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A study on the substituent effects of norbornadiene derivatives in iridium-catalyzed asymmetric [2 + 2] cycloaddition reactions†

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Employing a series of norbornadiene derivatives as substrates, the effects of various substituents on the Ir-catalyzed asymmetric [2 + 2] cycloaddition reactions with arylacetylenes were studied. It was found that the atom forming the short bridge chain had a great effect on the enantioselectivity of the reaction. Heteroatoms, such as oxygen and nitrogen, always resulted in excellent enantioselectivity. However, carbon atoms could decrease the enantioselective control ability of the catalyst over the reaction. The groups on the unreacted carbon–carbon double bond were found to have but a little effect on the reaction. Based on the results of the experiments, a mechanism was also hypothesized for the reaction.

Introduction

Promoted by extensive studies, transition metal catalyzed reactions of norbornadiene derivatives and terminal alkynes have shown high reactivity and amazing diversity in recent years. Catalyzed by different transition metals or under different catalytic conditions, norbornadiene derivatives and terminal alkynes can undergo hydroalkynylation reaction,[1] ring-opening reaction,[2] homo-Diels–Alder reaction,[3] cross coupling reaction,[4] [2 + 1],[5] [2 + 2],[6] [2 + 2 + 2][7] and other[8] cycloaddition reactions, leading to various cyclic products. Among all these reactions, the [2 + 2] cycloaddition reaction of norbornadiene derivatives with terminal alkynes is even more outstanding, since fused and strained cyclobutenes are generated as products, and four or more stereocenters can be formed at the same time.[9] However, maybe due to the high reactivity of the sp^1 C–H bond of terminal alkynes towards norbornadiene substrates, only limited progress had been achieved for the catalytic [2 + 2] cycloaddition reaction of norbornadiene derivatives with terminal alkynes.[6,10]

Recently, we found that iridium complexes employing planar chiral ligands, such as Xylyl-phanephos, can promote the asymmetric [2 + 2] cycloaddition reaction of oxabenzonorbornadienes with terminal alkynes, providing chiral cyclobutene products with up to 99% ee.[11] Interestingly, by simply changing the diphosphine ligand from planar chiral to axial chiral (*e.g.* SYNPHOS), no [2 + 2] cycloaddition products were observed; instead hydroalkynylation products were generated by direct addition of the C–H bond of terminal alkynes to the C=C bond of norbornadiene deratives.[12] We had noticed that the bridge atoms in norbornadiene derivatives had a strong effect on the enantioselectivity of hydroalkynylation reaction, since high to excellent enantioselectivities could be obtained for carbo-norbornadienes (up to 97% ee),[12a] and only moderate to good enantioselectivities were obtained for oxa-norbornadienes (up to 85% ee).[12b] Enlightened by these results, obvious substituent effects of norbornadiene derivatives on the Ir-catalyzed asymmetric [2 + 2] cycloaddition reaction with terminal alkynes were expected. In this paper, we report the results of applying a series of norbornadiene derivatives with various substituents as substrates in the Ir-catalyzed asymmetric [2 + 2] cycloaddition reaction with arylacetylenes. Additionally, based on the experimental results, a reaction mechanism was also hypothesized.

Results and discussion

Asymmetric [2 + 2] cycloaddition reaction of norbornadiene derivatives with arylacetylenes

Under the reaction conditions, which had been optimized in our previous work, a series of substituted oxabenzonorbornadienes were used in the asymmetric [2 + 2] cycloaddition reaction with phenylacetylene (Table 1). It seems that the

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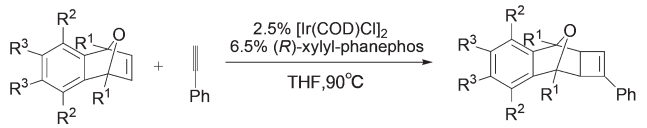
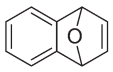
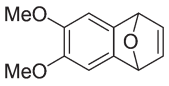
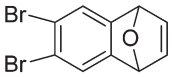
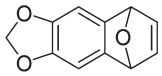
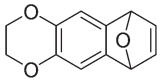
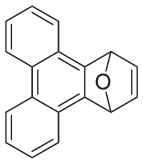
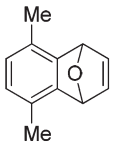
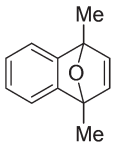
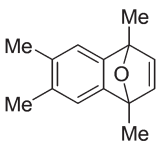
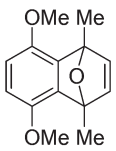
†Electronic supplementary information (ESI) available: Copies of ^1H and ^{13}C NMR spectra of new compounds, and HPLC chromatograms. See DOI: 10.1039/c3ob27382b

‡These two authors contributed equally to this paper.

