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Highly efficient synthesis of extended triptycenes via Diels–Alder cycloaddition in water under microwave radiation

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ABSTRACT

Microwave-irradiated Diels–Alder reactions of anthracene and endoxides (**6a–g**) in water afforded the cycloadducts (**8a–g**) with high efficiencies. The extended triptycenes (**2a–g**) were readily obtained by dehydration of **8a–g** in a mixture of AcOH and Ac_2O with good overall yields.

During the past decades, triptycene **1** and extended triptycenes **2** have attracted much attention for their unique geometrical and structural characters: rigidity, bulkiness, nonplanarity and π-electron richness.[1] They have been applied creatively in a range of fields, including studies of atropisomerism,[2] intramolecular charge transfer,[3] ligands design,[4] host-guest chemistry,[5] supramolecular chemistry[6] and molecular gear devices.[7]

Triptycenes are conventionally prepared by Diels–Alder reactions between anthracene or its derivatives (with its central ring serving as the diene component) and an appropriate dienophile (Scheme 1). The first synthesis of triptycene from anthracene **3** and *p*-benzoquinone **4** through a six-step reaction sequence was reported by Bartlett et al. in 1942.[8] Instead of using *p*-benzoquinone followed by complicated multistep manipulations for aromatization, Wittig and Ludwig later reported a single-step synthesis of triptycene by using benzyne **5** as the dienophile.[9] Using this approach, various triptycene derivatives had been synthesized through various aryne anthracene combinations.[10] Recently, the employ of benzofused endoxides **6** as dienophiles has provided a good method for the preparation of extended triptycene precursors **8** that can be readily dehydrated to corresponding extended triptycenes **2**.[11] However, the major drawback of this approach is a rather long reaction time at reflux. In many cases, the mixture of anthracene and the endoxide had to be refluxed in either xylene or decalin for more than two days.

Microwave radiation is an attractive alternative to conventional heating for introducing energy into reactions. It has been applied with success to many kinds of organic reactions.[12] Diels–Alder cycloaddition was the first reaction type to be examined in conjunction with microwave radiation. In general, these conditions reduce significantly the reaction times and improve the yields as compared to the conventional heating methods.[13] The short reaction time can also restrict the reversibility and prevent polymerization of the diene or dienophile. In this Letter, we report our findings on the Diels–Alder reactions of anthracene and endoxides under microwave radiation in water as an efficient approach to the preparation of extended triptycenes.

Our investigation started with the reaction between anthracene and oxadisilole-fused endoxide **6a**.[14] In a control experiment, the reaction was not completed and the cycloadduct **8a** could be isolated in 55% yield after refluxing in *p*-xylene for two days. The results in optimizing our microwave irradiation approach in a Chempower Reactor are summarized in Table 1.

The reactions were carried out in a sealed tube (10 mL) and the machine can control the reaction temperature by changing its power. We first used a mixture of *p*-xylene and water (volume ratio = 1:3) as a solvent. We found that at temperatures below 120 °C, there was almost no reaction (Table 1, entry 1). When the temperature increased, from 120 °C to 145 °C, the reactions gradually took place (entries 2–5). Within 20 min, isolated yields of 30–67% could be obtained. Further extending the reaction time to 40 min at 140 °C led to the completion of the reaction and product **8a** could be isolated in 92% yield (entry 6). Finally, we found that

