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# Chemoselectivity switch by mechanochemistry in the base-catalysed dione-acylation.

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## Table of Contents

**General experimental details** ..... 2
**General acylation procedure via ball-mill** ..... 2
**NMR and GC-MS spectra** ..... 3
**One-pot mechanochemical acylation (table 1)** ..... 7
**Mechanochemical acylation of in two-steps milling processes (table 2)** ..... 12
**Mechanochemical acylation of dimedone with various acids (table 3)** ..... 16
**Mechanochemical acylation of phenyl propanoic acid with various ketones (table 4)** 23
**Mechanically induced acylation of dimedone and 3-phenylpropanoic acid using scalable mills (table 5)** ..... 29
**Computational details** ..... 32
**Alternative paths for $TS_{3b}$** ..... 33
**Geometries** ..... 33
**References** ..... 45

**General experimental details**

All materials, unless otherwise stated, were purchased from commercial sources and utilised without further purification. Ball milling was performed using a home-made vortex mixer mixer[1] equipped with stainless steel 3/16-inch diameter under room thermal conditions and air. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometers at the Technion NMR facilities. Mass spectroscopy data were recorded in $CHCl_3$ medium using Bruker EVOQ SCION 456-GC equipped with an DB5 capillary column (VF-5ms, 30m 0.25mm 0.25µm) and a Bruker EVOQ triple quadrupole detector.

**General acylation procedure via ball-mill**

Diketone (1.0 equiv), acetic acid precursor (1.0 equiv), DCC (1.0 equiv), and catalytic base (0.1 equiv) were added to the 50 mL stainless steel milling jar containing 25 stainless steel 3/16-inch diameter griding balls. The mixture was grinded for 1 h at 1470 rpm (24.5 Hz). A small quantity of the final ground mixture was anaylsed by $^{1}H$ NMR without any purification.

**Acylation of dimedone with phenyl propanoic acid via ball-milling**

Dimedone (0.186 g, 1.0 equiv), phenyl propanoic acid (0.200 g, 1.0 equiv), DCC (0.274 g, 1.0 equiv), and DMAP (0.016 g, 0.1 equiv) were added to the 50 mL stainless steel milling jar containing 25 stainless steel 3/16-inch diameter griding balls. The mixture was grinded for 1 h at 1470 rpm (24.5 Hz). The final mixture was diluted in $CDCl_3$ and analysed by $^{1}H$ NMR without any purification. Prior to GC-MS injection, the solution was filtered to remove all solids.

**3-hydroxy-5,5-dimethyl-2-(3-phenylpropanoyl)cyclohex-2-en-1-one (*C*-acylation product 1):**

$^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm): 7.34 – 7.13 (m, 5H), 3.28 – 3.21 (m, 2H), 2.87 – 2.81 (m, 2H), 2.50 (s, 2H), 2.44 (s, 2H), 0.98 (s, 1H).$^{13}C$ NMR (101 MHz, DMSO-$d_6$) $\delta$ (ppm): 203.5, 195.8, 141.1, 128.3, 125.9, 111.9, 48.9, 42.0, 40.2, 33.4, 30.4, 29.9, 27.6, 25.3, 24.5.

**5,5-dimethyl-3-oxocyclohex-1-en-1-yl 3-phenylpropanoate (*O*-acylated product 2):**

$^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm): 7.40 – 7.10 (m, 5H), 5.74 (s, 1H), 2.99 – 2.78 (m, 4H), 2.34 (s, 2H), 2.21 (s, 2H), 0.99 (d, $J$ = 9.0 Hz, 6H). $^{13}C$ NMR (101 MHz, DMSO-$d_6$) $\delta$ (ppm): 199.1, 170.0, 168.9, 140.4, 128.9, 128.8, 126.7, 116.2, 50.6, 41.7, 35.6, 33.3, 30.4, 27.9.

## General product purification

If full conversion is reached (any milling procedure), the product can be isolated by dissolution in $CHCl_3$, which dissolved the product only while leaving behind the base, salt and urea by-products. A soxhlet was used in larger scale reactions.

## NMR and GC-MS spectra

$$\text{Conversion \%} = \frac{\sum \frac{Int(product\ peak)}{num\ of\ integrated\ protons}}{\frac{Int(reactant\ residues)}{num\ of\ integrated\ protons} + \sum \frac{Int(product)}{num\ of\ integrated\ protons}}$$

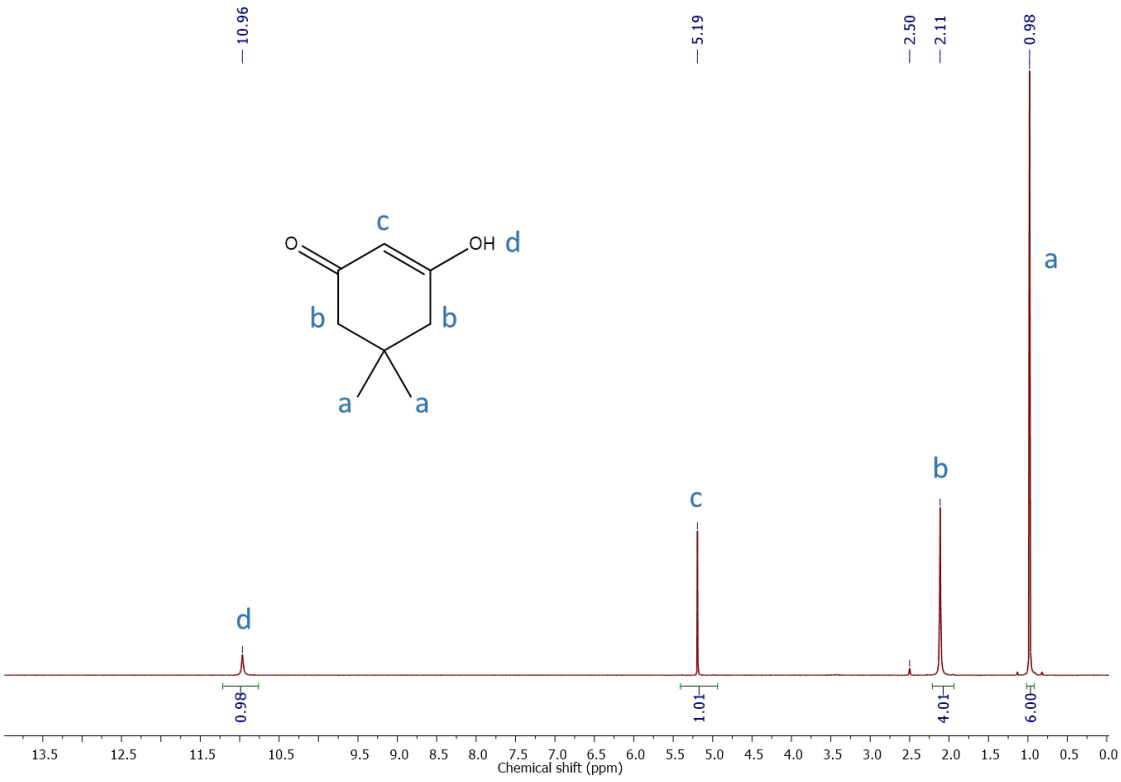



**Figure S1.** $^1$H NMR (400 MHz, DMSO-$d_6$) of dimedone.

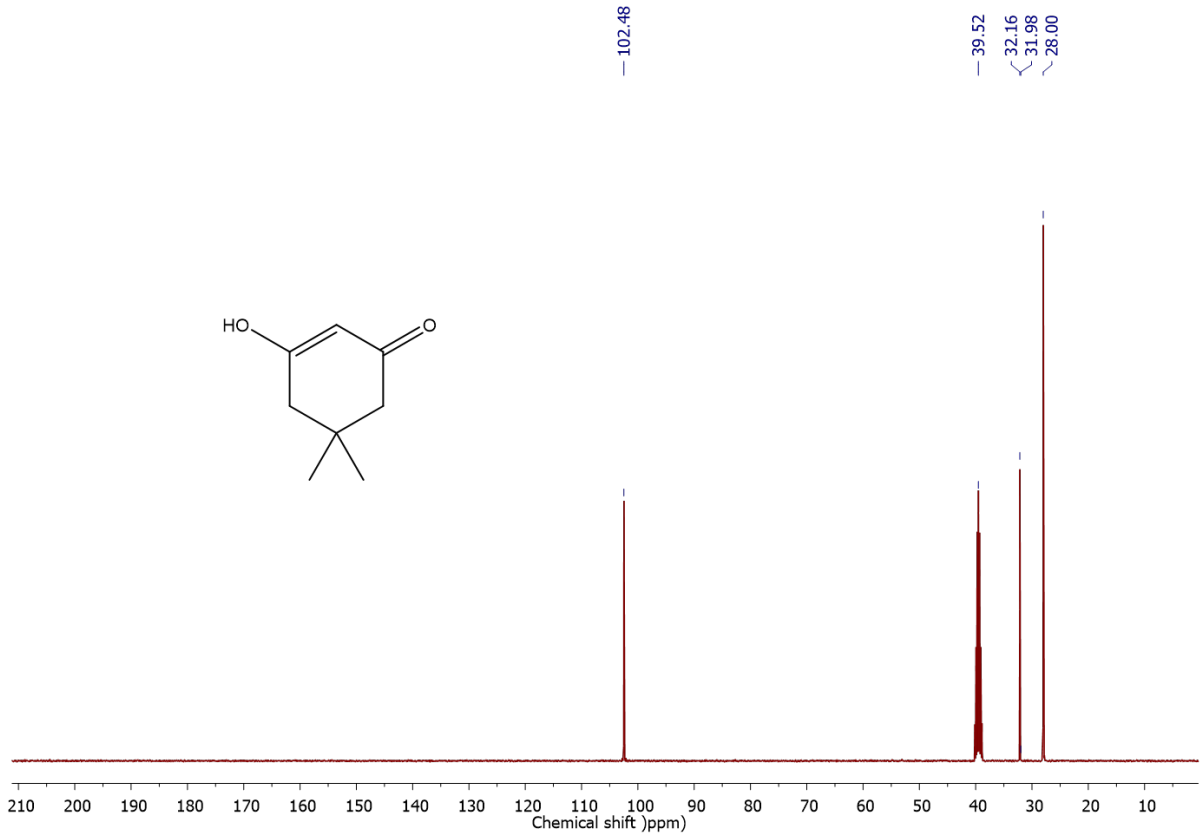



**Figure S2.** $^{13}C$ NMR (400 MHz, DMSO-$d_6$) of dimedone.

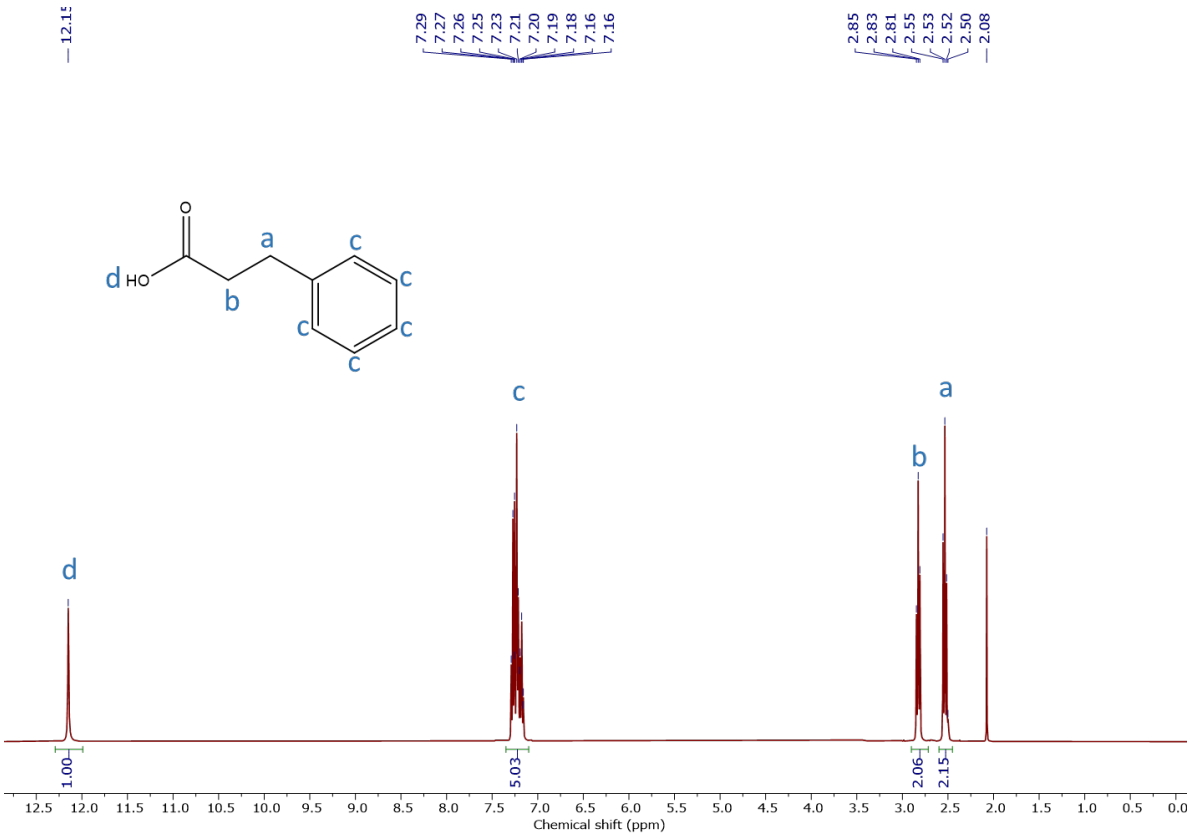



**Figure S3.** $^{1}H$ NMR (400 MHz, DMSO-$d_6$) of phenyl propanoic acid.

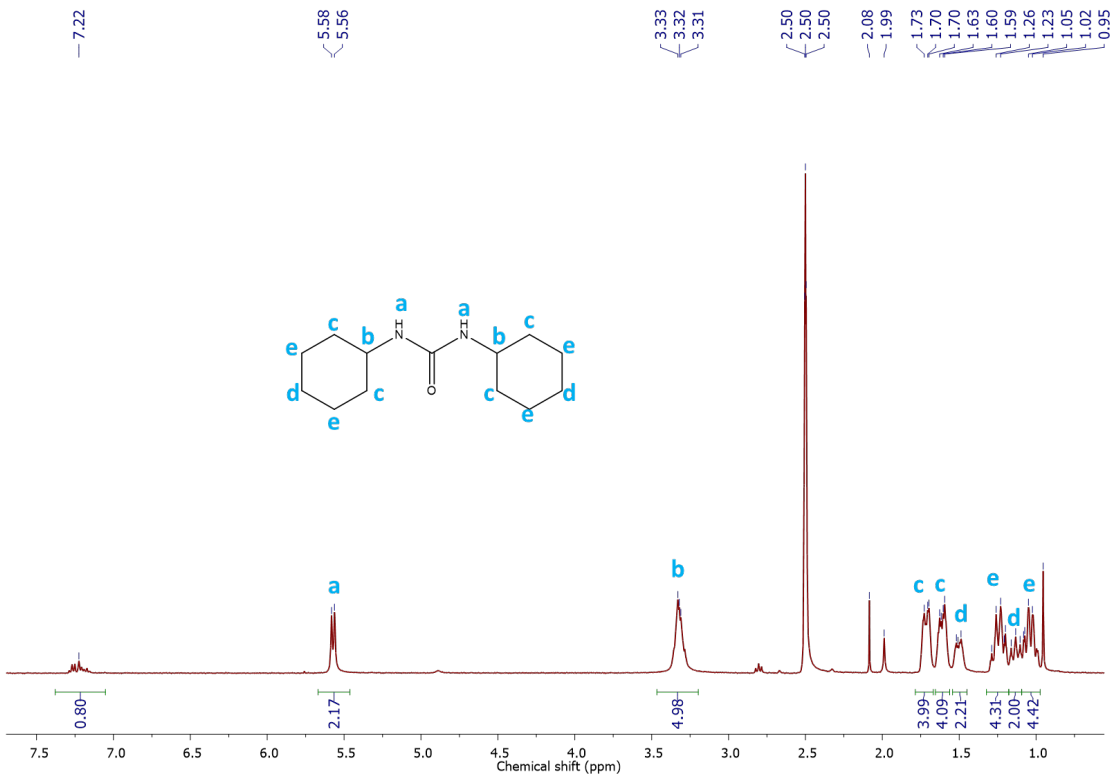



**Figure S4.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of 1,3-dicyclohexylurea precipitated at the end of each acylation reaction.

