Pseudo-Stilbene- and Azobenzene-Type Systems for Optical Frequency Conversion: Estimating the First-Order Molecular Hyperpolarizability

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S1. Optimized Geometries

Compound: PS-1

Cartesian coordinates (after OPT)

N	0.47997	0.57529	-0.00106
N	-0.24421	-0.44264	0.00123
C	1.87037	0.30933	-0.00073
C	2.42995	-0.96965	-0.00452
C	3.79840	-1.12078	-0.00417
C	4.60071	0.01088	-0.00007
C	4.06901	1.28777	0.00352
C	2.69652	1.42932	0.00301
C	-1.62027	-0.23509	0.00060
C	-2.24649	1.01798	-0.00254
C	-3.61207	1.11821	-0.00284
C	-4.43354	-0.03784	0.00000
C	-3.79085	-1.29494	0.00312
C	-2.41959	-1.37842	0.00340
N	6.04979	-0.15098	0.00031
O	6.50437	-1.28343	-0.00273
O	6.74316	0.85308	0.00370
N	-5.78505	0.06441	-0.00027
C	-6.42602	1.36663	-0.00300
C	-6.60828	-1.13032	0.00292
H	1.78372	-1.83459	-0.00782
H	4.25118	-2.10092	-0.00714
H	4.72176	2.14749	0.00658
H	2.24449	2.41194	0.00562
H	-1.64106	1.91364	-0.00473
H	-4.06174	2.09940	-0.00529
H	-4.37106	-2.20467	0.00533
H	-1.93542	-2.34719	0.00583
H	-6.15766	1.94502	-0.89048
H	-7.50288	1.23044	-0.00251
H	-6.15733	1.94886	0.88188
H	-6.42515	-1.74595	-0.88137
H	-7.65439	-0.84065	0.00205
H	-6.42530	-1.74117	0.89056

Compound: PS-2

Cartesian coordinates (after OPT)

C	0.49916	0.47195	-0.09704
N	-0.30291	-0.48452	0.12449
C	1.95616	0.29087	-0.06302
C	2.53428	-0.94515	0.23014
C	3.90380	-1.08888	0.25049
C	4.69379	0.01728	-0.02315
C	4.15251	1.25485	-0.31507
C	2.77731	1.38309	-0.33294
C	-1.69364	-0.28283	0.12123
C	-2.32086	0.93066	0.40251
C	-3.69469	1.04768	0.38266
C	-4.51896	-0.05247	0.08064
C	-3.87887	-1.27302	-0.19762
C	-2.50423	-1.37946	-0.15566
N	6.14723	-0.13009	-0.00186
O	6.61096	-1.22736	0.25923
O	6.82977	0.85052	-0.24635
N	-5.88974	0.05682	0.08594
C	-6.49488	1.37370	0.12200
C	-6.68761	-1.03136	-0.44318
H	0.15573	1.48113	-0.34079
H	1.89345	-1.78962	0.44075
H	4.36495	-2.03893	0.47453
H	4.79804	2.09461	-0.52301
H	2.33398	2.34439	-0.55985
H	-1.73327	1.80029	0.66851
H	-4.13104	2.00633	0.61939
H	-4.45742	-2.15158	-0.43961
H	-2.03346	-2.33316	-0.36068
H	-7.57596	1.26509	0.12649
H	-6.21297	1.98837	-0.74124
H	-6.21536	1.91114	1.02903
H	-7.73988	-0.78313	-0.33424
H	-6.48571	-1.22297	-1.50405
H	-6.50858	-1.95422	0.10976

Compound: PS-3

Cartesian coordinates (after OPT)

