



Recyclable organotungsten Lewis acid and microwave assisted Diels–Alder reactions in water and in ionic liquids

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Abstract—The water-soluble, organotungsten Lewis acid, $[O=P(2-py)_3W(CO)(NO)_2](BF_4)_2$ (**1**), was synthesized and characterized. A series of **1**-catalyzed Diels–Alder reactions were investigated under conventional heating or microwave heating conditions. The cycloaddition reactions were efficiently conducted in either water or in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate. The ionic liquid acts as a powerful medium not only for rate- and selectivity enhancements but also for facilitating catalyst recycling. Dramatic rate acceleration via microwave flash heating as compared to thermal heating was observed.

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1. Introduction

The Diels–Alder reaction is one of the most powerful synthetic tools for the construction of six-membered ring systems. Remarkable success in the rate acceleration and selectivity enhancement for various Diels–Alder reactions has been accomplished in the past two decades by the application of catalyst, high pressure, sonication, and solvent manipulation, etc.¹ Among these the effects provided by Lewis acid catalysts have been most widely studied. Special solvent effects of water which are almost equivalent to catalysis leading to dramatic enhancements of rate and stereoselectivity have also been demonstrated.^{2,3} Due to the limited miscibility of water with most organic substrates, the possibility of using ionic liquids as a solvent substitutes for water and also as Lewis acid catalysts on Diels–Alder reactions has been explored.⁴ A very recent trend in the development of environmentally benign processes is to use water⁵ or room temperature ionic liquids⁶ as solvent media for Diels–Alder catalysis. In the meantime, microwave technology is now a powerful and innovative tool for improving organic synthesis, because it is economical, efficient and provides better selectivity, higher reaction rates, milder reaction conditions, formation of cleaner products with higher yields and minor wastes. The successful application of microwave in chemistry dated since 1975.⁷ Numerous organic reactions such as acylation

and alkylation reactions, aromatic and nucleophilic substitutions, condensations, cycloadditions, protection and deprotection reactions, esterifications and transesterifications, heterocyclizations, rearrangements, organometallic reactions, oxidations and reductions assisted by microwave heating have been performed and reviewed in articles^{8,9} or books.¹⁰ In addition, ionic liquids have been demonstrated to couple very effectively with microwaves through an ionic conduction mechanism.^{11b} Also, small amounts of an ionic liquid can be used as additives to increase the dielectric constant of a molecular solvent.^{11b} Several recent studies in this area used ionic liquids, or mixtures of ionic liquids and molecular solvents, as reaction media in a number of important microwave-heated transformations,¹¹ including Diels–Alder reactions.¹²

We report herein the synthesis of a novel organotungsten Lewis acid **1** and a series of **1**-catalyzed Diels–Alder reactions with particular emphasis on the combined effects of this Lewis acid catalyst, the water or ionic liquid solvent system, and microwave radiation on the reaction rates and selectivity. The structures of dienes **2–7** and dienophiles **a–f** investigated in the current study are illustrated in Figure 1.

2. Results and discussion

The complex $[O=P(2-py)_3W(CO)(NO)_2](BF_4)_2$ (**1**) was easily synthesized in two steps within 30 min from the commercially available $W(CO)_6$ (Scheme 1). The precursor $O=P(2-py)_3W(CO)_3$ obtained in the first step can be prepared either through conventional heating or under

Keywords: Organotungsten Lewis acid; Diels–Alder; Microwave; Water; Ionic liquid.

