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Palladium-Catalyzed 1,2-Addition of Organic Halides and Terminal Alkynes to 7-Oxabenzonorbornadiene: An Efficient Route to Polyaromatic Hydrocarbons

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Keywords: Multicomponent reactions / Palladium / Oxabenzonorbornadiene / Alkynes

A three-component coupling reaction of organic halides with oxabicyclic alkenes 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-disubstituted 7-oxabenzonorbornene derivatives in good

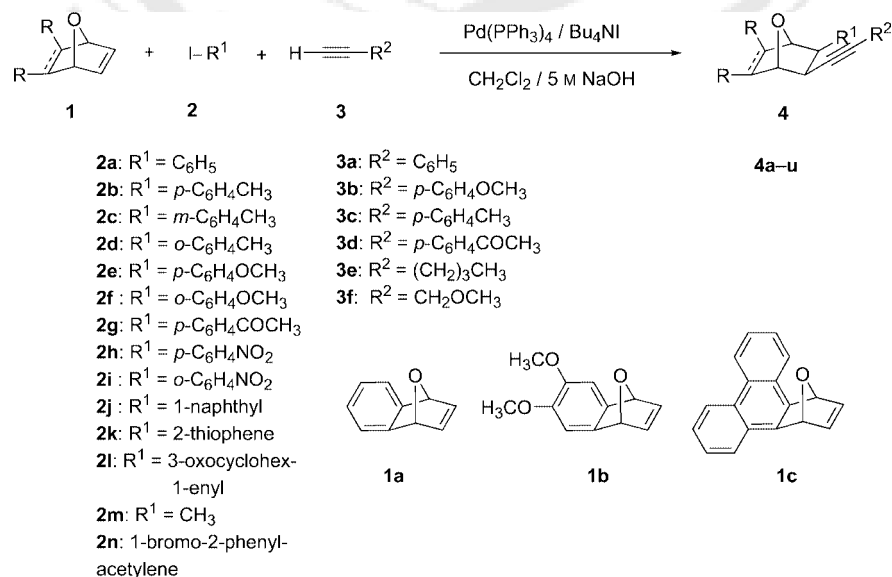
yields. The disubstituted products from oxabenzonorbornadiene can be readily converted into polyaromatic hydrocarbons by a Lewis acid mediated deoxyaromatization reaction.

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Introduction

Transition-metal-catalyzed ternary coupling reactions of organic halides, nucleophiles, and olefins is an important method for the construction of complex molecular structures in a single one-pot step.^[1] In this type of multicomponent reaction, the electrophiles employed include various aryl- and alkenyl halides, iodonium salts, and diazonium salts, and the nucleophiles^[2–5] typically used are 1-alkynes,

alkynols, organostannanes, and tetraphenylborate ions. However, there is great restriction on the type of olefin that can be used in the ternary coupling reactions. These olefins generally require high coordination and insertion ability, but they must also lack β -hydrogen atoms so that elimination after insertion is not possible. Bicyclic olefins such as norbornadienes and norbornenes are a class of olefins that show the above properties due to the angle strain of



Scheme 1. Oxabenzonorbornadiene treated with organic halides and 1-alkynes in the presence of Pd(PPh₃)₄, Bu₄NI, and NaOH to give 5,6-disubstituted 7-oxabenzonorbornene derivatives.

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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. Al-

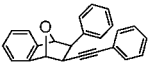
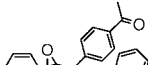
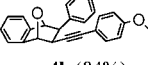
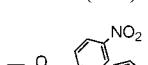
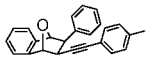
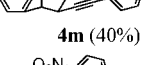
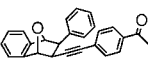
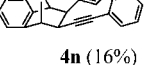
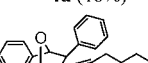
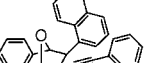
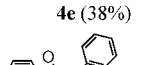
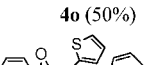
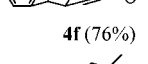
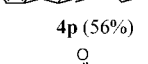
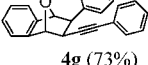
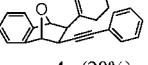
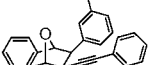
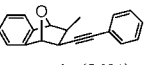
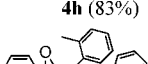

