Supplementary X-ray Crystallographic Data

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1 General Information.

Low temperature single crystal X-ray diffraction data were variously collected with a Nonius Kappa CCD Diffractometer or a (Rigaku) Oxford Diffraction SuperNova A diffractometer at 150 K. Data were reduced using the appropriate instrument manufacturer software, DENZO/SCALEPACK[1] or CrysAlisPro. For exceptionally small crystals data were collected using I19-1 at the Diamond Light Source at 100 K.[2] All structures were solved *ab initio* using SuperFlip[3] and the structures were refined using CRYSTALS.[4,5]

1.1 Synthesis of Ynamides from 1,2-Dichloroenamides.

Data for **53a** were collected with a Nonius Kappa CCD Diffractometer at 150 K by Dr Mike Jones. Data were reduced using DENZO/SCALEPACK[6], solved using SIR92[7] and the structure was refined using CRYSTALS, all by Dr Mike Jones.

Data for **66** were collected using I19-1 at the Diamond Light Source[8] at 100 K, and data for **71e** and **85e** were collected with a (Rigaku) Oxford Diffraction SuperNova A diffractometer at 150 K, all by Dr Kirsten Christensen. Data were reduced using CrysAlisPro, solved using SuperFlip and the structure was refined using CRYSTALS, all by Dr Kirsten Christensen.

The Flack x parameter was refined in all cases.[9,10]

Structure **60an** was found to be twinned which was modelled using ROTAX.[11]

Further details about the refinements, including disorder modelling and restraints, for the compounds pertaining to Chapter 1 are documented in the CIF files entitled "Chapter 1 - Ynamides Crystallographic Data" and "Chapter 1 - Dichloroenamides and Misc. Crystallographic Data".

1.2 Synthesis and Applications of Yndiamides.

Data for **148a** were collected with a Nonius Kappa CCD Diffractometer at 150 K by Dr Mike Jones. Data were reduced using DENZO/SCALEPACK, solved using SIR92 and the structure was refined using CRYSTALS, all by Dr Mike Jones.

Data for **148j** and **148k** were collected using I19-1 at the Diamond Light Source at 100 K by Dr Kirsten Christensen. Data were reduced using CrysAlisPro, solved using SuperFlip and the structures were refined using CRYSTALS by Dr Kirsten Christensen. Drs Kirsten Christensen and Amber Thompson aided in refinement of structure **148h**, **160a**, and **160b**.

Data for **155c** were collected using I19-1 at the Diamond Light Source[2] at 100 K by Dr Kirsten

Christensen. Data were reduced using CrysAlisPro, solved using SuperFlip and the structure was refined using CRYSTALS, all by Dr Kirsten Christensen. Drs Kirsten Christensen and Amber Thompson aided in refinement of structures **155b**, **162** and **206**.

The Flack x parameter was refined in all cases.[9,10] Bayesian analysis of the Bijvoet pairs was also carried out for enantiopure compound **148y** and (–)**-197** using all the data in the refinement.[12] This gave the Hooft y parameter, the P2 probability (the likelihood that the hand is correct given the crystal was enantiopure), and the P3 probability (the likelihood that the hand is correct given the crystal was enantiopure or racemic). The data for **148y** and (–)**-197** indicate that the handedness of these models is very likely correct.

The data for compound **148l** were extremely poor owing to the small, poor quality crystals grown. Synchrotron radiation was used for data collection, but the compound also suffered significant beam damage. Only data from the initial φ scan were used, data completeness is low (74.1%) and the final R indices are high. Similarly, the data for compound **160e** was extremely disordered, which was modelled using a split site model. Same distance, thermal similarity and vibrational restraints were necessary in order to maintain sensible geometric and displacement parameters. The occupancies of the individual components were refined competitively in the final refinement. Data for these compounds were not included in the data analysis, but are included here because the twisted nature of these compounds in the crystal lattice is evident.

Structure **160b** displays incommensurate modulation along the c-axis (**Figure SX1**). This was not modelled as the satellites were very weak, especially at high angle. On refinement, the displacement ellipsoids for the homoallyl sidechain were prolate, which is very likely to be a result of the modulation. This was modelled as disorder using a split site model.

Structure **155d**, **188** & **232a** contained large solvent accessible voids comprising weak, diffuse electron density. The discrete Fourier transforms of the void regions were treated as contributions to the A and B parts of the calculated structure factors using PLATON/SQUEEZE[13,14] integrated within the CRYSTALS software.

