

Supporting Information

Photo- and Thermal Isomerization of Shuttlecock- and Bowl-Equipped Phenylazopyridines

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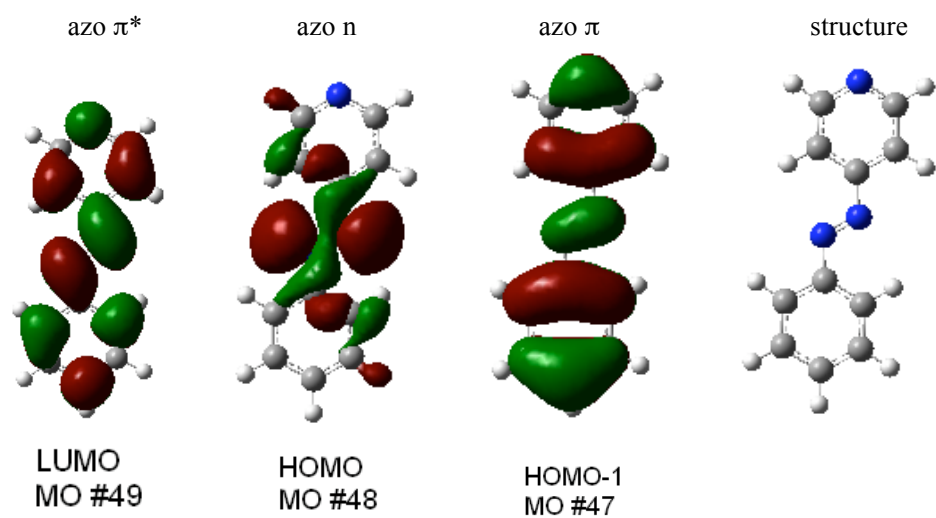
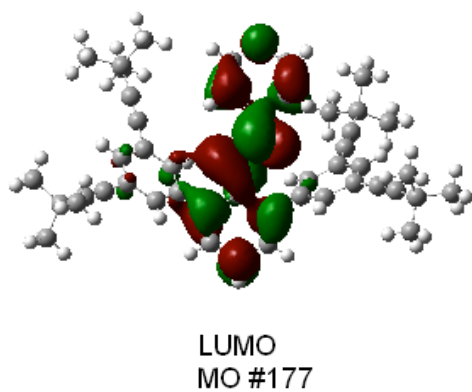
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Table of Contents

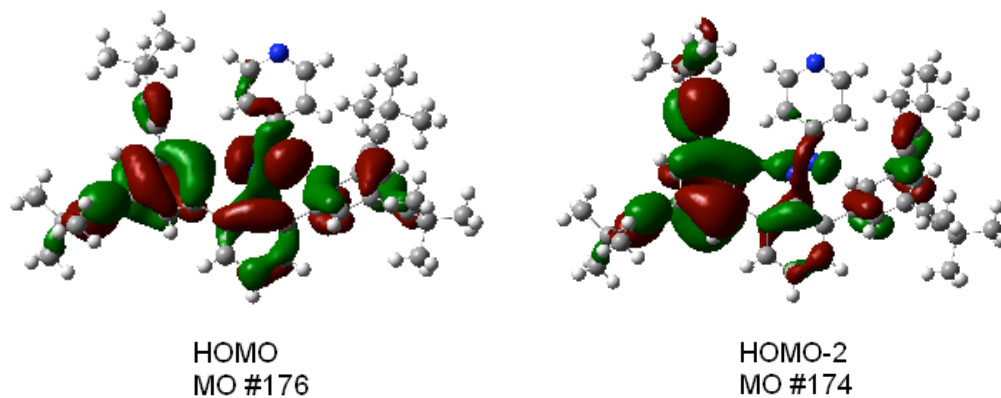
Figure S1. Representative molecular orbitals of 4-PhNNPy, TbetNNPy, BmtNNPy, and BmtNN(O)Py.

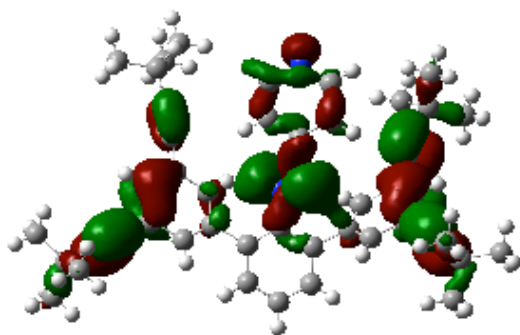
Figure S2. ^1H NMR spectra of TbetNNPy and BmtNNPy before and after irradiation in C_6D_6 and *trans*-BmtNN(O)Py in CDCl_3 .

