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# Highly Regioselective Syntheses of Substituted Triphenylenes from 1,2,4-Trisubstituted Arenes via a Co-Catalyzed Intermolecular Alkyne Cyclotrimerization

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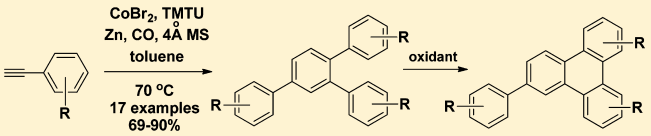
Supporting Information

**ABSTRACT:** Herein, we report the development of a new method for the syntheses of substituted triphenylenes from the corresponding 1,2,4-trisubstituted arenes, which were themselves generated in a highly regioselective manner according to an intermolecular alkyne cyclotrimerization reaction that was catalyzed by a novel Co−TMTU complex. This highly regioselective reaction for the formation of 1,2,4-trisubstituted arenes will be a valuable addition to the plethora of tools already available to synthetic chemists and encourage further mechanistic studies of this important alkyne trimerization process.




The transition-metal-catalyzed [2 + 2 + 2] cycloaddition reaction of alkynes has been reported as an effective tool for the synthesis of substituted arenes.[1] The formation of substituted arenes from alkynes, namely the Reppe cyclotrimerization,[2] has been studied extensively over the past three decades using a large number of elaborated transition-metal-catalyzed reactions.[3] Given that structurally defined aromatic compounds can be used as building blocks for the synthesis of new materials,[4] the purity levels of the aromatic compounds synthesized according to these cyclotrimerization procedures are particularly important in determining the practical value of the procedures themselves (Figure 1).

It should also be noted that the regioselective construction of polysubstituted arenes via homocyclotrimerizations of terminal alkynes can hardly be realized because it is difficult to control the region-selectivity during both the initial metallacycle formation and subsequent regioselective insertion of the third alkyne,[5] which usually results in the undesired formation of a mixture of 1,3,5-regioisomer and 1,2,4-regioisomer. Two methods have been utilized to solve this regioselective issue,[6] and these methods have been extensively applied to the construction of the core structures of numerous molecules with important biological activities.[7]

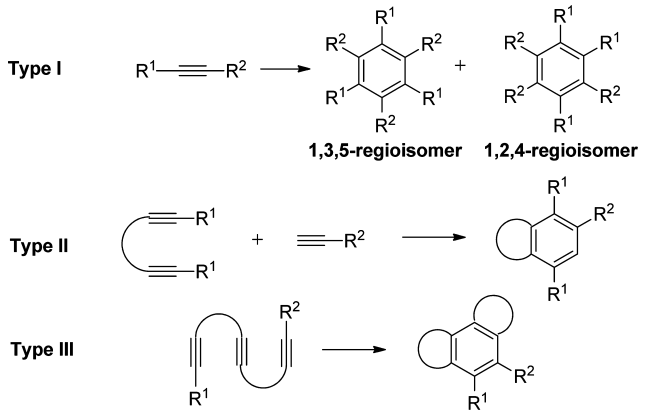



**Figure 1.** Three types of alkyne cyclotrimerization.

Of the many different metal catalysts available for the cyclotrimerization reactions of alkynes,[8] cobalt complexes such as $CpCo(CO)_2$[9] and $CpCo(C_2H_4)_2$[10] are two of the most widely used catalysts to affect transformation of this particular type. The practical application of these catalysts, however, has been limited by the air-sensitive nature of these materials and the requirement for distilled and degassed solvents. The development of a robust catalytic system capable of catalyzing the regioselective trimerization reaction of alkynes is therefore highly desired.

Herein, we report our latest efforts toward the development of a practical version of the regioselective synthesis of 1,2,4-trisubstituted arenes from aryl alkynes using a novel Co-complex derived from $CoBr_2$/tetramethylthiourea (TMTU)/Zn.

We recently reported the use of a Co−TMTU complex derived from the in situ reduction of $CoBr_2$ with Zn in the presence of TMTU as a catalyst for the Pauson−Khand reaction (PKR) under a balloon pressure of CO, with the

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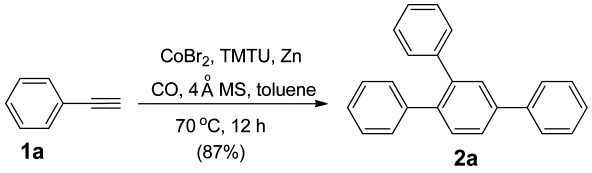
catalyst enabling the synthesis of a series of structurally diverse cyclopentenones.[11] To examine the effect of the substrate on the outcome of the observed PKR, the reaction conditions were subsequently applied to phenylacetylene and cyclopentene. Surprisingly, 1,2,4-triphenyl benzene was observed as the sole product of this reaction (Scheme 1). It is noteworthy that there

**Scheme 1. Synthesis of 1,2,4-Triphenylbenzene 2a**




are several advantages associated with the use of $CoBr_2$ and TMTU, including their stability toward air and moisture, as well as their inexpensive commercial availability. With all of these factors in mind, we decided to initiate a study toward the development of this transformation as a practical and robust strategy for the cyclotrimerization of alkynes.

Our research started with an investigation of the Co-catalyzed cyclotrimerization of phenylacetylene (Table 1, entry 1). Following a systematic investigation of the reaction conditions, the Co complex derived from the in situ reduction of $CoBr_2$ (5 mol %) with Zn[12] (1.0 equiv) in the presence of TMTU (30 mol %) was identified as an efficient catalyst for this intermolecular trimerization process, with the annulated product **2a** being obtained as the sole isomer in 87% yield (Scheme 2) (see the Supporting Information). To evaluate the scope of this reaction, a variety of different arylalkynes were annulated under the conditions listed in Table 1, and the desired products **2b–r** were obtained in good yields.