Structure **206** exhibited diffuse scattering indicating the presence of short range order within the disordered modelled (Figure **SX2**).

Further details about the refinements, including disorder modelling and restraints, for the compounds pertaining to Chapter 2 are documented in the CIF files entitled "Chapter 2 - Yndiamides Crystallographic Data" and "Chapter 2 - Bromoketene Aminals, Applications and Misc. Crystallographic Data".

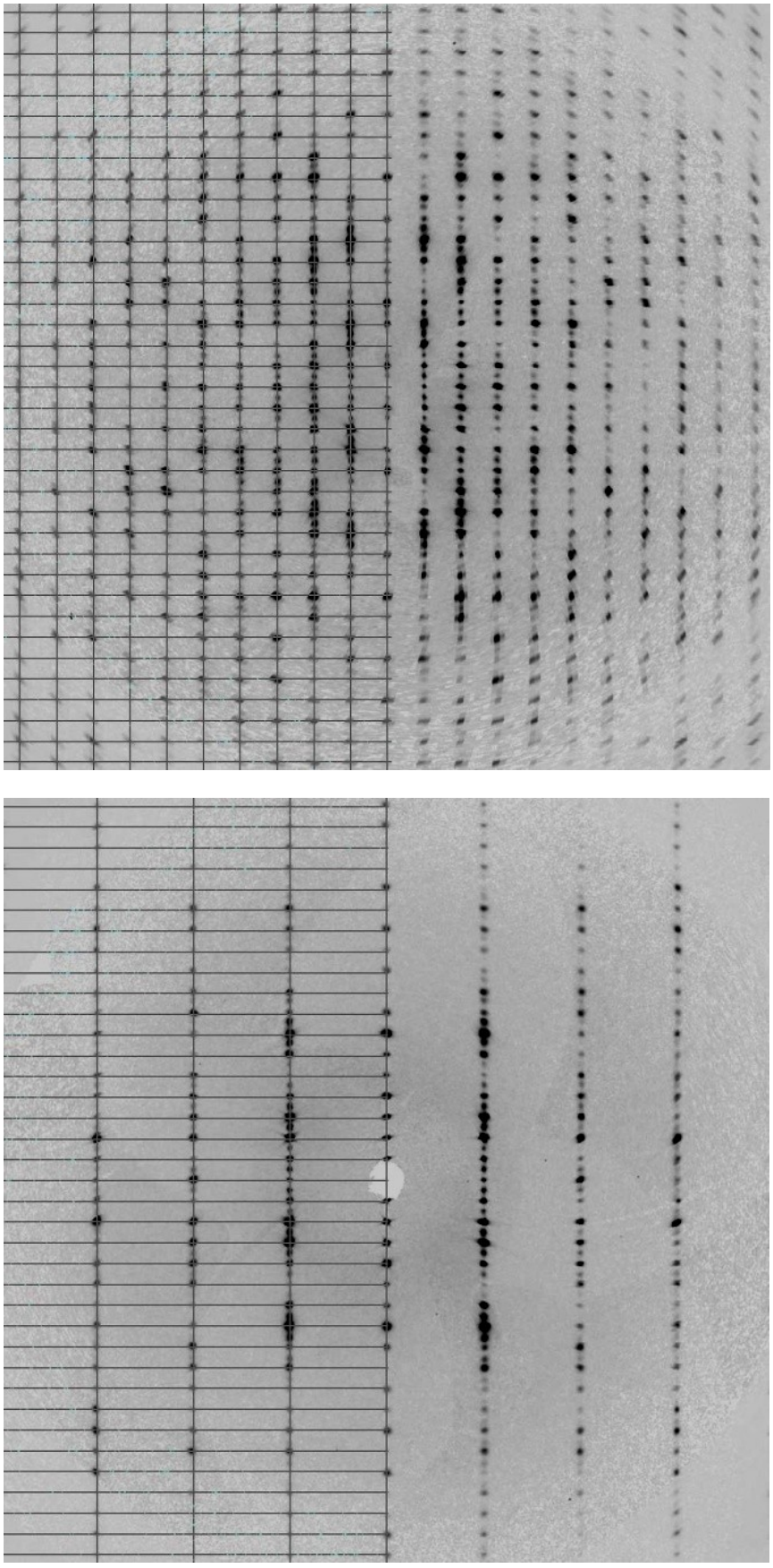

Figure SX1: The 1*kl* and *h*1*l* reciprocal lattice sections reconstructed to 1.5 Å, displayed with grid overlay on the left hand sides.

