

# Supporting Information

## Fluorinated azobenzenes with highly strained geometries for halogen bond-driven self-assembly

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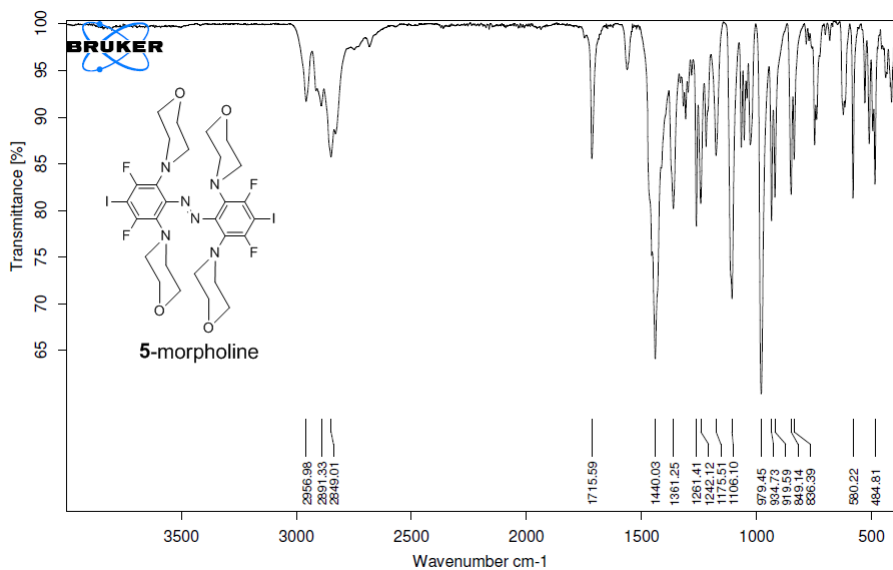
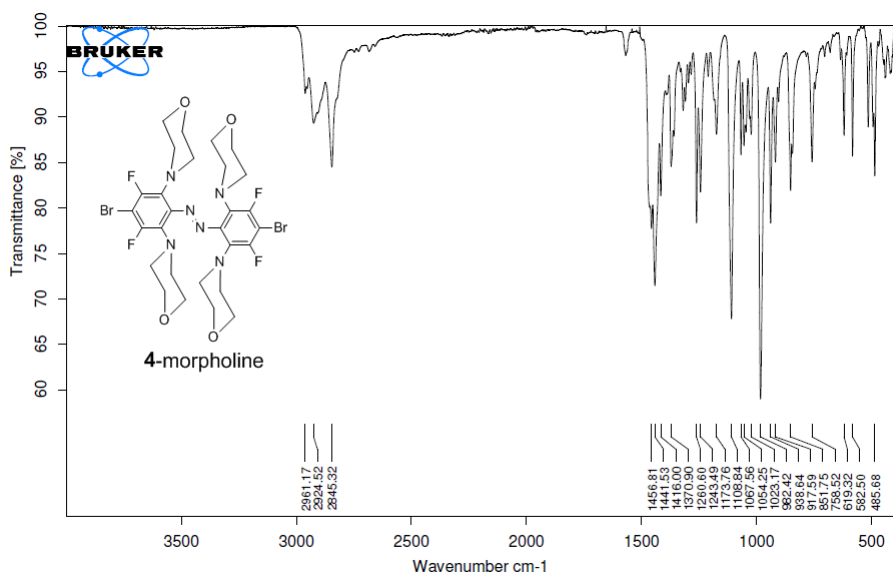
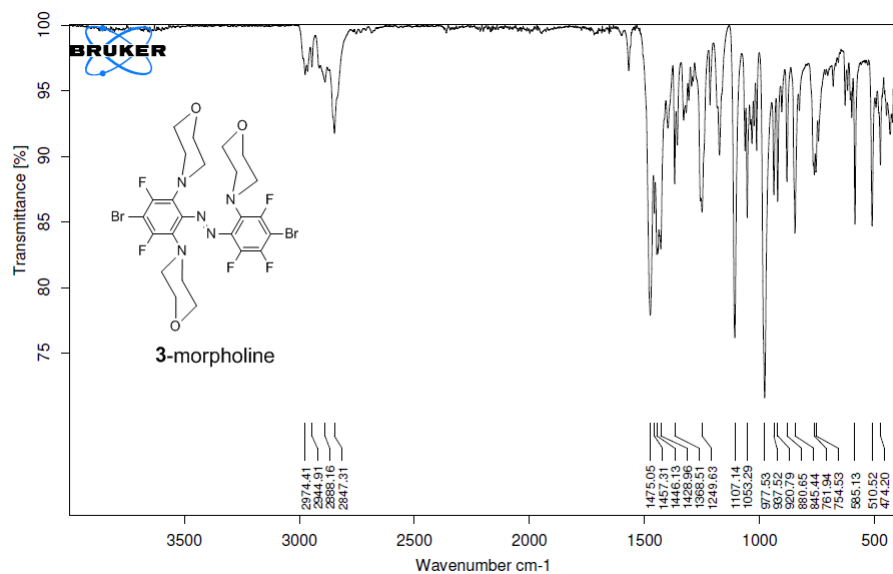
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### 1. X-ray diffraction studies

