Supporting Information for:

UV-induced benzyloxy rotamerization in a *ortho* OH-substituted aryl Schiff base

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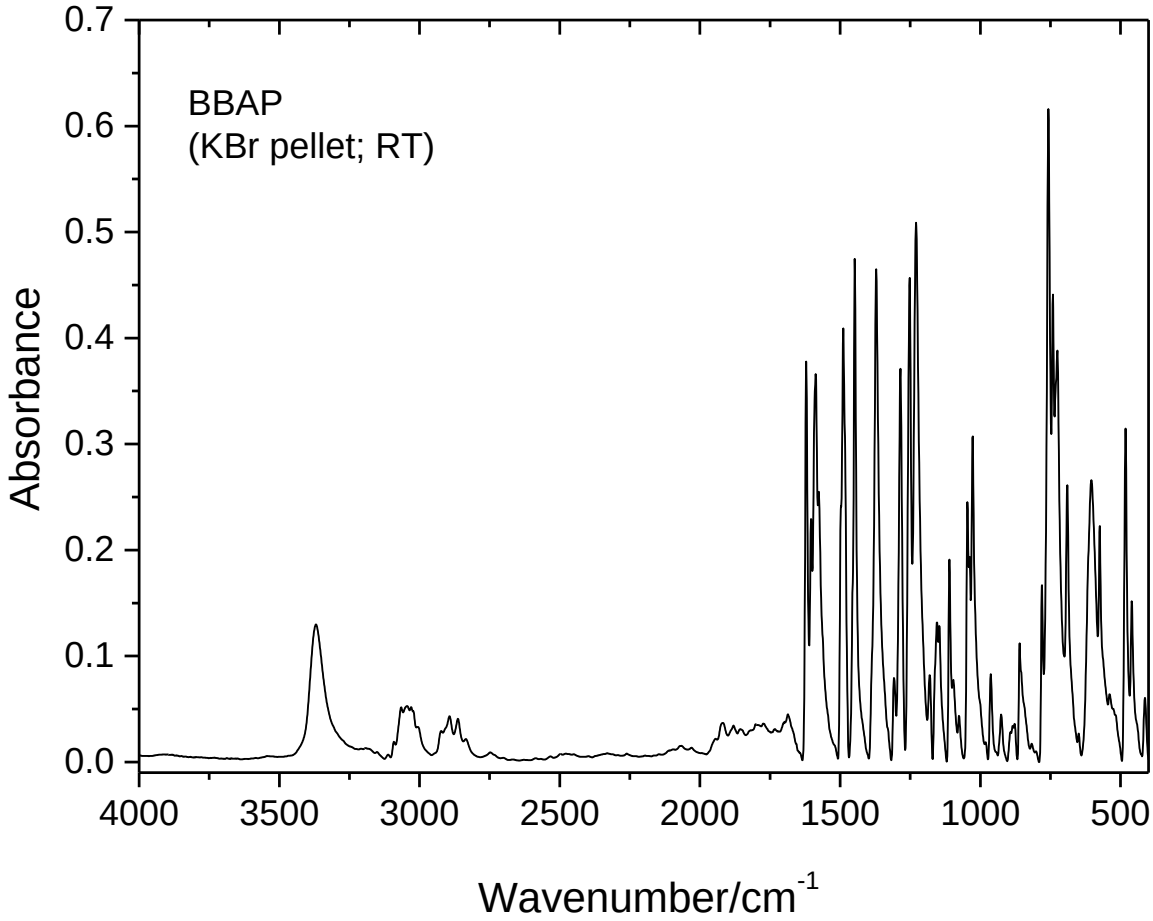

Figure S1. IR spectrum of BBAP in a KBr pellet at room temperature (RT).

