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The cyclopropyl effect on the regioselectivity of coupling reactions involving the lithiation of 1-cyclopropyl-2-arylacetylenes

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Abstract—The cyclopropyl effect controlled the regioselectivity of the cross coupling reactions of propargylic/allenylic metallic species with electrophiles affording alkynic cyclopropanes. It was proposed that the strain in cyclopropyl ring, which makes the formation of vinylidenecyclopropanes unfavorable, determined the regioselectivity. Control experiment of *i*-propyl, cyclobutyl, and cyclohexyl-phenylacetylenes were conducted to support the above speculation.

1. Introduction

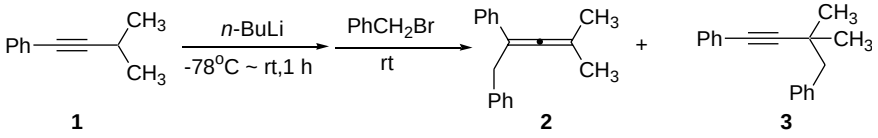
Selectivity control in a reaction is a very important issue in organic synthesis and remains to be a challenge to chemists.[1] Recently, tremendous attention has been paid to the selective synthesis of alkynes or allenes from propargylic/allenylic metallic species due to the presence of equilibrium mixture of propargylic and allenylic metallic derivatives.[2] Recently, we observed that the regioselectivity of Pd-catalyzed cross coupling reactions involving propargylic/allenylic species can be tuned by the steric, electronic, and ligand effects.[3] Herein, we report a cyclopropyl effect in the regioselectivity control in the lithiation of 1-aryl-1-alkynes and the subsequent cross coupling with electrophiles.

2. Results and discussion

First, it was observed that lithiation reaction of 1-phenyl-3-methyl-1-butyne **1**, a secondary alkyl substituted 1-aryl-1-alkyne, and the subsequent reaction with benzyl bromide afforded a mixture of 1,2-diphenyl-4-methyl-2,3-pentadiene **2** and 1,4-diphenyl-3,3-dimethylbut-1-yne **3** with a ratio of 70:30, a regioselectivity different from that of 1°-alkyl-substitute d 1-aryl-1-alkynes[3a,3b] (Scheme 1).

Furthermore, it was interesting to observe that the same reaction of 1-phenyl-2-cyclopropylacetylene **4a** afforded alkyne **5a** as the only product (entry 1, Table 1). The lithiation reaction of **4a** and the subsequent reaction with different electrophiles afforded alkynic products **5** highly selectively (Table 1), which is in accordance with the reported data.[4]

When a four-membered ring or six-membered ring was applied instead of the cyclopropyl ring, mixtures of alkynes and allenes were formed again (compare Table 1 with Scheme 2), indicating the strain in the three-membered ring may be the key factor determining the regioselectivity. With this observation, it was reasoned that the corresponding lithiation, transmetallation and subsequent Pd(0)-catalyzed cross coupling reaction with organic halides may also lead



1 2 3

Scheme 1. >99% (**2**:**3**=70:30). The yield and ratio are determined by 300 MHz ^{1}H NMR spectra analysis with CH_2Br_2 as the internal standard.

Keywords: Lithiation; Coupling; Palladium; Regioselectivity; Alkynes; Organic halides.
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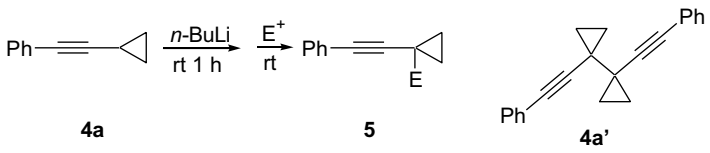
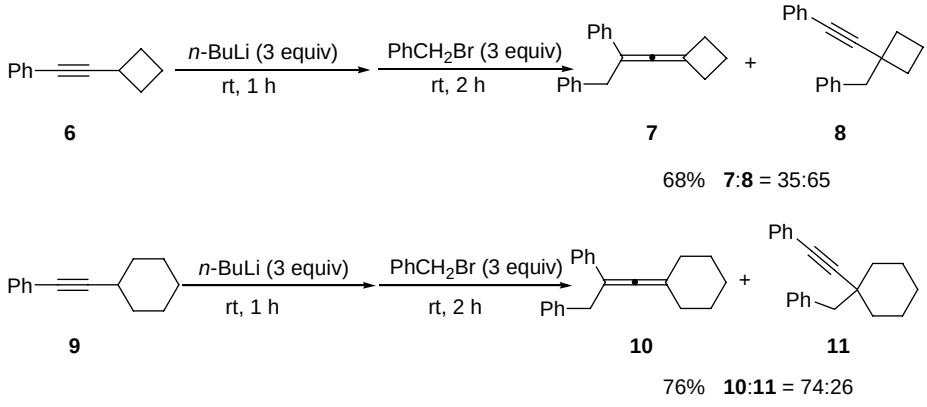
Table 1. The lithiation of 1-cyclopropyl-2-phenylacetylene **4a** and the subsequent reactions with electrophiles



4a **5** **4a'**

Entry	E^+	Yield of **5** (%)
1	$PhCH_2Br$	78 (**5a**)
2	$CH_2{=}CHCH_2Br$	77 (**5b**)[a]
3	n-C_4H_9Br	43 (**5c**)
4	PhCH=NTs	50 (**5d**)[b]
5	CH_3I	76 (**5e**)

[a] n-BuLi (2 equiv) and allyl bromide (4 equiv) were used. Compound **4a'** (2%) was also formed.
[b] The reaction was carried out at 0 °C.



Scheme 2.

to the highly selective formation of alkynes, instead of the usual products, allenes.

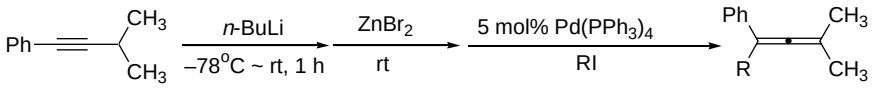
In fact, the lithiation of 1-phenyl-3-methyl-1-butyne **1**, transmetallation and the Pd(0)-catalyzed cross coupling[5] with aryl halides afforded allenes **12** as the only product as expected (Table 2).

However, in contrast to the results shown in Table 2, when 1-cyclopropyl-2-arylacetylene **4** was used in the same sequential reaction, substituted cyclopropyl alkynes **13** were afforded as the only products. The results listed in Table 3 indicated that: (1) the reactions gave alkynes exclusively; (2) the yields are very sensitive to the substituents of aryl halides. The more sterically hindered aryl halides afforded the products in lower yields (entries 2 and 3, Table 3); (3) the aryl halides with an electron-withdrawing substituent showed better results than those with an electron-donating group (compare entries 4 and 5 with entry 6 in Table 3).

When 1,4-diiodobenzene was used, the reaction produced 57% yield of the mono-cross coupling product **13l** and 18% yield of the double cross coupling product **13l'** (Scheme 3).

