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Article

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Cascade Multiple Diels–Alder Reactions of Styrene Derivatives with Maleimide or Maleic Anhydride

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Abstract

We developed novel one-pot multiple Diels–Alder reactions, which are frequently used in the construction of six-membered rings in functional molecular synthesis. We report triple and double Diels–Alder reactions with styrene derivatives, where the secondary Diels–Alder reaction takes place at a different position from that of the conventional Wagner-Jauregg reaction.

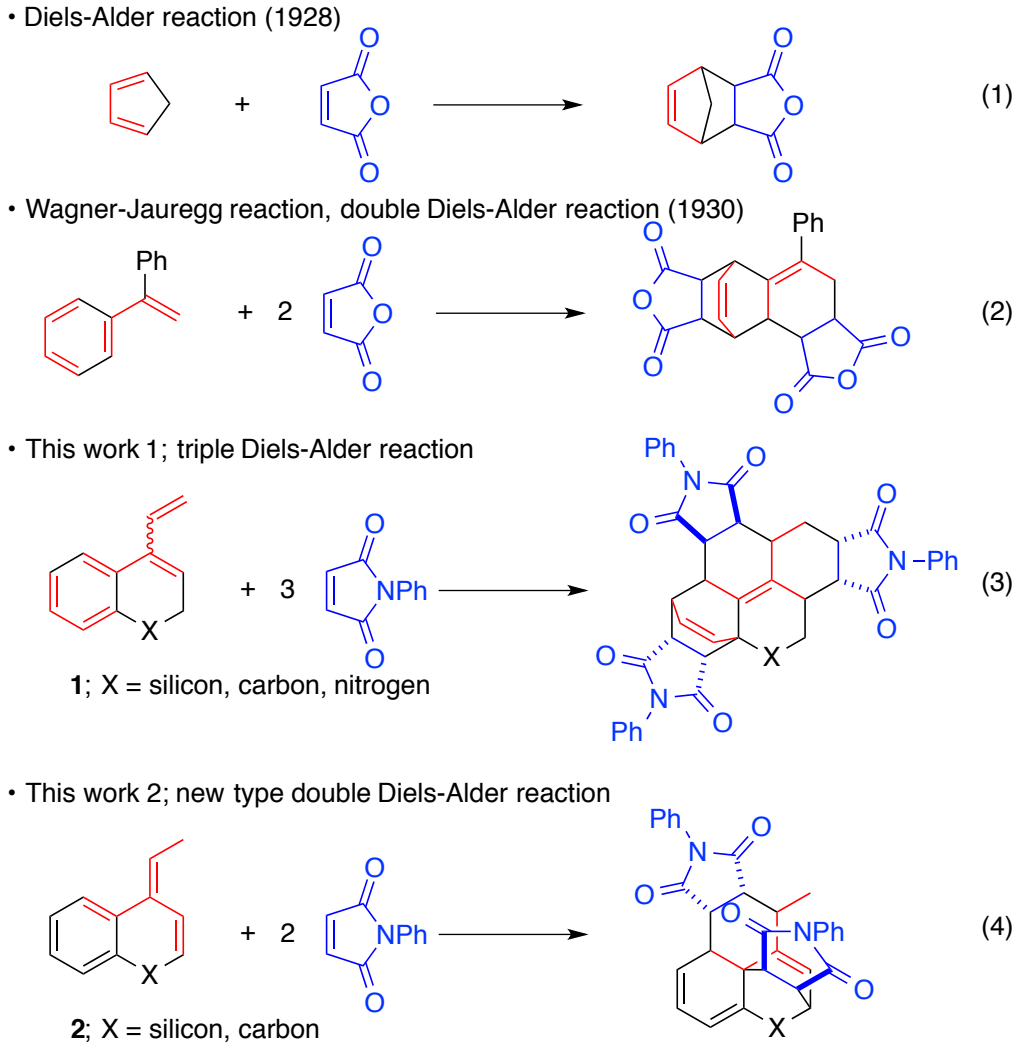
Keywords

pericyclic reaction, Diels–Alder reaction, theoretical calculation

Introduction

The Diels–Alder reaction is a reaction between a conjugated diene and an olefin to form the corresponding substituted cyclohexene, which was developed by Diels and Alder in 1928 (Scheme 1, eq. 1) and is now generally and widely used to synthesize structurally complex molecules, such as biologically active natural products.[1] The Wagner-Jauregg reaction is a double Diels–Alder reaction of two equivalents of maleic anhydride with one equivalent of 1,1-diarylethylene, which was reported by Wagner-Jauregg in 1930 but is rarely used in organic synthesis (Scheme 1, eq. 2).[2] Over 90 years, there have been only four reports based on the Wagner-Jauregg reaction.[3]

Scheme 1. Research background and this work.



Performing multiple reactions in one-pot is a useful ability for synthetic organic chemists, and can minimize solvent usage, time, and the number of purification steps compared with individual multi-step syntheses.[4] Although multiple Diels–Alder reactions could offer an effective approach to polycyclic compounds with six-membered rings, currently there have been relatively few reports of multiple Diels–Alder reactions. Several examples of triple Diels–Alder reactions exist in addition to the above the Wagner-Jauregg reaction.[5,6]

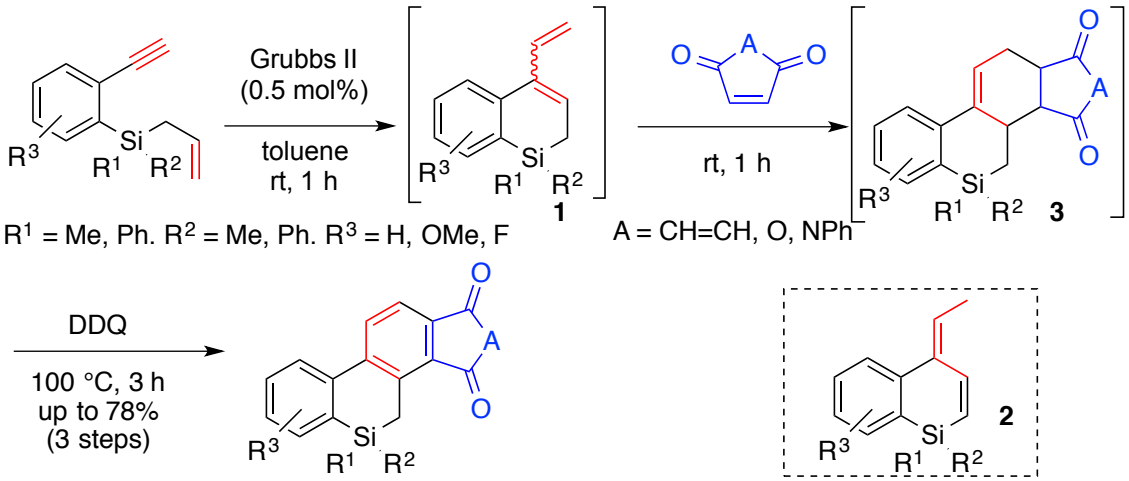
We envisioned that the triple Diels–Alder reaction and double Diels–Alder reaction, where a secondary Diels–Alder reaction takes place at a different position from that of the conventional Wagner-Jauregg reaction, of a styrene derivative might be possible with an appropriately designed diene moiety.

In this article we will describe a triple Diels–Alder reaction of **1** (Scheme 1, eq. 3) and a novel double Diels–Alder type reaction of **2** (Scheme 1 eq. 4), yielding six-membered cyclic compounds containing multiple rings. Results from our experiments are supported by

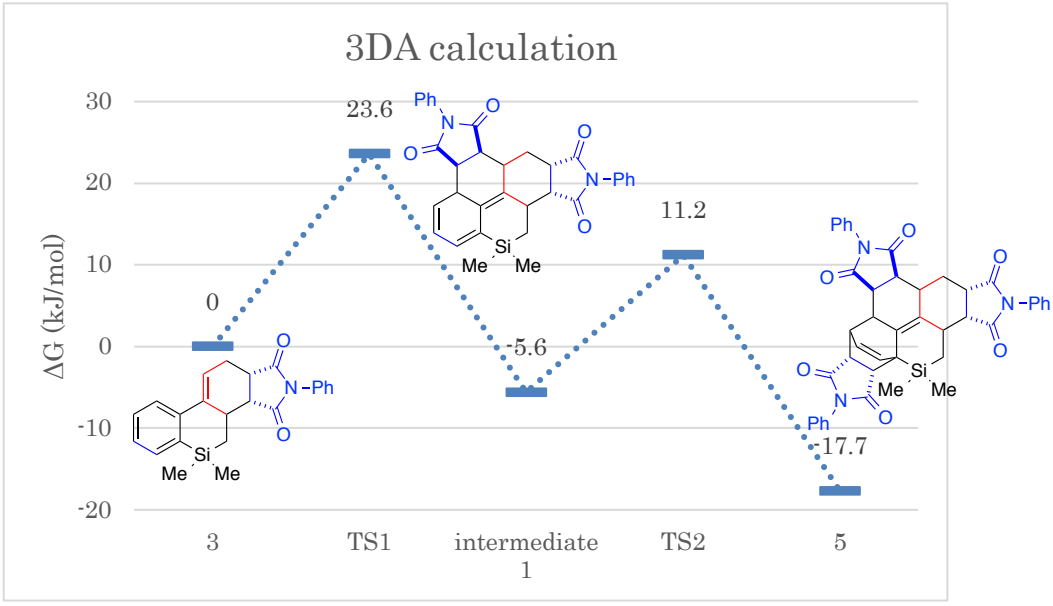
theoretical calculations.

