Synthesis of Itaconic Acid Derivatives via CO_2 Fixation into Allenes. Expanding Horizons in Electrosynthesis through Chemical Divergency

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1. General Methods

^{1}H-NMR spectra were recorded on a Bruker 600 spectrometer (600 MHz). Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= double doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, b = broad, m = multiplet), coupling constants (Hz).

^{13}C-NMR spectra were recorded on a Bruker 600 spectrometer (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard.

HRMS spectra were obtained with a G2XS QTof mass spectrometer using ESI ionization techniques, as specified case by case.

Chromatographic purification was done with 240-400 mesh silica gel.

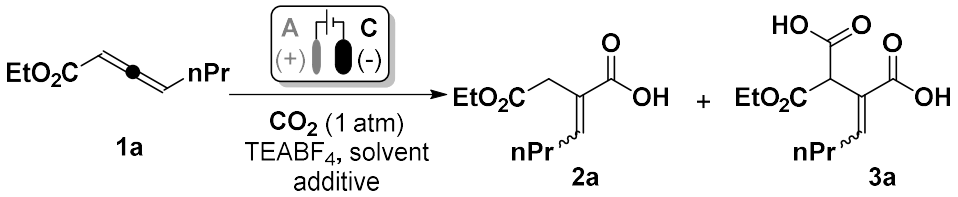
Anhydrous solvents, including DMSO, DMF and ACN for the electrochemical processes, were supplied by Merck in Sureseal® bottles and used without any further purification.

Compounds **1** [1] are known compounds and were synthesized according to the reported literature procedures.

Electrochemical characterization of **1a** and CO_2 were performed by cyclic voltammetry (CV). These experiments were carried out with a PGSTAT128N potentiostat driven by a Nova 2.0 software. The voltammetric responses were collected at room temperature in a three-electrode cell under N_2 flux. The working electrode consisted of a 3 mm diameter glassy carbon electrode (Metrohm), the counter electrode was a Pt wire (Metrohm) and an Ag wire was used as the pseudo-reference electrode. The potentials of the working electrode were finally referred to the ferrocene/ferrocenium redox couple ($E_{Fc^+/Fc}$ = +0.40 V vs. SCE) by adding a few crystals of ferrocene in the solution. The working electrode surface was polished with 1 and 0.3 μm alumina and sonicated in deionized water for 5 min before the use. The electrochemical experiments were recorded by dissolving the compound under investigation in a 0.1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) anhydrous DMF solution.

2. Additional Optimization Tables

2.1. **Table S1**: Additional reaction optimization results.[a]



Entry	*I* [mA] (F/mol$_{1a}$)	Solvent	Electrolyte	A(+) || C(-)	Additive	**2a**/**3a**[b]	(Yield [%]; *E*/*Z*)[c]
1	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	none	4.5:1	**2a** (46; 1.6:1)
2	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	$Sc(OTf)_3$	1.3:1	**2a** (38; 1.4:1)
3	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	AcOH	1:1.1	**2a** (28; 1.6:1)
4	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	Cs_2CO_3	2.5:1	**2a** (15; 2.5:1)
5	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	TBAOAc	2.1:1	**2a** (41; 1.4:1)
6	2.0 (5.0)	DMF	$TEABF_4$	Zn(+) || Ni(-)	H_2O	nd	<5
7	4.0 (5.0)	DMSO	$TEABF_4$	Zn(+) || Ni(-)	none	8.8:1	**2a** (87, 1.7:1)
8	4.0 (5.0)	DMSO	TEAI	Zn(+) || Ni(-)	none	8.7:1	**2a** (79, 1.7:1)
9	4.0 (5.0)	DMSO	$TBAClO_4$	Zn(+) || Ni(-)	none	nd	<5
10	4.0 (5.0)	DMSO	$TEABF_4$	Zn(+) || C(-)	none	7.0:1	**2a** (66, 1.7:1)
11	4.0 (5.0)	DMSO	$TEABF_4$	Zn(+) || SS(-)	none	7.2:1	**2a** (33, 1.6:1)
12	4.0 (5.0)	DMSO	$TEABF_4$	Mg(+) || Ni(-)	none	nd	decomposition
13[d]	60 (15)	ACN	$TEABF_4$	Zn(+) || Ni(-)	none	1:20	**3a** (75, 2.0:1)
14[d]	60 (15)	ACN	TEAI	Zn(+) || Ni(-)	none	1:20	**3a** (47, 2.1:1)
15[d]	60 (15)	ACN	$TBAClO_4$	Zn(+) || Ni(-)	none	1:20	**3a** (67, 2.1:1)
16[d]	60 (15)	ACN	$TEABF_4$	Zn(+) || C(-)	none	1:20	**3a** (31, 1.8:1)
17[d]	60 (15)	ACN	$TEABF_4$	Zn(+) || SS(-)	none	1:20	**3a** (18, 2.0:1)
18[d]	60 (15)	ACN	$TEABF_4$	Mg(+) || Ni(-)	none	nd	decomposition

[a] All reactions were carried out with ElectraSyn 2.0 apparatus under constant current electrolysis (CCE, A: anode, C: cathode). [b] Determined by ^1H NMR analysis on the crude mixture. [c] Isolated yields after flash chromatography. E/Z ratio determined on the isolated product. [d] Reaction run at 0 °C.

At the beginning of our investigation, we tested the possibility to influence the **2a**/**3a** ratio by using additives. With respect to the reaction run in their absence (entry 1), the use of Lewis acids (entry 2), Brønsted acids (entry 3), inorganic or organic bases (entries 4 and 5) or water (entry 6) did not influence the ratio significantly and proved detrimental to the reaction efficiency. Later on, at an advanced stage of optimization (entry 7 for comparison), different electrolytes (entries 9 and 10) or electrodic couples (entries 11, 12 and 13) were tested in the reaction leading selectively to mono-acid **2a**, confirming $TEABF_4$ and Zn(+) || Ni(-) as optimal.

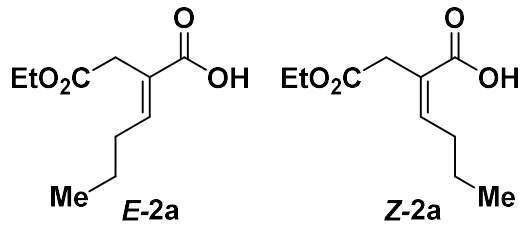
Similarly (entry 13 for comparison), different electrolytes (entries 14 and 15) or electrodic couples (entries 16, 17 and 18) were tested in the reaction leading selectively to di-acid **3a**, confirming $TEABF_4$ and Zn(+) || Ni(-) as optimal.

3. Electrochemical Carboxylation of Allenes

3.1 General procedure for the electrochemical monocarboxylation of allenes **1**.

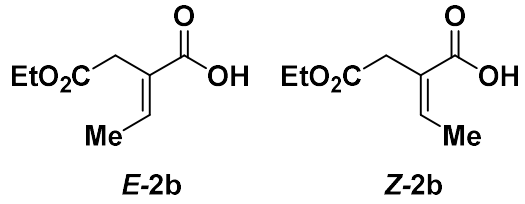
The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with allene **1** (0.15 mmol), and $TEABF_4$ (0.30 mmol, 65.1 mg). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ni), was inserted into the mixture, and closed with a rubber septum. The vessel was evacuated and backfilled with CO_2 (balloon) three times, then dry DMSO (3.0 mL) was added, and the mixture was stirred until complete dissolution of the solids occurred. Then, the solution was bubbled with CO_2 (balloon) under stirring for 1 min. The reaction mixture was electrolyzed (under CO_2, balloon) at a constant current of 4.0 mA, until a total charge of 0.75 mF (5.0 F/mol_1) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and $HCl_{(aq)}$ (2M, 10 mL), which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with $HCl_{(aq)}$ (0.1 M, 3 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was finally purified by FC to afford pure products **2**.

3.2 Characterization data of compounds **2**.



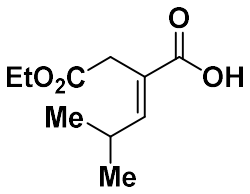
E-2a *Z*-2a

2a. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 87%, (0.131 mmol, 26.2 mg); *E*/*Z* = 1.7:1; **2a**/**3a** = 8.8:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.04 (t, *J* = 7.6 Hz, 1H *E*-**2a**), 6.13 (t, *J* = 7.4 Hz, 1H *Z*-**2a**), 4.08 (q, *J* = 7.2 Hz, 2H *Z*-**2a**) partially overlapped with 4.07 (q, *J* = 7.1 Hz, 2H *E*-**2a**), 3.27 (s, 2H *E*-**2a**), 3.19 (s, 2H *Z*-**2a**), 2.52 (q, *J* = 7.4 Hz, 2H *Z*-**2a**), 2.13 (q, *J* = 7.5 Hz, 2H *E*-**2a**), 1.50 – 1.37 (m, 2H *E*-**2a** + 2H *Z*-**2a**), 1.18 (t, *J* = 7.1 Hz, 3H *E*-**2a** + 3H *Z*-**2a**), 0.88 (t, *J* = 7.1 Hz, 3H *E*-**2a**) partially overlapped with 0.87 (t, *J* = 7.2 Hz, 3H *Z*-**2a**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.5 (*E*-**2a**), 172.3 (*Z*-**2a**), 171.5 (*Z*-**2a**), 170.7 (*E*-**2a**), 150.6 (*Z*-**2a**), 148.4 (*E*-**2a**), 125.2 (*E*-**2a**), 124.5 (*Z*-**2a**), 60.9 (*E*-**2a**), 60.9 (*Z*-**2a**), 40.0 (*Z*-**2a**), 32.1 (*E*-**2a**), 31.8 (*Z*-**2a**), 31.1 (*E*-**2a**), 22.4 (*Z*-**2a**), 21.6 (*E*-**2a**), 14.1 (*E*-**2a**), 14.1 (*Z*-**2a**), 13.8 (*E*-**2a**), 13.8 (*Z*-**2a**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{10}H_{15}O_4$ 199.0976; found 199.0985.

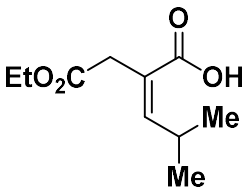


E-2b *Z*-2b

2b. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 60%, (0.090 mmol, 15.5 mg); *E*/*Z* = 3.2:1; **2b**/**3b** = 5.4:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.20 (q, *J* = 7.1 Hz, 1H *E*-**2b**), 6.32 (q, *J* = 7.3, 1H *Z*-**2b**), 4.15 (q, *J* = 7.1 Hz, 2H *E*-**2b** + 2H *Z*-**2b**), 3.35 (s, 2H *E*-**2b**), 3.25 (s, 2H *Z*-**2b**), 2.12 (d, *J* = 7.3 Hz, 3H *Z*-**2b**), 1.86 (d, *J* = 7.1 Hz, 3H *E*-**2b**), 1.25 (t, *J* = 7.1 Hz, 3H *E*-**2b**) partially overlapped with 1.24 (t, *J* = 7.1 Hz, 3H *Z*-**2b**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.2 (*E*-**2b**), 172.2 (*Z*-**2b**), 171.6 (*Z*-**2b**), 170.7 (*E*-**2b**), 144.9 (*Z*-**2b**), 143.3 (*E*-**2b**), 126.2 (*E*-**2b**), 125.5 (*Z*-**2b**), 60.9 (*E*-**2b**), 60.9 (*Z*-**2b**), 40.0 (*Z*-**2b**), 31.7 (*E*-**2b**), 16.2 (*Z*-**2b**), 14.9 (*E*-**2b**), 14.1 (*E*-**2b**), 14.1 (*Z*-**2b**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_8H_{11}O_4$ 171.0663; found 171.0669.

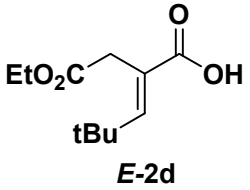


E-2c

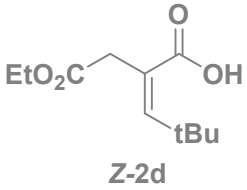


Z-2c

2c. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 57%, (0.086 mmol, 17.1 mg); *E*/*Z* = 4.2:1; **2c**/**3c** = 8.1:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 6.89 (d, *J* = 10.2 Hz, 1H *E*-**2c**), 5.95 (d, *J* = 9.9 Hz, 1H *Z*-**2c**), 4.14 (q, *J* = 7.1, 1.0 Hz, 2H *E*-**2c** + 2H *Z*-**2c**), 3.34 (s, 2H *E*-**2c**), 3.24 (s, 2H *Z*-**2c**), 2.64 – 2.57 (m, 1H *E*-**2c** + 1H *Z*-**2c**), 1.25 (t, *J* = 7.1 Hz, 3H *E*-**2c** + 3H *Z*-**2c**), 1.05 (d, *J* = 6.6 Hz, 6H *E*-**2c**), 1.02 (d, *J* = 6.6 Hz, 6H *Z*-**2c**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.4 (b, *E*-**2c** + *Z*-**2c** overlapped), 171.5 (*Z*-**2c**), 170.8 (*E*-**2c**), 156.7 (*Z*-**2c**), 154.6 (*E*-**2c**), 124.8 (*Z*-**2c**), 122.8 (*E*-**2c**), 60.9 (*E*-**2c**), 60.9 (*Z*-**2c**), 40.1 (*Z*-**2c**), 32.2 (*E*-**2c**), 28.6 (*E*-**2c**), 28.5 (*Z*-**2c**), 22.4 (2C *Z*-**2c**), 21.8 (2C *E*-**2c**), 14.1 (*E*-**2c**), 14.1 (*Z*-**2c**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{10}H_{15}O_4$ 199.0976; found 199.0969.

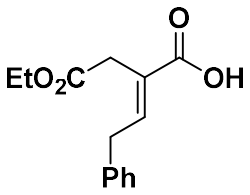


E-2d

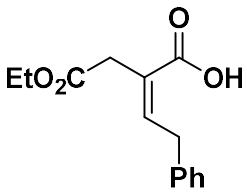


Z-2d

2d. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 60%, (0.090 mmol, 19.3 mg); *E*/*Z* = 18:1; **2d**/**3d** = 6.5:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.11 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 9H), only the peaks of *E*-**2d** are given, characteristic peak of *Z*-**2d**: 5.87 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 173.5, 170.9, 156.5, 123.3, 60.9, 33.7, 32.5, 30.1 (3C), 14.1, only the peaks relative to *E*-**2d** are given; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{17}O_4$ 213.1132; found 213.1137.



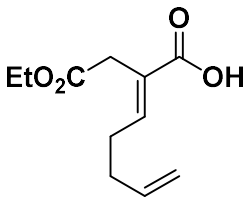
E-2e



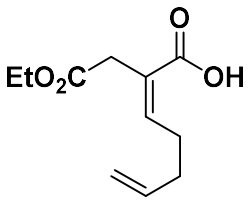
Z-2e

2e. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 57%, (0.086 mmol, 21.2 mg); *E*/*Z* = 3.8:1; **2e**/**3e** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.26 – 7.21 (m, 2H *E*-**2e** + 2H *Z*-**2e**), 7.20 – 7.10 (m, 4H *E*-**2e** + 3H *Z*-**2e**), 6.25 (t, *J* = 7.5 Hz, 1H *Z*-**2e**), 4.09 (q, *J* = 7.1 Hz, 2H *E*-**2e**) partially overlapped with 4.08 (q, *J* = 7.1 Hz, 2H *Z*-**2e**), 3.91 (d, *J* = 7.5 Hz, 2H *Z*-**2e**), 3.50 (d, *J* = 7.7 Hz, 2H *E*-**2e**), 3.38 (s, 2H *E*-**2e**), 3.22 (s, 2H *Z*-**2e**), 1.18 (t, *J* = 7.1 Hz, 3H *E*-**2e**) partially overlapped with 1.17 (t, *J* = 7.1 Hz, 3H *E*-**2e**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.1 (*E*-**2e**), 171.9 (*Z*-**2e**), 171.3 (*Z*-**2e**), 170.5 (*E*-**2e**), 148.1 (*Z*-**2e**), 146.2 (*E*-**2e**), 139.3 (*Z*-**2e**), 137.8 (*E*-**2e**), 128.8 (2C *E*-**2e**), 128.7 (2C

Z-**2e**), 128.7 (2C *Z*-**2e**), 128.6 (2C *E*-**2e**), 126.7 (*E*-**2e**), 126.4 (*Z*-**2e**), 125.6 (*E*-**2e**), 124.8 (*Z*-**2e**), 61.1 (*E*-**2e**), 61.0 (*Z*-**2e**), 40.0 (*Z*-**2e**), 36.1 (*Z*-**2e**), 35.2 (*E*-**2e**), 32.2 (*E*-**2e**), 14.1 (*E*-**2e**), 14.1 (*Z*-**2e**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{14}H_{15}O_4$ 247.0976; found 247.0968.

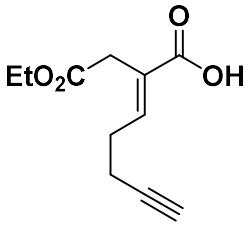


E-2f

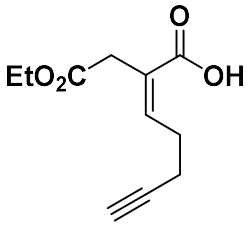


Z-2f

2f. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 71%, (0.107 mmol, 22.6 mg); *E*/*Z* = 4.6:1; **2f**/**3f** = 4.8:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.10 (t, *J* = 7.4 Hz, 1H *E*-**2f**), 6.19 (t, *J* = 7.3 Hz, 1H *E*-**2f**), 5.85 – 5.75 (m, 1H *E*-**2f** + 1H *Z*-**2f**), 5.06 (dq, *J* = 17.1, 1.6 Hz, 1H *E*-**2f**) partially overlapped with 5.05 (dq, *J* = 17.2, 1.6 Hz, 1H *Z*-**2f**), 5.02 (dq, *J* = 10.3, 1.4 Hz, 1H *E*-**2f**) partially overlapped with 5.01 (dq, *J* = 10.3, 1.4 Hz, 1H *Z*-**2f**), 4.14 (q, *J* = 7.1 Hz, 2H *E*-**2f** + 2H *Z*-**2f**), 3.34 (s, 2H *E*-**2f**), 3.26 (s, 2H *Z*-**2f**), 2.72 (q, *J* = 7.3 Hz, 2H *Z*-**2f**), 2.31 (q, *J* = 7.4 Hz, 2H *E*-**2f**), 2.26 – 2.19 (m, 2H *E*-**2f** + 2H *Z*-**2f**), 1.25 (t, *J* = 7.2 Hz, 3H *E*-**2f** + 3H *Z*-**2f**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.2 (*E*-**2f**), 171.9 (*Z*-**2f**), 171.4 (*Z*-**2f**), 170.6 (*E*-**2f**), 149.6 (*Z*-**2f**), 147.5 (*E*-**2f**), 137.5 (*Z*-**2f**), 136.9 (*E*-**2f**), 125.4 (*E*-**2f**), 124.8 (*Z*-**2f**), 115.8 (*E*-**2f**), 115.4 (*Z*-**2f**), 61.0 (*E*-**2f**), 60.9 (*Z*-**2f**), 39.9 (*Z*-**2f**), 33.0 (*Z*-**2f**), 32.2 (*E*-**2f**), 32.1 (*E*-**2f**), 29.0 (*Z*-**2f**), 28.5 (*E*-**2f**), 14.1 (*E*-**2f**), 14.1 (*Z*-**2f**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{15}O_4$ 211.0976; found 211.0983.

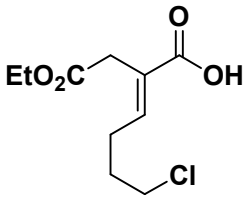


E-2g

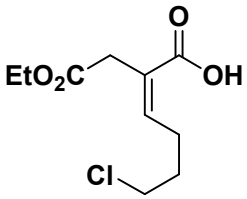


Z-2g

2g. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 43%, (0.065 mmol, 13.5 mg); *E*/*Z* = 4.5:1; **2g**/**3g** = 6.7:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.13 (t, *J* = 7.4 Hz, 1H *E*-**2g**), 6.29 (t, *J* = 7.1 Hz, 1H *Z*-**2g**), 4.17 – 4.12 (m, 2H *E*-**2g** + 2H *Z*-**2g**), 3.37 (s, 2H *E*-**2g**), 3.30 (s, 2H *Z*-**2g**), 2.84 (q, *J* = 7.1 Hz, 2H *Z*-**2g**), 2.45 (q, *J* = 7.2 Hz, 2H *E*-**2g**), 2.37 (td, *J* = 7.0, 2.6 Hz, 2H *E*-**2g**) partially overlapped with 2.34 (td, *J* = 7.1, 2.6 Hz, 2H *Z*-**2g**) 1.99 (t, *J* = 2.6 Hz, 1H *E*-**2g**), 1.98 (t, *J* = 2.6 Hz, 1H *Z*-**2g**), 1.25 (t, *J* = 7.1 Hz, 3H *E*-**2g** + 3H *Z*-**2g**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.9 (b, *E*-**2g** + *Z*-**2g** overlapped), 170.3 (*Z*-**2g**), 169.4 (*E*-**2g**), 146.5 (*Z*-**2g**), 144.6 (b, *E*-**2g**), 136.2 (*Z*-**2g**), 125.5 (b, *E*-**2g**), 82.2 (*Z*-**2g**), 81.6 (*E*-**2g**), 68.5 (*E*-**2g**), 68.2 (*Z*-**2g**), 60.0 (*E*-**2g**), 59.9 (*Z*-**2g**), 38.9 (b, *Z*-**2g**), 31.2 (b, *E*-**2g**), 27.6 (*Z*-**2g**), 27.1 (*E*-**2g**), 17.1 (*Z*-**2g**), 16.6 (*E*-**2g**), 13.1 (*E*-**2g**), 13.1 (*Z*-**2g**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{13}O_4$ 209.0819; found 209.0812.

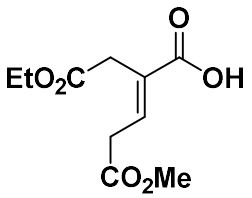


E-2h

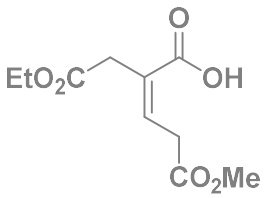


Z-2h

2h. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 73%, (0.110 mmol, 25.7 mg); *E*/*Z* = 3.6:1; **2h**/**3h** = 6.9:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 6.99 (t, *J* = 7.7 Hz, 1H *E*-**2h**), 6.11 (t, *J* = 7.5 Hz, 1H *Z*-**2h**), 4.08 (q, *J* = 7.1 Hz, 2H *E*-**2h** + 2H *Z*-**2h**), 3.50 (t, *J* = 6.3 Hz, 2H *Z*-**2h**) partially overlapped with 3.49 (t, *J* = 6.3 Hz, 2H *E*-**2h**), 3.31 (s, 2H *E*-**2h**), 3.21 (s, 2H *Z*-**2h**), 2.69 (q, *J* = 7.5 Hz, 2H *Z*-**2h**), 2.34 (q, *J* = 7.4 Hz, 2H *E*-**2h**), 1.93 – 1.85 (m, 2H *E*-**2h** + 2H *Z*-**2h**), 1.19 (t, *J* = 7.1 Hz, 3H *E*-**2h**) partially overlapped with 1.18 (t, *J* = 7.1 Hz, 3H *Z*-**2h**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.1 (b, *E*-**2h**), 170.8 (b, *Z*-**2h**), 170.3 (*Z*-**2h**), 169.5 (*E*-**2h**), 147.0 (*Z*-**2h**), 145.1 (*E*-**2h**), 125.5 (*E*-**2h**), 124.8 (*Z*-**2h**), 60.0 (*E*-**2h**), 60.0 (*Z*-**2h**), 43.2 (*Z*-**2h**), 43.0 (*E*-**2h**), 38.9 (*Z*-**2h**), 31.0 (*E*-**2h**), 31.0 (*Z*-**2h**), 29.9 (*E*-**2h**), 26.3 (*Z*-**2h**), 25.2 (*E*-**2h**), 13.1 (*E*-**2h**), 13.1 (*Z*-**2h**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{10}H_{14}{}^{35}ClO_4$ 233.0586; found 233.0593; calcd. for $C_{10}H_{14}{}^{37}ClO_4$ 235.0556; found 235.0561.

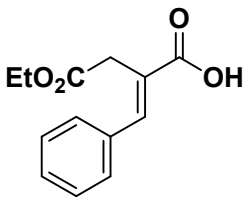


E-2i

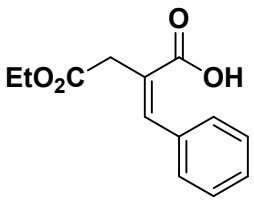


Z-2i

2i. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 77%, (0.116 mmol, 26.6 mg); *E*/*Z* > 20:1; **2i**/**3i** = 8.4:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.27 (t, *J* = 7.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.35 (s, 2H), 3.28 (d, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.4, 169.0, 168.9, 137.8, 126.8, 60.2, 51.3, 33.3, 31.3, 13.1; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{10}H_{13}O_6$ 229.0718; found 229.0724.

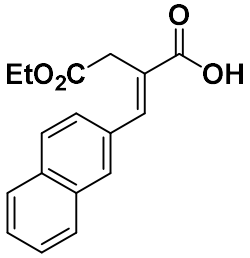


E-2j

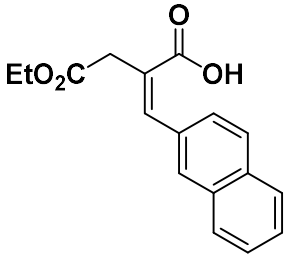


Z-2j

2j. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 57%, (0.110 mmol, 20.0 mg); *Z*/*E* = 2.0:1; **2j**/**3j** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.97 (s, 1H *E*-**2j**), 7.42 – 7.33 (m, 3H *E*-**2j** + 3H *Z*-**2j**), 7.32 – 7.25 (m, 2H *E*-**2j** + 2H *Z*-**2j**), 6.90 (s, 1H *Z*-**2j**), 4.22 – 4.12 (m, 2H *E*-**2j** + 2H *Z*-**2j**), 3.51 (s, 2H *E*-**2j**), 3.45 (s, 2H *Z*-**2j**), 1.25 (t, *J* = 6.9 Hz, 3H *E*-**2j** + 3H *Z*-**2j**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.5 (*E*-**2j**), 171.1 (*Z*-**2j**), 170.2 (*Z*-**2j**), 170.1 (*E*-**2j**), 142.8 (*E*-**2j**), 139.9 (*Z*-**2j**), 134.1 (*Z*-**2j**), 133.8 (*E*-**2j**), 128.2 (*E*-**2j**), 128.1 (*Z*-**2j**), 127.8 (2C *Z*-**2j**), 127.6 (2C *E*-**2j**), 127.4 (2C *E*-**2j**), 127.0 (2C *Z*-**2j**), 125.2 (*Z*-**2j**), 124.5 (*E*-**2j**), 60.2 (*Z*-**2j**), 60.1 (*E*-**2j**), 39.9 (*Z*-**2j**), 32.4 (*E*-**2j**), 13.1 (*E*-**2j**), 13.0 (*Z*-**2j**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{13}H_{13}O_4$ 233.0819; found 233.0825.

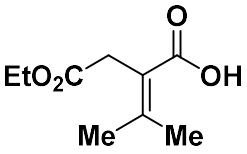


E-2k

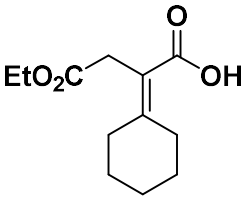


Z-2k

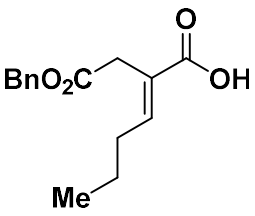
2k. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 49%, (0.078 mmol, 20.9 mg); *Z*/*E* = 2.4:1; **2k**/**3k** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.14 (s, 1H *E*-**2k**), 7.88 – 7.75 (m, 4H *E*-**2k** + 4H *Z*-**2k**), 7.56 – 7.43 (m, 3H *E*-**2k** + 3H *Z*-**2k**), 7.12 (s, 1H *Z*-**2k**), 4.25 – 4.15 (m, 2H *E*-**2k** + 2H *Z*-**2k**), 3.61 (s, 2H *E*-**2k**), 3.52 (s, 2H *Z*-**2k**), 1.28 (t, *J* = 7.1 Hz, 3H *E*-**2k** 3H *Z*-**2k**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.4 (*E*-**2k**), 170.6 (*Z*-**2k**), 170.1 (Z-**2k**), 170.0 (*E*-**2k**), 143.1 (*E*-**2k**), 140.9 (*Z*-**2k**), 132.3 (*E*-**2k**), 132.1 (*Z*-**2k**), 132.0 (*E*-**2k**), 131.9 (*Z*-**2k**), 131.6 (*Z*-**2k**), 131.2 (*E*-**2k**), 128.2 (*E*-**2k**), 127.7 (*Z*-**2k**), 127.4 (*E*-**2k**), 127.4 (*E*-**2k**), 127.3 (*Z*-**2k**), 126.7 (*E*-**2k**), 126.6 (*Z*-**2k**), 126.6 (*Z*-**2k**), 126.1 (*E*-**2k**), 125.6 (*E*-**2k**), 125.6 (*Z*-**2k**), 125.3 (*Z*-**2k**), 125.2 (*E*-**2k**), 125.2 (*Z*-**2k**), 124.8 (*Z*-**2k**), 124.4 (*E*-**2k**), 60.3 (*Z*-**2k**), 60.1 (*E*-**2k**), 39.9 (*Z*-**2k**), 32.5 (*E*-**2k**), 13.2 (*E*-**2k**), 13.1 (*Z*-**2k**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{17}H_{15}O_4$ 283.0976; found 283.0966.



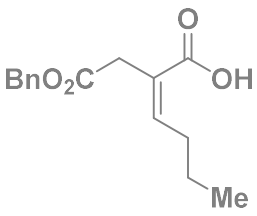
2l. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 43%, (0.065 mmol, 12.0 mg); **2l**/**3l** = 2.6:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 4.08 (q, *J* = 7.1 Hz, 2H), 3.32 (s, 2H), 2.15 (s, 3H), 1.84 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.7, 170.5, 152.2, 118.9, 59.8, 34.2, 22.9, 22.6, 13.1; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_9H_{13}O_4$ 185.0819; found 185.0810.



2m. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 36%, (0.054 mmol, 13.0 mg); **2m**/**3m** = 2.8:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 4.09 (q, *J* = 7.1 Hz, 2H), 3.33 (s, 2H), 2.70 – 2.64 (m, 2H), 2.22 – 2.17 (m, 2H), 1.62 – 1.51 (m, 6H), 1.19 (t, J= 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.8, 171.9, 158.5, 116.8, 61.0, 34.8, 33.0, 32.6, 28.4, 28.1, 26.3, 14.2; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{17}O_4$ 225.1132; found 225.1138.

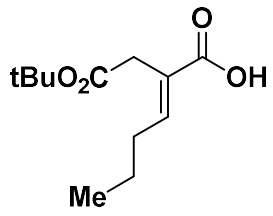


E-**2n**

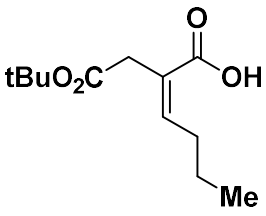


Z-2n

2n. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 65%, (0.098 mmol, 25.5 mg); *E*/*Z* = 8.1:1; **2n**/**3n** = 2.8:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.39 – 7.29 (m, 5H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.14 (s, 2H), 3.41 (s, 2H), 2.18 (q, *J* = 7.5 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), only the peaks of *E*-**2n** are given, characteristic peak of *Z*-**2n**: 6.22 (t, *J* = 7.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.2, 169.5, 147.6, 134.8, 127.5 (2C), 127.2, 127.1 (2C), 124.0, 65.6, 31.0, 30.1, 20.6, 12.8, only the peaks of *E*-**2n** are given; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{15}H_{17}O_4$ 261.1132; found 261.1141.

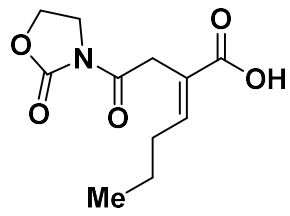


E-2o

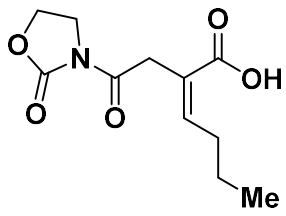


Z-2o

2o. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 46%, (0.069 mmol, 15.7 mg); *E*/*Z* = 4.0:1; **2o**/**3o** = 4.1:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.06 (t, *J* = 7.6 Hz, 1H *E*-**2o**), 6.13 (t, *J* = 7.5, 1H *Z*-**2o**), 3.26 (s, 2H *E*-**2o**), 3.18 (s, 2H *Z*-**2o**), 2.56 (q, *J* = 7.4 Hz, 2H *Z*-**2o**), 2.19 (q, *J* = 7.4 Hz, 2H *E*-**2o**), 1.54 – 1.45 (m, 2H *E*-**2o** + 2H *Z*-**2o**), 1.43 (s, 9H *Z*-**2o**), 1.43 (s, 9H *E*-**2o**), 0.94 (t, *J* = 7.4 Hz, 3H *E*-**2o**) partially overlapped with 0.94 (t, *J* = 7.4 Hz, 3H *Z*-**2o**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.5 (*E*-**2o**), 171.2 (*Z*-**2o**), 169.8 (*Z*-**2o**), 168.9 (*E*-**2o**), 148.5 (*Z*-**2o**), 146.6 (*E*-**2o**), 124.7 (*E*-**2o**), 124.0 (*Z*-**2o**), 80.0 (*Z*-**2o**), 79.9 (*E*-**2o**), 40.3 (*Z*-**2o**), 32.3 (*E*-**2o**), 30.7 (*Z*-**2o**), 30.0 (*E*-**2o**), 27.0 (3C *E*-**2o** + 3C *Z*-**2o**), 21.4 (*Z*-**2o**), 20.7 (*E*-**2o**), 12.8 (*E*-**2o**), 12.8 (*Z*-**2o**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{19}O_4$ 227.1289; found 227.1296.

