Contents

1 General information

All screening - and mechanistic reactions were carried out in a 12-slot carousel from Radleys if not mentioned otherwise. Reactions were monitored by ^{1}H-NMR and/or GC-FID.

To determine conversion via ^{1}H-NMR, signals of starting material (benzoic acid) and product (both regioisomers) have been compared or 1,3,5-trimethoxybenzene has been used as standard (if indicated).

For ^{1}H-NMR sample preparation, a small amount of sample was filtered through a pipette containing cotton, Merck 60 Å 230–400 mesh silica gel and Celite®, flushed with EtOAc. The solvent was removed in vacuo and the residue was analyzed via ^{1}H-NMR Spectroscopy ($CDCl_3$).

Purification of products was performed by reverse phase or normal phase column chromatography utilizing a Biotage Isolera Selekt autocolumn system with Biotage Sfaer C18, 100 Å, 30 µm, either 12g or 20g sized columns. For normal phase purification, silica colums from Biotage or Buchi were used in various sizes.

NMR data were collected either on a 400 MRDDC with OneMMR probe, A Mercury 400 with 400 Auto SW probe (^{1}H at 400.0 MHz; ^{13}C at 100.58 MHz, ^{19}F at 376 MHz), or on a Bruker NEO (^{1}H at 600 MHz; ^{19}F at 565 MHz; ^{13}C at 151 MHz; ^{15}N at 60.8 MHz), equipped with a SmartProbe BBFO or a BBO prodigy cryoprobe.

Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm; DMSO-d_6, ^{1}H: 2.50 ppm, ^{13}C: 39.52 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations (s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, m: multiplet).

GC-FID data were collected on a Agilent Technologies 7890 A GC System with a HP-5MS 5% phenyl-methyl polysiloxane column.

Concentrations of 1,2-epoxyhexane, benzoic acid and β-hydroxy ester products was determined via GC-FID measurement by addition of 0.1 mL of reaction solution to 1 mL of EtOAc, containing 1,3,5 Mesitylene (2 mL/L) as standard.

Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization.

Elemental analysis was conducted on Elementar micro cube to determine CHN compositions and on a Perkin Elmer Optima 7000DV spectrometer for iron content determination via ICP method. For ICP measurement, a sample was pretreated with HNO_3 and heated to 200 °C for 10 minutes, before it was diluted with 2 fold distilled water.

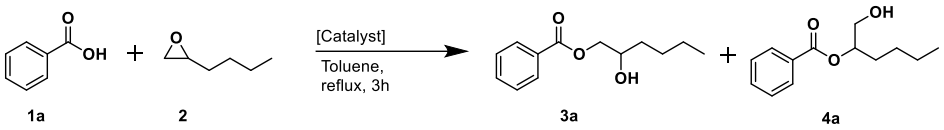
2 Chemicals

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. All reported compounds were characterized by ^{1}H- and ^{13}C-NMR and compared with literature data. All new compounds were fully characterized by ^{1}H- and ^{13}C-NMR, HRMS techniques or

X-Ray Crystallography, if applicable. For reaction, purification and analytic purposes, AR- or HPLC Grade solvents were used.

3 General procedure for Catalyst Screening

A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol) and solid catalyst component (2 mol% each, see Table **1-4**). The solids were suspended in toluene (3 mL) and 1,2-epoxyhexane was added (180.80 µL, 1.5 mmol). Catalyst components of liquid nature were introduced via stock solution with the reaction solvent. The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel, allowing the mixture to be stirred for 3 hours.



c = 0,5 mmol/mL ; V = 3 mL
1 eq. of both reactants

Table 1: Screening data of metallic Lewis acids.

Entry	Catalyst	Conversion (after 3h) (%) 3[a]	Regioisomer ratio after 3h **3/4**[a]	Amount (mol%)
1	No catalyst	3	/	/
2	$TiCp_2Cl_2$	14	71:29	2
3	$ZnCl_2$	10	60:40	2
4	$ZnOAc_2$	13	75:25	2
5	$Zr(acac)_4$	66	71:29	2
6	$ZrCp_2Cl_2$	51	70:30	2
7	$AlCl_3$	7	67:33	2
8	$MnCl_2$	7	67:33	2
9	$FeCl_3$	64	71:29	2
10	$FeCl_3$	32	69:31	1
11	$FeCl_3$+$FeBr_3$	52	67:33	1:1
12	$Fe(acac)_3$	37	67:33	2
13	$Fe(NO_3)_3 \cdot 9\ H_2O$	52	68:32	2
14	$Fe(OTf)_3$	n.d.	n.d.	2
15	$In(OTf)_3$	n.d.	n.d.	2
16	$Sc(OTf)_3$	n.d.	n.d.	2
17	$Y(OTf)_3$	n.d.	n.d.	2

[a] Determined by ^{1}H-NMR spectroscopy

Table 2: Screening data of nitrogen Lewis bases.

Entry	Catalyst	Conversion (after 3h) (%) 3[a]	Regioisomer ratio after 3h **3/4**[a]	Amount (mol%)
1	DIPEA	9	67:33	2
2	DABCO	30	71:29	2
3	1,8-Bis(dimethylamino)napthalene	13	70:30	2
4	1-Methylimidazole	36	71:29	2
5	1-Methylbenzimidazole	28	73:27	2
6	Pyridine	42	72:28	2
7	2,6-Lutidine	11	71:29	2
8	4-Methoxypyridine	46	72:28	2
9	DMAP	63	74:26	2
10	2,6-Diphenylpyridine	3	n.d.	2
11	Quinoline	32	71:29	2
12	Isoquinoline	39	73:27	2
13	2,2'-Bipyridine	8	67:33	2
14	4,4'-Bipyridine	40	73:27	2
15	Picolinic Acid	7	75:25	2
16	Barton's Base	42	74:26	2
17	PPh_3	66	74:26	2

[a] Determined by ^{1}H-NMR spectroscopy

Table 3: Screening data of metallic Lewis acids with DMAP.

Entry	Catalyst	Conversion (after 3h) (%) 3[a]	Regioisomer ratio[a] after 3h **3/4**	Amount (mol%)
1	$FeCl_3$+DMAP	82	73:27 (70:30)	1:1
2	$Fe(acac)_3$+DMAP	80	71:29	1:1
3	CP_2ZrCl_2+DMAP	51	70:30	1:1
4	$Zr(acac)_4$/DMAP	60	71:29	1:1
5	$CeCl_3$+DMAP	39	71:29	1:1
6	$MnCl_2$+DMAP	42	73:27	1:1
7	$Cu(CF_3acac)_2$+DMAP	44	71:29	1:1
8	$MoO_2(acac)_2$+DMAP	38	71:29	1:1

[a] Determined by ^{1}H-NMR spectroscopy; Regioisomer ratios observed after 20h depicted in parentheses.

Table 4: Screening data of $FeCl_3$ with nitrogen Lewis bases.

Entry	Catalyst	Conversion (after 3h) (%) 3[b]	Regioisomer ratio after 3h **3/4**	Amount (mol%)
1	$FeCl_3$+Pyridine	78	72:28 (71:29)	1:1

2	$FeCl_3$+Methylimidazole	73	71:29	1:1
3	$FeCl_3$+Quinoline	76	73:27	1:1
4	$FeCl_3$+benzmethylimidazole	63	70:30	1:1
5	$FeCl_3$+2,2'-bipyridyl	42	74:26	1:1
6	$FeCl_3$+4,4'-bipyridyl	58	73:27	1:1
7	$FeCl_3$+NPh_3	38	70:30	1:1
8	1,8-Bis(N,N-dimethylamino)naphthalin	70	71:29	1:1
9	$FeCl_3$+DIPEA	71	71:29	1:1
10	$FeCl_3$+2,6-Lutidine	73	72:28	1:1
11	$FeCl_3$+4-Methoxypyridine	69	71:29	1:1
12	$FeCl_3$+2-Picolinic Acid	40	71:29	1:1
13	$FeCl_3$+2,6-Phenylpyridine	38	69:31	1:1
14	$FeCl_3$+L-Proline	22	69:31	1:1
15	$FeCl_3$+Barton's Base	83	72:28	1:1
16	$FeCl_3$/PPh_3	81	71:29	1:1

[a] Determined by ^{1}H-NMR spectroscopy; Regioisomer ratios observed after 20h depicted in parentheses.

Table 5: Screening data of potassium hydroxide as standalone catalyst and in conjunction with $FeCl_3$.

Entry	Catalyst	Conversion (after 3h) (%) 3[b]	Regioisomer ratio after 3h **3/4**	Amount (mol%)
1	KOH	4	n.d.	1
2	KOH	4	n.d.	10
3	KOH[a]	4	n.d.	1
4	KOH[a]	15	74:26	10
5	$FeCl_3$+KOH	37	70:30	1:1
6	$FeCl_3$+KOH	53	71:29	1:10

[a] nBuOAc as solvent, [b] Determined by ^{1}H-NMR spectroscopy

4 General Procedure for Solvent Screening

A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol), $FeCl_3$ (2.43 mg, 1 mol%) and DMAP (1.83 mg, 1 mol%). The respective solvent was added (Figure **1**), followed by 1,2-epoxyhexane (180.80 µL, 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 °C) reaction carousel. If the boiling point of the solvent exceeded 120 ° C, the temperature was set to 115 °C instead. The mixture was allowed to stir for 3h.

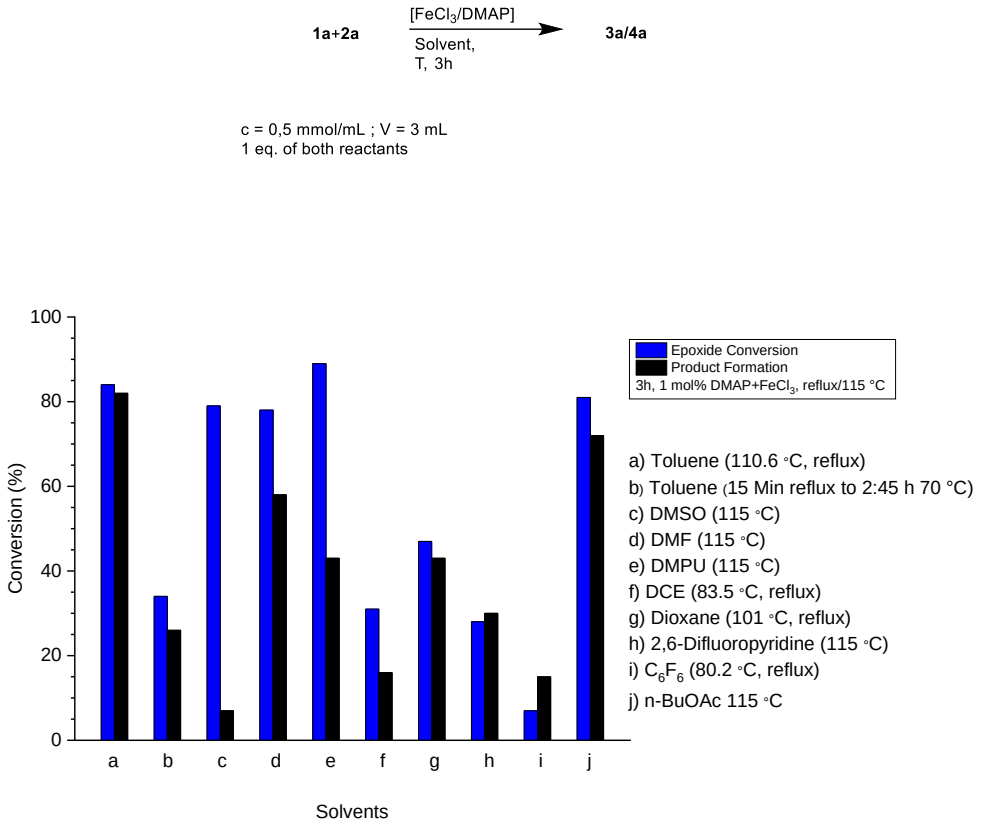


Figure 1. *Reaction conditions: benzoic acid (**1a**) (1 eq.), 1,2-epoxyhexane (**2**) (1 eq.), 1.5 mmol, v = 3 mL, reflux, 3h. Conversion determined by GC-FID.*

Toluene and n-Butyl acetate appeared to be most suitable as solvent for the model reaction.

5 Screening of different LA/LB ratios ($FeCl_3$/1-Methylimidazole; $FeCl_3$/DMAP)

A carousel vial from Radleys was charged with a stirrer, benzoic acid (180.18 mg, 1.5 mmol), $FeCl_3$ (x mol%) and 1-methylimidazole or DMAP (Figure 2) (y mol%) fitting the requirement of x + y = 2 mol %, 0.03 mmol. Toluene (3 mL) was added, followed by 1,2-epoxyhexane (180.80 µL, 1.5 mmol). Note: 1-methylimidazol was introduced via stock solution as reaction solvent. The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (60 °C or 120 °C) reaction carousel. The mixture was allowed to stir for 23 h. At 2h (3h and 23h), a sample was taken via syringe.

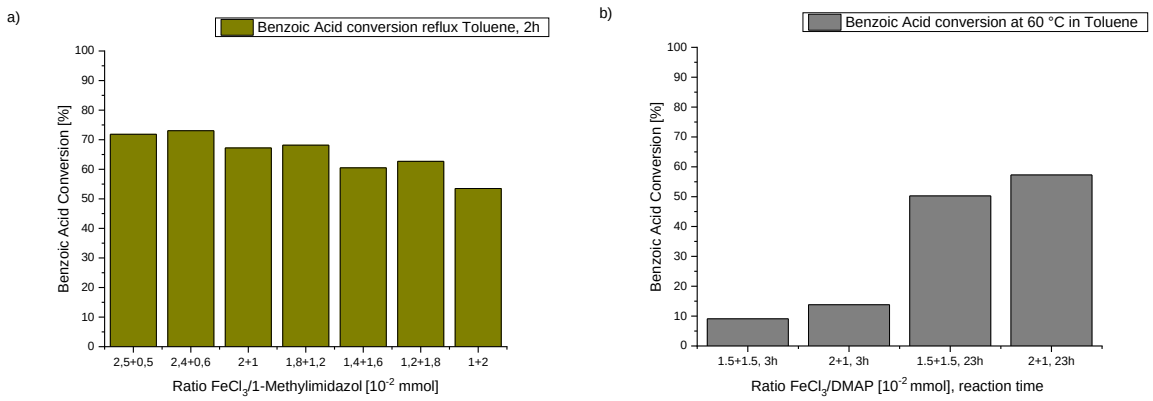
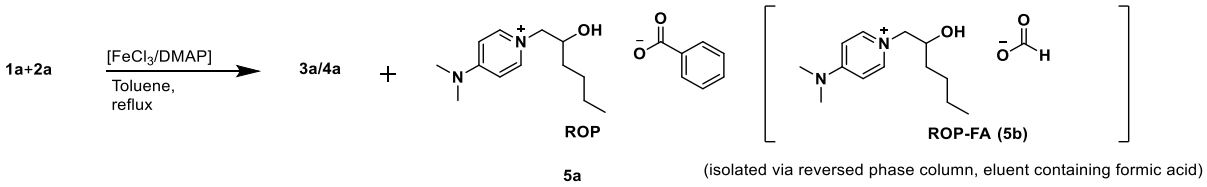


Figure 2. *Model reaction, benzoic acid (**1a**)(1 eq.), 1,2-epoxyhexane (**2**) (1 eq.) in toluene (v = 3 mL, c = 0.5 mmol/mL), a) reflux, b) 60 °C. Different ratios of LA/LB, total of 2 mol%. a) Model reaction with $FeCl_3$/1-methylimidazole as catalyst system at different ratios at reflux in toluene; b) $FeCl_3$/DMAP as catalyst system for the model reaction in different ratios at 60 °C in toluene. Different ratios of Lewis acid to Lewis base indicate a beneficial effect on conversion for higher amounts of $FeCl_3$ compared to Lewis base (1-methylimidazole or DMAP).*

The screening results suggest that higher amounts of $FeCl_3$ relative to the amount of Lewis base are slightly more effective for the catalytic activity compared to higher relative loadings of Lewis base.

6 Screening of DMAP in submolar amounts



A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol) and DMAP (25 mol%, 50 mol%, or 75 mol%). The solids were suspended in toluene (3 mL) and 1,2-epoxyhexane was added (180.80 µL, 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel, allowing the mixture to stir for 20h. A sample was taken via syringe. For ^{1}H-NMR preparation, the solvent was removed from a small amount of sample in vacuo and the residue was analyzed via ^{1}H-NMR spectroscopy (DMSO-d_6). For the reaction containing 50 mol% of DMAP as precatalyst, The mixture was concentrated in vacuo, adsorbed on Celite® and purified via automated reversed phase flash column chromatography using MeCN/H_2O (+0.1% FA) as gradient. The regioisomer mixture of the desired ring opening product (**3**+**4**) was isolated in 53% yield (177.7 mg), whereas the ROP was isolated in 52% (104.4 mg, based on DMAP Loading) with minor impurities of DMAP.

Table 6: Screening of DMAP in submolar amounts

Entry	Catalyst	Catalyst loading [%]	Product formation (both regioisomers) [%][a]	Isolated yield **(3+4)**	Isolated yield **ROP-Fa** [%]
1	DMAP	25	74	n.d.	n.d.
2	DMAP	50	51	53	52
3	DMAP	75	49	n.d.	n.d.

*Reaction conditions: Benzoic acid (**1a**) (1 eq.), 1,2-epoxyhexane (**2**) (1 eq.), 1.5 mmol, v = 3 mL, reflux, 20h,* [a] *Determined by GC-FID; n.d. = not determined.*

7 Presence of ROP under reaction conditions

A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol) and DMAP (91.63 mg, 50 mol%). The solids were suspended in toluene (3 mL) and 1,2-epoxyhexane was added (180.80 µL, 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel, allowing the mixture to stir for 3 hours. A sample was taken via syringe.

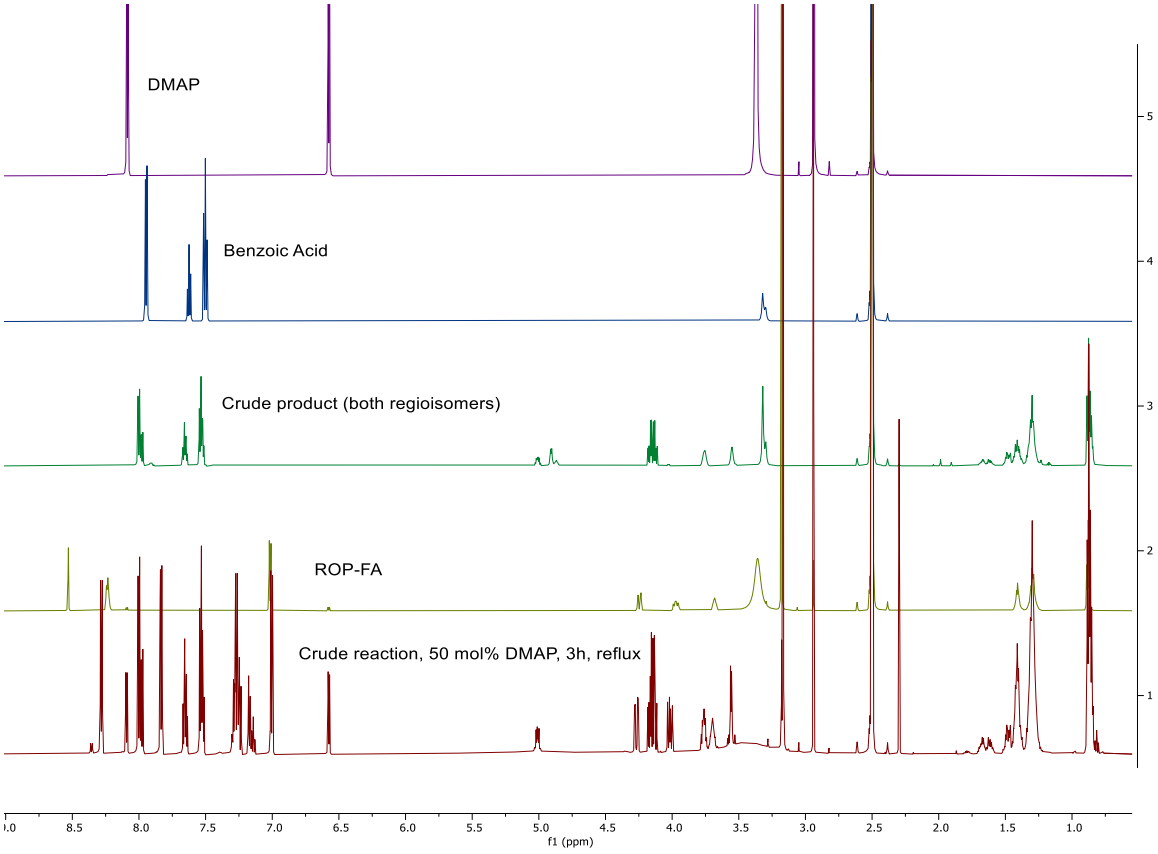
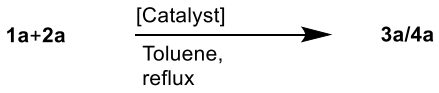
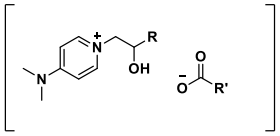


Figure 3. *^{1}H-NMR Spectrum in DMSO, crude reaction mixture with 50 mol% of DMAP as catalyst after 3h at reflux temperature in toluene. Comparison with the ^{1}H-NMR spectrum of ROP-FA shows presence of ROP structure in crude reaction mixture.*

The ^{1}H-NMR spectrum of the crude reaction mixture containing DMAP in 50 mol% of catalyst loading after 3 hours shows formation of the ring opening product (ROP), reaction product (both regioisomers), and remaining DMAP.

8 Role of ROP structure in the model reaction





R' = Ph (ROP) (5a), H (ROP-FA) (5b)

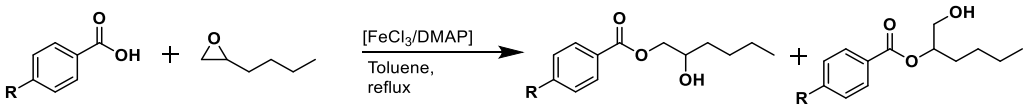
Table 7: Catalyst characteristics of the DMAP-epoxide ring opening product.

Entry	Catalyst	Catalyst loading [%]	Conversion (3h) [%][(a)]	Remark
1	ROP-FA	1	44	/
2	ROP-FA + $FeCl_3$	1/1	79	/
3	DMAP	50	0	No acid present, no formation of ROP observed[(a)]
4	DMAP	Traces	0	ROP as substrate[(b)]
5	DMAP+$FeCl_3$	Traces	0	ROP as substrate[(b)]
6	Sodium benzoate	Traces	0	ROP as substrate[(b)]

*[a] Reaction conditions: benzoic acid (**1a**) (1 eq.), 1,2-epoxyhexane (**2**) (1 eq.) in toluene (v=3 mL, c= 0.5 mmol/mL), reflux, 3h. [a] Conversion determined by ^{1}H-NMR [b] benzoic acid (**1a**) (1 eq.), toluene, v = 0.65 mL, c = 0.1 mmol/mL, reaction time of 19h.*

The isolated ring opening product (ROP-FA) showed similar catalytic activity as DMAP. No intermediate reactivity has been observed.

9 Conversion of para substituted benzoic acids



R = H (1a)[a], CF_3 (1b)[b], CH_3 (1f)[c] 2 R = H (3a)[a], CF_3 (3b)[b], CH_3 (3f)[c] R = H (4a)[a], CF_3 (4b)[b], CH_3 (4f)[c]

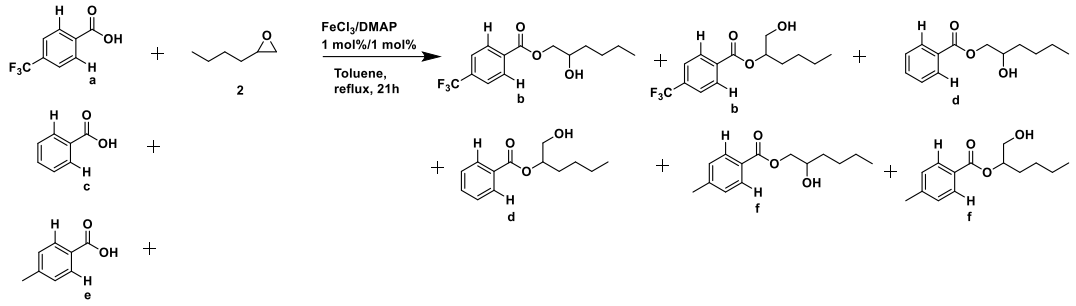
A carousel vial from Radleys was charged with a stirrer and the respective benzoic acid (549.54 mg, 4.5 mmol). $FeCl_3$ (1 mol%) and DMAP (1 mol%) were introduced via stock solutions (4.5 mL each, 0.01 mmol/mL in Toluene), followed by 1,2-epoxyhexane (542.40 µL, 4.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel and was stirred for 2 hours. The reaction progress was monitored by ^{1}H NMR and GC-FID analysis.

Table 8: Effect of para-substitutents on conversion of the benzoic acid

Entry	Substituent	1,2-Epoxyhexane conversion GC-FID [%][a]	Conversion benzoic acid (^{1}H NMR) [%][b]
1	*p*-CF_3	59	62
2	H	68	65
3	*p*-CH_3	69	67

[a] *Determined by GC-FID. Standard reaction conditions, reaction time: 2h.* [b] *Determined by ^{1}H-NMR. Average result of two runs.*

10 Direct competition experiment between substituted benzoic acids –$FeCl_3$/DMAP system



A carousel vial from radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol), 4-methylbenzoic acid (204.23 mg, 1.5 mmol), 4-trifluoromethylbenzoic acid (285.18 mg, 1.5 mmol), 1,3,5-trimethoxybenzene (285.29 mg, 1.5 mmol), $FeCl_3$ (7.29 mg, 1 mol%) and DMAP (5.49 mg, 1 mol%). Toluene (9 mL) was added. The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel. The mixture was stirred for 20 minutes, followed by addition of 1,2-epoxyhexane (542.40 µL, 4.5 mmol). The reaction progress was monitored by ^{1}H-NMR analysis.

Table 9: Direct competition experiments between differently para substituted carboxylic acids.

Entry	Time	Conversion *p*-CF_3 -benzoic acid **a** [%]	Product formation *p*-CF_3- benzoic ester (both regioisomers) **b** [%]	Conversion benzoic acid **c** [%]	Product formation Benzoic ester **d** (both regioisomers) [%]	Conversion *p*-toluic acid **e** [%]	Product formation *p*-toluic ester (both regioisomers) **f** [%]
1	20 min	39	30	7	9	5	6
2	3 hours	100	100	73	75	58	59
3	21 hours	100	93	100	99	100	92

Comparison of product ratios of *β*-hydroxyesters after 20 min, 3h and 21 h, determined by crude ^{1}H-NMR, 1,3,5-trimethoxybenzene (0.33 eq) as internal standard. (1 eq. 1,2-epoxyhexane (**2**), 0.33 eq. of each *para*-substituted carboxylic acid, toluene, reflux).

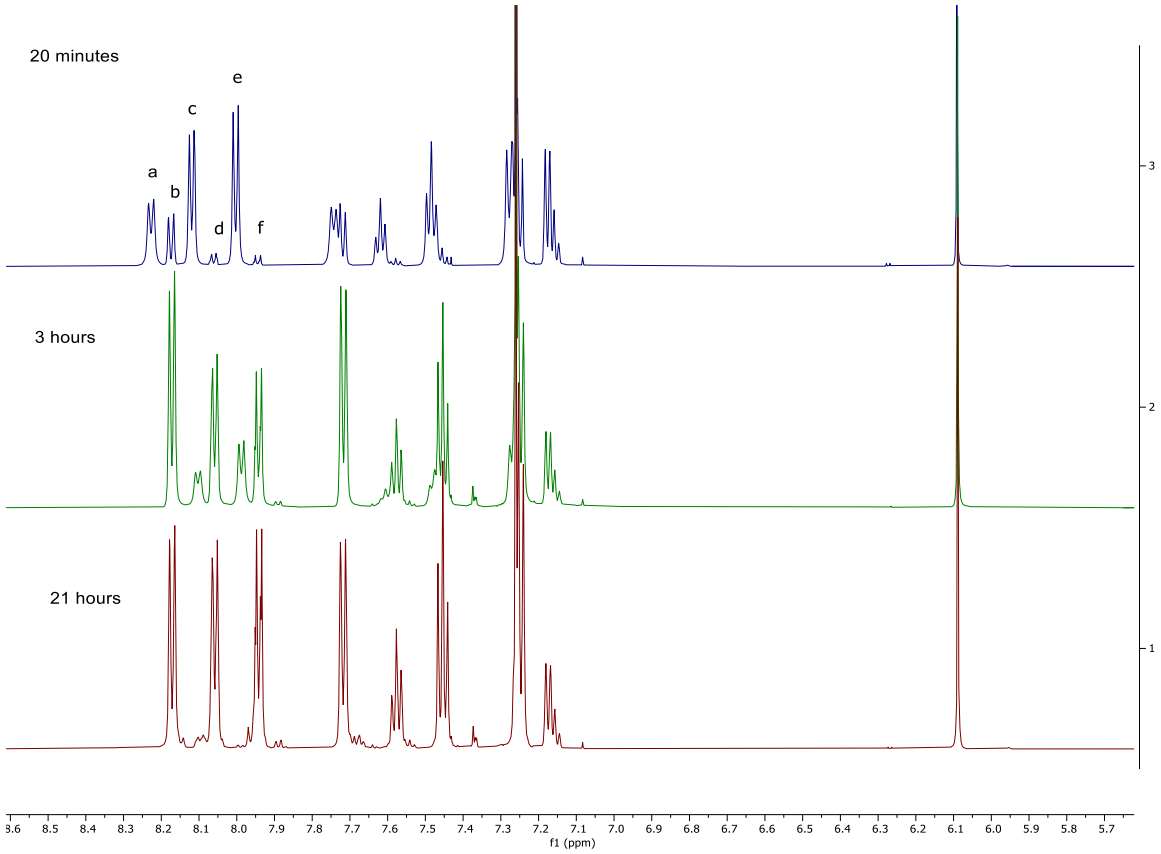
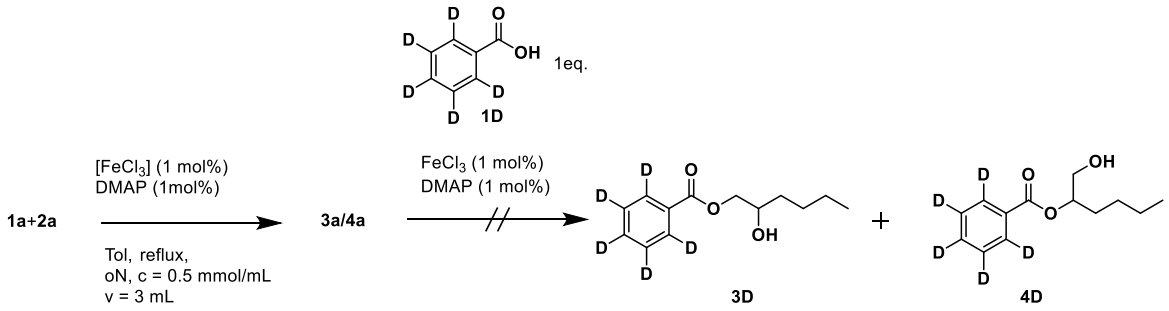


Figure 4. *^{1}H-NMR spectrum of direct competition experiment with differently para substituted carboxylic acids. 1,3,5-trimethoxybenzene as internal standard, 0.33 eq.*

Consumption of carboxylic acid: Conversion *p*-CF_3 - > *p*-H - > *p*-CH_3 - benzoic acid.

11 Potential equilibrium between starting material and products



A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol), $FeCl_3$ (2.43 mg, 1 mol%) and DMAP (1.83 mg, 1 mol%). Toluene (3 mL) was added, followed by addition of 1,2-epoxyhexane (180.80 µL, 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 °C) reaction carousel. After 22 hours, the reaction vessel was allowed to cool down to room temperature and the reaction progress was monitored by ^{1}H-NMR analysis to determine the ratios of both regioisomer products. Afterwards, 2,3,4,5,6-deuterobenzoic acid (190.73 mg, 1.5 mmol) was added to the crude reaction mixture, followed by $FeCl_3$ (2.43 mg, 1 mol%) and

DMAP (1.83 mg, 1 mol%). The reaction mixture was placed again into the preheated (120 ° C) reaction carousel for additional 5 hours, until another sample was taken for ^{1}H-NMR analysis to determine the product isomer ratio.

