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Novel synthesis of tetrahydro-2(1*H*)-quinolones using Diels–Alder reactions of 1-arylsulfonyl-2(1*H*)-pyridones having an electron-withdrawing group

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Abstract—A novel synthetic methodology of preparing tetrahydro-2(1*H*)-quinolones by Diels–Alder reactions between 2-methyl- and 2,3-dimethyl-1,3-butadienes and 1-arylsulfonyl-2(1*H*)-pyridones having an electron-withdrawing group at the 5-position is presented. Furthermore, the site-selectivity analyses based on MO calculations of the 5-substituted 2(1*H*)-pyridones acting as the dienophiles are described.

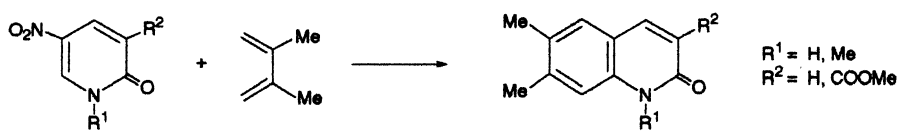
1. Introduction

There have been many reports describing the Diels–Alder (DA) reactions of 2(1*H*)-pyridones, which are aromatic, as dienes.[1] In contrast, we have previously reported on the DA reactions of 2(1*H*)-pyridones that have an electron-withdrawing group at the 4- or 6-position, acting as dienophiles, to give tetrahydro-1(2*H*)-isoquinolones.[2] To the best of our knowledge, there are not many reports on the syntheses of tetrahydro-2(1*H*)-quinolones using DA reactions of 2(1*H*)-pyridones. Recently, we have reported on the DA reactions of 1-methyl-5-nitro-2(1*H*)-pyridones to yield the aromatic 2(1*H*)-quinolones in 22–30% yields (Scheme 1).[3] From these results, we can assume that 2(1*H*)-pyridones that have two electron-withdrawing groups, at the 1- and 5-positions, would have higher reactivities as dienophiles than 2(1*H*)-pyridones with one group at the 5-position, since the additional electron-withdrawing group at the 1-position may actually decrease the delocalization of the unshared electrons on the nitrogen atom, and thus enhance the dienophilic character of the pyridone ring. Herein, we wish to report a novel method of preparing tetrahydro-2(1*H*)-quinolones by DA reactions between the 1-arylsulfonyl-2(1*H*)-pyridones having an electron-withdrawing group at the 5-position and a diene,[4] and examinations of the site-selectivity of 1,5-substituted 2(1*H*)-pyridones in terms of activation energy (E_a) using ab initio MO calculations.

2. Results and discussion

2.1. Arylsulfonylations of 2(1*H*)-pyridones

The reactions of 2(1*H*)-pyridones **1a**–**d** with arylsulfonyl chlorides **2a**–**h** (1.5 equiv.) using NaH (1.5 equiv.) as a base in THF were carried out at 30 or 60°C for 5 h, to yield the desired 1-arylsulfonyl-2(1*H*)-pyridones **3a**–**k** and 2-arylsulfonyloxypyridines **4i**,**j**, as shown in Table 1 and Scheme 2. Results showed that the yields of **3a** (94%), **3b** (60%), and **3c** (57%) from the reactions of 5-methoxycarbonyl-, 5-acetyl-, and 5-nitro-2(1*H*)-pyridones **1a**–**c**, with *p*-tosyl chloride **2a** decreased in the order of the electron-attracting properties of the R^1 substituents of **1** (entries 1–3).[5] The reactions of **1a** with 4-methoxy-, 4-chloro-, 2-methyl-, and unsubstituted (R^1=R^2=R^3=H)



Scheme 1.

Keywords: 1-arylsulfonyl-2(1*H*)-pyridone; tetrahydro-2(1*H*)-quinolone; Diels–Alder reaction; MO calculation.
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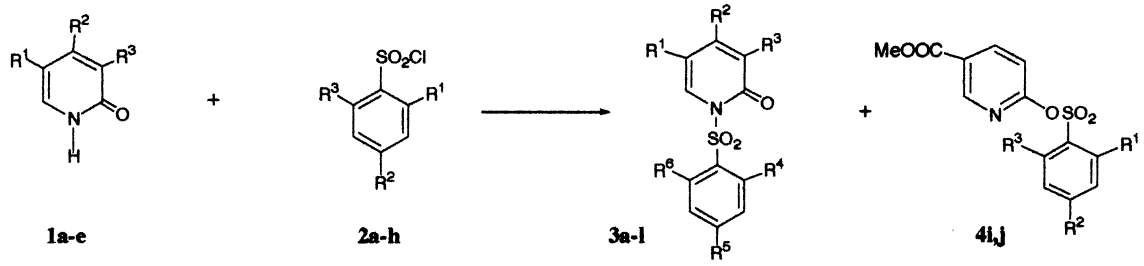
Table 1. Reactions of 2(1*H*)-pyridones **1a**–**e** with arylsulfonyl chlorides **2a**–**h** in the presence of NaH in THF

Entry	Compound **1**	Compound **2**	Temperature (°C)	Time (h)	Pyridone **3**	Yield (%)	Product **4**	Yield (%)
1	**a**	**a**	30	5	**a**	94		
2	**b**	**a**	60	5	**b**	60		
3	**c**	**a**	60	5	**c**	57		
4	**a**	**b**	60	5	**d**	91		
5	**a**	**c**	60	5	**e**	93		
6	**a**	**d**	60	5	**f**	43		
7	**a**	**e**	60	5	**g**	92		
8	**a**	**f**	30	5	**h**	90		
9	**a**	**g**	30	5	**i**	33	**i**	33
10	**a**	**h**	30	5	**j**	34	**j**	64
11	**d**	**a**	30	5	**k**	82		
12	**e**	**a**	30	5	**l**	69		



1a-e **2a-h** **3a-l** **4i,j**

1a : R^1 = COOMe; R^2 = R^3 = H
1b : R^1 = COMe; R^2 = R^3 = H
1c : R^1 = NO_2; R^2 = R^3 = H
1d : R^1 = COOMe; R^3 = Br; R^2 = H
1e : R^2 = COOMe; R^1 = R^3 = H

2a : R^2 = Me; R^1 = R^3 = H
2b : R^2 = OMe; R^1 = R^3 = H
2c : R^2 = Cl; R^1 = R^3 = H
2d : R^2 = NO_2; R^1 = R^3 = H
2e : R^1 = R^2 = R^3 = H
2f : R^1 = Me; R^2 = R^3 = H
2g : R^1 = R^2 = R^3 = Me
2h : R^1 = R^2 = R^3 = i-Pr

4i : R^1 = R^2 = R^3 = Me
4j : R^1 = R^2 = R^3 = *i*-Pr

3a : R^1 = COOMe; R^5 = Me; R^2 = R^3 = R^4 = R^6 = H
3b : R^1 = COMe; R^5 = Me; R^2 = R^3 = R^5 = H
3c : R^1 = NO_2; R^5 = Me; R^2 = R^3 = R^5 = H
3d : R^1 = COOMe; R^5 = OMe; R^2 = R^3 = R^4 = R^6 = H
3e : R^1 = COOMe; R^5 = Cl; R^2 = R^3 = R^4 = R^6 = H
3f : R^1 = COOMe; R^5 = NO_2; R^2 = R^3 = R^4 = R^6 = H
3g : R^1 = COOMe; R^2 = R^3 = R^4 = R^5 = R^6 = H
3h : R^1 = COOMe; R^4 = Me; R^2 = R^3 = R^4 = R^6 = H
3i : R^1 = COOMe; R^4 = R^5 = R^6 = Me; R^2 = R^3 = H
3j : R^1 = COOMe; R^4 = R^5 = R^6 = *i*-Pr; R^2 = R^3 = H
3k : R^1 = COOMe; R^3 = Br; R^5 = Me; R^2 = R^4 = R^6 = H
3l : R^2 = COOMe; R^5 = Me; R^1 = R^3 = R^4 = R^6 = H

Scheme 2.

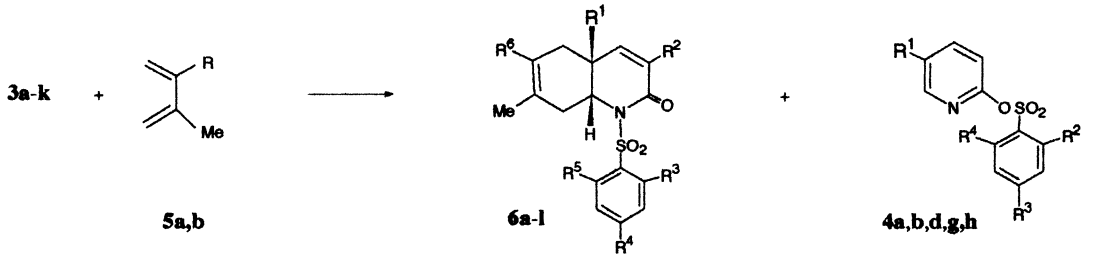
benzenesulfonyl chlorides **2b**,**c**,**f**,**e** afforded **3d** (91%), **3e** (93%), **3h** (90%), and **3g** (92%) in excellent yields (entries 4, 5, 8, and 7), whereas the reactions with 4-nitro-, 2,4,6-trimethyl-, and 2,4,6-triisopropylbenzene-sulfonyl chlorides (**2d**,**g**,**h**) afforded **3f** (43%), mixture of **3i** (33%) and **4i** (33%), and mixture of **3j** (34%) and **4j** (64%) in moderate to good total yields (entries 6,9, and 10). The reaction of **1d** (3-brominated **1a**) with **2a** gave **3k** (82%) in a high yield (entry 11). The reaction of 2(1*H*)-pyridones **1e**, which has an electron-withdrawing group at the 4-position, with **2a** gave 1-arylsulfonyl-2(1*H*)-pyridone **3l** in 69% yield (entry 12). These results indicate that arylsulfonyl chlorides bearing an electron-releasing group afford 1-arylsulfonyl-pyridones in higher yields than those bearing an electron-withdrawing group at the 4-position or alkyl groups at the 2,6-positions. Furthermore, a bromo substituent (R^3) at the 3-position on the pyridone ring of **1** was also found to be effective in providing good yield of **3k** (82%, entry 11).