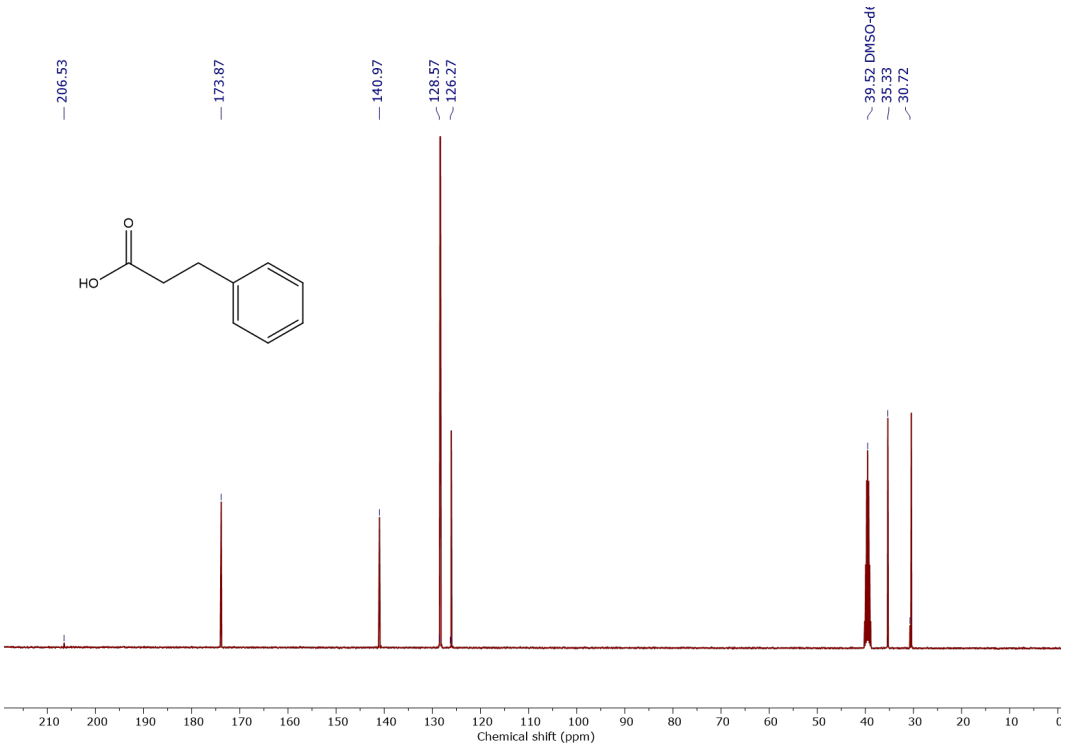



**Figure S5.** $^{13}$C NMR (101 MHz, DMSO-$d_6$) of phenyl propanoic acid.

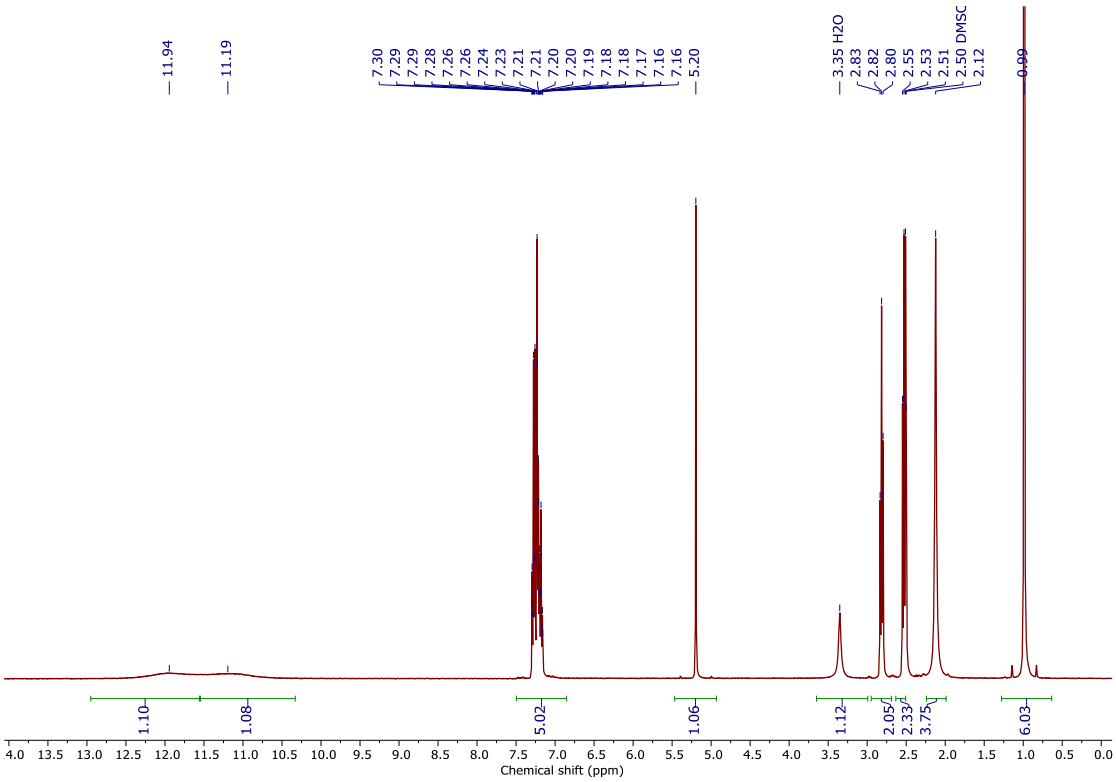



**Figure S6.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h without base nor DCC.

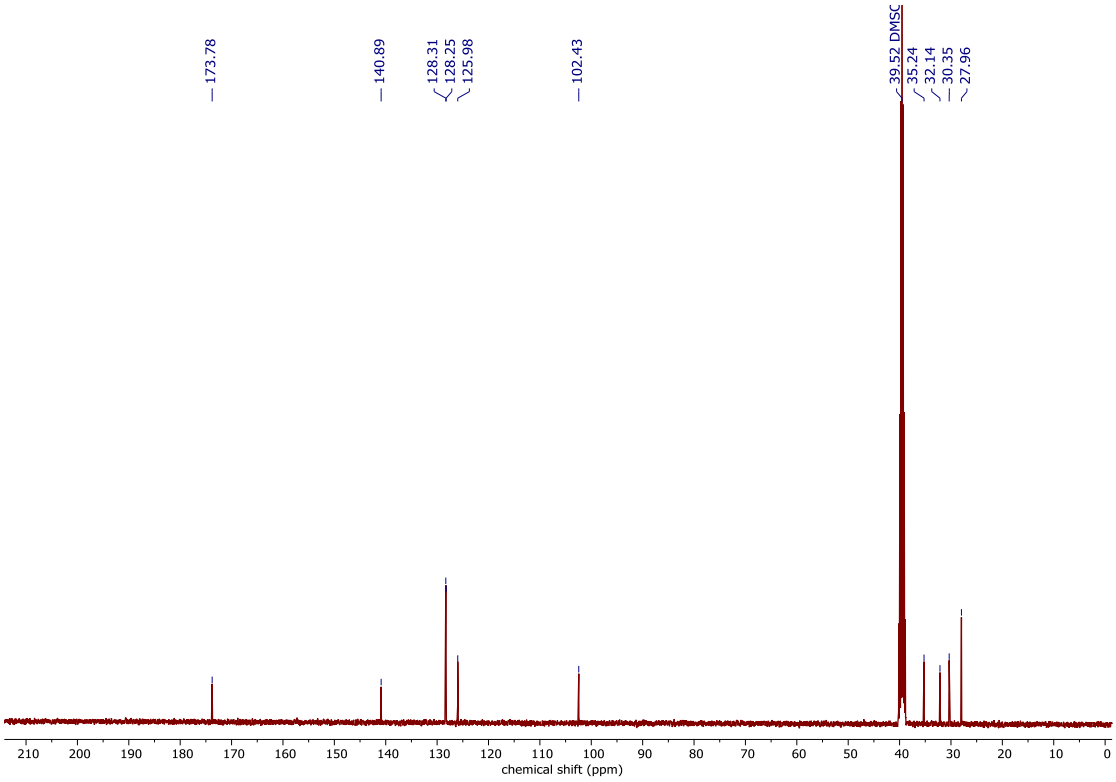



**Figure S7.** $^{13}$C NMR (101 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h without base nor DCC.

## One-pot mechanochemical acylation (table 1)

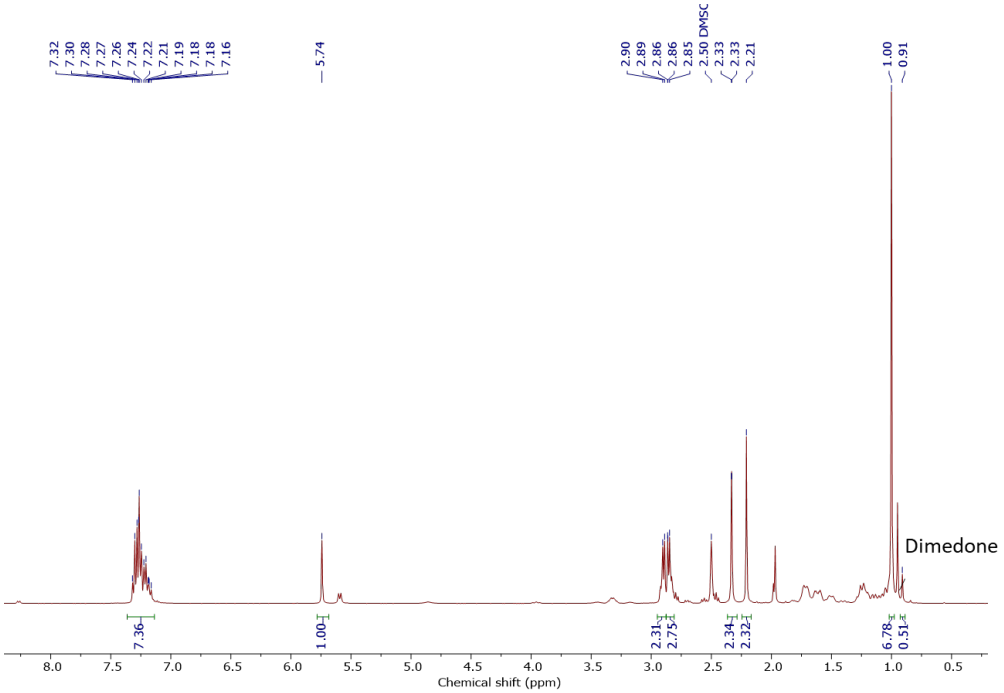



**Figure S8.** $^1$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% $K_2CO_3$.

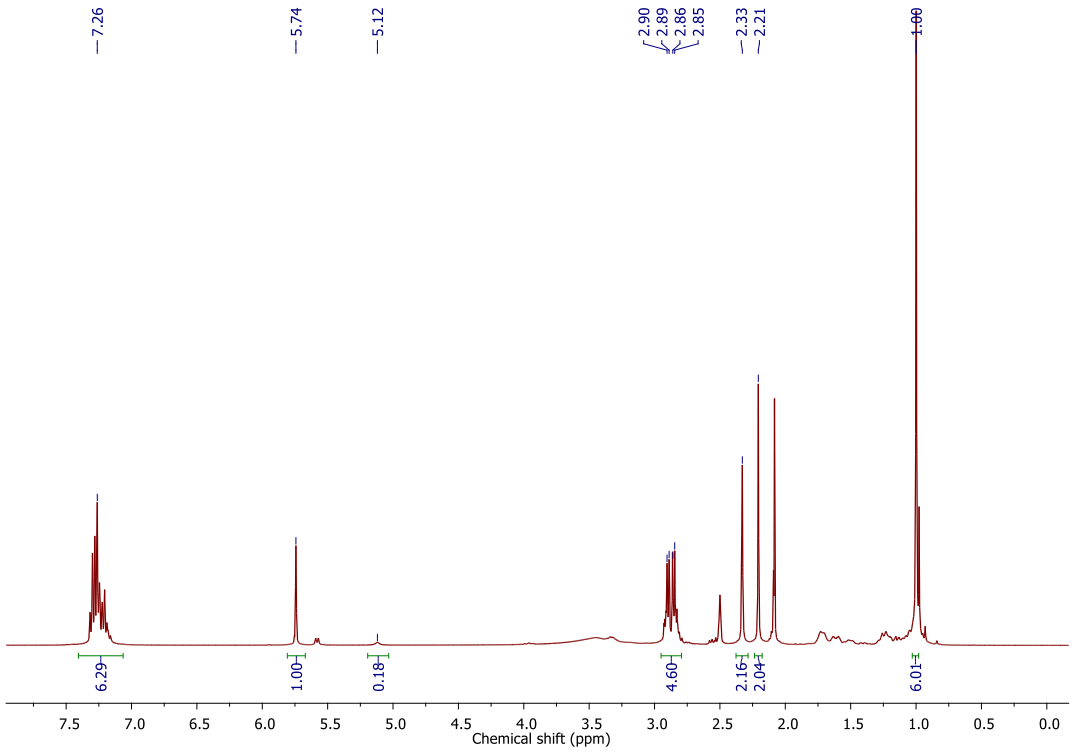



**Figure S9.** $^1$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% NaOH.

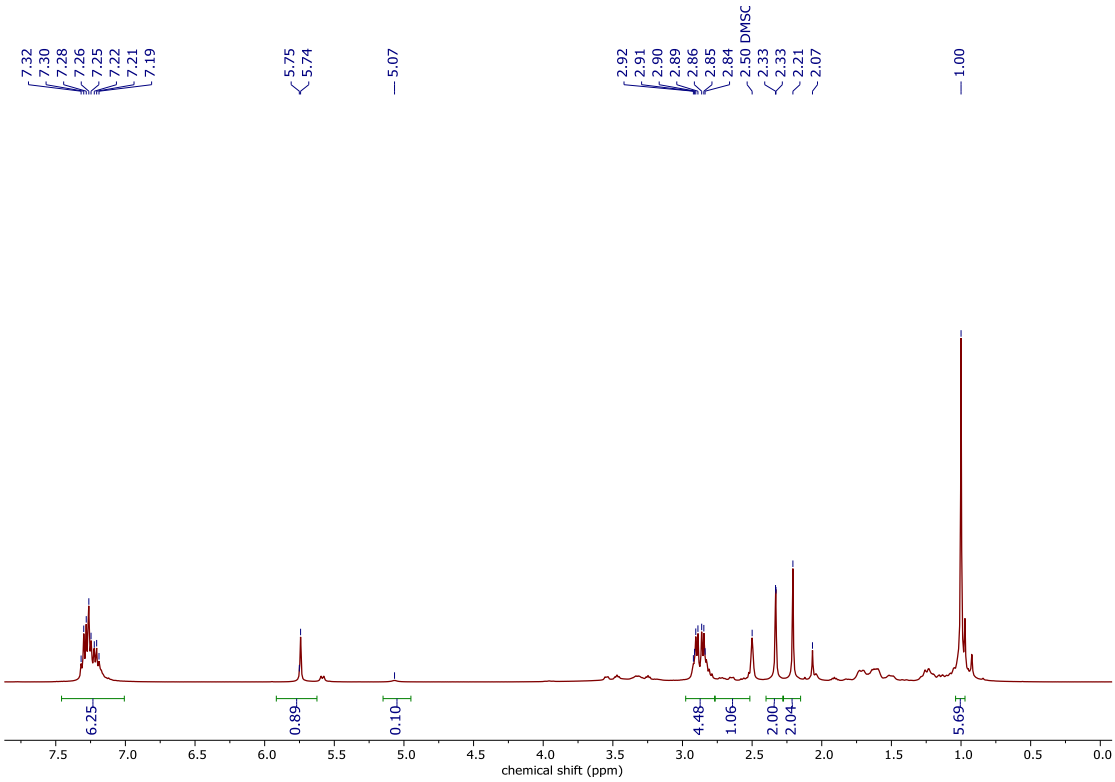



**Figure S10.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% DBU.

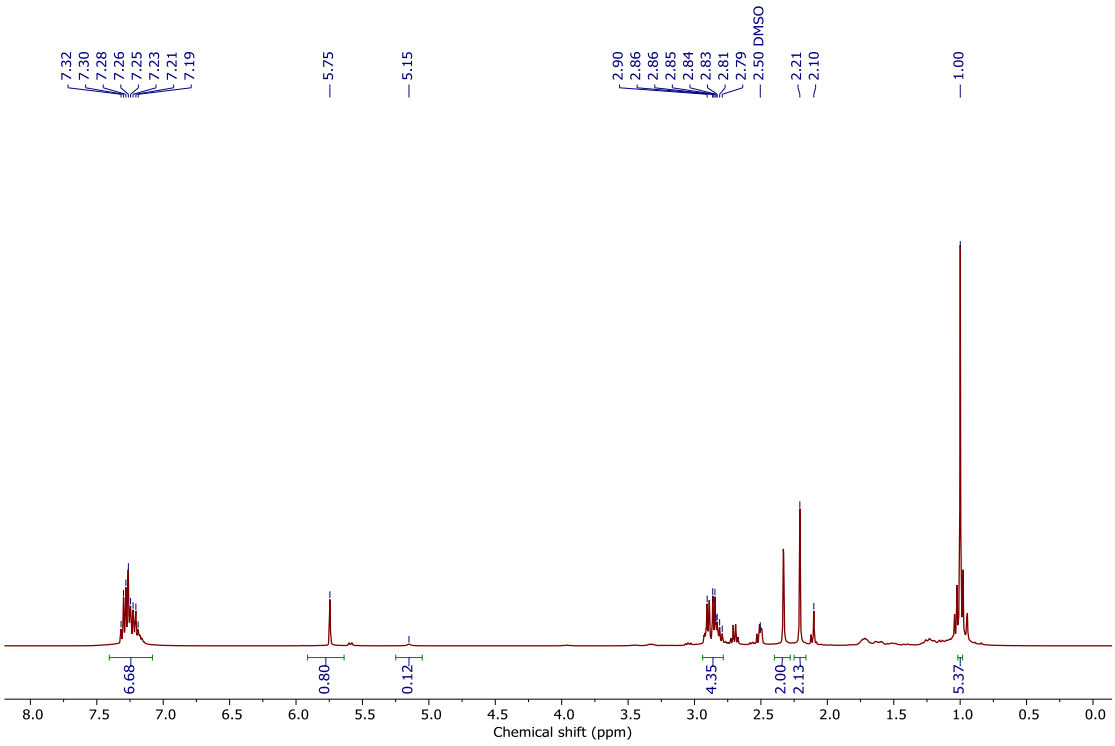



**Figure S11.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% $Et_3N$.

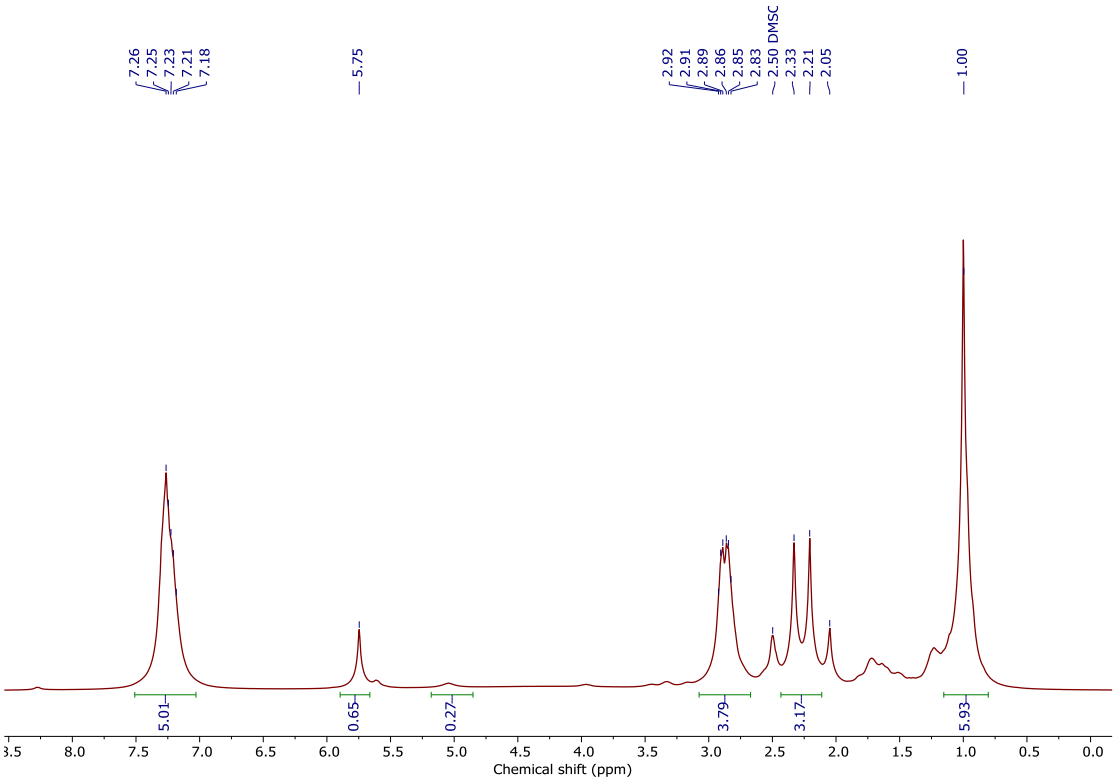



**Figure S12.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% KOtBu.

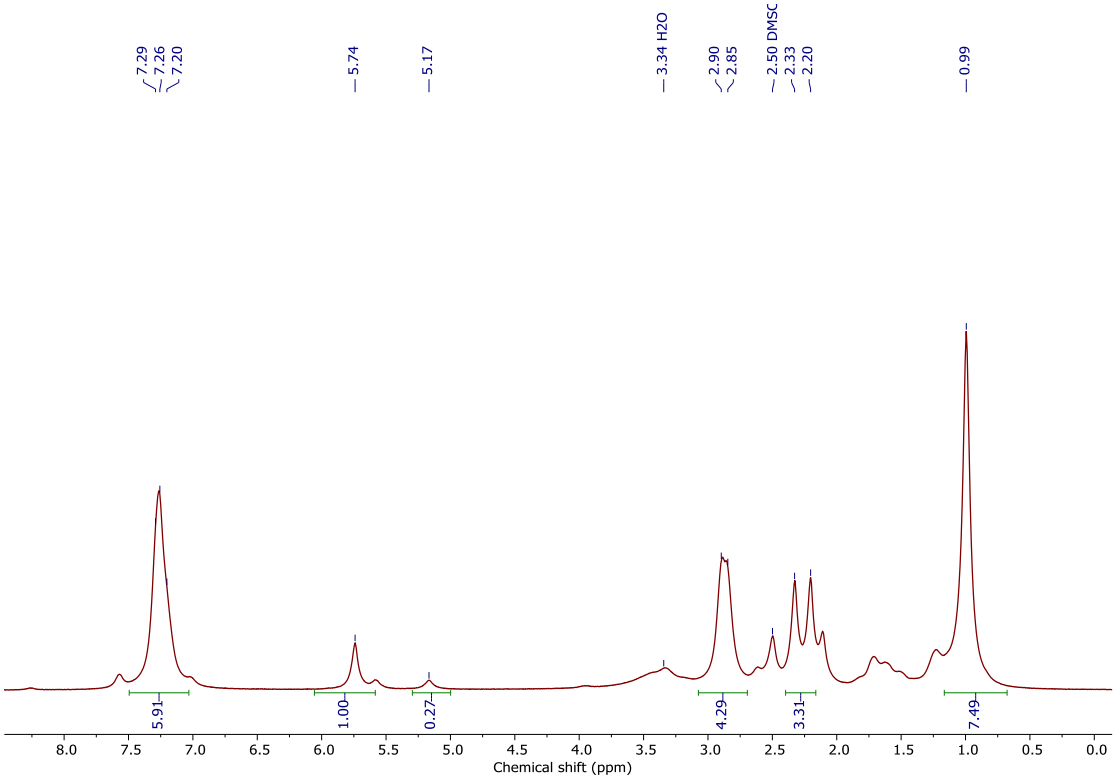



**Figure S13.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% aniline.

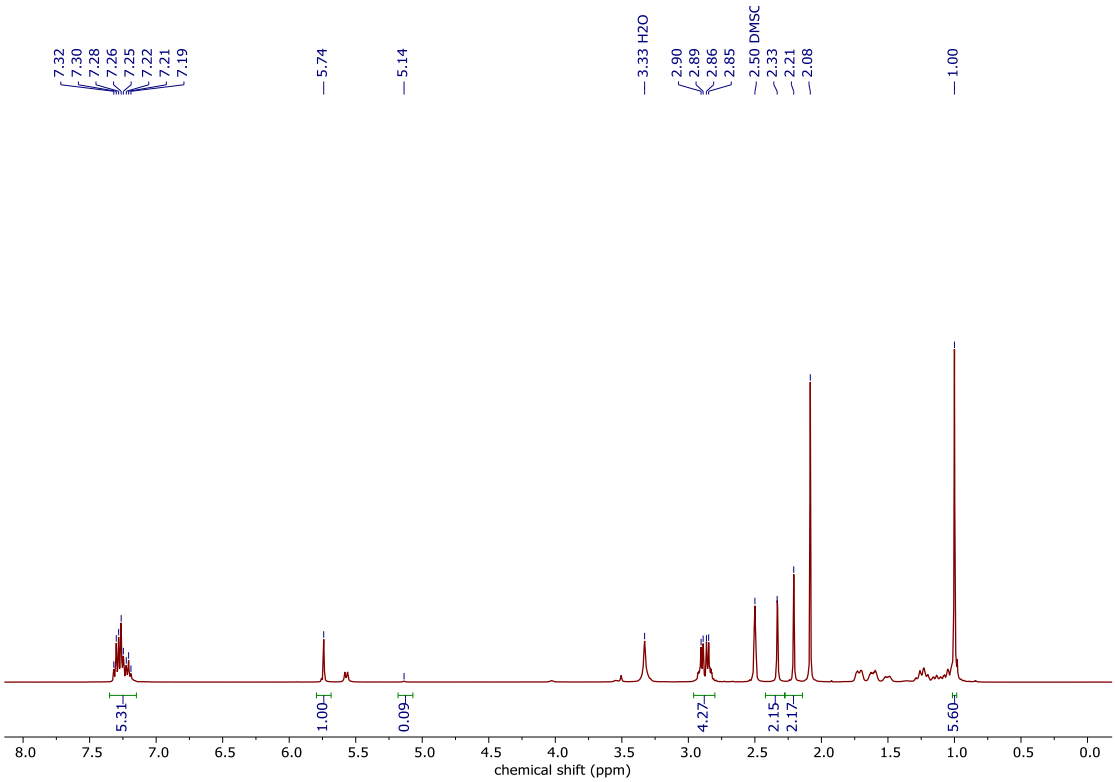



**Figure S14.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% pyridine.

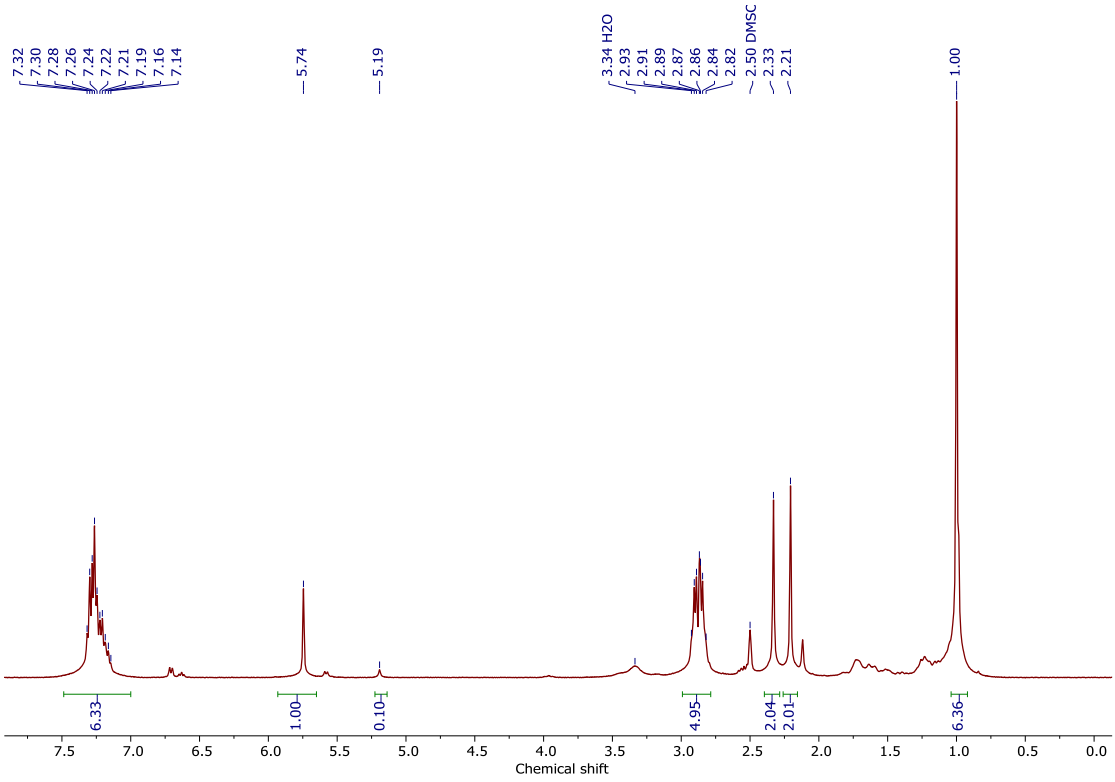



**Figure S15.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% *N,N*-dimethyl aniline (DMA).

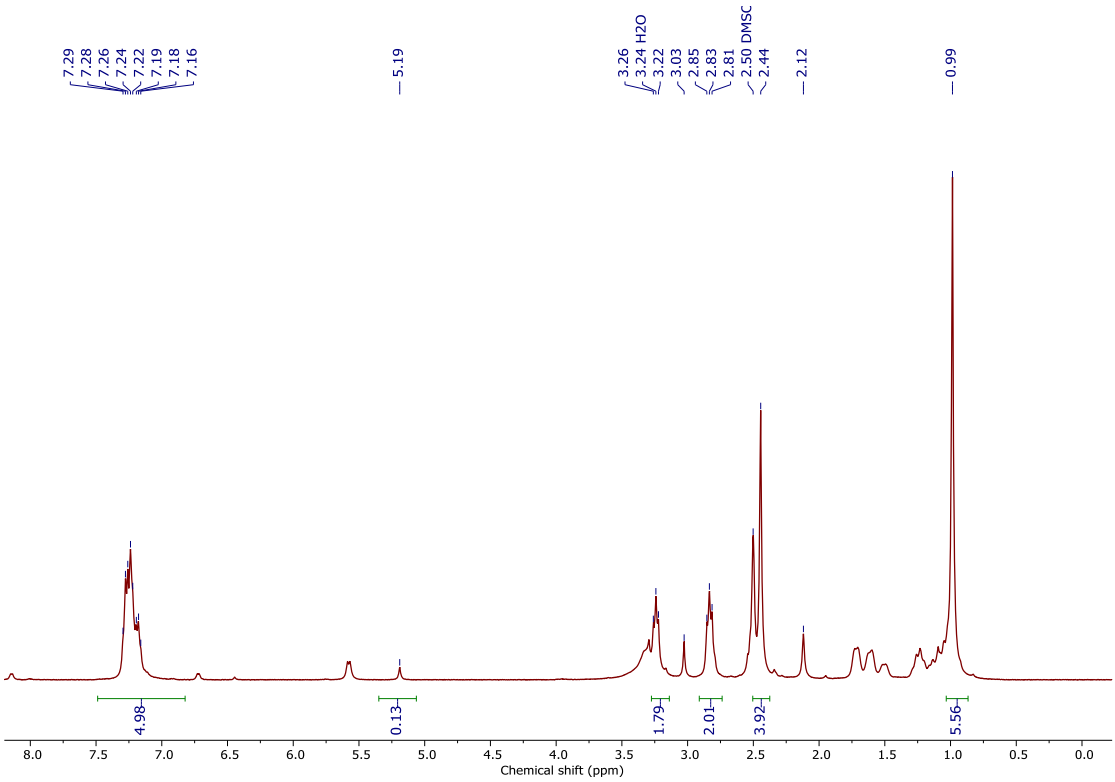



**Figure S16.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC and 10 mol% DMAP.

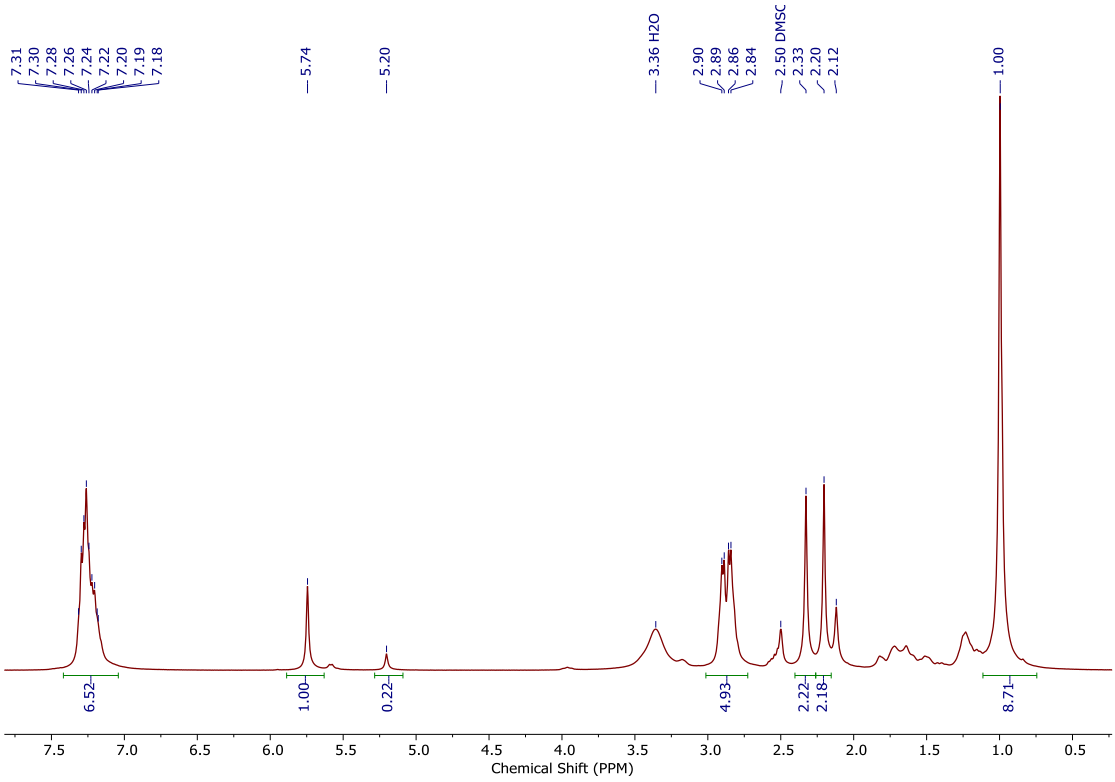



**Figure S17.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC without any catalytic base.

## Mechanochemical acylation of in two-steps milling processes (table 2)

**Step 1.1**

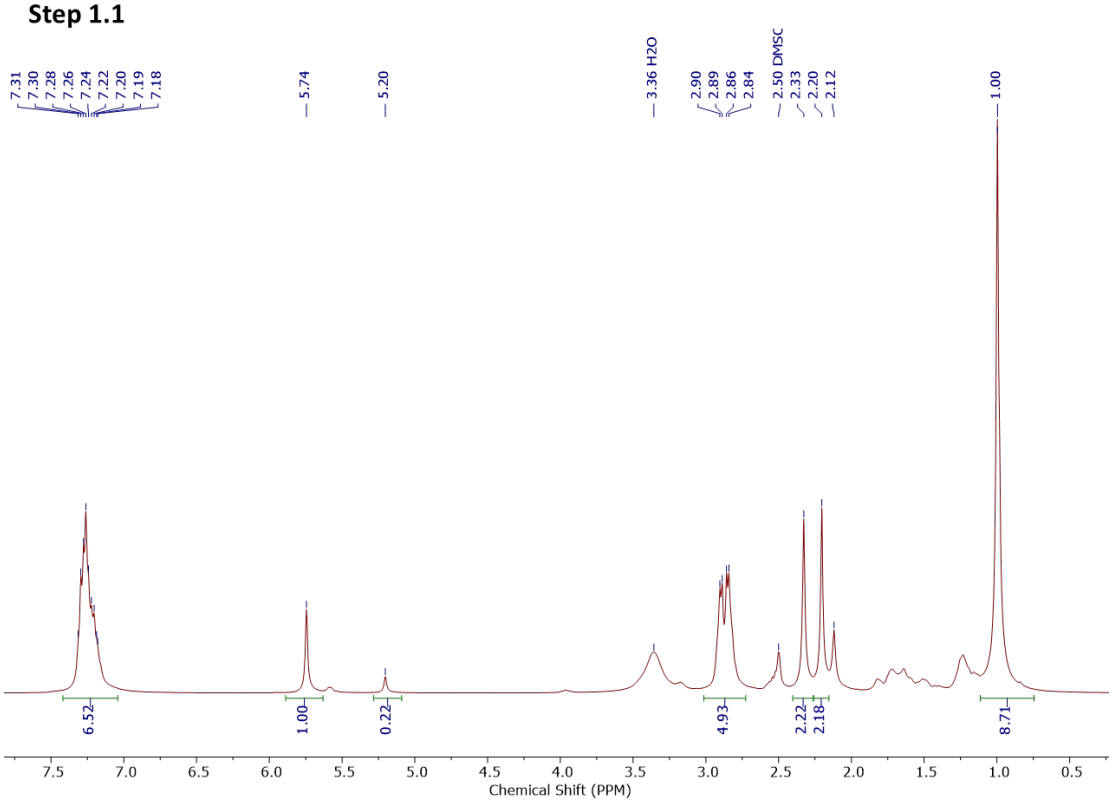



