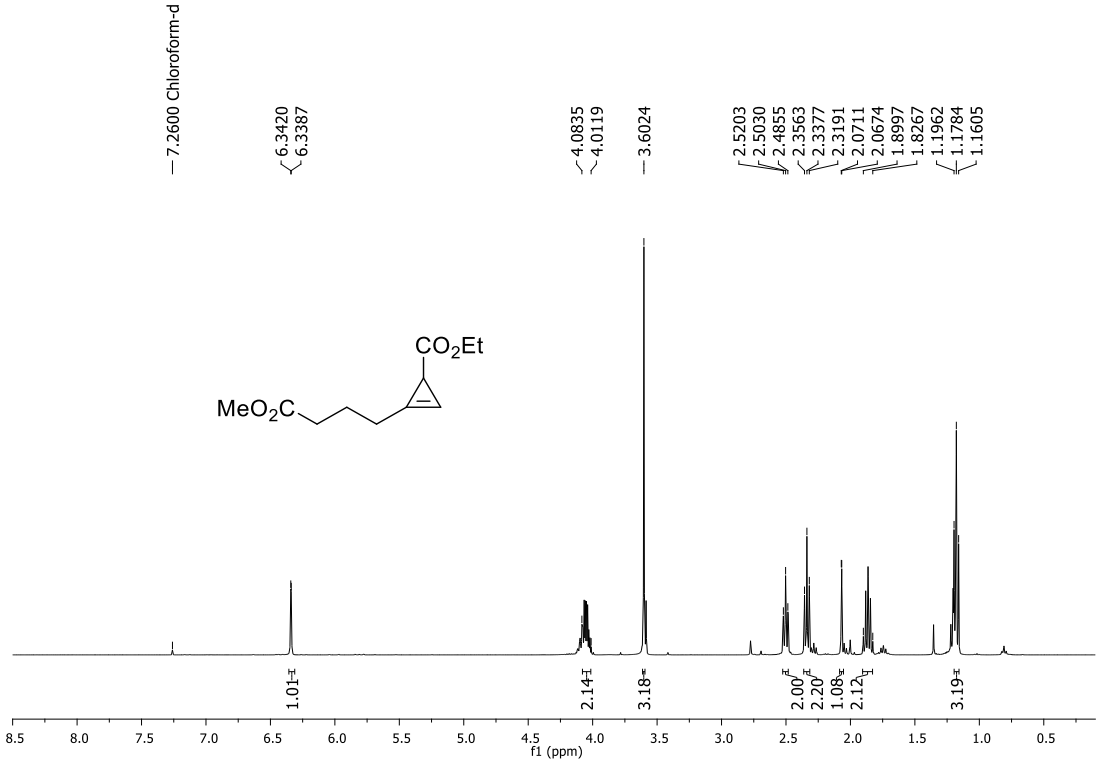


^{13}C NMR ($CDCl_3$, 101 MHz)

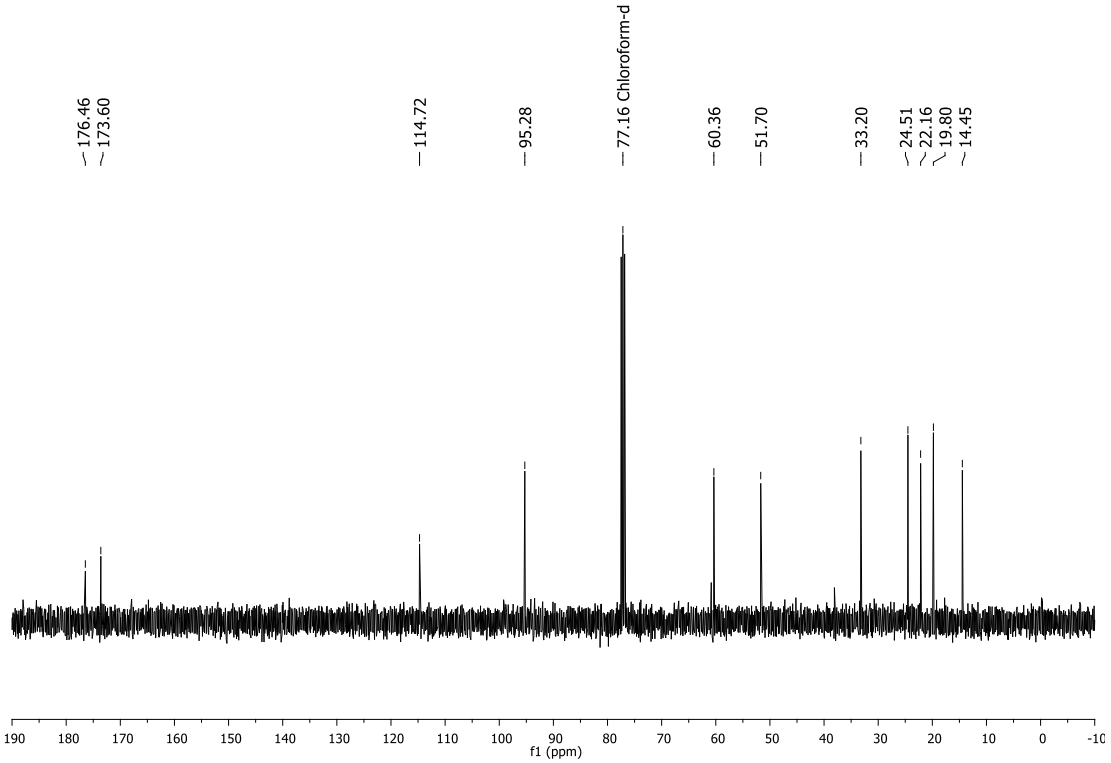


Ethyl 2-(4-methoxy-4-oxobutyl)cycloprop-2-ene-1-carboxylate (1f)

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

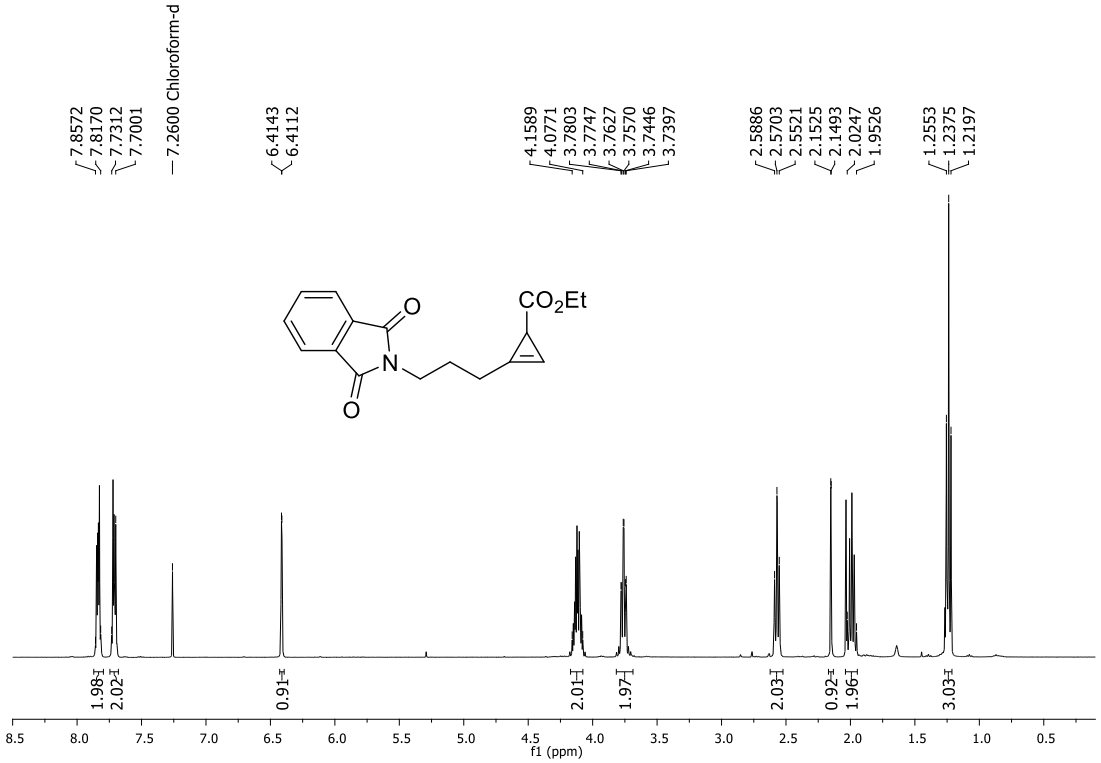


^{13}C NMR ($CDCl_3$, 101 MHz)

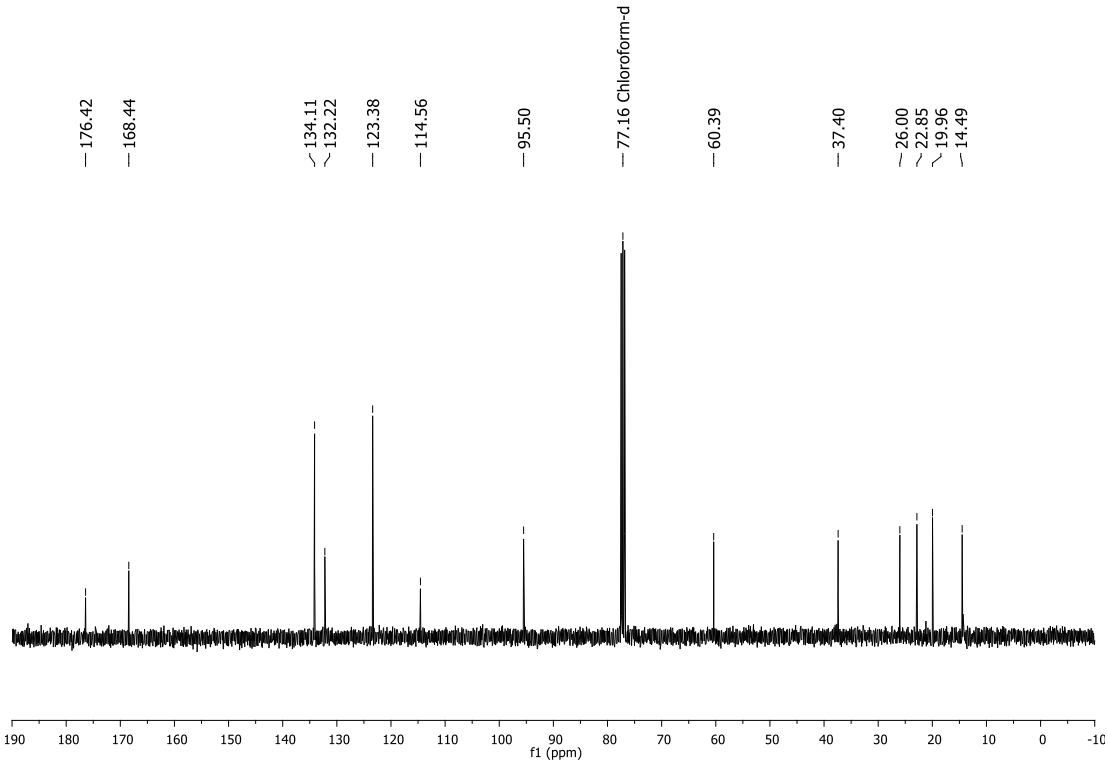


Ethyl 2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cycloprop-2-ene-1-carboxylate (1g)

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

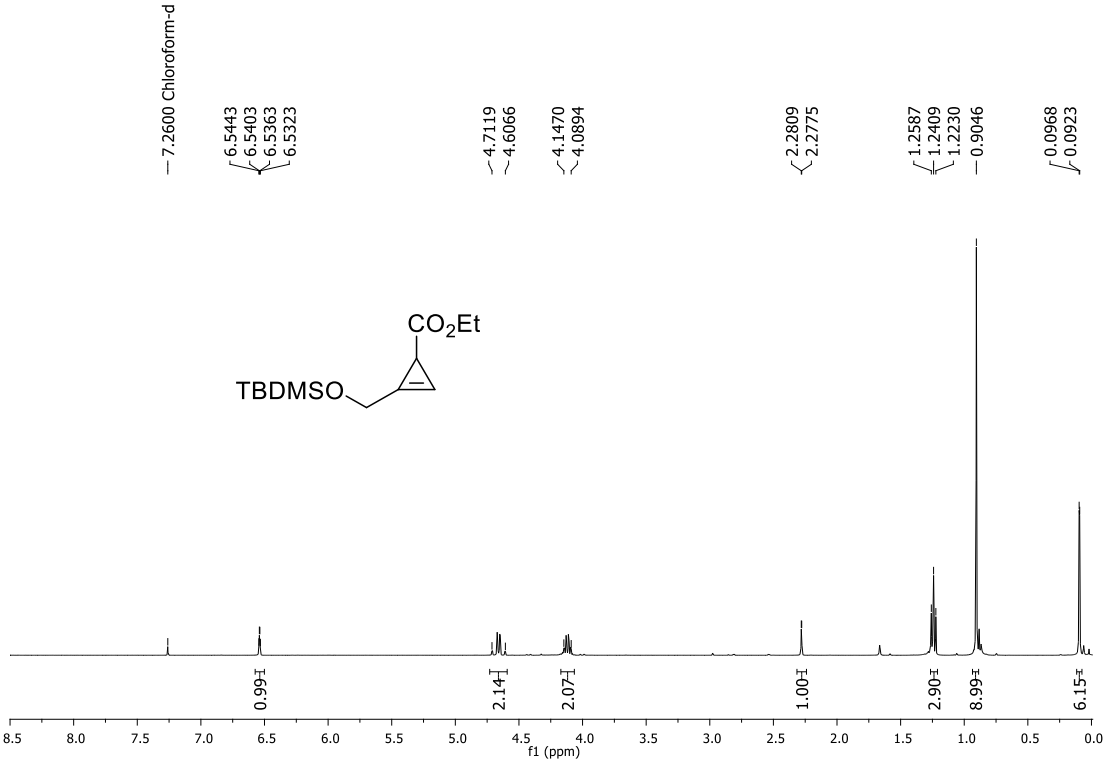


^{13}C NMR ($CDCl_3$, 101 MHz)

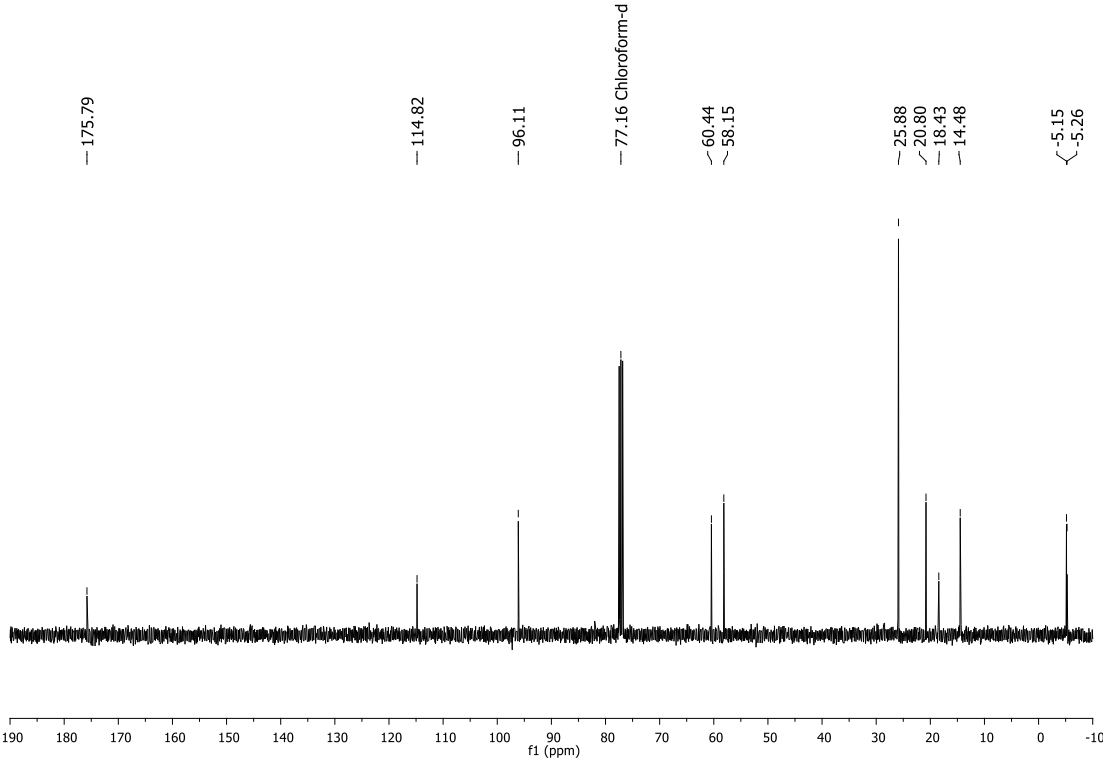


Ethyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)cycloprop-2-ene-1-carboxylate (1j)

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

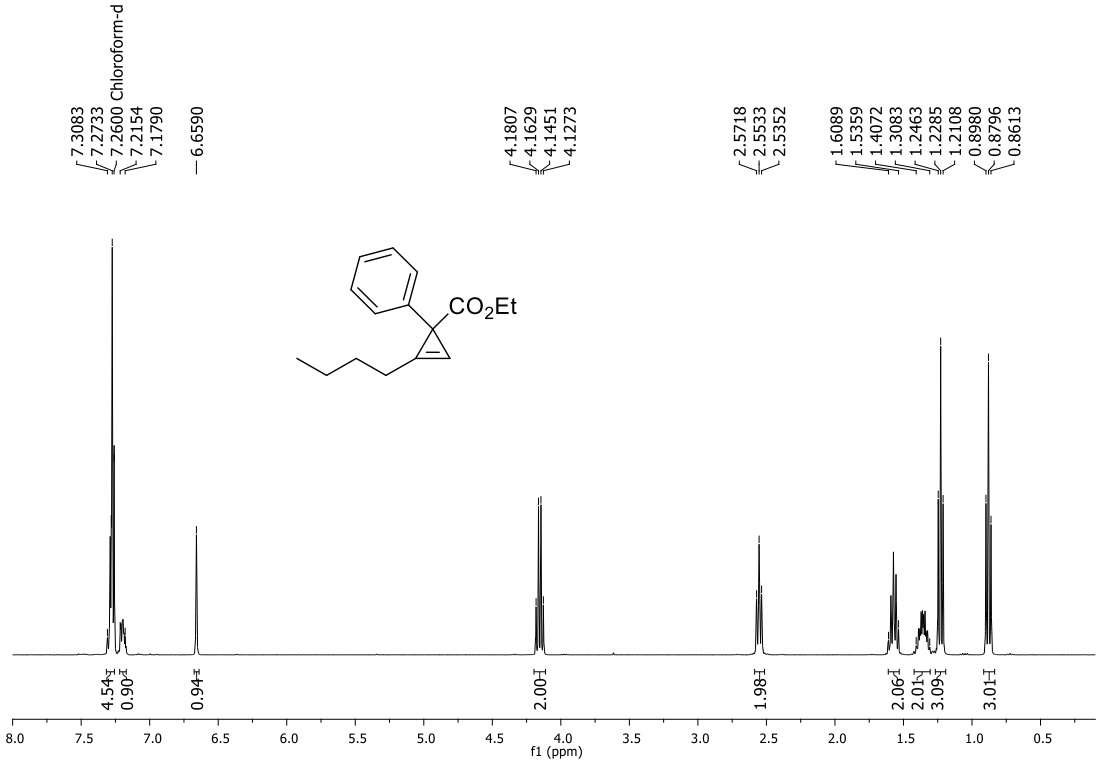


^{13}C NMR ($CDCl_3$, 101 MHz)

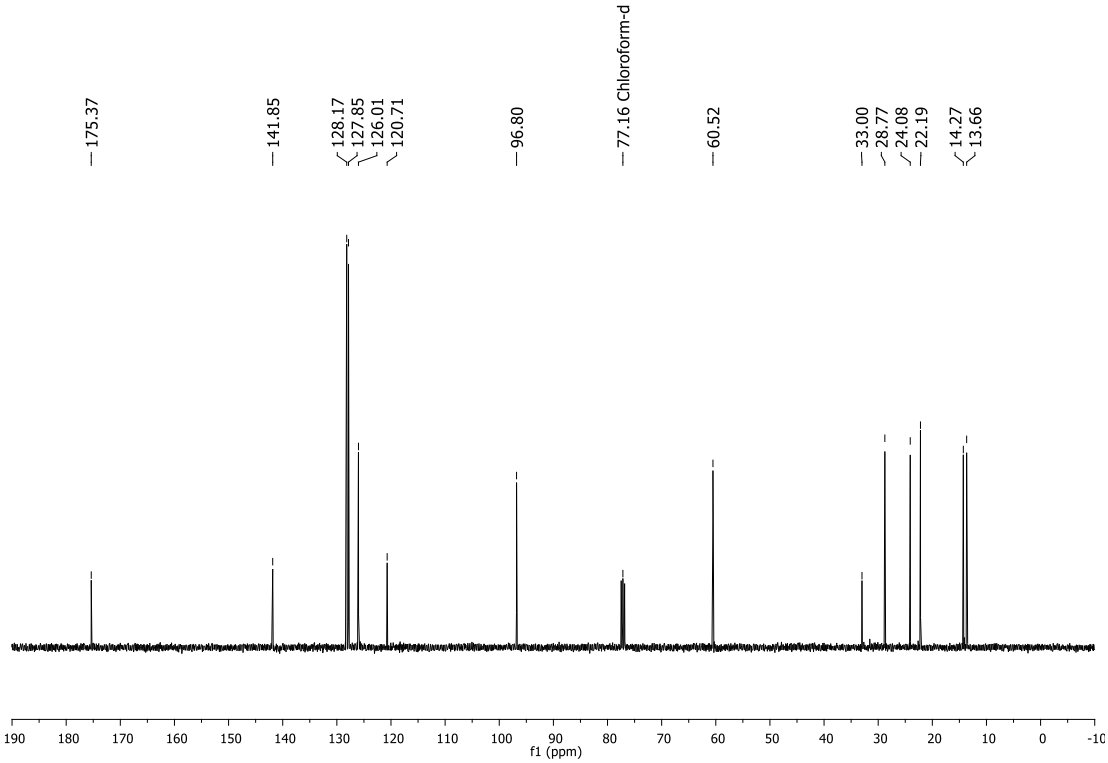


Ethyl 2-butyl-1-phenylcycloprop-2-ene-1-carboxylate (1o)

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

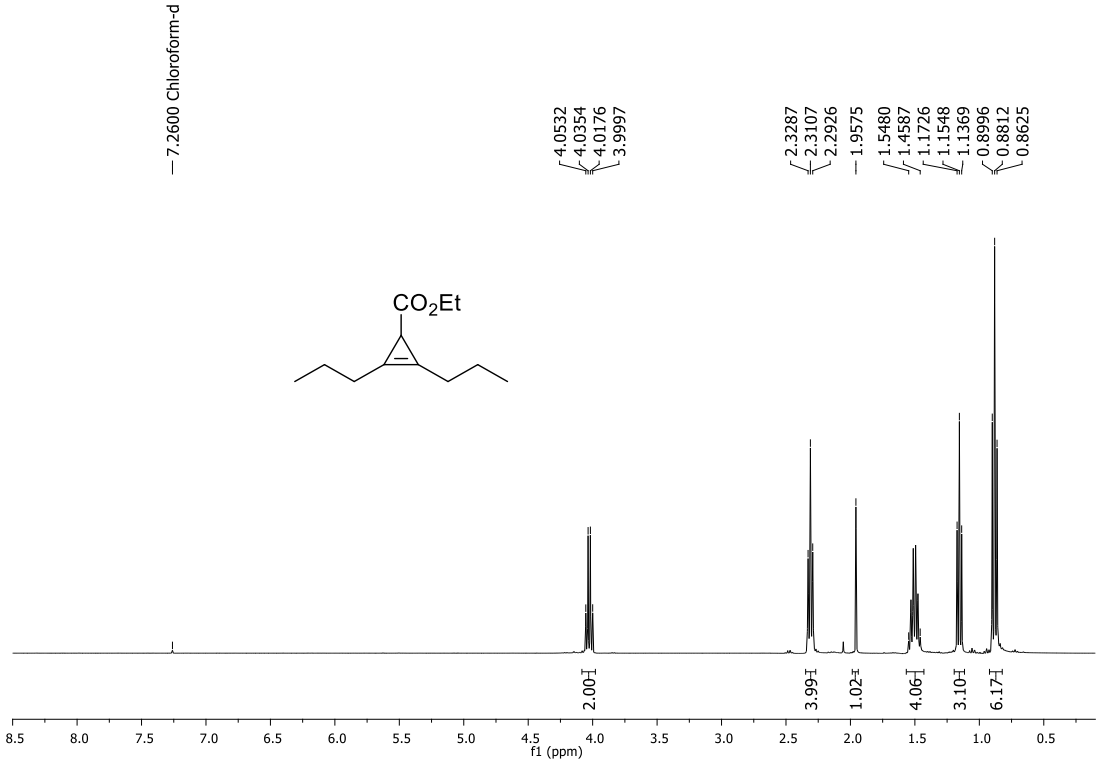


^{13}C NMR ($CDCl_3$, 101 MHz)

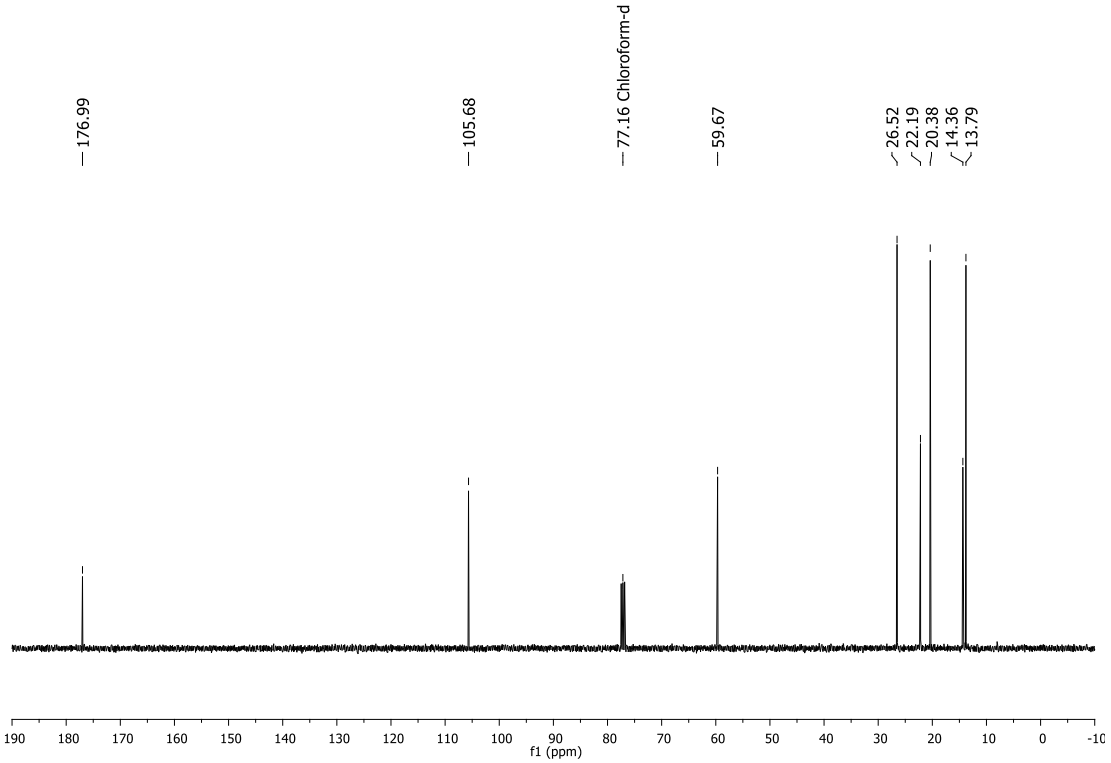


Ethyl 2,3-dipropylcycloprop-2-ene-1-carboxylate (1t)

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

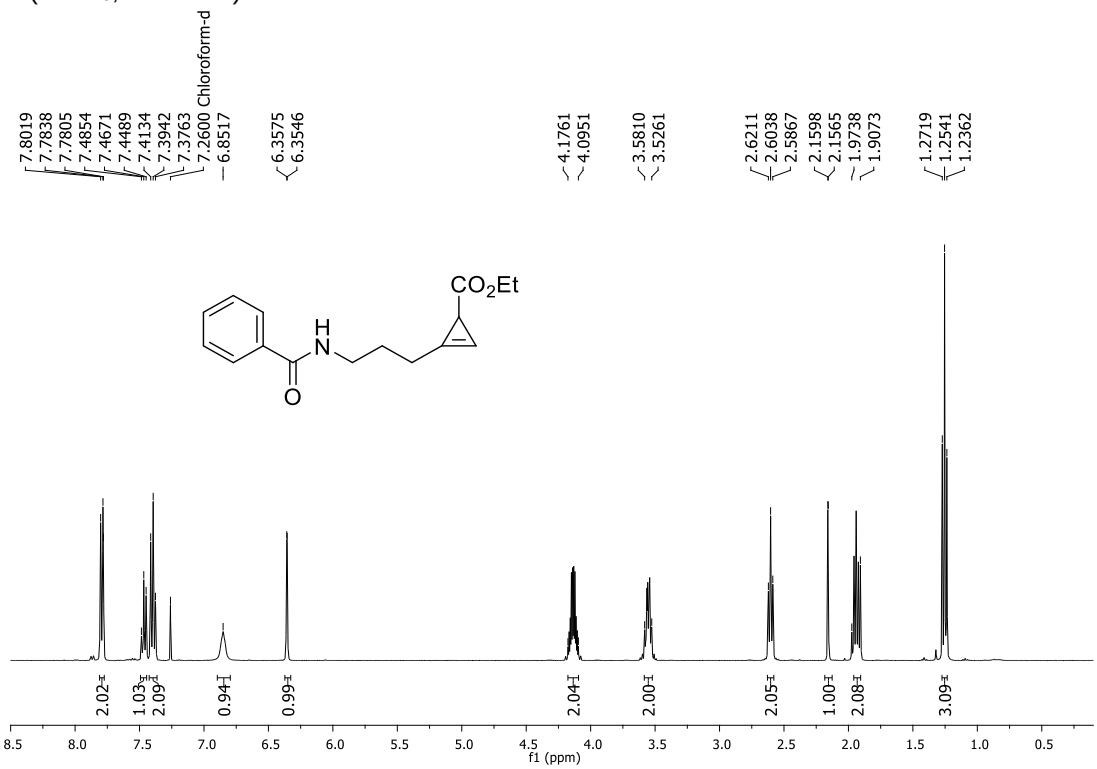


^{13}C NMR ($CDCl_3$, 101 MHz)