2.2. DA reactions

DA reactions of **3a**–**k** with 2,3-dimethyl-1,3-butadiene **5a** (5 equiv.) in *o*-xylene were carried out at 120–180°C for 2 days in a sealed tube to afford the desired tetrahydro-2(1*H*)-quinolones **6a**–**k** stereoselectively, and in some cases, the undesired 2-sulfonyloxypyridines **4a**,**b**,**d**,**g**,**h**, as shown in Table 2 and Scheme 3. The DA reactions of **3a**–**c** with **5a** afforded nearly identical yields [**6a** (46%), **6b** (43%), and **6c** (39%); entries 1–3], differences in the reactivities of **3a** and **3b** appear insignificant. The reactions of **3g**,**i**,**k** with **5a** gave **6g** (67%), **6i** (70%), and **6k** (81%), respectively (entries 7, 9, and 11) in satisfactory yields, whereas the reactions of **3d**–**f**,**h**,**j** produced **6d** (52%), **6e** (43%), **6f** (43%), **6h** (46%), and **6j** (53%) in moderate yields (entries 4–6, 8, and 10). In some cases, we were also able to isolate the corresponding byproducts, **4a**,**b**,**d**,**g**,**h** (entries 1, 2, 4, 7, and 8). Subsequently, the DA reaction between **3k** and **5a**, which afforded the adduct with the highest yield, as described above, was further studied using an unsymmetrical diene. The reaction of **3k** with 2-methyl-1,3-butadiene **5b** afforded the regio- and stereoselectively desired tetrahydro-2(1*H*)-quinolone **6l** in 35% yield. From these results, we presume that steric influences of the substituents at the nitrogen and at the 3-position of the pyridone ring of **3** play important roles in slowing down the migration. In view of the report by Afarinkia et al.[6] **4a**,**b**,**d**,**g**, and **h** seem to be the

Table 2. Diels–Alder reactions of 1-arylsulfonylpyridones **3a**–**k** with dienes **5a**,**b** in *o*-xylene

Entry	Pyridone **3**	Temperature (°C)	Time (d)	Adduct **6**	Yield (%)	Product **4**	Yield (%)
1	**a**	180	2	**a**	46	**a**	43
2	**b**	180	2	**b**	43	**b**	48
3	**c**	120	2	**c**	39		
4	**d**	180	2	**d**	52	**d**	35
5	**e**	140	2	**e**	43		
6	**f**	140	2	**f**	43		
7	**g**	180	2	**g**	67	**g**	31
8	**h**	140	2	**h**	46	**h**	44
9	**i**	160	2	**i**	70		
10	**j**	140	2	**j**	53		
11	**k**	160	4	**k**	81		
12	**k**	160	4	**l**	35		



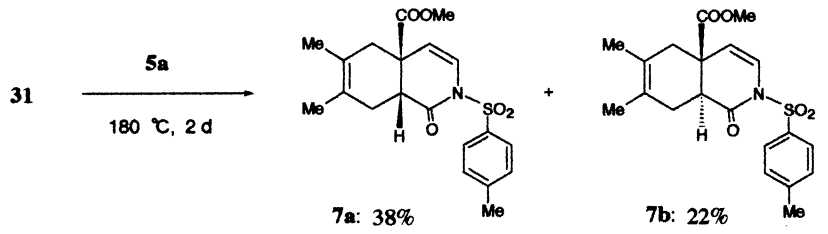
6a : R^1 = COOMe; $R^4 = R^6$ = Me; $R^2 = R^3 = R^5$ = H
6b : R^1 = COMe; $R^4 = R^6$ = Me; $R^2 = R^3 = R^5$ = H
6c : $R^1 = NO_2$; $R^4 = R^6$ = Me; $R^2 = R^3 = R^5$ = H
6d : R^1 = COOMe; R^4 = OMe; $R^2 = R^3 = R^5$ = H; R^6 = Me
6e : R^1 = COOMe; R^4 = Cl; $R^2 = R^3 = R^5$ = H; R^6 = Me
6f : R^1 = COOMe; $R^4 = NO_2$; $R^2 = R^3 = R^5$ = H; R^6 = Me
6g : R^1 = COOMe; $R^2 = R^3 = R^4 = R^5$ = H; R^6 = Me
6h : R^1 = COOMe; $R^3 = R^6$ = Me; $R^2 = R^4 = R^5$ = H
6i : R^1 = COOMe; $R^3 = R^4 = R^5 = R^6$ = Me; R^2 = H
6j : R^1 = COOMe; $R^3 = R^4 = R^5$ = *i*-Pr; R^2 = H; R^6 = Me
6k : R^1 = COOMe; R^2 = Br; $R^4 = R^6$ = Me; $R^3 = R^5$ = H
6l : R^1 = COOMe; R^2 = Br; R^4 = Me; $R^3 = R^5 = R^6$ = H

4a : R^1 = COOMe; R^3 = Me; $R^2 = R^4$ = H
4b : R^1 = COMe; R^3 = Me; $R^2 = R^4$ = H
4d : R^1 = COOMe; R^3 = OMe; $R^2 = R^4$ = H
4g : R^1 = COOMe; $R^2 = R^3 = R^4$ = H
4h : R^1 = COOMe; R^2 = Me; $R^3 = R^4$ = H

5a : R = Me
5b : R = H

Scheme 3.

products of intramolecular rearrangement of the arylsulfonyl group of **3a**,**b**,**d**,**g**,**h**. To investigate the site-selectivity of 1-arylsulfonyl-2(1*H*)-pyridones **3a**–**k**, we carried out the reaction of 1-arylsulfonyl-2(1*H*)-pyridone **3l**, which has an electron-withdrawing group at the 4-position. The reaction of **3l** with **5a** afforded tetrahydro-1(2*H*)-isoquinolone **7a** (38%) and **7b** (22%), site-selectively (Scheme 4). Assignment of the stereochemistry of the ring juncture in **6a**–**l** and **7a**,**b** were carried out as follow, the *cis*-stereochemistry of the ring juncture in **6a**–**l** was determined by NOE measurements and confirmed by X-ray analysis (Fig. 1) of **6a**. For **6a**,**b**, when H-8a was irradiated in each case, an NOE was observed between H-8a and CH_3OOC-4a (ca. 3.6%) in **6a**, and between H-8a and CH_3OC-4a (ca. 6.4%) in **6b**. The *cis*-stereochemistry of the ring juncture in **6c**–**l** was deduced by comparing their ^{1}H NMR spectra with those of **6a**,**b**. In a previous paper, we reported that the ^{1}H NMR signals produced by the proton of the ring juncture in the *cis*-isoquinolone adducts (δ 2.84–2.97) is located at a lower range than those of the corresponding *trans*-isoquinolone adducts (δ 2.00–2.80).[3] The signals assigned to the proton of the ring juncture in **7a**,**b** appeared at δ 2.95 and 2.72, and therefore,



Scheme 4.

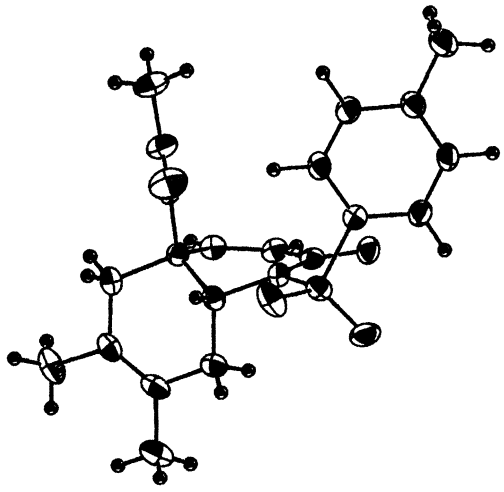


Figure 1. ORTEP drawing of **6a**.

the structure of the ring juncture in **7a** was confirmed as the *cis*- and **7b** as the *trans*-structure. Next, to assign the position of the methyl group in **3l**, $^1H-^1H$ correlation spectroscopy experiment for **3l** was carried out. Since correlation between the methylene protons at C-8 and the olefinic proton in their cyclohexene moiety was not observed, the methyl group in **3l** is located at C-7.