TABLE S1. List of Main Transitions by TD-DFT Calculations for 4-PhNNPy, TbetNNPy, BmtNNPy, and BmtNN(O)Py

4-PhNNPy**TbetNNPy**azo π^* 

azo n

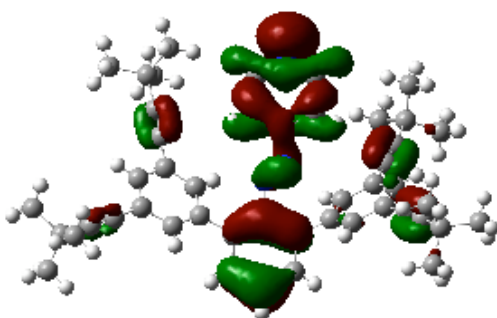




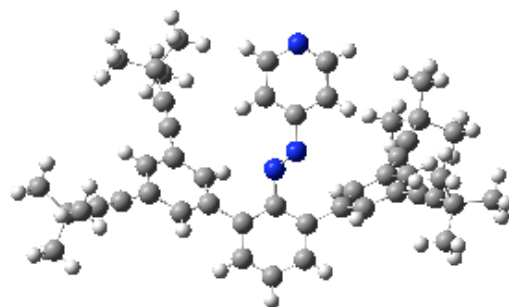
HOMO-4
MO #172

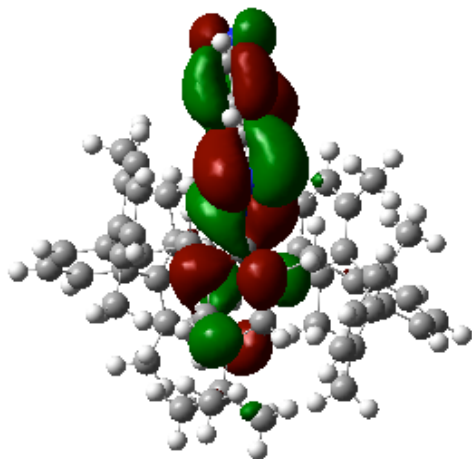
azo π

structure

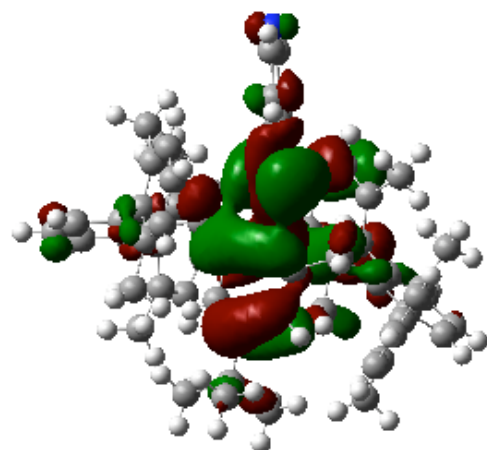
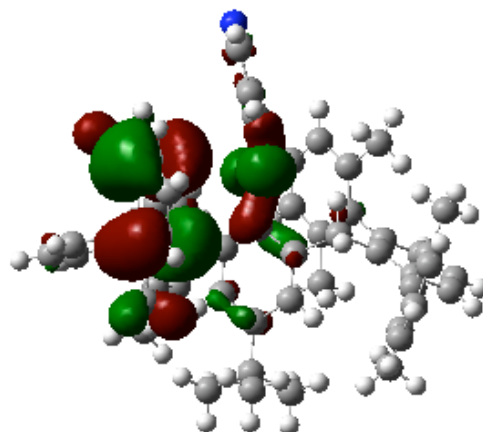


