

Electronic Supplementary Information (ESI)

Bio-based solvents as greener solvents replacement for hazardous hydrocarbon solvents for lipophilic β -diketone extraction from wheat straw wax

Pakin Noppawan^a, Suwivat Sangon^b, Petcharaphorn Chatsiri^c, Nutnicha Khunmood^d,
Suphatta Aintharabunya^b, Nontipa Supanchaiyamat^b, and Andrew J. Hunt^{b,*}

^a Department of Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham, 44150, Thailand.

^b Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand.

^c Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, 21210, Thailand.

^d Agilent Technologies, 22nd Floor, U Chu Liang Bldg, Rama IV Road, Bangrak, Bangkok, 10500, Thailand.

*Corresponding author: andrew@kku.ac.th

Contents

Page S3	Figure S1 The extraction procedure of the extraction of hentriacontane-14,16-dione from wheat straw wax
Page S3	Scheme S1 Formation of Cu(II) β -diketone complex and subsequent recovery of the β -diketone
Page S4	Table S1 Optimization results of hentriacontane-14,16-dione extraction from wheat straw wax with the extraction time = 20 min
Page S5	Figure S2 ^1H NMR spectrum of hentriacontane-14,16-dione
Page S5	Figure S3 ^{13}C NMR spectrum of hentriacontane-14,16-dione
Page S6	Figure S4 IR spectrum of hentriacontane-14,16-dione
Page S6	Figure S5 GC-FID chromatogram of the hentriacontane-14,16-dione
Page S6	Figure S6 GC-MS chromatogram of the hentriacontane-14,16-dione
Page S7	Figure S7 GC-MS of the hentriacontane-14,16-dione
Page S7	Figure S8 A proposed fragmentation scheme of the 14,16-hentriacontanedione (part 1)
Page S8	Figure S9 A proposed fragmentation scheme of the 14,16-hentriacontanedione (part 2)
Page S9	Green chemistry metrics analysis
Page S14	Table S2 Kamlet–Taft parameter of a combined measure of dipolarity and polarizability (π^*) of solvents
Page S14	Table S3 Contact angle of water on glass slide without wheat straw wax or diketone modification
Page S14	References

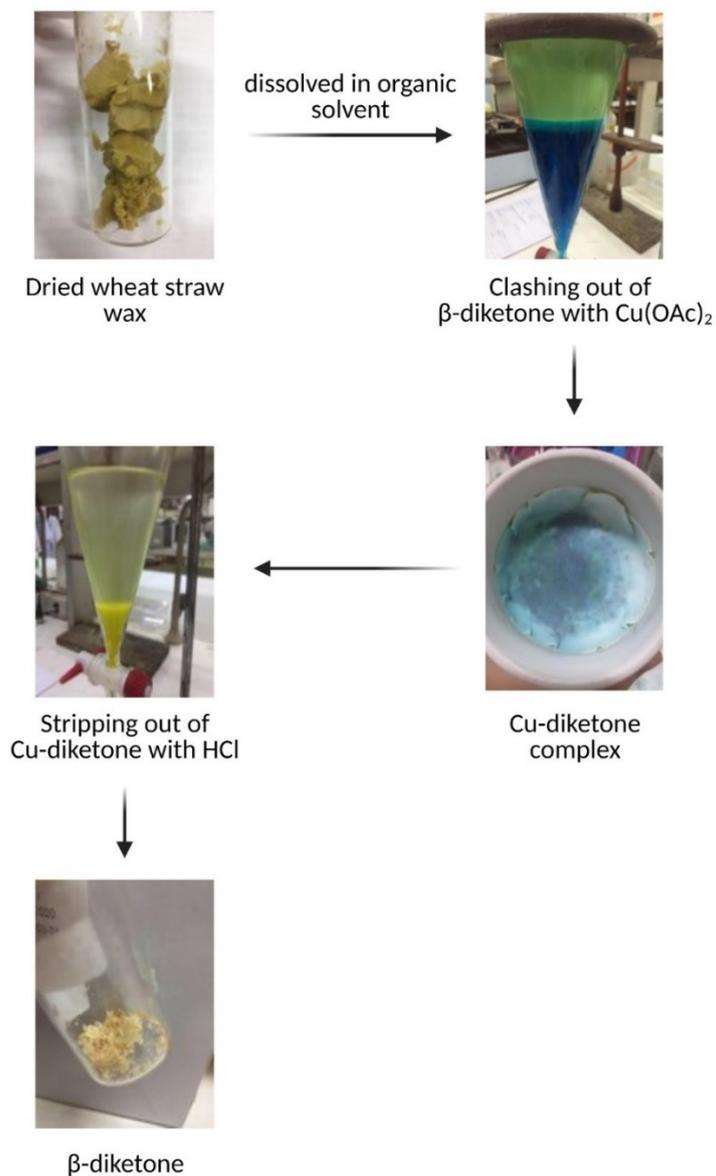
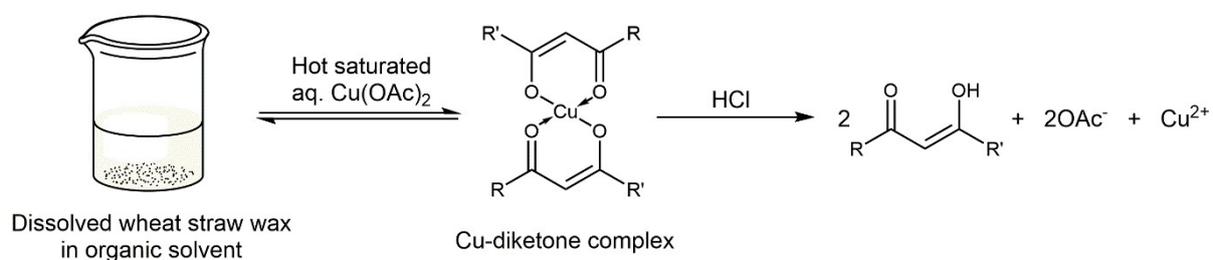