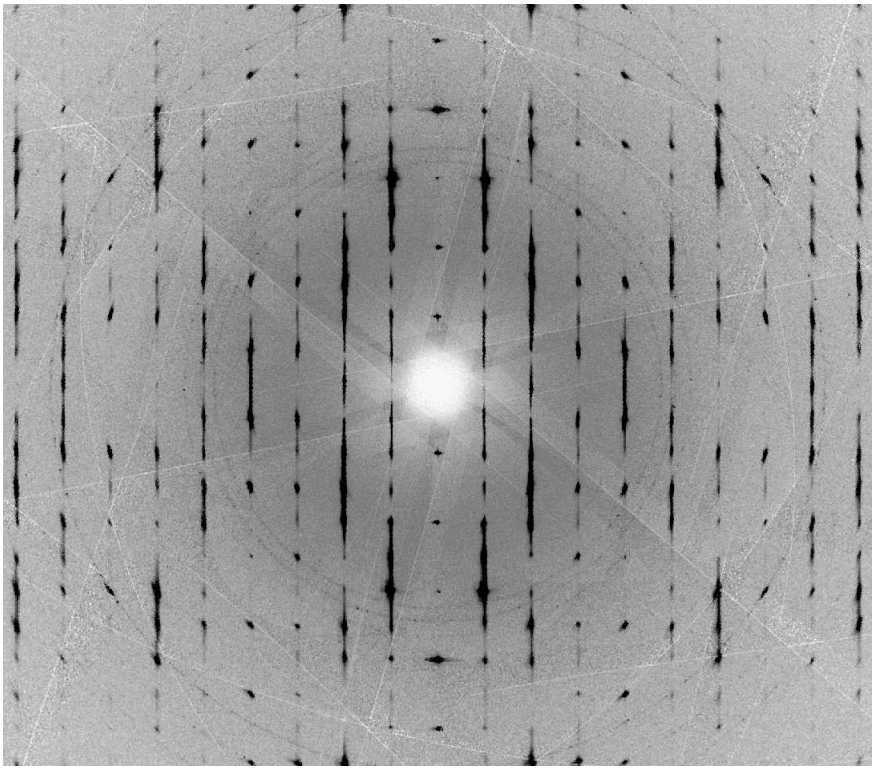

Figure SX2: The 0*kl* reciprocal lattice section reconstructed to 2.0 Å.

1.3 Physical and Spectroscopic Properties of Ynamides and Yndiamides.

Compounds (Ph*o*-CyTsYnMe) and (IndoleTsYnPh) were synthesised by Bethany Shire and Pavel Fedoseev, respectively, and were given as gifts for recrystallisation and X-ray diffraction analysis.

Further details about the refinements, including disorder modelling and restraints, for the ynamides *not* prepared in Chapter 1 are documented in the CIF files entitled "Chapter 3 - Ynamides Crystallographic Data".

The following CCDC entries contain additional data that was analysed in Chapter 3: 127101, 218160, 282619, 740499, 756647, 766232, 780116, 784155, 784156, 858296, 862235, 862236, 872579, 897472, 899755, 905007, 934067, 934068, 945285, 946186, 947100, 947101, 947102, 970596, 972880, 974565, 974566, 1002889, 1013242, 1013243, 1402829, 1414826, 1423446, 1425945, 1426144, 1500873, 1509490, 1518789, 1830665, 1833410, 1840581, 1840852, 1841828, 1862618. Data for these entries are not included here and can be obtained free of charge from the CCDC.

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2 X-ray Crystallographic Data.

2.1 Synthesis of Ynamides from 1,2-Dichloroenamides.

2.1a *Ynamides*.

Table S1 Crystal data and structure refinement for **56a**, PhTsYnCl.