X-ray crystallograpy (Fig. 1). The root mean square error of these structures was 0.04 Å for the ten heavy atoms (N_1, C_1-C_9) in the two rings.

In the DA reaction of **3a** with **5a**, for example, the calculated energies of the quinolone-type product was 28.74 kcal mol^{-1} lower than that of the initial state, and 4.57 kcal mol^{-1} higher than that of the isoquinolone-type product. The energy values of the other reactions in Table 3 showed the identical behavior. Therefore, we can assume that the retro-DA reactions do not occur and that these DA reactions are kinetically controlled, and therefore their activation energies (E_a) can be used as reaction indices.

Table 3 summarizes the calculated E_a values together with the experimental yields of adducts. For the DA reactions 1–7 in Table 3, where the dienophiles have an electron-withdrawing group at the 5-position, in each case, the calculated E_a value for 5,6-addition is much smaller than that for 3,4-addition. These results are consistent with the experimental findings that only the quinolone-type adducts were formed in these DA reactions. However, in the reaction 7, for dienophile **3m**, which has a methoxycarbonyl group at the 5-position and a methyl group at the 1-position but no arylsulfonyl group, quinolone-type adduct **6m** was produced in a poor yield.[8] This experimental result is supported by theoretical calculations, since the value of E_a for producting **6m** was 1.51 kcal mol^{-1} smaller than that for

Table 3. Experimental yields of adducts and activation energies (E_a) for the DA reactions calculated at the RHF/3-21G level

Reaction	Diene	Dienophile	Temperature (°C) (Time)	(3,4)-Addition		(5,6)-Addition	
				E_a (kcal mol^{-1})	Adduct (yield %)	E_a (kcal mol^{-1})	Adduct (Yield %)
1	**5a**	**3a**	180(2 d)	31.27	–	28.79	**6a**(46)
2	**5a**	**3b**	140(2 d)	31.64	–	29.20	**6b**(43)
3	**5a**	**3c**	120(2 d)	28.66	–	19.55	**6c**(39)
4	**5a**	**3l**	160(2 d)	31.59	–	28.05	**6i**(70)
5	**5a**	**3k**	160(4 d)	30.66	–	26.78	**6k**(81)
6	**5b**	**3k**	160(4 d)	32.80	–	27.71	**6l**(35)
7	**5a**	**3m**[a]	160(6 d)	35.25[b]	–	33.74[b]	**6m**(3)[a]
8	**5a**	**3l**	180(2 d)	27.29	**7a**,**b**(60%)	33.72	–

[a] **3m**=1-Methyl-5-methoxcarbonyl-2(1*H*)-pyridone; **6m**=4a,5,8,8a-Tetrahydro-*cis*4a-methoxcarbonyl-1,6,7-trimethyl-2(1*H*)-quinone.[8]
[b] Calculated at the RHF/3-21+G level.

2.3. Site-selectivity

It should be stressed that the quinolone derivatives **6a**–**l** were produced with high site-selectively via the DA reactions in which the dienes **5a**,**b** were cycloadded to the dienophiles **3a**–**k** on the 5,6-position. To study whether the quinolone or isoquinolone derivatives would be produced by way of the 5,6-addition or by 3,4-addition, we carried theoretical studies on the DA reactions listed in Table 3, searching and optimizing the structures of the transition states (TS) using Gaussian 98 at the RHF/3-21G level.[7] The optimized structures of the TS of the DA reaction of **3a** with **5a** are shown in Fig. 2. Furthermore, we also optimized the structures of the quinolone-type and the isoquinolone-type products. The optimized structures of the quinolone-type product from the 5,6-addition in the DA reaction of **3a** with **5a** coincide with the structure of adduct **6a**, which was experimentally determined using the

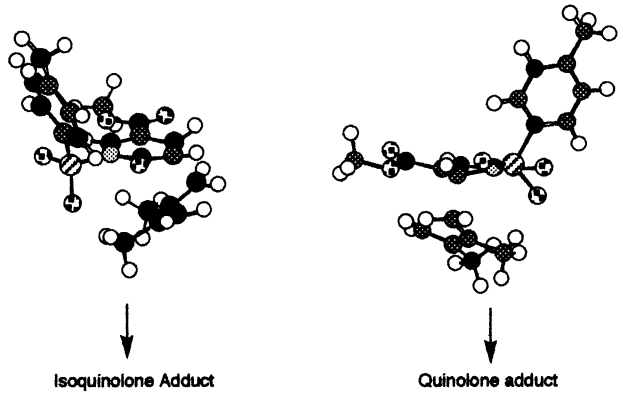


Figure 2. Calculated Structures of TS for 3,4-addition (left) and for 5,6-addition (right) in the DA reaction of **3a** with **5**. The calculated relevant interatomic distances are: C_1-C_3=2.258 Å, C_4-C_4=2.105 Å, (left); C_1-C_5=2.641 Å, C_4-C_6=1.848 Å, (right).

the isoquinolone-type adduct, and over 4.5 kcal mol^{-1} higher than those of the other reactions leading to the experimentally formed compounds in Table 3.

In contrast, in the reaction 8, for dienophile **3l**, which has a methoxycarbonyl group at the 4-position and arylsulfonyl group at the 1-position, the calculated E_a value for the 3,4-addition is much smaller than that for the 5,6-addition. These calculated values explain the experimental results, which show the formation of the isoquinolone-type adduct. We can conclude from above that the electron-withdrawing group at the 5-position and the arylsulfonyl group at the 1-position in the pyridone ring are important substituents that result in producing the quinolone-type adducts in these DA reactions.

In conclusion, we have developed a novel synthetic methodology of preparing tetrahydro-2(1*H*)-quinolones through DA reactions of 2(1*H*)-pyridones, that have electron-withdrawing groups at the 1- and 5-positions, acting as dienophiles. Furthermore, site-selectivity of 1,5-substituted 2(1*H*)-pyridones was explained by their activation energies (E_a) using ab initio MO calculations.

3. Experimental

3.1. General

The following instruments were used to obtain physical data: melting points, Yanaco micromelting point apparatus (values are uncorrected); IR spectra, Perkin Elmer ET-IR 1725X spectrometer; MS, JEOLJMN-DX 303/JMA-DA5000spectrometer; NMR spectra, JNM-GSX400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz), JNM-EX270 (^{1}H NMR, 270 MHz; ^{13}C NMR, 67.8 MHz) and JEOLJN-PMX 60SI spectrometer with tetramethylsilane (TMS) as an internal standard; elemental analyses, Perkin Elmer 2400 CHN Elemental Analyzer. The following experimental conditions were used for chromatography; column chromatography, Merk Kieselgel silica gel 60 (230–400 mesh); TLC, pre-coated TLC plates with $60F_{254}$ (2 mm, Merck).

3.1.1. Synthesis of 3-acetylpyridine 1-oxide. A suspension of 3-acetylpyridine (10.4 g, 85 mmol) and *m*-chloroperoxybenzoic acid (25.9 g, 150 mmol) in CH_2Cl_2 (50 ml) was stirred at room temperature for 3 days. The reaction mixture was diluted with $CHCl_3$ (200 ml), and treated with K_2CO_3 (138 g, 1 mol) and H_2O (45 ml). The organic layer was separated, dried over Na_2SO_4, and evaporated in vacuo to give 3-acetylpyridine 1-oxide (10.5 g, 90%) as colorless needles ($CHCl_3$), mp 140–142°C. IR (KBr): ν 1683, 1372, 1292, 916, 804, 719. ^{1}H NMR ($CDCl_3$) δ: 2.61 (3H, s, COMe), 7.41 (1H, dd, J=6.5, 7.9 Hz, H-5), 7.77 (1H, ddd, J=1.2, 1.5, 7.9 Hz, H-6), 8.35 (1H, ddd, J=1.2, 1.5, 6.5 Hz, H-4), 8.71(1H, dd, J=1.5, 1.5 Hz, H-2). ^{13}C NMR ($CDCl_3$) δ: 26.76, 124.44, 125.86, 135.47, 139.22, 142.11, 193.37. LMS *m/z*: 137 (M^+), 122, 95, 78. HRMS Calcd for $C_7H_7NO_2$: 137.0477. Found: 137.0500.

3.1.2. Reaction of 3-acetylpyridine 1-oxide with acetic anhydride. A solution of 3-acetylpyridine 1-oxide (9.3 g, 68 mmol) and acetic anhydride (110 ml) was refluxed for 14 h. After concentrating the reaction mixture in vacuo, the residue was purified using column chromatography (acetone–diisopropyl ether=2:1). The first fraction was evaporated to give 3-acetyl-2(1*H*)-pyridone (2.60 g, 28%) as pale yellow needles ($CHCl_3$), mp 160°C. IR (KBr): ν 1674, 1650, 1359, 774. ^{1}H NMR ($CDCl_3$) δ: 2.72 (3H, s, COMe), 6.46 (1H, dd, J=6.3, 7.3 Hz, H-5), 7.66 (1H, dd, J=2.3, 6.3 Hz, H-6), 8.25 (1H, dd, J=2.3, 7.3 Hz, H-4). ^{13}C NMR ($CDCl_3$) δ: 30.83, 107.05, 127.16, 140.28, 144.70, 163.68, 197.25. LMS *m/z*: 137 (M^+), 122, 94. HRMS Calcd for $C_7H_7NO_2$: 137.0477. Found: 137.0466. The solvent of the second fraction was evaporated to give 5-acetyl-2(1*H*)-pyridone (**1b**, 2.40 g, 15%) as pale yellow plates ($CHCl_3$), mp 203–205°C. IR (KBr): ν 1648, 1368, 833. ^{1}H NMR ($CDCl_3$) δ: 2.46 (3H, s, COMe), 6.60 (3H, s, dd, J=0.7, 9.6 Hz, H-3), 8.06 (1H, dd, J=2.7, 9.6 Hz, H-4), 8.13 (1H, dd, J=0.7, 2.7 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 25.68, 118.98, 119.95, 139.06, 139.76, 165.24, 192.63. LMS *m/z*: 137 (M^+), 122, 94. HRMS Calcd for $C_7H_7NO_2$: 137.0477. Found: 137.0514.