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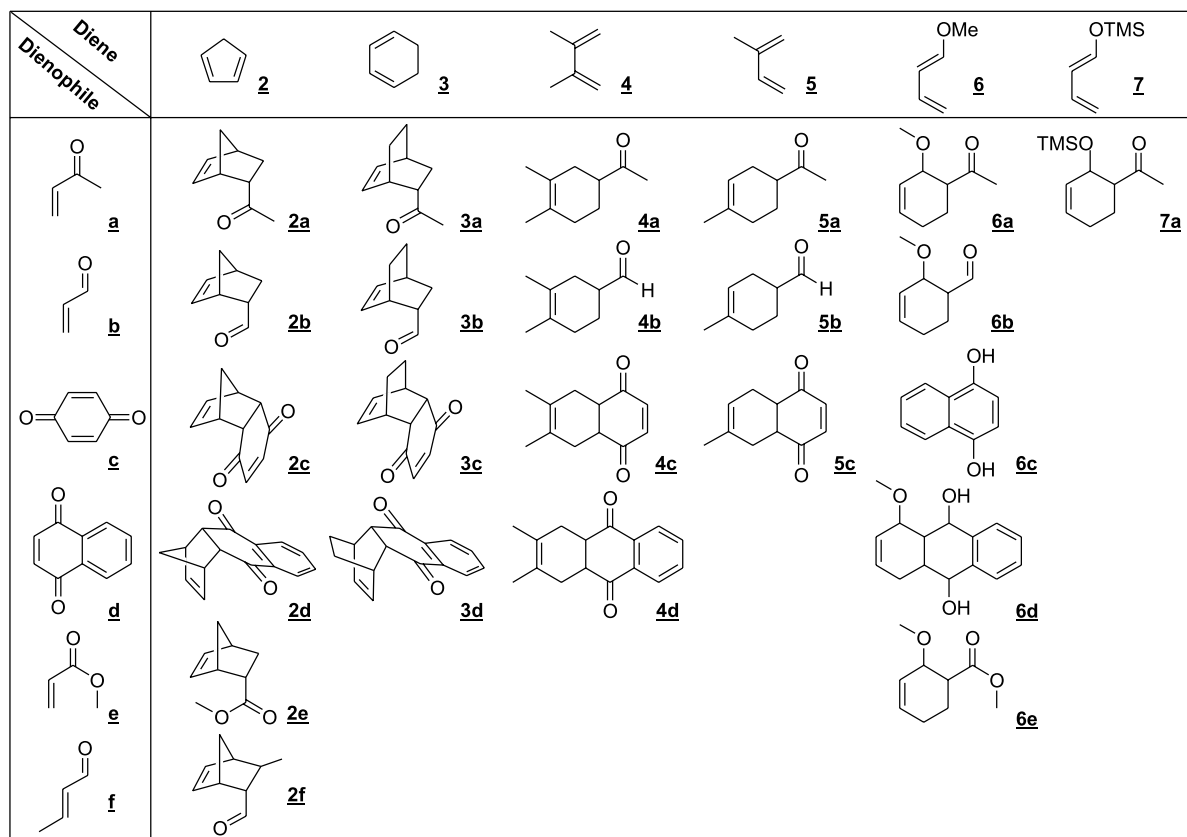
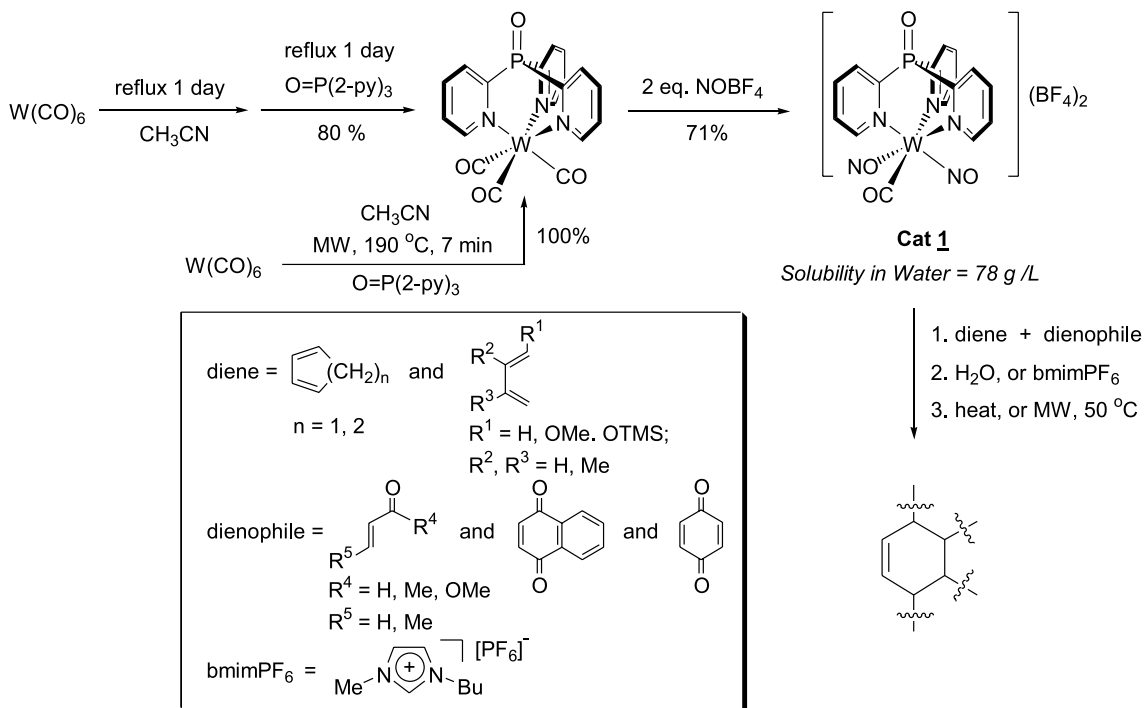


