Supporting Information

For

Cyclotrimerization of terminal alkynes catalyzed by the system of $NiCl_2$/Zn and (benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines

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Content

General Considerations

All the cyclotrimerization reactions were carried out in pre-dried a screwcapped test tube with a Teflon-lined septum or standard Schlenk tube. All solvents were purified by conventional methods, distilled and stored under nitrogen. Zinc powder was activated over dilute hydrochloric acid. Zinc iodide was prepared by the reaction of zinc powder with element iodine in diethyl ether. L4 was commercially available and the others were prepared according to literature procedures. The alkynes (**1c-1k**) were synthesized by the conventional reactions while the other alkynes (**1a**, **1b** and **1l-1s**) were commercially available and were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel purchased from commercial sources, and components were located by observation under UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM-ECA300 spectrometer at ambient temperature with $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of TMS (0), to the carbon resonance of the $CDCl_3$ (77.16). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d refer to multiplet, singlet, and doublet. GC-MS spectra were recorded on Hewlett Packard GC-MS system. Mass spectra were obtained using Bruker Esquire ion trap mass spectrometer in positive mode.

Experimental Procedures

A typical procedure for the cyclotrimerization reaction of alkynes: Zinc powder (6.5 mg, 0.10 mmol), 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)-pyridine **L2**(22 mg, 0.06 mmol), $NiCl_2 \cdot 6H_2O$ (12 mg, 0.05 mmol), and zinc iodide (32 mg, 0.10 mmol) were added to a standard Schlenk tube. The tube was then evacuated and backfilled with N_2 (3 cycles). Phenylacetylene **1a** (110 μL, 1 mmol) and acetonitrile (2.0 mL) were added by syringe at room temperature. The resulting mixture was stirred at the same temperature for 1 h. Then, the reaction mixture was quenched with dilute hydrochloric acid (3 M) followed by extraction with diethyl ether (3 × 5 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent to afford desired product **2a** (96 mg, 94%). The isomeric ratio was determined via careful integration of ^1H NMR-spectra of the products.

^{1}H NMR and ^{13}C NMR Data

1,2,4-Triphenylbenzene (**2a**).[1,2] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15-7.22 (m, 10H), 7.37-7.52 (m, 4H), 7.64-7.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.24, 126.66, 126.72, 127.26, 127.55, 128.04, 128.06, 128.96, 129.54, 130.00, 130.04, 131.24, 139.68, 140.49, 140.71, 141.13, 141.24, 141.63. GC-MS (EI, *m/z*, rel intensity): 306 (100, M^+), 289 (24), 228 (14).

1,3,5-Triphenylbenzene (**3a**).[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.41 (m, 3H), 7.48 (t, J = 7.6 Hz, 6H), 7.70 (d, J = 7.9 Hz, 6H), 7.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.32, 127.51, 127.69, 128.99, 141.28, 142.49. GC-MS (EI, *m/z*, rel intensity): 306 (100, M^+), 289 (11), 228 (12).

1,2,4-Tris(4-methylphenyl)benzene (**2b**).[3] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 6H), 2.40 (s, 3H), 7.03–7.11 (m, 8H), 7.26 (d, J = 6.9 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.55–7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.26, 125.84, 127.07, 128.80, 128.82 129.38, 129.67, 129.84, 129.88, 131.24, 136.12, 136.21, 137.23, 137.95, 138.53, 138.93, 139.30, 140.16, 140.95. GC-MS (EI, *m/z*, rel intensity): 348 (100, M^+), 333 (12), 318 (14).

1,3,5-Tris(4-methylphenyl)benzene (**3b**).[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 9H), 7.26 (d, J = 7.9 Hz, 6H), 7.58 (d, J = 7.9 Hz, 6H), 7.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.28, 124.71, 127.33, 129.67, 137.39, 138.56, 142.31. GC-MS (EI, *m/z*, rel intensity): 348 (100, M^+), 333 (16), 318 (20).