C	0.59418	0.50950	0.02195
C	-0.34328	-0.44615	0.01815
C	2.03709	0.29557	0.01095
C	2.63205	-0.97387	-0.00122
C	3.99992	-1.11927	-0.01130
C	4.79957	0.01449	-0.00958
C	4.25114	1.28524	0.00234
C	2.87908	1.41438	0.01267
C	-1.78713	-0.26409	0.02884
C	-2.41795	0.98406	0.03031
C	-3.78807	1.10595	0.04031
C	-4.62372	-0.03020	0.05801
C	-3.99256	-1.28646	0.04080
C	-2.61716	-1.38627	0.03121
N	6.24348	-0.13590	-0.02044
O	6.70961	-1.26560	-0.02706
O	6.93260	0.87322	-0.02252
N	-5.98792	0.08796	0.09749
C	-6.60241	1.38652	-0.09713
C	-6.81250	-1.08934	-0.08882
H	0.29253	1.55108	0.03420
H	-0.02918	-1.48524	0.00700
H	2.01945	-1.86436	-0.00269
H	4.45477	-2.09845	-0.02055
H	4.89418	2.15258	0.00355
H	2.44159	2.40454	0.02221
H	-1.82692	1.89126	0.01818
H	-4.21773	2.09628	0.03382
H	-4.57813	-2.19324	0.03506
H	-2.16794	-2.37315	0.02121
H	-6.37867	1.81093	-1.08255
H	-6.27325	2.09628	0.66313
H	-7.68012	1.28405	-0.00608
H	-6.60338	-1.84082	0.67397
H	-7.85756	-0.80759	0.00456
H	-6.66576	-1.54993	-1.07261

Compound: AB-1

Cartesian coordinates (after OPT)

N	-3.62357	0.61906	0.00397
N	-2.88179	-0.37436	0.00162
C	-5.01349	0.32372	-0.00066
C	-5.54016	-0.96619	-0.00831
C	-6.90618	-1.14614	-0.01233
C	-7.72948	-0.03183	-0.00865
C	-7.22859	1.25470	-0.00109
C	-5.85766	1.42616	0.00286
C	-1.49453	-0.10338	0.00601
C	-0.94298	1.17536	0.01167
C	0.42689	1.31872	0.01551
C	1.25867	0.20084	0.01381
C	0.70571	-1.07666	0.00816
C	-0.66509	-1.22120	0.00427
N	2.64947	0.47337	0.01806
N	3.37893	-0.53429	0.01714
C	4.76072	-0.29547	0.02130
C	5.35347	0.96784	0.01888
C	6.71961	1.09952	0.02194
C	7.56364	-0.03211	0.03352
C	6.95402	-1.29878	0.02558
C	5.58195	-1.41637	0.02256
N	-9.18538	-0.22605	-0.01286
O	-9.60297	-1.36859	-0.01960
O	-9.88812	0.76692	-0.00934
N	8.92635	0.10266	0.05518
C	9.52802	1.41173	-0.08024
C	9.76746	-1.06805	-0.06590
H	-4.86835	-1.81190	-0.01099
H	-7.34732	-2.13185	-0.01831
H	-7.90796	2.09388	0.00154
H	-5.41974	2.41520	0.00877
H	-1.59606	2.03612	0.01296
H	0.88613	2.29874	0.01996
H	1.36022	-1.93603	0.00688
H	-1.12327	-2.20190	-0.00019
H	4.72106	1.84462	0.01153
H	7.14432	2.09196	0.01486
H	7.55435	-2.19551	0.02122
H	5.11725	-2.39432	0.01823
H	10.60868	1.31380	-0.02174
H	9.27934	1.88723	-1.03558
H	9.21290	2.07899	0.72489
H	10.80954	-0.76612	-0.00480
H	9.61766	-1.59090	-1.01730
H	9.57986	-1.77589	0.74452

Compound: AB-2

Cartesian coordinates (after OPT)