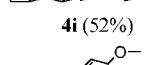
though 7-oxabicyclic alkenes are similar to norbornadienes and norbornenes, the transition-metal-catalyzed addition reaction of a nucleophilic^[7–13] or electrophilic^[14] reagent to a 7-oxabicyclic alkene often leads to ring opening of the oxabicyclic alkene because of facile β -oxygen elimination after the addition of an organic group to the oxabicyclic alkene. As a result, it is difficult to add a nucleophile or an electrophile in one pot to give a three-component coupling reaction product for reactions involving 7-oxabicyclic alkenes as substrates. In this study, we report a palladium-catalyzed three-component coupling reaction of oxabicyclic alkenes with organic halides and terminal alkynes to provide 5,6-disubstituted 7-oxabenzonorbornene derivatives 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 underwent deoxyaromatization readily in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ to provide an efficient method for the synthesis of variously 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 $\text{CH}_2\text{Cl}_2/\text{NaOH}$ (5 M in water) in the presence of tetrabutylammonium iodide (0.173 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.087 mmol) to give 5,6-disubstituted 7-oxabenzonorbornene derivative **4a** in 92% yield (Table 1, En-

Table 1. 5,6-Addition products of 1-alkyne **3** and aryl and alkenyl halides **2** to oxabicyclic alkene **1** in the presence of $\text{Pd}(\text{PPh}_3)_4$.

Entry	1	2	3	Product (yield)	Entry	1	2	3	Product (yield)
1	1a	2a	3a	 4a (92%)	12	1a	2g	3a	 4l (70%)
2	1a	2a	3b	 4b (84%)	13	1a	2h	3a	 4m (40%)
3	1a	2a	3c	 4c (68%)	14	1a	2i	3a	 4n (16%)
4	1a	2a	3d	 4d (18%)	15	1a	2j	3a	 4o (50%)
5	1a	2a	3e	 4e (38%)	16	1a	2k	3a	 4p (56%)
6	1a	2a	3f	 4f (76%)	17	1a	2l	3a	 4q (28%)
7	1a	2b	3a	 4g (73%)	18	1a	2m	3a	 4r (36%)
8	1a	2c	3a	 4h (83%)	19	1a	2n	3a	 4s (45%)
9	1a	2d	3a	 4i (52%)	20	1b	2a	3a	 4t (80%)
10	1a	2e	3a	 4j (77%)	21	1c	2a	3a	 4u (72%)
11	1a	2f	3a	 4k (65%)					

try 1). The structure of **4a** was characterized by NMR and IR spectroscopy and mass spectrometry. In the absence of a palladium complex or sodium hydroxide, product **4a** was not found, whereas the omission of a phase-transfer reagent, tetrabutylammonium iodide, afforded only a trace amount of desired product **4a**. The *exo* and *cis* stereochemistry of **4k** was confirmed by X-ray diffraction^[15] (Figure 1). The catalytic reaction is remarkably stereoselective and affords only to the *exo* and *cis* product.

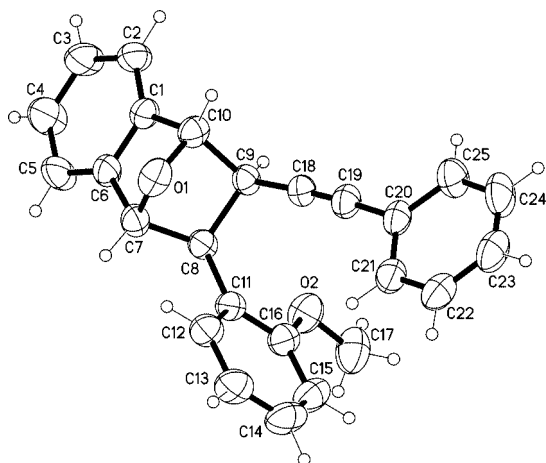


Figure 1. ORTER diagram of **4k**.

To understand the nature of this palladium-catalyzed 1,2-addition, the effect of solvent, base, and metal complex used in the three-component coupling reaction of **1a**, **2a**, and **3a** to give **4a** was investigated. The palladium complexes Pd(dba)₂ and Pd(dba)₂/2dppf afforded a trace amount of **4a** only, whereas Pd(dba)₂/2dppp gave product **4a** in 24% yield. Pd(PPh₃)₄ was found to be the best catalyst, as it afforded product **4a** in 92% yield. The solvent used for the catalytic reaction is also critical. Dichloromethane was more effective than toluene, and product **4a** was obtained in 92 and 74% yield, respectively. The use of Et₃N as base gave product **4a** in 45% yield, which is lower than the 92% yield obtained by using NaOH as the base. On the basis of these studies, the optimized reaction conditions for the three-component coupling reaction are: Pd(PPh₃)₄ in the presence of Bu₄NI in CH₂Cl₂/NaOH (5 M) at 40 °C. These reactions conditions were employed as the standard for the reactions shown in Table 1.

