

Tin-Free Three-Component Coupling Reaction of Aryl Halides, Norbornadiene (or Norbornene), and Alkynols Using a Palladium Catalyst

Cheol-Kyu Choi,^{†,*} Jin-Who Hong,^{†,*} Ikuyoshi Tomita,[‡] and Takeshi Endo[§]

Institute of Photonics and Surface Treatment, Q-sys Co., 985-18, Jangduk-dong, Gwangsan-gu, Kwangju 506-251, Korea

[†]*Department of Polymer Science and Engineering, Chosun University, 375, Susuk-dong, Dong-gu, Kwangju 501-759, Korea*

[‡]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,*

Tokyo Institute of Technology, Nagatuta-cho 4259, Midori-ku, Yokohama 226-8502, Japan

[§]*Department of Polymer Science and Engineering Faculty of Engineering Yamagata University 4-3-16 Jonan,*

Yonezawa, Yamagata 992-8510, Japan

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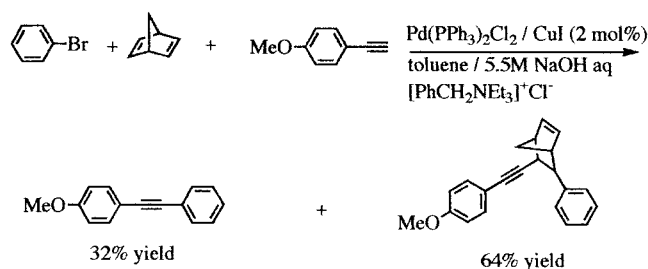
Good-to-excellent yields of 2,3-Disubstituted norbornenes (or norbornanes) were obtained using a Pd/Cu catalyzed three-component ternary coupling reaction of aryl halides, norbornadiene (or norbornene), and alkynols in toluene at 100 °C in the presence of 5.5 M NaOH as a base and benzyltriethylammonium chloride as a phase transfer catalyst. The results of experiments using various aromatic halides suggest that the ternary coupling reaction is promoted by bromide.

Keywords : Aryl halides, Norbornene, Alkynols, Palladium-catalyst, Three-component reaction.

Introduction

Transition metal-catalyzed multi-component coupling reactions are important in the single step construction of complex molecules.¹⁻⁷ They are also potentially of importance in the development of a new precision polycondensation technique in which more than three kinds of building block can be sequentially incorporated into polymer chains.⁸

In general, the reported ternary coupling systems consist of aromatic halides (or vinyl halides), nucleophiles, and unsaturated systems such as allenes, carbon monoxide, and olefins. To ensure that the objective reaction is selective, great efforts have been made to avoid the direct cross-coupling of organic halides with nucleophiles. For example, Kosugi *et al.*⁹⁻¹³ have reported that the reaction of aryl halides, norbornadiene (or norbornene), and organostannanes in the presence of a palladium complex provides an analogous overall transformation. Although acetylenes containing heteroatoms at their propargylic positions are also suitable for achieving the ternary coupling reaction,¹⁴⁻¹⁶ the use of terminal acetylenes might give rise to binary coupling products of aryl halides with the acetylenes in addition to the ternary coupling products (Scheme 1). Owing to the toxicity and rather high price of organotin compounds,¹⁷⁻¹⁸ it is of



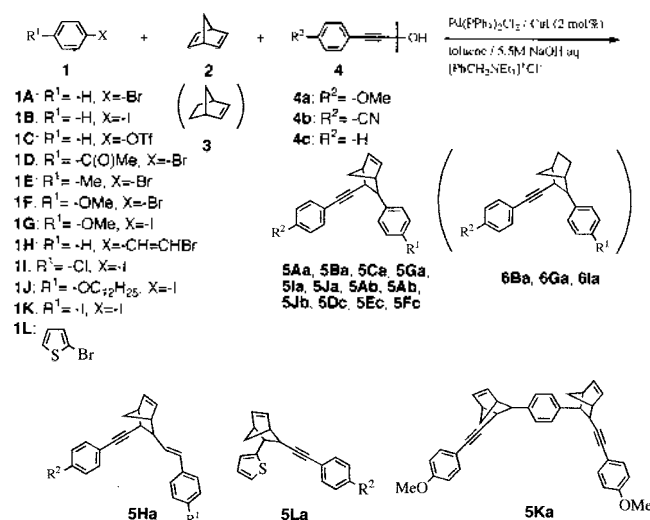
Scheme 1

practical importance to find an alternative candidate that could be employed in ternary coupling involving organic halides and norbornene.

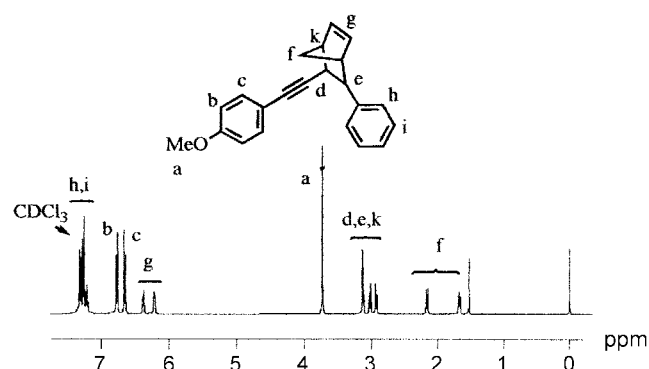
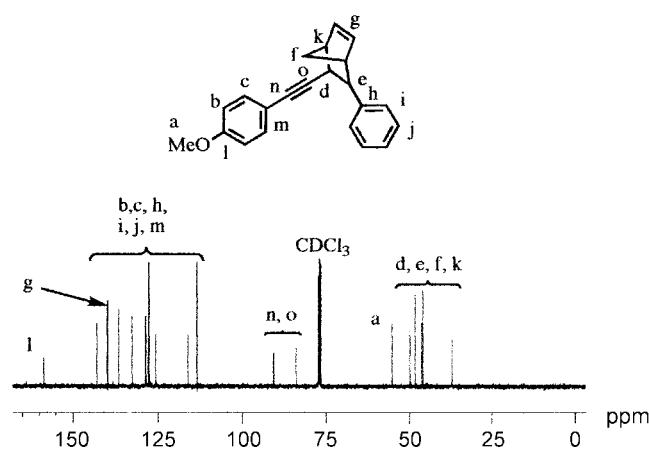
On the basis of the fact that alkynols serve as equivalence of terminal acetylenes,¹⁹ we report here technique for achieving three-component coupling of aromatic halides and norbornadiene using alkynols as one of the components (Scheme 2).

