Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Meinwald-Type Rearrangement of Monosubstituted Epoxides to Methyl Ketones Using an [Al porphyrin]$^+$[Co(CO)$_4$]$^-$ Catalyst

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General Considerations

Methods and Instruments

Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere or in an MBraun Unilab glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven-dried glassware cooled under vacuum. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Varian 300, 400, or 500 MHz instrument at 22 °C with shifts reported relative to the residual solvent peak ($CDCl_3$: 7.26 ppm (^{1}H), and 77.16 ppm (^{13}C)). All *J* values are given in Hertz. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and stored over K_2CO_3.

Gas chromatography (GC) analyses were performed on a Hewlett Packard 6890 gas chromatograph equipped with a Supelco β-Dex120 and a Supelco β-Dex225 column, and a flame ionization detector. Helium (Airgas, UHP grade) was used as carrier gas. Quantitative GC analysis to determine the yield of volatile products was performed by adding the internal standard dodecane to the reaction mixture. Response factors for the products relative to the internal standard were obtained using commercially available materials. HRMS analyses were performed on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source.

Gel permeation chromatography (GPC) analyses were carried out using an Agilent Technologies PL-GPC 50 Integrated GPC equipped with a UV detector and a refractive index detector as well as a Polymer Laboratories PL-AL RT GPC autosampler. The GPC used two PL gel Mini-MIX C columns (5 micron, 4.6 mm ID). The GPC columns were eluted with THF at 30 °C at 0.3 ml/min and were calibrated using monodisperse polystyrene standards.

Chemicals

Anhydrous 1,4-dioxane was purchased from Sigma-Aldrich and degassed via three freeze-pump-thaw cycles prior to use. Thiophene free benzene was purchased from EMD Millipore and dried over activated 3Å molecular sieves and sparged vigorously with nitrogen for 40 minutes prior to first use. Anhydrous toluene, dichloromethane (DCM), hexanes, diethyl ether, and tetrahydrofuran (THF) were purchased from Fischer Scientific and sparged vigorously with nitrogen for 40 minutes prior to first use. The solvents were further purified by passing them under nitrogen pressure through two packed columns of neutral alumina (tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Tetrahydrofuran, diethyl ether, and dichloromethane were degassed via three freeze-pump-thaw cycles prior to use. All

epoxides used in this study except **2n** were dried over calcium hydride and degassed via three freeze-pump-thaw cycles prior to use. Epoxide **2n** was dried overnight over activated 3Å molecular sieves, filtered, and degassed via three freeze-pump-thaw cycles prior to use. All non-dried solvents used were reagent grade or better and used as received.

All other chemicals were purchased from Aldrich, Alfa-Aesar, TCI America, or Macron and used as received.

The following compounds were prepared according to literature procedures:

a) catalysts and catalyst precursors

$NaCo(CO)_4$[1]

[*p*ClTPPAl(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ (**1**, *p*ClTPPAl(THF)$_2^+$ = bis(tetrahydrofuran)-*meso*-tetra(4-chlorophenyl)porphyrinato aluminum)[2]

(BDI)ZnOAc (BDI = *N*-(4-(((1*S*,2*S*)-2-(benyloxy)cyclohexyl)amino)-5,5,5-trifluoropent-3-en-2-ylidene)-2,6-dimethylaniline, ligand 5 from ref 3)[3]

b) epoxides

2-Propyl oxirane (**2d**)[4]

4,5-Epoxypentyl butyrate (**2j**)[5]

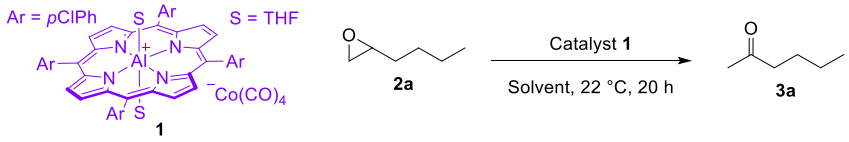
Ethyl 4,5-epoxypentanoate (**2k**)[6]

2-(4-Methoxybenzyl)oxirane (**2m**)[7]

1-(2-Oxiranylmethyl)-cyclopentanol (**2n**)[8]

Expanded Data Tables

Table S1 Expanded Table 1 – Evaluation of solvents and epoxide concentration in the isomerization of epoxide **2a** by $[p\text{ClTPPAl(THF)}_2]^+[\text{Co(CO)}_4]^-$ (**1**) and control experiments with added equivalents of ketone at 2.0 M.



Entry	Mol % **1**	Solvent	Concentration (M)	Acetone (equivalents)	Conversion (%)[a]
1	1	1,4-Dioxane	0.5	0	21
2	1	Benzene	0.5	0	27
3	1	Toluene	0.5	0	31
4	1	Ether	0.5	0	36
5	1	Hexanes	0.5	0	28
6	1	THF	0.5	0	45
7	1	THF	1.0	0	82
8	1	THF	1.5	0	72
9	1	THF	2.0	0	67
10	1	THF	4.0	0	71
11	1	none	8.7	0	38
12	2	THF	1.0	0	>99
13	1	THF	2.0	0	53
14	1	THF	2.0	1	54
15	1	THF	2.0	2	47

[a] Determined by ^{1}H NMR of the crude reaction mixture.

Proposed Cobalt Deactivation by β-Lactone Formation

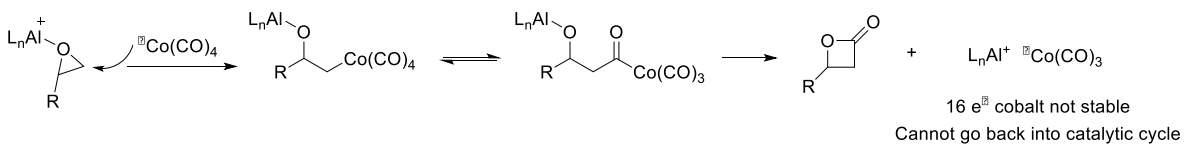
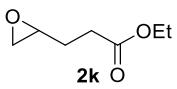
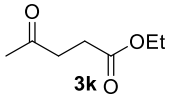
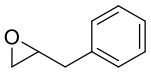
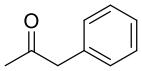
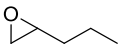
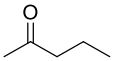
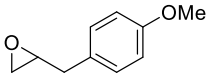
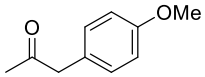
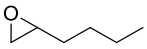
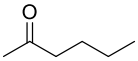
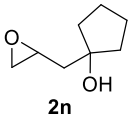
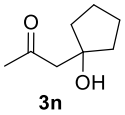
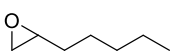
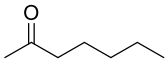
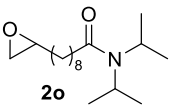
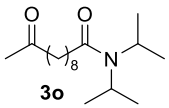
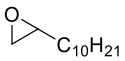
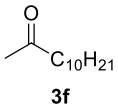
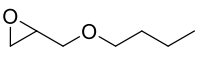
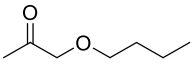
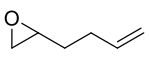
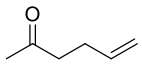
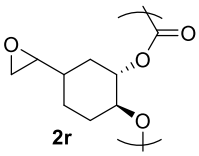
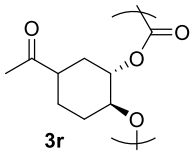
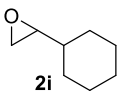
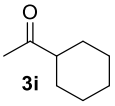
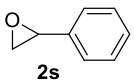
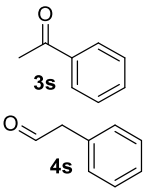
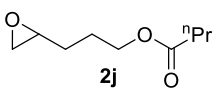
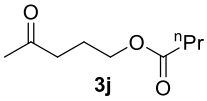
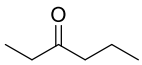


Table S2 Expanded Table 2 – Isolated yields and substrate scope for the rearrangement of monosubstituted epoxides catalyzed by **1**

Entry	Substrate	Product	Yield (%)	Entry	Substrate	Product	Yield (%)
1	 **2b**	 **3b**	96[b]	11	 **2k**	 **3k**	80
2	 **2c**	 **3c**	97[b]	12	 **2l**	 **3l**	86
3	 **2d**	 **3d**	90[b]	13	 **2m**	 **3m**	93
4	 **2a**	 **3a**	96[b]	14	 **2n**	 **3n**	83
5	 **2e**	 **3e**	92[b]	15	 **2o**	 **3o**	95
6	 **2f**	 **3f**	90	16	 **2p**	 **3p**	80
7	 **2g**	 **3g**	89[b]	17[c]	 **2q**	 **3q**	85[b]
8	 **2h**	 **3h**	97[b]	18	 **2r**	 **3r**	76
9	 **2i**	 **3i**	92[b]	19	 **2s**	 **3s** **4s**	Conversion (%)[d] 90 (**3s** : **4s** 1 : 1.6)[e]
10	 **2j**	 **3j**	90	20	 **2t**	 **3t**	31

[a] Conditions: [epoxide] = 1.0 M in THF, 2 mol % catalyst **1**, 22 °C, 18 h. [b] Quantitative GC yield versus dodecane internal standard. [c] 5 mol % catalyst used. [d] Conversion determined by GC or ^{1}H NMR analysis of the crude reaction mixture. [e] Determined by GC analysis.

Synthetic Procedures

General procedure A: Epoxidation of alkenes to epoxides using *m*CPBA

*m*CPBA (Aldrich, ≤77 %) was added in portions at 0 °C to a solution of the corresponding alkene in DCM and the resulting mixture was stirred at room temperature until TLC analysis indicated complete consumption of the alkene. After destroying excess *m*CPBA by adding aqueous $NaHSO_3$, the reaction mixture was filtered through celite, the organic phase washed with $NaHCO_3$ (sat., aq., 3x), dried with sodium sulfate, filtered, and concentrated under reduced pressure.

General procedure B: Isomerization of epoxides with quantitative GC yield

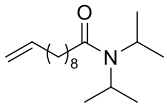
In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with **1**, dodecane, and THF. After 1 minute of stirring at 22 °C, the corresponding epoxide was added to the vial, which was then sealed and left to stir overnight at room temperature. After the indicated time, a drop of the reaction mixture was diluted with ether and passed through a neutral alumina plug to remove the catalyst before being subjected to quantitative GC analysis.

General procedure C: Isomerization of epoxides with isolation

In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with **1** and THF. After 1 minute of stirring at 22 °C, the corresponding epoxide was added to the vial, which was then sealed and left to stir overnight at room temperature. After the indicated time, the vial was taken out of the glove box and a saturated aqueous solution of Rochelle salt (potassium sodium L-(+)-tartrate tetrahydrate) was added and stirred at room temperature overnight. (Note: Rochelle salt binds the aluminum of the catalyst to help with isolation. It was found that stirring for only 1–2 hours resulted in slightly lower isolated yields.) The purple catalyst was filtered off using celite. The resulting green filtrate was extracted with ether 3x and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Ether was used to pass the resulting green oil through a small plug of decolorizing carbon to remove the color, followed by stripping off the solvent to give the pure ketone without the need of further purification.

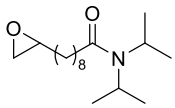
Synthesis of Starting Materials

N,*N*-Bis(1-methylethyl)-10-undecenamide (SM1)



10-Undecenoyl chloride (98%, 10.5 ml, 48.9 mmol) was taken up in benzene (46 ml) and added dropwise to a solution of diisopropyl amine (99%, 13.5 ml, 95.5 mmol) in tetrahydrofuran (80 ml). A white precipitate immediately formed, so an extra 50 ml THF was added throughout the addition to facilitate stirring. After stirring overnight at room temperature, the ammonium chloride salt was filtered off and the resulting solution was washed three times with water and dried over Na_2SO_4. Removing the solvent in vacuo followed by vacuum distillation afforded the title compound (12.6 g, 96%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 17.1, 10.3, 6.7, 1H), 4.89–5.02 (m, 2H), 3.96 (septuplet, *J* = 6.8, 1H), 3.48 (m, 1H), 2.26 (t, *J* = 7.7, 2H), 2.03 (q, *J* = 6.9, 2H), 1.60 (m, 2H), 1.24–1.40 (m, 18H), 1.18 (d, *J* = 6.7, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 171.6, 138.8, 113.9, 48.0, 45.2, 35.1, 33.6, 29.22, 29.21, 29.1, 28.8, 28.7, 25.2, 20.8, 20.5. **IR** (neat, cm^{-1}): 2966, 2924, 2852, 1639, 1437, 1368, 1301, 1214, 1134, 1043, 906. **HRMS** (DART) *m*/*z* calculated for $C_{17}H_{34}NO^+$ $(M + H)^+$ 268.26459, found 268.26341.

