

Supporting Information

for

Synthesis and Rotation Barriers in 2,6-Di-(*o*-anisyl)anisole

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TABLE OF CONTENTS

^1H NMR spectroscopic assignments for 1d	S2
Figure S1. ^1H - ^1H COSY spectrum for 1d .	S3
Figure S2. Partial ^1H - ^{13}C HMBC spectrum for 1d . (f_2 dimension: ^1H , f_1 dimension: ^{13}C)	S4
Figure S3. Partial ^1H - ^{13}C HMBC spectrum for 1d . (f_2 dimension: ^1H , f_1 dimension: ^{13}C)	S5
Figure S4. Partial ^1H - ^{13}C HMBC spectrum for 1d . (f_2 dimension: ^1H , f_1 dimension: ^{13}C)	S6
Figure S5. Partial ^1H - ^{13}C HSQC spectrum for 1d . (f_2 dimension: ^1H , f_1 dimension: ^{13}C)	S7
Figure S6. Partial ^1H - ^{13}C HSQC spectrum for 1d . (f_2 dimension: ^1H , f_1 dimension: ^{13}C)	S8
Figure S7. Partial 2-D ^1H - ^1H ROESY spectrum of 1d	S9
Figure S8. Two transition states for the interconversions of <i>anti</i> - 1d	S10
Table S1. Geometrical parameters for the species in Figure S8	S10
Table S2. Geometrical parameters for the species in Figure 3 of the paper	S11

1d, ^1H NMR (500 MHz, CD_2Cl_2) δ 3.143 (s, 3H, OMe), 3.816 (s, 6H, OMe), 7.016 (dd, $J = 8.3$, 1.2 Hz, 2H, *ortho* to OMe), 7.018 (dt, $J = 1.1$, 7.6 Hz, 2H, *para* to OMe), 7.147 (A, 1H, *para* to OMe in central ring) and 7.231 (B, 2H, *meta* to OMe in central ring), AB_2 system ($J_{\text{AB}} = 7.6$ Hz), 7.293 (dd, $J = 7.7$, 1.8 Hz, 2H, *meta* to OMe and *ortho* to central ring), 7.357 (ddd, $J = 8.2$, 7.5, 1.8 Hz, 2H, *meta* to OMe and *para* to central ring). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 56.00 (OMe), 60.75 (OMe of central ring), 111.34 (CH, *ortho* to OMe in outer ring), 120.79 (CH, *para* to OMe in outer ring), 123.17 (C_q , *ortho* to OMe in outer ring), 128.61 (C_q , *ortho* to OMe in central ring), 129.23 (CH, *meta* to OMe in outer ring), 131.66 / 131.85 (two CH, *meta* to OMe in central ring / *meta* to OMe and *ortho* to central ring in outer ring), 132.54 (CH, *para* to OMe in central ring), 156.72 ($\text{C}_q\text{-O}$ in central ring), 157.45 ($\text{C}_q\text{-O}$ in outer ring).

