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Biphenyl dicarboxylates from ethene and bifuran dimethyl esters

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ABSTRACT

The substrate scope of the Diels-Alder-Dehydration reaction was expanded to the deactivated bifuran structure. Dimethyl biphenyl-4,4′-dicarboxylate (**1**) and methyl 5- [4-(methoxycarbonyl)phenyl]-2-furoate (**2**) were synthesized from dimethyl 2,2′-bifuran-5,5′-dicarboxylate (**3**) via metal-triflate-catalyzed Diels-Alder-Dehydration reaction with ethene. A 31% yield of (**1**) was obtained using *Sc*(OTf)$_3$ catalyst, and a 76.6% yield of (**2**) was obtained using La(OTf)$_3$ catalyst under moderate reaction conditions. This approach is inherently selective to the 4,4′-dicarboxylates, and bypasses the methyl-group oxidation step of the dimethyl-biphenyl route.

1. Introduction

Dimethyl biphenyl dicarboxylate (**1**) and its acid, 4,4′-biphenyl dicarboxylic acid (BDA, **4**), are valuable as polymer additives, surface modifiers [1] and potentially many other applications. Copolymers of **1** (or **4**) with PET have improved thermal, mechanic, and gas-barrier properties [2]. **1** can also be used as a hepatoprotectant in the treatment of chronic hepatitis [3], and can be made into luminophore and liquid crystal precursors [4], and is a useful building block for metal-organic-frameworks (MOFs) and related materials [5].

Since **1** and **4** can be easily interconverted by esterification or hydrolysis [6], reported synthesis methods of both compounds are discussed here. In general, **1** was prepared by coupling *para*-pre-functionalized methyl benzoate. The syntheses of **4** are more diverse: it can be made by coupling of pre-functionalized p-benzoic acid, or by (hydro)alkylation and oxidation starting from benzene or toluene. Some characteristic examples are summarized below:

(1) Coupling of p-bromotoluene with magnesium in tetrahydrofuran (THF) to form 4,4′-dimethylbiphenyl, followed by oxidation with cobalt/bromine catalysts in acetic acid to form **4** (Fig. 1, a) [7] [8]. This Grignard reaction, however, consumes magnesium and produces large quantities of Mg salts, making it impractical above preparative scale.
(2) Reacting biphenyl with a halogenated cyclohexane to form 4,4′-dicyclohexyl biphenyl under iron chloride or aluminum chloride catalyst, followed by 4,4′-dicyclohexyl biphenyl oxidation with cobalt/manganese/bromine catalyst (Fig. 1, b) [9]. Besides using flammable and toxic solvents (nitrobenzene or carbon disulfide), the oxidation of 4,4′-dicyclohexyl biphenyl results in the loss of two cyclohexyl groups, which significantly reduces the atom efficiency and increases cost.
(3) Hydroalkylation of toluene to form (methylcyclohexyl) toluene (**5**), followed by the dehydrogenation and isomerization of **5**, to form dimethyl biphenyl that is then oxidized using NaBr catalyst to form **4** (Fig. 1, c) [10]. By our estimation, this hydroalkylation-isomerization method only produces 20.3% of 4, 4′- dimethyl biphenyl [11].

Tandem Diels-Alder dehydration of biomass-derivatized materials with ethene provides new venues for producing molecules containing benzoic ring(s) [12–18]. Lignocellulosic biomass is the most abundant renewable feedstock, and the source of a variety of furanic and phenyl-group containing acids [19]. Ethene can be produced by bioethanol dehydration [20,21]. Then benzoic compounds could be made from 100% renewable carbon by the tandem Diels-Alder dehydration reaction between furanic compounds and green ethene. In a previous report we described a convenient method of production of the dimethyl 2,2′-bifuran-5,5′-dicarboxylate (**3**) from methyl 2-furoate (Fig. 1, d) [22], which ultimately originates from non-edible C$_5$-sugar-derived furfural. Herein, we investigated the formation of dimethyl biphenyl-4, 4′-dicarboxylate (**1**) from **3** via the tandem Diels-Alder dehydration reaction with ethene.

