Electronic Supplementary Information (ESI)

Photocatalytic Reductive Incorporation of Carbon Dioxide into Double Bonds

Mark J. Deeprose,*[a] Thorsten Bach[a]*

[a] School of Natural Sciences, Department Chemie, and Catalysis Research Center (CRC), Technische Universität München, 85747 Garching, Germany

*** Corresponding author**

Email: thorsten.bach@ch.tum.de

Table of Contents

1. General Information

All reactions sensitive to air or moisture, were carried out in flame-dried glassware under positive pressure of argon using standard Schlenk techniques.

Commercially available chemicals were used without further purification, if not further mentioned. For moisture sensitive reactions, dichloromethane (CH_2Cl_2), diethylether (Et_2O) and tetrahydrofuran (THF) were purified using a MBSPS 800 *MBraun* solvent purification system. The following columns were used:

CH_2Cl_2: 2 × MB-KOL-A type (aluminium oxide)

Et_2O: 1 × MB-KOL-A type (aluminium oxide), 1 × MB-KOL-M type 2 (3 Å molecular sieve)

THF: 2 × MB-KOL-M type 2 (3 Å molecular sieve)

Anhydrous *N*,*N*-dimethylacetamide (DMA) *N*,*N*-dimethylformamide (DMF, supplied over 3 Å molecular sieves), were purchased from *Acros Organics*, and anhydrous dimethyl sulfoxide (DMSO), acetonitrile from *Sigma Aldrich* (*Merck*).

Technical solvents for column chromatography [dichloromethane (CH_2Cl_2), diethylether (Et_2O), ethyl acetate (EtOAc), methanol (MeOH), *n*-hexane (Hex), *n*-pentane (Pent)] were used after simple distillation.

Normal-phase flash column chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixture.

Photochemical reactions at $\lambda = 455$ nm were carried out using a Kessil Lamp (40 W Kessil Tuna Blue (A160WE)) with settings of colour and intensity set to maximum.

2. Analytical Methods

Thin layer chromatography (TLC) was performed on silica-coated aluminium plates (silica gel 60 F_{254}) with detection by UV-light (λ = 254 nm) and potassium permanganate [$KMnO_4$] or bromocreosole green stain.

UV/Vis spectra were recorded on a LAMBDA 365+ UV/Vis Spectrometer using acetonitrile as the solvent.

Infrared spectra (IR) were recorded on a JASCO IR-4100 or a *Perkin Elmer* Frontier IR-FTR spectrometer by ATR technique.

Melting points (M.p.) were determined using a Kofler ("Thermopan", Fs *Reichert*, Wien) apparatus.

Nuclear magnetic resonance (NMR) (^{1}H, ^{13}C and ^{19}F-NMR) spectra were recorded at room temperature on either a *Bruker* AVHD-400, a *Bruker* AVHD-500, or a *Bruker* AV-II-500 equipped with cryo probe head. Chemical shifts of the NMR spectra are reported relative to $CDCl_3$ (^{1}H-NMR: δ = 7.26 ppm, ^{13}C-NMR: δ = 77.16 ppm) or DMSO-d_6 (^{1}H-NMR: δ = 2.50 ppm, ^{13}C-NMR: δ = 39.52 ppm). The data are reported as follows: chemical shift (δ) [multiplicity, coupling constant *J* (Hz), relative integral, number of protons] where multiplicity is defined as: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, hept = heptuplet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tt = triplet of triplet, ddd = doublet of doublet of doublet.

High-resolution mass spectrometry (HRMS) using electrospray ionization (ESI) was performed on a SYNAPT XS High Resolution Mass Spectrometer (ESI) from *Waters* or on a *Thermo Scientific* LTQ-FT Ultra Spectrometer (ESI). For Liquid Injection Field Desorption Ionization (LIFDI) a *Linden* CMS LIFDI and a *ThermoFisher Scientific* Exactive Plus Orbitrap detector was used.

3. General Procedures

General Procedure 1 (GP 1): Oxygenated Conditions

In a glovebox, to an oven dried 7 mL black capped vial equipped with a stirrer bar, cesium acetate (200 mol%) and dimethyl methyl 4-mercaptobenzoate (15 mol%) were added. The substrate (100 mol%) was added at this point if it's in a solid form. The vial was sealed with a microwave cap and removed from the glovebox. To this, dimethyl sulfoxide (DMSO d_6, 0.1 M) was added and the solution was sparged with a balloon containing a mixture of CO_2 and air (approximately 1:1) for 30 seconds. To this solution, phenyl silane (200 mol%) was added and effervescence was observed. The headspace of the vial was vented with compressed air for a further 15 seconds, before the substrate (100 mol%) was added and the vial sealed with parafilm. The vial was irradiated with a Kessil lamp (Tuna Blue A160WE, 40 W, full intensity) for 16 hrs. Upon completion, the solution was quenched with HCl (3 M, 15 mL) before being diluted with EtOAc (10 mL) and extracted with EtOAc (3 x 25 mL). The resulting organic phase was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give the product as a crude oil. Trimethoxybenzene was added as an internal standard and an ^1H NMR was recorded to calculated the yield.

General Procedure 2 (GP 2): Activated alkenes

In a glovebox, to an oven dried 7 mL microwave vial equipped with a stirrer bar, cesium acetate (200 mol%) and dimethyl 4,4'-disulfanediyldibenzoate (10 mol%) were added. The substrate (100 mol%) was added at this point if it's in a solid form. The vial was sealed with a microwave cap and removed from the glovebox. To this, dimethyl sulfoxide (DMSO, 0.1 M) was added and the solution was sparged with a balloon containing pure CO_2 for 30 seconds. To this solution, phenyl silane (200 mol%) was added and effervescence was observed. The headspace of the vial was vented with the same balloon for a further 15 seconds, before the substrate (100 mol%) was added and the vial sealed with parafilm. The vial was irradiated with a Kessil lamp (Tuna Blue A160WE, 40 W, full intensity) for 16 hrs. Upon completion, the solution was quenched with HCl (3 M, 15 mL) before being diluted with EtOAc (10 mL) and extracted with EtOAc (3 x 25 mL). The resulting organic phase was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give the product as a crude oil. The crude product was purified by column chromatography, using a specified eluent system.

General Procedure 3 (GP 3): Internal Yield of Ammonium Triflate Complexes

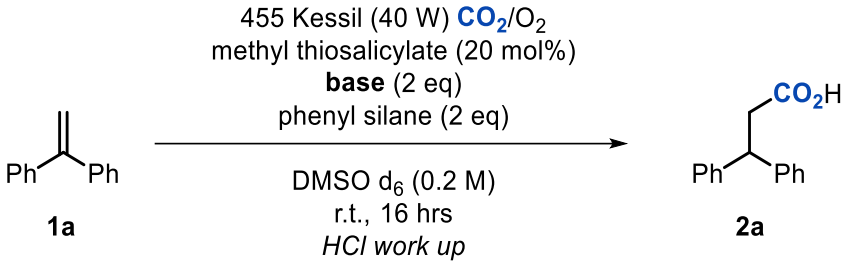
In a glovebox, to an oven dried 7 mL black capped vial equipped with a stirrer bar, cesium acetate (200 mol%) and dimethyl 4,4'-disulfanediyldibenzoate (10 mol%) were added. The vial was sealed with a microwave cap and removed from the glovebox. To this, dimethyl sulfoxide (DMSO d_6, 0.1 M) was added and the solution was sparged with a balloon containing pure CO_2 for 30 seconds. To this solution, phenyl silane (200 mol%) was added and effervescence was observed. The headspace of the vial was vented with the same balloon for a further 15 seconds, before the substrate (100 mol%) was added and the vial sealed with parafilm. The vial was irradiated with a Kessil lamp (Tuna Blue A160WE, 40 W, full intensity) for 16 hrs. Upon completion, the solution was quenched with triflic acid (300 mol%). Trimethoxybenzene was added as an internal standard and an ^{1}H NMR was recorded to calculated the yield.

General Procedure 4 (GP 4): Synthesis of Imines

Aniline was purified by filtering through a pad of silica immediately before the reaction. The aldehyde was purified by distillation if necessary.

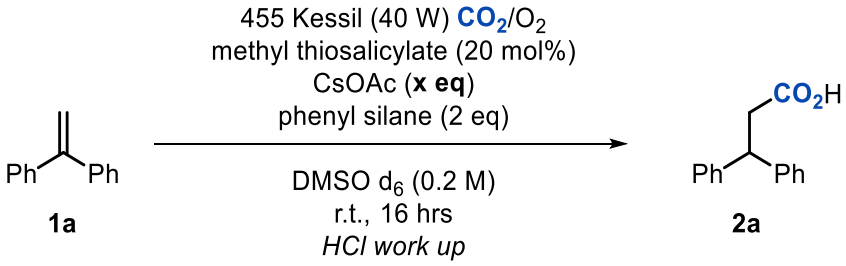
In an oven dried round bottomed flask, aniline (100 mol%) was added and stirred at room temperature. To this, the specified aldehyde (100 mol%) was added dropwise over 30 seconds. The resulting solution was left to stir for 30 mins at room temperature. In the case for imines that have a high bp, a vacuum was applied to remove water produced in the reaction. In all other cases, the imine was used without further purification.

4. Condition Optimisation and Control Studies



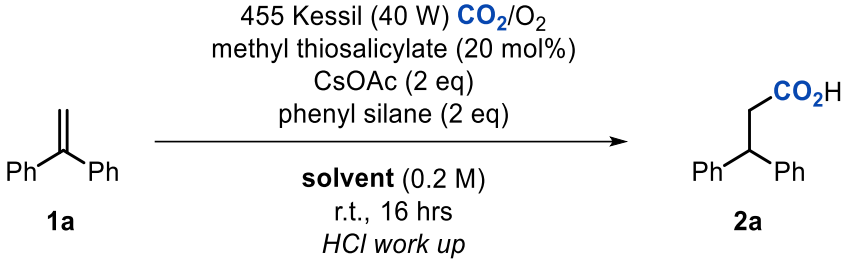
Base	Compound	NMR Yield (%)	SM (%)
1	K_3PO_4	66	0
2	**CsOAc**	**63**	**0**
3	KOAc	41	0
4	NaOAc	3	66
5	Cs_2CO_3	65	0
6	K_2CO_3	53	0

Trimethoxybenzene used as an internal standard. Upon screening of a small substrate scope, CsOAc was decided upon as giving the broadest reactivity.



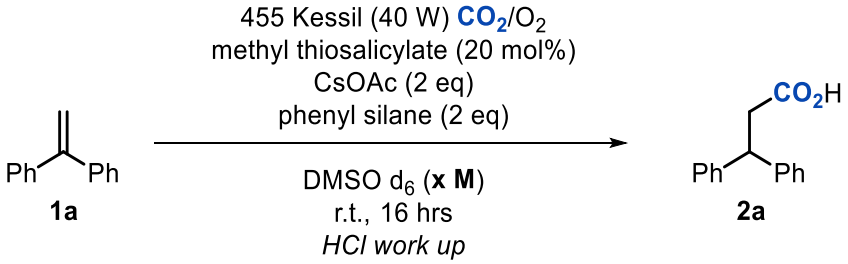
Base load.	Equiv.	NMR Yield (%)	SM (%)
1	1.1	33	0
2	1.5	36	0
3	**2.0**	**63**	**0**
4	2.5	47	0
5	3.0	46	0

Trimethoxybenzene used as an internal standard.



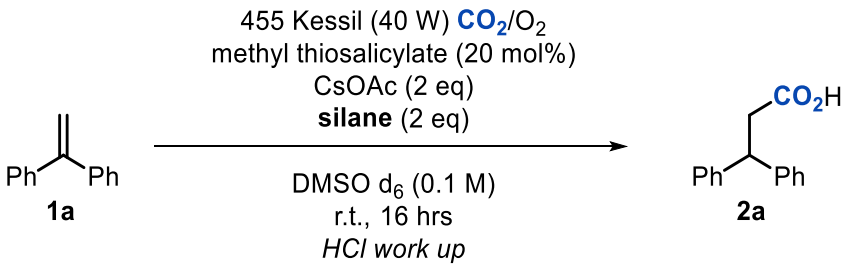
Solvent	Compound	NMR Yield (%)	SM (%)
1	THF	0	58
2	MeCN	0	62
3	DMF	53	0
4	DMA	54	6
5	**DMSO d_6**	**63**	**0**
7[a]	DMSO (mol. sieves)	49	0

Trimethoxybenzene used as an internal standard.
[a] stored with molecular sieves



Conc.	[M]	NMR Yield (%)	SM (%)
1	0.025	33	11
2	0.05	56	0
3	**0.1**	**64**	**0**
4	0.2	63	0
5	0.4	54	0

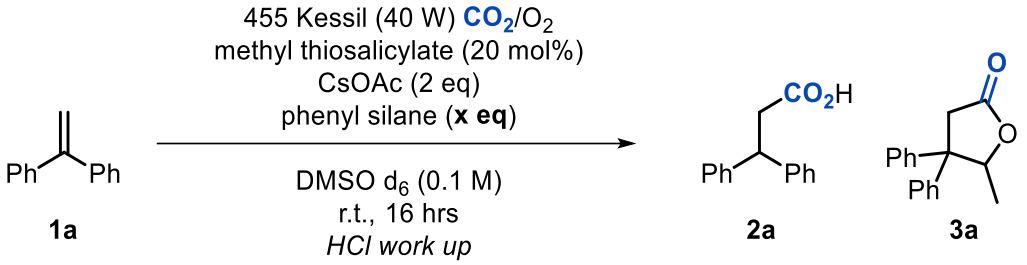
Trimethoxybenzene used as an internal standard.



Silane	Compound	NMR Yield (%)	SM (%)
1	**$PhSiH_3$**	**64**	**0**
2	Ph_2SiH_2	55	0
3	Ph_3SiH	54	16
4	$PhMeSiH_2$	48	0
5	$PhMe_2SiH$	37	0
6	Et_3SiH	4	79
7	$(EtO)_3SiH$	24	53
8	PMHS*	12	67

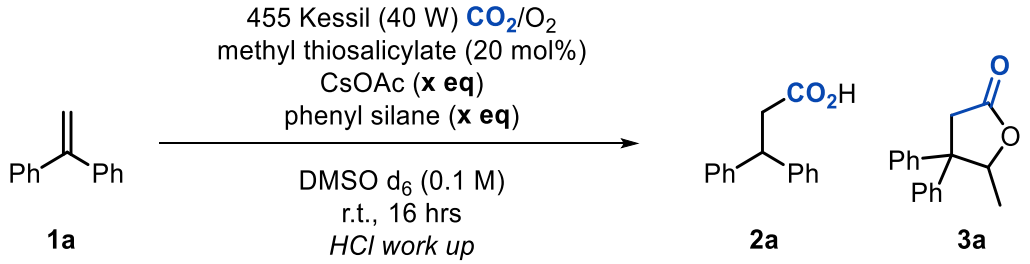
Trimethoxybenzene used as an internal standard.

*Polymethylhydrosiloxane.



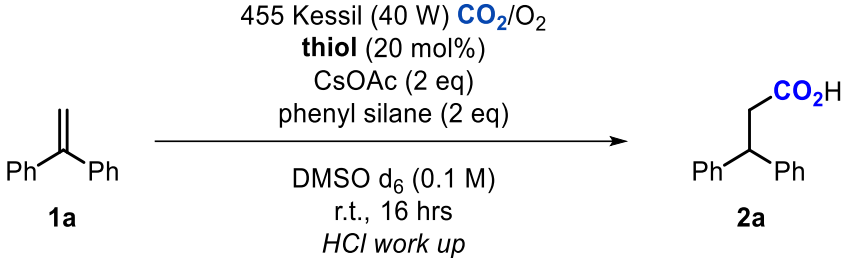
Silane loading	Equiv.	NMR Yield (%)	[3a] (%)	SM (%)
1	1.1	55	0	0
2	1.5	58	0	0
3	**2.0**	**64**	**0**	**0**
4	2.5	66	0	0
5	3.0	68	18	0

Trimethoxybenzene used as an internal standard.



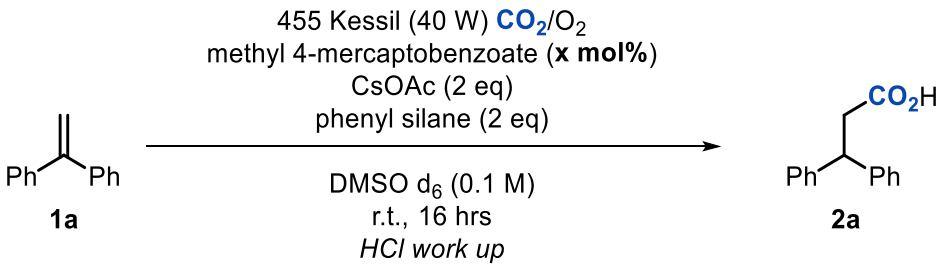
Base + Silane	Equiv.	NMR Yield (%)	[3b] (%)	SM (%)
1	1.1	44	0	0
2	1.5	55	0	0
3	**2.0**	**64**	**0**	**0**
4	2.5	59	18	0
5	3.0	58	25	0

Trimethoxybenzene used as an internal standard.



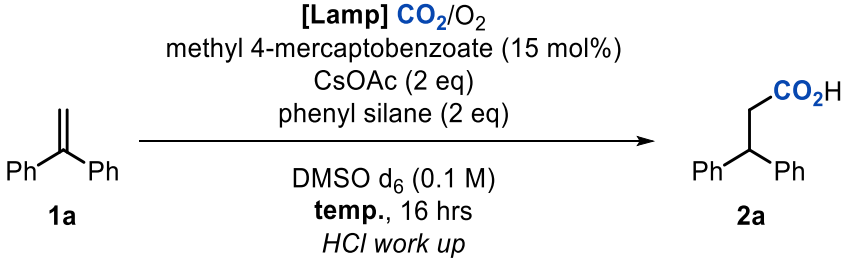
Thiol	Compound	NMR Yield (%)	SM (%)
1	methyl thiosalicylate	64	0
2	2,3-dichlorobenzenethiol	63	0
3	4-(tert-butyl)benzenethiol	51	0
4	2,6-dimethylbenzenethiol	26	21
5	2,4,6-triisopropylbenzenethiol	38	30
6	**methyl 4-mercaptobenzoate**	**79**	**0**
7	thiophenol	50	0
8	2,3,5,6-tetrafluorobenzenethiol	6	65
9	4-bromobenzenethiol	32	13
10	2-bromobenzenethiol	42	0

Trimethoxybenzene used as an internal standard.



Thiol loading	Equiv.	NMR Yield (%)	SM (%)
1	0.05	73	0
2	0.10	70	0
3	**0.15**	**79**	**0**
4	0.20	79	0
5	0.30	80	0

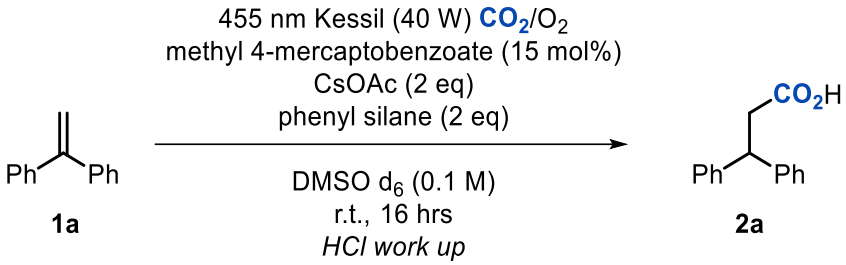
Trimethoxybenzene used as an internal standard.



