

## Supplementary Information

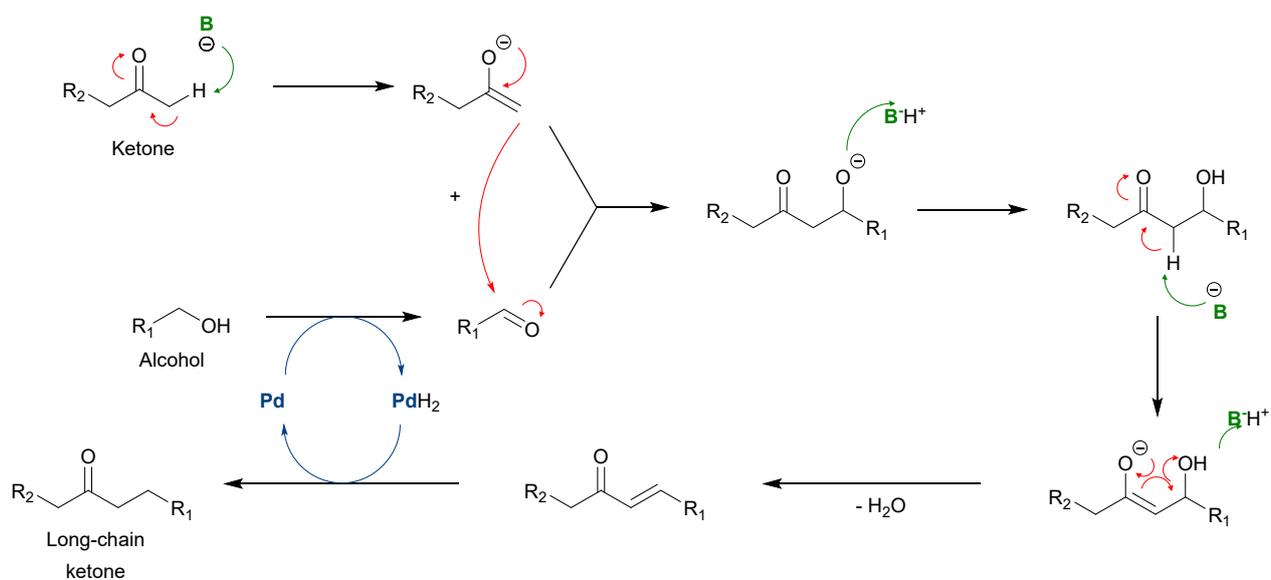
### **Production of Sustainable Aviation Fuel intermediates by Pd/C catalysed alkylation of combinations of fermentation-derived oxygenates**

