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# Convergent Synthesis of Azabicycloalkenones using Squaric Acid as Platform

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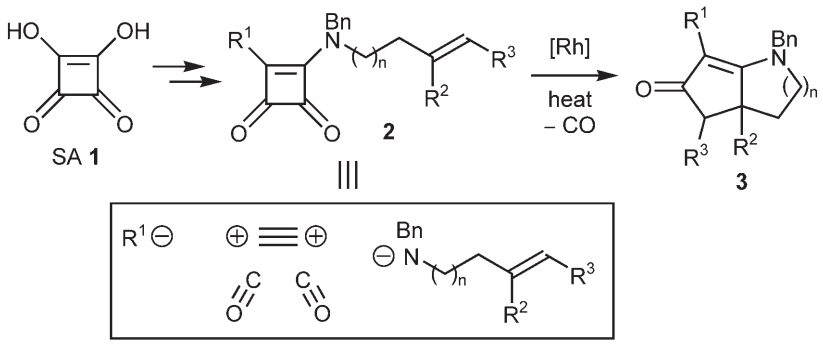
**Abstract:** The synthesis of azabicycloalkenones bearing a vinylogous amide moiety was achieved by means of the rhodium-catalyzed decarbonylative cycloaddition of cyclobutenediones with a pendant alkene. The starting cyclobutenediones were efficiently prepared from appropriate squaric acid monoesters and *N*-benzylalkenylamines under microwave heating conditions.

**Keywords:** C–C activation; cycloaddition; heterocycles; rhodium; small ring systems

## Introduction

The cobalt-mediated cycloaddition of an alkyne, an alkene, and CO leading to a cyclopentenone has been known as the Pauson–Khand (PK) reaction.[1] In particular, catalytic intramolecular PK reactions of enynes have received considerable attention to date, owing to their synthetic importance for giving the bicycloalkenone framework.[2] Furthermore, rhodium-catalyzed PK reactions that utilize aldehydes as CO sources have been developed recently to avoid the direct use of harmful CO gas.[3] In this context, we envisioned that an alternative catalytic intramolecular PK-type reaction without the direct use of CO gas would be realized using squaric acid (SA) **1** as a platform (Scheme 1). In other words, the cyclobutenedione ring might be fully utilized as an acetylene dication equivalent as well as a CO source. The products that might be obtained through this transformation are bicycloalkenones **3** bearing a vinylogous amide moiety. To the best of our knowledge, the *catalytic* PK reaction giving such products has so far remained unexplored, although Witulski and co-workers have reported the conventional cobalt-mediated PK reactions of *N*-butenylalkynylamides.[4]

Cyclobutenediones, specifically SA derivatives, are useful 4-carbon synthons in organic synthesis.[5] Highly substituted carbo- and heterocyclic compounds have been obtained by means of derivatizations and subsequent ring expansion of their strained four-membered rings. On the other hand, cyclobutenediones are also known as precursors of cyclopropenones and



