Supporting Information

Active Role of Proton in Excited State Intramolecular Proton Transfer Reaction

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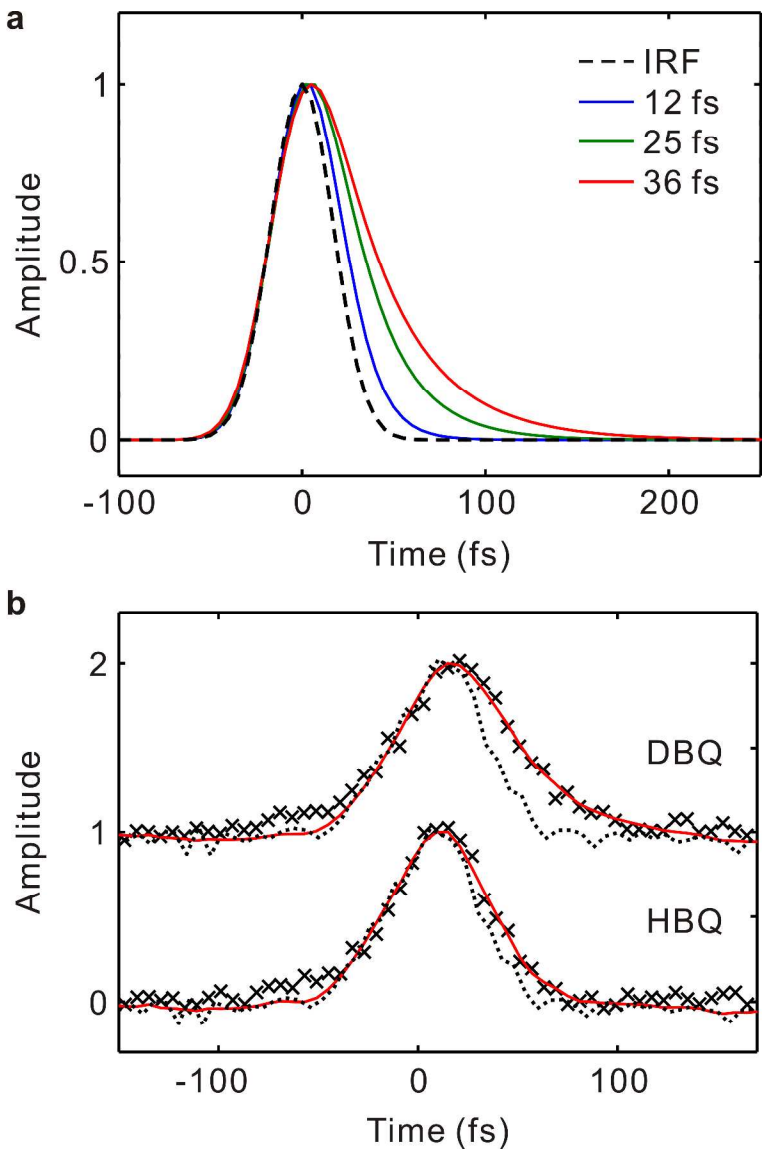

Figure S1. (a) Convolutions of a Gaussian function (FWHM 40 fs) with a single exponential function having time constant 12, 25, and 36 fs (b) Expanded view of the TRF signals of HBQ and DBQ. Crosses are the experimental TRF signals, and the dotted line is the cross-correlation between the solvent Raman scattering and the gate pulses. Red lines represent the nonlinear least-square fits of the TRFs to the convolution of the cross-correlation and an exponential function.