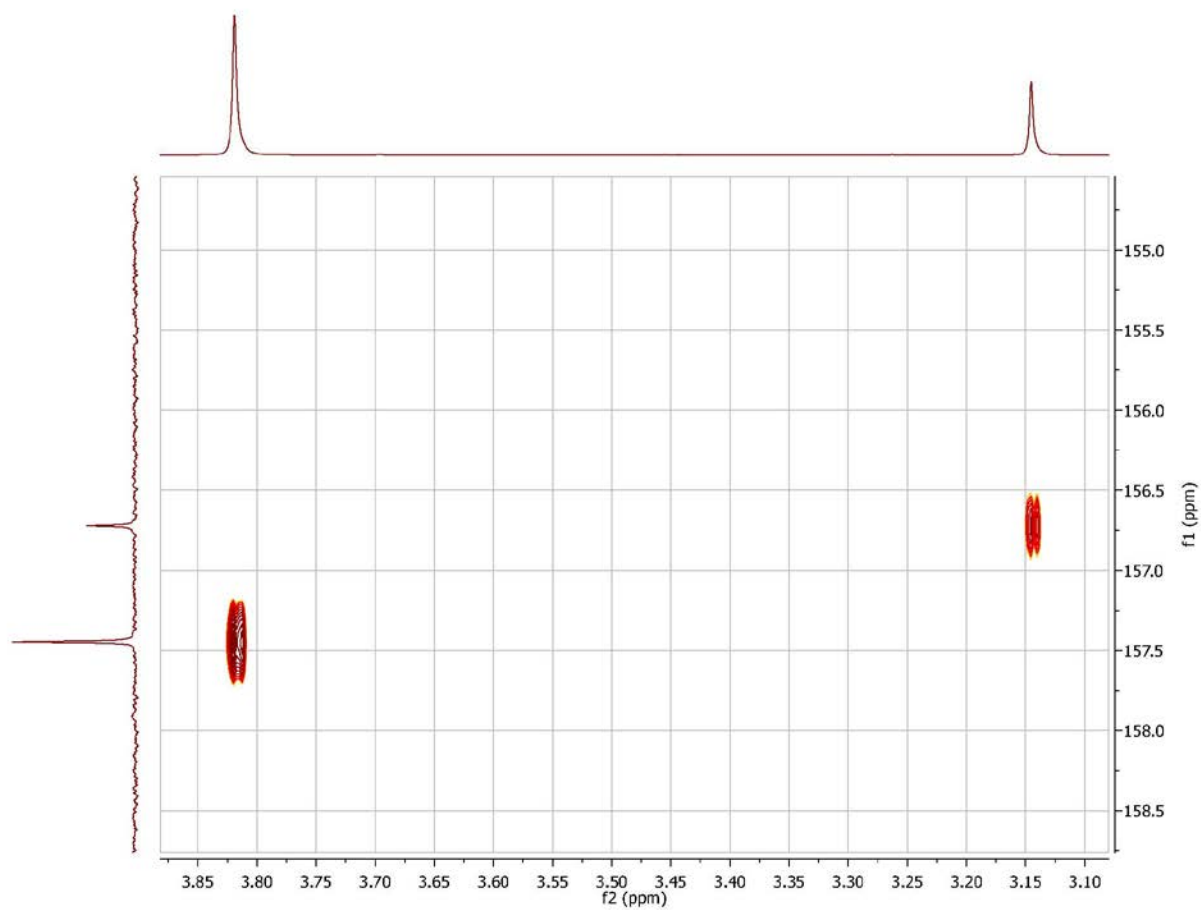


Figure S2. Partial ^1H - ^{13}C HMBC spectrum for **1d**.
(f_2 dimension: ^1H , f_1 dimension: ^{13}C)