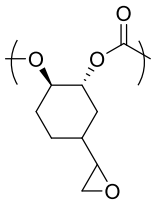
N,*N*-Bis(1-methylethyl)-2-oxiranenonanamide (2o)



Following general procedure A, *N*,*N*-Bis(1-methylethyl)-10-undecenamide (**SM1**, 2.442 g, 9.130 mmol), *m*CPBA (< 77%, 2.664 g, 11.89 mmol), and DCM (20 ml) were used to produce the title compound **2o** (2.304 g, 89%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.96 (septet, *J* = 6.7, 1H), 3.46 (m, 1H), 2.90 (m, 1H), 2.74 (dd, *J* = 5.0, 4.1, 1H), 2.46 (dd, *J* = 5.0, 2.7, 1H), 2.26 (m, 2H), 1.55–1.66 (m, 2H), 1.47–1.55 (m, 2H), 1.39–1.47 (m, 2H), 1.37 (d, *J* = 6.8, 6H), 1.24–1.33 (m, 8H), 1.18 (d, *J* = 6.7, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.1, 52.5, 48.3, 47.2, 45.6, 35.5, 32.6, 29.53, 29.49, 29.47, 26.0, 25.5, 21.1, 20.8. **IR** (neat, cm^{-1}): 2964, 2927, 2853, 1636, 1439, 1369, 1303, 1213, 1133, 1043832. **HRMS** (DART) *m*/*z* calculated for $C_{17}H_{34}NO_2^+$ $(M + H)^+$ 284.25895, found 284.25880.

Note: At this time we are unable to account for the three missing ^{13}C NMR signals except that they are overlapping with other signals. We are still confident in the identity of the product based on the ^{1}H NMR and HRMS data.

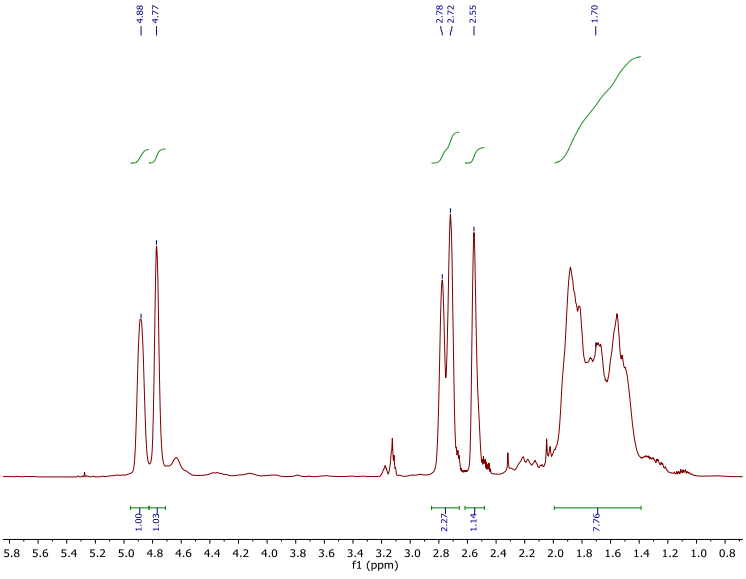
Poly(4-oxiranylcyclohexene carbonate) (2r)



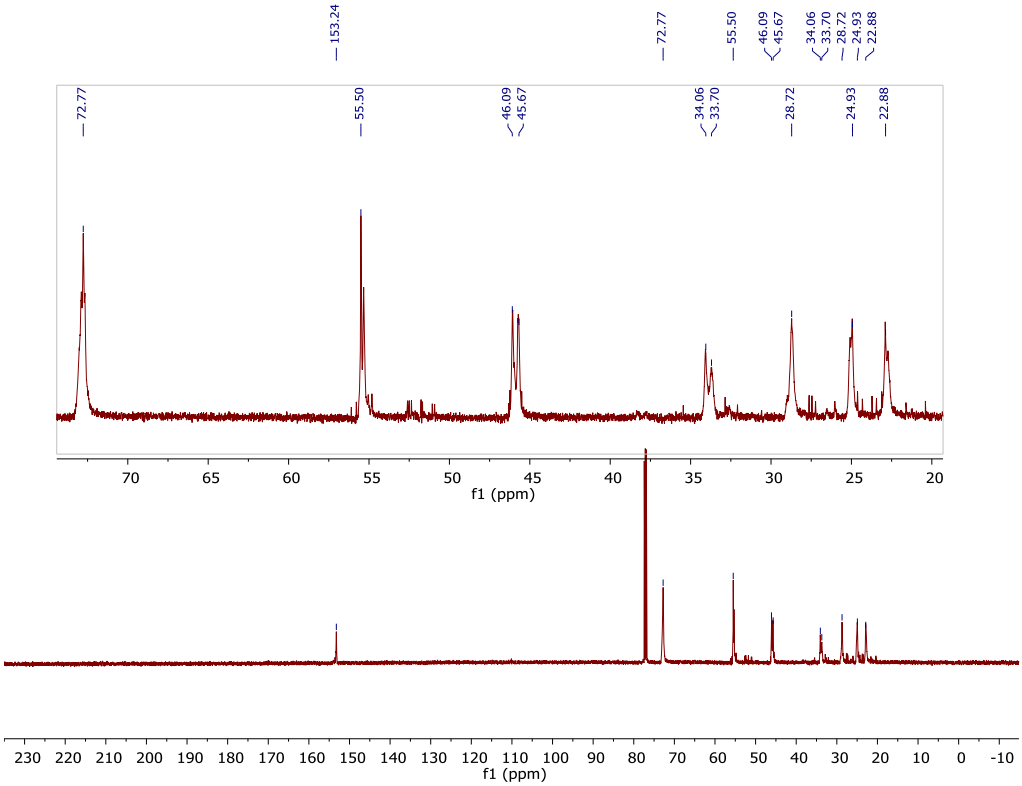
In a glove box, an oven dried Fischer-Porter bottle equipped with a Teflon-coated magnetic stir bar was charged with toluene (1.2 ml), vinylcyclohexene dioxide (0.5 ml, 3.9 mmol), and (BDI)ZnOAc (7.4 mg, 0.012 mmol, 0.31 mol %). The Fischer-Porter bottle was sealed with the reactor head and removed from the box. The vessel was placed in a 0 °C bath and allowed to equilibrate for 10 minutes. The vessel was charged to 100 psig CO_2 and vented to ~30 psig 3 times before being recharged to 100 psig. The vessel was left open to 100 psig for 5 minutes at 0 °C to allow saturation of the reaction mixture. The vessel was stirred at 0 °C for ~2 hours before being vented to atmospheric pressure and warmed to room temperature (Note: the polymerization was stopped at ~2 hours, corresponding to 10–20% conversion, to avoid crosslinking). The reaction mixture was diluted with ~1 mL DCM and precipitated into 100 mL rapidly stirring methanol. The polymer (106 mg, 15%) was isolated by vacuum filtration and dried in vacuo at 22 °C overnight to give a white powdery precipitate. **^{1}H NMR** (400 MHz, CDCl3): δ 4.88 (br m, 1H), 4.77 (br m, 1H), 2.78 (br m, 1H), 2.72 (br m, 1H), 2.55 (br m, 1H), 1.38–1.98 (br m, 7H). **IR** (neat, cm−1): 2936, 1739, 1228, 1153, 960, 854, 785. **GPC**: M_n = 15,300 g/mol, M_w = 25,500 g/mol, PDI = 1.67.

Note: broad ^{1}H NMR resonances are normal for polymers because of very similar, but not identical environments of each enchained monomer. This is exacerbated by the use of a diastereomeric mixture of monomers.

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



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



Isomerization of Monosubstituted Epoxides to Ketones

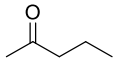
Acetone (3b)

Following general procedure B, **2b** (19.0 mg, 0.327 mmol), dodecane (18.7 mg, 0.110 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 7.5 mg, 0.0070 mmol, 2.1%) in THF (0.35 mL). Quantitative GC analysis resulted in 96% yield.

2-Butanone (3c)

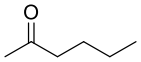
Following general procedure B, **2c** (25.9 mg, 0.359 mmol), dodecane (18.9 mg, 0.111 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 7.6 mg, 0.0071 mmol, 2.0%) in THF (0.35 mL). Quantitative GC analysis resulted in 97% yield.

2-Pentanone (3d)



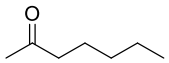
Following general procedure B, **2d** (33.9 mg, 0.394 mmol), dodecane (19.3 mg, 0.113 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 8.5 mg, 0.0079 mmol, 2.0%) in THF (0.4 mL). Quantitative GC analysis resulted in 90% yield.

2-Hexanone (3a)



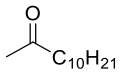
Following general procedure B, **2a** (36.7 mg, 0.367 mmol), dodecane (19.0 mg, 0.112 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 7.5 mg, 0.0070 mmol, 1.9%) in THF (0.35 mL). Quantitative GC analysis resulted in 96% yield.

2-Heptanone (3e)



Following general procedure B, **2e** (33.1 mg, 0.290 mmol), dodecane (17.2 mg, 0.101 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 6.6 mg, 0.0061 mmol, 2.1%) in THF (0.3 mL). Quantitative GC analysis resulted in 92% yield.

2-Dodecanone (3f)



Following general procedure C, **2f** (370.0 mg, 2.007 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 43.0 mg, 0.0399 mmol, 2.0%) in THF (2 mL) were used to produce **3f** (332.1 mg, 90%) as a colorless oil. Analytical data for **3f** matched those previously been reported.[9] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.40 (t, *J* = 7.5, 2H), 2.12 (s, 3H), 1.54 (m, 2H), 1.24 (m, 14H), 0.86 (t, *J* = 6.5, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 209.3, 43.9, 32.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 24.0, 22.8, 14.2.

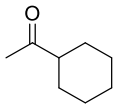
3-Methyl-2-butanone (3g)

Following general procedure B, **2g** (29.5 mg, 0.343 mmol), dodecane (18.6 mg, 0.109 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 7.6 mg, 0.0071 mmol, 2.1%) in THF (0.35 mL). Quantitative GC analysis resulted in 89% yield.

3,3-Dimethyl-2-butanone (3h)

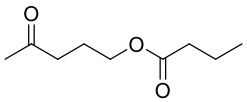
Following general procedure B, **2h** (33.1 mg, 0.330 mmol), dodecane (18.7 mg, 0.110 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 7.5 mg, 0.0070 mmol, 2.1 %) in THF (0.35 mL). Quantitative GC analysis resulted in 97% yield.

Cyclohexyl methyl ketone (3i)



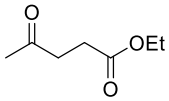
Following general procedure C, **2i** (109.2 mg, 0.865 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 21.5 mg, 0.020 mmol, 2.3%) in THF (1 mL) to give **3i** (79.3 mg, 73%). Quantitative GC analysis resulted in 92% yield. The difference is attributed to the volatility of the compound. Analytical data for **3i** matched those previously been reported.[10] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.27–2.26 (m, 1H), 2.12 (s, 3H), 1.83–1.90 (m, 2H), 1.73–1.80 (m, 2H), 1.63–1.69 (m, 1H), 1.14–1.38 (m, 5H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.4, 51.6, 28.6, 28.0, 26.0, 25.8.

4-Oxopentyl ester butanoic acid, (3j)



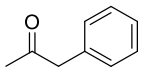
Following general procedure C, **2j** (347.6 mg, 2.018 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 43.3 mg, 0.0402 mmol, 2.0%) in THF (2 mL) were used to produce **3j** (313.6 mg, 90%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.07 (t, *J* = 6.4, 2H), 2.51 (t, *J* = 7.2, 2H), 2.27 (t, *J* = 7.4, 2H), 2.16 (s, 3H), 1.91 (app quintet, *J* = 6.6, 2H), 1.64 (sextet, *J* = 7.4, 2H), 0.94 (t, *J* = 7.4, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 207.6, 173.6, 63.3, 39.9, 36.1, 29.9, 22.9, 18.4, 13.7. **IR** (neat, cm^{-1}): 2959, 2873, 1710, 1714, 1354, 1163, 1087, 981, 729. **HRMS** (DART) *m*/*z* calculated for $C_9H_{16}O_3^+$ $(M + H)^+$ 173.11722, found 173.11745.

Ethyl-4-oxopentanoate (3k)



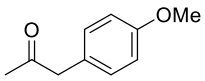
Following general procedure C, **2k** (54.8 mg, 0.380 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 8.6 mg, 0.00799 mmol, 2.1%) in THF (0.4 mL) were used to produce **3k** (44.0 mg, 80%) as a colorless oil. Analytical data for **3k** matched those previously been reported.[11] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.12 (q, *J* = 7.1, 2H), 2.4 (t, *J* = 6.6, 2H), 2.56 (t, *J* = 6.6, 2H), 2.19 (s, 3H), 1.25 (t, *J* = 7.1, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$): δ 206.8, 172.8, 60.6, 38.0, 29.9, 28.0, 14.2.