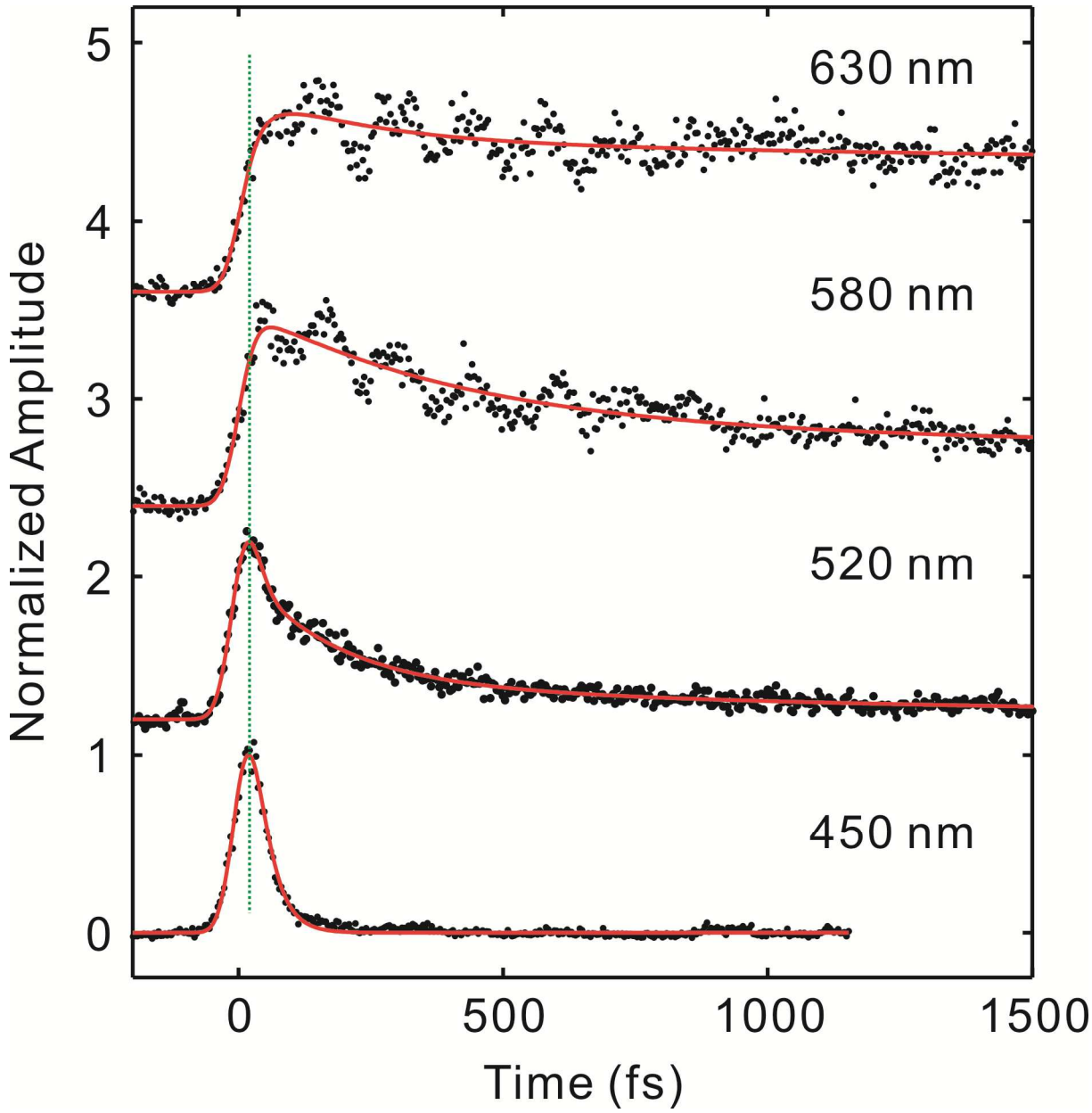

Figure S2. TRF signals of DBQ measured at 450, 520, 580, and 630 nm. Red lines represent exponential fits. At 450 nm, the enol emission was detected exclusively. At 520 nm, where both enol and keto isomers emit, an ultrafast decay was observed, but no delayed rise was verified. At longer wavelengths (580 and 630 nm), a fast rise and oscillations due to the wave packet motion on the potential surface of the keto isomer are apparent.