This palladium-catalyzed three-component coupling reaction was successfully extended to various organic halides and 1-alkynes. The results are summarized in Table 1. Treatment of iodobenzene and 7-oxabenzonorbornadiene (**1a**) with terminal alkynes **3a–f** (Table 1, Entries 1–6) furnished corresponding 5,6-disubstituted 7-oxabenzonorbornene derivatives **4a–f** in 18–92% yield. It is noteworthy that the yield of this three-component coupling reaction is substantially affected by the position of the substituent on the aryl iodide. *ortho*-Substituted aryl iodide gave a slightly lower yield relative to those of the *meta* and *para* derivatives (Table 1, Entries 7–11). In addition, aryl iodides bearing an electron-donating substituent in the *para* position (Table 1,

Entries 7, 10, and 12) gave higher product yields than that obtained with a substrate having a strong electron-withdrawing group (Table 1, Entry 13) in the ternary coupling reaction.

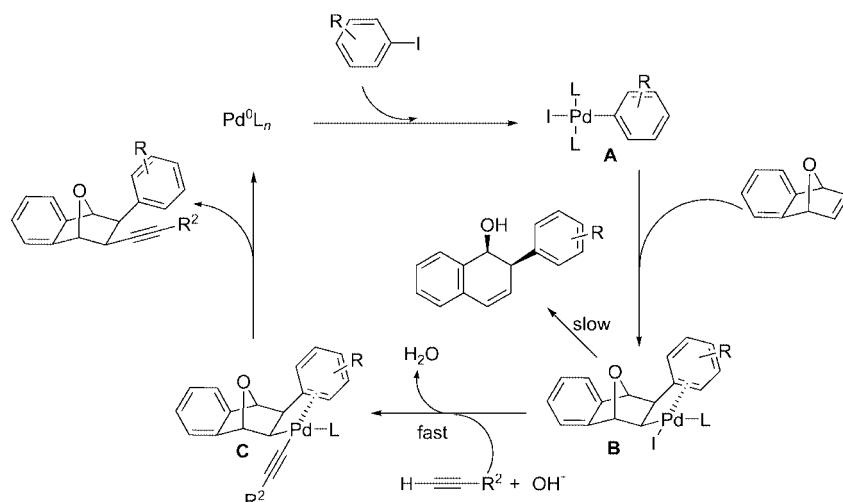
The reaction could be further applied to alkyl and alkynyl iodides and a 1-bromoalkyne. Under similar reaction conditions, 2-iodothiophene (**2k**) and 3-iodocyclohex-2-enone (**2l**) coupled to 7-oxabenzonorbornadiene (**1a**) and phenylacetylene (**3a**) to obtain **4p** and **4q** in 56 and 28% yield, respectively (Table 1, Entries 16 and 17). Similarly, the reactions of methyl iodide (**2m**) and 1-bromo-2-phenylacetylene (**2n**) with 7-oxabenzonorbornadiene (**1a**) and phenylacetylene (**3a**) afforded **4r** and **4s** in 36 and 45% yield, respectively (Table 1, Entries 18 and 19). In most of these three-component coupling reactions, direct coupling products between **2** and **3** were observed in various amounts. The side reactions likely account for the low yield of product **4** in some of the cases in Table 1.

Bicyclic alkenes could also be used in the ternary coupling reaction; thus, the coupling of **1b** with iodobenzene (**2a**) and phenylacetylene (**3a**) under similar reaction conditions afforded product **4t** in 80% yield (Table 1, Entry 20). In the same way, the coupling reaction of bulky 1,4-epoxy-1,4-dihydrotriphenylene (**1c**) with iodobenzene (**2a**) and phenylacetylene (**3a**) generated product **4u** in 72% yield (Table 1, Entry 21).

On the basis of the observed regiochemistry of the products and classical carbopalladation chemistry, a reasonable catalytic reaction mechanism was proposed (Scheme 2). The first step is likely the oxidative addition of the aryl halide to the Pd⁰ species to give arylpalladium(II) intermediate **A**. Substitution of a phosphane ligand in **A** by 7-oxabenzonorbornadiene (**1a**) by *exo* coordination followed by insertion of the carbon–carbon double bond into the oxabenzonorbornene moiety leads to intermediate **B**.^[16] Then, the coordinated iodine in intermediate **B** can be replaced by an acetylide to afford palladium intermediate **C**. Reductive elimination gives the final 5,6-disubstituted 7-oxabenzonorbornene derivative **4** to regenerate the Pd⁰ catalyst.