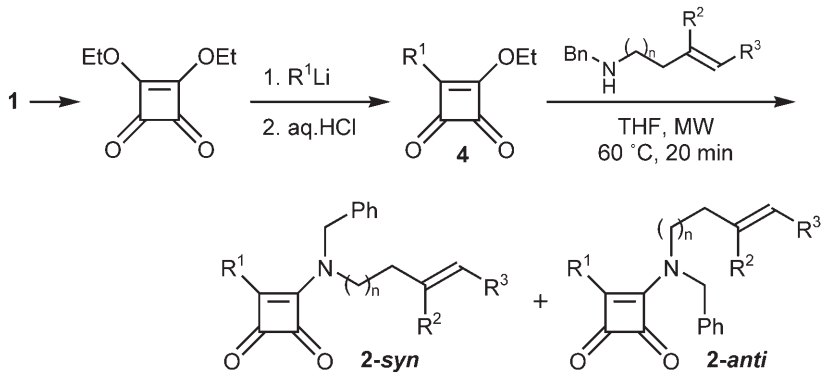

**Scheme 1.** Synthesis of azabicycloalkenones using squaric acid as platform.

alkynes. Under thermolysis or photolysis conditions, 3,4-disubstituted cyclobutenediones were converted to the corresponding cyclopropenones as a consequence of concomitant extrusion of one CO molecule.[6] Moreover, the complete loss of carbon monoxide from cyclobutenediones affording internal alkynes was utilized for the synthesis of polyalkyne materials.[7] With these reports in mind, one might consider that cyclobutenediones undergo decarbonylative transformation into other ring systems *via* the incorporation of additional unsaturated molecules. In fact, Kondo, Mitsudo, and co-workers have realized for the first time such a decarbonylative cycloaddition of alkoxycyclobutenediones with alkenes under ruthenium catalysis.[8] Although this reaction afforded interesting cyclopentenone derivatives, the scope of the alkene component is confined to norbornene or ethylene, and the harmful CO gas at a pressure of 3–15 atm is essential to suppress complete decarbonylation of the cyclobutenediones. To address these issues, we report herein the new rhodium-catalyzed decarbonylative transformation of cyclobutenediones **2** into azabicycloalkenones **3** (Scheme 1).

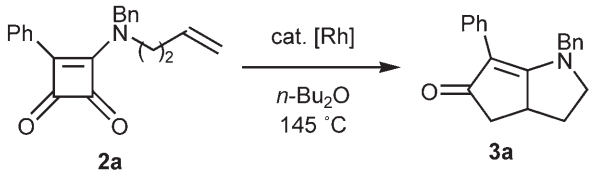
## Results and Discussion

Our synthetic strategy starts with the preparation of cyclobutenedione substrates **2** from appropriate squaric acid monoesters **4** (Scheme 2). Monoalkoxycyclobutenediones **4**, which were derived from diethyl squarate *via* known procedures,[9] were allowed to react with *N*-benzylalkenylamines in THF under microwave irradiation conditions (60 °C, 20 min) to furnish **2** in excellent yields (see Table 2). The $^1$H NMR analysis of the obtained products revealed that **2** exist




**Scheme 2.** Synthesis of cyclobutenedione substrates.

**Table 1.** Optimization of reaction conditions for conversion of **2a** to **3a.**[a]




| Run | Catalyst precursor | *t* [h] | Yield [%] |
|---|---|---|---|
| 1 | 10 mol% [RhCl(PPh$_3$)$_3$] | 58 | 42[b] |
| 2 | 5 mol% [{RhCl(cod)}$_2$], 25 mol% PPh$_3$ | 42 | 57[b] |
| 3 | 5 mol% [{RhCl(cod)}$_2$], 20 mol% PPh$_3$ | 38 | 62[b] |
| 4 | 5 mol% [{RhCl(cod)}$_2$], 10 mol% PPh$_3$ | 38 | 43[b,c] |
| 5 | 5 mol% [{RhCl(cod)}$_2$], 20 mol% P(*p*-MeOC$_6$H$_4$)$_3$ | 77 | 41[d] |
| 6 | 5 mol% [{RhCl(cod)}$_2$], 20 mol% P(*p*-FC$_6$H$_4$)$_3$ | 96 | 47[d] |
| 7 | 5 mol% [{RhCl(cod)}$_2$], 20 mol% PPh$_3$, 12 mol% AgPF$_6$ | 61 | 24[b] |
| 8 | 5 mol% [{RhCl(cod)}$_2$], 10 mol% dppe | 71 | 36[d] |

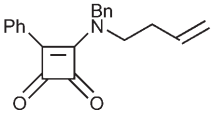
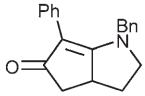
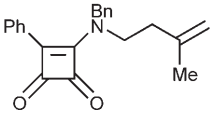
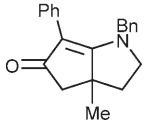
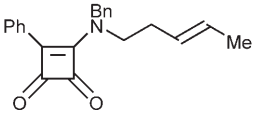
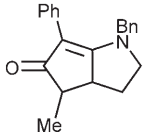
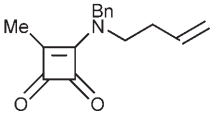
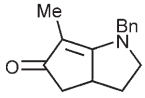
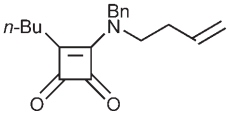
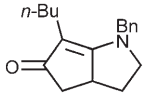
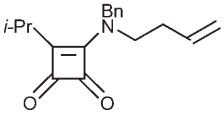
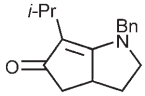
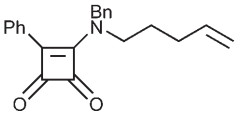
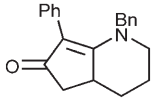
[a] All reactions were carried out in *n*-Bu$_2$O at 145 °C.
[b] Yields estimated by $^1$H NMR analysis of purified samples.
[c] 20% of **2a** was recovered.
[d] Isolated yields.