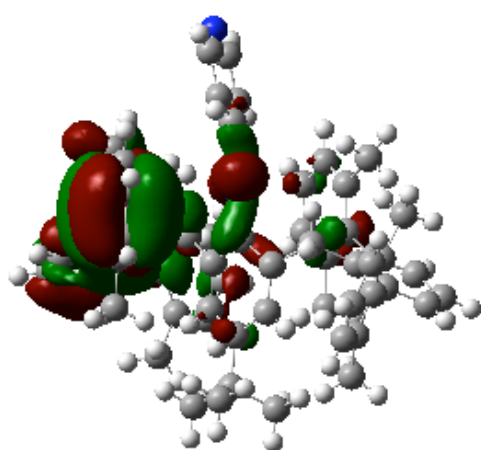
HOMO-5
MO #171



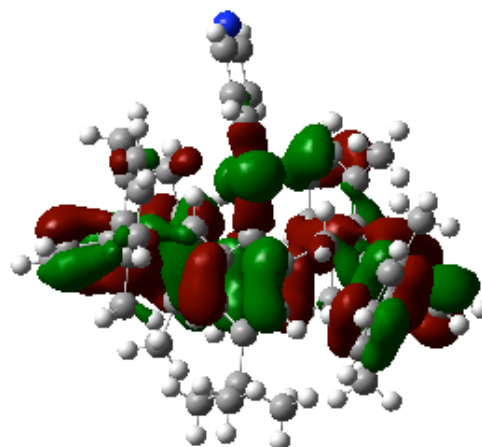
BmtNNPyazo π^* LUMO
MO #225

azo n

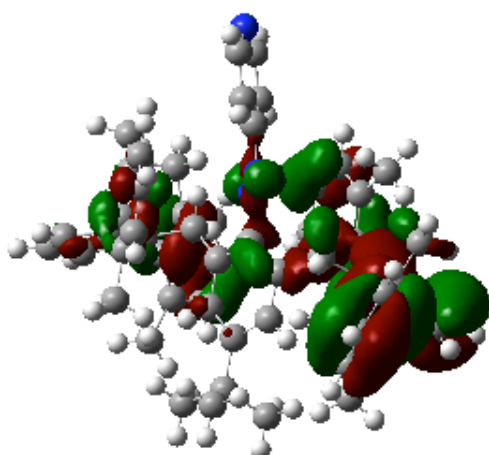
HOMO
MO #224HOMO-1
MO #223



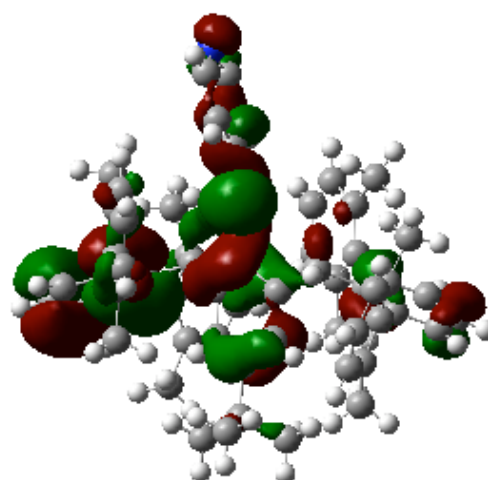
HOMO-2
MO #222



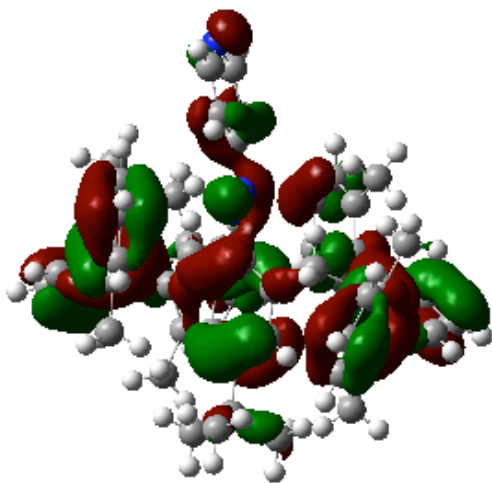
HOMO-5
MO #219



HOMO-9
MO #215

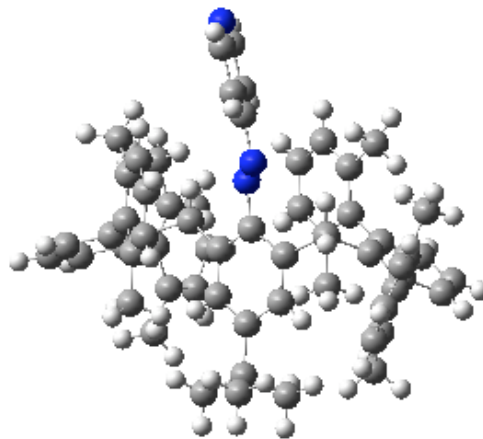
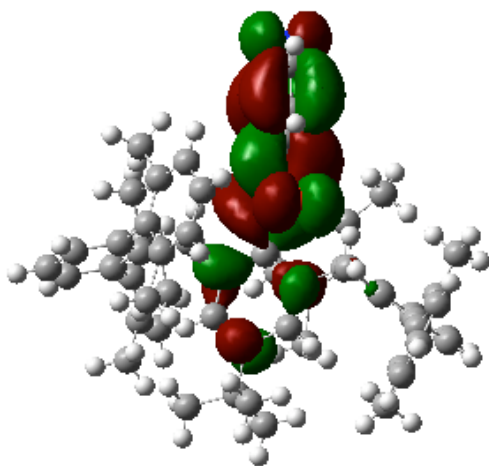