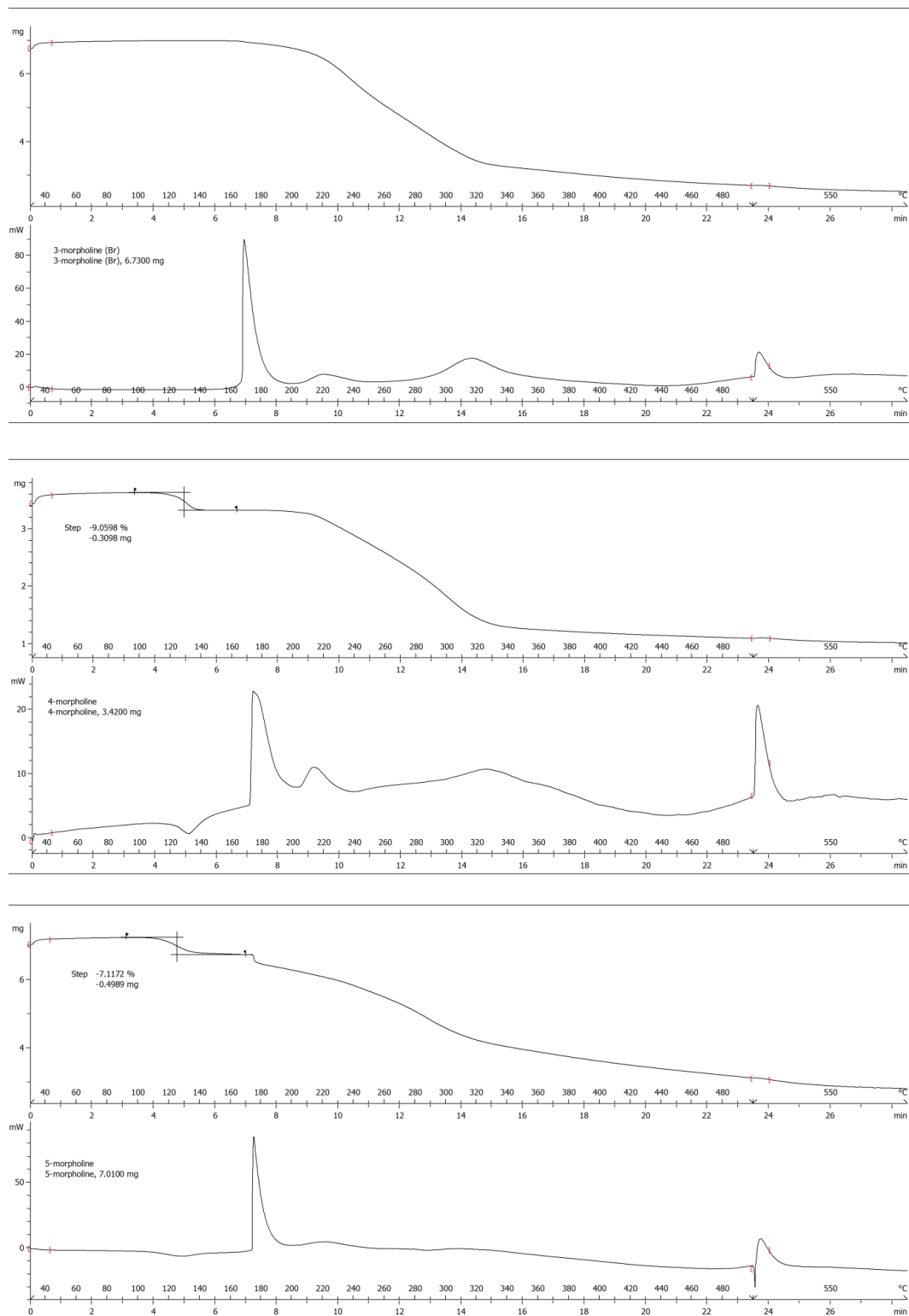
Single crystals of compounds **3-5** were grown from solutions of either *cis*- or *trans*-**1** or **-2** in morpholine by slow evaporation. X-ray single crystal diffraction data was obtained on Bruker D8 single-crystal X-ray diffractometer equipped with a MoK $\alpha$  X-ray source and a graphite monochromator. In all cases multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods and refined using SHELXL-2014/3 implemented within the WinGX 2013.3 integrated program system. Crystallographic data for all prepared cocrystals has been deposited with the Cambridge Structural Database CCDC deposition numbers 1007719-1007721.