Identification code	002mwj014	
Empirical formula	C15 H12 Cl1 N1 O2 S1	
Formula weight	305.78	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.93810(10) Å	α= 90°.
	b = 9.76990(10) Å	β= 93.7718(5)°.
	c = 16.5623(2) Å	γ = 90°.
Volume	1443.16(3) $Å^3$	
Z	4	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	0.409 mm^{-1}	
F(000)	632	
Crystal size	0.34 x 0.30 x 0.23 mm^3	
Theta range for data collection	5.103 to 27.488°.	
Index ranges	-11<=h<=11, -10<=k<=12, -21<=l<=21	
Reflections collected	24453	
Independent reflections	3277 [R(int) = 0.0161]	
Completeness to theta = 27.488°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3276 / 0 / 181	
Goodness-of-fit on F^2	1.0015	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0860	
R indices (all data)	R1 = 0.0406, wR2 = 0.0905	
Largest diff. peak and hole	0.32 and -0.40 e.$Å^{-3}$	

Table S2 Crystal data and structure refinement for **60a**, PhTsYnPh(P1).

Identification code	019eaa17	
Empirical formula	C21 H17 N1 O2 S1	
Formula weight	347.44	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 12.20120(10) Å	α= 90°.
	b = 18.6881(2) Å	β= 90°.
	c = 7.82410(10) Å	γ = 90°.
Volume	1784.03(3) $Å^3$	
Z	4	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	1.715 mm^{-1}	
F(000)	728	
Crystal size	0.43 x 0.36 x 0.18 mm^3	
Theta range for data collection	4.328 to 76.000°.	
Index ranges	-15<=h<=15, -23<=k<=21, -7<=l<=9	
Reflections collected	16490	
Independent reflections	3154 [R(int) = 0.0299]	
Completeness to theta = 76.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.73 and 0.46	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3154 / 1 / 228	
Goodness-of-fit on F^2	0.9960	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0968	
R indices (all data)	R1 = 0.0363, wR2 = 0.0969	
Extinction coefficient	56(7)	
Largest diff. peak and hole	0.26 and -0.26 e.$Å^{-3}$	
Absolute structure parameter	0.026(17)	

Table S3 Crystal data and structure refinement for **60a**, PhTsYnPh(P2).

Identification code	062eaa17	
Empirical formula	C21 H17 N1 O2 S1	
Formula weight	347.44	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.6012(4) Å	α= 90°.
	b = 10.3076(3) Å	β= 111.155(4)°.
	c = 14.3723(5) Å	γ = 90°.
Volume	1740.98(11) $Å^3$	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	1.758 mm^{-1}	
F(000)	728	
Crystal size	0.27 x 0.25 x 0.15 mm^3	
Theta range for data collection	4.009 to 76.283°.	
Index ranges	-15<=h<=15, -10<=k<=12, -17<=l<=16	
Reflections collected	8626	
Independent reflections	3573 [R(int) = 0.0147]	
Completeness to theta = 73.232°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3570 / 0 / 226	
Goodness-of-fit on F^2	1.0028	
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0873	
R indices (all data)	R1 = 0.0347, wR2 = 0.0885	
Largest diff. peak and hole	0.21 and -0.43 $e.Å^{-3}$	

Table S4 Crystal data and structure refinement for **60b**, PhTsYn*i*-Pr.

Identification code	035eaa17	
Empirical formula	C18 H19 N1 O2 S1	
Formula weight	313.42	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.9260(4) Å	α= 90°.
	b = 9.0582(2) Å	β= 98.130(2)°.
	c = 11.5806(3) Å	γ = 90°.
Volume	1653.84(7) $Å^3$	
Z	4	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	1.785 mm^{-1}	
F(000)	664	
Crystal size	0.20 x 0.17 x 0.04 mm^3	
Theta range for data collection	5.612 to 76.232°.	
Index ranges	-19<=h<=19, -11<=k<=11, -14<=l<=14	
Reflections collected	31085	
Independent reflections	3448 [R(int) = 0.0457]	
Completeness to theta = 76.232°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3447 / 0 / 199	
Goodness-of-fit on F^2	1.0054	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0905	
R indices (all data)	R1 = 0.0415, wR2 = 0.0991	
Largest diff. peak and hole	0.46 and -0.35 e.$Å^{-3}$	

Table S5 Crystal data and structure refinement for **60c**, PhTsYnCy.