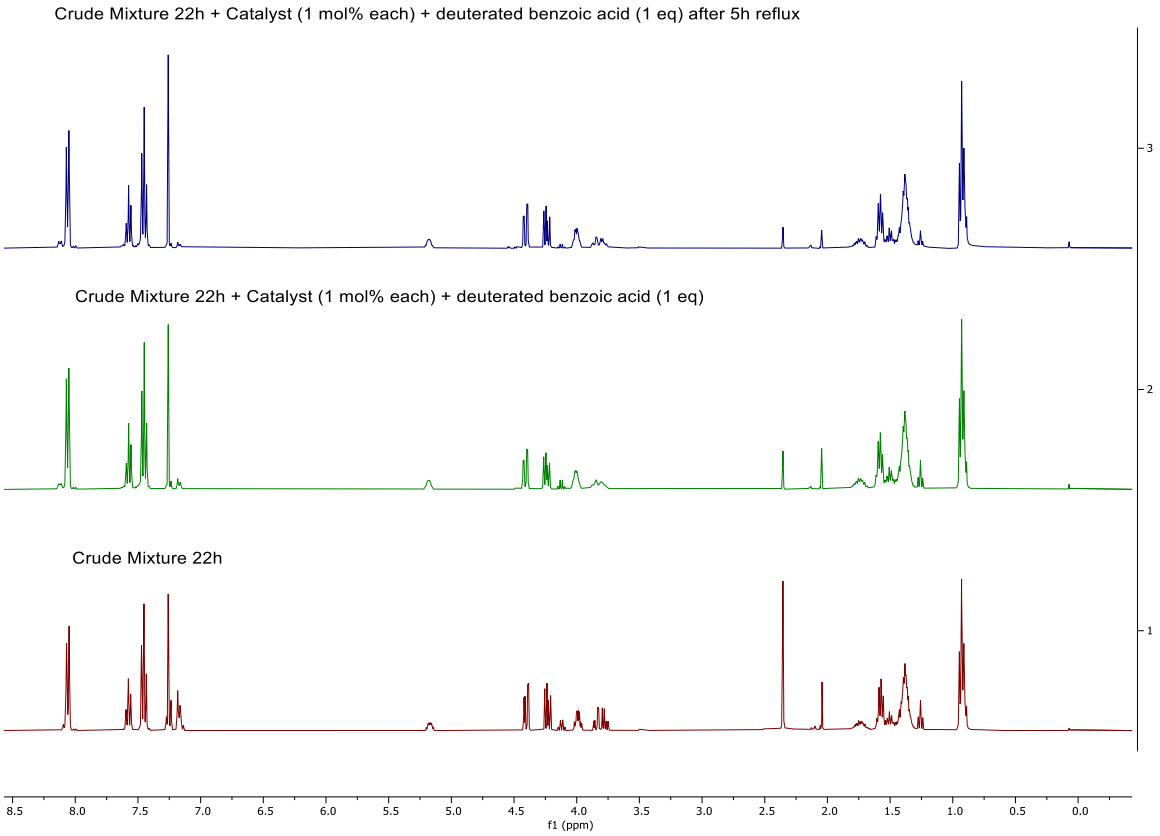
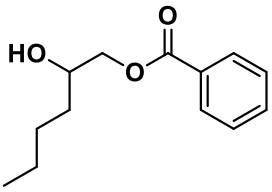


Figure 5. ^{1}H-NMR spectrum of crude reaction mixture after 22h at reflux and same mixture stirred for 5 additional hours in reflux in presence of 2,3,4,5,6-deuterobenzoic acid (1eq.) and an additional amount of $FeCl_3$+DMAP.

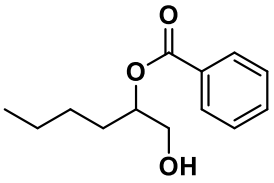
^{1}H-NMR shows that no significant equilibrium reaction between product regioisomers and starting material occurs. After 22h, the carboxylic acid is almost completely consumed. Addition of deuterated benzoic acid and 1 mol% of $FeCl_3$ and DMAP each does not result in release of benzoic acid after 5 hours under reflux conditions.

12 Equilibrium between product regioisomers

Synthesis and separation of Regioisomer products



3a



4a

A carousel vial from Radleys was charged with a stirrer, benzoic acid (4.5 mmol), $FeCl_3$ (7.29 mg, 1 mol%) and DMAP (5.49 mg, 1 mol%). Toluene (9 mL) was added, followed by

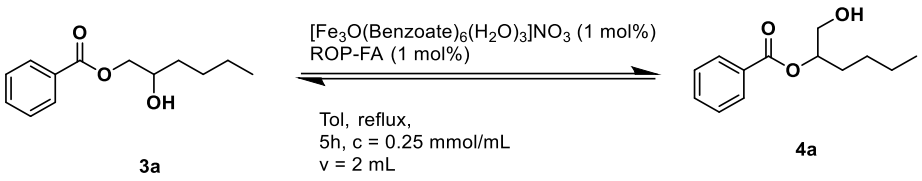
1,2-epoxyhexane (4.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 °C) reaction carousel. The mixture was allowed to stir overnight, was then concentrated in vacuo, adsorbed on Celite® and purified via automated column chromatography using a gradient of pentane/diethylether.

Yield **3**: 302.33 mg, 30 %

Yield **4**: 123.77 mg, 12 %

^{1}H and ^{13}C NMR spectra of both compounds were in alignment with previously reported literature[1,2]

Equilibrium experiment



3a **4a**

Table 10: Regioisomer equilibrium (**3a/4a**).

Entry	Time	Ratio 3/4
1	Start	1.00/1.56
2	5 h	1.00/0.41

A carousel vial from Radleys was charged with a stirrer, substrate **3a** (37.5 mg, 0.17 mmol), substrate **4a** (75 mg, 0.34 mmol) $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (0.33 mol%) (1.74 mg, 1 mol%) and ROP-Fa (1.36 mg, 1 mol%). Toluene (2 mL) was added, the reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel. The mixture was allowed to stir 5 hours until a sample was taken for analysis.

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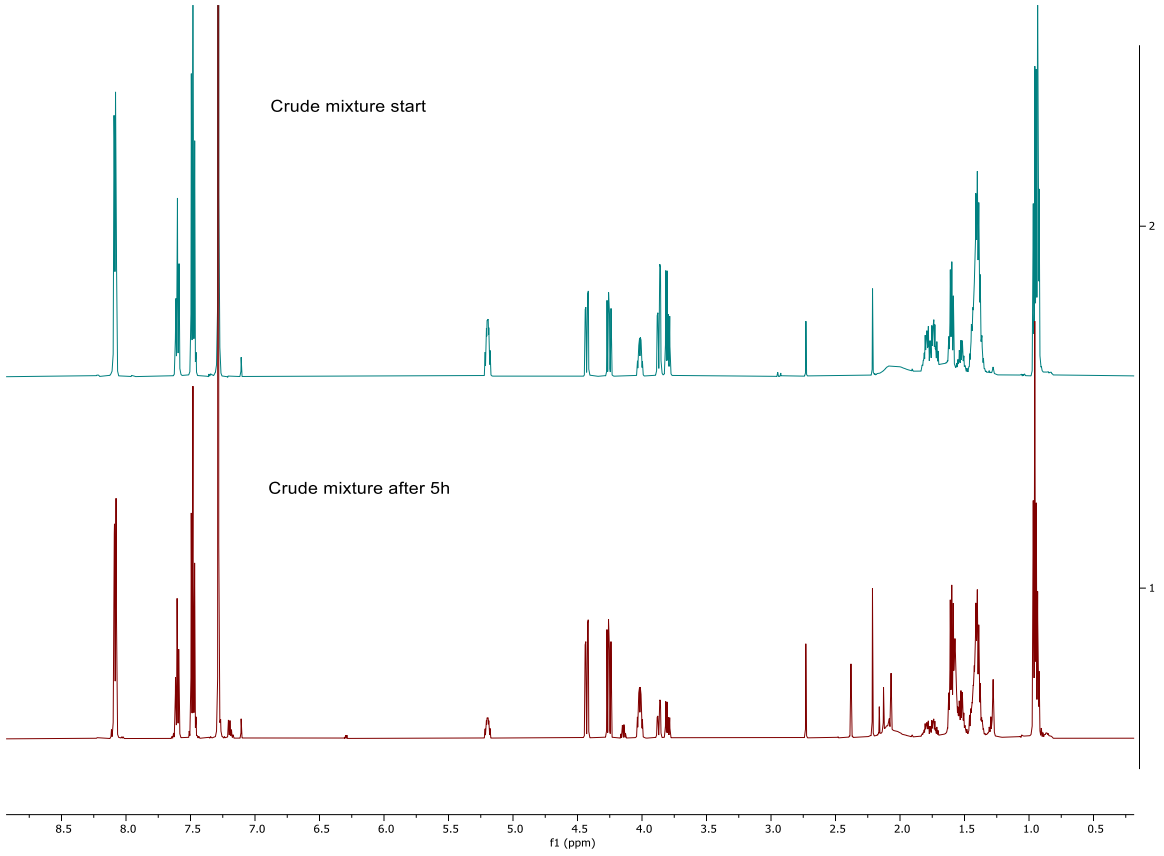
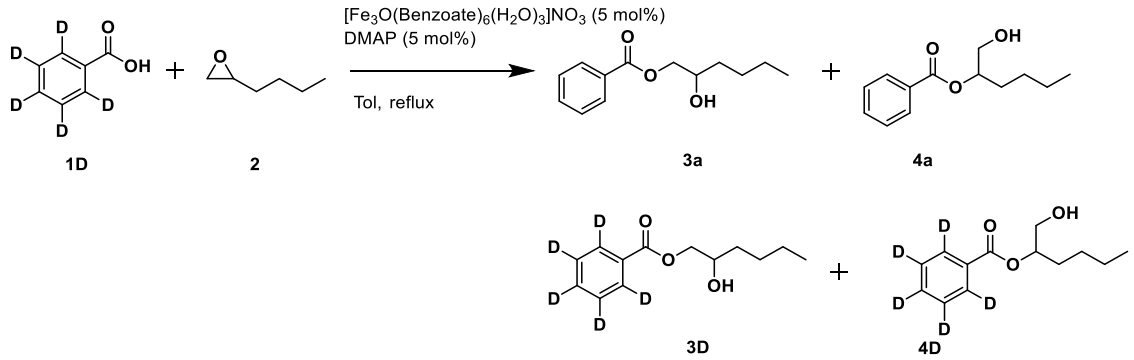


Figure 6. *^{1}H-NMR spectrum, reaction mixture of both regioisomer products and same mixture after 5h at reflux in presence of* $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (1 mol%) and ROP-Fa (1 mol%). Ratio of 3a to 4a changes towards higher amounts of compound 3 as less sterically hindered regioisomer.

13 $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ ligand product incorporation experiment



A carousel vial from Radleys was charged with a stirrer, 2,3,4,5,6-deuterobenzoic acid (190.73 mg, 1.5 mmol), $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (25.66 mg, 5 mol% iron loading), DMAP (9.15 mg, 5 mol%) and 1,3,5-trimethoxybenzene (84.09 mg, 0.5 mmol). Toluene (3 mL) was added, followed by 1,2-epoxyhexane (180.80 µL 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 °C) reaction carousel. After 1 h, a sample was taken for analysis.

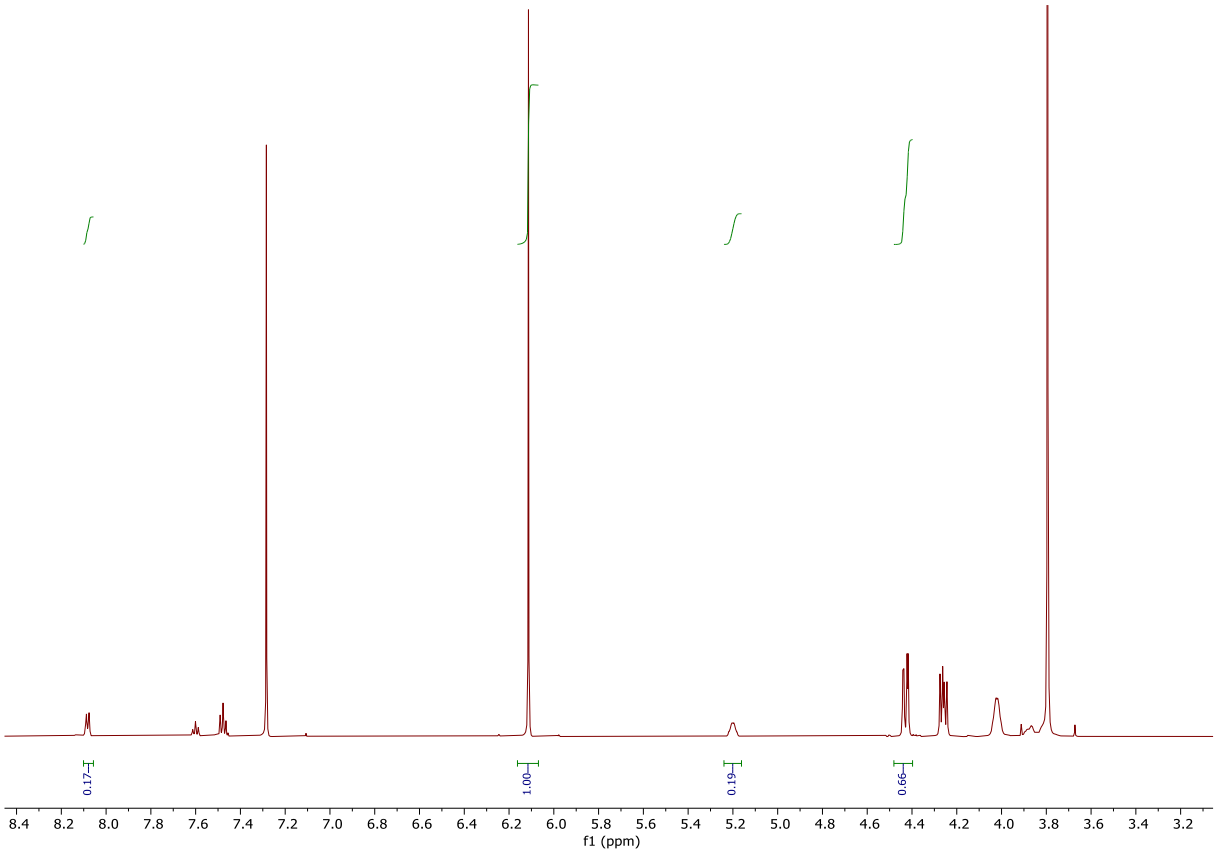


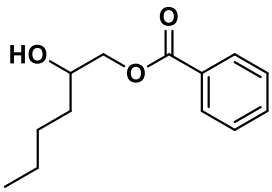
Figure 7. *^{1}H-NMR spectrum, reaction of 2,3,4,5,6-deuterobenzoic acid (1eq.), 1,2-epoxyhexane (1 eq.) in presence of* $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (5 mol%) and DMAP (5 mol%). 1,3,5-trimethoxybenzene (0.33 eq.) as internal standard. Non deuterated benzoic acid, introduced to the reaction as benzoate ligands, has been converted to product.

85% of Benzoic acid and 2,3,4,5,6-deuterobenzoic acid in total has been converted to product.

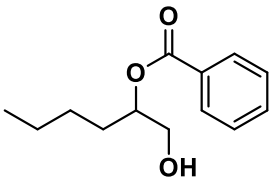
9% of product formed as a result of benzoate coordinated to the cluster reacting with the epoxide.

14 Substrate scope

A carousel vial from Radleys was charged with a stirrer, respective acid (1.5 mmol), TBAB (9.67 mg, 2 mol%) or $FeCl_3$ (2.43 mg, 1 mol%) and DMAP (1.83 mg, 1 mol%). Toluene (3 mL) was added, followed by the respective epoxide (1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel. The mixture was allowed to stir overnight, was then concentrated in vacuo, adsorbed on 2g of Celite® and purified via automated reversed phase flash column chromatography using a gradient of MeCN/H_2O (+0.1% FA).



3a (a)



4a (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 277.4 mg, 83%

Regioisomer Ratio a/b : 70:30

Catalyst System: TBAB

Yield: 288.8 mg, 87%

Regioisomer Ratio a/b : 70:30

Catalyst System: $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (0.33 mol%/1 mol%), 115 ° C, Anisole as solvent instead of Toluene.

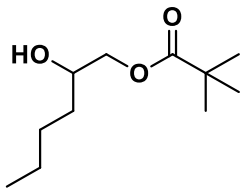
Yield: 275.7 mg, 83%

Regioisomer Ratio a/b : 71:29

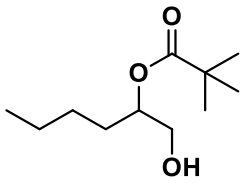
^{1}H NMR (600 MHz, CDCl3) δ = 8.07 – 8.05 (m, 2H, *a,b*), 7.59-7.56 (m, 1H, *a,b*), 7.47 – 7.44 (m, 2H, *a,b*), 5.19 – 5.14 (m, 1H, *b*), 4.40 (dd, *J*=11.4 Hz, 3.1 Hz, 1H, *a*), 4.23 (dd, *J*=11.4 Hz, 7.2 Hz, 1H, *a*), 4.02-3.96 (m, 1H, *a*), 3.87 – 3.61 (m, 2H, *b*), 2,11-1.97 (m, 1H, *a,b*), 1.81 – 1.30 (m, 6H, *a,b*), 0.96 – 0.87 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, CDCl3) δ = 167.1, 166.9, 133.3 (2x), 130.4, 130.1, 129.8 (x2), 128.6 (x2), 76.6, 70.3, 69.4, 65.2, 33.3, 30.6, 27.7 (x2), 22.8, 22.7, 14.1 (x2).

HRMS [$(M + H)^+$] calculated: 223.1329, found (m/z): 223.1329.



12 (a)



13 (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 229.5 mg, 76%

Regioisomer Ratio a/b : 70:30

Catalyst System: TBAB

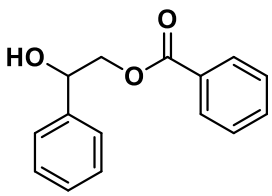
Yield: 253.5 mg, 84%

Regioisomer Ratio a/b : 71:29

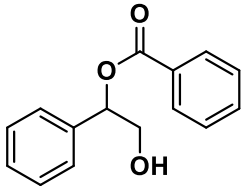
^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.00 – 4.75 (m, 1H, *b*), 4.13 (dd, *J*=11.4 Hz, 3.2 Hz, 1H, *a*), 3.97 (dd, *J*=11.4 Hz, 7.0 Hz, 1H, *a*), 3.87 – 3.80 (m, 1H, *a*), 3.73 – 3.56 (m, 2H, *b*), 1.97 (s, 1H, *a*), 1.90 (s, 1H, *b*), 1.63 – 1.28 (m, 6H, *a,b*), 1.23 (s, 9H, *a*), 1.22 (s, 9H, *b*), 1.00 – 0.82 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 179.3, 178.9, 75.7, 70.3, 68.8, 65.4, 39.1, 39.0, 33.2, 30.4, 27.7, 27.5, 27.4, 27.3, 22.8, 22.6, 14.1 (x 2).

HRMS [$(M + H)^+$] calculated: 203.1642, found (m/z): 203.1642.



14 (a)



15 (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 271.2 mg, 75%

Regioisomer Ratio a/b : 77:23

Catalyst System: TBAB

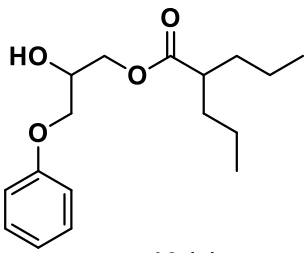
Yield: 273.0 mg ,75%

Regioisomer Ratio a/b : 76:24

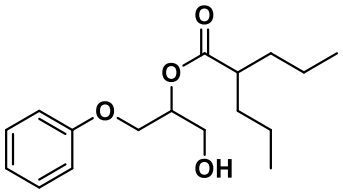
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 – 8.09 (m, 1H, *b*), 8.07 – 8.03 (m, 1H, *a*), 7.59 – 7.54 (m, 1H, *a,b*), 7.47 – 7.30 (m, 7H, *a,b*), 6.12 – 6.07 (m, 1H, *b*), 5.09 (dd, *J*=8.c1 Hz, 3.6 Hz, 1H, *a*), 4.51 (dd, *J*=11.5 Hz, 3.6 Hz, 1H, *a*), 4.42 (dd, *J*=11.5 Hz, 8.1 Hz, 1H, *a*), 4.05 – 3.86 (m, 2H, *b*), 3.08 (s, 1H, *a*), 2.51 (s, 1H, *b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 166.3, 140.1, 137.2, 133.3 (x2), 130.0, 129.9 (x2), 129.8 (x2), 128.7, 128.6, 128.5 (x2), 128.3, 126.7, 126.3, 77.5, 72.6, 69.9, 66.2.

HRMS [$(M + Na)^+$] calculated: 265.0835, found (m/z): 265.0835.



16 (a)



17 (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 329.1 mg, 75%

Regioisomer Ratio a/b : 82:18

Catalyst System: TBAB

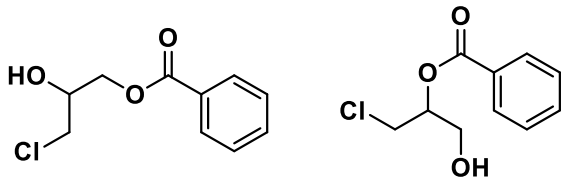
Yield: 326.7 mg, 74%

Regioisomer Ratio a/b : 82:18

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 – 7.27 (m, 2H, *a,b*), 7.00 – 6.95 (m, 1H, *a,b*), 6.94 – 6.88 (m, 2H, *a,b*), 5.25 (p, *J*=5.0 Hz, 1H, *b*), 4.36 – 4.26 (m, 2H, *a*), 4.25 – 4.20 (m, 1H, *a*), 4.16 (d, *J*=5.3 Hz, 2H, *b*) 4.03 (m, 2H, *a*), 3.93 – 3.87 (m, 2H, *b*), 2.59 (s, 1H, *a*), 2.47 – 2.40 (m, 1H, *a,b*), 1.95 (s, 1H, *b*), 1.66 – 1.56 (m, 2H, *a,b*), 1.48 – 1.39 (m, 2H, *a,b*), 1.36 – 1.24 (m, 4H, *a,b*), 0.92 – 0.84 (m, 6H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 177.0, 176.6, 158.5 (x2), 129.7 (x2), 121.5, 121.4, 114.7, (x2), 72.7, 68.9, 68.7, 66.4, 65.1, 62.4, 45.5, 45.4, 34.9, 34.8, 20.8, 20.7, 14.1 (x2).

HRMS [$(M + Na)^+$] calculated: 317.1723, found (m/z): 317.1726.



18 (a) **19 (b)**

Catalyst System: $FeCl_3$+DMAP

Yield: 76%

Regioisomer Ratio a/b : 83:17

Catalyst System: TBAB

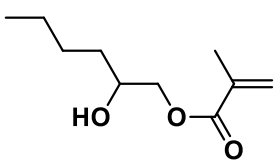
Yield: 77%

Regioisomer Ratio a/b : 87:13

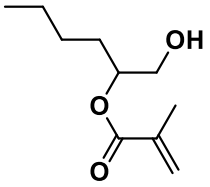
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 – 8.00 (m, 2H, *a,b*), 7.61 – 7.56 (m, 1H, *a,b*), 7.46 (t, *J*=7.8 Hz, 2H, *a,b*), 5.31 (p, *J*=5.1 Hz, 1H, *b*), 4.48 (d, *J*=5.2 Hz, 2H, *a*), 4.26 – 4.19 (m, 1H, *a*), 4.00 – 3.96 (m, 2H, *b*), 3.85 (m, 2H, *b*), 3.77 – 3.66 (m, 2H, *a*), 2.70 (d, 1H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 166.2, 133.6 (x2), 130.0 (x2), 129.9, 129.6, 128.7 (x2), 74.3, 70.0, 65.9, 62.0, 46.3, 42.4.

HRMS [(M + Na)$^+$] calculated: 237.0289, found (m/z): 237.0289.



20 (a)



21 (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 178.5 mg, 64%

Regioisomer Ratio a/b : 70:30

Catalyst System: TBAB

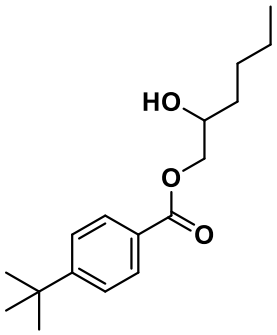
Yield: 189.7 mg, 68%

Regioisomer Ratio a/b : 71:29

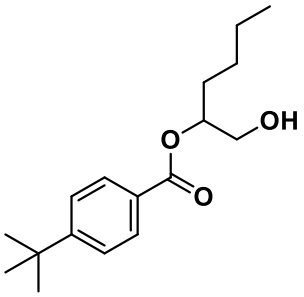
^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.13 (s, 1H, *a,b*), 5.60 (s, 1H, *a,b*), 5.00 – 4.93 (m, 1H, *b*), 4.22 (dd, *J*=11.5 Hz, 3.0 Hz, 1H, *a*), 4.05 (dd, *J*=11.4 Hz, 7.2 Hz, 1H, *a*), 3.92 – 3.85 (m, 1H, *a*), 3.78 – 3.63 (m, 2H, *b*), 2.14 – 1.98 (m, 1H, *a,b*), 1.96 (s, 3H, *a,b*), 1.72 – 1.20 (m, 6H, *a,b*), 0.95-0.85 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.0, 167.7, 136.5, 136.2, 126.1, 126.0, 76.3, 70.2, 69.1, 65.2, 33.2, 30.5, 27.7, 27.6, 22.8, 22.7, 18.5 (x2), 14.1 (x2).

HRMS [(M + H)$^+$] calculated: 187.1329, found (m/z): 187.1327.



3g (a)



4g (b)

Catalyst System: $FeCl_3$+DMAP

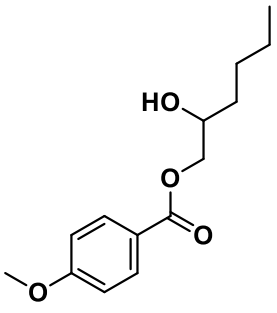
Yield: 233.9 mg, 56%

Regioisomer Ratio a/b : 72:28

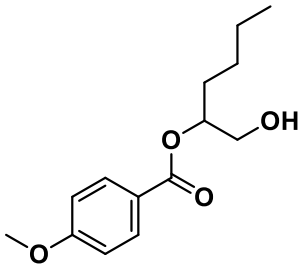
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 – 7.96 (m, 2H, *a,b*), 7.47 (d, *J*=8.5 Hz, 2H, *a,b*), 5.19 – 5.11 (m, 1H, *b*), 4.39 (dd, *J*=11.4 Hz, 3.1 Hz, 1H, *a*), 4.22 (dd, *J*=11.4 Hz, 7.1 Hz, 1H, *a*), 4.01 – 3.95 (m, 1H, *a*), 3.88 – 3.69 (m, 2H, *b*), 2.12 (s, 1H, *a*), 2.05 (s, 1H, *b*), 1.81 – 1.35 (m, 6H, *a,b*), 0.60 –0.87 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 166.9, 157.1, 157.0, 129.7 (x2), 127.5, 127.3, 125.6, 125.5, 76.4, 70.4, 69.2, 65.3, 35.3 (x2), 33.3, 31.3 (x2), 30.6, 27.7 (x2), 22.8, 22.7, 14.1 (x2).

HRMS [$(M + Na)^+$] calculated: 301.1775, found (m/z): 301.1774.



3e (a)



4e (b)

Catalyst System: $FeCl_3$+DMAP

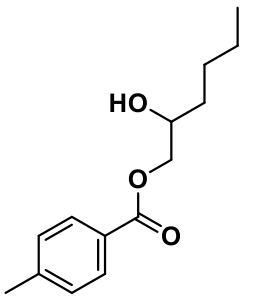
Yield: 306.6 mg, 81%

Regioisomer Ratio a/b : 70:30

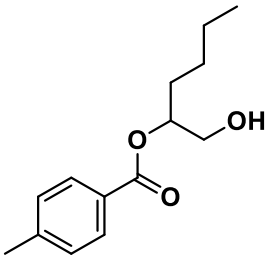
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J*=8.9 Hz, 2H, *a,b*), 6.92 (d, *J*=8.8 Hz, 2H, *a,b*), 5.17 – 5.06 (m, 1H, *b*), 4.36 (dd, *J*=11.4 Hz, 3.1 Hz, 1H, *a*), 4.19 (dd, *J*=11.4 Hz, 7.2 Hz, 1H, *a*), 4.00 – 3.92 (m, 1H, *a*), 3.86 (s, 3H, *a,b*), 3.81 (dd, *J*=12.1 Hz, 3.2 Hz, 1H, *b*), 3.75 (dd, *J*=12.1 Hz, 6.3 Hz, 1H, *b*), 2.23 (s, 1H, *a,b*), 1.80 – 1.27 (m, 6H, *a,b*), 0.95 – 0.84 (3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 166.7, 163.7 (x2), 131.9 (x2), 122.7, 122.4, 113.8 (x2), 76.3, 70.4, 69.2, 65.3, 55.6 (x2), 33.3, 30.6, 27.7 (x2), 22.8, 22.7, 14.1 (x2).

HRMS [$(M + Na)^+$] calculated: 275.1254, found (m/z): 275.1251.



3f (a)



4f (b)

Catalyst System: $FeCl_3$+DMAP

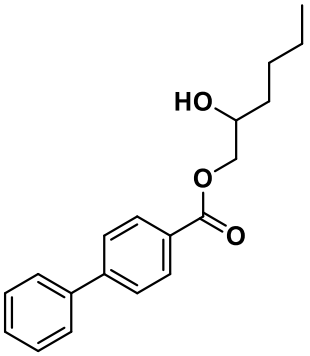
Yield: 284.4 mg, 80%

Regioisomer Ratio a/b : 70:30

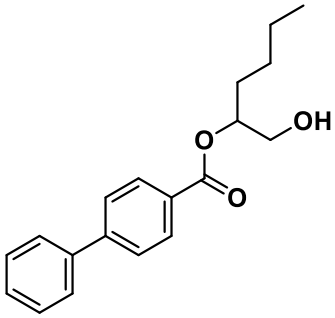
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, *J*=8.2 Hz, 2H), 7.28 (d, *J*=3.5 Hz, 2H), 5.21 – 5.12 (m, 1H, *b*), 4.40 (dd, *J*=11.4, 3.1 Hz, 1H, *a*), 4.23 (dd, *J*=11.4 Hz, 7.2 Hz, 1H, *a*), 4.03 – 3.96 (m, 1H, *a*), 3.85 (dd, *J*=12.1 Hz, 3.2 Hz, 1H, *b*), 3.78 (dd, *J*=12.1 Hz, 6.3 Hz, 1H, *b*), 2.44 (s, 3H, *a,b*), 2.13 (s, 1H, *a,b*), 1.83 – 1.32 (m, 6H, *a,b*), 0.98 – 0.88 (m, 3H, a,b).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 167.0, 144.1, 144.0, 129.9, 129.8, 129.30 (x2), 127.6, 127.3, 76.5, 70.4, 69.3, 65.3, 33.3, 30.6, 27.7 (x2), 22.8, 22.7, 21.8 (x2), 14.1 (x2).

HRMS [(M + H)$^+$] calculated: 237.1485, found (m/z): 237.1485.



3h (a)



4h (b)

Catalyst System: $FeCl_3$+DMAP

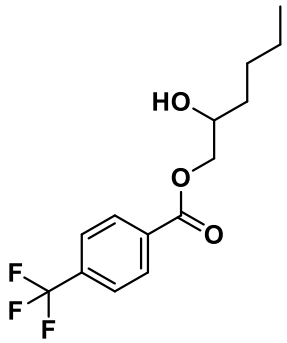
Yield: 298.6 mg, 67%

Regioisomer Ratio a/b : 63:37

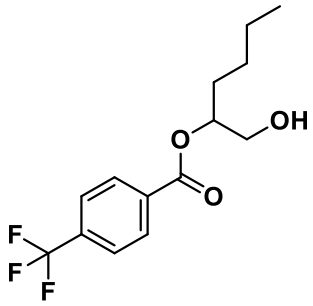
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 (d, *J*=8.0 Hz, 2H, *a,b*), 7.66 (d, *J*=8.0 Hz, 2H, *a,b*), 7.61 (d, *J*=7.6 Hz, 2H, *a,b*), 7.46 (t, *J*=7.5 Hz, 2H, *a,b*), 7.40 (t, *J*=7.3 Hz, 1H), 5.26 – 5.14 (m, 1H, *b*), 4.42 (dd, *J*=11.4 Hz, 3.2 Hz, 1H, *a*), 4.26 (dd, *J*=11.4 Hz, 7.1 Hz, 1H, *a*), 4.06 – 3.96 (m, 1H, *a*), 3.85 (dd, *J*=12.2 Hz, 3.4 Hz, 1H, *b*), 3.79 (dd, *J*=12.1 Hz, 6.3 Hz, 1H, *b*), 2.41 (s, 1H, *a,b*), 1.84 – 1.26 (m, 6H, *a,b*), 0.98 – 0.87 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 166.8, 146.0, 145.9, 140.0 (x2), 130.3 (x2), 129.0 (x2), 128.7 (x2), 128.3 (x2), 127.4 (x2), 127.2 (x2), 76.5, 70.2, 69.4, 65.0, 33.3, 30.5, 27.7, 27.6, 22.8, 22.7, 14.1 (x2).

HRMS [(M + H)$^+$] calculated: 299.1642, found (m/z): 299.1636.



3b (a)



4b (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 332.8 mg, 76%

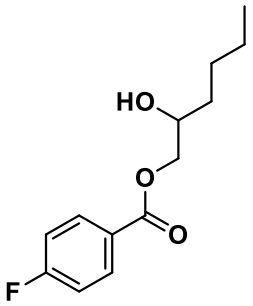
Regioisomer Ratio a/b : 73:27

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.15 (d, *J*=8.0 Hz, 2H, *a,b*), 7.69 (d, 2H, *J*=8.1 Hz, *a,b*), 5.22 –5.15 (m, 1H, *b*), 4.40 (dd, *J*=11.4 Hz, 3.2 Hz, 1H, *a*), 4.26 (dd, *J*=11.4 Hz, 7.1 Hz, 1H, *a*), 4.02-3.95 (m, 1H, *a*), 3.86 – 3.74 (m, 2H, *b*), 2.30 (s, 1H), 1.79 – 1.28 (m, 6H, *a,b*), 0.95 – 0.87 (m, 3H, *a,b*).

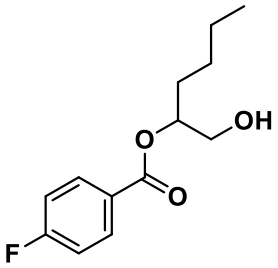
^{19}F NMR (565 MHz, $CDCl_3$) δ = -63.17 (s, 1F, b), -63.18 (s, 1F, a).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.8, 165.7, 134.7 (q, *J*=32.7 Hz), 134.7 (q, *J*=32.4 Hz), 133.6, 133.3, 130.2, 125.6-125.5 (m), 123.7 (q, *J*=273.1 Hz), 123.7 (q, *J*=272.5 Hz), 113.8 (x2), 77.1, 70.1, 69.7, 64.8, 33.3, 30.4, 27.7, 27.6, 22.7 (x2), 14.1, 14.0.

