

Supplementary Material for

Contrasting Behaviour of Exciplex Ensembles in Diastereodifferentiating Paternò-Büchi Reaction of Chiral Cyanobenzoate with Naphthyl- and Phenylethenes upon Direct or Charge-Transfer Excitation

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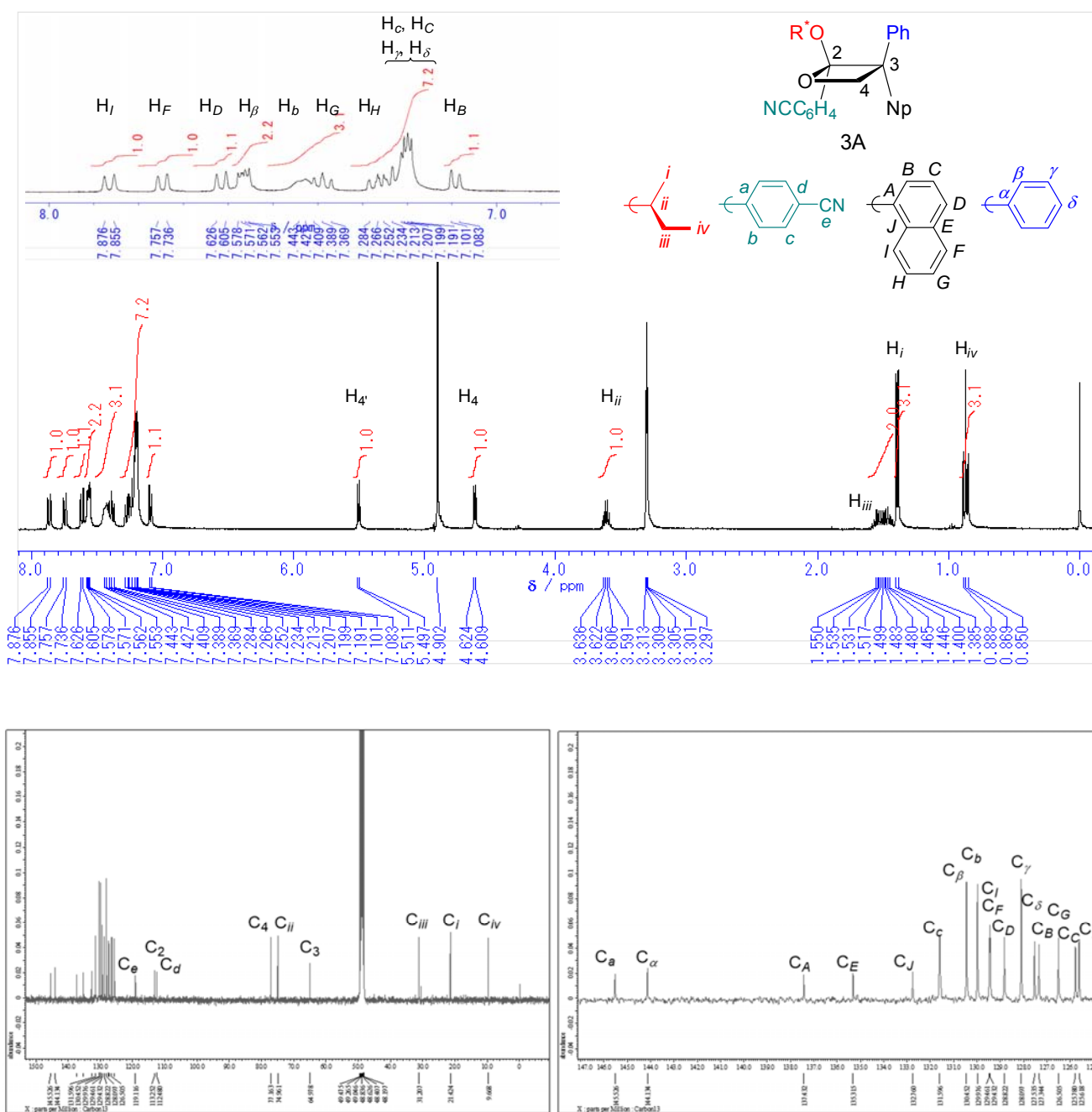


Figure S1. ^1H - and ^{13}C -NMR spectra of 3A in CD_3OD .

