嘉南藥理科技大學專題研究計畫成果報告

鈀金屬錯化物催化鹵化物及末端炔與7-異核雙環烯衍生物進行三分子偶合反應

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嘉南藥理科技大學專題研究計畫成果報告

bis(amino)distyrylbenzene 衍生物的合成與純化

計畫編號：CNAC-96-19

執行期限：96 年 01 月 01 日至 96 年 12 月 31 日

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Palladium-catalyzed 1,2-addition of organic halide and terminal alkyne to 7-oxabenzonorbornadiene; an efficient route to polyaromatic hydrocarbons

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Keywords: three-component coupling reaction / palladium-catalyzed / 7-oxabenzonorbornadiene / terminal alkyne

A three-component coupling reaction of organic halides with oxabicyclic alkene and terminal alkynes was catalyzed by a palladium complex and a phase transfer agent in the presence of aqueous NaOH. The reaction gave a series of 5,6-disubstituated 7-oxabenzonorbornene derivatives in good yields.

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Introduction

Transition metal-catalyzed ternary coupling reactions of organic halides, nucleophiles and olefins are an important methodology for the construction of complex molecular structure in a single one-pot step.[1] In this type of multi-component reaction, the electrophiles employed include various aryl and alkenyl halides, iodonium salts and diazonium salts and the nucleophiles[2-5] used are 1-alkynes, alkynols, organostannanes and tetraphenylborate ion. However, there is a great restriction of the olefins that are applicable in the ternary coupling reactions. These olefins generally require high coordination and insertion ability but no β-hydrogens to allow for elimination after insertion. Bicyclic olefins such as norbornadienes and norbornenes are a class of olefins that show the above properties due to the angle strain of the carbon-carbon double bonds. In our previous studies,[6] we observed a palladium-catalyzed three-component coupling reaction of norbornadiene with a 1-haloalkyne and a terminal alkyne to produce 5,6-dialkynyl norbornene. Although 7-oxabicyclic alkenes are similar to norbornadienes and norbornenes, the transition metal-catalyzed addition reaction of a nucleophilic[7-13] or electrophilic[14] reagent with a 7-oxabicyclic alkene often led to the ring-opening of the oxabicyclic alkene because the facile β-oxygen elimination of after the addition of an organic group to the oxabicyclic alkene. As a result, it is difficult for the reactions involving 7-oxabicyclic alkenes as substrates to add a nucleophile and electrophile in one pot to give a three component coupling reaction product. In this study, we report a palladium-catalyzed three-component coupling reaction of an oxabicyclic alkene with an organic halide and a terminal alkyne to provide 5, 6-disubstituated 7-oxabenzonorbornene derivative in good yields (Scheme 1). The catalytic reaction was carried out in the presence of aqueous NaOH and a phase transfer catalyst. The disubstituted products undergo deoxyaromatization readily in the presence of $BF_3{\cdot}OEt_2$ providing an efficient method for the synthesis of various substituted polyaromatics.

Results and Discussion

The three-component coupling reaction of iodobenzene **2a** (1.73 mmol), phenylacetylene **3a** (1.73 mmol) and 7-oxabenzonorbornadiene **1a** (1.73 mmol) was carried out at 40 °C for 24 h in CH_2Cl_2/5 M aqueous NaOH in the presence of tetrabutylammonium iodide (0.173 mmol) and palladium catalyst $Pd(PPh_3)_4$ (0.087 mmol) to give 5,6-disubstituated 7-oxabenzonorbornene derivative **4a** in 92% yield (Table 1, entry 1). The structure of **4a** was characterized by NMR, IR and mass spectroscopy. In the absence of a palladium complex or sodium hydroxide, no product **4a** was found, while the omission of phase transfer reagent, tetrabutylammoniun iodide, afforded only a trace amount of the desired product **4a**. The *exo* and *cis* stereochemistry of **4k** were conformed by X-ray diffraction[15] (Fig 1). The catalytic

reaction is remarkably stereoselective leading only to the *exo* and *cis* product.

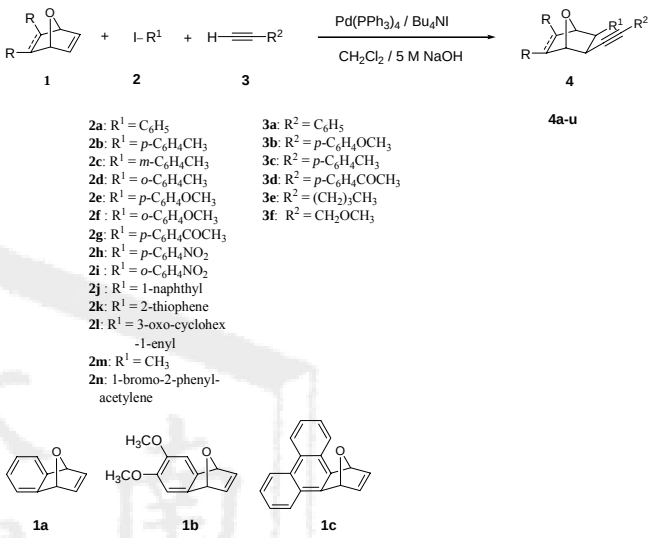
This palladium-catalyzed three-component coupling reaction is successfully extended to various organic halides and 1-alkynes. The results are summarized in Table 1. Treatment of iodobenzene and 7-oxabenzonorbornadiene **1** with different terminal alkynes **3a-f** (Table 1, entries 1-6) furnished the corresponding 5,6-disubstituated 7-oxabenzonorbornene derivatives **4a-f** in 18-92% yields. It is noteworthy that the yield of this three-component coupling reaction is substantial affected by the position of the substituent on the aryl iodide. *o*-Substituted aryl iodide gave a slightly lower yield relative to those of the *m*- and *p*-substituted ones (Table 1, entries 7-11). In addition, as shown in entries 7, 10, 12, and 13 (Table 1), aryl iodide bearing an electron-donating substitutent on para position gave higher product yield than that having an stronger electron-withdrawing group (entry 13) in the ternary coupling reaction