**Figure S18.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC without any catalytic base.

**Step 1.2**

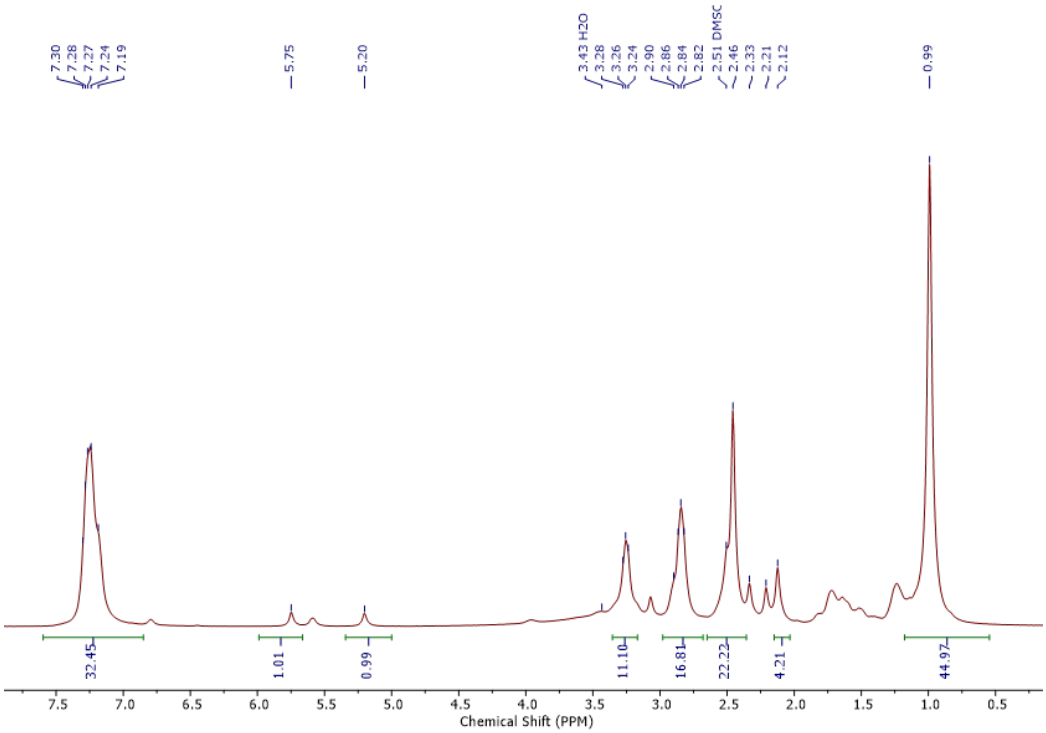



**Figure S19.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DCC followed by addition of DMAP and milled for an additional hour.

## Step 2.1

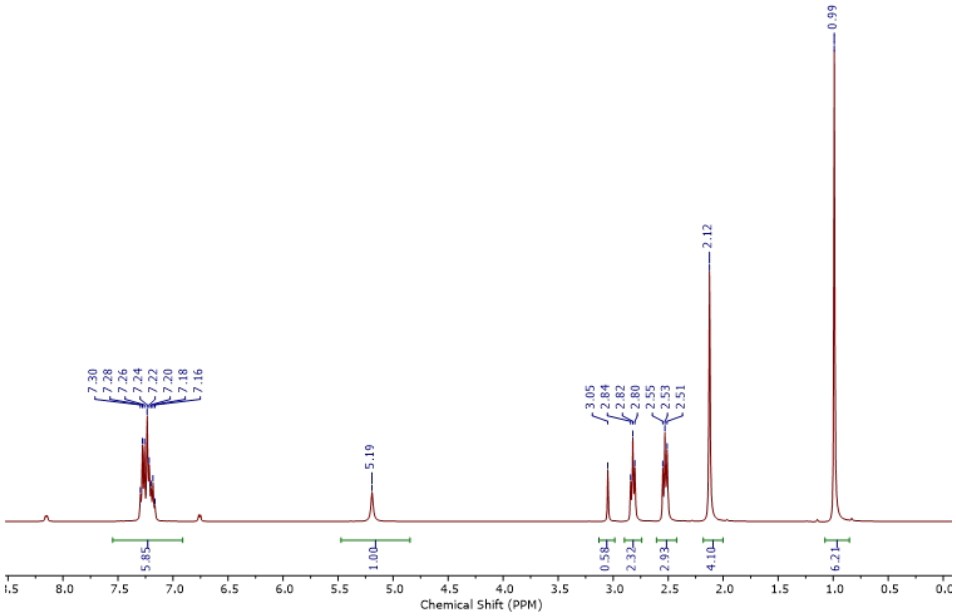



**Figure S20.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with 10 mol% DMAP without addition of DCC.

## Step 2.2

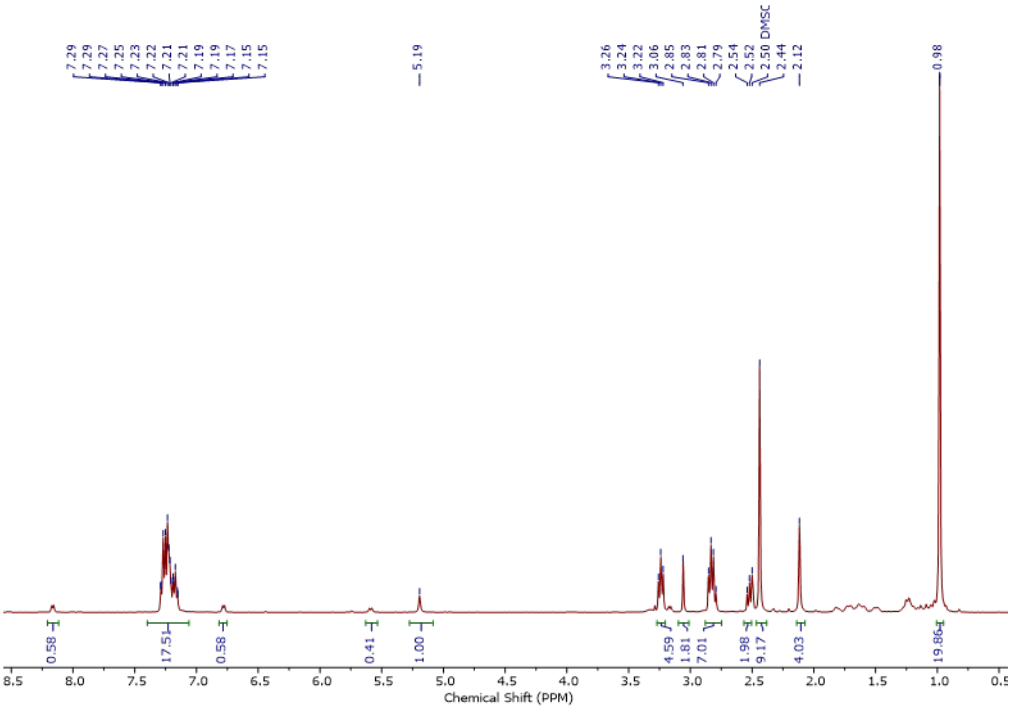



**Figure S21.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with DMAP followed by addition of DCC and milled for one additional hour.

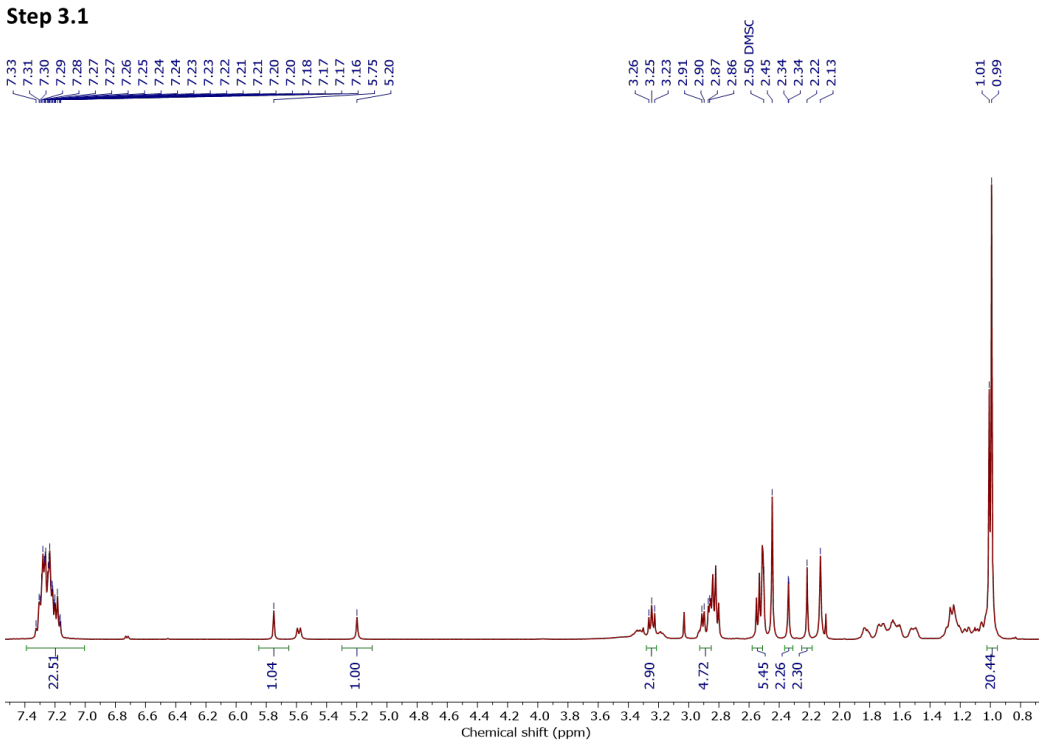



**Figure S22.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of one-pot acylation reaction of dimedone and phenyl propanoic acid milled for 1 h with DMAP and NaOH together (5 mol% each) in the presence of DCC.

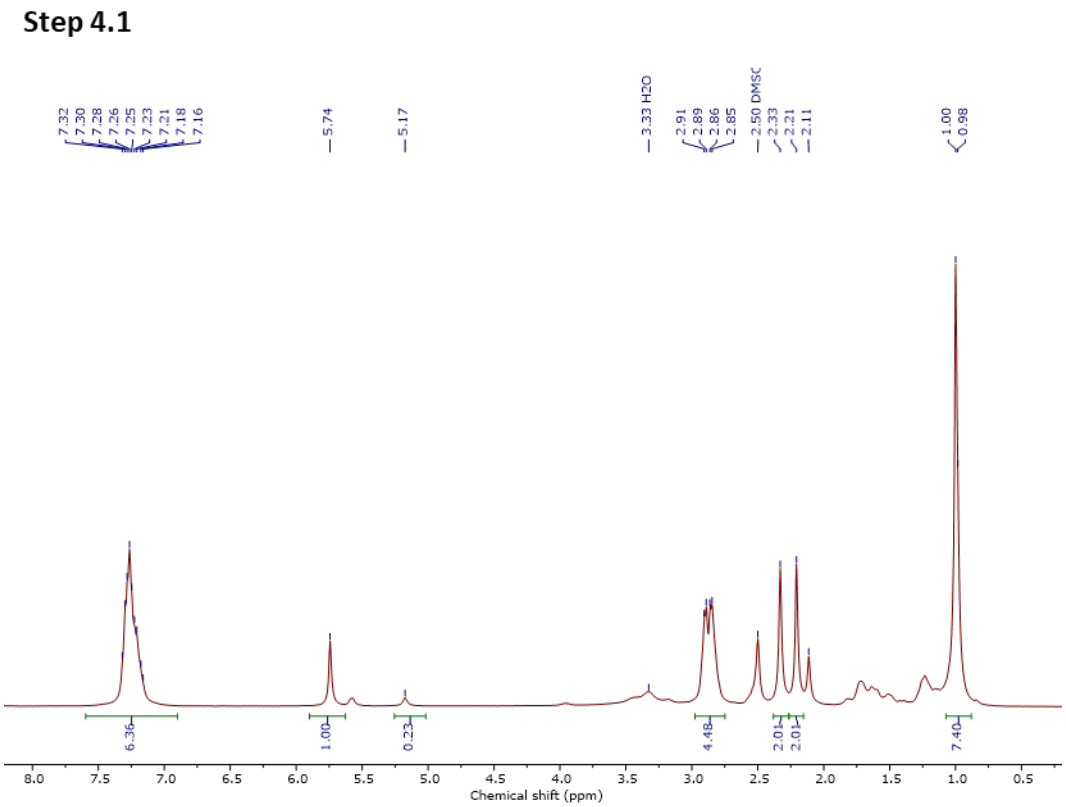



**Figure S23.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with NaOH in the presence of DCC.

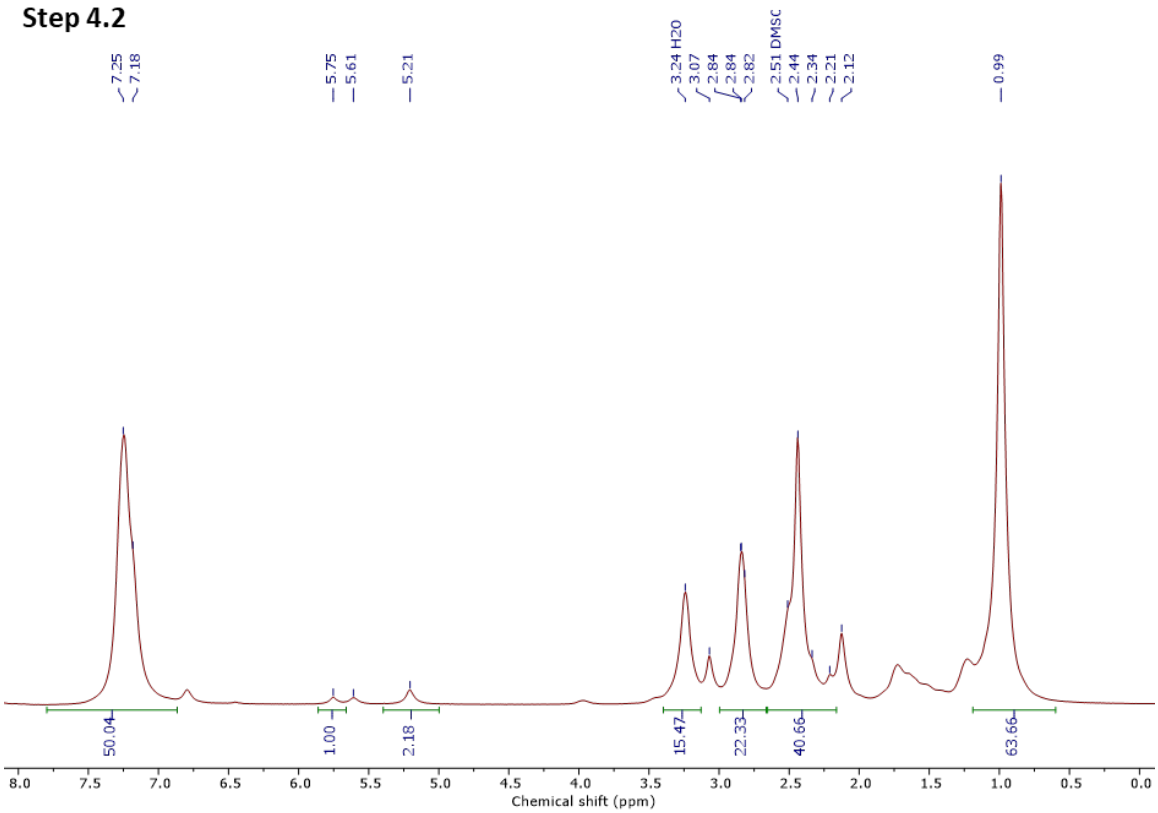



**Figure S24.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with 10 mol% NaOH followed by addition of 10 mol% DMAP and milled for one additional hour.

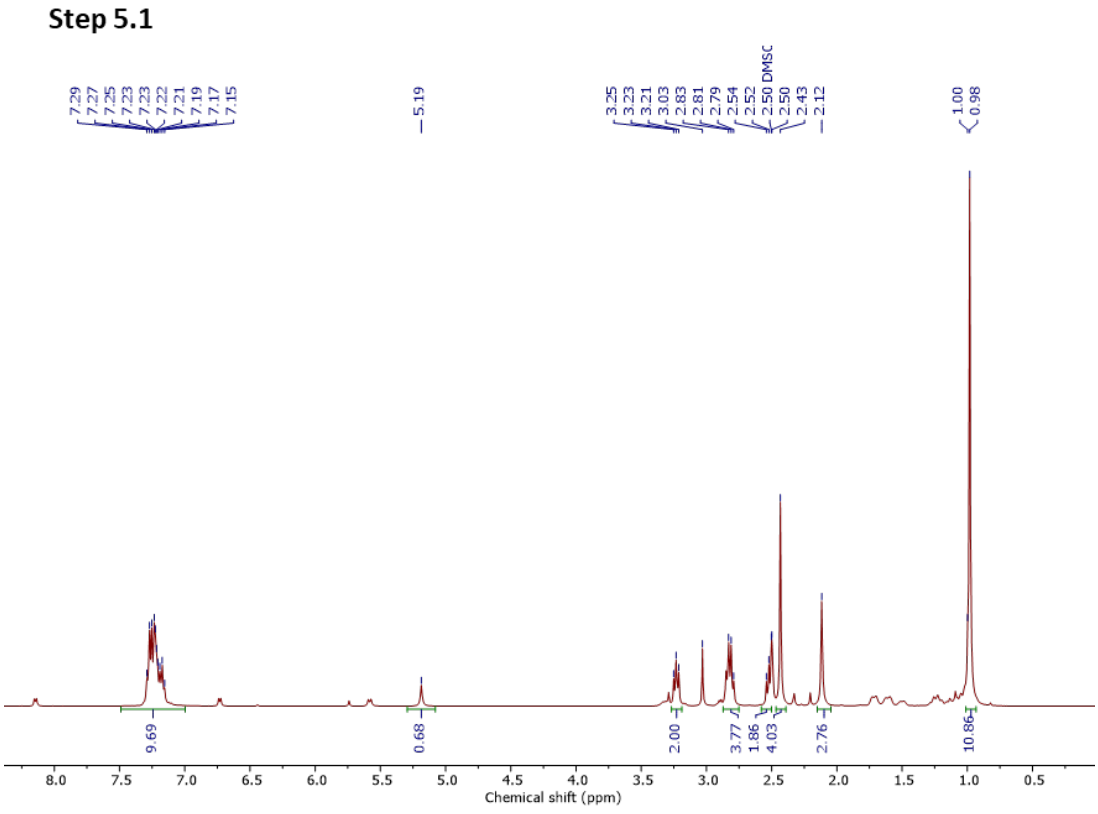



**Figure S25.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with 10 mol% DMAP in the presence of DCC.

Step 5.2

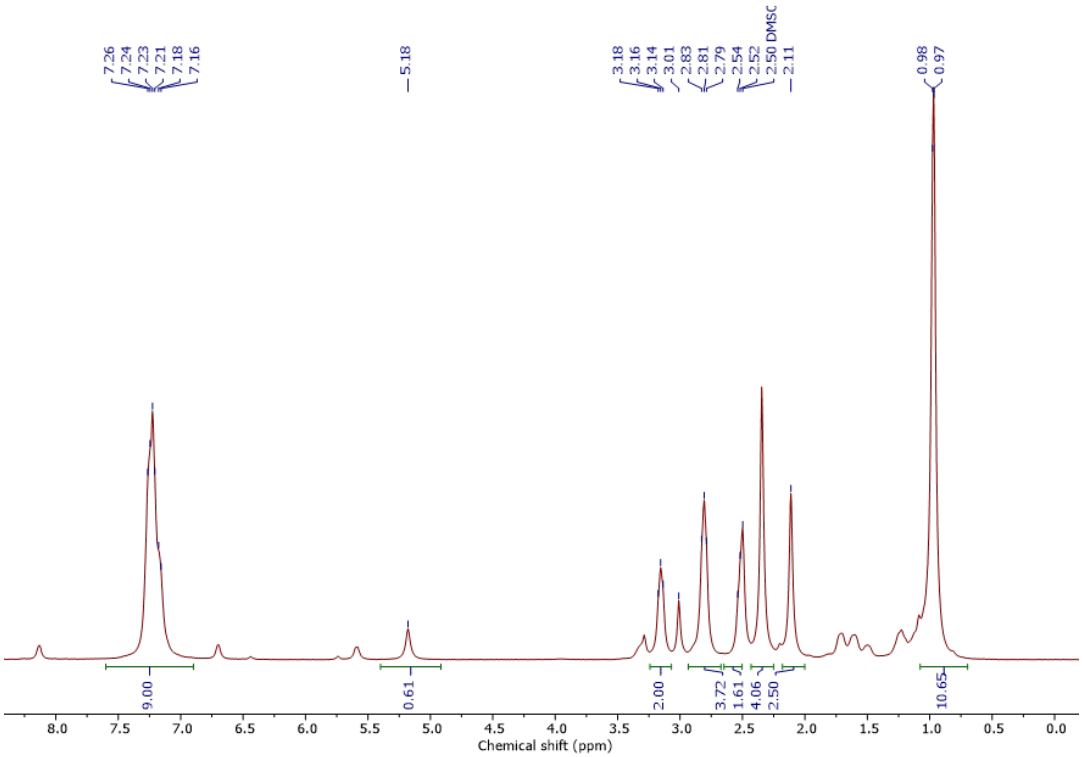



**Figure S26. .** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and phenyl propanoic acid milled for 1 h with 10 mol% DMAP and followed with addition of 10 mol% NaOH and milled for one additional hour.

