Electronic Supplementary Information
Calculation of linear and nonlinear optical properties of azobenzene derivatives with Kohn-Sham and coupled-cluster methods

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Table S1: Tuned RS parameters of a LC-PBE functional with different basis sets for investigated azobenzene systems.

Systems	Basis Sets	λ	ω	J^2 (ppm)	Curvature coefficients (eV)
Cis-AB	6-31G(d)	0.2864	0.1727	12	(0.06, 0.06)
	cc-pVDZ	0.2753	0.1727	11	(0.04, −0.04)
	6-311G(d,p)	0.2581	0.1747	14	(0.06, 0.05)
	6-311++G(d,p)	0.2500	0.1677	2	(0.03, −0.01)
Trans-AB	6-31G(d)	0.0859	0.2323	57	(0.13, 0.09)
	cc-pVDZ	0.0808	0.2273	34	(0.10, 0.06)
	6-311G(d,p)	0.0758	0.2273	22	(0.08, 0.04)
	6-311++G(d,p)	0.0505	0.2273	5	(0.02, −0.00)
Cis-DA-AB	6-31G(d)	0.2854	0.1697	47	(0.01, 0.07)
	cc-pVDZ	0.2551	0.1747	10	(0.05, 0.06)
	6-311G(d,p)	0.2530	0.1727	8	(−0.05, 0.05)
	6-311++G(d,p)	0.2510	0.1657	3	(0.01, 0.06)
Trans-DA-AB	6-31G(d)	0.0000	0.2162	566	(0.09, 0.05)
	cc-pVDZ	0.0000	0.2414	545	(0.07, 0.07)
	6-311G(d,p)	0.0000	0.2313	520	(0.08, 0.06)
	6-311++G(d,p)	0.0000	0.2323	408	(0.04, −0.11)

1 Romberg Iteration Procedure

Using Eq. (7), the procedure to stabilize the numerical γ_{zzzz} of *cis*-AB is shown in Table S2 of ESI. The respective iteration order errors (IOE) and field amplitude errors (FAE) are also given. The FAE is decreased (more negative) with an increase in the Romberg iteration number (r) and the IOE approaches zero correspondingly. In this process, the selection of minimum field amplitude is important as discussed earlier by Champagne and others.[3] Not only that, a stable finite differentiation is also needed with respect to the chosen upper and lower field amplitudes. The stable value can be chosen by considering the close agreement between the two nearest k and r as shown in bold in Table S2.

Table S2: Generation of Romberg iteration matrix[a] to estimate the γ_{zzzz} for *cis*-AB by using the TLC-PBE functional and 6-31G(d) basis sets.

Cis-AB	r=1	IOE	r=2	IOE	r=3	IOE	r=4	IOE	r=5
k=0	66707.4	(−18.6)	66726.0	(−3.5)	66729.5	(−0.8)	66730.4	(−0.2)	66730.6
FAE	(−90.0)		(−73.5)		(−71.0)		(−69.9)		(−69.7)
k=1	66797.4	(−2.3)	66799.7	(−0.5)	66800.2	(−0.1)	66800.3	(−0.0)	66800.3
FAE	(72.9)		(7.5)		(−4.9)		(−7.9)		
k=2	66724.5	(−67.7)	66792.2	(−12.9)	66805.1	(−3.1)	**66808.2**		
FAE	(5.0)		(−152.4)		(−241.9)				
k=3	66719.5	(−275.1)	66944.6	(−52.4)	67047.0				
FAE	(−53.6)		(−858.4)						
k=4	66737.1	(−1066.4)	67803.0						

[a]Minimum field amplitude (k=0) used of 4×10^{-4} a.u. IOE denotes the iteration order errors whereas FAE refers for field amplitude errors. The errors are in a.u. The bold value is considered as the numerically stable γ_{zzzz}.

Table S3: Calculated transition energies (eV) and oscillator sterngths (f, hartree), the energy gap between HOMO and LUMO, $\Delta\varepsilon_{\mathrm{HL}}$ (eV) and the major contributions in HOMO-LUMO transitions, %HL of AB isomers. The 6-311++G(d,p) basis set is used.

TDKST	*Cis*-AB				*Trans*-AB			
	H→L(f)	%HL	$\Delta\varepsilon_{\mathrm{HL}}$	H–1→L(f)	H→L(f)	%HL	$\Delta\varepsilon_{\mathrm{HL}}$	H–1→L(f)
CAM-B3LYP[a]	2.66 (0.03)	86	6.45	4.63 (0.16)	2.72 (0.00)	99	6.53	4.00 (0.79)
CAM-B3LYP[a,b]	2.73 (0.04)	85	6.52	4.51 (0.19)	2.75 (0.00)	98	6.44	3.85 (0.90)
PBE[a]	2.36 (0.04)	99	1.97	3.47 (0.01)	2.18 (0.00)	99	1.94	3.43 (0.53)
PBE[a,b]	2.42 (0.06)	99	2.04	3.39 (0.02)	2.24 (0.00)	99	2.01	3.29 (0.75)
LC-PBE[a]	2.68 (0.01)	65	9.13	5.12 (0.15)	2.79 (0.00)	95	8.85	4.38 (0.80)
LC-PBE[a,b]	2.76 (0.02)	62	9.14	5.02 (0.27)	2.81 (0.00)	95	8.80	4.24 (0.91)
TLC-PBE[a]	2.63 (0.03)	85	7.32	4.58 (0.14)	2.87 (0.00)	99	7.37	4.28 (0.82)
TLC-PBE[a,b]	2.69 (0.04)	84	7.34	4.46 (0.17)	2.89 (0.00)	96	7.42	4.14 (0.91)
RI-CC2[a]	2.92 (0.03)	94	-	4.59 (0.03)	2.85 (0.00)	92	-	4.23 (0.87)
CC2[c]	3.00 (0.03)	94	-	4.49 (0.06)	2.84 (0.00)	94	-	4.44 (0.02)
B3LYP[d]	2.57 (0.04)		3.91	4.51 (0.11)	2.54 (0.04)		3.77	3.68 (0.76)
RASPT2[e]	2.83	-	-	4.57	2.73	-		4.17
EOM-CCSD[f]	-	-	-	-	-	-	-	4.38
Expt.[g]	2.92	-	-	4.12	2.82	-	-	4.40
Expt.[h]	2.87 (0.02)	-	-	4.42 (0.17)	2.80 (0.02)	-	-	3.89 (0.56)

[a]Present work. [b]Calculations with a continuum model for ethanol. [c]From ref. [4], aug-cc-pVTZ basis set. [d]From ref. [5], 6-311++G(3df,3pd) basis set. [e]From ref. [6]. [f]From ref. [7] (in ethanol solution), 6-311++G(d,p) basis set. [g]Measured band peaks in the gas phase, from ref. [8]. [h]Measured band peaks in ethanol solution, from ref. [9].

