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Synthesis of Triphenylene Derivatives by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition: Application to the Synthesis of Highly Fluorescent Triphenylene-Based Long Ladder Molecules

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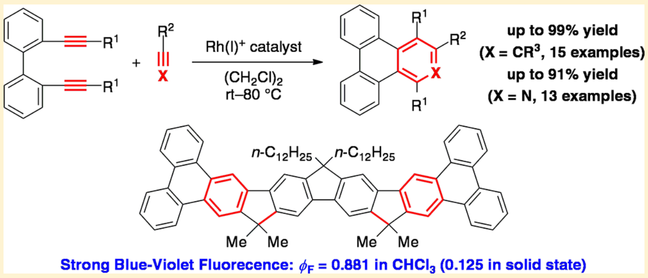
Supporting Information

ABSTRACT: The convenient synthesis of substituted triphenylenes and azatriphenylenes has been achieved by the cationic rhodium(I)/H_8-BINAP or BINAP complex-catalyzed [2 + 2 + 2] cycloaddition under mild conditions. Photophysical properties of representative triphenylenes and azatriphenylenes were examined, which revealed that azatriphenylenes showed higher fluorescence quantum yields than triphenylenes. This method was successfully applied to the synthesis of highly fluorescent triphenylene-based long ladder molecules.



INTRODUCTION

Triphenylene derivatives have attracted much attention in supramolecular and materials chemistry because of their rigid, planar, and conjugated structures and also their self-assembling character.[1] For example, triphenylenes possessing long aliphatic side chains form discotic liquid crystals as a result of their self-assembly.[2] Numbers of substituted triphenylenes have been synthesized, and their physical properties have been investigated to date,[1,2] while synthetic methods[3,4] of substituted azatriphenylenes have not been well investigated and no report has been published for their physical properties. As the transition-metal-catalyzed synthesis of substituted triphenylenes, the homo-[2 + 2 + 2] cycloaddition of three benzynes leading to symmetrically substituted triphenylenes has been reported.[5] For the transition-metal-catalyzed synthesis of unsymmetrically substituted triphenylenes, the Deiters group reported the [2 + 2 + 2] cycloaddition of a biaryl-linked diyne with alkynes using a nickel catalyst.[4] Importantly, this method could be applied to the synthesis of substituted azatriphenylenes by using a cobalt catalyst.[4] However, these reactions employed high reaction temperatures under microwave irradiation. On the other hand, our research group reported that the cationic rhodium(I)/H_8-BINAP or BINAP complex is able to catalyze the [2 + 2 + 2] cycloadditions[6,7] of 1,7-octadiyne derivatives with alkynes,[8,9] nitriles,[10,11] and isocyanates[12,13] leading to 6–6 fused carbocycles and heterocycles under mild conditions despite the absence of the Thorpe–Ingold effect[14] (Scheme 1).

These results prompted our investigation into the [2 + 2 + 2] cycloadditions of biaryl-linked diynes with alkynes, nitriles, and isocyanates leading to substituted triphenylenes and azatriphenylenes by using the cationic rhodium(I)/H_8-BINAP or BINAP complex as a catalyst (Scheme 2). Recently, our research group reported the rhodium-catalyzed enantioselective synthesis and photophysical properties of helically chiral 1,1′-bitriphenylenes.[15] In this paper, we disclose the rhodium-catalyzed synthesis and photophysical properties of substituted azatriphenylenes, as well as triphenylenes. The application of this method to the synthesis of highly fluorescent triphenylene-based long ladder molecules is also disclosed.

RESULTS AND DISCUSSION

We first examined the substituted triphenylene synthesis, as shown in Table 1. Pleasingly, the reaction of biaryl-linked terminal diyne **1a** and ethyl 2-butynoate (**2a**, 1.1 equiv) proceeded in the presence of the cationic rhodium(I)/H_8-BINAP complex (5 mol %) at room temperature to give the corresponding triphenylene **3aa** in high yield. The use of BINAP in place of H_8-BINAP afforded **3aa** in lower yield. Various electron-deficient unsymmetrical internal alkynes **2b–f** were able to react with **1a** to give the corresponding triphenylenes in good to high yields. Electron-rich propargyl alcohols **2g,h** were also suitable substrates for this process. For highly electron-deficient internal alkyne **2i** and terminal alkyne **2j**,[16] excess alkynes (2 equiv) were employed due to consumption of these alkynes by the undesired homo-[2 + 2 + 2] cycloaddition. In the case of **2i**, the use of BINAP in place of H_8-BINAP improved the product yield. Biaryl-linked internal diyne **1b** was also a suitable substrate for this process. Diyne **1b**

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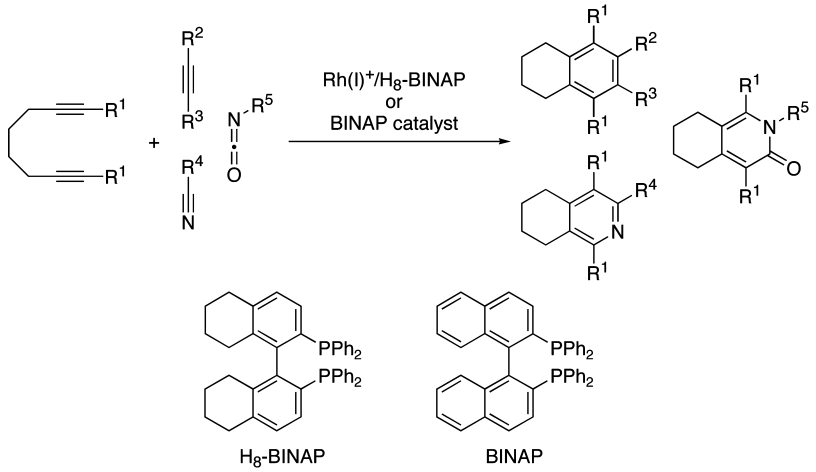
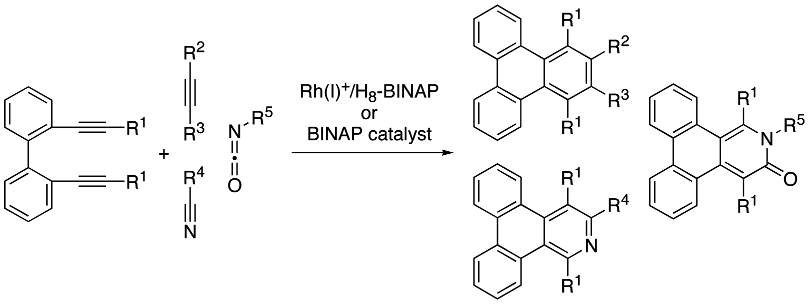
Scheme 1. Rhodium-Catalyzed [2 + 2 + 2] Cycloadditions of 1,7-Octadiyne Derivatives with Alkynes, Nitriles, and Isocyanates



Scheme 2. Rhodium-Catalyzed [2 + 2 + 2] Cycloadditions of Biaryl-Linked Diynes with Alkynes, Nitriles, and Isocyanates



reacted with both electron-deficient and -rich internal alkynes **2a**,**g** to give the corresponding triphenylenes in high yields.

