Supplementary Material

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

Raúl Balderrama-Martínez-Sotomayor, Mariana Flores-Jarillo, and Alejandro Alvarez-Hernandez*

Área Académica de Química. Universidad Autónoma del Estado de Hidalgo. Carr. Pachuca-Tulancingo Km 4.5. Pachuca, Hidalgo 42184 Mexico

Email: alvarez@uaeh.edu.mx
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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:

Sonogashira coupling. In a dry round bottom flask equipped with a stirring bar and septum under a N₂ atmosphere was added 405 mg (1 mmol, 1 equiv.) of 4,4'-diiodo-biphenyl, 23 mg (0.05 mmol, 0.05 equiv) of Pd₂(dba)₃, 6 mg (0.03 mmol, 0.03 equiv.) of Cul and 16 mg (0.06 mmol, 0.06 equiv.) of PPh₃ 10 mL of DMSO and 5 mL of THF. The flask was purged using vacuum, then a current of N₂. Then 240 µL (2.2 mmol, 2.2 equiv.) of trimethylsilylacetylene and 350 µL (2.5 mmol, 2.5 equiv.) of iPr₂NH 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. Na₂SO₄, 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, ¹H RMN (400 MHz, CDCl₃): δ 7.51 (s, 8H), 0.24 (d, J = 0.5 Hz, 18H); ¹³C RMN (100 MHz, CDCl₃): δ 140.2, 132.4, 126.7, 122.4, 104.8, 95.2, -0.1.

Deprotection. In a round bottom flask containing an stirring bar and under a N₂ 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 K₂CO₃ and 5 mL of methanol. The mixture was
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; Rf = 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](image)

**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-diiodo 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 of DMSO and the flask was purged with vacuum followed by a current of N₂. Then, 150 µL (1.05 mmol, 2.1 equiv.) of trimethylsililacetylene 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; Rf = 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,
Deprotection. In a round bottom flask containing an stirring bar, under a N\textsubscript{2} 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 K\textsubscript{2}CO\textsubscript{3} 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 \textit{3c} as a white solid. mp 129-131 °C; R\textsubscript{f} = 0.33 (40\% AcOEt/hexanes); IR (KBr) 3222, 3054, 2924, 2845, 2101, 1627, 1467 cm\textsuperscript{-1}; \textsuperscript{1}H RMN (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.49-7.41 (m, 3H), 3.76 (s, 2H), 3.29-3.27 (m, 4H), 3.26-3.23 (m, 4); \textsuperscript{13}C RMN (100 MHz, CDCl\textsubscript{3}): \(\delta\) 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
$^{13}$C NMR spectrum of 3a in CDCl$_3$, 100 MHz
$^1$H NMR spectrum of 3b in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of 3b in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of 3c in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of 3c in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of compound 3d in CDCl$_3$ 400 MHz
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$^1$H NMR spectrum of 4a in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of 4a in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of 4b in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of 4b in CDCl$_3$ 100 MHz
\textsuperscript{1}H NMR spectrum of compound 4c in CDCl\textsubscript{3} 400 MHz
$\text{Br-}\begin{array}{c} & \text{NH} \\ \text{O} & \text{O} \\ \text{O} & \text{O}
\end{array}\text{Br}$

$\text{13C NMR spectrum of compound 4c in CDCl}_3$ $100 \text{MHz}$
H NMR spectrum of compound 4d in CDCl₃ 400 MHz
$^{13}$C NMR spectrum of compound 4d in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of compound 4e in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of compound 4e in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of compound 4f in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of compound 4f in CDCl$_3$ 100 MHz
\(^1\)H NMR spectrum of compound 4g in CDCl\(_3\) 400 MHz
$\ ^{13}\text{C} \text{ NMR spectrum of compound 4g in CDCl}_3 \ 100 \text{ MHz}$
$^1$H NMR spectrum of compound 4h in CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of compound 4h in CDCl$_3$ 100 MHz
$^1$H NMR spectrum of compound 4i in CDCl$_3$ 400 MHz
$^{13}$C NMR spectrum of compound 4i in CDCl$_3$ 100 MHz.
$^{1}H$ NMR spectrum of compound 5d in DMSO-$d_6$ 400 MHz
$^{13}$C NMR spectrum of compound 5d in DMSO-d6 100 MHz
$^1$H NMR spectrum of compound 5e in DMSO-d$_6$ 400 MHz
$^{13}$C NMR spectrum of compound 5e in DMSO-$d_6$ 100 MHz
$^1$H NMR spectrum of compound 5f in DMSO-$d_6$ 400 MHz
$^{13}$C NMR spectrum of compound 5f in DMSO-$d_6$ 100 MHz
$^1$H NMR spectrum of compound 5g in DMSO-$d_6$ 400 MHz
$\text{C NMR spectrum of compound } 5g \text{ in DMSO-d6 100 MHz}$
$^1$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