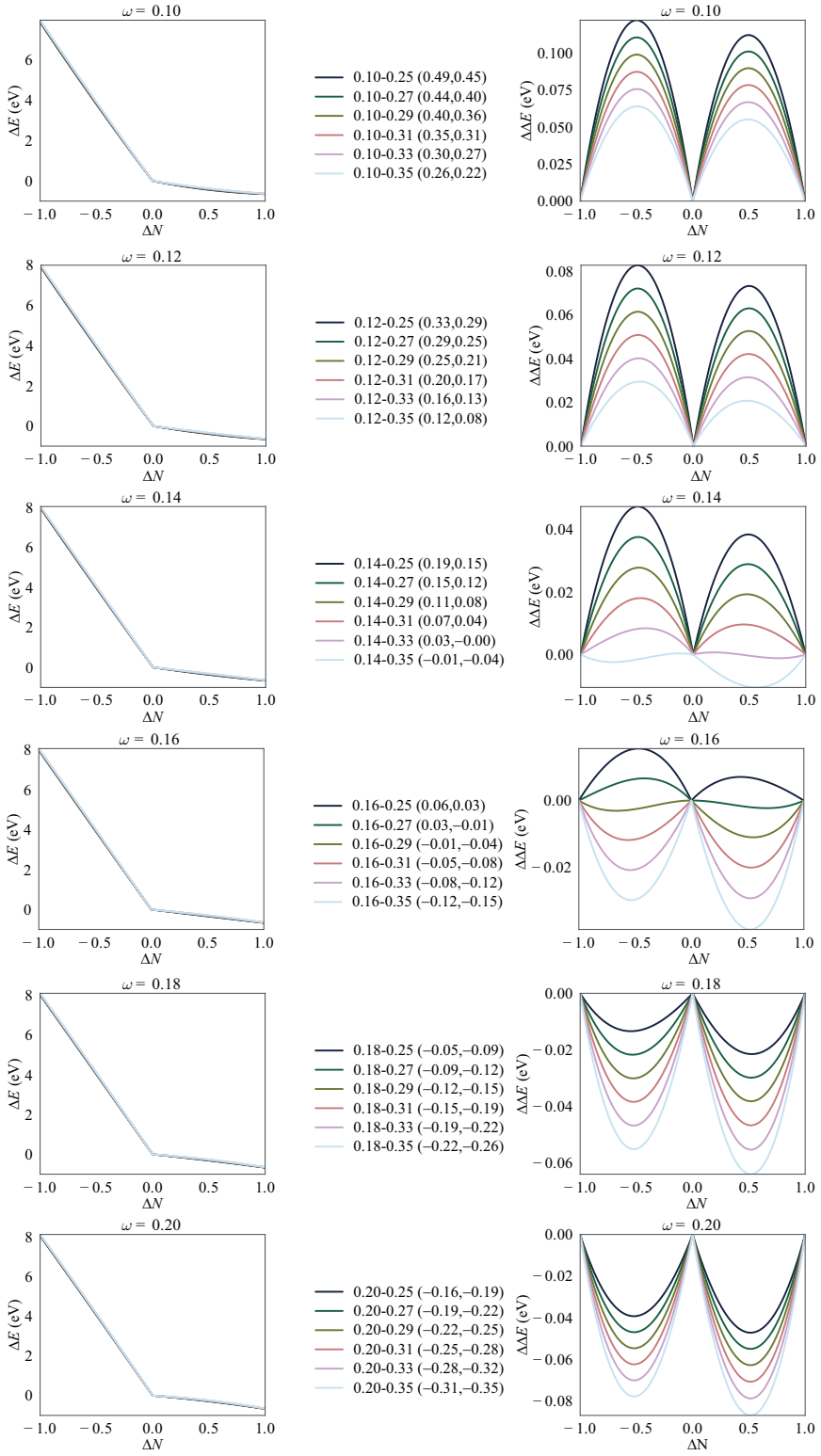


Figure S1: The 2DT curvature plots of *cis*-AB for each ω with different sets of λ.

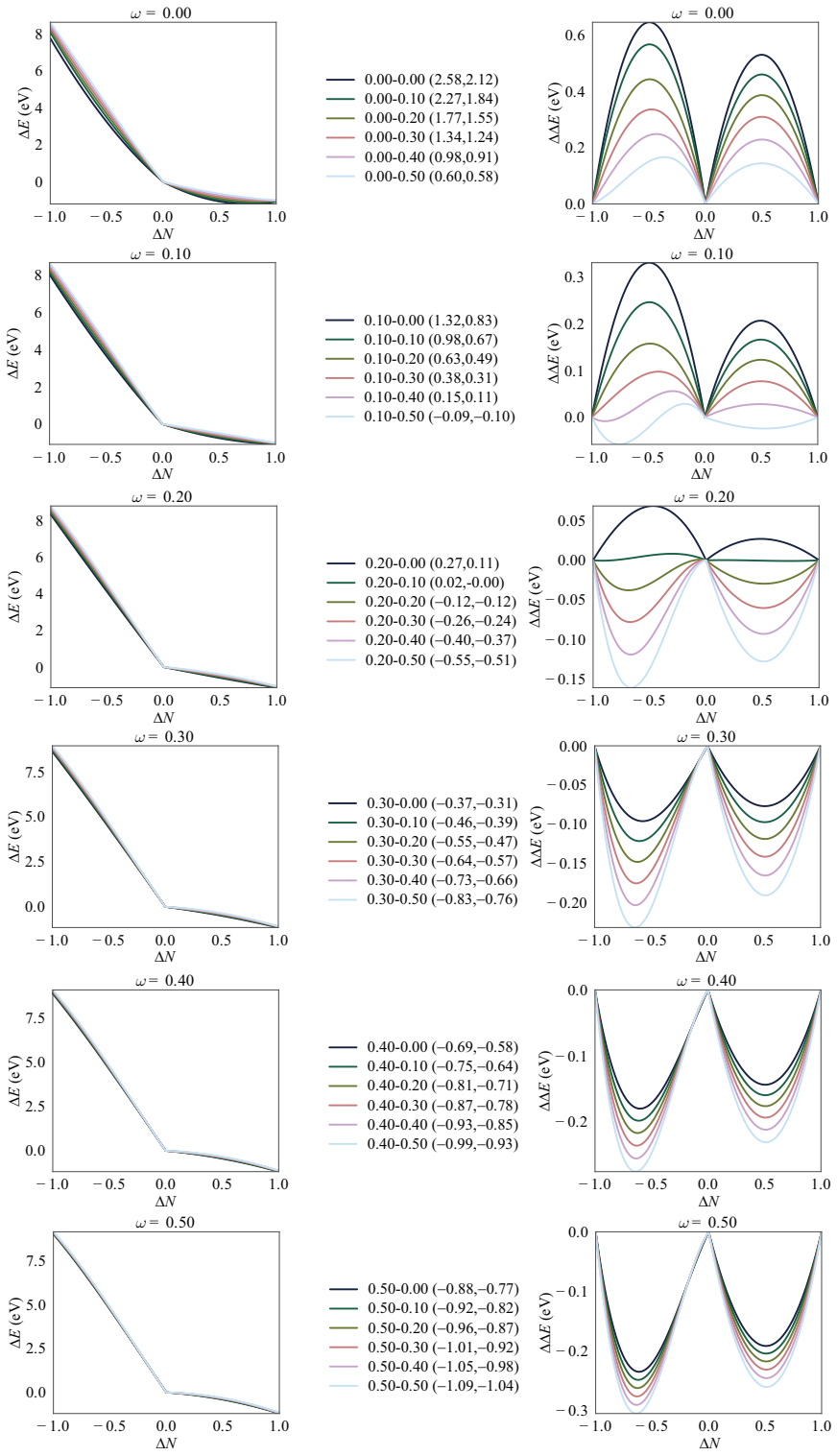


Figure S2: The 2DT curvature plots of *trans*-AB for each ω with different sets of λ.

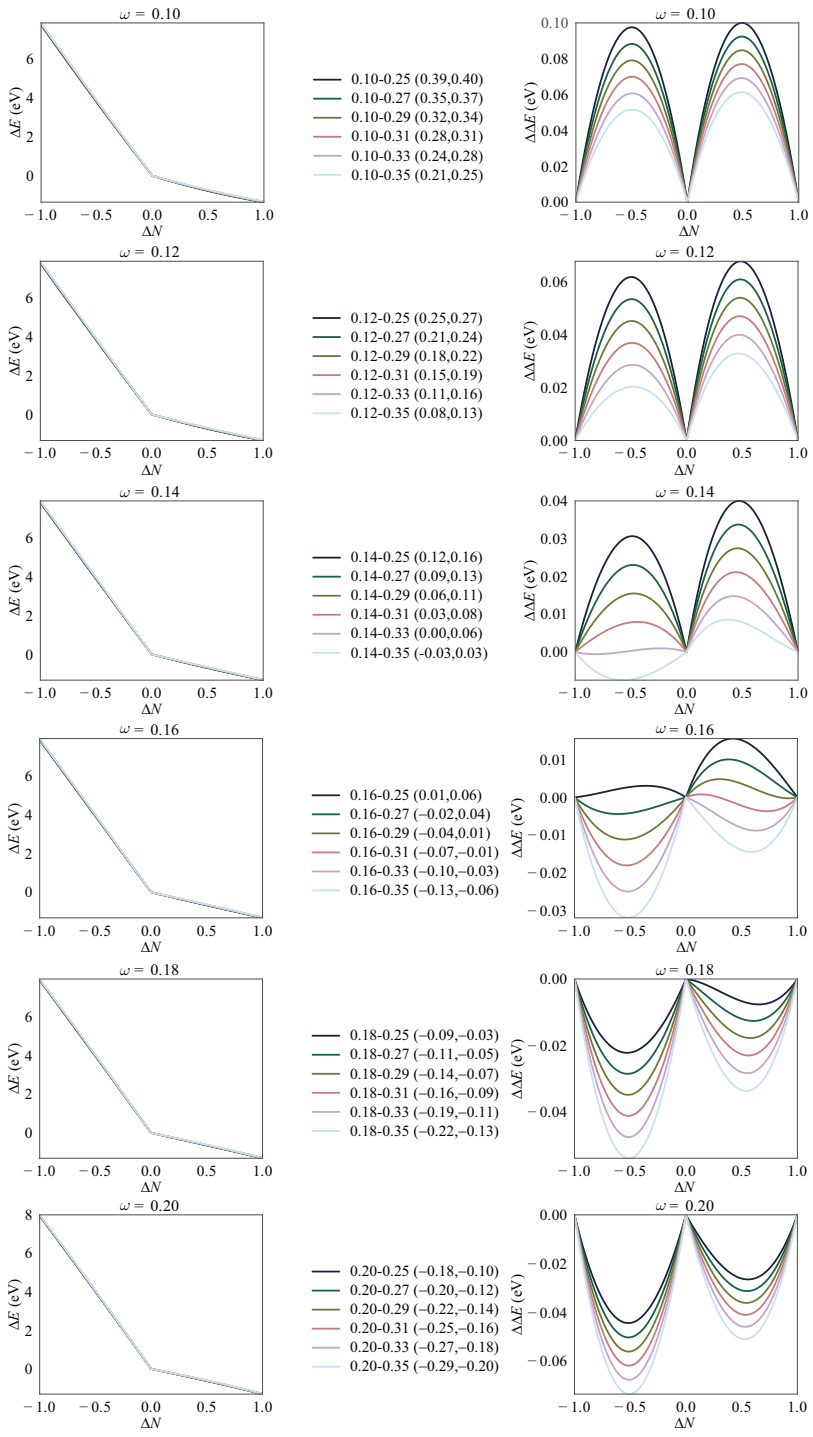


Figure S3: The 2DT curvature plots of *cis*-DA-AB for each ω with different sets of λ.