Figure 1. The numbering scheme for the dienes, dienophiles and the Diels–Alder adducts.

microwave irradiation conditions. The first method took more than 48 h and gave 80% yield of product after work-up procedures, while the second method gave 100% yield of high purity product in just 7 min. The direct reaction of $\text{O}=\text{P}(\text{2-py})_3\text{W}(\text{CO})_3$ and 2 equiv of NOBF_4 afforded **1**

which can be stored as a crystalline solid in air for months without significant decomposition. In addition, **1** is very water-soluble (78 g/L H_2O) and possesses strong Lewis acidity upon loss of the CO ligand. The relative Lewis acid strength of **1** was found to be comparable to that of AlCl_3 .¹³



Scheme 1.

Because of its high solubility and stability in water, we therefore decided to study the effects of using Lewis acid **1** in water on Diels–Alder reactions.

The results of **1**-catalyzed Diels–Alder reactions of dienes **2**, **6** and **7** with dienophiles **a–c** and **e** in water are summarized in Table 1. As shown in the table, the reactions at both room temperature and at 50 °C afforded the corresponding cycloadducts in good to excellent yields and selectivities. The reaction at room temperature in entry 1 completed in 2 h with a 95:5 of *endo*-to-*exo* ratio, while the controlled reaction in CH₃NO₂ under similar conditions completed in 5 h with a 97% *endo*-selectivity (entry 10). In addition, two other controlled reactions were performed without the presence of catalyst **1** to give 80% complete in 50 h in CH₃NO₂, and totally complete in 8 h in water (entries 11–12). This clearly demonstrated that both water and **1** can be applied independently to the reaction system to provide rate enhancement, and further acceleration can be made by combining the two in the same system. In addition, a 100% *endo*-selectivity was obtained in entries 3, 5, 6, 8 and 9. In particular, the reaction of 1-methoxybutadiene **6** and methyl vinyl ketone **a** in entry 5, as far as we know, has never been reported previously. It should be noted that the Diels–Alder adduct of **6** and quinone **c** was unstable, the aromatized product **6c** was obtained by loss of the methoxy substituent at C(1) position through elimination.¹⁴ Thus, the present catalytic process provides a potential route to the preparation of substituted dihydroxynaphthalene. The OTMS functionality of the Diels–Alder adduct **7a** in entry 9 was deprotected by the BF₄⁻ anion of **1** during catalysis. Reprotection of OTMS can be performed by treating the Diels–Alder mixture with TMSCl in the presence of NaHCO₃. The diene polymerization became competitive for the reaction between **6** and methyl acrylate **e** under catalytic conditions in water (entry 8). The use of isoprene **5** as the diene source in the Diels–Alder systems, however, resulted in the diene polymerization only.

