

# Synthesis of terephthalic acid via Diels-Alder reactions with ethylene and oxidized variants of 5-hydroxymethylfurfural

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Contributed by Mark E. Davis, May 7, 2014 (sent for review April 16, 2014)

Terephthalic acid (PTA), a monomer in the synthesis of polyethylene terephthalate (PET), is obtained by the oxidation of petroleum-derived p-xylene. There is significant interest in the synthesis of renewable, biomass-derived PTA. Here, routes to PTA starting from oxidized products of 5-hydroxymethylfurfural (HMF) that can be produced from biomass are reported. These routes involve Diels-Alder reactions with ethylene and avoid the hydrogenation of HMF to 2,5-dimethylfuran. Oxidized derivatives of HMF are reacted with ethylene over solid Lewis acid catalysts that do not contain strong Brønsted acids to synthesize intermediates of PTA and its equally important diester, dimethyl terephthalate (DMT). The partially oxidized HMF, 5-(hydroxymethyl)furoic acid (HMFA), is reacted with high pressure ethylene over a pure-silica molecular sieve containing framework tin (Sn-Beta) to produce the Diels-Alder dehydration product, 4-(hydroxymethyl)benzoic acid (HMBA), with 31% selectivity at 61% HMFA conversion after 6 h at 190 °C. If HMFA is protected with methanol to form methyl 5-(methoxymethyl)furan-2-carboxylate (MMFC), MMFC can react with ethylene in the presence of Sn-Beta for 2 h to produce methyl 4-(methoxymethyl)benzenecarboxylate (MMBC) with 46% selectivity at 28% MMFC conversion or in the presence of a pure-silica molecular sieve containing framework zirconium (Zr-Beta) for 6 h to produce MMBC with 81% selectivity at 26% MMFC conversion. HMBA and MMBC can then be oxidized to produce PTA and DMT, respectively. When Lewis acid containing mesoporous silica (MCM-41) and amorphous silica, or Brønsted acid containing zeolites (Al-Beta), are used as catalysts, a significant decrease in selectivity/yield of the Diels-Alder dehydration product is observed.

cycloaddition | dehydrative aromatization | heterogeneous catalysis

Terephthalic acid (PTA) is one of the monomers used for the synthesis of the polyester, polyethylene terephthalate (PET), that is used for the large-scale manufacture of synthetic fibers and plastic bottles. PTA is largely produced from the liquid-phase oxidation of petroleum-derived p-xylene (PX). However, there are now ongoing worldwide efforts exploring alternative routes for producing PTA from renewable biomass resources (1).

One approach to the synthesis of biomass-derived PTA has been to use a Diels-Alder reaction between a biomass-derived furanic diene and a dienophile as a way to build the six-carbon ring necessary for the synthesis of PTA. The Diels-Alder adduct is an oxabicyclic intermediate that must be further dehydrated to achieve the aromatic product. An important biomass-derived furan, 5-hydroxymethylfurfural (HMF), is a valuable platform chemical being considered for the production of many fuels and chemicals and can be obtained from glucose and other biomass feedstocks (2–4). HMF is now being manufactured at the commercial scale in Europe at 20 tons annually using a hydrothermal process (5). Thus, finding efficient routes to PTA from HMF is of great interest.

Diels-Alder routes to PTA from HMF have been investigated, and typically, they require the hydrogenation of HMF to 2,5-dimethylfuran (DMF) (6–12). It is known that DMF and ethylene

can react to form PX in a one-pot Diels-Alder dehydration reaction (7). This reaction has received much attention recently, and it is catalyzed by homogeneous Lewis acids and a wide variety of heterogeneous Brønsted acid-containing solids (7–12). Although nearly 100% PX yields from the Diels-Alder dehydration reaction can be achieved, the reduction step to convert HMF to DMF requires expensive metal catalysts and a hydrogen source, making this route challenging to commercially implement (13). Therefore, the discovery of routes to PTA from HMF that avoid any hydrogenation steps could be useful.

An oxidation route to PTA that has previously been considered is the Diels-Alder dehydration reaction of ethylene with the fully oxidized HMF, 2,5-furandicarboxylic acid (FDCA). This reaction is extremely slow and only negligible yields have been reported (14). The unreactivity of FDCA in the Diels-Alder dehydration reaction is presumably due to the strong electron-withdrawing effects of the two carboxyl (-CO<sub>2</sub>H) groups that result in a very electron-poor and deactivated diene.