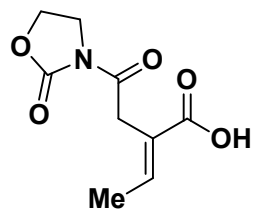


E-2p

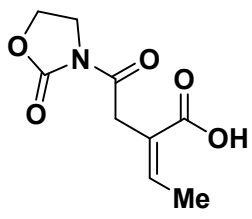


Z-2p

2p. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 60%, (0.090 mmol, 21.7 mg); *E*/*Z* = 3.8:1; **2p**/**3p** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.15 (t, *J* = 7.6 Hz, 1H *E*-**2p**), 6.17 (t, *J* = 7.4 Hz, 1H *Z*-**2p**), 4.47 – 4.40 (m, 2H *E*-**2p** + 2H *Z*-**2p**), 4.06 – 4.00 (m, 2H *E*-**2p** + 2H *Z*-**2p**), 3.93 (s, 2H *E*-**2p**), 3.87 (s, 2H *Z*-**2p**), 2.60 (q, *J* = 7.4 Hz, 2H *Z*-**2p**), 2.15 (q, *J* = 7.5 Hz, 2H *E*-**2p**), 1.54 – 1.44 (m, 2H *E*-**2p** + 2H *Z*-**2p**), 0.94 (t, *J* = 7.4 Hz, 3H *E*-**2p** + *Z*-**2p**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.2 (*E*-**2p**), 171.1 (*Z*-**2p**), 170.2 (*Z*-**2p**), 169.2 (*E*-**2p**), 152.8 (*E*-**2p**), 152.7 (*Z*-**2p**), 149.9 (*Z*-**2p**), 147.7 (*E*-**2p**), 123.7 (*E*-**2p**), 123.0 (*Z*-**2p**), 61.3 (*Z*-**2p**), 61.3 (*E*-**2p**), 41.5 (*E*-**2p**), 41.5 (*Z*-**2p**), 40.2 (*Z*-**2p**), 32.1 (*E*-**2p**), 30.8 (*Z*-**2p**), 30.1 (*E*-**2p**), 21.4 (*Z*-**2p**), 20.7 (*E*-**2p**), 12.8 (*E*-**2p**), 12.8 (*Z*-**2p**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{14}NO_5$ 240.0877; found 240.0868.

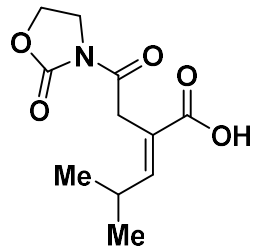


E-2q

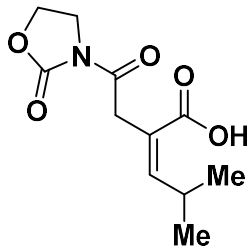


Z-2q

2q. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 57%, (0.086 mmol, 18.2 mg); *E*/*Z* = 3.2:1; **2q**/**3q** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.17 (q, *J* = 7.3 Hz, 1H *E*-**2q**), 6.22 (q, *J* = 7.2 Hz, 1H *Z*-**2q**), 4.41 – 4.32 (m, 2H *E*-**2q** + 2H *Z*-**2q**), 4.01 – 3.93 (m, *E*-**2q** + 2H *Z*-**2q**), 3.88 (s, 2H *E*-**2q**), 3.81 (s, 2H *Z*-**2q**), 2.06 (d, *J* = 7.2 Hz, 3H *Z*-**2q**), 1.77 (d, *J* = 7.1 Hz, 3H *E*-**2q**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.9 (*E*-**2q**), 171.8 (*Z*-**2q**), 171.3 (*Z*-**2q**), 170.2 (*E*-**2q**), 153.8 (*E*-**2q**), 153.7 (*Z*-**2q**), 145.0 (*Z*-**2q**), 143.5 (*E*-**2q**), 125.8 (*E*-**2q**), 125.2 (*Z*-**2q**), 62.3 (*E*-**2q** +*Z*-**2q** overlapped), 42.6 (*E*-**2q**), 42.5 (*Z*-**2q**), 41.2 (*Z*-**2q**), 32.8 (*E*-**2q**), 29.7 (*E*-**2q**), 29.7 (*Z*-**2q**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_9H_{10}NO_5$ 212.0564; found 212.0563.

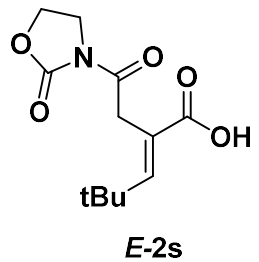


E-2r

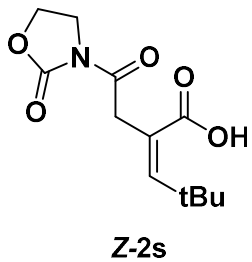


Z-2r

2r. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 53%, (0.080 mmol, 19.2 mg); *E*/*Z* = 5.9:1; **2r**/**3r** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 6.88 (d, *J* = 10.2 Hz, 1H *E*-**2r**), 5.87 (d, *J* = 9.9 Hz, 1H *Z*-**2r**), 4.44 – 4.31 (m, 2H *E*-**2r** + 2H *Z*-**2r**), 4.01 – 3.93 (m, 2H *E*-**2r** + 2H *Z*-**2r**), 3.86 (s, 2H *E*-**2r**), 3.79 (s, 2H *Z*-**2r**), 3.43 – 3.36 (m, 1H *Z*-**2r**), 2.52 – 2.41 (m, 1H *E*-**2r**), 0.98 (d, *J* = 6.6 Hz, 6H *E*-**2r**), 0.96 (d, *J* = 6.7 Hz, 6H *Z*-**2r**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.5 (*E*-**2r**), 172.1 (*Z*-**2r**), 171.2 (*Z*-**2r**), 170.3 (*E*-**2r**), 156.9 (*Z*-**2r**), 154.8 (*E*-**2r**), 153.8 (*E*-**2r**), 153.7 (*Z*-**2r**), 122.3 (*E*-**2r**), 121.8 (*Z*-**2r**), 62.3 (*E*-**2r**), 42.6 (*E*-**2r**), 42.5 (Z-**2r**), 41.3 (*Z*-**2r**), 33.2 (*E*-**2r**), 29.7 (*Z*-**2r**), 28.7 (*E*-**2r**), 28.5 (*Z*-**2r**), 22.4 (2C *Z*-**2r**), 21.9 (2C *E*-**2r**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{14}NO_5$ 240.0877; found 240.0882.



E-2s



Z-2s

2s. White solid. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 56%, (0.084 mmol, 21.4 mg); *E*/*Z* = 4.8:1; **2s**/**3s** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.18 (s, 1H *E*-**2s**), 5.91 (s, 1H *Z*-**2s**), 4.48 – 4.39 (m, 2H *E*-**2s** + 2H *Z*-**2s**), 4.08 (s, 2H *E*-**2s**), 4.06 – 4.00 (m, 2H *E*-**2s** + 2H *Z*-**2s**), 3.88 (s, 2H *Z*-**2s**), 1.19 (s, 9H *Z*-**2s**),

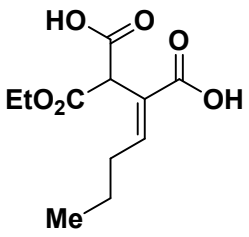
1.17 (s, 9H *E*-**2s**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 173.2 (*E*-**2s**), 172.7 (*Z*-**2s**), 171.4 (*Z*-**2s**), 170.5 (*E*-**2s**), 157.1 (*E*-**2s**), 154.2 (*Z*-**2s**), 153.8 (*E*-**2s**), 153.6 (*Z*-**2s**), 123.3 (*Z*-**2s**), 122.8 (*E*-**2s**), 62.3 (*Z*-**2s**), 62.3 (*E*-**2s**), 43.1 (*Z*-**2s**), 42.6 (*E*-**2s**), 42.5 (*Z*-**2s**), 33.7 (*Z*-**2s**), 33.6 (*E*-**2s**), 33.6 (*E*-**2s**), 30.1 (3C *E*-**2s**), 29.9 (3C *Z*-**2s**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{16}NO_5$ 254.1034; found 254.1043.

3.3 General procedure for the electrochemical double carboxylation of allenes **1**.

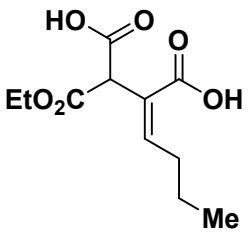
The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with allene **1** (0.15 mmol), and $TEABF_4$ (0.30 mmol, 65.1 mg). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ni), was inserted into the mixture, and closed with a rubber septum. The vessel was evacuated and backfilled with CO_2 (balloon) three times, then dry ACN (3.0 mL) was added, and the mixture was stirred until complete dissolution of the solids occurred. Then, the solution was bubbled with CO_2 (balloon) under stirring for 1 min. The reaction mixture was electrolyzed (under CO_2, balloon) at a constant current of 60.0 mA, until a total charge of 2.25 mF (15.0 F/mol_1) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and $HCl_{(aq)}$ (2M, 10 mL), which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with $HCl_{(aq)}$ (0.1 M, 3 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was finally purified by FC to afford pure products **3**.

Additional notes:
In some cases, cyanoacetic acid, formed form the carboxylation of ACN, may co-elute with the desired product from the FC. In this case, the impure mixture can be easily purified by dissolving it in a small amount of EtOAc (2-3 mL) and performing repeated washings with de-ionized water (4x10 mL).

3.4 Characterization data of compounds **3**.

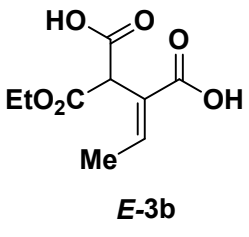


***E*-3a**

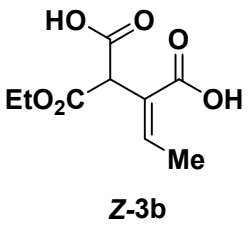


***Z*-3a**

3a. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 75%, (0.093 mmol); *E*/*Z* = 2.0:1; **3a**/**2a** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.57 (bs, 2H *E*-**3a** + 2H *Z*-**3a**), 7.16 (t, *J* = 7.7 Hz, 1H *E*-**3a**), 6.32 (t, *J* = 7.4 Hz, 1H *Z*-**3a**), 4.41 (s, 1H *E*-**3a**), 4.26 (s, 1H *Z*-**3a**), 4.23 – 4.14 (m, 2H *E*-**3a** + 2H *Z*-**3a**), 2.58 (qd, *J* = 7.4, 1.8 Hz, 2H *Z*-**3a**), 2.19 (ddt, *J* = 16.7, 15.1, 7.5 Hz, 2H *E*-**3a**), 1.54 – 1.41 (m, 2H *E*-**3a** + 2H *Z*-**3a**), 1.20 (t, *J* = 7.1 Hz, 3H *E*-**3a**) partially overlapped with 1.19 (t, *J* = 7.0 Hz, 3H *Z*-**3a**), 0.89 (t, *J* = 7.4 Hz, 3H *E*-**3a**) partially overlapped with 0.88 (t, *J* = 7.7 Hz, 3H *Z*-**3a**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.1 (*Z*-**3a**), 171.3 (*E*-**3a**), 171.3 (*Z*-**3a**), 170.3 (*E*-**3a**), 169.9 (*E*-**3a**), 169.1 (*Z*-**3a**), 153.2 (*Z*-**3a**), 150.8 (*E*-**3a**), 125.3 (*E*-**3a**), 124.2 (*Z*-**3a**), 62.8 (*E*-**3a**), 62.5 (*Z*-**3a**), 55.5 (*Z*-**3a**), 48.4 (*E*-**3a**), 31.9 (*Z*-**3a**), 31.4 (*E*-**3a**), 22.2 (*Z*-**3a**), 21.5 (*E*-**3a**), 13.9 (*Z*-**3a**), 13.8 (*E*-**3a**), 13.8 (*E*-**3a**), 13.7 (*Z*-**3a**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{15}O_6$ 243.0874; found 243.0881.

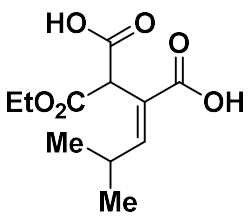


***E*-3b**

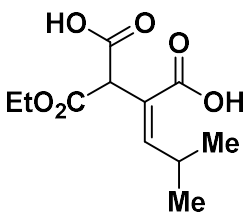


***Z*-3b**

3b. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 55%, (0.083 mmol); *E*/*Z* = 1.6:1; **3b**/**2b** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 9.34 (bs, 2H *E*-**3b** + 2H *Z*-**3b**), 7.27 (q, *J* = 7.2 Hz, 1H *E*-**3b**), 6.45 (q, *J* = 7.2 Hz, 1H *Z*-**3b**), 4.48 (s, 1H *E*-**3b**), 4.26 (s, 1H *Z*-**3b**), 4.26 – 4.19 (m, 2H *E*-**3b** + 2H *Z*-**3b**), 2.15 (d, *J* = 7.3 Hz, 3H *Z*-**3b**), 1.93 (d, *J* = 7.2 Hz, 3H *E*-**3b**), 1.26 (t, *J* = 7.2 Hz, 3H *E*-**3b**) partially overlapped with 1.25 (t, *J* = 7.3 Hz, 3H *Z*-**3b**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.9 (*Z*-**3b**), 170.9 (*E*-**3b**), 170.8 (*Z*-**3b**), 170.5 (*E*-**3b**), 170.2 (*E*-**3b**), 169.6 (*Z*-**3b**), 146.5 (*Z*-**3b**), 145.2 (*E*-**3b**), 126.8 (*E*-**3b**), 125.8 (*Z*-**3b**), 62.7 (*E*-**3b**), 62.5 (*Z*-**3b**), 56.3 (*Z*-**3b**), 48.5 (*E*-**3b**), 16.4 (*Z*-**3b**), 15.1 (*E*-**3b**), 13.9 (*Z*-**3b**), 13.8 (*E*-**3b**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_9H_{11}O_6$ 215.0561; found 215.0566.

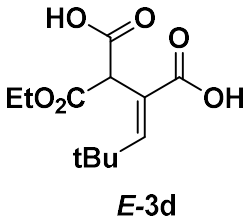


E-3c

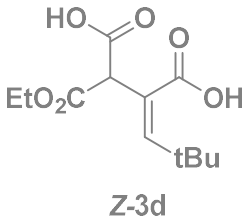


Z-3c

3c. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 49%, (0.074 mmol); *E*/*Z* = 3.2:1; **3c**/**2c** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.35 (s, 2H *E*-**3c** + 2H *Z*-**3c**), 6.93 (d, *J* = 10.4 Hz, 1H *E*-**3c**), 6.04 (d, *J* = 10.0 Hz, 1H *Z*-**3c**), 4.40 (s, 1H *E*-**3c**), 4.22 – 4.14 (m, 2H *E*-**3c** + 3H *Z*-**3c**), 3.47 – 3.37 (m, 1H *Z*-**3c**), 2.62 – 2.50 (m, 1H *E*-**3c**), 1.20 (t, *J* = 7.1 Hz, 3H *Z*-**3c**) partially overlapped with 1.19 (t, *J* = 7.1 Hz, 3H *E*-**3c**), 1.03 (d, *J* = 6.5 Hz, 3H *E*-**3c**), 1.00 (d, *J* = 6.6 Hz, 3H *E*-**3c**), 0.98 (d, *J* = 6.5 Hz, 3H *Z*-**3c**) partially overlapped with 0.97 (d, *J* = 6.6 Hz, 3H *Z*-**3c**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.0 (*Z*-**3c**), 171.6 (*E*-**3c**), 171.3 (*Z*-**3c**), 170.3 (*E*-**3c**), 170.1 (*E*-**3c**), 169.2 (*Z*-**3c**), 158.6 (*Z*-**3c**), 156.4 (*E*-**3c**), 123.1 (*E*-**3c**), 122.2 (*Z*-**3c**), 62.8 (*E*-**3c**), 62.5 (*Z*-**3c**), 55.8 (*Z*-**3c**), 48.5 (*E*-**3c**), 29.1 (*E*-**3c**), 28.8 (*Z*-**3c**), 22.2 (*Z*-**3c**), 22.1 (Z-**3c**), 21.6 (*E*-**3c**), 21.6 (*E*-**3c**), 13.9 (*Z*-**3c**), 13.8 (*E*-**3c**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{15}O_6$ 243.0874; found 243.0869.

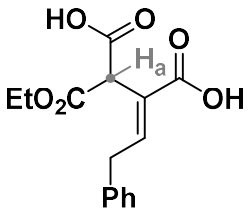


E-3d

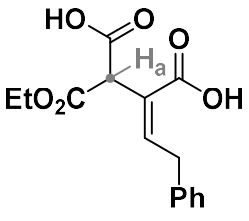


Z-3d

3d. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 61%, (0.092 mmol); *E*/*Z* > 20:1; **3d**/**2d** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, DMSO-d_6) δ = 6.83 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.40 (s, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 9H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ = 171.1, 169.4, 152.7, 125.1, 124.7, 60.5, 33.3, 32.9, 30.4 (3C), 14.5; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{17}O_6$ 257.1031; found 257.1040.



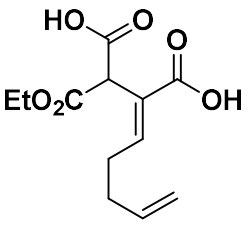
E-3e



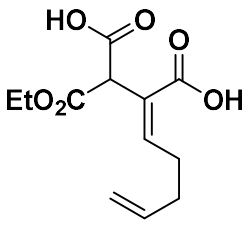
Z-3e

3e. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 54%, (0.081 mmol); *E*/*Z* = 3.5:1; **3e**/**2e** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, CD_3OD) δ = 7.21 – 7.15 (m, 2H *E*-**3e** + 2H *Z*-**3e**), 7.14 – 7.08 (m, 3H *E*-**3e** + 3H *Z*-**3e**), 7.04 (t, *J* = 7.8 Hz, 1H *E*-**3e**), 6.22 (t, *J* = 7.6 Hz, 1H *Z*-**3e**), 4.12 – 4.05 (m, 2H *E*-**3e** + 2H *Z*-**3e**), 3.88 (dd, *J* = 16.1, 7.7 Hz, 1H *Z*-**3e**) partially overlapped with 3.84 (dd, *J* = 16.1, 7.6 Hz, 1H *Z*-**3e**), 3.50 (d, *J* = 7.8 Hz, 2H *E*-**3e**), 1.15 (t, *J* = 7.2 Hz, 3H *E*-**3e**) partially

overlapped with 1.13 (t, *J* = 7.1 Hz, 3H *Z*-**3e**) the signal corresponding to H_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism, the -COOH peaks appear overlapped with the water signal at 4.81 ppm; **^{13}C NMR** (150 MHz, CD_3OD) δ = 170.0 (*Z*-**3e**), 169.7 (*E*-**3e**), 168.7 (*Z*-**3e**), 168.5 (*E*-**3e**), 168.2 (*E*-**3e**), 167.9 (*Z*-**3e**), 145.2 (*E*-**3e**), 144.9 (*Z*-**3e**), 139.4 (*Z*-**3e**), 138.2 (*E*-**3e**), 128.3 (2C *E*-**3e**), 128.3 (2C *E*-**3e**), 128.2 (2C *Z*-**3e**), 128.2 (2C *Z*-**3e**), 126.7 (*Z*-**3e**), 126.2 (*E*-**3e**), 126.2 (*Z*-**3e**), 126.0 (*E*-**3e**), 61.4 (*E*-**3e**), 61.3 (Z-**3e**), 35.3 (*Z*-**3e**), 34.7 (*E*-**3e**), 12.9 (*E*-**3e**), 12.9 (*Z*-**3e**) the signal corresponding to C_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{10}H_{15}O_6$ 291.0874; found 291.0877.

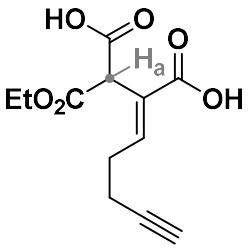


E-3f

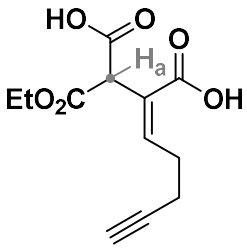


Z-3f

3f. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 58%, (0.087 mmol); *E*/*Z* = 2.7:1; **3f**/**2f** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 10.16 (bs, 2H *E*-**3f** + 2H *Z*-**3f**), 7.22 (t, *J* = 7.5 Hz, 1H *E*-**3f**), 6.38 (t, *J* = 7.2 Hz, 1H *Z*-**3f**), 5.85 – 5.74 (m, 1H *E*-**3f** + 1H *Z*-**3f**), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H *E*-**3f**), 5.04 – 4.99 (m, 1H *E*-**3f** + 2H *Z*-**3f**), 4.47 (s, 1H *E*-**3f**), 4.32 (s, 1H *Z*-**3f**), 4.30 – 4.21 (m, 2H *E*-**3f** + 2H *Z*-**3f**), 2.77 (qd, *J* = 7.4, 2.1 Hz, 2H *Z*-**3f**), 2.44 – 2.33 (m, 2H *E*-**3f**), 2.30 – 2.21 (m, 2H *E*-**3f** + 2H *Z*-**3f**), 1.27 (t, *J* = 7.1 Hz, 3H *Z*-**3f**) partially overlapped with 1.26 (t, *J* = 7.1 Hz, 3H *E*-**3f**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.0 (*Z*-**3f**), 171.2 (*E*-**3f**), 171.1 (*Z*-**3f**), 170.2 (*E*-**3f**), 169.8 (*E*-**3f**), 169.0 (*Z*-**3f**), 152.2 (*Z*-**3f**), 149.9 (*E*-**3f**), 137.1 (*Z*-**3f**), 136.5 (*E*-**3f**), 125.5 (*E*-**3f**), 124.4 (*Z*-**3f**), 116.2 (*E*-**3f**), 115.7 (*Z*-**3f**), 62.9 (*E*-**3f**), 62.6 (*Z*-**3f**), 55.4 (*Z*-**3f**), 48.4 (*E*-**3f**), 32.8 (*Z*-**3f**), 32.0 (*E*-**3f**), 29.1 (*Z*-**3f**), 28.7 (*E*-**3f**), 13.9 (*Z*-**3f**), 13.8 (*E*-**3f**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{15}O_6$ 255.0874; found 255.0868.



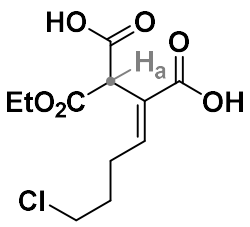
E-3g



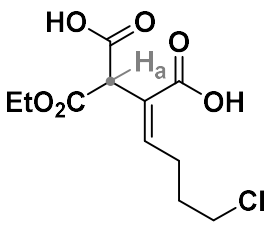
Z-3g

3g. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 52%, (0.078 mmol); *E*/*Z* = 3.9:1; **3g**/**2g** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.05 (t, *J* = 7.4 Hz, 1H *E*-**3g**), 6.21 (t, *J* = 7.2 Hz, 1H *Z*-**3g**), 4.09 (q, *J* = 7.1 Hz, 2H *Z*-**3g**) partially overlapped with 4.08 (q, *J* = 7.1 Hz, 2H *E*-**3g**), 2.77 (q, *J* = 7.1 Hz, 2H *Z*-**3g**), 2.42 – 2.37 (m, 2H *E*-**3g**), 2.32 – 2.25 (m, 2H *E*-**3g** + 2H *Z*-**3g**) 1.93 (t, *J* = 2.6

Hz, 1H *E*-**3g**), 1.92 (t, *J* = 2.6 Hz, 1H *Z*-**3g**), 1.19 (t, *J* = 7.1 Hz, 3H *E*-**3g** + 3H *Z*-**3g**) the signal corresponding to H_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism, the -COOH peaks were not detected; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.7 (*E*-**3g**), 171.4 (*Z*-**3g**), 171.4 (*Z*-**3g**), 170.5 (*E*-**3g**), 147.2 (*Z*-**3g**), 145.5 (*E*-**3g**), 126.4 (*E*-**3g**), 125.8 (*Z*-**3g**), 83.2 (*Z*-**3g**), 82.6 (*E*-**3g**), 69.5 (*E*-**3g**), 69.2 (*Z*-**3g**), 61.0 (*E*-**3g**), 61.0 (*Z*-**3g**), 28.6 (*Z*-**3g**), 28.1 (*E*-**3g**), 18.1 (*Z*-**3g**), 17.6 (*E*-**3g**), 14.1 (*E*-**3g**), 14.1 (*Z*-**3g**) the signals corresponding to C_a and to one -COOH carbon were not detected in the spectrum, probably due to a fast keto-enol tautomerism; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{12}H_{13}O_6$ 253.0718; found 253.0708.

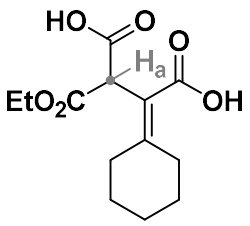


E-3h



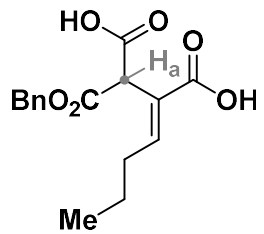
Z-3h

3h. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 47%, (0.071 mmol); *E*/*Z* = 3.6:1; **3h**/**2h** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 6.98 (t, *J* = 7.7 Hz, 1H *E*-**3h**), 6.10 (t, *J* = 7.6 Hz, 1H *Z*-**3h**), 4.09 (q, *J* = 7.1, 2H *E*-**3h** + 2H *Z*-**3h**), 3.51 – 3.48 (m, 2H *E*-**3h** + 2H *Z*-**3h**), 2.69 (q, *J* = 7.5 Hz, 2H *Z*-**3h**), 2.34 (q, *J* = 7.4 Hz, 2H *E*-**3h**), 1.93 – 1.85 (m, 2H *E*-**3h** + 2H *Z*-**3h**), 1.19 (t, *J* = 7.2 Hz, 3H *E*-**3h** + 3H *Z*-**3h**) the signal corresponding to H_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism, the -COOH peaks were not detected; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.4 (*Z*-**3h**), 171.4 (*E*-**3h**), 171.1 (*E*-**3h**), 171.1 (*Z*-**3h**), 171.1 (*Z*-**3h**), 170.6 (*E*-**3h**), 147.8 (*Z*-**3h**), 146.0 (*E*-**3h**), 126.4 (*E*-**3h**), 125.8 (*Z*-**3h**), 61.0 (*E*-**3h**), 61.0 (*Z*-**3h**), 44.3 (*Z*-**3h**), 44.1 (*E*-**3h**), 32.0 (*Z*-**3h**), 31.0 (*E*-**3h**), 27.3 (*Z*-**3h**), 26.2 (*E*-**3h**), 14.1 (*E*-**3h**), 14.1 (*Z*-**3h**) the signal corresponding to C_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{11}H_{14}{}^{35}ClO_6$ 277.0484; found 277.0488; calcd. for $C_{11}H_{14}{}^{37}ClO_6$ 279.0454; found 279.0461.

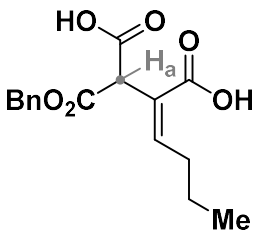


3m. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 47%, (0.071 mmol); **3m**/**2m** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, CD_3OD) δ = 4.08 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.49 (m, 2H), 2.23 – 2.13 (m, 2H), 1.60 – 1.50 (m, 6H), 1.16 (t, *J* = 7.1 Hz, 3H) the signal corresponding to H_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism, the -COOH peaks appear overlapped with the water signal at 4.76 ppm; **^{13}C NMR** (150 MHz, CD_3OD) δ

= 170.0, 169.1, 168.5, 154.3, 119.3, 61.3, 32.5, 32.3, 28.0, 27.6, 26.0, 12.9 the signal corresponding to C_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{13}H_{17}O_6$ 269.1031; found 269.1023.

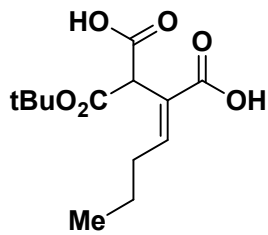


E-3n

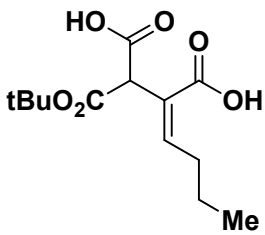


Z-3n

3n. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 62%, (0.093 mmol); *E*/*Z* = 3.1:1; **3n**/**2n** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, CD_3OD) δ = 7.31 – 7.17 (m, 5H *E*-**3n** + 5H *Z*-**3n**), 6.93 (t, *J* = 7.7 Hz, 1H *E*-**3n**), 6.07 (t, *J* = 7.5 Hz, 1H *Z*-**3n**), 5.10 – 5.04 (m, 2H *E*-**3n** + 2H *Z*-**3n**), 2.45 (q, *J* = 7.4 Hz, 2H *Z*-**3n**), 2.09 (qd, *J* = 7.4, 2.1 Hz, 2H *E*-**3n**), 1.39 – 1.30 (m, 2H *E*-**3n** + 2H *Z*-**3n**), 0.79 (t, *J* = 7.4 Hz, 3H *E*-**3n** + 3H *Z*-**3n**) the signal corresponding to H_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism, the -COOH peaks appear overlapped with the water signal at 4.80 ppm; **^{13}C NMR** (150 MHz, CD_3OD) δ = 170.0 (*Z*-**3n**), 169.7 (*E*-**3n**), 168.6 (*Z*-**3n**), 168.3 (*E*-**3n**), 168.2 (*E*-**3n**), 168.1 (*Z*-**3n**), 147.3 (*Z*-**3n**), 147.2 (*E*-**3n**), 135.7 (*Z*-**3n**), 135.7 (*E*-**3n**), 128.1 (2C *Z*-**3n**), 128.1 (2C *E*-**3n**), 127.9 (*Z*-**3n**), 127.8 (*E*-**3n**), 127.8 (2C *Z*-**3n**), 127.7 (2C *E*-**3n**), 126.5 (*E*-**3n**), 125.8 (*Z*-**3n**), 66.8 (*E*-**3n**), 66.8 (*Z*-**3n**), 31.2 (*Z*-**3n**), 30.6 (*E*-**3n**), 21.9 (*Z*-**3n**), 21.3 (*E*-**3n**), 12.7 (*E*-**3n**), 12.6 (*Z*-**3n**) the signal corresponding to C_a was not detected in the spectrum, probably due to a fast keto-enol tautomerism; **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{16}H_{17}O_6$ 305.1031; found 305.1035.



E-3o



Z-3o

3o. Colourless sticky oil. FC eluent: *n*-hexane/EtOAc: 7:3 + 1% HCOOH. Yield = 66%, (0.099 mmol); *E*/*Z* = 1.7:1; **3o**/**2o** > 20:1 in the crude mixture, > 20:1 after chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.13 (t, *J* = 7.7 Hz, 1H *E*-**3o**), 6.29 (t, *J* = 7.5 Hz, 1H *Z*-**3o**), 4.27 (s, 1H *E*-**3o**), 4.08 (s, 1H *Z*-**3o**), 2.61 (dq, *J* = 15.1, 7.5 Hz, 1H *Z*-**3o**), 2.54 (dq, *J* = 15.0, 7.3 Hz, 1H *Z*-**3o**), 2.26 – 2.12 (m, 2H *E*-**3o**), 1.53 – 1.41 (m, 2H *E*-**3o** + 2H *Z*-**3o**), 1.39 (s, 9H *Z*-**3o**), 1.38 (s, 9H *E*-**3o**), 0.90 (t, *J* = 7.4 Hz, 3H *E*-**3o**) partially overlapped with 0.88 (t, *J* = 7.4 Hz, 3H *Z*-**3o**) the -COOH peaks were not detected in the spectrum; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.5 (*E*-**3o**), 171.3 (*E*-**3o** + *Z*-**3o** overlapped), 170.2 (*E*-**3o**), 169.3 (*Z*-**3o**), 169.2 (*Z*-**3o**), 152.9 (*Z*-**3o**), 150.1 (*E*-**3o**), 126.0 (*E*-**3o**), 124.8

(*Z*-**3o**), 84.9 (*E*-**3o**), 84.2 (*Z*-**3o**), 56.2 (*Z*-**3o**), 48.5 (*E*-**3o**), 31.8 (*Z*-**3o**), 31.3 (*E*-**3o**), 27.7 (3C *Z*-**3o**), 27.7 (3C *E*-**3o**), 22.2 (*Z*-**3o**), 21.5 (*E*-**3o**), 13.8 (*E*-**3o**), 13.7 (*Z*-**3o**); **HRMS (ESI)** m/z: $[M-H]^-$ calcd. for $C_{13}H_{19}O_6$ 271.1187; found 271.1186.