1-Phenylpropan-2-one (3l)



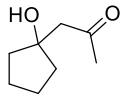
Following general procedure C, **2l** (40.1 mg, 0.299 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 6.5 mg, 0.00603 mmol, 2.0%) in THF (0.3 mL) were used to produce **3l** (34.4 mg, 86%) as a colorless oil. Analytical data for **3l** matched those previously been reported.[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.39 (m, 2H), 7.27–7.32 (m, 1H), 7.21–7.25 (m, 2H), 3.72 (s, 2H), 2.18 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 206.2, 134.3, 129.4, 128.7, 127.0, 50.9, 29.2.

1-(4-Methyoxyphenyl)-2-propanone (3m)



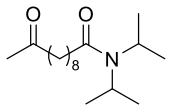
Following general procedure C, **2m** (65.2 mg, 0.397 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 8.5 mg, 0.00790 mmol, 2.0%) in THF (0.4 mL) were used to produce **3m** (60.6 mg, 93%) as a colorless oil. Analytical data for **3m** matched those previously been reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10–7.15 (m, 2H), 6.85–6.89 (m, 2H), 3.80 (s, 3H), 3.63 (s, 2H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 206.9, 158.7, 130.4, 126.3, 114.2, 55.3, 50.1, 29.2.

1-(1-Hydroxycyclopentyl)-2-propanone (3n)



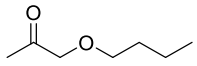
Following general procedure C, **2n** (285.1 mg, 2.00 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 43.2 mg, 0.0401 mmol, 2.0%) in THF (2 mL) were used to produce **3n** (238.0 mg, 83%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.46 (s, 1H), 2.76 (s, 2H), 2.18 (s, 3H), 1.77–1.87 (m, 4H), 1.56–1.64 (m, 2H), 1.40–1.50 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 210.9, 79.9, 52.9, 39.9, 31.4, 23.8. **IR** (neat, cm^{-1}): 3404 (br), 2951, 2866, 1697, 1355, 1162, 1025, 798. **HRMS** (DART) *m*/*z* calculated for $C_8H_{15}O_2^+$ $(M + H)^+$ 143.10666, found 143.10684.

***N*,*N*-Bis(1-methylethyl)-10-oxo-undecanamide (3o)**



Following general procedure C, **2o** (55.0 mg, 0.194 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 4.3 mg, 0.00399 mmol, 2.1%) in THF (0.2 mL) were used to produce **3o** (52.3 mg, 95%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.95 (septuplet, *J* = 6.7, 1H), 3.47 (m, 1H), 2.41 (t, *J* = 7.5, 2H), 2.25 (m, 2H), 2.13 (s, 3H), 1.50–1.64 (m, 4H), 1.37 (d, *J* = 6.8, 6H), 1.23–1.34 (m, 8H), 1.18 (d, *J* = 6.7, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 209.5, 172.1, 48.3, 45.6, 43.8, 35.5, 30.4, 29.9, 29.5, 29.4, 29.3, 29.2, 25.5, 23.9, 21.1, 20.8. **IR** (neat, cm^{-1}): 2923, 2852, 1714, 1634, 1441, 1368, 1044. **HRMS** (DART) *m*/*z* calculated for $C_{17}H_{34}NO_2^+$ $(M + H)^+$ 284.25841, found 284.25816.

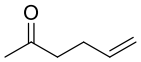
1-Butoxy-2-propanone (3p)



Following general procedure C, **2p** (195.6 mg, 1.502 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 32.3 mg, 0.0300 mmol, 2.0%) in THF (1.5 mL) were used to produce **3p** (157.3 mg, 80%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.01 (s, 2H), 3.48 (t, *J* = 6.6, 2H), 2.16 (s, 3H), 1.60 (m, 2H), 1.39 (m, 2H),

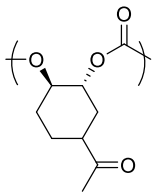
0.93 (t, J = 7.4, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 207.3, 76.4, 71.5, 31.6, 26.3, 19.2, 13.8. **IR** (neat, cm^{-1}): 2959, 2933, 2870, 1719, 1354, 1118. **HRMS** (DART) *m/z* calculated for $C_7H_{15}O_2^+$ $(M + H)^+$ 131.10666, found 131.10701.

5-Hexene-2-one (3q)



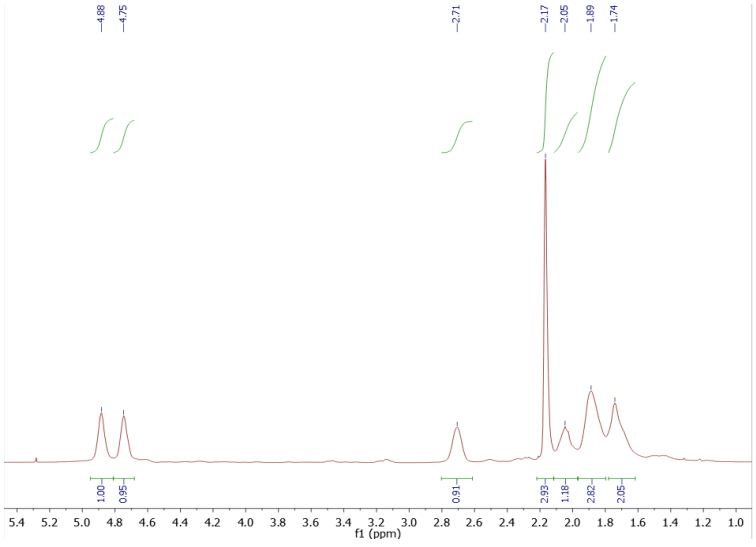
Following general procedure B, **2q** (36.2 mg, 0.369 mmol), dodecane (23.1 mg, 0.136 mmol), [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 21.6 mg, 0.0201 mmol, 5.4%) in THF (0.4 mL). Quantitative GC analysis resulted in 85% yield.

Poly(4-acetylcyclohexene carbonate) (3r)



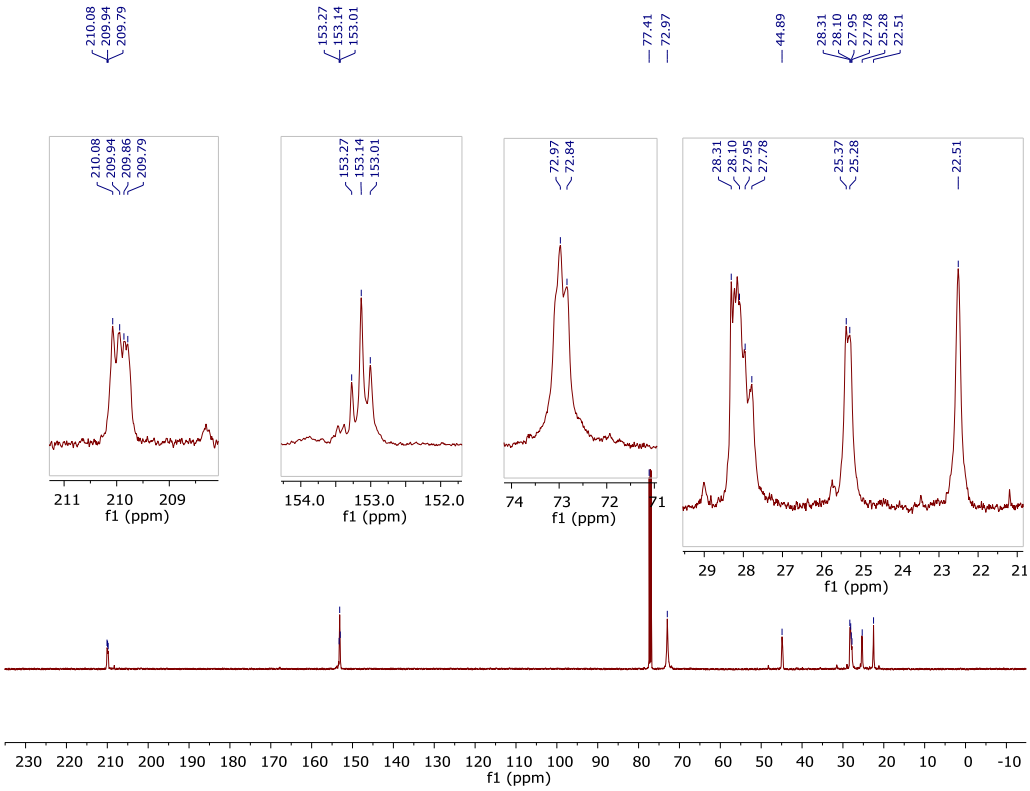
In a glove box, a 1 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with the epoxide-functionalized polycarbonate (**2r**, 48.6 mg, 0.264 mmol epoxide moieties) and [*p*ClTPPAl(THF)$_2$][Co(CO)$_4$] (**1**, 5.9 mg, 0.00548 mmol, 2.1% per epoxide group). THF (0.3 mL) was added and the solution was stirred for 18 hours at room temperature. Dichloromethane was used to dilute the reaction mixture and pass it through a plug of decolorizing carbon to remove the color. One ml methanol was added to promote precipitation before stripping off the solvent to produce **3r** (36.8 mg, 76%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.90 (br m, 1H), 4.76 (br m, 1H), 2.73 (br m, 1H), 2.19 (br s, 3H), 2.05 (br m, 1H), 1.90 (br m, 3H), 1.76 (br m, 2H). **IR** (neat, cm^{-1}): 2940, 1741, 1703, 1228, 1153, 959, 782. **GPC**: M_n = 15,500 g/mol, M_w = 27,600 g/mol, PDI = 1.78.

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



Note: broad ^{1}H NMR resonances are normal for polymers because of very similar, but not identical environments of each enchained monomer. This is exacerbated by the use of a diastereomeric mixture of monomers.

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



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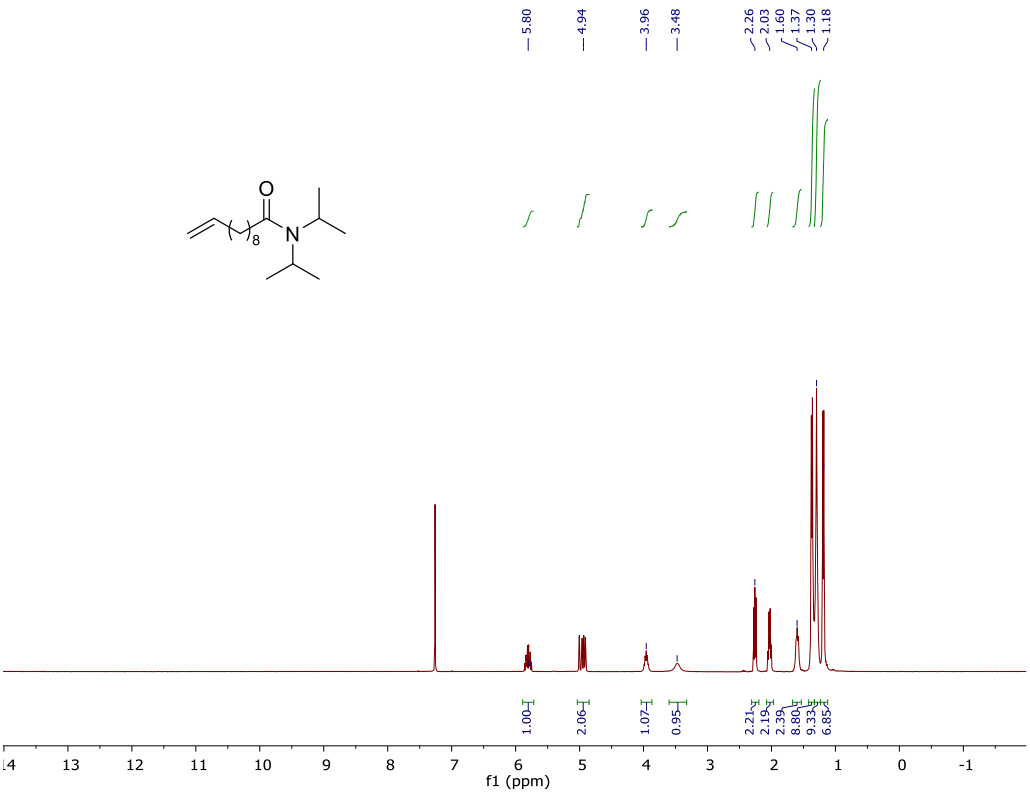
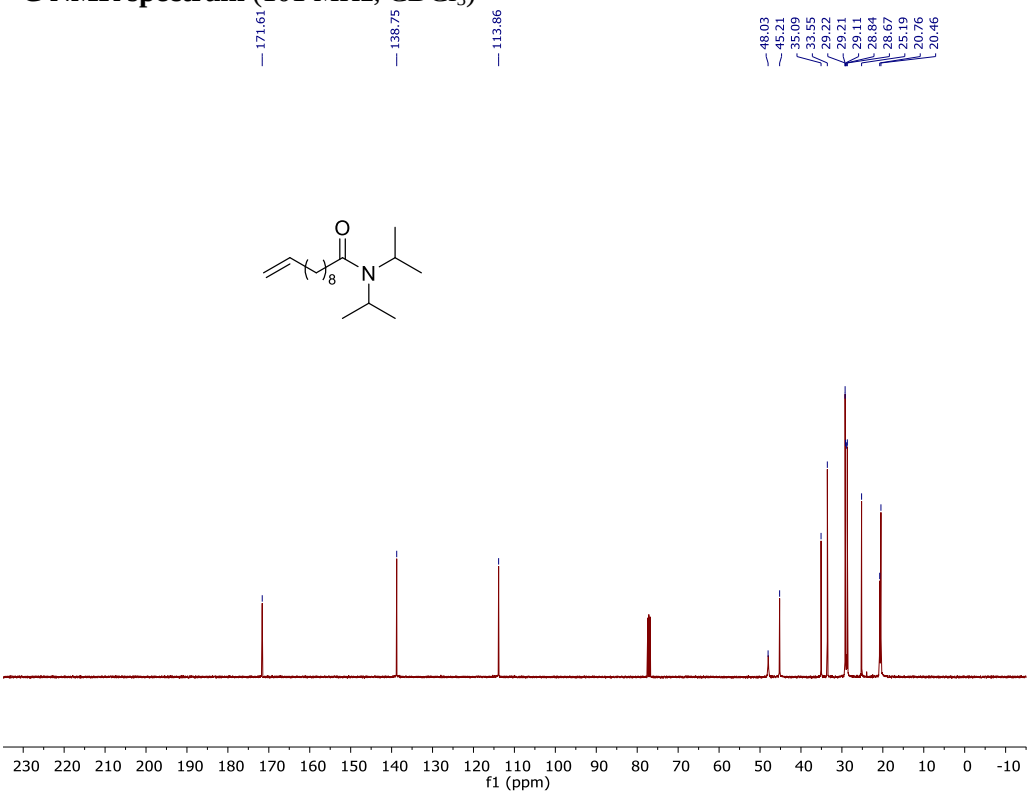
Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