Lamps	Type	NMR Yield (%)	SM (%)
1	1 W 455 nm LED **15 °C** (Direct light)	61	0
2	3 W 455 nm LED **25 °C** (Probe light)	13	61
3	3 W 455 nm LED **40 °C** (Probe light)	28	25
4	40 W **427 nm** Kessil (PR160L)	77	0
5	40 W **390 nm** Kessil (PR160L)	73	0
6	**40 W Kessil Tuna Blue (A160WE)**	**79**	**0**

Trimethoxybenzene used as an internal standard. See Figure S6 for lamp set up illustrations.

Control Studies



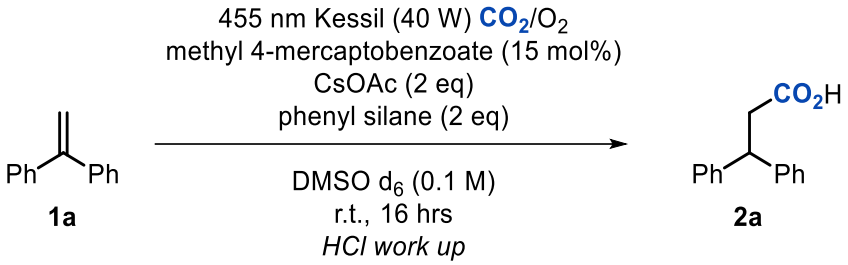
Entry	Change to Conditions	NMR Yield (%)	SM (%)
1	-	79	0
2	Presence of 4CzIPN (1 mol%)	73	0
3	Absence of CO_2	0	0
4	Absence of O_2	37	0
5	Absence of thiol	0	30
6	Absence of silane	< 1	18
7	Absence of base	0	63
8	Absence of light	0	0
9[a]	**Non-deuterated DMSO**[b,c]	**84**[d]	**0**
10[a]	Addition of water (1 eq.)	65	0
11[a]	Addition of water (1 M)	26	12
12[a]	Dry ice as CO_2 source[c,e]	50 (22)	0
13[a]	Scale up to 1 mmol[c]	70[d]	0

Trimethoxybenzene used as an internal standard. By-product **3a** yield in parentheses. [a] Anhydrous DMSO employed. [b] 0.2 mmol scale. [c] Disulphide **5** used as catalyst in the absence of oxygen (see GP1). [d] Isolated yield. [e] Crushed dry ice (approx. 100 mg, 2.2 mmol) added to reaction solution and allowed to warm to r.t. before sealing, no gas purging of reaction headspace.

5. Mechanistic Studies

Reaction Plot of Oxygenated Conditions Over Time.

We observed an initial delay in the reaction rate for the first two hours of the reaction. This is due to oxidation of the thiol into its catalytic form. Once a significant quantity of the thiol has been converted to the disulphide, the hydrocarboxylation of **1a** takes place until full consumption of the starting material. Evidence of thiol oxidation was obtained by synthesis of disulphide **5** under the reaction conditions in nearly quantitative yield with 3 hours irradiation.



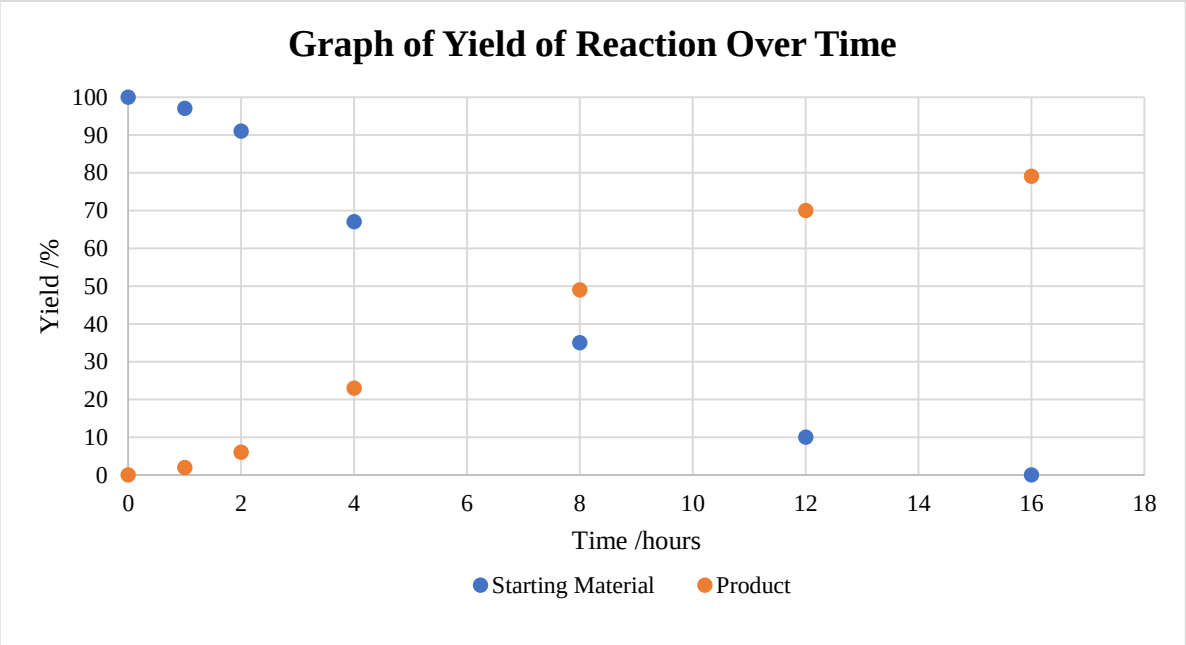
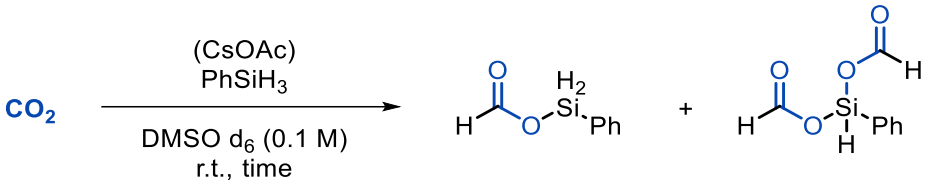


Figure S1 – Graph of the reaction yield vs time. The reaction was run with DMSO d_6 and an aliquot was taken at defined intervals, quenched with TFA (3 eq) and recorded by ^{1}H NMR. TMB was employed as the internal standard.

Reaction Plot of Phenylsilane in Presence/Absence of CsOAc



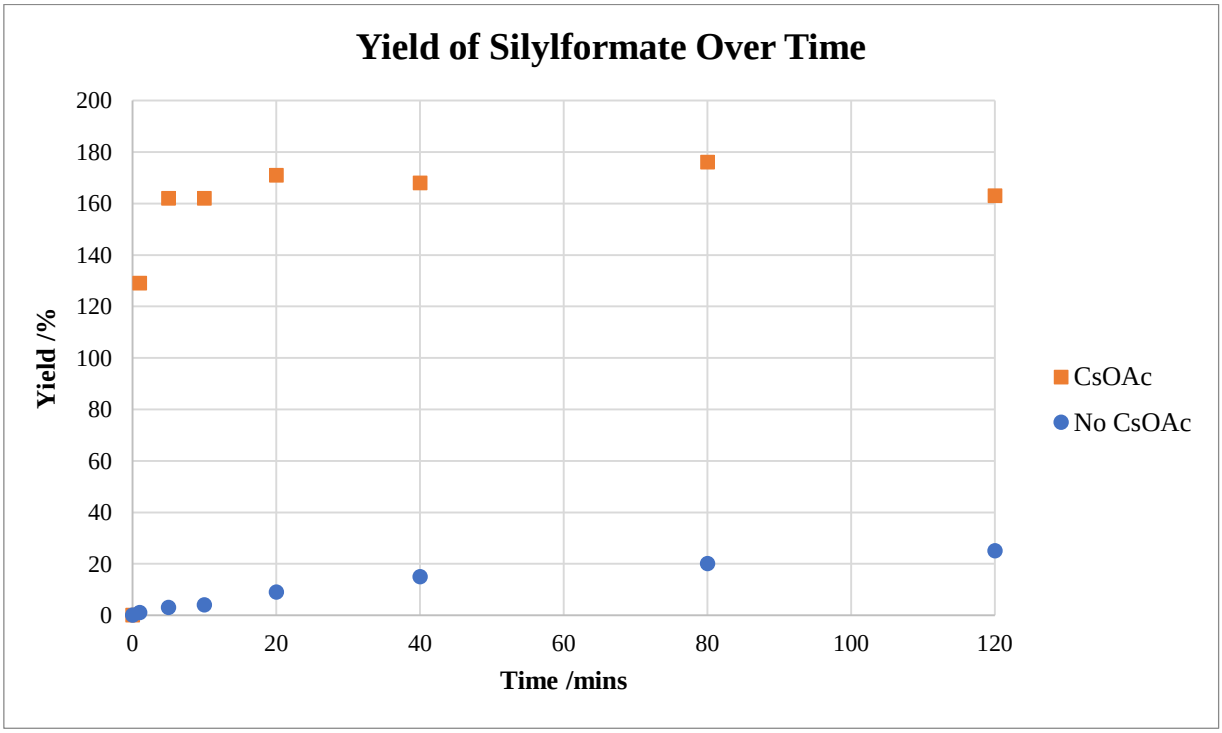
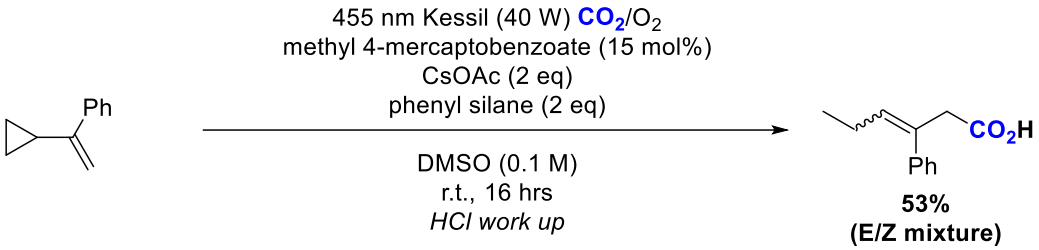


Figure S2 – Graph of the yield of silylformate formation vs time. Reaction was run with phenylsilane (0.2 mmol) in the presence/absence of CsOAc (0.2 mmol) in DMSO d_6, with aliquots of solution removed and sparged with Ar at each time interval. The internal standard used was dimethylacetamide.

The catalytic effect of caesium acetate is demonstrated in the above graph. The rate of reaction is rapidly increased and conversion of the silane to silylformate could be achieved within a 1-minute reaction time at room temperature.

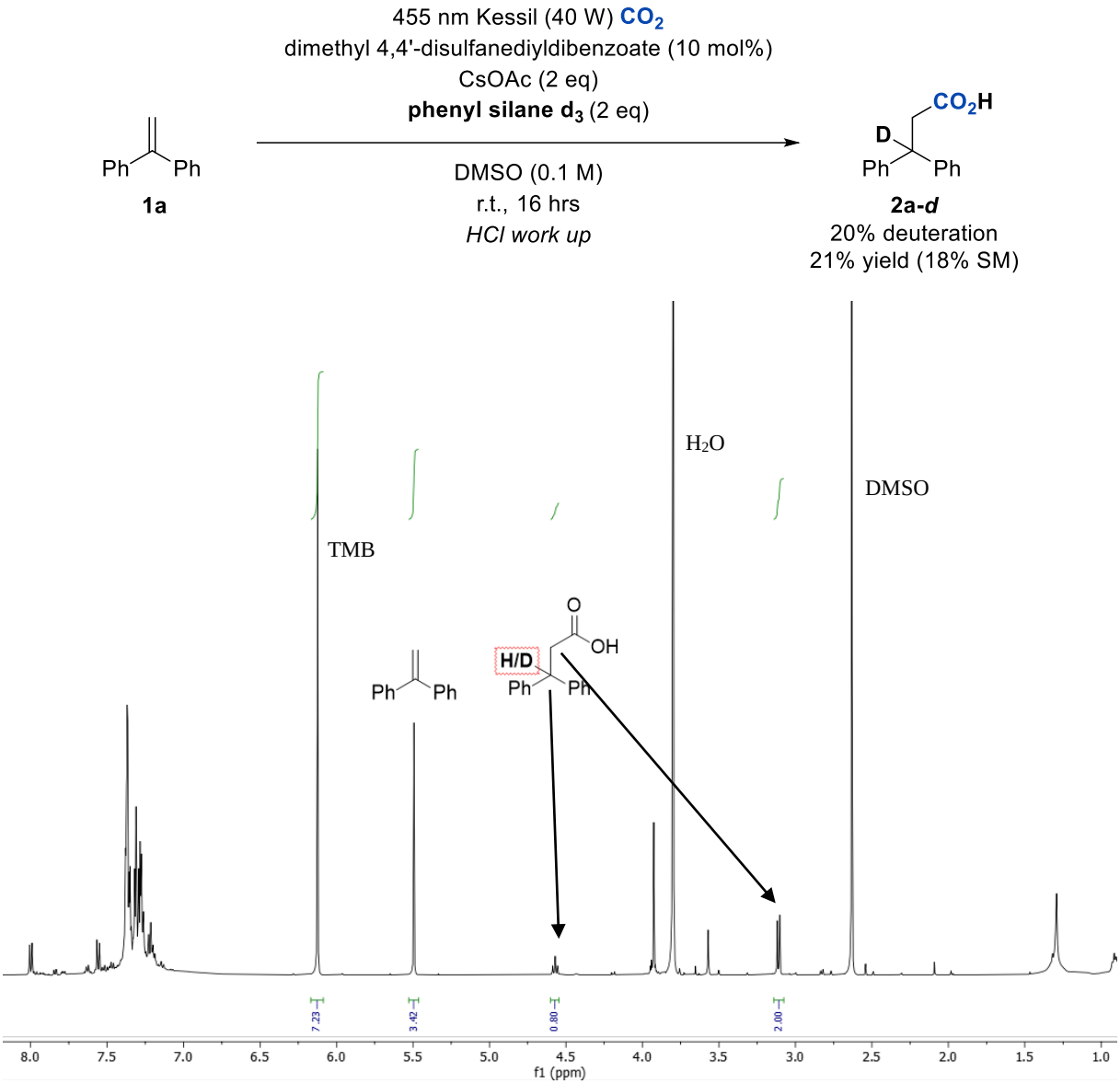
Radical Clock Test

To prove that a radical addition was taking place, a radical clock experiment was set up with substrate **S1**. The expected product was received in a 53% yield, giving further evidence towards a radical mechanism.

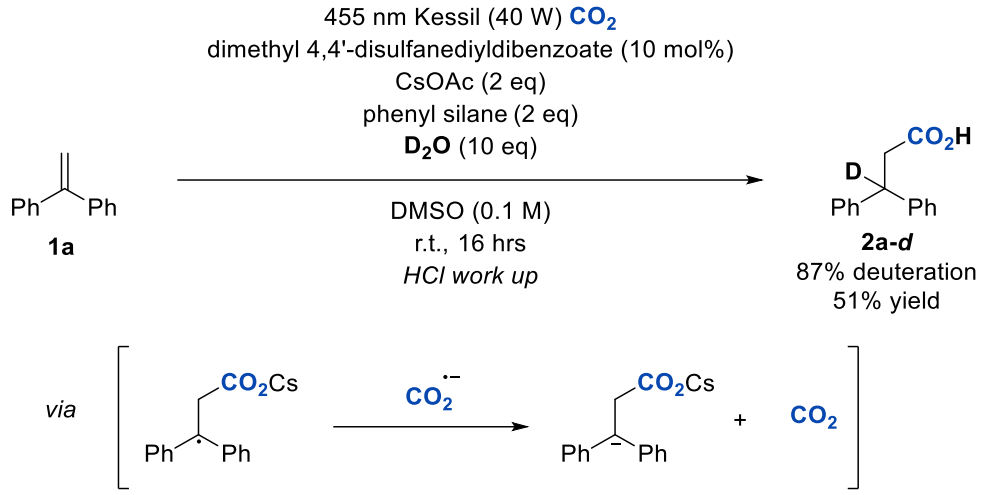


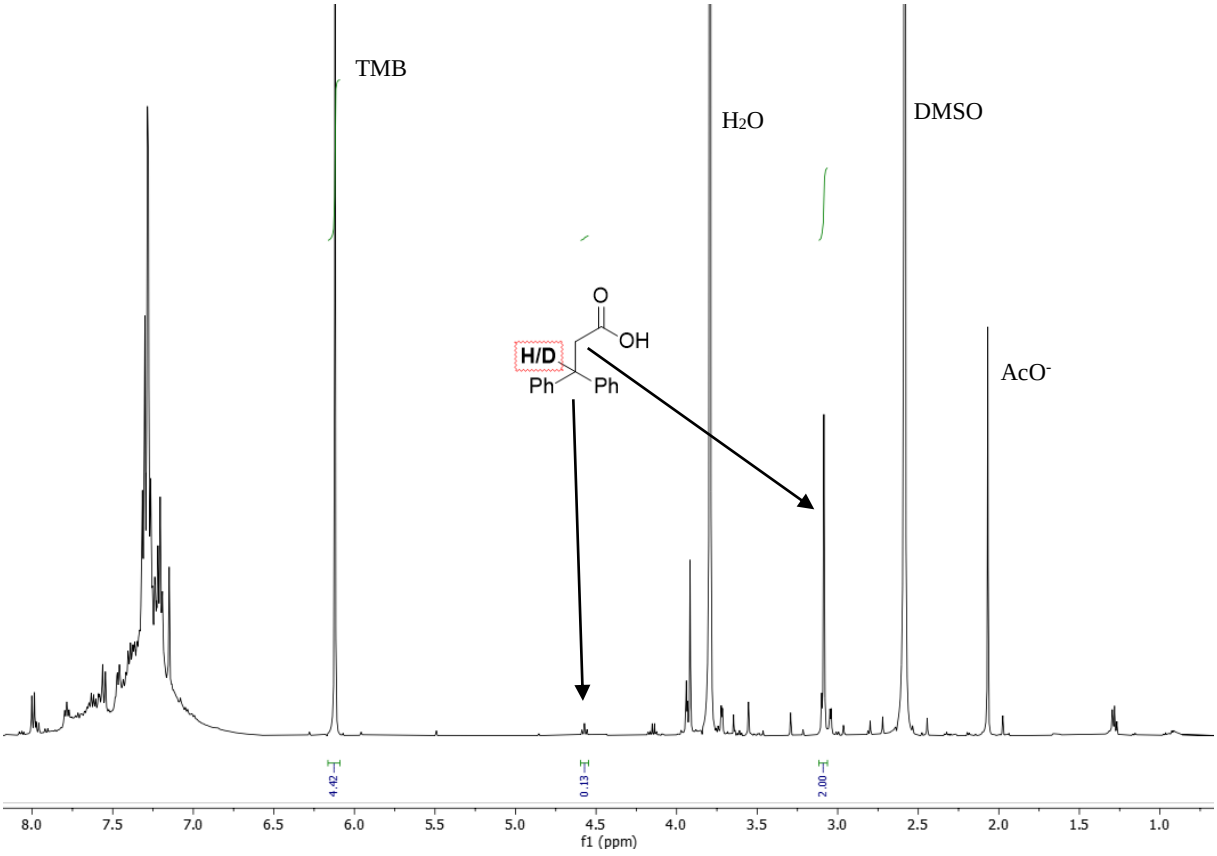
Deuterium Labelling

To demonstrate that CO_2 was sequentially reduced by silane, followed by HAT from a thiol radical, phenyl silane (d_3) was synthesised and employed into the reaction conditions. Deuteration in the *alpha*-position was observed, however only in low amounts. An alternative, favoured mechanism was therefore stipulated to be the major pathway.