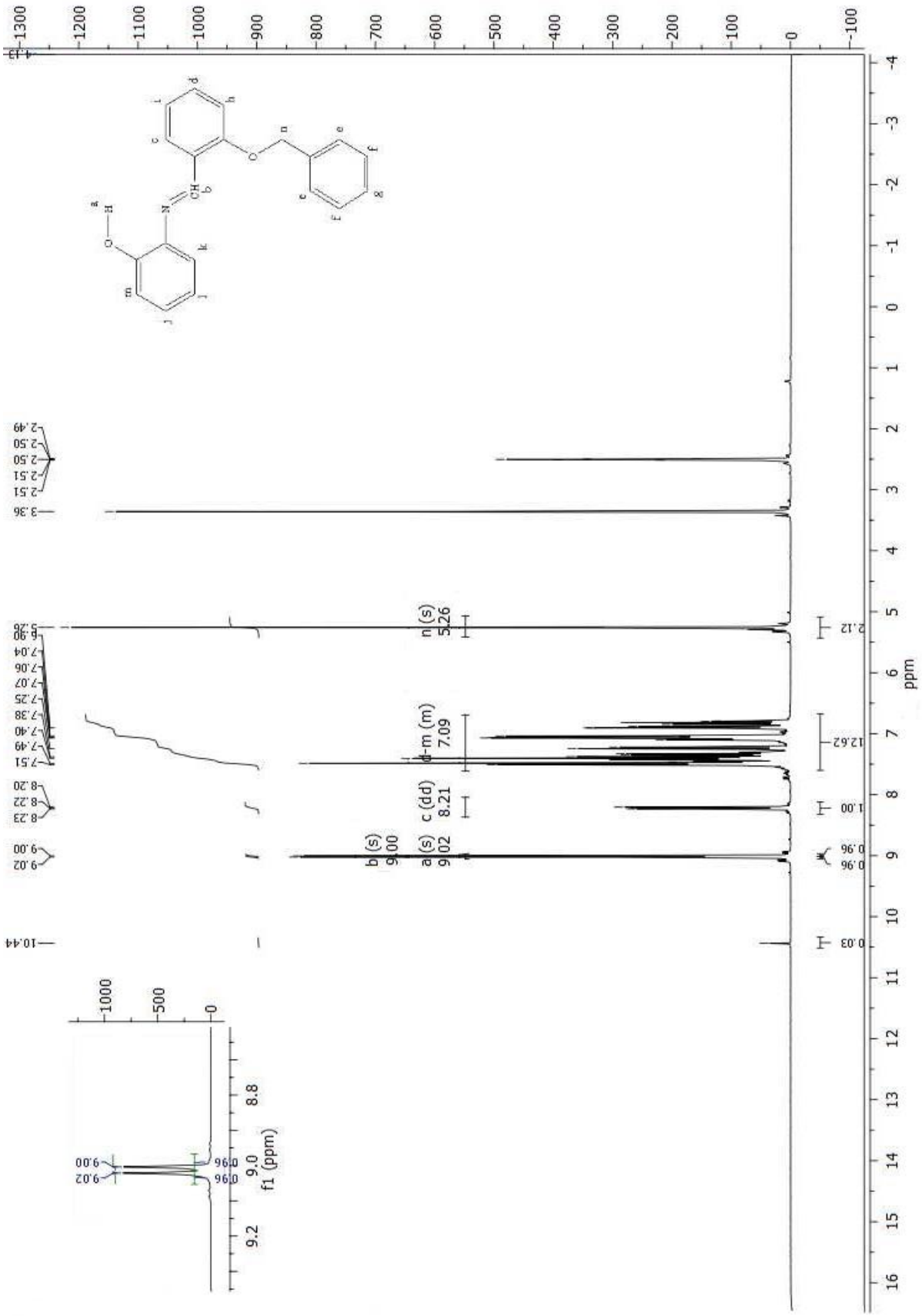

Figure S2. ^{1}H-NMR spectrum of BBAP in DMSO-d_6, at room temperature.