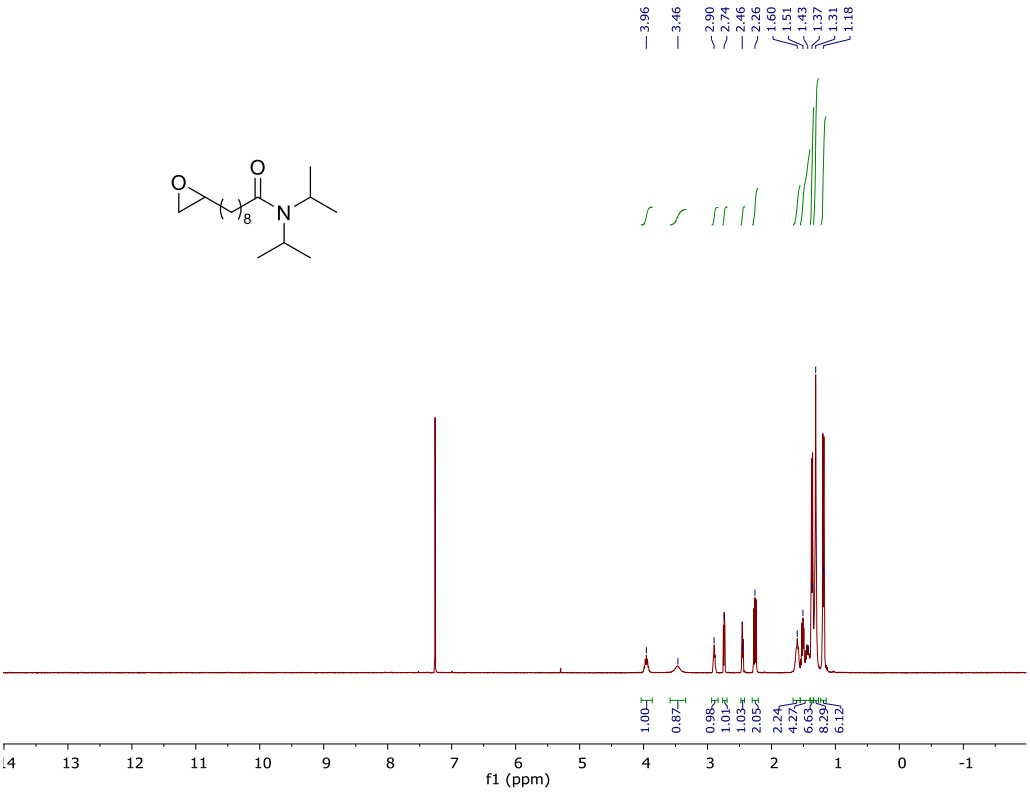
***N*,*N*-Bis(1-methylethyl)-10-undecenamide (SM1), ^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



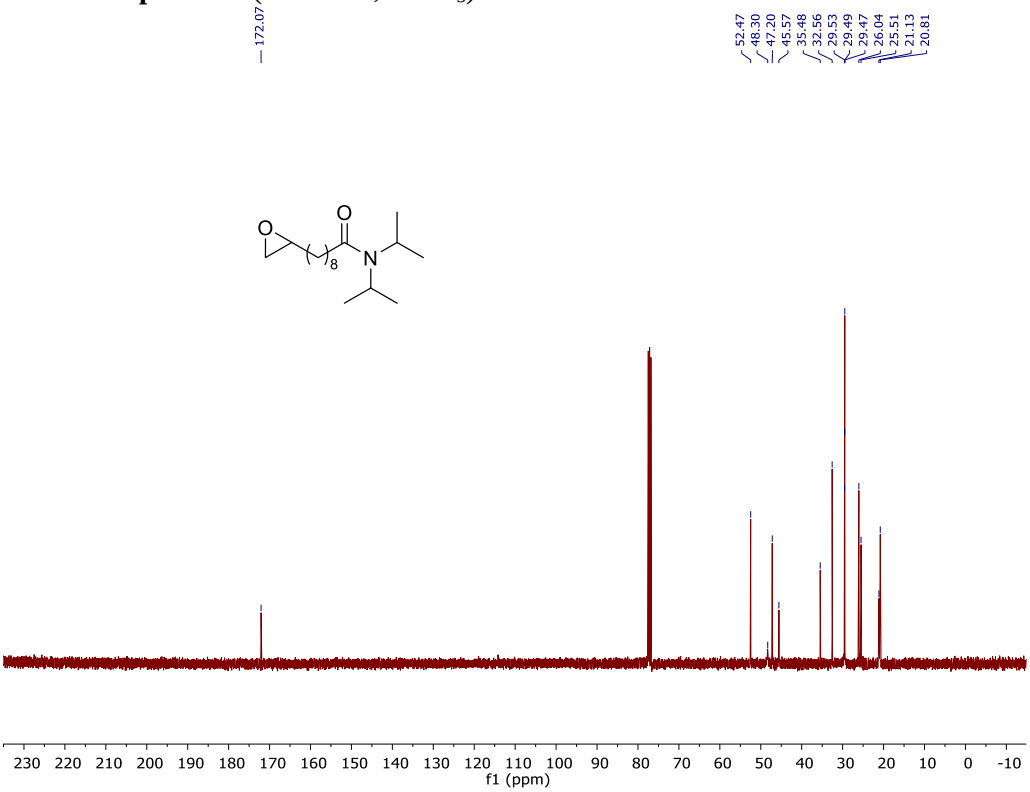
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



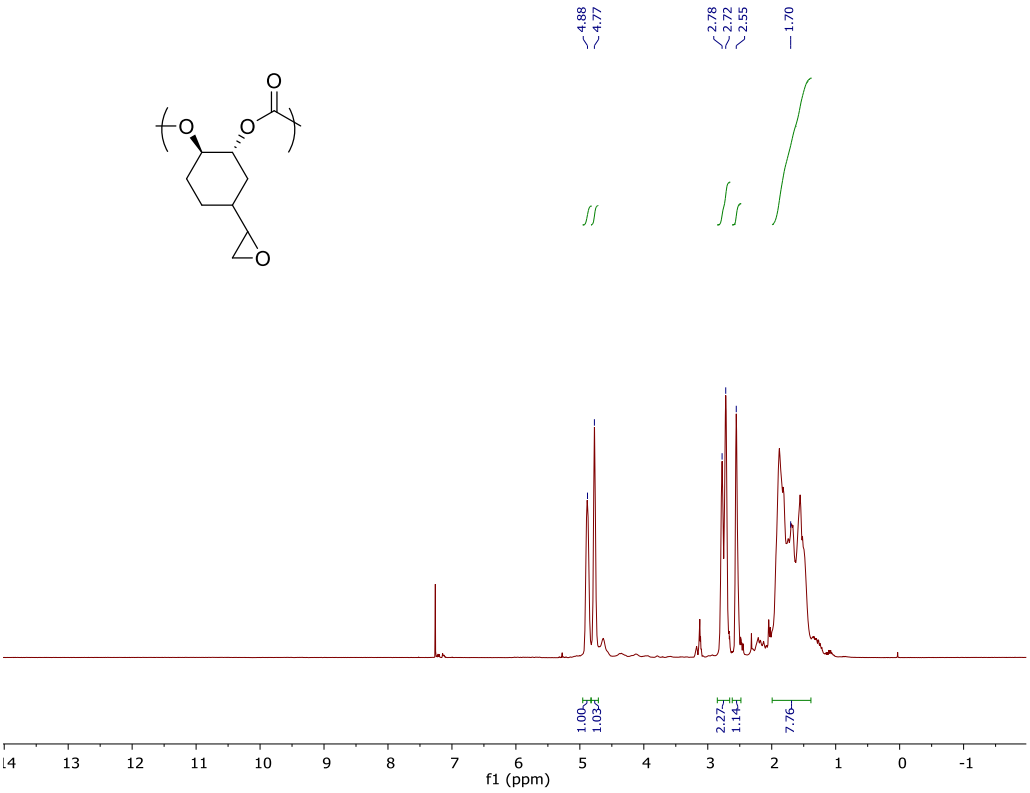
***N*,*N*-Bis(1-methylethyl)-2-oxiranenonanamide (2o), ^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



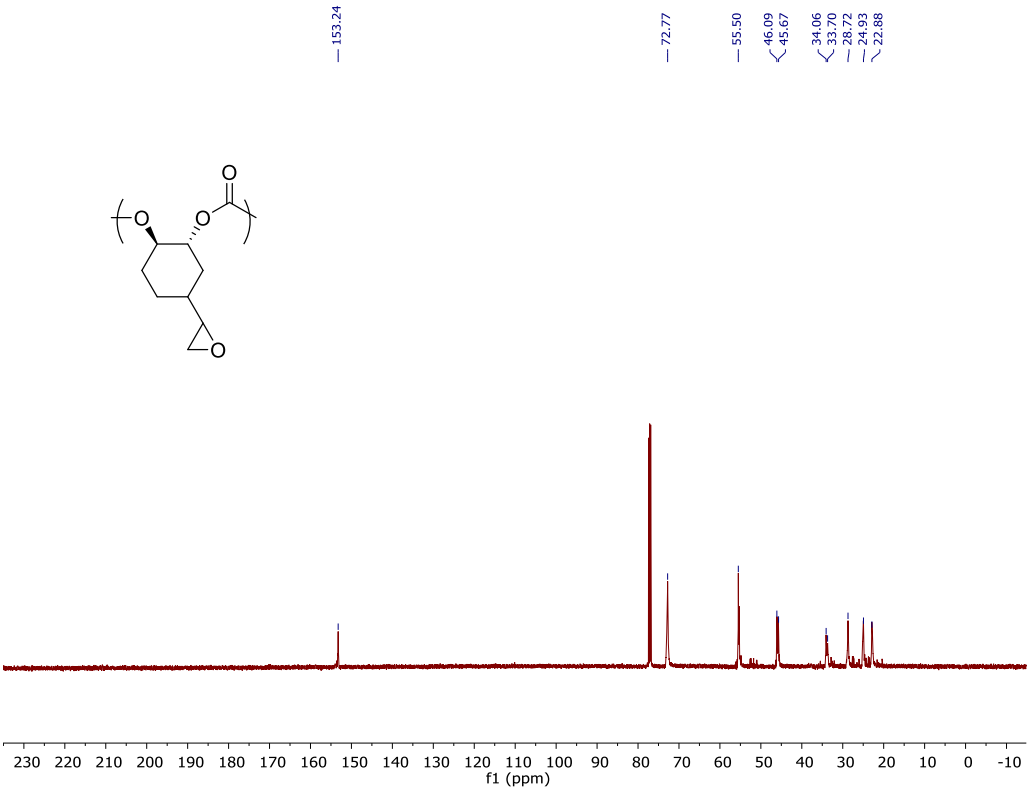
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