HRMS [$(M + H)^+$] calculated: 291.1203, found (m/z): 291.1203.



3c (a)



4c (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 302.0 mg, 84%

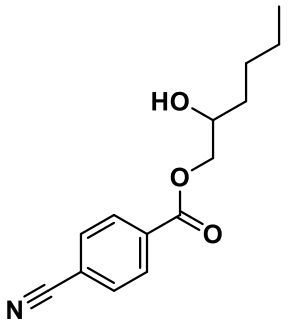
Regioisomer Ratio a/b : 69:31

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 – 7.03 (m, 2H, *a,b*), 7.12 (t, *J*=8.5 Hz, 2H, *a,b*), 5.18 – 5.11 (m, 1H, *b*), 4.38 (dd, *J*=11.4 Hz, 3.1 Hz, 1H, *a*), 4.22 (dd, *J*=11.4 Hz, 7.1 Hz, 1H, *a*), 4.00 – 3.94 (m, 1H, *a*), 3.83 (dd, *J*=12.1 Hz, 3.3 Hz, 1H, *b*), 3.76 (dd, *J*=12.1 Hz, 6.4 Hz, 1H, *b*), 1.80 – 1.30 (m, 6H, *a,b*), 0.95-0.87 (m, 3H, *a,b*).

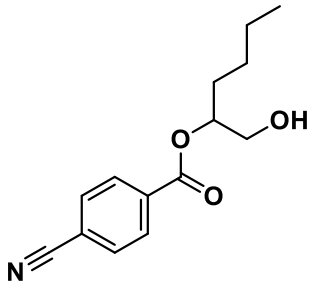
^{19}F NMR (565 MHz, $CDCl_3$) δ = -105.22 - -105.31(m, 1F, *a*), -105.41 - -105.48 (m, 1F, *b*).

^{13}C NMR (151 MHz, CDCl3) δ = 166.1, 166.0 (d, *J*=254.1 Hz), 166.0 (d, *J*=254.3 Hz), 165.9, 132.4 (d, *J*=9.3 Hz) (x2), 126.6 (d, *J*=3.1 Hz), 126.3 (d, *J*=2.9 Hz), 115.8 (d, *J*=21.9 Hz), 115.7 (d, *J*=22.1 Hz), 76.7, 70.3, 69.5, 65.1, 33.3, 30.5, 27.7, 27.6, 22.8, 22.7, 14.1 (x2).

HRMS [$(M + H)^+$] calculated: 241.1235, found (m/z): 241.1236.



3d (a)



4d (b)

Catalyst System: $FeCl_3$+DMAP

Yield: 308.6 mg, 83%

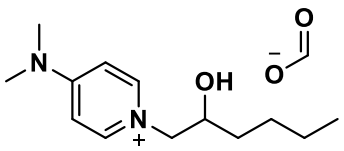
Regioisomer Ratio a/b : 69:31

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.15 (d, *J*=8.2 Hz, 2H, *a,b*), 7.74 (d, *J*=8.4 Hz, 2H, *a,b*), 5.23 – 5.15 (m, 1H, *b*), 4.41 (dd, *J*=11.4 Hz, 3.1 Hz, 1H, *a*), 4.26 (dd, *J*=11.4 Hz, 7.1 Hz, 1H, *a*), 4.03 – 3.95 (m, 1H, *a*), 3.85 (dd, *J*=12.1 Hz, 3.2 Hz, 1H, *b*), 3.77 (dd, *J*=12.2 Hz, 6.4 Hz, 1H, *b*), 2.06 (s, 1H, *a,b*), 1.82 – 1.28 (m, 6H, *a,b*), 0.95 – 0.87 (m, 3H, *a,b*).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.3, 165.2, 134.2, 133.9, 132.4 (x2), 130.3 (x2), 118.1, 118.0, 116.7, 116.6, 77.3, 70.1, 69.9, 64.8, 33.3, 30.4, 27.6 (x2), 22.7, 22.6, 14.1 (x2).

HRMS [$(M + H)^+$] calculated: 248.1281, found (m/z): 248.1283.

Ring Opening product (ROP-Fa)



ROP-Fa (5b)

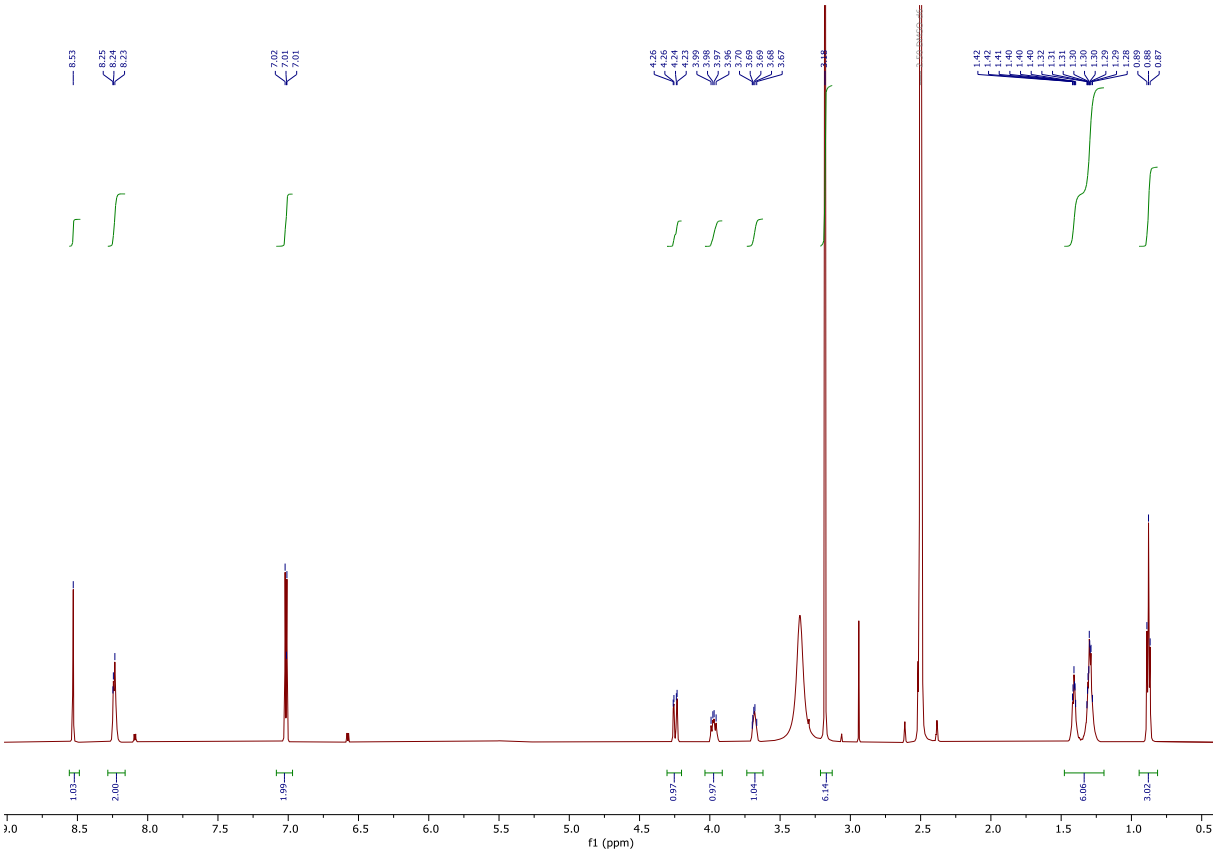
A carousel vial from Radleys was charged with a stirrer, benzoic acid (183.8 mg, 1.5 mmol), $FeCl_3$ (2.43 mg, 1 mol%) and DMAP (91.63 mg, 50 mol%). Toluene (3 mL) was added, followed by 1,2-epoxyhexane (180.8 µL, 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 °C) reaction carousel. The mixture was allowed to stir overnight, was then concentrated in vacuo, adsorbed on Celite® and purified via automated reversed phase flash column chromatography using a gradient of MeCN/H_2O (+0.1% FA).

Yield: 104.40 mg, 0.39 mmol, 52% (based on DMAP Loading)

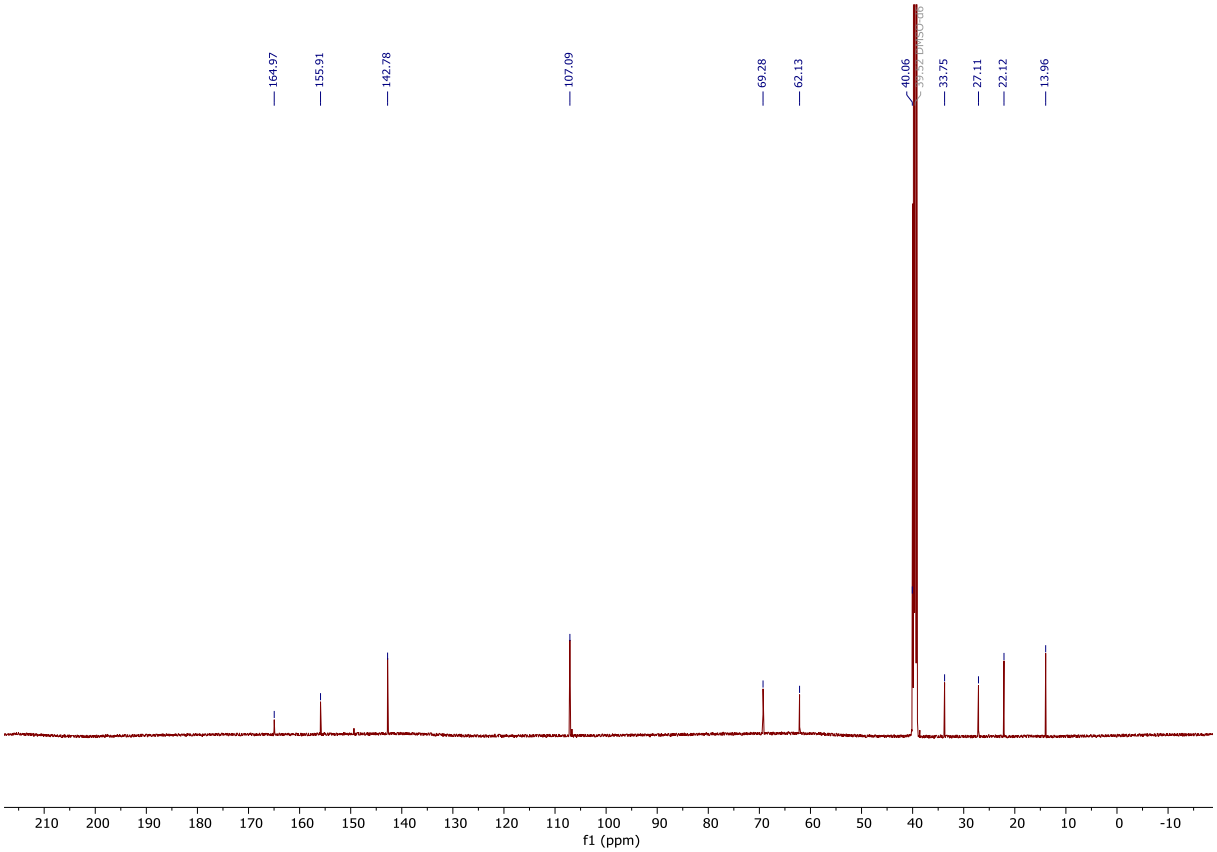
^{1}H NMR (600 MHz, DMSO) δ = 8.53 (s, 1H), 8.24 (d, *J*=6.3 Hz, 2H), 7.02 (d, *J*=7.7 Hz, 2H), 4.25 (dd, *J*=13.4 Hz, 3.1 Hz, 1H), 3.97 (dd, *J*=13.5 Hz, 8.2 Hz, 1H), 3.72-3.66 (m, 1H), 3.18 (s, 6H), 1.41 – 1.13 (m, 6H), 0.88 (t, J=6.9, 3H).

^{13}C NMR (151 MHz, DMSO) δ = 165.0, 155.9, 142.8, 107.1, 69.3, 62.1, 40.1, 33.8, 27.1, 22.1, 14.0.

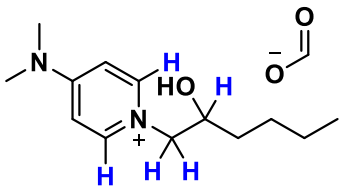
HRMS [$(M - FA)^+$] calculated: 223.1805, found (m/z): 223.1802.


8.53
8.25
8.24
8.23
7.02
7.01
7.01
4.26
4.26
4.24
4.23
3.98
3.98
3.97
3.96
3.70
3.69
3.69
3.68
3.67
3.18
1.42
1.42
1.41
1.40
1.40
1.40
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.28
0.89
0.88
0.87
1.03
2.00
1.99
0.97
0.97
1.04
6.14
6.06
3.02
f1 (ppm)

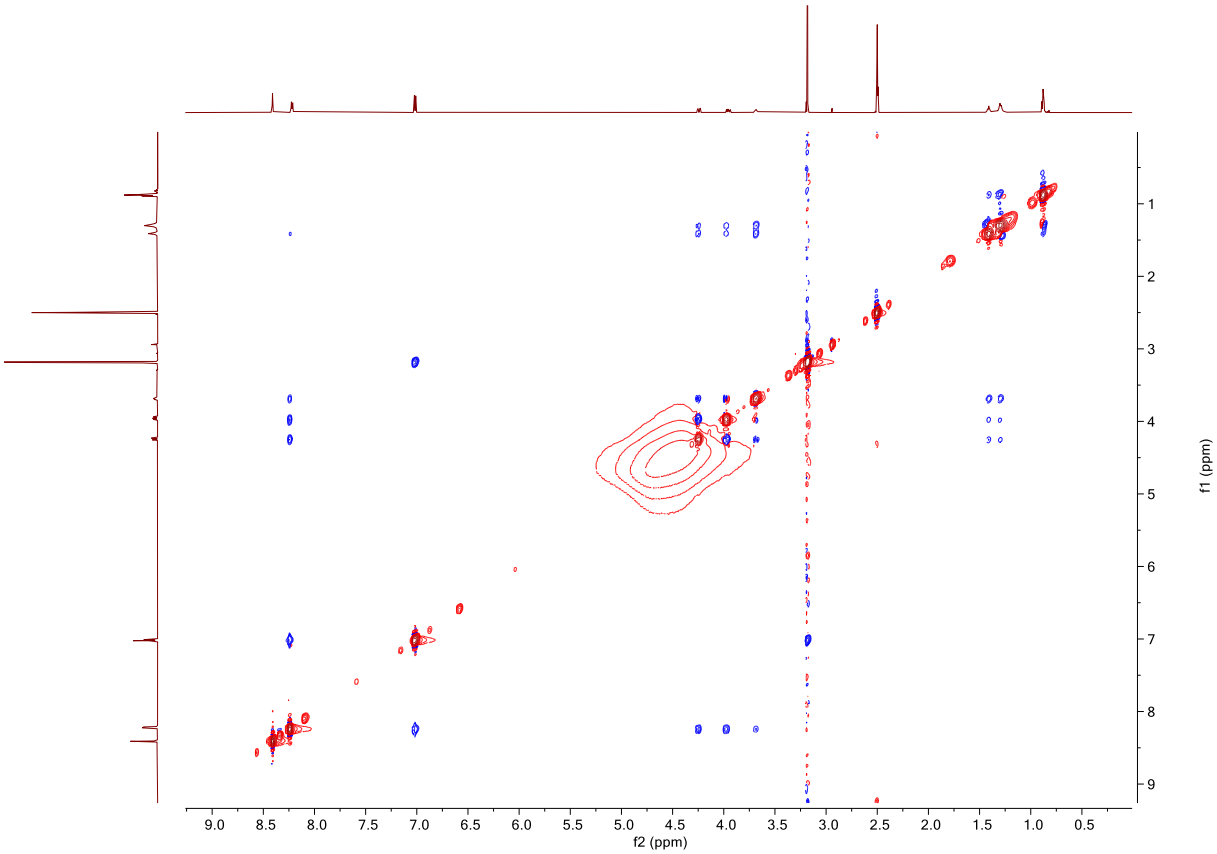
^{13}C-NMR


164.97
155.91
142.78
107.09
69.28
62.13
40.06
33.75
27.11
22.12
13.96
f1 (ppm)

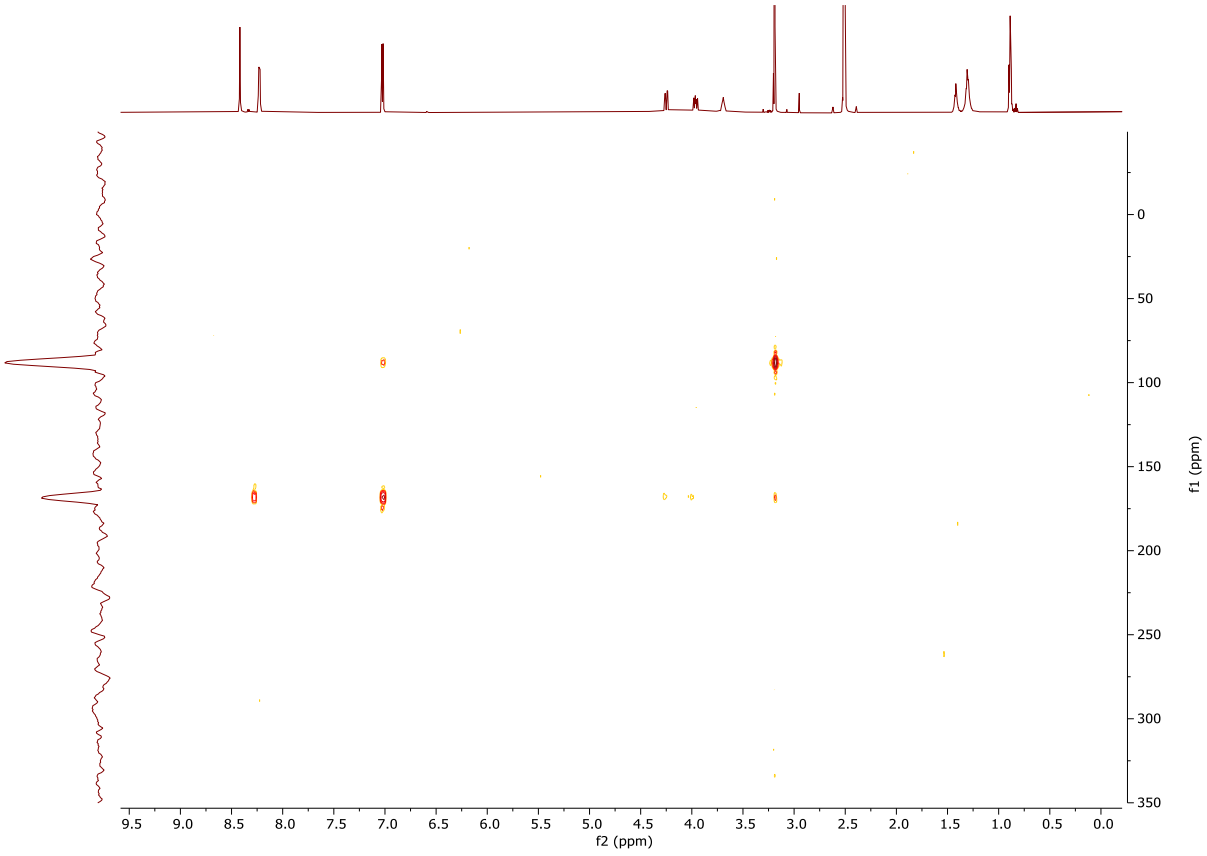
NOESY



5b



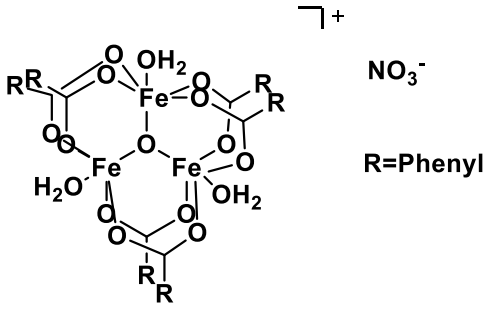
^{1}H-^{15}N-HMBC



Synthesis of Iron Clusters

Synthesis of cluster material was achieved by modification of a literature protocol[3]

Cluster 1 $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$



7

In a 100 mL round bottom flask, sodiumbenzoate (270.2 mg, 1.875 mmol) was dissolved in distilled water (18 mL). $Fe(NO_3)_3$ x 9 H_2O (300 mg, 0.74 mmol) was dissolved in distilled water (30 mL) and was added portionwise to the benzoate solution while stirring. The orange suspension was further stirred at room temperature overnight. The precipitate was then filtered and washed thoroughly with H_2O, before it was dried in high vacuum to obtain the product as pale orange solid.

Yield: 246.1 mg, 97%

HRMS [$(M - 3\ H_2O)^+$] calculated: 909.9729, found (m/z): 909.9736.

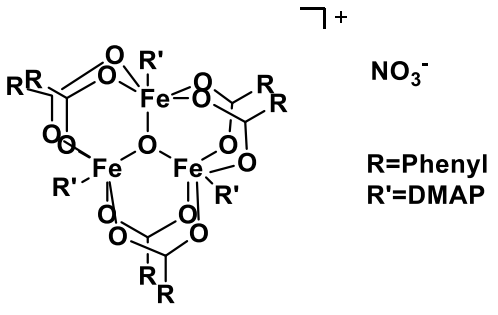
Elemental analysis calculated for $C_{42}H_{36}Fe_3NO_{19}$: C, 49.15; H, 3.54; N, 1.36; Fe, 16.32

Found: C, 49.52; H, 3.56; N, 1.20; Fe, 16.30

Gram scale synthesis:

In a 5 L three neck round bottom flask equipped with an overhead stirrer, sodiumbenzoate (24.97 g 123.3 mmol) was dissolved in distilled water (1.66 L). $Fe(NO_3)_3$ x 9 H_2O (28 g, 69.3 mmol) was dissolved in distilled water (2.81 L) in a beaker and was added portion wise to the benzoate solution while stirring. The orange suspension was further stirred at room temperature overnight. The precipitate was then filtered and washed thoroughly with H_2O, before it was dried in high vacuum in an Desiccator for several days until no further weight loss, to obtain the product as pale orange solid (20.65 g, 87%).

Cluster 2 (Modified Literature procedure of 4)



8

In a round bottom flask, $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (300 mg, 0.29 mmol) and sodium nitrate (35.6 mg, 0.42 mmol) were dissolved in EtOH (50 mL) and DMAP (260.2 mg, 2.13 mmol) was added. The

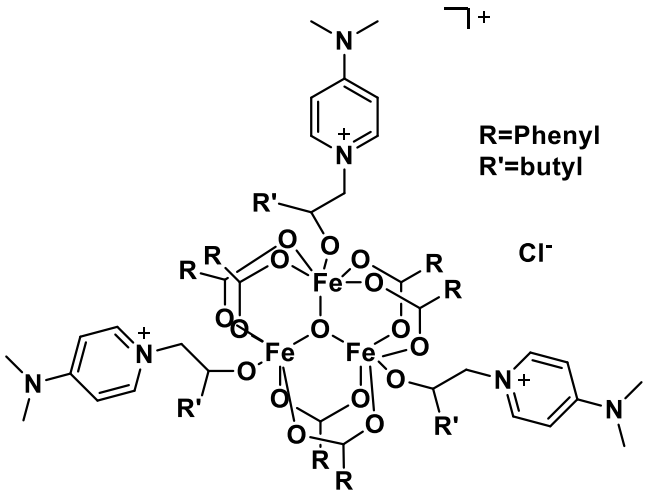
mixture was stirred overnight, filtered and the precipitate was washed gently with cold EtOH and dried in high vacuum.

Yield: 28.8 mg, 7 %

HRMS [$(M)^+$] calculated: 1276.2262, found (m/z): 1276.2295

HRMS [$(M - DMAP)^+$] calculated: 1154.1417, found (m/z): 1154.1455

Cluster 3



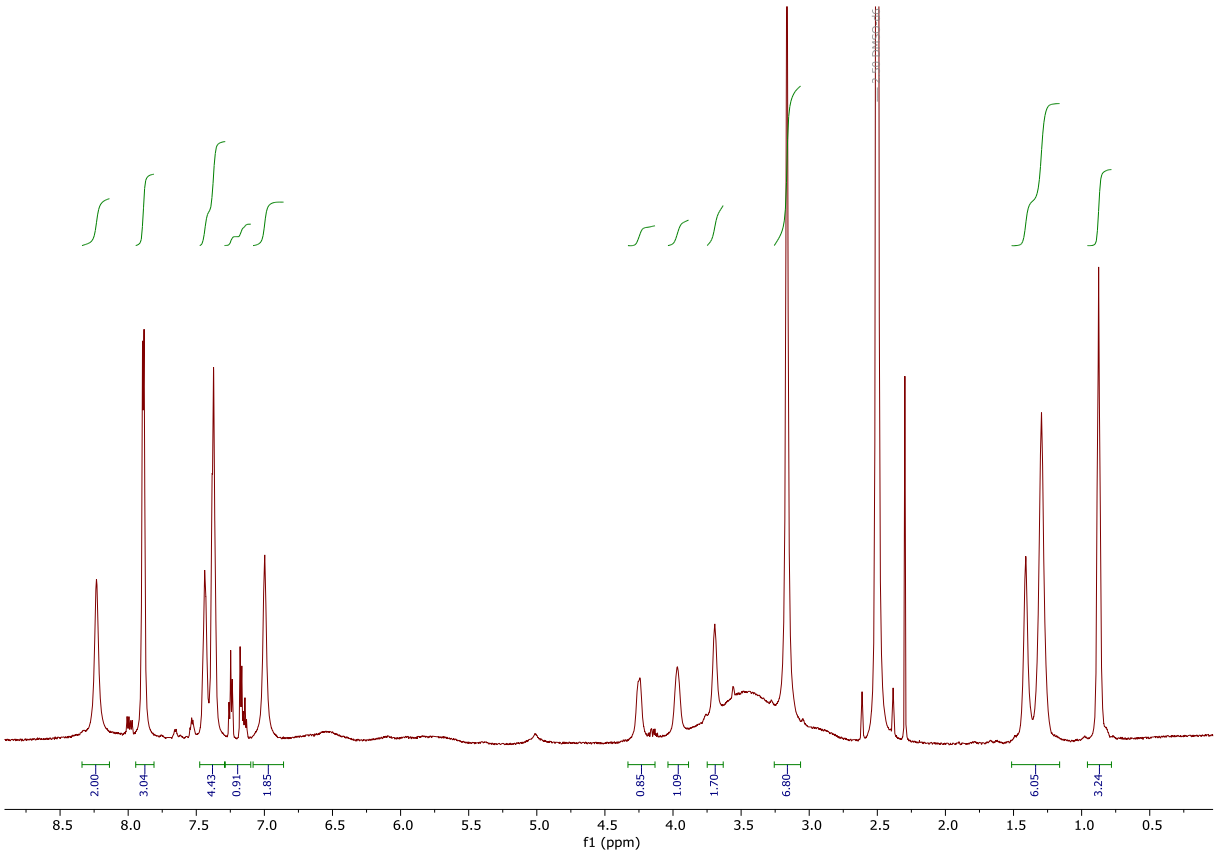
22

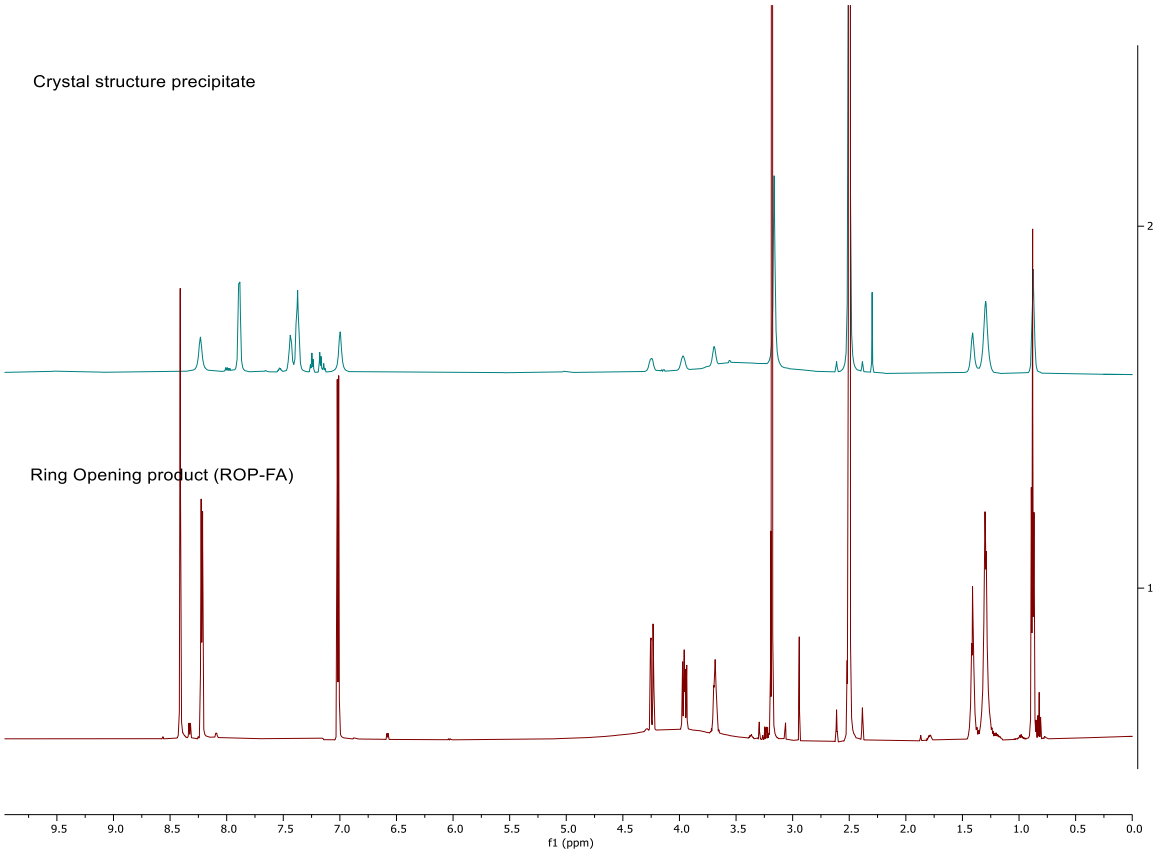
A carousel vial from Radleys was charged with a stirrer, benzoic acid (549.55 mg, 4.5 mmol), $FeCl_3$ (7.30 mg, 1 mol%) and DMAP (5.50 mg, 1 mol%). Toluene (9 mL) was added, followed by 1,2-epoxyhexane (542.37 µL, 4.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel. The reaction was stirred at reflux for 2 hours and was allowed to stand at room temperature for 2-5 days afterwards, which led to formation of red crystals. The solvent was decanted and the crystals were washed with Toluene, filtered and dried in high vacuum to obtain, 22.46 mg of material, 0.0142 mmol, 95% theoretical yield of assumed structure without residual solvent.

HRMS [$(M)^+$] calculated: 1576.4926, found (m/z): 1576.4889

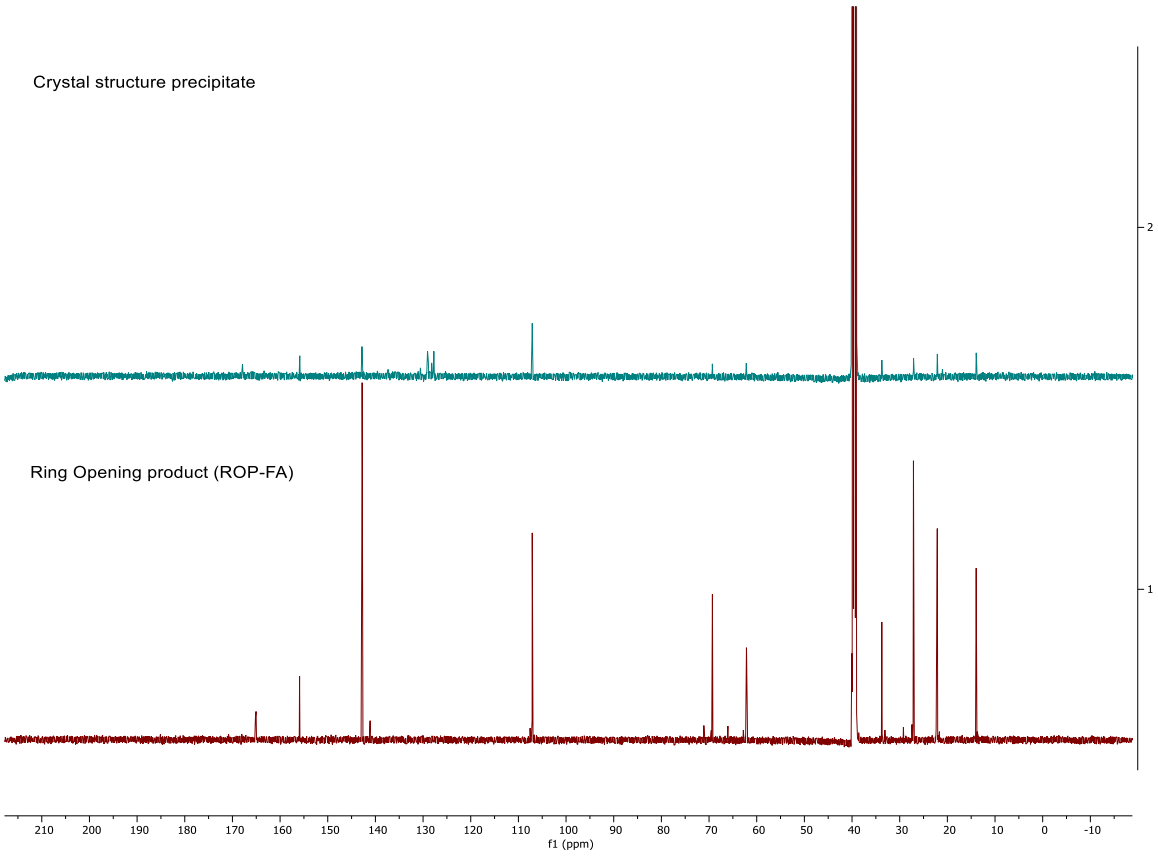
HRMS [$(M - ROP)^+$] calculated: 1354.3193, found (m/z): 1354.3200

^{1}H-NMR:


2.00
3.04
4.43
0.91
1.85
0.85
1.09
1.70
6.80
6.05
3.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



^{13}C NMR comparison between ROP and Crystal from finished reaction



HRMS, ^{1}H-NMR as well as ^{13}C NMR comparison shows the presence of ROP. Additionally, signals of toluene are observed in the ^{1}H-NMR spectrum.

