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Catalytic intramolecular decarbonylative coupling of 3-aminocyclobutenones and alkenes: a unique approach to [3.1.0] bicycles

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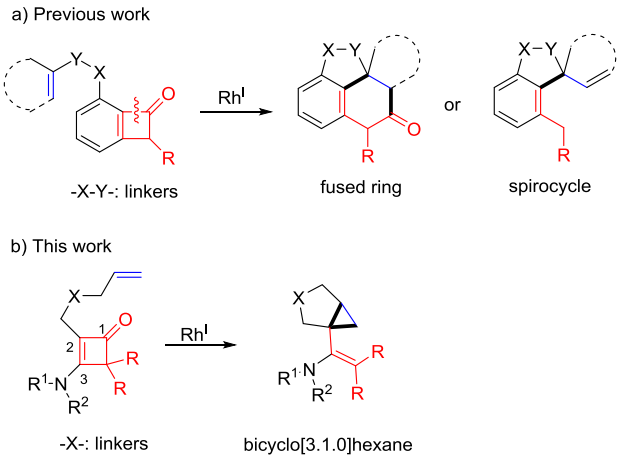
ABSTRACT

Here we describe a rhodium-catalyzed intramolecular decarbonylative coupling between 3-aminocyclobutenones and alkenes for synthesis of substituted [3.1.0] bicycles. This transformation represents a formal cyclopropanation reaction, in which the cyclobutenones serve as a one-carbon-unit synthon.

1. Introduction

Cyclobutenones are a unique class of compounds, and often serve as important synthetic intermediates due to their high reactivity driven by strain release.[1] Conventionally, cyclobutenones are often employed as a vinyl-ketene equivalent through a retro-4π cyclization.[2a] During the past two decades, novel transformations of cyclobutenones have been realized through transition metal-catalyzed carbon–carbon (C–C) bond cleavage followed by C–C bond formation.[2] These reactions often lead to complex scaffolds that are challenging to prepare using traditional approaches. For example, using Ni, Co, Ru and Rh as catalysts, intermolecular or intramolecular cyclization of cyclobutenones with alkenes, alkynes and other strained rings can provide five to eight-membered ring systems efficiently.[2]

Our group has been interested in applying catalytic C–C bond activation methods in complex molecule synthesis. Recently, we have demonstrated fused-ring and spirocycle synthesis through Rh-catalyzed C–C activation of benzocyclobutenones (Scheme 1a).[3] An intriguing question is whether non-benzo-type cyclobutenones will behave similarly in the catalytic intramolecular coupling reactions, which, to our knowledge, has not been explored previously. One potential challenge for this study is that regioselective synthesis of poly-substituted cyclobutenone substrates is non-trivial.[4,5] We were particularly inspired by an efficient method reported by Danheiser and co-workers for preparing multi-substituted 3-aminocyclobutenones[5] from readily available of ynamides[6] and ketenes.[7] Here, as an exploratory study, we describe our development of a Rh-catalyzed decarbonylative coupling of 3-aminocyclobutenones with alkenes leading to [3.1.0] bicycles



Scheme 1. Rh^{I}-catalyzed intramolecular cyclization between cyclobutenones and alkenes.

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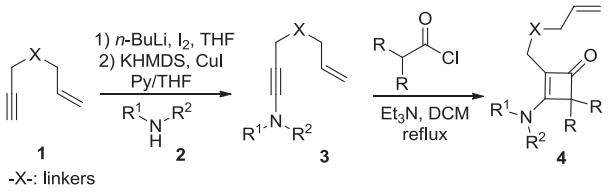
0040-4020/

(Scheme 1b). Compared to the corresponding benzocyclobutenones, a distinct reactivity with 3-aminocyclobutenones was discovered during this study.

2. Results and discussions

As illustrated in Scheme 2, the tethered alkene-cyclobutenone substrates can be efficiently synthesized in three steps from readily available enyne substrates.[5,8] Our initial study of the intramolecular cyclization reaction employed cyclobutenone **4a**[9] as the model substrate. When directly heating **4a** in 1,4-dioxane at 130 °C, vinyl cyclobutanones **6a** and **6a′** were slowly formed (their structures were unambiguously confirmed by X-ray crystallography)[10] (entry 1, Table 1). The reaction likely proceeds through a *retro*-[2+2] of the cyclobutenone to give a vinyl ketene and then a [2+2] cycloaddition with the alkene (vide infra, Scheme 3).[11] It is interesting to note that compounds **6a** and **6a′** represent a pair of conformational isomers and can be separated using regular silica-gel chromatography. The C3–N bond cannot freely rotate likely caused by the significant steric hindrance between the tetra-substituted olefin and the bulky cyclobutanone. $[Rh(cod)Cl]_2$ did not influence the reaction, because almost the same results were obtained when using $[Rh(cod)Cl]_2$ in combination with bidentate phosphine ligands (dppp, dppf and dppb) as well as monodentate $P(C_6F_5)_3$ ligand (entry 2). However, when the more electron-deficient $[Rh(CO)_2Cl]_2$ was employed as the catalyst, an interesting bicycle[3.1.0]-hexane compound **5** was observed as the dominating product in 68% yield (entry 3). The yield can be further improved to 84% by adding $P(C_6F_5)_3$ as an additional ligand, in which cyclobutanones **6a** and **6a′** (the major byproducts) only formed in 10% yield (entry 4); in contrast, using more electron-rich ligands gave diminished yields (entries 5–8). The solvent effect was also investigated (entries 9–12) and 1,4-dioxane remained to be optimal.

