

Supporting Information for

Investigation of new bis(carboxylate)triazole-based anchoring ligands for dye solar cell chromophore complexes

Alessandro Sinopoli,^a Fiona A. Black,^b Christopher J. Wood,^b Elizabeth A. Gibson^{b*} and Paul I. P. Elliott^{a*}

^a *Department of Chemistry, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK.*

^b *School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.*

Figure S1. ¹³ C NMR spectrum of detzbp y	p.S2
Figure S2. ¹ H NMR spectrum of detzbp y	p.S2
Figure S3. ¹³ C NMR spectrum of dctzbp y	p.S3
Figure S4. ¹ H NMR spectrum of dctzbp y	p.S3
Figure S5. ¹³ C NMR spectrum of AS16-Et ₂	p.S4
Figure S6. ¹ H NMR spectrum of AS16-Et ₂	p.S4
Figure S7. ¹³ C NMR spectrum of AS16	p.S5
Figure S8. ¹ H NMR spectrum of AS16	p.S5
Figure S9. ¹³ C NMR spectrum of AS17-Et ₂	p.S6
Figure S10. ¹ H NMR spectrum of AS17-Et ₂	p.S6
Figure S11. ¹³ C NMR spectrum of AS17	p.S7
Figure S12. ¹ H NMR spectrum of AS17	p.S7
Figure S13. ¹³ C NMR spectrum of AS18-Et ₂	p.S8
Figure S14. ¹ H NMR spectrum of AS18-Et ₂	p.S8
Figure S15. ¹ H NMR spectrum of AS18	p.S9
Figure S16. FT-IR spectrum of detzbp y	p.S10
Optimised geometry coordinates for AS16-18	p.S10-S17
Optimised geometry coordinates for 1-3	p.S17-S23
Table S1. Summarised TDDFT data for AS16-18 and 1-3	p.S23-S25
Figure S17. UV-vis abs spectra of 2 and AS16 adsorbed onto TiO ₂	p.S26
Figure S18. Infrared spectra of AS16 and AS16 immobilised on TiO ₂	p.S26

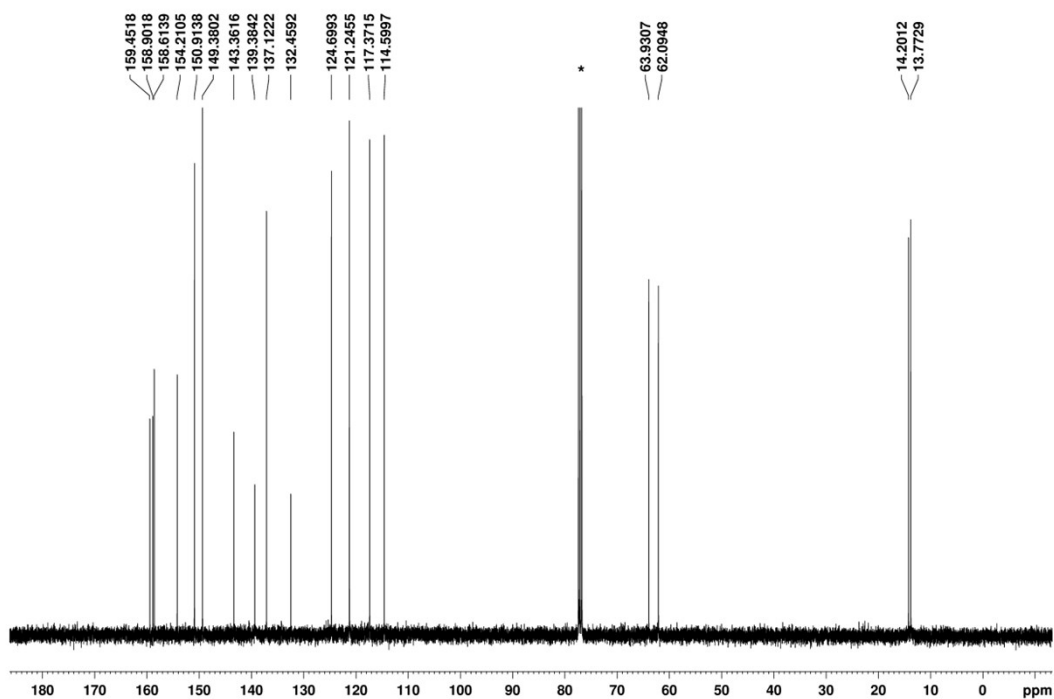


Figure S1. ^{13}C NMR spectrum of **detzbp** in d-chloroform (* residual solvent signals).

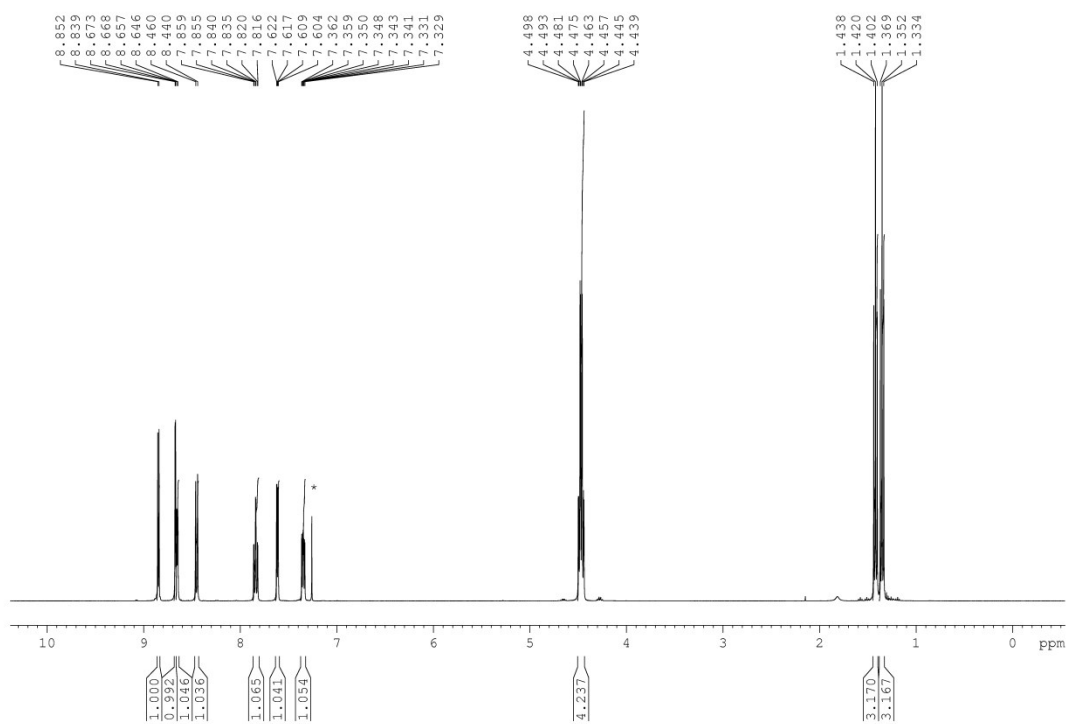


Figure S2. ^1H NMR spectrum of **detzbp** in d-chloroform (* residual solvent signals).

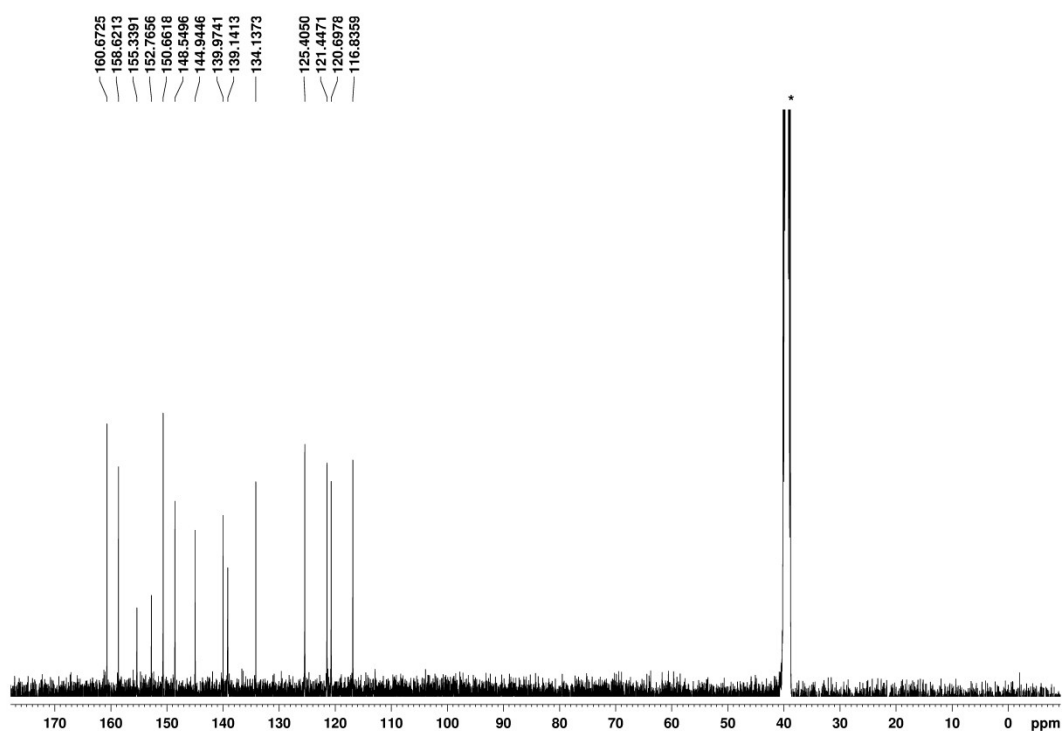


Figure S3. ^{13}C NMR spectrum of **dctzbp** in d_6 -DMSO (* residual solvent signals).