Figure S1 The extraction procedure of the extraction of hentriacontane-14,16-dione from wheat straw wax



Scheme S1 Formation of Cu(II) β -diketone complex and subsequent recovery of the β -diketone

Table S1 Optimization results of hentriacontane-14,16-dione extraction from wheat straw wax with the extraction time = 20 min

Solvent	Ratio of wax (g) to solvent (mL)					Precipitation temp.			Recovery yield of β -diketone (wt%)
	1:30	1:60	1:100	1:150	1:300	Room temperature	In fridge (h)		
							2	4	
Petroleum ether	-	-	-	-	✓	✓	-	-	12.12
	-	-	-	-	✓	-	✓	-	18.02
	-	-	-	-	✓	-	-	✓	19.62
	✓	-	-	-	-	-	-	✓	24.37
Toluene	-	-	-	-	✓	✓	-	-	-
	-	-	-	-	✓	-	✓	-	15.94
	-	-	-	-	✓	-	-	✓	29.01
	✓	-	-	-	-	-	-	✓	21.93
TMO	-	-	-	-	✓	-	-	✓	21.26
	-	-	-	✓	-	-	-	✓	20.37
	-	-	✓	-	-	-	-	✓	23.69
	-	✓	-	-	-	-	-	✓	20.38
	✓	-	-	-	-	-	-	✓	21.80
DEDMO	✓	-	-	-	-	-	-	✓	23.70

^bStandard deviation less than 0.5%.

