

Sulfonated Tetraphenylethylene-Based Hypercrosslinked Polymer as a Heterogeneous Catalyst for the Synthesis of Symmetrical Triarylmethanes via a Dual C–C Bond-Cleaving Path

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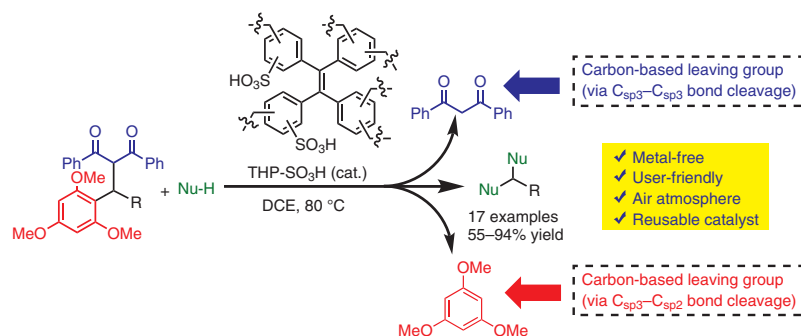
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Received: 12.07.2020

Accepted after revision: 01.10.2020

Published online: 01.10.2020

DOI: 10.1055/a-1277-3995; Art ID: st-2020-b0393-1

Abstract A sulfonic acid functionalized tetraphenylethylene-based hypercrosslinked polymer (THP-SO₃H) with a well-developed porous network and accessible sulfonic acid sites was synthesized and characterized by different analytical techniques. The catalytic prowess of the synthesized material THP-SO₃H was investigated in a challenging dual C–C bond-breaking reaction for the synthesis of symmetrical triarylmethanes (TRAMs) in high yield. The scope of the developed metal-free method was also explored with a wide variety of substrates. The organocatalyst can be easily recovered by filtration and reused up to five consecutive cycles without substantial loss in its catalytic efficacy.

Key words hypercrosslinked polymer, heterogeneous catalyst, reusable, C–C bond breaking, triarylmethane

Functionalization of porous organic polymers has provided an exciting platform for catering to a varied array of applications such as adsorption, energy applications, catalysis, etc.¹ The high thermal and chemical stability, high specific surface areas, and hierarchical pore networks of porous organic polymers have attracted significant attention over recent decades.² Moreover, they have an added advantage of the ease of preparation and functionalization using mild synthetic conditions. The proper selection of monomer units further aids in designing polymer materials with tailor-made properties for different applications. Based on the reactions involved in the synthetic process, porous organic polymers may be further classified into the categories such as hypercrosslinked polymers, microporous organic polymers, covalent organic framework, etc.³ Hypercrosslinked polymers possessing high surface areas, inherent porosity, good chemical and thermal stability, and a rigid skeleton for easy incorporation of catalytic sites have been proven to be a promising candidate for their use as hetero-

geneous catalysts.⁴ Heterogeneous catalysts are being gradually preferred over classical homogeneous catalysts owing to their noncorrosiveness, ease of recovery, and reusability.⁵ However, common limitations of heterogeneous catalysts include high cost, low yields, and catalyst poisoning in a hydrophilic environment. In this regard, the effective design of hypercrosslinked polymer-based catalysts may help to combine the advantages of both heterogeneous and homogeneous catalysts. Acid-functionalized hypercrosslinked polymers have been recently utilized as heterogeneous catalysts, mostly for the conversion of biomass into biofuel,⁶ biofuel additives,⁷ and hydroxymethylfurfural (HMF).⁸ Bhaumik and his group have recently employed a hypercrosslinked supermicroporous polymer as a heterogeneous catalyst for synthesizing biodiesel.⁶ However, the scope of such functionalized polymer-based catalysts has not been investigated much in other organic synthetic applications.

