Original Research Paper

# Urban waste upcycling to a recyclable solid acid catalyst for converting levulinic acid platform molecules into high-value products

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HIGHLIGHTS

➢One-pot upcycling of urban waste pine needles into an efficient sulphonated catalyst achieved.

➢The favored reaction pathway in alkyl levulinates synthesis was investigated.

➢Good to excellent levulinates yields (46-93%) were obtained across a broad substrate range.

➢Remarkable catalyst durability over a span of 10 consecutive cycles was demonstrated.

➢Waste-minimized purification protocol through Amberlyst® A-21 pad was verified by green metrics.

GRAPHICAL ABSTRACT
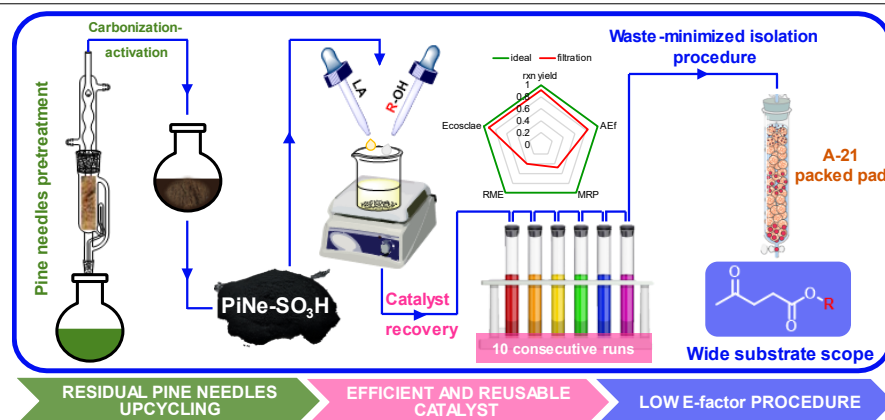
ARTICLE INFO

ABSTRACT

The conversion of levulinic acid (LA) into alkyl levulinates is highly significant due to the wide range of applications for these products, including their use as fuel additives, solvents, and fragrances. In order to meet the growing need for environmentally friendly chemical production, this study takes a circular economy approach by upcycling a common urban waste, i.e., pine needles, to synthesize a robust heterogeneous acid catalyst, subsequently used to efficiently upgrade LA into levulinates. By utilizing a single-step procedure under mild operating conditions, the resulting PiNe–SO₃H catalyst demonstrated good performances and flexibility in synthesizing diverse bio-derived levulinates. In fact, the catalyst showed an exceptionally broad range of applicability, resulting in isolated yields ranging from ~46% to ~93%, which is an unprecedented achievement. The catalyst's ability to be reused was tested, revealing remarkable performance for up to 10 consecutive cycles with negligible loss in efficiency. Additionally, a significant focus was directed towards developing a method that minimizes waste during the isolation process. This involved optimizing reaction conditions and rationalizing work-up procedures, resulting in low Environmental factor (E-factor) values ranging from 1.2 to 8.9. To comprehensively assess the overall environmental sustainability of the process, various additional green metrics were calculated, and the Ecoscale tool was employed as well. Furthermore, mechanistic investigations elucidated the favored reaction pathway, underscoring that, under the optimized conditions, the prevailing mechanism entails direct esterification, as opposed to the generation of a *pseudo*-ester intermediate.

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Abbreviations

A®-21	Amberlyst® A-21
AEf	Atom efficiency
ATR-IR	Attenuated total reflection-IR
α-AL	α-angelica lactone
EA	Elemental analysis
E-factor	Environmental factor
EL	Ethyl levulinate
FAME	Fatty acid methyl esters
FEMA	Flavor and Extract Manufacturers Association
FID	Flame ionization detector
GC-EIMS	Gas chromatography with electron impact mass spectrometry
GHG	Greenhouse gas
GLC	Gas-liquid chromatography
HMF	5-hydroxymethylfurfural
LA	Levulinic acid
MRP	Mass recovery parameter
NPs	Nanoparticles
PiNe	Pine needles derived biochar
RME	Reaction mass efficiency
TOF	Turnover frequency
UCC	Carbon cryogel

1. Introduction

The increasing energy demand driven by population growth has resulted in the over-exploitation of fossil feedstocks, leading to excessive greenhouse gas (GHG) emissions and global warming (Awasthi et al., 2020). To achieve long-term environmental sustainability and reduce GHG emissions, there is an urgent need to replace non-renewable raw materials and energy with alternative resources (Aghbashlo et al., 2022; Brandão et al., 2022). Biodiesel, which comprises fatty acid methyl esters (FAME) obtained from vegetable oil, animal oil/fats, and various waste oil resources (Bashir et al., 2022), offers intrinsic renewability, biodegradability, and non-toxicity. Additionally, it exhibits excellent lubricity, ignition characteristics, and zero sulphur content compared to petroleum-based diesel. However, it does have some drawbacks, including high viscosity, resulting in poor combustion quality (Vijay Kumar et al., 2018), and high pour and cloud points (Unlu et al., 2018; Krishnasamy and Bukkarapu, 2021), making cold engine starting challenging (Buoaid et al., 2014; Liu and Tao, 2022). To address these issues, the use of additives such as alkyl levulinates (Trombettoni et al., 2018a), notably ethyl levulinate (EL) (Heda et al., 2019) has been reported.

In addition to biodiesel and the value-added products generated through valorizing the byproduct of the biodiesel industry, i.e., glycerol (Hosseinzadeh-Bandbafha et al., 2018; Marrocchi et al., 2022; Wang et al., 2022; Keshavarzi et al., 2023), other bio-derived fuels and fuel additives (Alarcon et al., 2021; Shahbeik et al., 2022) and biomass-derived chemicals (Valentini et al., 2019; Lluna-Galán et al., 2021; Valentini et al., 2022) have also recently garnered significant attention in the shift towards a petroleum-free energy economy. Among the available bio-derived feedstocks, lignocellulosic biomass, agricultural residues, dedicated non-edible energy crops (Okolie et al., 2021; Raj et al., 2022), and aquaculture waste (Kiehbadroudinezhad et al., 2023) stand out as abundant resources that offer a viable and sustainable solution for industrial production. These feedstocks contain valuable compounds (*i.e.*, 5-hydroxymethylfurfural, furfural, sorbitol, xylitol, succinic acid, and levulinic acid), which are referred to as "platform molecules". The transformation of these "platform molecules" opens opportunities for producing a diverse array of value-added products, such as biofuels (Biddy et al., 2016; Correa et al., 2019), additives (Martìnez Aguilar et al., 2020; Perez et al., 2022), monomers for polymer synthesis (Kim et al., 2020; Zhu and Yin, 2021), and solvents (Lomba et al., 2019; Sheldon, 2019).

Levulinic acid (LA) stands as a prominent bio-derived platform chemical serving as a precursor to various valuable compounds in diverse fields (Trombettoni et al., 2018b; Di Menno Di Bucchianico et al., 2022). EL and alkyl levulinates, as a class, find application as fuel additives for biofuels, particularly biodiesel for diesel engines. Furthermore, these compounds serve as reaction media (Marcel et al., 2019; Uzunlu et al., 2023), solvents in various types of manufacturing processes (Campana et al., 2020a; Ho et al., 2020), and even as flavoring agents. In fact, the Flavor and Extract Manufacturers Association of the United States (FEMA) approves several levulinates (*i.e.,* ethyl, butyl, isoamyl, and benzyl levulinates) as food additives for flavoring beverages, ice creams, candies, puddings, chewing gums and more (Smith et al., 2009).

The current focus lies in developing environmentally friendly synthetic procedures for the upgrading of the bio-derived platforms. In this context, carbon-based low-cost catalytic systems play a pivotal role (Sevilla et al., 2021; Chen et al., 2022), aligning with the principles of a circular and sustainable economy. Of particular importance is the utilization of biomass raw materials to prepare heterogeneous catalytic systems capable of efficiently converting LA to ethyl levulinate. Representative examples of such heterogenous acidic catalysts include carbon cryogel (UCC) (Zainol et al., 2019a and b), sulphonated loofah-sponge derived carbon (Li et al., 2019a), sulphonated sugarcane bagasse (Liu et al., 2019), and carbon nanotubes (Oliveira et al., 2014). In recent studies, Peixoto et al. (2021) achieved an 84% yield of EL through the one-pot conversion of 5-hydroxymethylfurfural (HMF) using a sulphonated solid catalyst produced from vineyard pruning wastes. This highlights the significance of recycling (Kumar et al., 2021; Bohre et al., 2023) and valorizing waste materials into stable and durable catalysts, in line with the principles of upcycling, which are increasingly relevant in contemporary society (Ferlin et al., 2021; Moon et al., 2023). Among the lignocellulosic wastes, pine needles pose a significant concern in various geographical regions due to their economic impact on urbanized sites during disposal and their contribution to forest

fires, which in turn leads to GHG emissions. Furthermore, fallen pine needles create an acidic layer on the ground, reducing soil water absorbance and inhibiting the growth of other plant species (Rana et al., 2023). With approximately 30% of the pine tree mass consisting of pine needles, their conversion into valuable bio-products has garnered increasing interest.

Researchers have explored diverse options for utilizing pine needles, including producing bio-composites (Gairola et al., 2017), briquettes (Mandal et al., 2018; Nurek et al., 2019), biogas (Singh and Sharma, 2021; Eftaxias et al., 2022), bioethanol (Slathia et al., 2020), and carbonaceous materials through thermochemical processes. These carbonaceous materials, known as biochars, can be further functionalized and find application in soil amendments (Nascimento et al., 2023), as adsorbents (Mishra and Mohanty, 2022; Pandey et al., 2022), for enzyme immobilization and photocatalysis (Liu et al., 2015). Biochar-derived catalysts are also gaining attention since they can replace conventional heterogeneous active carbon-supported systems (Liu et al., 2021). In this context, sulphonated pine needles-derived biochars have been recently developed for catalyzing the synthesis of EL from LA. Li et al. (2019b) recently designed a highly efficient sulphonated catalytic system derived from pine needles, achieving a maximum of 96.1% LA conversion. Following a similar approach, Kumari et al. (2022) found that the chlorosulfonic acid-treated biochar, duly sulphonated, gave an impressive yield of 97% for the EL synthesis. Despite these good results, it is important to note that the surface functionalization of such biochars through the introduction of -SO$_3$H groups typically involves a significantly energy-intensive thermal treatment applied to the carbonaceous support originating from biomass (Table 1).

In continuation of our research group (Green S.O.C.)'s commitment to developing waste-minimized protocols (Campana et al., 2020b; Valentini et al., 2023), herein is reported the synthesis of various levulinates (**3a**: pentyl levulinate, **3b**: ethyl levulinate, **3c**: butyl levulinate, **3d**: octyl levulinate, **3e**: isoamyl levulinate, **3f**: isobutyl levulinate, **3g**: isopropyl levulinate, **3h**: *sec*-butyl levulinate, **3i**: cyclohexyl levulinate, **3j**: tetrahydrofurfuryl levulinate, **3k**: benzyl levulinate, and **3l**: 5-hexenyl levulinate) by reacting LA with both primary and secondary alcohols (**2a**: 1-pentanol, **2b**: ethanol, **2c**: butanol, **2d**: octanol, **2e**: isoamyl alcohol, **2f**: isobutyl alcohol, **2g**: isopropanol, **2h**: *sec*-butyl alcohol, **2i**: cyclohexanol, **2j**: tetrahydrofurfuryl alcohol, **2k**: benzyl alcohol, **2l**: 5-hexen-1-ol, **2m**: Geraniol and **2n**: furfuryl alcohol), employing the developed PiNe–SO$_3$H catalyst. This heterogeneous catalyst resulting from the valorization of pine needles urban waste, prepared through a one-pot chemical carbonization and functionalization process, demonstrated excellent

stability over 10 consecutive cycles. Notably, to the best of our knowledge, this work marks the first instance of a waste-derived acidic catalyst used for producing a range of levulinates beyond EL, showcasing the catalyst's broad applicability. The importance of the present study is evident when comparing it with the latest data concerning LA esterification involving sulfonated catalysts derived from bio-based feedstocks, as outlined in **Table 1**. Particularly, the developed procedure stands out by avoiding high-temperature multi-step synthetic protocols and the need for energy-intensive thermal treatments. In addition, a distinctive facet of this approach lies in the careful optimization of the work-up protocol to minimize waste generation, an aspect which is underscored in previous works. It is well established that waste mitigation directly translates to cost-effectiveness, as waste disposal stands as a prominently cost-impacting facet within synthetic processes. In the pursuit of assessing the environmental sustainability of diverse work-up procedures, a range of green metrics were employed, including atom efficiency (AEf), Mass Recovery Parameter (MRP), Reaction Mass Efficiency (RME), Environmental factor (E-factor), and Ecoscale, ultimately selecting the most environmentally friendly option. Moreover, investigations were conducted to understand the reaction mechanism involving PiNe–SO$_3$H.

2. Materials and Methods

All chemicals were purchased and used without additional purification unless specified otherwise. Gas-liquid chromatography (GLC) analyses were performed using a Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.22 mm, 0.25 µm), a Flame Ionization Detector (FID) and Helium as the gas carrier. N,O-Bis(trimethylsilyl)trifluoroacetamide was used as a GLC derivatizing agent for LA. Gas chromatography with electron impact mass spectrometry (GC-EIMS) analyses were carried out using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.

Elemental analysis (EA) was performed on the Elementar UNICUBE® elemental analyzer. ATR-IR spectra were recorded on Bruker Optics ALPHA-P spectrometer, equipped with a Platinum ATR module. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz and 100.6 MHz, respectively, on a Bruker DRX ADVANCE 400 MHz, using a CDCl$_3$ (99.8 atom% D or CDCl$_3$ 99.8 atom% D containing 0.05 % (v/v) TMS) as the deuterated solvent. Chemical shifts are reported in ppm (δ) and coupling

Table 1.
Comparison of this work with representative recent papers on LA esterification using SO$_3$H-functionalized biochars as catalysts.

Catalyst	Substrate	Preparation Method	Products	Ref.
CCOPF[a]	LOPF-IL[b] + furfural	(i) Catalytic (H$_2$SO$_4$) thermal treatment and (ii) subsequent calcination at 400 °C	1 (EL[c])	Zainol et al. (2019b)
LFCC[d]	Lignin + furfural	(i) Catalytic (H$_2$SO$_4$) thermal treatment and (ii) subsequent calcination at 500 °C	1 (EL[c])	Zainol et al. (2019a)
UCC-S[e]	Lignin + furfural	(i) Catalytic (H$_2$SO$_4$) thermal treatment, (ii) subsequent calcination at 500 °C followed by (iii) UCC sulphonation.	1 (EL[c])	Zainol et al. (2021)
Sulphonated LSAC[f]	Loofah sponge	(i) Pre-carbonization at 240 °C followed by (ii) calcination at 400–900 °C, and (iii) final hydrothermal sulphonation with H$_2$SO$_4$ at 180 °C	1 (EL[c])	Li et al. (2019a)
C-SO$_3$H[g]	Sugarcane bagasse	(i) Pre-carbonization at 450°C and (ii) sulphonation with H$_2$SO$_4$ at 150 °C.	1 (EL[c])	Liu et al. (2019)
SBC[h]	Pine needles	(i) Pre-carbonization at 240 °C in the presence of citric acid followed by (ii) sulphonation with HSO$_3$Cl	1 (EL[c])	Kumari et al. (2022)
s-PNAC[i]	Pine needles	(i) Pre-carbonization at 240 °C followed by (ii) carbonization at 700 °C and (iii) subsequent hydrothermal sulphonation with H$_2$SO$_4$ at 160 °C	1 (EL[c])	Li et al. (2019b)
PiNe-SO$_3$H	Pine needles	Sulphonation with H$_2$SO$_4$ at room temperature	12 alkyl levulinates	**This study**

[a] Carbon cryogel (UCC) liquefied oil palm frond. [b] Liquefied Oil Palm Frond ionic liquid. [c] Ethyl levulinate. [d] Lignin-furfural carbon cryogel. [e] Sulphonated urea-furfural carbon cryogel. [f] Sulphonated Loofah sponge activated carbon. [g] Sulphonated carbonized sugarcane bagasse powder. [h] Sulphonated biochar. [i] Sulphonated pine needles activated carbon.

constants (J) in Hertz, and multiplicity is reported as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *ddt* = doublet doublet of triplet, *m* = multiplet. Characterization data and copies of the ^{1}H and ^{13}C NMR spectra of the compounds can be found in the **Supplementary Material**.

