Synthesis

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Supporting Information

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Thieme

Donor–Acceptor Molecular Triangles

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S2. UV/Vis Spectroscopy

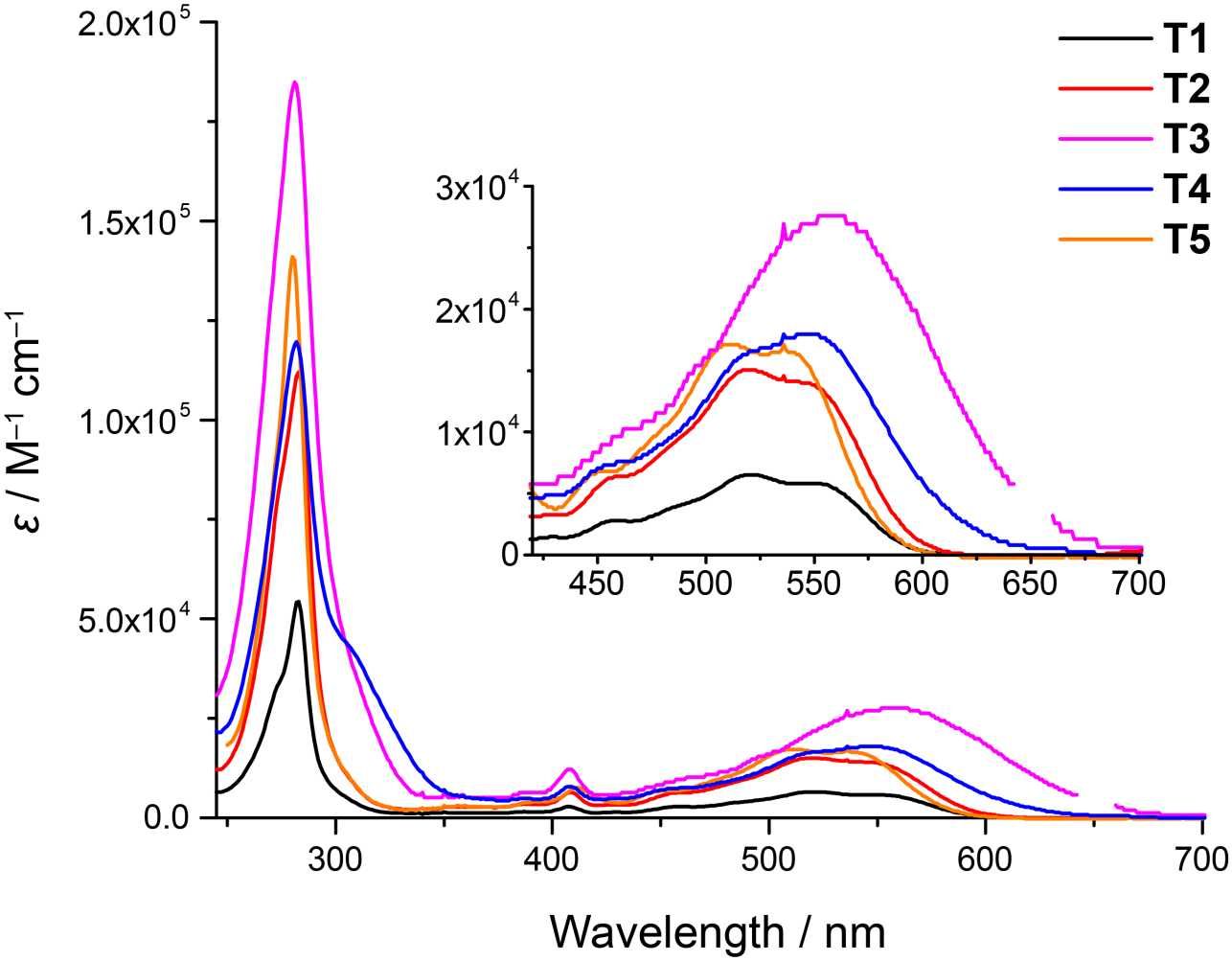


Figure S1 UV/Vis Absorption spectra of **T1**–**T5** in CH_2Cl_2 at room temperature

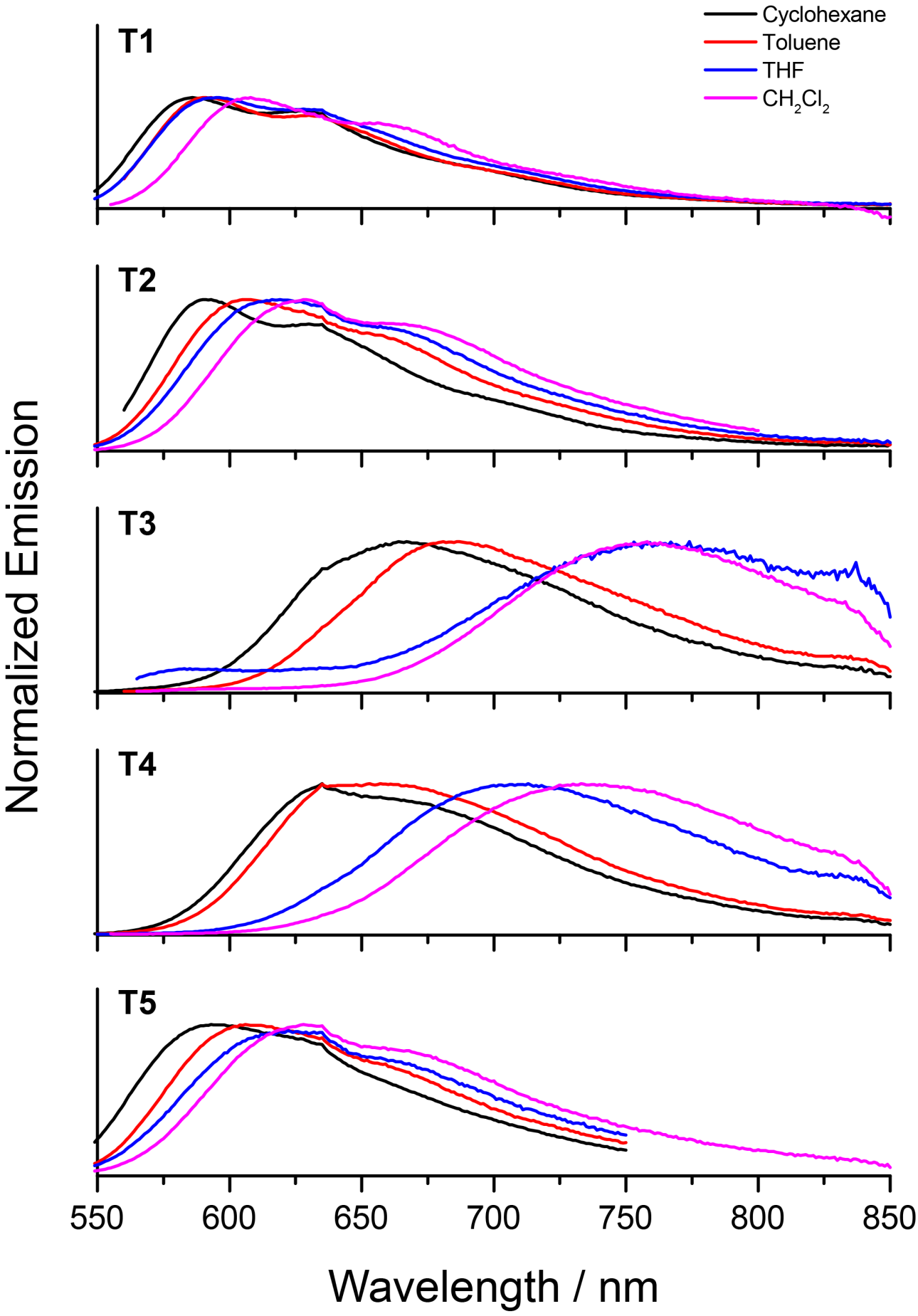


Figure S2 Fluorescence spectra of **T1**–**T5** in various solvents of different polarity

Table S1 Absorption and Emission Maxima, and Stokes Shifts[a] of **T1**–**T5** in Different Solvents

Compound		Cyclohexane	Toluene	THF	CH_2Cl_2
T1	$\lambda_{abs\text{-}max}$ (nm)	510 542	514 549	512 547	518 554
	$\lambda_{em\text{-}max}$ (nm)	585 628	590 630	596 628	608 657
	Stokes shift (nm)	43	41	49	54
T2	$\lambda_{abs\text{-}max}$ (nm)	509 546	515 546	510 548	522 551
	$\lambda_{em\text{-}max}$ (nm)	590 630	607 652	619 657	629 669
	Stokes shift (nm)	44	61	71	78
T3	$\lambda_{abs\text{-}max}$ (nm)	541	549	550	558
	$\lambda_{em\text{-}max}$ (nm)	664	686	774	758
	Stokes shift (nm)	123	137	224	200
T4	$\lambda_{abs\text{-}max}$ (nm)	540	542	542	554
	$\lambda_{em\text{-}max}$ (nm)	635	657	713	733
	Stokes shift (nm)	95	115	171	179
T5	$\lambda_{abs\text{-}max}$ (nm)	501 530	507 537	506 536	509 543
	$\lambda_{em\text{-}max}$ (nm)	593 628	606 657	625 663	628 662
	Stokes shift (nm)	63	69	89	85

[a] Stokes shift = $\lambda_{em\text{-}max}$(highest energy) – $\lambda_{abs\text{-}max}$(lowest energy).

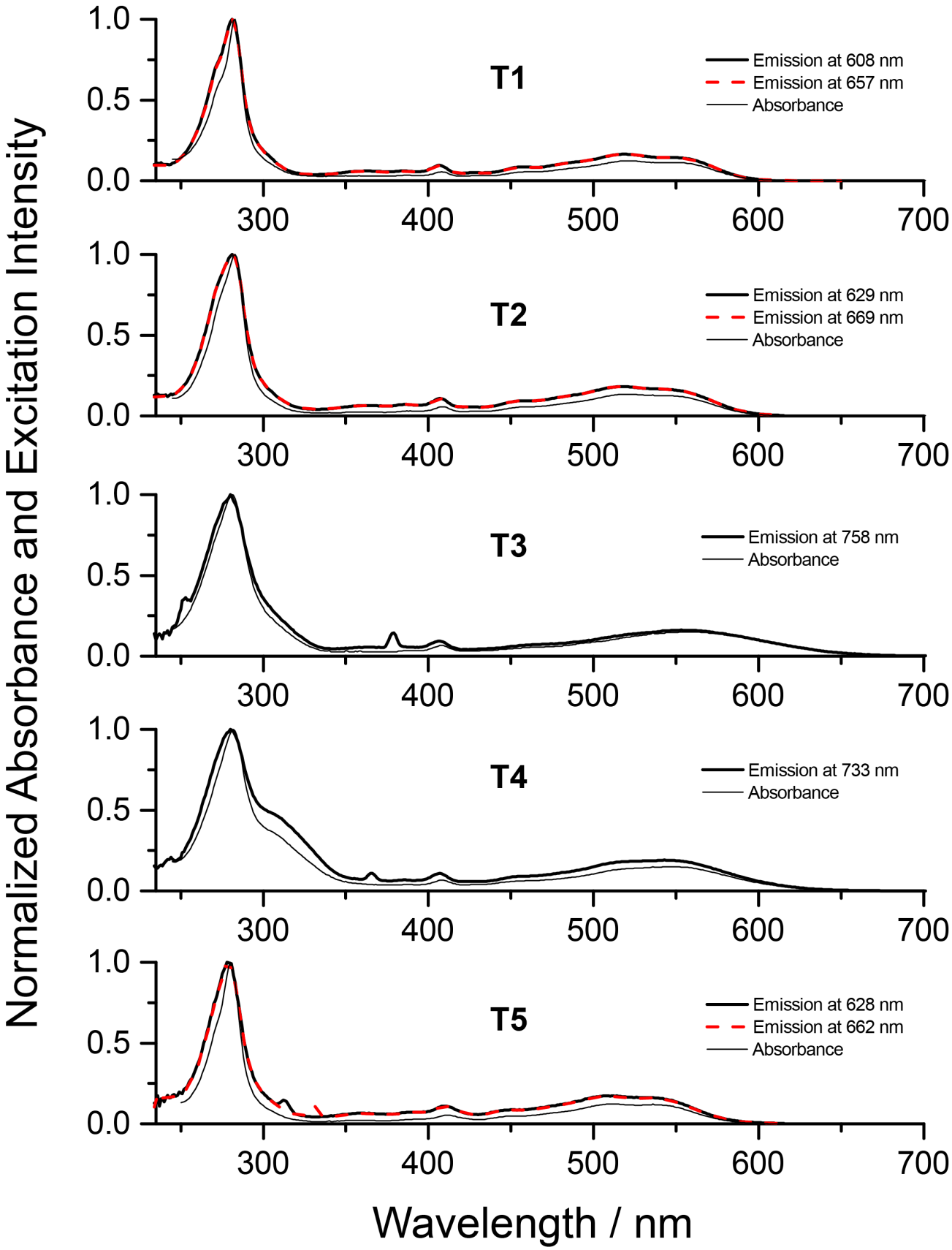


Figure S3 Normalized excitation and absorption spectra of **T1**–**T5** in CH_2Cl_2 at room temperature

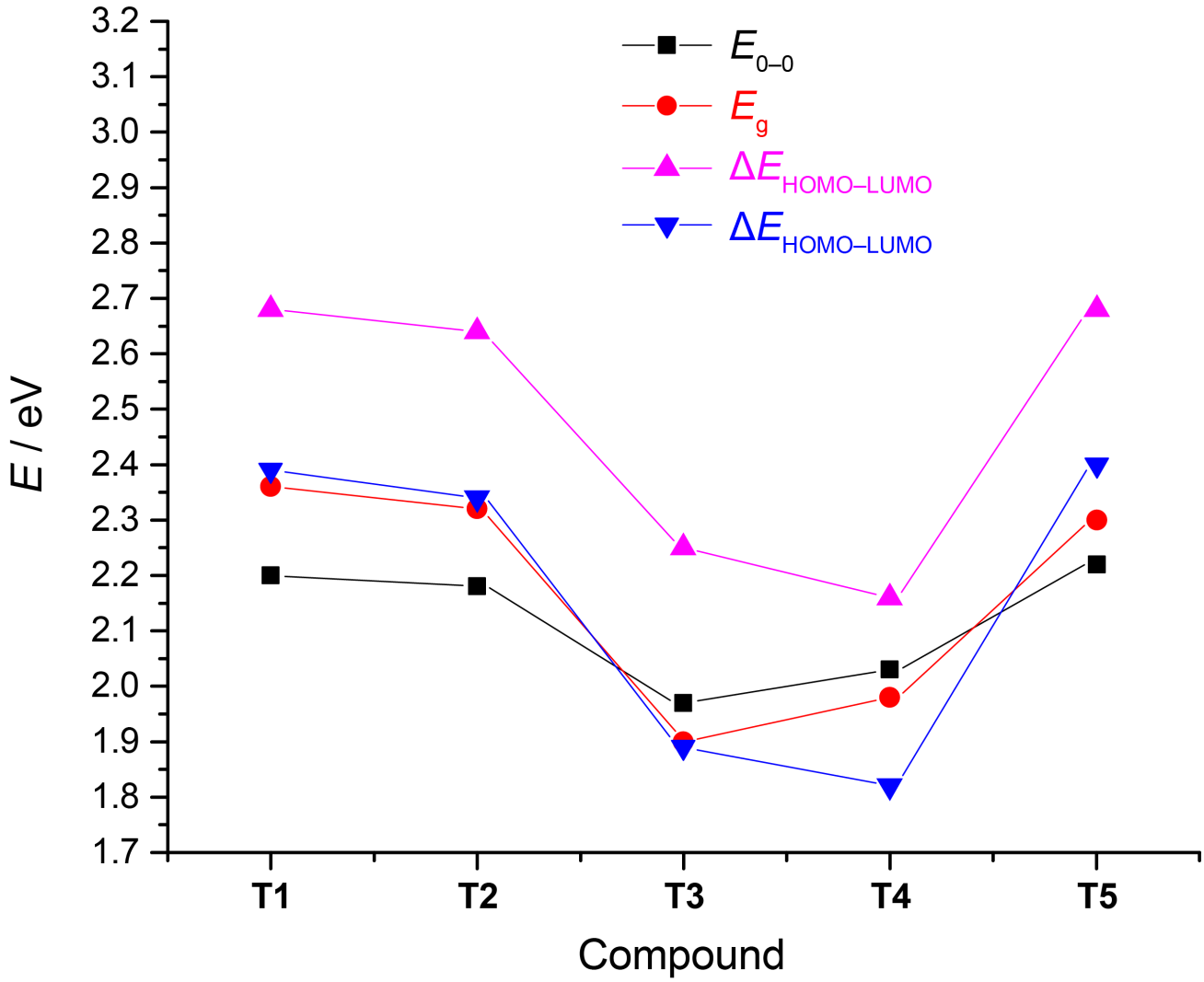


Figure S4 Comparison of E_{0-0} (black) obtained from UV/Vis spectroscopic measurements, E_g (red) obtained from cyclic voltammetry measurements, and $\Delta E_{HOMO-LUMO}$ obtained from DFT calculations (B3LYP/6-311+G(2d,p)/PCM(CH_2Cl_2) single point calculation in magenta and TD-B3LYP/6-31G(d)/PCM(CH_2Cl_2) calculation in blue) on B3LYP/6-31G(d) gas-phase geometries for **T1**–**T5**