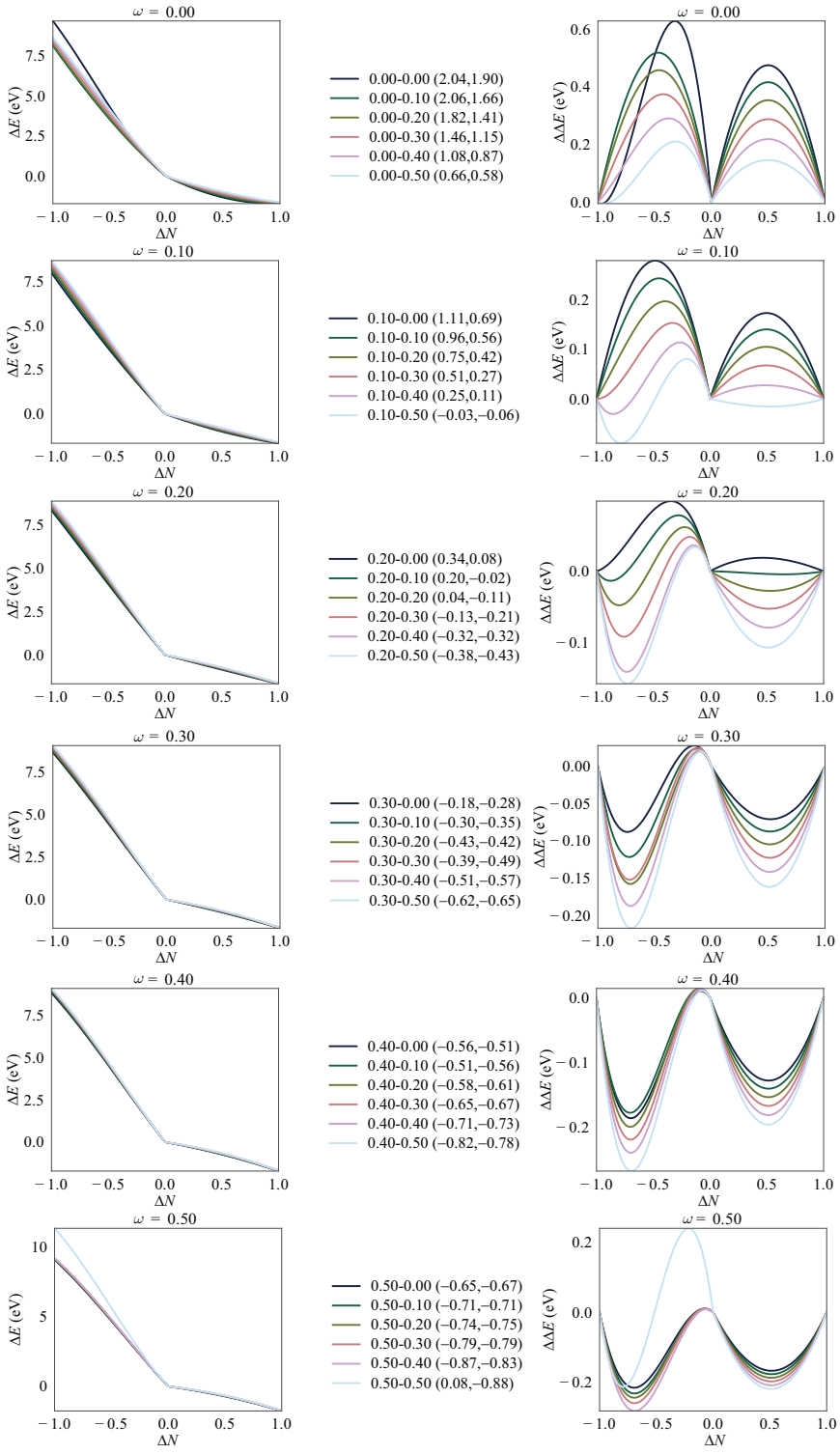


Figure S4: The 2DT curvature plots of *trans*-DA-AB for each ω with different sets of λ.

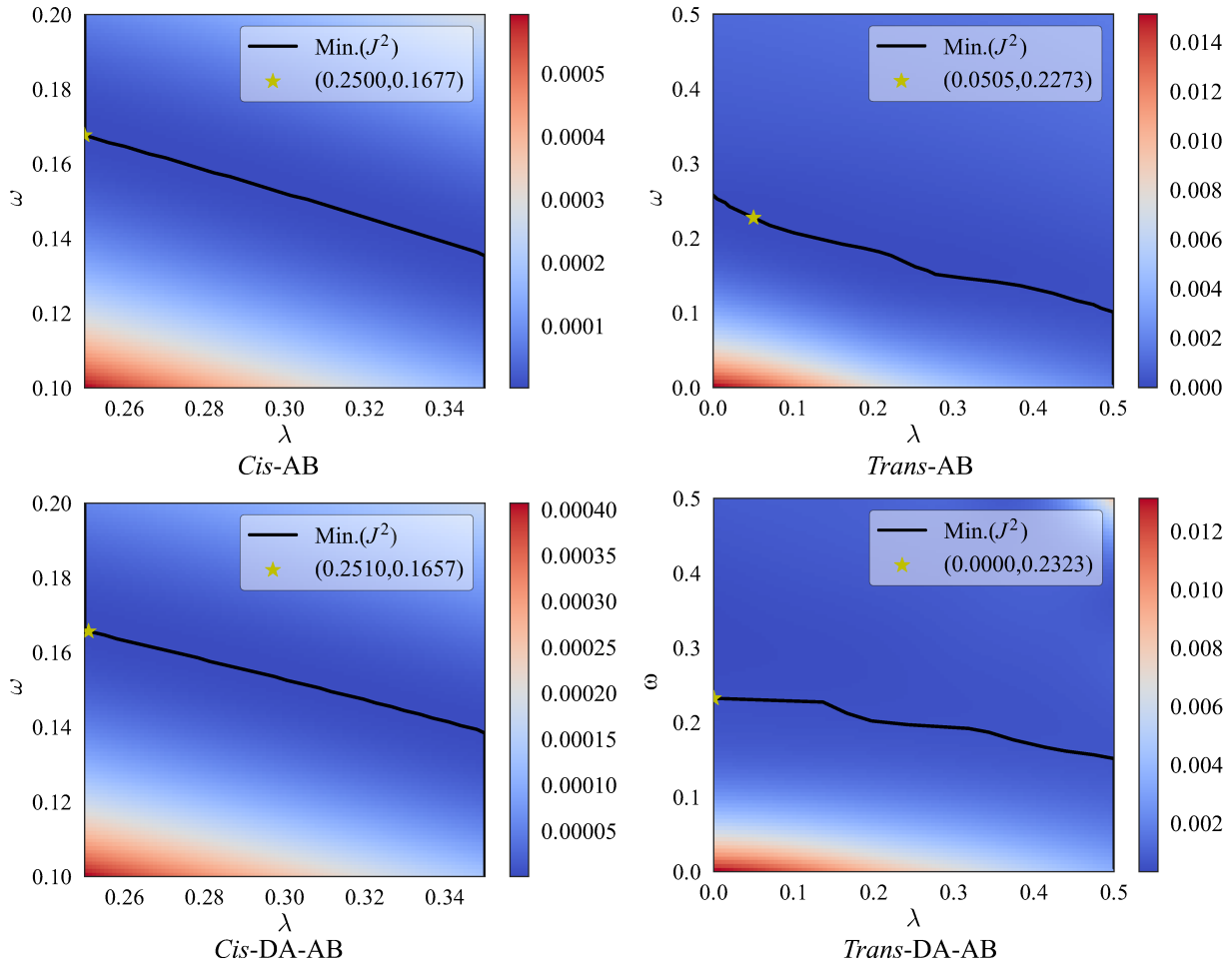


Figure S5: The J^2 surface plots from the tuning of separation parameters in LC-PBE functional for the investigated systems.