In order to clarify the cyclopropyl effect, the same sequential reaction of 1-cyclobutyl-2-phenylacetylene **6** and 1-cyclohexyl-2-phenylacetylene **9** were studied (Scheme 4). Here, again allenes were formed exclusively (compare Scheme 4 with Table 2).

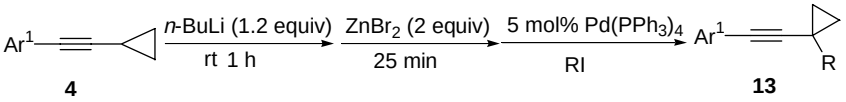
Table 2. The lithiation of 1-phenyl-3-methyl-1-butyne, transmetallation, and Negishi-type cross coupling with aryl halides



1 **12**

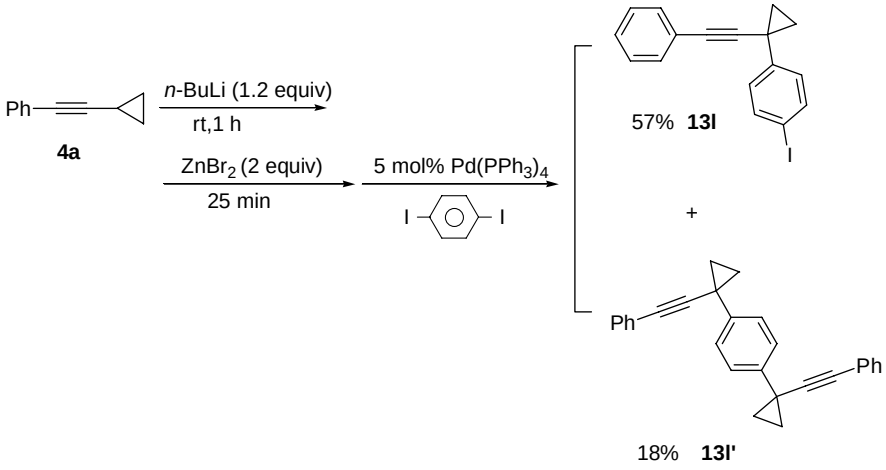
Entry	R	Yield of **12** (%)
1	Ph	47 (**12a**)
2	α-$C_{10}H_8$	25 (**12b**)
3	p-$MeOC_6H_4$	71 (**12c**)
4	p-$MeO_2CC_6H_4$	91 (**12d**)
5	o-$CH_3C_6H_4$	40 (**12e**)
6	(*E*)-CH=$CHCO_2CH_3$	37 (**12f**)

Table 3. The lithiation of 1-cyclopropyl-2-arylacetylenes, transmetallation, and Negishi-type cross coupling with aryl halides

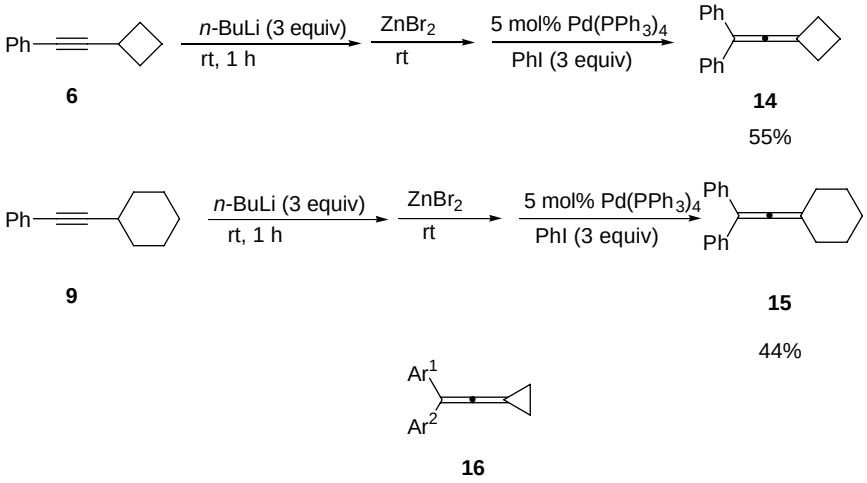


4 **13**

Entry	Ar^1	R	Yield of **13** (%)
1	Ph (**4a**)	Ph	72 (**13a**)
2	Ph (**4a**)	α-$C_{10}H_8$	27 (**13b**)
3	Ph (**4a**)	*o*-MeC_6H_4	25 (**13c**)
4	Ph (**4a**)	*p*-$MeO_2CC_6H_4$	98 (**13d**)
5	Ph (**4a**)	*p*-NCC_6H_4	88 (**13e**)
6	Ph (**4a**)	*p*-$MeOC_6H_4$	33 (**13f**)
7	Ph (**4a**)	(*E*)-CH=$CHCO_2Me$	34 (**13g**)
8	Ph (**4a**)	*p*-BrC_6H_4	64 (**13h**)
9	Ph (**4a**)	*p*-ClC_6H_4	55 (**13i**)
10	*p*-PhC_6H_4 (**4b**)	*p*-NCC_6H_4	70 (**13j**)
11	*p*-PhC_6H_4 (**4b**)	*p*-$MeO_2CC_6H_4$	51 (**13k**)



Scheme 3.



Scheme 4.

Based on these facts, it was quite clear that it was the enhanced ring strain in vinylidenecyclopropanes **16** caused by the direct connection of the carbon–carbon double bond with the cyclopropyl ring that led to the highly selective formation of alkynic cyclopopanes **5** and **13**.

In conclusion, the cyclopropyl effect tuned the selectivity in the reactions described above: the coupling reaction of cyclopropyl substituted 1-aryl-1-alkynes afforded alkynic cyclopropanes while that of other 1-aryl-1-(2°-alkyl)-substituted alkynes yielded a mixture of alkynes and allenes

or allenes exclusively. Further studies in this area are currently underway in our laboratory.

3. Experimental

3.1. Preparation of the starting materials 1, 4a, 4b, 6, and 9

3.1.1. Synthesis of 1-phenyl-3-methyl-1-butyne 1.[6] To 100 mL of anhydrous liquid ammonia was added lithium belt (0.47 g, 60 mmol) in portion and the mixture was stirred under −40 °C for 1 h. After evaporation of NH_3, phenylacetylene (5.5 mL, 50 mmol) and 20 mL of 1,4-dioxane were added. Then the mixture was kept under reflux for 20 min. After that, it was transferred into a glassware, which was put in an autoclave and *i*-propyl bromide (9.4 mL, 100 mmol) was added subsequently. The mixture was heated at 150 °C in the closed autoclave for 16 h. After the reaction was complete, the mixture was cooled down, poured into cold water and extracted with ether. Drying over anhydrous $MgSO_4$, rotary evaporation, and distillation afforded **1** as a liquid (1.418 g, 20%, bp 67 °C/5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.38–7.22 (m, 2H), 7.20–7.15 (m, 3H), 2.69 (heptet, J=6.7 Hz, 1H), 1.18 (d, J=6.7 Hz, 6H).