Results and Discussion

The three-component coupling reaction using bromobenzene (1A), 4-methoxyphenyl-2-methyl-3-butyn-2-ol (4a), and norbornadiene (2) was carried out at 100 °C for 2 days in toluene/5.5 M NaOH in the presence of benzyltriethylammonium chloride and Pd(PPh₃)₂Cl₂/CuI catalyst (2%



Scheme 2

Figure 1. $^1\text{H-NMR}$ spectrum of the **5Aa**.Figure 2. $^{13}\text{C-NMR}$ spectrum of the **5Aa**.

molality).

A 94% yield of 2,3-disubstituted norbornene (**5Aa**) was obtained (Table 1, run 1). The proposed structure of **5Aa** was confirmed objectively by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR spectrometry, and elemental analysis. For example, $^1\text{H-NMR}$ spectrum strongly supported that **5Aa** consists of building blocks originated from the three kinds of components (Figure 1). That is, peaks originated from three different components were observed at 6.22, 6.37 (the double bond in norbornene moieties), 6.65, 6.67 (phenylene originated from alkynol).

Table 1. Palladium-catalyzed ternary coupling reaction of **1A**, **2**, and **3a** in the presence of bases^a

| Run | Base | Yield/% ^b |
|-----|-----------------------------------|----------------------|
| 1 | NaOH | 94 |
| 2 | KOH | 91 |
| 3 | K_2CO_3 | 62 |
| 4 | $\text{CH}_3\text{CO}_2\text{K}$ | 14 |
| 5 | $\text{CH}_3\text{CO}_2\text{Na}$ | 5 |

^aReaction conditions: **1A** (0.5 mmol), **2** (10 mmol), **3a** (0.5 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.01 mmol), CuI (0.01 mmol), 5.5 M aq base (0.3 mL), benzyltriethylammonium chloride (0.015 mmol), toluene (2 mL), at 100 $^\circ\text{C}$ for 2 days. ^bIsolated yields by column chromatography (SiO_2 , *n*-hexane : ethyl acetate = 4 : 1).

and 7.27 ppm (phenyl from bromobenzene), respectively.

In the $^{13}\text{C-NMR}$ spectrum, the signals for three building blocks were also observed at 83.9, 93.7 (the carbon atoms of acetylene moieties), 139.8 (the carbon atoms of the double bond in norbornene), and 55.1 ppm (the carbon atom of methoxy), respectively (Figure 2). The structure of **5Aa** was identified as the *cis, exo* form on the basis of observations on the structure of the products obtained using the method of Kosugi *et al.*⁹⁻¹³ and Chiusoli *et al.*²⁻³

The rate of the ternary coupling reaction largely depends on the inorganic bases employed. Both NaOH and KOH - exhibiting strong basicity - are more suitable (Table 1, runs 1 and 2) than bases exhibiting weaker basicity (Table 1, runs 3-5). Thus, NaOH was used for the present study. The effect of NaOH on the ternary coupling reaction was investigated using bromobenzene (**1A**) and iodobenzene (**1B**) (Figures 3 and 4). The ternary coupling reaction did not take place in the absence of NaOH, but the presence of at least an equimolar amount of NaOH resulted in a smooth reaction. The addition of excess NaOH accelerated the reaction, although the yield of the product did not change significantly. From the conversion of **1A** and **1B** monitored by gas chromatography (GC), it was confirmed that the ternary coupling reaction proceeded smoothly to reach 100% conversion within 8 h. The results of the ternary coupling reactions of bromobenzene, iodobenzene, and phenyl triflate (**1A**, **1B**, and **1C**,

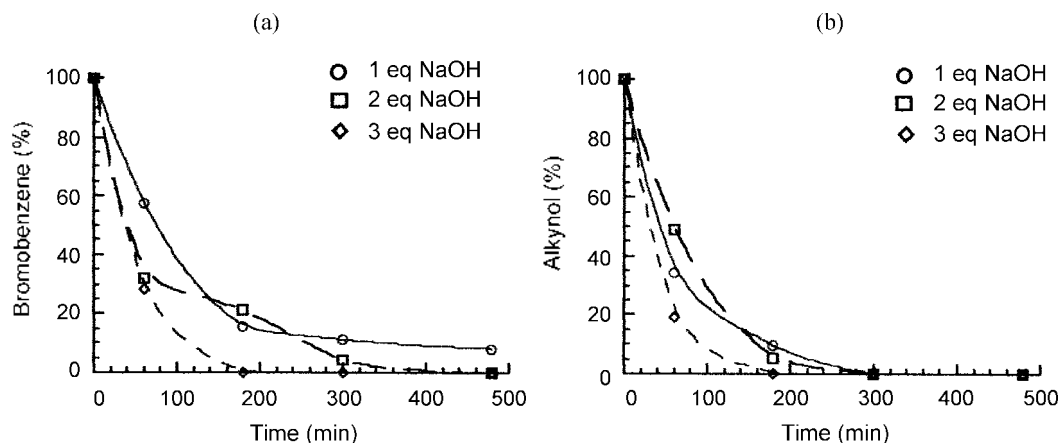


Figure 3. Time-conversion curves of bromobenzene (a) and alkynols (b) in the ternary coupling reaction.