## 2. Infrared spectroscopy



**Figure S1.** Fourier-transform infrared (FTIR) spectra for: (top) compound **3**; (middle) compound **4** and (bottom) compound **5**.

### 3. Combined thermal (TGA and DSC) analyses



**Figure S2.** Combined TGA and DSC plots of: (top) compound **3**; (middle) **4-morpholine** and (bottom) **5-morpholine**.

## 4. Mass Spectrometry

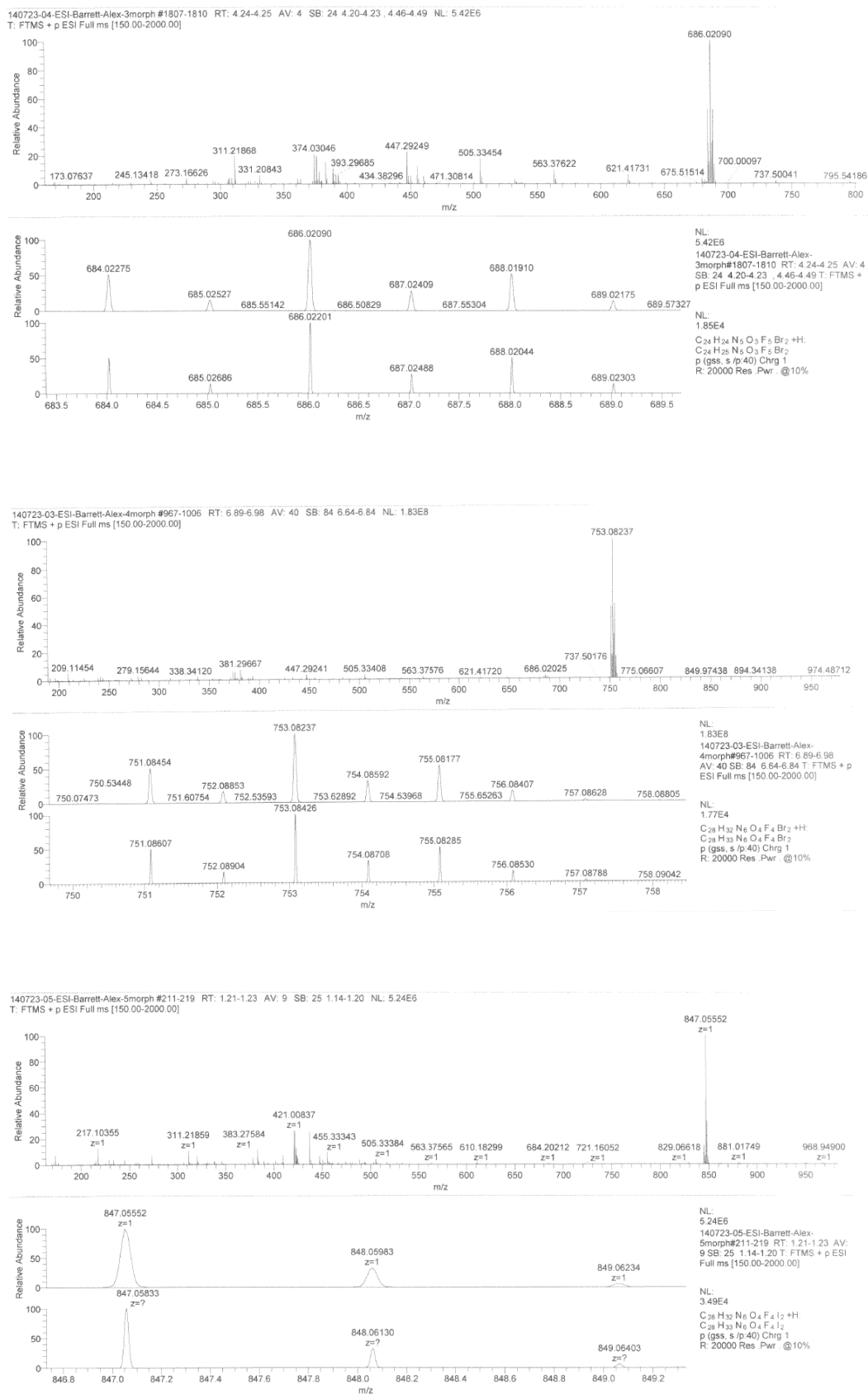
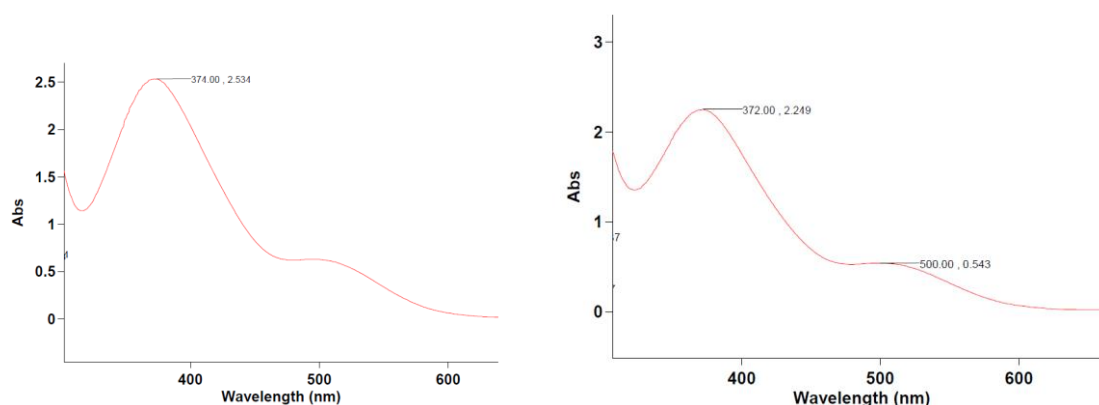