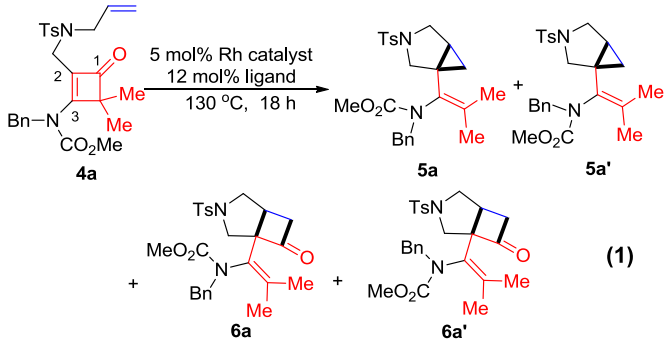


Scheme 2. General approach for synthesizing the 3-aminocyclobutenone substrates.

With the optimized conditions in hand, we next examined the scope of this decarbonylative cyclization reaction (Table 2).[12] First, change of the substituents on the nitrogen of the amino-cyclobutenones did not significantly affect the reactivity (entries 1–3). While the methyl formate substrates (**4a** and **4b**) all gave a pair of conformational isomers, the less hindered oxazolidone substrates afforded a single isomer (entries 3–10). Besides the nitrogen-based linker (entries 3–4), oxygen and carbon-based linkers are also effective (entries 5–7). Different substituents on the cyclobutenone C2 position were also examined. When replacing the *gem*-dimethyls to a cyclopentane group, the desired vinyl cyclopropane **5h** was isolated in 42% yield and a ring-opening diene (**5h′**) was found as the major byproduct (entry 8). The exact reason of forming diene **5h′** remains unclear. It is likely that **5h′** did not come from the decomposition of **5h** as treatment of **5h** under the reaction conditions did not yield any **5h′**. It was surprising to note that the diethyl analogue (**4i**) gave the ring-opening diene **5i** as the sole product (entry 9), which suggests the steric hindrance at the C2 position of the cyclobutenone plays an important role in the selectivity of the reaction.

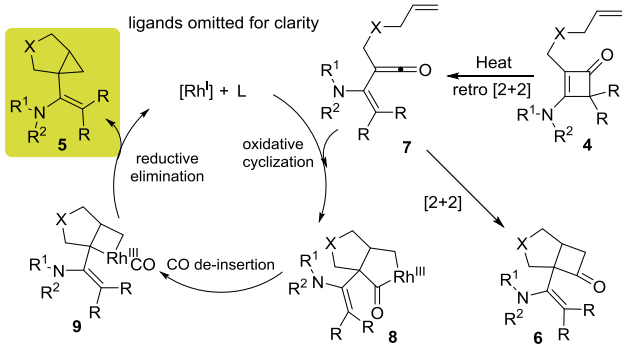
An interesting observation is that the substrate tethered with a 1,1-disubstituted olefin gave a complete selectivity for the [2+2]

Table 1
Selected reaction optimization conditions



Entry	Rh catalyst	Ligand	Solvent	Yield [%][a]
1	None	None	1,4-Dioxane	**6a**15%, **6a′**15%
2	$[Rh(cod)Cl]_2$	$P(C_6F_5)_3$	1,4-Dioxane	**6a**15%, **6a′**15%
3	$[Rh(CO)_2Cl]_2$	None	1,4-Dioxane	**5**[c] 68%
4	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	1,4-Dioxane	5 84%
5	$[Rh(CO)_2Cl]_2$	dppp[b]	1,4-Dioxane	**5** 60%
6	$[Rh(CO)_2Cl]_2$	dppm[b]	1,4-Dioxane	**5** 35%
7	$[Rh(CO)_2Cl]_2$	dppb[b]	1,4-Dioxane	**5** 50%
8	$[Rh(CO)_2Cl]_2$	PPh_3	1,4-Dioxane	**5** 43%
9	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	Toluene	**5** 78%
10	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	*m*-Xylene	**5** 80%
11	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	THF	**5** 65%
12	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	PhCl	**5** 81%

[a] Determined by ^1H NMR spectroscopy using mesitylene as the internal standard.
[b] 6 mol % of the ligand was used.
[c] **5** is a mixture of inseparable isomers: **5a** and **5a′** (1:1).



Scheme 3. Proposed catalytic cycle.

cyclobutanone product in 84% yield (entry 10).[13] In contrast, use of a 1,2-disubstituted olefin and elongation of the linkage led to a complex unidentifiable mixture (entries 11 and 12).

It is well known that decarbonylation of cyclobutanones to cyclopropanes can be catalyzed by transition metals, such as Rh(I) complexes.[14] Thus, it is natural to concern whether the [3.1.0] bicycle (e.g., **5a**/**5a′**) comes from the direct decarbonylation of a cyclobutanone intermediate (e.g., **6a**/**6a′**). Hence, the following experiment was conducted. When treating a mixture of **6a** and **6a′** under the standard reaction conditions, no decarbonylation product **5a**/**5a′** was observed (Eq. 2), suggesting that the [3.1.0] bicycle should come from a different reaction pathway.

