Supporting Information for

Photochemical Cyclopropanation in Aqueous Micellar Media – Experimental and Theoretical Studies

Joseph P. Milton,[a] Adam Milanowski,[a,b] Martin Peter Andersson[c]* and Dorota Gryko[a]*

[a]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[b]Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

[c]Center for Intergrative Petroleum Research, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

correspondence: dorota.gryko@icho.edu.pl

for correspondence regarding computational calculations: martin.andersson@kfupm.edu.sa

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1. General Information

General - Reactions were monitored by gas chromatography (GC) or TLC on Merck silica gel (GF254, 0.20 mm thickness), visualising with UV-light. Column chromatography was performed using Merck silica gel 60 (230 - 400 mesh) or with commercially available cartridges with a CombiFlash. Unless otherwise noted, all reactions were performed without the exclusion of air or moisture. Unless otherwise stated, all photochemical reactions were performed in 10 mL test tubes with a B14 neck and sealed with a rubber septum.

Materials - All solvents and commercially available reagents were purchased as reagent grade and were used without further purification. Methyl 2-diazo-2-phenylacetate (**1a**),[1] ethyl 2-diazo-2-phenylacetate (**1b**),[1] methyl 2-diazo-2-(4-methoxyphenyl)acetate (**1h**),[1] methyl 2-(4-(dodecyloxy)phenyl)acetate,[2] methyl 2-phenyl-2-(2-tosylhydrazineylidene)acetate (**4a**),[3] ethyl 2-phenyl-2-(2-tosylhydrazineylidene)acetate (**4b**),[4] ethyl 2-(4-fluorophenyl)-2-oxoacetate,[5] ethyl 2-oxo-2-(p-tolyl)acetate,[5] ethyl 2-(4-methoxyphenyl)-2-oxoacetate[5] and 3-chlorostyrene[6] were synthesised according to the literature.

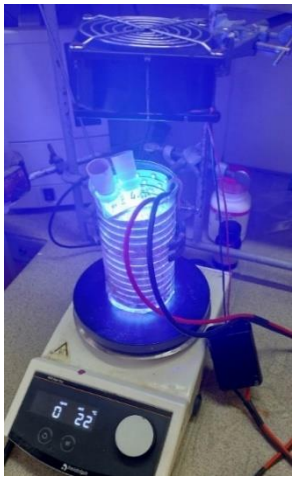
NMR - ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz, Bruker 500 MHz, Varian 500 MHz or a Varian 600 MHz instrument. NMR chemical shifts are reported in ppm and referenced to the residual solvent peak of $CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR or to TMS as an internal standard. Multiplicities are indicated by singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m). Coupling constants (J) are reported in Hertz. All data analysis was performed using the MestReNova software package.

GC - Gas chromatography coupled with a flame ionisation detector (GC-FID) were performed on a Shimadzu GCMS-QP2010 SE with helium as the carrier gas and a Zebron ZB 5MSi column.

EA - Elemental analysis (C, H, N, F, S, Br) were performed on a PERKIN-ELMER 240 Elemental Analyzer

HRMS - High resolution mass spectrometry was recorded on a Waters SYNAPT G2-S HDMS using ESI with a TOF detector.

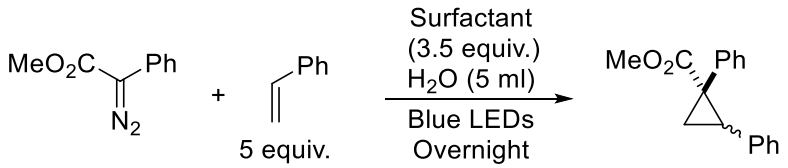
Setup for photoreactions



All photochemical reaction were performed in a beaker that contains blue LED tape (455 nm, 9 W) and are cooled with a fan.

2. Optimisation Details

2.1. Surfactant (by GC)



NOTE: The obtained yields are only approximate values and we found that more accurate values could be obtained when analysing the reactions by NMR. Nevertheless, we used GC as an initial screening for various surfactants.

Entry	Surfactant	Yield (%)[b]
1	DTAC	74
2	Aliquat 336	60
3	CTAB	50
4	CTAC	47
5	DOSS	44
6	DTAB	54
7	Potassium Laurate	54
8	None	>99
9	Tween 60	20
10	BZK	10
11	SDS	39
12	SLES	21
13	TPGS-750-M	16
14	Triton X-45	10
15	Triton X-100	12

[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 mmol, 1 equiv.), styrene (5 equiv.), surfactant (3.5 equiv.), H_2O (5 mL), blue LEDs (9W, 455 nm), overnight (~20 hours); [b]Yield determined by GC with dodecane as internal standard.

2.2. Surfactant (by NMR)[a]

Entry	Surfactant	Yield (%)[b]
1	DTAC	62
2	Aliquat 336	26
3	CTAB	36
4	CTAC	53
5	DOSS	39
6	DTAB	56
7	Potassium Laurate	43
8	None	53

[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 mmol, 1 equiv.), styrene (5 equiv.), surfactant (3.5 equiv.), H_2O (5 mL), blue LEDs (9W, 455 nm), overnight (~20 hours); [b]Yield determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

2.3. Concentration of DTAC[a]

Entry	DTAC Concentration (M)	Yield (%)[b]
1	0.14	44
2	0.07	62
3	0.0466	53
4	0.035	63

[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 mmol, 1 equiv.), styrene (5 equiv.), DTAC (3.5 equiv.), H_2O (X mL), blue LEDs (9W, 455 nm), overnight (~20 hours); [b]Yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

2.4. Co-solvent[a]

Entry	Co-Solvent	Equivalents	Yield (%)[b]
1	None	None	62
2	Acetone	10	47
3		30	53
4		50	43
5	THF	10	48
6		30	47
7		50	31
8	MeCN	10	51
9		30	52
10		50	43
11	^{i}PrOH	10	44
12		30	52
13		50	49
14	^{n}BuOH	10	54
15		30	47
16		50	37

[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 mmol, 1 equiv.), styrene (5 equiv.), DTAC (3.5 equiv.), H_2O (5 mL), Co-solvent (10 - 50 equiv.), blue LEDs (9W, 455 nm), overnight (~20 hours) [b]Yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

2.5. Light Source[a]

Entry	Light Source (Blue)	Yield (%)[b]
1	LED Tape, 9W, 455 nm, Beaker	62
2[c]	UOSlab 25% power	56
3[c]	UOSlab 50% power	46
4[c]	UOSlab75% power	38
5[c]	UOSlab 100% power	60
6[d]	Custom Photoreactor, 3 W	45
7[d]	Custom Photoreactor, 6 W	60
8[e]	Kessil Lamp, 440 nm, 100% power	46

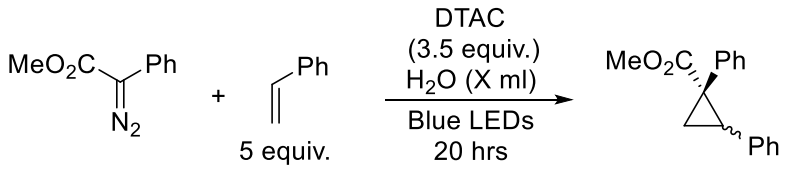
[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 mmol, 1 equiv.), styrene (5 equiv.), DTAC (3.5 equiv.), H_2O (5 mL), blue LEDs, overnight (~20 hours); [b]Yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard; [c]See the supporting information in reference 7 to find more detailed information on the photoreactor; [d]See the supporting information in reference 8 to find more detailed information on the photoreactor; [e]Reaction time: 1 hour.

2.6. Ratio of Reactants[a]

Entry	Diazo:styrene	Yield (%)[b]
1	1:10	48
2	1:5	62
3	1:3	40
4	1:2	21
5	1:1.5	20
6	1:1	26
7	1.5:1	29
8	2:1	44
9	3:1	46
10	5:1	66
11	10:1	59

[a]Reaction conditions: methyl 2-diazo-2-phenylacetate (0.1 - 1.0 mmol), styrene (0.1 - 1.0 mmol), DTAC (3.5 equiv.), H_2O (5 mL), blue LEDs (9W, 455 nm), overnight (~20 hours); [b]Yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

3. Experiments with the Concentration of DTAC



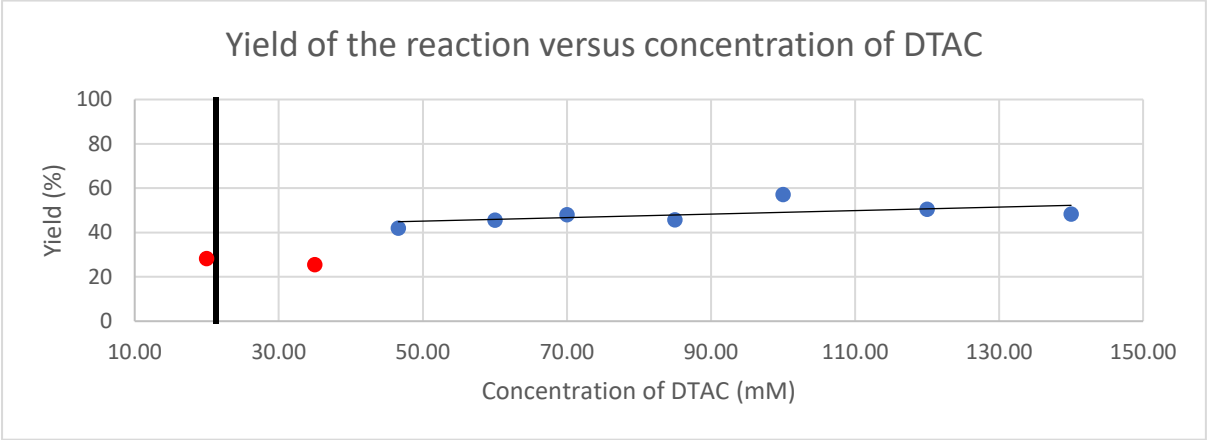
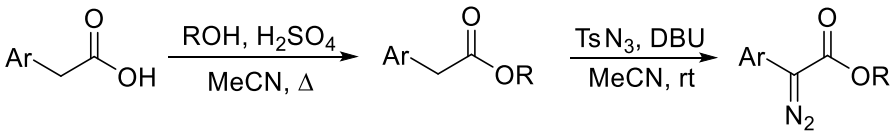


Figure S1: Yield of the reaction versus the concentration of DTAC. As the concentration of DTAC increases the yield gradually improves, particularly when surpassing 40 mM

All experiments used 0.1 mmol of diazo compound, 0.5 mmol of styrene and 0.35 mmol of DTAC with the concentration being modified by changing the amount of water. Yields were calculated by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. The solid black vertical line represents the CMC of DTAC at 25 °C (0.0213 mol/kg).[7] We can see an increase in the yield once the concentration surpasses 0.04 M; the average yield below 40 mM was 27% where as it was 48% when above 40 mM. This shows that once the reaction sufficiently surpasses the CMC of DTAC, the reaction can work more efficiently with a weak positive trend showing the higher concentration of DTAC, the higher the yield.

4. General Procedures

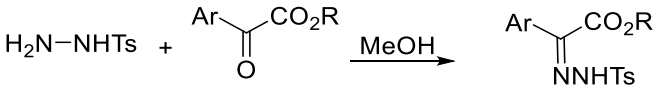
4.1. Synthesis of Diazo Compounds - General Procedure A



Esterification was performed by a modified procedure as reported by Claveau et al.[8] Diazo formation was performed analogously as reported by Keipour.[9]

The corresponding phenylacetic acid was dissolved in MeCN (0.5 M) followed by the addition of the corresponding alcohol (1.5 equiv.) and sulfuric acid (25 mol%), which was then refluxed overnight (~16 hours). The reaction was cooled down to room temperature and poured into a separating funnel. Water was added and the aqueous layer was extracted thrice with EtOAc. The organic layer was washed with water, saturated $NaHCO_3$, and brine successively, dried (Na_2SO_4) and filtered. EtOAc and residual MeCN was removed in vacuo. The corresponding crude mixture was then dissolved in MeCN (0.5 M) and DBU was added (1.5 equiv.). After 10 minutes, tosyl azide (1.5 equiv.) was then added, and the reaction was stirred until completed by TLC (~16 hours). MeCN was then removed in vacuo and the resultant crude was dissolved in EtOAc and washed with water once. The aqueous phase was extracted with EtOAc thrice and the combined organic layer was then washed twice with water, dried (Na_2SO_4), filtered and evaporated in vacuo. The crude mixture was subjected to column chromatography (SiO_2, 2-5% EtOAc in hexane) which, afforded the pure diazo compound typically as an orange compound.

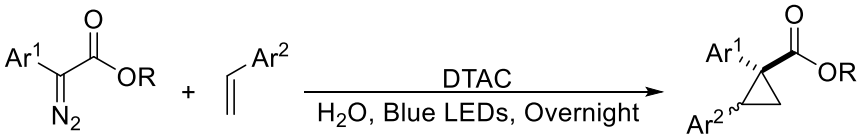
4.2. Synthesis of Hydrazones - General Procedure B



Hydrazones were synthesised according to the procedure by Li et al.[3]

p-Toluenesulfonyl hydrazide (1.1 equiv.) was dissolved in MeOH (1 M) followed by the corresponding β-keto ester dropwise/portionwise and stirred for 4 - 16 hours (sometimes the product will precipitate out of the solution indicating the end of the reaction). Upon completion, MeOH is removed in vacuo and the resultant solid was recrystallised in MeOH to afford the pure product. In cases where the product could not be recrystallised, it was purified by column chromatography (SiO_2, 10% EtOAc in hexane) instead.

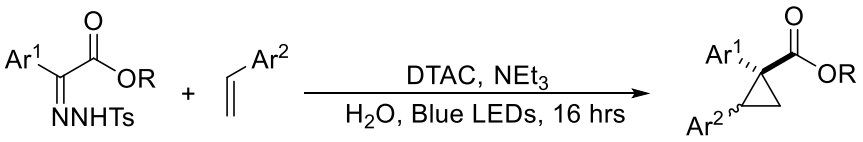
4.3. General Procedure C - Synthesis of Cyclopropanes from Diazo Compounds



A test tube was charged with DTAC (3.5 equiv.) followed by the addition of H_2O (0.07 M in respect to DTAC) and the solution was sonicated to ensure full dissolution. The diazo compound (0.1 mmol) was then added to the solution followed by the addition of olefin (5 equiv.) and the resulting mixture was then irradiated with blue LEDs overnight (16 - 24 hours). The reaction mixture was then diluted with brine and was extracted with EtOAc thrice. The combined organic phase was washed with water and brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude mixture was then subjected to

column chromatography (SiO_2, 0 -> 5% EtOAc in hexane gradient) to afford the corresponding cyclopropanes as a mixture of *cis*- and *trans*-isomers.

4.4. General Procedure D - Synthesis of Cyclopropanes from Hydrazones

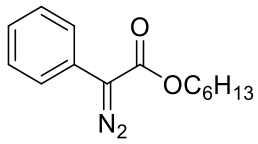


A test tube was charged with the corresponding hydrazone (0.1 mmol) and a 0.07 M solution of DTAC in water was added (5 mL per 0.1 mmol of hydrazone). Styrene (10 equiv.). and triethylamine (NEt_3, 1.5 equiv.) were sequentially added to the reaction vessel. The resulting mixture was stirred for 5 minutes without irradiation and then irradiated with blue LEDs for 16 hours. The reaction mixture was diluted with brine and extracted with EtOAc thrice. The combined organic phases were washed with water and brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude mixture was then subjected to column chromatography (SiO_2, 0 -> 5% EtOAc in hexane gradient) to afford the corresponding cyclopropanes as a mixture of *cis*- and *trans*-isomers.

5. Scope and Characterisation of Products

5.1. Diazo Compounds

hexyl 2-diazo-2-phenylacetate (**1c**)



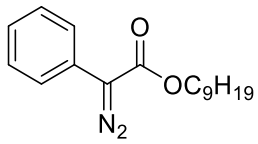
The title compound was synthesised according to General Procedure A from phenylacetic acid (5 mmol) in 24% yield (287 mg) as an orange oil (solidifies upon storage in a freezer).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.20 – 7.16 (m, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 1.71 (p, *J* = 6.9 Hz, 2H), 1.43 – 1.31 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 129.1, 125.9, 125.8, 124.1, 65.3, 31.5, 28.9, 25.7, 22.7, 14.1.

The spectroscopic data is consistent with that previously reported in the literature.[10]

nonyl 2-diazo-2-phenylacetate (**1d**)



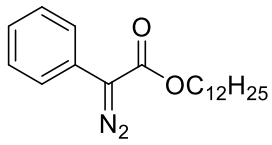
The title compound was synthesised according to General Procedure A from phenylacetic acid (5 mmol) in 34% yield (485 mg) as an orange oil (solidifies upon storage in a freezer).

^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 2H), 1.71 (p, *J* = 6.8 Hz, 2H), 1.42 – 1.28 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 129.1, 125.9, 125.8, 124.1, 65.3, 32.0, 29.6, 29.37, 29.36, 29.0, 26.0, 22.8, 14.2.

HRMS (EI$^+$): Calc'd for $C_{17}H_{24}N_2O_2^+$: 288.1838, found: 288.1833.

dodecyl 2-diazo-2-phenylacetate (**1e**)



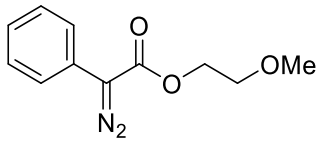
The title compound was synthesised according to General Procedure A from phenylacetic acid (20 mmol) in 59% yield (389 mg) as a pale orange solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 1.71 (p, *J* = 6.8 Hz, 2H), 1.41 – 1.28 (m, 19H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 129.0, 125.9, 125.8, 124.1, 65.3, 32.1, 29.78, 29.76, 29.69, 29.64, 29.5, 29.4, 28.9, 26.0, 22.8, 14.2.

The spectroscopic data is consistent with that previously reported in the literature.[10]

2-methoxyethyl 2-diazo-2-phenylacetate (**1f**)



The title compound was synthesised according to General Procedure A from phenylacetic acid (10 mmol) in 58% yield (1.27 g) as an orange solid.

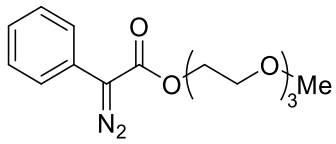
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 – 7.47 (m, 2H), 7.40 – 7.37 (m, 2H), 7.19 (tt, *J* = 7.4, 1.2 Hz, 1H), 4.43 – 4.42 (m, 2H), 3.68 – 3.66 (m, 2H), 3.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 165.2, 129.1, 126.0, 125.6, 124.2, 70.7, 64.0, 59.2.

HRMS (EI$^+$): Calc'd for $C_{11}H_{12}N_2O_3^+$: 220.0848; found: 220.0844.

The spectroscopic data is consistent with that previously reported in the literature.[11]

2-(2-(2-methoxyethoxy)ethoxy)ethyl 2-diazo-2-phenylacetate (**1g**)



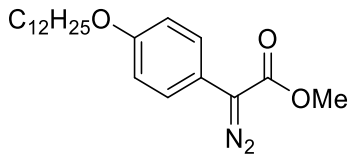
The title compound was synthesised according to General Procedure A from phenylacetic acid (5 mmol) in 50% yield (776 mg) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.44 (m, 2H), 7.34 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.40 – 4.38 (m, 2H), 3.75 – 3.73 (m, 2H), 3.66 – 3.61 (m, 6H), 3.52 – 3.50 (m, 2H), 3.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.0, 128.9, 125.8, 125.4, 124.0, 71.9, 70.65, 70.61, 70.56, 69.2, 63.9, 59.0.

HRMS (EI$^+$): Calc'd for $C_{15}H_{20}N_2O_5^+$: 308.1372; found: 308.1370.

methyl 2-diazo-2-(4-(dodecyloxy)phenyl)acetate (**1i**)



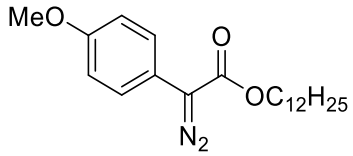
The title compound was synthesised according to General Procedure A from methyl 2-(4-(dodecyloxy)phenyl)acetate (1.0 mmol) in 17% yield (63 mg) as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.35 (m, 2H), 6.95 – 6.92 (m, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 1.77 (p, *J* = 6.7 Hz, 2H), 1.48 – 1.42 (m, 2H), 1.36 – 1.27 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 157.9, 126.1, 116.7, 115.4, 68.3, 52.1, 32.1, 29.80, 29.77, 29.73, 29.71, 29.53, 29.49, 29.38, 26.2, 22.8, 14.2.

HRMS (EI$^+$): Calc'd for $C_{21}H_{32}N_2O_3^+$: 360.2413; found: 360.2395.

dodecyl 2-diazo-2-(4-methoxyphenyl)acetate (**1j**)



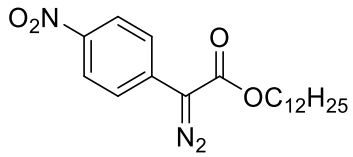
The title compound was synthesised according to General Procedure A from 4-methoxyphenylacetic acid (3 mmol) in 24% yield (262 mg) as an orange solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 2H), 6.95 – 6.93 (m, 2H), 4.25 (t, *J* = 6.7 Hz, 2H), 3.81 (s, 3H), 1.71 – 1.67 (m, 2H), 1.40 – 1.27 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.0, 158.2, 126.1, 117.2, 114.7, 65.2, 55.5, 32.1, 29.78, 29.78, 29.70, 29.65, 29.5, 29.4, 29.0, 26.0, 22.8, 14.3.

HRMS (EI$^+$): Calc'd for $C_{21}H_{32}N_2O_3^+$: 360.2413; found: 360.2407.

dodecyl 2-diazo-2-(4-nitrophenyl)acetate (**1k**)



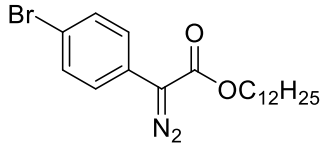
The title compound was synthesised according to General Procedure A from 4-nitrophenylacetic acid (5 mmol) in 30% yield (531 mg) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 – 8.21 (m, 2H), 7.67 – 7.65 (m, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 1.72 (p, *J* = 6.8 Hz, 2H), 1.40 – 1.26 (m, 19H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.9, 145.2, 134.2, 124.4, 123.3, 65.9, 32.1, 29.78, 29.77, 29.69, 29.63, 29.5, 29.3, 28.9, 26.0, 22.8, 14.2.

HRMS (EI$^+$): Calc'd for $C_{20}H_{29}N_3O_4^+$: 375.2158; found: 375.2166.

dodecyl 2-(4-bromophenyl)-2-diazoacetate (**1l**)



The title compound was synthesised according to General Procedure A from 4-bromophenylacetic acid (5 mmol) in 13% yield (273 mg) as an orange solid.

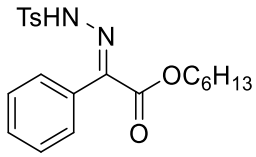
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 1.70 (p, *J* = 6.8 Hz, 2H), 1.39 – 1.27 (m, 19H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.0, 132.1, 125.5, 125.1, 119.4, 65.5, 32.1, 29.78, 29.77, 29.70, 29.6, 29.5, 29.4, 28.9, 26.0, 22.8, 14.2.

HRMS (EI^+): Calc'd for $C_{20}H_{29}N_2O_2Br^+$: 408.1412; found 408.1419.

5.2. Hydrazone Compounds

hexyl (E)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (*E*-**4c**)



The title compound was synthesised according to General Procedure B from hexyl 2-oxo-2-phenylacetate (3.83 mmol) in 65% yield (1.00 g). Purified by recrystallisation affording a white solid.

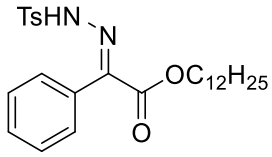
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.55 (s, 1H), 7.88 – 7.86 (m, 2H), 7.52 – 7.50 (m, 2H), 7.39 – 7.30 (m, 5H), 4.28 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.70 – 1.65 (m, 2H), 1.35 – 1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.3, 144.5, 138.4, 135.7, 134.2, 129.9, 129.5, 128.7, 128.14, 128.11, 66.6, 31.3, 28.3, 25.6, 22.6, 21.8, 14.0. [One peak from the alkyl region could not be found].

HRMS (ESI$^+$): Calc'd for $C_{21}H_{26}N_2O_4SNa^+$: 425.1511; found: 425.1515.

Elemental Anal.: Calc'd (%) for $C_{21}H_{26}N_2O_4S$: C - 62.66 H - 6.51 N - 6.96; found C - 62.45 H - 6.44 N - 6.99

dodecyl (E)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (*E*-**4d**)



The title compound was synthesised according to General Procedure B from dodecyl 2-oxo-2-phenylacetate (3.9 mmol) in 69% yield (1.31 g). Purified by recrystallisation affording a white solid.

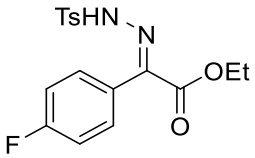
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.56 (s, 1H), 7.88 – 7.86 (m, 2H), 7.52 - 7.50 (m, 2H), 7.38 – 7.30 (m, 5H), 4.27 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.69 – 1.65 (m, 2H), 1.33 – 1.25 (m, 17H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.4, 144.5, 138.4, 135.7, 134.2, 129.9, 129.5, 128.7, 128.14, 128.11, 66.6, 32.1, 29.8, 29.63, 29.56, 29.48, 29.2, 28.4, 26.0, 22.8, 21.8, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{27}H_{38}N_2O_4SNa^+$: 509.2450; found: 509.2453.

Elemental Anal: Calc'd (%) for $C_{27}H_{36}N_2O_4S$: C - 66.64 H - 7.87 N - 5.76; found: C - 66.70 H - 7.90 N - 5.95.

ethyl (E)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate (*E*-**4e**)



The title compound was synthesised according to General Procedure B from ethyl 2-(4-fluorophenyl)-2-oxoacetate acid (0.55 mmol) in 39% yield for the *E*-isomer (26 mg). Purified by column chromatography affording a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.59 (s, 1H), 7.87 – 7.85 (m, 2H), 7.52 – 7.48 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.05 – 7.00 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

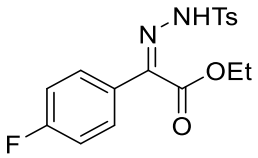
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.5 (d, *J* = 250.0 Hz), 162.0, 144.6, 137.1, 135.6, 130.7 (d, *J* = 8.4 Hz), 130.3 (d, *J* = 3.3 Hz), 129.9, 128.1, 115.3 (d, *J* = 21.9 Hz), 62.6, 21.8, 14.1.

^{19}F NMR (470 MHz, $CDCl_3$): δ MAJOR: -111.4 (tt, *J* = 8.5, 5.3 Hz), MINOR: -114.1 (tt, *J* = 8.7, 5.3 Hz).

HRMS (ESI$^+$): Calc'd for $C_{17}H_{18}N_2O_4SF^+$: 365.0971; found: 365.0970.

Elemental Anal: Calc'd (%) for $C_{17}H_{17}FN_2O_4S$: C - 56.04 H - 4.70 N - 7.69 S - 8.80 F - 5.21; found C - 56.03 H - 4.55 N - 7.65 S - 8.82 F - 5.10.

ethyl (Z)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4e**)



The title compound was synthesised according to General Procedure B from ethyl 2-(4-fluorophenyl)-2-oxoacetate acid (0.55 mmol) in 13% yield for the *Z*-isomer (26 mg). Purified by column chromatography and further purified by recrystallisation affording white crystals.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.86 – 7.84 (m, 2H), 7.35 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

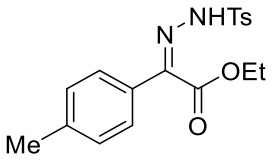
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.5 (d, *J* = 252.3 Hz), 163.1, 145.0, 143.2, 134.9, 130.8 (d, *J* = 8.6 Hz), 129.9, 128.3, 124.1 (d, *J* = 3.7 Hz), 117.0 (d, *J* = 21.9 Hz), 62.2, 21.8, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$): δ -108.3 (tt, *J* = 8.4, 5.3 Hz)

HRMS (ESI$^+$): Calc'd for $C_{17}H_{17}N_2O_4SFNa^+$: 387.0791; found 387.0793.

Elemental Anal: Calc'd (%) for $C_{17}H_{17}FN_2O_4S$: C - 56.04 H - 4.70 N - 7.69 S - 8.80 F - 5.21; found C - 56.05 H - 4.55 N - 7.72 S - 8.98 F - 5.08.

ethyl (Z)-2-(p-tolyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4f**)



The title compound was synthesised according to General Procedure B from ethyl 2-oxo-2-(*4*-tolyl)acetate (1.15 mmol) in 42% yield (152 mg) for the *E*-isomer. Purified by column chromatography affording a viscous yellow oil.

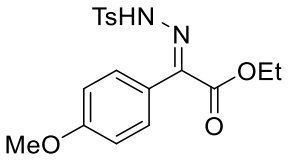
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.42 (s, 1H), 7.88 – 7.86 (m, 2H), 7.43 – 7.41 (m, 2H), 7.32 – 7.30 (m, 2H), 7.16 – 7.14 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.36 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.3, 144.4, 139.7, 138.7, 135.7, 131.3, 129.8, 128.9, 128.5, 128.1, 62.5, 21.7, 21.4, 14.1.

HRMS (EI^{+}): Calc'd for $C_{18}H_{20}N_2O_4S^{+}$: 360.1144; found: 360.1149.

Elemental Anal: Calc'd for $C_{18}H_{20}N_2O_4S$: C 59.98 H 5.59 N 7.77 S 8.89; found: C - 60.08 H - 5.55 N - 7.88 S - 8.78.

ethyl (E)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate (*E*-**4g**)



The title compound was synthesised according to General Procedure B from ethyl 2-(4-methoxyphenyl)-2-oxoacetate (3.37 mmol) in 34% yield (431 mg) for the *E*-isomer. Purified by column chromatography affording a brown oil.

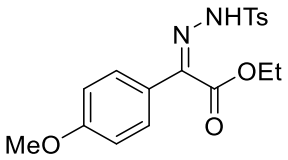
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.29 (s, 1H), 7.88 – 7.85 (m, 2H), 7.50 – 7.47 (m, 2H), 7.32 – 7.30 (m, 2H), 6.87 – 6.85 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.41 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.4, 160.8, 144.4, 138.6, 135.7, 130.1, 129.8, 128.1, 126.6, 113.7, 62.5, 55.5, 21.8, 14.2.

HRMS (ESI^{+}): Calc'd for $C_{18}H_{21}N_2O_5S^{+}$: 377.1171; found 377.1173.

Elemental Anal: Calc'd (%) for $C_{18}H_{20}N_2O_5S$: C - 57.43 H - 5.36 N - 7.44 S - 8.52; found: C - 57.41 H - 5.42 N - 7.36 S - 8.44.

ethyl (Z)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4g**)



The title compound was synthesised according to General Procedure B from ethyl 2-(4-methoxyphenyl)-2-oxoacetate (3.37 mmol) in 10% yield for the *Z*-isomer (126 mg). Purified by column chromatography affording a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.86 – 7.84 (m, 2H), 7.34 – 7.32 (m, 2H), 7.18 – 7.15 (m, 2H), 6.99 – 6.96 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.44 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.4, 161.2, 144.8, 144.3, 135.1, 130.1, 129.8, 128.2, 120.0, 115.0, 62.0, 55.6, 21.8, 14.2.

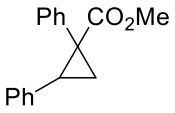
HRMS (EI^{+}): Calc'd for $C_{18}H_{20}N_2O_5S^{+}$: 376.1093; found 376.1088.

Elemental Anal: Calc'd (%) for $C_{18}H_{20}N_2O_5S$: C - 57.43 H - 5.36 N - 7.44 S - 8.52; found: C - 57.45, H - 5.50 N - 7.45 S - 8.58.

5.3. Cyclopropanes

NOTE CAREFULLY: Only the major diastereoisomer is reported due to the high number of overlapping peaks from the two diastereoisomers when the cyclopropane contains long alkyl chains. For ^{1}H NMR, only key peaks are identifiable such as those from the cyclopropane ring and the aromatic region.

methyl 1,2-diphenylcyclopropane-1-carboxylate (**3a**)



The title compound was synthesised according to General Procedure C from methyl 2-diazo-2-phenylacetate (0.1 mmol, 17.6 mg) in 59% yield (15 mg) as a white solid in 1:7 dr.

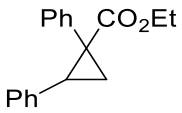
The title compound was synthesised according to General Procedure D from methyl 2-phenyl-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 33.2 mg) in 59% yield (15 mg) as a white solid in 1:10 dr.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.11 (m, 3H), 7.08 – 7.02 (m, 5H), 6.79 – 6.77 (m, 2H), 3.67 (s, 3H), 3.13 (dd, *J* = 9.4, 7.3 Hz, 1H), 2.15 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.89 (dd, *J* = 7.3, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5, 136.5, 134.9, 132.1, 128.2, 127.83, 127.81, 127.2, 126.4, 52.8, 37.5, 33.3, 20.6.

The spectroscopic data is consistent with that previously reported in the literature.[12]

ethyl 1,2-diphenylcyclopropane-1-carboxylate (**3b**)



The title compound was synthesised according to General Procedure C from ethyl 2-diazo-2-phenylacetate (0.1 mmol, 19.0 mg) in 71% yield (19 mg) as a white solid in 1:7 dr.

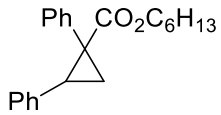
The title compound was synthesised according to General Procedure D from (*E*)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 34.6mg) in 91% yield (24 mg) as a white solid in 1:20 dr. The reaction with ethyl (*Z*)-2-phenyl-2-(2-tosylhydrazineylidene)acetate obtained the title compound in 69% yield (18 mg) in 1:8 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 – 7.10 (m, 3H), 7.06 – 7.01 (m, 5H), 6.78 – 6.76 (m, 2H), 4.20 – 4.07 (m, 2H), 3.10 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.13 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 136.6, 135.0, 132.0, 128.2, 127.8, 127.7, 127.0, 126.4, 61.4, 37.7, 33.0, 20.3, 14.3.

The spectroscopic data is consistent with that previously reported in the literature.[13]

hexyl 1,2-diphenylcyclopropane-1-carboxylate (**3c**)



The title compound was synthesised according to General Procedure C from hexyl 2-diazo-2-phenylacetate (0.1 mmol, 24.6 mg) in 77% yield (25 mg) as a yellow solid in 1:11 dr.

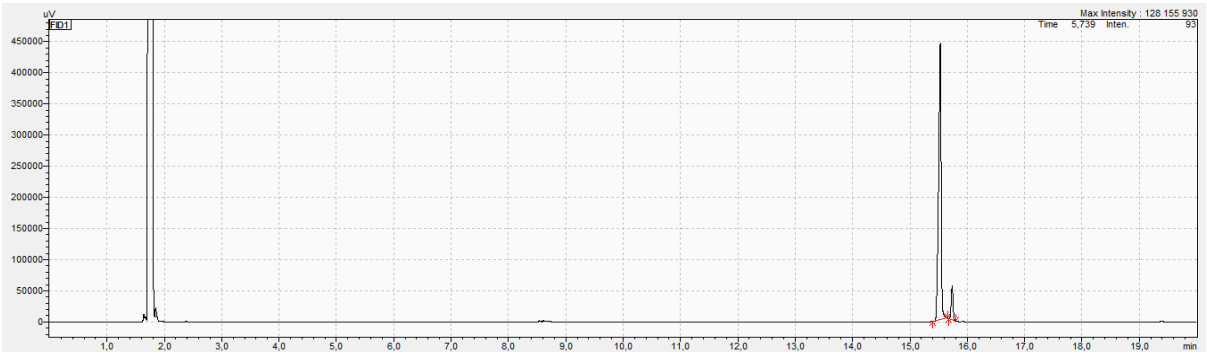
The title compound was synthesised according to General Procedure D from (*E*)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 40.3 mg) in 10% yield (3 mg) as a yellow solid in 1:9 dr. The reaction with ethyl (*Z*)-2-phenyl-2-(2-tosylhydrazineylidene)acetate obtained the title compound in 20% yield (6 mg) in 1:10 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 – 7.01 (m, 8H), 6.77 (dd, *J* = 6.4, 2.9 Hz, 2H), 4.06 (ddt, *J* = 40.7, 10.8, 6.6 Hz, 2H), 3.09 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.12 (dd, *J* = 9.2, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.3, 4.9 Hz, 1H).

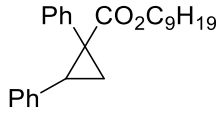
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 136.7, 135.0, 132.0, 128.2, 127.8, 127.7, 127.0, 126.4, 65.5, 37.8, 33.0, 31.4, 28.6, 25.5, 22.6, 20.3, 14.1.

HRMS (ESI$^+$): Calc'd for $C_{22}H_{26}O_2Na^+$: 345.1830; found: 345.1833.

GC (FID): 92% *cis* / 8% *trans*



nonyl 1,2-diphenylcyclopropane-1-carboxylate (**3d**)



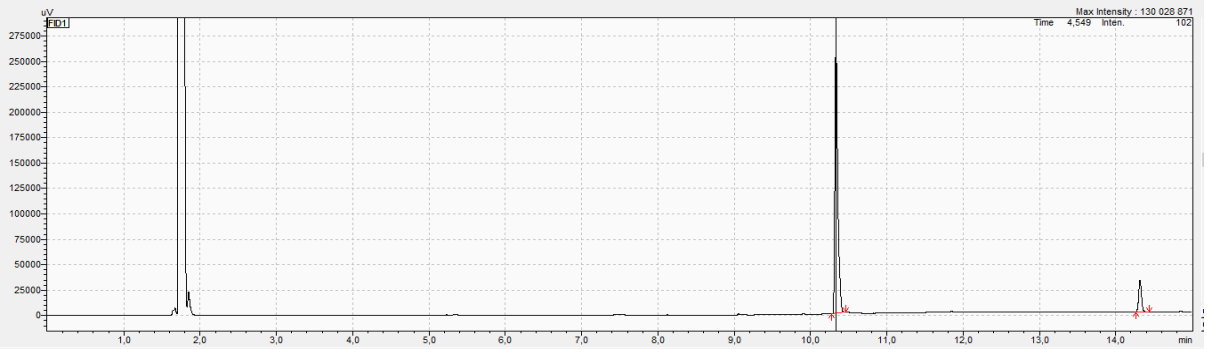
The title compound was synthesised according to General Procedure C from nonyl 2-diazo-2-phenylacetate (0.1 mmol, 28.8 mg), in 82% yield (30 mg) as a yellow oil in 1:10 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 – 7.01 (m, 8H), 6.78 (dd, *J* = 6.6, 3.0 Hz, 2H), 4.06 (ddt, *J* = 40.8, 10.7, 6.6 Hz, 2H), 3.10 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.13 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.3, 4.9 Hz, 1H).

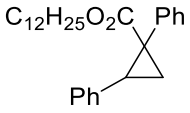
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 136.7, 135.0, 132.0, 128.2, 127.8, 127.7, 127.0, 126.4, 65.5, 37.8, 33.0, 32.0, 29.6, 29.3, 29.2, 28.6, 25.9, 22.8, 20.3, 14.2.

HRMS (ESI$^+$): Calc'd for $C_{25}H_{32}O_2Na^+$: 387.2300; found: 387.2298.

GC (FID): 90% *cis* / 10% *trans*



dodecyl 1,2-diphenylcyclopropane-1-carboxylate (**3e**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 93% yield (38 mg) as a yellow oil in 1:11 dr.

1 mmol scale reaction: dodecyl 2-diazo-2-phenylacetate (1.0 mmol, 330.4 mg), styrene (10.0 mmol, 1040 mg), DTAC (3.5 mmol, 924 mg) and water (50 mL) were charged in a 50 mL round bottomed flask and was subjected to blue light irradiation for 60 hours. The work up and purification procedures were analogous to General Procedure C, which obtained the title compound in 76% yield (309 mg) as a yellow oil in 1:11 dr.

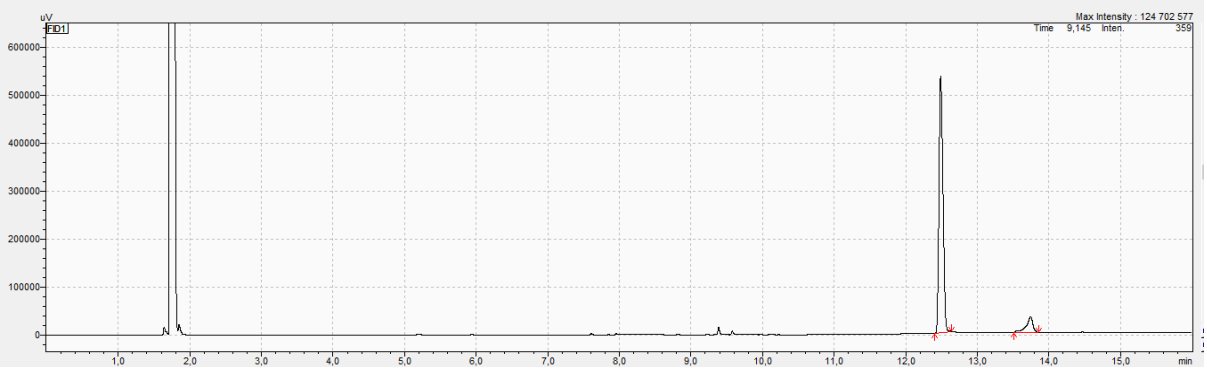
The title compound was synthesised according to General Procedure D from (*E*)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 34.6mg) in 31% yield (12 mg) as a yellow oil in 1:15 dr.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 – 7.00 (m, 8H), 6.79 – 6.76 (m, 2H), 4.14 – 3.99 (m, 2H), 3.10 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.13 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.87 (dd, *J* = 7.2, 4.9 Hz, 1H).

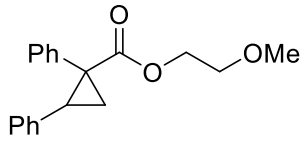
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 136.7, 135.0, 132.0, 128.2, 127.8, 127.7, 127.0, 126.4, 65.5, 37.8, 33.0, 32.1, 29.79, 29.78, 29.65, 29.63, 29.5, 29.2, 28.6, 25.9, 22.8, 20.3, 14.2.

HRMS (ESI$^+$): Calc'd for $C_{28}H_{38}O_2Na^+$: 429.2770; found: 429.2771.

GC (FID): 92% *cis* / 8% *trans*



2-methoxyethyl 1,2-diphenylcyclopropane-1-carboxylate (**3f**)



The title compound was synthesised according to General Procedure C from 2-methoxyethyl 2-diazo-2-phenylacetate (0.1 mmol, 22.0 mg) in 48% yield (14 mg) as a colourless semi-solid in 1:6 dr.

