Supplementary Material

Preparation of symmetrical C2-C2-linked bis- and tris-6-bromoindoles by Sonogashira couplings and 5-endo-dig cyclization induced by nBu₄NF

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**Experimental technique for preparation of compounds 3a-h** ........................................................... 2S

**1H and 13 C NMR spectra**

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Preparation of dialkynes 3a-h

3,6-diethynyl-9-hexyl-9H-carbazole (3a) was prepared according to the reported procedure: Zhang, W.; Cho, H. M.; Moore, J. S. Org. Synth. 2007, 84, 177-191. 1-Iodohexane was used instead of the 1-bromotetradecane used in the original report for N-alkylation of carbazole.

4,4'-diethynyl-1,1'-biphenyl (3b) was prepared according to the following procedure:

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\begin{align*}
\text{Sonogashira coupling.} & \quad \text{In a dry round bottom flask equipped with a stirring bar and septum under a N}_2 \text{ atmosphere was added 405 mg (1 mmol, 1 equiv.) of 4,4'-diido-biphenyl, 23 mg (0.05 mmol, 0.05 equiv.) of Pd}_2\text{(dba)}_3, 6 mg (0.03 mmol, 0.03 equiv.) of CuI and 16 mg (0.06 mmol, 0.06 equiv.) of PPh}_3 \text{ 10 mL of DMSO and 5 mL of THF. The flask was purged using vacuum, then a current of N}_2 \text{. Then 240 \mu L (2.2 mmol, 2.2 equiv.) of trimethylsilylilacetilene and 350 \mu L (2.5 mmol, 2.5 equiv.) of iPr}_2\text{NH were added to the flask. The mixture was left stirring at 45 °C during 1 h. Then the reaction mixture was diluted with 100 mL of ethyl acetate) and washed with water (2X100 mL) then with brine (1x100mL). The organic portion was dried over anh. Na}_2\text{SO}_4 \text{, filtered and concentrated under vacuum. Column chromatography eluting with hexane gave 236 mg (76%) of a yellow solid, mp 158-160 °C; R}_f = 0.60 (5% EtOAc/hexanes); IR (KBr) 3040, 2957, 2886, 2158, 1489 cm}^{-1}; \text{H RMN (400 MHz, CDCl}_3); \delta 7.51 (s, 8H), 0.24 (d, J = 0.5 Hz, 18H); \text{C RMN (100 MHz, CDCl}_3); \delta 140.2, 132.4, 126.7, 122.4, 104.8, 95.2, -0.1. \]

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\text{Deprotection.} & \quad \text{In a round bottom flask containing an stirring bar and under a N}_2 \text{ atmosphere was added 186 mg (0.78 mmol, 1 equiv) the bis protected acetylene from the previous step, 1.078 g (7.8 mmol, 10 equiv) de K}_2\text{CO}_3 \text{ and 5 mL of methanol. The mixture was}
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stirred for 15 min at room temperature and then concentrated under vacuum. The residue was chromatographed using 95:5 hexanes:EtOAc to obtain 99 mg (63%) of 3b as a yellow solid, mp 160-162 °C; R_f = 0.43 (5% EtOAc/hexanes); IR (KBr) ν 3275, 3038, 2922, 2852, 2107, 1490 cm⁻¹; ¹H RMN (400 MHz, CDCl₃): δ 7.56 (m, 8H), 3.15 (s, 2H); ¹³C RMN (100 MHz, CDCl₃): δ 140.5, 132.6, 126.9, 121.4, 83.4, 78.1.

2,5-diethynyl-morpholinebenzamide (3c) was prepared according to the following procedure:

Sonogashira coupling. In a round bottom flask equipped with a stirring bar and under a N₂ atmosphere was added 221 mg (0.49 mmol, 1 equiv.) of 2,5-diodo morpholine benzamide,* 13 mg (0.025 mmol, 0.05 equiv.) of Pd₂(dba)₃, 3 mg (0.015 mmol, 0.03 equiv) of CuI, and 8 mg (0.03 mmol, 0.06 equiv) of PPh₃. Then was added 5 mL de DMSO and the flask was purged with vacuum followed by a current of N₂. Then, 150 µL (1.05 mmol, 2.1 equiv.) of trimethylsililacetilene and 180 µL (1.25 mmol, 2.5 equiv.) of iPr₂NH were added and the mixture was stirred at 45 °C for 1 h. Then the crude was diluted with 100 mL of ethyl acetate and washed with water (3X60 mL) and brine 1x100 mL. The organic portion was dried over Na₂SO₄, filtered and concentrated under vacuum. Column chromatography using hexane:ethyl acetate gradients (95:5, 90:10, 80:20) gave 166.4 mg (86%) the compound 3c as a yellow solid. mp 155-157 °C; R_f = 0.83 (20% EtOAc/ 80% hexanes); IR (KBr) 3035, 2922, 2860, 2162, 1646, 1251 cm⁻¹; ¹H RMN (400 MHz, CDCl₃): δ 7.41 (m, 3H), 3.75, (m, 8H), 0.24 (m, 18H); ¹³C RMN (100 MHz, CDCl₃): δ 167.8, 139.0, 132.6, 132.2, 130.2, 124.1, 120.0,
103.7, 101.8, 100.6, 98.0, 67.1, 66.8, 47.4, 42.2, 0.1.

**Deprotection.** In a round bottom flask containing an stirring bar, under a N₂ atmosphere was added 133 mg (0.35 mmol, 1 equiv) of the coupling product from the previous step, 434 mg (3.5 mmol, 10 equiv) de K₂CO₃ and 5 mL of methanol and the mixture was stirred at room temperature for 15 min. Column chromatography using gradients of hexanes:ethyl acetate gave 70.4 mg (84%) of 3c as a white solid. mp 129-131 °C; R₇ = 0.33 (40% AcOEt/hexanes); IR (KBr) 3222, 3054, 2924, 2845, 2101, 1627, 1467 cm⁻¹; ¹H RMN (400 MHz, CDCl₃): δ 7.49-7.41 (m, 3H), 3.76 (s, 2H), 3.29-3.27 (m, 4H), 3.26-3.23 (m, 4); ¹³C RMN (100 MHz, CDCl₃): δ 167.44, 139.25, 132.9, 132.4, 129.94, 123.36, 119.28, 82.87, 80.29, 66.82, 66.64, 47.27, 42.11.


**Alkynes 3d-i.**
These compounds were prepared according to the reported procedure: Wang, Y.; Ji, K.; Lan, S.; Zhang, L. Angew. Chem. Int. Ed. 2012, 51, 1915-1918. See the supporting material.
$^1$H and $^{13}$C NMR Spectra
$^1$H NMR spectrum of 2 in acetone-$d_6$, 400 MHz.
$^{13}$C NMR spectrum of 2 in acetone-$d_6$ 100 MHz.
$^1$H NMR spectrum of 3a in CDCl$_3$ 400 MHz
\[ ^{13}\text{C} \text{NMR spectrum of 3a in CDCl}_3 \text{ 100 MHz} \]
$^1$H NMR spectrum of 3b in CDCl$_3$ 400 MHz
\(^{13}\text{C} \text{NMR spectrum of } 3b \text{ in CDCl}_3 \text{ 100 MHz} \)
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The 1H NMR spectrum of compound 4d in CDCl$_3$ at 400 MHz.
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C NMR spectrum of compound 4i in CDCl₃ 100 MHz
$^{1}H$ NMR spectrum of compound 5d in DMSO-$d_6$ 400 MHz
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$\text{H NMR spectrum of compound 5e in DMSO-d6 400 MHz}$
$^{13}$C NMR spectrum of compound 5e in DMSO-$d_6$ 100 MHz
H NMR spectrum of compound \(5f\) in DMSO-\(d_6\) 400 MHz

\[ ^1H \text{ NMR spectrum of compound } 5f \text{ in DMSO-}d_6 \text{ 400 MHz} \]
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$^1$H NMR spectrum of compound 5g in DMSO-$d_6$ 400 MHz
$^{13}$C NMR spectrum of compound \textit{5g} in DMSO-$d_6$ 100 MHz
$^1$H NMR spectrum of compound 5i in DMSO-$d_6$ 400 MHz
$^{13}$C NMR spectrum of compound 5i in DMSO-$d_6$ 100 MHz