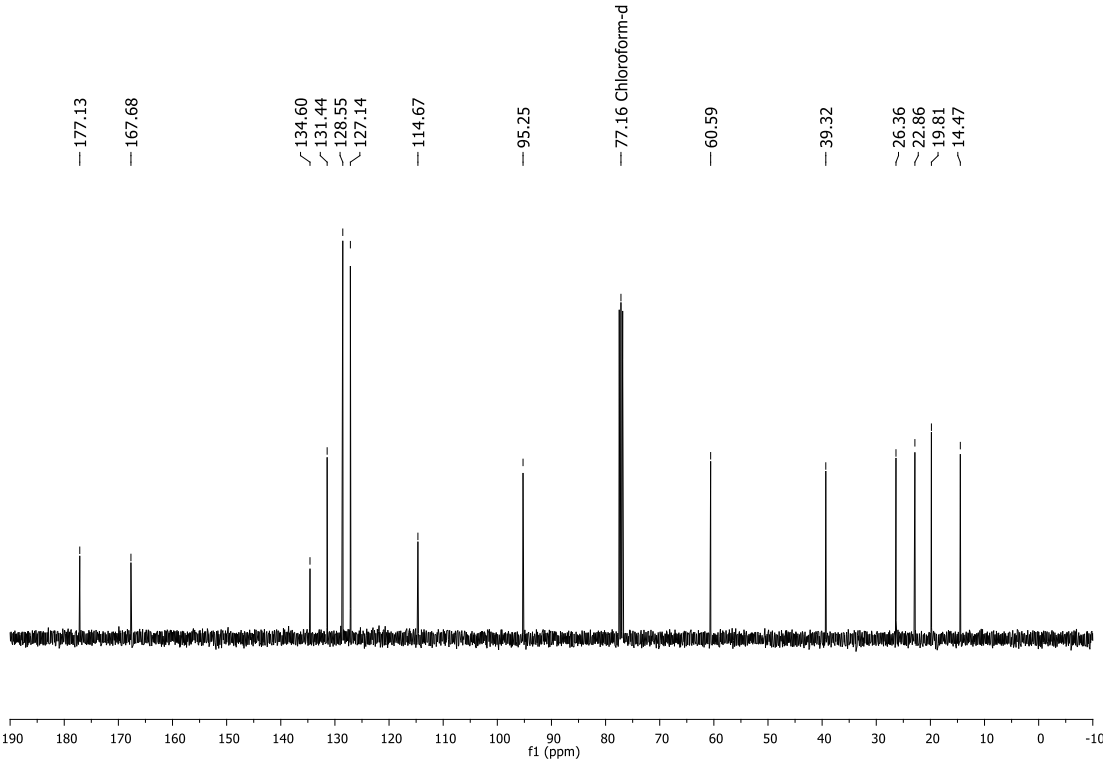


Ethyl 2-(3-benzamidopropyl)cycloprop-2-ene-1-carboxylate (1h)

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

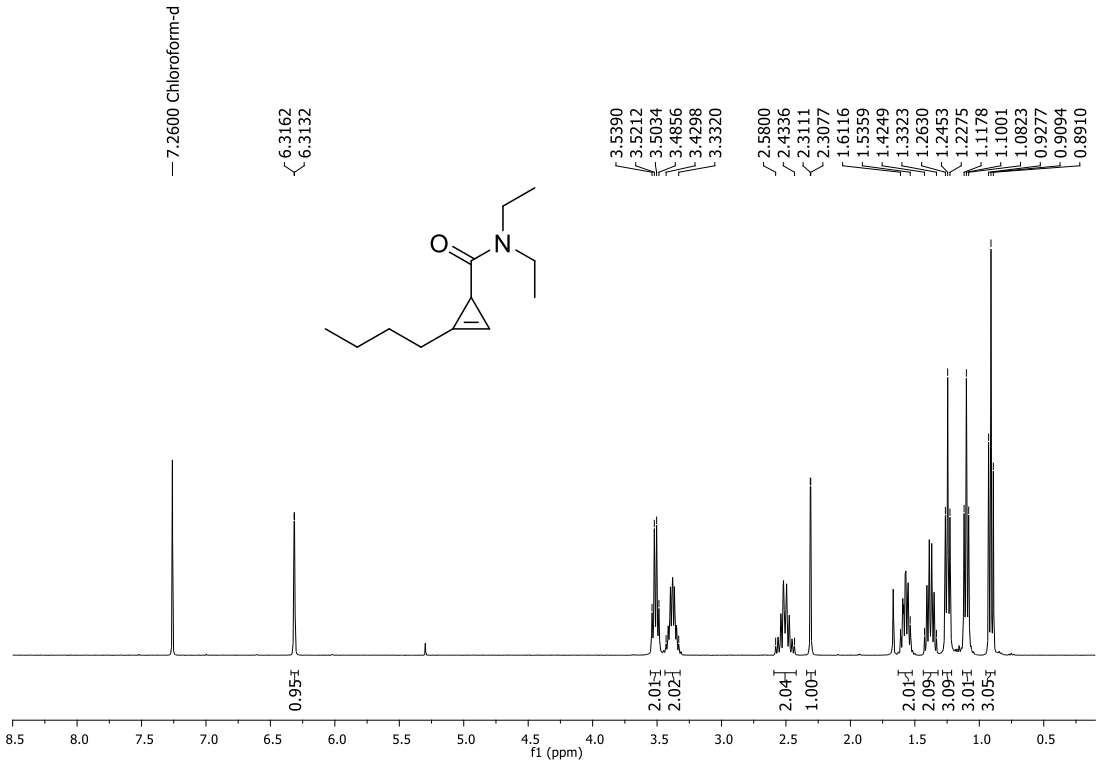


^{13}C NMR ($CDCl_3$, 101 MHz)



2-Butyl-*N*,*N*-diethylcycloprop-2-ene-1-carboxamide (1l)

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



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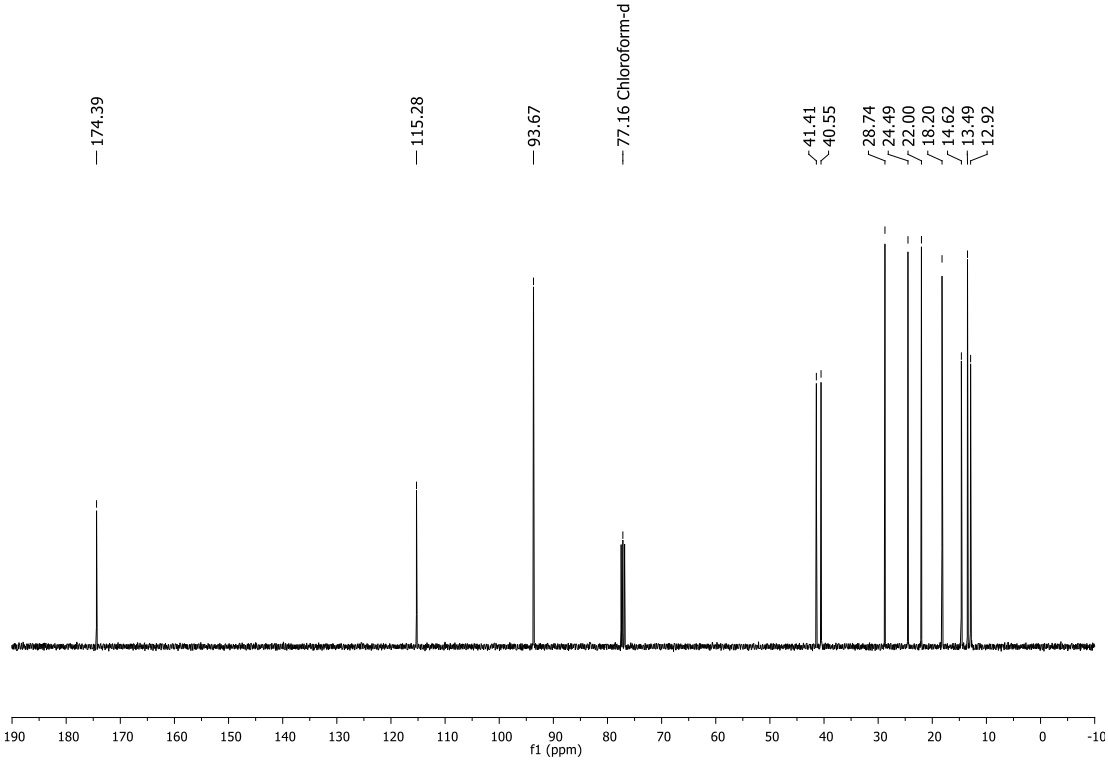
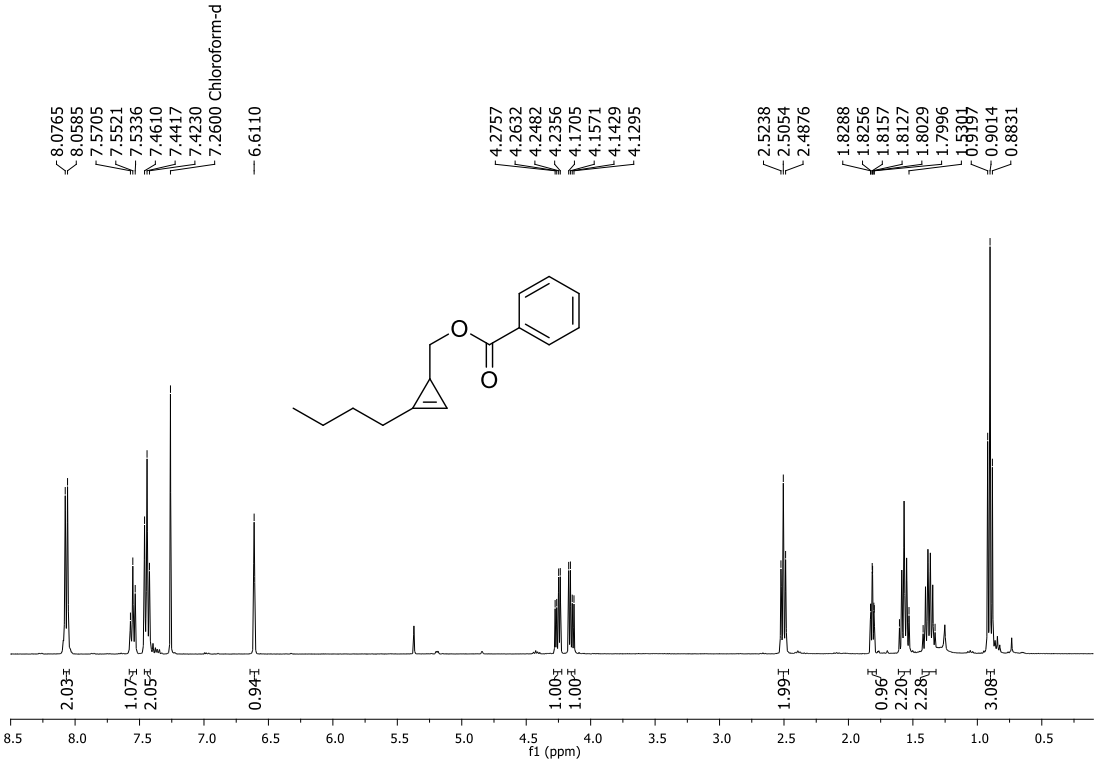


(2-Butylcycloprop-2-en-1-yl)methyl benzoate (1n)

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



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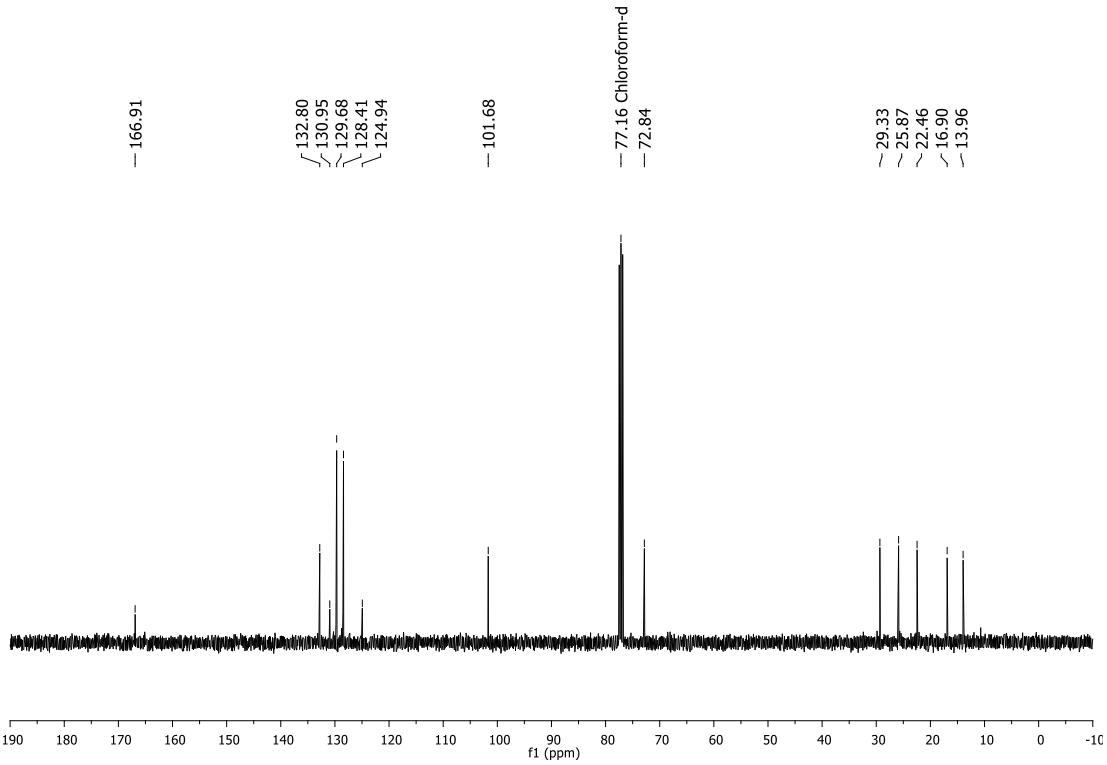
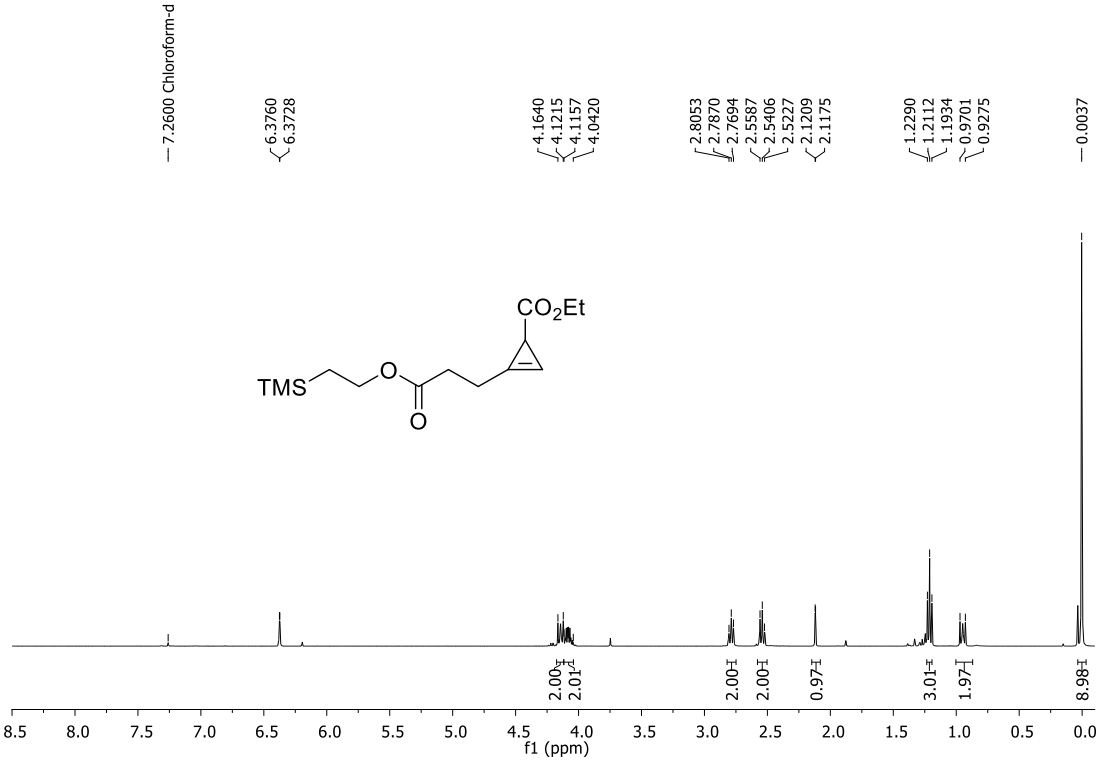
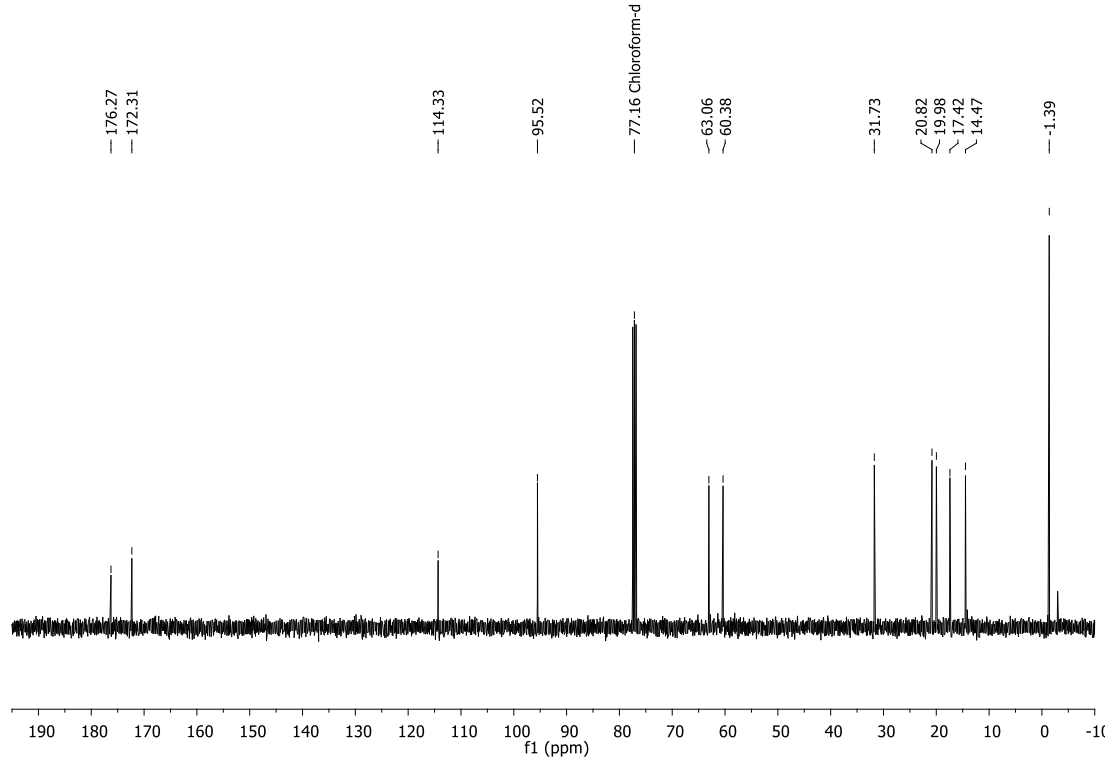


Ethyl 2-(3-oxo-3-(2-(trimethylsilyl)ethoxy)propyl)cycloprop-2-ene-1-carboxylate (IV)

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

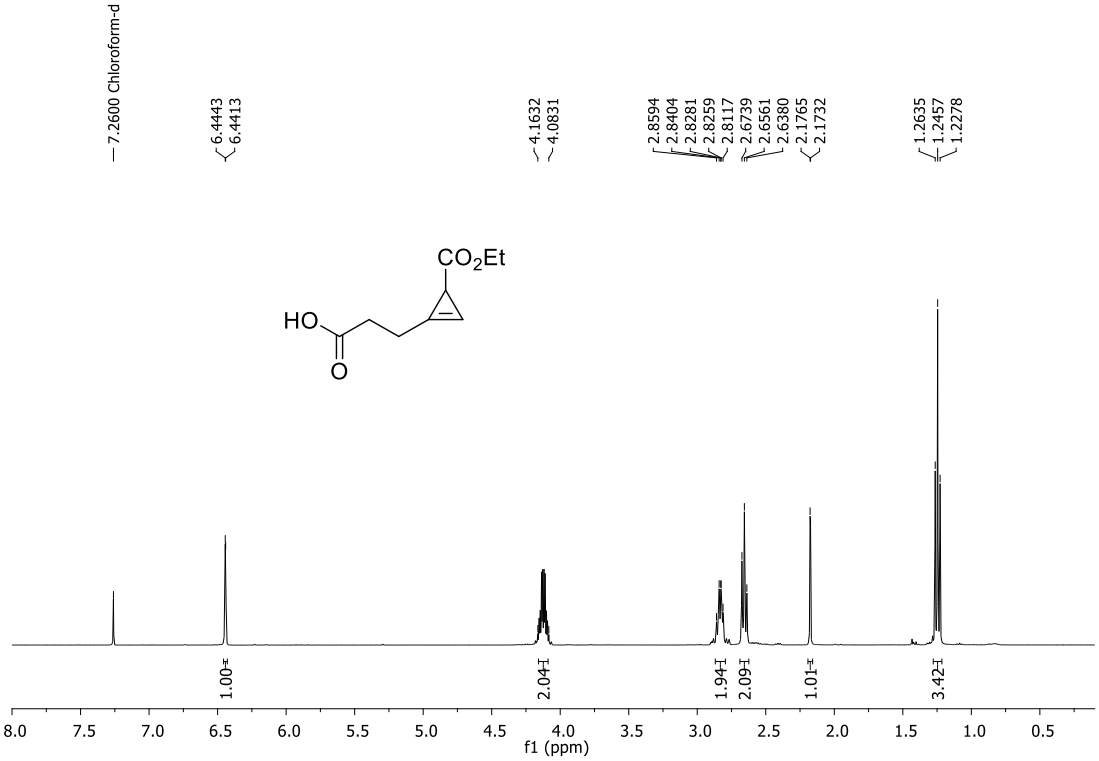


^{13}C NMR (101 MHz, $CDCl_3$)



3-(3-(Ethoxycarbonyl)cycloprop-1-en-1-yl)propanoic acid (1q)

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



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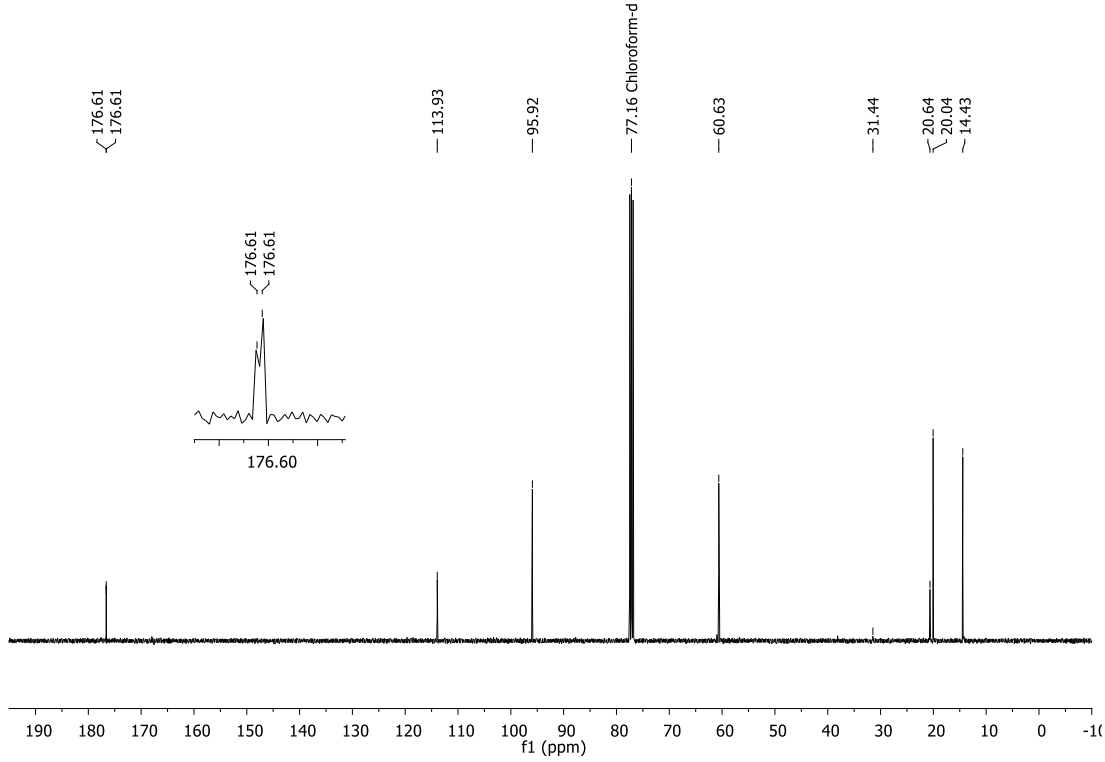
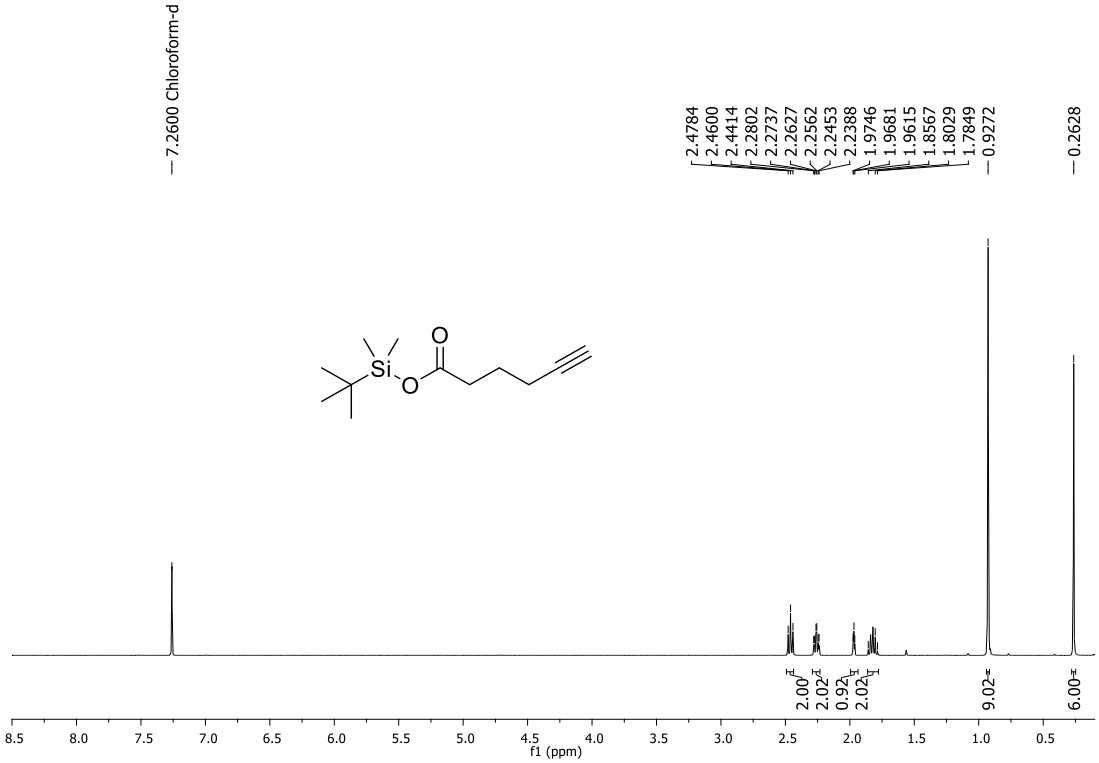
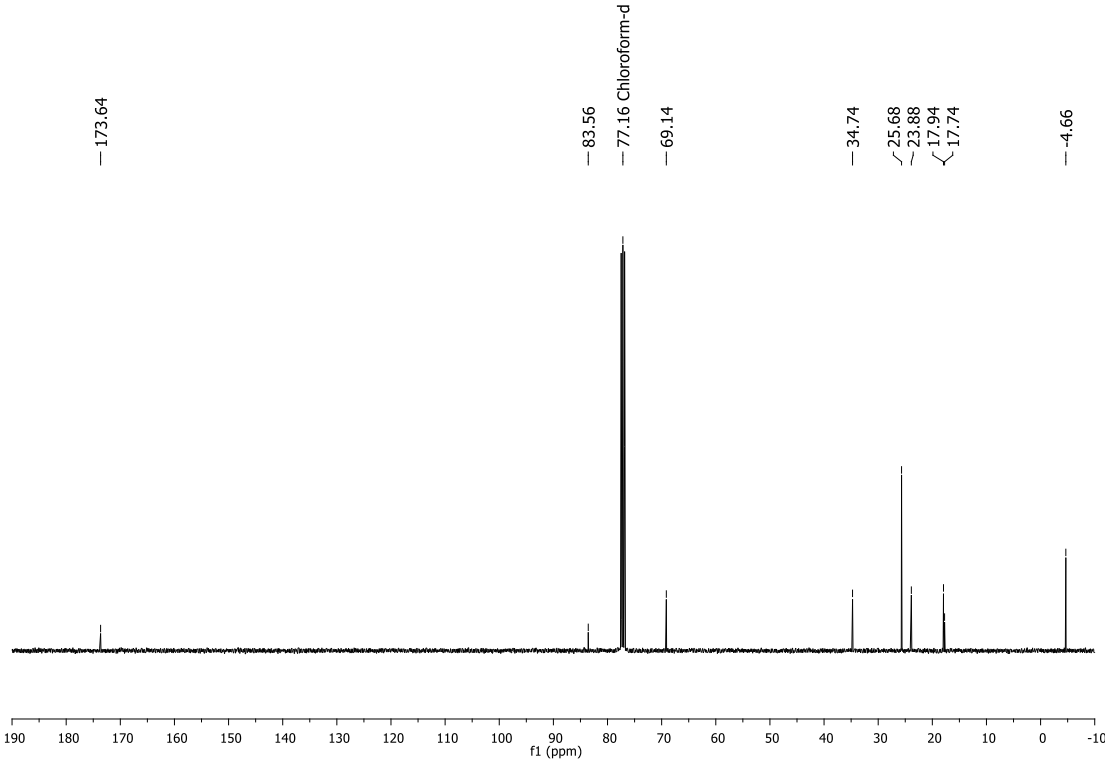


***tert*-Butyldimethylsilyl hex-5-ynoate (V)**

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

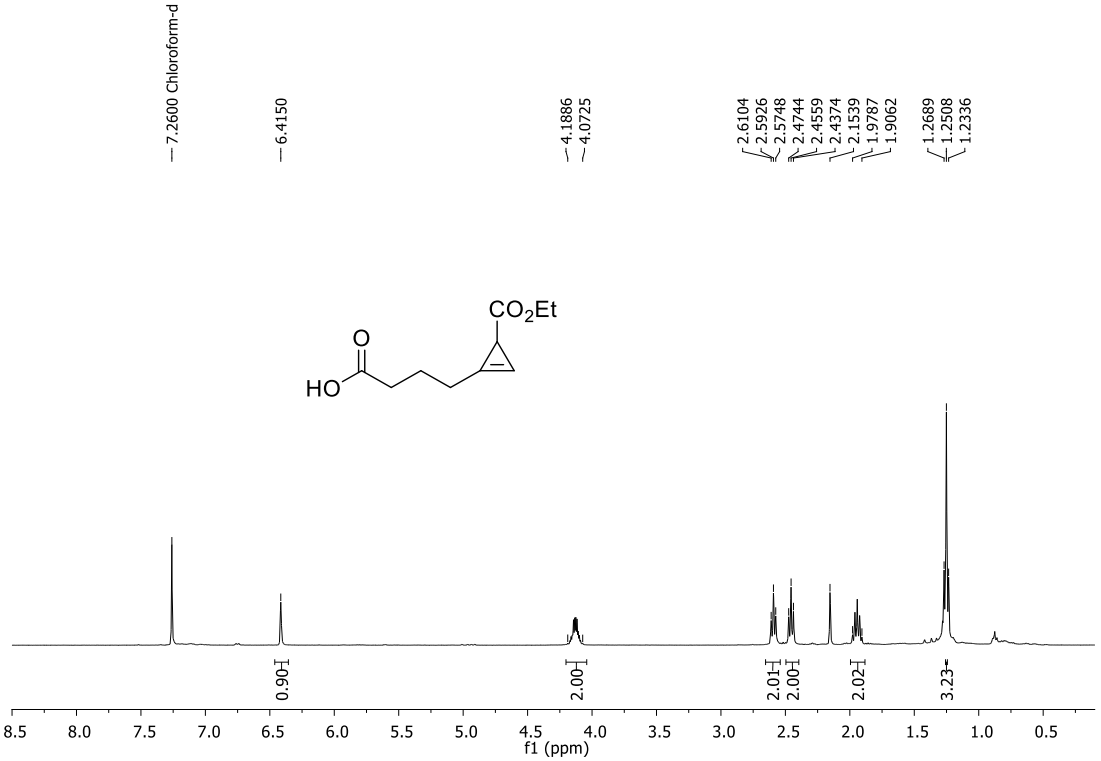


^{13}C NMR ($CDCl_3$, 101 MHz)