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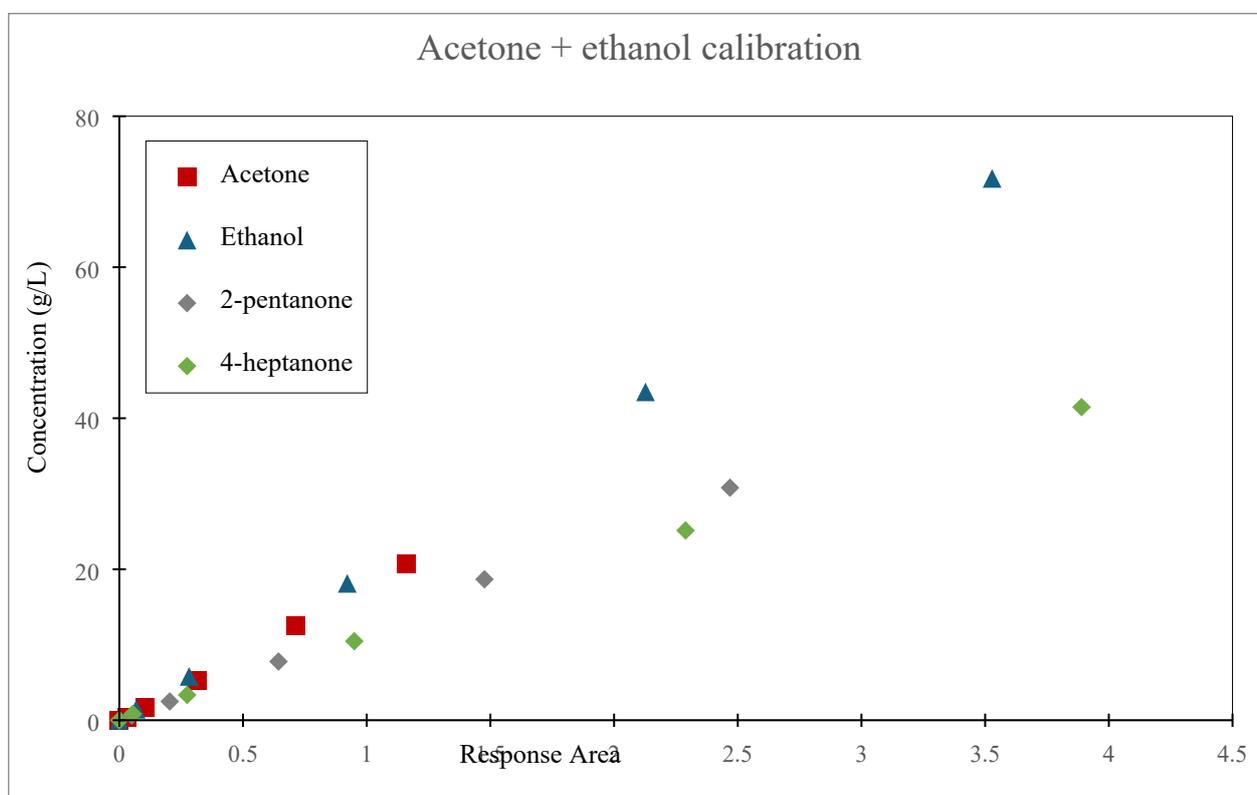
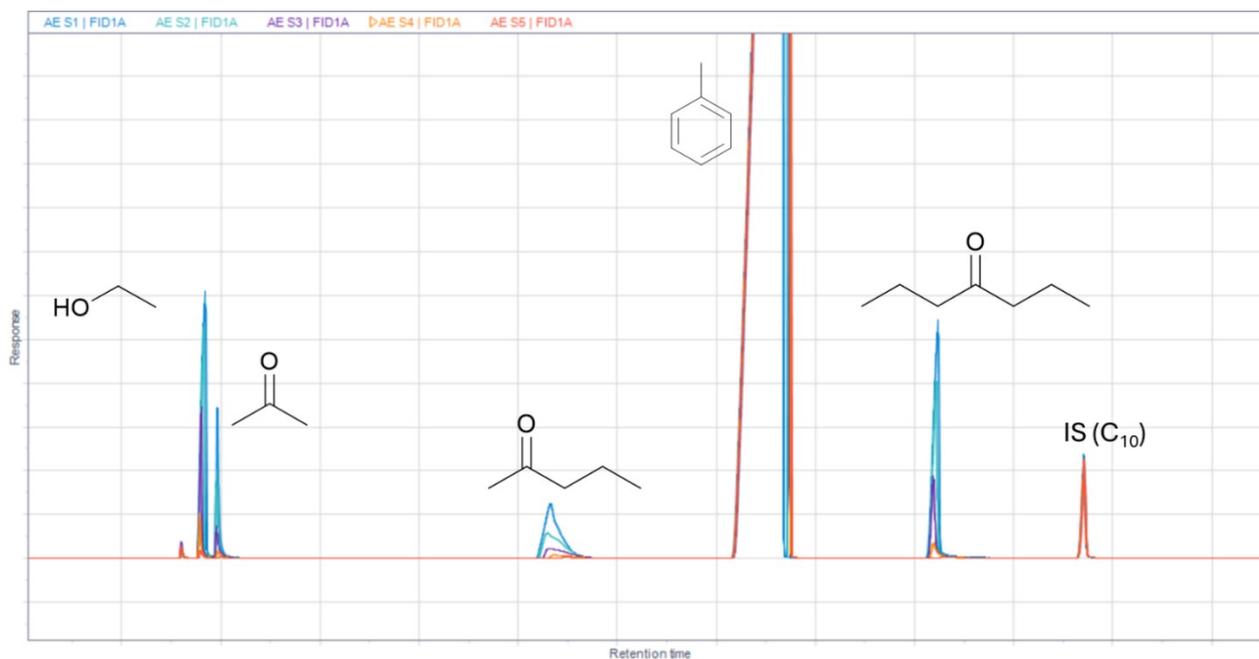
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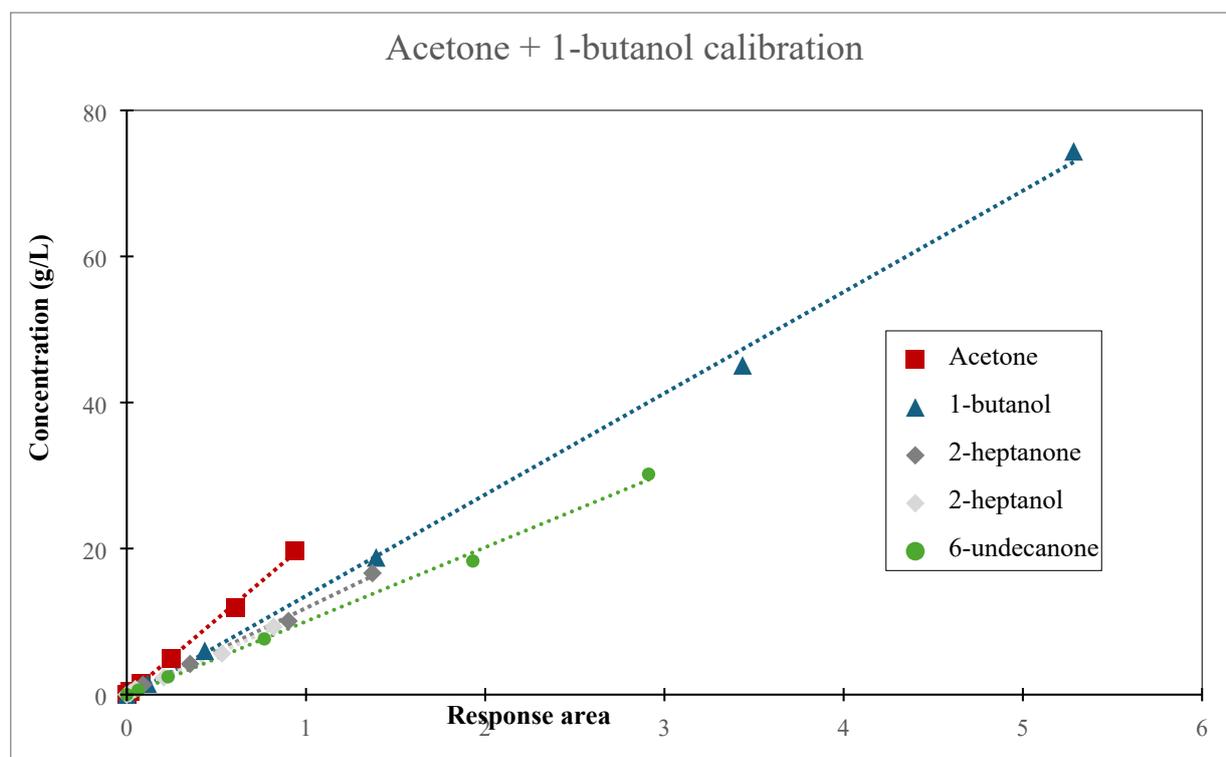
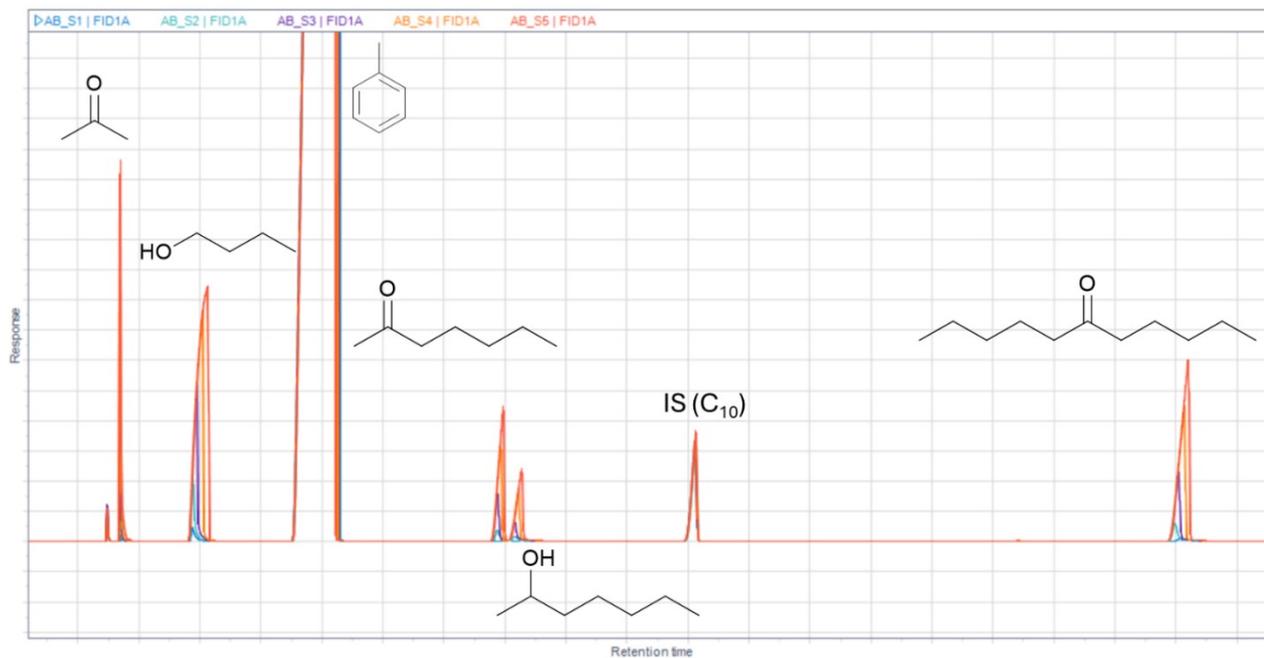
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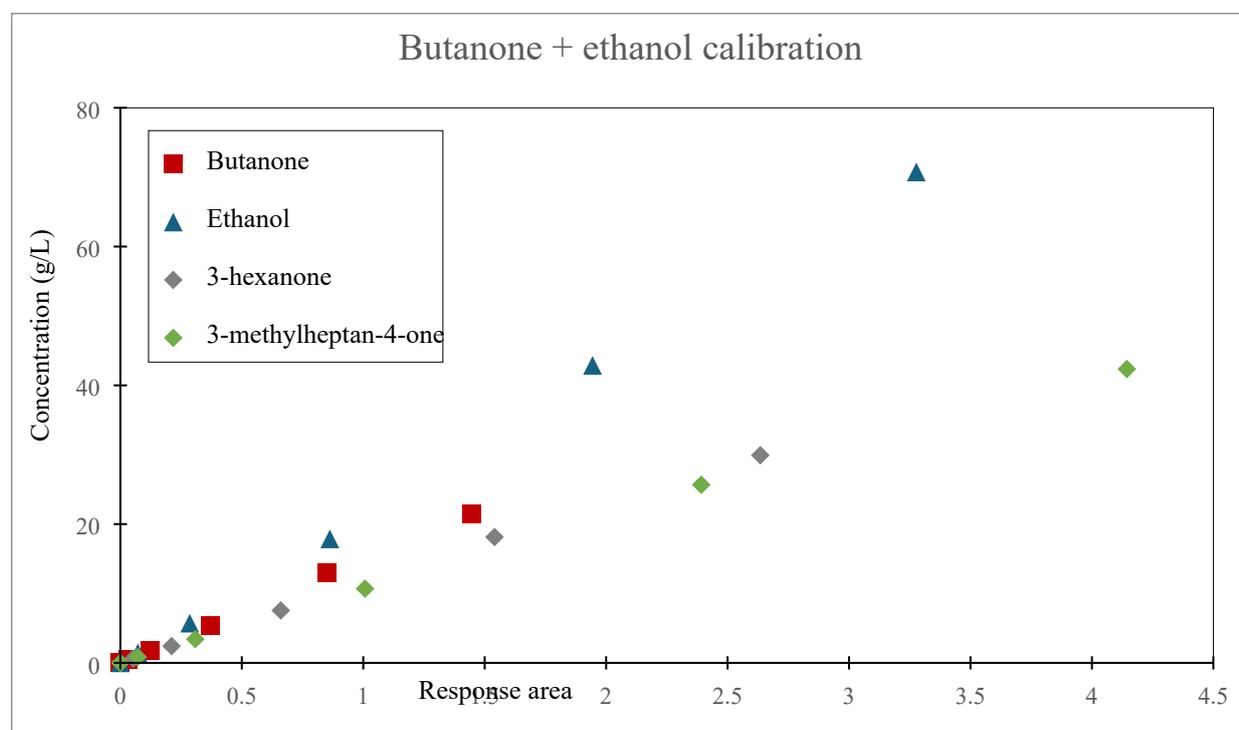
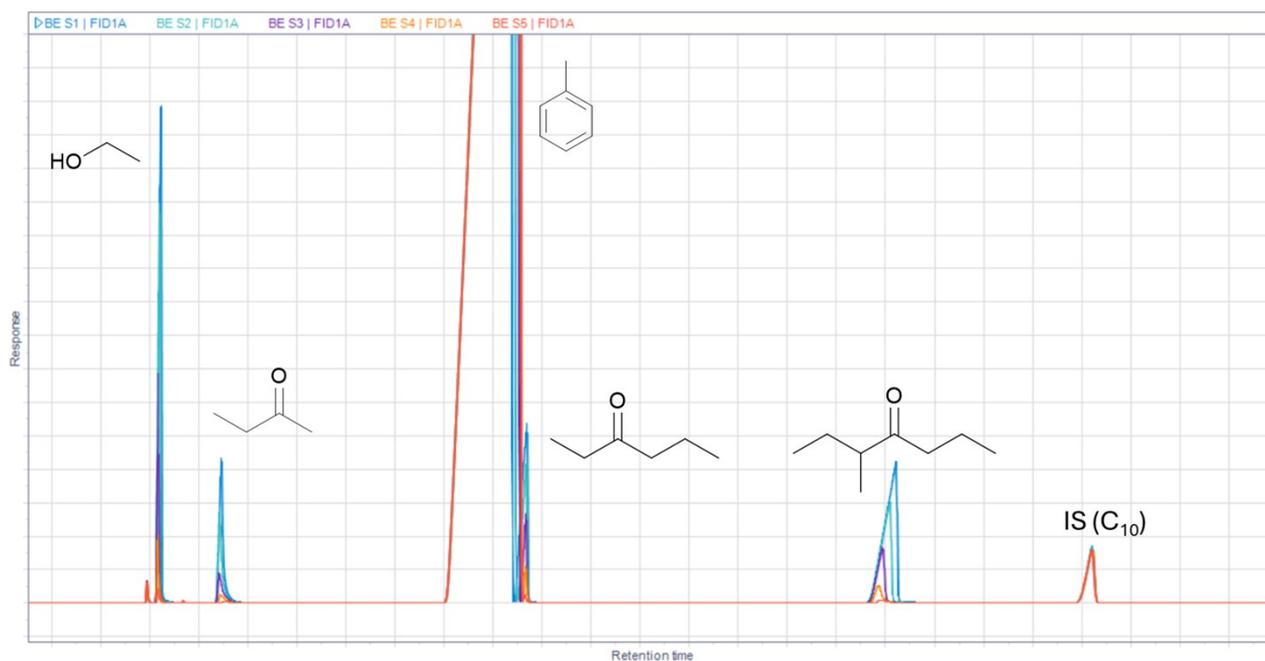
**Scheme S1.** Mechanism of the alkylation of ketones with alcohols catalysed by Pd (blue) and a base B (green). R<sub>1</sub>: CH<sub>3</sub> (ethanol) or (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> (1-butanol); R<sub>2</sub>: H (acetone) or CH<sub>3</sub> (butanone).