HOMO-10
MO# 214

azo π 

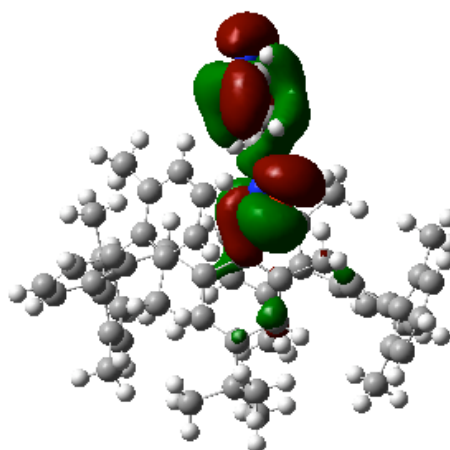
HOMO-11
MO #213

structure

**BmtNN(O)Py**azo π^* 

LUMO
MO #229

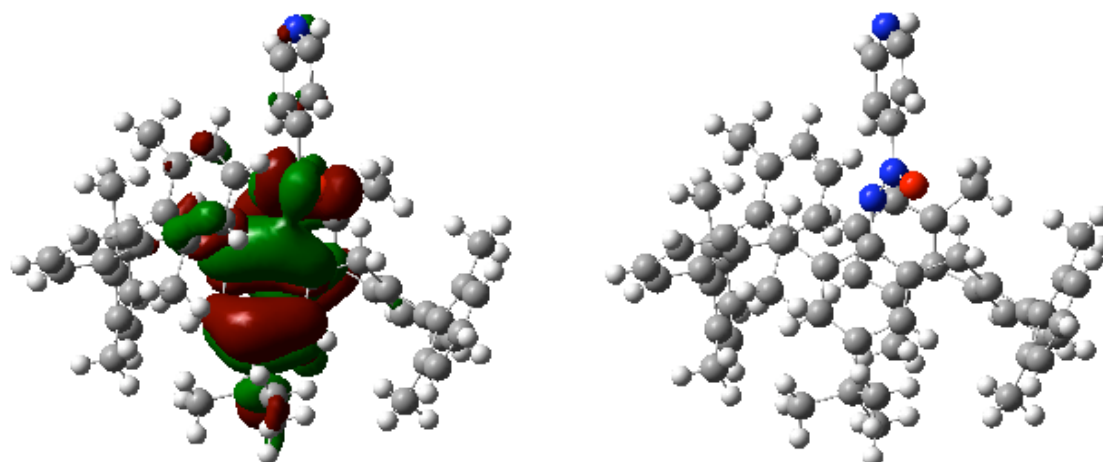
azo n



HOMO-16
MO #212

azo π

structure

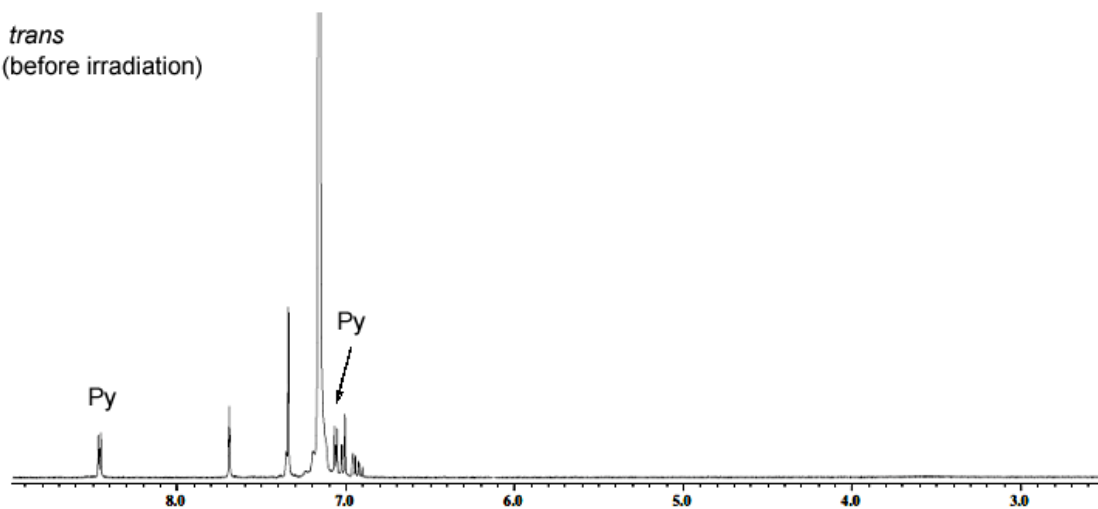


HOMO
MO #228

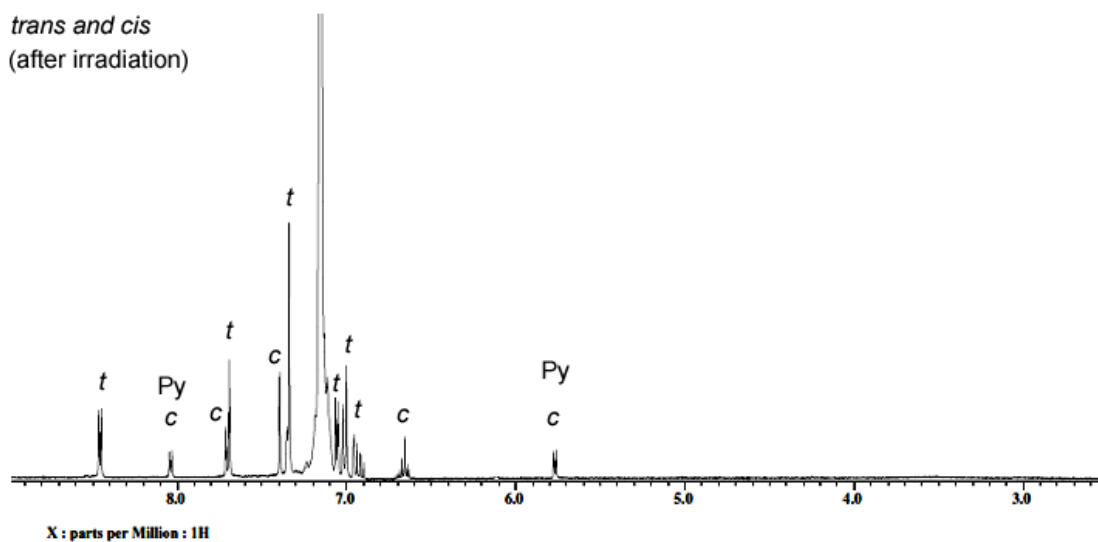
Figure S1. Representative molecular orbitals of 4-PhNNPy, TbetNNPy, BmtNNPy, and BmtNN(O)Py.