Identification code	021eaa17	
Empirical formula	C21 H23 N1 O2 S1	
Formula weight	353.48	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.9979(2) Å	α= 90°.
	b = 15.6744(3) Å	β= 107.064(2)°.
	c = 14.1236(3) Å	γ = 90°.
Volume	1904.26(7) $Å^3$	
Z	4	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	1.608 mm^{-1}	
F(000)	752	
Crystal size	0.30 x 0.25 x 0.21 mm^3	
Theta range for data collection	4.322 to 76.157°.	
Index ranges	-11<=h<=11, -18<=k<=19, -17<=l<=17	
Reflections collected	9744	
Independent reflections	3923 [R(int) = 0.0268]	
Completeness to theta = 72.349°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.71 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3923 / 158 / 272	
Goodness-of-fit on F^2	1.0069	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1110	
R indices (all data)	R1 = 0.0435, wR2 = 0.1142	
Largest diff. peak and hole	0.28 and -0.42 $e.Å^{-3}$	

Table S6 Crystal data and structure refinement for **60d**, PhTsYn*t*-Bu.

Identification code	020eaa17	
Empirical formula	C19 H21 N1 O2 S1	
Formula weight	327.45	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.2914(2) Å	α= 90°.
	b = 9.47850(10) Å	β= 102.1725(13)°.
	c = 11.50330(10) Å	γ = 90°.
Volume	1736.38(3) $Å^3$	
Z	4	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	1.721 mm^{-1}	
F(000)	696	
Crystal size	0.36 x 0.18 x 0.08 mm^3	
Theta range for data collection	2.775 to 76.055°.	
Index ranges	-19<=h<=20, -11<=k<=11, -14<=l<=14	
Reflections collected	42250	
Independent reflections	3624 [R(int) = 0.0556]	
Completeness to theta = 76.055°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3615 / 0 / 209	
Goodness-of-fit on F^2	1.0427	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1060	
R indices (all data)	R1 = 0.0427, wR2 = 0.1068	
Largest diff. peak and hole	0.27 and -0.47 $e.Å^{-3}$	

Table S7 Crystal data and structure refinement for **60e**, PhTsYnPh*p*-NMe_2.

Identification code	045eaa18	
Empirical formula	C23 H22 N2 O2 S1	
Formula weight	390.51	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.2727(2) Å	α= 90°.
	b = 8.46430(10) Å	β= 119.1762(17)°.
	c = 16.2146(2) Å	γ = 90°.
Volume	1949.99(5) $Å^3$	
Z	4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	1.642 mm^{-1}	
F(000)	824	
Crystal size	0.26 x 0.20 x 0.08 mm^3	
Theta range for data collection	5.457 to 75.976°.	
Index ranges	-18<=h<=20, -10<=k<=10, -17<=l<=20	
Reflections collected	20584	
Independent reflections	4051 [R(int) = 0.0259]	
Completeness to theta = 74.457°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4050 / 0 / 253	
Goodness-of-fit on F^2	1.0021	
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0910	
R indices (all data)	R1 = 0.0351, wR2 = 0.0934	
Largest diff. peak and hole	0.33 and -0.44 $e.Å^{-3}$	

Table S8 Crystal data and structure refinement for **60f**, PhTsYnPh*p*-NHAc.

Identification code	094eaa17	
Empirical formula	C23 H20 N2 O3 S1	
Formula weight	404.49	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.0923(3) Å	α= 90°.
	b = 9.6480(2) Å	β= 104.416(3)°.
	c = 10.6438(3) Å	γ = 90°.
Volume	1003.76(5) $Å^3$	
Z	2	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	1.656 mm^{-1}	
F(000)	424	
Crystal size	0.41 x 0.12 x 0.01 mm^3	
Theta range for data collection	4.289 to 75.024°.	
Index ranges	-12<=h<=8, -12<=k<=11, -13<=l<=13	
Reflections collected	9371	
Independent reflections	4017 [R(int) = 0.0358]	
Completeness to theta = 72.774°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.72	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4012 / 1 / 263	
Goodness-of-fit on F^2	1.0051	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0812	
R indices (all data)	R1 = 0.0368, wR2 = 0.0848	
Largest diff. peak and hole	0.16 and -0.27 $e.Å^{-3}$	
Absolute structure parameter	-0.020(15)	

Table S9 Crystal data and structure refinement for **60g**, PhTsYnPh*p*-OMe.