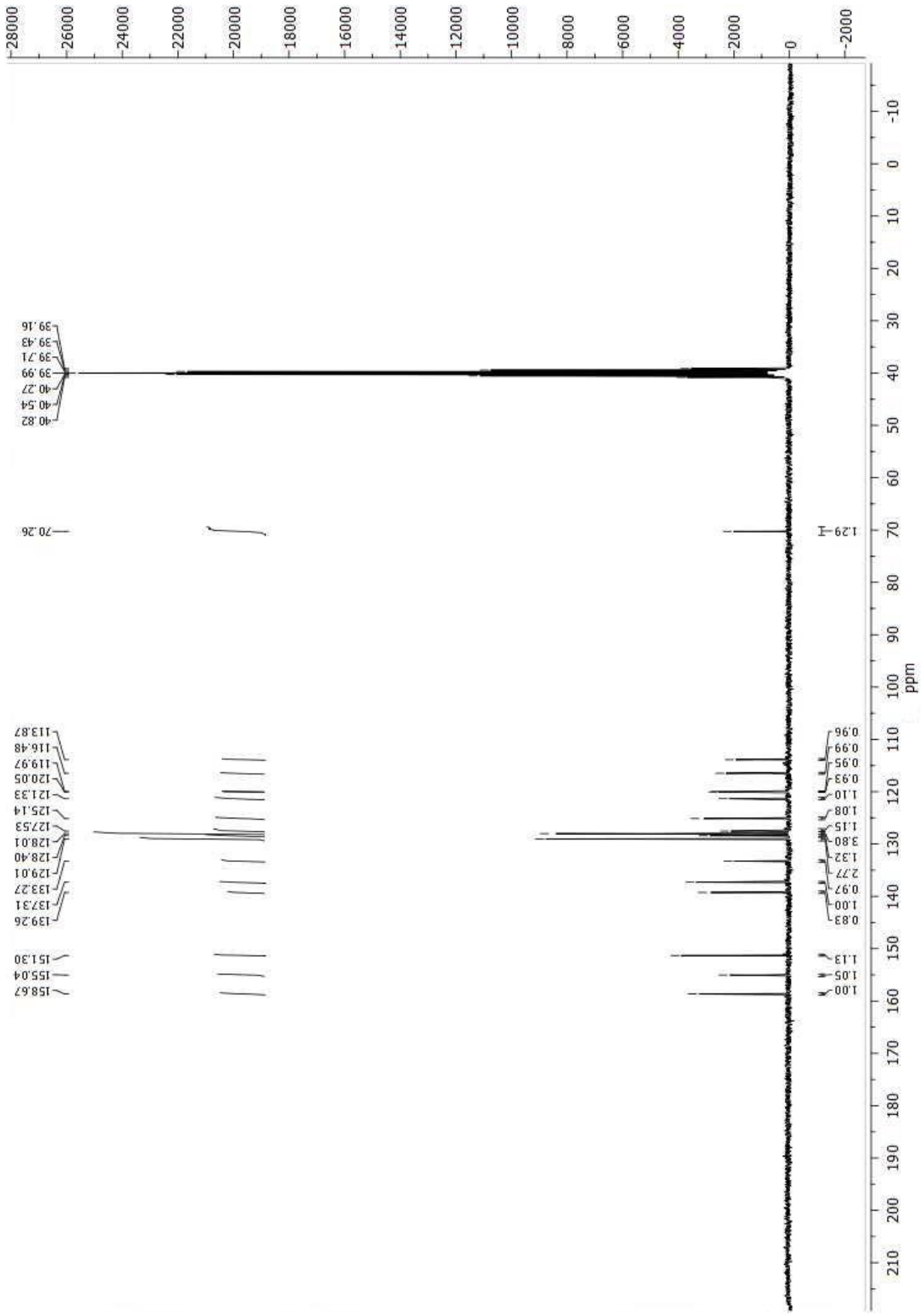

Figure S3. ^{13}C-NMR spectrum of BBAP in DMSO-d_6, at room temperature.