Recently, we have developed a one-pot enyne metathesis / Diels–Alder reaction / oxidation methodology to yield six-membered silacycles that contain multiple rings (Scheme 2).[7] We considered that the key intermediates **1** and **3** in the above one-pot reactions and the isomer of **1**, **2** might offer further examples of multiple Diels–Alder reaction.

Scheme 2. One-pot enyne metathesis / Diels–Alder reaction / oxidation.



Scheme 3. Diels–Alder reactions between **3** and *N*-phenylmaleimide.



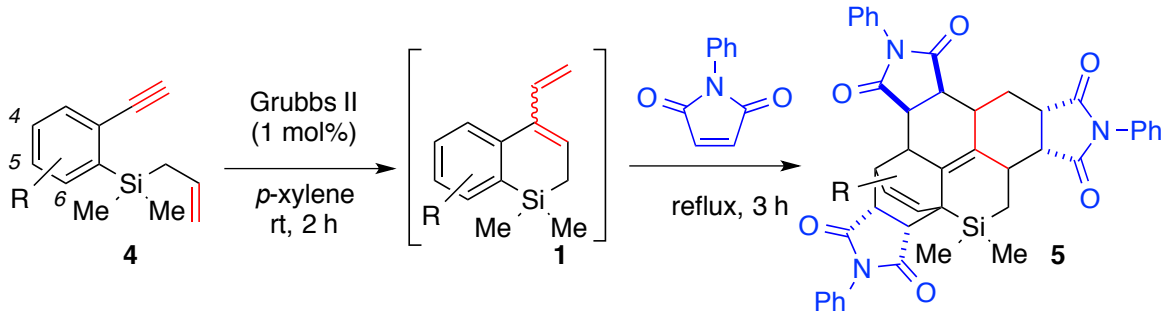
Results and Discussion

First, we calculated a Diels–Alder reaction between **3** and *N*-phenylmaleimide by density functional theory (DFT) using the B3LYP functional and the 6-31G* basis set.[8,9] We found

that two more domino Diels–Alder reactions on **3** are theoretically possible (Scheme 3). Then we used **1a**, generated by enyne metathesis of **4a**, and *N*-phenylmaleimide (10 equiv.) under refluxing xylene conditions (Scheme 4). As a result, we successfully obtained the expected product **5a**, via the theoretically predicted subsequent two extra Diels–Alder reactions on **3**, in 75% yield as a single diastereoisomer (Table 1, entry 2).

We continued our experiments to determine the substituent effects on the benzene ring (Table 1, runs 3–8). The enyne metathesis of **4** proceeded quantitatively, as determined by thin layer chromatography (TLC), regardless of the substituent attached to aromatic ring. However, the triple Diels–Alder reaction was affected by substituents on the aromatic ring. Therefore, the electronic effects of the substituents on the aromatic ring controlled the substrate reactivity toward the triple Diels–Alder reaction. Higher yields of triple Diels–Alder reaction products **5b**, **5c,** and **5d** were obtained with the use of substrates with an electron-releasing group on the aromatic ring.[10] The structure of **5c** was determined by single crystal X-ray diffraction (Figure 1).

Table 1. Triple Diels–Alder reaction of **1**.



Entry	Substrate		Product	
		R =		isolated yield (%, 4 steps)
1	**4a**	H	**5a**	0[a]
2	**4a**	H	**5a**	75
3	**4b**	4-OMe	**5b**	77
4	**4c**	5-OMe	**5c**	95
5	**4d**	6-OMe	**5d**	64
6	**4e**	4-F	**5e**	48
7	**4f**	5-F	**5f**	40
8	**4g**	6-F	**5g**	60

[a] The reaction was performed at room temperature.

Figure 1. X-ray structure of **5c**.[11]

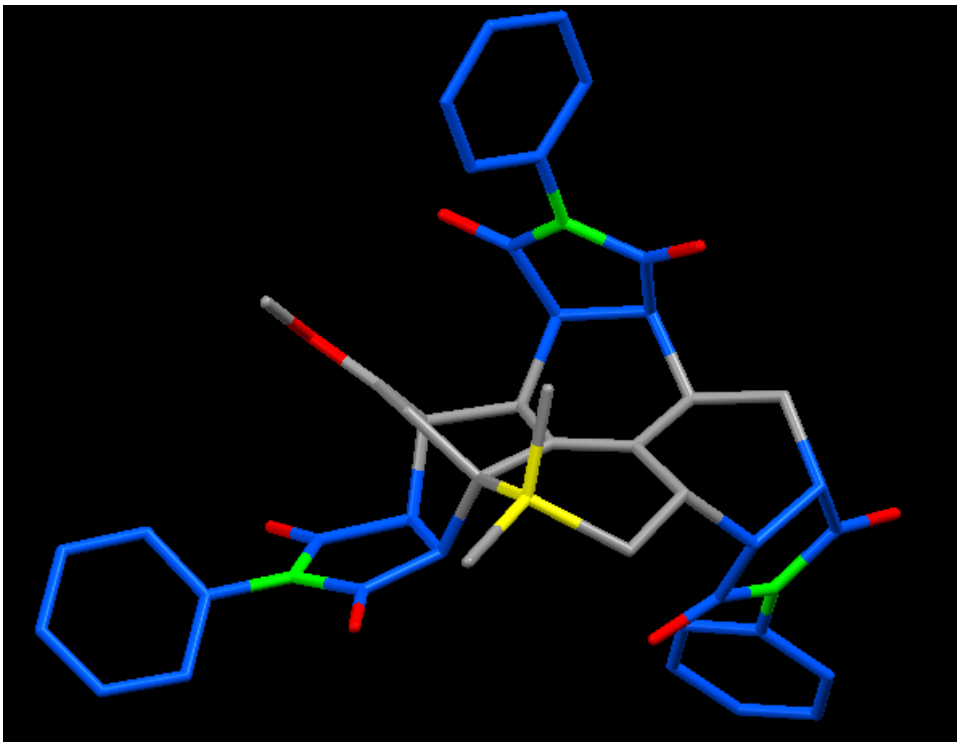
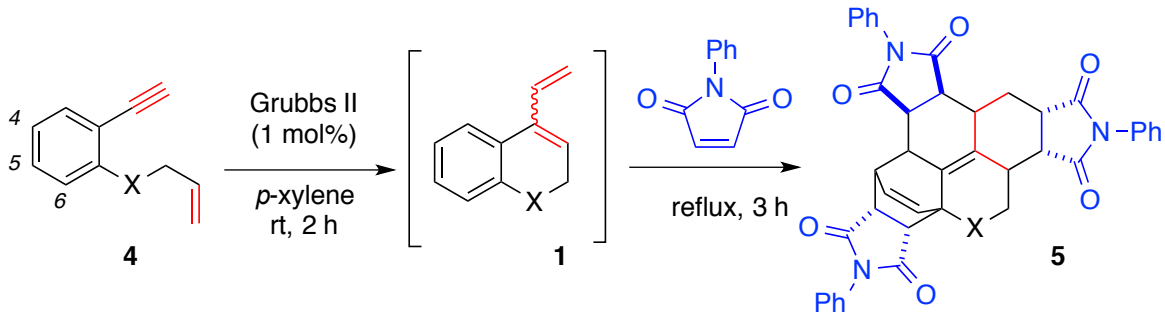


Table 2. One-pot enyne metathesis / triple Diels–Alder reaction of **4** to **5**.



