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^{31}P NMR Chemical Shifts of Solvents and Products Impurities in Biomass Pretreatments

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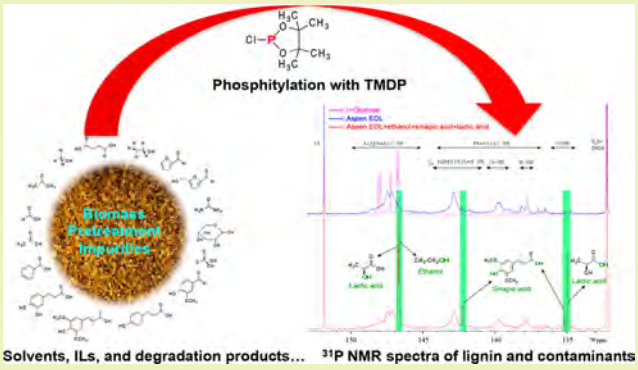
Supporting Information

ABSTRACT: The identification of chemical impurities is crucial in elucidating the structures of biorefinery products using nuclear magnetic resonance (NMR) spectroscopic analysis. In the current biorefinery platform, contaminants derived from pretreatment solvents and decomposition by-products may lead to misassignment of the NMR spectra of biorefinery products (e.g, lignin and bio-oils). Therefore, we investigated 54 commonly reported compounds including alcohols, carbohydrates, organic acids, aromatics, aldehydes, and ionic liquids associated with biomass pretreatment using ^{31}P NMR. The chemical shifts of these chemicals after derivatizing with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) were provided. The ^{31}P NMR signals of these derivatives could serve as valuable and informative spectral data in characterizing lignocellulose-based compounds.



KEYWORDS: *Biomass contaminants, Solvent impurities, Lignocellulose pretreatment, Lignin, NMR spectroscopy*

INTRODUCTION

^{31}P nuclear magnetic resonance (NMR) spectroscopic analysis of the phosphitylated labile proton proves to be a powerful technique in characterizing various types of functional groups including aliphatic alcohols and phenols (OHs), aliphatic and aromatic acids (COOH), amines (NHs), and thiols (SHs).[1] This facile and sensitive method enables a valuable and informative characterization in several biorefinery platforms, such as pretreatment, torrefaction, pyrolysis, and even biological conversion of biomass to biofuels and bioproducts.[2] The ^{31}P NMR method is capable of providing detailed quantitative information about, for example, the complex structure of lignin.[3] Combined with a depolymerizing method, derivatization followed by reductive cleavage, it allows an investigation of the interlinkages of native and technical lignins.[4,5] The quantitative analysis of lignin OHs via ^{31}P NMR has been further validated by ^{13}C NMR.[6] In addition to its wide use in lignin chemistry, ^{31}P NMR has also been applied to the measurements of cellulose substitution,[7] biodiesel production and contaminates,[8] pyrolysis bio-oils,[9] and natural metabolites (tannins and flavonoids, etc.).[10,11] More recently, ^{31}P NMR was successfully applied to distinguish tricin or tricin-like flavonoids incorporated with lignin.[12]

^{31}P NMR method becomes more important as renewable materials are vital to the emerging biobased economies.[13] Because of the natural cell wall recalcitrance, pretreatment of biomass is usually necessary to achieve high saccharification efficiency in the following biological conversion.[14] The pretreatment typically occurs in the presence of chemicals, such as acids, alkalines, organic solvents, and others. Diverse pretreatment technologies including ammonia recycled percolation, aqueous ammonia recycle, controlled pH, dilute acid, hydrothermal, lime, ionic liquid, and others have been widely investigated in the past decades.[15] Accompanied with a substantial deconstruction of cell wall, pretreatment usually brings byproducts and/or impurities from solvents and decomposed products during the process. A number of degradation compounds including carbohydrates, phenolics, organic acids, furans, alcohols, and others were discovered in the pretreated biomass.[16,17] The presence of these decomposition compounds as well as solvents could occur as impurities interfering in the biomass characterization process after pretreatment. Therefore, it is necessary to identify the ^{31}P NMR signals of trace impurities derived from commonly used pretreatment solvents and major decomposition products.

