

Catalytic One-Pot Conversion of Renewable Platform Chemicals to Hydrocarbon and Ether Biofuels through Tandem Hf(OTf)₄ + Pd/C Catalysis

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Efficient conversion of renewable biomass platform chemicals into high-quality fuels remains challenging. A one-pot catalytic approach has been developed to synthesize various structurally defined biofuels by using Hf(OTf)₄ and Pd/C for selective tandem catalysis and 2-methylfuran (2-MF) as a renewable feedstock. 2-MF first undergoes Lewis acid-catalyzed hydroxyal-kylation/alkylation (HAA) condensation with carbonyl compounds to afford intermediates containing the targeted carbon skeletons of hydrocarbon or ether products, and these intermediates then undergo hydrogenation or hydrodeoxygenation to afford the target products, catalyzed by metal triflate + Pd/C in the same pot. The present process can produce structurally defined alkanes and cyclic ethers under mild conditions.

The catalytic conversion of biomass-derived platform chemicals has emerged as a sustainable approach to renewable fuels and value-added commodity chemicals.^[1] Highly selective catalytic transformations may enable the production of single-component hydrocarbon fuel molecules with diversified molecular structures from simple biomass platform chemicals. If successful, these would greatly expand the scope for precisely optimizing "tailor-made" fuel performance by blending.^[2] Recent studies have shown that, based on current production technologies, 6-pentylundecane, 2-methyltetrahydrofuran, and ethyl levulinate are promising next-generation biofuels that could exceed the performance of bioethanol in both cost and environmental impact.^[3] Furthermore, efficient and precise new ways to produce hydrocarbon, cyclic ether, and levulinate biofuels from simple biomass platform chemicals may drive breakthroughs to next-generation biofuels. Upgrading strategies to convert platform chemicals into higher molecular weight fuels typically consist of two or three independent steps: (1) acid- or base-catalyzed condensation of simple fuel precursors into carbon-chain-extended complex fuel precursors, (2) hydrogena-

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tion to cyclic ethers, and/or (3) hydrodeoxygenation (HDO) of ethers to alkanes (Scheme 1 a).^[4] During HDO, the acid cocata-lysts^[5] may induce undesirable alkane isomerization, thereby compromising selectivity.^[6]

In marked contrast to the above scenario, a variety of alkyl ethers can be converted into the corresponding alkanes without significant isomerization by using tandem Hf(OTf)₄ and Pd/ C catalysis.^[7] These catalysts are also highly effective for the selective HDO of ethers with higher order complexity.^[5e,8] Furthermore, metal triflates also effectively catalyze hydroxyalkylation/alkylation (HAA) condensation of 2-MF and aldehydes or ketones, to produce complex furanoid structures.^[9] Upon complete Pd/C-catalyzed hydrogenation, such compounds can then be converted into cyclic ethers, which undergo catalytic HDO to alkanes. The efficacy of these separate transformations raises the intriguing question of whether HAA condensation, hydrogenation, and HDO can be carried out sequentially in a single reactor starting from simple platform chemicals.^[5c] Herein we report the realization of such a one-pot,^[10] highly selective tandem catalytic strategy to produce hydrocarbons and cyclic ether biofuels from simple carbonyls and 2-methylfuran (2-MF) as building blocks (Scheme 1 b).

HAA condensation of 2-MF and 5-methylfurfural is efficiently catalyzed by metal triflates under neat conditions (see the Supporting Information, Table S1). Hf(OTf)₄ is found to be the most active catalyst. Raising the reaction temperature to 45 °C affords 96% yield of the isolated condensation product in 2.5 h. The same conditions can also be applied to the HAA reactions of 2-MF with many aldehydes, as well as Michael reactions with many enals (Scheme S1). Typically, 0.5 mol% of catalyst is sufficient for aldehydes, whereas 1 mol % suffices for less reactive ketones or enones. Many of these aldehydes and ketones can be produced from biomass, such as furfural, valeraldehyde, levulinic acid, levulinate, 5-hydroxymethylfurfural (HMF), 5methylfurfural, and furan-2,5-dicarbaldehyde from C_5 and C_6 sugars;^[1g,11] acetone, 1-butanal, and aromatic aldehydes from fermentation;^[12] butanone from levulinic acid decarboxylation;^[13] cyclopentanone from furfural or furancarbinol isomerization;^[14] and cyclohexanone from lignocellulosic biomass.^[15] In general, more electrophilic aldehydes such as aromatic aldehydes bearing electron-withdrawing groups afford higher reactivity and higher yields. Nevertheless, extended reaction times may result in product decomposition, and sterically hindered aldehydes and ketones are less reactive.