We next examined the substituted azatriphenylene synthesis, as shown in Table 2. The reaction of the terminal diyne **1a** and acetonitrile (**4a**) proceeded at room temperature in the presence of the cationic rhodium(I)/BINAP complex (5 mol %) to give the corresponding azatriphenylene **5aa** in good yield. Both primary and secondary aliphatic nitriles **4b**,**c** could also participate in this reaction. Not only aliphatic nitriles but also aromatic nitriles **4d**−**g**[16] reacted with **1a** at room temperature to give the corresponding conjugated azatriphenylenes in good yields. Diyne **1a** selectively reacted with the cyano group of acrylonitrile (**4h**) to give vinylazatriphenylene **5ah** in high yield.[10] Although elevated reaction temperature (80 °C) was required, the reactions of activated nitriles **4i**−**k** and **1a** proceeded to give the corresponding azatriphenylenes in moderate to good yields. The internal diyne **1b** also reacted with **4d** and **4i** at 80 °C to give the corresponding azatriphenylenes **5bd** and **5bi** in moderate to high yields. Because the reactivity of nitriles **4** was lower than that of alkynes **2**, the yields of azatriphenylenes **5** were generally lower compared to triphenylenes **3**, and as a result, excess nitriles (5 equiv) were used in some cases.

Not only nitriles but also *n*-butylisocyanate (**6**) could be employed, as shown in Scheme 3. The internal diyne **1b** reacted with **6** in the presence of the cationic rhodium(I)/H_8-BINAP catalyst at room temperature to give the corresponding azatriphenylene **7b** in excellent yield.[17]

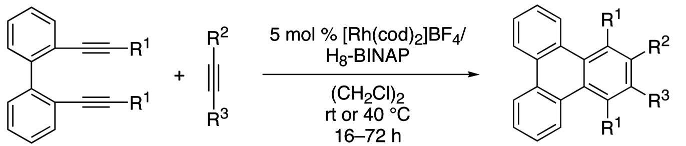
Absorption and emission data of representative triphenylenes and azatriphenylenes in $CHCl_3$ are shown in Table 3. Azatriphenylenes **5** and **7b** showed red shifts of absorption and emission maxima compared with triphenylenes **3**. Ethoxycarbonyl or diethoxyphosphinyl-substituted triphenylenes **3ad**, **3af**, and **3ai** showed higher fluorescence quantum yields (9.7−12.4%) than triphenylene-methanols **3ag** and **3ah** (2.9−3.0%), and that of diethoxyphosphinyl-substituted triphenylenes **3af** was the highest (12.4%).[18] In general, azatriphenylenes **5** showed higher fluorescence quantum yields (11.7−30.6%) than triphenylenes **3** (2.9−12.4%) and azatriphenylene **7b** (5.5%). Especially, π-extended 4-methoxyphenyl- and 4-cyanophenyl-substituted azatriphenylenes **5af** and **5ag** showed promising high fluorescence quantum yields (23.0 and 30.6%, respectively).

The present rhodium-catalyzed [2 + 2 + 2] cycloaddition of biaryl-linked diynes with alkynes was successfully applied to the synthesis of triphenylene-based ladder molecules. The reaction of the terminal diyne **1a** with phenyl-substituted propargyl alcohol **2k** in the presence of the cationic rhodium(I)/H_8-BINAP catalyst at room temperature afforded triphenylene **3ak**. Subsequent dehydration afforded triphenylene **8ak**, containing a fluorene skeleton, in good yield (Scheme 4). The rhodium-catalyzed double [2 + 2 + 2] cycloaddition of **1a** with benzene-linked bispropargyl alcohol **2l** followed by dehydration afforded triphenylene-based ladder molecule **8al**[19] in good yield (Scheme 5).

Longer ladder molecule **8am**[19,20] was also synthesized in good yield by the rhodium-catalyzed double [2 + 2 + 2] cycloaddition of **1a** with fluorene-linked bispropargyl alcohol **2m** followed by dehydration (Scheme 6).

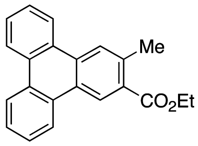
Single-crystal X-ray analyses of these ladder molecules **8al** and **8am** showed that the conjugated triphenylene-fluorene cores are almost flat as shown in the Supporting Information

Table 1. Synthesis of Triphenylenes by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition[a]

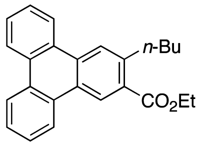


1a (R^1 = H)
1b (R^1 = Me)

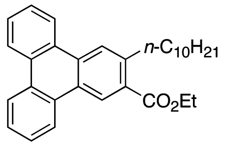
2a (R^2 = Me, R^3 = CO_2Et)
2b (R^2 = *n*-Bu, R^3 = CO_2Et)
2c (R^2 = *n*-$C_{10}H_{21}$, R^3 = CO_2Et)
2d (R^2 = Ph, R^3 = CO_2Et)
2e (R^2 = Ph, R^3 = Ac)
2f [R^2 = Ph, R^3 = $P(O)(OEt)_2$]
2g (R^2 = Ph, R^3 = CH_2OH)
2h (R^2 = $SiMe_3$, R^3 = CH_2OH)
2i (R^2 = R^3 = CO_2Et)
2j (R^2 = *n*-$C_{10}H_{21}$, R^3 = H)



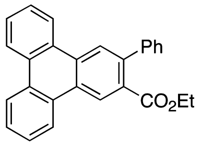
3aa / 89% yield
(**2a**: 1.1 equiv, rt, 16 h)
76% yield
(**2a**: 1.1 equiv, BINAP, rt, 16 h)



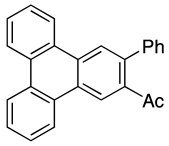
3ab / 87% yield
(**2b**: 1.1 equiv, rt, 16 h)



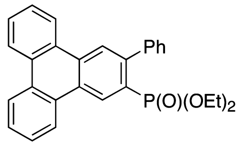
3ac / 89% yield
(**2c**: 1.1 equiv, rt, 16 h)



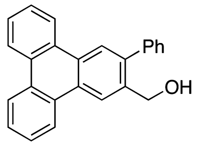
3ad / 94% yield
(**2d**: 1.1 equiv, rt, 16 h)



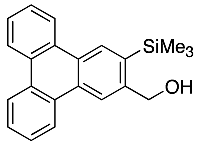
3ae / 74% yield
(**2e**: 1.1 equiv, rt, 16 h)



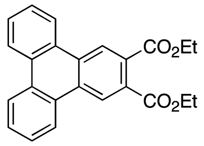
3af / 64% yield
(**2f**: 1.1 equiv, rt, 16 h)



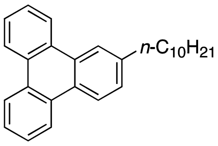
3ag / 94% yield
(**2g**: 1.1 equiv, rt, 16 h)



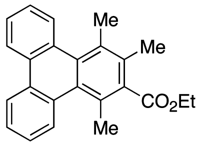
3ah / 93% yield
(**2h**: 1.1 equiv, rt, 16 h)



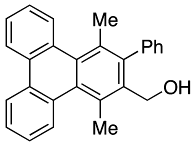
3ai / 76% yield
(**2i**: 2 equiv, BINAP, 40 °C, 16 h)



3aj / 73% yield
(**2j**: 2 equiv, rt, 16 h)



3ba / 99% yield
(**2a**: 1.1 equiv, rt, 16 h)



3bg / 89% yield
(**2g**: 1.1 equiv, rt, 72 h)

[a] $[Rh(cod)_2]BF_4$ (0.0050 mmol), H_8-BINAP or BINAP (0.0050 mmol), **1** (0.10 mmol), **2** (0.11−0.20 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. Cited yields are of isolated products.

(Figures S-7 and S-8, top). Ladder molecule **8al** is stacked along the *b*-axis with a mean interplanar distance of 3.51 Å (Figure S-7, bottom). On the other hand, ladder molecule **8am** is cocrystallized with *n*-hexane and stacked along the *a*-axis with a mean interplanar distance of 3.28 Å (Figure S-8, bottom).