4. CV Experiments

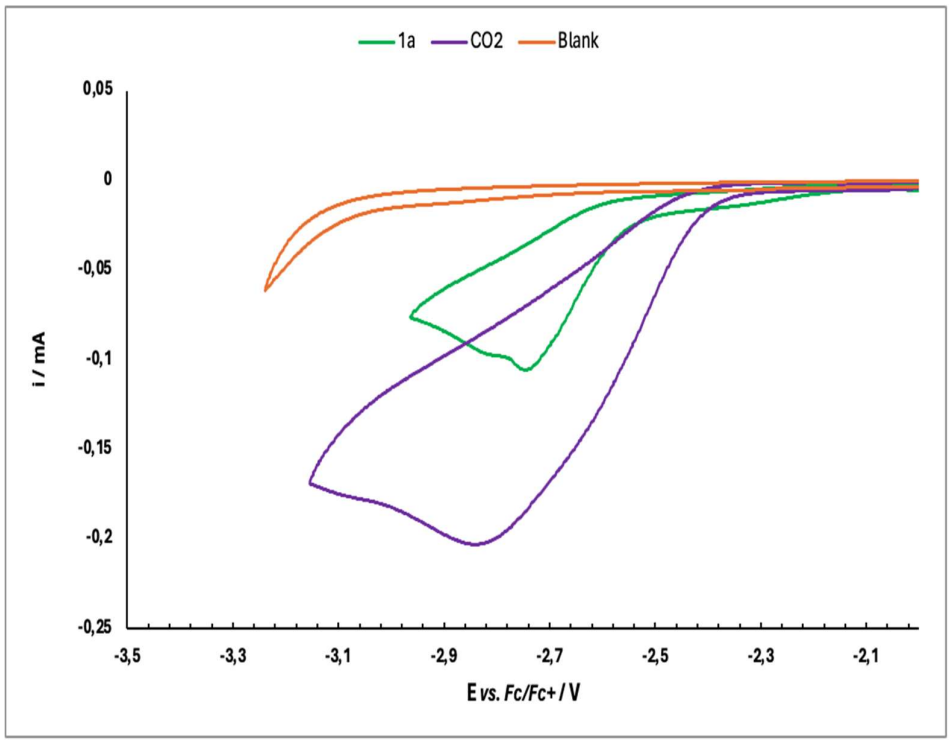


Figure S2. CV responses of 5 mM **1a** (grey line) and dissolved CO_2 (purple line) in 0.1 M $TEABF_4$, anhydrous DMF solution in comparison with the response obtained in the same solution before the addition of electroactive species (orange line). 0.050 Vs^{-1} potential scan rate. Potentials are reported versus the Fc/Fc^+ redox couple.

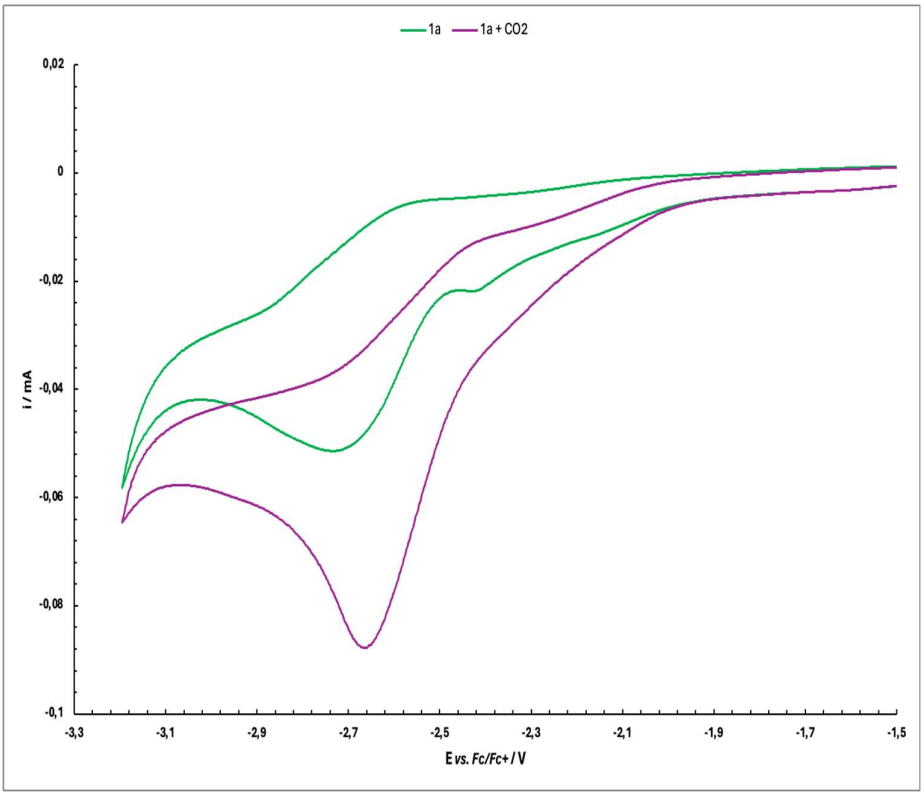
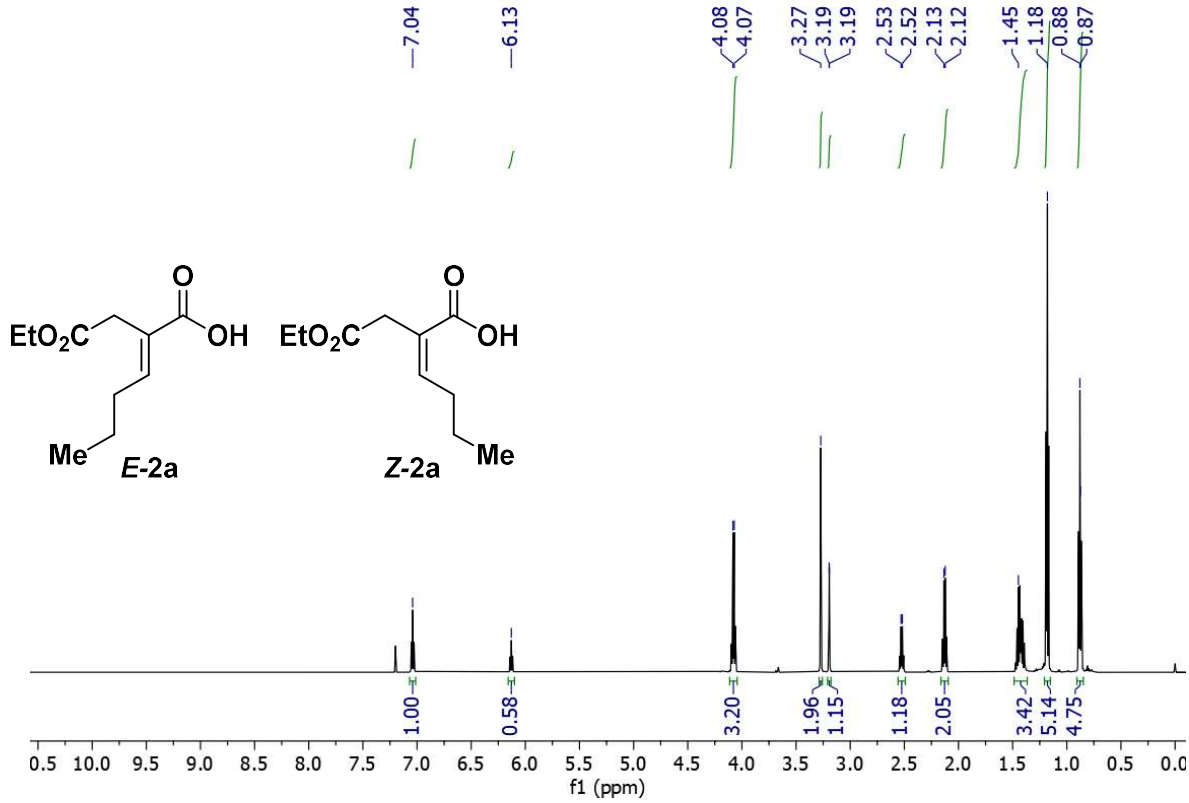


Figure S3. CV responses collected in a 5 mM **1a**, 0.1 M $TEABF_4$, anhydrous DMF solution before (green line) and after (purple line) bubbling CO_2 in solution for 4s. 0.05 Vs^{-1} potential scan rate. Potentials are reported versus the Fc/Fc^+ redox couple.

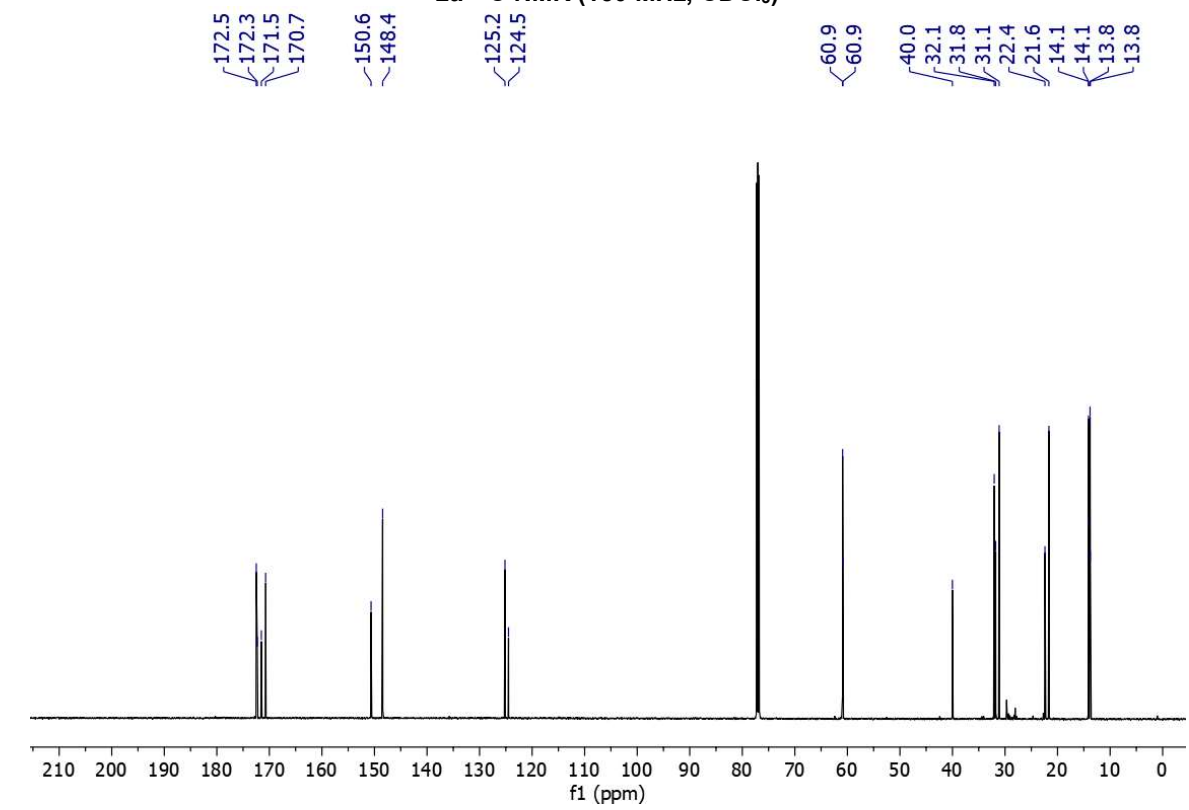
Compound **1a** shows two quite close reduction processes, the first occurring with a peak at -2.75 V *vs* Fc/Fc^+, and a second one at -2.82 V (Figure 2). Although the reduction of CO_2 is evidenced with a peak centered at more negative potential values (-2.84 V), this electrochemical process seems to require less negative potentials to occur, since the onset potential can be estimated at *ca.* -2.4 V. However, the difference in the reduction capability of the two species is not significant, as testified by voltammetric traces recorded in an analogous solution of **1a**, in absence and in presence of CO_2 (Figure 3): the addition of small amounts of CO_2 in solution does not affect the onset potential at which reduction processes start to occur. As a conclusion of these voltammetric experiments, we can assume that the reduction of the two species occurs simultaneously

5. ^{1}H-, and ^{13}C-NMR Spectra of New Compounds

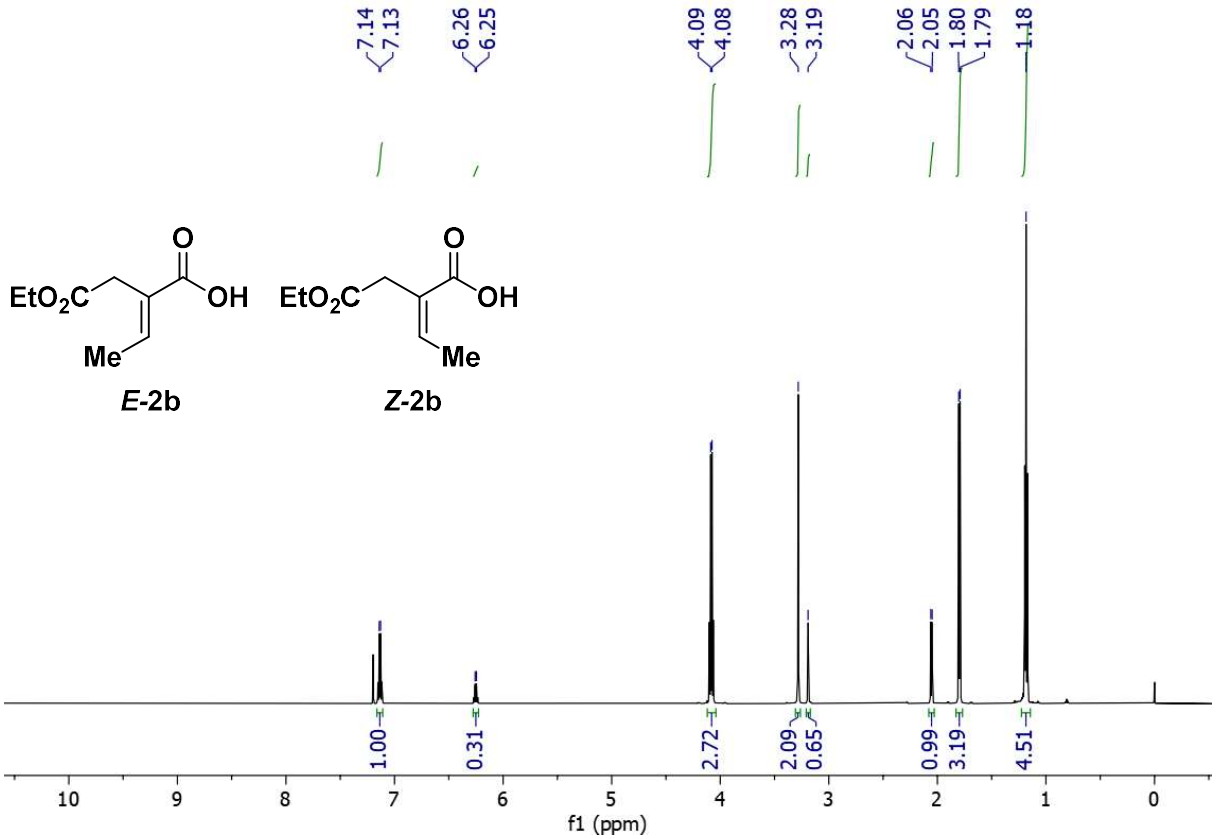
2a ^{1}H NMR (600 MHz, $CDCl_3$)



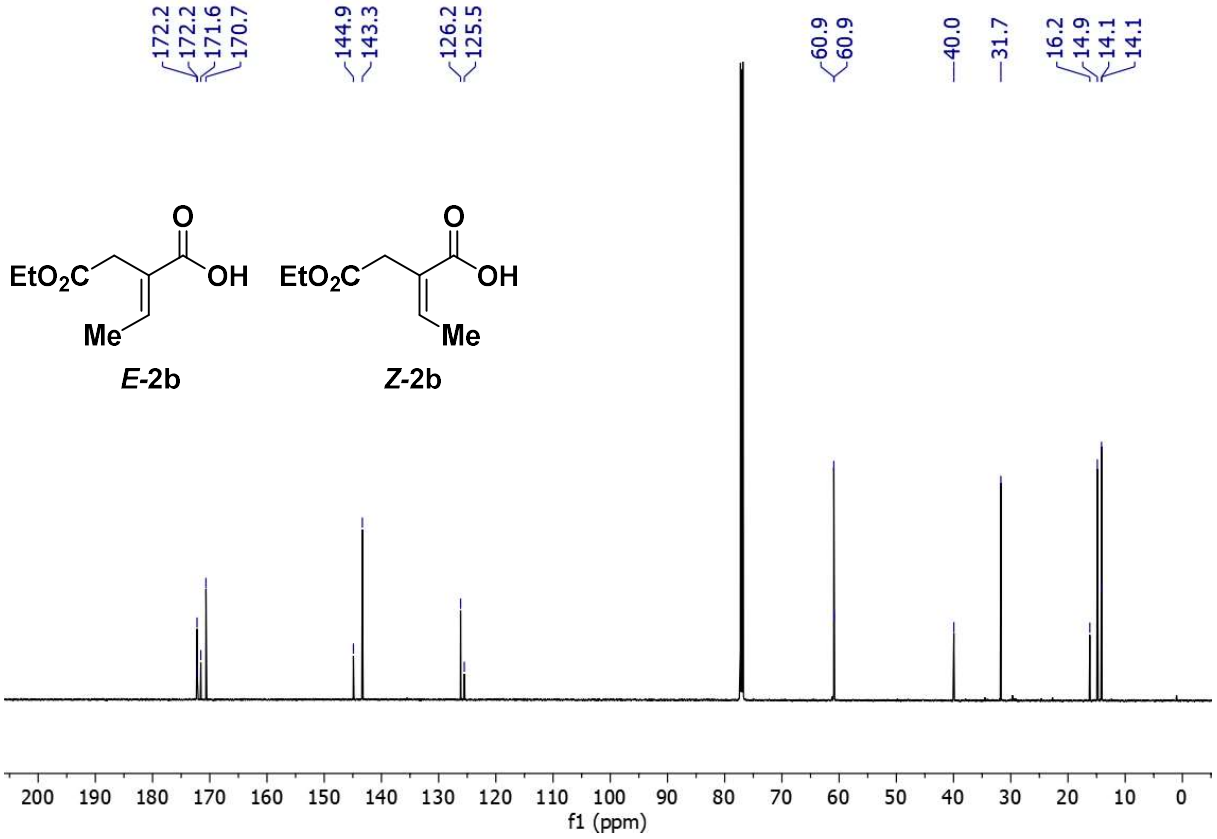
2a ^{13}C NMR (150 MHz, $CDCl_3$)



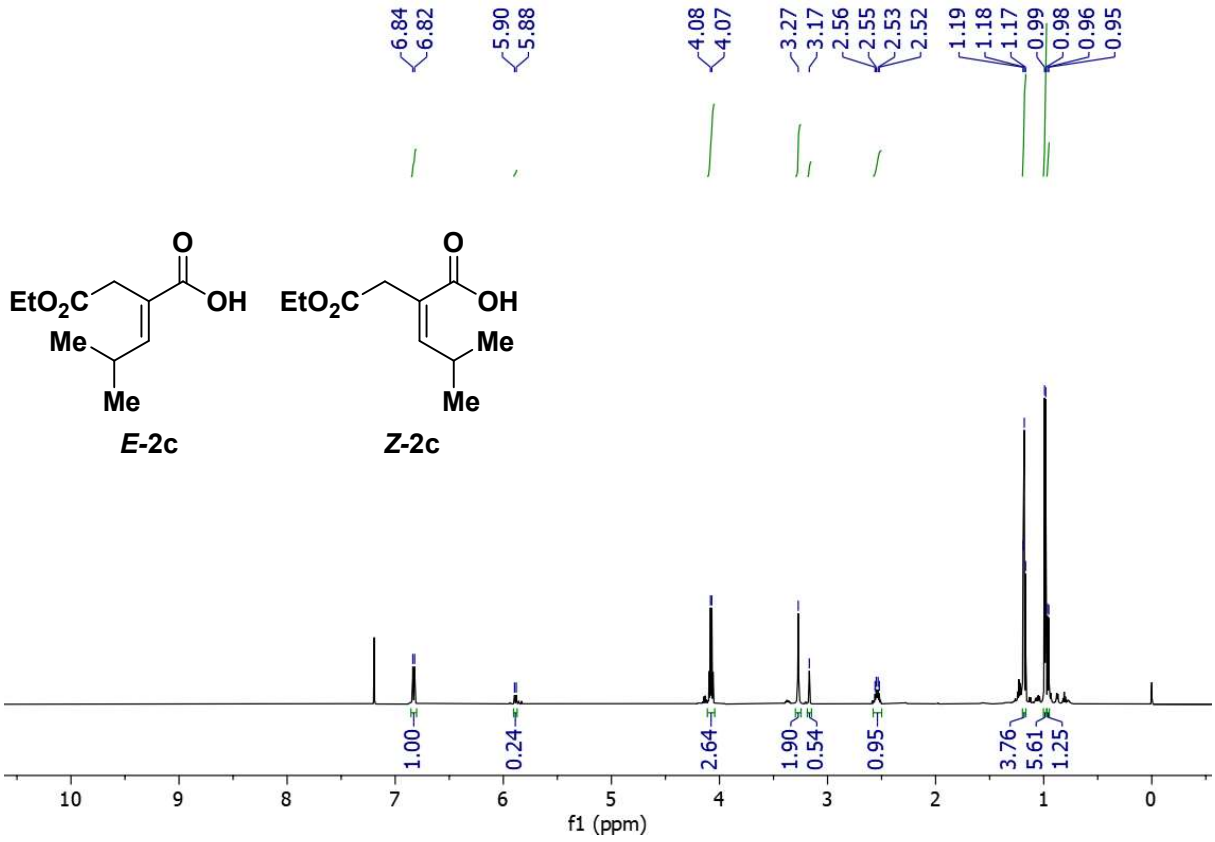
2b ^{1}H NMR (600 MHz, $CDCl_3$)



2b ^{13}C NMR (150 MHz, $CDCl_3$)



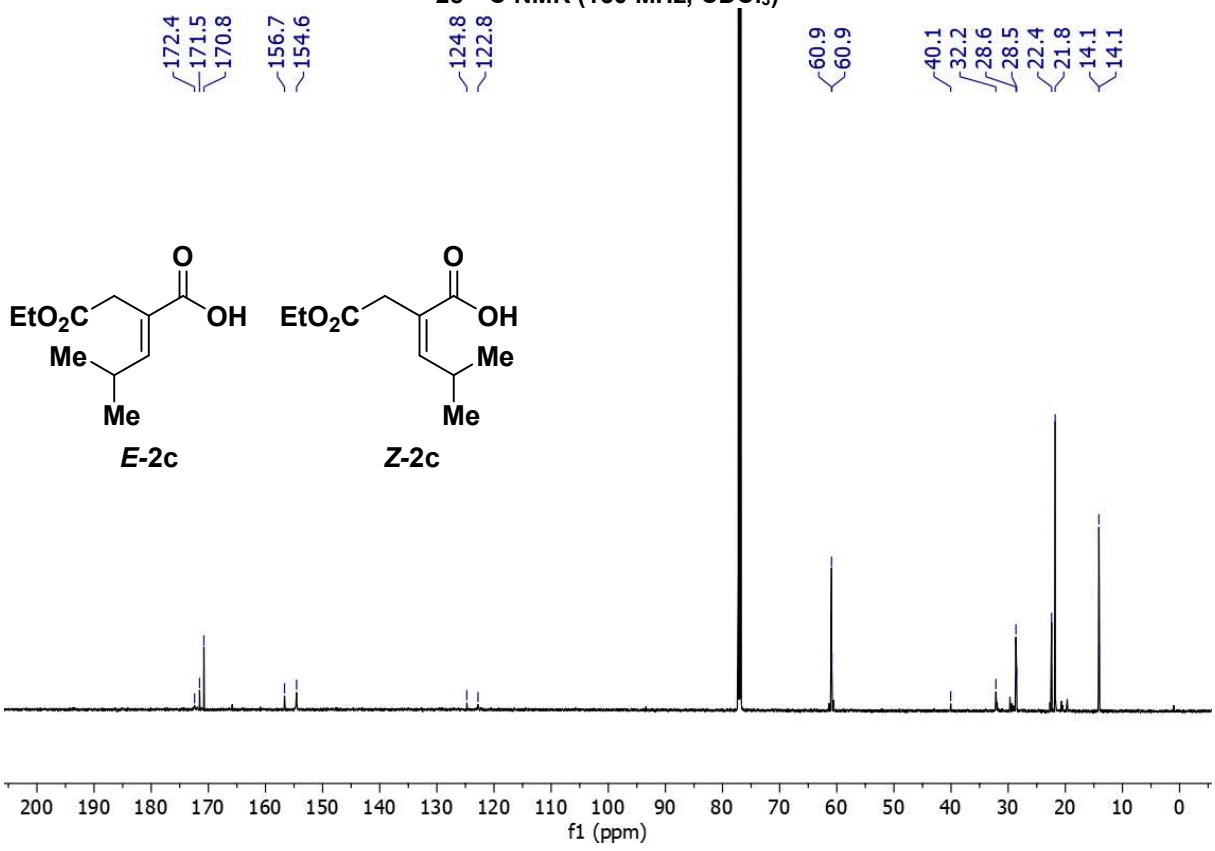
2c ^{1}H NMR (600 MHz, $CDCl_3$)



E-2c

Z-2c

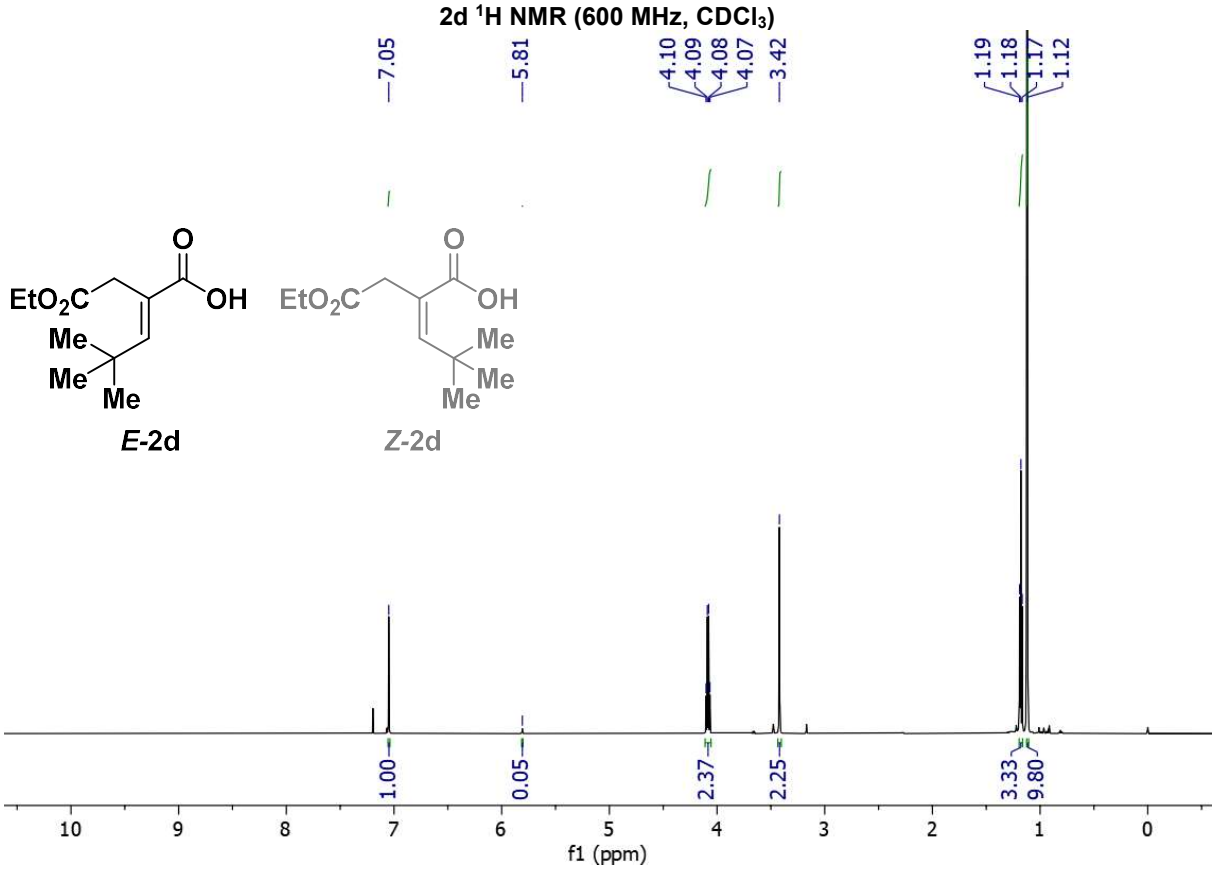
2c ^{13}C NMR (150 MHz, $CDCl_3$)



E-2c

Z-2c

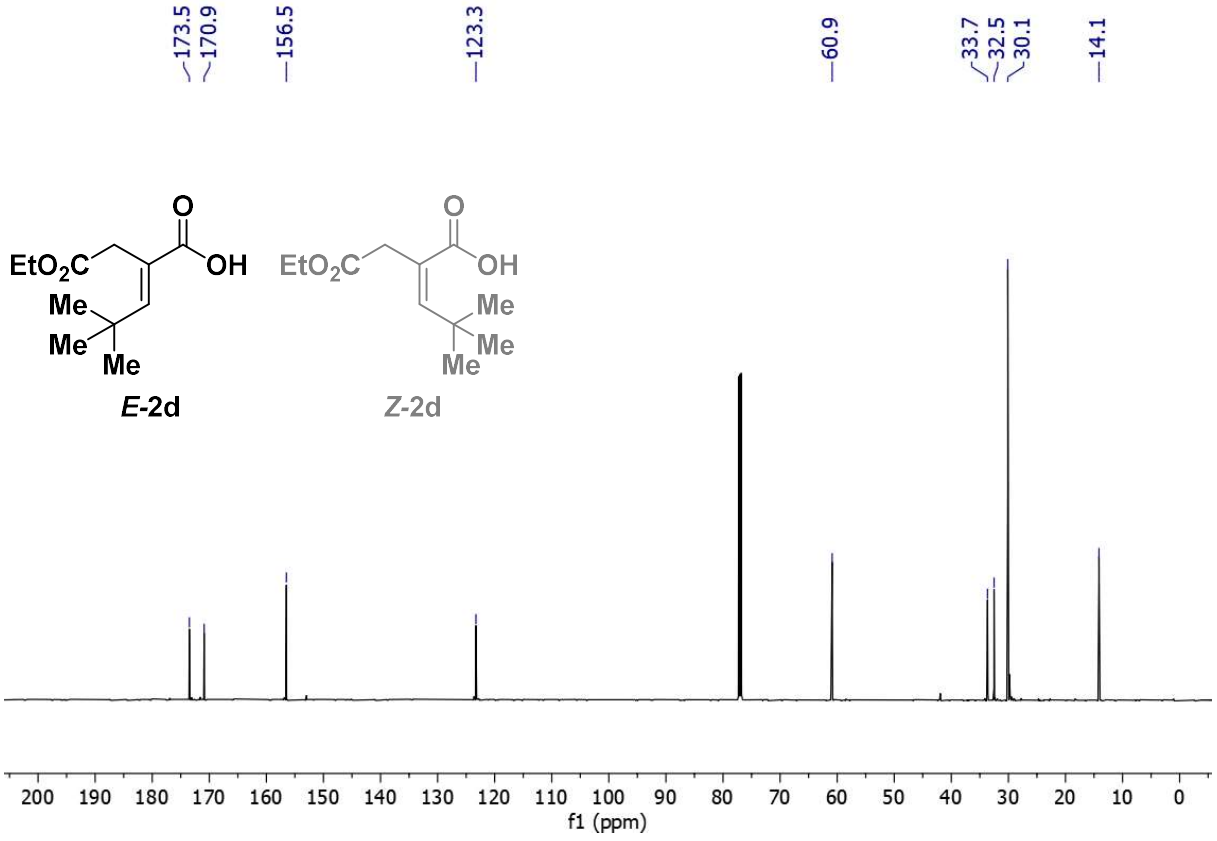
2d ^{1}H NMR (600 MHz, $CDCl_3$)