4 **1** **5**

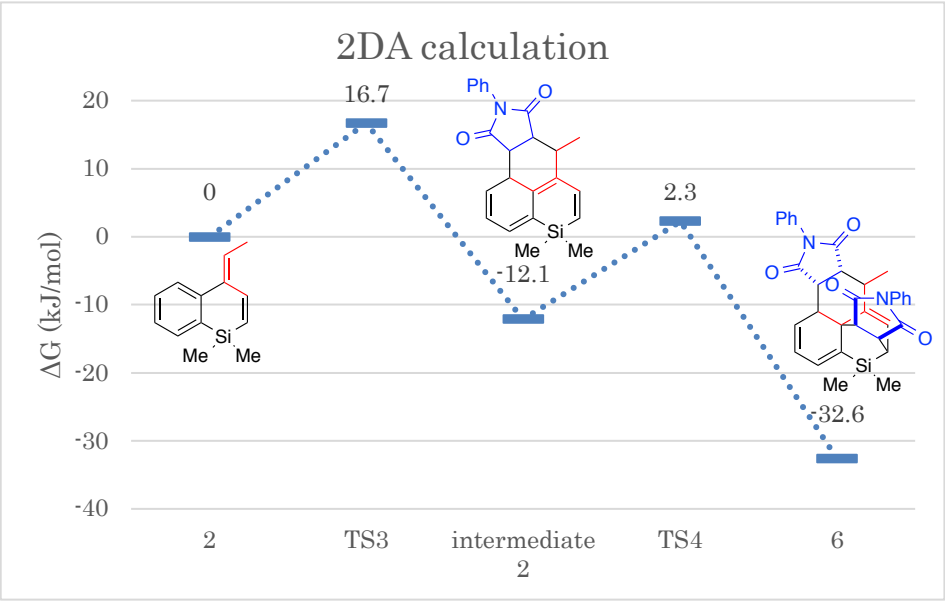
Entry	Substrate		Product	
		X =		isolated yield (%, 4 steps)
1	**4a**	$SiMe_2$	**5a**	75
2	**4h**	CMe_2	**5h**	59
3	**4i**	NTs	**5i**	49

The effects of a silane element on this reaction were then investigated (Table 2). Not only carbon analogue **4h** but also nitrogen analogue **4i** were converted to the corresponding products **5** in moderate to good yields through the same one-pot enyne metathesis / triple Diels–Alder reaction. Although we tried the same reaction between **1a** and other dienophiles, such as maleic anhydride and 1,4-benzoquinene, we could not obtain the corresponding products **5**.

Next, we calculated a Diels–Alder reaction between **2** and *N*-phenylmaleimide by DFT using the B3LYP functional and the 6-31G* basis set.[7] We found that a double Diels–Alder reaction was theoretically possible, with a secondary Diels–Alder reaction taking place with a styrene derivative at a different position from that of the conventional Wagner-Jauregg reaction (Scheme 4). Hence, we placed **2a**, generated by enyne metathesis / isomerization of **4a**, and *N*-phenylmaleimide in refluxing toluene (Scheme 4). As a result, we successfully obtained the corresponding product **6a**, *via* the theoretically expected double Diels–Alder reaction, in 82% yield as a single diastereoisomer (Table 3, Entry 2). The structure of **6a** was determined by single crystal X-ray diffraction (Figure 2).

Scheme 4. Diels–Alder reactions between **2** and *N*-phenylmaleimide.

(a) New type Diels–Alder reaction



(b) Conventional double Diels–Alder reaction (Wagner-Jauregg reaction).

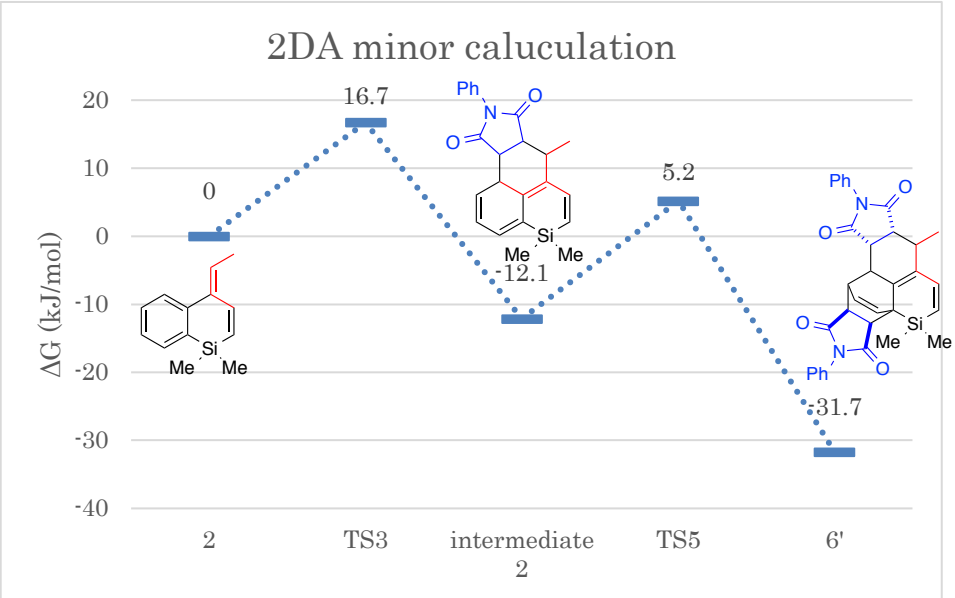
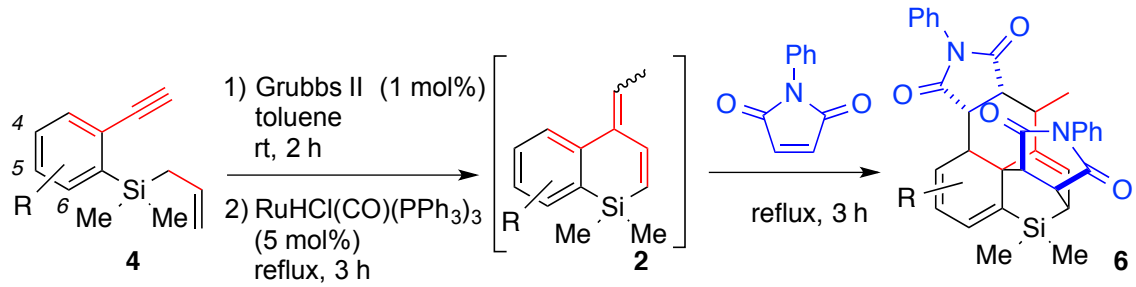


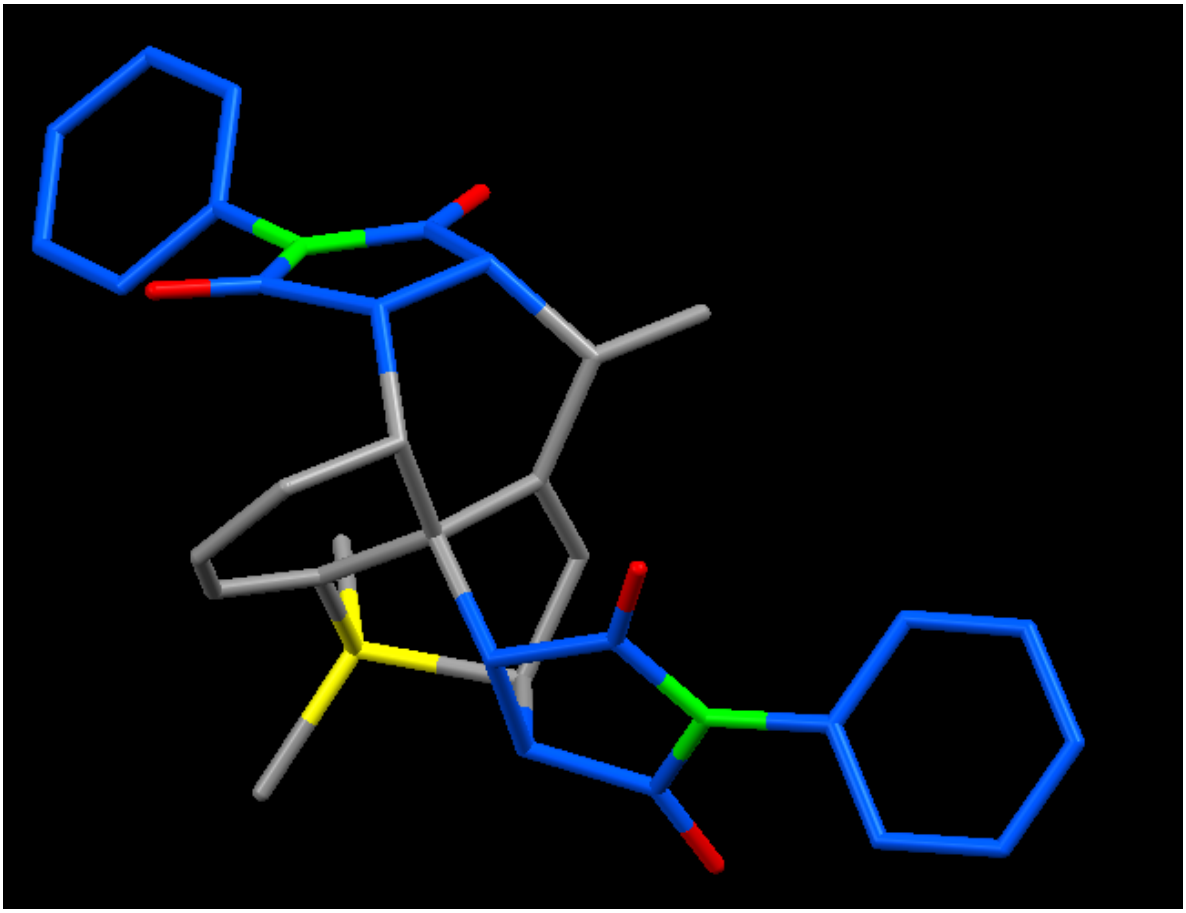
Table 3. Double Diels–Alder reaction of **2**.