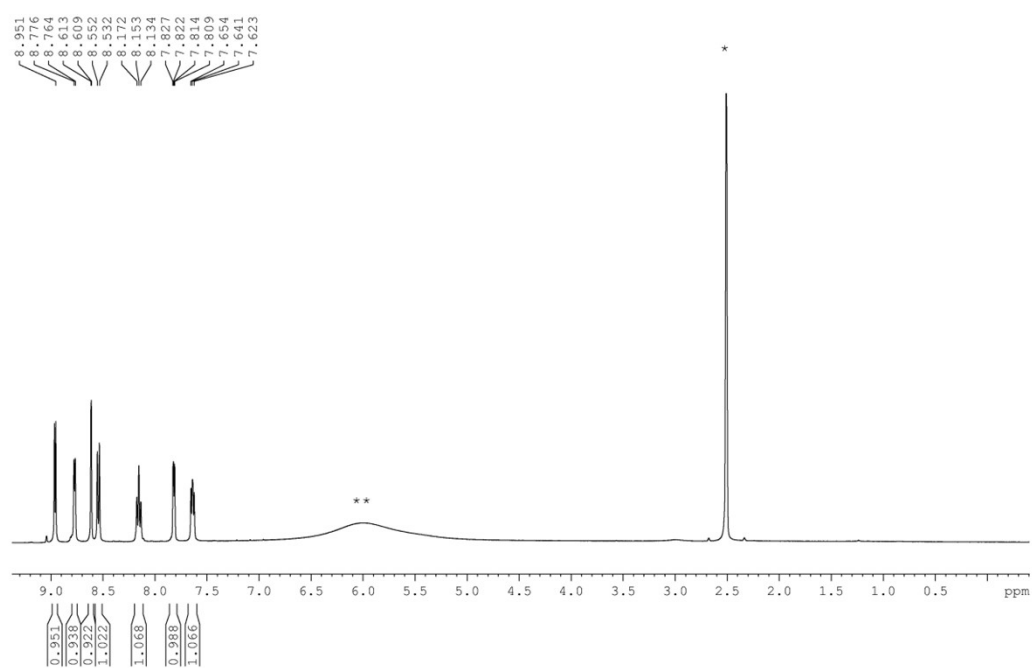


Figure S4. ^1H NMR spectrum of **dctzbp** in d_6 -DMSO (* residual solvent signals, ** impurity in solvent batch).

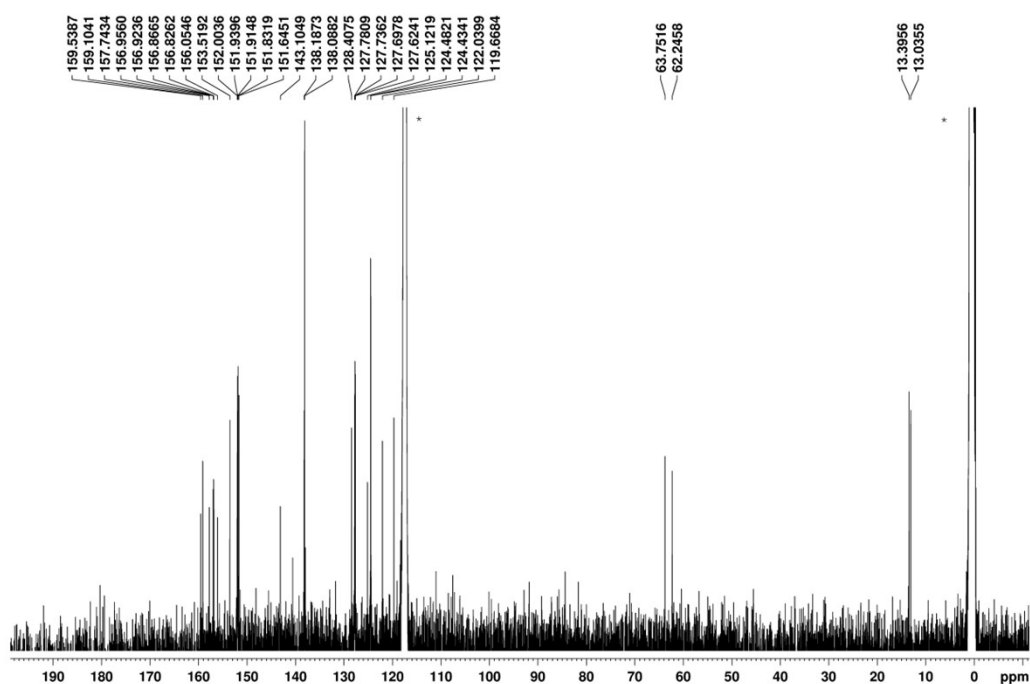


Figure S5. ^{13}C NMR spectrum of **AS16-Et₂** in d_3 -acetonitrile (* residual solvent signals).

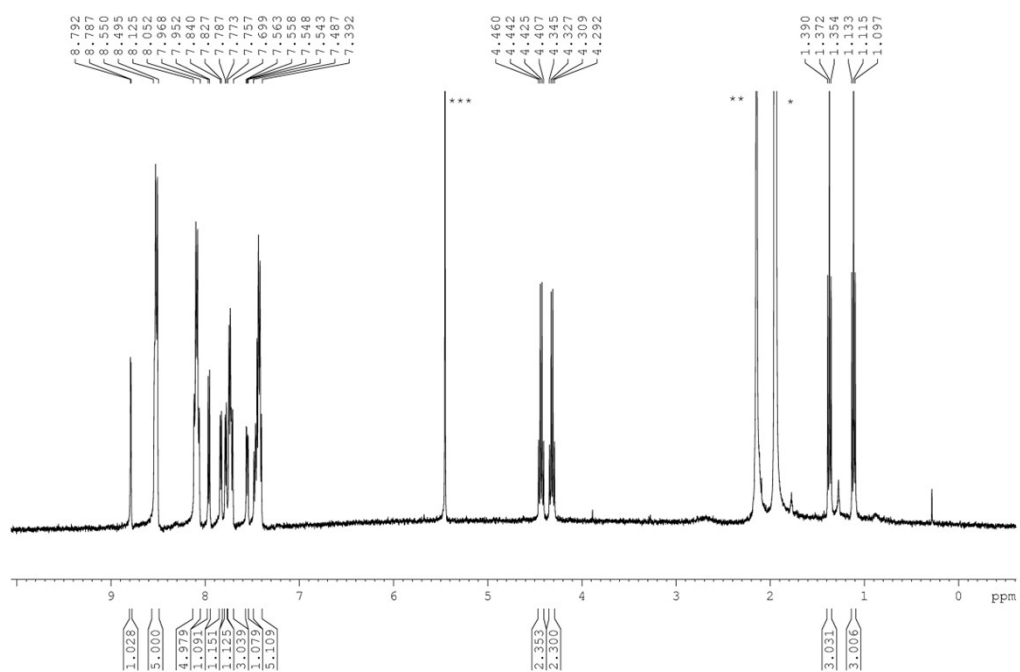


Figure S6. ^1H NMR spectrum of **AS16-Et₂** in d_3 -acetonitrile (* residual solvent signal, ** adventitious water signal, *** adventitious dichlorometane signal).