For example, organic reactions proceeding through unusual yet challenging C–C bond-breaking reactions still await the same level of interest as C–C bond-forming counterparts. Over the past years, several catalytic routes for the cleavage of the C–C bonds have been developed by researchers.⁹ Our interest on exploring new catalytic approaches for the activation of C–C bonds lead us to develop a facile FeCl₃-catalyzed dual C–C bond-breaking reaction in homogeneous medium for the synthesis of symmetrical and unsymmetrical triarylmethanes (TRAMs).¹⁰ In spite of tremendous reactivity and selectivity of homogeneous catalysts, it has limited applications in industrial processes due to the difficulties associated with the removal, recovery, and recycling of the active catalysts. Till date, several methods are reported in the literature on the synthesis of TRAMs.¹¹ To the best of our knowledge, the synthesis of TRAMs via a dual C–C bond-breaking reaction of diarylmethyl-substituted 1,3-dicarbonyl derivatives **1** has not

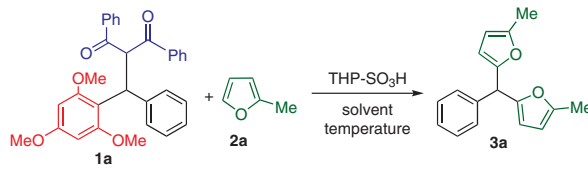
been attempted with heterogeneous catalysts. In this regard, acid-functionalized hypercrosslinked polymers can be used as reusable heterogeneous catalyst for the synthesis of TRAMs. Here, we have synthesized a sulfonic acid functionalized hypercrosslinked polymer derived from tetraphenylethylene (TPE). Hypercrosslinked polymers have been previously used by researchers as polymeric supports due to their porous natures and high thermal stabilities.¹² However, the choice of monomer units heavily influences the physico-chemical characteristics of the polymer. The tetraphenylethylene (TPE) moiety consists of peripheral phenyl rings, which prevents the π - π stacking of its polymerized form. Hence, the surface area of TPE-based hypercrosslinked polymers is usually very high and provides a suitable platform for the incorporation of numerous catalytic sites. Moreover, increasing the crosslinking between the monomer units improves the thermal stability of the polymeric catalyst. The synthesized TPE-based hypercrosslinked polymer (THP) has a high surface area and optimum pore dimensions, which make it a suitable framework for introducing sulfonic acid sites. The sulfonated polymer (THP-SO₃H) possesses high sulfonic acid content and good thermal stability. Also, THP-SO₃H shows high potential as a heterogeneous catalyst for the synthesis of symmetrical TRAMs via a dual C–C bond-breaking reaction of diarylmethyl-substituted 1,3-dicarbonyl derivatives **1**. It is noteworthy to mention that TRAM skeleton is found in several natural products, pharmaceuticals, dyes, etc.¹³ Moreover, the application of THP-SO₃H as a reusable heterogeneous catalyst in the dual C–C bond-breaking reaction enhances the practical utility of the present work.

The tetraphenylethylene-based hypercrosslinked polymer (THP) scaffold was synthesized via a simple Friedel-Crafts-based crosslinking reaction with tetraphenylethylene as the monomer and formaldehyde dimethylacetal as the crosslinker.¹⁴ Sulfonation of the polymer was successfully carried out in chlorosulfonic acid (ClSO₃H) at 25 °C under N₂ atmosphere [Scheme S1 of the Supporting Information (SI)].⁶ The details of the structural and morphological characterizations of THP-SO₃H are included in the SI.

After characterizing the THP-SO₃H material, we were interested to explore its catalytic prowess for the synthesis of symmetrical TRAMs via a challenging dual C–C bond-cleaving reaction of diarylmethyl-substituted 1,3-dicarbonyl derivatives **1** in a heterogeneous medium. To investigate the optimized reaction conditions, we chose 1,3-diphenyl-2-[phenyl(2,4,6-trimethoxyphenyl)methyl]propane-1,3-dione (**1a**) and 2-methylfuran (**2a**) as the model substrates for the synthesis of symmetrical TRAM **3a** by the cleavage of both C_{sp3}–C_{sp3} and C_{sp3}–C_{sp2} bonds in substrate **1a** (Table 1). Initially, we screened different solvents (entries 1–5) for the dual C–C bond cleavage in the presence of THP-SO₃H to find out the suitable solvent for the reaction. Among different solvents, the highest yield of the symmetrical TRAM **3a** was obtained in DCE solvent using the synthesized organocata-