S3. Cyclic Voltammetry

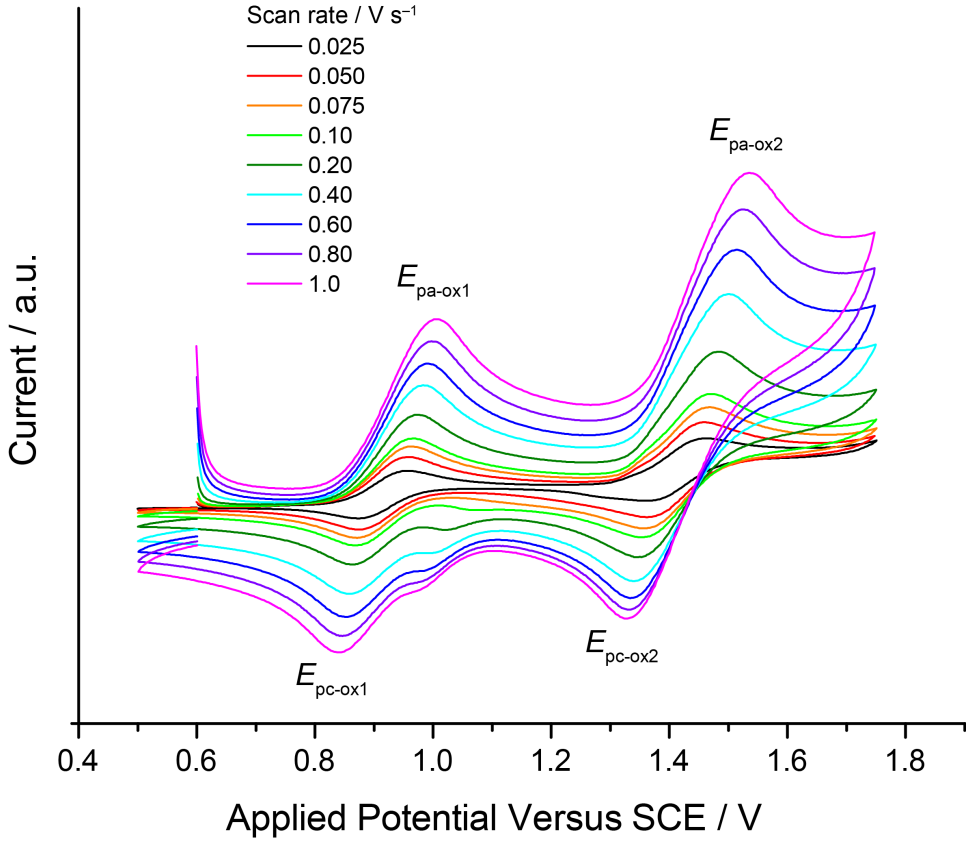


Figure S5 Cyclic voltammetry traces ($E > 0$V) for **T3** at different scan rates (CH_2Cl_2 / $TBAPF_6$)

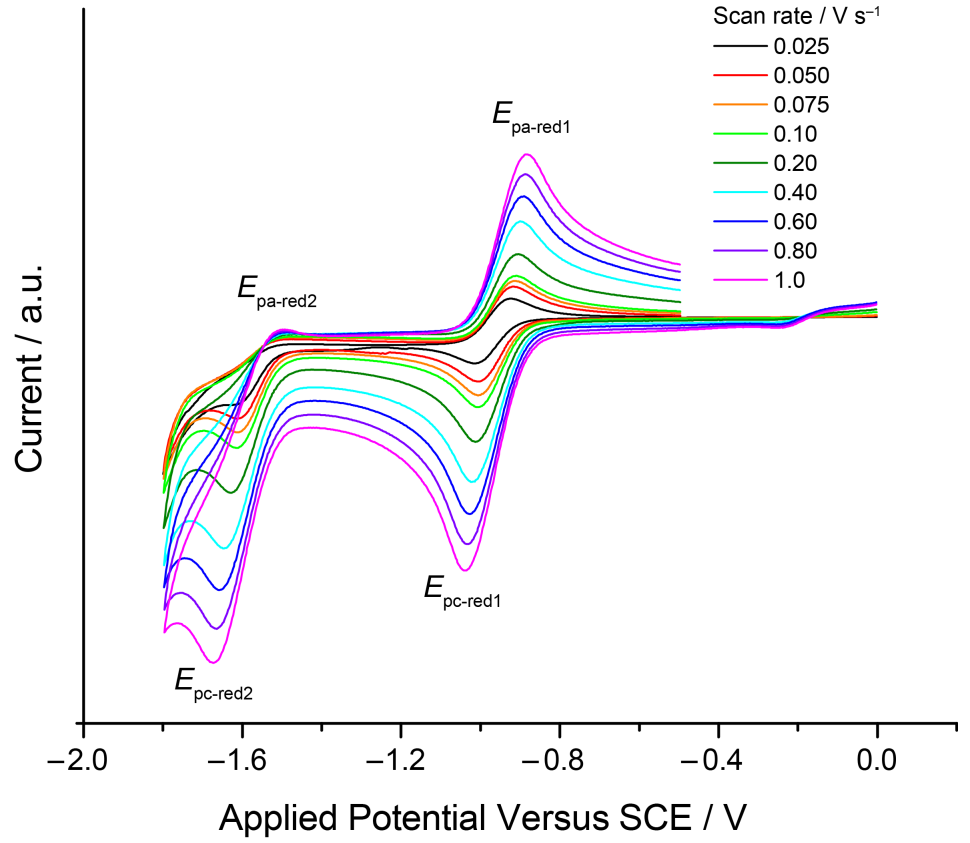


Figure S6 Cyclic voltammetry traces ($E < 0$V) for **T3** at different scan rates (CH_2Cl_2 / $TBAPF_6$)

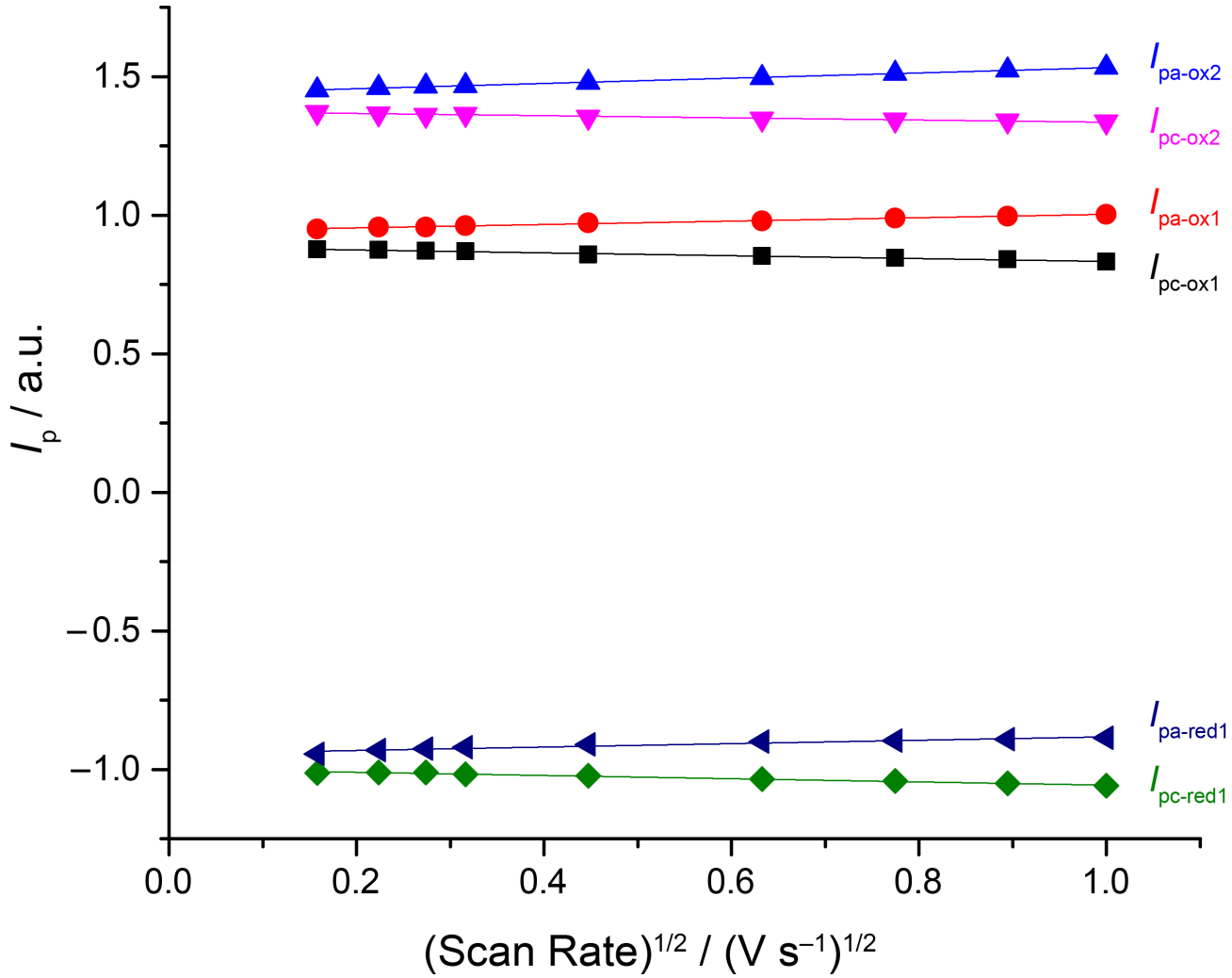


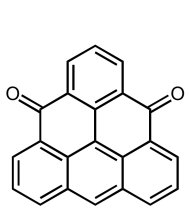
Figure S7 Plots of peak anodic (I_{pa}) and cathodic (I_{pc}) current versus (scan rate)$^{1/2}$ for the first ('ox1') and second ('ox2') oxidation and the first reduction ('red1') of **T3** by using the data from Figures S5 and S6

S4. Theoretical Calculations

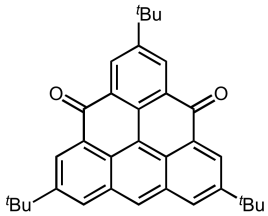
Molecules **T1**–**T5** were simplified to alleviate the computational costs by substitution of the three apex *tert*-butyl groups in positions 2, 6, and 10 (**$T1_H$**–**$T5_H$**) by hydrogen atoms. The effect of the *tert*-butyl groups on the calculated absorption spectra was tested on the parent triangulene-4,8-dione (**T0**) in the gas phase and CH_2Cl_2 as a model solvent. The results obtained with four different functionals (PBE1PBE, B3LYP, CAM-B3LYP, and M06-2X) are summarized in Table S2. The induction effect of the three *tert*-butyl groups causes a bathochromic shift of the energy of the first electronic transition by ~0.06 eV for all considered functionals irrespective of the solvation, and can therefore be neglected.

The first electronic transition in the series of donor–acceptor molecules **$T1_H$**–**$T5_H$** was calculated with the CAM-B3LYP and M06-2X functionals that showed[S1–S3] previously a balanced performance in evaluating both the local and charge-transfer (CT) electronic transitions. The results obtained from these calculations are summarized in Tables S3–S8.

Table S2 Comparison of Energies[a] of the First Electronic Transitions in **T0** and **T0-^{t}Bu$_3$**



T0



T0-^{t}Bu$_3$

Molecule	PBE1PBE		B3LYP		CAM-B3LYP		M06-2X	
	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)
T0-^{t}Bu$_3$ (gas)	494	2.5097	510	2.4327	445	2.7853	445	2.7886
T0-^{t}Bu$_3$ (PCM)	502	2.4680	518	2.3933	455	2.7267	454	2.7286
T0 (gas)	482	2.5699	498	2.4917	436	2.8409	435	2.8490
T0 (PCM)	490	2.5293	505	2.4527	446	2.7824	445	2.7887

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set in the gas phase and CH_2Cl_2 modeled as a polarizable continuum (PCM).

Table S3 The 10 Lowest Electronic Transitions[a] in $\mathbf{T1_H}$ in CH_2Cl_2 with Oscillator Strength Higher than 0.015 ($f > 0.015$)

Excited state	CAM-B3LYP			Excited state	M06-2X		
	λ (nm)	ΔE (eV)	f		λ (nm)	ΔE (eV)	f
1	457	2.7104	0.4396	1	457	2.7144	0.4315
2	350	3.5387	0.0377	4	352	3.5232	0.0472
5	336	3.6912	0.0952	5	333	3.7186	0.0818
8	295	4.1983	0.0196	8	294	4.2196	0.0134
9	285	4.3564	0.0333	9	285	4.3509	0.0333
11	262	4.7314	0.2958	10	273	4.5372	0.0038
16	240	5.1603	1.1426	11	263	4.7197	0.3356
17	240	5.1703	0.4324	15	241	5.1426	1.1057
18	231	5.3691	0.0157	17	239	5.1915	0.4466
19	229	5.4216	0.0455	18	230	5.3843	0.0444

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and CH_2Cl_2 modeled as a polarizable continuum.

Table S4 The 10 Lowest Electronic Transitions[a] in $\mathbf{T2_H}$ in CH_2Cl_2 with Oscillator Strength Higher than 0.015 ($f > 0.015$)

Excited state	CAM-B3LYP			Excited state	M06-2X		
	λ (nm)	ΔE (eV)	f		λ (nm)	ΔE (eV)	f
1	461	2.6885	0.4448	1	461	2.6903	0.4361
2	351	3.5275	0.0393	4	353	3.5109	0.0484
5	336	3.6908	0.0927	6	333	3.7202	0.0793
7	296	4.1953	0.0183	8	289	4.2956	0.0475
8	289	4.2878	0.0573	10	267	4.6392	0.1132
10	266	4.6693	0.1775	11	261	4.7432	0.2421
11	259	4.7886	0.1377	15	244	5.0915	0.0523
16	241	5.1486	0.8724	16	242	5.1338	1.0647
17	240	5.1578	0.3201	18	239	5.1882	0.445
18	240	5.1644	0.444	19	234	5.3091	0.043

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and CH_2Cl_2 modeled as a polarizable continuum.

Table S5 The 10 Lowest Electronic Transitions[a] in $\mathbf{T3_H}$ in CH_2Cl_2 with Oscillator Strength Higher than 0.015 ($f > 0.015$)

Excited state	CAM-B3LYP			Excited state	M06-2X		
	λ (nm)	ΔE (eV)	f		λ (nm)	ΔE (eV)	f
1	481	2.5772	0.4941	1	488	2.5397	0.4645
3	358	3.4648	0.0511	2	408	3.0372	0.0277
6	336	3.6943	0.0819	3	363	3.4185	0.0237
7	295	4.2065	0.0186	5	360	3.4471	0.0315
8	290	4.2774	0.0408	6	333	3.723	0.0715
11	271	4.5809	0.0378	9	288	4.3054	0.0165
12	263	4.7094	0.3378	11	272	4.5665	0.0295
13	258	4.8082	0.0447	12	265	4.6768	0.3861
14	255	4.8686	0.0406	13	258	4.8131	0.0449
16	246	5.0461	0.0165	14	256	4.8481	0.0932

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and CH_2Cl_2 modeled as a polarizable continuum.

Table S6 The 10 Lowest Electronic Transitions[a] in $\mathbf{T4_H}$ in CH_2Cl_2 with Oscillator Strength Higher than 0.015 ($f > 0.015$)

Excited state	CAM-B3LYP			Excited state	M06-2X		
	λ (nm)	ΔE (eV)	f		λ (nm)	ΔE (eV)	f
1	472	2.628	0.5524	1	477	2.5997	0.5266
3	353	3.5094	0.0432	5	356	3.4863	0.0492
6	336	3.6898	0.0858	6	333	3.7188	0.0738
7	296	4.1924	0.0236	8	294	4.2137	0.0172
8	290	4.2765	0.0478	9	289	4.2874	0.0423
10	281	4.4126	0.6266	10	284	4.3653	0.6408
11	275	4.5073	0.0182	13	271	4.5767	0.2206
13	269	4.6094	0.1947	14	269	4.6059	0.1493
14	267	4.6461	0.223	16	262	4.7238	0.3312
15	260	4.7601	0.233	18	249	4.9781	0.052

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and CH_2Cl_2 modeled as a polarizable continuum.

Table S7 The 10 Lowest Electronic Transitions[a] in $\mathbf{T5_H}$ in CH_2Cl_2 with Oscillator Strength Higher than 0.015 ($f > 0.015$)

Excited state	CAM-B3LYP			Excited state	M06-2X		
	λ (nm)	ΔE (eV)	f		λ (nm)	ΔE (eV)	f
1	456	2.7198	0.4129	1	455	2.7264	0.4048
4	344	3.6006	0.015	4	346	3.5871	0.037
5	338	3.6642	0.1231	6	335	3.6961	0.0857
8	294	4.214	0.07	8	296	4.1838	0.0431
11	260	4.7623	0.2279	9	283	4.3809	0.0203
12	249	4.9705	0.0184	11	261	4.7493	0.2811
16	240	5.1658	1.2704	15	241	5.1447	0.0199
17	239	5.1939	0.3639	16	241	5.1499	1.2055
18	228	5.4317	0.0605	17	238	5.2091	0.3834
21	221	5.5996	0.1366	19	228	5.4309	0.1006

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and CH_2Cl_2 modeled as a polarizable continuum.

Table S8 Energies[a] of the Lowest Electronic Transition in $\mathbf{T1_H}$– $\mathbf{T5_H}$ in different solvents

	CAM-B3LYP						M06-2X					
	Toluene		CH_2Cl_2		DMSO		Toluene		CH_2Cl_2		DMSO	
	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)
$\mathbf{T1_H}$	459 (0.4483)	2.7029	457 (0.4396)	2.7104	457 (0.4393)	2.7112	458 (0.4399)	2.7084	457 (0.4315)	2.7144	457 (0.4314)	2.7148
$\mathbf{T2_H}$	462 (0.4535)	2.6829	461 (0.4448)	2.6885	461 (0.4447)	2.6884	461 (0.4443)	2.6868	461 (0.4361)	2.6903	461 (0.4361)	2.6896
$\mathbf{T3_H}$	478 (0.5105)	2.5961	481 (0.4941)	2.5772	483 (0.4893)	2.5669	482 (0.4933)	2.5733	488 (0.4645)	2.5397	491 (0.4540)	2.5235
$\mathbf{T4_H}$	471 (0.5617)	2.6306	472 (0.5524)	2.6280	472 (0.5514)	2.6250	475 (0.5462)	2.6117	477 (0.5266)	2.5997	478 (0.5212)	2.5932
$\mathbf{T5_H}$	457 (0.4240)	2.7113	456 (0.4129)	2.7198	456 (0.4119)	2.7208	456 (0.4156)	2.7191	455 (0.4048)	2.7264	455 (0.4039)	2.7270

[a] Calculated with the TD-DFT formalism with the 6-31G(d) basis set and solvent modeled as a polarizable continuum.