TbetNNPy

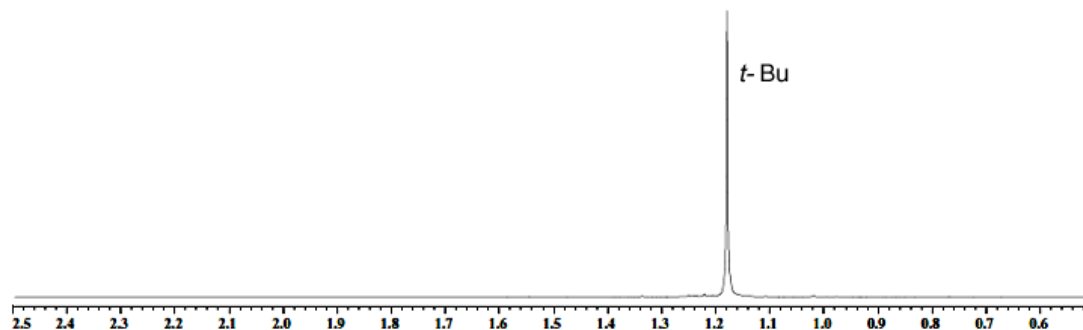
trans
(before irradiation)



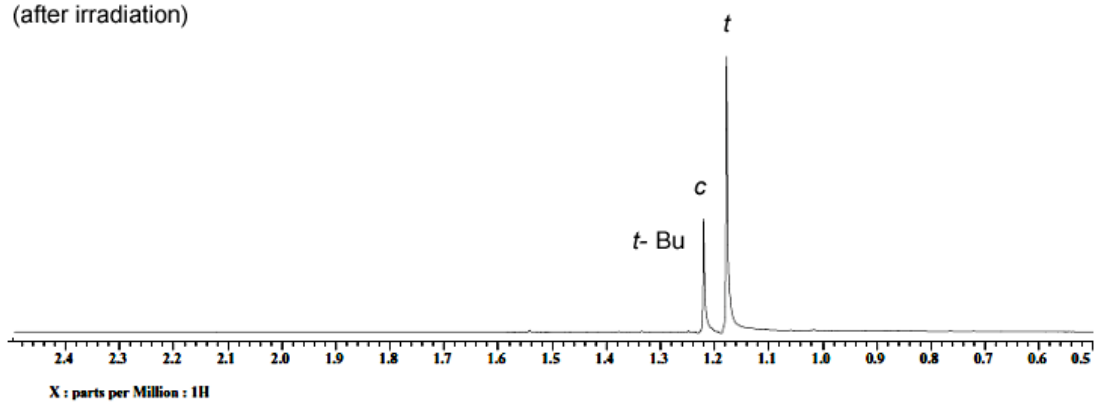
trans and cis
(after irradiation)

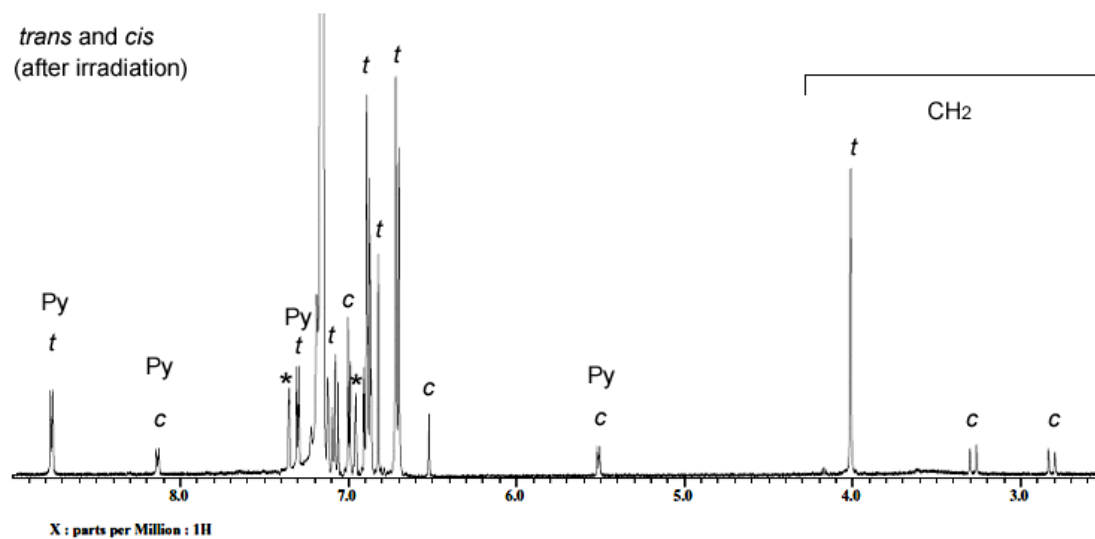
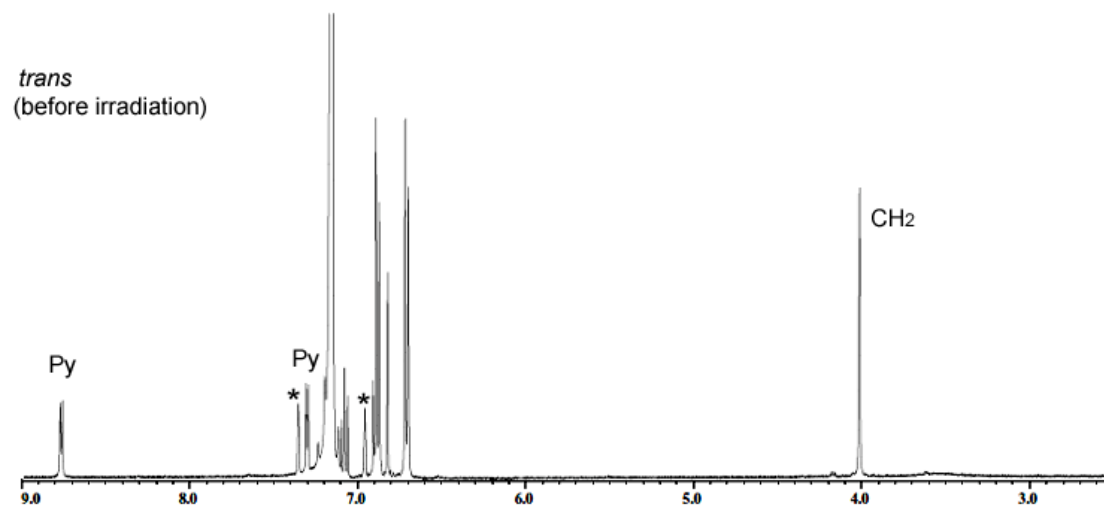


