Azo···phenyl stacking: a persistent self-assembly motif guides the assembly of fluorinated *cis*-azobenzenes into photo-mechanical needle crystals

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Supporting Information

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1. Experimental

1.1 Materials:

4,4'-diiodooctafluoroazobenzene (**1**) and 4,4'-dibromooctafluoroazobenzene (**2**) were synthesized according to the procedure outlined in our prior report.[1] Precursors such as 2-bromo-4,5,6-trifluoroaniline, and 2-bromo-3,4,6-trifluoroaniline were purchased from Santa Cruz Biotechnologies, 4-bromo-2,3,5,6-tetrafluoroaniline, 2,3,5,6-tetrafluoroaniline, pentafluoro-aniline, **dabco**, 4-vinylpyridine, dithiane, and HgO were obtained from Sigma-Aldrich Chemical Co. and used without purification.

1.2 Syntheses:

***cis-bis*(pentafluorophenyl)diazene (*cis*-3)** 300 mg of pentafluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 107 mg (35.7%) (*trans* and *cis* combined), MS *m/z* 363 $C_{12}N_2F_{10}$ (M + 1). Melting point (from hot-stage microscopy): 108 °C. ^{13}C NMR (126 MHz, toluene): δ 142.66 (s), 141.31 (s), 138.06 (s), 128.39 (s).

***cis-bis*(2-bromo-3H-4,5,6-trifluorophenyl)diazene (*cis*-4)** 300 mg of 2-bromo-4,5,6-trifluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 82 mg (27.5%), (*trans* and *cis* combined), MS *m/z* 449 $C_{12}H_2N_2F_6Br_2$ (M+1). Melting point (from hot-stage microscopy): 99 °C. ^1H NMR (500 MHz, toluene), 6.43 (ddd, J = 8.8, 6.7, 1.9 Hz, 1H) (*cis*-**4**); δ 6.55 (ddd, J = 9.1, 7.0, 2.2 Hz, 1H) (*trans*-**4**). ^{13}C NMR (126 MHz, toluene) δ 152.16 (d, J = 6.4 Hz), 150.36 (t, J = 6.5 Hz), 142.20 (s), 139.46 (s), 116.87 (d, J = 194.3 Hz), 113.02 (s).

***cis-bis*(2-bromo-5H-3,4,6-trifluorophenyl)diazene (*cis*-5)** 300 mg of 2-bromo-4,5,6-trifluoroaniline was stirred overnight with freshly prepared activated manganese dioxide (6 g) in petroleum ether. The solution was filtered through celite, evaporated and purified by column chromatography on silicagel (50:50 DCM/hexanes). Yield 95 mg (31.8%),(*trans* and *cis* combined), MS *m/z* 449 $C_{12}H_2N_2F_6Br_2$ (M+1). Melting point (from hot-stage microscopy): 101 °C. ^1H NMR (500 MHz, toluene) 5.72 (td, J = 9.5, 6.3 Hz, 1H) (*cis*-**5**); δ 6.09 (td, J = 10.2, 6.7 Hz, 1H) (*trans*-**5**). ^{13}C NMR (126 MHz, toluene) δ 150.45 (d, J = 6.8 Hz), 147.90 (d, J = 6.7 Hz), 145.67 (s), 136.69 (d, J = 6.1 Hz), 112.01 (s), 105.83 (d, J = 169.7 Hz).

1.3 Cocrystal preparation

Cocrystals were prepared **in the dark** by mixing equimolar quantities of halogen bond donors and acceptors in dichloromethane (DCM). Single crystals were grown by slow evaporation of the solvent.

(*cis*-**1**)(**dabco**): 10.0 mg (0.017 mmol) of *cis*-**1** was dissolved in 2.5 mL of DCM and added to the solution of 1.9 mg (0.017 mmol) of **dabco** in 2.5 ml of DCM. Resultant orange solution remained clear and small needle-shaped cocrystals were formed after solven evaporation.

(*cis*-**1**)(4-vinylpyridine)**:** 300 µL of 4-vinylpyridine (excess) was added to a solution of 10.0 mg (0.017 mmol) of **1** in 2.5 ml of DCM yielding long needle-like crystals upon solvent evaporation.

(*cis*-**1**)(dithiane)**:** 10.0 mg (0.017 mmol) of *cis*-**1** was dissolved in 2.5 mL of DCM and added to the solution of 4.7 mg (0.017 mmol) of dithiane in 2.5 ml of DCM resulting in yellow-orange needle-like crystals upon solvent evaporation.

2. Description of single crystal X-ray diffraction measurements and crystallographic summary

X-ray diffraction data was obtained on Bruker D8 single crystal X-ray diffractometer using a MoK_α X-ray source and a graphite monochromator. Multi-scan absorption correction (SADABS) was applied and structures were solved by direct methods and refined using SHELX-97.[2]

Table S1. General and crystallographic data for *cis*-azobenzene compounds.

Compound	*cis*-**3**	*cis*-**4**	*cis*-**5**	*cis*-**1**(**dabco**)	(*cis*-**1**)(4-vinylpyridine)	(*cis*-**1**)(dithiane)
formula	$C_{12}N_2F_{10}$	$C_{12}H_2N_2F_6Br_2$	$C_{12}H_2N_2F_6Br_2$	$C_{12}N_2F_8I_2{:}C_6H_{12}N_2$	$C_{12}N_2F_8I_2{:}2(C_7H_7N)$	$C_{12}N_2F_8I_2{:}C_4H_8S_2$
Formula, moiety	C_5NF_5	$C_{12}H_2N_2F_6Br_2$	$C_{12}H_2N_2F_6Br_2$	$C_{12}N_2F_8I_2{:}C_6H_{12}N_2$	$C_{12}N_2F_8I_2{:}2(C_7H_7N)$	$C_{12}N_2F_8I_2{:}C_4H_8S_2$
ρ_{calc} (g/cm^3)	2.008	2.205	2.218	2.127	1.926	2.321
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
T (K)	100	150	100	150	150	100
space group	C2	P 2_1/c	P 2_1/c	P 2/c	C 2/c	C 2/c
Unit cell parameters	a = 13.770(6) Å b = 5.569(6) Å c = 9.822(4) Å β = 127.333(4) °	a = 11.412(3) Å b = 10.891(3) Å c = 11.216(3) Å β = 104.541(3) °	a = 11.822(3) Å b = 5.6611(16) Å c = 20.062(5) Å β = 92.243(5) °	a = 20.390(4)Å b = 6.3311(13)Å c = 17.654(4) Å β = 108.999(2)°	a = 28.300(4)Å b = 5.4157(7)Å c = 17.841(2)Å β = 96.287(2)	a = 32.485(2)Å b = 5.4079(4)Å c = 11.3764(8)Å β = 91.0420(10)
Unit cell volume (Å^3)	598.9(5)	1349.3(5)	1341.6(5)	2154.8(8)	2718.0(6)	1998.2(2)
Z	4	4	4	4	4	4
resolution (°)	28.16	27.88	28.290	27.876	27.103	28.21
completeness (%)	98.7	98.8	95.5	99.3	99.7	95.0
collected/independent reflections	3440/1370	15542/3185	11476	23990/ 5121	8190/2982	12432/2336
data/parameters/restraints	1370/109/1	3185/199/0	3198/199/0	5121/289/0	2982/181/0	2336/136/0
S	1.049	1.004	1.021	1.017	1.058	1.049
R_1[for $I \geq 2\sigma(I)$]	0.0360	0.0365	0.0333	0.0365	0.0226	0.0156
wR_2 (for all data)	0.0842	0.0772	0.0738	0.0700	0.0500	0.0358
largest diff. peak, hole (e Å^{-3})	0.256, -0.173	0.554, -0.658	0.731, -0.523	1.142, -1.270	0.474, -0.438	0.419, -0.406

Table S2. General and crystallographic data for prepared *trans*-azobenzene compounds

Compound	*trans*-**3**	*trans*-**4**	*trans*-**5**
formula	$C_{12}N_2F_{10}$	$C_{12}H_2N_2F_6Br_2$	$C_{12}H_2N_2F_6Br_2$
ρ_{calc} (g/cm^3)	2.113	2.385	2.283
crystal system	Monoclinic	Monoclinic	Monoclinic
T (K)	100	100	150
space group	C 2/c	P 2_1/c	P 2_1/c
Unit cell parameters	a = 17.098(2) Å b = 7.5871(9) Å c = *8.8151(10)* Å β = 95.3090(13) °	a = 10.630(2) Å b = 4.7239(9) Å c = *12.695(2)* Å β = 101.917(2) °	a = 4.4460(10) Å b = 15.197(3) c = *9.650(2)* β = 91.628(3) °
Unit cell volume (Å^3)	1138.6(2)	623.7(2)	651.7(2)
Z	4	2	2
resolution (°)	27.484	27.933	27.101
completeness (%)	98.9	97.7	99.9
collected/independent reflections	6339/1289	6895/1462	5449/1444
data/parameters/restraints	1289/109/0	1462/100/0	1444/100/0
S	1.073	1.052	1.021
R_1[for $I \geq 2\sigma(I)$]	0.0284	0.0178	0.0336
wR_2 (for all data)	*0.0864*	0.0416	0.0771
largest diff. peak, hole (e Å^{-3})	0.399, -0.215	0.367, -0.370	0.442, -0.474

Table S3. Comparison of calculated crystal packing densities of *cis* and *trans*-forms for *cis*-**3**, *cis*-**4** and *cis*-**5**, and two of the best performing previously reported fluorinated *cis*-azobenzene photomechanical systems, *cis*-**2** and (*cis*-**1**)(*cis*-*bis*(4-pyridyl)ethylene).

Compound	density of *cis*-form, g/cm^3	density of *trans*-form g/cm^3	density difference, %	Direction of the overal photomechanical motion
(*cis*-**1**)(*cis*-**bpe**)[1]	2.006	2.058	2.6	away
cis-**2**[2]	2.373	2.470	4.1	away
cis-**3**	2.008	2.113	5.2	towards
cis-**4**	2.218	2.276	2.6	towards
cis-**5**	2.205	2.385	8.1	towards

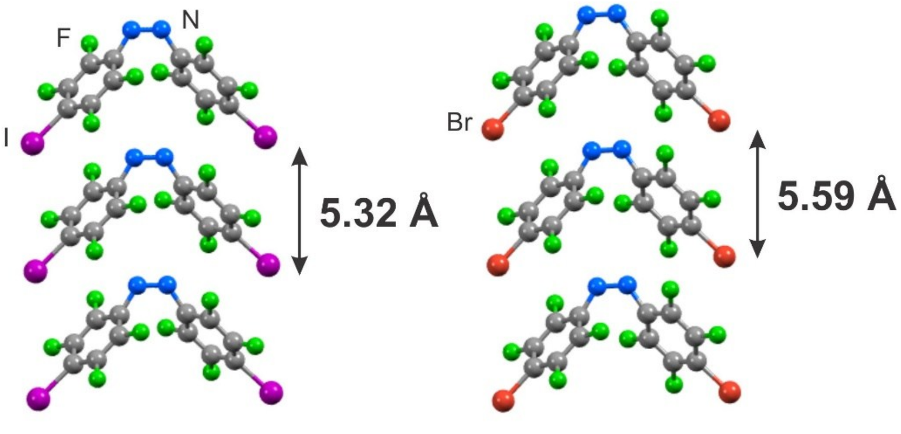


Figure S1. Illustration of azo···phenyl stacking in crystals of *cis*-**1** (left) *cis*-**2** (right).