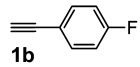
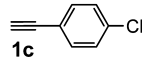
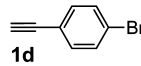
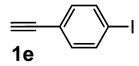
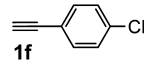
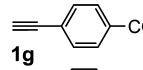
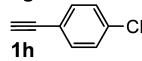
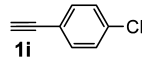
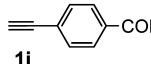
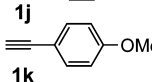
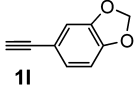
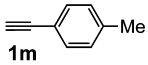
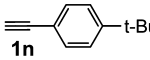
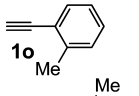
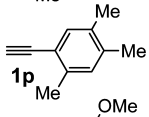
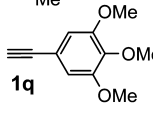
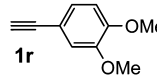
For the sake of comparison, we carried out cyclotrimerization of phenylacetylene under Hilt's conditions ($CoBr_2$, Zn, $ZnI_2$, diimine, $CH_3CN$, room temperature)[12] twice, and the ratio for 1,2,4-trisubstituted arene and 1,3,5-trisubstituted arene was 94:6, indicating our conditions provided better selectivity than Hilt's conditions (see the Supporting Information for details).

We also tested the cyclotrimerization with internal acetylene [trimethyl(phenylethynyl)silane] under the identical conditions listed in Table 1; however, no any cyclotrimerization was observed.

It is noteworthy that TMTU plays a pivotal role in this trimerization reaction of terminal arylalkynes. For example, when the reaction was carried out in the presence of $CoBr_2$–TMTU with a ratio of less than 1/3, none of the desired annulated product was obtained. The reaction also needs to be conducted in the presence of CO during the reductive formation of the Co–TMTU complex, with the CO presumably contributing to the formation of Co(I)[13]/TMTU complex.

On the basis of the results obtained from these experiments, the following general trends were confirmed: (1) substrates bearing electron-withdrawing (Table 1, entries 1–9) or electron-donating (Table 1, entries 10–11 and 16–17) groups proceeded smoothly through the cyclotrimerization reaction to give the annulated products as single isomers in good to excellent yields (see the Supporting Information for the NMR studies confirming the high regioselectivity); (2) a variety of different functional groups, including ester, aldehyde, ketone, nitrile, and acetal groups were well tolerated under the

**Table 1. Co–TMTU-Catalyzed Cyclotrimerization of Alkynes**


| entry | substrate | product | isolated yield[a] |
|---|---|---|---|
| 1 |  **1b** | **2b** | 86% |
| 2 |  **1c** | **2c** | 90% |
| 3 |  **1d** | **2d** | 82% |
| 4 |  **1e** | **2e** | 86% |
| 5 |  **1f** | **2f** | 66% |
| 6 |  **1g** | **2g** | 88% |
| 7 |  **1h** | **2h** | 85% |
| 8 |  **1i** | **2i** | 76% |
| 9 |  **1j** | **2j** | 82% |
| 10 |  **1k** | **2k** | 62%[b] |
| 11 |  **1l** | **2l** | 69% |
| 12 |  **1m** | **2m** | 86% |
| 13 |  **1n** | **2n** | 88% |
| 14 |  **1o** | **2o** | 87% |
| 15 |  **1p** | **2p** | 89% |
| 16 |  **1q** | **2q** | 87% |
| 17 |  **1r** | **2r** | 70% |

[a]Alkyne (1.0 mmol), $CoBr_2$ (5.0 mol %), TMTU (30 mol %), Zn (1.0 eqiv), toluene (2.0 mL), 90 °C, 4 Å MS, CO (balloon pressure), 12 h. [b]Using $CoBr_2$ (10 mol %), TMTU (60 mol %), Zn (2.0 equiv), toluene (2.0 mL), 90 °C, 4 Å MS, CO (balloon pressure), 12 h.

optimized conditions; (3) the selective formation of a benzene ring over the pyridine ring was observed when a nitrile group was present in the substrate (Table 1, entry 7);[14] and (4) in contrast to results previously published in the area,[15] *ortho*-substituted aryl arenes could also be formed effectively under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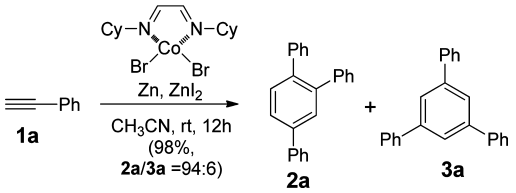
**Scheme 2. Synthesis of Triphenylbenzenes 2a and 3a**




the current conditions with a high level of regioselectivity (Table 1, entries 14 and 15).

The reaction mechanism[16] for this highly regioselective formation of 1,2,4-trisubstituted arenes remains unclear and we are currently working toward the development of a detailed understanding of the role of TMTU in this reaction in our laboratory. In line with the mechanisms proposed for the related reactions,[17] and in the absence of a detailed mechanism for the current transformation, we have proposed the following mechanism to account for the observed formation of the 1,2,4-triphenyl benzenes. Thus, the initially formed Co(I)−TMTU complex derived from the $CoBr_2$/TMTU/Zn mixture could form a Co(III) cobaltacycle **A** (see Figure 2) by oxidative addition of two alkynes, which could then insert a third equivalent of alkyne to give regioselectively the 1,2,4-triphenylbenzene after reductive elimination.