Entry	Substrate		Product	
		R =		isolated yield (%, 4 steps)
1	**4a**	H	**6a**	0[a]
2	**4a**	H	**6a**	82
3	**4b**	4-OMe	**6b**	95
4	**4c**	5-OMe	**6c**	quant.
5	**4d**	6-OMe	**6d**	85
6	**4e**	4-F	**6e**	59
7	**4f**	5-F	**6f**	51
8	**4g**	6-F	**6g**	55

[a] The reaction was performed at room temperature.

Figure 2. X-ray structure of **6a**.[9]

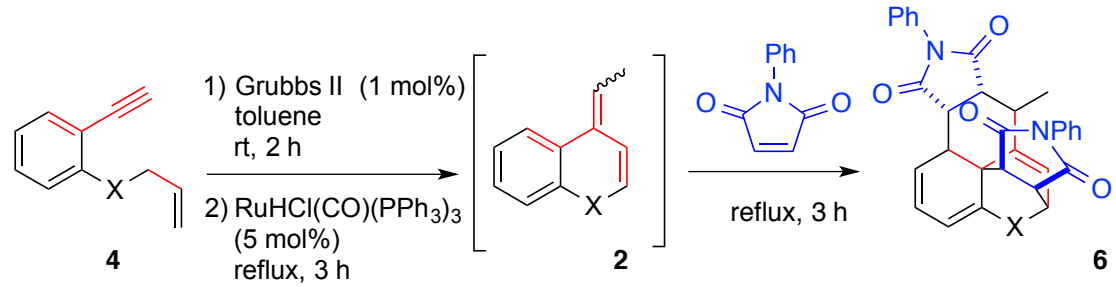


On the basis of these results, we next examined the effects of substituents on the benzene ring (Table 3, Entries 3–8). Methoxy derivatives **4b–d** were converted to the corresponding cyclized products **4b–4d** in excellent to quantitative yields; the variation of the yields was likely the result of electron donating effects. Derivatives **4e–4g**, with electron-withdrawing groups on the benzene ring, did not participate in the reaction well.[10]

We continued our experiments to determine the effects of substituents on the allyl silane moieties (Table 4). We found that both diphenylsilyl analogue **4j** and its carbon analogue **4h** were converted to the corresponding products **6** in moderate yields through one-pot enyne metathesis / isomerization / double Diels–Alder reaction (Entries 2 and 3). We tried the same reaction between **2a**, prepared from **4a**, and other dienophiles and found that we could also use

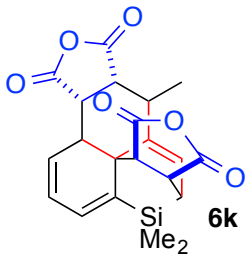
maleic anhydride as a dienophile. Thus, we obtained **6k** from **4a** in 71% yield (Figure 3).

Table 4. One-pot enyne metathesis / isomerization / double Diels–Alder reaction of **4** to **6**.



Entry	Substrate		Product	
		X =		isolated yield (%, 4 steps)
1	**4a**	$SiMe_2$	**6a**	82
2	**4h**	CMe_2	**6h**	62
3	**4j**	$SiPh_2$	**6j**	61

Figure 3. Structure of **6k**.



In summary, we have developed novel multiple Diels–Alder reactions based on theoretical considerations. Namely, a triple Diels–Alder reaction and a new type of double Diels–Alder reaction, for which the secondary Diels–Alder reaction takes place at a different position from that of a conventional Wagner-Jauregg reaction.

Experimental Section

General Information

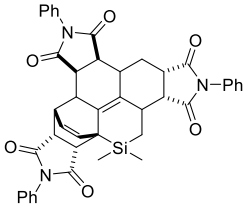
Chemicals and solvents were either purchased from commercial suppliers or purified by

standard techniques. All reactions were performed under N_2 atmosphere unless otherwise noted. For thin-layer chromatography (TLC), silica gel plates Merck 60 F_{254}. ^{1}H NMR were recorded at 300 MHz, 400 MHz and 500 MHz. ^{13}C NMR spectra were recorded at 101 MHz and 126 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and the coupling constants *J* are given in Hz. The spectra were recorded in $CDCl_3$ as solvent at room temperature unless otherwise noted. TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR, $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR. Column chromatography was performed with silica gel 60N (spherical, neutral, 63-210 μm, Kanto Chemical Co., Inc.), flash silica gel 60 (spherical, acid, 40-50 μm, Kanto Chemical Co., Inc.) and flash silica gel 60N (spherical, neutral, 40-50 μm, Kanto Chemical Co., Inc.) unless otherwise noted. Melting points were determined at heated plate and are uncorrected. HRMS (m/z) were measured using MALDI (Matrix Assisted Laser Desorption/Ionization) techniques unless otherwise noted. **4a**-**4c**, **4e**, **4f** and **4h** - **4j** are known compounds. [6] **4d** and **4g** are known compounds [13]

Triple Diels-Alder reaction

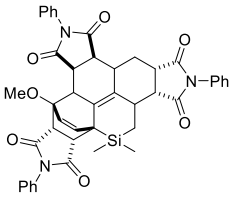
General procedure **A**

To a solution of **4** in *p*-xylene (0.2 M) was added Grubbs II (1 mol%) and the mixture was stirred at room temperature for 2 h. Then *N*-phenyl maleimide(10 eq.) was added to the reaction mixture and the mixture was refluxed for 3 h. The solvent was evaporated and the residue was subjected to column chromatography(*n*-hexane/AcOEt = 1/1) on neutral flash silica gel to give **5**.

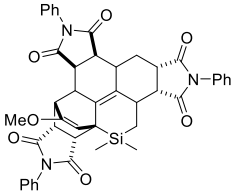


5a: Compound **5a** (75%, 0.0752 mmol, 54.1 mg) was prepared from **4a** (0.100 mmol, 20.0 mg) by a general procedure **A**. ^{1}H-NMR (DMSO-D_6, 500 MHz) δ: 7.52-7.50 (2H, m), 7.46-7.44 (5H, m), 7.40-7.35 (2H, m), 7.22 (2H, d, *J* = 7.4 Hz), 7.12 (4H, dd, *J* = 7.4, 7.4 Hz), 6.33-6.31 (1H, m), 6.20 (1H, d, *J* = 8.0 Hz), 3.56-3.54 (1H, m), 3.43 (1H, t, *J* = 7.7 Hz), 3.34-3.33 (1H, m), 3.27-3.25 (1H, m), 3.20 (1H, d, *J* = 8.0 Hz), 3.15 (1H, d, *J* = 7.4 Hz), 2.98 (1H, td, *J* = 13.2, 5.5 Hz), 2.86-2.84 (1H, m), 2.71 (1H, d, *J* = 6.9 Hz), 2.22 (1H, d, *J* = 14.0 Hz), 2.11 (1H, d, *J* = 13.2 Hz), 2.00 (1H, t, *J* = 13.2 Hz), 0.88 (1H, dd, *J* = 14.0, 5.5 Hz), 0.33 (3H, s), -0.18 (3H, s). ^{13}C-NMR (DMSO-D_6, 125 MHz) δ: 179.2, 178.4, 177.3, 177.2, 176.7, 175.7, 136.1, 135.2, 134.6, 132.5, 132.4, 132.2, 130.3, 129.0, 128.8, 128.8, 128.4, 128.3, 128.2, 127.4, 127.0, 126.8, 48.7, 47.7, 45.5, 45.4, 44.6, 43.6, 40.2, 35.8, 34.6, 34.2, 30.0, 24.8, 10.1, -2.2, -3.9. HRMS (MALDI-TOF) calcd for $C_{43}H_{38}N_3O_6Si$: 720.2524 ([M+H]$^+$), found 720.2532 ([M+H]$^+$). m.p. 294.0-295.0 °C (recrystallized from $CHCl_3$, a colorless column)

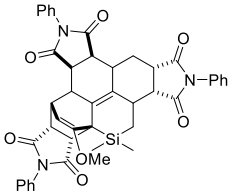
5b: Compound **5b** (77%, 0.0767 mmol, 57.5 mg) was prepared from **4b** (0.100 mmol, 23.0



mg) by a general procedure **A**. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.52-7.50 (2H, m), 7.44-7.42 (5H, m), 7.36-7.35 (2H, m), 7.15 (6H, dd, *J* = 15.5, 8.0 Hz), 6.71 (1H, d, *J* = 8.6 Hz), 6.09 (1H, d, *J* = 9.2 Hz), 3.79 (3H, s), 3.54 (1H, t, *J* = 8.3 Hz), 3.46 (1H, t, *J* = 7.2 Hz), 3.37 (1H, d, *J* = 8.0 Hz), 3.27 (1H, td, *J* = 14.4, 6.9 Hz), 3.22 (2H, td, *J* = 9.2, 4.1 Hz), 3.11 (1H, d, *J* = 8.0 Hz), 3.03-2.99 (1H, m), 2.62 (1H, dd, *J* = 7.5, 2.9 Hz), 2.39 (1H, dd, *J* = 14.3, 2.9 Hz), 2.25-2.20 (1H, m), 2.18-2.13 (1H, m), 0.96 (1H, dd, *J* = 14.9, 6.3 Hz), 0.47 (3H, s), -0.13 (3H, s). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 178.8, 178.1, 176.3, 175.4, 174.6, 173.6, 136.1, 135.4, 135.1, 131.7, 131.6, 131.5, 129.5, 129.2, 129.1, 129.0, 129.0, 128.7, 128.5, 126.5, 126.1, 125.9, 80.5, 52.7, 51.2, 50.3, 49.0, 45.1, 44.9, 40.7, 40.3, 35.8, 34.6, 30.5, 24.9, 10.6, -1.6, -3.9. HRMS (MALDI-TOF) calcd for $C_{44}H_{40}N_3O_7Si$: 750.2630 ($[M+H]^+$), found 750.2629 ($[M+H]^+$). m.p. 255.0-256.0 °C (recrystallized from $CHCl_3$, a colorless plate)