15 Kinetic Data general remarks

The concentration profiles have been analyzed and manipulated according to the Visual Time Normalization Analysis (VTNA) published by Burés and Nielsen[5] to achieve visual overlap of concentration profiles with different starting concentrations of the respective investigated parameters.

A Carousel vial from Radleys was charged with a stirrer, benzoic acid, and solid catalyst component. The solids were suspended in toluene (20 mL) and 1,2-epoxyhexane was added . The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel, allowing the mixture to be stirred overnight. The progress was followed via GC-FID by gradually taking samples over the course of the reaction.

16 ‘’Same excess’’ experiments for Visual Time Normalization Analysis

Table 11: Concentrations and catalyst loadings of ‘’same excess’’ experiments

Entry	Catalyst	Catalyst Loading	Starting concentration Benzoic Acid [mmol/mL]	Starting concentration 1,2-Epoxyhexane [mmol/mL]
1	$FeCl_3$/DMAP	1 mol% each	0.5	0.5
2	$FeCl_3$/DMAP	1 mol% each	0.25	0.25
3	DMAP	3 mol%	0.5	0.5
4	DMAP	3 mol%	0.25	0.25
5	$FeCl_3$	4 mol% each	0.5	0.5
6	$FeCl_3$	4 mol% each	0.25	0.25

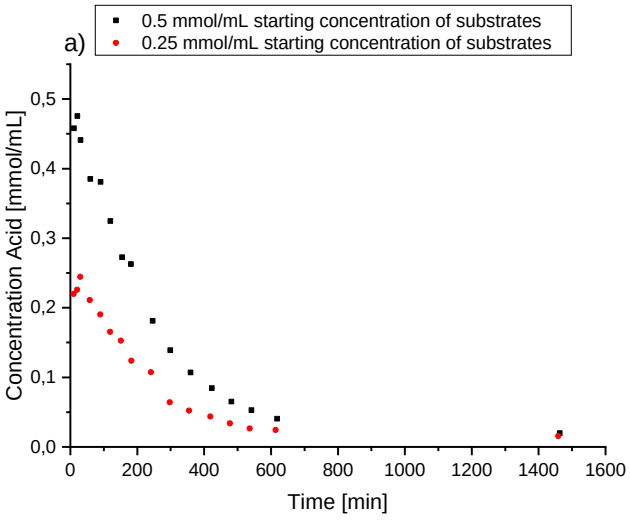
17 Table for Concentrations and Graphs

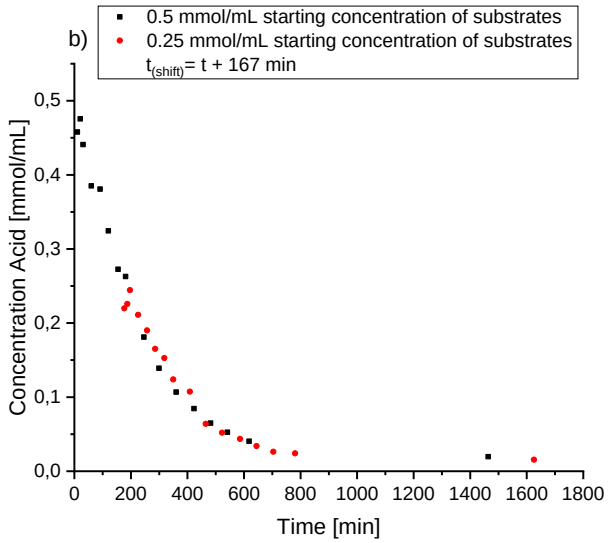
1. ‘’Different Excess’’ experiments for Visual Time Normalization Analysis

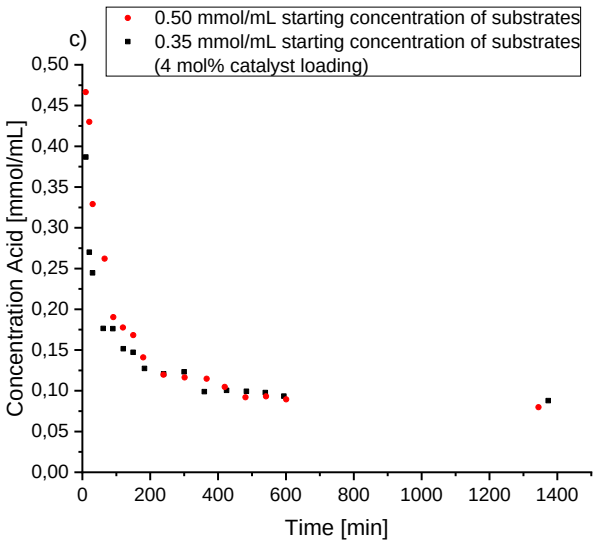
Table 12: Concentrations and catalyst loadings of ‘different excess’’ experiments.

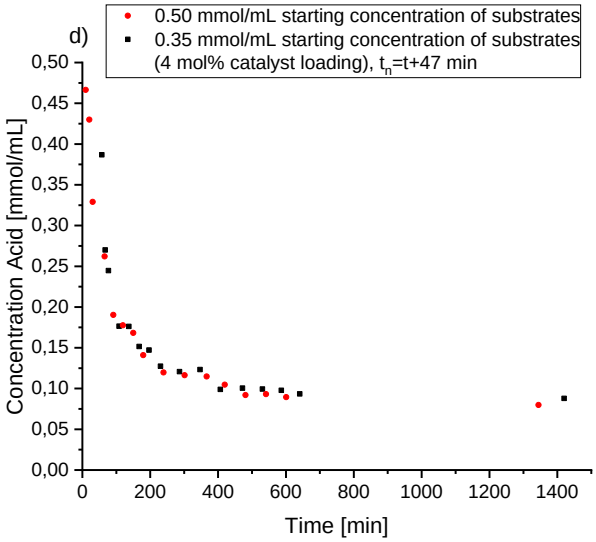
Entry	Catalyst	Catalyst Loading	Starting concentration Benzoic Acid [mmol/mL]	Starting concentration 1,2-Epoxyhexane [mmol/mL]	Remark
1	$FeCl_3$/DMAP	1 mol% each	0.5	0.5	Order in Acid/Catalyst
2	$FeCl_3$/DMAP	1 mol% each	0.4	0.5	Order in Acid
3	$FeCl_3$/DMAP	1 mol% each	0.25	0.5	Order in Acid
4	DMAP	3 mol%	0.5	0.5	Order in Acid/Catalyst
5	DMAP	3 mol%	0.35	0.5	Order in Acid
6	DMAP	3 mol%	0.25	0.5	Order in Acid
7	$FeCl_3$	4 mol% each	0.5	0.5	Order in Acid/Catalyst
8	$FeCl_3$	4 mol% each	0.35	0.5	Order in Acid
9	$FeCl_3$	4 mol% each	0.25	0.5	Order in Acid
10	$FeCl_3$/DMAP	1 mol% each	0.5	0.5	Order in Epoxide
11	$FeCl_3$/DMAP	1 mol% each	0.5	0.4	Order in Epoxide
12	$FeCl_3$/DMAP	1 mol% each	0.5	0.25	Order in Epoxide
13	DMAP	3 mol%	0.5	0.5	Order in Epoxide
14	DMAP	3 mol%	0.5	0.35	Order in Epoxide
15	DMAP	3 mol%	0.5	0.25	Order in Epoxide
16	$FeCl_3$/DMAP	0.5 mol% each	0.5	0.5	Order in Catalyst
17	$FeCl_3$/DMAP	2.5 mol% each	0.5	0.5	Order in Catalyst
18	DMAP	4 mol%	0.5	0.5	Order in Catalyst
18	DMAP	2 mol%	0.5	0.5	Order in Catalyst
19	$FeCl_3$	3 mol% each	0.5	0.5	Order in Catalyst
20	$FeCl_3$	2 mol% each	0.5	0.5	Order in Catalyst

18 Kinetic Data Catalyst deactivation






c)
0.50 mmol/mL starting concentration of substrates
0.35 mmol/mL starting concentration of substrates
(4 mol% catalyst loading)
Concentration Acid [mmol/mL]
0,00
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
0,50
0
200
400
600
800
1000
1200
1400
Time [min]


d)
0.50 mmol/mL starting concentration of substrates
0.35 mmol/mL starting concentration of substrates
(4 mol% catalyst loading), t$_n$=t+47 min
Concentration Acid [mmol/mL]
0,00
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
0,50
0
200
400
600
800
1000
1200
1400
Time [min]

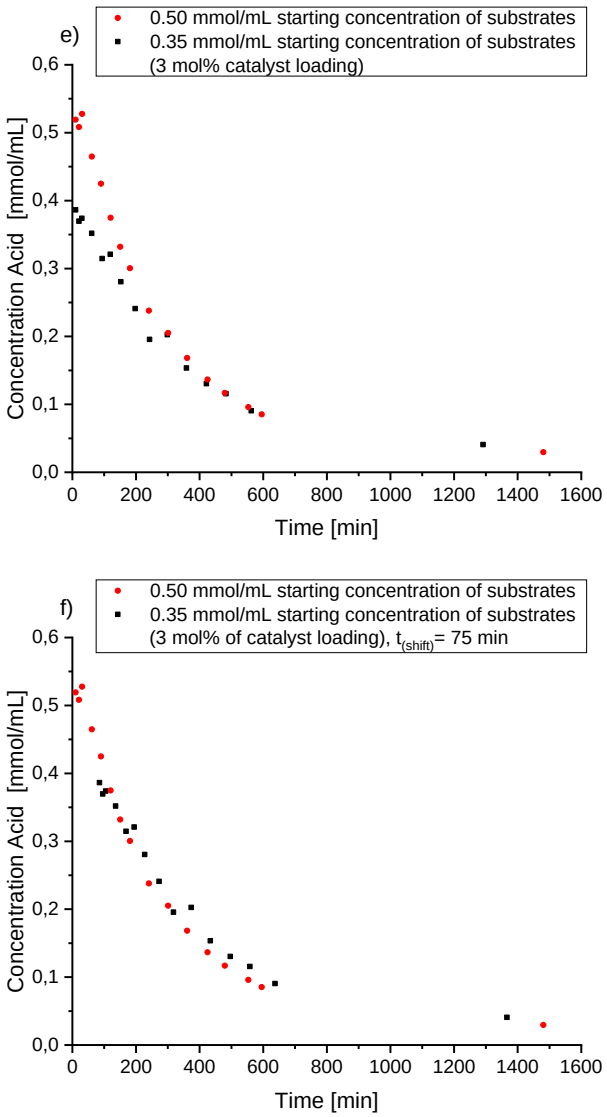


Figure 9: Concentration profiles of "same excess'' experiments with corresponding time shifts resulting in overlap of both concentration profiles for **a),b)**: $FeCl_3$/DMAP; **c),d)**: $FeCl_3$; **e),f)**: DMAP.

Figure 8. Concentration profiles of "same excess'' experiments with corresponding time shifts resulting in overlap of both concentration profiles for Top: $FeCl_3$+DMAP Middle: $FeCl_3$ Bottom: DMAP.

For ''same excess'' experiments depicted in Figure **3**, the concentration profiles of the datasets with lower starting concentrations have been shifted in time (x-axis) up to the point where both concentration profiles overlap. Successful overlap was achieved for all catalyst systems ($FeCl_3$/DMAP. $FeCl_3$, DMAP), indicating that catalyst degradation did not occur during the reaction.

19 Kinetic Data Order in Acid

$FeCl_3$/DMAP System

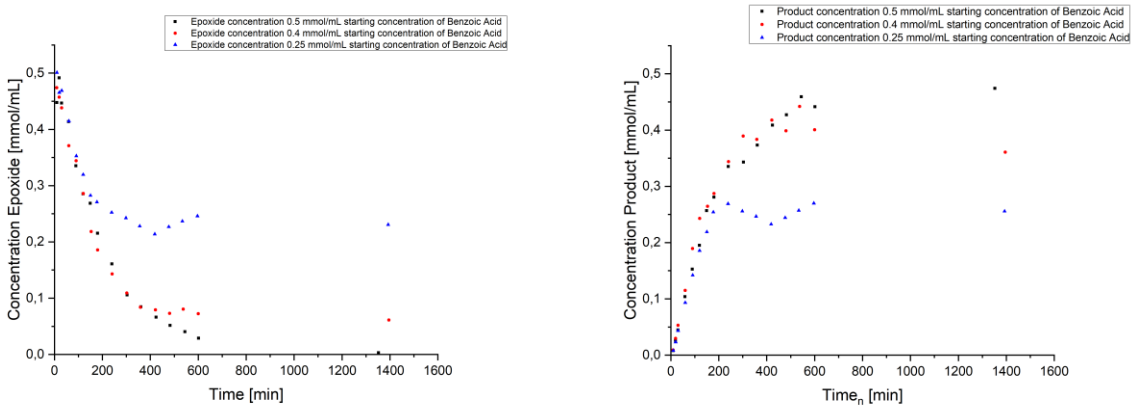


Figure 9. Determination of order in carboxylic acid for the $FeCl_3$+DMAP catalyst system. Concentration profiles of "different excess'' experiments **left:** Epoxide consumption. **right:** Product formation.

For the $FeCl_3$/DMAP system, the concentration profiles for three different starting concentrations overlap already without introducing a manipulation of the time scale, which indicates 0 order behavior for benzoic acid in this catalyst system.

DMAP Catalyst

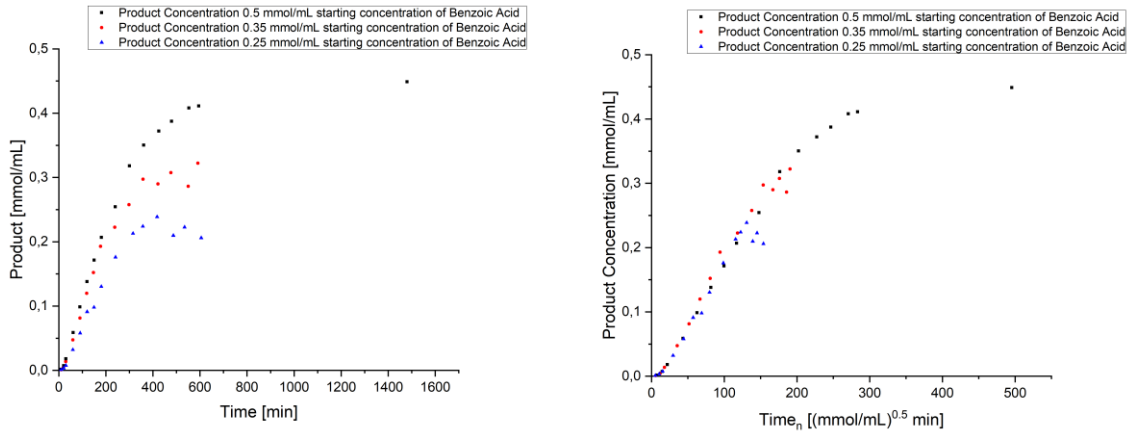


Figure 10. Determination of order in carboxylic acid with DMAP as catalyst. Concentration profiles of "different excess'' experiments **left:** Product formation. **right:** Product formation normalized to the order of 0.5.

For the DMAP system, the concentration profiles for three different starting concentrations of benzoic acid lead to overlap by alteration of the time scale, with iteration of $\beta = 0.5$, indicating 0.5 order behavior for benzoic acid in presence of DMAP as catalyst.

$FeCl_3$ Catalyst

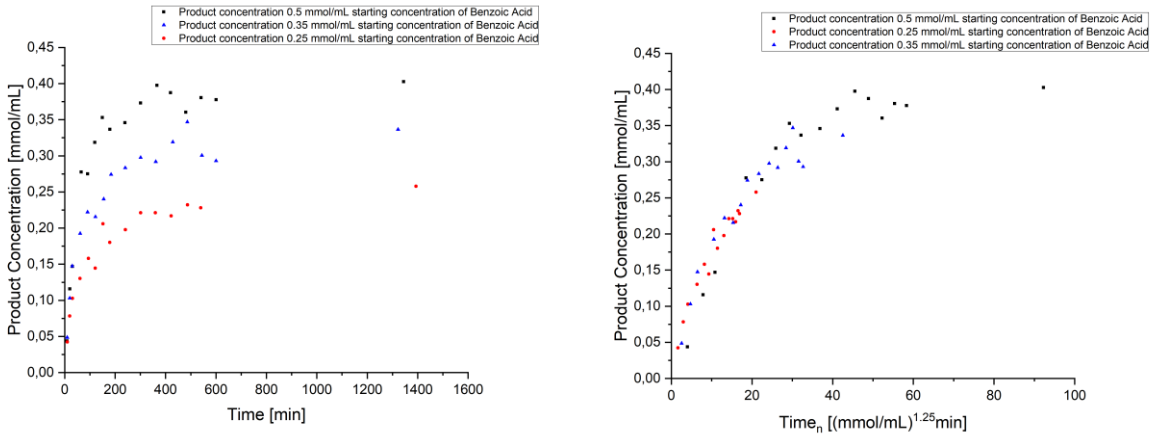


Figure 11. Determination of order in carboxylic acid with $FeCl_3$ as catalyst. Concentration profiles of "different excess'' experiments **left:** Product formation. **right:** Product formation normalized to the order of 1.25.

For the $FeCl_3$ system, the concentration profiles for three different starting concentrations of benzoic acid lead to best visual overlap by iteration of $\beta \approx 1.25$, indicating a non-integer order in acid for this catalyst.

20 Kinetic Data Order in Epoxide

$FeCl_3$/DMAP System

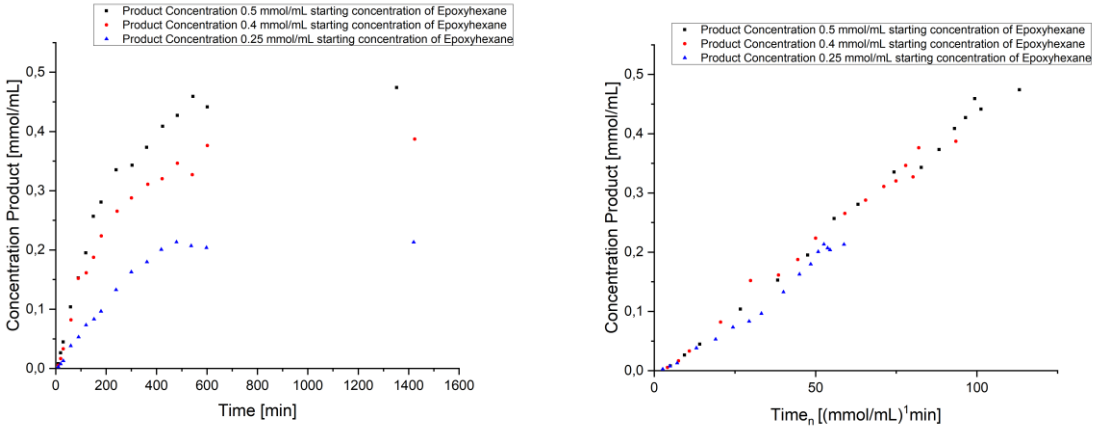


Figure 12. Determination of order in 1,2-epoxyhexane with $FeCl_3$/DMAP as catalyst system. Concentration profiles of "different excess'' experiments **left:** Product formation. **right:** Product formation normalized to the order of 1.

For the $FeCl_3$/DMAP system, the concentration profiles for three different starting concentrations of 1,2-epoxyhexane lead to overlap by alteration of the time scale, with iteration of $\beta = 1$, indicating first order behaviour for 1,2-epoxyhexane in presence of $FeCl_3$/DMAP as catalyst system.

DMAP Catalyst

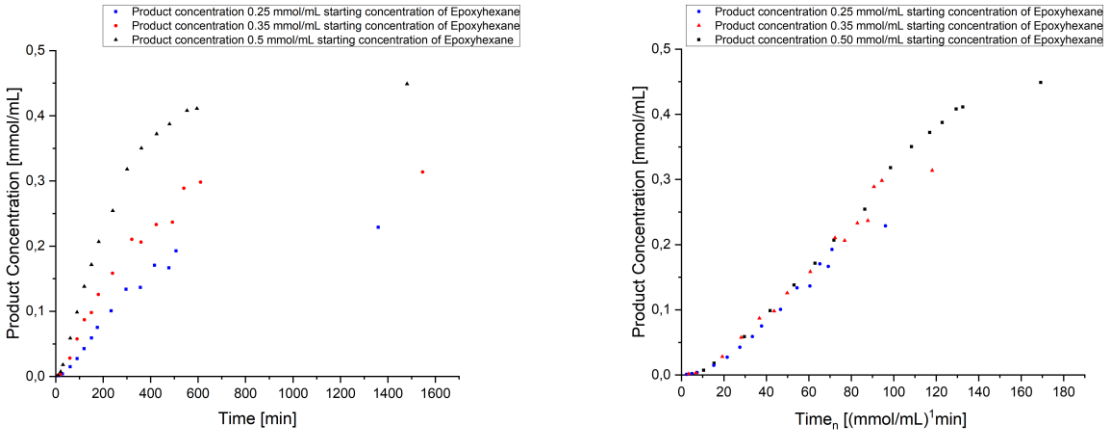


Figure 13. Determination of order in 1,2-Epoxyhexane with DMAP as catalyst. Concentration profiles of "different excess'' experiments **left:** Product formation. **right:** Product formation normalized to the order of 1.

For the DMAP system, the concentration profiles for three different starting concentrations of 1,2-epoxyhexane lead to overlap by alteration of the time scale, with iteration of β = 1, indicating first order behaviour for 1,2-epoxyhexane in presence of DMAP as catalyst.

For $FeCl_3$ as standalone catalyst, the order in epoxide has not been determined, because an increased tendency of the epoxide to engage in side reactions has been observed.

21 Kinetic Data Order in Catalyst

$FeCl_3$/DMAP System

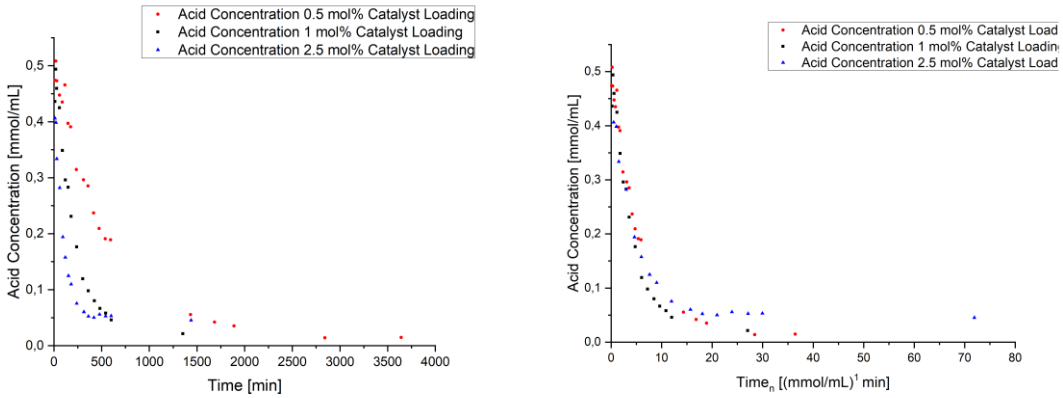


Figure 14. Determination of order in catalyst with $FeCl_3$/DMAP as catalyst system. Concentration profiles of "different excess'' experiments **left:** Acid consumption **right:** Acid consumption normalized to the order of 1.

For the $FeCl_3$/DMAP system, the concentration profiles for three different starting concentrations of $FeCl_3$ and DMAP (0.5 mol%, 1 mol% and 2.5 mol% each, equal ratios) lead to an overlap by alteration of the time scale, with iteration of β = 1, indicating first order behaviour in catalyst for this system.

$FeCl_3$ System

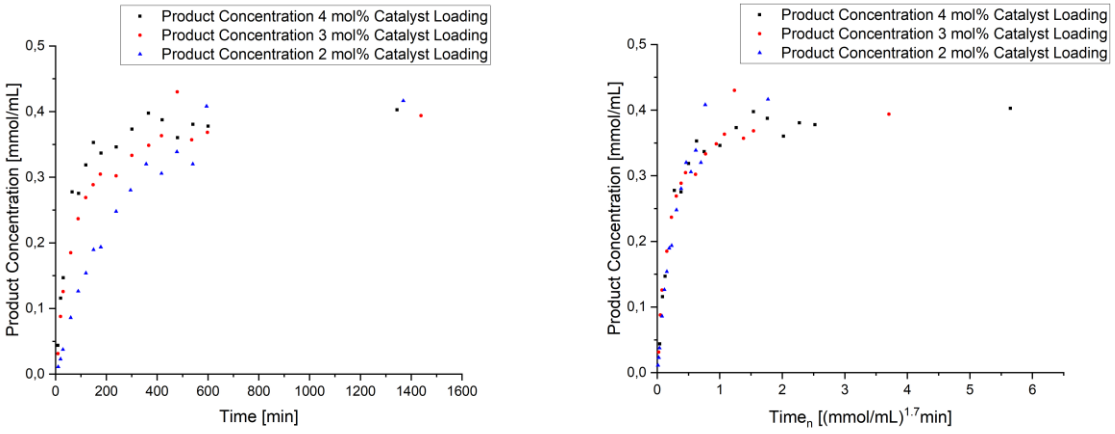


Figure 15. Determination of order in catalyst with $FeCl_3$ as catalyst. Concentration profiles of "different excess'' experiments **left:** Product formation **right:** product formation normalized to the order of 1.7.

For the $FeCl_3$ catalyst system, the concentration profiles for three different starting concentrations of $FeCl_3$ lead to an overlap by alteration of the time, with iteration to $\beta \approx 1.7$, indicating a more complex behavior in catalyst for this species.

DMAP System

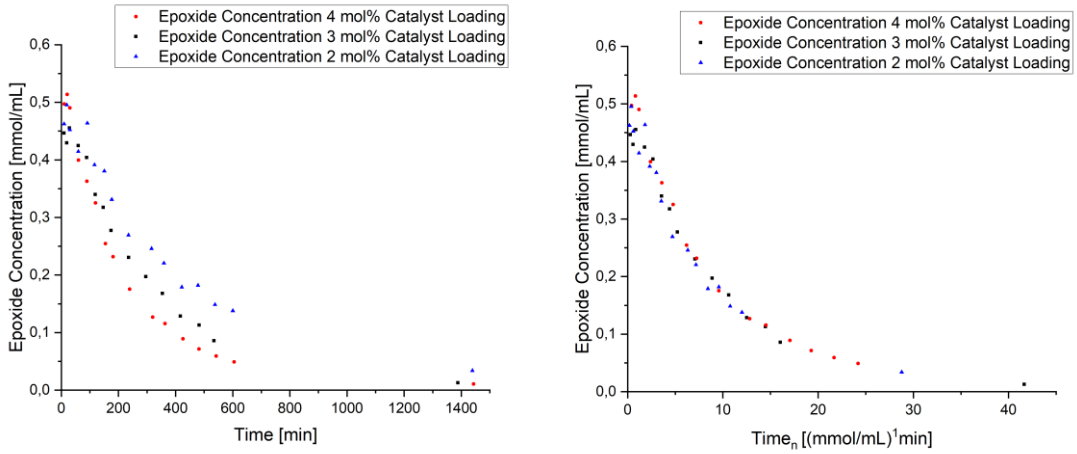
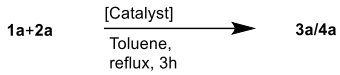


Figure 16. Determination of order in catalyst with DMAP as catalyst. Concentration profiles of "different excess'' experiments **left:** Epoxide consumption **right:** Epoxide consumption normalized to the order of 1.

For the DMAP catalyst system, the concentration profiles for three different starting concentrations of DMAP lead to an overlap by alteration of the time scale, with iteration of $\beta = 1$, indicating first order behaviour in catalyst for this system.

22 $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ /Guanidine Carbonate activity screen



c = 0,5 mmol/mL ; v = 9 mL
1 eq. of both reactants

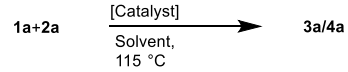
A carousel vial from Radleys was charged with a stirrer, benzoic acid (549.54 mg, 4.5 mmol), respective LA catalyst (1 mol% based on Iron) and guanidine carbonate (4.05 mg, 1 mol%). Toluene (9 mL) was added, followed by addition of 1,2-epoxyhexane (542.37 µL, 4.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (120 ° C) reaction carousel. At 1h and 3h, a sample was taken via syringe. A sample for GC-FID measurement was prepared by adding 0.1 mL of reaction mixture to 1 mL of stock solution consisting of EtOAc with mesitylene as external standard (2 mL/L). For ^{1}H-NMR preparation, the sample was filtered through a pipette containing Merck 60 Å 230–400 mesh silica gel and Celite®, flushed with EtOAc.

Table 13: Screening of guanidinium carbonate with iron sources**.**

Entry	Catalyst	Loading	1,2-epoxyhexane conversion GC-FID 1h [%][a]	Conversion benzoic acid (^{1}H NMR) 1h [%][b]	1,2-epoxyhexane conversion GC-FID 3h [%][a]	Conversion benzoic acid (^{1}H NMR) 3h [%][b]
1	$[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate	0.33/1	53 (69:31)	57	84	86
2	$FeCl_3$/ guanidinium carbonate	1/1	58 (69:31)	57	82	83

[a] *Determined by GC-FID, mesitylene as external standard. Temperature: reflux, c = 0.5 mmol/mL, v = 9 mL* [b] *Determined by ^{1}H-NMR signals of both regioisomers of product. Regioisomer ratios observed after 20h depicted in parentheses.*

23 $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ /Guanidine Carbonate Activity in Anisole, ^{n}BuOAc and (1-Methoxy-2-propyl) acetate



c = 0,5 mmol/mL ; v = 3 mL
1 eq. of both reactants

A Carousel vial from Radleys was charged with a stirrer, benzoic acid (183.18 mg, 1.5 mmol), and respective catalyst. Solvent (3 mL) was added, followed by addition of 1,2-epoxyhexane (180.80 µL 1.5 mmol). The reaction mixture was sealed with a Radleys screw cap and placed into a preheated (115 °C) reaction carousel. At 1h (and 3h), a sample was taken via syringe.

Table 14: Screening of catalyst systems in anisole.

Entry	Catalyst	Loading	Conversion benzoic acid (^{1}H	1,2-epoxyhexane conversion	Conversion benzoic acid (^{1}H	1,2-epoxyhexane conversion

			NMR) 1h [%][a]	GC-FID 1h [%][b]	NMR) 3h [%][a]	GC-FID 3h [%][b]
1	$[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate	0.33/1	51 (69:31)	52	83	89
2	$FeCl_3$/DMAP	1/1	30 (69:31)	30	63	66
3	TBAB	2	19 (69:31)	17	47	48
4	Et_3NBn	2	19 (70:30)	20	n.d.	n.d.
5	PPh_3	2	20 (69:31)	19	n.d.	n.d.
6	PPh_4Br	2	47 (69:31)	52	n.d.	n.d.

[a] *Determined by GC-FID,* [b] *Determined by ^{1}H-NMR, n.d. = not determined; Regioisomer ratios observed after 20h depicted in parentheses.*

Table 15: Screening of catalyst systems in nBuOAc.

Entry	Catalyst	Loading	Conversion benzoic acid (^{1}H NMR) 1h [%][a]	1,2-epoxyhexane conversion GC-FID 1h [%][b]
1	$[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate	0.33/1	66 (68:32)	63
2	$FeCl_3$/DMAP	1/1	41 (69:31)	50.
3	TBAB	2	26 (70:30)	27
4	Et_3NBn	2	24 (70:30)	27
5	PPh_3	2	16 (71:29)	11
6	PPh_4Br	2	55 (73:27)	53

[a] *Determined by GC-FID,* [b] *Determined by ^{1}H-NMR, n.d. = not determined; Regioisomer ratios observed after 20h depicted in parentheses.*

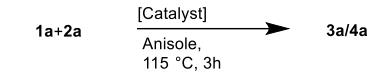
Table 16: Screening of catalyst systems in (1-Methoxy-2-propyl) acetate.