lyst at 80 °C in 30 min (entry 3). The reaction gave comparably lower yield of the desired TRAM **3a** in MeNO₂, MeCN, and toluene solvents (entries 1, 2, 4). However, polar protic solvent, such as EtOH, gave poor yield of **3a** even after 3 h (entry 5). The temperature also played a significant role in the dual C–C bond-breaking reaction. When we decreased the temperature from 80 °C to 55 °C, only 78% yield of the desired product **3a** was obtained after 3 h (entry 6). Further decreasing the temperature to room temperature, product **3a** was obtained only in 52% yield after 5 h (entry 7). Unlike our previous report,¹⁰ we did not isolate any unsymmetrical TRAM via the cleavage of C_{sp3}–C_{sp3} bond only,¹⁵ resulting dibenzoylmethane as the carbon-based leaving group. In addition, we varied the catalyst loading to determine the optimum amount of THP-SO₃H for the dual C–C bond cleavage in the reaction. It is noteworthy that the use of 96 mg catalyst at 80 °C produced the maximum yield of the product **3a** in 30 min (entry 3). An increase in the amount of catalyst loading (144 mg) did not affect the yield of the reaction significantly (entry 8). But a lower catalyst loading (48 mg) resulted in lesser yield of the product **3a** (entry 9). Besides, no dual C–C bond-breaking reaction was noticed in the absence of catalyst, and the starting materials were recovered quantitatively (entry 10). It is to be noted that the leaving 1,3-diphenylpropan-1,3-dione and 1,3,5-trimethoxybenzene were isolated in more than 90% yields (entry 3).

Table 1 Optimization of Reaction Conditions^a



Entry	Solvent	Temp. (°C)	Time (min)	Yield (%) ^b
1	MeNO ₂	80	45	89
2	MeCN	80	60	81
3	DCE	80	30	94
4	toluene	80	90	64
5	EtOH	80	180	56
6	DCE	55	180	78
7	DCE	RT	300	52
8 ^c	DCE	80	30	96
9 ^d	DCE	80	30	78
10 ^e	DCE	80	60	nil

^a Reaction conditions: **1a** (480 mg, 1.0 mmol), **2a** (246 mg, 3.0 mmol), catalyst (96 mg), and solvent (2 mL).

^b Isolated yields.

^c Catalyst (144 mg).

^d Catalyst (48 mg).

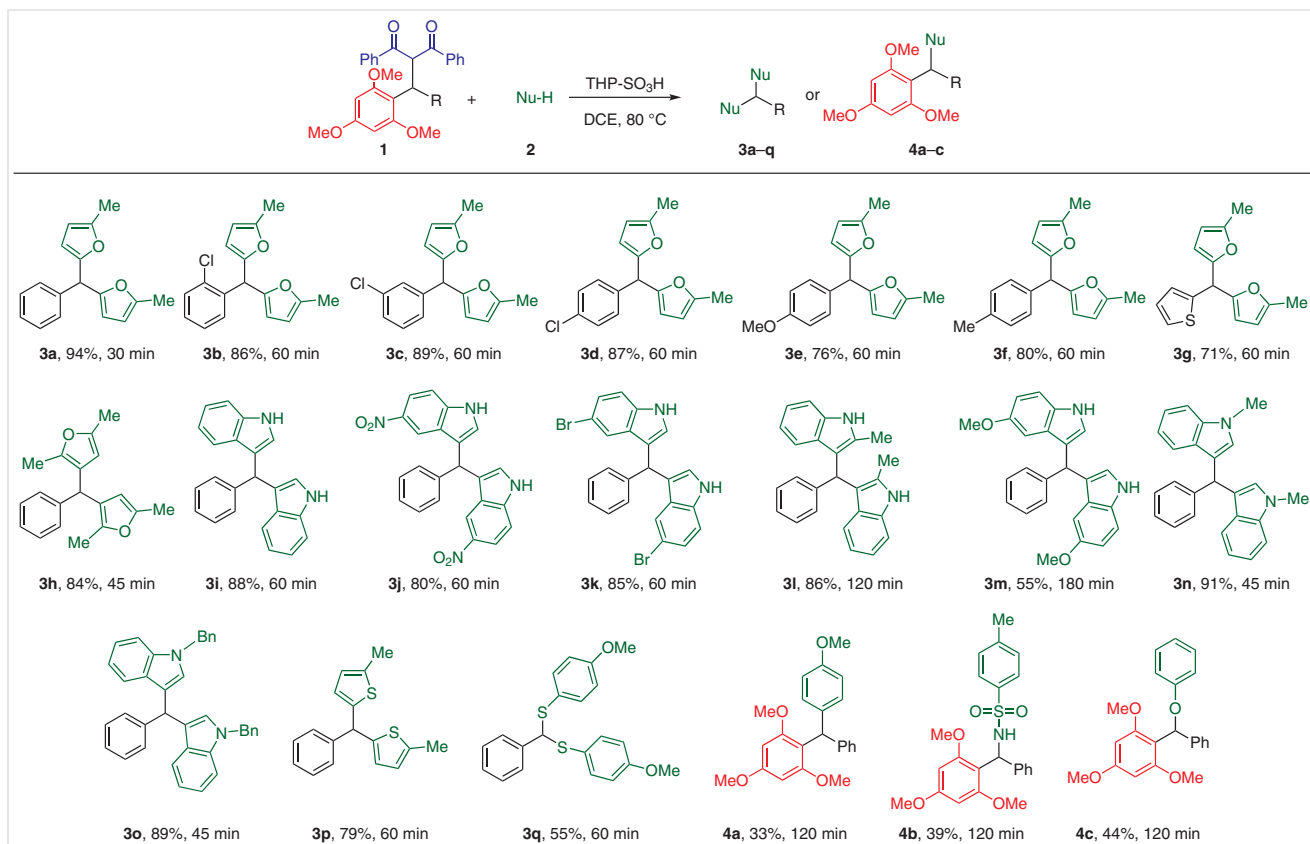
^e No catalyst.

