Supplementary Materials

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

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1. ^{1}H NMR spectra for 2a-5a and 2b-4b
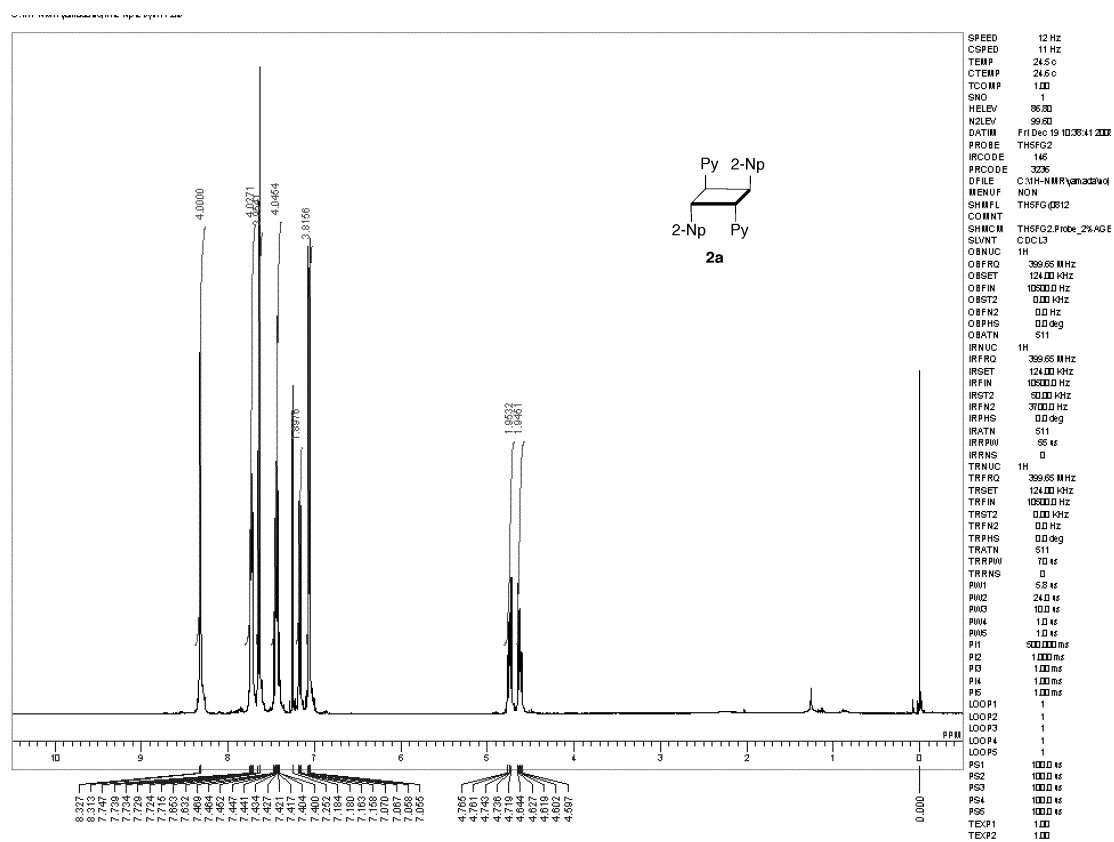
Figure S1. ^{1}H NMR spectrum for **2a**