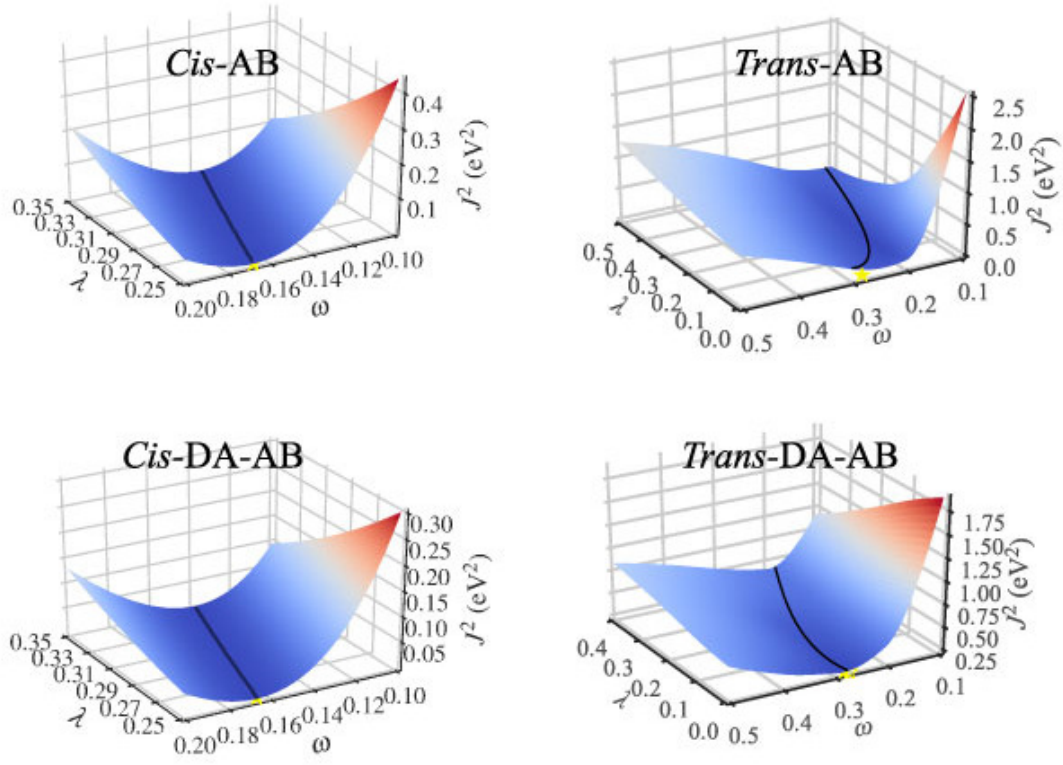


Figure S6: Slices of the contour plot shown in the top left of Figure S5.

Table S4: DA-AB isomers. Calculated first transition energies (eV) and oscillator sterngths (f, hartree).

Methods	6-31G*		6-311++G**	
	Cis-	*Trans-*	*Cis-*	*Trans-*
CAM-B3LYP[a]	2.63 (0.06)	2.68 (0.00)	2.61 (0.07)	2.71 (0.00)
CAM-B3LYP[a,b]	2.69 (0.11)	2.71 (0.00)	2.66 (0.13)	2.73 (0.00)
PBE[a]	2.11 (0.12)	1.77 (0.00)	2.03 (0.14)	1.79 (0.00)
PBE[a,b]	1.88 (0.23)	1.67 (0.00)	1.82 (0.18)	1.65 (0.00)
LC-PBE[a]	2.66 (0.04)	2.78 (0.00)	2.65 (0.04)	2.81 (0.00)
LC-PBE[a,b]	2.70 (0.08)	2.81 (0.00)	2.73 (0.07))	2.84 (0.00)
TLC-PBE[a]	2.60 (0.06)	2.41 (0.00)	2.57 (0.07)	2.46 (0.00)
TLC-PBE[a,b]	2.61 (0.15)	2.43 (0.00)	2.63 (0.12)	2.47 (0.00)
CC2[a]	2.79 (0.11)	2.85 (0.00)	2.86 (0.10)	2.81 (0.00)
B3LYP[c]	2.46 (0.11)	2.44 (0.00)	-	-
Expt.[d]	2.56	-	-	-

[a]Present work. [b]Calculations with a continuum model for ethanol. [c]From ref. [10], gas phase. [d]Measured band peaks for NHPh-azobenzene-NO_2 in cyclohexane, where Ph = phenyl [11].

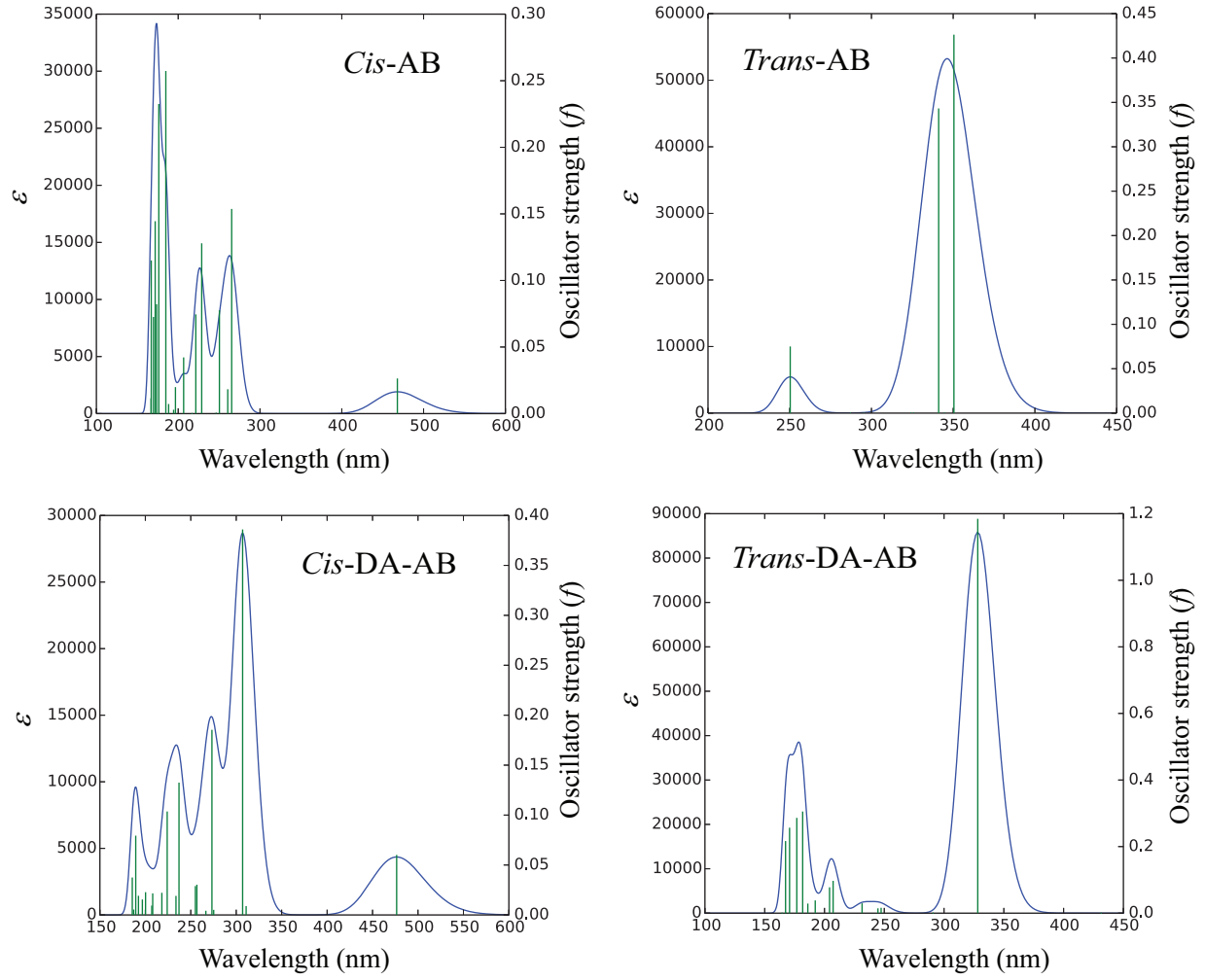
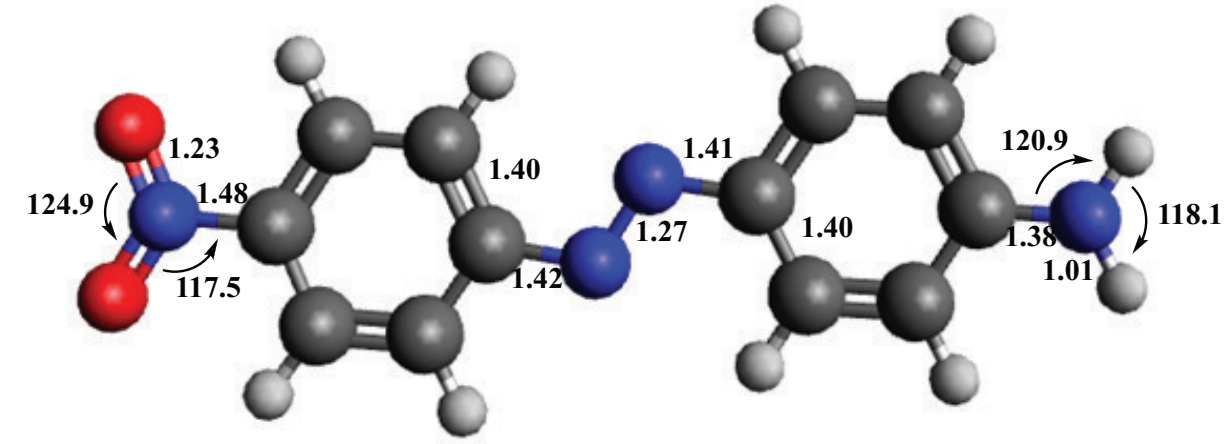