## Mechanochemical acylation of dimedone with various acids (table 3)

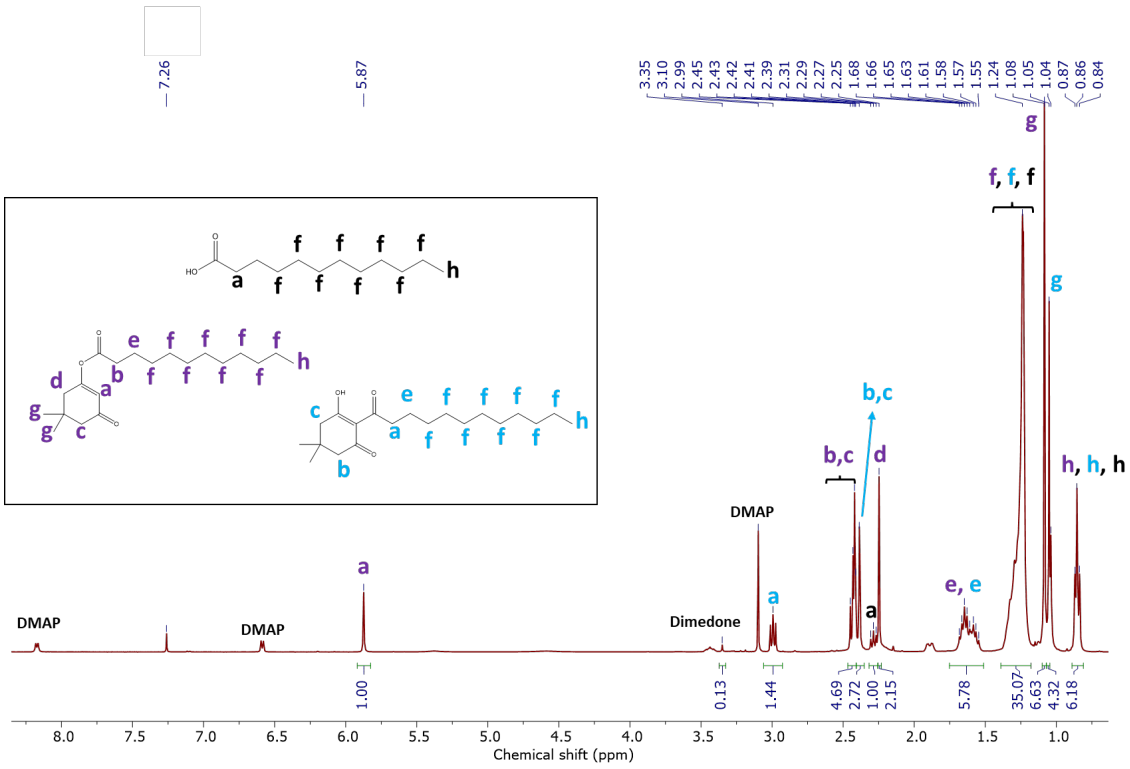



**Figure S27.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and lauric acid milled for 1 h with 10 mol% DMAP.

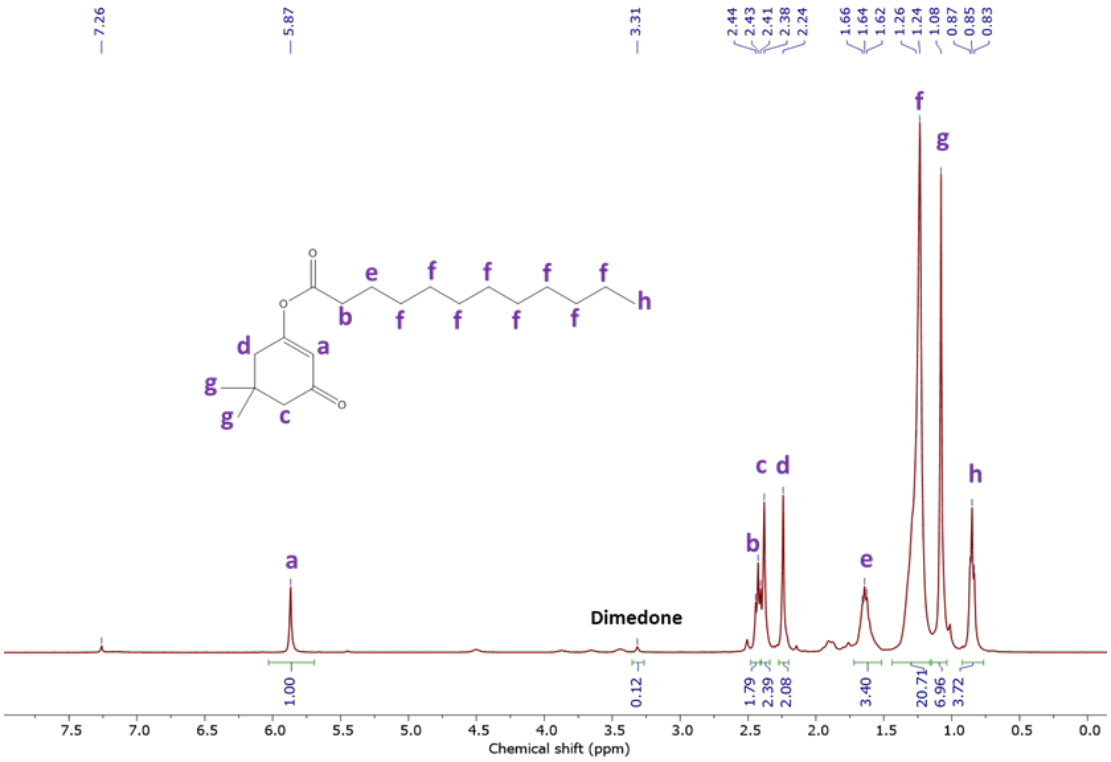



**Figure S28.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and lauric acid milled for 1 h with 10 mol% NaOH.

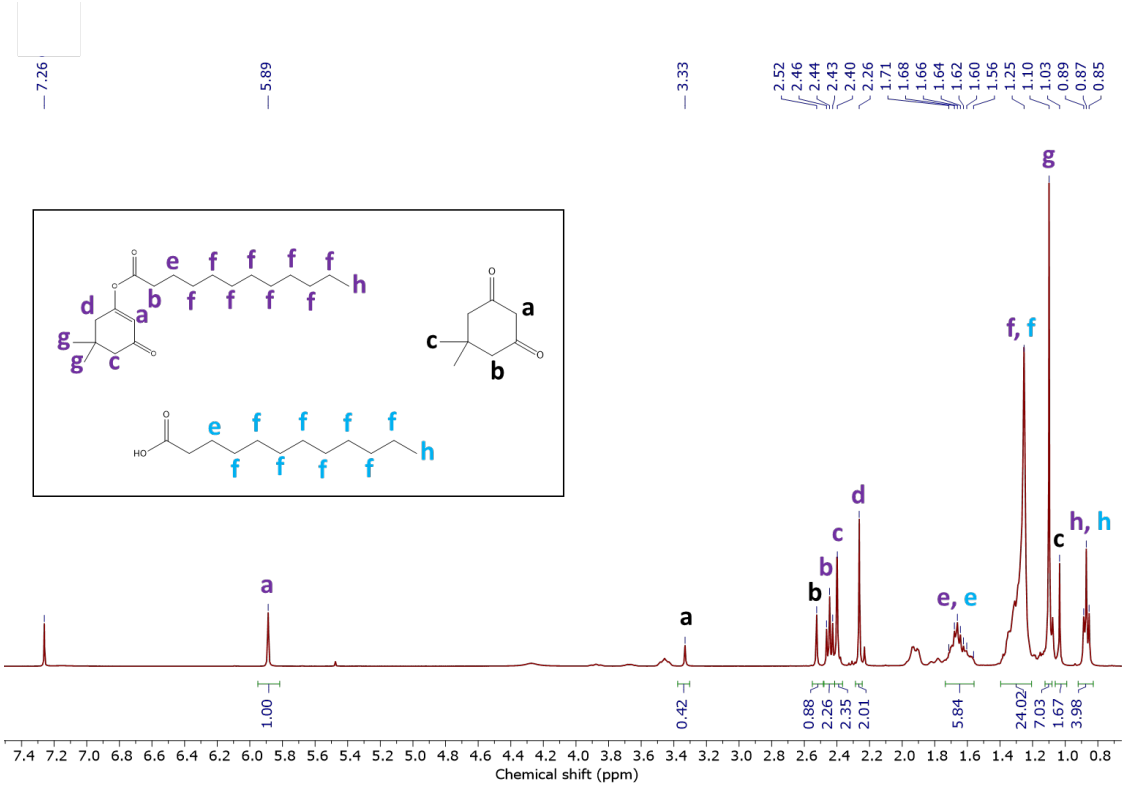



**Figure S29.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and lauric acid milled for 2 h with 10 mol% DMAP.

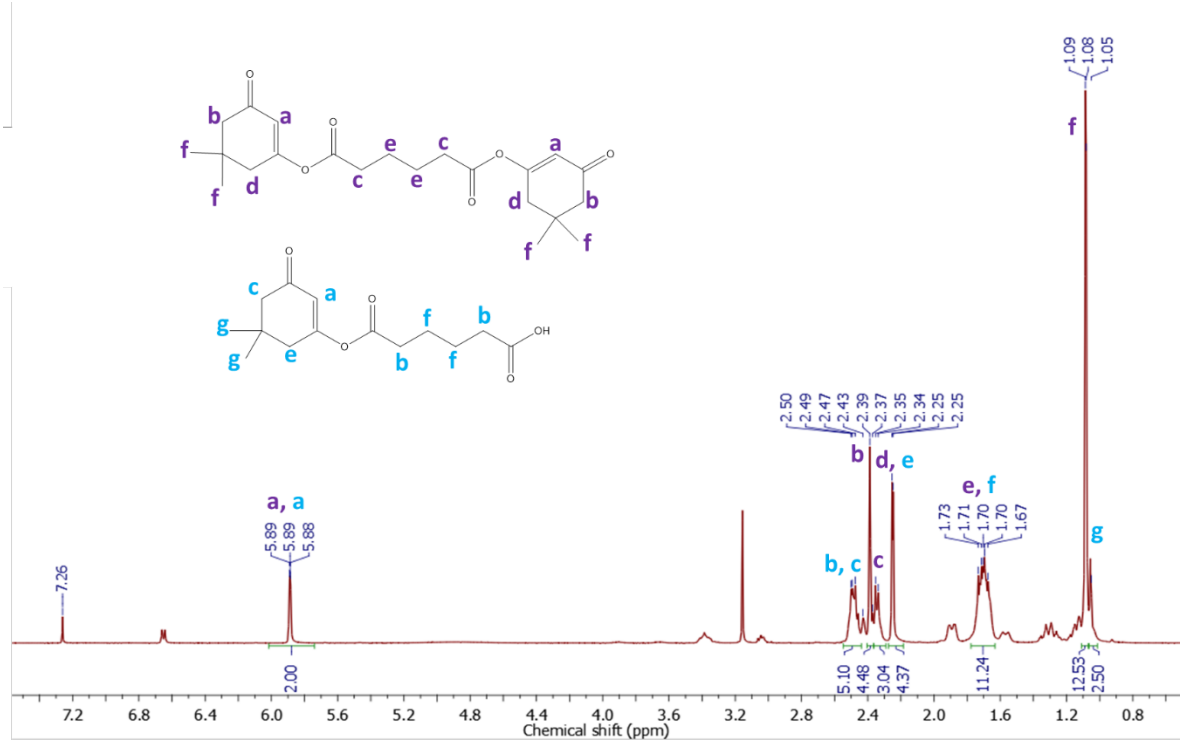



**Figure S30.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and adipic acid milled for 1 h with 10 mol% DMAP.

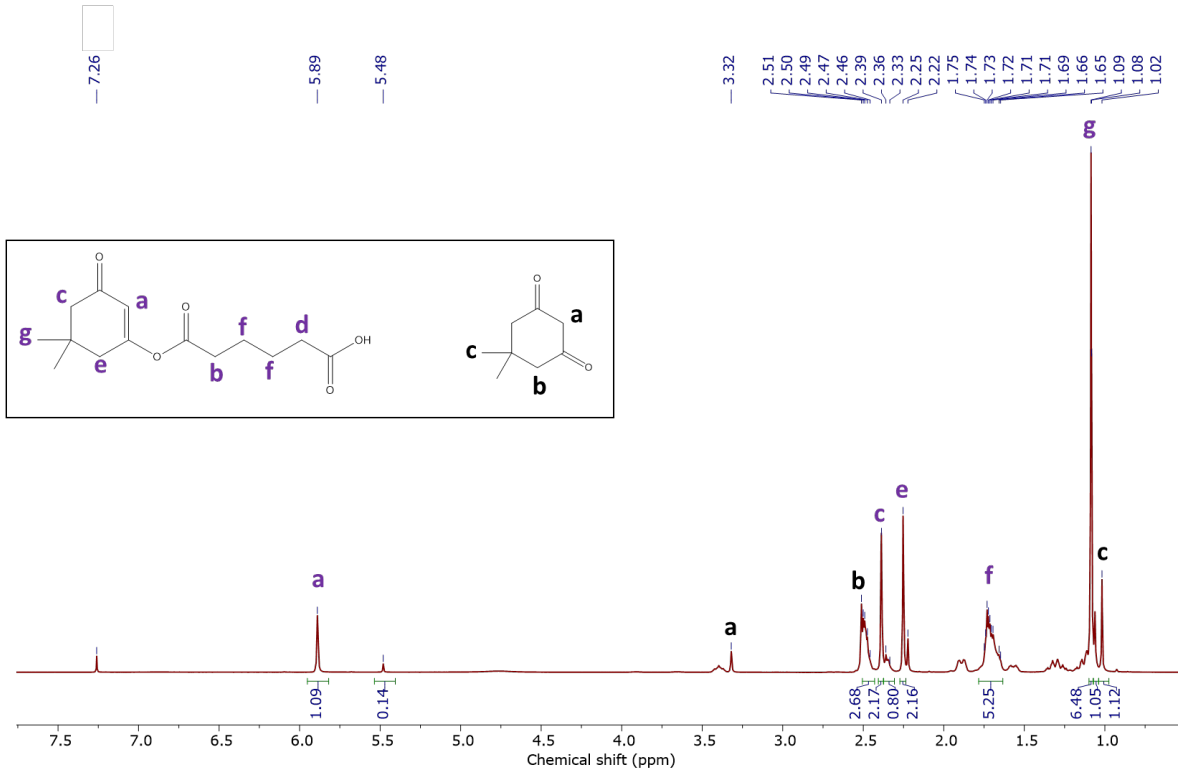



**Figure S31.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and adipic acid milled for 1 h with 10 mol% NaOH.

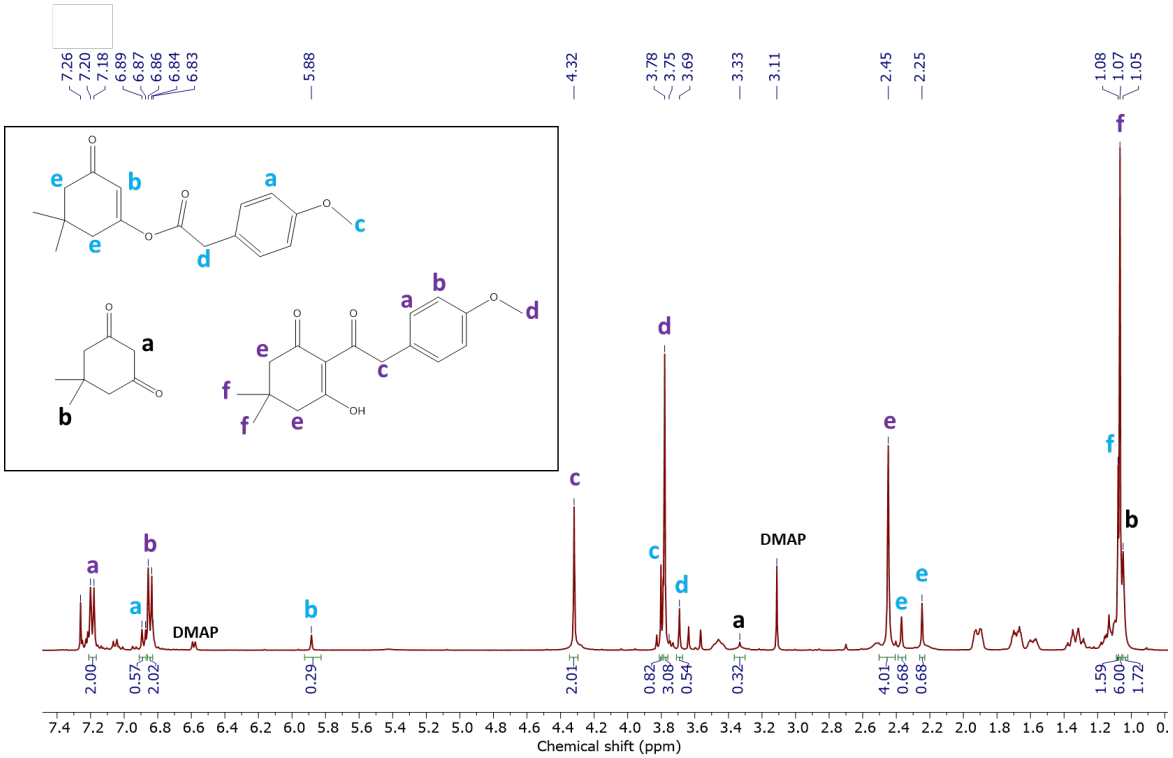



**Figure S32.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and 4-methoxyphenyl acetic acid milled for 1 h with 10 mol% DMAP.

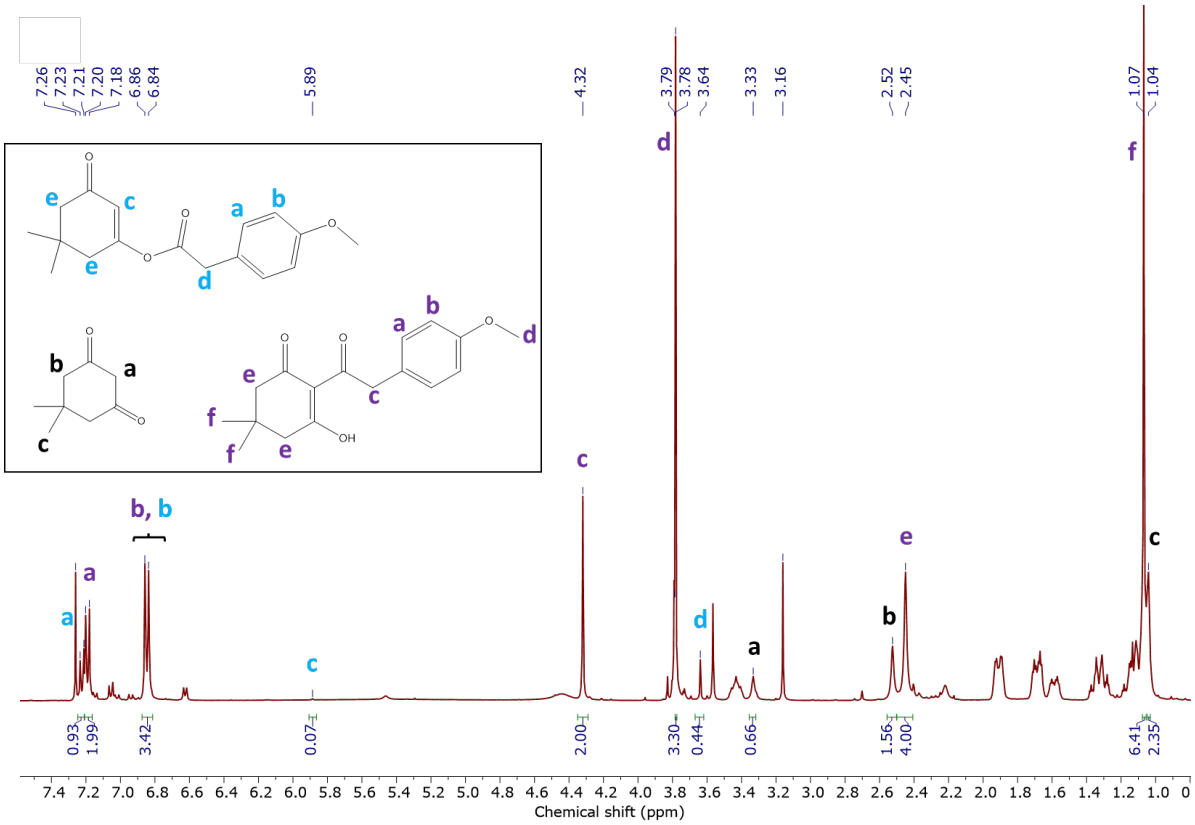



**Figure S33.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and 4-methoxyphenyl acetic acid milled for 2 h with 10 mol% DMAP.

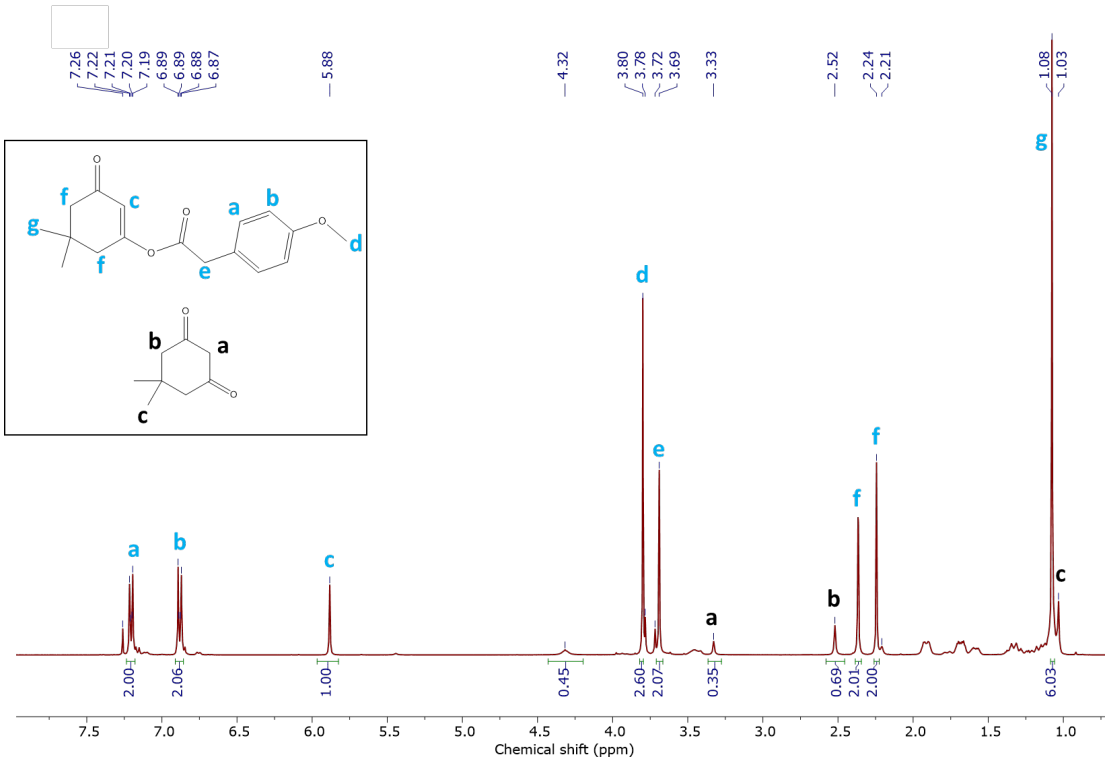



**Figure S34.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and 4-methoxyphenyl acetic acid milled for 1 h with 10 mol% NaOH.