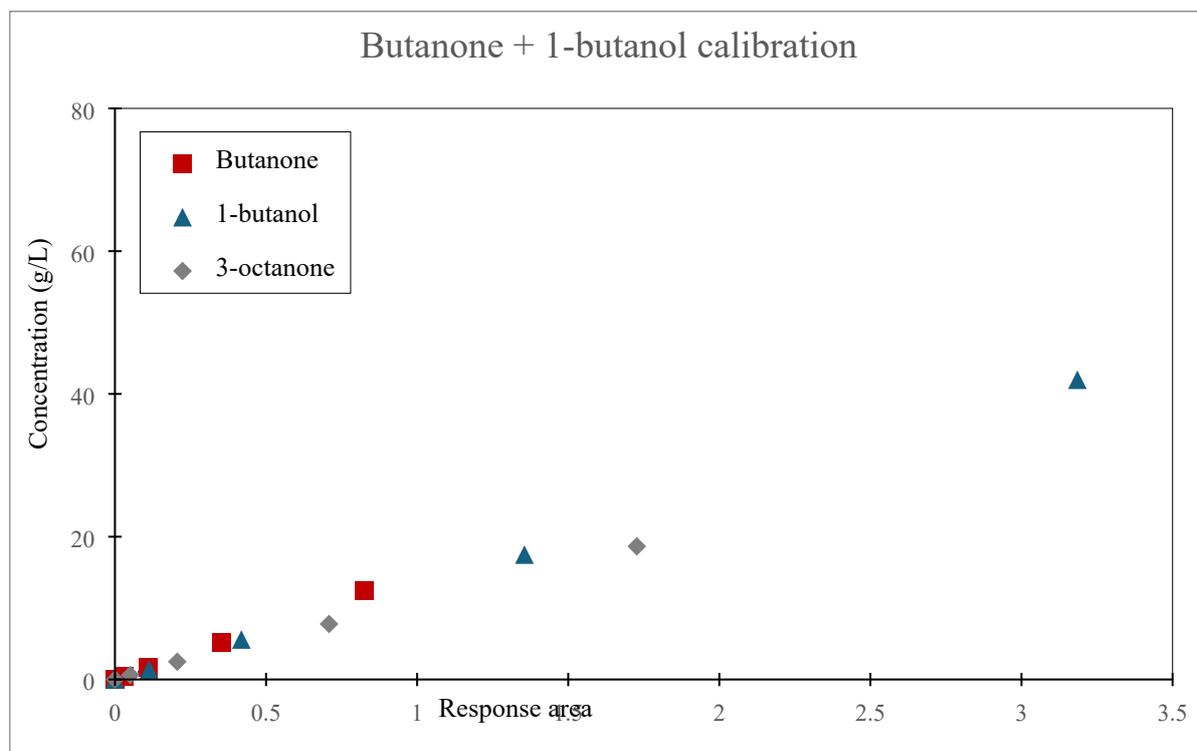
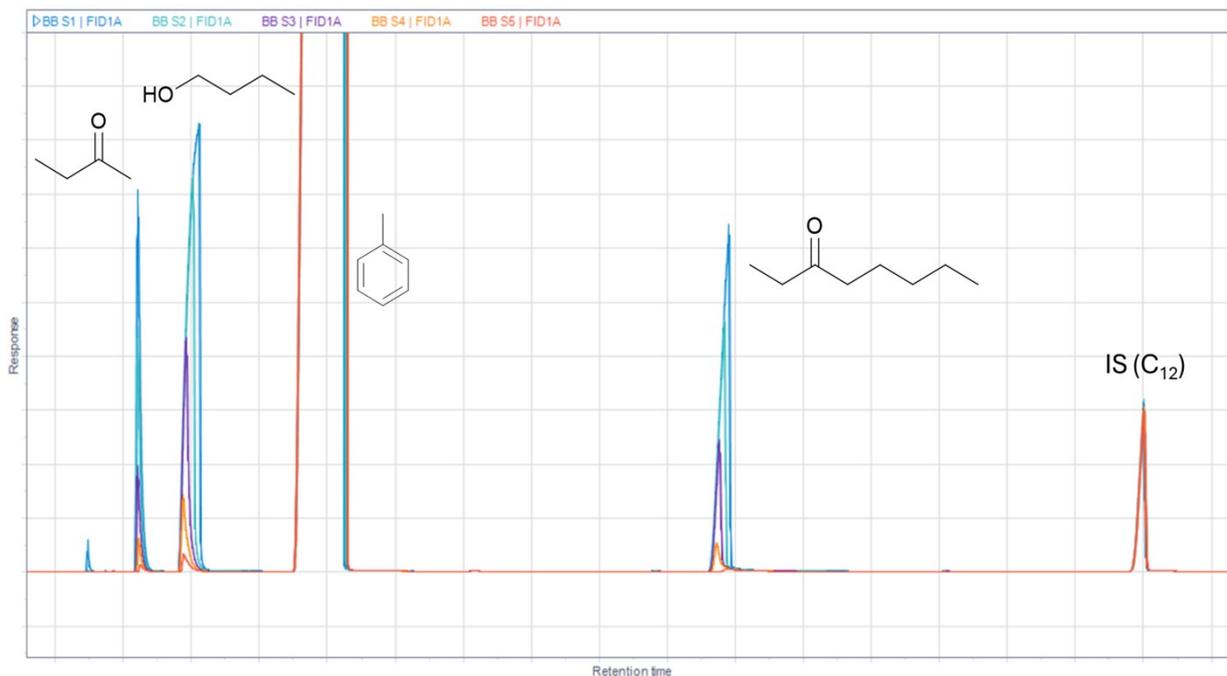
**Figure S1.** Calibration of acetone-ethanol mixtures for alkylation. Top: GC-FID standards chromatograms; bottom: calibration curves for ketone (red), alcohol (blue), monoalkylate (grey) and dialkylate (green).