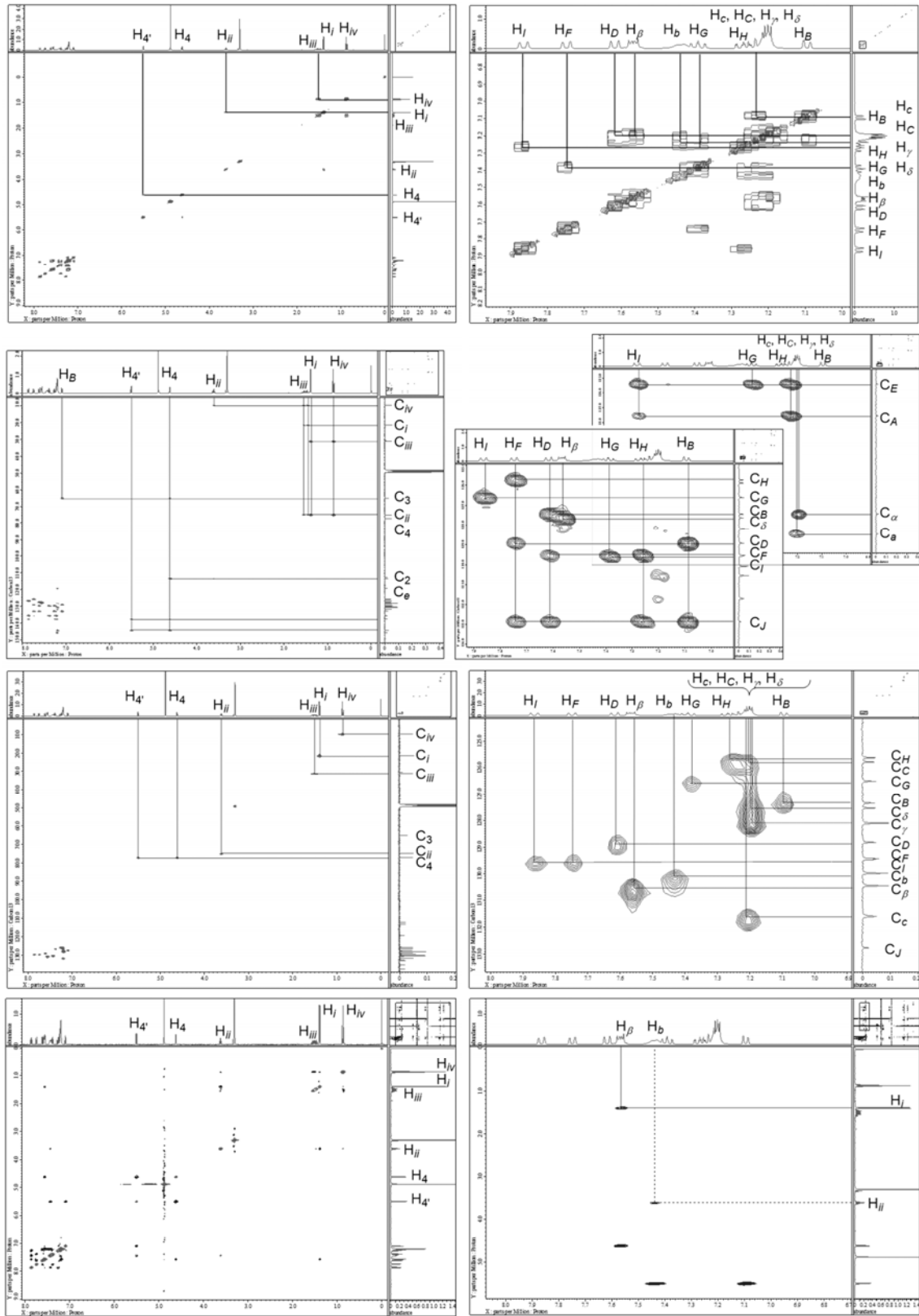


Figure S2. 2D-NMR (^1H - ^1H COSY, HBMC, HSQC, and NOESY, from top to bottom) spectra of 3A in CD_3OD .