Figure S2. ^{1}H NMR spectrum for **2b**

Figure S3. ^{1}H NMR spectrum for **3a**
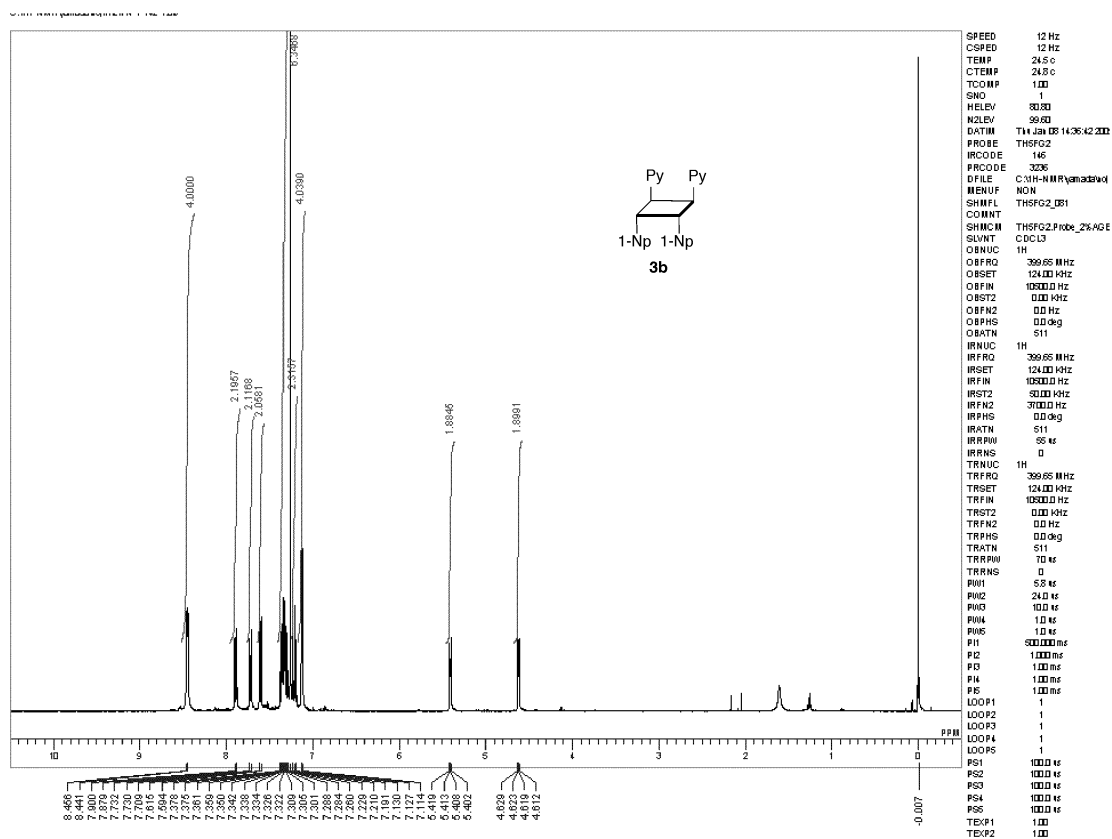
Figure S4. ^{1}H NMR spectrum for **3b**
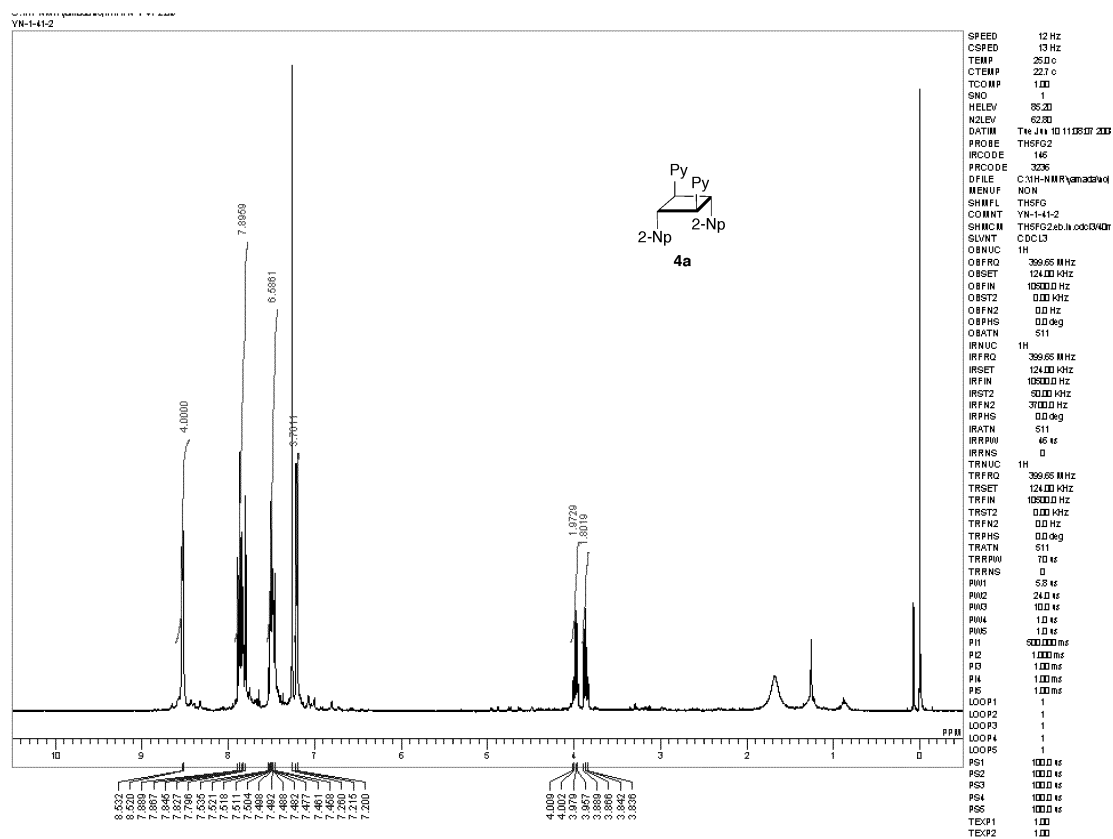
Figure S5. ^{1}H NMR spectrum for **4a**