The reaction could be further applied to reactants of alkyl, alkenyl iodides and 1-bromoalkyne. Under similar reaction conditions, 2-iodothiophene **2k** and 3-iodocyclohex-2-enone **2l** coupled to 7-oxabenzonorbornadiene **1a** and phenylacetylene **3a** obtained **4p** and **4q** in 56% and 28 % yields (Table 1, entry 16-17), respectively. Similarly, methyl iodine **2m** and 1-bromo-2-phenylacetylene **2n** reacted with 7-oxabenzonorbornadiene **1a** and phenylacetylene **3a** to afford **4r** and **4s** in 36% and 45 % yields (Table 1, entry 18-19), respectively.

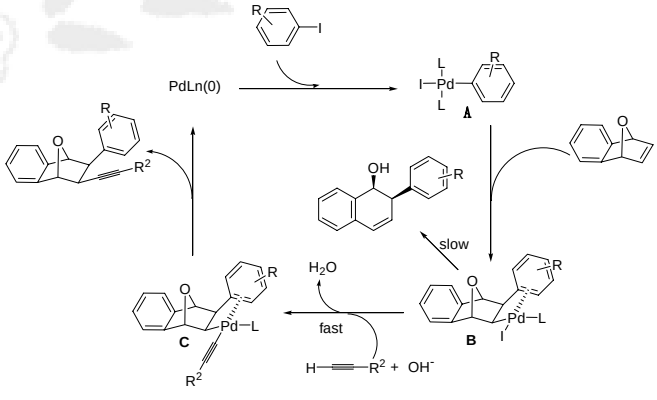
Compounds of bicyclic alkenes **1b-c** were also successfully used for the ternary coupling reaction with iodobenzene **2a** and phenylacetylene **3a**, under similar reaction conditions, a product of **4t** in 80% yields (Table 1, entry 20) was generated. The result came from substituted 7-oxabenzonorbornadiene **1b** having two strong electron-donating methoxy group on the aryl ring reacting with iodobenzene **2a** and phenylacetylene **3a**. In the same way, The coupling reaction was further applied to bulkier 1,4-oxa-1,4-dihydrotriphenylene **1c** with iodobenzene **2a** and phenylacetylene **3a** to give product **4u** in 72% yield (Table 1, entry 21).

Based on the observed regiochemistry of the products and the known palladium chemistry, a reasonable catalytic reaction mechanism is proposed as shown in Scheme 2. The first step is likely the oxidative addition of aryl halide to the Pd(0) species to give arylpalladium(II) intermediate A. (The first step relies on callassical carbopalladation of olefins at the oxidative addition of aryl halide to the Pd(0) species to give arylpalladium(II) intermediate A.)Substitution of a phosphane ligand in A by 7-oxabenzonorbornadiene 1 via exo-coordination followed by insertion of the carbon-carbon double bond in the oxabenzonorbornene moiety leads to intermediate B.[7h, 16] Then, the coordinated iodine in intermediate B was replaced by an acetylide to afford palladium intermediate C. Reductive elimination gave the final product 5,6-disubstituated 7-oxabenzonorbornene derivative 4 and regenerated the Pd(0) catalyst.

It is known that the addition of aryl halides to 7-oxabenzonorbornadiene **1** catalyzed by palladium and nickel complexes often resulted in the isolation of ring opening products because of the facile β-oxygen elimination of oxabicyclic alkene moiety in intermediate B.[13d, 14] However, in the present three-component coupling reaction, such ring opening due to C-O bond cleavage does not occur. The results indicate that the substitution of iodide ligand in intermediate B by the acetylide to give intermediate C is likely much faster than the β-oxygen elimination of B under the present catalytic reaction conditions.



Scheme 1. Oxabenzonorbornadiene reated with organic halide and 1-alkyne in the presence of $Pd(PPh_3)_4$, Bu_4NI, and NaOH to give 5,6-disubstituated 7-oxabenzonorbornene derivative.



Scheme 2. Proposed mechanism of the palladium-catalyzed 1,2-addition.