2.1. Error and uncertainty analysis

To avoid possible errors in weighing, the isolated product yields were determined and reported as the weighted average of three consecutive experiments. Specifically, a deviation in the isolated yields was observed across the three experiments conducted for each product, with fluctuations of approximately ± 0.5-1.5%.

2.2. PiNe–SO₃H catalyst preparation

The urban waste pine needles were collected, chopped into 1-2 cm pieces, and dried at 110 °C for 1 day. The dried biomass was then ground and sieved. The resulting material was extracted in a Soxhlet apparatus using a toluene methanol azeotrope (98% recovered) and subsequently dried at 80 °C under vacuum (Ferlin et al., 2021). For the preparation of PiNe-SO₃H, 2 g of the pretreated pine needles material was placed in an Erlenmeyer flask with 40 mL of sulphuric acid and sonicated for 30 min. After 3 d in H₂SO₄, the material was filtered and washed with water until reaching a neutral pH. The resulting PiNe-SO₃H was then dried under vacuum at 110 °C. The SO₃H loading was determined by CHNS analyses based on sulphur content (C: 40.04%, H: 5.12%, N: 0.56%, S: 2.6%; loading$_{SO_3H}$ = 0.81 mmol/g). The acidity of the PiNe-SO₃H was calculated using the titration method (1.26 meqH$^+$/g).

2.3. General procedure for levulinic acid esterification

In a 2 mL screw-capped vial equipped with a magnetic stirrer, LA (1 mmol), alcohol (1 eq.), and PiNe-SO₃H (1.5 mol%) were consecutively added. The resulting mixture was left under stirring at 90 °C for 5 h. After completion, the reaction mixture was allowed to cool to room temperature, then diluted with 0.5 mL of ethanol and subjected to centrifugation (6500 rpm, 10', 5 °C). PiNe-SO₃H was subsequently washed with 2 × 0.5 mL of ethanol (6500 rpm, 10 min, 5°C). The recovered ethanol was distilled (88%), yielding the crude levulinate.

2.4. Work-up procedure via extraction

This work-up procedure involved diluting the crude mixture with ethyl acetate (1 mL) and then washing it with sodium bicarbonate saturated solution (3 × 0.5 mL). The resulting organic phase was dried over sodium sulphate and concentrated under reduced pressure to afford the pure product as a pale-yellow oil, 87 ± 0.5% (162 mg, 0.87 mmol).

2.5. Work-up procedure via filtration on Amberlyst® A-21

In this work-up, before the recovery of ethanol, the organic layer was flushed through an Amberlyst® A-21 pad (80 mg) to remove residual LA. The remaining sample was dried under vacuum to afford the product as a pale-yellow oil, 91 ± 0.8% (170 mg, 0.91 mmol).

2.6. General procedure for PiNe–SO₃H recycling

After washing the catalyst and separating it from the reaction mixture by centrifugation, as described in *Section 2.3*, PiNe–SO₃H was dried under vacuum at 120 °C overnight and reused under the optimized reaction conditions.

3. Results and Discussion

The following sections report the preparation and characterization of PiNe-SO₃H, followed by the optimization of reaction conditions and a direct comparison of its catalytic activity with existing literature protocols. Finally, a comprehensive evaluation of the sustainability of the developed process, with particular emphasis on the work-up impact on environmental and cost sustainability, is provided.

3.1. PiNe–SO₃H synthesis and characterization

Initially, the pine needles waste underwent pretreatment to separate the extractive components from the lignocellulosic part, which could be utilized for different purposes, such as the preparation of bio-based monomers (Quilter et al., 2017; Stadler et al., 2019) and polymers (Winnacker and Sag, 2018; Winnacker, 2018). The extraction process employed an azeotropic mixture, which was subsequently recovered by distillation at 95% efficiency, thereby reducing waste associated with the pretreatment. The resulting lignocellulosic residue was then subjected to a one-pot chemical carbonization/functionalization in the presence of H₂SO₄ (see *Section 2.2*) to transform it into the PiNe–SO₃H catalyst. The catalyst was further characterized to determine its composition and surface functionalization.

Since the pretreated pine needles waste exhibited a negligible sulphur content (C: 43.87%, H: 5.104%, N: 0.39%, S: 0.097%), the SO₃H catalyst loading of 0.81 mmol/g was calculated based on the data collected from the elemental analysis on PiNe–SO₃H (see *Section 2.2*) and was confirmed by ATR-IR spectrum (**Supplementary Material**, **Fig. S1**). The material showed an acidity of 1.26 meqH$^+$/g, measured by titration. The higher acidity compared to the sulphonic groups loading was due to the presence of carboxylic moiety on the PiNe–SO₃H surface, as evidenced by the signal at 1701 cm^{-1}, associated with C=O stretching (Dawodu et al., 2014) observed in the ATR-IR spectrum (**Supplementary Material**, **Fig. S1**). The characteristic peaks of sulphonic groups were detected at 1023, 1097, and 1149 cm^{-1} and assigned to the SO₃$^-$ stretching, S–O, and S=O asymmetric stretching, respectively. Additionally, the signal at 1600 cm^{-1} was associated with the aromatic C=C stretching (Li et al., 2019a).

3.2. Catalytic tests: reaction between levulinic acid and 1-pentanol

With the PiNe–SO₃H acidic catalyst in hand, the study was started by optimizing the reaction conditions for the conversion of LA (**Fig. 1**; **1**) with 1-pentanol (**Fig. 1**; **2a**) as the model substrate. Different parameters were varied, and their effects were investigated (**Table 2**).

At 90 °C and a 1:10 ratio of **1:2a** without any catalyst, only traces of a 1:1 product mixture were detected after 24 h (**Table 2**; *entry 1*), highlighting the crucial role of the catalyst in yielding the desired product **3a**.
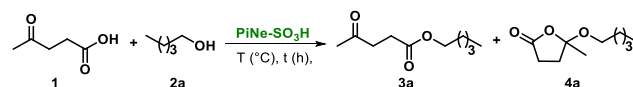

Fig. 1. Pentyl levulinate (**3a**) synthesis from the reaction between levulinic acid (**1**) and 1-pentanol (**2a**).

The catalyst performance was then tested employing a molar ratio of 1:10 between **1** and **2a** and by adding 3 mol% of PiNe-SO₃H at 50 °C (**Table 2**; *entries 2* and *3*). After 5 h, the catalyst enabled a 43% conversion with 83% selectivity towards the desired product pentyl levulinate (**3a**) (**Table 2**; *entry 2*). With prolonged reaction time, the catalyst achieved a 64% conversion, with a higher selectivity of 90% for **3a** (**Table 2**; *entry 3*). The esterification reaction can in fact proceed through both a classic Fisher esterification pathway and an initial dehydration and lactonization of LA into α-angelica lactone (AL), followed by nucleophilic addition of alcohol to form a pseudo-levulinate intermediate (**Fig. 2**), as also reported by Ciptonugroho et al. (2016) and Enumula et al. (2017). It is worth noting that under acidic conditions, the activation energy for *pseudo*-ester formation is lower (3 kJ·mol^{-1}) compared to the direct esterification (50 kJ·mol^{-1}) to produce the final product, as calculated by Al-Shaal et al. (2015) using Amberlyst-15 as a heterogenous acid catalyst with 1-butanol.

By increasing the reaction temperature to 70 °C (**Table 2**; *entry 4*) and 90 °C (**Table 2**; *entry 5*), higher conversions of 87% and 95%, with improved selectivity towards **3a** at 95% and >99%, were achieved, respectively. To further optimize the process and minimize waste generation, the catalyst amount was reduced to 1.5 mol%, resulting in the same conversion and selectivity as with 3 mol% (**Table 2**; *entry 6*). Gradually decreasing the molar ratio between **1** and **2a** to 1:5 (**Table 2**;

Table 2.
Optimization of reaction conditions for the reaction between levulinic acid (**1**) and 1-pentanol (**2a**).

Entry	1:2a	PiNe-SO$_3$H (mol%)[a]	T (°C)	t (h)	Conversion (%)[b]	3a (%)[b]	4a (%)[b]
1	1:10	-	90	24	5	55	45
2	1:10	3	50	5	43	83	17
3	1:10	3	50	8	64	90	10
4	1:10	3	70	5	87	94	6
5	1:10	3	90	5	95	>99	traces
6	1:10	1.5	90	5	95	>99	traces
7	1:5	1.5	90	5	95	100	-
8	1:1	1.5	90	5	96	100	-
9	1:1	1.5	90	8	96	100	-

[a]Calculated on -SO$_3$H loading (0.81 mmol/g).
[b]Determined by GLC analysis.
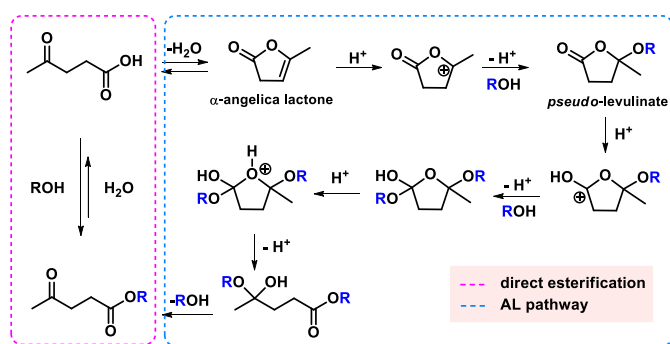
Fig. 2. Possible pathways for alkyl levulinates production from levulinic acid.

Fig. 3. ^{1}H-NMR spectra of (**A**) freshly isolated **4a**:**3a** mixture (91:9), (**B**) **4a**:**3a** mixture after 5 h at 90 °C without catalyst (91:9), (**C**) **4a**:**3a** mixture after 5 h at 90 °C with PiNe–SO$_3$H, and (**D**) pure **3a** in CDCl$_3$.

entry 7) and 1:1 (**Table 2**; *entry 8*) resulted in complete selectivity towards **3a** with conversions up to 96% when using a 1:1 molar ratio. Prolonging the reaction time did not significantly affect the conversion or selectivity, indicating the achievement of the thermodynamic equilibrium (**Table 2**; *entry 9*). The result suggests that a small amount of the PiNe–SO$_3$H catalyst effectively promoted the esterification product in 5 h at 90 °C, even without an excess of alcohol. Further investigation of the reaction mechanism was performed by monitoring the reaction evolution over time at different temperatures (50, 70, and 90 °C) and molar ratio of **1:2a** (1:10, 1:5, 1:2, 1:1) using both 3 mol% and 1.5 mol% of PiNe–SO$_3$H (**Fig. S2** in **Supplementary Material**). At low temperature (50 °C), the conversion decreased with the reduction of **2a** in excess, favoring the formation of *pseudo*-ester (**4a** in **Fig. 1**) initially. Over time, the selectivity shifted from intermediate **4a** to **3a** in all the conditions tested. However, at higher temperatures, the formation of **4a** was strongly inhibited when a stoichiometric amount of **2a** was used. It is noteworthy to mention that, with a molar ratio of 1:1, the reaction rate was even higher than using **2a** in excess, indicating the generation of a highly energetic reaction environment that favors direct esterification to **3a** and hinders its formation through the *pseudo*-ester (**4a**).

Attaining optimal reaction conditions while circumventing the need for excess alcohol, a distinctive trait particularly noteworthy in the context of carbonaceous catalysts (Gautam et al., 2022; Appaturi et al., 2022), emerges as a pivotal factor in establishing a thoroughly environmentally sustainable and waste-free synthetic methodology. To confirm the hypothesis regarding the reaction mechanism, intermediate **4a** was isolated by stopping the reaction performed in a molar ratio 1:10 at 50 °C after 30 min. The formation of *pseudo*-pentyl levulinate was confirmed through ^{1}H-NMR analysis, and a mixture of **4a**:**3a** (in a ratio of 91:9) was subjected to the optimized reaction conditions, both with and without catalyst. In the absence of the catalyst, the ratio between **4a** and **3a** remained unchanged (**Fig. 3**).
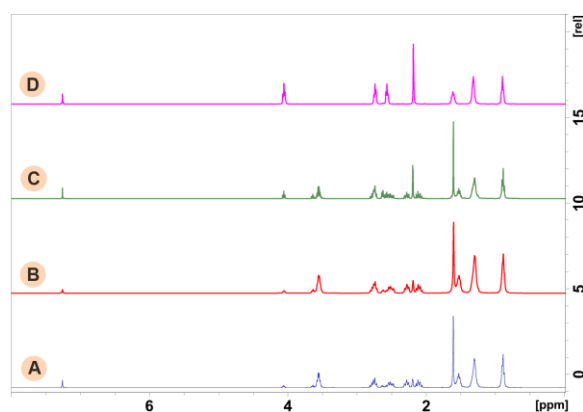
However, even when using a 1.5 mol% of PiNe–SO$_3$H at 90 °C for 5 h, the conversion into the desired product **3a** was unsatisfactory (23%). This result suggests that the catalyst operates through a direct esterification mechanism rather than the formation of the *pseudo*-ester **4a**. This is in contrast with the observations made by Zhou et al. (2022) concerning the use of TiO$_2$ nanoparticles.

The data discussed above clearly indicate that temperature and molar ratio are the key parameters influencing process reactivity and product selectivity. The efficiency of the developed catalytic system, Pine-SO$_3$H, was compared with other carbon-based, low-cost heterogeneous acid catalysts (Oliveira et al., 2014). Turnover frequency (TOF) values at ~50% LA conversion are reported in **Table S1** (**Supplementary Material**), demonstrating superior catalytic performances for PiNe-SO$_3$H under the optimized reaction conditions.

To evaluate the durability of the catalyst, thereby assessing the overall catalyst's efficiency in comparison to the existing alternatives (Li et al., 2019b; Liu et al., 2019), recycling experiments were conducted (**Fig. 4**). After each cycle, the solid catalyst was recovered, washed with ethanol, and dried under vacuum (see **Material and Methods**). PiNe-SO$_3$H showed impressive stability, remaining recyclable for up to 10 consecutive runs with only a slight decrease in conversion after the 9th cycle. This significant achievement stands out compared to the existing literature, reporting only a few examples of catalyst recycling with most of those catalysts losing efficiency after no more than 5 runs (Zainol et al., 2017; Li et al., 2019a). The recovered catalyst was characterized by ATR-IR (**Fig. S1** in **Supplementary Material**), showing shifts and increased intensity of the
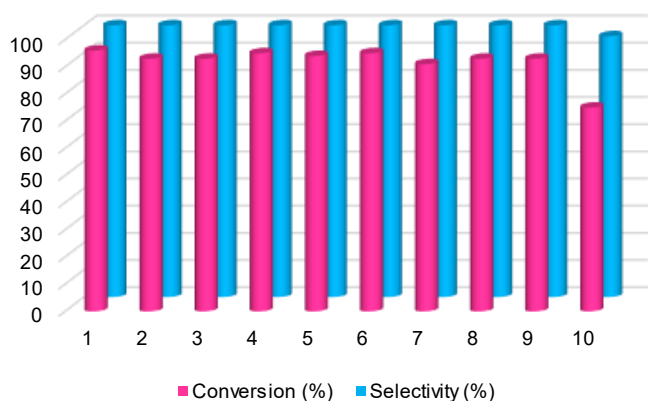
Fig. 4. Recycling test of PiNe-SO₃H for pentyl levulinate (**3a**) synthesis under optimized conditions.

C=O signal at 1710 cm⁻¹, indicating ester formation from the carboxylates present on PiNe–SO₃H's surface, while the signals assigned to the SO₃H groups remained unchanged, confirming their role in catalysis. Efforts were made to minimize waste during product isolation, enhancing the environmental sustainability of the process. To remove unreacted LA (4%), a liquid-liquid extraction of the crude mixture with ethyl acetate (1 mL), followed by washing with NaHCO₃ saturated aqueous phase (1.5 mL), was carried out (see *Section 2.4*). The desired product **3a** was obtained in 87 ± 0.5% isolated yield. This method led to an E-factor of 16.9 (See **Supplementary Material** for further details). On the contrary, using a supported ionic exchange resin, Amberlyst® A-21 (see *Section 2.5* and **Supplementary Material** for further details), reduced the E-factor to 1.5, leading to 91 ± 0.8% yield of product **3a**, along with 88% ethanol recovery. This reduction in the E-factor not only indicates waste minimization but also translates into tangible cost savings. Indeed, avoiding the utilization of a substantial quantity of solvent, which is essential for the liquid-liquid extraction process, serves a dual purpose. Beyond highlighting the establishment of a procedure characterized by reduced environmental impact, it concurrently leads to a notable cost reduction in the subsequent waste disposal stage. This is particularly noteworthy, considering that waste disposal typically constitutes approximately 90% of the total residues arising from a chemical process (Sheldon, 2019).