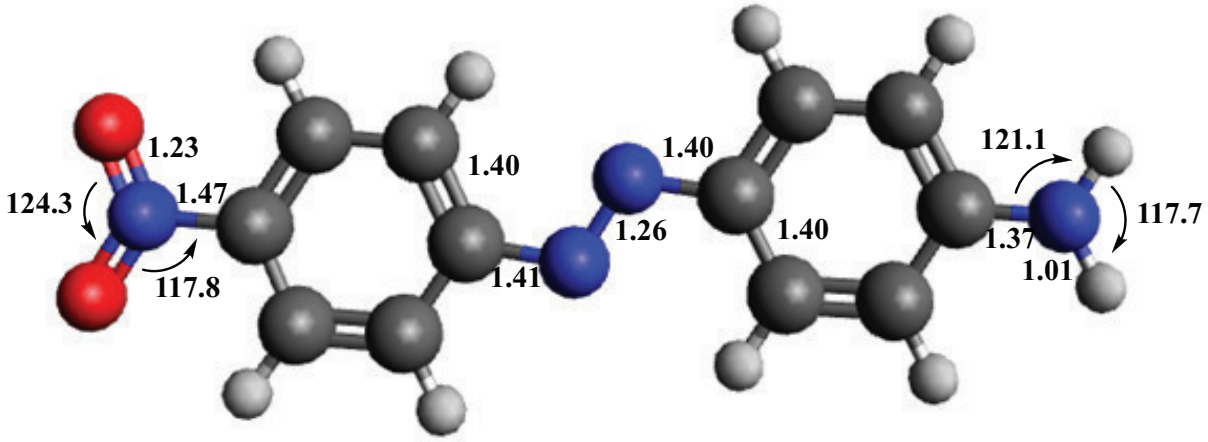
Figure S7: The UV-Visible spectrum of AB derivatives at TLC-PBE/6-31G(d) level. Gaussian base lines are used with a full width half maximum (FWHM) of 3000 cm^{-1}.

Table S5: Numerically (FF) calculated static longitudinal polarizabilities (a.u.) and second hyperpolarizabilities (103 a.u.) by using MP2/6-311+G** and B3LYP/6-311+G** optimized geometries of *trans*-DA-AB system.

Methods/6-31G*	Geom/MP2/6-311+G**		Geom/B3LYP/6-311+G**	
	α_{zz}	γ_{zzzz}	α_{zz}	γ_{zzzz}
CAM-B3LYP	394.2	1539	396.3	1522
B3LYP	446.7	2327	448.1	2254
PBE	493.1	2722	493.3	2600
LC-PBE	353.2	1154	356.6	1160
TLC-PBE	398.8	1412	401.2	1480
CCSD	343.3	1752	346.9	1777
CCSD(T)	357.2	2080	360.4	2096



MP2/6-311+G**



B3LYP/6-311+G**

Figure S8: Ground state optimized geometry of Trans-DA-AB system. Bond lengths are in .

Table S6: Calculated static α_{zz} (in a.u.) for AB isomers at various levels of theory.[a]

Methods/ Basis sets	6-31G(d)	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVDZ[b] +cc-pVDZ[c]	6-31G(d)	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVDZ[b] +cc-pVDZ[c]
AB	*Cis-*				*Trans-*			
M06-2X	175.4 (7)	196.0 (4)	203.1 (3)	202.7 (3)	266.5 (10)	284.4 (8)	291.2 (6)	290.8 (6)
B3LYP	183.8 (12)	207.0 (10)	213.7 (8)	213.3 (8)	288.3 (19)	306.5 (18)	316.4 (16)	316.0 (16)
CAM-B3LYP	175.3 (7)	197.7 (5)	204.8 (3)	204.4 (3)	267.5 (11)	284.0 (10)	295.1 (8)	294.7 (8)
PBE	193.2 (17)	216.9 (15)	223.1 (13)	223.6 (13)	305.5 (27)	325.3 (26)	334.3 (22)	334.7 (22)
LC-PBE	167.2 (2)	185.6 (1)	194.2 (2)	193.8 (2)	247.2 (2)	259.0 (0)	271.7 (1)	271.5 (1)
TLC-PBE	177.2 (8)	198.6 (6)	206.6 (4)	206.2 (4)	255.5 (6)	288.3 (11)	299.9 (10)	299.5 (10)
CCSD(T)	164.6	188.2	198.1	197.6	241.5	259.0	274.0	274.5
DA-AB								
M06-2X	243.5 (7)	266.9 (4)	276.5 (3)	276.1 (3)	396.2 (10)	420.3 (8)	435.9 (6)	435.4 (6)
B3LYP	268.1 (18)	296.9 (16)	305.7 (14)	305.3 (14)	447.3 (24)	481.9 (24)	495.4 (20)	495.0 (20)
CAM-B3LYP	244.9 (7)	270.9 (6)	280.8 (5)	280.4 (5)	396.0 (10)	424.4 (9)	440.6 (8)	440.2 (7)
PBE	296.2 (30)	329.9 (29)	338.1 (26)	337.6 (26)	492.3 (37)	534.3 (38)	546.6 (33)	546.2 (33)
LC-PBE	226.9 (1)	248.6 (3)	260.3 (3)	260.0 (3)	355.8 (1)	377.0 (3)	396.0 (3)	395.7 (4)
TLC-PBE	248.2 (9)	272.2 (6)	283.1 (5)	282.7 (6)	400.4 (11)	429.2 (10)	446.4 (9)	445.9 (8)
CCSD(T)	228.1	256.1	268.1	267.2	360.4	388.5	411.3	410.5

[a]Errors (in %) are calculated w.r.t. CCSD(T) values and are listed in parentheses. [b]For C, N and O atoms. [c]For H atoms.

Table S7: Calculated static numerical γ_{zzzz} for AB isomers at various levels of theory.[a]

Methods/ Basis sets	6-31G(d)	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVDZ[b] +cc-pVDZ[c]	6-31G(d)	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVDZ[b] +cc-pVDZ[c]
AB ($\times 10^2$ **au)**	*Cis-*				*Trans-*			
M06-2X	624 (4)	962 (8)	988 (6)	964 (10)	3600 (3)	4378 (8)	4352 (9)	4319 (9)
B3LYP	942 (45)	1436 (38)	1442 (37)	1412 (32)	4231 (14)	5378 (13)	5272 (11)	5230 (10)
CAM-B3LYP	645 (5)	1018 (2)	1017 (3)	1002 (6)	3535 (5)	4381 (8)	4309 (10)	4281 (10)
PBE	1267 (87)	1888 (81)	1870 (78)	1918 (80)	4574 (23)	5955 (26)	5810 (22)	5872 (23)
LC-PBE	451 (30)	693 (33)	694 (34)	682 (36)	2879 (22)	3398 (28)	3411 (29)	3393 (29)
TLC-PBE	668 (1)	1009 (3)	1015 (3)	995 (7)	3266 (12)	3978 (16)	3956 (17)	3928 (18)
CCSD(T)	677	1040	1049	1068	3710	4740	4771	4768
DA-AB ($\times 10^3$ **au)**								
M06-2X	296 (8)	367 (32)	359 (40)	356 (37)	1606 (23)	1933 (36)	1890	1875
B3LYP	583 (81)	769 (43)	745 (25)	739 (30)	2254 (8)	2919 (3)	2794	2783
CAM-B3LYP	299 (7)	384 (28)	375 (37)	373 (34)	1522 (27)	1899 (37)	1831	1832
PBE	876 (172)	1176 (118)	1157 (94)	1164 (104)	2600 (24)	3448 (14)	3157	2949
LC-PBE	187 (42)	231 (57)	228 (62)	227 (60)	1160 (45)	1370 (55)	1353	1347
TLC-PBE	295 (8)	368 (31)	360 (39)	358 (37)	1480 (29)	1694 (44)	1652	1643
CCSD(T)	322	537	595	568	2096	3017	3262	3198

[a]Errors (in %) are calculated w.r.t. CCSD(T) values and are listed in parentheses. [b]For C, N and O atoms. [c]For H atoms.

