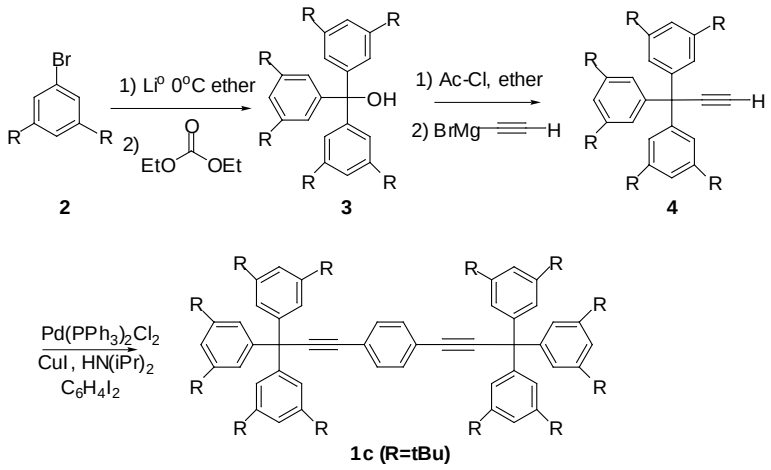
Supplementary Information

Molecular Compasses and Gyroscopes. Engineering Molecular Crystals with Fast Internal Rotation

*Tinh-Alfredo V. Khuong, Gerardo Zepeda,[#] Rebecca Ruiz, Saeed I. Khan, Miguel A. Garcia-Garibay**

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569,



Tris-(3,5-di-*tert*-butylphenyl)methanol (3). 3,5-Di-*tert*-butylphenyl lithium, prepared from bromo-3,5-di-*tert*-butylbenzene (**2**)[1] was reacted with diethyl carbonate to give compound **3** in 82% yield as a colourless crystalline solid after purification by silica gel chromatography using 2% diethyl ether in hexanes as eluant. M.p.=162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 54H), 2.76 (bs, 1H, -OH), 7.06 (d, 64H), 7.28 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.5, 34.9, 83.4, 120.4, 122.6, 146.7, 149.6. FTIR (KBr, cm^{-1}): 3611 (w, dil. -OH), 3414 (b), 2963, 1595, 1477, 1393, 1361, 1247, 1201, 880, 735. HRMS (CI) m/z calculated for $C_{43}H_{64}O$ (M^+) 596.4957; found: 596.4878.

(3,3,3-Tris-(3,5-di-*tert*-butylphenyl))propyne (4). Alcohol **3** was dissolved in a minimum of freshly distilled THF under argon and 5 eq of oxalyl chloride were slowly added at room temperature. The mixture was left under vigorous stirring for 2 hours before it was dried *in vacuo*. The light yellow crude chloride was redissolved in a minimum of THF and 5 eq of 0.5 M ethynylmagnesium bromide in THF were added and left to stir at room temperature for 48 hours. Conventional work up followed purification by silica gel column chromatography using pentane as eluant gave propyne **4** in 89% isolated yield as a colourless crystalline solid. M.p.=199-200 ^{o}C; ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 54H), 2.68 (s, 1H, terminal alkyne), 7.07 (d, 6H), 7.31 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 31.6, 34.8, 56.1, 72.0, 90.7, 119.9, 123.9, 144.8, 149.6. FTIR (KBr, cm^{-1}): 3307, 2965, 2242, 1592, 1477, 1393, 1362, 1249, 1183, 877, 724, 626. . HRMS (MALDI-TOF) m/z calculated for $C_{45}H_{64}$ (M^+) 604.5008; found: 604.4971.

1,4-Bis-[(3,3,3-tris-(3,5-di-*tert*-butylphenyl))propynyl]benzene (1c). The procedure reported by Glass *et al* was followed to complete conversion of the alkyne.[2] Silica gel chromatography with hexanes as the eluant gave **1c** as a crystalline white solid in 64% isolated yield. M.p.=332-334 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 108H), 7.07 (d, 12H J-1.76 Hz), 7.28 (t,6H), 7.44 (s, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 31.2, 34.7, 56.7, 83.7, 98.4, 119.7, 123.5, 123.8, 131.2, 145.1, 149.6. FTIR (KBr, cm^{-1}): 2964, 1593, 1508, 1477, 1430, 1393, 1362, 1248, 1184, 877, 835, 723. HRMS (MALDI-TOF) m/z calculated for $C_{96}H_{130}$ (M^+) 1283.02; found: 1283.65.

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1 Bartlett, P. D.; Roha, M.; Stiles, M. *J. Am. Chem. Soc.* **1954**, *76*, 2349.

2 (a) Z. Dominguez, H. Dang, M. J. Strouse, M. A. Garcia-Garibay, *J. Am. Chem. Soc*, **2001**, *124*, 2398-2399. (b) J. Raker, T. E. Glass, *Tetrahedron* **2001**, *57*, 10233-10240.