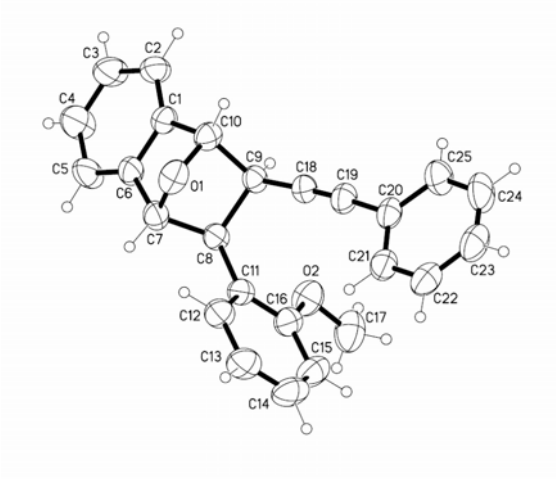
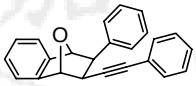
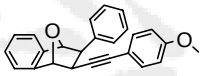
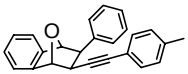
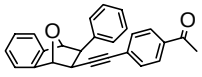
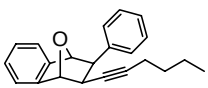
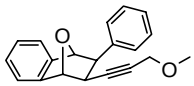
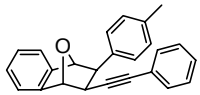
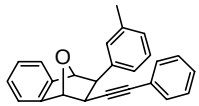
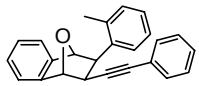
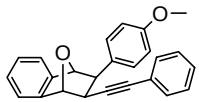
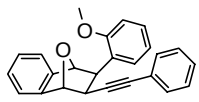
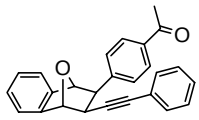
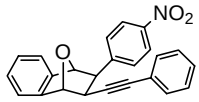
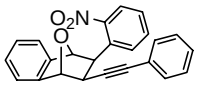
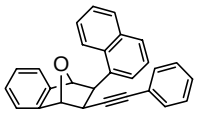
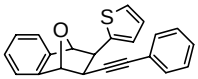
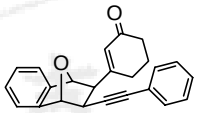
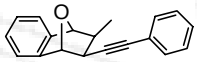
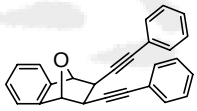
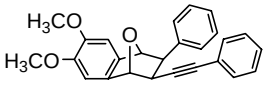
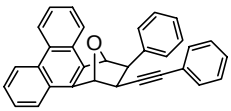


Figure 1. ORTER diagram of **4k**

Table 1. Products of 5,6-addition of 1-alkyne **3** and aryl, alkenyl halides **2** to oxabicyclic Alkene **1** in the presence of $Pd(PPh_3)_4$.

Entry	1	2	3	Product yield (%)
1	**1a**	**2a**	**3a**	 **4a** (92%)
2	**1a**	**2a**	**3b**	 **4b** (84%)
3	**1a**	**2a**	**3c**	 **4c** (68%)
4	**1a**	**2a**	**3d**	 **4d** (18%)
5	**1a**	**2a**	**3e**	 **4e** (38%)
6	**1a**	**2a**	**3f**	 **4f** (40%)
7	**1a**	**2b**	**3a**	 **4g** (73%)
8	**1a**	**2c**	**3a**	 **4h** (83%)
9	**1a**	**2d**	**3a**	 **4i** (52%)
10	**1a**	**2e**	**3a**	 **4j** (77%)
11	**1a**	**2f**	**3a**	 **4k** (65%)
12	**1a**	**2g**	**3a**	 **4l** (70%)
13	**1a**	**2h**	**3a**	 **4m** (40%)

14	**1a**	**2i**	**3a**	 **4n** (16%)
15	**1a**	**2j**	**3a**	 **4o** (50%)
16	**1a**	**2k**	**3a**	 **4p** (56%)
17	**1a**	**2l**	**3a**	 **4q** (28%)
18	**1a**	**2m**	**3a**	 **4r** (36%)
19	**1a**	**2n**	**3a**	 **4s** (45%)
20	**1b**	**2a**	**3a**	 **4t** (80%)
21	1c	2a	3a	 **4u** (72%)

Conclusions

We have developed a novel palladium-catalyzed three-component coupling reaction of organic halides with oxabicyclic alkene and terminal alkynes to afford products with extremely high stereoselectivity in good yields. The disubstituted products from oxabenzonorbornadiene can be further applied to the synthesis of polyaromatic hydrocarbons via deoxyaromatization reaction.

Experimental Section

General section

All reactions were performed under dry nitrogen atmosphere. ^{1}H and ^{13}C NMR experiments were performed on a Bruker 200 instrument at 200 MHz. Infrared spectra were obtained on a PerkinElmer System 2000 spectrometer. Mass spectra at high resolution were recorded on a Thermo Finnigan MAT 95 XL instrument.