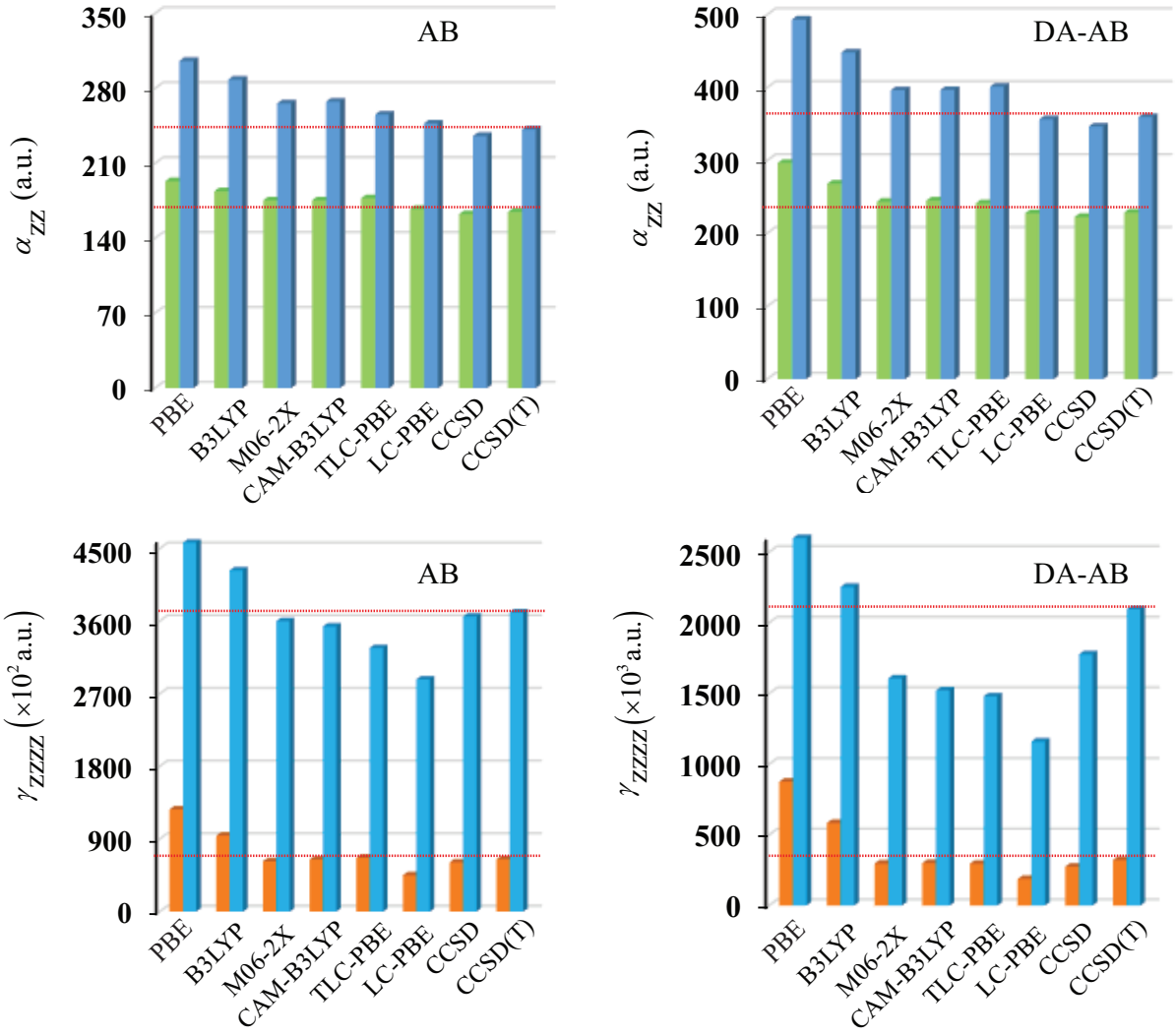


Figure S9: Variation of α_{zz} and γ_{zzzz} of investigated AB derivatives at different theoretical methods. α_{zz}: The light green bars are for *cis*-isomers and the accent blues are for the *trans*-isomers; γ_{zzzz}: The orange bars are for *cis*-isomers and the light blues are for the *trans*-isomers.

Table S8: Calculated static numerical α_{zz} and γ_{zzzz} for AB isomers at various KS functionals (KSF) with a 6-311++G(d,p) basis set.

KSF	α_{zz} (au)		γ_{zzzz} (au)	
AB	*Cis-*	*Trans-*	*Cis-*($\times 10^2$)	*Trans-*($\times 10^2$)
M062X	197.9	282.4	968	4422
B3LYP	208.8	308.5	1442	5408
CAM-B3LYP	199.6	286.2	1020	4389
PBE	218.4	327.6	1911	5996
LC-PBE	188.4	262.1	697	3438
TLC-PBE	200.6	270.7	1014	4018
DA-AB	*Cis-*	*Trans-*	*Cis-*($\times 10^3$)	*Trans-*($\times 10^3$)
M062X	269.4	423.4	374	1973
B3LYP	299.1	484.4	769	2929
CAM-B3LYP	273.3	427.4	384	1908
PBE	332.2	536.5	1165	3436
LC-PBE	251.8	380.7	232	1381
TLC-PBE	275.1	432.1	369	1702

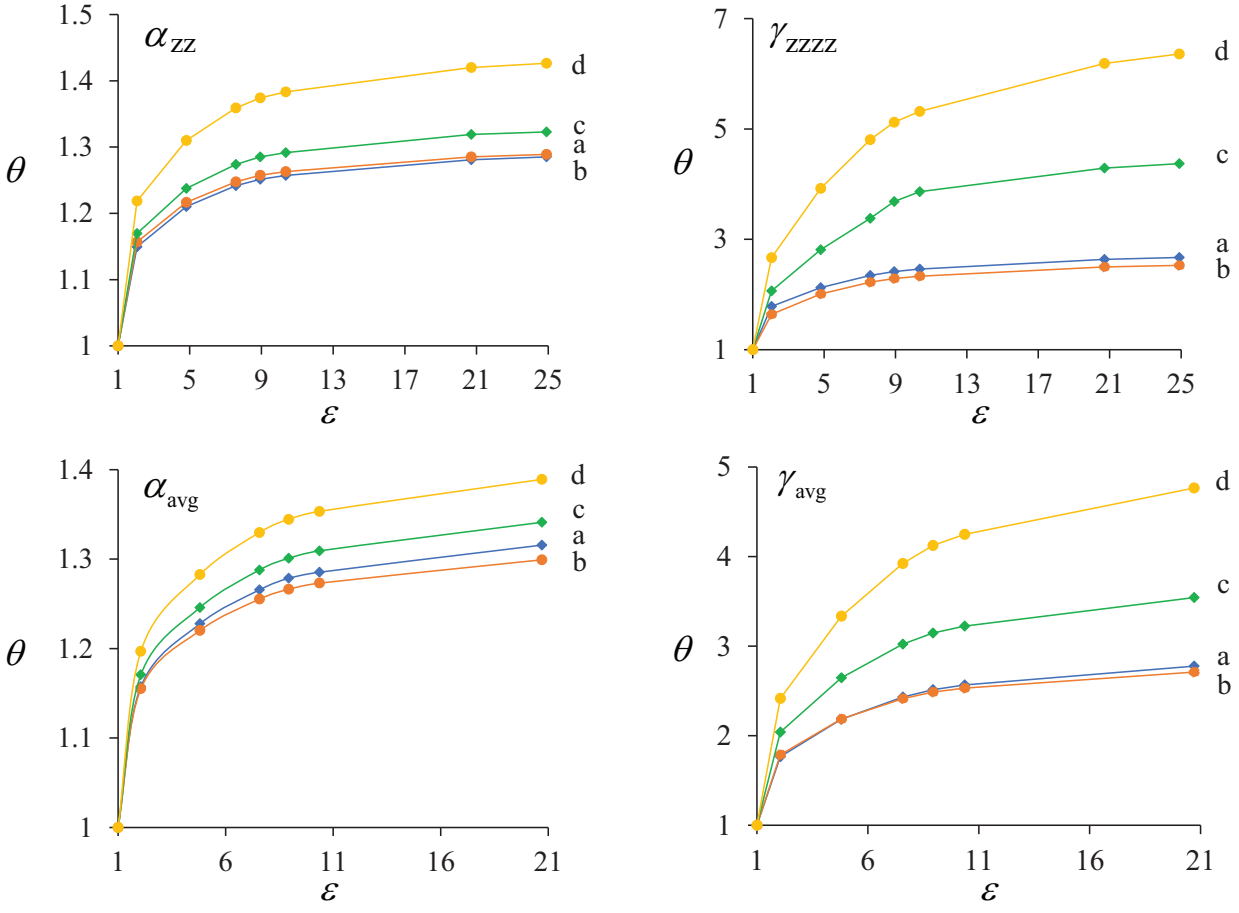


Figure S10: Plot of θ (unitless) versus ε for all systems at TLC-PBE / 6-31G(d) level: (a) *Cis*-AB, (b) *Trans*-AB, (c) *Cis*-DA-AB and (d) *Trans*-DA-AB.

Table S9: Calculated static longitudinal α_{zz} (a.u.) of AB derivatives in different solvents by using LC-PBE and TLC-PBE functionals with 6-31G(d) basis set. CCSD values are taken as a reference.

ε	DF	*Cis*-AB	*Trans*-AB	*Cis*-DA-AB	*Trans*-DA-AB
1	LC-PBE	167.2	247.2	226.9	355.8
	TLC-PBE	177.2	255.5	248.2	400.4
	CCSD	161.9	235.3	222.1	346.9
2.06	LC-PBE	190.9	284.5	262.0	424.2
	TLC-PBE	203.9	295.7	288.8	488.9
	CCSD	184.2	270.6	256.3	413.5
4.81	LC-PBE	200.2	298.7	275.7	451.4
	TLC-PBE	214.7	311.0	305.6	525.6
	CCSD	192.9	283.5	269.5	441.6
7.58	LC-PBE	205.1	306.0	282.8	465.7
	TLC-PBE	220.3	318.9	314.5	545.2
	CCSD	197.4	290.1	275.9	455.8
8.93	LC-PBE	206.6	308.2	285.0	470.0
	TLC-PBE	222.0	321.4	317.3	551.3
	CCSD	198.9	292.2	278.1	460.9
10.36	LC-PBE	207.6	309.5	286.3	472.8
	TLC-PBE	223.1	322.8	318.9	555.0
	CCSD	199.7	293.4	279.8	464.9
20.70	LC-PBE	211.2	314.7	291.5	483.3
	TLC-PBE	227.2	328.5	325.7	569.7
	CCSD	203.0	298.1	284.8	472.7
24.85	LC-PBE	211.8	315.6	292.5	485.1
	TLC-PBE	228.0	329.5	326.6	572.3
	CCSD	205.1	299.0	285.7	477.7

Table S10: Calculated static longitudinal γ_{zzzz} (a.u.) of AB derivatives in different solvents by using LC-PBE and TLC-PBE functionals with 6-31G(d) basis set. CCSD values are taken as a reference.

