Electronic Supplementary Material (ESI) for RSC Advances.

Symmetric Dicyanobenzothiadiazole (DCBT) Dyes with 1.5 V Excited State Reduction Potential Range

Qing Yun Li,[1] Ethan C. Lambert,[1] Ravinder Kaur,[1] Nathan I. Hammer,[1] and Jared H. Delcamp[*,1,2]

1. Department of Chemistry and Biochemistry, 322 Coulter Hall University of Mississippi, University, MS 38677, USA

2. Materials and Manufacturing Directorate, Air Force Research Laboratory, 2230 Tenth Street Wright-Patterson AFB, OH 45433, USA

Corresponding author email: delcamp@olemiss.edu

Table of Contents:

1. Computational Data

(XYZ coordinates, frequency information, and total energies are found at the end of this document.)

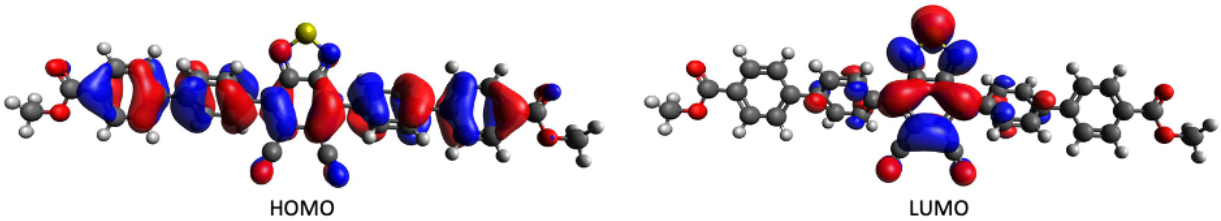

Figure S1: HOMO and LUMO orbitals of (Ar-Ar-Ester)$_2$DCBT.

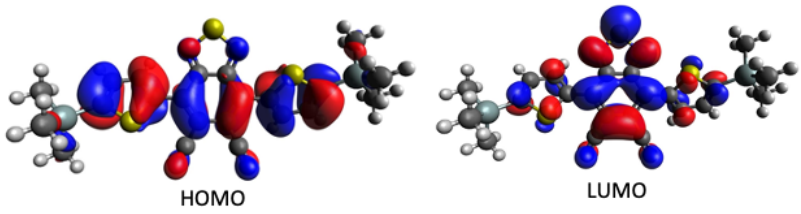

Figure S2: HOMO and LUMO orbitals of (TMS-thio)$_2$DCBT.

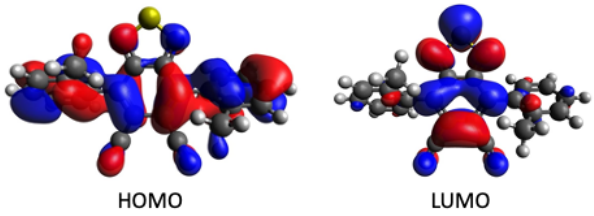

Figure S3: HOMO and LUMO orbitals of (tolyl)$_2$DCBT.

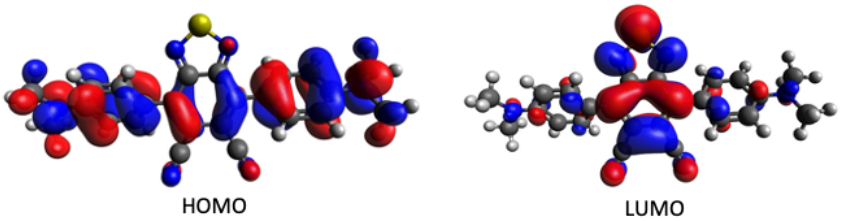

Figure S4: HOMO and LUMO orbitals of (DMA)$_2$DCBT.

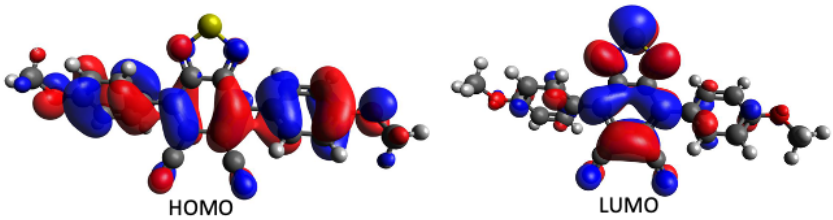

Figure S5: HOMO and LUMO orbitals of (*p*-OHx)$_2$DCBT.

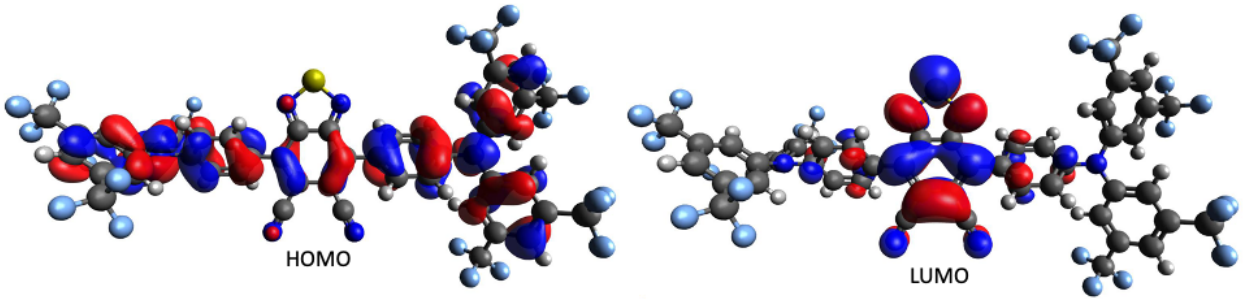

Figure S6: HOMO and LUMO orbitals of (TAA-(*m*-CF_3)$_4$)$_2$DCBT.

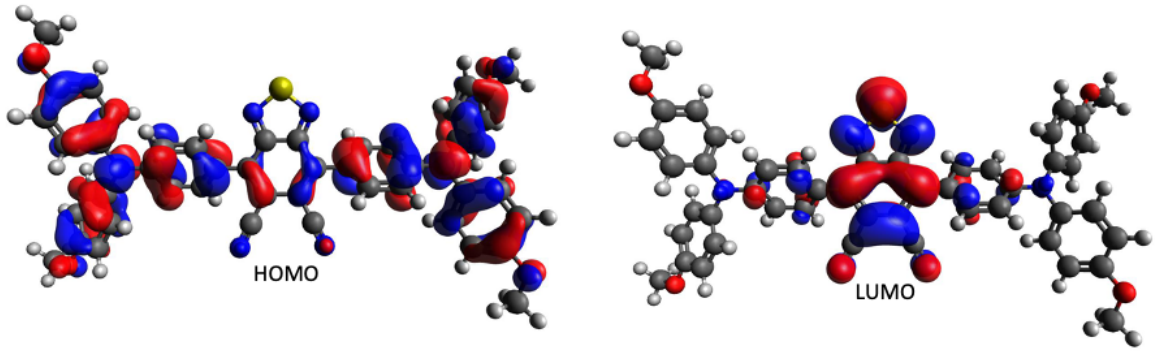

Figure S7: HOMO and LUMO orbitals of (TAA-(OHx))$_2$DCBT.

Table S1: Summary of dipole and dihedral angles at the two aryl-DCBT bonds for the DCBT dyes obtained after DFT geometry optimizations at the M06-2X/6-311G(d,p) level of theory.

Dye[a]	HOMO (eV)	LUMO (eV)	Orbitals[b]	% Cont.	Vert. Trans. (nm | eV)	Oscillator Strength	Dipole (D)	Dihedral (°)[c]
p-CN	-8.65	-3.23	H→L	96%	347 | 3.57	0.4667	6.1517	48.45
TMS-thio	-7.41	-2.68	H→L	98%	421 | 2.95	0.5452	6.3589	36.01
TAA-(OHx)	-6.13	-2.29	H→L H-2→L	91% 6%	495 | 2.51	0.7089	6.7772	45.33
Ar-Ar-Ester	-7.79	-2.75	H→L H-2→L H-4→L	90% 2% 4%	374 | 3.32	0.7356	3.0056	47.44
tolyl	-8.15	-2.60	H→L	97%	343 | 3.61	0.2192	6.2439	61.09
DMA	-6.50	-2.18	H→L	96%	456 | 2.72	0.5018	6.1511	44.29
TAA-(*m*-CF_3)$_4$	-7.58	-3.04	H→L H-2→L	87% 8%	406 | 3.05	0.7081	5.7463	47.36
p-OHx	-7.38	-2.47	H→L	97%	394 | 3.15	0.3991	6.6767	46.22

[a]Dyes are coded by their aryl substituents. [b]All transitions are S_0→S_1. HOMO is denoted by H and LUMO is denoted by L. [c]Dihedral is the average of both aryl-DCBT bonds.

2. Steady-state Optical Spectroscopy and Electrochemical Data

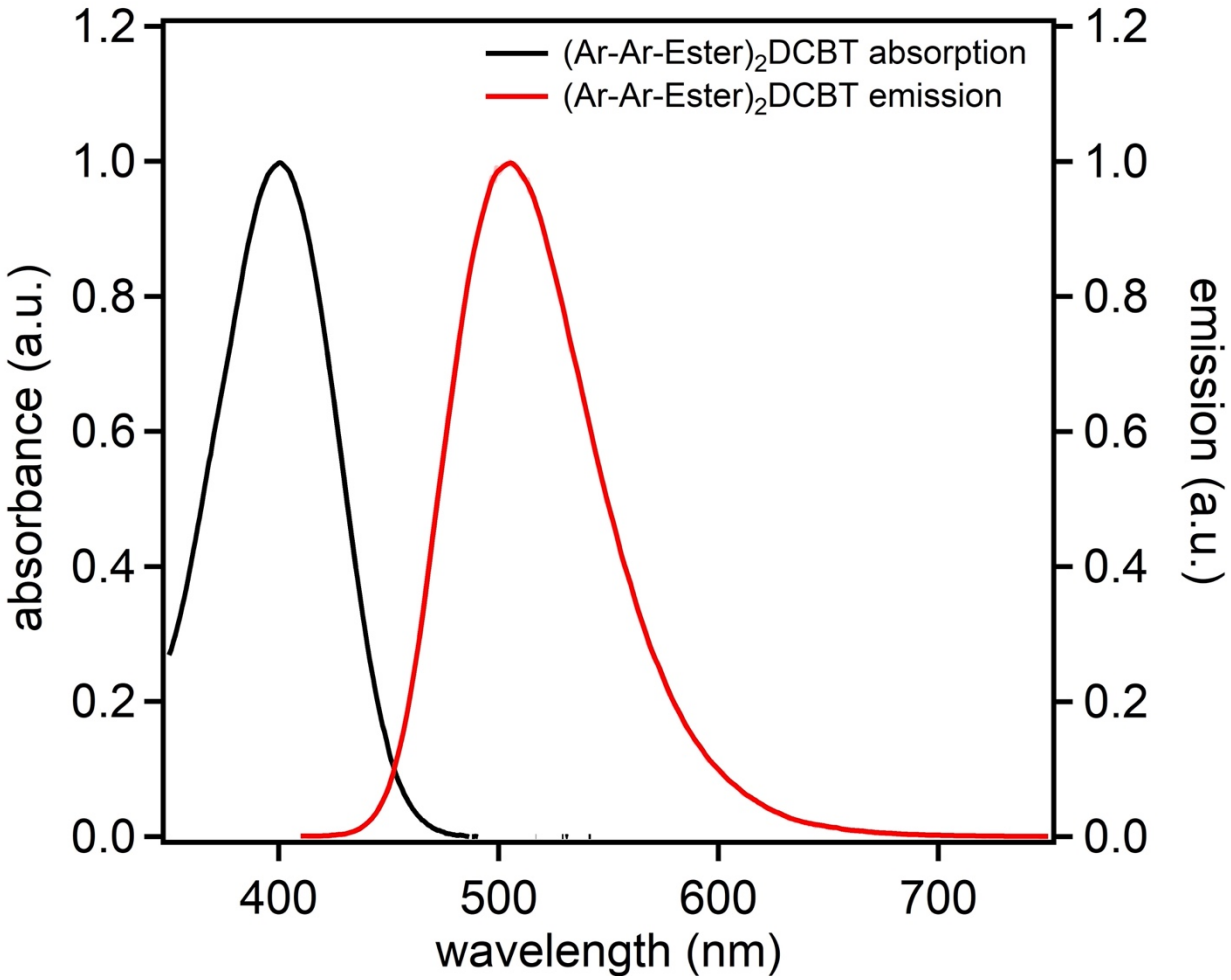

Figure S8: Normalized absorption and emission curve plot of (Ar-Ar-Ester)$_2$DCBT in dichloromethane.

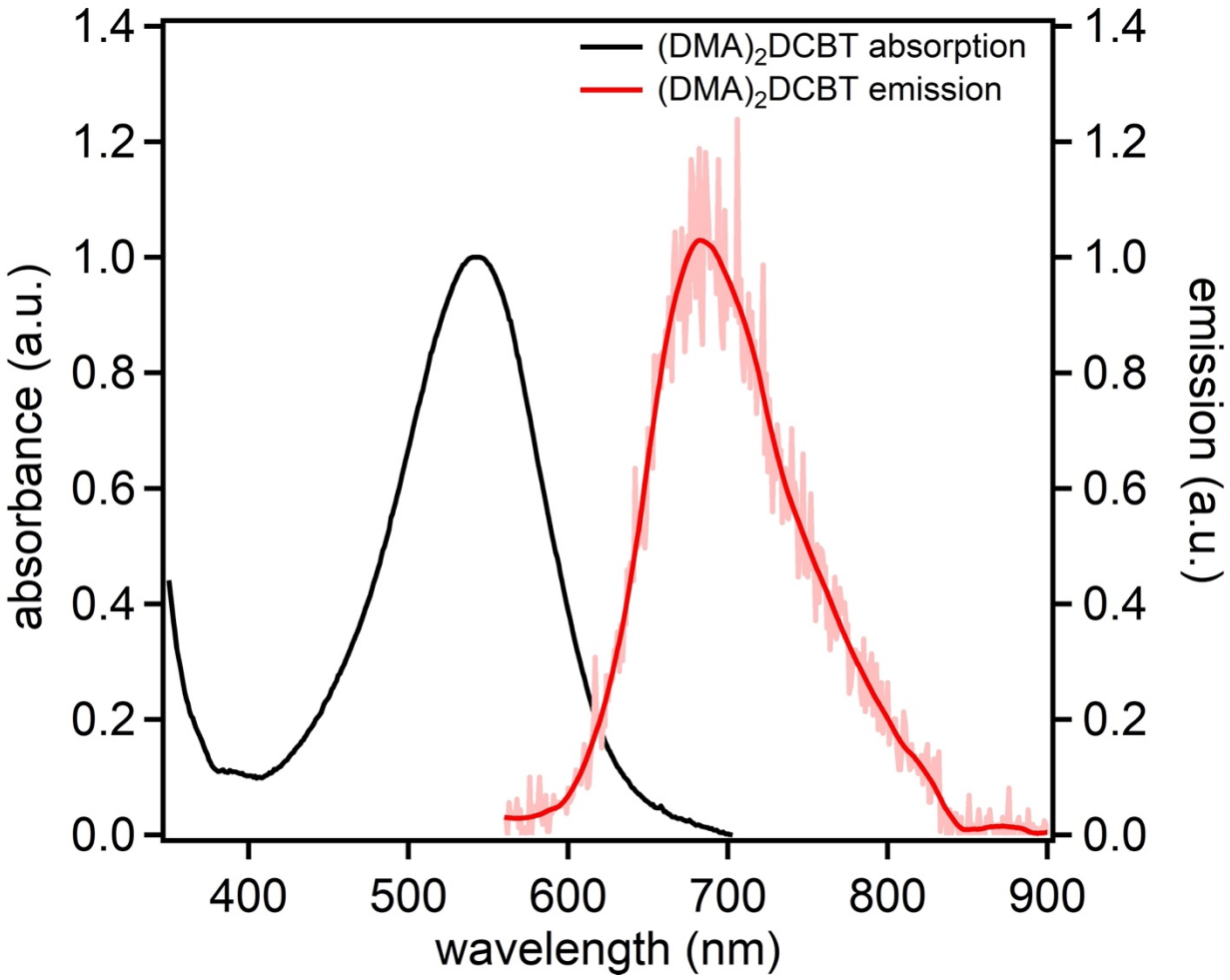

Figure S9: Normalized absorption and emission curve plot of $(DMA)_2DCBT$ in dichloromethane. Raw data is plotted in pink, and a fitted trace is shown in red.

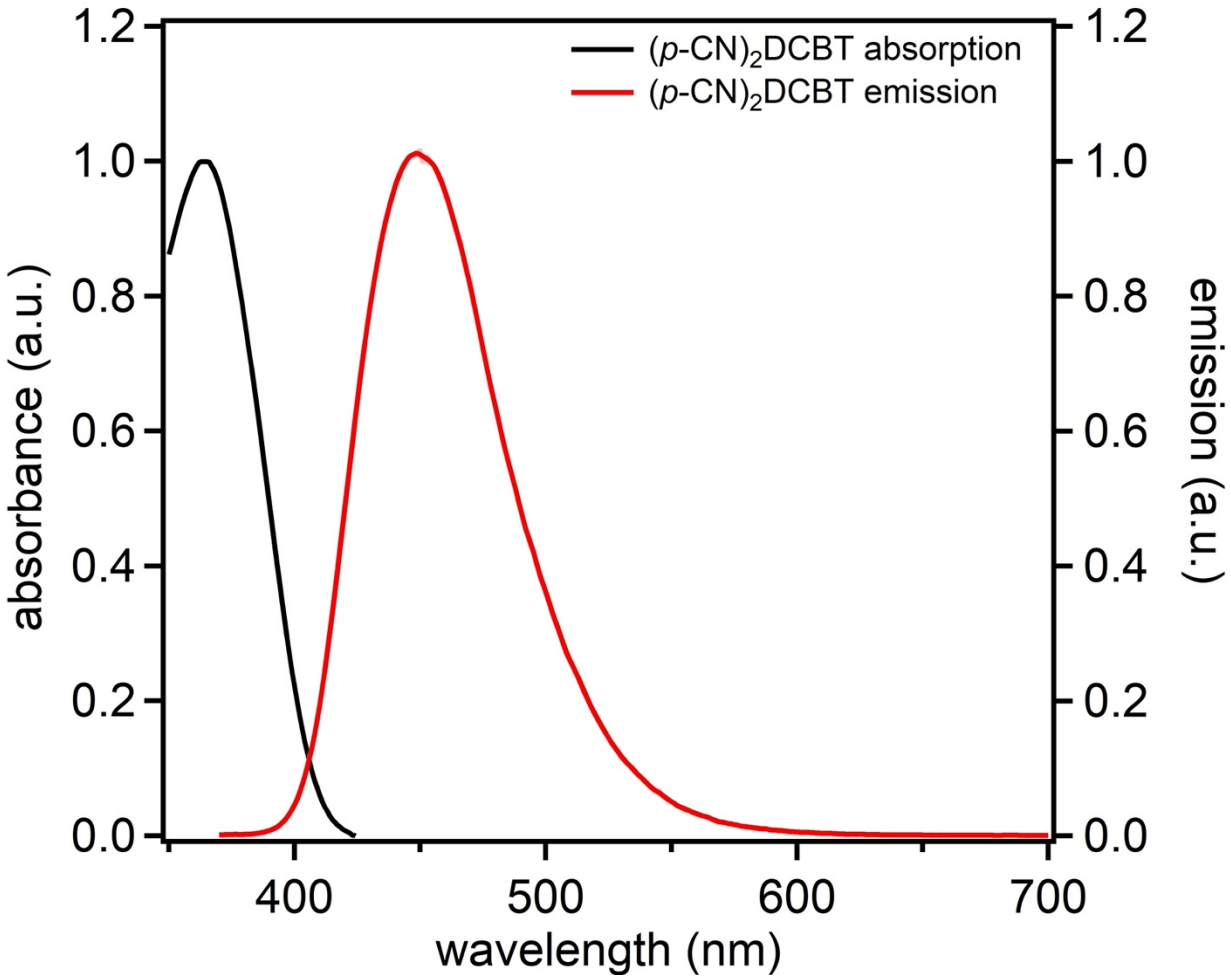

Figure S10: Normalized absorption and emission curve plot of (p-CN)$_2$DCBT in dichloromethane.