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Oxabenzonorbornadiene **1b-c** were prepared following literature procedures.[18] The complex $Pd(PPh_3)_4$ was prepared according to the published procedures.[19]

General procedure for the three-component coupling reaction.

In a typical procedure, a round-bottom flask containing $Pd(PPh_3)_4$ (0.087 mmol) and $(n\text{-butyl})_4NI$ (0.173 mmol) was purged with nitrogen three times. To the flask were added sequentially 7-oxabenzonorbornadiene (1.73 mmol), iodobenzene (1.73 mmol), 1-alkyne (1.73 mmol), CH_2Cl_2 (5 mL) and NaOH (5 M, 10 mL). The solution was then stirred at 40 °C for 24 h. After filtration through Celite, the filtrate was concentrated and then separated on a silica gel column using a mixture of hexane and ethyl acetate as the eluent to give the desired product 4. The spectral data of product 4 obtained by this procedure are listed below.

5-*Exo*-phenyl-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornene (4a): Yield: 513 mg (92%), m. p. 135-136 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.27 (s, 2H), 5.53 (s, 1H), 5.57 (s, 1H), 6.90-6.97 (m, 2H), 7.11-7.7.50 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.8 (d), 50.8 (d), 84.7 (d), 85.2 (d). 85.7 (s), 89.4 (s), 119.2 (d), 119.6 (d), 123.4 (s), 126.6 (d), 127.0 (d), 127.3 (d), 127.6 (d), 127.9 (d), 129.2 (d), 131.4 (d), 141.0 (s), 145.1 (s), 145.9 (s); IR (KBr): 3025.4, 1597.2, 1458.9, 1193.8, 750.3, 691.7 cm^{-1}; HRMS *(m/e)* calcd for $C_{24}H_{18}O$ 322.1358, found 322.1357. $C_{24}H_{18}O$ (322.40): calcd. C 89.41; H 5.63; Found: C 89.06; H 5.65.

5-*Exo*-(2-(4-methoxyphenyl)ethynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4b): Yield: 512 mg (84%), m. p. 152-153 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.26 (s, 2H), 3.74 (s, 3H), 5.53 (s, 1H), 5.56 (s, 1H), 6.68 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 7.18-7.51 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.7 (d), 50.7 (d), 55.1 (q), 84.8 (d), 85.2 (d). 85.5 (s), 87.8 (s), 113.5 (d), 115.5 (s), 119.2(d), 119.6 (d), 126.6 (d), 127.0 (d), 127.2 (d), 127.9 (d), 129.2 (d), 132.7 (d), 141.1 (s), 145.1 (s), 145.9 (s), 159.0 (s); IR (KBr): 3015.8, 2947.0, 1610.0, 1522.9, 1244.4, 836.7, 744.9, 698.4 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O_2$ 352.1463, found 352.1462. $C_{25}H_{20}O_2$ (352.43): calcd. C 85.20; H 5.72; Found: C 84.82; H 5.59.

5-*Exo*-phenyl-6-*exo*-(2-p-tolylethynyl)-7-oxabenzonorbornene (4c): Yield: 396 mg (68%), m. p. 137-139 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.18 (s, 3H), 3.18 (s, 2H), 5.45 (s, 1H), 5.49 (s, 1H), 6.76 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 7.10-7.43 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.3 (q), 40.7 (d), 50.7 (d), 84.7 (d), 85.2 (d). 85.7 (s), 88.6 (s), 119.1 (d), 119.6 (d), 120.3 (s), 126.6 (d), 127.0 (d), 127.2 (d), 127.9 (d), 128.7 (d), 129.2 (d), 131.2 (d), 137.5 (s), 141.00 (s), 145.1 (s), 145.9 (s); IR (KBr): 3026.8, 2923.9, 1603.2, 1494.7, 1264.1, 817.3, 753.3, 700.4 cm^{-1}.

HRMS *(m/e)* calcd for $C_{25}H_{20}O$ 336.1514, found 336.1515. $C_{25}H_{20}O$ (336.43): calcd. C 89.25; H 5.99; Found: C 89.05; H 6.03.

5-*Exo*-(2-(4-acetylphenyl)ethynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4d): Yield: 114 mg (18%), m. p. 149-151 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.54 (s, 3H), 3.30 (s, 2H), 5.57 (s, 1H), 5.59 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 7.21-7.50 (m, 9H), 7.77 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.5 (q), 40.9 (d), 50.8 (d), 84.5 (d), 85.1 (d). 93.2 (s), 119.2 (d), 119.7 (d), 126.7 (d), 127.1 (d), 127.4 (d), 127.9 (d), 128.0 (d), 128.3 (s), 129.1 (d), 131.4 (d), 135.7 (s), 140.8 (s), 144.9 (s), 145.8 (s), 197.3 (s); IR (KBr): 3062.7, 2998.8, 1669.8, 1598.7, 1460.8, 1273.2, 830.4, 776.5, 703.5 cm^{-1}; HRMS *(m/e)* calcd for $C_{26}H_{20}O_2$ 364.1463, found 364.1461. $C_{26}H_{20}O_2$ (364.44): calcd. C 85.69; H 5.53; Found: C 85.63; H5.32.