The DA/dehydration reaction between deactivated furan and a

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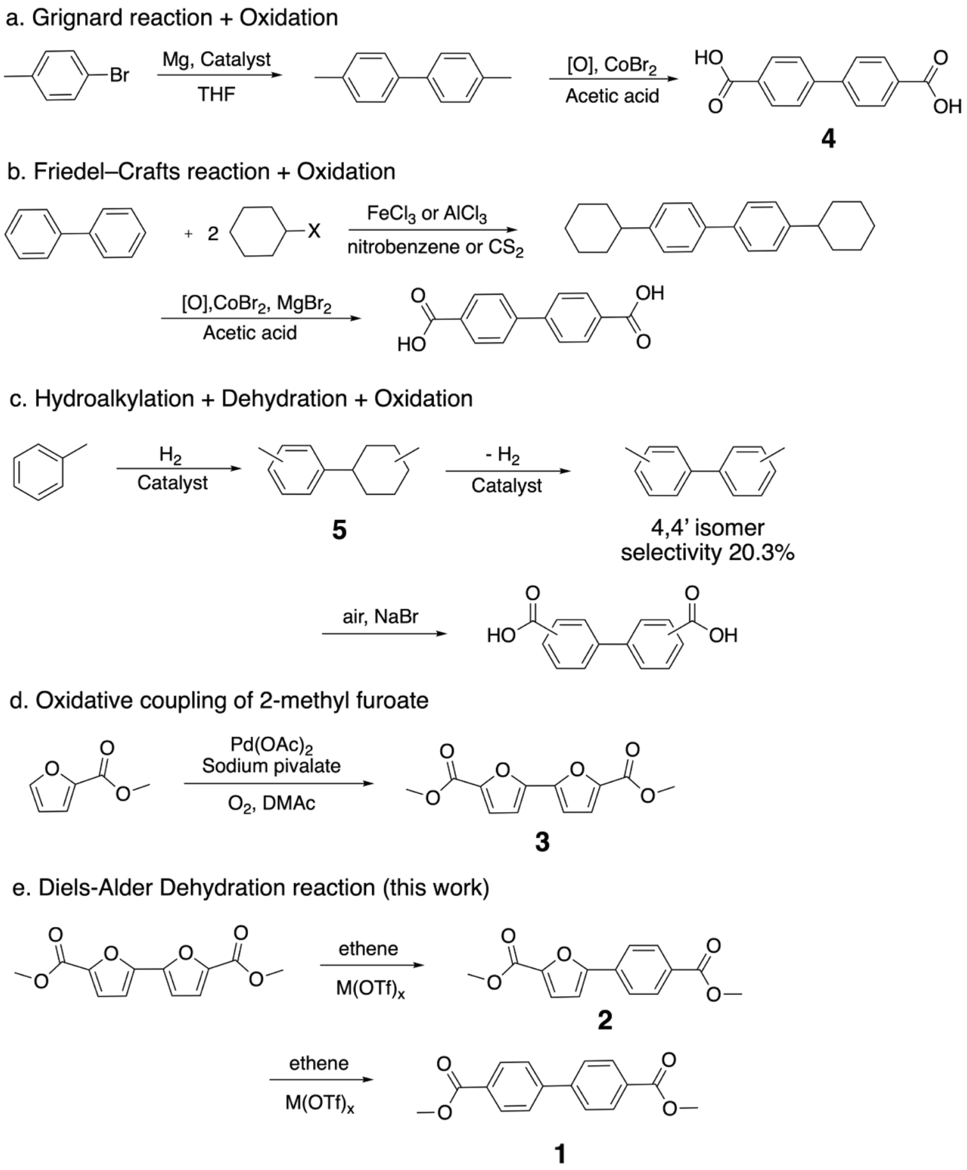
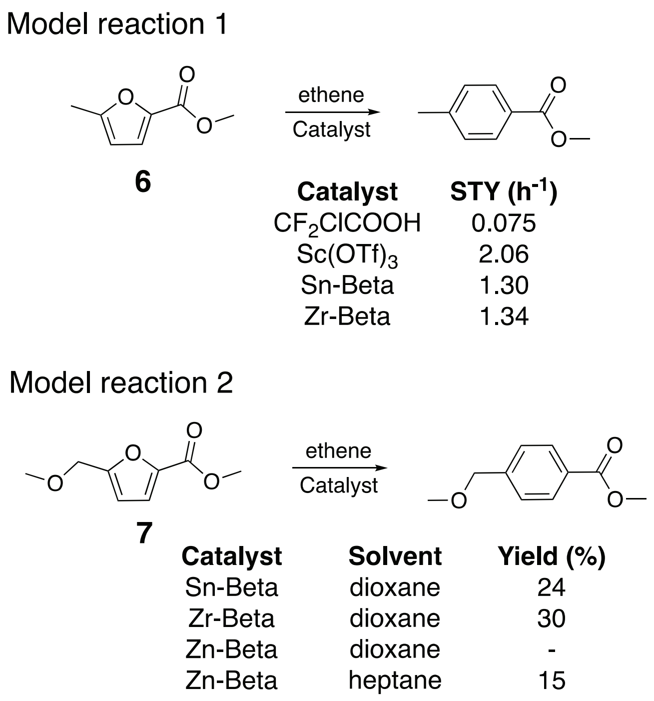