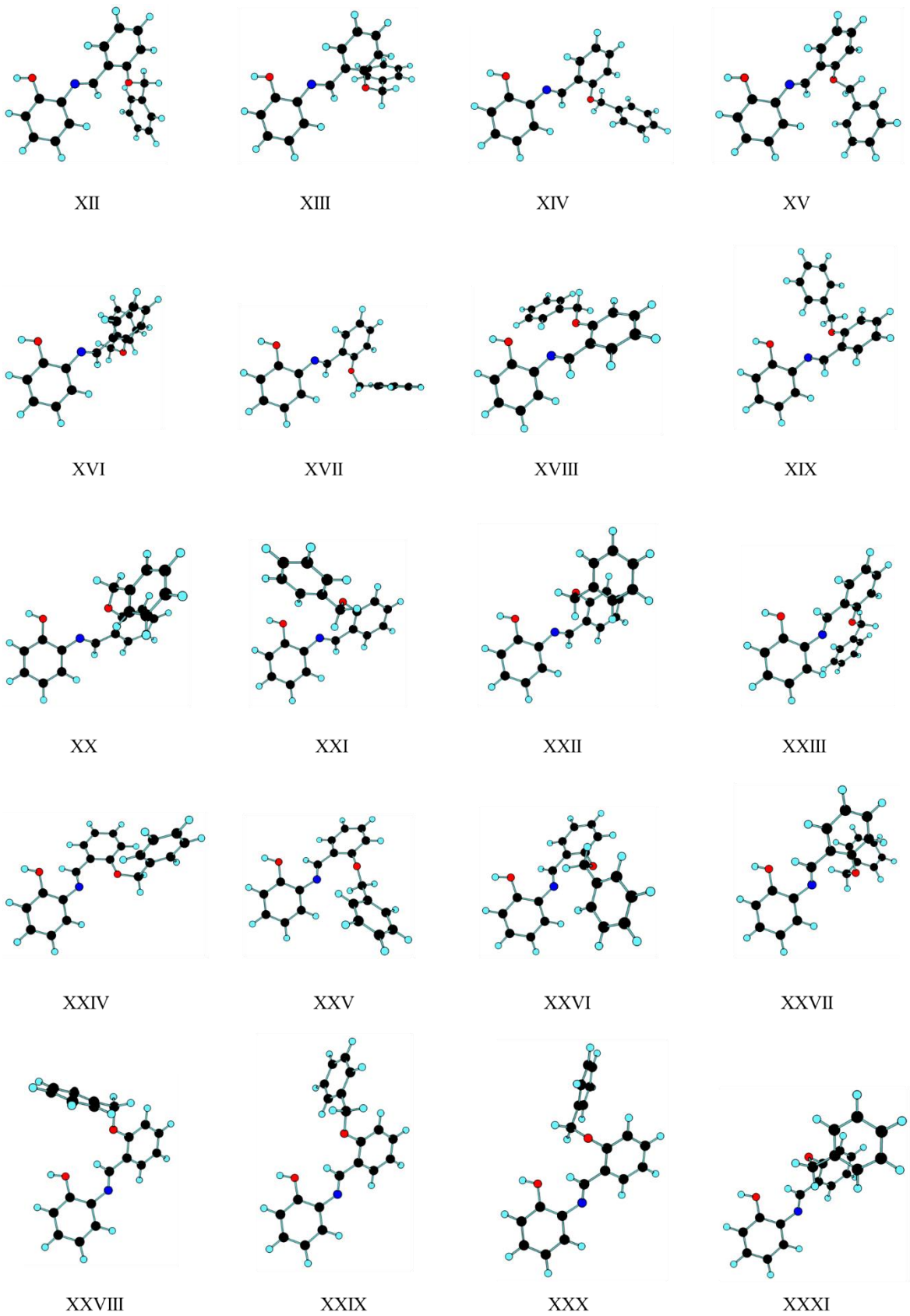

Figure S4. Structures of the non-intramolecularly H-bonded high-energy conformers of *trans* BBAP (forms XII to XXXI).

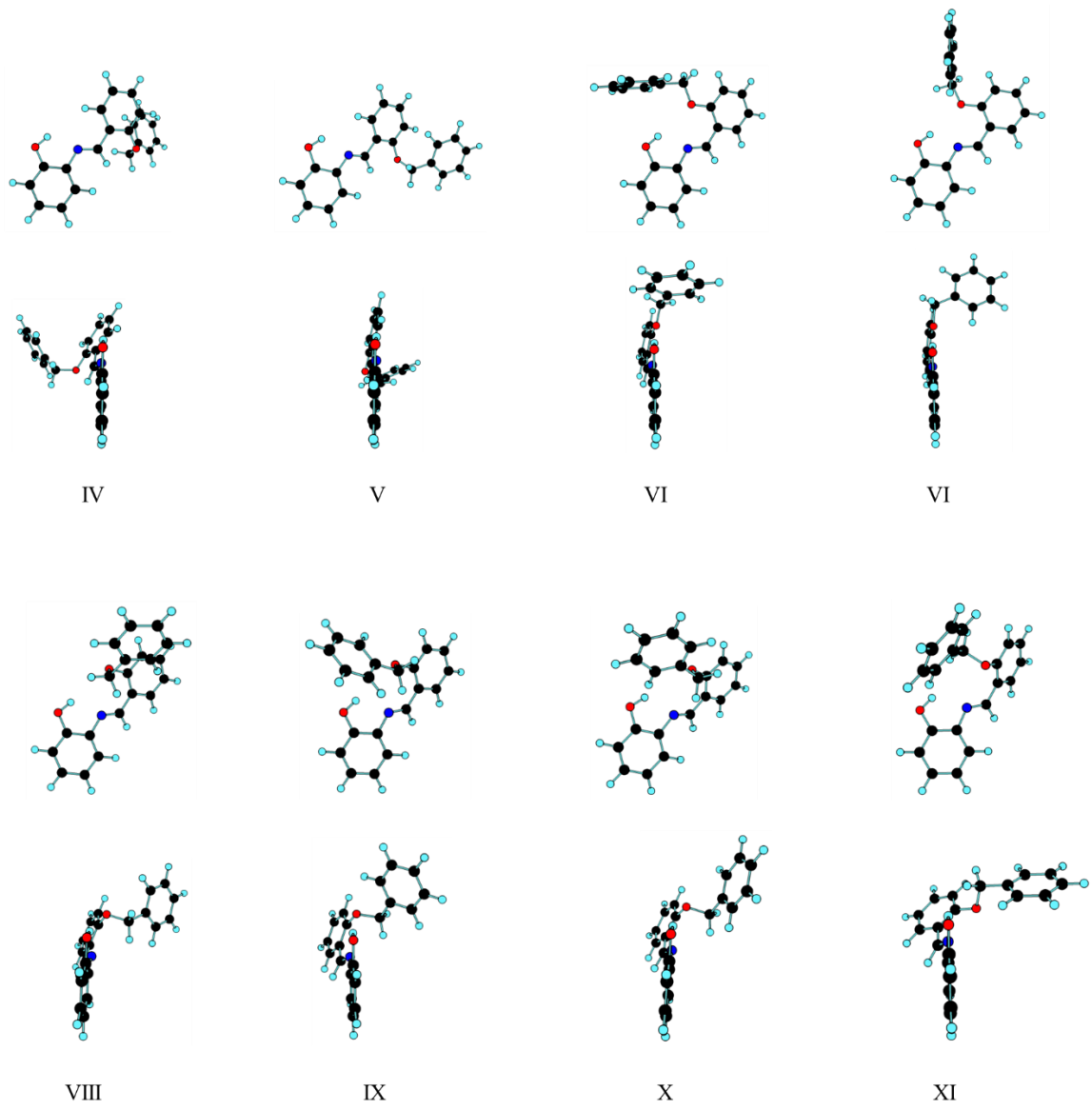

Figure S5. Structures of the higher-energy intramolecularly H-bonded conformers of *trans* BBAP (forms IV to XI; two perspectives).