5-*Exo*-(hex-1-ynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4e): Yield: 199 mg (38%); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.98 (t, J=7.2 Hz , 3H), 1.78-1.42 (m, 4H), 2.03-2.18 (m, 2H), 3.26 (dt, J=8.6, J=2.2 Hz , 1H), 3.36 (d, J=8.6 Hz , 1H), 5.65 (s, 1H), 5.67 (s, 1H), 7.27-7.77 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.6 (q), 18.3 (t), 21.6 (t), 30.5 (t), 40.1 (d), 50.5 (d), 79.3 (s), 85.1 (d), 85.2 (d), 85.9 (s), 119.1 (d), 119.6 (d), 126.4 (d), 126.9 (d), 127.1 (d), 127.7 (d), 129.2 (d), 141.2 (s), 145.2 (s), 145.9 (s); IR (neat): 3060.9, 2929.7, 1603.0, 1459.3, 1377.2, 1263.6, 758.6, 700.0 cm^{-1}; HRMS *(m/e)* calcd for $C_{22}H_{22}O$ 302.1671, found 302.1671.

5-*Exo*-(3-methoxyprop-1-ynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4f): Yield: 201 mg (40%); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.88 (s, 3H), 3.00 (dt, *J* = 8.6, *J* = 1.6 Hz, 1H), 3.08 (d, *J* = 8.6 Hz, 1H), 3.68-3.72 (m, 2H), 5.38 (s, 2H), 7.08-7.32 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 40.0 (d), 50.3 (d), 56.7 (q), 59.5 (t), 80.9 (s), 84.6 (d). 85.0 (d), 86.1 (s), 118.9 (d), 119.4 (d), 126.4 (d), 126.8 (d), 127.1 (d), 127.7 (d), 128.9 (d), 140.7 (s), 144.8 (s), 145.6 (s). IR (neat): 3060.5, 2927.8, 1602.1, 1459.9, 1357.2, 1095.4, 750.3, 700.7 cm^{-1}; HRMS *(m/e)* calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1305.

5-*Exo*-(2-phenylethynyl)-6-*exo*-p-tolyl-7-oxabenzonorbornene (4g): Yield: 425 mg (73%), m.p. 107-109 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.22 (s, 3H), 3.08 (s, 2H), 5.35 (s, 1H), 5.41 (s, 1H), 6.80-6.89 (m, 2H), 6.96-7.26 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.9 (q), 40.6 (d), 50.3 (d), 84.5 (d), 85.1 (d). 85.5 (s), 89.6 (s), 119.0(d), 119.5 (d), 123.4 (s), 126.8 (d), 127.1 (d), 127.4 (d), 127.8 (d), 128.4 (d), 128.9 (d), 131.3 (d), 135.9 (s), 137.8 (s), 144.9 (s), 145.8 (s); IR (KBr): 3011.5, 2936.1, 1596.1, 1461.5, 1194.0, 848.8, 759.2, 691.6 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O$ 336.1514, found 336.1517. $C_{25}H_{20}O$ (336.43): calcd. C 89.25; H 5.99; Found: C 89.18; H 5.96.

5-*Exo*-(2-phenylethynyl)-6-*exo*-m-tolyl-7-oxabenzonorbornene (4h): Yield: 483 mg (83%), m.p. 125-126 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.22 (d, AB type, *J* =8.6 Hz, 1H), 3.26(d, AB type *J* = 8.6 Hz, 1H), 5.51 (s, 1H), 5.57 (s, 1H), 6.92-7.02 (m, 2H), 7.05-7.41 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.5 (q), 40.7 (d), 50.8 (d), 84.8 (d), 85.3 (d). 85.7 (s), 89.5 (s), 119.1 (d), 119.7 (d), 123.5 (s), 126.4 (d), 126.9 (d), 127.2 (d), 127.4 (d), 127.5 (d), 127.8 (d), 127.9 (d), 129.9 (d), 131.4 (d), 137.4 (s), 140.8 (s), 145.1 (s), 146.00 (s). IR (KBr): 3048.5, 2927.8, 1597.1, 1459.7, 1153.0, 898.8, 758.4, 691.9 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O$ 336.1514, found 336.1513. $C_{25}H_{20}O$ (336.43): calcd. C 89.25; H 5.99; Found: C 89.01; H 6.02.

5-*Exo*-(2-phenylethynyl)-6-*exo*-o-tolyl-7-oxabenzonorbornene (4i): Yield: 303 mg (52%), m. p. 163-165 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.33 (d, AB type, *J* =8.5 Hz, 1H), 3.39(d, AB type, *J* = 8.5 Hz, 1H), 5.58 (s, 1H), 5.71 (s, 1H), 6.78-6.91 (m, 2H), 7.05-7.43 (m, 10H), 7.68 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.2 (q), 39.5 (d), 46.8 (d), 83.9 (d), 84.8 (d). 88.6 (s), 119.2(d), 119.7 (d), 123.3 (s), 126.0 (d), 126.4 (d), 127.0 (d), 127.3 (d), 127.5 (d), 127.8 (d), 129.6 (d), 131.5 (d), 136.8 (s), 139.5 (s), 145.3 (s), 146.2 (s); IR (KBr): 3021.0, 2915.5, 1598.9, 1487.6, 978.8, 900.2, 710.0 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O$ 336.1514, found 336.1511. $C_{25}H_{20}O$ (336.43): calcd. C 89.25; H 5.99; Found: C 88.93; H 5.87.