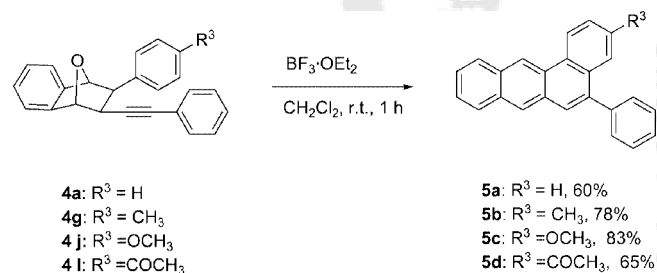
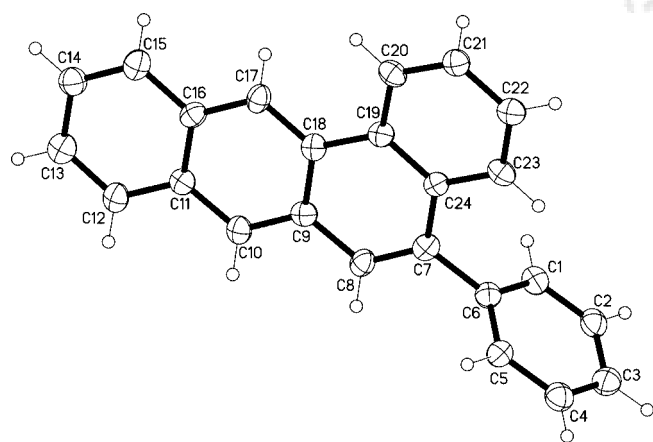
It is known that the addition of aryl halides to 7-oxabenzonorbornadiene (**1a**) catalyzed by palladium and nickel complexes often results in the isolation of ring-opening products because of facile β-oxygen elimination of the oxabicyclic alkene moiety in intermediate **B**.^[13d,14] However, in the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

5,6-Disubstituted 7-oxabenzonorbornene derivatives **4a**, **4g**, **4j**, and **4l** readily undergo deoxyaromatization in the presence of BF₃·OEt₂ (2 equiv.) as a Lewis acid in CH₂Cl₂ at room temperature over 1 h to provide polyaromatic compounds **5a**, **5b**, **5c**, and **5d** in 60, 78, 83, and 65% yield, respectively (Scheme 3). The structures of these polyaromatic compounds were characterized by NMR and IR spectroscopy and mass spectrometry. The structure of com-



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

compound **5a** was confirmed by X-ray diffraction^[15] (Figure 2). It is interesting to note that most of these polyaromatic hydrocarbon derivatives show strong photoluminescence in the solid state and in solution and are potentially useful as electroluminescent and photoluminescent materials.^[17]

Scheme 3. Deoxyaromatization reaction of compound **4** with BF₃·OEt₂ to afford corresponding product **5**.Figure 2. ORTER diagram of **5a**.

Conclusions

We developed a novel palladium-catalyzed three-component coupling reaction of organic halides with oxabicyclic

alkenes 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 by a deoxyaromatization reaction. Further application of the methodology in organic synthesis and detailed mechanistic studies of the catalytic reaction are in progress.

Experimental Section

General Section: All reactions were performed under a dry nitrogen atmosphere. All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Oxabenzonorbornadienes **1b,c** were prepared following literature procedures.^[18] The complex Pd(PPh₃)₄ was prepared according to the published procedures.^[19] ¹H and ¹³C NMR experiments were performed with a Bruker 200 instrument. Infrared spectra were obtained with a PerkinElmer System 2000 spectrometer. Mass spectra at high resolution were recorded with a Thermo Finnigan MAT 95 XL instrument.

General Procedure for the Three-Component Coupling Reaction: In a typical procedure, a round-bottom flask containing Pd(PPh₃)₄ (0.087 mmol) and (*n*-butyl)₄Ni (0.173 mmol) was purged with nitrogen three times. To the flask was added sequentially 7-oxabenzonorbornadiene (1.73 mmol), iodobenzene (1.73 mmol), 1-alkyne (1.73 mmol), CH₂Cl₂ (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 (hexane/ethyl acetate) to give desired product **4**.

5-*exo*-Phenyl-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornene (4a): Yield: 513 mg (92%), m.p. 135–136 °C. ¹H NMR (200 MHz, CDCl₃): δ = 3.27 (s, 2 H), 5.53 (s, 1 H), 5.57 (s, 1 H), 6.90–6.97 (m, 2 H), 7.11–7.750 (m, 12 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3025.4, 1597.2, 1458.9, 1193.8, 750.3, 691.7 cm⁻¹. HRMS: calcd. for C₂₄H₁₈O 322.1358; found 322.1357. C₂₄H₁₈O (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. ¹H NMR