Due to the usually low substrate solubility and the possibility of promoting the competing diene polymerization, the potential applications of water in the current **1**-catalyzed Diels–Alder systems are limited. We therefore chose the air-stable room-temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆),^{15,16} as a solvent alternative. The bmimPF₆ is in the same polarity region as the lower alcohols, such as methanol, ethanol and 1-butanol,¹⁷ but it provides miscibility with a much broader range of organic substrates. Also, due to its neutral and weakly coordinating nature,¹⁸ the bmimPF₆ does not interfere with the behavior of the Lewis acid catalyst employed. Table 2 shows the results of the **1**-catalyzed Diels–Alder reactions in bmimPF₆. As shown in the table, a much more variety of substrates can now be applied, and excellent yields and selectivities are obtained in all cases. It is also found that the enhancement in both the reaction rates and stereoselectivities in bmimPF₆ are not significantly different from those in water (Table 2, entries 1–3, 5, and 18–21). In contrast to the system in water, the **1**-in-bmimPF₆ system allowed the reactions of isoprene **5** and dienophiles **a–c** to undertake the Diels–Alder path with 78–91% isolated yields of the cycloaddition adducts (Table 2, entries 15–17). Similarly, the reaction of diene **6** and dienophile **e** in bmimPF₆ afforded a 1:1 mixture of products from both Diels–Alder and the competing diene polymerization pathways. On the contrary, the polymerization became dominant when the reaction of **6** and **e** was conducted in water (Table 2, entry 22 and Table 1, entry 8). Since the OTMS functionality of 1-methoxybutadiene **7** would be deprotected by the PF₆⁻ anion of the ionic liquid to give crotonaldehyde, diene **7** was not applied in the **1**-in-bmimPF₆ system. The cycloadduct from the reaction of **6** and naphthoquinone **d** was transformed to the more stable derivative **6d** with LiAlH₄ in Et₂O.

Finally, catalyst recycling can be readily accomplished in the **1**-in-bmimPF₆ system. The ionic liquid phase containing

Table 1. [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂-catalyzed Diels–Alder reactions in H₂O^a

Entry	Diene	Dienophile	Diels–Alder adduct	Room temperature/50 °C		
				Time (h) ^b	Yield (%) ^c	<i>endo</i> / <i>exo</i> ^d
1	2	a	2a	2/0.58	93/90	95:5/10:1
2	2	b	2b	2/0.67	94/92	10:1/19:2
3	2	c	2c	2/0.6	87/82	<i>endo</i> only
4	2	e	2e	8/3.5	99/96	4:1/3.7:1
5	6	a	6a	2/0.5	89/80	<i>endo-syn</i> only
6	6	b	6b	1/0.35	91/85	<i>endo-syn</i> only
7 ^e	6	c	6c	1.5/0.42	85/77	
8 ^f	6	e	6e	3/1	15/100	<i>endo-syn</i> only/polymer
9 ^g	7	a	7a	1/0.35	75/69	<i>endo-syn</i> only
10 ^h	2	a	2a	5	98	97:3
11 ⁱ	2	a	2a	50	80	95:5
12 ^j	2	a	2a	8	92	95:5

^a Reaction conditions: catalyst loading = 3 mol% at both room temperature and 50 °C, [substrate] = 0.1 M for entries 1–4 and 10–12; [substrate] = 0.2 M for entries 5–9.

^b Time was set for >99% conversion.

^c Isolated yield.

^d *endo*/*exo* ratios were estimated by ¹H NMR spectroscopy.

^e Compound **6c** was the aromatized product after DA reaction.

^f Diene polymerization was the only observable reaction path at 50 °C.

^g The overall yields after OTMS-reprotection.

^h The catalysis was carried out in CH₃NO₂ at room temperature.

ⁱ The reaction was carried out in CH₃NO₂ at room temperature without catalyst.

^j The reaction was carried out in water at room temperature without catalyst.