4-(3-(Ethoxycarbonyl)cycloprop-1-en-1-yl)butanoic acid (1r)

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



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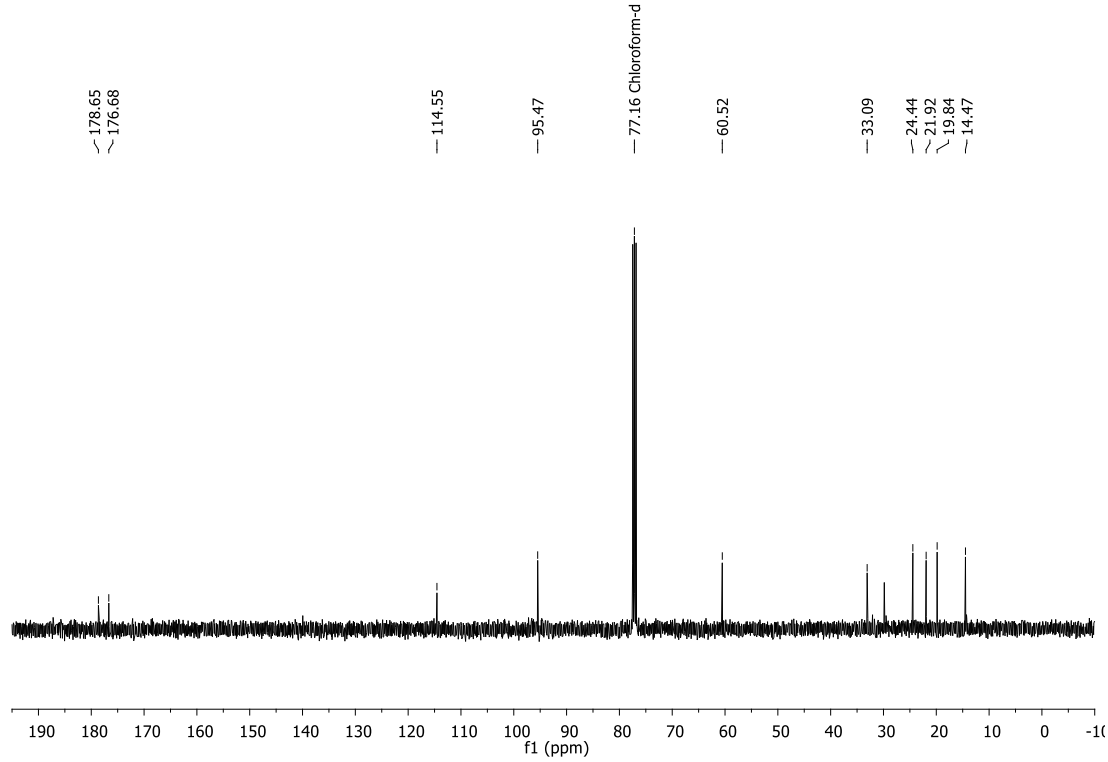
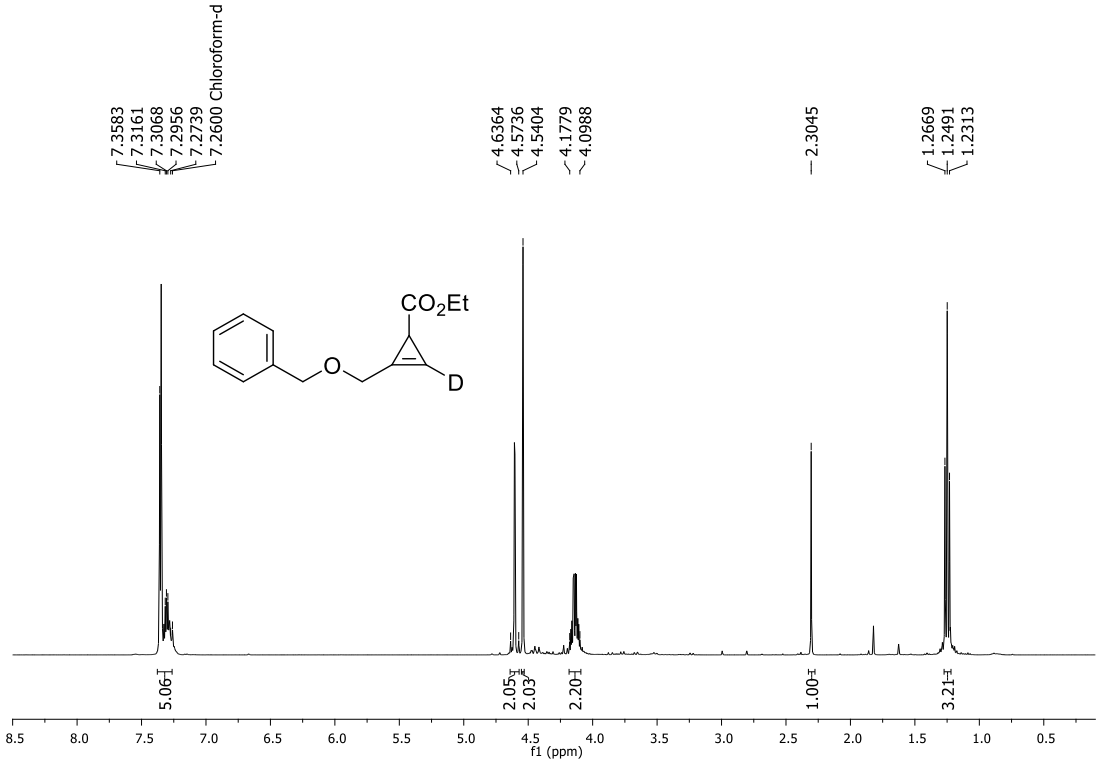
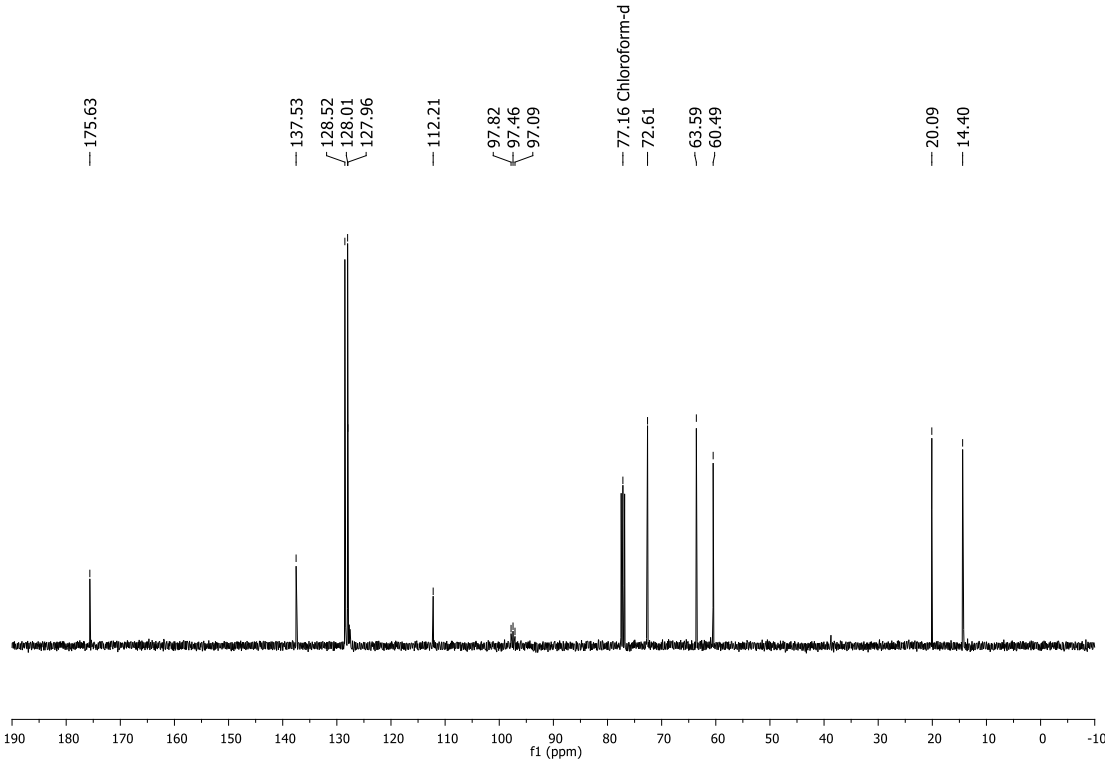


Ethyl 2-((benzyloxy)methyl)cycloprop-2-ene-1-carboxylate-3-*d* (1i-D)

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

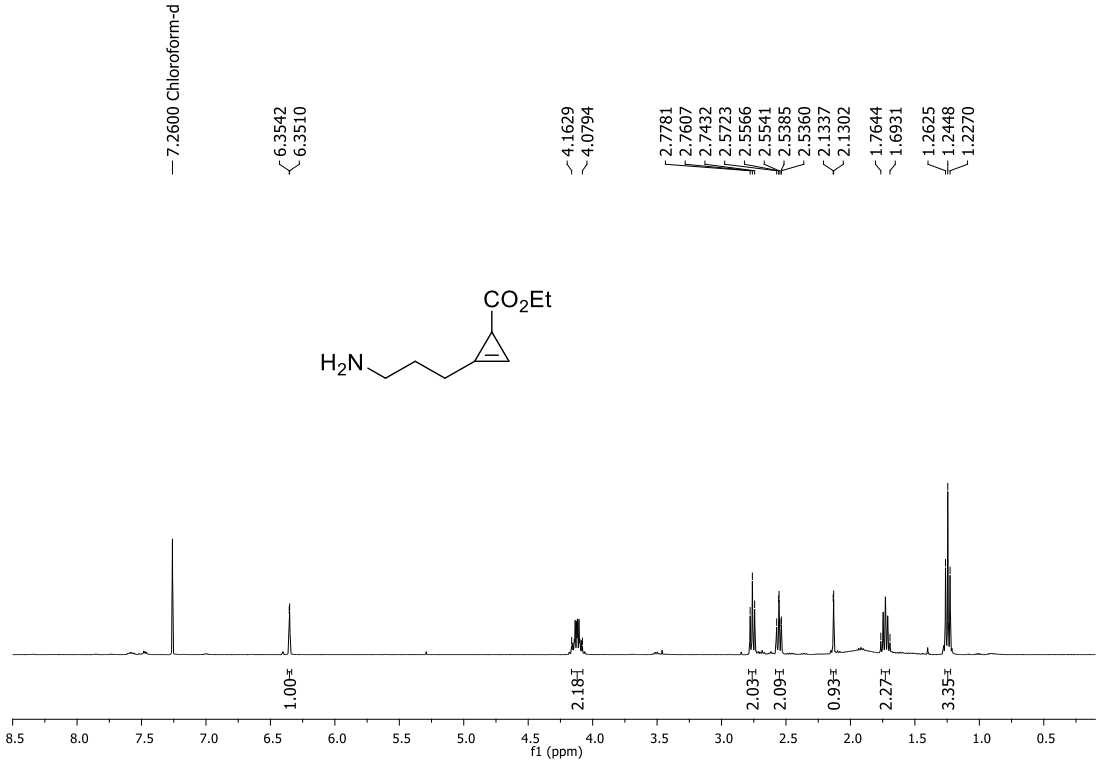


^{13}C NMR ($CDCl_3$, 101 MHz)

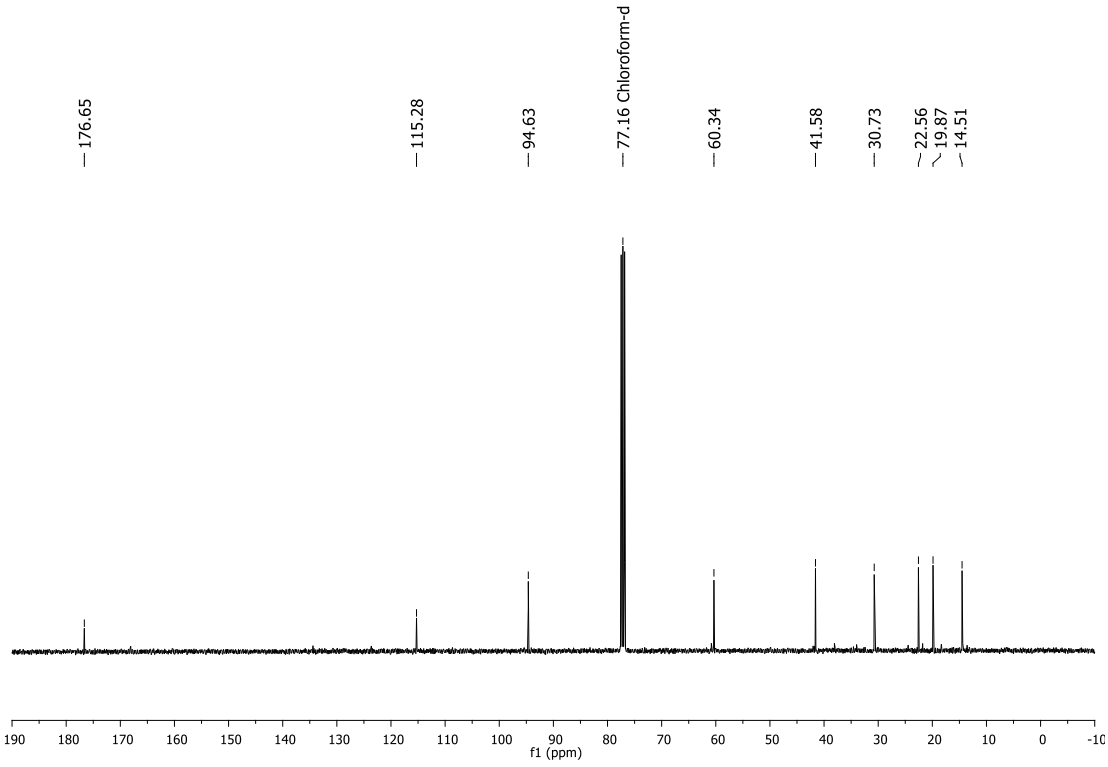


Ethyl 2-(3-aminopropyl)cycloprop-2-ene-1-carboxylate (1s)

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

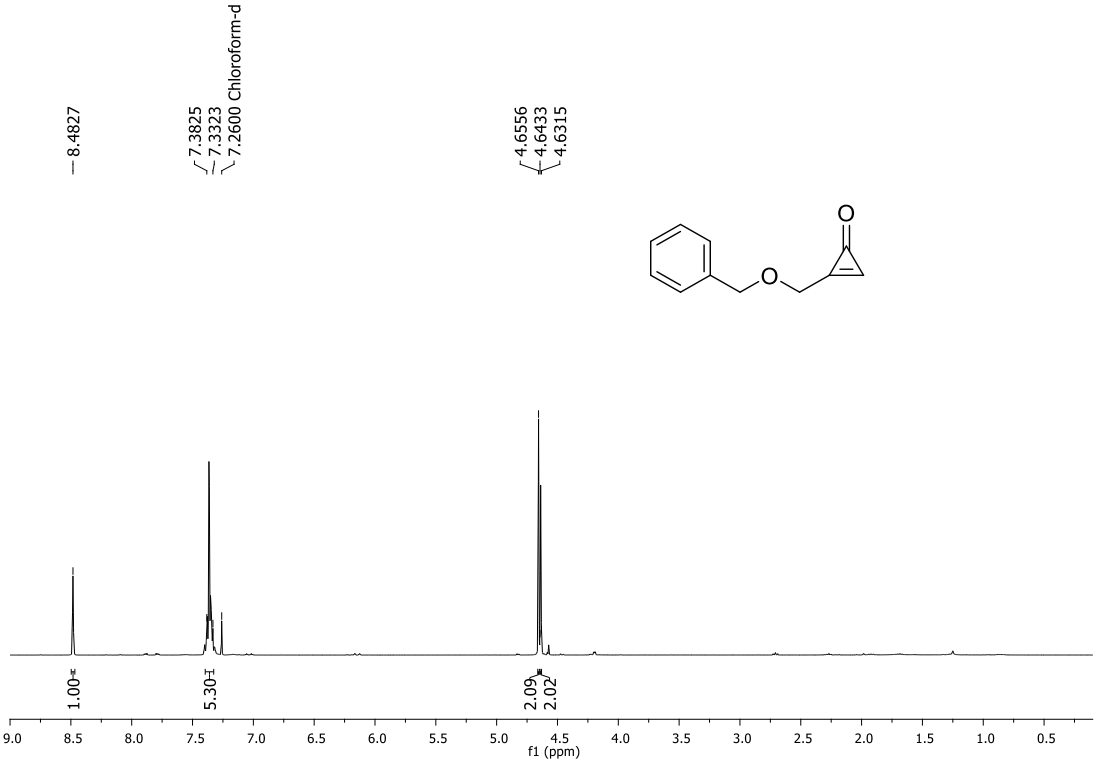


^{13}C NMR ($CDCl_3$, 101 MHz)

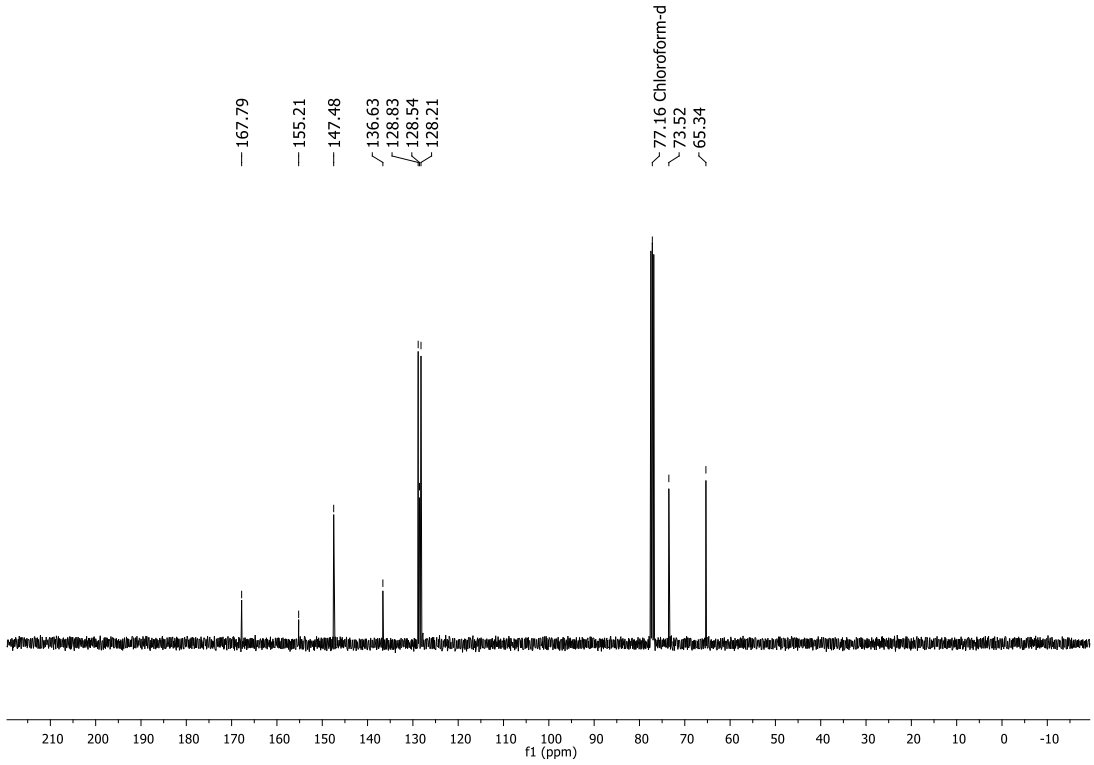


2-((Benzyloxy)methyl)cycloprop-2-en-1-one (1t)

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

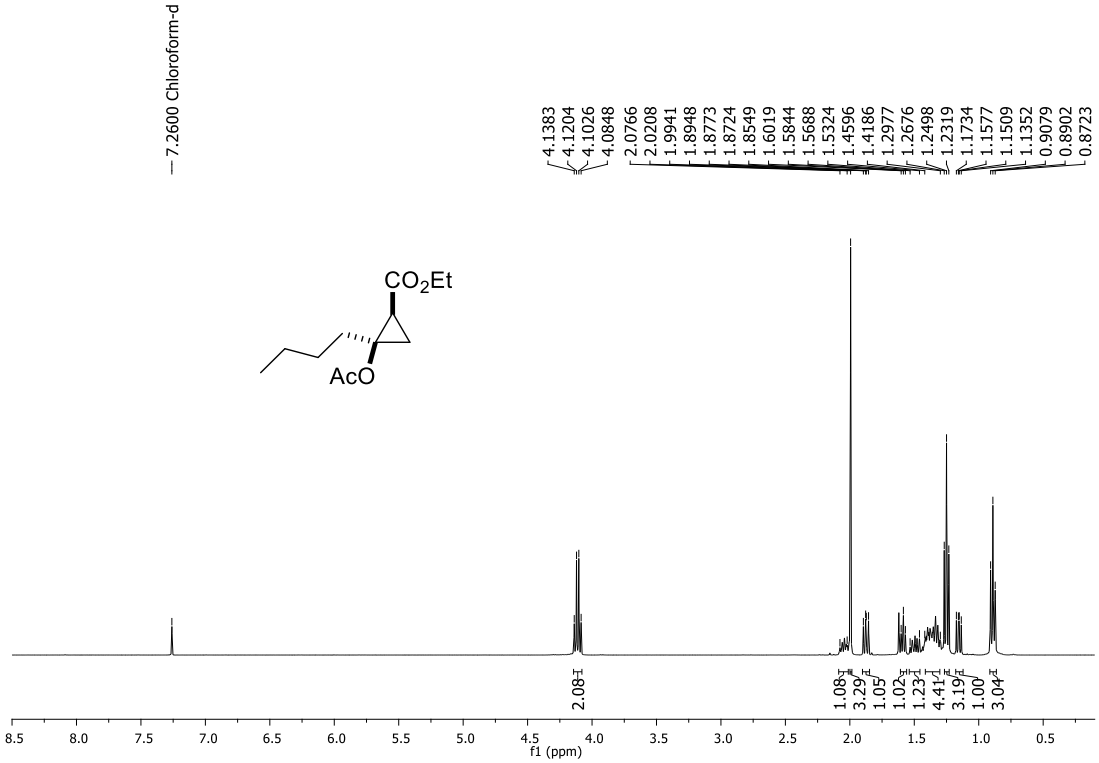


^{13}C NMR ($CDCl_3$, 101 MHz)

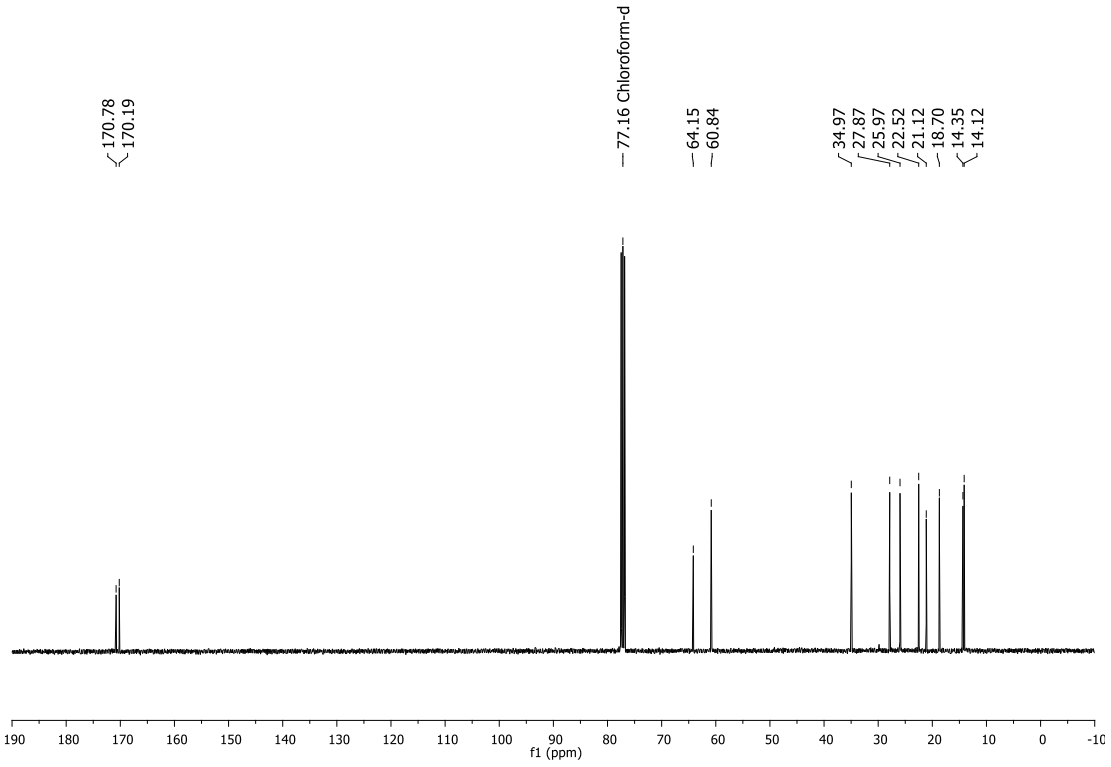


Ethyl (1*S,2*R**)-2-acetoxy-2-butylcyclopropane-1-carboxylate (3aa)**

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

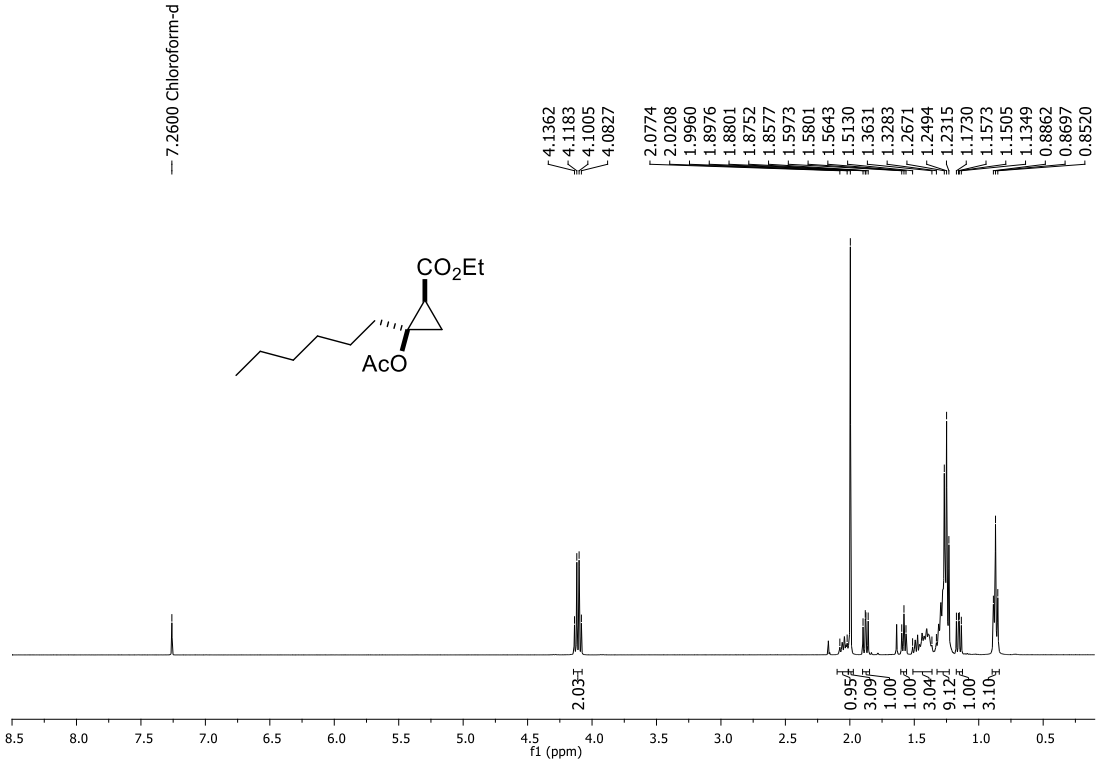


^{13}C NMR ($CDCl_3$, 101 MHz)