3.1.2. Synthesis of 1-cyclopropyl-2-phenylacetylene 4a.[7] $Pd(PPh_3)_4$ (500 mg, 0.5 mol%), CuI (270 mg, 1 mol%), and PhI (8.8 mL, 78.5 mmol) were dissolved in 250 mL of $(i\text{-Pr})_2NH$. A solution of cyclopropylacetylene (8 mL, 94 mmol) in 100 mL of $(i\text{-Pr})_2NH$ was added dropwise into the mixture under N_2 and stirred at rt. When the reaction was complete as monitored by TLC (eluent: petroleum ether (60–90 °C)), a brown precipitate appeared. Filtration, rotary evaporation, and flash chromatography on silica gel (petroleum ether) afforded **4a** (11.544 g, ~99%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.40–7.35 (m, 2H), 7.28–7.23 (m, 3H), 1.48–1.42 (m, 1H), 0.91–0.78 (m, 4H).

3.1.3. Synthesis of 1-cyclopropyl-2-(*p*-phenylphenyl)-acetylene 4b. The reaction of *p*-phenylphenyl bromide (1.165 g, 5 mmol), cyclopropylacetylene (0.85 mL, 10 mmol), and $Pd(PPh_3)_4$ (58 mg, 1 mol%) afforded **4b** as a solid (700 mg, 64%) according to the procedure for the synthesis of **4a**. Compound **4b**: mp 67–68 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.60–7.30 (m, 9H), 1.57–1.40 (m, 1H), 0.93–0.78 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=140.4, 140.1, 132.0, 128.8, 127.4, 126.9, 126.8, 122.8, 94.1, 75.6, 8.6, 0.2; MS (70 eV): *m*/*z* (%): 218 (M^+, 100.00); IR (neat): 2231, 1486 cm^{-1}. Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46; found C, 93.54; H, 6.54.

3.1.4. Synthesis of cyclobutylacetylene.[8] *n*-BuLi (21 mL, 0.034 mol, 1.6 M in hexanes) was added to a solution of 6-chloro-1-hexyne (1.855 g, 0.016 mol) in THF dropwise at −78 °C. After being stirred for 20 min at −78 °C, it was allowed to warm up naturally to rt and stirred overnight. When the reaction was complete, it was quenched with saturated aqueous solution of NH_4Cl and extracted with ether. Drying over anhydrous $MgSO_4$ and removing ether by distillation afforded a solution of the product in THF, which was submitted to next step directly.

3.1.5. Synthesis of 1-cyclobutyl-2-phenylacetylene 6.[7] The solution of cyclobutylacetylene in THF from above was added dropwise to a mixture of phenyl iodide (0.9 mL, 0.008 mol), CuI (15 mg, 1 mol%), $Pd(PPh_3)_4$ (46 mg, 0.5 mol%) and 3 mL $(i\text{-Pr})_2NH$ under N_2 and stirred at rt. When the reaction was complete as monitored by TLC (eluent: petroleum ether (60–90 °C)), a brown precipitate appeared. Filtration, rotary evaporation, and flash chromatography on silica gel (petroleum ether) afforded **6** as a liquid (0.373 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.42–7.37 (m, 2H), 7.30–7.25 (m, 3H), 3.30–3.20 (m, 1H), 2.40–2.19 (m, 4H), 2.05–1.91 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=131.5, 128.1, 127.5, 123.9, 93.9, 81.1, 30.0, 25.5, 19.2.

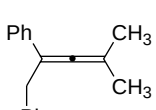
3.1.6. Synthesis of 1-cyclohexyl-2-phenylacetylene 9.[9] A suspension of zinc dust (2.24 g, 0.040 mol) in 20 mL of THF were added one drop each of 1,2-dibromoethane and TMSCl. After being stirred at rt for 20 min, cyclohexyl iodide (4.20 g, 20 mmol) was added and stirred overnight at 40–50 °C. After the excessive zinc dust was filtered under N_2, $CuCN\cdot 2LiCl$ (175 mg, 5 mol%) and phenylethynyl iodide (2.0 mL, 15 mmol) were added and stirred at rt. When the reaction was complete as monitored by TLC (eluent: petroleum ether (60–90 °C)), saturated aqueous solution of $FeSO_4$ was added and the mixture was extracted with ether. Drying over anhydrous $MgSO_4$, rotary evaporation and flash chromatography on silica gel (petroleum ether) afforded **9** (0.268 g, 9%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.42–7.37 (m, 2H), 7.30–7.24 (m, 3H), 2.62–2.54 (m, 1H), 1.91–1.85 (m, 2H), 1.81–1.72 (m, 2H), 1.60–1.48 (m, 3H), 1.42–1.31 (m, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=131.5, 128.1, 127.4, 124.1, 94.4, 80.4, 32.7, 29.6, 25.9, 24.9.

3.2. Typical procedure for the coupling reactions with or without Pd(0) catalyst

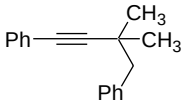
3.2.1. Synthesis of 1-(phenylethynyl)-1-benzylcyclopropane 5a. To a solution of 1-cyclopropyl-2-phenylacetylene (56 mg, 0.39 mmol) in THF (3 mL) in a dry Schlenk tube was added *n*-BuLi (0.30 mL, 1.6 M in hexanes, 0.47 mmol) at −78 °C under N_2. After being warmed up naturally and stirred 1 h at rt, benzyl bromide (0.056 mL, 0.47 mmol) was added. When the reaction was complete as monitored by TLC (eluent: petroleum ether (60–90 °C)), it was quenched with saturated aqueous solution of NH_4Cl and extracted with ether. Drying over anhydrous $MgSO_4$, rotary evaporation, and flash chromatography on silica gel (petroleum ether) afforded **5a** (71 mg, 78%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.37–7.18 (m, 10H), 2.77 (s, 2H), 1.04 (dd, J_1=6.6 Hz, J_2=4.2 Hz, 2H), 0.82 (dd, J_1=6.6 Hz, J_2=4.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=139.3, 131.5, 129.2, 128.1, 127.4, 126.3, 123.8, 94.9, 77.6, 43.4, 15.3, 13.4; MS (70 eV): *m*/*z* (%): 232 (M^+, 39.70), 115 (100.00); IR (neat) 2226, 1597, 1494 cm^{-1}; HRMS calcd for $C_{18}H_{16}Na$ [M^++Na]: 255.1150, found 255.1171.

The following compounds were prepared according to the procedure described in this section.