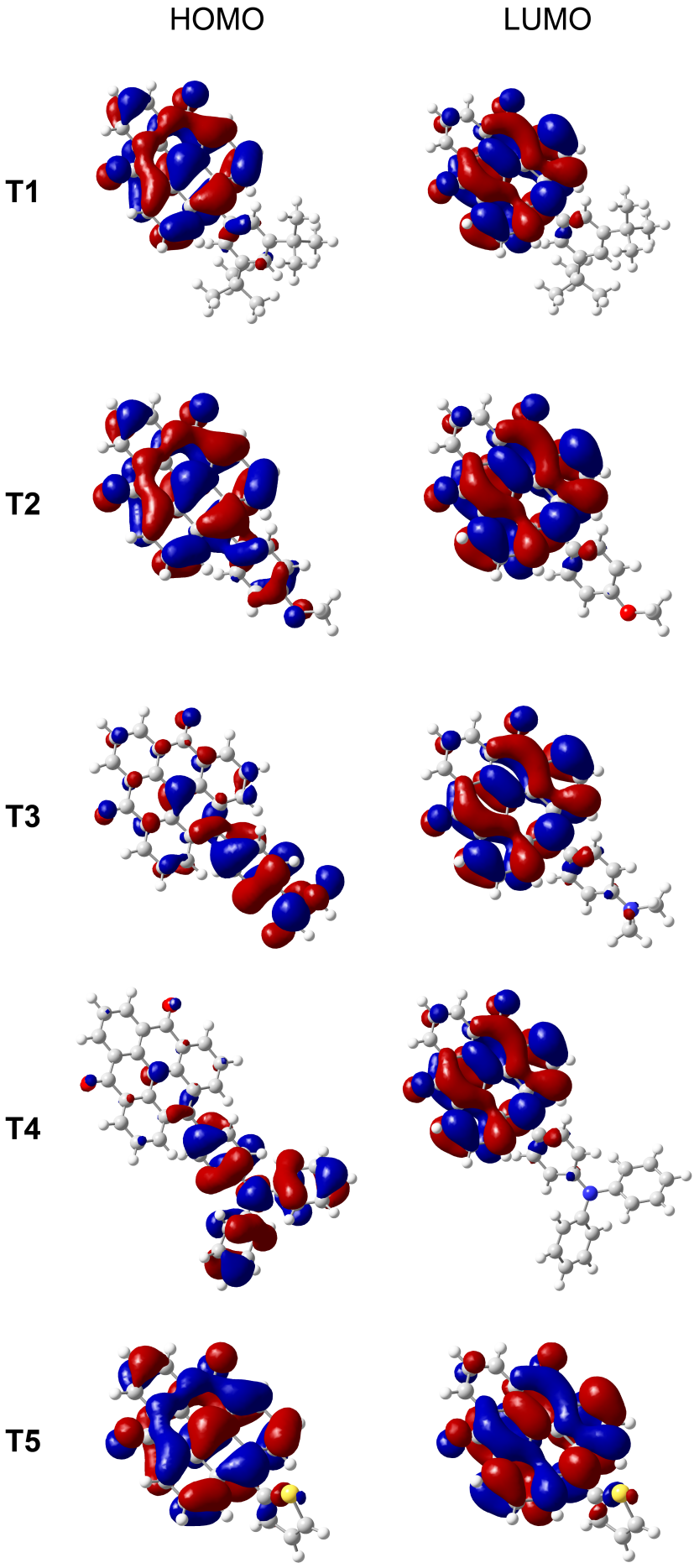
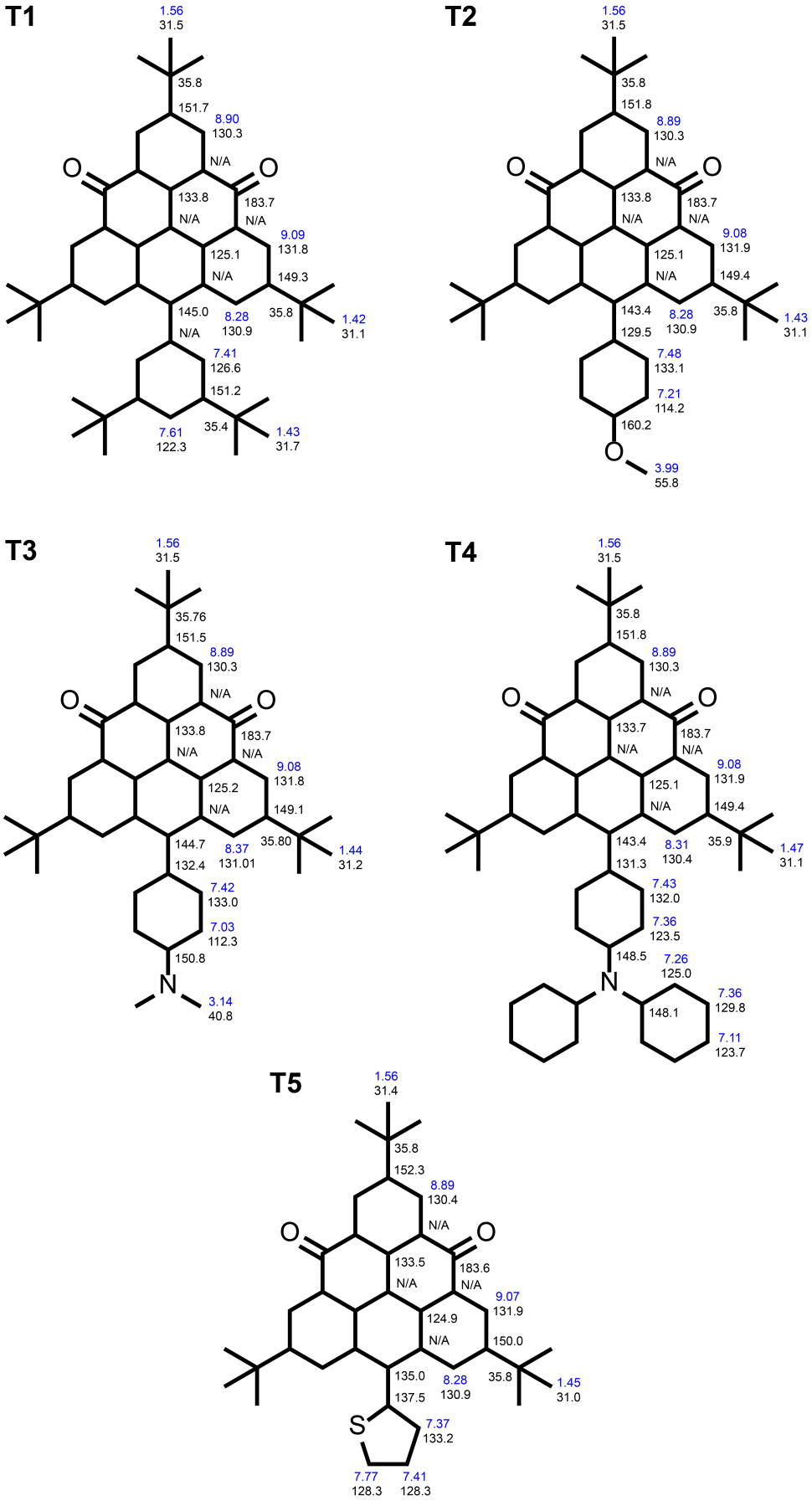


Figure S8 The HOMO and the LUMO of **T1**–**T5** (DFT, B3LYP/6-31G(d), gas phase)

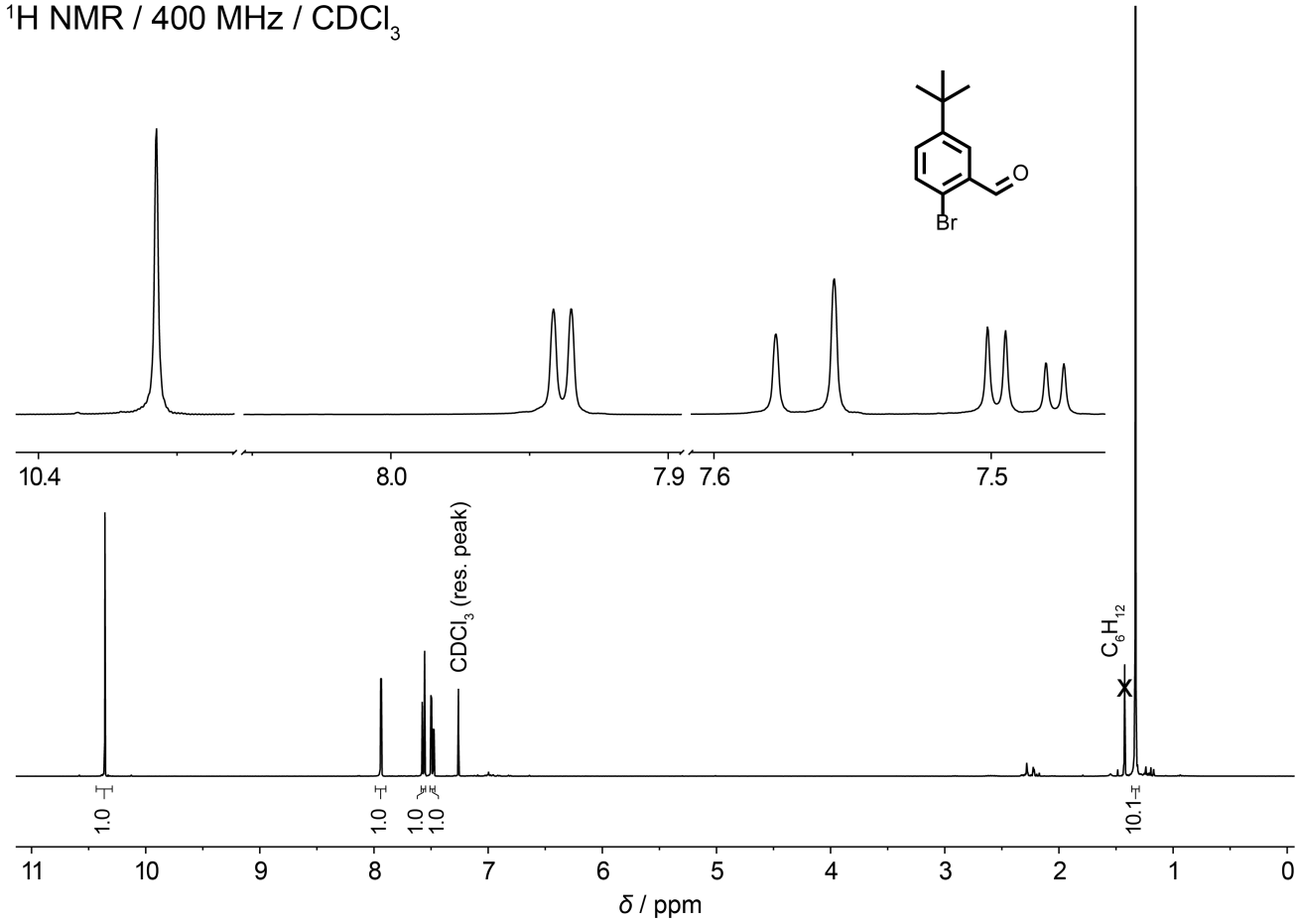
S5. Assignment of Proton and Carbon Resonances