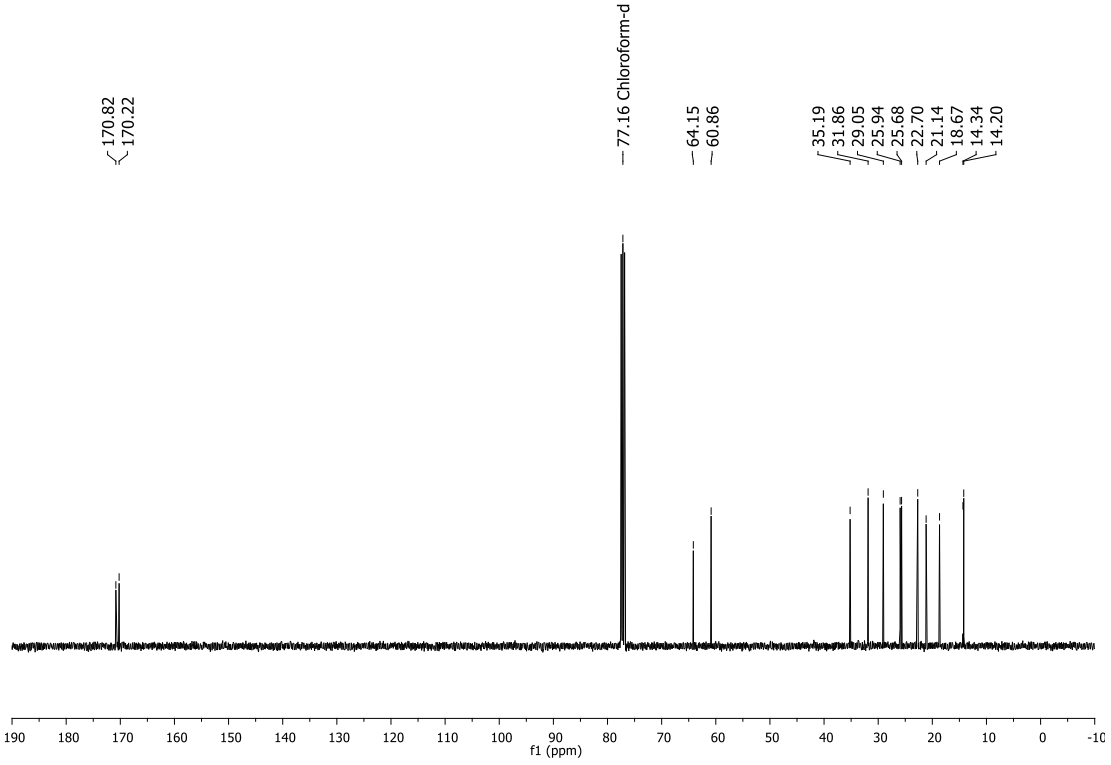


Ethyl (1*S,2*R**)-2-acetoxy-2-hexylcyclopropane-1-carboxylate (3ba)**

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

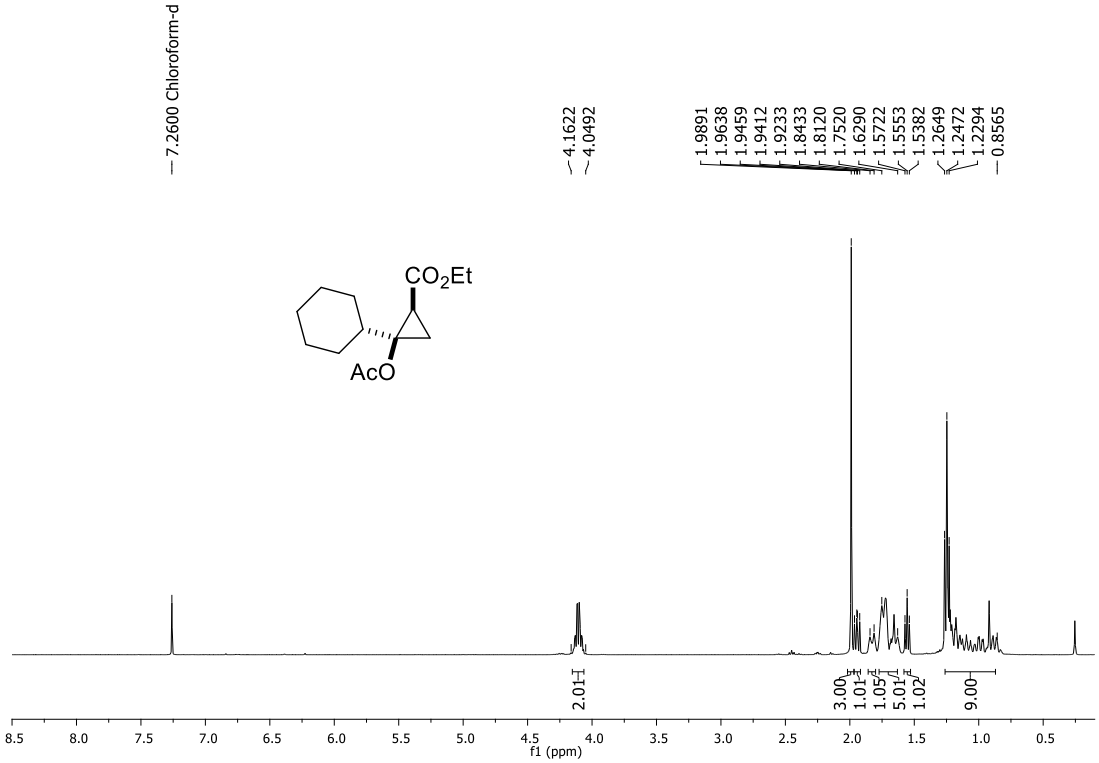


^{13}C NMR ($CDCl_3$, 101 MHz)

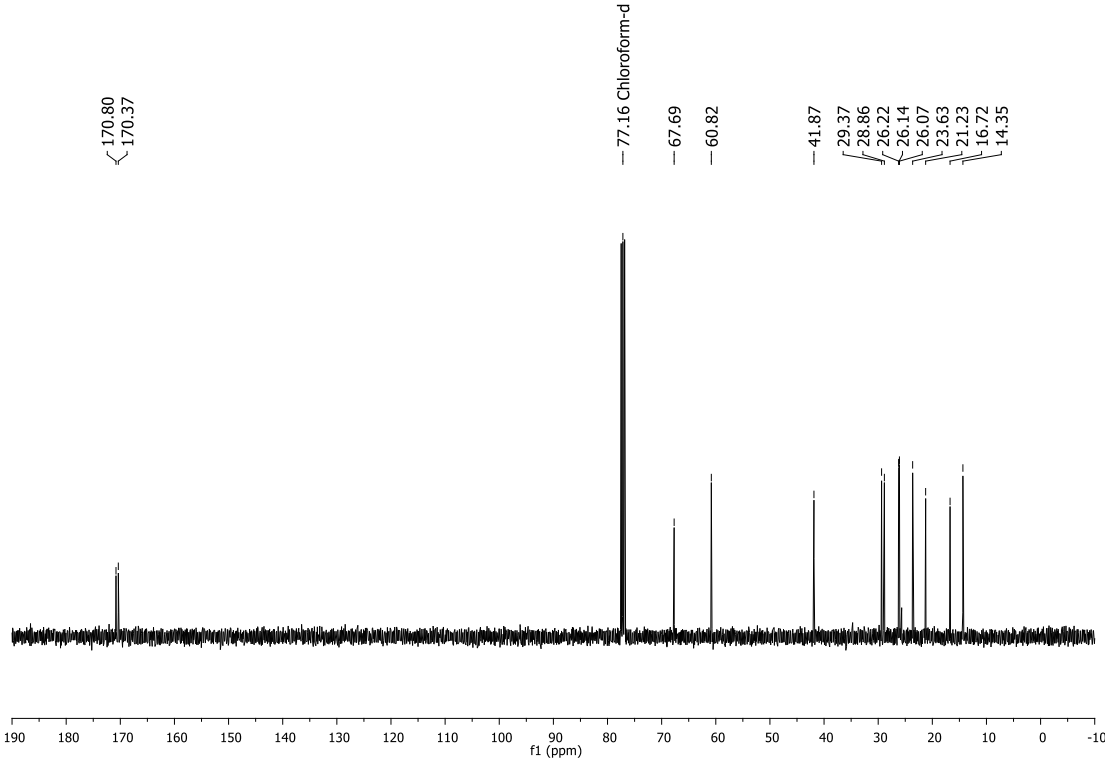


Ethyl (1*S,2*S**)-2-acetoxy-2-cyclohexylcyclopropane-1-carboxylate (3ca)**

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

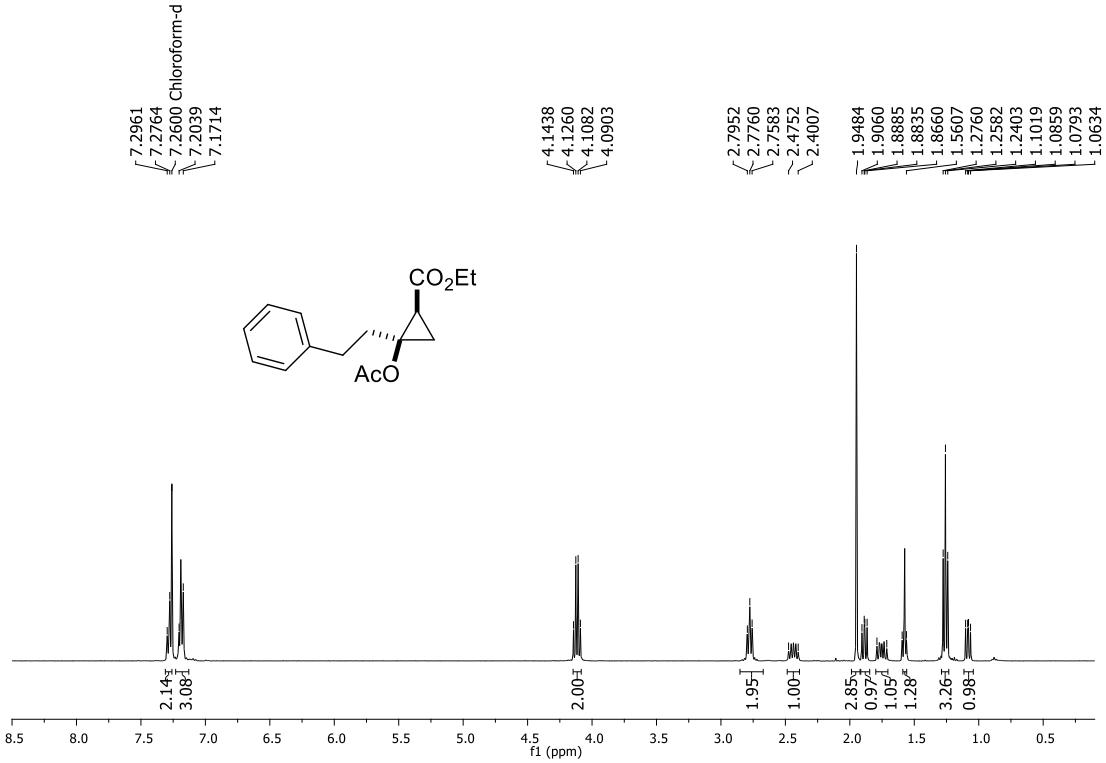


^{13}C NMR ($CDCl_3$, 101 MHz)

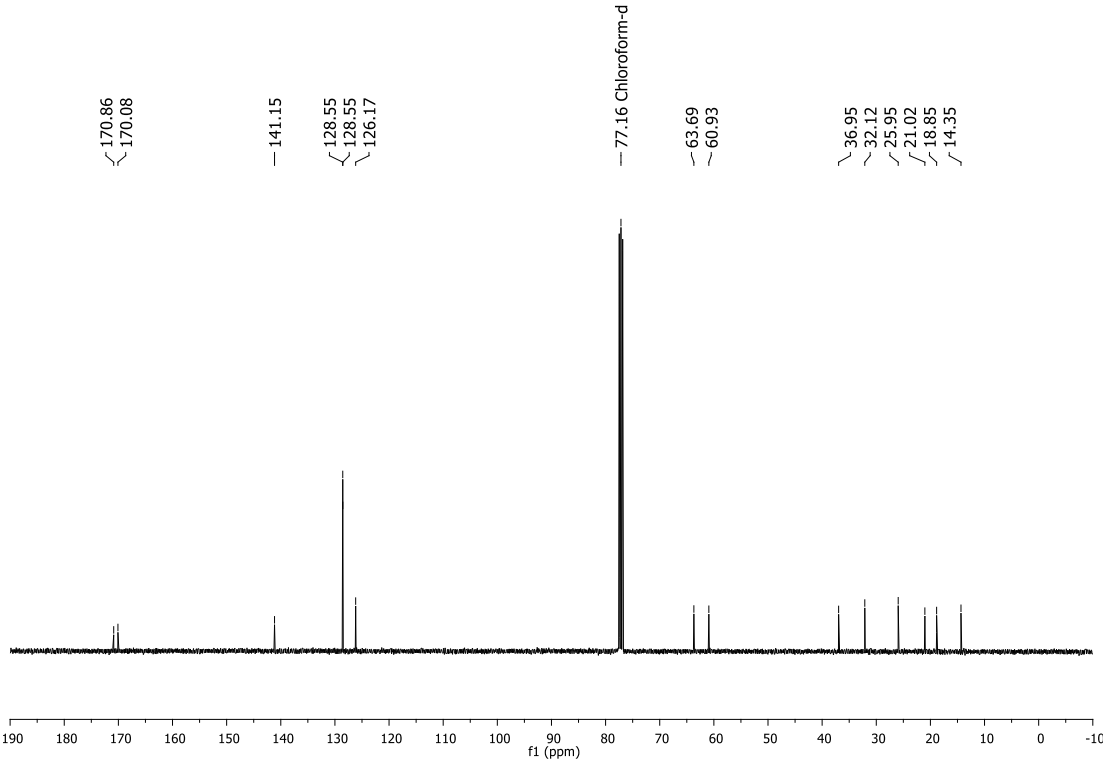


Ethyl (1*S,2*R**)-2-acetoxy-2-phenethylcyclopropane-1-carboxylate (3da)**

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

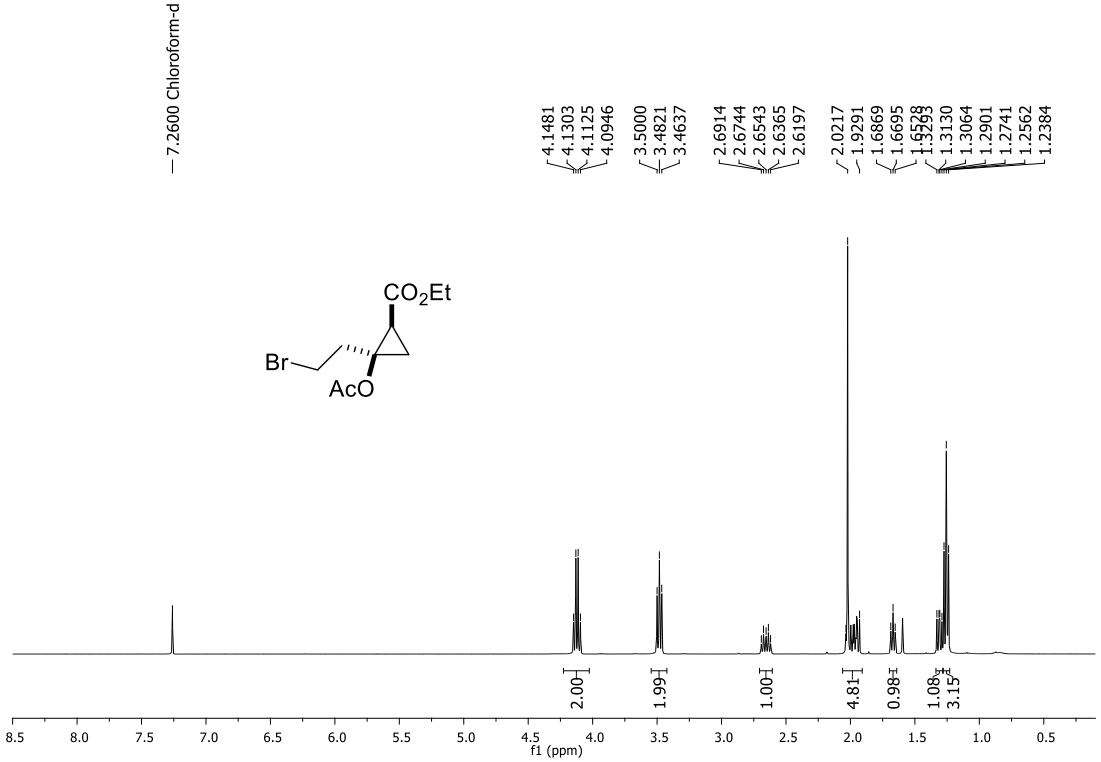


^{13}C NMR ($CDCl_3$, 101 MHz)

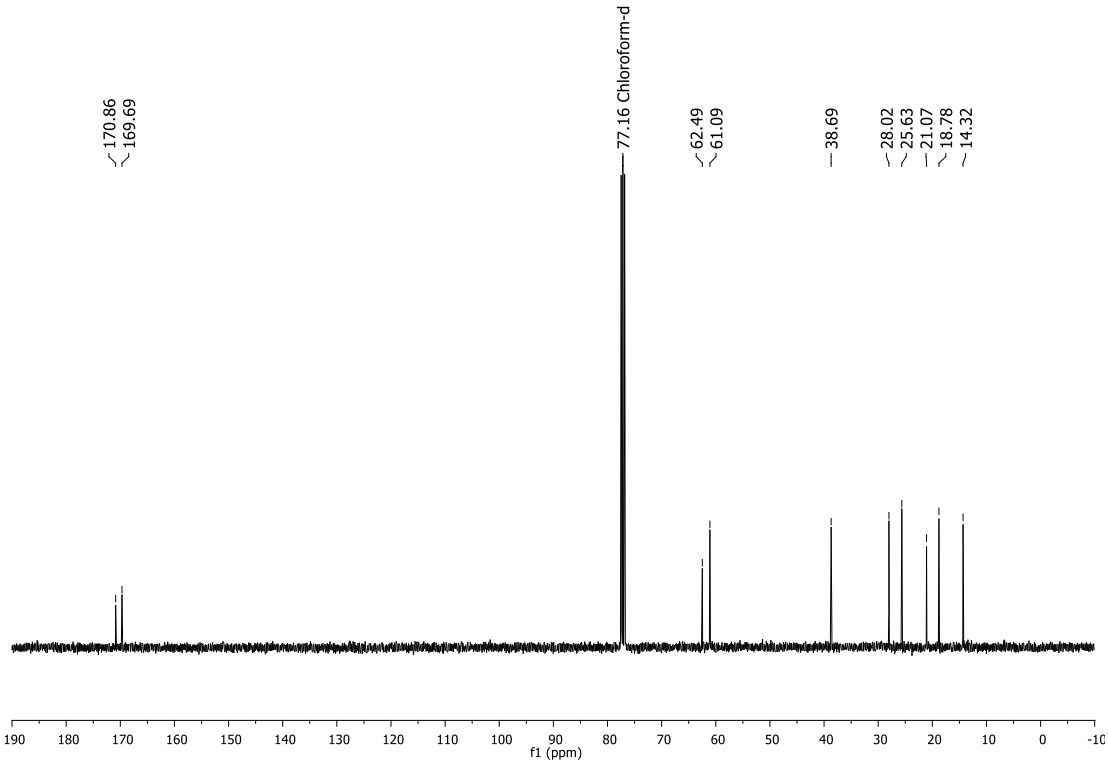


Ethyl (1*S,2*S**)-2-acetoxy-2-(2-bromoethyl)cyclopropane-1-carboxylate (3ea)**

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

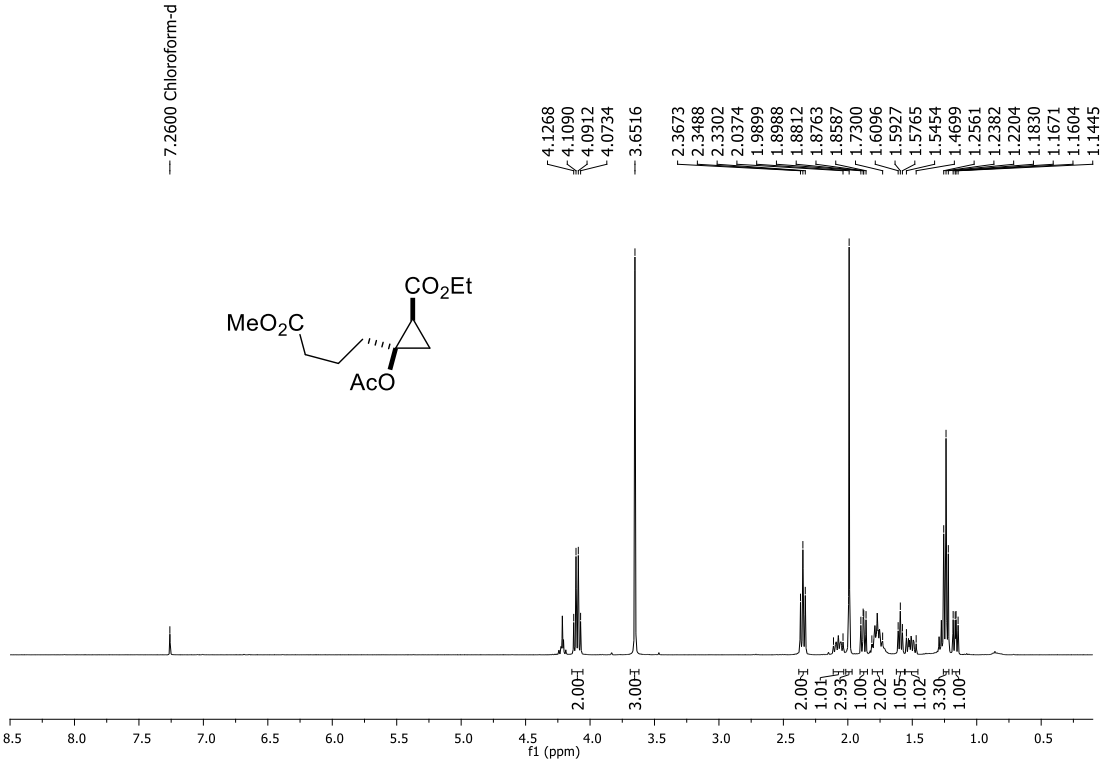


^{13}C NMR ($CDCl_3$, 101 MHz)

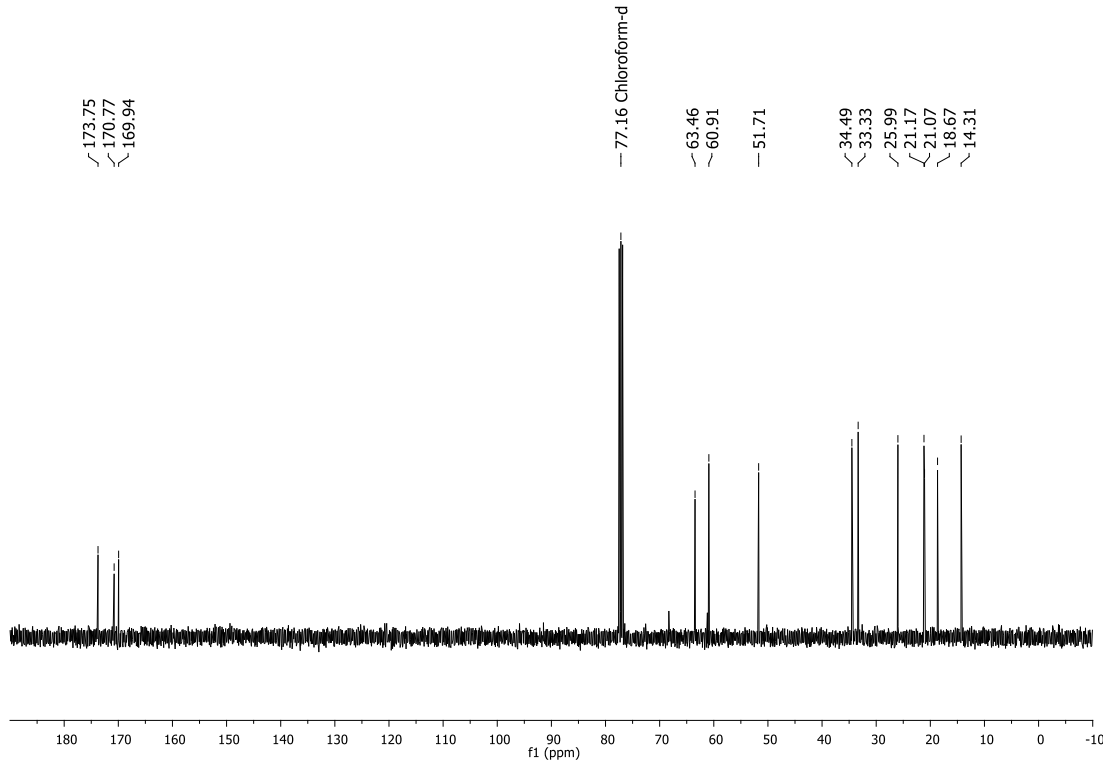


Ethyl (1*S,2*R**)-2-acetoxy-2-(4-methoxy-4-oxobutyl)cyclopropane-1-carboxylate (3fa)**

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

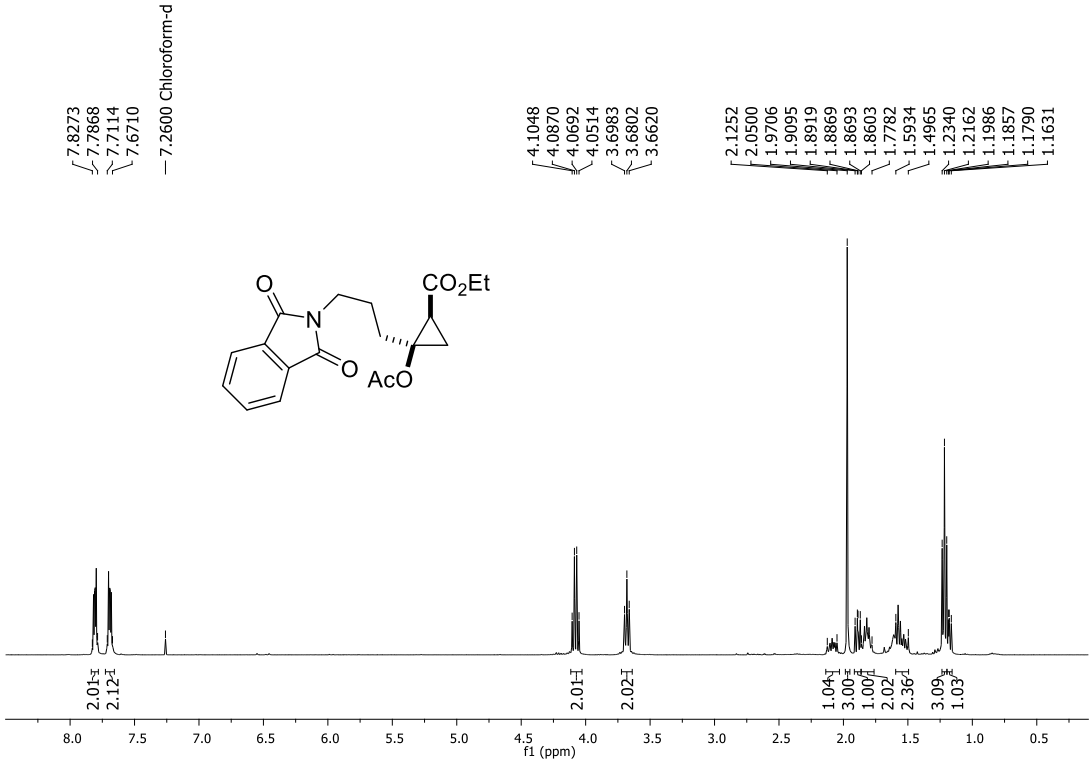


^{13}C NMR ($CDCl_3$, 101 MHz)

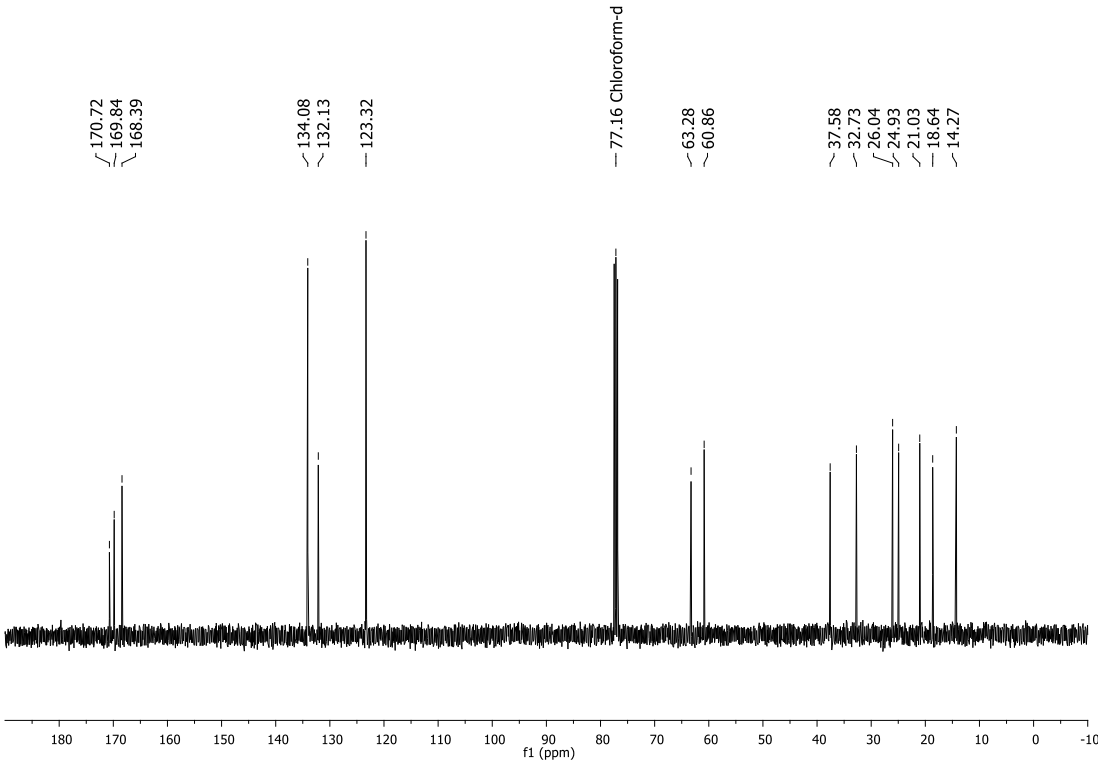


Ethyl (1*S,2*R**)-2-acetoxy-2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cyclopropane-1-carboxylate (3ga)**

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

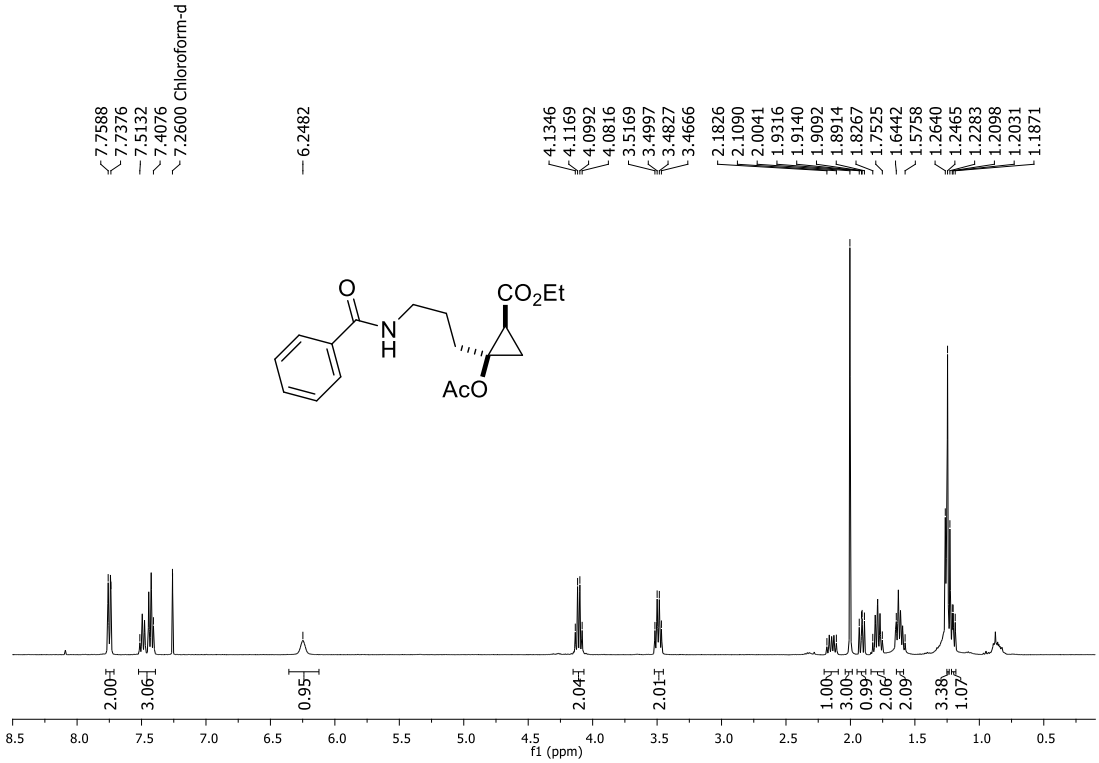


^{13}C NMR ($CDCl_3$, 101 MHz)