Further sustainability comparison between these work-up procedures was conducted using various green metrics (see **Supplementary Material**). The graphical representation of radial polygons (Andraos, 2012) in **Figure 5** clearly shows that the filtration work-up procedure approaches the ideal situation (*green line*) better than the extraction work-up. The optimized filtration method not only provides higher yield and AEf but also leads to increased values of RME and MRP, thereby providing additional confirmation of the enhanced benign nature inherent in the filtration procedure.
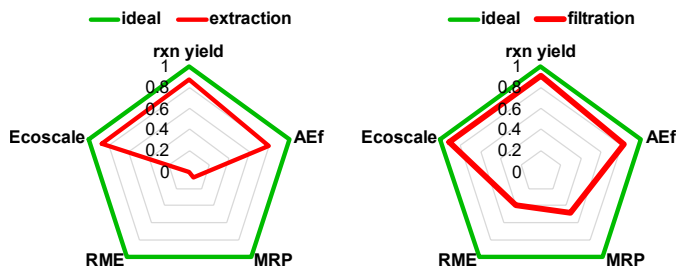

Fig. 5. Radial polygons comparing sustainability enhancement of work-up procedures (extraction *vs.* filtration). Abbreviations: rxn yield: isolated product yield, AEf: atom efficiency, MRP: mass recovery parameter, RME: reaction mass efficiency.

In addition, the sustainability enhancement achieved by exploiting Amberlyst® A-21 was further confirmed using "the Ecoscale" method. This is a powerful tool that quantifies the green quality of a synthetic method based on six categories (isolated product yield, cost of reagents, safety issues, technical setup, reaction conditions, and reaction work-up). An ideal process receives a score of 100, while penalty points indicate areas where the process could be improved in terms of sustainability (Van Aken et al., 2006). To integrate the Ecoscale rank (see **Supplementary Material** for further details) for the reference product **3a** isolation in the radial polygons representation, the ideal value was normalized to 1 (**Fig. 5**). Both of the investigated work-up procedures showed high values, with the filtration work-up demonstrating closer proximity to the ideal green situation.

3.3. Substrate scope

With the optimized conditions in hand, the versatility of the developed waste-derived sulphonated catalytic system was investigated in the synthesis of different bio-esters by reacting **1** with various alcohols (**2a-n**), including linear and branched, aliphatic, and aromatic alcohols (**Fig. 6**). When low-boiling point ethanol (**2b**) was reacted with LA under the optimized conditions at 90 °C, the conversion into **3b** reached only 66% due to limited contact between liquid LA and vaporized **2b** with the solid catalyst. However, by increasing the excess of **2b** to 10 eq., the conversion improved to 92%, resulting in an isolated yield of 86 ± 1%. Notably, the excess ethanol was recovered during the work-up procedure, minimizing waste and leading to a low E-factor value of 2.2 (see **Supplementary Material** for further details).
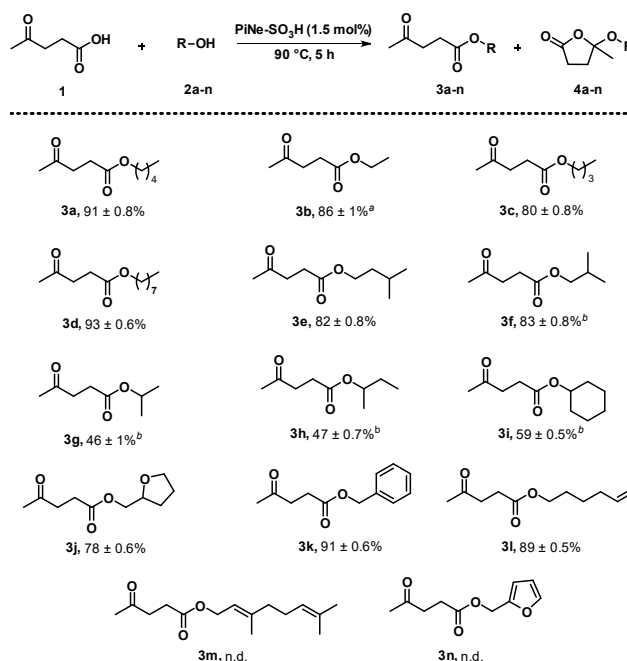

Fig. 6. Substrate scope for the synthesis of alkyl levulinates (**3a-n**). Reaction conditions: **1** (1 mmol), **2** (1 mmol), PiNe-SO₃H (1.5 mol%), 90 °C, 5 h; [a]**1** (1 mmol), **2** (10 mmol). [b]PiNe-SO₃H (3 mol%).

In contrast to the observations in the synthesis of **3b**, the optimized conditions worked well when linear alcohols **2c-e** were employed, resulting in high isolated yields of products **3c-e** (**Fig. 6**). Similarly, alcohols with increased complexity, such as tetrahydrofurfuryl alcohol (**2j**), benzyl alcohol (**2k**) and 5-hexen-1-ol (**2l**) led to high yields and low E-factor values (see **Supplementary Material** for further details).

The catalyst performance with secondary alcohols **2g-i** required an increase in catalyst amount to 3 mol% to achieve satisfactory conversions into alkyl levulinates **3g**, **3h**, and **3i** (46 ± 1%, 47 ± 0.7% and 59 ± 0.5%, respectively), overcoming steric hindrance issues during the nucleophilic addition. The effect of increased reaction time was negligible, confirming equilibrium attainment after 5 h, even with secondary alcohols. Geraniol (**2m**) and furfuryl alcohol (**2n**) did not produce the corresponding levulinates, likely due to the generation of degradation products under strongly acidic conditions and polymerization side reaction, respectively (Kim et al., 2011).

It is noteworthy to mention that, when synthesizing alkyl levulinates (**3a-n**) under the optimized reaction conditions, the formation of the corresponding *pseudo*-ester intermediate **4a-n** (**Fig. 6**) was never observed. To the best of our knowledge, PiNe–SO₃H is the first low-cost, heterogeneous carbon-based catalyst with the ability comparable to that of the polymeric solid catalytic system (Trombettoni et al., 2018b) in efficiently promoting the upgrading of the LA platform into a series of alkyl levulinates.

4. Limitations of the present study

Despite the noteworthy catalytic activity and durability exhibited by PiNe-SO₃H, forthcoming investigations should be directed toward addressing the limitations observed in reactions involving tertiary alcohols and complex substrates. As previously discussed, the utilization of secondary alcohols necessitated a catalyst quantity doubling to achieve satisfactory conversion rates, while tertiary alcohols failed to yield the desired product. The challenges associated with the conversion of complex substrates into levulinates, particularly those bearing unsaturated bonds or furanic rings within their structures, can be attributed to the high catalyst acidity, which could trigger the generation of degradation or oligomerization byproducts.

5. Policy and practical implications

The research presented in this study not only offers deeper insights into the chemistry surrounding alkyl levulinates but also directs attention toward the potential fully green development of fine chemicals with versatile applications, including fuel and food additives, fragrances, and environmentally benign solvents. Importantly, the study demonstrates the effective valorization of common urban waste into value-added products, effectively contributing to both economic welfare and environmental health. Through adopting a circular chemistry approach, waste materials are transformed into valuable resources, significantly enhancing the overall energy efficiency of the resultant chemical products throughout their life cycles. This approach conserves energy and notably reduces additional energy inputs (Keijer et al., 2019). Within this context, this research aligns perfectly with the EU Circular Economy Action Plan, particularly within the framework of the "EU's chemicals strategy for sustainability towards a toxic-free environment" section. This strategy aims not only to establish a new industrial production paradigm, emphasizing circularity in production processes and reducing the strain on natural resources but also to foster sustainable growth and employment opportunities while promoting the use of safer and sustainably designed chemicals.

It is important to highlight that the sulphonated heterogeneous catalyst developed in this study, as compared to catalysts like polymeric-based ones that are currently employed for levulinate production, is inherently safer and cleaner. This is due to its complete derivation from residual biomass, entirely devoid of any trace of petroleum derivatives.

6. Conclusions and outlooks

This work presents a step-economical preparation of a heterogeneous catalyst derived from the valorization of urban waste, pine needles. The synthesis of the PiNe–SO₃H catalyst occurred in a one-pot procedure under mild conditions, with its composition confirmed through various techniques (IR, elemental analysis, acidity measurement). The reaction conditions for the catalytic conversion of LA into alkyl levulinates were optimized, with a focus on minimizing waste during the work-up process. The greenness of the procedures was quantified using different green metrics (E-factor, AEf, RME, MRP) and the Ecoscale tool, highlighting the superior performance of the filtration work-up on Amberlyst® A-21 compared to the commonly used extraction procedure. The filtration method led to improved isolated yields. The

catalyst showed impressive durability and could be recycled for up to 10 consecutive runs.

The optimized reaction conditions were extended to synthesize different alkyl levulinates with good to excellent isolated yields (~46-93%) and low E-factor values (1.2-8.9) for both primary and secondary, aliphatic and aromatic alcohols. This is the first example of such broad applicability of a waste-derived acid catalyst. Furthermore, to fully understand the active reaction mechanism, several investigations were devoted to revealing a direct esterification pathway rather than involving a *pseudo*-levulinate intermediate derived from AL. Although LA dehydration and *pseudo*-ester formation are favored at low temperatures, the subsequent transformation into the desired product is kinetically unfavoured under the optimized conditions. Despite the impressive catalytic activity and durability, future studies should address the limitations observed in reactions with tertiary alcohols and complex substrates. In particular, it is advisable to conduct further studies aiming at developing a catalyst with a lower loading of sulfonic groups, i.e., having lower acidity. This modified catalyst configuration has the potential to be well-suited for the production of highly decorated esters.

Moreover, large-scale alkyl levulinate synthesis should be analyzed to thoroughly understand the catalyst behavior under stressed reaction conditions. In fact, given the primary applications of alkyl levulinates (fuel and food additives, fragrances, and more), it becomes imperative to understand the catalyst behavior under stressed and large reaction scales. Finally, this study contributes to the EU Circular Economy Action Plan, which is meant to set a new paradigm for industrial production, including circularity in production processes.
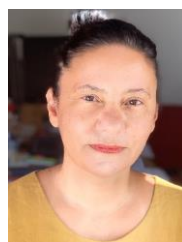
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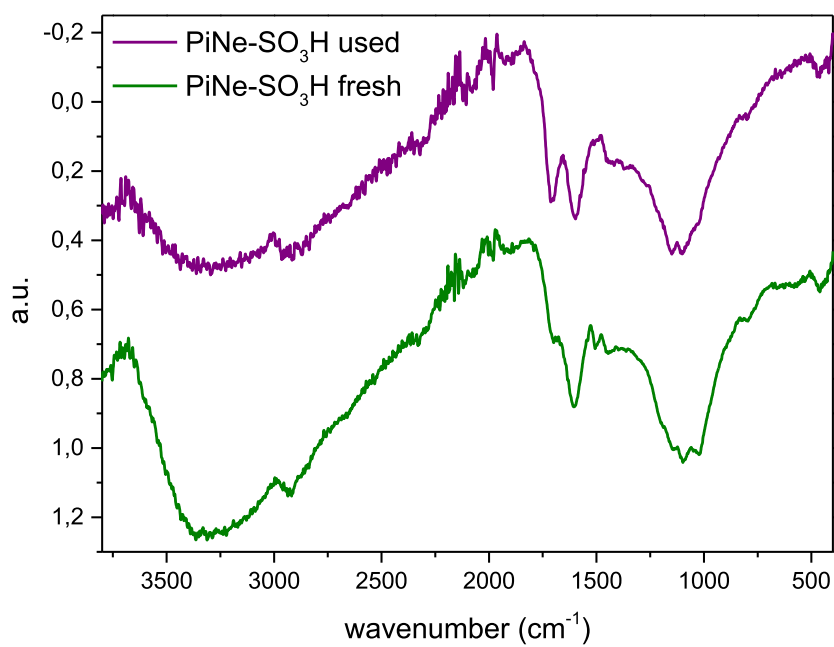
Supplementary Material

Fig. S1. ATR-IR spectra of fresh (green line) and used (purple line) PiNe–SO₃H catalyst.
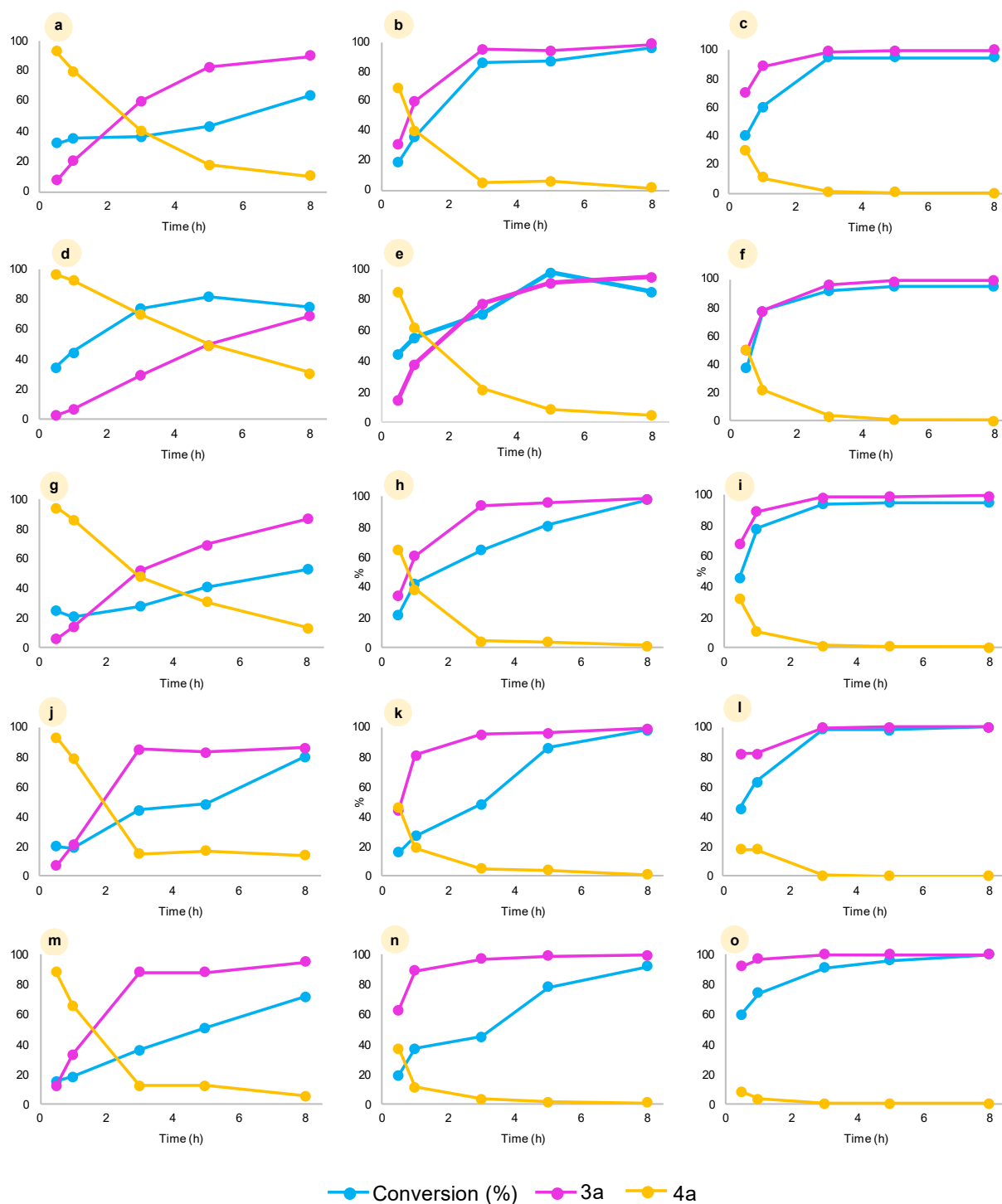
Fig. S2. Conversion of LA and selectivity for the reactions performed **(a)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (3 mol%) at 50 °C; **(b)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (3 mol%) at 70 °C; **(c)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (3 mol%) at 90 °C; **(d)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (1.5 mol%) at 50 °C; **(e)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (1.5 mol%) at 70 °C; **(f)** between LA (1 mmol) and **2a** (10 mmol) with PiNe–SO₃H (1.5 mol%) at 90 °C; **(g)** between LA (1 mmol) and **2a** (5 mmol) with PiNe–SO₃H (1.5 mol%) at 50 °C; **(h)** between LA (1 mmol) and **2a** (5 mmol) with PiNe–SO₃H (1.5 mol%) at 70 °C; **(i)** between LA (1 mmol) and **2a** (5 mmol) with PiNe–SO₃H (1.5 mol%) at 90 °C; **(j)** between LA (1 mmol) and **2a** (2 mmol) with PiNe–SO₃H (1.5 mol%) at 50 °C; **(k)** between LA (1 mmol) and **2a** (2 mmol) with PiNe–SO₃H (1.5 mol%) at 70 °C; **(l)** between LA (1 mmol) and **2a** (2 mmol) with PiNe–SO₃H (1.5 mol%) at 90 °C; **(m)** between LA (1 mmol) and **2a** (1 mmol) with PiNe–SO₃H (1.5 mol%) at 50 °C; **(n)** between LA (1 mmol) and **2a** (1 mmol) with PiNe–SO₃H (1.5 mol%) at 70 °C; **(o)** between LA (1 mmol) and **2a** (1 mmol) with PiNe–SO₃H (1.5 mol%) at 90 °C.