2555_Htd1.1.fid
2555_Htd1

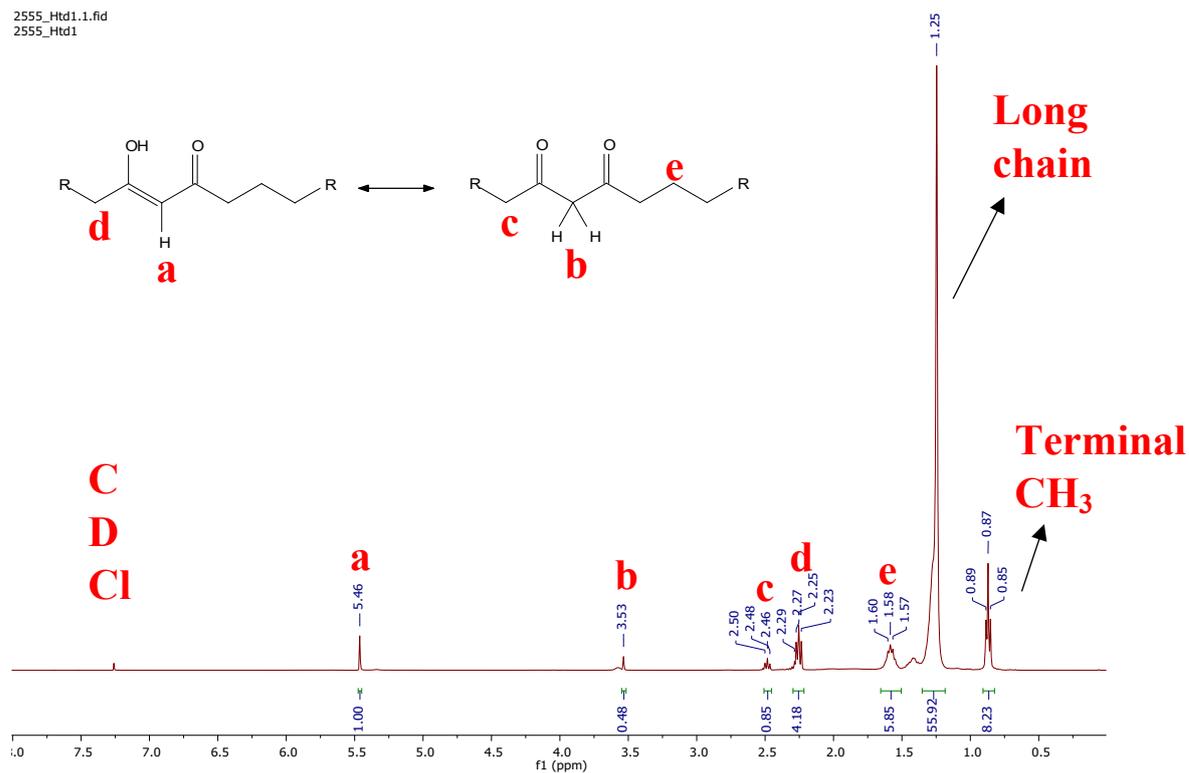


Figure S2 ^1H NMR spectrum of hentriacontane-14,16-dione

3299_Htd4_Tol_C.2.fid
3299_Htd4_Tol_C

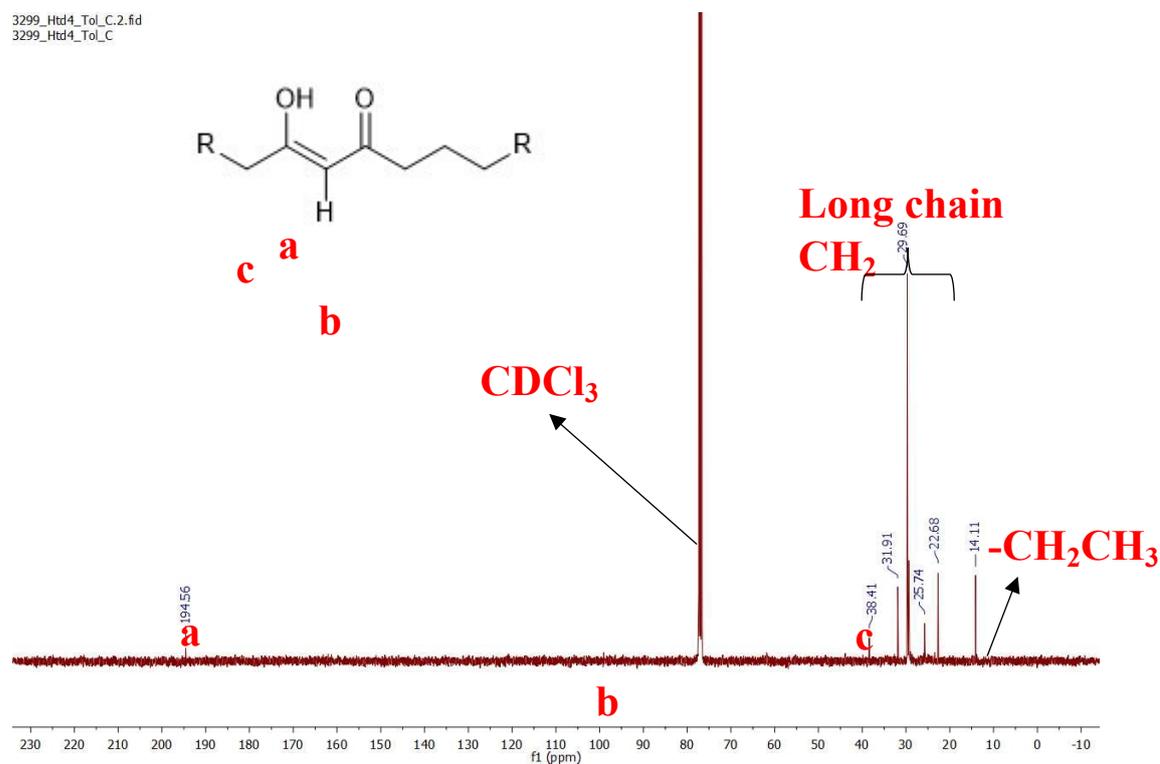


Figure S3 ^{13}C NMR spectrum of hentriacontane-14,16-dione

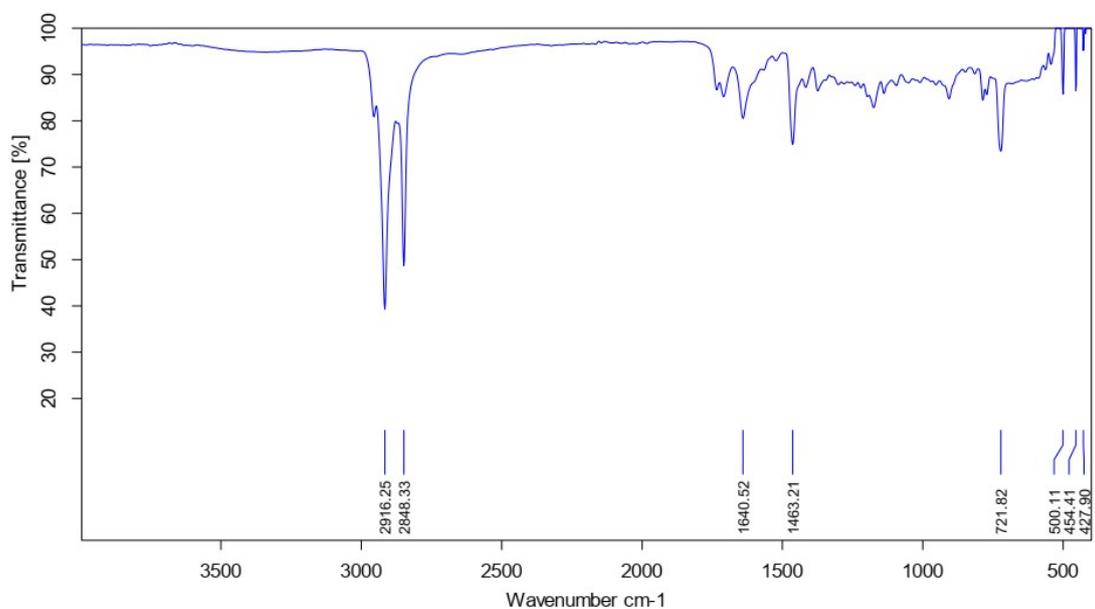