Here, we report new catalytic Diels-Alder dehydration routes to produce PTA and the equally important diester of PTA, dimethyl terephthalate (DMT), beginning with the oxidation, rather than the reduction, of HMF. The partially oxidized HMF, 5-(hydroxymethyl)furoic acid (HMFA), and each of the ether and ester derivatives of HMFA are shown to react with ethylene in a one-pot Diels-Alder dehydration reaction to produce the desired aromatic product (Fig. 1). The aromatic products of these reactions can be oxidized to produce PTA or DMT. Because HMFA can be formed easily and in quantitative yields through the air oxidation of HMF (15), HMFA is a much more attractive diene than DMF for the ethylene Diels-Alder dehydration step to produce the PTA intermediate. We explored a number of different catalytic materials and conditions, and the best catalysts we found at this time are pure-silica, large-pore

## Significance

**Current, plant-based polyethylene terephthalate (PET) is produced from biomass-derived ethylene glycol [the terephthalic acid (PTA) used is not from biomass]. To have a 100% biomass-derived PET, PTA must be produced from biomass. Here, pathways for the production of renewable PTA, using Diels-Alder reactions between ethylene and oxidized derivatives of 5-hydroxymethylfurfural, a biomass-derived chemical, are reported. These pathways are enabled by new catalytic chemistry that may provide routes for the production of 100% biomass-derived PET.**

Author contributions: J.J.P. and M.E.D. designed research; J.J.P. performed research; J.J.P. and M.E.D. analyzed data; and J.J.P. and M.E.D. wrote the paper.

The authors declare no conflict of interest.

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This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1408345111/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1408345111/-DCSupplemental).

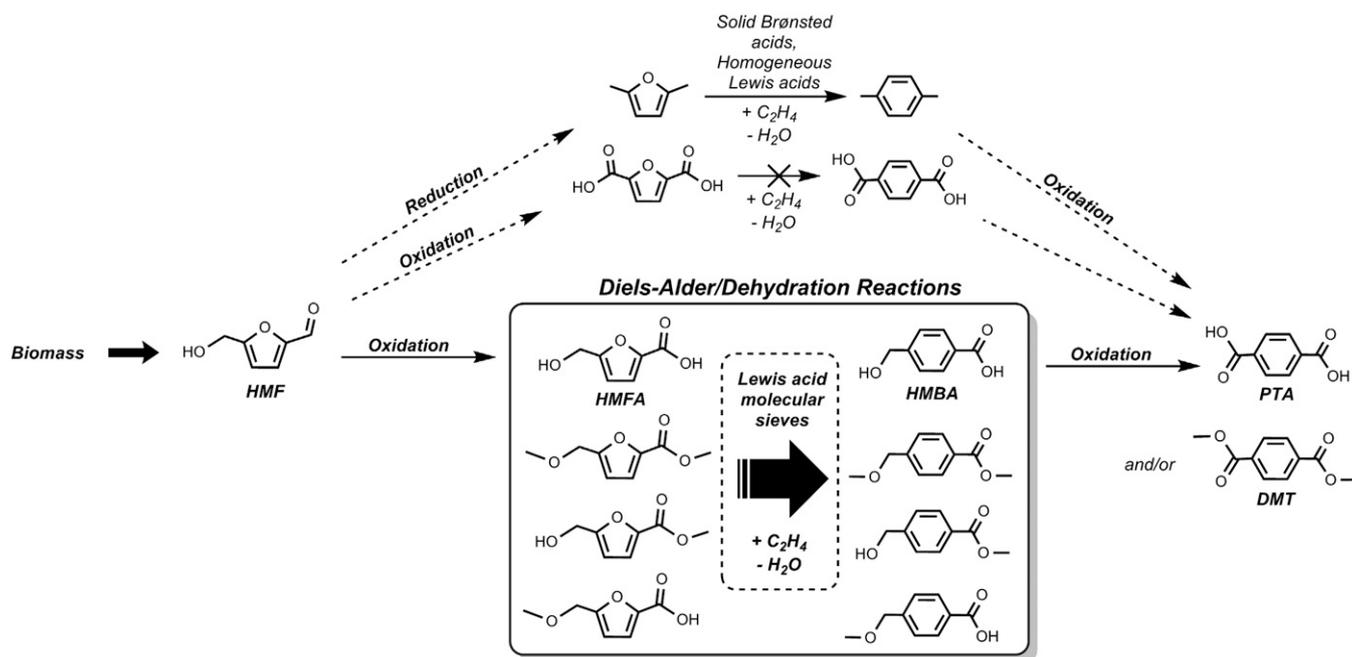


Fig. 1. Diels-Alder pathways to PTA and DMT starting from biomass-derived HMF using either reduction or oxidation steps.