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Fig. S3. Ecoscale values (http://ecoscale.cheminfo.org/) for **(a)** extraction isolation and **(b)** Amberlyst A-21 isolation procedure.

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Table S1.
Comparison of turnover frequency (TOF) values calculated at $t_{50\%}$.

LA:R–OH	-SO₃H Catalyst	T (°C)	$t_{50\%}$ (h)	LE$_{50\%}$ (%)^b	TOF (h^{-1})	Reference
1:5	50 wt% (loading 2.29 mmol/g)	80	2	43	16	Li et al. (2019b)
1:100	50 wt% (loading 0.06 mmol/g)^a	50	13	85	1	Kumari et al. (2022)
1:15	25 wt% (loading 0.59 mmol/g)^a	150	1	51	30	Zainol et al. (2017)
1:10	10 wt% (loading 0.63 mmol/g)^a	80	3	75	34	Zainol et al. (2021)
1:5	5 wt% (loading 1.59 mmol/g)	80	4	60	16	Li et al. (2019a)
1:5	5 wt% (loading 1.2 mmol/g)	120	3	56	56	Liu et al. (2019)
1:5	2.5 wt% (loading 0.49 mmol/g)	70	5	54	76	Oliveira et al. (2014)
1:1	16 wt% (loading 0.81 mmol/g)	90	0.5	60	80	**This study**

^{a} Calculated by the reported S%.

^{b} LE: Levulinic ester, R–OH: Alcohol stoichiometric excess, $t_{50\%}$: Reaction time at ∼50% LA conversion, LE$_{50\%}$: Levulinic ester conversion at $t_{50\%}$.

1. E-Factor and metrics calculation

1.1. E-factor calculation for the alkyl levulinates (3a-l) purification using extraction work-up

$13.6 <$ E-factor < 40.7

Reaction of levulinic acid (1) and pentanol (2a) to give pentyl levulinate (3a)

E-factor = ((116.11 mg (**1**) + 88.15 mg (**2a**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 162 mg (**3a**))) / 162 mg (**3a**) = 16.9

Reaction of levulinic acid (1) and ethanol (2b) to give ethyl levulinate (3b)

E-factor = ((116.11 mg (**1**) + 460.7 mg (**2b**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1440mg (**2b** + EtOH) + 118.2 mg (**3b**))) / 118.2 mg (**3b**) = 23.3

Reaction of levulinic acid (1) and butanol (2c) to give butyl levulinate (3c)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2c**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 130.5 mg (**3c**))) / 130.5 mg (**3c**) = 21.1

Reaction of levulinic acid (1) and octanol (2d) to give octyl levulinate (3d)

E-factor = ((116.11 mg (**1**) + 130.23 mg (**2d**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 202.1 mg (**3d**))) / 202.1 mg (**3d**) = 13.6

Reaction of levulinic acid (1) and isoamyl alcohol (2e) to give isoamyl levulinate (3e)

E-factor = ((116.11 mg (**1**) + 88.15 mg (**2e**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 147 mg (**3e**))) / 147 mg (**3e**) = 18.7

Reaction of levulinic acid (1) and isobutyl alcohol (2f) to give isobutyl levulinate (3f)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2f**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 135.3 mg (**3f**))) / 135.3 mg (**3f**) = 20.3

Reaction of levulinic acid 1) and isopropanol (2g) to give isopropyl levulinate (3g)

E-factor = ((116.11 mg (**1**) + 60.10 mg (**2g**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 69 mg (**3g**))) / 69 mg (**3g**) = 40.7

Reaction of levulinic acid (1) and *sec*-butyl alcohol (2h) to give *sec*-butyl levulinate (3h)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2h**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 77.5 mg (**3h**))) / 77.5 mg (**3h**) = 36.3

Reaction of levulinic acid (1) and cyclohexanol (2i) to give cyclohexyl levulinate (3i)

E-factor = ((116.11 mg (**1**) + 100.16 mg (**2i**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 111 mg (**3i**))) / 111 mg (**3i**) = 25.3

Reaction of levulinic acid (1) and tetrahydrofurfuryl alcohol (2j) to give tetrahydrofurfuryl levulinate (3j)

E-factor = ((116.11 mg (**1**) + 102.13 mg (**2j**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 148.5 mg (**3j**))) / 148.5 mg (**3j**) = 18.6

Reaction of levulinic acid (1) and benzyl alcohol (2k) to give benzyl levulinate (3k)

E-factor = ((116.11 mg (**1**) + 108.14 mg (**2k**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 177.5 mg (**3k**))) / 177.5 mg (**3k**) = 15.9

Reaction of levulinic acid (1) and 5-hexen-1-ol (2l) to give 5-hexenyl levulinate (3l)

E-factor = ((116.11 mg (**1**) + 100.16 mg (**2l**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 902 mg (EtOAc) + 1650 (NaHCO$_3$ aq.)) − (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 168.5 mg (**3l**))) / 168.5 mg (**3l**) = 16.3

1.2. E-factor calculation for the alkyl levulinates (3a-l) isolation using Amberlyst A-21 filtration work-up

$1.2 <$ E-factor < 8.9

Reaction of levulinic acid (1) and pentanol (2a) to give pentyl levulinate (3a)

E-factor = ((116.11 mg (**1**) + 88.15 mg (**2a**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) - (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 170 mg (**3a**))) / 170 mg (**3a**) = 1.5

Reaction of levulinic acid (1) and ethanol (2b) to give ethyl levulinate (3b)

E-factor = ((116.11 mg (**1**) + 460.7 mg (**2b**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1440mg (**2b** + EtOH) + 124 mg (**3b**))) / 124 mg (**3b**) = 2.2

Reaction of levulinic acid (1) and butanol (2c) to give butyl levulinate (3c)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2d**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 137 mg (**3c**))) / 137 mg (**3c**) = 2.0

Reaction of levulinic acid (1) and octanol (2d) to give octyl levulinate (3d)

E-factor = ((116.11 mg (**1**) + 130.23 mg (**2d**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 212 mg (**3d**))) / 212 mg (**3d**) = 1.2

Reaction of levulinic acid (1) and isoamyl alcohol (2e) to give isoamyl levulinate (3e)

E-factor = ((116.11 mg (**1**) + 88.15 mg (**2e**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 152.5 mg (**3e**))) / 152.5 mg (**3e**) = 1.8

Reaction of levulinic acid (1) and isobutyl alcohol (2f) to give isobutyl levulinate (3f)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2f**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 142 mg (**3f**))) / 142 mg (**3f**) = 1.9

Reaction of levulinic acid (1) and isopropanol (2g) to give isopropyl levulinate (3g)

E-factor = ((116.11 mg (**1**) + 60.10 mg (**2g**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 400 mg (Amberlyst A-21)) – (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 72.5 mg (**3g**))) / 72.5 mg (**3g**) = 8.9

Reaction of levulinic acid (1) and *sec*-butyl alcohol (2h) to give *sec*-butyl levulinate (3h)

E-factor = ((116.11 mg (**1**) + 74.12 mg (**2h**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 400 mg (Amberlyst A-21)) – (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 81 mg (**3h**))) / 81 mg (**3h**) = 8.1

Reaction of levulinic acid (1) and cyclohexanol (2i) to give cyclohexyl levulinate (3i)

E-factor = (116.11 mg (**1**) + 100.16 mg (**2i**) + 36.8 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 400 mg (Amberlyst A-21)) – (36.8 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 117 mg (**3i**))) / 117 mg (**3i**) = 5.5

Reaction of levulinic acid (1) and tetrahydrofurfuryl alcohol (2j) to give tetrahydrofurfuryl levulinate (3j)

E-factor = ((116.11 mg (**1**) + 102.13 mg (**2j**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 156 mg (**3j**))) / 156 mg (**3j**) = 1.9

Reaction of levulinic acid (1) and benzyl alcohol (2k) to give benzyl levulinate (3k)

E-factor = ((116.11 mg (**1**) + 108.14 mg (**2k**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 188 mg (**3k**))) / 188 mg (**3k**) = 1.4

Reaction of levulinic acid (1) and 5-hexen-1-ol (2l) to give 5-hexenyl levulinate (3l)

E-factor = ((116.11 mg (**1**) + 100.16 mg (**2l**) + 18.4 (PiNe-SO$_3$H) + 1184 mg (EtOH) + 80 mg (Amberlyst A-21)) – (18.4 mg (PiNe-SO$_3$H) + 1038 mg (EtOH) + 176.5 mg (**3l**))) / 176.5 mg (**3l**) = 1.5

1.3. Metrics calculations for the construction of radial polygons for different work-up

$AE = MW_{3a} / (MW_1 + MW_{2a}) = 186.25 / (116.11 + 88.15) * 100 = 0.9118$

Stoichiometric factor (SF) = Used mass (**1** + **2a**) / stoichiometric mass (**1** + **2a**) = (116.85 + 89.54) / (116.85 + 88.15) = 1.004

Extraction

Yield: 87% = 0.87
AEf: AE * Yield = 0.9118 * 0.87 = 0.7933
Reaction mass efficiency (RME) = 1 / (1 + E factor) = 1 / (1+16.9) = 0.0056
Mass recovery parameter (MRP) = RME * SF / Yield * AE = (0.0056 * 1.004) / (0.87 * 0.9118) = 0.071
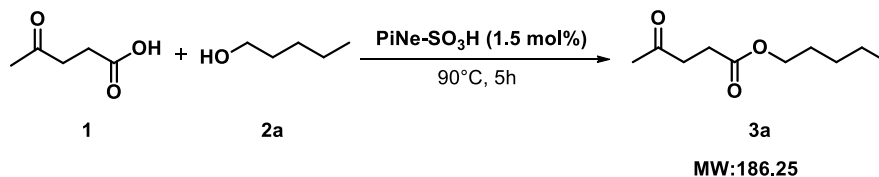
Filtration on Amberlyst A-21

Yield: 91% = 0.91
AEf = AE * Yield = 0.9118 * 0.91 = 0.8297
Reaction mass efficiency (RME) = 1 / (1 + E factor) = 1 / (1+1.53) = 0.395
Mass recovery parameter (MRP) = RME * SF / Yield * AE = (0.395 * 1.004) / (0.91 * 0.9118) = 0.478

2. Characterization data

Chem. Name	Pentyl 4-oxopentanoate (3a)
Reference	Trombettoni et al. (2018)

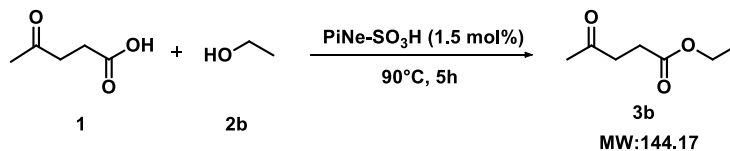**1**   **2a**   **3a**

MW:186.25

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), 1-pentanol (**2a**) (1 mmol, 88.15 mg), PiNe-SO$_3$H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO$_3$H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3a** as a pale-yellow oil, 91 ± 0.8% (170 mg).

Mol Formula	C$_{10}$H$_{18}$O$_3$			m.p.	oil
	δ value	No. H	Mult.	j value/Hz	
	4.05	2	*t*	6.67	
	2.74	2	*t*	6.42	
¹H-NMR	2.56	2	*t*	6.41	
400 MHz	2.18	3	*s*		
CDCl₃	1.65-1.58	2	*m*		
	1.33-1.30	4	*m*		
	0.89	3	*t*	6.8	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 173.0, 65.0, 38.1, 30.0, 28.4, 28.2, 22.4, 14.1

GC-EIMS (m/z, %): 186 (M +,<10), 114.1 (13.5), 117 (60.4), 101 (75.8), 100.1 (25.2), 99 (100), 98.1 (25.8), 75.1 (55.1), 74.1 (100), 73.1 (20.9), 72.1 (14.8), 71.1 (84.6), 70.1 (50.8), 57.1 (14.6), 56.1 (30.4), 55.1 (56.5)

Chem. Name	Ethyl 4-oxopentanoate (3b)
Reference	Trombettoni et al. (2018)

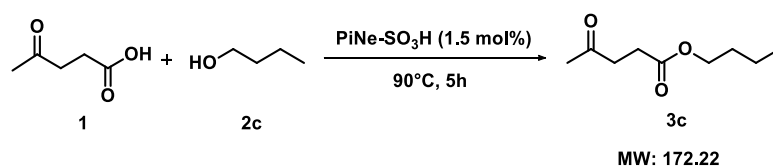**1**   **2b**   **3b**
MW:144.17

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), absolute ethanol (**2b**) (10 mmol, 460.7 mg), PiNe-SO$_3$H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO$_3$H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3b** as a pale-yellow oil, 86 ± 1% (124 mg).

Mol Formula	C$_7$H$_{12}$O$_3$		m.p.		oil

	δ value	No. H	Mult.	j value/Hz	
¹H-NMR	4.11	2	*q*	7.06	
400 MHz	2.73	2	*t*	6.47	
CDCl₃	2.55	2	*t*	6.47	
	2.17	3	*s*		
	1.23	3	*t*	7.12	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 172.9, 60.7, 38.0, 30.0, 28.1, 14.3

GC-EIMS (m/z, %): 144 (M+, <10), 129.1 (30.1), 102 (24.0), 101 (35.5), 99 (100), 98 (14.7), 74 (31.1), 73 (25.6), 71 (22.1), 57 (14.9), 56 (12.7), 55 (24.5)

Chem. Name	Butyl 4-oxopentanoate (3c)
Reference	Badgujar and Bhanage (2015)

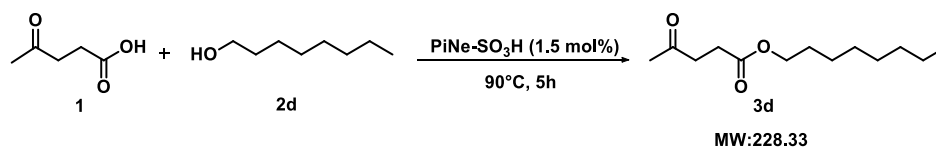**1**   **2c**   **3c**

MW: 172.22

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), butanol (**2c**) (1 mmol, 74.12 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3c** as a pale-yellow oil, 80 ± 0.8% (137 mg).

Mol Formula	$C_9H_{16}O_3$			m.p.		oil
	δ value	**No. H**	**Mult.**	**j value/Hz**		
	4.06	2	*t*	7.29		
	2.74	2	*t*	6.44		
¹H-NMR	2.56	2	*t*	6.44		
400 MHz	2.18	3	*s*			
CDCl₃	1.63-1.56	2	*m*			
	1.41-1.32	2	*m*			
	0.92	3	*t*	7.29		

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 173.0, 64.7, 38.1, 30.8, 30.0, 28.1, 19.2, 13.8

GC-EI, MS (m/z, %): 172.1 (M +,<10), 157.1 (24.0), 130.1 (33.4), 117.1 (73.6), 101.1 (100), 99.1 (100), 75.1 (51.6), 74.1 (100), 73.1 (32.1), 72.1 (12.4), 71.1 (44.7), 57.1 (70.0), 56.1 (80.0), 55.1 (33.6)

Chem. Name	Octyl 4-oxopentanoate (3d)
Reference	Trombettoni et al. (2018)

1 + **2d** → **3d**
MW:228.33

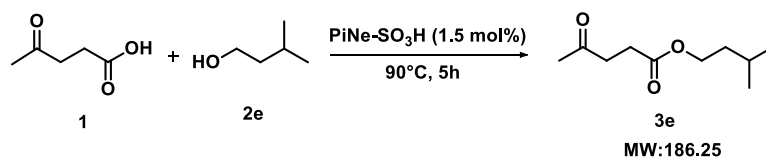PiNe-SO₃H (1.5 mol%)
90°C, 5h

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), octanol (**2d**) (1 mmol, 130.23 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature with ethanol (0.5 mL) and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3d** as a pale-yellow oil, 93 ± 0.6% (212 mg).