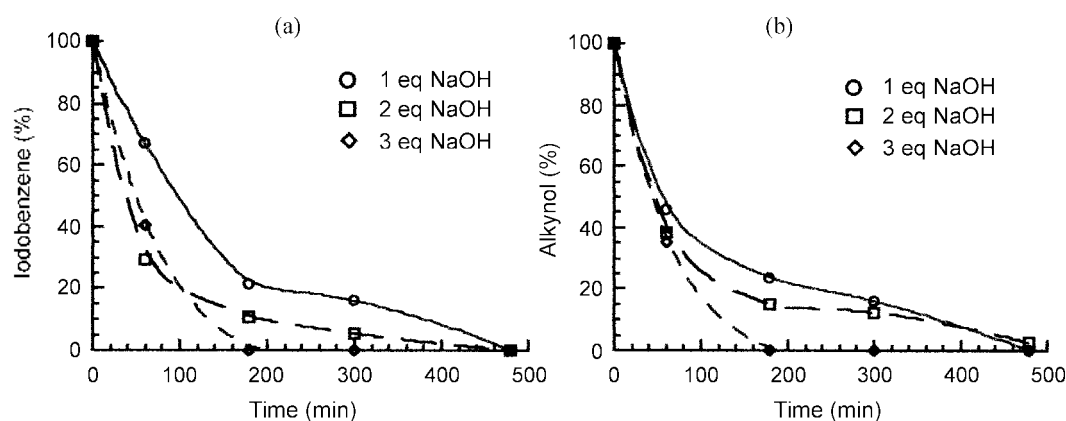


Figure 4. Time-conversion curves of iodobenzene (a) and alkynols (b) in the ternary coupling reaction.

respectively). **2**, and **4a** are summarized in Table 2 (runs 1-3). From **1B**, a 73% yield of the coupling product was obtained after the reaction had proceeded for 2 days. In the case of **1C**, the ternary coupling reaction at 100 °C for 2 days produced a low product yield (41%), although its conversion was complete within the reaction after 1 h, which might be due to the competitive hydrolysis of **1C**. In fact, when two equivalent amounts of **1C** were used under the same reaction conditions, the yield of the product increased to 79% (Table 2, run 4).

From the experiments using aryl halides bearing substituents on the para position in the ternary coupling reaction with **2** and alkynols (**4a** or **4c**), those having electron-donating substituents (**1A** and **1E-1G**) gave excellent yields of the desired products (Table 2, runs 1, 5, 10, 12, and 13), while that having an electron-withdrawing group gave a slightly lower yield of the product (Table 2, run 6). Likewise, alkynols having electron-withdrawing groups reduced

the yield of the products (Table 2, runs 7 and 9). It is noteworthy that the addition of NaBr to the reaction mixture led to a substantial increase in the yield of the products and the conversion of the starting materials (Figure 3 and Table 2, run 8). Although the role of NaBr remains unclear, one possible explanation is that the added bromide displaces the palladium ligand.²⁰

The palladium-catalyzed ternary coupling reaction was investigated using various aryl halides, norbornadiene (or norbornene), and alkynols. The results are summarized in Table 3. Aryl halides such as (*E*)- β -bromostyrene, 2-bromothiophene, para-substituted iodobenzene, and 1,4-diiodobenzene produced excellent yields of the corresponding ternary coupling products (Table 3, runs 1-4). As an olefin component, norbornene (**3**) also produced excellent yields of the corresponding ternary coupling products (Table 3, runs 5-7).

On the basis of the reported mechanism for the palladium-catalyzed coupling reaction,^{2,3,10} we propose that the present reaction pathway was as shown in Scheme 3. That is, the catalytic cycle may consist of four distinct stages: (a) oxidative addition of the aryl halide (**B**) to Pd(0) (**A**), (b) insertion of norbornadiene (**D**) to the aryl-Pd moieties (**C**), (c) formation of the complex (**H**) via transmetalation with a copper acetylide (**G**) generated by the reaction of alkynol (**F**) with copper (**I**) in the presence of base, and (d) reductive

Table 2. Palladium-catalyzed ternary coupling reaction of aryl halides (**1A-1G** and **1I**), **2**, and alkynols (**4a-4c**)^a

| Run | Aryl Halide | Alkynol | Yield (%) ^b |
|----------------|-------------|-----------|------------------------|
| 1 | 1A | 4a | 94 |
| 2 | 1B | 4a | 73 |
| 3 | 1C | 4a | 41 |
| 4c | 1C | 4a | 79 |
| 5 | 1G | 4a | 92 |
| 6 | 1I | 4a | 63 |
| 7 | 1B | 4b | 54 |
| 8 ^d | 1B | 4b | 61 |
| 9 | 1A | 4b | 65 |
| 10 | 1A | 4c | 93 |
| 11 | 1D | 4c | 73 |
| 12 | 1E | 4c | 99 |
| 13 | 1F | 4c | 98 |

^aReaction conditions: **1A-1F** (0.5 mmol), **4a-4c** (0.5 mmol), **2** (10 mmol), Pd(PPh₃)₂Cl₂ (0.01 mmol), CuI (0.01 mmol), 5.5 N aq NaOH (0.2 mL), benzyltriethylammonium chloride (0.015 mmol), toluene (2 mL), at 100 °C for 2 days. ^bIsolated yields by column chromatography (SiO₂, *n*-hexane:ethyl acetate = 4 : 1). ^cPhenyl triflate (1 mmol) was used. ^dSodium bromide (0.5 mmol) was used.

Table 3. Palladium-catalyzed coupling reaction of various aryl halides (**1B**, **1G-1L**), **2** (or **3**), and various alkynols (**4a-4b**)^a

| Run | Aryl Halide | Olefin | Alkynol | Yield (%) ^b |
|-----|-------------|----------|-----------|------------------------|
| 1 | 1H | 2 | 4a | 93 |
| 2 | 1J | 2 | 4b | 92 |
| 3 | 1K | 2 | 4a | 81 |
| 4 | 1L | 2 | 4a | 88 |
| 5 | 1B | 3 | 4a | 97 |
| 6 | 1G | 3 | 4a | 98 |
| 7 | 1I | 3 | 4a | 85 |

^aReaction conditions: **1B**, **1G-1L** (0.5 mmol) [or **1K** (0.25 mmol)], **4a-4b** (0.5 mmol), **2** (or **3**) (10 mmol), PdCl₂(PPh₃)₂ (0.01 mmol), CuI (0.01 mmol), 5.5 M aq NaOH (0.2 mL), benzyltriethylammonium chloride (0.015 mmol), toluene (2 mL) at 100 °C for 2 days. ^bIsolated yields by chromatography (SiO₂, *n*-hexane : ethyl acetate = 4 : 1).

elimination of complex (**H**) produces the 2,3-disubstituted norbornene product (**I**) with regeneration of the Pd(0) (**A**) species.

