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Rhodium(I)-Catalyzed [4+2] Cycloaddition Reactions of 2-Alkylenecyclobutanols with Alkyne and (*E*)-2-Nitroethenylbenzene through C(sp2)-C(sp3) Bond Cleavage

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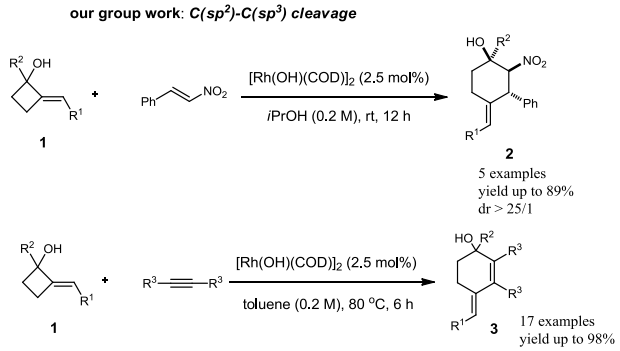
Summary of main observation and conclusion An intermolecular [4+2] cycloaddition was realized through C-C bond cleavage in the presence of Rh(I) catalyst. The selective ring opening of 2-alkylenecyclobutanols enables the generation of active alkenylrhodium species, which underwent smooth cross addition over alkynes and (*E*)-2-nitroethenylbenzene, leading to highly substituted all-carbon six-membered rings in a single step and in a complete atom economy.

Background and Originality Content

Organic motifs with all-carbon six-membered rings exist in numerous natural and unnatural products that exhibit important biological activities.[1] Intermolecular [4+2] cycloaddition has the high synthetic potential for the synthesis of structurally diverse and complex six-membered cyclic systems.[2] Despite the fact that many methods of [4+2] cycloaddition including Diels-Alder (DA) reaction[3] have been well-established, the synthesis of quaternary centers which are often present as the structural core in natural products of interesting biological activities remains a significant challenge for synthetic chemists.[4] As a result, the development of new and atom-economical approaches for the synthesis of all-carbon six-membered rings containing quaternary centers in a stereoselective manner are still highly desired.

Carbon–carbon bonds constitute the major framework of organic molecules. Such nonpolar σ-bonds are thermodynamically stable and kinetically inert in general. Over the past two decades, the difficulties associated with selective transformation of such nonpolar σ-bonds have motivated and inspired chemists to seek ways to activate these bonds. In such a way, organic skeletons could be constructed and/or functionalized in a more straightforward while efficient manner.[5] From an atom economic synthetic point of view, it would significantly streamline a unique atom-efficient method if a C-C single bond is cleaved and an unsaturated functionality is inserted therein to directly extend the carbon skeleton with two C-C single bonds newly formed. Cyclobutenols and cyclobutanols are privileged building blocks in this field.[6] Murakami pioneered in a series of studies on rhodium-catalyzed carbon–carbon bond cleavage/cycloaddition reactions of benzocyclobutenols with various functionalities including alkynes,[6d,6p] vinyl ketones,[6j] carbene precursors,[6l] and allenes.[6e] We have been interested in this field and recently reported a rhodium-catalyzed stereoselective [4+2] cycloaddition of oxetanols with alkynes[6b], and asymmetric [4+2] cycloaddition of 2- alkylenecyclobutanols[7] with α,β-unsaturated cyclic ketones, leading to synthetically valuable *trans*-bicyclic molecules.[8] In the latter case, ring opening of 2- alkylenecyclobutanol, a rarely exploited strained 4-carbon ring, selectively takes place on the C(sp3)-C(sp2) side. Notably, the following cross addition over C-C double bond represent the first example of utilization of internal alkenylrhodium species. Compared to well-studied benzocyclobutanol counterparts, 2-alkylenecyclobutanol host the potential utility as a versatile synthetic building block given its readily availability; 2-alkyledenecyclobutanols could be prepared from commercially available cyclobutanone via a 2-step procedure; an aldol condensation followed by 1,2-addition. Encouraged by the initial success, we envisioned that other two-carbon synthons could serve as coupling partners as well, leading to diverse molecular scaffolds through C(sp2)−C(sp3) bond cleavage and cycloaddition of 2-alkylenecyclobutanol.

Scheme 1 [4+2] cycloaddition of 2-alkylenecyclobutanol with 2-nitroethenylbenzene and alkyne



Herein, we report the successful expansion of this strategy to (*E*)-2-nitroethenylbenzene and alkynes, those reactions provide a rapid access to six-membered cyclic molecules with quaternary center and valuable functionalities including nitro, *exo*-alkene for facile derivatizations. Notably, (*E*)-2-nitroethenylbenzene has attracted much less attention in C-C bond cleavage field (Scheme 1).

Results and Discussion

We commenced our study by employing (*E*)-2-benzylidene-1-phenylcyclobutanol 1a and (*E*)-2-nitroethenylbenzene as the model substrates. The reaction conditions were adopted from our previous study, Rh(I) catalyst, in toluene at 70 ℃. As expected, screening of Rh(I)

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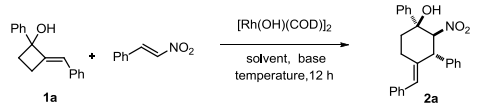
catalysts revealed that $[Rh(OH)(COD)]_2$ gave the best results, cyclic product (**2a**) was isolated in 38% yield as a single diastereomer (Table 1, entry 1). Examination of different additives did not provide better results. Switch of the solvent from toluene to THF improved the product yield. Reaction in 1,4-dioxane performed slightly better than that in THF. Interestingly, the reaction proceeded equally well at room temperature whereas raising the temperature to 110℃ resulted in decomposition of the starting material. To our delighted, 85% yield was attained when iPrOH was used instead of 1,4-dioxane as the solvent (entry 10).[9]

Table 1 Optimization of the reaction conditions for the rhodium (I)-catalyzed tandem ring-opening and cyclization.