To test if an anion intermediate was formed from two consecutive reactions with $CO_2^{\cdot-}$, D_2O was added to the solution as a protic deuterium source. From these results, it's clear that an anion is formed in the *alpha*-position as the major pathway. It is clear from these experiments however, that the delivery of the hydrogen atom takes place by both a radical abstraction from the carbon centred radical, and a proton abstraction from the carbon centred anion.





UV/Vis Spectra

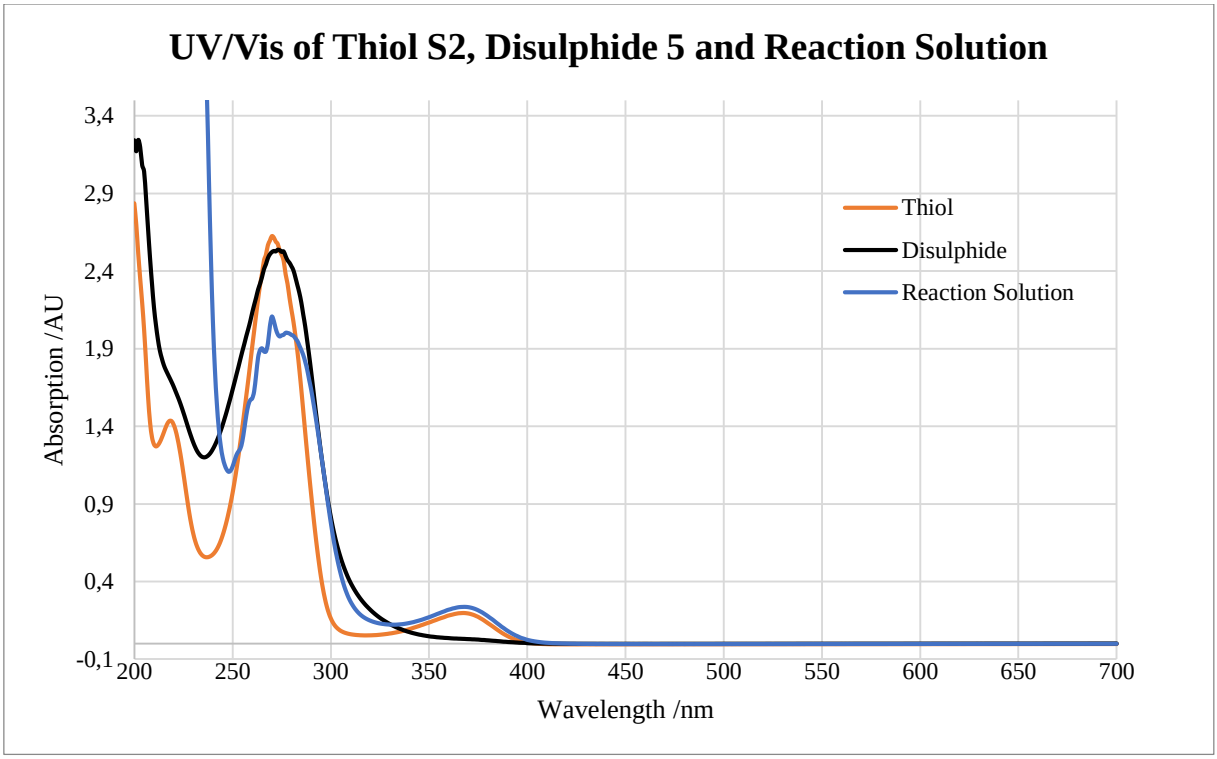
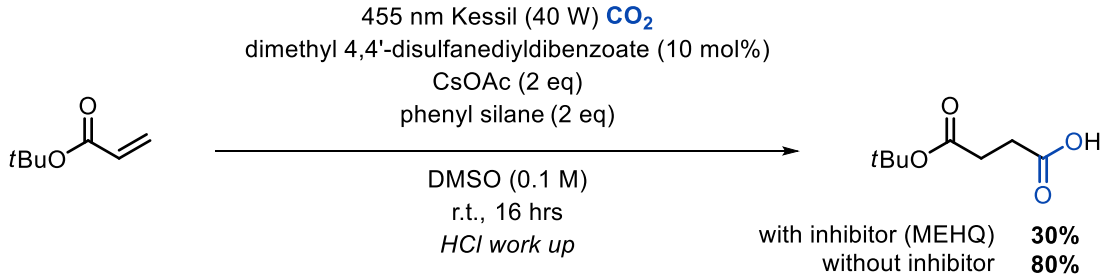


*Figure S3 – Graph of the absorbance vs wavelength of a) thiol **S2** in MeCN (1 mM), b) disulphide **5** in MeCN (1 mM), c) the reaction solution (pre irradiation) in MeCN (1 mM w.r.t. catalyst).*

Effect of Radical Inhibitors

While testing the scope of the reaction, it was found that the presence of radical inhibitors in commercial sources of alkenes (namely, styrenes and acrylates) had a detrimental effect on the reaction conditions. To prevent this, the pure substrate was obtained by filtering through 2.5 cm of neutral Al_2O_3 powder to remove the inhibitors.



Mechanism

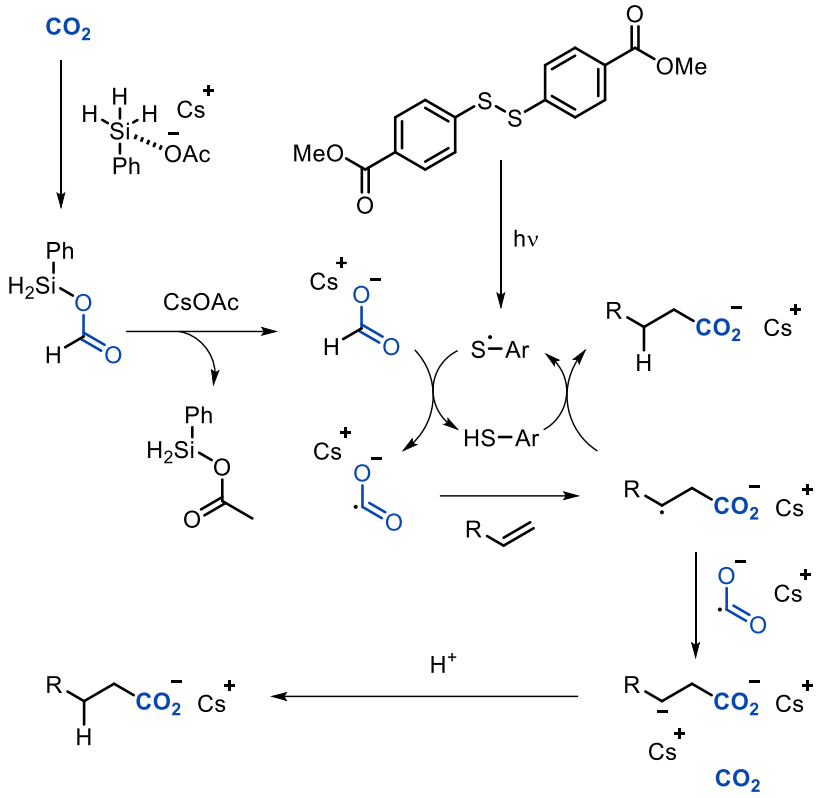


Figure S4 – A general mechanism towards the hydrocarboxylation of activated alkenes.

Illustration of Reaction and Lamp Set-up

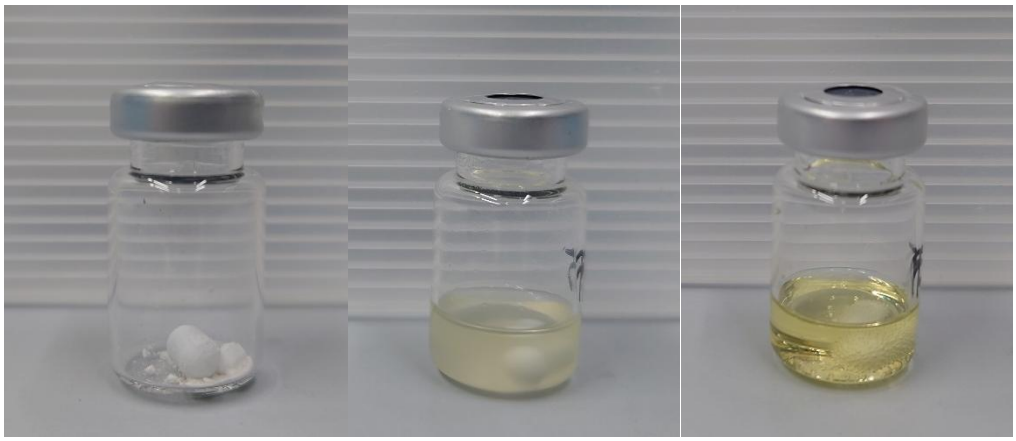


Figure S5 - a) Reaction vial after CsOAc and disulphide have been added and removed from the glovebox. b) Mixture after addition of DMSO and sparging with CO_2 for 30 s. c) Reaction mixture after addition of silane and substrate.

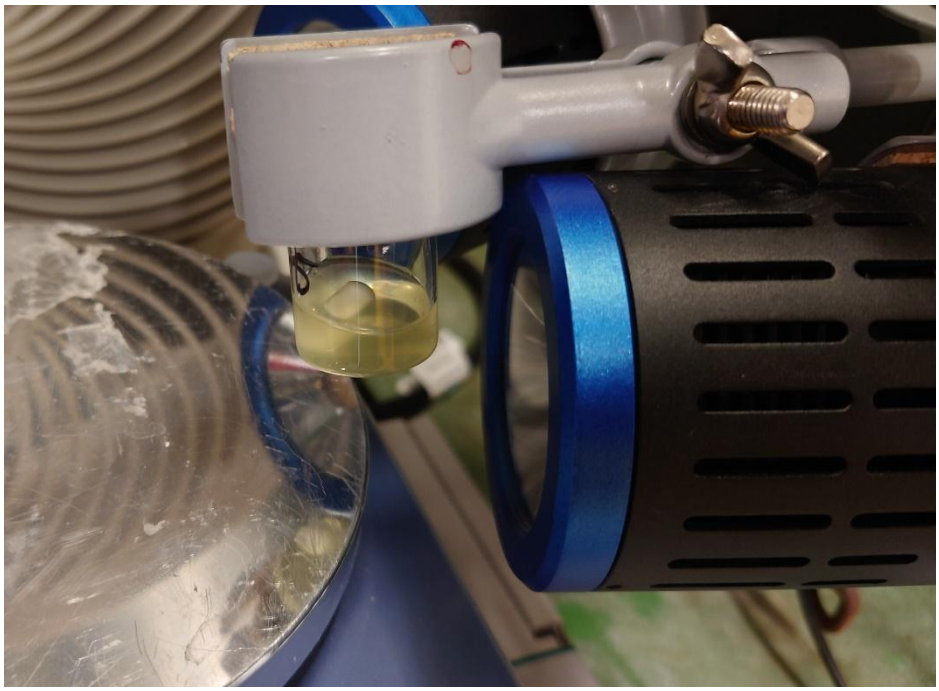
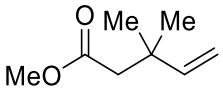


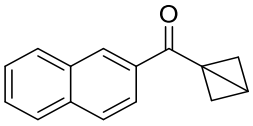
Figure S6 - Lamp set up with Kessil. Reaction mixture was clamped at approx. 2-4 cm from the light source. A fan was used to maintain the reaction temperature.

6. Additional Substrates

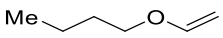


Following General procedure 1, methyl 3,3-dimethylpent-4-enoate (16 µL, 0.2 mmol) was employed. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (15 mg, 40%) as a colourless oil.

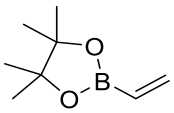
Note: Non-activated alkenes underperformed compared to their activated alkene counterparts. Due to the slower kinetics of the addition of $CO_2^{\bullet-}$ *(**7**) to generate **8** in the HAT cycle, the concentration of **8** remains very low, and therefore the regeneration of the thiol radical is stalled. The relatively fast over reduction of silyl acetate and silyl formate in the reaction conditions will therefore outcompete the formation of **7**, leading to a low conversion of the alkene.*



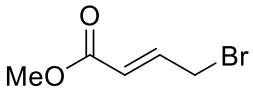
Degradation of starting material upon addition to reaction conditions.



No product observed, full consumption of starting material.



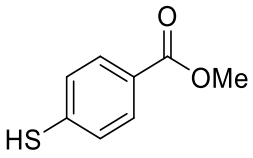
Product observed in ^{1}H NMR of the crude mixture in small quantities, but could not be purified.



Only hydrodehalogenated – hydrocarboxylation product **2j** observed.

7. Synthesis of Starting Materials

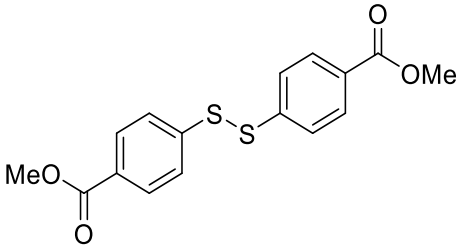
Methyl 4-mercaptobenzoate S2



A solution of 4-mercaptobenzoic acid (2.50 g, 16.2 mmol), H_2SO_4 (835 µL, 16.2 mmol) and MeOH (32.4 mL, 0.5 M) was heated to reflux over 15 hrs. The solution was cooled and MeOH was removed *in vacuo*. The crude mixture was diluted in ethyl acetate (100 mL) and $NaHCO_3$ sat. (200 mL). The organic layer was extracted with ethyl acetate (3 x 50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give the title compound (2.51 g, 92%) as a white powder. The compound was stored in a glovebox to avoid oxidation.

Analytical data matched those reported in the literature.[1]

Dimethyl 4,4'-disulfanediyldibenzoate 5



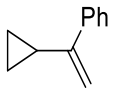
In a round-bottomed flask, methyl 4-mercaptobenzoate (1.00 g, 6.0 mmol) was added to dry DMSO (20 mL, 0.3 M). The solution was sparged with compressed air for 30 seconds before being irradiated with a 40 W Kessil Lamp (TUNA BLUE) for 3 hrs. The solution was diluted with EtOAc (150 mL) and washed with 1 M NaOH (3 x 100 mL) before being dried over $MgSO_4$ and reduced *in vacuo*. The resulting solid obtained was not purified any further and gave the title compound (971 mg, 97 % by mass) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.89 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.4, 142.1, 130.3, 128.9, 126.0, 52.2.

Analytical data matched those reported in the literature.[2]

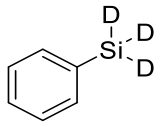
(1-Cyclopropylvinyl)benzene S1



In a flame-dried 2-neck round bottom flask methyltriphenylphosphonium bromide (3.57 g, 10 mmol) was dissolved in anhydrous THF (15 mL) and the mixture was cooled to -78 °C under an argon atmosphere. *n*-BuLi (4.0 mL, 2.5 M, 10 mmol) was added dropwise within 30 min, after which the reaction mixture was allowed to warm to room temperature. To this mixture cyclopropyl phenyl ketone (690 µL, 5.0 mmol) was added dropwise and the reaction was left to stir for 16 h. Brine (30 mL) was added and the phases were separated. The aqueous phase was extracted with pentane (3 × 20 mL), and the combined organic phases were dried over anhydrous $MgSO_4$, filtered and the crude mixture was further purified by flash chromatography using pure pentane as the eluent, giving compound the title compound (429 mg, 59%) as a colorless oil.

Analytical data matched those reported in the literature.[3]

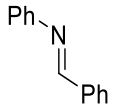
Phenylsilane-*d*$_3$ S3



$LiAlD_4$ (262 mg, 6.24 mmol) was suspended in dry Et_2O (6.2 mL) under an argon atmosphere and cooled to 0 °C. $PhSiCl_3$ (1.00 mL, 6.24 mmol) was added dropwise and the reaction mixture was warmed to r.t. and then refluxed at 45 °C for 15 h. The reaction mixture was then cooled to 0 °C, where it was carefully quenched with ice cold H_2O. The organic layer was separated and held at 0 °C and the aqueous layer extracted with ice cold Et_2O at 0 °C. The organic layers were combined, washed with ice cold brine at 0 °C, dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C at 40 mbar [CAUTION: concentrating below 40 mbar (e.g., 11 mbar) can result in the total loss of product] to furnish pure $PhSiD_3$ as a colourless oil (519 mg, 4.68 mmol, 75%).

Analytical data matched those reported in the literature.[4,5]

_N_-1-Diphenylmethanimine S4

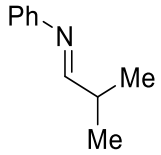


According to General Procedure 4, aniline (457 µL, 5 mmol) and benzaldehyde (500 µL, 5 mmol) were employed and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.49 (s, 1H), 7.99 – 7.89 (m, 2H), 7.51 (dd, J = 5.0, 1.9 Hz, 3H), 7.43 (dd, J = 8.3, 7.3 Hz, 2H), 7.31 – 7.21 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 160.4, 152.1, 136.3, 131.4, 129.2, 128.8, 128.8, 125.9, 120.9. Analytical data matched those reported in the literature.[6]

2-Methyl-*N*-phenylpropan-1-imine S5

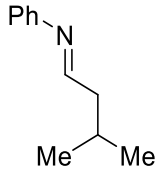


According to General Procedure 4, aniline (457 µL, 5 mmol) and isobutyraldehyde (456 µL, 5 mmol) were employed and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.73 (dd, J = 4.9, 0.6 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.21 – 7.12 (m, 3H), 7.02 (dq, J = 7.5, 1.2 Hz, 2H), 6.80 – 6.63 (m, 2H), 2.64 (pdd, J = 6.9, 4.9, 0.9 Hz, 1H), 1.20 (dd, J = 6.9, 0.7 Hz, 6H).

Due to the instability of the compound, no further analysis could be obtained.

3-Methyl-*N*-phenylbutan-1-imine S6

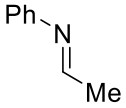


According to General Procedure 4, aniline (457 µL, 5 mmol) and isovaleraldehyde (536 µL, 5 mmol) were employed and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.92 – 7.84 (m, 1H), 7.42 – 7.33 (m, 2H), 7.29 – 7.12 (m, 2H), 7.10 – 7.01 (m, 1H), 2.39 (dt, *J* = 7.0, 4.7 Hz, 2H), 2.09 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.20 – 0.97 (m, 6H).

Due to the instability of the compound, no further analysis could be obtained.

N-Phenylethanimine S7

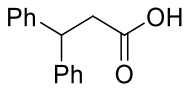


According to General Procedure 4, aniline (457 µL, 5 mmol) and acetaldehyde (250 µL, 5 mmol) were employed and used without further purification.

Due to the instability of the compound, no further analysis could be obtained.

8. Hydrocarboxylation of Styrenes

3,3-Diphenylpropanoic acid 2a



$C_{15}H_{14}O_2$
M: 226.27 g.mol^{-1}

According to General procedure 2, 1,1-diphenyl ethylene (36 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (38 mg, 84%) as colourless crystals.

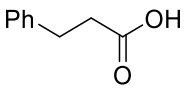
1.0 mmol scale: (158 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39 – 7.19 (m, 10H), 4.58 (t, J = 7.9 Hz, 1H), 3.14 (d, J = 7.9 Hz, 2H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 176.4, 143.2, 128.6, 127.6, 126.7, 46.7, 40.2. See spectrum.