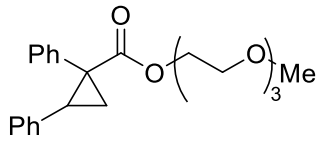
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 – 7.03 (m, 8H), 6.80 – 6.77 (m, 2H), 4.23 (ddt, *J* = 41.9, 11.9, 4.7 Hz, 2H), 3.52 (t, *J* = 4.9 Hz, 2H), 3.25 (s, 3H), 3.15 – 3.11 (m, 1H), 2.16 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.90 (dd, *J* = 7.2, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 136.5, 134.8, 132.1, 128.2, 127.8, 127.7, 127.1, 126.4, 70.4, 64.7, 59.2, 37.6, 33.2, 20.3.

HRMS (ESI$^+$): Calc'd for $C_{19}H_{20}O_3Na^+$: 319.1310; found: 319.1313.

Elemental Anal: Calc'd (%) for $C_{19}H_{20}O_3$: C - 77.00 H - 6.80; found: C - 76.59 H - 7.04.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 1,2-diphenylcyclopropane-1-carboxylate (**3g**)



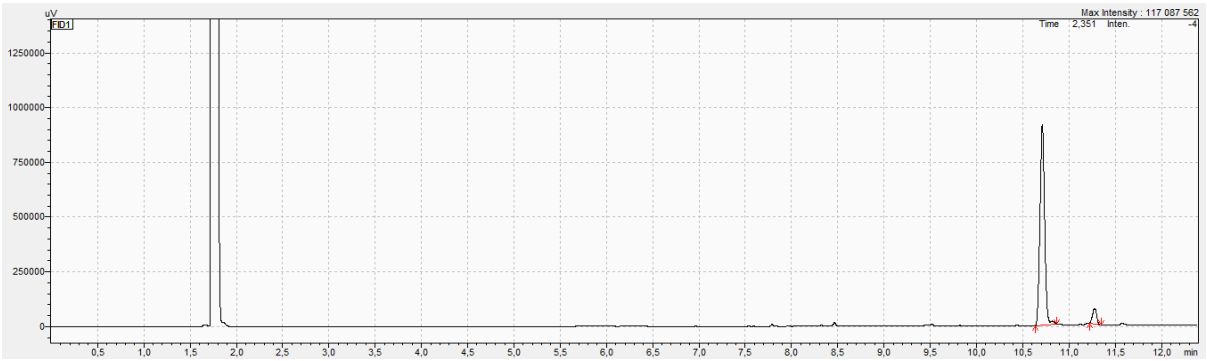
The title compound was synthesised according to General Procedure C from 2-(2-(2-methoxyethoxy)ethoxy)ethyl 2-diazo-2-phenylacetate (0.1 mmol, 30.8 mg), in 34% yield (13 mg) as a colourless semi-solid in 1:14 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 – 7.01 (m, 8H), 6.77 (dd, *J* = 6.7, 3.0 Hz, 2H), 4.22 (ddt, *J* = 36.0, 11.8, 4.9 Hz, 2H), 3.62 – 3.58 (m, 4H), 3.53 (dd, *J* = 5.5, 3.2 Hz, 4H), 3.47 – 3.45 (m, 2H), 3.37 (s, 3H), 3.12 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.15 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.88 (dd, *J* = 7.3, 4.9 Hz, 1H).

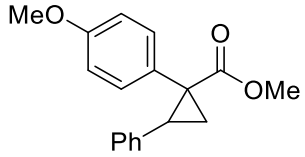
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 136.5, 134.9, 132.1, 128.2, 127.8, 127.7, 127.1, 126.4, 72.1, 70.81, 70.78, 70.68, 69.0, 65.0, 59.2, 37.6, 33.2, 20.4.

HRMS (ESI$^+$): Calc'd for $C_{23}H_{28}O_5Na^+$: 407.1834; found: 407.1841.

GC (FID): 93% *cis* / 7% *trans*



*methyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (***3h**)



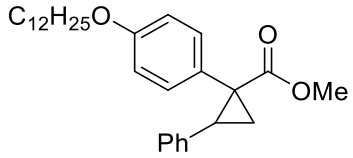
The title compound was synthesised according to General Procedure C from methyl 2-diazo-2-(4-methoxyphenyl)acetate (0.1 mmol, 20.6 mg) in 52% yield (15 mg) as a white solid in 1:12 dr.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09 – 7.04 (m, 3H), 6.94 – 6.92 (m, 2H), 6.78 – 6.76 (m, 2H), 6.68 – 6.65 (m, 2H), 3.72 (s, 3H), 3.66 (s, 3H), 3.07 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.12 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.82 (dd, *J* = 7.3, 4.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.8, 158.6, 136.6, 133.1, 128.2, 127.9, 126.9, 126.4, 113.3, 55.2, 52.8, 36.8, 33.3, 20.9.

The spectroscopic data is consistent with that previously reported in the literature.[14]

methyl 1-(4-(dodecyloxy)phenyl)-2-phenylcyclopropane-1-carboxylate (**3i**)



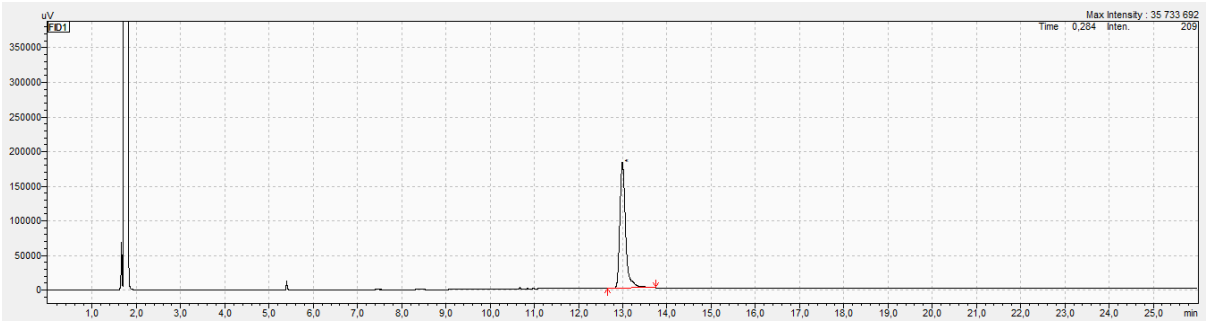
The title compound was synthesised according to General Procedure C from methyl 2-diazo-2-(4-(dodecyloxy)phenyl)acetate (0.1 mmol, 36.0 mg) in 41% yield (18 mg) as a colourless oil in >1:20 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 – 7.04 (m, 3H), 6.92 – 6.90 (m, 2H), 6.78 – 6.76 (m, 2H), 6.66 – 6.64 (m, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.67 (s, 3H), 3.08 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.13 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.81 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.74 – 1.69 (m, 1H).

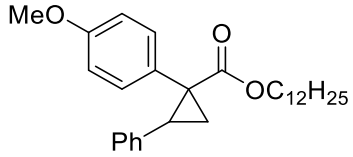
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 158.2, 136.7, 133.0, 128.2, 127.8, 126.7, 126.4, 113.9, 68.0, 52.7, 36.8, 33.3, 32.1, 29.81, 29.78, 29.75, 29.72, 29.6, 29.5, 29.4, 26.2, 22.8, 21.0, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_3Na^+$: 459.2875; found 459.2880.

GC (FID): Inseperable mixture of two diastereoisomers.



dodecyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3j**)



The title compound was synthesised according to General Procedure C from methyl dodecyl 2-diazo-2-(4-methoxyphenyl)acetate (0.1 mmol, 36.0 mg) in 65% yield (28 mg) as a colourless oil in 1:7 dr.

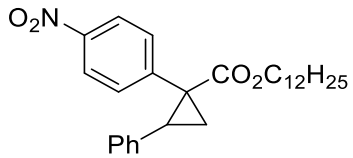
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 – 7.05 (m, 3H), 6.95 – 6.90 (m, 2H), 6.78 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.67 – 6.65 (m, 2H), 4.13 – 4.00 (m, 2H) 3.72 (s, 3H), 3.05 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.11 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.81 (dd, *J* = 7.2, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 158.5, 136.8, 133.0, 130.4, 128.2, 127.8, 126.3, 113.2, 65.5, 55.2, 40.7, 37.0, 33.0, 32.1, 29.77, 29.67, 29.66, 29.5, 29.3, 28.6, 25.9, 22.8, 20.5, 14.2.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_3Na^+$: 459.2875; found: 459.2878.

Elemental Anal: Calc'd (%) for $C_{29}H_{40}O_3$: C - 79.77 H - 9.23; found: C - 79.65 H - 9.31.

dodecyl 1-(4-nitrophenyl)-2-phenylcyclopropane-1-carboxylate (**3k**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-(4-nitrophenyl)acetate (0.1 mmol, 37.5 mg) in 73% yield (45 mg) as a yellow oil in 1:2 dr.

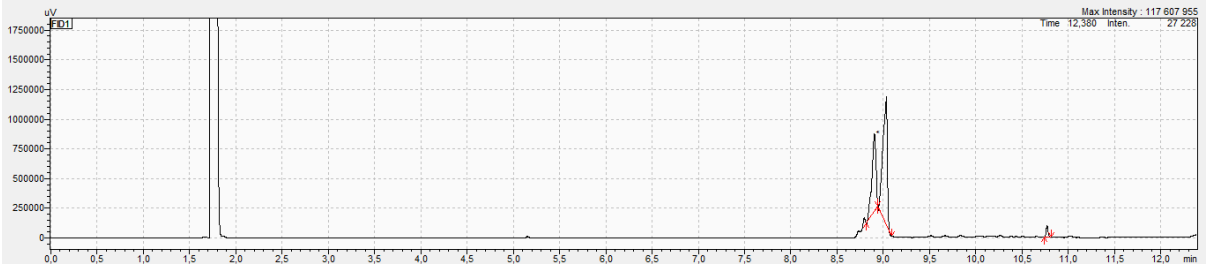
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.20 – 7.18 (m, 2H), 7.09 – 7.07 (m, 3H), 6.79 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.08 (ddt, *J* = 29.8, 10.8, 6.7 Hz, 2H), 3.19 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.21 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.94 (dd, *J* = 7.4, 5.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) Unable to unambiguously assign ^{13}C peaks due to the low dr.

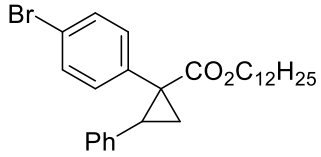
HRMS [APCI$^+$): Calc'd for $C_{28}H_{38}NO_4^+$: 452.2801; found: 452.2804.

Elemental Anal: Calc'd: (%) for $C_{28}H_{37}NO_4$ C - 74.47 H - 8.26 N - 3.10; found C - 74.46 H - 8.27 N - 3.20.

GC (FID): 64% *cis* / 36% *trans*



dodecyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3l**)



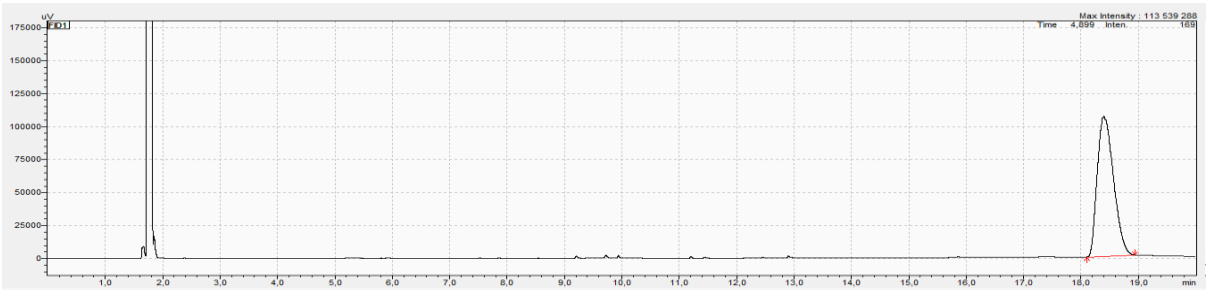
The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-(4-bromophenyl)acetate (0.1 mmol, 40.9 mg) in 80% yield (39 mg) as a colourless semi-solid in 1:13 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.22 (m, 2H), 7.10 – 7.06 (m, 3H), 6.89 – 6.87 (m, 2H), 6.78 – 6.77 (m, 2H), 4.05 (ddt, *J* = 33.5, 10.8, 6.6 Hz, 2H), 3.09 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.12 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.82 (dd, *J* = 7.3, 5.0 Hz, 1H).

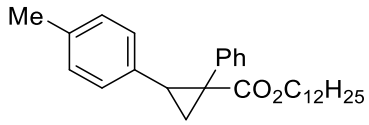
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 136.1, 134.3, 133.7, 130.9, 128.2, 128.0, 126.6, 121.2, 65.7, 37.1, 33.1, 32.1, 29.80, 29.77, 29.66, 29.64, 29.5, 29.2, 28.6, 25.9, 22.8, 20.2, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{28}H_{37}O_2BrNa^+$: 507.1875; found: 507.1877.

GC (FID): Inseperable mixture of two diastereoisomers.



dodecyl 1-phenyl-2-(p-tolyl)cyclopropane-1-carboxylate (**3m**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 68% yield (29 mg) as a colourless semi-solid in 1:8 dr.

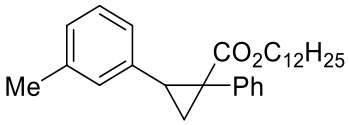
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 – 7.11 (m, 3H), 7.03 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.06 (ddt, *J* = 40.8, 10.8, 6.6 Hz, 2H), 3.06 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.21 (s, 3H), 2.11 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.82 (dd, *J* = 7.3, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 135.9, 135.2, 133.6, 132.1, 128.6, 128.0, 127.7, 126.9, 65.4, 37.6, 32.8, 32.1, 29.80, 29.78, 29.66, 29.64, 29.5, 29.2, 28.6, 25.9, 22.8, 21.1, 20.4, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_2Na^+$: 443.2926; found: 443.2923.

Elemental Anal: Calc'd (%) for $C_{29}H_{40}O_2$: C - 82.81 H - 9.59; found: C - 82.65 H - 9.70.

dodecyl 1-phenyl-2-(m-tolyl)cyclopropane-1-carboxylate (**3n**)



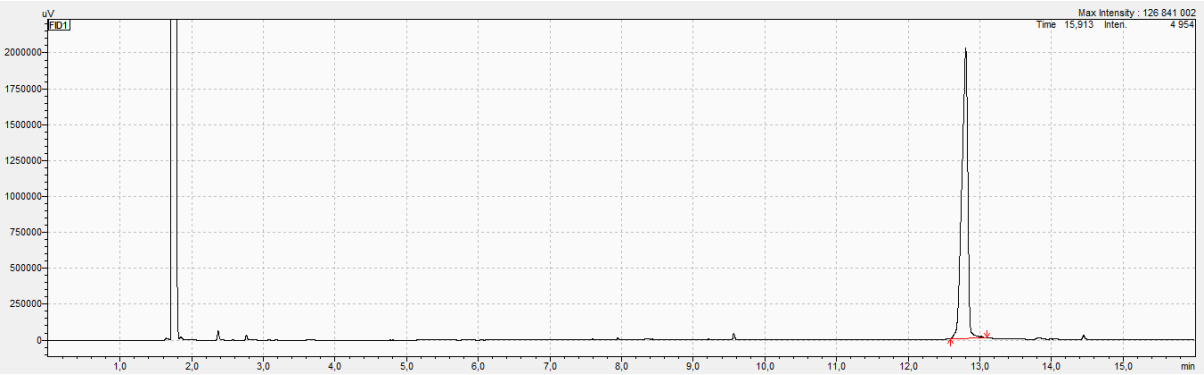
The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 74% yield (31 mg) as a yellow oil in 1:8 dr.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.04 – 7.02 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 4.06 (ddt, *J* = 48.4, 10.8, 6.6 Hz, 2H), 3.05 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.15 (s, 3H), 2.11 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.85 (dd, *J* = 7.3, 4.9 Hz, 1H).

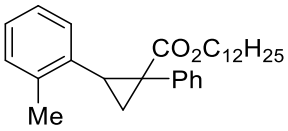
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.0, 137.3, 136.6, 135.1, 132.0, 129.2, 127.63, 127.62, 127.1, 127.0, 125.0, 65.5, 37.7, 33.0, 32.1, 29.79, 29.78, 29.65, 29.63, 29.5, 29.2, 28.6, 25.9, 22.8, 21.4, 20.4, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_2Na^+$: 443.2926; found: 443.2927.

GC (FID): Inseperable mixture of two diastereoisomers



dodecyl 1-phenyl-2-(o-tolyl)cyclopropane-1-carboxylate (**3o**)



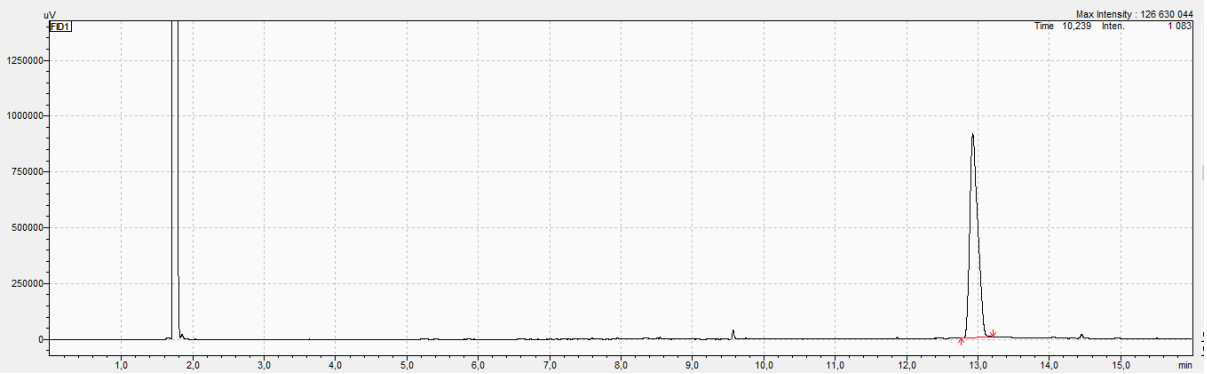
The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 76% yield (29 mg) as a colourless semi-solid in 1:14 dr.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 7.1 Hz, 1H), 7.05 (dd, *J* = 5.2, 2.0 Hz, 3H), 6.98 – 6.96 (m, 3H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.41 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.10 (ddt, *J* = 59.4, 10.8, 6.6 Hz, 2H), 3.12 (dd, *J* = 9.1, 7.6 Hz, 1H), 2.48 (s, 3H), 2.08 – 2.03 (m, 2H).

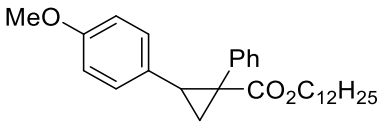
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.1, 137.9, 135.2, 134.5, 131.3, 129.8, 127.6, 126.9, 126.5, 125.8, 125.4, 65.4, 36.8, 32.1, 31.1, 29.80, 29.78, 29.67, 29.66, 29.5, 29.3, 28.7, 25.9, 22.8, 20.2, 18.5, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_2Na^+$: 443.2926; found: 443.2927.

GC (FID): Inseperable mixture of two diastereoisomers.



dodecyl 2-(4-methoxyphenyl)-1-phenylcyclopropane-1-carboxylate (**3p**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 73% yield (32 mg) as a yellow solid in 1:5 dr.

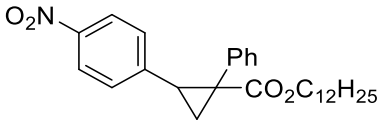
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (mHz, 3H), 7.03 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.71 – 6.68 (m, 2H), 6.62 – 6.59 (m, 2H), 4.06 (ddt, *J* = 41.0, 10.8, 6.6 Hz, 2H), 3.69 (s, 3H), 3.05 (dd, *J* = 9.4, 7.3 Hz, 1H), 2.11 (dd, *J* = 9.4, 4.8 Hz, 1H), 1.80 (dd, *J* = 7.3, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 158.2, 135.2, 132.1, 129.1, 128.6, 127.7, 126.9, 113.3, 65.4, 55.2, 37.4, 32.5, 32.1, 29.79, 29.77, 29.64, 29.62, 29.5, 29.2, 28.6, 25.9, 22.8, 20.3, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{29}H_{40}O_3Na^+$: 459.2875; found: 459.2881.

Elemental Anal: Calc'd (%) for $C_{29}H_{40}O_3$: C - 79.77 H - 9.23; found: C - 79.62 H - 9.39.

dodecyl 2-(4-nitrophenyl)-1-phenylcyclopropane-1-carboxylate (**3q**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 62% yield (28 mg) as a colourless semi-solid in 1:3 dr.

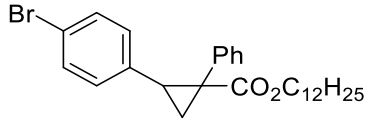
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 – 7.89 (m, 2H), 7.14 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.01 – 6.99 (m, 2H), 6.90 – 6.88 (m, 2H), 4.07 (ddt, *J* = 38.4, 10.8, 6.6 Hz, 2H), 3.18 (dd, *J* = 9.1, 7.1 Hz, 1H), 2.22 (dd, *J* = 9.1, 5.2 Hz, 1H), 1.94 (dd, *J* = 7.1, 5.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 146.5, 145.1, 134.0, 131.8, 128.7, 128.1, 127.6, 123.0, 65.9, 38.9, 32.3, 32.1, 29.78, 29.76, 29.63, 29.60, 29.5, 29.2, 28.5, 25.8, 22.8, 21.1, 14.3.

HRMS [APCI$^+$): Calc'd for $C_{28}H_{38}NO_4^+$: 452.2801; found: 452.2805.

Elemental Anal: Calc'd (%) for $C_{28}H_{37}NO_4$: C - 74.47 H - 8.26; found: C - 74.45 H - 8.28.

dodecyl 2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylate (**3r**)



The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 82% yield (40 mg) as a yellow oil in 1:4 dr.

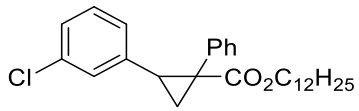
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 – 7.13 (m, 5H), 7.01 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.64 – 6.62 (m, 2H), 4.06 (ddt, *J* = 39.7, 10.8, 6.6 Hz, 2H), 3.04 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.13 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.81 (dd, *J* = 7.2, 5.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.7, 135.9, 134.6, 131.9, 130.9, 129.8, 127.9, 127.2, 120.3, 65.6, 37.9, 32.3, 32.1, 29.79, 29.77, 29.64, 29.62, 29.5, 29.2, 28.6, 25.9, 22.8, 20.5, 14.3.

HRMS (ESI$^+$): Calc'd for $C_{28}H_{37}O_2BrNa^+$: 507.1875; found: 507.1878.

Elemental Anal: Calc'd (%) for $C_{28}H_{37}BrO_2$: C - 69.27, H - 7.68 Br - 16.46; found C - 69.19, H - 7.67, Br - 16.42.

dodecyl 2-(3-chlorophenyl)-1-phenylcyclopropane-1-carboxylate (**3t**)



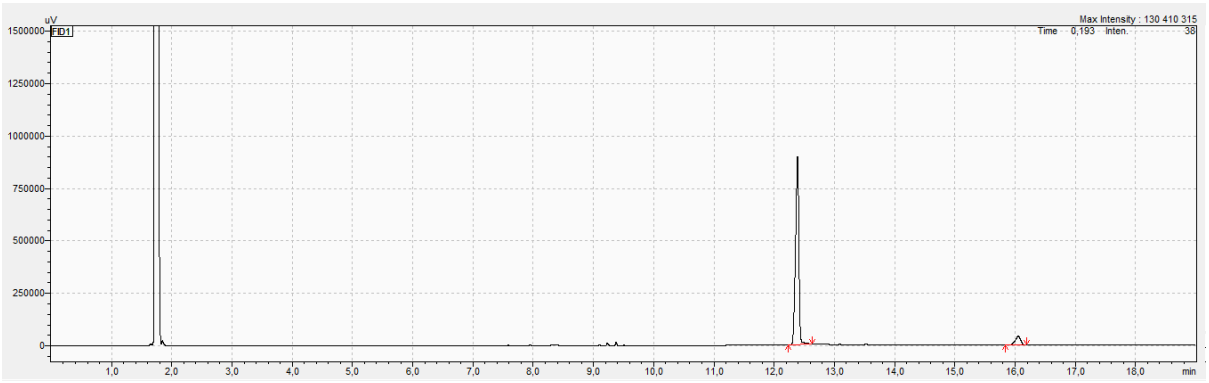
The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 34% yield (15 mg) as a yellow oil in 1:13 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 – 7.12 (m, 3H), 7.02 (dd, *J* = 6.7, 2.8 Hz, 3H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 1.9 Hz, 1H), 6.59 (dt, *J* = 7.8, 1.5 Hz, 1H), 4.06 (ddt, *J* = 41.3, 10.8, 6.6 Hz, 2H), 3.05 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.12 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.84 (dd, *J* = 7.2, 5.0 Hz, 1H).

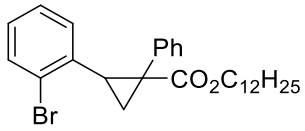
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.6, 139.0, 134.5, 133.7, 131.9, 128.9, 128.5, 127.9, 127.3, 126.5, 126.1, 65.7, 37.9, 32.4, 32.1, 29.79, 29.78, 29.65, 29.62, 29.5, 29.2, 28.6, 25.9, 22.8, 20.4, 14.3.

HRMS [APCI$^+$): Calc'd for $C_{28}H_{38}O_2Cl$: 441.2560; found: 441.2561.

GC (FID): 92% *cis* / 8% *trans*



dodecyl 2-(2-bromophenyl)-1-phenylcyclopropane-1-carboxylate (**3u**)



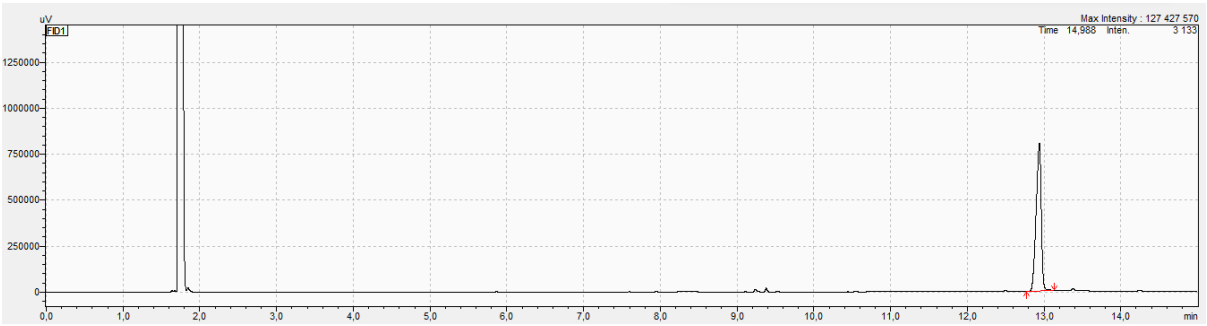
The title compound was synthesised according to General Procedure C from dodecyl 2-diazo-2-phenylacetate (0.1 mmol, 33.0 mg) in 62% yield (30 mg) as a yellow oil in 1:4 dr.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.12 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.09 – 7.05 (m, 3H), 6.91 (pd, *J* = 7.4, 1.8 Hz, 2H), 6.49 (dd, *J* = 7.4, 2.1 Hz, 1H), 4.12 (ddt, *J* = 77.0, 10.7, 6.6 Hz, 2H), 3.35 (dd, *J* = 7.9 Hz, 1H), 2.11 (dd, *J* = 9.1, 5.0 Hz, 1H), 2.02 (dd, *J* = 7.5, 5.1 Hz, 1H).

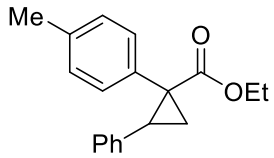
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.5, 136.1, 135.0, 132.5, 131.4, 128.1, 127.8, 127.7, 127.0, 126.8, 65.5, 36.9, 34.1, 32.1, 29.80, 29.78, 29.68, 29.5, 29.3, 28.7, 25.9, 22.8, 18.5, 14.3. [One peak from the aromatic region cannot be unambiguously assigned and the typical second peak around δ 29.7 is not observed].

HRMS (ESI$^+$): Calc'd for $C_{28}H_{37}O_2BrNa^+$: 507.1875; found 507.1872.

GC (FID): Inseperable mixture of two diastereoisomers.



ethyl 2-phenyl-1-(p-tolyl)cyclopropane-1-carboxylate (**3v**)



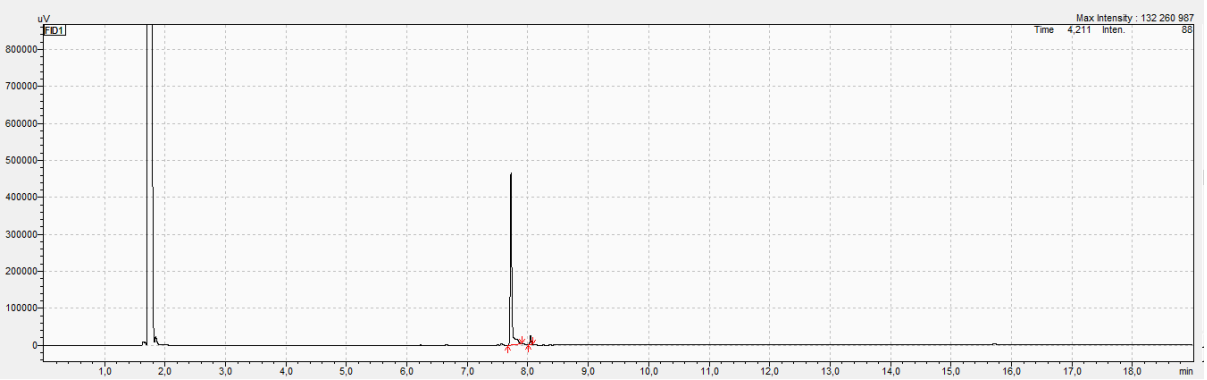
The title compound was synthesised according to General Procedure D from ethyl (*E*)-2-(*p*-tolyl)-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 36.0 mg), in 50% yield (14 mg) as a colourless semi-solid in 1:15 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (dd, *J* = 5.2, 1.9 Hz, 3H), 6.93 – 6.89 (m, 4H), 6.79 – 6.77 (m, 2H), 4.20 – 4.06 (m, 2H), 3.07 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.24 (s, 3H), 2.10 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.83 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

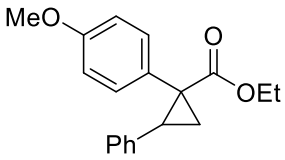
^{13}C NMR (126 MHz, $CDCl_3$): δ 174.1, 136.8, 136.6, 131.9, 131.8, 128.5, 128.2, 127.8, 126.3, 61.3, 37.4, 33.0, 21.3, 20.4, 14.3.

HRMS (EI$^+$): Calc'd for $C_{19}H_{20}O_2$: 280.1463; found 280.1470.

GC (FID): 96% *cis* / 4% *trans*



ethyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3w**)



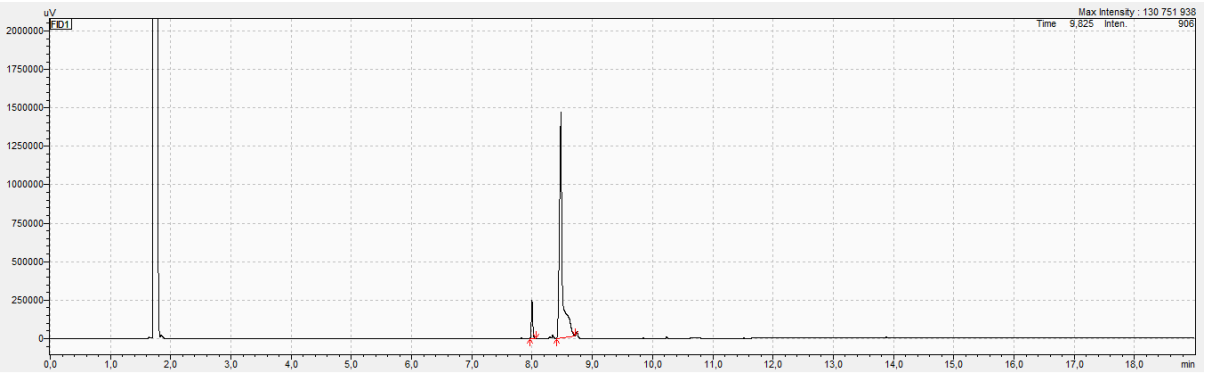
The title compound was synthesised according to General Procedure D from ethyl (*E*)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 37.6 mg) in 49% yield (15 mg) as a colourless semi-solid in 1:20 dr. The same reaction with ethyl (*Z*)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate obtained the title compound in 73% yield (22 mg) in 1:>20 dr.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 – 7.05 (m, 3H), 6.95 – 6.91 (m, 2H), 6.78 (dd, *J* = 7.5, 2.2 Hz, 2H), 6.67 – 6.64 (m, 2H), 4.20 – 4.05 (m, 2H), 3.72 (s, 3H), 3.06 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.11 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.81 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

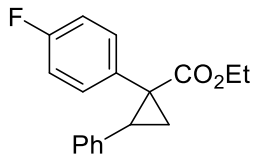
^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 158.5, 136.8, 133.0, 128.2, 127.8, 127.1, 126.3, 113.2, 61.3, 55.2, 37.0, 33.1, 20.6, 14.3.

HRMS (ESI^{+}): Calc'd for $C_{19}H_{20}O_3Na^{+}$: 319.1310; found 319.1316.

GC (FID): 93% *cis* / 7% *trans.*



ethyl 1-(4-fluorophenyl)-2-phenylcyclopropane-1-carboxylate (**3x**)



The title compound was synthesised according to General Procedure D from ethyl (*E*)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate (0.1 mmol, 36.4 mg) in 34% yield (10 mg) as a colourless oil in 1:>20 dr. The same reaction with ethyl (*Z*)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate obtained the title compound in 15% yield (4 mg) in 1:>20 dr.

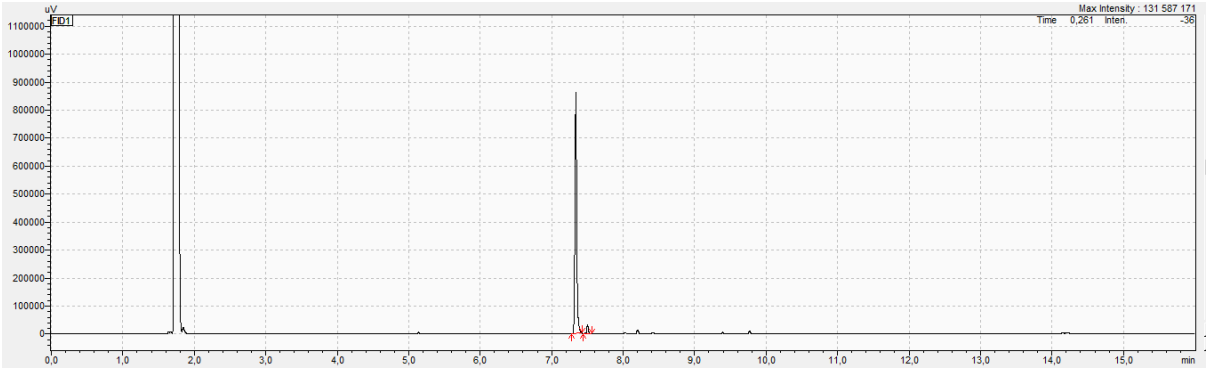
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 – 7.05 (m, 3H), 7.00 – 6.97 (m, 2H), 6.83 – 6.76 (m, 4H), 4.20 – 4.08 (m, 2H), 3.09 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.14 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.84 (dd, *J* = 7.2, 5.0 Hz, 1H) 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.7, 162.8, 160.9, 136.3, 133.6 (d, *J* = 8.2 Hz), 128.2, 127.9, 126.6, 114.7 (d, *J* = 21.5 Hz), 61.5, 36.9, 33.1, 20.3, 14.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ MINOR = -115.10 (tt, *J* = 8.5, 5.4 Hz), MAJOR = -115.33 (tt, *J* = 8.9, 5.4 Hz).

HRMS (ESI$^+$): Calc'd for $C_{18}H_{18}O_2F^+$: 285.1291; found: 285.1293.

GC (FID): 97% *cis* / 3% *trans*



6. Computational Methods and Additional Results

The density functional theory (DFT) calculations were performed using Turbomole 7.3[15]. We used the BP functional[16,17] and the TZVP basis set[18] along with the COSMO implicit solvent model[19] using an infinite dielectric constant, in order to allow for COSMO-RS[20] calculations. The ensuing COSMO-RS calculations were performed using COSMOtherm 21 and the BP_TZVP_C30_1601 parameterisation. The DTAC surfactant was modelled as a contact ion pair, to make it a neutral molecule, which is a requirement for the interfacial tension calculations.

We predicted the critical micellar concentration (CMC) using our recent method[21] with dodecane as the equivalent tail model for the surfactant. The method is based on our COSMO-RS based method for predicting liquid-liquid interfacial tension (IFT)[22] and allows to calculate the interfacial mole fraction of all components at the liquid-liquid interface, which in our case is the micelle-water interface. The first part of any liquid-liquid IFT calculation is a liquid extraction calculation, an equilibrium calculation between the two bulk phases, which were

1. Surfactant + water
2. Dodecane (modelling surfactant tail), styrene and diazo reagents (+ product)

In short, for the system including all components in the calculation (including the styrene and diazo reagents), the CMC was found by changing the surfactant concentration in the calculations until the computed IFT was equal to 0. Thermodynamically, this is the concentration at which the free energy cost for creating the micelle-water interface vanishes, and micelles can start to form spontaneously. For more details on the procedure, see [21]. This initial equilibration also allows for calculating the partition coefficient P between any compound in the calculation between the micellar core and the aqueous phase. All $\log(P_{water\text{-}core})$ values were lower than 0.00013, which means the concentration of diazo compounds in the aqueous phase are negligible, including the ones with more hydrophilic side chains.

7. References

1 H. Keipour, A. Jalba, L. Delage-Laurin and T. Ollevier, *J. Org. Chem.*, 2017, **82**, 3000–3010.

2 S. Y. Sit, C. M. Conway, K. Xie, R. Bertekap, C. Bourin and K. D. Burris, *Bioorganic Med. Chem. Lett.*, 2010, **20**, 1272–1277.

3 P. Li, J. Zhao, C. Wu, R. C. Larock and F. Shi, *Org. Lett.*, 2011, **13**, 3340–3343.

4 A. Y. Ji, A. Thirupathi, J. Y. Hwang, Y. Kim, G. Han, K.-H. Ahn, K. Kang and E. J. Kang, *Org. Lett.*, 2023, **25**, 1541–1546.

5 S. Xie, D. Li, H. Huang, F. Zhang and Y. Chen, *J. Am. Chem. Soc.*, 2019, **141**, 16237–16242.

6 N. Hu, H. Jung, Y. Zheng, J. Lee, L. Zhang, Z. Ullah, X. Xie, K. Harms, M. Baik and E. Meggers, *Angew. Chemie*, 2018, **130**, 6350–6354.

7 S. K. Mehta, K. K. Bhasin, R. Chauhan and S. Dham, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2005, **255**, 153–157.

8 R. Claveau, B. Twamley and S. J. Connon, *Chem. Commun.*, 2018, **54**, 3231–3234.

9 D. Y. Li, W. Fang, Y. Wei and M. Shi, *Chem. - A Eur. J.*, 2016, **22**, 18080–18084.

10 S. Zhou, B. Cai, C. Hu, X. Cheng, L. Li and J. Xuan, *Chinese Chem. Lett.*, 2021, **32**, 2577–2581.

11 S. Harada, K. Tanikawa, H. Homma, C. Sakai, T. Ito and T. Nemoto, *Chem. - A Eur. J.*, 2019, **25**, 12058–12062.

12 R. Sambasivan and Z. T. Ball, *Angew. Chemie - Int. Ed.*, 2012, **51**, 8568–8572.

13 J. D. Pizarro, F. Molina, M. R. Fructos and P. J. Pérez, *Chem. - A Eur. J.*, 2020, **26**, 10330–10335.

14 A. Dasgupta, R. Babaahmadi, B. Slater, B. F. Yates, A. Ariafard and R. L. Melen, *Chem*, 2020, **6**, 2364–2381.

15 R. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.

16 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

17 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.

18 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

19 A. Klamt and G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2*, 1993, 799–805.

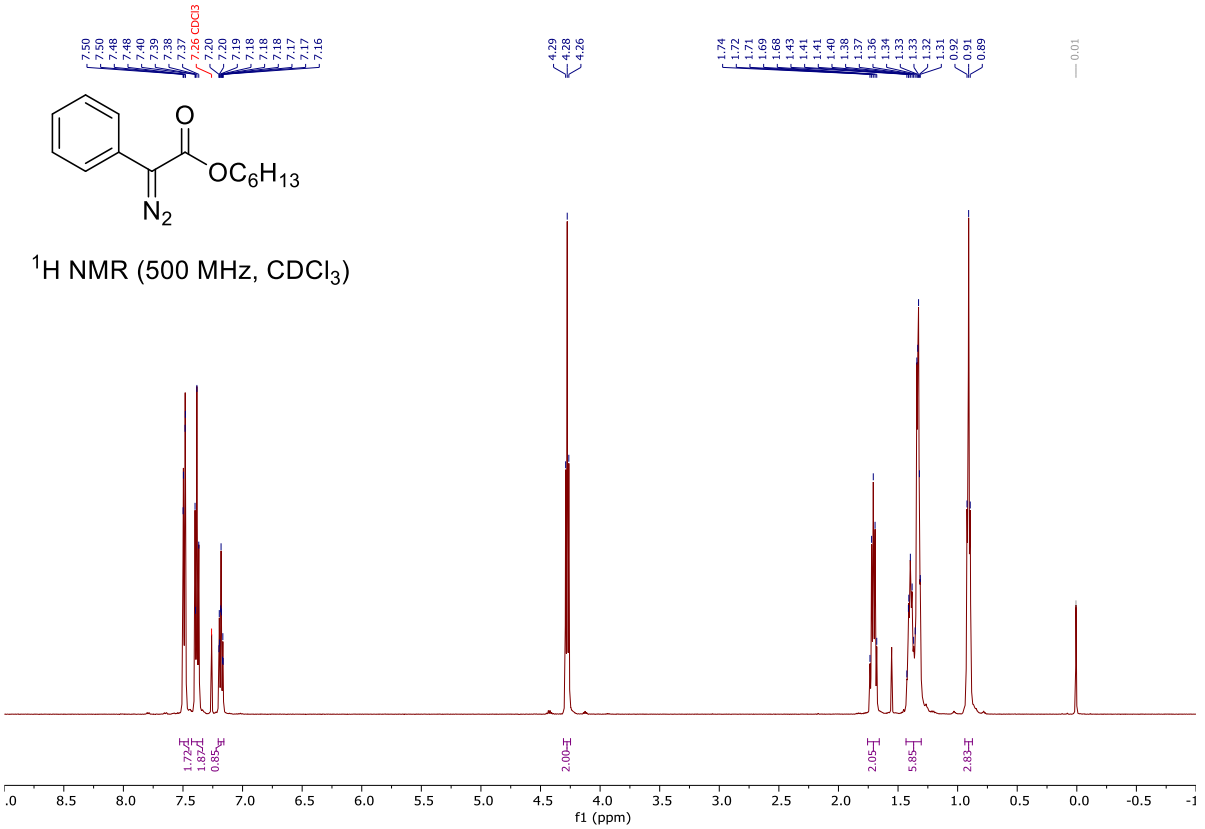
20 A. Klamt, F. Eckert and W. Arlt, in *Annual Review of Chemical and Biomolecular Engineering, Vol 1*, 2010, vol. 1, pp. 101–122.