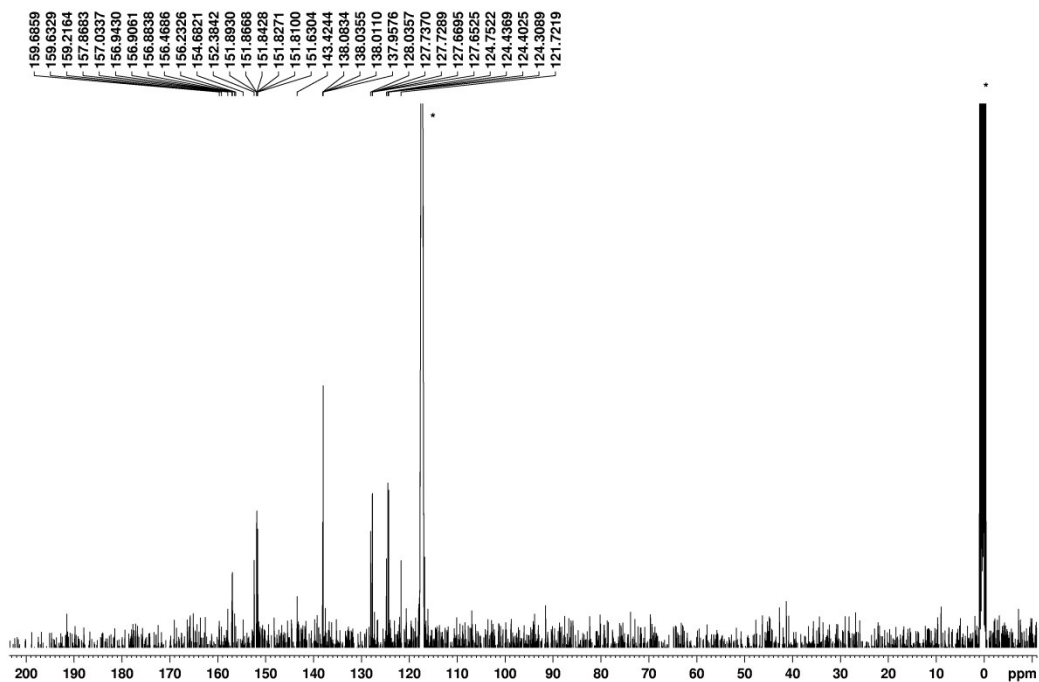


Figure S7. ^{13}C NMR spectrum of **AS16** in d_3 -acetonitrile (* residual solvent signals).

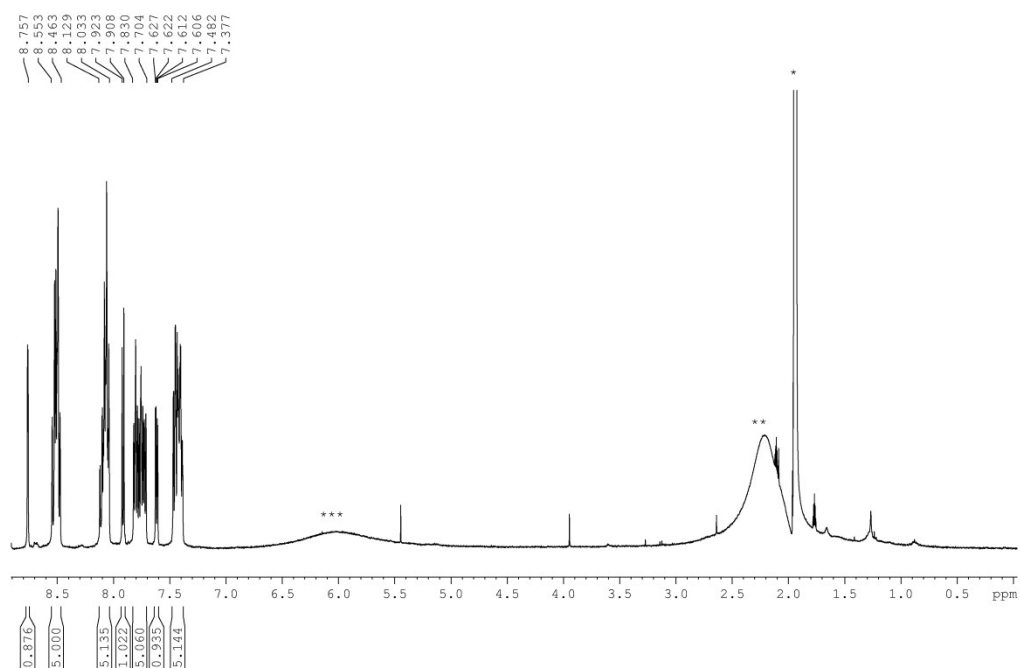


Figure S8. ^1H NMR spectrum of **AS16** in d_3 -acetonitrile (* residual solvent signal, ** adventitious water signal, *** impurity in solvent batch).

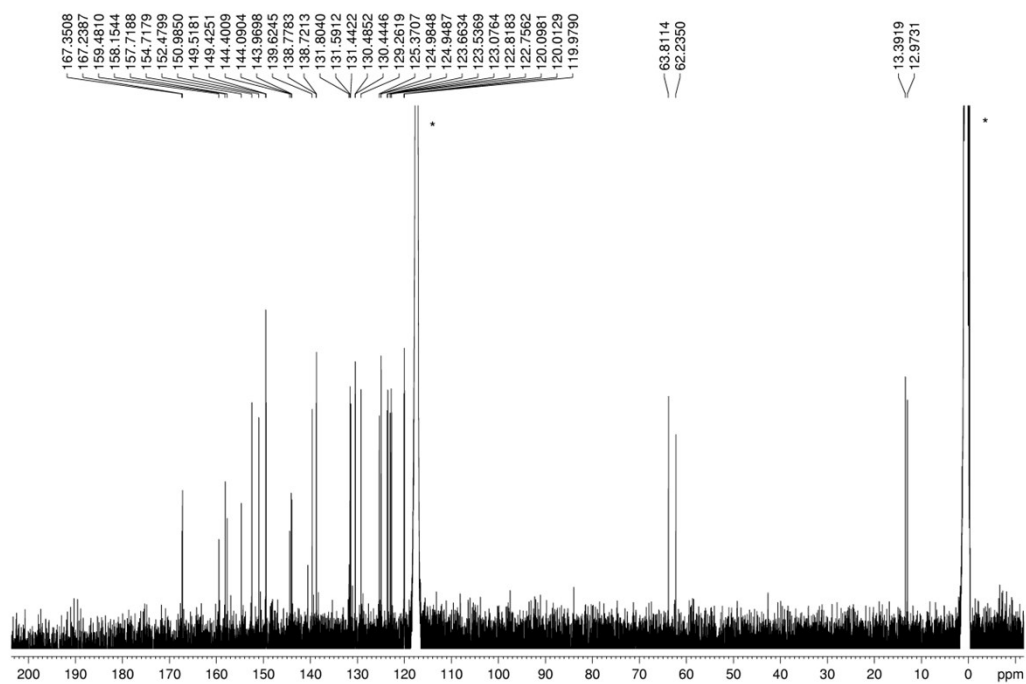


Figure S9. ^{13}C NMR spectrum of **AS17-Et₂** in d_3 -acetonitrile (* residual solvent signals).

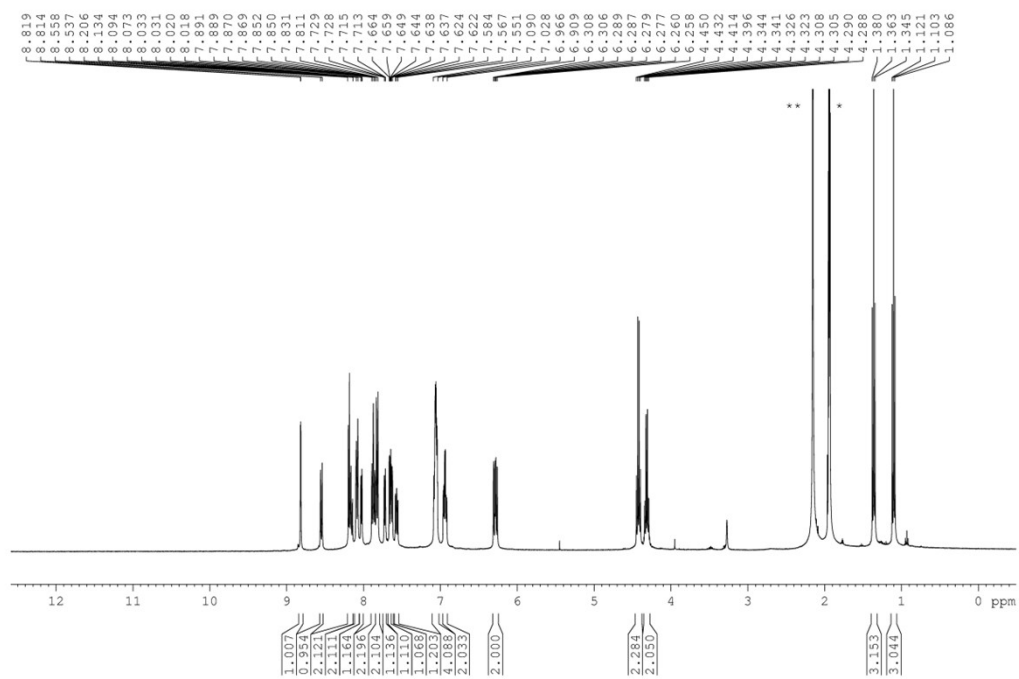


Figure S10. ^1H NMR spectrum of **AS17-Et₂** in d_3 -acetonitrile (* residual solvent signal, ** adventitious water signal).