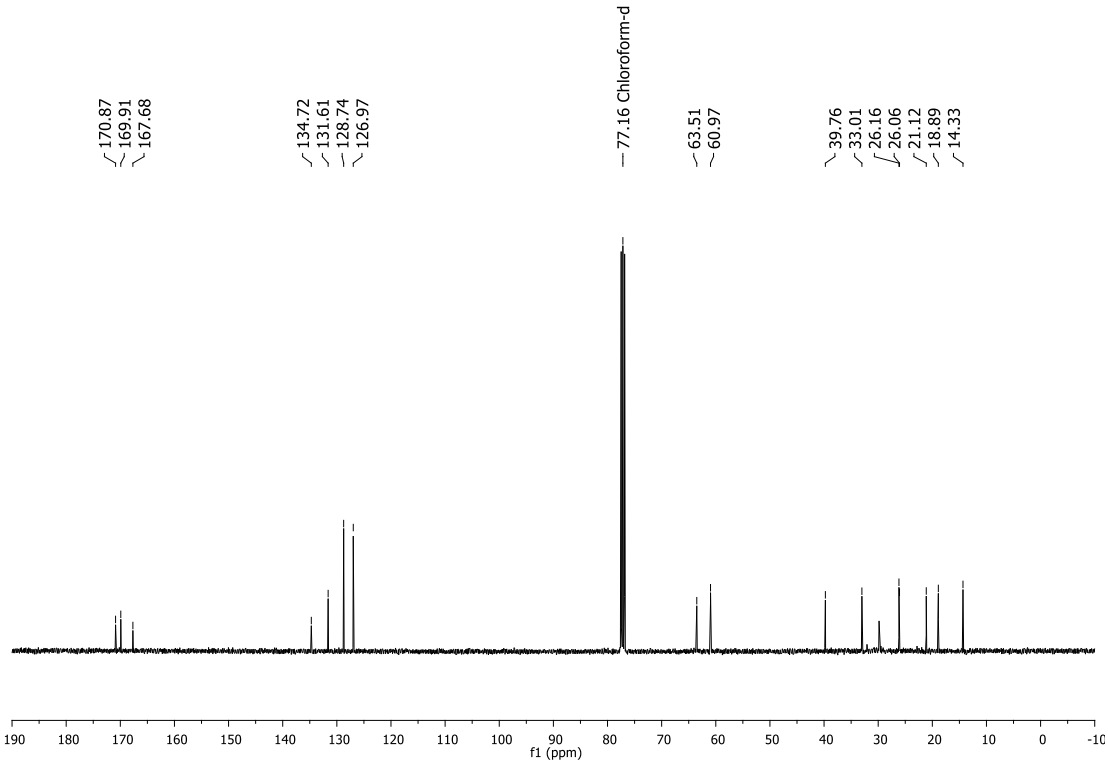


Ethyl (1*S,2*R**)-2-acetoxy-2-(3-benzamidopropyl)cyclopropane-1-carboxylate (3ha)**

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

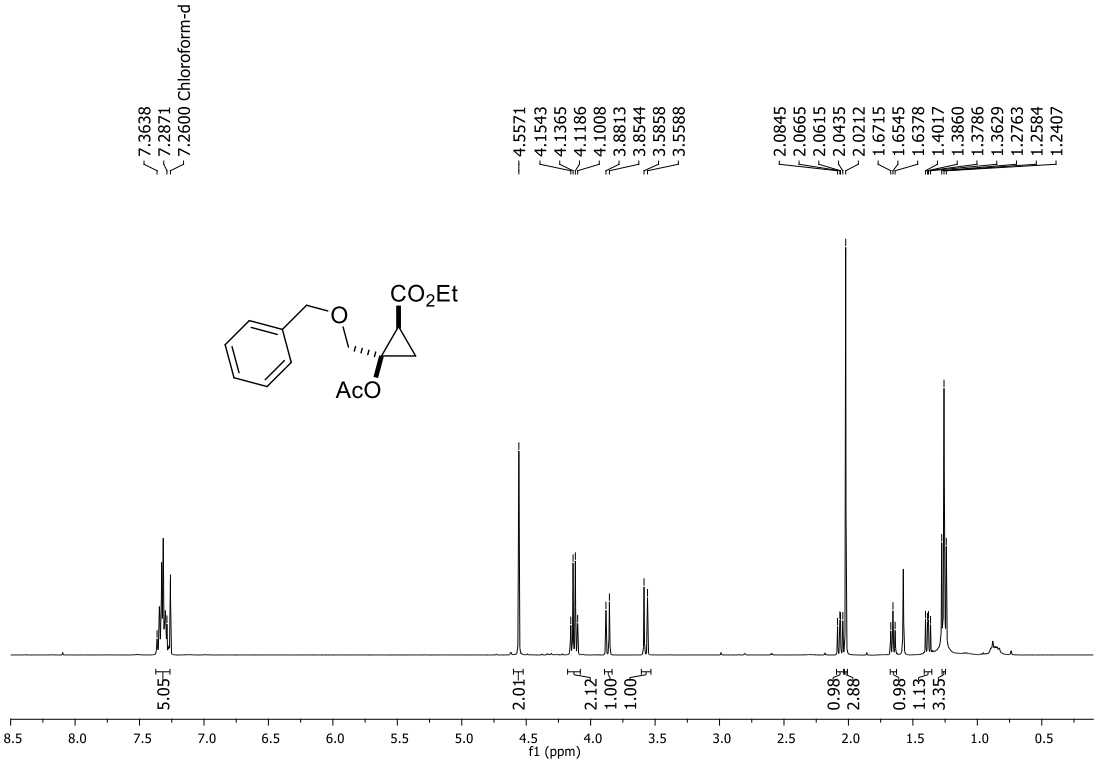


^{13}C NMR ($CDCl_3$, 101 MHz)

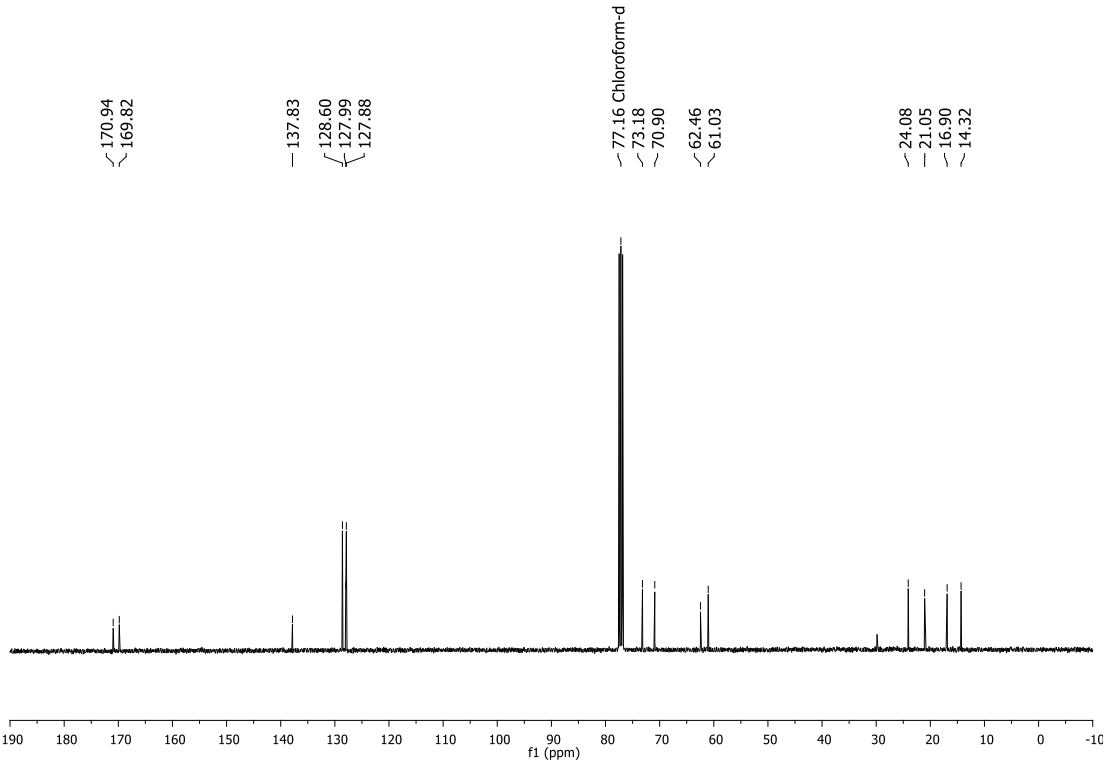


Ethyl (1*S,2*R**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate (3ia)**

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

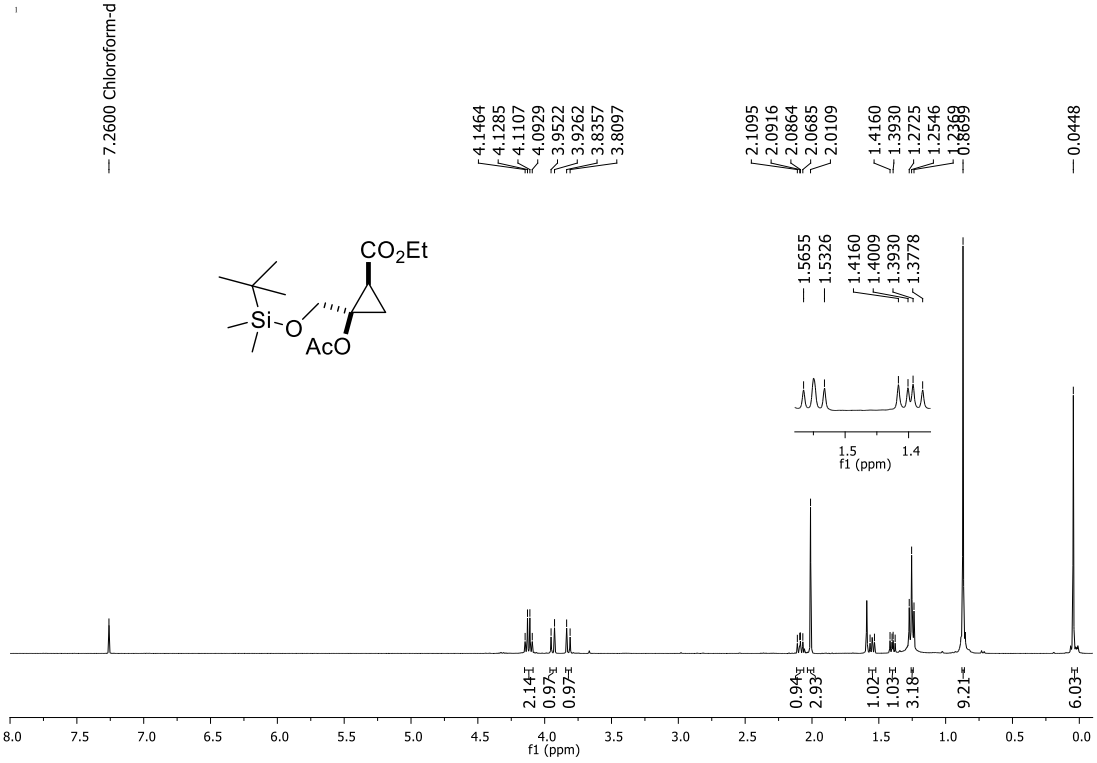


^{13}C NMR ($CDCl_3$, 101 MHz)

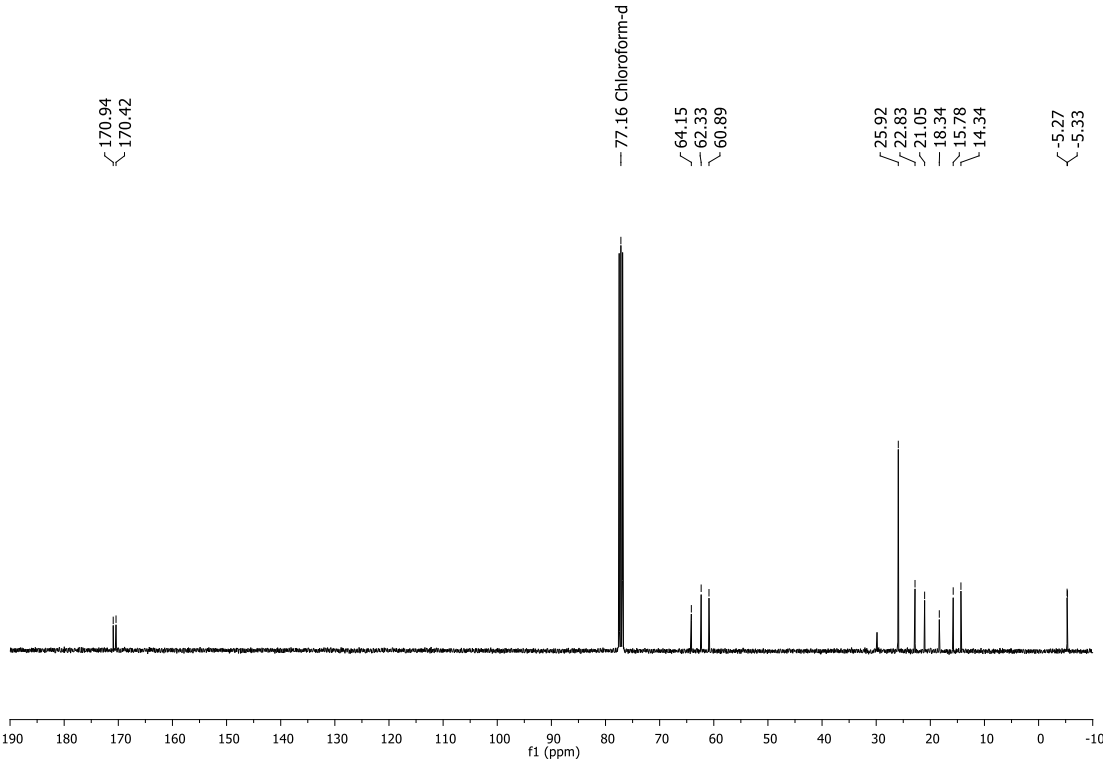


Ethyl (1*S,2*R**)-2-acetoxy-2-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopropane-1-carboxylate (3ja)**

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

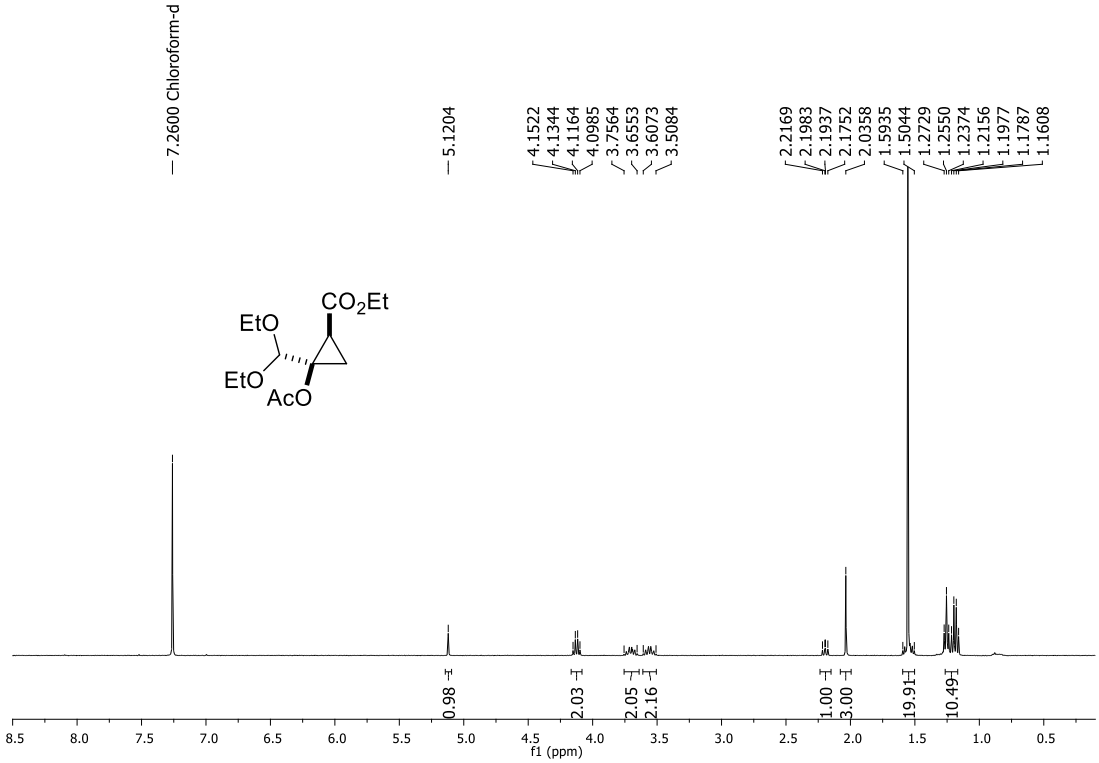


^{13}C NMR ($CDCl_3$, 101 MHz)

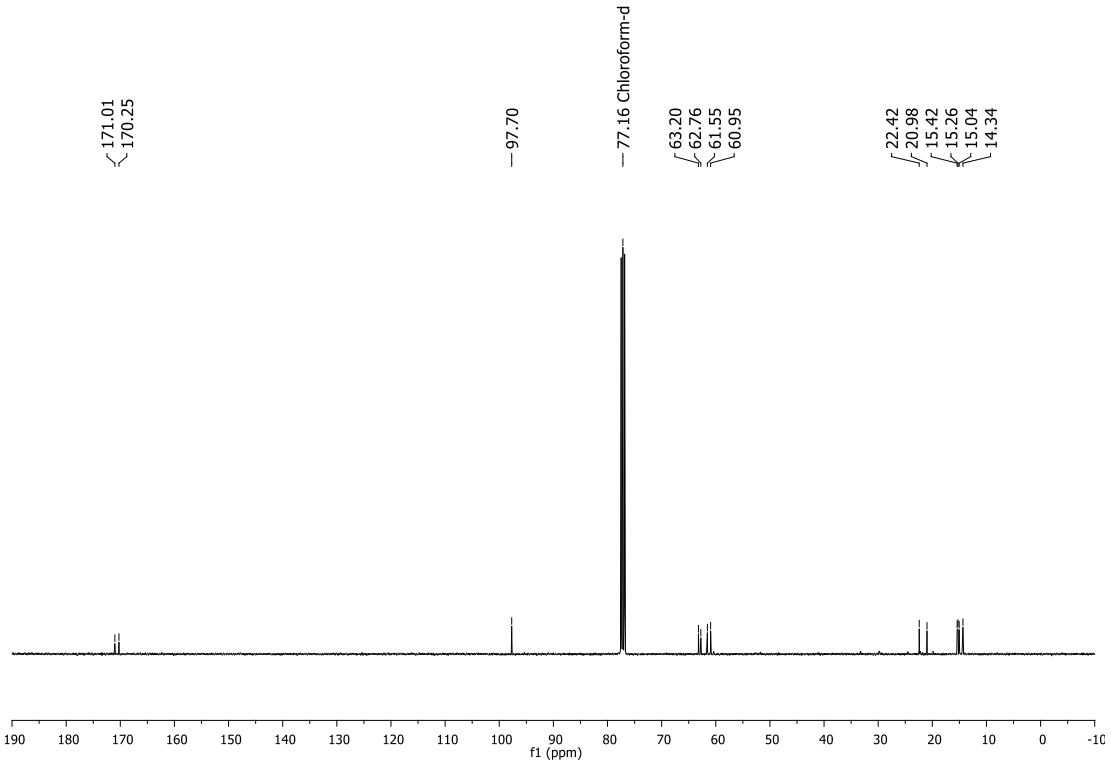


Ethyl (1*S,2*R**)-2-acetoxy-2-(diethoxymethyl)cyclopropane-1-carboxylate (3ka)**

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

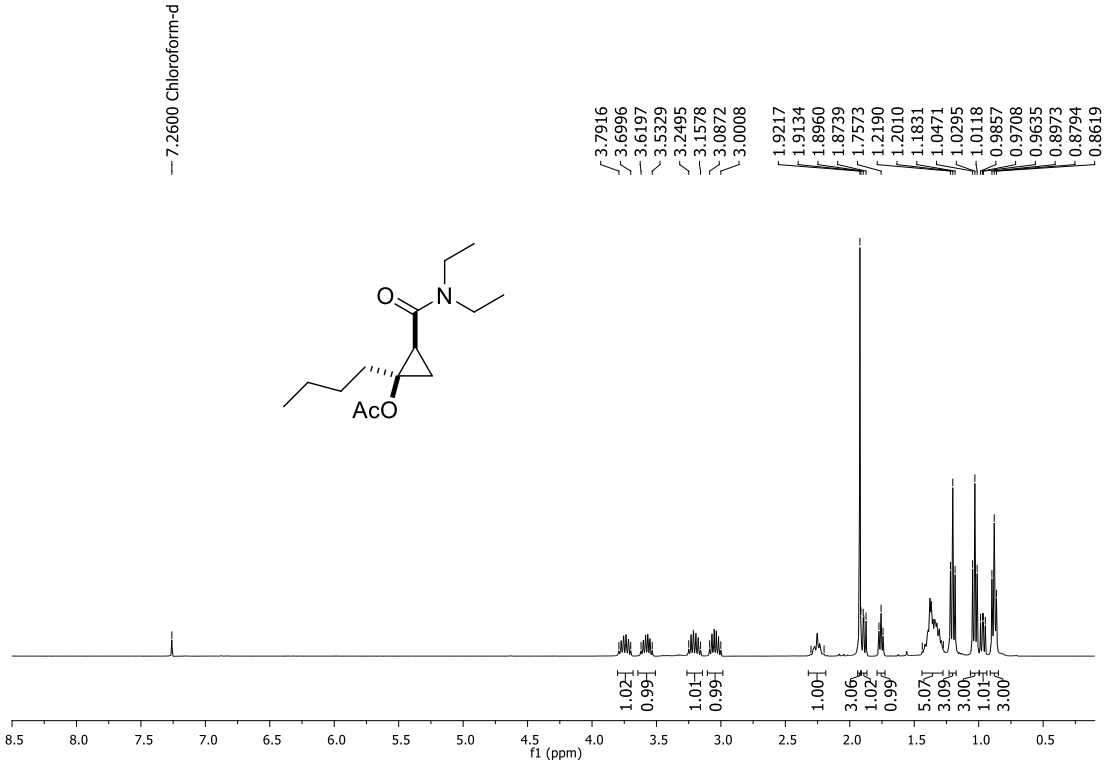


^{13}C NMR ($CDCl_3$, 101 MHz)

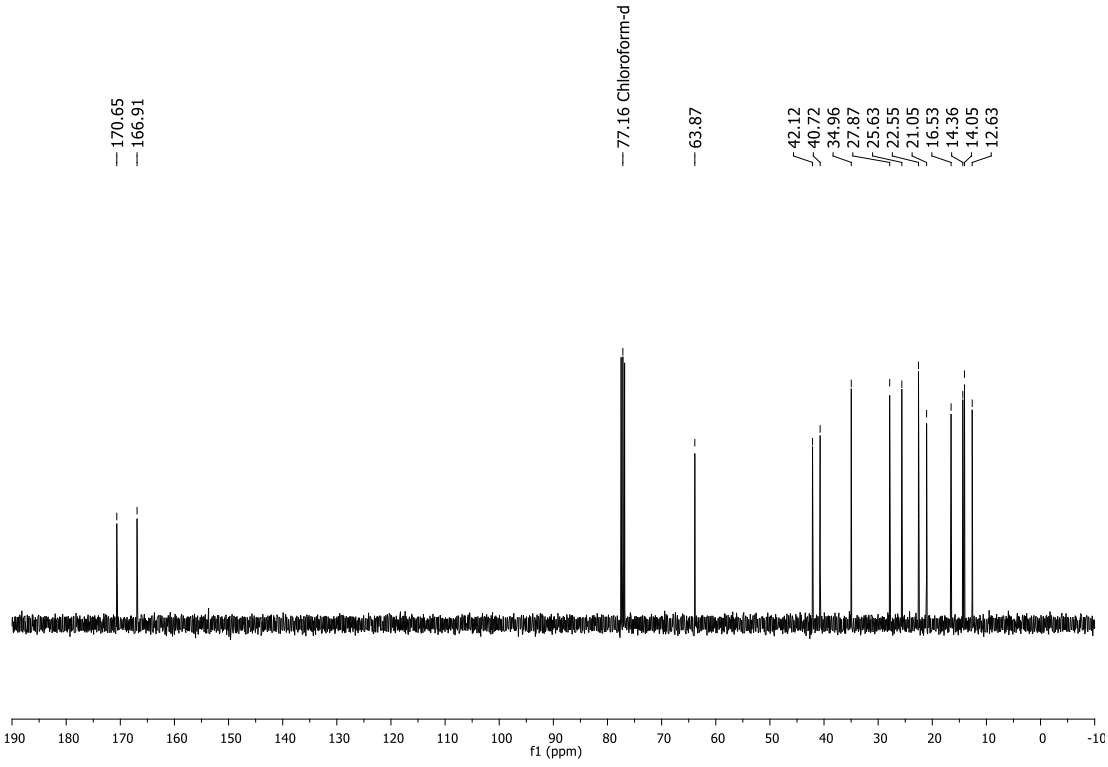


(1*R,2*S**)-1-Butyl-2-(diethylcarbamoyl)cyclopropyl acetate (3la)**

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

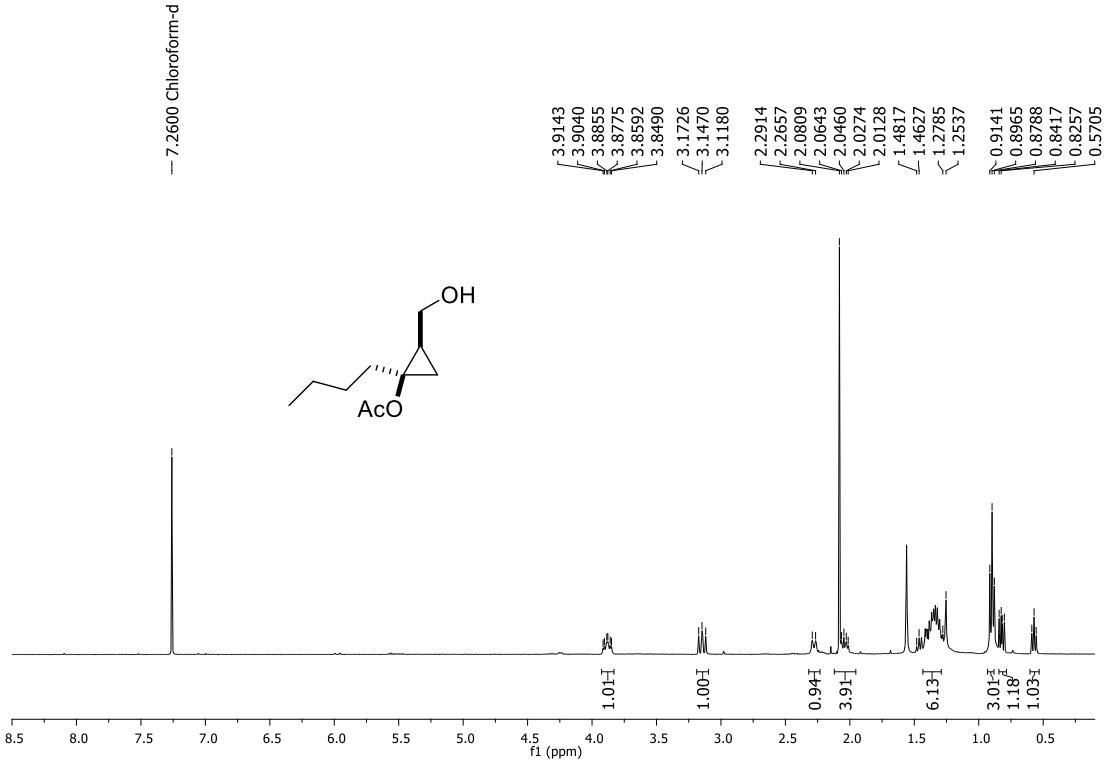


^{13}C NMR ($CDCl_3$, 101 MHz)

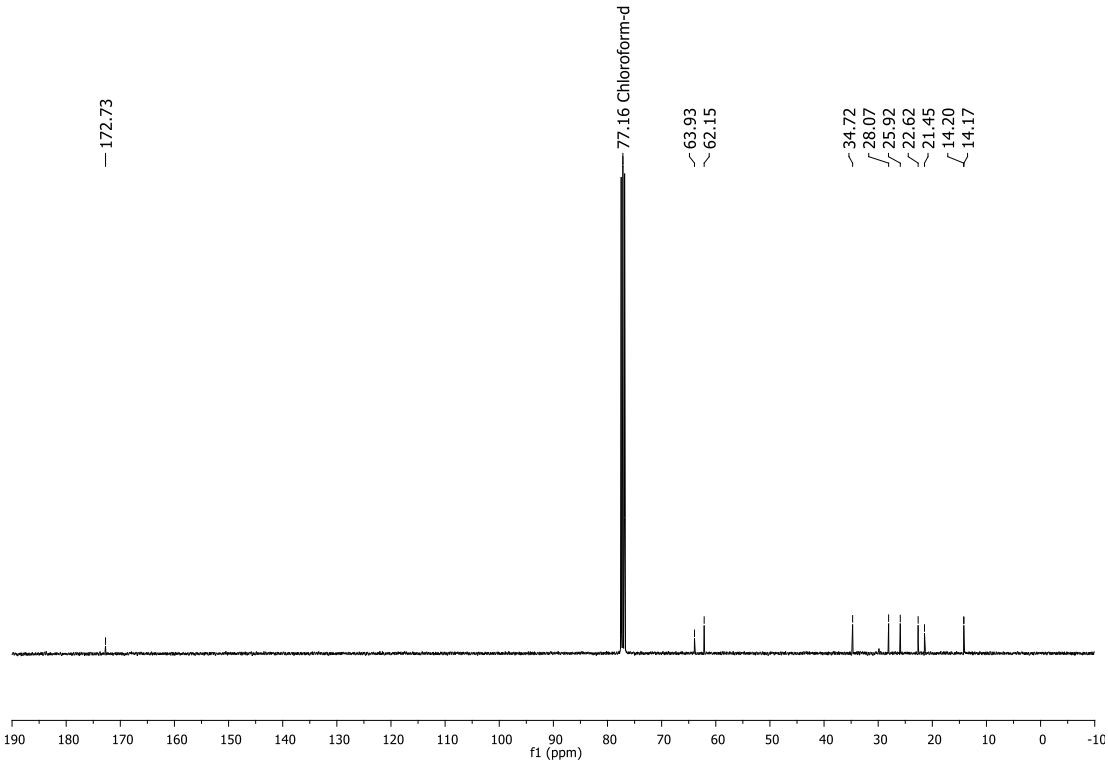


(1*R,2*R**)-1-Butyl-2-(hydroxymethyl)cyclopropyl acetate (3ma)**

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

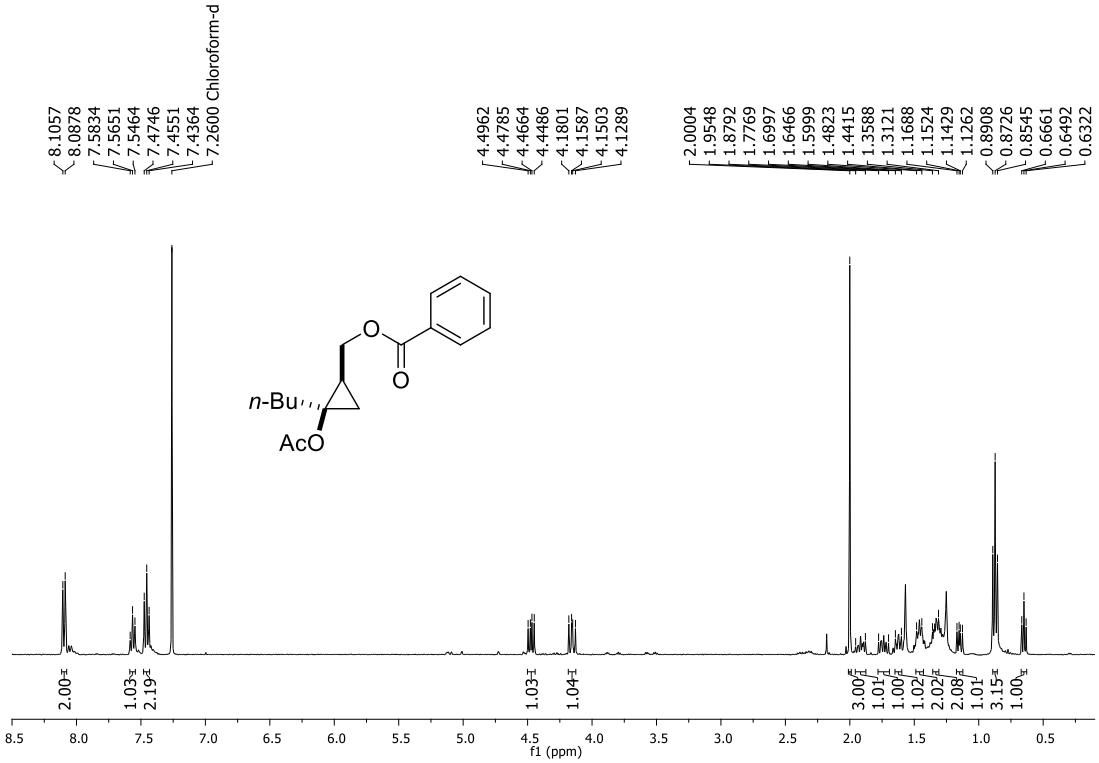


^{13}C NMR ($CDCl_3$, 101 MHz)