In summary, a convenient method for a tin-free three-component coupling reaction of aryl halides, norbornadiene (or norbornene) with alkynols has been successfully developed to provide good-to-excellent yields of the desired 2,3-disubstituted norbornenes (or norbornanes).

Experimental Methods

General Considerations. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ on a JNM-EX400 spectrometer (¹H NMR: 400 MHz and ¹³C NMR, 100 MHz). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. Gas chromatography (GC) analyses were performed out on a Shimadzu GC-14B equipment. Mass spectra were obtained by EI method or the FAB method using a Hitachi M-80 or a JEOL JMS-SX102 mass spectrometer. Toluene was dried and deoxygenated by refluxing and distilling from sodium/benzophenone ketyl under nitrogen. Bromobenzene (**1A**), iodobenzene (**1B**), phenyl trifluoromethanesulfonate (**1C**), 4-bromotoluene (**1E**), 4-bromoanisole (**1F**), (E)- β -bromostyrene (**1H**), and 2-bromothiophene (**1L**) were purified by distillation. 4-Bromoacetophenone (**1D**), 4-iodoanisole (**1G**), 4-chloriodobenzene (**1I**), and 1,4-diiodobenzene (**1K**) were purified by recrystallization from *n*-hexane. 4-Dodecyloxyiodobenzene (**1J**) was prepared by the reaction of 4-iodophenol with 12-bromododecane and was purified by recrystallization from *n*-hexane.

Norbornadiene (**2**) and norbornene (**3**) were dried over CaH₂ and distilled under nitrogen. All the reactions were carried out in a degassed sealed tube.

Synthesis of Alkynols.¹⁹ The typical procedure, for 4-Methoxyphenyl-2-methyl-3-butyn-2-ol (**4a**), was as follows. 4-Iodoanisole (4.680 g, 20 mmol), palladium(II) chloride (0.0469 g, 0.4 mmol) triphenylphosphine (0.3148 g, 1.2 mmol), copper (I) iodide (0.1524 g, 0.8 mmol), 2-methyl-3-butyn-2-ol (1.851 g, 22 mmol), diethylamine (20 mL), and THF (40 mL) were added to a 100-mL two-necked, round bottom flask equipped with a reflux condenser, magnetic stirrer chip, and nitrogen-gas inlet. The mixture was stirred at ambient temperature for 5 h under nitrogen, and then the solvent was evaporated under vacuum. After the addition of water (200 mL) and diethyl ether (100 mL), the organic layer was separated and dried over MgSO₄. After removal of the solvent *in vacuo*, the product was recrystallized from toluene to produce a 98% yield of white powders (3.73 g, 19.6 mmol). ¹H-NMR (400 MHz, δ , ppm) 1.64 (CH₃, s, 6H), 2.09 (-OH, s, 1H), 3.83 (-OCH₃, s, 3H), 6.86 (-C₆H₄-, d, *J* = 4.4 Hz, 2H), 7.38 (-C₆H₄-, d, *J* = 4.4 Hz, 2H); ¹³C-NMR (100 MHz, δ , ppm) 31.2 (-C(CH₃)₂OH), 54.9 (-C₆H₄OCH₃-), 65.3 (-C(CH₃)₂OH), 81.6, 92.0 (-C \equiv C-), 113.5, 114.4, 132.7, 159.2; IR (KBr) 3354 (-OH), 3057, 3034, 2982, 2934, 2870, 2231 (-C \equiv C-), 1952, 1880, 1807, 1720, 1672, 1599, 1574, 1491, 1444, 1363, 1275, 1163, 1070, 1026, 1001, 962, 906, 842, 808, 756, 692, 667 cm⁻¹

For 4-cyanophenyl-2-methyl-3-butyn-2-ol (**4b**) the procedure was as follows: from 4-bromobenzonitrile (1.82 g, 10.0 mmol) and 2-methyl-3-butyn-2-ol (925 mg, 11.0 mmol); yield 86% (1.59 g, 8.60 mmol); ¹H-NMR (400 MHz, δ , ppm) 1.62 (CH₃, s, 6H), 2.20 (-OH, s, 1H), 7.48 (-C₆H₄-, d, *J* = 8.8 Hz, 2H), 7.59 (-C₆H₄-, d, *J* = 8.8 Hz, 2H); ¹³C-NMR (100 MHz, δ , ppm) 31.2 (-C(CH₃)₂OH), 65.5 (-C(CH₃)₂OH), 80.5, 98.2 (-C \equiv C-), 111.5, 118.4 (-C \equiv N), 127.7, 132.1; IR (KBr) 3410 (-OH), 3045, 2980, 2932, 2876, 2797, 2241 (-C \equiv N), 2226 (-C \equiv C-), 1927, 1803, 1676, 1601, 1560, 1498, 1456, 1402, 1369, 1273, 1188, 1165, 1107, 1014, 962, 906, 839, 723, 625, 561, 486 cm⁻¹.

4-Phenyl-2-methyl-3-butyn-2-ol (4c): from bromobenzene (1.5702 g, 10 mmol) and 2-methyl-3-butyn-2-ol (0.9250 g, 11 mmol); Yield 91% (1.4580 g, 9.1 mmol); ¹H-NMR (400 MHz, δ , ppm) 1.61 (CH₃, s, 6H), 2.62 (-OH, s, 1H), 7.28 (-C₆H₄-, d, *J* = 2.4 Hz, 3H), 7.41 (-C₆H₄-, m, 2H); ¹³C-NMR (100 MHz, δ , ppm) 31.3 (-C(CH₃)₂OH), 65.4 (-C(CH₃)₂OH), 81.9, 93.8 (-C \equiv C-), 122.6, 128.1, 131.9, 132.1; IR (KBr) 3435 (-OH), 3119, 3074, 3022, 2988, 2935, 2841, 2532, 2226 (-C \equiv C-), 2050, 2008, 1896, 1772, 1649, 1606, 1570, 1508, 1454, 1440, 1363, 1304, 1286, 1248, 1168, 1107, 1030, 962 cm⁻¹.