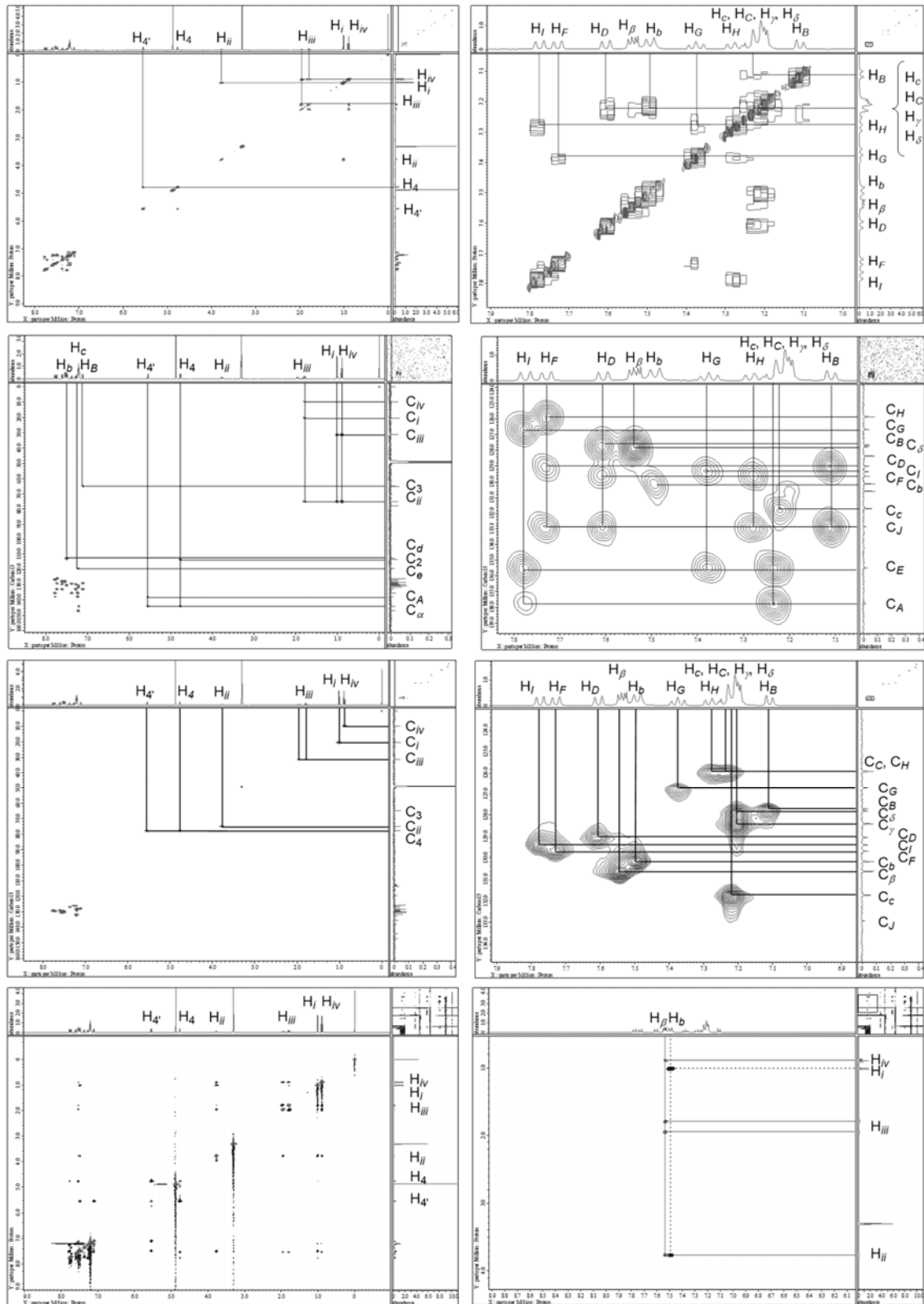


Figure S4. 2D-NMR (^1H - ^1H COSY, HBMBC, HSQC, and NOESY, from top to bottom) spectra of 3B in CD_3OD