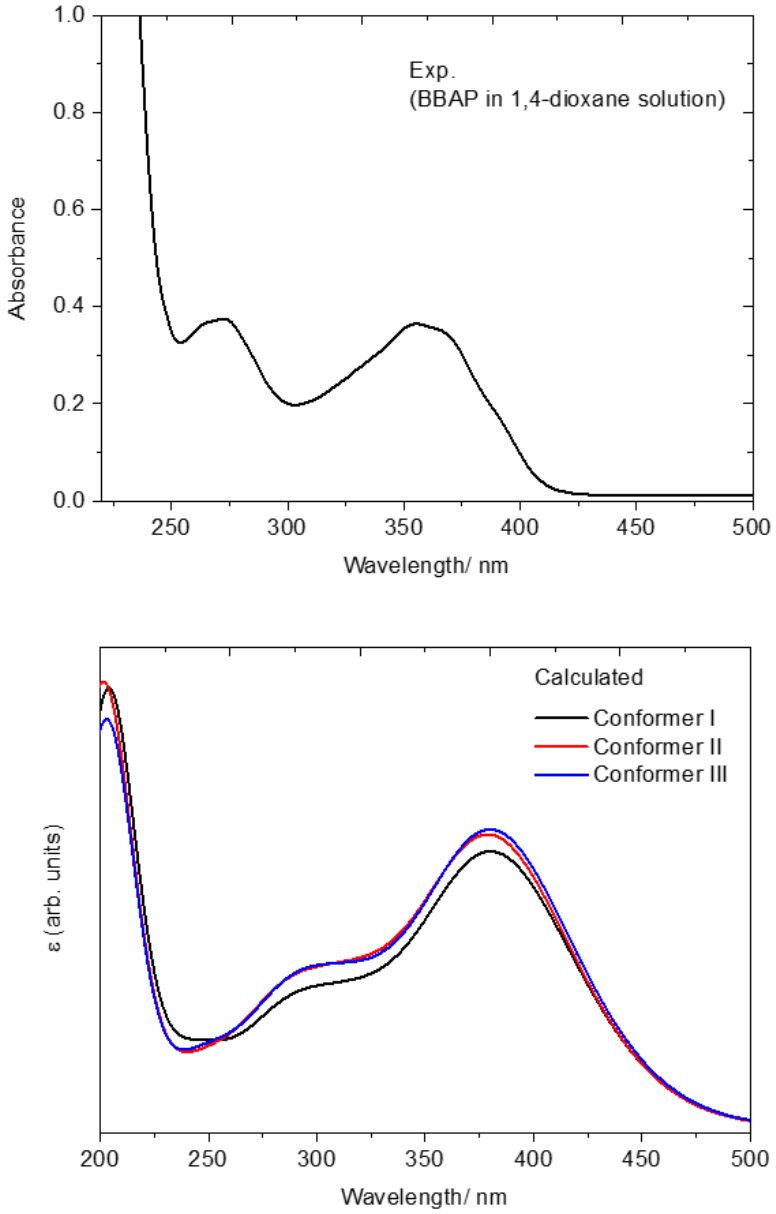

Figure S6. TD-DFT(B3LYP)/6-311++G(d,p) calculated UV-vis spectra of conformers I, II and III of BBAP (isolated molecule), and the experimental spectrum of the compound in 1,4-dioxane solution (5×10^{-4} M).