Ternary Coupling Reaction of Norbornadiene, Aromatic Halides, and Alkynols (General Procedure). A tube containing a mixture of norbornadiene (10 mmol), aromatic halide (0.5 mmol), alkynol (0.5 mmol), Pd(PPh₃)₂Cl₂ (0.01 mmol), triphenylphosphine (0.055 mmol), CuI (0.01 mmol), benzyltriethyl ammonium chloride (0.015 mmol), aqueous NaOH (5.5 N, 0.2 mL), and toluene (2 mL) was sealed *in vacuo*, immersed in an oil bath, and heated at 100 °C for 2 days. Products were isolated by silica gel column chromatography (*n*-hexane:ethyl acetate = 4 : 1 as eluent).

Products. *cis, exo*-2-Phenyl-3-(4-methoxyphenylethynyl)-bicyclo-[2,2,1]heptene (**5Aa**): ¹H NMR (400 MHz, CDCl₃) δ 1.68 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.17 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.94 (d, *J* = 8.8 Hz, 1H), 3.03 (d, *J* = 8.8 Hz, 1H), 3.14 (s, 2H), 3.75 (-OCH₃, s, 3H), 6.24 (-CH=CH- (5, 6), s, 1H), 6.39 (-CH=CH- (5, 6), s, 1H), 6.65 (-C₆H₄-, d, *J* = 8.8 Hz, 2H), 6.77 (-C₆H₄-, d, *J* = 8.8 Hz, 2H), 7.23-7.35 (-C₆H₅, m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 37.2, 45.9, 48.3, 49.8, 55.2 (-C₆H₄OCH₃-), 84.0, 90.7 (-C \equiv C-), 113.5, 116.1, 125.7, 127.7, 128.7, 132.6, 136.6, 143.0, 158.8 ppm; IR (KBr) 3053, 2970, 2872, 2837, 2222 (-C \equiv C-), 1890, 1606, 1568 (-CH=CH- (5, 6)), 1510, 1454, 1442, 1327, 1286, 1249, 1172, 1105, 1028, 912, 854, 829, 808, 756, 731, 715, 700, 655, 534, cm⁻¹; MS (EI) *m/z* 300.1414 (M⁺); Anal. Calcd for C₂₂H₂₀O: C, 87.96; H, 6.71; O, 5.33. Found: C, 87.52; H, 6.72.

cis, exo-2-(4-Methoxyphenyl)-3-(4-methoxyphenylethynyl)-bicyclo[2,2,1]-heptene (**5Ga**): ¹H NMR (400 MHz, CDCl₃) δ 1.66 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.15 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.90 (d, *J* = 8.8 Hz, 1H), 2.97 (d, *J* = 8.8 Hz, 1H), 3.08 (d, *J* = 17.6 Hz, 2H), 3.73 (-OCH₃, s, 3H), 3.81 (-OCH₃, s, 3H), 6.20 (-CH=CH- (5, 6), s, 1H), 6.37 (-CH=CH- (5, 6), s, 1H), 6.67 (-C₆H₄-, d, 2H), 6.85 (-C₆H₄-, m, 4H), 7.20 (-C₆H₄-, d, 2H) ppm; ¹³C NMR (100 MHz,

CDCl_3) δ 37.7, 46.2, 46.9, 47.9, 50.8, 56.2 ($-\text{C}_6\text{H}_4\text{OCH}_3-$), 84.6, 91.9 ($-\text{C}\equiv\text{C}-$), 113.8, 116.5, 130.0, 133.4, 136.2, 137.7, 140.9, 158.3, 159.3 ppm; IR (KBr) 3061, 3024, 2957, 2912, 2870, 2839, 2224 ($-\text{C}\equiv\text{C}-$), 1896, 1606, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1508, 1466, 1452, 1331, 1290, 1246, 1174, 1109, 1076, 1039, 910, 835, 785, 744, 723, 698, 663, 619, 538 cm^{-1} ; MS (EI) m/z 330.1526 (M^+); Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_2$: C, 83.60; H, 6.71; O, 9.68; Found: C, 83.69; H, 6.68.

cis,exo-2-Styryl-3-(4-methoxyphenylethynyl)bicyclo[2.2.1]-heptene (**5Ha**): ^1H NMR (400 MHz, CDCl_3) δ 1.53 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 1.98 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.46 (t, $J = 8$ Hz, 1H), 2.73 (t, 2H), 3.07 (s, 1H), 3.77 ($-\text{OCH}_3$, s, 3H), 6.18 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.24 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.48 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H), 6.75 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H), 7.18-7.29 (C_6H_5- and double bond in styrene, m, 5H), 7.39 (C_6H_5- , d, $J = 8.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 36, 44.5, 45.6, 48.8, 49.9, 55.2 ($-\text{C}_6\text{H}_4\text{OCH}_3-$), 83.3, 90.2 ($-\text{C}\equiv\text{C}-$), 113.8, 116.2, 126.1, 126.8, 128.5, 129.8, 132.8, 133.5, 133.7, 137.9, 138, 159 ppm; IR (KBr) 3059, 3026, 2972, 2872, 2835, 2220 ($-\text{C}\equiv\text{C}-$), 1606, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1510, 1450, 1288, 1248, 1172, 1105, 1070, 1030, 962 (E-double bond), 902, 831, 796, 769, 748, 711, 694 cm^{-1} ; MS (FAB) m/z 326.79 (M^+) Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}$: C, 88.31; H, 6.79; O, 4.90; Found: C, 88.23; H, 6.82.

cis,exo-2-(4-Chlorophenyl)-3-(4-methoxyphenylethynyl)-bicyclo[2.2.1]-heptene (**5Ia**): ^1H NMR (400 MHz, CDCl_3) δ 1.66 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.10 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.91 (d, $J = 8.8$ Hz, 1H), 2.97 (d, $J = 8.8$ Hz, 1H), 3.10 (d, $J = 17.6$ Hz, 2H), 3.74 ($-\text{OCH}_3$, s, 3H), 6.22 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.36 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.69 ($-\text{C}_6\text{H}_4-$, d, $J = 9.6$ Hz, 2H), 6.81 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H), 7.17 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H), 7.28 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 37.2, 45.8, 46.3, 47.7, 49.7, 55.2 ($-\text{C}_6\text{H}_4\text{OCH}_3-$), 84.4, 90.4 ($-\text{C}\equiv\text{C}-$), 113.6, 115.8, 127.8, 130.0, 131.4, 132.6, 136.7, 139.6, 141.6, 158.9 ppm; IR (KBr) 3140, 3063, 2982, 2955, 2934, 2914, 2837, 2224 ($-\text{C}\equiv\text{C}-$), 2054, 1898, 1608, 1583, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1510, 1462, 1442, 1329, 1288, 1248, 1176, 1109, 1032, 910, 837, 810, 796, 777, 767, 731 cm^{-1} ; MS (EI) m/z 334.1086 (M^+); Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{ClO}$: C, 78.91; H, 5.72; Cl, 10.59; O, 4.78; Found: C, 79.29; H, 5.83; Cl, 10.52.