3.2.1.1. Synthesis of 1,2-diphenyl-4-methyl-2,3-pentadiene (2) and 1,4-diphenyl-3,3-dimethyl-1-butyne (3).



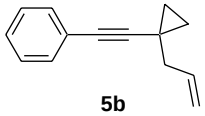
2



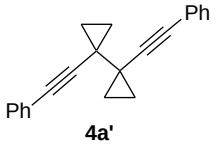
3

The reaction of 1-phenyl-3-methyl-1-butyne **1** (124 mg, 0.86 mmol), *n*-BuLi (0.54 mL, 1.6 M in hexanes, 1.0 mmol), and benzyl bromide (0.13 mL, 1.1 mmol) afforded a mixture of compounds **2** and **3**. The combined yield of **2** and **3** is >99% (**2**:**3**=70:30), which was determined by 300 MHz ^{1}H NMR spectra with CH_2Br_2 as the internal standard. Pure samples for the analysis were obtained by repeated chromatography on silica gel. Compound **2**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.48–7.44 (m, 2H), 7.36–7.31 (m, 6H), 7.27–7.21 (m, 2H), 3.83 (s, 2H), 1.78 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ= 203.4, 140.1, 137.7, 128.7, 128.2, 128.1, 126.1, 125.9, 102.7, 98.5, 37.3, 20.1; MS (70 eV): *m*/*z* (%): 234 (M^+, 52.99), 143 (100.00); IR (neat): 1952, 1598, 1493 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ [M^+]: 234.1409, found: 234.1410. Compound **3**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.40–7.20 (m, 10H), 2.77 (s, 2H), 1.27 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=138.3, 131.4, 130.6, 128.1, 127.6, 127.5, 126.3, 124.0, 96.9, 81.6, 49.1, 32.8, 29.1; MS (70 eV): *m*/*z* (%): 234 (M^+, 17.72), 143 (100.00); IR (neat): 2230, 1598, 1491 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ [M^+]: 234.14089, found: 234.1406.

3.2.1.2. Synthesis of 1-(2′-phenylethynyl)-1-allylcyclopropane (5b) and 1,1′-diphenylethynylbicyclopropyl (4a′).



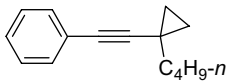
5b



4a'

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.49 mL, 0.79 mmol, 1.6 M in hexanes), and allyl bromide (0.14 mL, 1.58 mmol) afforded **5b** (55 mg, 77%) and **4a′** (2 mg, 2%). Compound **5b**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.42–7.37 (m, 2H), 7.32–7.25 (m, 3H), 6.09–5.95 (m, 1H), 5.22–5.11 (m, 2H), 2.24 (d, J=6.6 Hz, 2H), 1.04 (dd, J_1=6.9 Hz, J_2= 4.5 Hz, 2H), 0.76 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=135.5, 131.6, 128.1, 127.4, 123.9, 116.5, 94.7, 77.02, 42.0, 15.0, 12.1; MS (70 eV): *m*/*z* (%): 182 (M^+, 30.29), 115 (100.00); IR (neat) 2226, 1642, 1598, 1494 cm^{-1}; HRMS calcd for $C_{14}H_{14}Na$ [M^++Na]: 205.0993, found: 205.1001. Compound **4a′**: solid, mp 82–83 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.40–7.33 (m, 4H), 7.28–7.23 (m, 6H), 1.19 (dd, J_1= 7.5 Hz, J_2=4.8 Hz, 4H), 1.06 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=131.6, 128.1, 127.6, 123.6, 92.4, 77.8, 15.8, 14.6; MS (70 eV): *m*/*z* (%): 282 (M^+, 100.00); IR (neat) 2223, 1597, 1488 cm^{-1}; Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42; found: C, 93.61; H, 6.47.

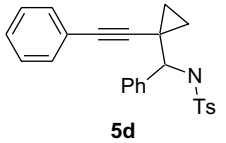
3.2.1.3. Synthesis of 1-(2′-phenylethynyl)-1-*n*-butylcyclopropane (5c).



5c

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (55 mg, 0.39 mmol), *n*-BuLi (0.29 mL, 0.46 mmol, 1.6 M in hexanes), and *n*-butyl bromide (0.059 mL, 0.55 mmol) afforded **5c** (33 mg, 43%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.40–7.35 (m, 2H), 7.28–7.20 (m, 3H), 1.63–1.52 (m, 2H), 1.44–1.30 (m, 4H), 0.97 (dd, J_1=6.6 Hz, J_2= 3.9 Hz, 2H), 0.92 (t, J=7.2 Hz, 3H), 0.65 (dd, J_1=6.6 Hz, J_2=3.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=131.6, 128.1, 127.3, 124.0, 95.3, 76.6, 38.0, 30.1, 22.6, 15.6, 14.1, 12.4; MS (70 eV): *m*/*z* (%): 198 (M^+, 18.38), 141 (100.00); IR (neat) 2220, 1598, 1491 cm^{-1}; HRMS calcd for $C_{15}H_{19}$ [M^++H]: 199.1487, found: 199.1507.

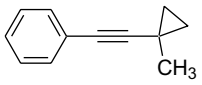
3.2.1.4. Synthesis of *N*-[phenyl-(1-(2′-phenylethynyl)-cyclopropyl)methyl]*p*-toluenesulfonamide (5d).



5d

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (58 mg, 0.41 mmol), *n*-BuLi (0.31 mL, 0.49 mmol, 1.6 M in hexanes), and *N*-benzylidene-*p*-toluenesulfonamide (127 mg, 0.49 mmol) afforded **5d** (82 mg, 50%) as a solid, mp 100–102 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.62 (d, J=8.4 Hz, 2H), 7.31–7.20 (m, 10H), 7.11 (d, J=8.4 Hz, 2H), 5.63 (d, J= 7.8 Hz, 1H), 3.87 (d, J=7.8 Hz, 1H), 2.34 (s, 3H), 1.04–0.86 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=143.0, 138.8, 137.7, 131.6, 129.2, 128.1, 128.0, 127.96, 127.6, 127.2, 127.0, 122.9, 90.4, 80.2, 63.3, 21.4, 19.1, 16.3, 14.7; MS (70 eV): *m*/*z* (%): 401 (M^+, 0.73), 260 (100.00); IR (neat) 3253, 2229, 1600 cm^{-1}. Anal. Calcd for $C_{25}H_{23}NO_2S$: C, 74.78; H, 5.77; N, 3.49; found: C, 75.08; H, 5.93; N, 3.42.

3.2.1.5. Synthesis of 1-(2′-phenylethynyl)-1-methylcyclopropane (5e).[10]

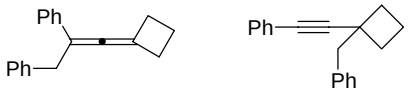


5e

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (59 mg, 0.42 mmol), *n*-BuLi (0.31 mL, 0.50 mmol, 1.6 M in hexanes), and CH_3I (0.052 mL, 0.83 mmol) afforded **5e** (50 mg, 76%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ= 7.40–7.33 (m, 2H), 7.26–7.21 (m, 3H), 1.35 (s, 3H), 0.99

(dd, $J_1=6.6$ Hz, $J_2=4.2$ Hz, 2H), 0.66 (dd, $J_1=6.6$ Hz, $J_2=4.2$ Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=131.6$, 128.1, 127.4, 123.9, 96.1, 75.7, 24.2, 16.6, 7.2; IR (neat) 2219, 1597, 1495 cm^{-1}.