In the same reactor, the above condensation products were next subjected to HDO in the presence of a hydrogenation catalyst and H_2 (Scheme 1 b). The products obtained from alde-





Scheme 1. Strategies for catalytic biofuel production from platform chemicals: a) Conventional stepwise biofuel production strategies. b) This work: One-pot conversion.

hydes and ketones diverge at this point: those from aldehydes undergo complete HDO to alkanes, whereas those from ketones are converted into cyclic ethers. The one-pot reaction between 2-MF and aldehydes was optimized first using 1-hexanal and Hf(OTf)₄ as the catalyst because the desired product 4a is a valuable biodiesel fuel.^[3, 16] Various hydrogenation catalysts were surveyed and $Hf(OTf)_4 + Pd/C$ was found to be the most effective combination (Table S2). Note that HDO requires higher loadings of Hf(OTf)₄ than does HAA; thus extra Hf(OTf)₄ is added along with Pd/C and solvent for the second reaction stage. Solvent screening showed that ethyl acetate is superior to other solvents (Table S3), possibly because it stabilizes cationic intermediates during HDO while not being so Lewis basic as to deactivate the metal triflate.^[17] In addition, ethyl acetate is inert towards HDO at 150 °C but capable of removing water by sacrificial hydrolysis to EtOH, ether, and AcOH (Scheme S2), which likely prevents inferior reaction pathways (Table S3, entries 7-10).

The one-pot conditions were thus optimized using ethyl acetate as the solvent (Table 1). The desired product $C_{16}H_{34}$ (**4a**) always comes with a C–C bond cleavage product $C_{11}H_{24}$ (**6a**) and many $C_{16}H_x$ (x < 34) isomers (**5a**), which seemed to be saturated monocyclic alkanes but could not be unambiguously identified. At high reagent concentrations and low catalyst loadings, the Hf/Pd ratio does not significantly impact the selectivity (Table 1, entries 1–4). Further lowering the catalyst

loading (Table 1, entry 5) results in lower overall yield, whereas lower concentrations of reagents and catalysts do not effect significant improvement (Table 1, entry 6). The conditions of Table 1, entry 2 were denoted as Modality A for further scope studies, for it provides a maximum combined yield of C₁₆ hydrocarbons 4a + 5a under the lowest loading of catalysts and solvent. A **4a** stability test under $Hf(OTf)_4 + Pd/C$ catalysis (Table S5) shows no isomerization, indicating that isomeric products are probably generated concurrently with 4a during the HDO step. Carbocation and olefin intermediates originating from C–O bond cleavage^[7b] might yield products 5 a and 6 a, especially when an adjacent tertiary or quaternary carbon center is present (Scheme S3).^[18] When the reagent concentration is decreased while that of the catalysts is held constant (Table 1, entries 7-9), the selectivity to product 4a is significantly enhanced. Meanwhile, reducing the Hf(OTf)₄ loading further increases selectivity to 4a, but at the expense of extended reaction times (Table 1, entries 9-16). Note that in these examples all Hf(OTf)₄ can be added in one portion along with the solvent in reaction stage 1 without diminishing yield and selectivity (Table 1, entries 13-16). In fact, the reaction time of stage 1 can be reduced to 40 min while achieving full conversion. The conditions for Table 1, entry 13 were denoted as Modality B in further studies, aiming to optimize selectivity to 4a with high catalyst loadings. A comparison of stepwise reaction selectivity to 4a, 5a, and 6a in Modalities A and B (Scheme S3)