3.2. General procedures for sulfonylations of 2(1*H*)-pyridones 1a–e with 2a–h

A solution of sulfonyl chloride **2a** (0.572 g, 3 mmol) in THF (10 ml) at −78°C was added to a stirred suspension of **1a** (0.306 g, 2 mmol) and NaH (0.072 g, 3 mmol) in THF (20 ml) at −78°C. After 1 h, the reaction mixture was allowed to warm to 60°C, and then was stirred for 5 h. The mixture was poured into ice water (10 ml), neutralized with K_2CO_3, then extracted with $CHCl_3$ (200 ml). The $CHCl_3$ extract was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (diethyl ether–hexane=2:1) to give sulfonylpyridone **3a** (0.866 g, 94%). Reactions of **1b–e** (2 mmol) with **2b–h** (5 mmol) were carried out under similar conditions, as listed in Table 1. The yields of **3a–l** and **4i,j** are summarized in Table 1.

3.2.1. 5-Methoxycarbonyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-pyridone (3a). Colorless needles (benzene), mp 130–132°C. IR (KBr): ν 1730, 1697, 1593, 1376, 1185, 839. ^{1}H NMR ($CDCl_3$) δ: 2.45 (3H, s, PhMe), 3.91 (3H, s, OMe), 6.42 (1H, dd, J=0.5, 9.7 Hz, 3-H), 7.36 (2H, d, J=8.5 Hz, H-Ph), 7.81 (1H, dd, J=2.4, 9.7 Hz, H-4), 8.00 (2H, d, J=8.5 Hz, H-Ph), 8.93 (1H, dd, J=0.5, 2.4 Hz, H-6). ^{13}C NMR ($CDC1_3$) δ: 21.81, 52.38, 110.34, 122.34, 129.46, 129.98 (C2), 132.42, 137.03, 139.66, 146.63, 159.33 (C-2), 163.74. LMS *m/z*: 307 (M^+), 276, 244, 185, 122. HRMS Calcd for $C_{14}H_{13}NO_5S$: 307.0514. Found: 307.0494.

3.2.2. 5-Acetyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-pyridone (3b). Pale yellow powder ($CHCl_3$), mp 161–163°C. IR (KBr): ν 1707, 1670, 1603, 1376, 1183, 1360, 821. ^{1}H NMR ($CDCl_3$) δ: 2.46 (3H, s, COMe), 2.53 (3H, s, PhMe), 6.43 (1H, dd, J=0.7, 9.7 Hz, H-3), 7.38 (2H, d, J=8.7 Hz, H-Ph), 7.87 (1H, dd, J=2.5, 9.7 Hz, H-4), 8.02 (2H, d, J=8.6 Hz, H-Ph), 8.83 (1H, dd, J=0.7, 2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.93, 25.61, 118.2, 122.79, 129.61 (C2), 130.10 (C2), 132.41, 136.56, 138.57, 146.86, 159.35, 192.43. LMS *m/z*: 291 (M^+), 227, 91. HRMS Calcd for $C_{14}H_{13}NO_4S$: 291.0565. Found: 291.0522.

3.2.3. 1-(4-Methylbenzenesulfonyl)-5-nitro-2(1*H*)-pyridone (3c). Colorless plates (benzene), mp 182°C. IR (KBr): ν 1696, 1619, 1563, 1380, 1186, 814. ^{1}H NMR ($CDCl_3$) δ: 2.48 (3H, s, PhMe), 6.47 (1H, dd, J=0.5, 10.0 Hz, H-3), 7.40 (2H, d, J=8.5 Hz, H-Ph), 8.02–8.08 (3H, m, H-4, Ph), 9.34 (1H, dd, J=0.5, 3.1 Hz, H-6). ^{13}C NMR ($CDC1_3$) δ: 22.00, 122.63, 129.83 (C2), 130.39 (C2), 131.55 (C2), 134.07, 134.30, 147.59, 158.33. LMS *m/z*: 294 (M^+), 231, 155. HRMS Calcd for $C_{12}H_{10}N_2O_5S$: 294.0310. Found: 294.0351.

3.2.4. 1-(4-Methoxylbenzenesulfonyl)-5-methoxycarbonyl-2(1*H*)-pyridone (3d). Colorless needles (benzene), mp 139–141°C. IR (KBr): ν 1728, 1616, 1591, 1382, 1171, 846. ^{1}H NMR ($CDCl_3$) δ: 3.89 (3H, s, OMe), 3.90 (3H, s, OMe), 6.42 (1H, dd, J=0.5, 9.6 Hz, H-3), 7.00 (2H, d, J=10.0 Hz, H-Ph), 7.81 (1H, dd, J=2.5, 9.6 Hz, H-4), 8.08 (2H, d, J=10.0 Hz, H-Ph), 8.93 (1H, dd, J=0.5, 2.5 Hz, H-6). ^{13}C NMR ($CDC1_3$) δ: 52.46, 55.88, 110.41, 114.17 (C2), 122.40, 126.32, 132.68 (C2), 137.17, 139.73, 159.50, 163.88, 164.94. LMS *m/z*: 323 (M^+), 292, 259. HRMS Calcd for $C_{14}H_{13}NO_6S$: 323.0464. Found: 323.0448.

3.2.5. 1-(4-Chlorobenzenesulfonyl)-5-methoxycarbonyl-2(1*H*)-pyridone (3e). Colorless needles (acetone), mp 158°C. IR (KBr): ν 1727, 1694, 1619, 1381, 1176, 830. ^{1}H NMR ($CDCl_3$) δ: 3.91 (3H, s, OMe), 6.45 (1H, dd, J=0.6, 9.6 Hz, H-3), 7.55 (2H, d, J=8.9 Hz, H-Ph), 7.83 (1H, dd, J=2.4, 9.6 Hz, H-4), 8.08 (2H, d, J=8.9 Hz, H-Ph), 8.89 (1H, dd, J=0.6, 2.4 Hz, H-6). ^{13}C NMR ($CDC1_3$) δ: 52.46, 110.80, 122.35, 129.20 (C2), 131.41 (C2), 133.81, 136.77, 139.89, 142.16, 159.23, 163.56. LMS *m/z*: 329 (M^++2), 327 (M^+), 297, 295, 265, 263. HRMS Calcd for $C_{13}H_{10}ClNO_5S$: 326.9968. Found: 326.9931.

3.2.6. 5-Methoxycarbonyl-1-(4-nitrobenzenesulfonyl)-2(1*H*)-pyridone (3f). Colorless plates (benzene), mp 135–137°C. IR (KBr): ν 1731, 1684, 1606, 1526, 1348, 1189, 846. ^{1}H NMR ($CDCl_3$) δ: 3.91 (3H, s, OMe), 6.45 (1H, d, J=0.6, 9.6 Hz, H-3), 7.55 (2H, d, J=8.9 Hz, H-Ph), 7.83 (1H, dd, J=2.4, 9.6 Hz, H-4), 8.08 (2H, d, J=8.9 Hz, H-Ph), 8.89 (1H, dd, J=0.6, 2.4 Hz, H-6). ^{13}C NMR ($CDCl_3$): 52.46, 110.80, 122.35 (C2), 129.20 (C2), 133.81, 136.77, 139.89, 142.16, 148.38, 159.23, 163.56. LMS *m/z*: 338 (M^+), 307, 274, 215, 122. HRMS Calcd for $C_{13}H_{10}N_2O_7S$: 338.0209. Found: 338.0181.

3.2.7. 1-Benzenesulfonyl-5-methoxycarbonyl-2(1*H*)-pyridone (3g). Colorless columns (acetone), mp 129–131°C. IR (KBr): ν 1728, 1683, 1619, 1581, 1341, 1186, 737. ^{1}H NMR ($CDCl_3$) δ: 3.91 (3H, s, OMe), 6.43 (1H, dd, J=0.6, 9.7 Hz, H-3), 7.55–7.62 (2H, m, H-Ph), 7.69–7.75 (1H, m, H-Ph), 7.82 (1H, dd, J=2.5, 9.7 Hz, H-4), 8.12–8.16 (2H, m, H-Ph), 8.93 (1H, dd, J=0.6, 2.5 Hz, H-6). ^{13}C NMR ($CDC1_3$) δ: 52.41, 110.59, 122.35, 128.83 (C2), 129.89 (C2), 135.06, 135.56, 136.98, 139.75, 159.26, 163.67. LMS*m/z*: 293 (M^+), 262, 229, 170. HRMS Calcd for $C_{13}H_{11}NO_5S$: 293.0358. Found: 293.0310.