Figure S4 IR spectrum of hentriacontane-14,16-dione

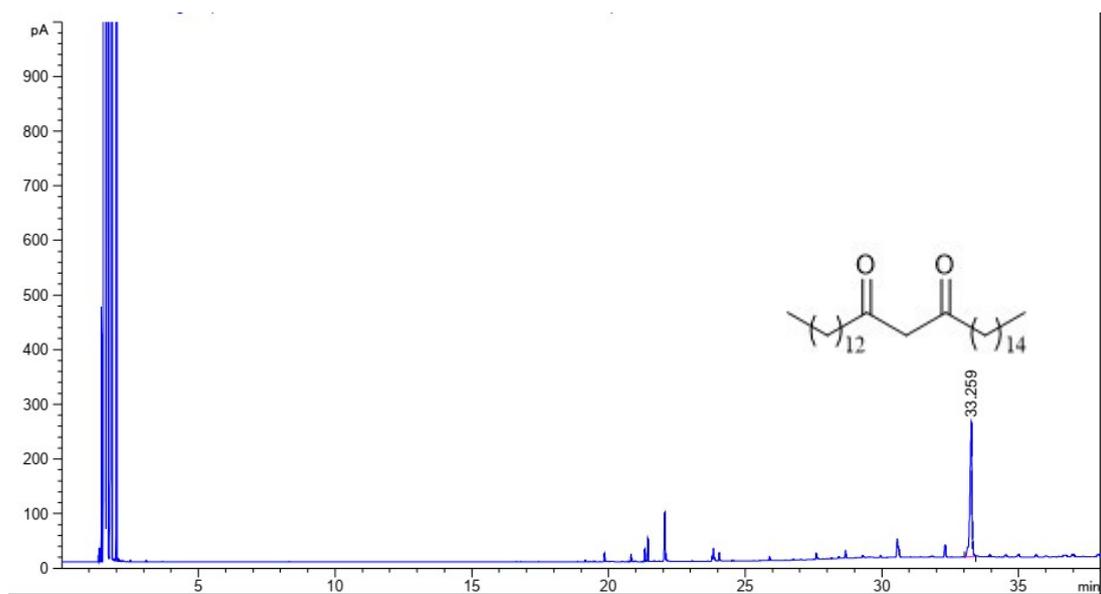


Figure S5 GC-FID chromatogram of the hentriacontane-14,16-dione

Figure S6 GC-MS chromatogram of the hentriacontane-14,16-dione

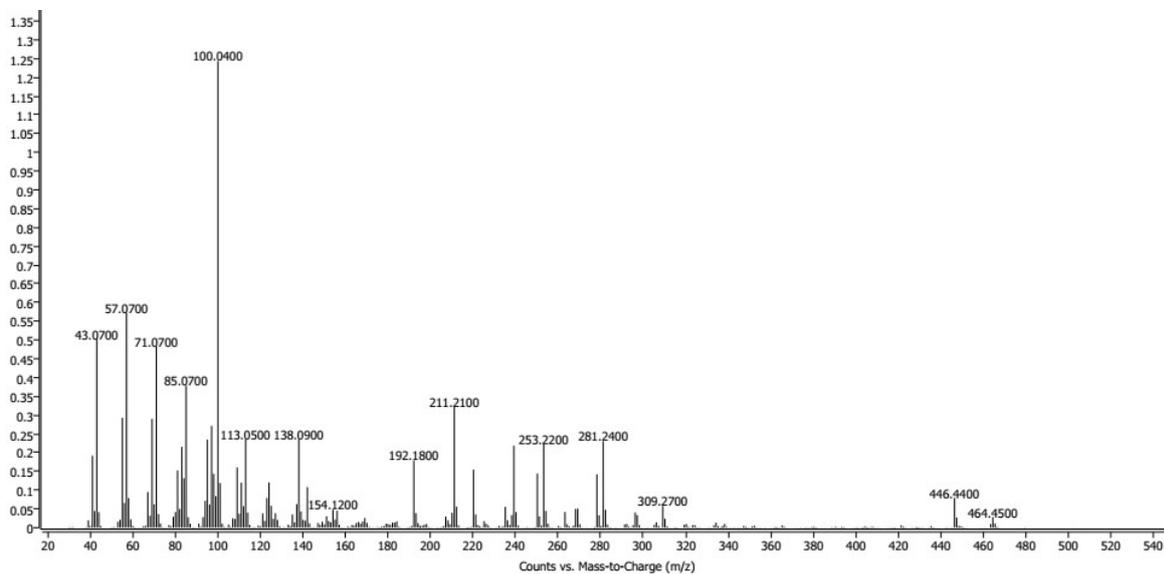
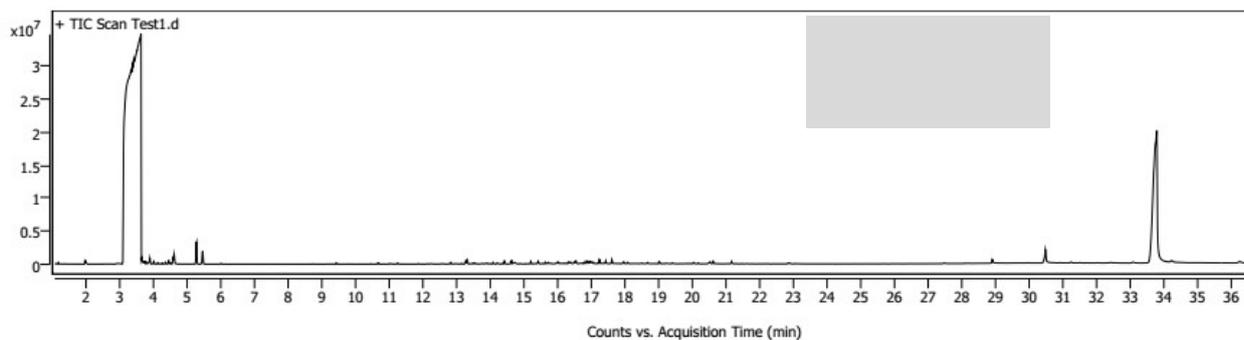