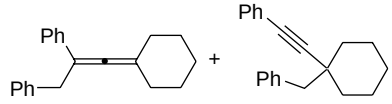
3.2.1.6. Synthesis of 2,3-diphenylpropenylidenecyclobutane (7) and 1-(phenylethynyl)-1-benzylcyclobutane (8).



7 **8**

The reaction of 1-cyclobutyl-2-phenylacetylene **6** (32 mg, 0.20 mmol), *n*-BuLi (0.38 mL, 0.60 mmol, 1.6 M in hexanes), and benzyl bromide (72 μL, 0.60 mmol) afforded **7** (12 mg, 24%) and **8** (22 mg, 44%). Compound **7**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.42$–7.39 (m, 2H), 7.32–7.12 (m, 8H), 3.78 (s, 2H), 3.02–2.90 (m, 2H), 2.82–2.70 (m, 2H), 2.02–1.80 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=196.9$, 139.9, 137.5, 128.8, 128.2, 128.1, 126.4, 126.2, 125.9, 107.0, 104.1, 37.6, 29.8, 17.4; MS (70 eV): *m*/*z* (%): 246 (M^+, 2.26), 91 (100.00); IR (neat): 1945, 1602, 1495 cm^{-1}; HRMS calcd for $C_{19}H_{18}$ [M^+]: 246.1409, found: 246.1381. Compound **8**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.42$–7.21 (m, 10H), 3.0 (s, 2H), 2.40–1.90 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=138.5$, 131.4, 130.0, 128.1, 127.8, 127.4, 126.3, 124.0, 96.5, 82.8, 45.8, 37.9, 34.1, 16.3; MS (70 eV): *m*/*z* (%): 246 (M^+, 16.02), 84 (100.00); IR (neat): 1598, 1492 cm^{-1}; HRMS calcd for $C_{19}H_{18}$ [M^+]: 246.1409, found: 246.1430.

3.2.1.7. Synthesis of 2,3-diphenylpropenylidenecyclohexane (10) and 1-(phenylethynyl)-1-benzylcyclohexane (11).



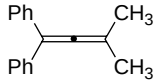
10 **11**

The reaction of 1-cyclohexyl-2-phenylacetylene **9** (37 mg, 0.20 mmol), *n*-BuLi (0.38 mL, 0.60 mmol, 1.6 M in hexanes), and benzyl bromide (72 μL, 0.60 mmol) afforded **10** and **11** as a mixture (42 mg, 76%) with a ratio of **10**:**11**=74:26, which was determined by 300 MHz ^{1}H NMR spectra. The mixture is a solid. Compound **10**: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.42$–7.14 (m, 10H), 3.73 (s, 2H), 2.20–2.00 (m, 2H), 1.80–1.20 (m, 8H), (a signal at 2.8 (s, 2H) was observed for **11**); MS (70 eV): *m*/*z* (%): 274 (M^+, 28.76), 91 (100.00); IR (neat): 1946 cm^{-1}. Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08; found: C, 92.02; H, 8.14.

3.2.2. Synthesis of 1-(phenylethynyl)-1-phenylcyclopropane 13a. To a solution of 1-cyclopropyl-2-phenylacetylene (56 mg, 0.39 mmol) in THF (3 mL) in a dry Schlenk tube was added *n*-BuLi (0.30 mL, 1.6 M in hexanes, 0.47 mmol) at −78 °C under N_2. After being warmed up naturally and stirred 1 h at rt, a solution of dry $ZnBr_2$ (178 mg, 0.79 mmol) in THF (4 mL) was added. After being stirred for 25 min at this temperature, $Pd(PPh_3)_4$ (15 mg, 5 mol%) and iodobenzene (29 μL, 0.26 mmol) were added subsequently at rt with stirring. After the reaction was complete as monitored by TLC (eluent: petroleum ether (60–90 °C)), it was quenched with saturated aqueous solution of NH_4Cl and extracted with ether. Drying over anhydrous $MgSO_4$, rotary evaporation, and flash chromatography on silica gel (petroleum ether) afforded **13a** (41 mg, 72%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.50$–7.15 (m, 10H), 1.54 (dd, $J_1=6.9$ Hz, $J_2=4.5$ Hz, 2H), 1.33 (dd, $J_1=6.9$ Hz, $J_2=4.5$ Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=141.9$, 131.7, 128.3, 128.2, 127.7, 126.0, 125.5, 123.7, 93.7, 78.3, 20.5, 16.2; MS (70 eV): *m*/*z* (%): 218 (M^+, 100.00); IR (neat) 2235, 1598, 1491 cm^{-1}; HRMS calcd for $C_{17}H_{14}$ [M^+]: 218.1096, found 218.1088.

The following compounds were prepared according to the procedure described in this section

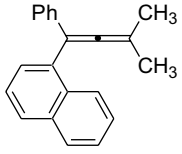
3.2.2.1. Synthesis of 1,1-diphenyl-3-methylbuta-1,2-diene (12a).[11]



12a

The reaction of 1-phenyl-3-methyl-1-butyne **1** (58 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), and iodobenzene (30 μL, 0.27 mmol) afforded **12a** (28 mg, 47%) as a solid, mp 54–55 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.34$–7.20 (m, 10H), 1.88 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=203.7$, 138.0, 128.5, 128.2, 126.7, 107.7, 98.3, 20.4; MS (70 eV): *m*/*z* (%): 220 (M^+, 58.75), 205 (100.00); IR (neat): 1948, 1595, 1489 cm^{-1}.

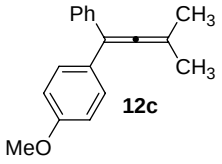
3.2.2.2. Synthesis of 1-phenyl-1-(1′-naphthyl)-3-methylbuta-1,2-diene (12b).



12b

The reaction of 1-phenyl-3-methyl-1-butyne **1** (57 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), 1-naphthyl iodide (40 μL, 0.27 mmol) afforded **12b** (18 mg, 25%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta=7.97$–7.80 (m, 3H), 7.52–7.35 (m, 4H), 7.26–7.14 (m, 5H), 1.88 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta=203.1$, 138.6, 135.5, 133.8, 132.1, 128.25, 128.22, 127.70, 127.66, 126.8, 126.31, 126.27, 125.8, 125.7, 125.6, 104.6, 98.2, 20.3; MS (70 eV): *m*/*z* (%): 270 (M^+, 27.72), 255 (100.00); IR (neat): 1948, 1596, 1490 cm^{-1}; HRMS calcd for $C_{21}H_{18}$ [M^+]: 270.1409, found: 270.1434.

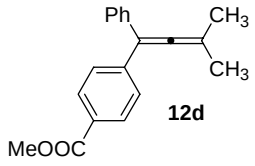
3.2.2.3. Synthesis of 1-phenyl-1-(4′-methoxyphenyl)-3-methylbuta-1,2-diene (12c).



