

Supporting Information

Switching from Dimerization to Cyclotrimerization Selectivity by FeCl₃ in the Y[N(TMS)₂]₃-Catalyzed Transformation of Terminal Alkynes: A New Strategy for Controlling the Selectivity of Organolanthanide-based Catalysis

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Table of contents

Contents:	pages
1. General experimental details	S1
2. General procedure	S2
3. Experimental characterization data for products	S2-S5
4. NMR spectra of all new compounds	S6-S8

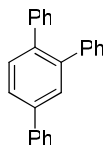
General experimental details

All reactions were carried out under argon atmosphere using the standard Schlenk techniques. The solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen. All substrates were commercially available and purified by standard procedure. ¹H NMR spectra and ¹³C NMR spectra were recorded at a Bruker 400 MHz using CDCl₃ as solvent. GC-MS were obtained on a Hewlett Packard 6890/5973 instrument. High resolution mass spectra (HRMS) were recorded using ESI ionization sources.

General procedure for the cyclotrimerization of alkyne: To a mixture of Y[N(TMS)₂]₃ (23 mg, 0.04 mmol) and FeCl₃ (6 mg, 0.04 mmol) in 5 mL toluene was added 0.80 mmol of alkyne. The mixture was stirred at 50 °C for 24 h. Then the reaction was quenched with water and the aqueous layer was extracted with ether (3×10 mL) and subsequent ethyl acetate (3×10 mL). The combined organic layer was dried over Na₂SO₄. After filtration and removal of solvents in vacuum, the crude product was purified with flash chromatography using petroleum ether as eluent.

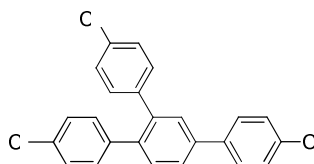
Experimental characterization data for products:

1,2,4-Triphenylbenzene (2a)¹



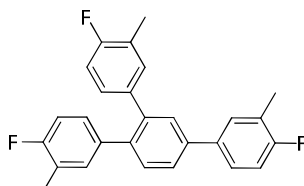
¹H NMR (CDCl₃, 400 MHz) δ 7.71-7.59 (m, 4H), 7.54-7.40 (m, 3H), 7.39-7.30 (m, 1H), 7.16-7.21 (m, 10H). ¹³C NMR (CDCl₃, 100MHz) δ 141.62, 141.25, 141.12, 140.71, 140.49, 139.68, 131.25, 130.04, 130.01, 129.56, 128.96, 128.07, 128.04, 127.57, 127.27, 126.73, 126.66, 126.26.

1,2,4-Tris(4-chlorophenyl)benzene (2b)²



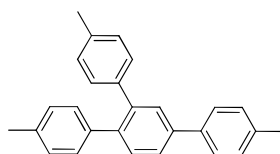
¹H NMR (CDCl₃, 400 MHz) δ 7.64 – 7.54 (m, 4H), 7.49 – 7.40 (m, 3H), 7.25 – 7.21 (m, 4H), 7.12 – 7.05 (m, 4H). ¹³C NMR (CDCl₃, 100MHz) δ 139.96, 139.71, 139.53, 139.17, 138.76, 138.65, 133.93, 133.20, 133.11, 131.28, 131.20, 131.16, 129.22, 129.20, 128.54, 128.50, 128.44, 126.49.

1,2,4-tri(3-methyl-4-fluorophenyl)benzene(2c)³



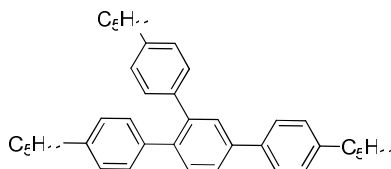
¹H NMR (CDCl₃, 400 MHz) δ 7.64 – 7.57 (m, 2H), 7.56 – 7.42 (m, 3H), 7.17 – 7.03 (m, 3H), 7.00 – 6.80 (m, 4H), 2.40 (d, J = 1.7, 3H), 2.31 – 2.22 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 162.53, 161.77, 161.72, 160.09, 159.33, 159.28, 137.18, 137.15, 136.76, 132.89, 132.87, 132.84, 132.82, 131.11, 130.31, 130.25, 129.22, 128.97, 128.92, 128.89, 128.84, 126.09, 126.07, 126.01, 125.40, 125.38, 125.23, 125.21, 124.61, 124.55, 124.44, 124.37, 115.59, 115.37, 114.73, 114.70, 114.51, 114.48, 14.83, 14.80, 14.66, 14.62.