Similar work, such as NMR chemical shifts recorded for laboratory[18] and industry[19] commonly used solvents, has provided valuable information for chemists. These well-established databases of chemical shifts (δ) allow identification

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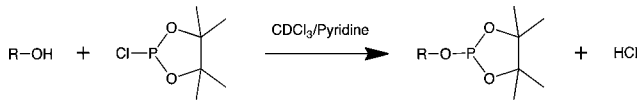
of common contaminants for ^{1}H and ^{13}C NMR analyses. However, comparable results of contaminant chemical shifts for ^{31}P NMR are not fully established. In this study, we compiled the ^{31}P NMR chemical shifts of 54 chemicals, typically used or generated in biomass pretreatment, including pretreatment solvents, carbohydrates, aromatics, carboxylic acids, aldehydes, amines, and others after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP; Scheme 1).

Scheme 1. Phosphitylation of the Hydroxyl Groups in Contaminants (R−OH) with TMDP



EXPERIMENTAL SECTION

All the reagents and chemicals were obtained from commercial sources and, unless otherwise noted, were used as received. To prevent potential ambiguities in assignment, all the chemicals were added in approximately equal amounts (0.02 mmol of chemicals was added into 0.5 mL of solvent in a 5 mm NMR tube) and run at the same temperature. ^{31}P NMR analyses of these solvents/chemicals were performed after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) in a solvent of pyridine/$CDCl_3$ (1.6/1.0, v/v) according to a published method.[20] The ^{13}C NMR acquisition was performed using a Bruker Avance III HD 500-MHz spectrometer equipped with a N_2 cryoprobe (BBO ^{1}H&^{19}F-5 mm) and a 12 s pulse delay, and 1024 scans at 300 K. More details regarding chemicals and NMR analysis are given in the Supporting Information.

RESULTS AND DISCUSSION

Commonly Used Pretreatment Solvents. A few commonly used pretreatment solvents[21] (e.g., acetone, ethanol, and others) have been investigated for their δ after phosphitylation with TMDP (Table 1). The ^{31}P NMR chemical shifts range of these phosphitylated alcohols was located at 145.2−147.1 ppm which overlapped with the aliphatic OHs in lignin (usually from 145.4 to 150.0 ppm, Figure 1). The ammonia solution derivative yielded a peak at 142.4 ppm (data not shown) falling into the range of lignin phenolic OHs (usually from 137.6 to 144.0 ppm). However, no ^{31}P signals were detected for solvents without a labile proton, such as acetone, dimethylformamide, dioxane, dimethyl sulfoxide, tetrahydrofuran, and toluene.

Table 1. ^{31}P NMR Chemical Shifts (δ/ppm) of Phosphitylated Pretreatment Solvents

Compound	Formula	OH
Ethanol	CH_3CH_2OH	146.7
Ethylene glycol	$HOCH_2CH_2OH$	147.0
Glycerol[8]	$HOCH_2CH(OH)CH_2OH$	147.4
	$HOCH_2CH(OH)CH_2OH$	146.3[a]
1-Hexanol	$CH_3(CH_2)_4CH_2OH$	147.1
Isopropyl alcohol	$CH_3CH(OH)CH_3$	145.2
Methanol	CH_3OH	148.1
1-Propyl alcohol	$CH_3CH_2CH_2OH$	147.1

[a]Denotes the 2nd OH in glycerol.

Lignocellulose-Derived Carbohydrates. Monosaccharides (e.g., glucose, xylose, mannose, arabinose, and galactose), disaccharides (e.g., cellobiose), and even oligomers can be generated from cellulose and hemicellulose depolymerization during biomass pretreatments. An earlier endeavor using ^{31}P NMR spectra of 2-chloro-1,3,2-dioxaphospholane phosphitylatives has elucidated structural details of molecules of carbohydrates and lignin−carbohydrate complexes.[22] In our present study, the signals of TMDP phosphitylated carbohydrates are summarized in Table 2. The chemical shifts of studied carbohydrates are in the range 145.5−148.5 ppm which could intervene in the quantification of lignin aliphatic OHs (e.g., the spectrum of D-glucose derivative in pink had signals that fall into the aliphatic OH region of aspen lignin in blue in Figure 1).