(200 MHz, CDCl₃): δ = 3.26 (s, 2 H), 3.74 (s, 3 H), 5.53 (s, 1 H), 5.56 (s, 1 H), 6.68 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.18–7.51 (m, 9 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3015.8, 2947.0, 1610.0, 1522.9, 1244.4, 836.7, 744.9, 698.4 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O₂ 352.1463; found 352.1462. C₂₅H₂₀O₂ (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. ¹H NMR (200 MHz, CDCl₃): δ = 2.18 (s, 3 H), 3.18 (s, 2 H), 5.45 (s, 1 H), 5.49 (s, 1 H), 6.76 (d, J = 8.1 Hz, 2 H), 6.88 (d, J = 8.1 Hz, 2 H), 7.10–7.43 (m, 9 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3026.8, 2923.9, 1603.2, 1494.7, 1264.1, 817.3, 753.3, 700.4 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O 336.1514; found 336.1515. C₂₅H₂₀O (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. ¹H NMR (200 MHz, CDCl₃): δ = 2.54 (s, 3 H), 3.30 (s, 2 H), 5.57 (s, 1 H), 5.59 (s, 1 H), 7.00 (d, J = 8.2 Hz, 2 H), 7.21–7.50 (m, 9 H), 7.77 (d, J = 8.1 Hz, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3062.7, 2998.8, 1669.8, 1598.7, 1460.8, 1273.2, 830.4, 776.5, 703.5 cm⁻¹. HRMS: calcd. for C₂₆H₂₀O₂ 364.1463; found 364.1461. C₂₆H₂₀O₂ (364.44): calcd. C 85.69, H 5.53; found C 85.63, H 5.32.

5-*exo*-(Hex-1-ynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4e): Yield: 199 mg (38%). ¹H NMR (200 MHz, CDCl₃): δ = 0.98 (t, J = 7.2 Hz, 3 H), 1.78–1.42 (m, 4 H), 2.03–2.18 (m, 2 H), 3.26 (dt, J = 8.6, 2.2 Hz, 1 H), 3.36 (d, J = 8.6 Hz, 1 H), 5.65 (s, 1 H), 5.67 (s, 1 H), 7.27–7.77 (m, 9 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (neat): 3060.9, 2929.7, 1603.0, 1459.3, 1377.2, 1263.6, 758.6, 700.0 cm⁻¹. HRMS: calcd. for C₂₂H₂₂O 302.1671; found 302.1671.

5-*exo*-(3-Methoxyprop-1-ynyl)-6-*exo*-phenyl-7-oxabenzonorbornene (4f): Yield: 382 mg (76%). ¹H NMR (200 MHz, CDCl₃): δ = 2.88 (s, 3 H), 3.00 (dt, J = 8.6, 1.6 Hz, 1 H), 3.08 (d, J = 8.6 Hz, 1 H), 3.68–3.72 (m, 2 H), 5.38 (s, 2 H), 7.08–7.32 (m, 9 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (neat): 3060.5, 2927.8, 1602.1, 1459.9, 1357.2, 1095.4, 750.3, 700.7 cm⁻¹. HRMS: calcd. for C₂₀H₁₈O₂ 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. ¹H NMR (200 MHz, CDCl₃): δ = 2.22 (s, 3 H), 3.08 (s, 2 H), 5.35 (s, 1 H), 5.41 (s, 1 H), 6.80–6.89 (m, 2 H), 6.96–7.26 (m, 11 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3011.5, 2936.1, 1596.1, 1461.5, 1194.0, 848.8, 759.2, 691.6 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O

336.1514; found 336.1517. C₂₅H₂₀O (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. ¹H NMR (200 MHz, CDCl₃): δ = 2.35 (s, 3 H), 3.22 (d, AB type, J = 8.6 Hz, 1 H), 3.26 (d, AB type J = 8.6 Hz, 1 H), 5.51 (s, 1 H), 5.57 (s, 1 H), 6.92–7.02 (m, 2 H), 7.05–7.41 (m, 11 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3048.5, 2927.8, 1597.1, 1459.7, 1153.0, 898.8, 758.4, 691.9 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O 336.1514; found 336.1513. C₂₅H₂₀O (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. ¹H NMR (200 MHz, CDCl₃): δ = 2.20 (s, 3 H), 3.33 (d, AB type, J = 8.5 Hz, 1 H), 3.39 (d, AB type, J = 8.5 Hz, 1 H), 5.58 (s, 1 H), 5.71 (s, 1 H), 6.78–6.91 (m, 2 H), 7.05–7.43 (m, 10 H), 7.68 (d, J = 7.6 Hz, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3021.0, 2915.5, 1598.9, 1487.6, 978.8, 900.2, 710.0 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O 336.1514; found 336.1511. C₂₅H₂₀O (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. ¹H NMR (200 MHz, CDCl₃): δ = 3.15 (s, 2 H), 3.73 (s, 3 H), 5.39 (s, 1 H), 5.48 (s, 1 H), 6.81 (d, J = 8.7 Hz, 2 H), 6.87–6.98 (m, 2 H), 7.04–7.34 (m, 7 H), 7.30 (d, J = 8.7 Hz, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3016.8, 2930.0, 1609.0, 1462.9, 1246.2, 846.7, 765.2, 695.6 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O₂ 352.1463; found 352.1463. C₂₅H₂₀O₂ (352.43): calcd. C 85.20, H 5.69.