E-2d

Z-2d

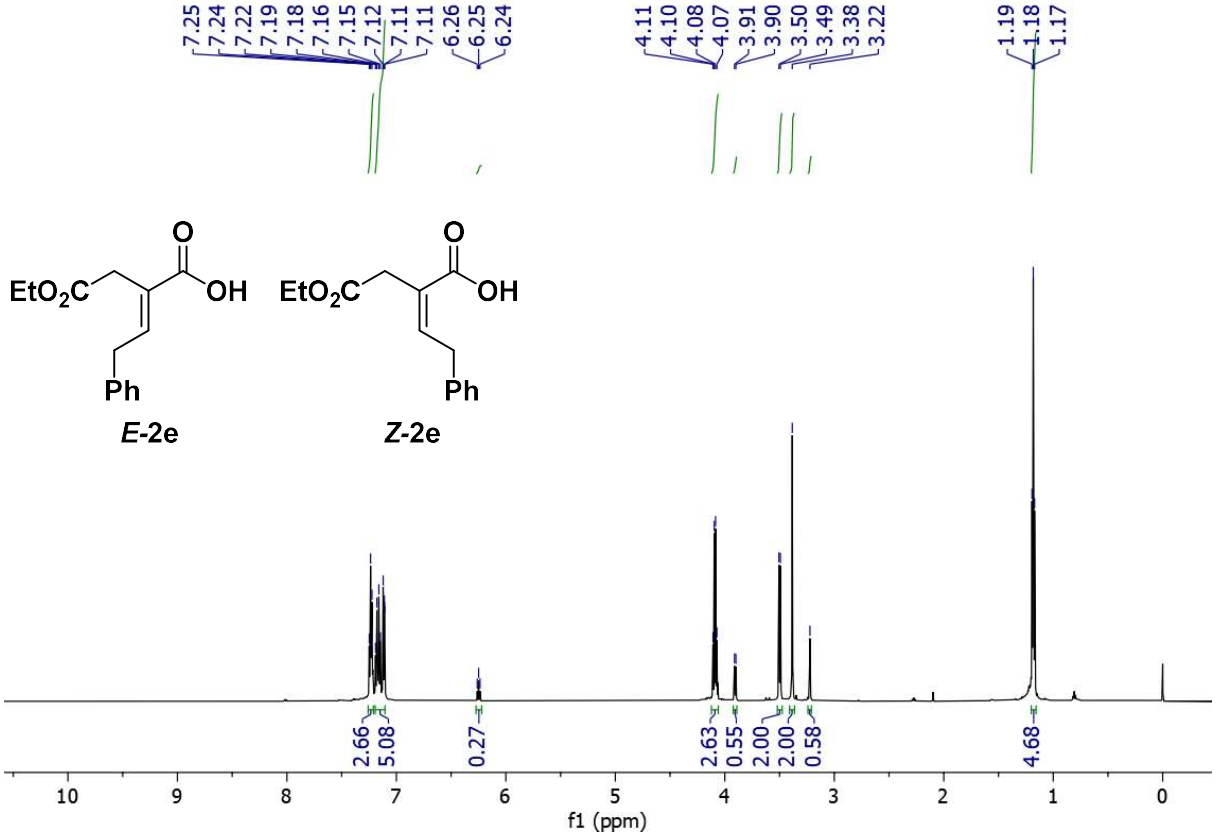
2d ^{13}C NMR (150 MHz, $CDCl_3$)



E-2d

Z-2d

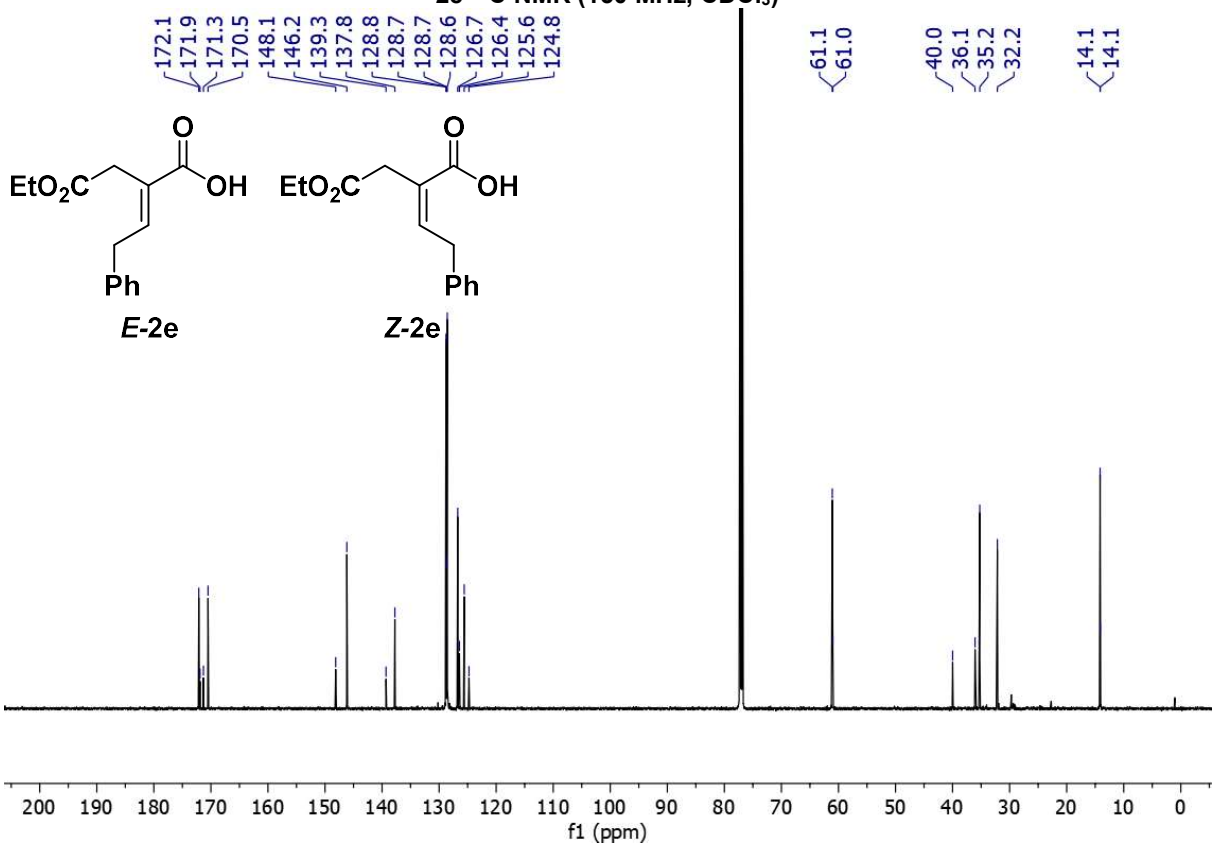
2e ^{1}H NMR (600 MHz, $CDCl_3$)



E-2e

Z-2e

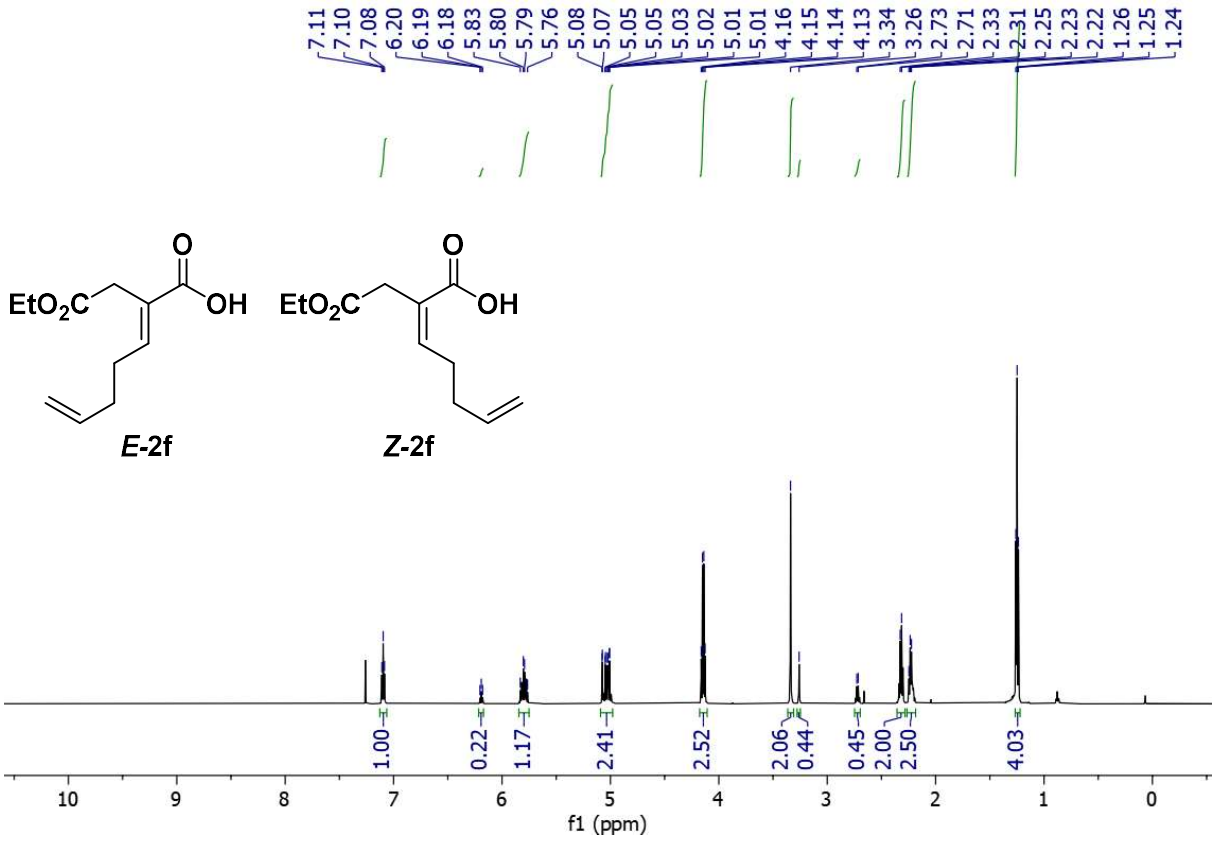
2e ^{13}C NMR (150 MHz, $CDCl_3$)



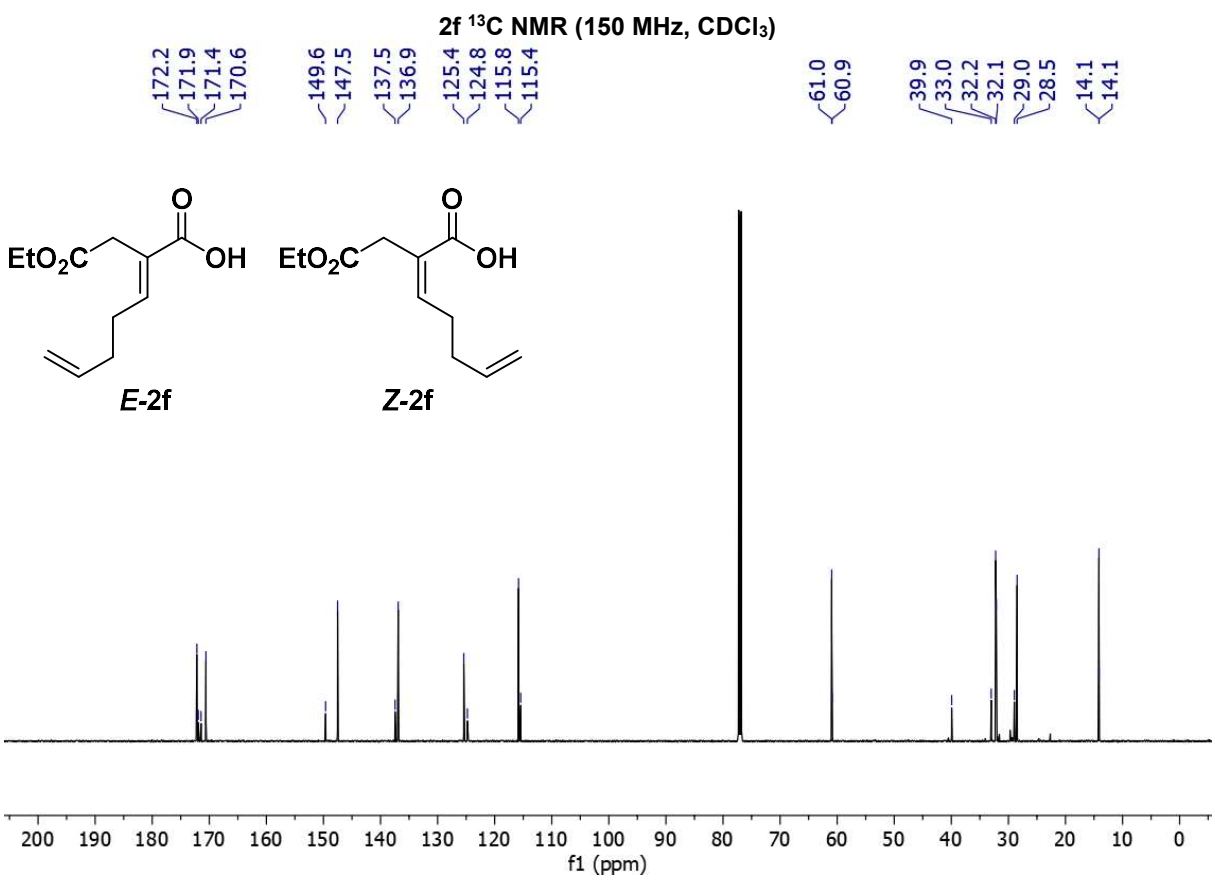
E-2e

Z-2e

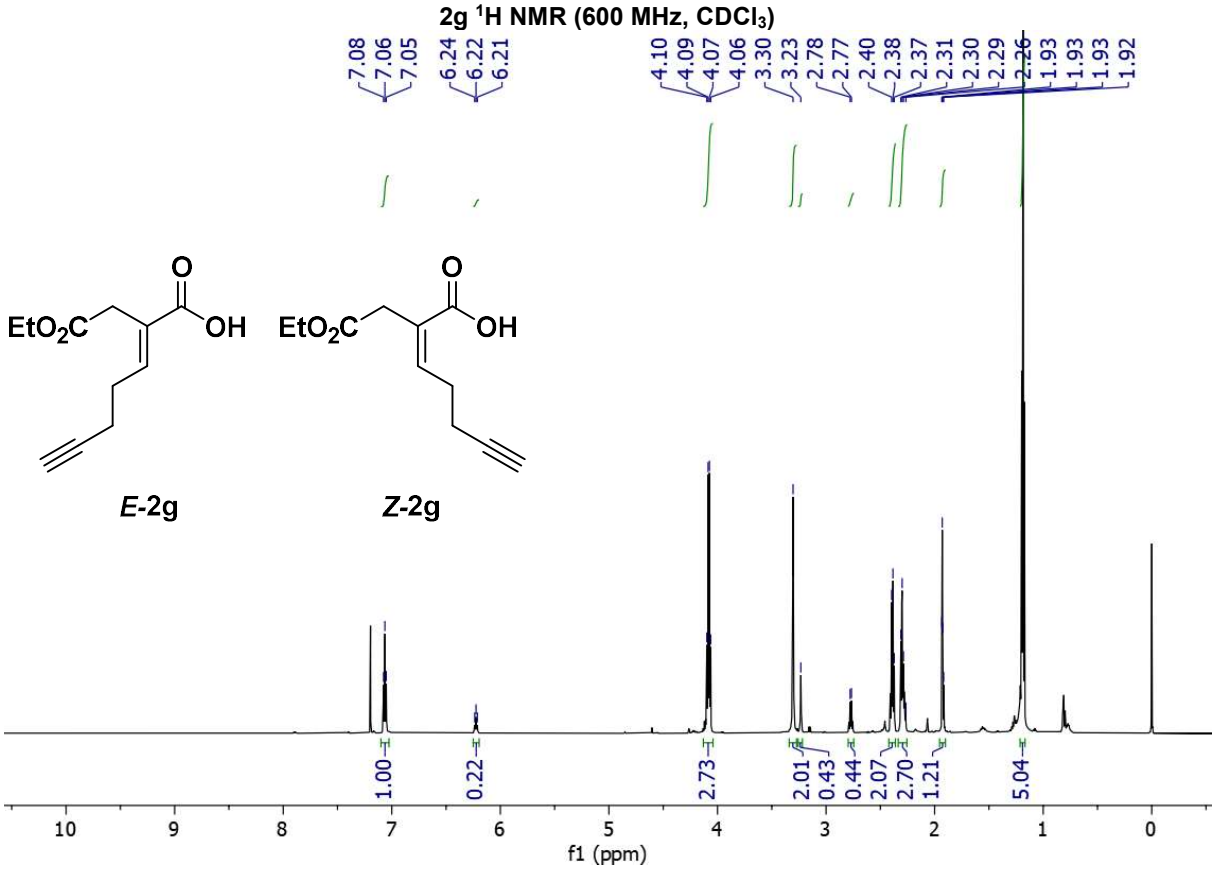
2f ^{1}H NMR (600 MHz, $CDCl_3$)



2f ^{13}C NMR (150 MHz, $CDCl_3$)

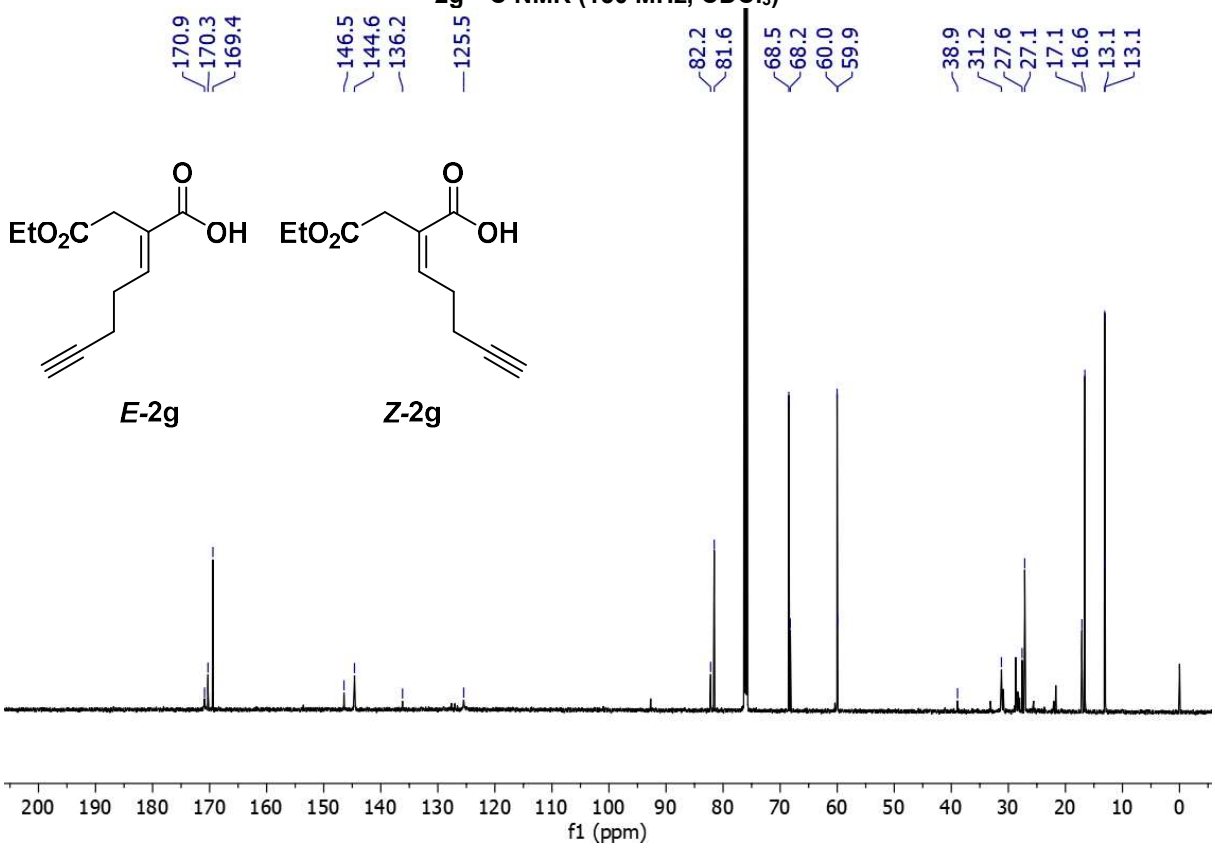


2g ^{1}H NMR (600 MHz, $CDCl_3$)



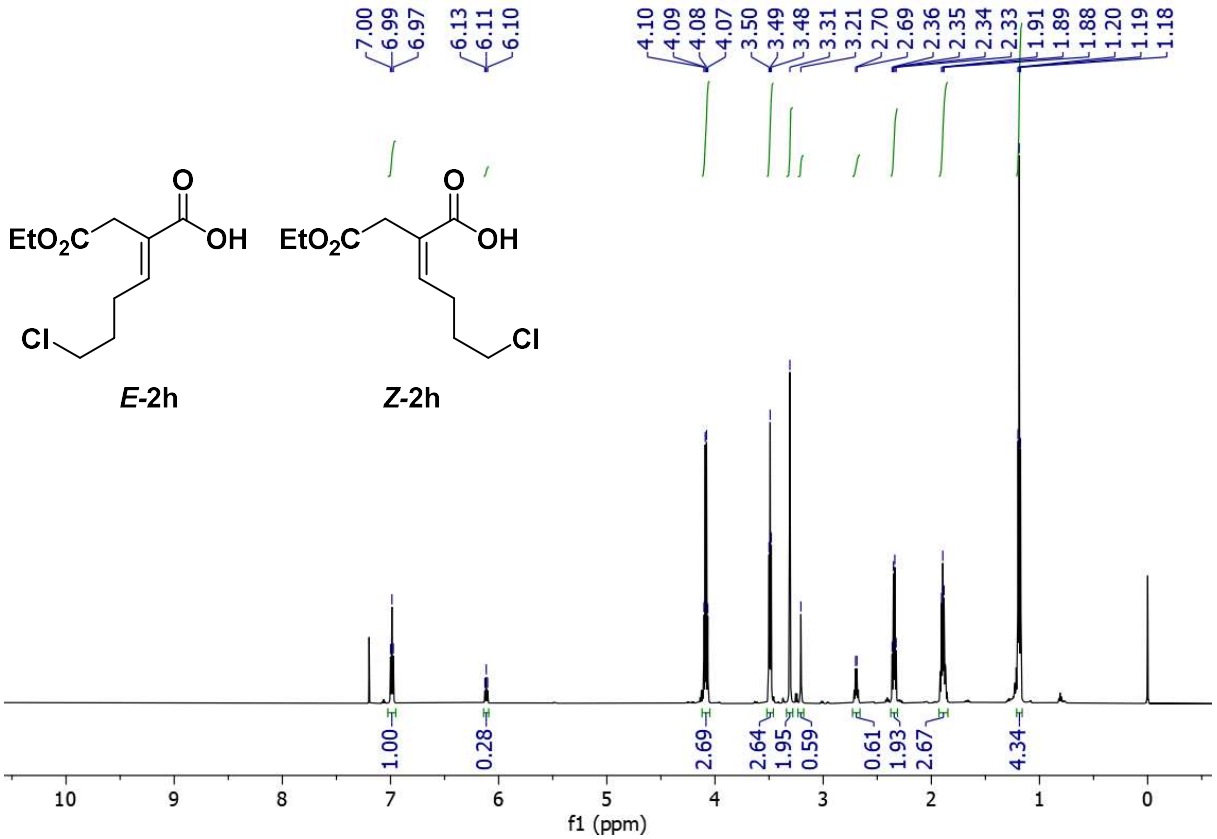
E-2g *Z*-2g

2g ^{13}C NMR (150 MHz, $CDCl_3$)



E-2g *Z*-2g

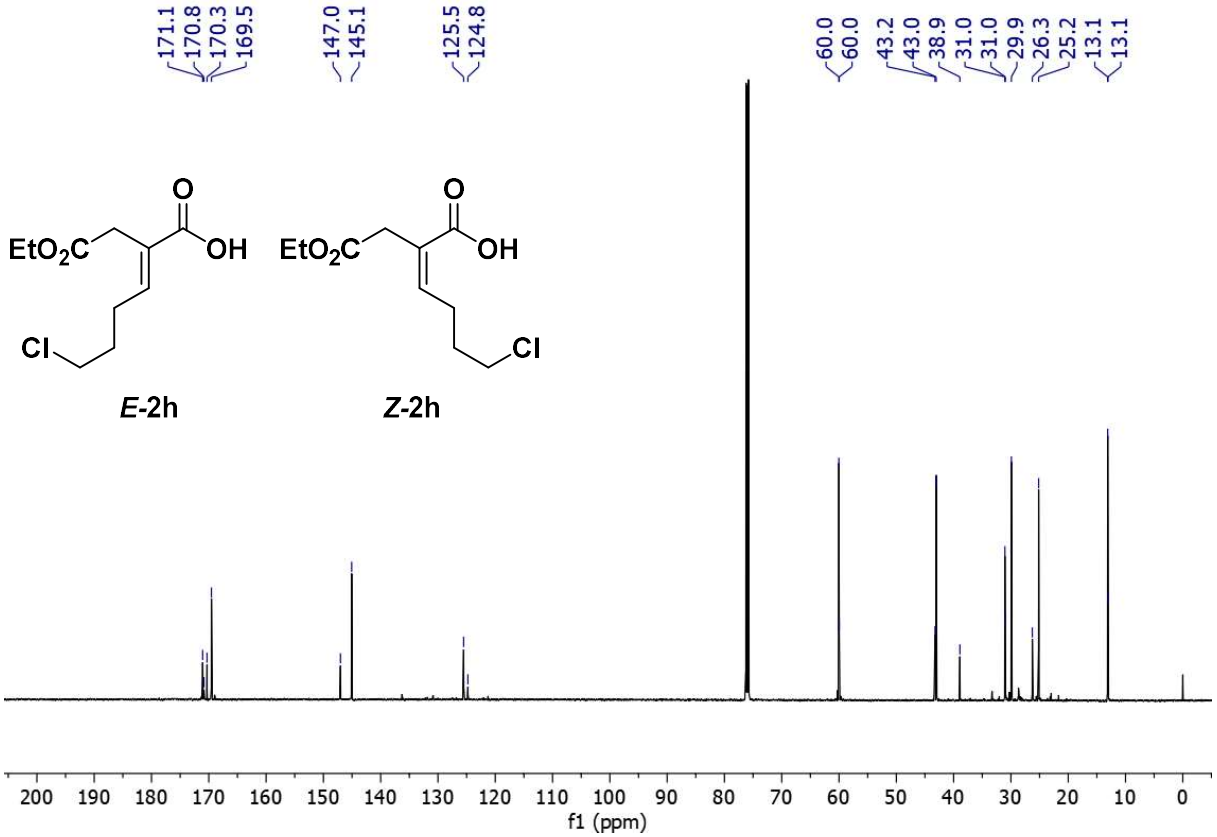
2h ^{1}H NMR (600 MHz, $CDCl_3$)



E-2h

Z-2h

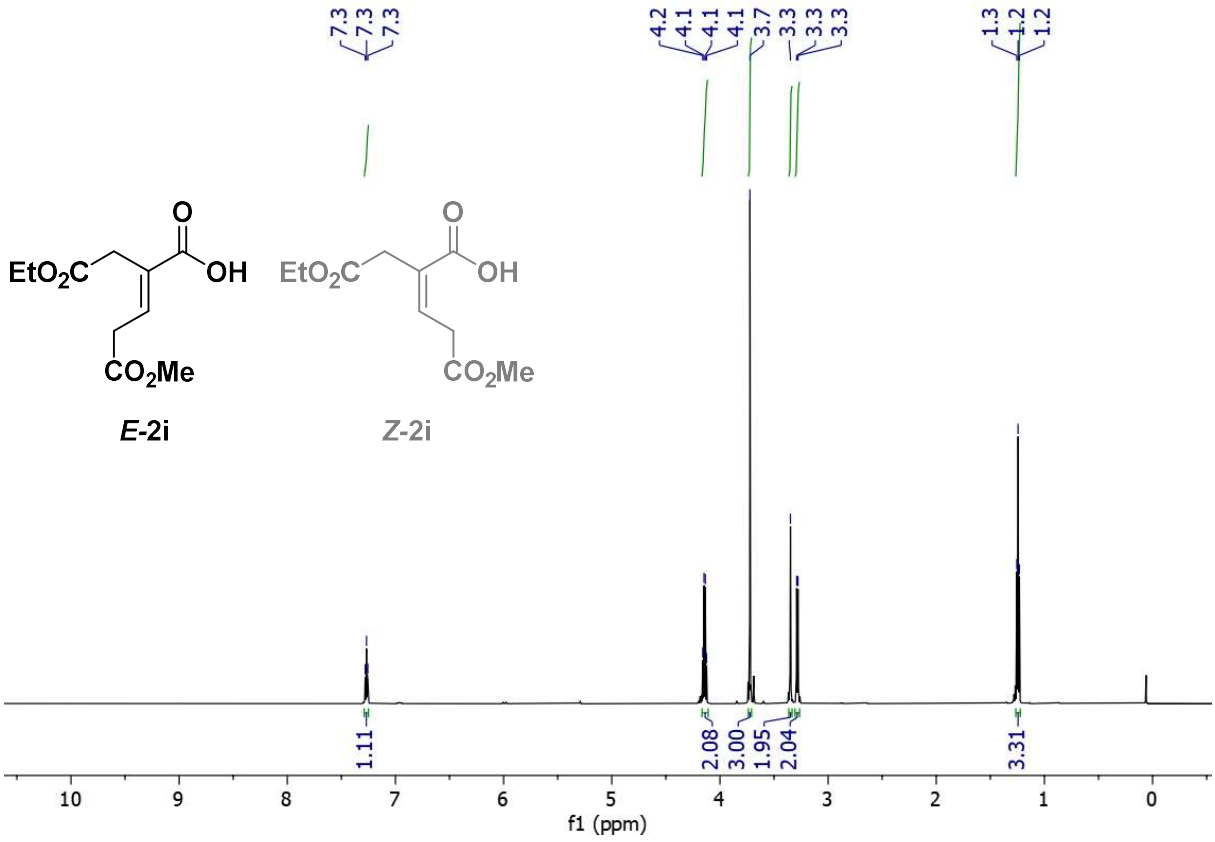
2h ^{13}C NMR (150 MHz, $CDCl_3$)



E-2h

Z-2h

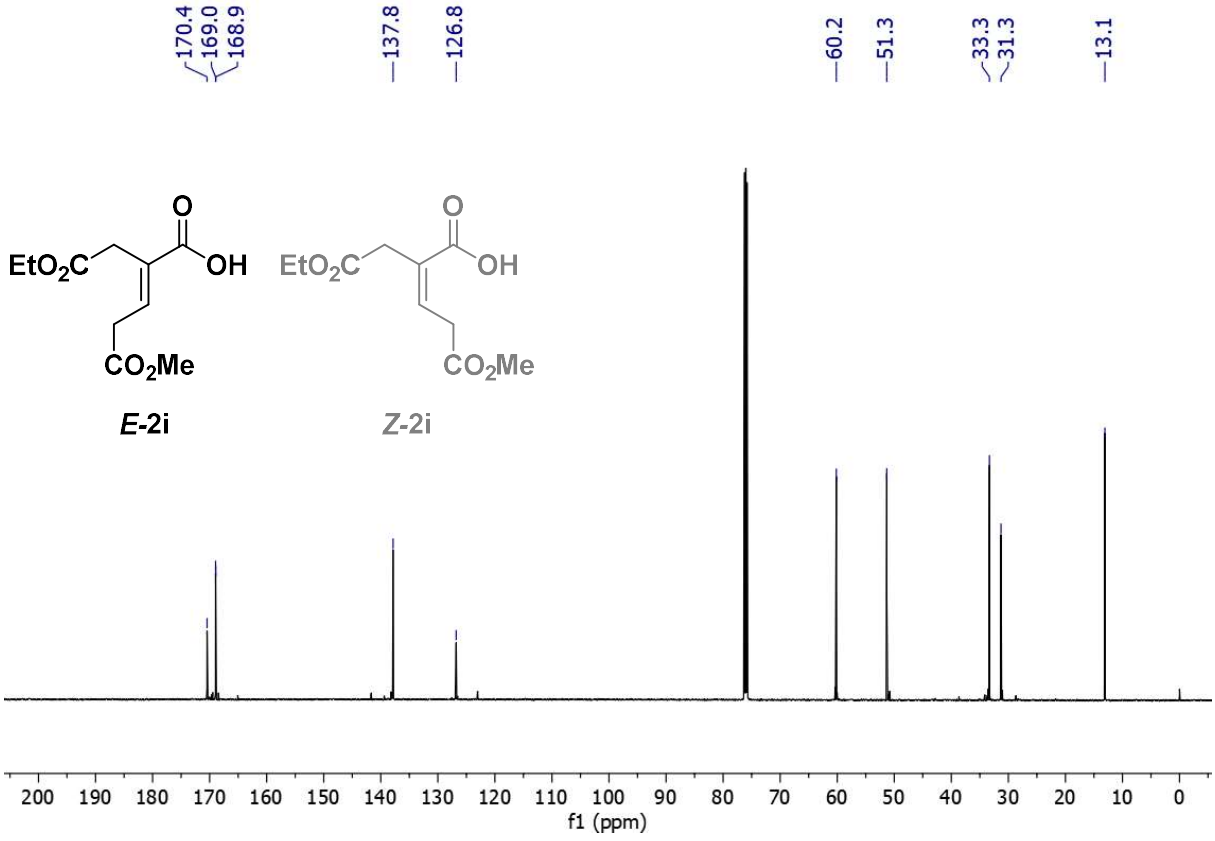
2i ^{1}H NMR (600 MHz, $CDCl_3$)