Table 1. Conditions optimization for one-pot production of hydrocarbon- $c^{[a]}$									
+ 2	$ \begin{array}{c} 0 \\ 1a \\ 2) + l \\ EtO \end{array} $	(OTf) ₄ , neat 5 °C, 5 h Hf(OTf) ₄ , Pd/C Ac, 40 bar H ₂ + 150 °C, <i>t</i>	4a (C ₁₆ H ₃₄) • Isomeric C ₁₆ products 5a + 6a (C ₁₁ H ₂₄)						
Entry	Conc. (1 a /Hf/Pc	l) [mм] t [h]	Yields ^[b] (4 a/5 a/6 a) [%]						
$\begin{array}{c} 1 \\ 2^{[c]} \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13^{[e,f]} \\ 14^{[e]} \\ 15^{[e]} \\ 16^{[e]} \end{array}$	2000:40:12 2000:40:16 2000:40:20 2000:40:24 2000:20:16 1000:20:8 1000:40:16 200:40:16 200:40:16 200:20:16 200:20:16 200:10:16 200:10:16 200:10:24 200:6:16 200:4:16	5 5 5 5 5 5 5 5 5 5 20 20 20 20 20 20 20 20 20 20 20 20 20	59:31:2 69:27:1 58:28:1 58:25:1 40:20:1 57:26:1 66:21:2 63:27:2 77:17:2 60% alkanes ^(d) 76: 10:1 84:10:1 87:8:1 87:6:1 6% alkanes ^(d) ethers ^(d)						
[a] Reaction conditions, unless otherwise stated: 1) 1a (1.0 mmol), 2 (2.0 mmol), and first 0.5 mol% $Hf(OTf)_4$ were stirred at 45 °C in a high- pressure reactor for 5 h; 2) remaining $Hf(OTf)_4$, Pd/C (5% Pd on activated carbon), ethyl acetate were added and heated at 150 °C for a specified time under 40 bar of H ₂ . [b] Yields of 4a and 6a determined by GC-FID calibrated by authentic samples. 5a calibrated with respect to 4a . [c] Conditions employed as Modality A. [d] Incomplete conversion of cyclic ethers observed. [e] At stage 1, all $Hf(OTf)_4$ added along with sol-									

indicates that Modality B prevents generation of **5***a* from cyclic ethers.

vent and stirred, for 40 min. Stage 2 remains the same. [f] Conditions em-

ployed as Modality B.

At this stage, TfOH was investigated as a catalyst to determine whether the observed catalytic reactions were the result of metal triflate hydrolysis.^[19] Although results comparable to those with 0.5 mol% Hf(OTf)₄ were obtained in HAA using 1– 2 mol% TfOH (Table S1, entries 11–13), significantly lower selectivity and carbon balance were observed in the one-pot reactions catalyzed by a series of TfOH concentrations following either Modality A or B, mimicking partial hydrolysis scenarios (Table S4).^[8b] These results demonstrate the distinctive role of Hf(OTf)₄ beyond that of a mere Brønsted acid precursor.^[20] Nevertheless, the true catalytic species remains elusive in that the reaction system is a dynamic mixture and any component may influence the activity/selectivity of the catalyst. This report focuses on overall strategy and scope, leaving detailed mechanistic studies to future efforts.

Both Modalities A and B were investigated in the aldehyde scope study. Modality A produces jet fuel hydrocarbons in the

 C_{13} – C_{17} range as C_n and isomeric C_n mixtures along with small amounts of lower carbon number components (Table 2, entries 1–9). Modality B is capable of precise production of target C_n hydrocarbons (e.g., **4a**) in the C_{13} – C_{28} jet fuel and diesel range (Table 2, entries 1–12). Note that for entry 7, the reaction requires higher temperature and longer time to enable HDO of a primary C–O bond. EtOAc also underwent HDO to AcOH in this case. When starting from enals, significant isomerization products are still observed, even with Modality B (Table 2, entries 13–19). For entries 15 and 17, target C_n could not be distinguished from their isomers by GC. As a comparison, 5-methylfurfuryl alcohol achieves high selectivity to linear alkanes with Modality A (Table 2, entry 20) without isomerization.

In contrast to the above results, the fuel precursors obtained from ketones and 2-MF are not suitable for alkane production. Substantial C-C bond cleavage occurred in several examples at high temperature under either Modality A or B, probably due to the quaternary carbon center (Scheme S4).^[6d] Nevertheless, these are excellent precursors for the production of cyclic ethers, which are valuable fuel additives,^[2] and oxygen-containing diesel fuels.^[21] In contrast to alkane biofuels, ethers containing more oxygen atoms should provide better performance as fuels.^[22] Moreover, cyclic and polycyclic ethers are excellent solvents for chemical reactions and lithium battery electrolytes.^[23] Many bioactive natural products and antibodies contain ether rings as well.^[24] Nevertheless, selective production of renewable cyclic ethers from biomass-derived platform chemicals remains a challenge. Hydrogenation of furan precursors often results in unwanted C-O bond hydrogenolysis to alcohols, even if the Pd hydrogenation catalyst is optimized and acid catalysts from previous steps removed.^[21] New strategies for selective production of cyclic ethers are therefore highly desirable.