Entry	Catalyst	Loading	Conversion benzoic acid (^{1}H	1,2-epoxyhexane conversion

			NMR) 1h [%][a]	GC-FID 1h [%][b]
1	$[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate	0.33/1	50	56
2	$FeCl_3$/DMAP	1/1	33	50
3	TBAB	2	24	31
4	Et_3NBn	2	23	29
5	PPh_3	2	14	14
6	PPh_4Br	2	46	54

[a] *Determined by GC-FID*, [b] *Determined by ^{1}H-NMR, n.d. = not determined.*

24 $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ /Guanidine Carbonate Recyclability



c = 0,5 mmol/mL ; v = 9 mL
1 eq. of both reactants

A carousel vial from Radleys was charged with a stirrer, benzoic acid (549.54 mg, 4.5 mmol), $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (15.39 mg, 0.33 mol%) and guanidine carbonate (4.05 mg, 1 mol%). Anisole (9 mL) was added, followed by addition of 1,2-epoxyhexane (542.37 µL, 4.5 mmol). The reaction mixture was sealed with a Radleys Screw Cap and placed into a preheated (115 ° C) reaction carousel.

a) First catalytic run

Sample taken after 3h

b) Readdition of substrates

A catalytic run was allowed to cool to room temperature after 16h, additional benzoic acid (1eq.) and 1,2-epoxyhexane (1eq.) has been added and the reaction was run for additional 3h at 115 ° C, until a sample was taken

c) Recycled catalyst

Three catalytic runs have been reacted for 16h and were allowed to cool to rt. Pentane (15 mL) was added. After allowing the suspensions to stand overnight, the precipitated catalyst material was filtered, washed with pentane and dried in vacuum. The recycled material has been isolated in 51.3 mg, 72% yield. (Isolation of same ratio of $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ to guanidinium salt assumed, calculation based on guanidinium benzoate). A catalytic run has been performed with 2 mol% of the isolated material (1.5 mmol of substrates, v=3 mL,)

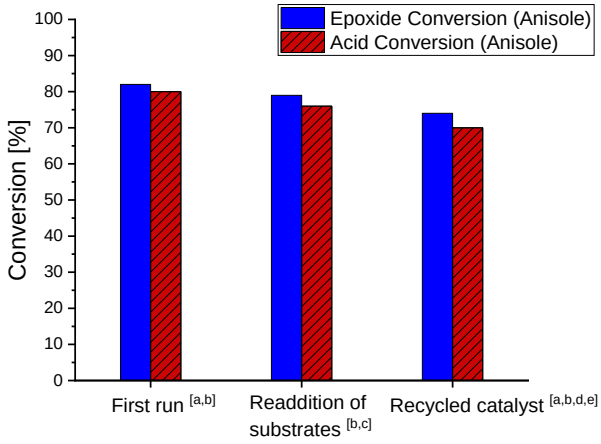
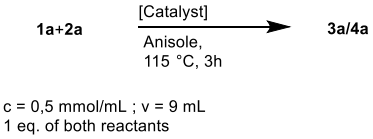


Figure 17 Reaction conditions: **1a** (4.5 mmol), **2** (4.5 mmol), 1/1 mol%, $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate , toluene, reflux, v = 9 mL, [a] Determined by ^{1}H-NMR spectroscopy, [b] Determined by GC-FID, [c] readdition to reaction after 16h [d] equal isolated mol ratio (1/1) of $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ and guanidinium benzoate assumed, [e] **1a** (1.5 mmol), **2** (1.5 mmol), v = 3 mL.

25 Different ratios $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ /Guanidine carbonate



c = 0,5 mmol/mL ; v = 9 mL
1 eq. of both reactants

A Carousel vial from Radleys was charged with a stirrer, benzoic acid (549.54 mg, 4.5 mmol), $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ (x mol%) and Guanidine Carbonate (1 mol). Toluene or anisole (9 mL) was added, followed by 1,2-epoxyhexane (542.37 µL, 4.5 mmol). The reaction mixture was sealed with a Radleys Screw Cap and placed into a preheated (120 ° C) reaction carousel and was stirred for 1 hour. The reaction progress was monitored by ^{1}H NMR and GC-FID analysis.

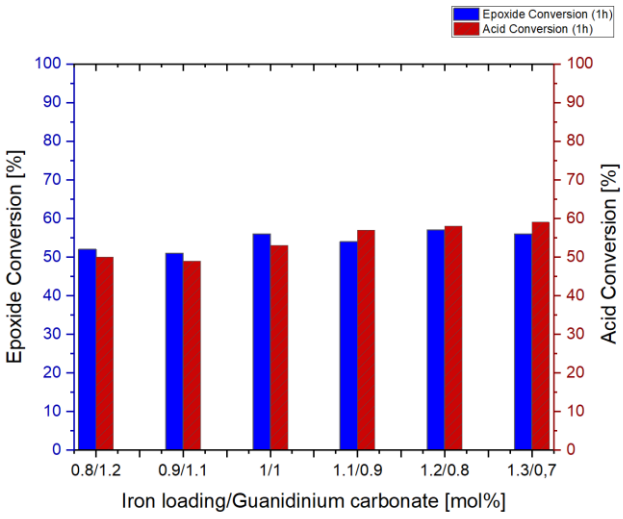


Figure 18. Different ratios of $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ to guanidine carbonate. Screening against model reaction, c = 0.5 mol/L, v = 9 mL, reflux, 1h. Epoxide conversion determined by GC-FID. Acid conversion determined by ^{1}H-NMR.

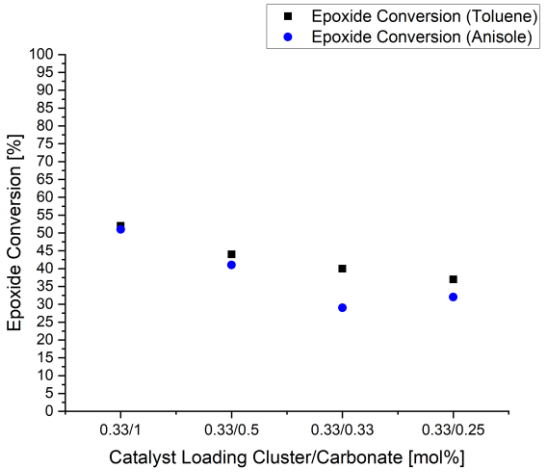
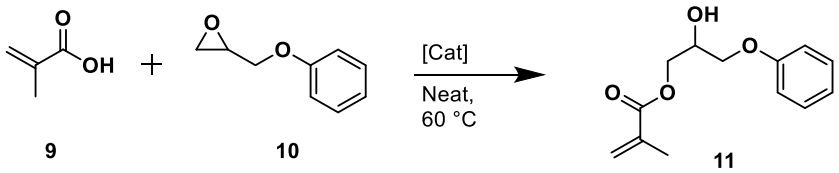


Figure 19. Different ratios (a/b) of $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$ to guanidine carbonate. Screening against model reaction, c = 0.5 mol/L, v = 9 mL, reflux, 1h of reaction time. Epoxide conversion determined by GC-FID. Acid conversion determined by ^{1}H-NMR.

26 Application – Synthesis of 2-hydroxy-3-phenoxypropyl methacrylate



9 10 11

To a 2 mL LCMS Vial, charged with catalyst and stirrer, was added methacrylic acid (126.60 µL 1.5 mmol) and phenyl glycidyl ether (202.95 µL, 1.5 mmol). The vial was sealed with a crimp cap, purged with nitrogen via a needle and put in a preheated oil bath (65 °C). After 3 hours, 1 mL of a stock solution of $CDCl_3$, containing 1,3,5-trimethoxybenzene (0.5 mmol/mL) was added to the vial and 50 mikroliter were diluted with $CDCl_3$ (0.6 mL) for ^{1}H-NMR analysis.

The product was isolated via automated column chromatography (pentane/diethylether) for the $[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate system in 92 % yield after reacting the neat mixture for 3h in a sand bath at 65 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 – 7.27 (m, 2H), 6.98 (t, *J*=7.6, 1H), 6.95 – 6.91 (m, 2H), 6.18-6.14 (m, 1H), 5.63-5.60 (m, 1H), 4.44 – 4.33 (m, 2H), 4.29 (p, *J*=5.1, 1H), 4.10 – 4.01 (m, 2H), 1.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.7, 158.5, 136.0, 129.7, 126.3, 121.5, 114.7, 68.8 (x2), 65.8, 18.5.

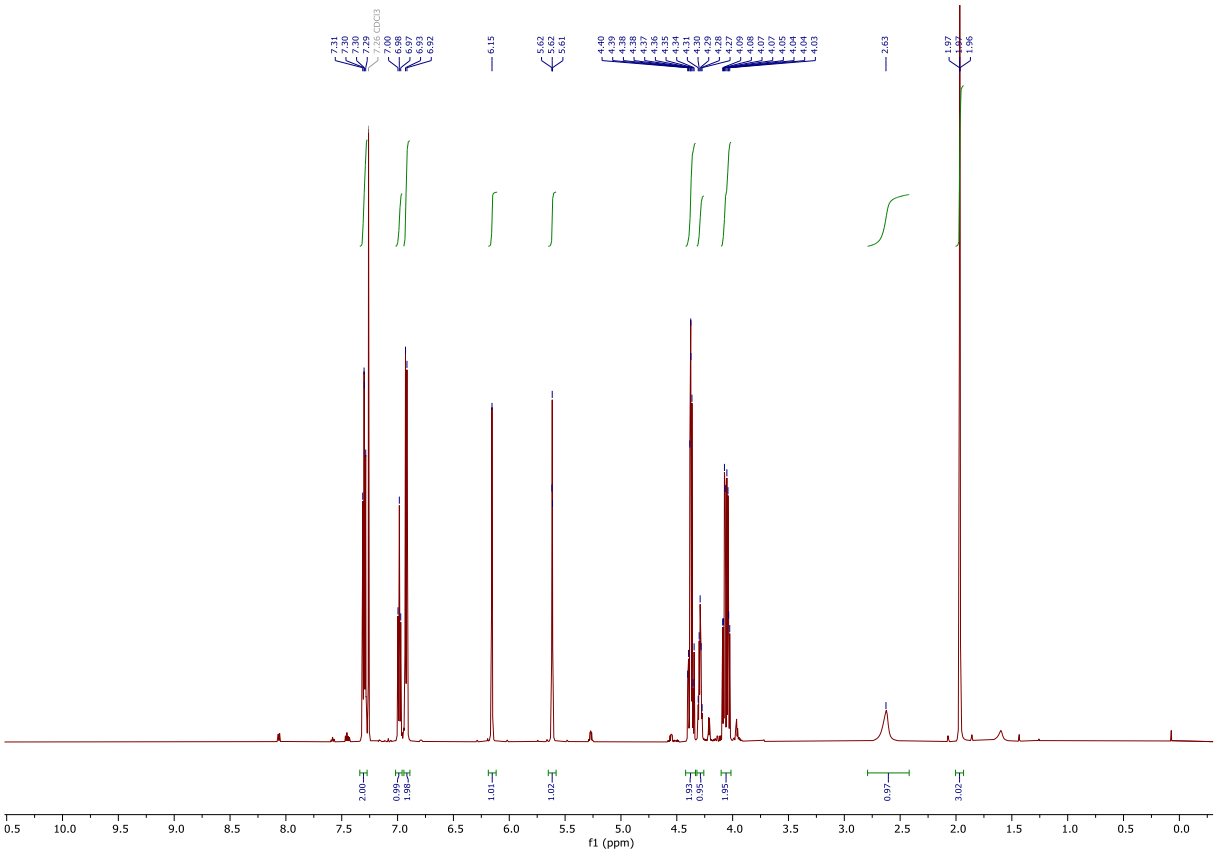
HRMS [$(M + H)^+$] calculated: 237.1121, found (m/z): 237.1122.

Table 17: Conversion towards 2-hydroxy-3-phenoxypropyl methacrylate

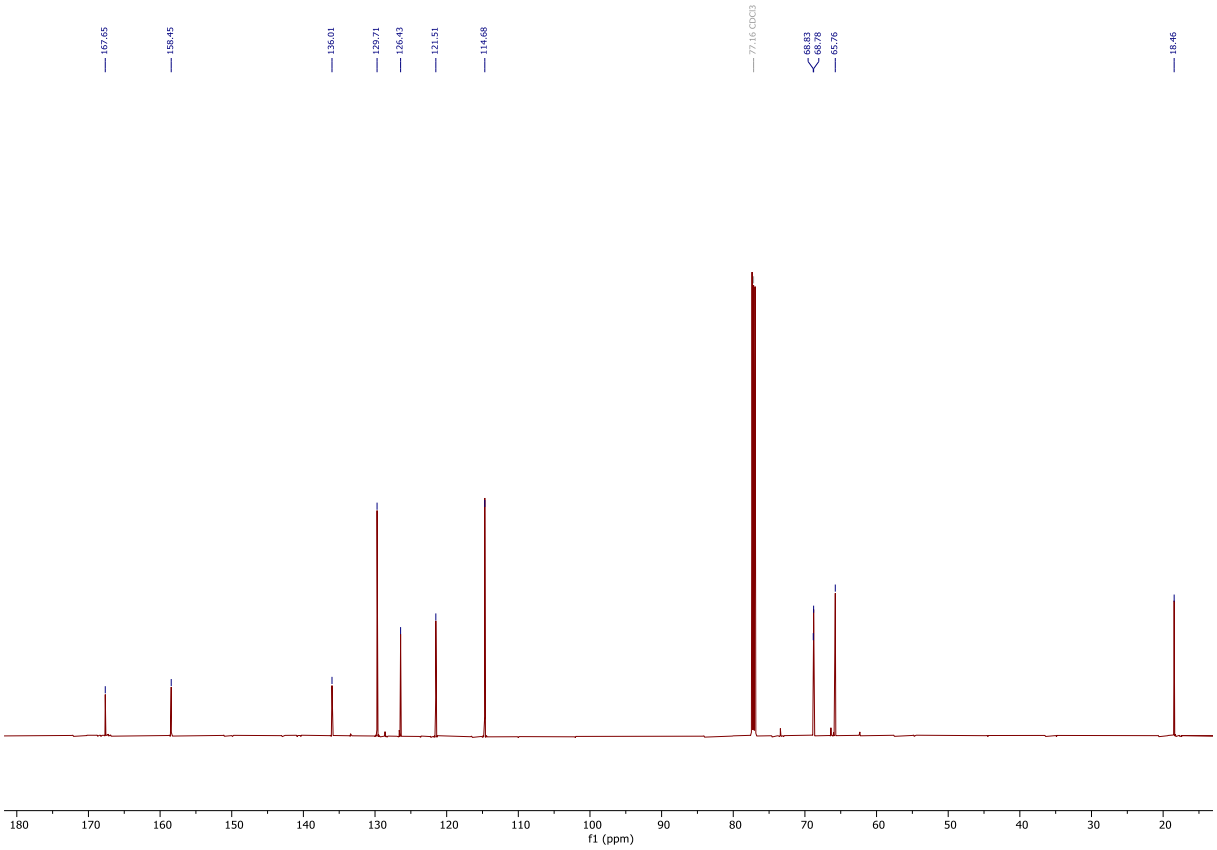
Entry	Catalyst	Loading [mol%]	2-hydroxy-3-phenoxypropyl methacrylate formation, 1h [%][a]	2-hydroxy-3-phenoxypropyl methacrylate formation, 3h [%][a]
1	$[Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate	0.33/1	59	88
2	TBAB	1/1	24	47
3	Et_3N	2	3	8
4	Et_3NBn	2	22	48
5	PPh_3	2	26	51
6	PPh_4Br	2	36	60

[a] *Determined by ^{1}H-NMR, 1,3,5-trimethoxybenzene as external standard. Temperature: 60 °C, 1.5 mmol, neat, 3h.*

^{1}H NMR of **11**


7.31
7.30
7.30
7.29
7.26 CDCl3
7.00
6.98
6.97
6.93
6.92
6.15
5.62
5.62
5.61
4.40
4.39
4.38
4.38
4.37
4.36
4.35
4.34
4.31
4.30
4.29
4.28
4.27
4.09
4.08
4.07
4.07
4.05
4.04
4.04
4.03
2.63
1.97
1.97
1.96
2.00
0.99
1.98
1.01
1.02
1.93
0.95
1.95
0.97
3.02
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C NMR of **11**



27 Sustainability comparison of relevant Catalysts

Most severe drawbacks of state of the art catalysts compared to $Fe_3O(Benzoate)_6(H_2O)_3]NO_3$/guanidinium carbonate:

Generally, all tested catalysts showed lower catalytic activity in several solvents and under neat conditions.

TBAB: Classified as “harmful to aquatic life” and “suspected of damaging fertility”, is potentially adversely affecting tropospheric ozone concentrations and requires haloalkanes for synthesis.

PPh_3: Classified as “harmful if swallowed” and “causes damage to organs”, lower biodegradability and requires halogenated aromatic compounds for synthesis.

Et_3N: Classified as “Harmful if swallowed”, “toxic in contact with skin or inhaled”, volatile and may form secondary organic aerosols through reaction with ozone.

Benzyltriethylammoniumchloride: Classified as “harmful to aquatic life” and requires haloalkanes for synthesis.

Compiled data

Information concluded and compared according to literature[6]

Table 18: Discussion of relevant and applicable concerns for the Iron (III) benzoate cluster.

Iron (III) benzoate cluster	
Concern	**Assessment**
Bio-accumulation	- Benzoate ligands abundant in nature[7], used as food additive[8], biodegradable[9] - Nitrate used as fertilizer[10]
Ecotoxicity	Not expected; Ligands, counterion and iron are abundantly present in environment and biodegradable[7-10]
Eutrophication	Nitrate present, but unlikely to be released in large quantities into the environment
Human toxicity	Practically not toxic; Ligands, counterion and iron are abundantly present in environment, ligand used as food additive, nitrate used as fertilizer[7-10]
Human carcinogenicity	Not expected, ligands, counterion and iron is abundantly present in environment[7-10]
Ozone depletion	Not expected, low volatility
Persistence	Not expected, ligand is degradable[9]
Ressource depletion	Ligands, counterion and iron is abundantly present in environment[7-10]

Table 19: Discussion of relevant and applicable concerns for guanidinium carbonate.

Guanidinium Carbonate	
Concern	**Assessment**
Bio-accumulation	Considered as no thread[11]
Ecotoxicity	Considered as no thread[11]
Eutrophication	Nitrogen containing compound, but unlikely to be released in large quantities (currently no regulatory needs,[11] compound used in consumer product)[12]
Human toxicity	Considered as no thread[11]
Human carcinogenicity	Considered as no thread[11]
Ozone depletion	Not expected, low volatility
Persistence	Not expected, degradable[11]
Ressource depletion	No thread

Table 20: Discussion of relevant and applicable concerns for tetrabutylammoniumbromide.

Tetrabutylammoniumbromide	
Concern	**Assessment**
Bio-accumulation	Biodegradable[13]
Ecotoxicity	H412 Harmful to aquatic life with long lasting effects[13]
Eutrophication	Nitrogen containing compound, but unlikely to be released in large quantities
Human toxicity	Considered as not toxic[13]
Human carcinogenicity	H361fd Suspected of damaging fertility. Suspected of damaging the unborn child.[13]
Ozone depletion	Surface active compound, contains bromide, may promote adverse effects[14]
Persistence	Not expected[13]
Ressource depletion	No thread, but requires haloalkanes for synthesis[15]

Table 21: Discussion of relevant and applicable concerns for benzyltriethylammoniumchloride.

Benzyltriethylammoniumchloride	
Concern	**Assessment**
Bio-accumulation	Low potential for bioaccumulation[16]
Ecotoxicity	H412: Harmful to aquatic life with long lasting effects[16]
Eutrophication	Nitrogen containing compound, but unlikely to be released in large quantities
Human toxicity	Considered as no thread[16]
Human carcinogenicity	Considered as no thread[16]
Ozone depletion	Requires halogenated aromatic compound for synthesis[17]
Persistence	Considered as No thread[16]
Ressource depletion	No thread

Table 22: Discussion of relevant and applicable concerns for triethylamine.

Triethylamine	
Concern	**Assessment**
Bio-accumulation	Considered as not accumulative[18]

Ecotoxicity	Not classified as ecotoxic[18]
Eutrophication	Nitrogen containing compound, but unlikely to be released in large quantities
Human toxicity	H302 Harmful if swallowed. H311 + H331 Toxic in contact with skin or if inhaled.[18]
Human carcinogenicity	Considered as no thread.[118]
Ozone depletion	Volatile, potentially contributing to formation of secondary organic aerosols (SOAs)[19]
Persistence	Not expected[18]
Ressource depletion	No thread

Table 23: Discussion of relevant and applicable concerns for triphenylphosphine.

Triphenylphosphine	
Concern	**Assessment**
Bio-accumulation	Not readily biodegradable according to criteria of ''The Organization for Economic Cooperation and Development (OECD) ''[20]
Ecotoxicity	chronic hazard to aquatic environments - category 4, poor solubility[20]
Eutrophication	Phosphorous containing compound, but unlikely to be released in large quantities.
Human toxicity	H302 Harmful if swallowed. H372 Causes damage to organs (Central nervous system, Peripheral nervous system) through prolonged or repeated exposure if inhaled.[20]
Human carcinogenicity	Considered as no thread[20]
Ozone depletion	Low volatility
Persistence	Slow degradation[20]
Ressource depletion	Requires halogenated aromatic compounds for synthesis[21]

Table 24: Log K_{OW}, toxicity data and hazard statements for relevant catalyst systems.

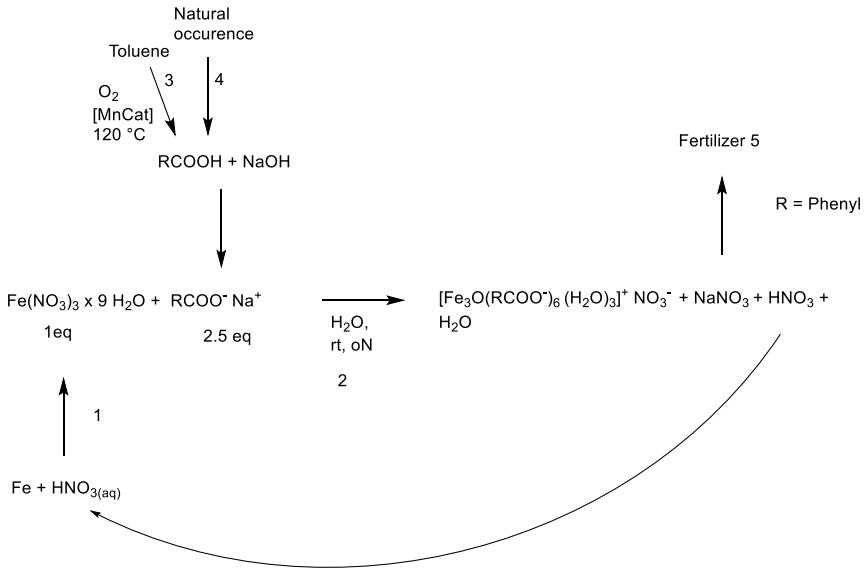
Bioaccumulation and toxicity of catalyst systems				
Substrate	**Bio-accumulation**	**Ecotoxicity**	**Human toxicity**	**Hazard statements**

NaOBenz	Log K_{OW}=-2.27 (estimate[a])	LC_{50} (daphnia magna 96h) > 100 mg/L[9] LC_{50} (fathead minnow 96h): 484 mg/L[9]	No data	H319 Causes serious eye irritation.[9]
Guanidinium Carbonate	Log K_{OW}=-9.61 (estimate[a])	LC_{50} (daphnia magna 48h): 41 mg/L[22]	LD_{50} (rat, oral): 1045 mg/kg[22]	H318: Causes serious eye damage.[11] H302: Harmful if swallowed.[11]
TBAB	Log K_{OW}=1.71 (estimate[a])	LC_{50} (Danio rerio 96h) > 100 mg/L[23] EC_{50} (Vibrio fischeri 0.25h): 1.862 mg/L[23]	LD_{50} (rat, oral): >300 mg/kg, < 2000 mg/kg[23]	H302: Harmful if swallowed.[13] H315: Causes skin irritation.[13] H319: Causes serious eye irritation.[13] H361: Suspected of damaging fertility or the unborn child.[13] H412: Harmful to aquatic life with long lasting effects.[13]
Et_3N	Log K_{OW}= 1.45	LC_{50} (Oryzias latipes 96h) 24 mg/L[24] LC_{50} (Ceriodaphnia dubi 48h):17 mg/L[24]	LD_{50} (rat, oral): 730 mg/kg[24] LC_{50} (rat, inhalation 4h): 3.63 mg/L[24]	H225 Highly flammable liquid and vapor.[18] H302 Harmful if swallowed.[18] H311 + H331 Toxic in contact with skin or if inhaled.[18] H314 Causes severe skin burns and eye damage.[18] H335 May cause respiratory irritation.[18]
Benzyltriethylammoniumchloride	Log K_{OW}=-1.00 (estimate[a])	LC_{50} (fathead minnow 96h): 161 mg/L[25]	LD_{50} (rat, oral): 2219 mg/kg[25]	H302: Harmful if swallowed.[16] H412: Harmful to aquatic life with long lasting effects.[16] H317: May cause an allergic skin reaction.[16]
PPh_3	Log K_{OW}=5.69	LC_{50} (Leuciscus idus 96h) > 10000 mg[26]	LD_{50} (rat, oral): 700 mg/kg[26]	H302 Harmful if swallowed.[20] H317 May cause an allergic skin reaction.[20]

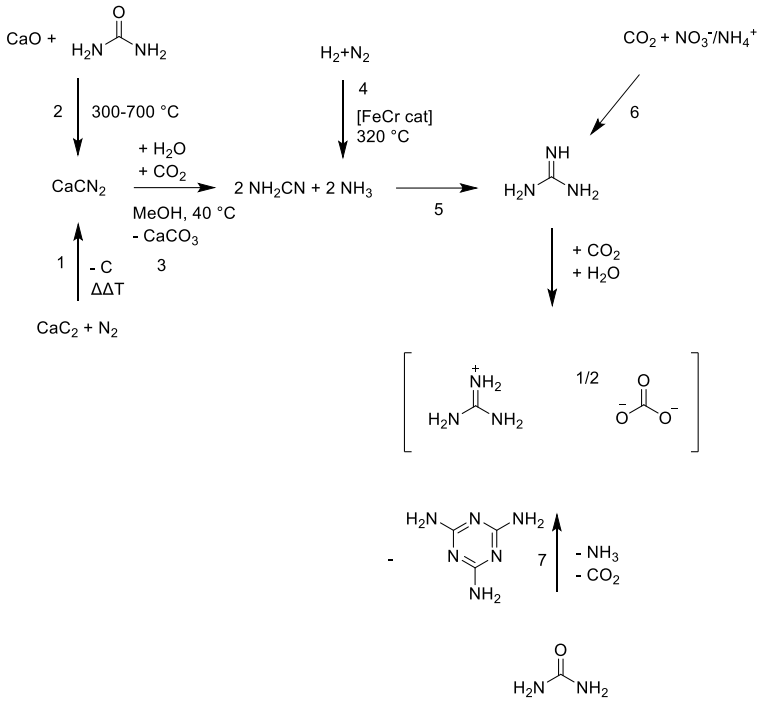
	EC_{50} (Daphnia magna 48h)> 5 mg/L (above solubility limit)[26]	LC_{50} (rat, inhalation 4h): 12.5 mg/L[26]	H372 Causes damage to organs (Central nervous system, Peripheral nervous system) through prolonged or repeated exposure if inhaled.[20]

[a] Estimated values calculated with Episuite.

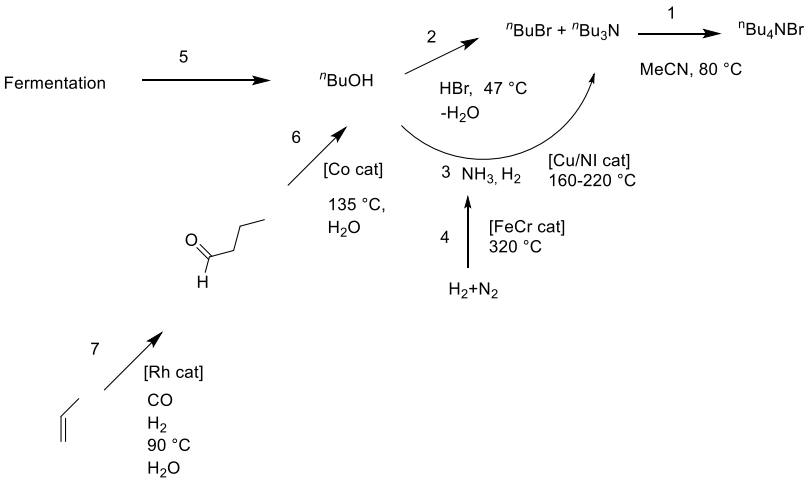
Potential synthesis pathways of relevant catalysts



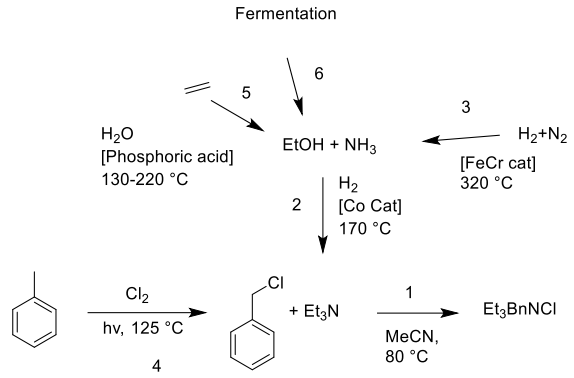
Scheme 1. Synthesis of iron (III) benzoate cluster; **1**.C.C. Lewchalermwong, (1989), *Process for manufacture of ferric nitrate*, US4808393A, United States Patent and Trademark Office; **2**.F.F. Moreira, T. Hasegawa, D.J. Evans and F.S. Nunes, *J. Coord. Chem*, 2007, 60, 185-191; **3**.D. Jihad, A. Zorran, S. Yoel (1988), *Process for the manufacture of benzoic acid and salts thereof*, US4965406A, United States Patent and Trademark Office; **4**. A. del Olmo, J. Calzada and M. Nuñez, *Crit. Rev. Food Sci. Nutr.,* 2017, 57, 3084-3103; **5**.J. Davidson, J.A. Le Clerc, *J. Agron.,* 1917, 9, 145.



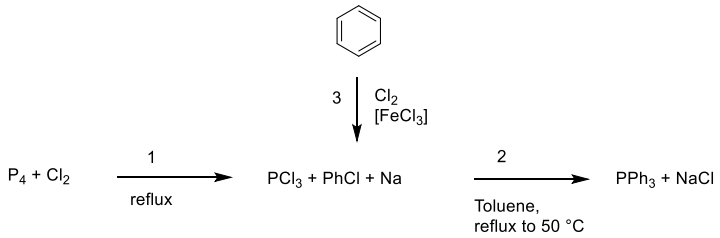
Scheme 2. Synthesis pathways for guanidinium carbonate; **1.** T. Güthner; B. Mertschenk, "Cyanamides". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH, 2006; **2.** P.J. Picard, (1965), *Synthesis of calcium cyanamide*, US3173755A, United States Patent and Trademark Office; **3**. J. Houben, T. Weyl, E. Mueller, *Methoden der organischen Chemie*, 4. Aufl., Bd. 8, Stuttgart 1952, S. 96, **4.** M. Appl, "Ammonia". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH**,** 2006; **5.** S. Li, L. Cai, (2005), *Process for the preparation of guanidine carbonate*, CN1560031A, A China National Intellectual Property Administration; **6.** B. Wang, T. Dong, A. Myrlie, L. Gu, H. Zhu, W. Xiong, P. Maness, R. Zhou, J. Yu, *Green Chem.*, 2019, 21, 2928-2937; **7. a)** A.Schmidt, K. Wegleitner, J. H. Hatzl, R. Sykora, F. Weinrotter (1972), *Process for the preparation of guanidine carbonate,* US3952057A, United States Patent and Trademark Office. **b)** J.M. Lee, (1993), *Process for manufacturing melamine from urea,* US5384404A, United States Patent and Trademark Office. **c)** H. Gabriel and R. Dicke, (2020), *Method for increasing the guanidine carbonate yield in a combined melamine process and guanidine carbonate treatment process*, EP3626706A1, European Patent Office.



Scheme 3. Synthesis pathways for tetrabutylammoniumbromide; **1.** J. Wu, F. Xiang, Z. Chen, J. Lu, X. Wang, Q. Li, X. Shi, Y. Shen, (2020), *Synthesis process of tetrabutylammonium bromide*, CN111960948A, A China National Intellectual Property Administration; **2.** Y. Jinting, S. Zhang, (2018), *Preparation method of alkyl bromide*, CN107973692A, A China National Intellectual Property Administration; **3.** A. Ying, H. Hou, L. Feng, F. Zheng, Z. Sun, Q. Qi, H. Zhou (2015), *Preparation method of n-butylamine*, CN104262165A, A China National Intellectual Property Administration; **4.** M. Appl, "Ammonia". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH, 2006; **5.** E.M. Green, COBIOT, 2011, **22**, 337-343; **6.** J. Unruh, D.A. Ryan, S. Dugan, (2000), *Process for the production of n-butanol*, EP1027315A1, European Patent Office; **7.** D.H. Ko, S.-S. Eom, Y.-J. Choe, C.H. Lee, M.-H. Hong, O.-H. Kwon, D.-C. Kim, J.-H. Choi, (2011), *Apparatus for producing alcohols from olefins*, US2011282108A1, United States Patent and Trademark Office.

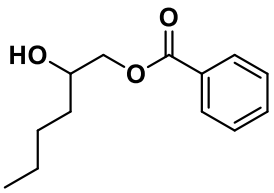


Scheme 4. Synthesis pathways for benzyltriethylammoniumchloride; **1.** Y. Yu, C. Zhou, H. Ying, J. Liu and P. Chen, (2022), *Synthesis method of benzyltriethylammonium chloride*, CN115521209A, A China National Intellectual Property Administration; **2.** T. Bailiang, D. Wei, T. Guoqi, L. Baoqin, Z. Guiying, Z. Qi, (2010), *Production method of ethylamine*, CN101671254A, A China National Intellectual Property Administration; **3.** M. Appl, "Ammonia". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH, 2006; **4.** M. Rossberg, W. lendle, G. Pfleiderer, A. Tögel, E.-L. Dreher, E. Langer, H. Rassaerts, P. Kleinschmidt, H. Strack, R. Cook, U. Beck, K.-A. Upper, T.R. Torkelson, E. Löser, K.K. Beutel, T. Mann, "Chlorinated Hydrocarbons". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH, 2006; **5.** M. Naito, M. Osawa, S. Tanaka, (2018), *Method of producing ethanol*, JP2020002015A, Japan Patent Office; **6.** F.W. Hayes, (1980), *Production of ethanol from sugar cane*, US4326036A, United States Patent and Trademark Office.