Figure S3. Mass spectra: (top) compound **3**; (middle) compound **4** and (bottom) compound **5**.

## 5. UV-Vis spectroscopy

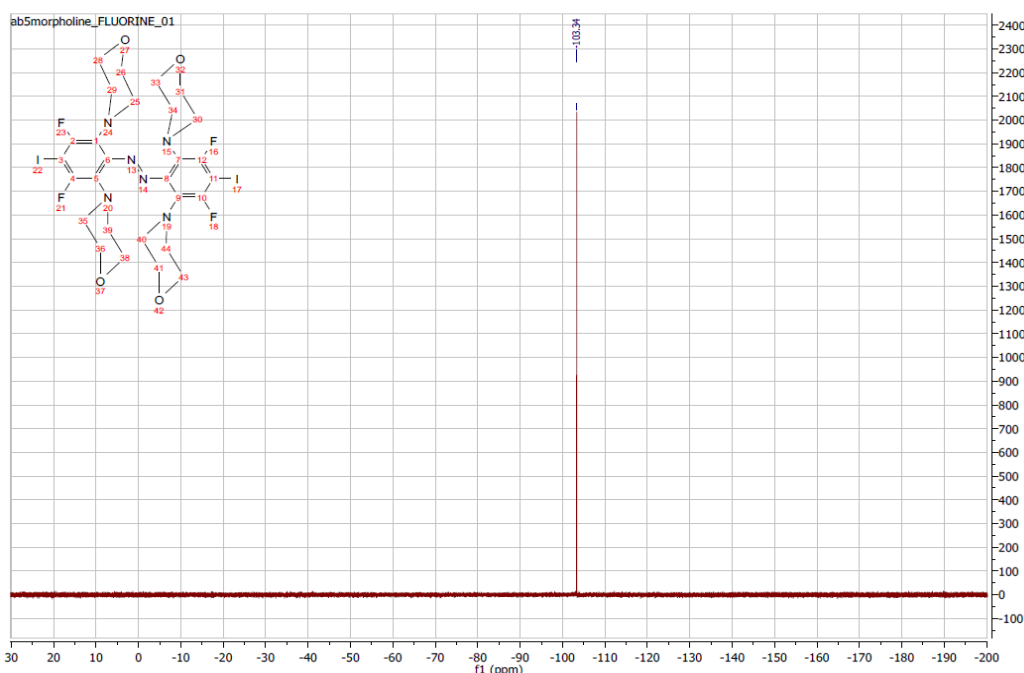
UV-Vis studies of compounds **4** and **5** were performed on a Cary 300 Bio UV-Vis spectrometer in THF solution at 0.078 ML<sup>-1</sup> for compound **4** 0.065 ML<sup>-1</sup> for compound **5**. Both compounds exhibit nearly identical spectra including a shoulder at 500 nm of coalescing  $\pi$ - $\pi^*$  and n-  $\pi^*$  transitions. Nearly identical behavior was observed in CH<sub>2</sub>Cl<sub>2</sub> and in cyclohexane solutions, indicating the absence of solvatochromism.