5-*exo*-(2-Methoxyphenyl)-6-*exo*-(2-phenylethynyl)-7-oxabenzonorbornene (4k): Yield: 396 mg (65%), m.p. 127–129 °C. ¹H NMR (200 MHz, CDCl₃): δ = 3.31 (d, J = 8.5 Hz, 1 H), 3.69 (d, J = 8.5 Hz, 1 H), 3.74 (s, 3 H), 5.55 (s, 1 H), 5.64 (s, 1 H), 6.83–6.93 (m, 3 H), 7.00–7.43 (m, 9 H), 7.66 (d, J = 6.9 Hz, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3053.5, 2920.9, 1595.3, 1465.7, 1243.2, 751.9, 695.0 cm⁻¹. HRMS: calcd. for C₂₅H₂₀O₂ 352.1463; found 352.1461. C₂₅H₂₀O₂ (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. ¹H NMR (200 MHz, CDCl₃): δ = 2.60 (s, 3 H), 3.32 (s, 2 H), 5.53 (s, 1 H), 5.60 (s, 1 H), 6.89–6.96 (m, 2 H), 7.08–7.44 (m, 7 H), 7.56 (d, J = 8.2 Hz, 2 H), 7.95 (d, J = 8.2 Hz, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3002.5, 2931.4, 1671.2, 1606.0, 1488.8, 1272.6, 849.8, 757.4, 691.7 cm⁻¹. HRMS: calcd. for C₂₆H₂₀O₂ 364.1463; found 364.1465. C₂₆H₂₀O₂ (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. ¹H NMR (200 MHz, CDCl₃): δ = 3.35 (s, 2 H), 5.50 (s, 1 H), 5.61 (s, 1 H), 6.90–6.98 (m, 2 H), 7.11–7.44 (m, 7 H), 7.64 (d, *J* = 8.7 Hz, 2 H), 8.20 (d, *J* = 8.7 Hz, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3064.5, 1596.6, 1506.0, 1489.3, 1342.1, 847.3, 755.0, 691.9 cm⁻¹. HRMS: calcd. for C₂₄H₁₇NO₃ 367.1208; found 367.1205. C₂₄H₁₇NO₃ (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. ¹H NMR (200 MHz, CDCl₃): δ = 3.53 (d, *J* = 8.3 Hz, 1 H), 3.73 (d, *J* = 8.3 Hz, 1 H), 5.50 (s, 1 H), 5.60 (s, 1 H), 6.76–6.85 (m, 2 H), 6.99–7.39 (m, 8 H), 7.58 (t, *J* = 7.7 Hz, 1 H), 7.84 (dd, *J* = 8.1, 1.1 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3086.5, 1523.3, 1347.2, 1263.2, 755.6, 691.8 cm⁻¹. HRMS: calcd. for C₂₄H₁₇NO₃ 367.1208; found 367.1206. C₂₄H₁₇NO₃ (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-oxabenzonorbornene (4o): Yield: 322 mg (50%), m.p. 226–228 °C. ¹H NMR (200 MHz, CDCl₃): δ = 3.52 (d, *J* = 8.5 Hz, 1 H), 4.02 (d, *J* = 8.5 Hz, 1 H), 5.64 (s, 1 H), 5.87 (s, 1 H), 6.47–6.57 (m, 2 H), 6.94–7.08 (m, 3 H), 7.22–7.62 (m, 7 H), 7.76–7.95 (m, 4 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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, 2 C), 128.7 (d), 131.1 (d, 2 C), 132.8 (s), 133.5 (s), 137.0 (s), 145.3 (s), 146.1 (s) ppm. IR (KBr): 3043.8, 1596.8, 1459.6, 1153.7, 745.0, 689.1 cm⁻¹. HRMS: calcd. for C₂₈H₂₀O 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. ¹H NMR (200 MHz, CDCl₃): δ = 3.17 (d, *J* = 8.2 Hz, 1 H), 3.54 (d, *J* = 8.2 Hz, 1 H), 5.48 (s, 1 H), 5.51 (s, 1 H), 6.79–7.75 (m, 12 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3004.0, 1597.7, 1461.7, 1265.6, 760.4, 692.4 cm⁻¹. HRMS: calcd. for C₂₂H₁₆OS 328.0922; found 328.0921. C₂₂H₁₆OS (328.43): calcd. C 80.45, H 4.91, S 9.76; found C 80.22, H 4.66, S 10.08.