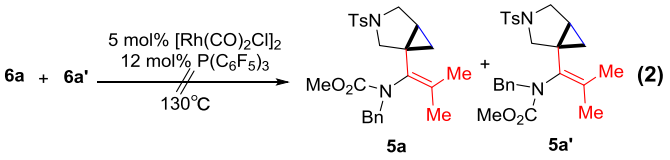
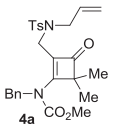
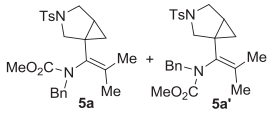
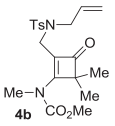
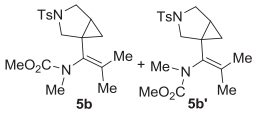
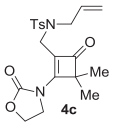
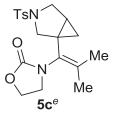
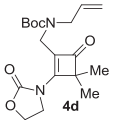
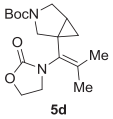
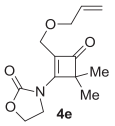
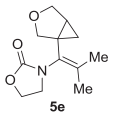
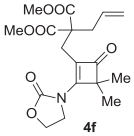
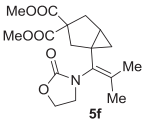
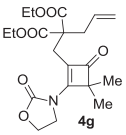
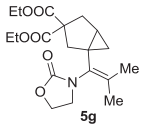
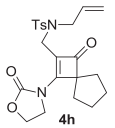
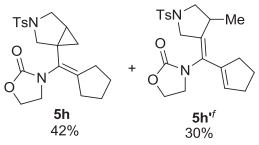
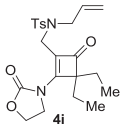
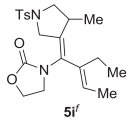
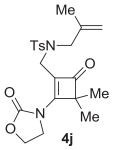
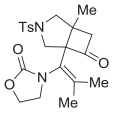
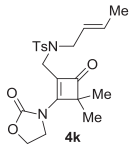
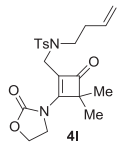


Table 2
Substrate scope[a]

Entry	Substrate	Product	Yield [%][b]
1	 **4a**	 **5a** + **5a'**	80 **5a:5a′**=1:1[d]
2	 **4b**	 **5b** + **5b'**	75 **5b:5b′**=1:1[d]
3	 **4c**	 **5c**[e]	72
4	 **4d**	 **5d**	45
5	 **4e**	 **5e**	65
6	 **4f**	 **5f**	72 (86)[c]
7	 **4g**	 **5g**	76 (90)
8	 **4h**	 **5h** 42% + **5h'**[f] 30%	
9	 **4i**	 **5i**[f]	45
10	 **4j**	 **6j**	84
11	 **4k**		0
12	 **4l**		0

[a]Each reaction was ran on a 0.1 mmol scale in a sealed 4 mL vial, using 5 mol% $[Rh(CO)_2Cl]_2$ and 12 mol% $P(C_6F_5)_3$, in 1,4-dioxane (1.5 mL), at 130 °C, for 18 h.
[b]Yields of isolated products.
[c]The number in parentheses represents the yield based on recovered starting material (brsm).
[d]The ratio was determined by ^{1}H NMR.
[e]The structure of **5c** was confirmed by a series of 2D NMRs, DEPT, and HRMS.
[f]**5h**′ and **5i** were isolated as a single olefin-geometric isomer; the exact olefin geometry for each was not determined.

The proposed catalytic cycle is depicted in Scheme 3.[15] First, a retro-4π cyclization of cyclobutenones should give a reactive vinyl ketene intermediate (**7**), which can undergo either a [2+2] cycloaddition with the tethered alkene to give cyclobutanone **6** (background reaction) or a cyclometalation reaction mediated by Rh to give a five-membered metallacycle **8** (catalytic reaction). Subsequent CO de-insertion from complex **8** followed by reductive elimination should provide cyclopropane **5**.

3. Conclusion

In summary, a Rh-catalyzed intramolecular coupling of 3-aminocyclobutenones with alkenes has been studied. In this transformation, the cyclobutenone serves as a one-carbon synthon leading to an unprecedented cyclopropanation reaction. This reaction offers a unique approach for synthesizing heavily substituted vinyl cyclopropanes and [3.1.0]-bicycle skeletons. Stimulated by this work, efforts on investigating the coupling of less substituted cyclobutenones with alkenes, alkynes and allenes are ongoing in this laboratory.

4. Experimental

4.1. General

THF, 1,4-dioxane and toluene were purchased from Fischer Scientific, distilled freshly over sodium and freeze-pump-thawed. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. All reactions were carried out under nitrogen with stirring bar in a rubber septum sealed flask. Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glove-box with standard techniques. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15×45 mm 1 dram (4 mL)/ 27.75×95 mm 10 dram (40 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight and cooled in a dessicator. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as *m*/*z* (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, $[M-H]^-$ or $[M]^+$. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with a Varian Gemini (400 MHz, ^{1}H at 400 MHz, ^{13}C at 100 MHz). Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ=7.26 ppm (^{1}H) and 77.00 ppm (^{13}C)). Couplingconstants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, dd=doublet of doublets, td=triplet of doublets, ddd=doublet of doublet of doublets, m=multiplet, coupling constant (Hz), and integration.