Since cyclic ethers are intermediates in alkane production, the same Hf+Pd catalyst system and condensation-hydrogenation multistep strategy should also apply in these cases. The reaction between 2-butanone and 2-MF was chosen to optimize the reaction conditions (Table 3). Surprisingly, unlike other reported catalytic protocols,^[21] alcohol byproducts do not form under the current conditions. When ethyl acetate is used as the solvent in the one-pot procedure, the C-C bond cleavage byproduct 9a is generated in 24% yield (Table 3, entry 1). This product is not observed if Hf(OTf)₄ is removed before hydrogenation (Table 3, entry 7), indicating that 9a formation is likely due to the Lewis acid. Hence, when water (a stronger Lewis base than EtOAc) is used as the solvent, generation of 9a is less significant (Table 3, entries 2-6), but hydrolysis product 8a is formed in 11% yield (Table 3, entry 3). In temperature screening within the range 60° C-100°C, the best selectivity to **7a** is obtained at 80°C (Table 3, entries 2-4). Although the reaction at 100 °C provides far more 8a and 9a byproducts than that at 80°C, we found that two-stage heating-first at 80°C and then at 120°C-can effectively transform 8a into the desired product 7a (Table 3, entries 5 and 6, and Scheme S5).

The reaction conditions given for Table 3, entries 6 (one-pot in water) and 7 (stepwise), were denoted as Modalities C and D, respectively, for further investigation of cyclic ether produc-



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Table 2. One-pot production of designer fuels from aldehydes and 2-MF.												
Aldehyde + $Modality A \text{ or } B$ Target C_n + Isomeric C_n + C-C cleaved C_{n-5}												
Entry	aldehyde	Structures target C _n		AA LIYAD	Product distribution ^[b] [%]							
				Modality $A^{(0)}$ target $C_n^{[d]}$	isomeric C _n mixture ^[e]	$C-C$ cleaved $C_{n-5}^{[e]}$	target $C_n^{[d]}$	isomeric C _n mixture ^[e]	C—C cleavage C _{n-5} ^[e]			
1	<i>∕</i> √µ0	\sim	C ₁₃	51	26	ND	78	4	ND			
2	~~~¢0	\sim	C ₁₄	60	22	ND	93	5	ND			
3		\sim	C ₁₄	75	15	ND	92	3	ND			
4		\sim	C ₁₅	63	23	ND	76	10	ND			
5		\sim	C ₁₆	69	27	1	87	8	1			
6 ^[f]	_°>°	\sim	C ₁₆	42	21	4	86	1	5			
7 ^[g]	©°	\sim	C ₁₅	46	30	ND	82	6	ND			
8		\sim	C ₁₆	37	20	9	90	4	2			
9	✓ ^o	~	C ₁₇	62	11	7	90	4	4			
10 ^[h]	но		C ₂₁	-	-	-	42	8	7 ^[k]			
11 ⁽¹⁾	0~~0~~0	\sim	C ₂₆	-	-	-	40	8	22 ^[k]			
12 ^[j]	0~~~~0	\sim	C ₂₈	-	-	-	55	6	38 ^[k]			
13	×	\sim	C ₁₉	-	-	-	15 ⁰⁾	35	1			
14	~~~ ⁰	\sim		-	-	-	26 ^[I]	56	3			
15	∩) _o	\sim	C ₂₁	-	-	-	97 ^[m]		2			
16	~~~¢0	\sim	C ₂₁	-	-	-	36 ^[1]	44	4			
17	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	\sim		-	-	-	59 ^[m]		12			
18	~~~~~o	\sim	C ₂₂	-	-	-	23 ^[I]	60	4			
19		\sim	C ₂₃	-	-	-	26 ^[1]	55	6 ^[k]			
20	O OH	~	C ₁₁	94	0	ND		-	-			