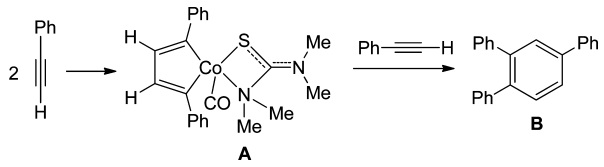


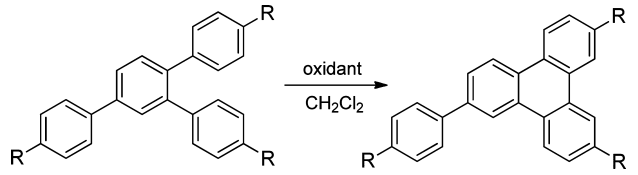

**Figure 2.** Intermolecular Co-catalyzed [2 + 2 + 2] cycloaddition.

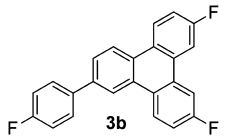
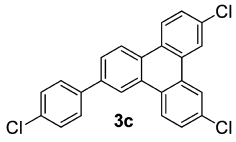
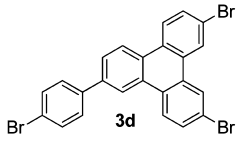
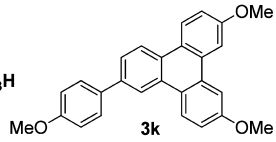
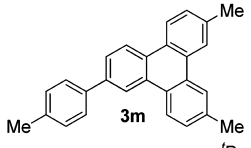
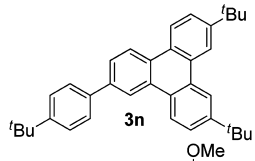
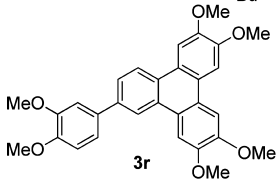
With a highly regioselective method for the synthesis of 1,2,4-trisubstituted arenes in hand, we proceeded to investigate the use of these 1,2,4-trisubstituted arenes as starting materials for the construction of substituted triphenylenes (TPs), which are useful building blocks for the construction of complex materials in the field of materials science.[18]

With this in mind, we began to profile different oxidative reagents for the proposed cyclodehydrogenation reaction of the trisubstituted arenes. Although $FeCl_3$ is well-known as an effective oxidative agent[19] to mediate this type of oxidative coupling reaction, its application to the current annulation reaction was unsuccessful, with none of the desired product detected. We later found out that the use of phenyliodine(III) bis(trifluoroacetate) (PIFA)[20] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under acidic conditions[21] could effectively promote the desired annulation reaction, with the expected products being obtained in good to acceptable yields (Table 2). It is noteworthy that electron-rich substrates **2k** and **2r** were oxidatively converted to the substituted TP's in yields of 68−72% using DDQ in the presence of methyl sulfonic acid.. For the other substrates, PIFA was found to be the most effective oxidative reagent for the oxidative annulations.

In summary, we have identified a novel type of Co complex derived from $CoBr_2$/TMTU/Zn that is capable of catalyzing the highly regioselective cyclotrimerization of terminal arylalkynes for the formation of structurally diverse 1,2,4-trisubstituted arenes in good to excellent yields. Furthermore, the resulting arenes could be oxidatively converted to the

**Table 2. Oxidative Cyclodehydrogenation**[a]




| entry | substrate | oxidant | product | yield (%) |
|---|---|---|---|---|
| 1 | **2b** | **PIFA** |  **3b** | 46 |
| 2 | **2c** | **PIFA** |  **3c** | 75 |
| 3 | **2d** | **PIFA** |  **3d** | 76 |
| 4 | **2k** | **DDQ/MeSO$_3$H** |  **3k** | 68 |
| 5 | **2m** | **PIFA** |  **3m** | 74 |
| 5 | **2n** | **PIFA** |  **3n** | 51 |
| 5 | **2r** | **DDQ/MeSO$_3$H** |  **3r** | 72 |

[a]The experimental details are provided in the Supporting Information.

substituted TPs. Given the practical and robust nature of this new $CoBr_2$/TMTU/Zn-catalyzed trimerization process, it is envisaged that this reaction could be used for the synthesis of structurally diverse of substituted TPs, which could find application in the synthesis of new materials.

## EXPERIMENTAL SECTION

**General Procedure for the Intermolecular [2 + 2 + 2] Reaction.** To a solution of molecular sieves (4 Å, 160 mg) in toluene (1.5 mL) in Schlenk tube were added anhydrous $CoBr_2$ (0.050 mmol, 10.9 mg, 5 mol %), TMTU (0.3 mmol, 39.7 mg, 0.30 equiv), and zinc dust (1.0 mmol, 65 mg, 1.0 equiv), the mixture was stirred under a balloon pressure of CO at 70 °C for 3 h, and the color of the reaction mixture was changed from its original deep green to colorless or yellowish. To this solution was added the alkyne (1.00 mmol, 1.0 equiv), and the resulting mixture was stirred at 90 °C for an additional 12 h. After being cooled to room temperature, the reaction mixture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was worked up by addition of a saturated $NH_4Cl$ solution and extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were dried with $Na_2SO_4$, The solution was filtered, the solvent was removed under pressure, and the residue was purified by a flash column chromatography on silica gel with gradient solvent (petroleum ether and ethyl acetate) to give the corresponding product.

**Synthesis of 4′-Phenyl-1,1′:2′,1″-terphenyl (2a).**[22] Alkyne (158.1 mg, 1.55 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 137.5 mg (0.449 mmol) in 87% yield. White solid. Mp: 100−101 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.69−7.64 (m, 4H), 7.52 (d, $J$ = 8.0 Hz, 1H), 7.48−7.44 (m, 2H), 7.38−7.34 (m, 1H), 7.25−7.16 (m, 10H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.5, 141.1, 140.9, 140.6, 140.3, 139.5, 131.1, 129.9, 129.8, 129.4, 128.8, 127.9, 127.9, 127.4, 127.1, 126.6, 126.5, 126.1. IR (neat): 3059 (w), 3024 (w), 1470, 1258, 1076, 1026, 794, 760, 695 cm$^{-1}$. EI-MS ($m/z$): 306 ($M^+$).