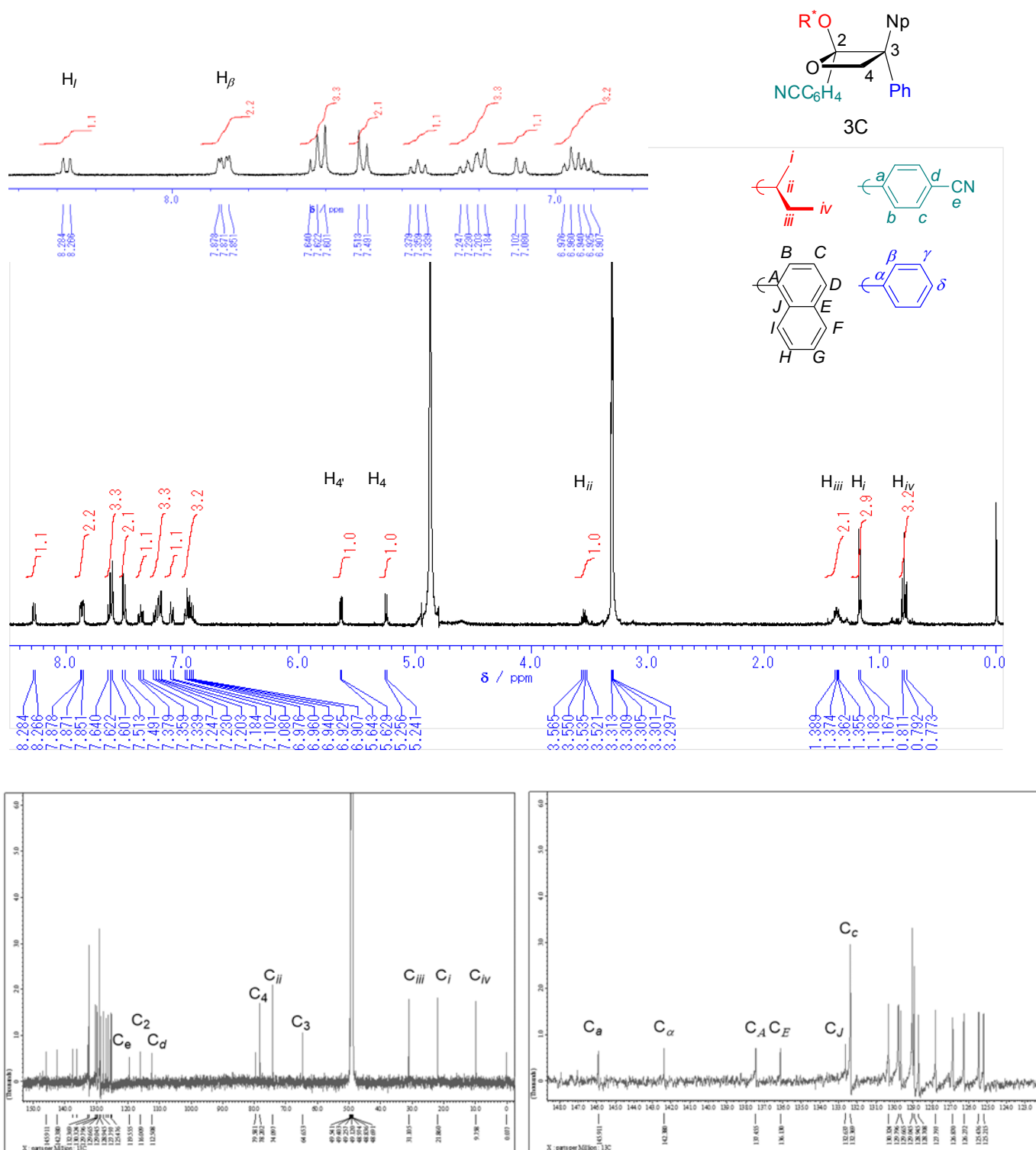


Figure S5. ^1H - and ^{13}C -NMR spectra of 3C in CD_3OD .