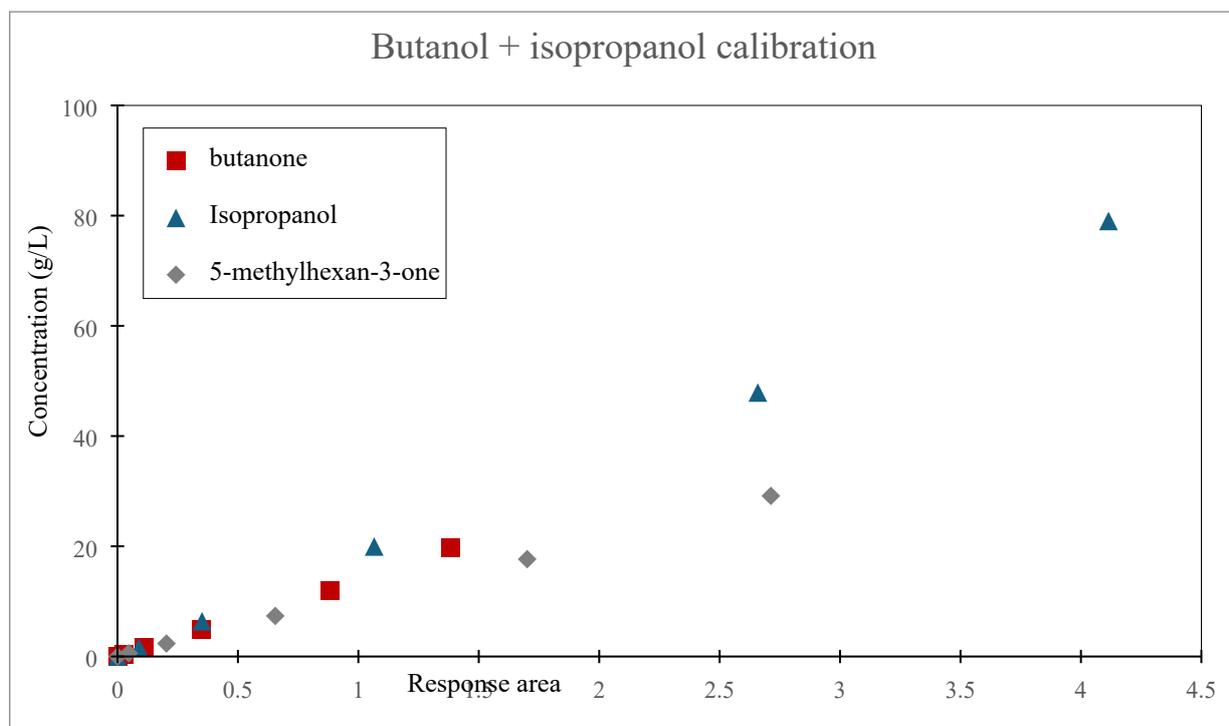
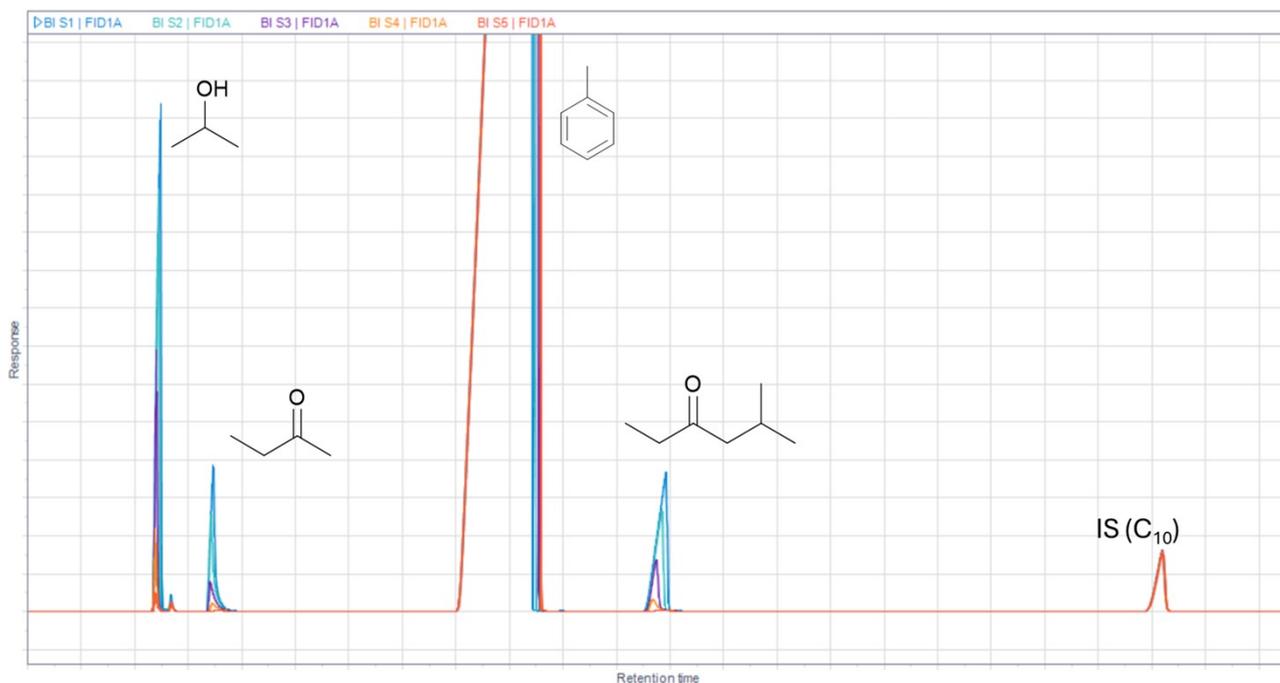
**Figure S2.** Calibration of acetone-butanol mixtures for alkylation. Top: GC-FID standards chromatograms; bottom: calibration curves for ketone (red), alcohol (blue), monoalkylate (grey), alcohol from monoalkylate (light grey) and dialkylate (green).