Identification code	098eaa17	
Empirical formula	C22 H19 N1 O3 S1	
Formula weight	377.46	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.3188(2) Å	α= 90°.
	b = 7.6203(2) Å	β= 97.928(3)°.
	c = 19.6737(6) Å	γ = 90°.
Volume	938.26(5) $Å^3$	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	1.715 mm^{-1}	
F(000)	396	
Crystal size	0.23 x 0.14 x 0.01 mm^3	
Theta range for data collection	4.538 to 75.688°.	
Index ranges	-7<=h<=7, -9<=k<=5, -24<=l<=22	
Reflections collected	8169	
Independent reflections	2811 [R(int) = 0.0321]	
Completeness to theta = 74.174°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2811 / 1 / 245	
Goodness-of-fit on F^2	1.0005	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0855	
R indices (all data)	R1 = 0.0369, wR2 = 0.0879	
Largest diff. peak and hole	0.24 and -0.35 $e.Å^{-3}$	
Absolute structure parameter	-0.02(2)	

Table S10 Crystal data and structure refinement for **60h**, PhTsYnPh*o*-OMe.

Identification code	100eaa17	
Empirical formula	C25 H22 N O3 S	
Formula weight	416.52	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.5545(3) Å	α= 90°.
	b = 10.1069(2) Å	β= 91.6279(17)°.
	c = 15.4427(3) Å	γ = 90°.
Volume	2114.70(8) $Å^3$	
Z	4	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	1.573 mm^{-1}	
F(000)	876	
Crystal size	0.21 x 0.06 x 0.04 mm^3	
Theta range for data collection	4.280 to 75.784°.	
Index ranges	-15<=h<=16, -8<=k<=12, -18<=l<=19	
Reflections collected	15582	
Independent reflections	4366 [R(int) = 0.0282]	
Completeness to theta = 74.268°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.82	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4365 / 108 / 299	
Goodness-of-fit on F^2	0.9969	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0885	
R indices (all data)	R1 = 0.0401, wR2 = 0.0943	
Largest diff. peak and hole	0.37 and -0.37 $e.Å^{-3}$	

Table S11 Crystal data and structure refinement for **60i**, PhTsYnPh*o*-F,OMe.

Identification code	007eaa18	
Empirical formula	C22 H18 F1 N1 O3 S1	
Formula weight	395.45	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4619(8) Å	α= 62.180(6)°.
	b = 10.8579(8) Å	β= 66.752(6)°.
	c = 11.6128(6) Å	γ = 68.711(7)°.
Volume	945.71(13) $Å^3$	
Z	2	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	1.807 mm^{-1}	
F(000)	412	
Crystal size	0.16 x 0.13 x 0.07 mm^3	
Theta range for data collection	4.476 to 76.002°.	
Index ranges	-11<=h<=11, -13<=k<=12, -14<=l<=12	
Reflections collected	8678	
Independent reflections	3895 [R(int) = 0.0249]	
Completeness to theta = 72.962°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.81	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3894 / 0 / 253	
Goodness-of-fit on F^2	0.9984	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0903	
R indices (all data)	R1 = 0.0381, wR2 = 0.0946	
Largest diff. peak and hole	0.44 and -0.45 $e.Å^{-3}$	

Table S12 Crystal data and structure refinement for **60j**, PhTsYnMes.

Identification code	084eaa17	
Empirical formula	C24 H23 N1 O2 S1	
Formula weight	389.52	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.8227(4) Å	α= 88.212(3)°.
	b = 14.6906(5) Å	β= 79.334(4)°.
	c = 14.7062(6) Å	γ = 86.406(3)°.
Volume	2080.94(14) $Å^3$	
Z	4	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	1.523 mm^{-1}	
F(000)	824	
Crystal size	0.15 x 0.12 x 0.11 mm^3	
Theta range for data collection	4.253 to 76.364°.	
Index ranges	-12<=h<=12, -7<=k<=18, -18<=l<=18	
Reflections collected	20999	
Independent reflections	8626 [R(int) = 0.0403]	
Completeness to theta = 74.073°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.74	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8624 / 0 / 505	
Goodness-of-fit on F^2	1.0056	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1078	
R indices (all data)	R1 = 0.0547, wR2 = 0.1201	
Largest diff. peak and hole	0.38 and -0.40 $e.Å^{-3}$	

Table S13 Crystal data and structure refinement for **60k**, PhTsYnPh*o*-Me,*p*-Cl.