5-*Exo*-(4-methoxyphenyl)-6-*exo*-(2-phenylethynyl) -7-oxabenzonorbornene (4j): Yield: 450 mg (77%), m. p. 99-100 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.15 (s, 2H), 3.73 (s, 3H), 5.39 (s, 1H), 5.48 (s, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.87-6.98 (m, 2H), 7.04-7.34 (m, 7H), 7.30 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.8 (d), 50.1 (d), 55.4 (q), 84.8 (d), 85.5 (d). 85.7 (s), 89.6 (s), 113.4 (d), 119.2(d), 119.6 (d), 123.5 (s), 127.0 (d), 127.3 (d), 127.6 (d), 127.9 (d), 130.2 (d), 131.4 (d), 133.1 (s), 145.1 (s), 145.9 (s), 158.6 (s); IR (KBr): 3016.8, 2930.0, 1609.0, 1462.9, 1246.2, 846.7, 765.2, 695.6 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O_2$ 352.1463, found 352.1463. $C_{25}H_{20}O_2$ (352.43): calcd. C 85.20; H 5.72; Found: C 85.27; H 5.69.

5-*Exo*-(2-methoxyphenyl)-6-*exo*-(2-phenylethynyl)-7-oxabenzonorborne ne (4k): Yield: 396 mg (65%), m. p. 127-129 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.31 (d, *J* = 8.5 Hz, 1H), 3.69 (d, *J* = 8.5 Hz, 1H), 3.74 (s, 3H), 5.55 (s, 1H), 5.64 (s, 1H), 6.83-6.93 (m, 3H), 7.00-7.43 (m, 9H), 7.66 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.8 (d), 43.2 (d), 55.3 (q), 83.4 (d), 84.4 (s). 84.7 (d), 89.5 (s), 109.9 (d), 119.1 (d), 119.5 (d), 123.5 (s), 126.8 (d), 127.1 (d), 127.3 (d), 127.4 (d), 127.7 (d), 128.3 (d), 129.6 (d), 131.3 (s), 145.2 (s), 146.1 (s), 157.5 (s); IR (KBr): 3053.5, 2920.9, 1595.3, 1465.7, 1243.2, 751.9, 695.0 cm^{-1}; HRMS *(m/e)* calcd for $C_{25}H_{20}O_2$ 352.1463, found 352.1461. $C_{25}H_{20}O_2$ (352.43): calcd. C 85.20; H 5.72; Found: C 85.25; H 5.69.

5-*Exo*-(4-acetylphenyl)-6-*exo*-(2-phenylethynyl) -7-oxabenzonorbornene (4l): Yield: 441 mg (70%), m. p. 150-151 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.60 (s, 3H), 3.32 (s, 2H), 5.53 (s, 1H), 5.60 (s, 1H), 6.89-6.96 (m, 2H), 7.08-7.44 (m, 7H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.6 (q), 40.8 (d), 50.7 (d), 84.7 (d), 84.8 (d). 85.9 (s), 88.8 (s), 119.2 (d), 119.6 (d), 123.0 (s), 127.2 (d), 127.4 (d), 127.7 (d), 127.9 (d), 128.0 (d), 129.4 (d), 131.1 (d), 135.6 (s), 144.9 (s), 145.3 (s), 146.7 (s), 197.9 (s). IR (KBr): 3002.5, 2931.4, 1671.2, 1606.0, 1488.8, 1272.6, 849.8, 757.4, 691.7 cm^{-1}; HRMS *(m/e)* calcd for $C_{26}H_{20}O_2$ 364.1463, found 364.1465. $C_{26}H_{20}O_2$ (364.44): calcd. C 85.69; H 5.53; Found: C 85.80; H 5.55.

5-*Exo*-(4-nitrophenyl)-6-*exo*- (2-phenylethynyl)-7-oxabenzonorbornene (4m): Yield: 252 mg (40%), m. p. 215-216 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.35 (s, 2H), 5.50 (s, 1H), 5.61 (s, 1H), 6.90-6.98 (m, 2H), 7.11-7.44 (m, 7H), 7.64 (d, *J* = 8.7 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.9 (d), 50.7 (d), 84.9 (d), 86.4 (s), 88.3 (s), 119.3 (d), 119.7 (d), 122.7 (s), 122.9 (d), 127.4 (d), 127.6 (d), 128.0 (d), 128.2 (d), 130.1 (d), 131.1 (d), 144.8 (s), 145.0 (s), 146.8 (s), 148.9 (s). IR (KBr): 3064.5, 1596.6, 1506.0, 1489.3, 1342.1, 847.3, 755.0, 691.9 cm^{-1}; HRMS *(m/e)* calcd for $C_{24}H_{17}NO_3$ 367.1208, found 367.1205. $C_{24}H_{17}NO_3$ (367.40): calcd. C 78.46; H 4.66; N 3.81; Found: C 78.07; H 4.69; N 3.78..