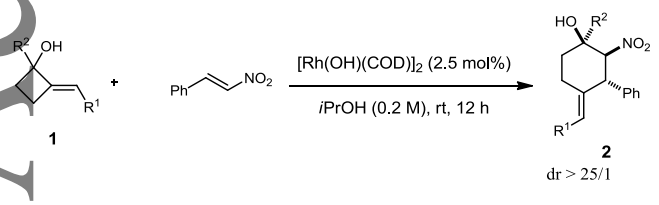
1a 2a

Entry[a]	Additives	solvent	Temp (°C)	Yield (**2a**)[%][b]
1	-	toluene	70	38
2	K_2CO_3	toluene	70	-
3	10% ^{i}PrOH	toluene	70	34
4	-	THF	70	58
5	-	xylene	70	34
6	-	1,4-dioxane	70	60
7	-	1,4-dioxane	110	-
8	-	1,4-dioxane	r.t	50
9	-	*t*-BuOH	r.t	50
10	-	^{i}PrOH	r.t	85

[a]Reaction conditions: 2-alkylenecyclobutanol (0.2 mmol), (*E*)-2-nitroethenylbenzene (1.1 equiv), $[Rh(OH)(COD)]_2$ (2.5 mol%), solvent (0.2M), 12 h. [b] Isolated yield.

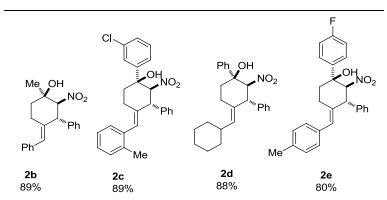
Efforts were then devoted to exploring the substrate scope with regard to diversity of 2-alkylenecyclobutanols (Table 2). The reaction seemed not sensitive to the electronic and steric properties of the substitutions at either the R^1 or R^2 positions. Both aryl and alkyl groups were compatible under current reaction conditions. A chloro and fluoro group on the phenyl ring remained intact. Those highly functionalized cyclic products were obtained in generally over 80% yield.

Table 2 Scope studies: cycloadditions of nitrostyrene [a,b]



1 2

dr > 25/1

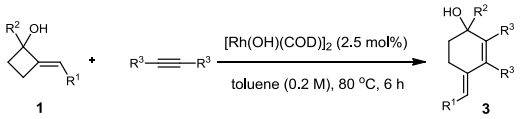


2b 89% **2c** 89% **2d** 88% **2e** 80%

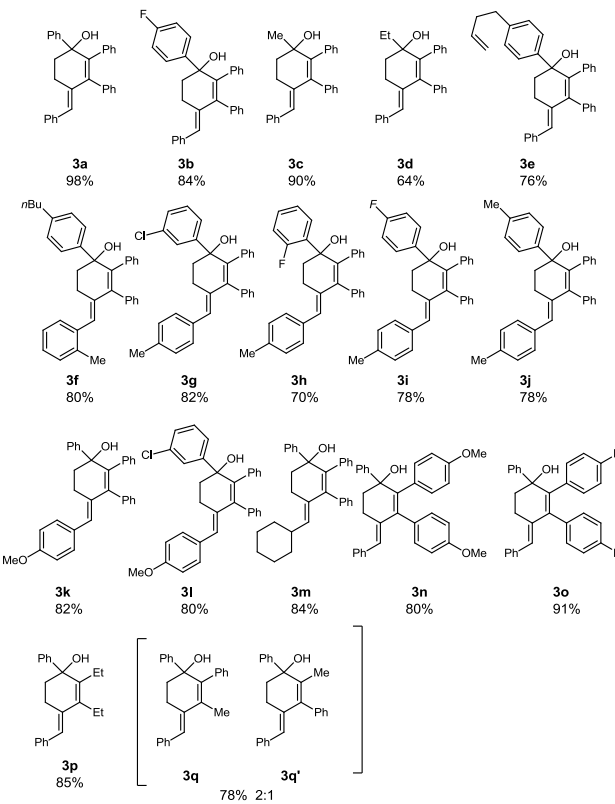
[a]Reaction conditions: 2-alkylenecyclobutanol (0.2 mmol), (E)-2-nitroethenylbenzene (1.1 equiv), $[Rh(OH)(COD)]_2$ (2.5 mol%), 2-PrOH (0.2M), rt , 12 h. bIsolated yield.

Motivated by the success with (*E*)-2-nitroethenylbenzene, our attention was then focused on alkyne counterpart. The cycloaddition of 2-alkylenecyclobutanol with alkynes would allow expedient access to alkylenecyclohexenols,[10] which represent an interesting molecular scaffold and would be difficult to be prepared by other means. We tested the reaction using 1,2-diphenylethyne with (*E*)-2-benzylidene-1-phenylcyclobutanol **1a**. Benefit from previous investigations, it did not take long to identify the optimal conditions. Simple heating of 1a with diphenylethyne in toluene at 80 °C in the presence of $[Rh(OH)(COD)]_2$ provided the desired cycloadduct **3a** in almost quantitative yield.