Figure S7 GC-MS of the hentriacontane-14,16-dione



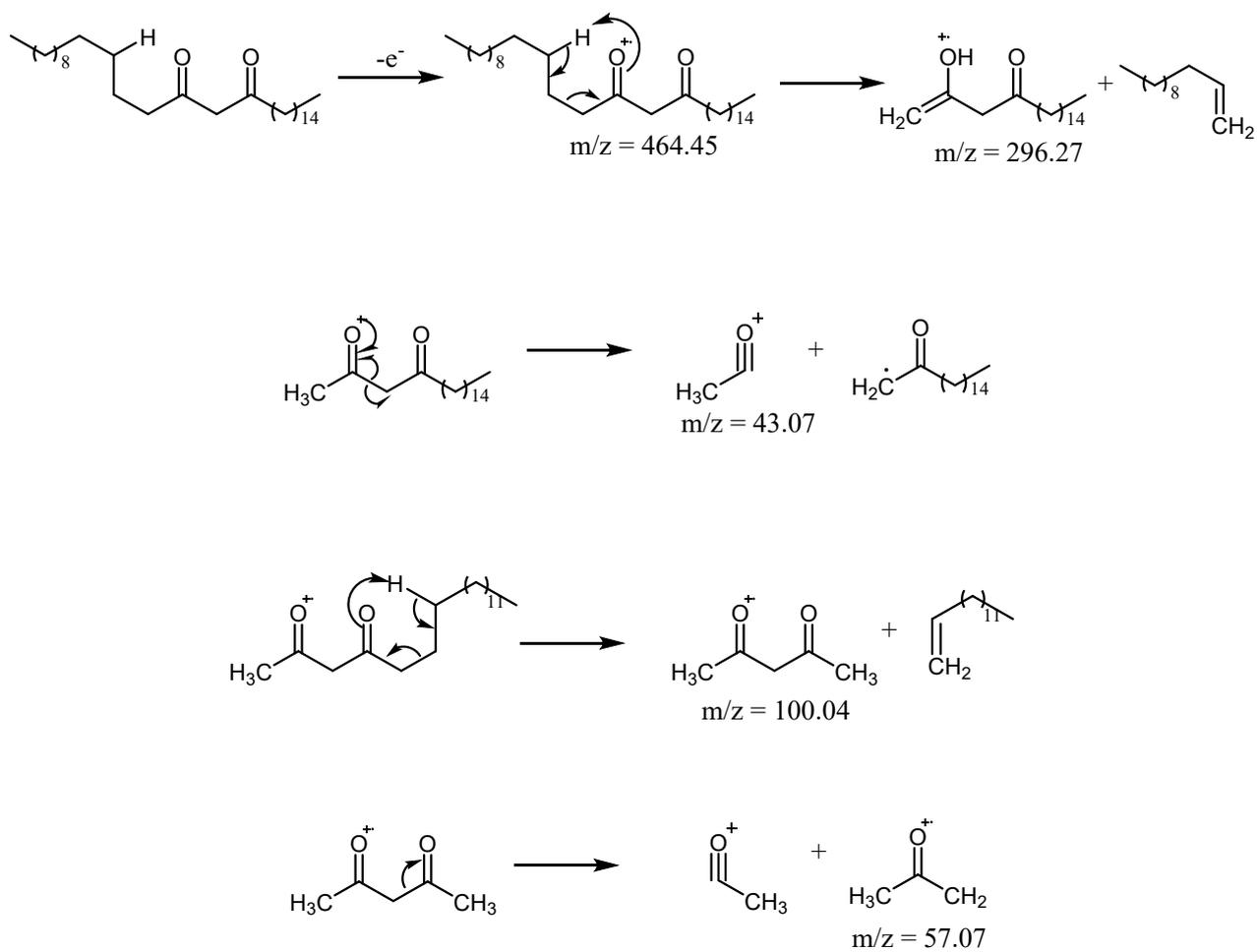
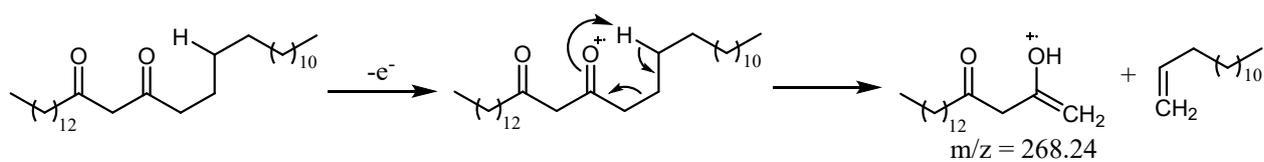