as *ca.* 1:1 *syn/anti*-isomer mixtures at room temperature, due to the partial double bond character of the vinylogous amide C–N bonds.[10]

With desired cyclobutenediones in hand, we explored the decarbonylative transformation of these substrates. Toward this aim, we decided to use rhodium complexes as catalyst precursors for following reasons: (1) rhodium complexes catalyze intramolecular PK reactions under a CO pressure of less than 1 atm,[11] (2) rhodium catalysts are able to utilize carbonyl compounds as CO sources,[3] and finally, (3) rhodium complexes have proved to be effective for the ring transformation of cyclobutanones *via* C–C bond cleavage.[12] Thus, cyclobutenedione **2a** was treated with 10 mol% of Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$], in dibutyl ether (0.1 M) at 145 °C for 58 h to give rise to the expected azabicyclo[3.3.0]octenone **3a** (Table 1). It is noteworthy that the Wilkinson's catalyst was reported to be totally ineffective for the prototypical intermolecular reaction.[8a] Although **3a** was formed in 42% yield by $^1$H NMR analysis (run 1), its isolation was unfortunately hampered by inseparable triphenylphosphine oxide. With the combination of 5 mol% [{RhCl(cod)}$_2$] (10 mol% Rh) and 25 mol% PPh$_3$, the reaction went to completion after 42 h to give **3a** in a higher yield (run 2). The highest yield of 62% was obtained with a decreased PPh$_3$ loading of 20 mol% (run 3), whereas a 10 mol% loading of the phosphine slowed the reaction rate and the yield was not further improved (run 4). Thus, the Rh/phosphine ratio of 1/2 was found to be optimal. The use of more electron-rich tri(*p*-methoxyphenyl)phosphine or more electron-deficient tri(*p*-fluorophenyl)phosphine in place of PPh$_3$ slowed the reaction, resulting in lower yields of **3a** (runs 5 and 6). In these cases, however, **3a** was isolated in pure form without contamination of the corresponding phosphine oxides. In striking contrast to the neutral catalysts, a relevant cationic system *in-situ* produced from [RhCl(cod)]$_2$, PPh$_3$, and AgPF$_6$ proved to be much less effective, causing the

**Table 2.** Synthesis of azabicycloheptenones **3** from cyclobutenediones **2**.[a]

| Run | Compound **2** | | | *t* [h] | Compound **3** | | |
|---|---|---|---|---|---|---|---|
| | No. | Structure | Yield [%] | | No. | Structure | Yield [%] |
| 1 | **2a** |  | 98 | 38 | **3a** |  | 62[b] |
| 2 | **2b** |  | 99 | 60 | **3b** |  | 67[b] |
| 3 | **2c** |  | quant. | 72 | **3c** |  | 29[c,d] |
| 4 | **2d** |  | 92 | 33 | **3d** |  | 45[d] |
| 5 | **2e** |  | 96 | 34 | **3e** |  | 56[d] |
| 6 | **2f** |  | 96 | 96 | **3f** |  | 37[b,c] |
| 7 | **2g** |  | 97 | 48 | **3g** |  | 51[d] |

[a] All reactions were carried out with 5 mol% [{RhCl(cod)}$_2$] and 20 mol% PPh$_3$ in *n*-Bu$_2$O at 145 °C.
[b] Yields estimated by $^1$H NMR analysis of purified samples.
[c] Starting materials **2c** and **2f** were recovered in 10% and 17% for runs 3 and 6, respectively.
[d] Isolated yields.

extensive decomposition of the product (run 7). Although two equivalents of triphenylphosphine per rhodium metal are optimal, a bidentate phosphine, diphenylphosphinoethane (dppe), was less effective, resulting in a decrease of both the reaction rate and the yield of **3a** (run 8). Among the solvents tested, xylene, DMF, chlorobenzene, and 1,1,2,2-tetrachloroethane were found to be ineffective compared to dibutyl ether.