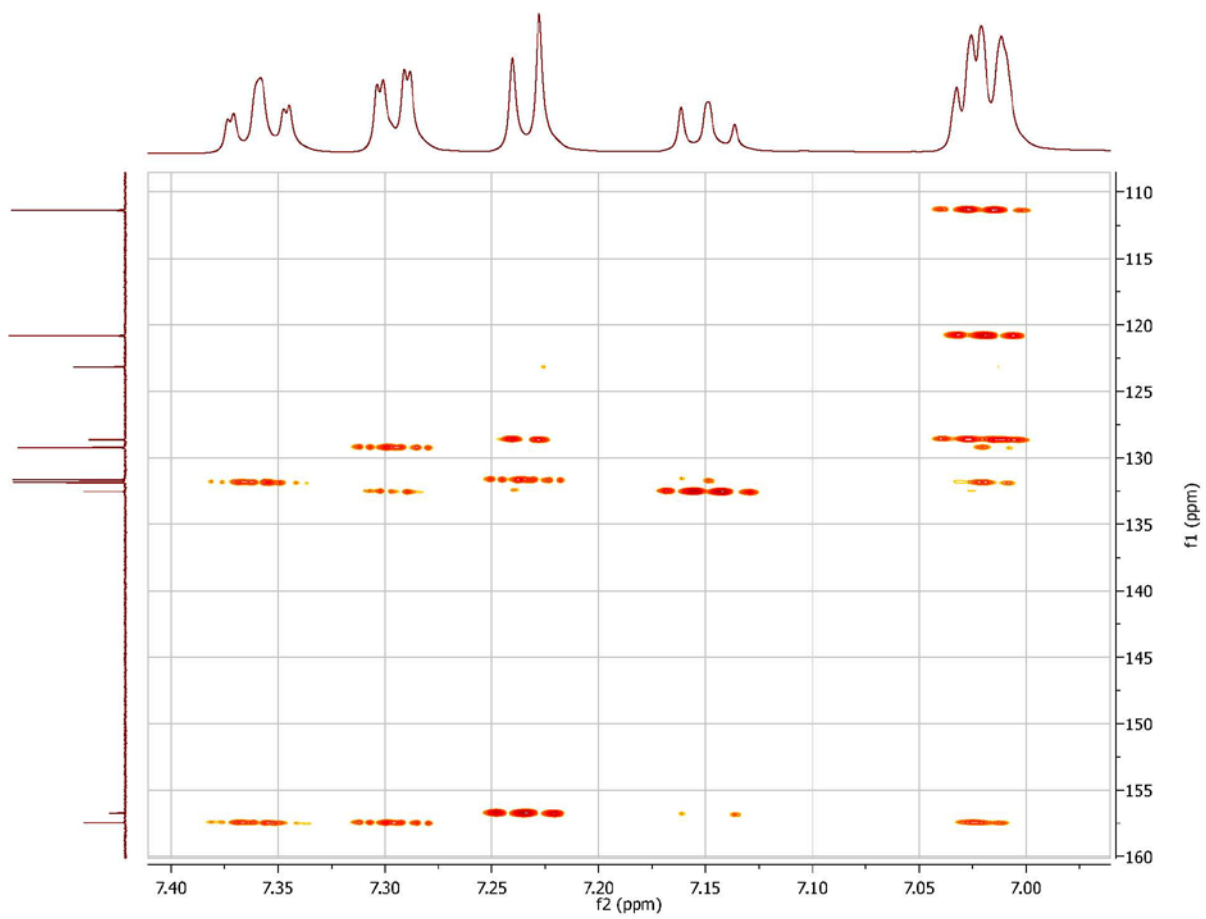


Figure S3. Partial ^1H - ^{13}C HMBC spectrum for **1d**.
(f_2 dimension: ^1H , f_1 dimension: ^{13}C)