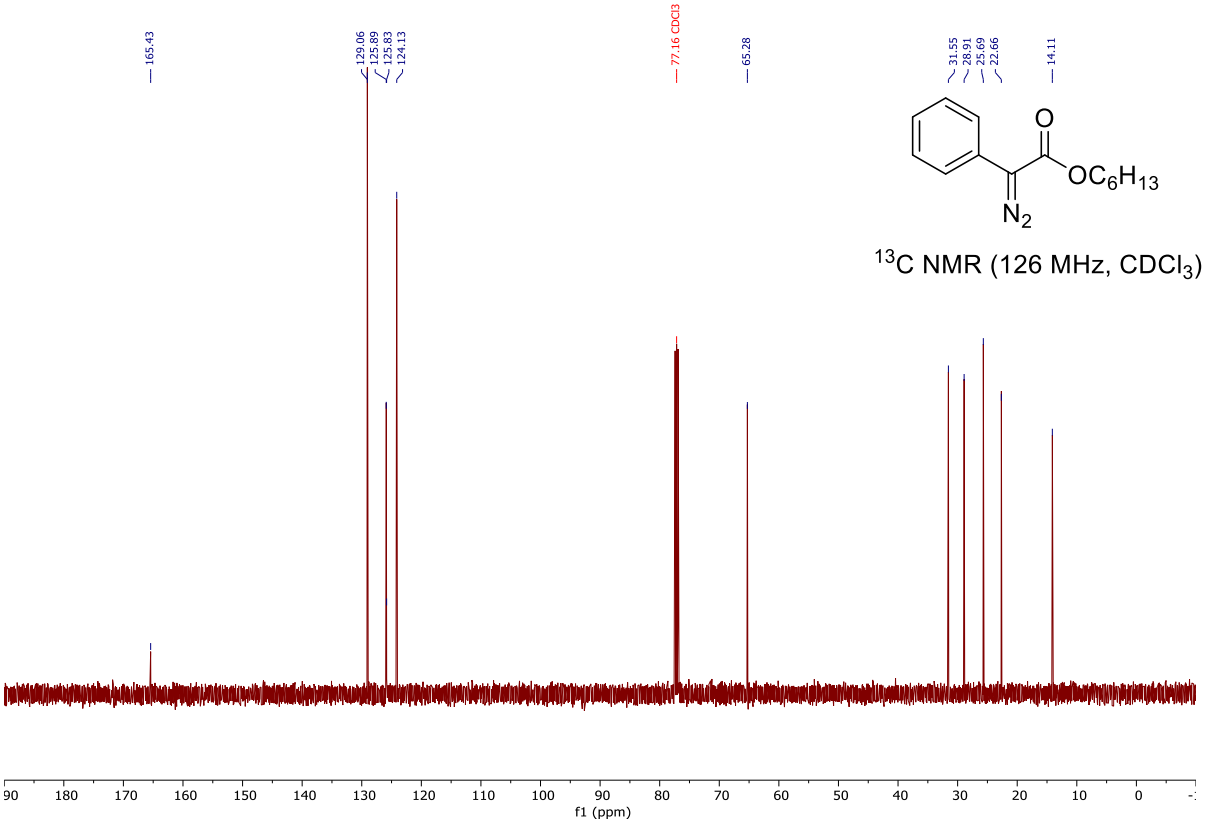
21 M. Turchi, A. P. Karcz and M. P. Andersson, *J. Colloid Interface Sci.*, 2022, **606**, 618–627.

22 M. P. Andersson, M. Bennetzen, A. Klamt and S. L. S. Stipp, *J. Chem. Theory Comput.*, 2014, **10**, 3401–3408.

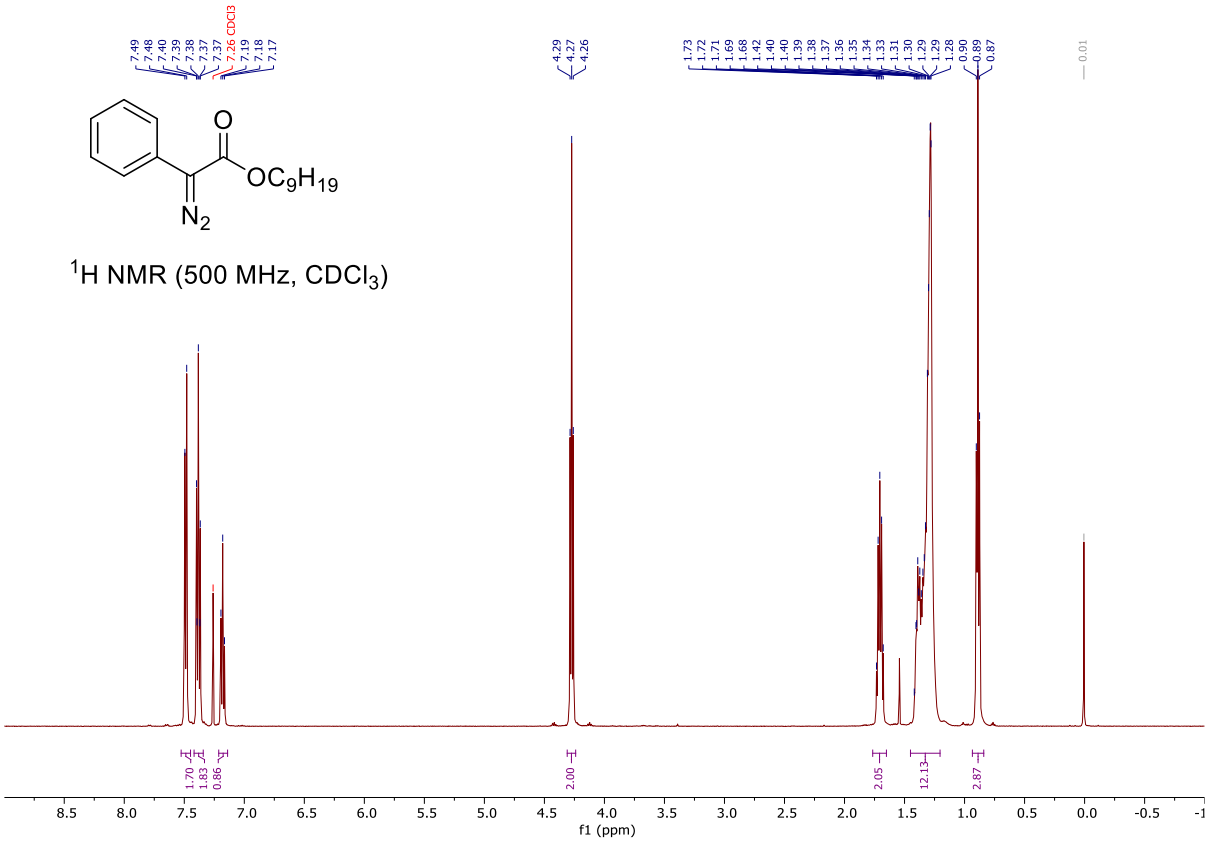
8. NMR Spectra

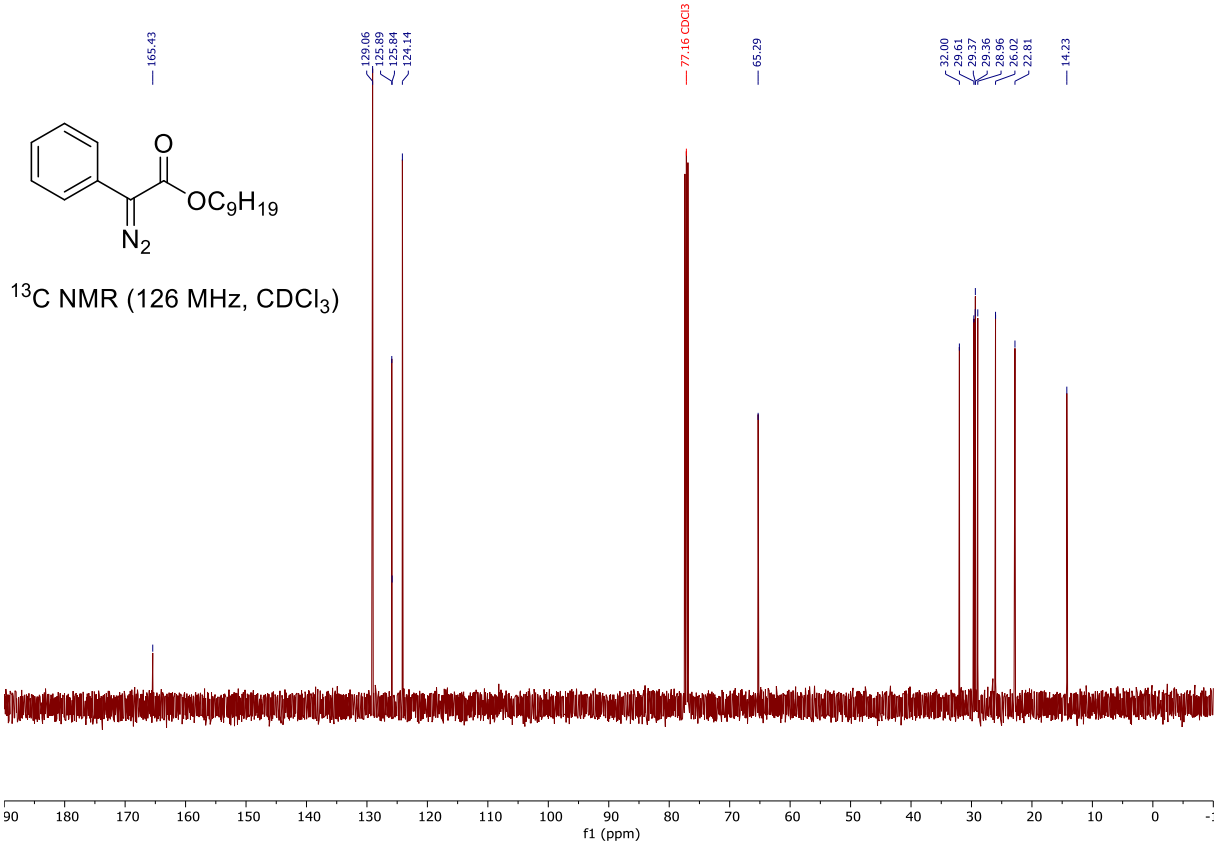
hexyl-2-diazo-2-phenylacetate (**1c**)



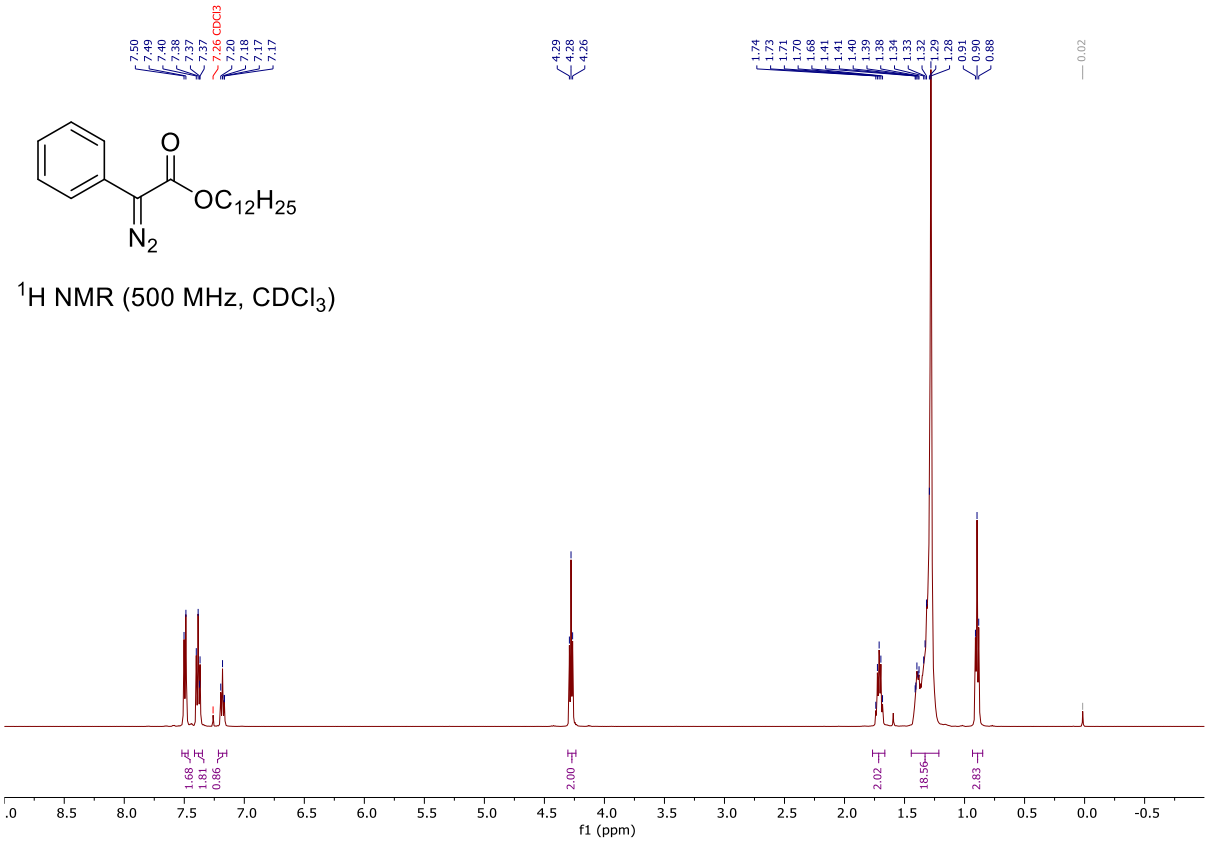


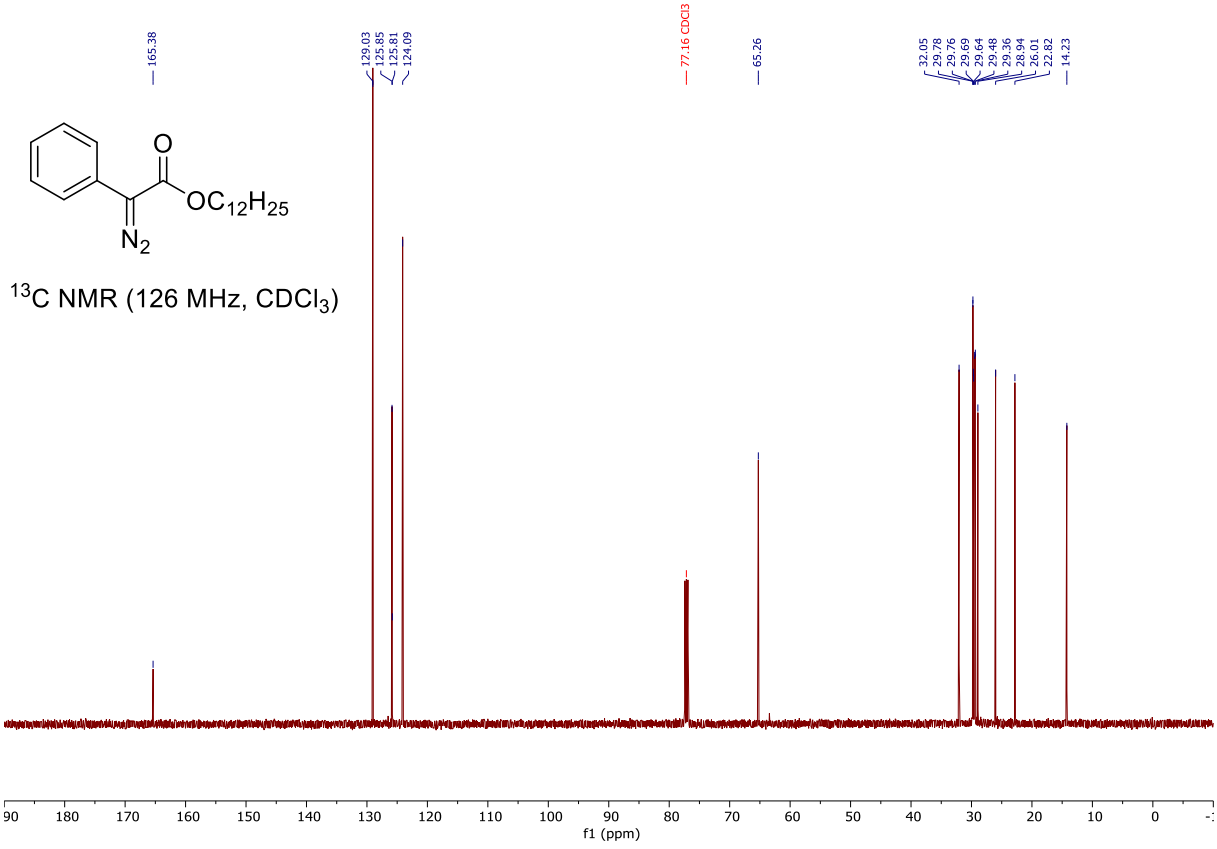
nonyl 2-diazo-2-phenylacetate (**1d**)



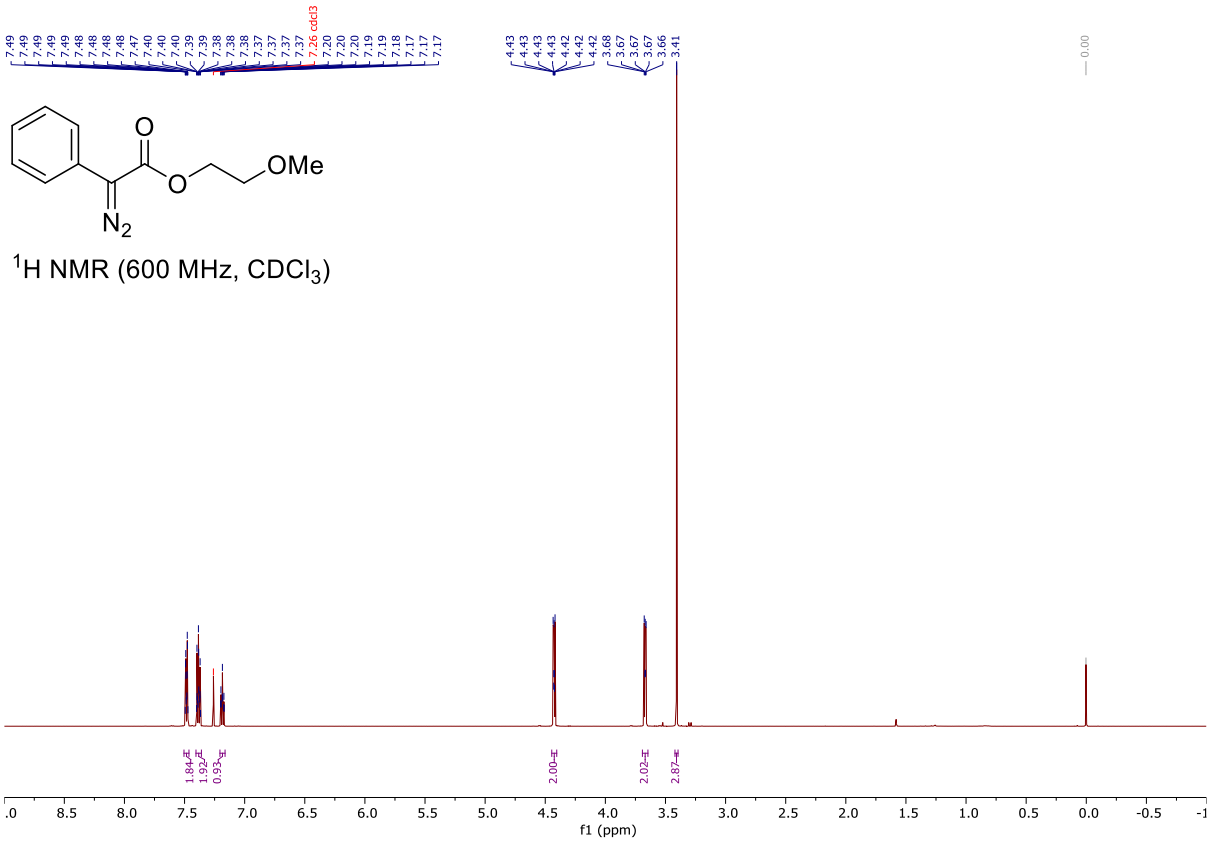


dodecyl 2-diazo-2-phenylacetate (**1e**)

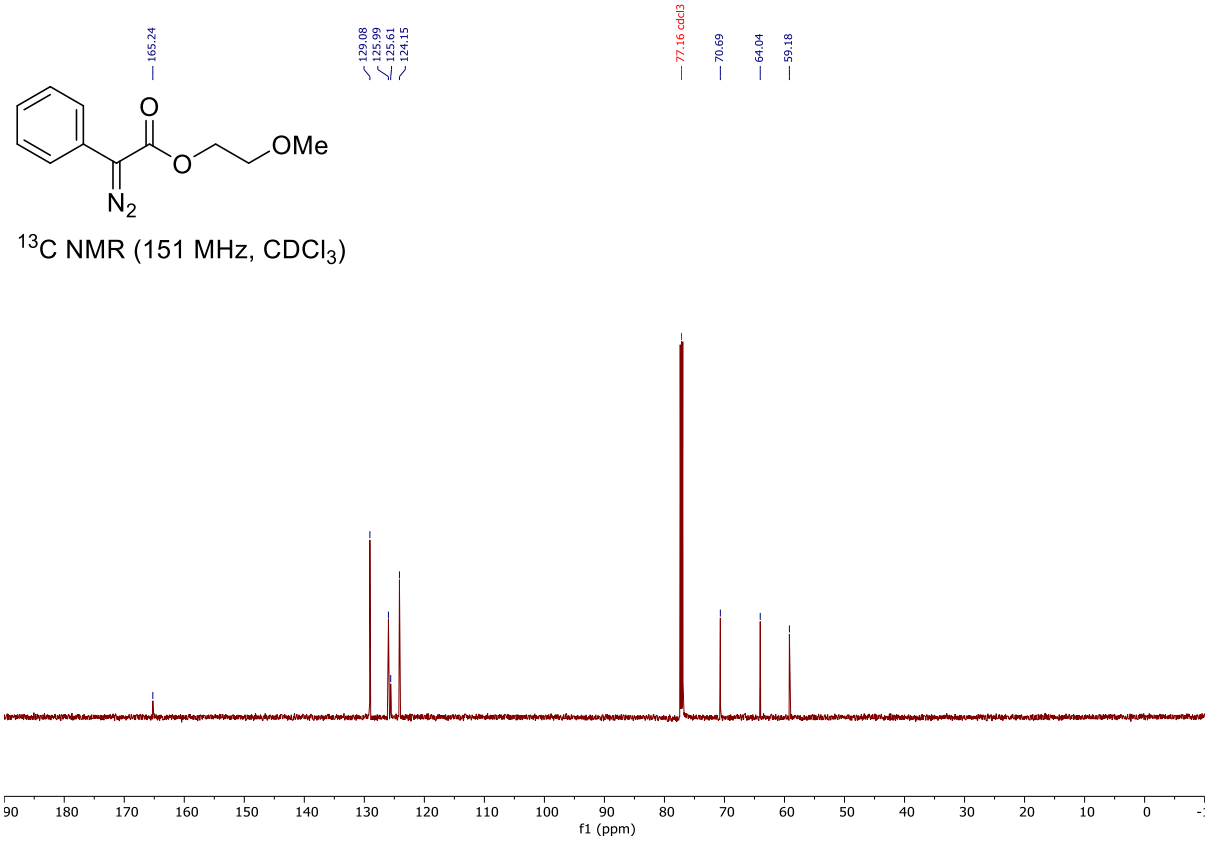




2-methoxyethyl 2-diazo-2-phenylacetate (**1f**)

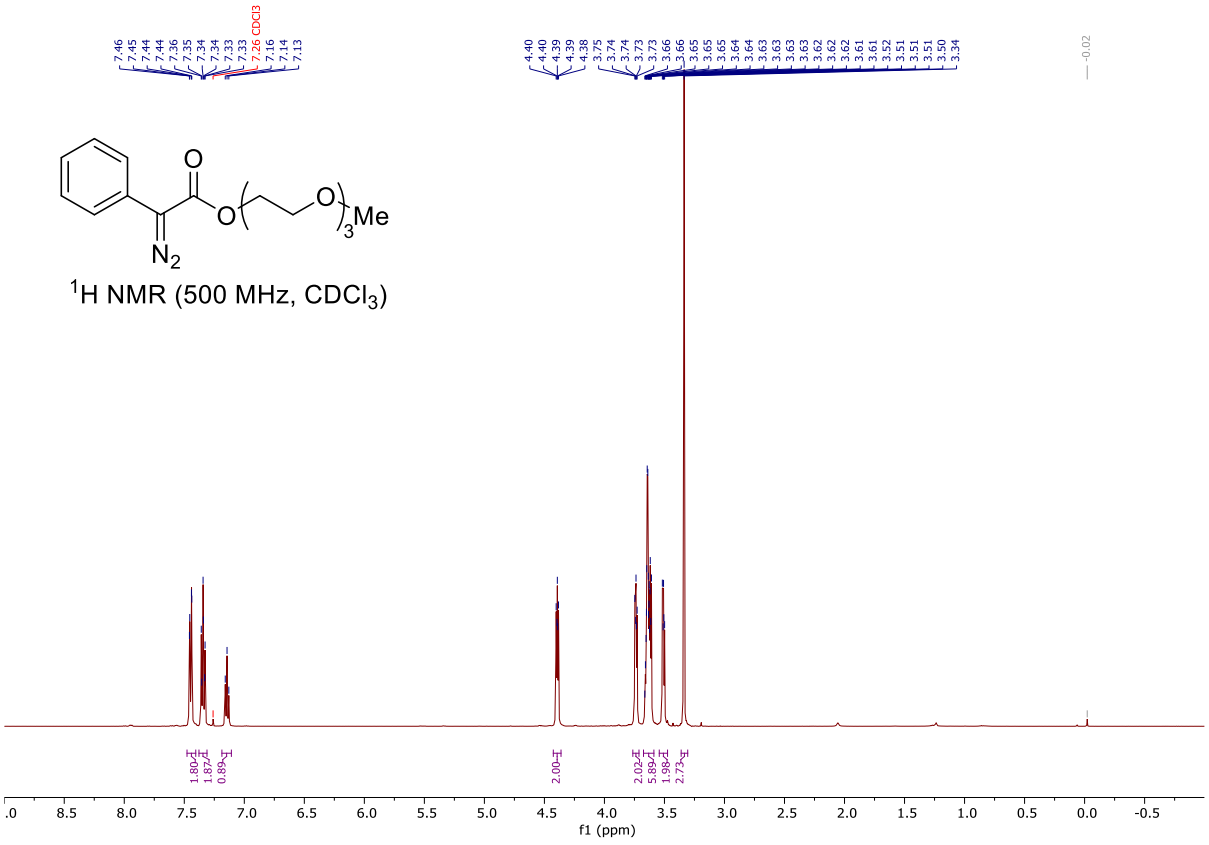


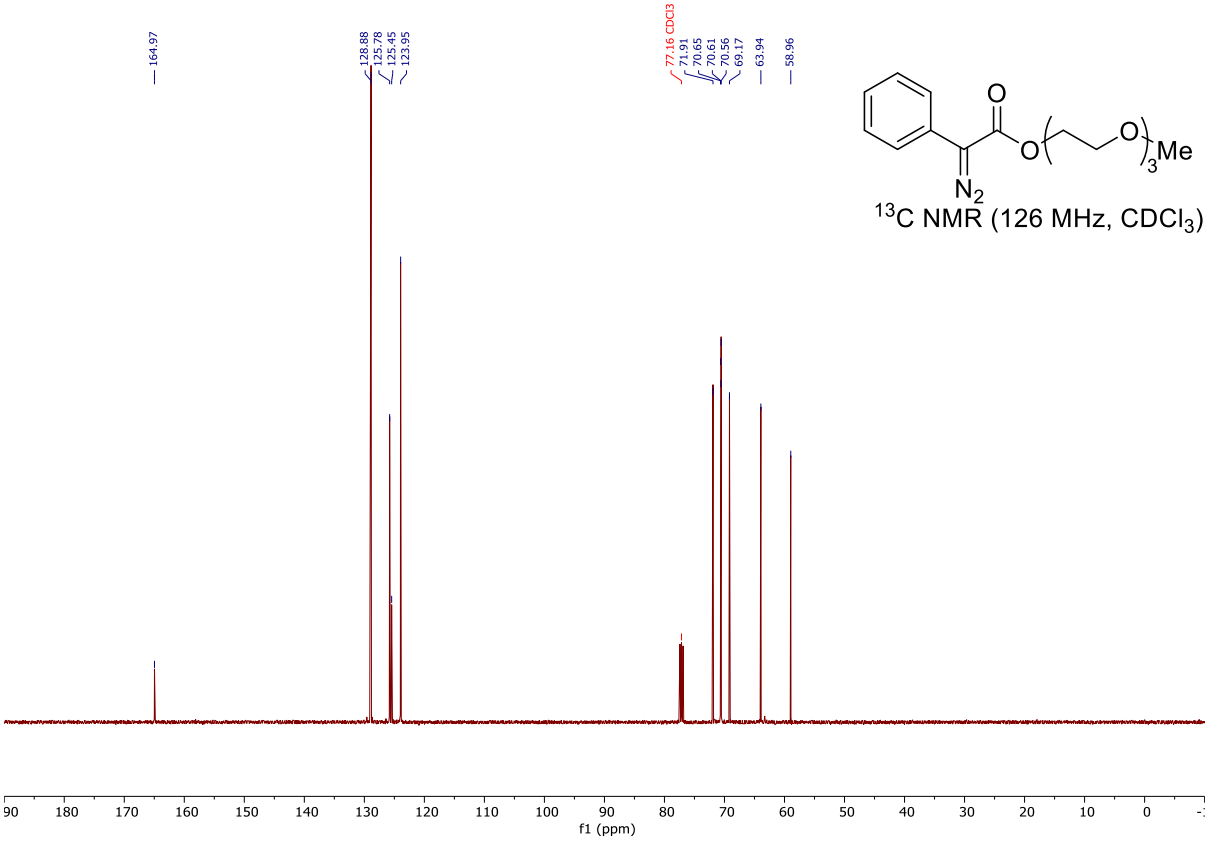
^{1}H NMR (600 MHz, $CDCl_3$)



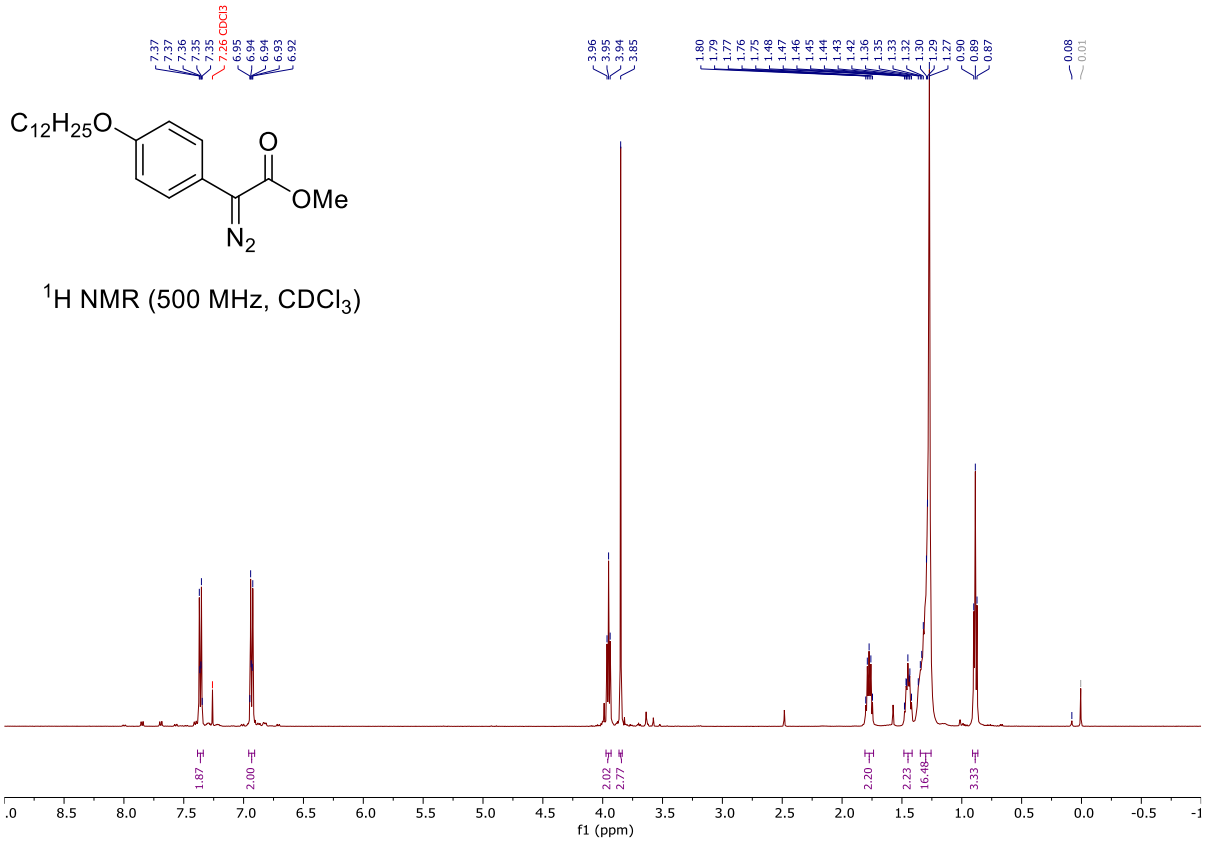
^{13}C NMR (151 MHz, $CDCl_3$)

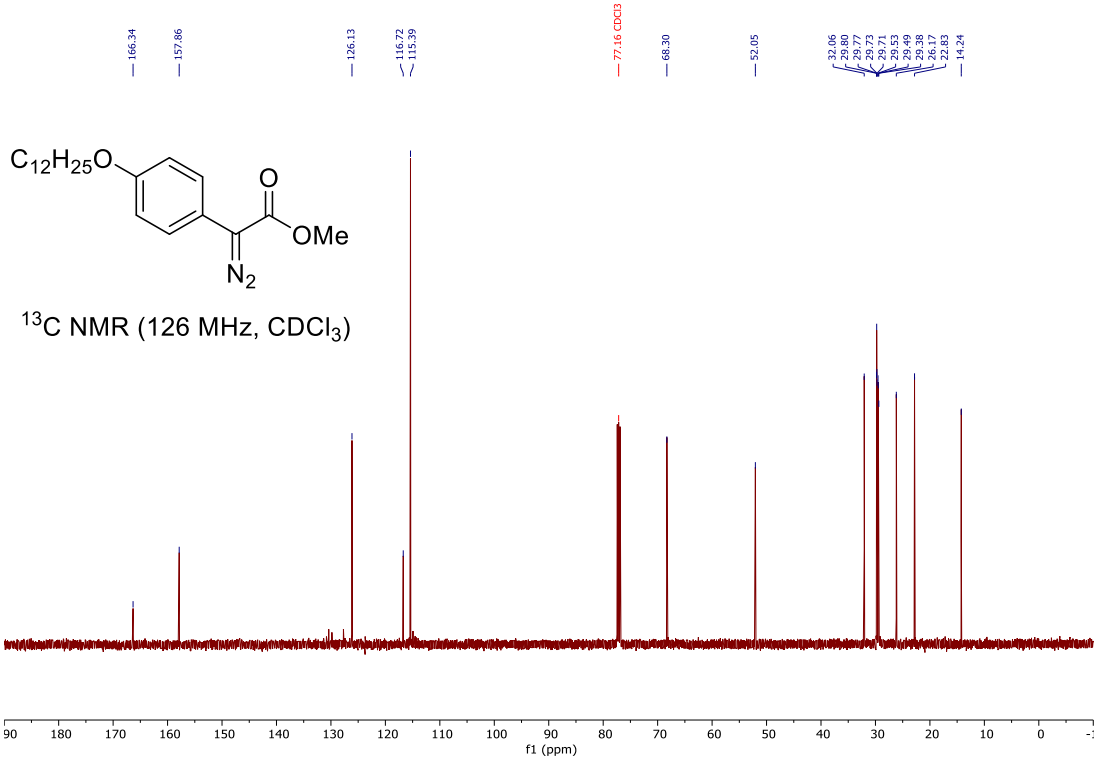
2-(2-(2-methoxyethoxy)ethoxy)ethyl 2-diazo-2-phenylacetate (**1g**)



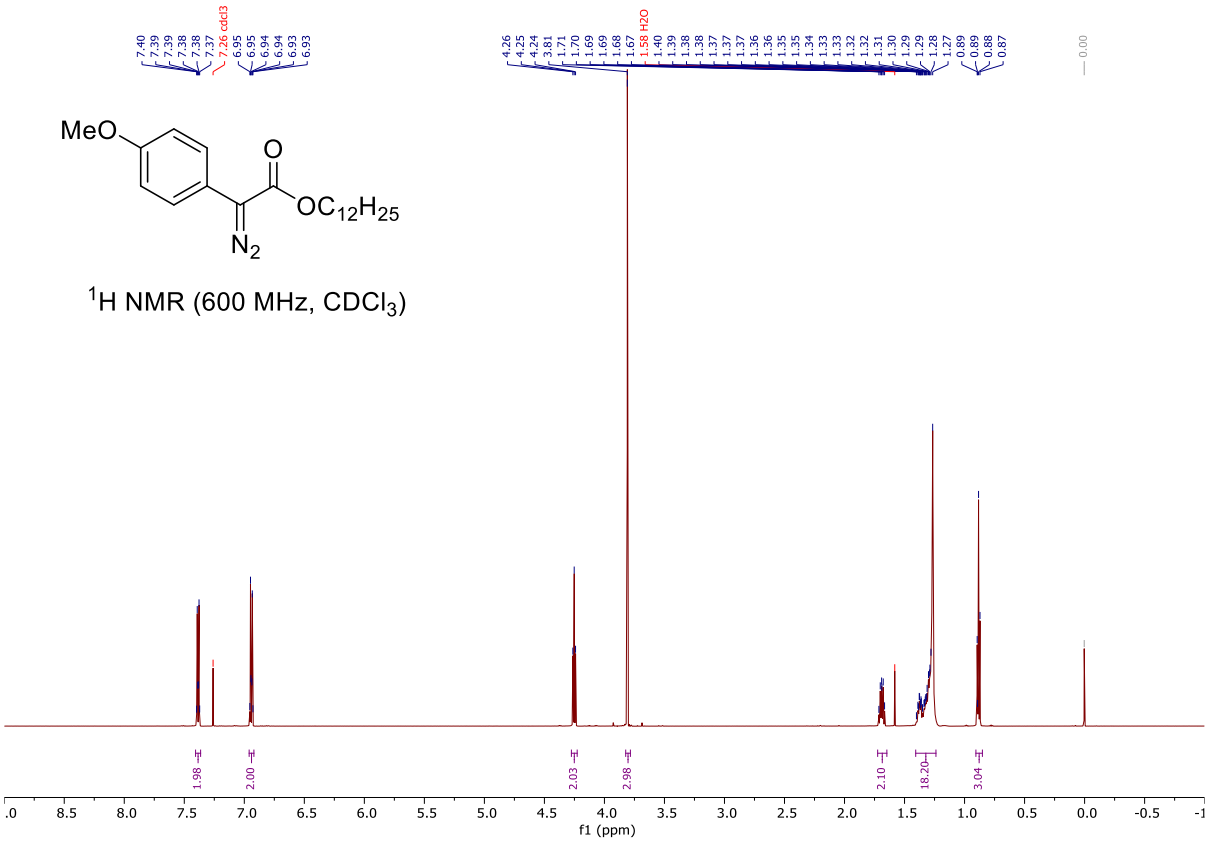


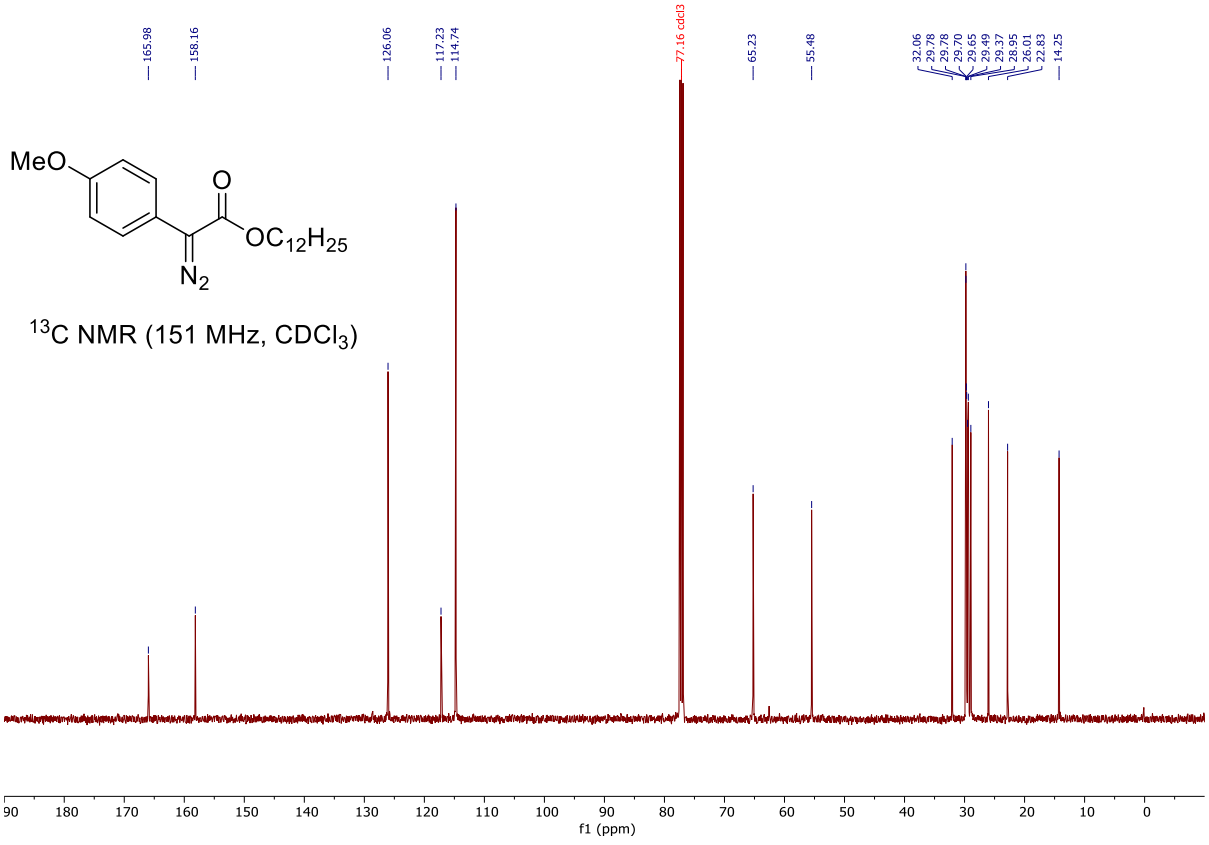
methyl 2-diazo-2-(4-(dodecyloxy)phenyl)acetate (**1i**)