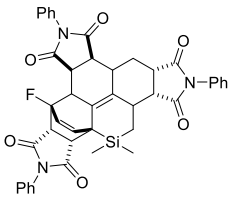


5c: Compound **5c** (95%, 0.0945 mmol, 70.9 mg) was prepared from **4c** (0.100 mmol, 23.0 mg) by a general procedure **A**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.47-7.38 (9H, m), 7.18-7.08 (6H, m), 4.74 (1H, d, *J* = 2.3 Hz), 3.69 (1H, d, *J* = 2.3 Hz), 3.49-3.42 (1H, m), 3.45 (3H, s), 3.38 (1H, t, *J* = 8.3 Hz), 3.33 (1H, d, *J* = 7.5 Hz), 3.25-3.19 (3H, m), 3.08-2.98 (1H, m), 3.00 (1H, dd, *J* = 7.5, 2.6 Hz), 2.46-2.34 (2H, m), 2.26-2.14 (2H, m), 0.96 (1H, dd, *J* = 14.6, 6.0 Hz), 0.47 (3H, s), -0.07 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 179.2, 178.5, 176.7, 175.8, 175.5, 174.2, 160.5, 137.1, 135.2, 132.2, 132.1, 132.0, 129.8, 129.6, 129.3, 129.2, 129.0, 128.9, 126.7, 126.6, 126.5, 93.6, 54.9, 50.7, 49.0, 46.2, 45.6, 45.3, 43.6, 40.9, 40.8, 35.5, 34.9, 30.0, 25.5, 11.0, -1.6, -3.1. HRMS(MALDI-TOF) calcd for $C_{44}H_{40}N_3O_7Si$: 750.2630 ($[M+H]^+$), found 750.2639 ($[M+H]^+$). m.p. 228.0-229.0 °C (recrystallized from $CHCl_3$, a colorless column)

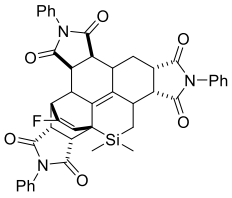


5d:Compound **5d** (64%, 0.0652 mmol, 48.1 mg) was prepared from **4d** (0.100 mmol, 23.0 mg) by a general procedure **A**. ^{1}H-NMR (DMSO-D_6, 400 MHz) δ: 7.52-7.43 (7H, m), 7.43-7.36 (2H, m), 7.21 (2H, d, *J* = 7.8 Hz), 7.09 (2H, d, *J* = 7.8 Hz), 6.99 (2H, d, *J* = 7.8 Hz), 4.84 (1H, d, *J* = 7.3 Hz), 3.49-3.42 (2H, m), 3.39 (3H, s), 3.38-3.37 (1H, m), 3.33-3.31 (1H, m), 3.25 (1H, dd, *J* = 9.2, 5.0 Hz), 3.17 (1H, d, *J* = 7.3 Hz), 3.08 (1H, dd, *J* = 7.3, 2.4 Hz), 2.95 (1H, td, *J* = 13.7, 6.4 Hz), 2.92-2.84 (1H, m), 2.60-2.56 (1H, m), 2.21 (1H, d, *J* = 13.7 Hz), 2.10-2.07 (1H, m), 1.95 (1H, dd, *J* = 14.0, 12.3 Hz), 0.78 (1H, dd, *J* = 14.0, 5.5 Hz), 0.38 (3H, s), -0.04 (3H, s). ^{13}C-NMR (DMSO-D_6, 100 MHz) δ: 179.2, 178.5, 177.4, 176.8, 176.7, 175.2, 157.8, 135.9, 135.7, 132.5, 132.4, 129.0, 128.9, 128.9, 128.5, 128.5, 128.3, 127.4, 127.2, 127.0, 95.7, 54.9, 49.5, 48.9, 45.6, 45.2, 44.6, 43.5, 36.1, 35.2, 34.7, 34.5, 24.9, 11.1, -1.0, -2.3. HRMS (MALDI-TOF) calcd for $C_{44}H_{39}N_3O_7Si$: 749.2552 (M^+), found 749.2559 (M^+). m.p. >300 °C (recrystallized from

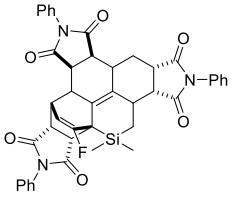
$CHCl_3$, a colorless column)



5e: Compound **5e** (48%, 0.0479 mmol, 35.3 mg) was prepared from **4e** (0.100 mmol, 21.8 mg) by a general procedure **A.** ^{1}H-NMR (DMSO-D_6, 500 MHz) δ: 7.52-7.36 (9H, m), 7.28-7.27 (2H, m), 7.13-7.10 (4H, m), 6.46 (1H, dd, J = 11.7, 8.9 Hz), 6.18 (1H, dd, J = 8.9, 5.4 Hz), 3.51 (1H, t, J = 8.3 Hz), 3.45-3.42 (2H, m), 3.39-3.37 (1H, m), 3.29-3.27 (1H, m), 3.21 (1H, d, J = 8.0 Hz), 3.03-2.97 (2H, m), 2.88-2.82 (1H, m), 2.35-2.29 (1H, m), 2.11 (1H, dd, J = 11.7, 4.0 Hz), 1.98 (1H, dd, J = 14.6, 11.7 Hz), 0.90 (1H, dd, J = 14.6, 6.0 Hz), 0.32 (3H, s), -0.20 (3H, s). ^{13}C-NMR (DMSO-D_6, 125 MHz) δ: 179.1, 178.4, 177.1, 176.1, 174.6, 173.0, 135.9, 135.8, 134.8 (J = 25 Hz), 133.7 (J = 7 Hz), 132.5, 132.4, 132.2, 128.9, 128.9, 128.8, 128.6 (J = 7 Hz), 128.5, 128.2, 127.6, 127.1, 126.9, 96.0 (J =199 Hz), 51.0 (J = 17 Hz), 49.5 (J = 20 Hz), 48.9, 48.9, 45.0, 44.4, 40.8, 34.7, 34.2, 30.1, 24.5, 9.9, -2.2, -4.0. ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: -185.10. HRMS(MALDI-TOF) calcd for $C_{43}H_{36}N_3O_6FNaSi$:760.2250 ($[M+Na]^+$), found 760.2245 ($[M+Na]^+$). m.p. 226.0-227.0 °C (recrystallized from $CHCl_3$, a colorless needle)



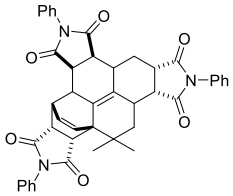
5f: Compound **5f** (40%, 0.0400 mmol, 29.5 mg) was prepared from **4f** (0.100 mmol, 21.8 mg) by a general procedure **A**. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.52-7.33 (9H, m), 7.17-7.13 (6H, m), 5.42 (1H, dd, J = 5.3, 2.5 Hz), 3.87-3.84 (1H, m), 3.49-3.45 (1H, m), 3.39 (1H, t, J = 8.5 Hz), 3.34 (1H, dd, J = 7.6, 2.1 Hz), 3.27-3.21 (3H, m), 3.13-3.10 (1H, m), 3.04-2.97 (1H, m), 2.51-2.47 (1H, m), 2.39 (1H, ddd, J = 14.2, 4.1, 1.4 Hz), 2.25-2.22 (1H, m), 2.22-2.15 (1H, m), 0.97 (1H, dd, J = 14.7, 6.0 Hz), 0.44 (3H, s), -0.20 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 179.0, 178.4, 176.5, 175.3, 174.9, 174.5, 162.6 (J = 288 Hz), 136.9, 135.4, 131.9 (J = 2 Hz), 131.7, 129.8, 129.6, 129.4, 129.3, 129.2, 128.8, 126.9, 126.4, 126.0, 104.1, 104.0, 49.6, 49.2, 46.5, 45.3 (J = 27 Hz), 43.4, 40.6, 39.1 (J = 22 Hz), 35.6, 35.0, 30.9, 30.839, 25.439, 10.9, -1.8, -3.6. ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: 98.70 (J = 12 Hz). HRMS(MALDI-TOF) calcd for $C_{43}H_{36}N_3O_6FNaSi$:760.2250 ($[M+Na]^+$), found 760.2246 ($[M+Na]^+$). m.p. 228.0-229.0 °C (recrystallized from $CHCl_3$, a colorless column)