Analytical data matched those reported in the literature.[7]

3-Phenylpropanoic acid 2b



$C_9H_{10}O_2$
M: 150.18 g.mol^{-1}

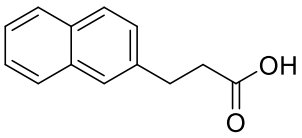
According to General procedure 2, styrene (23 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (17 mg, 57%) as colourless crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35 – 7.17 (m, 5H), 2.97 (t, J = 7.8 Hz, 2H), 2.70 (t, J = 7.8 Hz, 2H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.7, 140.2, 128.6, 128.3, 126.4, 35.5, 30.6. See spectrum.

Analytical data matched those reported in the literature.[8]

3-(Naphthalen-2-yl)propanoic acid 2c

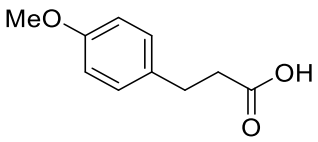


$C_{13}H_{12}O_2$
M: 200.24 g.mol^{-1}

According to General procedure 2, 2-vinylnaphthalene (31 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (15 mg, 37%) as colourless crystals.

Analytical data matched those reported in the literature.[11]

3-(4-Methoxyphenyl)propanoic acid 2d

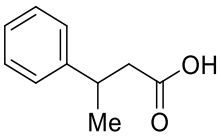


$C_{10}H_{12}O_3$
M: 180.20 g.mol^{-1}

According to General procedure 2, 4-vinyl anisole (27 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (12 mg, 33%) as a colourless oil.

Analytical data matched those reported in the literature.[11]

3-Phenylbutanoic acid 2e



$C_{10}H_{12}O_2$
M: 164.20 g.mol^{-1}

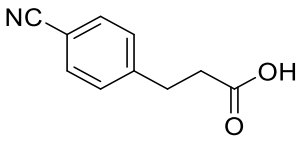
According to General procedure 2, *a*-methyl styrene (26 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (5 mg, 14%) as colourless crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 – 7.19 (m, 5H), 3.30 (dt, J = 8.1, 6.7 Hz, 1H), 2.75 – 2.55 (m, 2H), 1.35 (d, J = 7.0 Hz, 3H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 177.8, 145.4, 128.6, 126.7, 126.5, 42.4, 36.8, 21.9. See spectrum.

Analytical data matched those reported in the literature.[9]

3-(4-Cyanophenyl)propanoic acid 2f

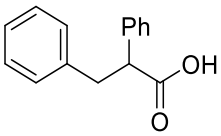


$C_{10}H_9NO_2$
M: 175.19 g.mol^{-1}

According to General procedure 2, 4-cyano styrene (26 mg, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (12 mg, 34%) as a colourless oil.

Analytical data matched those reported in the literature.[10]

2,3-Diphenylpropanoic acid 2g



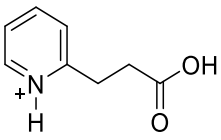
$C_{15}H_{14}O_2$
M: 226.27 g.mol^{-1}

According to General procedure 2, *trans*-stilbene (36 mg, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5

Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (19 mg, 42%) as colourless crystals.

Analytical data matched those reported in the literature.[7]

2-(2-Carboxyethyl)pyridin-1-ium 2h



$C_8H_{10}NO_2^+$
M: 152.17 g.mol^{-1}

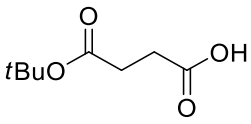
According to General Procedure 3, 2-vinylpyridine (21 µL, 0.2 mmol) was employed into the reaction conditions. The internal yield from the crude solution was 37%.

^{1}H NMR (400 MHz, DMSO d_6) δ_H 8.82 (dd, *J* = 6.0, 1.7 Hz, 1H), 8.48 (td, *J* = 7.9, 1.7 Hz, 1H), 7.87 (ddd, *J* = 7.3, 5.8, 1.2 Hz, 1H), 7.68 – 7.64 (m, 1H), 3.22 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H).

Analytical data matched those reported in the literature.[12]

9. Hydrocarboxylation of Giese-type Substrates

4-(*tert*-Butoxy)-4-oxobutanoic acid 2i



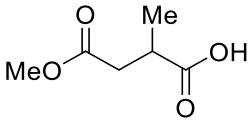
$C_8H_{14}O_4$
M: 174.20 g.mol^{-1}

According to General procedure 2, *tert*-butyl acrylate (29 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (28 mg, 80%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.66 – 2.58 (m, 2H), 2.58 – 2.50 (m, 2H), 1.44 (s, 9H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 177.8, 171.4, 81.0, 30.1, 29.1, 28.0. See spectrum.
Analytical data matched those reported in the literature.[13]

4-Methoxy-2-methyl-4-oxobutanoic acid 2j

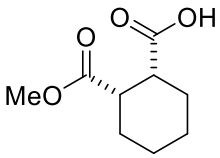


$C_6H_{10}O_4$
M: 146.14 g.mol^{-1}

According to General procedure 2, methyl (*E*)-but-2-enoate (21 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (26 mg, 89%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.69 (s, 3H), 2.96 (ddd, J = 8.0, 7.1, 6.0 Hz, 1H), 2.75 (dd, J = 16.7, 8.0 Hz, 1H), 2.43 (dd, J = 16.8, 6.0 Hz, 1H), 1.26 (d, J = 7.2 Hz, 3H). See spectrum.
^{13}C NMR (100 MHz, $CDCl_3$) δ_C 181.1, 172.2, 51.8, 37.1, 35.6, 16.8. See spectrum.
Analytical data matched those reported in the literature.[15]

2-(Methoxycarbonyl)cyclohexane-1-carboxylic acid 2k



75:25 d.r.
$C_9H_{14}O_4$
M: 186.21 g.mol^{-1}

According to General procedure 2, methyl cyclohex-1-ene-1-carboxylate (27 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (28 mg, 75%) as a colourless oil.

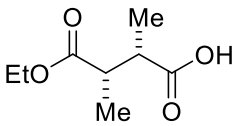
A mixture of diasterioisomers are reported:

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.67 (s, 3H), 2.89 – 2.80 (m, 1.5H), 2.61 (dtd, J = 26.4, 11.0, 3.7 Hz, 0.5H), 2.16 – 1.94 (m, 2H), 1.84 – 1.70 (m, 2H), 1.61 – 1.16 (m, 4H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 181.1, 180.0, 180.0, 180.0, 175.4, 174.1, 51.9, 51.7, 44.6, 44.5, 42.5, 42.4, 28.8, 26.3, 26.0, 25.2, 25.1, 23.8, 23.6. See spectrum.

Analytical data matched those reported in the literature.[14]

4-Ethoxy-2,3-dimethyl-4-oxobutanoic acid 2l



73:27 d.r.
$C_8H_{14}O_4$
M: 174.20 g.mol^{-1}

According to General procedure 2, ethyl tiglate (28 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (15 mg, 44%) as a colourless oil.

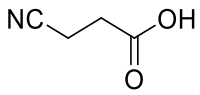
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 4.24 – 4.09 (m, 2H), 2.93 – 2.71 (m, 2H), 1.34 – 1.11 (m, 9H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 180.1, 179.2, 175.2, 174.8, 60.8, 60.8, 42.2, 42.1, 41.5, 41.4, 14.7, 14.6, 14.1, 13.6, 13.6. See spectrum.

IR ν 3074, 2982, 1730, 1707, 1430, 1131, 1079, 729, 698 cm^{-1}.

HRMS (ESI) m/z calcd for $C_8H_{13}Na_2O_4$ [(M+2Na-H)+] 219.0604, found 219.0603.

3-Cyanopropanoic acid 2m

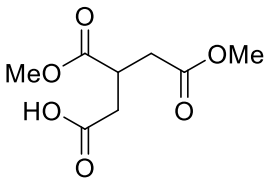


$C_4H_5NO_2$
M: 99.09 g.mol^{-1}

According to General procedure 2, acrylonitrile (13 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (17 mg, 86%) as a colourless oil.

Analytical data matched those reported in the literature.[10]

5-Methoxy-3-(methoxycarbonyl)-5-oxopentanoic acid 2n



$C_8H_{12}O_6$
M: 204.18 g.mol^{-1}

According to General procedure 2, dimethylitaconate (32 mg, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (24 mg, 59%) as a colourless oil.

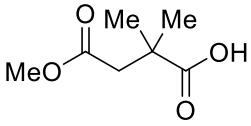
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.71 (d, J = 10.0 Hz, 6H), 3.33 – 3.22 (m, 1H), 2.83 (ddd, J = 18.2, 16.9, 6.8 Hz, 2H), 2.66 (ddd, J = 16.8, 12.8, 6.5 Hz, 2H). See spectrum.

^{13}C NMR (125 MHz, $CDCl_3$) δ_C 74.8, 173.5, 171.8, 52.5, 52.0, 37.1, 35.0, 34.5. See spectrum.

IR ν 3074, 2956, 2258, 1735, 1431, 1130, 1092, 1028, 908, 727, 696 cm^{-1}.

HRMS (ESI) m/z calcd for $C_8H_{11}Na_2O_6$ [(M+2Na-H)+] 249.0346, found 249.0343.

4-Methoxy-2,2-dimethyl-4-oxobutanoic acid 2o



$C_7H_{12}O_4$
M: 160.17 $g.mol^{-1}$

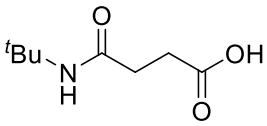
According to General procedure 2, methyl 3-methylbut-2-enoate (26 µL, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (14 mg, 44%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.67 (s, 3H), 2.62 (s, 2H), 1.31 (s, 6H). See spectrum.

^{13}C NMR (100 MHz, $CDCl_3$) δ_C 182.1, 171.7, 58.2, 51.6, 43.8, 40.4, 25.2. See spectrum.

Analytical data matched those reported in the literature.[16]

4-(*tert*-Butylamino)-4-oxobutanoic acid 2p



$C_8H_{15}NO_3$
M: 173.21 $g.mol^{-1}$

According to General procedure 2, *tert*-butylacrylamide (25 mg, 0.2 mmol) was employed into the reaction conditions. The crude product was purified by column chromatography (95:5 Pent.:EtOAc – 80:19:1 Pent.:EtOAc:AcOH) to give the title compound (15 mg, 43%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.59 (s, 1H), 2.73 – 2.60 (m, 2H), 2.52 – 2.45 (m, 2H), 1.37 (s, 9H). See spectrum.

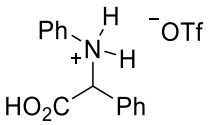
^{13}C NMR (125 MHz, $CDCl_3$) δ_C 174.1, 172.6, 52.2, 31.6, 30.6, 28.7. See spectrum.

IR ν 3329, 3074, 2928, 2251, 1718, 1650, 1547, 1260, 1132, 1095, 1027, 907, 801, 728, 696 cm^{-1}.

HRMS (ESI) m/z calcd for $C_8H_{14}NNa_2O_3$ [(M+2Na-H)+] 218.0764, found 218.0761.

10. Hydrocarboxylation of Imines

***N*-(Carboxy(phenyl)methyl)benzenaminium trifluoromethanesulfonate 4a**
N-Phenyl-2-phenylglycine ammonium triflate



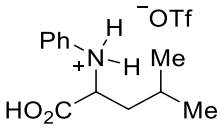
According to General Procedure 3, *N*-1-diphenylmethanimine (36 mg, 0.2 mmol) was employed into the reaction conditions. The internal yield from the crude solution was 100%.

^{1}H NMR (400 MHz, DMSO d_6) δ_H 7.47 – 7.40 (m, 1H), 7.28 – 7.19 (m, 2H), 7.14 (dt, *J* = 14.9, 7.4 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.99 – 6.91 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.54 – 6.43 (m, 1H), 4.75 (d, *J* = 1.9 Hz, 1H). See spectrum.

^{13}C NMR (100 MHz, DMSO d_6) δ_C 172.5, 147.4, 141.8, 129.3, 129.2, 128.3, 128.2, 127.3, 122.8, 119.6, 113.9, 55.6. See spectrum.

Analytical data matched those reported in the literature.[17]

***N*-(1-Carboxy-3-methylbutyl)benzenaminium trifluoromethanesulfonate 4b**
N-Phenyl-leucine ammonium triflate



According to General Procedure 3, 2-methyl-*N*-phenylpropan-1-imine (32 mg, 0.2 mmol) was employed into the reaction conditions. The internal yield from the crude solution was 49%.

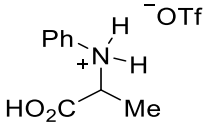
^{1}H NMR (400 MHz, DMSO d_6) δ_H 7.32 (t, *J* = 7.7 Hz, 1H), 7.15 – 7.03 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 3.58 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.27 (dd, *J* = 13.3, 5.3 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.02 – 1.92 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H). See spectrum.

^{13}C NMR (100 MHz, DMSO d_6) δ_C 172.5, 129.9, 129.6, 122.8, 119.6, 55.6, 27.4, 23.6, 21.5. See spectrum.

Analytical data matched those reported in the literature.[18]

N-(1-Carboxyethyl)benzenaminium trifluoromethanesulfonate 4c

N-Phenyl-alanine ammonium triflate



According to General Procedure 3, *N*-phenylethanimine (24 mg, 0.2 mmol) was employed into the reaction conditions. The internal yield from the crude solution was 62%.

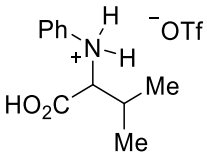
^{1}H NMR (400 MHz, DMSO d_6) δ_H 7.58 – 7.24 (m, 5H), 5.07 (q, J = 5.1 Hz, 1H), 1.23 (d, J = 5.1 Hz, 3H). See spectrum.

^{13}C NMR (100 MHz, DMSO d_6) δ_C 172.5, 141.8, 130.3, 123.6, 119.6, 55.6, 20.8. See spectrum.

Analytical data matched those reported in the literature.[17]

N-(1-Carboxy-2-methylpropyl)benzenaminium trifluoromethanesulfonate 4d

N-Phenyl-valine ammonium triflate



According to General Procedure 3, 3-methyl-*N*-phenylbutan-1-imine (29 mg, 0.2 mmol) was employed into the reaction conditions. The internal yield from the crude solution was 88%.

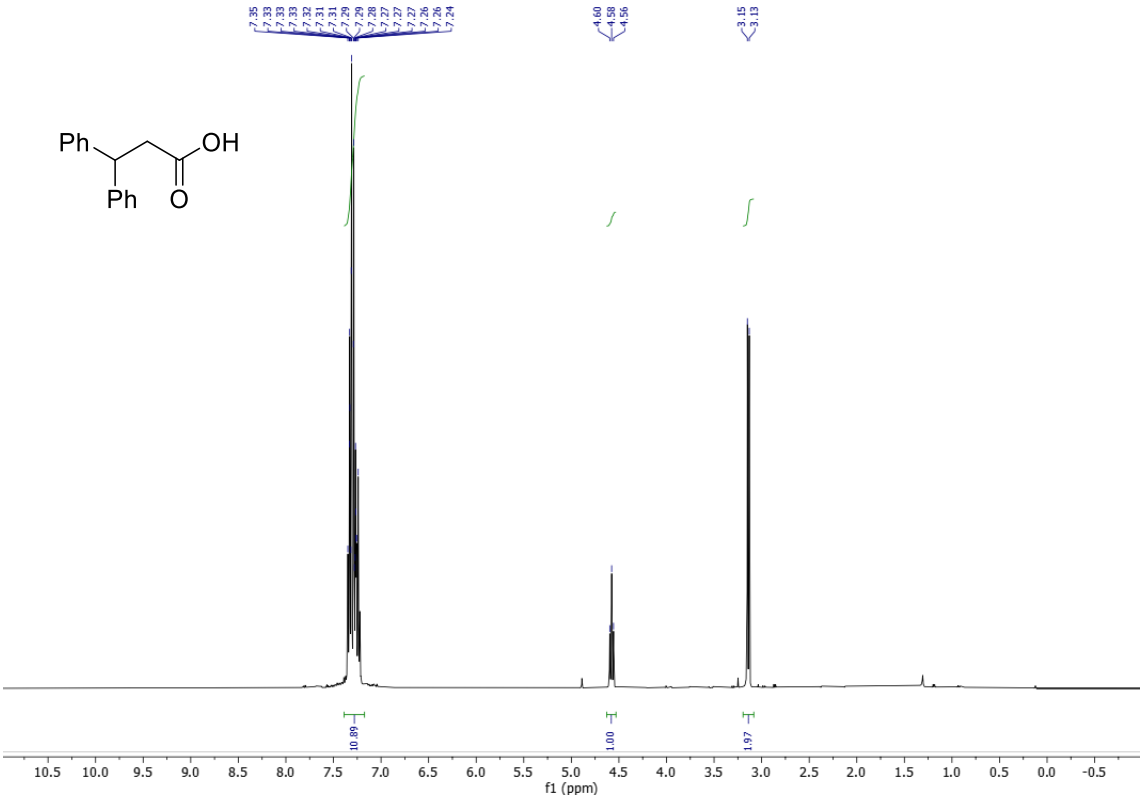
^{1}H NMR (400 MHz, DMSO d_6) δ_H 7.50 – 7.40 (m, 2H), 7.35 – 7.24 (m, 3H), 3.12 (d, J = 7.0 Hz, 1H), 1.99 – 1.84 (m, 1H), 0.98 (d, J = 6.7 Hz, 6H). See spectrum.

^{13}C NMR (100 MHz, DMSO d_6) δ_C 172.5, 141.8, 130.3, 122.8, 119.6, 55.6, 26.3, 21.5, 20.4. See spectrum.