Table 1 The iridium-catalyzed asymmetric [2 + 2] cycloaddition reaction of oxabenzonorbornadienes with phenylacetylene[a]



1a-j 2a-j

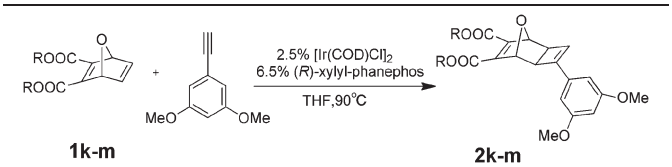
Entry	Oxanorbornadienes	Time (h)	Yield[b] (%)	ee[c] (%)
1	 1a	20	79	99
2	 1b	48	76	94
3	 1c	12	60	96
4	 1d	24	52	93
5	 1e	36	85	95
6	 1f	20	50	94
7	 1g	24	52	93
8	 1h	30	N. R.	/
9	 1i	30	N. R.	/
10	 1j	30	N. R.	/

[a] Reaction conditions: **1** (0.3 mmol), **1** : phenylacetylene : [Ir(COD)-Cl]$_2$: xylyl-phanephos = 1 : 2 : 0.025 : 0.065, in THF (2 mL) at 90 °C under Ar for the indicated period of time. [b] Isolated yield by column chromatography. [c] ee % were determined by chiral HPLC using a Chiralcel OD-H or AS-H column.

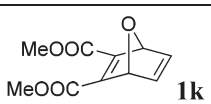
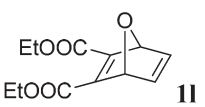
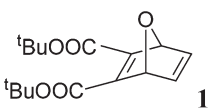
substituents on the phenyl ring have little effect on the enantioselectivity of the reaction, since all of the substrates **1b–1g** could react with phenylacetylene smoothly to generate the corresponding cyclobutene products with excellent ee values (entries 2 to 7). Though the MeO group and Br group on the phenyl ring gave comparable yields and similar ee values for the reaction products, they did affect the reaction rate greatly (entry 2 and entry 3). 48 hours were needed to complete the reaction for substrate **1b** and only 12 hours for **1c**, which means that electron-donating groups could decrease the reaction rate, however electron-withdrawing groups increased it. The steric hindrance effect of the substituents on the phenyl ring was not very obvious, since substrates bearing different bulky substituents on the phenyl ring got similar reaction results (entry 4 to entry 7). However, the steric hindrance on the bridge head carbons of the substrate was fatal for the reaction. For example, the methyl groups in substrates **1h–1j** blocked the reactions completely, and no transformation took place at all (entry 8 to entry 10).

Besides oxabenzonorbornadienes, three oxanorbornadienes **1k–1m** without a benzo group were also tested in this iridium-catalyzed asymmetric [2 + 2] cycloaddition reaction (Table 2). Instead of phenylacetylene, 3,5-dimethoxyphenylacetylene was used here in order to make the purification of products easier. From the results, it could be seen that the benzo group in the substrates was not necessary for the reaction to take place. Promoted by the Ir-catalyst, all of these three substrates could

Table 2 The expansion of oxanorbornadienes as substrates for the iridium-catalyzed asymmetric [2 + 2] cycloaddition reaction with 3,5-dimethoxyphenylacetylene[a,b]



1k-m 2k-m

Entry	Oxanorbornadienes	Time (h)	Yield[c] (%)	ee[d] (%)
1	 1k	24	35	89
2	 1l	24	30	92
3	 1m	20	22	94

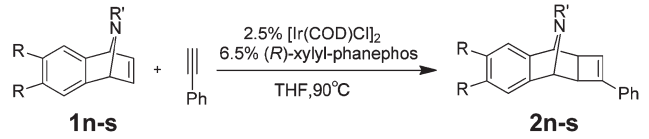
[a] Reaction conditions: **1** (0.3 mmol), **1** : arylacetylene : [Ir(COD)-Cl]$_2$: xylyl-phanephos = 1 : 2 : 0.025 : 0.065, in THF (2 mL) at 90 °C under Ar for the indicated period of time. [b] Under the same reaction conditions, 92%, 94% and 96% ee values could be obtained for the [2 + 2] cycloaddition products of **1k**, **1l** and **1m** with phenylacetylene respectively. [c] Isolated yield by column chromatography. [d] ee % were determined by chiral HPLC using a Chiralcel AD-H or OJ-H column.

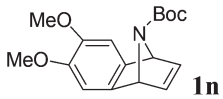
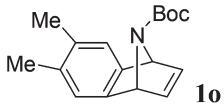
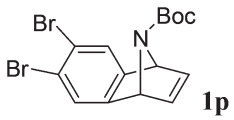
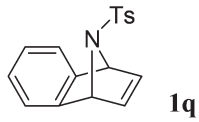
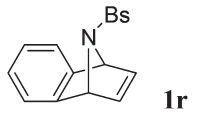
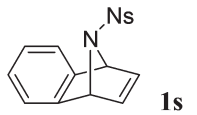
react readily with 3,5-dimethoxyphenylacetylene to generate the desired [2 + 2] cycloaddition products with high enantioselectivities. Though the products' ee values were distributed in a narrow range, it could still be concluded that bulky substituents on the unreacted carbon–carbon double bond were favourable for high enantioselective control of the reaction, since the products' ee values increased slightly from 89% to 94%, with the change of the ester groups from –COOMe to –COOEt and then to –COOBu^t.