4.2. General procedure for synthesis of cyclobutenone compounds through [2+2] cyclization

Acyl chloride (3.0 mmol) and Et_3N (0.70 ml, 5.0 mmol) were added drop wise to a solution of ynamide (1.0 mmol) in anhydrous DCM (10 mL) at 0 °C under N_2. The resulting mixture was stirred for 48 h at 40 °C, and then quenched with saturated aqueous $NaHCO_3$ solution. The layers were separated, and the aqueous layers were extracted with EtOAc (3×20 mL). The organic layers were combined and washed with brine (20 mL), which were then dried over $MgSO_4$ and concentrated. Compounds **4a**–**4l** were purified via silica gel flash chromatography. (For details, see Supplementary data).

*4.2.1. Compound **4a**.* Compound **4a** was obtained in 85% yield as a white solid. R_f=0.60, hexans/EtOAc=2:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.40–7.39 (m, 2H), 7.32–7.30 (m, 1H), 7.30–7.21 (m, 4H), 5.66–5.56 (m, 1H), 5.28 (s, 2H), 5.26–5.21 (m, 1H), 5.06–5.03 (m, 1H), 3.86 (s, 3H), 3.71 (d, J=6.0 Hz, 2H), 3.49 (s, 2H), 2.39 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 173.0, 152.3, 143.6, 136.1, 135.1, 132.9, 129.6, 128.8, 127.5, 127.3, 125.2, 118.5, 115.9, 63.1, 54.4, 51.0, 39.7, 21.4, 20.6. IR: ν 1752, 1595, 1437, 1395, 1346, 1305, 1262, 1185, 1160, 1090, 1044, 743 cm^{-1}. HRMS calcd for $C_{26}H_{30}N_2NaO_5S^+$ $[M+Na]^+$: 505.1773, found: 505.1765. Mp (°C): 100–102.

*4.2.2. Compound **4b**.* Compound **4b** was obtained in 55% yield (90% brsm yield) as a white solid. R_f=0.30, hexans/EtOAc=5:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J=8.0 Hz, 2H), 7.28 (d, J=8.0 Hz, 2H), 5.69–5.59 (m, 1H), 5.21–5.15 (m, 1H), 5.07–5.04 (m, 1H), 3.87 (s, 3H), 3.81 (s, 2H), 3.73 (dt, J=1.2, 6.0 Hz, 2H), 3.55 (s, 3H), 2.39 (s, 3H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 173.4, 152.2, 143.6, 135.3, 133.0, 129.7, 127.3, 118.5, 115.6, 62.8, 54.2, 50.9, 39.8, 36.3, 21.4, 20.5. IR: ν 2959, 2927, 1494, 1428, 1263, 1090, 1043, 955, 916 cm^{-1}. HRMS calcd for $C_{20}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 429.1460, found: 429.1456. Mp (°C): 83–85.

*4.2.3. Compound **4c**.* Compound **4c** was obtained in 60% yield (86% brsm yield) as a colorless oil. R_f=0.55, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.31–7.26 (m, 2H), 5.65–5.56 (m, 1H), 5.25–5.23 (m, 1H), 5.15–5.12 (m, 1H), 4.62–4.60 (m, 2H), 4.47–4.45 (m, 2H), 3.77–3.74 (m, 4H), 2.42 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 168.7, 151.9, 144.0, 135.2, 132.3, 129.9, 127.1, 119.5, 115.8, 63.2, 62.3, 51.0, 45.0, 38.7, 21.5, 20.3. IR: ν 1784, 1754, 1344, 1223, 1192, 1159, 1121, 1091, 913, 743 cm^{-1}. HRMS calcd for $C_{20}H_{25}N_2O_5S^+$ $[M+H]^+$: 405.1484, found: 405.1482.

*4.2.4. Compound **4d**.* Compound **4d** was obtained in 86% yield as a colorless oil. R_f=0.40, DCM/Acetone=10:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76–5.69 (m, 1H), 5.16–5.11 (m, 2H), 4.58–4.54 (m, 2H), 4.41–4.38 (m, 2H), 3.90 (d, J=5.6 Hz, 2H), 3.83 (s, 2H), 1.40 (s, 9H), 1.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 166.7, 155.2, 152.1, 133.4, 118.4, 116.6, 80.0, 63.1, 61.9, 49.6, 44.3, 37.1, 28.3, 20.6. IR: ν 2978, 2928, 1754, 1687, 1611, 1458, 1366, 1166, 1145, 1102 cm^{-1}. HRMS calcd for $C_{18}H_{26}N_2NaO_5^+$ $[M+Na]^+$: 373.1739, found: 373.1736.

*4.2.5. Compound **4e**.* Compound **4e** was obtained in 79% yield as a colorless oil. R_f=0.25, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.80 (m, 1H), 5.28–5.23 (m, 1H), 5.20–5.17 (m, 1H), 4.59–4.55 (m, 2H), 4.31–4.27 (m, 2H), 3.96–3.93 (m, 2H), 3.92 (s, 2H), 1.39 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 168.9, 151.8, 133.9, 118.7, 117.9, 71.4, 63.0, 62.4, 58.3, 44.5, 20.7. IR: ν 2926, 1782, 1755, 1410, 1218, 1190, 1121, 1072 cm^{-1}. HRMS calcd for $C_{13}H_{18}NO_4^+$ $[M+H]^+$: 252.1236, found: 252.1227.