N	-3.691255	0.601407	-0.136866
N	-2.949088	-0.369167	0.070459
C	-5.081407	0.313911	-0.067754
C	-5.607295	-0.946025	0.209636
C	-6.973311	-1.120750	0.254205
C	-7.796565	-0.031295	0.020362
C	-7.296306	1.225303	-0.256217
C	-5.925344	1.391821	-0.298970
C	-1.560815	-0.102772	0.005538
C	-1.013727	1.147058	-0.269474
C	0.356773	1.288866	-0.307129
C	1.199735	0.201289	-0.074320
C	0.641277	-1.044401	0.201257
C	-0.728652	1.193201	0.239285
C	2.652823	0.395720	-0.126636
N	3.470406	-0.554524	0.050244
C	4.854646	-0.322250	0.034834
C	5.457582	0.853247	0.473057
C	6.828672	1.010311	0.441575
C	7.666013	-0.002473	-0.050008
C	7.052769	-1.198623	-0.453949
C	5.683749	-1.350811	-0.398191
N	9.03668	0.168051	-0.128116
C	9.873488	-0.991129	-0.348998
C	9.640376	1.297572	0.543463
N	-9.252838	-0.219897	0.068477
O	-9.669854	-1.335776	0.314077
O	-9.955329	0.750949	-0.140081
H	-4.935387	-1.772887	0.386875
H	-7.414358	-2.083420	0.466374
H	-7.975995	2.045590	-0.432036
H	-5.487710	2.357820	-0.511830
H	-1.669488	1.986679	-0.449676
H	0.790339	2.258932	-0.521748
H	1.300992	-1.881913	0.382334
H	-1.182725	-2.152598	0.451045
H	2.987939	1.416129	-0.345678
H	4.851843	1.649866	0.886940
H	7.247881	1.930722	0.818913
H	7.648346	-2.026402	-0.807737
H	5.229231	-2.284738	-0.703547
H	10.912281	-0.673587	-0.399781
H	9.780052	-1.741126	0.447348
H	9.633887	-1.471666	-1.298437
H	10.710822	1.293072	0.351951
H	9.484242	1.280733	1.630326
H	9.245053	2.238129	0.157594

Compound: AB-3

Cartesian coordinates (after OPT)

N	3.766897	-0.620995	0.028724
N	3.024564	0.370712	-0.047722
C	5.155851	-0.325084	0.016979
C	5.682756	0.962004	-0.071483
C	7.048590	1.142964	-0.075221
C	7.873005	0.032650	0.009708
C	7.372224	-1.251105	0.098168
C	6.001588	-1.423518	0.101308
C	1.640428	0.103890	-0.037841
C	1.079929	-1.168514	0.045476
C	-0.289093	-1.307557	0.045320
C	-1.144630	-0.200185	-0.033732
C	-0.561972	1.066668	-0.123232
C	0.807945	1.214906	-0.123040
C	-2.587056	-0.428197	-0.021402
C	-3.537976	0.509423	0.017142
C	-4.981175	0.304695	0.029406
C	-5.592760	-0.945105	-0.083626
C	-6.960946	-1.090381	-0.063163
C	-7.810711	0.021093	0.081458
C	-7.201415	1.280368	0.175106
C	-5.827633	1.404547	0.152180
N	-9.180399	-0.124603	0.135467
C	-10.018024	1.051136	0.045838
C	-9.771523	-1.398569	-0.211610
N	9.328098	0.227786	0.005580
O	9.745571	1.367901	-0.072969
O	10.031855	-0.761854	0.080936
H	5.010632	1.804958	-0.136279
H	7.488950	2.126760	-0.142541
H	8.051876	-2.087598	0.162601
H	5.564418	-2.410592	0.169068
H	1.728087	-2.030981	0.108956
H	-0.722976	-2.298385	0.111168
H	-1.184654	1.947564	-0.200990
H	1.262107	2.195051	-0.192873
H	-2.877863	-1.473389	-0.033147
H	-3.237663	1.552177	0.053966
H	-4.987423	-1.834969	-0.201020
H	-7.374665	-2.082445	-0.163229
H	-7.800049	2.173850	0.266918
H	-5.394483	2.395514	0.230564
H	-9.809723	1.743653	0.862922
H	-11.059907	0.752246	0.130305
H	-9.889707	1.590931	-0.901027
H	-9.557788	-1.696957	-1.245774
H	-9.417044	-2.189481	0.451142
H	-10.850070	-1.333357	-0.091300