Figure S8 A proposed fragmentation scheme of the 14,16-hentriacontanedione (part 1)



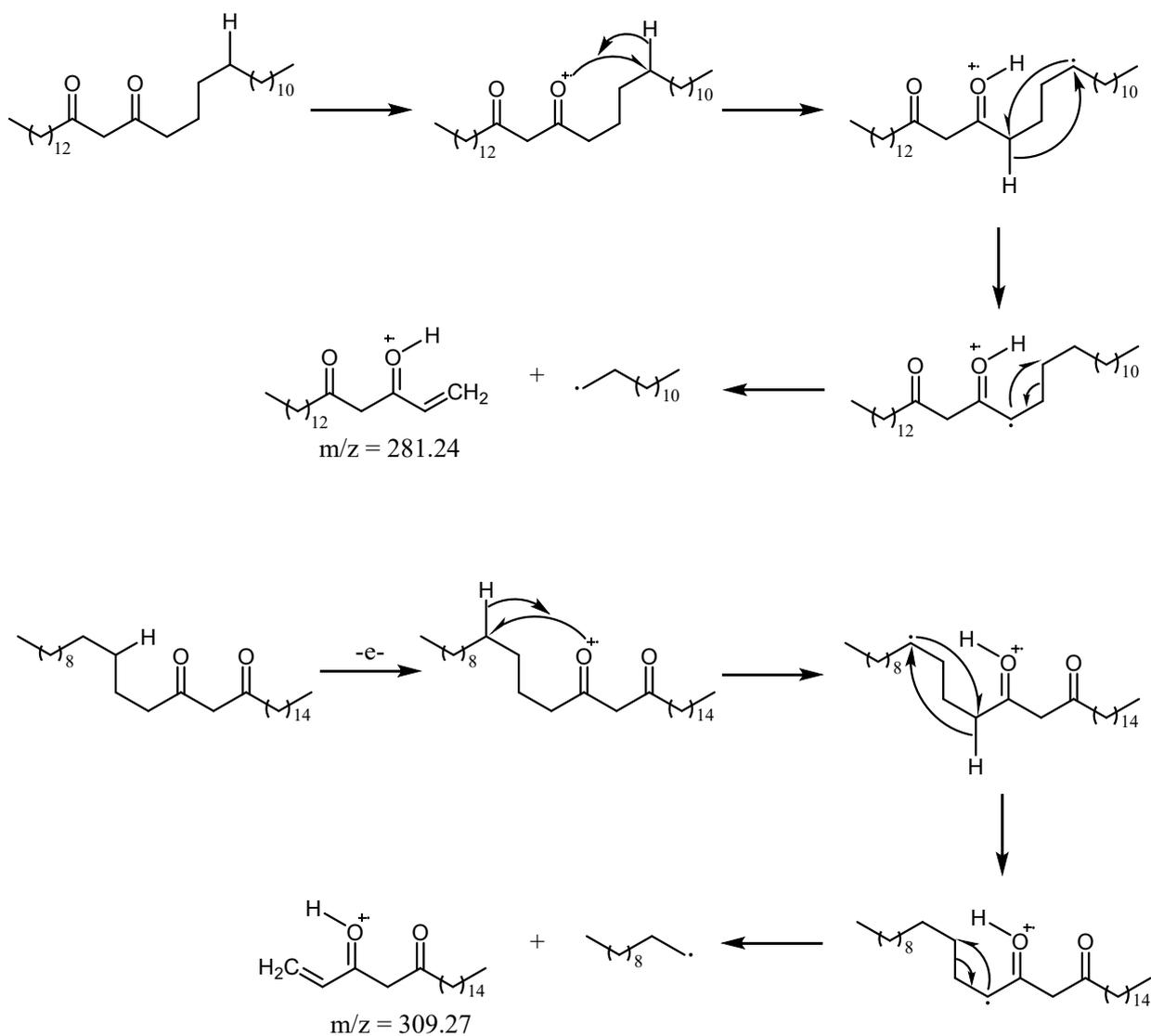


Figure S9 A proposed fragmentation scheme of the 14,16-hentriacontanedione (part 2)