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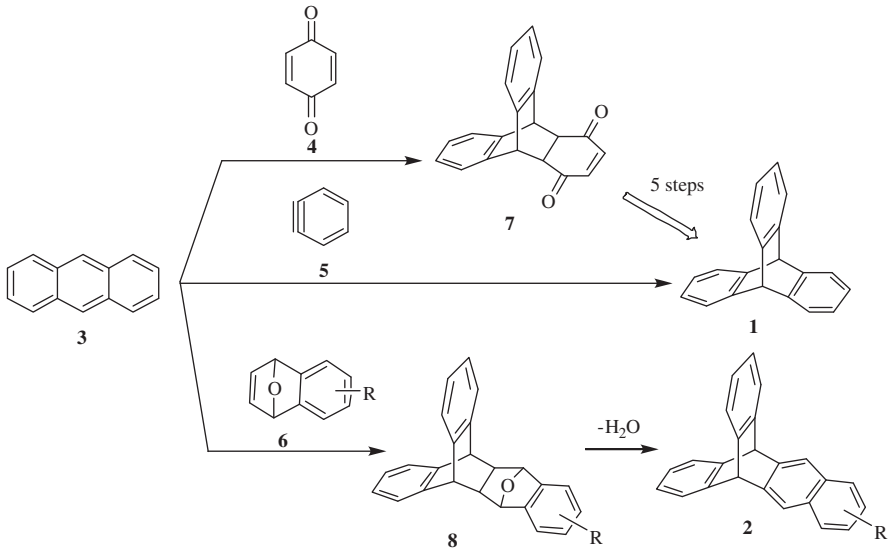
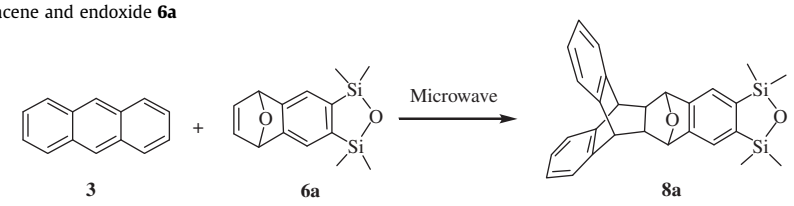


Scheme 1.

Table 1
Diels–Alder reaction between anthracene and endoxide **6a**



Entry	Solvents	Temperature (°C)	Time (min)	Yield (%)
1[a]	*p*-Xylene/H_2O	100–115	20	<5
2[a]	*p*-Xylene/H_2O	120	20	30
3[a]	*p*-Xylene/H_2O	130	20	44
4[a]	*p*-Xylene/H_2O	140	20	65
5[a]	*p*-Xylene/H_2O	145	20	67
6[a]	*p*-Xylene/H_2O	140	40	92
7[a]	H_2O[d]	135	40	93
8[b]	H_2O[d]	135	90	<5
9[c]	*p*-Xylene	—	30	56

[a] Chempower reactor, a mixture of H_2O (3.0 mL) and *p*-xylene (1.0 mL) as solvent; 0.36 mmol anthracene and 0.3 mmol endoxide **6a** were used.
[b] The reaction mixture in a 10 mL sealed tube was heated in an oil bath.
[c] The reaction mixture in an open beaker was heated in a domestic microwave oven (800 W).
[d] 4 mL H_2O as solvent.

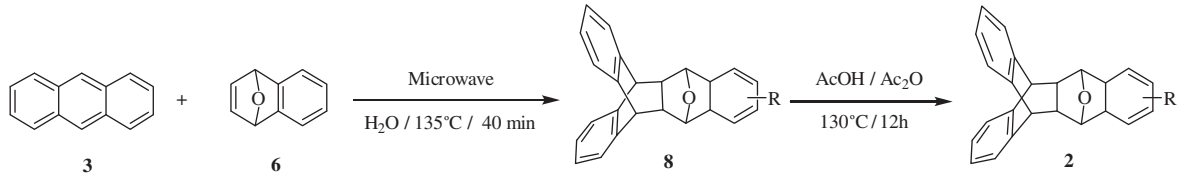
with only water as the solvent, the reaction could be completed in 40 min at 135 °C with isolated yield of cycloadduct **8a** in 93% (entry 7). The use of microwave is crucial for these Diels–Alder reactions. When the reaction mixture was heated in a sealed tube in an oil bath at 135 °C for 90 min, only trace amount of product could be detected (entry 8). The reaction could also be carried out in an open beaker using a domestic microwave oven with isolated yield of 56% in 30 min (entry 9).

With the optimized reaction conditions in hand, we then examined the scope of this microwave-irradiated Diels–Alder reaction of anthracene with various endoxides.[15] The results are summarized in Table 2. All the benzofused endoxide (**6b–e**) and naphthofused endoxides (**6f** and **6g**) reacted with anthracene completely to afford the corresponding cycloadducts **8a–g** in very high isolated yields (91–95%) within 40 min. The reactions were very clean. Both the yields and efficiency are much higher than the conventional approaches.