*4.2.6. Compound **4f**.* Compound **4f** was obtained in 61% yield (76% brsm yield) as a colorless oil. R_f=0.40, DCM/Acetone=10:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70–5.59 (m, 1H), 5.21–5.17 (m, 1H), 5.12–5.09 (m, 1H), 4.57–4.53 (m, 2H), 4.28–4.24 (m, 2H), 3.69 (s, 6H), 2.73 (d, J=7.2 Hz, 2H), 2.66 (s, 2H), 1.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 170.9, 167.3, 152.3, 132.2, 119.8, 118.0, 63.0, 61.5, 57.5, 52.6, 44.1, 37.8, 26.5, 20.7. IR: ν 2957, 1784, 1734, 1611, 1437, 1371, 1328, 1207, 1126, 1042, 913 cm^{-1}. HRMS calcd for $C_{18}H_{23}NNaO_7^+$ $[M+Na]^+$: 388.1372, found: 388.1370.

*4.2.7. Compound **4g**.* Compound **4g** was obtained in 72% yield as a colorless oil. R_f=0.50, DCM/Acetone=10:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73–5.63 (m, 1H), 5.23–5.19 (m, 1H), 5.13–5.10 (m, 1H), 4.57–4.53 (m, 2H), 4.30–4.26 (m, 2H), 4.21–4.09 (m, 4H), 2.75 (d, J=7.6 Hz, 2H), 2.65 (s, 2H), 1.31 (s, 6H), 1.32 (t, J=7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 170.5, 167.3, 152.3, 132.3, 119.8, 118.2, 62.9, 61.6, 61.5, 57.4, 44.1, 37.6, 26.3, 20.8, 13.9. IR: ν 2982, 1785, 1730, 1612, 1395, 1203, 1042, 913 cm^{-1}. HRMS calcd for $C_{20}H_{27}NNaO_7^+$ $[M+Na]^+$: 416.1685, found: 416.1681.

*4.2.8. Compound **4h**.* Compound **4h** was obtained in 7% yield (70% brsm yield) as a colorless oil. R_f=0.60, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=8.0 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 5.64–5.56 (m, 1H), 5.26–5.21 (m, 1H), 5.12–5.09 (m, 1H), 4.63–4.58 (m, 2H), 4.47–4.43 (m, 2H), 3.76 (s, 2H), 3.76 (d, J=6.8 Hz, 2H), 2.41 (s, 3H), 1.99–193 (m, 2H), 1.78–1.70 (m, 2H), 1.69–1.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 165.7, 152.0, 143.9, 135.4, 132.3, 129.9, 127.1, 119.5, 117.6, 70.2, 63.2, 51.0, 44.9, 38.7, 31.4, 26.5, 21.5. IR: ν 2924, 1781, 1751, 1607, 1401, 1275, 1260, 913 cm^{-1}. HRMS calcd for $C_{22}H_{27}N_2O_5S^+$ $[M+H]^+$: 431.1641, found: 431.1636.

*4.2.9. Compound **4i**.* Compound **4i** was obtained in 35% yield (81% brsm yield) as a colorless oil. R_f=0.60, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J=6.4 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 5.52–5.44 (m, 1H), 5.25–5.20 (m, 1H), 5.12–5.10 (m, 1H), 4.63–4.59 (m, 2H), 4.47–4.43 (m, 2H), 3.85 (s, 2H), 3.81 (d, J=6.4 Hz, 2H), 2.43 (s, 3H), 1.85–175 (m, 4H), 0.83 (d, J=7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.1, 152.2, 143.9, 135.5, 131.1, 129.8, 127.3, 120.2, 119.5, 72.2, 63.3, 50.2, 45.1, 37.7, 25.5, 21.5, 10.1. IR: ν 2965, 1784, 1752, 1607, 1401, 1340, 1186, 1157, 1120, 913 cm^{-1}. HRMS calcd for $C_{22}H_{29}N_2O_5S^+$ $[M+H]^+$: 433.1797, found: 433.1780.

*4.2.10. Compound **4j**.* Compound **4j** was obtained in 60% yield (89% brsm yield) as a colorless oil. R_f=0.50, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J=8.0 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H), 5.27 (d, J=0.8 Hz, 1H), 4.98 (s, 1H), 4.62–4.58 (m, 2H), 4.45–4.41 (m, 2H), 3.73 (s, 2H), 3.66 (s, 2H), 2.39 (s, 3H), 1.68 (s, 3H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 168.1, 151.9, 143.9, 140.3, 135.2, 129.8, 127.1, 116.0, 114.3, 63.2, 62.2, 55.0, 44.8, 39.5, 21.4, 19.9. IR: ν 2926, 1784, 1753, 1610, 1272, 1224, 1191, 1119, 1046, 913 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 441.1460, found: 441.1456.