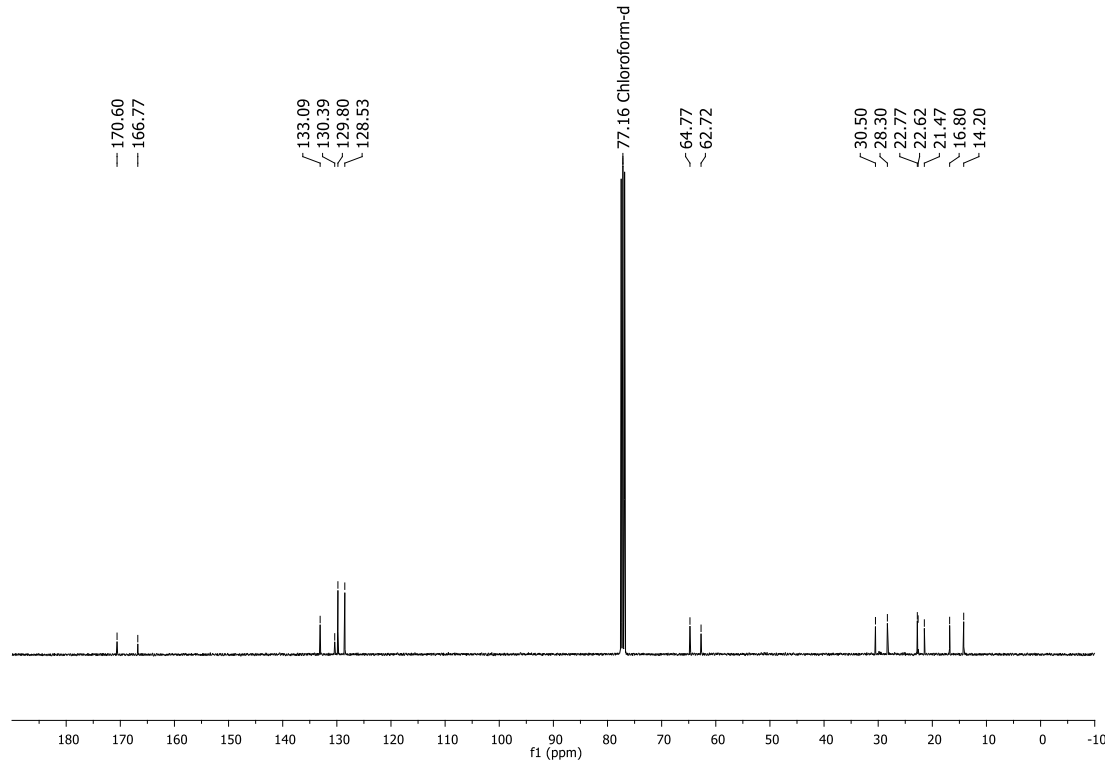


(1*R,2*R**)-2-Acetoxy-2-butylcyclopropyl)methyl benzoate (3na)**

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

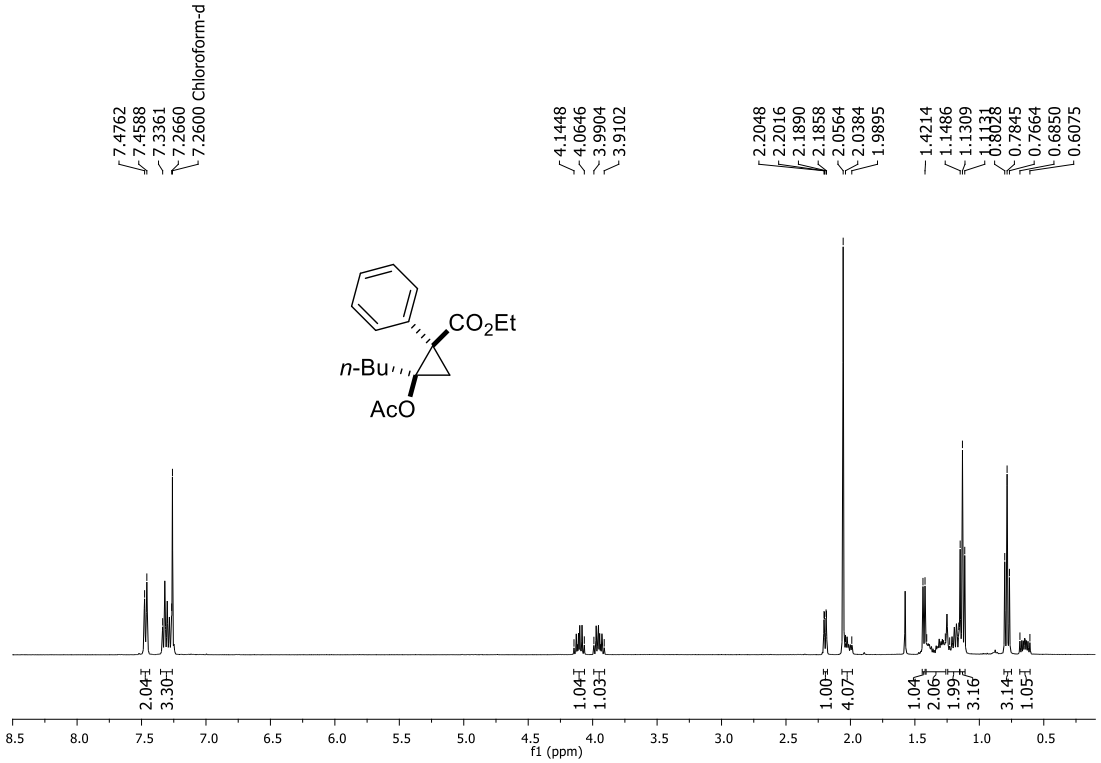


^{13}C NMR ($CDCl_3$, 101 MHz)

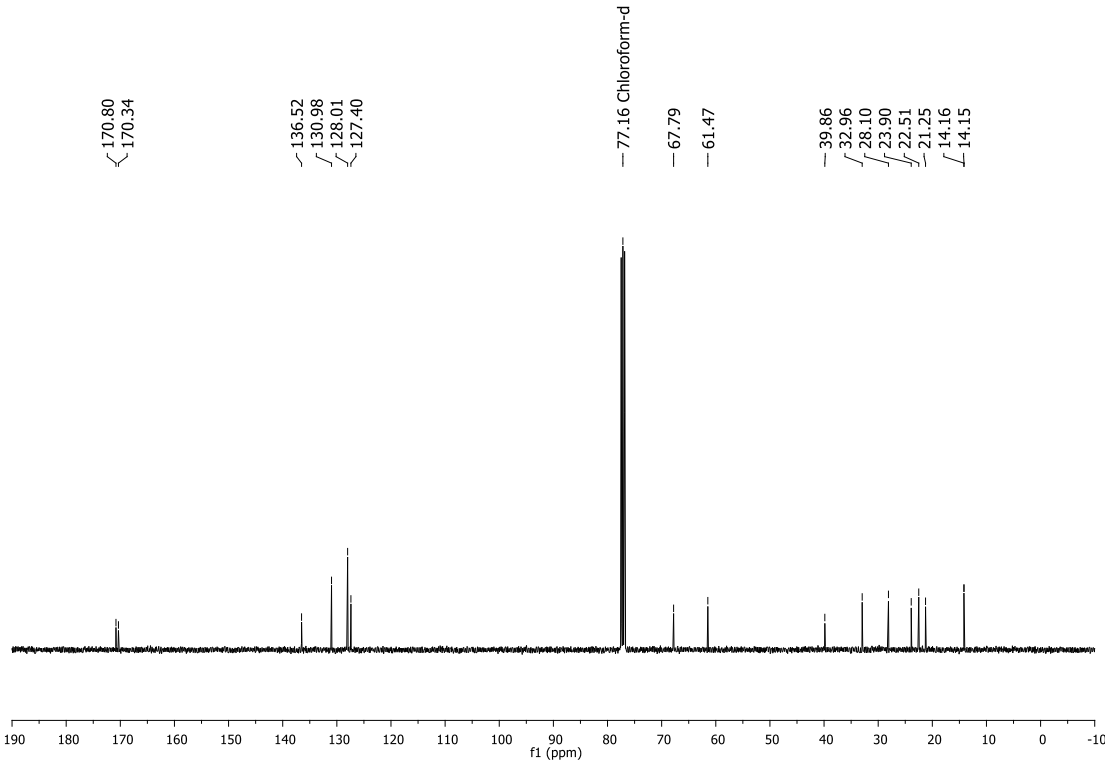


Ethyl (1*R, 2*R**)-2-acetoxy-2-butyl-1-phenylcyclopropane-1-carboxylate (3oa)**

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

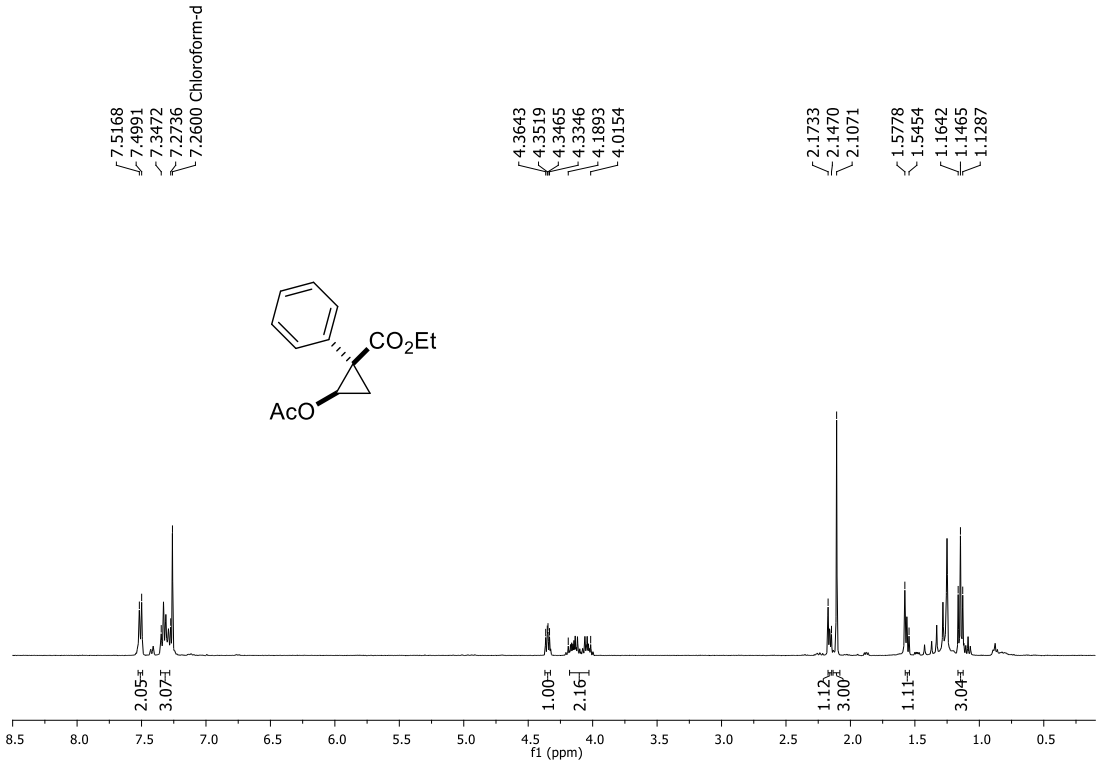


^{13}C NMR ($CDCl_3$, 101 MHz)

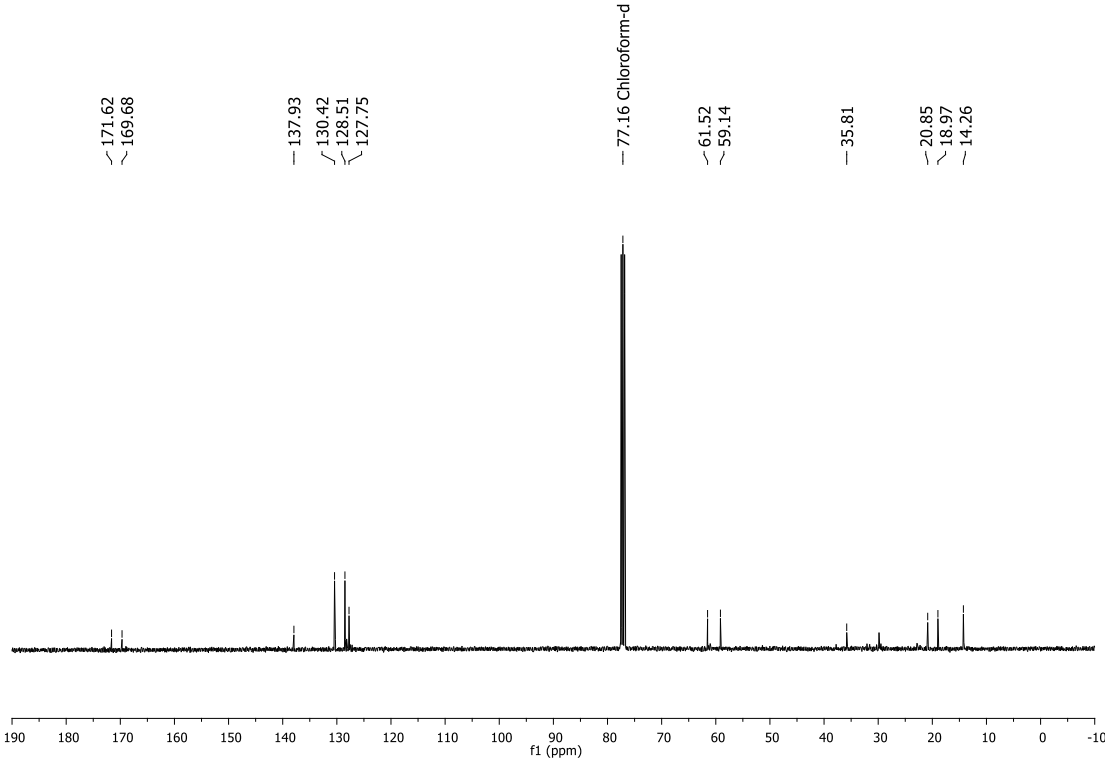


Ethyl (1*R,2*R**)-2-acetoxy-1-phenylcyclopropane-1-carboxylate (3pa)**

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

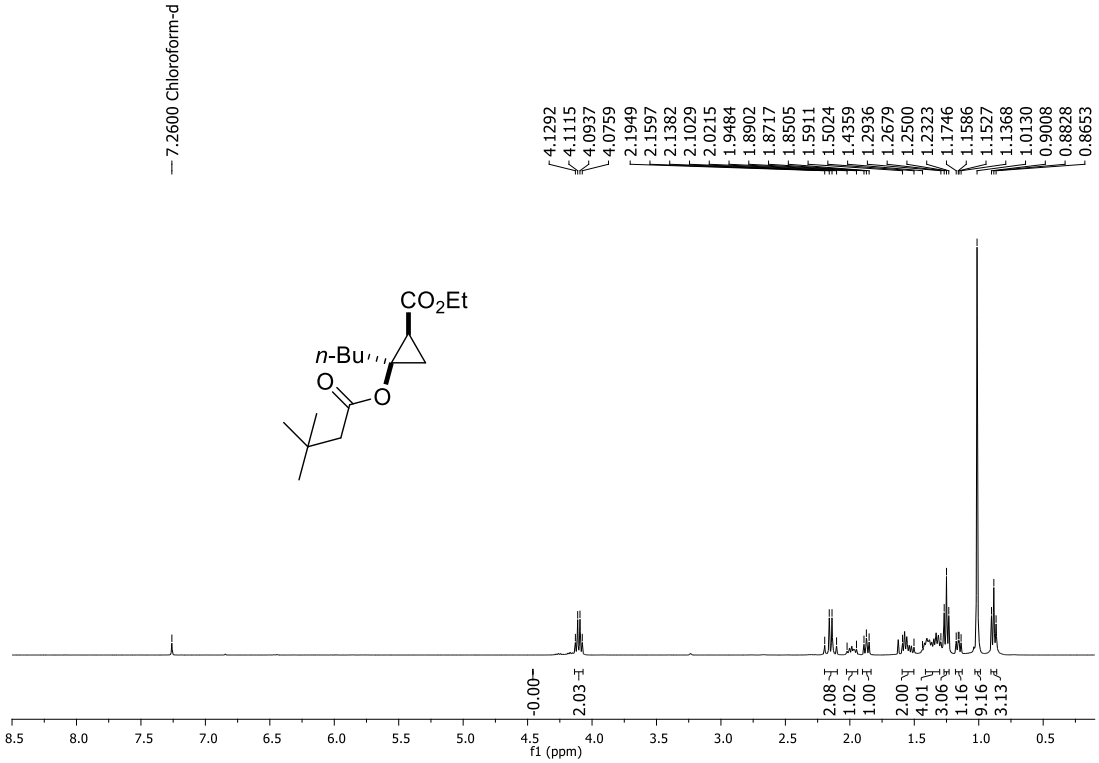


^{13}C NMR ($CDCl_3$, 101 MHz)

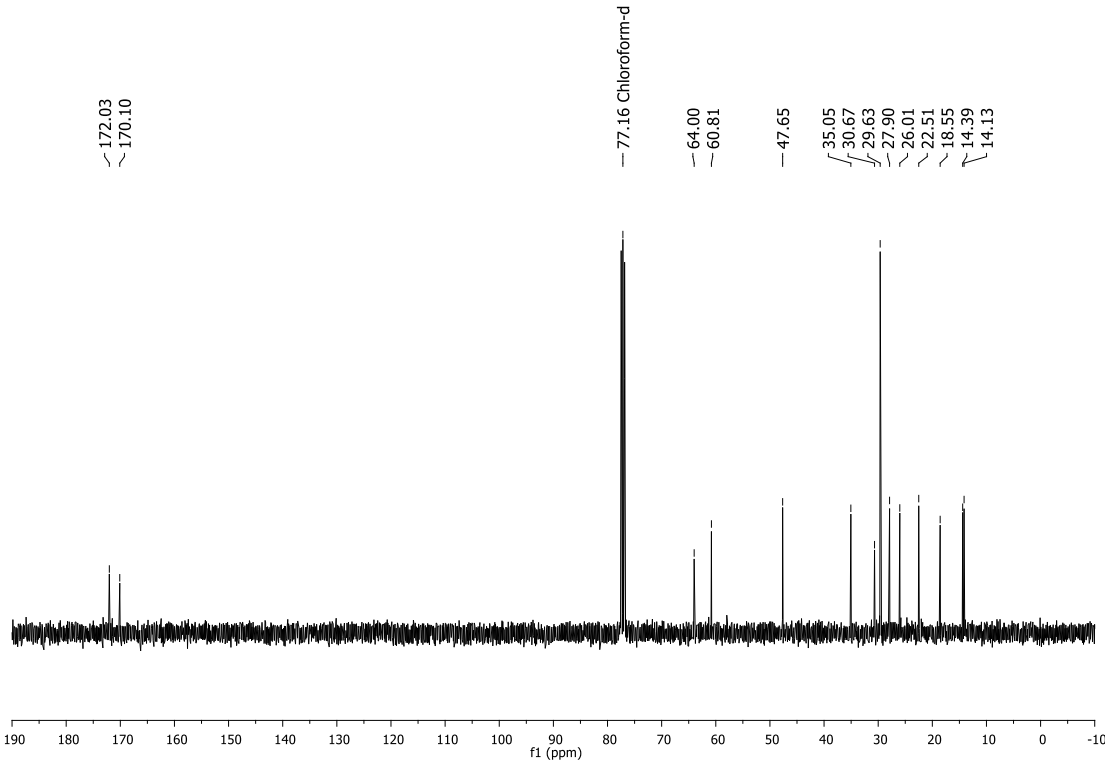


Ethyl (1*S,2*R**)-2-butyl-2-((3,3-dimethylbutanoyl)oxy)cyclopropane-1-carboxylate (3ab)**

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

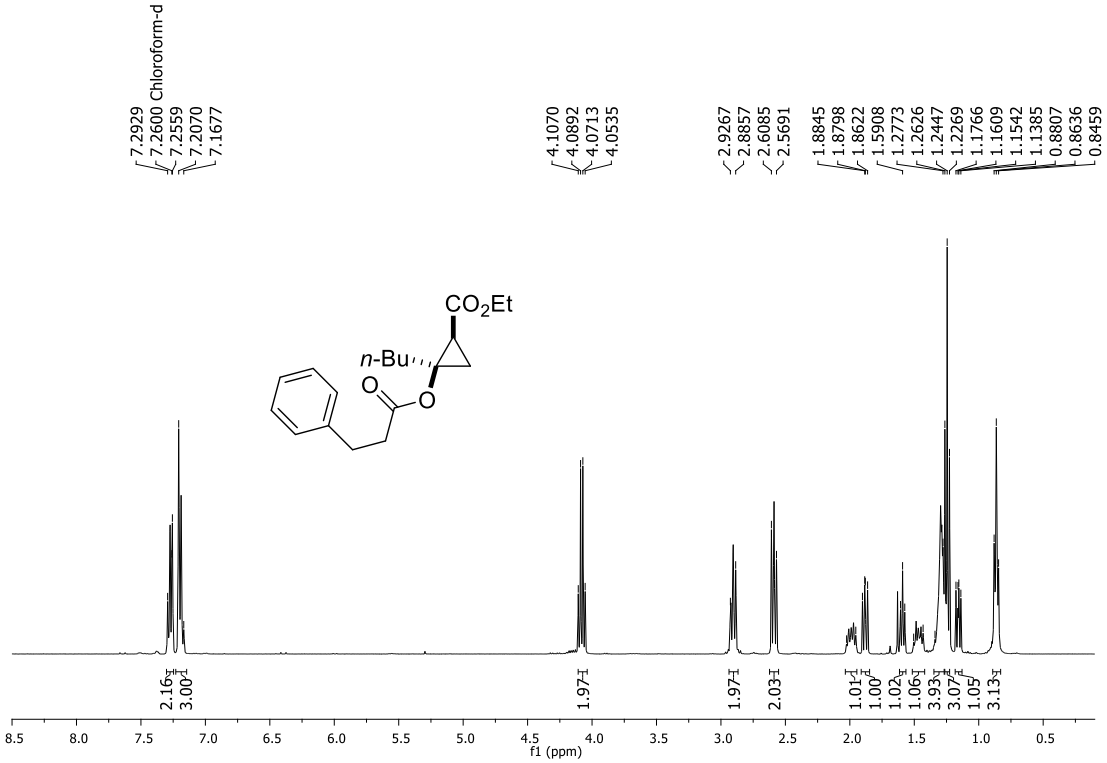


^{13}C NMR ($CDCl_3$, 101 MHz)

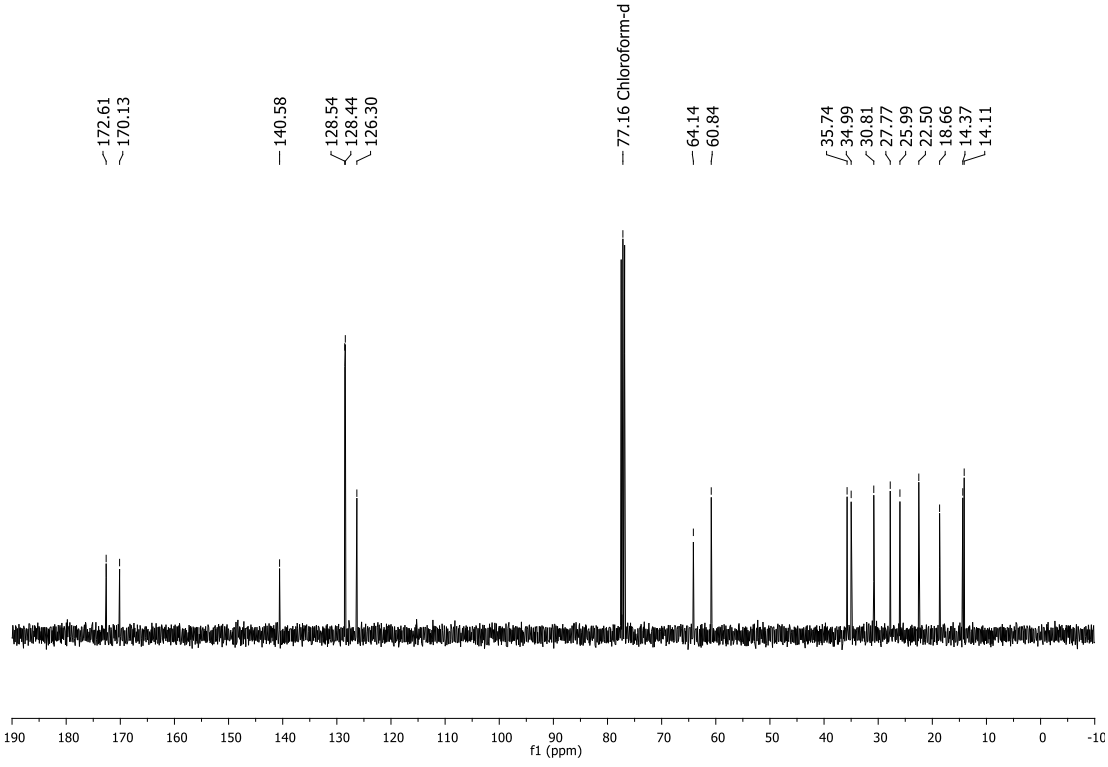


Ethyl (1*S,2*R**)-2-butyl-2-((3-phenylpropanoyl)oxy)cyclopropane-1-carboxylate (3ac)**

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

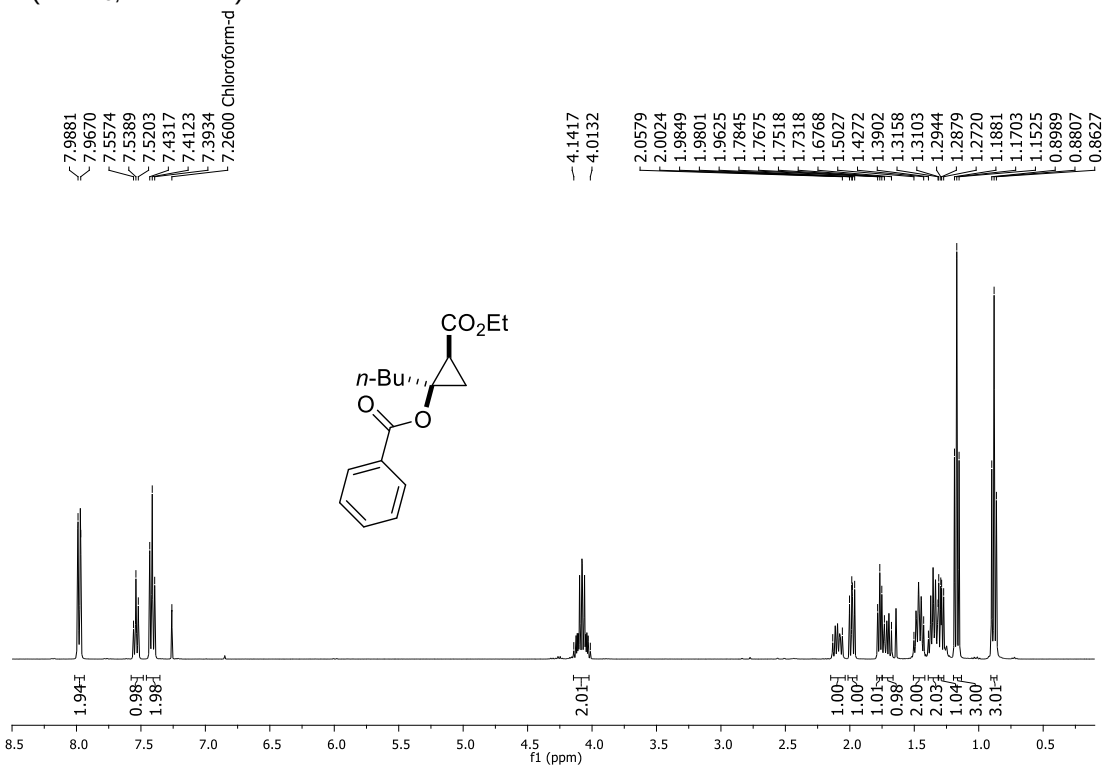


^{13}C NMR ($CDCl_3$, 101 MHz)