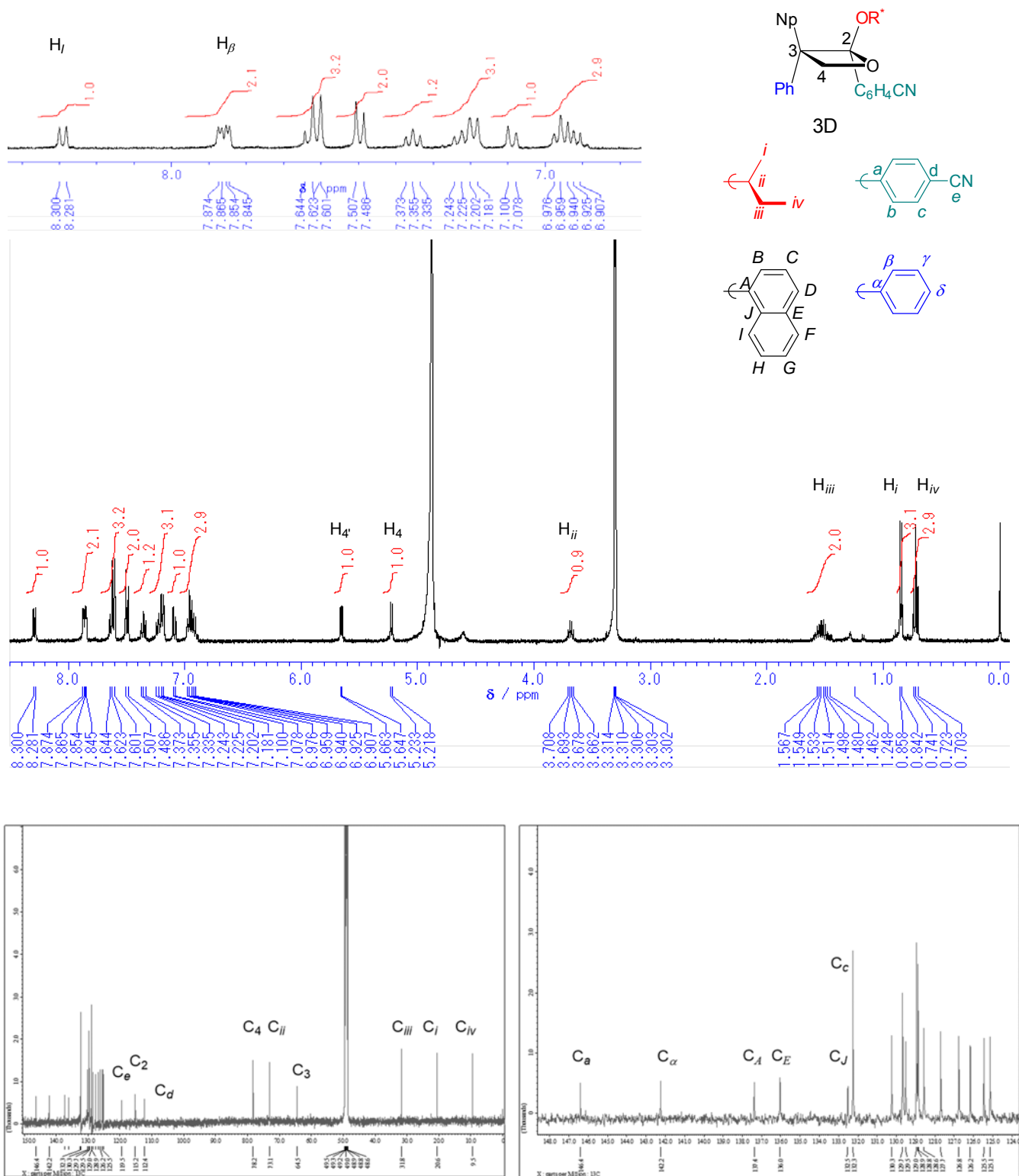


Figure S5. ^1H - and ^{13}C -NMR spectra of 3D in CD_3OD .

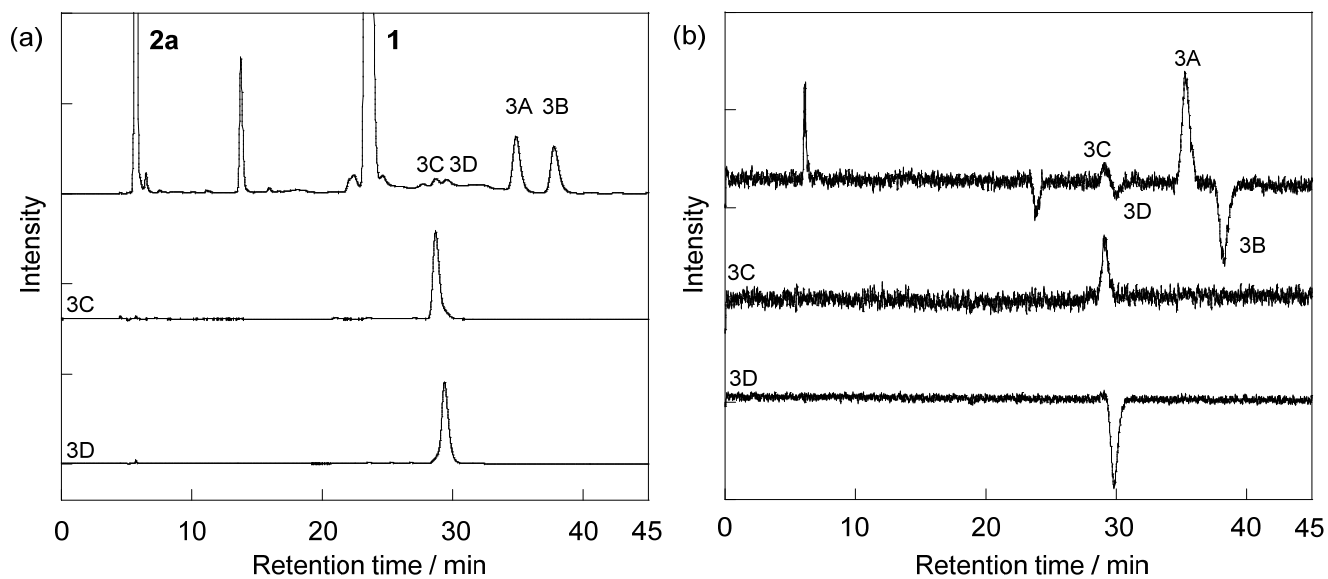


Figure S6. HPLC chromatogram of crude mixture of photoproducts and isolated 3C and 3D in diastereodifferentiating [2+2] photocycloaddition of **1** with **2a**. Conditions: Column: Mightysil ($\phi = 4.6$ mm \times 250 mm), 40 °C. Eluent: 98 : 2 (v/v) mixture of *n*-hexane and ethyl acetate, 0.8 mL min⁻¹. Left: UV detector at 254 nm. Right: CD detector at 254 nm.