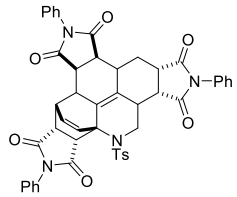
5g: Compound **5g** (60%, 0.0603 mmol, 44.5mg) was prepared from **4g** (0.100 mmol, 21.8 mg) by a general procedure **A.** ^{1}H-NMR (DMSO-D_6, 300 MHz) δ: 7.48-7.43 (9H, m), 7.23-7.21 (2H, m), 7.11-7.07 (4H, m), 5.56 (1H, t, J = 6.7 Hz), 3.62-3.57 (1H, m), 3.47-3.38 (3H, m), 3.30-3.24 (2H, m), 3.20-3.16 (1H, m), 2.98 (1H, td, J = 14.1, 6.5 Hz), 2.93-2.84 (1H, m), 2.69-2.63 (1H, m), 2.28-2.08 (2H, m), 1.99 (1H, t, J = 14.1 Hz), 0.88 (1H, dd, J = 14.1, 5.1 Hz), 0.39 (3H, s), -0.10 (3H, s). ^{13}C-NMR (DMSO-D_6, 100 MHz) δ: 179.2, 178.5, 177.4, 177.0, 176.3, 175.0, 160.8 (J = 271 Hz), 136.4, 134.8 (J = 3 Hz), 132.4, 132.3, 132.2, 129.0, 129.0, 128.9, 128.5,

128.4, 127.5, 127.0, 126.7, 105.7, 105.6, 50.0, 48.1, 45.6, 44.8, 44.4, 43.4, 35.5 (J = 5 Hz), 35.3, 34.9, 34.9, 34.3, 24.7, 10.2, -1.4, -3.3 (J = 7 Hz)

^{19}F-NMR ($CDCl_3$, 376 MHz) δ: -101.85. HRMS(MALDI-TOF) calcd for $C_{43}H_{37}N_3O_6FSi$:738.2430 (M^+), found 738.2430 (M^+). m.p. 242.0-243.0 °C (recrystallized from $CHCl_3$, a colorless needle)



5h: Compound **5h** (59%, 0.0593 mmol, 41.7 mg) was prepared from **4h** (0.100 mmol, 18.4 mg) by a general procedure **A**. ^{1}H-NMR (DMSO-D_6, 400 MHz) δ: 7.52-7.35 (9H, m), 7.22-7.19 (2H, m), 7.11-7.06 (4H, m), 6.35 (1H, d, J = 8.2 Hz), 6.14 (1H, dd, J = 8.2, 6.2 Hz), 3.53-3.46 (2H, m), 3.44-3.39 (2H, m), 3.31-3.27 (2H, m), 3.15 (1H, d, J = 7.8 Hz), 2.95 (1H, td, J = 13.3, 5.5 Hz), 2.75-2.65 (3H, m), 2.29-2.14 (2H, m), 1.43 (1H, d, J = 7.8 Hz), 1.29 (3H, s), 0.81 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 178.8, 177.6, 176.6, 175.8, 175.6, 174.4, 135.8, 132.8, 132.7, 132.7, 131.9, 131.6, 131.5, 129.4, 129.2, 129.1, 128.9, 128.7, 128.7, 126.6, 126.2, 126.1, 49.7, 49.6, 48.5, 44.8, 44.6, 43.6, 41.1, 40.3, 35.6, 35.1, 34.7, 33.7, 31.9, 28.6, 26.7, 24.3. HRMS(MALDI-TOF) calcd for $C_{44}H_{37}N_3O_6Na$:726.2575 ([M+Na]$^+$), found 726.2573 ([M+Na]$^+$). m.p. 251.0-252.0 °C (recrystallized from $CHCl_3$, a colorless needle)



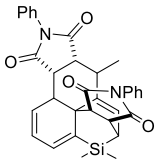
5i: Compound **5i** (49%, 0.0485 mmol, 40.3 mg) was prepared from **4i** (0.100 mmol, 31.1 mg) by a general procedure **A**. ^{1}H-NMR (DMSO-D_6, 400 MHz) δ: 7.54-7.37 (11H, m), 7.28 (2H, d, J = 7.3 Hz), 7.21 (2H, d, J = 7.3 Hz), 7.01 (2H, d, J = 8.2 Hz), 6.92 (2H, dd, J = 6.4, 3.0 Hz), 6.76 (1H, d, J = 8.8 Hz), 6.04 (1H, dd, J = 8.8, 6.4 Hz), 4.35 (1H, dd, J = 15.0, 5.5 Hz), 4.22 (1H, dd, J = 11.0, 15.0 Hz), 3.61-3.59 (1H, m), 3.56-3.45 (5H, m), 3.27 (1H, d, J = 8.2 Hz), 2.93-2.91 (2H, m), 2.90-2.80 (1H, m), 2.41-2.33 (1H, m), 2.20-2.15 (1H, m), 2.15 (3H, s). ^{13}C-NMR (DMSO-D_6, 100 MHz) δ: 178.9, 177.5, 177.0, 176.7, 176.1, 172.8, 142.4, 140.8, 134.0, 132.3, 132.3, 132.0, 130.2, 129.8, 129.0, 128.9, 128.8, 128.6, 128.3, 128.3, 127.4, 126.7, 126.7, 125.2, 63.4, 46.8, 45.9, 44.6, 43.4, 42.3, 40.2, 39.0, 33.5, 31.2, 31.0, 23.9, 20.9. HRMS(MALDI-TOF) calcd for $C_{48}H_{38}N_4O_8NaS$: 853.2303 ([M+Na]$^+$), found 853.2298 ([M+Na]$^+$). m.p. 222.0-223.0 °C (recrystallized from $CHCl_3$, a colorless column)

Double Diels-Alder reaction

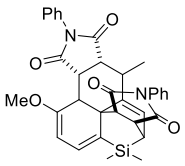
general procedure **B**

To a solution of **4** in toluene (0.2 M) was added Grubbs II (1 mol%) and the mixture was stirred at room temperature for 2 h. Then $RuHCl(CO)(PPh_3)_3$ (5 mol%) was added to the mixture and the mixture was refluxed for 3 h. *N*-phenyl maleimide(5.0 eq.) was added to the

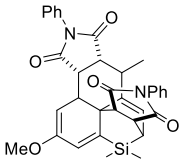
reaction mixture and the mixture was refluxed for 3 h. The solvent was evaporated and the residue was subjected to column chromatography(*n*-hexane/AcOEt = 2/1) on neutral flash silica gel to give **6**.



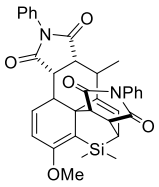
6a: Compound **6a** (82%, 0.0820 mmol, 44.8 mg) was prepared from **4a** (0.100 mmol, 20.0 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.48-7.28 (6H, m), 7.19-7.16 (2H, m), 7.11-7.07 (2H, m), 6.50-6.43 (2H, m), 6.40-6.34 (1H, m), 6.12 (1H, dd, *J* = 8.3, 2.4 Hz), 4.27 (1H, t, *J* = 6.4 Hz), 3.31-3.28 (1H, m), 3.23-3.19 (2H, m), 2.96 (1H, d, *J* = 8.3 Hz), 2.76-2.70 (1H, m), 2.66 (1H, d, *J* = 8.3 Hz), 1.54 (3H, d, *J* = 2.8 Hz), 0.25 (3H, s), -0.26 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 179.0, 176.3, 175.7, 174.9, 138.2, 137.7, 136.4, 132.0, 131.8, 129.2, 128.8, 128.7, 128.0, 128.4, 127.4, 126.5, 125.5, 123.7, 48.7, 45.2, 44.3, 41.6, 40.4, 32.5, 32.5, 28.4, 15.2, -2.7, -4.2. HRMS (MALDI-TOF) calcd for $C_{33}H_{31}N_2O_4Si$: 547.2048 ($[M+H]^+$), found 547.2043 ($[M+H]^+$). m.p. 281.5-282.0 °C (recrystallized from $CHCl_3$, a colorless column).