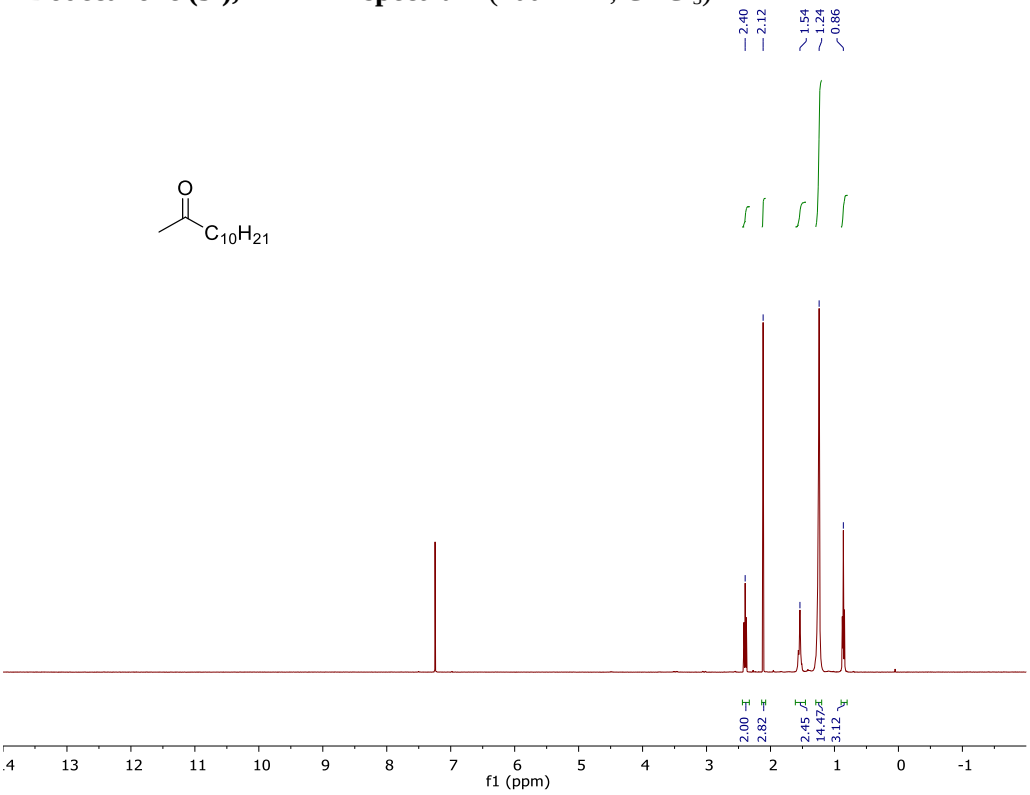
Poly(4-oxiranylcyclohexene carbonate) (2r), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



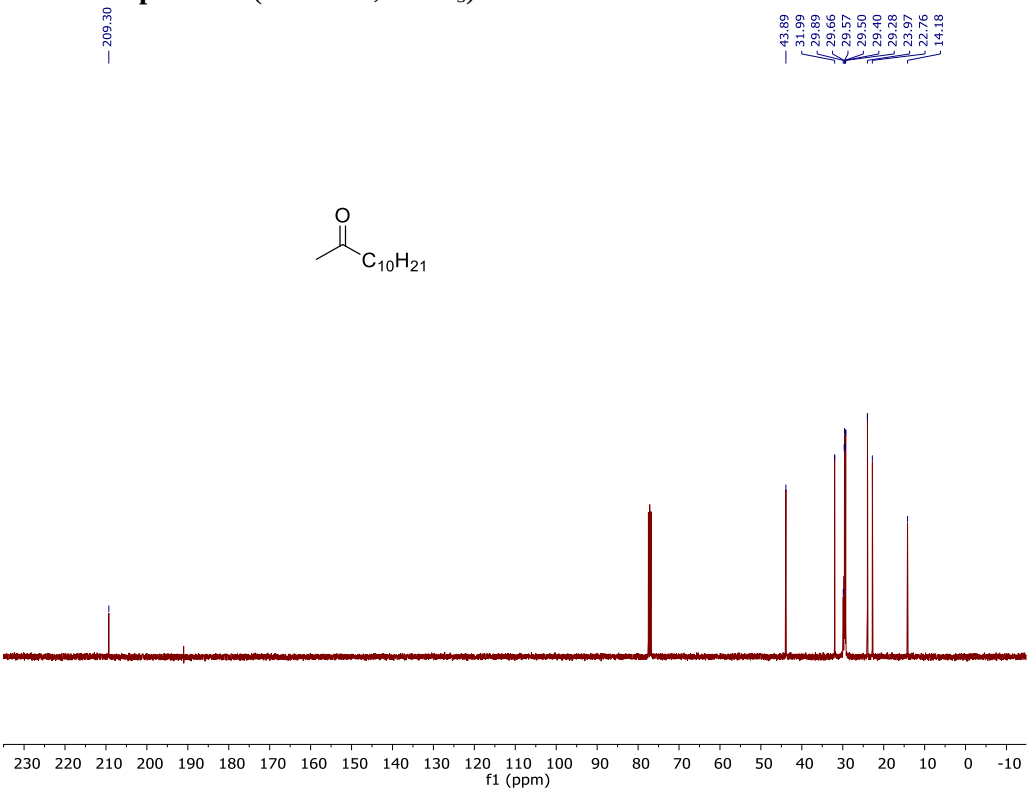
^{13}C NMR spectrum (126 MHz, $CDCl_3$)



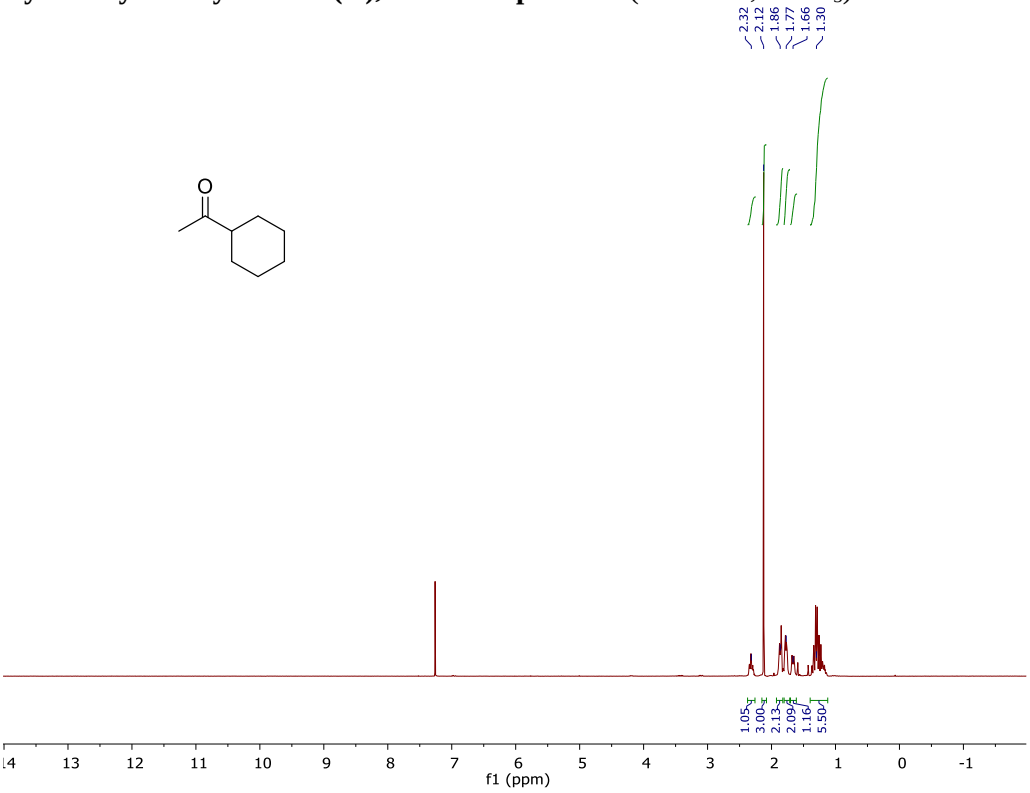
2-Dodecanone (3f), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



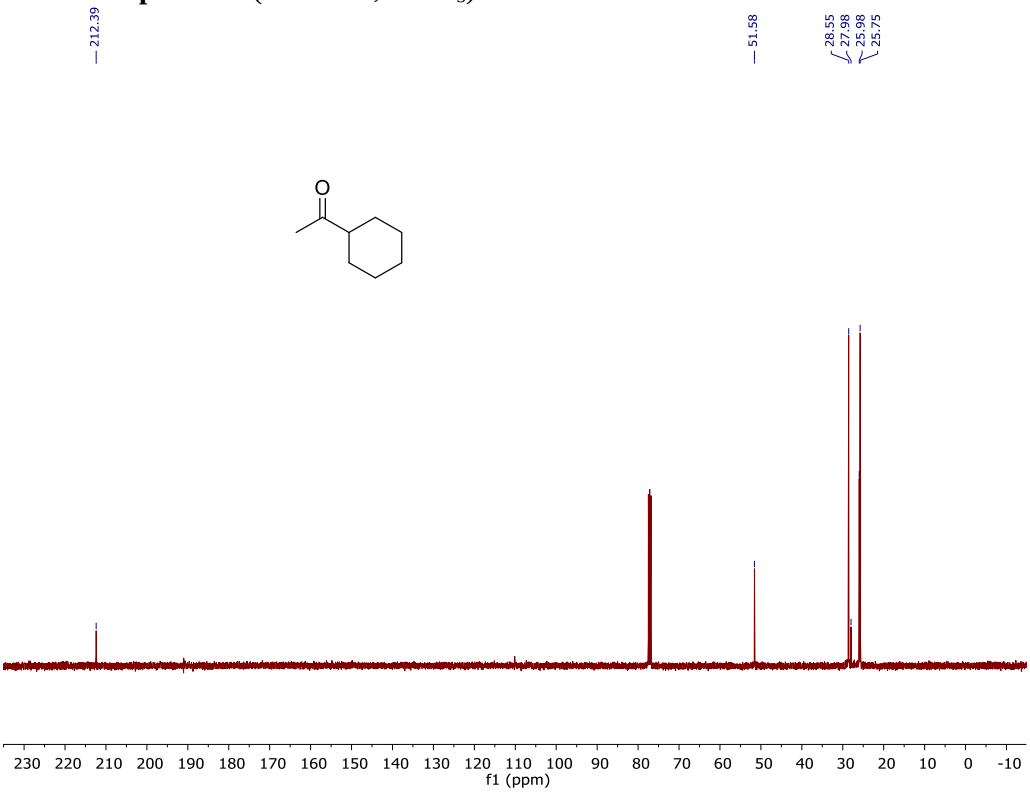
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



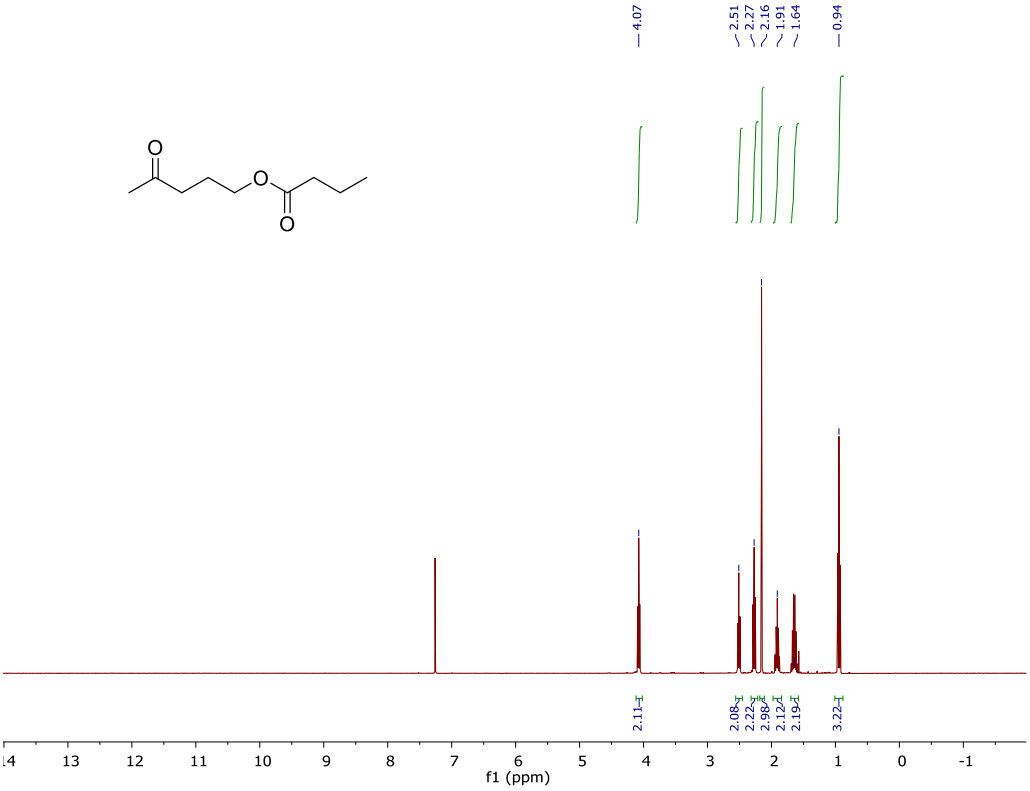
Cyclohexyl methyl ketone (3i), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