**Synthesis of 4′-Phenyl-1,1′:2′,1″-terphenyl (2a) via Hilt's Conditions.** To a solution of dry $CH_3CN$ (1.0 mL) in a flame-dried Schlenk tube were added $CoBr_2$ (cy-diimine) (44 mg, 0.1 mmol, 5.0 mol %), zinc dust (13 mg, 0.2 mmol, 10.0 mol %), and anhydrous $ZnI_2$ (64 mg, 0.2 mmol, 10.0 mol %), and the mixture was refluxed under $N_2$ atmosphere for 1 min. After the mixture was cooled to room temperature, phenylacetylene (204 mg, 0.22 mL, 2.0 mmol) was added, and the newly generated mixture was stirred at room temperature for 15 min. The reaction mixture was worked up by addition of a saturated $NH_4Cl$ solution (3 mL), and the mixture was extracted with EtOAc (3 × 3 mL). The combined extracts were dried with $Na_2SO_4$. The solution was filtered, solvent was removed under pressure, and the residue was purified by a flash chromatography on silica (petroleum ether/EtOAc = 50/1) to give product **2a** (200 mg, 0.654 mmol) in 98% yield, the ratio of **2a**/**3a** is 94:6 according to the $^1$NMR analysis.

**Synthesis of 4,4″-Difluoro-4′-(4-fluorophenyl)-1,1′:2′,1″-terphenyl (2b).**[22] Alkyne (200.7 mg, 1.67 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 173.3 mg (0.481 mmol) in 86% yield. White solid. Mp: 148−149 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.62−7.55 (m, 4H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.16−7.08 (m, 6H), 6.96−6.91 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.6, 162.9, 162.8, 161.7, 160.9, 160.9, 140.0, 139.6, 138.5, 137.2, 136.8, 136.5, 131.4, 131.3, 131.2, 131.1, 129.1, 128.7, 128.6, 126.1, 115.8, 115.7, 115.1, 114.9. $^{19}$F NMR (470.6 MHz, $CDCl_3$): δ −114.96 (s), −115.43 (s), −115.55 (s) ppm. IR (neat): 1604, 1523, 1509, 1482, 1223, 1158, 836, 821 cm$^{-1}$. EI-MS ($m/z$): 360 ($M^+$).

**Synthesis of 4,4″-Dichloro-4′-(4-chlorophenyl)-1,1′:2′,1″-terphenyl (2c).**[23] Alkyne (235.5 mg, 1.72 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 211.9 mg (0.517 mmol) in 90% yield. White solid. Mp: 190−191 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60−7.54 (m, 4H), 7.45−7.40 (m, 3H), 7.23−7.20 (m, 4H), 7.09−7.05 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.8, 139.6, 139.4, 139.0, 138.6, 138.5, 133.8, 133.0, 132.9, 131.1, 131.0, 131.0, 129.0, 129.0, 128.4, 128.3, 128,2, 126.3. IR (neat): 1473, 1090, 1013, 1004, 828, 811, 741 cm$^{-1}$. EI-MS ($m/z$): 408 ($M^+$), 338 ($M^+$-2Cl).

**Synthesis of 4,4″-Dibromo-4′-(4-bromophenyl)-1,1′:2′,1″-terphenyl (2d).**[24] Alkyne (234.7 mg, 1.30 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 193.6 mg (0.357 mmol) in 82% yield. White solid. Mp: 172−173 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.61−7.55 (m, 4H), 7.51−7.49 (m, 2H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.40−7.36 (m, 4H), 7.04−7.00 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.8, 139.8, 139.6, 139.5, 139.1, 138.5, 132.0, 131.4, 131.4, 131.3, 131.3, 131.1, 129.0, 128.6, 126.3, 122.0, 121.3, 121.2. IR (neat): 1488, 1470, 1074, 1009, 1002, 811, 750 cm$^{-1}$. EI-MS ($m/z$): 542 ($M^+$), 544 ($M^+$), 382 ($M^+$ − 2Br), 384 ($M^+$ − 2Br).

**Synthesis of 4,4″-Diiodo-4′-(4-iodophenyl)-1,1′:2′,1″-terphenyl (2e).**[25] Alkyne (167.6 mg, 0.735 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 143.6 mg (0.210 mmol) in 86% yield. White solid. Mp: 256−257 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, $J$ = 8.4 Hz, 2H), 7.60−7.53 (m, 6H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.38 (d, $J$ = 8.4 Hz, 2H), 6.91−6.87 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.4, 140.0, 139.8, 139.7, 139.6, 138.6, 138.0, 137.3, 137.3, 131.6, 131.6, 131.1, 129.0, 128.9, 126.3, 93.5, 92.9, 92.8. IR (neat): 1466, 1261, 1068, 1005, 999, 823, 814, 809, 751 cm$^{-1}$; EI-MS ($m/z$): 684 ($M^+$), 558 ($M^+$ − I).

**Synthesis of 4,4″-Bis(trifluoromethyl)-4′-(4-(trifluoromethyl)phenyl)-1,1′:2′,1″-terphenyl (2f).** Alkyne (211.4 mg, 1.24 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 140.2 mg (0.274 mmol) in 66% yield. White solid. Mp: 170−171 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.78−7.71 (m, 5H), 7.66 (s, 1H), 7.56−7.52 (m, 5H), 7.31−7.25 (m, 4H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.3, 144.0, 143.5, 139.9, 139.0, 131.4, 130.1, 130.3, 130.0, 129.8, 127.4, 127.1, 125.9, 125.3, 125.3, 125.2, 123.1, 123.0. $^{19}$F NMR (470.6 MHz, $CDCl_3$): δ −62.44, −62.45. IR (neat): 1617, 1323, 1163, 1122, 1107, 1074, 845, 825 cm$^{-1}$. HRMS (EI-TOF): $m/z$ calcd for $C_{27}H_{15}F_9$ $[M]^+$ 510.1030, found 510.1035.

**Synthesis of Dimethyl 4′-(4-(Methoxycarbonyl)phenyl)-[1,1′:2′,1″-terphenyl]-4,4″-dicarboxylate (2g).**[25] Alkyne (222.2 mg, 1.39 mmol); eluent: petroleum ether/acetone = 20/1 to $CH_2Cl_2$/acetone = 50/1, product obtained 196.0 mg (0.408 mmol) in 88% yield. White solid. Mp: 224−225 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, $J$ = 8.4 Hz, 2H), 7.93−7.90 (m, 4H), 7.75−7.70 (m, 4H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.26−7.21 (m, 4H), 3.95 (s, 3H), 3.90 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.7, 166.7, 145.5, 145.1, 144.4, 140.2, 139.9, 139.3, 131.1, 130.2, 129.8, 129.7, 129.4, 129.4, 129.3, 129.3, 128.7, 128.6, 127.0, 126.9, 52.1, 52.0. IR (neat): 2952, 2925, 1719, 1608, 1435, 1276, 1113, 1103, 770, 731 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{30}H_{24}NaO_6$ $[M + Na]^+$ 503.1465, found 503.1458.