Further, we examined the generality of the present transformation with respect to various cyclobutenediones **2** (Table 2). Upon heating under the optimized conditions, **2b** possessing a *gem*-disubstituted alkene was completely consumed within a reaction time of 60 h. Although the desired azabicycle **3b** was again not separated from triphenylphosphine oxide, the yield of **3b** proved to be 67% according to the $^1$H NMR analysis (run 2). A pure sample of **3b** was obtained in 36% yield using tri(*p*-methoxyphenyl)-phosphine instead of $PPh_3$. In contrast, the reaction of the more sterically demanding *vic*-disubstituted alkene **2c** did not reach to completion after 72 h and **3c** was obtained in 29% isolated yield together with recovered **2c** (run 3). In addition to cyclobutenediones bearing an aromatic substituent, methyl-substituted **2d** and *n*-butyl-substituted **2e** underwent decarbonylative cycloaddition with comparable reaction times, although the isolated yields of **3d** and **3e** were moderate (runs 4 and 5). When a more sterically demanding isopropyl substituent was introduced on the cyclobutenedione ring, the reaction was considerably slowed, resulting in an incomplete reaction even after 96 h (run 6). The corresponding product **3f** was formed in 37% NMR yield. Piperidine-fused cyclopentenone **3g** was similarly obtained from **2g** having a longer tether in 51% isolated yield (run 7).

To our surprise, cyclobutenediones **2h** and **2i** bearing a 2-furyl or an alkynyl substituent were found to be resistent under the optimal conditions, leading to their almost complete recovery after heating for 24 h (Figure 1). Ethoxy-substituted **2j** also proved to be totally resistent under the same reaction conditions. According to the resonance structure **5**, the carbon-carbon bond to be cleaved might have partial double bond character, which renders the rhodium insertion difficult (*vide infra*).

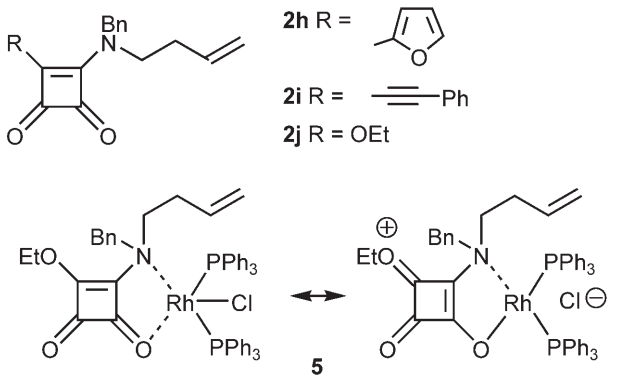
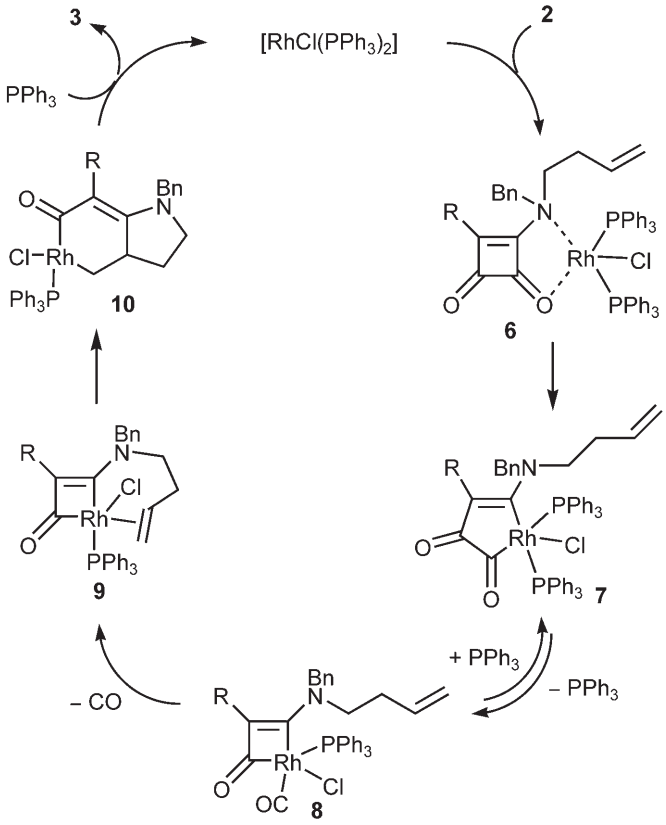