Table 3 Scope studies: cycloaddition of alkyne.[a, b]



1 3

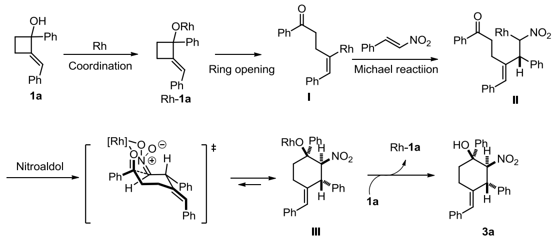


[a] Reaction conditions: 2-alkylenecyclobutanol (0.2 mmol), alkyne (1.1 equiv), $[Rh(OH)(COD)]_2$ (2.5 mol%), Toluene (0.2M), 80 °C , 6 h. [b] Isolated yield.

The six-membered ring forming reaction proceeded successfully with various combinations of 2-alkylenecyclobutanols **1** and alkynes, demonstrating the generality of the unique site-selective and efficient insertion of triple bond to the C(sp2)-C(sp3) bond of four-membered ring (Table 3). With R^1 as a phenyl, the alkyl groups (R^2) showed the same site-selectivity to give cyclic products in satisfactory yields (**3c** - **3d**). Notably, a carbon-carbon double bond remained intact (**3e**). The presence of electron-donating and withdrawing groups on the benzene ring scarcely affected the reaction (**3b**, **3f** - **3l**). The effects of variations of substitutions on the alkylene (R^1) were then

examined. To our delight, arenes bearing electron-donating methyl and methoxy at the either *para*, or *ortho* positions with various combinations of benzene substitutions (R^1) are compatible with the reaction conditions (**3f** - **3l**). Even the alkyl -substituted derivative **1m** reacted well to afford **3M** in 84% yield. Furthermore, the variations of diaryl alkynes were then briefly investigated, alkynes with electron-donating methyl and methoxy at the para position serve as the suitable substrates (**3n** - **3o**). To our delight, with R^2 as a phenyl, a cyclohexyl of the R^1 was well tolerated, giving the corresponding product **3m** in 84% yield. The reaction of an unsymmetric alkyne bearing methyl and phenyl substitution groups (**3q**) gave two separable regioisomers at a ratio of 2 : 1 indicating that the steric properties of the alkyne substitution groups has less effect on the site-selectivity of insertion.

Scheme 2 Proposed catalytic cycle.



According to previous studies and our observations,[7f,j] The mechanistic scenario for the synthesis of **2a** is depicted in Scheme 2. At the beginning, a well-established rhodium(I) cyclobutanolate formation and β-carbon elimination of the C(sp2)-C(sp3) bond occur to afford the vinylrhodium species **I**. Next, a *cis*- migratory insertion of C(sp2)-Rh(I) across the (*E*)-2-nitroethenylbenzene occurs to give **II**.[9] The last ring closing takes place in a highly stereoselective manner.

Conclusions

In conclusion, two types of highly functionalized all-carbon six-membered ring have been synthesised by an stepwise [4+2]cycloaddition of 2-alkylenecyclobutanols with nitrostyrene and alkynes using rhodium(I) complexes as catalyst. The excellent site-selectivity and diastereoselectivity are remarkable. The synthetic application of the methodology established in this work to material and pharmaceutical science is positively expected.

Experimental

Generally information

NMR spectra were recorded at room temperature on the following spectrometers: Agilent (400 MHz) and VARIAN (400 MHz). Chemical shifts are given in ppm and coupling constants in Hz. ^{1}H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the largest coupling constant. High performance liquid chromatography (HPLC) was carried out with Agilent 1260 Infinity on a UV spectrophotometric detector (210 nm, Agilent). For ESI^+-spectra and EI^-HR (GC-TOF) spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR spectrometer named Nicolet 380. The method is denoted in brackets. For the most significant bands the wave number ṽ (cm^{-1}) is given.

Chemicals were purchased from commercial suppliers. Unless stated otherwise, all the substrates and solvents were purified and dried according to standard methods prior to use. Reactions requiring inert conditions were carried out in glove box.

Generation procedure for cyclic products 2

To an oven-dried sealed tube equipped with a stirrer bar was added $[Rh(OH)(COD)]_2$ (2.3 mg, 5.0 umol, 2.5 mol%), 2-alkylenecyclobutanol 1 (0.20 mmol, 1.0 equiv), (*E*)-2-nitroethenylbenzene (0.40 mmol, 2.0 equiv) in glove box. Then dry isopropanol (1.0 ml) was added. After the mixture was stirred at room temperature for 12h , The resulting mixture was passed through a pad of silica gel and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/EtOAc = 10:1) to afford the product **2** .

(1*S*,2*S*,3*S*,*E*)-4-benzylidene-2-nitro-1,3-diphenylcyclohexanol (**2a**) was obtained as white solid (85.1 mg, 0.22 mmol, 85%). mp = 125 - 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.26 (m, 10H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 5.87 (s, 1H), 5.48 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.13 (d, *J* = 2.4 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.78 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.08 – 2.14 (m, 1H), 1.93 (dd, *J* = 17.9, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 139.6, 137.1, 135.1, 129.6, 128.8, 128.76, 128.7, 128.4, 128.13, 128.1, 126.7, 124.5, 95.6, 75.1, 51.1, 39.2, 24.6. IR (neat) cm^{-1} ṽ: 3475, 3024, 2918, 2856, 1704, 1600, 1493, 1447, 1306, 1058, 1036, 950, 752, 695, 658, 611, 532, 477. HRMS (EI(+), 70 eV) : $C_{25}H_{23}NO_3$ $[M-HNO_2]^+$: calcd. 338.1678, found: 338.1663.