^{1}H NMR of HBQ

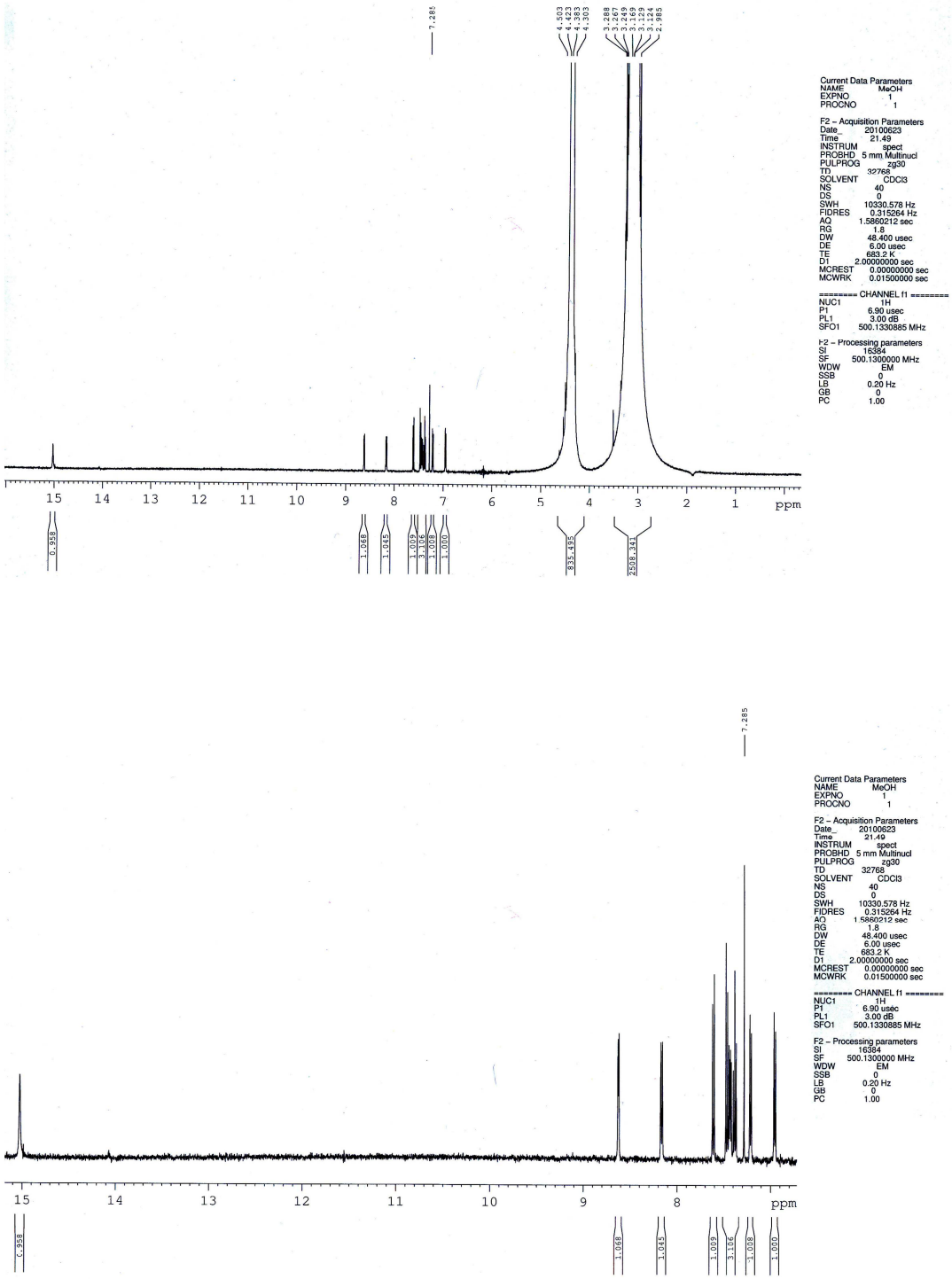

Figure S3. ^{1}H NMR (500 MHz, chloroform-*d*) of HBQ : δ 15.055 (1H, s).