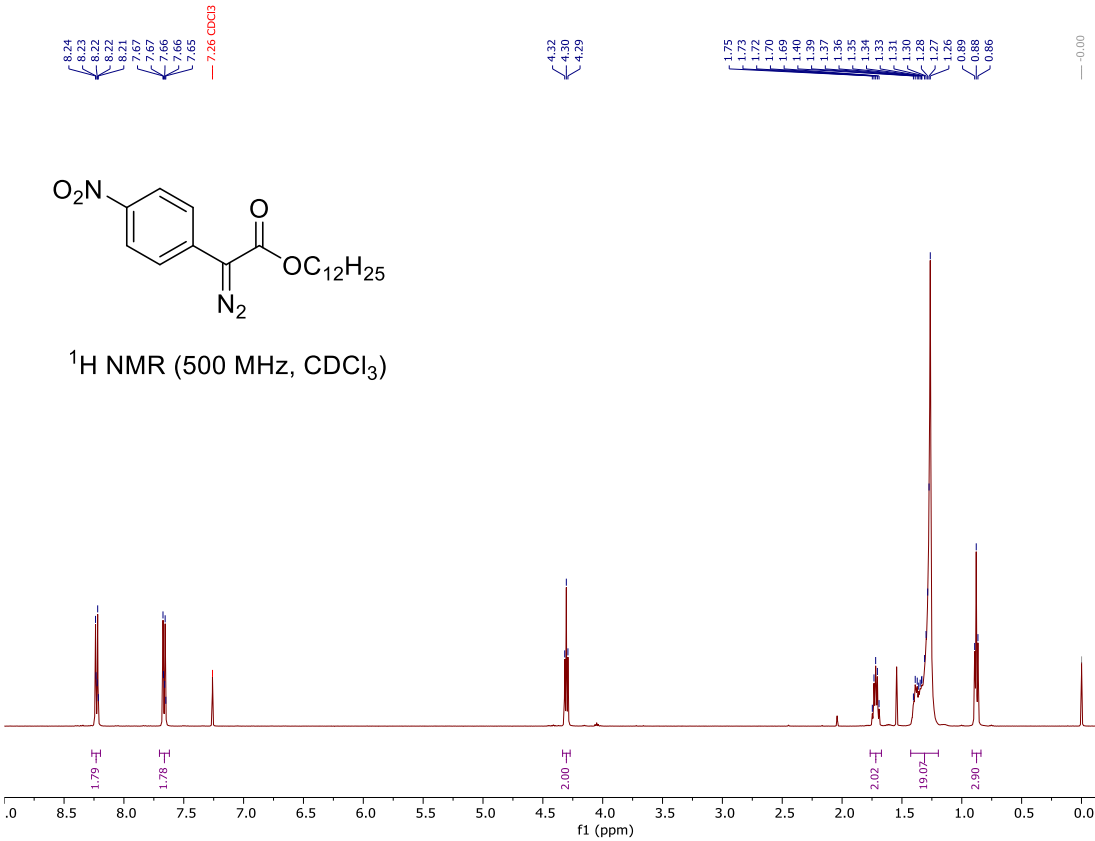


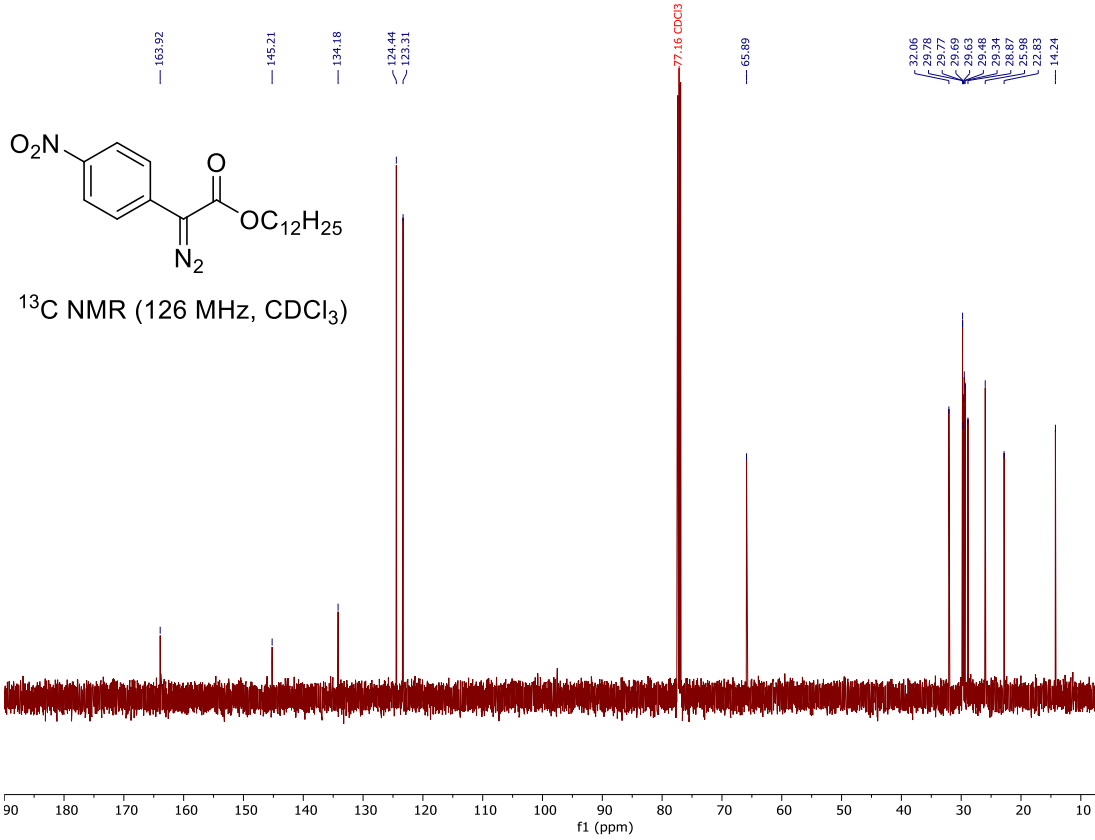
dodecyl 2-diazo-2-(4-methoxyphenyl)acetate (**1j**)



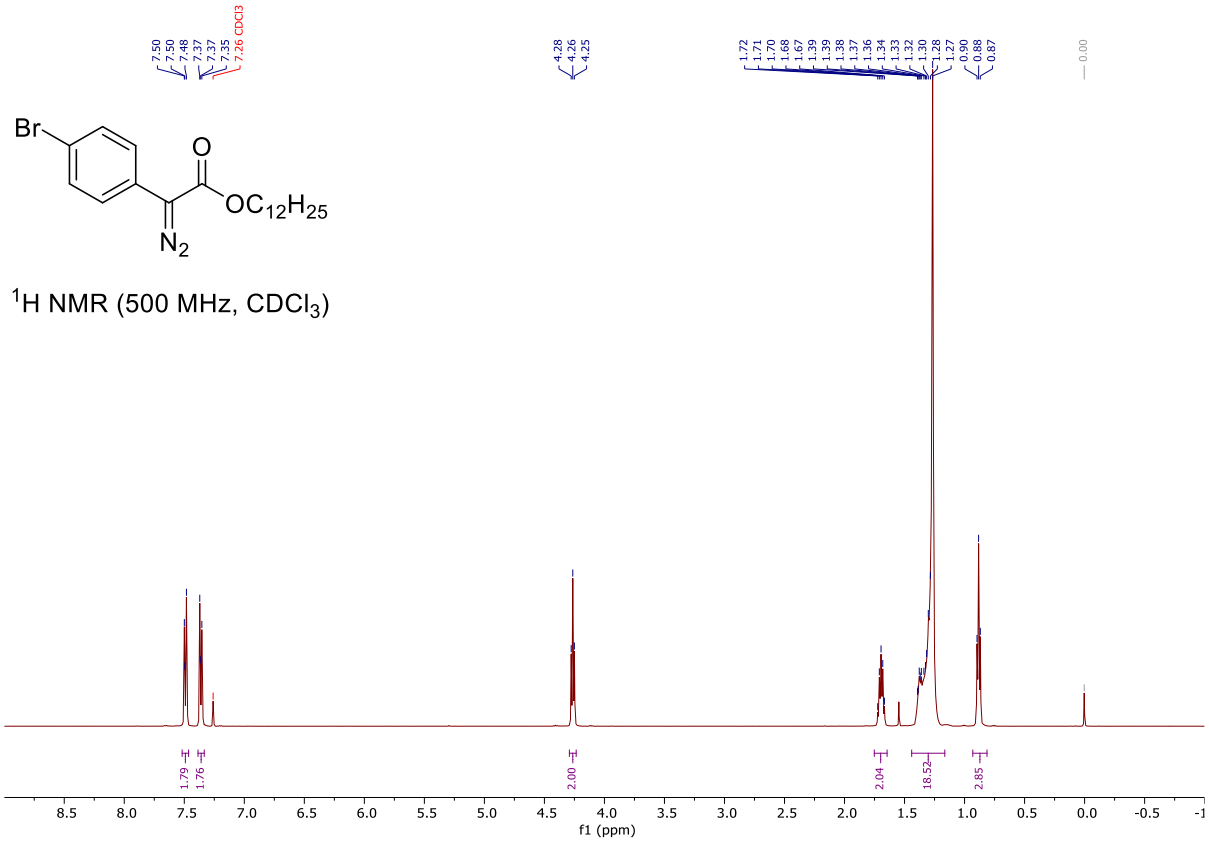


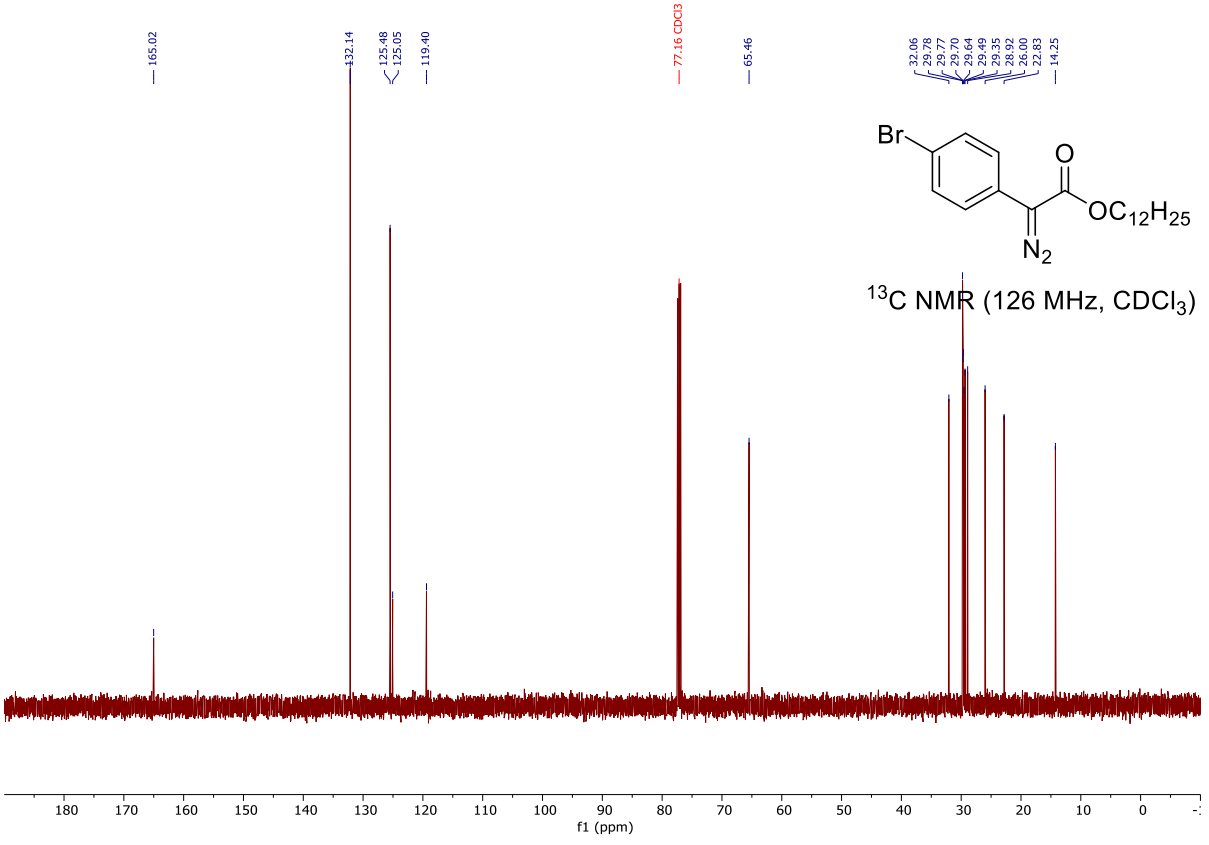
dodecyl 2-diazo-2-(4-nitrophenyl)acetate (**1k**)



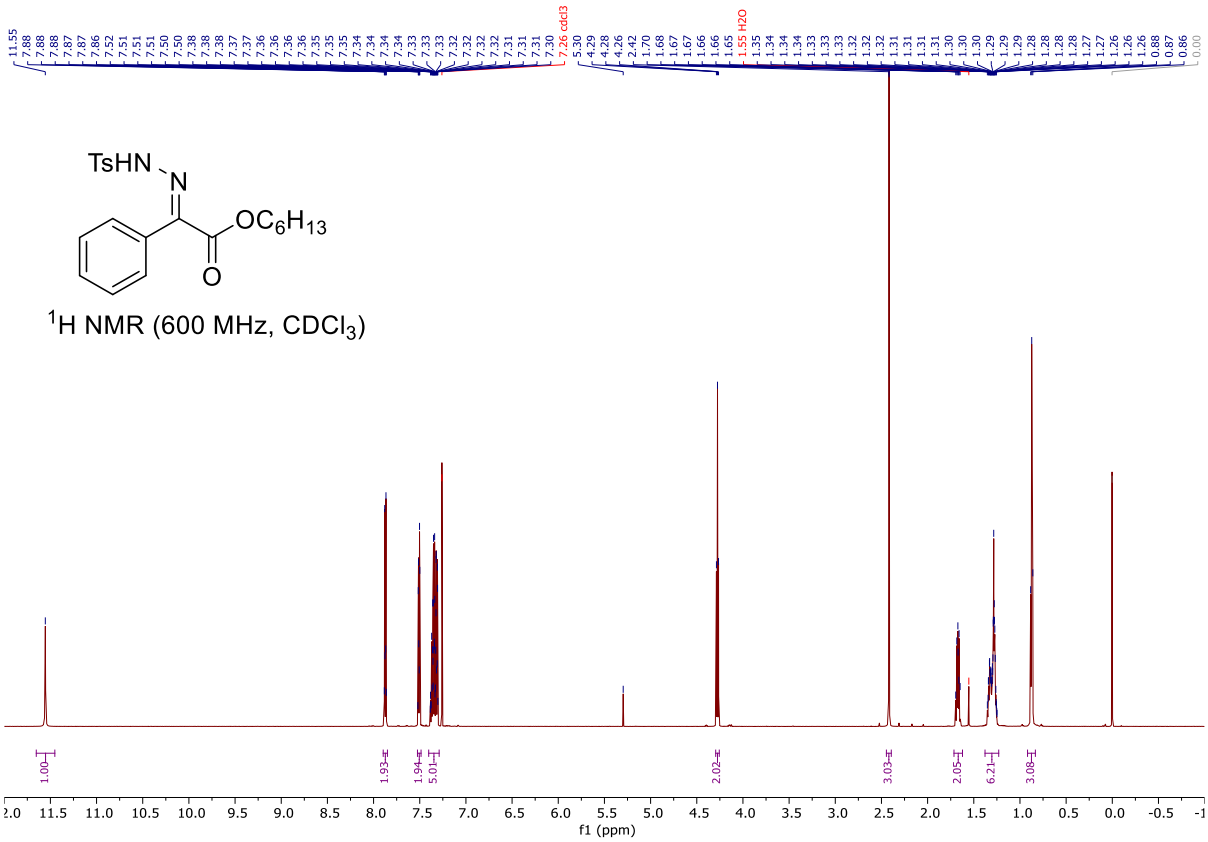


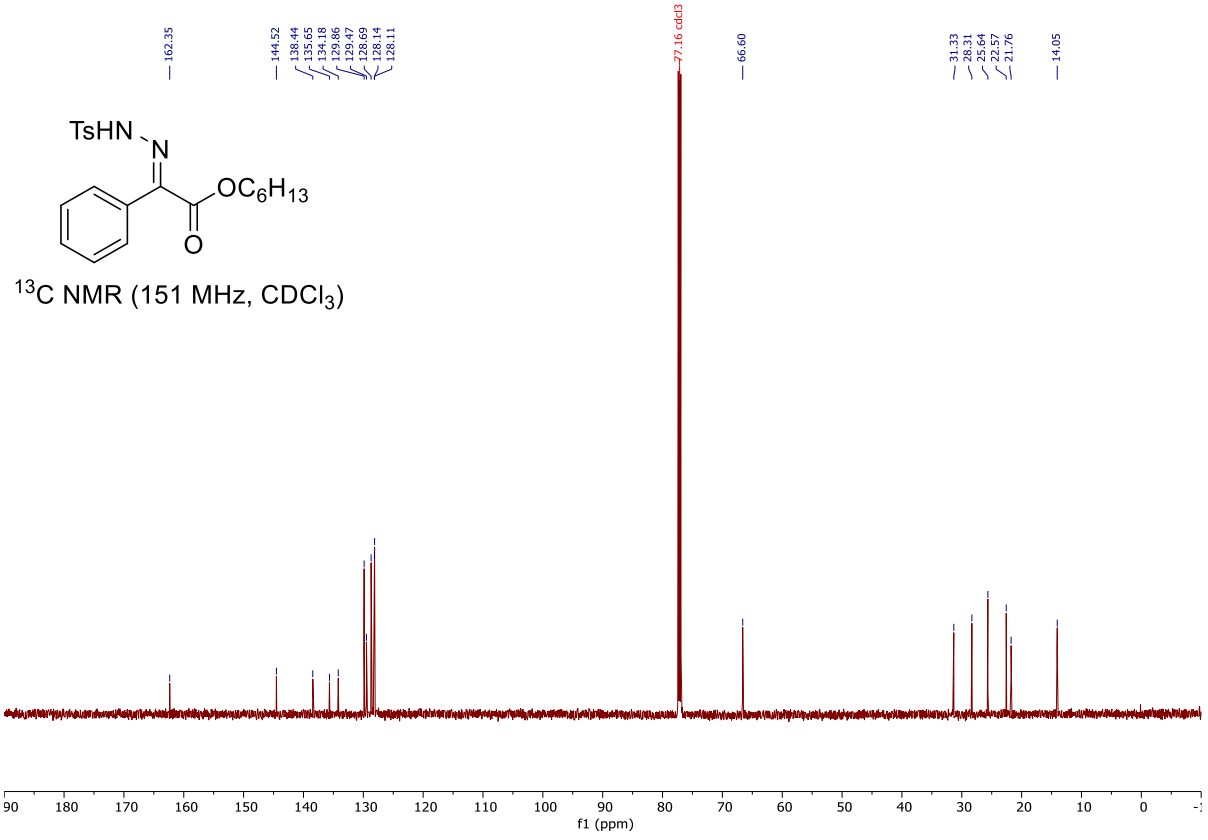
dodecyl 2-(4-bromophenyl)-2-diazoacetate (**1l**)



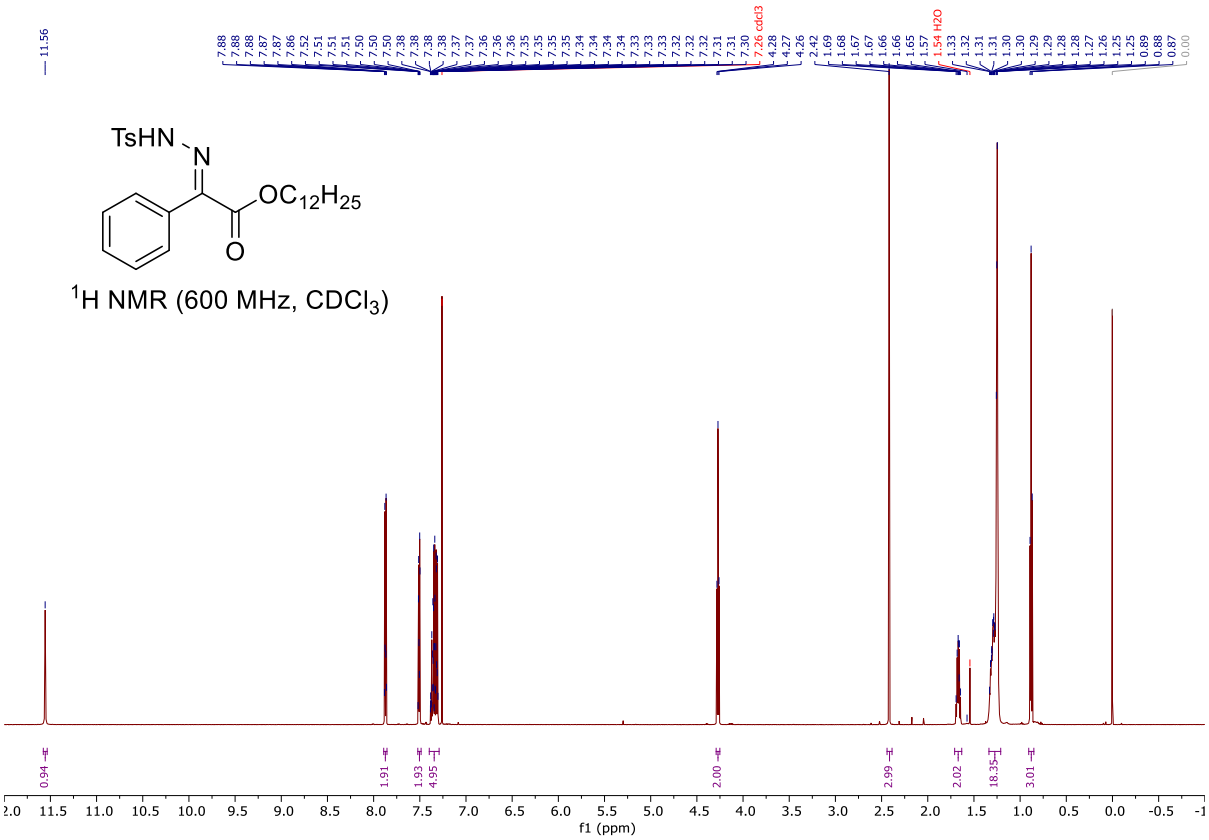


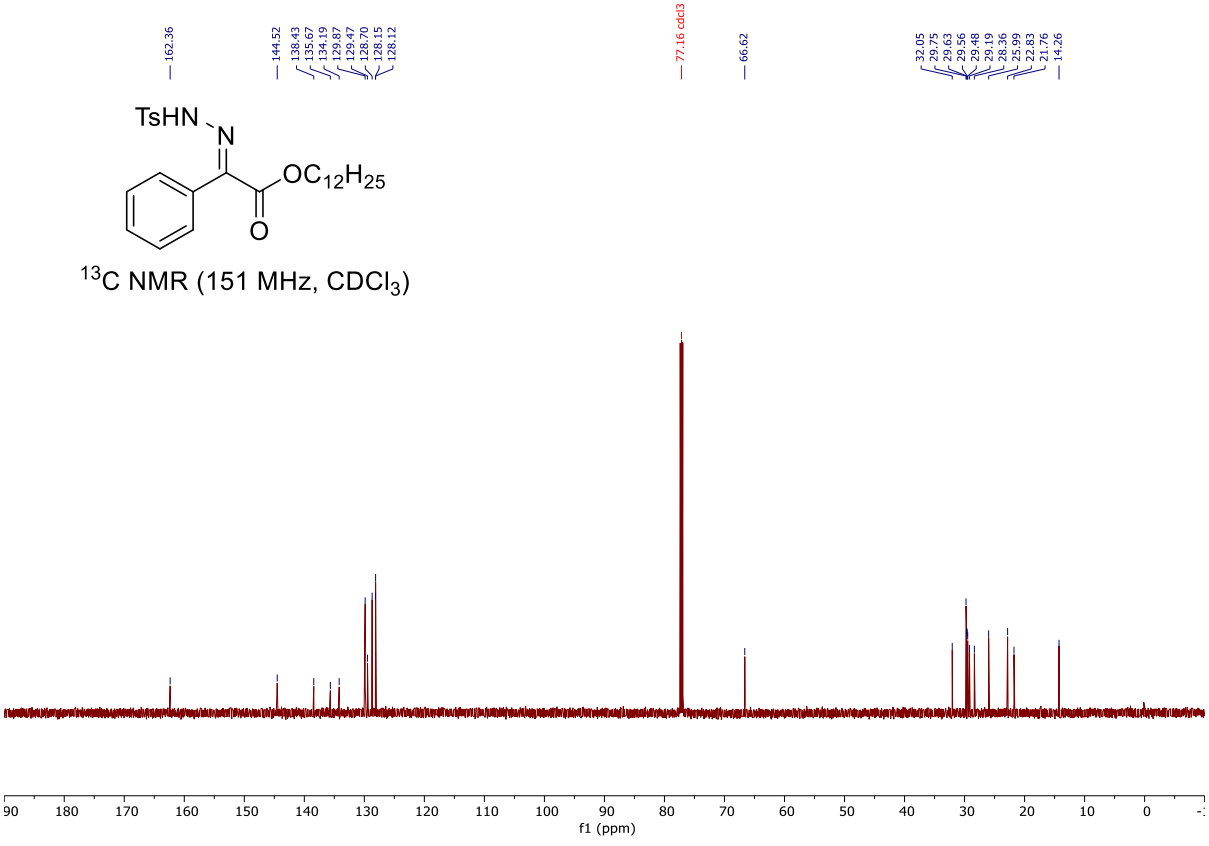
hexyl (E)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (*E*-**4c**)



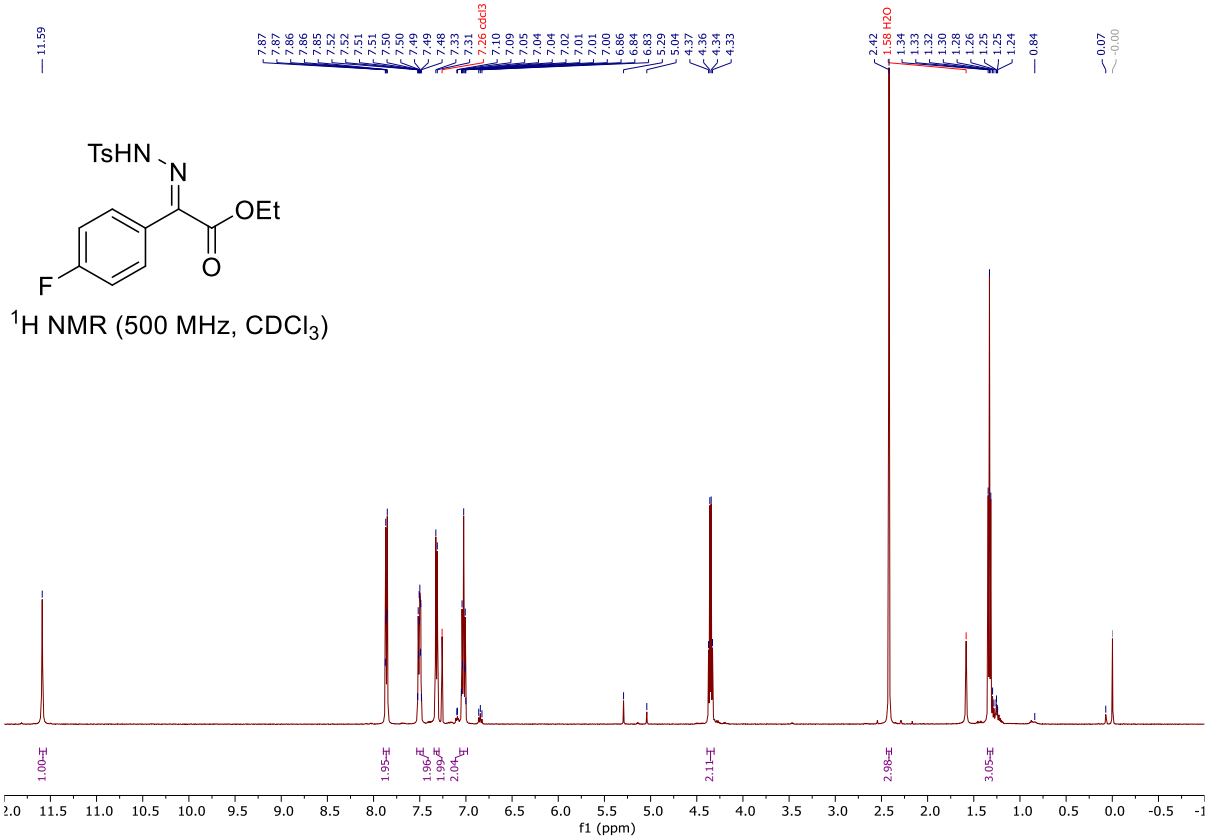


dodecyl (E)-2-phenyl-2-(2-tosylhydrazineylidene)acetate (*E*-**4d**)

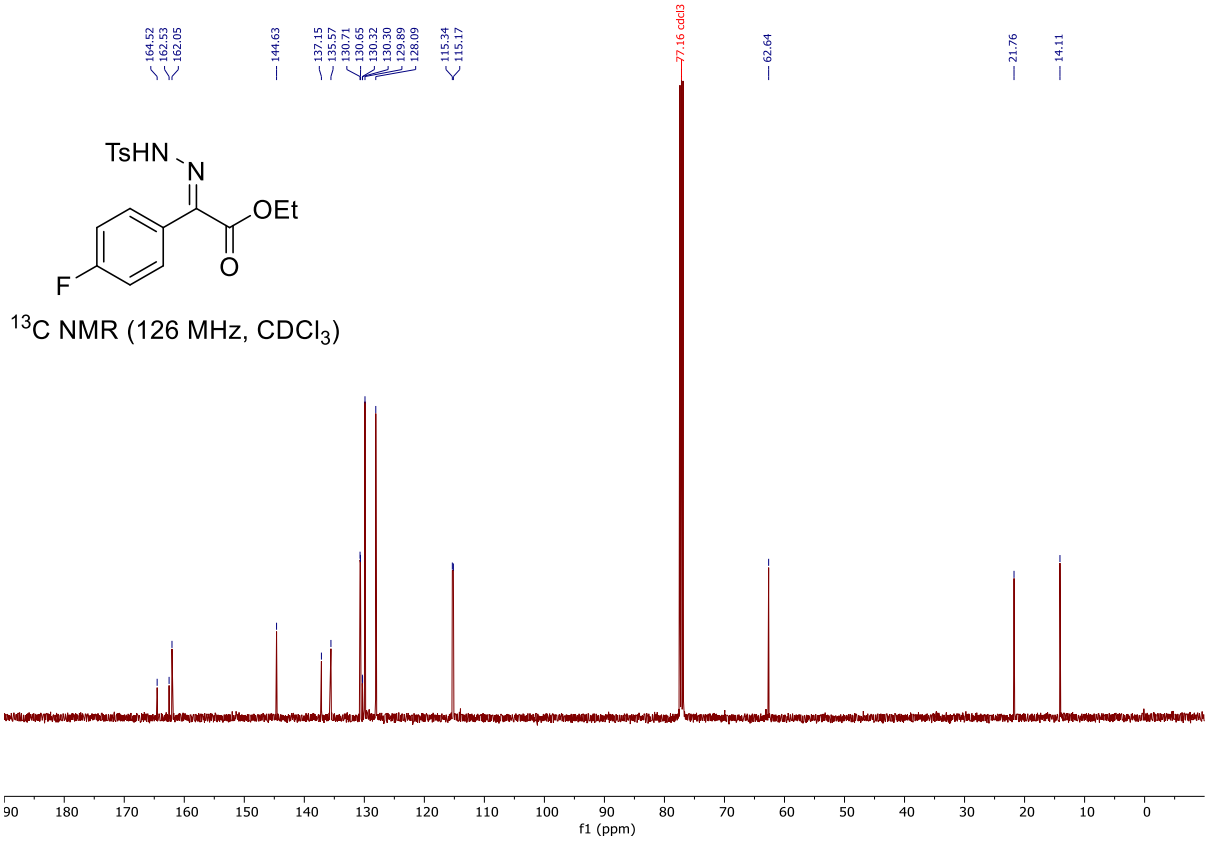




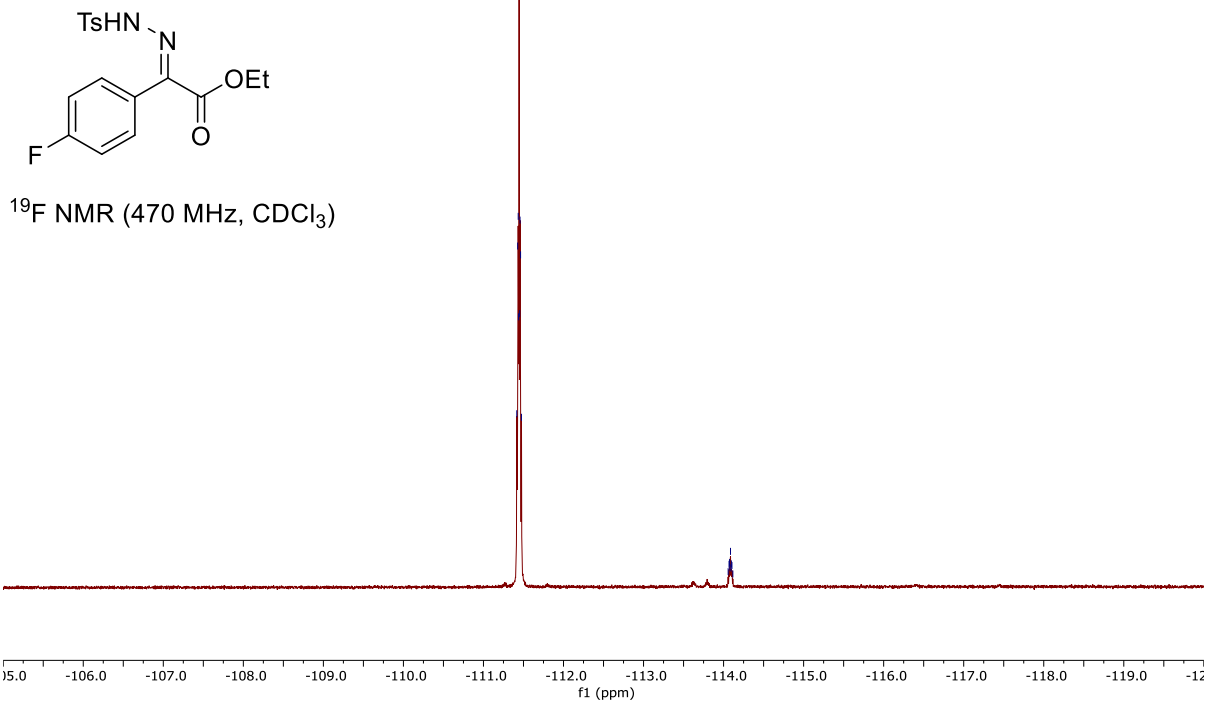
ethyl (E)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate (*E*-**4e**)



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

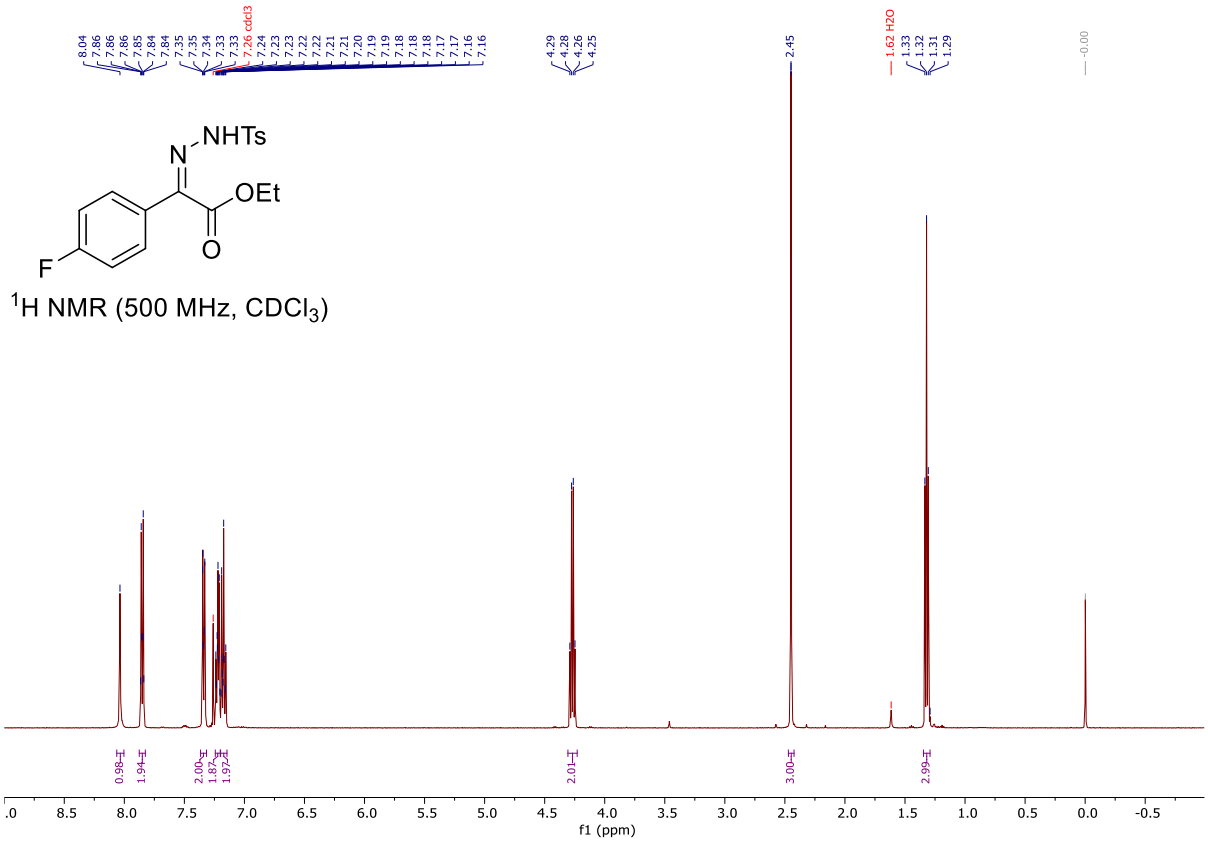


^{13}C NMR (126 MHz, $CDCl_3$)

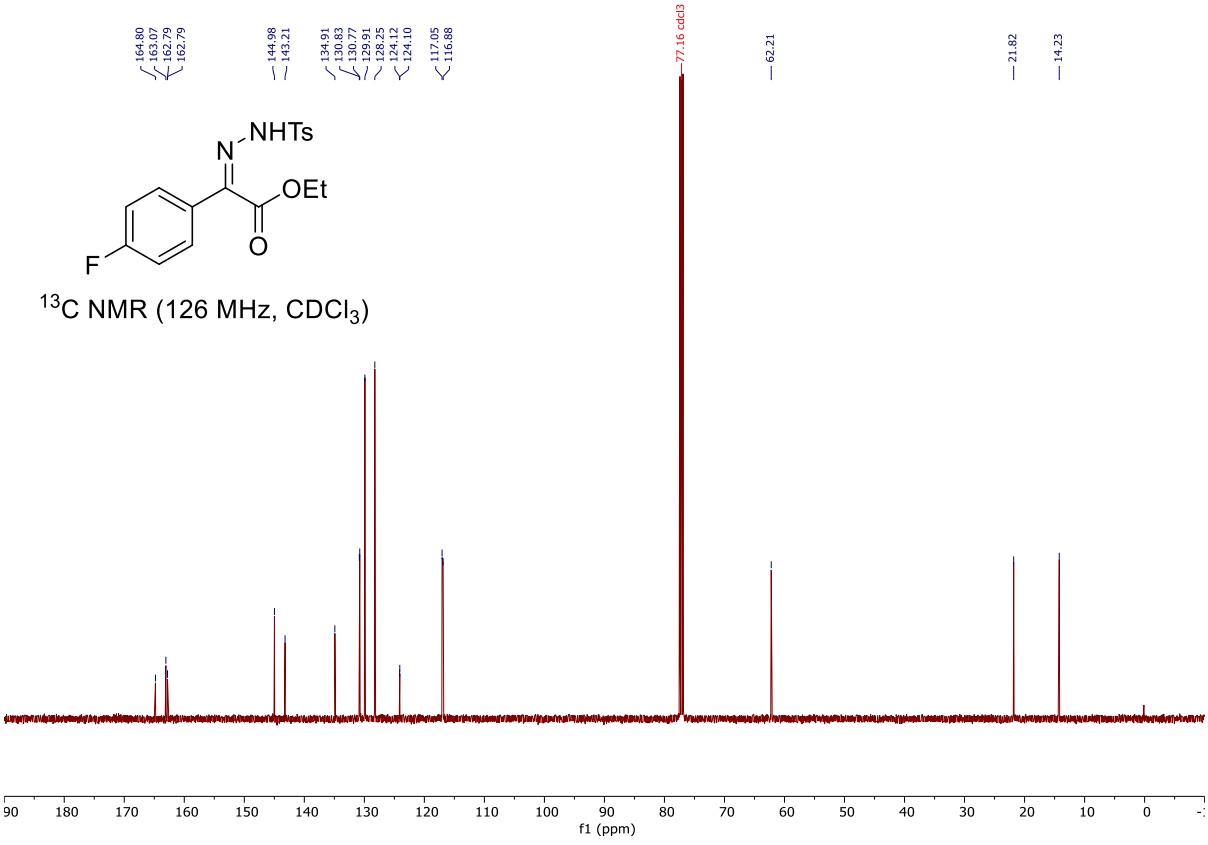


^{19}F NMR (470 MHz, $CDCl_3$)