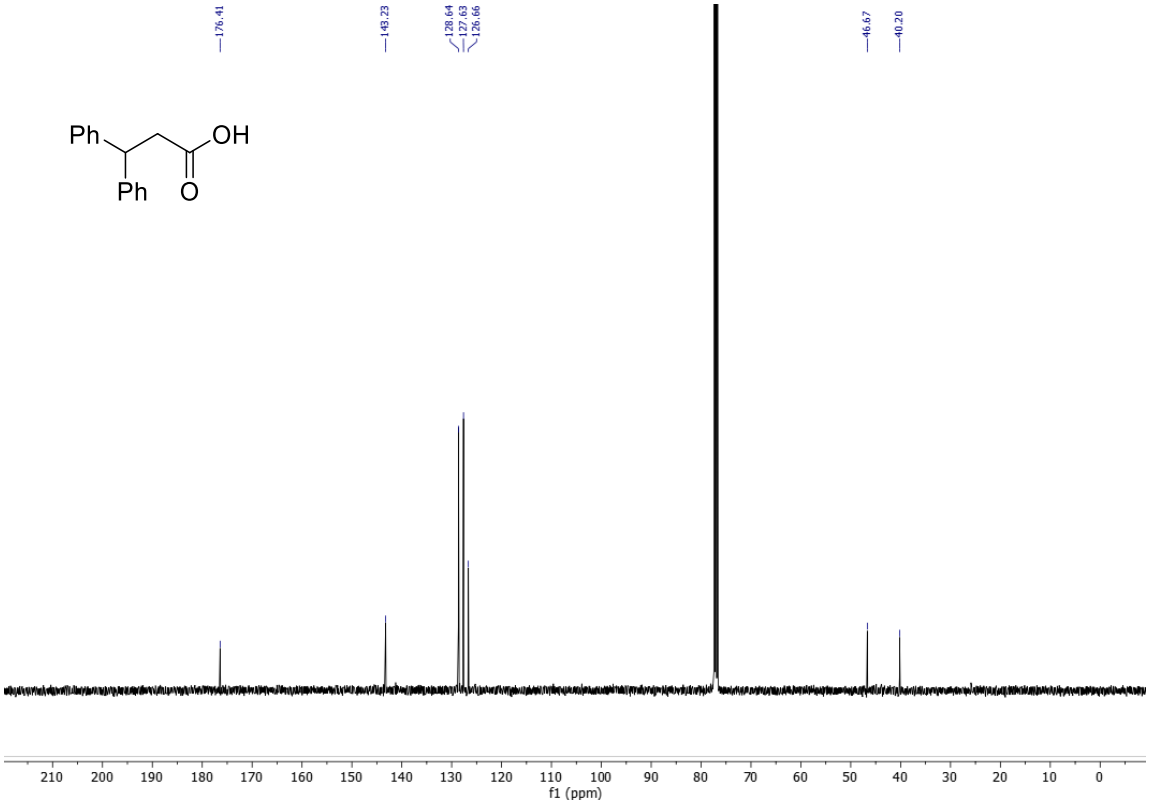
Analytical data matched those reported in the literature.[17]

11. NMR Spectra of Synthesised Compounds

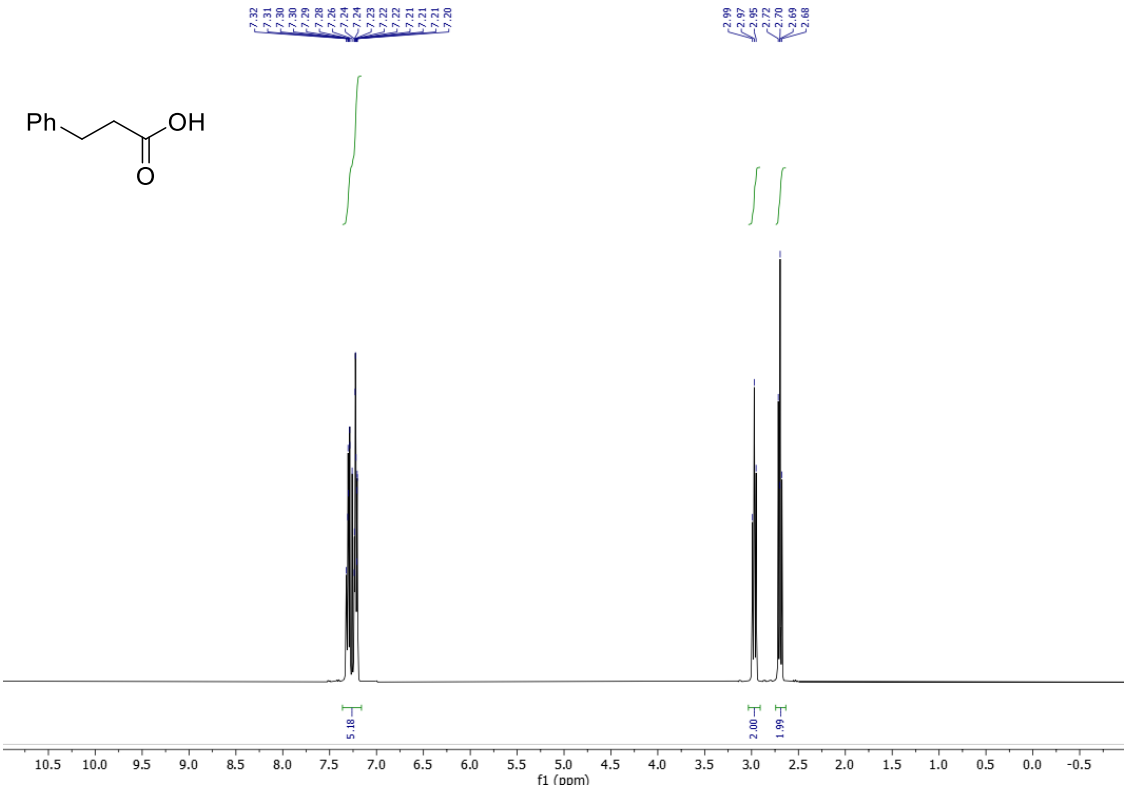
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a** (see procedure).



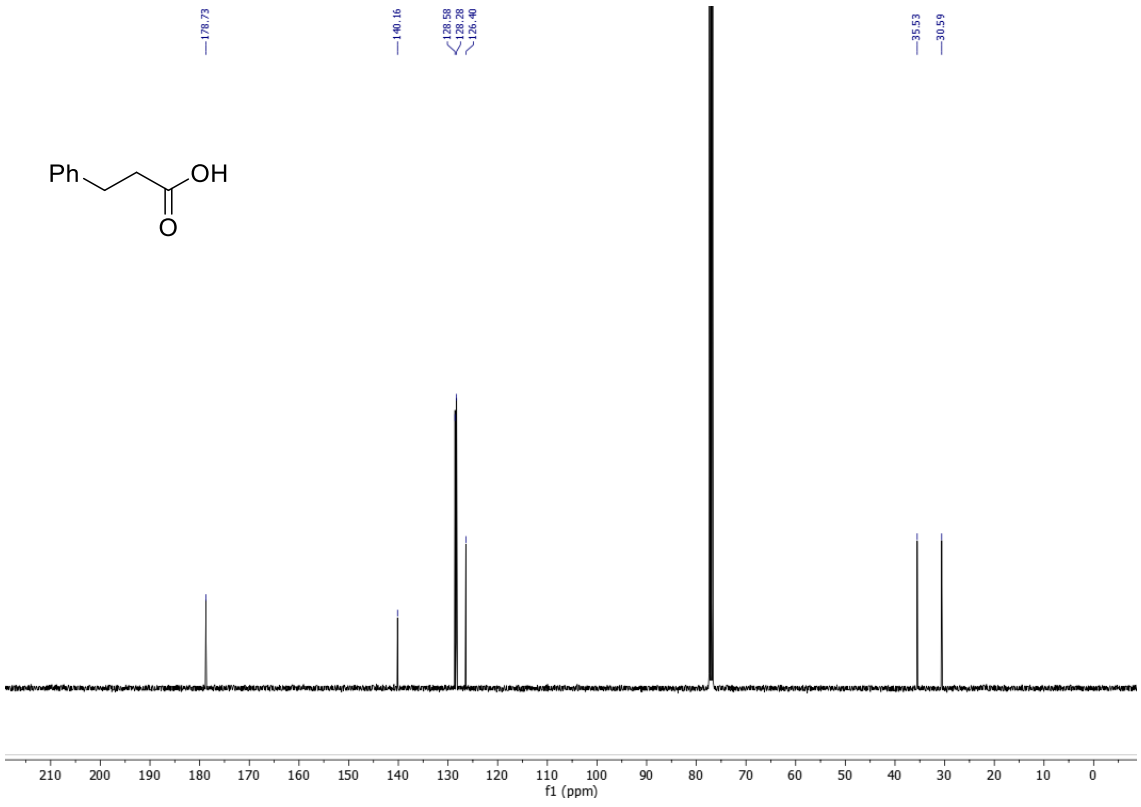
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2a** (see procedure).



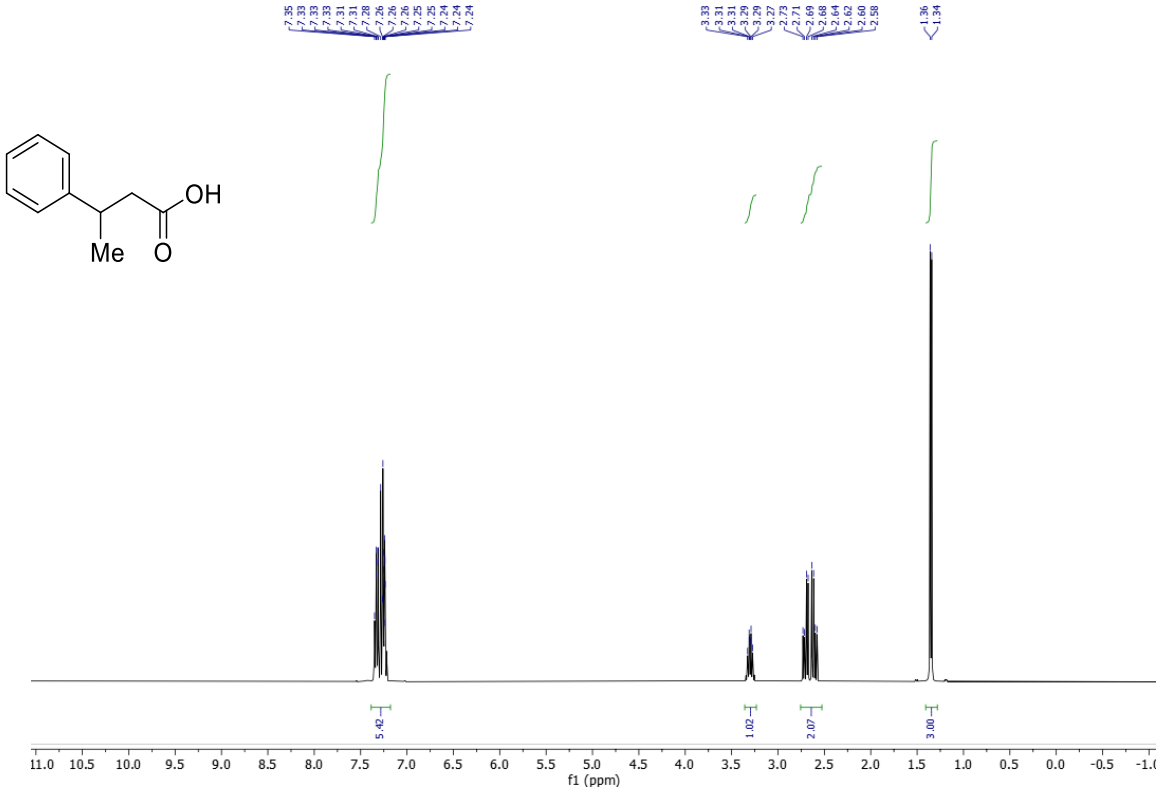
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b** (see procedure).



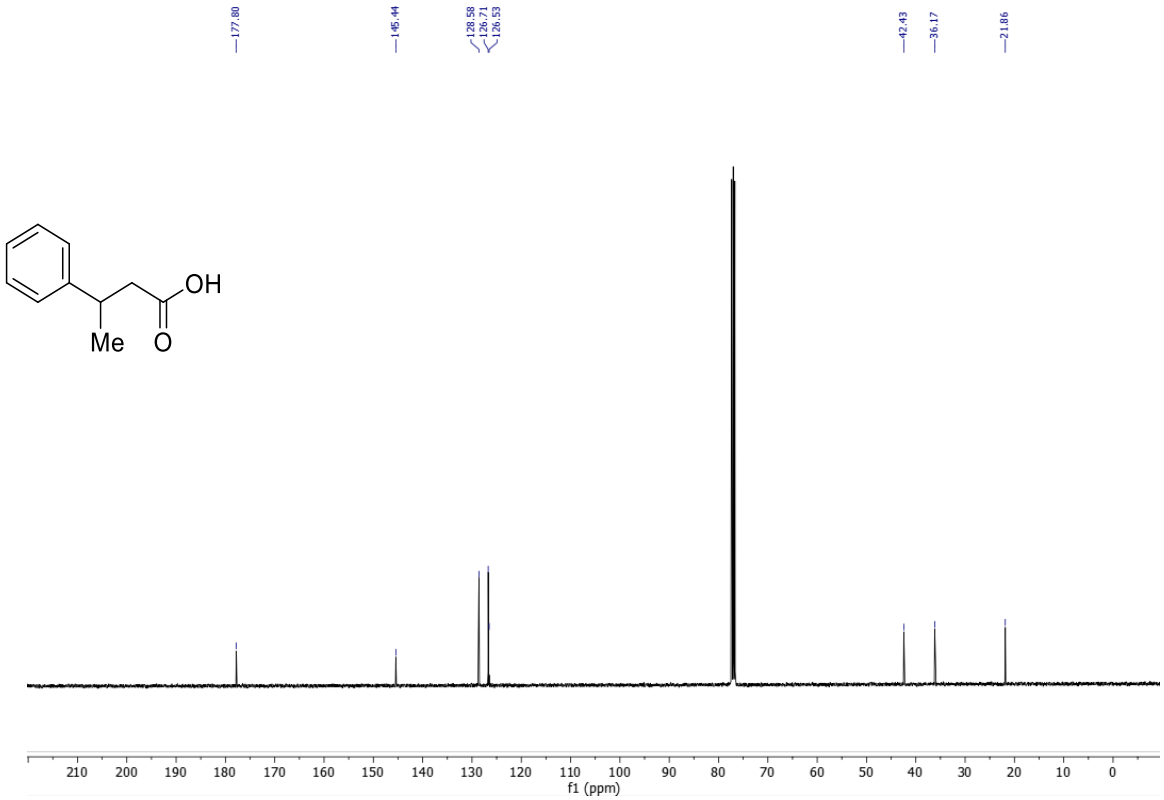
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2b** (see procedure).



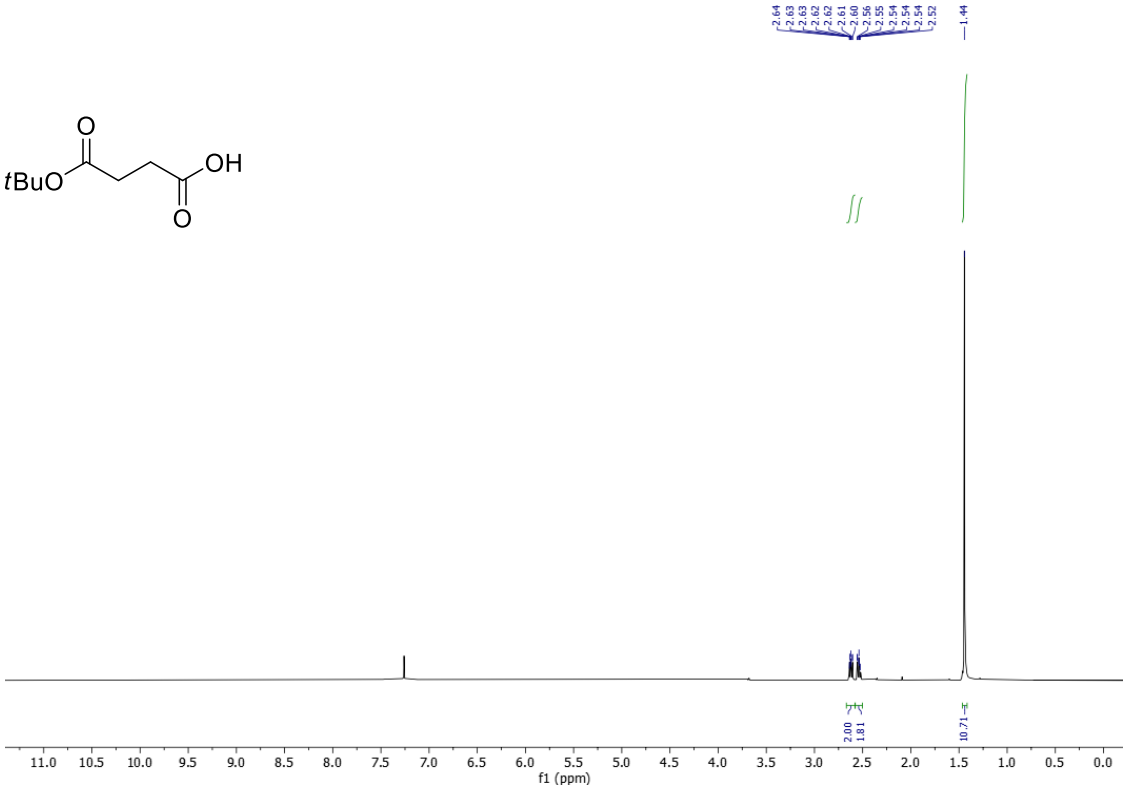
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e** (see procedure).



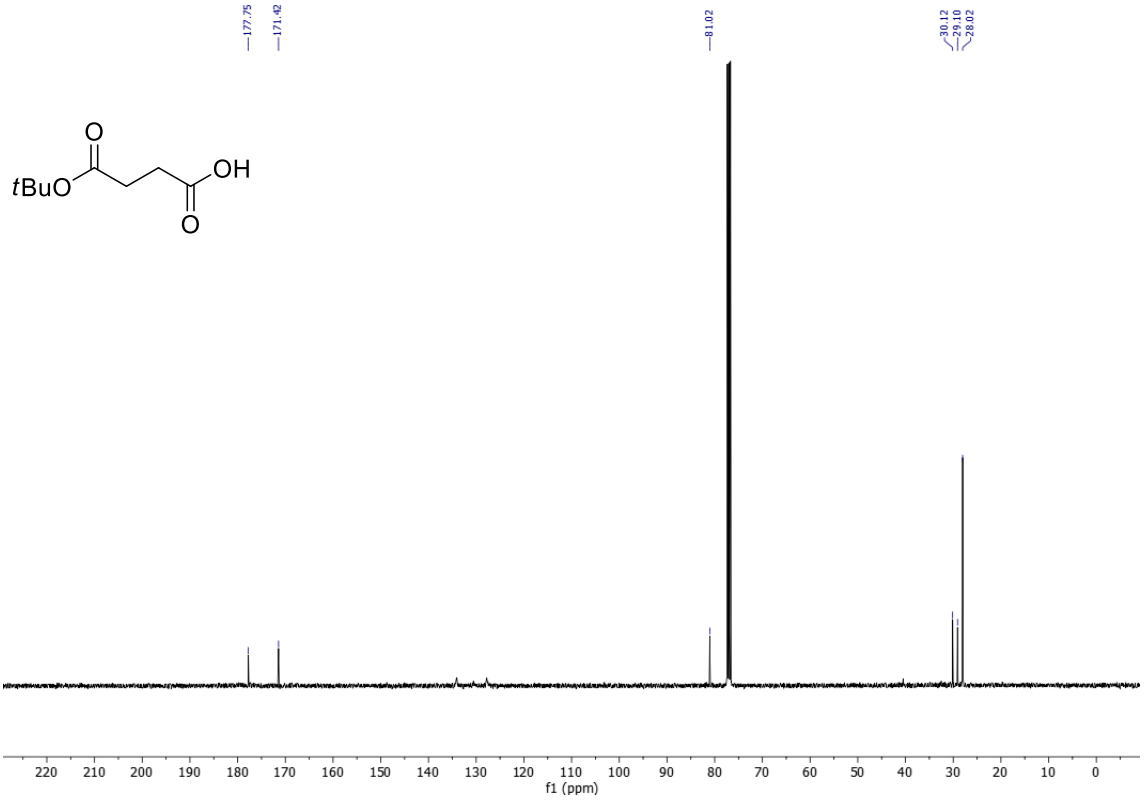
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2e** (see procedure).