Cycloadduct **8a** can be dehydrated to afford the extended triptycene **2a** under acidic conditions (Table 2). Typical acids such as TsOH, HCl and H_3PO4 used in the literatures gave poor results. The extended triptycene **2a** was isolated in less than 50% yield and a large amount of retro Diels–Alder products were obtained.[16] After much modification, we found that $AcOH/Ac_2O$ (ratio = 2:1) system gave the best result. Compound **2a** could be isolated in 81% yield with very little amount of retro Diels–Alder products after refluxed for 12 h.[17] Under these conditions, cycloadducts **8b–g** were readily dehydrated to provide the corresponding extended triptycenes **2b–g** in good yields (70–83%). In case of **8e–g**, addition of few drops of concentrated H_2SO_4 speeded up the dehydration processes. It is worth noting that both **2f** and **2g** contain an anthracene moiety. They will be useful precursors for large iptycenes via cycloaddition reactions.[11a]

In summary, we have developed a highly efficient microwave-mediated Diels–Alder reaction of anthracene and endoxides with

Table 2
Diels–Alder reactions between anthracene and various endoxides under microwave radiation followed by dehydration



6a	**8a** 93%	**2a** 81%
6b	**8b** 93%	**2b** 80%
6c	**8c** 95%	**2c** 70%
6d	**8d** 91%	**2d** 83%
6e	**8e** 95%	**2e** 71%
6f	**8f** 94%	**2f** 72%
6g	**8g** 91%	**2g** 73%

water as the solvent. Dehydration of the cycloadducts in AcOH/Ac_2O afforded the extended triptycenes in good yields.

Acknowledgement

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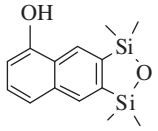
15. *General experimental procedure of Diels–Alder reaction between anthracene and endoxides* **6** *under microwave radiation*: Anthracene (64 mg, 0.36 mmol), endoxide **6** (0.3 mmol) and H_2O (4 mL) were added into a 10 mL glass vessel which was then sealed with rubber septa and put into the Chempower Reactor machine (750 W, Shanghai, China). The highest power (750 W) was set at the beginning so that the targeted temperature can be reached within 4 min. During the reaction, the temperature (135 °C) and the pressure (1.0–1.2 MPa) in the vessel were steady. After 40 min, the mixture was cooled to room temperature and then extracted with CH_2Cl_2 (2 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4. After being filtered and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel with 15–30% CH_2Cl_2 in petroleum ether as eluent to afford product **8**.
Compound **8a**: mp 205–206°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 6H), 0.30 (s, 6H), 2.30 (s, 2H), 4.44 (s, 2H), 4.95 (s, 2H), 7.00 (m, 2H), 7.16 (m, 2H), 7.22 (m, 2H), 7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.9, 1.0, 47.4, 48.9, 81.2, 120.8, 123.5, 123.8, 125.7, 126.0, 141.4, 144.2, 146.6, 148.0. HRMS (MALDI-TOF) calcd for $C_{28}H_{28}O_2Si_2Na$ [M+Na]$^+$: 475.1520; found 475.1522.
Compound **8b**: mp 261–262°; ^{1}H NMR ($CDCl_3$, ppm): δ 2.25 (s, 2H), 4.42 (s, 2H), 4.93 (s, 2H), 7.01 (m, 4H), 7.13 (m, 4H), 7.22 (m, 2H), 7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.4, 48.8, 81.2, 118.6, 123.5, 123.7, 125.7, 126.0, 126.2, 141.4, 144.2, 146.7.
Compound **8c**: mp 266–267°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 2H), 4.42 (s, 2H), 4.91 (s, 2H), 7.03 (m, 2H), 7.15 (m, 2H), 7.23 (m, 2H), 7.28 (m, 2H), 7.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.1, 48.4, 80.8, 122.1, 123.6, 123.8, 124.2, 125.9, 126.2, 141.1, 143.8, 147.7.
Compound **8d**: mp 217–218°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 6H), 2.21 (s, 2H), 4.40 (s, 2H), 4.88 (s, 2H), 6.91 (s, 2H), 6.99 (m, 2H), 7.14 (m, 2H), 7.22 (m, 2H), 7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 47.5, 49.4, 81.1, 120.1, 123.4, 123.7, 125.6, 125.9, 134.2, 141.5, 144.3, 144.7.
Compound **8e**: mp >350°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (s, 2H), 4.15 (s, 2H), 4.61 (s, 2H), 5.33 (s, 2H), 6.95 (m, 6H), 7.08 (m, 4H), 7.14 (m, 2H), 7.18 (m, 2H), 7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.2, 48.7, 54.2, 80.9, 115.0, 123.4, 123.5, 123.6, 125.0, 125.1, 125.5, 125.8, 141.4, 143.9, 144.0, 144.2, 145.2, 145.5. HRMS (MALDI-TOF) calcd for $C_{38}H_{26}ONa$ [M+Na]$^+$: 521.1886; found 521.1887.
Compound **8f**: mp 281° (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 2H), 4.50 (s, 2H), 5.08 (s, 2H), 7.03 (m, 2H), 7.18 (m, 2H), 7.25 (m, 2H), 7.33 (m, 2H), 7.40 (m, 2H), 7.51 (s, 2H), 7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.5, 49.2, 81.2, 116.8, 123.5, 123.8, 125.6, 125.7, 126.1, 128.1, 132.6, 141.4, 144.0, 144.5.
Compound **8g**: mp >350°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 2H), 4.45 (s, 2H), 5.00 (s, 2H), 5.49 (s, 2H), 7.01 (m, 6H), 7.148 (m, 2H), 7.23 (m, 2H), 7.29 (m, 2H), 7.38 (m, 6H), 7.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.5, 49.0, 53.6, 81.2, 116.6, 122.0, 123.5, 123.6, 123.7, 125.3, 125.4, 125.7, 126.0, 130.7, 141.4, 142.1, 144.0, 144.4, 144.5, 144.6.
16. The retro Diels–Alder products are anthracene and oxadisilole fused naphthol which is confirmed by NMR spectra.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.44 (s, 6H), 0.45 (s, 6H), 6.10 (b, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6, 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 8.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.2, 1.3, 109.0, 120.8, 124.7, 124.8, 126.5, 130.9, 134.8, 142.8, 144.2, 151.8.