(1*R*,2*S*,3*S*,*E*)-4-benzylidene-1-methyl-2-nitro-3-phenylcyclohexanol (**2b**) was obtained as white solid (71.9 mg, 0.22 mmol, 89%). mp = 105 - 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.3 Hz, 2H), 7.32 – 7.25 (m, 5H), 7.19 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 5.75 (s, 1H), 4.94 (d, J = 12.3 Hz, 1H), 4.48 (d, J = 12.3 Hz, 1H), 3.04 (d, J = 2.3 Hz, 1H), 2.85 (s, 1H), 2.59 (dd, J = 16.4, 11.7 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.56 (d, J = 6.4 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 137.2, 135.7, 129.4, 128.8, 128.7, 128.1, 128.0, 127.9, 126.6, 96.8, 70.1, 50.3, 37.7, 27.4, 24.1. IR (neat) cm^{-1} ṽ: 3538, 2920, 2855, 1537, 1493, 1455, 1365, 1274, 1202, 1152, 1124, 1076, 1000, 943, 920, 886, 761, 734, 698, 602, 571, 542, 443. HRMS (EI(+), 70 eV) : $C_{20}H_{21}NO_3$ [M]+: calcd. 323.1521, found: 323.1528.

(1*S*,2*S*,3*S*,*E*)-1-(3-chlorophenyl)-4-(2-methylbenzylidene)-2-nitro-3-phenylcyclohexanol (**2c**) was obtained as white solid (81.7 mg, 0.19 mmol, 82%). mp = 115 - 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 6.5, 1.8 Hz, 1H), 7.41 – 7.34 (m, 5H), 7.33 – 7.28 (m, 2H), 7.28 – 7.26 (m, 1H), 7.12 (t, J = 4.3 Hz, 3H), 7.04 (dd, J = 6.2, 3.1 Hz, 1H), 5.81 (s, 1H), 5.44 (d, J = 12.1 Hz, 1H), 4.67 – 4.61 (m, 1H), 4.17 (d, J = 2.7 Hz, 1H), 2.72 (dd, J = 7.8, 3.0 Hz, 2H), 2.07 (d, J = 6.9 Hz, 3H), 2.05 – 2.02 (m, 1H), 1.71 – 1.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.6, 136.4, 136.2, 135.1, 134.8, 130.0, 129.8, 129.4, 128.8, 128.7, 128.4, 128.2, 127.1, 125.4, 125.1, 122.7, 95.3, 74.9, 50.9, 39.2, 24.6, 19.8. IR (neat) cm^{-1} ṽ: 3574, 2922, 2854, 1574, 1539, 1453, 1418, 1356, 1294, 1260, 1081, 1064, 968, 938, 897, 786, 740, 722, 696, 597, 569, 535, 451. HRMS (EI(+), 70 eV) : $C_{26}H_{24}ClNO_3$ [M-HNO_2]+: calcd. 386.1445, found: 386.1447.

(1*S*,2*S*,3*S*,*E*)-4-(cyclohexylmethylene)-2-nitro-1,3-diphenylcyclohexanol (**2d**) was obtained as white solid (84.8 mg, 0.22 mmol, 88%). mp = 95 - 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.26 (s, 1H), 7.21 (d, J = 6.8 Hz, 2H), 5.32 (d, J = 12.1 Hz, 1H), 4.60 (d, J = 9.1 Hz, 1H), 4.42 (d, J = 11.8 Hz, 1H), 4.11 (d, J = 2.8 Hz, 1H), 2.69 (s, 2H), 2.35 (d, J = 4.5 Hz, 1H), 2.22 (d, J = 8.8 Hz, 1H), 2.10 (s, 1H), 1.86 (t, J = 12.9 Hz, 1H), 1.65 (d, J = 23.3 Hz, 2H), 1.46 (d, J = 13.2 Hz, 1H), 1.33 – 1.18 (m, 3H), 1.07 (d, J = 12.3 Hz, 1H), 1.00 (s, 1H), 0.84 (dd, J = 24.1, 12.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 135.4, 134.6, 129.5,

128.6, 128.5, 128.0, 127.7, 124.5, 96.0, 75.1, 50.8, 39.4, 36.8, 33.5, 32.7, 25.82, 25.8, 24.1. IR (neat) cm^{-1} ṽ: 3523, 2921, 2850, 1667, 1540, 1444 1364, 1268, 1204, 1110, 1063, 983, 900, 886, 742, 697, 603, 550, 532, 453.HRMS (EI(+), 70 eV) : $C_{25}H_{29}NO_3$ $[M\text{-}HNO_2]^+$: calcd. 344.2147, found: 344.2126.

(1*S*,2*S*,3*S*,*E*)-1-(4-fluorophenyl)-4-(4-methylbenzylidene)-2-nitro-3-phenylcyclohexanol (**2e**) was obtained as white solid (86.8 mg, 0.21 mmol, 80%). mp = 100 - 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 7.13 – 7.08 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 (d, J = 8.0 Hz, 2H), 5.84 (s, 1H), 5.43 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.12 (t, J = 4.9 Hz, 1H), 3.02 – 2.92 (m, 1H), 2.75 (d, J = 4.9 Hz, 1H), 2.32 (d, J = 5.7 Hz, 3H), 2.13 – 2.03 (m, 1H), 1.91 – 1.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$= 248.5 Hz), 138.7, 138.2, 136.5, 135.1, 134.1, 129.5, 128.83, 128.8, 128.6, 128.4, 128.1, 126.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 95.6, 74.9, 51.1, 39.4, 24.6, 21.1. IR (neat) cm^{-1} ṽ: 3537, 2923, 1602, 1539, 1509, 1451, 1350, 1304, 1229, 1160, 1067, 970, 894, 836, 746, 701, 556, 521, 505.
HRMS (EI(+), 70 eV) : $C_{26}H_{24}NO_3$ $[M\text{-}HNO_2]^+$: calcd. 370.1740, found: 370.1727.