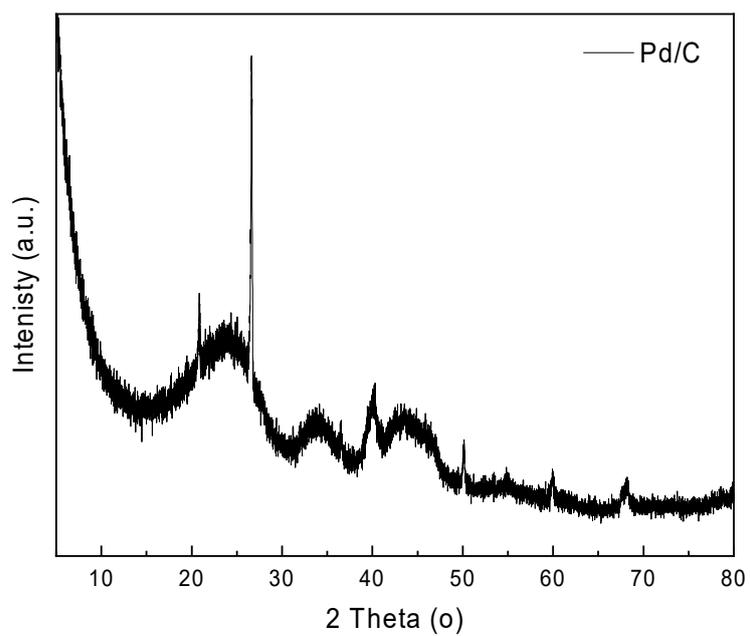
**Figure S3.** Calibration of butanone-ethanol mixtures for alkylation. Top: GC-FID standards chromatograms; bottom: calibration curves for ketone (red), alcohol (blue), monoalkylate (grey), and dialkylate (green).