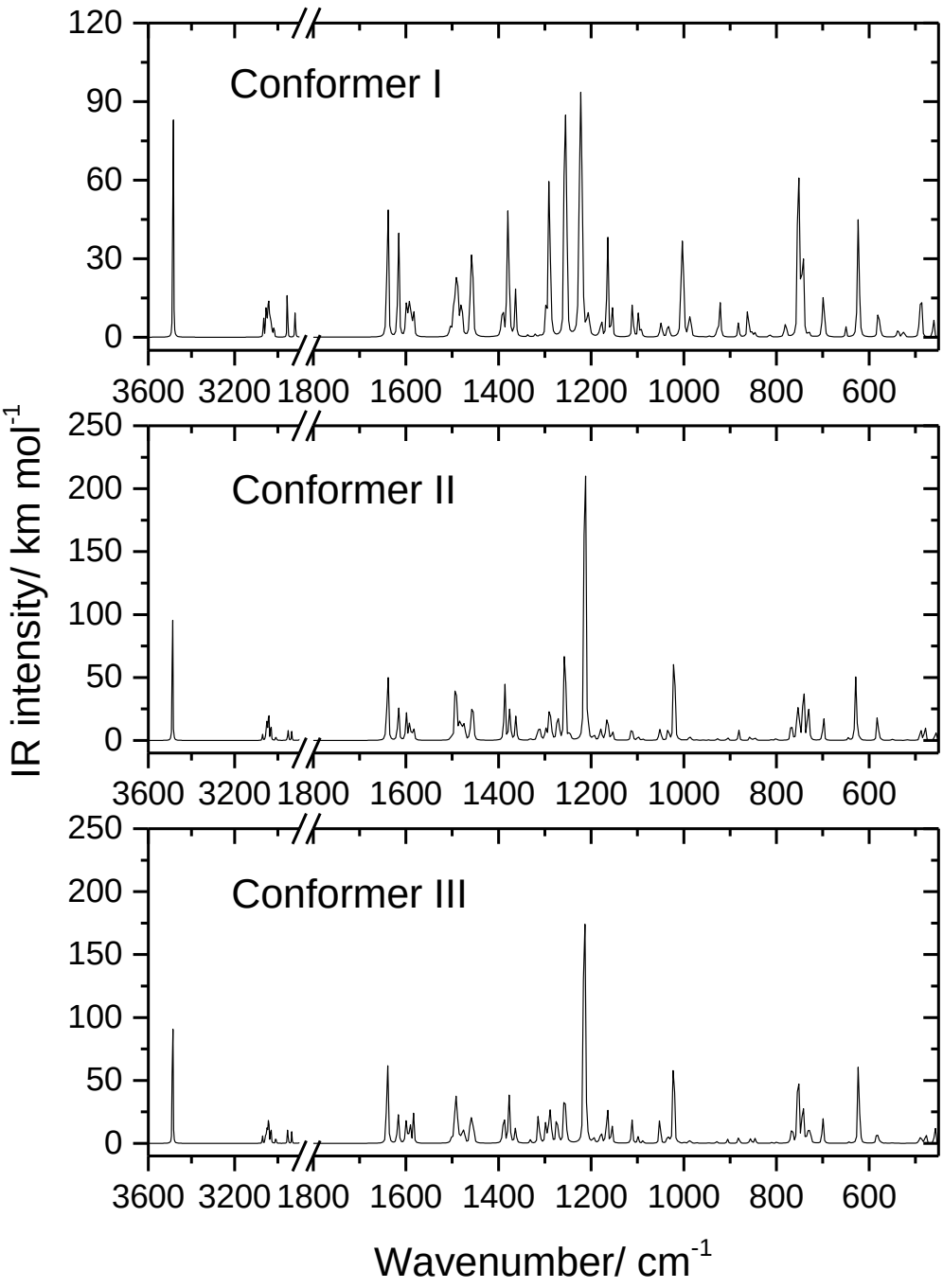

Figure S7. DFT(B3LYP)/6-311++G(d,p) calculated IR spectra of conformers I, II and II of BBAP. Calculated wavenumbers were scaled as described in Section 2.3 of the manuscript.

Table S1. B3LYP/6-311++G(d,p) calculated relative electronic energies (ΔE_{el}), zero-point corrected electronic energies ($\Delta E_{(0)}$), and standard Gibbs energies ($\Delta G_{298.15}$) for the high-energy conformers of *trans* BBAP.[a]

Conformer	ΔE_{el}	$\Delta E_{(0)}$	$\Delta G_{298.15}$
XII	28.44	26.65	27.54
XIII	31.55	30.22	32.93
XIV	31.79	30.27	32.55
XV	38.87	36.75	36.48
XVI	41.14	38.74	38.77
XVII	42.44	39.89	38.19
XVIII	41.77	39.57	43.49
XIX	46.39	44.56	45.89
XX	48.04	45.90	48.02
XXI	48.25	46.22	50.92
XXII	51.99	49.39	50.69
XXIII	43.04	40.41	43.21
XXIV	48.01	45.79	46.74
XXV	49.58	46.75	47.48
XXVI	50.30	47.54	48.73
XXVII	50.76	48.10	48.91
XXVIII	29.24	27.26	27.57
XXIX	32.07	30.51	32.36
XXX	40.77	38.25	37.33
XXXI	41.65	39.31	39.26

[a] Energies in kJ mol^{-1} relative to conformer I (See Figure 1). See also Figure S5 for structures of the conformers.

Table S2. Tentative assignment of the infrared spectra of BBAP isolated in an argon and N_2 matrices (10 K), and the B3LYP/6-311++G(d,p) calculated infrared spectra for conformers I, II and III.[a]