Absorption and emission data of these triphenylene-based π-conjugated molecules in $CHCl_3$ are shown in Table 4. As expected, longer π-conjugated molecules showed larger red shifts of absorption and emission maxima. The fluorescence quantum yields of **8al** and **8am** are very high in $CHCl_3$: 88.1% for **8al** and 84.6% for **8am**. Importantly, **8al** and **8am** also emit in the solid state. The fluorescence quantum yields are 9.2% for **8al** and 12.5% for **8am**.

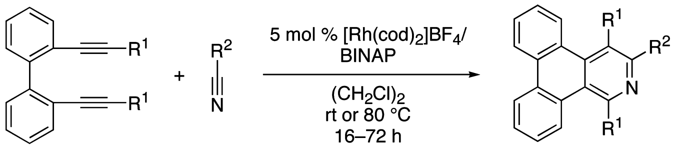
■ CONCLUSION

In conclusion, we have achieved the convenient synthesis of substituted triphenylenes and azatriphenylenes by the cationic rhodium(I)/H_8-BINAP or BINAP complex-catalyzed [2 + 2 + 2] cycloaddition under mild conditions. Photophysical properties of representative triphenylenes and azatriphenylenes were examined, which revealed that azatriphenylenes showed higher fluorescence quantum yields than triphenylenes. This method was successfully applied to the synthesis of highly fluorescent triphenylene-based long ladder molecules.

■ EXPERIMENTAL SECTION

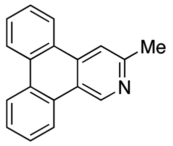
General. Anhydrous CH_2Cl_2 (No. 27,099-7) and $(CH_2Cl)_2$ (No. 28,450-5) were obtained from Sigma-Aldrich and used as received. Solvents for the synthesis of substrates were dried over molecular sieves 4 Å (Wako) prior to use. H_8-BINAP was obtained from Takasago International Corporation. Diynes (**1a**,[21,22] **1b**,[23] and **2m**[24]) and monoynes (**2c**[25] and **2k**[26]) were prepared according to the literature. All other reagents were obtained from commercial sources

Table 2. Synthesis of Azatriphenylenes by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition[a]

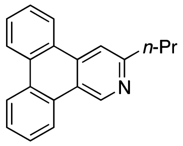


1a (R^1 = H)
1b (R^1 = Me)

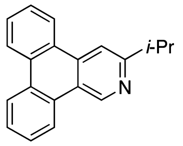
4a (R = Me)
4b (R = *n*-Pr)
4c (R = *i*-Pr)
4d (R = Ph)
4e (R = 4-$F_3CC_6H_4$)
4f (R = 4-$MeOC_6H_4$)
4g (R = 4-NCC_6H_4)
4h (R = CH=CH_2)
4i (R = CO_2Et)
4j (R = CH_2CN)
4k (R = Bz)



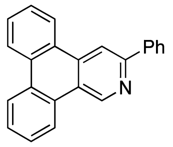
5aa / 61% yield
(**4a**: 5 equiv, rt, 40 h)



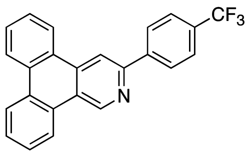
5ab / 73% yield
(**4b**: 5 equiv, rt, 40 h)



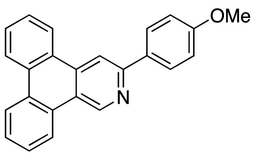
5ac / 71% yield
(**4c**: 5 equiv, rt, 40 h)



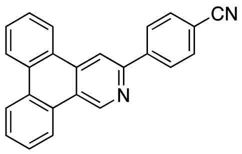
5ad / 58% yield
(**4d**: 1.1 equiv, rt, 40 h)



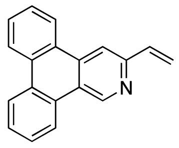
5ae / 76% yield
(**4e**: 1.1 equiv, rt, 40 h)



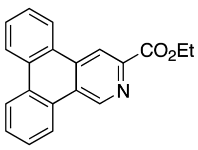
5af / 66% yield
(**4f**: 1.1 equiv, rt, 40 h)



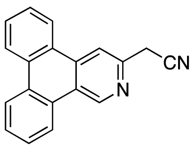
5ag / 58% yield
(**4g**: 1.1 equiv, rt, 40 h)



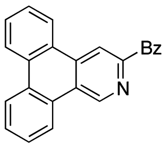
5ah / 86% yield
(**4h**: 5 equiv, rt, 72 h)



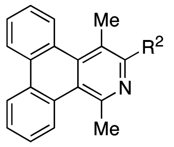
5ai / 65% yield
(**4i**: 1.1 equiv, 80 °C, 40 h)
86% yield
(**4i**: 5 equiv, 80 °C, 65 h)



5aj / 88% yield[b]
(**4j**: 5 equiv, 80 °C, 16 h)



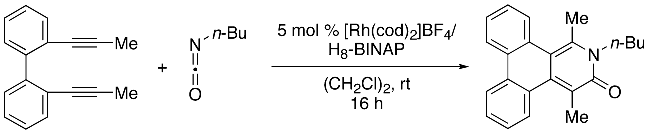
5ak / 40% yield[b,c]
(**4k**: 1.1 equiv, 80 °C, 72 h)



5bd / 52% yield[b,d]
(**4d**, R^2 = Ph: 1.1 equiv, 80 °C, 72 h)
5bi / 91% yield
(**4i**, R^2 = CO_2Et: 2 equiv, 80 °C, 16 h)

[a] $[Rh(cod)_2]BF_4$ (0.0050 mmol), BINAP (0.0050 mmol), **1** (0.10 mmol), **4** (0.11–0.50 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. Cited yields are of isolated products. [b] Catalyst: 10 mol %. [c] Conv of **1a** ≈ 85%. [d] Conv of **1b** ≈ 85%.

Scheme 3. Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Biaryl-Linked Internal Diyne 1b with Isocyanate 6



1b **6** (2 equiv) **7b** / 92%

and used as received. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

*5-[4-(3-Butyl-3-hydroxyhept-1-ynyl)phenylethynyl]nonan-5-ol (**2l**).* To a stirred solution of $PdCl_2(PPh_3)_2$ (8.6 mg, 0.012 mmol) and CuI (9.3 mg, 0.049 mmol) in di-isopropylamine (30 mL) and toluene (10 mL) were added 1,4-diiodobenzene (0.402 g, 1.22 mmol) and 5-ethynyl-5-nonanol (0.430 g, 2.56 mmol). The resulting mixture was stirred at 60 °C for 4 h. The reaction mixture was filtered and concentrated. The crude product was purified by a silica gel column chromatography (hexane/EtOAc = 10:1) to give **2l** (0.329 g, 0.800 mmol, 66% yield). Pale orange solid, mp 52.6−54.4 °C; IR (KBr) 3347, 3077, 2963, 2861, 1507, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.35 (s, 4H), 1.95 (s, 2H), 1.80−1.66 (m, 8H), 1.62−1.47 (m, 8H), 1.38 (sext, J = 7.2 Hz, 8H), 0.95 (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 131.5, 122.7, 94.0, 83.9, 71.7, 41.8, 26.5, 22.9, 14.1; HRMS (ESI-TOF) calcd for $C_{28}H_{42}O_2Na$ $[M + Na]^+$ 433.3077, found 433.3071.