Since the corresponding cyclobutene products have great potential to be useful intermediates for the synthesis of polycyclic alkaloids, the use of azabenzonorbornadienes as substrates in this reaction has particular importance for organic chemistry. Some azabenzonorbornadienes (**1n** to **1s**) were then tested in this Ir-catalyzed system (Table 3). Fortunately, all of these azabenzonorbornadienes were proven suitable substrates for this reaction. To the three *N*-Boc protected substrates **1n**, **1o** and **1p**, their cyclobutene products generated with phenylacetylene had high optical purities and moderate to good yields (entry 1 to entry 3). The complex of $[Ir(COD)Cl]_2$ and Xylyl-phanephos also showed excellent enantioselective control ability in the [2 + 2] cycloaddition reaction of sulfonyl protected azabenzonorbornadienes **1q**, **1r** and **1s** (entry 4 to entry 6). Though the corresponding cyclobutene product had 90% ee value, the drawback of the *p*-nitrobenzenesulfonyl group (Ns) was evident. The lowest yield was obtained for the reaction of azabenzonorbornadiene **1s**, as well as the lowest enantioselectivity (entry 6). It seems that the reduction of the electron cloud density on the nitrogen atom is disfavourable for the reaction, which implies that the nitrogen atoms on the bridge chains of these substrates maybe participate in the coordination to Ir metal during the catalytic process.

Benzonorbornadienes, which have no heteroatoms on the bridge chain, were then employed in this catalytic cycloaddition reaction (Table 4). Promoted by the chiral Ir-catalyst, several benzonorbornadienes with different substituents on the benzo-ring (**1t** to **1x**) reacted with phenylacetylene smoothly to generate the desired cyclobutene products in high yield. However, lower enantioselective control ability of the chiral iridium catalyst for these carbon-bridged norbornadiene substrates was shown, since only 69% to 80% ee values were obtained (entry 1 to entry 5). Benzonorbornadienes **1y** and **1z**, which have bulky substituents on the carbon-bridge, were inert in this catalytic system, since no reactions took place after heating and stirring for a long time (entries 6 and 7).

Table 3 The application of azabenzonorbornadienes as substrates for the iridium-catalyzed asymmetric [2 + 2] cycloaddition reaction with phenylacetylene[a]



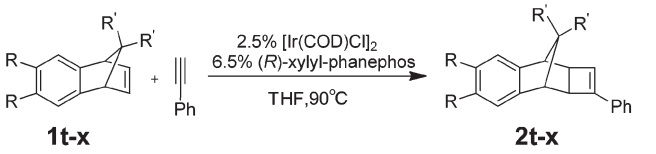
Entry	Benzonorbornadiene	Time (h)	Yield[b] (%)	ee[c] (%)
1	 **1n**	48	45	94
2	 **1o**	16	63	92
3	 **1p**	16	44	93
4	 **1q**	12	64	94
5	 **1r**	20	57	95
6	 **1s**	24	31	90

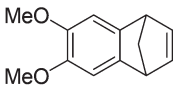
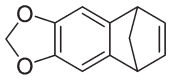
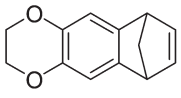
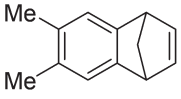
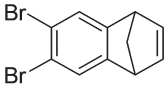
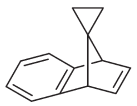
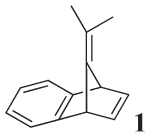
[a] Reaction conditions: **1** (0.3 mmol), **1** : phenylacetylene : [Ir(COD)-Cl]$_2$: xylyl-phanephos = 1 : 2 : 0.025 : 0.065, in THF (2 mL) at 90 °C under Ar for the indicated period of time. [b] Isolated yield by column chromatography. [c] ee % were determined by chiral HPLC using a Chiralcel OD-H or AD-H column. Boc = *t*-butoxycarbonyl group, Ts = *p*-toluenesulfonyl group, Bs = benzenesulfonyl group, Ns = *p*-nitrobenzenesulfonyl group.

Mechanism for Ir-catalyzed [2 + 2] cycloaddition

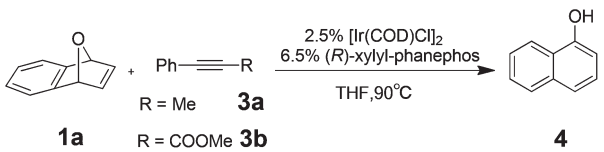
To hypothesize the [2 + 2] cycloaddition reaction mechanism, the following two reactions should be mentioned. (a) During our expanding of the scope of alkynes, two representative internal alkynes **3a** and **3b** had been explored in the Ir-catalytic system to react with oxabenzonorbornadiene **1a**. Surprisingly, after two days' heating and stirring, only 1-naphthol **4** (about 30% yield) and some unreacted oxabenzonorbornadiene **1a** were separated out, and none of the targeted [2 + 2] cycloaddition products could be detected. Independent experiments had proved that the complex of $[Ir(COD)Cl]_2$ and (*R*)-Xylyl-phanephos can catalyze the isomerization of oxabenzonorbornadiene **1a** to 1-naphthol. So, it can be concluded that, different from the Rh-catalyzed [2 + 2] cycloaddition reaction of norbornadiene derivatives,[10p] this Ir-catalyzed one is effective only for terminal but not internal alkynes. (b) Under the optimized reaction conditions, when spiro chiral diphosphine ligand (*R*)-xyl-SDP[13] was used instead of (*R*)-xylyl-phanephos, oxabenzonorbornadiene **1a** could also react with phenylacetylene. However, not only [2 + 2] cycloaddition product **2a**, but also the hydroalkynylation product **5**, were generated. The former was isolated in 12% yield with 28% ee, and the latter was isolated in 20% yield with 44% ee (Schemes 1–3).