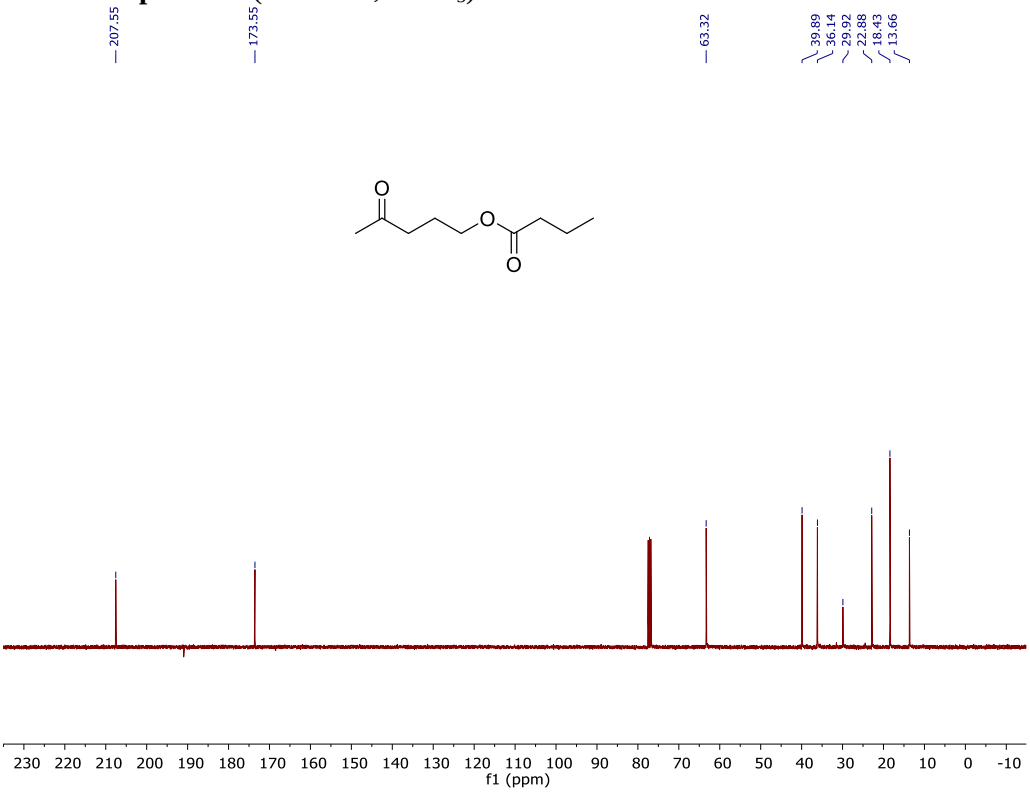
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



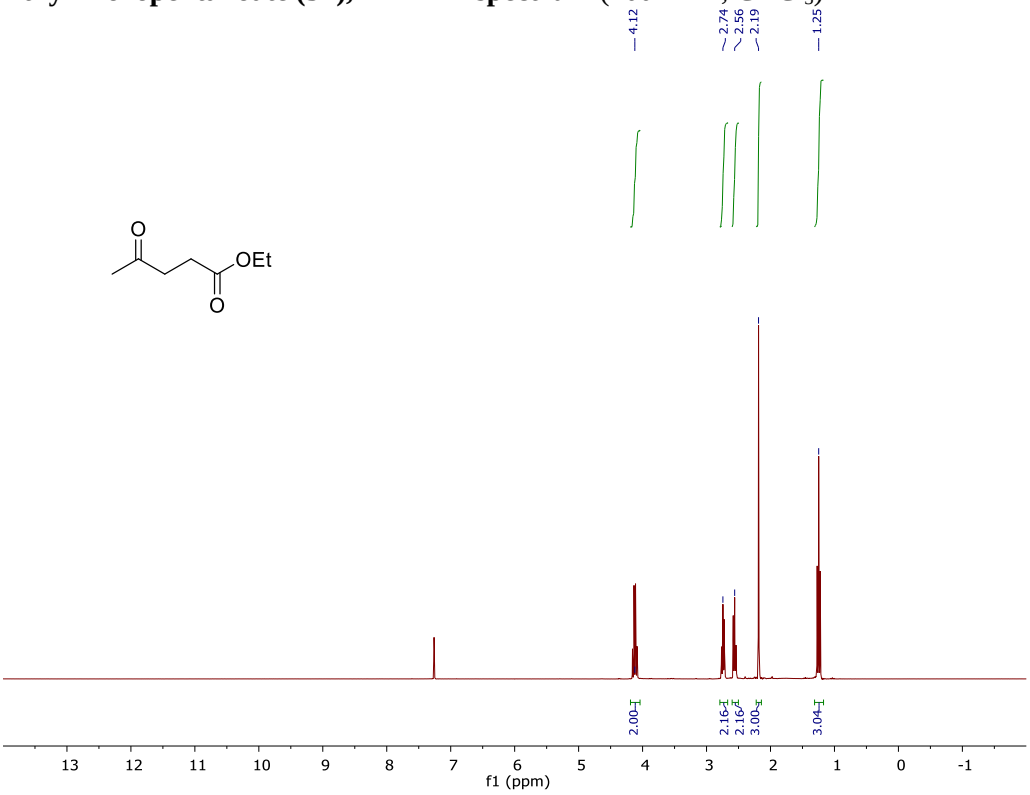
4-Oxopentyl ester butanoic acid, (3j), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



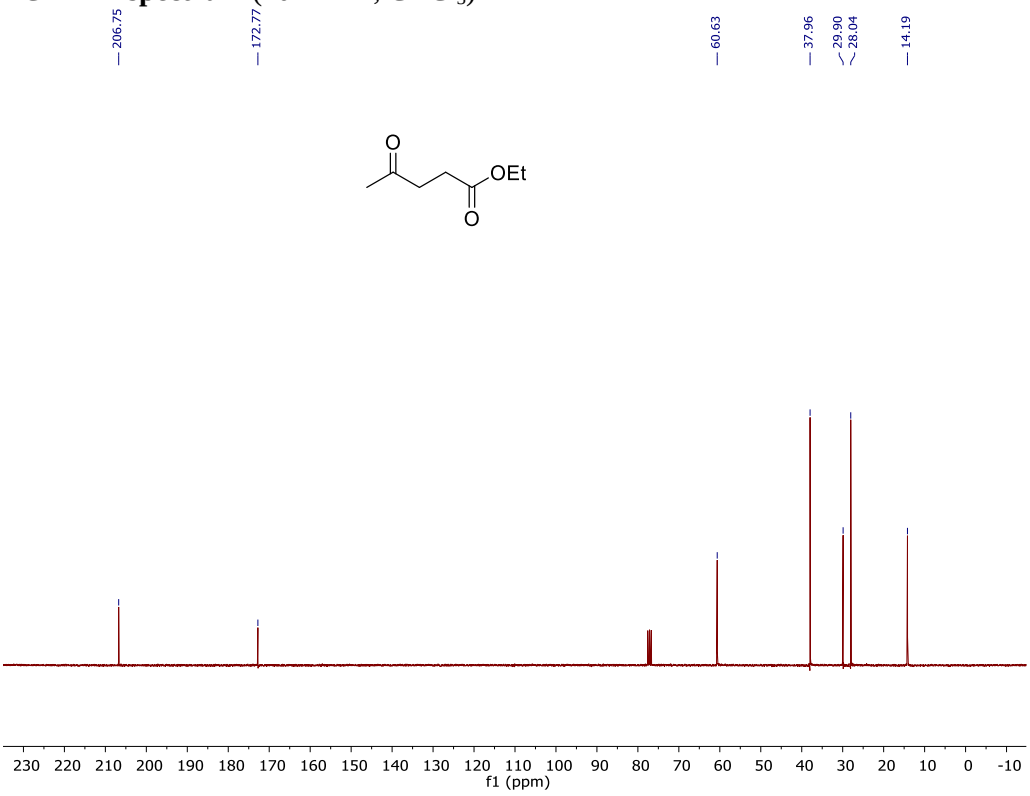
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



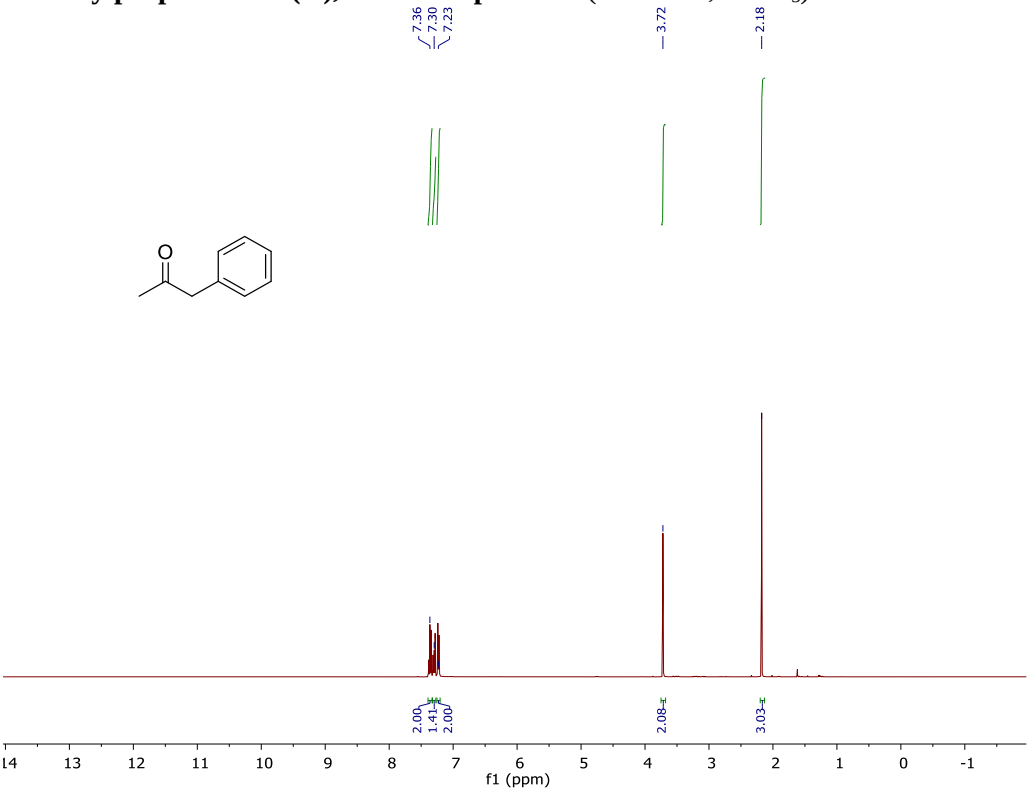
Ethyl-4-oxopentanoate (3k), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