5-*exo*-(2-Phenylethynyl)-6-*exo*-(3-oxocyclohex-1-enyl)-7-oxabenzonorbornene (4q): Yield: 165 mg (28%), m.p. 179–180 °C. ¹H NMR (200 MHz, CDCl₃): δ = 1.91–2.08 (m, 2 H), 2.31–2.54 (m, 3 H), 2.60–2.75 (m, 1 H), 2.80 (d, *J* = 8.7 Hz, 1 H), 3.23 (d, *J* = 8.7 Hz, 1 H), 5.49 (s, 1 H), 5.53 (s, 1 H), 6.16 (s, 1 H), 7.17–7.43 (m, 9 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3084.7, 1665.8, 1598.3, 1490.5, 1460.8, 1256.3, 760.9, 692.5 cm⁻¹. HRMS: calcd. for C₂₄H₂₀O₂ 340.1463; found 340.1465. C₂₄H₂₀O₂ (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%). ¹H NMR (200 MHz, CDCl₃): δ = 1.32 (d, *J*

= 7.2 Hz, 3 H), 1.92–2.07 (m, 1 H), 2.80 (d, *J* = 8.1 Hz, 2 H), 4.92 (s, 1 H), 5.34 (s, 1 H), 7.04–7.24 (m, 6 H), 7.32–7.40 (m, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (neat): 3046.1, 2925.6, 1598.1, 1461.8, 1377.5, 1153.8, 752.8, 691.3 cm⁻¹. HRMS: calcd. for C₁₉H₁₆O 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. ¹H NMR (200 MHz, CDCl₃): δ = 3.16 (s, 2 H), 5.60 (s, 2 H), 7.18–7.30 (m, 8 H), 7.30–7.38 (m, 2 H), 7.38–7.75 (m, 4 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3059.1, 1597.6, 1490.1, 1227.9, 758.1, 691.6 cm⁻¹. HRMS: calcd. for C₂₆H₁₈O 346.1358; found 346.1359. C₂₆H₁₈O (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. ¹H NMR (200 MHz, CDCl₃): δ = 3.21 (s, 2 H), 3.88 (s, 3 H), 3.90 (s, 3 H), 5.47 (s, 1 H), 5.52 (s, 1 H), 6.89–7.01 (m, 4 H), 7.11–7.49 (m, 8 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3062.0, 2998.8, 1597.8, 1490.5, 1307.7, 1218.9, 1090.3, 757.5, 693.4 cm⁻¹. HRMS: calcd. for C₂₆H₂₂O₃ 382.1569; found 382.1570. C₂₆H₂₂O₃ (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. ¹H NMR (200 MHz, CDCl₃): δ = 3.20 (s, 2 H), 6.05 (s, 1 H), 6.08 (s, 1 H), 6.89–6.98 (m, 2 H), 7.07–7.16 (m, 3 H), 7.24–7.38 (m, 4 H), 7.42–7.50 (m, 2 H), 7.56–7.69 (m, 4 H), 7.81–7.88 (m, 1 H), 7.96–8.06 (m, 1 H), 8.65–8.75 (m, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): 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) ppm. IR (KBr): 3034.0, 1592.1, 1488.1, 1213.9, 752.4, 693.7 cm⁻¹. HRMS: calcd. for C₃₂H₂₂O 422.1671; found 422.1670. C₃₂H₂₂O (422.52): calcd. C 90.97, H 5.25; found C 90.67, H 5.13.

General Procedure for the Deoxyaromatization Reaction: In a typical procedure, a round-bottom flask containing compound **4** (0.55 mmol) was purged with nitrogen three times. To the flask was added sequentially CH₂Cl₂ (5 mL) and BF₃·OEt₂ (1.10 mmol). The solution was then stirred at room temperature for 1 h. After filtration through Celite, the filtrate was concentrated and then separated on a silica gel column (hexane/ethyl acetate) to give desired product **5**.