KDP			PNA			UREA		
Cartesian coordinates (after OPT)			Cartesian coordinates (after OPT)			Cartesian coordinates (after OPT)		
K	-2.39124	0.00174	C	-0.02582	-1.20635	N	-1.13114	0.61613
P	0.79578	-0.00581	C	1.35328	-1.20455	C	-0.00210	-0.13840
O	0.02263	-0.15766	C	2.06905	-0.00003	O	-0.02511	-1.36434
O	1.80237	-1.26907	C	1.35330	1.20451	N	1.15576	0.57359
O	1.79891	1.25405	C	-0.02580	1.20634	H	-1.11595	1.62369
O	0.04509	0.14456	C	-0.69614	0.00001	H	-1.99200	0.12584
H	2.13841	-1.39159	N	3.43338	-0.00011	H	1.97504	0.08373
H	2.00632	1.67062	N	-2.16096	0.00002	H	1.17410	1.58376
			O	-2.72419	0.02783			
			O	-2.72649	-0.02780			
			H	-0.57175	-2.14068			
			H	1.88871	-2.14554			
			H	1.88879	2.14546			
			H	-0.57172	2.14070			
			H	3.94859	0.86023			
			H	3.94863	-0.85936			

S2. Geometric parameters of the compounds

Table S1. Bond length, bond angle, and torsion angle of all compounds investigated in this work after geometry optimization in the gas phase. Between parentheses, CIF 234915 (PS-1) and 1217889 (PS-2) refer to experimental X-ray values.

Compounds		Bond length (Å)			Bond angle (Å)	Torsion angle (°)	
System Type I	PS-1	C1-N1	1.416 (1.423)	C1-N1-N2	114.60 (112.57)	C1-N1-N2-C7	-179.98 (-179.94)
		N1-N2	1.249 (1.258)	N1-N2-C7	116.85 (114.98)	N1-N2-C7-C8	-0.01 (-3.62)
		C4-N3	1.458 (1.434)	C4-N3-O1	118.24 (118.63)	C3-C4-N3-O2	179.98 (173.79)
		C10-N4	1.355 (1.371)	C4-N3-O2	118.25 (117.59)	C4-N3-O1-O2	180.00 (-179.72)
		N4-C13	1.451 (1.453)	C10-N4-C13	120.24 (121.10)	C10-N4-C14-C13	179.97 (179.37)
	PS-2	N3-O1	1.220 (1.226)	C5-C4-N3	118.98 (118.17)	C11-10-N4-C14	0.01 (9.61)
		C5-N1	1.375 (1.387)	C11-N2-O1	118.21 (118.17)	C11-N2-O1-O2	-179.98 (179.42)
		N1-C2	1.445 (1.446)	C5-N1-C1	119.18 (119.53)	C10-C11-N1-O2	0.09 (-3.50)
		C11-N2	1.461 (1.477)	C5-N1-C2	119.23 (118.39)	C5-N1-C2-C1	157.09 (-157.27)
		N2-O1	1.212 (1.229)	C10-C11-N2	118.88 (118.79)	C6-C5-N1-C2	13.19 (-8.66)
	PS-3	C1-C2	1.339	C1-C2-C3	126.01	C1-C2-C3-C9	180.00
		C1-C3	1.459	C2-C9-C10	124.00	C12-N2-C15-C16	161.00
		C12-N2	1.370	C12-N2-C16	119.52	C13-C12-N2-C15	10.02
		N2-C15	1.450	C4-C3-C1	123.55	C6-N1-O1-O2	180.00
		N1-O2	1.222	C6-N1-O2	118.38	C5-C6-N1-O1	-0.20
		C1-C2	1.339	C1-C2-C3	126.01	C1-C2-C3-C9	180.00
System Type II	AB-1	C1-N1	1.421	C1-N1-N2	114.91	C1-N1-N2-C7	180.00
		N1-N2	1.240	N1-N2-C7	115.80	C10-N3-N4-C13	180.00
		C10-N3	1.416	C10-N3-N4	114.93	C4-N4-O1-O2	180.00
		N3-N4	1.246	N3-N4-C13	116.71	C18-N3-C22-C21	179.92
		N4-C13	1.396	C16-N6-C19	120.50	C18-N3-C21-C22	-179.92
		C4-N5	1.463	C16-N6-C20	120.22	C17-C16-N6-C19	-0.04
		C16-N6	1.357	C4-N5-O2	118.13	C17-C18-N6-C20	0.05
		N6-C19	1.451	C5-C4-N5	118.80	C18-C17-C16-N3	180.00
		N5-O2	1.216	C15-C16-N6	121.40	C5-C4-N4-O1	179.99
	AB-2	C1-N1	1.421	C1-N1-N2	114.78	C1-N1-N2-C7	179.98
		N1-N2	1.239	N1-N2-C7	115.62	C10-C13-N3-C14	-177.97
		N2-C7	1.415	C10-C13-N3	122.63	C17-N4-C19-C20	154.47
		C10-C13	1.467	C12-N3-C14	120.73	C17-N4-C19-C20	-154.48
		C13-N3	1.266	C17-N4-C19	118.92	C4-N5-O2-O1	-180.00
		C17-N4	1.383	C4-N5-O2	117.67	C16-C17-N4-C20	166.11
		N6-C20	1.446	C4-N5-O2	117.66	C3-C4-N5-O2	-179.99
		N5-O2	1.216	C16-C17-N4	121.47	C17-N4-C19-C20	154.47
	AB-3	C1-N1	1.420	C1-N1-N2	114.71	C1-N1-N2-C7	-179.99
		N1-N2	1.241	N1-N2-C7	115.82	C10-C13-C14-C15	179.96
		N2-C7	1.410	C10-C13-C14	126.42	C4-N4-O2-O1	180.00
		C13-C14	1.336	C18-N3-C22	119.32	C18-N3-C22-C21	157.74
		C18-N3	1.378	C4-N4-O2	117.71	C17-C18-N3-C22	-11.76
		N3-C22	1.447	C4-N4-O1	117.70	C17-C18-N3-C21	11.22
		N4-O2	1.217	C13-C14-C15	127.53	C18-N3-C22-C22	-157.70