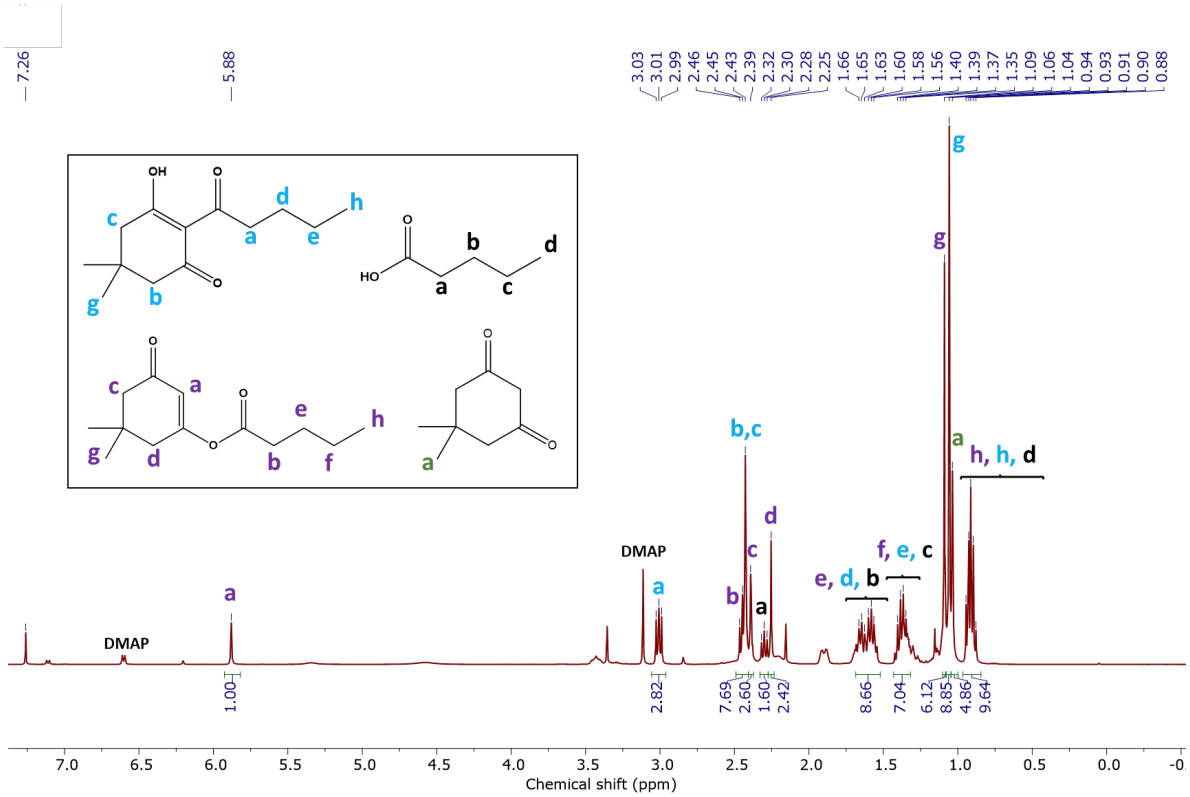



**Figure S35.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and pentanoic acid milled for 1 h with 10 mol% DMAP.

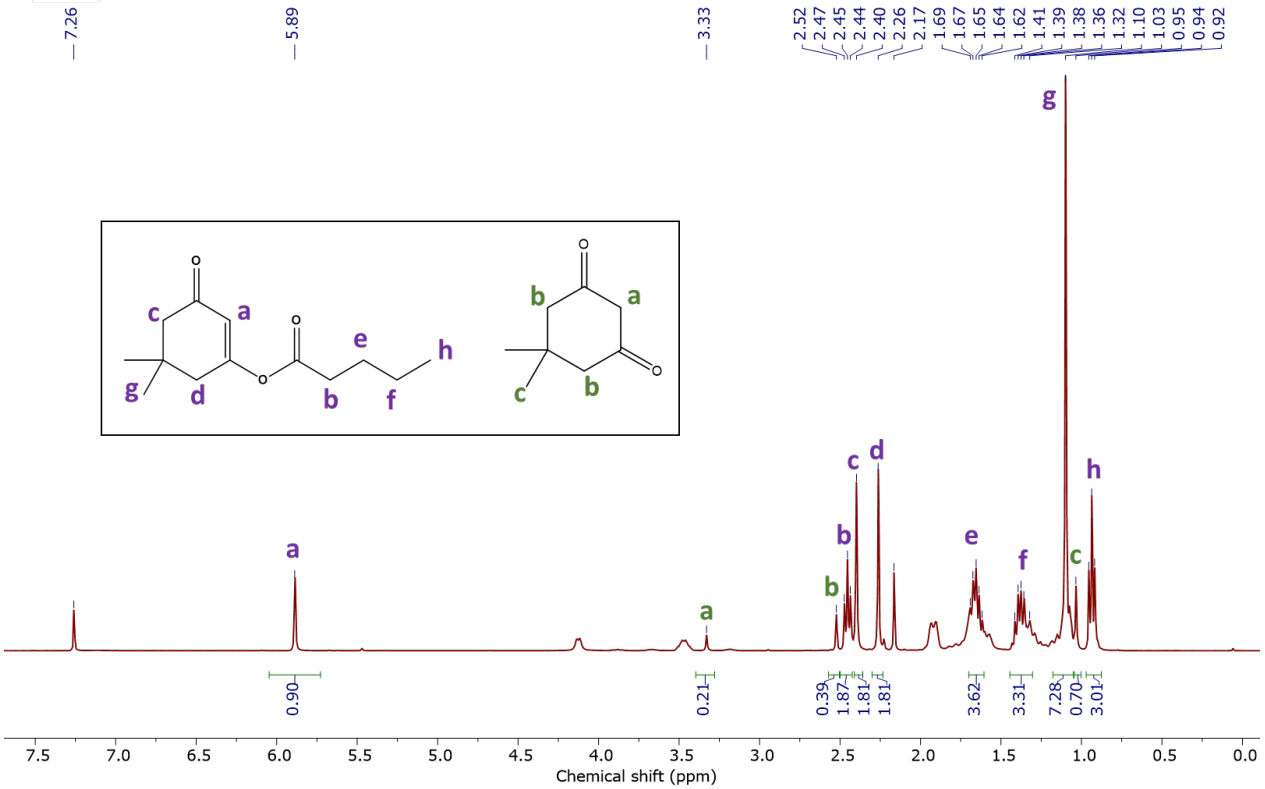



**Figure S36.** $^{1}$H NMR (400 MHz, $CDCl_3$) of dimedone and pentanoic acid milled for 1 h with 10 mol% NaOH.

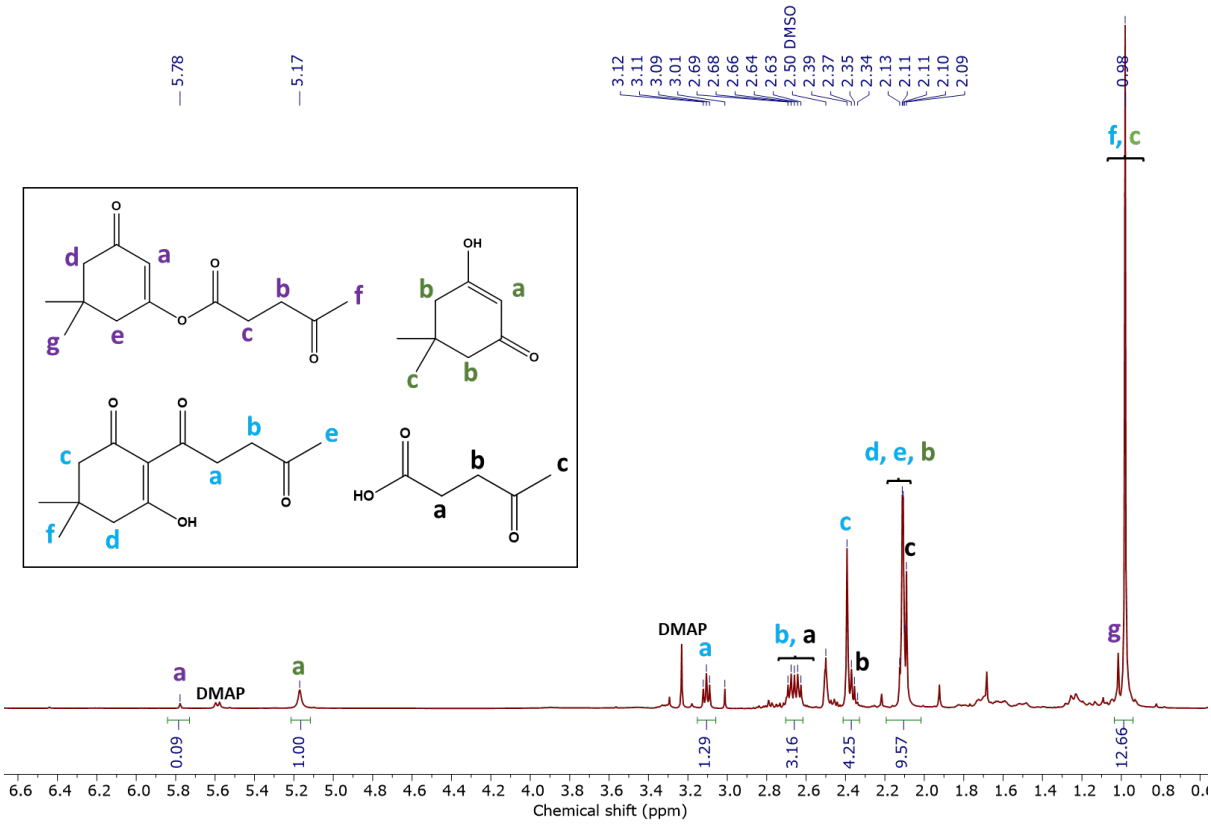



**Figure S37.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and levulinic acid milled for 1 h with 10 mol% DMAP.

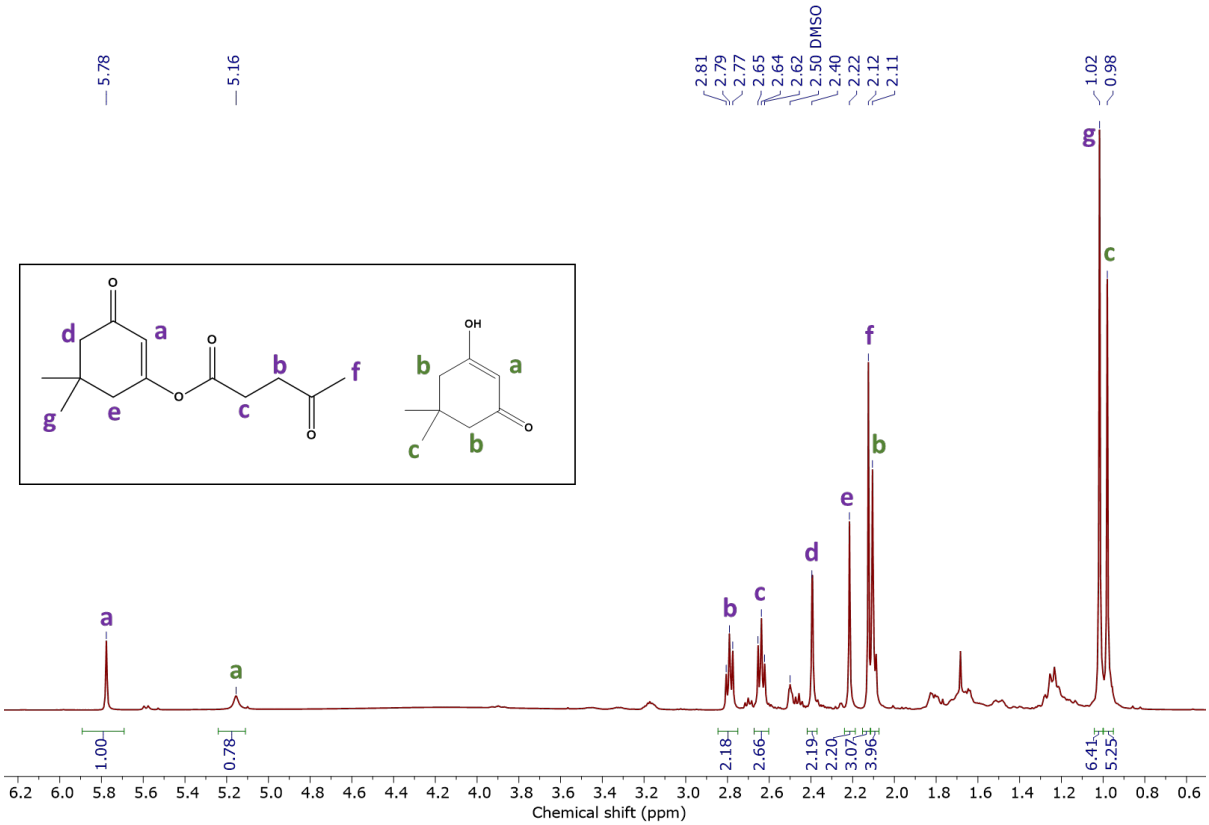



**Figure S38.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and levulinic acid milled for 1 h with 10 mol% NaOH.

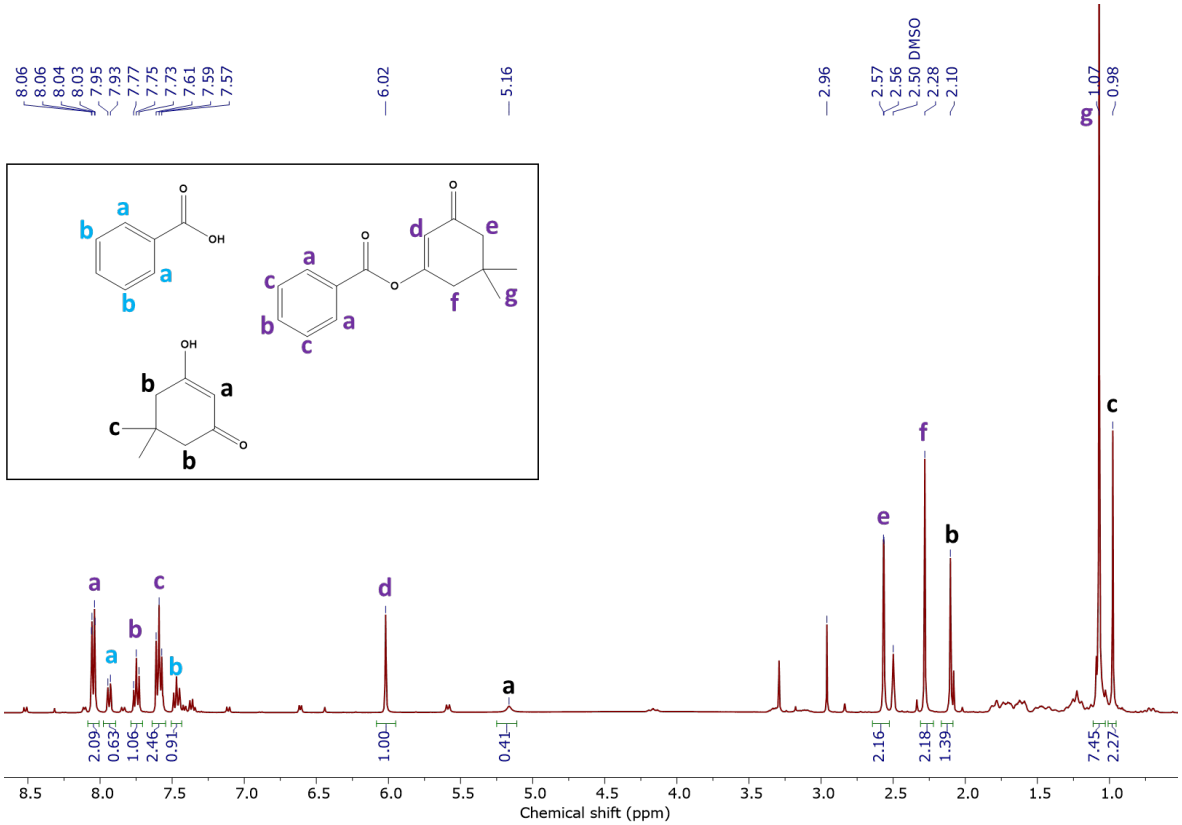



**Figure S39.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and benzoic acid milled for 1 h with 10 mol% DMAP.

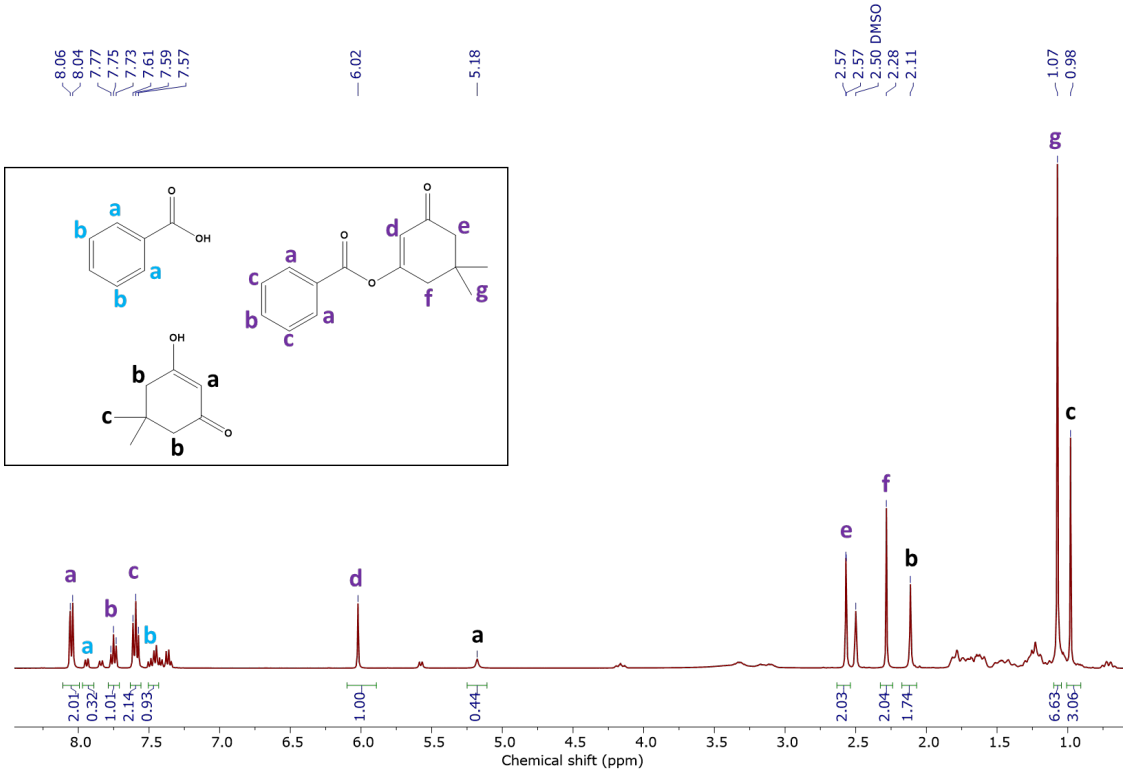



**Figure S40.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of dimedone and benzoic acid milled for 1 h with 10 mol% NaOH.

## Mechanochemical acylation of phenyl propanoic acid with various ketones (table 4)

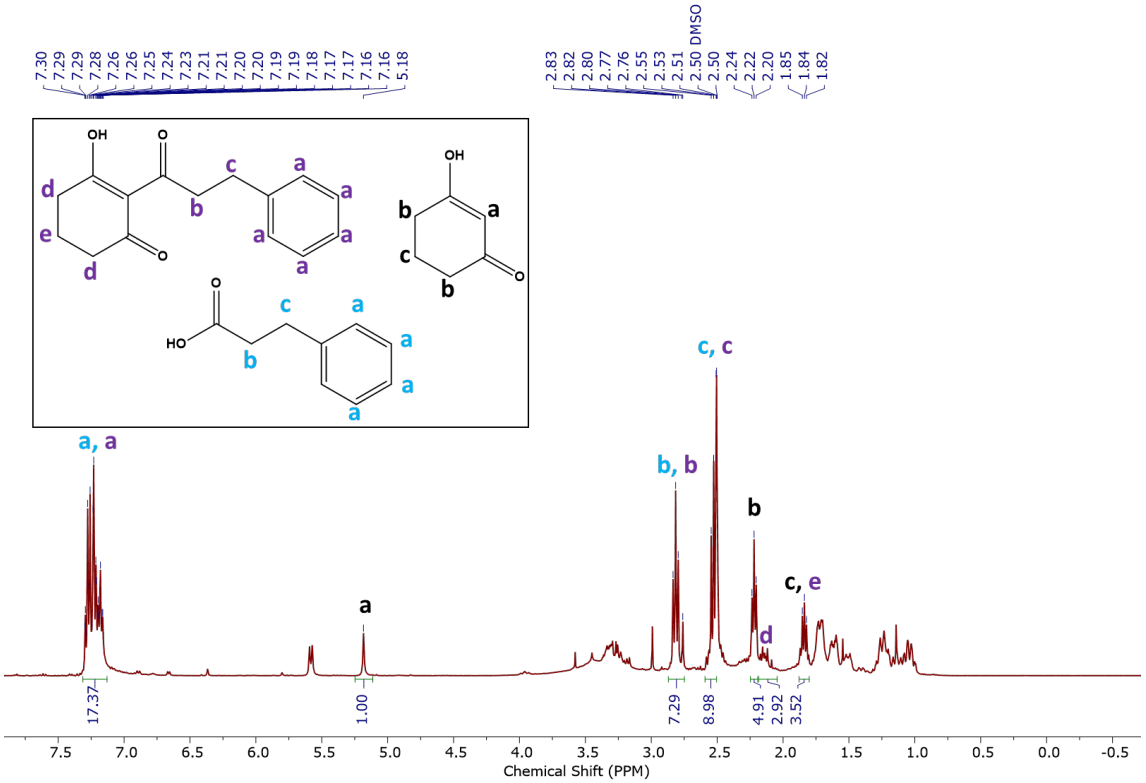



**Figure S41.** $^{1}$H NMR (400 MHz, DMSO) of phenyl propanoic acid and 1,3-cyclohexanedione milled for 1 h with 10 mol% DMAP.

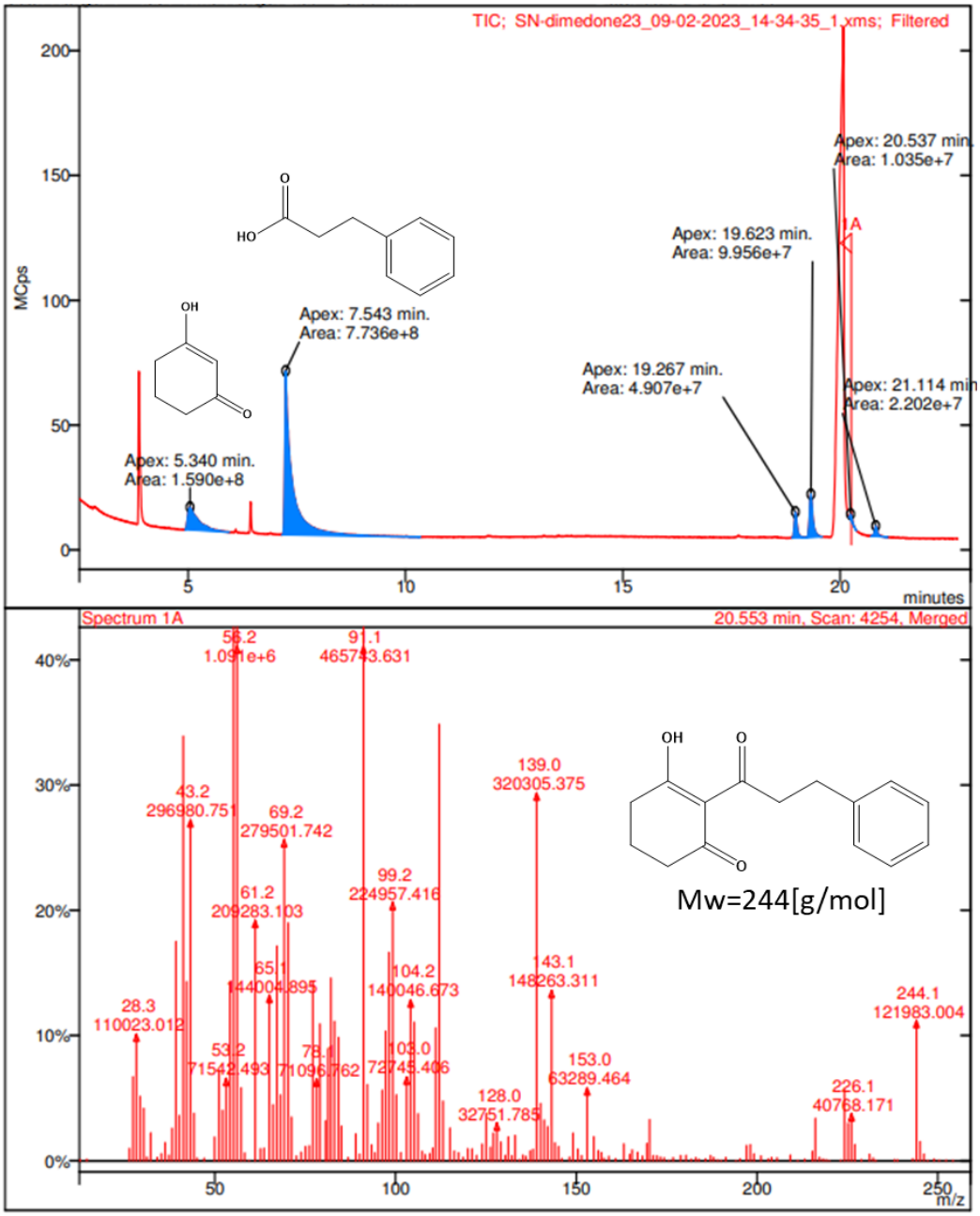



***Figure* S42.** GC-MS of phenyl propanoic acid and 1,3-cyclohexanedione milled for 1 h with 10 mol% DMAP.

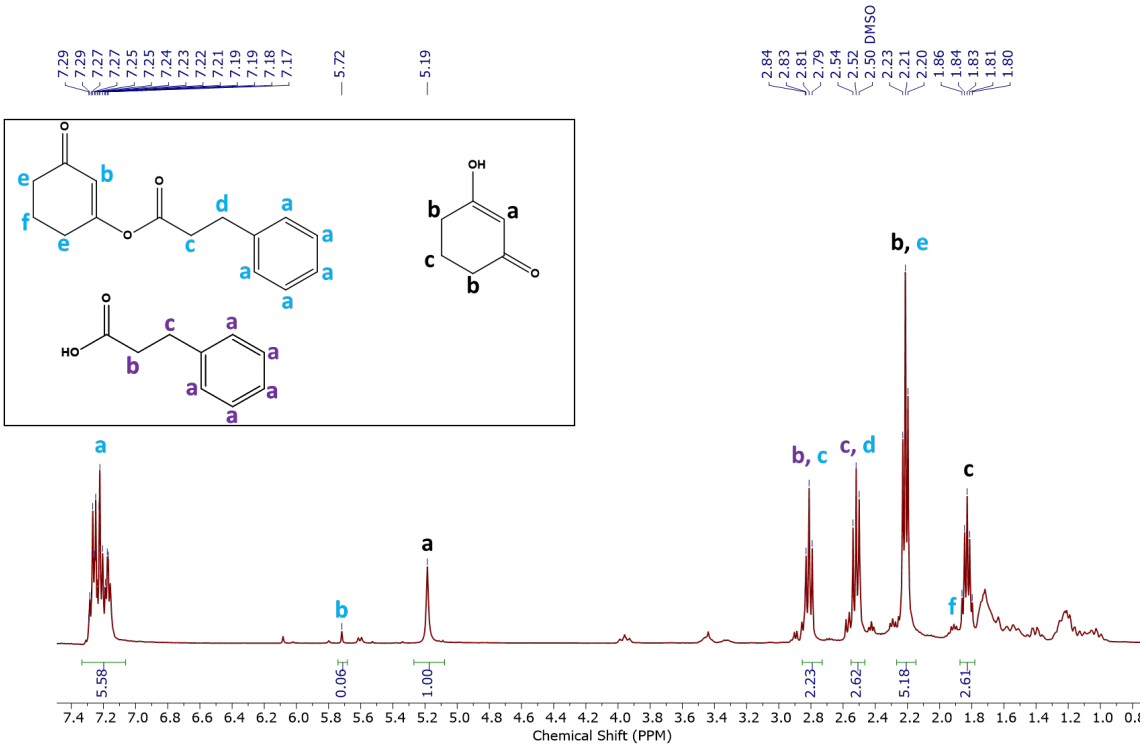



**Figure S43.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of phenyl propanoic acid and 1,3-cyclohexanedione milled for 1 h with 10 mol% NaOH.