General Procedure for Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition. H_8-BINAP or BINAP (0.0050 mmol) and $[Rh(cod)_2]BF_4$ (0.0050 mmol) were dissolved in CH_2Cl_2, and the mixture

Table 3. Photophysical Properties of Representative Triphenylenes and azatriphenylenes[a]

entry	compound	UV absorption λ_{max} (nm)	fluorescence λ_{max} (nm)	ϕ_F
1	**3ad**	270	384	0.099
2	**3af**	267	359, 375	0.124
3	**3ag**	266	369	0.030
4	**3ah**	266	368	0.029
5	**3ai**	269	365, 381	0.097
6	**5ad**	274	361, 379	0.176
7	**5ae**	274	360, 378	0.193
8	**5af**	259, 279	377, 387	0.230
9	**5ag**	277	363, 381	0.306
10	**5ai**	267	358, 375	0.117
11	**7b**	278, 288	498	0.055

[a]Measured in $CHCl_3$ at 25 °C.

was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After being stirred at room temperature for 1 h, the resulting solution was concentrated to dryness. The residue was redissolved in $(CH_2Cl)_2$ (0.5 mL), and a $(CH_2Cl)_2$ (0.5 mL) solution of **2**, **4**, or **6** (0.110−0.500 mmol) was added. A $(CH_2Cl)_2$ (1.0 mL) solution of **1** (0.100 mmol) was added dropwise to this solution, and the mixture was stirred at rt−80 °C for 16−72 h. The resulting solution was concentrated and purified by a preparative TLC, which furnished **3**, **5**, or **7**.

*3-Methyltriphenylene-2-carboxylic Acid Ethyl Ester (**3aa**):* Colorless solid, mp 118.3−119.1 °C, H_8-BINAP 28.1 mg (89%), BINAP 24.0 mg (76%); IR (KBr) 3074, 2973, 1710, 1271, 1095, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.13 (s, 1H), 8.66−8.47 (m, 4H), 8.32 (s, 1H), 7.72−7.54 (m, 4H), 4.49 (q, J = 7.2 Hz, 2H), 2.80 (s, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 137.7, 132.1, 130.6, 129.4, 129.3, 128.6, 128.5, 127.9, 127.30, 127.25, 127.2, 126.3, 125.9, 123.7, 123.3, 123.2, 123.1, 60.9, 22.3, 14.5; HRMS (ESI-TOF) calcd for $C_{22}H_{18}O_2Na$ [M + Na]$^+$ 337.1199, found 337.1194.

*3-Butyltriphenylene-2-carboxylic Acid Ethyl Ester (**3ab**):* Colorless solid, mp 85.0−85.9 °C, 30.9 mg (87%); IR (KBr) 3078, 2952, 1719, 1269, 1086, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.15 (s, 1H), 8.69−8.55 (m, 4H), 8.42 (s, 1H), 7.72−7.59 (m, 4H), 4.50 (q, J = 7.2 Hz, 2H), 3.20 (t, J = 7.8 Hz, 2H), 1.81−1.67 (m, 2H), 1.58−1.42 (m, 5H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 142.3, 132.1, 130.6, 129.5, 129.4, 128.8, 128.7, 127.9, 127.4, 127.3, 127.22, 127.20, 126.5, 125.3, 123.7, 123.3, 123.2, 61.0, 34.8, 34.2, 22.9, 14.4, 14.1; HRMS (ESI-TOF) calcd for $C_{25}H_{24}O_2Na$ [M + Na]$^+$ 379.1669, found 379.1674.

*3-Decyltriphenylene-2-Carboxylic Acid Ethyl Ester (**3ac**).* Colorless solid, mp 80.5−81.4 °C, 39.4 mg (89%); IR (KBr) 3078, 2923, 1721, 1271, 1091, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.16 (s, 1H), 8.69−8.56 (m, 4H), 8.43 (s, 1H), 7.72−7.60 (m, 4H), 4.50 (q, J = 7.2 Hz, 2H), 3.19 (t, J = 7.8 Hz, 2H), 1.80−1.67 (m, 2H), 1.56−1.18 (m, 17H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 142.3, 132.1, 130.7, 129.5, 129.4, 128.8, 128.7, 128.0, 127.4, 127.3, 127.23, 127.21, 126.5, 125.3, 123.7, 123.3, 123.2, 61.0, 35.1, 32.1, 31.9, 29.9, 29.7, 29.63, 29.62, 29.3, 22.7, 14.4, 14.1; HRMS (ESI-TOF) calcd for $C_{31}H_{36}O_2Na$ [M + Na]$^+$ 463.2608, found 463.2611.

*3-Phenyltriphenylene-2-carboxylic Acid Ethyl Ester (**3ad**):* Colorless solid, mp 156.0−157.9 °C, 35.3 mg (94%); IR (KBr) 3088, 2980, 2935, 1953, 1709, 1249 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.14 (s, 1H), 8.79−8.47 (m, 5H), 7.81−7.56 (m, 4H), 7.56−7.34 (m, 5H), 4.22 (q, J = 6.9 Hz, 2H), 1.09 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.7, 141.8, 140.5, 131.7, 130.6, 129.8, 129.7, 129.1, 128.8, 128.7, 128.4, 128.1, 128.0, 127.6, 127.5, 127.3, 127.2, 125.8, 125.6, 123.8, 123.5, 123.4, 123.3, 61.1, 13.7; HRMS (ESI-TOF) calcd for $C_{27}H_{20}O_2Na$ [M + Na]$^+$ 399.1356, found 399.1356.

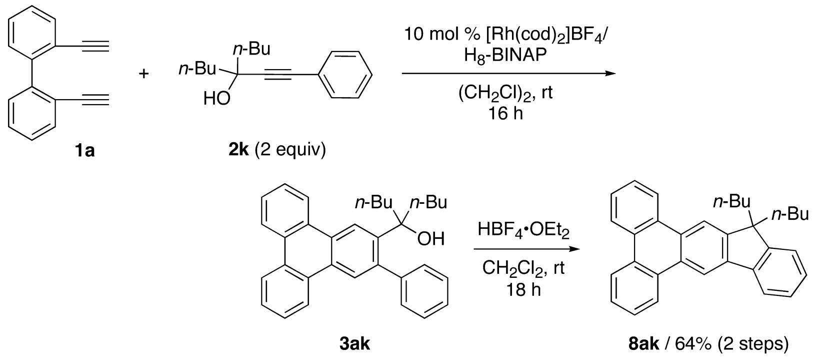
*1-(3-Phenyltriphenylen-2-yl)ethanone (**3ae**):* Colorless solid, mp 200.2−201.9 °C, 25.5 mg (74%); IR (KBr) 3070, 3031, 2925, 1959, 1678, 761 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.85 (s, 1H), 8.74−8.56 (m, 4H), 8.59 (s, 1H), 7.75−7.60 (m, 4H), 7.59−7.43 (m, 5H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.5, 141.0, 139.4, 138.9, 131.4, 130.6, 129.9, 129.2, 129.1, 128.9, 128.8, 128.6, 128.1, 128.0, 127.7, 127.5, 127.4, 125.3, 123.8, 123.7, 123.5, 123.4, 123.3, 30.6; HRMS (ESI-TOF) calcd for $C_{26}H_{18}ONa$ [M + Na]$^+$ 369.1250, found 369.1256.