1,2,4-Tris(4-methylphenyl)benzene(2d)^{1,2}



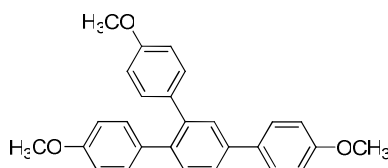
^1H NMR (CDCl_3 , 400 MHz) δ 7.63 – 7.54 (m, 4H), 7.46 (d, J = 7.8, 1H), 7.25-7.29 (m, 2H), 7.12 – 7.02 (m, 8H), 2.41 (s, 3H), 2.33 (d, J = 1.4, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.95, 140.20, 139.31, 138.93, 138.53, 137.96, 137.28, 136.26, 136.17, 131.27, 129.90, 129.86, 129.70, 129.42, 128.85, 128.82, 127.10, 125.88, 21.30, 21.29.

1,2,4-Tris(4-phenylphenyl)benzene(2e)



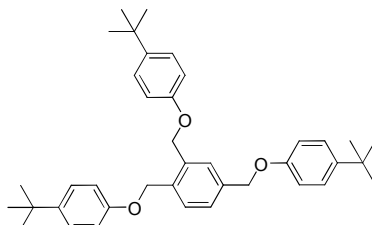
^1H NMR (CDCl_3 , 400 MHz) δ 7.64 – 7.57 (m, 4H), 7.47 (d, J = 8.4Hz, 1H), 7.27 – 7.25 (m, 3H), 7.10-7.01 (m, 7H), 2.66-2.54 (m, 6H), 1.67 – 1.55 (m, 6H), 1.38 – 1.25 (m, 12H), 0.92-0.87 (m, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 142.29, 141.21, 141.13, 141.02, 140.15, 139.37, 139.09, 138.69, 138.17, 131.13, 129.88, 129.84, 129.34, 129.01, 128.99, 128.05, 128.01, 127.07, 125.82, 35.76, 35.68, 31.73, 31.64, 31.62, 31.33, 31.15, 31.14, 22.73, 22.70, 14.22, 14.20. HRMS-ESI: Calcd for $\text{C}_{39}\text{H}_{48}$: 516.3756, found: 516.3758.

1,2,4-Tris(4-methoxyphenyl)benzene (2f)²



^1H NMR (CDCl_3 , 400 MHz) δ 7.61-7.55 (m, 5H), 7.44 (d, J = 7.6, 1H), 7.14 – 7.08 (m, 4H), 7.00 – 6.98 (m, 2H), 6.80 – 6.77 (m, 4H), 3.86 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (CDCl_3 , 100MHz) δ 159.31, 158.43, 158.35, 140.49, 139.70, 138.56, 134.24, 133.83, 133.31, 131.13, 131.04, 130.99, 129.02, 128.21, 125.48, 114.35, 113.54, 113.51, 55.42, 55.25.

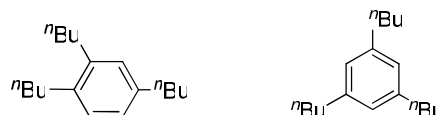
1,2,4-Tris(4-tert-butylphenoxy)methyl)benzene (2g)



^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (s, 1H), 7.59 (d, J = 7.4Hz, 1H), 7.49 (d, J =7.4Hz), 7.38-7.35 (m, 6H), 6.99-6.96 (m, 6H), 5.21 (s, 4H), 5.12 (s, 2H), 1.37 (s, 27H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.65, 156.56, 156.53, 143.92, 143.88, 143.83, 143.79, 138.25, 137.64, 135.78, 135.18, 129.28, 128.04, 127.40, 126.40, 114.46, 114.44,

114.43 , 69.75, 68.10, 67.89, 34.22, 31.67. HRMS-ESI: Calcd for C₃₉H₄₈O₃: 564.3603, found: 564.3600.