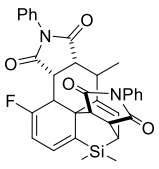
6b: Compound **6b** (95%, 0.0953 mmol, 55.0 mg) was prepared from **4b** (0.100 mmol, 23.0 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.45-7.36 (6H, m), 7.32-7.29 (1H, m), 7.19-7.16 (2H, m), 7.12-7.09 (2H, m), 6.44 (1H, d, *J* = 6.3 Hz), 6.10 (1H, dd, *J* = 8.0, 2.3 Hz), 5.53 (1H, d, *J* = 6.3 Hz), 4.25 (1H, d, *J* = 8.0 Hz), 3.80 (3H, s), 3.39 (1H, dd, *J* = 9.7, 8.0 Hz), 3.34 (1H, d, *J* = 8.0 Hz), 3.25 (1H, dd, *J* = 9.7, 4.6 Hz), 2.93 (1H, d, *J* = 8.0 Hz), 2.72-2.67 (1H, m), 2.63 (1H, d, *J* = 8.0 Hz), 1.53 (3H, d, *J* = 6.9 Hz), 0.24 (3H, s), -0.26 (3H, s). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 179.2, 176.5, 175.9, 174.6, 159.8, 138.3, 136.9, 132.0, 131.8, 129.2, 128.7, 128.0, 126.5, 126.5, 125.6, 123.6, 97.2, 55.5, 48.6, 47.5, 44.2, 40.8, 40.6, 37.7, 32.5, 28.6, 15.1, -2.4, -4.2. HRMS (MALDI-TOF) calcd for $C_{33}H_{32}N_2O_5NaSi$: 599.1973 ($[M+Na]^+$), found 599.1981 ($[M+Na]^+$). m.p. 237.0-238.0 °C (recrystallized from $CHCl_3$, a colorless needle)



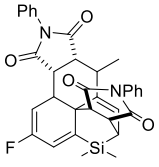
6c: Compound **6c** (quant, 0.100 mmol, 57.6 mg) was prepared from **4c** (0.100 mmol, 23.0 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 500 Hz) δ: 7.45 (2H, dd, *J* = 7.7, 7.7 Hz), 7.40-7.37 (3H, m), 7.30 (1H, dd, *J* = 7.4, 7.4 Hz), 7.17 (2H, d, *J* = 7.4 Hz), 7.10 (2H, d, *J* = 7.4 Hz), 6.29 (1H, d, *J* = 2.3 Hz), 6.11 (1H, dd, *J* = 8.6, 2.3 Hz), 5.15 (1H, dd, *J* = 6.9, 2.3 Hz), 4.35 (1H, t, *J* = 7.2 Hz), 3.75 (3H, s), 3.39 (1H, d, *J* = 8.6 Hz), 3.24-3.16 (2H, m), 2.97 (1H, d, *J* = 8.6 Hz), 2.77-2.73 (1H, m), 2.66 (1H, d, *J* = 8.6 Hz), 1.54 (3H, d, *J* = 6.9 Hz), 0.27 (3H, s), -0.25 (3H, s). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 178.9, 176.2, 175.8, 175.3, 154.6, 140.5, 138.7, 135.8, 132.1, 131.8, 129.2, 128.8, 128.7, 127.9, 126.5, 125.5, 123.6, 92.9, 54.7, 48.7, 46.0, 44.3, 42.7, 40.3, 32.6, 32.5, 28.5, 15.1, -2.9, -4.3. HRMS (MALDI-TOF) calcd for $C_{34}H_{33}N_2O_5Si$: 577.2153 ($[M+H]^+$), found 577.2156 ($[M+H]^+$). m.p. 226.0-227.0 °C (recrystallized from $CHCl_3$, a colorless needle)



6d: Compound **6d** (85%, 0.0850 mmol, 49.0 mg) was prepared from **4d** (0.100 mmol, 23.0 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.47-7.32 (6H, m), 7.17-7.15 (2H, m), 7.11-7.07 (2H, m), 6.62 (1H, d, *J* = 10.0 Hz), 6.54 (1H, dd, *J* = 10.0, 6.2 Hz), 6.10 (1H, dd, *J* = 8.3, 2.4 Hz), 4.22 (1H, t, *J* = 6.7 Hz), 3.71 (3H, s), 3.27-3.20 (2H, m), 3.13 (1H, dd, *J* = 9.8, 7.0 Hz), 2.99 (1H, dd, *J* = 8.3, 0.7 Hz), 2.74-2.68 (1H, m), 2.57 (1H, d, *J* = 8.3 Hz), 1.52 (3H, d, *J* = 6.9 Hz), 0.32 (3H, s), -0.21 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 179.4, 176.4, 175.8, 161.8, 138.1, 132.1, 132.0, 130.6, 129.3, 128.8, 128.8, 128.3, 126.5, 124.4, 123.1, 107.9, 55.7, 48.8, 46.2 44.4, 41.1, 40.8, 33.3, 32.7, 29.1, 15.2, -2.1, -3.9. HRMS (MALDI-TOF) calcd for $C_{34}H_{32}N_2O_5NaSi$: 599.1973 ($[M+Na]^+$), found 599.1970 ($[M+Na]^+$). m.p. 226.0-227.0 °C (recrystallized from $CHCl_3$, a colorless column)

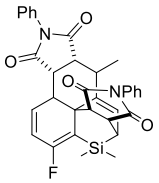


6e: Compound **6e** (59%, 0.0591 mmol, 49.0 mg) was prepared from **4e** (0.100 mmol, 21.8 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.47-7.37 (5H, m), 7.33-7.30 (1H, m), 7.19-7.15 (2H, m), 7.11-7.07 (2H, m), 6.39 (1H, dd, *J* = 6.9, 6.0 Hz), 6.14 (1H, dd, *J* = 8.2, 1.8 Hz), 6.04 (1H, dd, *J* = 11.0, 6.4 Hz), 4.44 (1H, dd, *J* = 12.6, 7.7 Hz), 3.40 (1H, dd, *J* = 10.1, 7.7 Hz), 3.33 (1H, d, *J* = 8.2 Hz), 3.27 (1H, dd, *J* = 9.8, 4.8 Hz), 2.96 (1H, d, *J* = 8.2 Hz), 2.69-2.65 (1H, m), 2.67 (1H, d, *J* = 8.2 Hz), 1.54 (3H, d, *J* = 6.9 Hz), 0.25 (3H, s), -0.25 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 178.7, 176.1, 175.5, 173.9, 162.3 (*J* = 255 Hz), 137.1 (*J* = 3 Hz), 134.8 (*J* = 8 Hz), 132.7 (*J* = 5 Hz), 131.7 (*J* = 18 Hz), 129.2, 128.9, 128.7, 128.1, 126.4, 125.5, 124.3, 105.1, 105.0, 49.0, 48.8 (*J* = 6 Hz), 43.7, 40.4, 39.8 (*J* = 4 Hz), 35.3 (*J* = 23.8 Hz), 32.6, 28.5, 15.1, -2.7, -4.3. ^{19}F-NMR ($CDCl_3$, 470 MHz) δ: -107.48. HRMS (MALDI-TOF) calcd for $C_{33}H_{29}N_2O_4FNaSi$: 587.1773 ($[M+Na]^+$), found 587.1768 ($[M+Na]^+$). m.p. 299.0-300 °C (recrystallized from $CHCl_3$, a colorless needle)

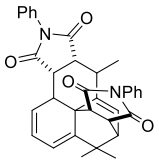


6f: Compound **6f** (51%, 0.0512 mmol, 28.9 mg) was prepared from **4f** (0.100 mmol, 21.8 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.48-7.38 (5H, m), 7.34-7.27 (1H, m), 7.17 (2H, d, *J* = 7.6 Hz), 7.09 (2H, d, *J* = 7.2 Hz), 6.36 (1H, dd, *J* = 6.5, 2.1 Hz), 6.15 (1H, dd, *J* = 8.3, 2.1 Hz), 5.74 (1H, ddd, *J* = 11.0, 6.5, 2.4 Hz), 4.43-4.37 (1H, m), 3.38 (1H, d, *J* = 8.3 Hz), 3.27-3.20 (2H, m), 2.99 (1H, d, *J* = 8.3 Hz), 2.75-2.68 (1H, m), 2.70 (1H, d, *J* = 8.3 Hz), 1.55 (3H, d, *J* = 6.9 Hz), 0.29 (3H, s), -0.23 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 178.5, 175.8, 175.5, 174.8, 158.1 (*J* = 254 Hz), 143.7 (*J* = 6 Hz), 137.8, 131.9 (*J* = 32 Hz), 131.7 (*J* = 20 Hz), 129.3, 128.9, 128.7, 128.1, 126.4, 125.4, 124.1, 102.0, 101.8, 48.6, 45.8, 43.9, 41.8 (*J* = 4 Hz), 40.2, 32.5, 32.2 (*J* = 7 Hz), 28.4, 15.1, -3.0, -4.4. HRMS (MALDI-TOF) calcd for $C_{33}H_{29}N_2O_4FNaSi$: 587.1773 ($[M+Na]^+$), found 587.1774 ($[M+Na]^+$). ^{19}F-NMR ($CDCl_3$, 470 MHz) δ: -121.01. Anal. calcd for

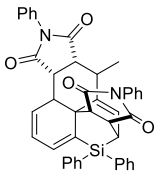
$C_{33}H_{29}N_2O_4FSi$: C, 70.19; H, 5.18; N, 4.96, found: C, 69.90; H, 5.25; N, 4.97. m.p. 241.0-242.0 °C (recrystallized from $CHCl_3$, column)