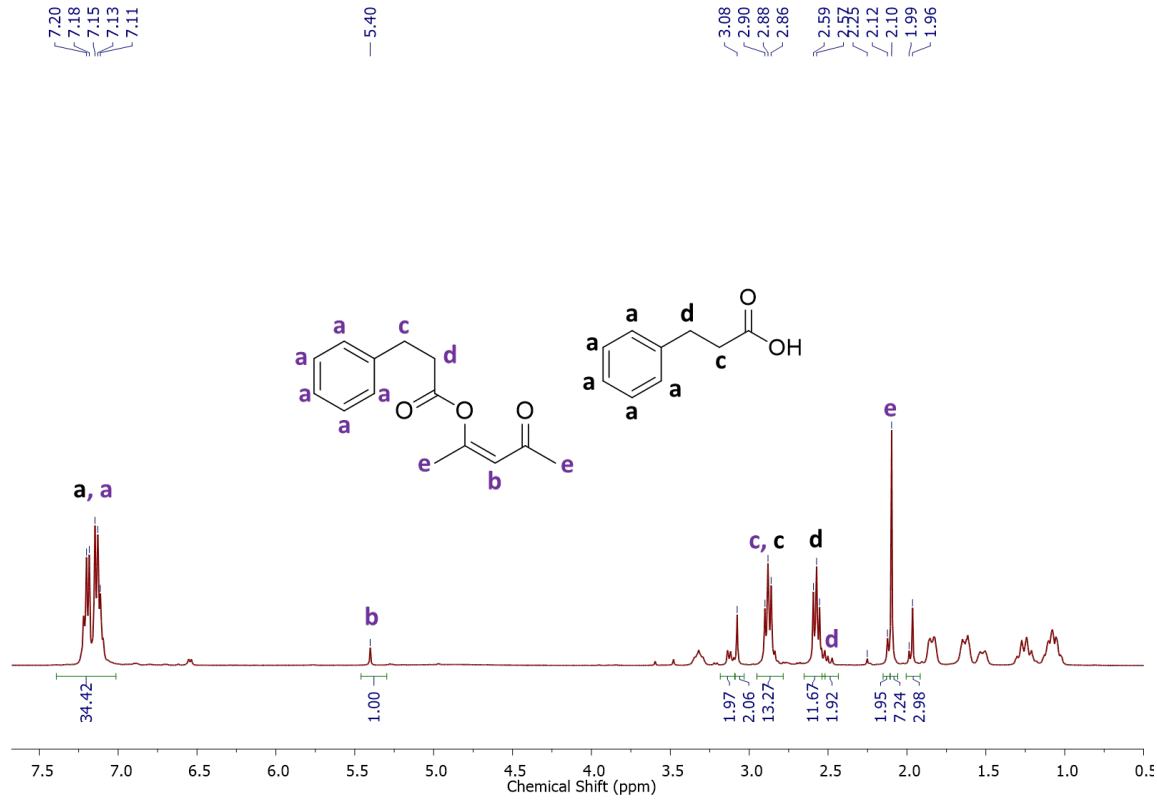



**Figure S44.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and acetyl acetone milled for 1 h with 10 mol% DMAP.

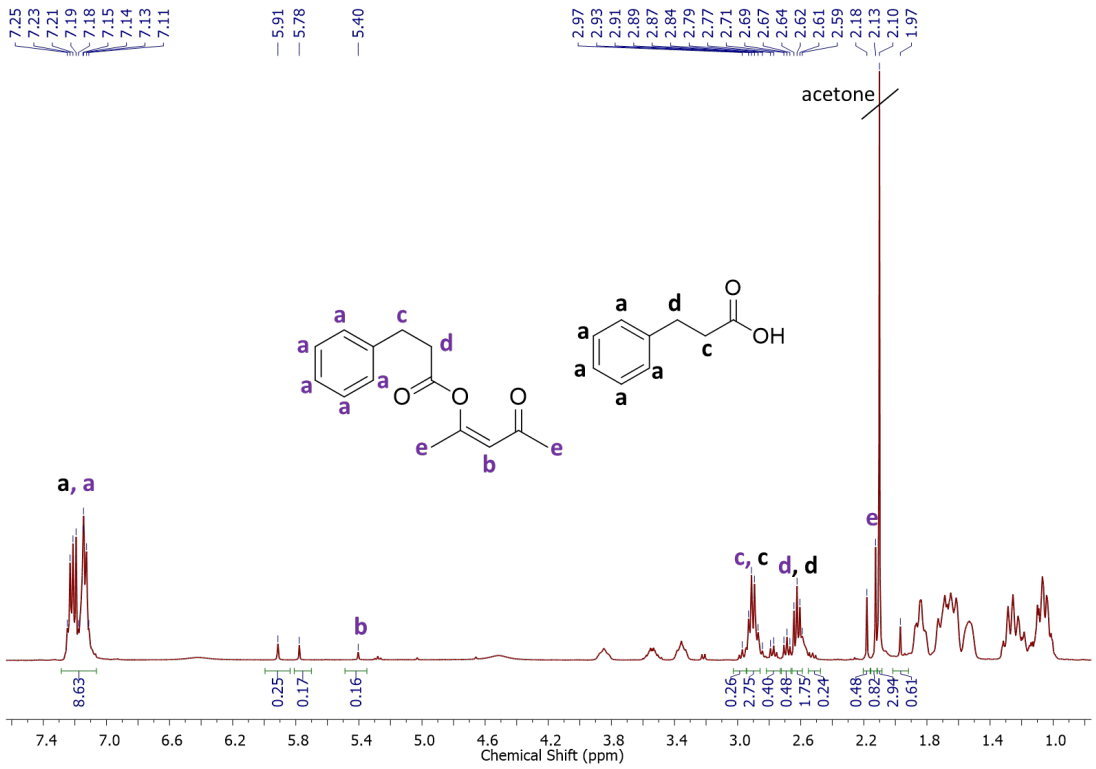



**Figure S45.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and acetyl acetone milled for 1 h with 10 mol% NaOH.

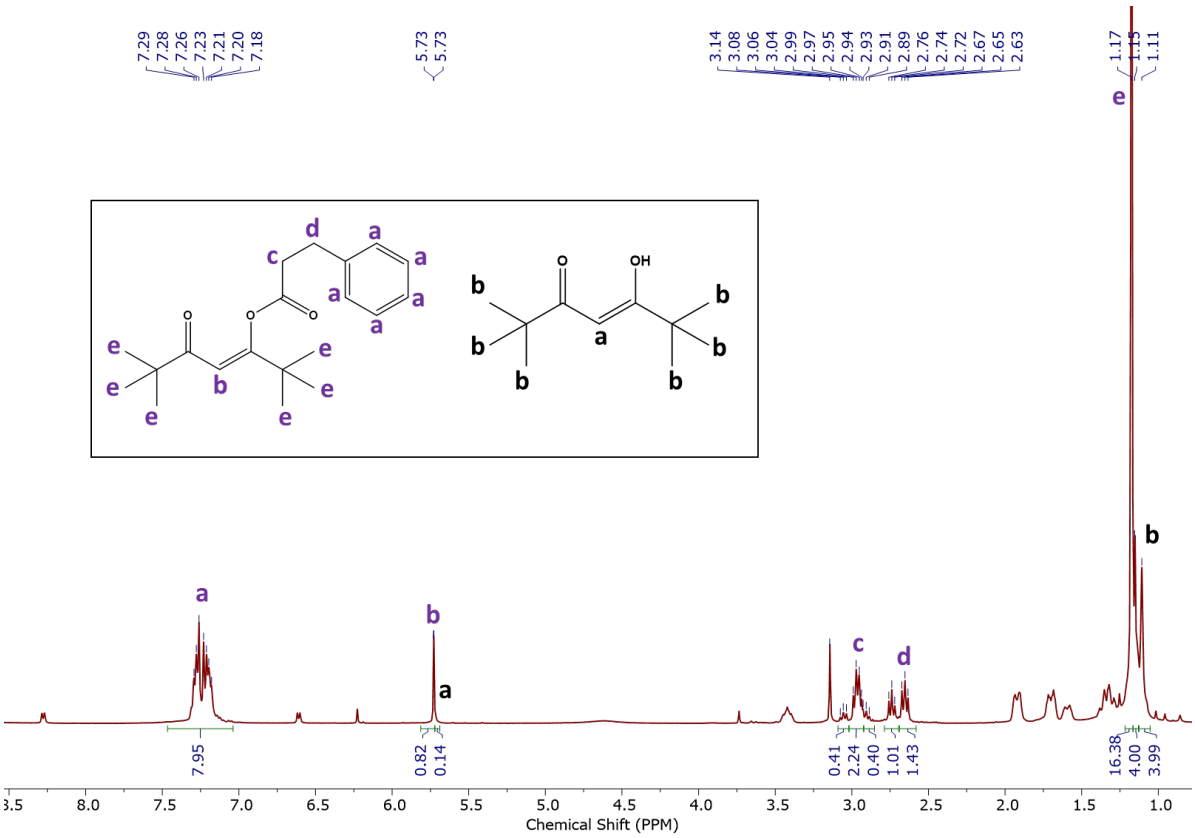



**Figure S46.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and tetramethylheptane-3,5-dione milled for 1 h with 10 mol% DMAP.

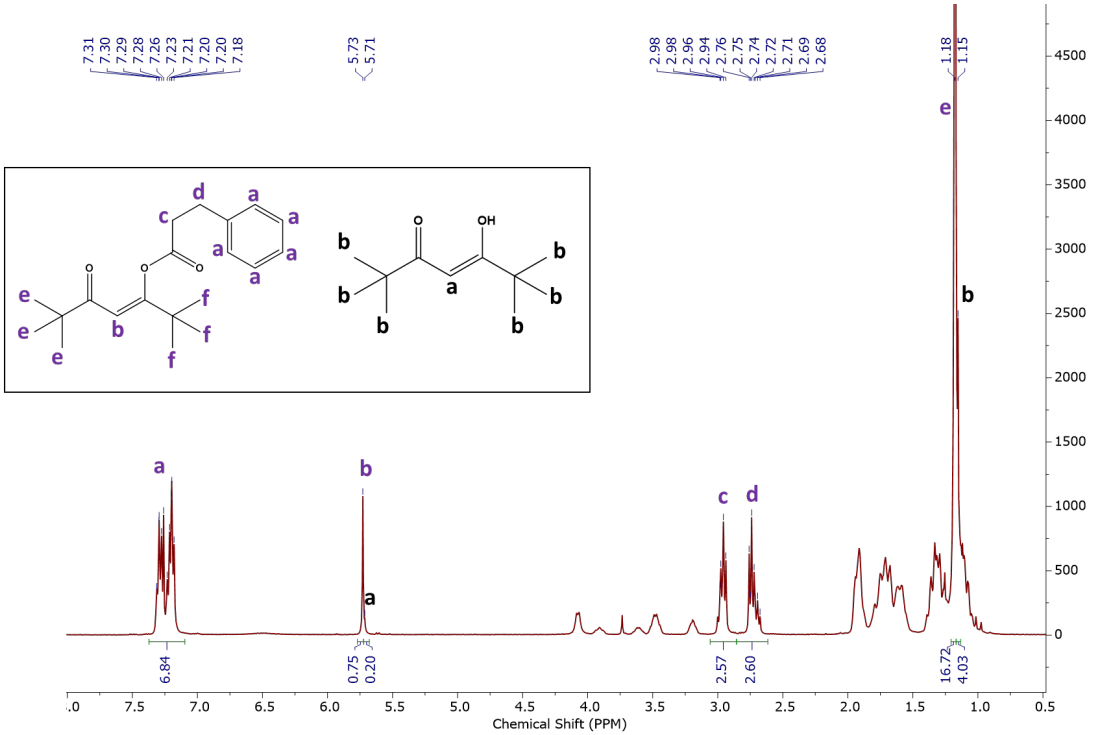



**Figure S47.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and tetramethylheptane-3,5-dione milled for 1 h with 10 mol% NaOH.

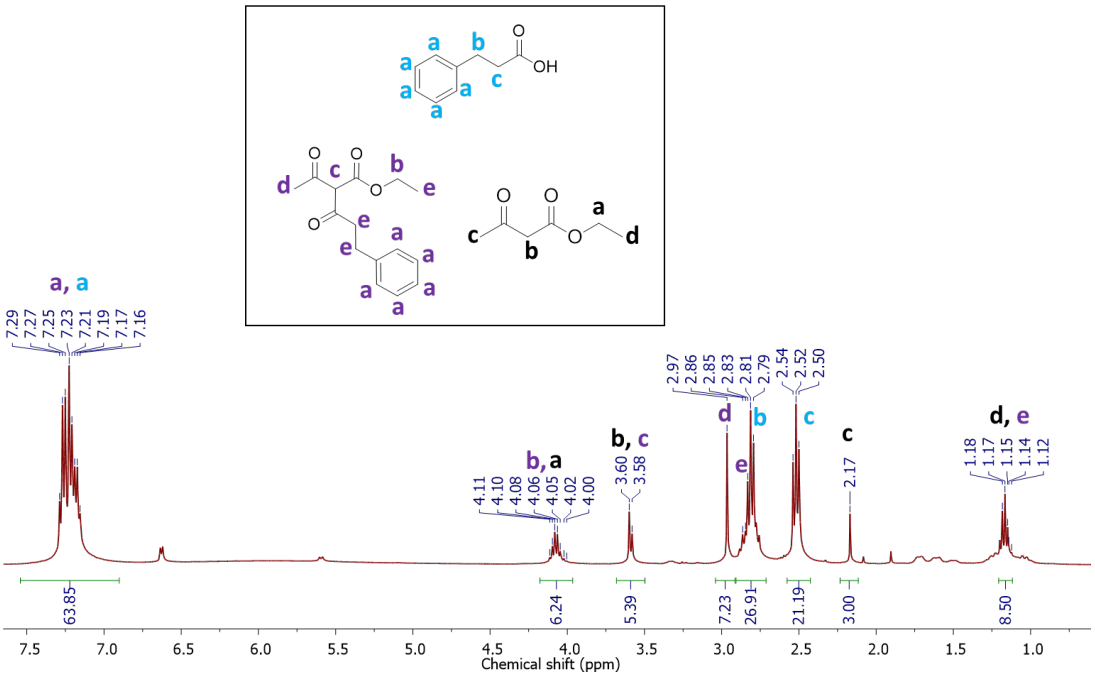



**Figure S48.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and ethyl acetoacetate milled for 1 h with 10 mol% DMAP.

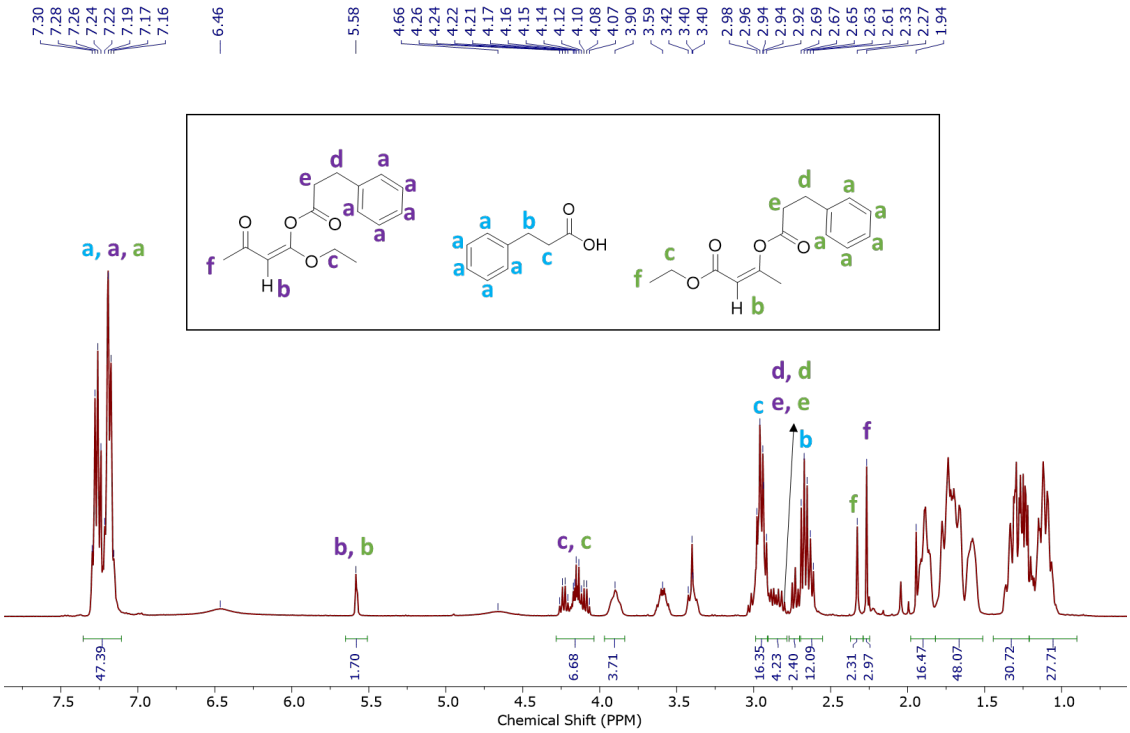



**Figure S49.** $^{1}$H NMR (400 MHz, $CDCl_3$) of phenyl propanoic acid and ethyl acetoacetate milled for 1 h with 10 mol% NaOH.

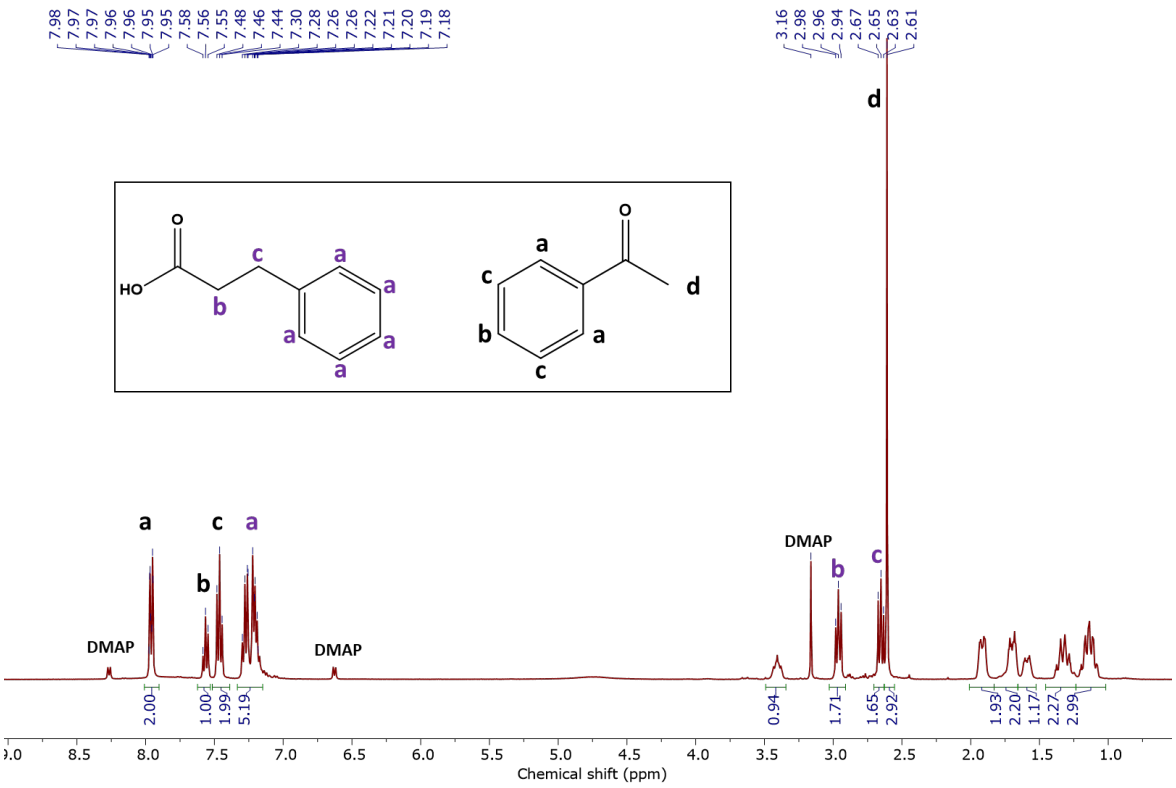



**Figure S50.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of phenyl propanoic acid and acetophenone milled for 1 h with 10 mol% DMAP.

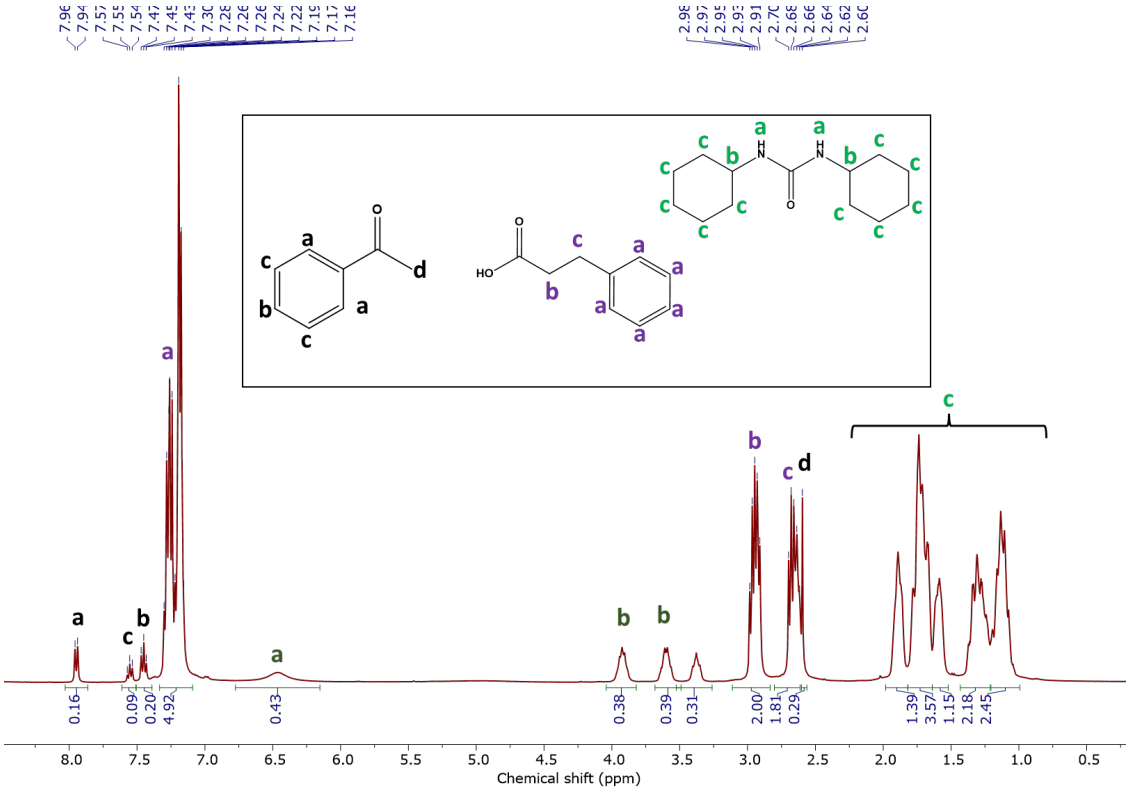



**Figure S51.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of phenyl propanoic acid and acetophenone milled for 1 h with 10 mol% NaOH.

## Mechanically induced acylation of dimedone and 3-phenylpropanoic acid using scalable mills (table 5)

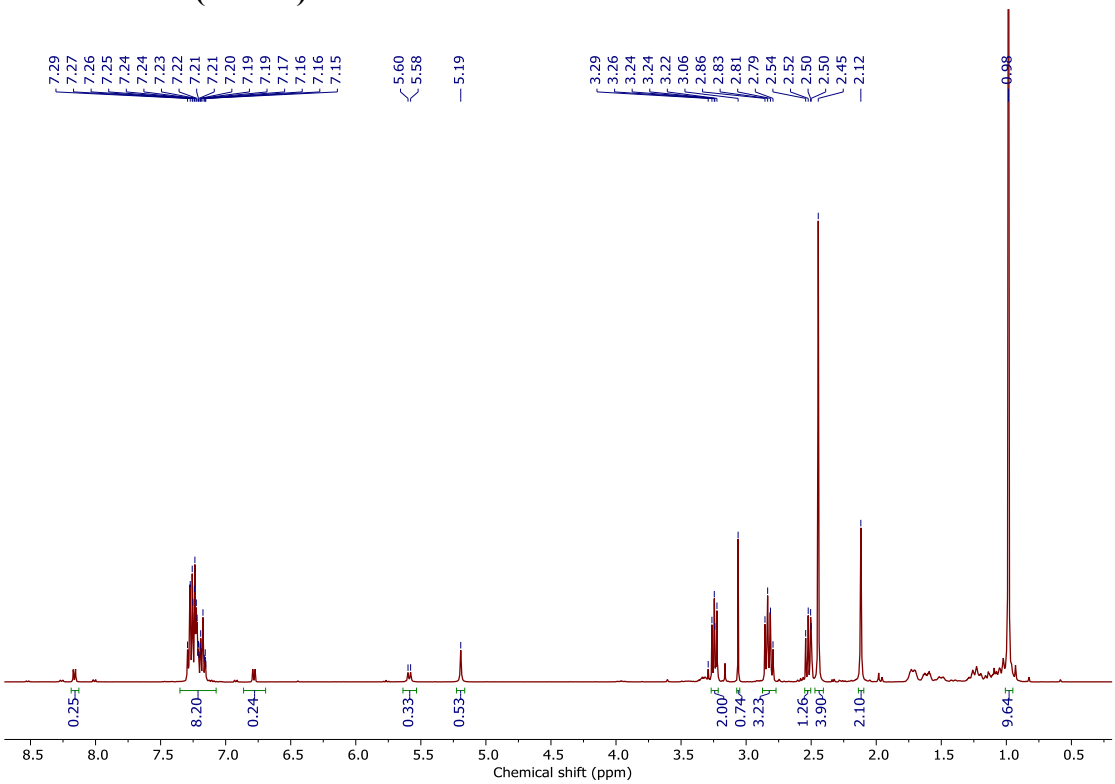



**Figure S52.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 30 min with 10 mol% DMAP using planetary mill.

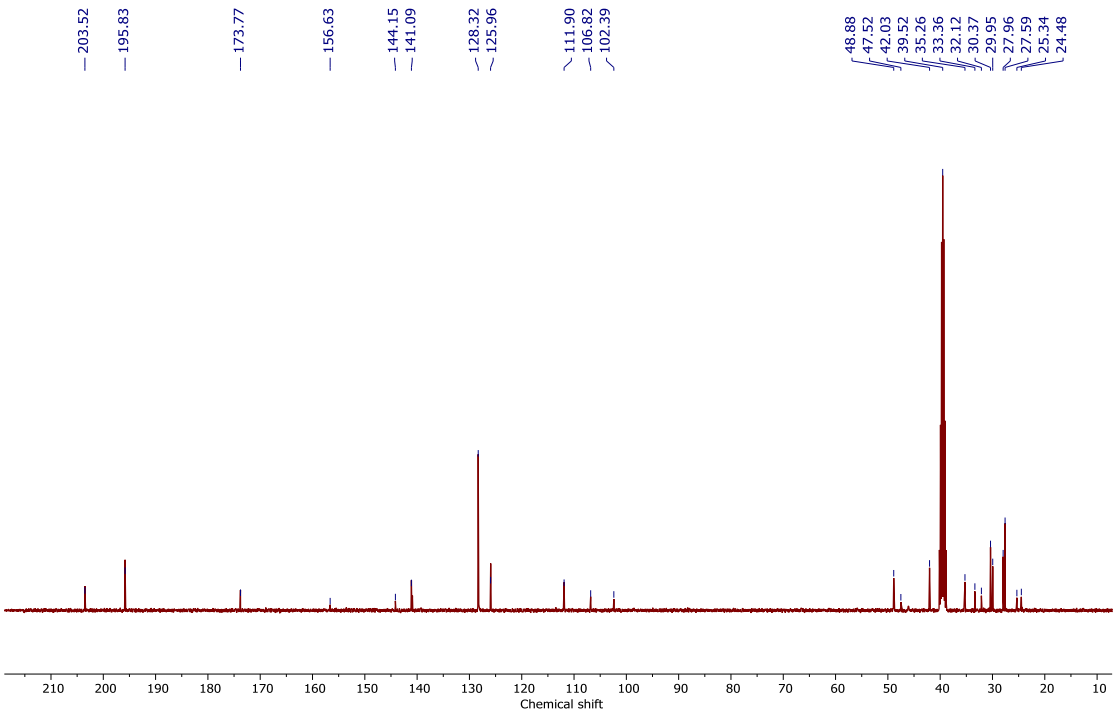



**Figure S53.** $^{13}$C NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 30 min with 10 mol% DMAP using planetary mill.

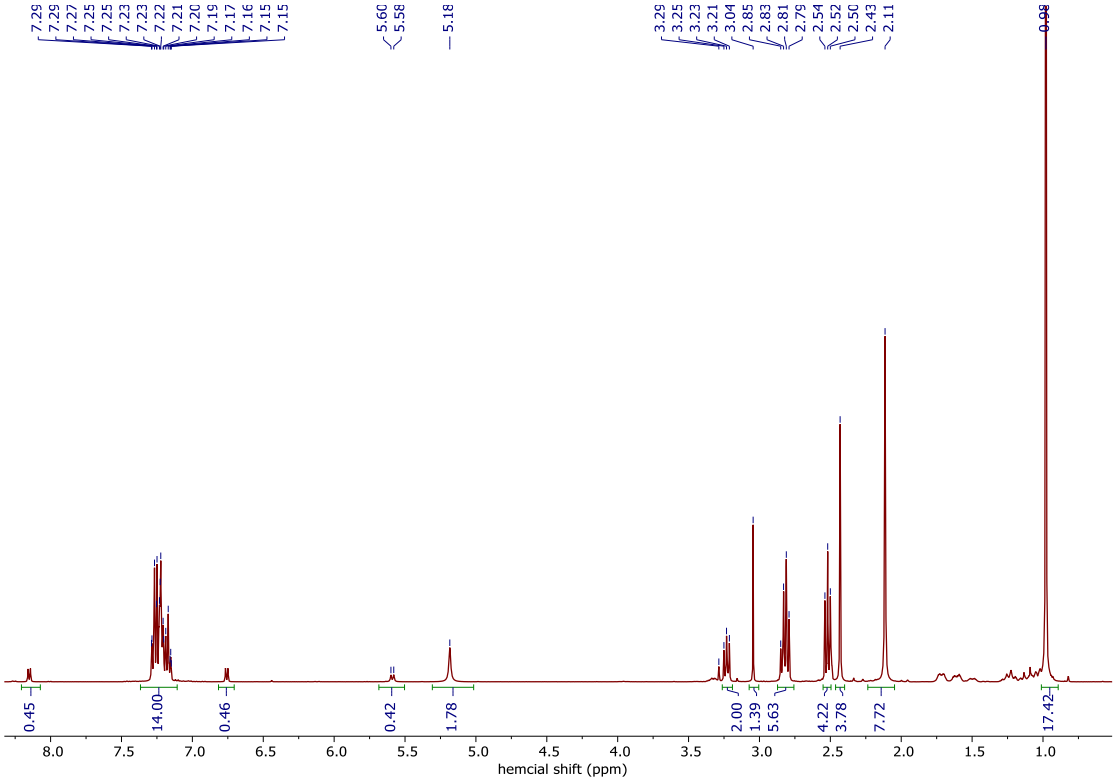



**Figure S54.** $^{1}$H NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 30 min with 10 mol% DMAP using hammer mill.