cis,exo-1,4-bis[3-{2-(4-methoxyphenylethynyl) bicyclo[2.2.1]heptenyl}]-benzene (**5Ka**): ^1H NMR (400 MHz, CDCl_3) δ 1.68 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 2H), 2.17 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 2H), 2.94-3.14 ($-\text{CH}$ (1), CH (2), CH (3), and CH (4), m, 8H), 3.74 ($-\text{OCH}_3$, s, 6H), 6.23 ($-\text{CH}=\text{CH}-$ (5, 6), s, 2H), 6.39 ($-\text{CH}=\text{CH}-$ (5, 6), s, 2H), 6.67 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 4H), 6.79 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 4H), 7.28 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 37.5, 46.2, 47.2, 48.4, 50.1, 55.5 ($-\text{C}_6\text{H}_4\text{OCH}_3-$), 84.5, 91.4 ($-\text{C}\equiv\text{C}-$), 113.7, 116.6, 128.5, 133.0, 136.9, 140.1, 140.5, 159.0 ppm; IR (KBr) 3138, 3057, 2980, 2937, 2901, 2872, 2837, 2222 ($-\text{C}\equiv\text{C}-$), 2056, 1901, 1730, 1608, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1510, 1491, 1454, 1410, 1327, 1292, 1249, 1170, 1107, 1087, 1039, 1030, 1012, 904, 839, 812, 779, 765, 715, 650, 540, 505 cm^{-1} ; MS (EI) m/z 522.2531 (M^+); Anal. Calcd for

$\text{C}_{38}\text{H}_{34}\text{O}_2$: C, 87.32; H, 6.56; O, 6.12; Found: C, 87.21; H, 6.51.

cis,exo-2-(2-Thiophenyl)-3-(4-methoxyphenylethynyl)-bicyclo[2.2.1]heptene (**5La**): ^1H NMR (400 MHz, CDCl_3) δ 1.68 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.23 ($>\text{CH}_2$ (7), d, $J = 9.2$ Hz, 1H), 2.87 (d, $J = 8.8$ Hz, 1H), 3.13 (d, $J = 8.8$ Hz, 2H), 3.25 (d, 1H), 3.75 ($-\text{OCH}_3$, s, 3H), 6.2 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.3 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.70 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H), 6.91 ($-\text{C}_4\text{H}_3\text{S}-$, s, 1H), 6.98 ($-\text{C}_6\text{H}_4-$, d, $J = 8.8$ Hz, 2H), 7.19 ($-\text{C}_4\text{H}_3\text{S}-$, s, 1H), 7.25 ($-\text{C}_4\text{H}_3\text{S}-$, s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 37.6, 44.2, 45.9, 49.1, 50.1, 55.2 ($-\text{C}_6\text{H}_4\text{OCH}_3-$), 83.8, 89.9 ($-\text{C}\equiv\text{C}-$), 113.6, 116.1, 123.2, 124.8, 126.1, 132.7, 136.7, 139, 146.8, 158.9 ppm; IR (KBr) 3063, 2974, 2874, 2835, 2224 ($-\text{C}\equiv\text{C}-$), 1606, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1510, 1462, 1440, 1413, 1367, 1325, 1288, 1246, 1172, 1105, 1076, 1039, 902, 864, 831, 810, 779, 763, 723, 694 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{OS}$: C, 78.39; H, 5.92; O, 5.22; S, 10.46; Found: C, 78.46; H, 6.14; S, 10.22.

cis,exo-2-Phenyl-3-(4-cyanophenylethynyl)bicyclo[2.2.1]-heptene (**5Ab**): ^1H NMR (400 MHz, CDCl_3) δ 1.70 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.11 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.94 (d, $J = 9.6$ Hz, 1H), 3.06 (d, $J = 8.8$ Hz, 1H), 3.15 (d, 2H), 6.24 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.41 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.87 ($-\text{C}_6\text{H}_5$, d, $J = 8.4$ Hz, 2H), 7.25 ($-\text{C}_6\text{H}_5$, d, $J = 8.4$ Hz, 3H), 7.31 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H), 7.40 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 37.7, 46.3, 46.4, 48.6, 49.9, 83.4, 97.9 ($-\text{C}\equiv\text{C}-$), 110.7, 119 ($-\text{C}\equiv\text{N}$), 126.2, 128.2, 128.9, 129.2, 131.9, 132.1, 136.7, 140.3, 142.9 ppm; IR (KBr) 3063, 3024, 2962, 2943, 2920, 2874, 2224 ($-\text{C}\equiv\text{N}$ and $-\text{C}\equiv\text{C}-$), 1602, 1570 ($-\text{CH}=\text{CH}-$ (5, 6)), 1545, 1498, 1452, 1406, 1311, 1253, 1178, 1138, 1103, 1076, 1008, 910, 841 cm^{-1} ; MS (FAB) m/z 295.81 (M^+); Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}$: C, 89.46; H, 5.80; N, 4.74; Found: C, 88.61; H, 5.94; N, 4.51.