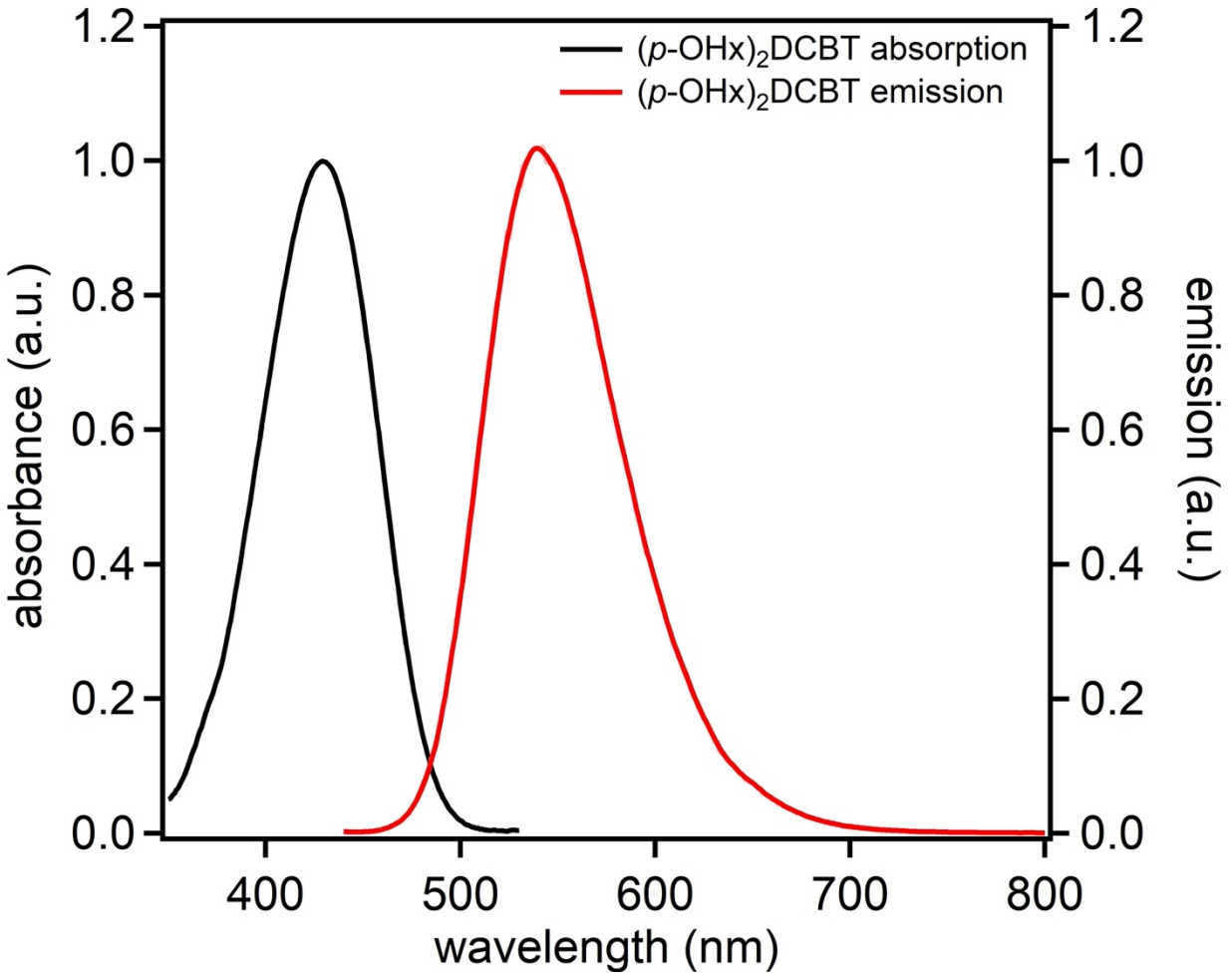

Figure S11: Normalized absorption and emission curve plot of (p-OHx)$_2$DCBT in dichloromethane.

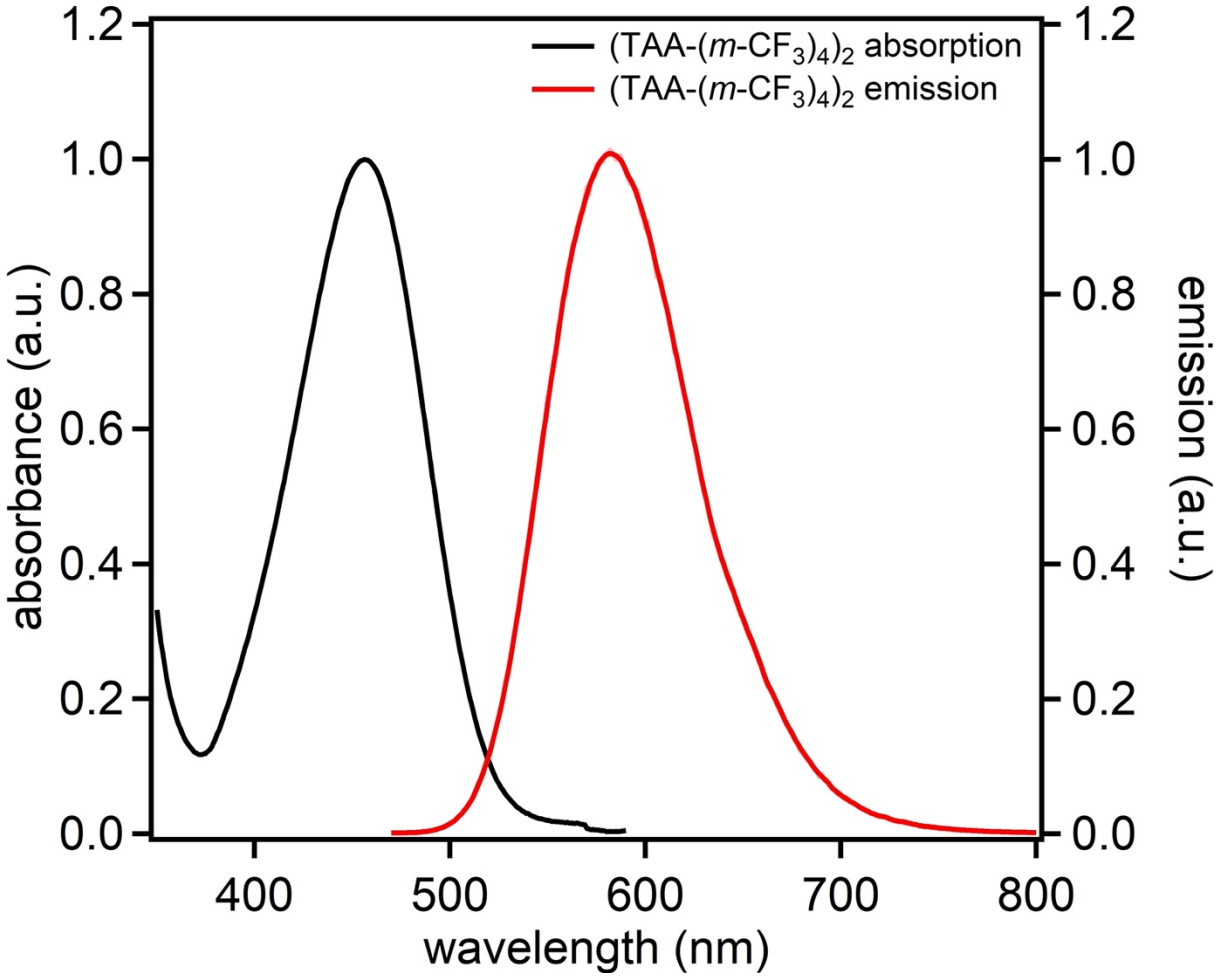

Figure S12: Normalized absorption and emission curve plot of (TAA-(m-CF_3)$_4$)$_2$DCBT in dichloromethane.

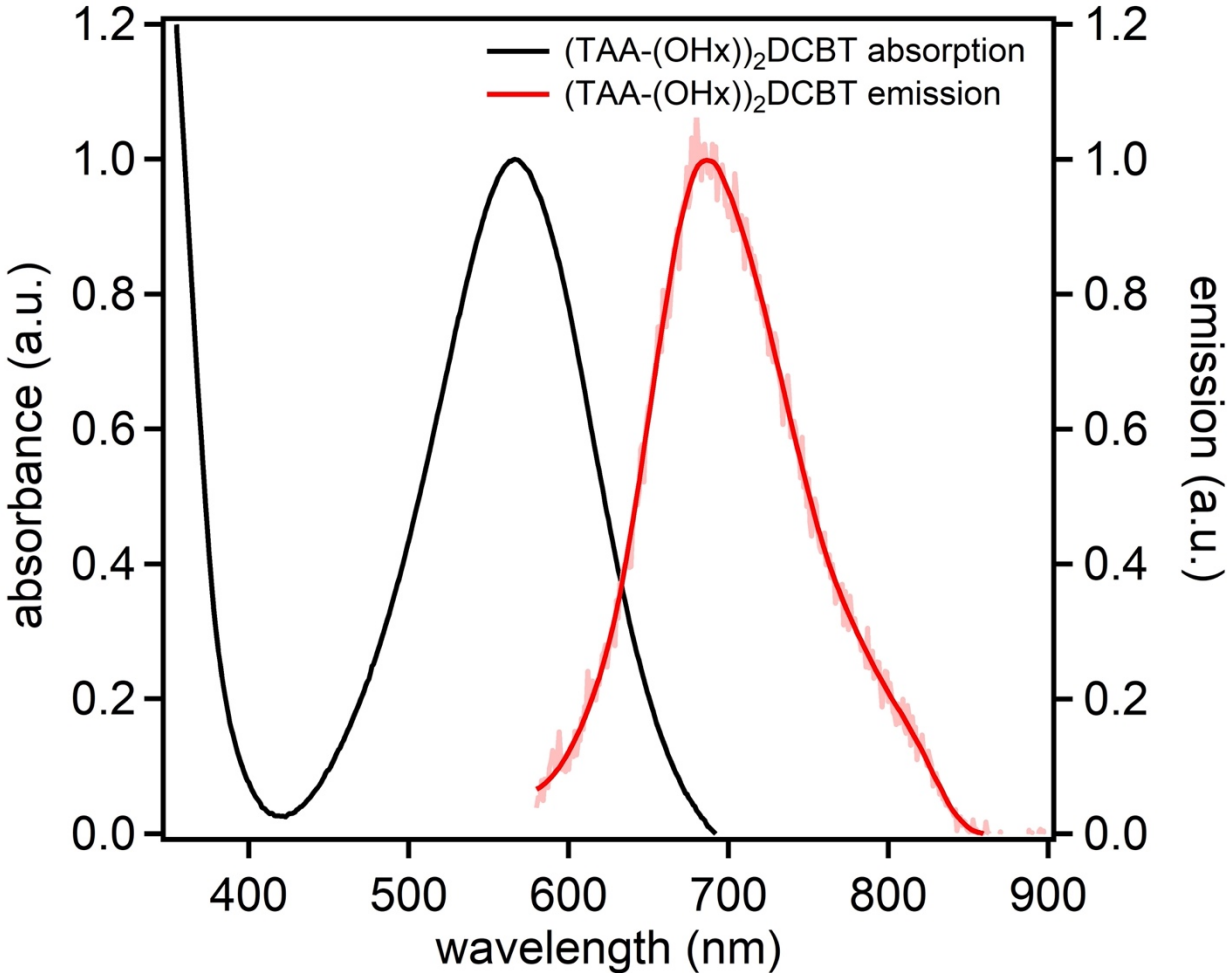

Figure S13: Normalized absorption and emission curve plot of $(TAA\text{-}(OHx))_2DCBT$ in dichloromethane. Raw data is plotted in pink, and a fitted trace is shown in red.

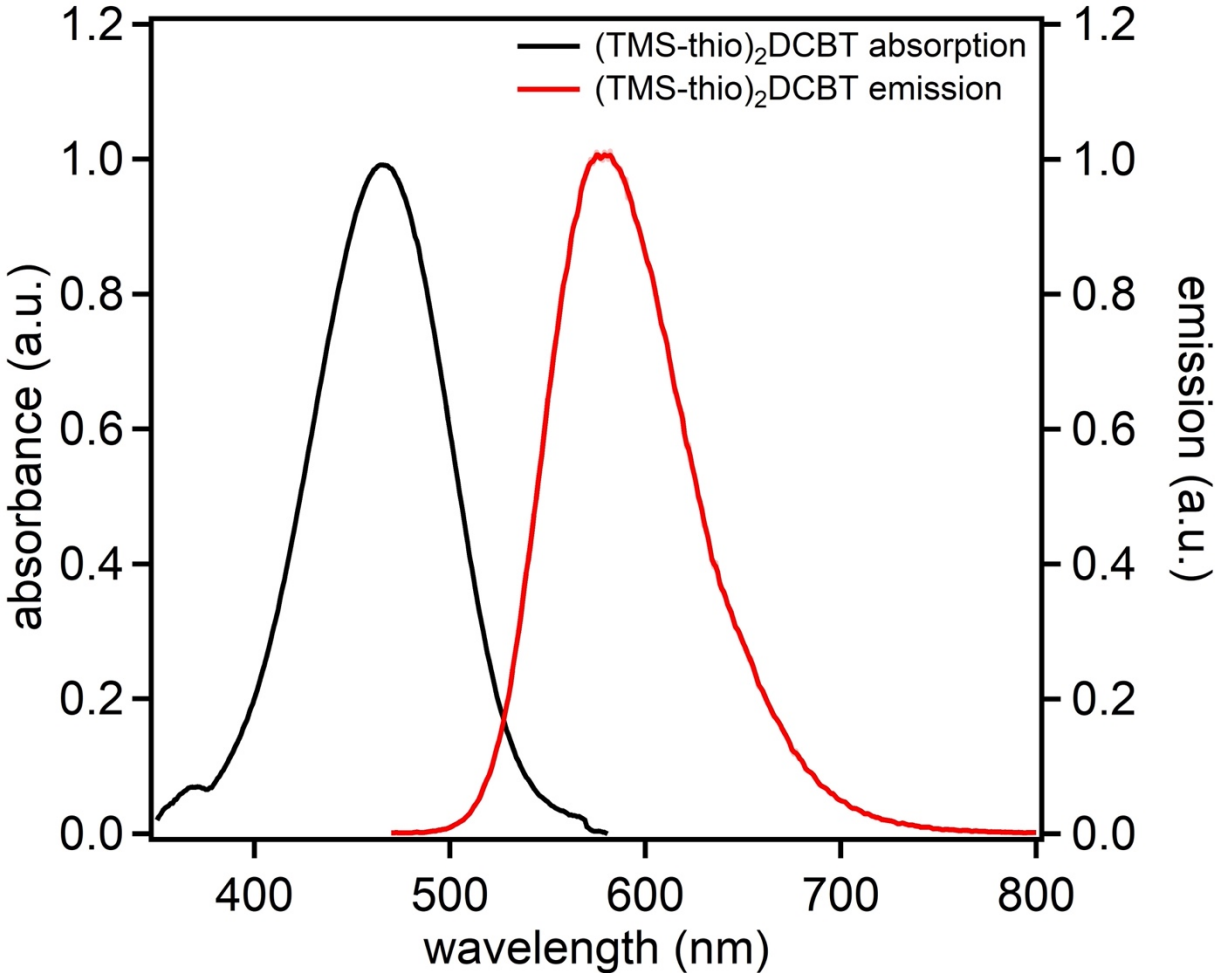

Figure S14: Normalized absorption and emission curve plot of (TMS-thio)$_2$DCBT in dichloromethane.

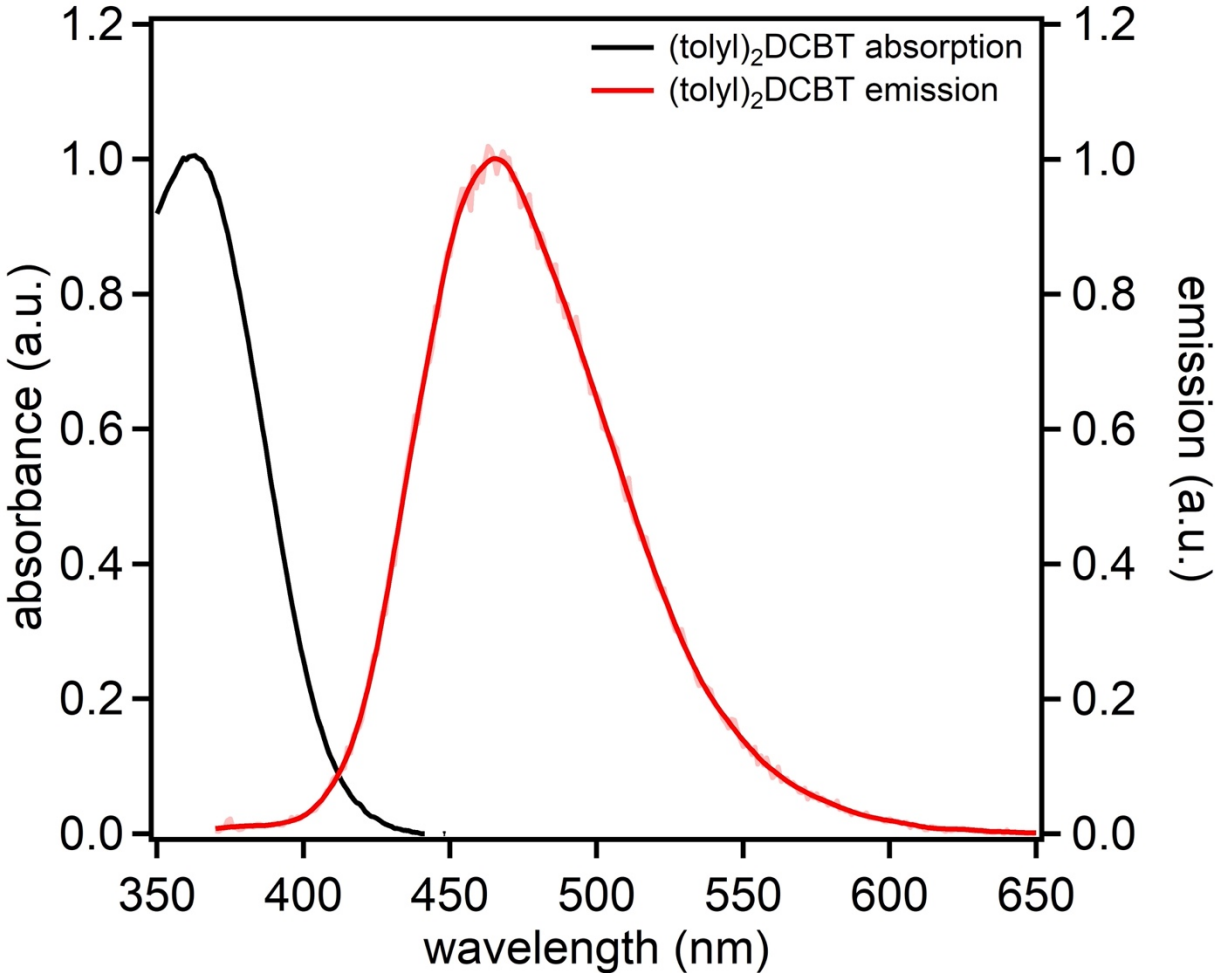

Figure S15: Normalized absorption and emission curve plot of $(tolyl)_2$DCBT in dichloromethane. Raw data is plotted in pink, and a fitted trace is shown in red.