Table 2. [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂-catalyzed Diels–Alder reactions in bmimPF₆^a

Entry	Diene	Dienophile	Diels–Alder adduct	Room temperature/50 °C		
				Time (h) ^b	Yield (%) ^c	<i>endo:exo</i> ^d
1	2	a	2a	0.75/0.35	97/90	10:1/10:1
2	2	b	2b	0.75/0.42	91/88	10:1/8:1
3	2	c	2c	2/0.5	87/80	<i>endo</i> only
4	2	d	2d	2/0.5	87/83	<i>endo</i> only
5	2	e	2e	8/3.5	99/97	4:1/4:1
6 ^c	2	f	2f	8/4	40/28	4:1/3.5:1
7	3	a	3a	1.25/0.58	92/90	6:1/11:2
8	3	b	3b	1.25/0.58	80/76	6:1/5:1
9	3	c	3c	8/0.66	81/78	<i>endo</i> only
10	3	d	3d	8/0.66	93/85	<i>endo</i> only
11	4	a	4a	4/1.1	81/80	
12	4	b	4b	4/1.1	92/87	
13	4	c	4c	2/0.58	83/78	
14	4	d	4d	2/0.58	91/85	
15	5	a	5a	5/1.7	80/78	
16	5	b	5b	5/1.7	91/85	
17	5	c	5c	6/2.5	78/70	
18	6	a	6a	1/0.35	78/72	<i>endo-syn</i> only
19	6	b	6b	0.5/0.25	79/72	<i>endo-syn</i> only
20 ^f	6	c	6c	1/0.35	77/73	
21 ^g	6	d	6d	1/0.42	71/65	<i>endo-syn</i> only
22 ^h	6	e	6e	48/3	40/100	4:1/polymers

^a Reaction conditions: catalyst loading = 3 mol% at both room temperature and 50 °C, [substrate] = 1.0 M for entries 11–17; [substrate] = 0.67 M for other entries.

^b Time was set for >99% conversion.

^c Isolated yield.

^d *endo:exo* ratios were estimated by ¹H NMR spectroscopy.

^e Diene polymerization dominated over DA reactions.

^f The yields for the aromatized product **6c**.

^g Compound **6d** was the derivatized product.

^h Diene polymerization was the only observable reaction at 50 °C.

bmimPF₆ and catalyst **1** was quantitatively recovered after the removal of the etherated extract of products. Figure 2 showed the results of catalyst recycling experiments. The recovered **1**-in-bmimPF₆ can be reused many times without significant loss of activity even after the tenth application, while the recovered **1**-in-water showed a 20% of decay in catalytic activity after being recycled six times.¹⁹

Microwave radiation is an alternative to conventional heating for transforming electromagnetic energy into heat. There are some documented examples involving the use of ionic liquids as additives for microwave heated Diels–Alder reactions in molecular solvents.^{9b,c} However, to our knowledge, there has been no report on the microwave-assisted

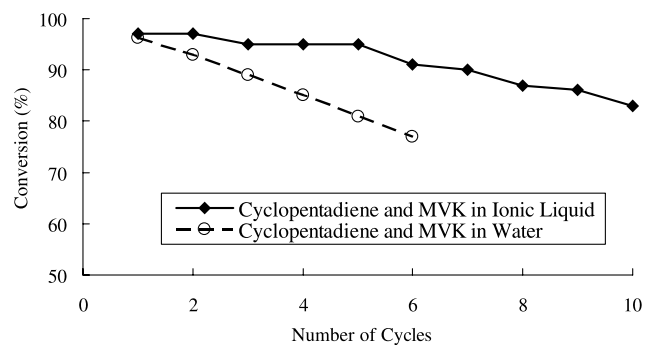


Figure 2. Catalyst systems recycling in bmimPF₆ (◆, upper curve) and in H₂O (○, lower curve). Experiments were conducted in a sealed process vial containing 1.5 mL of bmimPF₆ or 5 mL of H₂O. Reaction conditions: 3.4 mmol of **2**, 3.4 mmol of **a**, 3 mol% of **1**, 5 mL of bmimPF₆ for 45 min or 34 mL of water for 2 h at room temperature.