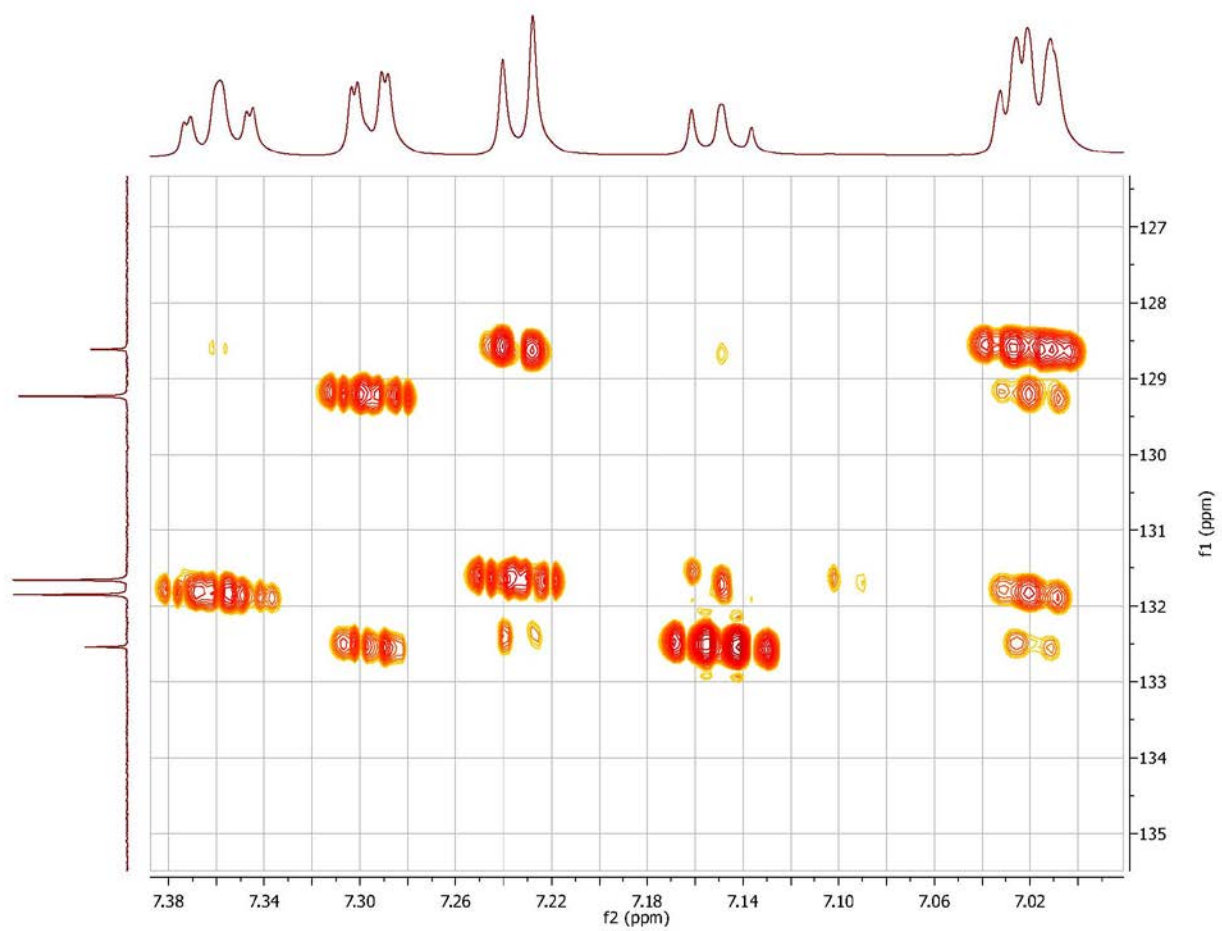


Figure S4. Partial ^1H - ^{13}C HMBC spectrum for **1d**.
(f_2 dimension: ^1H , f_1 dimension: ^{13}C)