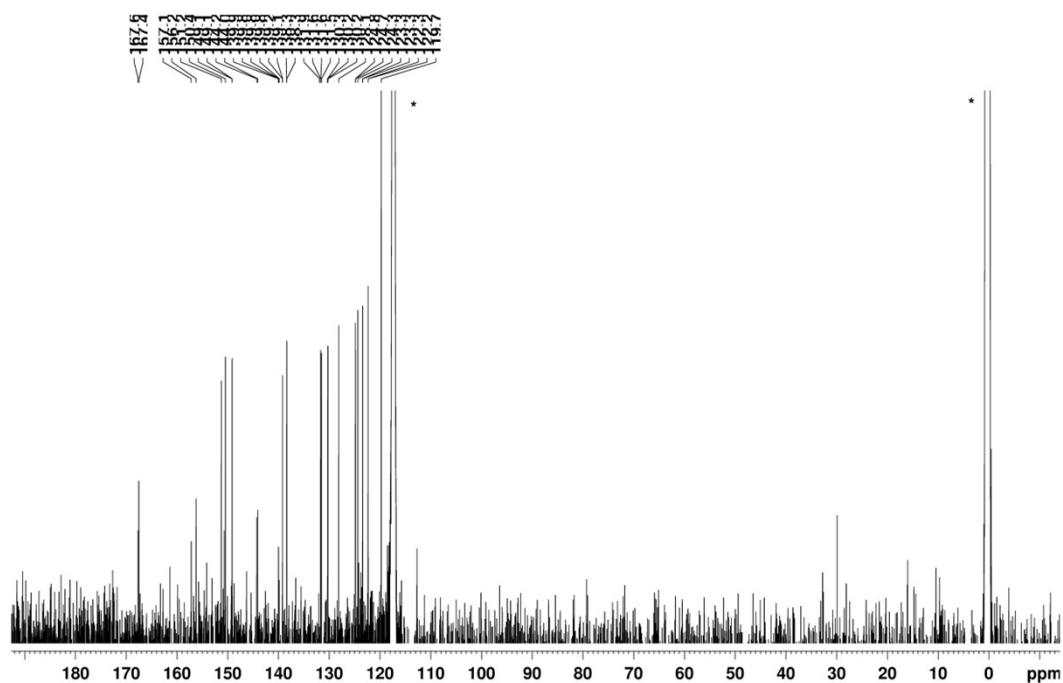


Figure S11. ¹³C NMR spectrum of **AS17** in d₃-acetonitrile (* residual solvent signal, ** adventitious acetone signal).

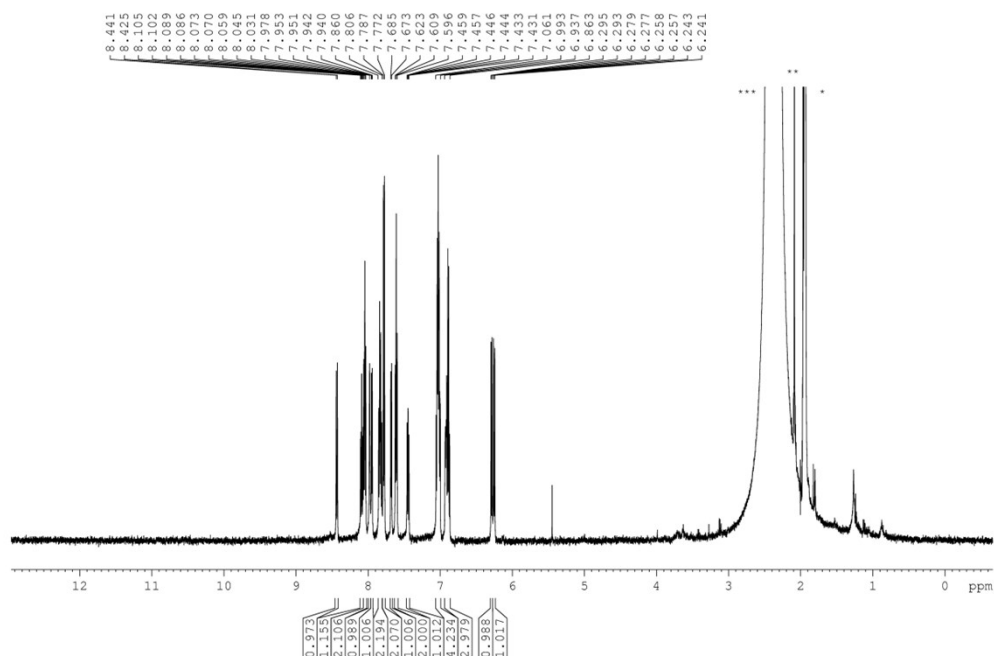


Figure S12. ¹H NMR spectrum of **AS17** in d₃-acetonitrile (* residual solvent signal, ** adventitious acetone signal, *** adventitious water signal).

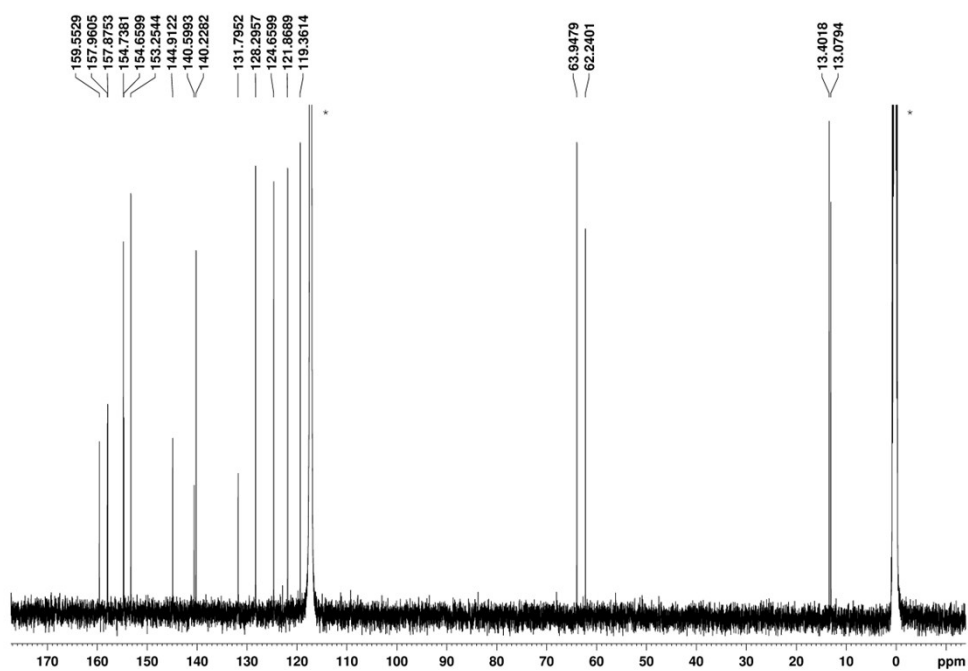


Figure S13. ^{13}C NMR spectrum of **AS18-Et₂** in d_3 -acetonitrile (* residual solvent signal).