E-2i

Z-2i

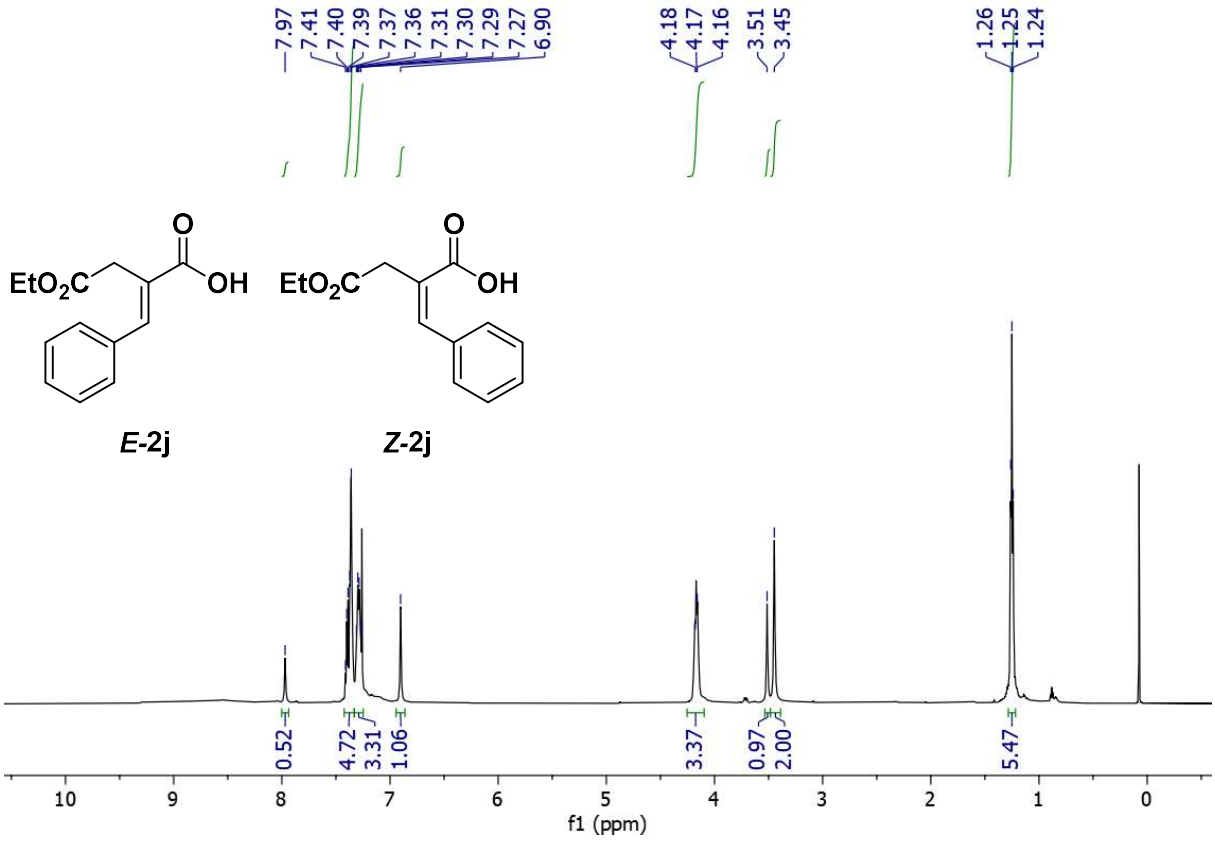
2i ^{13}C NMR (150 MHz, $CDCl_3$)



E-2i

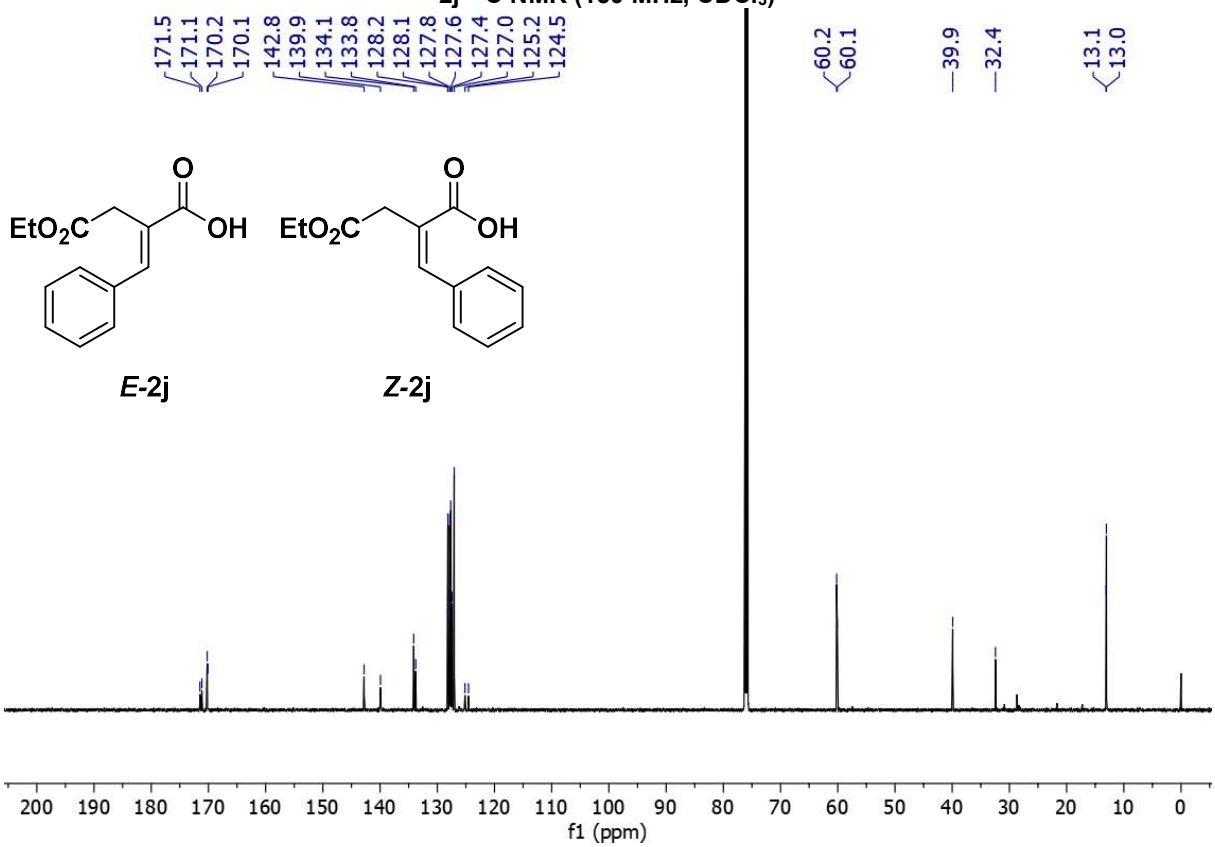
Z-2i

2j ^{1}H NMR (600 MHz, $CDCl_3$)



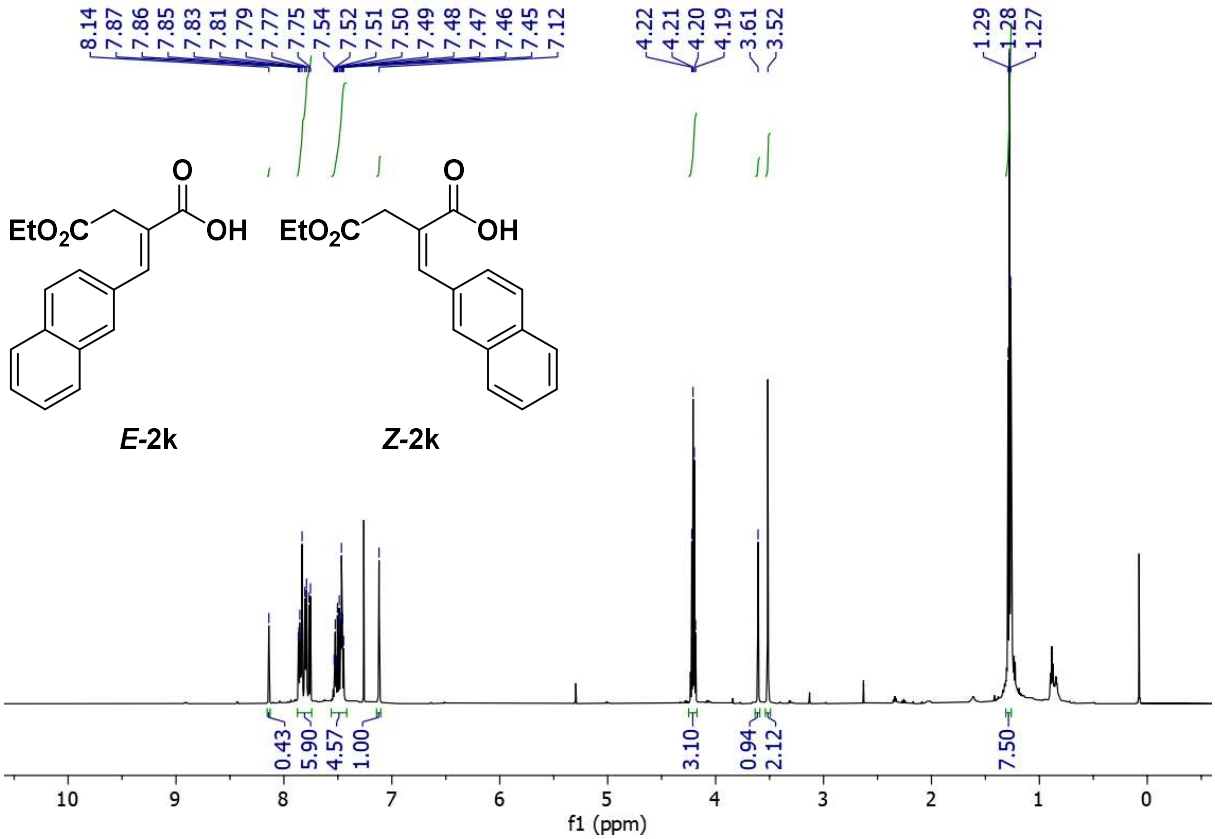
E-2j *Z*-2j

2j ^{13}C NMR (150 MHz, $CDCl_3$)

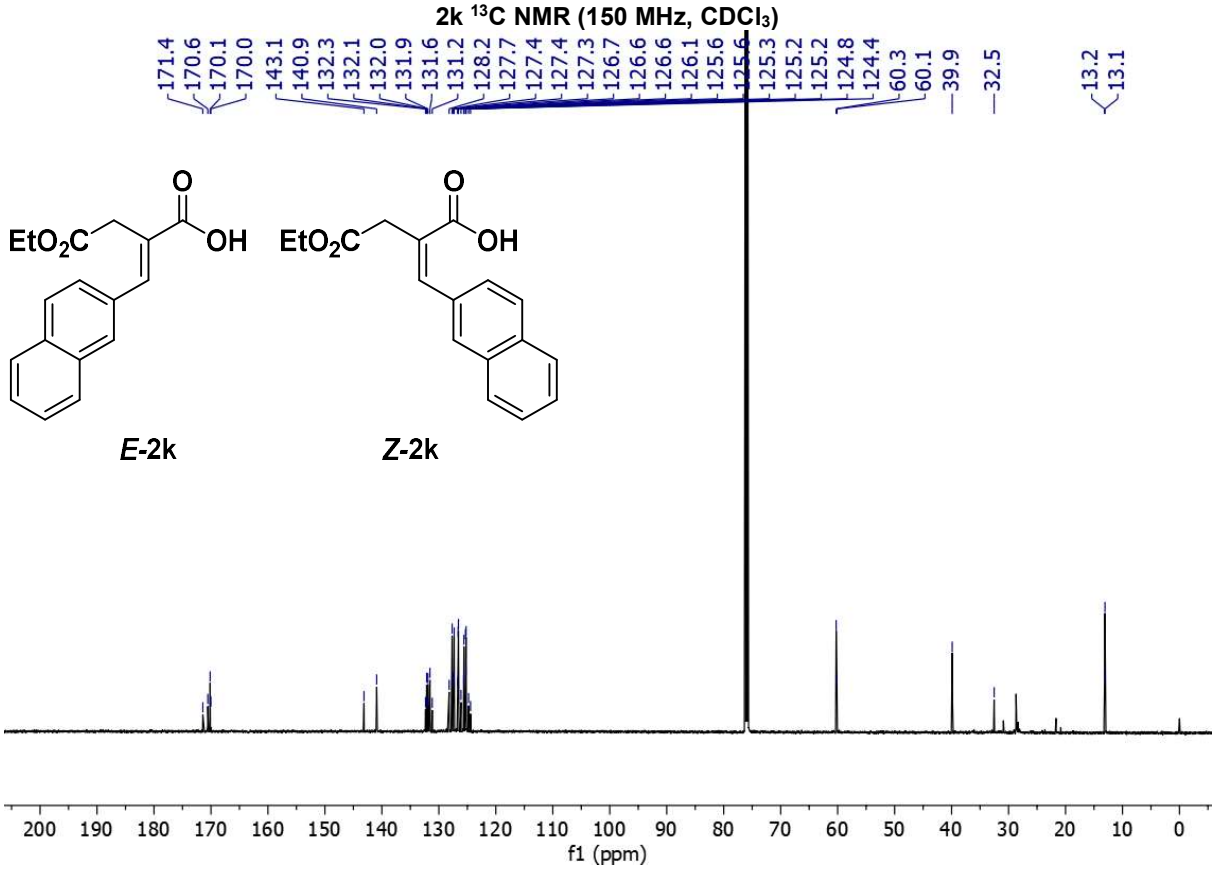


E-2j *Z*-2j

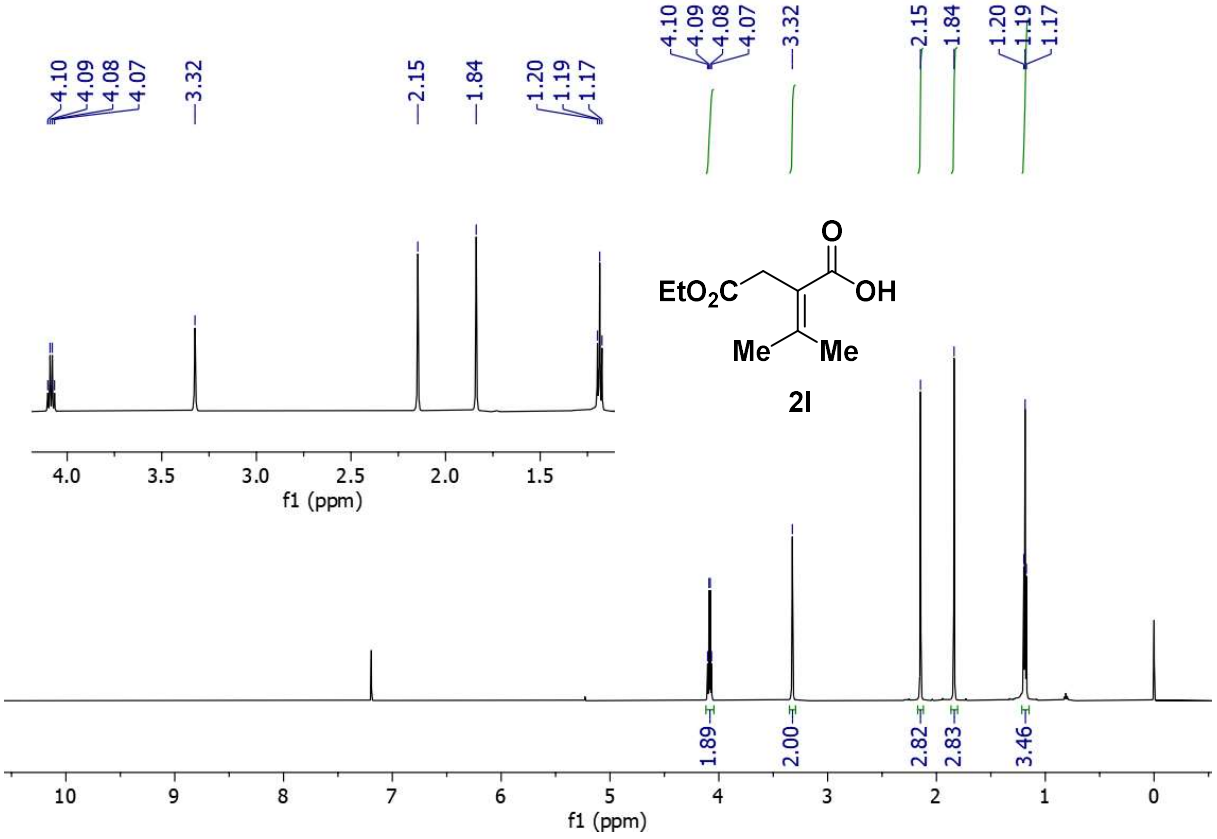
2k ^{1}H NMR (600 MHz, $CDCl_3$)



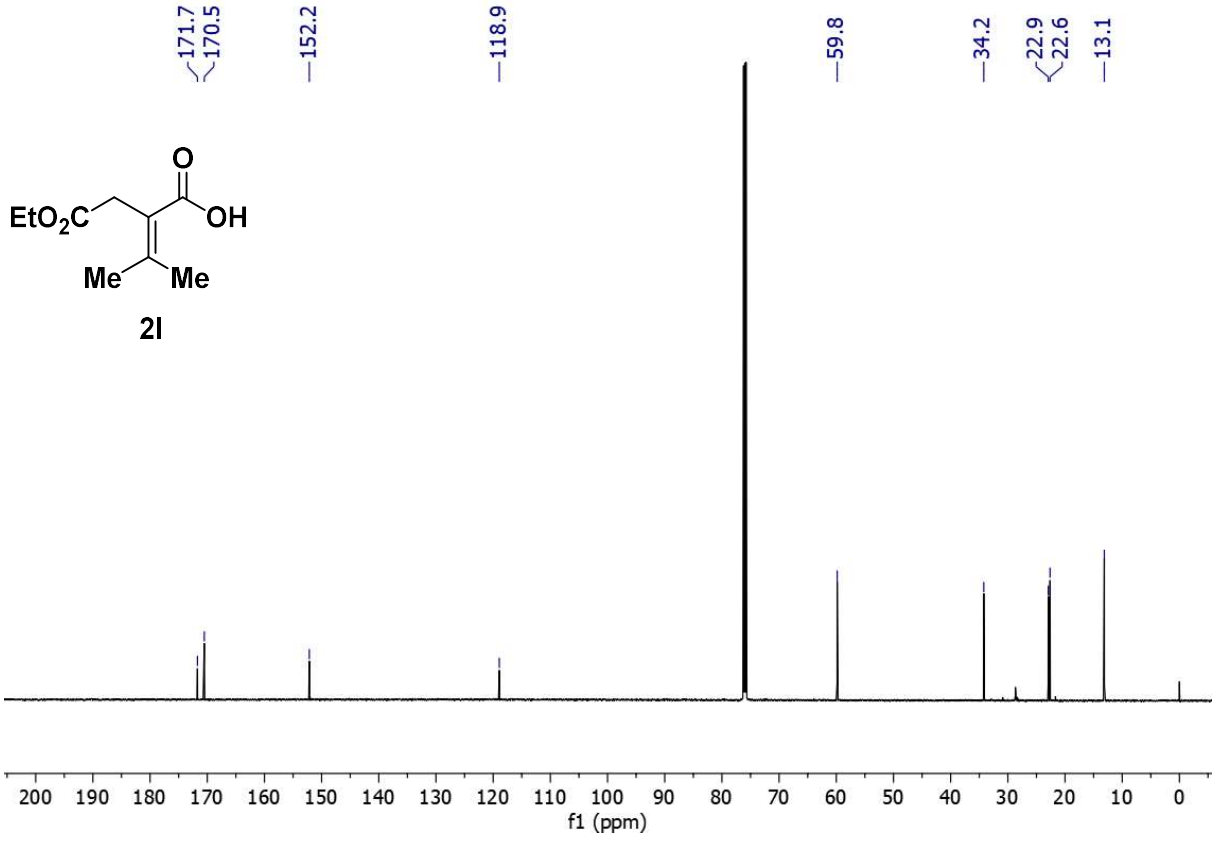
2k ^{13}C NMR (150 MHz, $CDCl_3$)



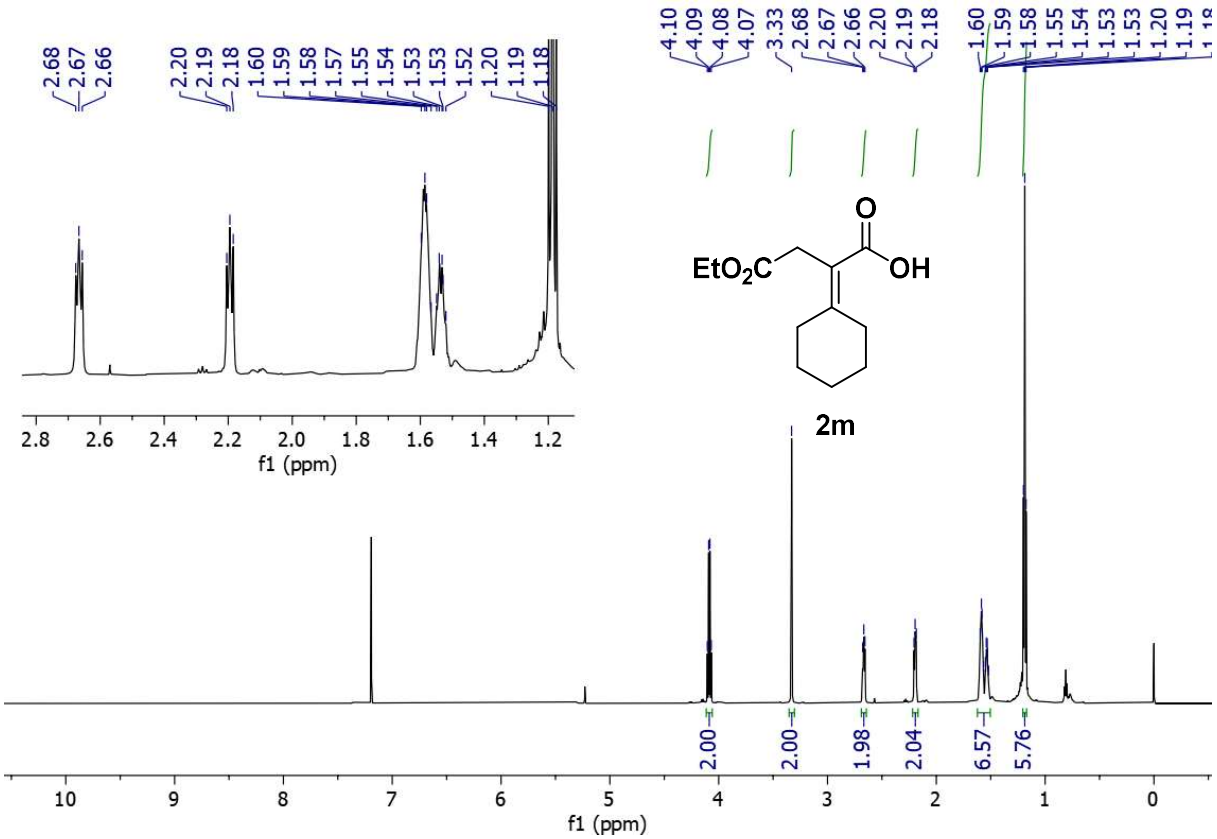
2l ^{1}H NMR (600 MHz, $CDCl_3$)



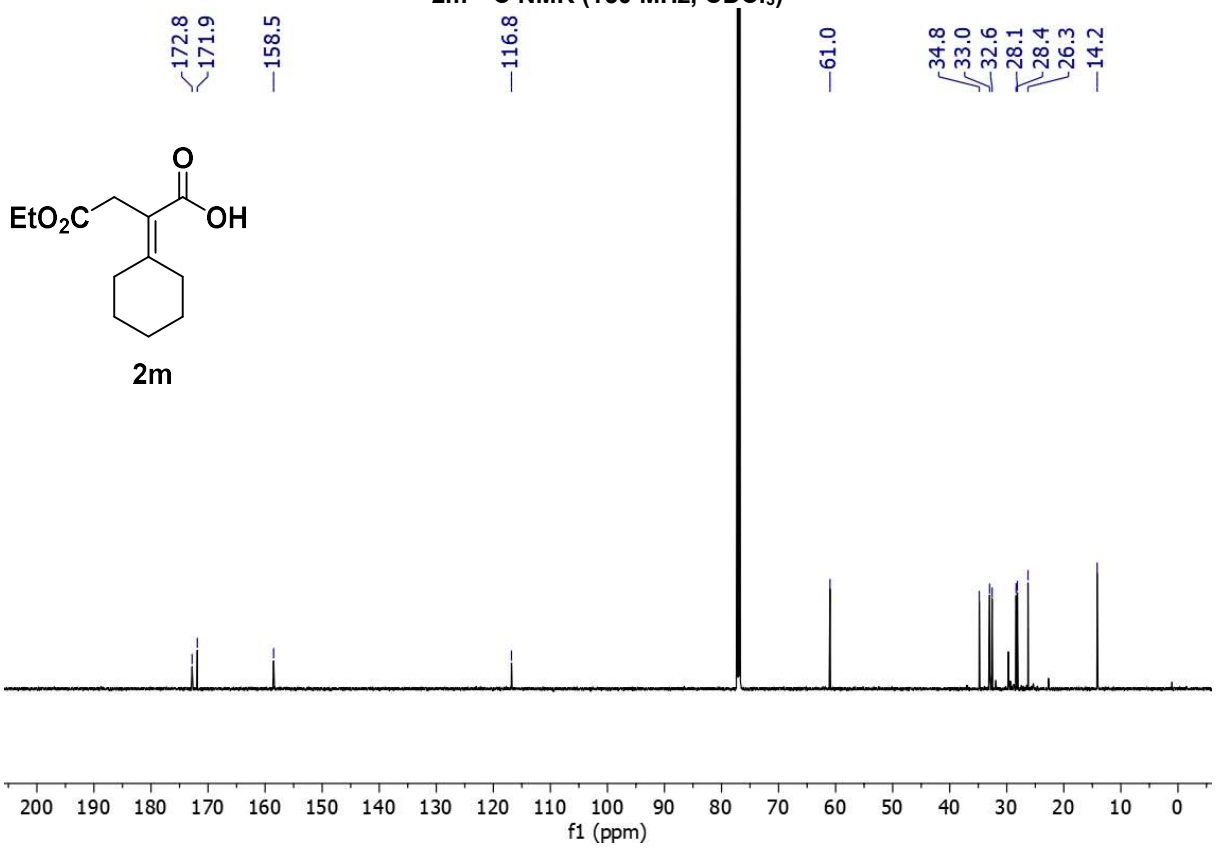
2l ^{13}C NMR (150 MHz, $CDCl_3$)



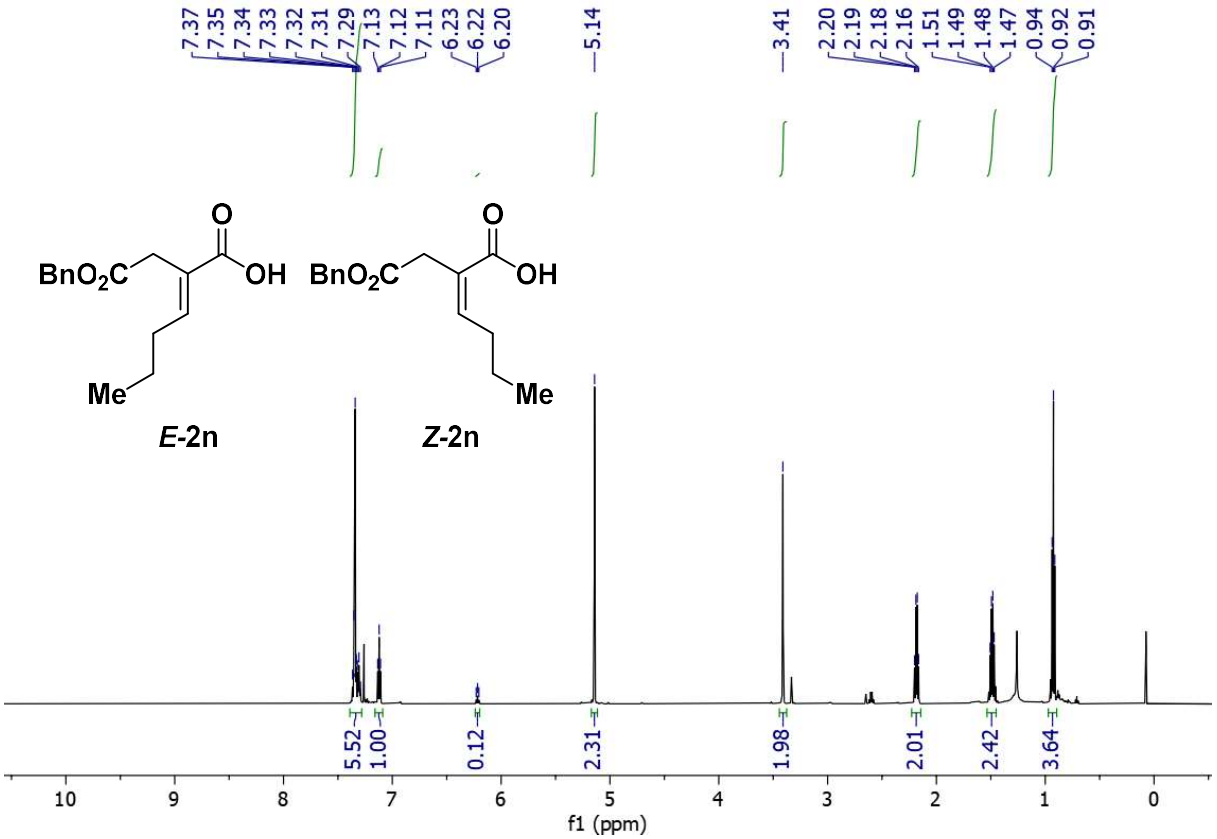
2m ^{1}H NMR (600 MHz, $CDCl_3$)



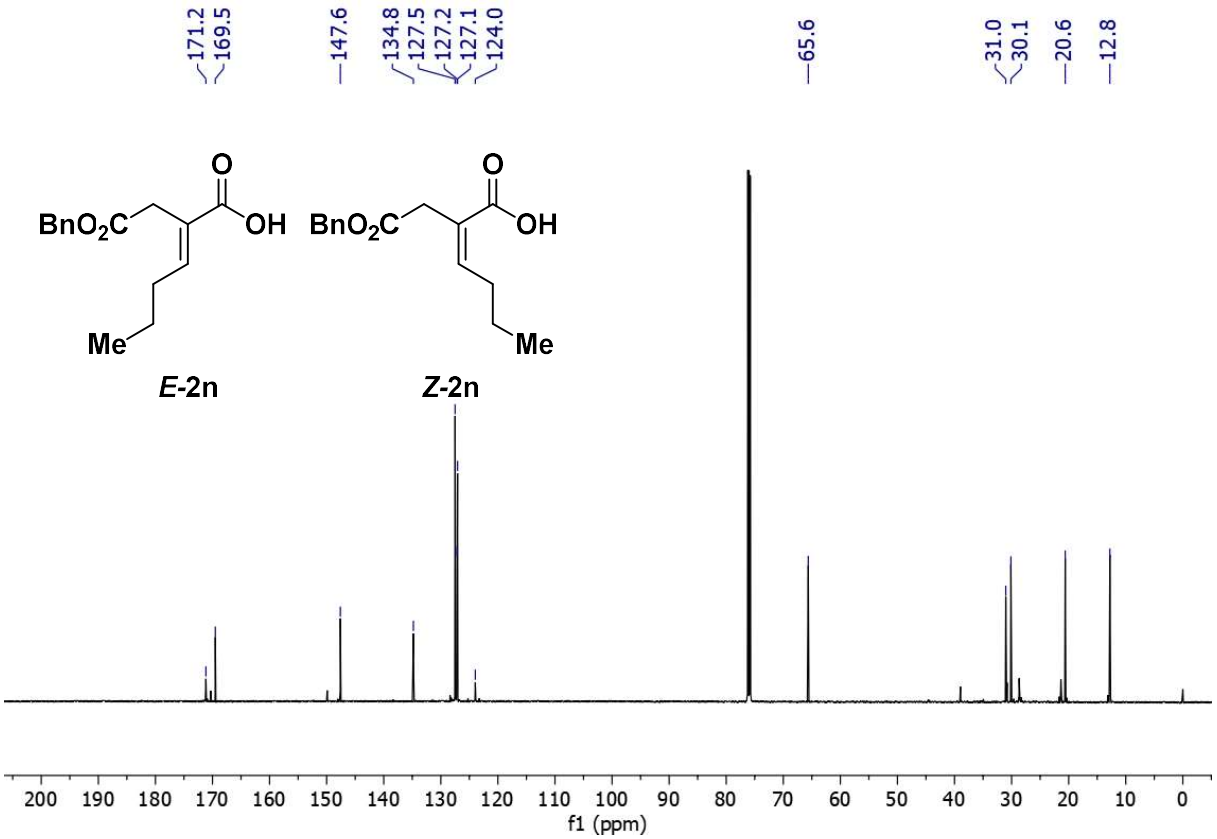
2m ^{13}C NMR (150 MHz, $CDCl_3$)