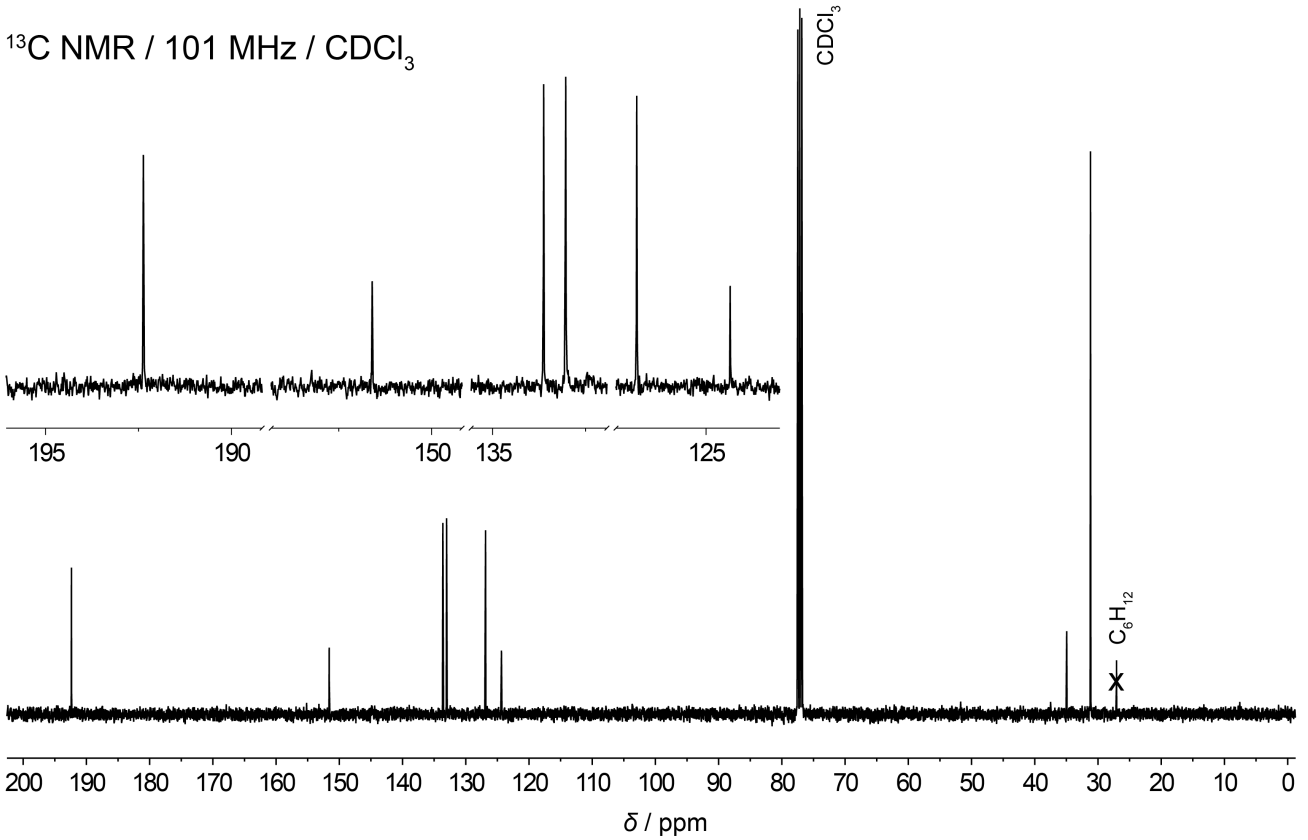
^{1}H / ^{13}C NMR



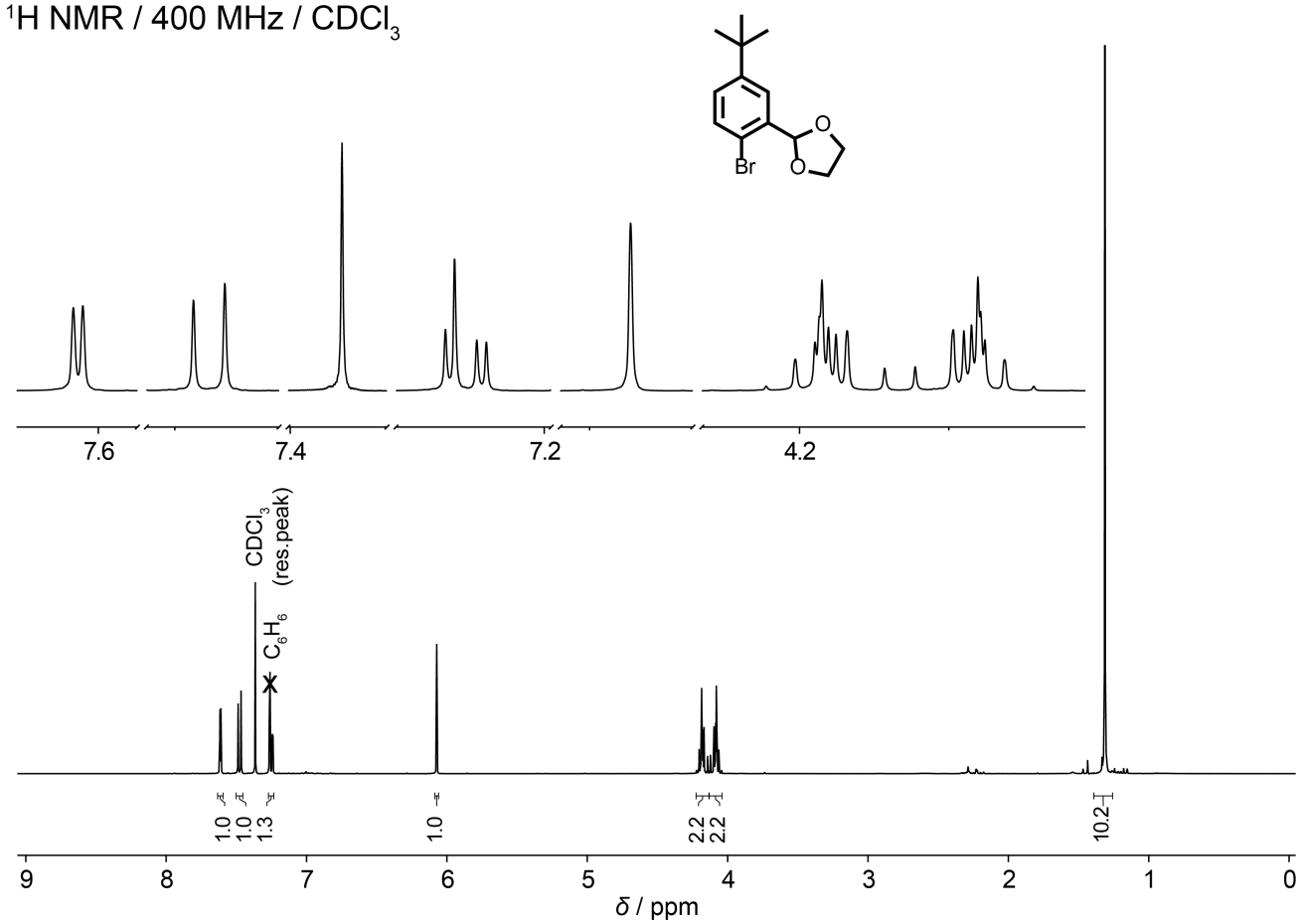
S6. Copies of the NMR Spectra

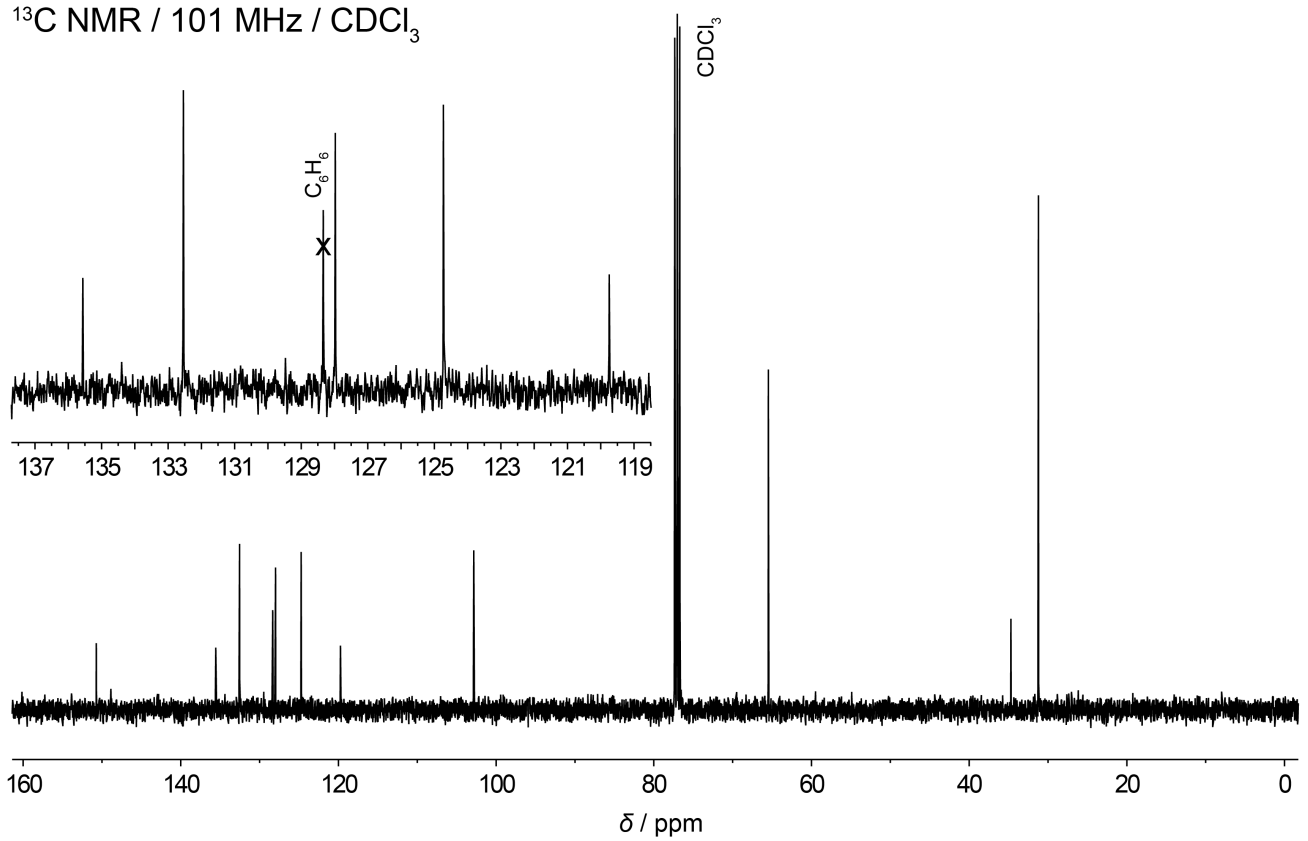
2-Bromo-5-(*tert*-butyl)benzaldehyde (2)



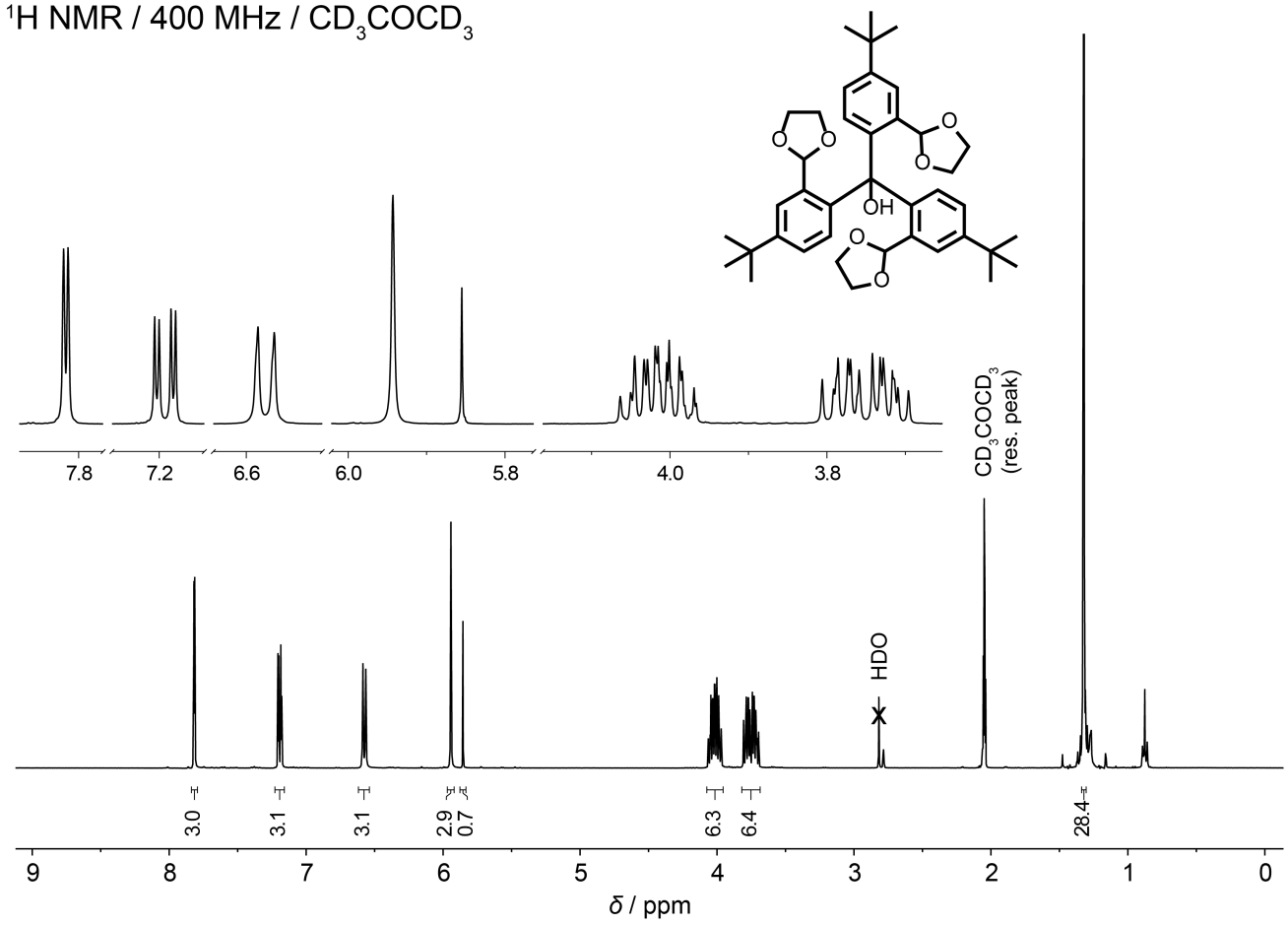


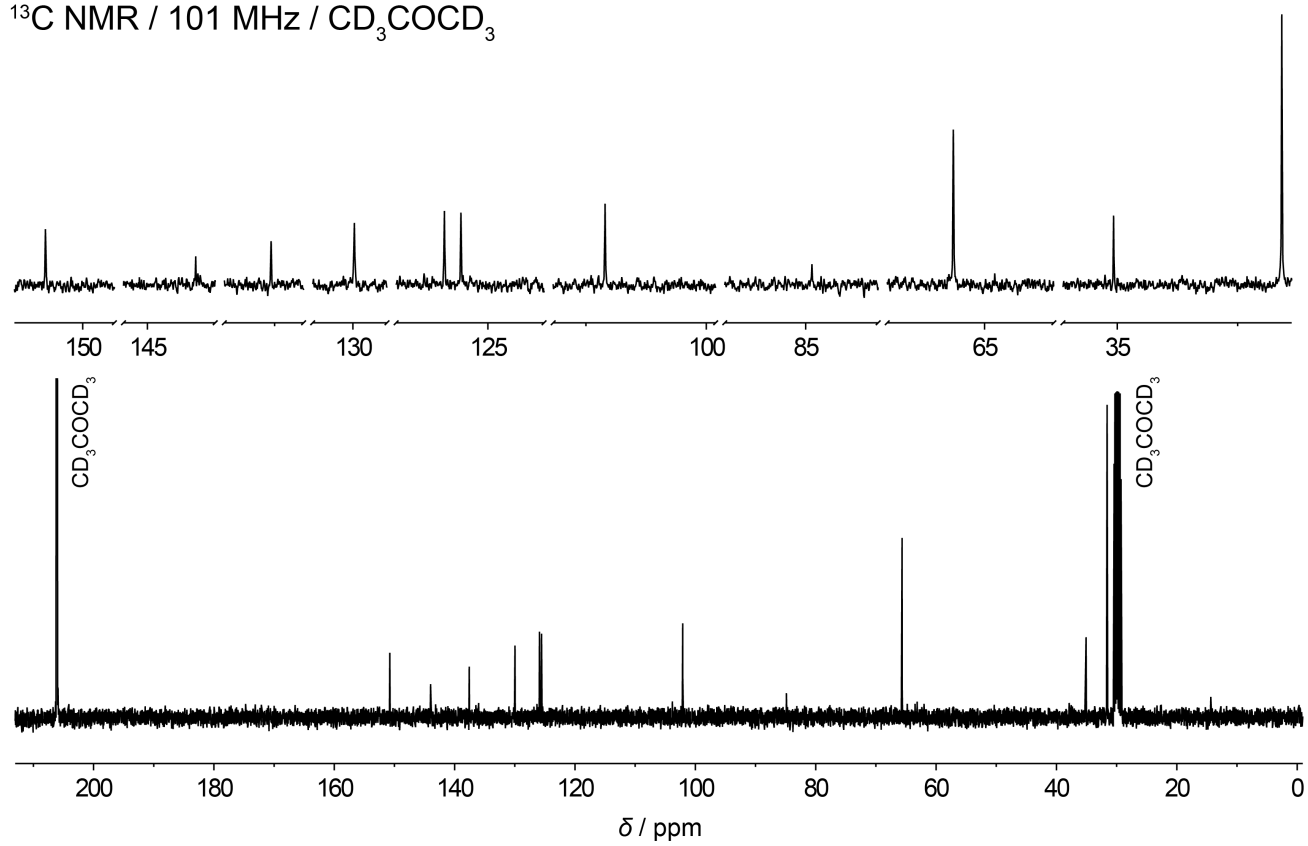
2-(2-Bromo-5-(*tert*-butyl)phenyl)-1,3-dioxolane (3)





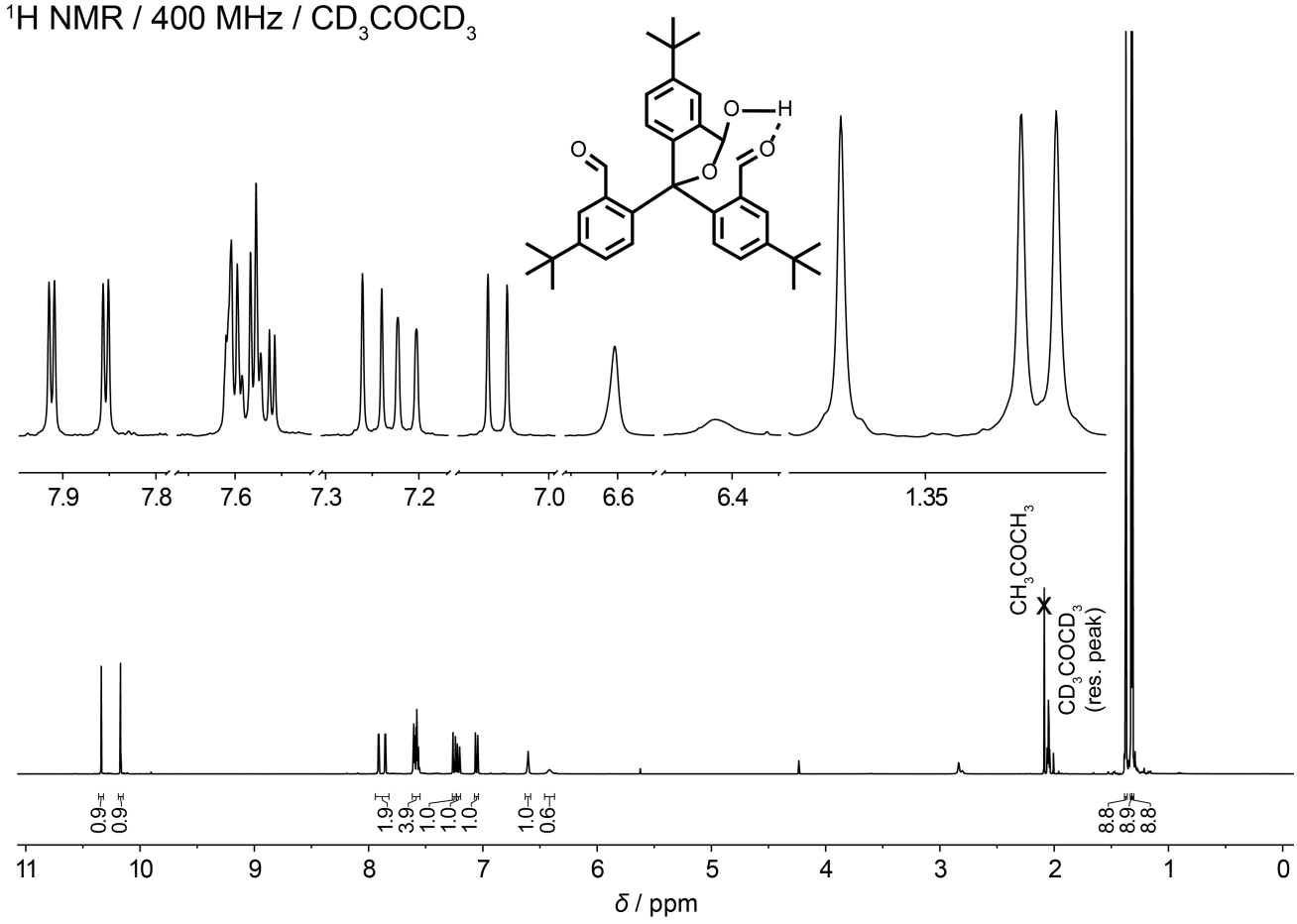
Tris(4-(*tert*-butyl)-2-(1,3-dioxolan-2-yl)phenyl)methanol (4)



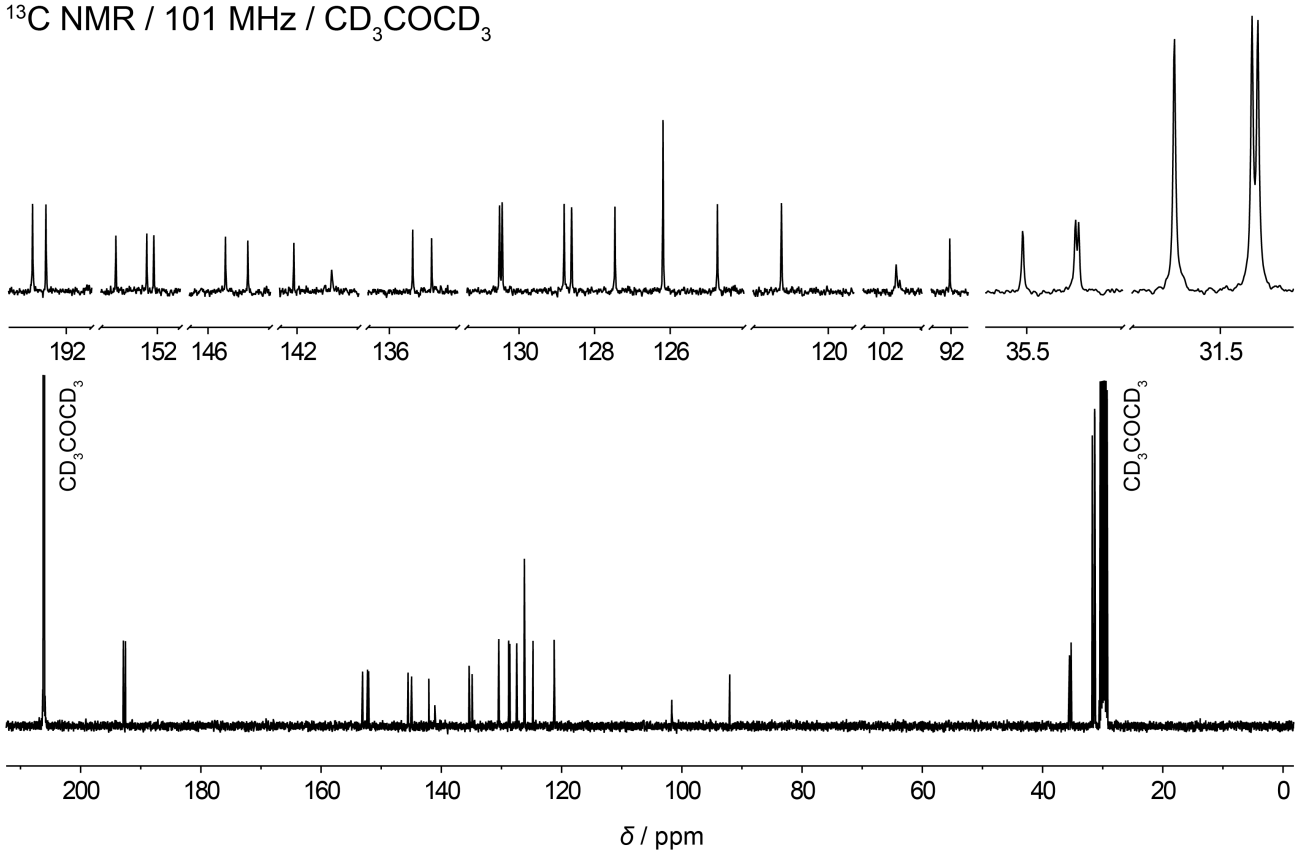


2,2'-(5-(*tert*-Butyl)-3-hydroxy-1,3-dihydroisobenzofuran-1,1-diyl)bis(5-(*tert*-butyl)benzaldehyde) (5)