5-Phenyltetraphene (5a): Yield: 100 mg (60%), m.p. 133–135 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.41–7.62 (m, 8 H), 7.68 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.73 (s, 1 H), 7.87 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.99–8.19 (m, 2 H), 8.36 (s, 1 H), 8.92 (d, *J* = 8.0 Hz, 1 H), 9.20 (s, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 121.4 (d), 123.2 (d), 125.7 (d), 125.8 (d), 126.7 (d), 126.8 (d), 126.9 (d), 127.1 (d), 127.4 (d), 127.7 (d), 127.9 (d), 128.3 (d, 2 C), 128.5 (d), 128.6 (s), 129.9 (d, 2 C), 130.2 (s), 130.9 (s), 131.4 (s), 131.9 (s), 132.2 (s), 138.7 (s), 140.7 (s) ppm. IR (KBr): 3053.5, 1601.2, 1471.2, 903.1, 741.7, 700.5 cm⁻¹. HRMS: calcd. for C₂₄H₁₆ 304.1252; found 304.1249. C₂₄H₁₆ (304.38): calcd. C 94.70, H 5.30; found C 94.78, H 5.30.

3-Methyl-5-phenyltetraphene (5b): Yield: 137 mg (78%), m.p. 160–161 °C. ¹H NMR (200 MHz, CDCl₃): δ = 2.41 (s, 3 H), 7.35–7.60 (m, 9 H), 7.63 (s, 1 H), 7.92–8.11 (m, 2 H), 8.27 (s, 1 H), 8.74 (d, *J* = 8.4 Hz, 1 H), 9.08 (s, 1 H) ppm. ¹³C NMR (50 MHz, [D₈]-THF): δ = 21.8 (q), 122.1 (d), 124.4 (d), 126.5 (d, 2 C), 127.7 (d), 127.7 (d), 128.3 (d), 128.6 (d), 128.8 (d), 129.1 (d), 129.3 (d, 2 C), 129.4 (d), 129.9 (s), 130.9 (d, 2 C), 131.2 (s), 132.5 (s), 133.3 (s), 133.4 (s), 137.6 (s), 139.8 (s), 142.1 (s) ppm. IR (KBr): 3051.9, 2945.8, 1620.2, 1467.2, 902.1, 739.9, 700.6 cm⁻¹. HRMS: calcd. for C₂₅H₁₈ 318.1409; found 318.1410.

3-Methoxy-5-phenyltetraphene (5c): Yield: 153 mg (83%), m.p. 133–134 °C. ¹H NMR (200 MHz, CDCl₃): δ = 3.81 (s, 3 H), 7.26–7.35 (m, 2 H), 7.44–7.63 (m, 7 H), 7.72 (s, 1 H), 7.98–8.15 (m, 2 H), 8.33 (s, 1 H), 8.82 (d, *J* = 9.7 Hz, 1 H), 9.07 (s, 1 H) ppm. ¹³C NMR (50 MHz, [D₈]-THF): δ = 55.5 (q), 109.9 (d), 116.4 (d), 121.5 (d), 125.9 (d, 2 C), 126.2 (d), 126.5 (d), 127.8 (d), 128.4 (d), 128.6 (d), 129.2 (d), 129.4 (d, 2 C), 123.0 (s), 130.7 (d, 2 C), 132.9 (s), 133.5 (s), 133.8 (s), 139.5 (s), 142.0 (s), 160.0 (s) ppm. IR (KBr): 3053.6, 2924.1, 1609.1, 1463.7, 1219.1, 741.7, 701.0 cm⁻¹. HRMS: calcd. for C₂₅H₁₈O 334.1358; found 334.1356. C₂₅H₁₈O (334.41): calcd. C 89.79, H 5.43; found C 89.60, H 5.23.

1-(5-Phenyltetraphen-3-yl)ethanone (5d): Yield: 124 mg (65%), m.p. 131–132 °C. ¹H NMR (200 MHz, CDCl₃): δ = 2.61 (s, 3 H), 7.38–7.62 (m, 7 H), 7.73 (s, 1 H), 7.92–8.13 (m, 2 H), 8.36 (dd, *J* = 8.6, 1.9 Hz, 1 H), 8.40 (s, 1 H), 8.46–8.52 (m, 1 H), 8.98 (d, *J* = 8.6 Hz, 1 H), 9.24 (s, 1 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 26.6 (q), 122.6 (d), 123.6 (d), 125.4 (d), 126.0 (d), 126.5 (d), 127.1 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.5 (d, 2 C), 128.7 (d, 2 C), 129.8 (d, 2 C), 130.5 (s), 131.0 (s), 132.0 (s), 132.7 (s), 134.4 (s), 135.1 (s), 138.6 (s), 140.0 (s), 198.0 (s) ppm. IR (KBr): 3095.4, 2924.6, 1673.8, 1624.5, 1493.6, 1372.4, 742.6, 699.4 cm⁻¹. HRMS: calcd. for C₂₆H₁₈O 346.1358; found 346.1359. C₂₆H₁₈O (346.42): calcd. C 90.14, H 5.24; found C 90.02, H 5.25.

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