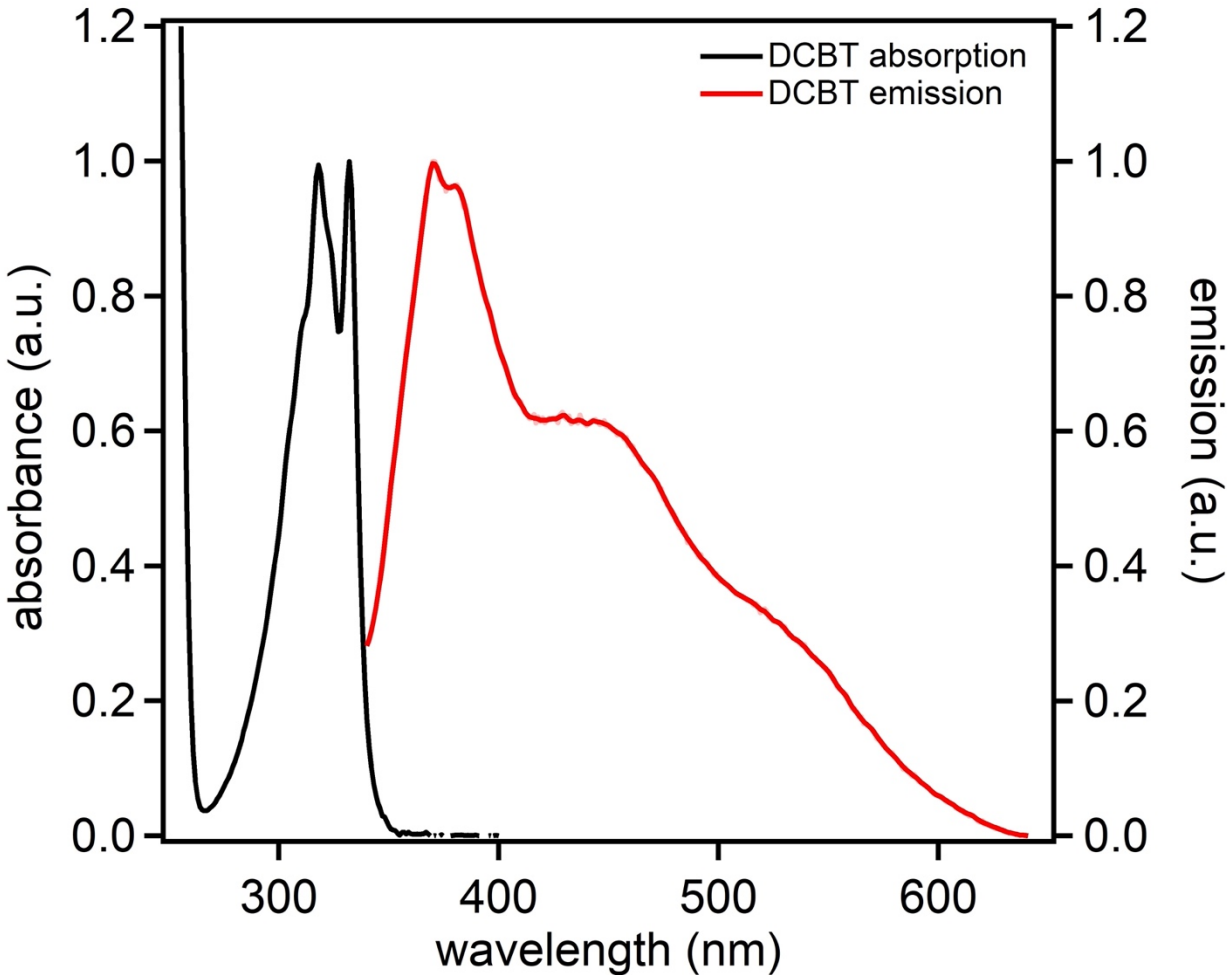

Figure S16: Normalized absorption and emission curve plot of DCBT core in dichloromethane.

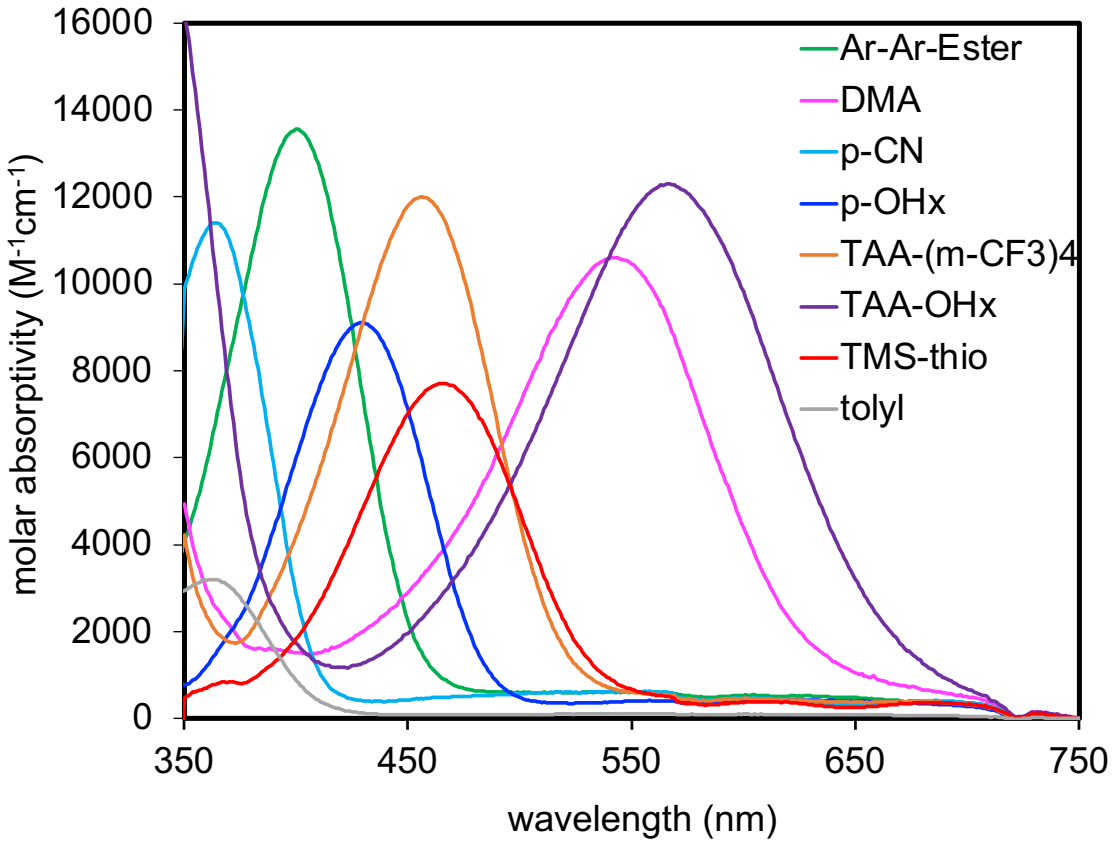

Figure S17: Absorption spectra of DCBT dyes in DCM plotted as molar absorptivity coefficients.

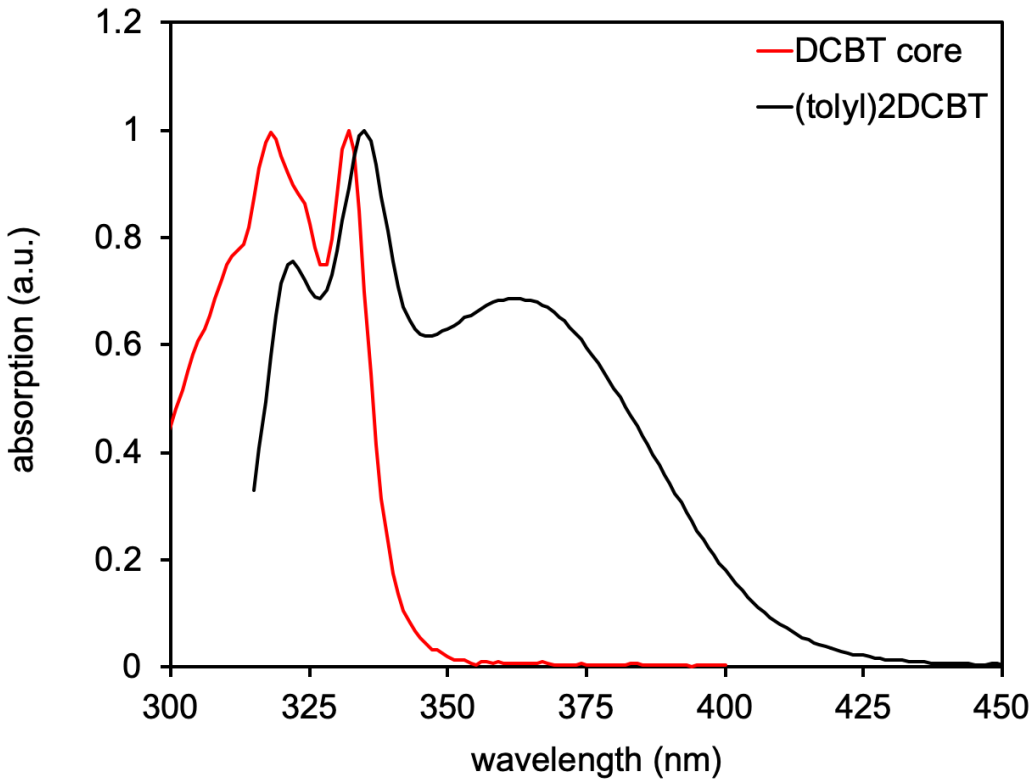

Figure S18: Normalized absorption spectra of DCBT core and $(tolyl)_2$DCBT in dichloromethane.

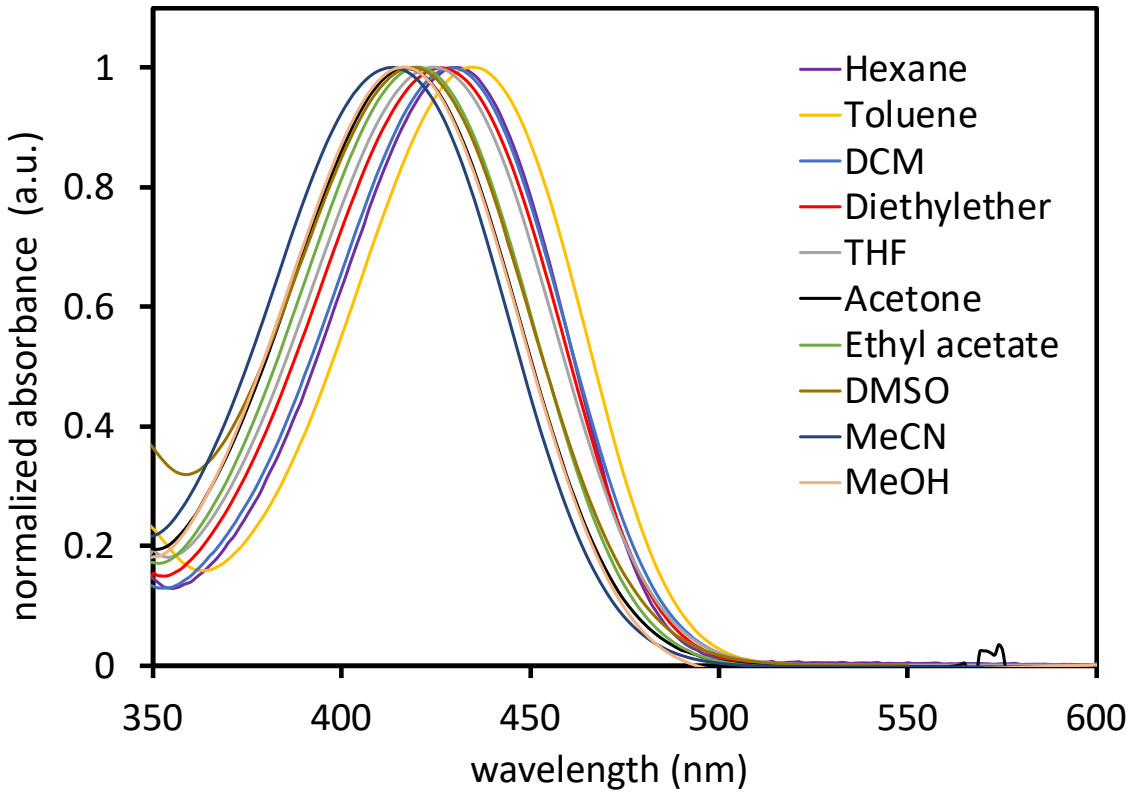

Figure S19: Normalized absorption spectra of (*p*-OHx)$_2$DCBT in solvents of varying polarity.

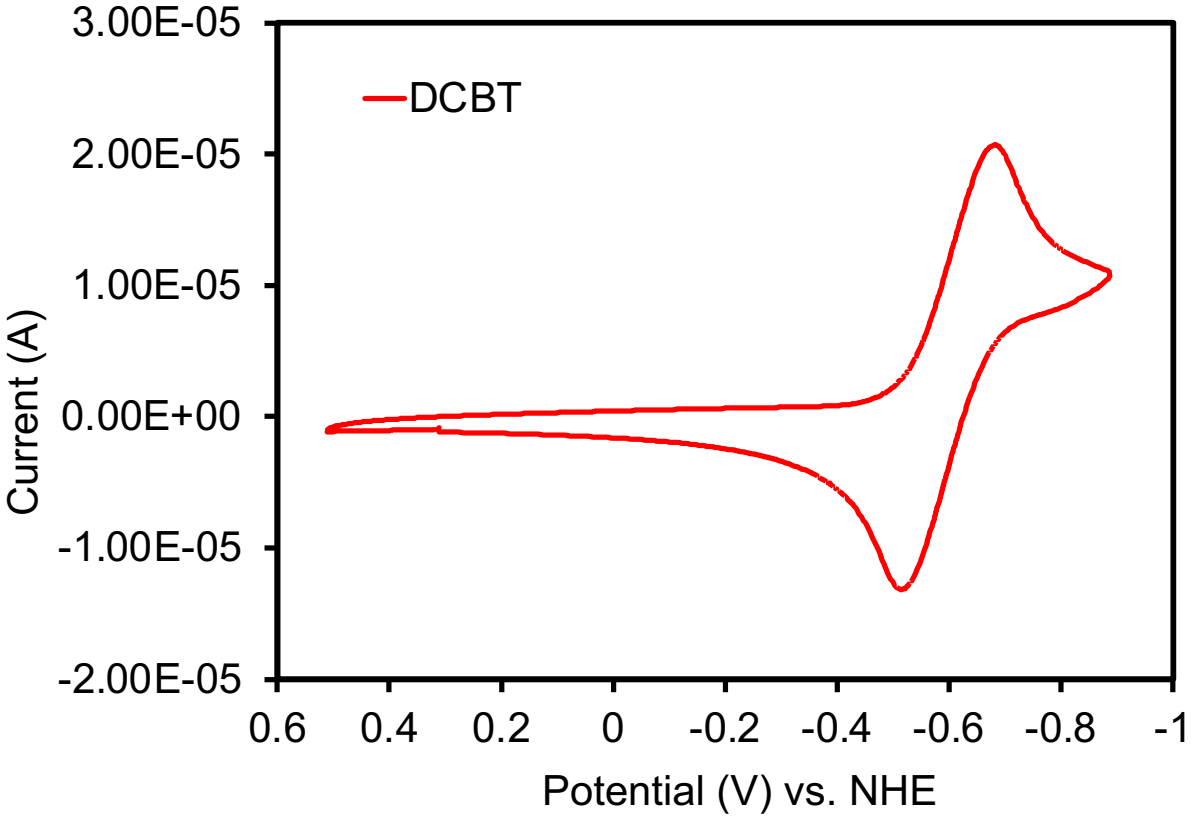

Figure S20. Cyclic voltammogram collected for DCBT core in dichloromethane solution with 0.1 M Bu_4NPF_6 as electrolyte, platinum counter electrode, Ag wire reference electrode and a glassy carbon working electrode. Ferrocenium/Ferrocene was used as a reference standard, taken as 0.70 V versus NHE in DCM and oxidation potentials are reported versus normal hydrogen electrode (NHE).

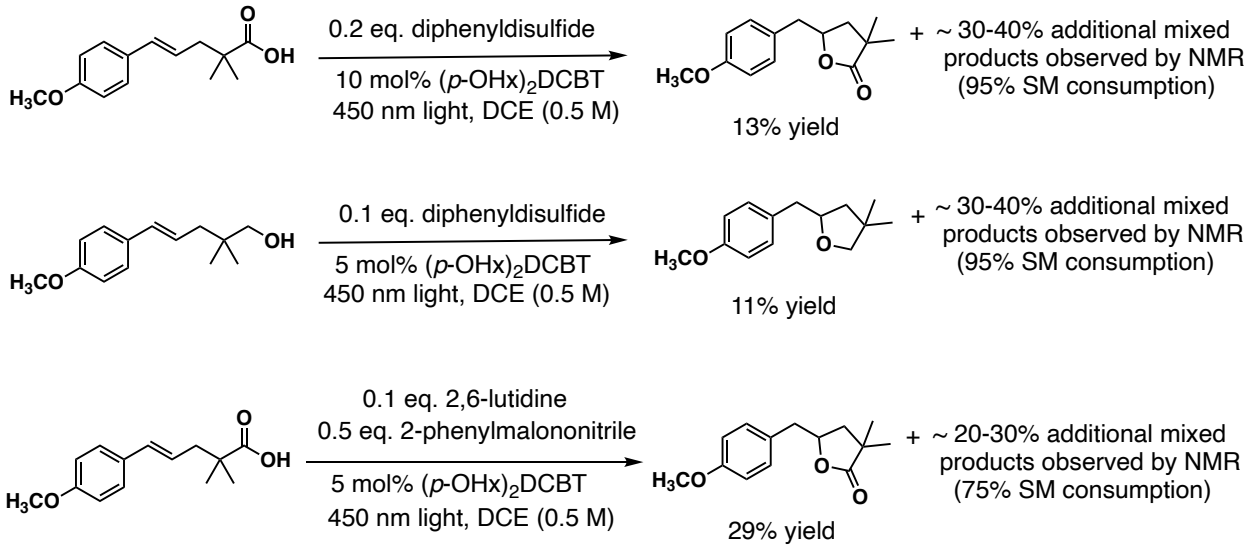

Figure S21. Example photochemical transformations driven by (p-OHx)$_2$DCBT.

3. NMR Spectra

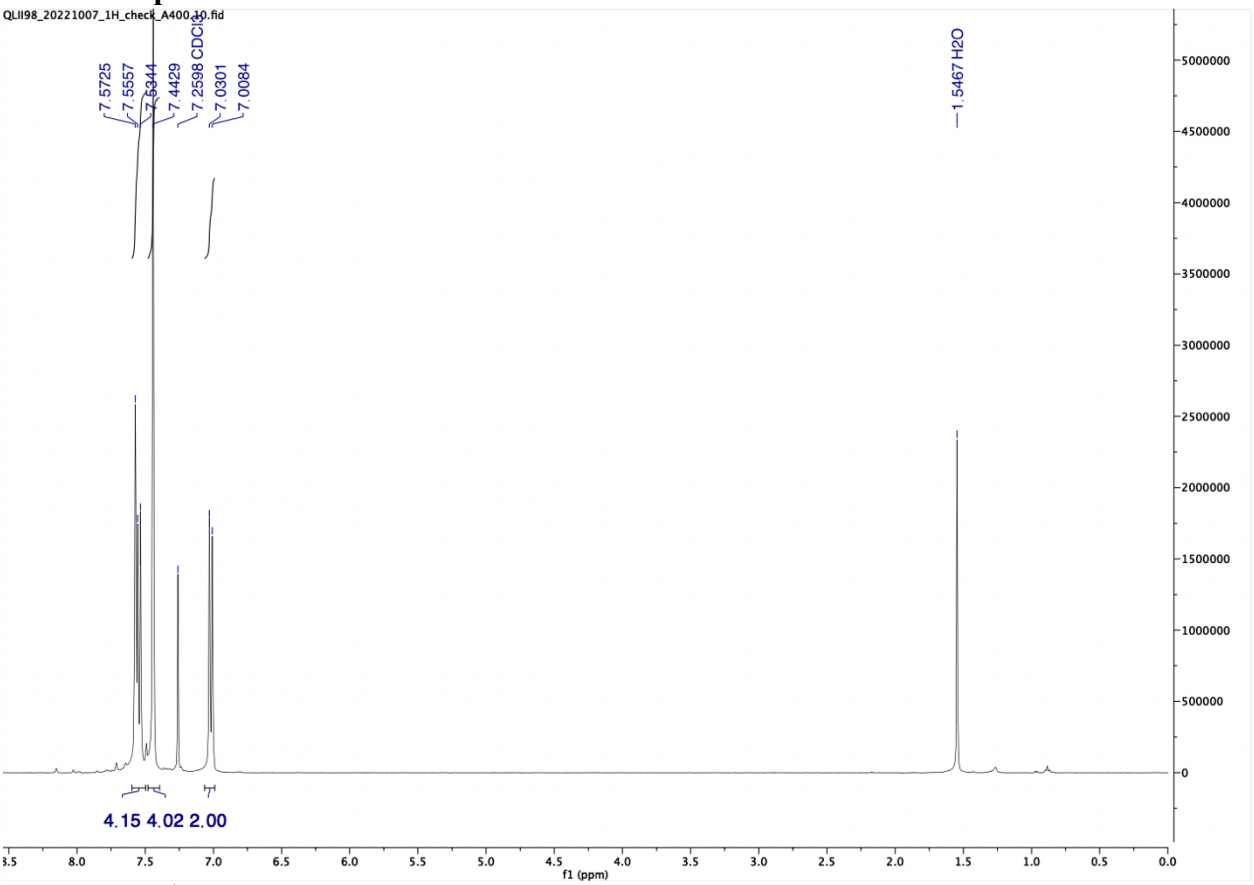

Figure S22: ^{1}H NMR of (TAA-(*m*-CF_3)$_4$)-Br in $CDCl_3$ at 400 MHz.