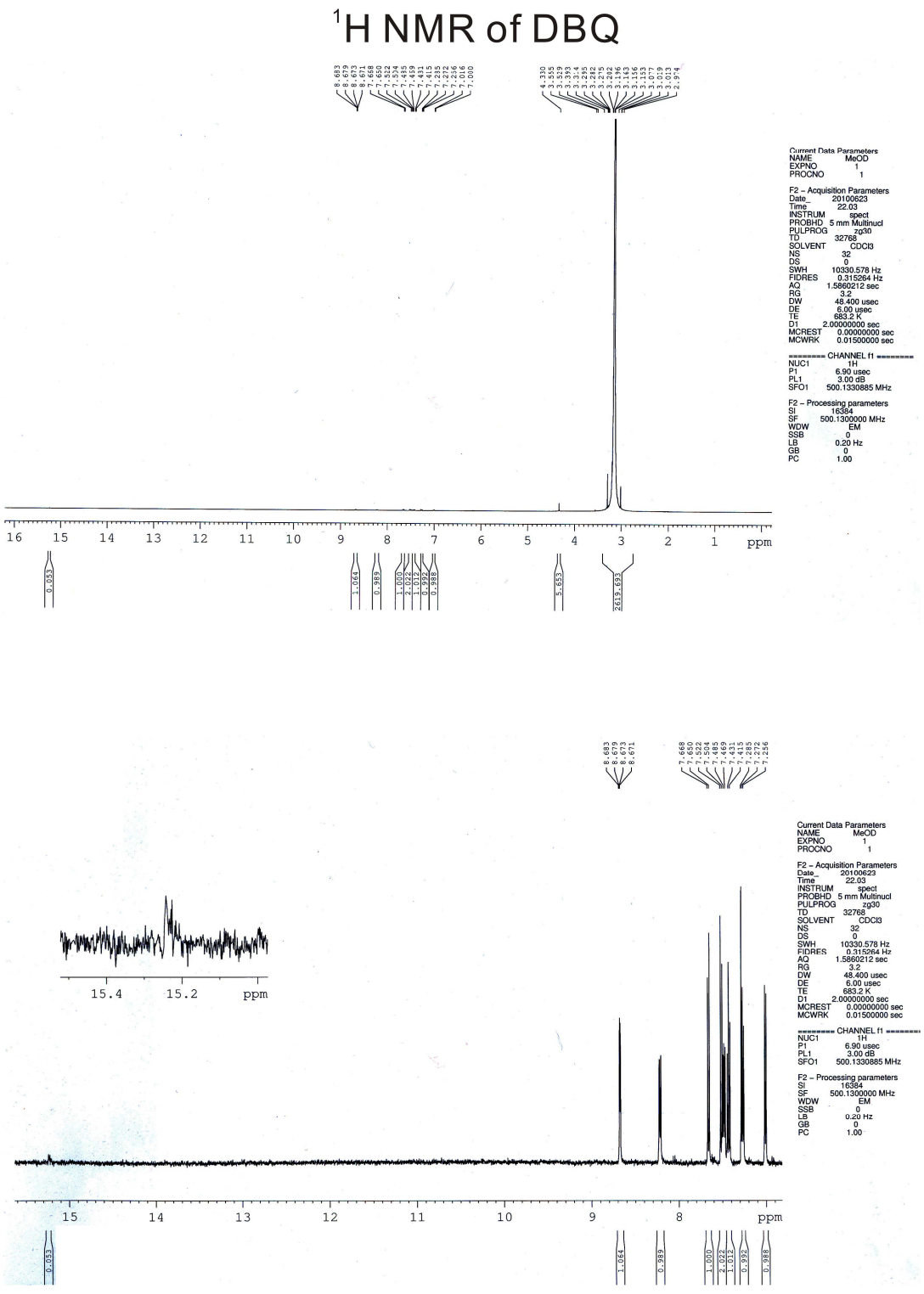

Figure S4. ^{1}H NMR (500 MHz, chloroform-*d*) of DBQ : δ 15.248 (1H, s).