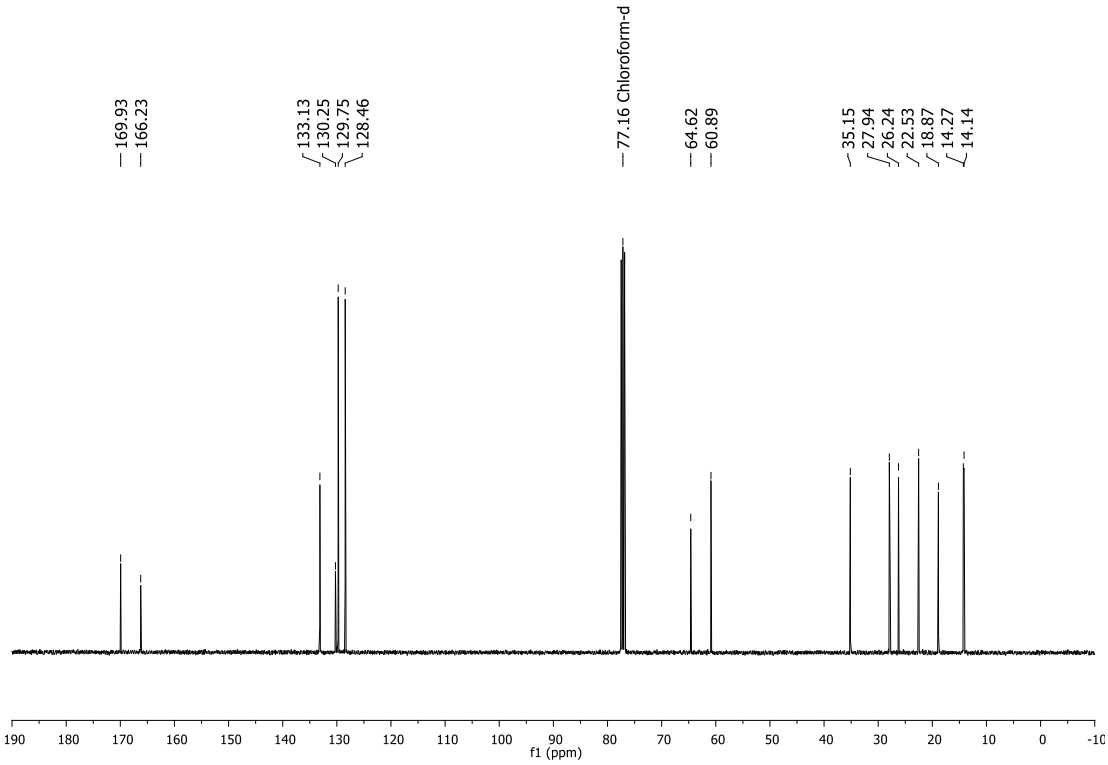


(1*R,2*S**)-1-Butyl-2-(ethoxycarbonyl)cyclopropyl benzoate (3ad)**

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

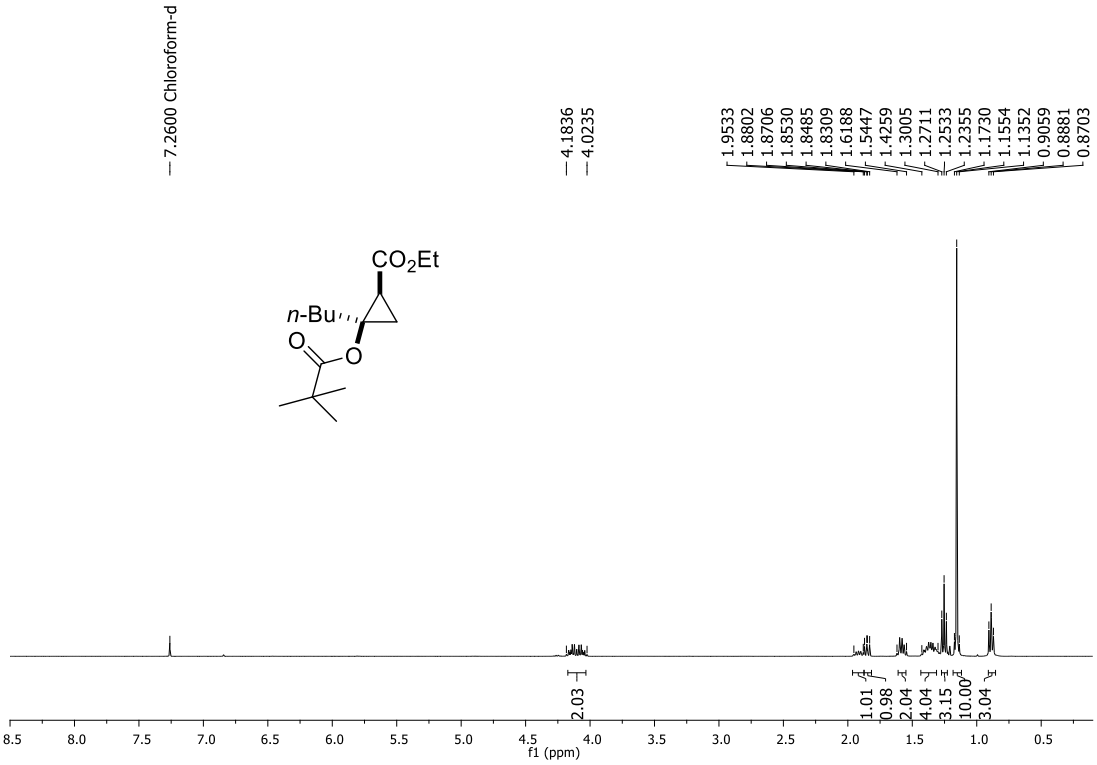


^{13}C NMR ($CDCl_3$, 101 MHz)

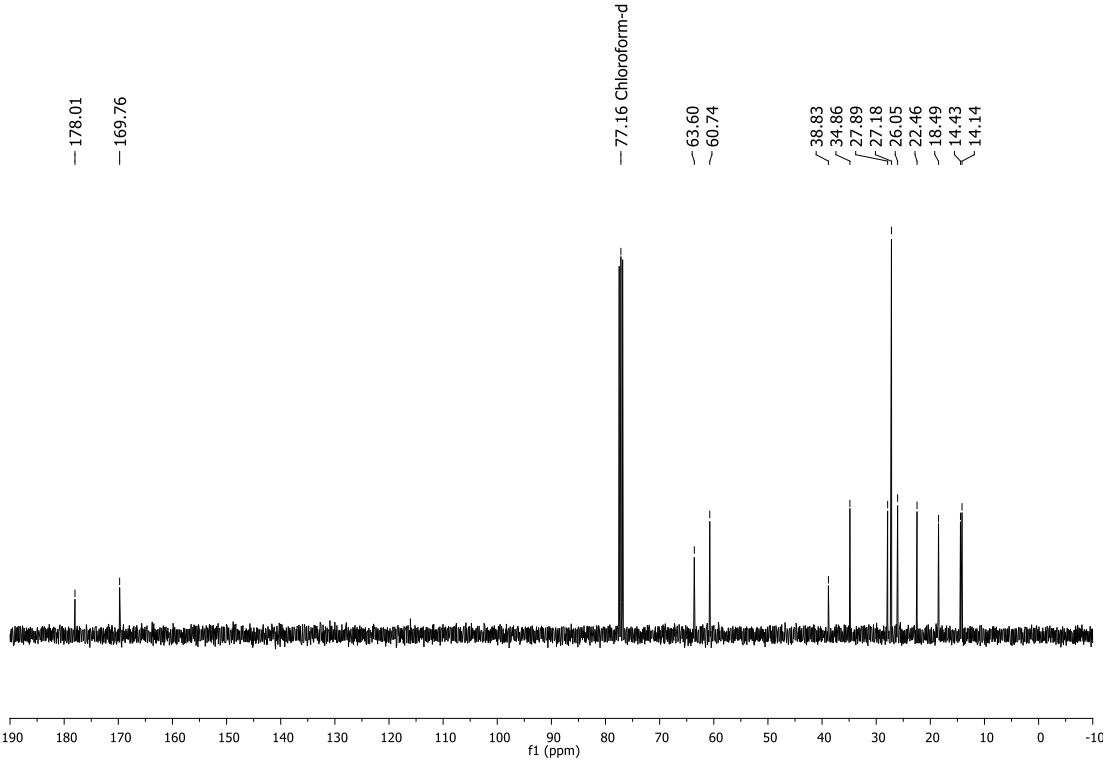


Ethyl (1*S,2*R**)-2-butyl-2-(pivaloyloxy)cyclopropane-1-carboxylate (3ae)**

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

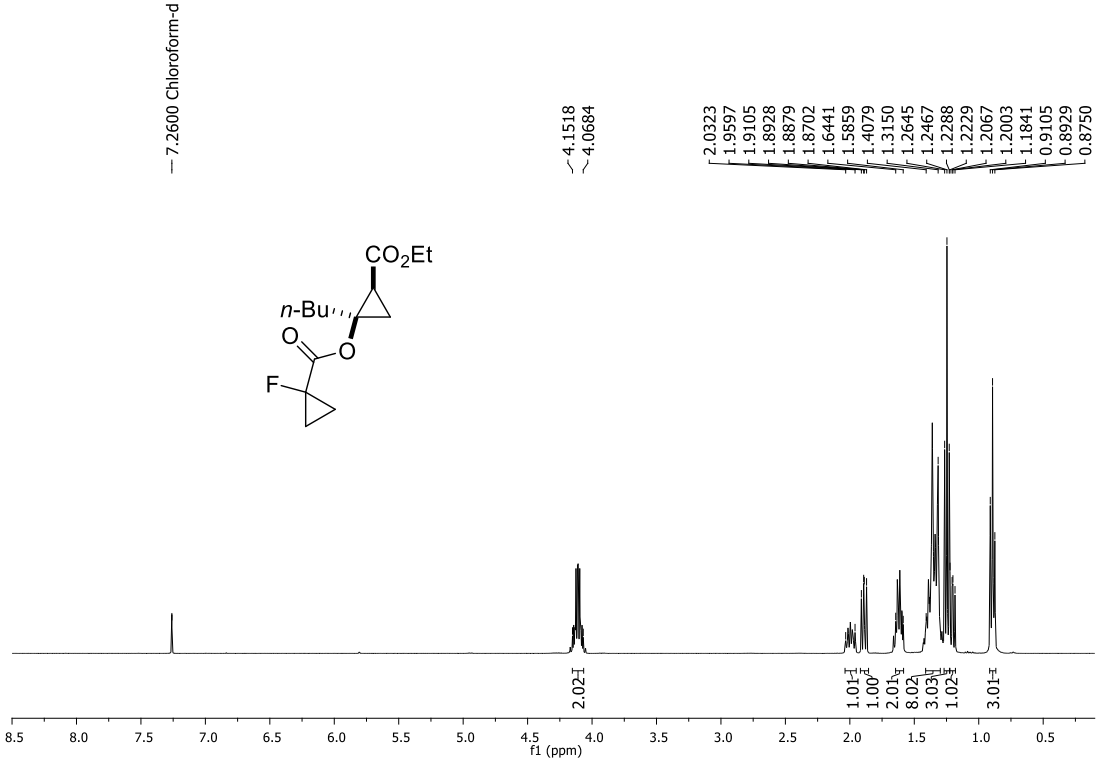


^{13}C NMR ($CDCl_3$, 101 MHz)

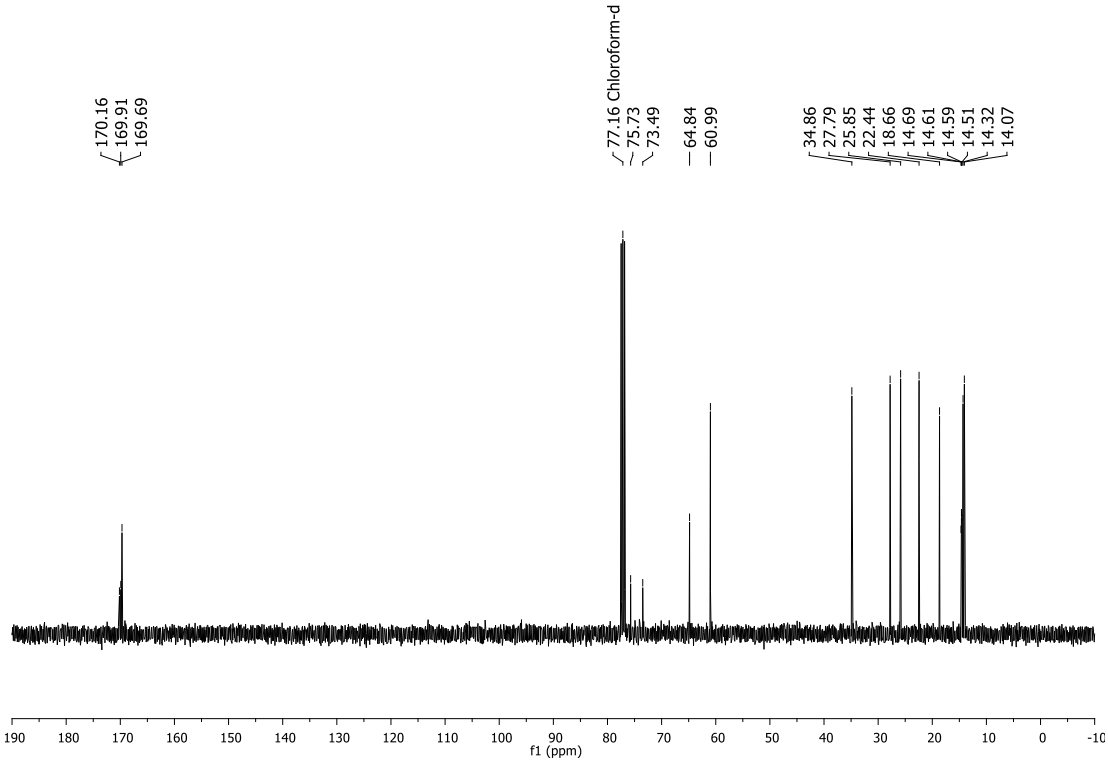


Ethyl (1*S,2*R**)-2-butyl-2-((1-fluorocyclopropane-1-carbonyl)oxy)cyclopropane-1-carboxylate (3af)**

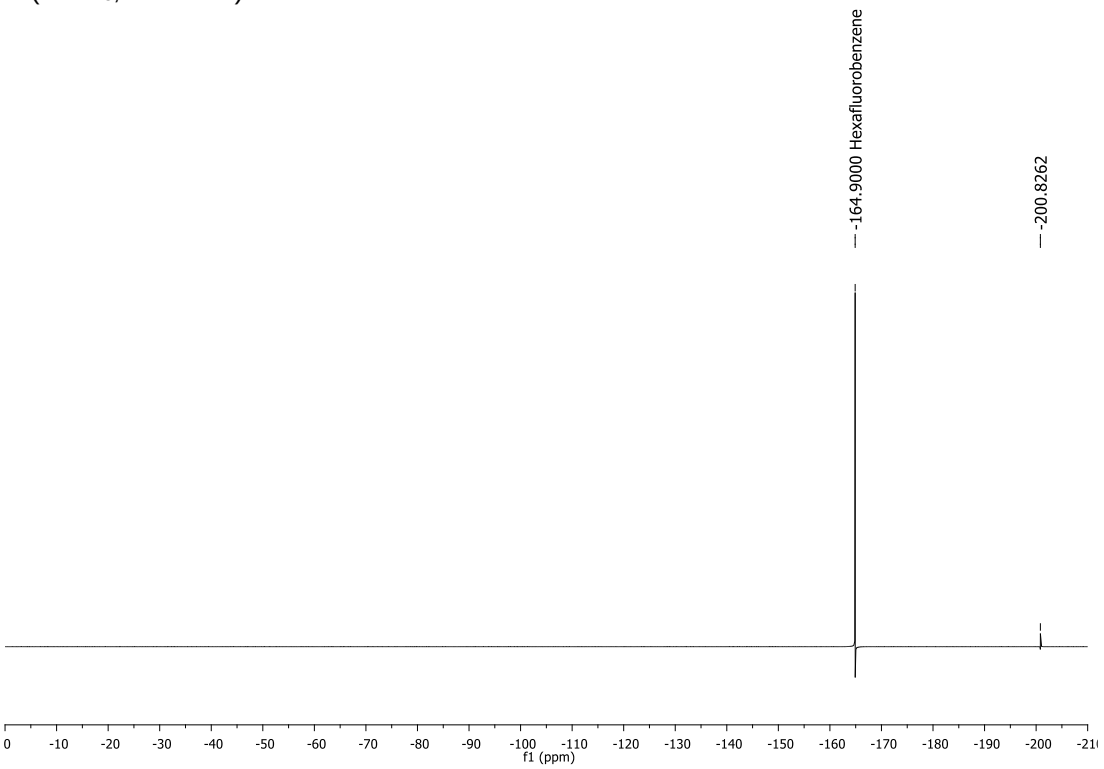
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

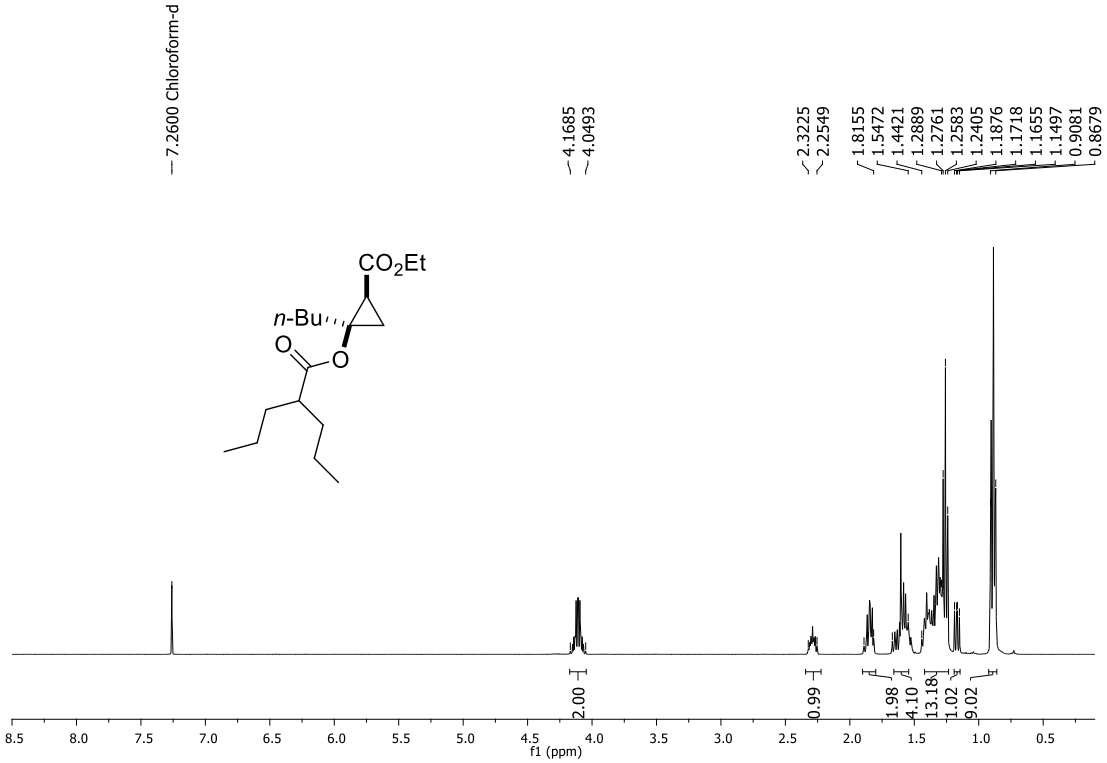


^{19}F NMR ($CDCl_3$, 337 MHz)

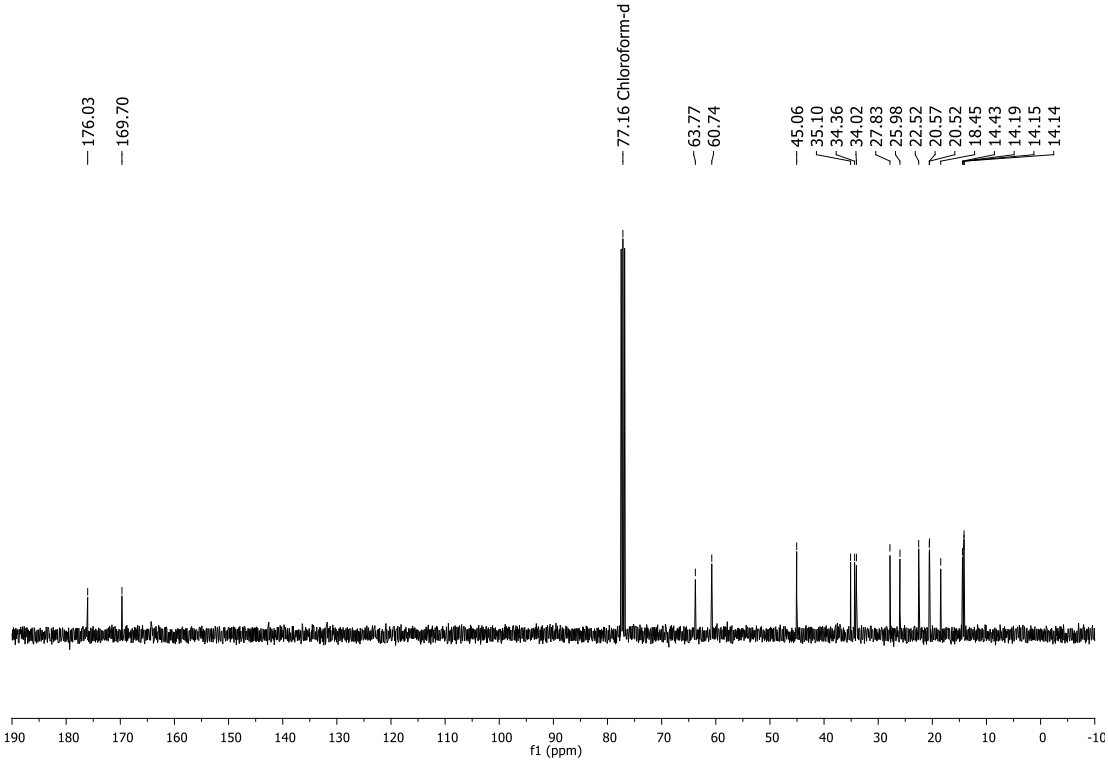


Ethyl (1*S,2*R**)-2-butyl-2-((2-propylpentanoyl)oxy)cyclopropane-1-carboxylate (3ag)**

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

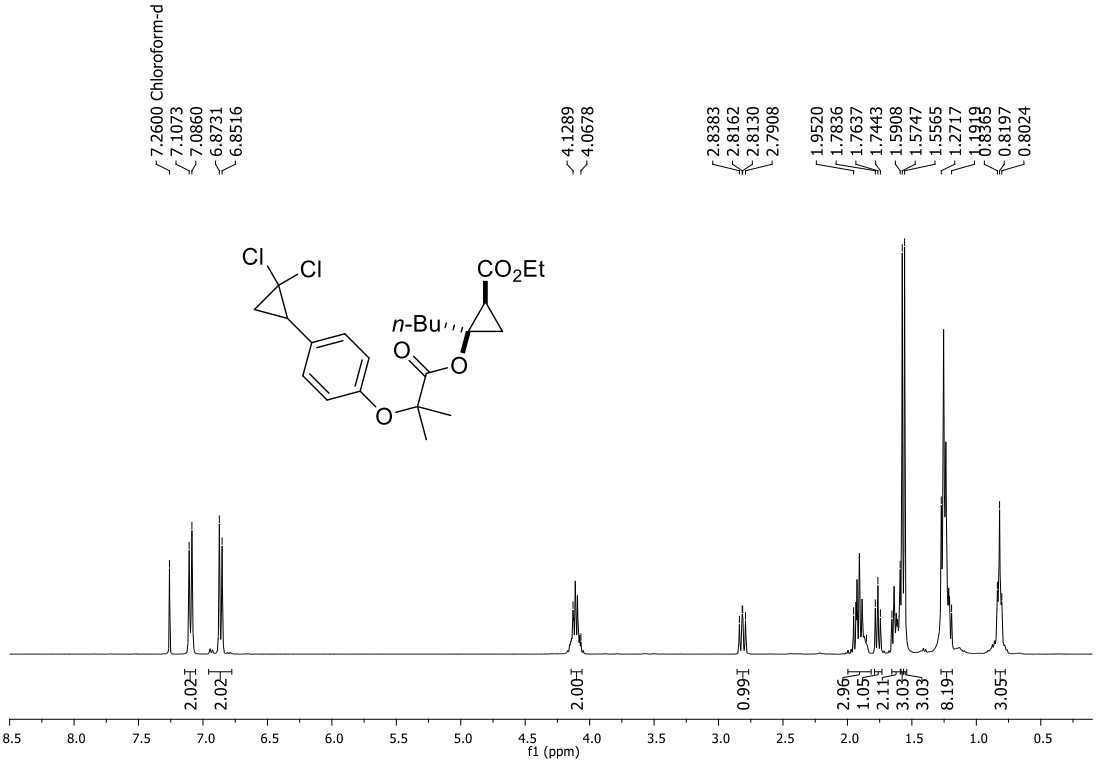


^{13}C NMR ($CDCl_3$, 101 MHz)

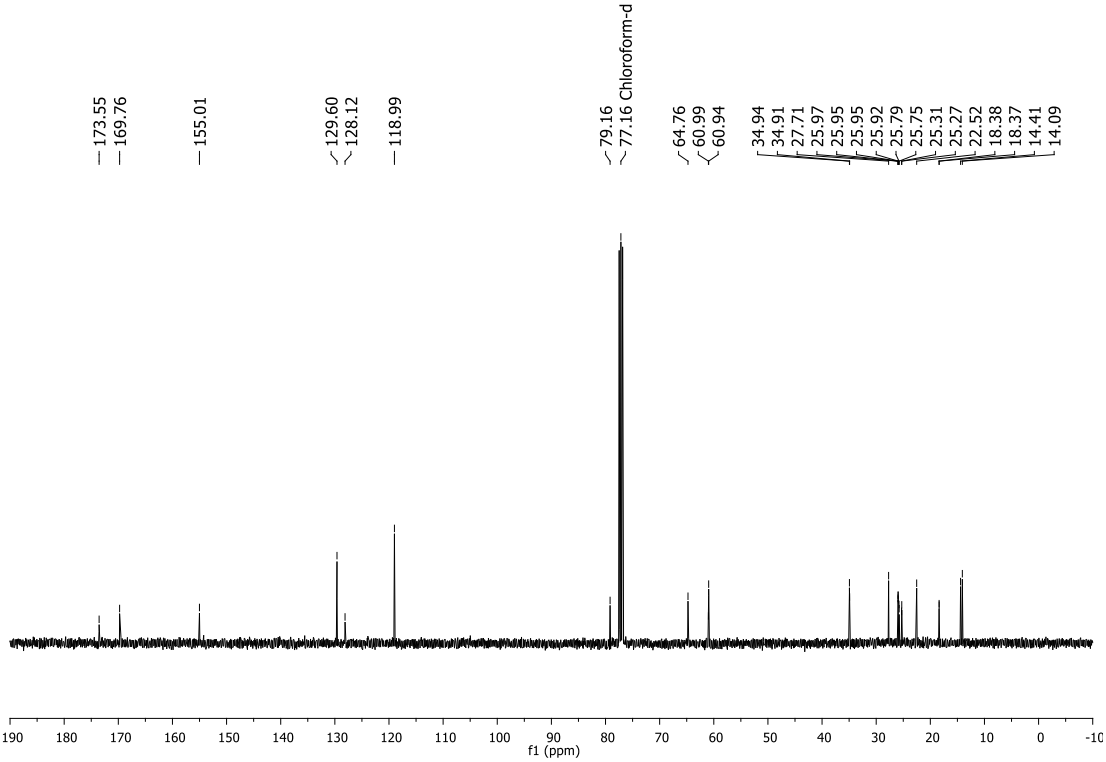


Ethyl (1*S,2*R**)-2-butyl-2-((2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl)oxy) cyclopropane-1-carboxylate (3ah)**

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

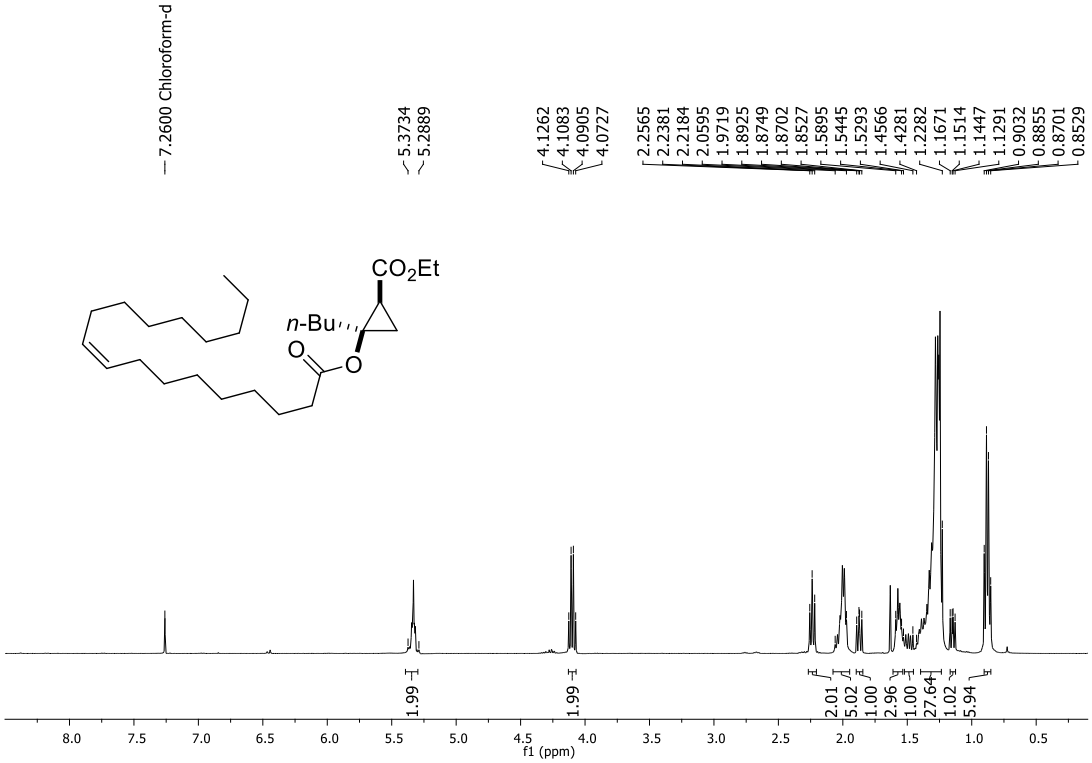


^{13}C NMR ($CDCl_3$, 101 MHz)