Table 4 The using of benzonorbornadienes as substrates for the iridium-catalyzed asymmetric [2 + 2] cycloaddition reaction with phenylacetylene[a]



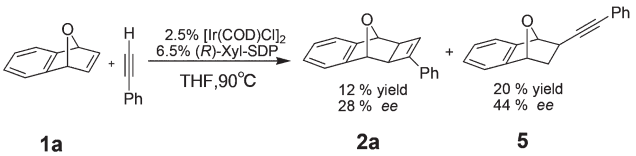
Entry	Benzonorbornadiene	Time (h)	Yield[b] (%)	ee[c] (%)
1	 1t	60	85	76
2	 1u	24	86	69
3	 1v	60	89	73
4	 1w	24	26	80
5	 1x	24	26	71
6	 1y	60	N. R.	/
7	 1z	60	N. R.	/

[a] Reaction conditions: 1 (0.3 mmol), **1** : phenylacetylene : [Ir(COD)Cl]$_2$: xylyl-phanephos = 1 : 2 : 0.025 : 0.065, in THF (2 mL) at 90 °C under Ar for the indicated period of time. [b] Isolated yield by column chromatography. [c] ee % were determined by chiral HPLC using a Chiralcel OD-H column.

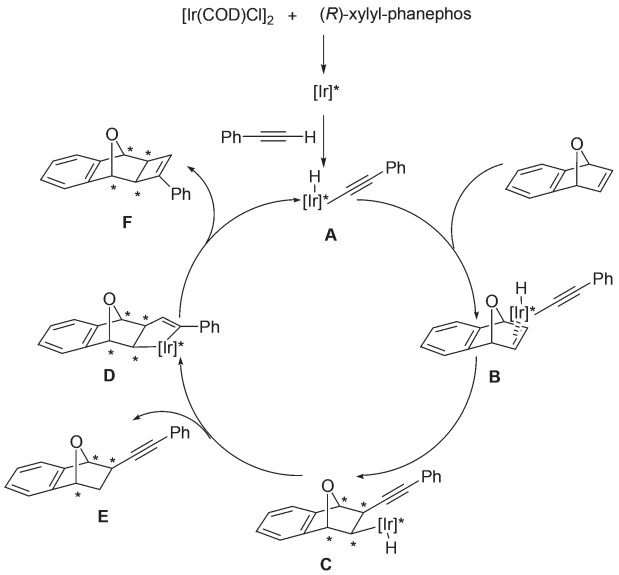


Scheme 1 Exploration of internal alkynes in the Ir-catalyzed [2 + 2] cycloaddition reaction.

Based on the results of all experiments, a mechanism was hypothesized for this [2 + 2] cycloaddition reaction. The catalytic cycle is started by the oxidative addition of terminal alkyne to the chiral Ir(I) complex to generate the intermediate **A**. The coordination of the alkene moiety to the chiral iridium(III) complex **A** forms **B**. After the migratory insertion of the phenylethynyl group to the carbon–carbon double bond in an *exo* manner, the intermediate **C** is produced. Although the



Scheme 2 The use of (*R*)-xyl-SDP as chiral ligand in the Ir-catalyzed [2 + 2] cycloaddition reaction.



Scheme 3 Hypothesized mechanism for the Ir-catalyzed asymmetric [2 + 2] cycloaddition reaction.

reductive elimination of the iridium(III) part will give the hydroalkynylation product **E**, further addition of the Ir–H bond to the triple bond in **C** is going on in this cycle, and the metallocyclopentenyl intermediate **D** is constructed. As the last step, the reductive elimination of iridium from **D** produces the [2 + 2] cycloaddition product **F** and the intermediate **A** to complete the cycle.

Conclusions

A series of norbornadiene derivatives had been employed as substrates in Ir-catalyzed asymmetric [2 + 2] cycloaddition reaction with arylacetylenes to investigate the substituent effects on the reaction. It was found that the kind of atoms on the bridge chain was decisive to the enantioselective level of the reaction. Heteroatoms with a weak coordinating ability, such as oxygen and nitrogen, always resulted in excellent enantioselectivity for the [2 + 2] cycloaddition reaction, and the products generally had more than 90% ee values. However, carbon atoms on the bridge chain decreased the enantioselectivity of the reaction greatly, and the corresponding products' ee values mainly ranged from 69% to 80%. The groups on the unreacted carbon–carbon double bond, including various substituted benzo-rings and ester groups, had but a little effect on

the reaction. Bulky steric hindrance on the bridge-head carbons or bridge chains could block the reaction completely. Based on all the experiment results, an interesting reaction mechanism had also been hypothesized. Further efforts to understand and improve this Ir-catalyzed asymmetric [2 + 2] cycloaddition reaction are still ongoing.