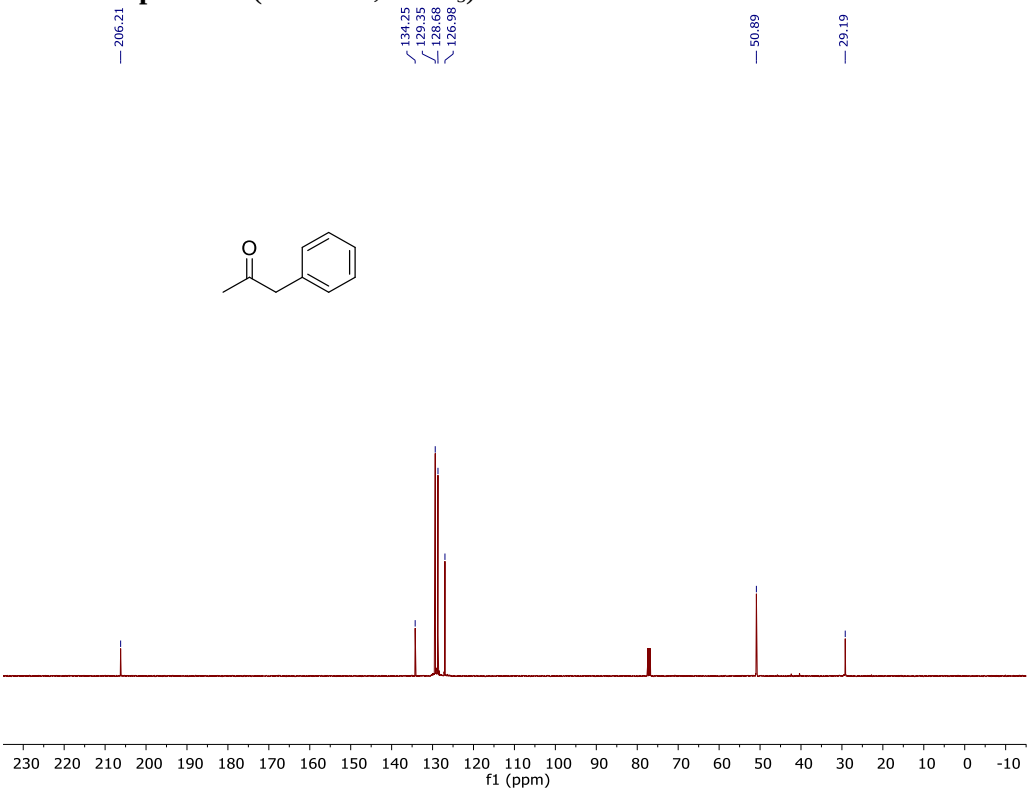
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



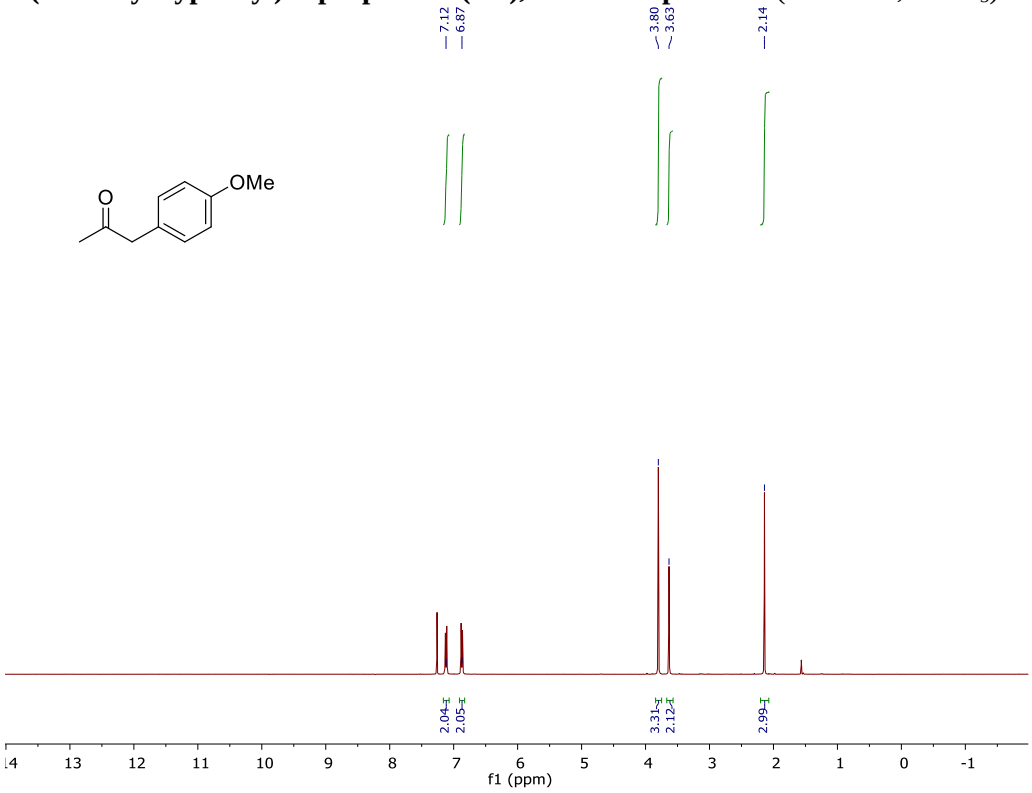
1-Phenylpropan-2-one (3l), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



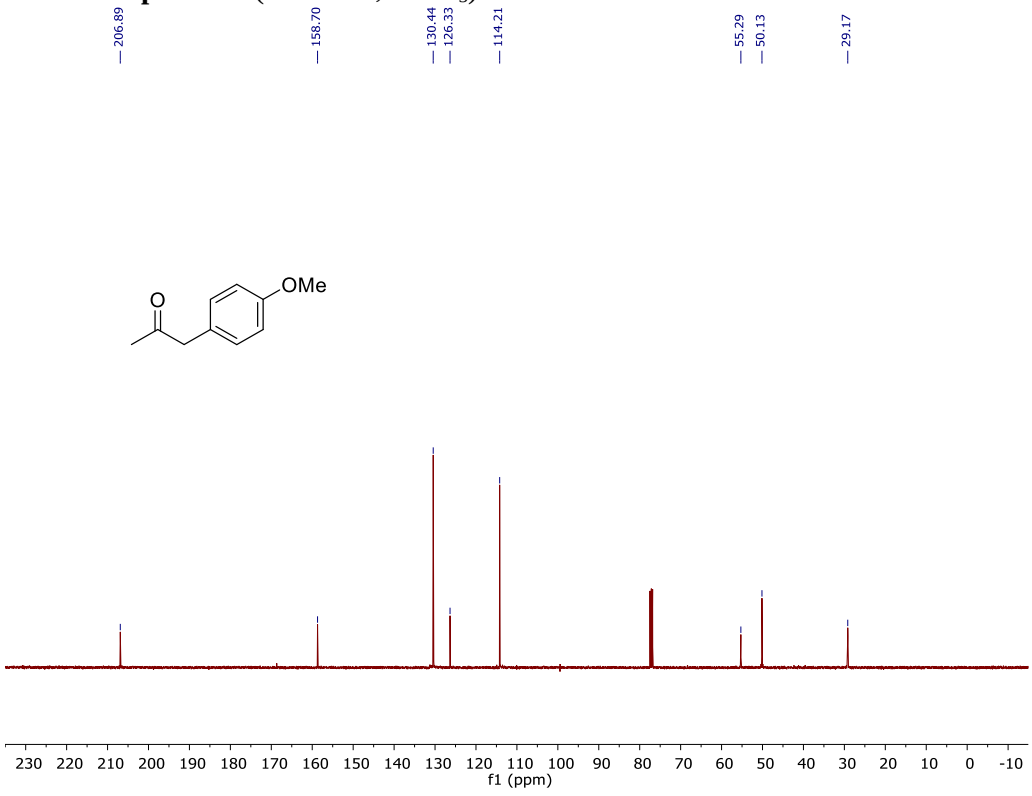
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



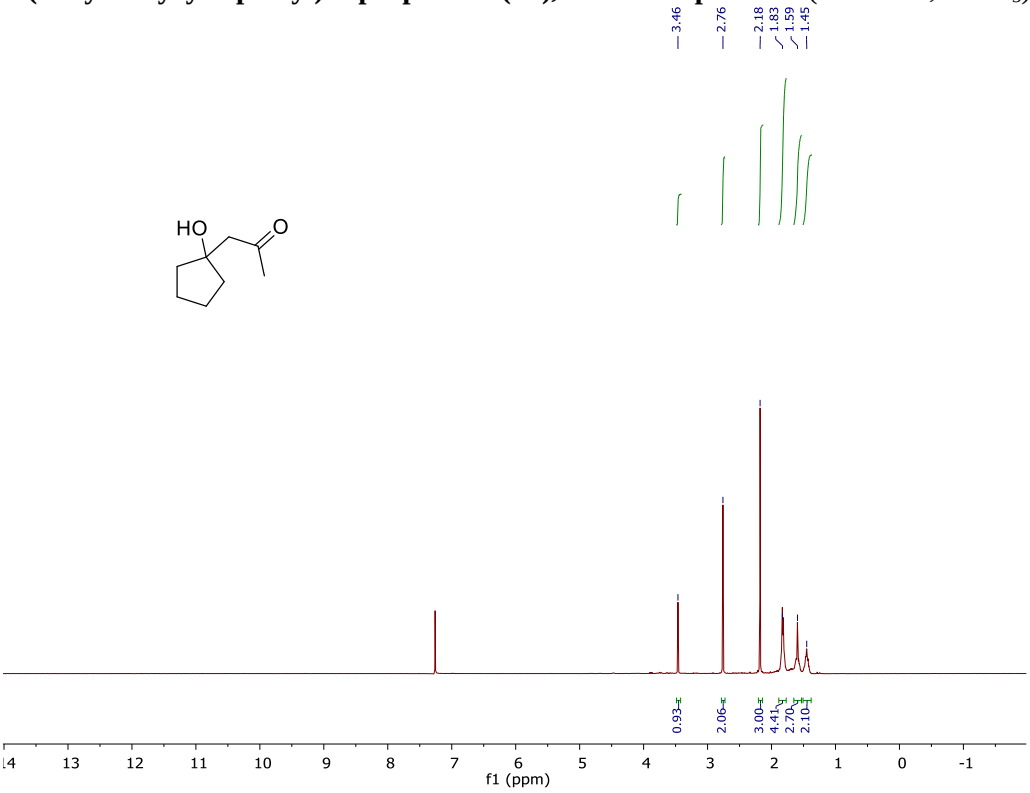
1-(4-Methyoxyphenyl)-2-propanone (3m), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



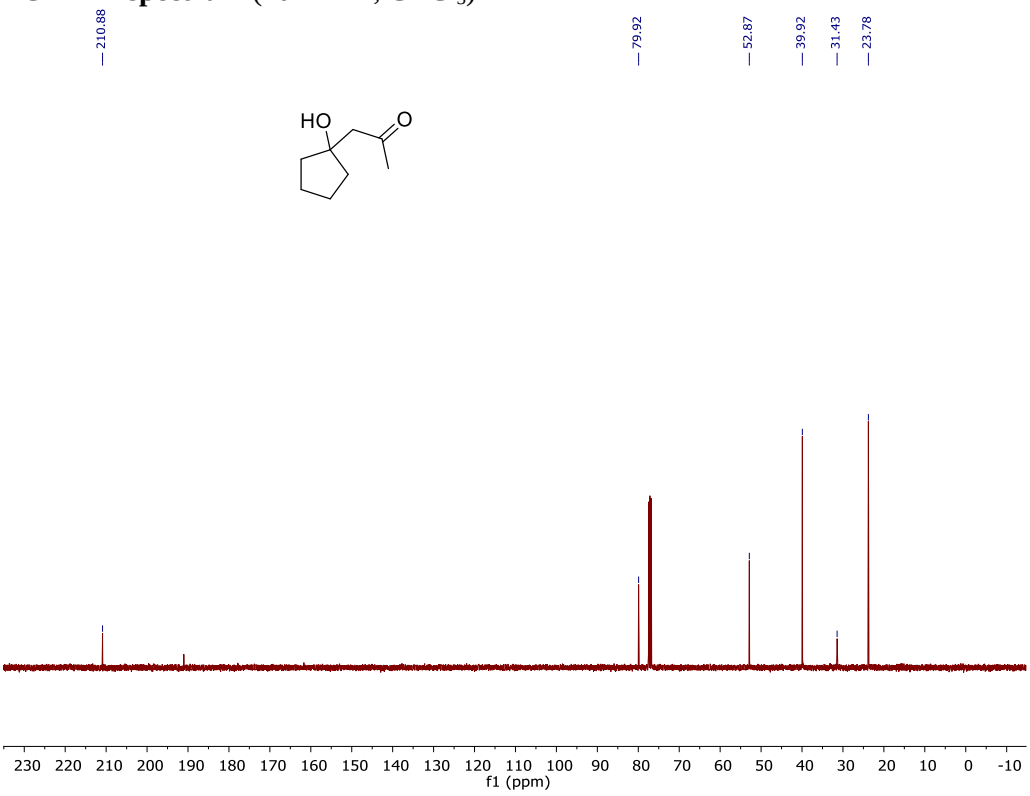
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