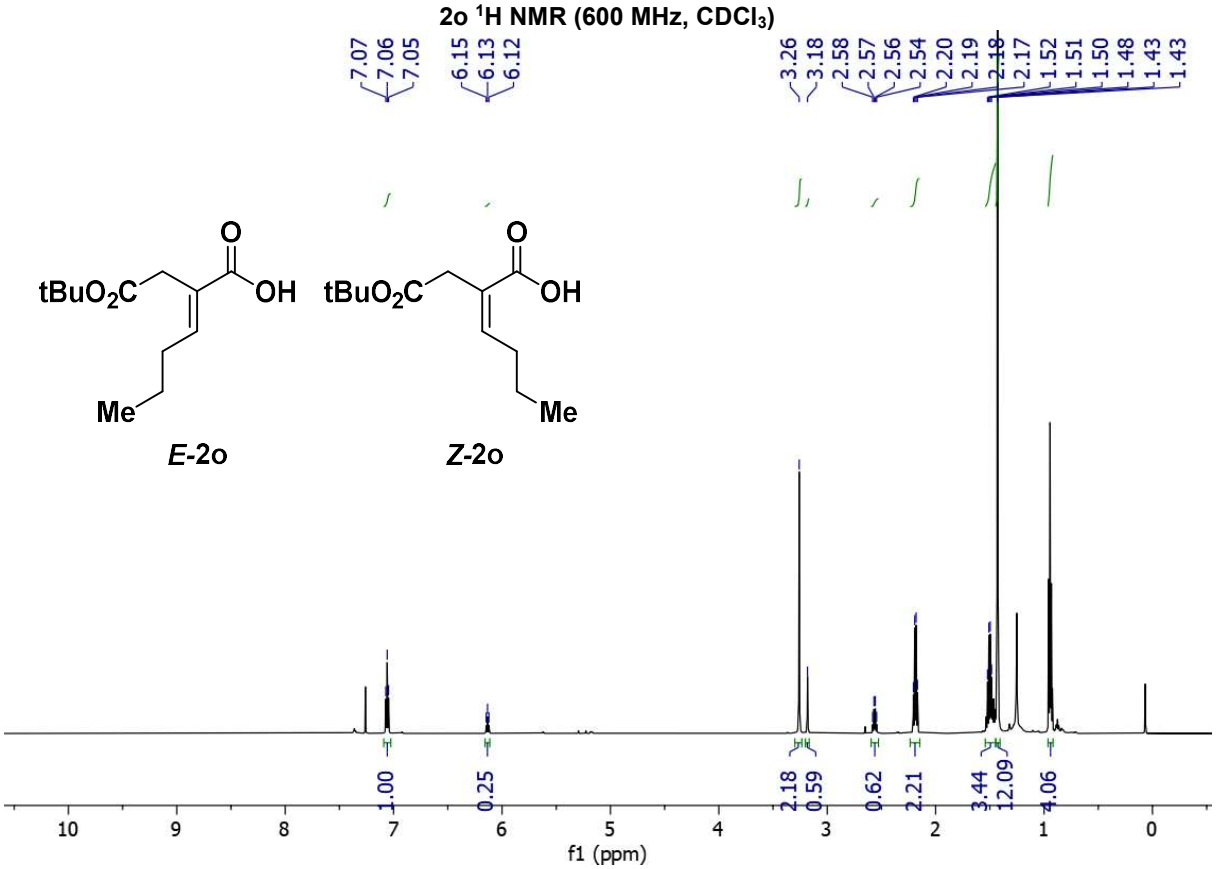
2n ^{1}H NMR (600 MHz, $CDCl_3$)



2n ^{13}C NMR (150 MHz, $CDCl_3$)



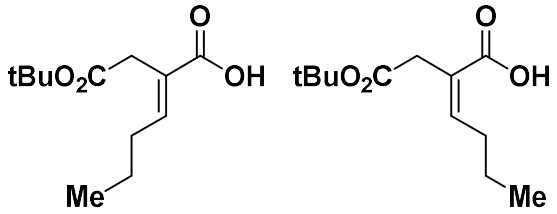
2o ^{1}H NMR (600 MHz, $CDCl_3$)



E-2o

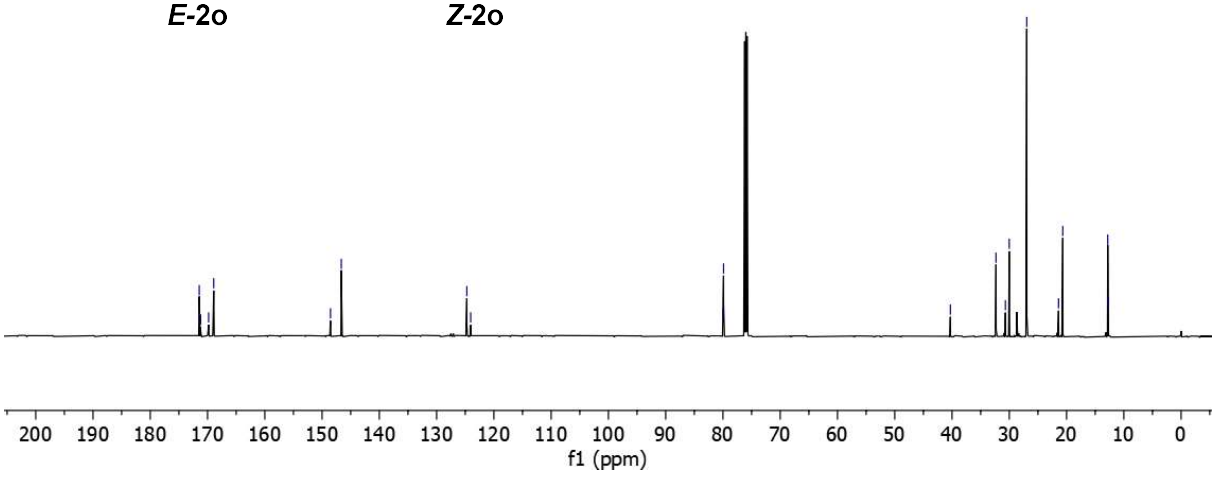
Z-2o

2o ^{13}C NMR (150 MHz, $CDCl_3$)

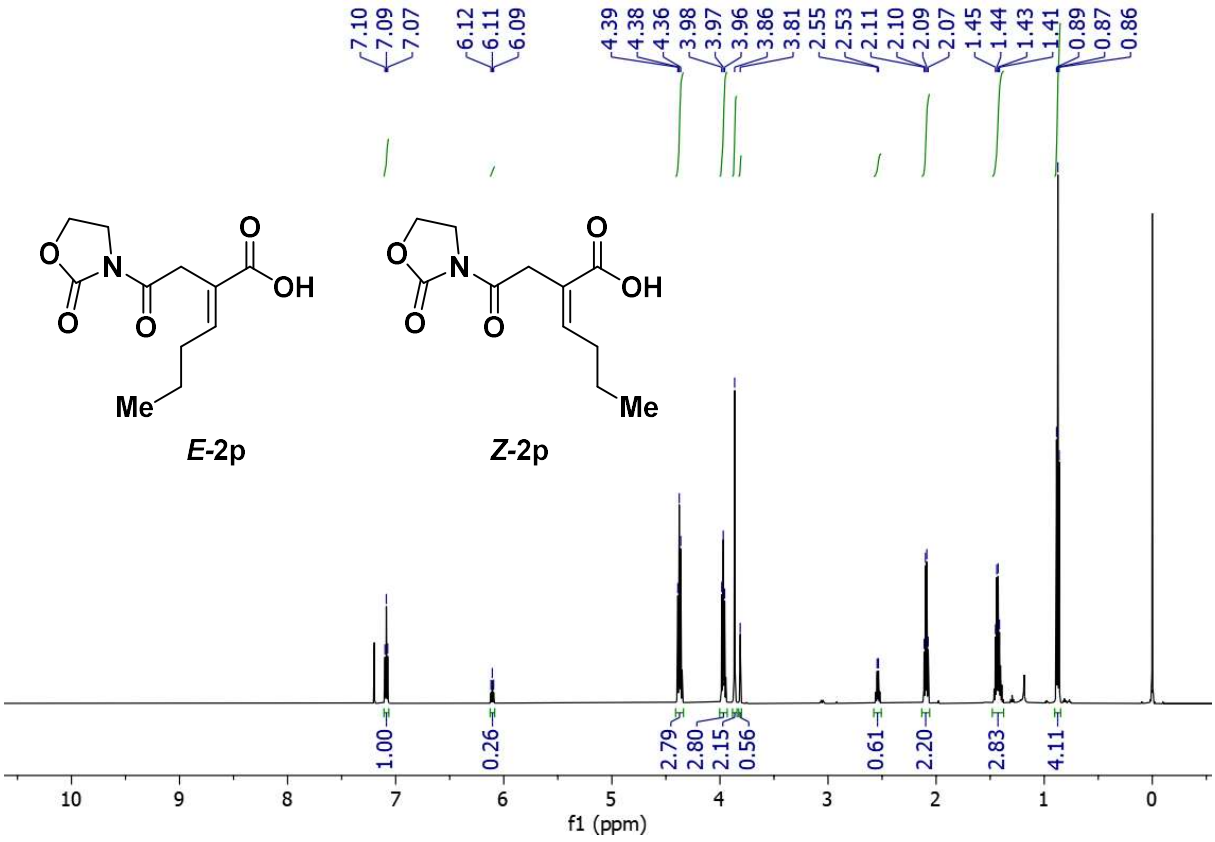


E-2o

Z-2o



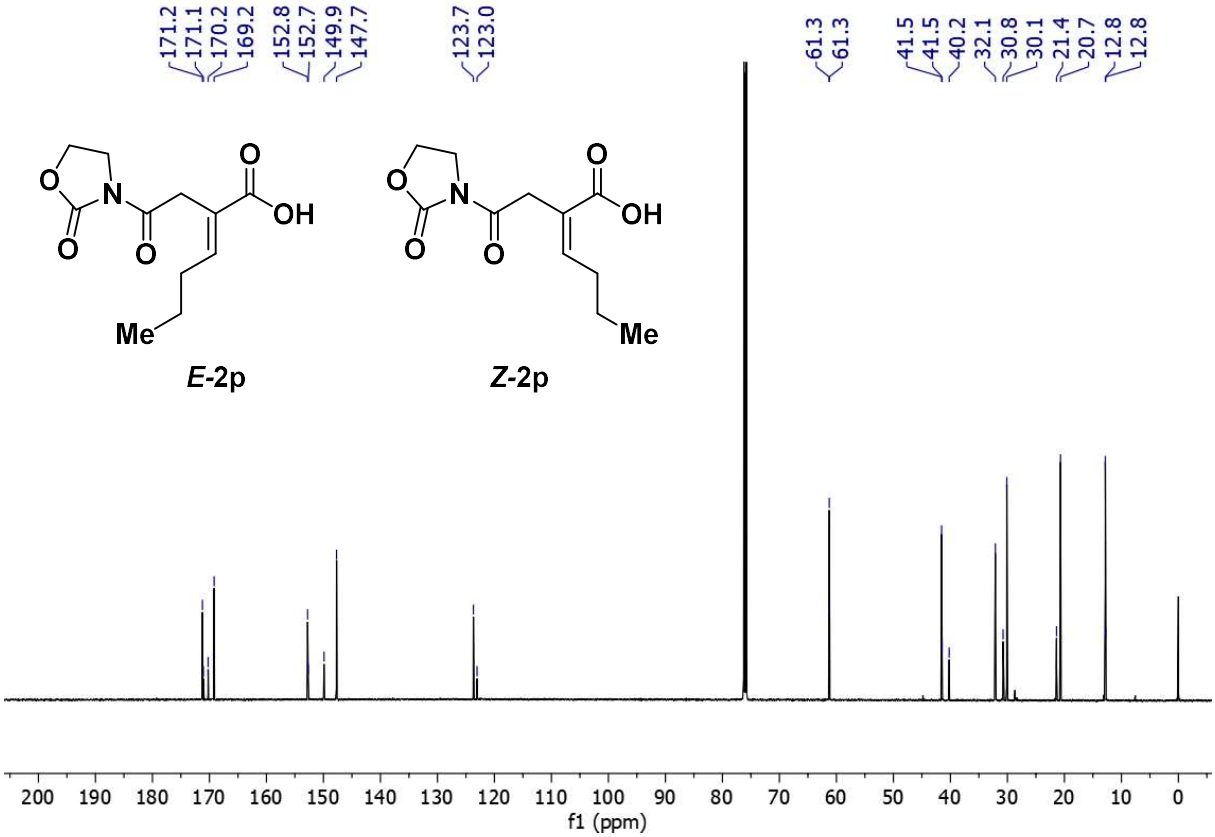
2p ^{1}H NMR (600 MHz, $CDCl_3$)



E-2p

Z-2p

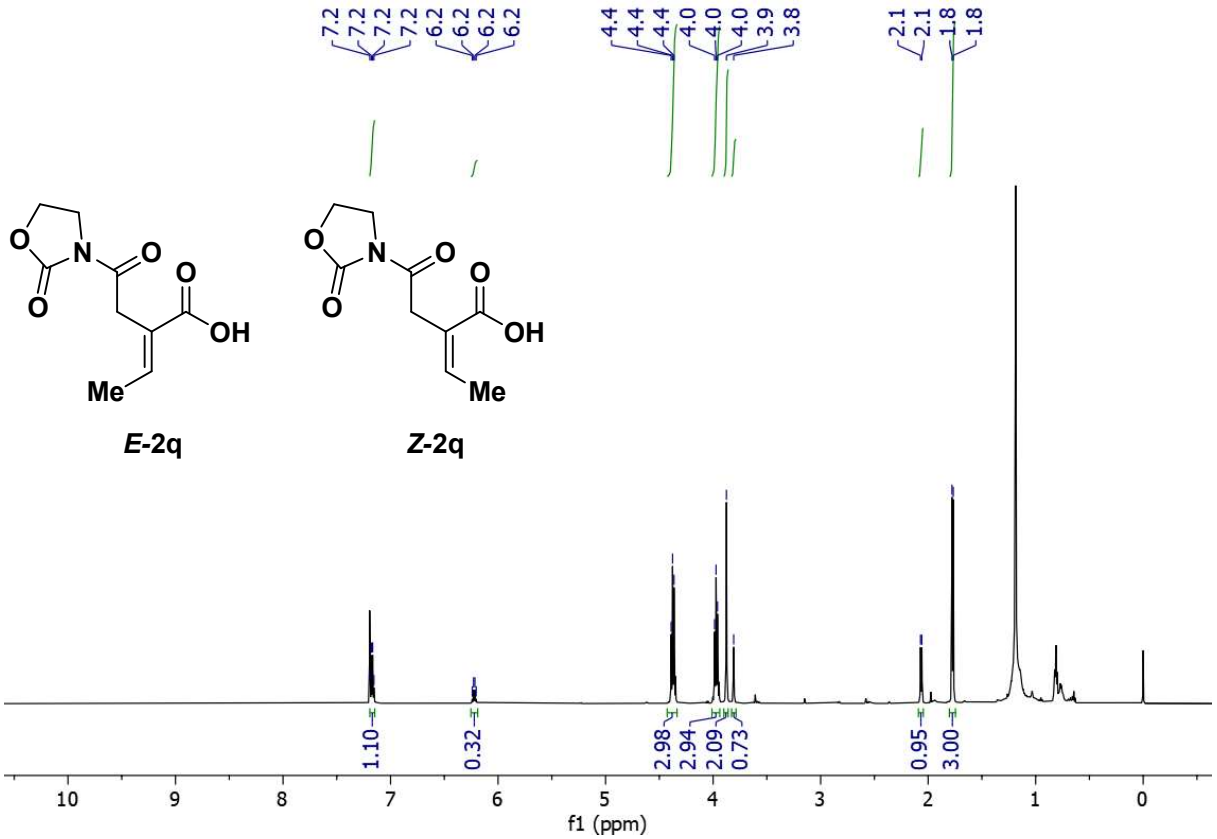
2p ^{13}C NMR (150 MHz, $CDCl_3$)



E-2p

Z-2p

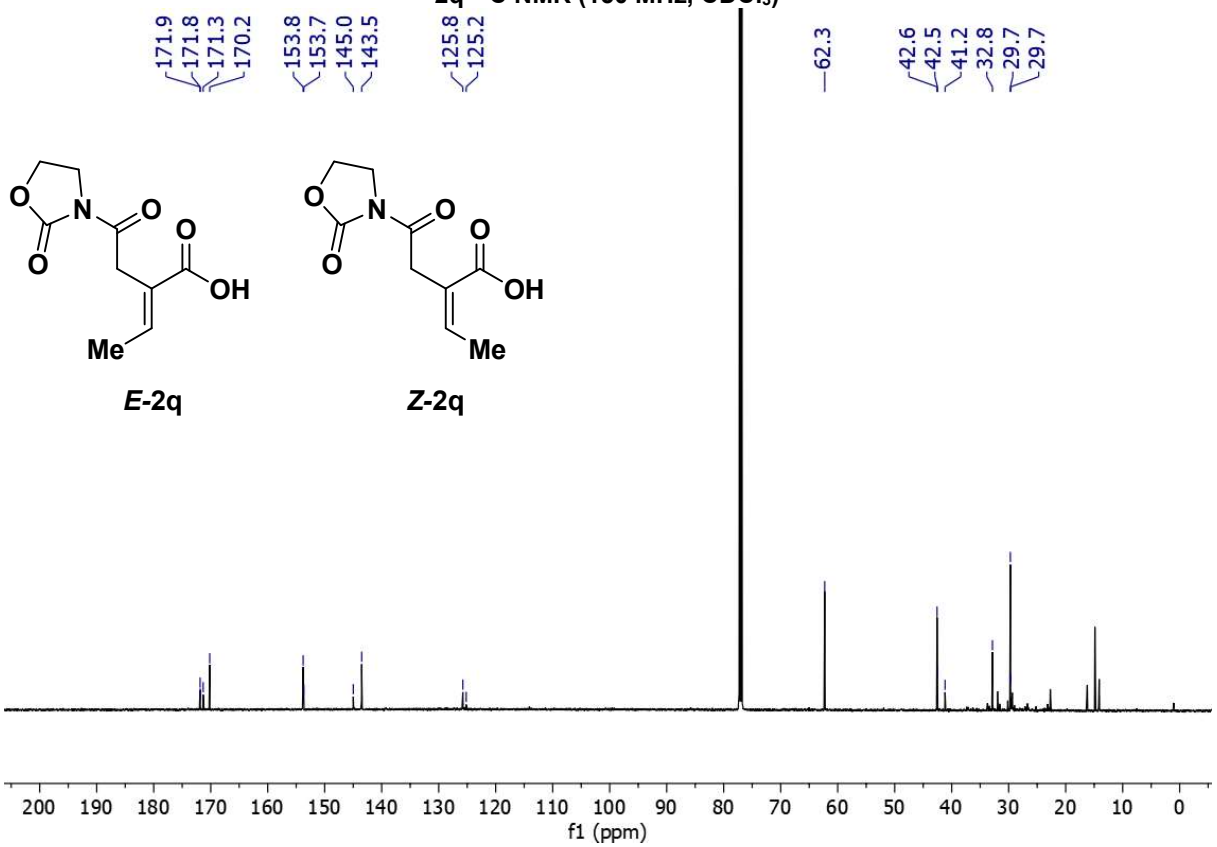
2q ^{1}H NMR (600 MHz, $CDCl_3$)



***E*-2q**

***Z*-2q**

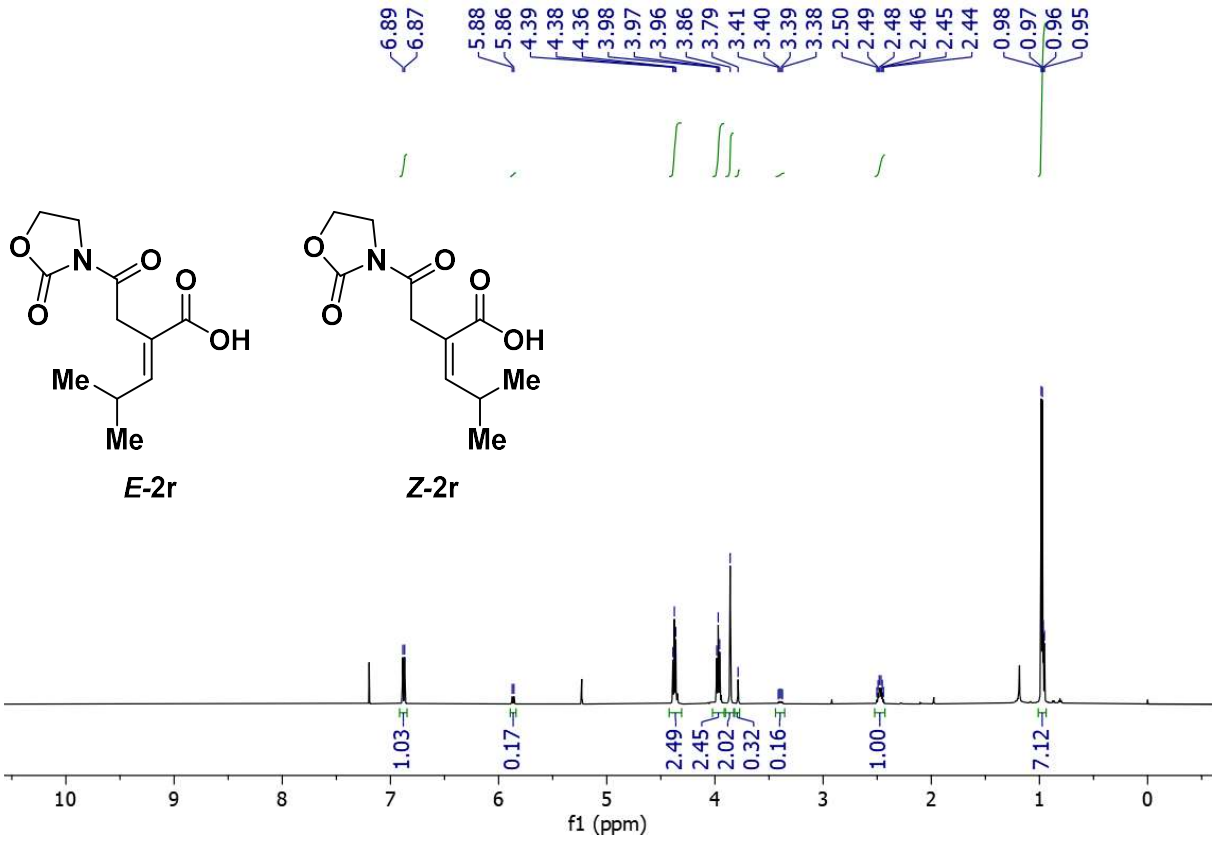
2q ^{13}C NMR (150 MHz, $CDCl_3$)



***E*-2q**

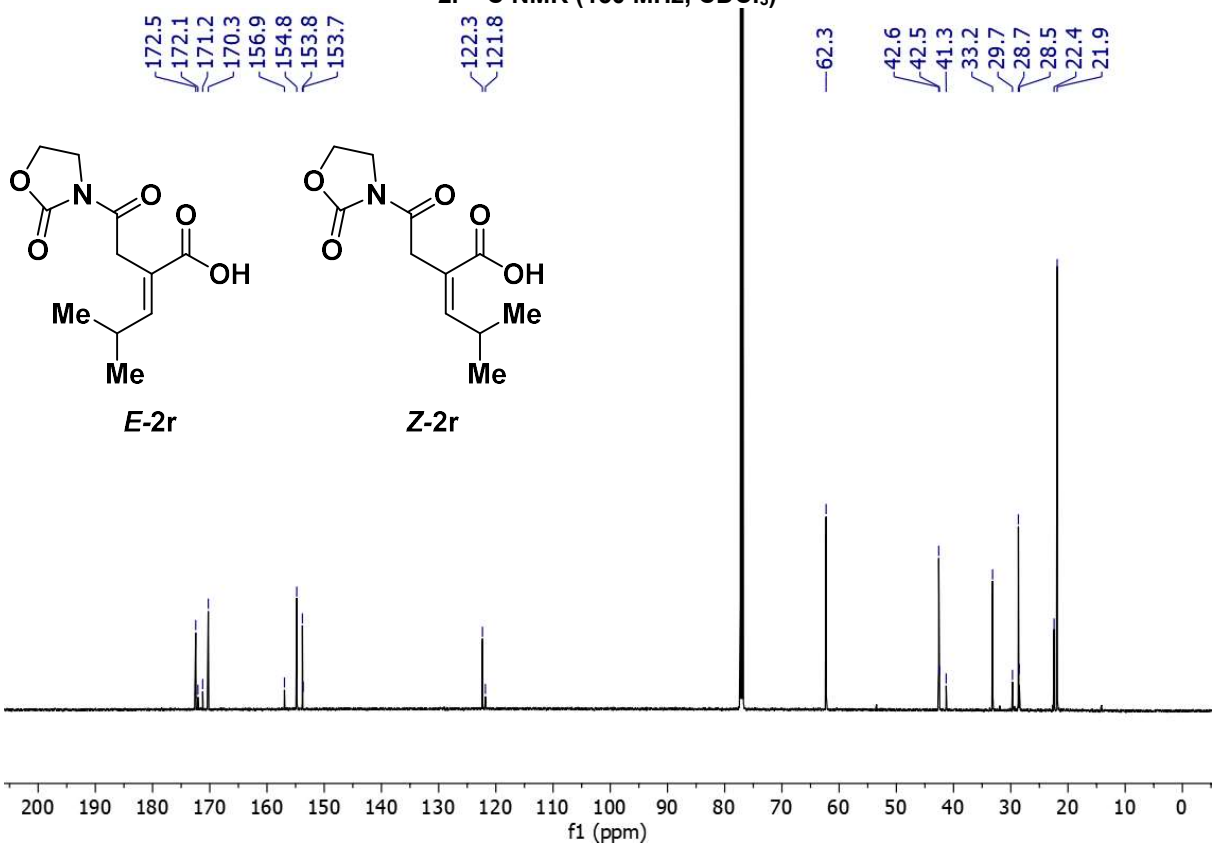
***Z*-2q**

2r ^{1}H NMR (600 MHz, $CDCl_3$)



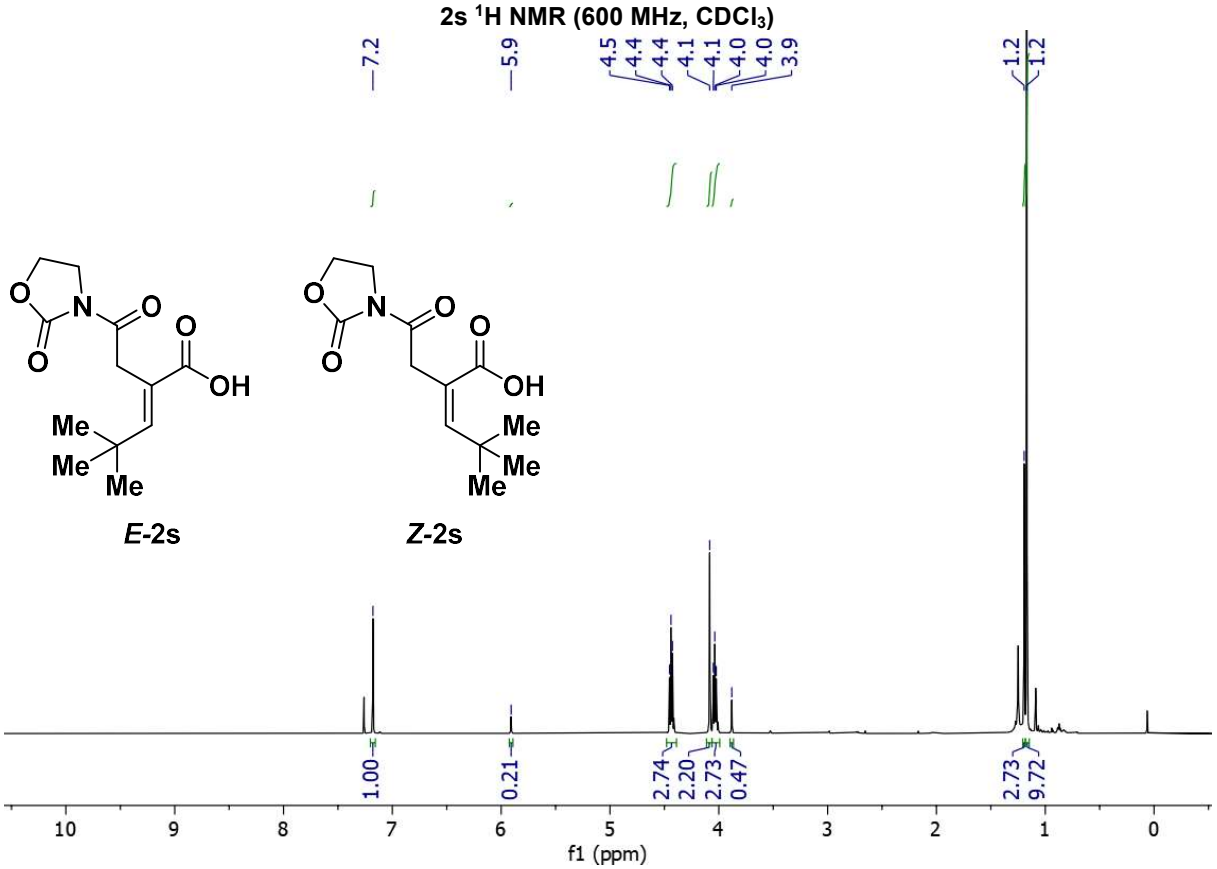
E-2r *Z*-2r

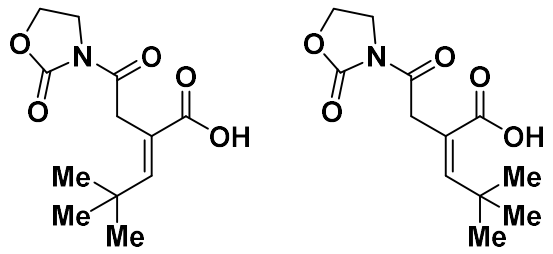
2r ^{13}C NMR (150 MHz, $CDCl_3$)



E-2r *Z*-2r

2s ^{1}H NMR (600 MHz, $CDCl_3$)





E-2s

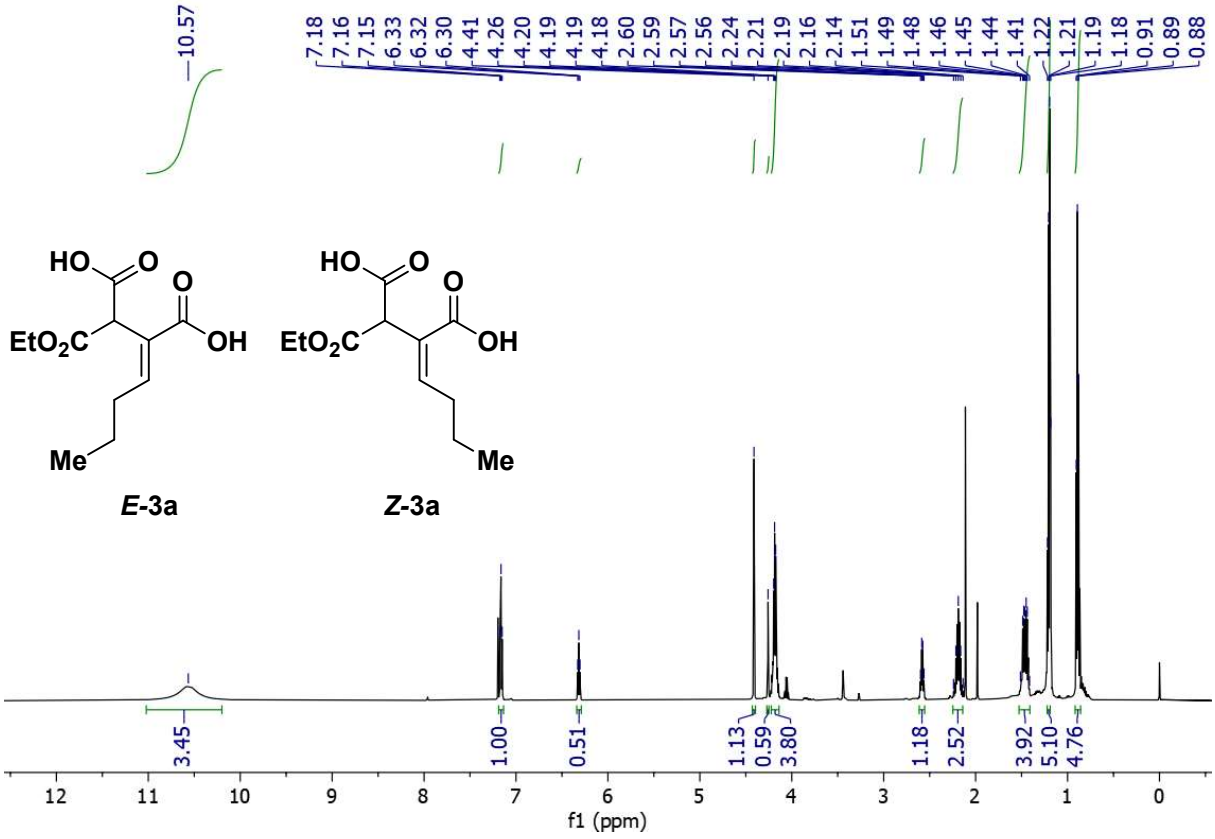
Z-2s

2s ^{13}C NMR (150 MHz, $CDCl_3$)