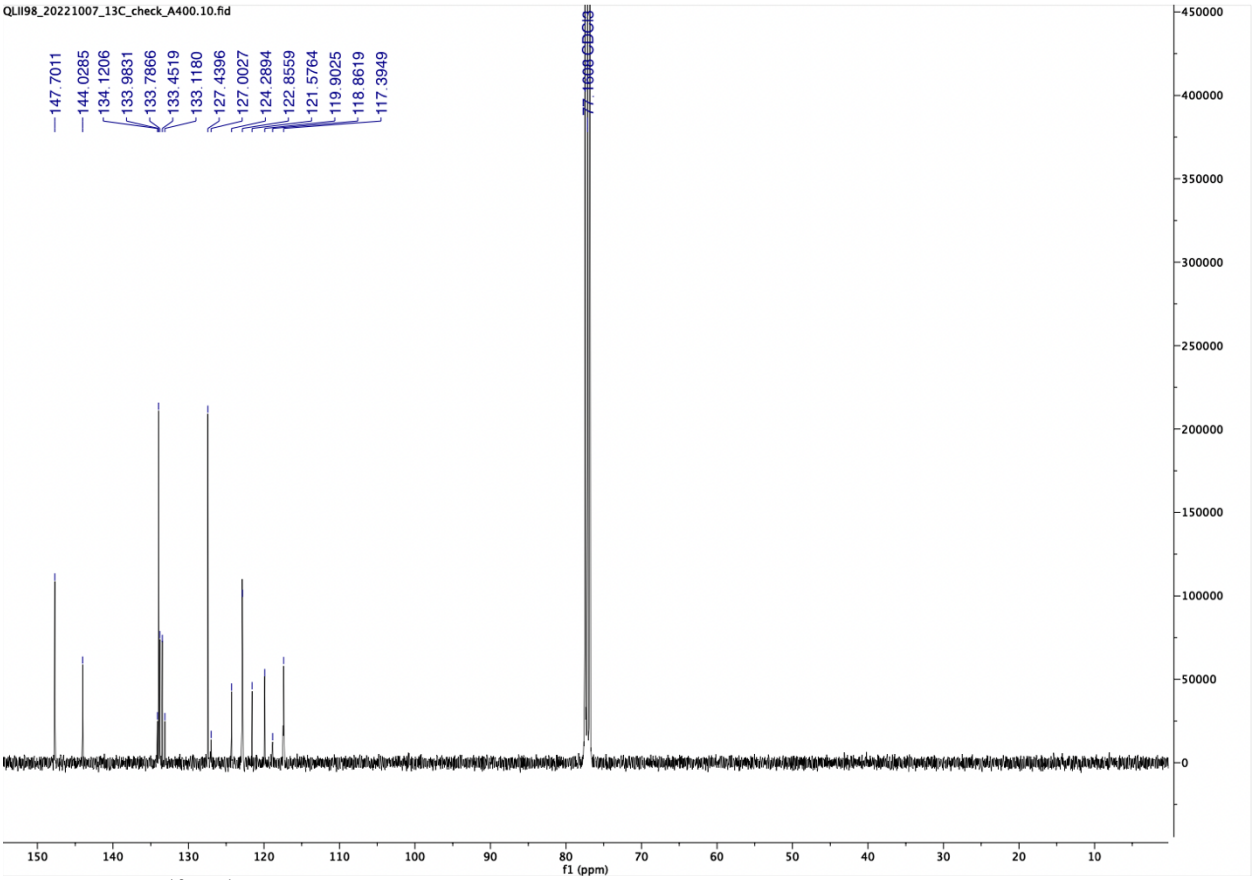

Figure S23: $^{13}C\{^{1}H\}$ NMR of (TAA-(*m*-CF_3)$_4$)$_2$-Br in $CDCl_3$ at 100 MHz.

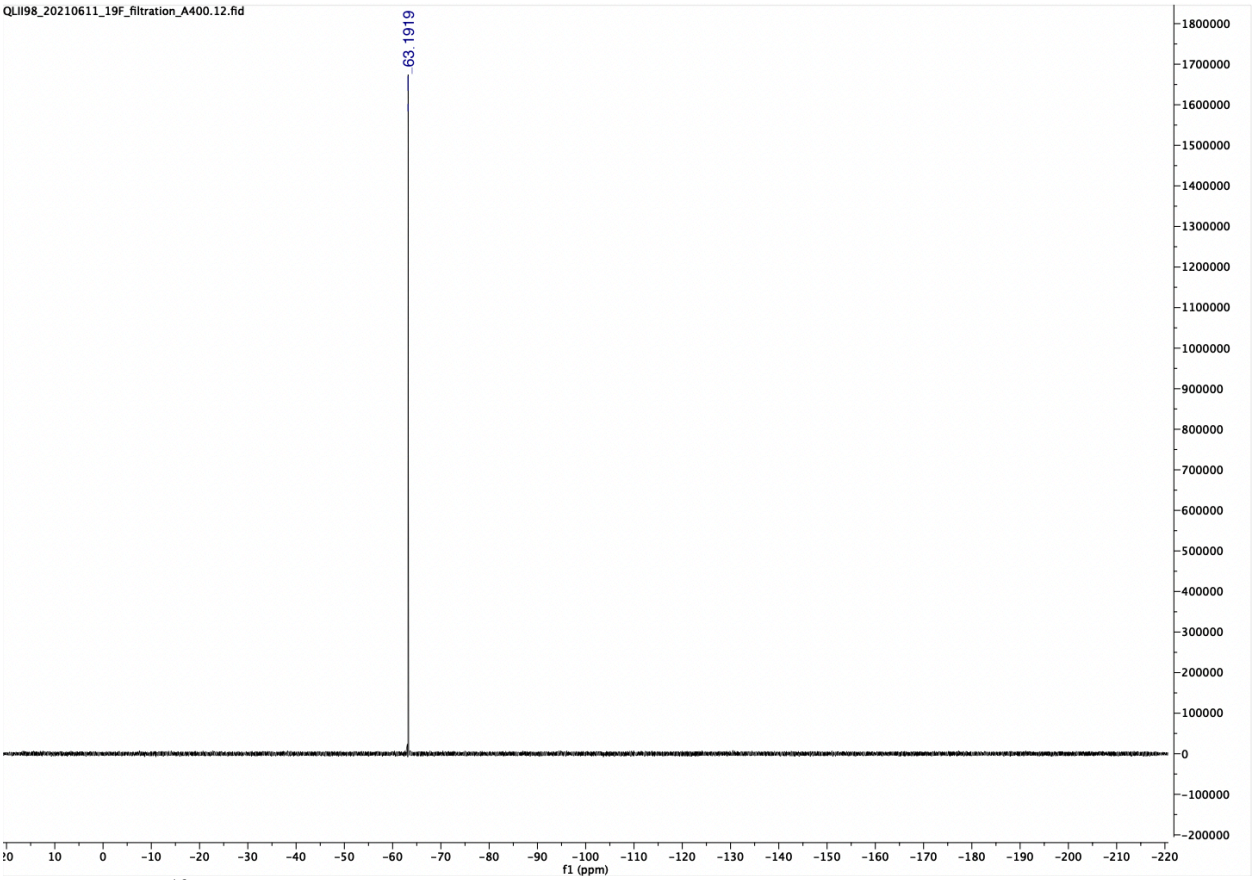

Figure S24: ^{19}F NMR of (TAA-(*m*-CF_3)$_4$)$_2$-Br in $CDCl_3$ at 376 MHz.

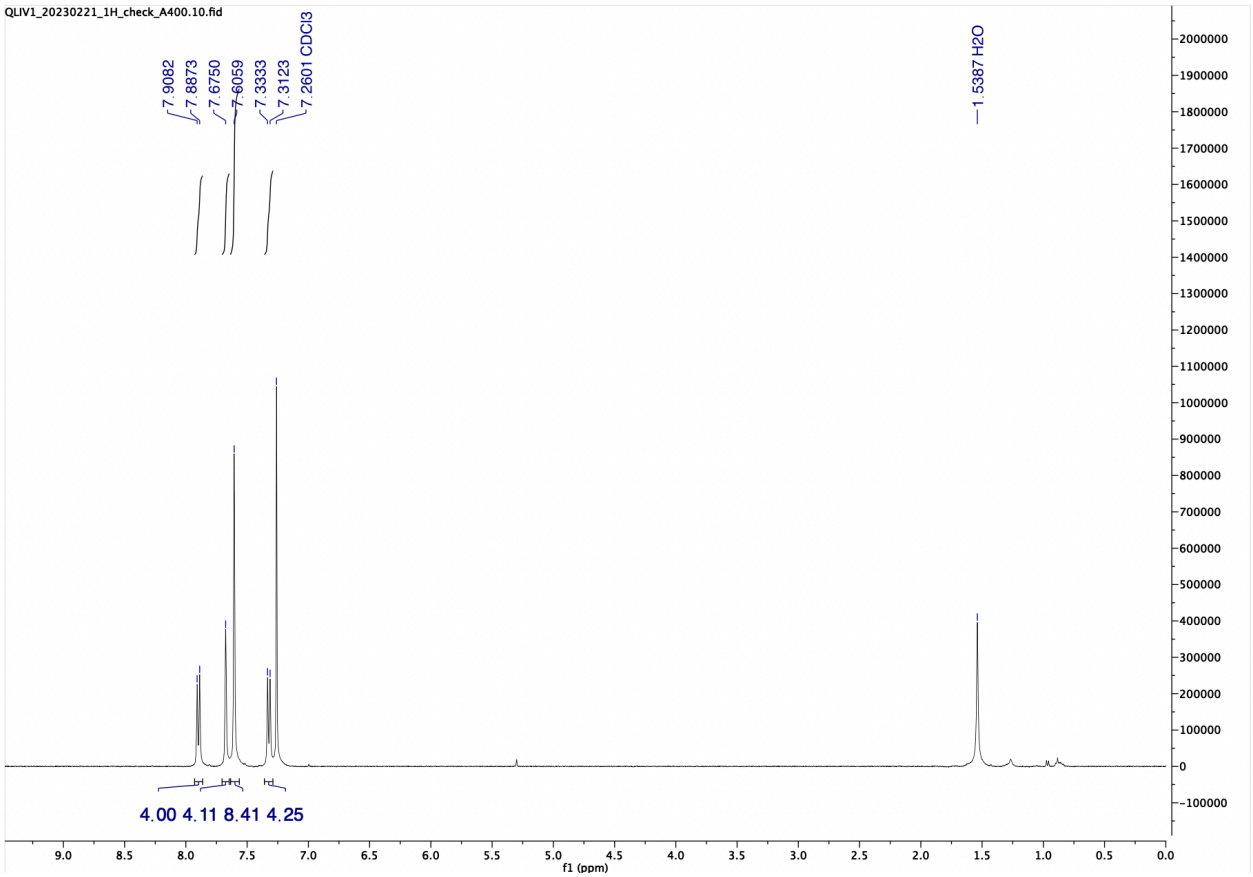

Figure S25: ^{1}H NMR of (TAA-(*m*-CF_3)$_4$)$_2$DCBT in $CDCl_3$ at 400 MHz.

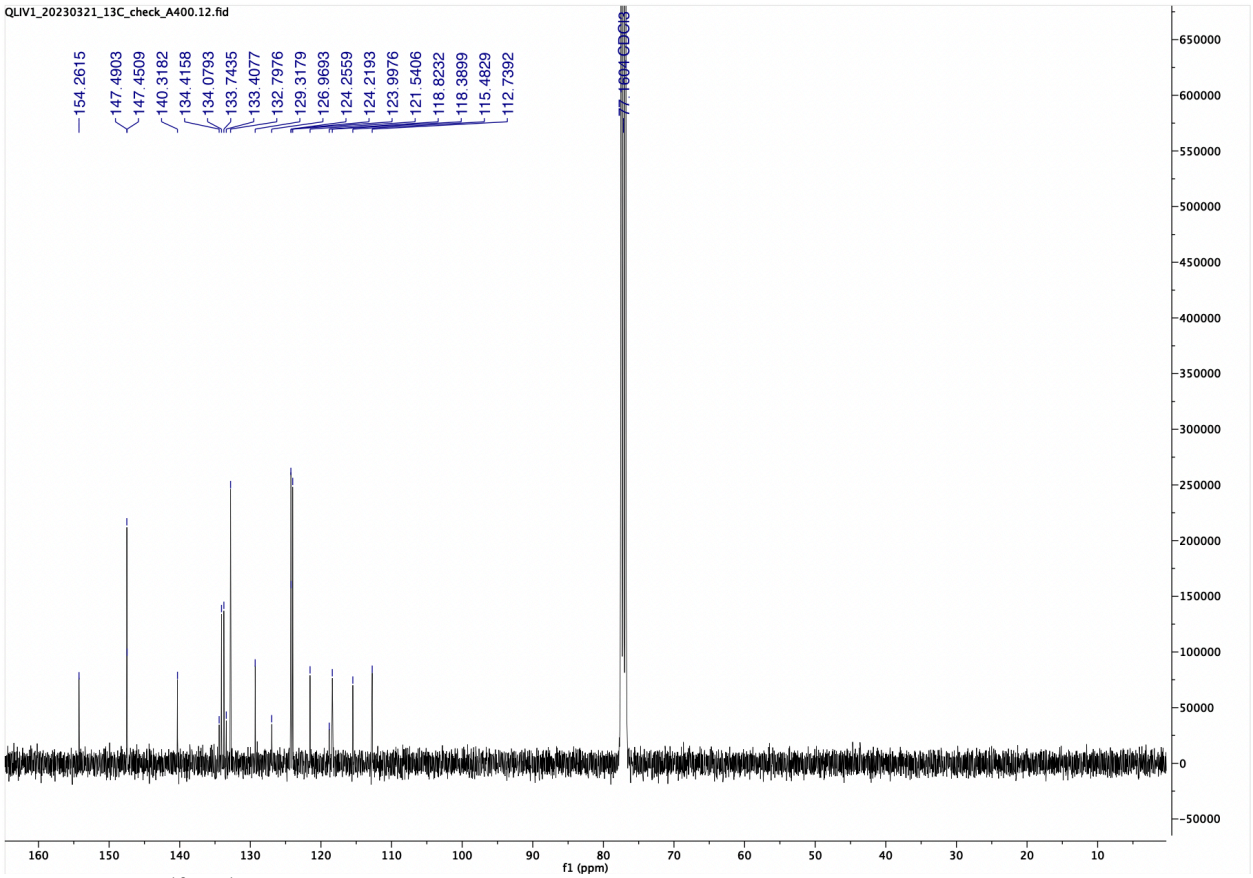

Figure S26: $^{13}C\{^{1}H\}$ NMR of (TAA-(*m*-CF_3)$_4$)$_2$DCBT in $CDCl_3$ at 100 MHz.

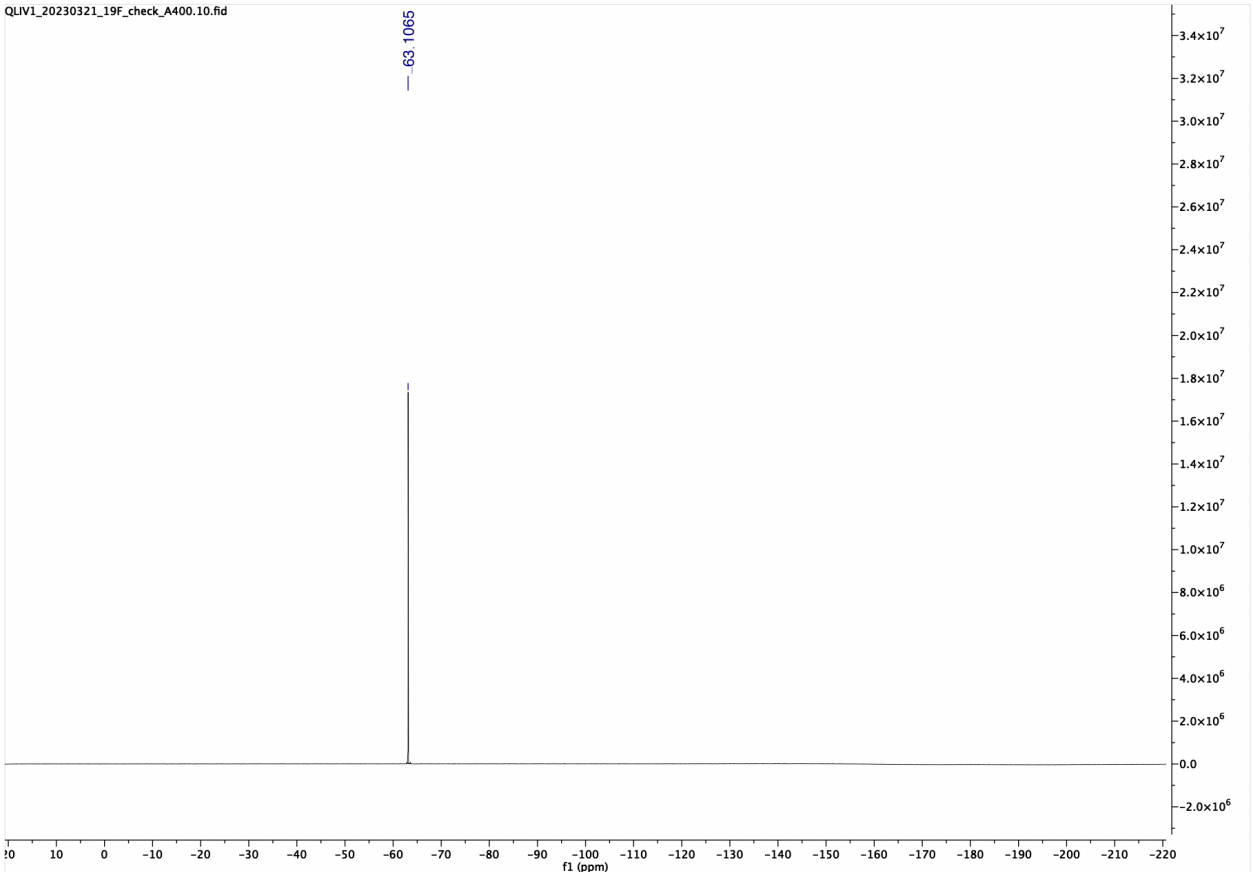

Figure S27: ^{19}F NMR of (TAA-(*m*-CF_3)$_4$)$_2$DCBT in $CDCl_3$ at 376 MHz.

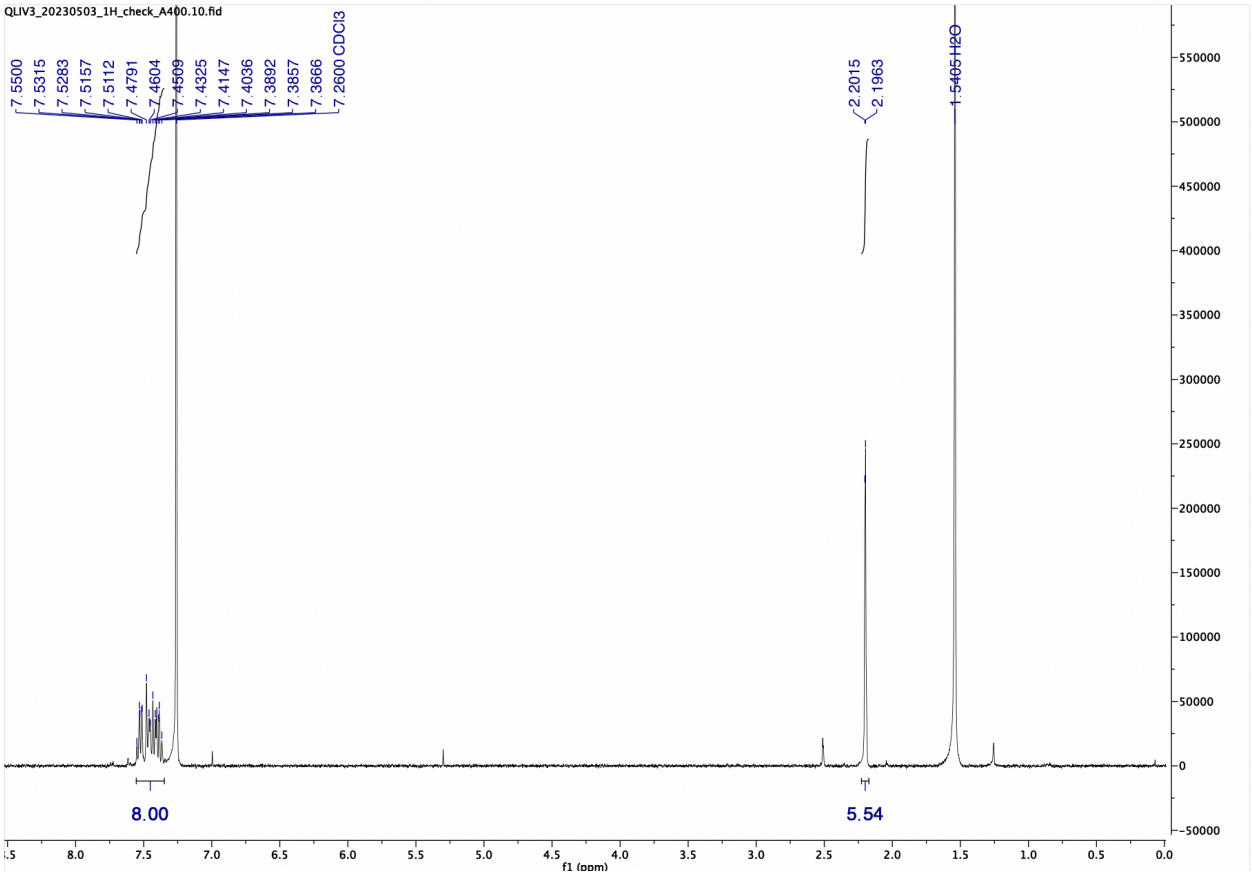

Figure S28: ^{1}H NMR of $(tolyl)_2DCBT$ in $CDCl_3$ at 400 MHz.

