Tandem reactions for the synthesis of high-density polycyclic biofuels with double/triple hexane ring

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Table of Contents

General
Information..................................................................................................S3
Measurements of fuel properties.................................................................S3
General procedures.....................................................................................S4-S8
Spectral data of Intermediates...............................................................S9-S13
Copies of $^1$H NMR and $^{13}$C NMR Spectra of Intermediates........S14-S24
Copies of $^1$H, $^{13}$C, DEPT-135 NMR and GC-MS Spectra of Products.................................................................S25-S44
$^1$H, $^{13}$C, DEPT-135 NMR Spectra and GC-MS of 3b after vacuum distillation................................................................................S45-S46
References..............................................................................................S47
General Information

All reagents and solvents were purchased from commercial suppliers (Energy Chemical, 99%) and used without further purification. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF 254 plates. The silica gel (200-300 meshes, Qingdao Haiyang Chemical) was used for column chromatography, and the distillation range of petroleum ether was 60-90°C. $^1$H, $^{13}$C spectra were recorded on Bruker AV-III 400 MHz spectrometers and spectral data were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quadruplet; dd, doublet of doublets; m, multiple for proton spectra. Coupling constants ($J$) are reported in hertz (Hz). MS data were obtained on Thermo scientific ISQ 7000 with electron ionization (EI). Infrared spectra were obtained on Thermo-Fisher Nicolet 6700 FI-IR spectrometer.

In the manuscript, the yields of intermediates and the yields of HDO products were calculated according to the following equations. For intermediates, isolated yield was used, which is the ratio of the mass of the target compound obtained after post-treatment to the theoretical mass: Isolated yield (%$\) = \frac{\text{actual quality of target product}}{\text{theoretical quality of target product}} \times 100%.

For the HDO product, carbon yield was used: Carbon yield of specific product in the HDO reaction (%) = \frac{\text{carbon in the specific product obtained in the HDO reaction}}{\text{carbon in the intermediates consumed during the HDO reaction}} \times 100%.

Measurements of fuel properties

The samples of biofuels were purified by vacuum distillation before the test. The freezing point was measured by DSC 250 according to ASTM D2368. The samples were ramped from -90 °C to 50 °C, down to -90 °C, and then back to 50 °C, all at 10 °C /min. The heat of combustion was measured by IKA-C6000 isoperibol Package 2/10 Calorimeter according to ASTM D240-02. Elemental analysis was measured by Elementar Vario Micro cube.
General procedure

The synthesis of tetraketones 2
Furfural/benzaldehyde derivatives (1 mmol, 1.0 eq.), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol, 2.0 eq.) and water (5 mL) were stirred at room temperature for 2 h to obtain white precipitate. Then, the resultant precipitates were filtered, washed by cold water and dried in a vacuum affording the product as white solid.

The one-pot condensation reaction of octahydroxanthenes-1,8-diones
A mixture of 5,5-dimethyl-1,3-cyclohexanedione (2.0 mmol, 2.0 eq.), benzaldehyde derivatives (1.0 mmol, 1.0 eq.), PTSA (0.1 mmol, 0.1 eq.) was stirred at 80°C for 2 h under solvent-free condition. Upon completion of the reaction (monitored by TLC), the product was purified by column chromatography.

The HDO reaction
The HDO reaction was carried out in a 60 ml stainless autoclave with 5 mL cyclohexane as solvent, and a mixture of the substrate (0.5 mmol), Pd/C\textsubscript{10\%} (50 mg) and AcOH (1 drop) as catalysts. (As for products of furfural/methyl furfural and 5,5-dimethyl-1,3-cyclohexanedione, reaction conditions: substrate (0.5 mmol), Pd/C\textsubscript{10\%} (50 mg), Hf(OTf)\textsubscript{4} (0.025 mmol) and AcOH (1 drop) as catalysts)
The reactor was sealed and the hydrogen was filled under the pressure of 40 MPa after replacing air with pure H\textsubscript{2}. The reaction was heated at 220°C for 24 hours. The HDO products were purified by vacuum distillation. Finally, the properties of obtained fuels were tested by related instruments.