Procedure for cyclic products 3

To an oven-dried sealed tube equipped with a stirrer bar was added $[Rh(OH)(COD)]_2$ (2.3 mg, 5.0 umol, 2.5 mol%), 2-alkylenecyclobutanol 1 (0.20 mmol, 1.0 equiv) and alkyne (0.40 mmol, 2.0 equiv) in glove box. Then dry toluene (1.0 ml) was added. After the mixture was stirred at 80 °C for 6h, the resulting mixture was cooled to room temperature. The resulting mixture was passed through a pad of silica gel and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/EtOAc = 10:1) to afford **3**.

(*E*)-4'-benzylidene-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3a**) was obtained as yellow oil (52.2 mg, 0.13 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.17 (m, 5H), 7.16 – 7.07 (m, 5H), 6.93 (d, *J* = 4.8 Hz, 3H), 6.84 – 6.79 (m, 2H), 6.17 (s, 1H), 2.96 (d, *J* = 16.2 Hz, 1H), 2.62 (t, *J* = 14.4 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.19 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 142.1, 141.5, 139.4, 137.9, 137.6, 130.8, 130.62, 130.6, 130.4, 129.1, 128.1, 128.0,127.45, 127.4, 127.2, 126.5, 126.4, 126.2, 76.2, 39.0, 24.4. HRMS (ESI(+), 70 eV) : $C_{31}H_{26}O$ [M-Na]+: calcd. 437.1984, found: 437.1876.

(*E*)-4'-benzylidene-4-fluoro-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3b**) was obtained as yellow oil (82.0 mg, 0.19 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.29 – 7.04 (m, 12H), 6.98 – 6.90 (m, 3H), 6.84 – 6.76 (m, 2H), 6.18 (s, 1H), 2.97 (dd, *J* = 12.3, 3.9 Hz, 1H), 2.60 (s, 1H), 2.38 – 2.30 (m, 1H), 2.11 (dd, *J* = 10.7, 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 246.4 Hz), 141.9, 141.7, 141.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 139.3, 137.8, 137.6, 137.5, 131.0, 130.8, 130.5, 129.2, 128.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.1, 127.6, 127.5, 126.7, 126.6, 126.4, 116.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 75.9, 39.1, 24.4. IR (neat) cm^{-1} ṽ: 2926, 1599, 1501, 1440, 1328, 1223, 1156, 1057, 1031, 1010, 907, 837, 759, 731, 696. HRMS (ESI(+), 70 eV) : $C_{31}H_{25}FO$ [M+Na]+: calcd. 455.1889, found: 455.1778.

(*E*)-6'-benzylidene-3'-methyl-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-3'-ol (**3c**) was obtained as yellow oil (54.1 mg, 0.15 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2H), 7.17 (dd, J = 17.5, 7.4 Hz, 3H), 7.11 – 6.95 (m, 10H), 6.01 (s, 1H), 3.09 – 3.00 (m, 1H), 2.92 – 2.82 (m, 1H), 2.12 – 1.98 (m, 2H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 139.5, 139.4, 138.6, 138.3, 137.7, 130.52, 130.5, 129.9, 129.0, 127.9, 127.2, 126.4, 126.2, 126.0, 70.6, 37.7, 28.2, 24.8. IR (neat) cm^{-1} ṽ: 2920, 1508, 1488, 1439, 1327, 1183, 1155, 1110, 1054, 908, 876, 818, 758, 732, 698. HRMS (EI(+), 70 eV) : $C_{26}H_{24}O$ [M]+: calcd. 352.1827, found: 352.1821.

(*E*)-6'-benzylidene-3'-ethyl-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-3'-ol (**3d**) was obtained as yellow oil (36.0 mg, 0.098 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.18 (dd, *J* = 17.3, 7.8 Hz, 3H), 7.11 – 6.92 (m, 10H), 6.01 (s, 1H), 3.06 – 2.94 (m, 1H), 2.84 (t, *J* = 10.7 Hz, 1H), 2.11 (dd, *J* = 12.5, 5.8 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.84 – 1.75 (m, 1H), 1.62 – 1.54 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 140.0, 139.7, 138.4, 138.3, 137.8, 130.7, 130.6, 129.8, 129.1, 128.0, 127.24, 127.2, 126.4, 126.2, 125.9, 72.8, 32.5, 32.0, 24.4, 7.7. IR (neat) cm^{-1} ṽ: 3564, 2936, 1597, 1571, 1488, 1440, 1369, 1330, 1271, 1116, 1073, 982, 913, 878, 759, 739, 695. HRMS (EI(+), 70 eV) : $C_{27}H_{26}O$ [M]+: calcd. 366.1984, found: 366.1977.

(*E*)-6'-benzylidene-3'-(but-3-en-1-yl)-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-3'-ol (**3e**) was obtained as yellow oil (36.0 mg, 0.092 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.3 Hz, 3H), 7.23 – 7.15 (m, 3H), 7.13 – 6.93 (m, 9H), 6.01 (s, 1H), 5.77 (dd, *J* = 17.0, 6.7 Hz, 1H), 4.96 (dd, *J* = 31.0, 13.5 Hz, 2H), 2.99 (s, 1H), 2.86 (d, *J* = 10.6 Hz, 1H), 2.17 (s, 3H), 2.00 (d, *J* = 10.5 Hz, 1H), 1.89 (d, *J* = 10.1 Hz, 1H), 1.64 (d, *J* = 14.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 140.0, 139.6 138.6, 138.2, 138.1, 137.7, 130.7, 130.6, 130.0, 129.1, 128.0, 127.3, 127.27, 126.4, 126.3, 126.0, 114.6, 72.6, 38.5, 33.2, 27.8, 24.5. IR (neat) cm^{-1} ṽ: 2924, 1640, 1599, 1573, 1488, 1440, 1368, 1330, 1266, 1072, 1029, 908, 870, 761, 731, 696. HRMS (EI(+), 70 eV) : $C_{29}H_{28}O$ [M]+: calcd. 392.2140, found: 392.2128.