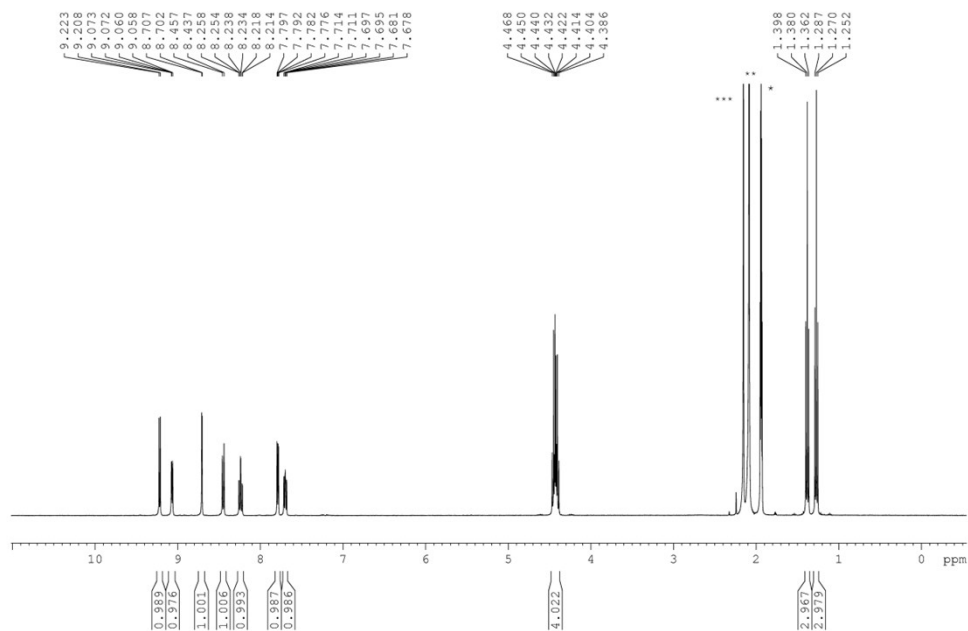


Figure S14. ^1H NMR spectrum of **AS18-Et₂** in d_3 -acetonitrile (* residual solvent signal, ** adventitious acetone signal, *** adventitious water signal).

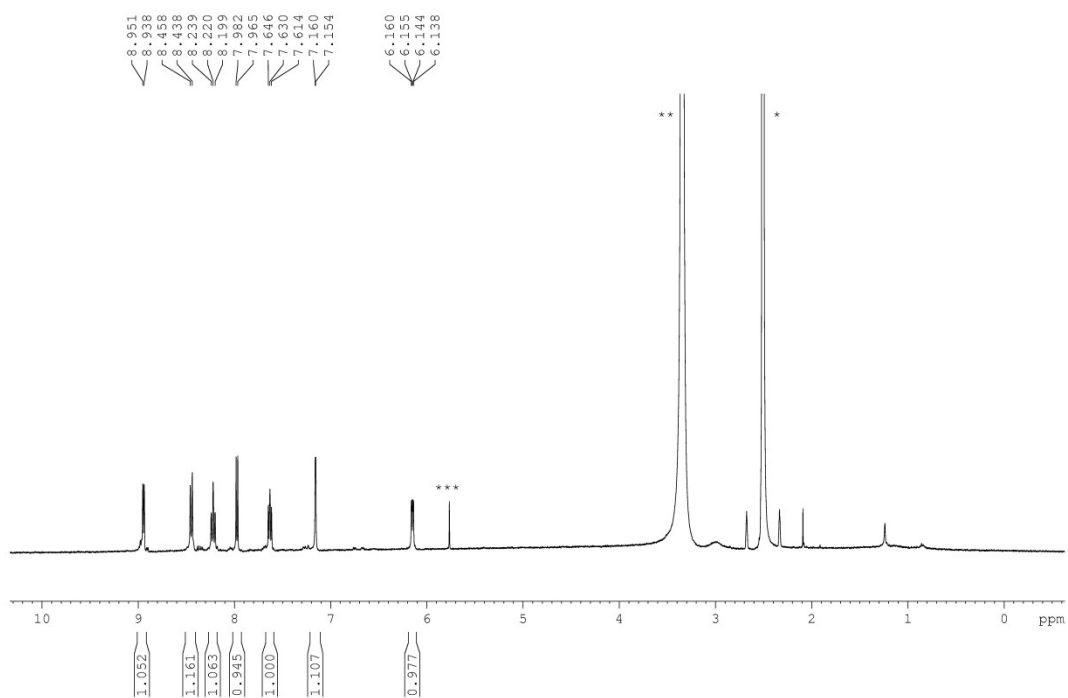


Figure S15. ^1H NMR spectrum of **AS18** in $\text{d}_6\text{-DMSO}$ (* residual solvent signal, ** adventitious water signal, *** adventitious dichloromethane signal).

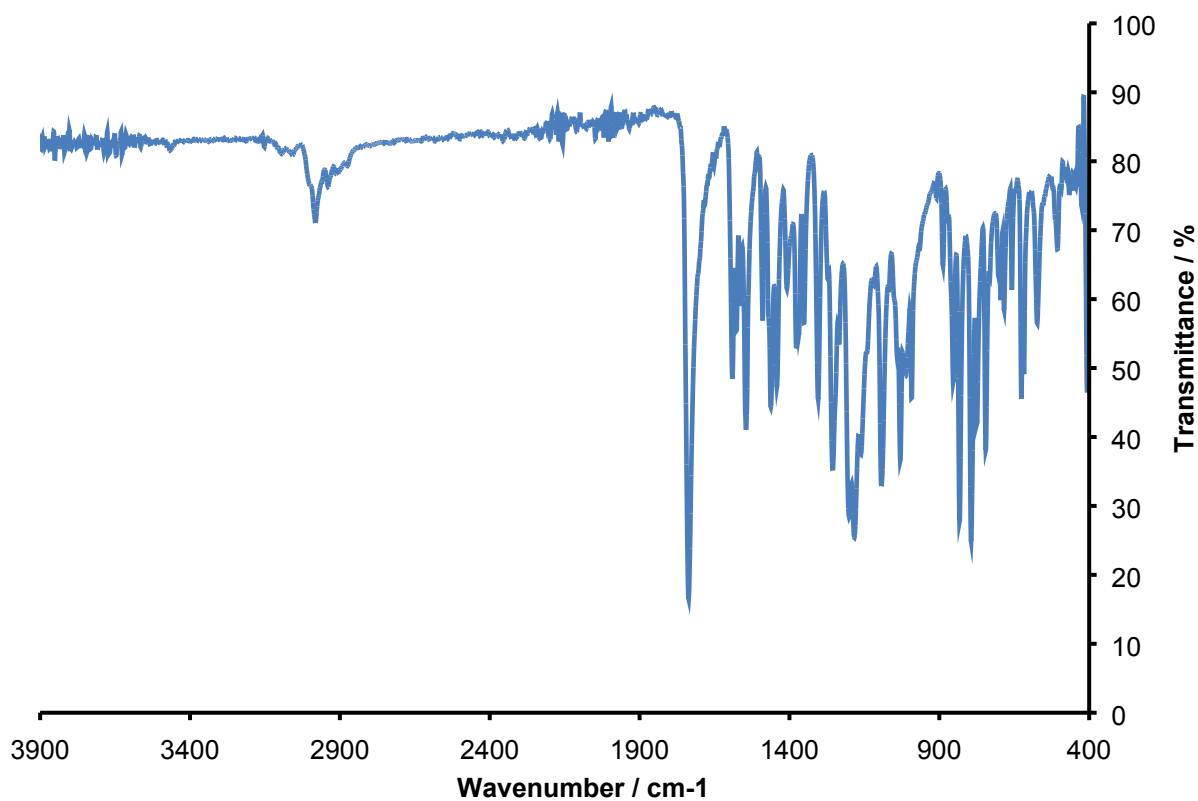


Figure S16. FT-IR spectrum of **detzbp**.