^{1}H NMR / 400 MHz / CD_3COCD_3

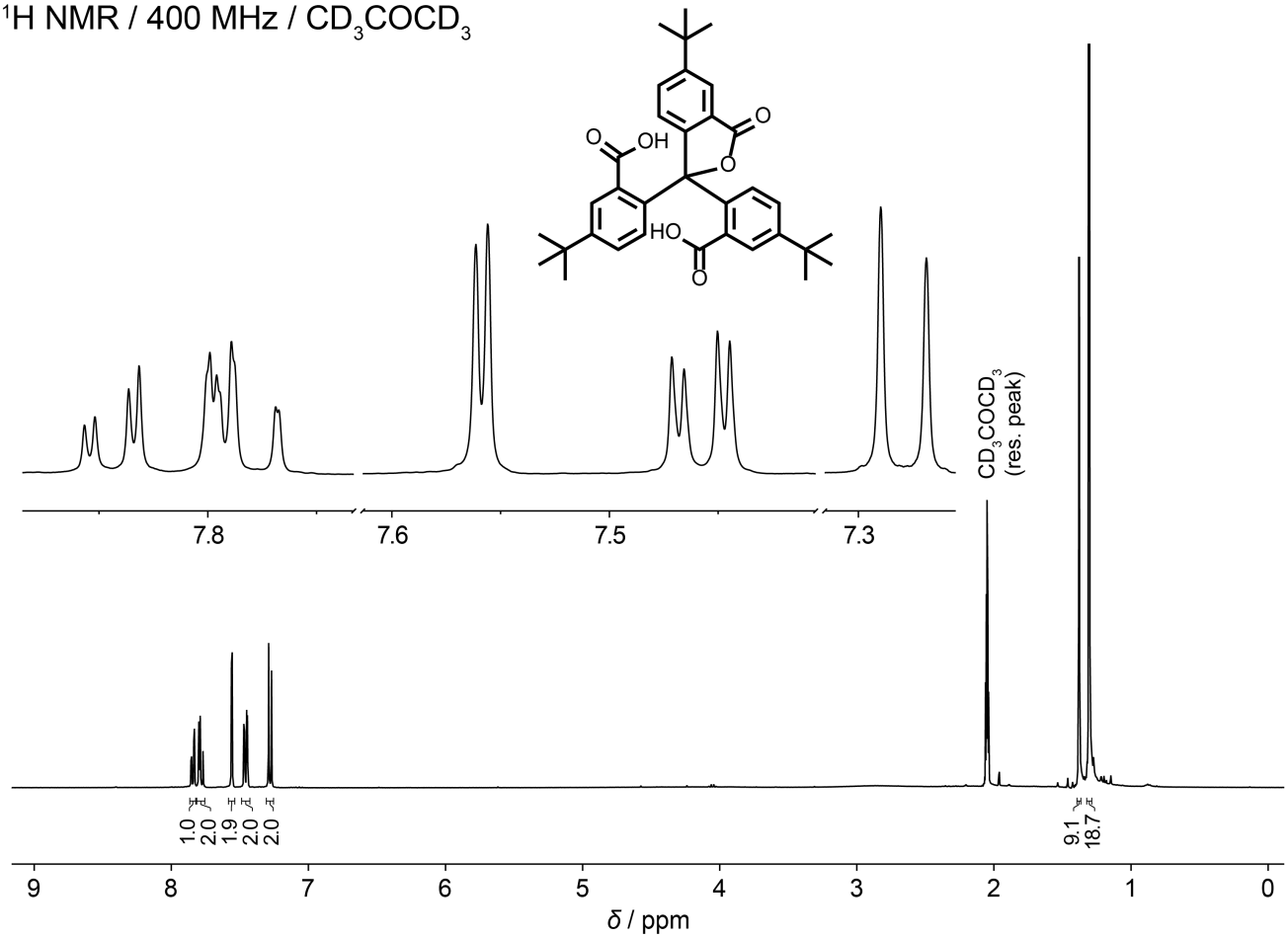


^{13}C NMR / 101 MHz / CD_3COCD_3

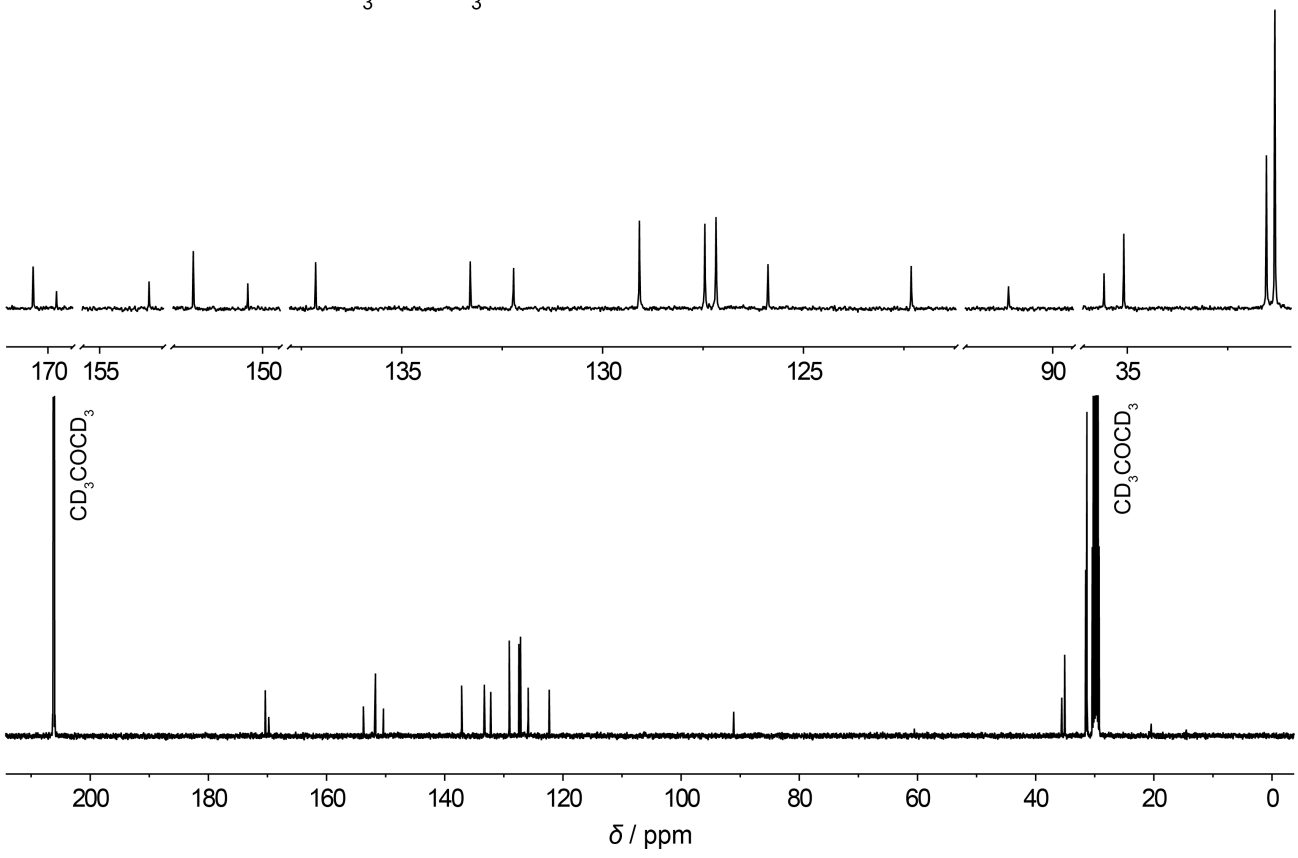


6,6'-(5-(*tert*-Butyl)-3-oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(3-(*tert*-butyl)benzoic acid) (6)

^{1}H NMR / 400 MHz / CD_3COCD_3

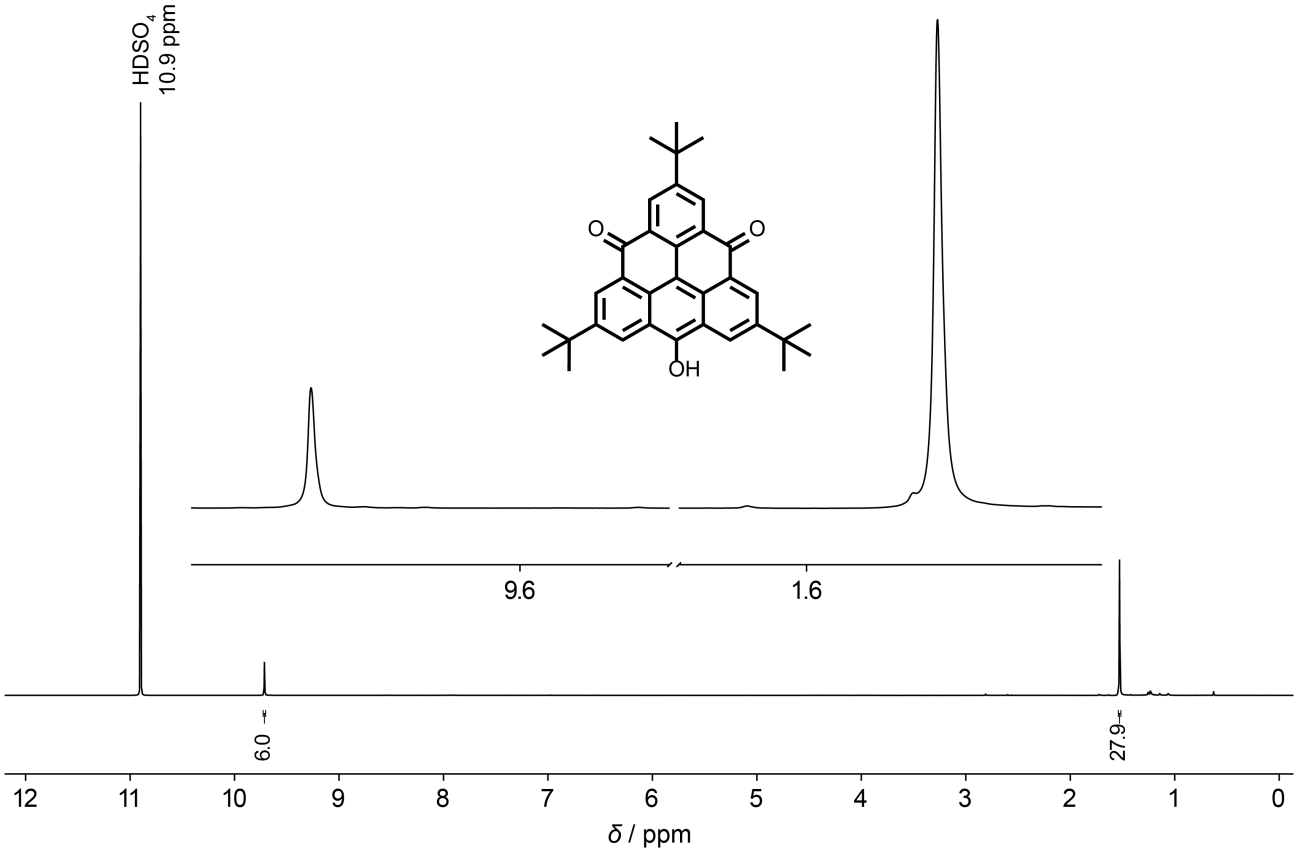


^{13}C NMR / 101 MHz / CD_3COCD_3

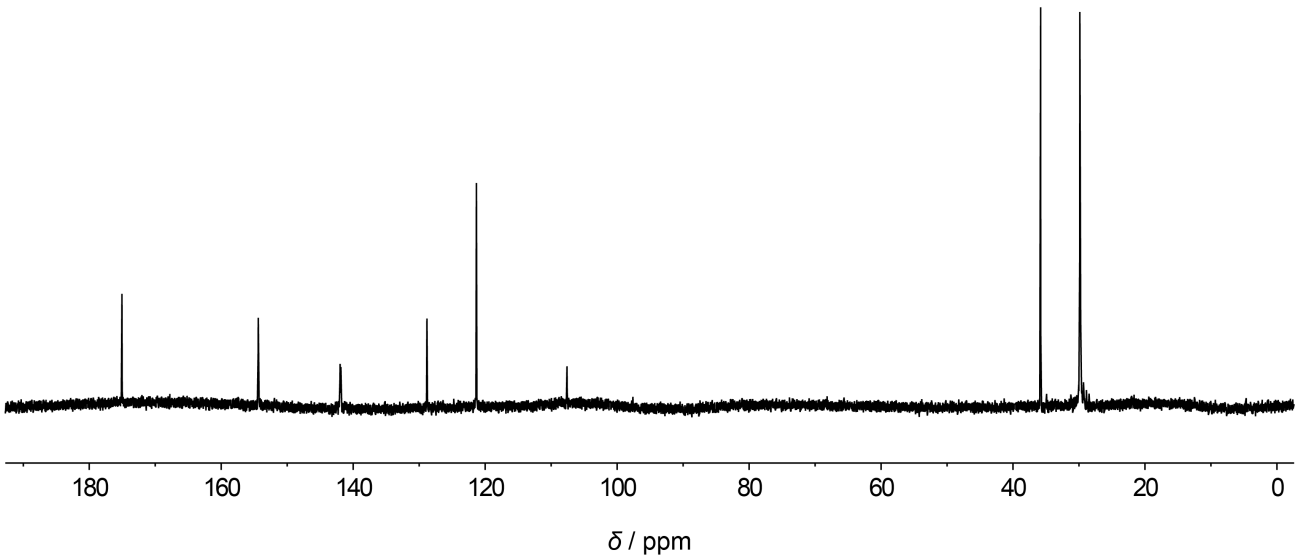


2,6,10-Tri-*tert*-butyl-12-hydroxydibenzo[*cd*,*mn*]pyrene-4,8-dione (7)