*(3-Phenyltriphenylen-2-yl)phosphonic Acid Diethyl Ester (**3af**):* Colorless solid, mp 206.8−209.0 °C, 28.3 mg (64%); IR (KBr) 3073, 2980, 2864, 1599, 1242, 1032 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.40 (d, J = 16.0 Hz, 1H), 8.84−8.75 (m, 1H), 8.70−8.63 (m, 2H), 8.62 (d, J = 8.5 Hz, 1H), 8.56 (d, J = 5.0 Hz, 1H), 7.76−7.67 (m, 3H), 7.66−7.56 (m, 3H), 7.52−7.42 (m, 3H), 4.09−3.89 (m, 4H), 1.20 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.44, 143.37, 141.61, 141.58, 132.21, 132.18, 130.9, 130.5, 130.4, 129.8, 129.6, 129.0, 128.7, 128.3, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 126.2, 126.1, 124.7, 123.8, 123.6, 123.4, 123.3, 61.95, 61.90, 16.14, 16.08; ^{31}P NMR ($CDCl_3$, 202 MHz) δ 19.2; HRMS (ESI-TOF) calcd for $C_{28}H_{25}O_3PNa$ [M + Na]$^+$ 463.1434, found 463.1435.

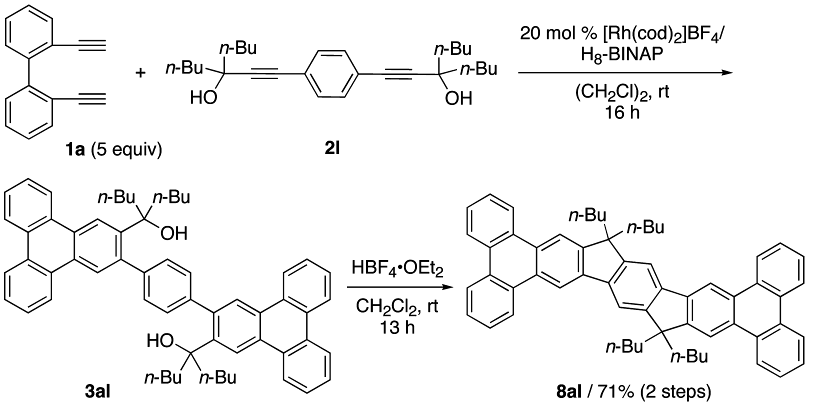
*(3-Phenyltriphenylen-2-yl)methanol (**3ag**):* Colorless solid, mp 195.9−197.2 °C, 31.6 mg (94%); IR (KBr) 3339, 3052, 2927, 2242, 1601, 1438 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.82 (s, 1H), 8.77−8.71 (m, 1H), 8.70−8.64 (m, 2H), 8.62 (d, J = 8.0 Hz, 1H), 8.52 (s, 1H), 7.76−7.59 (m, 4H), 7.57−7.43 (m, 5H), 4.87 (s, 2H), 1.79 (br, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.7, 140.2, 137.2, 130.0, 129.8, 129.47, 129.46, 129.3, 129.1, 129.0, 128.4, 127.5, 127.3, 127.2, 124.9, 123.44, 123.36, 123.3, 122.9, 63.6; HRMS (ESI-TOF) calcd for $C_{25}H_{18}ONa$ [M + Na]$^+$ 357.1250, found 357.1255.

*(3-Trimethylsilanyltriphenylen-2-yl)methanol (**3ah**):* Colorless solid, mp 151.7−152.3 °C, 30.6 mg (93%); IR (KBr) 3276, 3085, 2941, 1606, 1245, 839 cm^{-1};^1H NMR ($CDCl_3$, 300 MHz) δ 8.81 (s, 1H), 8.76−8.54 (m, 5H), 7.73−7.58 (m, 4H), 5.02 (s, 2H), 1.93 (br, 1H), 0.50 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.5, 136.6, 130.3, 130.2, 130.0, 129.7, 129.6, 129.4, 127.8, 127.4, 127.2, 127.1,

Scheme 4. Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Biaryl-Linked Terminal Diyne 1a with Phenyl-Substituted Propargyl Alcohol 2k



Scheme 5. Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Biaryl-Linked Terminal Diyne 1a with Phenyl-Substituted Bispropargyl Alcohol 2l



Scheme 6. Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Biaryl-Linked Terminal Diyne 1a with Fluorene-Substituted Bispropargyl Alcohol 2m

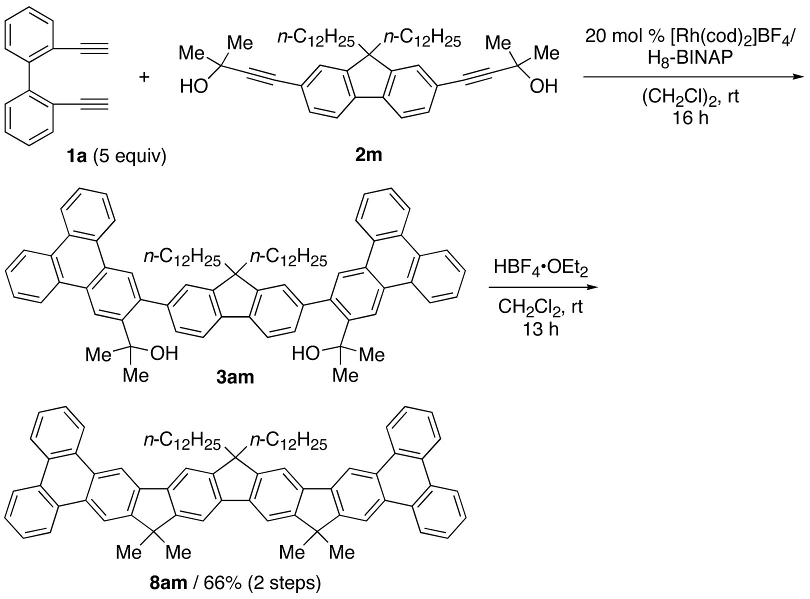


Table 4. Photophysical Properties of Triphenylene-Based π-Conjugated Molecules[a]

entry	compound	UV absorption λ_{max} (nm)	fluorescence λ_{max} (nm)	ϕ_F
1	**8ak**	278	362, 381	0.265
2	**8al**	392	396, 419	0.859 (0.092[b])
3	**8am**	407	412, 437	0.881 (0.125[b])

[a]Measured in $CHCl_3$ at 25 °C. [b]Fluorescence quantum yields in the solid state.

127.0, 123.35, 123.27, 123.2, 123.0, 121.6, 65.6, 0.4; HRMS (ESI-TOF) calcd for $C_{22}H_{22}OSiNa$ $[M + Na]^+$ 353.1332, found 353.1342.

*Triphenylene-2,3-dicarboxylic Acid Diethyl Ester (**3ai**):* A $(CH_2Cl)_2$ solution of **1a** and **2i** was added dropwise to a $(CH_2Cl)_2$ solution of the Rh catalyst. Colorless solid, mp 106.9−108.4 °C, 28.3 mg (76%); IR (KBr) 3081, 2980, 2937, 2904, 1721, 1251 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.97 (s, 2H), 8.75−8.57 (m, 4H), 7.79−7.63 (m, 4H), 4.49 (q, J = 7.2 Hz, 4H), 1.47 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.9, 131.3, 130.5, 130.0, 128.6, 128.5, 127.6, 124.8, 123.9, 123.4, 61.8, 14.2; HRMS (ESI-TOF) calcd for $C_{24}H_{20}O_4Na$ $[M + Na]^+$ 395.1254, found 395.1255.

*2-Decyltriphenylene (**3aj**):* Colorless solid, mp 57.7−59.5 °C, 26.8 mg (73%); IR (KBr) 3071, 2919, 2849, 1620, 1469, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.78−8.59 (m, 4H), 8.57 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 1.5 Hz, 1H), 7.77−7.58 (m, 4H), 7.50 (dd, J = 8.4, 1.5 Hz, 1H), 2.87 (t, J = 7.5 Hz, 2H), 1.79 (quint, J = 7.5 Hz, 2H), 1.51−1.20 (m, 14H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.9, 129.9, 129.8, 129.7, 129.4, 128.0, 127.7, 127.4, 127.1, 127.03, 127.02, 126.7, 123.27, 123.25, 123.2, 123.1, 122.7, 36.3, 31.9, 31.6, 29.62, 29.57, 29.4, 29.3, 22.7, 14.1; HRMS (APCI-TOF) calcd for $C_{28}H_{33}$ $[M + H]^+$ 369.2577, found 369.2592.