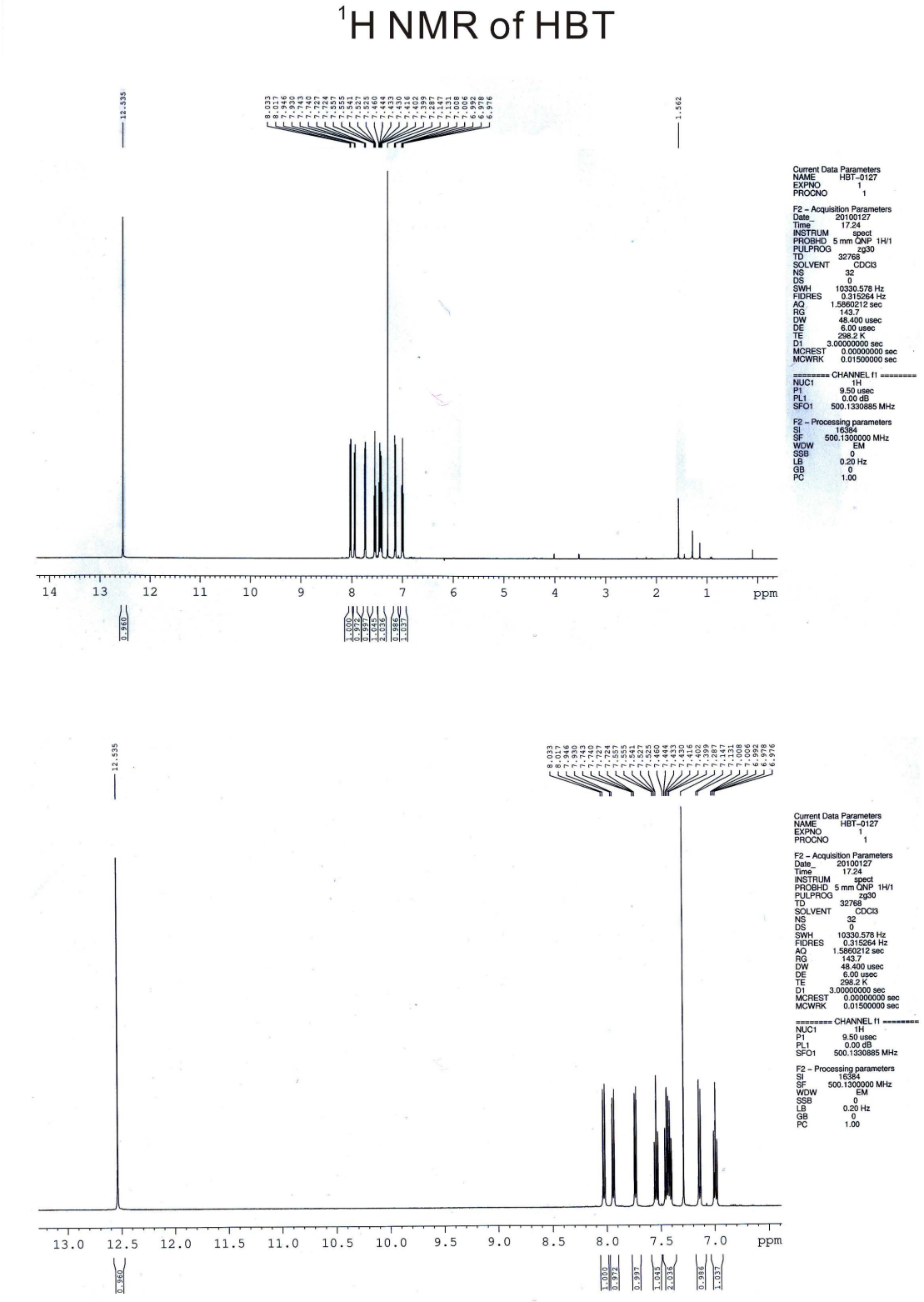

Figure S5. ^{1}H NMR (500 MHz, chloroform-*d*) of HBT : δ 12.535 (1H, s).