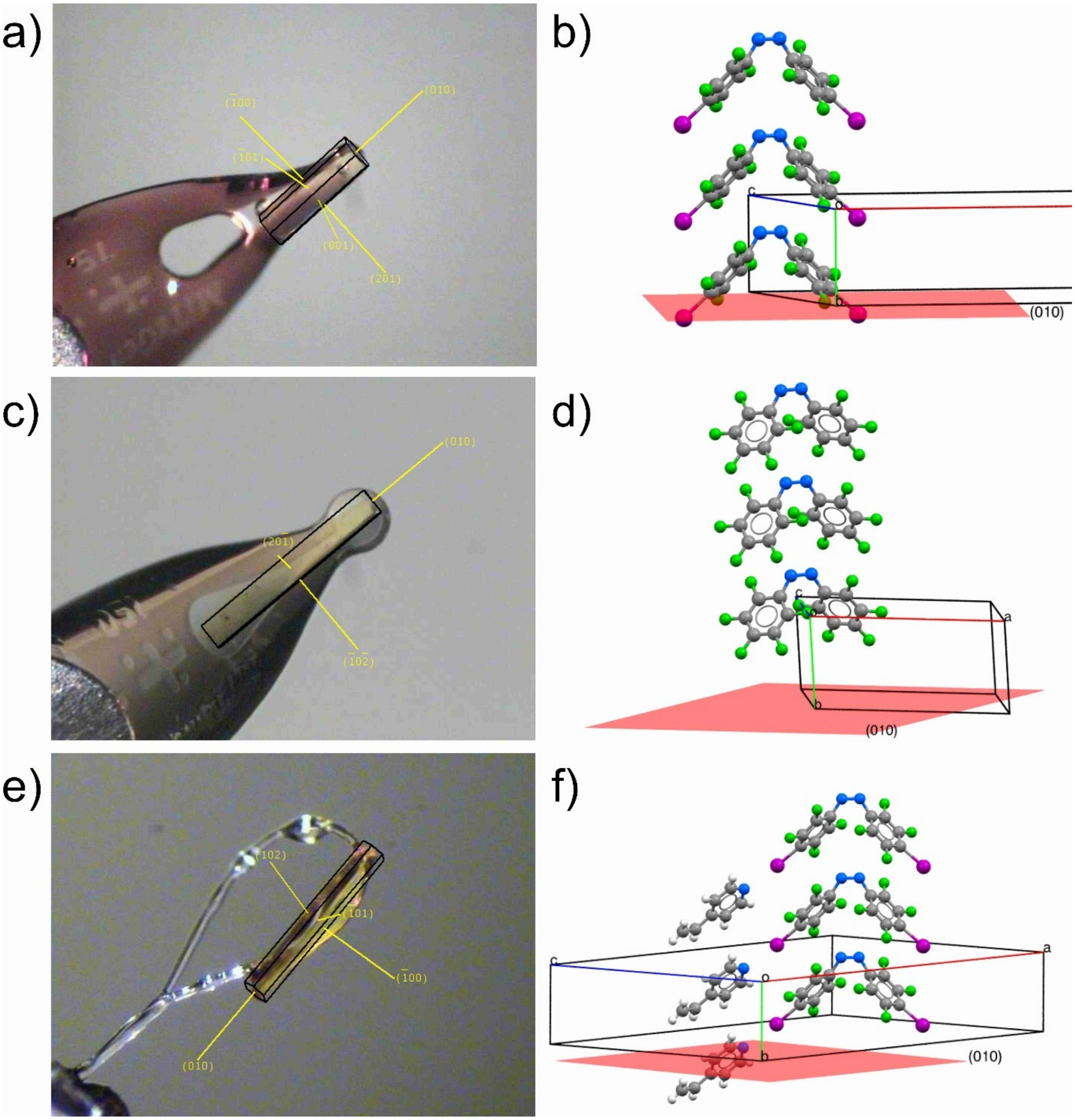


Figure S2. Images of face-indexed crystals (left) and azo···phenyl stacking (right) in corresponding crystal structures of *cis*-**1** (a and b); *cis*-**3** (c and d) and *cis*-**1**:4-vinylpyridine (e and f), demonstrating preferrential growth of needle-like crystals along the direction of the azo···phenyl interaction. The (010) planes (shown in red) correspond to the capping faces of the needle crystals.

3. Theoretical Method for QM calculations

QM software: GAMESS-US (v. 1 May 2013 (R1)),[3, 4], NBO[5] and NCIplot[6, 7]
Visualization software: MacMolPlt (v.7.4.4)[8], Avogadro (v.1.1.1)[9, 10], VMD [11]
Functional : B3LYP
Basis set : 6-31+G(d,p)

XYZ coordinates of structures

Table S4. Coordinates for the *cis*-**1** dimer assembly

I	53.0	16.61602974	6.47869968	7.75998020
F	9.0	17.75452042	4.42334986	5.59773970
F	9.0	20.48154068	3.72641015	10.23962021
F	9.0	18.61495972	5.62395000	10.07635021
F	9.0	19.59556007	2.47202992	5.78036022
N	7.0	20.86380005	1.86186993	8.13302040
C	6.0	18.12708092	5.05799007	7.83587980
C	6.0	18.42729950	4.26575041	6.74747038
C	6.0	19.37583923	3.27705002	6.83872986
C	6.0	20.10567856	3.07472992	7.99502039
C	6.0	18.85367966	4.86365986	8.99440002
C	6.0	19.82390976	3.89785004	9.07563972
I	53.0	26.29218102	6.47869968	8.93340969
F	9.0	25.15369034	4.42334986	11.09565067
F	9.0	22.42667007	3.72641015	6.45378017
F	9.0	24.29324913	5.62395000	6.61704016
F	9.0	23.31264877	2.47202992	10.91303062
N	7.0	22.04441071	1.86186993	8.56037045
C	6.0	24.78112984	5.05799007	8.85750961
C	6.0	24.48090935	4.26575041	9.94591999
C	6.0	23.53236961	3.27705002	9.85466957
C	6.0	22.80253029	3.07472992	8.69836998
C	6.0	24.05452919	4.86365986	7.69898987
C	6.0	23.08429909	3.89785004	7.61775017
I	53.0	16.61602974	1.15449989	7.75998020
F	9.0	17.75452042	-0.90085000	5.59773970
F	9.0	20.48154068	-1.59779000	10.23962021
F	9.0	18.61495972	0.29975000	10.07635021
F	9.0	19.59556007	-2.85216999	5.78036022
N	7.0	20.86380005	-3.46232986	8.13302040
C	6.0	18.12708092	-0.26621002	7.83587980
C	6.0	18.42729950	-1.05844998	6.74747038
C	6.0	19.37583923	-2.04716015	6.83872986
C	6.0	20.10567856	-2.24947023	7.99502039
C	6.0	18.85367966	-0.46054000	8.99440002
C	6.0	19.82390976	-1.42635000	9.07563972
I	53.0	26.29218102	1.15449989	8.93340969

F	9.0	25.15369034	-0.90085000	11.09565067
F	9.0	22.42667007	-1.59779000	6.45378017
F	9.0	24.29324913	0.29975000	6.61704016
F	9.0	23.31264877	-2.85216999	10.91303062
N	7.0	22.04441071	-3.46232986	8.56037045
C	6.0	24.78112984	-0.26621002	8.85750961
C	6.0	24.48090935	-1.05844998	9.94591999
C	6.0	23.53236961	-2.04716015	9.85466957
C	6.0	22.80253029	-2.24947023	8.69836998
C	6.0	24.05452919	-0.46054000	7.69898987
C	6.0	23.08429909	-1.42635000	7.61775017

Table S5. Coordinates for the *cis*-**2** dimer assembly

Br	35.0	1.04705000	6.57418013	17.04198074
Br	35.0	6.42224979	6.57418013	9.44032001
Br	35.0	1.04705000	0.97718000	17.04198074
Br	35.0	6.42224979	0.97718000	9.44032001
F	9.0	-0.40123001	8.76490021	15.48243046
F	9.0	0.63112998	10.70425987	13.93587017
F	9.0	4.98354006	9.10687923	14.82903004
F	9.0	3.95938015	7.15687990	16.34081078
F	9.0	7.87052011	8.76490021	10.99986076
F	9.0	6.83816004	10.70425987	12.54642963
F	9.0	2.48574996	9.10687923	11.65326977
F	9.0	3.50992012	7.15687990	10.14147949
F	9.0	-0.40123001	3.16790009	15.48243046
F	9.0	0.63112998	5.10726023	13.93587017
F	9.0	4.98354006	3.50988007	14.82903004
F	9.0	3.95938015	1.55988002	16.34081078
F	9.0	7.87052011	3.16790009	10.99986076
F	9.0	6.83816004	5.10726023	12.54642963
F	9.0	2.48574996	3.50988007	11.65326977
F	9.0	3.50992012	1.55988002	10.14147949
N	7.0	3.29572010	11.14195061	13.68992996
N	7.0	4.17357016	11.14195061	12.79236031
N	7.0	3.29572010	5.54495001	13.68992996
N	7.0	4.17357016	5.54495001	12.79236031
C	6.0	0.92590004	8.82423019	15.30605984
C	6.0	1.45035005	9.81826019	14.52095032
C	6.0	2.82629013	9.93523026	14.31015015
C	6.0	3.64917994	9.00612926	14.93548012
C	6.0	3.12270999	8.01210022	15.73613071
C	6.0	1.75355995	7.90575981	15.93033981
C	6.0	6.54340029	8.82423019	11.17623997
C	6.0	6.01894999	9.81826019	11.96135044
C	6.0	4.64300966	9.93523026	12.17214966

C	6.0	3.82011986	9.00612926	11.54681015
C	6.0	4.34658003	8.01210022	10.74616051
C	6.0	5.71574020	7.90575981	10.55195999
C	6.0	0.92590004	3.22723007	15.30605984
C	6.0	1.45035005	4.22126007	14.52095032
C	6.0	2.82629013	4.33822966	14.31015015
C	6.0	3.64917994	3.40913010	14.93548012
C	6.0	3.12270999	2.41509986	15.73613071
C	6.0	1.75355995	2.30875993	15.93033981
C	6.0	6.54340029	3.22723007	11.17623997
C	6.0	6.01894999	4.22126007	11.96135044
C	6.0	4.64300966	4.33822966	12.17214966
C	6.0	3.82011986	3.40913010	11.54681015
C	6.0	4.34658003	2.41509986	10.74616051
C	6.0	5.71574020	2.30875993	10.55195999

Table S6. Coordinates for the *cis*-**3** dimer assembly

F	9.0	8.36487961	2.41917014	0.59197998
F	9.0	6.69394016	0.55634004	1.65799999
F	9.0	7.71161032	-1.49416006	3.11216998
F	9.0	12.07126045	0.16762999	2.37493014
F	9.0	11.03822994	2.19028997	0.93403995
N	7.0	10.35966015	-1.89959002	3.44408011
C	6.0	8.86237907	1.40005004	1.30891001
C	6.0	8.00932980	0.46333998	1.85324001
C	6.0	8.54257011	-0.57471997	2.58580017
C	6.0	9.90474033	-0.69501001	2.82009006
C	6.0	10.74150085	0.26341000	2.24294996
C	6.0	10.22232914	1.29701996	1.49555993
F	9.0	13.21860981	2.41917014	7.21773005
F	9.0	14.88953972	0.55634004	6.15171003
F	9.0	13.87187004	-1.49416006	4.69754028
F	9.0	9.51221943	0.16762999	5.43477964
F	9.0	10.54524994	2.19028997	6.87566996
N	7.0	11.22381973	-1.89959002	4.36563015
C	6.0	12.72109985	1.40005004	6.50080013
C	6.0	13.57415009	0.46333998	5.95647001
C	6.0	13.04091072	-0.57471997	5.22391987
C	6.0	11.67875004	-0.69501001	4.98961973
C	6.0	10.84197998	0.26341000	5.56676006
C	6.0	11.36114979	1.29701996	6.31414986
F	9.0	8.36487961	-3.14983010	0.59197998
F	9.0	6.69394016	-5.01266003	1.65799999

F	9.0	7.71161032	-7.06315994	3.11216998
F	9.0	12.07126045	-5.40137005	2.37493014
F	9.0	11.03822994	-3.37871003	0.93403995
N	7.0	10.35966015	-7.46858978	3.44408011
C	6.0	8.86237907	-4.16895008	1.30891001
C	6.0	8.00932980	-5.10565996	1.85324001
C	6.0	8.54257011	-6.14372015	2.58580017
C	6.0	9.90474033	-6.26400995	2.82009006
C	6.0	10.74150085	-5.30559015	2.24294996
C	6.0	10.22232914	-4.27197981	1.49555993
F	9.0	13.21860981	-3.14983010	7.21773005
F	9.0	14.88953972	-5.01266003	6.15171003
F	9.0	13.87187004	-7.06315994	4.69754028
F	9.0	9.51221943	-5.40137005	5.43477964
F	9.0	10.54524994	-3.37871003	6.87566996
N	7.0	11.22381973	-7.46858978	4.36563015
C	6.0	12.72109985	-4.16895008	6.50080013
C	6.0	13.57415009	-5.10565996	5.95647001
C	6.0	13.04091072	-6.14372015	5.22391987
C	6.0	11.67875004	-6.26400995	4.98961973
C	6.0	10.84197998	-5.30559015	5.56676006
C	6.0	11.36114979	-4.27197981	6.31414986