*1,3,4-Trimethyltriphenylene-2-carboxylic Acid Ethyl Ester (**3ba**):* Colorless solid, mp 171.6−173.9 °C, 33.9 mg (99%); IR (KBr) 3412, 3063, 2970, 2865, 1721, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.62−8.36 (m, 2H), 8.33−8.06 (m, 2H), 7.79−7.36 (m, 4H), 4.51 (q, J = 7.5 Hz, 2H), 2.85 (s, 3H), 2.79 (s, 3H), 2.42 (s, 3H), 1.47 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.1, 135.2, 133.9, 131.3, 131.1, 130.8, 130.7, 130.6, 130.5, 130.3, 129.0, 128.2, 126.9, 126.7, 126.6, 126.1, 125.9, 123.4, 61.2, 21.39, 21.37, 17.4, 14.3; HRMS (ESI-TOF) calcd for $C_{24}H_{22}O_2Na$ $[M + Na]^+$ 365.1512, found 365.1512.

*(1,4-Dimethyl-3-phenyltriphenylen-2-yl)methanol (**3bg**):* Colorless solid, mp 87.3−89.0 °C, 32.4 mg (89%); IR (KBr) 3578, 3386, 3062, 2922, 1725, 1439 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.52 (dd, J = 8.1, 1.5 Hz, 2H), 8.31 (dt, J = 8.1, 1.5 Hz, 2H), 7.68−7.40 (m, 7H), 7.38−7.29 (m, 2H), 4.61 (s, 2H), 3.05 (s, 3H), 2.55 (s, 3H), 1.42

(br, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 142.2, 141.1, 135.9, 133.05, 132.96, 131.1, 130.92, 130.90, 130.8, 129.6, 129.3, 128.9, 128.6, 127.2, 126.7, 126.6, 125.95, 125.92, 123.45, 123.42, 61.0, 23.5, 20.7; HRMS (ESI-TOF) calcd for $C_{27}H_{22}ONa$ [M + Na]$^+$ 385.1563, found 385.1568.

*3-Methyl-2-azatriphenylene (**5aa**)*[4]*:* Colorless solid, 14.8 mg (61%); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.81 (s, 1H), 8.77−8.51 (m, 4H), 8.17 (s, 1H), 7.81−7.59 (m, 4H), 2.79 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 155.0, 146.2, 135.5, 131.3, 129.4, 129.1, 128.2, 127.7, 127.54, 127.46, 127.3, 123.6, 123.35, 123.31, 122.3, 122.1, 115.1, 24.6; HRMS (ESI-TOF) calcd for $C_{18}H_{14}N$ [M + H]$^+$ 244.1121, found 244.1121.

*3-Propyl-2-azatriphenylene (**5ab**):* Pale yellow solid, mp 121.0−122.6 °C, 19.8 mg (73%); IR (KBr) 3076, 2959, 2871, 1725, 1606, 1437 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.85 (s, 1H), 8.77−8.51 (m, 4H), 8.17 (s, 1H), 7.78−7.58 (m, 4H), 3.01 (t, J = 7.2 Hz, 2H), 1.93 (sext, J = 7.2 Hz, 2H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.0, 146.4, 135.5, 131.3, 129.4, 129.1, 128.3, 127.7, 127.6, 127.5, 127.3, 123.6, 123.35, 123.30, 122.3, 114.6, 40.5, 23.4, 14.0; HRMS (ESI-TOF) calcd for $C_{20}H_{18}N$ [M + H]$^+$ 272.1434, found 272.1445.

*3-Isopropyl-2-azatriphenylene (**5ac**):* Pale yellow solid, mp 116.5−117.7 °C, 19.3 mg (71%); IR (KBr) 3079, 2954, 2869, 1730, 1604, 1437 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.88 (s, 1H), 8.74−8.51 (m, 4H), 8.21 (s, 1H), 7.78−7.58 (m, 4H), 3.32 (sept, J = 7.2 Hz, 1H), 1.49 (d, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 164.1, 146.3, 135.6, 131.3, 129.4, 129.0, 128.3, 127.73, 127.71, 127.5, 127.3, 123.6, 123.4, 123.3, 122.4, 122.3, 112.5, 36.4, 22.8; HRMS (ESI-TOF) calcd for $C_{20}H_{18}N$ [M + H]$^+$ 272.1434, found 272.1440.

*3-Phenyl-2-azatriphenylene (**5ad**)*[4]*:* Colorless solid, 17.6 mg (58%); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 9.90 (d, J = 4.5 Hz, 1H), 8.72−8.45 (m, 5H), 8.19 (d, J = 8.0 Hz, 2H), 7.76−7.61 (m, 4H), 7.61−7.54 (m, 2H), 7.51−7.46 (m, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 154.1, 146.7, 139.6, 135.6, 131.3, 129.7, 129.1, 128.81, 128.78, 128.0, 127.7, 127.6, 127.4, 127.0, 123.5, 123.35, 123.29, 123.1, 122.4, 112.6; HRMS (ESI-TOF) calcd for $C_{23}H_{16}N$ [M + H]$^+$ 306.1277, found 306.1278.

*3-(4-Trifluoromethylphenyl)-2-azatriphenylene (**5ae**):* Colorless solid, mp 231.8−233.3 °C, 28.4 mg (76%); IR (KBr) 3075, 2933, 2364, 1615, 1328, 1111 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 10.04 (s, 1H), 8.82 (s, 1H), 8.85−8.57 (m, 4H), 8.33 (d, J = 8.1 Hz, 2H), 7.87−7.65 (m, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 152.6, 147.0, 142.9, 135.8, 131.5, 130.0, 129.5, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 125.79, 125.76, 123.9, 123.63, 123.58, 123.5, 122.7, 113.2; HRMS (ESI-TOF) calcd for $C_{24}H_{15}F_3N$ [M + H]$^+$ 374.1151, found 374.1153.

*3-(4-Methoxyphenyl)-2-azatriphenylene (**5af**):* Pale yellow solid, mp 234.1−235.8 °C, 22.3 mg (66%); IR (KBr) 3069, 3012, 2940, 2842, 1602, 1250 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 9.96 (s, 1H), 8.75−8.66 (m, 3H), 8.66−8.56 (m, 2H), 8.17 (d, J = 8.5 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.73−7.63 (m, 3H), 7.09 (d, J = 8.5 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 160.4, 154.1, 146.7, 135.8, 132.2, 131.4, 129.7, 129.2, 128.3, 127.9, 127.8, 127.7, 127.5, 123.7, 123.5, 123.4, 122.8, 122.5, 114.2, 111.8, 55.4; HRMS (ESI-TOF) calcd for $C_{24}H_{18}NO$ [M + H]$^+$ 336.1383, found 336.1395.