ε	DF	*Cis*-AB ($\times 10^2$)	*Trans*-AB ($\times 10^2$)	*Cis*-DA-AB ($\times 10^3$)	*Trans*-DA-AB ($\times 10^3$)
1	LC-PBE	451	2879	187	1160
	TLC-PBE	668	3266	295	1480
	CCSD	610	3657	274	1777
2.06	LC-PBE	772	5117	355	3080
	TLC-PBE	1188	5363	580	3964
	CCSD	1168	5646	427	4937
4.81	LC-PBE	908	6210	443	4346
	TLC-PBE	1413	6568	749	5824
	CCSD	1456	6809	579	6362
7.58	LC-PBE	995	6830	494	5203
	TLC-PBE	1560	7257	850	7135
	CCSD	1631	7524	748	7839
8.93	LC-PBE	1023	7030	526	5503
	TLC-PBE	1607	7480	1058	7604
	CCSD	1690	7782	1042	7860
10.36	LC-PBE	1040	7150	591	5690
	TLC-PBE	1636	7615	1086	7899
	CCSD	1725	7868	1068	7901
20.70	LC-PBE	1109	7637	643	6496
	TLC-PBE	1754	8160	1206	9190
	CCSD	1872	8421	1183	9056
24.85	LC-PBE	1122	7725	652	6652
	TLC-PBE	1776	8259	1228	9443
	CCSD	1899	8497	1204	9949

Table S11: Calculated static α_{avg} (a.u.) of unsubstituted AB isomers in different solvents by using CAM-B3LYP and TLC-PBE functionals with 6-31G(d) basis set.

Solvents (ε)	*Cis*-AB			*Trans*-AB		
	CAM-B3LYP	TLC-PBE	LC-PBE	CAM-B3LYP	TLC-PBE	LC-PBE
Gas phase (1.00)	130.9	132.1	127.1	150.0	145.7	142.6
CS_2 (2.06)	151.4	152.9	146.3	174.0	168.3	164.1
$CHCl_3$ (4.81)	160.4	162.2	154.7	184.2	177.8	173.2
THF (7.58)	165.4	167.2	159.4	189.6	182.9	178.0
CH_2Cl_2 (8.93)	167.0	168.9	160.9	191.3	184.5	179.6
$CH_3CH_2Cl_2$ (10.36)	168.0	169.8	161.8	192.4	185.5	180.5
CH_3COCH_3 (20.70)	171.8	173.8	165.4	196.5	189.3	184.2

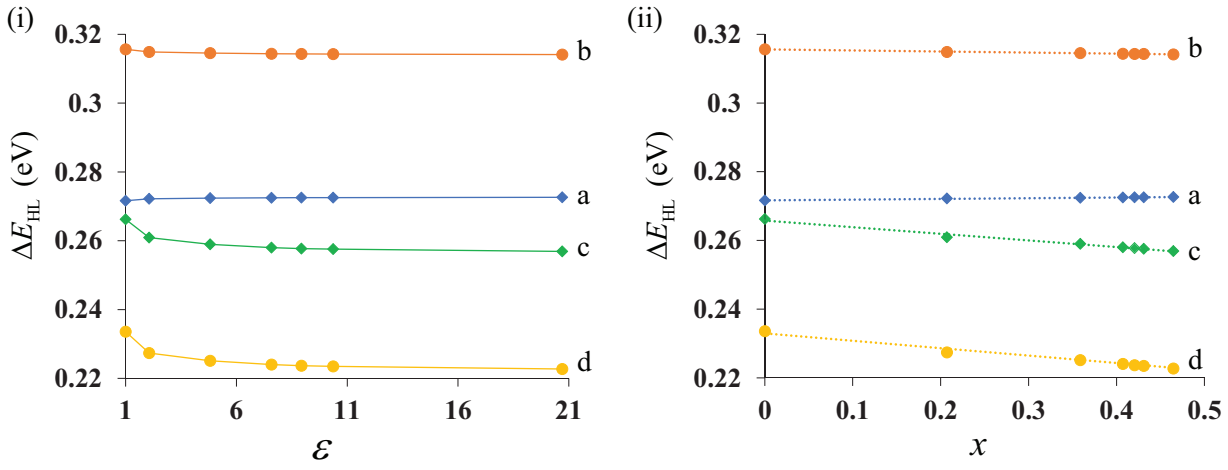


Figure S11: Plot of (i) ΔE_{HL} versus ε and (ii) ΔE_{HL} versus $x[= (\varepsilon - 1)/(2\varepsilon + 1)]$ for all systems at TLC-PBE / 6-31G(d) level: (a) *Cis*-AB, (b) *Trans*-AB, (c) *Cis*-DA-AB and (d) *Trans*-DA-AB.

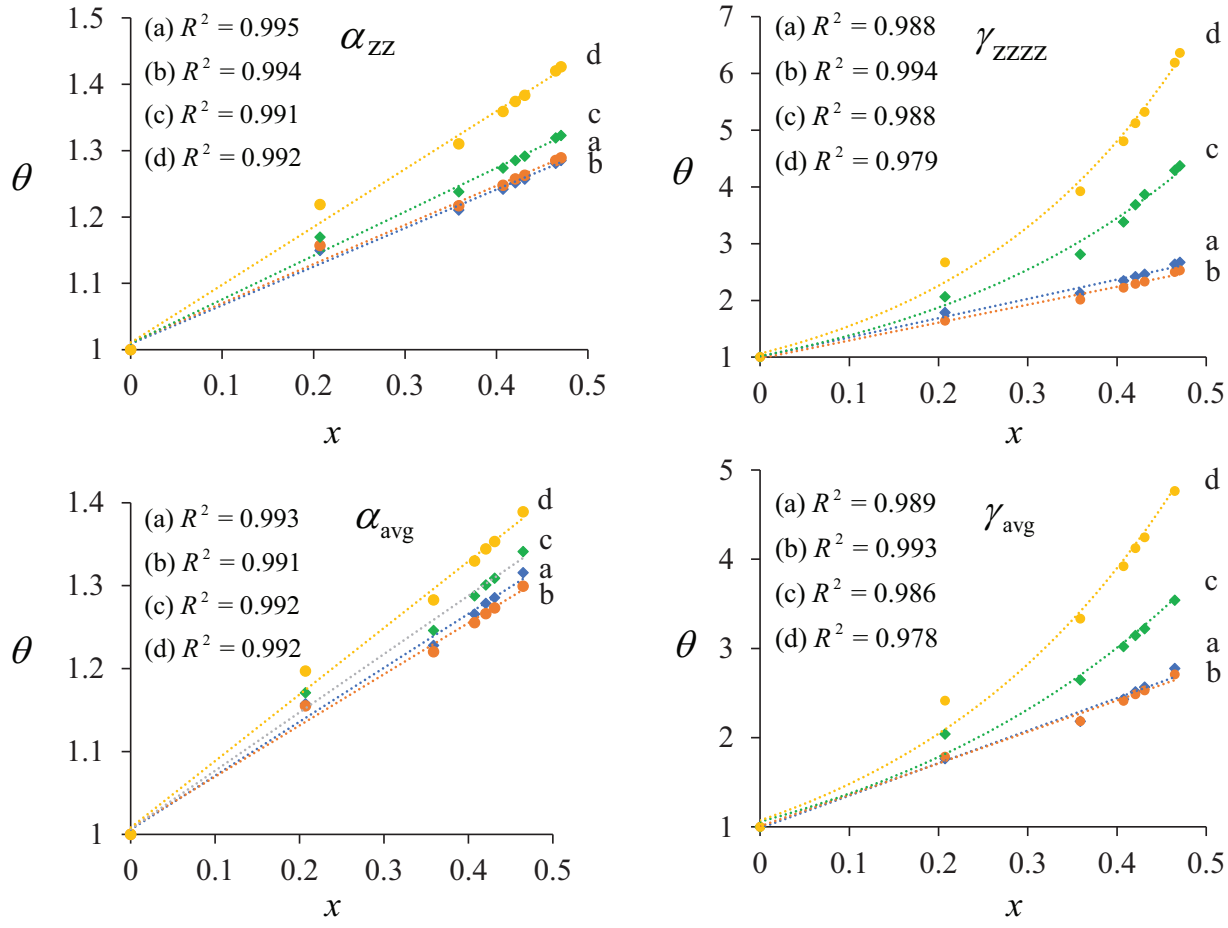


Figure S12: Plot of θ (unitless) versus $x[= (\varepsilon - 1)/(2\varepsilon + 1)]$[1,2] for all systems at TLC-PBE / 6-31G(d) level: (a) *Cis*-AB, (b) *Trans*-AB, (c) *Cis*-DA-AB and (d)*Trans*-DA-AB.