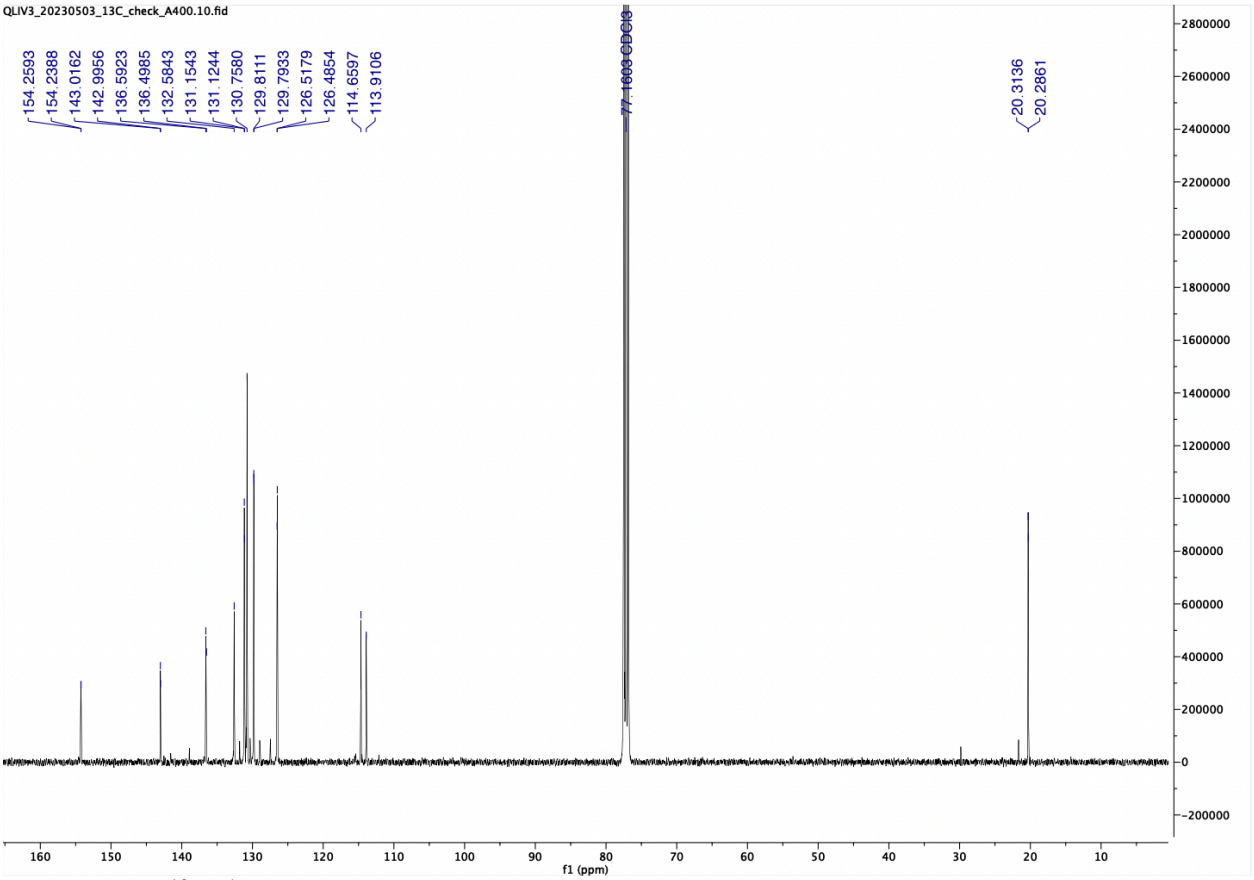

Figure S29: $^{13}C\{^{1}H\}$ NMR of $(tolyl)_2DCBT$ in $CDCl_3$ at 100 MHz.

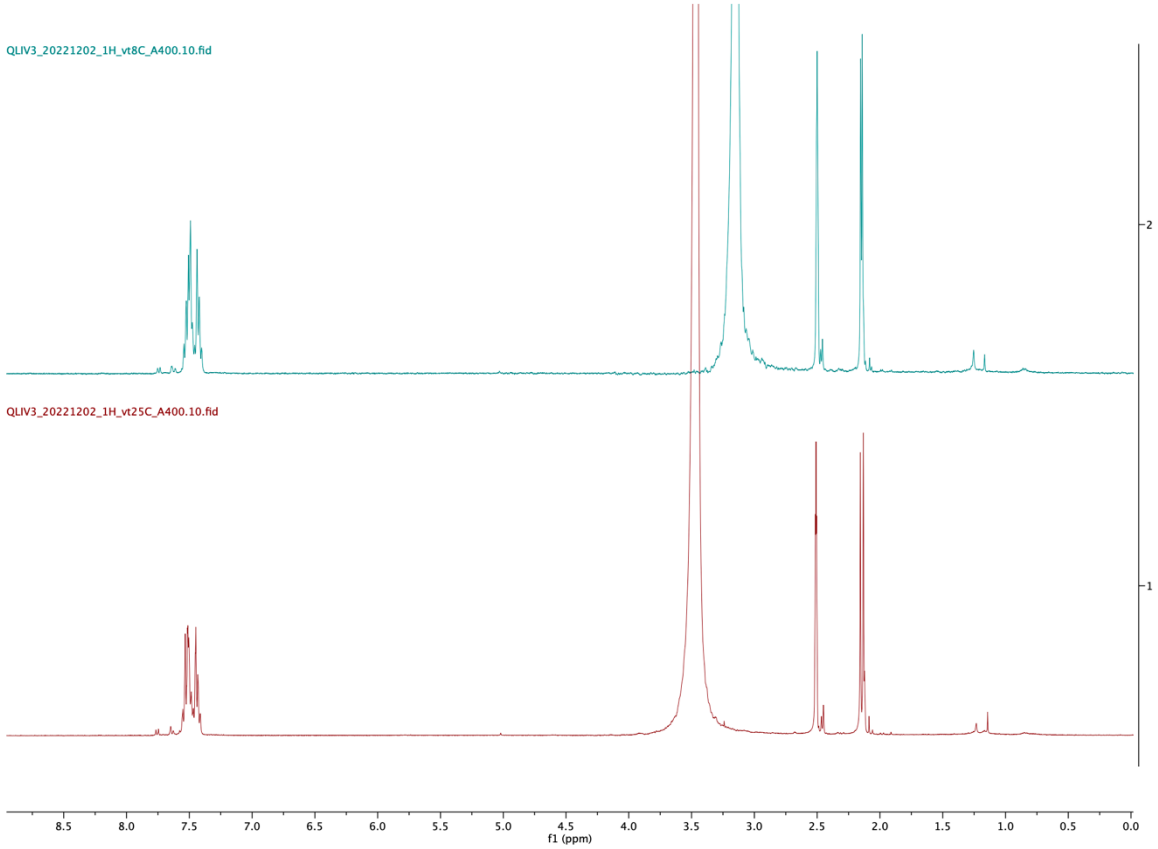

Figure S30: Variable temperature ^{1}H NMR of (tolyl)$_2$DCBT at 80ºC (top, blue) and 25ºC (bottom, red) in $(CD_3)_2SO$ at 400 MHz.

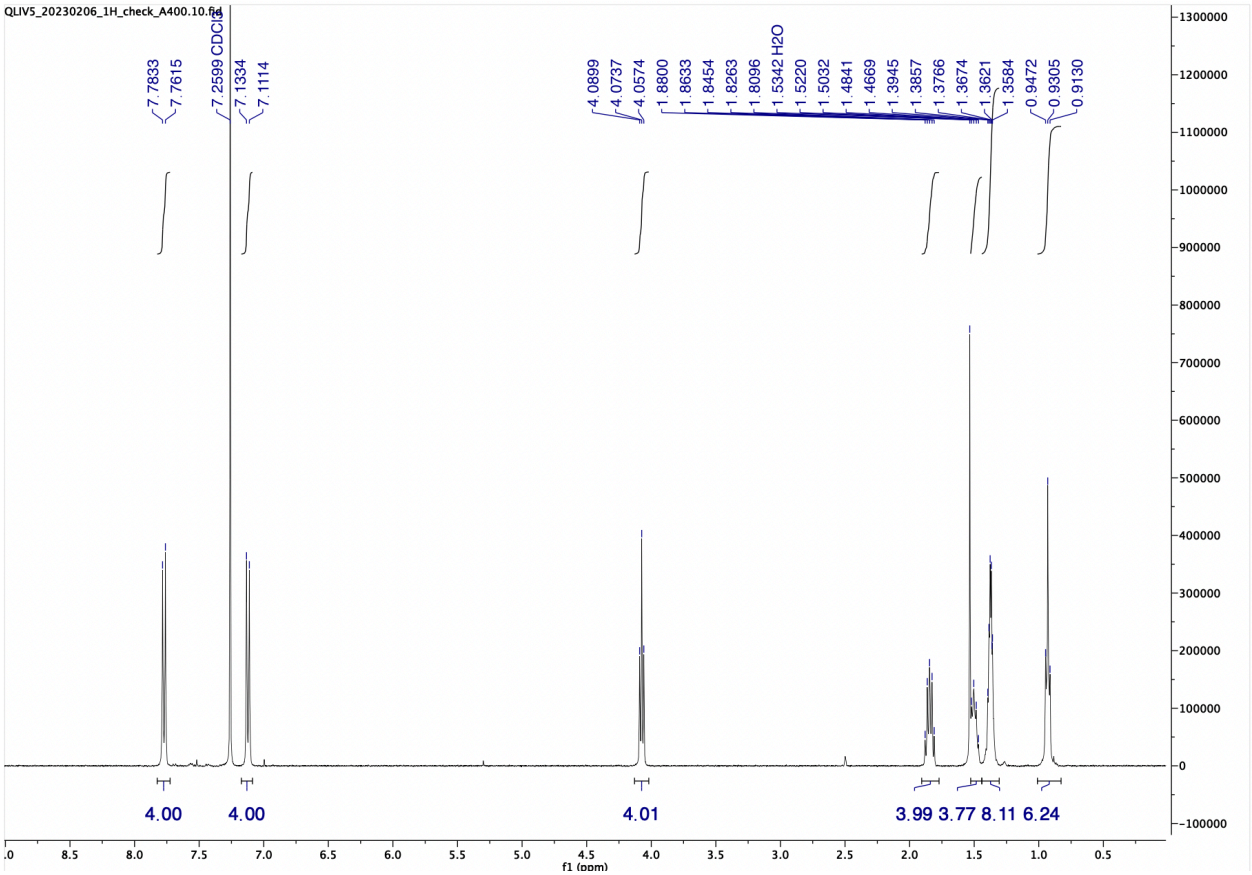

Figure S31: ^{1}H NMR of (p-OHx)$_2$DCBT in $CDCl_3$ at 400 MHz.

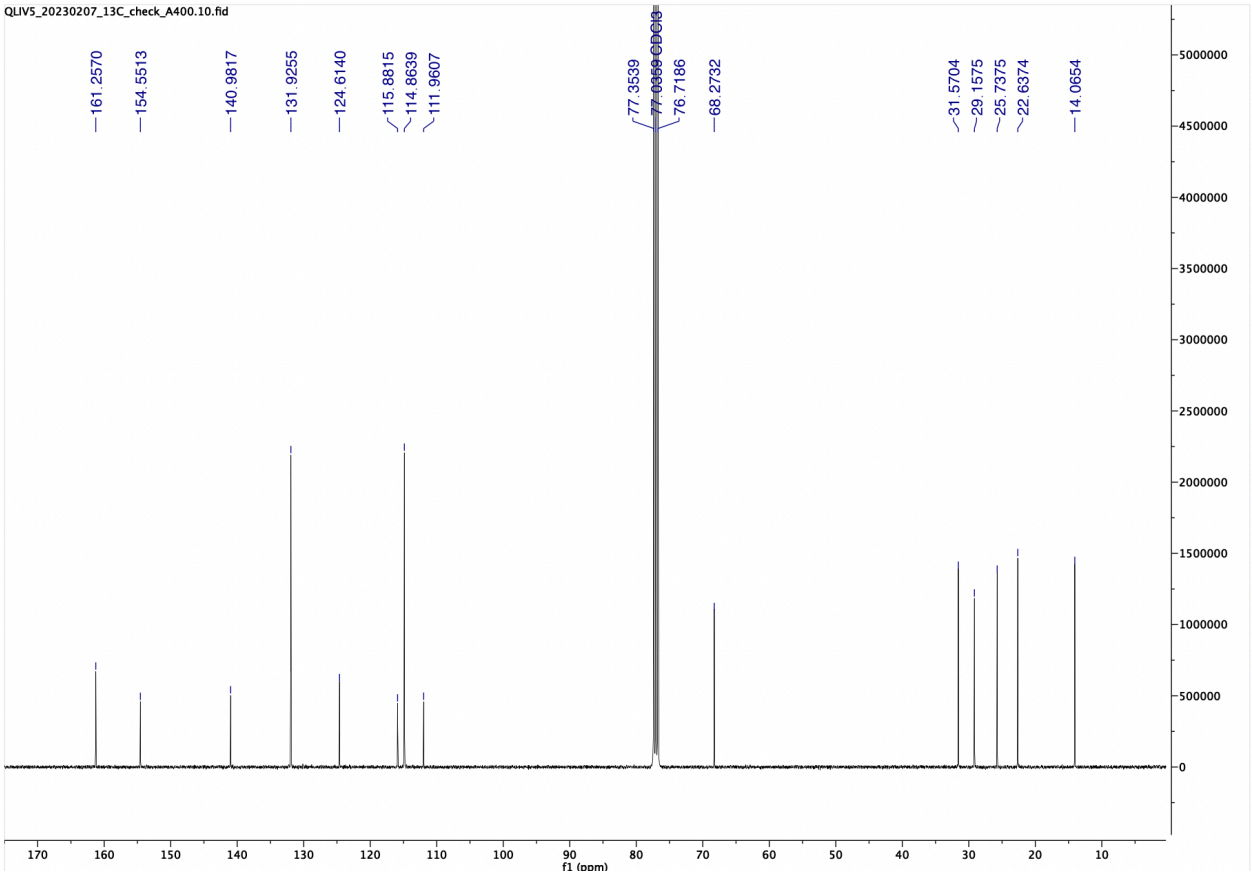

Figure S32: $^{13}C\{^{1}H\}$ NMR of (*p*-OHx)$_2$DCBT in $CDCl_3$ at 100 MHz.

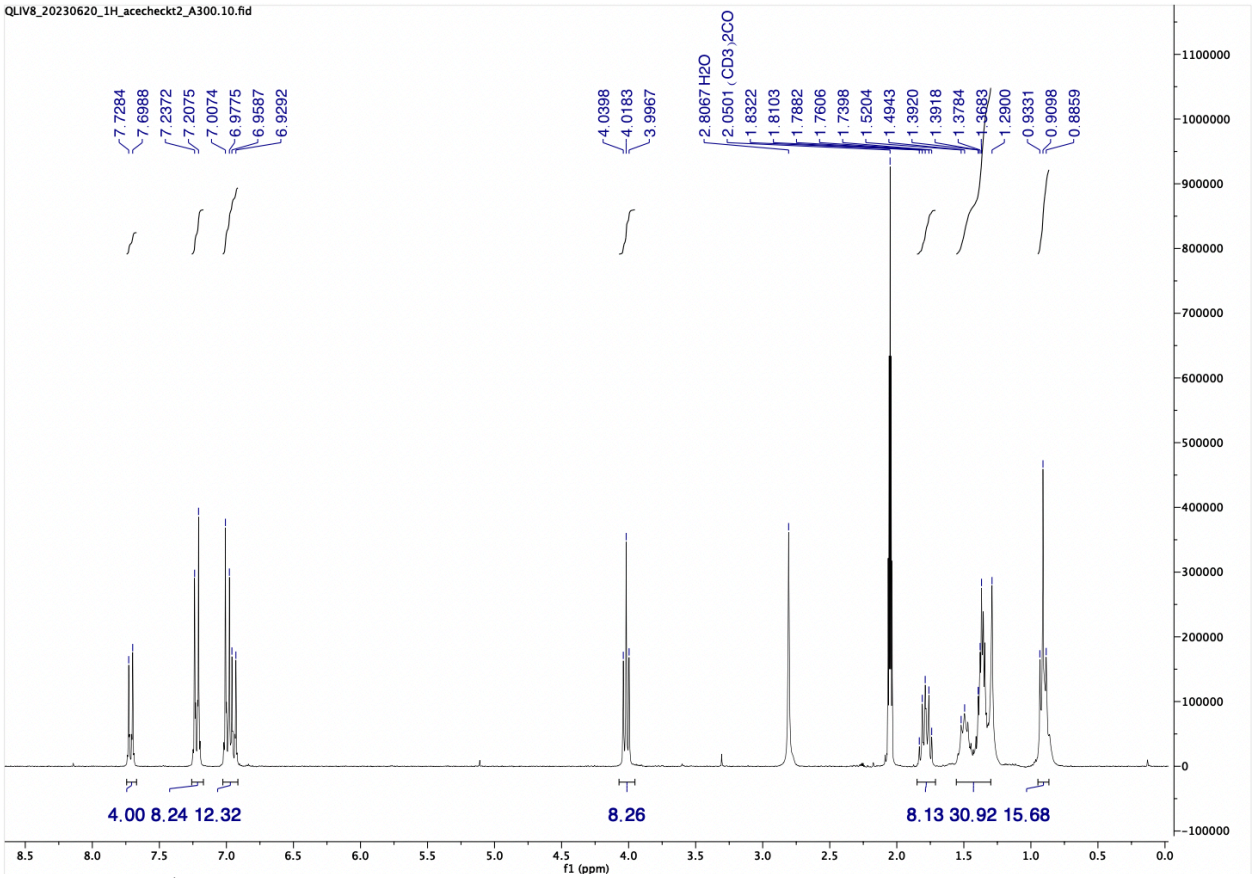

Figure S33: ^{1}H NMR of (TAA-(OHx))$_2$DCBT in $(CD_3)_2CO$ at 300 MHz.