Figure S6. ^{1}H NMR spectrum for **4b**

Figure S7. ^{1}H NMR spectrum for **5a**

2. MS spectra for 3a, 4b and 5a

[Mass Spectrum]
Data : YN-2-Np-synHH2002   Date : 09-Dec-2008 11:46
Sample: 0
Note : -
Inlet : Direct   Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 3.85 min   Scan# : 232
BP : m/z 231.0000   Int. : 1599.98
Output m/z range : 20.0000 to 500.0000   Cut Level : 0.50 %
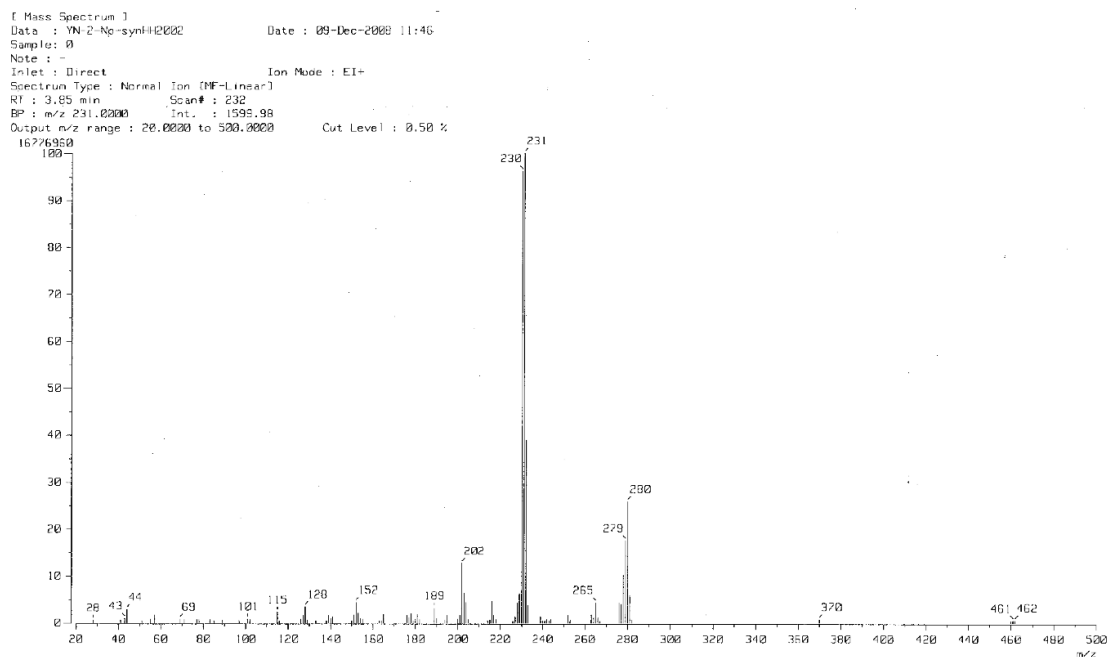
Figure S8. MS spectrum of 3a
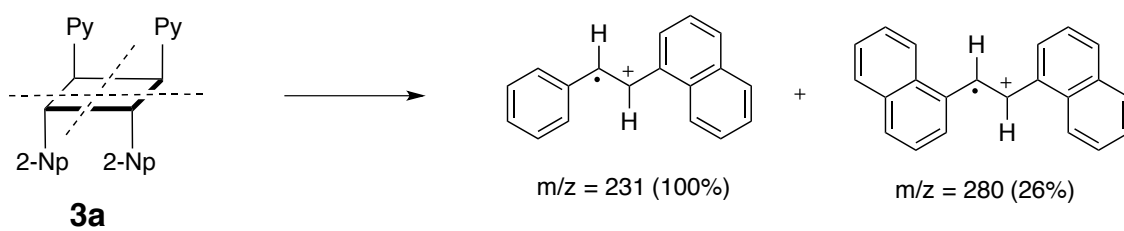
Figure S9. Determination of a head-to-head structure of **3a**