Caution: High-pressure and high-temperature experiments represent a significant risk and must be conducted with appropriate safety procedures and in conjunction with the use of suitable equipment.
The synthesis of 5,5-dimethyl-1,3-cyclohexanenedione

\[
s + \text{malonic acid} \rightarrow 5,5\text{-dimethyl-1,3-cyclohexanenedione}
\]

**Figure S1.** The synthetic route of 5,5-dimethyl-1,3-cyclohexanenedione.

5,5-dimethyl-1,3-cyclohexanenedione can be obtained from biomass-derived chemicals: acetone and malonic acid, as reported in the literature. The detailed synthesis route is shown in Figure S1. Similar synthesis route was shown in the previously reported references. \(^1,2\)

**Figure S2.** The proposed mechanism of catalyst-free tandem reaction and reverse Michael addition reaction of 2d.

In the system, water helps enolization of 5,5-dimethyl-1,3-cyclohexanenedione through making hydrogen bonds interact with -OH and it increases the nucleophilic activity of methylene carbon of 5,5-dimethyl-1,3-cyclohexanenedione. Meanwhile, it also increases the electrophilic activity of carbonyl carbon of benzaldehyde through forming hydrogen bonds with
carbonyl group. After the Knoevenagel condensation reaction, the α, β-unsaturated ketene intermediate is afforded. By the following Michael addition reaction of 5,5-dimethyl-1,3-cyclohexanedione and α, β-unsaturated ketene, 2d is obtained. But the Michael addition reaction is a reversible process, and it is beneficial to the reverse reaction when the temperature rises. Under the hydrodeoxygenation conditions, it is beneficial to the decomposition process of 2d, and then the α, β-unsaturated ketene is rapidly hydrodeoxygenated to 3d. Similar mechanism of catalyst-free tandem reaction and reverse Michael addition reaction was reported in the previously literature.³

![Diagram](image)

**Figure S3.** The proposed mechanism of cyclization reaction of 2d'. In the reaction, the carbonyl group of 2d' is first activated by proton, and then the enolized hydroxyl group attacks the carbonyl group of 2d' to obtain a ring-closing compound. In alkaline conditions, the activation energy of cyclization reaction comes from enol oxygen attacking carbonyl without protonation is too high, which makes the process impossible. Under the acidic condition, the activation energy of dehydration and deprotonation is obviously lower. Therefore, the acidic condition is favorable for the cyclization reaction of 2d'.

S6
Similar mechanism of catalyst-free tandem reaction and reverse Michael addition reaction was reported in the previously literature.  

**Calculation method of NHOC (gross) and NHOC (net)**

On this basis, the enthalpies of formation for molecules were calculated by atomization reactions.

Take \( C_xH_y \) as an example. The following atomization reaction was used to calculate the enthalpies of formation:

\[
C_xH_y \rightarrow xC + yH
\]  

(1)

The atomization energy was calculated by following equation:

\[
\sum D_0(C_xH_y) = x\varepsilon_0(C) + y\varepsilon_0(H) - \varepsilon_0(C_xH_y) - \varepsilon_{ZPE}
\]  

(2)

Where \( \varepsilon_0 \) is the total electronic energy, and \( \varepsilon_{ZPE} \) stands for zero-point energy. Then calculate \( \Delta fH^0(C_xH_y,0K) \) and \( \Delta fH^0(C_xH_y,298K) \) for each molecule:

\[
\Delta fH^0(C_xH_y,0K) = x \Delta fH^0(C,0K) + y \Delta fH^0(H,0K) - \sum D_0(C_xH_y)
\]  

(3)

\[
\Delta fH^0(C_xH_y,298K) = \Delta fH^0(C_xH_y,0K) + H^0(C_xH_y,298K) - H^0(C_xH_y,0K) - [x(H^0(C,298K) - H^0(C,0K)) + y(H^0(H,298K) - H^0(H,0K))]
\]  

(4)

Where \( \Delta fH^0(C,0K) \), \( \Delta fH^0(H,0K) \), \( H^0(C,298K) - H^0(C,0K) \) and \( H^0(H,298K) - H^0(H,0K) \) can be attained by Table S1.

**Table S1**  Experimental enthalpies of formation of atoms (kcal/mol).

| Atoms | \( \Delta fH^0(0K) \) | \( H^0(298K) - H^0(0K) \) |
|-------|-----------------|-----------------|
| H     | 51.63±0.001    | 1.01            |
| C     | 169.98±0.1     | 0.25            |
| N     | 112.53±0.02    | 1.04            |
| O     | 58.99±0.02     | 1.04            |
| F     | 18.47±0.07     | 1.05            |
Once the enthalpies of formation are determined, we can calculate the enthalpies of combustion by using the enthalpies of formation. The combustion reaction per mole of compound is:

\[
C_xH_y(g) + (x + y/4)O_2(g) = xCO_2(g) + y/2H_2O(l)
\] (5)

In order to calculate the enthalpies of combustion, the enthalpies of formation of oxygen, carbon dioxide and liquid water should be needed. The values are 0, -393.51, -285.83kJ/mol, respectively.