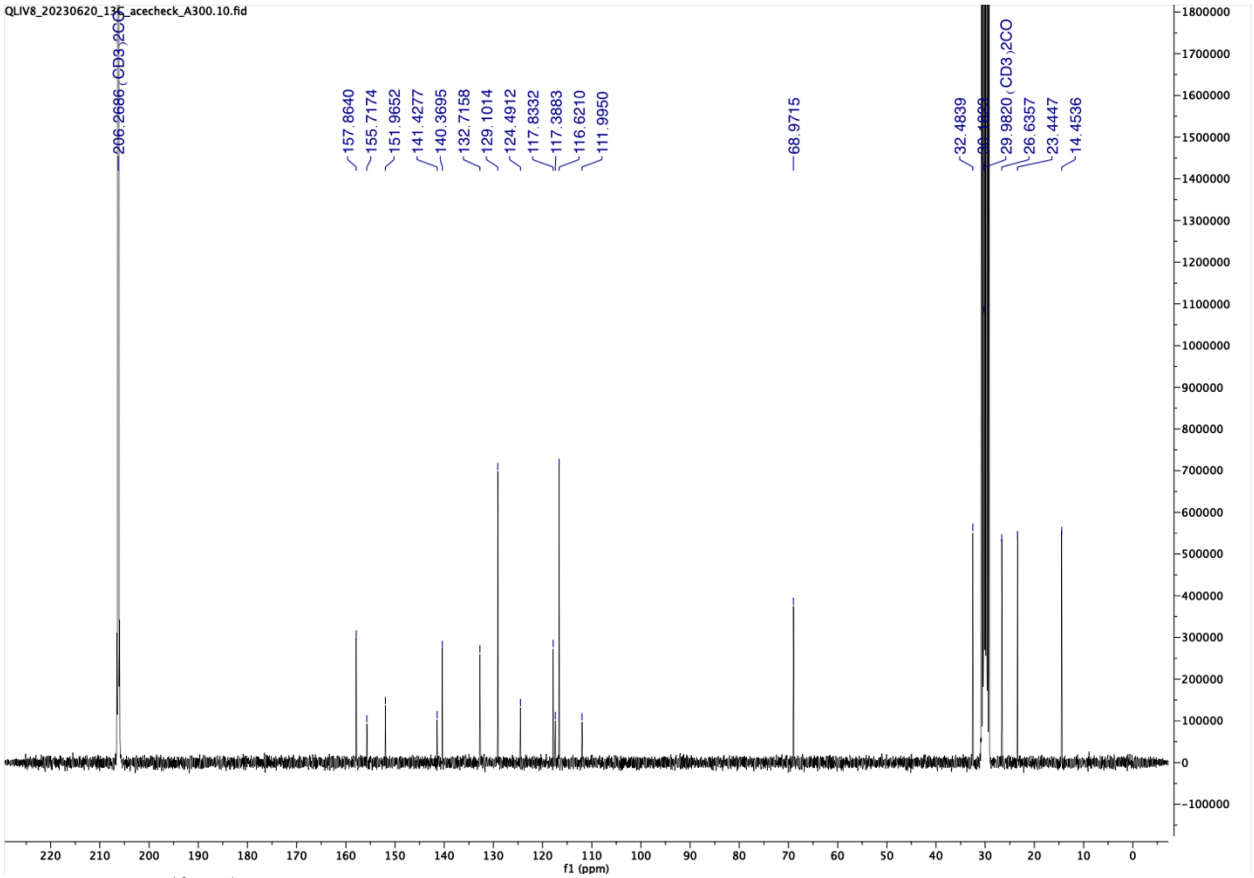

Figure S34: $^{13}C\{^{1}H\}$ NMR of $(TAA\text{-}(OHx))_2DCBT$ in $(CD_3)_2CO$ at 75 MHz.

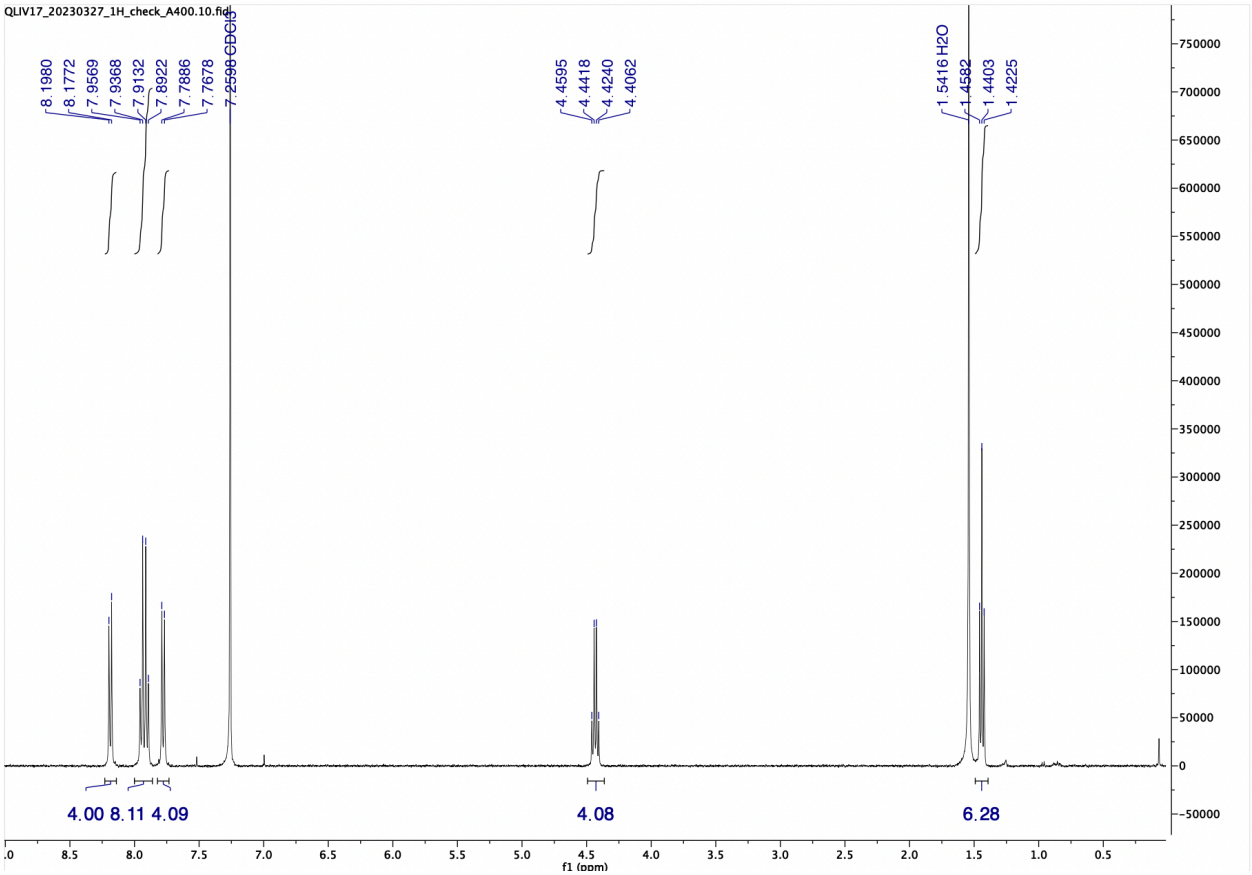

Figure S35: ^{1}H NMR of (Ar-Ar-Ester)$_2$DCBT in $CDCl_3$ at 400 MHz.

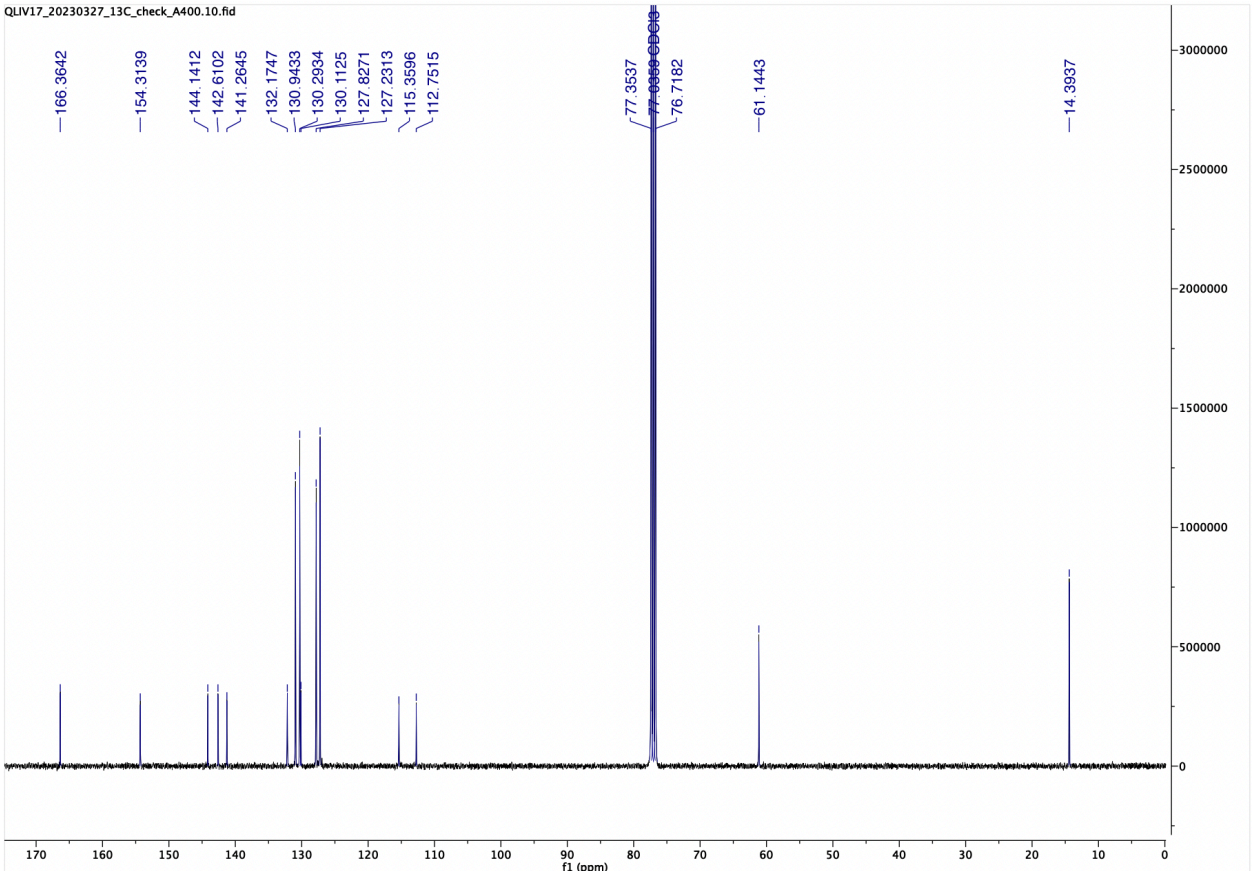

Figure S36: $^{13}C\{^{1}H\}$ NMR of (Ar-Ar-Ester)$_2$DCBT in $CDCl_3$ at 100 MHz.

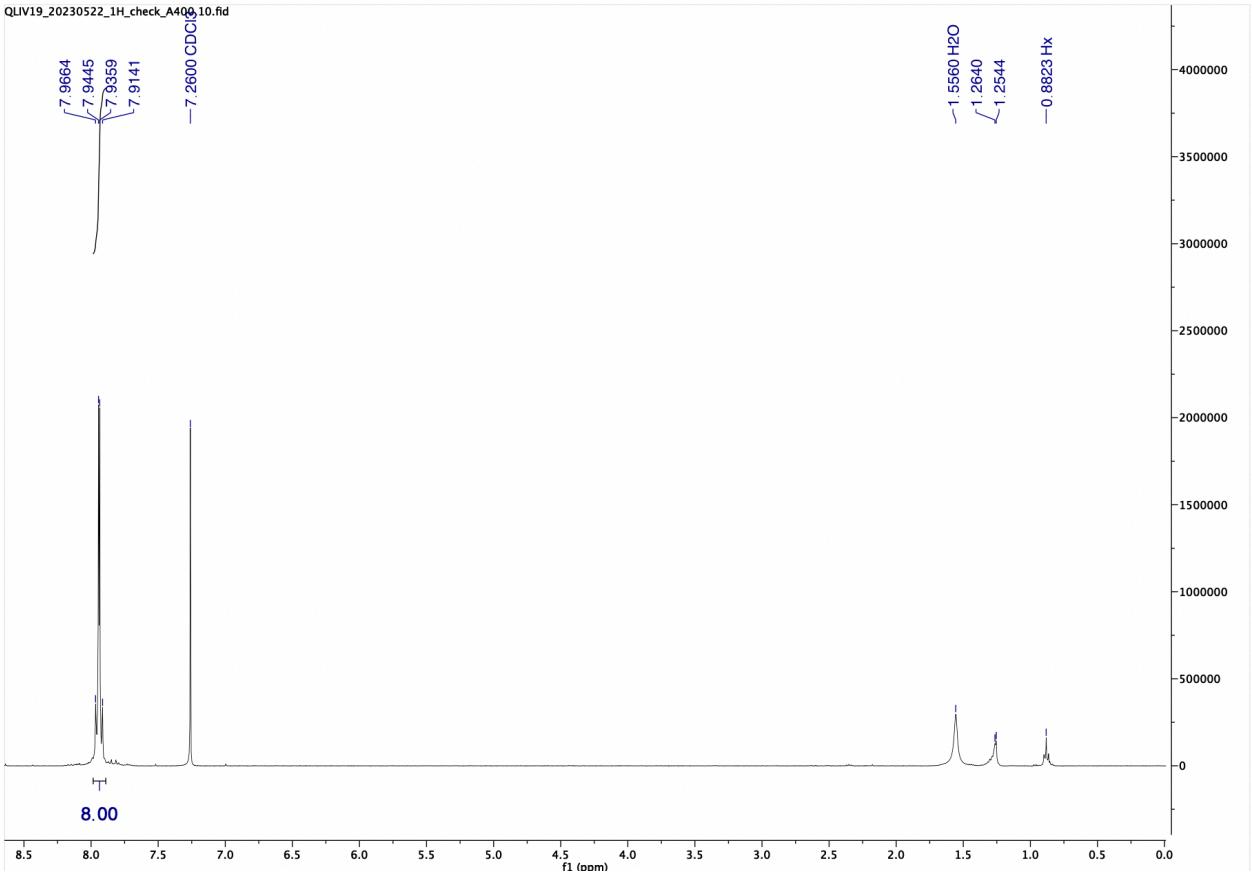

Figure S37: ^{1}H NMR of (p-CN)$_2$DCBT in $CDCl_3$ at 400 MHz.

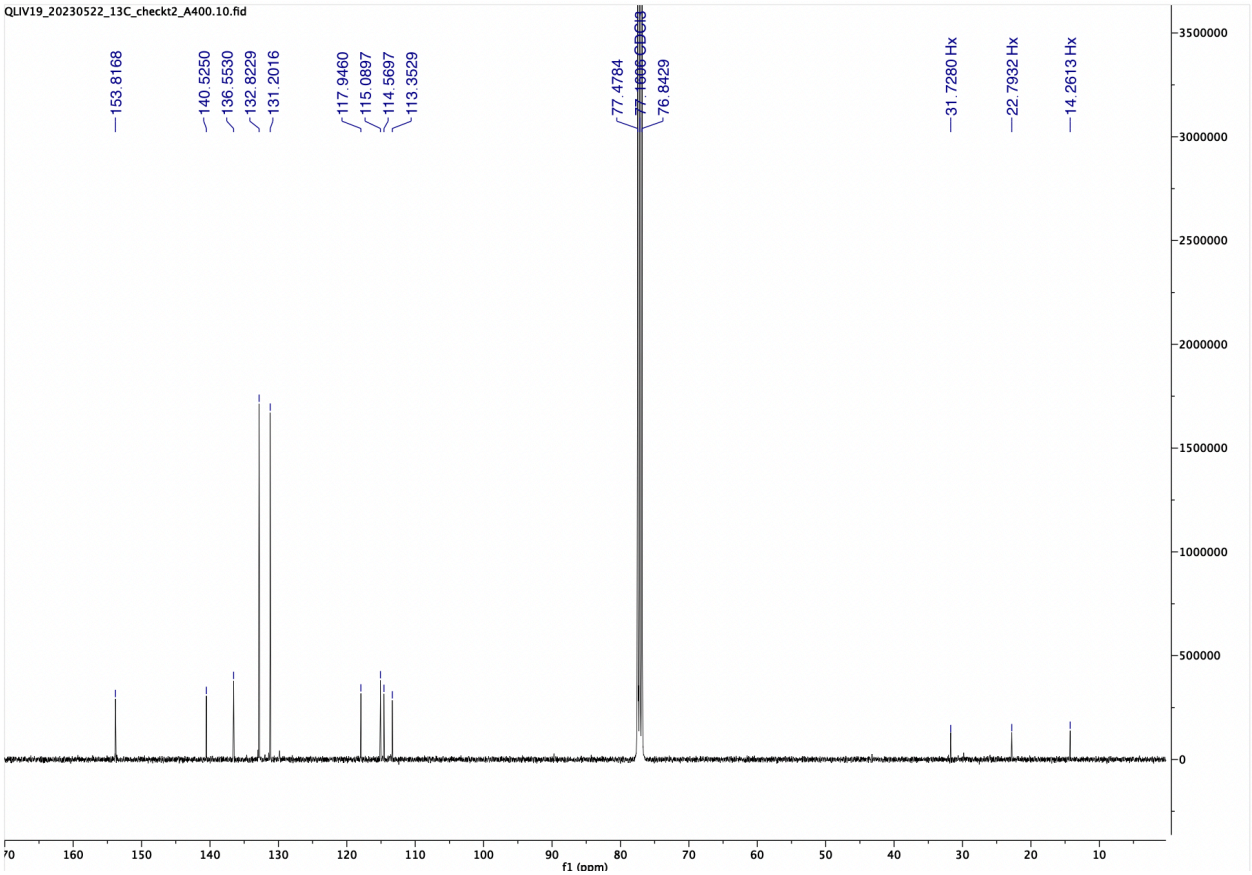

Figure S38: $^{13}C\{^{1}H\}$ NMR of (p-CN)$_2$DCBT in $CDCl_3$ at 100 MHz.

4. XYZ coordinates, Frequency, and Total Energy Information

(Ar-Ar-Ester)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -2302.8941114 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	-1.23925	2.42184	-0.00062
C	-0.71987	1.19799	0.00327
C	0.71987	1.19799	-0.00329
N	1.23925	2.42183	0.00061
S	0.00001	3.46163	-0.00003
C	-1.47186	-0.02483	0.00293
C	-0.72519	-1.17972	0.0076
C	0.72518	-1.17972	-0.0076
C	1.47186	-0.02484	-0.00293
C	-2.94907	-0.00066	-0.00723
C	2.94907	-0.00067	0.00723
C	-3.64767	0.82959	0.87434
C	-5.03284	0.83841	0.87893
C	-5.75861	0.03335	-0.00417
C	-5.05551	-0.78197	-0.89462
C	-3.66987	-0.80167	-0.89621
C	3.66987	-0.80165	0.89624
C	5.05551	-0.78195	0.89464
C	5.75861	0.03334	0.00417
C	5.03284	0.83838	-0.87895
C	3.64767	0.82956	-0.87436
C	-7.24028	0.04513	0.0033
C	7.24028	0.04513	-0.0033
C	7.94253	1.24451	-0.16407
C	9.32789	1.25416	-0.17128
C	10.03438	0.06273	-0.02008
C	9.34682	-1.13892	0.13972
C	7.95993	-1.14426	0.14864
C	-7.95993	-1.14427	-0.14861
C	-9.34682	-1.13892	-0.13969
C	-10.03438	0.06273	0.02008
C	-9.32789	1.25416	0.17125
C	-7.94253	1.24452	0.16404
C	-11.52314	0.13011	0.03695
O	-12.09183	-1.07401	-0.11762
O	-12.15454	1.14391	0.1732
C	11.52314	0.13011	-0.03695
O	12.15454	1.1439	-0.17322
O	12.09183	-1.07401	0.11765
C	13.52	-1.07314	0.10853

C	-13.51999	-1.07314	-0.1085
C	-1.37686	-2.45937	0.06173
N	-1.87758	-3.49296	0.1114
C	1.37685	-2.45938	-0.06172
N	1.87755	-3.49297	-0.11139
H	-3.10277	1.45462	1.56984
H	-5.56126	1.45801	1.59396
H	-5.599	-1.38783	-1.60988
H	-3.14548	-1.42929	-1.60649
H	3.14548	-1.42925	1.60653
H	5.59901	-1.3878	1.60992
H	5.56126	1.45796	-1.59399
H	3.10277	1.45458	-1.56988
H	7.39556	2.17555	-0.25716
H	9.88367	2.17679	-0.2853
H	9.90206	-2.0614	0.24735
H	7.42571	-2.08218	0.24673
H	-7.42571	-2.08218	-0.24667
H	-9.90205	-2.0614	-0.24729
H	-9.88367	2.1768	0.28525
H	-7.39556	2.17556	0.25711
H	13.81692	-2.10961	0.24165
H	13.90256	-0.45403	0.92025
H	13.89146	-0.6833	-0.83939
H	-13.89145	-0.68328	0.83941
H	-13.81691	-2.10962	-0.24158
H	-13.90256	-0.45405	-0.92023

$(DMA)_2DCBT$ Ground State XYZ from DFT Geometry Optimization
Energy = -1653.0329906 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	-1.23917	2.36851	-0.01257
C	-0.72089	1.14524	-0.00182
C	0.72091	1.14523	0.00182
N	1.23922	2.36848	0.01257
S	0.00004	3.41071	-0.00004
C	-1.47972	-0.07742	-0.00258
C	-0.72539	-1.23004	0.01005
C	0.72536	-1.23005	-0.01004
C	1.47972	-0.07745	0.00261
C	-2.95008	-0.05164	-0.0249
C	2.95008	-0.05168	0.02492
C	3.68004	-0.89654	0.86724
C	5.06123	-0.88273	0.8867
C	5.78875	-0.01495	0.0458
C	5.05046	0.83499	-0.80521
C	3.66925	0.82098	-0.79972
C	-3.66925	0.82104	0.79971
C	-5.05047	0.83504	0.8052
C	-5.78875	-0.01492	-0.04579
C	-5.06123	-0.88273	-0.88666
C	-3.68004	-0.89654	-0.8672
N	-7.16115	0.00622	-0.06002
C	-7.87401	0.80829	0.91334
C	-7.88246	-0.99111	-0.8255
N	7.16115	0.0062	0.06003
C	7.88248	-0.99108	0.82555
C	7.874	0.80826	-0.91336
C	-1.37143	-2.51118	0.08436
N	-1.86528	-3.54726	0.15549
C	1.37137	-2.51121	-0.08439
N	1.86516	-3.54731	-0.15556
H	3.15966	-1.57127	1.5363
H	5.57444	-1.55302	1.56107
H	5.55766	1.511	-1.47868
H	3.13667	1.48987	-1.46338
H	-3.13668	1.48995	1.46337
H	-5.55767	1.51106	1.47865
H	-5.57443	-1.55305	-1.561
H	-3.15965	-1.57129	-1.53623
H	-7.62476	1.86785	0.80634
H	-7.64996	0.50404	1.94344