3.2.8. 5-Methoxycarbonyl-1-(2-methylbenzenesulfonyl)-2(1*H*)-pyridone (3h). Colorless plates (ether), mp 99–100°C. IR (KBr): ν 1727, 1697, 1594, 1366, 1183, 767. ^{1}H NMR ($CDCl_3$) δ: 2.47 (3H, s, PhMe), 3.92 (3H, s, OMe), 6.40 (1H, dd, J=0.5, 9.6 Hz, 3-H), 7.29 (1H, d, J=7.4 Hz, H-Ph), 7.42–7.47 (1H, m, H-Ph), 7.57–7.60 (1H, m, H-Ph), 7.85 (1H, dd, J=0.5, 9.6 Hz, 4-H), 8.28 (1H, m, H-Ph), 8.96 (1H, dd, J=0.5, 2.4 Hz, 6-H). ^{13}C NMR ($CDC1_3$) δ: 20.29, 52.45, 110.30, 122.38, 126.38, 132.36, 132.93, 134.22, 134.96, 137.10, 137.97, 139.75, 159.21, 163.67. LMS *m/z*; 307 (M^+), 276, 226, 91. HRMS Calcd for $C_{14}H_{13}NO_5S$: 307.0514. Found: 307.0478.

3.2.9. 5-Methoxycarbonyl-1-(2,4,6-trimethylbenzenesulfonyl)-2(1*H*)-pyridone (3i). Colorless needles (ether), mp 195°C. IR ($CHCl_3$): ν 1726, 1689, 1602, 1367, 839. ^{1}H NMR ($CDCl_3$) δ: 2,31 (3H, s, PhMe), 2.58 (6H, s, PhMe, PhMe), 3.91 (3H, s, OMe), 6.41 (1H, dd, J=0.4, 9.8 Hz, 3-H), 6.98 (2H, s, H-Ph), 7.85 (1H, dd, J=2.5, 9.8 Hz, 4-H), 8.95 (1H, dd, J=0.4, 2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.22, 22.66 (C2), 52.51, 109.86, 116.01, 122.46, 130.32, 132.13 (C2), 137.10, 139.69, 141.20, 145.15, 160.02, 163.91. LMS *m/z*: 336 (M^++1), 271, 254, 119, 91. HRMS Calcd for $C_{16}H_{17}NO_5S$: 335.0828. Found: 335.0771.

3.2.10. 5-Methoxycarbonyl-1-(2,4,6-triisopropylbenzenesulfonyl)-2(1*H*)-pyridone (3j). Colorless needles (ether), mp 151–152°C. IR ($CHCl_3$): ν 1728, 1693, 1599, 1379, 883, 839. ^{1}H NMR ($CDCl_3$) δ: 1.18–1.26 (18H, m, J=6.9 Hz, Me×6), 2.91 (1H, m, J=6.9 Hz, CH), 3.93 (3H, s, OMe), 3.93–4.05 (2H, m, J=6.9 Hz, CH×2), 6.42 (1H, d, J=9.6 Hz, H-3), 7.19 (2H, s, H-Ph), 7.85 (1H, dd, J=2.3, 9.6 Hz, H-4), 8.95 (1H, dd, J=2.3 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 23.3, 24.27 (C4), 219.43 (C2), 34.24, 52.42, 110.22, 122.15, 124.07 (C2), 129.36, 136.12, 139.48, 151.71 (C2), 155.04, 159.92, 163.78, 172.82. LMS *m/z*: 420 (M^++1), 355, 338, 312, 203, 91. HRMS Calcd for $C_{22}H_{29}NO_5S$: 419.1767. Found: 419.1744.

3.2.11. 3-Bromo-5-methoxycarbonyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-pyridone (3k). Colorless plates (ether), mp 147°C. IR (KBr): ν 1722, 1697, 1593, 1536, 1374, 1175, 740. ^{1}H NMR ($CDCl_3$) δ: 2.46 (3H, s, PhMe), 3.92 (3H, s, OMe), 7.37 (2H, d, J=8.1 Hz, H-Ph), 8.03 (2H, d, J=8.1 Hz, H-Ph), 8.23 (1H, d, J=2.2 Hz, H-4), 8.93 (1H, d, J=2.2 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.97, 52.75, 110.65, 117.92, 129.76 (C2), 130.37 (C2), 131.83, 136.12, 141.35, 147.18, 155.77, 162.92. LMS *m/z*: 387 (M^++2), 385 (M^+), 323, 301, 155, 91. HRMS Calcd for $C_{14}H_{12}BrNO_5S$: 384.9620. Found: 384.9652.

3.2.12. 4-Methoxycarbonyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-pyridone (3l). Colorless needles (ether), mp 120–121°C. IR ($CHCl_3$): ν 1734, 1682, 1614, 1334, 1122, 815. ^{1}H NMR ($CDCl_3$) δ: 2.45 (3H, s, C-Me), 3.95 (3H, s, OMe), 6.71 (1H, dd, J=1.7, 7.3 Hz, H-5), 7.03 (1H, d, J=1.7 Hz, H-3), 7.35 (2H, d, J=8.1 Hz, H-3′,5′), 7.99 (2H, d, J=8.1 Hz, H-2′,6′), 8.14 (1H, d, J=7.3 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.79, 53.08, 104.56, 125.53, 129.59 (C2), 130.03 (C2), 132.06, 132.87, 141.86, 146.61, 159.87, 164.11. LMS *m/z*: 308 (M^++1), 276, 243, 184, 91. HRMS Calcd for $C_{14}H_{13}NO_5S$: 307.0562. Found: 307.0610.

3.2.13. 5-Methoxycarbonylpyridin-2yl-2,4,6-trimethylbenzenesulfonate (4i). Colorless needles (ether), mp

73–74°C. IR ($CHCl_3$): ν 1730, 1595, 1369, 1175, 823. ^{1}H NMR ($CDCl_3$) δ: 2.32 (3H, s, PhMe), 2.68 (6H, s, PhMe), 3.92 (3H, s, OMe), 6.98 (2H, s, H-Ph), 7.12 (1H, dd, J=0.5, 8.5 Hz, H-3), 8.32 (1H, dd, J=2.4, 8.5 Hz, H-4), 8.80 (1H, dd, J=0.5, 2.4 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.21, 22.77 (C2), 52.52, 114.25, 124.43, 131.63 (C2), 140.15 (C3), 141.05, 143.83, 150.03, 159.89, 164.57. LMS *m/z*: 335 (M^+), 271, 254, 119, 91. HRMS Calcd for $C_{16}H_{17}NO_5S$: 335.0828. Found: 335.0792.

3.2.14. 5-Methoxycarbonylpyridin-2yl-2,4,6-triisopropylbenzenesulfonate (4j). Colorless needles (ether), mp 115°C. IR ($CHCl_3$): ν 1725, 1595, 1383, 1116, 825. ^{1}H NMR ($CDCl_3$) δ:1.25 (12H, d, J=6.9 Hz, CMe×4), 1.26 (6H, d, J=6.9 Hz, CMe×2), 2.92 (1H, m, J=6.9 Hz, CH), 3.9 2 (3H, s, OMe), 4.24 (2H, m, J=6.9 Hz, PhCH×2), 7.09 (1H, dd, J=0.8, 8.6 Hz, H-3), 7.20 (2H, s, PhCH), 8.32 (1H, dd, J=2.5, 8.6 Hz, H-4), 8.80 (1H, dd, J=0.8, 2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 23.58 (C2), 24.60 (C4), 29.82 (C2), 34.32, 52.51, 114.09, 123.79 (C2), 124.36, 130.78, 141.02, 150.02 (C2), 150.74, 154.13, 160.10, 164.62. LMS *m/z*: 420 (M^++1), 355, 338, 312, 203, 91. HRMS Calcd for $C_{22}H_{29}NO_5S$: 419.1767. Found: 419.1766.

3.3. General procedures for DA reactions of 1-arylsulfonylpyridones 3a–l with 5a,b

A solution of **3a** (0.307 g, 1 mmol) and **5a** (0.410 g, 5 mmol) in *o*-xylene (3 ml) was heated at 180°C for 2 days in a sealed tube. The reaction mixture was concentrated in vacuo, and then purified by column chromatography (acetone–hexane=1:2). The first fraction was evaporated to give **4a** (0.200 g, 43%). The second fraction was evaporated, then further purified by preparative TLC over silica gel (ether–hexane=3:1) to afford **6a** (0.268 g, 46%). Reactions of **3b**–**l** (1 mmol) with **5a**,**b** (5 mmol) were carried out under similar the conditions, as listed in Table 2, to afford **6b**–**l**, respectively. Yields of **6a**–**l** and **4a**,**b**,**d**,**g**,**h** are summarized in Table 2.