17. *General experimental procedure for dehydration of cycloadducts* **8** *to extended triptycenes* **2**: Compound **8** (40–150 mg) was dissolved in a mixture of AcOH (2.0 mL) and Ac_2O (1.0 mL) (for **8e–g**, 3–6 drops of concentrated H_2SO_4 (96%) was added to the mixture). The reaction mixture was stirred at 130 °C for 12 h and then poured into 10 mL ice water. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the organics were dried over anhydrous Na_2SO_4. After being filtered and concentrated, the residue was purified by column chromatography on silica gel with 10–25% CH_2Cl_2 in petroleum ether as eluent to afford product **2**.
Compound **2a**: mp 296–297°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.36 (s, 12H), 5.54 (s, 2H), 7.02 (m, 4H), 7.42 (m, 4H), 7.77 (s, 2H), 7.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.2, 53.7, 121.9, 123.7, 125.5, 130.6, 132.1, 142.7, 143.5, 144.4. HRMS (MALDI-TOF) calcd for $C_{28}H_{26}OSi_2$ [M]$^+$: 434.1517; found 434.1496.
Compound **2b**: mp 258–259°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (s, 2H), 7.04 (m, 4H), 7.38 (m, 2H), 7.45 (m, 4H), 7.72 (m, 2H), 7.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.7, 121.7, 123.7, 125.5, 125.6, 127.4, 131.7, 142.0, 144.5.
Compound **2c**: mp >350°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (s, 2H), 7.04 (m, 4H), 7.43 (m, 4H), 7.63 (s, 2H), 7.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.5, 120.6, 121.4, 123.9, 125.8, 131.5, 131.6, 143.5, 144.0.
Compound **2d**: mp 275–276°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6H), 5.53 (s, 2H), 7.04 (m, 4H), 7.45 (m, 6H), 7.69 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 53.7, 120.8, 123.6, 125.4, 127.0, 130.5, 135.1, 141.0, 144.8.
Compound **2e**: mp >350°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.44 (s, 4H), 6.96 (m, 8H), 7.35 (m, 8H), 7.62 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.7, 121.4, 123.6, 125.3, 129.7, 142.1, 144.6.
Compound **2f**: mp 289–290°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.58 (s, 2H), 7.08 (m, 4H), 7.42 (m, 2H), 7.48 (m, 4H), 7.90 (s, 2H), 7.95 (m, 2H), 8.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.5, 121.3, 123.8, 124.9, 125.6, 125.7, 128.0, 130.4, 131.6, 141.0, 144.1.
Compound **2g**: mp >350°; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (s, 4H), 7.02 (m, 8H), 7.42 (m, 8H), 7.81 (s, 4H), 8.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.6, 121.3, 123.8, 125.0, 125.6, 130.4, 140.6, 144.2.