Fig. 1. Protocols for the synthesis of **1**, **4** and **3**, and this work.

nonactivated dienophile is a major scientific challenge for its slow kinetics and unfavorable thermodynamics [23]. Several attempts to carry out this reaction have been reported with both homogeneous and heterogeneous catalysts. Song et al. reported that homogeneous haloacetic acids (Brønsted acids) and rare-earth metal triflates (Lewis acids) could catalyze the reaction of various furans, including the ester group-containing methyl 5-methyl-2-furoate (**6**) [24]. *Sc*(OTf)$_3$ was a particularly effective catalyst. A 49.5% yield of Methyl 4-methylbenzoate can be achieved in a 24-h reaction in 1,4-dioxane (Fig. 2). Pacheco and Davis reported that a silica molecular sieve catalysts containing framework Lewis acid centers (Sn-Beta and Zr-Beta) could catalyze the reaction of ethene with various deactivated furans such as **6**, and methyl 5-(methoxymethyl)furan-2-carboxylate (**7**) (Fig. 2) [25, 26]. Dioxane was also used as the solvent. Sn-Beta and Zr-Beta displayed similar space-time-yield (STY) in the case of **6** under similar reaction conditions (besides reaction time). While for the reaction of **7**, conversion under Zr-Beta (39%, 24 h) was lower than that of Sn-Beta (50%, 6 h), the selectivity under Zr-Beta (76%) was higher than under Sn-Beta (48%) (Fig. 2). This could be partially explained by the higher Si/Zr ratio (185) in Zr-Beta than the Si/Sn ratio (106) in Sn-Beta. Orazov and Davis reported that CIT-6, a zincosilicate with the zeolite Beta topology (Zn-Beta), was a versatile catalyst in the DA/Dehydration reaction among many other reactions [27]. However, in contrast to Sn- and Zr-Beta, heptane was used as the solvent. Oxygenated solvents bind too strongly to the catalyst even at relative high temperature, resulting in no **7** reaction in dioxane (Fig. 2). Heptane was then used as the solvent and 15.6% yield was achieved. Zn-Beta has no Brønsted acid sites by IR, therefore, the reaction was purely catalyzed by Lewis acid sites. Selectivity of reaction of **7** in Zn-Beta (51%, heptane) is higher than that with Sn-Beta (48%, dioxane), but lower than that of Zr-Beta (76%, dioxane) (Fig. 2). Interestingly, due to its high Lewis acidity, Zn-Beta was able to catalyze reactions not previously observed with Sn-, Ti- and Zr- based Lewis acid silicate catalysts such as the reaction of ethene with dimethyl 2,5-furandicarboxylate to produce dimethyl terephthalate (DMT), although the yield (3.4%) and selectivity (5%) were low [27].

Based on reported data on the reaction of **6** [24–26], we estimate that (see Appendix A) the STY of the homogeneous *Sc*(OTf)$_3$ catalyst is about 1.5 times higher than that of the Sn-Beta and Zr-Beta. However, the **6** concentration was two times higher in the *Sc*(OTf)$_3$ experiment than that of Sn-Beta and Zr-Beta experiments, plus the temperature in *Sc*(OTf)$_3$ experiment (200 °C) was 10° higher than that of Sn-Beta and Zr-Beta experiments (190 °C). We conclude that these three catalysts have



Catalyst	STY (h^{-1})
$CF_2ClCOOH$	0.075
$Sc(OTf)_3$	2.06
Sn-Beta	1.30
Zr-Beta	1.34

Catalyst	Solvent	Yield (%)
Sn-Beta	dioxane	24
Zr-Beta	dioxane	30
Zn-Beta	dioxane	-
Zn-Beta	heptane	15

Fig. 2. Model DA-Dehydration reactions of furoates (**6** and **7**) with ethene for catalyst screening.

similar (same order of magnitude) catalytic reactivity. Because dioxane was not a compatible solvent with Zn-Beta [27], and **3** is hardly soluble in hydrocarbons, we did not pursue the reaction of **3** with Zn-Beta catalyst. The simplicity of the system, together with the consideration that **3** is a relatively large molecule, led to the selection of homogeneous metal triflate catalysts for the investigations described below.