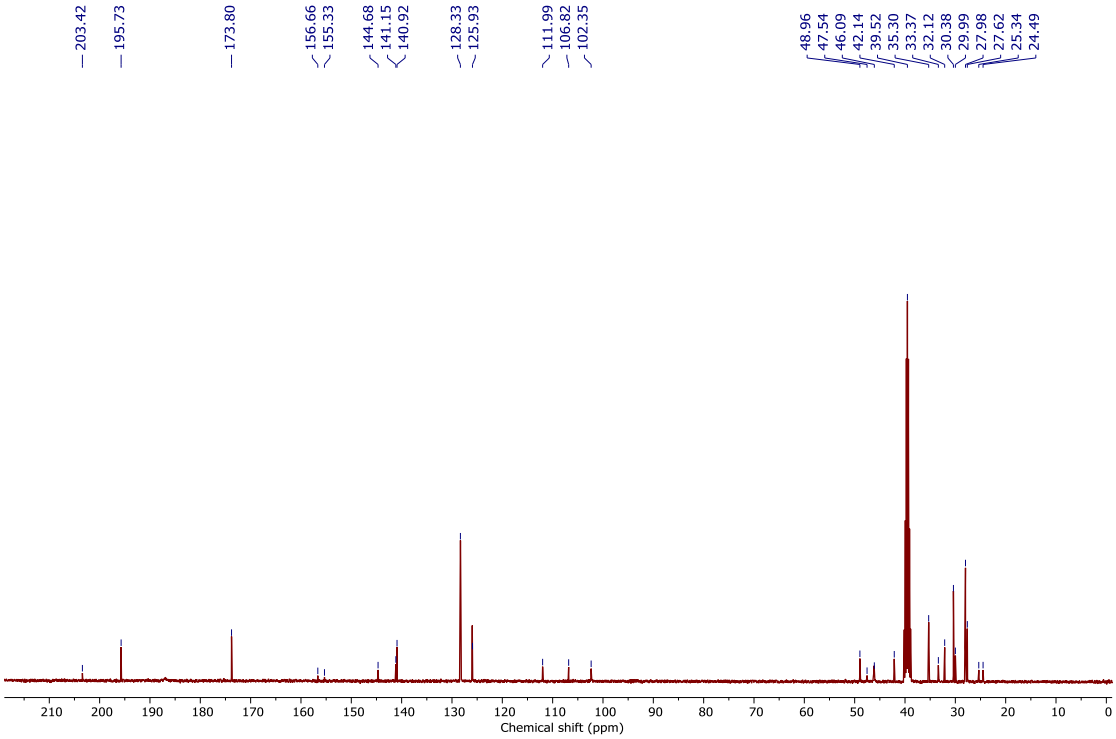



**Figure S55.** $^{13}C$ NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 30 min with 10 mol% DMAP using hammer mill.

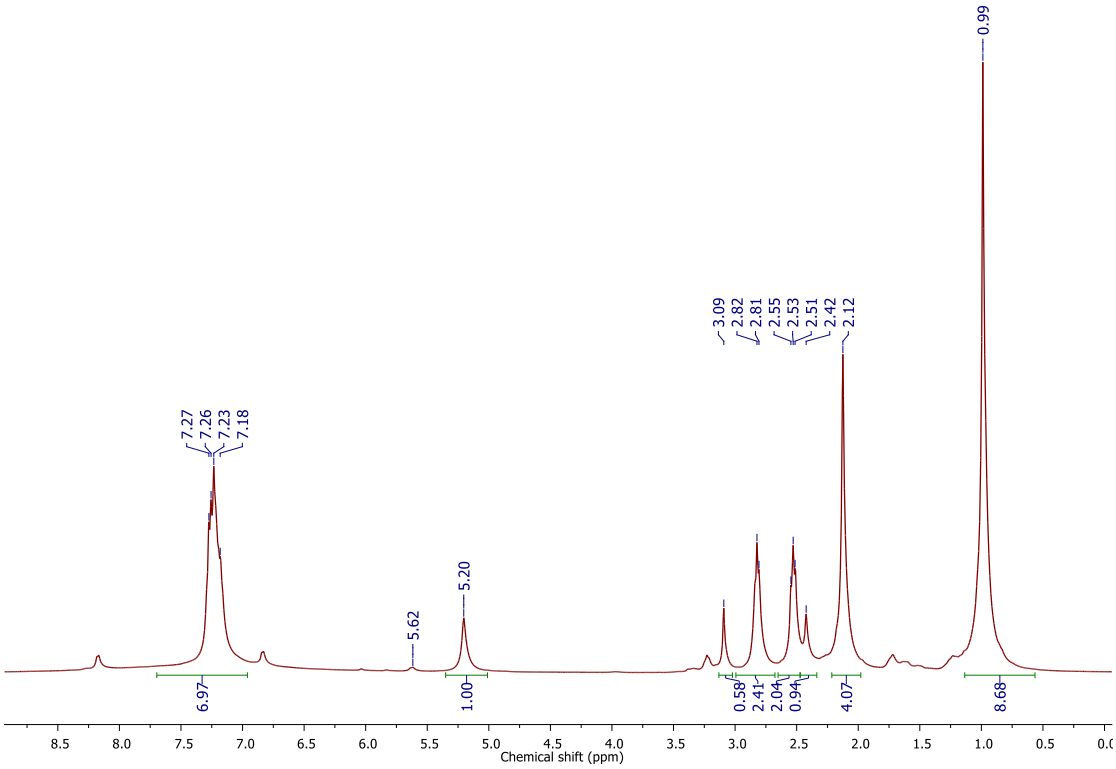



**Figure S56.** $^{1}H$ NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 10 min with 10 mol% DMAP using attritor.

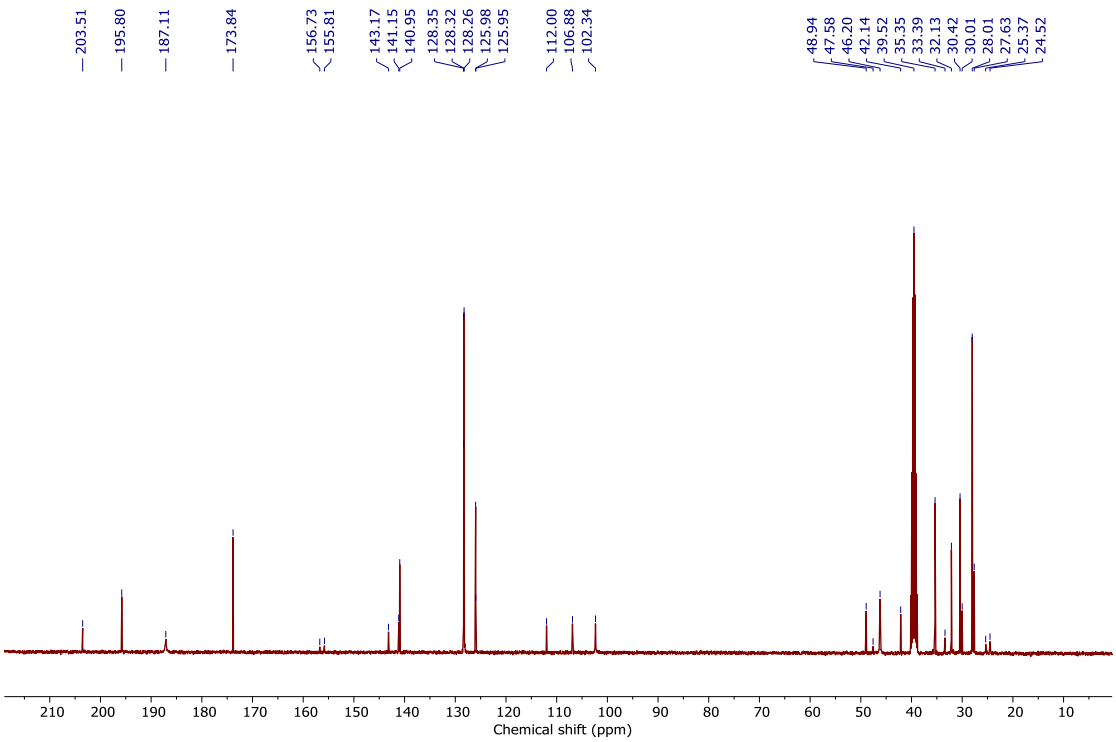
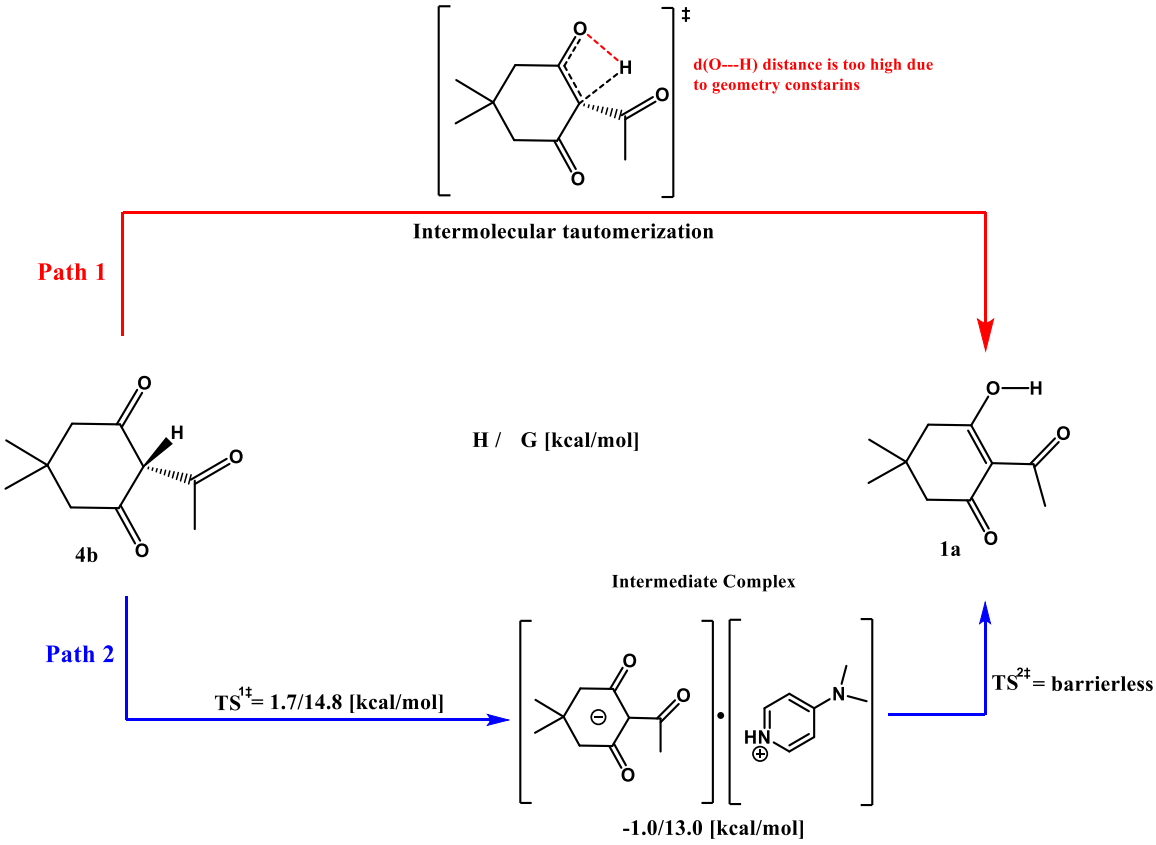



**Figure S57.** $^{13}$C NMR (400 MHz, DMSO-$d_6$) of acylation of dimedone with phenyl propanoic acid milled for 10 min with 10 mol% DMAP using attritor.

## Computational details

The calculations were performed using Orca 5.0.[2] For geometry optimizations and frequency calculations functional BP86[3]-D3(bj)[4] with def2-SVP[5] basis were used, denoted as M2 method. For single point calculations ωB97M-V[6] with def2-TZVP[5] were used, denoted as M1 method. The ωB97M-V functional was selected for the optimization of the reaction pathways due to its robust performance,[7] accuracy in representing non-covalent interactions and electronic properties.[8] All calculations (optimizations, frequency calculations and single point energies) were performed in hexane using conductor-like polarizable continuum solvation model (CPCM)[9]. PB86 functional in ORCA was treated with the RI-J approximation, whereas hybrid, ωB97M-V was treated with the chain-of-sphere approximation to evaluate exchange integrals (RIJCOSX).[10] The optimized minima and transition states were verified by harmonic vibrational analysis to have no and one proper imaginary frequency, respectively. All transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations.[11] The quoted energies electronic single point energies by M1 with inclusion of zero-point, enthalpy, and entropic corrections determined from vibrational frequencies calculated at M2 method (M1//M2) at 298.15K. Conformational search and analysis were performed using CREST package.[12]

**Alternative paths for $TS_{3b}$**




**Scheme S1.** Alternative paths for $TS_{3b}$

**Table S1.** Gibbs free energy (kcal/mol) for Scheme 2 values at different temperatures

| Temp | reverse barrier | 2a_CO | TS2a | Start | TS1a | 1a_CC | reverse barrier |
|---|---|---|---|---|---|---|---|
| 25 | 33.2 | -14.2 | 19.0 | 0.0 | 24.4 | -23.4 | 47.8 |
| 45 | 33.0 | -13.3 | 20.9 | 0.0 | 26.3 | -22.3 | 48.1 |
| 65 | 32.7 | -12.4 | 22.8 | 0.0 | 28.3 | -21.3 | 48.3 |
| 85 | 32.5 | -11.5 | 24.7 | 0.0 | 30.2 | -20.2 | 48.6 |
| 105 | 32.2 | -10.6 | 26.6 | 0.0 | 32.2 | -19.2 | 48.8 |
| 125 | 32.0 | -9.8 | 28.5 | 0.0 | 34.1 | -18.1 | 49.1 |
| 145 | 31.8 | -8.9 | 30.4 | 0.0 | 36.1 | -17.1 | 49.4 |
| 165 | 31.5 | -8.0 | 32.3 | 0.0 | 38.1 | -16.0 | 49.6 |
| 185 | 31.3 | -7.1 | 34.2 | 0.0 | 40.0 | -15.0 | 49.9 |
| 205 | 31.0 | -6.2 | 36.1 | 0.0 | 42.0 | -13.9 | 50.2 |
| 225 | 30.8 | -5.3 | 38.0 | 0.0 | 43.9 | -12.9 | 50.4 |
| 245 | 30.5 | -4.4 | 39.9 | 0.0 | 45.9 | -11.8 | 50.7 |
| 265 | 30.3 | -3.5 | 41.8 | 0.0 | 47.8 | -10.8 | 50.9 |

**Table S2.** Scheme 2 kinetics at different temperatures

| | Free energy activation differences (kcal/mol) | Rate constants ratio |
|---|---|---|
| T[°C] | ΔΔG(TS1a-TS2a) | k(TSa1)/k(TSa2) |
| 25 | -5.4 | 9015 |
| 45 | -5.4 | 5510 |
| 65 | -5.5 | 3569 |
| 85 | -5.5 | 2427 |
| 105 | -5.6 | 1719 |
| 125 | -5.6 | 1261 |
| 145 | -5.7 | 952 |
| 165 | -5.7 | 738 |
| 185 | -5.8 | 585 |
| 205 | -5.9 | 473 |
| 225 | -5.9 | 388 |
| 245 | -6.0 | 324 |
| 265 | -6.0 | 274 |

**Table S3.** Scheme 2 thermodynamics at different temperatures

| | Products free energy differences (kcal/mol) | Thermodynamic equilibrium |
|---|---|---|
| T[°C] | ΔΔG(2a-1a) | K1a/2a |
| 25 | 9.2 | 2.E-07 |
| 45 | 9.0 | 6.E-07 |
| 65 | 8.9 | 2.E-06 |
| 85 | 8.7 | 5.E-06 |
| 105 | 8.5 | 1.E-05 |
| 125 | 8.4 | 3.E-05 |
| 145 | 8.2 | 5.E-05 |
| 165 | 8.0 | 1.E-04 |
| 185 | 7.9 | 2.E-04 |
| 205 | 7.7 | 3.E-04 |
| 225 | 7.5 | 5.E-04 |
| 245 | 7.4 | 8.E-04 |
| 265 | 7.2 | 1.E-03 |

**Table S4.** Gibbs free energy (kcal/mol) for Scheme 3 values at different temperatures

| Temp | 2a | TS1b | 3b | TS2b | 4b | TS3b | 1a | Highest activation | 2a-1a |
|---|---|---|---|---|---|---|---|---|---|
| 25 | 0.0 | 24.6 | 17.2 | 25.8 | 6.2 | 14.8 | -9.2 | 25.8 | -9.2 |
| 45 | 0.0 | 25.7 | 18.2 | 26.9 | 7.1 | 15.7 | -9.1 | 26.9 | -9.1 |
| 65 | 0.0 | 26.8 | 19.3 | 27.9 | 8.0 | 16.6 | -9.0 | 27.9 | -9.0 |
| 85 | 0.0 | 27.9 | 20.3 | 29.0 | 8.9 | 17.4 | -8.9 | 29.0 | -8.9 |
| 105 | 0.0 | 29.0 | 21.4 | 30.0 | 9.8 | 18.3 | -8.8 | 30.0 | -8.8 |
| 125 | 0.0 | 30.1 | 22.4 | 31.1 | 10.7 | 19.2 | -8.7 | 31.1 | -8.7 |
| 145 | 0.0 | 31.2 | 23.4 | 32.2 | 11.6 | 20.1 | -8.6 | 32.2 | -8.6 |
| 165 | 0.0 | 32.3 | 24.5 | 33.2 | 12.5 | 21.0 | -8.5 | 33.2 | -8.5 |

## Geometries

37

**DCC**.xyz -618.063649609

| | | | |
|---|---|---|---|
| C | -0.55948301564082 | -0.62915578794993 | -0.54223707481176 |
| N | -0.23092280058599 | -0.12673035588881 | -1.62051397470091 |
| N | -0.89601680469823 | -1.28616833144116 | 0.44599341609620 |
| C | 0.84548219649669 | 0.82751504048391 | -1.88052788305319 |
| C | 1.11027423121570 | 1.77815575907342 | -0.69995202833420 |
| C | 2.13569763087030 | 0.08526328681510 | -2.28269834374094 |
| H | 0.52311313491109 | 1.43731660487714 | -2.75499278518080 |
| C | 2.24571762701707 | 2.76403470957013 | -1.01358643989892 |
| H | 1.38381572738570 | 1.16254977741379 | 0.18717739707721 |
| H | 0.17415509115308 | 2.31641555273683 | -0.44079989744429 |
| C | 3.27101661458250 | 1.07066786992321 | -2.59923488156079 |
| H | 2.43153650441606 | -0.57436842508855 | -1.43597285710373 |
| H | 1.92592346444673 | -0.57756433522227 | -3.14759325452636 |
| C | 3.53011095840333 | 2.02670826939169 | -1.42429876868086 |
| H | 2.43359976540842 | 3.41859098048605 | -0.13649714768290 |
| H | 1.92795926298904 | 3.43648418619515 | -1.84248782283992 |
| H | 4.19478392651844 | 0.51260484689463 | -2.86006097941820 |
| H | 2.99913721925089 | 1.66425351452830 | -3.50144810710954 |
| H | 4.32771150694959 | 2.75409132746229 | -1.68508784961087 |
| H | 3.90817799377913 | 1.44182106884787 | -0.55527769732170 |
| C | -1.93625394021492 | -0.98993889065966 | 1.42855630480686 |
| C | -2.34939763579617 | 0.49144386128959 | 1.45946242775340 |
| C | -3.16227639317044 | -1.89375618601364 | 1.19196959760091 |
| H | -1.51534161103124 | -1.25641441364036 | 2.42543779362030 |
| C | -3.43906534596288 | 0.74907746936401 | 2.51116762875033 |
| H | -2.72956177118990 | 0.76824982382832 | 0.44989217785080 |
| H | -1.45474460589177 | 1.12180194998041 | 1.64906217486415 |
| C | -4.25129744086114 | -1.63955873318224 | 2.24526097923119 |
| H | -3.55942802761932 | -1.67805629106169 | 0.17471169298129 |
| H | -2.84214105603158 | -2.95622946135660 | 1.19248794940910 |
| C | -4.65916765111466 | -0.15834638134018 | 2.28782874727438 |
| H | -3.73803680357410 | 1.81837571957565 | 2.49498252555637 |
| H | -3.02027829917882 | 0.55760886730086 | 3.52516060326856 |
| H | -5.13357137572805 | -2.28200920590968 | 2.04128385935307 |
| H | -3.86859920448161 | -1.94256542436874 | 3.24625138073139 |
| H | -5.41838422866484 | 0.01191812153394 | 3.08022883665475 |
| H | -5.14400244222129 | 0.11374614213819 | 1.32288675950565 |

22

**3a**.xyz -462.522325041

| | | | |
|---|---|---|---|
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| C | -4.13322753542131 | 1.12908921385742 | 0.24522252795163 |
| C | -2.66817172211796 | 1.45635860986791 | 0.54438102702649 |
| C | -1.67840226060161 | 0.49227829868367 | 0.06150536461532 |
| C | -2.04865847334551 | -0.67878864852482 | -0.54315728466212 |
| C | -3.48222605349444 | -1.06986292425421 | -0.76370165689526 |

H -4.36313715111949 1.57154425807984 -0.75172056627690
H -4.75971864136737 1.66851290835475 0.98409382239655
H -0.61601491679338 0.74274009144416 0.21865714674884
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H -4.98042905413109 -0.47688021268886 2.34745055169765
H -4.53873291728937 -2.06188470682389 1.63191560751960
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8
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H -2.73260594705653 -3.61270149243522 0.48091542329804
H -2.27089254933910 -2.92336930820945 -1.09658410125147
H -1.22939921920336 -2.60774866469510 0.35289596780512
O -2.64780808249627 -0.48896408161537 0.86102806887584
O -4.35267601076171 -1.60538048641076 -0.11964599451441
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H -4.038836000000 -0.745984000000 -1.058703500000
H -0.574589000000 -2.182123500000 0.204070000000
H -2.512398500000 1.326927500000 1.727157500000
H -2.658089500000 1.162540000000 -0.051640500000
O -0.277022000000 0.214409500000 1.284069500000
O -2.806132000000 -3.343117500000 -0.513597000000
C -5.140407000000 0.728912000000 0.918417500000
H -5.137357500000 1.247125500000 -0.063267500000
H -6.096086500000 0.170826500000 1.006276500000
H -5.124629000000 1.503863500000 1.713583000000
C -3.975306500000 -0.914948000000 2.423622500000
H -4.905195500000 -1.510061500000 2.536441500000
H -3.114776000000 -1.602233000000 2.555218500000

| | | | |
|---|---|---|---|
| H | -3.943574000000 | -0.169764000000 | 3.245723000000 |
| C | -0.947867000000 | -0.637479000000 | -1.992107000000 |
| C | -1.275103000000 | -1.881990500000 | -2.762309000000 |
| H | -0.749747000000 | -1.822528000000 | -3.739728000000 |
| H | -0.974962500000 | -2.803037500000 | -2.233914000000 |
| H | -2.363368000000 | -1.913399000000 | -2.942951500000 |
| O | -1.490086500000 | 0.456297000000 | -2.123218000000 |
| H | -0.205994500000 | 1.607133500000 | -1.592201000000 |
| O | 0.500397500000 | -0.705544000000 | -1.661321000000 |
| C | 1.160367000000 | 0.284273500000 | -1.075012000000 |
| N | 0.735138000000 | 1.546961500000 | -1.158000000000 |
| N | 2.328726000000 | -0.057206000000 | -0.510279500000 |
| H | 2.866157500000 | 0.703631500000 | -0.086799500000 |
| C | 1.195204000000 | 2.632186000000 | -0.285775000000 |
| C | 2.231708000000 | 3.532945000000 | -0.989251500000 |
| C | -0.019679000000 | 3.433654000000 | 0.211898500000 |
| H | 1.662698500000 | 2.163320500000 | 0.613261500000 |
| C | 2.665266000000 | 4.691214500000 | -0.077747500000 |
| H | 1.768396500000 | 3.934336500000 | -1.920774500000 |
| H | 3.109967500000 | 2.928078000000 | -1.307137500000 |
| C | 0.420812000000 | 4.597356500000 | 1.111295500000 |
| H | -0.578221000000 | 3.826367000000 | -0.672164000000 |
| H | -0.690330000000 | 2.737331500000 | 0.758835000000 |
| C | 1.451010000000 | 5.502004500000 | 0.409590500000 |
| H | 3.387834500000 | 5.344739500000 | -0.614756000000 |
| H | 3.210954000000 | 4.279466500000 | 0.805095500000 |
| H | -0.469938000000 | 5.183580500000 | 1.425934500000 |
| H | 0.869359500000 | 4.182876000000 | 2.045525000000 |
| H | 1.780883000000 | 6.313864000000 | 1.091595500000 |
| H | 0.967715000000 | 5.998954000000 | -0.465447500000 |
| C | 2.664110500000 | -1.417710000000 | -0.063984500000 |
| C | 4.054867000000 | -1.835847500000 | -0.563185500000 |
| C | 2.549777000000 | -1.523254000000 | 1.465704000000 |
| H | 1.907280000000 | -2.084394500000 | -0.522493000000 |
| C | 4.400672000000 | -3.253898000000 | -0.079737000000 |
| H | 4.808762500000 | -1.113445000000 | -0.173691000000 |
| H | 4.089937500000 | -1.772874500000 | -1.670994500000 |
| C | 2.893903000000 | -2.942220500000 | 1.939357000000 |
| H | 3.259885000000 | -0.795394500000 | 1.923645500000 |
| H | 1.526944500000 | -1.211748500000 | 1.760827500000 |
| C | 4.283275000000 | -3.378264000000 | 1.447811000000 |
| H | 5.420902500000 | -3.530274500000 | -0.418895000000 |
| H | 3.704133500000 | -3.977721000000 | -0.559876500000 |
| H | 2.834909500000 | -2.995738500000 | 3.046514000000 |
| H | 2.125946500000 | -3.649528000000 | 1.552493000000 |
| H | 4.498525000000 | -4.420168000000 | 1.765457000000 |
| H | 5.057844000000 | -2.736605000000 | 1.926491500000 |