5-*Exo*-(2-nitrophenyl)-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornene (4n): Yield: 102 mg (16%),m. p. 155-156 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.53 (d, *J* = 8.3 Hz, 1H), 3.73 (d, *J* = 8.3 Hz, 1H), 5.50 (s, 1H), 5.60 (s, 1H), 6.76-6.85 (m, 2H), 6.99-7.39 (m, 8H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.84 (dd, *J* = 8.1, *J* = 1.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.4 (d), 46.6 (d), 83.8 (d), 84.6 (d), 85.0 (s), 88.5 (s), 119.3 (d), 119.7 (d), 123.0 (s), 124.0 (d), 127.3 (d), 127.4 (d), 127.5 (d), 127.7 (d), 127.9 (d) 130.3 (d), 131.2 (d), 132.7 (d), 136.6 (s), 145.0 (s), 145.1 (s), 145.0 (s); IR (KBr): 3086.5, 1523.3, 1347.2, 1263.2, 755.6, 691.8 cm^{-1}; HRMS *(m/e)* calcd for $C_{24}H_{17}NO_3$ 367.1208, found 367.1206. $C_{24}H_{17}NO_3$(367.40): calcd. C 78.46; H 4.66; N 3.81; Found: C 78.17; H 4.68; N 3.77.

5-*Exo*-(naphthalen-1-yl)-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornen e (4o): Yield: 322 mg (50%), m. p. 226-228 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.52 (d, *J* = 8.5 Hz, 1H), 4.02 (d, *J* = 8.5 Hz, 1H), 5.64 (s, 1H),

5.87 (s, 1H), 6.47-6.57 (m, 2H), 6.94-7.08 (m, 3H), 7.22-7.62 (m, 7H), 7.76-7.95 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.4 (d), 46.0 (d), 84.0 (d), 84.7 (s), 85.0 (d), 88.7 (s), 119.3 (d), 119.7 (d), 123.0 (s), 123.3 (d), 124.9 (d), 125.2 (d), 125.5 (d), 125.8 (d), 127.0 (d), 127.1 (d), 127.3 (d), 127.4 (d), 127.6 (d, 2C), 128.7 (d), 131.1 (d, 2C), 132.8 (s), 133,5 (s), 137.0 (s), 145.3 (s), 146.1 (s). IR (KBr): 3043.8, 1596.8, 1459.6, 1153.7, 745.0, 689.1 cm^{-1}; HRMS *(m/e)* calcd for $C_{28}H_{20}O$ 372.1514, found 372.1512.

5-*Exo*-(2-phenylethynyl)-6-*exo*-(2-thienyl)-7-oxabenzonorbornene (4p): Yield: 318 mg (56%), m. p. 127-128 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.17 (d, *J* = 8.2 Hz, 1H), 3.54 (d, *J* = 8.2 Hz, 1H), 5.48 (s, 1H), 5.51 (s, 1H), 6.79-7.7.51 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.1 (d), 46.3 (d), 85.0 (d), 85.3 (s), 85.8 (d), 88.6 (s), 119.4 (d), 119.5 (d), 123.3 (s), 124.3 (d), 126.1 (d), 126.2 (d), 127.3 (d), 127.6 (d), 127.9 (d) 131.4 (d), 143.8 (s), 144.7 (s), 144.9 (s); IR (KBr): 3004.0, 1597.7, 1461.7, 1265.6, 760.4, 692.4 cm^{-1}; HRMS *(m/e)* calcd for $C_{22}H_{16}OS$ 328.0922, found 328.0921. $C_{22}H_{16}OS$ (328.43): calcd. C 80.45; H 4.91; S 9.76. Found: C 80.22; H 4.66; S10.08.

5-*Exo*-(2-phenylethynyl)-6-*exo*-(3-Oxo-cyclohex-1-enyl)-7-oxabenzonorbornene (4q): Yield: 165 mg (28%), m. p. 179-180 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.91-2.08 (m, 2H), 2.31-2.54 (m, 3H), 2.60-2.75 (m, 1H), 2.80 (d, *J* = 8.7 Hz, 1H), 3.23 (d, *J* = 8.7 Hz, 1H), 5.49 (s, 1H), 5.53 (s, 1H), 6.16 (s, 1H), 7.17-7.43 (m, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.6 (t), 29.5 (t), 37.6 (t), 39.6 (d), 52.3 (d), 81.9 (d), 84.3 (s), 84.8 (d), 88.1 (s), 119.3 (d), 119.6 (d), 123.0 (s), 127.3 (d), 127.5 (d), 128.0 (d), 128.1 (d), 128.3 (d), 131.5 (d), 144.7 (s), 144.9 (s), 164.5 (s), 199.7 (s). IR (KBr): 3084.7, 1665.8, 1598.3, 1490.5, 1460.8, 1256.3, 760.9, 692.5 cm^{-1}; HRMS *(m/e)* calcd for $C_{24}H_{20}O_2$ 340.1463, found 340.1465. $C_{24}H_{20}O_2$ (340.41): calcd. C 84.68; H 5.92; Found: C 84.60; H 5.94.