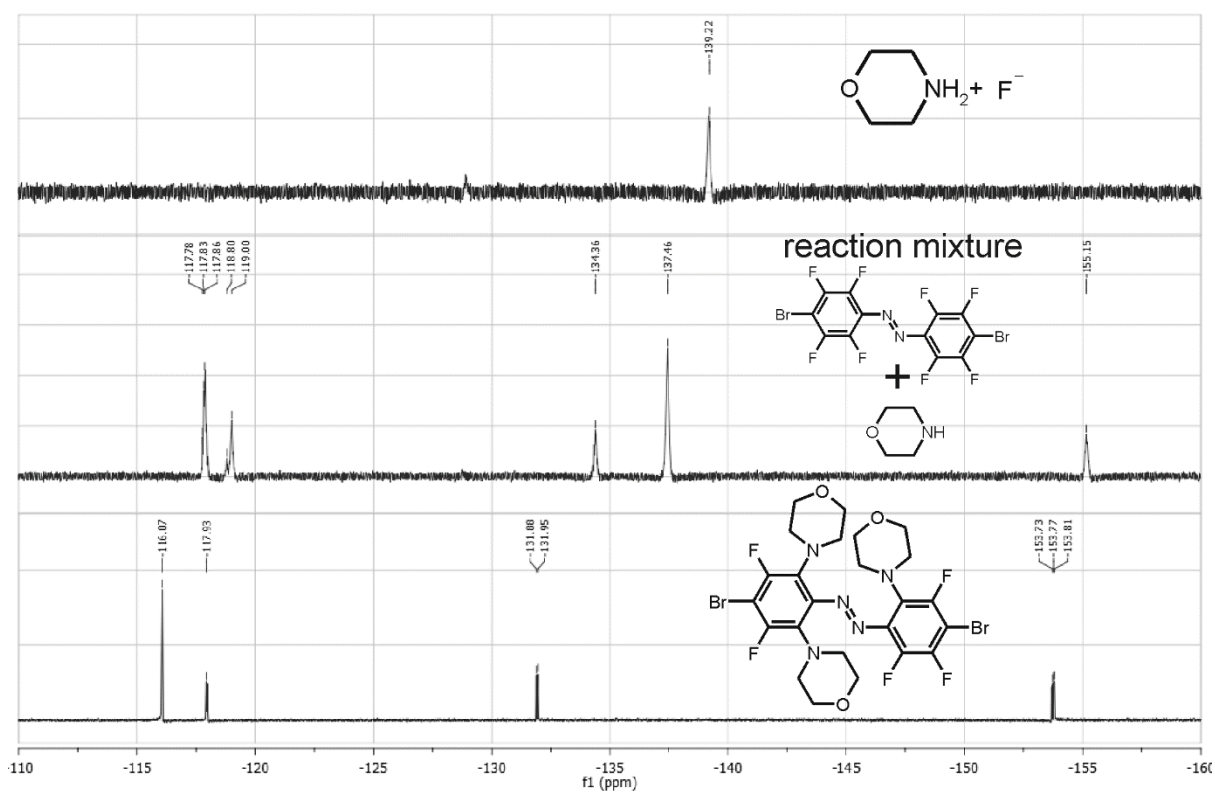
**Figure S4.** UV-Vis profiles of: (left) compound **4** and (right) compound **5** in THF.