*4-(2-Azatriphenylen-3-yl)benzonitrile (**5ag**):* Colorless solid, mp 291.2−292.0 °C, 19.3 mg (58%); IR (KBr) 3055, 2923, 2364, 2221, 1604, 1435 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 10.03 (s, 1H), 8.82 (s, 1H), 8.80−8.64 (m, 4H), 8.33 (d, J = 8.0 Hz, 2H), 7.89−7.78 (m, 3H), 7.78−7.69 (m, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 152.0, 147.2, 143.8, 135.9, 132.7, 131.6, 130.2, 129.7, 128.4, 128.1, 127.8, 127.7, 127.53, 127.51, 124.2, 123.7, 123.6, 122.8, 118.9, 113.5, 112.2; HRMS (ESI-TOF) calcd for $C_{24}H_{15}N_2$ [M + H]$^+$ 331.1230, found 331.1244.

*3-Vinyl-2-azatriphenylene (**5ah**):*[4] Pale yellow solid, 21.9 mg (86%);[1] H NMR (CDCl$_3$, 500 MHz) δ 9.85 (s, 1H), 8.69−8.63 (m, 1H), 8.62−8.52 (m, 3H), 8.25 (s, 1H), 7.78−7.62 (m, 4H), 7.04 (dd, J = 17.0, 10.5 Hz, 1H), 6.45 (dd, J = 17.0, 1.0 Hz, 1H), 5.59 (dd, J = 10.5, 1.0 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 152.4, 146.7, 136.8, 135.5, 131.3, 129.7, 129.2, 128.2, 127.8, 127.6, 127.4, 123.63, 123.57, 123.40, 123.39, 122.5, 117.9, 114.1; HRMS (ESI-TOF) calcd for $C_{19}H_{14}N$ [M + H]$^+$ 256.1121, found 256.1126.

*2-Azatriphenylene-3-carboxylic Acid Ethyl Ester (**5ai**):* Colorless solid, mp 170.1−171.6 °C, **4i**: 1.1 equiv, 19.6 mg (65%), **4i**: 5 equiv, 25.9 mg (86%); IR (KBr) 3076, 2976, 2869, 1712, 1262, 1129 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.93 (s, 1H), 9.15 (s, 1H), 8.72−8.51 (m, 4H), 7.81−7.61 (m, 4H), 4.60 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 165.7, 146.9, 144.6, 135.3, 131.2, 130.7, 129.7, 128.9, 128.0, 127.8, 127.3, 127.2, 126.6, 124.0, 123.45, 123.36, 123.2, 118.7, 62.0, 14.5; HRMS (ESI-TOF) calcd for $C_{20}H_{15}NO_2Na$ [M + Na]$^+$ 324.0995, found 324.1006.

*(2-Azatriphenylen-3-yl)acetonitrile (**5aj**):* Pale yellow solid, mp 176.8−177.7 °C, 23.5 mg (88%); IR (KBr) 3082, 2916, 2851, 2252, 1609, 1399 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.78 (s, 1H), 8.70−8.47 (m, 4H), 8.38 (s, 1H), 7.83−7.62 (m, 4H), 4.13 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 147.1, 147.0, 136.1, 131.5, 130.0, 129.8, 128.4, 128.0, 127.7, 127.6, 126.9, 123.9, 123.8, 123.5, 122.6, 117.3, 114.6, 26.7; HRMS (ESI-TOF) calcd for $C_{19}H_{12}N_2Na$ [M + Na]$^+$ 291.0893, found 291.0904.

*(2-Azatriphenylen-3-yl)phenylmethanone (**5ak**):* Pale yellow solid, mp 194.2−194.8 °C, 13.4 mg (40%); IR (KBr) 3060, 2925, 2854, 1652, 1390, 1266 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 10.02 (s, 1H), 9.20 (s, 1H), 8.85−8.59 (m, 4H), 8.24−8.14 (m, 2H), 7.87−7.70 (m, 4H), 7.69−7.50 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 151.6, 145.8, 136.9, 135.7, 132.8, 131.3, 131.1, 130.8, 129.8, 129.0, 128.2, 128.1, 127.9, 127.54, 127.50, 126.3, 124.2, 123.6, 123.5, 123.3, 118.4; HRMS (ESI-TOF) calcd for $C_{24}H_{15}NONa$ [M + Na]$^+$ 356.1046, found 356.1047.

*1,4-Dimethyl-3-phenyl-2-azatriphenylene (**5bd**):* Pale yellow solid, mp 188.0−190.0 °C, 17.3 mg (52%); IR (KBr) 3059, 2963, 2927, 1731, 1542, 1393 m^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.67−8.42 (m, 4H), 7.79−7.38 (m, 9H), 3.21 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 155.6, 152.0, 141.5, 139.3, 132.3, 130.9, 129.65, 129.58, 129.5, 129.1, 128.4, 128.3, 127.8, 127.7, 127.2, 126.8, 126.1, 125.8, 123.5, 123.3, 122.6, 28.6, 22.7; HRMS (ESI-TOF) calcd for $C_{25}H_{20}N$ [M + H]$^+$ 334.1590, found 334.1607.

*1,4-Dimethyl-2-azatriphenylene-3-carboxylic Acid Ethyl Ester (**5bi**):* Colorless oil, 29.8 mg (91%); IR (KBr) 3068, 2978, 2931, 1718, 1213, 1080 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.54 (d, J = 8.1 Hz, 2H), 8.45 (d, J = 7.5 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H), 7.79−7.50 (m, 4H), 4.55 (q, J = 7.2 Hz, 2H), 3.17 (s, 3H), 2.98 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 167.8, 152.4, 145.8, 139.2, 132.2, 131.3, 129.00, 128.98, 128.8, 128.1, 128.0, 127.8, 126.9, 126.3, 124.7, 123.6, 123.4, 61.8, 28.5, 20.8, 14.3; HRMS (ESI-TOF) calcd for $C_{22}H_{19}NO_2Na$ [M + Na]$^+$ 352.1308, found 352.1315.

*2-Butyl-1,4-dimethyl-2H-2-azatriphenylen-3-one (**7b**):* Yellow solid, mp 79.7−82.3 °C, 30.3 mg (92%); IR (KBr) 3062, 2958, 2871, 1622, 1599, 760 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.31−8.08 (m, 3H), 7.77−7.67 (m, 1H), 7.62−7.52 (m, 1H), 7.52−7.34 (m, 3H), 4.31 (t, J = 7.8 Hz, 2H), 2.92 (s, 3H), 2.68 (s, 3H), 1.76 (quint, J = 7.2 Hz, 2H), 1.51 (sext, J = 7.2 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 162.2, 140.6, 137.6, 133.3, 130.55, 130.53, 129.9, 129.7, 129.2, 127.8, 126.9, 126.7, 126.2, 123.8, 123.5, 119.6, 113.8, 45.5, 30.7, 20.7, 20.5, 18.0, 13.8; HRMS (ESI-TOF) calcd for $C_{23}H_{23}NONa$ [M + Na]$^+$ 352.1672, found 352.1673.