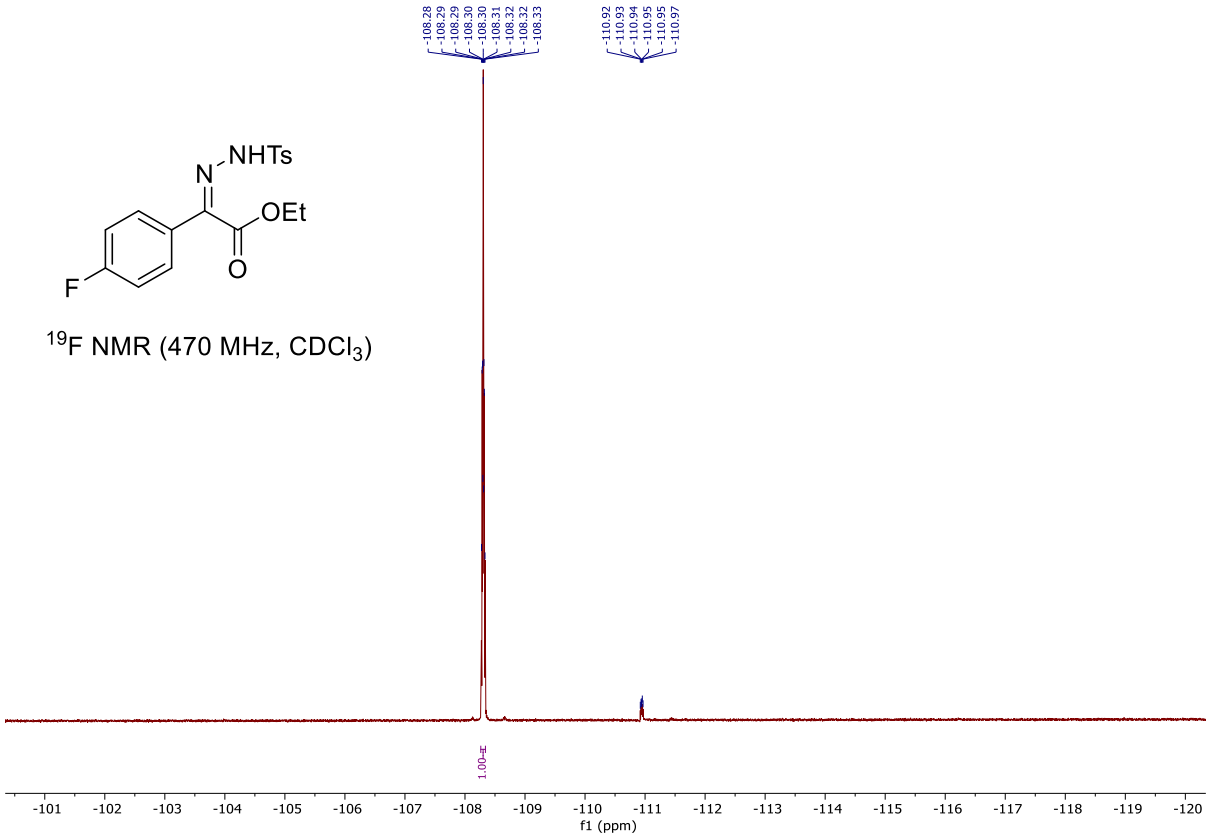
ethyl (Z)-2-(4-fluorophenyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4e**)



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

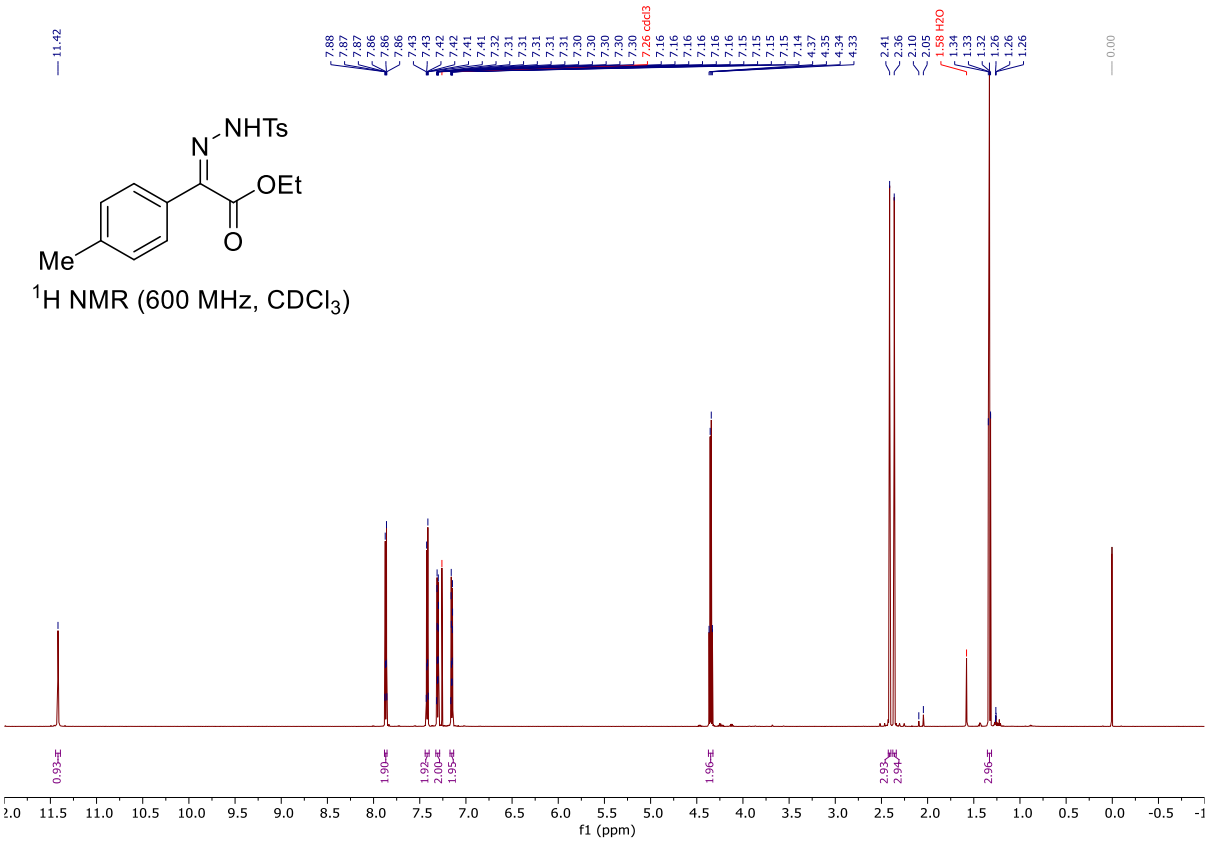


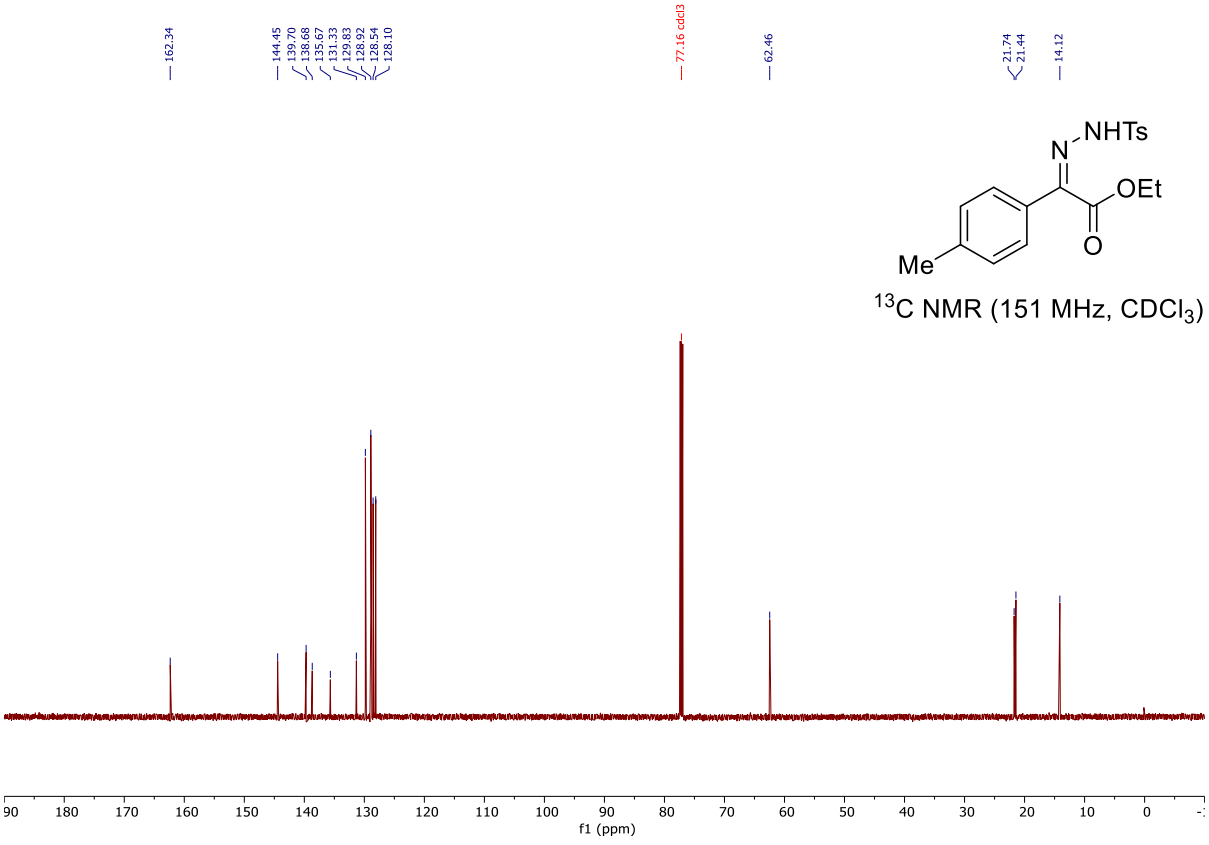
^{13}C NMR (126 MHz, $CDCl_3$)



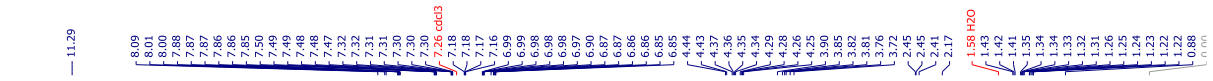
^{19}F NMR (470 MHz, $CDCl_3$)

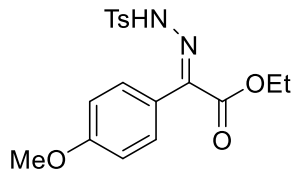
ethyl-(Z)-2-(p-tolyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4f**)



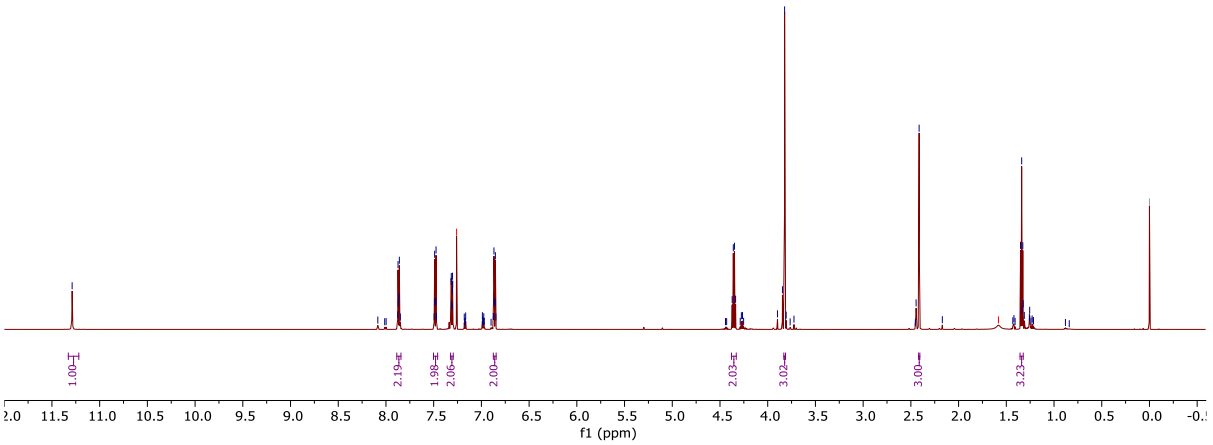


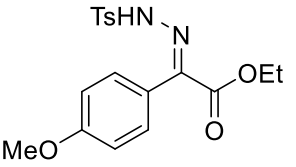
ethyl (E)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate (*E*-**4g**)





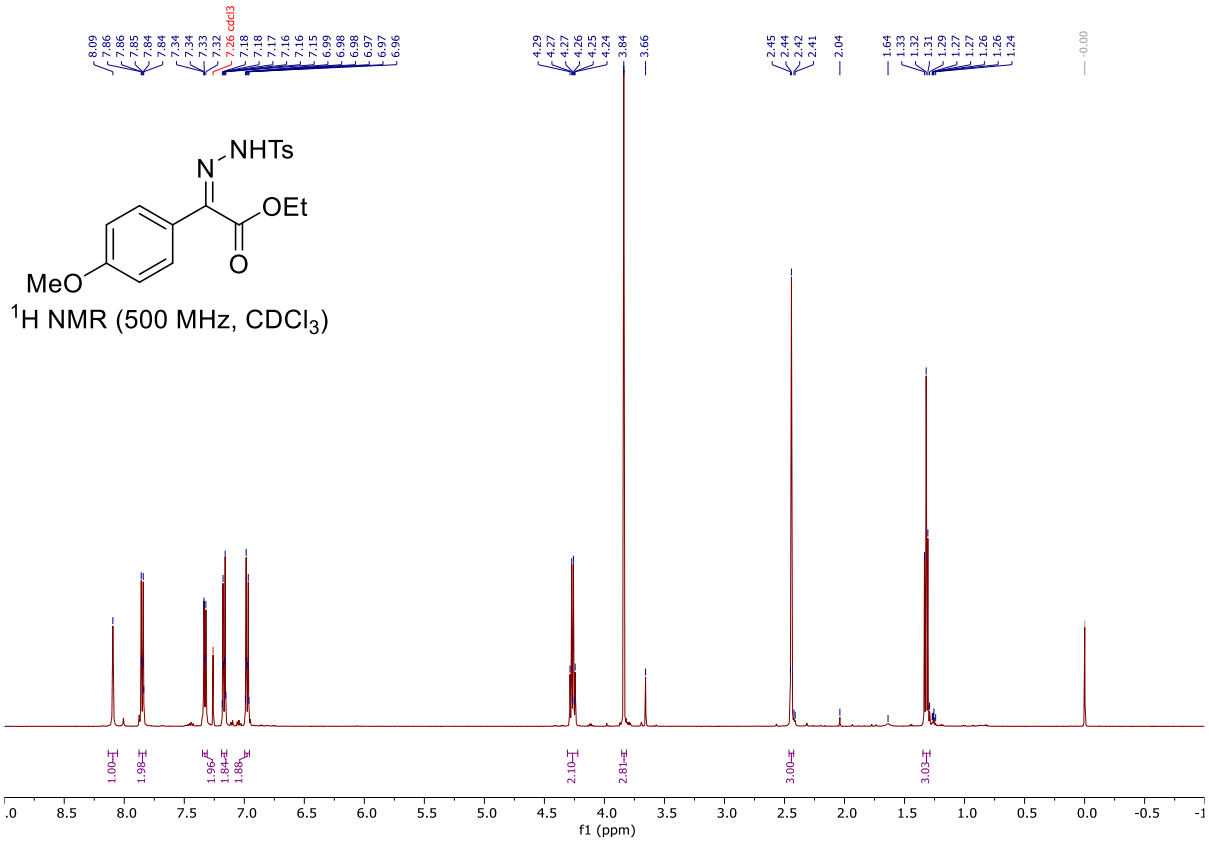
^{1}H NMR (600 MHz, $CDCl_3$)

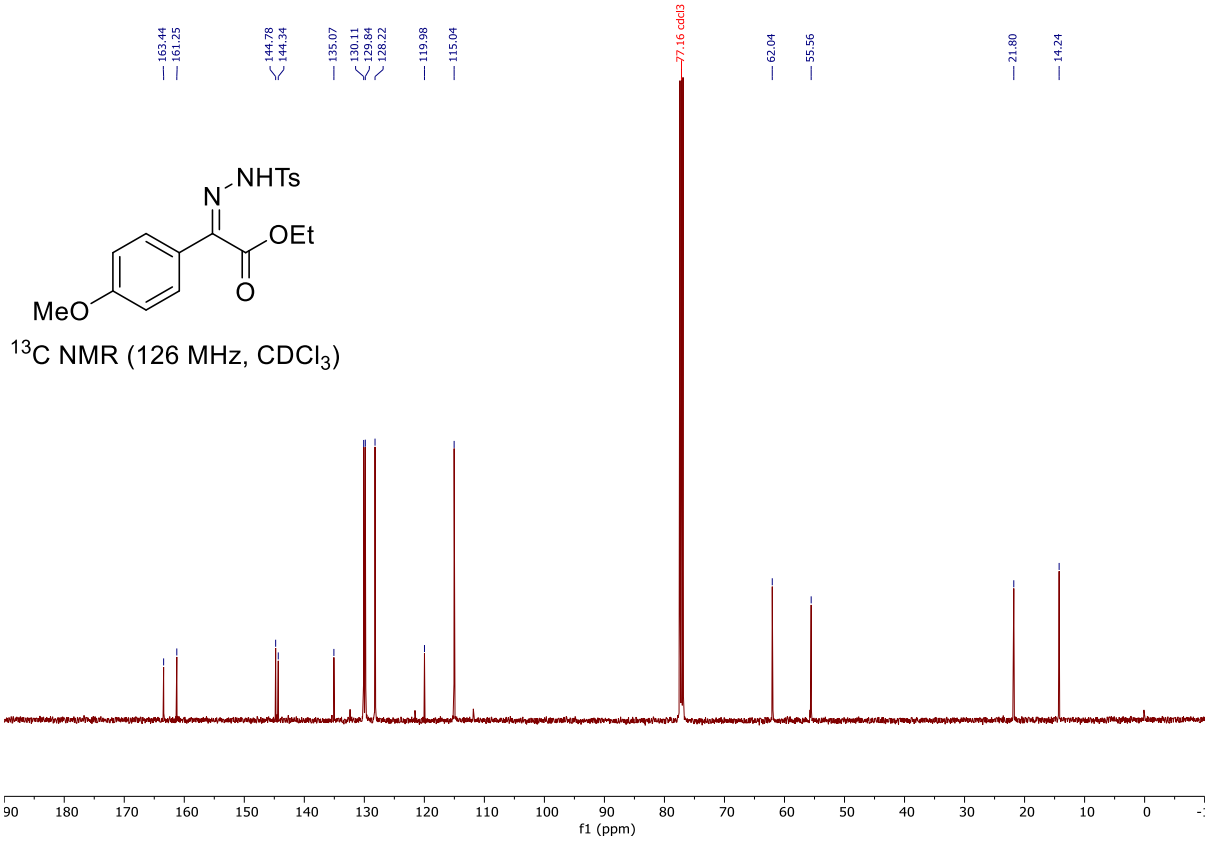




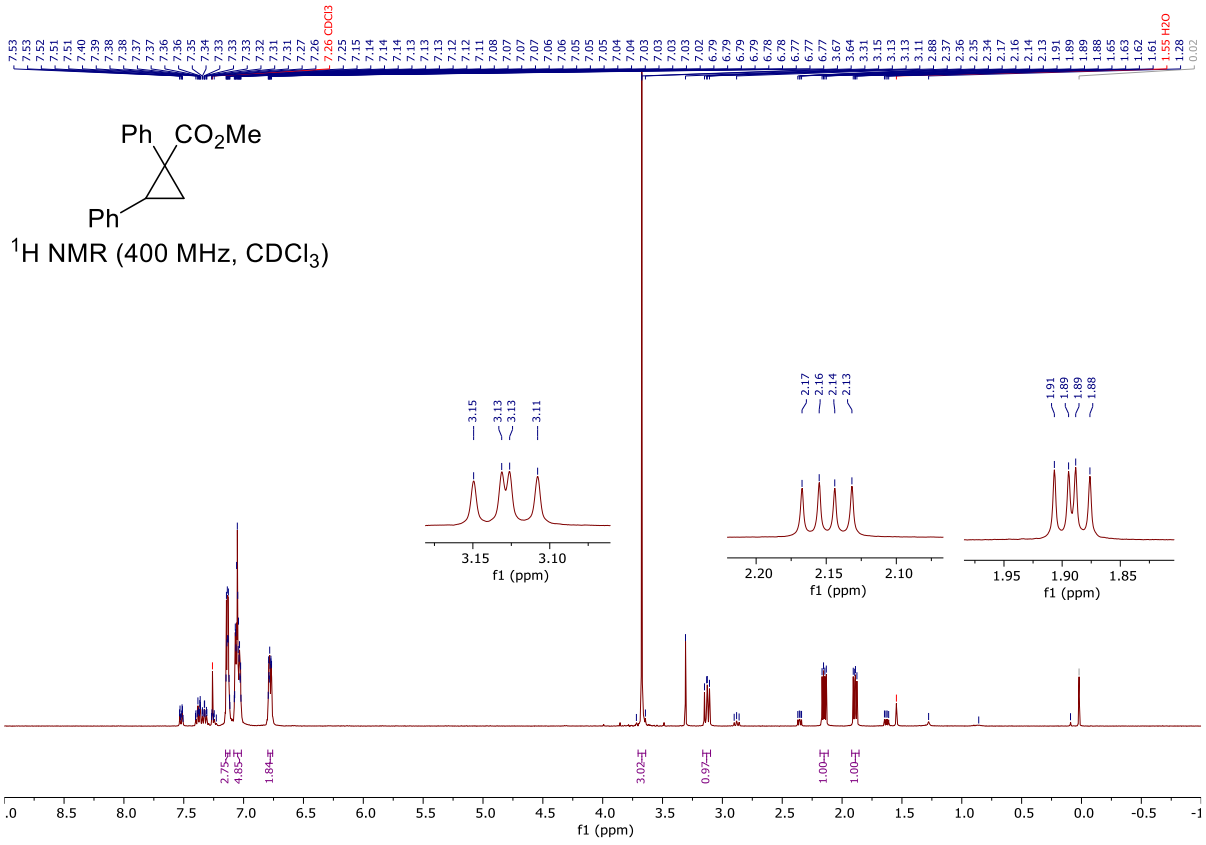
^{13}C NMR (151 MHz, $CDCl_3$)

ethyl (Z)-2-(4-methoxyphenyl)-2-(2-tosylhydrazineylidene)acetate (*Z*-**4g**)

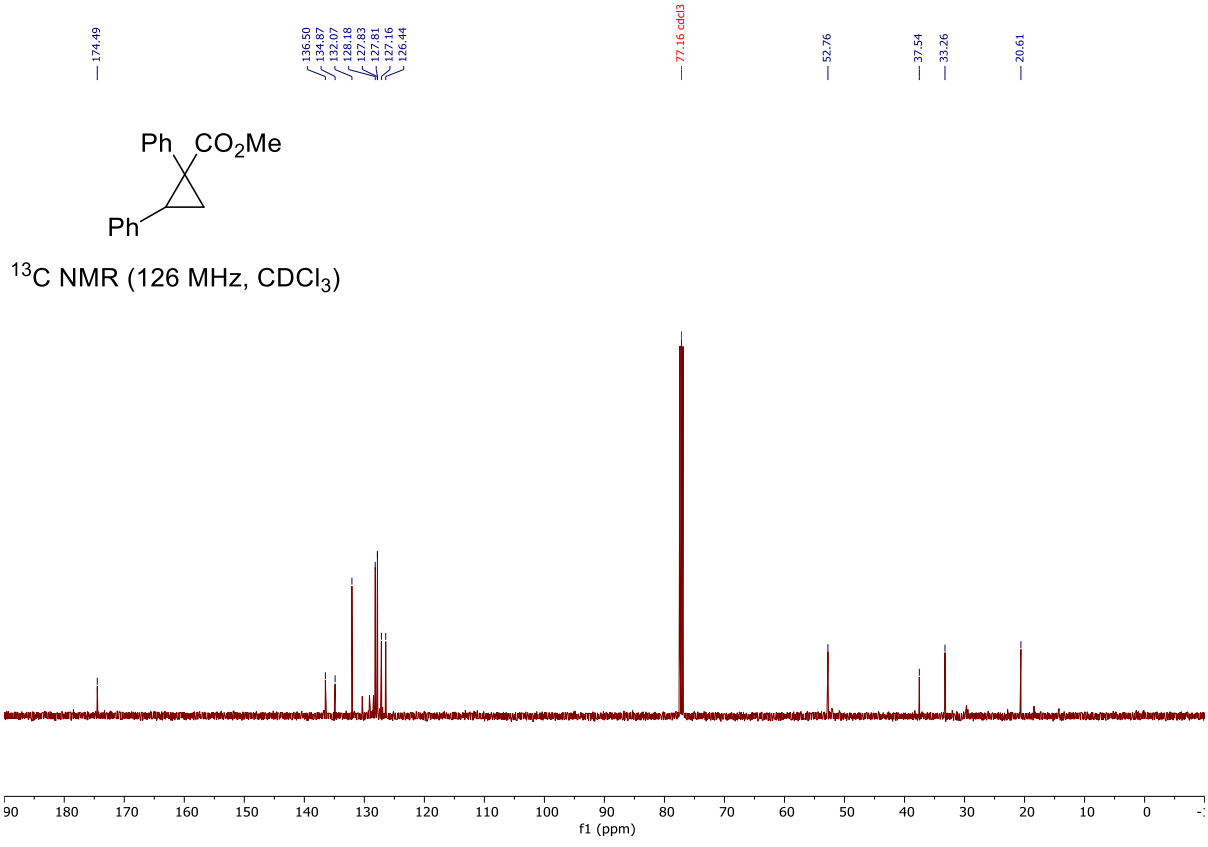




methyl-1,2-diphenylcyclopropane-1-carboxylate (**3a**) (dr 1:7)

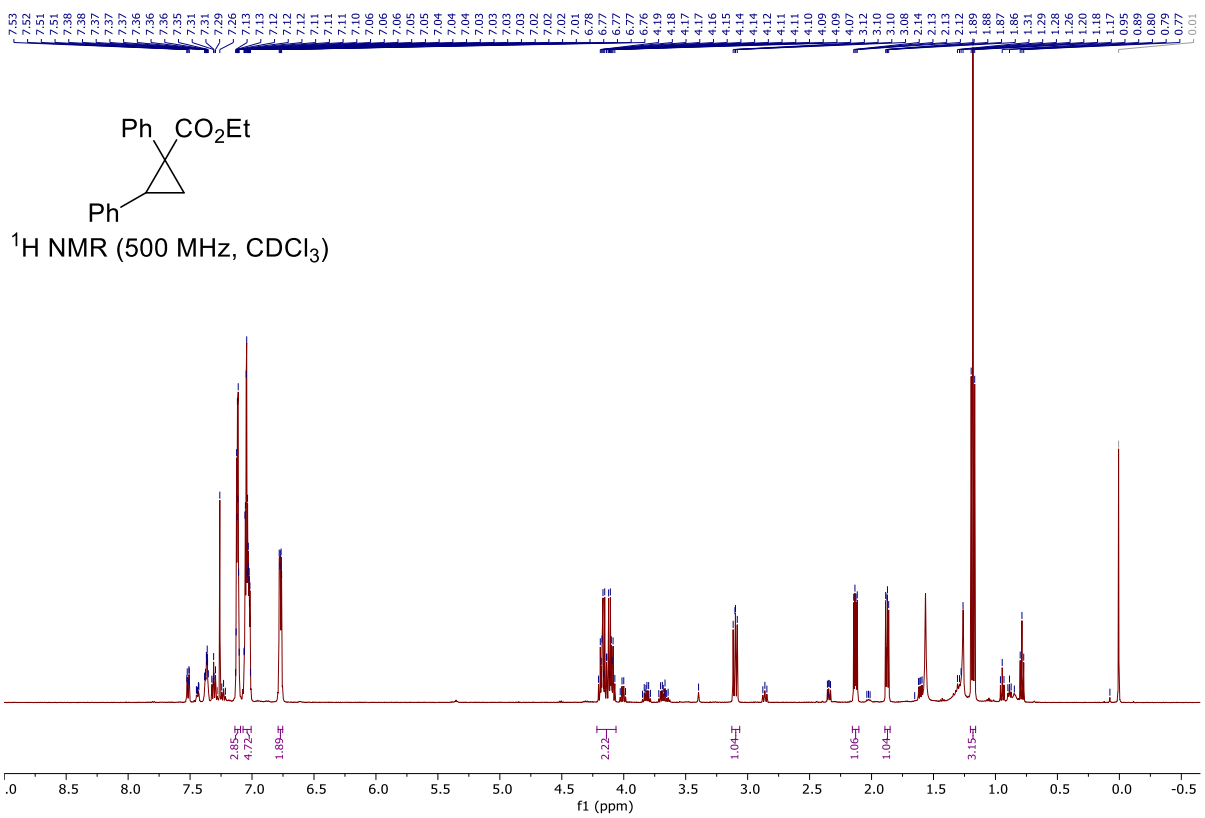


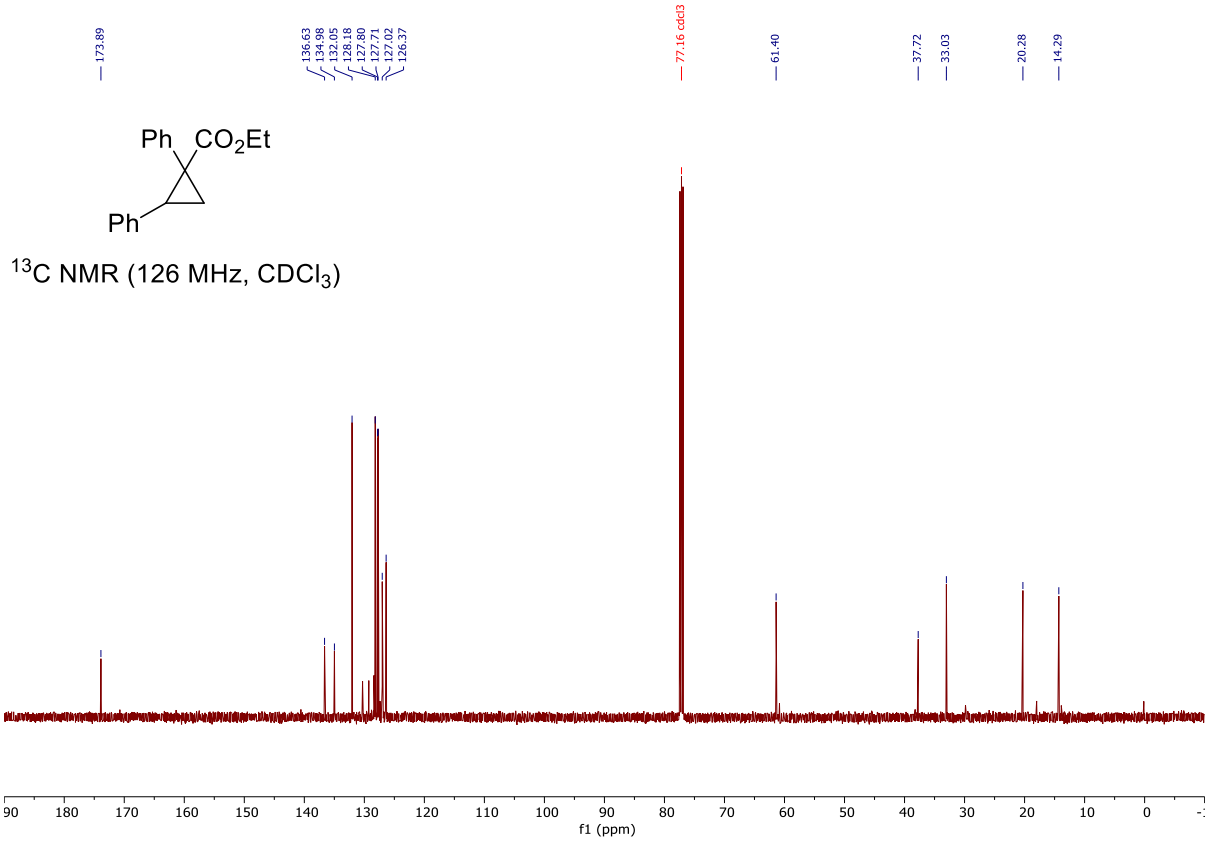
^{1}H NMR (400 MHz, $CDCl_3$)



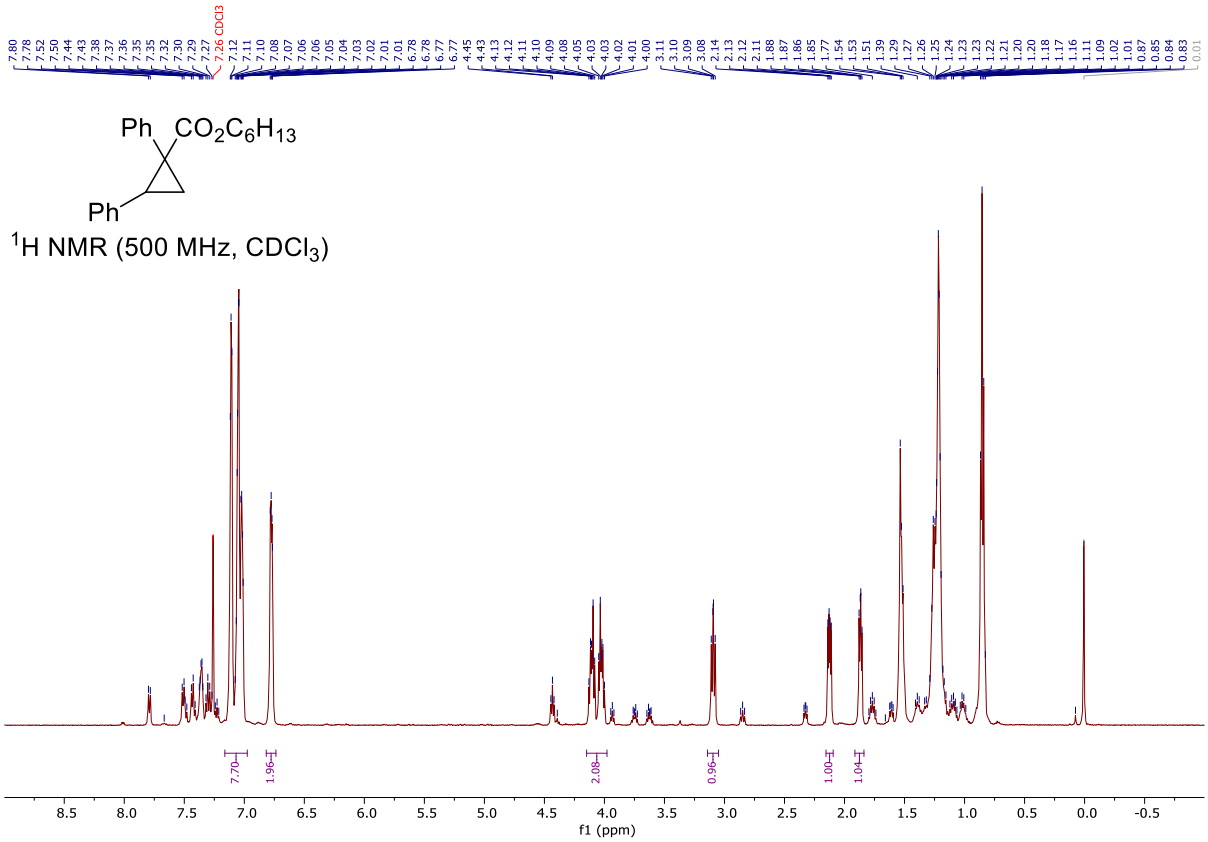
^{13}C NMR (126 MHz, $CDCl_3$)

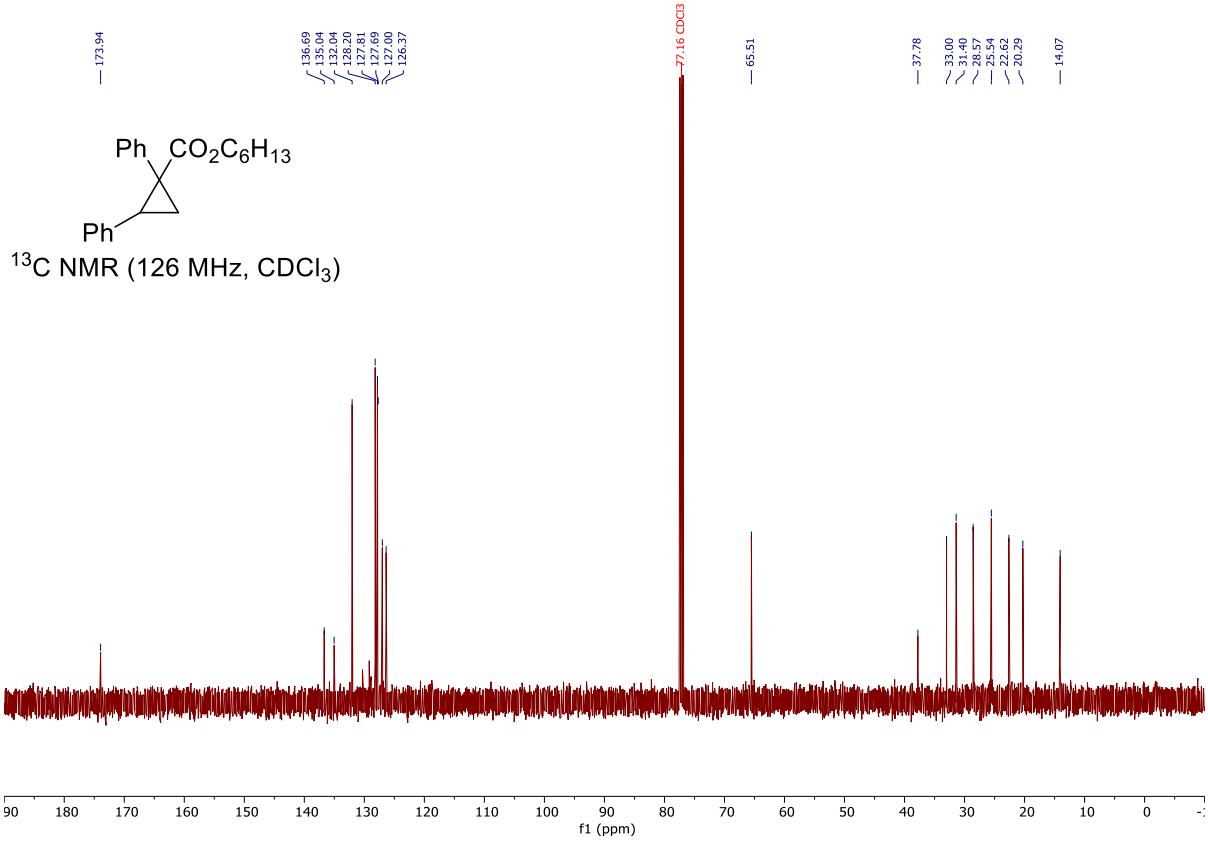
ethyl 1,2-diphenylcyclopropane-1-carboxylate (**3b**) (dr 1:7)



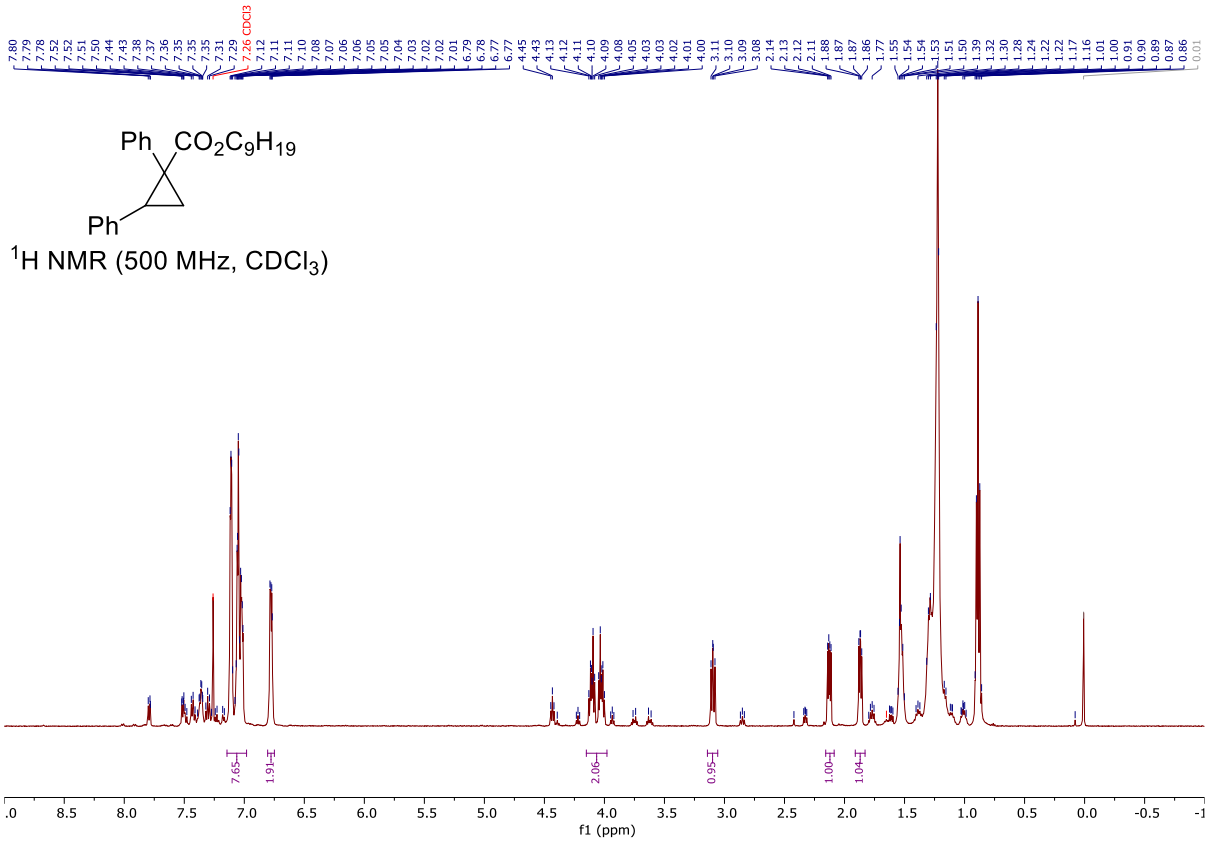


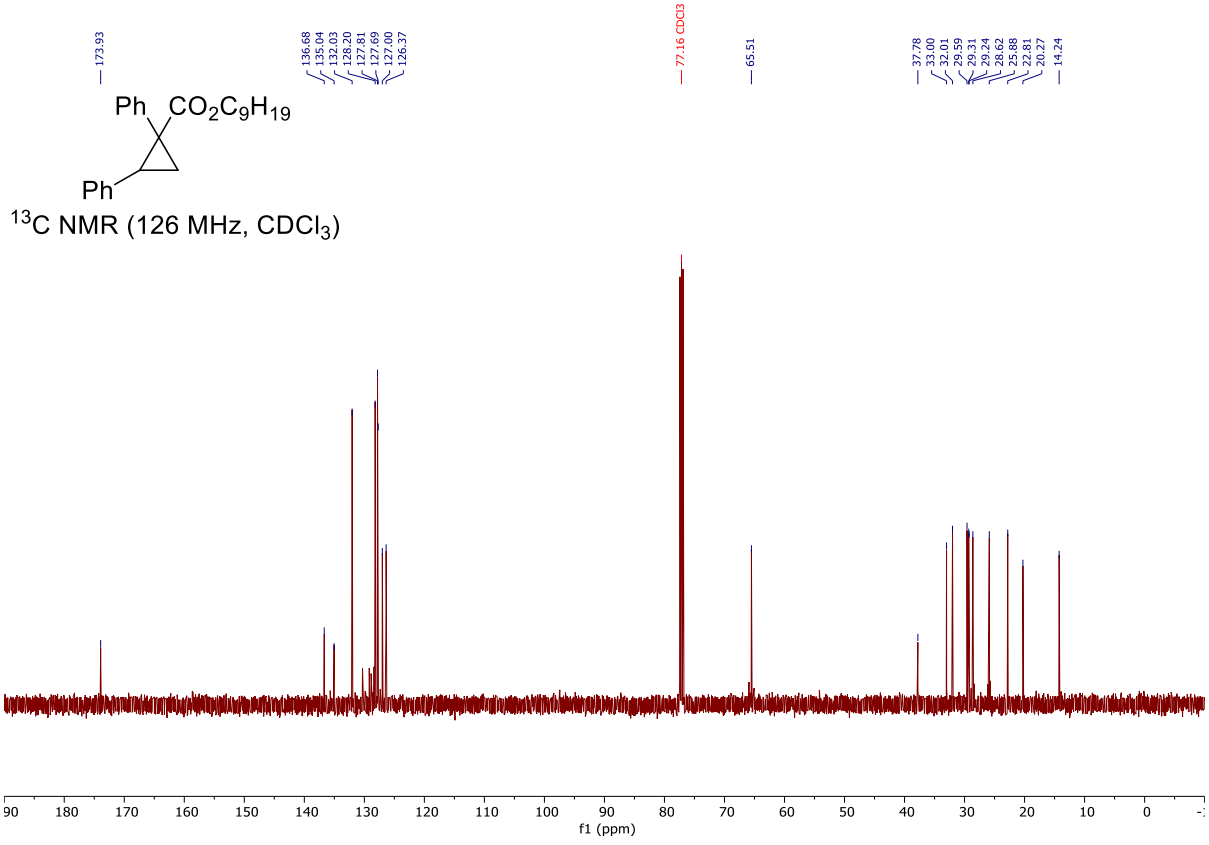
hexyl 1,2-diphenylcyclopropane-1-carboxylate (**3c**) (dr 1:11)