molecular sieves (having the zeolite Beta topology) containing Lewis acidic centers that are created by substituting metal (M) cations in a +4 oxidation state for a small amount of the framework Si<sup>4+</sup> (denoted as M-Beta). The absence of strong Brønsted acidity is of particular importance to avoid unwanted side reactions of the oxygenated and functionalized furans at the high reaction temperature (190 °C) and pressure (70 bar) required for the activation of ethylene in the Diels-Alder step.

An important example of a Lewis acid molecular sieve is Sn-Beta, which contains isolated Sn<sup>4+</sup> within the pure-silica Beta framework. This material is known to behave as a Lewis acid catalyst in a variety of other reactions, such as the Meerwein-Ponndorf-Verley (MPV) reduction of carbonyl compounds and the isomerization of glucose (16, 17). For the isomerization of glucose, <sup>13</sup>C NMR studies using glucose deuterated at the C-2 position proved that Sn-Beta performs the isomerization via a Lewis acid mechanism (18). The use of microporous molecular sieves containing Lewis acids in the absence of strong Brønsted acidity (e.g., Sn-Beta) as catalysts for Diels-Alder cycloadditions have not been reported, but a recent review from our laboratory discussing the use of and future outlook of solid Lewis acids as catalysts for the upgrading of biomass to fuels and chemicals suggested the high potential of Lewis acidic microporous molecular sieves as Diels-Alder catalysts in biomass-related conversions (19).

## Results and Discussion

Several oxygenated furans were contacted with high pressure ethylene to screen for activity in the Diels-Alder dehydration reaction using Sn-Beta as catalyst. The results shown in Table 1 summarize the furans used in this study and their reactivities. Entries 5, 6, 8, and 9 are furans that are not readily obtained from HMF by oxidation steps only but were included in the study to assist in the understanding of the effects of different functional groups on reactivity. Dioxane was found to be the preferred solvent, and data reported in Table 1 were obtained using this solvent.

The HMF oxidation product, HMFA (entry 1), is shown to be active in the Diels-Alder dehydration reaction with ethylene to produce 4-(hydroxymethyl)benzoic acid (HMBA) with 31% se-

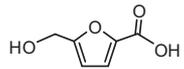
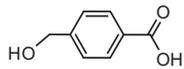
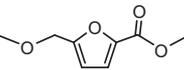
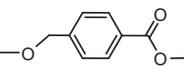
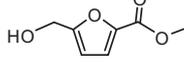
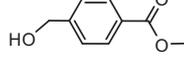
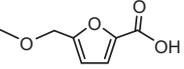
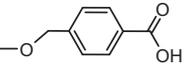
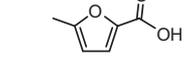
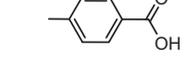
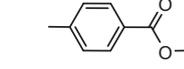
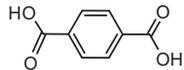
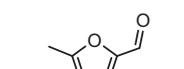
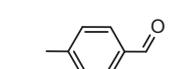
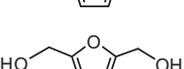
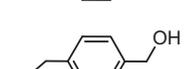
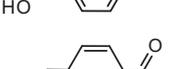
lectivity at 61% HMFA conversion using the Sn-Beta catalyst. By protecting the hydroxymethyl and acid groups of HMFA with an alcohol (i.e., methanol) to produce the corresponding ether and ester groups, a 48% selectivity to the desired product at 50% furan conversion was achieved (entry 2). Each of the HMFA functionalities were protected with methanol independently (entries 3 and 4). When the acid function was protected the selectivity increased relative to the HMFA case along with a significant decrease in conversion, but when the hydroxymethyl function was protected the selectivity decreased along with a decrease in conversion. By using methanol to protect both functionalities, the highest yield (24%) of the Diels-Alder-dehydration product was obtained using the current Sn-Beta catalyst.