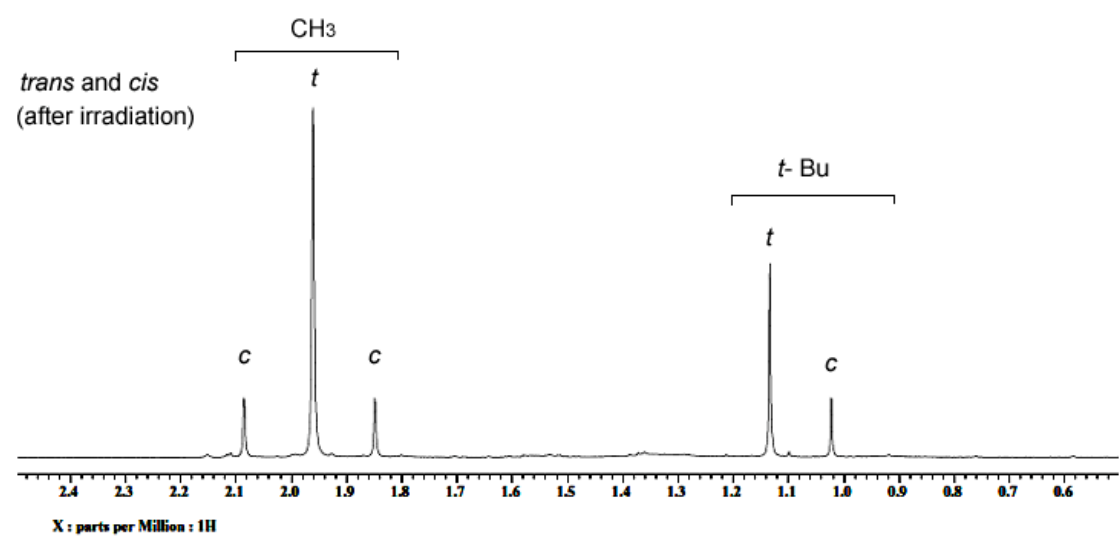
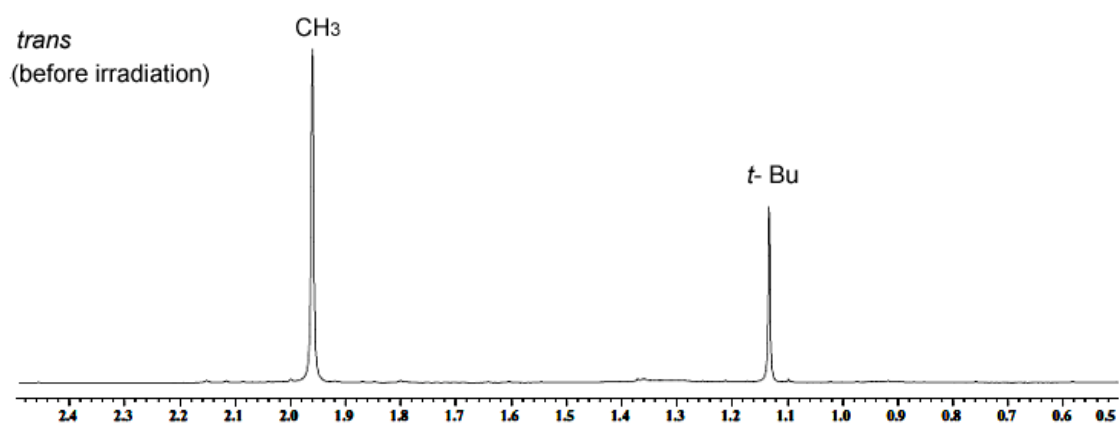
trans
(before irradiation)



trans and cis
(after irradiation)