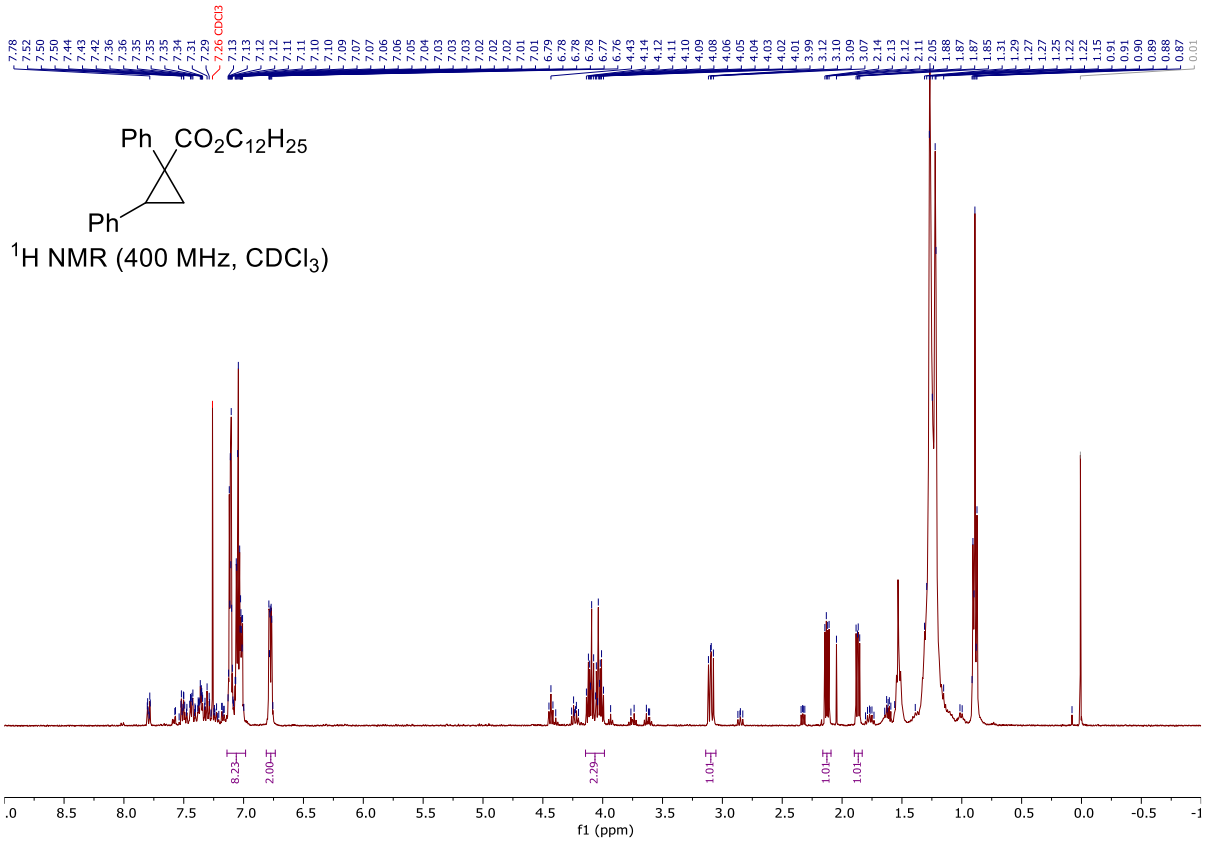


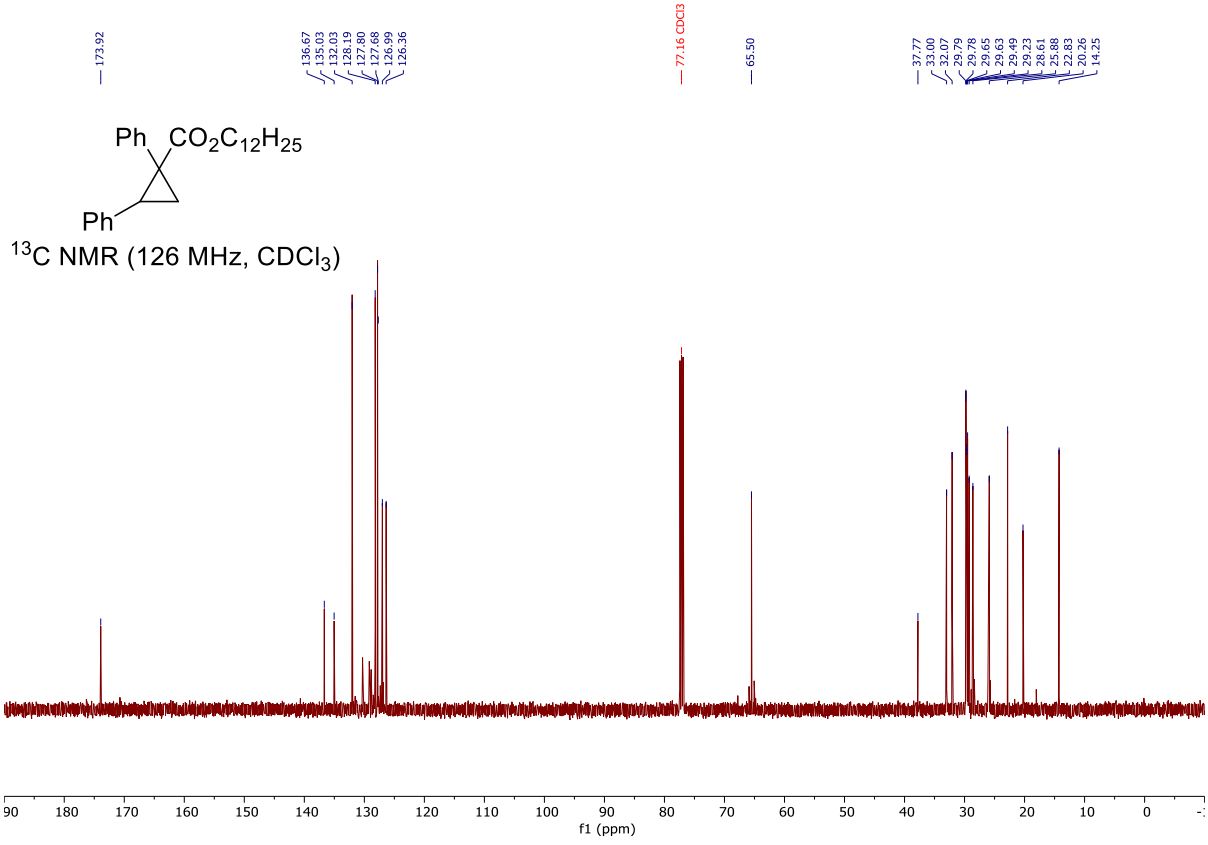
nonyl 1,2-diphenylcyclopropane-1-carboxylate (**3d**) (dr 1:10)



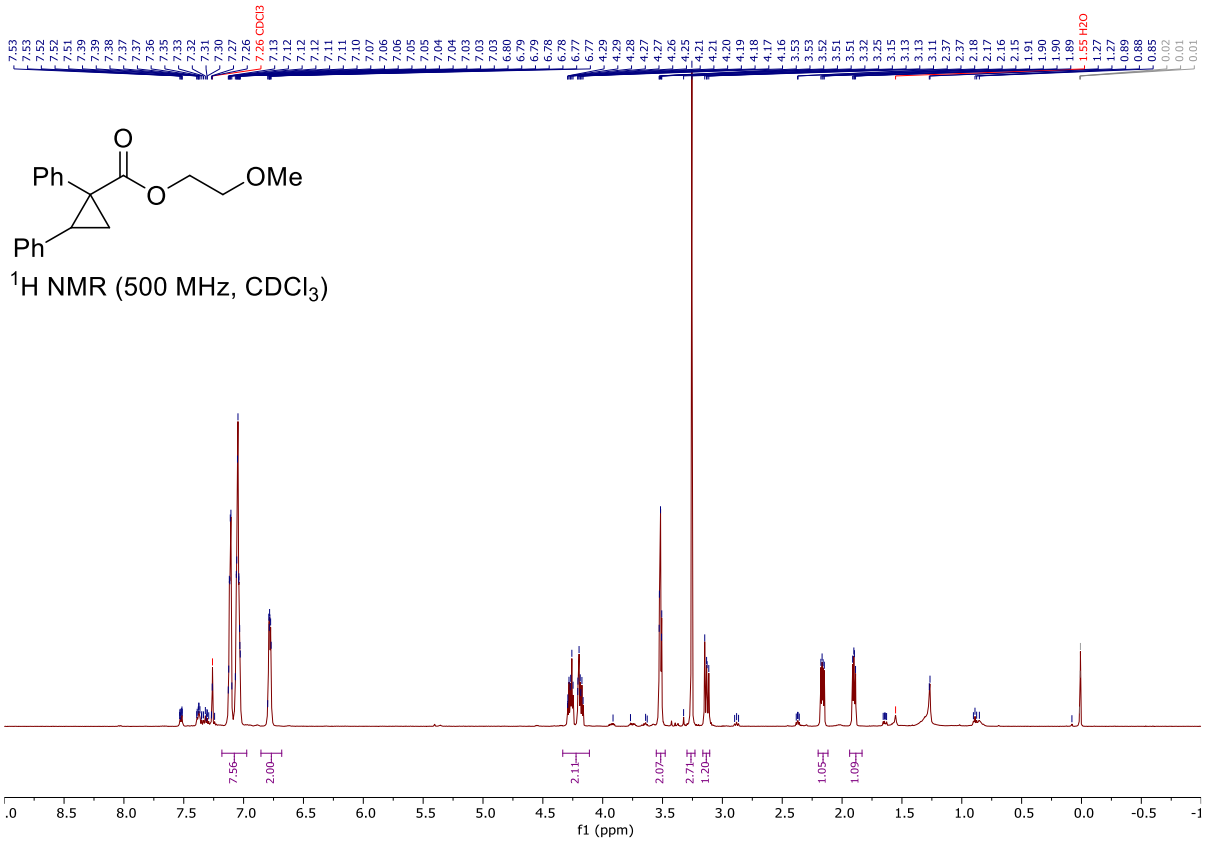


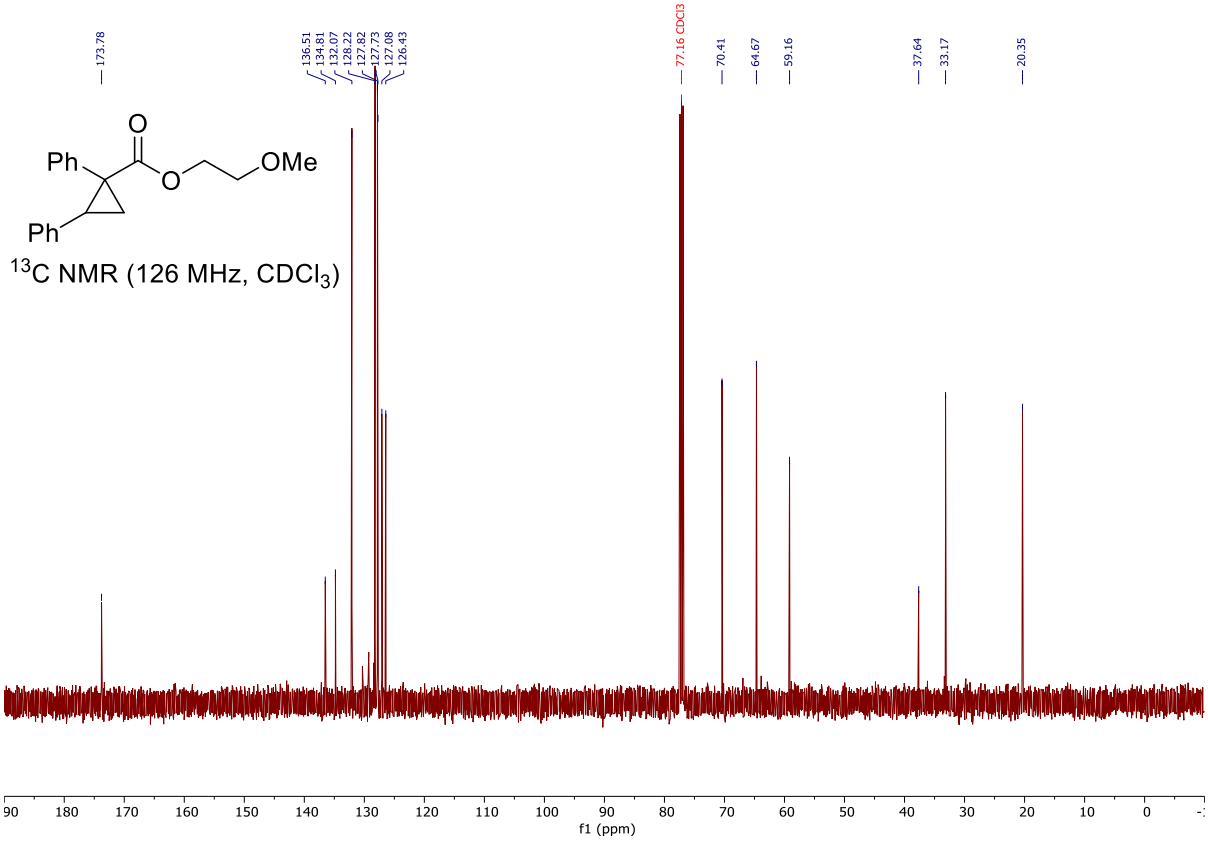
dodecyl 1,2-diphenylcyclopropane-1-carboxylate (**3e**) (dr 1:11)



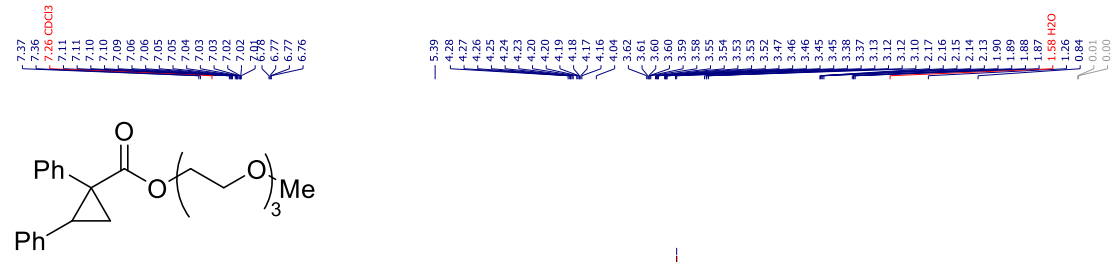


2-methoxyethyl 1,2-diphenylcyclopropane-1-carboxylate (**3f**) (dr 1:6)

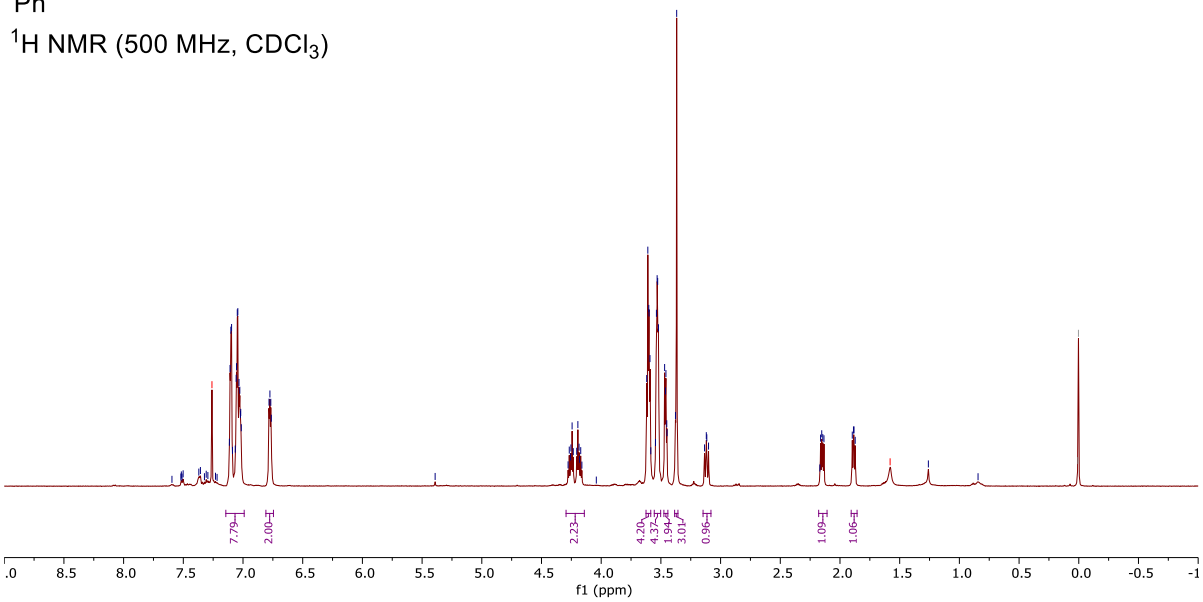


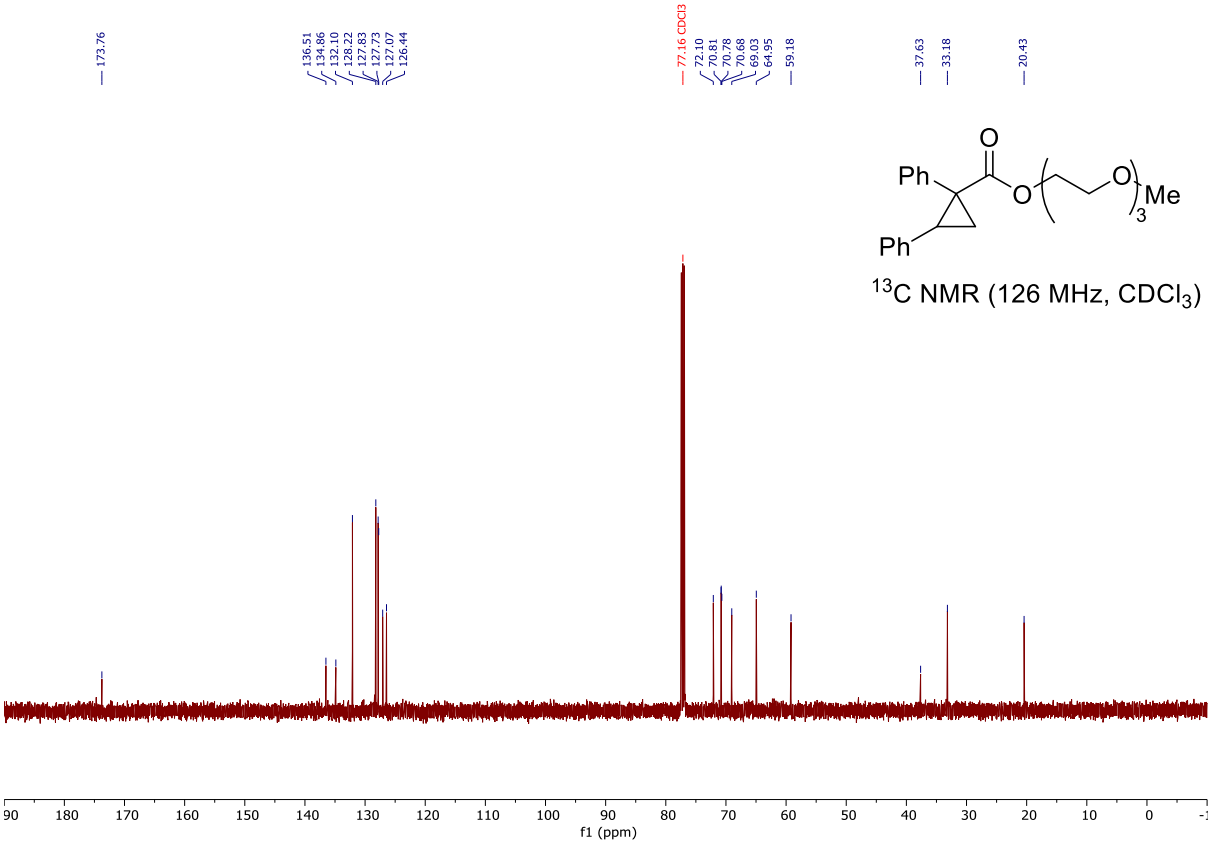


2-(2-(2-methoxyethoxy)ethoxy)ethyl 1,2-diphenylcyclopropane-1-carboxylate (**3g**) (dr 1:14)



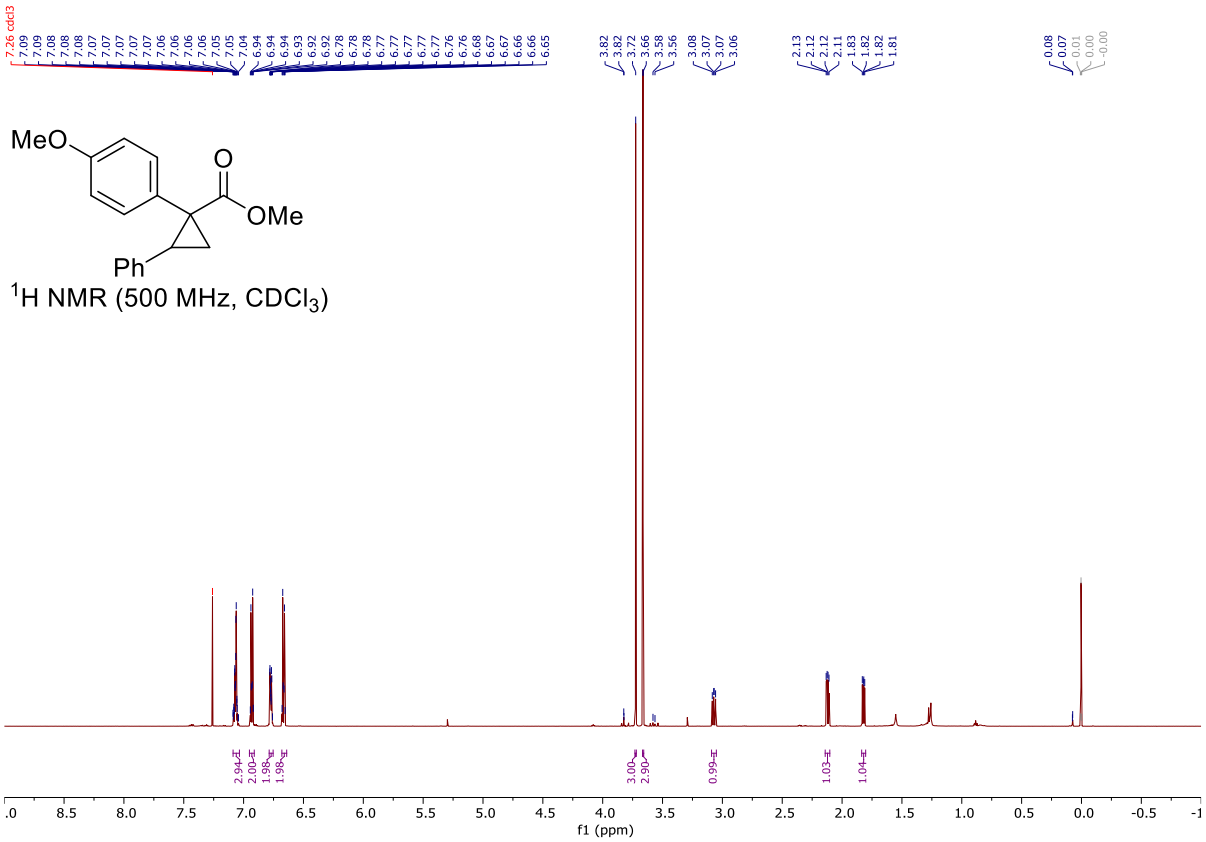
^{1}H NMR (500 MHz, $CDCl_3$)

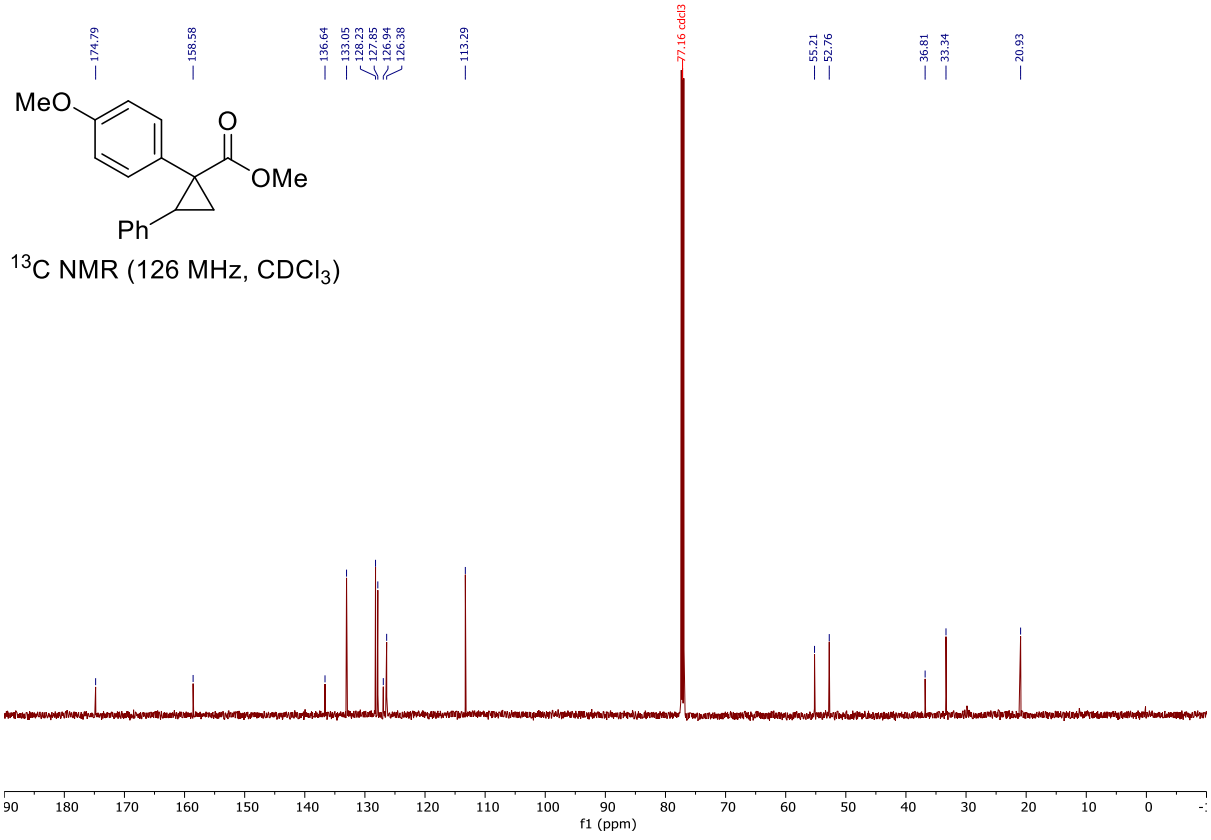




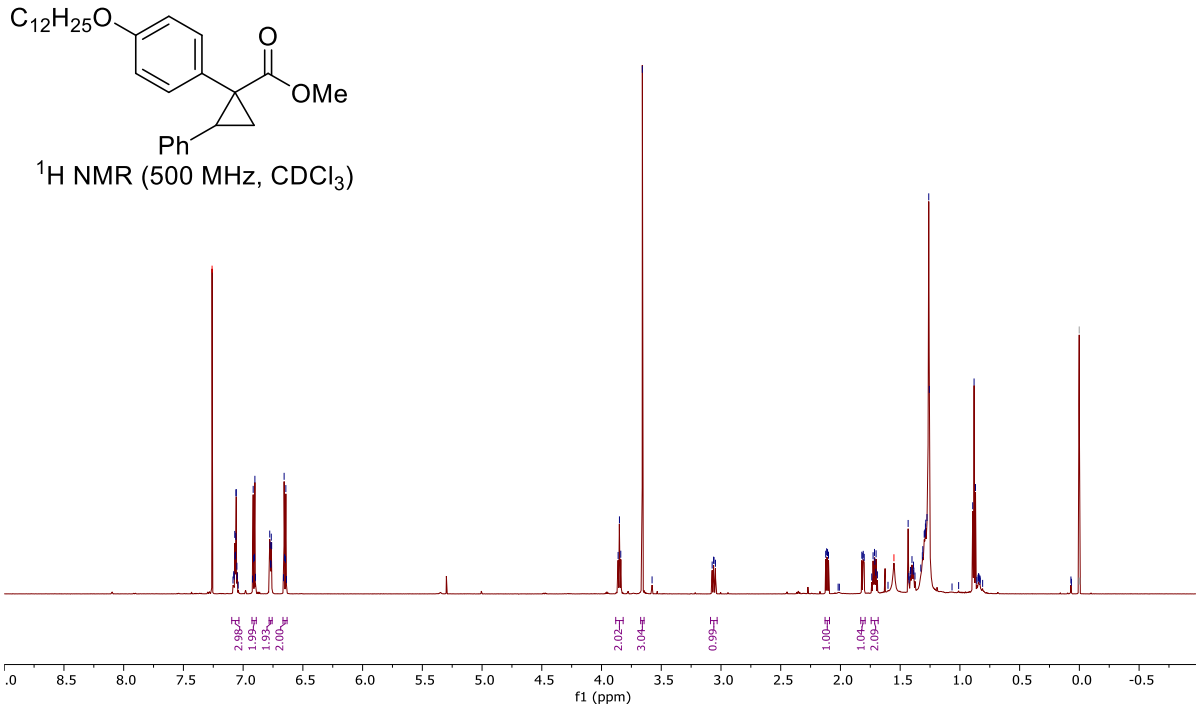
^{13}C NMR (126 MHz, $CDCl_3$)

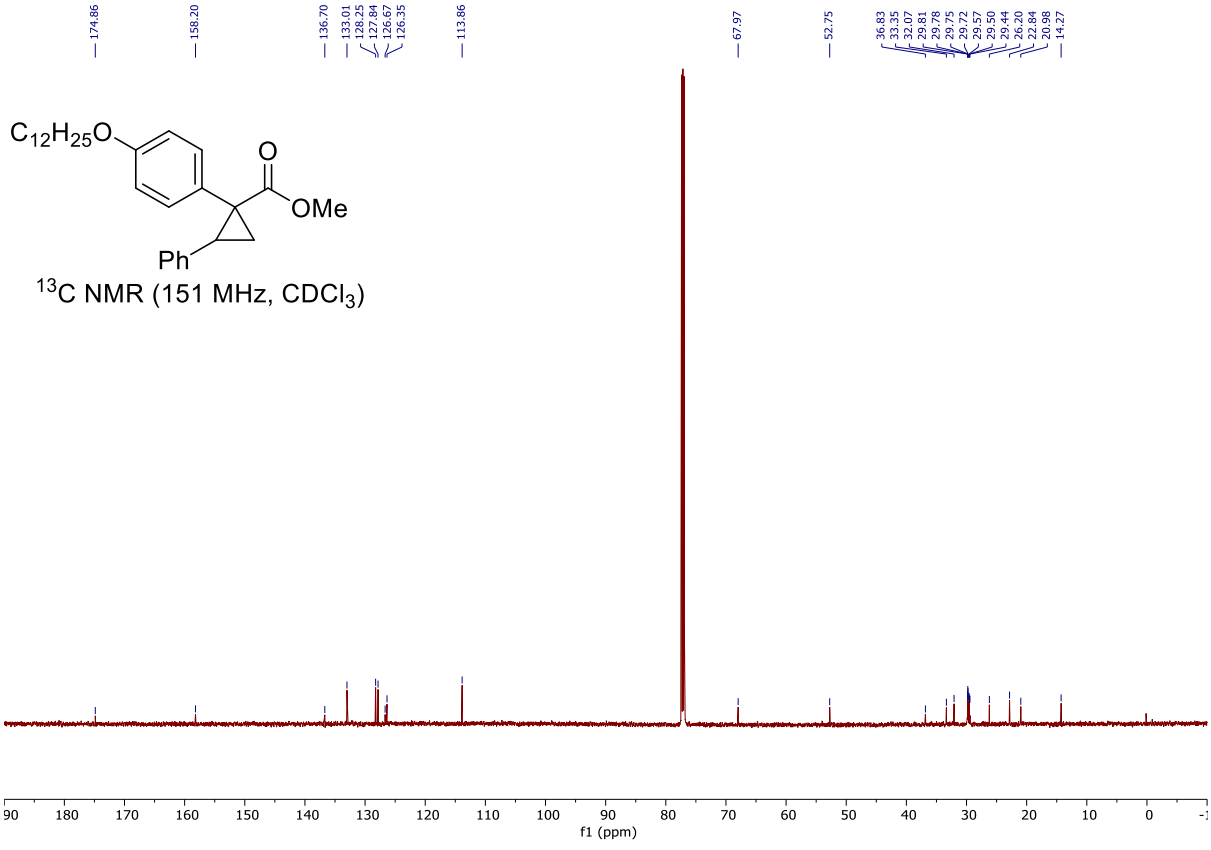
methyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3h**) (dr 1:12)



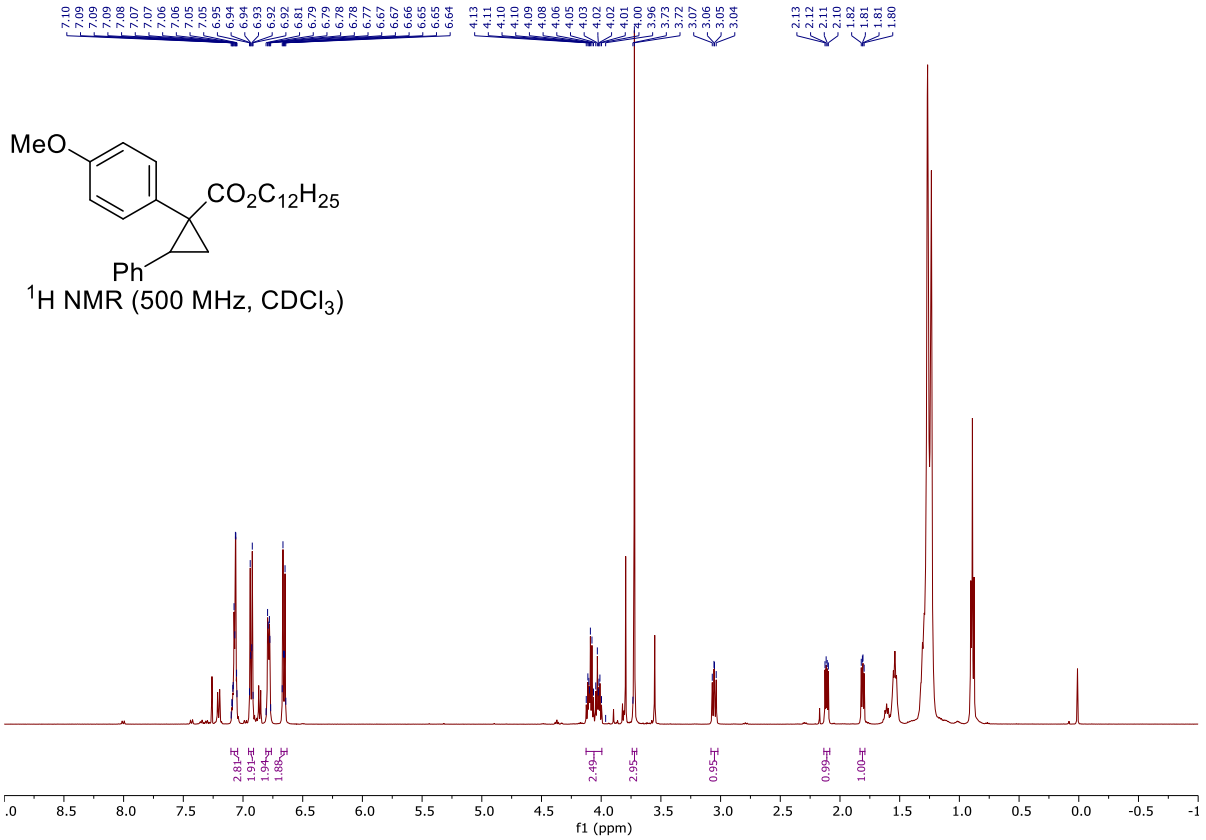


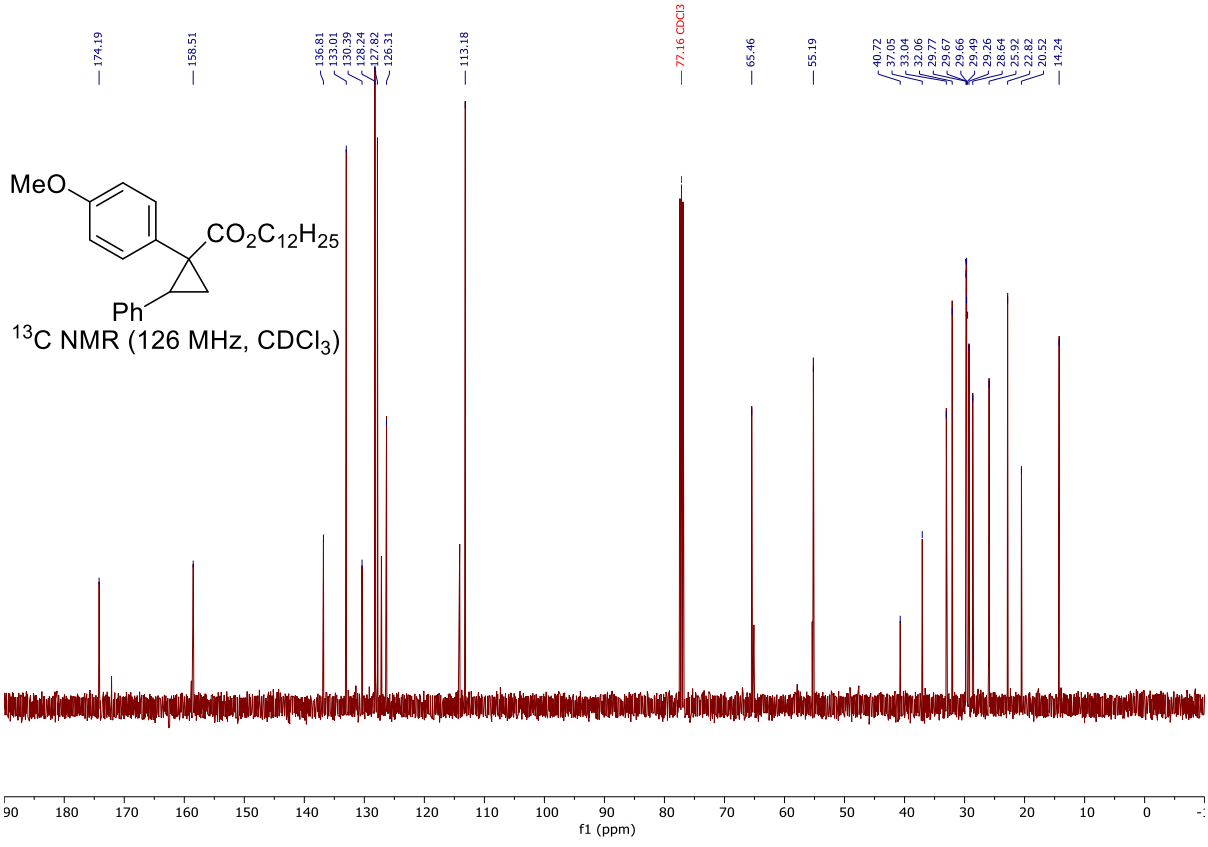
methyl 1-(4-(dodecyloxy)phenyl)-2-phenylcyclopropane-1-carboxylate (**3i**) (dr 1:>20)