Substituting the hydroxymethyl group at the 5-position with a methyl (entries 5 and 6) produced an interesting result. When the acid function remained the selectivity to *p*-toluic acid was only 27%. When the acid was converted to the ester functionality, an increase in selectivity was expected and, indeed, nearly 100% selectivity to methyl *p*-toluate was obtained at diene conversions of 12%. The 100% selectivity obtained for entry 6 suggests that only the carboxylic acid, hydroxymethyl, and methoxymethyl groups in entries 1–5 are resulting in side reactions, and the presence of the carboxylate ester group alone does not cause any side reactions.

The Diels-Alder dehydration reaction of the fully oxidized HMF, FDCA, was investigated (entry 7), and FDCA was found to be generally unreactive. PTA yields of only ~2% could be obtained by using higher temperatures (225 °C) and longer times (14 h). It is noteworthy that the product solution showed little sign visually (and also by <sup>1</sup>H NMR) of any side or degradation reactions of the FDCA reactant or of “coking” of the Sn-Beta catalyst; even after a reaction held at 225 °C for 14 h, the catalyst and undissolved FDCA remained nearly white and the dioxane solution remained nearly colorless. We conclude that the strong deactivating effects of the two carboxyl groups rendered the Diels-Alder step with ethylene too slow for practical application, so no further testing was performed.

Entries 8–10 are furans that are without a carboxylic acid or carboxylate ester functionality, and results from these experiments showed no measurable yields of the Diels-Alder

**Table 1. Results for the Diels-Alder dehydration of oxygenated furans with ethylene**

Entry	Diene	Product	Diene conversion (%)	Product yield (%)	Product selectivity (%) <sup>*</sup>
1			61	19	31
2			50	24	48
3			12	5	42
4			52	9	17
5			45	12	27
6			12	12	100
7			0 <sup>†</sup>	0	0
8			2	0	0
9			100	<1	<1
10			16	0	0

All experiments were carried out with 70 bar of ethylene gas at 190 °C for 6 h; the reactor was charged with 10 g of a 0.1 M diene solution in dioxane and 100 mg of Sn-Beta catalyst.

<sup>\*</sup>Selectivity defined as yield (product)/conversion (diene).

<sup>†</sup>The diene, FDCA, was mostly insoluble in dioxane at room temperature; the 0.1 M solution was prepared as if all of the FDCA were dissolved. Due to the insoluble nature of FDCA, concentrations (and therefore, conversions) were difficult to accurately measure with the method used. No PTA was produced per <sup>1</sup>H NMR analysis.

dehydration products. Numerous additional attempts using these furans at various reaction conditions typically resulted in significant coke formation on the catalyst, presumably preventing any formation of the desired product. Clearly, the

presence of a single carboxylic acid or carboxylate ester function seems to be playing a critical role in the ability of oxygenated furans to selectively react with ethylene in the Diels-Alder dehydration reaction in the presence of Sn-Beta.

**Table 2. Results for the Diels-Alder dehydration of MMFC and ethylene**

Entry	Catalyst	Solvent	Time (h)	Temperature (°C)	MMFC conversion (%)	MMBC yield (%)	MMBC selectivity (%)
1	None	Dioxane	6	190	1	0	0
2	Sn-Beta	Dioxane	2	190	28	13	46
3	Sn-Beta	Dioxane/hexane (1:1 vol/vol)	2	190	33	12	36
4	Sn-Beta	Dioxane	2	210	44	13	30
5	Sn-Beta	Dioxane	6	190	50	24	48
6	Zr-Beta	Dioxane	6	190	26	21	81
7	Ti-Beta	Dioxane	12	190	2	1	50
8	Sn-MCM-41	Dioxane	6	190	5	1	20
9	Sn-SiO <sub>2</sub> (amorphous)	Dioxane	6	190	16	2	13
10	Sn-MFI	Dioxane	6	190	9	1	11
11	H-Al-Beta (Si/Al = 13.5)	Dioxane	6	190	100	2	2

Experiments were carried out with 70 bar of ethylene gas and the reactor was charged with 10 g of a 0.1 M solution of MMFC and 100 mg of catalyst. Powder XRD patterns are provided in *SI Appendix, Fig. S1*, and the silicon/metal ratios for solids are provided in *SI Appendix, Table S1*.