4. Calculated molecular electrostatic potential & NCI plots for *cis*-1 and *cis*-2

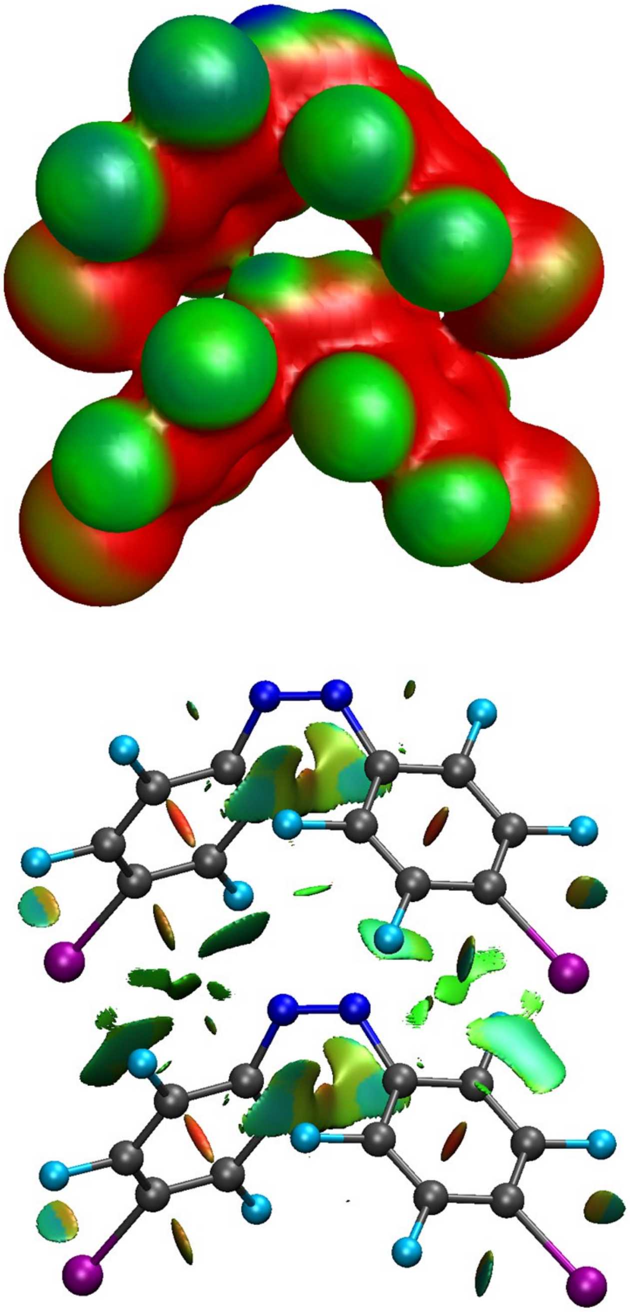


Figure S3. MEP plot iso = 0.007 (top) and NCI plot (bottom) of *cis*-**1** (RHO THRESHOLD(au): 0.20; RDG THRESHOLD (au): 2.00)

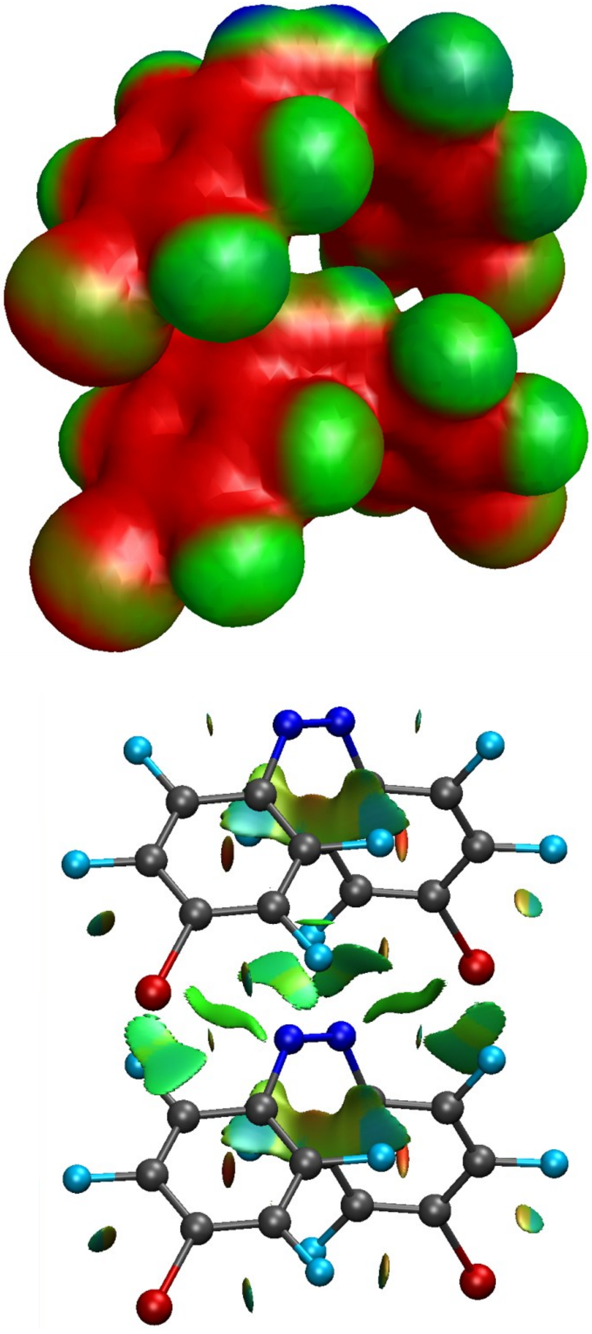


Figure S4. MEP plot iso = 0.007 (top) and NCI plot (bottom) of *cis*-**2** (RHO THRESHOLD (au): 0.20; RDG THRESHOLD (au): 2.00)

5. Calculations of intermolecular potentials

Table S7. Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-**1** (CSD code DOCCOP)

mol1	mol2	distance	energy (kJ/mol)
0	1	5.3242	-54.4191
0	2	6.41114	-25.1655
0	3	6.56237	-19.9726

Packing Energy:
PE = -135.61 kJ/mol 40 interactions
PE = -138.47 kJ/mol 120 interactions
PE = -138.74 kJ/mol 160 interactions
PE = -138.83 kJ/mol 180 interactions
PE = -138.87 kJ/mol 190 interactions
PE = -138.90 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S8. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
I1	15	I1	15	1505374.0	3.11	26517.0
I1	15	F1	6	507240.7	3.67	3870.1
I1	15	N1	23	1302038.0	3.64	20663.5
I1	15	C1	3	583466.5	3.29	8007.4
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
F1	6	C1	3	196600.9	3.84	1168.8
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	C1	3	491494.0	3.86	2791.0
C1	3	C1	3	226145.2	3.47	2418.0

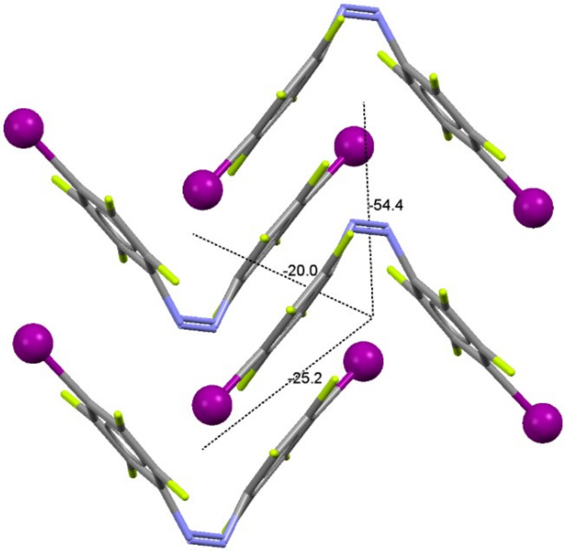


Figure S5. Fragment of crystal structure of *cis*-**1** (CSD code DOCCOP), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl is oriented vertically.

Table S9. Three most negative calculated inter-molecular potentials for crystal structure of cis-2 (CSD code DOCCEF):

mol1	mol2	distance	energy (kJ/mol)
0	1	5.3155	-49.628
0	2	6.33694	-21.9495
0	3	6.4965	-19.8855

Packing Energy:
PE = -129.39 kJ/mol 40 interactions
PE = -131.85 kJ/mol 120 interactions
PE = -132.10 kJ/mol 160 interactions
PE = -132.18 kJ/mol 180 interactions
PE = -132.22 kJ/mol 190 interactions
PE = -132.25 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S10. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
Br1	13	Br1	13	2017608.0	3.57	10786.0
Br1	13	C1	3	675479.4	3.52	5106.9
Br1	13	F1	6	587232.7	3.89	2468.3
Br1	13	N1	23	651019.0	3.53	12358.4
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	F1	6	196600.9	3.84	1168.8
C1	3	N1	23	491494.0	3.86	2791.0
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
N1	23	N1	23	365263.0	3.65	2891.0

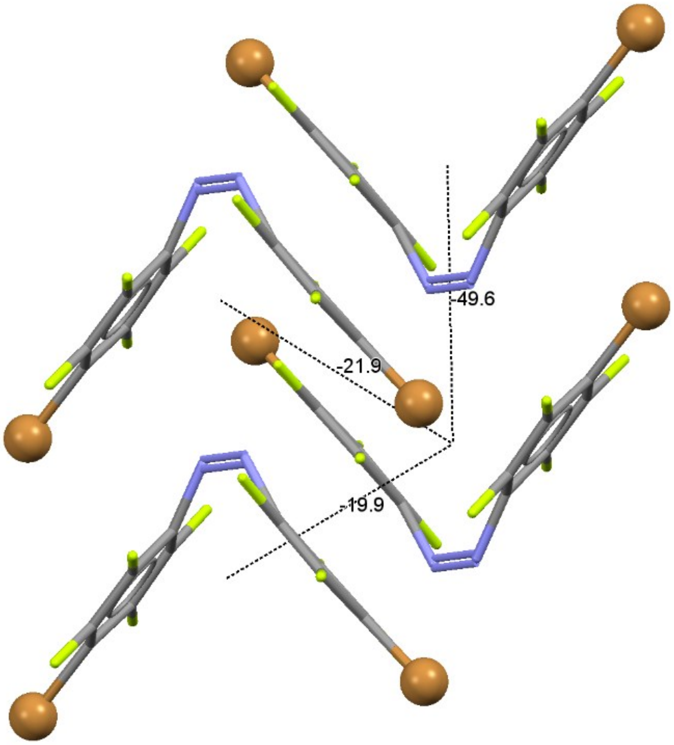


Figure S6. Fragment of crystal structure of *cis*-**2** (CSD code DOCCEF), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl is oriented vertically.

Table S11. Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-**2** (CSD code DOCCEF01):

mol1	mol2	distance	energy (kJ/mol)
0	1	5.597	-43.5418
0	2	9.12777	-22.137
0	3	7.40284	-19.3471

Packing Energy:
PE = -129.47 kJ/mol 40 interactions
PE = -131.74 kJ/mol 120 interactions
PE = -131.99 kJ/mol 160 interactions
PE = -132.08 kJ/mol 180 interactions
PE = -132.11 kJ/mol 190 interactions
PE = -132.14 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S12. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
Br1	13	Br1	13	2017608.0	3.57	10786.0
Br1	13	C1	3	675479.4	3.52	5106.9
Br1	13	F1	6	587232.7	3.89	2468.3
Br1	13	N1	23	651019.0	3.53	12358.4
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	F1	6	196600.9	3.84	1168.8
C1	3	N1	23	491494.0	3.86	2791.0
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
N1	23	N1	23	365263.0	3.65	2891.0

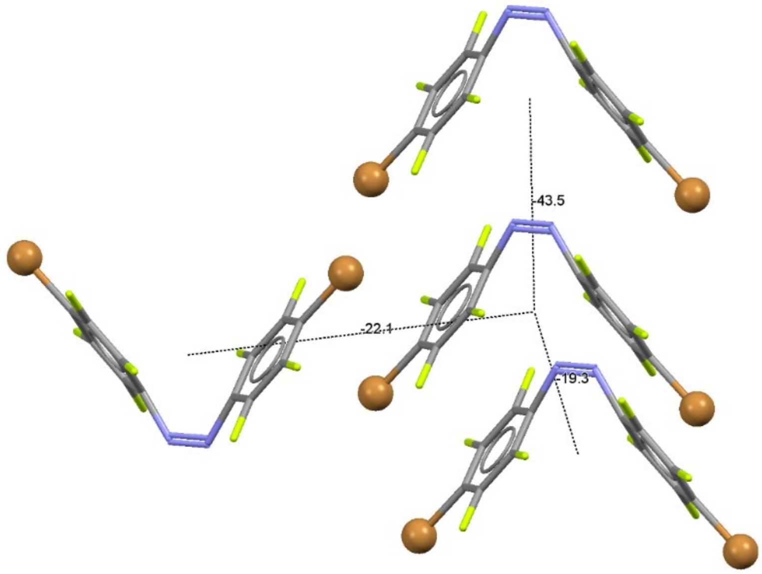


Figure S7. Fragment of crystal structure of *cis*-**2** (CSD code DOCCEF01), displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is oriented vertically.