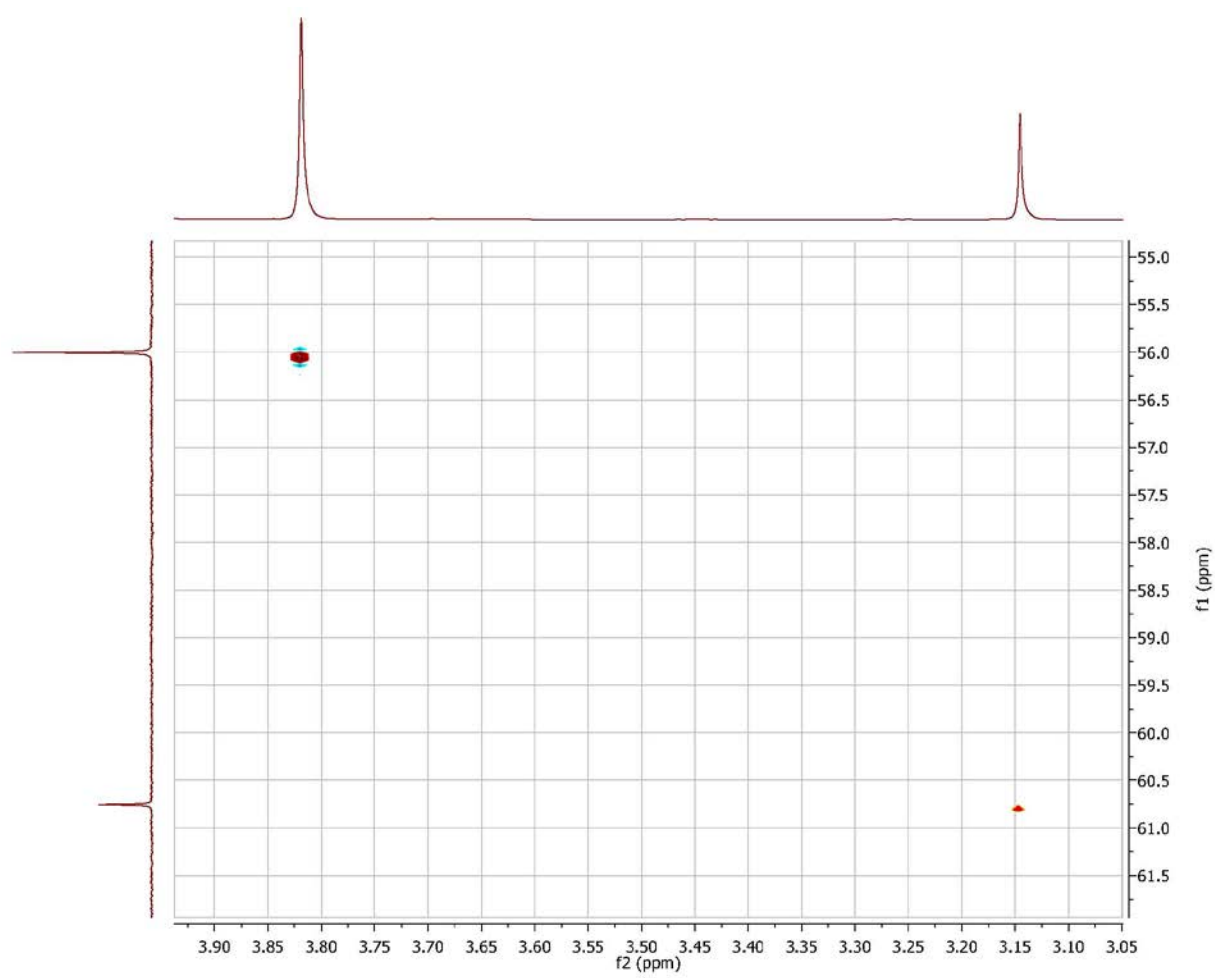


Figure S5. Partial ^1H - ^{13}C HSQC spectrum for **1d**.
(f_2 dimension: ^1H , f_1 dimension: ^{13}C)

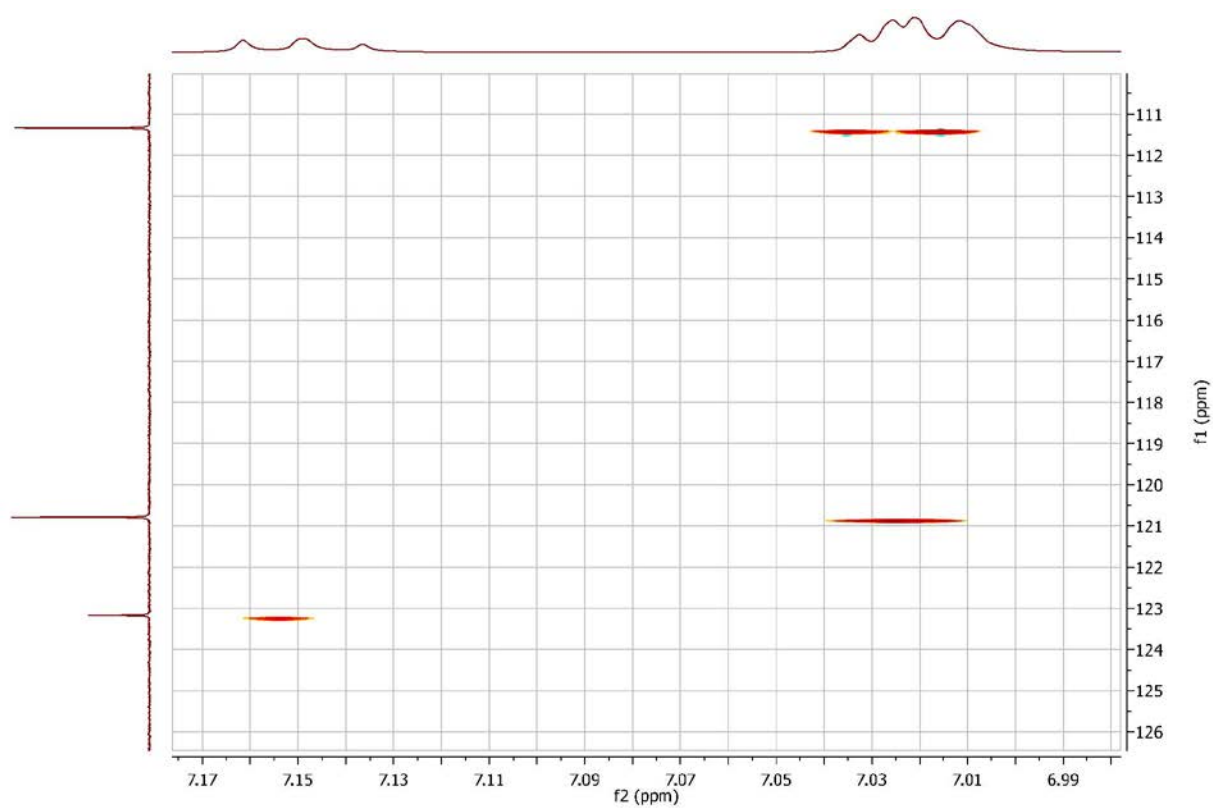


Figure S6. Partial ^1H - ^{13}C HSQC spectrum for **1d**.
(f_2 dimension: ^1H , f_1 dimension: ^{13}C)