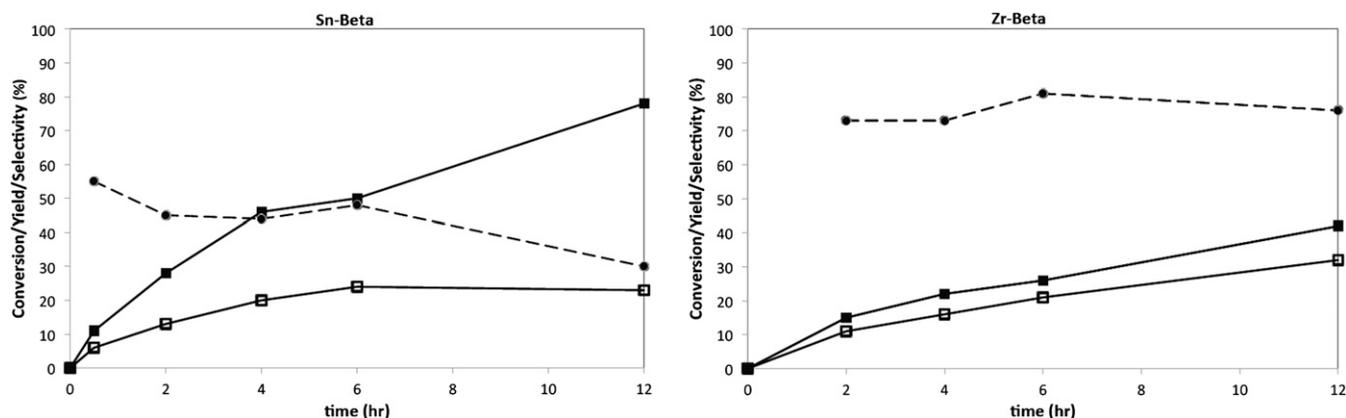


Fig. 2. MMFC conversion (■) and MMBC yield (□) and selectivity (●) as a function of time at 190 °C using Sn-Beta and Zr-Beta as catalyst. Experiments were carried out with 70 bar of ethylene gas, and the reactor was charged with 10 g of a 0.1 M solution of MMFC in dioxane and 100 mg of catalyst.

Of the four HMFA related compounds (Table 1, entries 1–4), the furan that gave the highest selectivity, methyl 5-(methoxymethyl) furan-2-carboxylate (MMFC, entry 2), was further investigated by measuring the effects of temperature, reaction time, solvent, and catalyst type on conversion, yield, and selectivity. The results are summarized in Table 2. An aliphatic solvent (hexane) was used with dioxane (entry 3) and a higher temperature was tested (entry 4), and in both cases the methyl 4-(methoxymethyl)benzenecarboxylate (MMBC) yield after 2 h of reaction remained about the same (however, the MMBC selectivity decreased) as when dioxane alone is used at 190 °C (entry 2).

The performances of other catalytic materials were compared with Sn-Beta (Table 2, entries 5–11). The type of Lewis acid metal center was varied (entries 6 and 7), and it was found that pure-silica Beta molecular sieves with Zr<sup>4+</sup> centers (Zr-Beta) were more selective catalysts for producing the Diels-Alder dehydration product, MMBC, than Sn-Beta. Zr-Beta was 81% selective for MMBC at 26% MMFC conversion. Ti<sup>4+</sup> centers in Beta (Ti-Beta) were found to be much less active than Sn<sup>4+</sup> and Zr<sup>4+</sup>. The spatial environment around the Sn<sup>4+</sup> was varied by preparing Sn<sup>4+</sup> containing mesoporous silica (MCM-41) and Sn<sup>4+</sup> containing amorphous silica (entries 8 and 9, respectively). Both materials produced lower yields and lower selectivities than Sn-Beta, suggesting that confinement effects within the microporous Beta framework are playing an important role in the selective formation of the Diels-Alder dehydration product. Smaller micropore size was tested with a pure-silica medium pore molecular sieve (having the MFI zeolite topology) containing Sn<sup>4+</sup> (entry 10), and only a small amount of MMBC was formed. A commercial, calcined Al-Beta sample (Tosoh, Si/Al = 13.5) was tested (entry 11), and complete conversion of MMFC with only 2% yield of MMBC was observed. Significant amounts of degradation reactions were apparent by the dark product solution and black solids obtained after reaction. Al-Beta contains a high concentration of Brønsted acid sites that catalyze many undesired side reactions (coke formation) involving the oxygenated functional groups of the furan and therefore resulted in poor selectivities.