Optimised geometry coordinates for AS16 (.xyz file format)

73

C	1.84510631	5.62075785	0.32443377
C	1.23425005	6.45206306	-0.60566133
C	0.23642413	5.92623165	-1.42054661
C	-0.11205688	4.5917148	-1.27086094
C	1.45351129	4.28446865	0.42684599
H	2.62108543	6.01625576	0.96615473
H	1.53251495	7.4904772	-0.69107355
H	-0.88252491	4.14408297	-1.88450657
C	-3.97415578	2.79784932	1.25302497
C	-3.87232709	3.16170913	2.58958735

C	-2.62319249	3.12167067	3.20137001
C	-1.52686138	2.72044699	2.45202165
C	-2.83466947	2.4001101	0.55079328
H	-4.93844472	2.82647233	0.76355835
H	-4.75244244	3.47063622	3.14134126
H	-0.53860259	2.6753652	2.88995121
C	-2.84854714	1.99407044	-0.86742008
C	-1.57070481	1.2859044	-2.6821674
C	-4.00580818	1.94367556	-1.64695823
C	-2.68491828	1.21868751	-3.50603527
H	-0.58631524	1.03441842	-3.05407089
H	-4.96600405	2.20440026	-1.22231519
H	-2.57283129	0.90777703	-4.53751777
C	-3.92799991	1.5526521	-2.97757533
H	-4.82218524	1.50938724	-3.58834821
N	-1.63578485	1.66325216	-1.39206019
C	2.01269516	1.14787393	2.19870469
C	2.04875984	3.32863369	1.37986264
C	3.03612237	1.41346842	3.09670381
H	1.55989625	0.16687644	2.14228331
C	3.08233993	3.65497843	2.26020377
H	3.39255781	0.62935041	3.75342183
H	3.49919175	4.65317845	2.27142066
N	1.51967914	2.07355782	1.35548442
C	3.58329969	2.69258569	3.12740455
H	4.38602648	2.93806669	3.8128621
H	-0.26916286	6.53426637	-2.16071926
H	-2.49284645	3.39648664	4.24090593
C	1.52270326	-0.42005345	-1.37218145

C	2.47558041	-1.08102243	-2.14997584
C	3.34643475	-0.34389462	-2.9428531
C	3.24732022	1.04415962	-2.93765122
C	2.28808269	1.6425204	-2.13290666
N	1.43883175	0.93920478	-1.36188275
H	4.08979699	-0.84623793	-3.55073909
H	2.54883073	-2.16088557	-2.12970959
H	3.90361292	1.66060577	-3.53976443
H	2.18383441	2.7188833	-2.09558776
C	0.55339488	-1.11782421	-0.50713142
C	0.43758823	-2.50560006	-0.47906878
C	-0.48360062	-3.09778562	0.37942605
H	1.03966539	-3.12891444	-1.122364
C	-1.13252492	-0.9052879	1.07355087
H	-1.74343742	-0.24040743	1.66932435
N	-0.23880782	-0.31719584	0.25470589
C	-1.2841814	-2.27542838	1.17962116
H	-2.0195035	-2.69926695	1.84896342
N	-0.68275512	-4.49495663	0.42460483
C	0.13341271	-5.58101858	0.22434195
C	-0.70022093	-6.66468132	0.41596587
N	-1.95348727	-4.93174163	0.74384166
N	-1.95124664	-6.2095575	0.7242231
C	-0.36571956	-8.10039722	0.2059757
O	0.60090695	-8.45747587	-0.41653774
O	-1.26776159	-8.90646492	0.76719412
H	-1.02127189	-9.82437295	0.56983027
C	1.58935071	-5.55516655	-0.1073378
O	2.08104437	-4.88937831	-0.98873751

O	2.26614557	-6.35757019	0.70390299
H	3.18054637	-6.44155616	0.38747464
Ru	-0.00766077	1.7526669	-0.05757478
N	0.47460361	3.77802936	-0.37391348
N	-1.61554098	2.36290874	1.15762758

Optimised geometry coordinates for AS17 (.xyz file format)

73

C	-1.92651534	-5.46305998	0.19781784
C	-1.32690242	-6.28100272	-0.74823173
C	-0.27243718	-5.78314971	-1.51610995
C	0.17774183	-4.47510236	-1.34167267
C	-0.41117195	-3.62312842	-0.39929562
C	-1.47700836	-4.14531329	0.37846605
H	-2.74272163	-5.85807478	0.79378791
H	-1.67213364	-7.29972619	-0.88504901
H	1.00686906	-4.12579448	-1.94737286
C	3.95773564	-2.61940047	1.35970282
C	3.83791147	-2.95331403	2.70064579
C	2.57616621	-2.95158978	3.29818350
C	1.44144467	-2.61542207	2.56069655
C	1.53081172	-2.26832702	1.20713222
C	2.81884001	-2.28089168	0.61193600
H	4.94122207	-2.62599950	0.90139332
H	4.71760019	-3.21753512	3.27685326
H	0.47583196	-2.63557962	3.05439503
Ir	0.03184237	-1.67483637	-0.03029339

C	2.86426141	-1.92541714	-0.80435309
C	1.57425418	-1.27121280	-2.65317410
C	4.01184700	-1.90709366	-1.60849929
C	2.67776690	-1.24147636	-3.48620517
H	0.58441012	-1.03685411	-3.02188077
H	4.96936653	-2.16831971	-1.17743997
H	2.56006686	-0.97431250	-4.52902873
C	3.92343834	-1.56590835	-2.94728443
H	4.81257879	-1.55562976	-3.56790560
N	1.65466171	-1.59874959	-1.34979612
C	-1.93682406	-1.05624659	2.24150296
C	-2.05150419	-3.22815469	1.35926430
C	-2.94592189	-1.30988852	3.15244333
H	-1.44465913	-0.09355133	2.20030685
C	-3.07943236	-3.53203799	2.26232389
H	-3.26067182	-0.53461201	3.83993609
H	-3.51556998	-4.52233090	2.26009907
N	-1.49734816	-1.97900047	1.36543946
C	-3.52891009	-2.57786100	3.15883738
H	-4.32119471	-2.81725832	3.85947444
H	0.20665306	-6.42183742	-2.25189447
H	2.47553514	-3.22035846	4.34530869
C	-1.54474046	0.60533500	-1.35987243
C	-2.52332553	1.28646112	-2.08827435
C	-3.42456698	0.56547766	-2.86263852
C	-3.33324544	-0.82200684	-2.88916566
C	-2.34789161	-1.43886452	-2.12855008
N	-1.47371112	-0.74853413	-1.38059443
H	-4.18823097	1.08309282	-3.43188049

H	-2.59740724	2.36532624	-2.04238987
H	-4.01423816	-1.42384884	-3.47867256
H	-2.23950297	-2.51646477	-2.10296634
C	-0.54089682	1.29953766	-0.51746976
C	-0.40243180	2.68767525	-0.52547959
C	0.54036128	3.27834770	0.30804048
H	-1.00105307	3.30588434	-1.17554156
C	1.17469981	1.09837693	1.03522627
H	1.78482677	0.42528384	1.62495213
N	0.25308203	0.51624925	0.25018548
C	1.34889110	2.47043986	1.10913563
H	2.10270701	2.90070903	1.75354781
N	0.74336326	4.68257308	0.32272940
C	-0.10585190	5.74799503	0.20277908
C	0.71964559	6.84925971	0.32498661
N	2.02583923	5.13756126	0.52873926
N	2.00013806	6.41862775	0.51694390
C	0.32753920	8.27137738	0.16953514
O	-0.73312483	8.61311939	-0.29046643
O	1.28650985	9.10695909	0.58107593
H	0.97719327	10.01309491	0.42425348
C	-1.58343528	5.68859302	-0.00419336
O	-2.12739106	5.09091887	-0.90116771
O	-2.21785055	6.38041156	0.93895488
H	-3.15975964	6.43390044	0.70914519

Optimised geometry coordinates for AS18 (.xyz file format)

C	1.78565719	0.55422290	0.36812885
C	3.03231340	-0.06568080	0.47461322
C	4.18122495	0.71112769	0.52304915
C	4.05932126	2.09492504	0.46451040
C	2.79205885	2.64677759	0.34759130
N	1.67595819	1.90309945	0.29954928
H	5.15483758	0.24046029	0.59959774
H	3.11281994	-1.14425920	0.50015841
H	4.92582095	2.74407685	0.49585547
H	2.65280403	3.71732837	0.28057185
C	0.51473915	-0.19545994	0.31943966
C	0.46515215	-1.58607342	0.42118607
C	-0.76312735	-2.22495937	0.33362906
H	1.36254468	-2.16613690	0.56479710
C	-1.79561188	-0.09036744	0.13271150
H	-2.66857839	0.53805957	0.02077001
N	-0.61162613	0.54315677	0.18515231
C	-1.92452591	-1.46620631	0.19432375
H	-2.89712414	-1.93457335	0.13937774
N	-0.86834180	-3.64165816	0.41783224
C	-0.09462544	-4.64508688	-0.08473389
C	-0.75696549	-5.79939296	0.28868981
N	-1.96282203	-4.17586172	1.05351573
N	-1.88140602	-5.45479881	0.97908635
C	-0.29812775	-7.18525443	0.05889438
O	0.80975024	-7.45962901	-0.33442727
O	-1.24174693	-8.09336265	0.34460628
H	-0.85437388	-8.96812075	0.18659739

C	1.17575466	-4.48293768	-0.85445834
O	2.16709774	-3.94519531	-0.42886899
O	1.06112263	-5.01085999	-2.07292394
H	1.92691223	-4.96579142	-2.50982702
Re	-0.35069616	2.72379935	-0.09454024
Cl	0.18141248	2.03431479	-2.46492173
C	-0.69497027	3.15249262	1.76098055
O	-0.89689970	3.40442508	2.87039100
C	-2.18187622	3.15138159	-0.58213020
O	-3.27453212	3.35575583	-0.87872966
C	0.16137057	4.56193325	-0.46723015
O	0.50570945	5.63580723	-0.69336911