H	-8.94366	0.70026	0.74749
H	-7.6546	-0.90837	-1.89209
H	-8.951	-0.83025	-0.7004
H	-7.6439	-2.01118	-0.50062
H	7.64393	-2.01116	0.50072
H	7.65461	-0.90829	1.89214
H	8.95101	-0.83021	0.70045
H	7.64995	0.50398	-1.94344
H	8.94365	0.70023	-0.74751
H	7.62475	1.86782	-0.80637

(p-CN)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -1569.6138547 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	1.23865	2.34188	-0.00507
C	0.71924	1.11775	-0.00575
C	-0.71925	1.11775	0.00572
N	-1.23865	2.34187	0.00499
S	0.	3.3813	-0.00005
C	1.46812	-0.1053	-0.0048
C	0.72485	-1.26177	-0.00628
C	-0.72485	-1.26177	0.00631
C	-1.46812	-0.1053	0.0048
C	2.94735	-0.07908	0.00259
C	-2.94735	-0.07908	-0.00259
C	3.63557	0.73982	-0.8979
C	5.01968	0.76216	-0.90535
C	5.72953	-0.02525	0.00362
C	5.0513	-0.83601	0.91446
C	3.66619	-0.86197	0.90933
C	-3.6662	-0.86199	-0.90931
C	-5.0513	-0.83603	-0.91444
C	-5.72953	-0.02525	-0.00362
C	-5.01967	0.76218	0.90533
C	-3.63557	0.73984	0.89788
C	1.37938	-2.53998	-0.05153
N	1.88766	-3.57014	-0.0907
C	-1.37938	-2.53998	0.0516
N	-1.88765	-3.57014	0.09081
C	-7.16601	0.00555	-0.00371
N	-8.31531	0.03394	-0.00362
C	7.16601	0.00555	0.00372
N	8.31531	0.03394	0.00362
H	3.08439	1.35338	-1.59804
H	5.55665	1.38565	-1.60837
H	5.60989	-1.43825	1.61901
H	3.14241	-1.48641	1.62224
H	-3.14242	-1.48645	-1.6222
H	-5.6099	-1.43829	-1.61897
H	-5.55665	1.38569	1.60834
H	-3.08439	1.35341	1.598

(p-OHx)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -1614.16766 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	-1.1543	-2.39113	-0.06746
C	-0.67877	-1.15003	-0.07411
C	0.7609	-1.09907	-0.06817
N	1.32255	-2.3037	-0.07215
S	0.12067	-3.38782	-0.0692
C	-1.47725	0.04472	-0.07684
C	-0.76862	1.22418	-0.08423
C	0.68129	1.27573	-0.06133
C	1.47217	0.14986	-0.06609
C	-2.94971	-0.03473	-0.06376
C	2.9467	0.17756	-0.0761
C	-3.62508	-0.91419	-0.92407
C	-5.00225	-0.97698	-0.92757
C	-5.74741	-0.17466	-0.05603
C	-5.09061	0.69053	0.81827
C	-3.70249	0.75484	0.80303
C	3.64712	1.02267	-0.9489
C	5.02604	1.04832	-0.95311
C	5.74737	0.23331	-0.0749
C	5.06582	-0.61534	0.79807
C	3.67693	-0.64316	0.78258
O	-7.08924	-0.31173	-0.1326
O	7.09271	0.33389	-0.14909
C	7.86522	-0.46738	0.72254
C	-7.88486	0.49326	0.71547
C	-1.46293	2.48064	-0.14812
N	-1.99783	3.49676	-0.20563
C	1.28471	2.5781	0.00392
N	1.74597	3.62944	0.06569
H	-3.06051	-1.54216	-1.60081
H	-5.53661	-1.63934	-1.59647
H	-5.63901	1.31479	1.5095
H	-3.20467	1.42522	1.49303
H	3.10483	1.65463	-1.64157
H	5.57694	1.69089	-1.62762
H	5.59829	-1.25509	1.4878
H	3.15679	-1.30818	1.45966
H	8.9037	-0.23189	0.50399
H	7.68703	-1.53191	0.54226
H	7.65056	-0.23165	1.76927
H	-8.9169	0.23976	0.48683

H	-7.71783	1.55663	0.51978
H	-7.68143	0.27764	1.76876

(TAA-(*m*-CF_3)$_4$)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -5116.2161653 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	-1.23913	-2.14176	0.73554
C	-0.71801	-0.99964	0.29766
C	0.72082	-0.99395	0.31817
N	1.2383	-2.13662	0.75899
S	-0.00203	-3.11019	1.12079
C	-1.46784	0.14066	-0.14684
C	-0.72035	1.21953	-0.55814
C	0.72909	1.22812	-0.52974
C	1.47373	0.14951	-0.1126
C	-2.94374	0.11626	-0.1357
C	2.95052	0.12515	-0.09603
C	-3.63649	-0.98165	-0.65662
C	-5.0198	-1.00798	-0.6585
C	-5.74357	0.05033	-0.10299
C	-5.05964	1.1424	0.43362
C	-3.67502	1.1769	0.40491
C	3.68842	0.55215	-1.20307
C	5.07333	0.5375	-1.18042
C	5.74957	0.0847	-0.0467
C	5.01974	-0.35407	1.06032
C	3.63581	-0.33457	1.03284
N	-7.16009	0.0061	-0.07777
C	-7.81956	-1.1993	0.24707
C	-7.90862	1.18139	-0.31086
N	7.16774	0.06539	-0.02019
C	7.88821	-0.36958	-1.1532
C	7.85324	0.45613	1.15054
C	9.08446	0.25668	-1.51477
C	9.78643	-0.18539	-2.62492
C	9.3153	-1.22999	-3.41141
C	8.12114	-1.83604	-3.04991
C	7.4125	-1.42774	-1.92825
C	8.99274	-0.23311	1.5693
C	9.65931	0.16758	2.71841
C	9.20368	1.2312	3.48494
C	8.06124	1.90095	3.06607
C	7.39222	1.53564	1.90757
C	-7.51036	2.08262	-1.30376
C	-8.24795	3.23401	-1.52249
C	-9.3969	3.51025	-0.78822
C	-9.78495	2.60705	0.18812

C	-9.04857	1.45658	0.44241
C	-9.00871	-1.55084	-0.40092
C	-9.64888	-2.73352	-0.0711
C	-9.12377	-3.60153	0.88073
C	-7.94021	-3.24774	1.50888
C	-7.29207	-2.05526	1.21304
C	-1.37327	2.39129	-1.07263
N	-1.88291	3.3323	-1.49246
C	1.3848	2.44153	-0.93178
N	1.89654	3.42001	-1.25136
C	-11.03989	2.83632	0.98485
F	-12.0246	2.0254	0.57762
F	-10.8441	2.58696	2.28574
F	-11.4823	4.09122	0.87299
C	-7.78603	4.22996	-2.55189
F	-8.82157	4.80054	-3.17805
F	-7.07758	5.21417	-1.98666
F	-7.01054	3.66251	-3.48048
C	-10.95582	-3.0874	-0.72702
F	-11.01946	-4.39258	-1.01393
F	-11.98978	-2.81198	0.07694
F	-11.14427	-2.41081	-1.86436
C	-7.30572	-4.17583	2.50763
F	-6.29336	-4.85915	1.95578
F	-6.79903	-3.50481	3.54894
F	-8.17616	-5.07006	2.98345
C	7.54487	-2.93775	-3.89605
F	7.01651	-3.90982	-3.14222
F	6.56253	-2.47889	-4.68321
F	8.46484	-3.49232	-4.68963
C	11.10603	0.45412	-2.9615
F	12.11828	-0.18388	-2.36094
F	11.34629	0.42613	-4.27621
F	11.15353	1.73038	-2.56472
C	7.50316	3.02139	3.90043
F	6.9622	3.97985	3.14124
F	6.53852	2.5778	4.7183
F	8.44162	3.5864	4.66543
C	10.91937	-0.55571	3.10829
F	11.97151	-0.10201	2.41619
F	11.19991	-0.40228	4.40559
F	10.82693	-1.86849	2.86353
H	-3.08791	-1.81112	-1.08308
H	-5.54723	-1.85182	-1.08658
H	-5.61378	1.95995	0.8785
H	-3.1597	2.02631	0.83627

H	3.17933	0.90147	-2.09287
H	5.63452	0.87818	-2.04203
H	5.54154	-0.71231	1.93952
H	3.08137	-0.68391	1.89392
H	9.45984	1.08912	-0.93184
H	9.86441	-1.55934	-4.28343
H	6.49177	-1.92928	-1.65423
H	9.3544	-1.08234	1.00147
H	9.72435	1.53067	4.3846
H	6.51521	2.08621	1.588
H	-6.62887	1.87856	-1.89939
H	-9.97363	4.4059	-0.97779
H	-9.36098	0.77633	1.22634
H	-9.42559	-0.90102	-1.1605
H	-9.62569	-4.52946	1.12198
H	-6.37737	-1.79135	1.73068

(TAA-(OHx))$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -2877.9147101 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	1.22083	-2.39289	-0.07656
C	0.71297	-1.16508	-0.06658
C	-0.72835	-1.1521	-0.06531
N	-1.25783	-2.37079	-0.05612
S	-0.02767	-3.4235	-0.06667
C	1.48062	0.05083	-0.06676
C	0.73876	1.21121	-0.05361
C	-0.71144	1.22447	-0.07289
C	-1.47416	0.07761	-0.06414
C	2.95142	0.01411	-0.08835
C	-2.94553	0.06641	-0.04766
C	3.66134	-0.85159	0.75148
C	5.04369	-0.86601	0.76021
C	5.77306	-0.02968	-0.09973
C	5.06334	0.81743	-0.96519
C	3.68202	0.84205	-0.94805
C	-3.6662	0.90569	0.80838
C	-5.0486	0.90223	0.82089
C	-5.76784	0.06551	-0.04612
C	-5.04784	-0.7815	-0.90428
C	-3.66623	-0.78787	-0.89122
N	7.17009	-0.04098	-0.09933
C	7.89129	-1.18965	0.32814
C	7.9104	1.11587	-0.47216
N	-7.16471	0.07486	-0.0561
C	-7.89177	1.22736	0.35354
C	-7.90128	-1.07591	-0.4514
C	-7.55191	2.49525	-0.13292
C	-8.26797	3.6094	0.25818
C	-9.3579	3.48259	1.12529
C	-9.713	2.22232	1.6003
C	-8.97152	1.10614	1.21921
C	-8.96112	-0.95365	-1.35621
C	-9.69666	-2.06228	-1.72761
C	-9.38018	-3.32486	-1.21739
C	-8.32267	-3.45657	-0.31969
C	-7.60028	-2.32993	0.06679
C	9.00066	0.99919	-1.3406
C	9.73842	2.11292	-1.69217
C	9.39309	3.37488	-1.19943
C	8.30538	3.50038	-0.3376

C	7.58124	2.3692	0.03079
C	7.57218	-2.45705	-0.1729
C	8.2808	-3.57016	0.235
C	9.34316	-3.44232	1.13541
C	9.67845	-2.18231	1.62534
C	8.9444	-1.0676	1.22613
O	10.17103	4.40669	-1.61466
O	9.98288	-4.59395	1.46384
O	-10.00256	4.63529	1.43855
O	-10.15512	-4.35127	-1.65246
C	-11.10143	4.54987	2.31995
C	-9.87044	-5.6408	-1.15448
C	11.05953	-4.50577	2.37235
C	9.84929	5.69788	-1.1424
C	1.39944	2.48491	0.023
N	1.90727	3.51382	0.09866
C	-1.34765	2.51074	-0.14484
N	-1.83382	3.55041	-0.21556
H	3.12302	-1.50324	1.42752
H	5.5702	-1.52089	1.44245
H	5.60448	1.45284	-1.65424
H	3.16232	1.49719	-1.63682
H	-3.13939	1.55342	1.49872
H	-5.58141	1.54611	1.50855
H	-5.58272	-1.42817	-1.58787
H	-3.13558	-1.44687	-1.56616
H	-6.71396	2.59783	-0.81282
H	-8.014	4.59718	-0.10515
H	-10.55141	2.09151	2.27054
H	-9.24382	0.1253	1.59148
H	-9.20368	0.02383	-1.75678
H	-10.52063	-1.98421	-2.42569
H	-8.05799	-4.41849	0.09745
H	-6.78383	-2.42951	0.77289
H	9.26497	0.02267	-1.72965
H	10.58548	2.03946	-2.36256
H	8.01503	4.46159	0.0636
H	6.73948	2.46726	0.70667
H	6.75721	-2.55768	-0.8805
H	8.04502	-4.55755	-0.14161
H	10.49592	-2.05062	2.3208
H	9.20132	-0.08687	1.60939
H	-11.46762	5.56606	2.44454
H	-10.79896	4.1505	3.2934
H	-11.89773	3.92523	1.90222
H	-10.59144	-6.30933	-1.61874

H	-9.98597	-5.68055	-0.06651
H	-8.85705	-5.95547	-1.42409
H	11.42811	-5.52042	2.5025
H	10.73124	-4.11134	3.33942
H	11.8623	-3.87546	1.97627
H	10.57579	6.37192	-1.58975
H	9.92654	5.75201	-0.05174
H	8.84122	5.99301	-1.45052

(TMS-thio)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -2843.9624482 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	0.89636	-2.46236	-0.40357
C	0.55432	-1.1796	-0.41693
C	-0.87273	-0.98236	-0.41606
N	-1.55373	-2.12114	-0.41541
S	-0.47287	-3.32471	-0.40202
C	1.47205	-0.06907	-0.42003
C	0.87912	1.17615	-0.41535
C	-0.55695	1.37202	-0.38756
C	-1.46053	0.32998	-0.4095
C	2.91082	-0.32177	-0.41945
C	-2.90909	0.51251	-0.42344
C	-3.62193	1.51265	-1.03993
C	-5.01448	1.41916	-0.80796
C	-5.37539	0.36065	-0.00837
S	-3.98439	-0.55058	0.43274
C	3.56037	-1.35606	-1.05064
C	4.95654	-1.3484	-0.82327
C	5.3816	-0.33075	-0.00187
S	4.04511	0.64263	0.47274
Si	7.13998	0.04411	0.55797
Si	-7.10727	-0.11179	0.55648
C	-7.17213	-0.05196	2.42925
C	-8.28807	1.13376	-0.1956
C	-7.48811	-1.84781	-0.04195
C	7.18065	0.07118	2.43205
C	8.22858	-1.32357	-0.11909
C	7.654	1.71224	-0.12335
C	1.67887	2.3674	-0.46972
N	2.28461	3.343	-0.52617
C	-1.0153	2.73005	-0.30754
N	-1.3554	3.82614	-0.23844
H	-3.1648	2.28074	-1.64722
H	-5.73165	2.11694	-1.22083
H	3.04614	-2.08931	-1.65364
H	5.63248	-2.07782	-1.25106
H	-6.92245	0.94567	2.79714
H	-6.46405	-0.75794	2.87052
H	-8.17082	-0.30899	2.79183
H	-8.05995	2.14901	0.13768
H	-9.31502	0.90824	0.10259
H	-8.24611	1.11441	-1.28723

H	-6.78001	-2.57016	0.37203
H	-7.42933	-1.90824	-1.13092
H	-8.49282	-2.15213	0.26274
H	6.85329	-0.88554	2.84501
H	6.52413	0.84982	2.82865
H	8.19197	0.27136	2.79534
H	7.91739	-2.30217	0.25414
H	9.26636	-1.16484	0.18461
H	8.20272	-1.34903	-1.21119
H	6.99194	2.50457	0.23467
H	7.61825	1.71683	-1.21498
H	8.67277	1.96066	0.18551

(tolyl)$_2$DCBT Ground State XYZ from DFT Geometry Optimization
Energy = -1463.757354 Hartrees
No imaginary frequencies were observed

XYZ coordinates

N	1.32793	-2.31339	-0.15777
C	0.76327	-1.10972	-0.14816
C	-0.67484	-1.16011	-0.14812
N	-1.15329	-2.40109	-0.14603
S	0.12327	-3.3952	-0.15577
C	1.46803	0.13754	-0.1536
C	0.68667	1.26594	-0.17478
C	-0.76321	1.21512	-0.18239
C	-1.46573	0.03583	-0.15271
C	2.95049	0.17696	-0.17711
C	-2.94591	-0.04591	-0.15997
C	3.70634	-0.34959	0.88137
C	5.09585	-0.28072	0.78963
C	5.72518	0.28299	-0.31263
C	4.96731	0.80792	-1.35205
C	3.58344	0.75764	-1.27804
C	-3.72992	0.51629	0.85883
C	-5.11816	0.40277	0.75141
C	-5.71715	-0.23997	-0.32069
C	-4.92993	-0.80961	-1.31658
C	-3.55161	-0.71986	-1.22644
C	3.06583	-0.95728	2.10274
C	-3.14986	1.20925	2.06612
C	1.3095	2.56122	-0.17451
N	1.79076	3.60505	-0.17257
C	-1.47627	2.45953	-0.24734
N	-2.04175	3.45912	-0.29909
H	5.6925	-0.6707	1.60712
H	6.80708	0.32167	-0.35402
H	5.44747	1.25893	-2.21123
H	2.98067	1.16713	-2.0808
H	-5.73504	0.82853	1.53542
H	-6.79716	-0.30561	-0.37552
H	-5.38674	-1.32203	-2.15391
H	-2.92608	-1.16514	-1.99101
H	2.13022	-0.45595	2.35895
H	3.736	-0.88076	2.95923
H	2.84366	-2.01345	1.93395
H	-2.12358	0.90012	2.26686
H	-3.75027	0.98217	2.94798
H	-3.15258	2.29319	1.92752

5. Time-Correlated Single Photon Counting Kinetics/Fitting

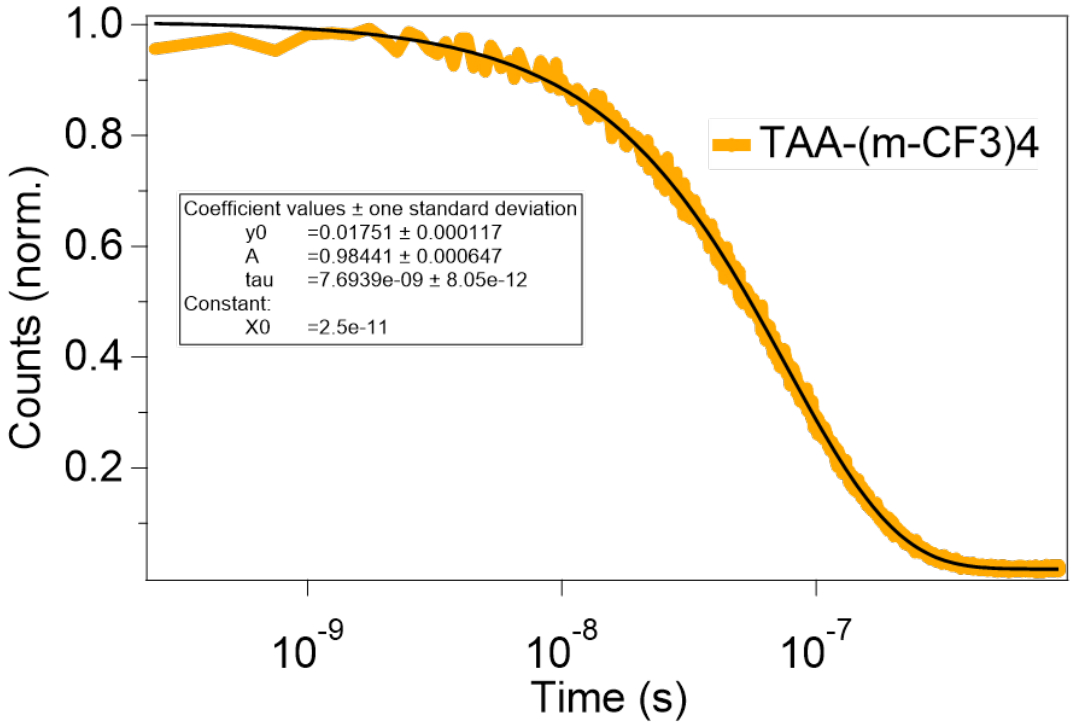

Figure S39. TCSPC decay and fitting parameters for $(TAA\text{-}(m\text{-}CF_3)_4)_2DCBT$.