12c

The reaction of 1-phenyl-3-methyl-1-butyne **1** (58 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), and 4-iodoanisole (63 mg, 0.27 mmol) afforded **12c** (48 mg, 71%) as a solid, mp 45–46 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.44–7.22 (m, 7H), 6.86 (d, J=8.7 Hz, 2H), 3.80 (s, 3H), 1.87 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=203.3, 158.6, 138.4, 130.4, 129.6, 128.4, 128.2, 126.7, 113.7, 107.1, 98.2, 55.3, 20.6; MS (70 eV): *m*/*z* (%): 250 (M^+, 80.10), 235 (100.00); IR (neat): 1948, 1605, 1508 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25; found: C, 86.30; H, 6.98.

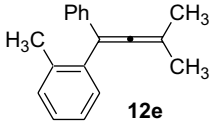
3.2.2.4. Synthesis of 1-phenyl-1-(4′-methoxycarbonylphenyl)-3-methylbuta-1,2-diene (12d).



12d

The reaction of 1-phenyl-3-methyl-1-butyne **1** (58 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (8 mg, 5 mol%), and methyl 4-iodobenzoate (35 mg, 0.13 mmol) afforded **12d** (33 mg, 91%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.91 (d, J=8.4 Hz, 2H), 7.33–7.17 (m, 7H), 3.83 (s, 3H), 1.82 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=204.5, 167.0, 143.1, 137.4, 129.5, 128.5, 128.3, 128.24, 128.19, 127.0, 107.3, 99.1, 52.0, 20.3; MS (70 eV): *m*/*z* (%): 278 (M^+, 91.82), 263 (100.00); IR (neat): 1946, 1720, 1606, 1491 cm^{-1}; HRMS calcd for $C_{19}H_{19}O_2$ [M^++H]: 279.1385, found: 279.1382.

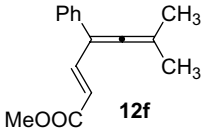
3.2.2.5. Synthesis of 1-phenyl-1-(2′-methylphenyl)-3-methylbuta-1,2-diene (12e).



12e

The reaction of 1-phenyl-3-methyl-1-butyne **1** (57 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), and 2-methylphenyl iodide (34 μL, 0.27 mmol) afforded **12e** (25 mg, 40%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.32–7.16 (m, 9H), 2.24 (s, 3H), 1.87 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=202.2, 138.3, 137.2, 136.8, 130.4, 130.2, 128.2, 127.3, 126.7, 126.2, 125.8, 105.4, 97.9, 20.3, 20.2; MS (70 eV): *m*/*z* (%): 234 (M^+, 25.04), 219 (100.00); IR (neat): 1951, 1598, 1489 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ [M^+]: 234.1409, found: 234.1435.

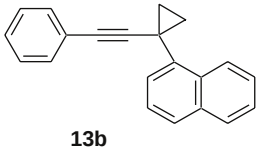
3.2.2.6. Synthesis of 1-phenyl-1-(*E*-methoxycarbonylethenyl)-3-methylbuta-1,2-diene (12f).



12f

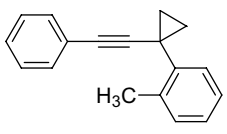
The reaction of 1-phenyl-3-methyl-1-butyne **1** (58 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), and methyl (*E*)-3-iodopropenoate[3] (57 mg, 0.27 mmol) afforded **12f** (23 mg, 37%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.50 (d, J=15.9 Hz, 1H), 7.40–7.20 (m, 5H), 5.93 (d, J=15.9 Hz, 1H), 3.75 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=207.8, 167.5, 143.9, 135.7, 128.5, 127.9, 127.3, 119.0, 104.8, 98.5, 51.5, 19.9; MS (70 eV): *m*/*z* (%): 228 (M^+, 100.00); IR (neat): 1942, 1720, 1622 cm^{-1}; HRMS calcd for $C_{15}H_{16}O_2$ [M^+]: 228.1150, found: 228.1171.

3.2.2.7. Synthesis of 1-(phenylethynyl)-1-(1′-naphthyl)cyclopropane (13b).


13b

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.30 mL, 0.47 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol%), and 1-naphthyl iodide (38 μL, 0.26 mmol) afforded **13b** (19 mg, 27%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.66 (d, J=9.0 Hz, 1H), 7.89 (d, J=8.1 Hz, 1H), 7.86 (d, J=8.1 Hz, 1H), 7.80–7.15 (m, 9H), 1.62 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H), 1.33 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=138.2, 134.2, 132.8, 131.9, 128.7, 128.3, 128.2, 127.7, 126.5, 126.2, 126.0, 125.7, 125.6, 123.9, 95.3, 76.7, 17.5, 15.7; MS (70 eV): *m*/*z* (%): 268 (M^+, 1.63), 84 (100.00); IR (neat) 2227, 1596, 1491 cm^{-1}; HRMS calcd for $C_{21}H_{17}$ [M^++H]: 269.1330, found: 269.1332.

3.2.2.8. Synthesis of 1-(phenylethynyl)-1-(2′-methylphenyl)cyclopropane (13c).

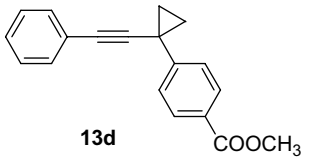


13c

The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.30 mL, 0.47 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol%), and 2-iodotoluene (33 μL, 0.26 mmol) afforded **13c** (15 mg, 25%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.38–7.30 (m, 3H), 7.25–7.11 (m, 6H), 2.60 (s, 3H), 1.44 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H), 1.19 (dd, J_1=6.9 Hz,

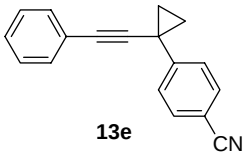
J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=139.8, 139.0, 131.6, 130.3, 128.9, 128.0, 127.4, 127.2, 125.8, 123.8, 94.3, 76.0, 19.6, 17.1, 16.1; MS (70 eV): *m/z* (%): 232 (M^+, 34.12), 202 (100.00); IR (neat) 2232, 1597, 1488 cm^{-1}; HRMS calcd for $C_{18}H_{16}$ [M^+]: 232.1252, found: 232.1266.

3.2.2.9. Synthesis of 1-(phenylethynyl)-1-(4′-methoxycarbonylphenyl)cyclopropane (13d).



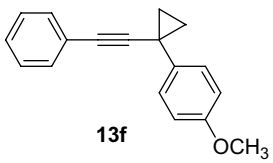
The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.30 mL, 0.47 mmol, 1.6 M in hexanes), $ZnBr_2$ (178 mg, 0.79 mmol), $Pd(PPh_3)_4$ (8 mg, 5 mol%), and methyl 4-iodobenzoate (34 mg, 0.13 mmol) afforded **13d** (35 mg, 98%) as a solid, mp 79–81 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.98 (d, J=9.0 Hz, 2H), 7.49–7.40 (m, 4H), 7.33–7.29 (m, 3H), 3.90 (s, 3H), 1.64 (dd, J_1=7.2 Hz, J_2=4.2 Hz, 2H), 1.40 (dd, J_1=7.2 Hz, J_2=4.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=166.9, 147.5, 131.7, 129.6, 128.2, 127.9, 127.7, 125.0, 123.3, 92.5, 79.1, 52.0, 21.7, 16.5; MS (70 eV): *m/z* (%): 276 (M^+, 70.56), 217 (100.00); IR (neat) 2230, 1717, 1282 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_2$ C, 82.58; H, 5.84; found: C, 82.31; H, 5.60.