3.3.1. 4a,5,8,8a-Tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-1-(4-methylbenzene-sulfonyl)-2(1*H*)-quinolone (6a). Colorless plates (benzene), mp 172–173°C. IR (KBr): ν 1734, 1687, 1596, 1344, 1169, 831. ^{1}H NMR ($CDCl_3$) δ:1.60 (3H, s, CMe), 1.65 (3H, s, CMe), 2.16 (1H, d, J=17.0 Hz, H-8), 2.33 (1H, d, J=17.5 Hz, H-5), 2.63–2.70 (2H, m, H-5,8), 3.65 (3H, s, OMe), 5.23 (1H, ddd, J=2.1, 7.2, 9.3 Hz, H-8a), 5.88 (1H, d, J=9.6 Hz, H-3), 6.45 (1H, dd, J=2.1, 9.6 Hz, H-4), 7.29 (2H, d, J=8.6 Hz, H-Ph), 7.97 (2H, d, J=8.6 Hz, H-Ph). ^{13}C NMR ($CDCl_3$): 18.51, 18.53, 21.63, 36.70, 40.59, 47.74, 52.84, 55.41, 122.12, 125.67, 126.06, 129.03 (C2), 129.26 (C2), 136.28, 144.64, 146.24, 161.27, 172.82. LMS *m/z*: 389 (M^+), 243, 159, 91. HRMS Calcd for $C_{20}H_{23}NO_5S$: 389.1297. Found: 389.1314. X-Ray analytical data (Fig. 1): 2θ range (23.2–30.0), crystal system: monoclinic, temperature: 23°C, space group: $P21/c$, D_{calc} (g/cm): 1.311, lattice parameters (Å): a=15.257 (3), b=8.380 (2), c=15.439 (2), V=1973.8 (5) Å3, β=90.99 (1)°. Z=4. μ (Cu Kα): 16.73 cm^{-1}. Further details have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambrige CB2 1EW, UK.

3.3.2. *cis*-4a-Acetyl-4a,5,8,8a-tetrahydro-6,7-dimethyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-quinolone (6b). Colorless powder ($CHCl_3$), mp 197–198°C. IR (KBr): ν 1710, 1689, 1597, 1381, 1345, 1170, 831. ^{1}H NMR ($CDCl_3$) δ: 1.61 (3H, s, CMe), 1.66 (3H, s, CMe), 2.12 (3H, s, COMe), 2.12, 2.27 (2H, m, H-5,8), 2.38 (1H, dd, J=7.1, 7.1 Hz, H-5), 2.41 (3H, s, PhMe), 2.70 (1H, dd, J=7.1, 17.1 Hz, H-8), 5.25 (1H, ddd, J=2.0, 7.1, 7.1 Hz, H-8a), 5.92 (1H, d, J=9.7 Hz, H-3), 6.55 (1H, dd, J=2.0, 9.7 Hz, H-4), 7.30 (2H, d, J=8.1 Hz, H-Ph), 7.98 (2H, d, J=8.4 Hz, H-Ph). ^{13}C NMR ($CDCl_3$) δ: 18.67, 18.75, 21.75, 27.18, 36.95, 40.03, 53.37, 54.68, 121.88, 126.41, 126.46, 128.97 (C2), 129.32 (C2), 135.89, 144.57, 146.63, 160.90, 204.79. LMS *m/z*: 373 (M^+), 330, 266, 176, 227. HRMS Calcd for $C_{20}H_{23}NO_4S$: 373.1348. Found: 373.1305.

3.3.3. 4a,5,8,8a-Tetrahydro-6,7-dimethyl-1-(4-methylbenzenesulfonyl)-*cis*-4a-nitro-2(1*H*)-quinolone (6c). Brown powder ($CHCl_3$), mp 180°C. IR (KBr): ν 1672, 1620, 1594, 816. ^{1}H NMR ($CDCl_3$) δ: 1.57 (3H, s, CMe), 1.65 (3H, s, CMe), 1.97 (1H, dd, J=9.7, 17.4 Hz, H-8), 2.30 (1H, d, J=17.2 Hz, H-5), 2.42 (3H, s, PhMe), 2.57 (1H, d, J=17.2 Hz, H-5), 2.75 (1H, dd, J=7.2, 17.4 Hz, H-8), 4.77 (1H, ddd, J=1.8, 7.2, 9.7 Hz, H-8a), 5.86 (1H, d, J=9.5 Hz, H-3), 6.50 (1H, dd, J=1.8, 9.5 Hz, H-4), 7.30 (2H, d, J=8.4 Hz, H-Ph), 7.97 (2H, d, J=8.4 Hz, H-Ph). ^{13}C NMR ($CDCl_3$) δ: 18.18, 18.90, 21.74, 40.44, 43.78, 60.69, 67.27, 122.91, 125.65, 126.40, 128.80 (C2), 129.19 (C2), 136.00, 144.70, 147.69, 161.17. MS *m/z*: 376 (M^+), 330, 266, 174, 159, 91. HRMS Calcd for $C_{18}H_{20}N_2O_5S$: 376.1093. Found: 376.1121.

3.3.4. 4a,5,8,8a-Tetrahydro-1-(4-methoxybenzenesulfonyl)-*cis*-4a-methoxycarbonyl-6,7-dimethyl-2(1*H*)-quinolone (6d). Colorless plates (benzene), mp 167°C. IR (KBr): ν 1733, 1624, 1594, 1343, 1163, 834. ^{1}H NMR ($CDCl_3$) δ: 1.59 (3H, s, CMe), 1.60 (3H, s, CMe), 2.19 (1H, d, J=7.1, 11.5 Hz, 8-H), 2.32 (1H, d, J=17.2 Hz, 5-H), 2.62–2.68 (2H, m, 5,8-H), 3.64 (3H, s, OMe), 3.86 (3H, s, PhOMe), 5.22 (1H, ddd, J=2.0, 7.1, 9.1 Hz, 8a-H), 5.87 (1H, d, J=9.7 Hz, 3-H), 6.43 (1H, dd, J=2.0, 9.7 Hz, 4-H), 6.93–6.98 (2H, m, H-Ph), 8.00–8.06 (2H, m, H-Ph). ^{13}C NMR ($CDCl_3$): 18.63, 18.65, 36.77, 40.67, 47.78, 52.89, 55.46, 55.65, 113.48 (C2), 122.02 (C2), 125.61, 126.00, 130.50, 131.52, 146.03, 161.12, 163.52, 172.68. LMS *m/z*: 405 (M^+), 341, 259. HRMS Calcd for $C_{20}H_{23}NO_6S$: 405.1246. Found: 405.1230.

3.3.5. 1-(4-Chlorobenzenesulfonyl)-4a,5,8,8a-tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-2(1*H*)-quinolone (6e). Colorless plates (ether–hexane), mp 173°C. IR (KBr): ν 1734, 1696, 1598, 1538, 1357, 1131, 826. ^{1}H NMR ($CDCl_3$) δ: 1.61 (3H, s, CMe), 1.66 (3H, s, CMe), 2.14–2.24 (1H, brm, H-8), 2.34 (1H, d, J=17.0 Hz, H-5), 2.61–2.67 (2H, brd, H-5, 8), 3.65 (3H, s, OMe), 5.22 (1H, ddd, J=2.0, 7.2, 9.4 Hz, H-8a), 5.89 (1H, d, J=9.6 Hz, H-3), 6.48 (1H, dd, J=2.0, 9.6 Hz, H-4), 7.47 (2H, d, J=9.2 Hz, H-Ph), 8.04 (2H, d, J=9.2 Hz, H-Ph). ^{13}C NMR ($CDCl_3$) δ: 18.62, 18.65, 36.82, 40.64, 47.74, 53.02, 55.66, 122.10, 125.27, 125.94, 127.44, 128.95, 129.53, 133.64, 134.45, 140.67, 146.56, 161.05, 172.59. LMS *m/z*: 411 (M^++2), 409 (M^+), 350, 263. HRMS Calcd for $C_{19}H_{20}ClNO_5S$: 409.0751. Found: 409.0699.

3.3.6. 4a,5,8,8a-Tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-1-(4-nitrobenzenesul-fonyl)-2(1*H*)-quinolone (6f). Colorless needles (benzene), mp 181–182°C. IR (KBr): ν 1724, 1696, 1607, 1530, 1357, 1168, 829. ^{1}H NMR ($CDCl_3$) δ:1.62 (3H, s, CMe), 1.66 (3H, s, CMe), 2.20 (1H, d, J=17.6 Hz, H-8), 2.38 (1H, d, J=17.6 Hz, H-5), 2.60–2.72 (2H, m, H-5,8), 3.66 (3H, s, OMe), 5.24 (1H, ddd, J=2.1, 7.2, 9.2 Hz, H-8a), 5.87 (1H, d, J=9.7 Hz, H-3), 6.51 (1H, dd, J=2.1, 9.7 Hz, H-4), 8.32 (4H, s, H-Ph). ^{13}C NMR ($CDCl_3$): 18.63, 18.64, 36.81, 40.57, 47.58, 53.04, 55.62, 122.22 (C2), 123.46 (C2), 124.95, 126.88, 130.71, 144.46, 146.98, 150.41, 161.02, 172.31. LMS *m/z*: 420 (M^+), 388, 361, 274. HRMS Calcd for $C_{19}H_{20}N_2O_7S$: 420.0991. Found: 420.0976.