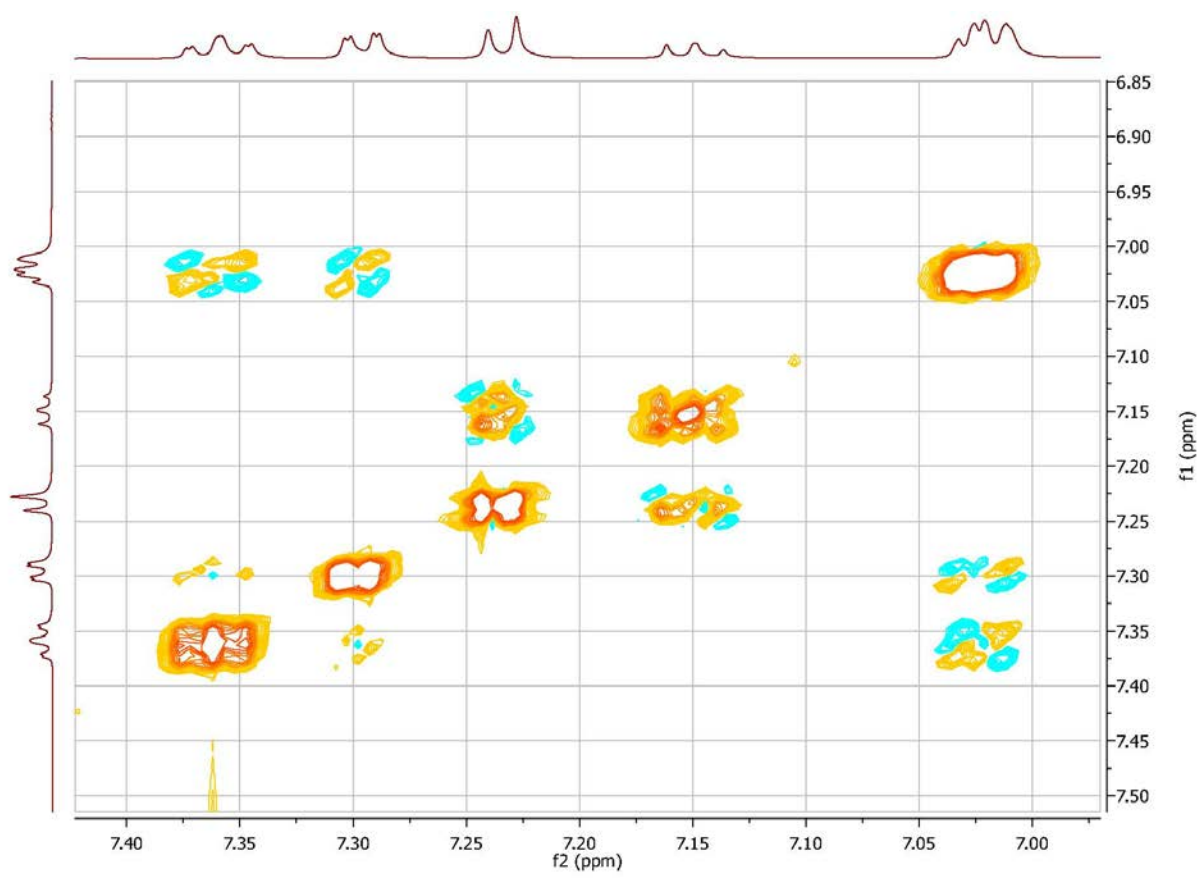
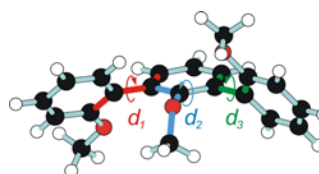


Figure S7. Partial 2-D ^1H - ^1H ROESY spectrum of **1**

Table S1. Geometrical parameters of the species in Figure 3.



Conformers		Dihedral angles ^a		
		<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃
<i>syn-a</i>		<i>118.81</i>	<i>-89.84</i>	<i>-118.81</i>
		123.23	-89.08	-123.23
<i>syn-s</i>		<i>-54.36</i>	<i>-90.56</i>	<i>54.36</i>
		-51.54	-89.97	51.54
<i>anti</i>		<i>53.21</i>	<i>84.56</i>	<i>118.26</i>
		50.82	81.64	122.10
TS(<i>syn-s</i> → <i>anti</i>)		<i>6.26</i>	<i>-100.31</i>	<i>57.57</i>
		5.64	-100.47	56.07
TS(<i>syn-a</i> → <i>syn-s</i>)		<i>-100.80</i>	<i>-1.34</i>	<i>116.23</i>
		-103.75	-5.20	120.06
TS(<i>anti</i> → <i>syn-a</i>)		<i>-7.78</i>	<i>95.94</i>	<i>118.49</i>
		-7.38	95.82	121.39
TS(<i>anti</i> → <i>anti</i>) ^b		<i>95.32</i>	<i>-179.12</i>	<i>114.92</i>
		96.75	-177.22	118.05