Table S13. Three most negative calculated inter-molecular potentials for crystal structure of *cis*-**3**:

mol1	mol2	distance	energy (kJ/mol)
0	1	5.569	-33.876
0	2	7.42675	-15.9682
0	3	8.34309	-12.882

Packing Energy:
PE = -108.13 kJ/mol 40 interactions
PE = -110.03 kJ/mol 120 interactions
PE = -110.24 kJ/mol 160 interactions
PE = -110.32 kJ/mol 180 interactions
PE = -110.34 kJ/mol 190 interactions
PE = -110.37 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S14. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
F1	6	C1	3	196600.9	3.84	1168.8
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	C1	3	491494.0	3.86	2791.0
C1	3	C1	3	226145.2	3.47	2418.0

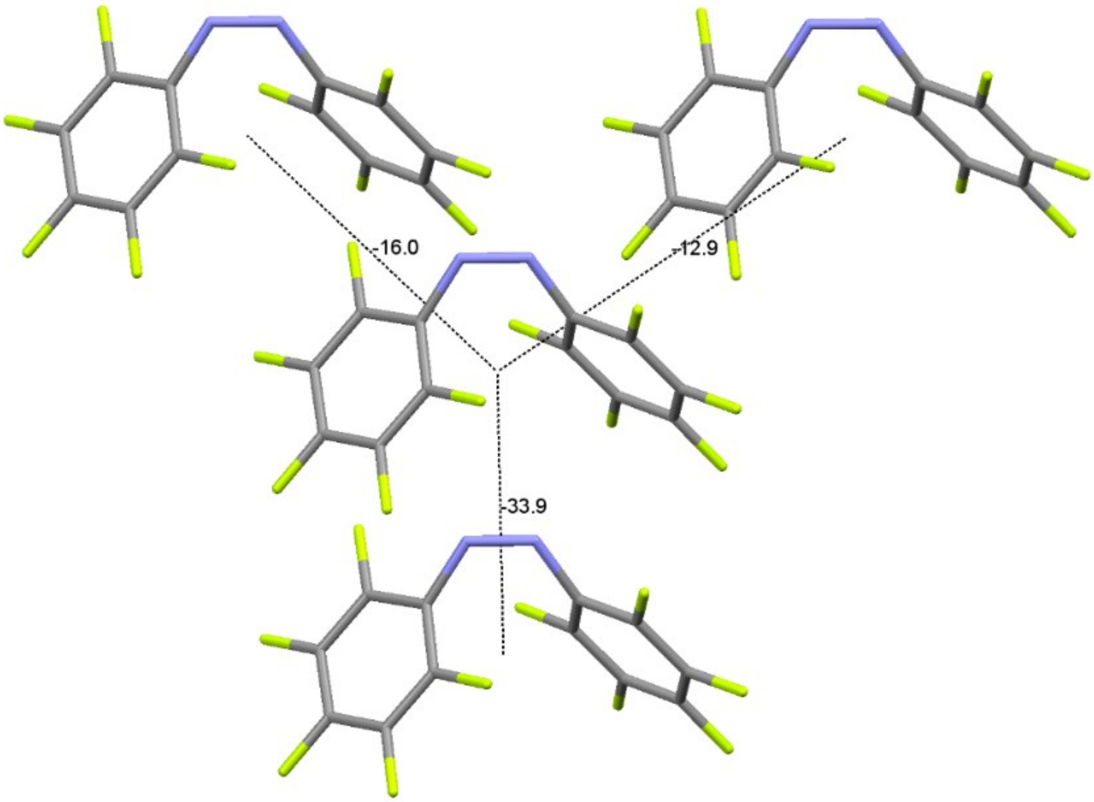


Figure S8. Fragment of crystal structure of *cis*-**3**, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is oriented vertically.

Table S15. Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-**4**:

mol1	mol2	distance	energy(kJ/mol)
0	1	5.6611	-40.3024
0	2	7.74331	-20.4451
0	3	7.45	-15.2718

Packing Energy:
PE = -115.55 kJ/mol 40 interactions
PE = -117.67 kJ/mol 120 interactions
PE = -117.90 kJ/mol 160 interactions
PE = -117.97 kJ/mol 180 interactions
PE = -118.00 kJ/mol 190 interactions
PE = -118.03 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S16. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
Br1	13	Br1	13	2017608.0	3.57	10786.0
Br1	13	C1	3	675479.4	3.52	5106.9
Br1	13	H1	1	220774.5	3.79	1085.3
Br1	13	F1	6	587232.7	3.89	2468.3
Br1	13	N1	23	651019.0	3.53	12358.4
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	H1	1	120792.1	4.10	472.8
C1	3	F1	6	196600.9	3.84	1168.8
C1	3	N1	23	491494.0	3.86	2791.0
H1	1	H1	1	24158.0	4.01	109.2
H1	1	F1	6	64257.8	4.11	248.4
H1	1	N1	23	228279.0	4.52	502.1
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
N1	23	N1	23	365263.0	3.65	2891.0

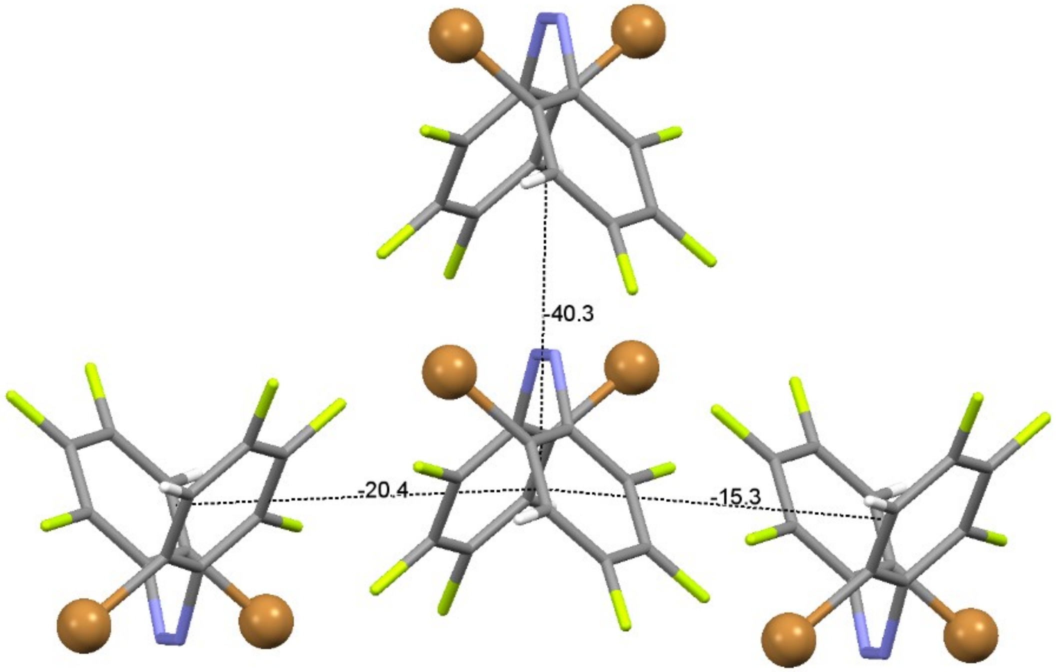


Figure S9. Fragment of crystal structure of *cis*-**4**, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is oriented vertically.

Table S17. Three most negative calculated inter-molecular potentials for the crystal structure of *cis*-**5**:

mol1	mol2	distance	energy(kJ/mol)
0	1	5.88969	-34.3962
0	2	8.37817	-28.3839
0	3	8.96892	-22.8244

Packing Energy:
PE = -113.75 kJ/mol 40 interactions
PE = -115.80 kJ/mol 120 interactions
PE = -116.02 kJ/mol 160 interactions
PE = -116.09 kJ/mol 180 interactions
PE = -116.12 kJ/mol 190 interactions
PE = -116.14 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Table S18. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
Br1	13	Br1	13	2017608.0	3.57	10786.0
Br1	13	F1	6	587232.7	3.89	2468.3
Br1	13	N1	23	651019.0	3.53	12358.4
Br1	13	C1	3	675479.4	3.52	5106.9
Br1	13	H2	1	220774.5	3.79	1085.3
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
F1	6	C1	3	196600.9	3.84	1168.8
F1	6	H2	1	64257.8	4.11	248.4
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	C1	3	491494.0	3.86	2791.0
N1	23	H2	1	228279.0	4.52	502.1
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	H2	1	120792.1	4.10	472.8
H2	1	H2	1	24158.0	4.01	109.2

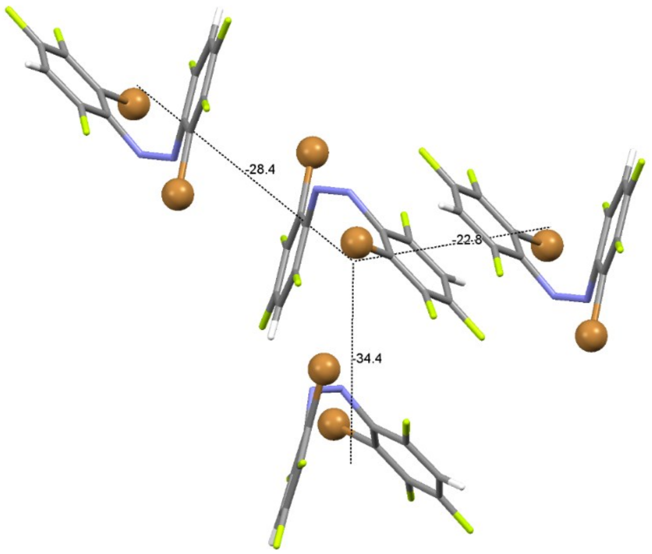


Figure S10. Fragment of crystal structure of *cis*-**5**, displaying the directions and magnitudes of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is vertical.

