Supporting information

One-step preparation of novel 1-(N-indolyl)-1,3-butadienes by base-catalysed isomerization of alkynes as an access to 5-(N-indolyl)-naphthoquinones

C. M. Pis Diez, a,b J. F. Fernandez, a,b G. Di Venosa, c A. Casas, c R. Pis Diez d and J. A. Palermo a,b*

a. Universidad de Buenos Aires, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Ciudad Universitaria, Pabellón 2 – (1428), Buenos Aires, Argentina.
b. CONICET-Universidad de Buenos Aires, Unidad de Microanálisis y Métodos Físicos en Química Orgánica (UMYMFOR), Buenos Aires, Argentina.
c Centro de Investigaciones sobre Porfirinas y Porfirias (CIPYP) CONICET and Hospital de Clínicas José de San Martín, Universidad de Buenos Aires, Córdoba 2351, 1er subsuelo, Ciudad de Buenos Aires, 1120 AAF Buenos Aires, Argentina.
d. CEQUINOR (CONICET-CCT-La Plata, UNLP), Bvd 120 N1465, 1900 La Plata, Argentina.

| Content                                              | Page Number |
|------------------------------------------------------|-------------|
| 1^H and 1^3C spectra of 1a                           | 2           |
| 1^H and 1^3C spectra of 1b                           | 3           |
| 1^H and 1^3C spectra of 2a                           | 4           |
| 1^H and 1^3C spectra of 2b                           | 4           |
| 1^H and 1^3C spectra of 3a                           | 5           |
| 1^H and 1^3C spectra of 3b                           | 6           |
| 1^H and 1^3C spectra of 4a                           | 7           |
| 1^H and 1^3C spectra of 4b                           | 8           |
| 1^H and 1^3C spectra of 5a                           | 9           |
| 1^H and 1^3C spectra of 5b                           | 10          |
| 1^H and 1^3C spectra of 6a                           | 11          |
| 1^H and 1^3C spectra of 6b                           | 11          |
| 1^H and 1^3C spectra of 7a                           | 12          |
| 1^H and 1^3C spectra of 7b                           | 12          |
| 1^H and 1^3C spectra of 1c                           | 13          |
| 1^H and 1^3C spectra of 2c                           | 14          |
| 1^H and 1^3C spectra of 3c                           | 15          |
| 1^H and 1^3C spectra of 4c                           | 16          |
| 1^H and 1^3C spectra of 5c                           | 17          |
| 1^H and 1^3C spectra of 7c                           | 18          |
| 1^H and 1^3C spectra of 1-(but-2-yn-1-yl)-1H-indole | 19          |
| 1^H and 1^3C spectra of 5-bromo-1-(but-2-yn-1-yl)-1H-indole | 20 |
| 1^H and 1^3C spectra of 1-(but-2-yn-1-yl)-6-fluoro-1H-indole | 21 |
| Geometric parameters for species involved in C4 isomerization | 22 |
| Energy diagram of C5 alkyne isomerization            | 22          |
(E)-N-(1,3-butadienyl)-indole (1a): $^1$H NMR (500MHz, CDCl$_3$):

(E)-N-(1,3-butadienyl)-indole (1a): $^{13}$C NMR (125MHz, CDCl$_3$):
(Z)-N-(1,3-butadienyl)-indole (1b): $^1$H NMR (500MHz, CDCl$_3$):

$\text{\begin{figure}[h]}
\centering
\includegraphics[width=0.8\textwidth]{figure1}
\caption{NMR spectrum of (Z)-N-(1,3-butadienyl)-indole (1b).}
\end{figure}\end{equation}$

(Z)-N-(1,3-butadienyl)-indole (1b): $^{13}$C NMR (125MHz, CDCl$_3$):

$\text{\begin{figure}[h]}
\centering
\includegraphics[width=0.8\textwidth]{figure2}
\caption{NMR spectrum of (Z)-N-(1,3-butadienyl)-indole (1b).}
\end{figure}\end{equation}$
(E)-N-(1,3-butadienyl)-5-bromoindole (2a); (Z)-N-(1,3-butadienyl)-5-bromoindole (2a): $^1$HNMR (500MHz, CDCl$_3$)

(E)-N-(1,3-butadienyl)-5-bromoindole (2a); (Z)-N-(1,3-butadienyl)-5-bromoindole (2a): $^{13}$C NMR (125MHz, CDCl$_3$)
(E)-1-(buta-1,3-dien-1-yl)-5-chloro-1H-indole (3a): $^1$H NMR (500MHz, CDCl3)

(3a): $^{13}$C NMR (125MHz, CDCl3)
(E)-1-(buta-1,3-dien-1-yl)-5-chloro-1H-indole (3b): $^1$H NMR (500MHz, CDCl3)

(E)-1-(buta-1,3-dien-1-yl)-5-chloro-1H-indole (3b): $^{13}$C NMR (125MHz, CDCl3)
(Z)-1-(buta-1,3-dien-1-yl)-5-fluoro-1H-indole (4a): $^1$H NMR (500MHz, CDCl₃)

$^{13}$C NMR (125MHz, CDCl₃)
(E)-1-(buta-1,3-dien-1-yl)-5-fluoro-1H-indole (4b): $^1$H NMR (500MHz, CDCl3)

$^1$H NMR (500MHz, CDCl3)