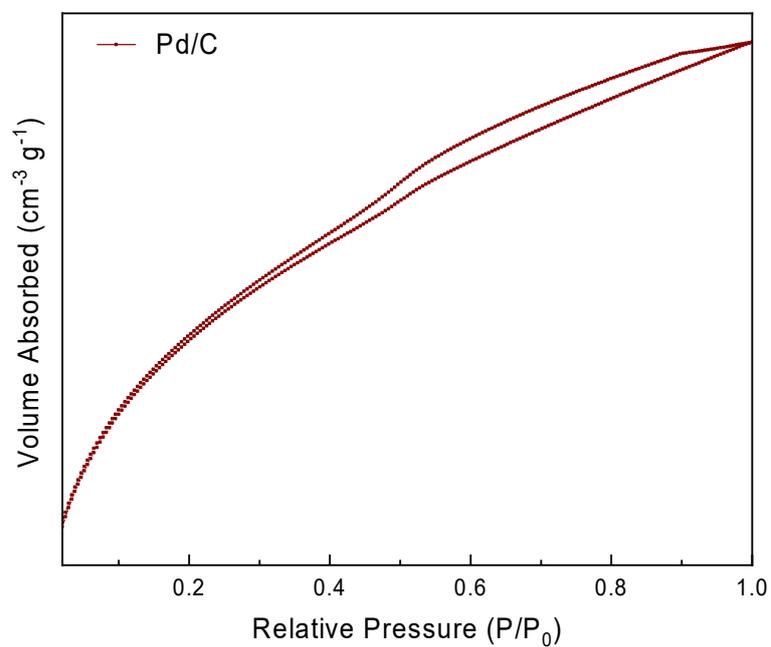
**Figure S4.** Calibration of butanone-butanol mixtures for alkylation. Top: GC-FID standards chromatograms; bottom: calibration curves for ketone (red), alcohol (blue), and monoalkylate (grey). Composition of the dialkylate was estimated via the ECN method elsewhere described.



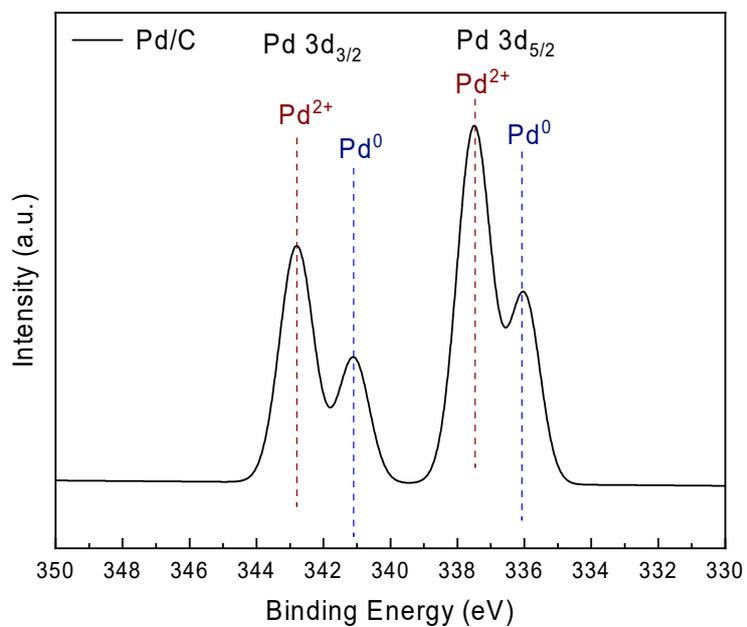
**Figure S5.** Calibration of butanone-isopropanol mixtures for alkylation. Top: GC-FID standards chromatograms; bottom: calibration curves for ketone (red), alcohol (blue), and monoalkylate (grey).



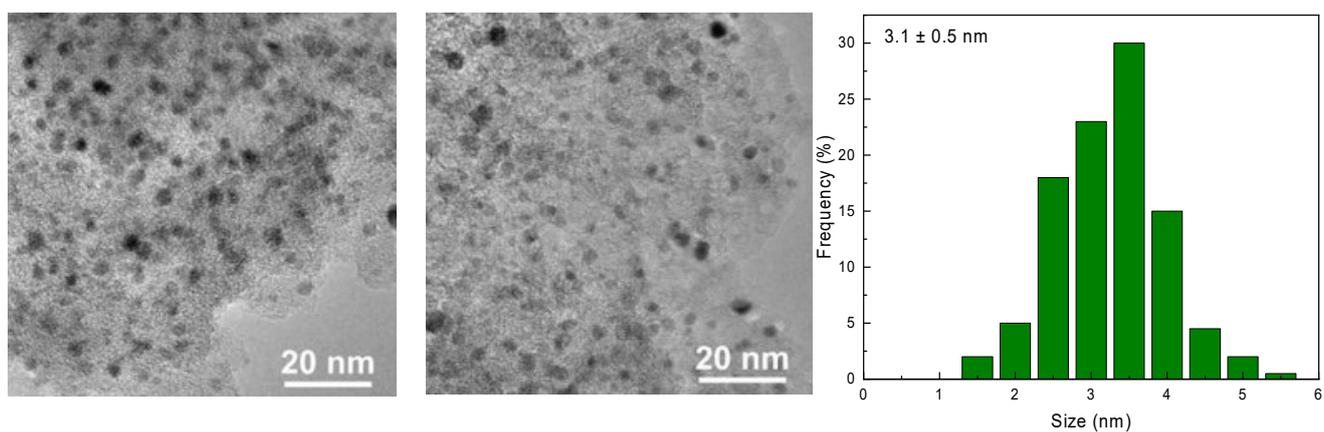
**Figure S6.** XRD diffractogram of the 5 wt% Pd/C catalyst.