1,2,4-Tris-(4-methoxyphenyl)benzene (**2c**).[4,5] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 6H), 3.85 (s, 3H), 6.77 (d, J = 2.8 Hz, 2H), 6.79 (d, J = 2.8 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 7.08–7.13 (m, 4H), 7.43 (d, J = 7.9 Hz, 1H), 7.53-7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.25, 55.41, 113.53, 113.56, 114.37, 125.47, 128.19, 129.00, 130.99, 131.03, 131.11, 133.32, 133.85, 134.28, 138.58, 139.70, 140.51, 158.38, 158.45, 159.34.

1,3,5-Tris(4-(*N*,*N*-dimethylamino)phenyl)benzene (3d).[4] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.01 (s, 18H), 6.85 (d, J = 8.9 Hz, 6H), 7.62 (d, J = 8.9 Hz, 6H), 7.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.72, 112.92, 122.68, 128.03, 129.93, 142.14, 150.13.

1,2,4-Tris(4-methoxycarbonylphenyl)benzene (**2f**). Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 6H), 3.95 (s, 3H), 7.21-7.26 (m, 4H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.70-7.75 (m, 4H), 7.86-7.92 (m, 4H), 8.14 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.1, 52.25, 127.06, 127.13, 128.78, 128.84, 129.52, 129.55, 129.89, 129.93, 130.34, 131.28, 139.48, 140.02, 140.37, 144.55, 145.30, 145.62, 166.90. ESI-MS (*m/z*): 503 ($M + Na^+$).

1,3,5-Tris(4-methoxycarbonylphenyl)benzene (**3f**). White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 9H), 7.74 (d, *J* = 8.3 Hz, 6H), 7.83 (s, 3H), 8.14 (d, *J* = 8.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.30, 126.08, 127.34, 129.55, 130.34, 141.64, 144.99, 166.91.

1,2,4-Tris(4-acetylphenyl)benzene (**2g**).[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, 6H), 2.66 (s, 3H), 7.25-7.31 (m, 4H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.71-7.78 (m, 4H), 7.83-7.87 (m, 4H), 8.07 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.60, 26.67, 127.04, 127.23, 128.26, 128.28, 129.06, 129.40, 129.97, 130.04, 131.29, 135.58, 135.64, 136.25, 139.31, 139.86, 140.17, 144.51, 145.36, 145.70, 197.62, 197.69. ESI-MS (*m/z*): 433 ($M + H^+$).

1,3,5-Tris(4-acetylphenyl)benzene (**3g**).[6] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66 (s, 9H), 7.79 (d, *J* = 8.3 Hz, 6H), 7.87 (s, 3H), 8.09 (d, *J* = 8.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.80, 126.19, 127.58, 129.18, 136.49, 141.67, 145.13, 197.70.

1,2,4-Tris(4-chlorophenyl)benzene (**2h**).[2] Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.09 (m, 4H), 7.19-7.23 (m, 4H), 7.39–7.45 (m, 3H), 7.54-7.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.47, 128.43, 128.48, 128.52, 129.19, 131.15, 131.20, 131.26, 133.09, 133.19, 133.91, 138.63, 138.75, 139.16, 139.52, 139.70, 139.94. GC-MS (EI, *m/z*, rel intensity): 410 (100, M^+), 338 (71), 302 (47)

1,3,5-Tris(4-chlorophenyl)benzene (**3h**).[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.6 Hz, 6H), 7.59 (d, *J* = 8.6 Hz, 6H), 7.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.17, 128.70, 129.23, 134.09, 139.34, 141.60.

1,2,4-Tris(4-bromophenyl)benzene (**2i**).[2] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99-7.04 (m, 4H), 7.36-7.40 (m, 4H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.51-7.61

(m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.37, 121.44, 122.14, 126.50, 128.80, 129.03, 129.17, 131.28, 131.49, 132.18, 138.66, 139.24, 139.63, 139.74, 139.81, 139.97.

1,2,4-Tris(4-biphenyl)benzene (2j).[4] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.80 (m, 30H).

1,3,5-Tris(4-biphenyl)benzene (3j).[4] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.50 (m, 9H), 7.67 (d, *J* = 7.2 Hz, 6H), 7.73 (d, *J* = 8.3 Hz, 6H), 7.81 (d, *J* = 8.3 Hz, 6H), 7.89 (s, 3H).