(E)-1-(buta-1,3-dien-1-yl)-5-fluoro-1H-indole (4b): $^{13}$C NMR (125MHz, CDCl3)
(Z)-1-(buta-1,3-dien-1-yl)-6-fluoro-1H-indole (5a): $^1$H NMR (500MHz, CDCl3)

$^{13}$C NMR (125MHz, CDCl3)
(E)-1-(buta-1,3-dien-1-yl)-6-fluoro-1H-indole (5b): $^1$H NMR (500MHz, CDCl3)

(1H NMR (500MHz, CDCl3) spectrum)

(13C NMR (125MHz, CDCl3) spectrum)
(E)-5-(benzyl)oxy-1-(buta-1,3-dien-1-yl)-1H-indole (6a); (Z)-5-(benzyl)oxy-1-(buta-1,3-dien-1-yl)-1H-indole (6b) ¹H NMR (500MHz, CDCl₃) and ¹³C NMR (125MHz, CDCl₃)
(E)-9-(buta-1,3-dien-1-yl)-9H-carbazole (7a); (Z)-9-(buta-1,3-dien-1-yl)-9H-carbazole (7b): $^1$H NMR (500MHz, CDCl3)

(E)-9-(buta-1,3-dien-1-yl)-9H-carbazole (6a); (Z)-9-(buta-1,3-dien-1-yl)-9H-carbazole (6b) $^{13}$C NMR(125MHz, CDCl3)
5-(1H-indol-1-yl)naphthalene-1,4-dione (1c): $^1$H NMR (500MHz, CDCl$_3$)
5-(5-bromo-1H-indol-1-yl)naphthalene-1,4-dione (2c): $^1$H NMR (500MHz, CDCl$_3$)

5-(5-bromo-1H-indol-1-yl)naphthalene-1,4-dione (2c): $^{13}$C NMR (125MHz, CDCl$_3$)
5-(5-chloro-1H-indol-1-yl)naphthalene-1,4-dione (3c): $^1$H NMR (500MHz, CDCl$_3$)

$^{13}$C NMR (125MHz, CDCl$_3$)
5-(5-fluoro-1H-indol-1-yl)naphthalene-1,4-dione (4c): $^1$H NMR (500MHz, CDCl$_3$)

$^1$C NMR (125MHz, CDCl$_3$)
5-(6-fluoro-1H-indol-1-yl)naphthalene-1,4-dione (5c): $^1$H NMR (500MHz, CDCl$_3$):

5-(6-fluoro-1H-indol-1-yl)naphthalene-1,4-dione (5c): $^13$C NMR (125MHz, CDCl$_3$):
5-(9H-carbazol-9-yl)naphthalene-1,4-dione (7c): $^1$H NMR (500MHz, CDCl$_3$)

$^1$H NMR (500MHz, CDCl$_3$)

5-(9H-carbazol-9-yl)naphthalene-1,4-dione (7c): $^{13}$C NMR (125MHz, CDCl$_3$)

$^{13}$C NMR (125MHz, CDCl$_3$)
1-(but-2-yn-1-yl)-1H-indole: $^1$H NMR (500MHz, CDCl$_3$)

1-(but-2-yn-1-yl)-1H-indole: $^{13}$C NMR (125MHz, CDCl$_3$)
5-bromo-1-(but-2-yn-1-yl)-1H-indole: $^1$H NMR (500 MHz, CDCl$_3$)

5-bromo-1-(but-2-yn-1-yl)-1H-indole: $^{13}$C NMR (125 MHz, CDCl$_3$)
1-(but-2-yn-1-yl)-6-fluoro-1H-indole: $^1$H NMR (500MHz, CDCl$_3$)

1-(but-2-yn-1-yl)-6-fluoro-1H-indole: $^{13}$C NMR (125MHz, CDCl$_3$)
Geometric parameters of the lowest-energy conformers of the molecules studied in the present work. Distances ($r$) are in angstroms and dihedral angles ($\tau$) are in degrees.

|           | 7     | 8     | 9     | 10    | 11    | 12    | 1a, 1b |
|-----------|-------|-------|-------|-------|-------|-------|--------|
| $r(C'_1-C'_2)$ | 1.534 | 1.492 | 1.505 | 1.489 | 1.457 | 1.352 | 1.341  |
| $r(C'_2-C'_3)$ | 1.452 | 1.342 | 1.301 | 1.275 | 1.202 | 1.429 | 1.443  |
| $r(C'_3-C'_4)$ | 1.203 | 1.277 | 1.300 | 1.341 | 1.448 | 1.337 | 1.337  |
| $r(N-C'_1)$   | 1.441 | 1.474 | 1.447 | 1.460 | 1.447 | 1.414 | 1.383  |
| $r(C'_2-N)$   | 1.372 | 1.366 | 1.370 | 1.366 | 1.371 | 1.373 | 1.382  |
| $r(C'_7a-N)$  | 1.373 | 1.370 | 1.372 | 1.367 | 1.370 | 1.375 | 1.385  |
| $\tau(C'_2-N-C'_1-C'_2)$ | -86.80 | -39.05 | 93.8 | 117.18 | -113.80 | -5.35 | 10.82  |
| $\tau(N-C'_1-C'_2-C'_3)$ | -169.14 | 98.42 | 110.91 | 164.59 | -144.90 | 167.69 | -179.05 |
| $\tau(C'_1-C'_2-C'_3-C'_4)$ |       |       |       | 75.20 |        |       | -178.79 |

Energy diagram for the C5 alkyne isomerization. Species are numbered in analogy with those in C4.