Table S19. Four most negative calculated inter-molecular potentials for the crystal structure of (*cis*-**1**)(**dabco**) cocrystal:

mol1	mol2	distance	energy (kJ/mol)
0	1	6.3311	-38.6093
2	3	6.3311	-37.5472
2	4	8.84633	-17.9562
2	5	5.71033	-17.5944

Packing Energy:
Cluster 1 PE = -41.76 kJ/mol 440 interactions
PE = -41.77 kJ/mol 520 interactions
PE = -41.78 kJ/mol 560 interactions
PE = -41.78 kJ/mol 580 interactions
PE = -41.78 kJ/mol 590 interactions
PE = -41.78 kJ/mol 600 interactions
Cluster 2 PE = -119.29 kJ/mol 440 interactions
PE = -119.33 kJ/mol 520 interactions
PE = -119.34 kJ/mol 560 interactions
PE = -119.34 kJ/mol 580 interactions
PE = -119.35 kJ/mol 590 interactions
PE = -119.35 kJ/mol 600 interactions
Cluster 3 PE = -116.32 kJ/mol 440 interactions
PE = -116.36 kJ/mol 520 interactions
PE = -116.37 kJ/mol 560 interactions
PE = -116.37 kJ/mol 580 interactions
PE = -116.37 kJ/mol 590 interactions
PE = -116.37 kJ/mol 600 interactions

Total packing energy = -277.5 kJ/mol
Inter-fragment energy (1-2): -17.6 kJ/mol
Inter-fragment energy (1-3): -7.73 kJ/mol
Inter-fragment energy (2-3): -0.717 kJ/mol

Potential = A*exp(-Br) - Cr(-6)

Table S20. Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	H4	1	120792.1	4.10	472.8
C1	3	N1	23	491494.0	3.86	2791.0
C1	3	F1	6	196600.9	3.84	1168.8
C1	3	I1	15	583466.5	3.29	8007.4
H4	1	H4	1	24158.0	4.01	109.2
H4	1	N1	23	228279.0	4.52	502.1
H4	1	F1	6	64257.8	4.11	248.4
H4	1	I1	15	190700.9	3.56	1701.7
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	F1	6	249858.9	3.93	1277.9
N1	23	I1	15	1302038.0	3.64	20663.5
F1	6	F1	6	170916.4	4.22	564.8
F1	6	I1	15	507240.7	3.67	3870.1
I1	15	I1	15	1505374.0	3.11	26517.0

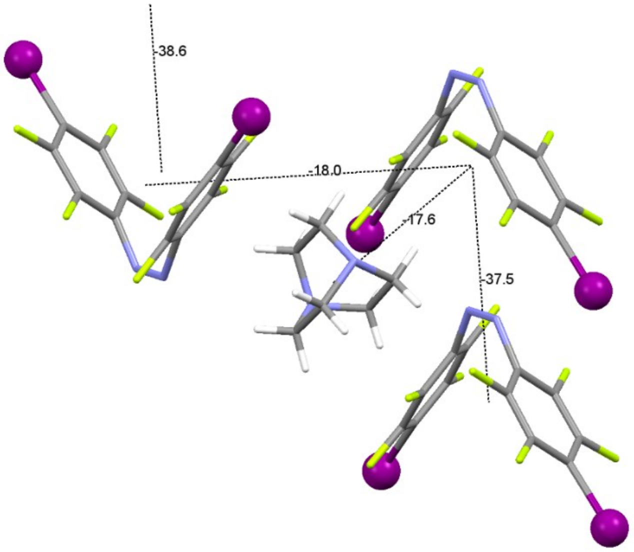


Figure S11. Fragment of crystal structure of (*cis*-**1**)(**dabco**) cocrystal, displaying the directions and magnitudes (in kJ mol^{-1}) of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is always vertical. The structure contains two symmetrically independent molecular stacks, hence two values for the intermolecular potential in the azo···phenyl stacking direction

Table S21. Three most negative calculated inter-molecular potentials for (*cis*-**1**)(dithiane):

mol1	mol2	distance	energy (kJ/mol)
0	1	5.4079	-51.0623
0	2	6.22387	-26.0184
0	3	6.37657	-21.9186

Packing Energy:

Cluster 1	PE = -51.27 kJ/mol 240 interactions
	PE = -51.33 kJ/mol 320 interactions
	PE = -51.34 kJ/mol 360 interactions
	PE = -51.35 kJ/mol 380 interactions
	PE = -51.35 kJ/mol 390 interactions
	PE = -51.35 kJ/mol 400 interactions
Cluster 2	PE = -133.96 kJ/mol 240 interactions
	PE = -134.10 kJ/mol 320 interactions
	PE = -134.14 kJ/mol 360 interactions
	PE = -134.15 kJ/mol 380 interactions
	PE = -134.15 kJ/mol 390 interactions
	PE = -134.15 kJ/mol 400 interactions

Total packing energy = -185.5 kJ/mol
Inter-fragment energy (1-2): -0.41 kJ/mol

Table S22. Unified (UNI) pair-potential parameters, Potential = A*exp(-Br) - Cr(-6):

atom1	code1	atom2	code2	A	B	C
I1	15	I1	15	1505374.0	3.11	26517.0
I1	15	C1	3	583466.5	3.29	8007.4
I1	15	F1	6	507240.7	3.67	3870.1
I1	15	N1	23	1302038.0	3.64	20663.5
I1	15	H7A	1	190700.9	3.56	1701.7
I1	15	S1	9	1279591.6	3.31	16889.2
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	F1	6	196600.9	3.84	1168.8
C1	3	N1	23	491494.0	3.86	2791.0
C1	3	H7A	1	120792.1	4.10	472.8
C1	3	S1	9	529108.6	3.41	6292.7
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N1	23	249858.9	3.93	1277.9
F1	6	H7A	1	64257.8	4.11	248.4
F1	6	S1	9	431162.5	3.87	2465.0
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	H7A	1	228279.0	4.52	502.1
N1	23	S1	9	630306.9	3.59	5576.8
H7A	1	H7A	1	24158.0	4.01	109.2
H7A	1	S1	9	268571.0	4.03	1167.3
S1	9	S1	9	1087673.0	3.52	10757.1

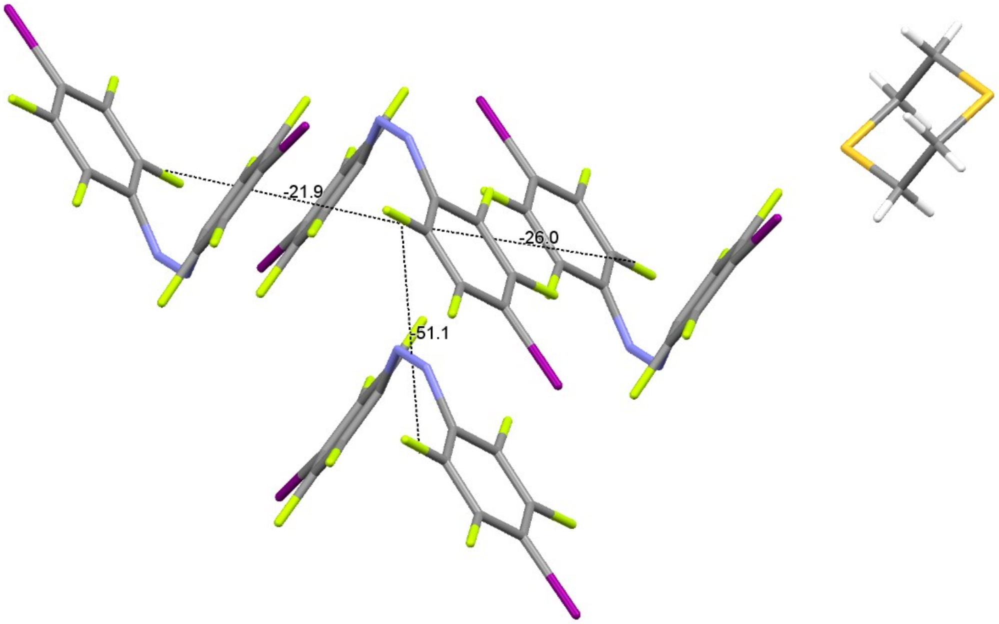


Figure S12. Fragment of crystal structure of (*cis*-**1**)(dithiane) cocrystal, displaying the directions and magnitudes (in kJ mol^{-1}) of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is always vertical.

Table S23. Three most negative calculated inter-molecular potentials for the crystal structure of the (*cis*-**1**)(4-vinylpyridine)$_2$ cocrystal :

mol1	mol2	distance	energy(kJ/mol)
0	1	5.4157	-52.6147
0	2	9.07845	-19.3498
3	4	6.13737	-13.3963

Packing Energy:

Cluster 1	PE = -130.56 kJ/mol 240 interactions
	PE = -130.72 kJ/mol 320 interactions
	PE = -130.76 kJ/mol 360 interactions
	PE = -130.78 kJ/mol 380 interactions
	PE = -130.78 kJ/mol 390 interactions
	PE = -130.79 kJ/mol 400 interactions

Cluster 2	PE = -54.39 kJ/mol 240 interactions
	PE = -54.44 kJ/mol 320 interactions
	PE = -54.46 kJ/mol 360 interactions
	PE = -54.46 kJ/mol 380 interactions
	PE = -54.46 kJ/mol 390 interactions
	PE = -54.46 kJ/mol 400 interactions

Total packing energy = -185.3 kJ/mol
Inter-fragment energy (1-2): -5.41 kJ/mol

Table S24. Unified (UNI) pair-potential parameters, Potential = A*exp(-Br) - Cr(-6):

atom1	code1	atom2	code2	A	B	C
I1	15	I1	15	1505374.0	3.11	26517.0
I1	15	F1	6	507240.7	3.67	3870.1
I1	15	N2	23	1302038.0	3.64	20663.5
I1	15	C8	3	583466.5	3.29	8007.4
I1	15	H1	1	190700.9	3.56	1701.7
F1	6	F1	6	170916.4	4.22	564.8
F1	6	N2	23	249858.9	3.93	1277.9
F1	6	C8	3	196600.9	3.84	1168.8
F1	6	H1	1	64257.8	4.11	248.4
N2	23	N2	23	365263.0	3.65	2891.0
N2	23	C8	3	491494.0	3.86	2791.0
N2	23	H1	1	228279.0	4.52	502.1
C8	3	C8	3	226145.2	3.47	2418.0
C8	3	H1	1	120792.1	4.10	472.8
H1	1	H1	1	24158.0	4.01	109.2

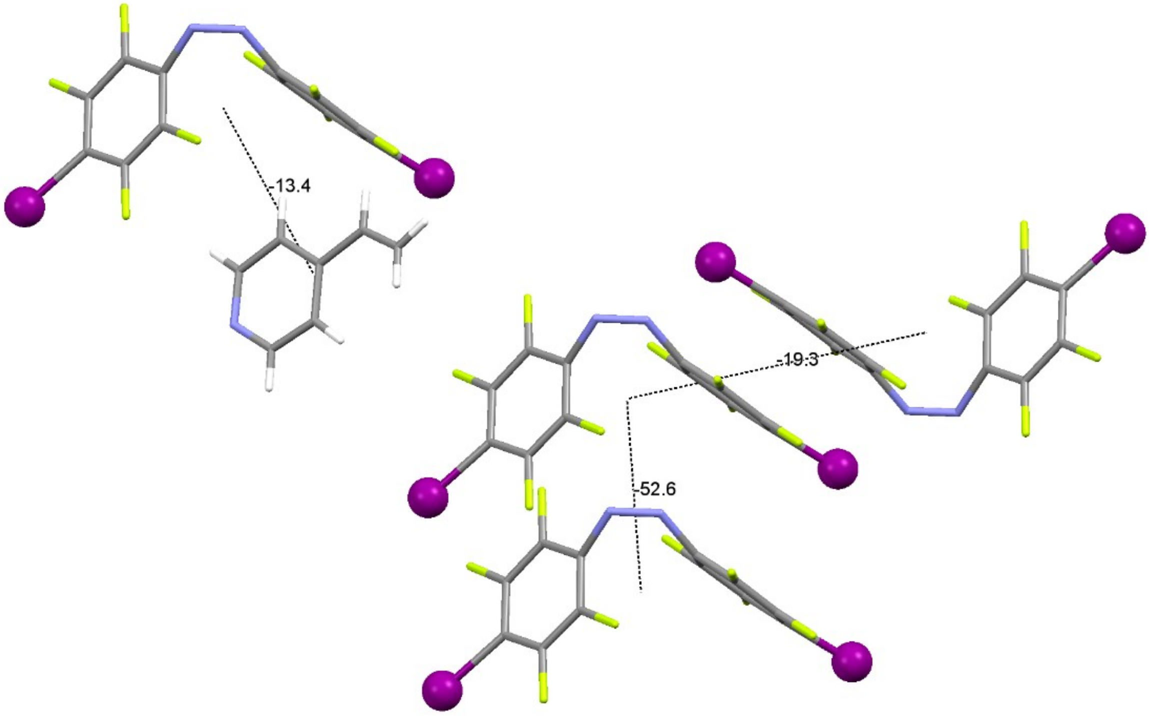


Figure S13. Fragment of crystal structure of (*cis*-**1**)(4-vinylpyridine)$_2$ cocrystal, displaying the directions and magnitudes (in kJ mol^{-1}) of three most negative intermolecular potentials. For clarity, the direction of the azo···phenyl stacking is always vertical.