*4.2.11. Compound **4k**.* Compound **4k** was obtained in 52% yield (82% brsm yield) as a colorless oil. R_f=0.50, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H), 5.63–5.56 (m, 1H), 5.27–5.20 (m, 1H), 4.62–4.58 (m, 2H), 4.45–4.41 (m, 2H), 3.73 (s, 2H), 3.69 (d, J=6.4 Hz, 2H), 2.40 (s, 3H), 1.57 (dd, J=0.8, 6.4 Hz, 3H),1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 168.6, 152.0, 143.8, 135.4, 131.2, 129.7, 127.2, 124.5, 116.1, 63.3, 62.1, 50.4, 45.0, 38.3, 21.4, 20.4, 17.7. IR: ν 2963, 1785, 1754, 1468, 1341, 1221, 1191, 1158, 1130, 1048 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 441.1460, found: 441.1453.

*4.2.12. Compound **4l**.* Compound **4l** was obtained in 75% yield as a colorless oil. R_f=0.40, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.31–7.29 (m, 2H), 5.70–5.60 (m, 1H), 5.04–4.97 (m, 2H), 4.63–4.59 (m, 2H), 4.47–4.43 (m, 2H), 3.74 (s, 2H), 3.11–3.07 (m, 2H), 2.41 (s, 3H), 2.28–2.23 (m, 2H), 1.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 169.4, 151.9, 144.0, 134.7, 134.5, 129.9, 127.2, 117.1, 115.4, 63.3, 62.5, 48.1, 45.0, 39.4, 33.4, 21.4, 20.4. IR: ν 2962, 2926, 1785, 1754, 1609, 1404, 1314, 1290, 1220, 1133, 1090 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 441.1460, found: 441.1458.

4.3. General procedure for synthesis of Bicyclo[3.1.0]hexane and its analogues

Cyclobutenone substrates (0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.95 mg, 0.05 mmol), $P(C_6F_5)_3$ (6.4 mg, 0.12 mmol), and anhydrous 1,4-Dioxane (1.5 mL) were added into a 4.0 mL vial in glove box, which were then stirred at 130 °C under N_2 for 18 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL). The layers were then separated, and the aqueous layers were extracted with EtOAc (3×10 mL). The organic layers were combined, washed with brine (20 mL), dried over $MgSO_4$ and concentrated. The decarbonylative coupling products were purified via silica gel flash chromatography.

*4.3.1. Compounds **5a** and **5a**′.* Compounds **5a** and **5a**′ were obtained from **4a** in 80% yield as a colorless oil, **5a** and **5a**′ in a 1:1 ratio (the ratio of **5a** and **5a**′ was determined by crude ^{1}H NMR). R_f=0.55, hexans/EtOAc=2:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 4H), 7.33–7.30 (m, 4H), 7.27–7.20 (m, 4H), 7.12–7.07 (m, 6H), 4.70 (d, J=14.4 Hz, 1H), 4.43 (d, J=14.4 Hz, 1H), 4.21 (d, J=14.4 Hz, 1H), 4.16 (d, J=14.4 Hz, 1H), 3.70–3.62 (m, 2H), 3.62 (s, 3H), 3.40–3.34 (m, 2H), 3.32 (s, 3H), 3.03–2.99 (m, 2H), 2.85–2.79 (m, 2H), 2.42 (s, 6H), 1.69 (s, 3H), 1.62 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.29–1.23 (m, 1H), 1.12–1.08 (m, 1H), 0.73 (t, J=4.4 Hz, 1H), 0.65 (dd, J=4.4, 8.0 Hz, 1H), 0.48 (t, J=4.4 Hz, 1H), 0.35 (dd, J=4.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.6, 143.4, 143.3, 137.6, 137.5, 136.3, 134.8, 134.0, 133.5, 130.4, 130.1, 129.6, 129.5, 129.0, 128.5, 128.3, 128.2, 127.9, 127.7, 127.5, 127.3, 53.7, 53.5, 52.8, 52.4, 49.7, 49.6, 29.9, 29.8, 24.7, 23.0, 21.5, 21.5, 20.4, 20.2, 20.1, 20.1, 16.7, 14.9. IR: ν 2360, 2342, 1700, 1347, 1294, 1165, 1131, 1093, 913 cm^{-1}. HRMS calcd for $C_{25}H_{30}N_2NaO_4S^+$ $[M+Na]^+$: 477.1824, found: 477.1816.

*4.3.2. Compounds **5b** and **5b**′.* Compound **5b** and **5b**′ were obtained in 75% yield as a colorless oil from **4b**, **5b** and **5b**′ in a 1:1 ratio determined by crude ^{1}H NMR. R_f=0.50, hexans/EtOAc=2:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.63 (m, 4H), 7.32–7.29 (m, 4H), 3.65–3.62 (m, 2H), 3.59 (s, 3H), 3.53–3.50 (m, 2H), 3.25 (s, 3H), 3.21–3.16 (m, 1H), 3.06–3.02 (m, 3H), 2.83 (s, 3H), 2.77 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H), 1.51–1.46 (m, 1H), 1.43–1.39 (m, 1H), 0.92–0.90 (m, 1H), 0.82–0.79 (m, 1H), 0.74–0.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.5, 134.9, 134.2, 133.1, 132.9, 131.8, 131.4, 129.6, 129.5, 127.6, 127.4, 53.9, 53.4, 52.6, 52.2, 50.0, 49.7, 36.5, 36.4, 30.1, 30.0, 23.5, 23.1, 21.5, 21.4, 19.9, 19.8, 19.7, 15.9, 15.6. IR: ν 1773, 1418, 1346, 1275, 1260, 1161, 1113, 913 cm^{-1}. HRMS calcd for $C_{19}H_{27}N_2O_4S^+$ $[M+H]^+$: 379.1692, found: 379.1693.