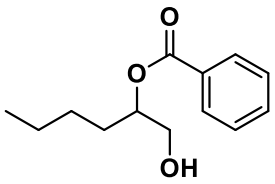


Scheme 5. Synthesis pathway for tripehnylphosphine **1.** Forbes, M. C.; Roswell, C. A.; Maxson, R. N.Fernelius, W. C., *Inorganic Syntheses*, Bd. 2, New York-London 1946, S. 145/7; **2.** S. Guangri, B. Caifeng, S. Youmei, (1993), *Synthesis of triphenyl phosphine*, CN1069273A, A China National Intellectual Property Administration; **3.** B. Philipp, P. Stevens: *Grundzüge der Industriellen Chemie.* VCH Verlagsgesellschaft, Weinheim 1987, ISBN 3-527-25991-0, S. 176.

28 NMR Spectra

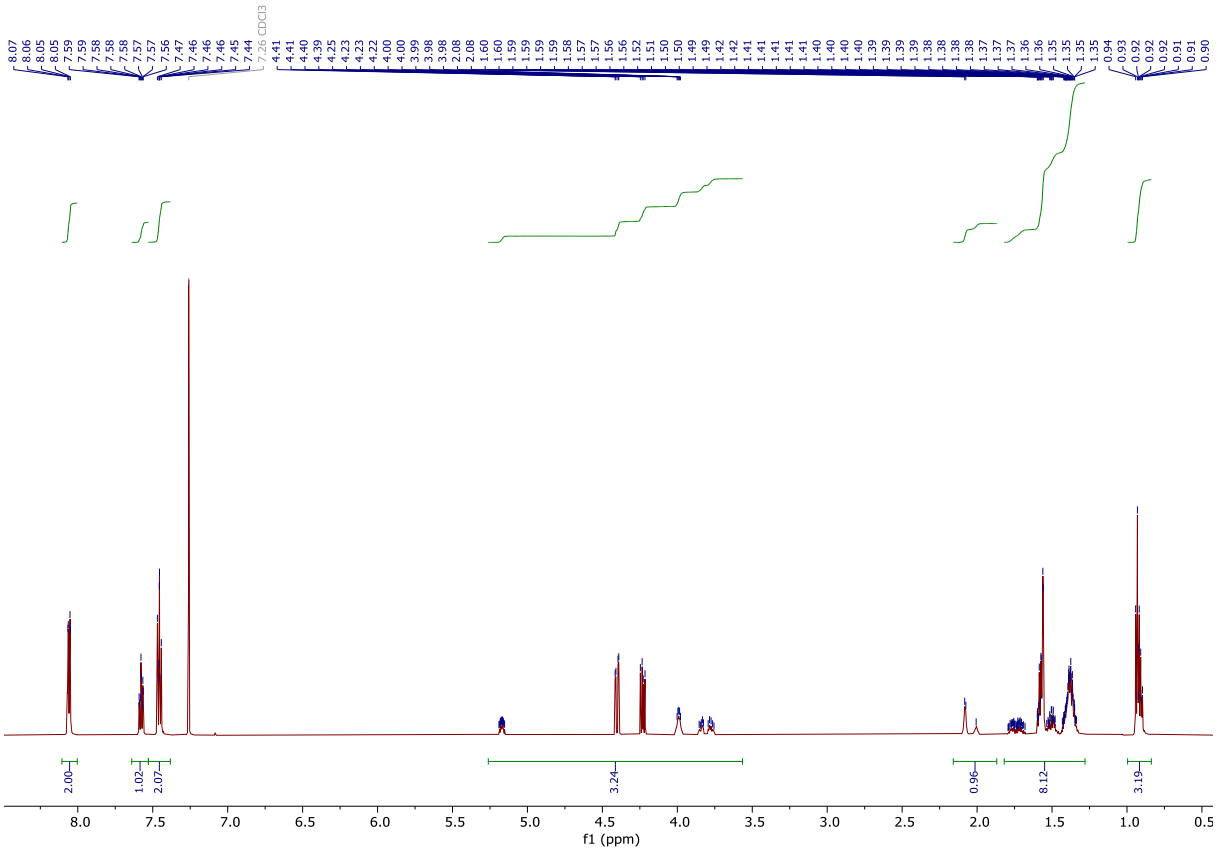


3a (a)

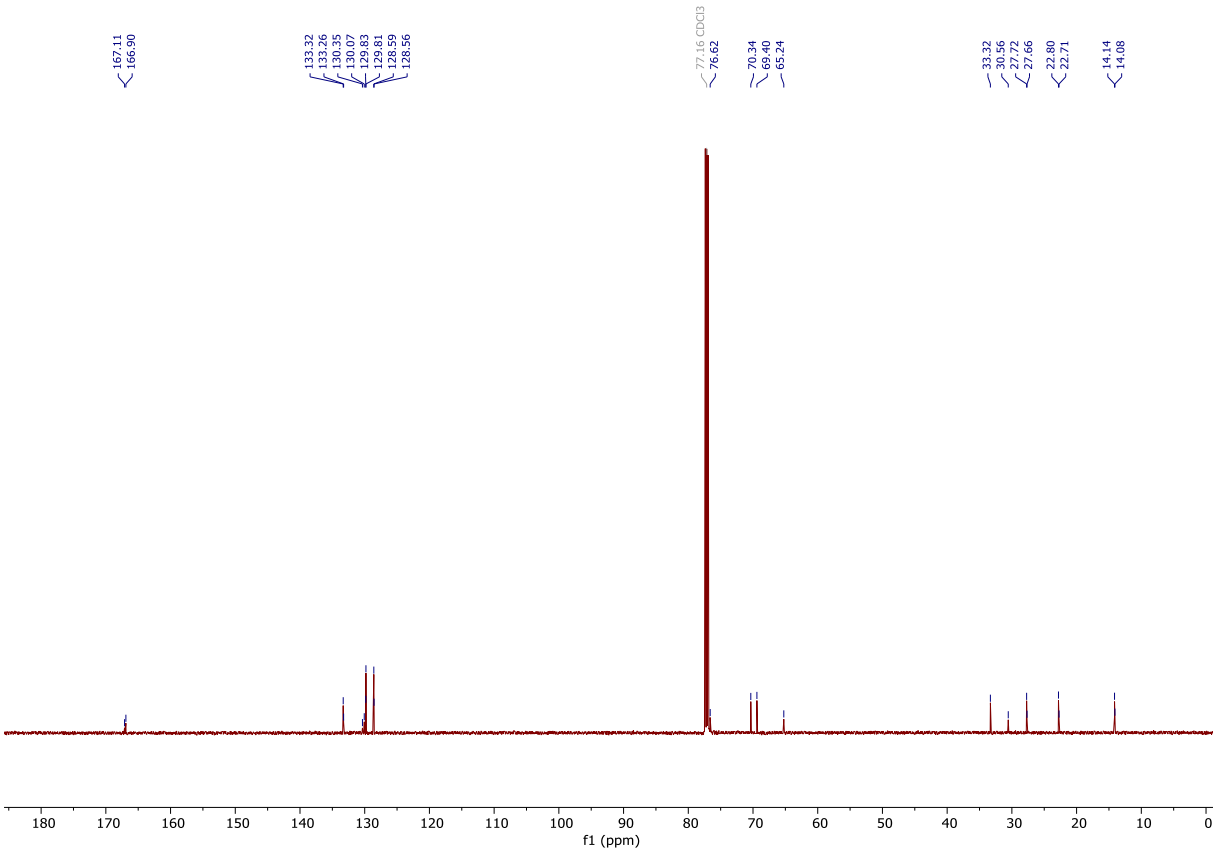


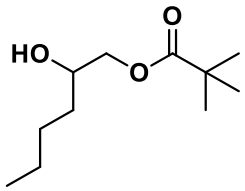
4a (b)

^{1}H-NMR spectrum of **3a** + **4a**

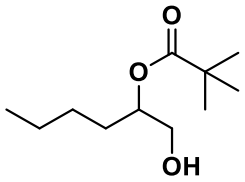


^{13}C-NMR spectrum of **3a**+**4a**



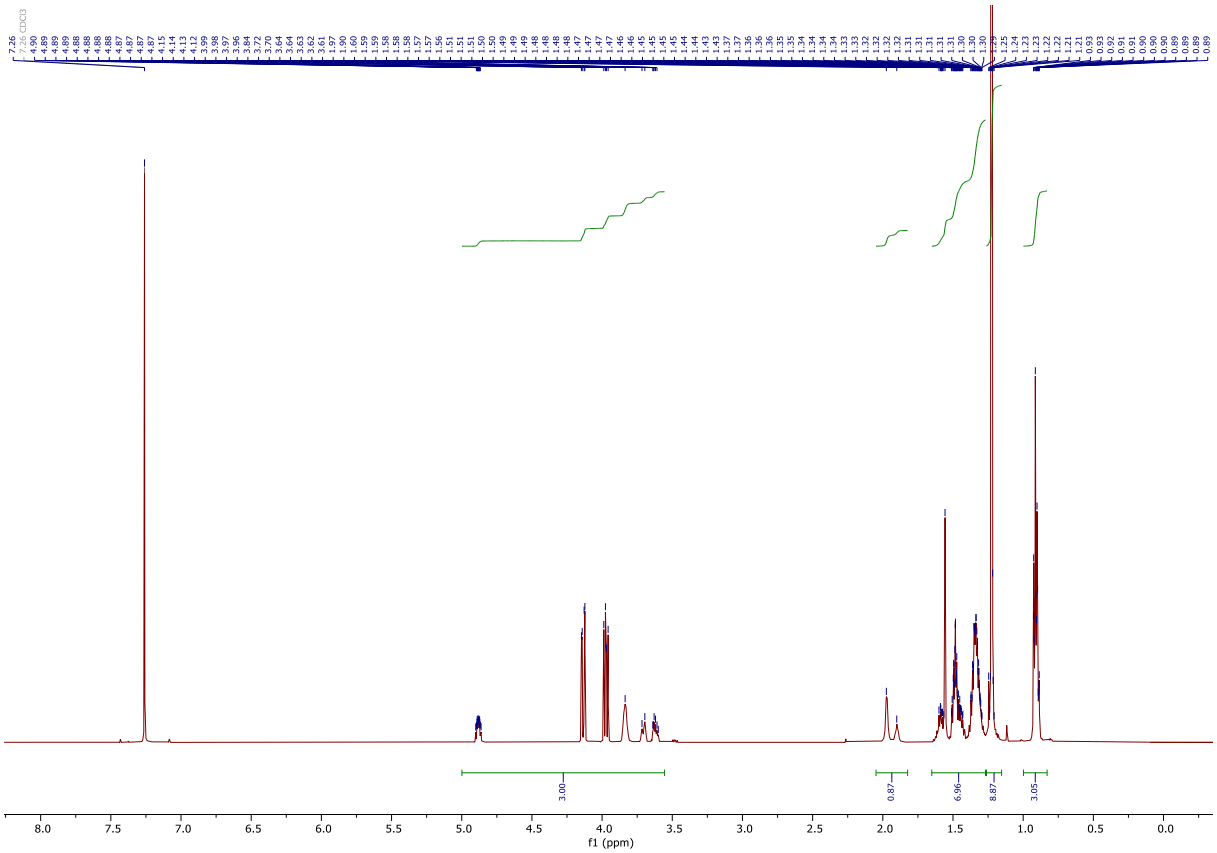


12 (a)

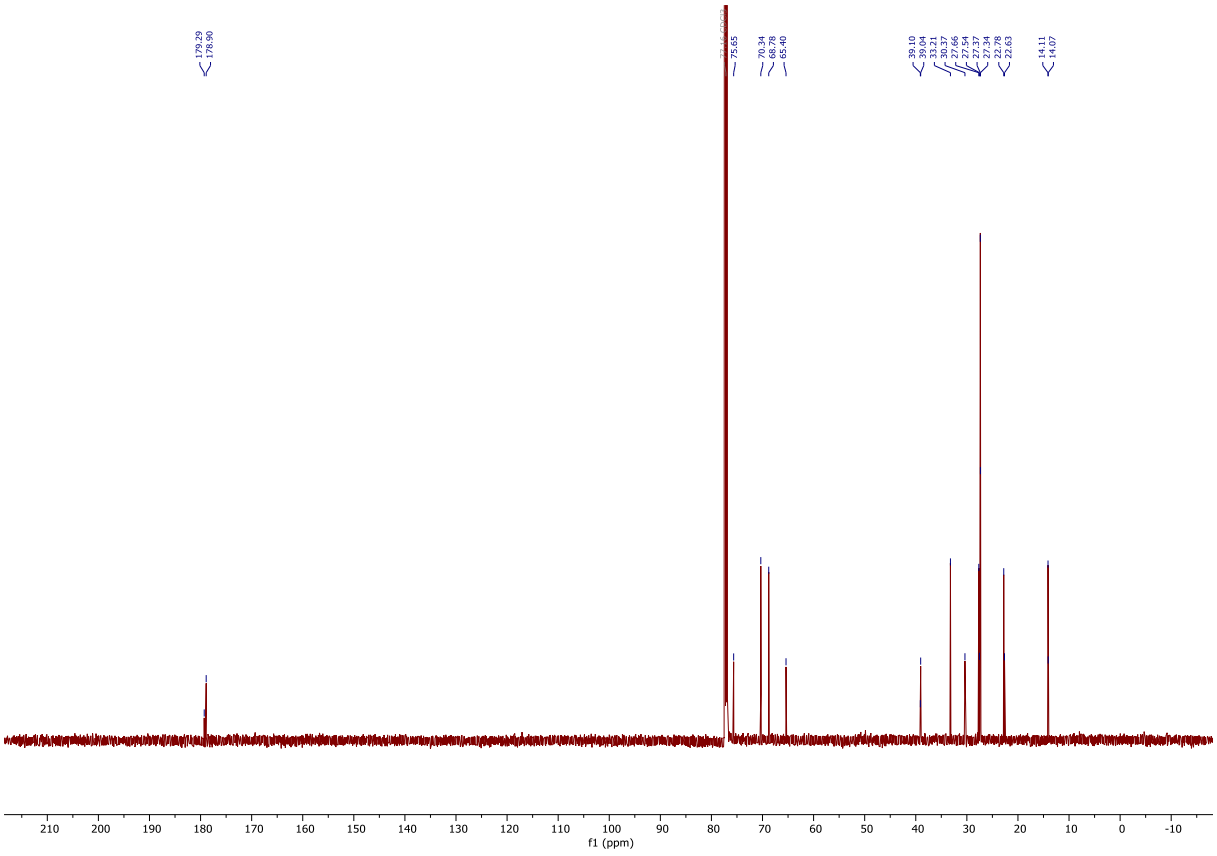


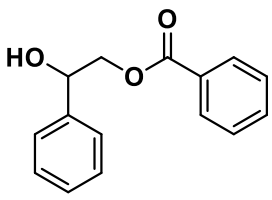
13 (b)

^{1}H-NMR spectrum of **12**+**13**

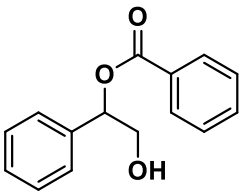


^{13}C-NMR spectrum of **12**+**13**



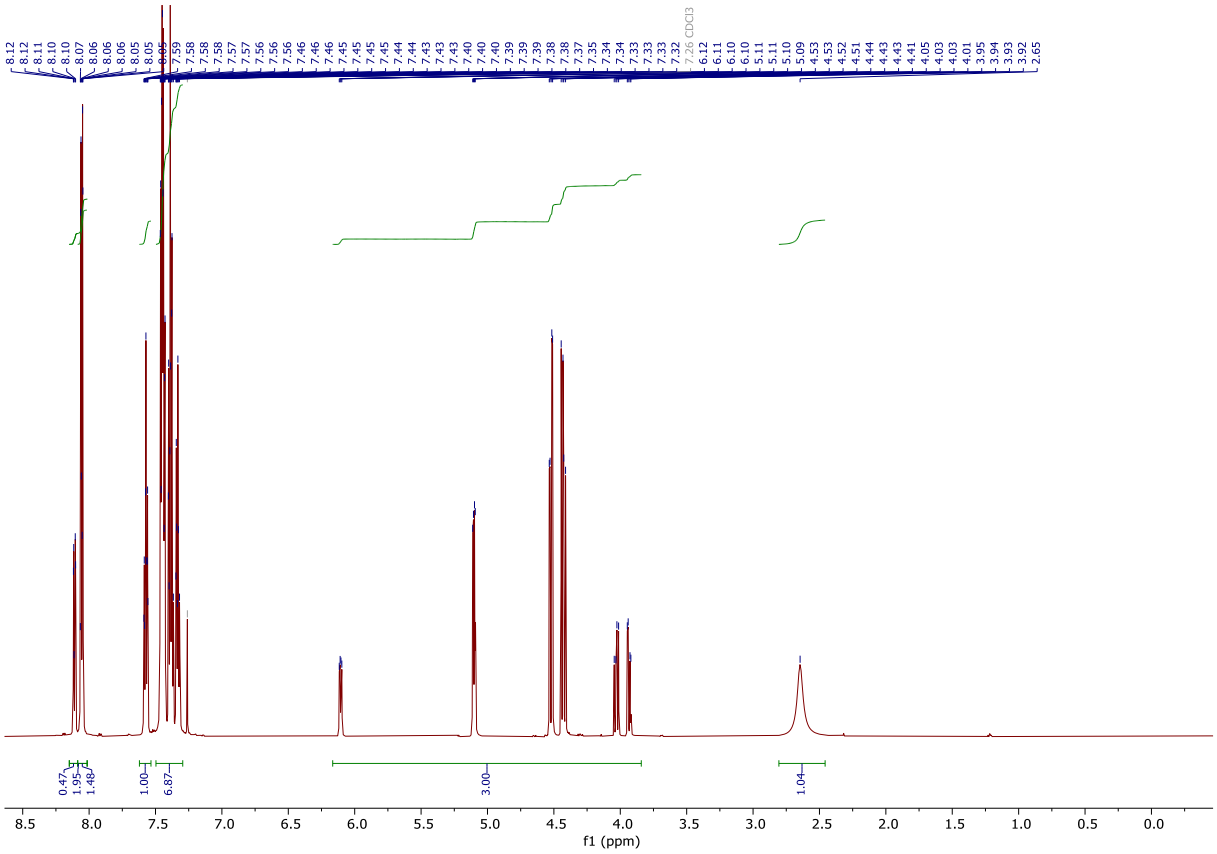


14 (a)



15 (b)

^{1}H-NMR spectrum of **14+15**



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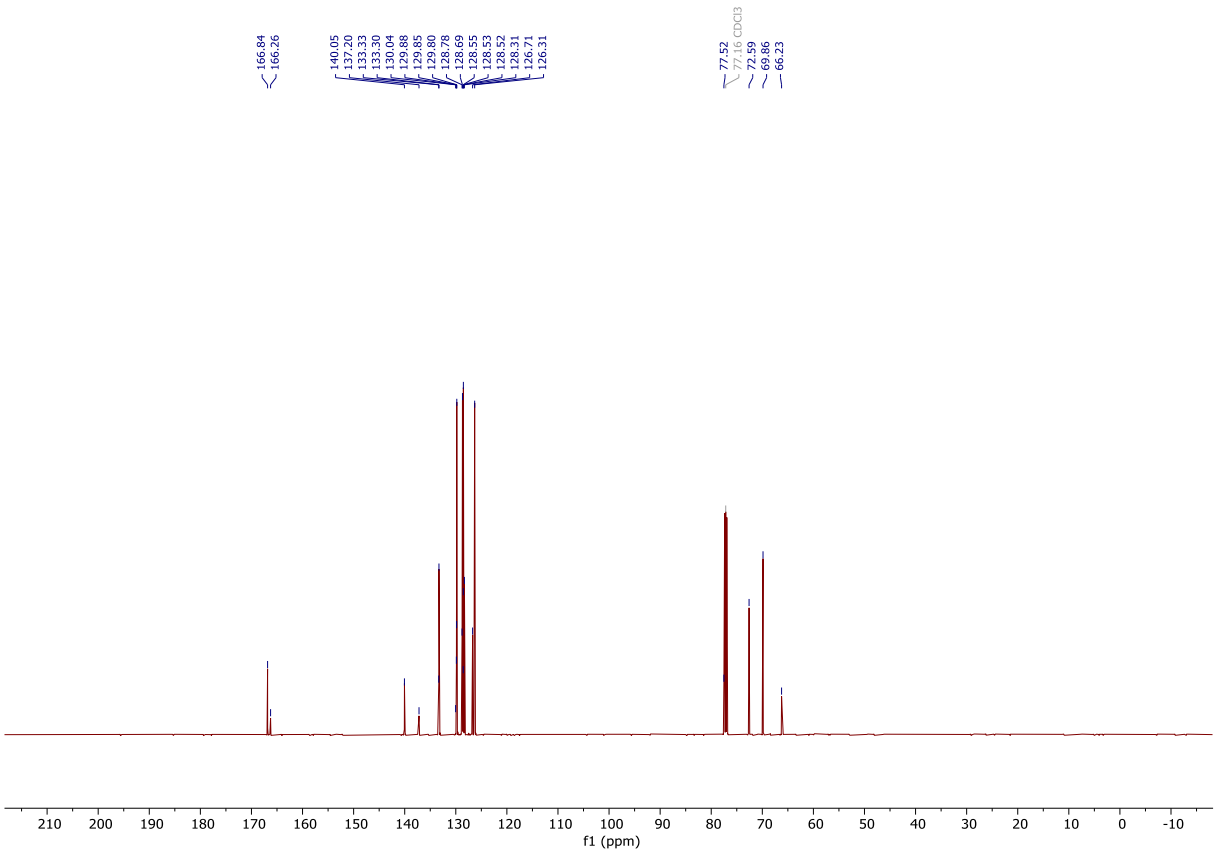
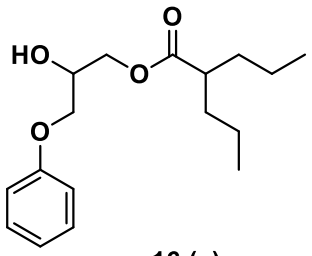
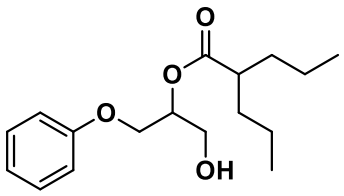


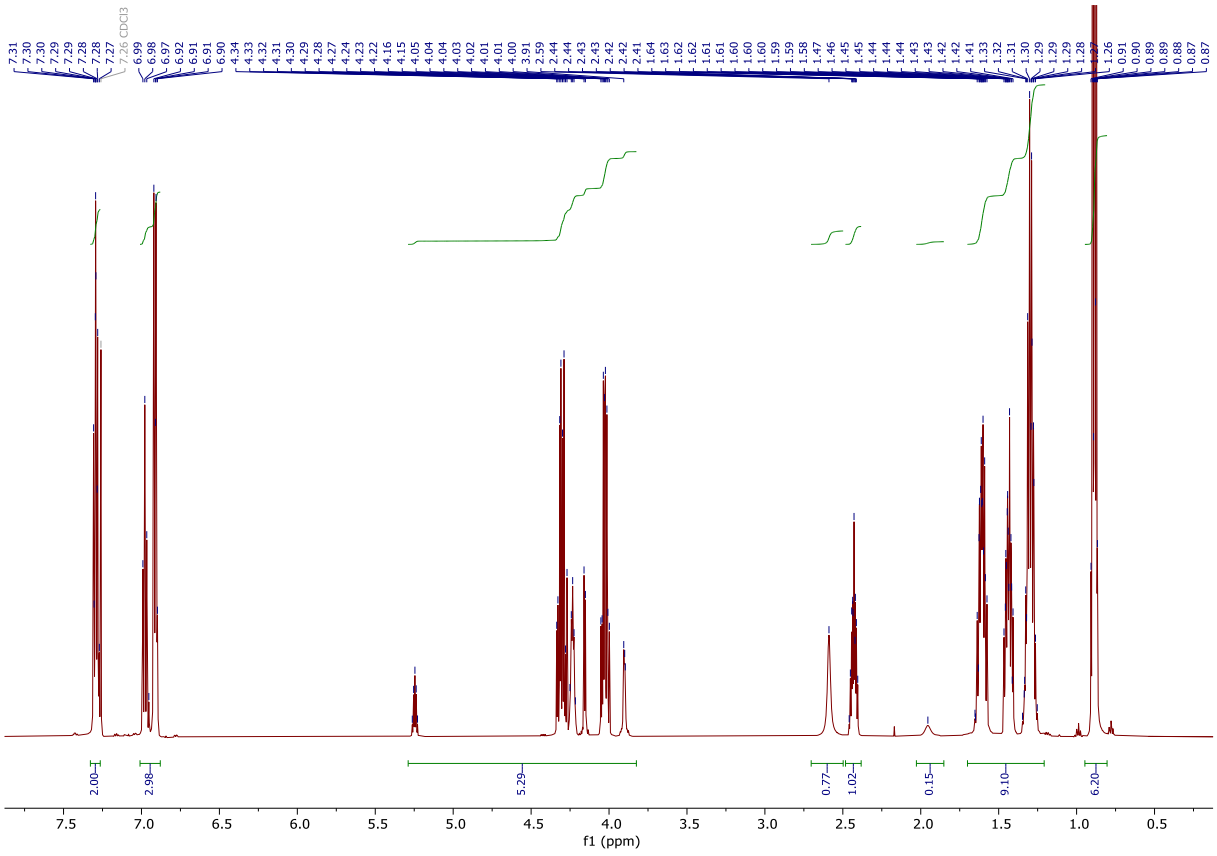


16 (a)



17 (b)

^{1}H-NMR spectrum of **16+17**



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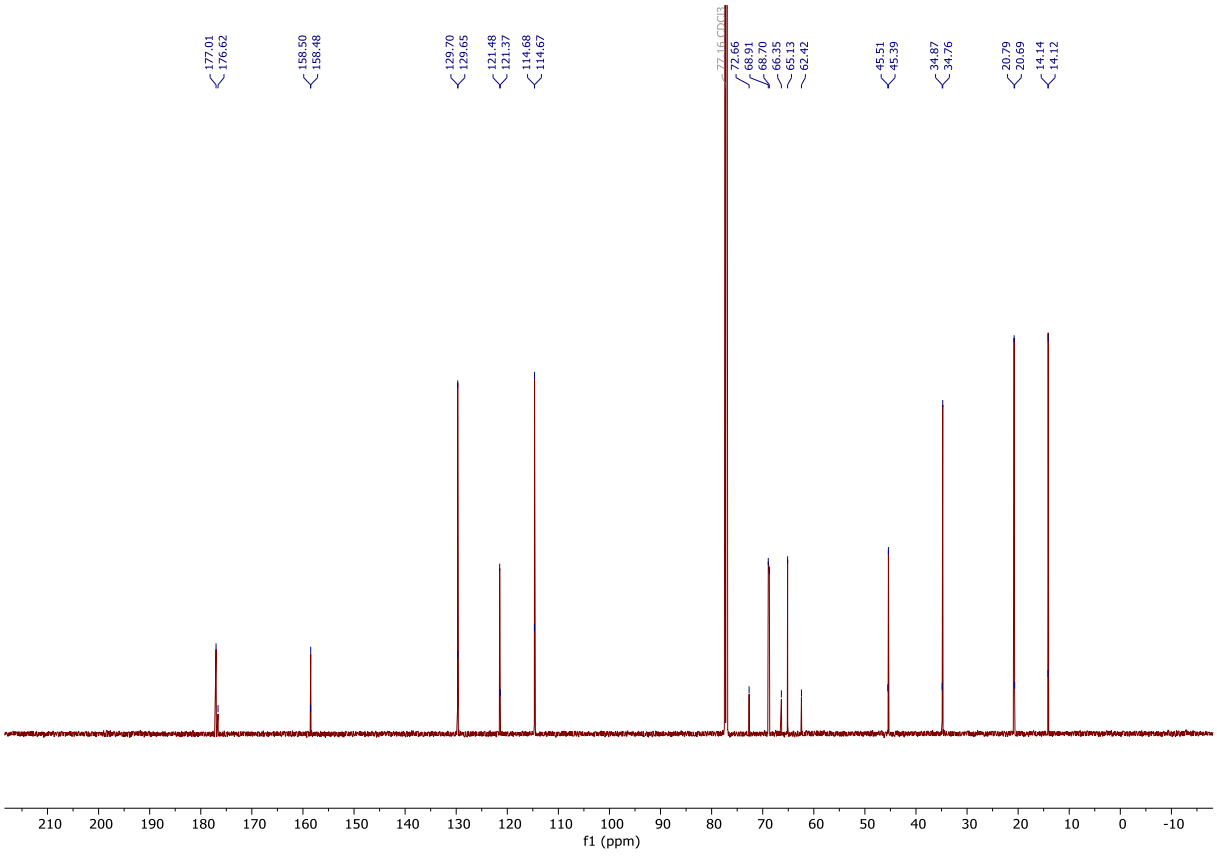
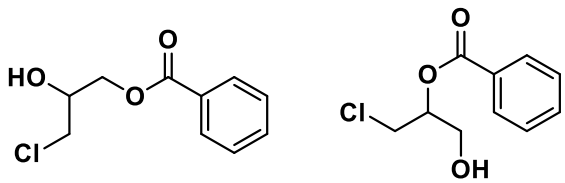
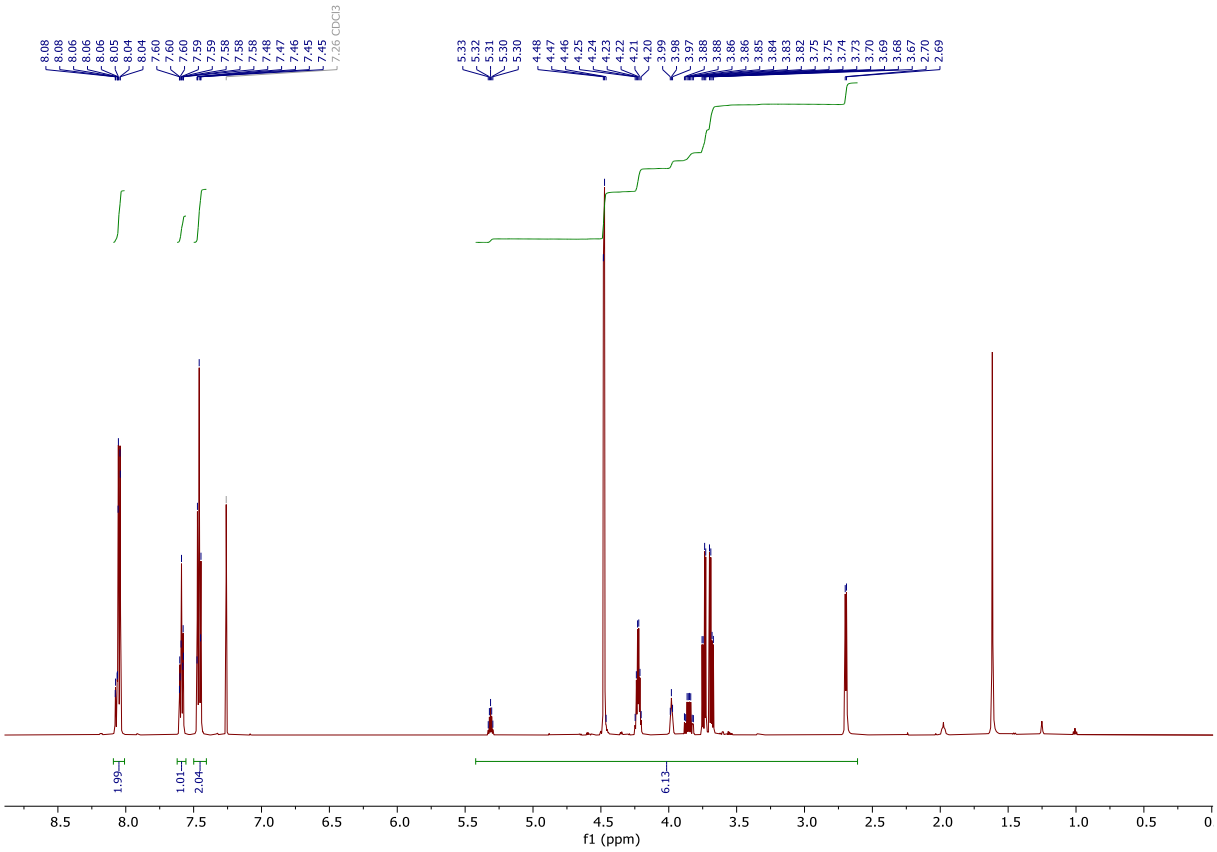