**Synthesis of 4′-(4-Cyanophenyl)[1,1′:2′,1″-terphenyl]-4,4″-dicarbonitrile (2h).** Alkyne (153.5 mg, 1.21 mmol); eluent: petroleum ether/acetone = 30/1 to 10/1, product obtained 134.0 mg (0.351 mmol), yield 87%. White solid. Mp: 243−244 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.80−7.78 (m, 5H), 7.65 (br, 1H), 7.60−7.56 (m, 5H), 7.29−7.25 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 144.9, 144.6, 144.1, 139.8, 139.6, 138.9, 132.8, 132.2, 132.1, 131.4, 130.4, 130.4, 129.4, 127.7, 127.5, 118.6, 118.4, 118.4, 111.8, 111.4, 111.3. IR (neat): 2227, 1606, 1480, 910, 821, 733 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{16}N_3$ $[M + H]^+$: 382.1339, found 382.1340.

**Synthesis of 4′-(4-Formylphenyl)[1,1′:2′,1″-terphenyl]-4,4″-dicarbaldehyde (2i).** Alkyne (228.7 mg, 1.76 mmol); eluent: petroleum ether/acetone = 30/1 to $CH_2Cl_2$/acetone = 40/1, product obtained 173 mg (0.443 mmol) in 76% yield. White solid. Mp: 216−217 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 10.00 (s, 1H), 9.99 (s, 1H), 8.02 (d, $J$ = 8.0 Hz, 1H), 7.86 (d, $J$ = 8.0 Hz, 1H), 7.80−7.74 (m, 6H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.38−7.33 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 191.6, 146.8, 146.5, 145.8, 140.1, 140.0, 139.4, 135.6, 135.0, 134.9, 131.3, 130.5, 130.4, 130.3(5), 129.6, 129.6, 129.5, 127.7, 127.3. IR (neat): 2955, 2924, 2852, 1701, 1603, 1210, 1170, 837, 817 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{19}O_3$ $[M + H]^+$: 391.1329, found 391.1335.

**Synthesis of 1,1′-(4′-(4-Acetylphenyl)[1,1′:2′,1″-terphenyl]-4,4″-diyl)diethanone (2j).**[25] Alkyne (180.7 mg, 1.25 mmol); eluent: petroleum ether/acetone = 30/1 to $CH_2Cl_2$/acetone = 40/1, product obtained 148.9 mg (0.344 mmol) in 82% yield. White solid. Mp: 258−259 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, $J$ = 8.0 Hz, 2H), 7.87−7.83 (m, 4H), 7.78−7.71 (m, 4H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.30−7.25 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.6, 197.5, 145.6, 145.2, 144.4, 140.1, 139.8, 139.2, 136.2, 135.5, 135.5, 131.2, 129.9, 129.9, 129.3, 129.0, 128.2, 128.2, 127.1, 126.9, 26.6, 26.5. IR (neat): 1680, 1603, 1358, 1267, 958, 912, 820, 732 cm$^{-1}$. EI-MS ($m/z$): 432 ($M^+$), 417 ($M^+$ − Me).

**Synthesis of 4,4″-Dimethoxy-4′-(4-methoxyphenyl)-1,1′:2′,1″-terphenyl (2k).**[25] Alkyne (160.8 mg, 1.22 mmol); eluent: petroleum ether/EtOAc = 30/1 to 25/1, product obtained 100.1 mg (0.252 mmol) in 62% yield. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60−7.54 (m, 4H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.13−7.08 (m, 4H), 6.99 (d, $J$ = 8.4 Hz, 1H), 6.79−6.76 (m, 4H), 3.84 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.2, 158.3, 158.2, 140.4, 139.6, 138.4, 134.1, 133.7, 133.2, 131.0, 130.9, 130.8, 128.9, 128.1, 125.3, 114.2, 113.4, 113.4, 55.3, 55.1. IR (neat): 2962, 2917, 1609, 1524, 1481, 1259, 1247, 1177, 1091, 1031, 1019, 821, 800, 749 cm$^{-1}$.


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HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{25}O_3$ $[M + H]^+$ 397.1798, found 397.1808.

**Synthesis of 5,5′,5″-(Benzene-1,2,4-triyl)tris(benzo[*d*][1,3]-dioxole) (2l).** Alkyne (259 mg, 1.77 mmol); eluent: petroleum ether/EtOAc = 30/1 to 25/1, product obtained 179.7 mg (0.410 mmol). Yield 69%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.50−7.49 (m, 2H), 7.39 (d, $J$ = 8.4 Hz, 1H), 7.12−7.10 (m, 2H), 6.89 (d, $J$ = 8.0 Hz, 1H), 6.72−6.65 (m, 6H), 5.98 (s, 2H), 5.92 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.2, 147.2, 147.2, 147.2, 146.4, 146.3, 140.4, 139.8, 138.7, 135.4, 135.1, 134.8, 131.0, 129.0, 125.6, 123.3, 123.2, 120.6, 110.3, 110.2, 108.6, 108.0, 108.0, 107.5, 101.2, 100.9, 100.9; IR (neat): 2896, 1472, 1223, 1038, 806, 732 cm$^{-1}$; HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{18}NaO_6$ $[M + Na]^+$ 461.0996, found 461.0997.