Nº	Exp. (Ar)	Exp. (N_2)	Calc. I		Calc. II		Calc. III		
	ν	ν	ν	I^{IR}	ν	I^{IR}	ν	I^{IR}	Approximate Description[b]
114	3454/3422	3439	3485	138	3488	144	3487	146	νOH
113	3095	3111	3066	11	3071	8	3071	7	νCH_{sym}
112	3090	3096	3057	11	3057	9	3058	9	νCH_{asym}
111	3078	3075	3052	15	3052	16	3052	16	$\nu CH_{p\text{-}sym}$
110			3048	12	3049	9	3049	9	νCH_{sym}
109	3045	3055/3044	3045	16	3044	17	3044	17	$\nu CH_{p\text{-}asym}$
108			3043	14	3043	13	3043	14	νCH_{asym}
107			3038	24	3043	18	3043	19	νCH_{asym}
106			3033	7	3033	13	3033	13	$\nu CH_{p\text{-}asym}$
105	3016	3016	3029	8	3032	6	3033	6	νCH_{asym}
104			3028	1	3028	1	3028	1	νCH_{asym}
103			3024	0	3024	0	3024	0	$\nu CH_{p\text{-}asym}$
102			3021	2	3023	0	3024	0	νCH_{asym}
101			3017	4	3009	8	3009	8	νCH_{asym}
100	2952	2954	2956	21	2953	21	2954	21	$\nu C\text{-}H_{am}$
99	2935	2936	2920	20	2936	11	2936	11	$\nu CH_{2\ asym}$
98	2879	2888/2882	2877	37	2893	36	2893	35	$\nu CH_{2\ sym}$
97	1632/1624	1624	1640	79	1640	91	1639	90	$\nu CC_{p\text{-}po}$; νN=C; $\delta CH_{p\text{-}po}$
96	1620	1632/1624	1619	2	1617	12	1618	12	νCC_b; δCH_b
95	1610/1608	1607	1616	46	1616	26	1616	29	$\nu CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; δOH
94	1602/1600/1598	1600/1597	1599	1	1600	25	1599	22	νCC_b; δCH_b
93			1598	34	1597	8	1597	6	$\nu CC_{p\text{-}po}$; νN=C; $\delta CH_{p\text{-}po}$; $\delta C\text{-}H_{am}$
92	1593	1592	1591	38	1591	32	1591	34	νCC_p; δCH_p; δOH
91	1586/1581	1585/1580	1584	23	1584	24	1583	23	νCC_{po}; δCH_{po}
90	1506	1503	1504	9	1501	7	1501	7	νCC_b; δCH_b
89	1501	1502	1495	48	1492	121	1492	134	$\delta CH_{p\text{-}po}$; scis-CH_2
88	1494	1494	1488	67	1482	26	1483	14	δCC_p; δCH_p; scis-CH_2
87	1486/1483	1487/1484	1480	17	1476	14	1476	14	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; scis-CH_2
86	1465	1459	1475	2	1474	17	1474	9	δCC_p; δCH_p; δOH
85	1461	1454/1452	1460	9	1460	20	1460	23	δCC_b; δCH_b; twist-CH_2
84	1455/1451		1458	90	1456	48	1456	50	$\delta CC_{p\text{-}o}$; $\delta CH_{p\text{-}o}$
83	1383/1372	1383/1373	1392	31	1387	63	1389	60	$\delta C\text{-}H_{am}$; wag-CH_2
82	1351	1349	1379	124	1375	51	1377	67	$\delta C\text{-}H_{am}$; wag-CH_2
81			1363	23	1362	31	1363	27	δCC_p; δCH_p; δC-H; δOH
80	1339/1331	n.obs.	1337	1	1331	3	1331	3	δCH_b; twist-CH_2
79	1311	1314	1320	1	1315	23	1314	24	νCC_b; δCH_b; twist-CH_2
78	1304	1306	1311	0	1310	7	1310	9	$\nu CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$
77	1294	1296	1296	22	1298	24	1298	22	$\nu CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; $\delta C\text{-}H_{am}$
76	1285	1288/1285	1290	113	1289	75	1289	83	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; νC-(OH)
75	1262	1263	1257	121	1272	63	1273	53	δCC_p; δCH_p; νC-(OH)
74	1257	1258	1254	68	1257	110	1257	111	$\delta CC_{p\text{-}po}$; δCH_{po}; δOH; νC-N; νC-O
73	1248	1250	1226	12	1246	11	1246	2	twist-CH_2
72	1225	1228/1221	1223	342	1214	343	1214	375	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; δOH; νC-N; νC-O
71	1210	1215	1217	12	1207	14	1208	2	δCC_b; δCH_b; νC-N; νC-CH_2; wag-CH_2
70	1200	1193	1206	27	1194	6	1194	7	$\delta CH_{p\text{-}po}$; δOH
69	1191	1189	1182	3	1180	9	1180	11	δCH_b
68	1179	1181	1178	9	1178	12	1179	9	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; δOH
67	1162	1167/1163	1165	49	1165	56	1166	56	δCH_{po}
66			1163	0	1163	1	1163	1	δCH_b
65	1151	1152	1155	13	1155	14	1155	15	δCH_p
64	1113	1113/1110	1110	25	1112	27	1112	26	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; δOH
63	1096	1097	1097	13	1099	7	1099	8	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; δOH
62	n.obs.	n.obs.	1092	4	1088	2	1088	2	δCC_b; δCH_b; rock-CH_2
61	1052/1048	1052	1049	14	1052	22	1052	23	δCC_{po}; δCH_{po}
60			1034	10	1034	12	1034	11	δCC_p; δCH_p
59	1034	1034/1030	1032	2	1033	2	1033	4	δCC_b; δCH_b
58	1028	1027	1004	98	1021	94	1022	90	δCC_{po}; δCH_{po}; $\nu O\text{-}CH_2$; γCC_b; γCH_b
57			1001	21	1011	1	1012	1	δCC_b; δCH_b; $\nu O\text{-}CH_2$
56			989	5	999	1	999	1	$\gamma C\text{-}H_{am}$; γCH_{po}
55	1018/1013	1013	987	4	989	0	988	0	γCH_b
54			986	9	986	8	987	7	rock-CH_2
53			973	0	973	1	973	1	$\gamma C\text{-}H_{am}$; γCH_{po}
52	972	965/956	968	0	971	0	971	0	γCC_b; γCH_b
51			960	0	957	0	960	0	γCH_p
50	n.obs.	n.obs.	946	1	946	1	947	1	$\gamma C\text{-}H_{am}$; γCH_{po}
49	928	933	928	3	926	3	928	3	γCC_p; γCH_p
48	915	926/918	921	23	906	5	905	5	γCC_b; γCH_b
47	886	885	882	8	882	11	881	10	δCC_{po}; δCH_{po}; δC-CH=N-C
46	863/859	863	861	26	857	6	857	7	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta O\text{-}CH_2$