^{1}H NMR / 600 MHz / D_2SO_4

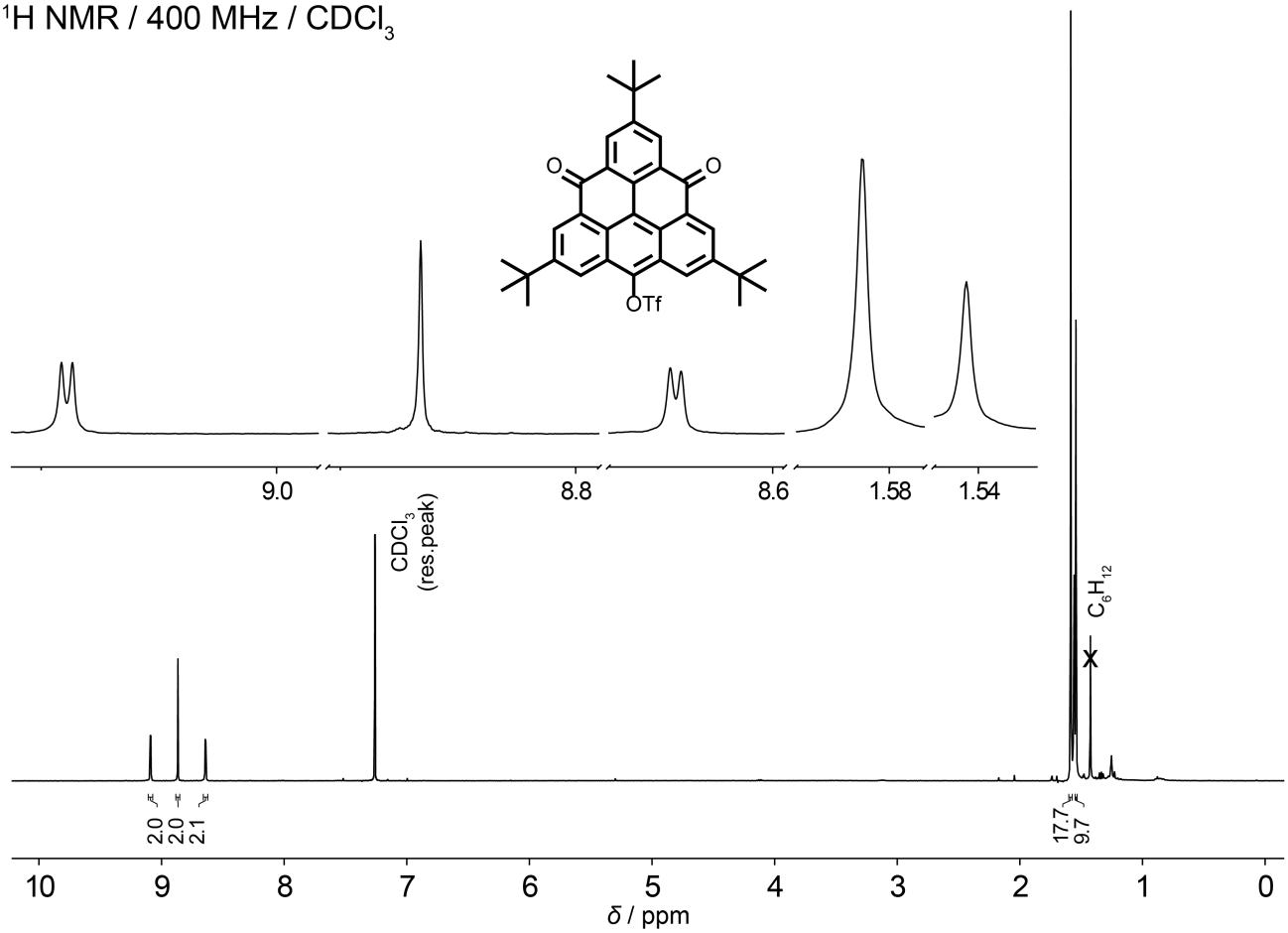


^{13}C NMR / 151 MHz / D_2SO_4

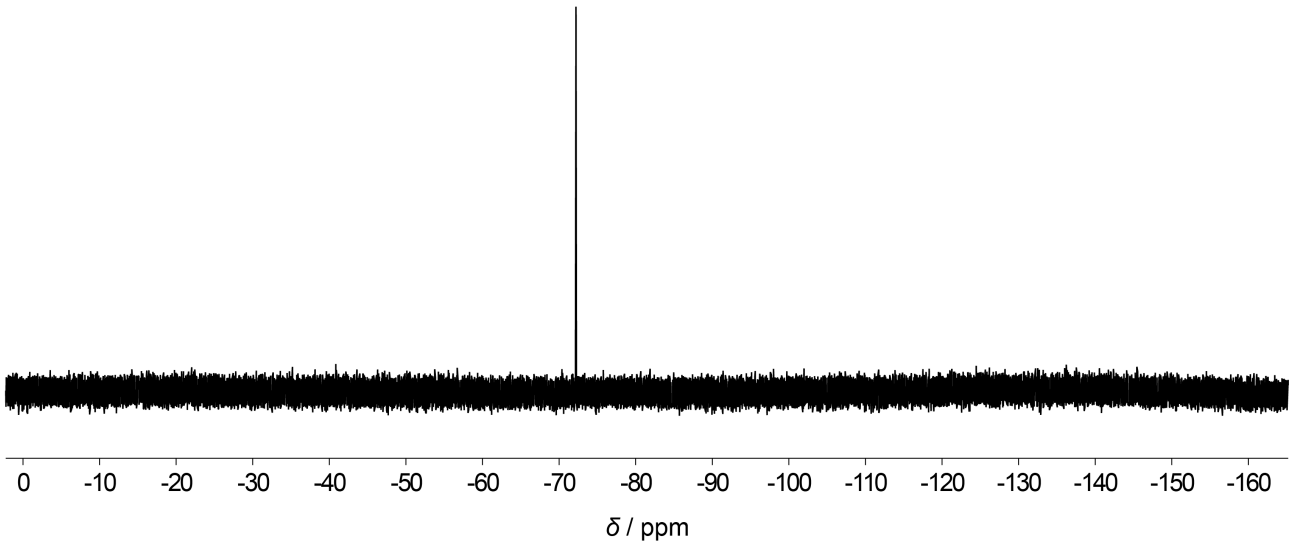


2,6,10-Tri-*tert*-butyl-8,12-dioxo-8,12-dihydrodibenzo[*cd*,*mn*] pyren-4-yl trifluoromethanesulfonate (8)

^{1}H NMR / 400 MHz / $CDCl_3$

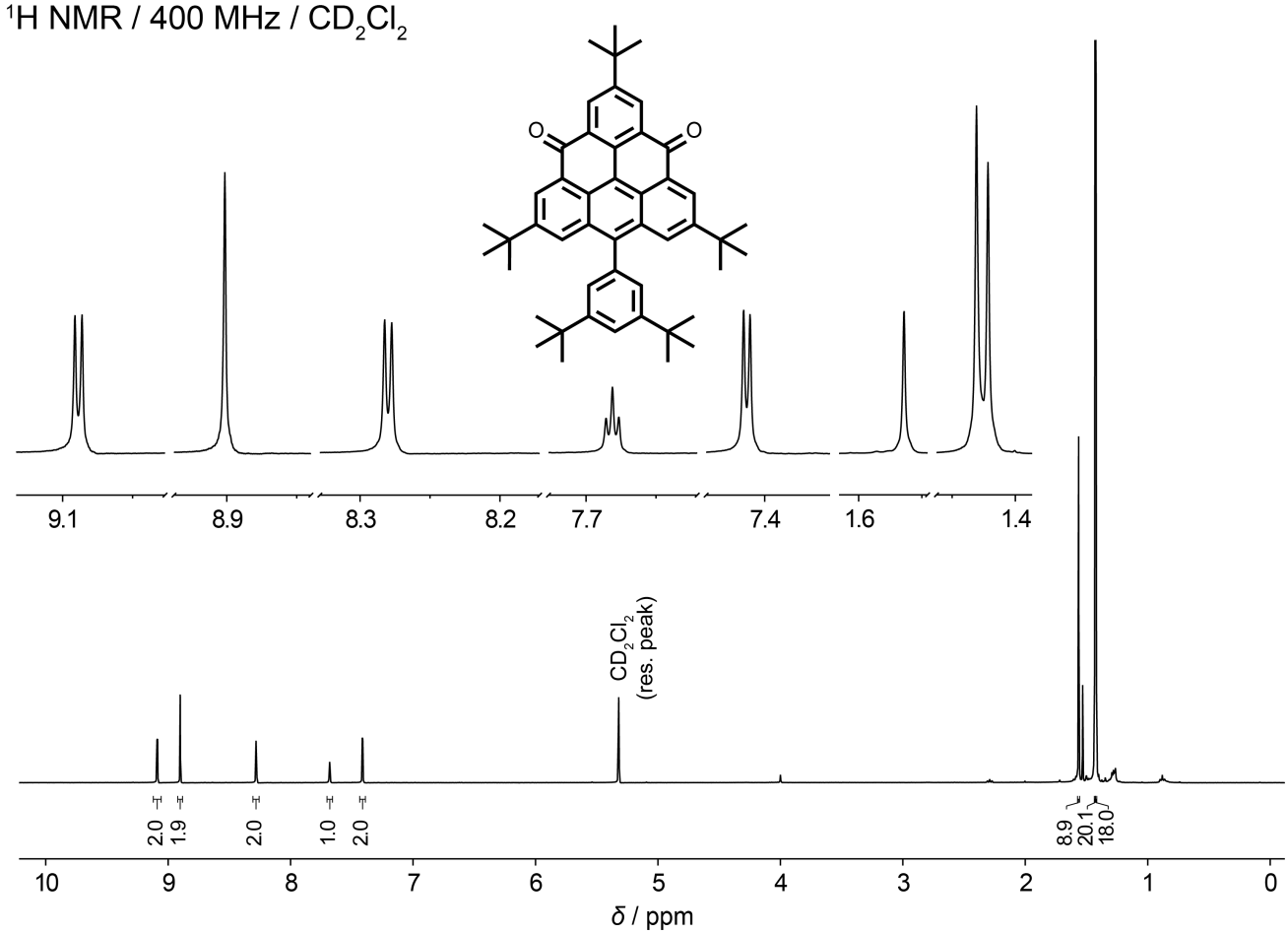


^{19}F NMR / 376.5 MHz / $CDCl_3$

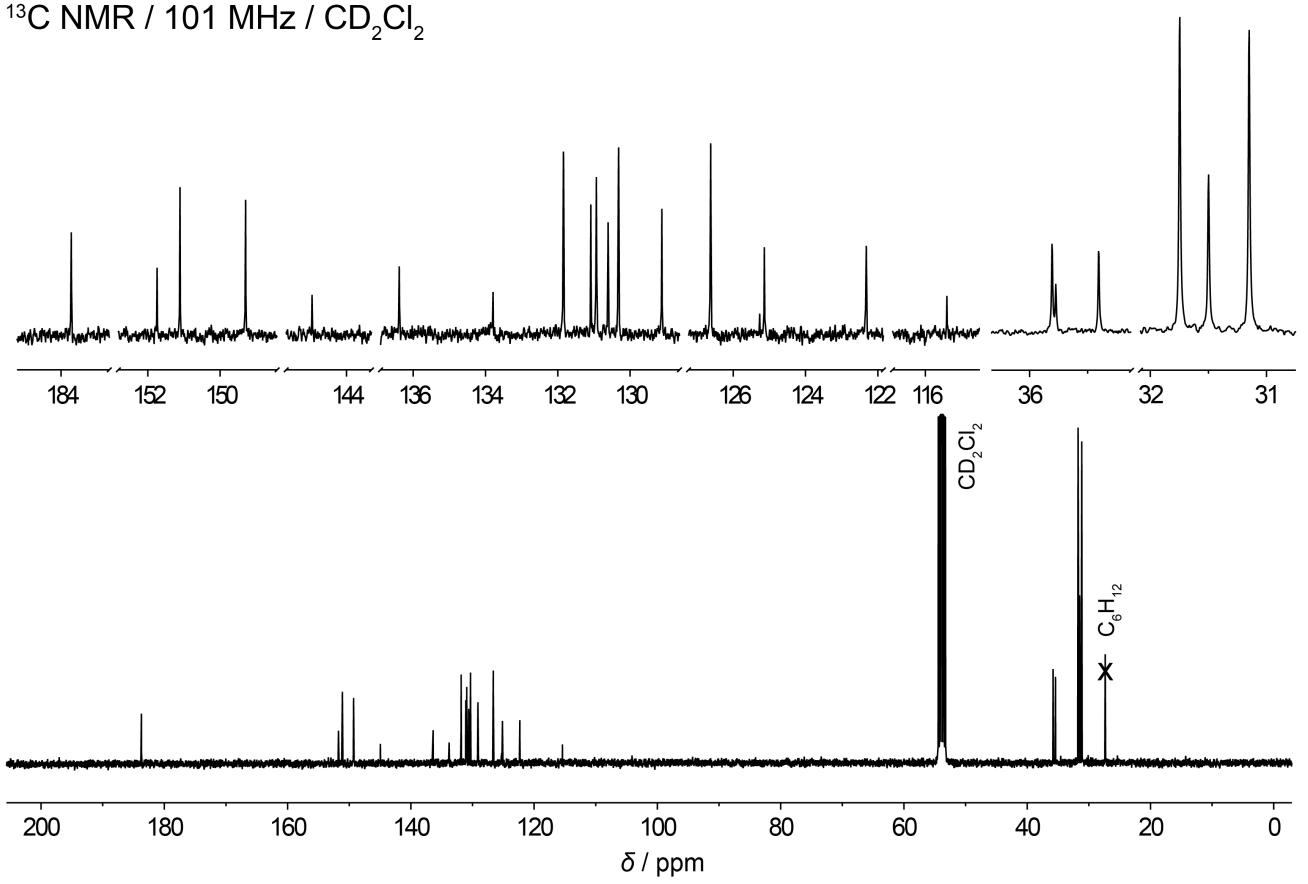


2,6,10-Tri-*tert*-butyl-12-(3,5-di-*tert*-butylphenyl)dibenzo[*cd*,*mn*] pyrene-4,8-dione (T1)