Diels–Alder reaction with the employment of catalysts in water or in ionic liquids. We next considered applying the Lewis acid **1** in water or in bmimPF₆ solvent with microwave heating on a series of Diels–Alder reactions. Table 3 shows the results of microwave heated **1**-catalyzed Diels–Alder reactions in water. As shown in the table, the system provided significant rate acceleration as compared to the data obtained from the system without microwave heating shown in Table 1. In all cases the reactions were complete within 1 min with similar selectivity to those obtained for the thermal reactions in the **1**-in-water system. Table 4 shows the results of microwave heated **1**-catalyzed Diels–Alder reactions in bmimPF₆. Interestingly, the **1**-in-bmimPF₆ system under microwave irradiation brought about even more acceleration. As shown in Table 4, most of the reactions were complete within 30 s (entries 1–4, 6–13 and 17–20), and even the reaction with a less reactive dienophile methylacrylate **e** took only one minute to complete (entry 5). These results suggested that while water is an excellent medium for microwave irradiation, the ionic liquid bmimPF₆ coupled with microwave even more effectively. To compare the efficiency in microwave conductance between the media water and bmimPF₆, the following experiments were carried out. A maximum temperature of 50 °C and a maximum power of 20% of 300 W were preselected to afford heating profiles and power supply curves for both solvents shown in Figure 3. As seen in the figure, the bmimPF₆ reached 50 °C after being heated for 30 s under sealed vessel conditions, while the water took 48 s to get to 50 °C under the same conditions. Meanwhile, the preset maximum power of 60 W was inputted to both

Table 3. [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂-catalyzed Diels–Alder reactions in H₂O under microwave irradiation^a

Entry	Diene	Dienophile	Diels–Alder adduct	Time (s)	Conversion ^b (%)	Yield ^c (%)	<i>endo/exo</i> ^d
1	2	a	2a	50	94	90	93:4
2	2	b	2b	50	92	87	8:1
3	2	c	2c	50	92	84	<i>endo</i> only
4	2	e	2e	60	>99	97	7:2
5	6	a	6a	50	94	86	<i>endo-syn</i> only
6	6	b	6b	50	94	88	<i>endo-syn</i> only
7	6	c	6c	50	92	83	

^a Reaction conditions: catalyst loading = 3 mol%, [reactant] = 0.1 M for entries 1–4; [reactant] = 0.2 M for entries 5–7.

^b Determined by ¹H NMR.

^c Isolated yield.

^d *endo/exo* selectivities were estimated by ¹H NMR spectroscopy.

systems in the first 6 s, and the power was found to decrease gradually to zero at 30 s in bmimPF₆ and at 48 s in water to prevent the temperature from rising over 50 °C. This is consistent with the results obtained from both Tables 3 and 4.

In conclusion, we have synthesized a water-soluble organotungsten Lewis acid catalyst, [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂ and have demonstrated a highly effective methodology for the construction of 6-membered ring systems via the combined effects of the Lewis acid catalyst in water or in bmimPF₆ under controlled microwave irradiation. The ionic liquid bmimPF₆ acts as a powerful reaction media not only for rate acceleration and chemoselectivity enhancement but also for facilitating catalyst recycling in the [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂-catalyzed Diels–Alder reaction systems. Therefore, this novel methodology involving the use of catalysts, ionic liquids, and microwave radiation is expected to have significant impact in organic synthesis via Diels–Alder reactions that relied on conventional homogeneous catalysts. Further applications of this methodology to other catalytic reactions are under investigations.

3. Experimental

3.1. General method

O=P(2-py)₃ were synthesized by the oxidation of P(2-py)₃²⁰ with 30% H₂O₂ in acetone. 1-Butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) was synthesized by modification of a reported procedure.¹⁶ All cycloaddition products have previously been characterized, and the data obtained corresponded satisfactorily with the reported NMR data, and comparison with authentic samples.

3.1.1. Synthesis of O=P(2-py)₃W(CO)₃ via microwave process. To a solution of 25 mL CH₃CN in Teflon container, W(CO)₆ (300 mg, 0.85 mmol) and O=P(2-py)₃ (239 mg, 0.85 mmol) were added. The container was sealed in the acid digestion vessel and placed into microwave (a CEM MARS 5™). The microwave was programmed to give a maximum internal temperature of 190 °C, the reaction mixture was irradiated at 100% of 300 W power for 7 min. All volatiles were removed at room temperature and the crude was dried in vacuo to afford O=P(2-py)₃W(CO)₃ (468 mg, 100% yield).