**Synthesis of 4,4″-dimethyl-4′-(p-tolyl)-1,1′:2′,1″-terphenyl (2m).**[26] Alkyne (157.6 mg, 1.36 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 135.2 mg (0.388 mmol) in 86% yield; 1H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62−7.55 (m, 4H), 7.46 (d, $J$ = 7.6 Hz, 1H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.11−7.02 (m, 8H), 2.40 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 140.8, 140.0, 139.1, 138.8, 138.4, 137.8, 137.1, 136.1, 136.0, 131.1, 129.7, 129.7, 129.5, 129.2, 128.7, 128.6, 126.9, 125.7, 21.1. IR (neat): 3023, 2919, 2016, 1513, 1481, 1265, 1111, 819, 807, 739 cm$^{-1}$. EI-MS ($m/z$): 348 ($M^+$), 333 ($M^+$ − Me), 318 ($M^+$ − 2Me), 303 ($M^+$ − 3Me).

**Synthesis of 4,4″-Di-*tert*-butyl-4′-(4-(*tert*-butyl)phenyl)-1,1′:2′,1″-terphenyl (2n).**[26] Alkyne (147.2 mg, 0.930 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 129.7 mg (0.273 mmol) in 88% yield. White solid. Mp: 145−146 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.66 (d, $J$ = 1.6 Hz, 1H), 7.60 (d, $J$ = 8.0 Hz, 3H), 7.47−7.44 (m, 3H), 7.23−7.20 (m, 4H), 7.12−7.07 (m, 4H), 1.35 (s, 9H), 1.29 (s, 9H), 1.28 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.2, 149.3, 149.2, 140.8, 139.9, 139.2, 138.7, 138.3, 137.9, 131.0, 129.5, 129.5, 129.2, 126.8, 125.7, 124.7, 124.6, 34.5, 34.4, 31.4, 31.4. IR (neat): 2962, 1482, 1362, 1270, 1112, 1005, 835, 819 cm$^{-1}$. EI-MS ($m/z$): 474 ($M^+$).

**Synthesis of 2,2″-Dimethyl-4′-(*o*-tolyl)-1,1′:2′,1″-terphenyl (2o.**[22] Alkyne (145.2 mg, 1.25 mmol); eluent: petroleum ether/EtOAc = 100/1 to 80/1, product obtained 126.9 mg (0.364 mmol). Yield: 87%. $^1$H NMR (500 MHz, DMSO-$d_6$, 363 K): $\delta$ 7.38 (dd, $J$ = 6.4 Hz, 1.6 Hz, 1H), 7.34 (d, $J$ = 6.4 Hz, 1H), 7.31−7.28 (m, 2H), 7.27−7.25 (m, 2H), 7.19 (d, $J$ = 1.6 Hz, 1H), 7.11−7.04 (m, 4H), 6.99−6.95 (m, 4H), 2.33 (s, 3H), 2.11 (6H). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 363 K): $\delta$ 140.4, 140.0, 139.8, 139.6, 139.5, 138.4, 134.6, 134.5, 134.3, 130.3, 129.8, 129.8, 129.6 (br), 129.1, 128.9, 126.9, 126.7, 126.3, 126.3, 125.3, 124.2, 19.4, 19.2, 19.2. IR (neat): 3060, 3019, 2921, 1472, 1457, 1010, 756, 725 cm$^{-1}$. EI-MS ($m/z$): 348 ($M^+$), 333 ($M^+$ − Me), 318 ($M^+$ − 2Me).

**Synthesis of 2,2″,4,4″,5,5″-Hexamethyl-4′-(2,4,5-trimethylphenyl)-1,1′:2′,1″-terphenyl (2p).** Alkyne (198.7 mg, 1.38 mmol); eluent: petroleum ether/EtOAc = 80/1, product obtained 177.2 mg (0.410 mmol) in 89% yield. $^1$H NMR (500 MHz, DMSO-$d_6$, 363 K): $\delta$ 7.29 (d, $J$ = 6.0 Hz, 1H), 7.24 (d, $J$ = 6.0 Hz, 1H), 7.09 (s, 1H), 7.05 (s, 2H), 6.84−6.80 (m, 4H), 2.50 (s, 9H), 2.24 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.99 (s, 6H). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 363 K): $\delta$ 139.7, 139.3, 138.3, 137.9, 137.7, 137.6, 134.4, 133.7, 133.7, 132.8, 131.6, 131.5, 131.2, 131.0, 130.4, 130.3, 130.2, 129.7, 126.6, 18.9, 18.6, 18.6, 18.1, 18.1, 18.0, 17.9. IR (neat): 2920, 1480, 1450, 1020, 909, 871, 842, 736 cm$^{-1}$. EI-MS ($m/z$): 432 ($M^+$), 417 ($M^+$ − Me).

**Synthesis of 3,3″,4,4″,5,5″-Hexamethoxy-4′-(3,4,5-trimethoxyphenyl)-1,1′:2′,1″-terphenyl (2q).**[25] Alkyne (148.5 mg, 0.773 mmol); eluent/petroleum ether/EtOAc/$CH_2Cl_2$ = 13/1/1 to petroleum ether/EtOAc = 2/1, product obtained 129.3 mg (0.224 mmol) in 87% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.66 (d, $J$ = 1.6 Hz, 1H), 7.63 (dd, $J$ = 8.0 Hz, 1.6 Hz, 1H), 7.56 (d, $J$ = 8.0 Hz, 1H), 6.85 (s, 2H), 6.45 (s, 2H), 6.42 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H), 3.84 (s, 3H), 3.84 (s, 3H), 3.68 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 153.5, 152.8, 152.7, 140.7, 140.7, 139.4, 137.8, 137.0, 136.9, 136.8, 136.4, 136.4, 130.4, 128.6, 126.2, 107.2, 107.1, 104.4, 60.9, 60.9, 56.2, 56.1, 56.0. IR (neat): 2936, 1582, 1484, 1239, 1124, 1006, 822, 730 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{33}H_{40}NO_9$ $[M + NH_4]^+$ 594.2698, found 594.2698.