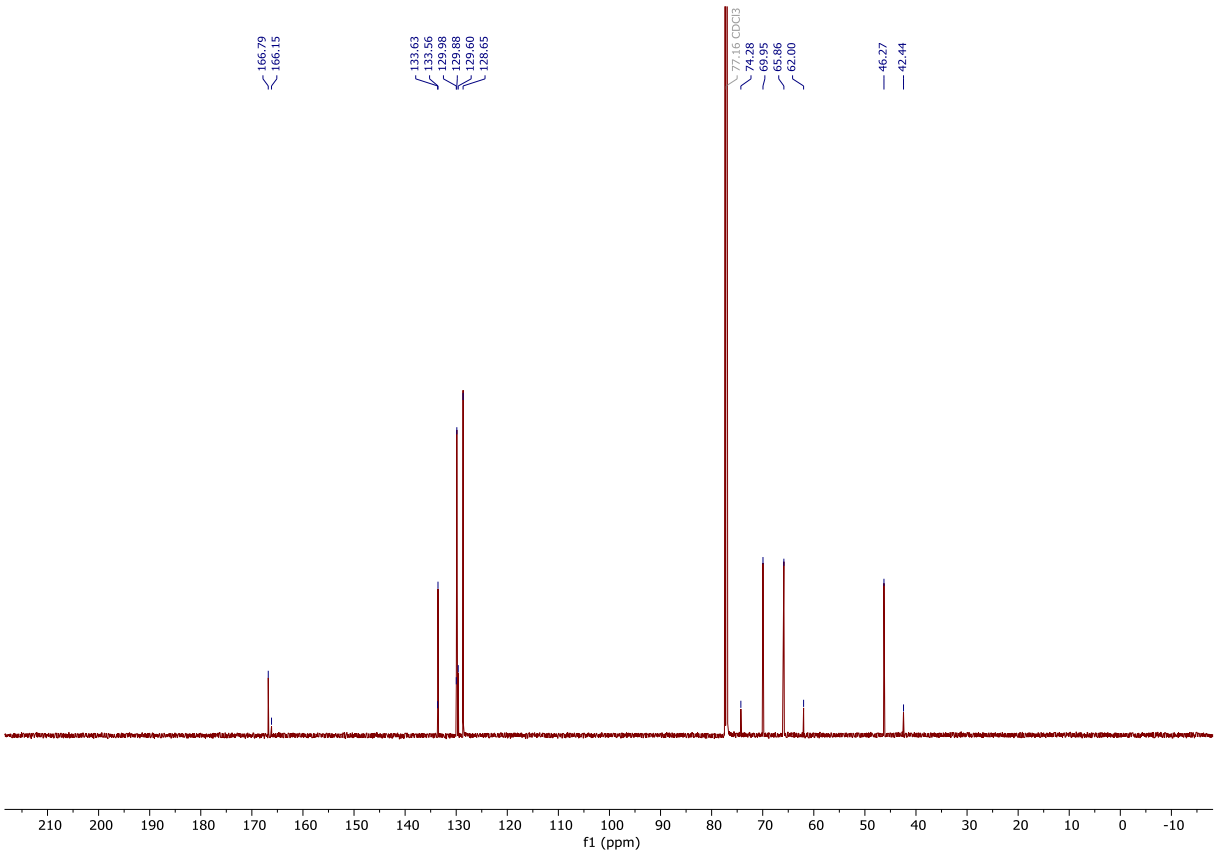


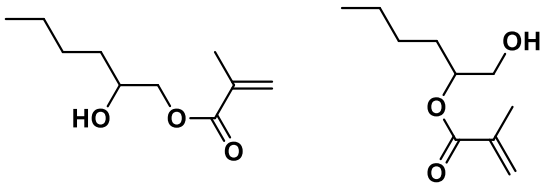
18 (a) **19 (b)**

^{1}H-NMR spectrum of **18**+**19**



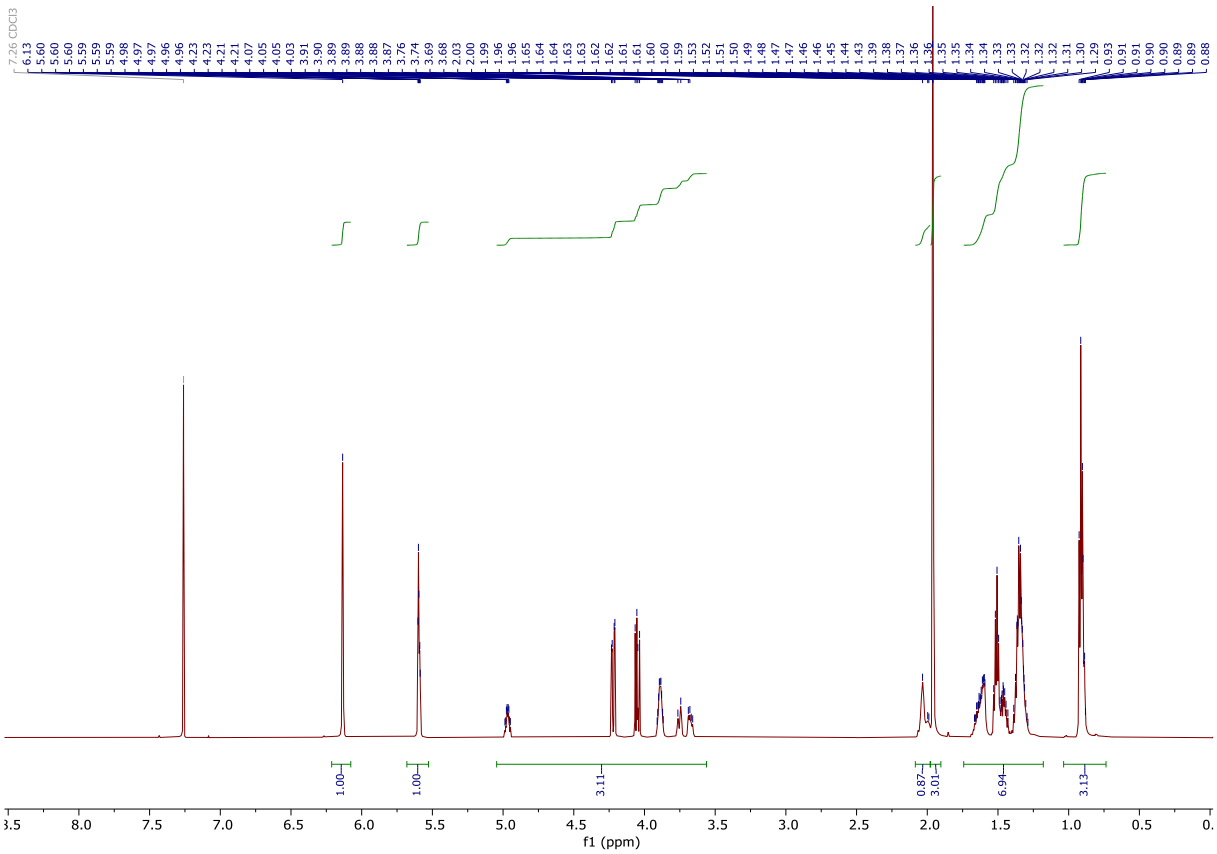
^{13}C-NMR spectrum of **18**+**19**





20 (a) **21 (b)**

^{1}H-NMR spectrum of **20+21**



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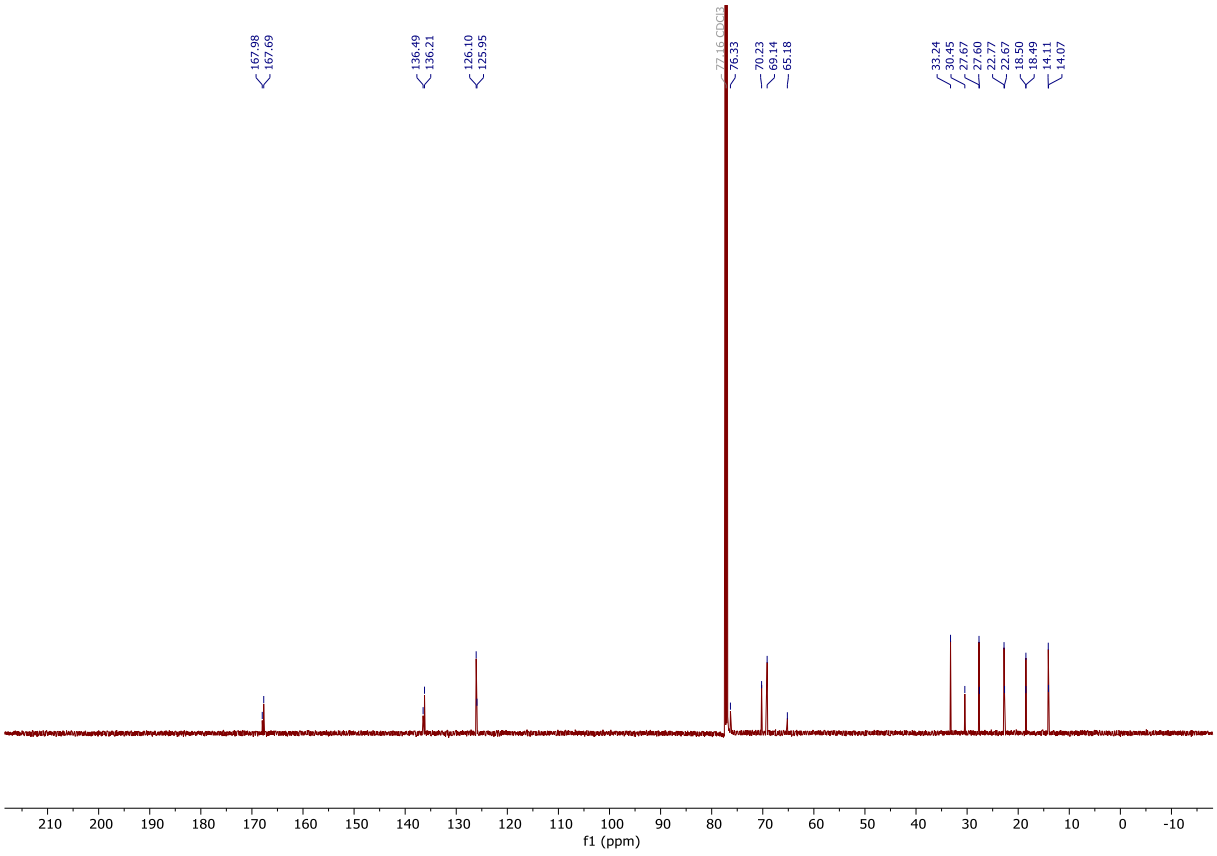
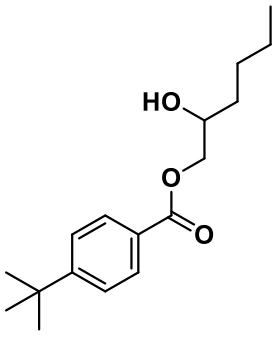
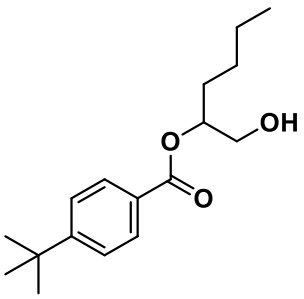


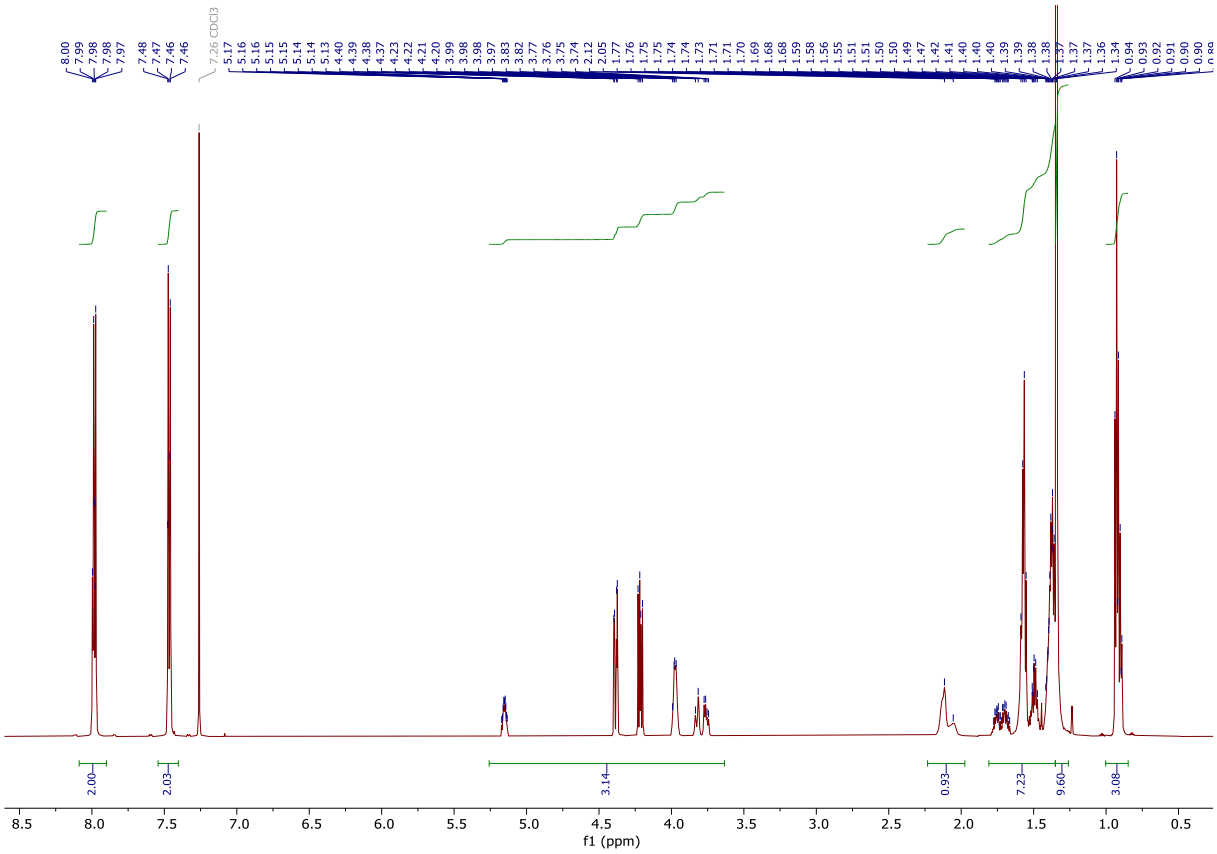


3g (a)

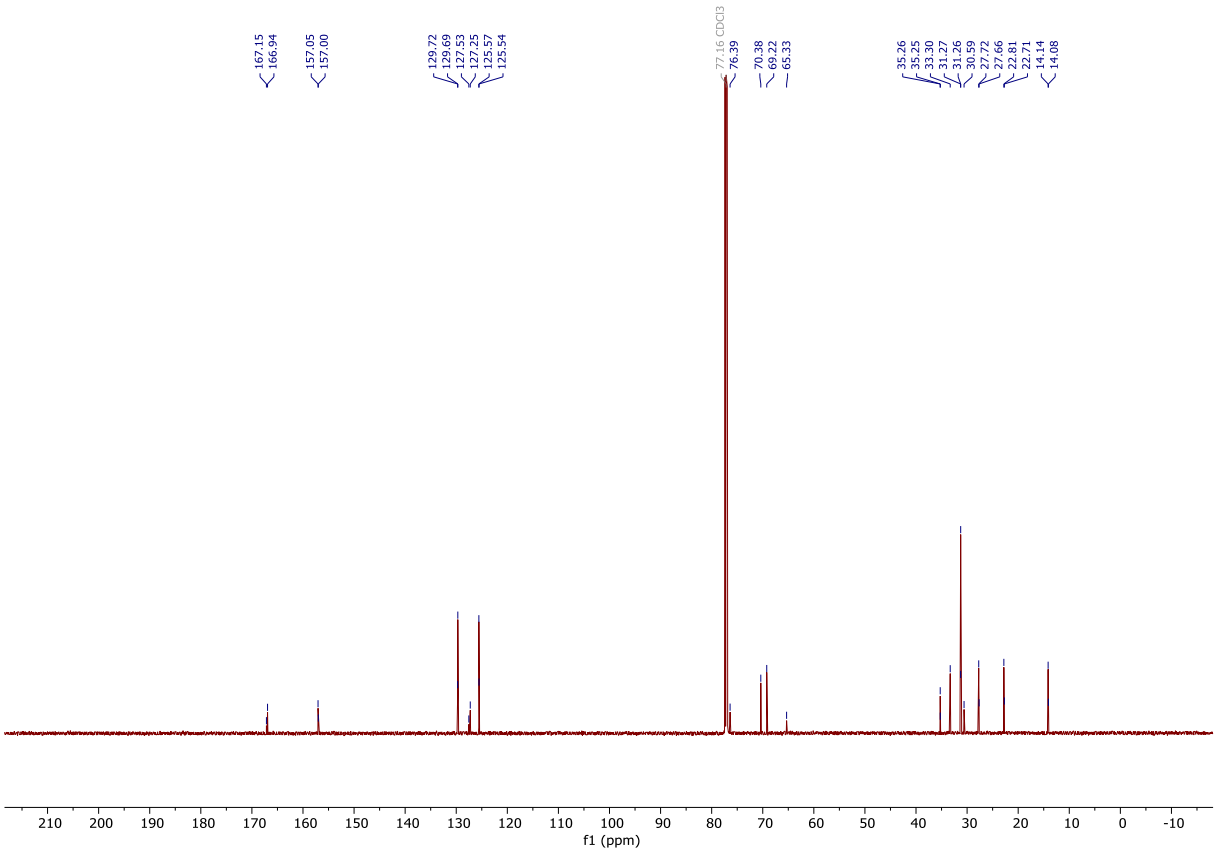


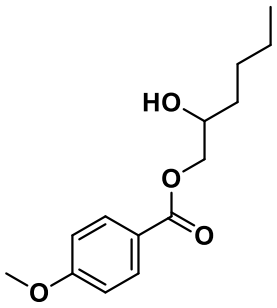
4g (b)

^{1}H-NMR spectrum of **3g**+**4g**

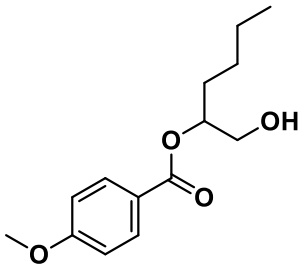


^{13}C-NMR spectrum of **3g**+**4g**



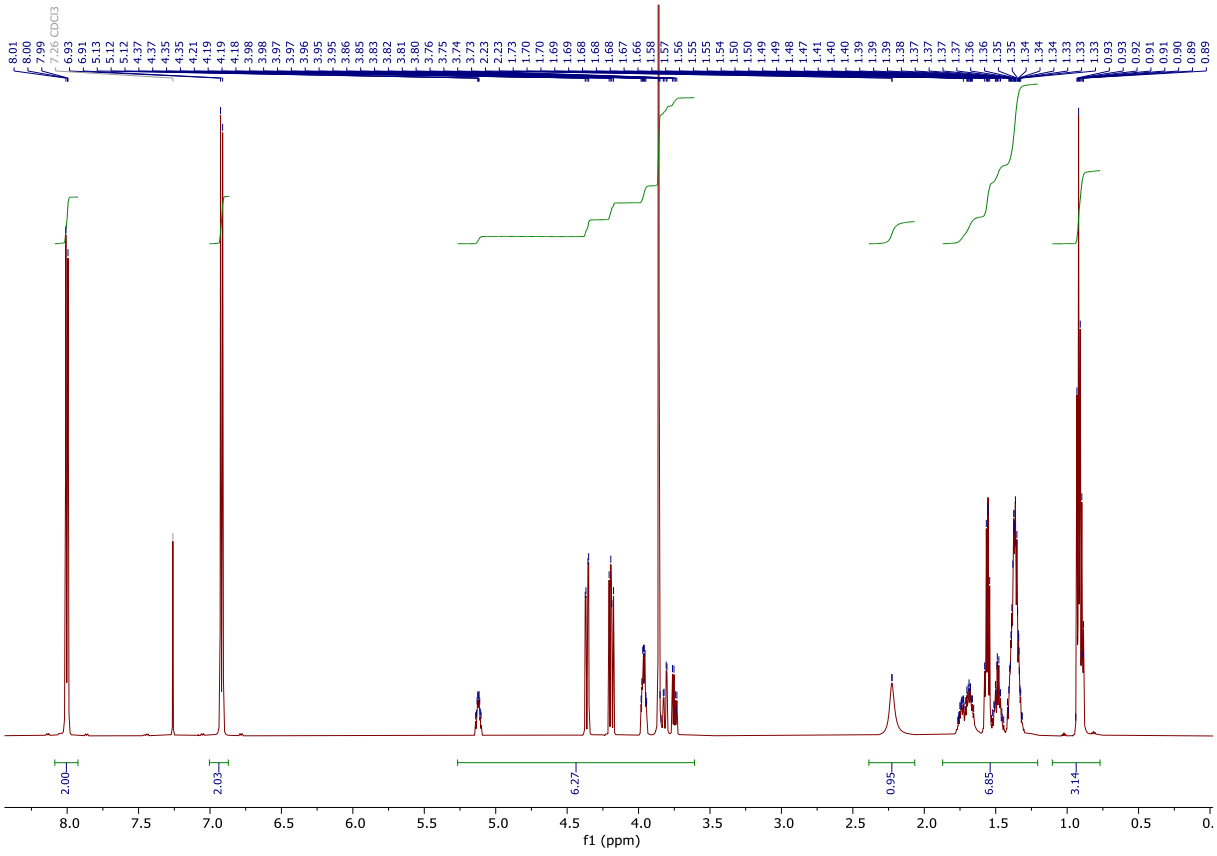


3e (a)

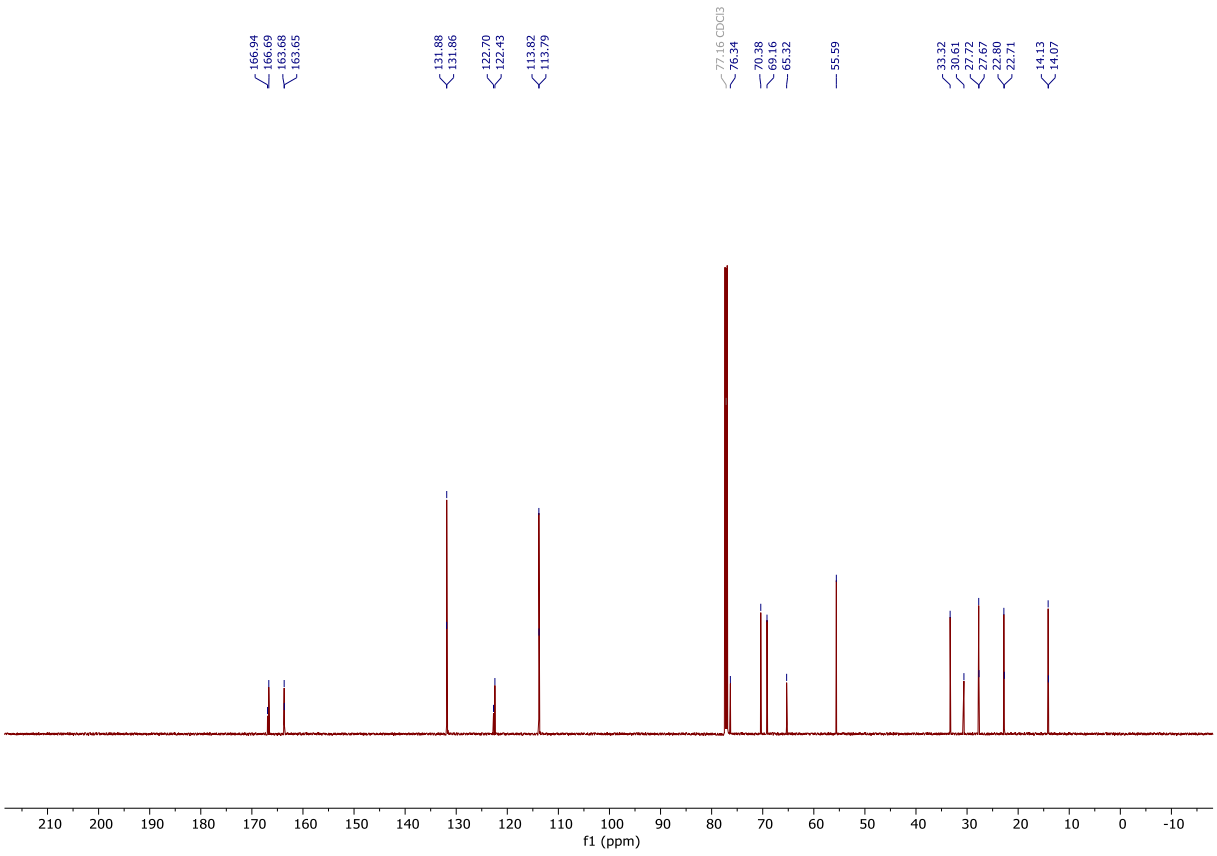


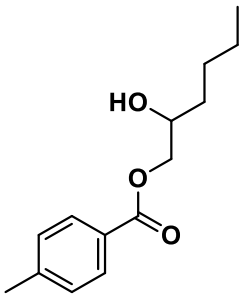
4e (b)

^{1}H-NMR spectrum of **3e**+**4e**

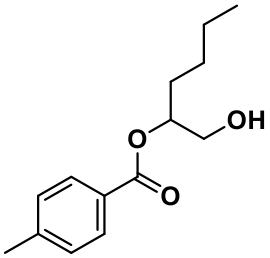


^{13}C-NMR spectrum of **3e**+**4e**



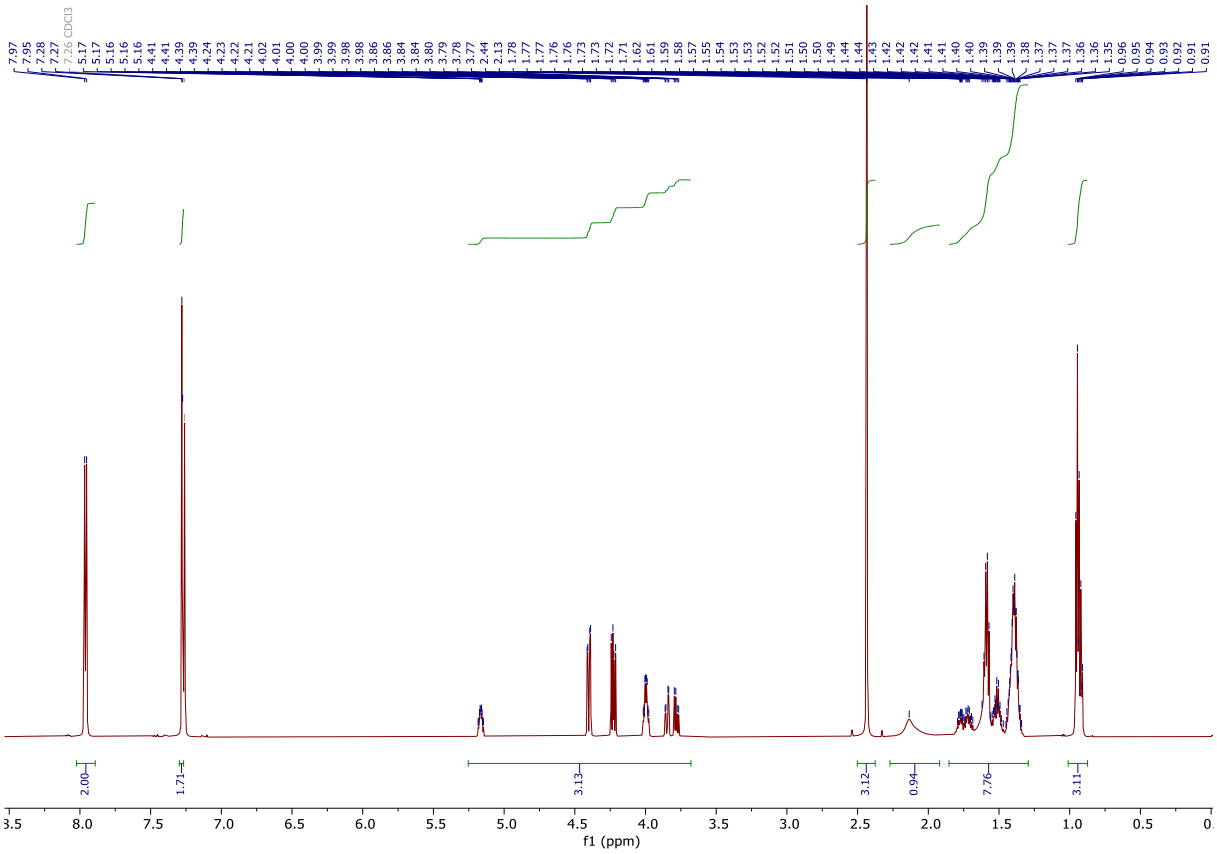


3f (a)

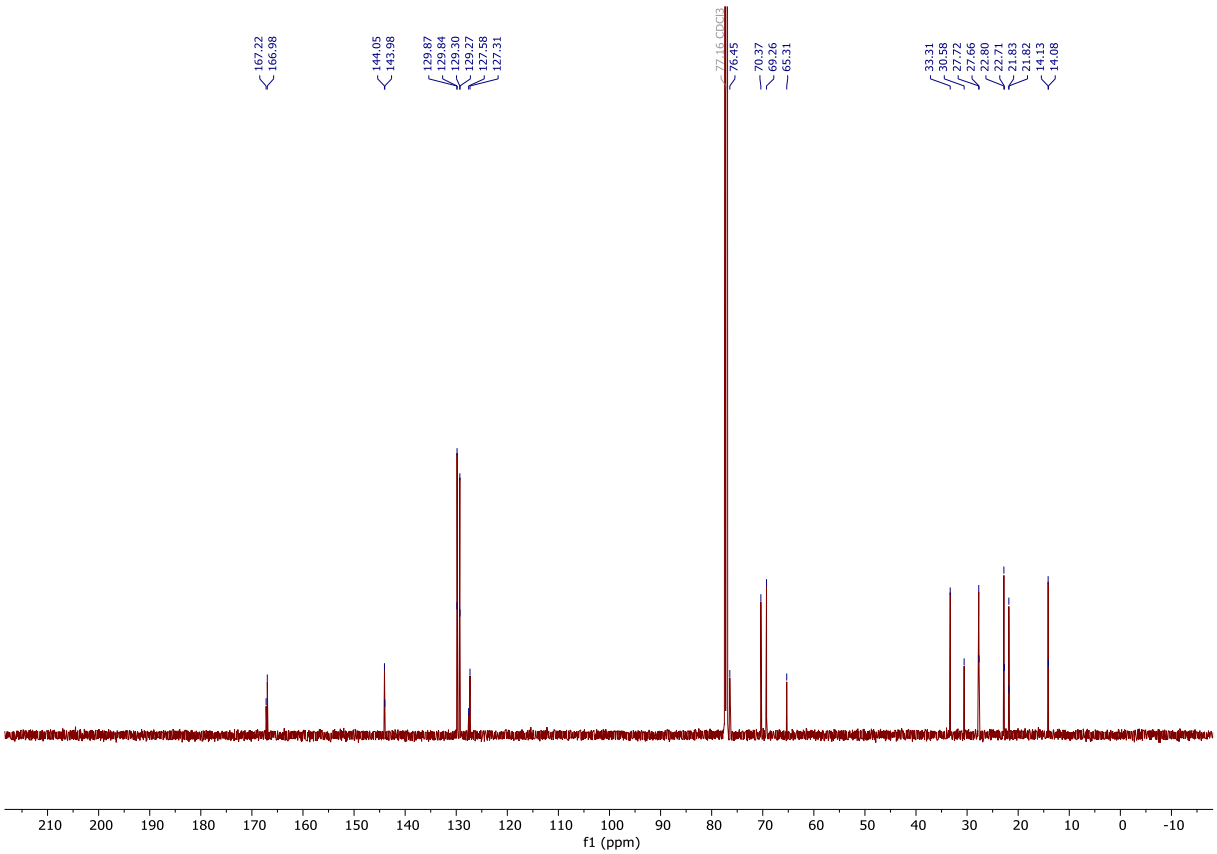


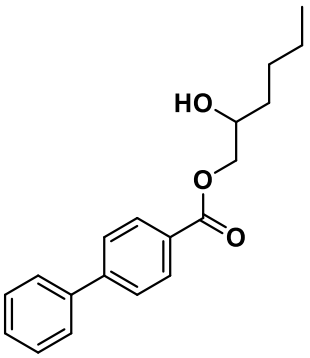
4f (b)

^{1}H-NMR spectrum of **3f**+**4f**

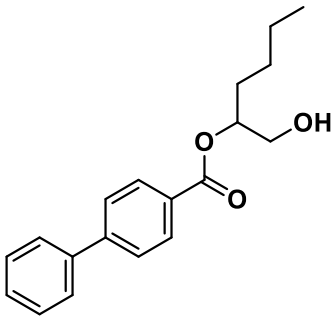


^{13}C-NMR spectrum of **3f**+**4f**



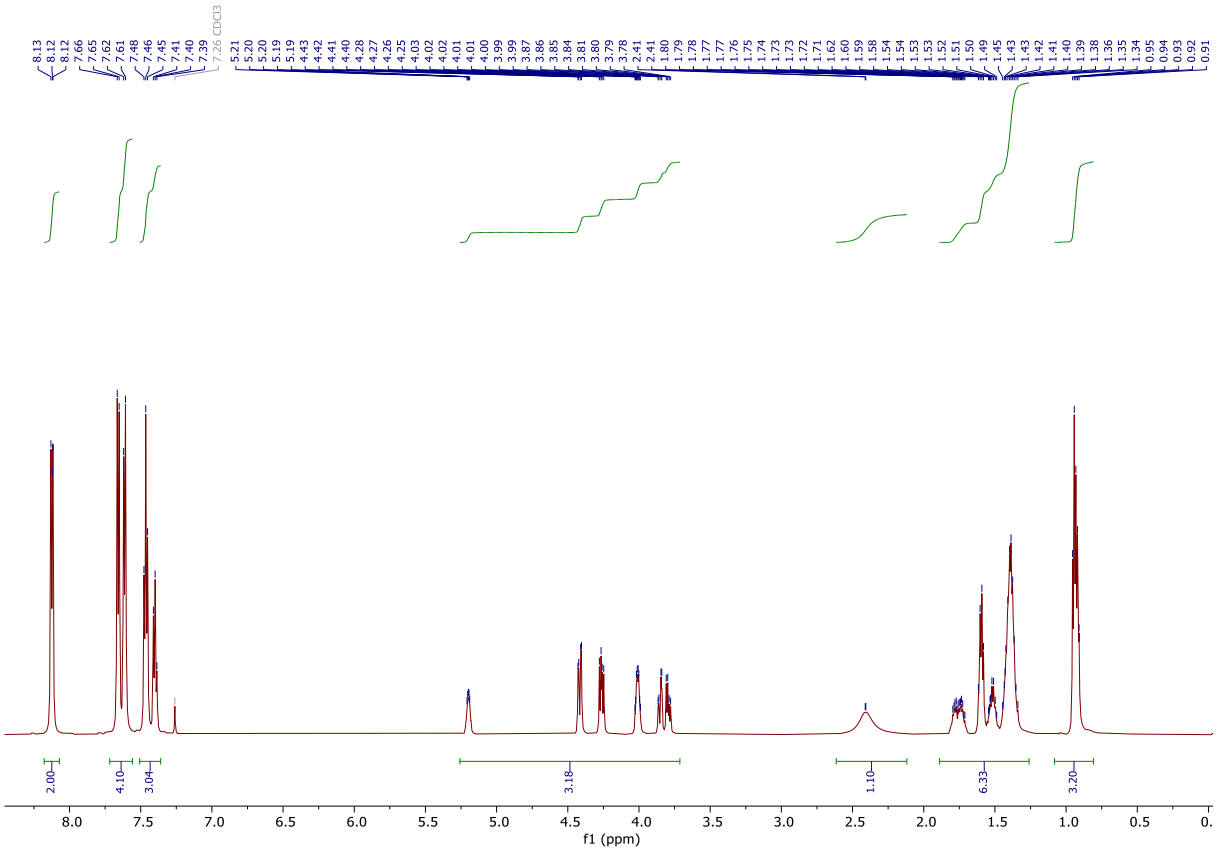


3h (a)