Table 4. [O=P(2-py)₃W(CO)(NO)₂](BF₄)₂-catalyzed Diels–Alder reactions in bmimPF₆ under microwave irradiation^a

Entry	Diene	Dienophile	Diels–Alder adduct	Time (s)	Conversion ^b (%)	Yield ^c (%)	<i>endo/exo</i> ^d
1	2	a	2a	25	95	92	8:1
2	2	b	2b	25	89	85	8:1
3	2	c	2c	30	95	81	<i>endo</i> only
4	2	d	2d	30	92	90	<i>endo</i> only
5	2	e	2e	60	>99	96	4:1
6	3	a	3a	25	95	90	6:1
7	3	b	3b	25	82	77	6:1
8	3	c	3c	30	95	80	<i>endo</i> only
9	3	d	3d	30	93	90	<i>endo</i> only
10	4	a	4a	30	81	80	
11	4	b	4b	30	93	88	
12	4	c	4c	30	92	80	
13	4	d	4d	30	91	86	
14	5	a	5a	35	86	83	
15	5	b	5b	35	90	88	
16	5	c	5c	40	84	75	
17	6	a	6a	25	82	75	<i>endo-syn</i> only
18	6	b	6b	25	82	78	<i>endo-syn</i> only
19 ^e	6	c	6c	25	81	78	
20 ^f	6	d	6d	25	81	71	<i>endo-syn</i> only

^a Reaction conditions: catalyst loading = 3 mol%, [reactant] = 1.0 M for entries 10–16; [reactant] = 0.67 M for other entries.

^b Determined by ¹H NMR.

^c Isolated yield.

^d *endo/exo* selectivities were estimated by ¹H NMR spectroscopy.

^e The yields for the aromatized product **6c**.

^f Compound **6d** was the derivatized product.

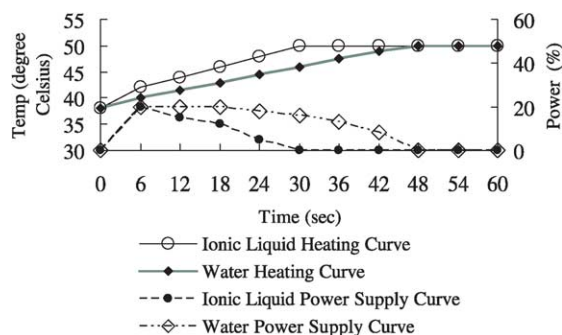


Figure 3. Upper curves: heating profiles for microwave-heated (○) bmimPF_6 and (◆) H_2O . Lower curves: power supply profiles for (●) bmimPF_6 and (◇) H_2O . Experiments were conducted in a sealed process vial containing 1.5 mL of bmimPF_6 or 5 mL of H_2O .

3.1.2. Synthesis of $[\text{O}=\text{P}(\text{2-py})_3\text{W}(\text{CO})(\text{NO})_2](\text{BF}_4)_2$ (**1**).

A CH_3NO_2 suspension of NOBF_4 (43 mg, 0.36 mmol in 3 mL) was cooled to 0°C before adding $\text{O}=\text{P}(\text{2-py})_3\text{W}(\text{CO})_3$ (100 mg, 0.18 mmol). The mixture was stirred at 0°C for 20 min before filtration. 20 mL of CH_2Cl_2 was transferred into the filtrate, and the mixture was allowed to sit at 0°C for 0.5 h to give green crystalline solids. The crude was washed with CH_2Cl_2 (3×5 mL) and dried in vacuo (94 mg, 71% yield). $^1\text{H NMR}$ (400 MHz, CD_3NO_2): δ = 9.41 (3H, m), 8.78 (3H, m), 8.63 (3H, m), 8.09 (3H, m). $^{13}\text{C NMR}$ (100 MHz, CD_3NO_2): δ = 190.5 (CO). $^{31}\text{P NMR}$ (160 MHz, CD_3NO_2): δ = 7.2. IR (CaF_2): ν_{CO} = 2156, ν_{NO} = 1852, 1763 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{B}_2\text{F}_8\text{N}_5\text{O}_4\text{PW}$: C, 26.44; H, 1.66; N, 9.64. Found: C, 26.74; H, 1.70; N, 9.85%.