2. Experimental

2.1. Materials

3 can be synthesized by our previous reported methods [22], or can be purchased from commercial sources. Here, to reduce our workload, commercial **3** purchased from Boron Molecular was used. Ethene (polymer grade) was purchased from Matheson Tri-Gas. Scandium triflate was purchased from Sigma-Aldrich. Yttrium(III) trifluoromethanesulfonate, lanthanum(III) trifluoromethanesulfonate, 1, 4-dioxane, diethylene glycol diethyl ether (DGDE), dimethyl 4, 4′-biphenyldicarboxylate (DMBP) and diethyl 4,4′-biphenyldicarboxylate were purchased from TCI America. Methyl 4-biphenylcarboxylate, dibromomethane, iron triflate, acetic acid, and Chloroform-d were purchased from Alfa Aesar. Methanol was purchased from Fisher Chemicals. H-Beta zeolite (HCZB 150) was kindly supported from Clariant. Phosphorus-containing silica (P-SiO_2) was synthesized by our previously reported method [15].

2.2. Methods and product analysis

The reaction was conducted in a stainless-steel batch reactor (50 mL, 4790 pressure vessel, Parr Instrument Company) with a PTFE liner (1431HCHA, Parr Instrument Company) and a magnetic stir bar. Heat shrinkable probe cover was purchased from Tef Cap Industries Inc. to protect the thermocouple. In a typical experiment, the reactor was charged with **3** (125 mg), metal triflate (0.01 mmol), solvent (5 mL) in sequence at room temperature and sealed. The vessel was purged with ethene (34.5 bar) three times to remove all the air inside. Then the reactor was charged with 34.5 bar ethene, and was heated to the reaction temperature by a heating band (Omegalux® MB mica insulated band heaters, NHL00144) controlled by a PID temperature controller (Cole- Parmer 89000-10) under magnetic stirring. Then the reaction was proceeded to specific length of time. After the reaction, reactor was quenched in water batch. Ethene was carefully released in a fume hood.

Table 1
Catalyst and solvent screening.

Entry	Catalyst	Solvent	Conversion (%)	Y_2 (%)	Y_1 (%)
1	H-Beta	1,4-Dioxane	53.5	1.4	0
2	P-SiO_2	1,4-Dioxane	22.0	12.2	0
3[a]	$Sc(OTf)_3$	1,4-Dioxane	84.5	52.5	11.5
4	$La(OTf)_3$	1,4-Dioxane	74.1	60.7	3.3
5	$Nd(OTf)_3$	1,4-Dioxane	68.6	27.0	1.1
6	$Fe(OTf)_3$	1,4-Dioxane	55.4	6.6	0
7[b]	$Cu(OTf)_2$	1,4-Dioxane	43.0	13.2	0.2
8[b]	$Sc(OTf)_3$	Tetrahydropyran	78.8	6.5	0.2
9	$Sc(OTf)_3$	Acetic acid	63.6	30.8	0.9

Reaction conditions: **3** 0.5 mmol, solvent 5 mL, metal triflate 0.01 mmol, H-Beta zeolite 100 mg, P-SiO_2 100 mg, ethene 34.5 bar, 200 °C, 3 h. Y_2: yield of **2**. Y_1: yield of **1**. a: 4 h. b: 180 °C.

To determine the product distribution and quantity after reaction, the reaction mixture was diluted and fully mixed with 30 mL of dibromomethane and 15 mL of methanol. A known weight of DGDE (~90 mg) was also added to the mixture and fully mixed as an GC internal standard. Products was identified with GC/MS (Agilent 8890 GC, Agilent 5977B GC/MSD) and quantified with GC (Agilent 7890B) with an FID detector and an Agilent DB-17HT column. The concentration of **3, 1** and byproducts were calibrated with DGDE with commercial samples. The effective carbon number (ECN) of **3** and **1** was averaged and used as the ECN of **2**. Similarly, ECN of the ethyl methyl 4,4′-biphenyldicarboxylate was taken as the average of the ECN of dimethyl 4,4′-biphenyl dicarboxylate (**1**) and diethyl 4,4′-biphenyl dicarboxylate. Due to the lack of commercial sample, the ECN for methyl 2,2′-bifuran-5-carboxylate was represented by the ECN of **3** in calculating the carbon balance.