(*E*)-4-butyl-4'-(2-methylbenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3f**) was obtained as yellow oil (30.0 mg, 0.062 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 (s, 4H), 7.08 (dd, *J* = 8.0, 4.0 Hz, 4H), 6.94 (d, *J* = 1.6 Hz, 3H), 6.83 (d, *J* = 3.4 Hz, 2H), 6.15 (s, 1H), 2.77 – 2.62 (m, 3H), 2.47 (s, 1H), 2.30 (d, *J* = 3.7 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 1H), 1.64 (dd, *J* = 15.2, 7.8 Hz, 2H), 1.39 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 141.9, 141.8, 141.1, 139.6, 138.0, 137.6, 136.9, 136.6, 130.7, 130.5, 129.7, 129.6, 128.6, 128.1, 127.4, 126.7, 126.45, 126.4, 126.2, 125.1, 76.3, 39.2, 35.2, 33.5, 24.0, 22.4, 19.9, 14.0. IR (neat) cm^{-1} ṽ: 2924, 2854, 1600, 1484, 1439, 1409, 1326, 1258, 1182, 1104, 1054, 938, 888, 834, 788, 748, 698. HRMS (ESI(+), 70 eV) : $C_{36}H_{36}O$ [M+Na]+: calcd. 507.2766, found: 507.2662.

(*E*)-3-chloro-4'-(4-methylbenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3g**) was obtainedas yellow oil (53.0 mg, 0.11 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.06 – 7.15 (m, 9H), 7.00 – 6.91 (m, 3H), 6.84 – 6.74 (m, 2H), 6.16 (s, 1H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.61 (s, 1H), 2.35 (dd, *J* = 12.6, 4.3 Hz, 1H), 2.30 (s, 3H), 2.12 (d, *J* = 12.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 142.1, 140.1, 139.3, 137.6, 136.8, 136.5, 134.6, 134.4, 131.1, 130.7, 130.5, 129.2, 129.1, 128.7, 127.5, 127.48, 127.4, 126.8, 126.6, 126.3, 124.9, 75.9, 38.9, 24.3, 21.2. IR (neat) cm^{-1} ṽ: 3610, 3528, 3174, 2342, 2166, 2107, 1588, 1485, 1440, 1322, 1097, 1056, 997, 895, 808, 788, 755, 729, 698, 633. HRMS (ESI(+), 70 eV) : $C_{32}H_{27}ClO$ [M+Na]+: calcd. 485.1750, found: 485.1643.

(*E*)-2-fluoro-4'-(4-methylbenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3h**) was obtained as yellow oil (88.0 mg, 0.20 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.13 – 6.97 (m, 11H), 6.87 (s, 5H), 6.14 (s, 1H), 2.97 (d, *J* = 10.3 Hz, 1H), 2.92 – 2.81 (m, 1H), 2.50 (dd, *J* = 19.4, 7.1 Hz, 2H), 2.30 (s, 3H), 2.22 – 2.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, $J_{C\text{-}F}$ = 247.5 Hz), 141.50, 140.2, 139.7, 138.4, 137.4, 136.3, 134.7, 133.2 (d, $J_{C\text{-}F}$ = 10.1 Hz), 130.7, 130.3, 129.1, 128.9, 128.8, 128.7, 128.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.3, 127.0, 126.1, 123.8, 123.7, 115.9(d, $J_{C\text{-}F}$ = 23.2 Hz), 74.18, 37.2, 24.0, 21.1. IR (neat) cm^{-1} ṽ: 2930, 1605, 1506, 1442, 1286, 1242, 1176, 1107, 1032, 908, 824, 757, 732, 697, 622. HRMS (ESI(+), 70 eV) : $C_{32}H_{27}FO$ [M+Na]+: calcd. 469.2046, found: 469.1935.

(*E*)-4-fluoro-4'-(4-methylbenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3i**) was obtained as yellow oil (42.0 mg, 0.094 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.21 – 7.03 (m, 11H), 6.94 (s, 3H), 6.79 (d, *J* = 3.6 Hz, 2H), 6.14 (s, 1H), 2.98 (d, *J* = 16.3 Hz, 1H), 2.58 (t, *J* = 14.7 Hz, 1H), 2.40 – 2.25 (m, 4H), 2.13 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$= 246.4 Hz), 141.8, 141.4, 139.4, 137.7, 136.9, 136.5, 134.6, 130.9, 130.8, 130.4, 129.1, 128.7, 128.3 (d, $J_{C\text{-}F}$= 8.1 Hz), 127.5, 126.5, 126.2, 114.90 (d, $J_{C\text{-}F}$ = 21.2 Hz), 75.8, 39.1, 24.4, 21.1. IR (neat) cm^{-1} ṽ: 2733, 1599, 1503,, 1440, 1327, 1222, 1156, 1057, 836, 759, 739, 697, 618. HRMS (ESI(+), 70 eV) : $C_{32}H_{27}FO$ [M+Na]+: calcd. 469.2046, found: 469.1936.