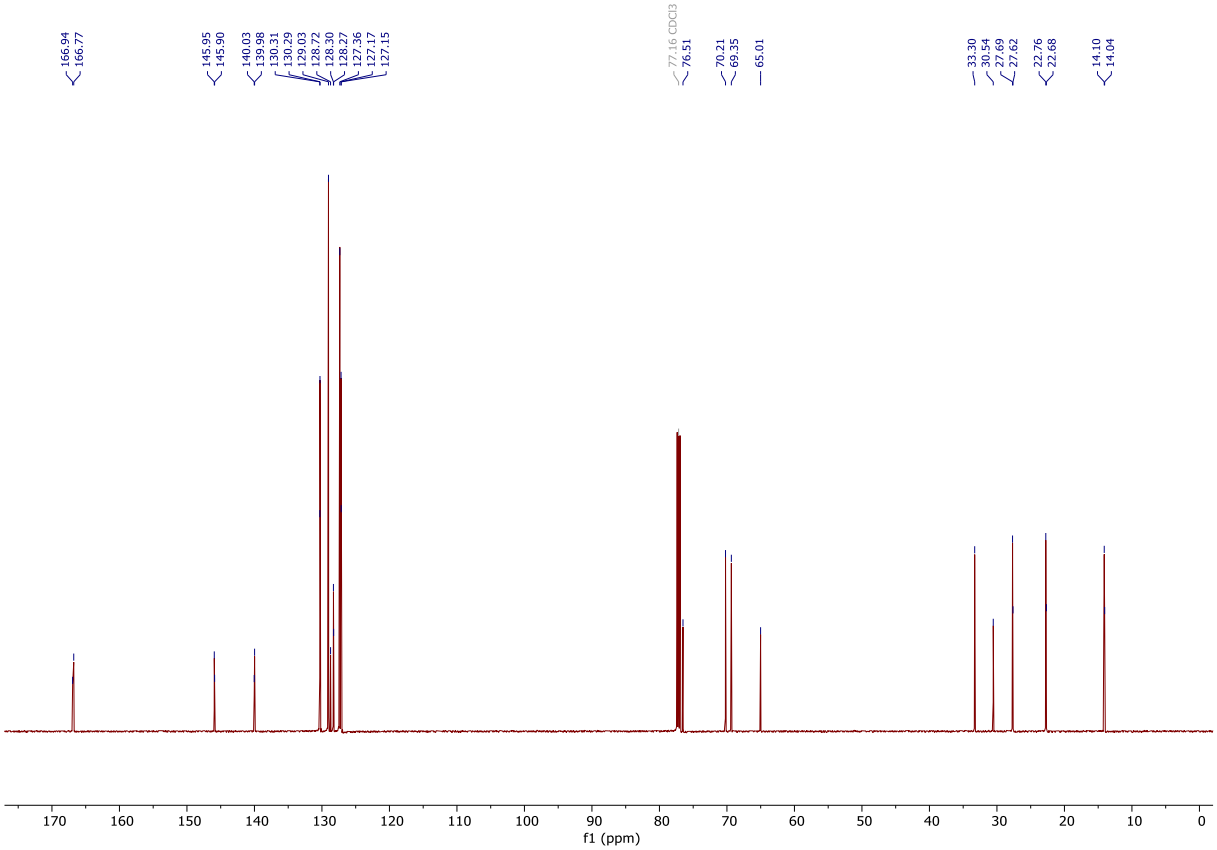


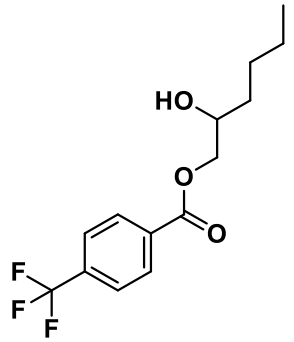
4h (b)

^{1}H-NMR spectrum of **3h**+**4h**

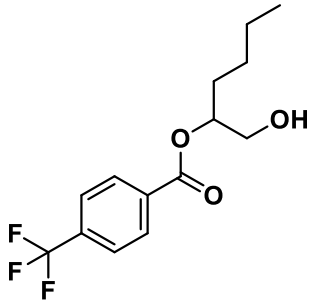


^{13}C-NMR spectrum of **3h**+**4h**



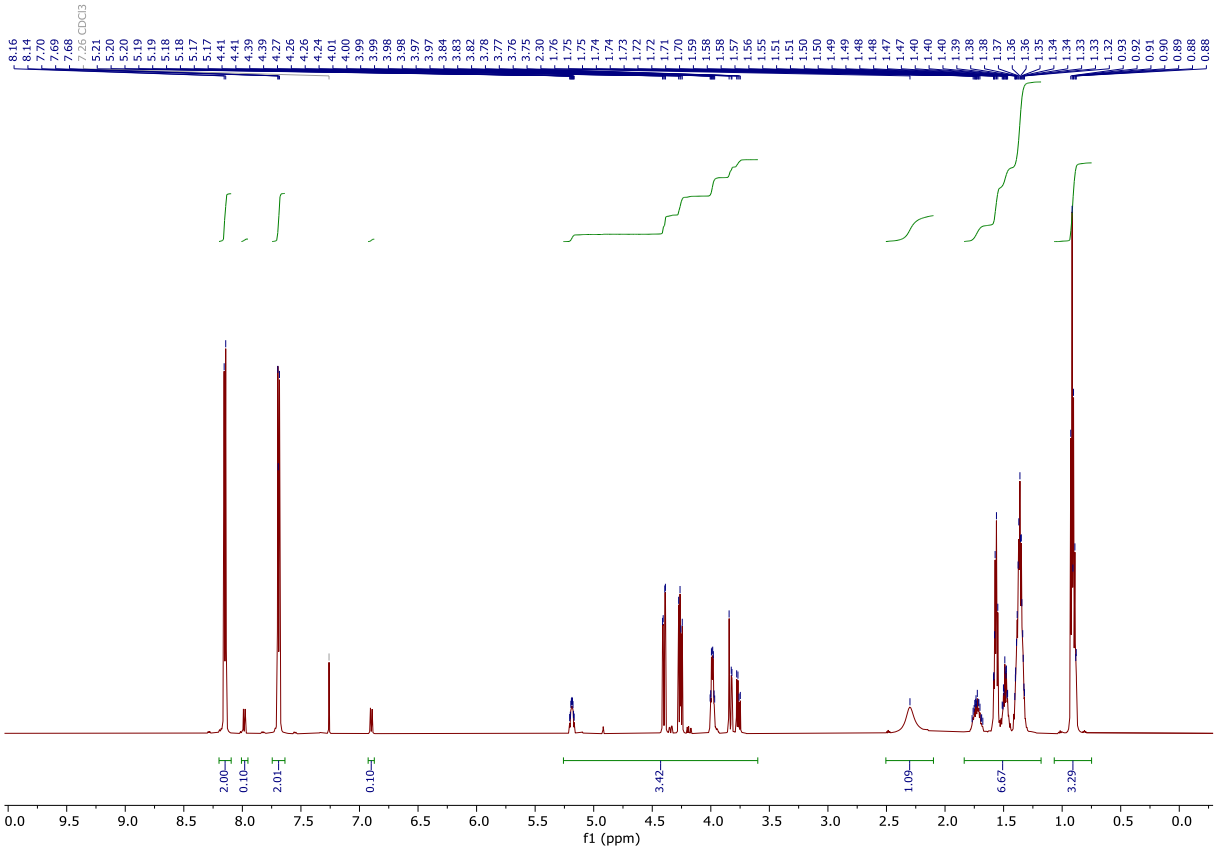


3b (a)

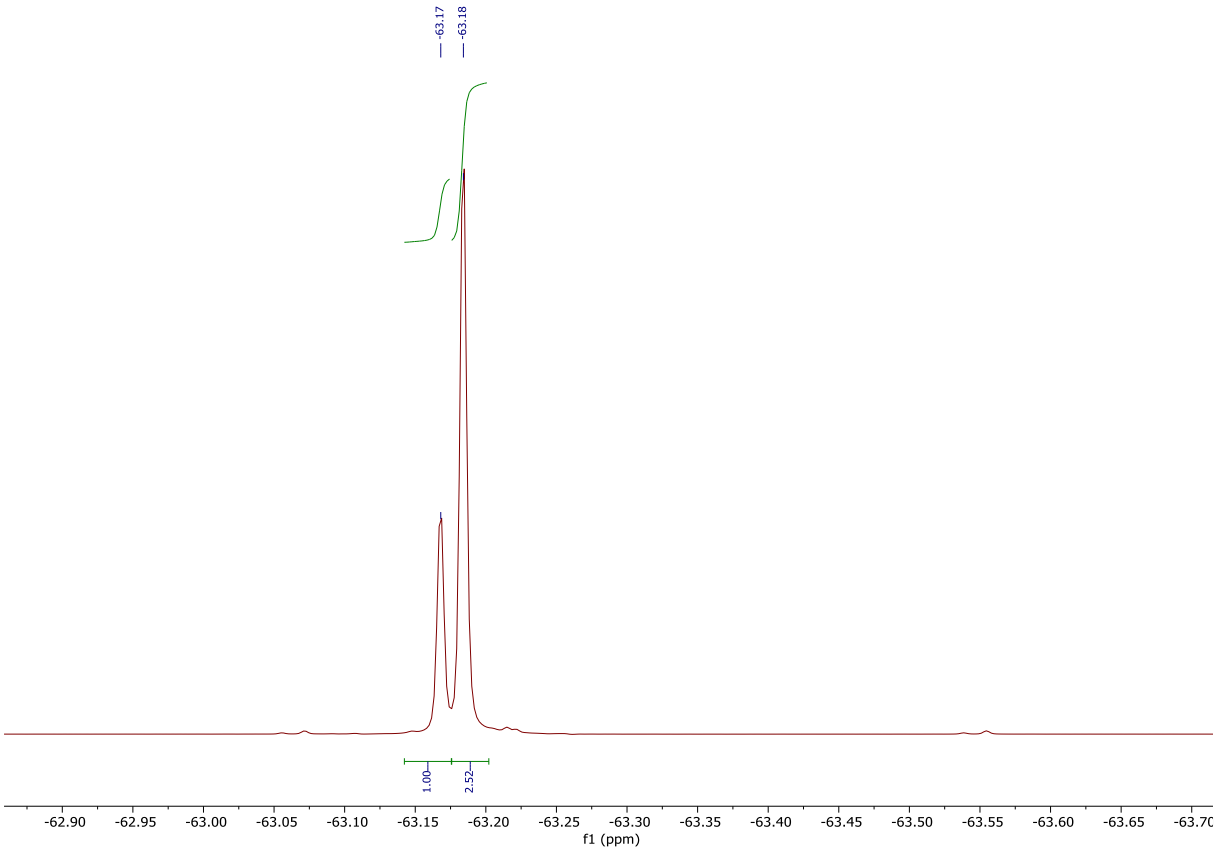


4b (b)

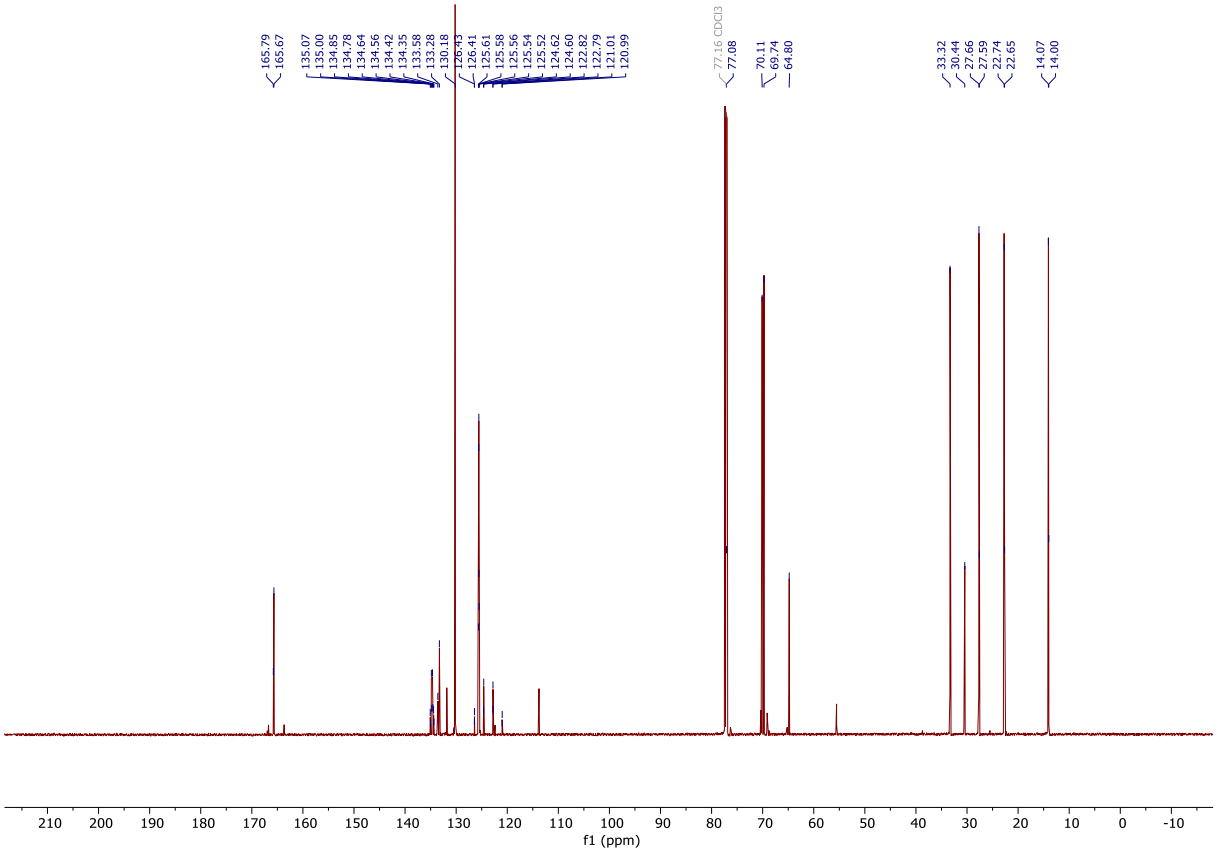
^{1}H-NMR spectrum of **3b**+**4b**

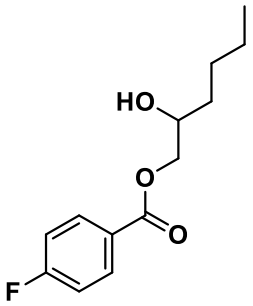


^{19}F-NMR spectrum of **3b**+**4b**

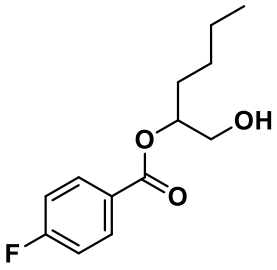


^{13}C-NMR spectrum of **3b**+**4b**



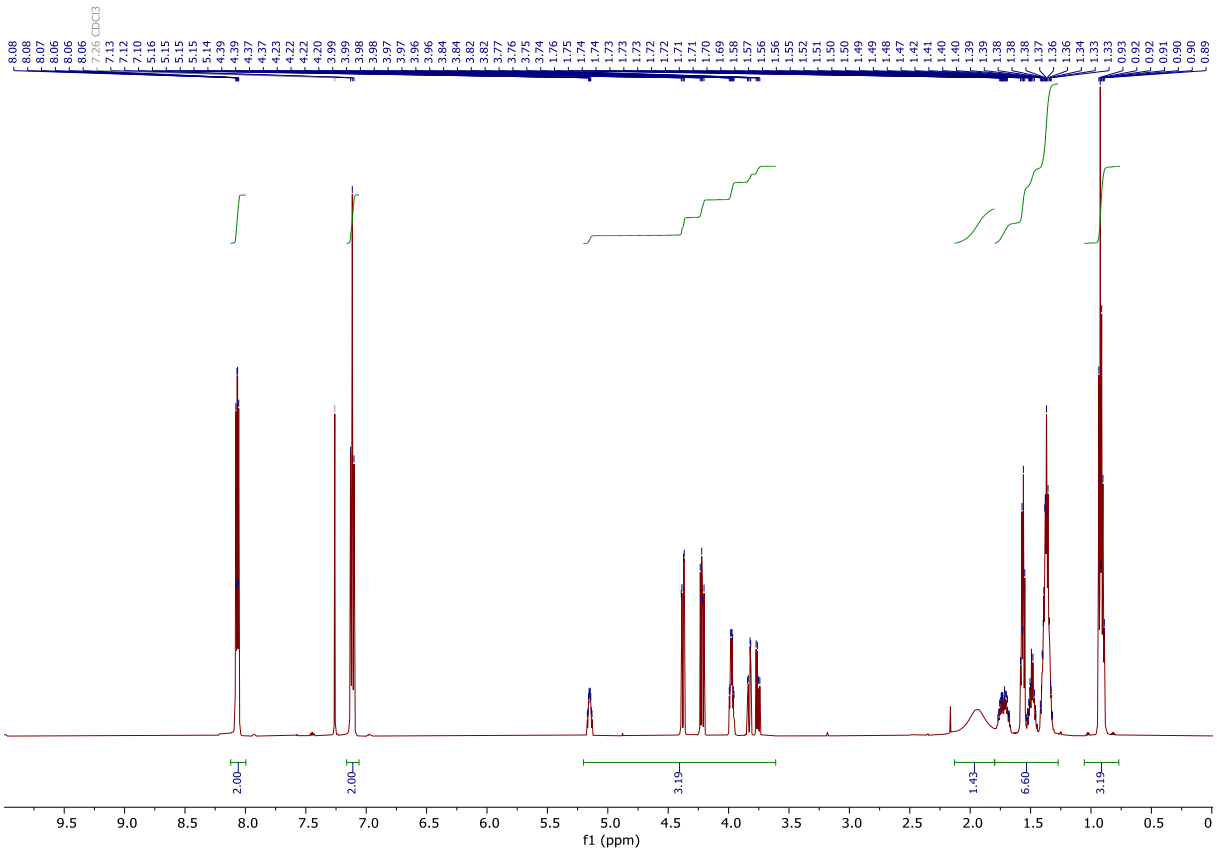


3c (a)

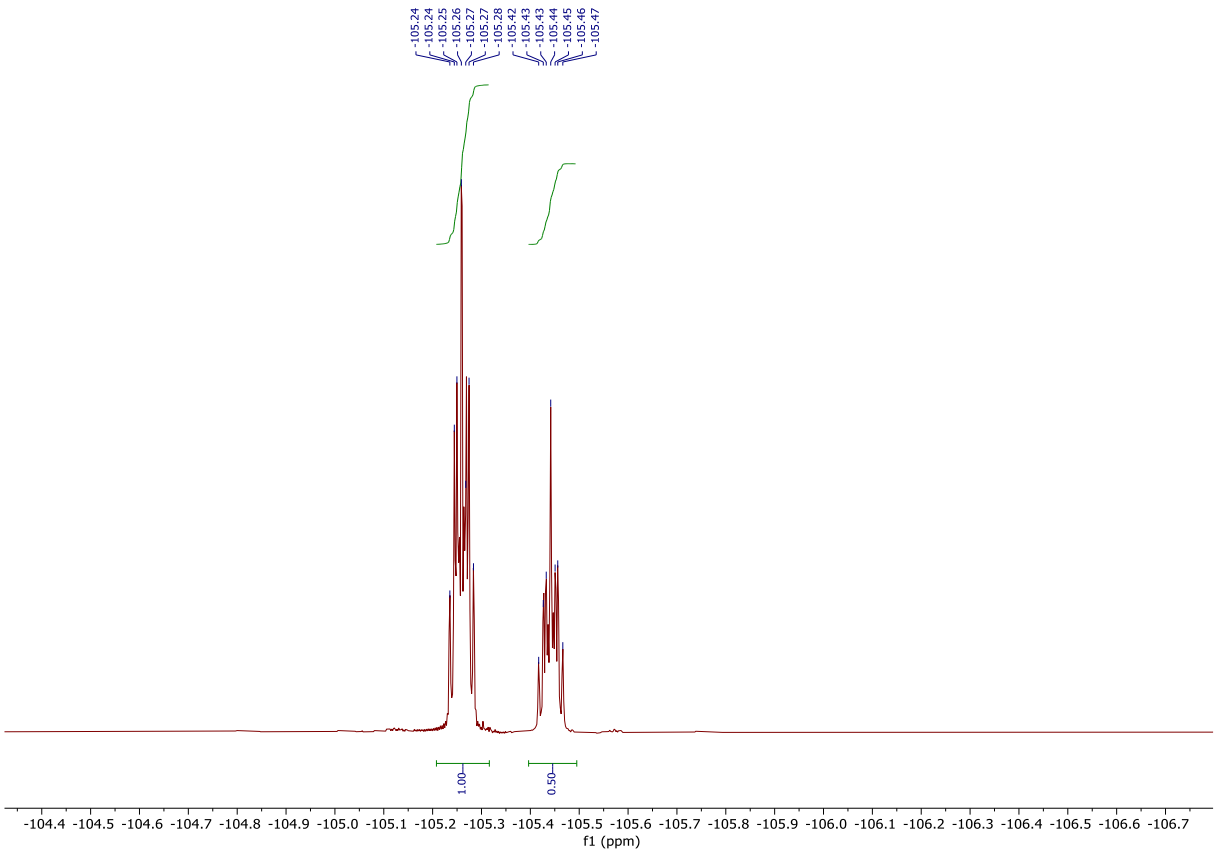


4c (b)

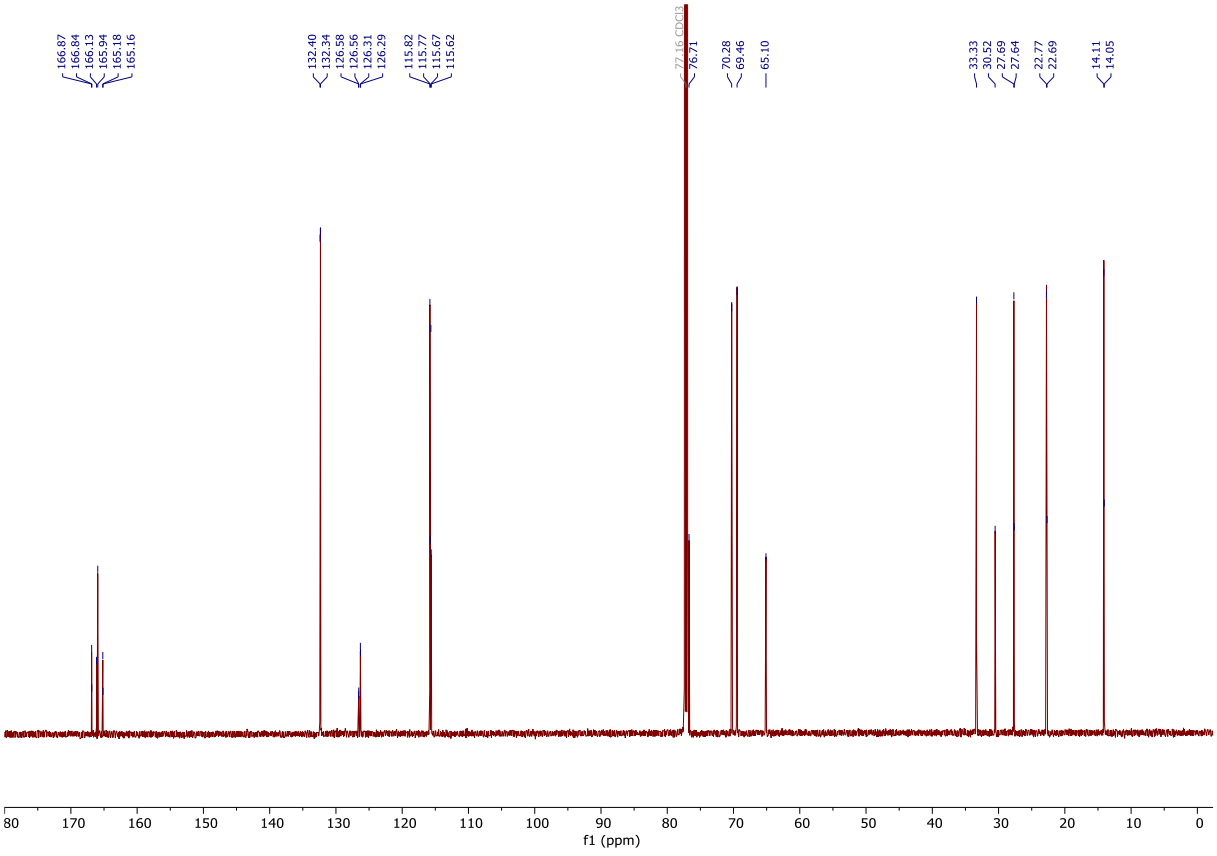
^{1}H-NMR spectrum of **3c**+**4c**

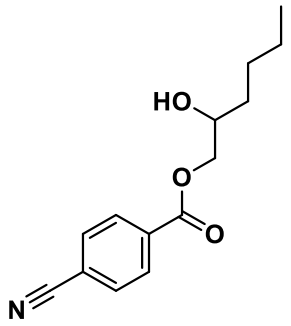


^{19}F-NMR spectrum of **3c**+**4c**

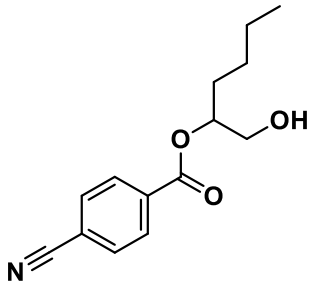


^{13}C-NMR spectrum of **3c**+**4c**



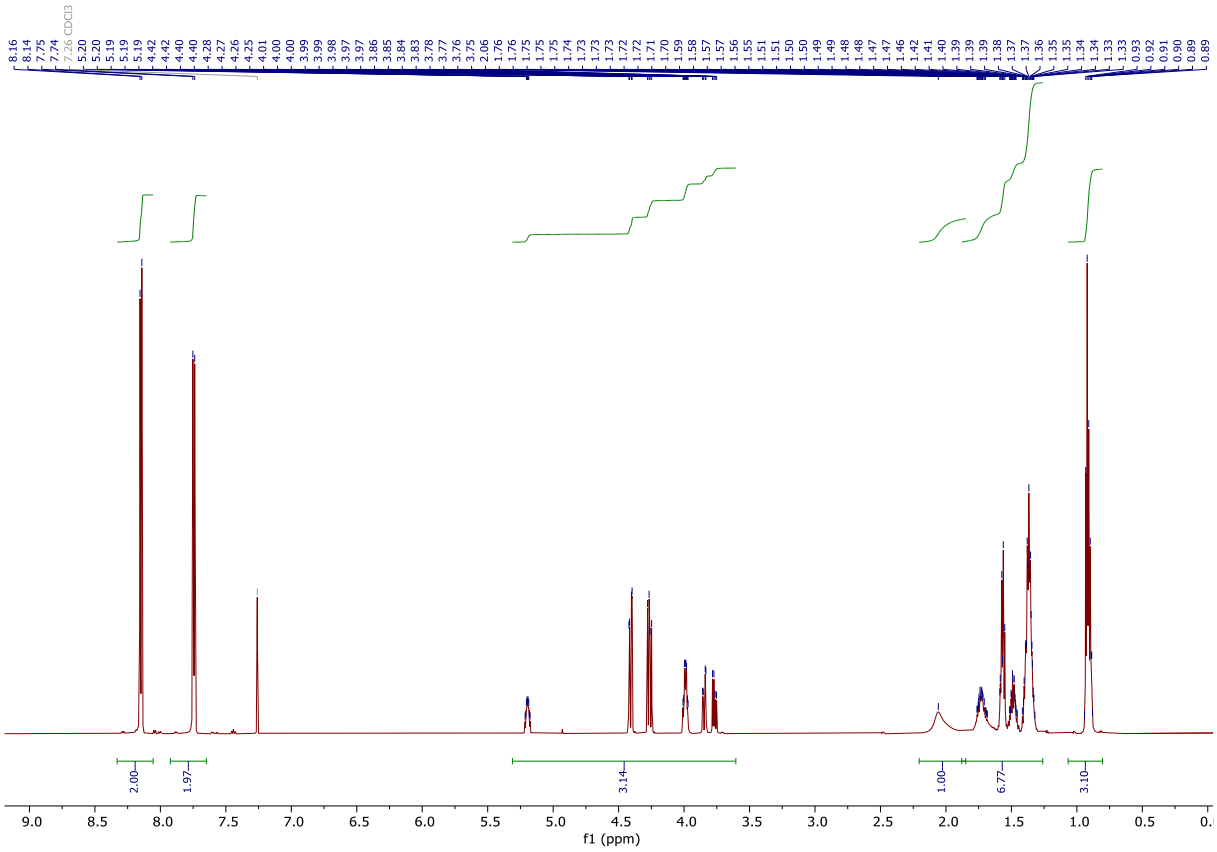


3d (a)

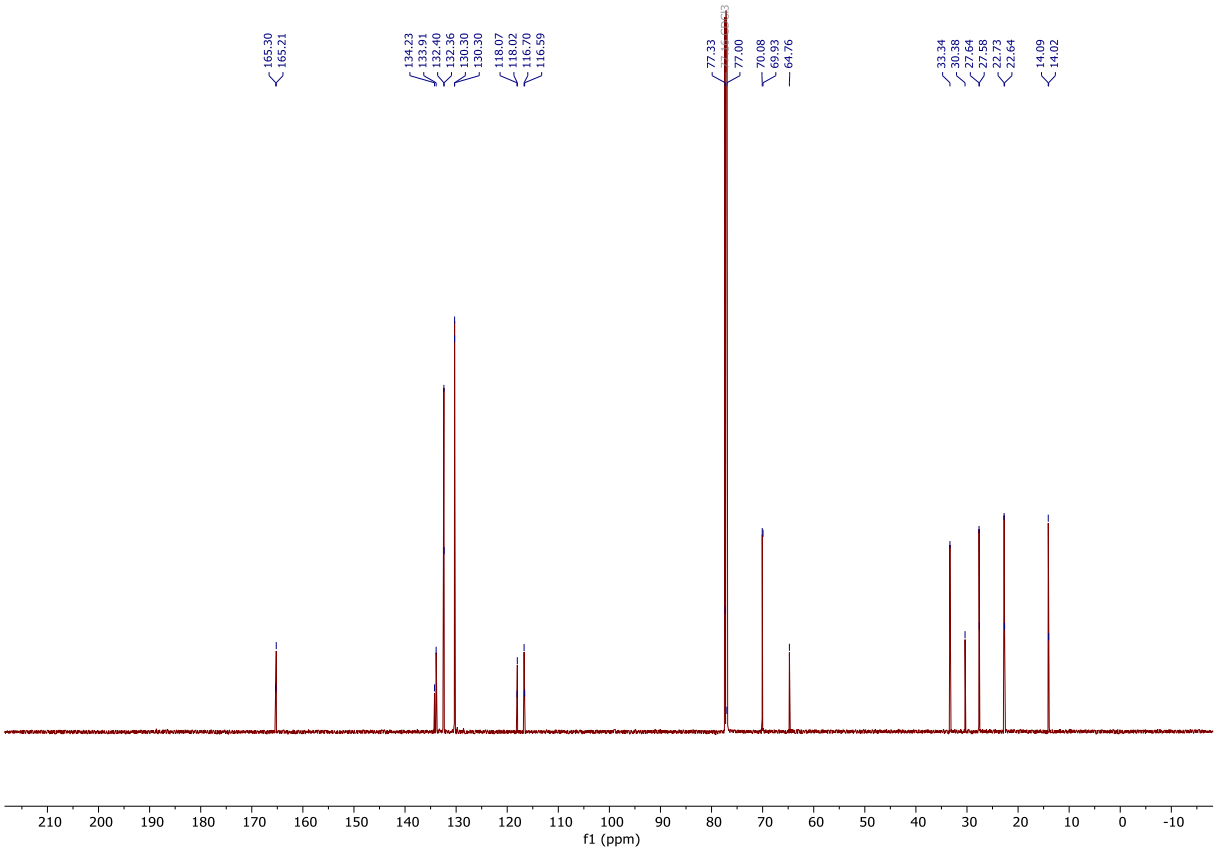


4d (b)

^{1}H-NMR spectrum of **3d**+**4d**



^{13}C-NMR spectrum of **3d**+**4d**



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