The **NHOC (net)** was calculated as follows:

\[
Q_{n,(net,298K)} = Q_{g,(gross,298K)} - 0.2122^\Delta H_{\text{combustion}}(298K) - 0.2122^\Delta H
\] (6)

Where \( Q_{g,(gross,298K)} \) is the gross heat of combustion, \( Q_{n,(net,298K)} \) is the net heat of combustion, \( H \) is the hydrogen content of fuels. The density was calculated by ACD Labs (1. ACD/ChemSketch, version 2020.1.1, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, 2020.).
Spectral data of Intermediates

2-(1-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)butyl)-5,5-dimethylcyclohexane-1,3-dione (2a)

![Molecular structure of 2a.](image)

Prepared according to the general procedure as described above in 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.48 (s, 1H), 4.76 (s, 2H), 3.93 (t, $J = 8.0$ Hz, 1H), 2.27 (d, $J = 5.6$ Hz, 8H), 1.98 (q, $J = 7.6$ Hz, 2H), 1.24-1.15 (m, 2H), 1.05 (s, 12H), 0.86 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.9, 189.6, 116.5, 46.9, 46.1, 31.2, 31.0, 29.8, 29.2, 26.5, 22.0, 13.7.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.

2-(furan-2-yl(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2b)

![Molecular structure of 2b.](image)

Prepared according to the general procedure as described above in 96% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.15 (s, 1H), 11.43 (s, 1H), 7.24 (s, 1H), 6.27 (q, $J = 1.6$ Hz, 1H), 5.93 (s, 1H), 5.37 (s, 1H), 2.41-2.22 (m, 8H), 1.16 (s, 6H), 1.08 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.4, 151.6, 141.0, 114.1, 110.1, 106.2, 46.8, 46.1, 31.3, 29.6, 29.1, 26.4.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.

2-((2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(5-methylfuran-2-yl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2c)
Figure S6. Molecular structure of 2c.
Prepared according to the general procedure as described above in 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.19 (s, 1H), 11.45 (s, 1H), 5.84 (d, $J = 2.0$ Hz, 2H), 5.80 (d, $J = 2.0$ Hz, 2H), 5.34 (s, 1H), 2.34 (s, 8H), 2.16 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.3, 150.3, 149.4, 114.1, 106.8, 105.8, 46.8, 46.2, 31.3, 29.7, 29.1, 26.3, 13.4.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.\textsuperscript{6}

$2$-((2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(phenyl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2d)

Figure S7. Molecular structure of 2d.
Prepared according to the general procedure as described above in 96% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.87 (s, 1H), 7.23 (d, $J = 7.6$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, ), 7.07 (d, $J = 8.0$ Hz, 2H), 5.51 (s, 1H), 4.75 (m, 1H), 2.46-2.26 (m, 8H), 1.21 (s, 6H), 1.07 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.4, 189.3, 138.0, 128.1, 126.7, 125.8, 115.5, 47.0, 46.4, 32.7, 31.3, 29.6, 27.3.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.\textsuperscript{3}

$2$-((2-hydroxy-4,4-dimethyl-6-oxocyclohexyl)(p-tolyl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2e)

Figure S8. Molecular structure of 2e.
Prepared according to the general procedure as described above in 92% yield. 

1H NMR (400 MHz, CDCl₃): δ 11.90 (s, 1H), 7.07 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.6 Hz, 2H), 5.50 (s, 1H), 2.47-2.29 (m, 11H), 1.22 (s, 6H), 1.09 (s, 6H).

13C NMR (100 MHz, CDCl₃): δ 190.3, 189.3, 135.2, 134.8, 128.9, 126.6, 115.7, 47.0, 46.4, 32.3, 31.3, 29.6, 27.3, 20.8.

All the resonances of 1H and 13C NMR spectra were consistent with reported values.⁷

2-((2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(o-tolyl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2f)

![Molecular structure of 2f.](image)

Prepared according to the general procedure as described above in 90% yield.

White solid, m.p.: 165-166°C.

1H NMR (400 MHz, CDCl₃): δ 11.66 (s, 1H), 7.25-7.09 (m, 4H), 5.51 (s, 1H), 2.52-2.16 (m, 11H), 1.10 (s, 12H).

13C NMR (100 MHz, CDCl₃): δ 189.4, 136.7, 135.8, 131.1, 127.6, 126.3, 125.6, 116.2, 47.0, 31.8, 31.7, 28.3, 20.5.