S3. First-Order Molecular Hyperpolarizability Calculation

Table S2-A. Calculated values of static (β_0) and dynamic (β_{HRS}) first-order molecular hyperpolarizability of all compounds using the CAM-B3LYP level of theory with an incident wavelength of 1064 nm. All values are presented in units of $10^{-30}\ cm^4\ statvolt^{-1}$ both in the gas phase and solvent medium.

Compound	In a vacuum		In DMSO	
	β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
KDP	0.8	0.9	0.3	0.2
Urea	0.4	0.4	0.6	0.5
PNA	5.5	8.6	22.0	21.5

Table S2-B. Calculated values of static (β_0) and dynamic (β_{HRS}) first-order molecular hyperpolarizability of all compounds using the CAM-B3LYP level of theory with an incident wavelength of 1330 nm. All values are presented in units of $10^{-30}\ cm^4\ statvolt^{-1}$ both in the gas phase and solvent medium.

Compound	In a vacuum		In DMSO	
	β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
KDP	0.8	0.8	0.3	0.2
Urea	0.3	0.3	0.6	0.5
PNA	5.5	7.3	22.0	17.2

Table S2-C. Calculated values of static (β_0) and dynamic (β_{HRS}) first-order molecular hyperpolarizability of all compounds using the CAM-B3LYP level of theory with an incident wavelength of 1550 nm. All values are presented in units of $10^{-30}\ cm^4\ statvolt^{-1}$ both in the gas phase and solvent medium.

Compound	In a vacuum		In DMSO	
	β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
KDP	0.8	0.9	0.3	0.2
Urea	0.4	0.4	0.6	0.5
PNA	5.5	6.7	22.0	15.2

Table S3-A. Calculated values of static (β_0) and dynamic (β_{HRS}) first-order molecular hyperpolarizability of all compounds using the B3LYP level of theory with an incident wavelength of 1064 nm. All values are presented in units of $10^{-30}\ cm^4\ statvolt^{-1}$ both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	73.2	394.0	356.0	18744.9
	PS-2	103.4	2001.4	434.6	1658.8
	PS-3	95.9	620.4	463.7	3900.6
System II	**AB-1**	233.0	11153.9	871.3	3943.2
	AB-2	322.2	1795.4	1004.6	2844.0
	AB-3	337.4	3635.5	1434.4	3978.1