^a*italics*B3LYP/6-31G*; **bold** B2PLYPD/cc-pVDZ; ^b lower of the two T

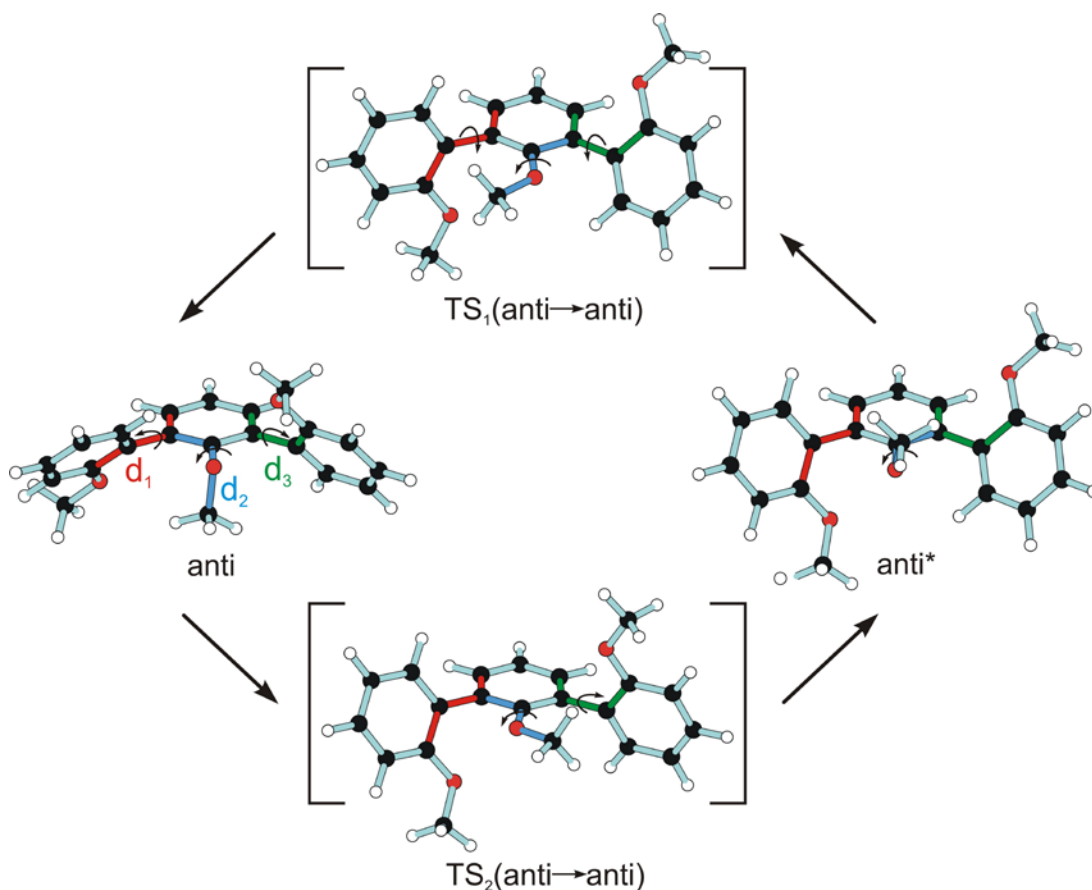


Figure S8. Interconversion of *anti* atropisomer of **1d** (structures from B2PLYPD/cc-pVDZ calculations; note that the two *anti* structures are identical); the TS₁ lies 2.82 kJ/mol higher than TS₂; (for geometrical parameters see Table S1).

Table S1. Geometrical parameters of the species in Figure S8.

Conformers	Dihedral angles		
	d_1	d_2	d_3
<i>anti</i>	50.82	81.64	122.10
TS(<i>anti</i> → <i>anti</i>) ^a	96.75	-177.22	118.05
<i>anti</i> *	122.10	81.64	50.82
TS(<i>anti</i> → <i>anti</i>) ^b	99.36	175.76	55.20