3.3.7. 1-Benzenesulfonyl-4a,5,8,8a-tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-2(1*H*)-quinolone (6g). Colorless plates (acetone), mp 158°C. IR (KBr): ν 1732, 1687, 1585, 1344, 1173, 758. ^{1}H NMR ($CDCl_3$) δ:1.60 (3H, s, CMe), 1.65 (3H, s, CMe), 2.15 (1H, dd, J=7.3, 17.0 Hz, H-8), 2.33 (1H, d, J=17.0 Hz, H-5), 2.63–2.69 (2H, m, H-5,8), 3.63 (3H, s, OMe), 5.20–5.24 (1H, ddd, J=2.0, 7.3, 7.3 Hz, H-8a), 5.88 (1H, d, J=9.5 Hz, H-3), 6.46 (1H, dd, J=2.0, 9.5 Hz, H-4), 7.47–7.63 (3H, m, H-Ph), 8.09 (2H, d, J=8.4 Hz, H-Ph). ^{13}C NMR ($CDCl_3$): 18.51, 18.54, 36.70, 40.55, 47.07, 52.80, 55.46, 121.96, 125.42, 125.86, 128.21 (C2), 129.00, 133.40, 139.01, 146.13, 161.00, 172.53. LMS *m/z*: 375 (M^+), 316, 229, 159. HRMS Calcd for $C_{19}H_{21}NO_5S$: 375.1141. Found: 375.1171.

3.3.8. 4a,5,8,8a-Tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-1-(2-methylbenzene-sulfonyl)-2(1*H*)-quinolone (6h). Colorless needles (ether), mp 137–139°C. IR (KBr): ν 1729, 1652, 1596, 1341, 1168, 749. ^{1}H NMR ($CDCl_3$) δ: 1.62 (3H, s, CMe), 1.66 (3H, s,CMe), 2.21 (1H, brm, H-8), 2.33 (1H, d, J=17.0 Hz, H-5), 2.70 (3H, s, PhMe), 2.74–2.87 (2H, brm, H-5,8), 3.68 (3H, s, OMe), 5.22 (1H, ddd, J=2.2, 7.4, 9.6 Hz, H-8a), 5.91 (1H, d, J=9.7 Hz, H-3), 6.47 (1H, dd, J=2.2, 9.7 Hz, H-4), 7.26 (1H, dd, J=0.8, 7.6 Hz, H-Ph), 7.32 (1H, ddd, J=0.8, 7.6, 18.0 Hz, H-Ph), 7.45 (1H, ddd, J=1.2, 7.6, 7.6 Hz, H-Ph), 8.04 (1H, dd, J=1.2, 8.0 Hz, H-Ph). ^{13}C NMR ($CDCl_3$): 18.50, 18.55, 20.76, 36.97, 40.85, 47.88, 52.91, 55.44, 121.99, 125.71, 126.02, 126.17, 131.14, 132.29, 133.46, 137.87, 139.39, 146.35, 162.28, 173.06. LMS *m/z*: 389 (M^+), 358. HRMS Calcd for $C_{20}H_{23}NO_5S$: 389.1297. Found: 389.1337.

3.3.9. 4a,5,8,8a-Tetrahydro-*cis*-4a-methoxycarbonl-6,7-dimethyl-1-(2,4,6-trimethylben-zenesulfonyl)-2(1*H*)-quinolone (6i). Colorless needles (ether–$CHCl_3$), mp 158–159°C. IR ($CHCl_3$): ν 1736, 1695, 1602, 1336, 887, 825. ^{1}H NMR ($CDCl_3$) δ: 1.61 (3H, s, CMe), 1.66 (3H, s, CMe), 2.24–2.30 (5H, m, PhMe, H-5,8), 2.63 (6H, s, PhMe×2), 2.76–2.90 (2H, m, H-5,8), 3.74 (3H, s, OMe), 5.18 (1H, ddd, J=2.0, 5.3, 7.3 Hz, H-8a), 5.92 (1H, d, J=9.8 Hz, H-3), 6.44 (1H, dd, J=2.0, 9.8 Hz, H-4), 6.93 (2H, s, H-Ph). ^{13}C NMR ($CDCl_3$) δ: 18.4, 18.55, 21.01, 22.64 (C2), 37.25, 41.13, 47.87, 52.83, 55.36, 121.46, 125.65, 126.05, 131.56 (C2), 133.35, 140.86 (C2), 143.24, 145.81, 163.33, 173.07. LMS *m/z*: 418 (M^++1), 353, 321, 294, 271, 261, 139, 91. HRMS Calcd for $C_{22}H_{27}NO_5S$: 417.1610. Found: 417.1559.

3.3.10. 4a,5,8,8a-Tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-1-(2,4,6-triisopropylbenzene-sulfonyl)-2(1*H*)-quinolone (6j). Colorless needles (ether–$CHCl_3$), mp 181–182°C. IR ($CHCl_3$): ν 1741, 1693, 1599, 1331, 883, 825. ^{1}H NMR ($CDCl_3$) δ: 1.29 (12H, d, J=6.9 Hz, CMe×4), 1.32 (6H, d, J=6.9 Hz, CMe×2), 1.61 (3H, s, CMe), 1.65 (3H, s, CMe), 2.28–2.35 (2H, brd, H-5,8), 2.70 (1H, d, J=16.6 Hz, H-5), 2.83–2.93 (2H, m, H-8, CH), 3.74 (3H, s, OMe), 4.10 (2H, m, J=6.9 Hz, CH×2), 5.30 (1H, m, J=2.0, 7.4, 9.4 Hz, H-8a), 5.92 (1H, d, J=9.6 Hz, H-3), 6.49 (1H, dd, J=2.0, 9.6 Hz, H-4), 7.16 (2H, s, H-Ph). ^{13}C NMR ($CDCl_3$) δ: 18.59, 18.63, 23.56 (C2), 23.60 (C2), 24.52 (C2), 29.63 (C2), 34.22, 37.10, 41.65, 47.99, 52.93, 54.90, 121.51, 123.95 (C2), 125.16, 126.36, 133.23, 146.10, 152.03 (C2), 153.44, 163.48, 172.82. LMS *m/z*: 502 (M^++1), 437, 355, 338, 312, 203. HRMS Calcd for $C_{28}H_{39}NO_5S$: 501.2519. Found: 501.2175.

3.3.11. 3-Bromo-4a,5,8,8a-tetrahydro-*cis*-4a-methoxycarbonyl-6,7-dimethyl-1-(4-methylbenzene-sulfonyl)-1(2*H*)-quinolone (6k). Colorless plates ($CHCl_3$). IR ($CHCl_3$): ν 1736, 1697, 1597, 1356, 815, 750. ^{1}H NMR ($CDCl_3$) δ: 1.62 (3H, s, C-Me), 1.65 (3H, s, C-Me), 2.17 (1H, dd, J=7.3, 17.1 Hz, 8-H), 2.31 (1H, d, J=17.1 Hz, 5-H), 2.42 (3H, s, Ph-Me), 2.63–2.73 (2H, m, J=17.1 Hz, 5, 8-H), 3.65 (3H, s, OMe), 5.22 (1H, m, J=2.0, 7.3, 9.3 Hz, 8a-H), 6.83 (1H, d, J=2.0 Hz, 4-H), 7.30 (2H, d, J=8.4 Hz, 3′,5′-H), 7.97 (2H, d, J=8.4 Hz, 2′,6′-H). ^{13}C NMR ($CDCl_3$) δ: 18.57, 18.65, 21.73, 36.78, 40.57, 49.69, 53.13, 55.81, 118.38, 121.97, 125.99, 129.06, 129.34, 135.38, 144.93, 145.76, 156.73, 171.77. LMS *m/z*: 469 (M^++2), 467 (M^+), 403, 388, 321, 91. HRMS Calcd for $C_{20}H_{22}BrNO_5S$: 467.0402. Found: 467.0366.

3.3.12. 3-Bromo-4a,5,8,8a-tetrahydro-*cis*-4a-methoxycarbonyl-7-methyl-1-(4-methylbenzenesulfonyl)-1(2*H*)-quinolone (6l). Colorless needles (Et_2O), mp 198°C. IR ($CHCl_3$): ν 1736, 1697, 1620, 1597, 1358, 1143, 814. ^{1}H NMR ($CDCl_3$) δ: 1.69 (3H, s, C-Me), 2.00 (1H, dd, J=3.4, 16.0 Hz, 8-H), 2.02–2.16 (2H, m, 5, 5-H), 2.19 (1H, d, J=16.0 Hz, H-8), 2.42 (3H, s, Ph-Me), 3.71 (3H, s, OMe), 5.37 (1H, brs, H-6), 5.76 (1H, dd, J=1.7, 3.4 Hz, H-8a), 6.90 (1H, d, J=1.7 Hz, 4-H), 7.30 (2H, d, J=8.1 Hz, 3′,5′-H), 7.98 (2H, d, J=8.4 Hz, 2′,6′-H). ^{13}C NMR ($CDCl_3$) δ: 21.65 (C-Me), 22.69 (C-Me), 26.00, 31.24 (C-8), 48.68 (C-5), 53.13 (O-Me), 57.56 (C-8a), 119.08 (C-3), 120.56 (C-6 or 7), 129.21 (C2), 129.43 (C2), 135.77, 136.52, 143.15, 145.05, 156.75, 171.50. LMS *m/z*: 455 (M^++2), 453 (M^+). HRMS Calcd for $C_{19}H_{20}BrNO_5S$: 453.0246. Found: 453.0215.