Mol Formula	$C_{13}H_{24}O_3$				m.p.	oil
	δ value	**No. H**	**Mult.**	**j value/Hz**		
	4.05	2	*t*	6.82		
	2.74	2	*t*	6.58		
¹H-NMR	2.57	2	*t*	6.44		
400 MHz	2.19	3	*s*			
CDCl₃	1.62-1.57	2	*m*			
	1.30-1.27	10	*m*			
	0.88	3	*m*			

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 172.9, 65.0, 38.1, 31.9, 30.0, 29.3, 29.3, 28.7, 28.1, 26.0, 22.7, 14.2

GC-EI, MS (m/z, %): 229.2(M +,<10), 112.2 (25.1), 101.1 (45.4), 100.1 (33.5), 99.1 (100), 82.2 (10.1), 75.1 (39.0), 74.1 (81.0), 73.2 (12.9), 72.2 (16.9), 71.2 (100), 70.2 (37.1), 69.2 (30.4), 56.2 (55.0), 55.2 (62.4)

Chem. Name	Isoamyl 4-oxopentanoate (3e)
Reference	Yang and Tang (2019)

1   **2e**   **3e**
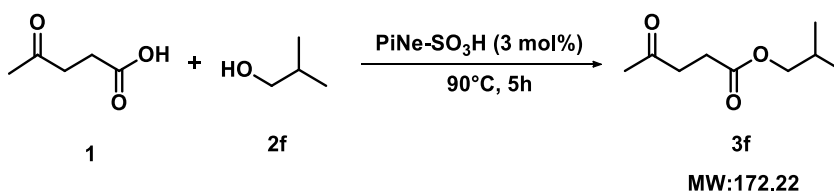**MW:186.25**

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), isoamyl alcohol (**2e**) (1 mmol, 88.15 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature with ethanol (0.5 mL) and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3e** as a pale-yellow oil, $82 \pm 0.8\%$ (152.5 mg).

Mol Formula	$C_{10}H_{18}O_3$			**m.p.**	oil
	δ value	**No. H**	**Mult.**	**j value/Hz**	
	4.09	2	*t*	6.88	
	2.74	2	*t*	6.51	
¹H-NMR	2.56	2	*t*	6.51	
400 MHz	2.19	3	*s*		
CDCl₃	1.72-1.62	1	*m*		
	1.51	2	*q*	6.90	
	0.91	6	*d*	6.58	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 173.0, 63.4, 38.0, 37.4, 38.0, 37.4, 30.0, 28.1, 25.1, 22.5

GC-EI, MS (m/z, %): 186.2 (M +,<10), 171.1 (10.1), 144.2 (24.5), 143.1 (11.2), 117.1 (71.6), 101.1 (31.7), 100.1 (32.2), 99.1 (100), 74.1 (21.9), 73.1 (11.3), 72.2 (31.3), 71.1 (100), 70.2 (100), 56.1 (32.3), 55.1 (98.2)

Chem. Name	Isobutyl 4-oxopentanoate (3f)
Reference	Zhu et al. (2014)

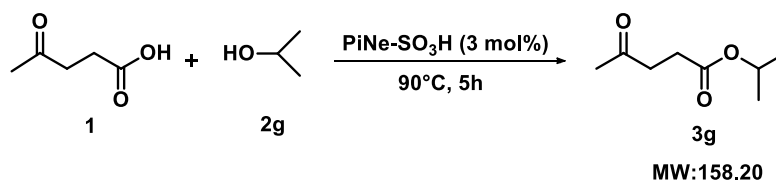**1**   **2f**   **3f**
MW:172.22

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), isobutyl alcohol (**2f**) (1 mmol, 74.12 mg), PiNe-SO₃H (3 mol%, 36.8 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (400 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3f** as a pale-yellow oil, 83 ± 0.8% (142 mg).

Mol Formula	$C_9H_{16}O_3$			m.p.	oil
	δ value	No. H	Mult.	j value/Hz	
	3.85	2	*d*	6.64	
¹H-NMR	2.74	2	*t*	6.42	
400 MHz	2.58	2	*t*	6.61	
CDCl₃	1.91	1	*m*		
	0.91	6	*d*	6.66	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.8, 172.9, 70.9, 38.1, 30.0, 28.1, 27.8, 19.2

GC-EI, MS (m/z, %): 172.2 (M +,<10), 130.2 (18.2), 117.1 (78.5), 101.1 (50.6), 100.1 (35.2), 99 (100), 75.1 (14.9), 74.2 (78.2), 73.2 (19.0), 72.2 (11.5), 71.2 (53.2), 58.2 (12.7), 56.2 (79.4), 55.2 (26.0)
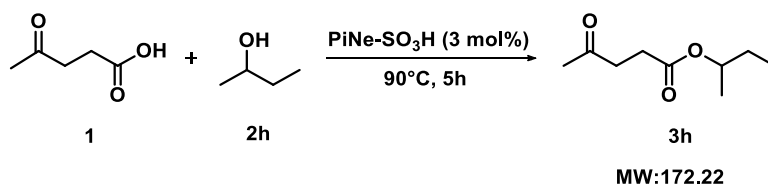
Chem. Name	Isopropyl 4-oxopentanoate (3g)
Reference	Trombettoni et al. (2018)

3g
MW:158.20

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), isopropanol (**2g**) (1 mmol, 60.01 mg), PiNe-SO₃H (3 mol%, 36.8 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (400 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3g** as a pale-yellow oil, 46 ± 1% (72.5 mg).

Mol Formula	$C_8H_{14}O_3$			m.p.	oil
	δ value	No. H	Mult.	j value/Hz	
¹H-NMR **400 MHz** **CDCl₃**	5.02-4.93	1	*m*	6.26	
	2.72	2	*t*	6.58	
	2.52	2	*t*	6.63	
	2.18	3	*s*		
	1.21	6	*d*	6.29	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.9, 172.4, 68.1, 38.1, 30.0, 28.5, 21.9

GC-EIMS (m/z, %): 158 (M +,<10), 143.1 (24.5), 130.2 (13.9), 116.2 (110.7), 101 (67.5), 100.2 (25.3), 99.1 (100), 75.2 (16.0), 74.2 (100), 73.2 (32.2), 72.2 (16.3), 71.2 (43.1), 61.2 (13.6), 59.2 (11.9), 57.2 (13.9), 56.2 (46.6)

Chem. Name	*Sec*-butyl 4-oxopentanoate (3h)
Reference	Trombettoni et al. (2018)

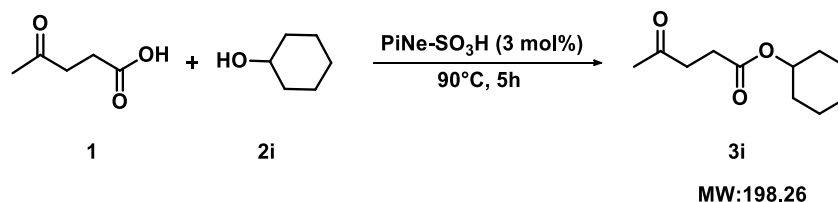**1**   **2h**   **3h**

MW:172.22

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), *sec*-butyl alcohol (**2h**) (1 mmol, 74.12 mg), PiNe-SO₃H (3 mol%, 36.8 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (400 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3h** as a pale-yellow oil, 47 ± 0.7% (81 mg).

Mol Formula	$C_9H_{16}O_3$			m.p.	oil
	δ value	**No. H**	**Mult.**	**j value/Hz**	
	4.86-4.78	1	*m*		
	2.73	2	*t*	6.59	
¹H-NMR	2.54	2	*t*	6.63	
400 MHz	2.18	3	*s*		
CDCl₃	1.63-1.46	2	*m*		
	1.18	3	*d*	6.29	
	0.88	3	*t*	7.46	

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.9, 172.5, 72.7, 38.2, 30.0, 28.9, 28.5, 19.5, 9.8

GC-EI, MS (m/z, %): 172.1 (M +,<10), 117.1 (69.1), 116.2 (16.4), 101.1 (52.6), 100.1 (33.8), 99.1 (100), 74.1 (71.1), 73.2 (38.9), 72.2 (18.9), 71.2 (49.7), 61.1 (11.5), 57.2 (80.8), 56.2 (82.2), 55.32 (26.9)

Chem. Name	Cyclohexyl 4-oxopentanoate (3i)
Reference	Jia et al. (2020)

1   **2i**   PiNe-SO₃H (3 mol%) 90°C, 5h   **3i**
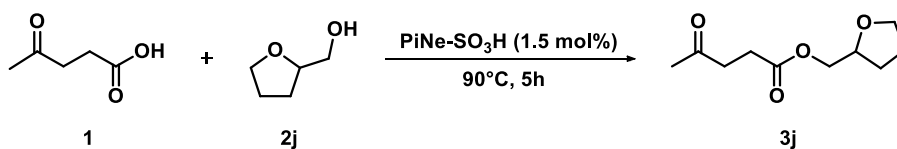
MW:198.26

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), cyclohexanol (**2i**) (1 mmol, 100.16 mg), PiNe-SO₃H (3 mol%, 36.8 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (400 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3l** as a pale-yellow oil, 59 ± 0.5% (117 mg).

Mol Formula	$C_{11}H_{18}O_3$				m.p.	oil
	δ value	**No. H**	**Mult.**	**j value/Hz**		
	4.77-4.70	1	*m*			
	2.73	2	*t*	6.56		
	2.55	2	*t*	6.56		
¹H-NMR **400 MHz** **CDCl₃**	2.18	3	*s*			
	1.83-1.81	2	*m*			
	1.72-1.69	2	*m*			
	1.54-1.51	1	*m*			
	1.44-1.32	4	*m*			
	1.30-1.23	1	*m*			

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.9, 172.3, 73.1, 38.2, 31.7, 30.0, 28.6, 25.5, 23.8

GC-EI, MS (m/z, %): 198.2 (M +,<10), 117.1 (62.8), 101.1 (17.1), 100.1 (22.1), 99.1 (100), 83.2 (48.5), 82.2 (25.6), 81.1 (14.8), 74.1 (13.6), 71.1 (29.7), 67.1 (40.0), 56.1 (38.7), 55.1 (75.7), 54.2 (15.9)

Chem. Name	(tetrahydrofuran-2-yl)methyl 4-oxopentanoate (3j)
Reference	Trombettoni et al. (2018)

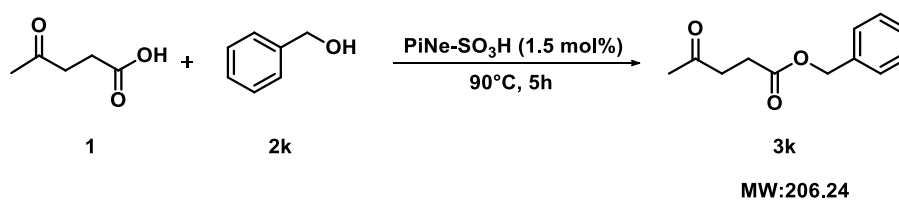**1**   **2j**   PiNe-SO₃H (1.5 mol%)   90°C, 5h   **3j**

MW:200.23

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), tetrahydrofurfuryl alcohol (**2j**) (1 mmol, 102.13 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL) and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3j** as a pale-yellow oil, 78 ± 0.6% (156 mg).

Mol Formula	$C_{10}H_{16}O_4$		m.p.		oil
	δ value	**No. H**	**Mult.**	**j value/Hz**	
	4.15-4.06	2	*m*		
	4.01-3.97	1	*m*		
	3.89-3.83	1	*m*		
¹H-NMR **400 MHz** **CDCl₃**	3.80-3.74	1	*m*		
	2.74	2	*t*	6.40	
	2.60	2	*t*	6.40	
	2.17	3	*s*		
	2.02-1.86	3	*m*		
	1.62-1.54	1	*m*		

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.7, 172.8, 76.6, 68.5, 66.7, 38.0, 29.9, 28.1, 28.0, 25.8

GC-EI, MS (m/z, %): 200.1 (M +,<10), 117.1 (12.7), 99.1 (73.6), 85.1 (19.0), 84.1 (86.2), 72.1 (17.7), 71.1 (100), 57.2 (10.6),56.1 (15.0), 55.1 (22.7)

Chem. Name	Benzyl 4-oxopentanoate (3k)
Reference	Badgujar and Bhanage (2015)

1   **2k**   PiNe-SO₃H (1.5 mol%), 90°C, 5h   **3k**   **MW:206.24**

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), benzyl alcohol (**2k**) (1 mmol, 108.14 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3k** as a pale-yellow oil, 91 ± 0.6% (188 mg).

Mol Formula	$C_{12}H_{14}O_3$				m.p.	oil
	δ value	**No. H**	**Mult.**	**j value/Hz**		
¹H-NMR **400 MHz** **CDCl₃**	7.38-7.30	5	*m*			
	5.12	2	*s*			
	2.77	2	*t*	6.57		
	2.63	2	*t*	6.57		
	2.18	3	*s*			

¹³C-NMR (100.6 MHz, CDCl₃) δ: 206.4, 172.7, 136.0, 128.7, 128.4, 128.3, 66.6, 38.0, 30.0, 28.1

GC-EI, MS (m/z, %): 206.1 (M +,<10), 108.1 (20.1), 107.1 (54.7), 99 (43.9), 77.1 (11.6), 65.1 (18.6)