The MMFC conversion and MMBC yield as a function of reaction time using both Sn-Beta and Zr-Beta as catalysts are shown in Fig. 2. Both catalysts give similar MMBC yield profiles, producing 21–24% MMBC yield after 6 h, but it is apparent from the MMFC conversion profiles that MMFC reacts faster on Sn-Beta relative to Zr-Beta. This may be in part explained by the higher amount of Sn in the Sn-Beta material compared with Zr in the Zr-Beta; energy dispersive X-ray spectroscopy (EDS) measurements show a Si/Sn ratio of 106 for the Sn-Beta catalyst, whereas the Si/Zr ratio is 185 for the Zr-Beta catalyst. Fewer side reactions occur with

the Zr-Beta catalyst, resulting in selectivities to the Diels-Alder dehydration product of more than 70%, compared with the ~50% selectivities when using Sn-Beta.

The exact mechanism of how the Lewis acid centers catalyze the Diels-Alder dehydration reactions of oxygenated furans and ethylene is not clear at this time. A recent computational study using density functional theory (DFT) experiments to elucidate the role of different acid sites in the Diels-Alder dehydration reaction between DMF and ethylene has suggested that Lewis acids can coordinate with ethylene to catalyze the [4 + 2]-Diels-Alder reaction, but there is no prior experimental evidence of the catalysis of ethylene in Diels-Alder cycloadditions (20). Additionally, the DFT study also suggested the usefulness of Lewis acids in the dehydration of cycloadducts between ethylene and furans. Several examples of Lewis acid catalysis of dehydrative aromatizations of oxabicyclic compounds, including the use of heterogeneous Lewis acids involving Fe<sup>3+</sup>-exchanged montmorillonite K10 clay, have been reported (21–23). Our current efforts are directed at understanding the reaction mechanism and the identification of the side products. Elucidation of this information may allow for the creation of even more selective catalysts for the synthesis of renewable PTA from biomass.

## Materials and Methods

**Synthesis of Catalytic Materials.** Synthesis procedures for all of the solids used as catalytic materials are given in *SI Appendix*.

**Characterization of Catalytic Materials.** Powder X-ray diffraction (XRD) confirmed that the Sn-Beta and Zr-Beta materials had the zeolite Beta topology. The XRD patterns are provided in *SI Appendix*, Fig. S1. EDS results are provided in *SI Appendix*, Table S1.

**Diels-Alder Dehydration Reactions.** Experiments were carried out in a 50-mL high pressure stainless steel batch reactor (Parr Series 4590) equipped with a magnetic stirrer and heater. The reactor setup allowed for ethylene gas (Matheson, 99.995% purity) or helium to be charged to the reactor. In a typical experiment, 100 mg of catalyst and 10 g of a 0.1 M diene solution in dioxane (Sigma-Aldrich, 99.8%) was loaded into the reactor. The magnetic stirrer was operated at 200 rpm and the head space of the reactor was purged with helium gas with a fill/vent cycle (10×). Next, the reactor was pressurized to 37 bar (room temperature) with ethylene gas, the inlet valve was closed, and the reaction was performed in batch operation. The reactor was heated to 190 °C within 15 min while the pressure increased autogenously to 70 bar. At the end of the reaction time, the reactor was allowed to cool to room temperature and the reactor gases were vented. The product was then collected for analysis.

For each reaction, the starting diene solution and product solution were both analyzed by <sup>1</sup>H NMR spectroscopy as follows: 0.2 g of each solution (the starting diene solution and product solution) was added to separate 1 g of DMSO-d<sub>6</sub> solutions containing 5 mM tetraethylsilane as an internal standard. The two

mixtures were transferred through filtering pipettes into NMR tubes, and the  $^1\text{H}$  NMR spectra were collected at room temperature. By using the tetraethylsilane peak, the concentrations could be determined, and conversions and yields were calculated. For example, the signals used for calculating the conversion of MMFC and the yield of MMBC are as follows: tetraethylsilane  $\delta = 0.49$  ppm (q, 8 H); MMFC  $\delta = 6.63$  ppm (d, 1 H)

and  $\delta = 7.26$  ppm (d, 1 H); MMBC  $\delta = 7.46$  ppm (d, 2 H) and  $\delta = 7.95$  ppm (d, 2 H), where d denotes doublet and q denotes quartet.

Details regarding the chemical suppliers of the diene reactants and Diels-Alder dehydration product standards can be found in *SI Appendix, Table S2*.

**ACKNOWLEDGMENTS.** This work was funded by Toray Industries.

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