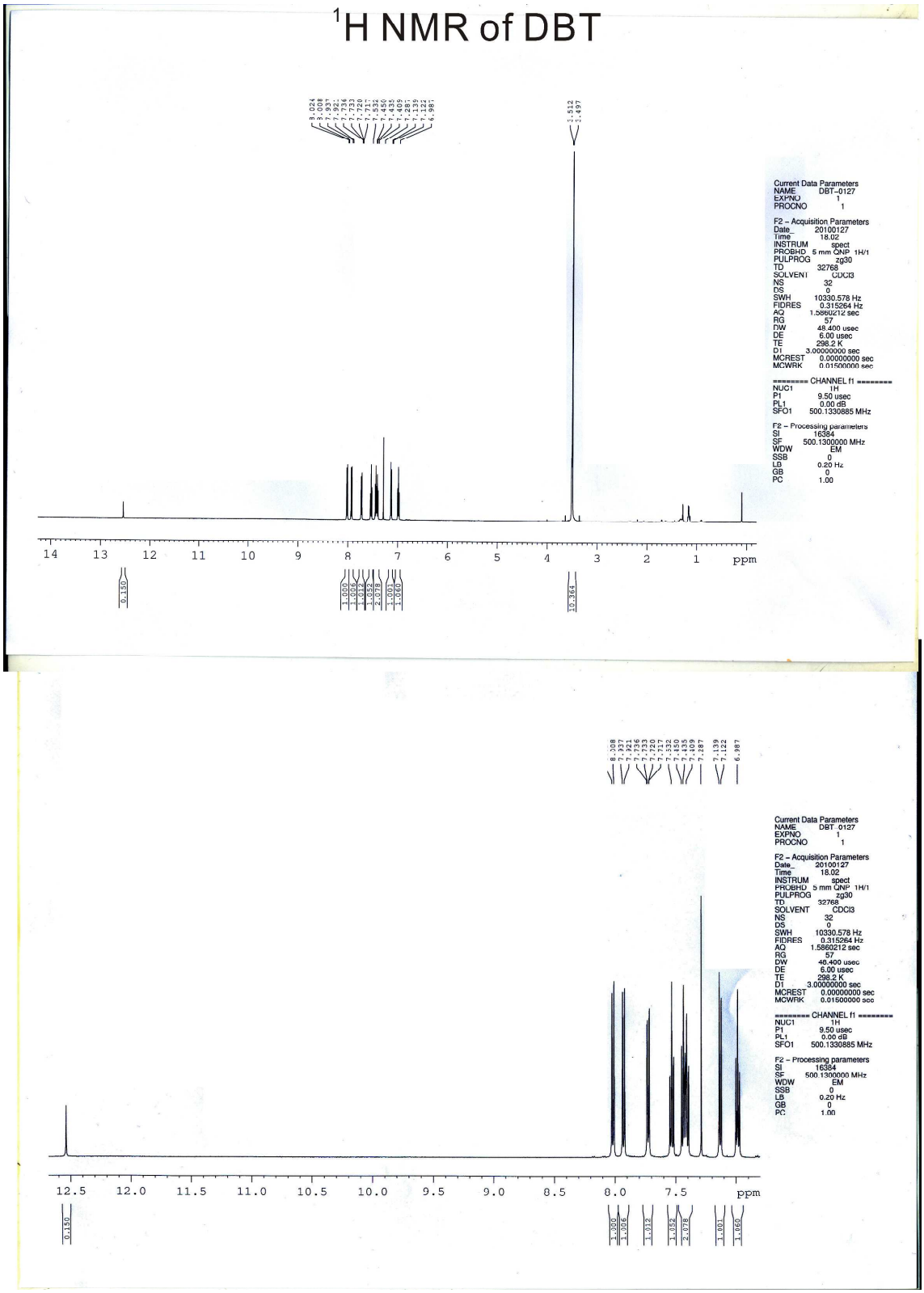

Figure S6. [1]H NMR (500 MHz, chloroform-*d*) of DBT : δ 12.578 (1H, s).

Table S1. Results of the nonlinear least-square fits with exponential functions for the TRF signals in Figure S2.

	λ (nm)	A_1	τ_1 (fs)	A_2	τ_2 (fs)	A_3	τ_3 (ps)
DBQ	450	1.0	25				
	520	0.82	8	0.14	176	0.04	1.5
	580	-1.0	41	0.65	428	0.35	16
	630	-1.0	34	0.27	237	0.73	20

Table S2. Optimized geometry of ground state enol form of HBQ : DFT 6-31+G(d,p).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-0.982832	-3.432168	0.000000
2	6	0.355879	-3.075607	0.000000
3	6	0.723842	-1.715764	0.000000
4	6	-0.320494	-0.743071	0.000000
5	6	-1.944283	-2.409423	0.000000
6	6	2.090727	-1.279387	0.000000
7	6	0.000000	0.668380	0.000000
8	6	1.373884	1.062832	0.000000
9	6	2.394355	0.048262	0.000000
10	6	1.715545	2.430787	0.000000
11	1	2.762939	2.717332	0.000000
12	6	0.716940	3.394989	0.000000
13	6	-0.634413	3.029664	0.000000
14	6	-1.005877	1.684824	0.000000
15	1	2.877171	-2.029354	0.000000
16	1	-1.292616	-4.471830	0.000000
17	1	1.132580	-3.836276	0.000000
18	1	-3.005871	-2.644884	0.000000
19	1	3.432174	0.370471	0.000000
20	1	0.981777	4.448538	0.000000
21	1	-1.420564	3.777330	0.000000
22	8	-2.320493	1.389393	0.000000
23	1	-2.400157	0.395046	0.000000
24	7	-1.629017	-1.118203	0.000000