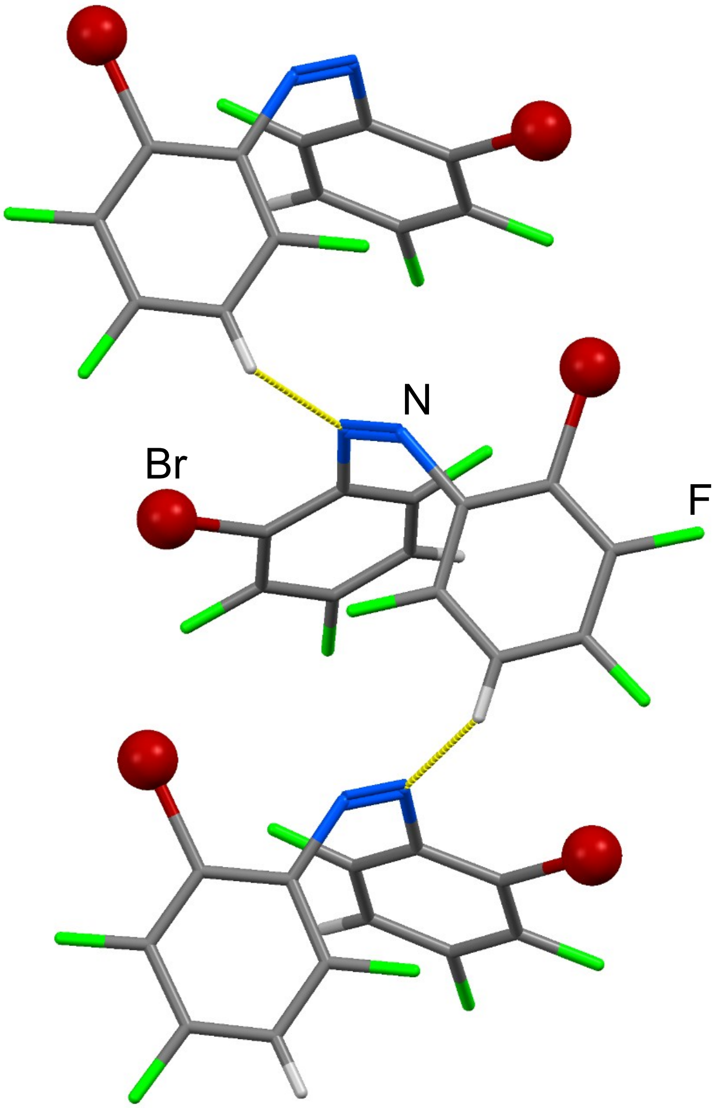


Figure S14. View of a fragment of a single azo···phenyl stack in the crystal structure of *cis*-**5**, highlighting the C-H···N interactions that might be responsible for directing the orientation of nearest-neighbour molecules in the stack. The C···N distance is 3.22 Å, the C-H···N angle 116°.

6. Fourier-transform attenuated total reflectance (FTIR-ATR) spectroscopy

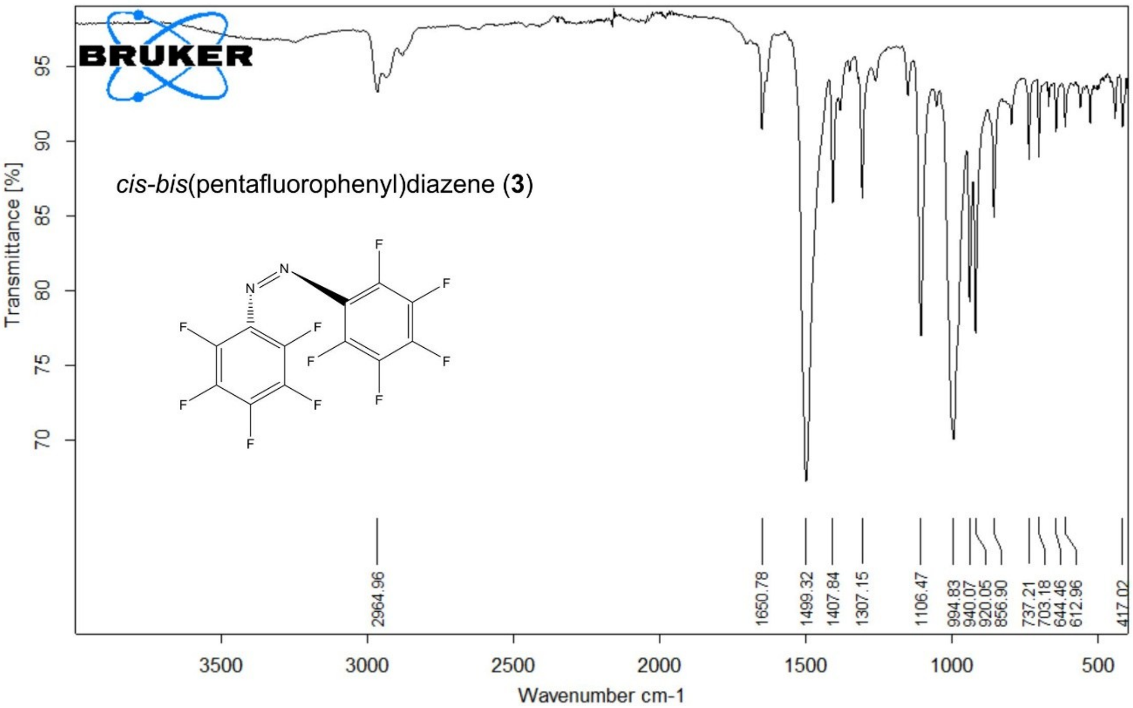


Figure S15. FTIR-ATR spectrum of *cis-bis*(pentafluorophenyl)diazene (**3**)

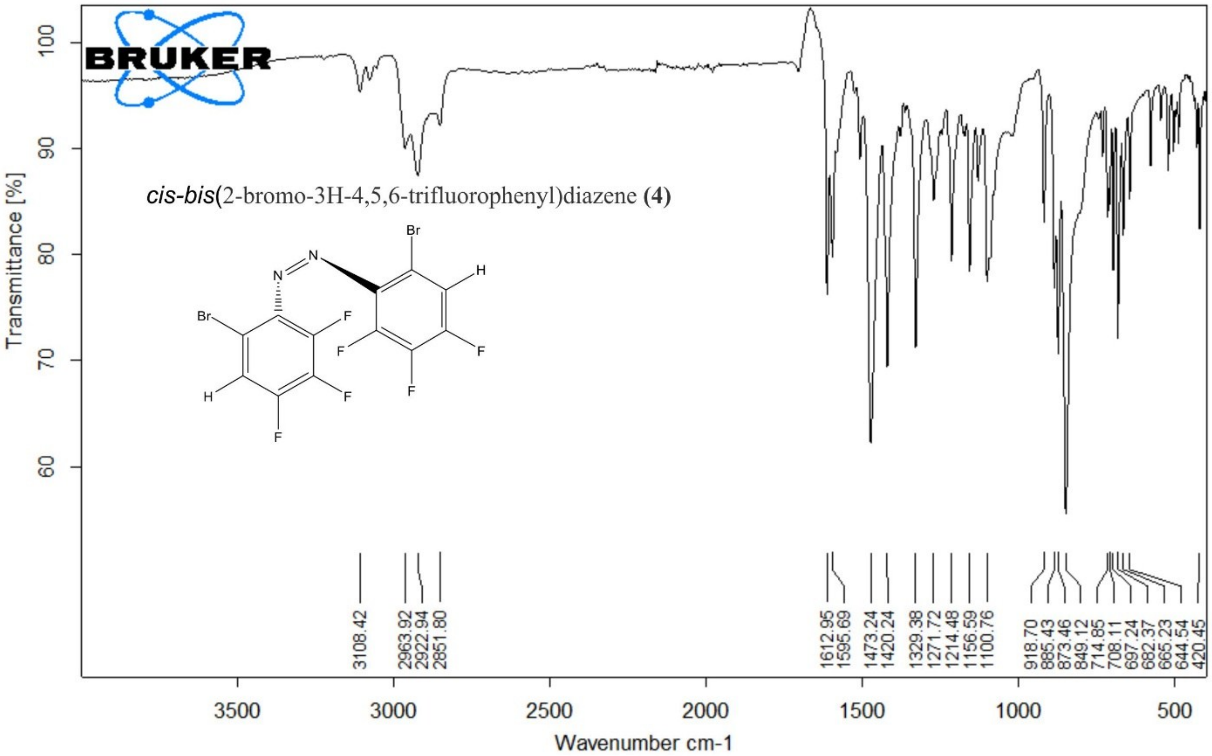


Figure S16. FTIR-ATR spectrum of *cis-bis*(2-bromo-3H-4,5,6-trifluorophenyl)diazene (**4**)

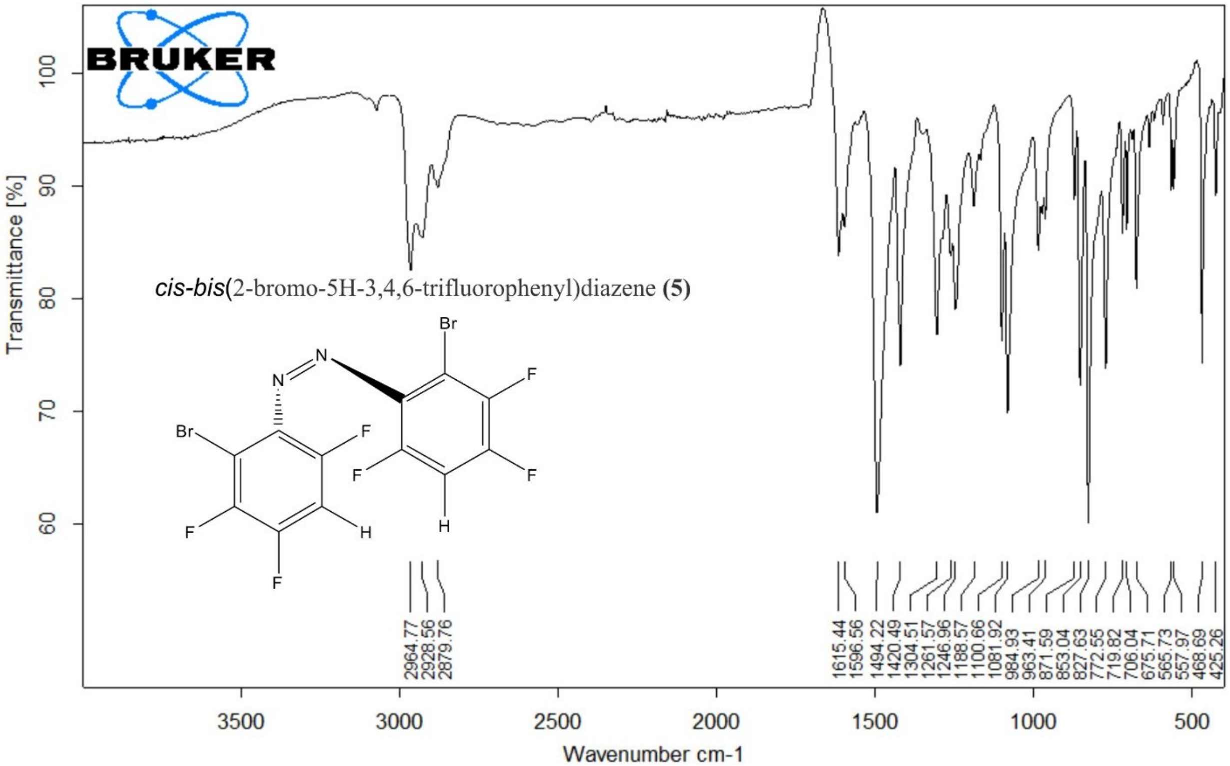


Figure S17. FTIR-ATR spectrum of *cis-bis*(2-bromo-5H-3,4,6-trifluorophenyl)diazene (**5**)