Green chemistry metrics analysis

The following formulae were used for calculating Process Mass Intensity (PMI), E-factor, Solvent and Water Intensity (SI and WI).¹⁻¹³

Total mass of input material in the whole process

$$\text{PMI} = \frac{\text{Mass of product}}$$

$$\text{E Factor} = \text{PMI} - 1$$

SI =

Total mass of solvents excl. water in the whole process

Mass of product

Total mass of water used in the whole process

$$\text{WI} = \frac{\text{Mass of product}}$$

Reported procedures for process A do not always contain all the required information; therefore, some realistic assumptions were used where appropriate and are italicized in the calculations given below.

Experimental procedures: 1 g of wheat straw wax was crushed with a spatula in a beaker and dissolved in 200 mL of solvent. The mixture was stirred at room temperature for 30 min and transferred to a separatory funnel, followed by the addition of 100 mL hot excess saturated aqueous $\text{Cu}(\text{OAc})_2$. Then the mixture was shaken for 20 min and allowed to stand for 1 hour. The organic phase becomes green, while the aqueous phase becomes light blue with a dark blue of Cu-diketones in between the two phases. The system was heated with a heat-gun to afford proper separation. The organic phase was collected and kept for 2 hours at room temperature. The precipitate was then filtered and washed with 5 mL of extraction solvent. The copper salt was re-dissolved in 100 mL of hot chosen solvent and transferred to a separating flask followed by the addition of 2 mL of hydrochloric acid. The mixture was shaken for 10 min to strip out the Cu(II) ions from hentriacontane-14,16-dione in the organic phase and washed with 100 mL deionized distilled water. The product was recovered from the organic layer by removing the solvent under a vacuum in a rotary evaporator.

Materials used for metrics calculations: wheat straw wax (1g), petroleum ether (A1, 305 mL, 199.2 g), cyclohexane (A2, 305 mL, 237.6 g), p-cymene (A3, 305 mL, 261.4 g), CPME (A4, 305 mL, 263.2), $\text{Cu}(\text{OAc})_2$ (10 g), HCl (2 mL, 2.4 g), water (200 mL, 200 g), product A1 (0.18 g), product A2 (0.06 g), product A3 (0.082 g), product A4 (0.078 g)

Petroleum ether (process A1)

$$\text{PMI} = \frac{199.2 + 10 + 2.4 + 200}{0.18} = 2292$$

$$\text{E Factor} = 2292 - 1 = 2291$$

$$\text{SI} = \frac{199.2}{0.18} = 1106$$

$$\text{WI} = \frac{200}{0.18} = 1111$$

Cyclohexane (process A2)

$$\text{PMI} = \frac{237.6 + 10 + 2.4 + 200}{0.06} = 7516$$

$$\text{E Factor} = 7516 - 1 = 7515$$

$$\text{SI} = \frac{237.6}{0.06} = 3960$$

$$\text{WI} = \frac{200}{0.06} = 3333$$

p-Cymene (process A3)

$$\text{PMI} = \frac{261.4 + 10 + 2.4 + 200}{0.082} = 5790$$

$$\text{E Factor} = 5790 - 1 = 5789$$

$$\text{SI} = \frac{261.4}{0.082} = 3188$$

$$WI = \frac{200}{0.082} = 2439$$

CPME (process A4)

$$PMI = \frac{263.2 + 10 + 2.4 + 200}{0.078} = 6110$$

$$E \text{ Factor} = 6110 - 1 = 6109$$

$$SI = \frac{263.2}{0.078} = 3375$$

$$WI = \frac{200}{0.078} = 2564$$

Current work (This work)

Experimental procedures: 1 g of wheat straw wax was crushed with a spatula in a beaker and dissolved in 20 mL of solvent. The mixture was stirred at room temperature for 30 min and transferred to a separatory funnel, followed by the addition of 10 mL hot excess saturated aqueous $\text{Cu}(\text{OAc})_2$. Then the mixture was shaken for 20 min and allowed to stand for 1 hour. The organic phase becomes green, while the aqueous phase become light blue with a dark blue of Cu-diketones in between the two phases. The system was heated with a heat-gun to afford proper separation. The organic phase was collected and kept for 2 hours at room temperature followed by kept in the refrigerator for 4 hours for the complete crashing of Cu-diketones. The precipitate was then filtered and washed with 5 mL of extraction solvent. The copper salt was re-dissolved in 10 mL of hot chosen solvent and transferred to a separating flask followed by the addition of 0.2 mL of hydrochloric acid. The mixture was shaken for 10 min to strip out the Cu(II) ions from hentriacontane-14,16-dione in the organic phase and

washed with 10 mL deionized distilled water. The product was recovered from the organic layer by removing the solvent under a vacuum in a rotary evaporator.