Carboxylic Acids. There are a number of byproducts including acids that could be generated from the pretreatment of lignocellulosic materials depending on the pretreatment techniques and conditions.[23] In general, organic acids, such as formic, acetic, lactic, levulinic, and succinic acids, are present at relatively elevated levels among those lignocellulose-based byproducts. These commonly reported carboxylic acids were phosphitylated and analyzed for the chemical shifts of their derivatives (Table 3). A few other carboxylic acids such as palmitic, oleic, and stearic acids representing fatty acids from lignocellulosic materials have also been derivatized and recorded. Except for formic and acetic acids, the phosphitylated carboxylic OHs were located in a small chemical shift span of 134.3−134.9 ppm no matter the bulky size to which the carboxylic group attached. However, the peaks had 0.5−1 ppm downfield shift when the carboxylic group in the parent compound connected to an unsaturated C=C bond (e.g., derivatized *trans*-aconitic acid at 135.2 and 135.4 ppm and fumaric acid at 135.2 ppm) likely because of a deshielding effect. It seems that this effect from the C=C group diminished when it is located a few bonds away; e.g., the chemical shifts of derivatized linoleic, linolenic, oleic, and palmitic acids are identical at 134.3−134.4 ppm.[8] The chemical shifts of these carboxylic acids could likely lead to the misassignment and overestimation of the carboxylic contents in lignin. Unless they are removed prior to analysis, for example, the spectra of lactic acid and sinapic acid derivatives fell in the spectral range of derivatized aspen EOL (Figure 1).

Aromatic Compounds. A large number of aromatic compounds are relevant for lignocellulose in thermochemical pretreatment. Phenolic and other aromatic byproducts could be derived from lignin units as well as hemicellulose sugars.[24] A variety of lignin-like model compounds were derivatized with 2-chloro-1,3,2-dioxaphospholane by the Argyropoulos group.[25,26] In later research, TMDP was recommended and widely used as a phosphitylating reagent for quantitative ^{31}P NMR analysis of the phenolic OHs in lignins, especially for an accurate determination of uncondensed and condensed lignin phenolic OHs.[2,20] In this study, the ^{31}P NMR chemical shifts of several aromatic model compounds derivatized by TMDP were investigated (Table 4). The environment of the adjacent carbon had an effect on the chemical shifts of the derivatized carboxylic OHs. For example, the aromatic carboxylic acid derivatives peaking at 135.0−136.0 ppm (Table 4) were about 1−1.5 ppm downfield shift compared with the aliphatic carboxylic acids at 134.0−135.0 ppm (Table 3). This indicated that the benzene ring also had a deshielded effect, similar to the previously mentioned C=C, on the derivatized carboxylic group. In addition, the benzene ring showed larger downfield shift effect than the C=C. For example, benzoic and vanillic acids with benzene ring adjacent to carboxylic groups had δ 136.0 ppm