cis,exo-2-(4-Dodecyloxy)phenyl-3-(4-cyanophenylethynyl)-bicyclo[2.2.1]-heptene (**5Jb**): ^1H NMR (400 MHz, CDCl_3) δ 0.88 ($-\text{CH}_3$, t, $J = 6.4$ Hz, 3H), 1.27-1.43 ($-\text{CH}_2-$, m, 18H), 1.69 ($-\text{CH}_2$ (7), d, 1H), 1.76 ($-\text{CH}_2-$, m, 2H), 2.1 ($-\text{CH}_2$ (7), d, $J = 8$ Hz, 1H), 2.9 (d, $J = 8.8$ Hz, 1H), 3.0 (d, $J = 8.8$ Hz, 1H), 3.1 (d, $J = 10.8$ Hz, 2H), 3.94 ($-\text{OCH}_2-$, t, $J = 6.4$ Hz, 2H), 6.21 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.39 ($-\text{CH}=\text{CH}-$ (5, 6), s, 1H), 6.85 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H), 6.94 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H), 7.15 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H), 7.41 ($-\text{C}_6\text{H}_4-$, d, $J = 8.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 26.1, 29.3-29.6, 31.9, 37.4, 45.9, 46.5, 47.6, 49.5, 68.1, 83.2, 97.9 ($-\text{C}\equiv\text{C}-$), 110.2, 113.9, 118.7, 129, 129.4, 131.6, 131.8, 134.4, 136.3, 140.0, 157.4 ppm; IR (KBr) 3061, 2962, 2918, 2849, 2224 ($-\text{C}\equiv\text{C}-$), 1602, 1581 ($-\text{CH}=\text{CH}-$ (5, 6)), 1545, 1510, 1469, 1394, 1329, 1305, 1292, 1248, 1205, 1176, 1140, 1107, 1024, 918, 904, 842, 810, 783 cm^{-1} ; MS (FAB) m/z 479.8 (M^+); Anal. Calcd for $\text{C}_{34}\text{H}_{41}\text{NO}$: C, 85.13; H, 8.61; N, 2.92; O, 3.34; Found: C, 84.59; H, 8.69; N, 2.43.

cis,exo-2-Phenyl-3-phenylethynylbicyclo[2.2.1]heptene (**5Ac**): ^1H NMR (400 MHz, CDCl_3) δ 1.67 (CH_2 (7), d, $J = 8.8$ Hz, 1H), 2.16 ($>\text{CH}_2$ (7), d, $J = 8.8$ Hz, 1H), 2.93 (d, $J = 8.8$ Hz, 1H), 3.02 (d, $J = 8.8$ Hz, 1H), 3.13 (s, 2H), 6.22

(-CH=CH- (5, 6), s, 1H), 6.38 (-CH=CH- (5, 6), s, 1H), 6.85 (-C₆H₅, d, *J* = 8.8 Hz, 2H), 7.12 (-C₆H₅, m, 3H), 7.27 (-C₆H₅, m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 37.3, 45.9, 46.3, 48.3, 49.8, 84.2, 92.4 (-C≡C-), 125.7, 128.5, 129.4, 131.3, 136.6, 139.9, 142.9 ppm; IR (KBr) 3059, 3026, 2974, 2872, 2224 (-C≡C-), 1946, 1878, 1803, 1726, 1599, 1574 (-CH=CH- (5, 6)), 1491, 1452, 1315, 1253, 1217, 1182, 1157, 1099, 1070, 1028, 1012, 910, 817, 792, 756, 711, 692, cm⁻¹; Anal. Calcd for C₂₁H₁₈: C, 93.29; H, 6.71; Found: C, 93.37; H, 6.75.

cis, exo-2-(4-Acetylphenyl)-3-phenylethynylbicyclo[2.2.1]-heptene (**5Dc**): ¹H NMR (400 MHz, CDCl₃) δ 1.73 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.14 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.58 (-CH₃, s, 3H), 2.99 (d, *J* = 8.8 Hz, 1H), 3.05 (d, *J* = 8.8 Hz, 1H), 3.16 (s, 2H), 6.25 (-CH=CH- (5, 6), s, 1H), 6.39 (-CH=CH- (5, 6), s, 1H), 6.80 (-C₆H₅, d, *J* = 8.0 Hz, 2H), 7.12 (-C₆H₅, m, 3H), 7.36 (-C₆H₄-, d, *J* = 8.4 Hz, 2H), 7.91 (-C₆H₄-, d, *J* = 8.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 37.4, 45.9, 46.1, 48.5, 49.8, 84.5, 91.8 (-C≡C-), 123.5, 127.4, 127.9, 128.9, 131.1, 134.9, 136.8, 139.6, 149.0, 197.9 (>C=O) ppm; IR (KBr) 3059, 2986, 2972, 2945, 2930, 2874, 2220 (-C≡C-), 1680, 1604, 1570 (-CH=CH- (5, 6)), 1543, 1523, 1508, 1489, 1452, 1440, 1413, 1358, 1332, 1307, 1269, 1186 cm⁻¹; MS (FAB) *m/z* 312.15 (M⁺); Anal. Calcd for C₂₃H₂₀O: C, 88.43; H, 6.45; O, 5.12; Found: C, 87.09; H, 6.17.

cis, exo-2-(4-Methylphenyl)-3-phenylethynylbicyclo[2.2.1]-heptene (**5Ec**): ¹H NMR (400 MHz, CDCl₃) δ 1.66 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.15 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.29 (-CH₃, s, 3H), 2.90 (d, *J* = 8.8 Hz, 1H), 2.99 (d, *J* = 8.8 Hz, 1H), 3.11 (d, *J* = 8.0 Hz, 2H), 6.21 (-CH=CH- (5, 6), s, 1H), 6.37 (-CH=CH- (5, 6), s, 1H), 6.84 (-C₆H₅, d, *J* = 8.0 Hz, 2H), 7.14 (-C₆H₄- and -C₆H₅, m, 7H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 37.2, 45.9, 46.4, 47.9, 49.7, 84.2, 92.6 (-C≡C-), 123.9, 127.1, 127.8, 128.5, 131.3, 135.1, 136.5, 139.8 ppm; IR (KBr) 3057, 2974, 2945, 2922, 2872, 2224 (-C≡C-), 1599, 1572 (-CH=CH- (5, 6)), 1514, 1491, 1450, 1377, 1329, 1315, 1253, 1219, 1155, 1111, 1068, 1012, 912, 837, 804, 756 cm⁻¹; MS (FAB) *m/z* 284.16 (M⁺); Anal. Calcd for C₂₂H₂₀: C, 92.91; H, 7.09; Found: C, 92.00; H, 6.86.