3.1.3. Representative procedure for the 1-catalyzed Diels–Alder reaction in water.

Cat. **1** (22 mg, 0.03 mmol) was dissolved in water (5 mL). A mixture of **6** (100 μL , 1.0 mmol) and **a** (80 μL , 1.0 mmol) was transferred into the solution. The solution was stirred at room temperature and monitored by $^1\text{H NMR}$. When the $^1\text{H NMR}$ data showed the reaction to be completed (a total disappearance of reactants' signals), the mixture was extracted with ether (3×15 mL). MgSO_4 was added to the extract for dehydration. The crude was purified by flash chromatography on SiO_2 using hexane/ether (10:1) as eluent to give **6a** (139 mg, 90% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 5.99 (2H, m), 4.05 (1H, m), 3.30 (3H, s), 2.46 (1H, m), 2.22 (1H, m), 2.18 (3H, s), 1.91 (1H, m), 1.83 (2H, m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 208.96, 132.97, 124.27, 72.59, 56.30, 52.27, 28.01, 25.15, 18.35; MS (EI) m/e : 154, 153, 139, 122, 107, 84, 79, 78, 43, 42; M^+ / e calcd: 154.0994, found: 154.0992. IR (CaF_2): 3206, 2934, 1713, 1650 cm^{-1} .

3.1.4. Representative procedure for the 1-catalyzed Diels–Alder reaction in bmimPF_6 .

Cat. **1** (22 mg, 0.03 mmol) was dissolved in bmimPF_6 (1.5 mL). A mixture of **6** (100 μL , 1.0 mmol) and **a** (80 μL , 1.0 mmol) was transferred into this ionic solution. The mixture was stirred at room temperature and monitored by $^1\text{H NMR}$. The resulting mixture was extracted with ether (3×10 mL). MgSO_4 was added to the extract, and the mixture was stirred and allowed to sit for 30 min. Trace amount of ionic solids containing bmim^+ , SO_4^{2-} , Mg^{2+} , and PF_6^- were filtered off, and the filtrate was dried and purified by flash chromatography on SiO_2 using hexane/ether (10:1) as eluent to give **6a** (128 mg, 78% yield).

3.1.5. Representative procedure for the 1-catalyzed Diels–Alder reaction in water under controlled microwave irradiation.

A 10 mL sealed microwave process vial containing an aqueous solution of **1** (22 mg, 0.03 mmol, in 5 mL of H_2O) was added compounds **6** (100 μL , 1.0 mmol) and **a** (80 μL , 1.0 mmol). The mixture was subjected for microwave heating (20% of 300 W maximum power, 50°C preselected maximum temperature). The process was monitored by $^1\text{H NMR}$. When the reaction showed $>90\%$ completion, the mixture was extracted with ether (3×10 mL). MgSO_4 was added to the extract for dehydration. The crude was purified by flash chromatography on SiO_2 using hexane/ether (10:1) as eluent to give **6a** (132 mg, 86% yield).

3.1.6. Representative procedure for the 1-catalyzed Diels–Alder reaction in bmimPF_6 under controlled microwave irradiation.

A 5 mL sealed microwave process vial containing bmimPF_6 solution of **1** (22 mg, 0.03 mmol, in 1.5 mL of bmimPF_6) was added compounds **6** (100 μL , 1.0 mmol) and **a** (80 μL , 1.0 mmol). The mixture was subjected for microwave heating (20% of 300 W maximum power, 50°C preselected maximum temperature). The process was monitored by $^1\text{H NMR}$. When the reaction showed $>90\%$ completion, the mixture was extracted with ether (3×10 mL), and MgSO_4 was added to the extract. The mixture was stirred and allowed to sit for 30 min. The ionic solids containing bmim^+ , SO_4^{2-} , Mg^{2+} , and PF_6^- were filtered off. The filtrate was purified by flash chromatography on SiO_2 using hexane/ether (10:1) to give **6a** (116 mg, 75% yield).

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