After optimizing the reaction conditions, we explored the substrate scope of the developed method with our in-house synthesized organocatalyst THP-SO₃H. From our previous work, we experienced that the combination of 1,3-diphenylpropan-1,3-dione (as the 1,3-dicarbonyl substituent) and 2,4,6-trimethoxyphenyl unit (as the electron-rich arene substituent) in the starting substrates **1** showed the best results during dual C–C bond-breaking reaction.¹⁰

Hence, to study the catalytic efficacy of THP-SO₃H for the synthesis of symmetrical TRAMs, we varied only the R group in **1**, keeping 1,3-diphenylpropan-1,3-dione and 2,4,6-trimethoxyphenyl units intact in the precursor **1** (Scheme 1). We found that the aromatic ring bearing EWG in substrate **1** generated slightly higher yields of the symmetrical TRAMs **3b–d** than the aromatic ring bearing EDG **3e,f**. A heteroaryl substituent in substrate **1g** provided the corresponding product **3g** in 71% yield. Furthermore, the reaction performed well when 2,5-dimethylfuran (**2b**, Figure 1) was used as nucleophile producing the desired TRAM **3h** in good yield. Then, we examined other nucleophiles based on their performance in the dual C–C bond-cleaving reaction. In the presence of indole derivatives **2c–i**, the corresponding bisindolylmethanes **3i–o** were obtained in good yield. Surprisingly, 5-methoxyindole (**2g**) gave a lower yield

of the desired bisindolylmethane derivative **3m** after prolonged reaction time. The N-substituted indoles **2h,i** were effective in the dual C–C bond-cleaving reaction generating the symmetrical TRAMs **3n,o** in excellent yields. 2-Methylthiophene (**2j**) also reacted well with substrate **1a** to give the symmetrical TRAM **3p** in 79% yield. It is important to note that 4-methoxythiophenol (**2k**) took part in the reaction producing 55% yield of the product **3q** with two new C_{sp3}–S bonds at the cost of two C–C bonds. While examining the scope of nucleophiles, we noticed that the symmetrical TRAM did not form during the reactions between substrate **1a** and nucleophiles **2l–n** via the dual C–C bond-breaking reaction. Instead, we isolated unsymmetrical TRAMs **4** due to the exclusive C_{sp3}–C_{sp3} bond-cleaving reaction of **1a** in the presence of the above-mentioned nucleophiles. We previously noted the similar observations in our FeCl₃-catalyzed dual C–C bond-breaking work.¹⁰ These results indicate that the C_{sp3}–C_{sp3} bond is relatively easier to cleave than C_{sp3}–C_{sp2} bond in substrate **1** in our developed reaction conditions.¹⁶

In view of commercial applications, we also explored the potential for reusability of the synthesized organocatalyst THP-SO₃H in the dual C–C bond-breaking reaction of substrate **1a** and **2a**. After 30 min of the reaction time in each cycle, the catalyst was recovered by filtration, washed



Scheme 1 Substrate scope of the C–C bond-breaking reaction for the synthesis of TRAMs. Reagents and conditions: (a) **3a–h**: **1** (1.0 mmol), **2** (3.0 mmol), THP-SO₃H (96 mg), DCE (2 mL), 80 °C. (b) **3i–q** and **4a–c**: **1** (1.0 mmol), **2** (2.0 mmol), THP-SO₃H (96 mg), DCE (2 mL), 80 °C.