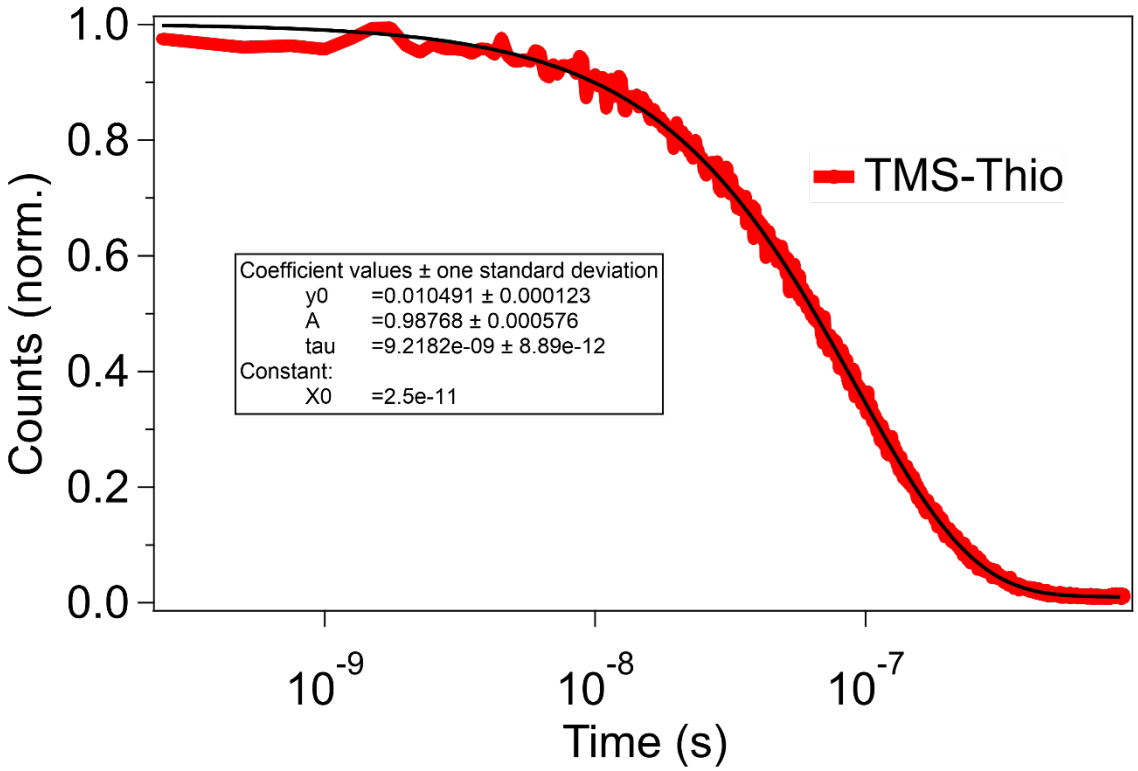

Figure S40. TCSPC decay and fitting parameters for $(TMS\text{-}thio)_2DCBT$.

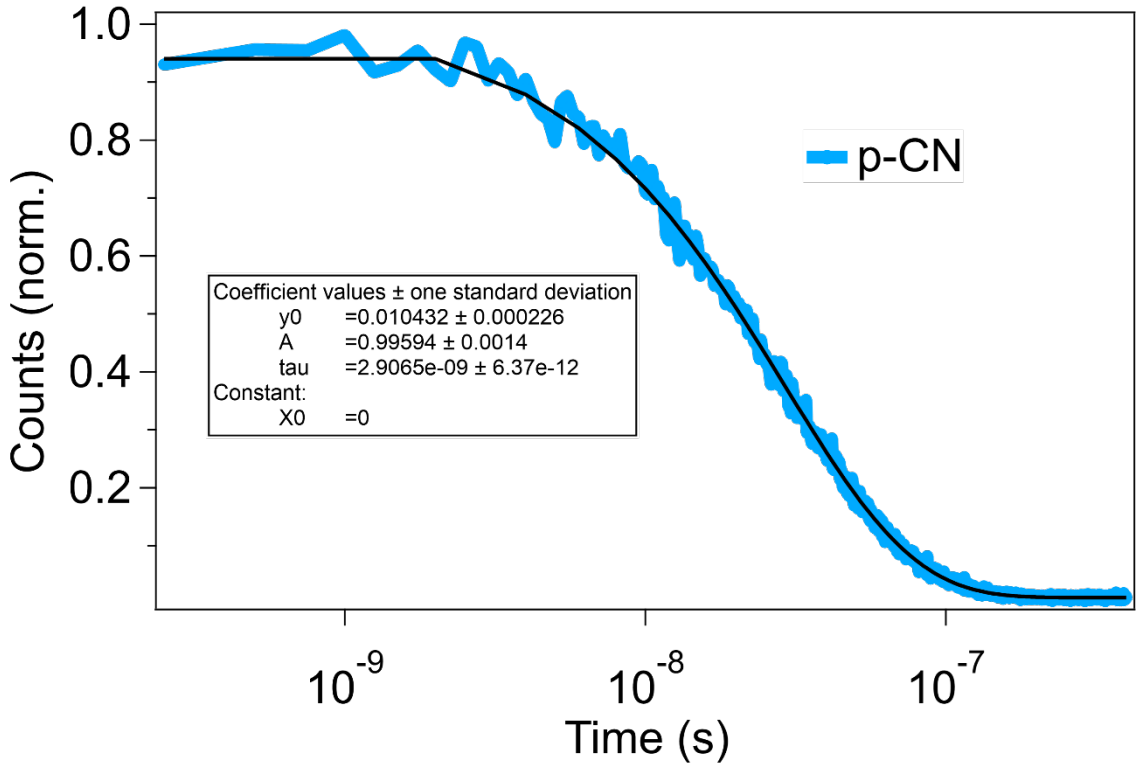

Figure S41. TCSPC decay and fitting parameters for (*p*-CN)$_2$DCBT.

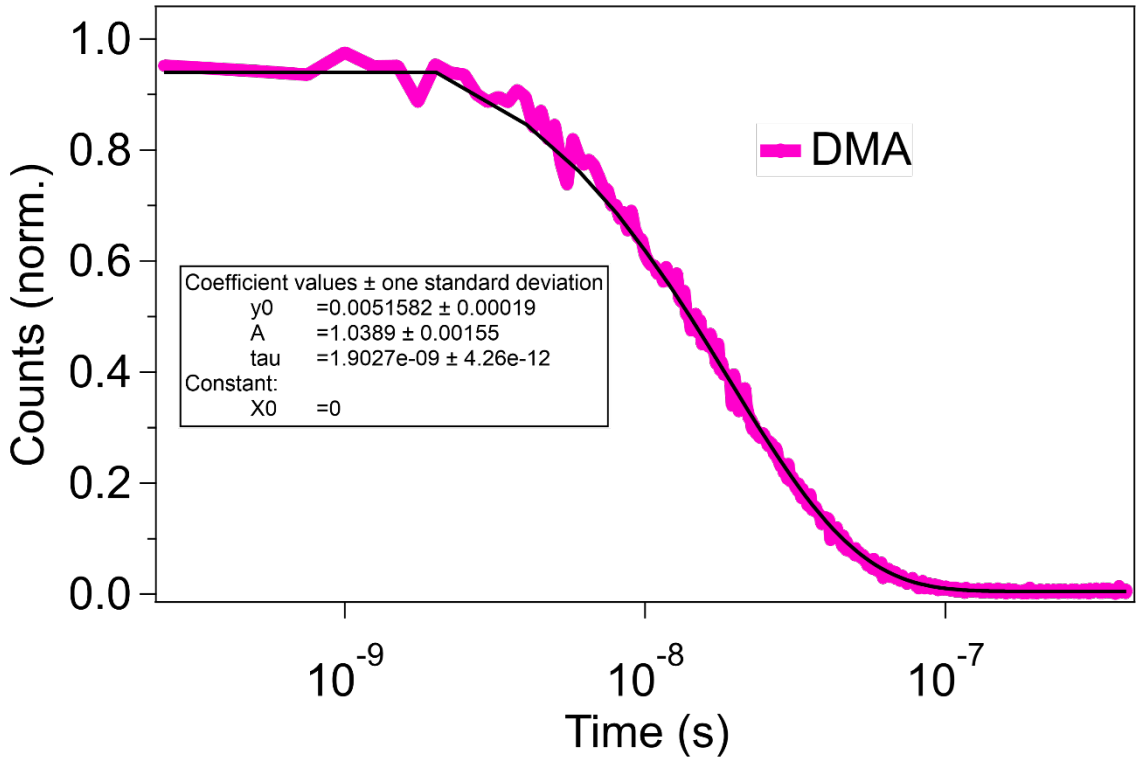

Figure S42. TCSPC decay and fitting parameters for (DMA)$_2$DCBT.

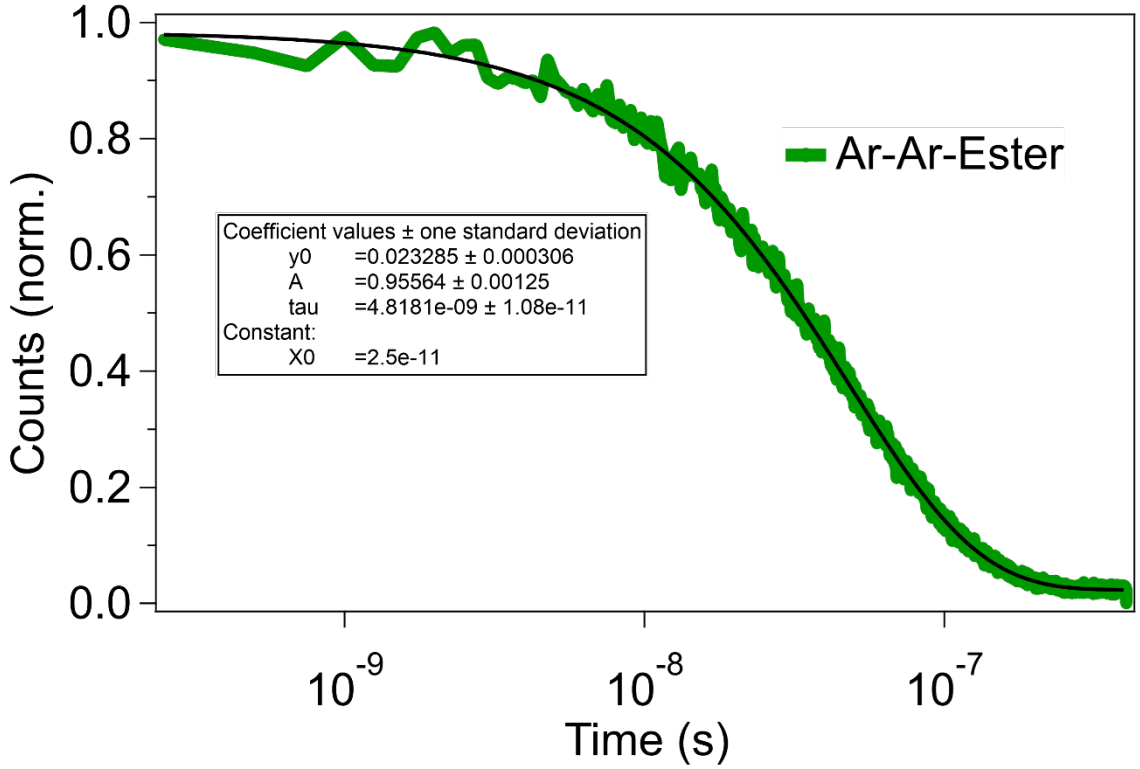

Figure S43. TCSPC decay and fitting parameters for (Ar-Ar-Ester)$_2$DCBT.

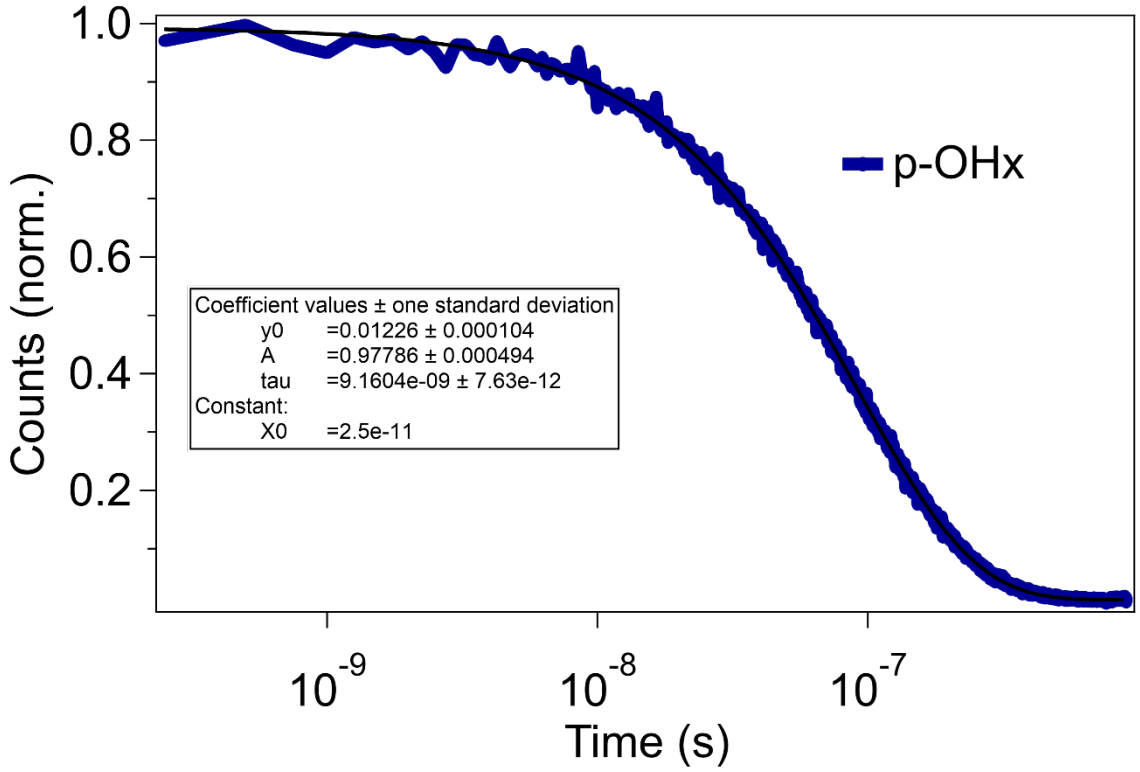

Figure S44. TCSPC decay and fitting parameters for (*p*-OHx)$_2$DCBT.

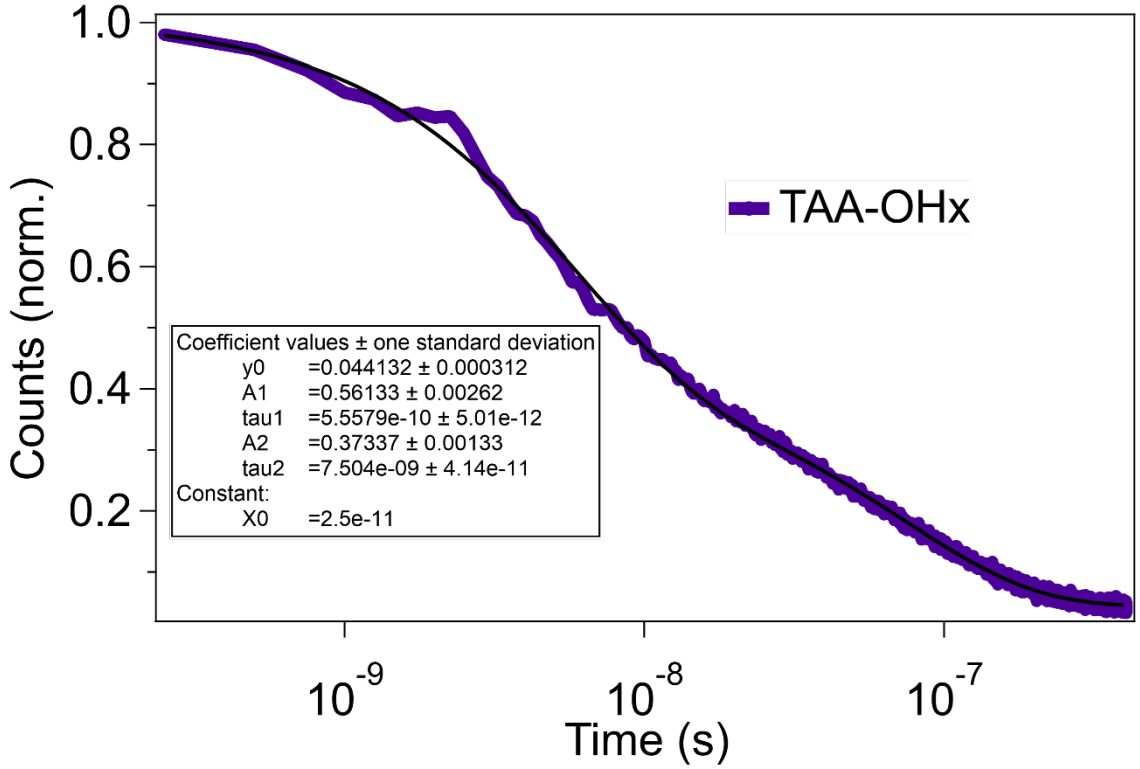

Figure S45. TCSPC decay and fitting parameters for $(TAA\text{-}OHx)_2DCBT$.

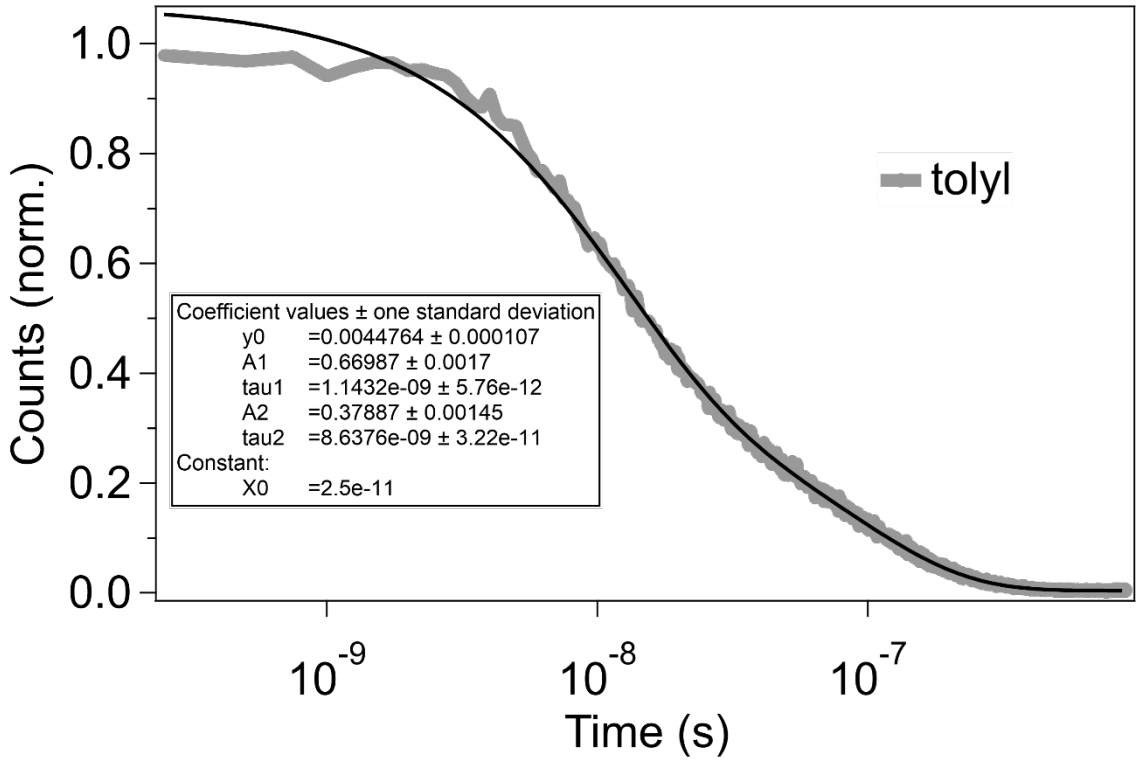

Figure S46. TCSPC decay and fitting parameters for $(tolyl)_2DCBT$.