Table S3-B. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the B3LYP level of theory with an incident wavelength of 1310 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	73.2	179.6	356.0	800.0
	PS-2	103.4	350.1	434.6	2375.2
	PS-3	95.9	251.8	463.7	1321.7
System II	**AB-1**	106.0	221.0	871.3	12721.1
	AB-2	322.2	10205.2	1004.6	5981.5
	AB-3	337.4	2608.2	1434.4	11313.6

Table S3-C. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the B3LYP level of theory with an incident wavelength of 1550 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	73.2	131.8	356.0	451.6
	PS-2	103.4	222.2	434.6	812.2
	PS-3	95.9	179.7	463.7	659.9
System II	**AB-1**	233.0	616.6	871.3	2244.0
	AB-2	322.2	1382.2	1004.6	6912.3
	AB-3	337.4	1129.5	1434.4	6596.7

Table S3-D. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the CAM-B3LYP level of theory with an incident wavelength of 1064 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.0	131.4	181.5	411.6
	PS-2	42.5	112.5	127.6	285.5
	PS-3	50.5	124.8	187.4	417.0
System II	**AB-1**	100.10	351.0	284.4	1011.3
	AB-2	91.4	333.3	193.4	613.1
	AB-3	132.30	505.1	356.6	1423.5

Table S3-E. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the CAM-B3LYP level of theory with an incident wavelength of 1310 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.0	88.7	181.5	227.5
	PS-2	42.5	76.0	127.6	170.9
	PS-3	50.5	87.1	187.4	242.0
System II	**AB-1**	100.10	206.3	284.4	469.3
	AB-2	91.4	193.2	193.4	324.0
	AB-3	132.30	284.9	356.6	630.9

Table S3-F. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the CAM-B3LYP level of theory with an incident wavelength of 1550 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.0	73.8	181.5	176.6
	PS-2	42.5	63.1	127.6	135.8
	PS-3	50.5	73.3	187.4	190.4
System II	**AB-1**	100.10	162.70	284.4	344.5
	AB-2	91.4	151.2	193.4	245.9
	AB-3	132.30	221.1	356.6	456.2

Table S3-G. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the M06-2X level of theory with an incident wavelength of 1064 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.3	132.9	185.4	418.6
	PS-2	47.4	129.0	130.5	297.4
	PS-3	56.0	144.7	188.9	421.2
System II	**AB-1**	106.0	378.8	269.1	912.6
	AB-2	97.0	376.2	191.3	641.3
	AB-3	138.6	554.3	344.7	1353.7