**Figure 1.** Substrates which failed to undergo decarbonylative transformation.

Scheme 3 outlines a proposed mechanism of the present rhodium(I)-catalyzed decarbonylative cycloaddition of the cyclobutenediones with a pendant



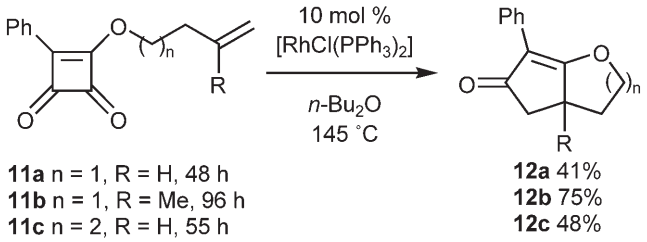

**Scheme 3.** Proposed mechanism for decarbonylative cycloaddition.

alkene. In the exploratory study summarized in Table 1, it was revealed that two equivalents of $PPh_3$ per rhodium metal was optimal for the decarbonylative cycloaddition. In addition, the chlorine abstraction had a deteriorative effect on the product yield. These results suggest that $[RhCl(PPh_3)_2]$ is a plausible active species. As proposed by Kondo, Mitsudo, and co-workers,[8a] the rhodium fragment might be inserted into one of the two C(vinyl)-C(carbonyl) bond of the cyclobutenediones *via* **6**, resulting in the formation of rhodacyclopentenedione **7**. Subsequent dissociation of $PPh_3$ induces CO migration from the rhodacycle skeleton onto the rhodium center to give rise to rhodacyclobutenone **8**. Similar rhodacyclobutenones are proposed as intermediates of the rhodium-catalyzed decarbonylation of cyclopropenones.[13] The ligand exchange from CO to the pendant olefin might

give **9**, which undergoes olefin insertion to produce rhodacyclohexenone **10**. Finally, the extrusion of the products **3** and association of $PPh_3$ restores the catalytic active species, $[RhCl(PPh_3)_2]$.

Next, the impact of the heteroatom of the tether was briefly examined (Scheme 4). Cyclobutenediones