(*E*)-4-methyl-4'-(4-methylbenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3j**) was obtained as yellow oil (81.0 mg, 0.18 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.01 (m, 9H), 6.96 – 6.89 (m, 3H), 6.86 – 6.79 (m, 2H), 6.13 (s, 1H), 2.95 (d, *J* = 16.3 Hz, 1H), 2.60 (t, *J* = 14.0 Hz, 1H), 2.38 (s, 3H), 2.32 (dd, *J* = 12.8, 3.8 Hz, 1H), 2.28 (s, 3H), 2.11 (dd, *J* = 8.1, 4.2 Hz, 1H), 2.02 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.9, 141.4, 139.6, 138.0, 137.2, 136.8, 136.3, 134.7, 130.8, 130.5, 130.4, 129.1, 128.8, 128.7 127.4, 127.3, 126.5, 126.3, 126.1, 76.1, 39.0, 24.6, 21.1, 21.0. IR (neat) cm^{-1} ṽ: 2920, 1601, 1574, 1509, 1439, 1411, 1328, 1182, 1057, 1006, 907, 815, 759, 731, 698. HRMS (ESI(+), 70 eV) : $C_{33}H_{30}O$ [M+Na]+: calcd. 465.2297, found: 465.2185.

(*E*)-4'-(4-methoxybenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol(**3k**) was obtained as yellow oil (90.0 mg, 0.20 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.02 (m, 7H), 6.92 (dd, *J* = 6.9, 3.4 Hz, 3H), 6.85 – 6.75 (m, 4H), 6.11 (s, 1H), 3.74 (s, 3H), 2.95 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.60 (d, *J* = 2.4 Hz, 1H), 2.40– 2.32 (m, 1H), 2.18 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 145.6, 141.6, 141.3, 139.6, 138.0, 136.3, 130.8, 130.5, 130.2, 128.1, 127.4, 127.35, 127.2, 126.6, 126.3, 126.2, 113.4, 76.2, 55.2, 39.0, 24.5. IR (neat) cm^{-1} ṽ: 2896, 2049, 1973, 1601, 1506, 1441, 1327, 1247, 1175, 1082, 1030, 888, 830, 764, 741, 697, 624. HRMS (ESI(+), 70 eV) : $C_{32}H_{28}O_2$ [M+Na]+: calcd. 467.2089, found: 467.1981.

(*E*)-3-chloro-4'-(4-methoxybenzylidene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3l**) was obtained as yellow oil (45.0 mg, 0.097 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.18 – 7.03 (m, 7H), 6.94 (s, 3H), 6.80 (d, *J* = 7.5 Hz, 4H), 6.12 (s, 1H), 3.76 (s, 3H), 2.97 (d, *J* = 16.2 Hz, 1H), 2.60 (t, *J* = 14.1 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.12 (d, *J* = 11.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 148.1, 142.1, 140.6, 139.4, 137.6, 135.9, 134.4, 130.7, 130.5, 130.46, 130.1, 129.2, 127.5, 127.46, 127.4 , 126.8, 126.6, 126.3, 124.9, 113.5, 75.8, 55.2, 38.9, 24.3. IR (neat) cm^{-1} ṽ: 2927, 1599, 1506, 1465, 1439, 1414, 1301, 1247, 1175, 1097, 1031, 888, 830, 787, 754, 733, 697, 627. HRMS (ESI(+), 70 eV) : $C_{32}H_{27}ClO_2$ [M+Na]+: calcd. 501.1700, found: 501.1591.

(*E*)-4'-(cyclohexylmethylene)-3'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3m**) was obtained from as yellow oil (35.0 mg, 0.083 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.13 – 6.97 (m, 5H), 6.91 (s, 3H), 6.75 (s, 2H), 4.99 (d, *J* = 9.2 Hz, 1H), 2.70 (d, *J* = 14.9 Hz, 1H), 2.28 (t, *J* = 11.3 Hz, 3H), 2.11 (s, 1H), 2.04 (s, 1H), 1.56 (dd, *J* = 39.4, 13.4 Hz, 5H), 1.27 – 1.17 (m, 2H), 1.07 (d, *J* = 11.5 Hz, 1H), 0.98 – 0.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 141.1, 139.8, 139.6, 138.2, 133.7, 130.8, 130.5, 128.0, 127.4, 127.2, 127.0, 126.5, 126.2, 125.9, 76.7, 76.2, 39.0, 37.2, 32.8, 32.3, 26.0, 25.9, 25.8, 22.2. IR (neat) cm^{-1} ṽ: 2921, 2848, 1598, 1488, 1442, 1328, 1256, 1178, 1050, 1004, 906, 761, 734, 697, 630. HRMS (ESI(+), 70 eV) : $C_{31}H_{32}O$ [M+Na]+: calcd. 443.2453, found: 443.2344.

(*E*)-4'-benzylidene-4''-methoxy-3'-(4-methoxyphenyl)-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3n**) was obtained as yellow oil (50.0 mg, 0.11 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.22 (dd, *J* = 15.5, 7.0 Hz, 4H), 7.15 (d, *J* = 6.6 Hz, 1H), 7.04 (d, *J* = 6.3 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 4H), 6.49 (d, *J* = 8.5 Hz, 2H), 6.20 (s, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 2.94 (d, *J* = 16.2 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.36 – 2.28 (m, 1H), 2.12 (d, *J* = 11.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 157.7, 145.8 141.8, 141.1, 138.4, 137.7, 131.9, 131.6, 130.1, 130.0, 129.1, 128.1, 127.9, 127.1, 126.5, 126.4, 113.0, 112.9, 76.2 55.0, 54.8, 39.0, 24.4. IR (neat) cm^{-1} ṽ: 2931, 2834, 1605, 1505, 1442, 1329, 1285, 1241, 1175, 1106, 1083, 1032, 907, 823, 791, 764, 729, 698, 645. HRMS (ESI(+), 70 eV) : $C_{33}H_{30}O_3$ [M+Na]+: calcd. 497.2195, found: 497.2081.