E-2s

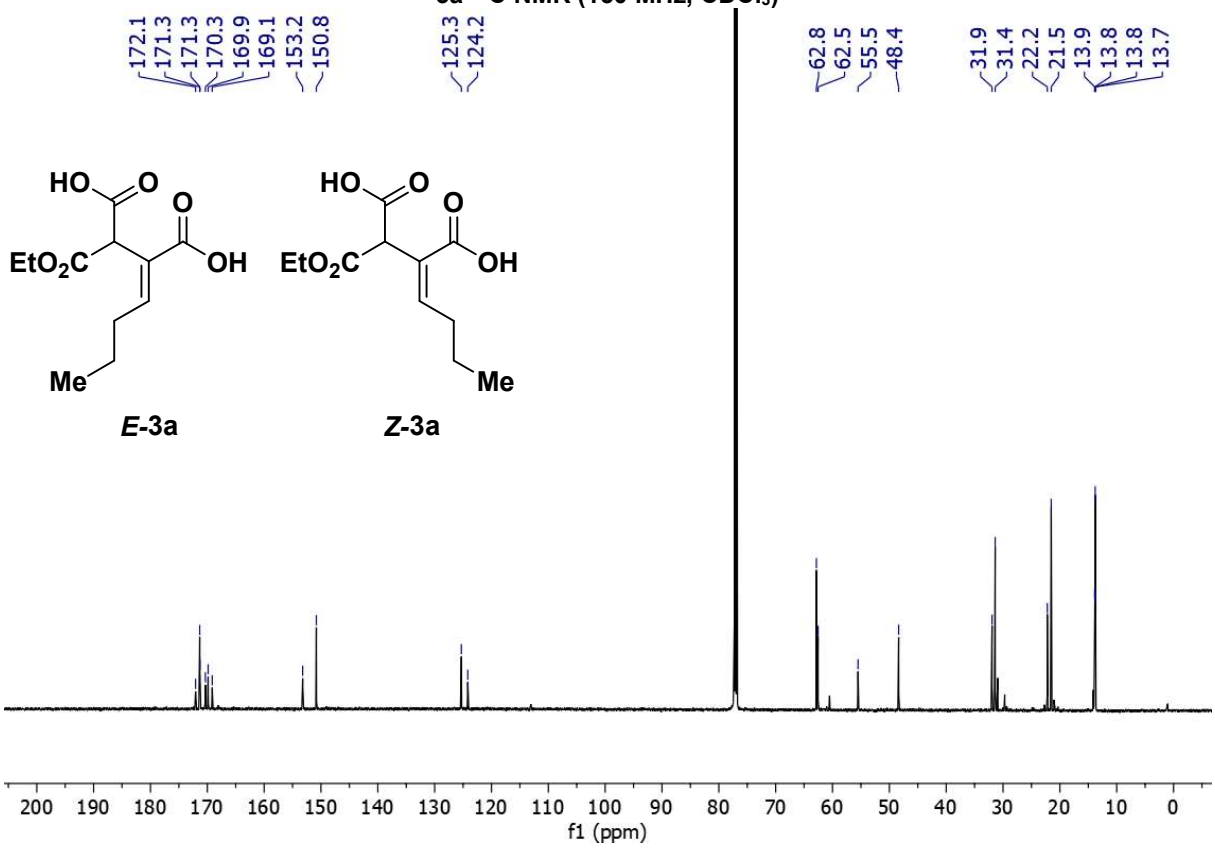
Z-2s

3a ^{1}H NMR (600 MHz, $CDCl_3$)



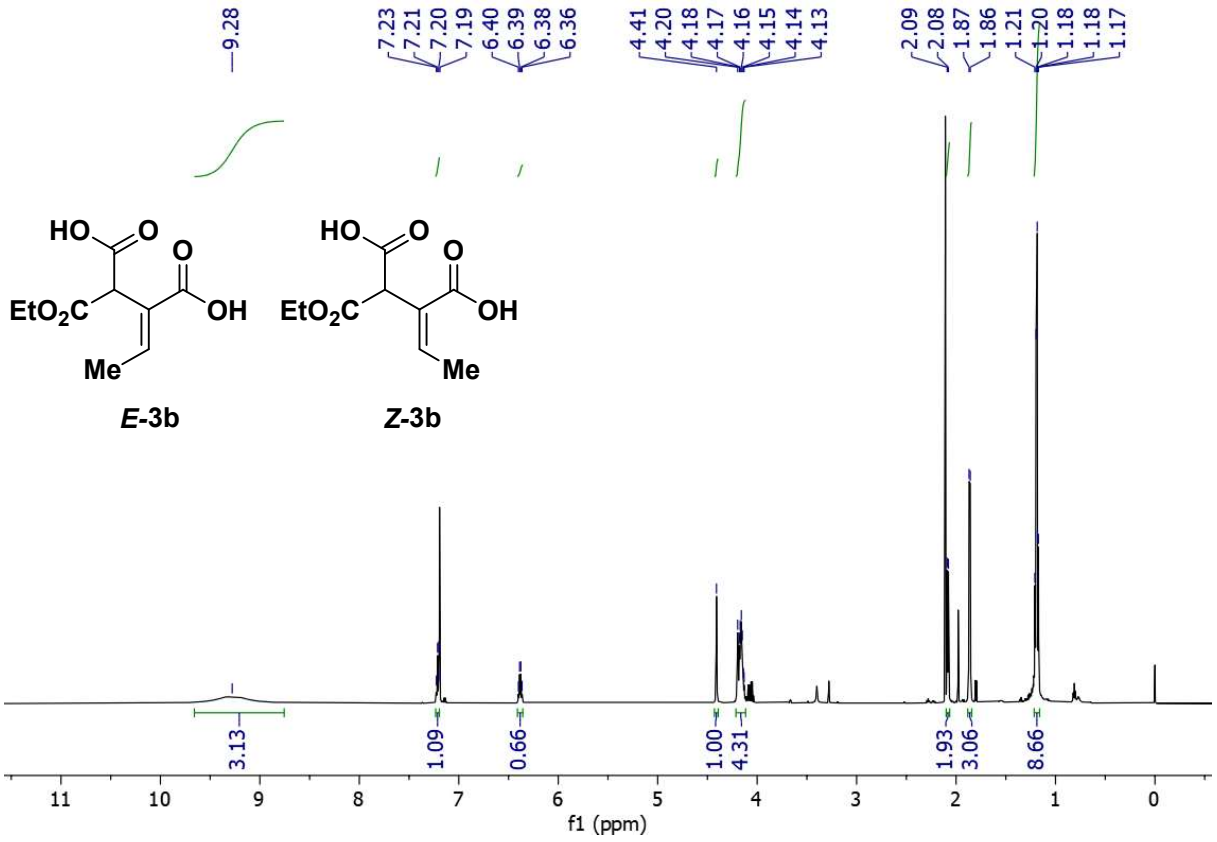
E-3a *Z*-3a

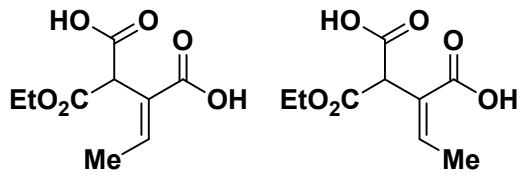
3a ^{13}C NMR (150 MHz, $CDCl_3$)



E-3a *Z*-3a

3b ^{1}H NMR (600 MHz, $CDCl_3$)





***E*-3b**

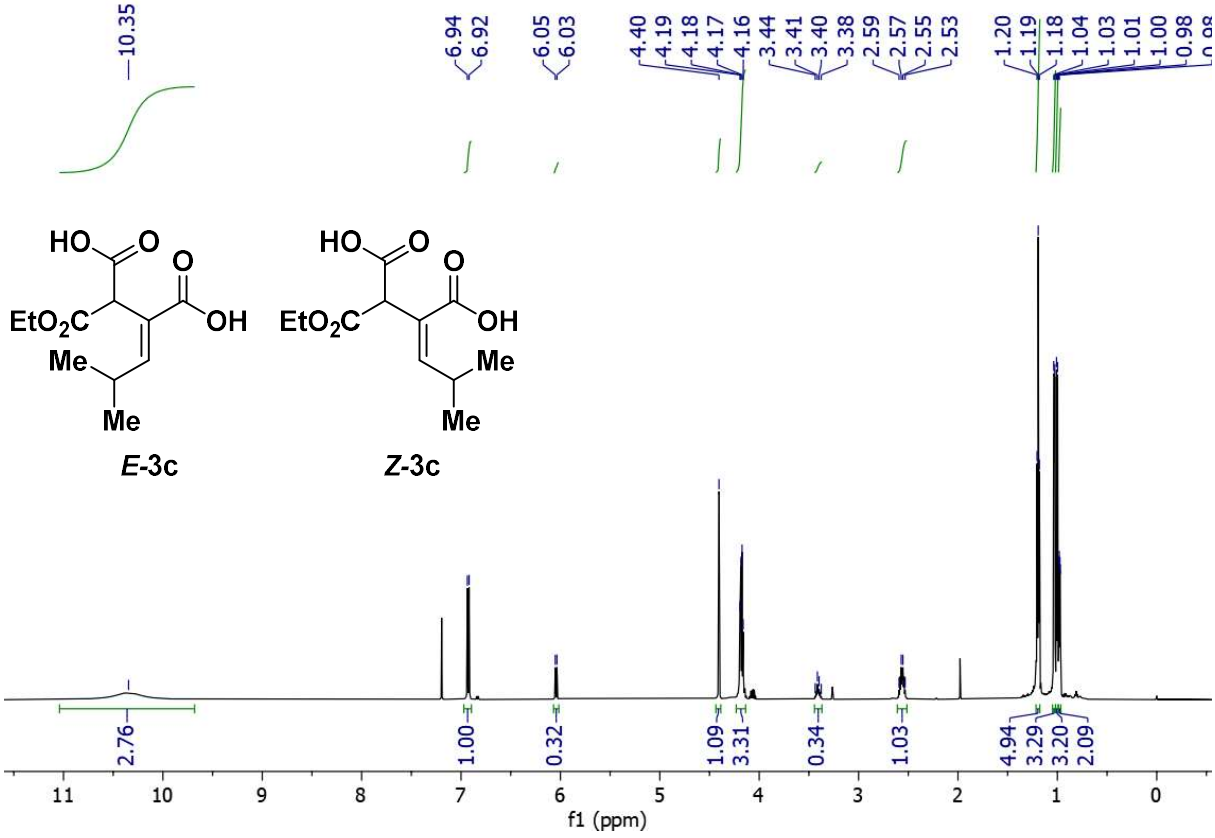
***Z*-3b**

3b ^{13}C NMR (150 MHz, $CDCl_3$)

***E*-3b**

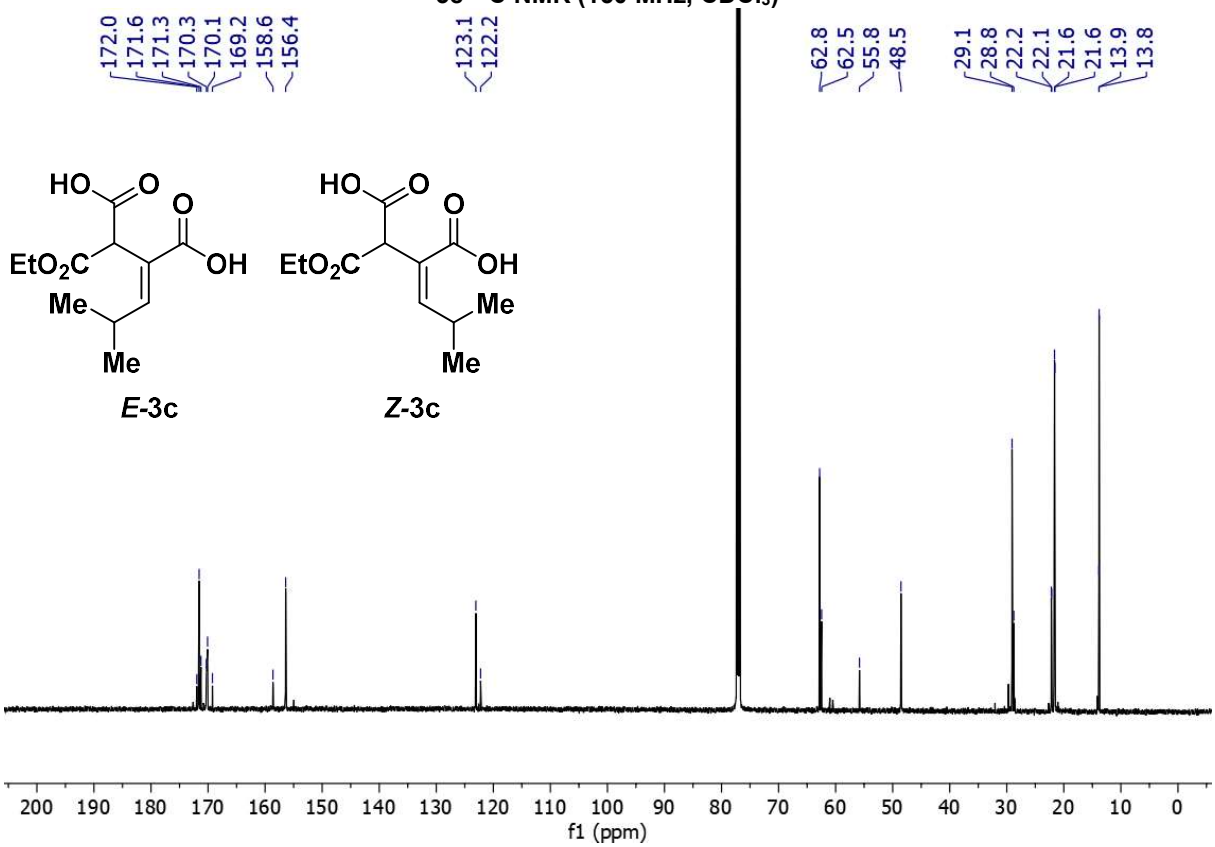
***Z*-3b**

3c ^{1}H NMR (600 MHz, $CDCl_3$)



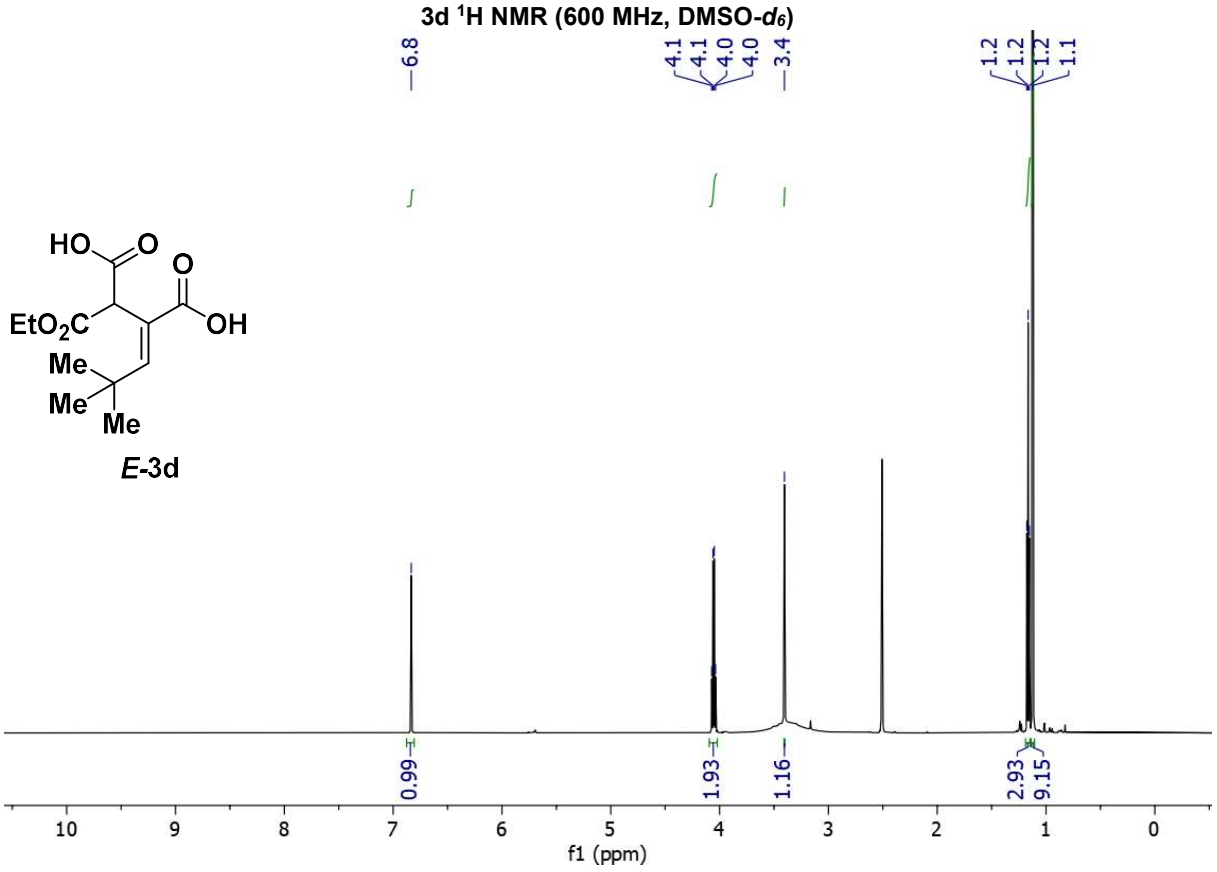
E-3c *Z*-3c

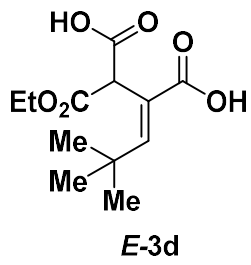
3c ^{13}C NMR (150 MHz, $CDCl_3$)



E-3c *Z*-3c

3d ^{1}H NMR (600 MHz, DMSO-d_6)



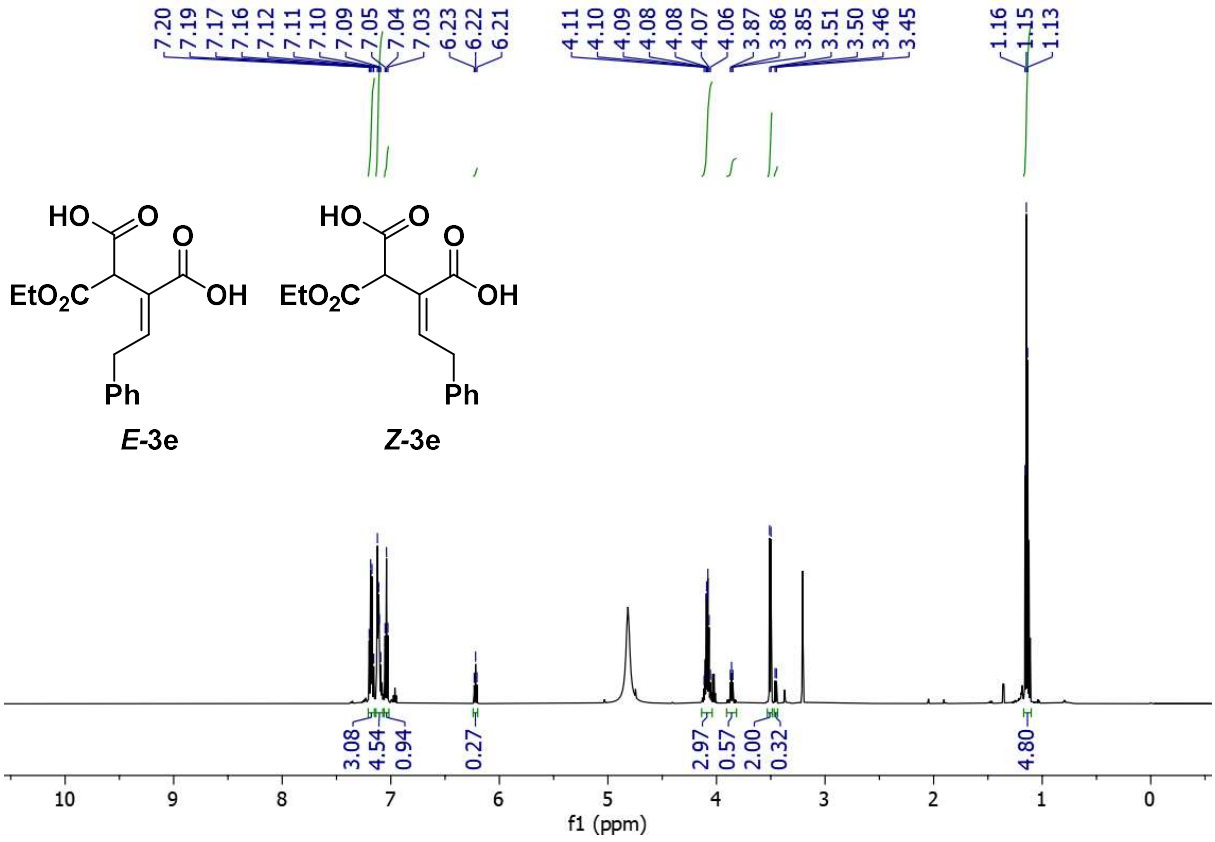


E-3d

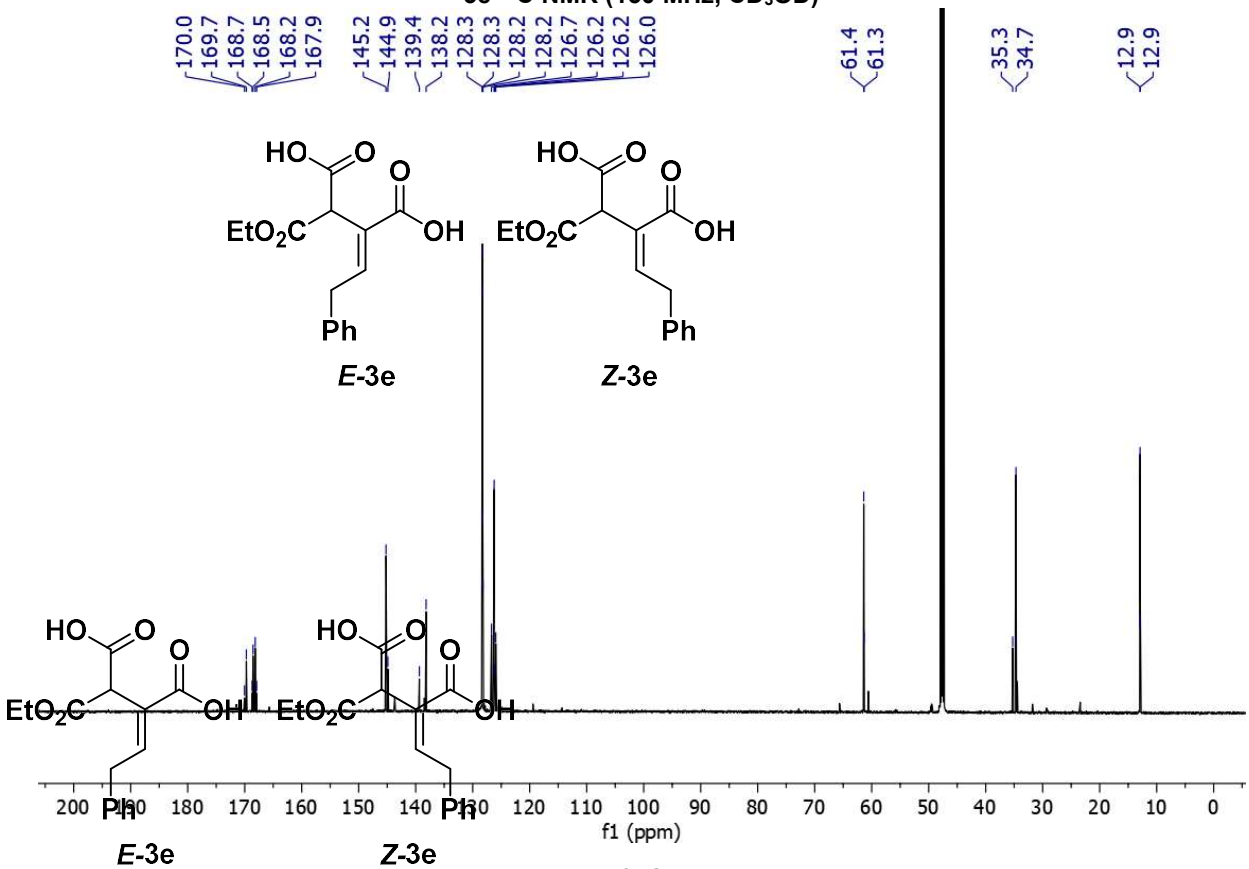
3d ^{13}C NMR (150 MHz, DMSO-d_6)

E-3d

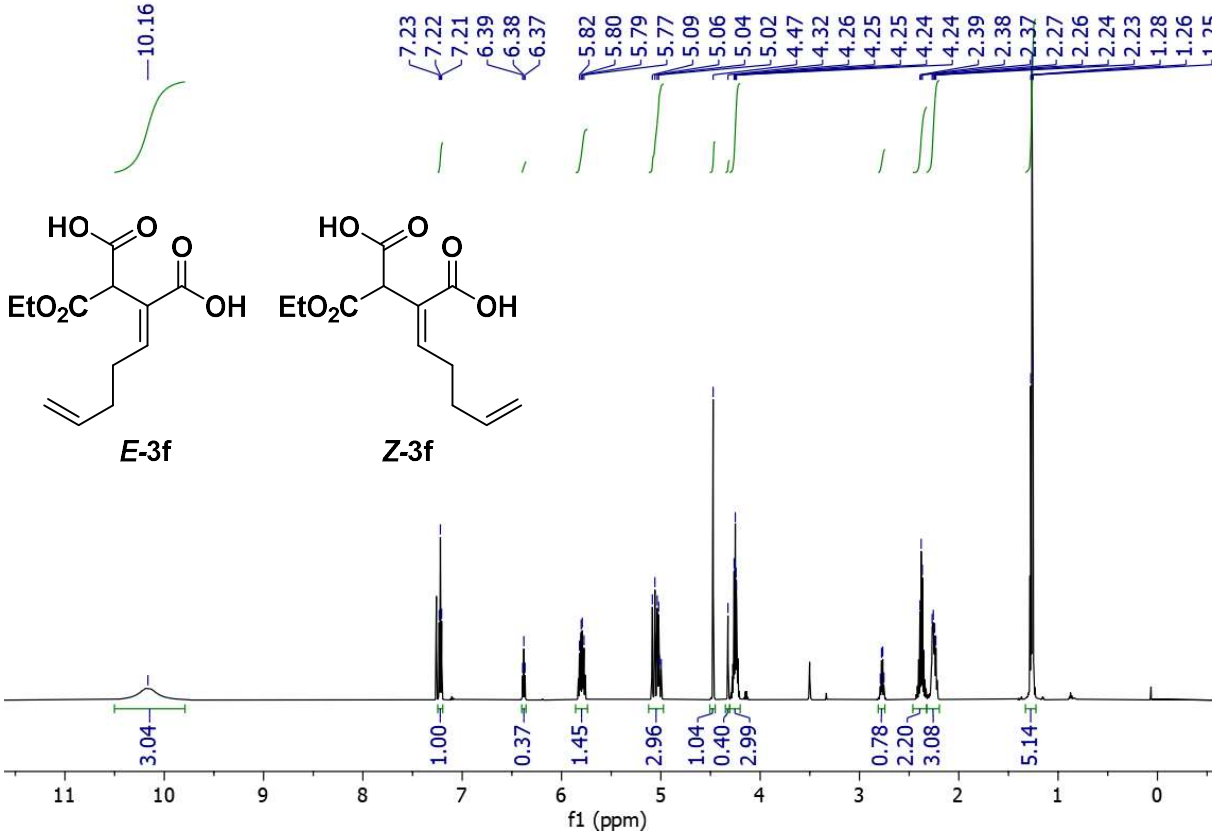
3e ^{1}H NMR (600 MHz, CD_3OD)



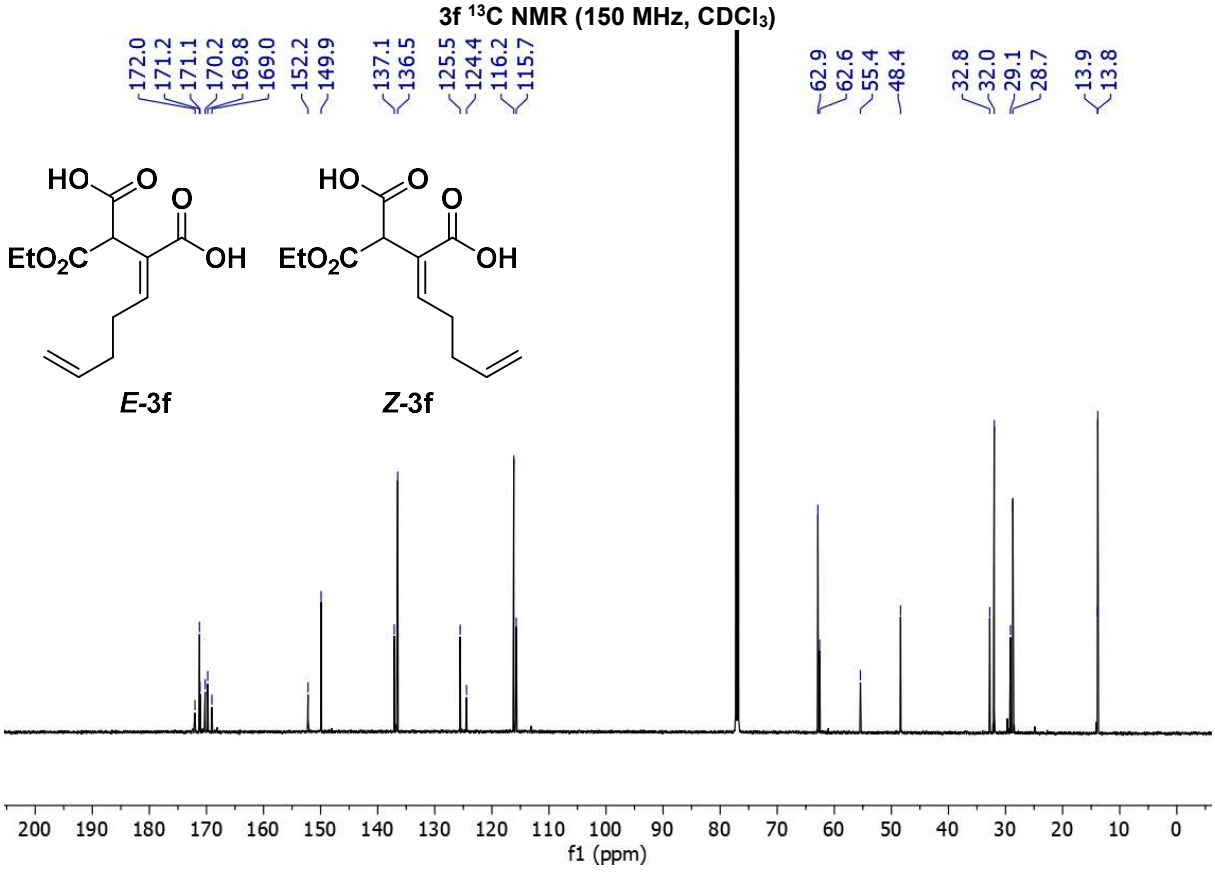
3e ^{13}C NMR (150 MHz, CD_3OD)