*4.3.3. Compounds **5c**.* Compound **5c** was obtained in 72% yield as a white solid from **4c**. R_f=0.50, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=8.4 Hz, 2H), 7.33 (d, J=8.0 Hz, 2H), 4.33 (d, J=8.4 Hz, 1H), 4.31 (d, J=7.6 Hz, 1H), 3.63–3.46 (m, 4H), 3.23 (dd, J=3.6, 9.6 Hz, 1H), 3.04 (d, J=9.2 Hz, 1H), 2.42 (s, 3H), 1.68–1.58 (m, 7H), 0.86–0.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 143.6, 137.5, 133.2, 129.6, 127.4, 125.6, 61.9, 53.2, 49.7, 45.9, 28.5, 24.3, 21.5, 20.2, 20.0, 14.9. IR: ν 2918, 2361, 1748, 1410, 1344, 1165, 1107, 1033, 913 cm^{-1}. HRMS calcd for $C_{19}H_{24}N_2NaO_4S^+$ $[M+Na]^+$: 399.1354, found: 399.1349. Mp (°C): 103–105.

*4.3.4. Compounds **5d**.* Compound **5d** was obtained in 45% yield as a colorless oil from **4d**. R_f=0.30, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41–4.37 (m, 2H), 3.77–3.74 (m, 2H), 3.65–3.55 (m, 2H), 3.49–3.46 (m, 1H), 3.27–3.24 (m, 1H), 1.86 (d, J=4.0 Hz, 3H), 1.69 (s, 3H), 1.69–1.67 (m, 1H), 1.42 (s, 9H), 0.99 (dd, J=4.4, 8.0 Hz, 1H), 0.66–0.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.8, 136.8, 126.3, 79.6, 61.9, 52.1, 48.2, 47.9, 46.1, 45.9, 28.4, 24.0, 20.2, 16.5. IR: ν 2360, 2342, 1750, 1690, 1406, 1259, 1171, 913 cm^{-1}. HRMS calcd for $C_{17}H_{26}N_2NaO_4^+$ $[M+Na]^+$: 345.1790, found: 345.1786.

*4.3.5. Compounds **5e**.* Compound **5e** was obtained in 65% yield as a colorless oil. R_f=0.20, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42–4.34 (m, 2H), 3.87–3.84 (m, 3H), 3.80–3.77 (m, 1H), 3.64–3.58 (m, 2H), 1.87 (s, 3H), 1.82–1.76 (m, 1H), 1.70 (s, 3H), 0.89 (dd, J=4.4, 8.0 Hz, 1H), 0.82 (t, J=4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 126.4, 125.2, 72.4, 69.6, 61.9, 46.1, 29.7, 25.1, 20.2, 14.0. IR: ν 2919, 1746, 1410, 1297, 1275, 1105, 1039, 913 cm^{-1}. HRMS calcd for $C_{12}H_{17}NNaO_3^+$ $[M+Na]^+$: 246.1106, found: 246.1101.

*4.3.6. Compounds **5f**.* Compound **5f** was obtained in 72% yield as a colorless oil from **4f**. R_f=0.30, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (t, J=8.0 Hz, 2H), 3.74–3.68 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 2.83 (d, J=13.6 Hz, 1H). 2.64–2.58 (m, 2H), 2.41 (dd, J=1.6, 13.6 Hz, 1H), 1.84 (s, 3H), 1.66 (s, 3H), 1.60–1.55 (m, 1H), 0.77–0.73 (m, 1H), 0.44–0.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.1, 156.5, 128.2, 61.9, 59.4, 53.0, 52.9, 45.9, 41.3, 36.1, 29.8, 20.2, 20.0. IR: ν 2953, 1734, 1436, 1256, 1203, 1098, 913 cm^{-1}. HRMS calcd for $C_{17}H_{23}NNaO_6^+$ $[M+Na]^+$: 360.1423, found: 360.1420.

*4.3.7. Compounds **5g**.* Compound **5g** was obtained in 76% yield as a colorless oil from **4g**. R_f=0.45, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (t, J=7.6 Hz, 2H), 4.21–4.10 (m, 4H), 3.79–3.82 (m, 1H), 3.72–3.65 (m, 1H), 2.82 (d, J=14.0 Hz, 1H), 2.64–2.56 (m, 2H), 2.38 (dd, J=1.2, 13.6 Hz, 1H), 1.84 (s, 3H), 1.66 (s, 3H), 1.63–1.55 (m, 1H), 1.26 (t, J=7.2 Hz, 3H), 1.20 (t, J=7.2 Hz, 3H), 0.75–0.72 (m, 1H), 0.47–0.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 171.7, 156.5, 128.3, 61.9, 61.8, 61.6, 59.6, 45.8, 41.2, 36.0, 29.7, 20.2, 20.0, 13.9. IR: ν 2983, 1729, 1444, 1410, 1251, 1197, 1096, 1069, 913 cm^{-1}. HRMS calcd for $C_{19}H_{27}NNaO_6^+$ $[M+Na]^+$: 388.1736, found: 388.1732.