*14,14-Dibutyl-14H-indeno[1,2-b]triphenylene (**8ak**):* H$_8$-BINAP (3.2 mg, 0.0050 mmol) and [Rh(cod)$_2$]BF$_4$ (2.0 mg, 0.0050 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H$_2$ was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness. The residue was redissolved in $(CH_2Cl)_2$ (0.4 mL) and a $(CH_2Cl)_2$ (0.6 mL) solution of **2k** (24.4 mg, 0.100 mmol) was added. A $(CH_2Cl)_2$ (1.0 mL) solution of **1a** (10.1 mg, 0.050 mmol) was added dropwise to this solution, and the mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/CH_2Cl_2 = 5:6), which furnished adulterated **3ak**. Tetrafluoroboric acid diethyl ether complex (12.3 μL, 0.090 mmol) was added to a stirred solution of this adulterated **3ak** (13.4 mg, 0.030 mmol) in CH_2Cl_2 (3.0 mL), and the mixture was stirred at room temperature for 18 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/CH_2Cl_2 = 12:1), which furnished **8ak** (13.7 mg, 0.0319 mmol, 64% yield from **1a**): Colorless solid, mp 170.0−172.3 °C; IR (KBr) 3063, 2958, 2928, 2858, 1458, 1436 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.98 (s, 1H), 8.82 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.72−8.65 (m, 2H), 8.60 (s, 1H), 8.01−7.95 (m, 1H), 7.77−7.63 (m, 4H), 7.46−7.37 (m, 3H), 2.22−2.07 (m, 4H), 1.10 (sext, J = 7.5 Hz, 4H), 0.71−0.62 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.3, 150.0, 140.9, 140.7, 130.3, 129.6, 129.2, 127.7, 127.2, 127.1, 127.0, 126.92, 126.90, 123.4, 123.35, 123.32, 123.1, 120.1, 117.0, 113.8, 55.2, 40.8, 26.1, 23.1, 13.8; HRMS (APCI-TOF) calcd for $C_{33}H_{33}$ $[M + H]^+$ 429.2577, found 429.2573.

*Triphenylene-Based Ladder Molecule **8al**.* H_8-BINAP (6.3 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness. The residue was redissolved in $(CH_2Cl)_2$ (0.4 mL), and a $(CH_2Cl)_2$ (0.6 mL) solution of **2l** (20.5 mg, 0.0500 mmol) was added. A $(CH_2Cl)_2$ (1.0 mL) solution of **1a** (50.6 mg, 0.250 mmol) was added dropwise to this solution, and the mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/CH_2Cl_2 = 35:90), which furnished adulterated **3al**. Tetrafluoroboric acid diethyl ether complex (26.3 μL, 0.193 mmol) was added to a stirred solution of this adulterated **3al** in CH_2Cl_2 (3 mL), and the mixture was stirred at room temperature for 13 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (hexane/CH_2Cl_2 = 5:1) to give **8al** (27.8 mg, 0.0357 mmol, 71% yield from **2l**): Colorless solid, mp >300 °C; IR (KBr) 3080, 2953, 2927, 2858, 1723, 1421 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.09 (s, 2H), 8.93 (d, J = 7.5 Hz, 2H), 8.81 (d, J = 7.5 Hz, 2H), 8.71 (d, J = 7.5 Hz, 4H), 8.65 (s, 2H), 7.99 (s, 2H), 7.83−7.58 (m, 8H), 2.44−2.09 (m, 8H), 1.30−1.01 (m, 8H), 0.90−0.64 (m, 8H), 0.66 (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.0, 150.5, 141.2, 140.9, 130.34, 130.32, 129.8, 129.6, 129.3, 129.2, 127.2, 127.1, 126.93, 126.89, 123.5, 123.4, 123.3, 117.1, 114.5, 113.7, 55.0, 41.3, 26.2, 23.2, 13.9; HRMS (APCI-TOF) calcd for $C_{60}H_{59}$ $[M + H]^+$ 779.4611, found 779.4608.

*Triphenylene-Based Ladder Molecule **8am**.* H_8-BINAP (6.3 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After being stirred at room temperature for 1 h, the resulting solution was concentrated to dryness. The residue was redissolved in $(CH_2Cl)_2$ (0.4 mL), and a $(CH_2Cl)_2$ (0.6 mL) solution of **2m** (33.4 mg, 0.0500 mmol) was added. A $(CH_2Cl)_2$ (1.0 mL) solution of **1a** (50.6 mg, 0.250 mmol) was added dropwise to this solution, and the mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/CH_2Cl_2 = 1:2), which furnished **3am**. Tetrafluoroboric acid diethyl ether complex (30.0 μL, 0.220 mmol) was added to a stirred solution of this adulterated **3am** in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 13 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The residue was purified by a preparative TLC (hexane/CH_2Cl_2 = 10:1) to give **8am** (34.0 mg, 0.0329 mmol, 66% yield from **2m**): Yellow solid, mp 122.4−124.5 °C; IR (KBr) 3077, 2925, 2852, 1609, 1421, 1289 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.10 (s, 2H), 8.94 (d, J = 8.0 Hz, 2H), 8.81 (d, J = 7.0 Hz, 2H), 8.75 (s, 2H), 8.71 (d, J = 8.0 Hz, 4H), 7.99 (s, 2H), 7.97 (s, 2H), 7.80−7.65 (m, 8H), 2.38−2.19 (m, 4H), 1.81 (s, 12H), 1.29−1.04 (m, 36H), 0.94−0.83 (m, 4H), 0.79 (t, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.7, 153.4, 151.0, 141.5, 139.4, 138.1, 130.2, 129.6, 129.4, 129.1, 127.1, 126.9, 126.8, 123.5, 123.4, 123.3, 117.0, 114.7, 113.8, 54.7, 46.7, 41.2, 31.8, 30.2, 29.7, 29.60, 29.55, 29.3, 29.2, 28.1, 23.9, 22.6, 14.0; HRMS (ESI-TOF) calcd for $C_{79}H_{87}$ $[M + H]^+$ 1035.6802, found 1035.6766.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed conditions for measurement of photophysical properties, absorption and emission spectra, X-ray crystallographic structures, copies of ^1H and ^{13}C NMR spectra, and X-ray crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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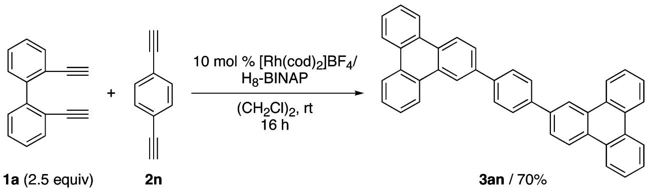
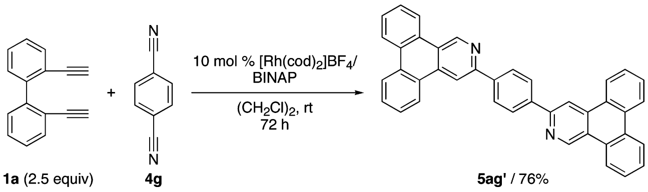
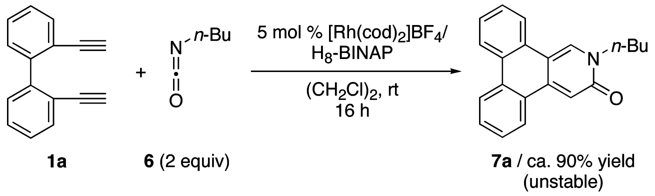
(16) The double [2 + 2 + 2] cycloaddition of **1a** with terminal diyne **2k** proceeded in the presence of the cationic rhodium(I)/H_8-BINAP catalyst at room temperature to give the known benzene-linked bis-triphenylene **3an**. For a report of **3an**, see: Yu, J.-Y.; Huang, M.-J.; Chen, C.-H.; Lin, C.-S.; Cheng, C.-H. *J. Phys. Chem. C.* **2009**, *113*, 7405. The double [2 + 2 + 2] cycloaddition of **1a** with dinitrile **4g** also proceeded in the presence of the cationic rhodium(I)/BINAP catalyst at room temperature to give benzene-linked bis-azatriphenylene **5ag′**. Unfortunately, these cycloadducts could not be fully characterized due to their insolubility in common organic solvents.





(17) The reaction of the terminal diyne **1a** with *n*-butylisocyanate **6** was also examined in the presence of the cationic rhodium(I)/H_8-BINAP catalyst at room temperature. The desired azatriphenylene **7a** was generated with high yield, while this cycloadduct could not be isolated in a pure form due to its instability.



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