BmtNNPy



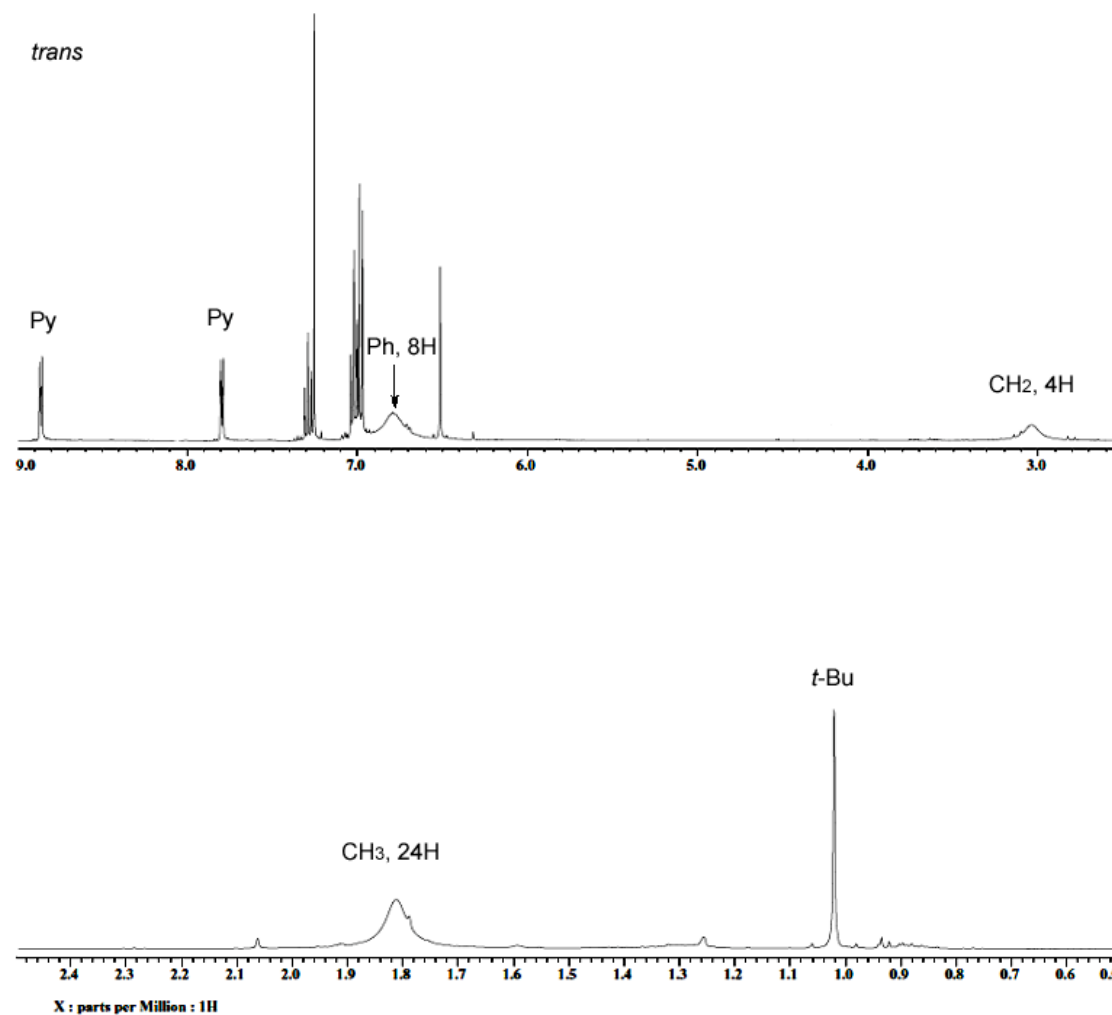
BmtNN(O)Py

Figure S2. ^1H NMR spectra of TbetNNPy and BmtNNPy before and after irradiation in C_6D_6 and *trans*-BmtNN(O)Py in CDCl_3 . The *t*, *c*, and asterisks indicate *trans*, *cis*, and spinning side bands, respectively.