*4.3.8. Compounds **5h** and **5h**′.* Compound **5h** was obtained in 42% yield as a colorless oil from **4h**. R_f=0.30, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J=6.8 Hz, 2H), 7.34 (d, J=8.4 Hz, 2H), 4.33 (t, J=8.0 Hz, 2H), 3.66–3.61 (m, 2H), 3.56–3.52 (m, 2H), 3.21 (dd, J=3.6, 9.6 Hz, 1H), 3.06 (d, J=9.2 Hz, 1H), 2.43 (s, 3H), 2.23–2.15 (m, 3H), 2.04–1.99 (m, 1H), 1.65–1.59 (m, 5H), 0.87 (dd, J=4.4, 8.0 Hz, 1H), 0.80 (t, J=4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.2, 143.5, 133.3, 129.6, 127.4, 122.3, 62.0, 52.5, 49.7, 45.4, 30.9, 30.5, 29.2, 26.4, 25.7, 23.9, 21.5, 14.6. IR: ν 2954, 2869, 1747, 1410, 1343, 1164, 1095, 1036 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_4S^+$ $[M+Na]^+$: 425.1511, found: 425.1508.

Compound **5h**′ was obtained in 30% yield as colorless oil: R_f=0.45, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J=6.4 Hz, 2H), 7.33 (d, J=8.0 Hz, 2H), 5.76–5.75 (m, 1H), 4.42 (t, J=8.0 Hz, 2H), 3.96 (d, J=15.2 Hz, 1H), 3.83 (d, J=15.2 Hz, 2H), 3.66–3.57 (m, 2H), 3.32 (dd, J=6.4, 9.2 Hz, 1H), 3.14–3.11 (m, 1H), 3.04 (dd, J=3.2, 9.2 Hz, 1H), 2.44–2.39 (m, 7H), 1.95–1.89 (m, 2H), 1.08 (d, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 143.8, 140.8, 137.0, 132.6, 131.9, 129.7, 127.8, 124.9, 62.1, 55.2, 50.5, 44.8, 35.3, 33.7, 32.3, 23.5, 21.5, 19.6. IR: ν 2923, 2342, 1750, 1409, 1343, 1161, 1092, 913 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_4S^+$ $[M+Na]^+$: 425.1511, found: 425.1505.

*4.3.9. Compounds **5i**.* Compound **5i** was obtained in 45% yield as a colorless oil from **4i**. R_f=0.45, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J=7.6 Hz, 2H), 7.33 (d, J=7.6 Hz, 2H), 5.54

(t, J=6.8 Hz, 1H), 4.39–4.30 (m, 2H), 3.92 (d, J=14.4 Hz, 1H), 3.77 (dd, J=1.6, 14.4 Hz, 1H), 3.54–3.49 (m, 2H), 3.44–3.40 (m, 1H), 3.09–3.03 (m, 1H), 2.79 (dd, J=5.6, 9.6 Hz, 1H), 2.43 (s, 3H), 2.23–2.16 (m, 1H), 1.88–1.79 (m, 1H), 1.69 (d, J=6.8 Hz, 3H), 0.95 (d, J=6.8 Hz, 3H), 0.92 (t, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.7, 137.6, 135.6, 132.2, 129.7, 129.5, 128.1, 127.8, 62.0, 55.2, 50.6, 44.5, 35.4, 21.5, 21.4, 18.4, 13.4, 12.5. IR: ν 2968, 2924, 1750, 1407, 1343, 1161, 1092, 913 cm^{-1}. HRMS calcd for $C_{21}H_{29}N_2O_4S^+$ $[M+H]^+$: 405.1848, found: 405.1839.

*4.3.10. Compounds **6j**.* Compound **6j** was obtained in 84% yield as a colorless oil from **4j**. R_f=0.2, hexans/EtOAc=1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J=8.0 Hz, 2H), 7.36 (d, J=8.0 Hz, 2H), 4.44–4.39 (m, 1H), 4.35–4.28 (m, 1H), 3.87–3.80 (m, 2H), 3.68 (d, J=9.6 Hz, 1H), 3.52–3.46 (m, 1H), 3.19 (d, J=18.4 Hz, 1H), 3.05 (d, J=6.4 Hz, 1H), 2.98–2.92 (m, 2H), 2.44 (s, 3H), 1.67 (s, 3H), 1.48 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 157.4, 144.2, 139.1, 131.4, 129.7, 127.9, 123.1, 76.1, 62.5, 59.7, 57.6, 57.2, 46.5, 44.1, 21.5, 21.2, 20.2, 19.4. IR: ν 1780, 1742, 1419, 1347, 1252, 1167, 1091, 1037, 913 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 441.1460, found: 441.1456.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.02.087.

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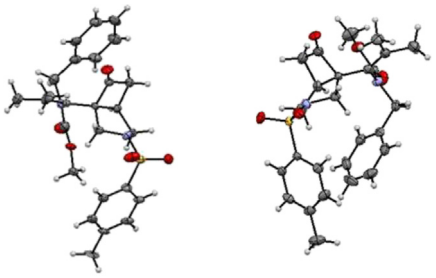

6a 6a'

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