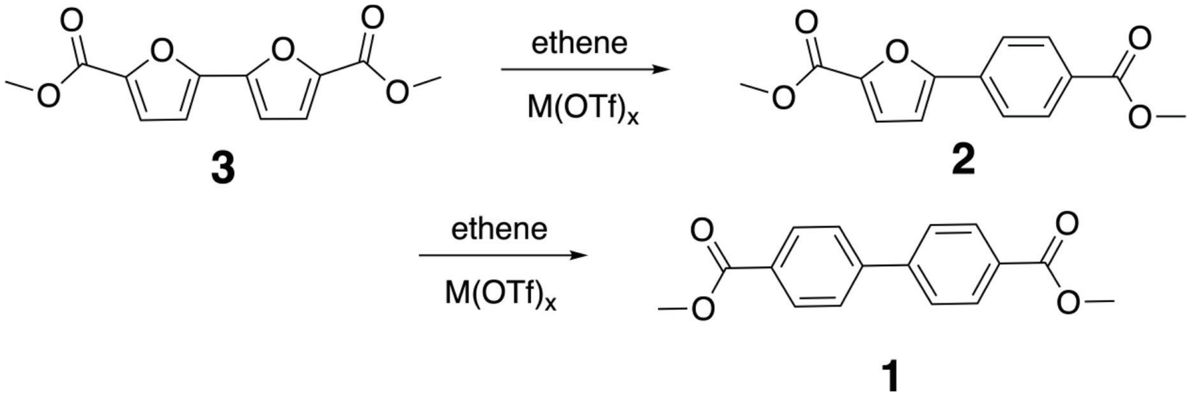
Yield was defined as $Yield = \frac{mol\ of\ desired\ product(s)}{mol\ of\ converted\ 3} \times 100\%$. Selectivity reported in this paper was defined as $Selectivity = \frac{mol\ of\ 2\ +\ mol\ of\ 1}{mol\ of\ converted\ 3} \times 100\%$. Space-time yield (STY) was defined as $STY = \frac{mol\ of\ 2\ +\ 2\times mol\ of\ 1}{(mol\ of\ active\ sites)\times(reaction\ time\ h)}$. Carbon balance (C.B.) was defined as $C.B. = \frac{\sum carbon\ numbers\ in\ all\ recovered\ liquid\ phase\ reactant\ and\ products}{(12\times mol\ of\ input\ 3)+(2\times mol\ of\ ethene\ added\ to\ the\ substrates)} \times 100\%$ in this paper.

2.3. Product separation test

The reaction conditions of $La(OTf)_3$ catalyst (220 °C for 4 h of reaction) were used to assess the proposed separation method. Reaction procedure was the same as described above. After the prescribed reaction time, once the reactor was cooled down and ethene was released, the reactor was opened and placed in a fume hood overnight to evaporate the 1,4-dioxane. Once the dioxane was removed, 30 mL of water was added and fully stirred to dissolve the $La(OTf)_3$, and then the liquid and solid were separated by centrifugation. The solid was transferred to a 50 mL flask, and any residual water in the solid was removed using a rotavap. The solids were then fully dissolved by CH_2Br_2 and methanol, and 0.1 mL of DGDE was added to the flask as the GC internal standard. The product was quantified by GC-FID using the same method described above.