[Mass Spectrum]
Data : YN1-Npanti1001   Date : 02-Feb-2009 10:50
Sample: MS-4-95-11)
Note : -
Inlet : Direct   Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.90 min   Scan# : 115
BP : m/z 231.0000   Int. : 1599.90
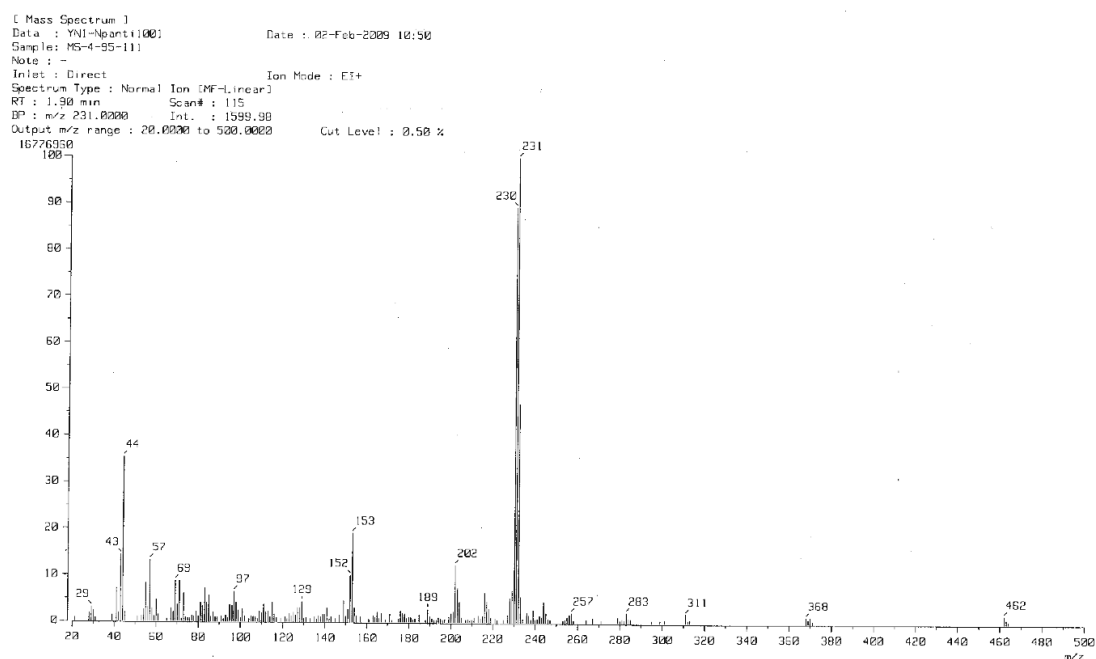Output m/z range : 20.0000 to 500.0000   Cut Level : 0.50 %