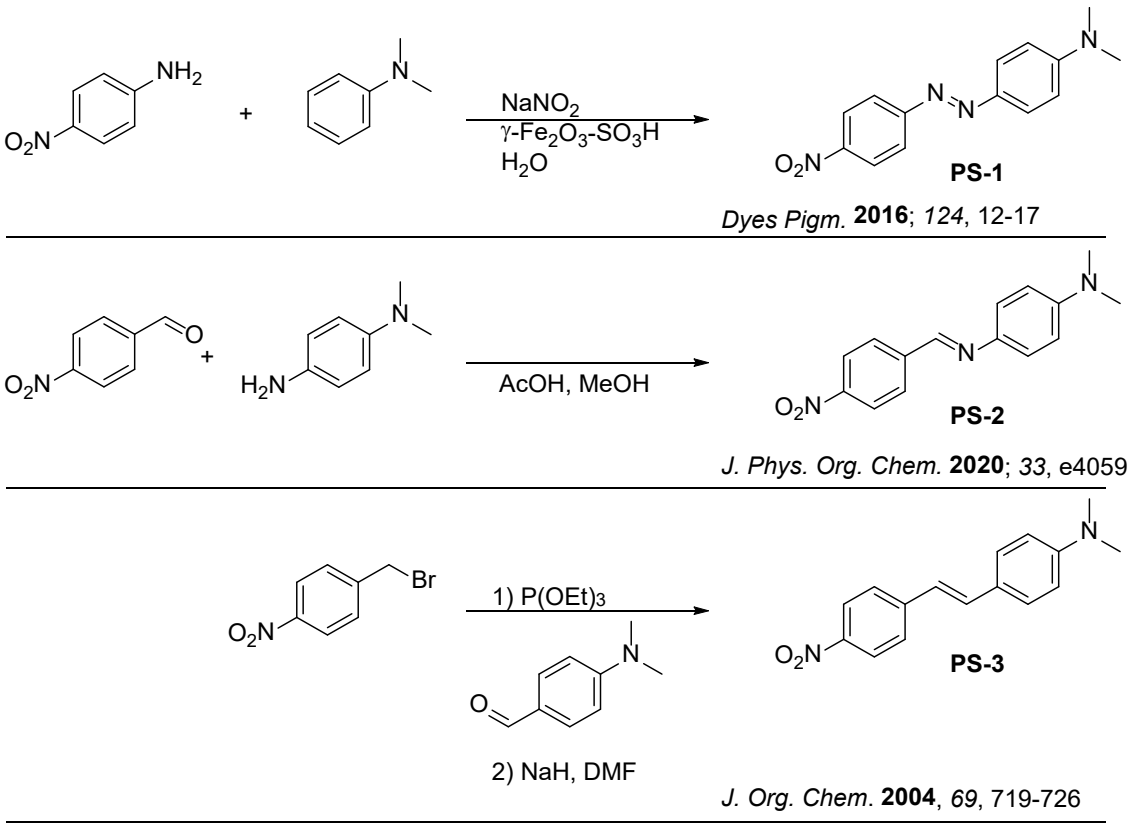
Table S3-H. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the M06-2X level of theory with an incident wavelength of 1310 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.3	132.9	185.4	418.6
	PS-2	47.4	85.9	130.5	176.1
	PS-3	56.0	98.9	188.9	244.8
System II	**AB-1**	106.0	221.0	269.1	441.9
	AB-2	97.0	210.8	191.3	329.1
	AB-3	138.6	305.2	344.7	607.7

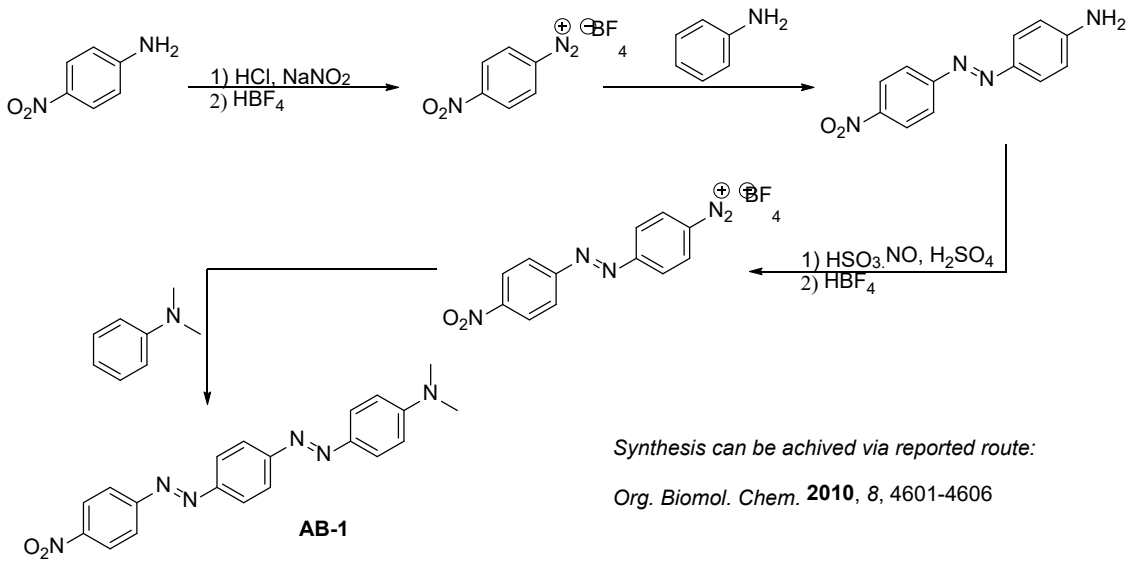
Table S3-I. Calculated static (β_0) and dynamic first-order molecular hyperpolarizability (β_{HRS}) of the investigated compounds using the M06-2X level of theory with an incident wavelength of 1550 nm. β values are presented in units of 10^{-30}cm^4 statvolt^{-1} both in the gas phase and solvent medium.