3. Results and discussion

An initial catalyst and solvent screening (Table 1) revealed that rare earth metal triflate and 1,4-dioxane were effective catalysts and solvents for this reaction. To find the optimal reaction conditions, the reaction was conducted with $Sc(OTf)_3$, $Y(OTf)_3$ and $La(OTf)_3$ at 180 °C, 200 °C,



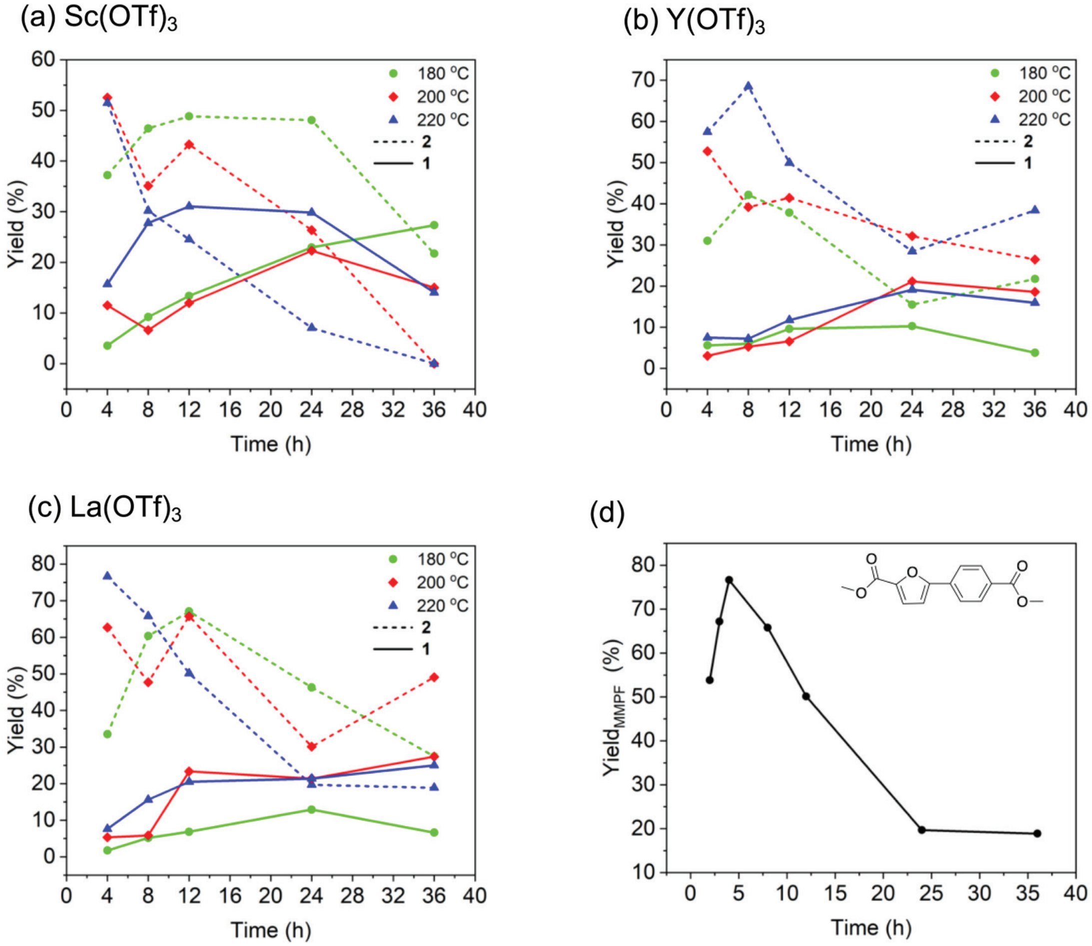


Fig. 3. Yield for **2** and **1** with (a) *Sc*(OTf)$_3$ catalyst, (b) Y(OTf)$_3$ catalyst, (c) La(OTf)$_3$ catalyst; and Yield for **2** with La(OTf)$_3$ catalyst, and (d) Yield of **2** over time string with La(OTf)$_3$ catalyst at 220 °C. Conditions: **3** 125 mg (0.5 mmol), metal triflate (0.01 mmol), 1,4-dioxane 5 mL, ethene 34.5 bar.

and 220 °C from 4 h to 36 h (Fig. 3). The intermediate, methyl 5-[4-(methoxycarbonyl)phenyl]-2-furoate (**2**) was formed rapidly with high yield and good selectivity; the transformation of **2** into **1**, however, was much slower. The yield for **1** first increased with time but then decreased rapidly. Initially, because **2** concentration was low, the reaction to form **1** was also slow, and as **2** accumulated in the solution, the reaction from **2** to **1** increased proportionally. However, competing reactions such as decarboxylation and polymerization, unavoidably reduce selectivity and the carbon balance (C.B.). The optimal conditions for producing **2** were La(OTf)$_3$ as catalyst, at 220 °C for 4 h in dioxane. The conversion of **3** was 85.3% with **2** yield of 76.6% and **1** yield of 7.6%. The optimal conditions for producing **1** uses *Sc*(OTf)$_3$ as catalyst, at 220 °C for 12 h. In this case, **3** reacted to completion with **2** yields of 24.5% and **1** yield of 31.0%.