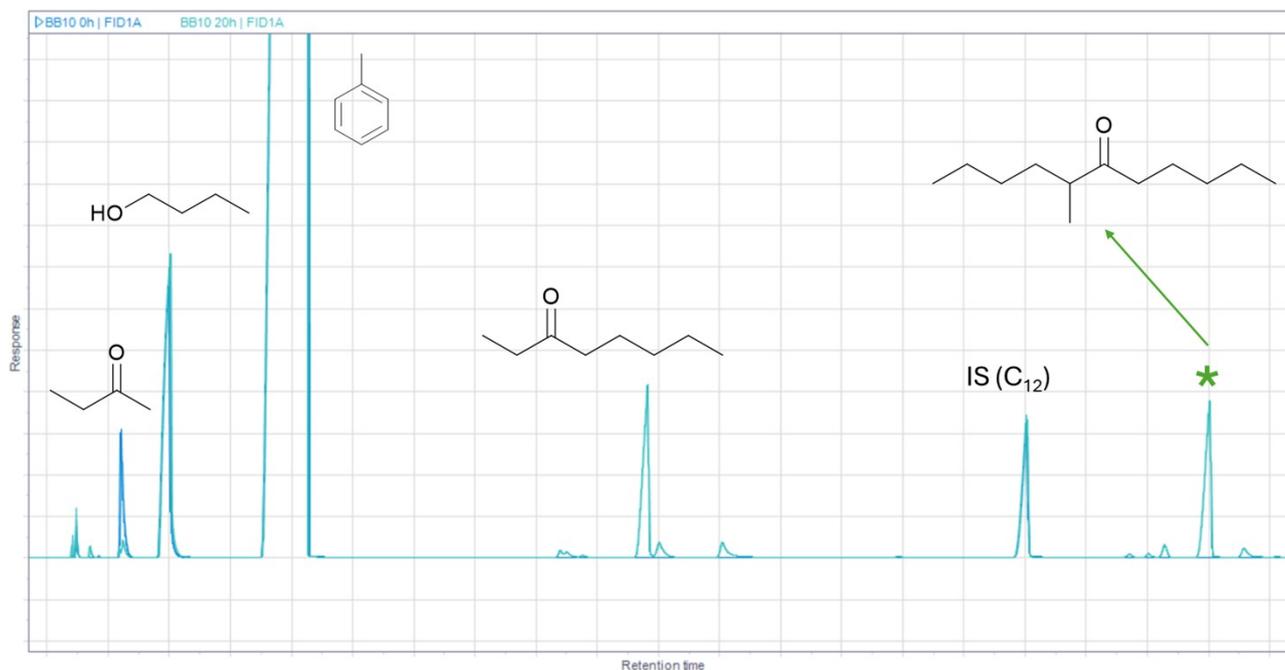
**Figure S7.** Nitrogen adsorption-desorption isotherms of the 5 wt% Pd/C catalyst.



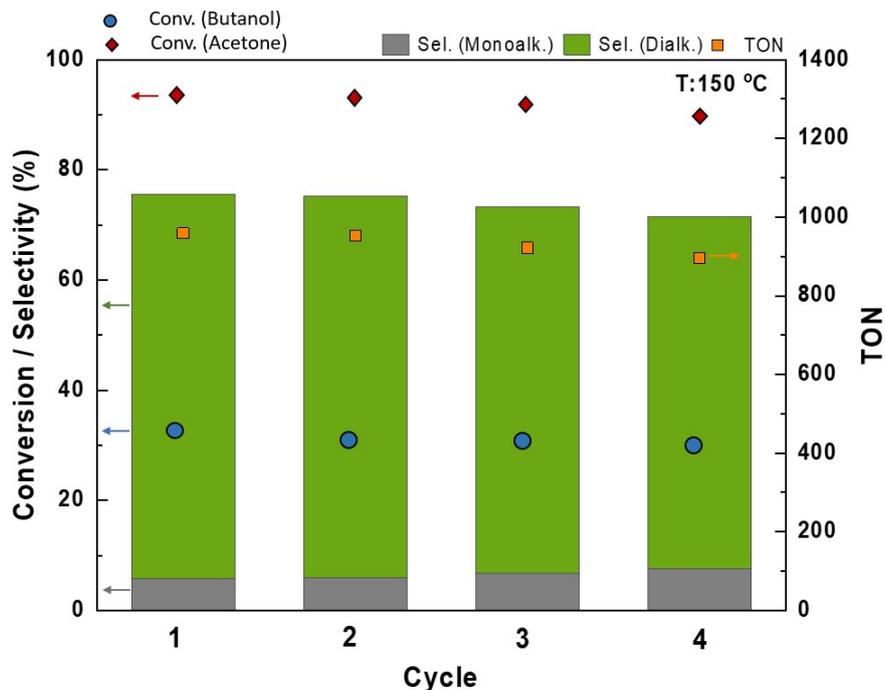
**Figure S8.** High-resolution XPS spectrum of the Pd 3d region for the 5 wt% Pd/C catalyst.