[c] Yields determined by GC-FID calibrated with 6-pentylhexadecane (for $C_{19}-C_{28}$ products), 6-pentylundecane (for $C_{14}-C_{18}$ products), and *n*-undecane (for $C_{9}-C_{13}$ products). ND = not determined. [b] Reaction conditions according to Modality A. Catalyst loading: 1 mol% of Hf(OTf)₄ and 0.4 mol% of Pd/C per MF unit. Reaction time for stage 1 varies depending on aldehyde. See the Supporting Information for details. [c] Reaction conditions according to Modality B. Catalyst loading: 5 mol% of Hf(OTf)₄ per carbonyl, and 4 mol% of Pd/C per MF unit, unless otherwise stated. Reaction time for stage 1 was 40 min for all aldehydes. [d] Structures identified by NMR spectroscopy and GCMS unless otherwise stated. [e] Components identified by NMR spectroscopy, GCMS, and comparison with authenticated samples; target molecules excluded from isomeric C_n mixtures, unless otherwise stated. [f] Modified procedures and loadings of catalysts applied for both Modalities A and B: stage 1: 0.5 mol% Hf(OTf)₄, 45 °C, 2.5 h; stage 2: ethyl acetate along with 24 mM Pd/C (1.2 mol% for Modality A, 12 mol% for Modality B), 80 °C, 40 bar H₂, 3 h; stage 3: Hf(OTf)₄ added up to 60 mM (3 mol%) for Modality A or 10 mM (5 mol%) for Modality B; then 150 °C, 40 bar H₂, 5 h for Modality A or 20 h for Modality B. [g] 180 °C, 80 h for stage 2 of both Modalities A and B. [h] 6 mol% of Hf(OTf)₄ used. [i] 8 mol% of Hf(OTf)₄ used. [k] $C_{n-5}+C_{n-10}$. [I] GC yield of the suspected target C_n . Structure not identifiable by NMR spectroscopy. (cpy. [m] All C_n products combined.

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[a] Reaction conditions: 1) **3a** (1.0 mmol), **2** (2.0 mmol), Hf(OTf)₄ (1 mol%), were stirred under 45 °C in a high pressure reactor for 6 h (without H₂); 2) Pd/C (5% Pd on activated carbon) and specified solvent (0.5 mL) added and stirred at indicated temperature under 30 bar H₂ following indicated temperature program. [b] Total yield from isolated product mixture. Selectivity determined by GC-FID. [c] Conditions employed as Modality C. [d] Hf(OTf)₄ removed by silica gel column before stage 2. Conditions employed as Modality D.

tion from biomass-derived ketones (Scheme 2). Compounds **7a–d** are obtained by Modality C in good yields, among which **7b–d** are obtained with nearly 100% selectivity. However, Modality C performs poorly when applied to compounds **7e–g**, whereas stepwise Modality D affords satisfactory overall yields and selectivities. Additionally, 2-cyclohexenone is converted in high selectivity and efficiency in tandem Michael–HAA–hydrogenation reactions with 3 equivalents of 2-MF into cyclic ether **7 h** when Modality D is applied (Scheme 3). Interestingly, cyclopentenone only participates in the Michael reaction stage with 1 equivalent of 2-MF. When carrying out hydrogenation/HDO, Modality A affords alkane **7 i** in high selectivity, which is derived from extrusion of oxygen atoms of both the furan ring and the Michael product carbonyl.^[5k] In contrast, enals give mixtures of cyclic ether **7 j** and byproducts under Modality D. Note from Table 2 that they also provide alkane mixtures under Modality B.

Lastly, we investigated the reaction of 2-MF with ethyl levulinate. Modalities A, B, and C all afford complex mixtures of products, whereas Modality D gives about 50% yield of the desired cyclic ether (Scheme 4).

In summary, we have developed a facile, efficient, and selective strategy for the one-pot catalytic conversion of biomassderived platform chemicals into well-designed biofuels. Four optimized reaction modalities were developed to meet the requirements of producing either hydrocarbons or cyclic ethers of desired quality.

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Scheme 2. Cyclic ether production from ketones and 2-MF.

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Scheme 3. Products from α , β -unsaturated carbonyl compounds and 2-MF.



Scheme 4. Conversion of ethyl levulinate and 2-MF.

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Conflict of interest

The authors declare no conflict of interest.

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COMMUNICATIONS

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Catalytic One-Pot Conversion of Renewable Platform Chemicals to Hydrocarbon and Ether Biofuels through Tandem Hf(OTf)₄ + Pd/C Catalysis



Fueling good: A one-pot catalytic approach has been developed to synthesize biofuels by using Hf(OTf)₄ and Pd/C for selective tandem catalysis and 2-methylfuran (2-MF) as a renewable feedstock. 2-MF undergoes Lewis acid-cata-

lyzed hydroxyalkylation/alkylation condensation and the intermediates then undergo hydrogenation or hydrodeoxygenation to afford structurally defined alkanes and cyclic ethers under mild conditions.