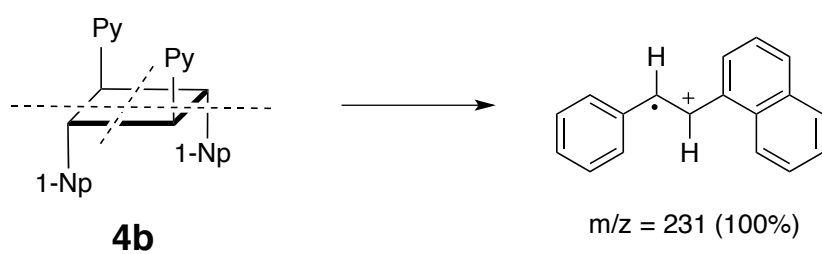**Figure S10.** MS spectra for **4b**

Figure S11. Determination of a head-to-tail structure of **4b**

Figure S12. MS spectrum of **5a**

m/z = 231 (100%) m/z = 280 (44%)
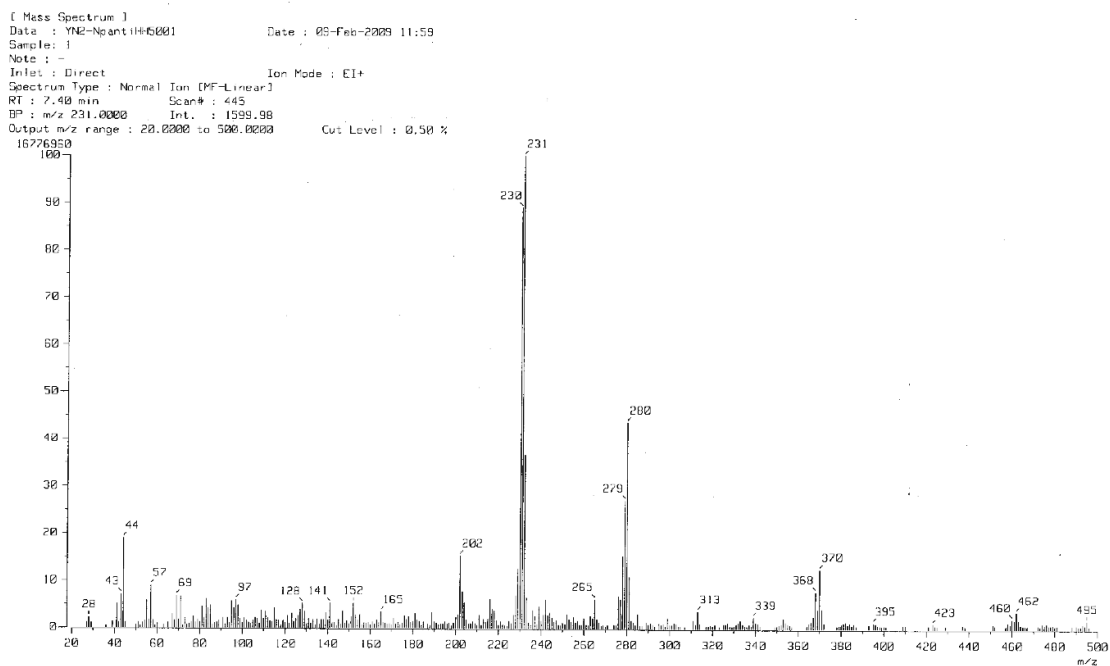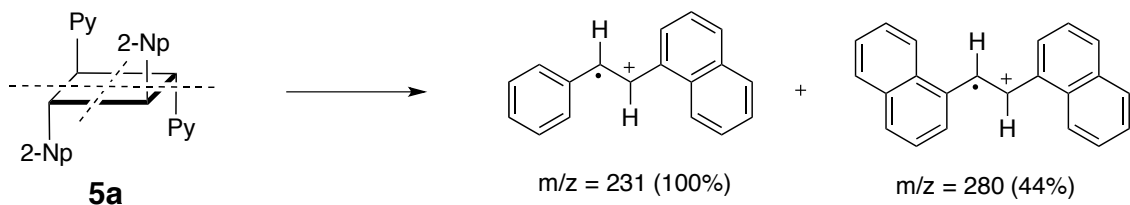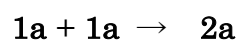
Figure S13. Determination of a head-to-head structure of **5a**

S11

3. Plot of second-order kinetics for the formation of 2a

1a + **1a** $\longrightarrow$ **2a**

$d[\mathbf{1a}]/dt = -k[\mathbf{1a}]^2$

$-d[\mathbf{1a}]/[\mathbf{1a}]^2 = -kdt$

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

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

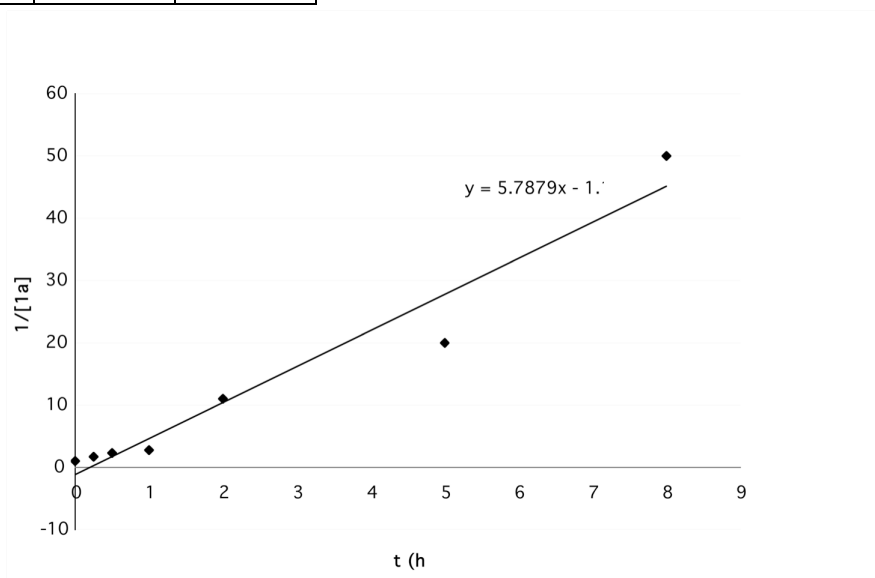| Time (h)	[1a] (M)	1/[1a]
0	1	1
0.25	0.59	1.7
0.5	0.43	2.3
1	0.36	2.8
2	0.09	11
5	0.05	20
8	0.02	50

Figure S14. Plot of second-order kinetics for the formation of **2a**