cis, exo-2-(4-Methoxyphenyl)-3-phenylethynylbicyclo[2.2.1]-heptene (**5Fc**): ¹H NMR (400 MHz, CDCl₃) δ 1.67 ((CH₂) (7), d, *J* = 8.8 Hz, 1H), 2.16 (>CH₂ (7), d, *J* = 8.8 Hz, 1H), 2.91 (d, *J* = 8.8 Hz, 1H), 2.97 (d, *J* = 8.8 Hz, 1H), 3.10 (d, *J* = 20 Hz, 2H), 3.80 (-OCH₃, s, 3H), 6.21 (-CH=CH- (5, 6), s, 1H), 6.37 (-CH=CH- (5, 6), s, 1H), 6.88 (-C₆H₄- and -C₆H₅, m, 4H), 7.16 (-C₆H₄- and -C₆H₅, m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 37.2, 45.8, 46.6, 47.6, 49.7, 55.4, 84.3, 92.6 (-C≡C-), 123.5, 113.3, 123.9, 127.2, 127.8, 129.5, 131.3, 134.9, 136.5, 139.9, 157.8 ppm; IR (KBr) 3059, 2974, 2872, 2833, 2224 (-C≡C-), 1612, 1583 (-CH=CH- (5, 6)), 1512, 1491, 1462, 1442, 1329, 1305, 1290, 1249, 1180, 1157, 1111, 1068, 1037, 912, 841, 806, 785, 756, 736, 690 cm⁻¹; MS (FAB) *m/z* 300.15 (M⁺); Anal. Calcd for C₂₂H₂₀O: C, 87.96; H, 6.71; O, 5.33; Found: C, 88.04; H, 6.87.

cis, exo-2-Phenyl-3-(4-methoxyphenylethynyl)bicyclo[2.2.1]-

heptane (**6Ba**): ¹H NMR (400 MHz, CDCl₃) δ 1.39 (>CH₂-CH₂< (5, 6), m, 3H), 1.66 (>CH₂ (7) and C (5), s, 2H), 2.10 (>CH₂ (7), s, 1H), 2.53 (s, 1H), 2.59 (s, 1H), 3.04 (s, 2H), 3.73 (-OCH₃, s, 3H), 6.64 (-C₆H₄-, d, *J* = 7.2 Hz, 2H), 6.76 (-C₆H₄-, m, 2H), 7.27 (-C₆H₅, m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 28.4, 31.3, 36.8, 41.5, 43.2, 44.4, 52.2, 55.5, 84.5, 90.6 (-C≡C-), 113.8, 116.5, 125.9, 128.0, 128.7, 132.9, 143.9, 159.0 ppm; IR (KBr) 3061, 3026, 3003, 2955, 2912, 2868, 2837, 2224 (-C≡C-), 1606, 1508, 1464, 1450, 1413, 1352, 1327, 1294, 1280, 1246, 1197 cm⁻¹; MS (EI) *m/z* 302.1622 (M⁺); Anal. Calcd for C₂₂H₂₂O: C, 87.38; H, 7.33; O, 5.29; Found: C, 87.09; H, 7.45.

cis, exo-2-(4-Methoxyphenyl)-3-(4-methoxyphenylethynyl)-bicyclo[2.2.1]heptane (**6Ga**): ¹H NMR (400 MHz, CDCl₃) δ 1.37 (>CH₂-CH₂< (5, 6), m, 3H), 1.64 (>CH₂ (7) and C (5), s, 2H), 2.10 (>CH₂ (7), s, d, *J* = 6.4 Hz, 1H), 2.52 (s, 2H), 2.99 (m, 2H), 3.73 (s, 3H), 3.79 (s, 3H), 6.76 (-C₆H₄-, d, *J* = 8.0 Hz, 2H), 6.86 (-C₆H₄-, d, *J* = 8.4 Hz, 2H), 7.26 (-C₆H₄-, d, *J* = 8.4 Hz, 2H), 7.37 (-C₆H₄-, d, *J* = 8.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 28.1, 30.9, 36.4, 41.5, 42.9, 44.1, 51.1, 55.2, 55.4, 84.2, 90.5 (-C≡C-), 113.1, 113.5, 116.2, 129.3, 132.6, 135.9, 157.6, 158.7 ppm; IR (KBr) 3013, 2995, 2957, 2912, 2870, 2837, 2226 (-C≡C-), 1606, 1583, 1510, 1462, 1440, 1356, 1329, 1290, 1277, 1246, 1176 cm⁻¹; MS (EI) *m/z* 330.1675 (M⁺); Anal. Calcd for C₂₃H₂₄O₂: C, 83.10; H, 7.28; O, 9.63; Found: C, 82.91; H, 7.36.

cis, exo-2-(4-Chlorophenyl)-3-(4-methoxyphenylethynyl)-bicyclo[2.2.1]heptane (**6Ia**): ¹H NMR (400 MHz, CDCl₃) δ 1.37 (>CH₂-CH₂< (5, 6), t, *J* = 11.2 Hz, 3H), 1.64 (>CH₂ (7) and C (5), s, 2H), 2.05 (>CH₂ (7), d, *J* = 10 Hz, 1H), 2.52 (s, 1H), 3.01 (q, *J* = 8.8 Hz, 2H), 3.73 (-OCH₃, s, 3H), 6.68 (-C₆H₄-, d, *J* = 8.8 Hz, 2H), 6.79 (-C₆H₄-, d, *J* = 8.0 Hz, 2H), 7.16 (-C₆H₄-, d, *J* = 8.8 Hz, 2H), 7.25 (-C₆H₄-, d, *J* = 8.0 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 27.9, 30.8, 36.3, 41.2, 42.7, 44.1, 51.3, 55.2, 84.6, 89.9 (-C≡C-), 113.6, 115.9, 127.7, 129.8, 131.3, 132.5, 142.1, 158.8 ppm; IR (KBr) 3007, 2955, 2922, 2872, 2837, 2224 (-C≡C-), 1608, 1510, 1493, 1460, 1412, 1329, 1294, 1248, 1194, 1170, 1138, 1105, 1089, 1037, 1012, 987, 956, 922, 883, 837 cm⁻¹; MS (EI) *m/z* 336.1226 (M⁺); Anal. Calcd for C₂₂H₂₁ClO: C, 78.44; H, 6.28; Cl, 10.52; O, 4.75; Found: C, 78.87; H, 6.10; Cl, 11.74.

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