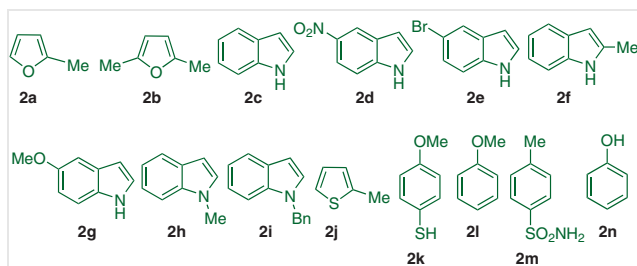


Figure 1 List of nucleophiles used in the dual C–C bond cleavage reaction

with DCE, and dried at 100 °C under vacuum oven for 3 h (the detailed procedure is given in the SI). The recovered catalyst was reused for four consecutive cycles without significant loss in its catalytic efficiency (Figure 2).

The FT-IR spectrum of the reused catalyst after the fifth cycle shows the same pattern as the synthesized THP-SO₃H material (Figure S7 of the SI), which indicates that the active site of the heterogeneous catalyst remains intact even after the fifth cycle.

Based on the above observations and the related literature about the dual C–C bond-breaking reaction, we propose a plausible reaction mechanism for the reaction between substrate **1a** and **2a** in Scheme 2. THP-SO₃H has abundant acidic sites due to the presence of a large number of –SO₃H groups at the surface of the hypercrosslinked polymer and provides ample H⁺ ion in the reaction medium.

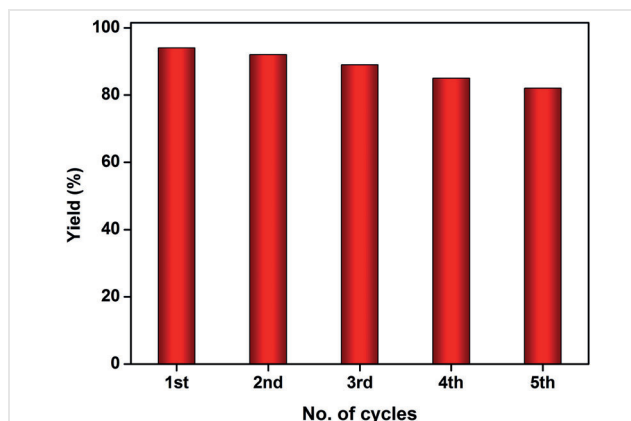
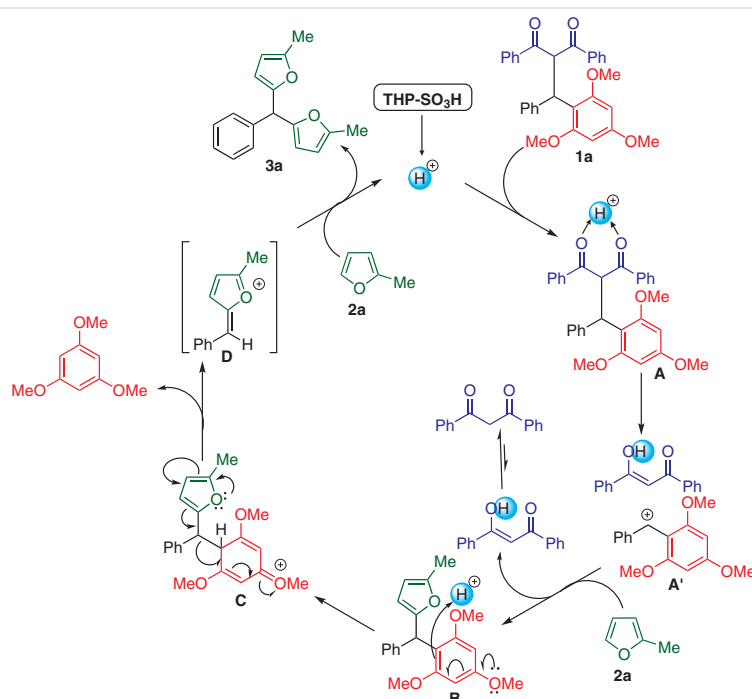