Table S12: Calculated static α_{avg} (a.u.) of DA-AB isomers in different solvents by using CAM-B3LYP and TLC-PBE functionals with 6-31G(d) basis set.

Solvents (ε)	*Cis*-DA-AB			*Trans*-DA-AB		
	CAM-B3LYP	TLC-PBE	LC-PBE	CAM-B3LYP	TLC-PBE	LC-PBE
Gas phase (1.00)	170.3	169.2	162.5	201.9	204.1	188.0
CS_2 (2.06)	199.8	198.1	188.8	241.7	244.3	221.1
$CHCl_3$ (4.81)	212.9	210.8	200.4	259.1	261.8	235.2
THF (7.58)	220.1	217.9	206.7	268.5	271.4	242.8
CH_2Cl_2 (8.93)	222.4	220.1	208.8	271.5	274.4	245.3
$CH_3CH_2Cl_2$ (10.36)	223.8	221.5	210.0	273.3	276.2	246.7
CH_3COCH_3 (20.70)	229.3	226.9	214.9	280.6	283.5	252.5

Table S13: Calculated static γ_{avg} (10^2 a.u.) of unsubstituted AB isomers in different solvents by using CAM-B3LYP and TLC-PBE functionals with 6-31G(d) basis set.

Solvents (ε)	*Cis*-AB			*Trans*-AB		
	CAM-B3LYP	TLC-PBE	LC-PBE	CAM-B3LYP	TLC-PBE	LC-PBE
Gas phase (1.00)	199	206	147	712	593	580
CS_2 (2.06)	397	364	252	1313	1061	1015
$CHCl_3$ (4.81)	433	450	308	1621	1297	1229
THF (7.58)	482	501	342	1799	1431	1351
CH_2Cl_2 (8.93)	498	518	353	1857	1475	1390
$CH_3CH_2Cl_2$ (10.36)	508	529	359	1892	1501	1414
CH_3COCH_3 (20.70)	549	572	387	2034	1607	1509

Table S14: Calculated static γ_{avg} (10^2 a.u.) of DA-AB isomers in different solvents by using CAM-B3LYP and TLC-PBE functionals with 6-31G(d) basis set.

Solvents (ε)	*Cis*-DA-AB			*Trans*-DA-AB		
	CAM-B3LYP	TLC-PBE	LC-PBE	CAM-B3LYP	TLC-PBE	LC-PBE
Gas phase (1.00)	836	717	586	3003	2715	2271
CS_2 (2.06)	1754	1463	1154	7392	6560	5045
$CHCl_3$ (4.81)	2298	1898	1477	10642	9052	6717
THF (7.58)	2636	2167	1674	12135	10653	7754
CH_2Cl_2 (8.93)	2749	2256	1739	12770	11197	8101
$CH_3CH_2Cl_2$ (10.36)	2818	2311	1780	13161	11533	8314
CH_3COCH_3 (20.70)	3107	2540	1946	14806	12942	9602

Table S15: Calculated CT energies (E_{CT}, eV) and oscillator strengths (f, Hartree), and dipole moment (Debye) from TDKST calculations with TLC-PBE functional and a 6-31G(d) basis set.

ε	*Cis*-DA-AB		*Trans*-DA-AB	
	$E_{CT}(f)$	Debye	$E_{CT}(f)$	Debye
1	3.99 (0.28)	11.89	3.45 (1.08)	15.64
2.06	3.82 (0.44)	16.25	3.18 (1.27)	18.99
4.81	3.75 (0.46)	16.86	3.08 (1.33)	20.34
7.58	3.72 (0.47)	17.15	3.03 (1.37)	21.05
8.93	3.71 (0.47)	17.23	3.01 (1.37)	21.26
10.36	3.71 (0.47)	17.28	3.01 (1.37)	21.39
20.70	3.69 (0.48)	17.45	2.97 (1.39)	21.90
24.85	3.68 (0.48)	17.48	2.97 (1.40)	21.99
Expt.[11]	3.73	-	2.85	-

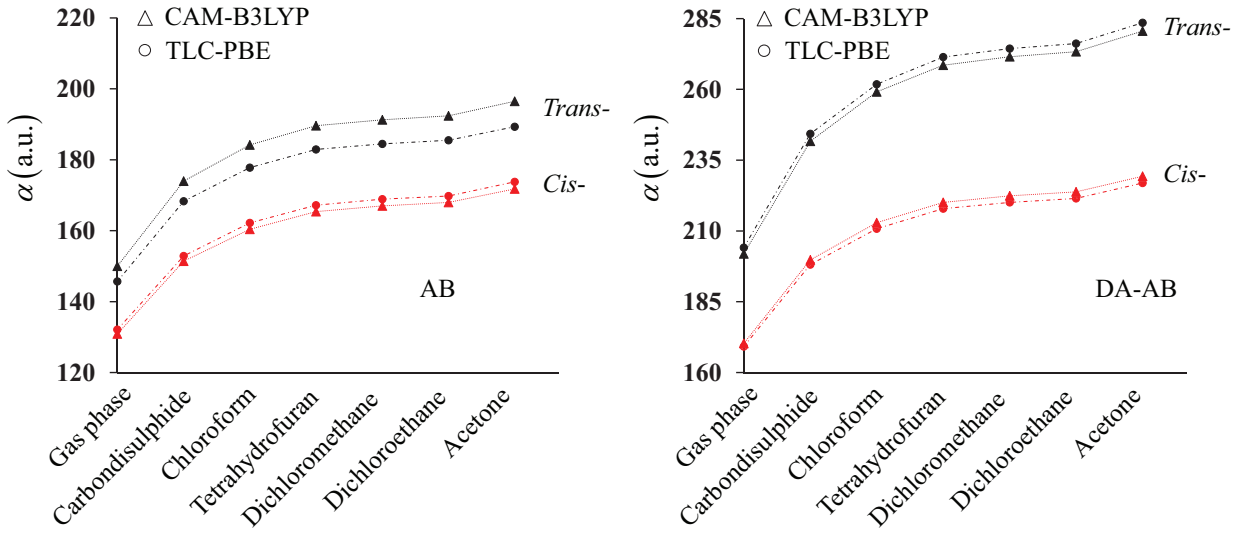


Figure S13: Variation plot of α_{avg} with different solvents calculated by TLC-PBE and CAM-B3LYP funtionals and 6-31G(d) basis set.

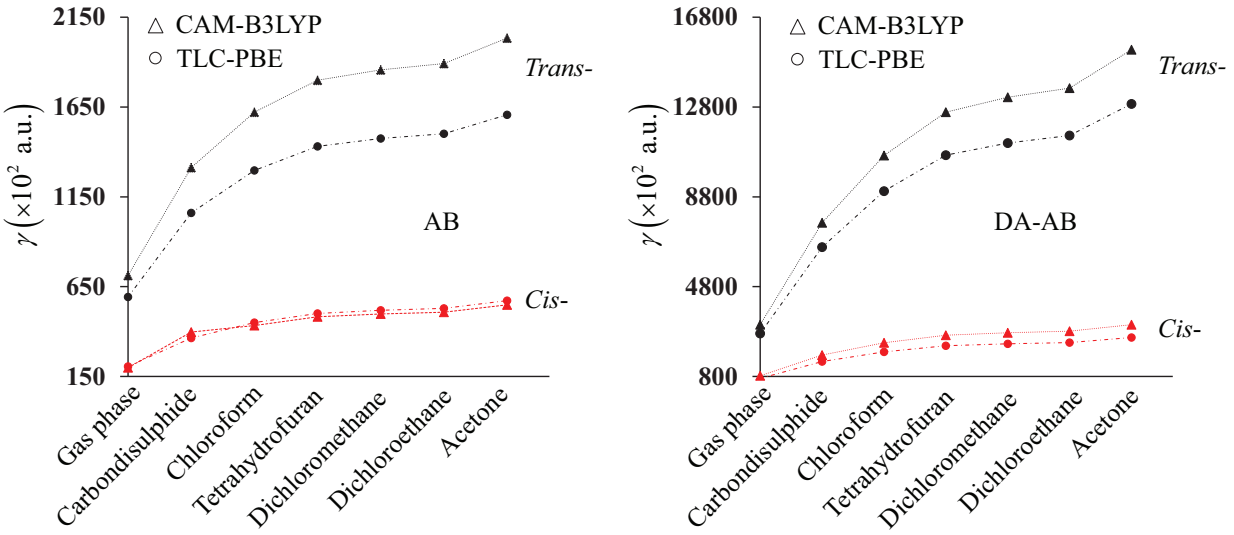


Figure S14: Variation plot of γ_{avg} with different solvents calculated by TLC-PBE and CAM-B3LYP funtionals and 6-31G(d) basis set.

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