1,2,4-Tri-*n*-butylbenzene (2h) and 1,3,5-Tri-*n*-butylbenzene (3h)²



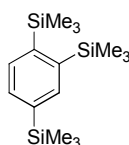
¹H NMR (CDCl₃, 400 MHz) of the mixture of the two products: δ 7.10 (d, *J* = 7.2Hz, 1H), 7.01-7.97 (m, 2H), 6.87 (s, 3H), 2.65-2.58 (m, 12H), 1.68-1.57 (m, 12H), 1.50-1.37 (m, 12H), 1.02-0.96 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz) of the mixture of the two products: δ 142.80, 140.43, 140.24, 137.77, 129.38, 129.10, 125.98, 125.85, 35.84, 35.46, 33.95, 33.92, 33.76, 33.74, 32.62, 32.17, 23.06, 23.02, 22.69, 22.65, 14.18, 14.14.

1,2,4-Tri-*n*-hexylbenzene (2i) and 1,3,5-Tri-*n*-hexylbenzen (3i)²



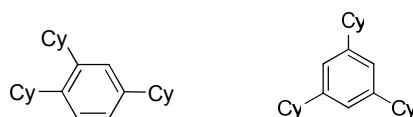
¹H NMR (CDCl₃, 400 MHz) of the mixture of the two products: δ 7.11 (d, *J* = 7.6Hz, 1H), 7.00 (m, 2H), 6.87 (s, 3H), 2.66-2.59 (m, 12H), 1.66-1.59 (m, 12H), 1.38-1.33 (m, 36H), 0.97-0.94 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz) of the mixture of the two products: δ 142.81, 140.42, 140.26, 137.79, 129.35, 129.08, 125.96, 125.83, 36.15, 35.78, 32.94, 32.51, 31.95, 31.75, 31.56, 29.69, 29.30, 22.81, 22.79, 14.24, 14.18.

1,2,4-tris(trimethylsilyl)benzene(2j)^{3,4}



¹H NMR (CDCl₃, 400 MHz) δ 7.84 (s, 1H), 7.66 (d, *J* = 7.6Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 0.38 (s, 9H), 0.36 (s, 9H), 0.27 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 146.70, 144.95, 140.12, 139.47, 138.98, 138.44, 134.51, 132.94, 2.13, 2.03, -0.89, -1.06.

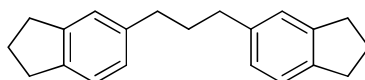
1,2,4-tri(cyclohexylphenyl) benzene (2k) and 1,3,5- tri(cyclohexylphenyl) benzene (3k)



¹H NMR (CDCl₃, 400MHz) of the mixture of the two products: δ 7.16 (d, *J* = 8Hz,

1H), 7.08 (d, $J = 2\text{ Hz}$, 1H), 7.01 (dd, $J = 8.0, 1.6\text{ Hz}$, 1H), 6.89 (s, 3H), 2.81-2.76 (m, 2H), 2.51-2.44 (m, 4H), 1.91-1.74 (m, 24H), 1.50-1.25 (m, 36H). ^{13}C NMR (CDCl_3 , 100MHz) of the mixture of the two products: δ 147.93, 145.16, 144.63, 142.19, 125.72, 124.60, 123.99, 123.05, 44.96, 44.46, 39.42, 39.15, 34.88, 34.85, 34.73, 34.65, 27.47, 27.46, 27.19, 27.18, 26.52, 26.42, 26.41. HRMS-ESI: Calcd for $\text{C}_{24}\text{H}_{36}$: 324.2817, found: 324.2825.

1,3-bis(2,3-dihydro-1H-inden-5-yl)propane (3l)⁵



^1H NMR (CDCl_3 , 400 MHz) δ 7.14 (d, $J = 8\text{ Hz}$, 2H), 7.07 (s, 2H), 6.97 (d, $J = 8\text{ Hz}$, 2H), 2.96-2.86 (t, $J = 7.4\text{ Hz}$, 8H), 2.65-2.61 (t, $J = 7.8\text{ Hz}$, 4H), 2.10-2.03 (m, 4H), 1.97-1.92 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.40, 141.57, 140.38, 126.37, 124.56, 124.21, 35.53, 33.74, 32.94, 32.60, 29.87, 25.66.

References:

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