Optimised geometry coordinates for 1 (.xyz file format)

67

C	3.16933984	-3.56657702	-0.69589279
C	3.36807446	-4.24867110	0.49774310
C	2.58700138	-3.91291928	1.59921937
C	1.63732223	-2.91090241	1.46202577
N	1.43803480	-2.24371799	0.31051052
C	2.19937210	-2.56519896	-0.77230856
H	3.76797778	-3.81846281	-1.56103767
H	4.11861015	-5.02762034	0.56454862
H	2.70452514	-4.41578820	2.55130639
H	1.01000388	-2.61997141	2.29410299
C	-3.17668071	-3.55898360	0.70401368
C	-3.37677670	-4.24314259	-0.48821323
C	-2.59504260	-3.91122026	-1.59038263

C	-1.64341419	-2.91077257	-1.45527722
N	-1.44280343	-2.24160843	-0.30514248
C	-2.20471542	-2.55938637	0.77836290
H	-3.77583286	-3.80787437	1.56966979
H	-4.12885785	-5.02073622	-0.55341339
H	-2.71354321	-4.41583990	-2.54142114
H	-1.01554893	-2.62277040	-2.28796100
C	0.70072060	2.12955411	0.23097910
C	1.43429856	3.29093587	0.45989861
C	2.75014120	3.20481854	0.90270596
C	3.30653770	1.94341037	1.10848490
C	2.52459544	0.82443217	0.86100402
N	1.25054859	0.89843332	0.43354377
H	1.01111263	4.27444762	0.30147685
H	4.32653173	1.83232915	1.45219346
H	2.91948761	-0.17171842	1.00906849
C	-0.69686506	2.13037947	-0.23595183
C	-1.42799683	3.29266599	-0.46808578
C	-2.74395902	3.20809817	-0.91083796
H	-1.00276309	4.27571636	-0.31230385
C	-2.52340280	0.82736577	-0.86262356
C	-3.30297052	1.94730050	-1.11324812
H	-2.92035642	-0.16835275	-1.00805253
H	-4.32314444	1.83742256	-1.45681185
N	-1.24923676	0.89986251	-0.43525542
Ru	-0.00095238	-0.73458966	0.00106069
C	3.49819240	4.48906530	1.13299932
O	3.00957335	5.57100322	0.95190248
O	4.74945931	4.26619924	1.55619832

H	5.19306769	5.11936684	1.69081227
C	-3.48927242	4.49327292	-1.14480494
O	-2.99840388	5.57468110	-0.96664921
O	-4.74094301	4.27186412	-1.56757630
H	-5.18274025	5.12558332	-1.70462546
C	-1.92597438	-1.77936066	1.99924826
C	-0.60941654	-0.11908662	2.96802829
C	-2.62539749	-1.94029339	3.19688431
C	-1.26706821	-0.23515399	4.18403958
H	0.19634706	0.59073663	2.83614537
H	-3.42547279	-2.66448273	3.27253058
H	-0.97448758	0.39388993	5.01582360
C	-2.29668710	-1.16376566	4.30076112
H	-2.83605011	-1.28204798	5.23329903
N	-0.91975335	-0.86732514	1.89339661
C	0.60888803	-0.12635730	-2.96709758
C	1.92227348	-1.78707956	-1.99478440
C	1.26665174	-0.24590547	-4.18270804
H	-0.19566073	0.58513076	-2.83678552
C	2.62172667	-1.95153290	-3.19192423
H	0.97540179	0.38206379	-5.01577064
H	3.42057147	-2.67724486	-3.26595662
N	0.91766202	-0.87304667	-1.89094017
C	2.29469099	-1.17652151	-4.29736413
H	2.83413186	-1.29748023	-5.22951295

Optimised geometry coordinates for 2 (.xyz file format)

C	3.21416565	-3.46888691	-0.73180128
C	3.47239825	-4.11615960	0.46737983
C	2.69670310	-3.81780605	1.58910836
C	1.67046827	-2.87673164	1.51314764
C	1.38881431	-2.20357498	0.31814749
C	2.18187088	-2.52110691	-0.81439502
H	3.81965296	-3.70787563	-1.59992174
H	4.26762116	-4.85061263	0.52954469
H	2.88915764	-4.32737876	2.52832954
H	1.08097824	-2.67808293	2.40170876
C	-3.23929983	-3.43572560	0.76072460
C	-3.50258083	-4.09318114	-0.43180746
C	-2.72425531	-3.81274470	-1.55631535
C	-1.69033883	-2.87934354	-1.48968542
C	-1.40340022	-2.19626284	-0.30157274
C	-2.19926217	-2.49568685	0.83396331
H	-3.84701570	-3.66058648	1.63104025
H	-4.30378723	-4.82170509	-0.48666356
H	-2.92084680	-4.33028816	-2.49032650
H	-1.09914931	-2.69453113	-2.38010972
C	0.72104873	2.22147229	0.19026978
C	1.45816609	3.39058098	0.37087219
C	2.79620875	3.31250822	0.74543026
C	3.37386920	2.05760554	0.92845749
C	2.58461459	0.93227002	0.73080750
N	1.29266563	1.00434320	0.37573280
H	1.02368236	4.37085382	0.22755464
H	4.41151047	1.95503520	1.21687873

H	2.98118115	-0.06746304	0.85864565
C	-0.70682243	2.22446311	-0.20848556
C	-1.43779165	3.39668024	-0.39374256
C	-2.77568973	3.32420287	-0.76994137
H	-0.99865591	4.37520689	-0.25269951
C	-2.57631360	0.94298647	-0.74683891
C	-3.35935706	2.07167773	-0.95019019
H	-2.97804225	-0.05516237	-0.87100282
H	-4.39694512	1.97338868	-1.24032697
N	-1.28467007	1.00964487	-0.38962700
Ir	-0.00178514	-0.75434205	0.00096554
C	3.54745959	4.59771517	0.93082760
O	3.05626163	5.68401743	0.77288827
O	4.82387306	4.38798923	1.29279234
H	5.25623864	5.25024862	1.39682926
C	-3.52023094	4.61269061	-0.95967658
O	-3.02443474	5.69685970	-0.80164833
O	-4.79656759	4.40840504	-1.32518878
H	-5.22460488	5.27253070	-1.43175288
C	-1.85920528	-1.76795093	2.05393301
C	-0.42828405	-0.15585747	2.98274166
C	-2.47882889	-1.92473462	3.30130642
C	-1.00780078	-0.27648176	4.23246072
H	0.39439687	0.52499892	2.80899960
H	-3.28656354	-2.63652756	3.41002448
H	-0.64166339	0.32189119	5.05745254
C	-2.05745527	-1.18235341	4.39104436
H	-2.53648388	-1.30819580	5.35570649
N	-0.83539069	-0.87313804	1.91847354

C	0.43050294	-0.18789152	-2.98627153
C	1.84740829	-1.80298810	-2.04150621
C	1.00855274	-0.32639229	-4.23483684
H	-0.38582303	0.50223549	-2.81922264
C	2.46520844	-1.97797178	-3.28728869
H	0.64766275	0.26697062	-5.06571289
H	3.26670403	-2.69785319	-3.38853249
N	0.83121981	-0.89821447	-1.91492135
C	2.04981661	-1.24341997	-4.38456265
H	2.52695999	-1.38401201	-5.34812523

Optimised geometry coordinates for 3 (.xyz file format)

34

Re	-0.00249836	1.71017522	-0.05247418
C	-0.00858698	1.97868420	-1.97127669
O	-0.01235433	2.13413063	-3.11588192
C	-1.37486807	3.06907360	0.18644078
O	-2.21600218	3.83785654	0.33965324
C	1.36846429	3.07198309	0.17755361
O	2.20902263	3.84258582	0.32476991
Cl	0.00499387	1.22246414	2.42099736
C	2.88587647	-2.35913610	-0.06160693
C	3.48654921	-1.10159423	-0.10323331
C	2.67200577	0.01883602	-0.14006215
C	0.73815311	-1.27118075	-0.09216975
C	1.49812587	-2.43819438	-0.05647223
H	4.56254883	-0.99293318	-0.10251848
H	3.09661113	1.01305650	-0.16596583

S22

H	1.03852561	-3.41632727	-0.01905998
C	-0.73711354	-1.27274998	-0.08957679
C	-1.49449360	-2.44143128	-0.05304602
C	-2.88241683	-2.36531389	-0.05336099
H	-1.03269839	-3.41865088	-0.01893411
C	-2.67386286	0.01321820	-0.12910749
C	-3.48589761	-1.10898403	-0.09098911
H	-3.10064390	1.00657660	-0.15230531
H	-4.56211785	-1.00261470	-0.08648412
N	-1.33243675	-0.05410735	-0.13296038
N	1.33072464	-0.05132457	-0.13908327
C	-3.65744149	-3.64250566	-0.01048703
O	-3.15718228	-4.73773717	0.01329184
O	-4.98851026	-3.43219742	-0.00283474
H	-5.42211071	-4.29860761	0.02925032
C	3.66374844	-3.63460587	-0.01905479
O	3.16588081	-4.73081424	0.00954153
O	4.99439371	-3.42152549	-0.01770998
H	5.42992396	-4.28695883	0.01461316

Table S1. Summarised TDDFT data for **AS16-18** and **1-3** for selected transitions.