1,2,4-Tris(3-thienyl)benzene (**2k**).[7] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80-6.85 (m, 2H), 7.08-7.09 (m, 1H), 7.12-7.14 (m, 1H), 7.17-7.22 (m, 2H), 7.40-7.44 (m, 2H), 7.47-7.51 (m, 2H), 7.57-7.61 (m, 1H), 7.67 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.62, 122.96, 123.11, 124.84, 124.97, 125.59, 126.37, 126.47, 128.37, 128.94, 129.05, 130.74, 134.23, 135.09, 135.84, 141.70, 142.10. GC-MS (EI, *m/z*, rel intensity): 324 (100, M^+), 290 (31), 279 (22).

Tri-*n*butylbenzene (**2l+3l**).[2] Colorless liquid. **1,2,4-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90-0.97 (m, 9H), 1.32-1.42 (m, 6H), 1.51-1.61 (m, 6H), 2.52-2.59 (m, 6H), 6.91-6.94 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.14, 14.18, 14.35, 22.69, 23.03, 23.06, 32.17, 32.63, 33.75, 33.95, 35.46, 125.85, 129.10, 129.39, 137.78, 140.25, 140.44. GC-MS (EI, *m/z*, rel intensity): 246 (29, M^+), 203 (29), 161 (100). **1,3,5-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90-0.97 (m, 9H), 1.32-1.42 (m, 6H), 1.51-1.61 (m, 6H), 2.52-2.59 (m, 6H), 6.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.14, 22.69, 33.95, 35.85, 125.99, 142.81. GC-MS (EI, *m/z*, rel intensity): 246 (38, M^+), 204 (100), 147 (51).

Triphenethylbenzene (**2m+3m**). Colorless liquid. **1,2,4-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95-7.01 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H). GC-MS (EI, *m/z*, rel intensity): 390 (41, M^+), 299 (100), 91 (56). **1,3,5-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82 (s, 3H). GC-MS (EI, *m/z*, rel intensity): 390 (25, M^+), 299 (28), 105 (100). ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.59, 34.98, 37.73, 37.89, 38.11, 38.18, 38.24, 126.03, 126.12, 126.45, 126.50, 128.47, 128.56, 128.66, 129.40, 129.71, 137.18, 139.52, 139.70, 141.93, 142.11.

Tris(3-chloropropyl)benzene (**2n+3n**).[7] Colorless liquid. **1,2,4-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02-2.11 (m, 6H), 2.70-2.80 (m, 6H), 3.50-3.60 (m, 6H), 6.98-7.00 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 1H). GC-MS (EI, *m/z*, rel intensity): 308 (33, M^+), 244 (100), 167 (49). **1,3,5-isomer:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02-2.12 (m, 6H), 2.71-2.80 (m, 6H), 3.51-3.60 (m, 6H), 6.87 (s, 3H). GC-MS (EI, *m/z*, rel intensity): 308 (33, M^+), 243 (73), 181 (100). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.29, 29.73, 32.45, 32.81, 33.97, 34.00, 34.16, 44.38, 44.67, 126.70, 129.73, 129.82, 136.52, 138.90, 141.25.

1,3,5-Tris(trimethylsilyl)benzene (**3o**).[8] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 27H), 7.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -0.92, 138.44, 138.97. GC-MS (EI, *m/z*, rel intensity): 294 (12, M^+), 280 (38), 279 (100).

1,2,4-Triethoxycarbonylbenzene (**2p**).[3] Pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36-1.44 (m, 9H), 4.36-4.46 (m, 6H), 7.76 (d, *J* = 7.9Hz, 1H), 8.19 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.15, 14.19, 14.36, 61.78, 62.03, 62.08, 128.96, 130.20, 132.09, 132.20, 132.79, 136.37, 165.08, 166.70, 167.24. GC-MS (EI, *m/z*, rel intensity): 294 (5, M^+), 249 (45), 221 (100).

Hexamethoxycarbonylbenzene (**2s**).[3] White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.54, 133.98, 165.18. GC-MS (EI, *m/z*, rel intensity): 426 (0.7, M^+), 395 (100), 349 (6).

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