45	849	853/840	854	4	850	1	851	2	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta O\text{-}CH_2$
44	837	836	850	0	846	5	846	4	γCC_{po}; γCH_{po}
43			846	3	845	0	844	0	γCC_{p}; γCH_{p}
42			841	0	810	1	810	1	γCC_{b}; γCH_{b}
41	811	810	814	2	801	2	799	1	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta C\text{-}CH_2$
40	782/776/768	782	781	16	767	23	767	26	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta C\text{-}CH_2$
39	760/754	760/755	754	13	753	82	753	85	$\gamma CC_{po\text{-}p}$; $\gamma CH_{po\text{-}p}$
38			752	82	750	11	751	11	$\gamma CH_{po\text{-}p\text{-}b}$
37	748/744	748	750	24	741	61	742	51	γCC_{b}; $\gamma CH_{po\text{-}p\text{-}b}$
36	737	741	743	50	731	35	731	35	γCC_{p}; $\gamma CH_{po\text{-}p}$
35	731	736/733	729	2	727	4	727	8	$\gamma CC_{po\text{-}b}$; $\gamma CH_{po\text{-}p}$
34	696/693	702/700	698	47	699	26	700	26	γCC_{b}; γCH_{b}
33	649	648	650	4	644	3	644	2	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta O\text{-}CH_2$; $\delta N{=}CH$
32	n.obs.	n.obs.	625	4	629	75	626	1	δCC_{b}; γOH
31	618	618	624	70	625	5	623	73	γOH
30	n.obs.	n.obs.	620	9	620	4	620	12	$\delta CC_{p\text{-}po\text{-}b}$; $\delta CH_{p\text{-}po\text{-}b}$; $\delta O\text{-}CH_2$
29	580	580	579	22	582	24	582	25	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; $\delta N{=}CH$
28	576	576	576	4	575	2	575	2	$\delta CC_{p\text{-}po}$; $\delta CH_{p\text{-}po}$; $\delta N{=}CH$; $\delta C\text{-}OH$
27	n.obs.	n.obs.	563	0	563	0	564	0	$\gamma CC_{po\text{-}p}$; $\gamma CH_{po\text{-}p}$
26	537	538	540	0	550	3	549	1	$\gamma CC_{po\text{-}p}$; $\gamma CH_{po\text{-}p}$
25			538	5	536	1	538	0	Skeletal
24	526/508	527	526	7	517	2	517	0	Skeletal
23	489/480/477	490/483	490	16	488	16	489	16	$\gamma CC_{po\text{-}p}$; $\gamma CH_{po\text{-}p}$; $\gamma N{=}CH$; γOH
22			487	16	479	13	478	14	Skeletal
21	462/458	465/459	461	8	457	15	458	16	Skeletal

[a] Frequencies (ν, in cm^{-1}) were scaled by 0.983 or 0.955, below and above 1800 cm^{-1}, respectively. Calculated infrared intensities (I^{IR}) in km mol^{-1}. [b] Approximate descriptions were obtained by visual inspection of the animated vibrations using ChemCraft. ν, stretching; δ, bending; γ, torsion; wag, wagging; twist, twisting; rock, rocking; n.obs., not observed. Subscript "p" refers to the phenol ring, "b" to ring of benzyl group, "am" to the azomethine bridging group, "po" to the phenol group. The calculated spectra of the 3 experimentally relevant conformers of BBAp are provided in Figure S7.