Supplementary Materials

[2+2] Photodimerization of Naphthylvinylpyridines through Cation-π Interactions in Acidic Solution

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Table of Contents

1. $^1$H NMR spectra for 2a-5a and 2b-4b S1-S8
2. MS spectra for 3a, 4b and 5a S9-S11
3. Plots of second-order kinetics for the formation of 2a S12
1. $^1$H NMR spectra for 2a-5a and 2b-4b

Figure S1. $^1$H NMR spectrum for 2a
Figure S2. $^1$H NMR spectrum for 2b
Figure S3. $^1$H NMR spectrum for 3a
Figure S4. $^1$H NMR spectrum for 3b
Figure S5. $^1$H NMR spectrum for 4a
Figure S6. $^1$H NMR spectrum for 4b
**Figure S7.** $^1$H NMR spectrum for 5a
2. MS spectra for 3a, 4b and 5a

**Figure S8. MS spectrum of 3a**

**Figure S9. Determination of a head-to-head structure of 3a**

m/z = 231 (100%)  
m/z = 280 (26%)
**Figure S10.** MS spectra for 4b

**Figure S11.** Determination of a head-to-tail structure of 4b
Figure S12. MS spectrum of 5a

Figure S13. Determination of a head-to-head structure of 5a
3. Plot of second-order kinetics for the formation of 2a

\[ 1a + 1a \rightarrow 2a \]

\[
\frac{d[1a]}{dt} = -k[1a]^2
\]

\[
-\frac{d[1a]}{[1a]^2} = -kdt
\]

\[
\frac{1}{[1a]} - 1/[1a]_0 = kt
\]

\[
\frac{1}{[1a]} = kt + 1/[1a]_0 \quad ([1a] = [1a]_0/1+kt[1a]_0)
\]

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<th>[1a] (M)</th>
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**Figure S14.** Plot of second-order kinetics for the formation of 2a