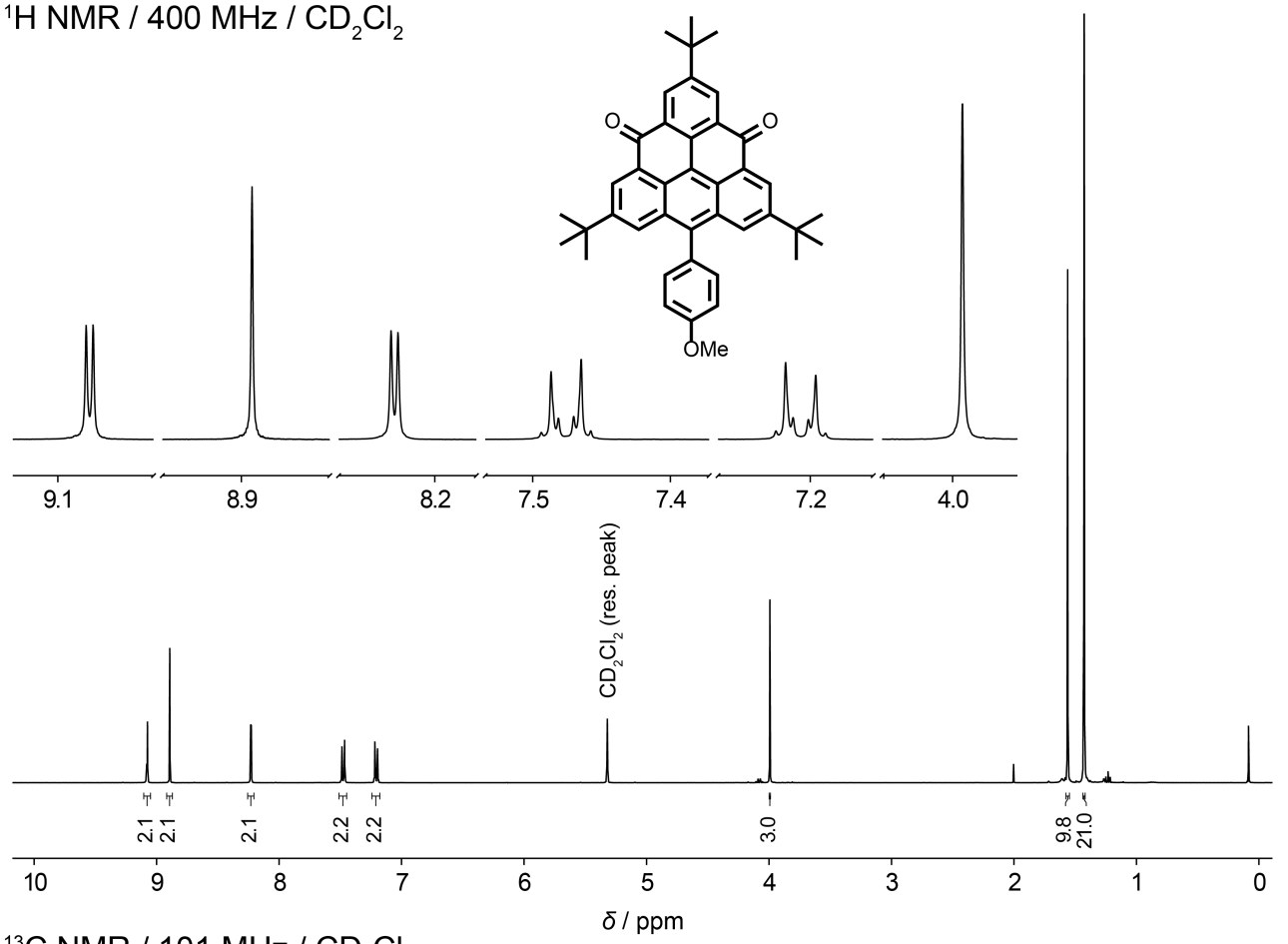
^{1}H NMR / 400 MHz / CD_2Cl_2

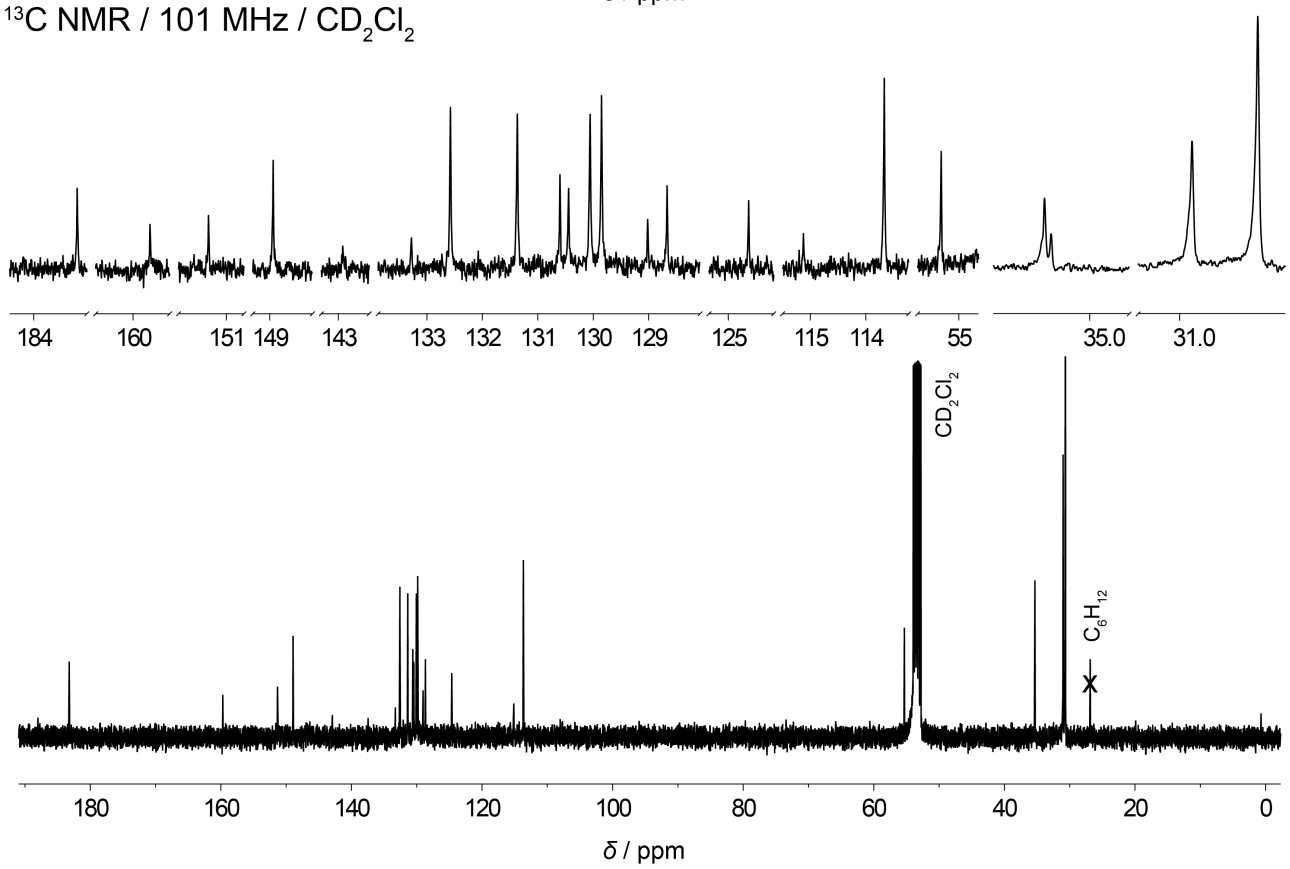


^{13}C NMR / 101 MHz / CD_2Cl_2

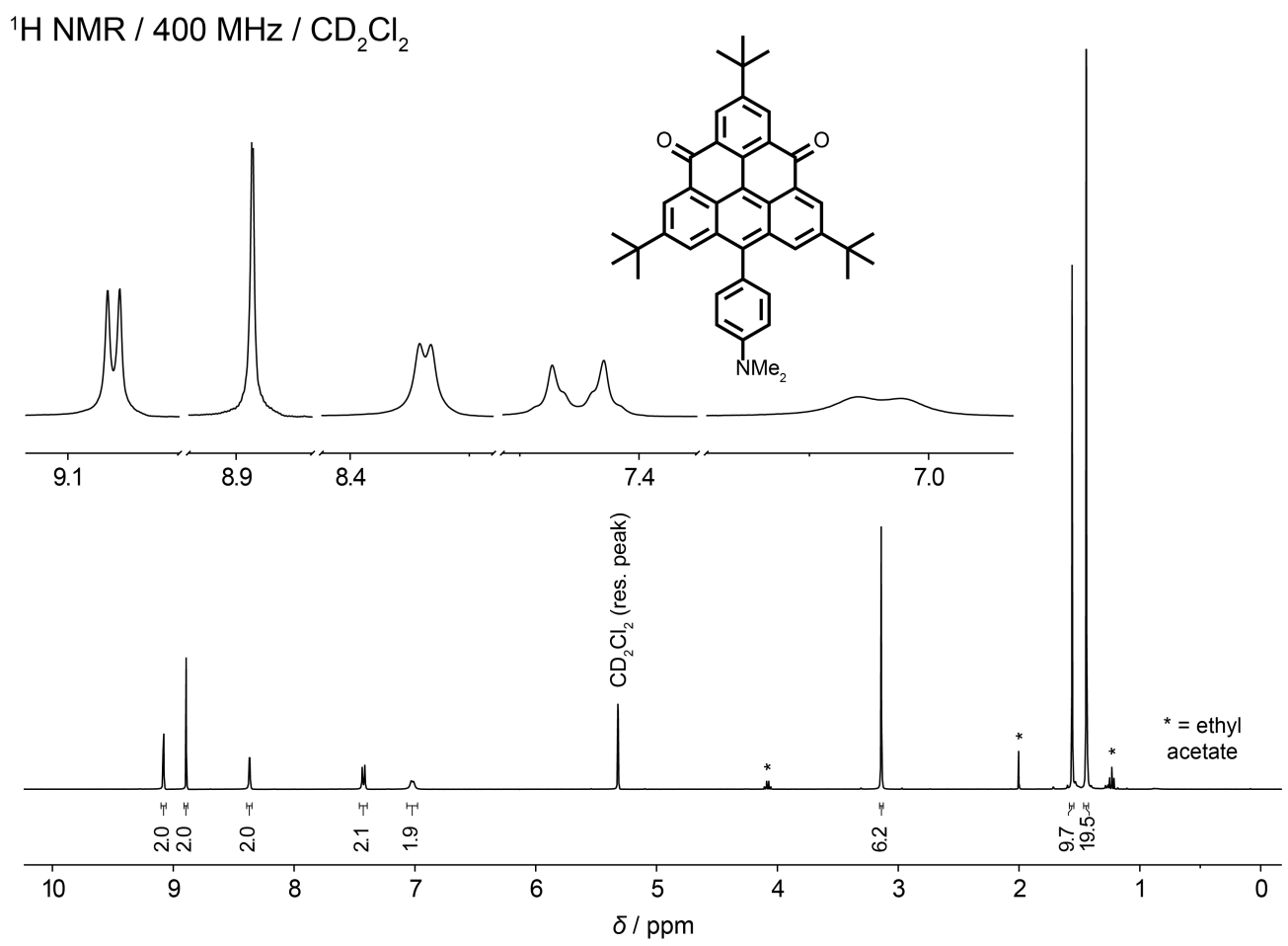


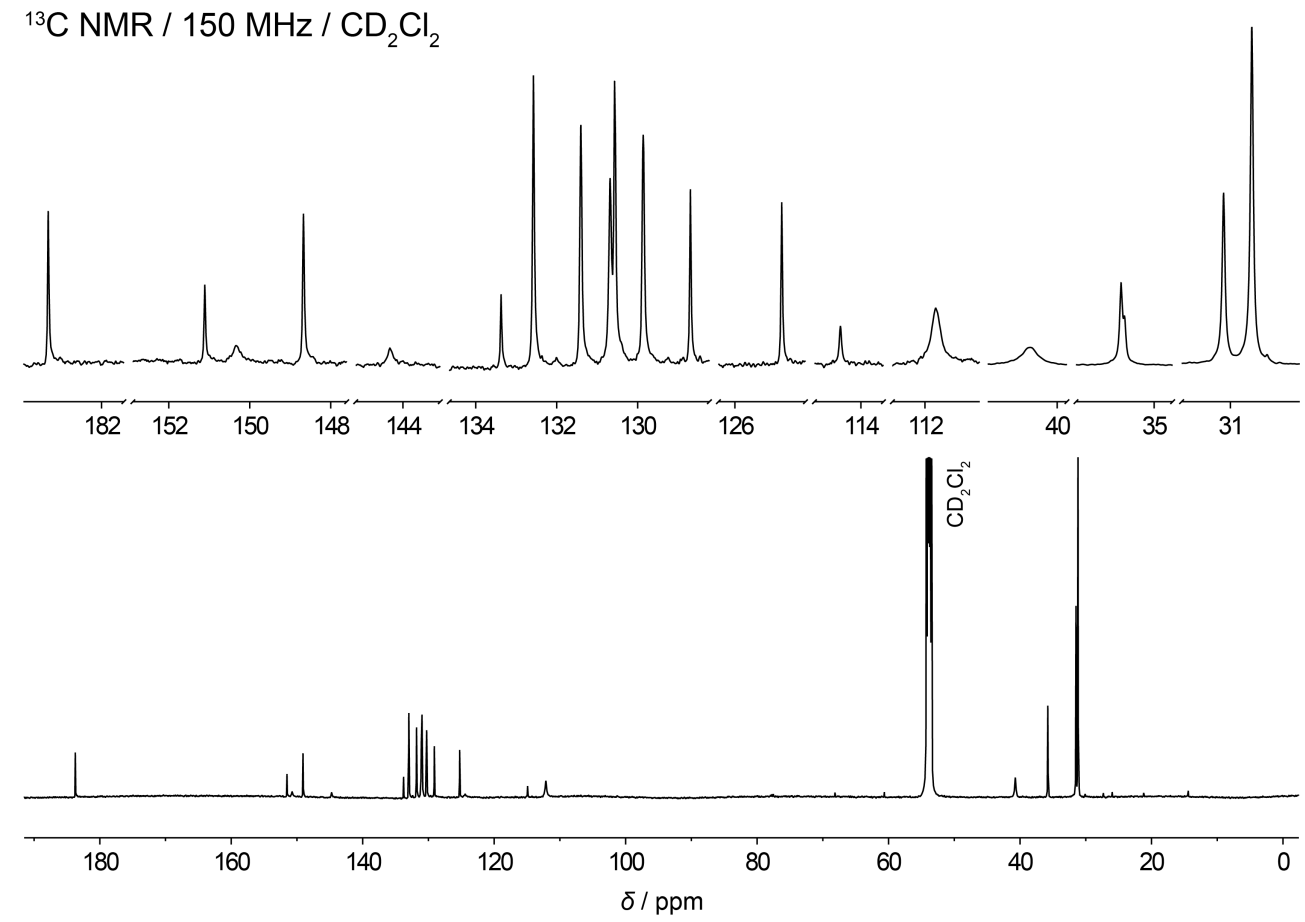
2,6,10-Tri-*tert*-butyl-12-(4-methoxyphenyl)dibenzo[*cd*,*mn*]pyrene-4,8-dione (T2)



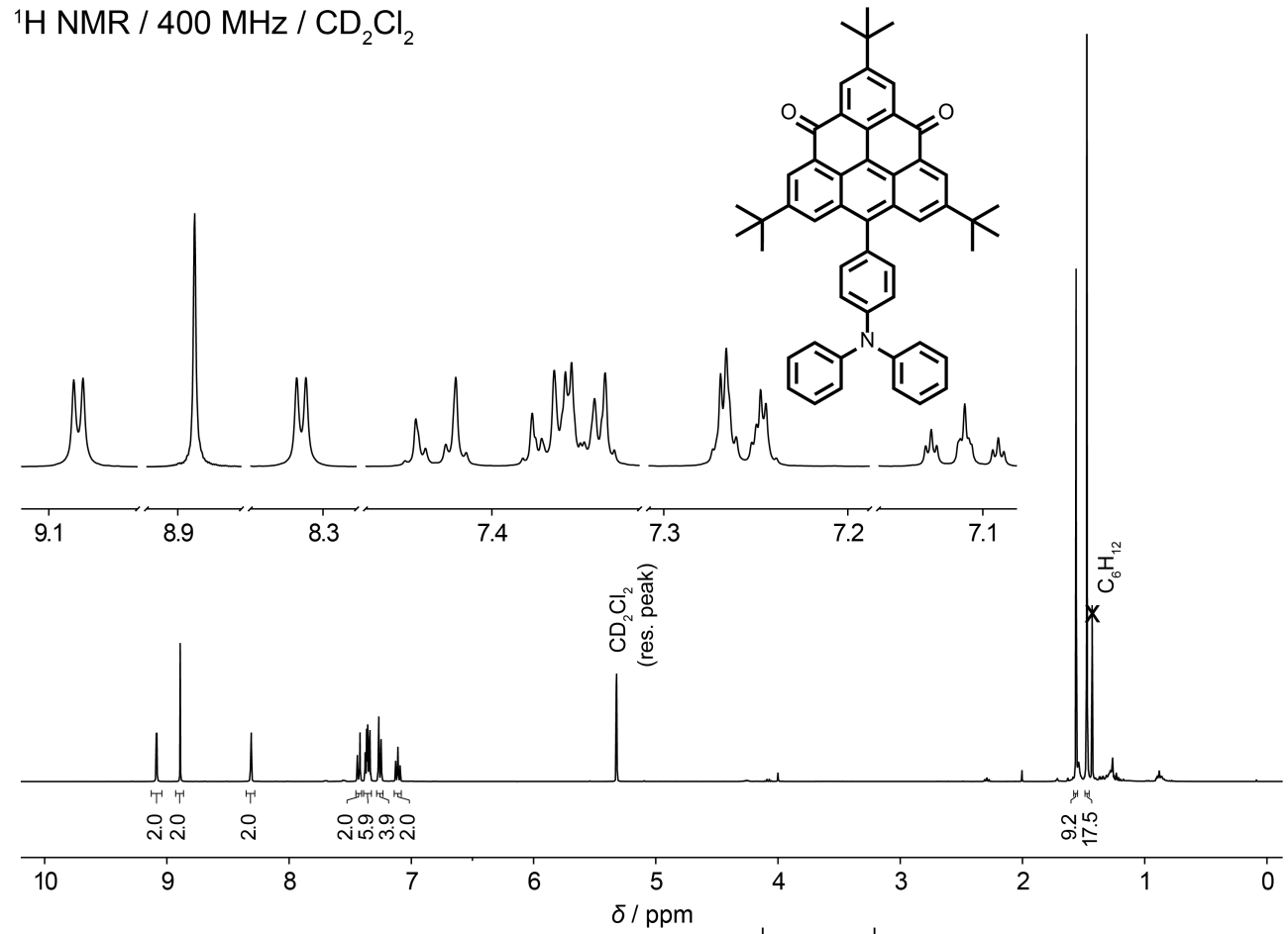


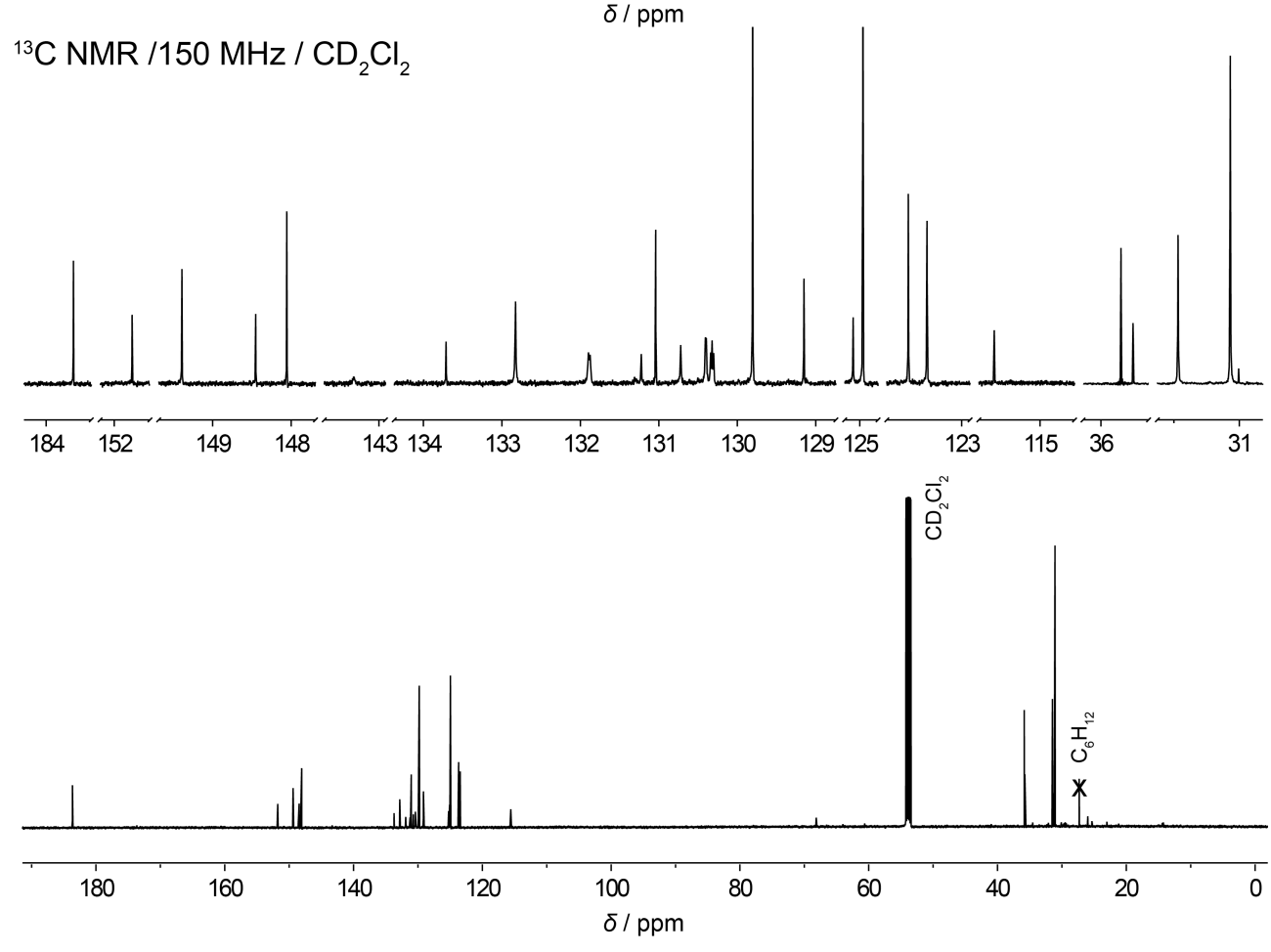
2,6,10-Tri-*tert*-butyl-12-(4-(dimethylamino)phenyl)dibenzo [*cd*,*mn*]pyrene-4,8-dione (T3)





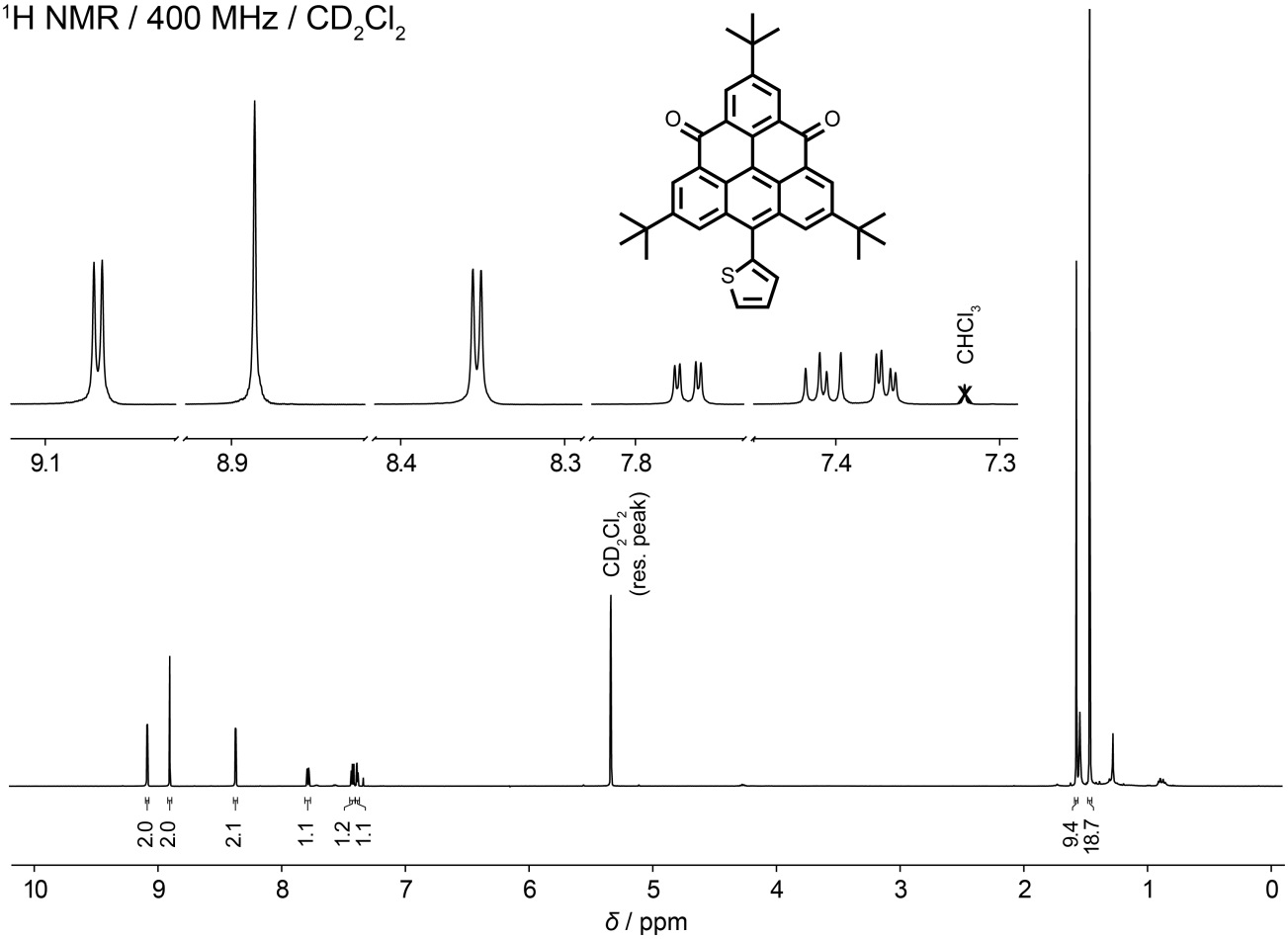
2,6,10-Tri-*tert*-butyl-12-(4-(diphenylamino)phenyl)dibenzo[*cd*,*mn*] pyrene-4,8-dione (T4)