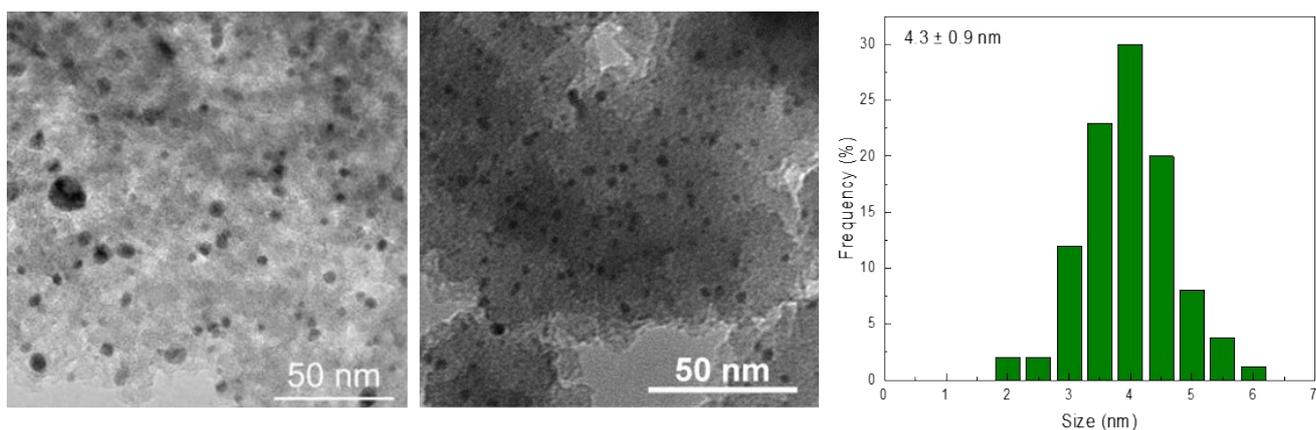
**Figure S9.** TEM images of the 5 wt% Pd/C catalyst and bar chart with the measured sizes of Pd nanoparticles on carbon (ca. 100 particles) before the alkylation reaction.



**Figure S10.** GC-FID chromatograms of reaction mixtures from the alkylation of butanone with 1-butanol at 180°C after 0 h (blue) and 20 h (turquoise). Identification of the dialkylate iso-C<sub>12</sub> (green asterisk) was performed by GC-MS, and its quantity was estimated via the ECN method elsewhere described.



**Figure S11.** Alkylation of acetone with 1-butanol with the Pd/C-K<sub>3</sub>PO<sub>4</sub> catalyst system over four reaction cycles to check the deactivation of the catalyst. Reaction conditions: Alcohol-to-ketone molar ratio 3.9 (total volume 5.6 mL), 0.017 mol% Pd, 5.0 mol% K<sub>3</sub>PO<sub>4</sub>, 20 h. Red diamonds: Conversion of acetone; Blue circles: Conversion of 1-butanol; Grey bars: Selectivity towards monoalkylated 2-C<sub>7</sub> product; Green bars: Selectivity towards dialkylated C<sub>11</sub> product; Yellow squares: turnover number (TON).



**Figure S12.** TEM images of the 5 wt% Pd/C catalyst and bar chart with the measured sizes of Pd nanoparticles on carbon (ca. 100 particles) after the four cycles of alkylation reaction. Reaction conditions as in Figure S11.

**Table S1.** Mass of reagents and catalysts used for the alkylation reactions.<sup>a,b</sup>

Ketone		Alcohol		Pd/C (mg)	K <sub>3</sub> PO <sub>4</sub> (mg)
Compound	Mass (g)	Compound	Mass (g)		
Acetone	1.08	Ethanol	3.34	32.2	968.7
Acetone	0.75	1-butanol	3.75	22.5	675.0
Butanone	1.27	Ethanol	3.17	30.6	919.1
Butanone	0.91	1-butanol	3.63	21.7	654.3
Butanone	1.04	Isopropanol	3.38	25.0	751.7

<sup>a</sup> All reactions were carried out with a constant volume of 5.6 mL, with a molar alcohol-to-ketone ratio of 3.9, Pd loading of 0.017 mol%, and K<sub>3</sub>PO<sub>4</sub> loading of 5 mol%. <sup>b</sup> Factors supporting that mass-transfer limitations did not affect the reactions: Reactions were performed in well-stirred liquid-phase autoclaves (10 mL), ensuring good dispersion and minimal external diffusion resistance, reactions proceeded homogeneously with fully dissolved oxygenates, eliminating gas-liquid or multiphase transfer barriers, and higher reaction temperatures (see Figure 2) increased selectivity and alcohol conversion, consistent with kinetic rather than mass-transfer control.

**Table S2.** N<sub>2</sub> physisorption results of the 5 wt% Pd/C catalyst.

Catalyst	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)
Pd/C	890	0.10	0.07

**Table S3.** Amount of water added to the acetone, 1-butanol reaction mixture to obtain initial water contents of 1-10 wt% relative to the total liquid phase (organics + water), calculated for a fixed organic feed consisting of 0.75 g acetone and 3.75 g 1-butanol.

Water content (wt%)	Water mass (g)	Water volume (mL)
1	0.046	0.046
3	0.139	0.14
5	0.237	0.24
7	0.339	0.34
10	0.500	0.50

**Table S4.** Pd/C-K<sub>3</sub>PO<sub>4</sub>-catalyzed alkylation of acetone with 1-butanol at 150 °C with different water contents.<sup>a</sup>

Water content (wt%)	Conversion (%)		Product Selectivity (%)		TON	TOF (h <sup>-1</sup> )
	Acetone	1-Butanol	2-C <sub>7</sub>	C <sub>11</sub>		
0	94.1	32.0	5.8	69.8	959	48.0
1	93.9	31.8	6.0	68.7	957	48.9
3	90.0	30.0	10.0	63.2	918	45.9
5	78.2	26.4	22.0	50.0	795	39.8
7	68.3	23.0	32.0	40.4	693	34.7
10	55.0	18.9	45.0	28.0	561	28.1

<sup>a</sup> Conversions, product selectivities, and turnover numbers (TONs) were determined after 20 h.

**Table S5.** Catalyst recycling results for the Pd/C-K<sub>3</sub>PO<sub>4</sub>-catalyzed alkylation of acetone with 1-butanol at 150°C over four consecutive reaction cycles.<sup>a</sup>

Cycle	Conversion (%)		Product Selectivity (%)		TON	TOF (h <sup>-1</sup> )
	Acetone	1-Butanol	2-C <sub>7</sub>	C <sub>11</sub>		
1	94.1	32.0	5.8	69.8	959	48.0
2	93.7	31.6	6.0	69.2	952	47.6
3	91.5	30.4	6.8	66.5	922	46.1
4	89.6	29.1	7.5	64.0	895	44.8

<sup>a</sup> Conversions, product selectivities, and turnover numbers (TONs) were determined after 20 h for each cycle. The catalyst was recovered by filtration, washed, dried, and reused under identical reaction conditions (see Section 2.3 in manuscript).