Experimental section

General remarks

The reactions were carried out under argon atmosphere by using Drybox (Mikrouna, Supper 1220/750). Norbornadiene derivatives were synthesized according to the published procedures.[14] Arylacetylenes were purchased from reagent companies and distilled before use, and other commercial reagents were used as received without further purification. Anhydrous THF was distilled from sodium benzophenone ketyl prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-Avance 400 spectrometer. Chemical shifts (δ) were reported in ppm with tetramethylsilane as an internal standard, and J values were given in Hz. The ee values were determined by an Agilent 1260 Series HPLC using Daicel AD-H, OD-H, OJ-H or AS-H chiral columns with a mixture of i-propyl alcohol and *n*-hexane as the eluent. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200–300 mesh) with petroleum ether and ethyl acetate as eluents.

General procedure for the Ir-catalyzed [2 + 2] cycloaddition reactions

Under the protection of argon in a drybox, the mixture of $[Ir(COD)Cl]_2$ (5.1 mg, 0.0075 mmol), (*R*)-xylyl-phanephos (13.4 mg, 0.0195 mmol) and THF (2 mL) was stirred at room temperature for 30 minutes in a reaction tube. After the addition of a norbornadiene derivative (0.3 mmol), the stirring was continued for another 20 minutes. After the addition of arylacetylene (0.6 mmol), the reaction tube was sealed with a rubber septum, and then moved out of the drybox to an oil bath. The mixture was stirred at 90 °C (bath temperature) until the reaction was complete. After vacuum evaporation of the solvent, the residue was purified by column chromatography through silica gel to yield the aimed product. The ee value of the product was determined by chiral HPLC analysis.

Cyclobutene 2b. White solid, 76% yield, mp 173–175 °C, 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.47 (m, 2H), 7.37–7.34 (m, 2H), 7.29–7.25 (m, 1H), 6.98 (s, 1H), 6.92 (s, 1H), 6.48 (s, 1H), 5.10 (s, 1H), 4.97 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.05 (d, J = 3.6 Hz, 1H), 2.72 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.79, 147.76, 147.15, 137.58, 136.99, 133.22, 128.47, 128.12, 127.20, 124.94, 104.82, 104.74, 76.82, 76.07, 56.39, 47.41, 44.84; HRMS (ESI) calcd for $C_{20}H_{18}O_3$ $[M]^+$, 306.1256, found 306.1259; HPLC (Chiralcel AS-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 16.8 min, t_{major} = 22.7 min.

Cyclobutene 2c. White solid, 60% yield, mp 149–150 °C, 96% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.55 (s, 1H), 7.47–7.45 (m, 2H), 7.39–7.35 (m, 2H), 7.32–7.26 (m, 1H), 6.44 (s, 1H), 5.10 (s, 1H), 4.98 (s, 1H), 3.09 (d, J = 3.6 Hz, 1H), 2.76 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.56, 146.27, 145.76, 132.76, 128.59, 128.44, 126.45, 125.23, 125.13, 124.95, 122.32, 76.19, 75.45, 46.48, 43.94; HRMS (ESI) calcd for $C_{18}H_{12}OBr_2$ $[M]^+$, 401.9255, found 401.9260; HPLC (Chiralcel OD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 13.0 min, t_{minor} = 14.8 min.

Cyclobutene 2d. White solid, 52% yield, mp 149–151 °C, 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.49 (m, 2H), 7.40–7.37 (m, 2H), 7.33–7.31 (m, 1H), 6.89 (s, 1H), 6.84 (s, 1H), 6.50 (s, 1H), 6.00–5.97 (m, 2H), 5.08 (s, 1H), 4.95 (s, 1H), 3.07 (d, J = 3.6 Hz, 1H), 2.74 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.13, 146.06, 138.90, 138.29, 133.13, 128.49, 128.16, 127.15, 124.94, 102.13, 102.06, 101.21, 75.88, 47.13, 44.58; HRMS (ESI) calcd for $C_{19}H_{14}O_3Na$ $[M + Na]^+$, 313.0840, found 313.0849; HPLC (Chiralcel OD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 23.6 min, t_{major} = 25.8 min.

Cyclobutene 2e. White solid, 85% yield, mp 113–115 °C, 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.49 (m, 2H), 7.40–7.37 (m, 2H), 7.33–7.31 (m, 1H), 6.87 (s, 1H), 6.82 (s, 1H), 6.46 (s, 1H), 5.06 (s, 1H), 4.93 (s, 1H), 4.23 (s, 4H), 3.06 (d, J = 3.6 Hz, 1H), 2.74 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.01, 141.72, 138.15, 137.57, 133.15, 128.48, 128.14, 127.11, 124.95, 109.69, 109.59, 76.44, 75.70, 64.32, 47.40, 44.88; HRMS (ESI) calcd for $C_{20}H_{16}O_3$ $[M]^+$, 304.1099, found 304.1100; HPLC (Chiralcel OD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 24.8 min, t_{minor} = 31.8 min.