## 6. <sup>19</sup>F NMR spectroscopy

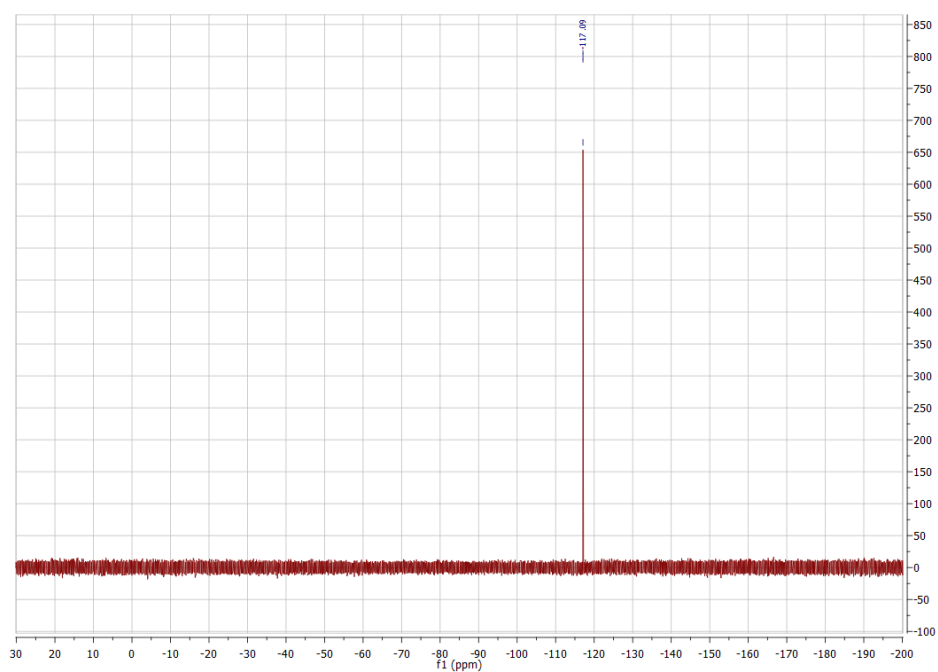
The <sup>19</sup>F NMR spectrum for the reaction between *trans*-**1** and morpholine was recorded in a 6:4 respective mixture of morpholine and (CD<sub>3</sub>)<sub>2</sub>CO. Spectra of pure compounds **3**, **4** and **5** were recorded in CDCl<sub>3</sub> due to solubility limitations.



**Figure S5.** <sup>19</sup>F NMR spectrum of compound **5** in CDCl<sub>3</sub>.



**Figure S6.**  $^{19}\text{F}$  NMR spectra for the reaction of *trans*-1 and morpholine: (a) solution of morpholinium fluoride in  $(\text{CD}_3)_2\text{CO}$ ; (b) solution of *trans*-1 in a 6:4 mixture of morpholine and  $(\text{CD}_3)_2\text{CO}$  after 20 minutes at room temperature and (c) compound **3** in  $\text{CDCl}_3$ .

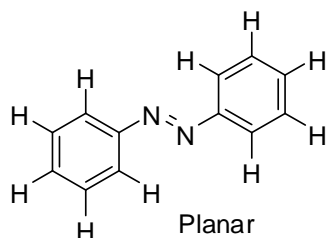


**Figure S7.**  $^{19}\text{F}$  NMR spectrum of compound **5** in  $\text{CDCl}_3$ .

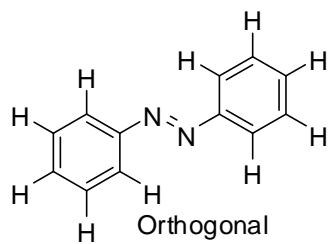
## 7. Computational Studies

### Cartesian coordinates of calculated structures

B3LYP/6-31+G(d) optimized geometries, given in standard XYZ format: coordinates are Cartesian coordinates in the usual order (units are in ångstroms). All calculations were performed in the gas phase.