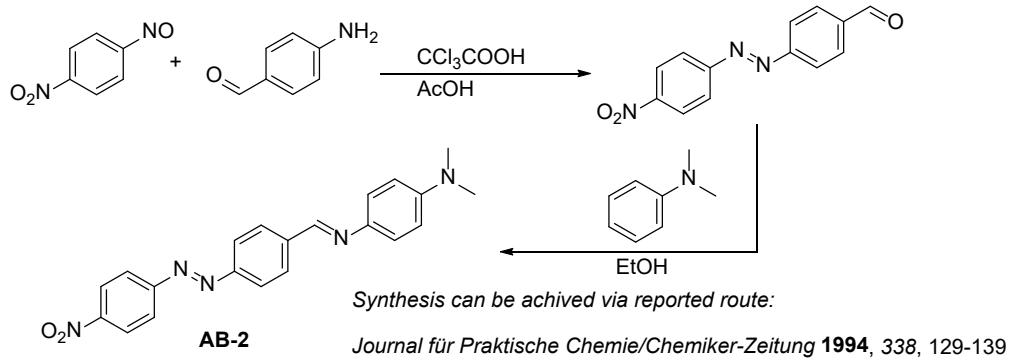
Compound		In a vacuum		In DMSO	
		β (0,0,0)	β (−2ω, ω, ω)	β (0,0,0)	β (−2ω, ω, ω)
System I	**PS-1**	50.3	74.4	185.4	180.6
	PS-2	47.4	71.0	130.5	139.4
	PS-3	56.0	82.5	188.9	192.5
System II	**AB-1**	106.0	173.6	269.1	327.5
	AB-2	97.0	163.2	191.3	247.6
	AB-3	138.6	235.0	344.7	440.7

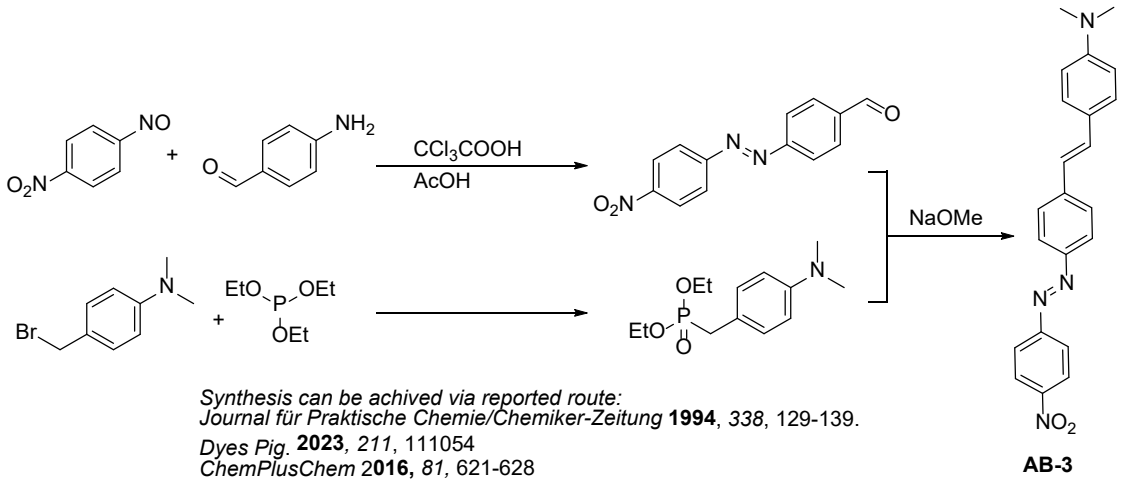
S4. Methods of Synthesis for the Investigated Compounds



Scheme S1: Synthetic approach to access **PS-01**, **PS-02**, **PS-03**







Scheme S2: Possible synthetic approach to access **AB-01**, **AB-02**, **AB-03**