Table S3. Optimized geometry of excited state keto form of HBQ : TDDFT 6-31+G(d,p).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-0.923785	-3.468034	0.000000
2	6	0.401380	-3.101223	0.000000
3	6	0.775643	-1.694612	0.000000
4	6	-0.271307	-0.737810	0.000000
5	6	-1.934907	-2.480291	0.000000
6	6	2.117332	-1.233050	0.000000
7	6	0.000000	0.687570	0.000000
8	6	1.357114	1.101254	0.000000
9	6	2.412699	0.111390	0.000000
10	6	1.648660	2.501049	0.000000
11	1	2.687923	2.813449	0.000000
12	6	0.629700	3.448520	0.000000
13	6	-0.713749	3.064148	0.000000
14	6	-1.076099	1.691101	0.000000
15	1	2.917412	-1.967827	0.000000
16	1	-1.214090	-4.512348	0.000000
17	1	1.186217	-3.850020	0.000000
18	1	-2.992732	-2.695803	0.000000
19	1	3.441059	0.454491	0.000000
20	1	0.883753	4.504261	0.000000
21	1	-1.519550	3.787901	0.000000
22	8	-2.337298	1.332530	0.000000
23	1	-2.254618	-0.379142	0.000000
24	7	-1.567582	-1.165040	0.000000

Table S4. Optimized geometry of ground state enol form of HBT : DFT 6-31+G(d,p).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.842224	-1.313443	0.000000
2	6	-0.512128	-1.842435	0.000000
3	6	-0.338498	-3.258488	0.000000
4	6	-1.441731	-4.058998	0.000000
5	6	-2.750072	-3.514656	0.000000
6	6	-2.949136	-2.145466	0.000000
7	1	0.656566	-3.663234	0.000000
8	1	-1.324524	-5.127789	0.000000
9	1	-3.597383	-4.175970	0.000000
10	1	-3.944083	-1.738768	0.000000
11	6	1.087354	3.879788	0.000000
12	6	2.487509	3.736370	0.000000
13	6	3.062410	2.476177	0.000000
14	6	2.275106	1.337909	0.000000
15	6	0.277824	2.777657	0.000000
16	1	0.652417	4.862604	0.000000
17	1	3.115587	4.608802	0.000000
18	1	4.128855	2.347589	0.000000
19	1	-0.788862	2.904109	0.000000
20	6	0.000000	0.320777	0.000000
21	6	0.819939	1.453174	0.000000
22	8	2.880282	0.166848	0.000000
23	1	2.242763	-0.550473	0.000000
24	7	0.460521	-0.949670	0.000000
25	16	-1.779084	0.422239	0.000000

Table S5. Optimized geometry of excited state keto form of HBT : CIS 6-31+G(d,p).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.834630	-1.342295	0.000000
2	6	-0.551075	-1.889465	0.000000
3	6	-0.371951	-3.272478	0.000000
4	6	-1.496327	-4.074937	0.000000
5	6	-2.780270	-3.527527	0.000000
6	6	-2.956065	-2.152159	0.000000
7	1	0.615933	-3.696264	0.000000
8	1	-1.377959	-5.143596	0.000000
9	1	-3.638098	-4.174700	0.000000
10	1	-3.942783	-1.725534	0.000000
11	6	1.169143	3.914055	0.000000
12	6	2.555907	3.773947	0.000000
13	6	3.121858	2.509640	0.000000
14	6	2.324106	1.322202	0.000000
15	6	0.327577	2.786452	0.000000
16	1	0.723545	4.892008	0.000000
17	1	3.183379	4.646450	0.000000
18	1	4.187125	2.368572	0.000000
19	1	-0.735422	2.949653	0.000000
20	6	0.000000	0.353825	0.000000
21	6	0.835561	1.491427	0.000000
22	8	2.816226	0.192882	0.000000
23	1	1.408963	-1.094733	0.000000
24	7	0.422212	-0.932488	0.000000
25	16	-1.748311	0.412899	0.000000