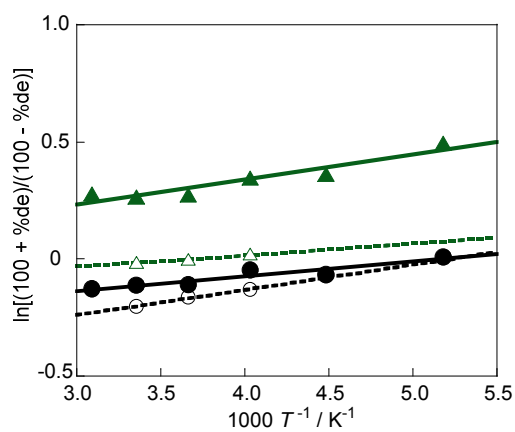


Figure S7. Temperature dependence of the de values obtained upon the direct excitation (black) or the C-T excitation (green) of **1** and **2a** in dichloromethane (dotted lines) and in toluene (solid lines).

TABLE S1. Optimized Geometries of the Complex Formed between **1** and **2a** (Precursor to **3A**) at the Ground (C-T) and the Excited States (EX).

C-T (ground-state)				EX (excited-state)			
C	0.3174300	4.3162360	2.1442930	C	0.0860084	4.3837059	0.8984851
C	0.5221219	3.4772601	-0.2616105	C	0.5640808	-4.5100608	0.2546132
C	0.7805658	-4.3474988	0.1602735	C	0.7166346	3.6485084	-0.2679755
C	0.9282307	-2.4979197	-1.4145320	C	0.8095828	-2.5912030	-1.2027628
C	1.0884162	-0.6807820	-3.0138156	C	1.0441436	4.6331362	2.0495529
C	1.4968667	-3.6235623	-0.7652848	C	1.0801089	-0.6630872	-2.6390486
C	1.6639941	-1.7495195	-2.3683481	C	1.3587921	-3.6902369	-0.5306947
C	1.6881760	-0.2184288	1.4041810	C	1.6185783	-1.7711132	-1.9896335
C	2.0540755	-1.4402805	1.9507798	C	1.9345711	0.0424934	1.4336580
C	2.1491858	1.7057905	-0.1802373	C	2.1908887	1.7696782	-0.3661986
C	2.5085088	0.4060824	0.4565515	C	2.3115584	-1.1446123	1.9764941
C	3.2582448	-2.0449766	1.5569449	C	2.6126243	0.5882602	0.3100744
C	3.6209707	-3.3199887	2.0884115	C	3.4083864	-1.8769846	1.4497417
C	3.7108082	-0.1979485	0.0696466	C	3.6984859	-3.1668513	1.9089063
C	4.0911208	-1.4145542	0.6162489	C	3.7675304	-0.1032282	-0.1518031
C	-0.1759525	3.2529466	-1.5953091	C	4.1540246	-1.2848138	0.3955673
C	-0.2492961	-0.3250133	-2.7373513	C	-0.2273996	3.5098961	-1.4441550
C	-0.3834496	4.0844879	0.8032852	C	-0.2580469	-0.3810137	-2.5209678
C	-0.4226139	-2.1205238	-1.1076985	C	-0.5698199	-2.2926384	-1.0560871
C	-0.5468570	-3.9741020	0.4679433	C	-0.7825617	-4.2438655	0.3668577
C	-1.0082065	-1.0135379	-1.8055279	C	-1.1046374	-1.1562171	-1.7257246
C	-1.1355514	-2.8947619	-0.1554331	C	-1.3473329	-3.1510402	-0.2799040
C	-1.9262899	0.3830834	0.6548561	C	-2.2933055	0.1576271	0.7047658
C	-2.3060426	0.7831305	1.9335594	C	-2.5196750	-0.7468495	-1.6021593
C	-2.4248237	-0.6078627	-1.5818939	C	-2.8202772	0.4599900	1.9442537
C	-2.8468366	-0.2209059	-0.2138524	C	-3.0735783	-0.4752239	-0.2552002
C	-3.2738446	-0.5456430	-2.6235489	C	-3.2392068	-0.5917387	-2.7081383