3.3.13. 5-Methoxycarbonylpyridin-2yl-4-methylbenzenesulfonate (4a). Colorless needles (acetone), mp 71–73°C. IR (KBr): ν 1724, 1597, 1375, 1302, 1130, 881, 817. ^{1}H NMR ($CDCl_3$) δ: 2.46 (3H, s, PhMe), 3.93 (3H, s, OMe), 7.15 (1H, dd, J=0.7, 8.4 Hz, H-3), 7.35 (2H, d, J=8.6 Hz, H-Ph), 7.92 (2H, d, J=8.6 Hz, H-Ph), 8.34 (1H, dd, J=2.3, 8.4 Hz, H-4), 8.86(1H, dd, J=0.7, 2.3 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.77, 52.58, 114.99, 124.97, 128.78 (C2), 129.78 (C2), 133.46, 141.35, 145.68, 150.23, 159.71, 164.70. LMS *m/z*: 306 (M^+−1), 243. HRMS Calcd for $C_{14}H_{13}NO_5S$: 307.0515. Found: 307.0531.

3.3.14. 5-Acetylpyridin-2yl-4-methylbenzenesulfonate (4b). Colorless powder ($CHCl_3$), mp 103–105°C. IR (KBr): ν 1686, 1587, 1371, 1316, 819. ^{1}H NMR ($CDCl_3$) δ: 2.46 (3H, s, COMe), 2.60 (3H, s, PhMe), 7.16 (1H, d, J=8.6 Hz, H-3), 7.36 (2H, d, J=8.4 Hz, H-Ph), 7.93 (2H, d, J=8.4 Hz, H-Ph), 8.29 (1H, dd, J=2.5, 8.6 Hz, H-4), 8.80 (1H, d, J=2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.93, 25.61, 118.25, 122.79, 129.61 (C2), 130.10 (C2), 132.41, 136.56, 138.57, 146.86, 159.35, 192.43. LMS *m/z*: 291 (M^+), 227, 91. HRMS Calcd for $C_{14}H_{13}NO_4S$: 291.0565. Found: 291.0522.

3.3.15. 5-Methoxycarbonylpyridin-2yl-4-methoxylbenzenesulfonate (4d). Colorless needles (ether–hexane), mp 89–92°C. IR (KBr): ν 1739, 1596, 1371, 1300, 1175, 1129, 843, 832, 807. ^{1}H NMR ($CDCl_3$) δ: 3.89 (3H, s, PhOMe), 3.93 (3H, s, COOMe), 7.00 (2H, d, J=9.1 Hz, H-Ph), 7.15 (1H, dd, J=0.7, 8.4 Hz, H-3), 7.97 (2H, d, J=9.1 Hz, H-Ph), 8.34 (1H, dd, J=2.5, 8.4 Hz, H-4), 8.86 (1H, dd, J=0.7, 2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 52.57, 55.76, 114.97, 114.33 (C2), 124.88, 127.65, 131.16 (C2), 141.32, 150.22, 159.79, 164.34, 164.73. LMS *m/z*: 323 (M^+), 259. HRMS Calcd for $C_{14}H_{13}NO_6S$: 323.0464. Found: 323.0442.

3.3.16. 5-Methoxycarbonylpyridin-2yl-benzenesulfonate (4g). Colorless needles (ether–hexane), mp 50°C. IR (KBr): ν 1728, 1590, 1386, 1182, 1133, 830, 794, 746. ^{1}H NMR ($CDCl_3$) δ: 3.93 (3H, s, OMe), 7.16 (1H, dd, J=0.7, 8.4 Hz, H-3), 7.45–7.60 (2H, m, H-Ph), 7.66–7.72 (1H, m, H-Ph), 7.92–8.08 (2H, m, H-Ph), 8.35 (1H, dd, J=2.4, 8.4 Hz, H-4), 8.86 (1H, dd, J=0.7, 2.4 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 52.60, 114.95, 125.07, 128.74 (C2), 129.14 (C2), 134.44, 136.54, 141.42, 150.21, 159.47, 164.66. LMS *m/z*: 294 (M^++1), 293 (M^+), 229. HRMS Calcd for $C_{13}H_{11}NO_5S$: 293.0358. Found: 293.0358.

3.3.17. 5-Methoxycarbonylpyridin-2yl-2-methylbenzenesulfonate (4h). Colorless oil (acetone). IR (KBr): ν 1730, 1594, 1319, 1176,748. ^{1}H NMR ($CDCl_3$) δ: 2.78 (3H, s, PhMe), 3.92 (3H, s, OMe), 7.18 (1H, dd, J=0.7, 8.5 Hz, H-3), 7.30–7.40 (2H, m, H-Ph), 7.54 (1H, ddd, J=1.3, 8.1, 8.1 Hz, H-Ph), 8.99 (1H, dd, J=1.3, 8.1 Hz, H-Ph), 8.34 (1H, dd, J=2.5, 8.5 Hz, H-4), 8.81(1H, dd, J=0.7, 2.5 Hz, H-6). ^{13}C NMR ($CDCl_3$) δ: 21.77, 52.58, 114.99, 124.97, 128.78 (C2), 129.78 (C2), 133.46, 141.35, 145.68, 150.23, 159.71, 164.70. LMS *m/z*: 307 (M^+), 243. HRMS Calcd for $C_{14}H_{13}NO_5S$: 307.0515. Found: 307.0549.

3.3.18. 4a,5,8,8a-Tetrahydro-6,7-dimethyl-*cis*-4a-methoxycarbonyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-isoquinolone (7a). Colorless needles (ether), mp 70°C. IR (KBr): ν 1736, 11359, 1172, 754. ^{1}H NMR ($CDCl_3$) δ: 1.56 (6H, s, C-Me), 1.96 (1H, d, J=17.4 Hz, 5-H), 2.14 (1H, dd, J=6.9, 17.0 Hz, 8-H), 2.26 (1H, dd, J=6.9, 17.0 Hz, 8-H), 2.37 (1H, d, J=17.4 Hz, 5-H), 2.44 (3H, s, Ph-Me), 2.95 (1H, ddd, J=1.0, 6.9, 6.9 Hz, 8a-H), 3.50 (3H, s, OMe), 5.16 (1H, dd, J=1.0, 8.1 Hz, 4-H), 7.03 (1H, d, J=8.1 Hz, 3-H), 7.32 (2H, dd, J=1.8, 6.8 Hz, 3′,5′-H), 7.86 (2H, dd, J=1.8, 6.8 Hz, 2′,6′-H). ^{13}C NMR ($CDCl_3$) δ: 17.41, 17.90, 20.68, 28.39, 35.75, 42.43, 43.92, 51.50, 111.30, 121.17, 122.86, 124.11, 127.54, 128.42, 134.24, 144.14, 168.64, 172.34. LMS *m/z*: 389 (M^+), 330, 174, 91. HRMS Calcd for $C_{20}H_{23}NO_5S$: 389.1297. Found: 389.1307.

3.3.19. 4a,5,8,8a-Tetrahydro-*trans*-4a-methoxycarbonyl-6,7-dimethyl-1-(4-methylbenzenesulfonyl)-2(1*H*)-isoquinolone (7b). Colorless plates (ether), mp 155°C. IR (KBr): ν 1732, 1597, 1359, 1172, 814. ^{1}H NMR ($CDCl_3$) δ: 1.56 (3H, s, C-Me), 1.61 (3H, s, C-Me), 2.11 (1H, d, J=16.8 Hz, 5-H), 2.17–2.24 (1H, m, 8-H), 2.27–2.33 (1H, m, 8-H), 2.44 (3H, s, Ph-Me), 2.67 (1H, d, J=16.8 Hz, 5-H), 2.72 (1H, dd, J=5.1, 11.2 Hz, 8a-H), 3.50 (3H, s, OMe), 5.16 (1H, d, J=8.1 Hz, 4-H), 7.09 (1H, d, J=8.1 Hz, 3-H), 7.33 (2H, d, J=8.3 Hz, 3′,5′-H), 7.91 (2H, d, J=8.3 Hz, 2′,6′-H). ^{13}C NMR ($CDCl_3$) δ: 18.72, 18.73, 21.66, 29.29, 39.54, 44.79, 45.84, 52.05, 112.08, 123.46, 124.35, 125.69, 128.72 (C2), 129.32 (C2), 135.47, 145.00, 168.94, 171.74. LMS *m/z*: 389 (M^+), 330, 174, 91. HRMS Calcd for $C_{20}H_{23}NO_5S$: 389.1297. Found: 389.1283.

3.4. Calculation of activation energy

The structures of the initial and the transition states (TS) were optimized using the restricted Hartree–Fock (RHF) method at the 3-21G level in the Gaussian 98 program package.[7] Solvent effects were not considered. Assuming that the diene and the dienophile were significantly separated at the initial state, the activation energy was calculated as the energy difference between the TS and the initial state. After optimizing the TS structure, vibrational calculations were performed to confirm that the TS has exactly one imaginary vibrational frequency. Intrinsic reaction coordinate calculations were also carried out to confirm that the TS connected the initial with the intended final state.

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