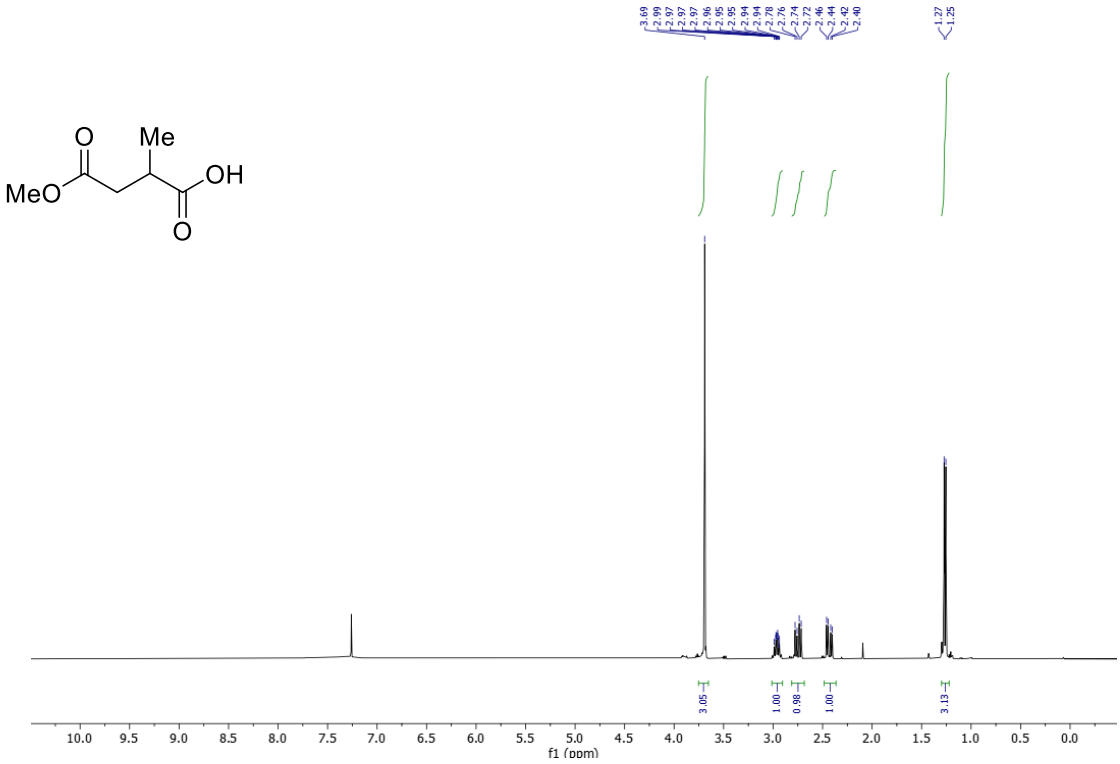
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i** (see procedure).



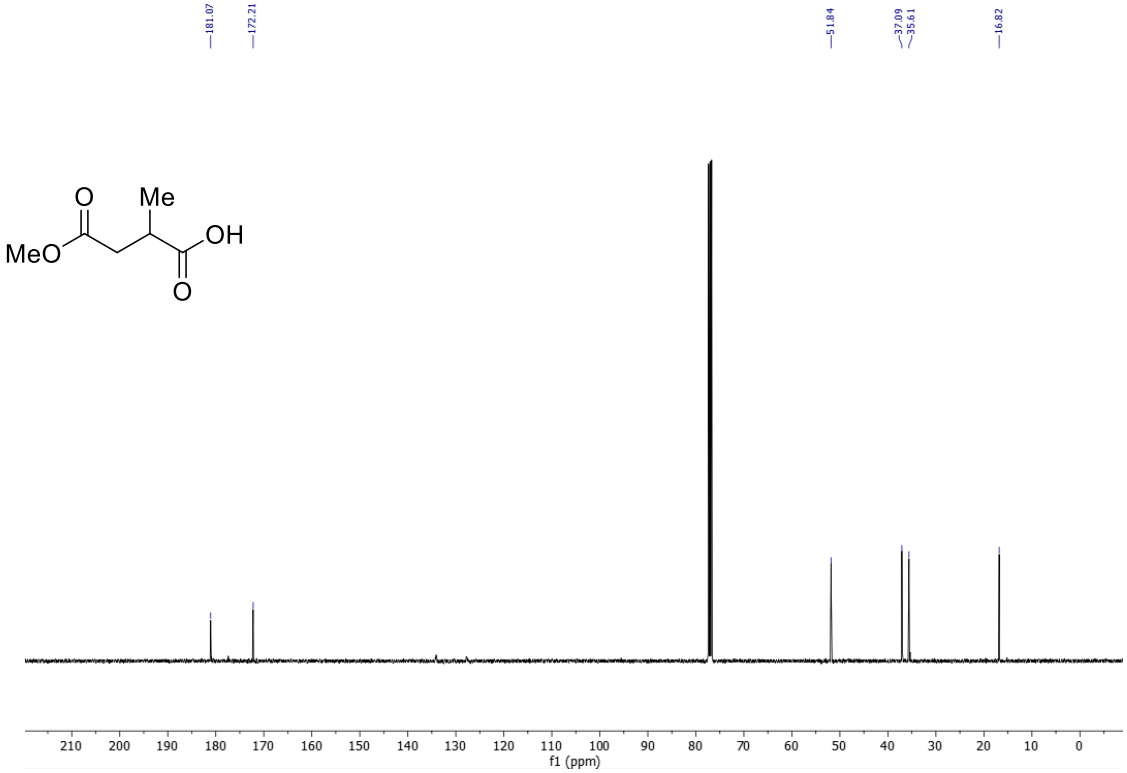
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2i** (see procedure).



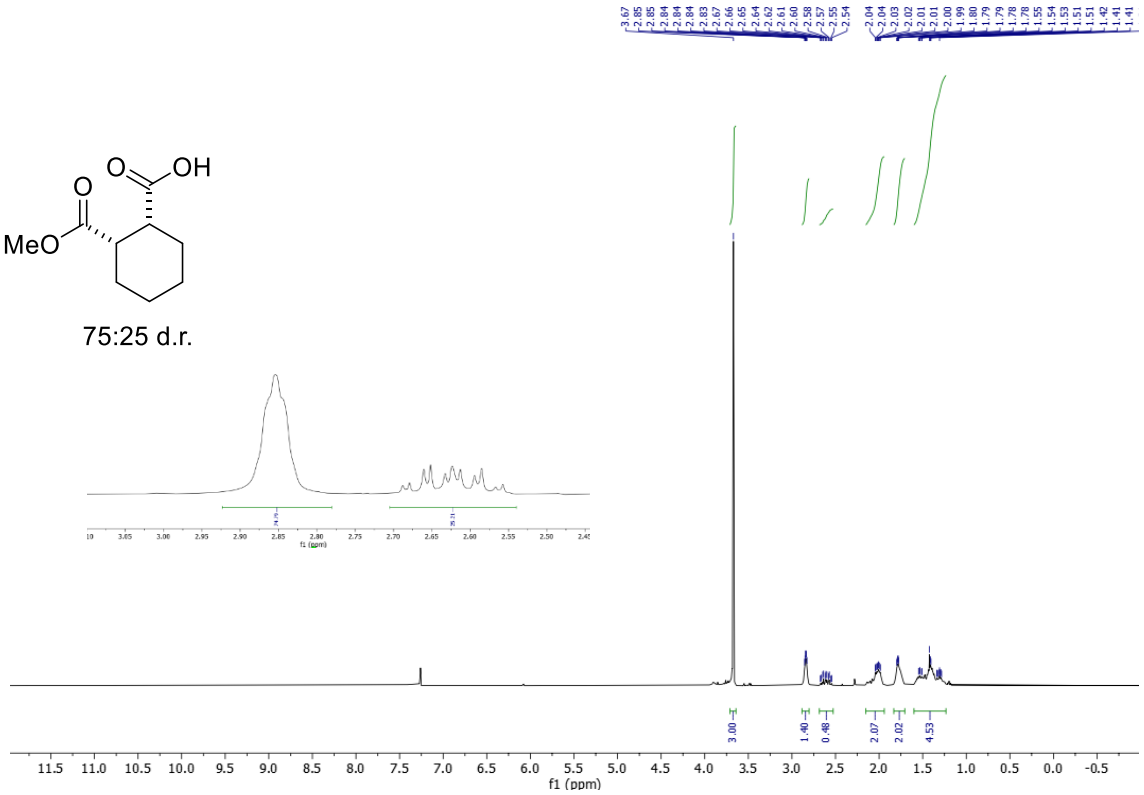
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2j** (see procedure).



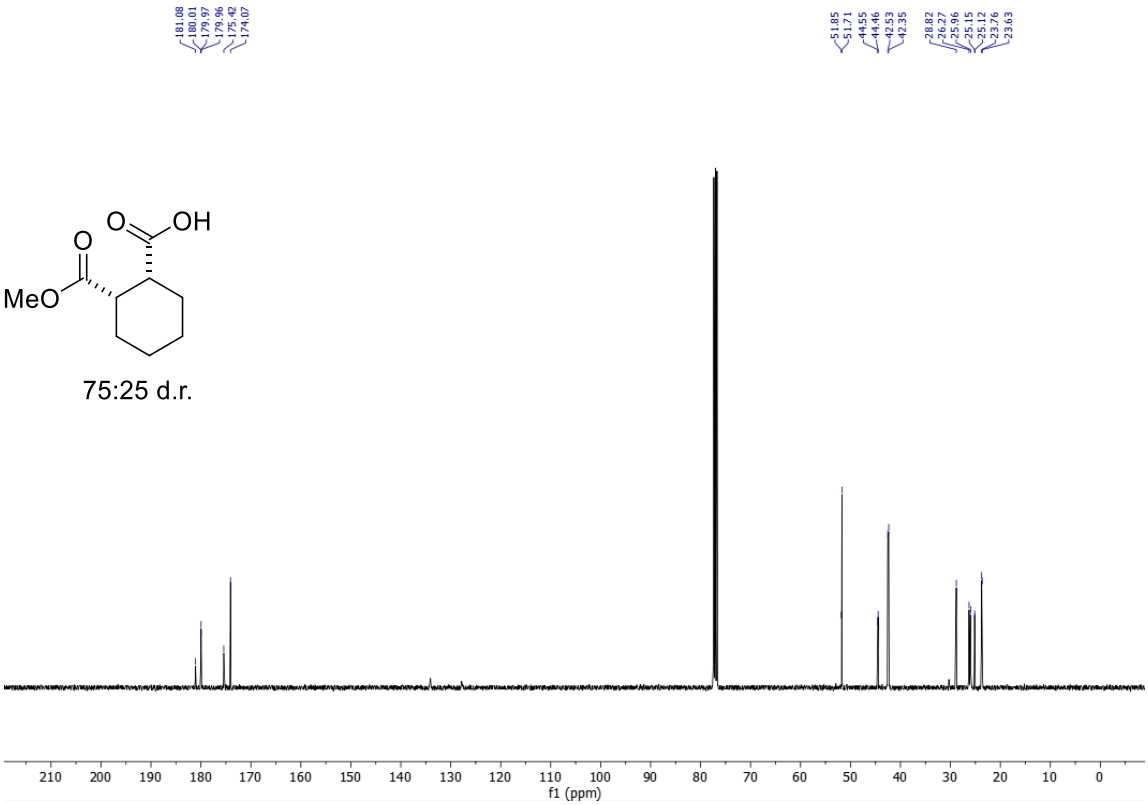
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2j** (see procedure).



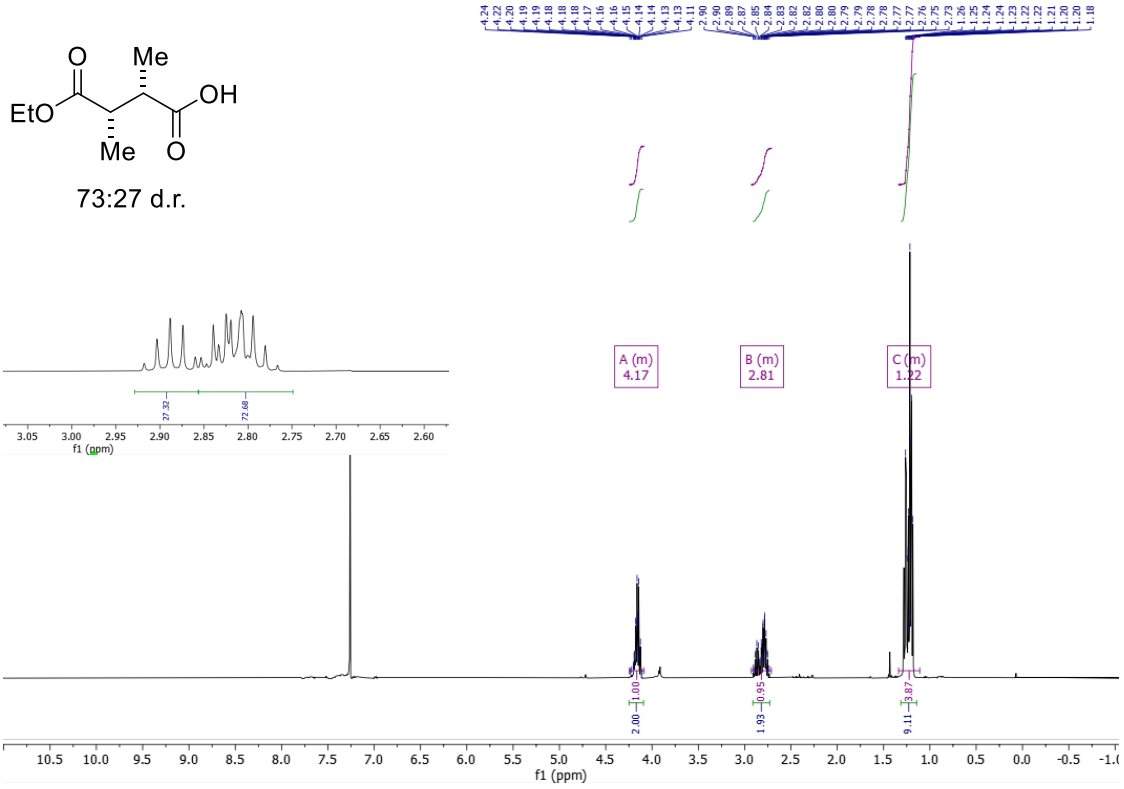
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k** (see procedure).



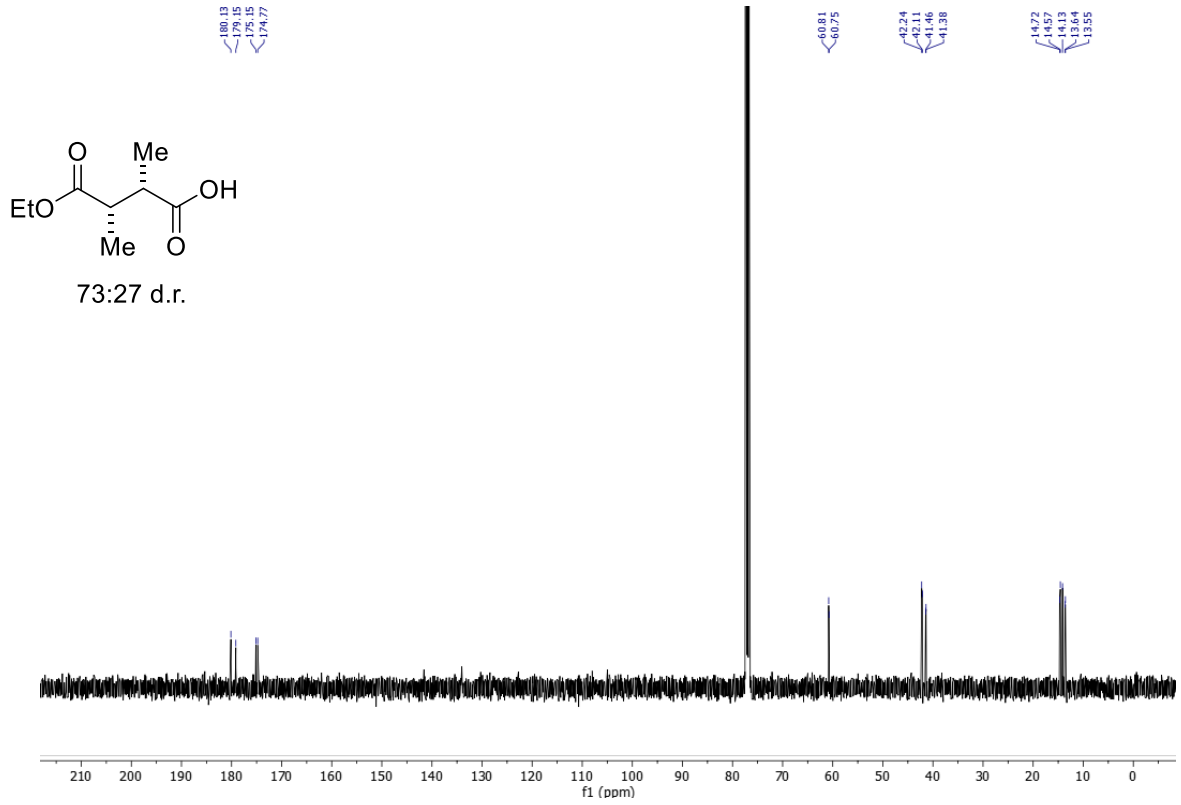
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2k** (see procedure).



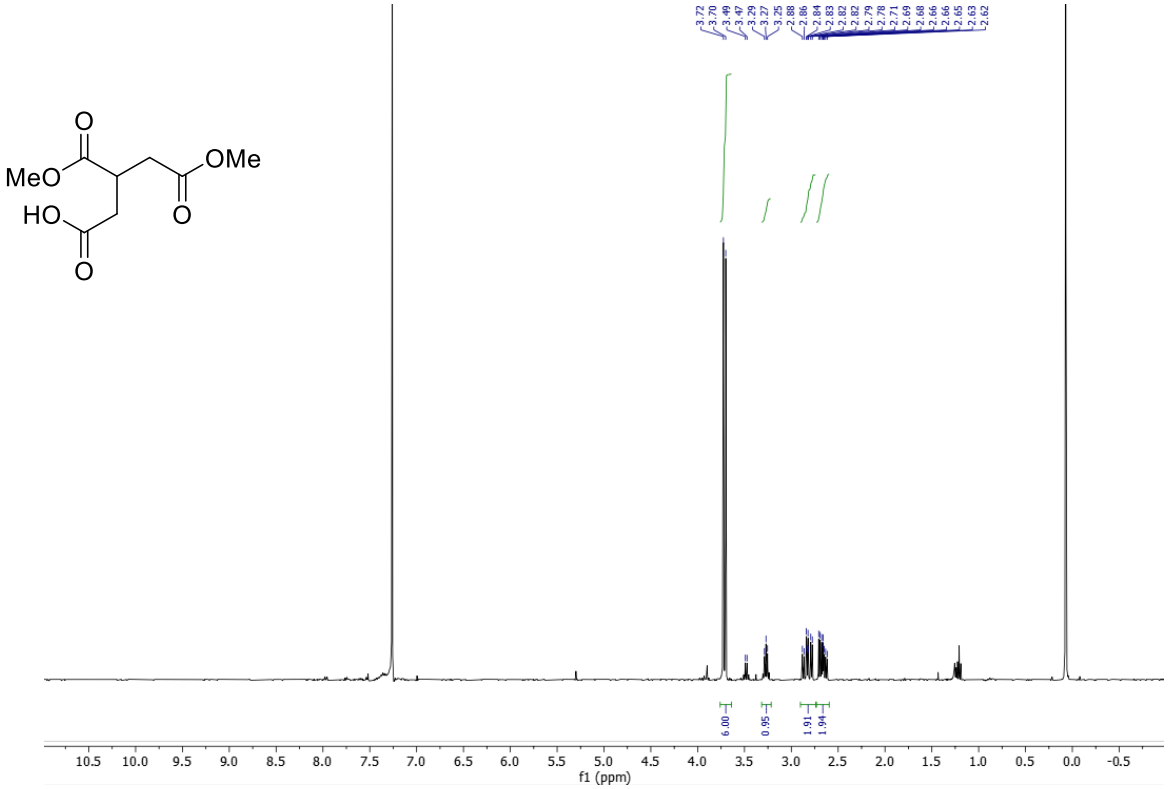
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2l** (see procedure).