3.2.2.10. Synthesis of 1-(phenylethynyl)-1-(4′-cyanophenyl)cyclopropane (13e).



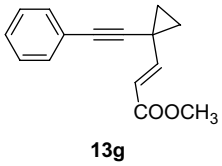
The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.30 mL, 0.47 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (8 mg, 5 mol%), and 4-iodobenzonitrile (31 mg, 0.13 mmol) afforded **13e** (29 mg, 88%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.57 (d, J=9.0 Hz, 2H), 7.46–7.40 (m, 4H), 7.31–7.22 (m, 3H), 1.66 (dd, J_1=7.8 Hz, J_2=4.5 Hz, 2H), 1.38 (dd, J_1=7.8 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=147.8, 132.1, 131.7, 128.3, 128.1, 125.8, 123.0, 119.0, 109.5, 91.7, 79.6, 22.0, 16.6; MS (70 eV): *m/z* (%): 243 (M^+, 100.00); IR (neat) 2227, 1609, 1507 cm^{-1}; HRMS calcd for $C_{18}H_{14}N$ [M^++H]: 244.1126, found: 244.1136.

3.2.2.11. Synthesis of 1-(phenylethynyl)-1-(4′-methoxylphenyl)cyclopropane (13f).



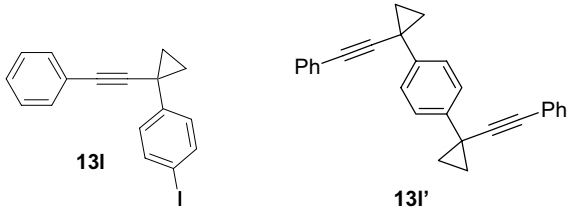
The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (57 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol%), and 4-iodoanisole (63 mg, 0.27 mmol) afforded **13f** (22 mg, 33%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.45–7.40 (m, 2H), 7.35–7.23 (m, 5H), 6.85 (d, J=9.0 Hz, 2H), 3.79 (s, 3H), 1.48 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H), 1.26 (dd, J_1=6.9 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=158.0, 134.0, 131.7, 128.2, 127.6, 127.0, 123.7, 113.7, 94.3, 77.8, 55.3, 19.7, 15.6; MS (70 eV): *m/z* (%): 248 (M^+, 100.00); IR (neat) 2232, 1248 cm^{-1}; HRMS calcd for $C_{18}H_{16}O$ [M^+]: 248.1201, found: 248.1216.

3.2.2.12. Synthesis of 1-(phenylethynyl)-1-(*E*-methoxycarbonylethenyl)cyclopropane (13g).



The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (56 mg, 0.39 mmol), *n*-BuLi (0.30 mL, 0.47 mmol, 1.6 M in hexanes), $ZnBr_2$ (178 mg, 0.79 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol%), and methyl (*E*)-3-iodopropenate[12] (55 mg, 0.26 mmol) afforded **13g** (20 mg, 34%) as a solid, mp 80–81 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.44–7.38 (m, 2H), 7.32–7.24 (m, 3H), 6.38 (d, J=15.0 Hz, 1H), 6.31 (d, J=15.0 Hz, 1H), 3.74 (s, 3H), 1.53 (dd, J_1=7.2 Hz, J_2=4.2 Hz, 2H), 1.25 (dd, J_1=7.2 Hz, J_2=4.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=167.1, 151.9, 131.7, 128.2, 128.0, 123.0, 119.2, 89.3, 80.8, 51.5, 19.9, 15.7; MS (70 eV): *m/z* (%): 226 (M^+, 41.01), 165 (100.00); IR (neat) 2230, 1716, 1645, 1201, 1165 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_2$ C, 79.62; H, 6.24; found: C, 79.63; H, 6.27.

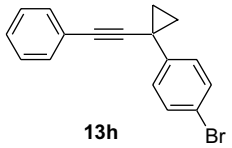
3.2.2.13. Synthesis of 1-(phenylethynyl)-1-(4′-iodophenyl)cyclopropane (13l) and 1,4-bis(1′-phenylethynyl-1′-cyclopropyl)benzene (13l′).



The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (64 mg, 0.45 mmol), *n*-BuLi (0.34 mL, 0.54 mmol, 1.6 M in hexanes), $ZnBr_2$ (203 mg, 0.90 mmol), $Pd(PPh_3)_4$ (26 mg, 5 mol%), and 1,4-diiodobenzene (74 mg, 0.23 mmol) afforded **13l** (45 mg, 57%) and **13l′** (15 mg, 18%). Compound **13l**: liquid, ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.61 (d, J=8.7 Hz, 2H), 7.45–7.38 (m, 2H), 7.31–7.23 (m, 3H), 7.13 (d, J=8.7 Hz, 2H), 1.55 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H), 1.29 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=141.8, 137.3, 131.7, 128.2, 127.8, 127.6, 123.4, 92.9, 91.0, 78.7, 20.7, 16.0; MS (70 eV): *m/z* (%): 344 (M^+, 46.09), 202 (100.00); IR (neat) 2232, 1598, 1486 cm^{-1}; HRMS calcd for $C_{17}H_{13}I$

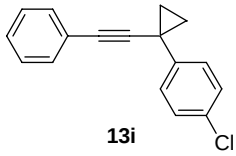
[M^+]: 344.0062, found: 344.0086. Compound **13l′**: solid, mp 97–100 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.50–7.40 (m, 4H), 7.35 (s, 4H), 7.31–7.24 (m, 6H), 1.53 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 4H), 1.32 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=139.7, 131.7, 128.2, 127.6, 125.6, 123.7, 93.8, 78.2, 20.3, 15.9; MS (70 eV): *m/z* (%): 358 (M^+, 20.6), 217 (100.00); IR (neat) 2231, 1597, 1491 cm^{-1}; HRMS calcd for $C_{28}H_{23}$ [M^++1]: 359.1800, found: 359.1809.