Cyclobutene 2f. Yellow solid, 50% yield, mp 201–202 °C, 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78–8.75 (m, 2H), 8.13–8.00 (m, 1H), 7.96–7.94 (m, 1H), 7.71–7.66 (m, 4H), 7.58–7.56 (m, 2H), 7.44–7.40 (m, 2H), 7.34–7.33 (m, 1H), 6.64 (s, 1H), 5.78 (s, 1H), 5.65 (s, 1H), 3.16 (d, J = 3.2 Hz, 1H), 2.83 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.42, 140.55, 139.86, 133.12, 130.11, 130.07, 128.60, 128.29, 127.52, 126.94, 126.27, 126.21, 124.97, 124.10, 124.04, 123.71, 123.66, 76.32, 75.48, 47.34, 44.89; HRMS (ESI) calcd for $C_{26}H_{18}O$ $[M]^+$, 346.1358, found 346.1354; HPLC (Chiralcel AS-H, i-propanol–hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 24.4 min, t_{major} = 28.7 min.

Cyclobutene 2g. White solid, 52% yield, mp 168–170 °C, 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.47 (m, 2H), 7.39–7.35 (m, 2H), 7.30–7.24 (m, 1H), 6.89 (s, 2H), 6.49 (s, 1H), 5.20 (s, 1H), 5.07 (s, 1H), 3.05 (d, J = 3.6 Hz, 1H), 2.72 (d, J = 3.6 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.81, 143.13, 142.60, 133.20, 128.51, 128.17, 128.08, 128.06, 126.98, 126.85, 126.82, 124.90, 75.46, 74.70, 46.12, 43.65, 18.13, 18.08; HRMS (ESI) calcd for $C_{20}H_{18}O$ $[M]^+$, 274.1358, found 274.1357; HPLC (Chiralcel OD-H,

i-propanol–hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 7.6 min, t_{major} = 10.1 min.

Cyclobutene 2k. Yellow Oil, 35% yield, 89% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, J = 2.3 Hz, 2H), 6.47 (s, 1H), 6.41 (t, J = 2.16 Hz, 1H), 5.00 (s, 1H), 4.90 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.81 (s, 6H), 3.19 (d, J = 3.4 Hz, 1H), 2.88 (d, J = 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.10, 163.06, 161.00, 146.99, 143.82, 143.30, 134.38, 127.36, 103.19, 100.49, 78.57, 77.88, 55.41, 52.44, 52.36, 44.56, 41.91. HRMS (ESI) calcd for $C_{20}H_{20}O_7$ $[M]^+$, 372.1209, found 372.1205; HPLC (Chiralcel AD-H, i-propanol–hexane = 30/70, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 8.4 min, t_{major} = 18.3 min.

Cyclobutene 2l. White solid, 30% yield, mp 89–90 °C, 92% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, J = 2.1 Hz, 2H), 6.47 (s, 1H), 6.41 (t, J = 2.28 Hz, 1H), 5.00 (s, 1H), 4.89 (s, 1H), 4.35–4.26 (m, 4H), 3.81 (s, 6H), 3.19 (d, J = 3.56 Hz, 1H), 2.88 (d, J = 3.50 Hz, 1H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.86, 162.81, 161.00, 147.01, 143.60, 143.19, 134.43, 127.40, 103.12, 100.61, 78.59, 77.91, 61.44, 55.38, 44.68, 42.03, 14.12. HRMS (ESI) calcd for $C_{22}H_{24}O_7$ $[M]^+$, 400.1522, found 400.1528; HPLC (Chiralcel OJ-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 25.3 min, t_{minor} = 30.0 min.

Cyclobutene 2m. Yellow oil, 22% yield, 94% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, J = 2.2 Hz, 2H), 6.46 (s, 1H), 6.40 (t, J = 2.26 Hz, 1H), 4.92 (s, 1H), 4.80 (s, 1H), 3.80 (s, 6H), 3.19 (d, J = 3.48 Hz, 1H), 2.86 (d, J = 3.50 Hz, 1H), 1.55 (s, 9H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.99, 161.90, 160.97, 147.09, 144.08, 143.12, 134.54, 127.52, 103.01, 100.64, 82.42, 82.32, 78.69, 55.36, 44.85, 42.20, 28.17, 28.14. HRMS (ESI) calcd for $C_{26}H_{32}O_7$ $[M]^+$, 456.2148, found 456.2156; HPLC (Chiralcel OD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 5.6 min, t_{major} = 11.6 min.