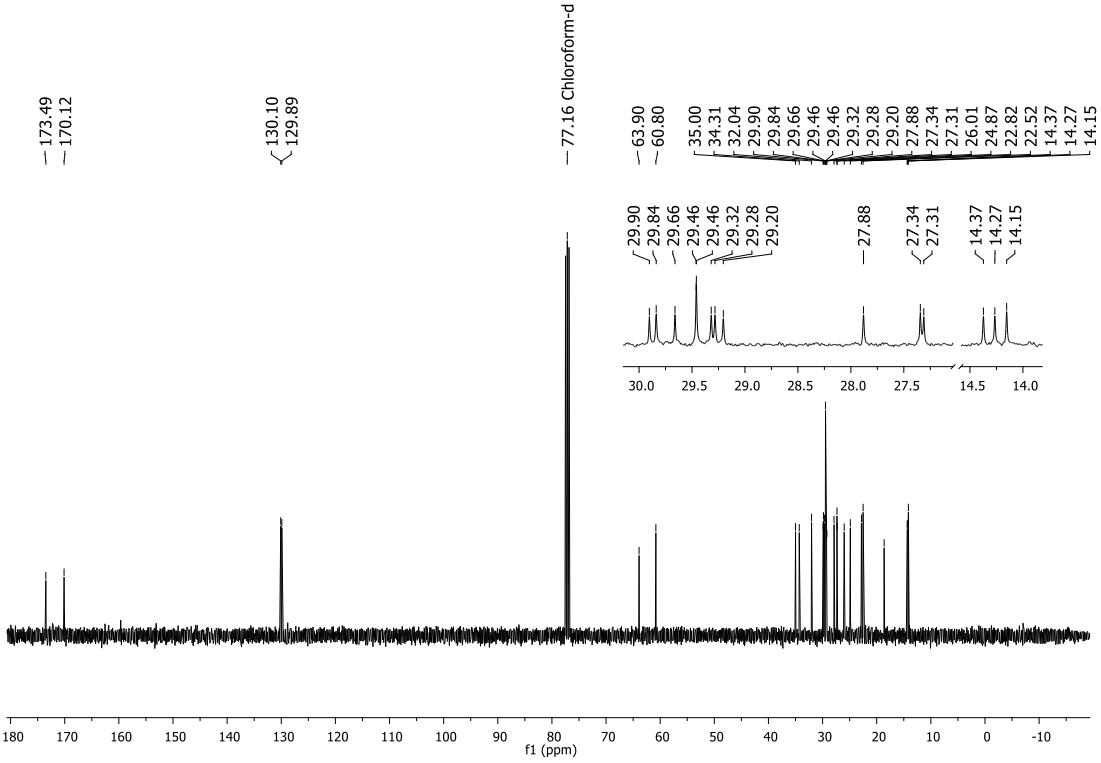


Ethyl (1*S,2*R**)-2-butyl-2-(oleoyloxy)cyclopropane-1-carboxylate (3ai)**

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

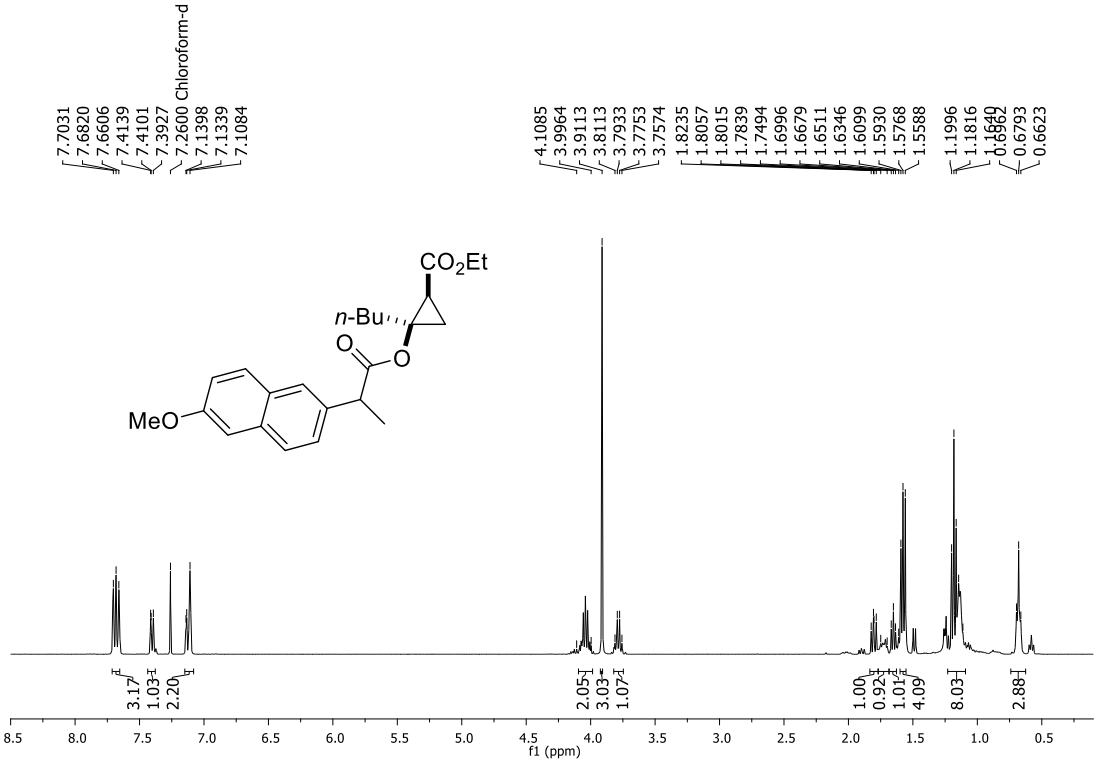


^{13}C NMR ($CDCl_3$, 101 MHz)

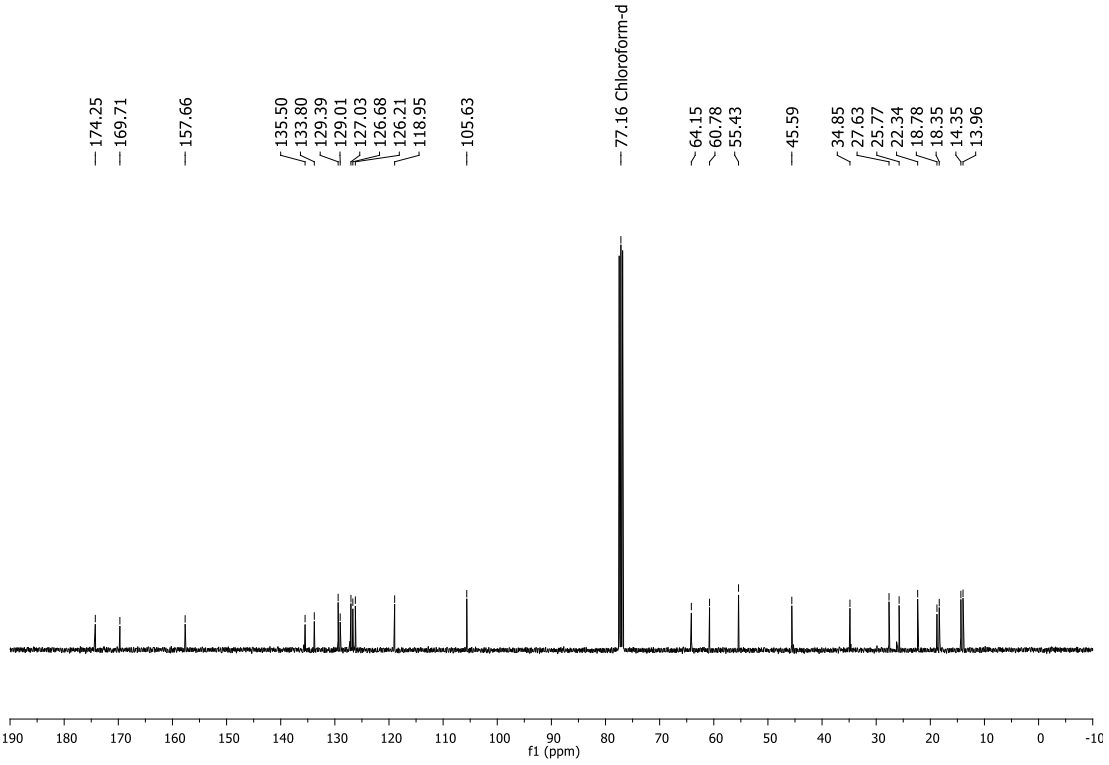


Ethyl (1*S,2*R**)-2-butyl-2-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)cyclopropane-1-carboxylate (3aj) – *major isomer***

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

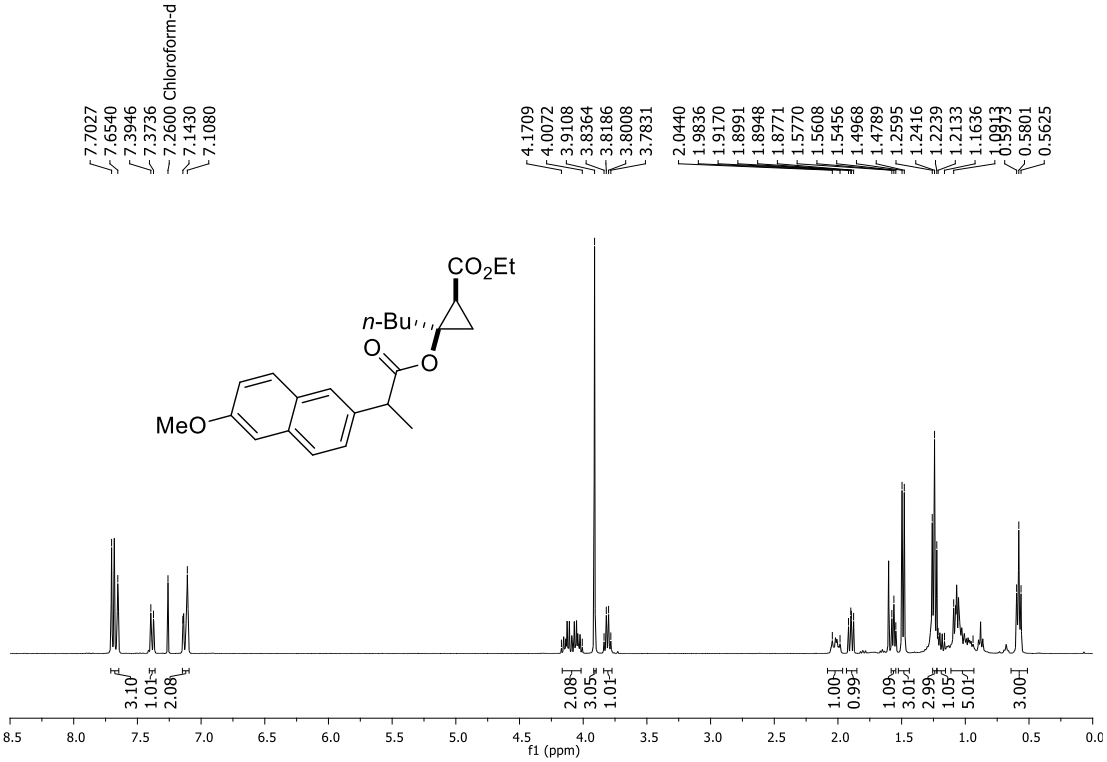


^{13}C NMR ($CDCl_3$, 101 MHz)

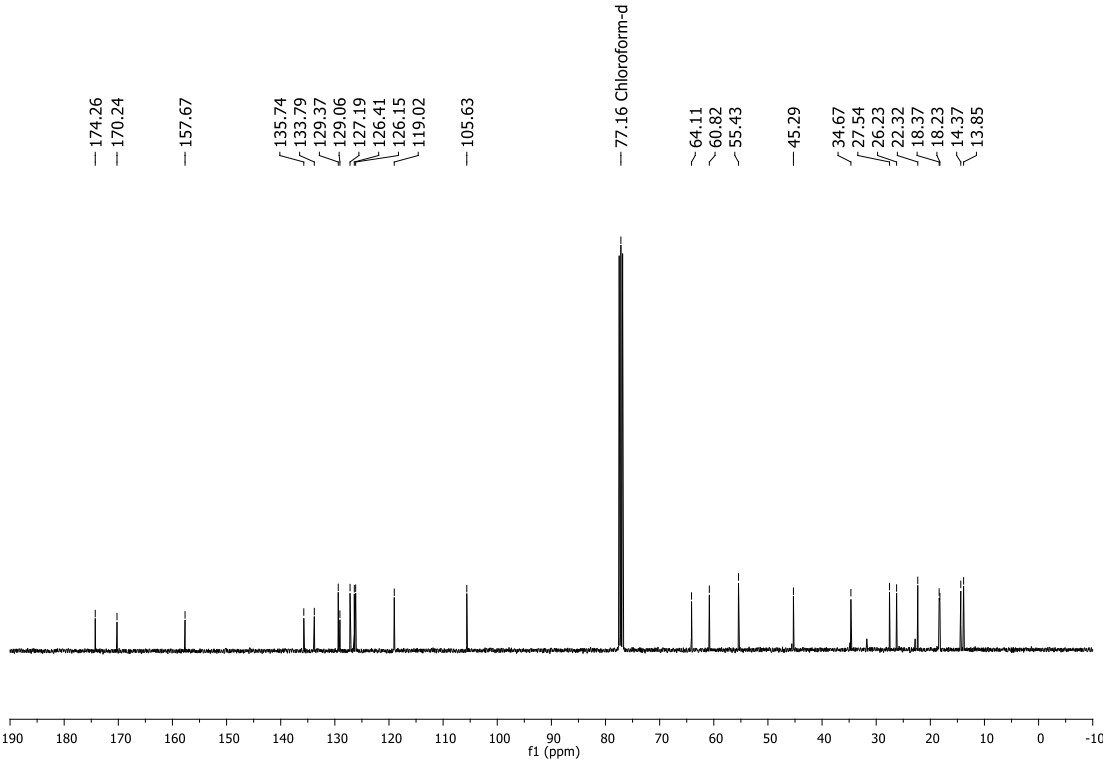


Ethyl (1*S,2*R**)-2-butyl-2-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)cyclopropane-1-carboxylate (3aj) – *minor isomer***

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

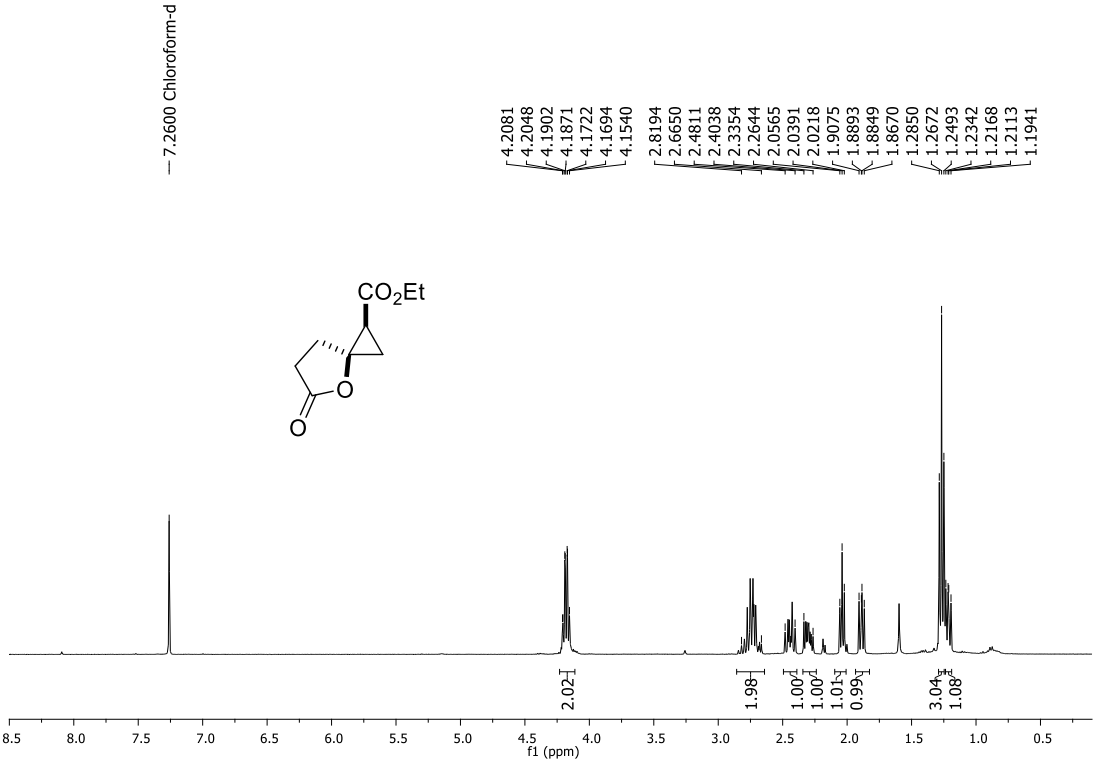


^{13}C NMR ($CDCl_3$, 101 MHz)

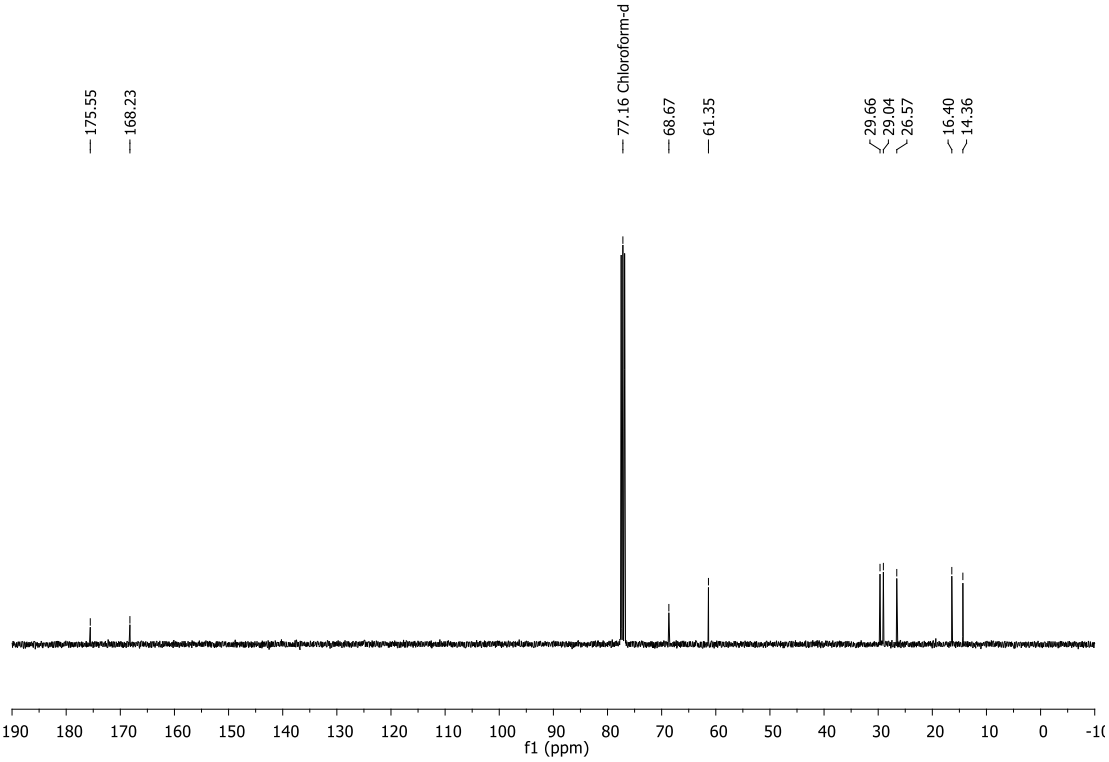


Ethyl (1*S,3*R**)-5-oxo-4-oxaspiro[2.4]heptane-1-carboxylate) (3q)**

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

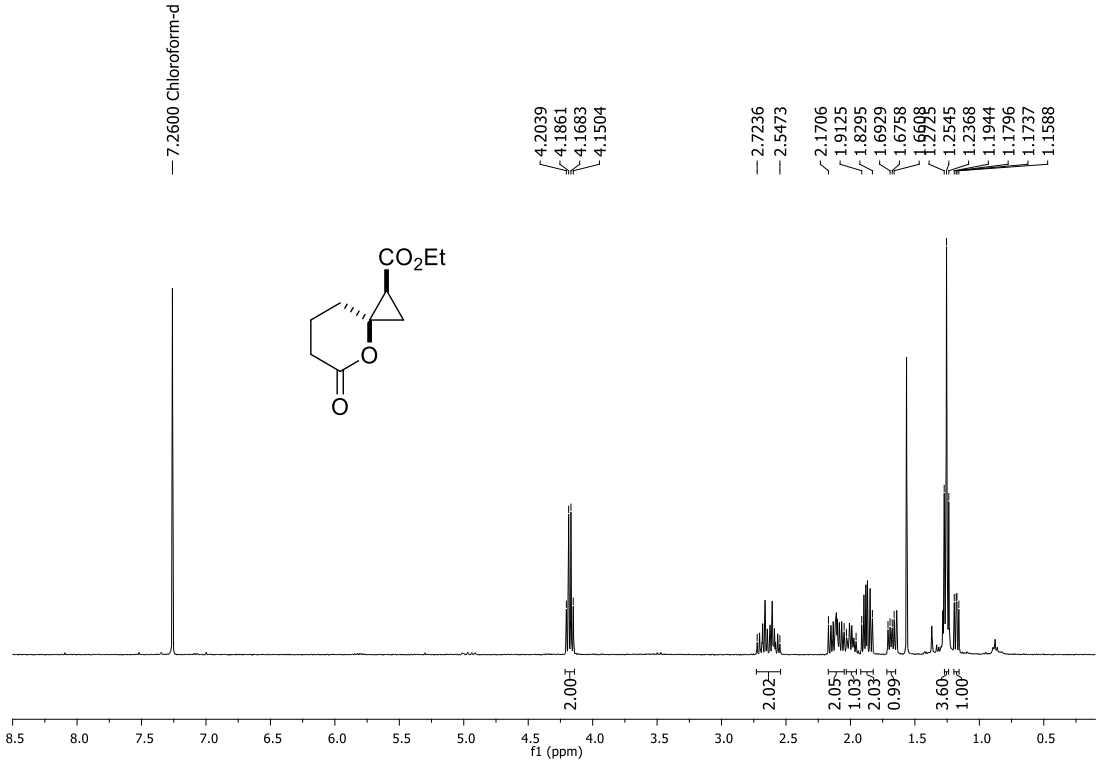


^{13}C NMR ($CDCl_3$, 101 MHz)

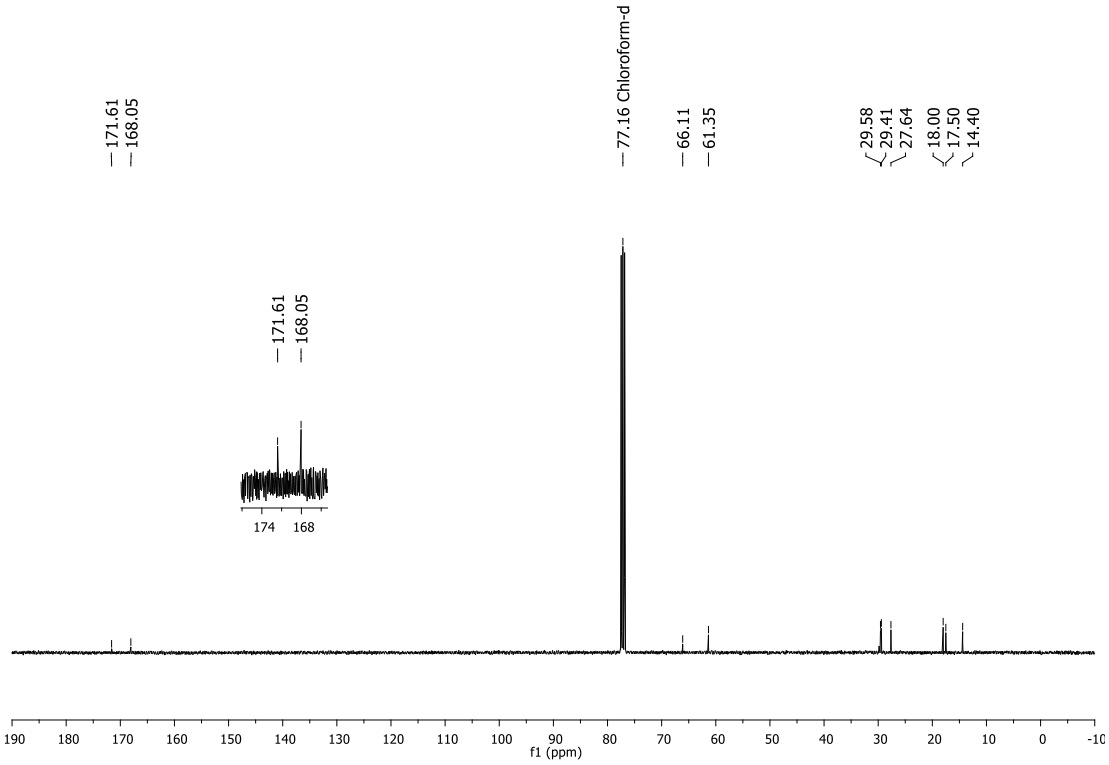


Ethyl (1*S,3*R**)-5-oxo-4-oxaspiro[2.5]octane-1-carboxylate) (3r)**

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

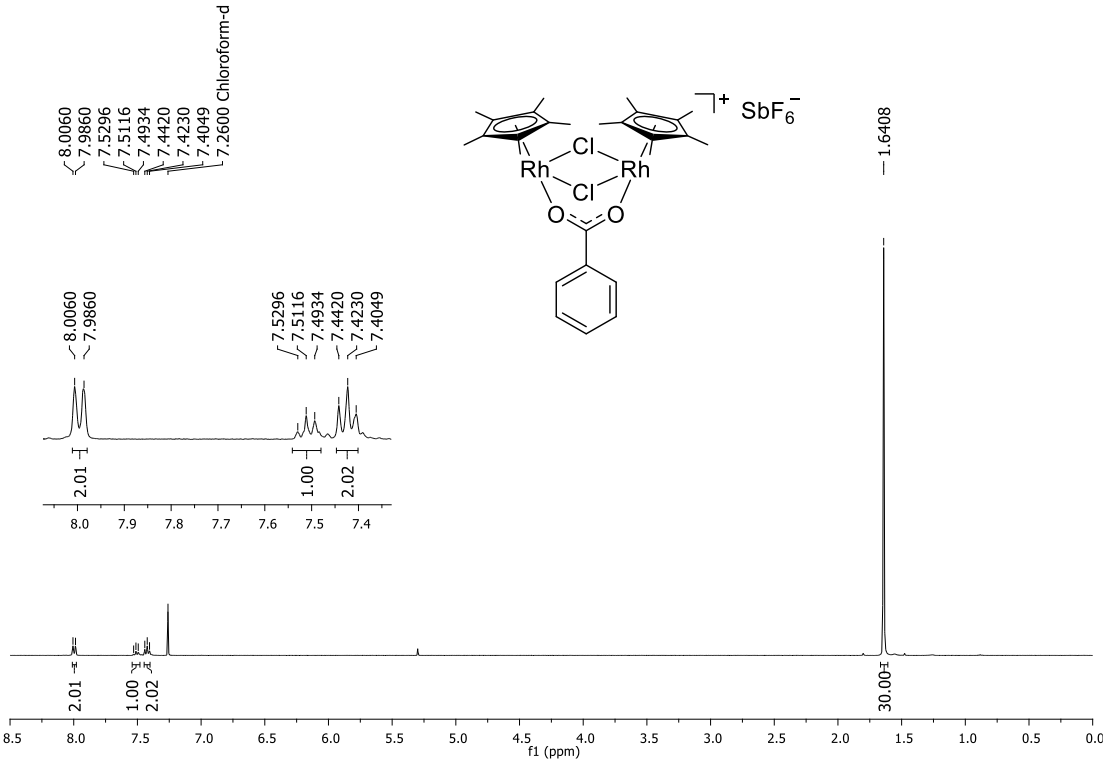


^{13}C NMR ($CDCl_3$, 101 MHz)

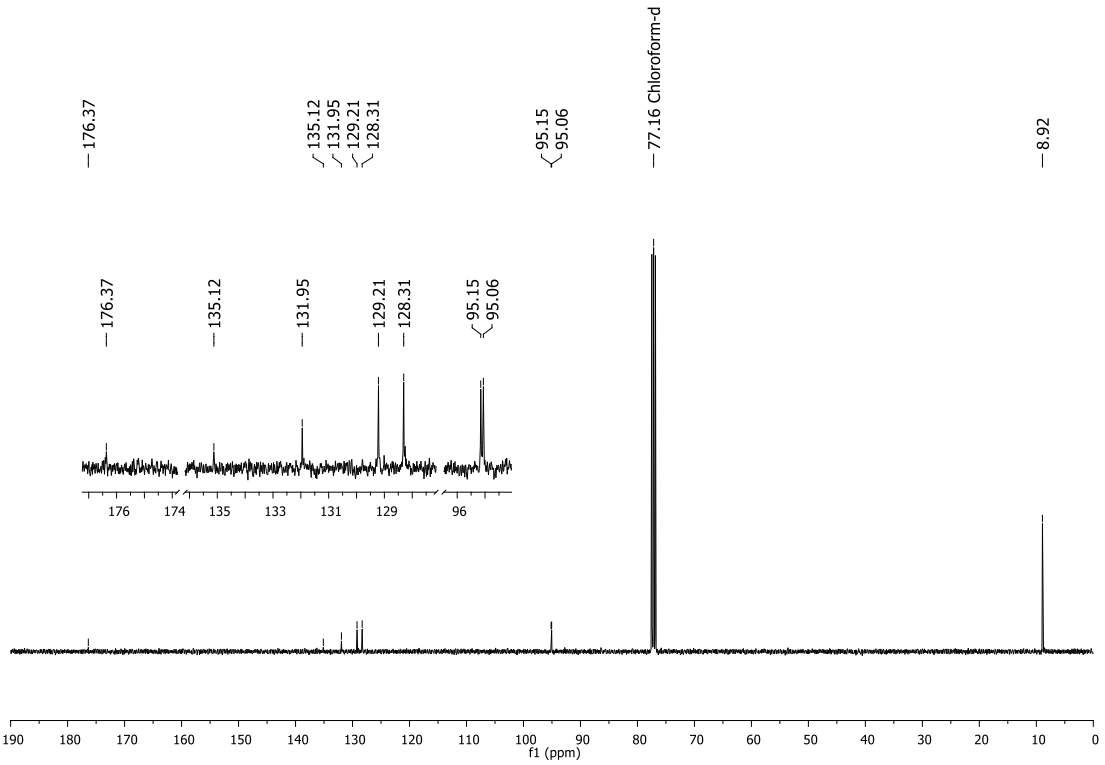


μ-(Benzoato-κ^2*O*:*O*′)-di-μ-chloro-bis[(pentamethyl-η^5-cyclopentadienyl)rhodium(III)] hexafluoroantimonate(V) (Rh-A)

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

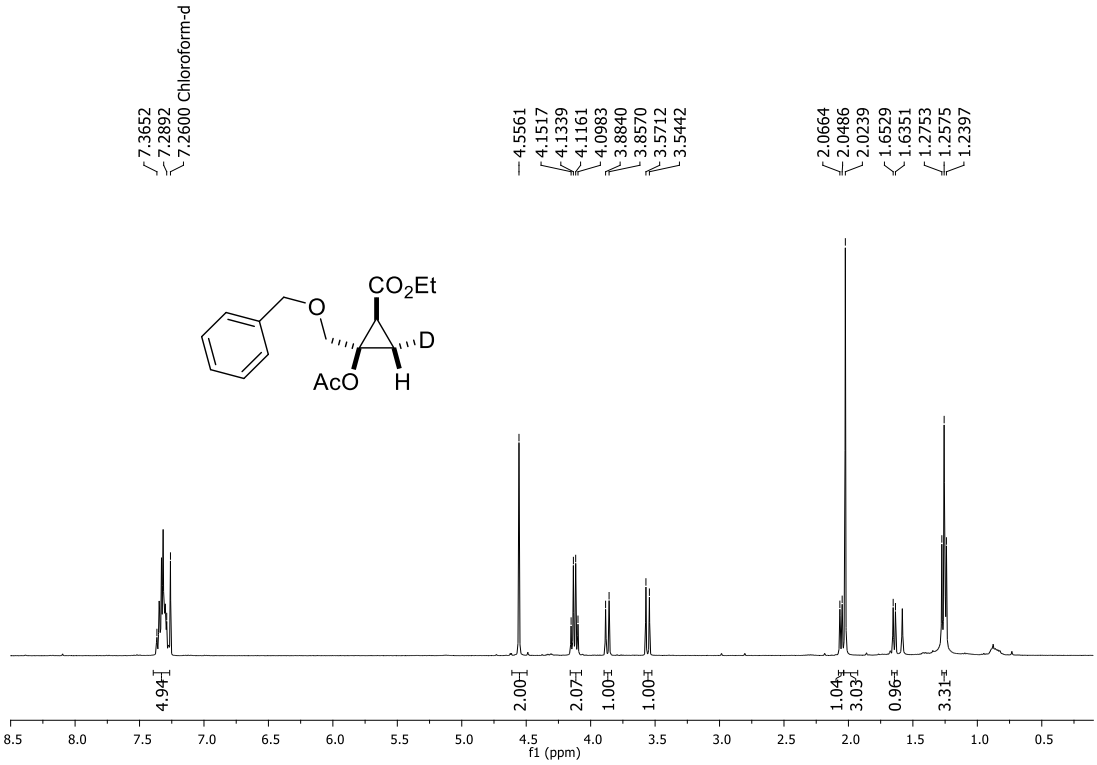


^{13}C NMR ($CDCl_3$, 101 MHz)



Ethyl (1*S,2*R**,3*S**)-2-acetoxy-2-((benzyloxy)methyl)cyclopropane-1-carboxylate-3-*d* (3ia-D)**

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



^{13}C NMR ($CDCl_3$, 101 MHz)