C	-3.6138664	0.5757087	2.3742308	C	-4.1270663	0.1279430	2.2460953
C	-4.1585017	-0.4297256	0.2421318	C	-4.3851421	-0.8091119	0.0587935
C	-4.5378225	-0.0335998	1.5223197	C	-4.9080175	-0.5087993	1.3001657
N	3.9082892	-4.3659772	2.5071443	N	3.8929080	-4.2510337	2.2431498
O	0.9673195	2.1797322	0.2762435	O	1.1054384	2.3653777	0.2119088
O	2.8420968	2.2721806	-1.0064513	O	2.6931803	2.2354629	-1.3746226
H	0.5071124	2.7933491	-2.3130178	H	0.2644627	2.9890766	-2.2555408
H	0.6803969	3.3731508	2.5639057	H	0.5497839	5.1563113	2.8612139
H	0.7604557	0.2498651	1.7059135	H	1.0106849	-5.3308117	0.7828272
H	1.1775609	4.9855287	2.0285607	H	1.1109148	0.5833935	1.8590429
H	1.2350723	-5.1987088	0.6581247	H	1.4355979	3.7008360	2.4374556
H	1.4099274	-1.9411555	2.6646367	H	1.6084100	4.1719736	-0.5936077
H	1.4246195	4.0806913	-0.4021826	H	1.7224968	-0.0087370	-3.1965005
H	1.6581708	-0.1015449	-3.7344899	H	1.7795131	-1.5417663	2.8225024
H	2.5183378	-3.9029197	-1.0108274	H	1.8867081	5.2388280	1.7303143
H	2.6915918	-2.0363340	-2.5762356	H	2.4091505	-3.8884740	-0.6157004
H	4.3287379	0.3032532	-0.6677898	H	2.6646290	-1.9866756	-2.0744396
H	5.0189655	-1.8914200	0.3185415	H	4.3420496	0.3427043	-0.9433503
H	-0.3676184	4.7693528	2.8677487	H	5.0390156	-1.7812292	0.0376862
H	-0.5071779	4.2154030	-1.9996303	H	-0.2987012	5.3302352	0.5275449
H	-0.6986191	0.5178058	-3.2537324	H	-0.5302776	4.4879891	-1.8034430
H	-0.7556393	5.0368147	0.4050558	H	-0.6615278	0.4903000	-2.9997274
H	-0.9129344	0.5532148	0.3086210	H	-0.7732690	3.8139058	1.2448187
H	-1.0518920	2.6099189	-1.4668510	H	-1.1201294	2.9641165	-1.1535674
H	-1.1116176	-4.5502425	1.1956116	H	-1.2769575	0.4332092	0.4836541
H	-1.2571930	3.4350198	0.9351345	H	-1.4075904	-4.8763602	0.9697144
H	-1.5805451	1.2597373	2.5879289	H	-2.2072110	0.9591958	2.6724867
H	-2.1608540	-2.6305899	0.0792286	H	-2.3962468	-2.9607541	-0.1629229
H	-2.9642174	-0.8524349	-3.6175413	H	-2.8297989	-0.7938809	-3.6812417
H	-3.9098802	0.8785228	3.3744727	H	-4.2626462	-0.2676386	-2.6661190
H	-4.2911650	-0.1832702	-2.5069679	H	-4.5336053	0.3607127	3.2137440
H	-4.8736172	-0.9308688	-0.4042212	H	-4.9937338	-1.3207234	-0.6655093
H	-5.5544449	-0.2116652	1.8618528	H	-5.9231811	-0.7780927	1.5306568