Materials used for metrics calculations: wheat straw wax (1g), petroleum ether (B1, 35 mL, 22.9 g), toluene (B2, 35 mL, 30.3 g), TMO (B3, 35 mL, 28.1 g), DEDMO (B4, 35 mL, 29.3), Cu(OAc)₂ (1 g), HCl (0.2 mL, 0.2 g), water (20 mL, 20 g), product B1 (0.244 g), product B2 (0.219 g), product B3 (0.218 g), product B4 (0.237 g)

Petroleum ether (process B1)

$$\text{PMI} = \frac{22.9 + 1 + 0.2 + 20}{0.244} = 185$$

$$\text{E Factor} = 185 - 1 = 184$$

$$\text{SI} = \frac{22.9}{0.244} = 94$$

$$\text{WI} = \frac{20}{0.244} = 82$$

Cyclohexane (process B2)

$$\text{PMI} = \frac{30.3 + 1 + 0.2 + 20}{0.219} = 240$$

$$\text{E Factor} = 240 - 1 = 239$$

$$\text{SI} = \frac{30.3}{0.219} = 139$$

$$WI = \frac{20}{0.219} = 91$$

TMO (process B3)

$$PMI = \frac{28.1 + 1 + 0.2 + 20}{0.218} = 231$$

$$E \text{ Factor} = 231 - 1 = 230$$

$$SI = \frac{28.1}{0.218} = 129$$

$$WI = \frac{20}{0.218} = 92$$

DEDMO (process B4)

$$PMI = \frac{29.3 + 1 + 0.2 + 20}{0.237} = 217$$

$$E \text{ Factor} = 217 - 1 = 216$$

$$SI = \frac{29.3}{0.237} = 124$$

$$WI = \frac{20}{0.237} = 84$$

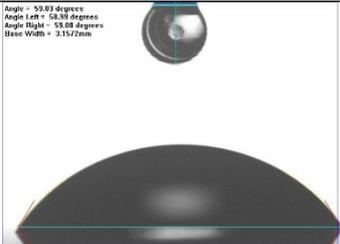
Table S2 Kamlet–Taft parameter of a combined measure of dipolarity and polarizability (π^*) of solvents

Solvent	π^*
Petroleum ether	-0.16 [#]
Toluene	0.51 ^{15,16}

TMO	0.35 ^{15,16}
DEDMO	0.31 ¹⁶

This work

Table S3 Contact angle of water on glass slide without wheat straw wax or β -diketone modification

Contact angle (degree)	Standard deviation	Picture
59.32	0.42	

References

- 1 C. R. McElroy, A. Constantinou, L. C. Jones, L. Summerton and J. H. Clark, *Green Chem.*, 2015, **17**, 3111–3121.
- 2 F. Roschangar, R. A. Sheldon and C. H. Senanayake, *Green Chem.*, 2015, **17**, 752–768.
- 3 C. Jimenez-Gonzalez, C. S. Ponder, Q. B. Broxterman and J. B. Manley, *Org. Process Res. Dev.*, 2011, **15**, 912–917.
- 4 C. Jiménez-González, D. J. C. Constable and C. S. Ponder, *Chem. Soc. Rev.*, 2012, **41**, 1485–1498.
- 5 J. Augé, *Green Chem.*, 2008, **10**, 225–231.
- 6 J. Andraos, *Org. Process Res. Dev.*, 2005, **9**, 149–163.
- 7 D. J. C. Constable, A. D. Curzons and V. L. Cunningham, *Green Chem.*, 2002, **4**, 521–527.
- 8 X. Zhang, X. Ma, W. Qiu, J. Evans and W. Zhang, *Green Chem.*, 2019, **21**, 349–354.
- 9 A. Muthengi, X. Zhang, G. Dhawan, W. Zhang, F. Corsini and W. Zhang, *Green Chem.*, 2018, **20**, 3134–3139.
- 10 S. Abou-Shehada, P. Mampuy, B. U. W. Maes, J. H. Clark and L. Summerton, *Green Chem.*, 2017, **19**, 249–258.
- 11 N. J. Willis, C. A. Fisher, C. M. Alder, A. Harsanyi, L. Shukla, J. P. Adams and G. Sandford, *Green Chem.*, 2016, **18**, 1313–1318.
- 12 T. V. T. Phan, C. Gallardo and J. Mane, *Green Chem.*, 2015, **17**, 2846–2852.
- 13 P. Noppawan, S. Sangon, N. Supanchaiyamat and A. J. Hunt, *Green Chem.*, , DOI:10.1039/D1GC00872B.
- 14 K. Asemave, phd, University of York, 2016.
- 15 F. Byrne, B. Forier, G. Bossaert, C. Hoebbers, T. J. Farmer, J. H. Clark and A. J. Hunt, *Green Chem.*, 2017, **19**, 3671–3678.
- 16 P. Noppawan, S. Sangon, N. Supanchaiyamat, J. Sherwood and A. J. Hunt, *ACS Sustainable Chem. Eng.*, 2022, **10**, 4486–4493.