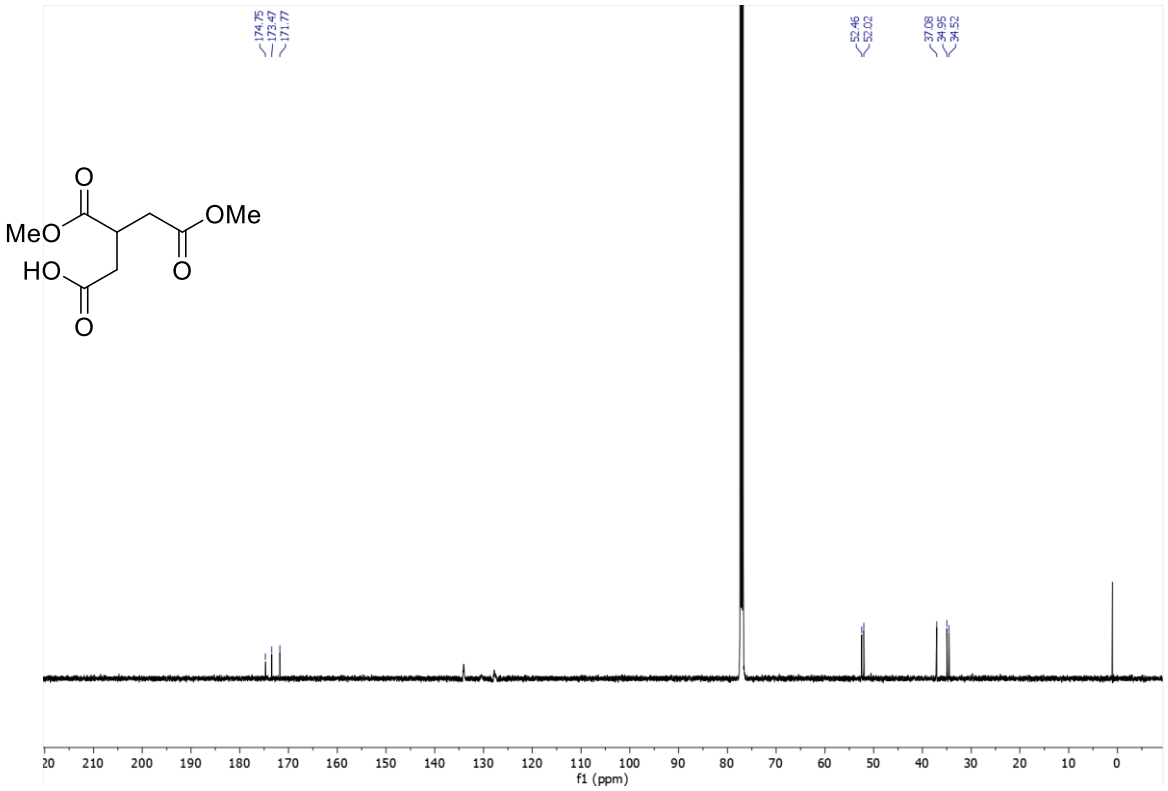
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2l** (see procedure).



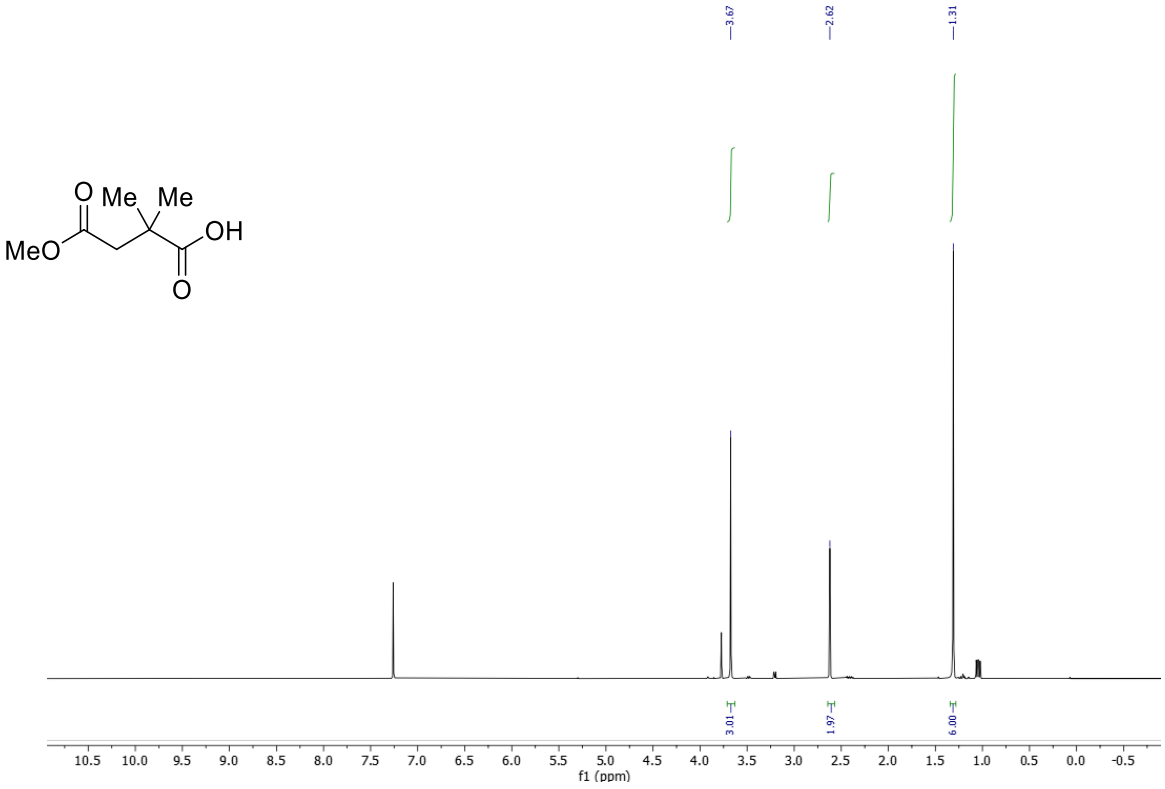
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2n** (see procedure).



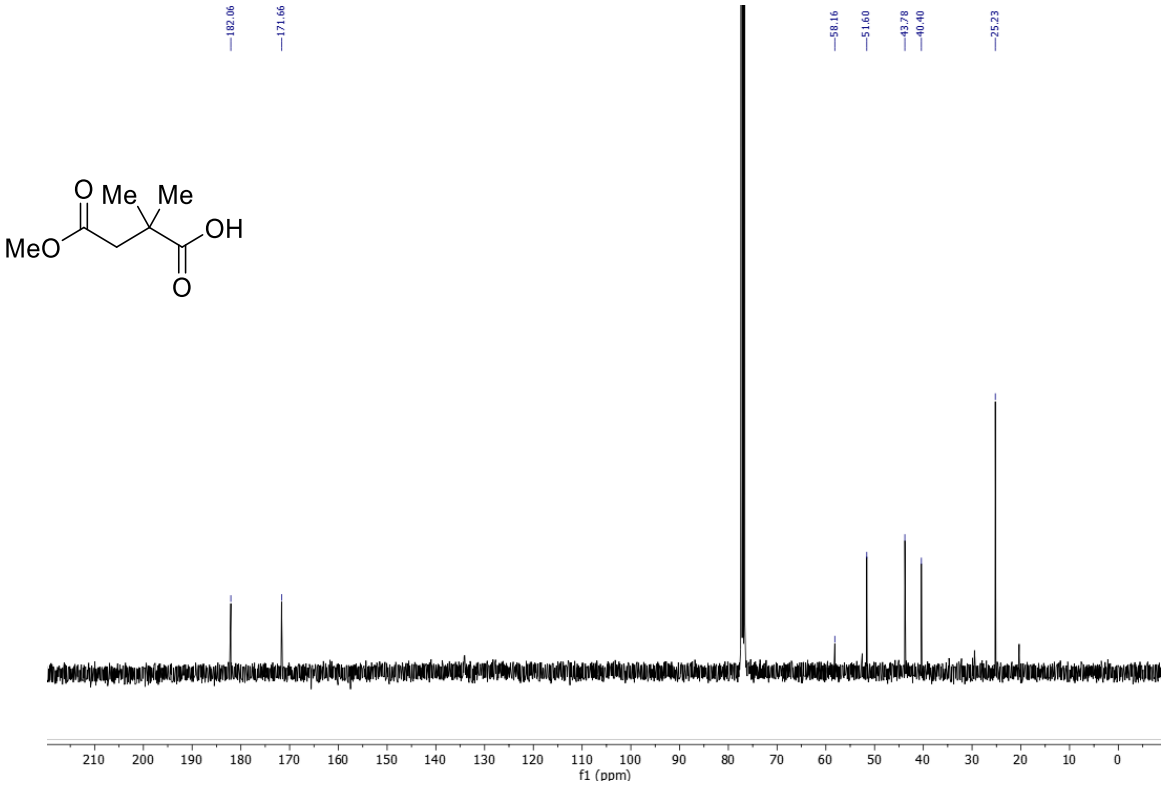
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2n** (see procedure).



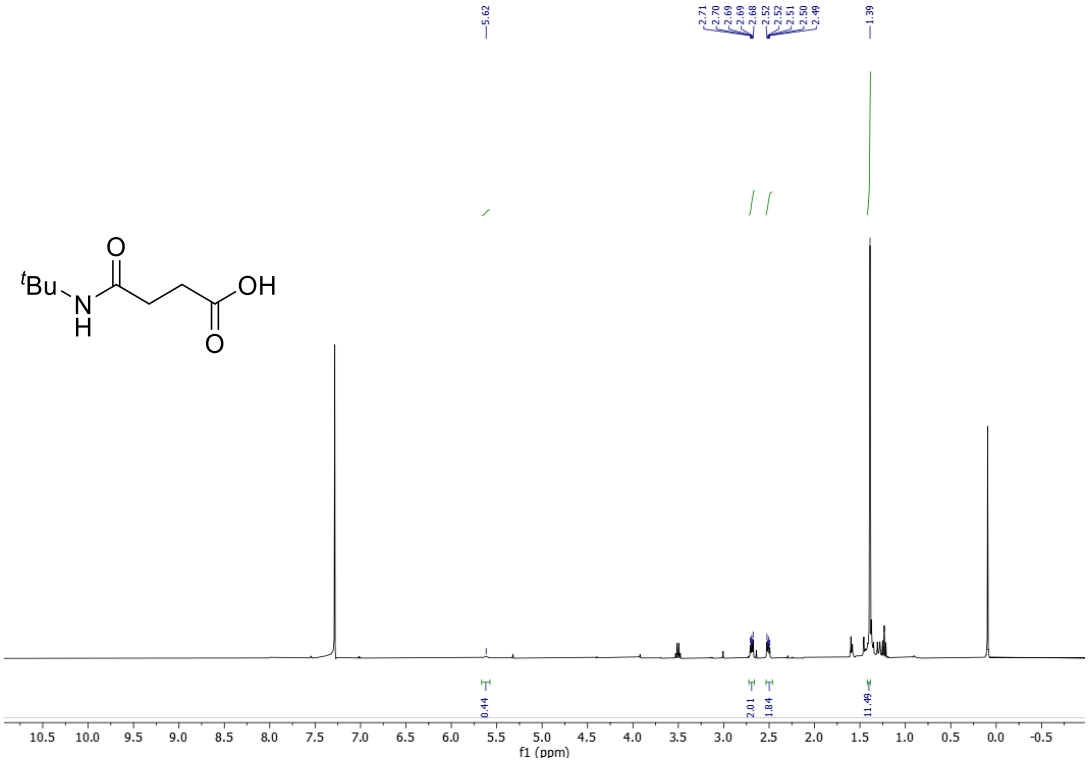
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2o** (see procedure).



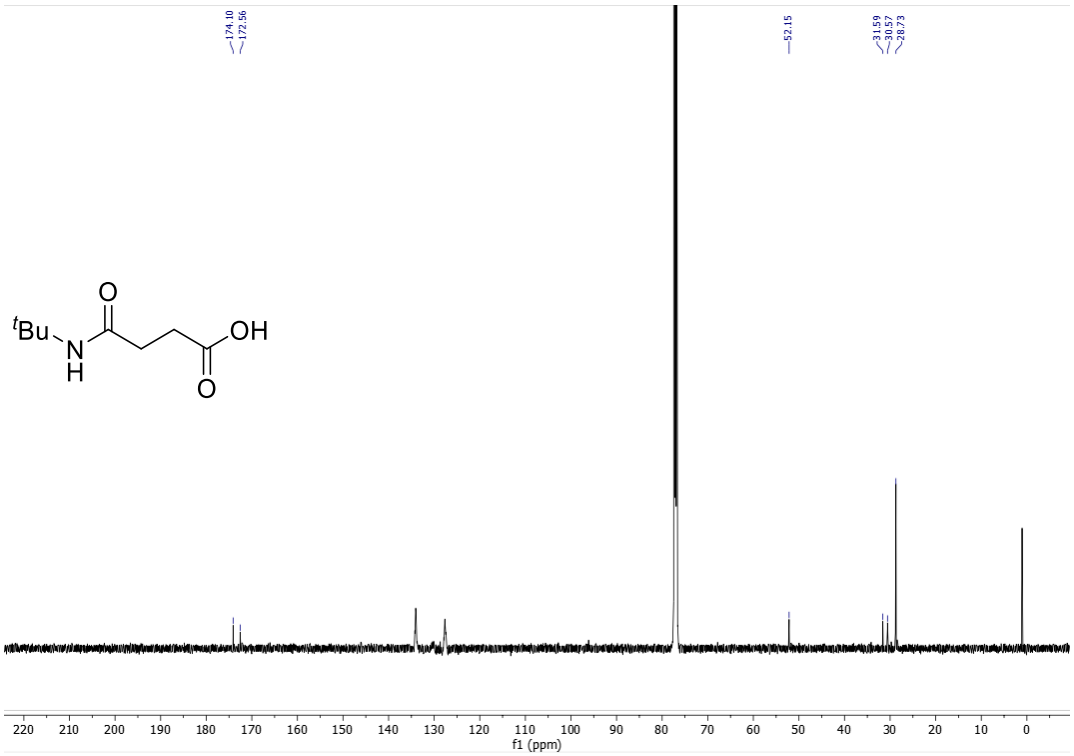
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2o** (see procedure).



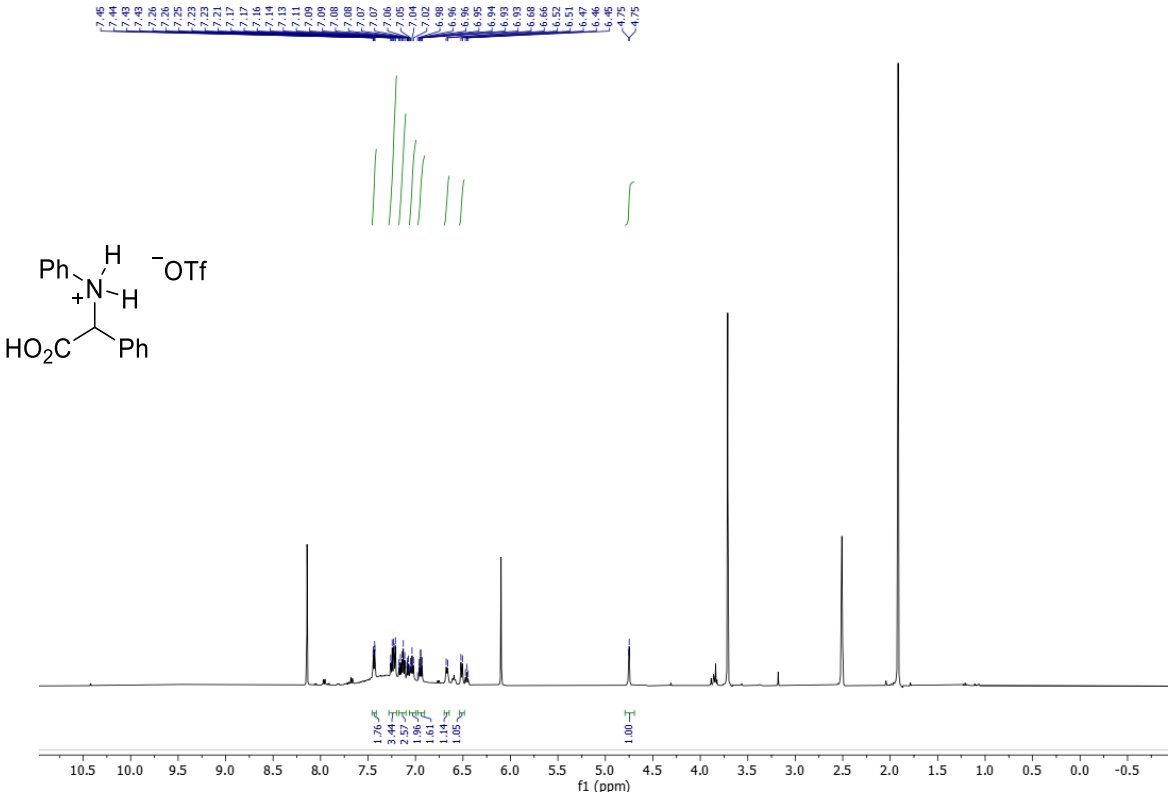
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2p** (see procedure).



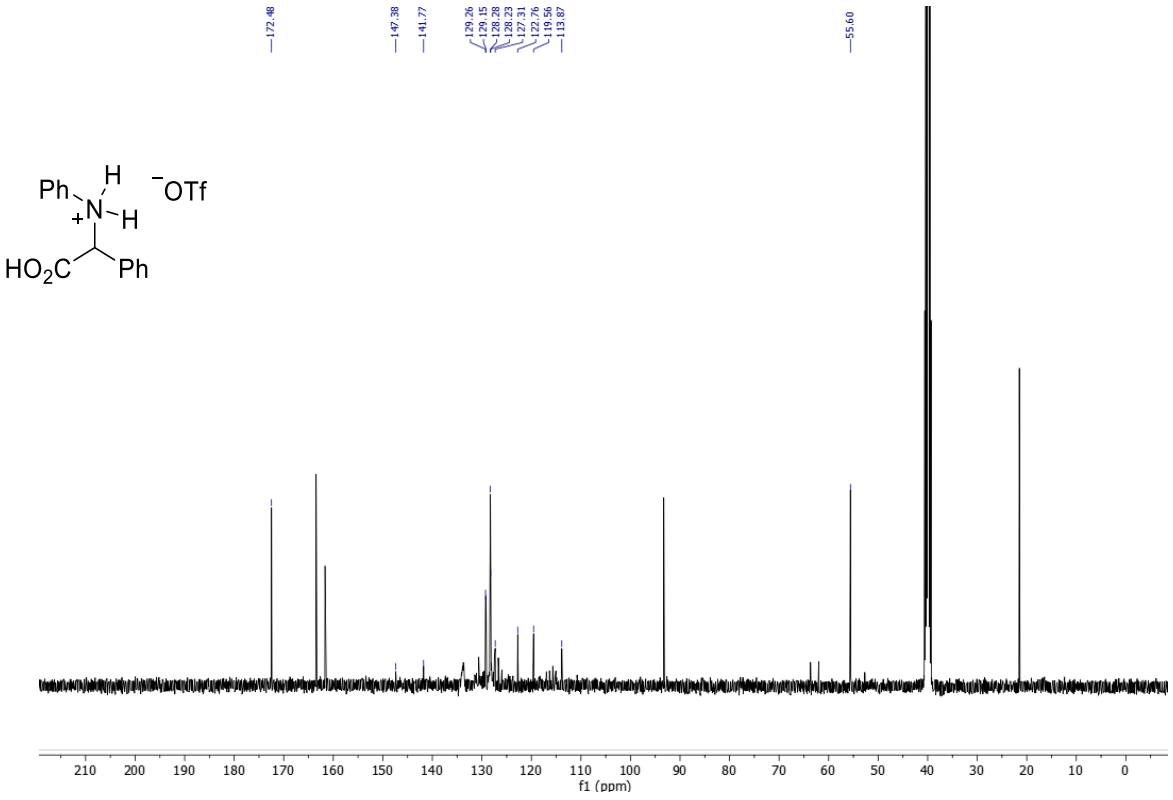
^{13}C NMR (400 MHz, $CDCl_3$) of compound **2p** (see procedure).