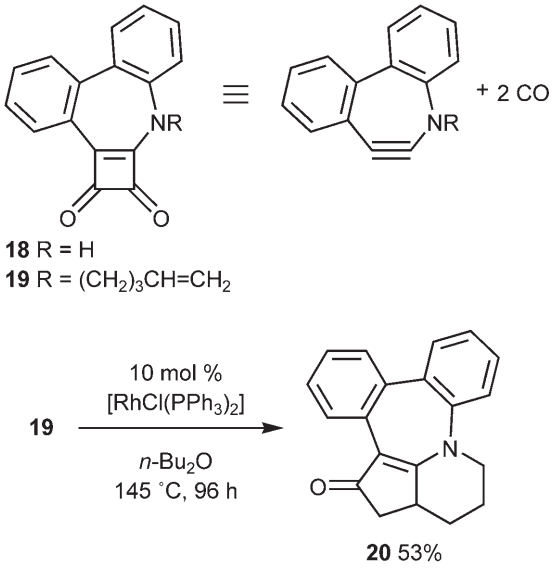



**Scheme 4.** Synthesis of oxabicycloalkenones **12** from cyclobutenediones **11**.

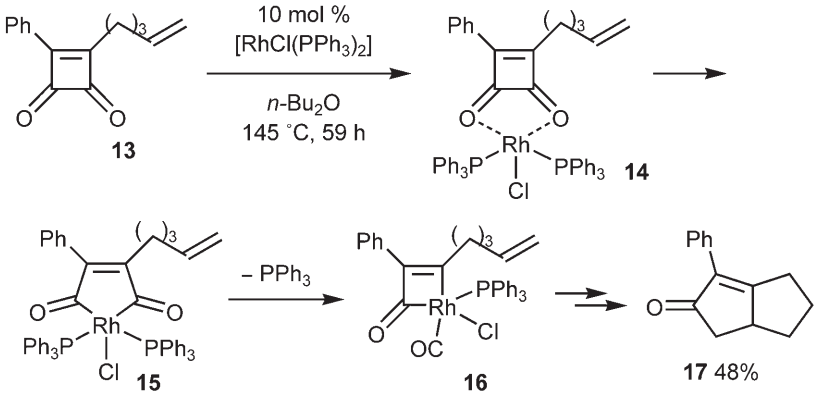
**11a** and **11c** bearing a 3-butenoxy or a 4-pentenoxy side chain were subjected to the rhodium-catalyzed ring transformation to afford oxabicycloalkenones **12a** and **12c** in 41% and 48% isolated yields, respectively.[14] It was revealed that longer reaction times were required for the complete conversions of these substrates compared to those for **2a** or **2g** having a nitrogen tether. As a result, the product yields were lowered due to their decomposition. In fact, when the isolated bicycloalkenone **12a** was returned to the identical conditions with the conversion of **11a**, it led to 33% decomposition after 12 h. Gratifyingly, the yield was improved for cyclobutenedione **11b** possessing a *gem*-disubstituted olefin terminal. The desired product **12b** was isolated in 75% yield, although the prolonged heating for 96 h was required for the total conversion of **11b**.

Under the ruthenium-catalyzed conditions, a dialkylcyclobutenone with norbornene gave a hydroquinone derivative instead of the expected cyclopentenone.[8a] In contrast, 3-(4-pentenyl)cyclobutenedione **13** similarly underwent the decarbonylative cycloaddition, resulting in the formation of bicyclooctenone **17** in 48% isolated yield (Scheme 5). This result shows that the heteroatom in the olefinic side chain is not imperative. The oxidative addition of the rhodium species is probably able to occur at the C–C bond between the two carbonyl groups *via* **14** to produce maleoylrhodium complex **15**,[13,15] which might be subsequently converted to the final product **17** *via* rhodacyclobutenone **16**.

Finally, we examined the possibility of a fused cyclobutenedione as a cycloalkyne equivalent. Toward this aim, the known azacyclic compound **18**[16] was converted to **19** bearing a 4-pentenyl side chain on its nitrogen atom, which was subsequently heated under optimal conditions (Scheme 6). The interesting pentacyclic product **20** was eventually obtained in 53% isolated yield.




**Scheme 6.** Cyclobutenedione **18** as dibenzoazacycloheptadienyne equivalent in decarbonylative ring transformation.




**Scheme 5.** Decarbonylative transformation of **13** into **17**.

## Conclusions

In conclusion, we have successfully developed rhodium(I)-catalyzed decarbonylative cycloaddition of cyclobutenediones with a pendant alkene, leading to the formation of intramolecular PK-type products with a vinylogous amide moiety. The starting cyclobutenediones were also efficiently prepared from appropriate SA monoesters and *N*-benzylalkenylamines by means of microwave heating. Overall, the present method provides a highly convergent strategy to assemble interesting azaheterocycles starting from SA as a synthetic platform. In addition to the azabicycloalkenones, oxa- and carbo-analogues were also synthesized from corresponding cyclobutenonediones having an ether or an alkyl tether, indicative of a heteroatom of tether chain being unnecessary.

## Experimental Section

### General Considerations

Column chromatography were performed on silica gel (Cica silica gel 60N) with mixed solvents [hexane/ethyl acetate]. $^1$H and $^{13}$C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 °C. $^1$H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. $^{13}$C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at $\delta = 77.0$ ppm for $CDCl_3$. Elemental analyses were performed by the Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes and are uncorrected. *n*-$Bu_2O$ was distilled from $CaH_2$, and degassed before use. [{RhCl(cod)}$_2$] was prepared according to the literature procedures.[17] 2-Phenylbicyclo[3.3.0]oct-1-en-3-one (**18**) was prepared as reported in the literature.[18]