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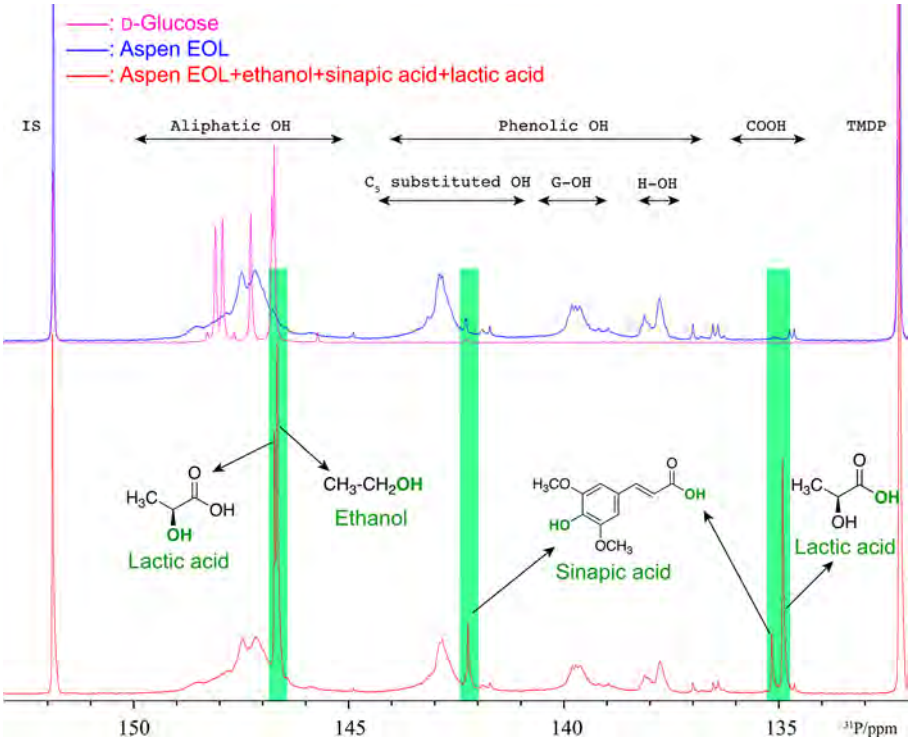
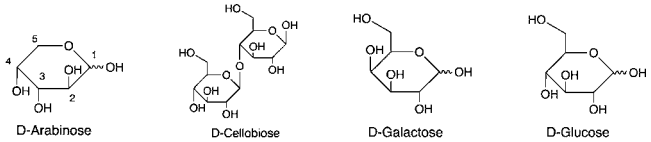


Figure 1. ^{31}P NMR spectra of TMDP phosphitylated D-glucose, aspen lignin, and aspen lignin spiked with impurities. EOL, ethanol organosolv lignin; IS, internal standard; G−OH, guaiacyl hydroxyls; H−OH, *p*-hydroxyphenyl hydroxyls. The chemical shift regions were assigned according to the literature.[2]

Table 2. ^{31}P NMR Chemical Shifts[a] (δ/ppm) of Carbohydrates Phosphitylated with TMDP



Compound	OH_1	OH_2	OH_3	OH_4	OH_6
D-Arabinose	146.5	146.9	147.1	146.7	—[b]
D-Cellobiose[c]	145.7	147.3	147.6	—	146.7
	—	147.9	148.3	148.5	146.2
D-Galactose	146.6	147.2	147.2	147.7	146.9
D-Glucose	146.7	147.2	147.9	148.1	146.8
D-Mannose	145.6	146.5	147.5	148.2	146.4
L-Threitol	147.1	147.2	147.2	147.0	—
Xylitol	147.3	146.4	148.0	146.4	147.3 (OH_5)
D-Xylose	145.8	146.8	147.2	146.6	—

[a]Chemical shifts were assigned in ^{31}P NMR of TMDP phosphitylated sugars according to the relative position in the literature.[22] [b]—: not applicable/detectable. [c]Individual assignments at $OH_{3/3'}$ and $OH_{4/4'}$ are not distinguished.

whereas *trans*-cinnamic, caffeic, coumaric, ferulic, and sinapic acids showed chemical shifts at about 135.1 ppm. Phenolic OH derivatives located at 137.5−143.0 ppm varied with their adjacent substituents.