Cyclobutene 2n. White solid, 45% yield, mp 116–117 °C, 94% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.36 (m, 5H), 6.98 (s, 1H), 6.94 (s, 1H), 6.47 (s, 1H), 5.07 (s, 1H), 4.97 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.92 (d, J = 3.6 Hz, 1H), 2.72 (d, J = 3.2 Hz, 1H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.37, 147.68, 147.41, 147.35, 136.56, 136.04, 133.60, 129.58, 128.38, 128.23, 125.15, 124.96, 105.18, 105.09, 104.96, 79.32, 59.86, 59.40, 56.32, 47.87, 46.02, 28.34, 27.75; HRMS (ESI) calcd for $C_{25}H_{27}NO_4$ $[M]^+$, 405.1940, found 405.1938; HPLC (Chiralcel OD-H, i-propanol–hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 14.3 min, t_{minor} = 18.7 min.

Cyclobutene 2o. White solid, 63% yield, mp 202–204 °C, 92% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.35 (m, 5H), 7.11 (s, 1H), 7.09 (s, 1H), 6.45 (s, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 2.92 (d, J = 3.2 Hz, 1H), 2.72 (d, J = 3.2 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.49, 147.57, 141.88, 141.48, 134.36, 134.24, 133.68, 129.48, 128.35, 128.16, 125.14, 124.97, 121.57, 121.33, 79.15, 59.62, 59.09, 47.80, 45.96, 28.35, 27.77, 19.97; HRMS (ESI) calcd for $C_{25}H_{27}NO_2$ $[M]^+$, 373.2042, found 373.2043; HPLC (Chiralcel AD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 6.1 min, t_{minor} = 8.6 min.

Cyclobutene 2p. White solid, 44% yield, mp 197–198 °C, 93% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.56 (m, 2H), 7.46–7.36 (m, 5H), 6.42 (s, 1H), 5.07 (s, 1H), 5.00 (s, 1H), 2.93 (d, J = 3.2 Hz, 1H), 2.74 (d, J = 3.2 Hz, 1H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.25, 147.17, 145.14, 144.80, 133.17, 128.72, 128.51, 128.46, 125.56, 125.39, 125.12, 122.09, 79.87, 59.32, 58.86, 46.96, 45.07, 28.28, 27.70; HRMS (ESI) calcd for $C_{23}H_{21}NO_2Br_2$ $[M]^+$, 500.9939, found 500.9952; HPLC (Chiralcel AD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 7.6 min, t_{minor} = 9.2 min.

Cyclobutene 2q. White solid, 64% yield, mp 186–188 °C, 94% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.28 (m, 3H), 7.07–7.05 (m, 1H), 7.00–6.92 (m, 3H), 6.86 (s, 1H), 6.84 (s, 1H), 6.47 (s, 1H), 4.92 (s, 1H), 4.80 (s, 1H), 2.99 (d, J = 3.2 Hz, 1H), 2.67 (d, J = 3.2 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.66, 143.33, 142.59, 142.50, 136.05, 132.97, 128.79, 128.53, 128.31, 127.62, 126.68, 126.49, 125.06, 120.68, 120.59, 62.27, 61.72, 47.58, 45.00, 21.33; HRMS (ESI) calcd for $C_{25}H_{21}NO_2S$ $[M]^+$, 399.1293, found 399.1299; HPLC (Chiralcel AD-H, i-propanol–hexane = 10/90, flow rate 1 mL min^{-1}, λ = 254 nm): t_{minor} = 14.5 min, t_{major} = 27.5 min.

Cyclobutene 2r. White solid, 57% yield, mp 166–168 °C, 95% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.35 (m, 8H), 7.10–7.04 (m, 3H), 6.99–6.89 (m, 3H), 6.48 (s, 1H), 4.95 (s, 1H), 4.83 (s, 1H), 3.00 (d, J = 4.1 Hz, 1H), 2.69 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.15, 142.43, 139.01, 132.95, 132.91, 131.81, 128.93, 128.56, 128.38, 128.21, 127.29, 126.63, 126.30, 125.43, 125.07, 123.26, 121.32, 120.64, 120.56, 62.35, 61.83, 47.60, 45.00; HRMS (ESI) calcd for $C_{24}H_{19}NO_2S$ $[M]^+$, 385.1137, found 385.1139; HPLC (Chiralcel AD-H, i-propanol–hexane = 20/80, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 7.2 min, t_{major} = 14.4 min.

Cyclobutene 2s. White solid, 31% yield, mp 210–211 °C, 90% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92–7.89 (m, 2H), 7.62–7.58 (m, 2H), 7.45–7.42 (m, 2H), 7.39–7.32 (m, 3H), 7.09 (m, 1H), 7.02 (m, 1H), 6.98–6.93 (m, 2H), 6.47 (s, 1H), 4.98 (s, 1H), 4.88 (s, 1H), 3.04 (d, J = 3.6 Hz, 1H), 2.74 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.29, 146.75, 145.01, 143.03, 142.32, 132.60, 128.68, 128.63, 126.88, 126.49, 124.99, 123.36, 120.85, 120.75, 62.78, 62.06, 47.44, 44.90; HRMS (ESI) calcd for $C_{24}H_{18}N_2O_4S$ $[M]^+$, 430.0987, found 430.0990; HPLC (Chiralcel AD-H, i-propanol–hexane = 10/90, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 18.0 min, t_{major} = 30.3 min.