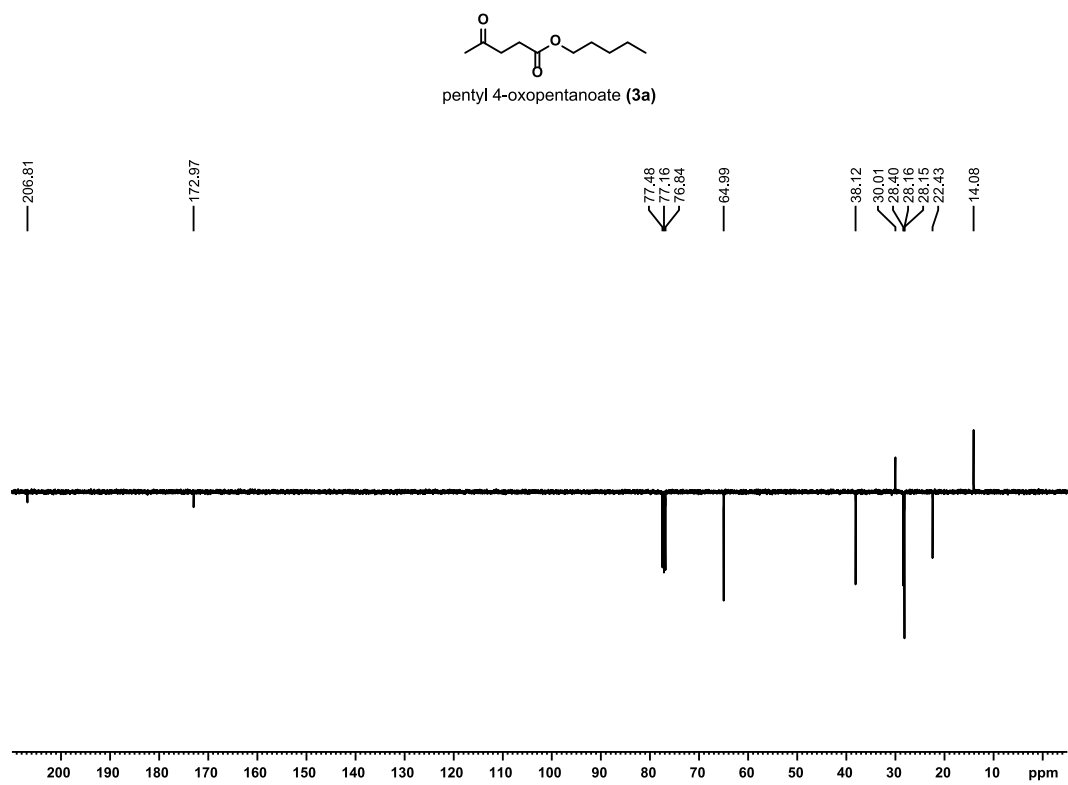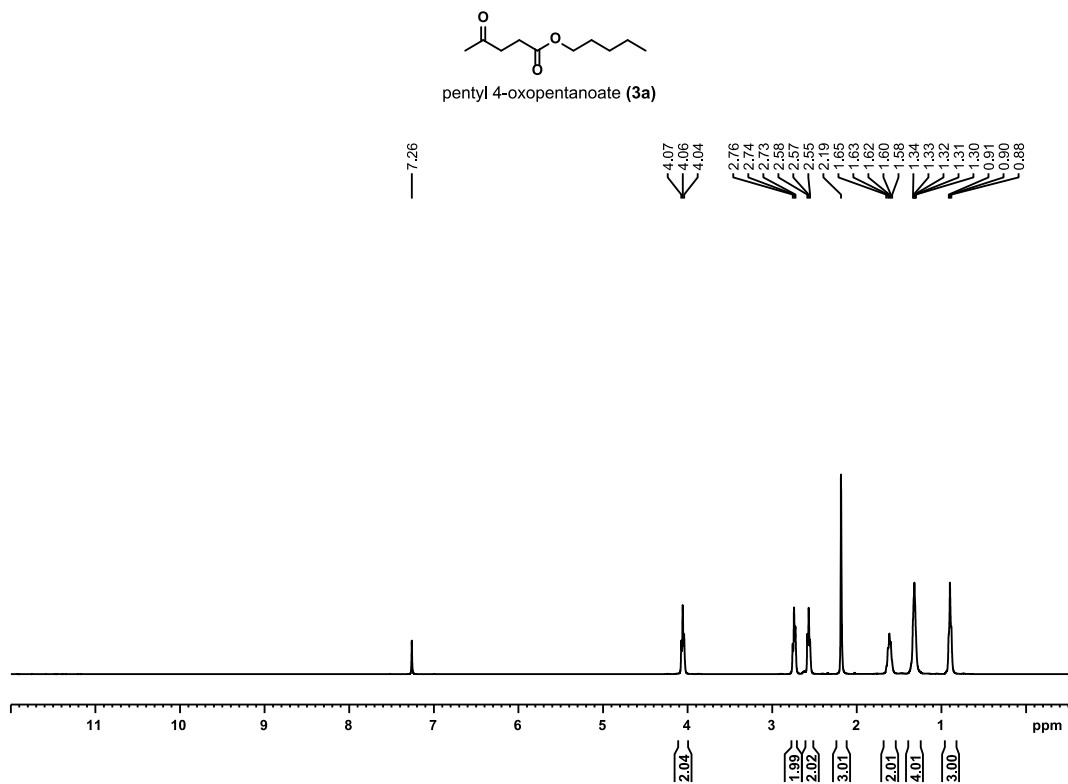| Chem. Name	5-hexenyl 4-oxopentanoate (3l)
Reference	This study
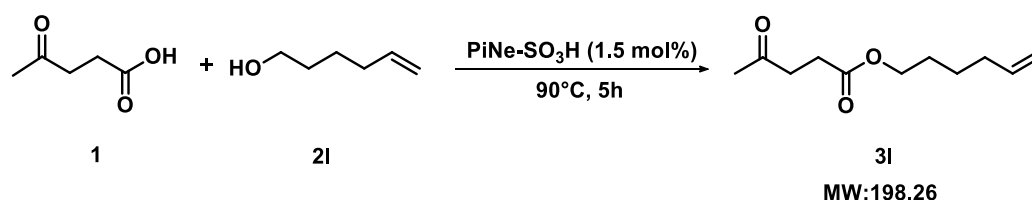
1 **2l** **3l**
MW:198.26

Method:

In a 2 mL screw-capped vial equipped with a magnetic stirrer, levulinic acid (**1**) (1 mmol, 116.11 mg), 5-hexen-1-ol (**2l**) (1 mmol, 100.16 mg), PiNe-SO₃H (1.5 mol%, 18.4 mg), were consecutively added and the resulting mixture was left under stirring at 90 °C for 5 h. The reaction mixture was left to cool to room temperature, diluted with ethanol (0.5 mL), and centrifuged (6500 rpm, 10', 5 °C) to recover the reaction crude. PiNe-SO₃H was subsequently washed with additional ethanol (2 × 0.5 mL; 6500 rpm, 10', 5 °C), and the combined organic layer was flushed through an Amberlyst® A-21 pad (80 mg). Finally, ethanol was recovered by distillation (88%) under reduced pressure (97 mBar, 50 °C) to afford the product **3l** as a pale-yellow oil, 89 ± 0.5% (176.5 mg).
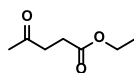
Mol Formula	$C_{11}H_{18}O_3$			m.p.	oil
	δ value	No. H	Mult.	j value/Hz	
¹H-NMR **400 MHz** **CDCl₃**	5.84-5.73	1	*ddt*	16.94; 10.27; 6.67	
	5.03-4.94	2	*m*		
	2.74	2	*t*	6.61	
	2.56	2	*t*	6.61	
	2.18	3	*s*		
	2.10-2.04	2	*m*		
	1.67-1.60	2	*m*		
	1.48-1.40	2	*m*		

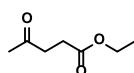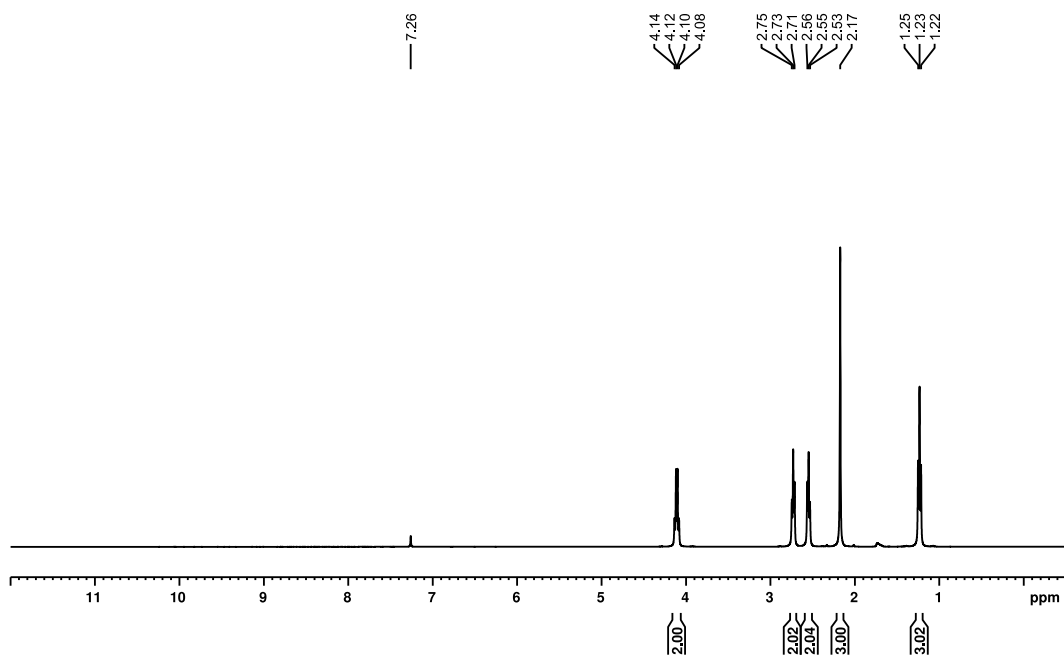**¹³C-NMR (100.6 MHz, CDCl₃) δ:** 206.7, 172.8, 138.4, 114.9, 64.6, 38.0, 33.3, 29.9, 28.0, 28.0, 25.2

GC-EI, MS (m/z, %): 197.2 (M +,<10), 101.1 (23.6), 100.1 (36.8), 99.1 (100), 98.9 (100), 83.2 (57.7), 82.2 (100), 81.2 (25.6), 74.1 (24.4), 71.1 (57.5), 67.1 (100), 56.1 (21.7), 55.2 (100), 54.2 (100), 53.2 (17.9)
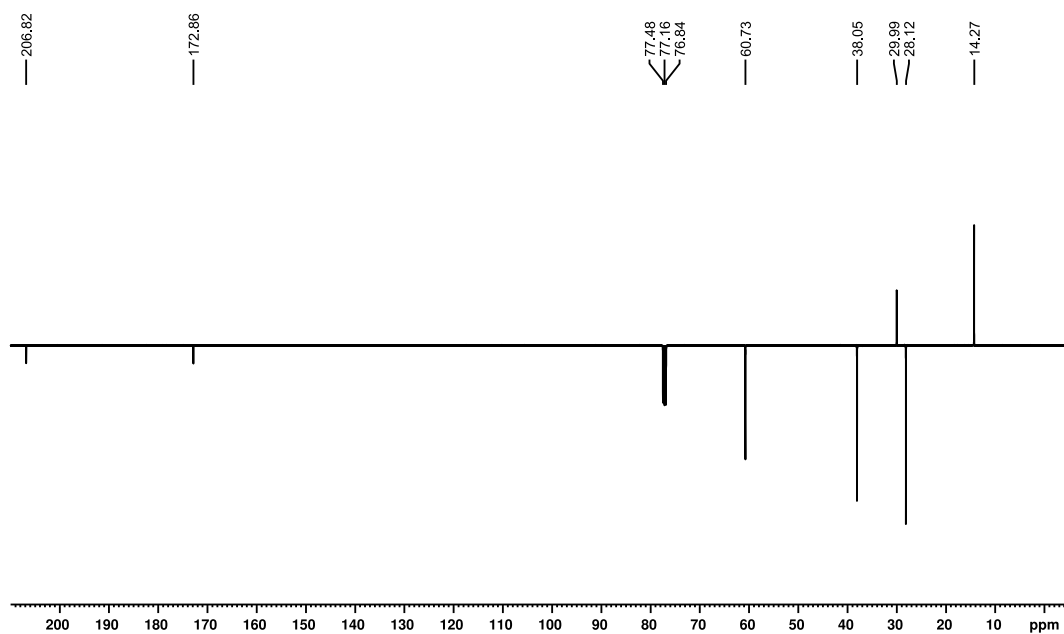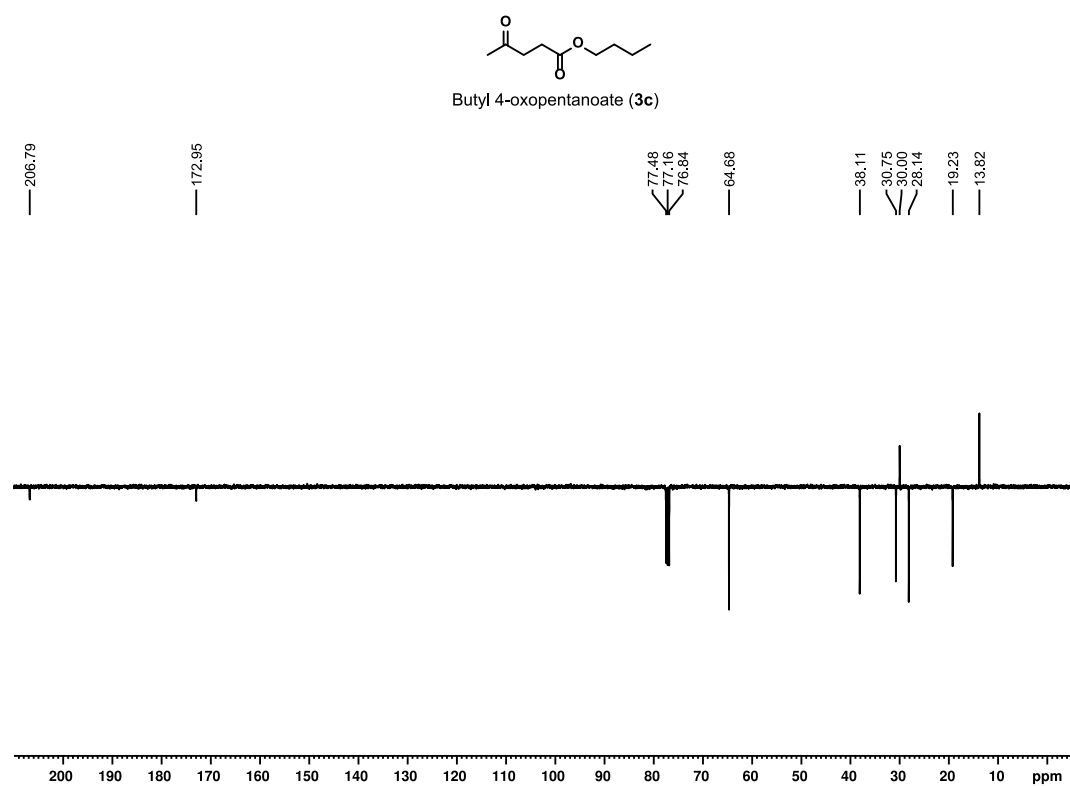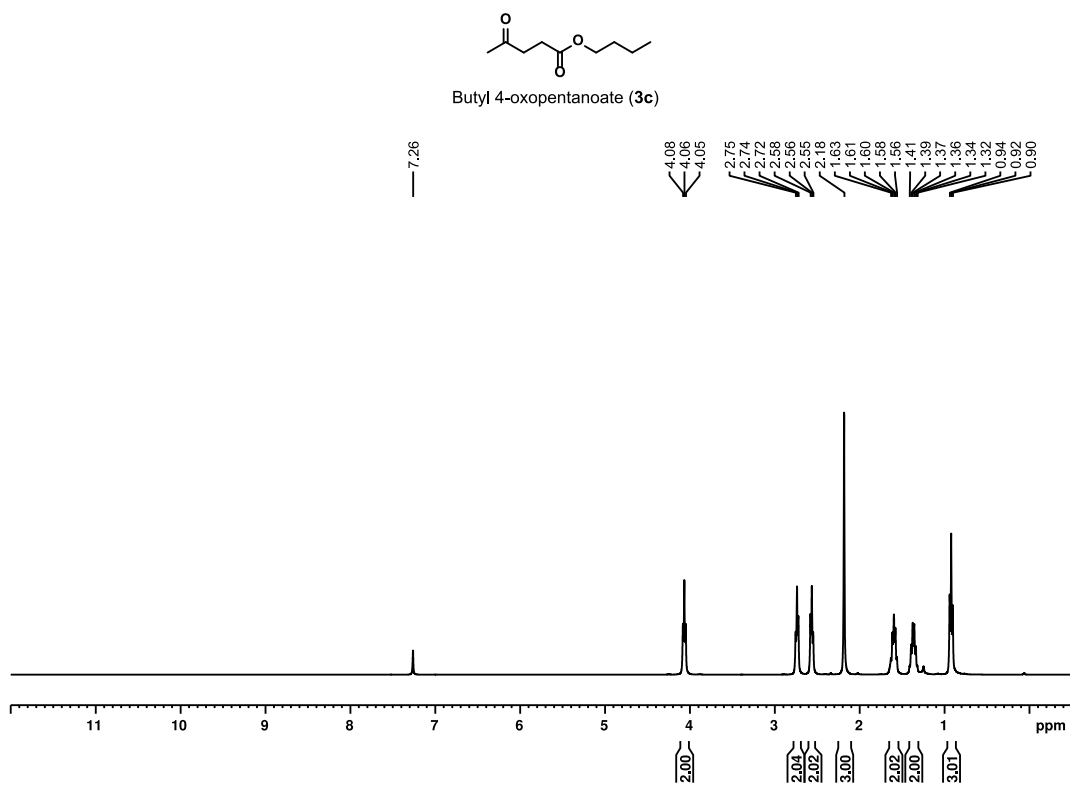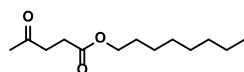
3. NMR spectra

pentyl 4-oxopentanoate **(3a)**

7.26

4.07
4.06
4.04

2.76
2.74
2.73
2.58
2.57
2.55
2.19
1.65
1.63
1.62
1.60
1.58
1.34
1.33
1.32
1.31
1.30
0.91
0.90
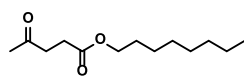0.88

| 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | ppm |

2.04

1.99
2.02

3.01

2.01
4.01

3.00

pentyl 4-oxopentanoate **(3a)**

206.81

172.97

77.48
77.16
76.84

64.99

38.12

30.01
28.40
28.16
28.15
22.43

14.08

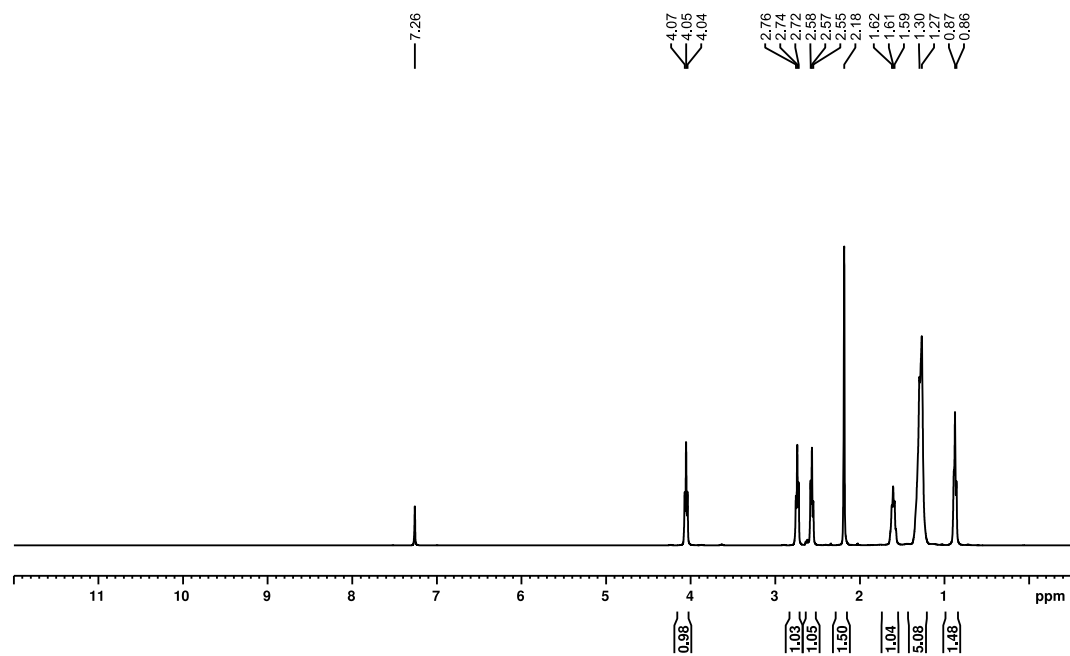| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | ppm |