**Synthesis of 4′-(3,4-Dimethoxyphenyl)-3,3″,4,4″-tetramethoxy-1,1′:2′,1″-terphenyl (2r).** Alkyne (267.1 mg, 1.64 mmol); eluent: petroleum ether/EtOAc = 2/1 to 1/1, product obtained 187 mg (1.13 mmol) in 70% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.64 (d, $J$ = 1.6 Hz, 1H), 7.59 (dd, $J$ = 8.0 Hz, 1.6 Hz, 1H), 7.50 (d, $J$ = 8.0 Hz, 1H), 7.23−7.18(m, 2H), 6.96 (d, $J$ = 8.0 Hz, 1H), 6.87−6.77 (m, 4H), 6.68−6.64 (m, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.85 (s, 6H), 3.62 (s, 3H), 3.60 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.0, 148.5, 148.1, 148.0, 147.6, 147.6, 140.3, 139.8, 138.6, 134.2, 133.7, 133.4, 130.5, 128.5, 125.4, 121.6, 121.6, 119.2, 113.3, 113.2, 111.4, 110.7, 110.6, 110.2, 55.7, 55.7, 55.6, 55.6, 55.5, 55.4. IR (neat): 2929, 2361, 2342, 1522, 1486, 1249, 1141, 1026, 806 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{30}H_{31}O_6$ $[M + H]^+$ 487.21152, found 487.21174.

**Synthesis of 2,11-Difluoro-6-(4-fluorophenyl)triphenylene 3b.** To a stirring solution of **2b** (102 mg, 0.28 mmol) and PIFA (3 equiv) in dry $CH_2Cl_2$ (20 mL) was added $BF_3{\cdot}Et_2O$ (6 equiv) in a dropwise fashion at room temperature, and the mixture was stirred at room temperature until the substrate was fully converted (as monitored by TLC). The reaction was quenched with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with $CH_2Cl_2$ and the combined organic layers were dried with anhydrous $Na_2SO_4$. The solvent was filtered, and the solvent was removed under pressure, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/EtOAc = 300/1 to 100/1) to give product **3b** (47 mg, 0.13 mmol, 46%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.53−8.50 (m, 2H), 8.46−8.40 (m, 2H), 7.96−7.93 (m, 2H), 7.72−7.65 (m, 3H), 7.33−7.30 (m, 2H), 7.24−7.17 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 323 K): $\delta$ 163.8, 163.3, 163.2, 161.8, 161.3, 161.2, 139.0, 137.1, 137.0, 131.3, 131.3, 131.2, 131.2, 131.0, 130.9, 130.9, 130.9, 129.2, 128.9, 128.9, 127.9, 126.6, 126.4, 126.1, 125.7, 125.6, 125.6, 123.8, 121.4, 116.2, 116.2, 116.1, 115.9, 115.9, 115.8, 109.1, 109.1, 108.9, 108.9. IR (neat): 2922, 2850, 1234, 1223, 1158, 822, 803, 799 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{24}H_{13}F_3$ $[M + H]^+$ 358.0964, found 358.0966.

**Synthesis of 2,11-Dichloro-6-(4-chlorophenyl)triphenylene 3c.** To a stirring solution of **2c** (188 mg, 0.461 mmol) and PIFA (3 equiv) in dry $CH_2Cl_2$ (20 mL) was added $BF_3{\cdot}Et_2O$ (6 equiv) in a dropwise fashion at room temperature, and the mixture was stirred at room temperature until the substrate was fully converted (as monitored by TLC). The reaction was worked up and purified by the same procedure in the synthesis of compound **3b** with the eluting solvent system (petroleum ether/EtOAc = 200/1 to 50/1) to give product **3c** (140 mg, 0.345 mmol, 75%). Mp =239−240 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.66 (d, $J$ = 1.2 Hz, 1H), 8.59 (dd, $J$ = 9.2, 1.6 Hz, 2H), 8.53 (d, $J$ = 8.8 Hz, 1H), 8.46 (dd, $J$ = 2.4, 2.4 Hz, 2H), 7.85 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.64 (dd, $J$ = 8.8, 1.6 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, $d_5$-pyridine): $\delta$ 139.9, 139.6, 134.5, 131.3, 131.1, 130.3, 129.9, 129.7, 129.5, 129.3, 129.2, 129.1, 128.9, 127.4, 126.5, 126.4, 125.3, 124.5, 124.5, 122.5. IR (neat): 2976, 1084, 1042, 877 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{24}H_{13}Cl_3$ $[M]^+$ 406.0077, found 406.0082.

**Synthesis of 2,11-Dibromo-6-(4-bromophenyl)triphenylene 3d.** To a stirring solution of **2d** (220 mg, 0.405 mmol) and PIFA (3 equiv) in dry $CH_2Cl_2$ (10 mL) was added $BF_3{\cdot}Et_2O$ (6 equiv) in a dropwise fashion at room temperature, and the mixture was stirred at room temperature until the substrate was fully converted (as monitored by TLC). The reaction was worked up and purified by the same procedure in the synthesis of compound **3b** with the eluting solvent system (petroleum ether/EtOAc = 100/1 to DCM/MeOH = 10/1) to give product **3d** (167 mg, 0.309 mmol, 76%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.66−8.44 (m, 4H), 8.52 (d, $J$ = 8.8 Hz, 1H), 8.46 (d, $J$ = 8.4 Hz, 1H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.77 (d, $J$ = 8.4 Hz, 2H), 7.67−7.62 (m, 4H). $^{13}$C NMR (125 MHz, pyridine-$d_5$, 363 K): $\delta$ 140.3, 139.9, 135.7, 132.6, 131.7, 131.6, 131.4, 131.2, 130.3, 129.7, 129.5, 129.2, 127.2, 127.2, 127.2, 126.3, 126.2, 124.9, 122.8, 122.6, 122.5, 122.3. IR (neat): 2920, 2849, 1739, 1365, 1217, 804, 676 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{24}H_{13}Br_3$ $[M + H]^+$ 537.8562, found 537.8550.