FTIR (Neat) cm⁻¹: 3202, 3011, 2955, 2870, 1731, 1638, 1607, 1378, 1226, 1166, 1122, 1061, 965, 939, 912, 893, 749.

EIMS: m/z 382.4 (M⁺, 11).

2-((2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(4-isopropylphenyl)methyl)-5,5-dimethylcyclohexane-1,3-dione (2g)

![Molecular structure of 2g.](image)

Prepared according to the general procedure as described above in 89% yield. 

1H NMR (400 MHz, CDCl₃): δ 11.91 (s, 1H), 11.58 (s, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.50 (s, 1H), 2.89-2.82 (m, 1H), 2.47-2.29 (m, 8H), 1.23 (s, 12H), 1.10 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.3, 189.2, 146.1, 135.1, 126.6, 126.2, 115.6, 47.0, 46.4, 33.4, 32.3, 31.3, 29.6, 27.3, 23.9.
All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.$^7$

3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (2d')

Figure S11. Molecular structure of 2d'.
Prepared according to the general procedure as described above in 93% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.21 (d, $J$ = 7.6Hz, 2H), 7.12 (t, $J$ = 7.6Hz, 2H), 7.00 (t, $J$ = 7.2Hz, 1H), 4.67 (s, 1H), 2.39 (s, 1H), 2.10 (q, $J$ = 16.4Hz, 4H), 1.01 (s, 1H), 0.90 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.1, 162.1, 143.9, 128.1, 127.8, 126.1, 115.4, 50.5, 40.6, 31.9, 31.6, 29.0, 27.1.
All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.$^8$

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (2e')

Figure S12. Molecular structure of 2e'.
Prepared according to the general procedure as described above in 87% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17 (d, $J$ = 8.0Hz, 2H), 7.00 (d, $J$ = 8.0Hz, 2H), 4.70 (s, 1H), 2.45 (s, 4H), 2.24-2.13 (m, 7H), 1.09 (s, 6H), 0.98 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.3, 162.0, 141.1, 135.6, 128.7, 128.1, 115.6, 50.6, 40.7, 32.1, 31.3, 29.1, 27.2, 20.9.
All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.$^8$
3,3,6,6-tetramethyl-9-(o-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (2f’)

![Figure S13. Molecular structure of 2f’.](image1)

Prepared according to the general procedure as described above in 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.05-6.89 (m, 4H), 4.83 (s, 1H), 2.84 (s, 3H), 2.46 (s, 4H), 2.15 (q, $J$ = 16.4Hz, 4H), 1.07 (s, 6H), 0.94 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.3, 161.9, 143.0, 137.0, 129.8, 127.4, 125.8, 125.3, 116.4, 50.4, 40.5, 31.9, 29.0, 27.5, 26.9, 19.5.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.$^8$

9-(4-isopropylphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (2g’)

![Figure S14. Molecular structure of 2g’.](image2)

Prepared according to the general procedure as described above in 86% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17 (d, $J$ = 8.0Hz, 2H), 7.04 (d, $J$ = 8.0Hz, 2H), 4.72 (s, 1H), 2.82-2.75 (m, 1H), 2.45 (s, 4H), 2.19 (d, $J$ = 7.6Hz, 4H), 1.17 (s, 3H), 1.15 (s, 3H), 1.09 (s, 6H), 0.99 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.4, 162.1, 146.4, 141.3, 128.0, 126.0, 115.7, 50.7, 40.8, 33.5, 32.1, 31.2, 29.1, 27.4, 23.8.

All the resonances of $^1$H and $^{13}$C NMR spectra were consistent with reported values.$^8$
Copies of $^1$H NMR and $^{13}$C NMR Spectra of Intermediates

Figure S15. $^1$H NMR Spectra of 2a.

Figure S16. $^{13}$C NMR Spectra of 2a.
Figure S17. $^1$H NMR Spectra of 2b.

Figure S18. $^{13}$C NMR Spectra of 2b.
Figure S19. $^1$H NMR Spectra of 2c.

Figure S20. $^{13}$C NMR Spectra of 2c.
**Figure S21.** $^1$H NMR Spectra of 2d.

**Figure S22.** $^{13}$C NMR Spectra of 2d.
Figure S23. $^1$H NMR Spectra of 2e.

Figure S24. $^{13}$C NMR Spectra of 2e.
Figure S25. $^1$H NMR Spectra of 2f.

Figure S26. $^{13}$C NMR Spectra of 2f.
Figure S27. $^1$H NMR Spectra of 2g.

Figure S28. $^{13}$C NMR Spectra of 2g.
Figure S29. $^1$H NMR Spectra of 2d'.