Aldehydes. We phosphitylated several aromatic aldehydes, furfural, and 5-hydroxymethyl-furfural as these are commonly mentioned aldehydes derived from lignin and polysaccharides in pretreatment hydrolysates.[23] The TMDP derivatized aldehydes yielded signals in the range 146.7−148.0 ppm (Table 5). A previous study has shown that the reagent 2-chloro-1,3,2-dioxaphospholane reacted with aliphatic and aromatic aldehydes in a peculiar manner.[25] The authors found that the phosphitylation of aldehyde functional group was likely an addition reaction rather than a substitution reaction shown in Scheme 1 depicted for hydroxyl groups. Moreover, the adduct of phosphitylation reagent with the carbonyl group appeared to be relatively unstable and underwent further decomposition. Our results showed that the ^{31}P NMR spectra of aldehydes had a single peak at a narrow range of 146−148 ppm after the addition of TMDP. In addition, we observed that there were two peaks in these aldehydes that bear OHs, such as 2,3-dihydroxybenzaldehyde, 4-hydroxy-3-methoxycinnamaldehyde, HMF, and vanillin (Figure S1). These two peaks with 0.1−0.6 ppm separation likely corresponded to the OHs with two different chemistry environments. For instance, the reaction of TMDP with the aldehydes group could generate two types of compounds so that the same phosphitylated OH in these two compounds presented a different chemical shifts. To confirm this, we then run a ^{13}C NMR of phosphitylated vanillin to monitor the status of the aldehyde group. The ^{13}C NMR spectra of phosphitylated vanillin showed a peak at 188.9 ppm assigned to the unreacted aldehyde group (Figure S2). This suggested that the aldehyde was not completely reacted with TMDP while the OHs were completely phosphitylated (at least by the time of NMR aquisition). Therefore, the TMDP derivatives of aldehydes were affected (i.e., exhibited two different chemical shifts for its OHs in this scenario).

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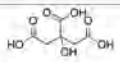
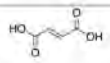
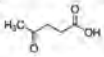
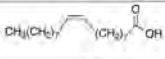
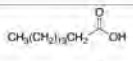
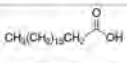
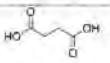
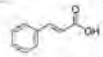
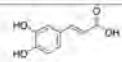
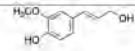
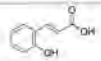
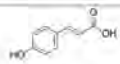
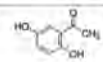
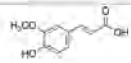
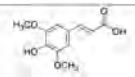
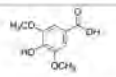
Table 3. ^{31}P NMR Chemical Shifts (δ/ppm) of Carboxylic Acids Phosphitylated with TMDP[a]

Compounds	Formula/structure	COOH
Acetic acid	CH_3COOH	134.6
trans-Aconitic acid		134.6 135.2 135.4
Citric acid		134.8 134.9
Formic acid[9]	HCOOH	137.4
Fumaric acid		135.2
Glucuronic acid*		134.5 (β) 135.3(α)
Hexanoic acid[8]		134.3
Isobutyric acid		134.8
L-lactic acid		134.9
Levulinic acid		134.6
Linoleic acid[8]	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	134.3
Linolenic acid[8]	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	134.3
Malonic acid		134.8
Oleic acid[8]		134.4
Palmitic acid[8]		134.4
Stearic acid		134.7
Succinic acid		134.6
cis-Vaccenic acid		134.7

[a]* indicates where one should refer to D-glucose in Table 2 for aliphatic OH assignments in glucuronic acid (α and β configurations).

Table 4. ^{31}P NMR Chemical Shifts (δ/ppm) of Aromatic Compounds Phosphitylated with TMDP[a]

Compounds	Structure	COOH	OH
Benzoic acid[9]		136.0	—
trans-Cinnamic acid		135.0	—
Caffeic acid		135.1	138.6 (*p*) 139.6 (*m*)
Coniferyl alcohol		—	139.7 148.1*
o-Coumaric acid		134.9	138.9
p-Coumaric acid		135.1	137.7
2',5'-Dihydroxyacetophenone		—	138.7(*m*) 138.8 (*o*)
Ferulic acid		135.1	139.4
3-Methoxycatechol		—	142.7(*m*) 138.6(*o*)
4-Methyl catechol		—	139.3 (*p*) 138.9 (*m*)
Phenol		—	138.0
Sinapic acid		135.2	142.2
Syringic acid		135.1	141.9
Vanillic acid[9]		136.0	139.8

[a]* refers to Aliphatic OH. *o*, *ortho*; *m*, *meta*; *p*, *para*. —: not applicable/detectable.