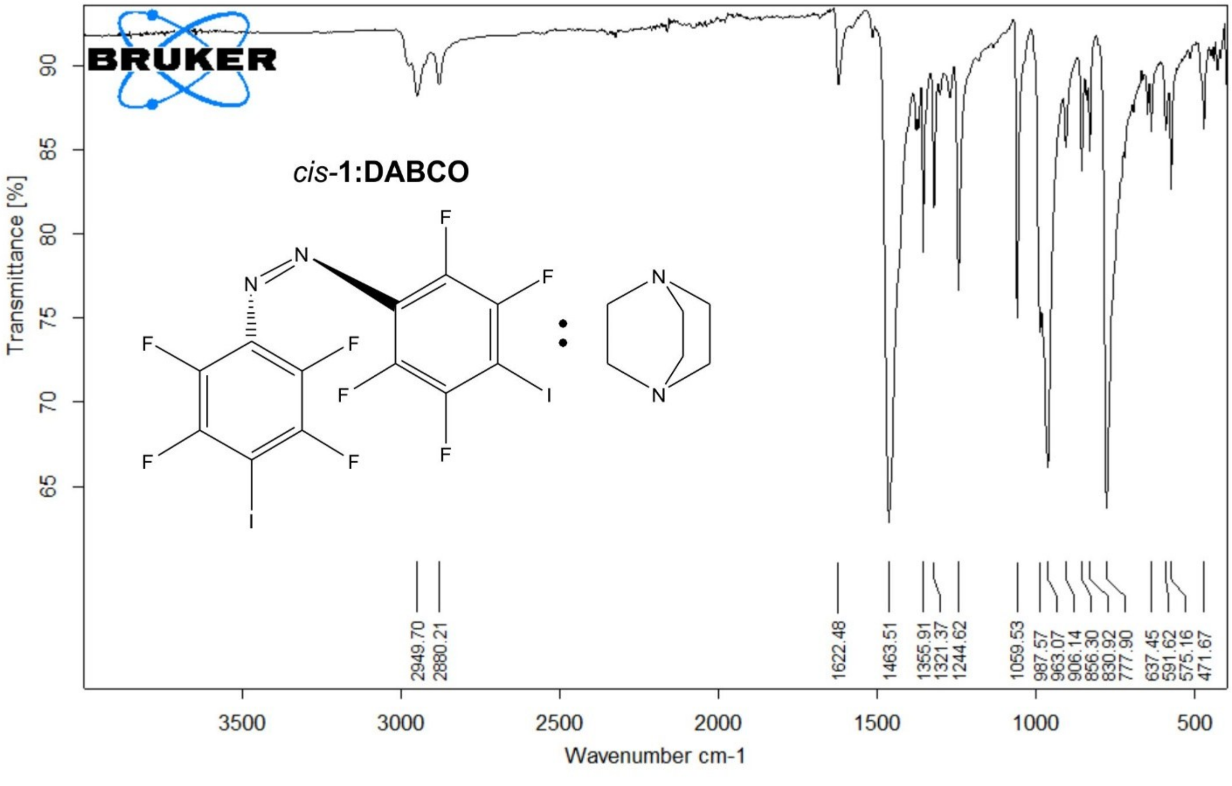


Figure S18. FTIR-ATR spectrum of *cis*-**1**:DABCO cocrystal.

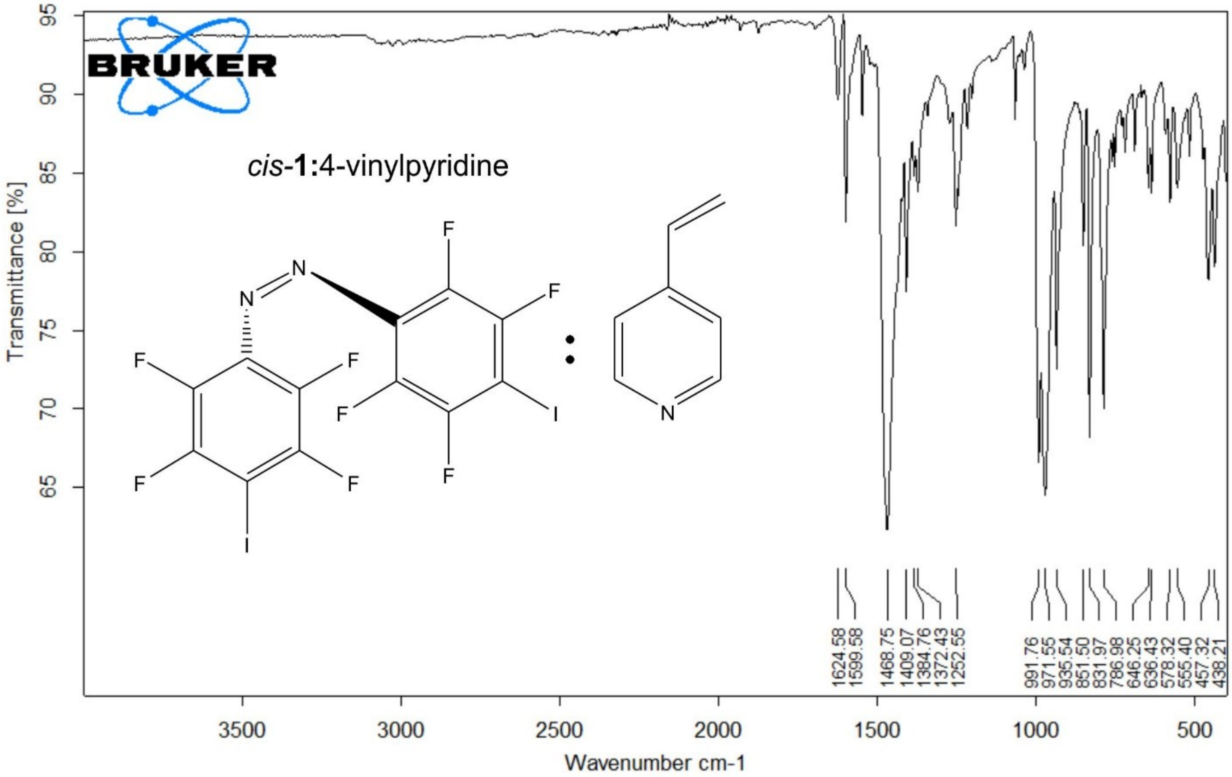


Figure S19. FTIR-ATR spectrum of *cis*-**1**:4-vinylpyridine cocrystal.

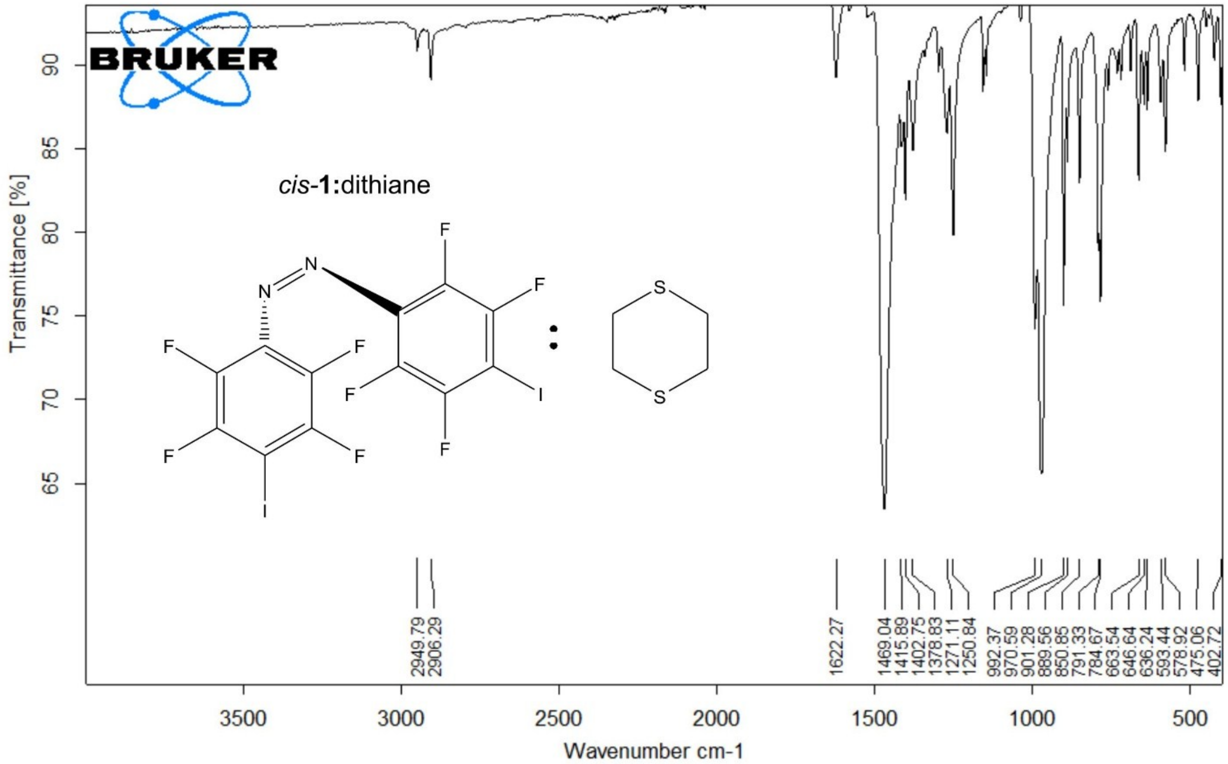
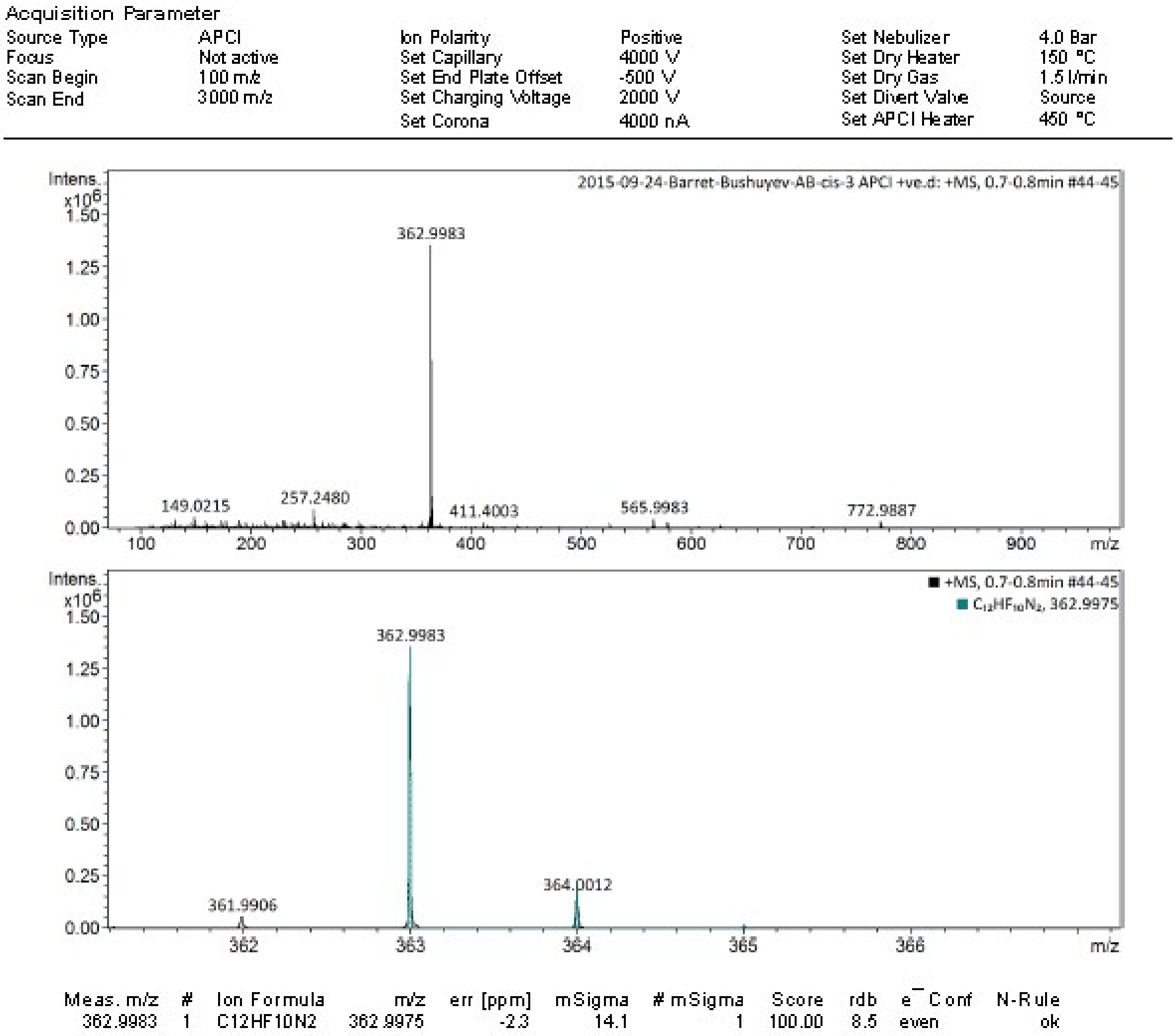


Figure S20. FTIR-ATR spectrum of *cis*-**1**:dithiane cocrystal.