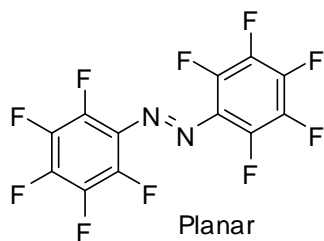


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C	0.30232900	-1.07244300	-1.38978700
C	1.46162900	-1.57785200	-1.99564800
C	-1.05275200	-2.26524800	-2.99814200
C	-1.46125100	1.58677400	1.98871900
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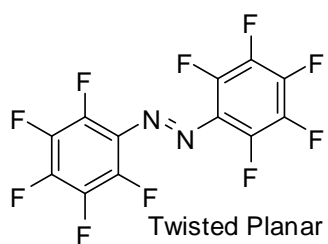


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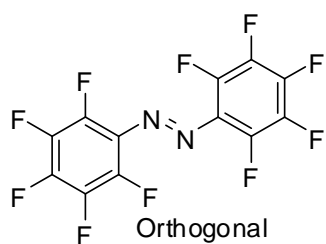




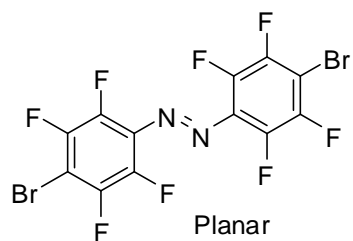
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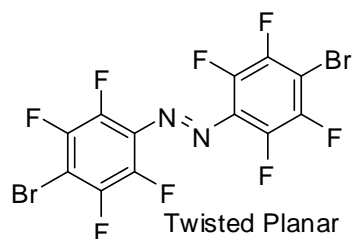
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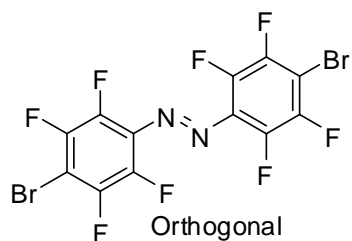
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C	0.73039800	1.00494300	2.13740900
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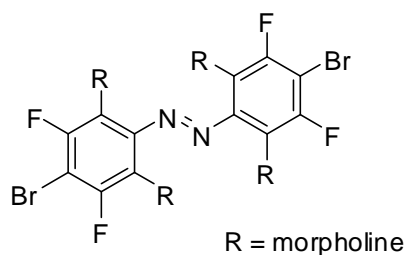
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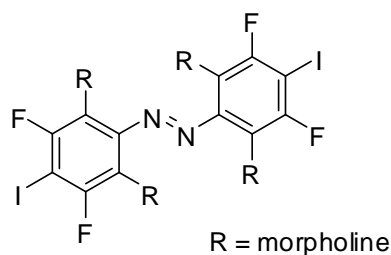
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C	0.79039800	-1.44705700	-3.32959100
C	0.05839800	3.03594300	3.29940900
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O	1.85144000	3.38495100	-2.47483300
N	1.06514200	0.67455200	-2.20747400
N	1.74660900	-0.03649600	1.95677400
N	-2.37168500	2.36099900	0.70521300
C	-0.63154500	-4.48031800	0.45161200
H	-0.14851500	-4.15428500	1.38853000
H	0.12115200	-4.97794200	-0.16245300
C	-2.27561300	-2.67016600	0.44513300
H	-2.69893200	-1.89049800	-0.19446500
H	-1.94352200	-2.20466500	1.38486600
C	-1.75987500	-5.45533300	0.78252900
H	-2.15951400	-5.89087400	-0.14644300
H	-1.39766200	-6.26052600	1.42775700

O	-2.80479400	-4.80385100	1.50145400
C	-3.42994600	1.34176700	0.67693400
H	-4.14713200	1.50586200	1.50032000
H	-2.98499800	0.35281000	0.80407700
C	-4.16893400	1.41110800	-0.65847100
H	-3.48850000	1.11650600	-1.47339900
H	-5.03322900	0.74073900	-0.65599800
C	-2.90320900	3.70473300	0.44682200
H	-2.07559700	4.41933900	0.40955400
H	-3.60495700	4.03038200	1.22860600
O	-4.67745500	2.71840400	-0.90260600
N	-1.17091500	-3.31720700	-0.26008600
C	-3.34760900	-3.71907100	0.75495400
H	-4.13885900	-3.28548700	1.37379000
H	-3.78955900	-4.09366500	-0.18232800
C	1.56017600	-1.35205800	2.58882700
H	0.51860700	-1.65554000	2.46194100
H	1.78929500	-1.30771700	3.66734900
C	3.15614000	0.38606700	1.97423300
H	3.53735000	0.53639700	2.99457700
H	3.24810400	1.33114900	1.42863600
C	2.47645900	-2.37049300	1.91410200
H	2.44178300	-3.32699500	2.44347000
H	2.15321100	-2.52309100	0.87295400
O	3.83844800	-1.94981100	1.93774100
C	3.99790700	-0.69095800	1.29150300
H	3.71461100	-0.77813400	0.23027400
H	5.06094000	-0.44227600	1.35720700
C	-3.63528000	3.69045100	-0.89531600
H	-4.11469400	4.65629200	-1.07711900
H	-2.92613700	3.48359200	-1.71243100