Ethyl 4-oxopentanoate (**3b**)

7.26

4.14
4.12
4.10
4.08

2.75
2.73
2.71
2.56
2.55
2.53
2.17

1.25
1.23
1.22

11 10 9 8 7 6 5 4 3 2 1 ppm

2.00

2.02
2.04

3.00

3.02

Ethyl 4-oxopentanoate (**3b**)

206.82

172.86

77.48
77.16
76.84

60.73

38.05

29.99
28.12

14.27

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Butyl 4-oxopentanoate (**3c**)

7.26

4.08
4.06
4.05

2.75
2.74
2.72
2.58
2.56
2.55
2.18
1.63
1.61
1.60
1.58
1.56
1.41
1.39
1.37
1.36
1.34
1.32
0.94
0.92
0.90

2.00

2.04
2.02

3.00

2.02
2.00

3.01

Butyl 4-oxopentanoate (**3c**)

206.79

172.95

77.48
77.16
76.84

64.68

38.11

30.75
30.00
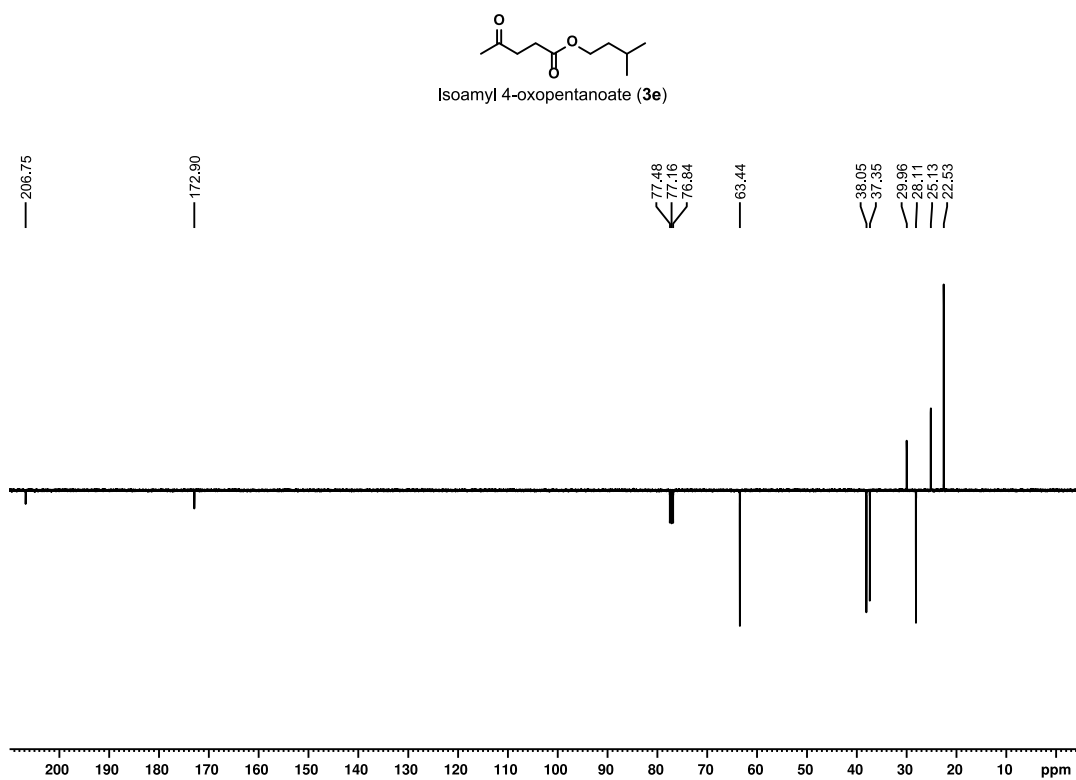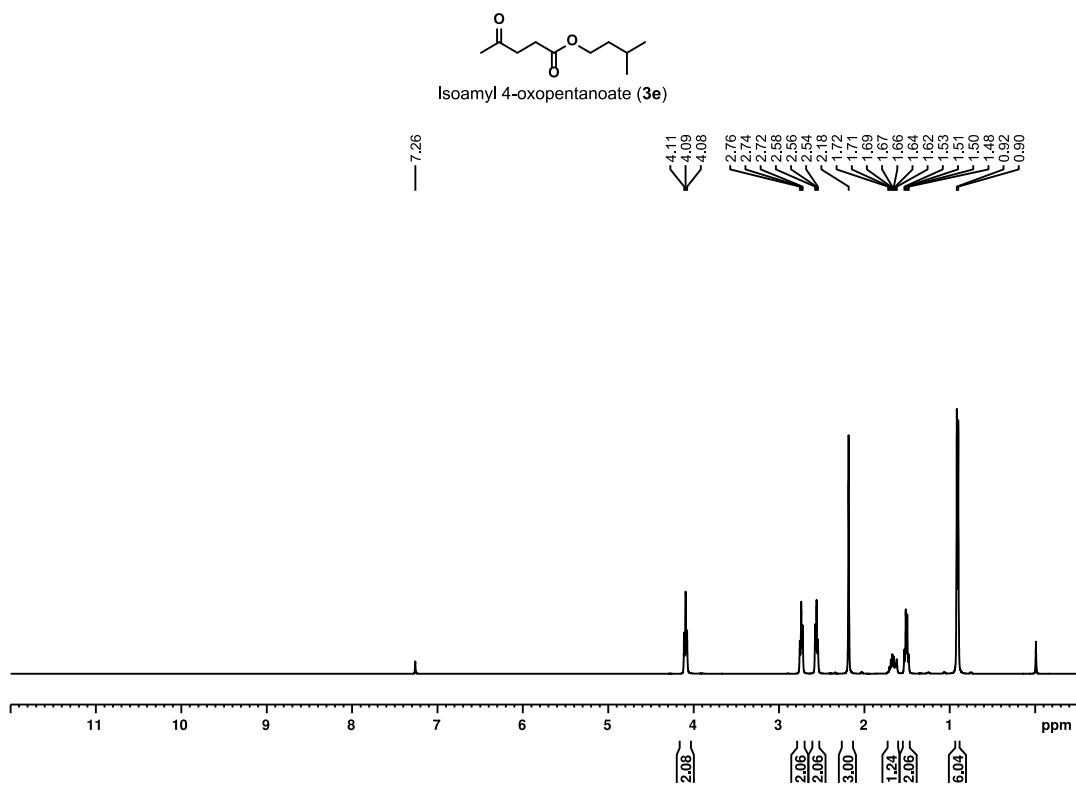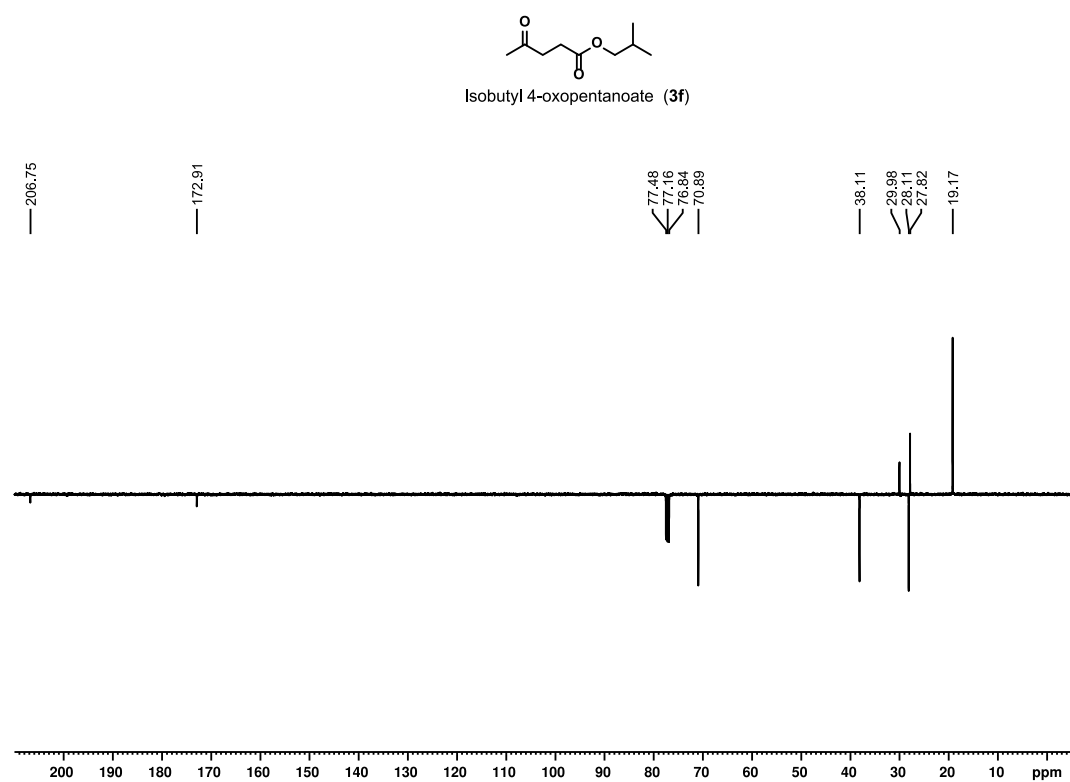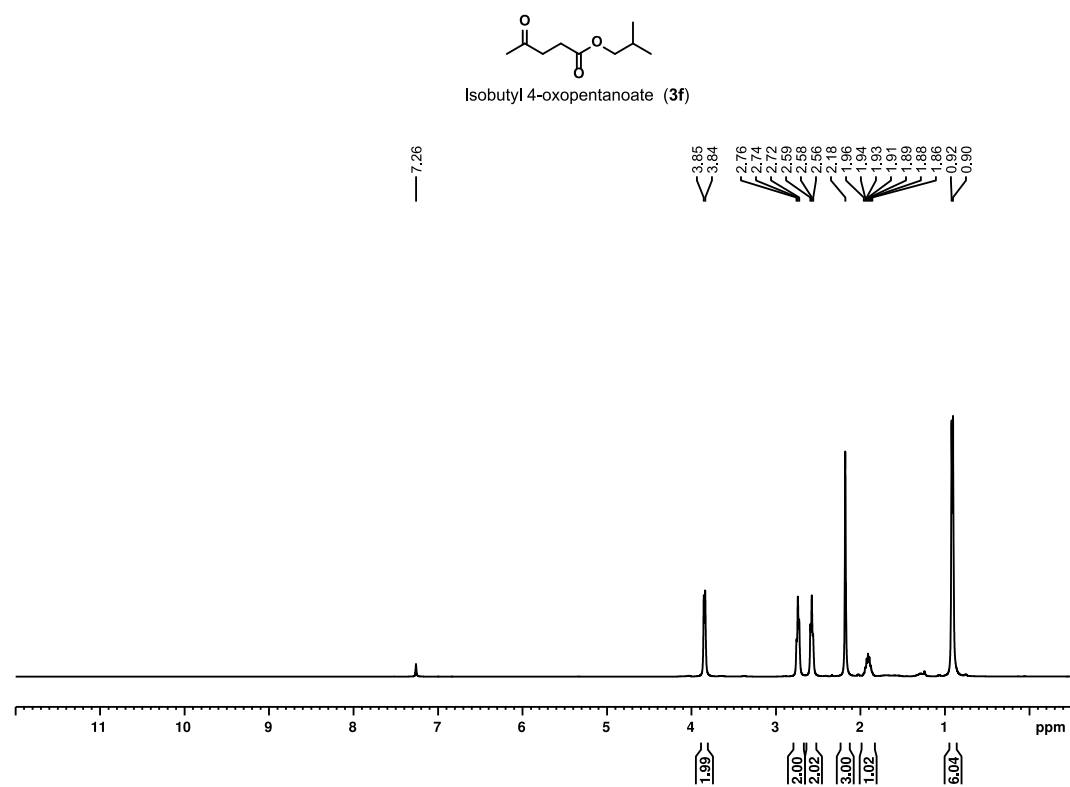28.14

19.23

13.82

Octyl 4-oxopentanoate (**3d**)

Octyl 4-oxopentanoate (**3d**)

Isoamyl 4-oxopentanoate (**3e**)

7.26 | 4.11 4.09 4.08 | 2.76 2.74 2.72 2.58 2.56 2.54 2.18 1.72 1.71 1.69 1.67 1.66 1.64 1.62 1.53 1.51 1.50 1.48 0.92 0.90

11 10 9 8 7 6 5 4 3 2 1 ppm

2.08 | 2.06 2.06 | 3.00 | 1.24 2.06 | 6.04

Isoamyl 4-oxopentanoate (**3e**)

206.75 | 172.90 | 77.48 77.16 76.84 | 63.44 | 38.05 37.35 | 29.96 28.11 25.13 22.53