7. Mass Spectrometry

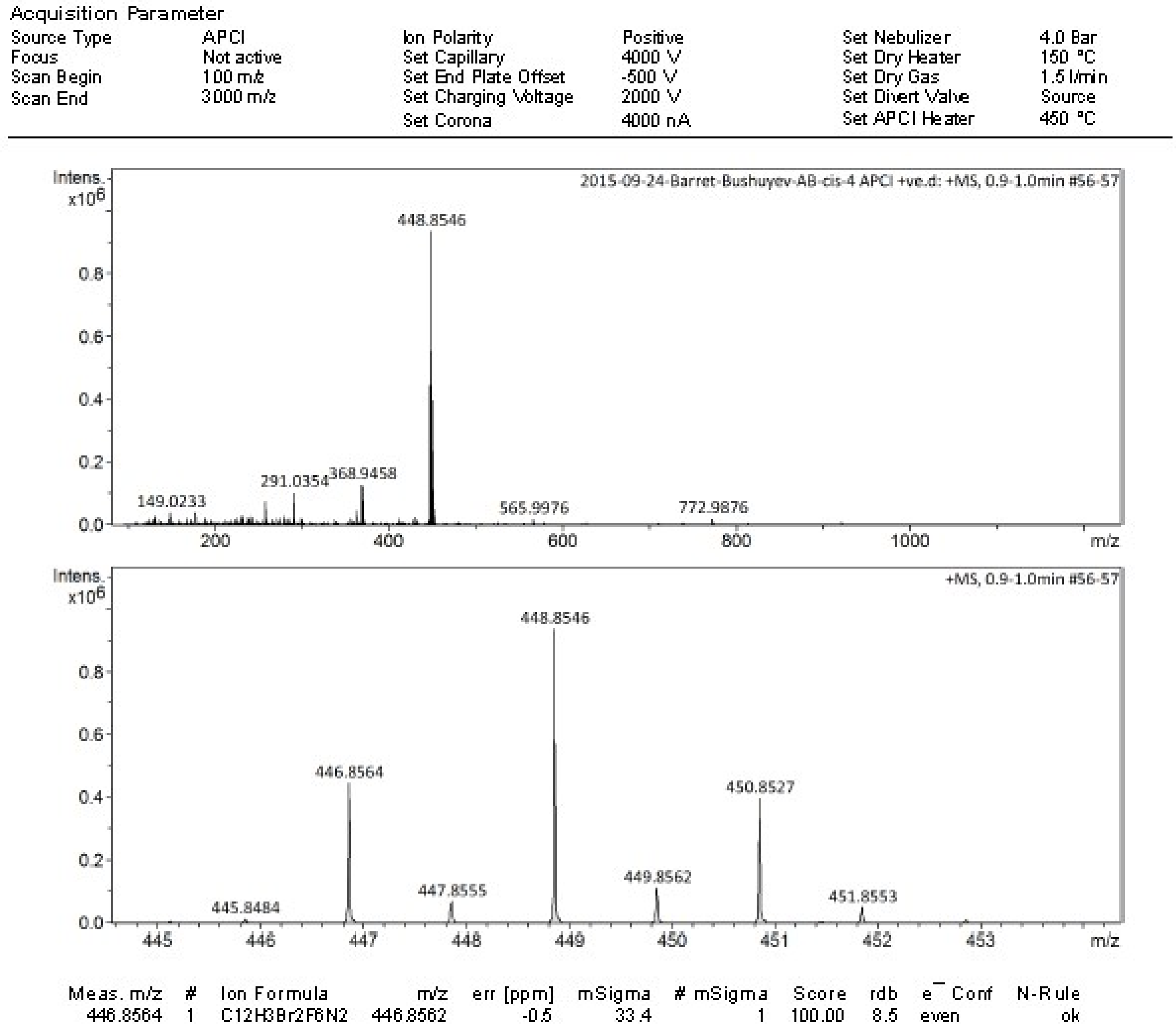


Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	4.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	150 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	4000 nA	Set APCI Heater	450 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e^- Conf	N-Rule
362.9983	1	C12HF10N2	362.9975	-2.3	14.1	1	100.00	8.5	even	ok

Figure S21. High Resolution Mass spectrum for compound *cis*-**3**

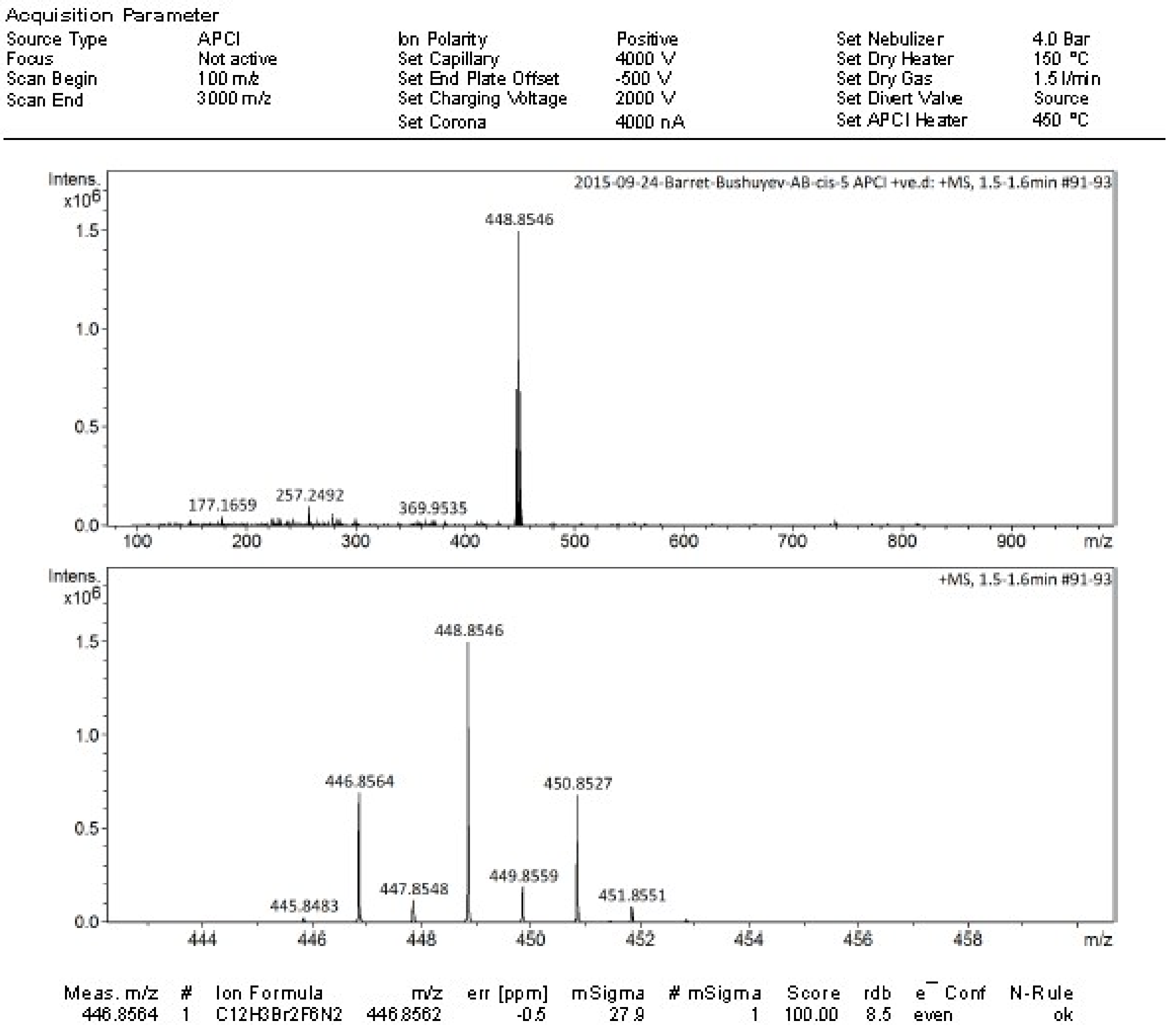


Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	4.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	150 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	4000 nA	Set APCI Heater	450 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
446.8564	1	C12H3Br2F6N2	446.8562	-0.5	33.4	1	100.00	8.5	even	ok

Figure S22. High Resolution Mass spectrum for compound *cis*-**4**



Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	4.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	150 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	4000 nA	Set APCI Heater	450 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
446.8564	1	C12H3Br2F6N2	446.8562	-0.5	27.9	1	100.00	8.5	even	ok

Figure S23. High Resolution Mass spectrum for compound *cis*-**5**

8. UV-Vis spectroscopy

UV-Vis spectroscopy studies of compounds **3-5** were performed on a Cary 300 Bio UV-Vis spectrometer in hexane solution.

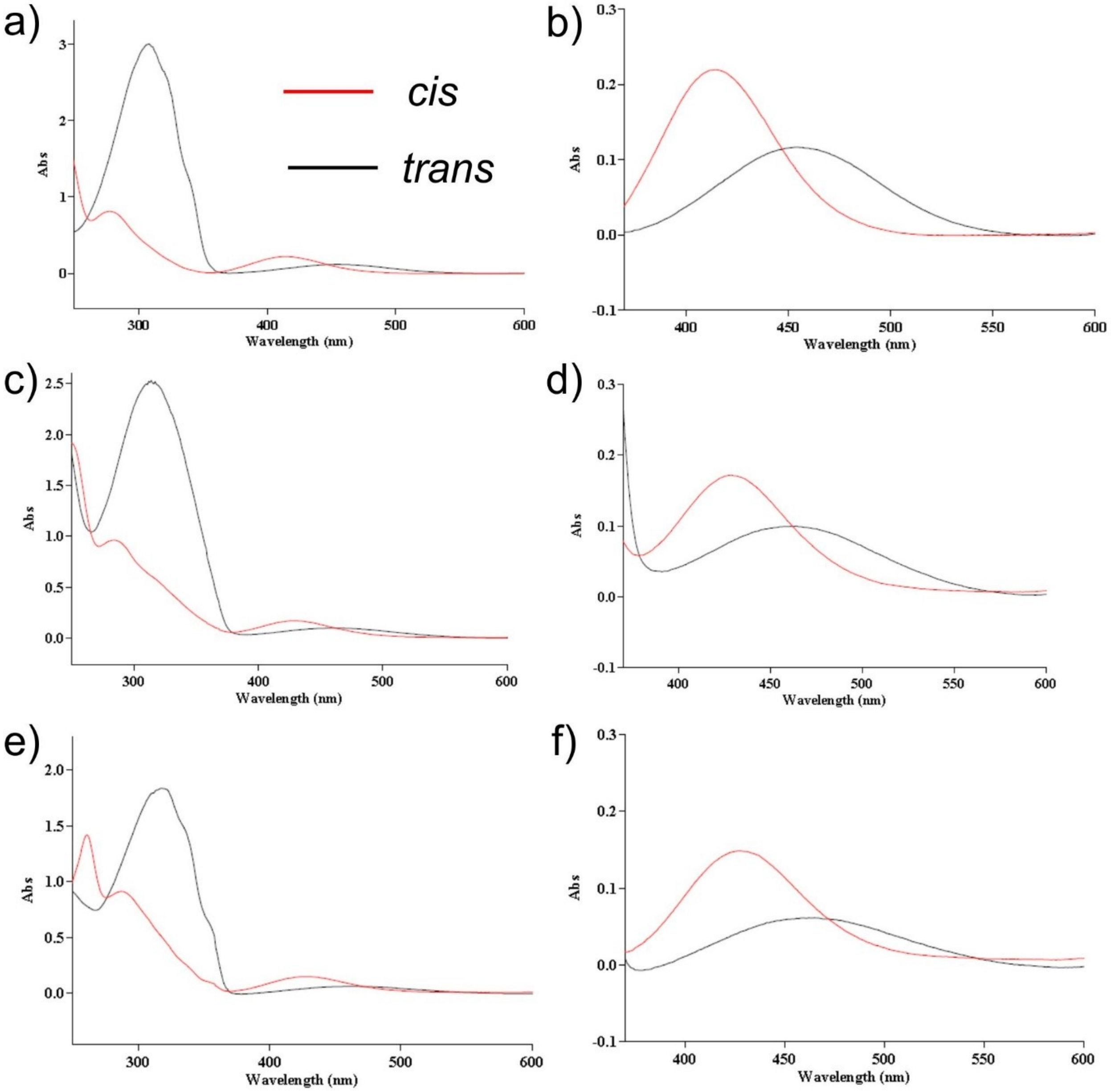


Figure S24. UV-Vis absorption spectra of *cis* and *trans*-isomers of compound **3** (a, b) **4** (c, d) **5** (e, f) in hexanes. In all figures red line denotes the *cis*-isomer and black line the *trans*-isomer.

9. References

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