Ionic Liquids. Ionic liquids (ILs) have recently been applied to biomass pretreatment because of their strong dissolution ability of biopolymers.[27] Several ILs were also studied in this work to find any contaminant peak in their ^{31}P NMR spectra (Table 6). Choline chloride (Ch:Cl) showed a peak at 148.1 after reaction with TMDP whereas the mixture of Ch:Cl with glycerol and urea had other peaks corresponding to glycerol and urea, respectively. In the case of Ch:Cl: urea, another two small peaks observed at 142.3 and 142.6 ppm were probably due to the further phosphitylation of the primary amine in urea.[28] The spectra of ILs 1-butyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium acetate showed one peak at 134.6 ppm likely corresponding to acetic acid derivatives. The other four ILs containing no labile protons, such as 1-butyl-3-methylimidazolium chloride, 1,3-dimethylimidazolium dimethyl phosphate, 1-ethyl-3-methylimidazolium diethyl phosphate, and tetrabutylphosphonium chloride, have no detected phosphitylated peaks. However, the latter three ILs containing phosphor element had a peak at −7.3, −9.6, and 33.3 ppm, respectively, after TMDP was added (Figure S3).

It has been reported that phosphitylated derivatives from lignin and carboxylic acids are not stable in the ^{31}P NMR solution after an extended time of storage.[2,9] We selectively monitored five representative model compounds, such as ethanol, xylose, acetic acid, ferulic acid, and vanillin representing impurities from solvents, carbohydrates, carboxylic acids, aromatics, and aldehydes, respectively, to investigate the relative stabilities of their TMDP derivatives (Figures S4−S8). We found that the phosphitylated carboxylic and phenolic hydroxyls were not stable as revealed by the weakened peak intensity at 22 h whereas the phosphitylated aliphatic hydroxyls

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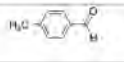
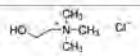
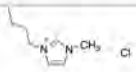
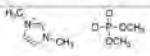
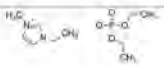
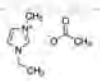
Table 5. ^{31}P NMR Chemical Shifts (δ/ppm) of Aldehydes Phosphitylated with TMDP[a]

Compounds	Structure	CHO	OH
2,3-Dihydroxybenzaldehyde		147.8	138.4 138.8
Furfural		147.2	—
4-Hydroxy-3-methoxycinnamaldehyde		147.0	139.3 139.7
5-Hydroxymethyl-furfural		147.1	148.6 148.7
Vanillin		147.1	139.0 139.4
p-Tolualdehyde		147.4	—

[a]—: not applicable/detectable.

Table 6. ^{31}P NMR Chemical Shifts (δ/ppm) of Several Other Compounds Phosphitylated with TMDP

Compounds	Formula/Structure	OH/NH
Choline Chloride (Ch:Cl)		148.0
Choline Chloride:glycerol	Ch:Cl•	146.3
	$HOCH_2CH(OH)CH_2OH$	147.4
		148.0
Choline Chloride:urea	Ch:Cl•	133.5
	$NH_2C(=O)NH_2$	148.0
1-Butyl-3-methylimidazolium acetate		134.6
1-Butyl-3-methylimidazolium chloride		—
1,3-Dimethylimidazolium dimethyl phosphate		-7.3
1-Ethyl-3-methylimidazolium diethyl phosphate		-9.6
1-Ethyl-3-methylimidazolium acetate		134.6
Tetrabutylphosphonium chloride		33.3

were relatively stable. Therefore, a short-time preparation and storage, e.g., <2 h, was recommended for quantitative analysis of these compounds using the ^{31}P NMR method.

In summary, the identification of signals arising from common contaminants during lignocellulose pretreatment is crucial for accurate characterization of biorefinery polymers and bioproducts. We studied 54 chemicals including alcohols, carbohydrates, organic acids, aromatics, and ionic liquids which represent a variety of pretreatment contaminants derived from pretreatment solvents and biomass decomposition. These chemicals were phosphitylated with TMDP, and their chemical shifts were identified by ^{31}P NMR spectroscopy. The chemical shifts recorded in this study could serve as a practical resource that facilitates the identification of trace impurities in structural elucidation of biorefinery products and quantitation of their functional groups.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03602.

Additional experimental details and supplemental NMR spectra (PDF)

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Author Contributions

Y.P. and A.R. conceived and designed the research. M.L. and C.G.Y. carried out the experiment. M.L. wrote the manuscript. All the authors discussed data and revised the paper. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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