Figure 2 Recyclability of THP-SO₃H catalyst in the dual C–C bond-breaking reaction

The reaction may be initiated by the activation of carbonyl groups of the starting material **1a** in the presence of H⁺ to produce a species **A**.¹⁰ 2-Methylfuran (**2a**) combines with the electrophilic species **A'** to form unsymmetrical TRAM **B** and consequently releases 1,3-diphenylpropan-1,3-dione by the cleavage of C_{sp3}–C_{sp3} bond. The electron-donating –OMe group of the species **B** undergoes conjugation and gets protonated in the acidic medium to generate an ionic species **C** which may decompose to species **D** via the elimination of 1,3,5-trimethoxybenzene.¹⁷ Subsequently, a second molecule of **2a** reacts with the electrophilic center in spe-



Scheme 2 Plausible reaction mechanism for the reaction between **1a** and **2a** catalyzed by THP-SO₃H

cies **D** to produce the desired symmetrical TRAM **3a** via a $C_{sp^3}-C_{sp^2}$ bond-breaking reaction, and a proton is consequently released in the reaction medium.

In conclusion, we have synthesized a novel sulfonic acid functionalized tetraphenylethylene-based hypercrosslinked polymer (THP-SO₃H) with a porous network and accessible sulfonic acid sites. Due to the abundant accessible acidic sites in the material, its catalytic property was examined on a dual C–C bond-breaking reaction in diarylmethyl-substituted 1,3-dicarbonyl derivatives. THP-SO₃H showed promising catalytic activity in the synthesis of symmetrical TRAMs via the cleavage of both $C_{sp^3}-C_{sp^3}$ and $C_{sp^3}-C_{sp^2}$ bonds in mild reaction conditions.¹⁸ The generality of the reaction was explored on a diverse range of substrates, and the desired product was obtained in high yield. Due to its heterogeneity in the reaction medium, the catalyst could be recycled for further use. The catalyst was reused up to five reaction cycles without any substantial decrease in its catalytic efficiency. The results described here demonstrate the first-ever synthesis of symmetrical TRAMs via a metal-free, dual C–C bond-breaking strategy using sulfonated tetraphenylethylene-based hypercrosslinked polymer as a heterogeneous catalyst.

Funding Information

The Science and Engineering Research Board (SERB, Grants SB/FT/CS-075/2014 and SB/FT/CS-115/2014) is gratefully acknowledged for financial support to G.K.D. and P.N.C. We also thank NIT Meghalaya for financial support to G.K., N.D., and D.P. SAIF, NEHU.

Acknowledgment

The NMR Research Centre, IISc Bangalore; SAIC, TU; Centre for Energy, IIT Guwahati; MSE, IIT Kanpur and SAIF, IIT Bombay are also acknowledged for analytical facilities.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/a-1277-3995>.

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- (15) The following unsymmetrical TRAM (via only $C_{sp^3}-C_{sp^3}$ bond cleavage) was not isolated in the reaction (Figure 3).

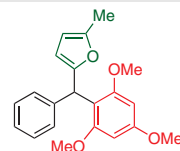


Figure 3

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- (18) **Typical Procedure for the Synthesis of 3a**
A 25 mL round-bottomed flask equipped with a magnetic bar and water condenser were charged with **1a** (1.0 mmol), **2a** (3.0 mmol), DCE (2.0 mL), and THP-SO₃H (96 mg) in an air atmosphere. The flask was placed in a constant temperature oil bath at 80 °C, and the progress of the reaction was monitored by TLC. After 30 min, the mixture was filtered to separate the catalyst and washed twice with DCE (2 × 5 mL). Then the filtrate was removed under reduced pressure, and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60–80 °C/EtOAc) to give a yellow oily liquid; yield 94%.
¹H NMR (400 MHz, CDCl₃): δ = 2.158 (s, 6 H), 5.256 (s, 1 H), 5.788 (d, J = 3.2 Hz, 4 H), 7.159–7.243 (m, 5 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.65, 45.12, 106.08, 108.19, 126.97, 128.40, 128.44, 140.00, 151.46, 152.85 ppm.