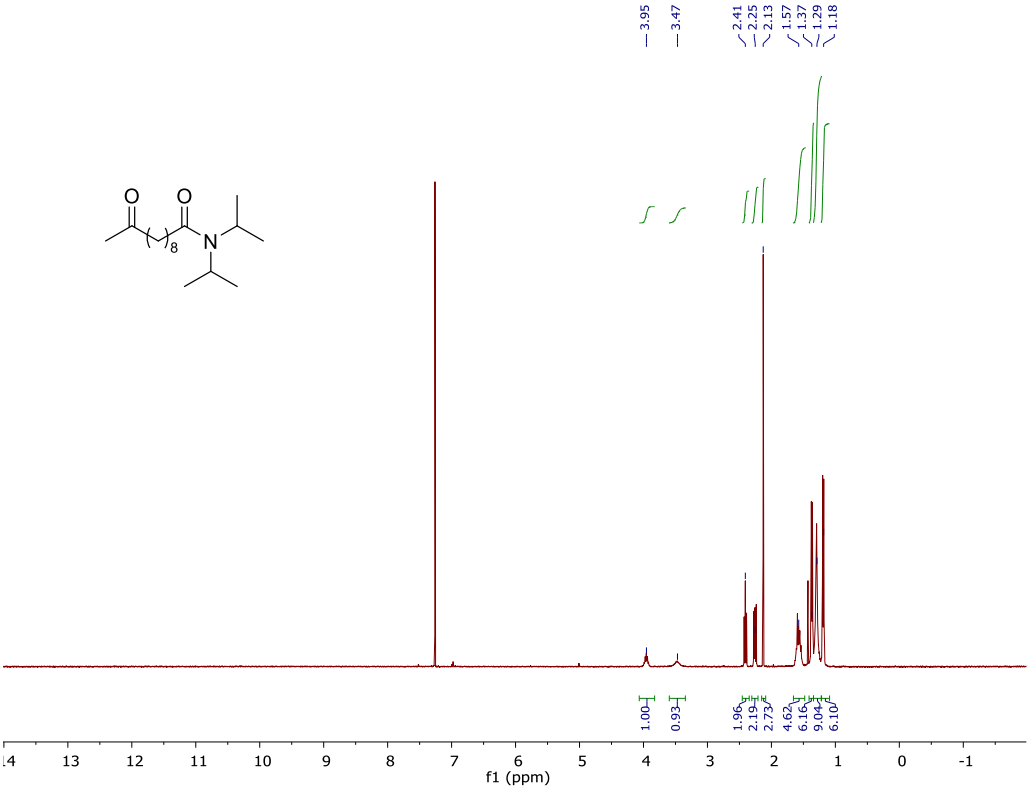
1-(1-Hydroxycyclopentyl)-2-propanone (3n), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



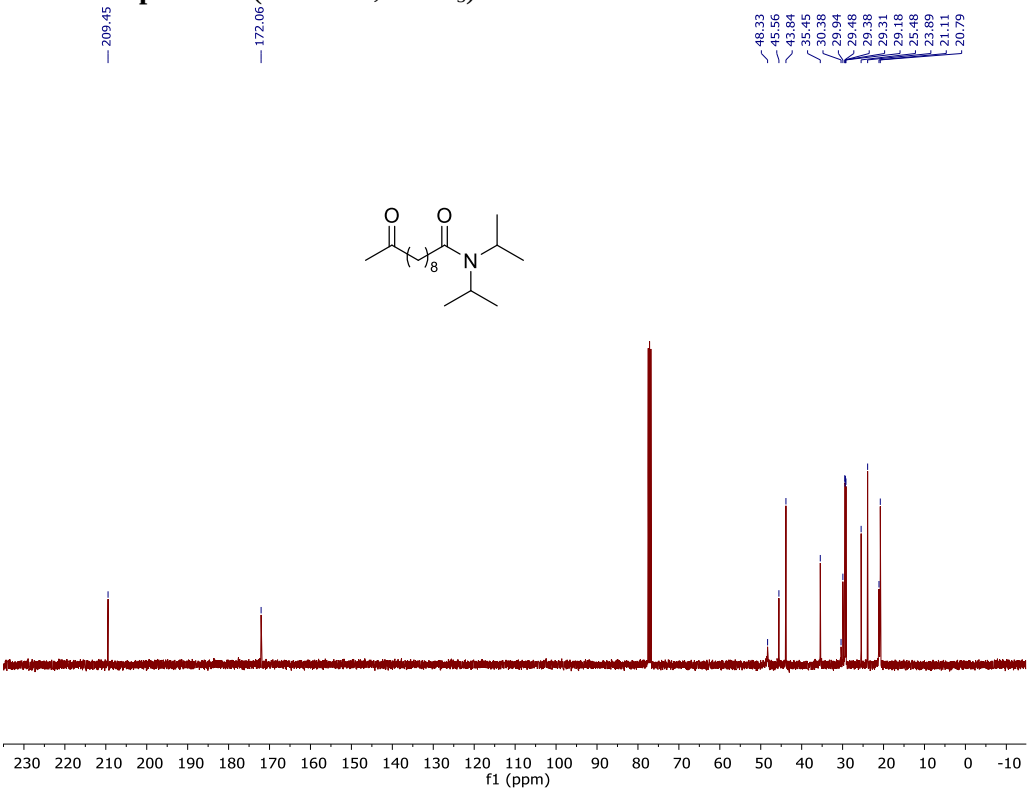
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



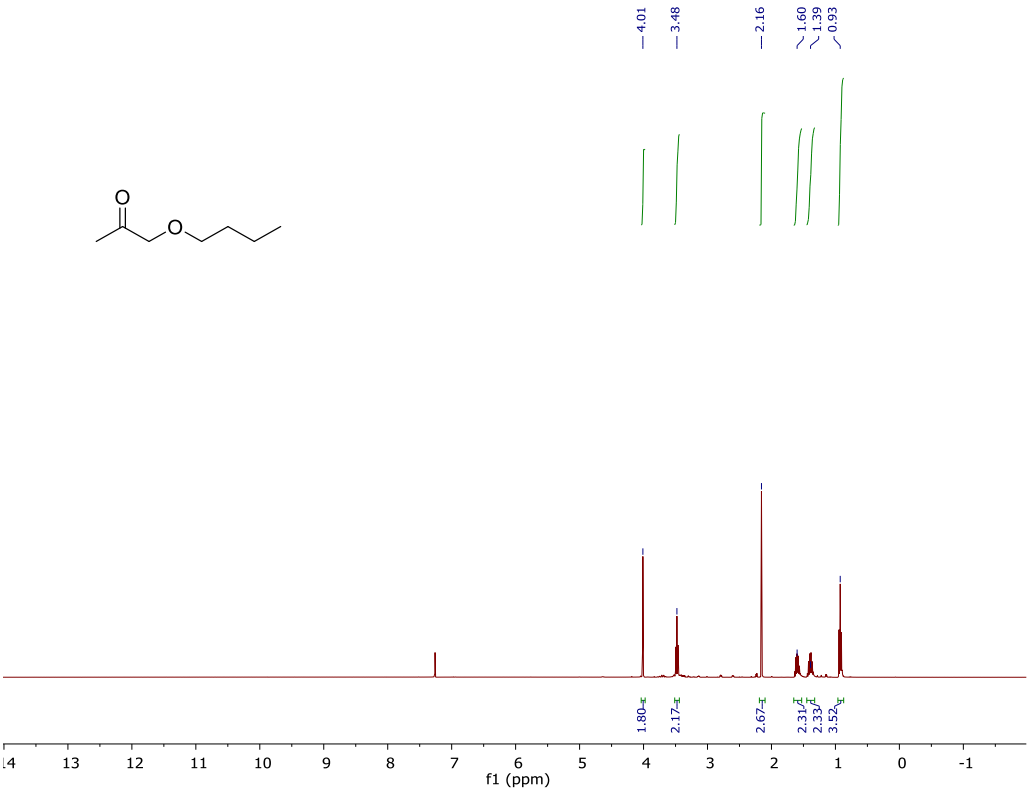
***N*,*N*-Bis(1-methylethyl)-10-oxo-undecanamide (3o), ^{1}H NMR spectrum** (400 MHz, $CDCl_3$)



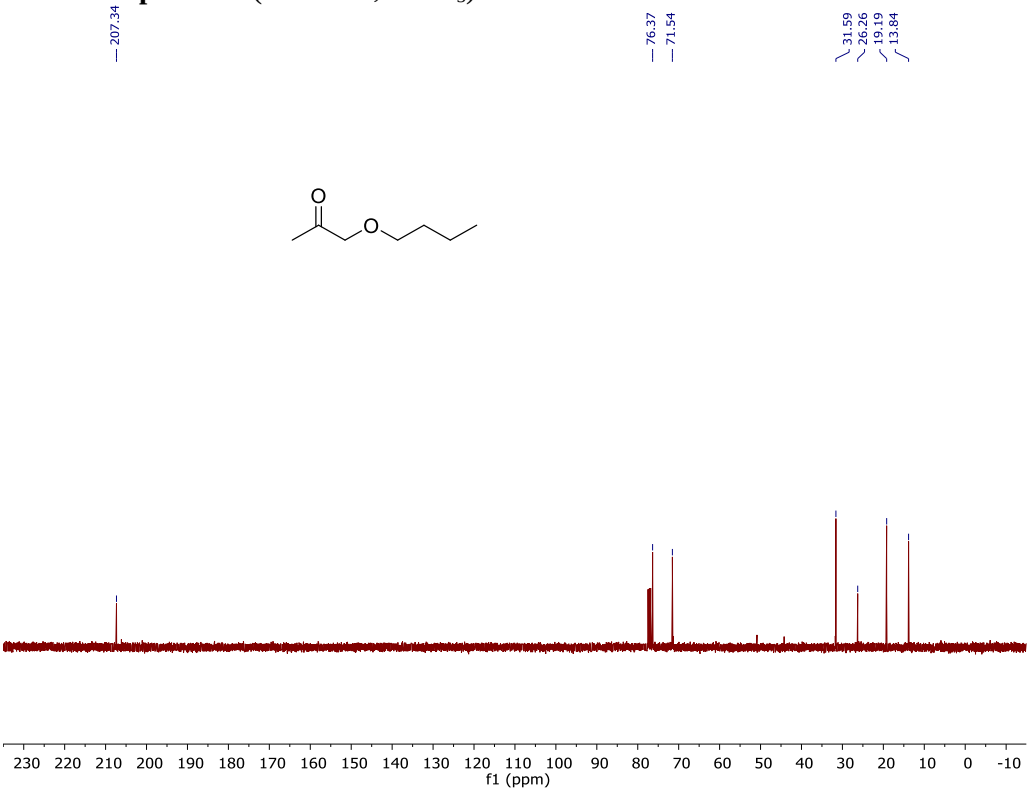
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



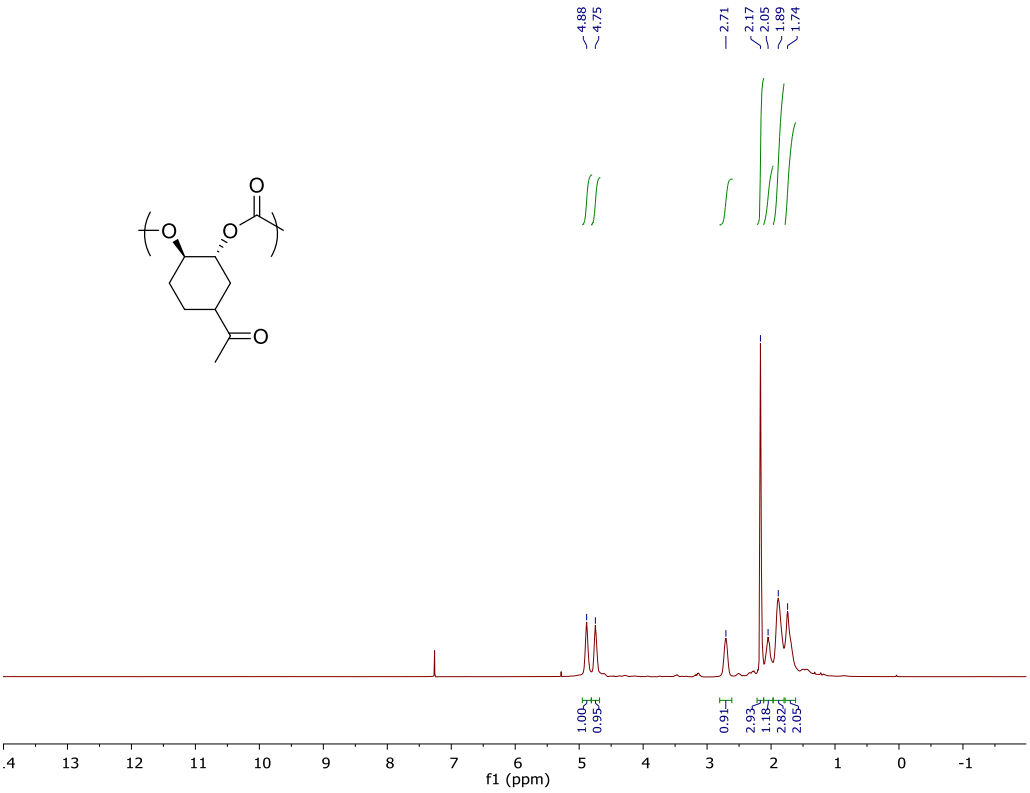
1-Butoxy-2-propanone (3p), ^{1}H NMR spectrum (400 MHz, $CDCl_3$)



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



Poly(4-acetylcyclohexene carbonate) (3r), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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