Because of its relevance to scale up, we also developed a process to recover the metal triflate of this homogeneous reaction: After reacting to completion, dioxane was removed and water was added to the product mixture. **3, 2** and **1** were precipitated as a mixture of solids. The metal triflate, however, remained dissolved in the aqueous phase. The liquid and solid phases were easily separated by filtration or centrifugation. Water could be removed from the aqueous solution by distillation and then recycled, leaving metal triflate as a solid that can be reused. Many reports have demonstrated that rare-metal triflates are robust catalysts even in aqueous phase [28–30]. Therefore, the catalyst activity would not be affected once water is completely removed. The water-resistance feature of metal triflates is also beneficial towards water produced as byproduct of the desired reaction. The recovered solid phase (from filtration or centrifugation) typically contains a mixture of **2**/**3** or **2**/**1** (Fig. 3). In a separation experiment, 75% of the organics (16% **3** and 59% **2**) were successfully retrieved compared to direct quantification under the same reaction conditions (see Appendix A). It was presumed the experimental handling loss was the major contributor to the loss in recovery, suggesting the feasibility of this separation method.

The melting points for **3** and **1** were 220.4 °C and 224 °C, respectively [22,31]. Interestingly, the m.p. for **2** is 157–158 °C [32], much lower than that of **3** and **1**, probably due to the lower symmetry of this molecule [33]. The differences in m.p. provide a plausible separation strategy through melting crystallization [34], and should lead to differences in solubility in polar solvents that can be used for selective dissolution/recrystallization [33]. Any leftover **3** would be recycled to the reactor. And if **2** is a desired product, it could be either recycled by for further reaction or used as a product. In principle, this approach can separate the metal triflate catalyst as well. The catalyst recycling enables scaling-up of the reaction process, making this homogeneous process more advantageous that using heterogeneous Lewis acid catalysts, including but not limited to higher activity, selectivity [35], and no coking-dependent deactivation.

4. Conclusions

In summary, we established catalyst and reaction conditions for the tandem Diels-Alder/dehydration reaction of biomass-derived **3** with ethene to produce species **2** and **1**. This is the first report on the DA-Dehydration reaction on deactivated bifurans. The optimal yield (76.6%) and selectivity for **2** are high under La(OTf)$_3$ catalyst at 220 °C after 4 h of reaction. The highest yield (31%) for **1** was achieved under *Sc*(OTf)$_3$ catalyst at 220 °C for 12 h. While the yield and selectivity for **1** are lower, these reaction results are comparable to other reports where reactant pre-functionalization was not used (See Appendix) [9,10]. The decarboxylation of reactants and products were identified as the main competing reactions, resulting in lower yields and carbon balance for **1**. The second Diels-Alder/dehydration step (from **2** to **1**) has higher activation energy than the first, leading to product decarboxylation and formation of other undesired species. The decrease in cation size from La^{3+}, to Y^{3+} and to Sc^{3+} [36], resulting increases in their triflate salts Lewis acidity, which possibly making *Sc*(OTf)$_3$ more effective in catalyzing the second DA/dehydration reaction (from **2** to **1**). However, when comparing the reaction from **3** to **2**, which is comparatively easier, the gentle Lewis acidity of La(OTf)$_3$ was found suitable, while the strong Lewis acidity of *Sc*(OTf)$_3$ promoted the decarboxylation during the DA/dehydration reaction, leading to lower selectivity to the formation of **2**. Species **2** is expected to be more stable than **3** due to the stabilization provided by the phenyl group, and it is potentially a substitute to **1** for several of the applications for which the biphenyl dicarboxylate has been investigated. Our findings provide not only a new practical synthesis method for the **1**, but also a facile and high-yield method for the preparation of **2**, which previously could only be obtained from heterocoupling of methyl furoate with methyl benzoate [37,38]. Our results also allow for the evaluation of **2** as a biomass-derived diacid for a multitude of applications.

CRediT authorship contribution statement

Mingchun Ye: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft. **Mi Jen Kuo:** Investigation. **Raul F. Lobo:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.112949.

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