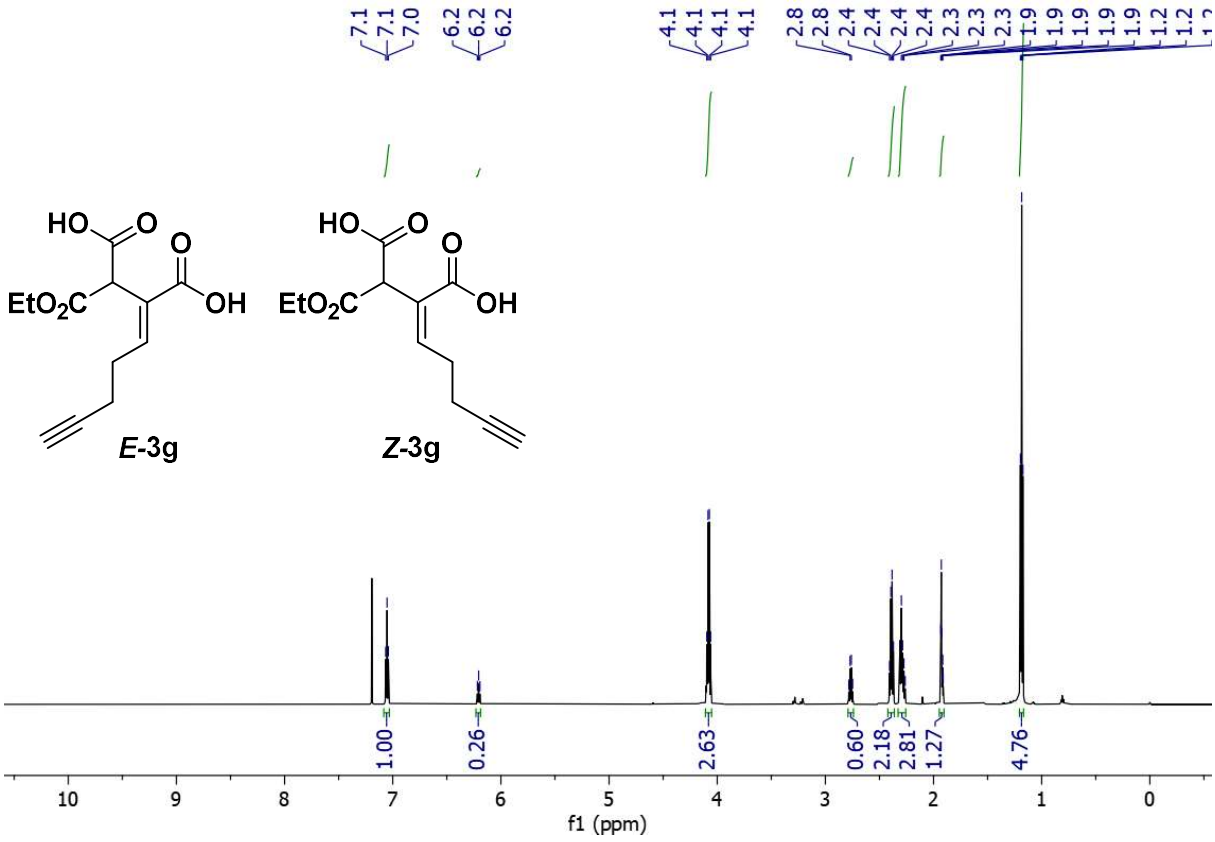
3f ^{1}H NMR (600 MHz, $CDCl_3$)



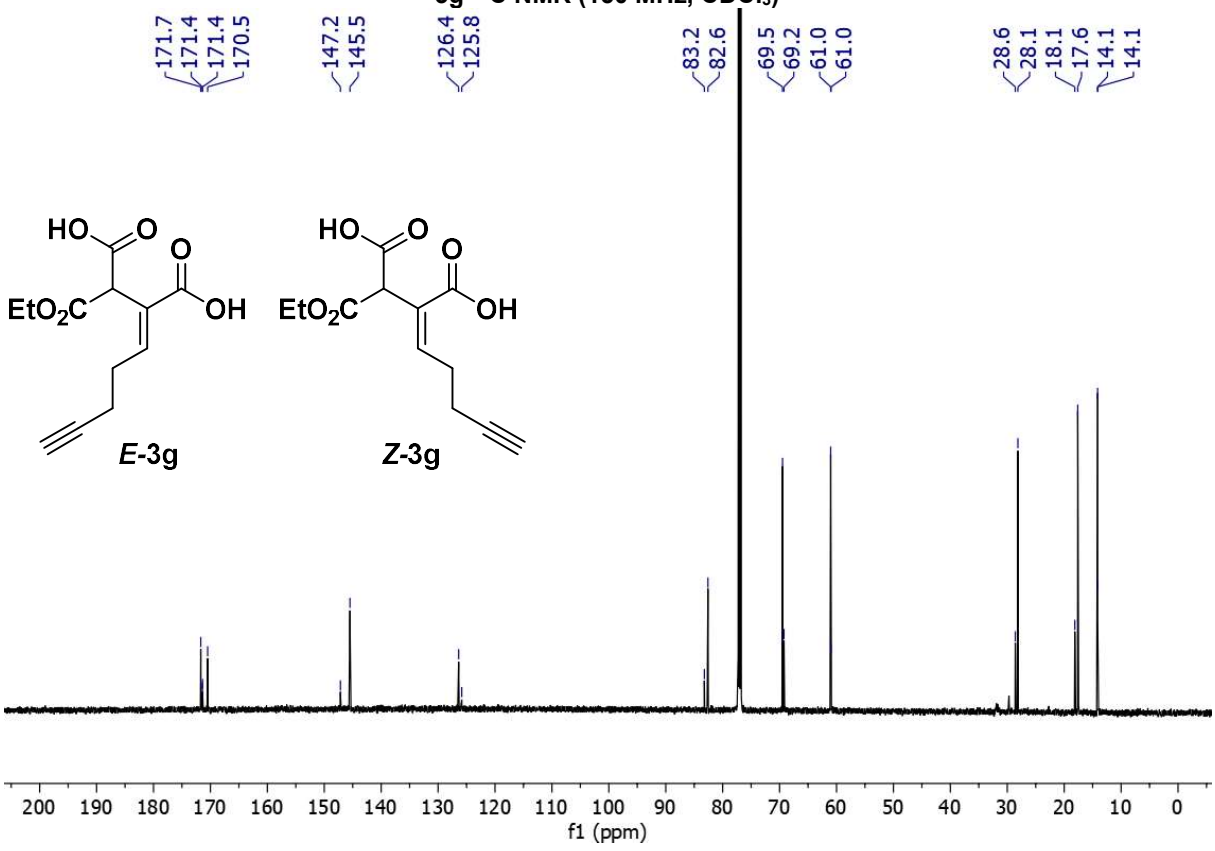
3f ^{13}C NMR (150 MHz, $CDCl_3$)



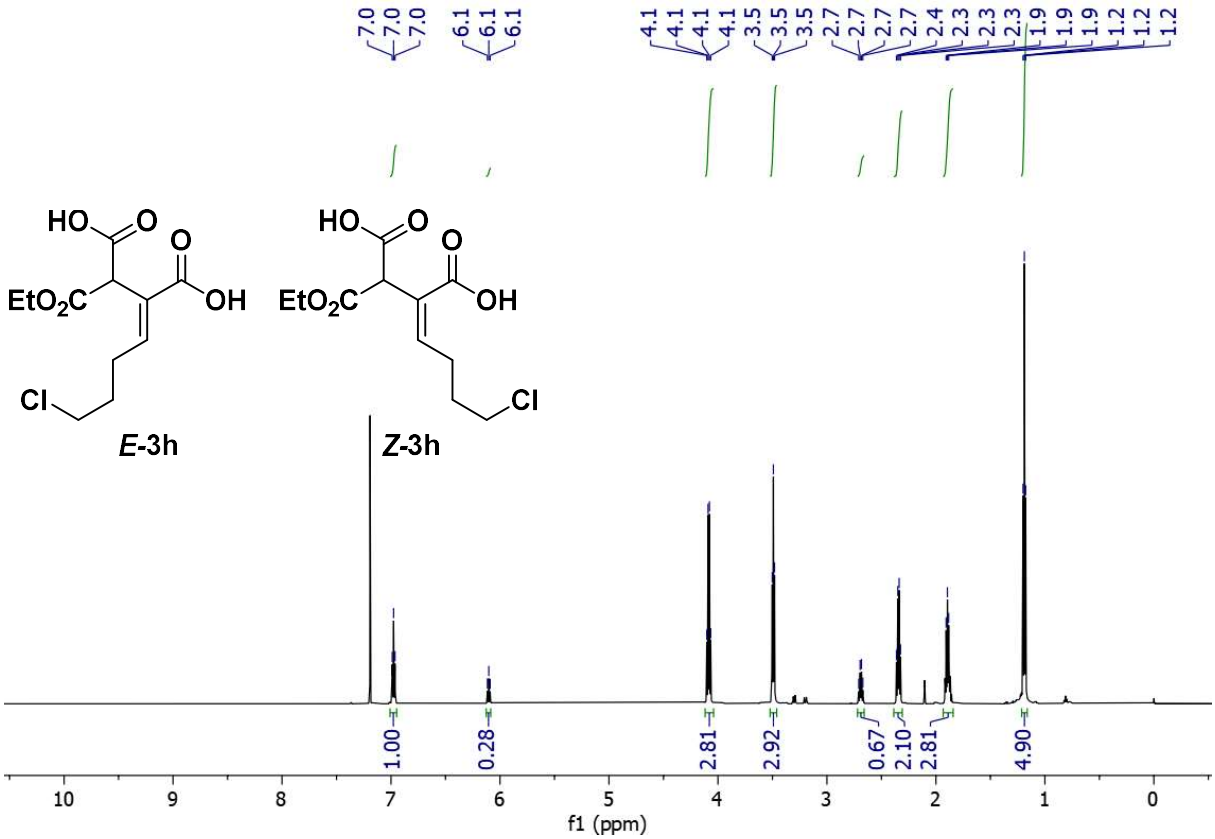
3g ^{1}H NMR (600 MHz, $CDCl_3$)



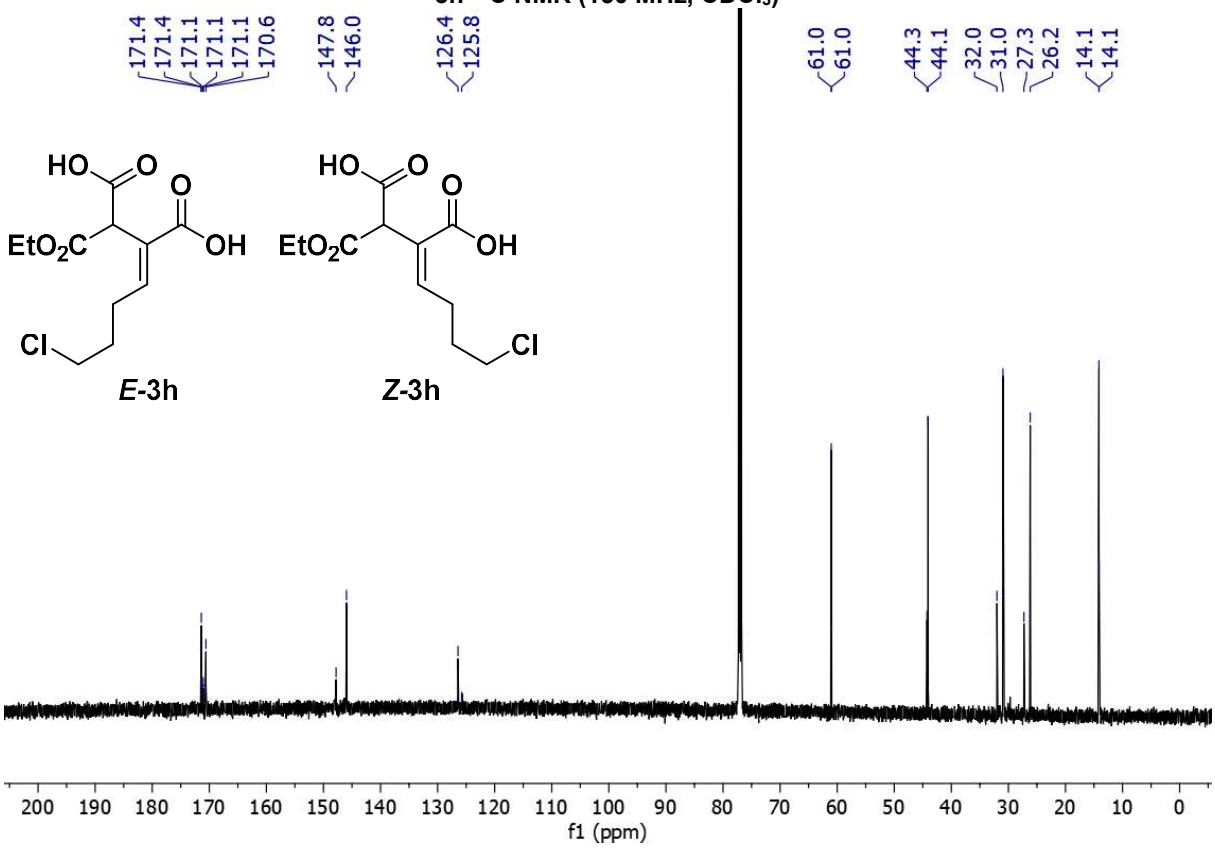
3g ^{13}C NMR (150 MHz, $CDCl_3$)



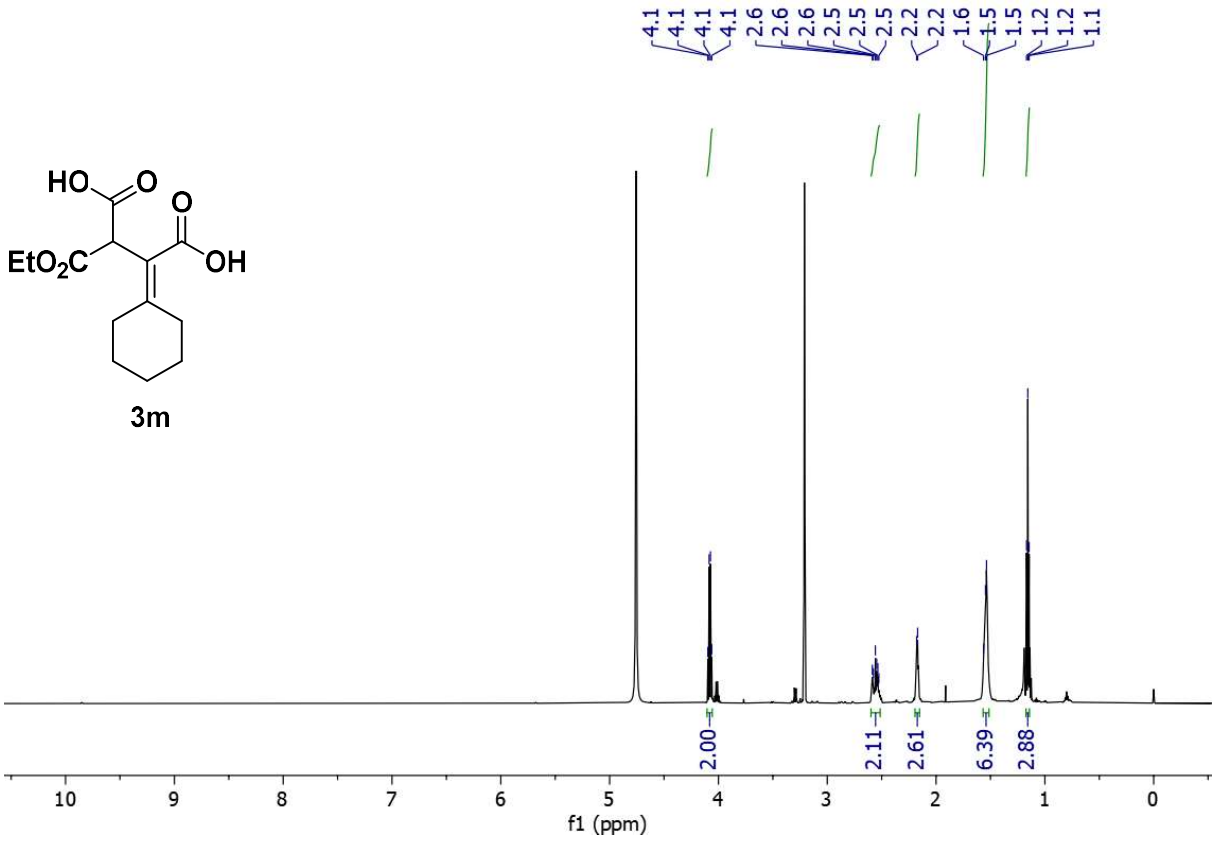
3h ^{1}H NMR (600 MHz, $CDCl_3$)



3h ^{13}C NMR (150 MHz, $CDCl_3$)

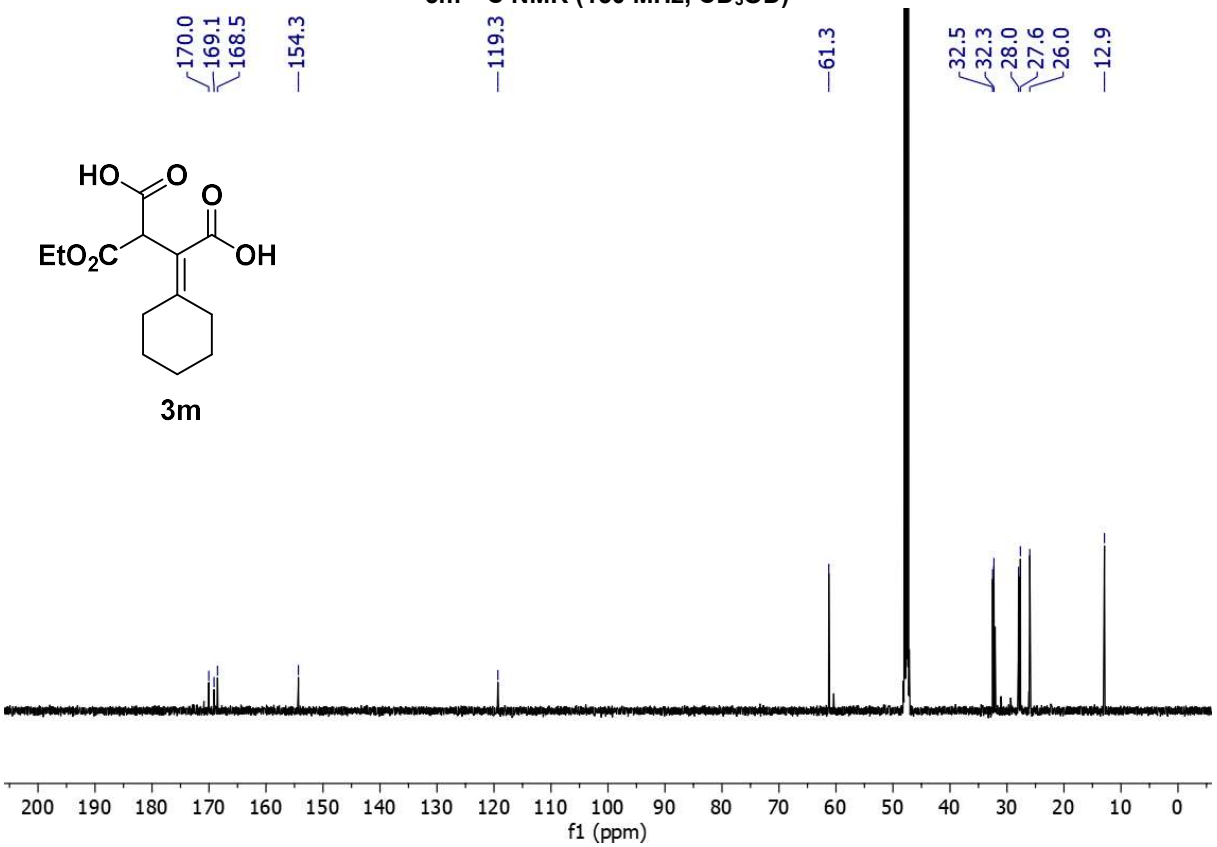


3m ^{1}H NMR (600 MHz, CD_3OD)



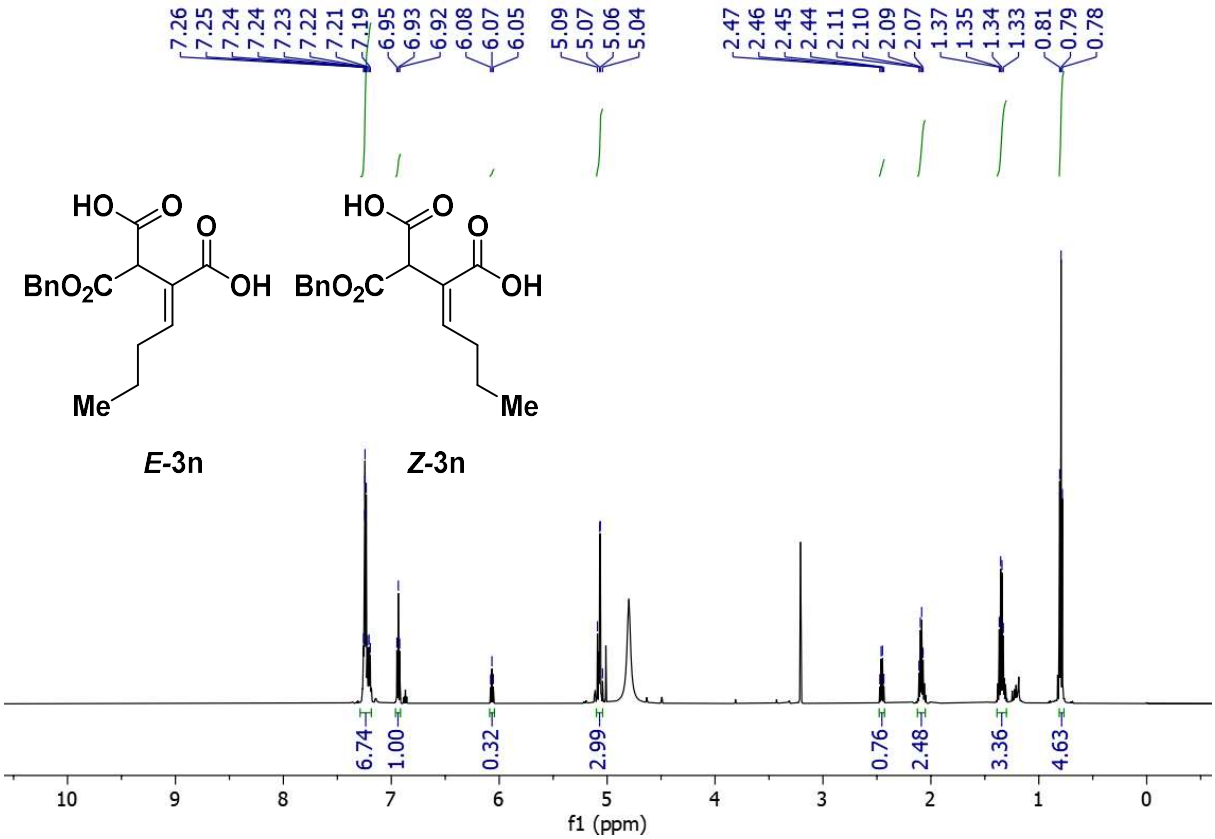
3m

3m ^{13}C NMR (150 MHz, CD_3OD)

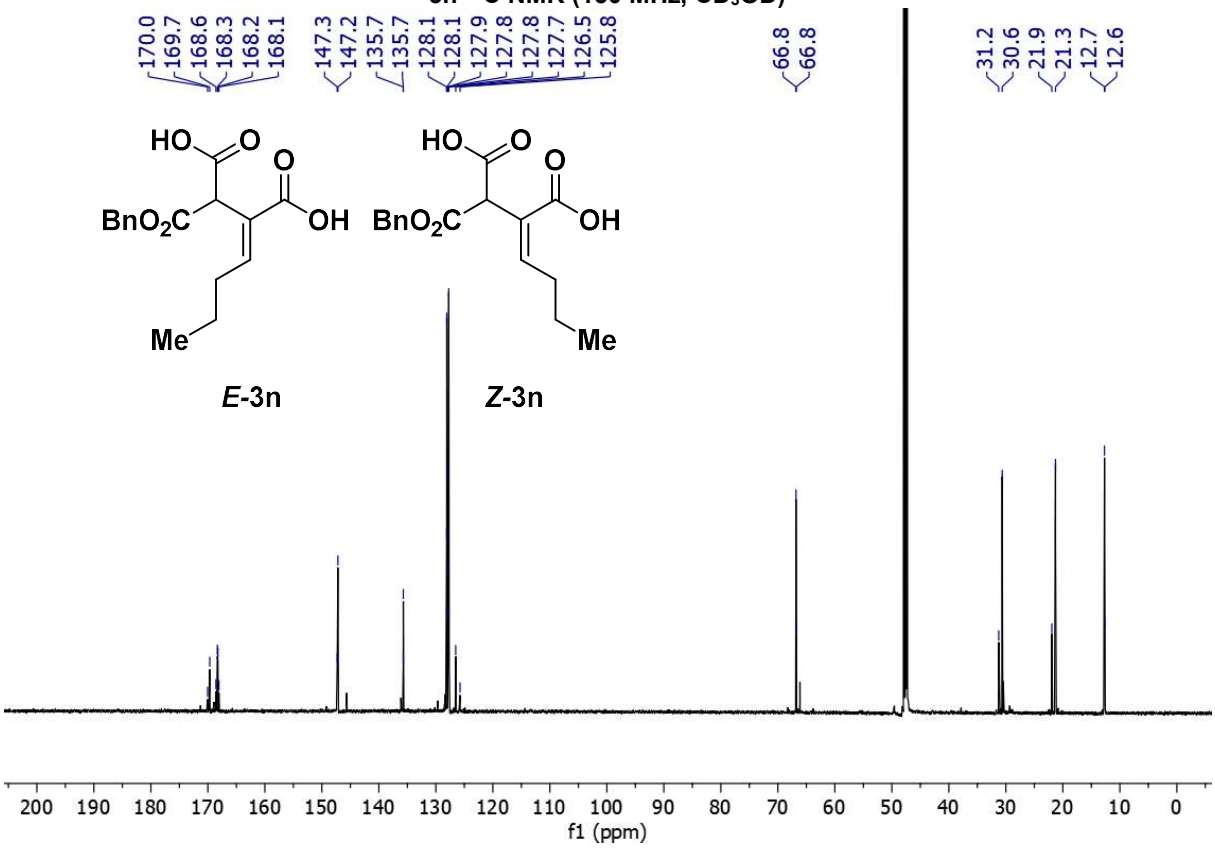


3m

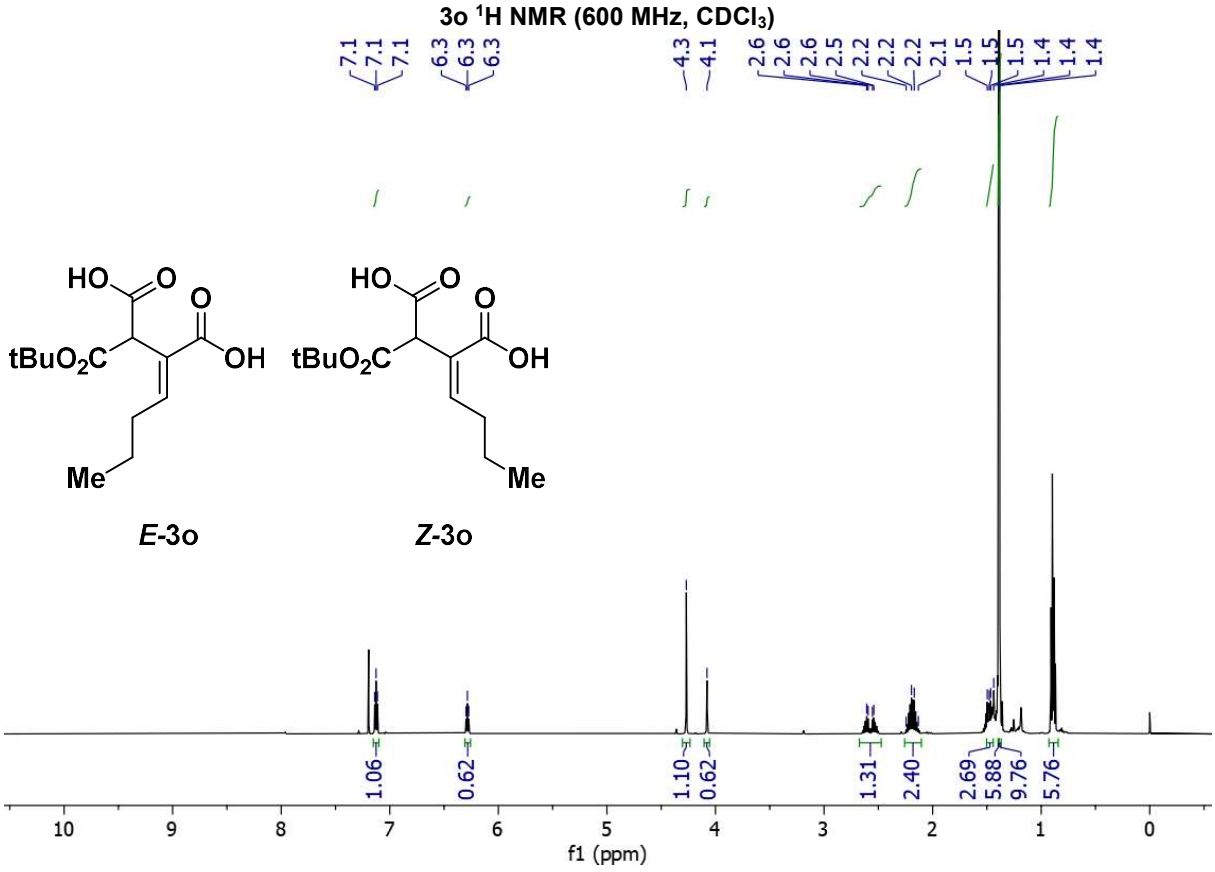
3n ^{1}H NMR (600 MHz, CD_3OD)



3n ^{13}C NMR (150 MHz, CD_3OD)

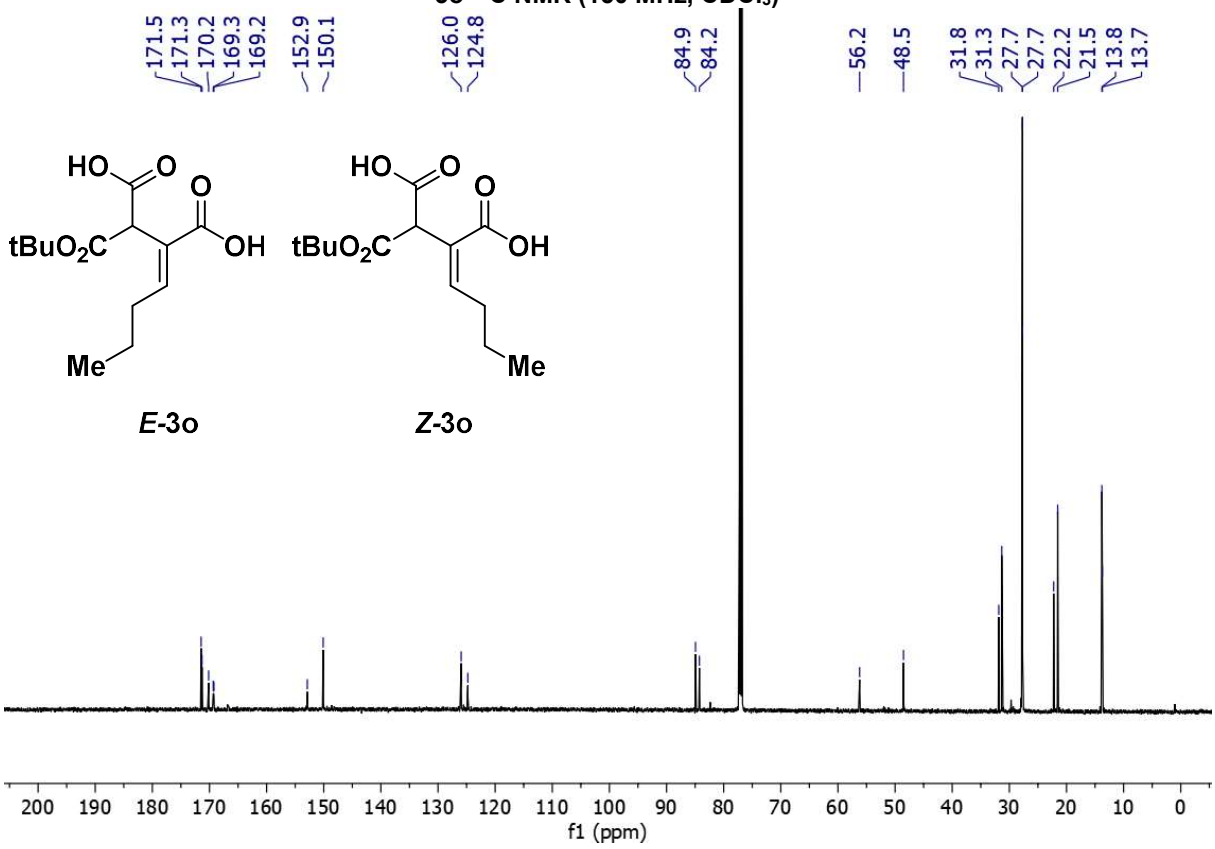


3o ^{1}H NMR (600 MHz, $CDCl_3$)



E-3o *Z*-3o

3o ^{13}C NMR (150 MHz, $CDCl_3$)



E-3o *Z*-3o

6. References

[1] For substrates **1a**-**1o** see: a) J. Sun, G. C. Fu, *J. Am. Chem. Soc.* **2010**, *132*, 4568-4569; b) L. Rout, A. M. Harned, *Chem. Eur. J.* **2009**, *15*, 12926-12928; c) G. E. Keck, R. L. Giles, V. J. Cee, C. A. Wager, T. Yu, M. B. Kraft, *J. Org. Chem.* **2008**, *73*, 9675-9691. For substrates **1p**-**1s** see: d) A. Parodi, S. Battaglioli, Y. Liu, M. Monari, M. Marìn-Luna, C. Silva-Lòpez, M. Bandini, *Chem. Commun.* **2019**, *55*, 9669-9672.