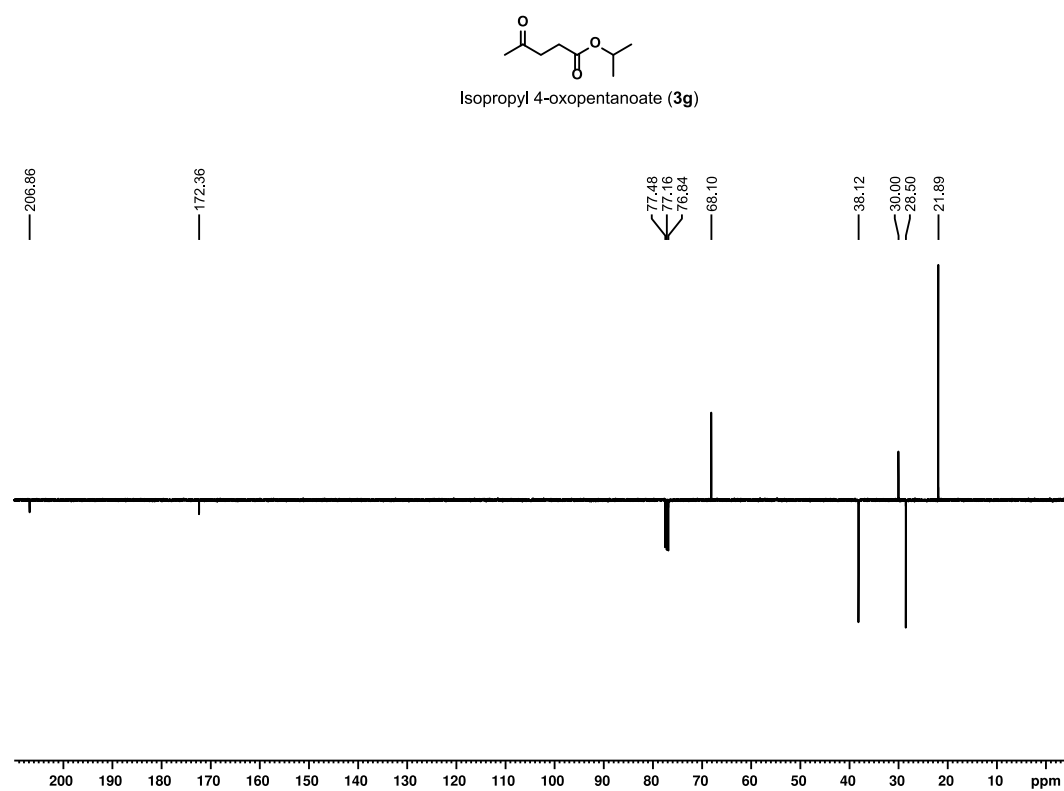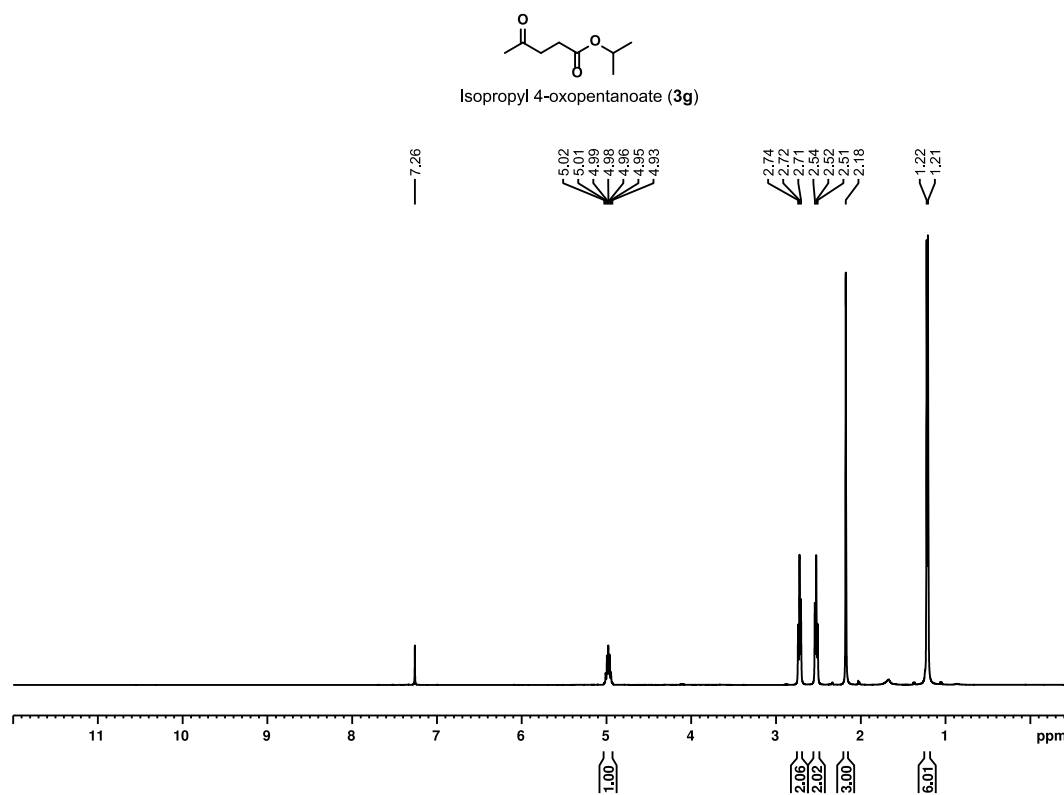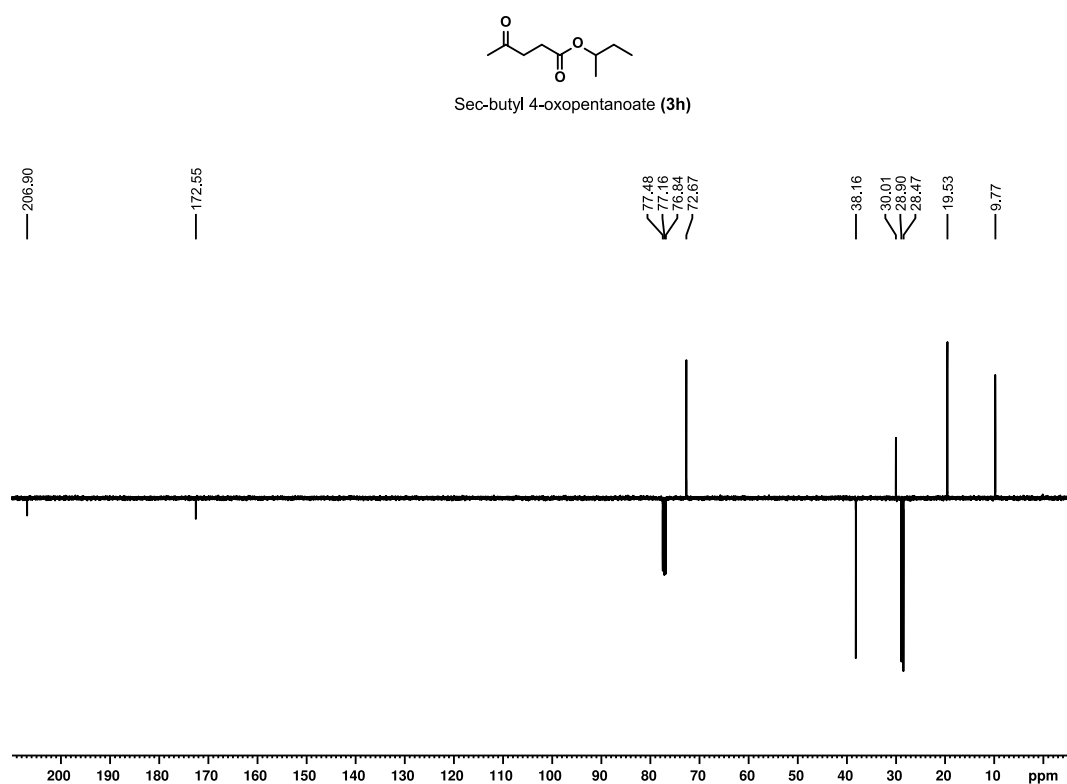200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Isobutyl 4-oxopentanoate (**3f**)

Isobutyl 4-oxopentanoate (**3f**)

Isopropyl 4-oxopentanoate (**3g**)

7.26

5.02
5.01
4.99
4.98
4.96
4.95
4.93

2.74
2.72
2.71
2.54
2.52
2.51
2.18

1.22
1.21

1.00

2.06
2.02
3.00
6.01

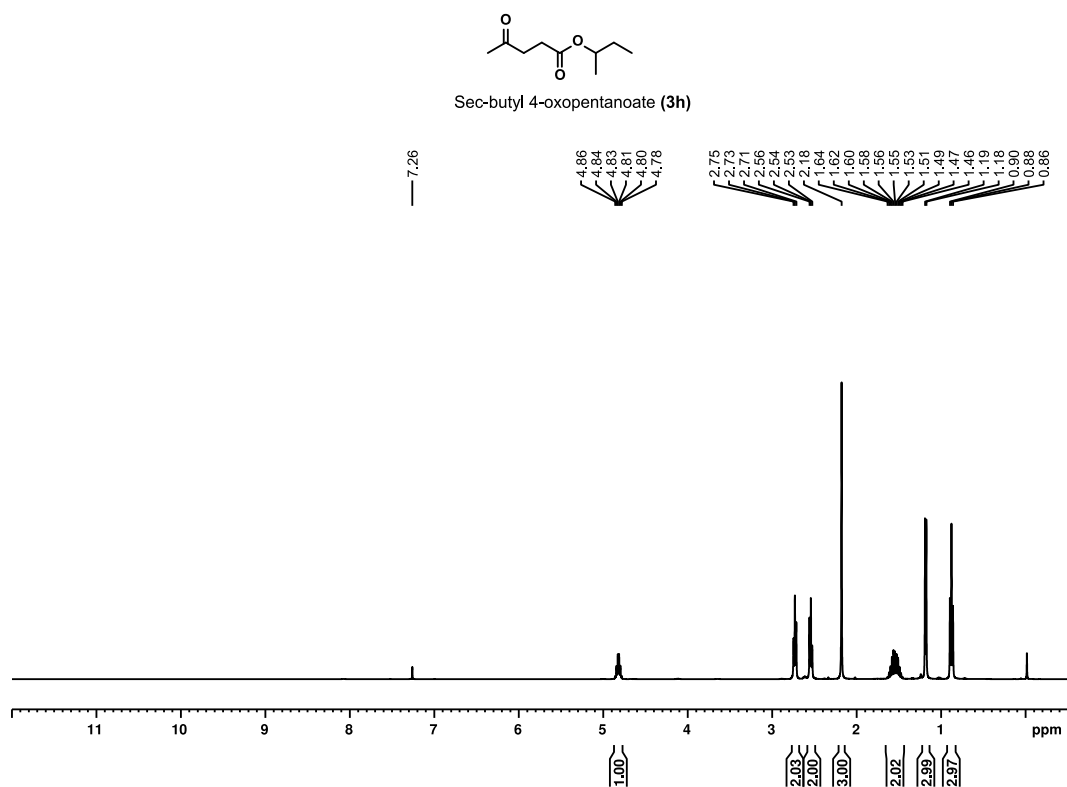Isopropyl 4-oxopentanoate (**3g**)

206.86

172.36

77.48
77.16
76.84
68.10

38.12

30.00
28.50
21.89

Sec-butyl 4-oxopentanoate **(3h)**

7.26

4.86
4.84
4.83
4.81
4.80
4.78

2.75
2.73
2.71
2.56
2.54
2.53
2.18
1.64
1.62
1.60
1.58
1.56
1.55
1.53
1.51
1.49
1.47
1.46
1.19
1.18
0.90
0.88
0.86

11 10 9 8 7 6 5 4 3 2 1 ppm

1.00   2.03 3.00   2.02 2.99 2.97
       2.00

Sec-butyl 4-oxopentanoate **(3h)**

206.90

172.55

77.48
77.16
76.84
72.67

38.16

30.01
28.90
28.47

19.53

9.77

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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Cyclohexyl 4-oxopentanoate (**3i**)

7.26

4.77
4.76
4.75
4.73
4.72
4.71
4.70
2.75
2.73
2.71
2.56
2.55
2.53
2.18
1.83
1.81
1.72
1.71
1.70
1.69
1.54
1.53
1.51
1.51
1.44
1.41
1.38
1.37
1.35
1.32
1.30
1.29

1.00

2.00
2.00

3.00

1.99
2.02
1.01
4.06
1.08

Cyclohexyl 4-oxopentanoate (**3i**)

206.92

172.30

77.48
77.16
76.84
73.08

38.18
31.69
30.04
28.56
25.49
23.85

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(tetrahydrofuran-2-yl)methyl 4-oxopentanoate (**3j**)

(tetrahydrofuran-2-yl)methyl 4-oxopentanoate (**3j**)

Benzyl 4-oxopentanoate (**3k**)

7.39
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.26

5.12

2.78
2.77
2.75
2.65
2.63
2.62
2.18

11 10 9 8 7 6 5 4 3 2 1 ppm

5.00

2.00

2.01
2.01
3.06

Benzyl 4-oxopentanoate (**3k**)

206.65

172.70

135.98
128.68
128.35
128.29

77.48
77.16
76.84

66.60

38.03

29.98
28.13

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
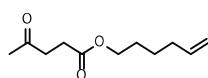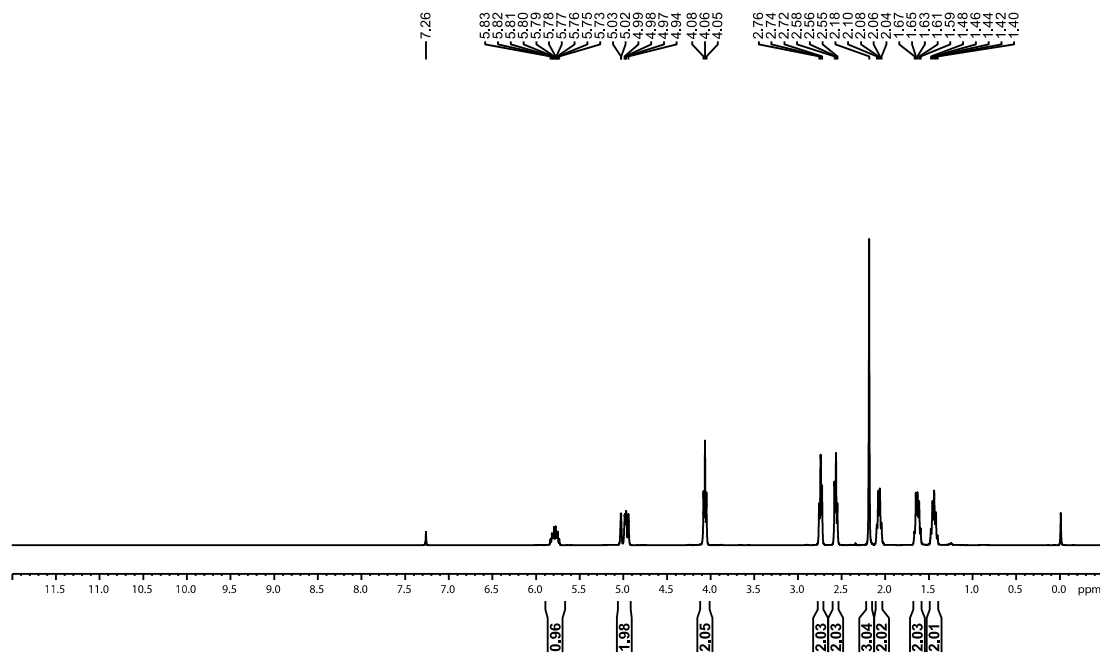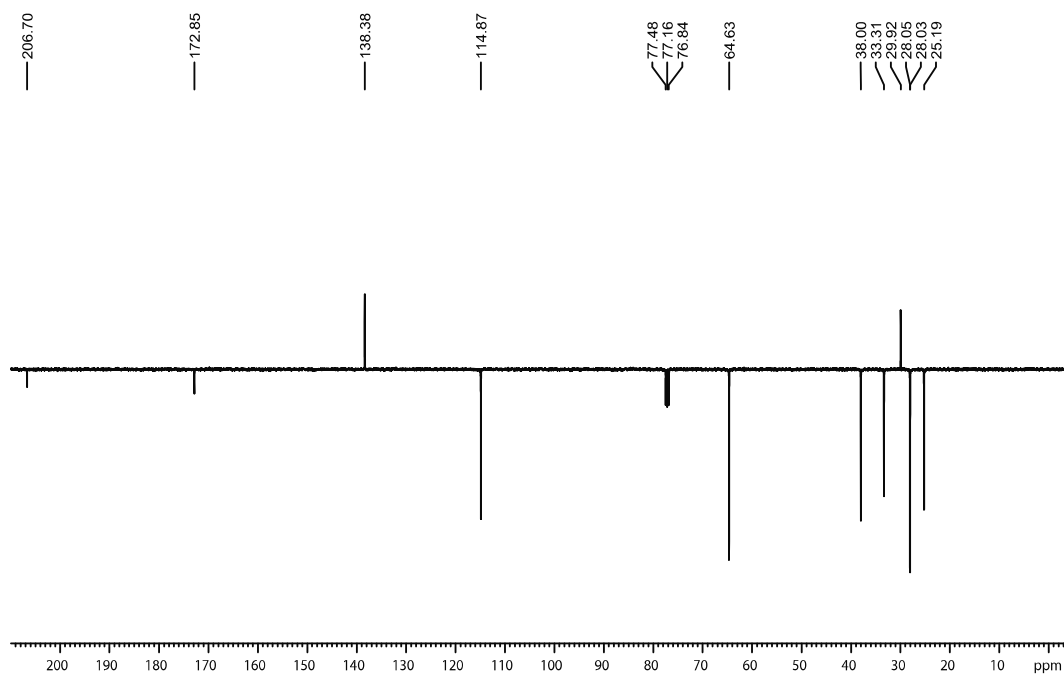
5-hexenyl 4-oxopentanoate (3**l**)

5-hexenyl 4-oxopentanoate (3**l**)

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