Figure S30. $^{13}$C NMR Spectra of 2d'.
Figure S31. $^1$H NMR Spectra of 2e'.

Figure S32. $^{13}$C NMR Spectra of 2e'.
Figure S33. $^1$H NMR Spectra of 2f'.

Figure S34. $^{13}$C NMR Spectra of 2f'.
Figure S35. $^1$H NMR Spectra of 2g'.

Figure S36. $^{13}$C NMR Spectra of 2g'.
Copies of $^1\text{H}$, $^{13}\text{C}$, DEPT-135 NMR and GC-MS Spectra of Products

**Figure S37. $^1\text{H}$ NMR Spectra of 3a.**

**Figure S38. $^{13}\text{C}$ NMR Spectra of 3a.**
Figure S39. DEPT-135 Spectra of 3a.

Figure S40. GC-MS Spectra of 3a.

Mass spectrum of 3a. MS (EI, 70ev): m/z, 278.29 [M⁺].
Figure S41. $^1$H NMR Spectra of $3c$.

Figure S42. $^{13}$C NMR Spectra of $3c$. 
Figure S43. DEPT-135 Spectra of 3c.

Figure S44. GC-MS Spectra of 3c.

Mass spectrum of 3c. MS (EI, 70ev): m/z, 306.36 [M⁺].
Figure S45. $^1$H NMR Spectra of 3d.

Figure S46. $^{13}$C NMR Spectra of 3d.
**Figure S47.** DEPT-135 Spectra of 3d.

**Figure S48.** GC-MS Spectra of 3d.

Mass spectrum of 3d. MS (EI, 70ev): m/z, 208.23 [M⁺].
Figure S49. $^1$H NMR Spectra of 3e.

Figure S50. $^{13}$C NMR Spectra of 3e.
**Figure S51.** DEPT-135 Spectra of 3e.

**Figure S52.** GC-MS Spectra of 3e.

Mass spectrum of 3e. MS (EI, 70ev): m/z, 222.26 [M⁺].
Figure S53. $^1$H NMR Spectra of 3f.

Figure S54. $^{13}$C NMR Spectra of 3f.
Figure S55. DEPT-135 Spectra of 3f.

Figure S56. GC-MS Spectra of 3f.

Mass spectrum of 3f. MS (EI, 70ev): m/z, 222.24 [M+].
Figure S57. $^1$H NMR Spectra of 3g.

Figure S58. $^{13}$C NMR Spectra of 3g.
Figure S59. DEPT-135 Spectra of 3g.

Figure S60. GC-MS Spectra of 3g.

Mass spectrum of 3g. MS (EI, 70ev): m/z, 250.28 [M⁺].
Figure S61. $^1$H NMR Spectra of 3d'.

Figure S62. $^{13}$C NMR Spectra of 3d'.
Figure S63. DEPT-135 Spectra of 3d'.

Figure S64. GC-MS Spectra of 3d'.

Mass spectrum of 3d’. MS (EI, 70ev): m/z, 318.30 [M⁺].
Figure S65. $^1$H NMR Spectra of 3e'.

Figure S66. $^{13}$C NMR Spectra of 3e'.
Figure S67. DEPT-135 Spectra of 3e'.

Figure S68. GC-MS Spectra of 3e'.

Mass spectrum of 3e’. MS (EI, 70ev): m/z, 332.34 [M*].
Figure S69. $^1$H NMR Spectra of 3f'.

Figure S70. $^{13}$C NMR Spectra of 3f'.
Figure S71. DEPT-135 Spectra of 3f'.

Figure S72. GC-MS Spectra of 3f'.

Mass spectrum of 3f’. MS (EI, 70ev): m/z, 332.34 [M⁺].
Figure S73. $^1$H NMR Spectra of 3g’.

Figure S74. $^{13}$C NMR Spectra of 3g’.
**Figure S75.** DEPT-135 Spectra of 3g'.

**Figure S76.** GC-MS Spectra of 3g'.

Mass spectrum of 3g'. MS (EI, 70ev): m/z, 360.36 [M$^+$.]
$^{1}$H, $^{13}$C, DEPT-135 NMR and GC-MS Spectra of 3c after vacuum distillation

Figure S77. $^{1}$H NMR Spectra of 3c after vacuum distillation.

Figure S78. $^{13}$C NMR Spectra of 3c after vacuum distillation.
Figure S79. DEPT-135 Spectra of 3c after vacuum distillation.

Figure S80. GC-MS Spectra of 3c after vacuum distillation.

Mass spectrum of 3c. MS (El, 70ev): m/z, 306.32 [M+].
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