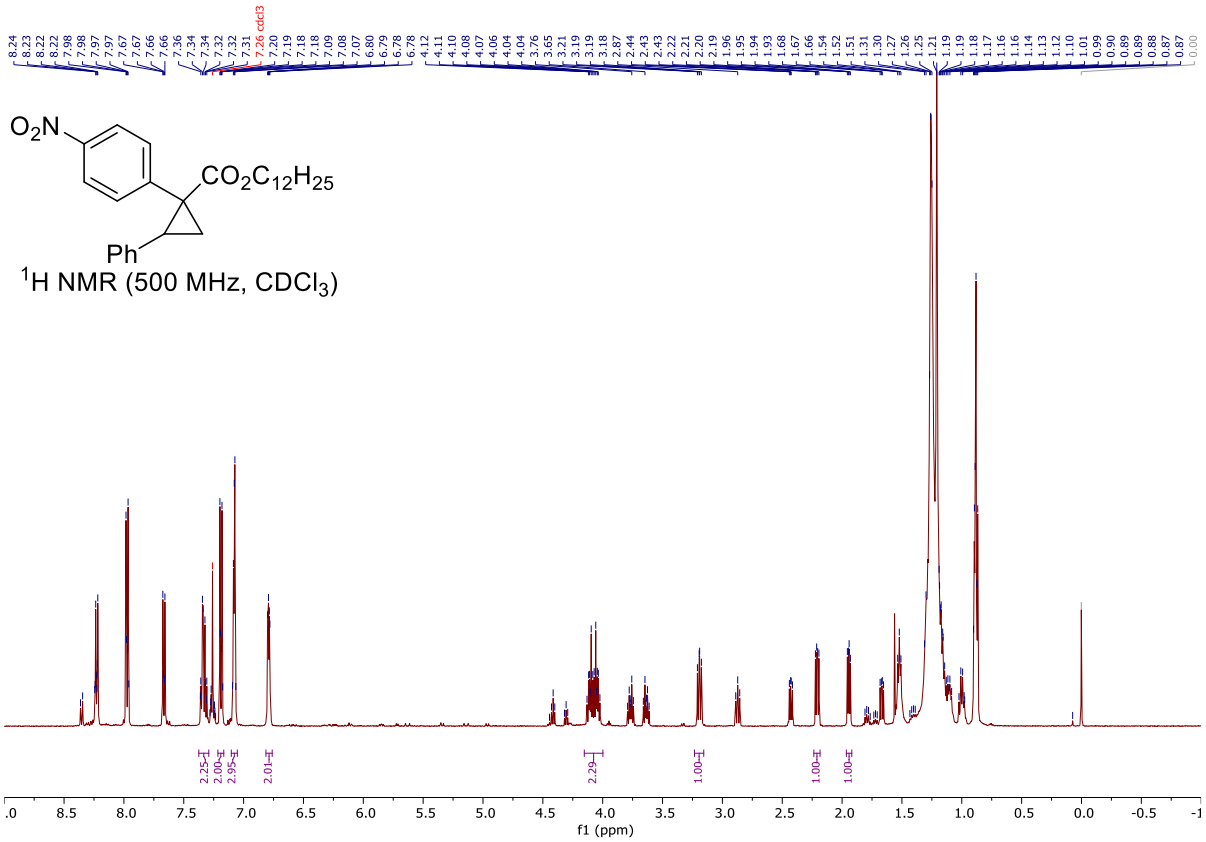


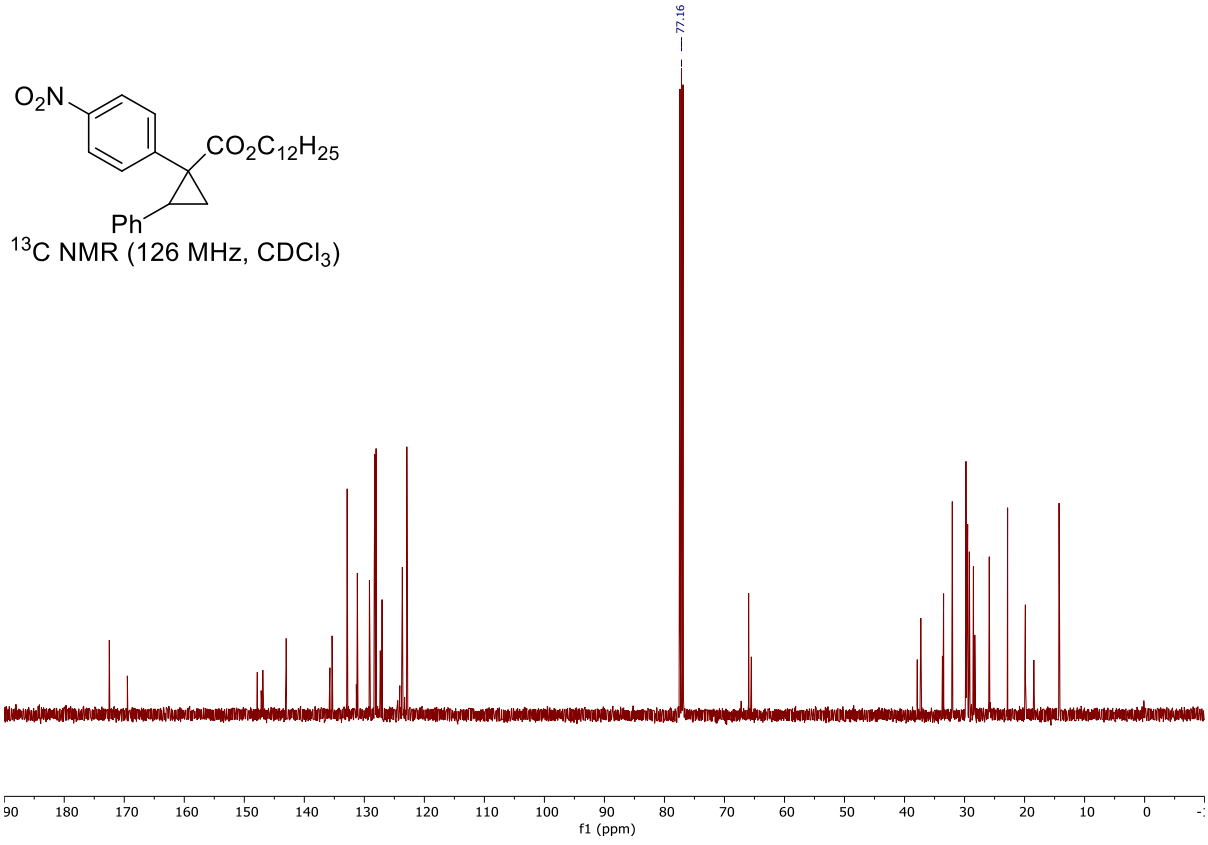
dodecyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3j**) (dr 1:7)



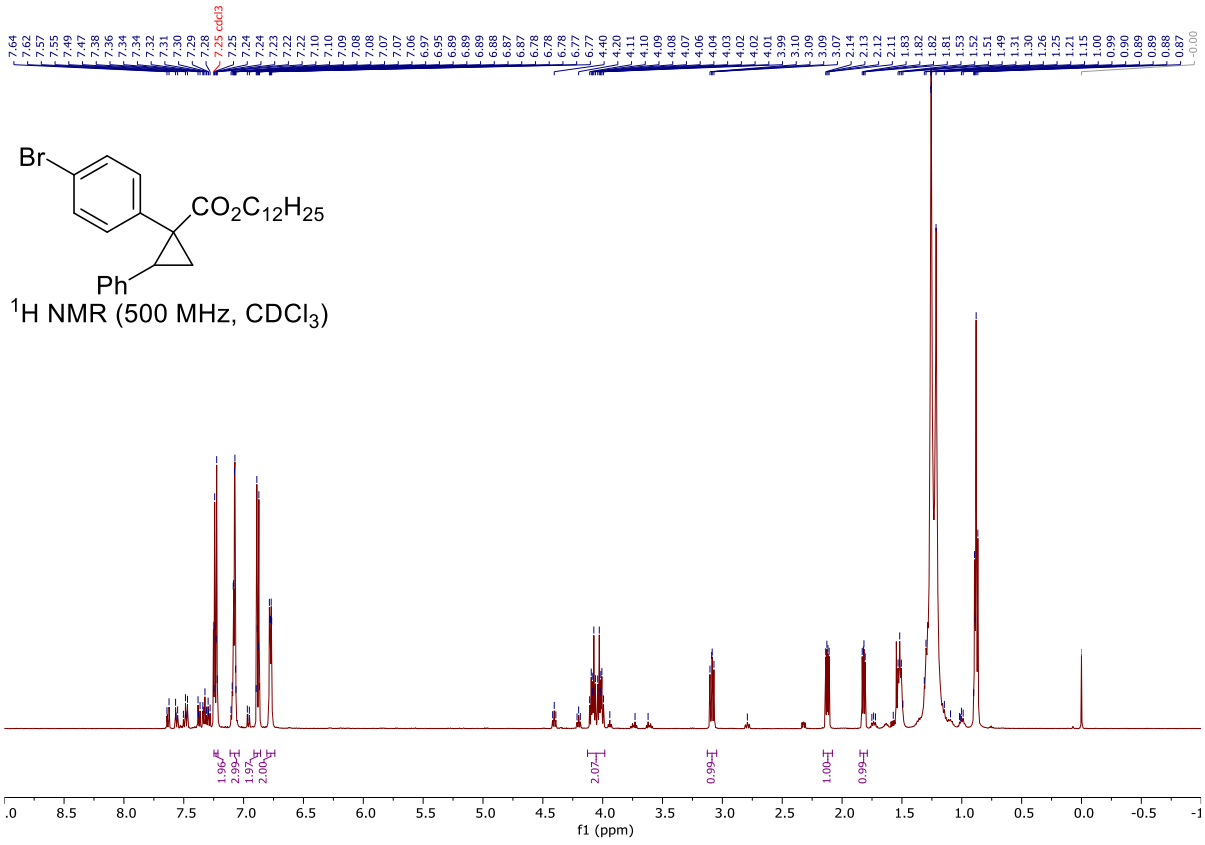


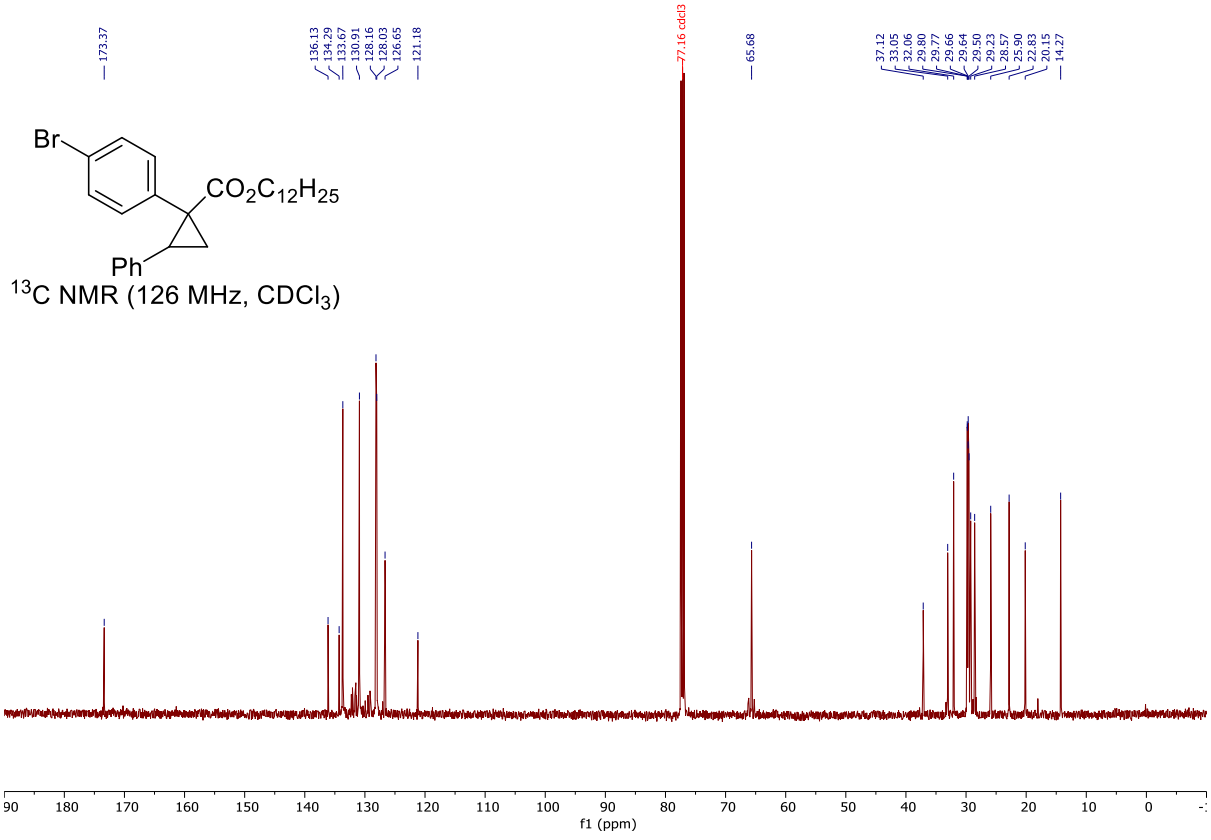
dodecyl 1-(4-nitrophenyl)-2-phenylcyclopropane-1-carboxylate (**3k**) (dr 1:2)



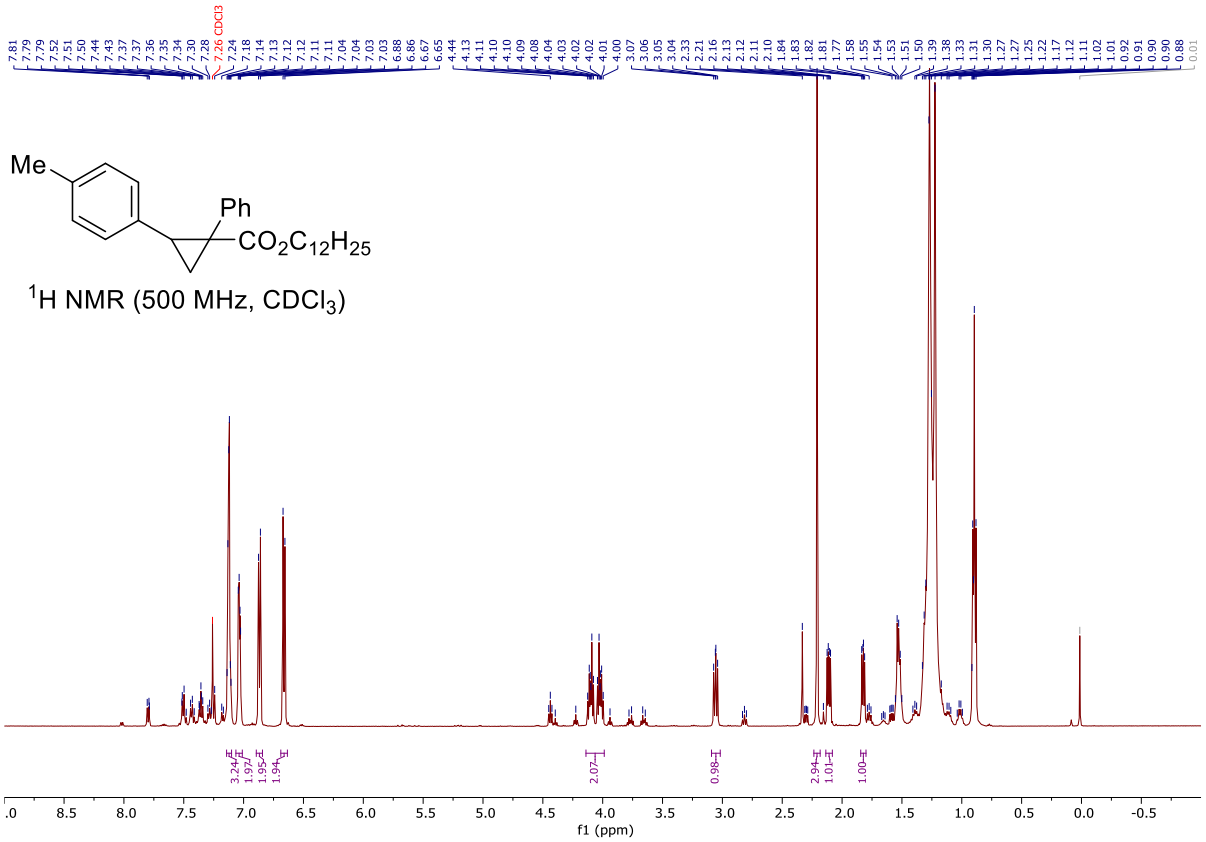


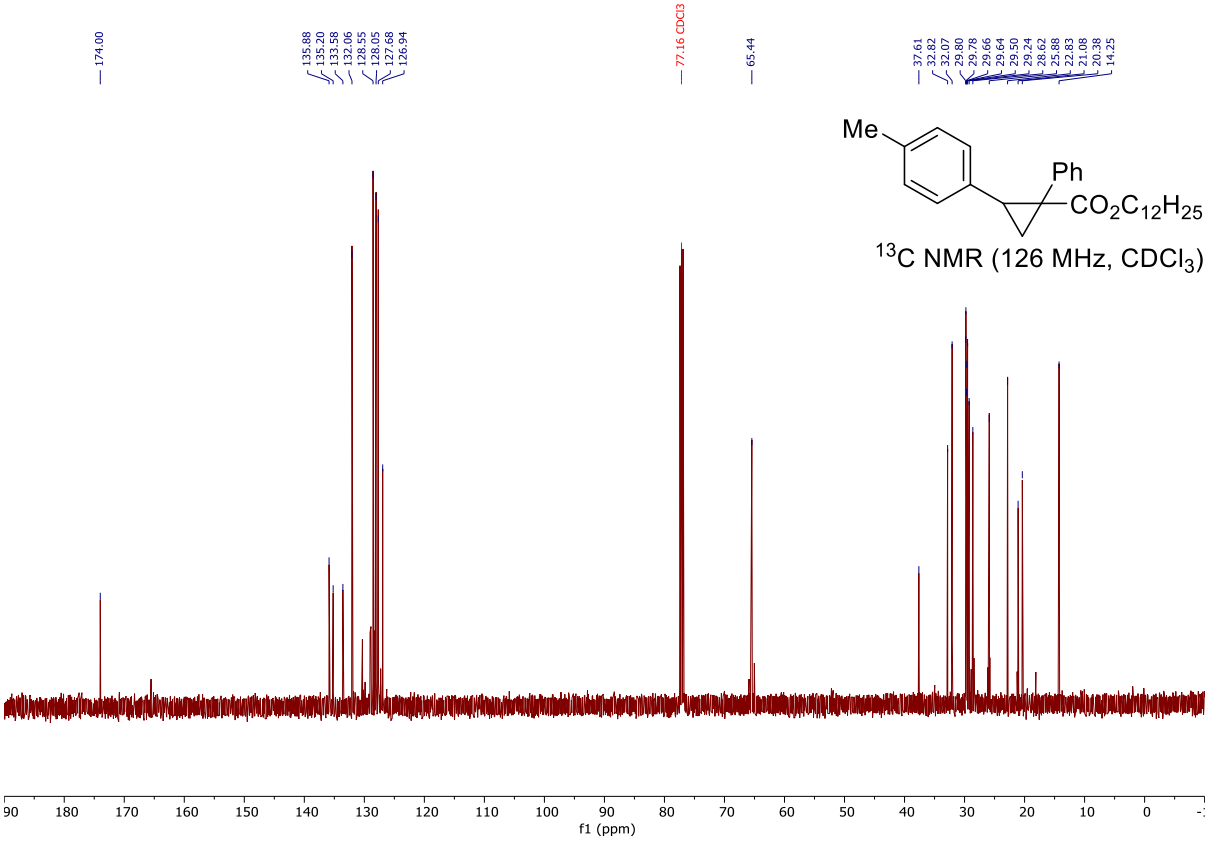
dodecyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3l**) (dr 1:13)



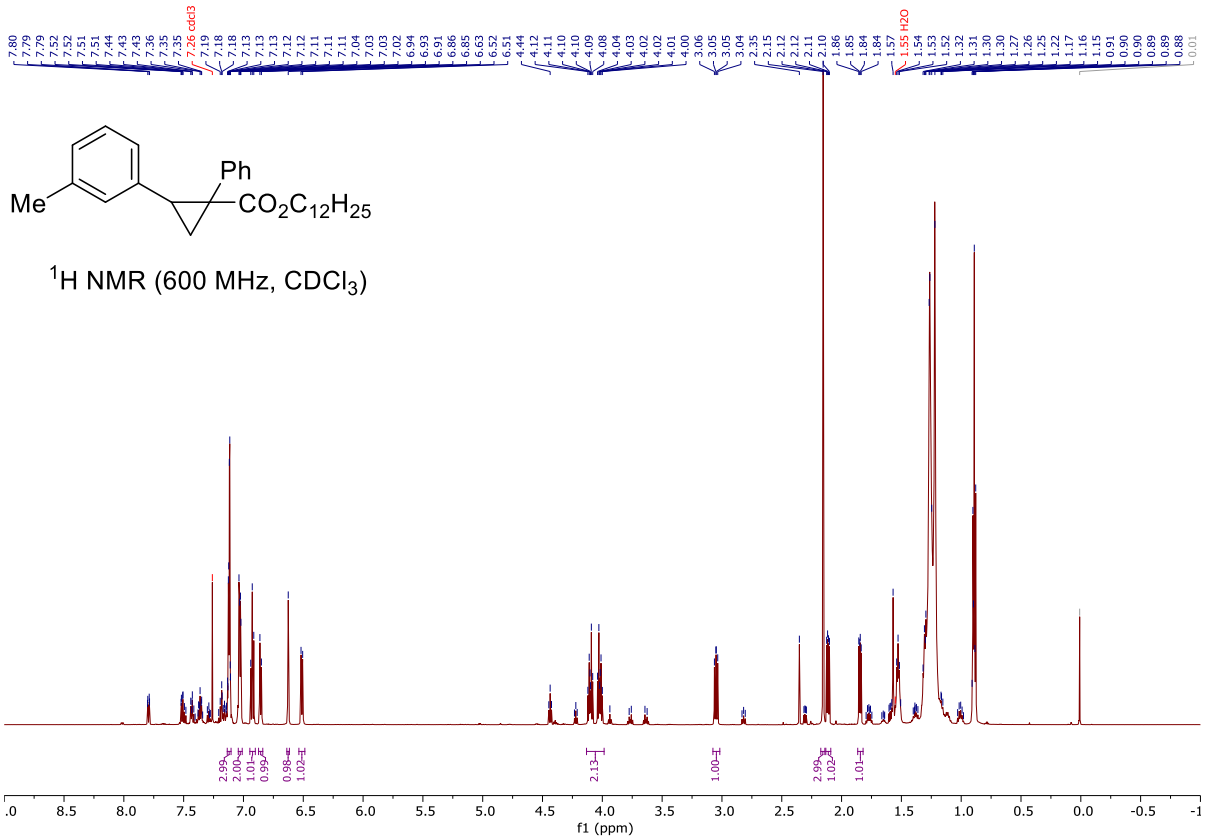


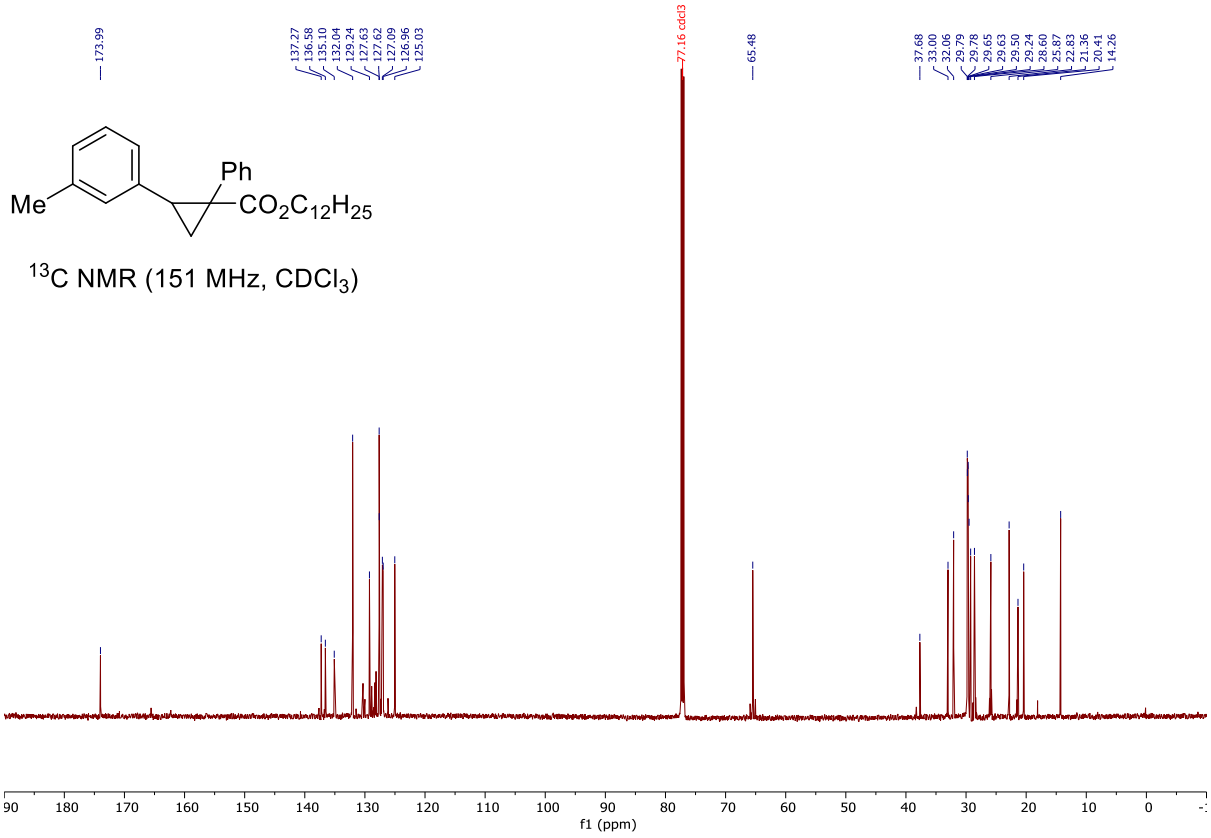
dodecyl 1-phenyl-2-(p-tolyl)cyclopropane-1-carboxylate (**3m**) (dr 1:8)



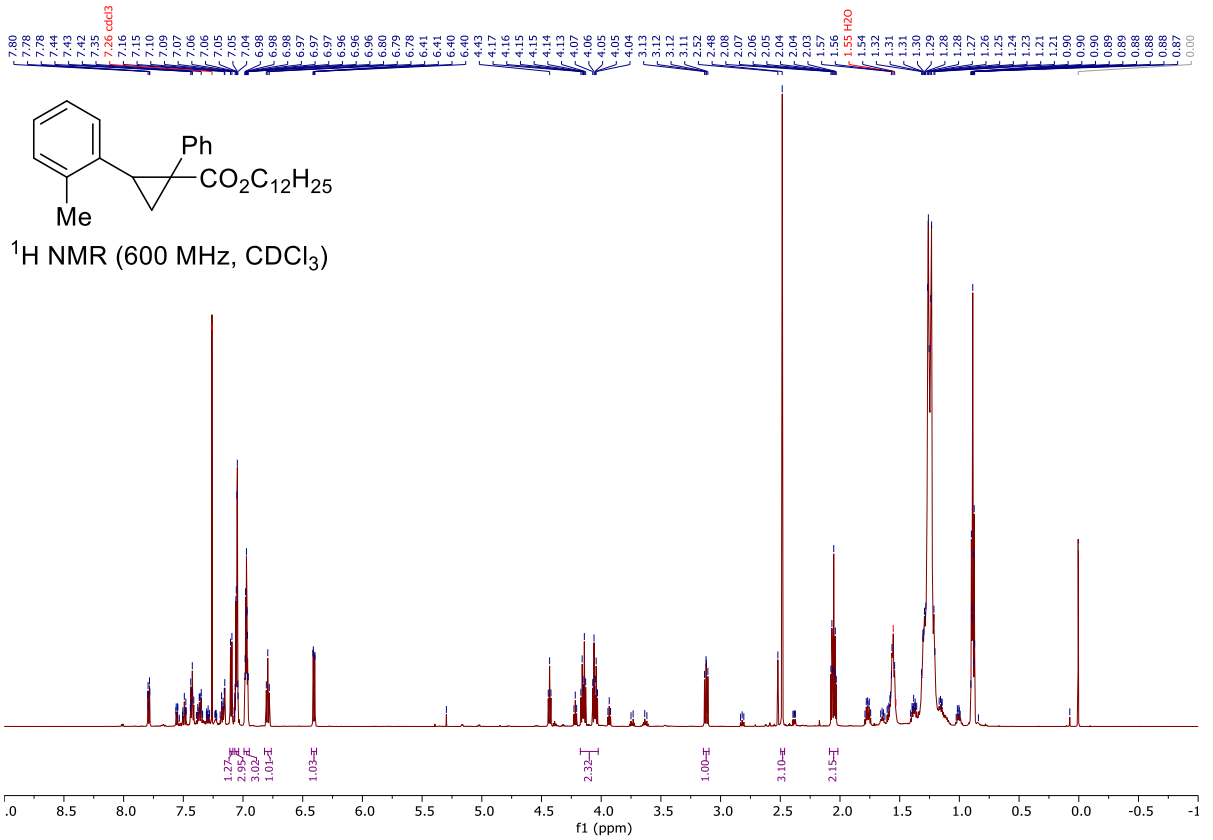


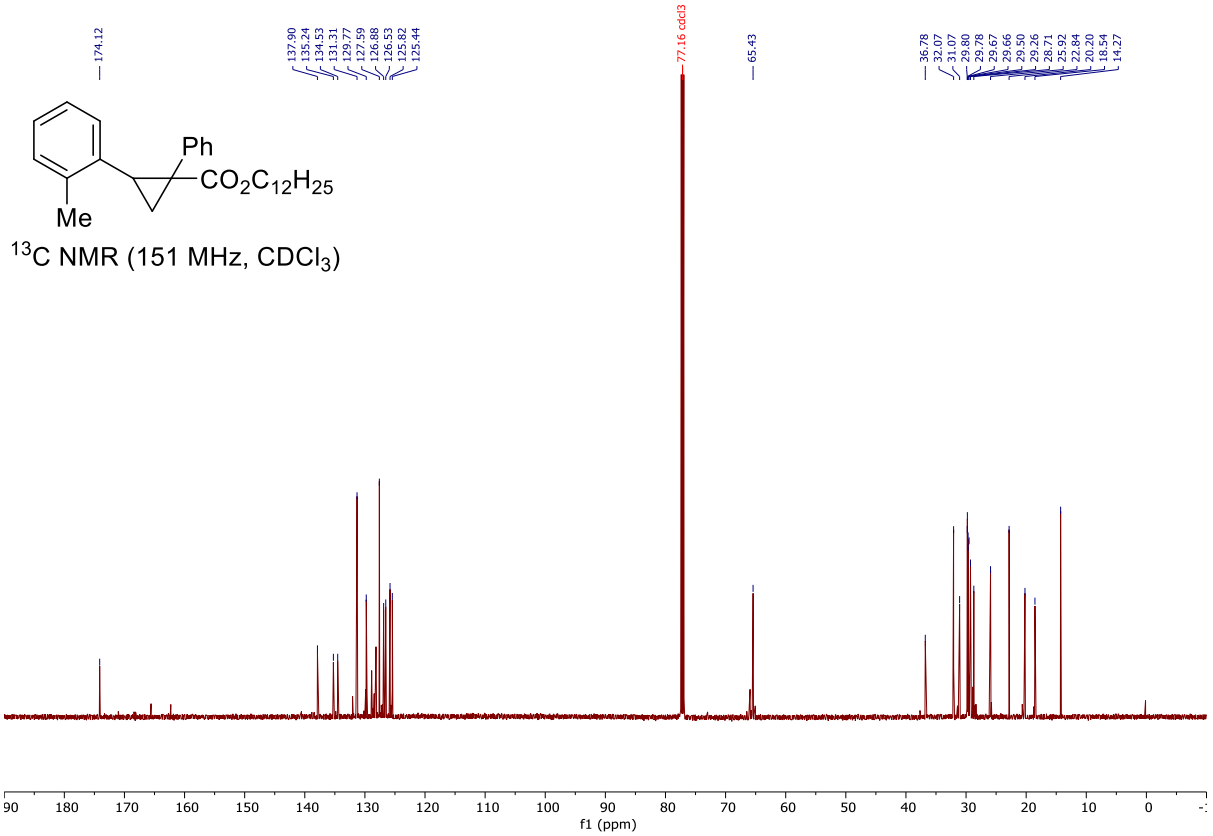
dodecyl 1-phenyl-2-(m-tolyl)cyclopropane-1-carboxylate (**3n**) (dr 1:8)



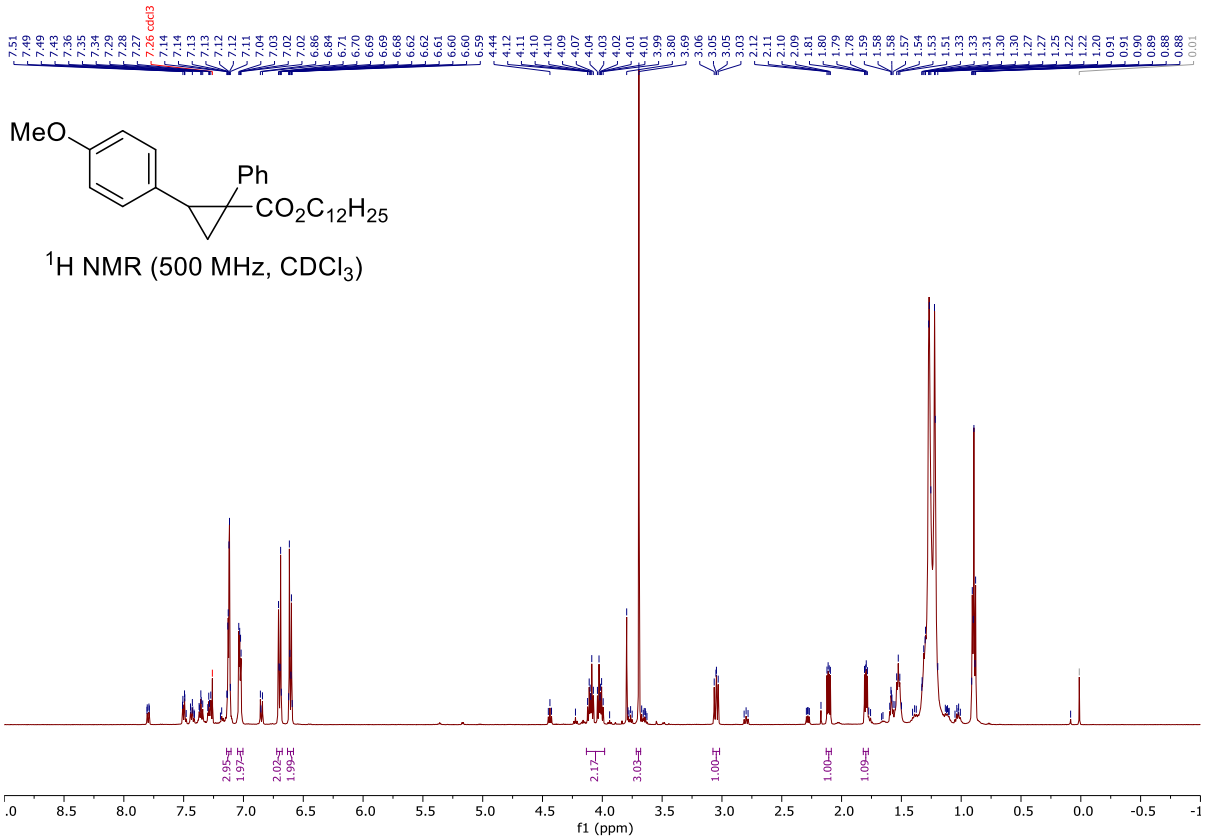


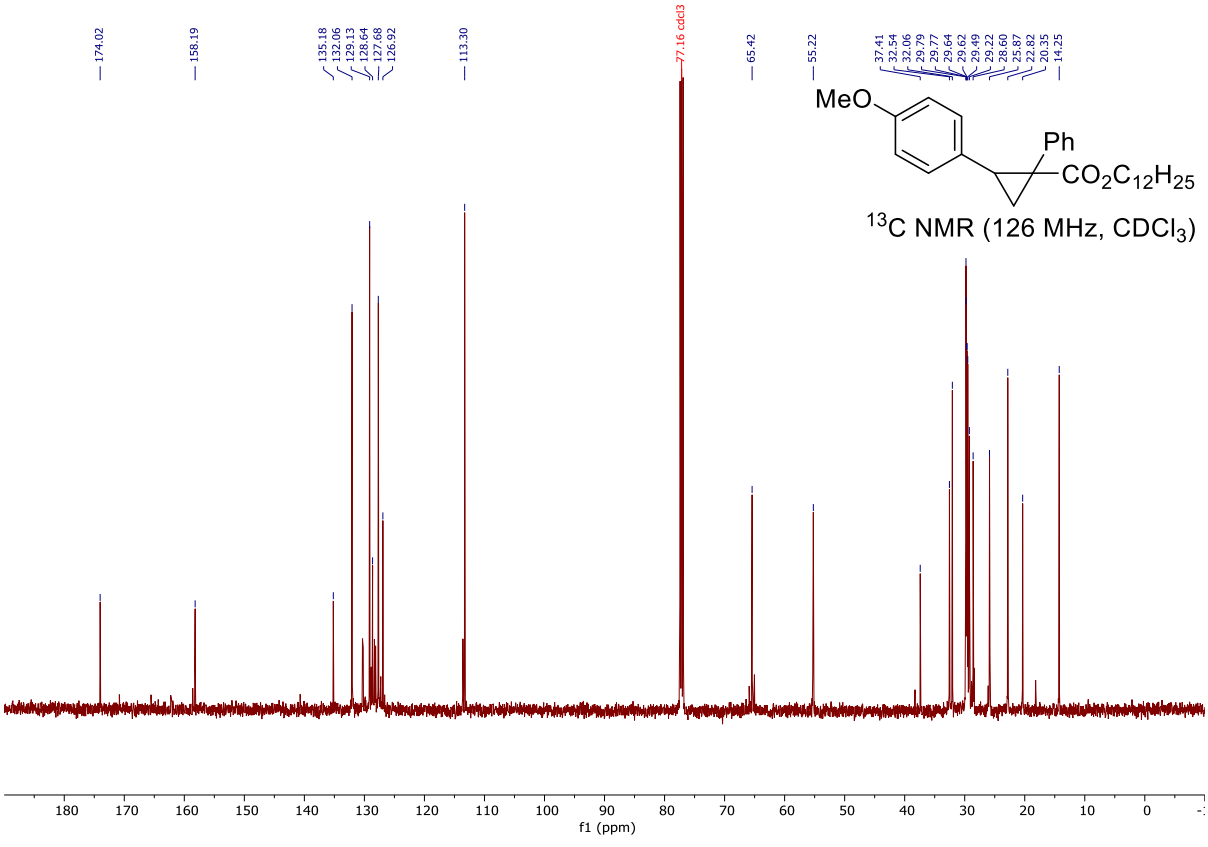
dodecyl 1-phenyl-2-(o-tolyl)cyclopropane-1-carboxylate (**3o**) (dr 1:14)



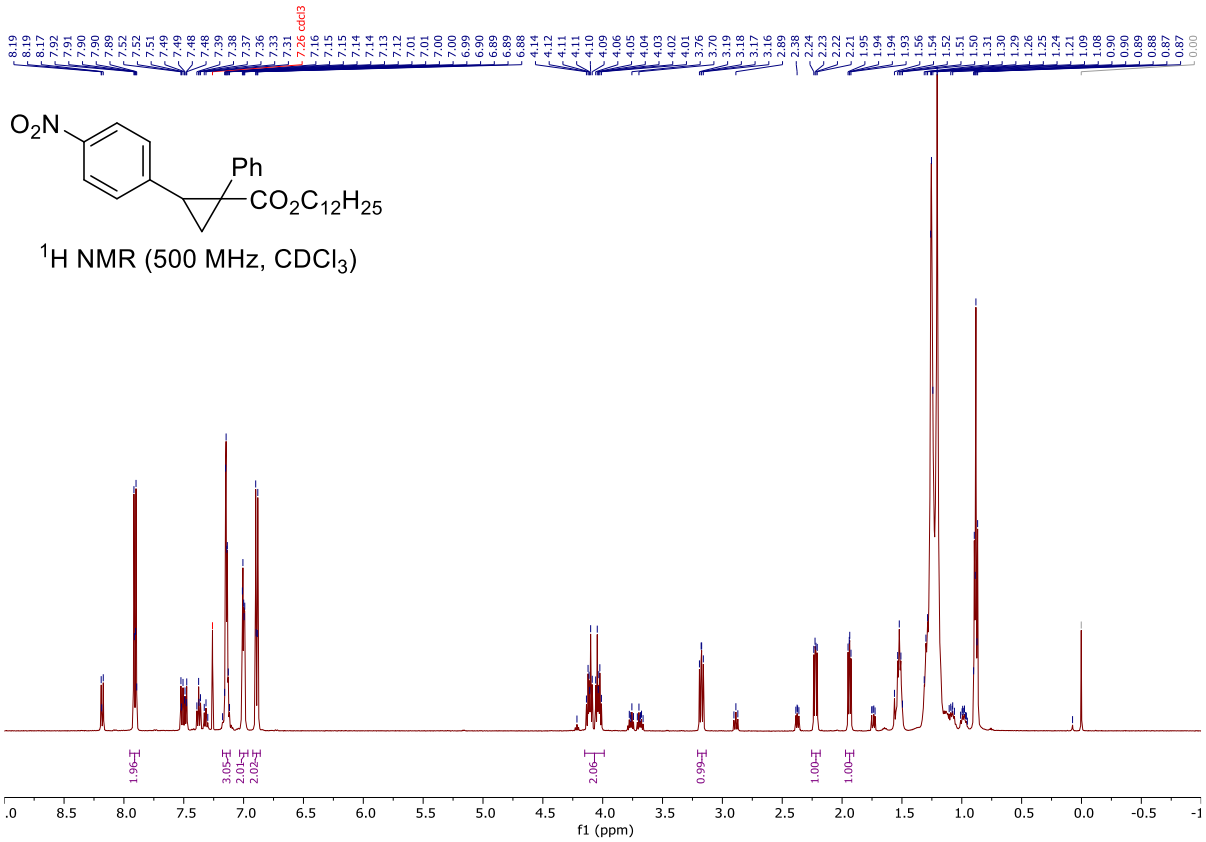


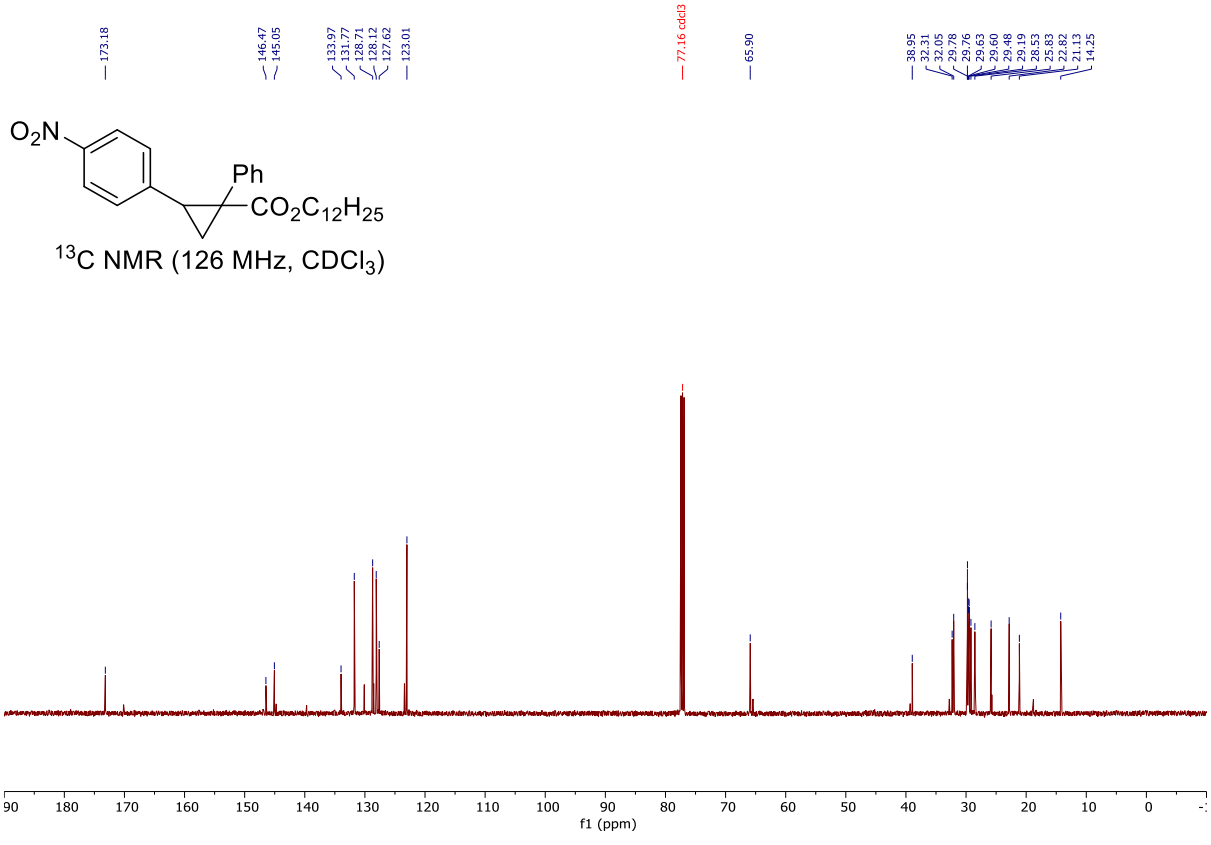
dodecyl 2-(4-methoxyphenyl)-1-phenylcyclopropane-1-carboxylate (**3p**) (dr 1:5)