67

**TS2a**.xyz -1309.7238977

| | | | |
|---|---|---|---|
| C | 1.75517862141104 | 2.35111881311229 | 1.20029160686757 |
| C | 0.58752625364902 | 3.36235874393113 | 1.17831446213436 |
| C | -0.58387603501282 | 2.96096062551195 | 0.27697538100988 |
| C | -0.28337680611066 | 2.15912931436266 | -0.88306251552088 |
| C | 0.97577301037419 | 1.61587748714153 | -1.13149638848474 |
| C | 2.15012234728368 | 2.04063855944082 | -0.26095630553813 |
| H | 0.18855099109410 | 3.54667770245074 | 2.19726061076415 |
| H | 0.96541152910338 | 4.34172000754745 | 0.80411061237039 |
| H | -1.13261366092585 | 1.91195554741665 | -1.53166543789896 |
| H | 2.92347747264367 | 1.24584913202550 | -0.30106457815402 |
| H | 2.60656428905909 | 2.94650305730588 | -0.72050075443468 |
| O | 1.28118382030826 | 0.75836860277565 | -2.06130499290087 |
| O | -1.74608641628426 | 3.32181038496721 | 0.56279284313516 |
| C | 2.95899967629452 | 2.95576172256908 | 1.94317814934972 |
| H | 3.81481910318551 | 2.24835004936200 | 1.96091309325126 |
| H | 3.29996905891127 | 3.89250204562587 | 1.45558817434566 |
| H | 2.69458709747949 | 3.19633382248902 | 2.99400434970331 |
| C | 1.32531469809692 | 1.05141956543979 | 1.90998011534728 |
| H | 0.47245703735155 | 0.57060302549914 | 1.39078000745953 |
| H | 2.16278758784031 | 0.32300143379391 | 1.93419613309786 |
| H | 1.01711430175392 | 1.25460887291407 | 2.95612056200368 |
| C | 0.06842062139230 | -0.23745741122489 | -3.12439148040067 |
| C | -0.59115801967148 | 0.80028509975040 | -3.99689674548999 |
| H | 0.15471976218888 | 1.57628414800669 | -4.24808414447227 |
| H | -0.92091519468924 | 0.30500054326345 | -4.93148869009640 |
| H | -1.45734291814687 | 1.27527677198941 | -3.50530225530440 |
| O | 0.72926592154727 | -1.18270434689053 | -3.52434853134399 |
| H | -1.12718088999901 | -1.90025210130595 | 0.89156850077743 |
| O | -0.96022006691106 | -0.55990255446923 | -1.97914624013912 |
| C | -0.55717366529666 | -1.26354772818629 | -0.94566382019047 |
| N | -1.31207361068324 | -1.20531807613737 | 0.16479864123640 |
| N | 0.55247607546291 | -2.00898236196866 | -1.00360393441641 |
| H | 0.98594125468805 | -1.98927699890589 | -1.95067318356566 |
| C | 1.34292354681359 | -2.43332663649845 | 0.15278791594869 |
| C | 1.14090402595976 | -3.91868010477757 | 0.50133171707368 |
| C | 2.82393055666979 | -2.11465586734069 | -0.10670892907360 |
| H | 1.01239501407338 | -1.82175563406719 | 1.02224407170401 |
| C | 2.01041808718959 | -4.31783104857198 | 1.70376482036492 |
| H | 1.41086948444724 | -4.52964884747839 | -0.38842488056341 |
| H | 0.06699447373575 | -4.11780536323762 | 0.70631491646436 |
| C | 3.69422402029926 | -2.51878231914165 | 1.09045026953911 |
| H | 3.14902024674911 | -2.67232929052658 | -1.01388193357740 |
| H | 2.92421213284212 | -1.03576314377474 | -0.34260435581017 |
| C | 3.49353389471245 | -3.99750500831369 | 1.45821922605802 |
| H | 1.87453298287546 | -5.39590411216641 | 1.92963776761168 |
| H | 1.66164612529025 | -3.76213007734324 | 2.60381078147303 |
| H | 4.76141668277279 | -2.31231668426997 | 0.86653522376625 |

| | | | |
|---|---|---|---|
| H | 3.43018629842108 | -1.88060951661899 | 1.96428129019285 |
| H | 4.09665057954888 | -4.25859307537043 | 2.35291431971530 |
| H | 3.87166107700620 | -4.63431768412072 | 0.62688895430267 |
| C | -2.36010096333816 | -0.20522780191878 | 0.42271803961587 |
| C | -3.69191013880154 | -0.53068386496331 | -0.27062618120054 |
| C | -2.54037030252926 | -0.04515758998727 | 1.93855245023806 |
| H | -1.98162905571787 | 0.75482651494964 | 0.02060733796753 |
| C | -4.71871039502690 | 0.57268436099489 | 0.03004222993119 |
| H | -4.06549943195528 | -1.51383560152038 | 0.09669947469115 |
| H | -3.52434421751086 | -0.62935477081001 | -1.36213532516025 |
| C | -3.58766299222507 | 1.03478832918693 | 2.24988491725990 |
| H | -2.85825641229956 | -1.02360431886419 | 2.37069656535458 |
| H | -1.56616914949650 | 0.21779385699940 | 2.40133635004701 |
| C | -4.92158118209856 | 0.74915764456608 | 1.54288767106103 |
| H | -5.68158770387637 | 0.34395909986561 | -0.47284987971956 |
| H | -4.35028471150204 | 1.53103474323485 | -0.39893238769346 |
| H | -3.73367267198884 | 1.10885537326466 | 3.34798032386446 |
| H | -3.18681378531368 | 2.01242952970442 | 1.90512736981021 |
| H | -5.64169634137214 | 1.57054540984929 | 1.74148652967240 |
| H | -5.37580214334229 | -0.17821223163693 | 1.96190871396826 |

35

**TS3b**_withACOH.xyz -844.273284071

| | | | |
|---|---|---|---|
| C | -6.42916966340875 | -0.89946814321691 | -0.39829610687689 |
| C | -4.90467779372803 | -1.13245304023519 | -0.43486890920283 |
| C | -4.09171570434509 | 0.14580280506859 | -0.26390385565640 |
| C | -4.61957126332812 | 1.17380918030439 | 0.68921279733212 |
| C | -5.87736128213046 | 0.88274349048237 | 1.38888323972880 |
| C | -6.75063868966685 | -0.28101781677792 | 0.97388338710779 |
| H | -4.61959688474744 | -1.82707005791058 | 0.38892237429590 |
| H | -4.57501178212262 | -1.60647425674946 | -1.38106134919988 |
| H | -3.74822794602807 | 1.16692368908088 | 1.76752656002501 |
| H | -6.63357949369607 | -1.05134511401455 | 1.77099258849585 |
| H | -7.80523731264321 | 0.06032217951283 | 1.04741589883941 |
| O | -6.26080307720585 | 1.55561015542368 | 2.38280591426205 |
| O | -3.01960726472542 | 0.28322247928445 | -0.85490342121989 |
| C | -6.85345816041029 | 0.05433525482766 | -1.53384429334464 |
| H | -6.58579403757800 | -0.37110121172815 | -2.52258826052222 |
| H | -7.95019639780736 | 0.21951903782580 | -1.51703354432673 |
| H | -6.36481555179417 | 1.04697184703595 | -1.45127311188337 |
| C | -7.17027472678316 | -2.23849975164139 | -0.54763944349430 |
| H | -8.26857338705338 | -2.09395046012393 | -0.47888166963306 |
| H | -6.94899354196603 | -2.70477132673688 | -1.52957628746653 |
| H | -6.86959053698957 | -2.95417123192416 | 0.24547154055503 |
| C | -4.38083281880684 | 2.65758525624595 | 0.40738087523327 |
| C | -3.60581698408379 | 3.04091866282757 | -0.83582414409505 |
| H | -4.04120824178960 | 2.57440276545034 | -1.74218618763725 |

| | | | |
|---|---|---|---|
| H | -3.61668296037070 | 4.14278146537131 | -0.92149898352435 |
| H | -2.57026808463661 | 2.65707487098928 | -0.76941431418310 |
| O | -4.81109690218243 | 3.52014732231149 | 1.16748240567373 |
| O | -2.97647618116701 | 1.30137972088576 | 2.74778468015554 |
| C | -3.36067879254062 | 2.06158996524700 | 3.69588113757159 |
| O | -4.54984642226700 | 2.52322629223611 | 3.84119636686578 |
| H | -5.29233030712446 | 2.19292155471114 | 3.08158711558031 |
| C | -2.34170766626899 | 2.48194327415446 | 4.71863235392120 |
| H | -1.55937716674997 | 1.70906794251165 | 4.82460620222667 |
| H | -1.85818535631260 | 3.41348864115368 | 4.35613888528155 |
| H | -2.82654620254111 | 2.69936812211675 | 5.68723789111484 |

46

**TS1b**.xyz -997.401476059

| | | | |
|---|---|---|---|
| C | -5.71844391179918 | -0.37554777345726 | 1.32909564810793 |
| C | -4.33729453433042 | -0.81103517923556 | 0.79393461545426 |
| C | -3.51975080176052 | 0.30025564970589 | 0.16874075714490 |
| C | -3.85650047317450 | 1.63112568771655 | 0.35445017301146 |
| C | -4.77838466515197 | 2.03319563885894 | 1.39581242907368 |
| C | -5.51859539290985 | 0.92095313010311 | 2.14133517253639 |
| H | -3.72941841017622 | -1.23519574480061 | 1.62577791679852 |
| H | -4.43235633151933 | -1.62955051274022 | 0.04771868984104 |
| H | -3.30121508003095 | 2.41813953032742 | -0.16875676970577 |
| H | -4.91522041539302 | 0.69293185254070 | 3.05085282067612 |
| H | -6.48270052246773 | 1.33455835929605 | 2.50299619422890 |
| O | -4.90880940280914 | 3.21964873121666 | 1.75708696467792 |
| O | -2.44557451181736 | -0.14355589209707 | -0.45951825757249 |
| C | -6.69929421952078 | -0.13265181374957 | 0.16351630991008 |
| H | -6.85688293200208 | -1.06617374668036 | -0.41549733548511 |
| H | -7.68588294656977 | 0.20081176885538 | 0.54673613073645 |
| H | -6.32500212830310 | 0.64206335561847 | -0.53444102562585 |
| C | -6.28137634660867 | -1.48007566923395 | 2.24066746899194 |
| H | -7.27651957328982 | -1.19519117721138 | 2.64094496150854 |
| H | -6.39805523098950 | -2.43435931845383 | 1.68534288681336 |
| H | -5.60769563342292 | -1.66788971585289 | 3.10320480102004 |
| C | -1.05892957488741 | 0.82936359569817 | -0.59490145814901 |
| C | -0.02063486014167 | -0.24112425307474 | -0.86422381232176 |
| H | -0.20252011700936 | -0.64792938102850 | -1.87750432783724 |
| H | 0.98078804528157 | 0.23061225216734 | -0.84351758812360 |
| H | -0.05466422788068 | -1.07588989754796 | -0.14144782629788 |
| O | -1.18244588448015 | 1.85384979678590 | -1.24885902689530 |
| C | -1.20771711304131 | 0.26940201513049 | 2.06702367425982 |
| C | -1.74962846911866 | 0.59466766046173 | 3.30012435385088 |
| C | -2.11338240219458 | 1.95174117457053 | 3.58040761702756 |
| C | -1.74187633506501 | 2.92178161784483 | 2.59972892954430 |
| C | -1.22404529060896 | 2.49907002057679 | 1.38826343428492 |
| H | -0.99641007976933 | -0.77541927046327 | 1.79776673347186 |
| H | -1.94423724358105 | -0.21273070539426 | 4.01570039564070 |
| H | -1.95398133104347 | 3.98732179304462 | 2.73729010343605 |

H -1.04708887875464 3.18239361960927 0.54295995103879
N -0.98562282169721 1.19822656157400 1.10919301989336
N -2.81682521016416 2.29469060375127 4.69464721692643
C -3.21077831806788 1.27125638054273 5.65391039628521
H -2.33116723731135 0.69564954340018 6.00810466463871
H -3.67435801420080 1.75642696712877 6.53073561768987
H -3.94544975466915 0.55306051410746 5.22282319841024
C -3.41856440637888 3.62683487843427 4.78230268902291
H -4.08111935234304 3.80914779165169 3.90722004443165
H -4.01607677000560 3.68833024525421 5.70855809069653
H -2.64250088882030 4.41953831504798 4.82313335693266
21
**3b**.xyz -462.017691941
C -6.28603608960727 -0.84507252446547 -0.06147896646389
C -4.74676373355128 -0.89060891070678 0.02507175035857
C -4.06051879885154 0.47654065383226 0.25312838716877
C -4.81769193297875 1.46200513890407 0.95450287729180
C -6.15366873695853 1.29158644548002 1.42608914251714
C -6.80316158520662 -0.09008984956421 1.18015085490294
H -4.45192088933962 -1.55868111111893 0.86860837181689
H -4.30033536314752 -1.33242110507196 -0.89236498534855
H -4.33441950225800 2.43776726505416 1.13919939639367
H -6.61731604856738 -0.71421483657029 2.08607732813274
H -7.90259103413461 0.06847578030744 1.13164862371231
O -6.82651207226621 2.15547500039414 2.04660457774219
O -2.88067751428975 0.61887384691555 -0.16145182882204
C -6.72148103241734 -0.10939501660808 -1.34589712300969
H -6.34257405224556 -0.63280510278784 -2.24971746943551
H -7.82916250690920 -0.05941314509609 -1.41721459334239
H -6.32767788740065 0.92616182101148 -1.35589395888875
C -6.85709067389450 -2.27447800222077 -0.08804444377181
H -7.96771555890202 -2.26239044264762 -0.13952220197367
H -6.48162771482156 -2.84072903945302 -0.96817575151090
H -6.56755157225169 -2.83818171558802 0.82450898253016
46
**TS2b**.xyz -997.398853533
C -6.08905866236615 -0.41508442564541 1.13561978542402
C -4.64237503098768 -0.90553662366411 0.89750470994759
C -3.78562015586342 0.06373329191684 0.09296749113334
C -3.94014843466296 1.47216040051279 0.42071590669336
C -5.15177123466518 1.98989882599814 1.05242990623077
C -6.01067648132029 0.97762668580710 1.79826896317210
H -4.14368890846121 -1.01266453968386 1.88988431849705
H -4.61611279382054 -1.89499088951425 0.39730931979523
H -3.42722572030230 2.17948160232574 -0.25240432168348
H -5.52526615426981 0.87314273644350 2.79691876915821
H -7.01516676989935 1.42004543357751 1.95578562533832
O -5.42867004226508 3.20224962092120 1.07120453184642

| | | | |
|---|---|---|---|
| O | -2.93718437698090 | -0.35236208205769 | -0.72084263067292 |
| C | -6.84079760459687 | -0.32340253233132 | -0.20719860477634 |
| H | -6.89368518501911 | -1.31641413402349 | -0.70044862900094 |
| H | -7.87832339092331 | 0.03960710727189 | -0.05410613194331 |
| H | -6.33863511335411 | 0.37609555713731 | -0.90680411424591 |
| C | -6.81935181904572 | -1.39365646366228 | 2.07082893852868 |
| H | -7.85700252065658 | -1.05288740835395 | 2.27007697192768 |
| H | -6.87390349130299 | -2.40811330604137 | 1.62254775600160 |
| H | -6.29606446937145 | -1.47769370120248 | 3.04599085015337 |
| C | -2.64801805874654 | 1.62233368075048 | 2.19594507068443 |
| C | -2.40414947363811 | 3.11696983711588 | 2.11459540300654 |
| H | -3.38607417833039 | 3.62827306248049 | 2.10931755598313 |
| H | -1.84052356298969 | 3.41918559057201 | 3.02203834751891 |
| H | -1.84859693369238 | 3.44225668903242 | 1.21776603007057 |
| O | -3.18236867348644 | 1.09040829733405 | 3.17510190966115 |
| C | -0.80371121239741 | 1.11330620549690 | 0.45463566462540 |
| C | 0.18704121362997 | 0.30543076666520 | -0.06719239529630 |
| C | 0.49593244672164 | -0.94727105057414 | 0.54927318510284 |
| C | -0.25642839575382 | -1.27576909238449 | 1.72120866282338 |
| C | -1.21973807759907 | -0.40595137847989 | 2.19340296696474 |
| H | -1.08199691897255 | 2.05753899571498 | -0.02679845707851 |
| H | 0.68853551346770 | 0.63558853107002 | -0.98354954238621 |
| H | -0.09844380346774 | -2.21547742184541 | 2.26274906181214 |
| H | -1.84020982246802 | -0.59215901155954 | 3.08219299559293 |
| N | -1.48204266334877 | 0.78171189504820 | 1.58639274807935 |
| N | 1.44274624794245 | -1.78271464461808 | 0.04352703772373 |
| C | 2.16041157533460 | -1.42451256943848 | -1.17622301716479 |
| H | 2.72056562352107 | -0.47337381193324 | -1.05242699029952 |
| H | 2.88516959694255 | -2.22159420079496 | -1.41571201049076 |
| H | 1.46875811949388 | -1.31213307402407 | -2.03853810306146 |
| C | 1.70526927259518 | -3.06617323360092 | 0.68667832202437 |
| H | 0.80753922742570 | -3.72126306302688 | 0.67522453232440 |
| H | 2.51662331014415 | -3.58256058000036 | 0.14521378703579 |
| H | 2.02537798780708 | -2.93289457473199 | 1.74184482321890 |

27

**4b**.xyz

| | | | |
|---|---|---|---|
| C | -6.24818793338175 | -0.23438148454811 | 1.05495297326852 |
| C | -4.76660379853890 | -0.38809678230431 | 0.61222011684498 |
| C | -4.16288382520301 | 0.92156707930699 | 0.16365018309805 |
| C | -4.31552551404902 | 2.08217913820187 | 1.17070310427000 |
| C | -5.74769461503073 | 2.16235210366074 | 1.73951776632732 |
| C | -6.32834201464866 | 0.83921074818161 | 2.17642235475394 |
| H | -4.17238414364096 | -0.74009126748149 | 1.48458429384081 |
| H | -4.66563007661473 | -1.12265642539169 | -0.21029306971479 |
| H | -4.09509247970983 | 3.02864871150353 | 0.64514547466506 |
| H | -5.72269994053539 | 0.48705814718671 | 3.04053736644159 |
| H | -7.37300806625916 | 0.99996673519400 | 2.50631202671312 |
| O | -6.32796720633683 | 3.23464433960444 | 1.79779487790124 |

O -3.59681445415448 1.10154582438858 -0.90252075249193
C -7.10965995982709 0.19842154479879 -0.14797892653910
H -7.06348406986534 -0.55983453830715 -0.95594988295874
H -8.17054308531150 0.32051723898085 0.15115349294958
H -6.77084375398417 1.16455160562101 -0.57763870255378
C -6.74999727854083 -1.57793948159526 1.60845788687143
H -7.80652062922175 -1.49799707144924 1.93722267199765
H -6.69244505216032 -2.36837242293459 0.83215695417941
H -6.14264522368007 -1.90359546854313 2.47755751883400
C -3.30470575848414 1.87920053561807 2.32643286355182
C -2.25675153382512 2.95833068759063 2.43633608847334
H -2.75315343754036 3.93867988725121 2.59696390676144
H -1.56232467009462 2.73836408988011 3.26714601787604
H -1.70296801293409 3.03723050762471 1.47714183332738
O -3.35857846642714 0.91640801796109 3.07929956131162
25
**DMAP_COMe**.xyz -535.31232972
C -0.28376685028192 1.08536498071701 -0.36792306017081
C 0.19663765676627 -0.31282340704993 -0.62580896286664
H 0.69116909080417 -0.32205352040605 -1.61213648265289
H 0.92015858618371 -0.63993890748677 0.14837980364503
H -0.64747358263093 -1.03225207847557 -0.63507819404266
O -0.15536360805957 2.02757614528571 -1.11314162718640
C -1.19673618439771 0.32930546564413 1.85376479456265
C -1.84642108885051 0.58105442809268 3.03742371744480
C -2.32496673834679 1.90394319828582 3.34316493144058
C -2.07603279968187 2.91281030227401 2.34618863234750
C -1.42086921714810 2.59666047584188 1.18337858402459
H -0.82915156773651 -0.67389221641280 1.60863436610709
H -1.98565488006638 -0.25452712153636 3.73281427996214
H -2.39972106727862 3.95058553447987 2.48678911166365
H -1.20500351190877 3.32446906427074 0.38920911200397
N -0.97785873266419 1.31878306832868 0.92320481718516
N -2.96709917208430 2.18063228517789 4.49231192558090
C -3.19952093820485 1.12769847069366 5.48707423103636
H -2.24054340191761 0.71401376420379 5.86087648837593
H -3.75017553565656 1.55655344693454 6.34045252687362
H -3.80503559289160 0.30326453206568 5.05867260644493
C -3.43731013843869 3.54262499109761 4.77111497870400
H -4.16679226968293 3.87483649654993 4.00472603589517
H -3.93457964423257 3.55557918377697 5.75494722610997
H -2.59018781159312 4.25800541764686 4.79633815751130
27
**2b**.xyz -615.18043921
C -3.06102347931938 -0.13418274033354 -0.53920109456016
C -3.11891035602890 0.81043630429205 0.68139700363259
C -1.75005485924471 1.14677090013076 1.26672405098618
C -0.71702572118538 0.09529335329792 1.20798281470100

| | | | |
|---|---|---|---|
| C | -0.96076226665604 | -1.07802167258973 | 0.55980484962219 |
| C | -2.25856144863028 | -1.39206235010843 | -0.13256383226300 |
| H | -3.63397921300590 | 1.76250112367879 | 0.44194193742064 |
| H | -3.70503831494942 | 0.32426761727678 | 1.49578402095160 |
| H | 0.23916232900509 | 0.30355018814537 | 1.69815670041364 |
| H | -2.04256267335402 | -2.02622039681457 | -1.01795828685007 |
| H | -2.86958907980175 | -2.02407729343845 | 0.55327067370775 |
| O | -0.09296208029407 | -2.14386700288518 | 0.43542119158063 |
| O | -1.52339807116313 | 2.23626317633754 | 1.79752998370629 |
| C | -4.48253214029648 | -0.55020365386684 | -0.95230578455304 |
| H | -5.01435423392634 | -1.05109519639088 | -0.11694444177471 |
| H | -5.07860065675849 | 0.33522138684063 | -1.25394764570827 |
| H | -4.45664603372258 | -1.25222020206377 | -1.81181294898060 |
| C | -2.37194230294742 | 0.57587387432276 | -1.72289922474613 |
| H | -1.33411701062183 | 0.87881477996373 | -1.47739472364574 |
| H | -2.33259642161826 | -0.08829362335565 | -2.61080859361612 |
| H | -2.93235724968337 | 1.49034753893449 | -2.00521797127390 |
| C | 1.14762357486125 | -2.25624200466962 | 1.05559100936186 |
| C | 1.77350058833456 | -3.56675742502216 | 0.65511684367330 |
| H | 2.74758251063550 | -3.68061667855047 | 1.16107758031956 |
| H | 1.10173113269179 | -4.40680799482973 | 0.92207017597834 |
| H | 1.91122427202701 | -3.59613647339919 | -0.44463065546344 |
| O | 1.62471718065256 | -1.42270461290259 | 1.79089038337962 |

27

**1b**.xyz -615.182231223

| | | | |
|---|---|---|---|
| C | -1.92321007773650 | -0.10506864042107 | -0.55679712503064 |
| C | -0.82012893564108 | -0.97545421064747 | -1.22155662299722 |
| C | 0.13497622742579 | -1.55592932300896 | -0.20647874380026 |
| C | 0.76501558296549 | -0.52382137984134 | 0.75198612941201 |
| C | -0.28795121195296 | 0.45832977042164 | 1.30940749203348 |
| C | -1.24219738844255 | 1.01416324173045 | 0.27925051803929 |
| H | -1.26117548264137 | -1.80441638164305 | -1.80844281222706 |
| H | -0.22233913411184 | -0.32675715133245 | -1.89969976177896 |
| H | 1.21706358546671 | -1.06691564291326 | 1.60109555512400 |
| H | -1.99195662918332 | 1.64398514181851 | 0.79653555369984 |
| H | -0.64756709234832 | 1.65409014139242 | -0.40972334309118 |
| O | -0.31127947721626 | 0.72686315899997 | 2.49977938014880 |
| O | 0.40894378431287 | -2.74075351871525 | -0.10158947269076 |
| C | -2.78555402155761 | 0.53937178414030 | -1.65404255152621 |
| H | -3.27959268487855 | -0.23767017619112 | -2.27290067457413 |
| H | -3.57808186705501 | 1.17466216588464 | -1.20787212870496 |
| H | -2.17142778867196 | 1.17456368580479 | -2.32467263822131 |
| C | -2.79984955090762 | -0.98134505275598 | 0.35973335971737 |
| H | -2.20977732189628 | -1.45706510813809 | 1.17110259177343 |
| H | -3.59540238131917 | -0.37462209424425 | 0.83804677842811 |
| H | -3.28543841705331 | -1.79292851476338 | -0.21941089692541 |
| C | 1.85793088976048 | 0.28190204771950 | 0.00734410125064 |
| C | 3.23246584333978 | 0.17977851507520 | 0.61990643410832 |

| | | | |
|---|---|---|---|
| H | 3.19149244609505 | 0.51855462847194 | 1.67663537578044 |
| H | 3.55001186478753 | -0.88408153038631 | 0.64074036462084 |
| H | 3.95694655256071 | 0.78691846583947 | 0.04764376498634 |
| O | 1.61355038989929 | 0.94750181170316 | -0.98964914255480 |

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