TABLE S1: List of Main Transitions by TD-DFT Calculations for 4-PhNNPy, TbetNNPy, BmtNNPy, and BmtNN(O)Py

compound	wavelength	osillator strength	main transition	orbital number	coefficient
4-PhNNPy	501.4 nm	0	$n(\text{azo}) \rightarrow \pi^*(\text{azo})$	#48 (H) $\rightarrow$ 49 (L)	0.66465
	322.9 nm	0.6202	$\pi(\text{azo}) \rightarrow \pi^*(\text{azo})$	#47 (H-1) $\rightarrow$ 49 (L)	0.60473
TbetNNPy	504.7 nm	0.0012	$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#176 (H) $\rightarrow$ 177 (L)	0.59973
			$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#174 (H-2), $\rightarrow$ 177 (L)	-0.15211
			$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#172 (H-4), $\rightarrow$ 177 (L)	-0.19962
			$\pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#175 (H-1) $\rightarrow$ 177 (L)	0.70382
	391.5 nm	0.005	$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#174 (H-2) $\rightarrow$ 177 (L)	0.65373
	378.4 nm	0.0228	$\pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#173 (H-3) $\rightarrow$ 177 (L)	0.68143
	373.2 nm	0.0287	$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#176 (H) $\rightarrow$ 177 (L)	0.22283
	342.2 nm	0.0239	$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#174 (H-2) $\rightarrow$ 177 (L)	-0.12358
			$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#172 (H-4) $\rightarrow$ 177 (L)	0.60102
			$\pi(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#171 (H-5) $\rightarrow$ 177 (L)	0.16765
			$\pi(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#171 (H-5) $\rightarrow$ 177 (L)	0.55424
	325.0 nm	0.0042	$\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#170 (H-6) $\rightarrow$ 177 (L)	0.28281
			$\pi(\text{azo}) + n(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#169 (H-7) $\rightarrow$ 177 (L)	0.26662
			$\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#170 (H-6) $\rightarrow$ 177 (L)	0.45251
			$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{Ph})$	#176 (H) $\rightarrow$ 178 (L+1)	0.33417
	309.2 nm	0.0744	$\pi(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#171 (H-5) $\rightarrow$ 177 (L)	-0.27127
			$n(\text{azo}) + \pi(\text{Ph}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{Ph})$	#176 (H) $\rightarrow$ 178 (L+1)	0.52421
			$\pi(\text{azo}) + n(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#169 (H-7) $\rightarrow$ 177 (L)	-0.27616
			$\pi(\text{azo}) + \pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{azo})$	#171 (H-5) $\rightarrow$ 177 (L)	0.20500
	302.3 nm	0.1079			
BmtNNPy	501.8 nm	0.0188	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#224 (H) $\rightarrow$ 225 (L)	0.56424
	378.4 nm	0.0284	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#223 (H-1) $\rightarrow$ 225 (L)	0.61657
	369.3 nm	0.0136	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#222 (H-2) $\rightarrow$ 225 (L)	0.60728
	362.0 nm	0.0289	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#221 (H-3) $\rightarrow$ 225 (L)	0.64796
	358.6 nm	0.0143	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#220 (H-4) $\rightarrow$ 225 (L)	0.61866
	348.8 nm	0.012	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#219 (H-5) $\rightarrow$ 225 (L)	0.51607
	330.8 nm	0.0852	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#218 (H-6) $\rightarrow$ 225 (L)	0.60079
	327.1 nm	0.03	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#214 (H-10) $\rightarrow$ 225 (L)	-0.55095
	322.9 nm	0.0015	$n(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#215 (H-9) $\rightarrow$ 225 (L)	0.62113
	320.5 nm	0.0001	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#217 (H-7) $\rightarrow$ 225 (L)	0.70497
	318.1 nm	0.0007	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#216 (H-8) $\rightarrow$ 225 (L)	-0.69014
	313.7 nm	0.0048	$\pi(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#213 (H-11) $\rightarrow$ 225 (L)	-0.52437
	307.2 nm	0.1048	$\pi(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#213 (H-11) $\rightarrow$ 225 (L)	0.59588
	300.0 nm	0.0067	$\pi(\text{azo}) + \pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#213 (H-11) $\rightarrow$ 225 (L)	0.57942
BmtNN(O)Py	420.0 nm	0.0818	$\pi(\text{azo}) \rightarrow \pi^*(\text{azo})$	#228 (H) $\rightarrow$ 229 (L)	0.65932
	389.0 nm	0.0174	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#227 (H-1) $\rightarrow$ 229 (L)	0.68741
	373.0 nm	0.0049	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#226 (H-2) $\rightarrow$ 229 (L)	0.57373
	369.0 nm	0.0043	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#225 (H-3) $\rightarrow$ 229 (L)	0.54067
	359.1 nm	0.0023	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#224 (H-4) $\rightarrow$ 229 (L)	0.53306
	349.6 nm	0.023	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#223 (H-5) $\rightarrow$ 229 (L)	0.50632
	336.5 nm	0	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#220 (H-8) $\rightarrow$ 229 (L)	0.51378
	334.1 nm	0.0125	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#221 (H-7) $\rightarrow$ 229 (L)	0.56445
	331.4 nm	0.0002	$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#222 (H-6) $\rightarrow$ 229 (L)	0.64969
	327.0 nm	0.0037	$n(\text{azo}) \rightarrow \pi^*(\text{azo})$	#212 (H-16) $\rightarrow$ 229 (L)	0.37419
			$n + \pi(\text{azo}) \rightarrow \pi^*(\text{azo})$	#214 (H-14) $\rightarrow$ 229 (L)	-0.35523
			$\pi(\text{Ph}) \rightarrow \pi^*(\text{azo})$	#221 (H-7) $\rightarrow$ 229 (L)	-0.33692