Complex	Transition	Energy	λ	f	Composition	Character
AS16	S ₁	2.364	524	0.00362	HOMO→LUMO 90%	MLCT
	S ₅	2.743	452	0.15	HOMO-1→LUMO 54%	MLCT
					HOMO-1→LUMO+1 27%	MLCT
	S ₈	3.004	412	0.11	HOMO-2→LUMO+1 49%	MLCT
					HOMO-1→LUMO+2 36%	MLCT
					HOMO-1→LUMO+1 7%	MLCT

	S ₉	3.105	399	0.05	HOMO→LUMO+3 54%	MLCT
					HOMO-2→LUMO+2 21%	MLCT
					HOMO-1→LUMO+2 8%	MLCT
	S ₁₁	3.296	376	0.02	HOMO-1→LUMO+3 68%	MLCT
					HOMO-2→LUMO+3 21%	MLCT
AS17	S ₁	2.199	563	0.00061	HOMO→LUMO 96%	MLCT/LLCT
	S ₄	2.947	421	0.03	HOMO-1→LUMO 68%	MLCT/LLCT
					HOMO-2→LUMO 21%	MLCT/LLCT
	S ₅	3.144	394	0.05	HOMO→LUMO+2 92%	MLCT/ILCT
	S ₆	3.152	393	0.08	HOMO-3→LUMO 81%	MLCT/LLCT
	S ₉	3.399	365	0.02	HOMO-5→LUMO 88%	MLCT/LLCT
	S ₁₂	3.611	343	0.03	HOMO-4→LUMO+1 12%	MLCT/LLCT
					HOMO-2→LUMO+1 77%	MLCT/LLCT
AS18	S ₁	2.599	476	0.0037	HOMO→LUMO 96%	MLCT/LLCT
	S ₂	2.796	443	0.08	HOMO-1→LUMO 96%	MLCT/LLCT
	S ₄	3.360	369	0.02	HOMO→LUMO+1 94%	LLCT/MLCT
	S ₉	4.062	305	0.05	HOMO-3→LUMO 38%	ILCT
					HOMO-5→LUMO 28%	LLCT/MLCT
					HOMO-4→LUMO 20%	LLCT/MLCT
1	S ₁	2.257	549	0.00345	HOMO→LUMO 96%	MLCT
	S ₃	2.697	460	0.10	HOMO-2→LUMO 81%	MLCT
	S ₅	2.769	448	0.01	HOMO→LUMO+2 90%	MLCT
	S ₈	3.077	403	0.10	HOMO-2→LUMO +2 47%	MLCT
					HOMO-1→LUMO+1 49%	MLCT
	S ₉	3.119	397	0.08	HOMO→LUMO+3 56%	MLCT
					HOMO-1→LUMO+2 30%	MLCT

	S ₁₀	3.250	382	0.10	HOMO-1→LUMO+4 54%	MLCT
					HOMO-2→LUMO+2 6%	MLCT
					HOMO-1→LUMO+2 23%	MLCT
					HOMO→LUMO+3 10%	MLCT
	S ₁₂	3.349		0.04	HOMO-2→LUMO+3 72%	MLCT
					HOMO→LUMO+4 21%	MLCT
	S ₁₃	3.398	365	0.04	HOMO-1→LUMO+3 36%	MLCT
					HOMO→LUMO+3 21%	MLCT
					HOMO-1→LUMO+2 12%	MLCT
	S ₁₅	3.527	352	0.04	HOMO-2→LUMO+4 87%	MLCT
2	S ₁	2.024	612	0.00036	HOMO→LUMO 99%	MLCT/LLCT
	S ₆	3.033	409	0.08	HOMO-3→LUMO 84%	MLCT/LLCT
	S ₈	3.166	392	0.05	HOMO→LUMO+3 86%	MLCT/ILCT
	S ₁₂	3.602	344	0.06	HOMO-4→LUMO+1 12%	MLCT/LLCT
					HOMO-2→LUMO+1 81%	MLCT/LLCT
3	S ₁	2.411	514	0.00525	HOMO→LUMO 99%	MLCT/LLCT
	S ₂	2.631	471	0.07	HOMO-1→LUMO 96%	MLCT/LLCT
	S ₄	3.253	381	0.04	HOMO→LUMO+1 96%	MLCT/LLCT
	S ₅	3.311	374	0.02	HOMO-1→LUMO+1 96%	MLCT/LLCT
	S ₉	3.905	318	0.04	HOMO-5→LUMO 49%	LLCT/MLCT
					HOMO-3→LUMO 47%	ILCT
	S ₁₀	3.977	312	0.07	HOMO-4→LUMO 94%	LLCT

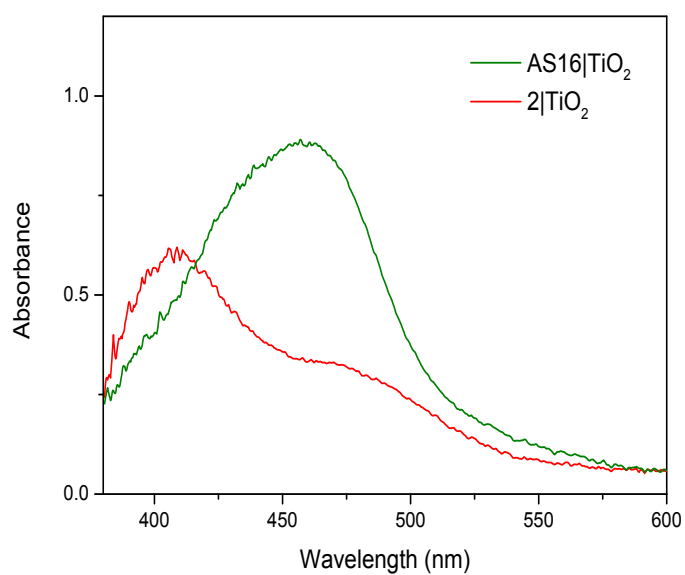


Figure S17. UV-vis absorption spectra of **2** and **AS16** adsorbed onto a TiO_2 electrode.

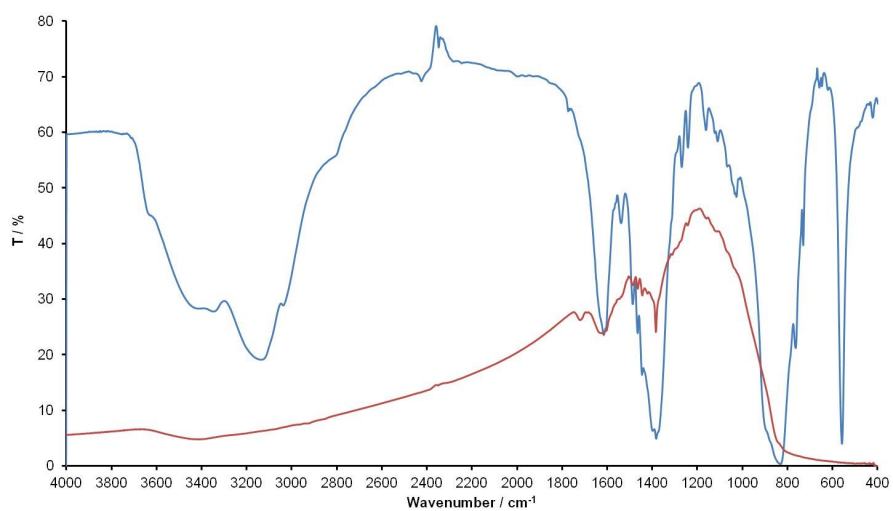


Figure S18. Infrared spectra of **AS16** (KBr disc, blue trace) and **AS16** immobilised on TiO_2 (KBr disc, red trace).