### General Procedure for Synthesis Cyclobutenediones 2

A solution of 3-ethoxy-4-phenyl-3-cyclobutene-1,2-dione (176.5 mg, 0.873 mmol) and *N*-benzyl-3-butenylamine (168.9 mg, 1.05 mmol) in THF (4.5 mL) was irradiated by microwave reactor (30 W) at 60 °C for 20 min. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt (10:1) to give **2a** as a yellow oil (*ca.* 1:1 *syn*/anti isomer mixture); yield: 275.4 mg (99 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 2.13$ and 2.43 (br q, $J = 7.5$ Hz, 2H), 3.39 and 3.88 (br t, $J = 7.5$ Hz, 2H), 4.64 and 5.09 (s, 2H), 4.80–5.19 (m, 2H), 5.32–5.86 (m, 1H), 7.15–7.50 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 31.6$ and 33.0, 48.1 and 49.2, 53.2 and 54.2, 118.2 and 118.4, 127.2, 127.4 and 127.5, 128.2 and 128.4, 128.5 and 128.6, 128.9 and 129.0, 129.7, 164.3 and 164.8, 179.6 and 180.5, 188.7 and 188.9, 192.2 and 192.8; IR ($CHCl_3$): ν = 1778 (C=O), 1738 (C=O) cm$^{-1}$; MS (EI): *m*/*z* (%) = 317 (32) [M$^+$], 289 (68) [M$^+$−CO], 260 (100) [M$^+$−H−2CO], 220 (32) [M$^+$−2CO−$CH_2$=$CHCH_2$]; anal. calcd. (%) for $C_{21}H_{19}NO_2$ (317.38): C 79.47, H 6.03, N 4.41; found: C 79.72, H 5.94, N 4.25.

### General Procedure for Decarbonylative Transformation of Cyclobutenediones

To a solution of cyclobutenedione **2e** (60.4 mg, 0.203 mmol) in dry degassed *n*-$Bu_2O$ (2.0 mL) was added [{RhCl(cod)}$_2$] (4.97 mg, 0.0102 mmol) and $PPh_3$ (10.7 mg, 0.0408 mmol), and the resultant mixture was degassed at −78 °C and stirred at 145 °C for 34 h. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 2:1) to give **3e** as a brown oil; yield: 30.7 mg (56 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 0.82$ (t, $J = 7.2$ Hz, 3H), 1.20–1.38 (m, 4H), 1.62 (ddt, $J = 12.0$, 11.4, 8.4 Hz, 1H), 2.10–2.21 (m, 2H), 2.25 (quint, $J = 7.2$ Hz, 2H), 2.54 (dd, $J = 16.2$, 6.9 Hz, 1H), 3.05 (sext, $J = 6.6$ Hz, 1H), 3.41 (dd, $J = 10.5$, 8.1 Hz, 1H), 3.63 (dt, $J = 10.8$, 4.8 Hz, 1H), 4.61 (d, $J = 16.2$ Hz, 1H), 4.67 (d, $J = 16.2$ Hz, 1H), 7.17–7.20 (m, 2H), 7.26–7.39 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 21.9, 22.8, 29.9, 33.0, 40.0, 43.5, 51.2, 55.7, 106.8, 126.8, 127.7, 128.8, 136.6, 177.6, 204.1; IR ($CHCl_3$): ν = 1592 (enone) cm$^{-1}$; MS (EI): *m*/*z* (%) = 269 (65) [M$^+$], 226 (100) [M$^+$−$C_3H_7$]; anal. calcd. (%) for $C_{18}H_{23}NO$ (269.38): C 80.26, H 8.61, N 5.20; found: C 80.34, H 8.81, N 4.91.

### General Procedure for Synthesis Cyclobutenediones 11

To a solution of 3-(3-butenoxy)-4-chloro-3-cyclobutene-1,2-dione[19] (1.255 g, 6.73 mmol) in dry THF (20 mL) was added PhMgBr (2.0 M in THF, 3.70 mL, 7.40 mmol) at −78 °C under an argon atmosphere. The solution was stirred at this temperature for 30 min, and then the reaction was quenched with saturated $NH_4Cl$ solution (20 mL). After evaporation of the organic solvent, the residue was extracted with AcOEt (30 mL × 3). The organic layer was washed with brine (20 mL), dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by silica gel flash column chromatography (hexane-AcOEt, 30:1 to 10:1) to give 3-(3-butenoxy)-2-chloro-4-hydroxy-4-phenyl-2-cyclobutenone as a colorless oil; yield: 823 mg, (46 %).