3.2.2.14. Synthesis of 1-(phenylethynyl)-1-(4′-bromophenyl)cyclopropane (13h).



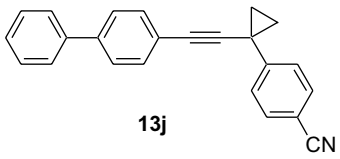
The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (66 mg, 0.46 mmol), *n*-BuLi (0.35 mL, 0.56 mmol, 1.6 M in hexanes), $ZnBr_2$ (203 mg, 0.90 mmol), $Pd(PPh_3)_4$ (18 mg, 5 mol%), and 1-bromo-4-iodobenzene (87 mg, 0.31 mmol) afforded **13h** (59 mg, 64%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.48–7.41 (m, 4H), 7.33–7.24 (m, 5H), 1.57 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H), 1.32 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=141.1, 131.7, 131.3, 128.2, 127.8, 127.3, 123.4, 119.8, 93.0, 78.7, 20.6, 16.0; MS (70 eV): *m/z* (%):298 (M^+(^{81}Br), 296 (M^+(^{79}Br), 20.79), 17.88), 217 (79.30), 215 (100.00); IR (neat) 2233, 1598, 1488 cm^{-1}; HRMS calcd for $C_{17}H_{13}^{79}Br$ [M^+]: 296.0201, found: 296.0193.

3.2.2.15. Synthesis of 1-(phenylethynyl)-1-(4′-chlorophenyl)cyclopropane (13i).



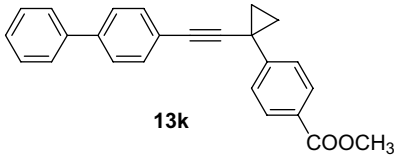
The reaction of 1-cyclopropyl-2-phenylacetylene **4a** (65 mg, 0.46 mmol), *n*-BuLi (0.34 mL, 0.55 mmol, 1.6 M in hexanes), $ZnBr_2$ (203 mg, 0.90 mmol), $Pd(PPh_3)_4$ (18 mg, 5 mol%), and 1-chloro-4-iodobenzene (73 mg, 0.31 mmol) afforded **13i** (43 mg, 55%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.50–7.42 (m, 2H), 7.36–7.24 (m, 7H), 1.57 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H), 1.32 (dd, J_1=7.5 Hz, J_2=4.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=140.5, 131.75, 131.67, 128.4, 128.2, 127.8, 126.9, 123.4, 93.1, 78.6, 20.6, 15.9; MS (70 eV): *m/z* (%): 254 (M^+(^{37}Cl), 14.06), 252 (M^+(^{35}Cl), 42.85), 217 (100.00); IR (neat) 2233, 1598, 1492 cm^{-1}; HRMS calcd for $C_{17}H_{13}^{35}Cl$ [M^+]: 252.0706, found: 252.0725.

3.2.2.16. Synthesis of 1-(*p*-phenylphenyl)ethynyl-1-(4′-cyanophenyl)cyclopropane (13j).



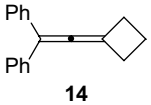
The reaction of 1-cyclopropyl-2-(*p*-phenylphenyl)acetylene **4b** (87 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol%), and 4-iodobenzonitrile (46 mg, 0.20 mmol) afforded **13j** (45 mg, 70%) as a solid, mp 118–119 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.62–7.35 (m, 13H), 1.70 (dd, J_1=7.5 Hz, J_2=4.5 Hz, 2H), 1.42 (dd, J_1=7.5 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=147.8, 140.8, 140.3, 132.2, 132.1, 128.8, 127.6, 127.0, 125.8, 121.9, 119.0, 109.6, 92.4, 79.5, 22.1, 16.7; MS (70 eV): *m/z* (%): 319 (M^+, 100.00); IR (neat) 2227, 1606, 1486 cm^{-1}. Anal. Calcd for $C_{24}H_{17}N$: C, 90.25; H, 5.36; N, 4.39; found: C, 90.06; H, 5.20; N, 4.19.

3.2.2.17. Synthesis of 1-(*p*-phenylphenyl)ethynyl-1-(4′-methoxycarbonylphenyl)cyclopropane (13k).



The reaction of 1-cyclopropyl-2-(*p*-phenylphenyl)acetylene **4b** (87 mg, 0.40 mmol), *n*-BuLi (0.30 mL, 0.48 mmol, 1.6 M in hexanes), $ZnBr_2$ (180 mg, 0.80 mmol), $Pd(PPh_3)_4$ (8 mg, 5 mol%), and methyl 4-iodobenzoate (38 mg, 0.13 mmol) afforded **13k** (26 mg, 51%) as a solid, mp 156 °C (petroleum ether–Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.00 (d, J=8.7 Hz, 2H), 7.62–7.24 (m, 11H), 3.91 (s, 3H), 1.67 (dd, J_1=7.5 Hz, J_2=4.5 Hz, 2H), 1.43 (dd, J_1=7.5 Hz, J_2=4.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=166.9, 147.5, 140.6, 140.3, 132.1, 129.7, 128.8, 127.8, 127.6, 127.0, 126.9, 125.1, 122.3, 93.3, 79.0, 52.0, 21.8, 16.6; MS (70 eV): *m/z* (%): 352 (M^+, 100.00); IR (neat) 2215, 1714, 1282 cm^{-1}. Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72; found: C, 85.01; H, 5.71.

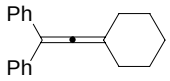
3.2.2.18. Synthesis of 2,2-diphenyl vinylidenecyclobutane (14).



The reaction of 1-cyclobutyl-2-phenylacetylene **6** (79 mg, 0.50 mmol), *n*-BuLi (0.94 mL, 1.51 mmol, 1.6 M in hexanes), $ZnBr_2$ (340 mg, 1.51 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), and iodobenzene (169 μL, 1.51 mmol) afforded **14** (64 mg, 55%) as a solid, mp 54–55 °C (petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.40–7.20 (m, 10H), 3.05 (t, J=8.1 Hz, 4H), 2.03 (pentet, J=7.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=197.2, 138.0, 128.5, 128.2, 127.0, 111.6, 103.6, 30.1, 17.5; MS (70 eV): *m/z* (%): 232

(M^+, 18.60), 204 (100.00); IR (neat): 1940, 1596, 1491 cm^{-1}. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94; found: C, 92.92; H, 7.05.

3.2.2.19. Synthesis of 2,2-diphenyl vinylidenecyclohexane (15).



15

The reaction of 1-cyclohexyl-2-phenylacetylene **9** (94 mg, 0.51 mmol), *n*-BuLi (0.95 mL, 1.52 mmol, 1.6 M in hexanes), $ZnBr_2$ (343 mg, 1.52 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), and iodobenzene (171 μL, 1.52 mmol) afforded **15** (59 mg, 44%) as a solid, mp 97–98 °C (petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ=7.40–7.20 (m, 10H), 2.32–2.28 (m, 4H), 1.73–1.65 (m, 4H), 1.61–1.55 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=200.4, 138.2, 128.4, 128.2, 126.6, 107.4, 105.6, 31.4, 27.6, 26.1; MS (70 eV): *m/z* (%): 260 (M^+, 90.62), 217 (100.00); IR (neat): 1945, 1597, 1488 cm^{-1}. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74; found: C, 92.24; H, 7.86.

Acknowledgements

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