Product **3q, 3q'** was obtained as yellow oil (29.5 mg, 0.083 mmol, 78%, 2:1).

(*E*)-4'-benzylidene-4''-methyl-3'-(p-tolyl)-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3o**) was obtained as yellow oil (52.0 mg, 0.12 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.3 Hz, 2H), 7.41 (t, *J* = 6.7 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 4H), 6.72 (dd, *J* = 19.4, 7.0 Hz, 4H), 6.16 (s, 1H), 2.94 (d, *J* = 15.9 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.38 – 2.28 (m, 2H), 2.23 (s, 3H), 2.10 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 141.8, 141.2 138.2, 137.7, 136.5, 135.8, 135.5, 134.8, 130.6, 130.2, 129.2, 128.2, 128.1, 127.9, 127.1, 126.6, 126.4, 76.2, 39.0, 24.4, 21.1, 20.97. IR (neat) cm^{-1} ṽ: 3022, 2921, 1598, 1489, 1443, 1328, 1181, 1108, 1082, 1049, 907, 815, 760, 730, 698, 641. HRMS (ESI(+), 70 eV) : $C_{33}H_{30}O$ [M+Na]+: calcd. 465.2297, found: 465.2188.

(*E*)-4-benzylidene-5,6-diethyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-1-ol (**3p**) was obtained as yellow oil (30.0 mg, 0.094 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.25 (m, 7H), 7.19 (d, *J* = 6.8 Hz, 1H), 6.67 (s, 1H), 2.66 (d, *J* = 15.2 Hz, 1H), 2.55 (dd, *J* = 14.6, 7.2 Hz, 2H), 2.40 – 2.23 (m, 3H), 2.02 – 1.90 (m, 4H), 1.23 (t, *J* = 7.4 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 141.0, 138.3, 138.1, 136.1, 129.2, 128.0, 126.9, 126.2, 126.15, 123.4, 76.7, 40.8, 24.6, 23.3, 21.2, 15.5, 14.3. IR (neat) cm^{-1} ṽ: 2962, 1599, 1490, 1444, 1373, 1320, 1154, 1017, 983, 911, 851, 763, 732, 697, 622. HRMS (EI(+), 70 eV) : $C_{23}H_{26}O$ [M]+: calcd. 318.1984, found: 318.1990.

(*E*)-4'-benzylidene-3'-methyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-1'-ol (**3q**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.27 (m, 7H), 7.23 (dd, *J* = 17.3, 5.3 Hz, 4H), 7.00 (s, 2H), 6.76 (s, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 2.50 (t, *J* = 14.4 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.08 – 1.98 (m, 1H), 1.89 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 141.6, 138.8, 137.9, 137.5, 132.7, 129.3, 128.1, 128.0, 127.1, 127.0, 126.6, 126.5, 125.8, 77.4, 39.4, 24.3, 17.3. IR (neat) cm^{-1} ṽ: 3564, 3055, 2924,, 2860, 2245, 1601, 1488, 1442, 1328, 1261, 1102, 1064, 1018, 986, 907, 860, 799, 760, 730, 699, 645. HRMS (ESI(+), 70 eV) : $C_{26}H_{24}O$ [M-H_2O]+: calcd. 335.1827, found: 335.1792.

(E)-4'-benzylidene-2'-methyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-1'-ol (**3q'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 2H), 7.41 (q, J = 7.5 Hz, 4H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 4H), 7.14 (d, J = 6.7 Hz, 3H), 5.90 (s, 1H), 2.82 (dd, J = 13.5, 7.1 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.18 – 2.08 (m, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 140.7, 140.3, 138.6, 137.8, 136.7, 129.9, 129.0, 128.6, 128.3, 128.2, 127.9, 127.1, 126.7, 126.3, 126.0, 76.4, 40.2, 24.3, 17.0. IR (neat) cm^{-1} ṽ: 3384, 3056, 3023, 2923, 2855, 1599, 1491, 1444, 1328, 1179, 1046, 1028, 918, 876, 764, 736, 700. HRMS (ESI(+), 70 eV) : $C_{26}H_{24}O$ [M-H_2O]+: calcd. 335.1827, found: 335.1794.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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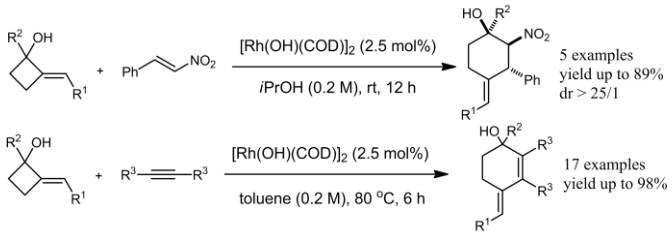
Rhodium(I)-Catalyzed [4+2] Cycloaddition Reactions of 2-Alkylenecyclobutanols with Alkynes and (E)-2-Nitroethenylbenzene through C(sp2)-C(sp3) Bond Cleavage

Xinxin Zheng, Guozhu Zhang*, Dayong Zhang*



An intermolecular [4+2] cycloaddition was realized through C-C bond cleavage in the presence of Rh(I) catalyst. The selective ring opening of 2-alkylenecyclobutanols enables the generation of active alkenylrhodium species, which underwent smooth cross addition over alkynes and (*E*)-2-nitroethenylbenzene, leading to highly substituted all-carbon six-membered rings in a single step.