The obtained alcohol was dissolved in $CHCl_3$ (25 mL), and treated with trifluoroaccetic anhydride (6.53 g, 31.1 mmol) and pyridine (738 mg, 9.33 mmol) at ambient temperature overnigt. To the reaction mixture was added saturated $NaHCO_3$ solution (20 mL) and $H_2O$ (20 mL), and the crude materials were extracted with AcOEt (30 mL × 3). The organic layer was washed with brine (15 mL × 2), dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by silica gel flash column chromatography (hexane-AcOEt, 30:1) to give 3-(3-butenoxy)-4-phenyl-3-cyclobutene-1,2-dione (**11a**) as yellow needles; yield: 522 mg (74 %); mp 69.6–69.9 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta =$ 2.67 (qt, $J = 6.6$, 1.5 Hz, 2H), 4.97 (t, $J = 6.6$ Hz, 2H), 5.16–5.27 (m, 2H), 5.80–5.94 (m, 1H), 7.48–7.55 (m, 3H), 8.02–8.06 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 34.5$, 73.9, 119.0, 127.6, 129.0, 131.9, 132.6, 173.6, 192.2, 192.5, 194.2; IR ($CHCl_3$): ν = 1787 (C=O), 1750 (C=O) cm$^{-1}$; MS (EI): *m*/*z* (%) = 228 (13) [M$^+$], 200 (75) [M$^+$−CO], 145 (100)

$[M^+-CO-(CH_2)_2CH=CH_2]$, 117 (33) $[M^+-2\,CO-(CH_2)_2CH=CH_2]$, 89 (64) $[M^+-3\,CO-(CH_2)_2CH=CH_2]$; anal. calcd. (%) for $C_{14}H_{12}O_3$ (228.24): C 73.67, H 5.30; found: C 73.57, H 5.36.

### Synthesis Cyclobutenedione 13

To a solution of 2-(4-pentenyl)-3,4,4-triethoxy-2-cyclobutenone[20] (217 mg, 0.81 mmol) in dry THF (8 mL) was added PhLi (1.05 M in THF, 1.54 mL, 1.62 mmol) at −78 °C under an argon atmosphere. The solution was stirred at this temperature for 30 min, and then the reaction was quenched with saturated $NH_4Cl$ solution (10 mL). The aqueous solution was extracted with $Et_2O$ (20 mL × 3). The organic layer was washed with brine (10 mL × 2), dried with $MgSO_4$, and concentrated under vacuum. The residue was diluted with $CH_2Cl_2$ (4 mL), and treated with concentrated HCl (2 drops) at room temperature for 45 min. The solution was dried with $K_2CO_3$ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography (hexane-AcOEt, 25:1) to give 3-(4-pentenyl)-4-phenyl-3-cyclobutene-1,2-dione (**13**) asa yellow solid; yield: 110 mg (60%); mp 38.2–39.1 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.97 (quint, $J$ = 7.5 Hz, 2H), 2.22 (q, $J$ = 7.2 Hz, 2H), 3.06 (t, $J$ = 7.5 Hz, 2H), 5.02–5.11 (m, 2H), 5.75–5.89 (m, 1H), 7.53–7.64 (m, 3H), 7.99–8.03 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 25.0, 27.1, 33.6, 116.1, 128.2, 128.3, 129.3, 133.3, 136.7, 190.3, 197.0, 197.4, 198.0; IR ($CHCl_3$): $\nu$ = 1783 (C=O), 1767 (C=O) cm$^{-1}$; MS (EI): $m/z$ (%) = 226 (29) $[M^+]$, 198 (24) $[M^+-CO]$, 184 (100) $[M^+-H-CH_2CH=CH_2]$, 169 (56) $[MH^+-2\,CO]$, 155 (100) $[M^+-2\,H-CO-CH_2CH=CH_2]$; anal. calcd. (%) for $C_{15}H_{14}O_2$ (226.27): C 79.62, H 6.24; found: C 79.60, H 6.26.

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