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**Synthesis of 2,11-Dimethoxy-6-(4-methoxyphenyl)-triphenylene (3k).** To a stirring solution of **2k** (134 mg, 0.338 mmol) in dry $CH_2Cl_2$ (10 mL) containing $MeSO_3H$ (10% v/v) was added DDQ (1.5 equiv) at 0 °C. After the solution was stirred at 0 °C for 40 min, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with $CH_2Cl_2$, and the combined organic layers were washed with brine and dried with anhydrous $Na_2SO_4$. The solution was filtered, solvent was removed under pressure, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 8/1) to give product **3k** (90 mg, 0.230 mmol, 68%). Mp = 182−183 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.54 (s, 1H), 8.50 (d, $J$ = 8.8 Hz, 1H), 8.37 (dd, $J$ = 8.0, 8.0 Hz, 2H), 7.81 (d, $J$ = 2.0 Hz, 2H), 7.65−7.61 (m, 3H), 7.18−7.12 (m, 2H), 7.00 (d, $J$ = 8.4 Hz, 2H), 3.91 (s, 6H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.2, 158.6, 158.5, 138.3, 133.8, 131.0, 130.6, 129.0, 128.2, 127.4, 125.0, 124.9, 124.8, 124.1, 124.0, 123.1, 120.4, 115.4(5), 115.4(3), 114.3, 106.0(6), 106.0(2), 55.4, 55.3. IR (neat): 2962, 2917, 1609, 1524, 1481, 1259, 1247, 1177, 1091, 1031, 1019, 821, 800, 749 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{25}O_3$ $[M + H]^+$ 397.1798, found 397.1808.

**Synthesis of 2,11-Dimethyl-6-(*p*-tolyl)triphenylene 3m.** To a stirring solution of **2m** (168 mg, 0.482 mmol) and PIFA (1.2 equiv) in dry $CH_2Cl_2$ was added $BF_3{\cdot}Et_2O$ (2.4 equiv) in a dropwise fashion at −78 °C, and the mixture was stirred at −78 °C until the substrate was fully converted (as monitored by TLC). The reaction was worked up and purified by the same procedure in the synthesis of compound **3b** with the eluting solvent system (petroleum ether/EtOAc = 100/1) to give product **3m** (123 mg, 0.355 mmol, 74%). Mp: 179−180 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.72 (d, $J$ = 1.6 Hz, 1H), 8.55 (d, $J$ = 8.8 Hz, 2H), 8.45 (d, $J$ = 8.0 Hz, 1H), 8.37 (br, 2H), 7.77 (dd, $J$ = 8.8, 1.6 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 2H), 7.42−7.39 (m, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H), 2.57 (s, 6H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 139.2, 138.4, 137.1, 136.7, 136.6, 129.8, 129.7, 129.6, 128.5, 128.5, 128.4, 127.6, 127.4, 127.2, 125.6, 123.5, 123.3, 123.2, 123.2, 121.1, 21.8, 21.1. IR (neat): 2921, 2850, 1260, 1091, 1018, 807, 802 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{27}H_{22}$ $[M + H]^+$ 347.1794, found 347.1796.

**Synthesis of 2,11-Di-*tert*-butyl-6-(4-(*tert*-butyl)phenyl)-triphenylene 3n.** To a stirring solution of **2n** (120 mg, 0.253 mmol) and PIFA (1.5 equiv) in dry $CH_2Cl_2$ was added $BF_3{\cdot}Et_2O$ (3 equiv) in dropwise fashion at −40 °C, and the mixture was stirred at 0 °C until the substrate was fully converted (as monitored by TLC). The reaction was worked up and purified by the same procedure in the synthesis of compound **3b** with the eluting solvent system (petroleum ether/EtOAc = 150/1) to give product **3n** (61.5 mg, 0.130 mmol, 51%). Mp = 239−240 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.80 (d, $J$ = 1.2 Hz, 1H), 8.68−8.61 (m, 4H), 8.57 (d, $J$ = 8.8 Hz, 1H), 7.84 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.74−7.69 (m, 4H), 7.56 (d, $J$ = 8.4 Hz, 2H), 1.52 (s, 18H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.4, 149.8, 149.6, 139.2, 138.5, 129.8, 129.8, 129.6, 128.5, 127.7, 127.5, 127.0, 125.8, 125.1, 125.0, 123.6, 123.2, 121.4, 119.0, 118.9, 35.0, 34.6, 31.5, 31.4. IR (neat): 2961, 1486, 1362, 1265, 908, 813, 737 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{36}H_{40}$ $[M + H]^+$ 473.3203, found 473.3207.

**Synthesis of 10-(3,4-Dimethoxyphenyl)-2,3,6,7-tetramethoxytriphenylene 3r.** To a stirring solution of substrate **2r** (49 mg, 0.101 mmol) in dry $CH_2Cl_2$ containing $MeSO_3H$ (10% v/v) was added DDQ (1.5 equiv) at 0 °C. After the solution was stirred at 0 °C for 40 min, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with $CH_2Cl_2$, and the combined organic layers were washed with brine and dried with anhydrous $Na_2SO_4$. The solution was filtered, the solvent was removed under pressure, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/EtOAc = 3/2 to 1/1) to give product **3r** (35 mg, 0.072 mmol) in 72% yield. Mp = 235−236 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.48 (d, $J$ = 1.4 Hz, 1H), 8.44 (d, $J$ = 8.6 Hz, 1H), 7.90 (s, 1H), 7. 87 (s, 1H), 7.75 (dd, $J$ = 8.6, 1.4 Hz, 1H), 7.64 (s, 2H), 7.34 (dd, $J$ = 8.2, 2.0 Hz, 1H), 7.28 (d, $J$ = 2.0 Hz, 1H), 7.04 (d, $J$ = 8.2 Hz, 1H), 4.09 (s, 12H), 4.02 (s, 3H), 3.97 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.3, 149.2, 148.8, 148.7, 148.6, 138.5, 134.4, 128.9, 127.5, 125.0, 124.0, 123.6, 123.3, 123.2, 120.7, 119.8, 111.6, 110.9, 104.5, 104.4, 104.0, 56.1, 56.0, 55.9, 55.9, 55.8. IR (neat): 2932, 1507, 1465, 1413, 1263, 1250, 1216, 1156, 1026 cm$^{-1}$. HRMS (FT-ICR): $m/z$ calcd for $C_{30}H_{28}NaO_6$ $[M + Na]^+$ 507.17781, found 507.17728.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H NMR and $^{13}$C NMR spectra. 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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