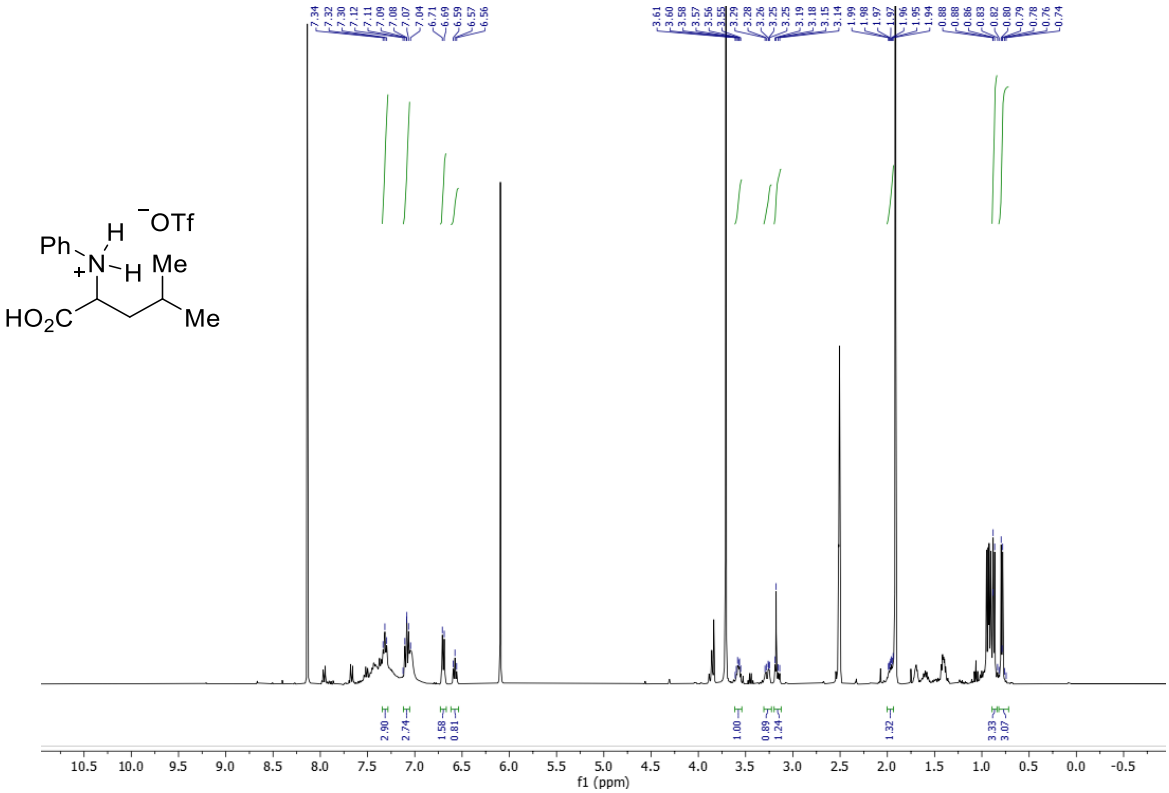
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a** (see procedure).



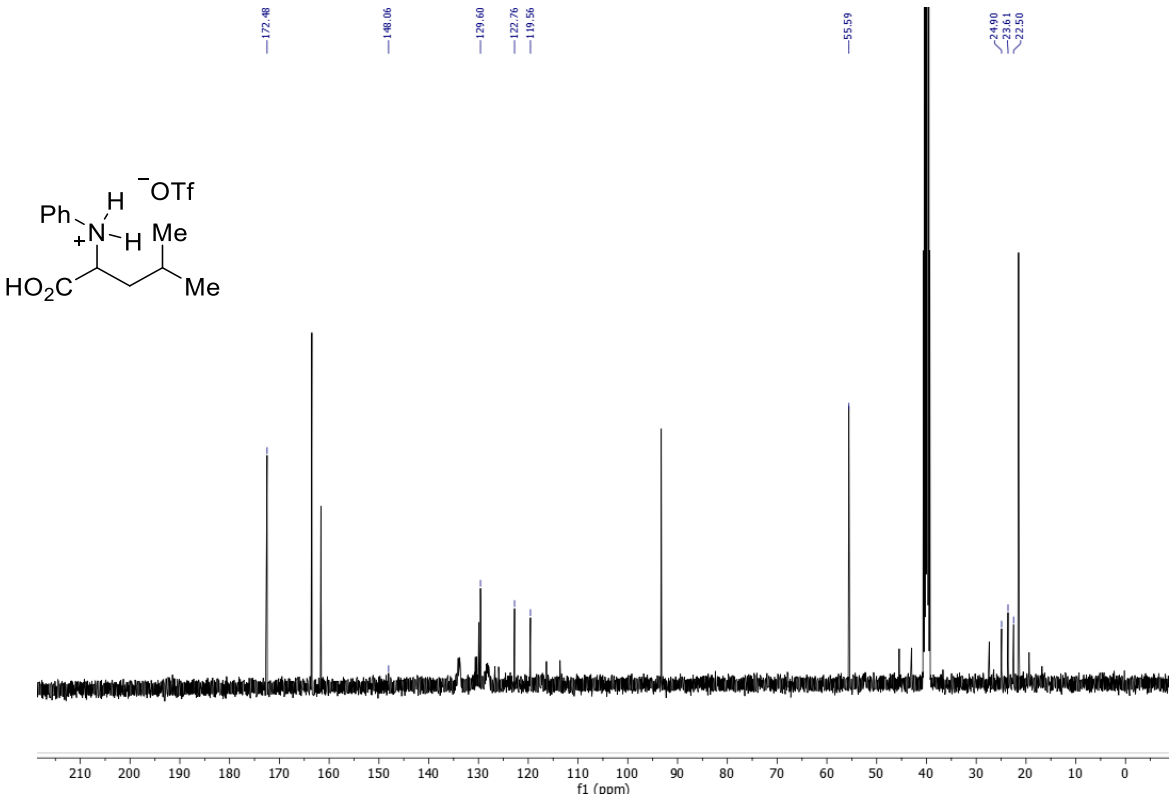
^{13}C NMR (400 MHz, $CDCl_3$) of compound **4a** (see procedure).



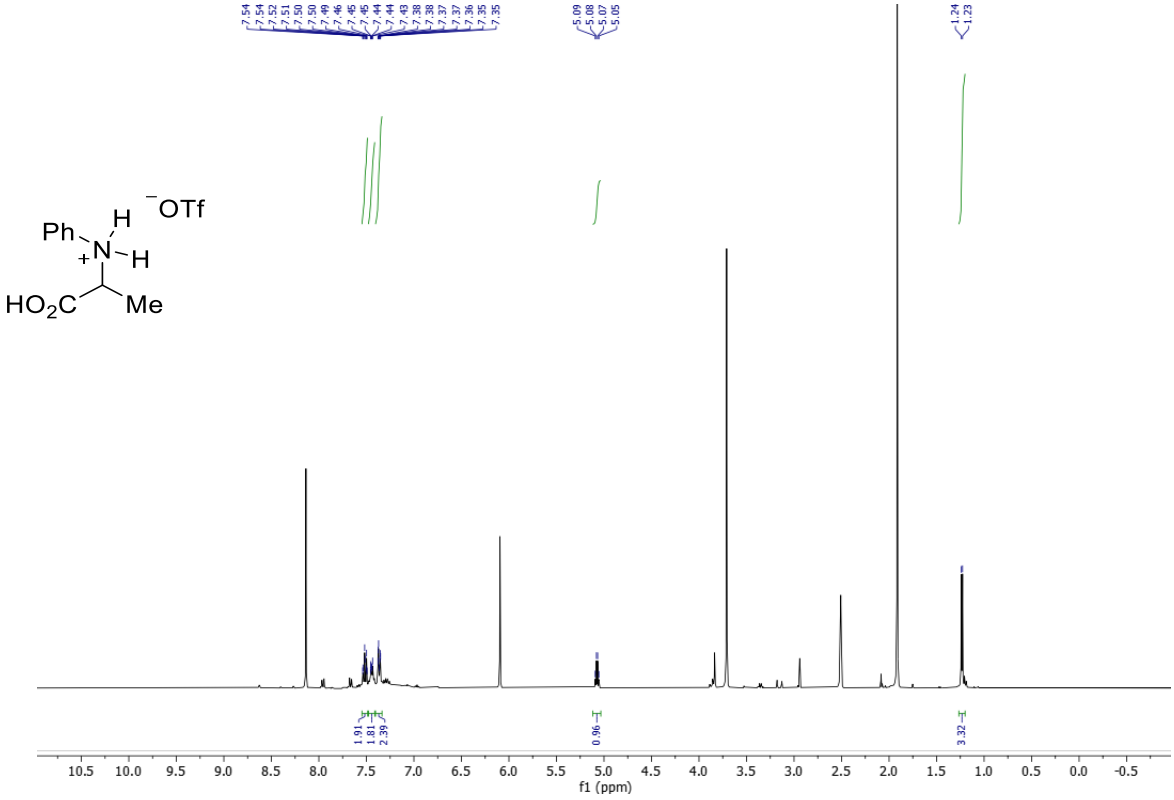
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b** (see procedure).



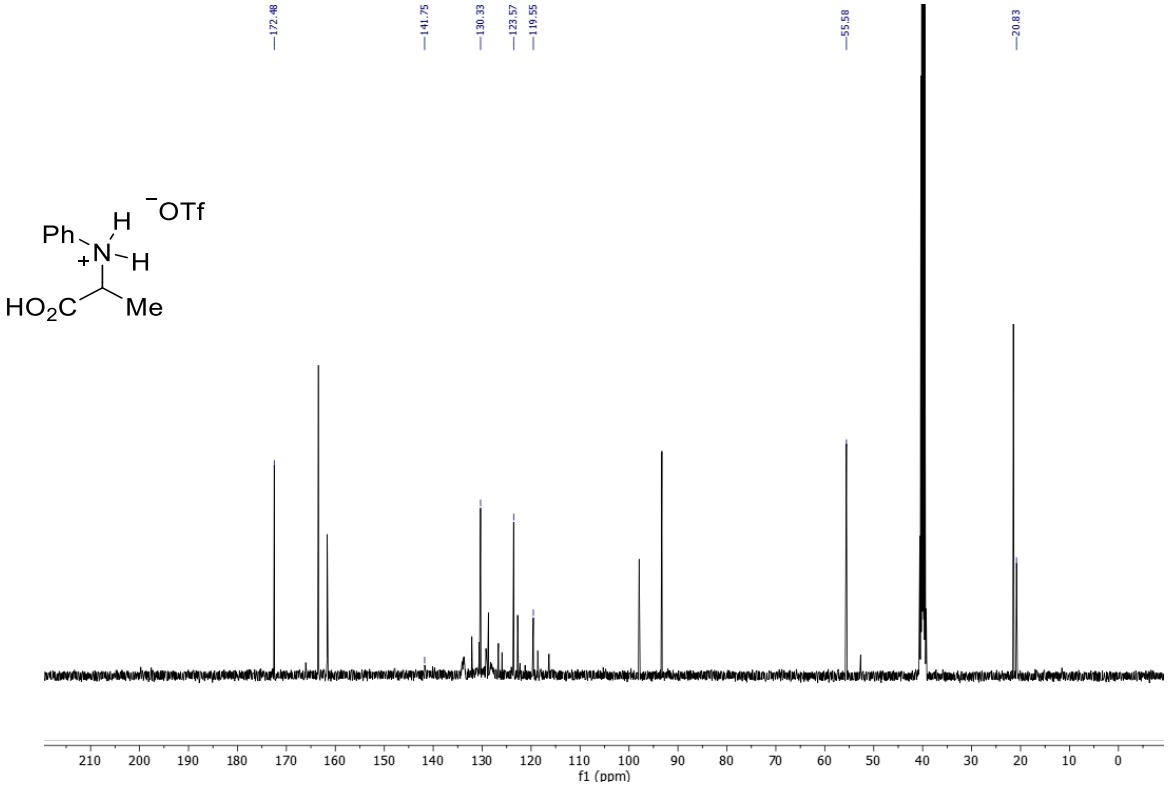
^{13}C NMR (400 MHz, $CDCl_3$) of compound **4b** (see procedure).



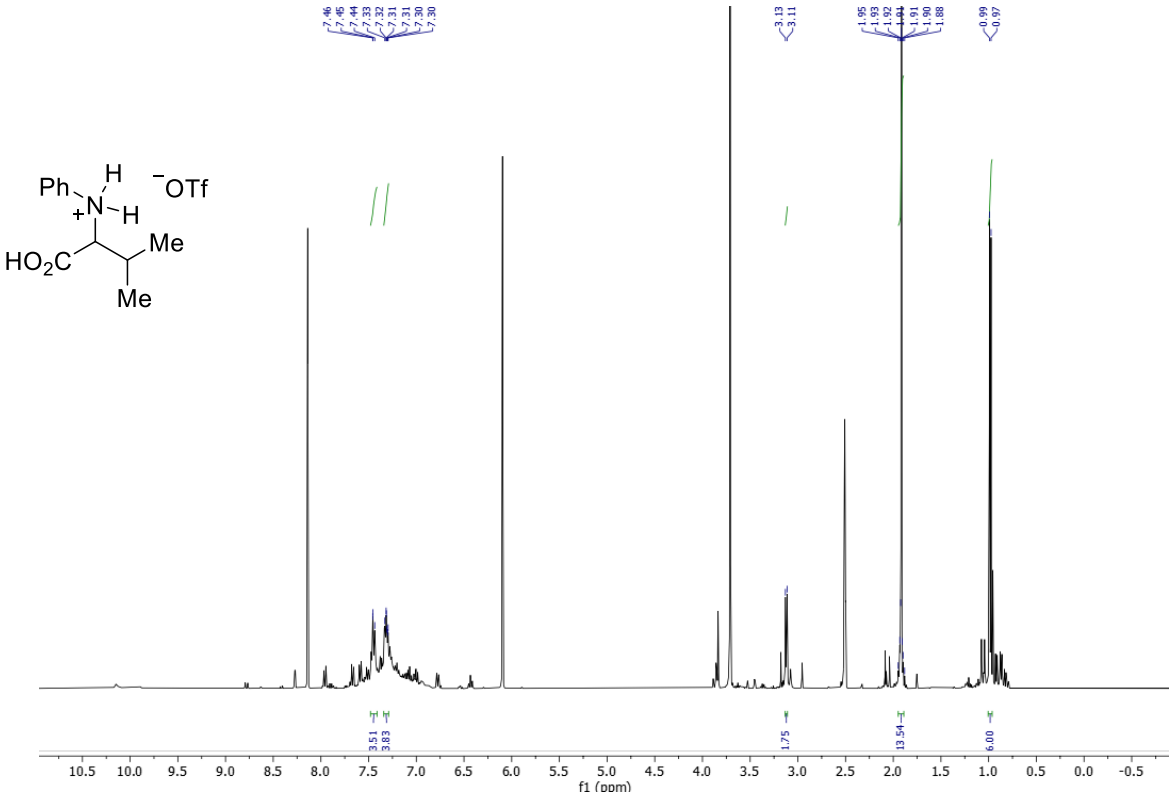
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c** (see procedure).



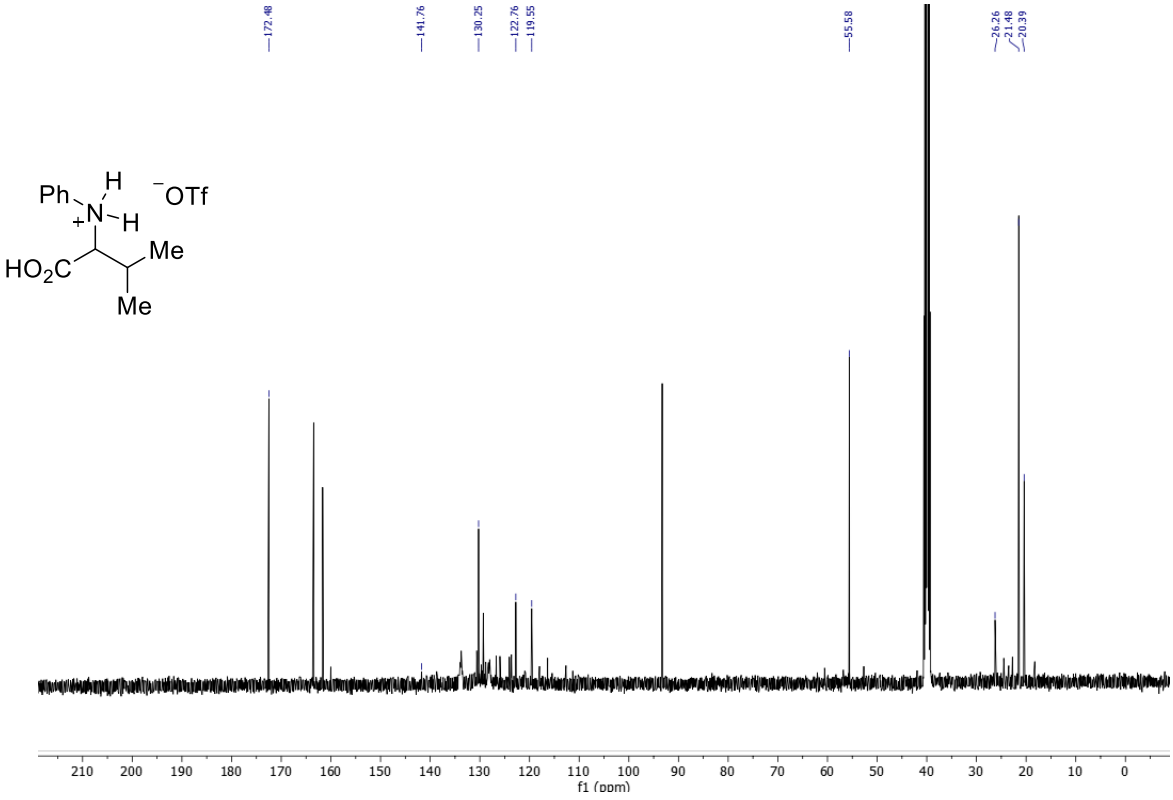
^{13}C NMR (400 MHz, $CDCl_3$) of compound **4c** (see procedure).



^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d** (see procedure).



^{13}C NMR (400 MHz, $CDCl_3$) of compound **4d** (see procedure).



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