5-*Exo*-(2-phenylethynyl)-6-*exo*-methyl-7-oxabenzonorbornene (4r): Yield: 162 mg (36%); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.32 (d, *J* = 7.2 Hz, 3H), 1.92-2.07 (m, 1H), 2.80 (d, *J* = 8.1 Hz, 2H), 4.92 (s, 1H), 5.34 (s, 1H),7.04-7.24 (m, 6H), 7.32-7.40 (m, 2H) . ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.5 (q), 38.1 (d), 38.3 (d), 83.8 (s), 85.3 (d), 85.4 (d), 89.2 (s), 119.1 (d), 119.2 (d), 123.7 (s), 126.7 (d), 127.0 (d), 127.7 (d), 128.1 (d), 131.6 (d), 144.6 (s), 145.6 (s). IR (neat):3046.1, 2925.6, 1598.1, 1461.8, 1377.5, 1153.8, 752.8, 691.3 cm^{-1}; HRMS *(m/e)* calcd for $C_{19}H_{16}O$ 260.1201, found 260.1199.

5-*Exo*-(2-phenylethynyl)-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornene (4s): Yield: 270 mg (45%), m. p. 160-162 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.16 (s, 2H), 5.60 (s, 2H), 7.18-7.30 (m, 8H), 7.30-7.38 (m, 2H), 7.38-7.75 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.5 (d), 85.0 (d), 88.6 (s), 119.6 (d), 123.5 (s), 127.5 (d), 127.9 (d), 128.1 (d), 131.8 (d), 144.3 (s). IR (KBr): 3059.1, 1597.6, 1490.1, 1227.9, 758.1, 691.6 cm^{-1}; HRMS *(m/e)* calcd for $C_{26}H_{18}O$ 346.1358, found 346.1359. $C_{26}H_{18}O$ (346.42): calcd. C 90.14; H 5.24; Found: C 89.77; H 5.21.

1, 2, 3, 4-tetrahydro-6, 7-dimethoxy-1, 4-epoxynaphthalene-2-exo-phenyl-3-exo-(2-phenylethynyl) (4t): Yield: 529 mg (80%), m. p. 150-153 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.21 (s, 2H), 3.88 (s, 3H), 3.90 (s, 3H), 5.47 (s, 1H), 5.52 (s, 1H), 6.89-7.01 (m, 4H), 7.11-7.49 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.2 (d), 51.3 (d), 56.3 (q), 85.0 (d), 85.5 (d), 89.6 (s), 103.9 (d), 104.4 (d), 123.4 (s), 126.6 (d), 127.5 (d), 127.9 (d), 129.2 (d), 131.4 (d), 137.4 (s), 138.3 (s), 141.1 (s), 148.3 (s), 148.5 (s). IR (KBr): 3062.0, 2998.8, 1597.8, 1490.5, 1307.7, 1218.9, 1090.3, 757.5, 693.4 cm^{-1}; HRMS *(m/e)* calcd for $C_{26}H_{22}O_3$ 382.1569, found382.1570. $C_{26}H_{22}O_3$ (382.45): calcd. C 81.65; H 5.80; Found: C 81.46; H 5.79.

1, 2, 3, 4-tetrahydro-1, 4-epoxytriphenylene-2-exo-phenyl-3-exo-(2-phenylethynyl) (4u): Yield: 526 mg (72%), m. p. 209-211 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.20 (s, 2H), 6.05 (s, 1H), 6.08 (s, 1H), 6.89-6.98 (m, 2H), 7.07-7.16 (m, 3H), 7.24-7.38 (m, 4H), 7.42-7.50 (m, 2H), 7.56-7.69 (m, 4H), 7.81-7.88 (m, 1H), 7.96-8.06 (m, 1H), 8.65-8.75 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.8 (d), 50.9 (d), 84.4 (d), 84.8 (d), 85.5 (s), 89.7 (s), 123.4 (s), 123.7 (d), 124.4 (d), 125.4 (s), 125.7 (s), 126.60 (d), 126.7 (d), 126.8 (d), 127.2 (d), 127.60 (d), 127.9 (d), 128.0 (d), 129.4 (d), 130.3 (s), 130.4 (s), 131.4 (d), 140.5 (s), 141.1 (s), 141.4 (s). IR (KBr): 3034.0, , 1592.1, 1488. 1, 1213.9, 752.4, 693.7 cm^{-1}; HRMS *(m/e)* calcd for $C_{32}H_{22}O$ 422.1671, found 422.1670. $C_{32}H_{22}O$ (422.52): calcd. C 90.97; H 5.25; Found: C 90.67; H 5.13.

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[15] For **4k**: CCDC-656613 [cell parameters: a = 16.122(3), b = 11.678(2), c = 19.930(3)]; contains the supplementary crystallographie data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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