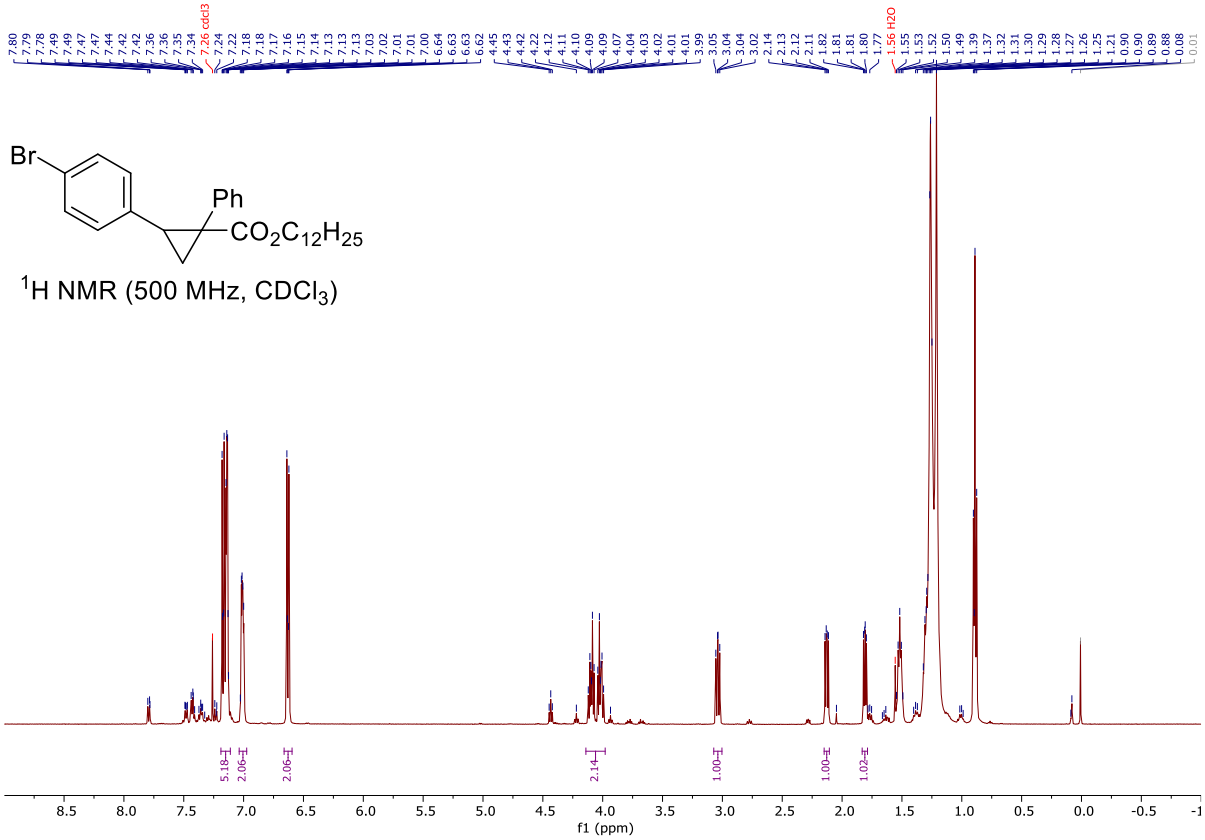


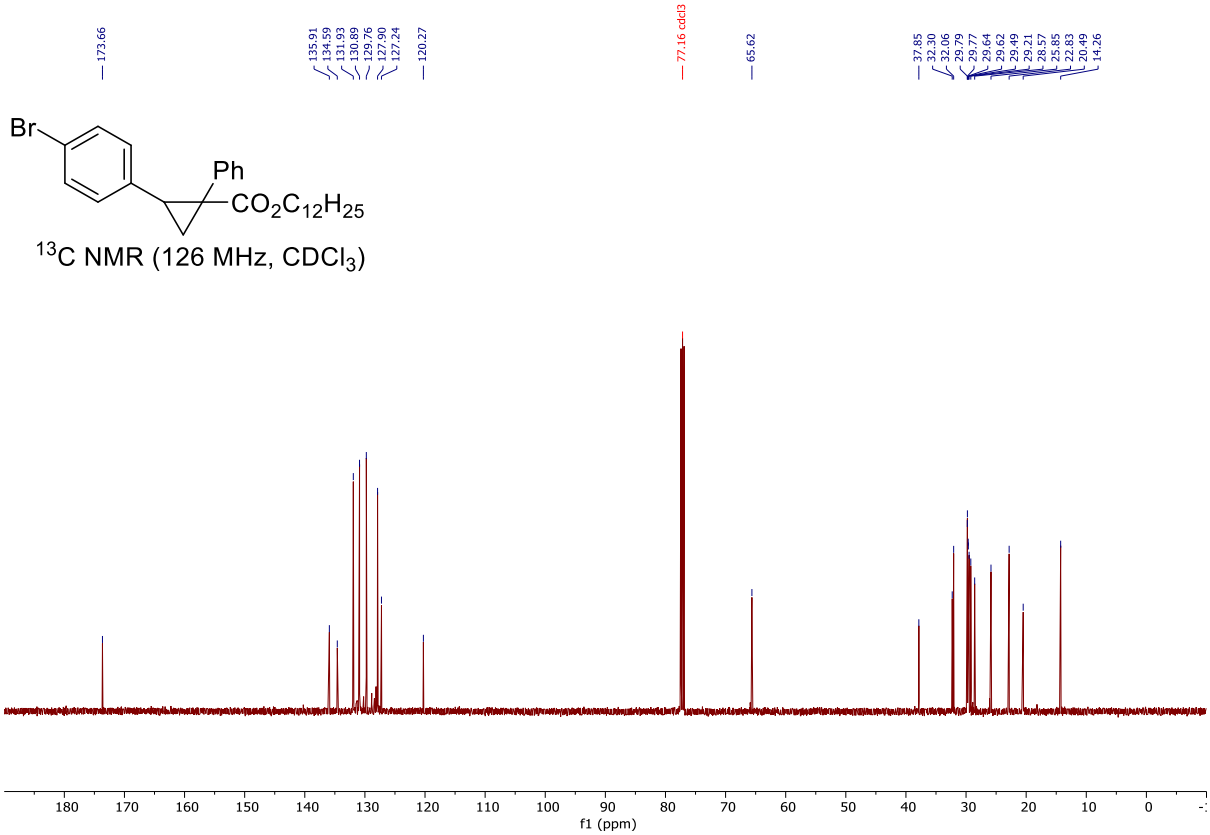
dodecyl 2-(4-nitrophenyl)-1-phenylcyclopropane-1-carboxylate (**3q**) (dr 1:3)



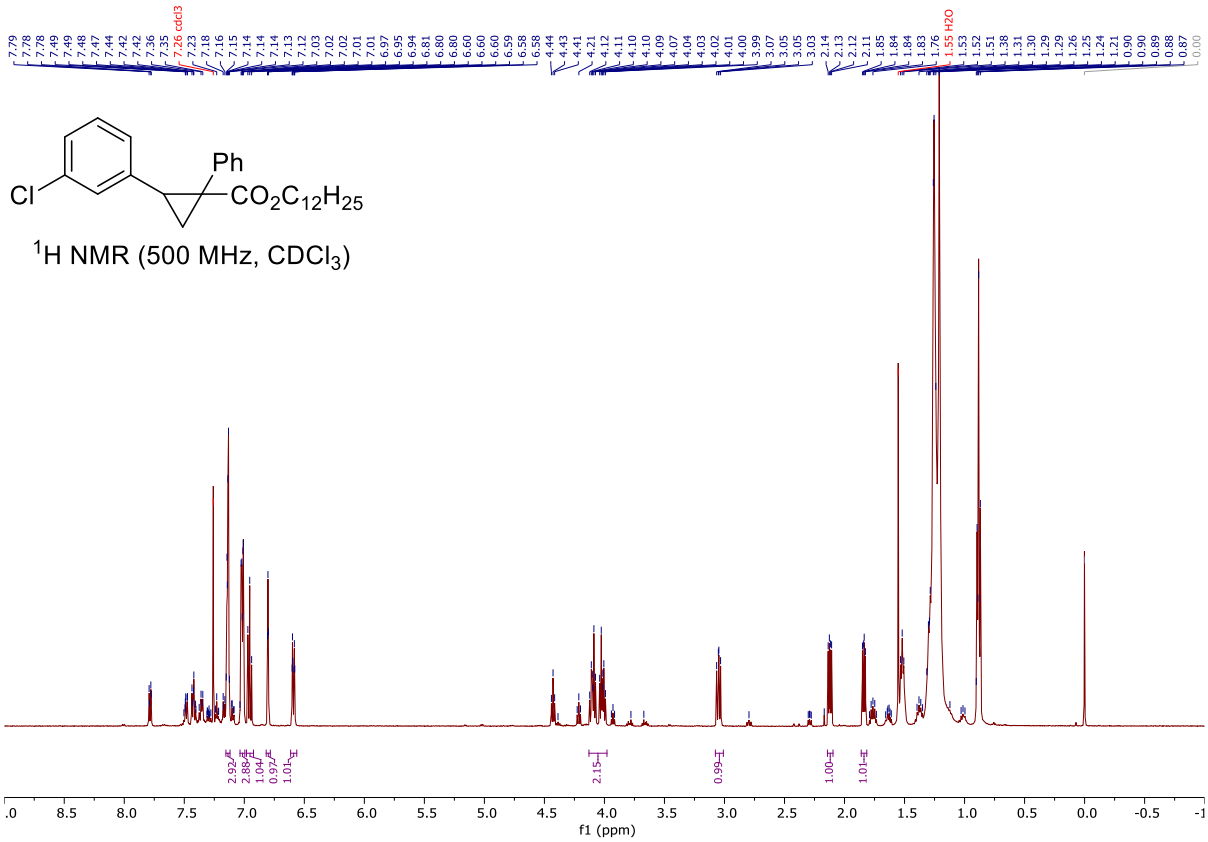


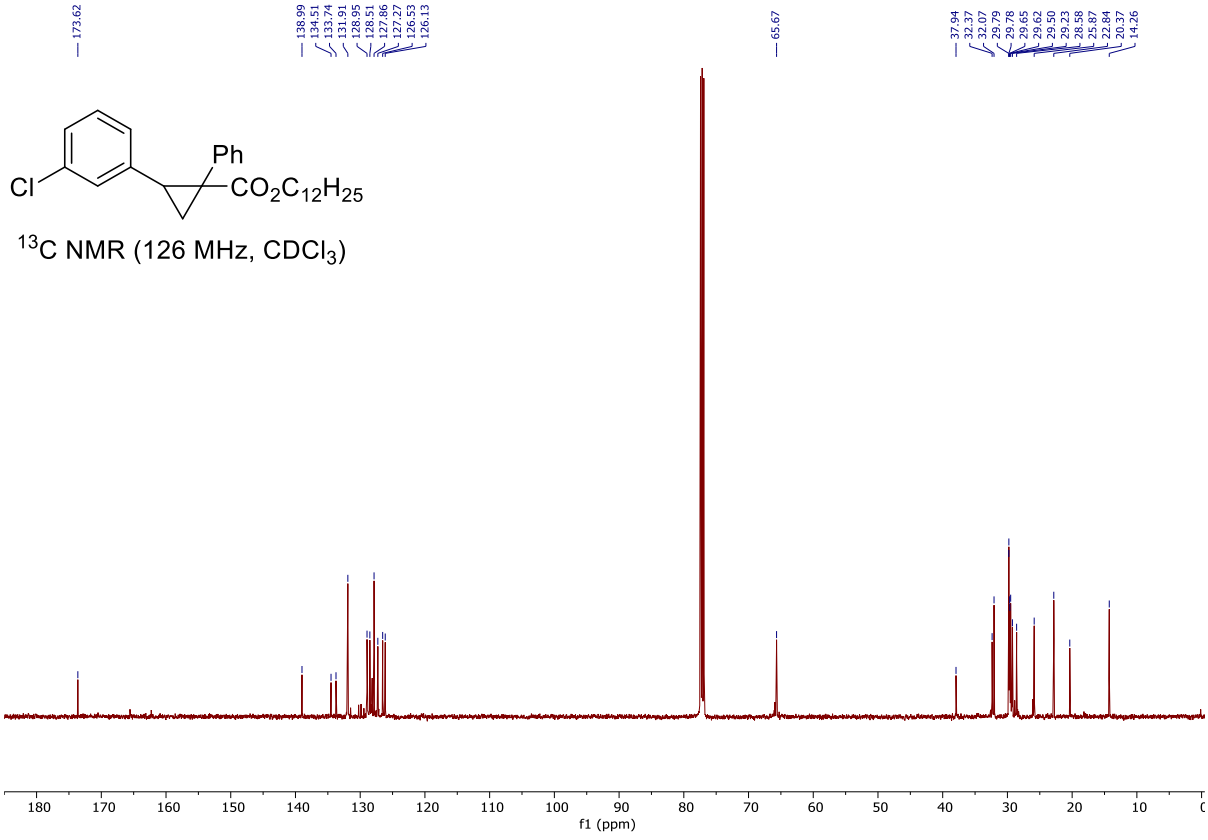
dodecyl 2-(4-bromophenyl)-1-phenylcyclopropane-1-carboxylate (**3r**) (dr 1:4)



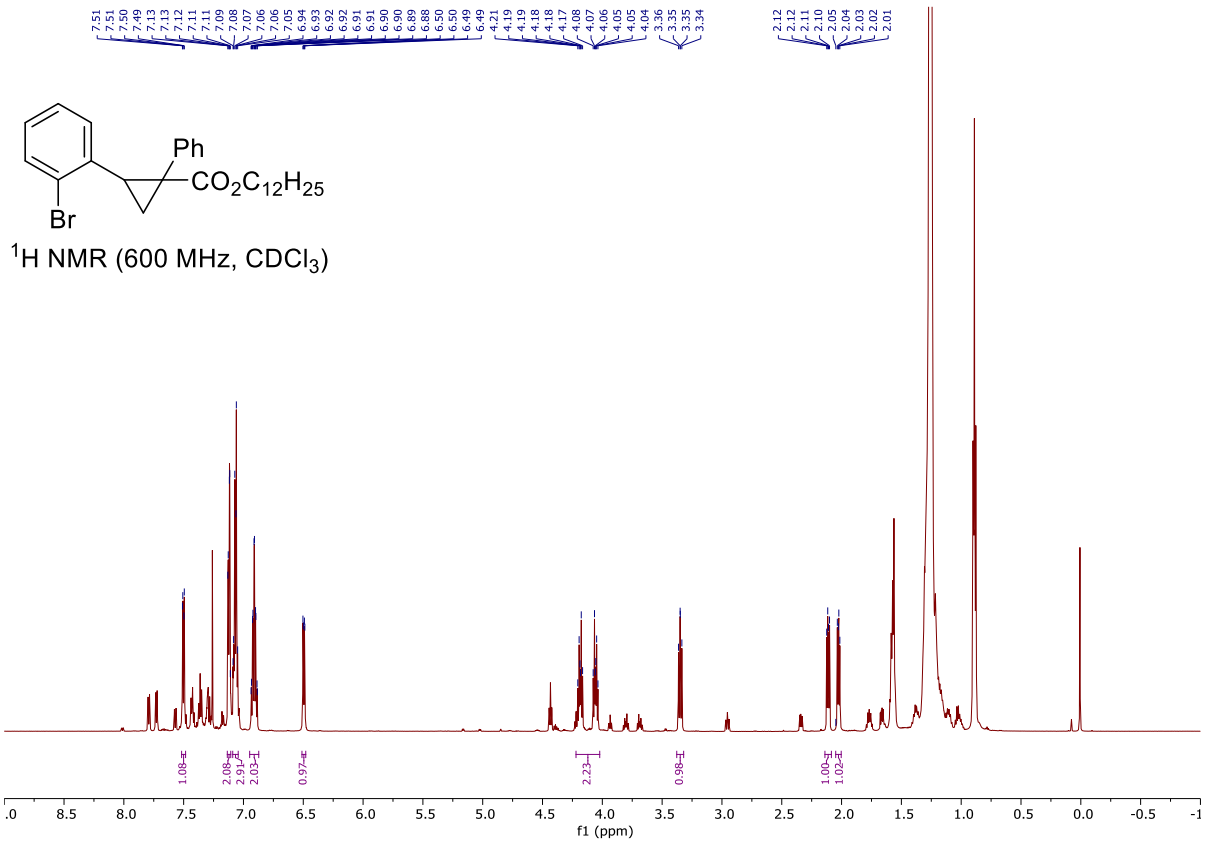


dodecyl 2-(3-chlorophenyl)-1-phenylcyclopropane-1-carboxylate (**3t**) (dr 1:13)

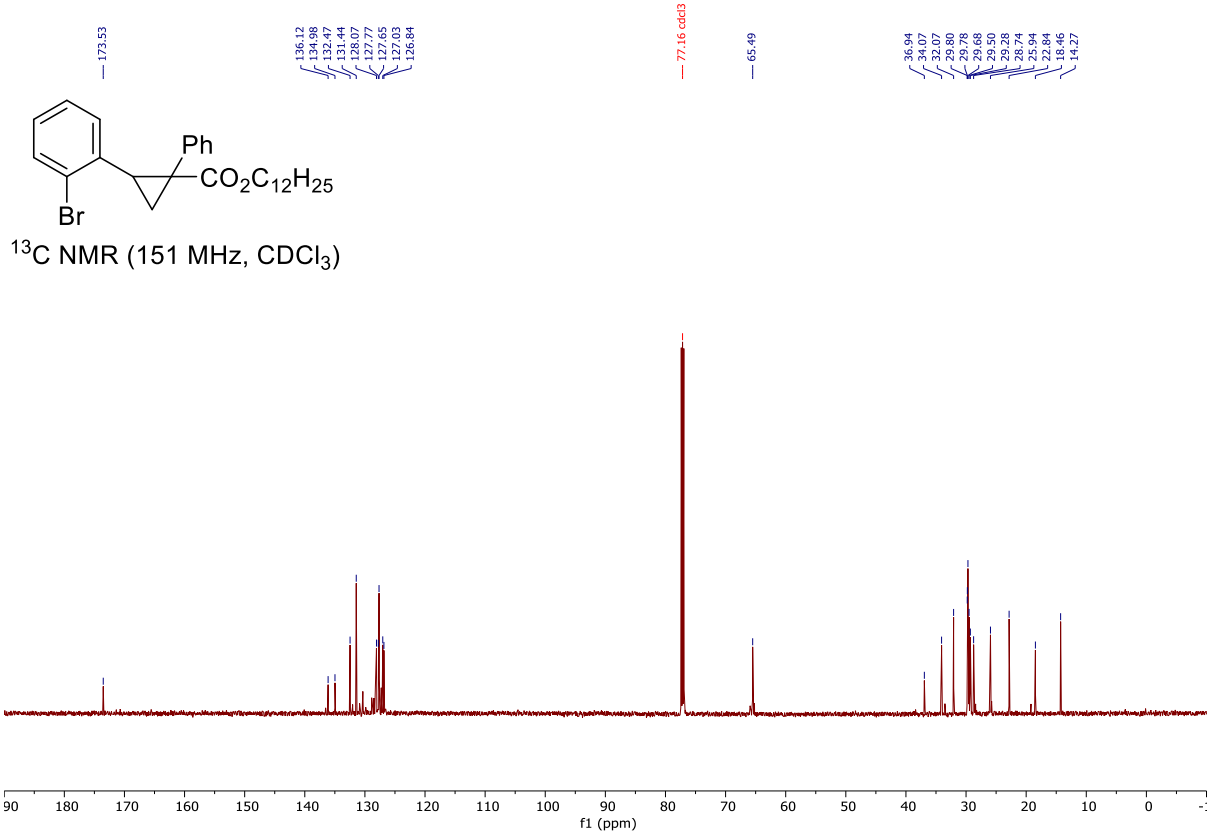




dodecyl 2-(2-bromophenyl)-1-phenylcyclopropane-1-carboxylate (**3u**) (dr 1:4)

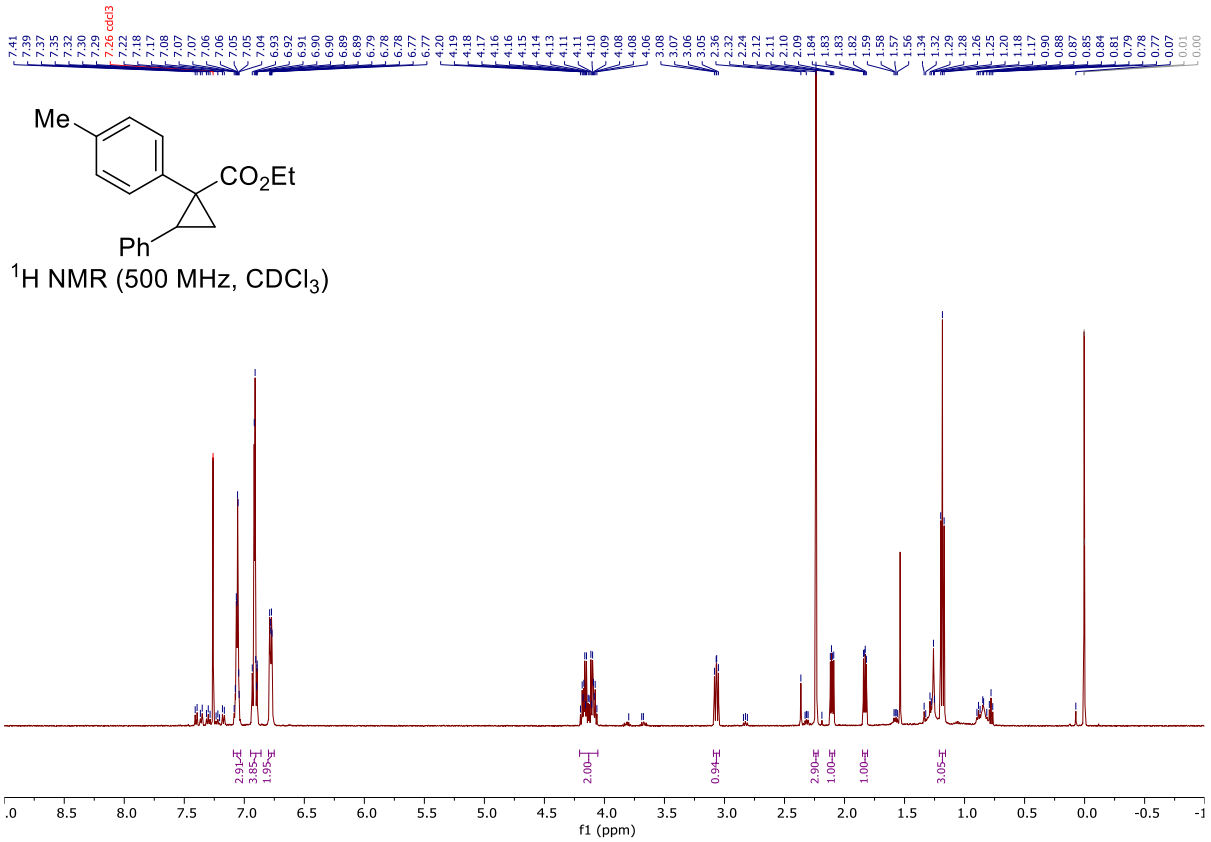


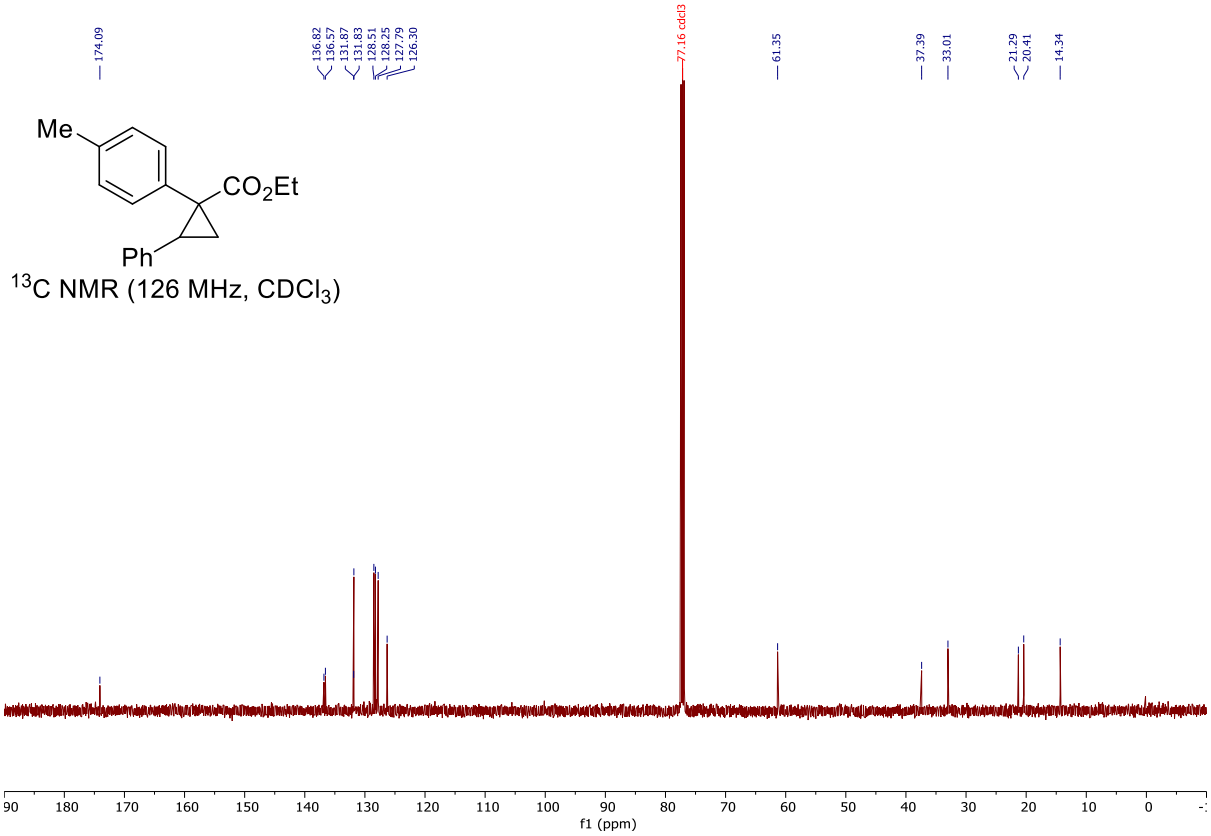
^{1}H NMR (600 MHz, $CDCl_3$)



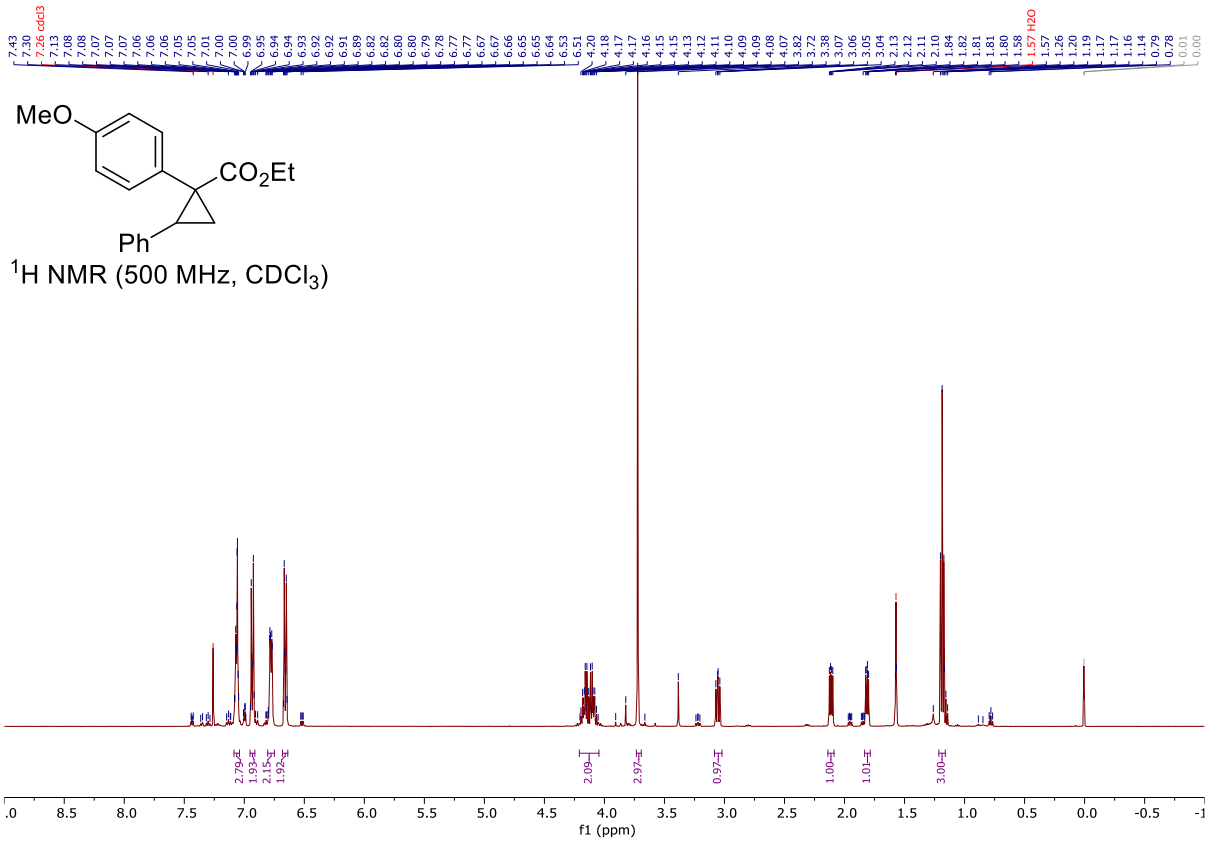
^{13}C NMR (151 MHz, $CDCl_3$)

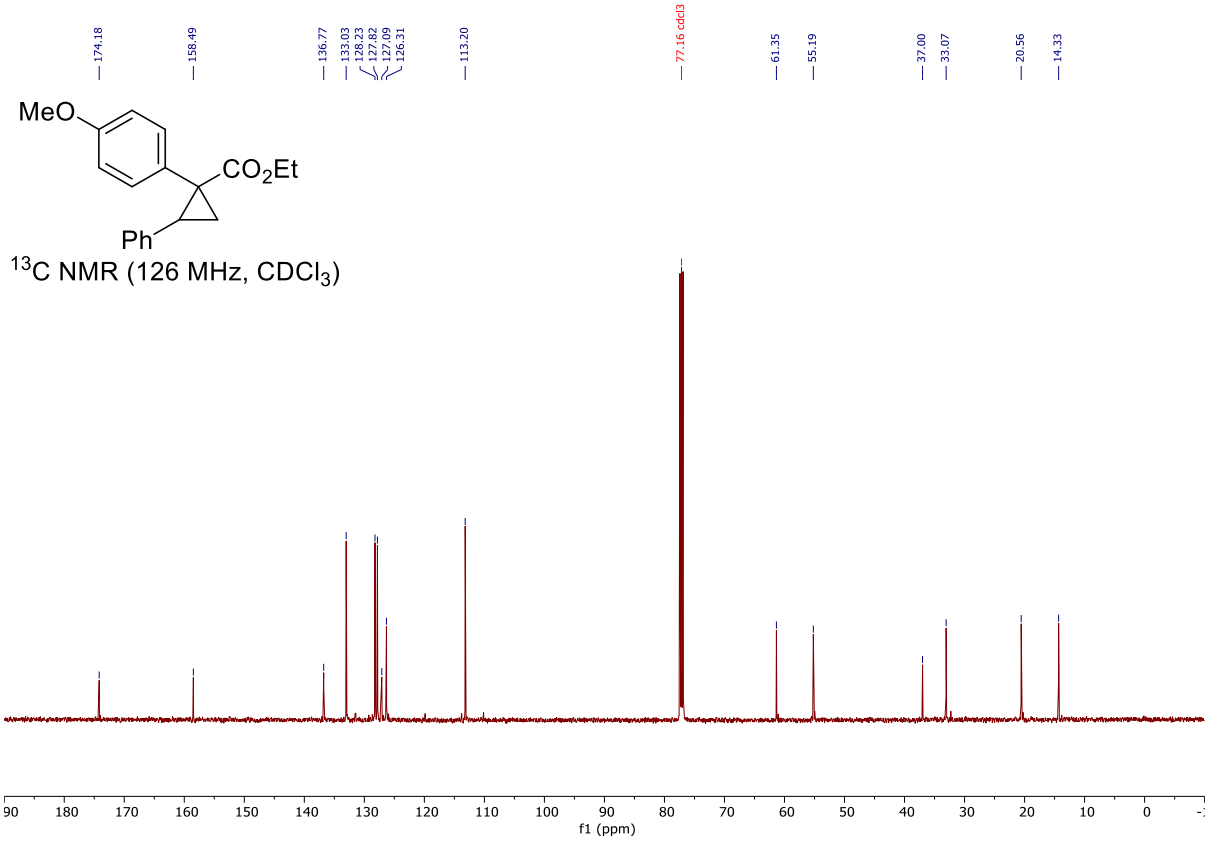
ethyl 2-phenyl-1-(p-tolyl)cyclopropane-1-carboxylate (**3v**) (dr 1:15)



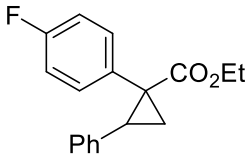


ethyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3w**) (dr 1:>20)

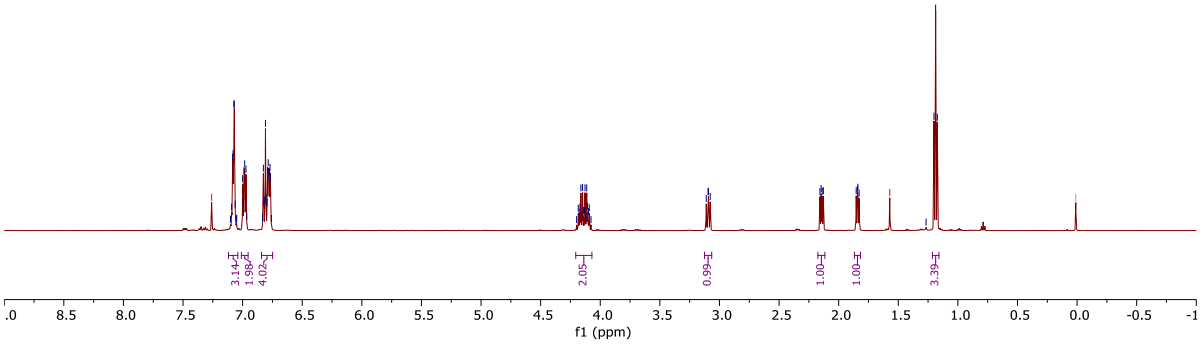


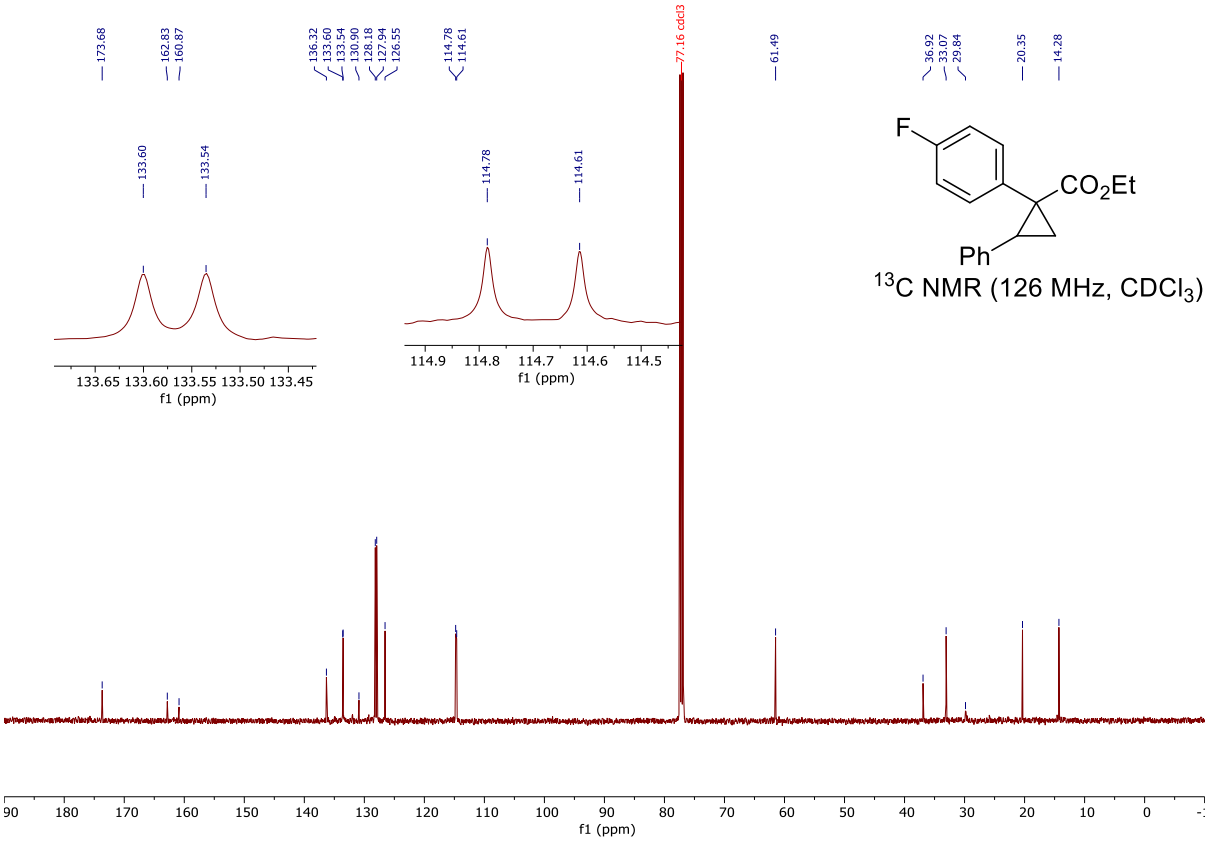


ethyl 1-(4-fluorophenyl)-2-phenylcyclopropane-1-carboxylate (**3x**) (dr 1:>20)

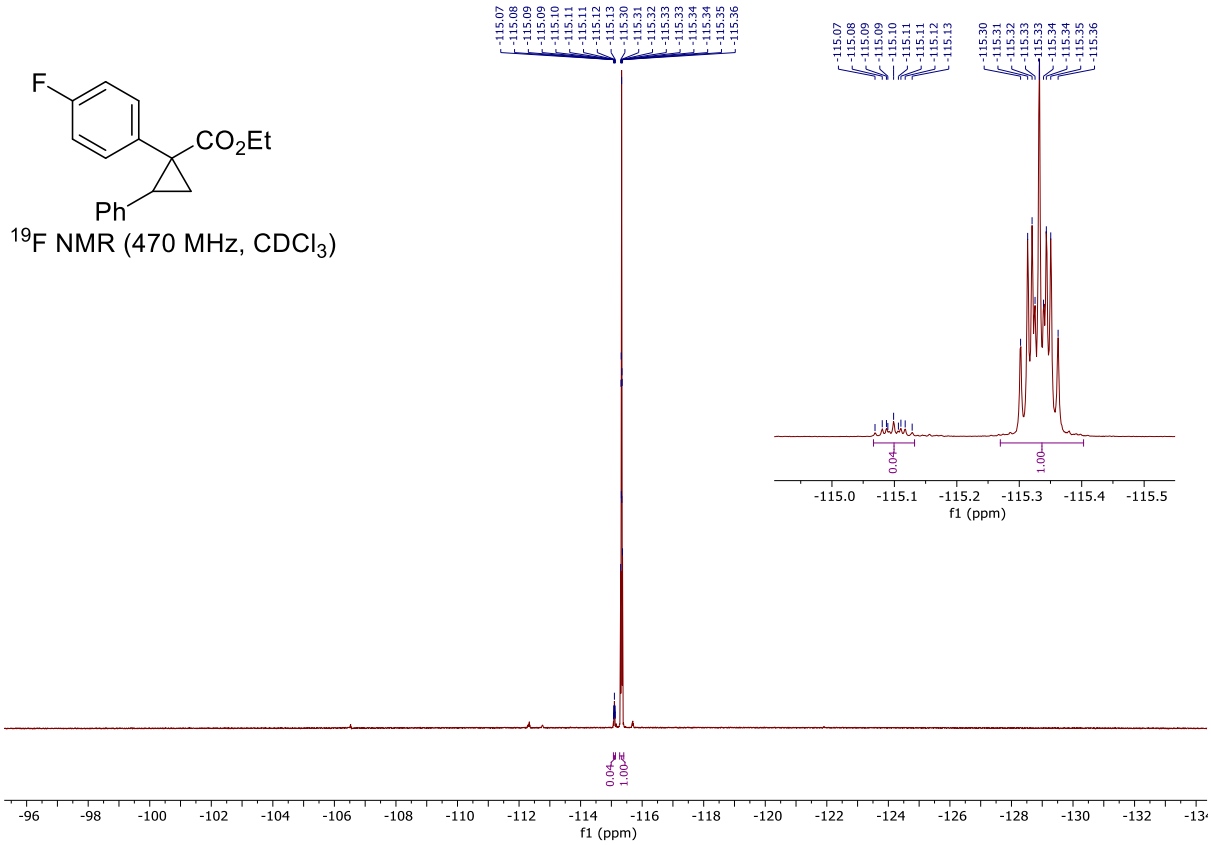


^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)