	X	Y	Z
I	1.08091700	-4.15490000	-5.03458800
I	0.18651600	4.07390000	5.28170800
N	-0.47115500	0.50575200	0.10292100
N	-0.24868400	-0.73796000	0.10601500
C	-0.10616500	-1.36104700	-1.14733200
C	-0.50811500	-2.72650200	-1.17997000
C	-0.14324300	-3.48489500	-2.30374100
C	0.58921300	-2.96350900	-3.36285400
C	0.92294500	-1.61165900	-3.31745100
C	0.59582400	-0.76644000	-2.24561900
C	-0.35559700	1.15520600	1.34645700
C	0.74496500	0.93627600	2.22623500
C	0.86420300	1.81027100	3.31861100
C	-0.03137700	2.84222300	3.58043700
C	-1.11703000	2.98935900	2.72076300
C	-1.30352200	2.19078800	1.58442100
F	-0.54526400	-4.77482000	-2.36276500
F	1.56953800	-1.08327500	-4.38405600
F	-2.04324200	3.93013600	3.01760600
F	1.88654900	1.61985000	4.18502200
N	1.02573100	0.57582700	-2.20947500
C	0.07832200	1.60188600	-2.67148000
H	-0.91206400	1.37067600	-2.27697600
H	0.03333100	1.61740400	-3.77417500
C	2.76338700	2.27149000	-2.04297900
H	2.73928100	2.25284100	-0.94159900
H	3.76262400	2.56937700	-2.37350500
C	2.40744900	0.89302400	-2.59860400
H	2.54190000	0.90957000	-3.68950500
H	3.07867100	0.13587900	-2.18032500
C	0.52086600	2.96921000	-2.15677000
H	-0.09666800	3.76022800	-2.59186700
H	0.42265200	2.99506200	-1.06165600
O	1.86614500	3.26423500	-2.52935200
N	-1.26461200	-3.34274600	-0.17669800
N	1.71902900	-0.05764200	1.96315400
N	-2.37407100	2.36815700	0.68708300
C	3.95865900	-0.75105200	1.29768000
H	3.66768600	-0.85785100	0.24035300
H	5.02474300	-0.51264900	1.35143700
C	2.42305400	-2.39981100	1.96617300
H	2.38132800	-3.34435100	2.51613900
H	2.09077600	-2.57093300	0.93077700
C	3.13295600	0.34954000	1.96233300
H	3.52256100	0.51766400	2.97676700

H	3.23186900	1.28165100	1.39598700
C	1.52305200	-1.35678200	2.62500400
H	0.47731800	-1.65167100	2.51228400
H	1.76044200	-1.29169300	3.70069700
O	3.78991000	-1.99419300	1.97159200
C	-0.72426100	-4.49039400	0.55866100
H	0.01367900	-5.01193900	-0.05364000
H	-0.22322400	-4.14406000	1.47873500
C	-3.42819000	-3.69568500	0.88233700
H	-4.20590900	-3.23822000	1.50115100
H	-3.88765900	-4.09075200	-0.03794900
C	-1.85588600	-5.44559100	0.93299700
H	-1.49103000	-6.23636700	1.59442000
H	-2.27330600	-5.90241500	0.02222600
C	-2.35111500	-2.66613700	0.52872300
H	-2.77687000	-1.89906200	-0.12448600
H	-1.99994700	-2.17982500	1.45088500
O	-2.88433900	-4.76567900	1.64945200
C	-2.88323100	3.71427600	0.39975700
H	-3.57742900	4.06970400	1.17536500
H	-2.04363000	4.41359500	0.34468900
C	-3.44892500	1.36652400	0.68449500
H	-4.16099200	1.56042900	1.50589500
H	-3.01985700	0.37337200	0.83225800
C	-3.61873100	3.68214600	-0.94018000
H	-4.08193900	4.65166900	-1.14332000
H	-2.91525300	3.44399300	-1.75363900
C	-4.19068100	1.41821000	-0.65027600
H	-3.51794100	1.09351700	-1.46013700
H	-5.06635300	0.76303200	-0.63022600
O	-4.67758500	2.72821800	-0.92295000