6g: Compound **6g** (55%, 0.0552 mmol, 31.2 mg) was prepared from **4g** (0.100 mmol, 21.8 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.48-7.29 (7H, m), 7.17-7.13 (2H, m), 7.11-7.07 (2H, m), 6.53 (1H, ddd, J = 10.0, 6.5, 6.5 Hz), 6.37 (1H, dd, J = 10.0, 5.5 Hz), 6.12 (1H, dd, J = 8.3, 2.4 Hz), 4.31 (1H, t, J = 6.7 Hz), 3.30 (1H, d, J = 8.3 Hz), 3.26 (1H, dd, J = 9.9, 4.5 Hz), 3.18 (1H, dd, J = 9.9, 7.1 Hz), 3.03 (1H, d, J = 8.3 Hz), 2.74-2.70 (1H, m), 2.64 (1H, d, J = 8.3 Hz), 1.54 (3H, d, J = 6.9 Hz), 0.39 (3H, d, J = 1.4 Hz), -0.24 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 178.6, 175.9, 175.4, 174.9, 165.0 (J = 250 Hz), 137.8, 132.1 (J = 10 Hz), 131.7, 131.7, 129.0 (J = 39 Hz), 128.8, 128.1, 126.4, 125.7, 124.2, 123.9 (J = 39 Hz), 109.3, 109.0, 48.5 (J = 3.8 Hz), 46.0 (J = 12.4 Hz), 44.2, 41.3, 40.3, 33.4, 32.6, 28.4, 15.1, -3.0, -4.5 (J = 3 Hz). ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: -100.45. HRMS (MALDI-TOF) calcd for $C_{33}H_{29}N_2O_4FNaSi$: 587.1773 ($[M+Na]^+$), found 587.1771 ($[M+Na]^+$). Anal. calcd for $C_{33}H_{29}N_2O_4FSi$: C, 70.19; H, 5.18; N, 4.96, found: C, 70.25; H, 5.33; N, 5.05. m.p. 287.0-288.0 °C (recrystallized from $CHCl_3$, a colorless column)

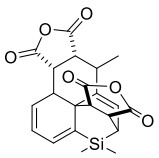


6h: Compound **6h** (62%, 0.0616 mmol, 32.7 mg) was prepared from **4h** (0.100 mmol, 18.4 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.45 (2H, dd, J = 7.7, 7.7 Hz), 7.38 (3H, dd, J = 7.7, 7.7 Hz), 7.29 (1H, dd, J = 7.4, 7.4 Hz), 7.18 (2H, d, J = 8.3 Hz), 7.08 (2H, d, J = 8.3 Hz), 6.38 (1H, dd, J = 9.4, 5.7 Hz), 6.20 (1H, dd, J = 6.9, 2.3 Hz), 6.08 (1H, dd, J = 9.4, 6.3 Hz), 5.92 (1H, d, J = 6.3 Hz), 4.20 (1H, t, J = 6.6 Hz), 3.24-3.21 (3H, m), 3.13 (1H, d, J = 7.4 Hz), 3.00 (1H, dd, J = 6.6, 2.6 Hz), 2.75-2.72 (1H, m), 1.54 (3H, d, J = 6.8 Hz), 1.26 (3H, s), 0.76 (3H, s). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ:178.0, 175.8,175.6, 174.4, 145.9, 138.9, 131.8, 131.7, 129.3, 128.8, 128.7, 128.0, 126.9, 126.3, 125.7, 124.9, 122.0, 119.6, 47.2, 45.5, 45.3, 44.2, 41.8, 41.1, 40.2, 33.1, 32.1, 28.7, 27.8, 14.6. HRMS (MALDI-TOF) calcd for $C_{34}H_{30}N_2O_4Na$: 553.2098 ($[M+Na]^+$), found 553.2108 ($[M+Na]^+$). m.p. 267.0-268.0 °C (recrystallized from $CHCl_3$, a colorless needle)



6j: Compound **6j** (61%, 0.0605 mmol, 40.6 mg) was prepared from **4j** (0.100 mmol, 32.5 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.49-7.42 (6H, m), 7.41-7.36 (3H, m), 7.30-7.25 (2H, m), 7.21-7.16 (4H, m), 7.10 (2H, d, J = 7.3 Hz), 6.91 (2H, dd, J = 7.3, 7.3 Hz), 6.80-6.76 (3H, m), 6.60 (1H, dd, J = 9.3, 5.1 Hz), 6.50 (1H, dd, J = 9.3, 6.4 Hz), 6.42 (1H, d, J = 8.2 Hz), 4.38 (1H, t, J = 6.9 Hz), 3.48 (1H, d, J = 8.7 Hz), 3.24-3.13 (4H, m), 2.73-2.68 (1H, m), 1.53 (3H, d, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 178.6, 175.9, 174.9, 174.6, 139.1, 138.9, 135.9, 135.4, 133.8, 132.2, 131.9, 131.8, 130.4, 130.3, 129.9, 129.3, 128.8, 128.4, 128.4, 128.2, 127.8, 127.4, 126.9, 126.4,

125.4, 124.4, 48.9, 45.8, 43.9, 41.4, 40.6, 32.7, 32.6, 27.6, 15.3. HRMS (MALDI-TOF) calcd for $C_{43}H_{34}N_2O_4NaSi$: 693.2180 ($[M+Na]^+$), found 693.2185 ($[M+Na]^+$). m.p. 281.0-282.0 °C (recrystallized from $CHCl_3$, a colorless needle)



6k: Compound **6k** (71%, 0.0711 mmol, 28.2 mg) was prepared from **4a** (0.100 mmol, 20.0 mg) by a general procedure **B**. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 6.46 (1H, dd, *J* = 9.6, 5.2 Hz), 6.38 (1H, dd, *J* = 5.2, 1.6 Hz), 6.24 (1H, ddd, *J* = 9.6, 6.6, 1.6 Hz), 6.22 (1H, dd, *J* = 8.3, 2.4 Hz), 3.98 (1H, t, *J* = 6.6 Hz), 3.39 (1H, d, *J* = 10.0 Hz), 3.38-3.25 (3H, m), 3.07 (1H, dd, *J* = 8.8, 1.1 Hz), 2.71-2.64 (1H, m), 2.66 (1H, dd, *J* = 8.1, 1.1 Hz), 1.48 (3H, d, *J* = 6.9 Hz), 0.24 (3H, s), 0.12 (3H, s). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 174.0, 171.2, 171.1, 170.5, 138.1, 137.6, 135.7, 128.4, 125.8, 125.7, 49.9, 45.2, 44.7, 41.0, 40.9, 32.2, 32.2, 28.6, 14.7, -3.1, -4.1. HRMS (MALDI-TOF) calcd for $C_{21}H_{20}O_6NaSi$: 419.0929 ($[M+Na]^+$), found 419.0921 ($[M+Na]^+$). m.p. 281.0-282.0 °C (recrystallized from $CHCl_3$, a colorless column)

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxx. Spectral data for all new compounds, computational details and x-ray crystallographic analysis data .

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8. Computational details and citations are given in the Supporting Information. B3LYP/6-31G* gives activation energies that are about 5 kcal/mol too high and reaction energies about 10 kcal/mol too endergonic. We calculated the stereoisomers which might be more stable due to the steric repulsion.

9. See also a) Domingo, L. R.; Ríos-Gutiérrez, M.; Silvi, B.; Pérez, P. The Mysticism of Pericyclic Reactions: A Contemporary Rationalisation of Organic Reactivity Based on Electron Density Analysis. *Eur. J. Org. Chem.* **2018**, 1107 - 1120. b) Domingo, L. R.; Sáez, J. A. Understanding the Mechanism of Polar Diels–Alder Reactions. *Org. Biomol. Chem.* **2009**, *7*, 3576 – 3583. c) Domingo, L. R.; Ríos-Gutiérrez, M.; Pérez, P. Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity. *Molecules* **2016**, *21*, 748.

10. The experimental results can be explained in terms of the P-DA mechanism. Due to the electrophilic character of N-phenylmaleimida, these P-DA reactions are favored with the increase of the nucleophilic character of the diene. See reference 8b.

11. CCDC 1831909

12. CCDC 1831910

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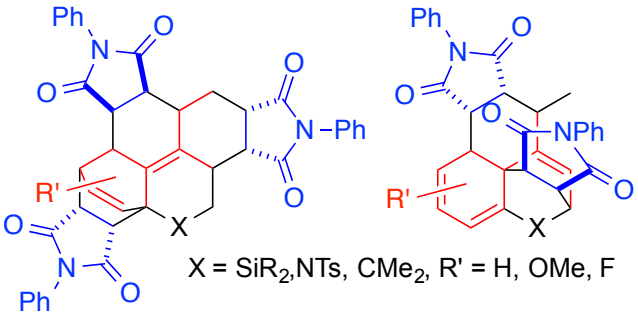

X = SiR_2,NTs, CMe_2, R' = H, OMe, F

via Domino Diels-Alder Reactions of Styrene