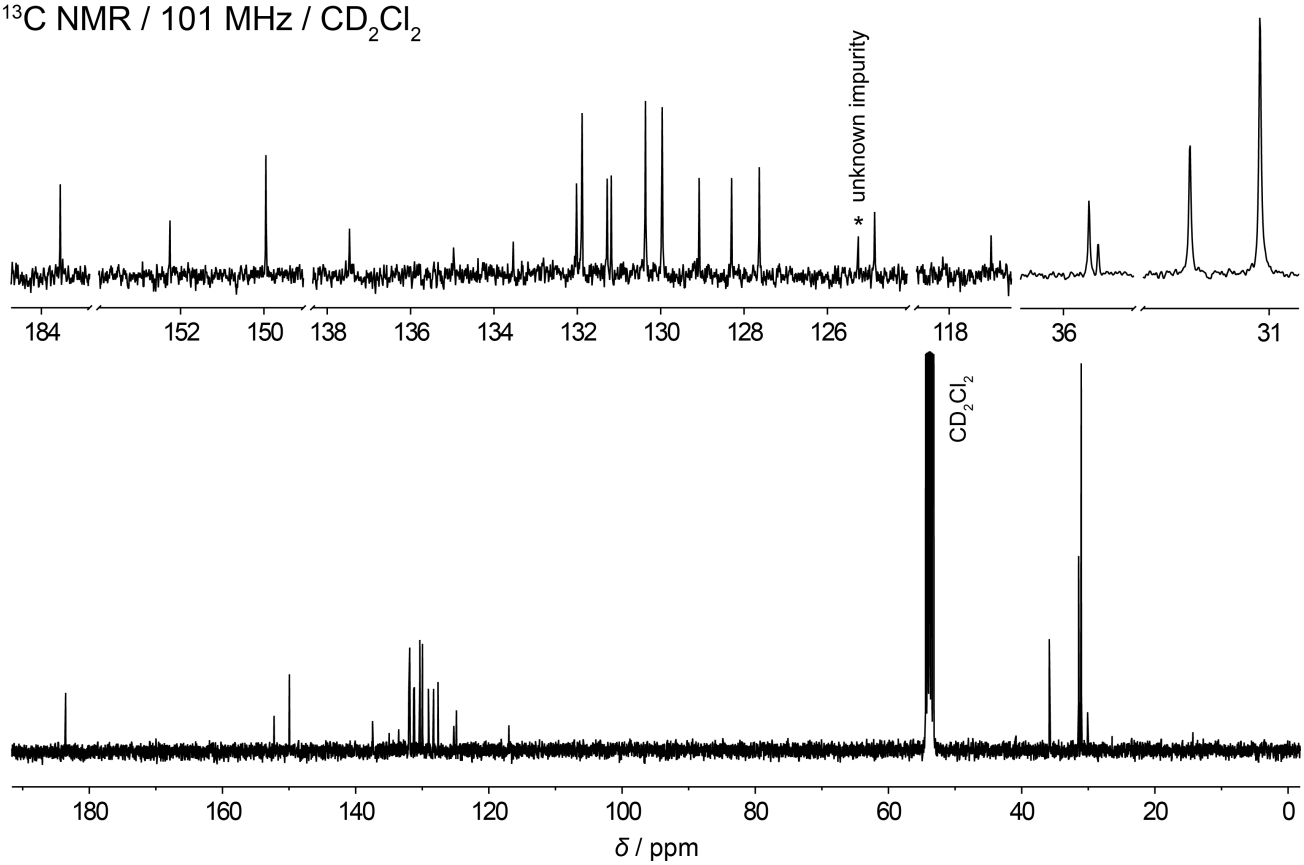


2,6,10-Tri-*tert*-butyl-12-(thiophen-2-yl)dibenzo[*cd*,*mn*]pyrene-4,8-dione (T5)

^{1}H NMR / 400 MHz / CD_2Cl_2



^{13}C NMR / 101 MHz / CD_2Cl_2



S7. Cartesian Coordinates

$T1_H$, E = –1540.44332001 Hartree

6	-6.186800	1.151292	-0.341519
6	-4.787652	1.163508	-0.344906
6	-4.064043	-0.003509	-0.005215
6	-4.786768	-1.171199	0.334096
6	-6.185920	-1.160287	0.329830
6	-6.888122	-0.004829	-0.006079
6	-4.082641	2.416045	-0.710629
6	-2.596699	2.368471	-0.704426
6	-1.899661	1.168445	-0.349086
6	-2.607445	-0.002822	-0.004768
6	-0.458031	1.171057	-0.353922
6	0.214414	2.372569	-0.736330
6	-0.483324	3.507969	-1.073775
6	-1.894591	3.505826	-1.053286
6	-1.898865	-1.173465	0.340121
6	-0.457369	-1.174633	0.346027
6	0.254302	-0.001483	-0.003592
6	-4.080842	-2.423056	0.700427
6	-2.594942	-2.374102	0.695176
6	-1.891907	-3.510720	1.044604
6	-0.480647	-3.511436	1.066067
6	0.216127	-2.375320	0.729008
8	-4.692461	-3.449601	0.995748
8	-4.695029	3.442063	-1.006214
6	1.750853	-0.002071	-0.004539
1	-2.458307	-4.398827	1.307308
1	0.053725	-4.412034	1.354402
1	1.299941	-2.376737	0.753026
1	-6.700176	2.069584	-0.608535
1	-7.974284	-0.005344	-0.006429
1	-6.698609	-2.079047	0.596559
1	1.298213	2.375393	-0.758911
1	0.050383	4.409167	-1.361448
1	-2.461724	4.393399	-1.316215
6	2.459115	0.608520	1.032114
6	3.864196	0.617323	1.051292
6	4.529367	-0.004677	-0.009167
6	3.852398	-0.629145	-1.073220
6	2.455662	-0.618711	-1.051569
1	1.899586	1.077823	1.836140
6	4.604831	1.297508	2.218860
1	5.612805	-0.009277	-0.017362
6	4.660814	-1.290015	-2.206475
1	1.886902	-1.084045	-1.848494
6	3.756030	-1.925550	-3.279232
6	5.547453	-0.225250	-2.895434
6	5.560611	-2.402340	-1.616887

1	4.375221	-2.382013	-4.059456
1	3.118177	-2.713203	-2.862328
1	3.111428	-1.182961	-3.762945
1	6.147331	-2.878111	-2.411996
1	6.263635	-2.010385	-0.874496
1	4.957789	-3.177642	-1.130178
1	6.133691	-0.682455	-3.701738
1	4.935061	0.572253	-3.331515
1	6.250226	0.237787	-2.194898
6	6.136225	1.213596	2.074797
6	4.209240	2.792374	2.277481
6	4.208762	0.610744	3.547810
1	6.613106	1.710666	2.926836
1	6.489596	0.176276	2.059224
1	6.489589	1.710514	1.164067
1	4.723206	1.087874	4.390725
1	3.132107	0.674715	3.736475
1	4.484425	-0.450006	3.538440
1	4.722661	3.289561	3.109326
1	4.486959	3.308197	1.351017
1	3.132469	2.925429	2.425204

T2$_{H}$, E = –1340.45634450 Hartree

6	5.221115	-1.155980	-0.098508
6	3.822635	-1.184657	-0.064352
6	3.085376	0.022159	-0.032617
6	3.794486	1.246129	-0.036978
6	5.193222	1.250643	-0.072643
6	5.908751	0.055657	-0.103072
6	3.132694	-2.497276	-0.063897
6	1.646568	-2.466919	-0.038310
6	0.935220	-1.223994	0.001281
6	1.629251	0.004872	0.003633
6	-0.506094	-1.244668	0.028803
6	-1.163246	-2.512880	-0.014977
6	-0.452168	-3.688823	-0.054114
6	0.958695	-3.664631	-0.059931
6	0.907247	1.216854	0.041402
6	-0.533865	1.203343	0.084847
6	-1.233420	-0.029121	0.073354
6	3.074457	2.541984	-0.002170
6	1.590061	2.476337	0.046870
6	0.876037	3.657394	0.104816
6	-0.533512	3.648098	0.170001
6	-1.217680	2.455695	0.163709
8	3.673692	3.617163	-0.010966
8	3.756967	-3.557866	-0.087521
6	-2.726621	-0.047480	0.109135
1	1.432976	4.589236	0.107911
1	-1.076899	4.586516	0.232082

1	-2.299819	2.453231	0.225196
1	5.744900	-2.106356	-0.121691
1	6.994500	0.068525	-0.130082
1	5.694833	2.213182	-0.074956
1	-2.246886	-2.536495	-0.021803
1	-0.975632	-4.639937	-0.087122
1	1.536677	-4.583069	-0.090347
6	-3.419605	-0.462349	1.261707
6	-4.807210	-0.479165	1.299186
6	-5.549317	-0.083360	0.175659
6	-4.878601	0.330632	-0.981349
6	-3.481665	0.346563	-1.002057
1	-2.858321	-0.768002	2.140495
1	-5.342220	-0.792942	2.190022
8	-6.903561	-0.137663	0.312075
1	-5.425225	0.637318	-1.865680
1	-2.971610	0.666061	-1.906909
6	-7.708909	0.251089	-0.791127
1	-8.742580	0.130638	-0.462809
1	-7.535581	1.299493	-1.066858
1	-7.529315	-0.387343	-1.665973

T3$_{H}$, E = –1359.90173496 Hartree

6	-5.487533	1.228510	-0.030975
6	-4.088373	1.231730	-0.029357
6	-3.372266	0.011765	-0.002646
6	-4.104096	-1.198890	0.021145
6	-5.503092	-1.177669	0.017280
6	-6.197318	0.029935	-0.008201
6	-3.374961	2.530991	-0.058726
6	-1.889875	2.473031	-0.072241
6	-1.199817	1.217931	-0.033079
6	-1.916360	0.002389	0.000278
6	0.241981	1.212376	-0.042119
6	0.918466	2.467405	-0.133929
6	0.227897	3.656003	-0.172813
6	-1.181923	3.657931	-0.133074
6	-1.215666	-1.222279	0.036383
6	0.226033	-1.235284	0.051390
6	0.951169	-0.016068	0.006404
6	-3.407570	-2.507251	0.053056
6	-1.921948	-2.468408	0.072417
6	-1.229481	-3.662314	0.135610
6	0.180087	-3.678548	0.180825
6	0.886048	-2.498924	0.145267
8	-4.026840	-3.571404	0.067569
8	-3.980370	3.603056	-0.075892
6	2.441358	-0.026085	0.010224
1	-1.804209	-4.582932	0.162235
1	0.707133	-4.625550	0.253369

1	1.968395	-2.516208	0.196413
1	-5.994004	2.188311	-0.051440
1	-7.283492	0.036914	-0.010317
1	-6.021938	-2.130881	0.035682
1	2.001136	2.470720	-0.180831
1	0.767332	4.596139	-0.243709
1	-1.744677	4.585839	-0.162225
6	3.175385	0.484210	1.092719
6	4.565320	0.476512	1.105951
6	5.303594	-0.049435	0.019576
6	4.564115	-0.549246	-1.078263
6	3.174121	-0.541270	-1.070785
1	2.645587	0.889888	1.950803
1	5.076017	0.880176	1.971895
7	6.687971	-0.079945	0.033379
1	5.073841	-0.943697	-1.949003
1	2.643389	-0.931187	-1.935588
6	7.410086	-0.473710	-1.164544
6	7.410866	0.597028	1.096732
1	8.481536	-0.458181	-0.957262
1	7.146524	-1.494587	-1.467469
1	7.215299	0.195192	-2.017574
1	8.482482	0.452523	0.948609
1	7.210553	1.679641	1.124006
1	7.153486	0.180084	2.078298

T4$_{H}$, E = –1743.38226158 Hartree

6	-1.298374	-0.663537	1.001598
6	-0.570602	-0.000003	0.000002
6	-1.298372	0.663533	-1.001594
6	-2.689418	0.657615	-1.012128
6	-3.411269	-0.000001	0.000001
6	-2.689419	-0.657618	1.012131
6	0.921249	-0.000002	0.000003
6	1.636117	1.197806	0.255976
6	3.077908	1.195669	0.245876
6	3.786357	0.000000	0.000001
6	3.077910	-1.195671	-0.245873
6	1.636119	-1.197811	-0.255971
6	5.242920	0.000001	-0.000001
6	5.966654	1.192041	0.237450
6	5.261591	2.470562	0.495256
6	3.775843	2.420822	0.500138
6	5.966656	-1.192038	-0.237453
6	7.365789	-1.180346	-0.234367
6	8.067718	0.000003	-0.000004
6	7.365787	1.180351	0.234361
6	3.775846	-2.420823	-0.500136
6	5.261594	-2.470560	-0.495257
6	0.967111	2.423776	0.558217

6	1.665391	3.583113	0.800247
6	3.075667	3.582073	0.763536
6	3.075671	-3.582075	-0.763533
6	1.665395	-3.583118	-0.800241
6	0.967114	-2.423781	-0.558211
8	5.873535	3.519096	0.698779
8	5.873539	-3.519093	-0.698781
1	3.644098	-4.487643	-0.951494
1	1.132132	-4.501490	-1.028246
1	-0.115773	-2.427727	-0.601245
1	7.878579	2.118629	0.420875
1	9.153880	0.000004	-0.000005
1	7.878581	-2.118623	-0.420882
1	-0.115775	2.427720	0.601253
1	1.132127	4.501484	1.028253
1	3.644093	4.487642	0.951497
1	-0.764671	1.172361	-1.799872
1	-3.224500	1.159861	-1.811119
7	-4.824561	0.000000	0.000001
1	-3.224503	-1.159863	1.811121
1	-0.764674	-1.172366	1.799876
6	-5.545819	-1.142691	0.452558
6	-5.545817	1.142693	-0.452559
6	-6.648666	-0.990764	1.306865
6	-7.363702	-2.107856	1.735162
6	-6.982815	-3.390409	1.335131
6	-5.881363	-3.544585	0.490531
6	-5.171723	-2.431853	0.042440
1	-6.939832	0.003988	1.629153
1	-8.215570	-1.973461	2.396481
1	-7.538228	-4.259247	1.676373
1	-5.579452	-4.536164	0.163712
1	-4.326494	-2.554118	-0.627683
6	-6.648661	0.990767	-1.306869
6	-7.363694	2.107860	-1.735169
6	-6.982806	3.390413	-1.335137
6	-5.881357	3.544587	-0.490533
6	-5.171720	2.431854	-0.042439
1	-6.939827	-0.003985	-1.629159
1	-8.215560	1.973466	-2.396491
1	-7.538217	4.259251	-1.676380
1	-5.579445	4.536166	-0.163713
1	-4.326494	2.554117	0.627686

T5$_{H}$, E = –1546.68754812 Hartree

6	-4.608727	1.203691	-0.085964
6	-3.210522	1.215587	-0.036075
6	-2.488361	-0.000001	-0.010891
6	-3.210519	-1.215592	-0.036073
6	-4.608725	-1.203699	-0.085962

6	-5.309796	-0.000005	-0.111274
6	-2.505436	2.520710	-0.009451
6	-1.020327	2.473313	0.043590
6	-0.324615	1.221379	0.066770
6	-1.031669	0.000000	0.040662
6	1.115224	1.225333	0.116909
6	1.789862	2.484053	0.145264
6	1.093357	3.668514	0.122183
6	-0.317712	3.661985	0.069996
6	-0.324612	-1.221377	0.066773
6	1.115227	-1.225327	0.116914
6	1.824446	0.000004	0.139259
6	-2.505430	-2.520713	-0.009445
6	-1.020322	-2.473313	0.043598
6	-0.317704	-3.661983	0.070012
6	1.093366	-3.668508	0.122206
6	1.789867	-2.484045	0.145282
8	-3.117399	-3.587906	-0.030119
8	-3.117408	3.587902	-0.030126
6	3.307803	0.000007	0.182307
1	-0.883069	-4.588496	0.050745
1	1.627356	-4.613983	0.144760
1	2.873209	-2.489499	0.191736
1	-5.121596	2.160074	-0.103946
1	-6.395220	-0.000006	-0.150231
1	-5.121591	-2.160083	-0.103942
1	2.873204	2.489509	0.191711
1	1.627346	4.613990	0.144727
1	-0.883080	4.588497	0.050725
6	4.131325	0.000050	1.280130
6	5.522048	0.000042	0.952250
6	5.746661	-0.000007	-0.395780
16	4.260969	-0.000044	-1.291364
1	6.693920	-0.000023	-0.918655
1	6.315575	0.000071	1.691647
1	3.748644	0.000085	2.295353

S8. References

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(S2) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Account* **2008**, *120*, 215.

(S3) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51.