Cyclobutene 2t. White solid, 85% yield, mp 103–104 °C, 76% ee; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.46 (m, 2H), 7.38–7.34 (m, 2H), 7.29–1.26 (m, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.46 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.13 (s, 1H), 2.98 (s, 1H), 2.88 (d, J = 3.2 Hz, 1H), 2.55 (d, J = 3.2 Hz, 1H), 1.94 (d, J = 9.6 Hz, 1H), 1.67 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.74, 146.76, 140.62, 139.83, 133.88, 128.61, 128.51, 127.98, 125.06, 106.75, 106.61, 56.41, 47.79, 45.23, 41.86, 41.46, 40.73; HRMS (ESI) calcd for $C_{21}H_{20}O_2$ $[M]^+$, 304.1463, found 304.1467; HPLC (Chiralcel OD-H, i-propanol–hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 13.7 min, t_{minor} = 15.3 min.

Cyclobutene 2u. White solid, 86% yield, mp 144–146 °C, 69% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H), 7.46–7.43 (m, 2H), 7.33–7.29 (m, 1H), 6.85 (s, 1H), 6.80 (s, 1H), 6.48 (s, 1H), 5.94–5.91 (dd, J = 9.8, 1.6 Hz, 2H), 3.12 (s, 1H), 2.98 (s, 1H), 2.88 (d, J = 3.2 Hz, 1H), 2.56 (d, J = 3.6 Hz, 1H), 1.94 (d, J = 9.2 Hz, 1H), 1.71 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.61, 144.70, 141.70, 140.89, 133.70, 128.48, 128.32, 127.87, 124.92, 103.88, 103.74, 100.52, 47.41, 44.85, 41.68, 41.32, 40.54; HRMS (ESI) calcd for $C_{20}H_{16}O_2$ $[M]^+$, 288.1150, found 288.1153; HPLC (Chiralcel OD-H, i-propanol–hexane = 3/97, flow rate 0.5 mL min^{-1}, λ = 254 nm): t_{major} = 12.3 min, t_{minor} = 14.2 min.

Cyclobutene 2v. White solid, 89% yield, mp 105–107 °C, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.38–7.33 (m, 2H), 7.28–7.26 (m, 1H), 6.80 (s, 1H), 6.75 (s, 1H), 6.43 (s, 1H), 4.22 (s, 4H), 3.09 (s, 1H), 2.94 (s, 1H), 2.88 (d, J = 3.2 Hz, 1H), 2.55 (d, J = 3.2 Hz, 1H), 1.91 (d, J = 9.6 Hz, 1H), 1.65 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.47, 141.34, 140.69, 140.57, 133.72, 128.47, 128.23, 127.84, 124.93, 111.09, 110.92, 64.36, 47.55, 45.00, 41.30, 40.78, 40.19; HRMS (ESI) calcd for $C_{21}H_{18}O_2$ $[M]^+$, 302.1307, found 302.1300; HPLC (Chiralcel OD-H, i-propanol–hexane = 5/95, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{major} = 5.8 min, t_{minor} = 10.9 min.

Cyclobutene 2w. White solid, 26% yield, mp 162–163 °C, 80% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.47 (m, 2H), 7.38–7.34 (m, 2H), 7.29–7.27 (m, 1H), 7.08 (s, 1H), 7.02 (s, 1H), 6.45 (s, 1H), 3.13 (s, 1H), 2.98 (s, 1H), 2.89 (d, J = 3.2 Hz, 1H), 2.56 (d, J = 3.2 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 1.90 (d, J = 9.6 Hz, 1H), 1.65 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.43, 146.05, 145.29, 133.78, 133.15, 128.48, 128.28, 127.83, 124.93, 122.94, 122.78, 47.50, 44.96, 41.36, 40.98, 40.25, 19.91; HRMS (ESI) calcd for $C_{21}H_{20}$ $[M]^+$, 272.1565, found 272.1563; HPLC (Chiralcel OD-H, i-propanol–hexane = 3/97, flow rate 0.5 mL min^{-1}, λ = 254 nm): t_{minor} = 8.0 min, t_{major} = 8.9 min.

Cyclobutene 2x. White solid, 26% yield, mp 140–142 °C, 71% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.47–7.44 (m, 3H), 7.39–7.35 (m, 2H), 7.32–7.29 (m, 1H), 6.43 (s, 1H), 3.16 (s, 1H), 3.03 (s, 1H), 2.89 (d, J = 3.2 Hz, 1H), 2.57 (d, J = 3.2 Hz, 1H), 1.92 (d, J = 10.0 Hz, 1H), 1.70 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.41, 148.74, 147.01, 133.26, 128.57, 128.16, 127.53, 126.78, 126.61, 124.94, 120.66, 46.48, 43.93, 41.48, 40.89, 40.38; HRMS (ESI) calcd for $C_{19}H_{14}Br_2$ $[M]^+$, 399.9462, found 399.9457; HPLC (Chiralcel OD-H, i-propanol–hexane = 3/97, flow rate 0.5 mL min^{-1}, λ = 254 nm): t_{major} = 9.5 min, t_{minor} = 10.4 min.

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