Identification code	099eaa17	
Empirical formula	C22 H18 Cl1 N1 O2 S1	
Formula weight	395.91	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.1085(2) Å	α= 90°.
	b = 13.3591(2) Å	β= 90°.
	c = 18.4947(4) Å	γ = 90°.
Volume	2003.39(7) $Å^3$	
Z	4	
Density (calculated)	1.313 Mg/m^3	
Absorption coefficient	2.791 mm^{-1}	
F(000)	824	
Crystal size	0.16 x 0.13 x 0.11 mm^3	
Theta range for data collection	5.819 to 76.045°.	
Index ranges	-9<=h<=10, -14<=k<=16, -21<=l<=23	
Reflections collected	10167	
Independent reflections	4130 [R(int) = 0.0334]	
Completeness to theta = 73.763°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.74 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4129 / 0 / 245	
Goodness-of-fit on F^2	0.9991	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0977	
R indices (all data)	R1 = 0.0413, wR2 = 0.1017	
Absolute structure parameter	0.004(16)	
Largest diff. peak and hole	0.55 and -0.42 $e.Å^{-3}$	

Table S14 Crystal data and structure refinement for **60l**, PhTsYnFc.

Identification code	108eaa18	
Empirical formula	C25 H21 Fe1 N1 O2 S1	
Formula weight	455.36	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.0920(3) Å	α= 64.447(3)°.
	b = 10.1937(3) Å	β= 85.899(2)°.
	c = 10.8227(3) Å	γ = 87.988(2)°.
Volume	1001.89(6) $Å^3$	
Z	2	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	7.189 mm^{-1}	
F(000)	472	
Crystal size	0.37 x 0.15 x 0.13 mm^3	
Theta range for data collection	4.392 to 76.014°.	
Index ranges	-12<=h<=12, -12<=k<=12, -13<=l<=13	
Reflections collected	17453	
Independent reflections	4141 [R(int) = 0.0284]	
Completeness to theta = 73.734°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.39 and 0.17	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4127 / 0 / 271	
Goodness-of-fit on F^2	1.0036	
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0661	
R indices (all data)	R1 = 0.0252, wR2 = 0.0665	
Largest diff. peak and hole	0.32 and -0.42 $e.Å^{-3}$	

Table S15 Crystal data and structure refinement for **60m**, PhTsYn1-Np.

Identification code	012eaa18	
Empirical formula	C25 H19 N1 O2 S1	
Formula weight	397.50	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.0622(2) Å	α= 90°.
	b = 11.31990(10) Å	β= 98.0347(13)°.
	c = 13.6438(2) Å	γ = 90°.
Volume	1997.61(5) $Å^3$	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	1.604 mm^{-1}	
F(000)	832	
Crystal size	0.17 x 0.13 x 0.11 mm^3	
Theta range for data collection	4.390 to 76.180°.	
Index ranges	-14<=h<=16, -14<=k<=13, -17<=l<=17	
Reflections collected	17523	
Independent reflections	4145 [R(int) = 0.0287]	
Completeness to theta = 74.656°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.81	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4142 / 0 / 262	
Goodness-of-fit on F^2	0.9979	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0856	
R indices (all data)	R1 = 0.0371, wR2 = 0.0904	
Largest diff. peak and hole	0.37 and -0.42 $e.Å^{-3}$	

Table S16 Crystal data and structure refinement for **60n**, PhTsYn2-Np.

Identification code	014eaa18	
Empirical formula	C25 H19 N1 O2 S1	
Formula weight	397.50	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.78260(10) Å	α= 90°.
	b = 8.65700(10) Å	β= 103.0072(13)°.
	c = 18.5908(2) Å	γ = 90°.
Volume	2004.45(4) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	1.599 mm^{-1}	
F(000)	832	
Crystal size	0.33 x 0.13 x 0.09 mm^3	
Theta range for data collection	3.549 to 76.175°.	
Index ranges	-10<=h<=15, -10<=k<=10, -23<=l<=22	
Reflections collected	10881	
Independent reflections	4121 [R(int) = 0.0251]	
Completeness to theta = 73.890°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4115 / 0 / 262	
Goodness-of-fit on F^2	1.0002	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0898	
R indices (all data)	R1 = 0.0370, wR2 = 0.0933	
Largest diff. peak and hole	0.29 and -0.35 $e.Å^{-3}$	

Table S17 Crystal data and structure refinement for **60o**, PhTsYnPhen.

Identification code	008eaa18	
Empirical formula	C29 H21 N1 O2 S1	
Formula weight	447.56	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.3811(2) Å	α= 90°.
	b = 17.7083(2) Å	β= 114.613(2)°.
	c = 12.2129(2) Å	γ = 90°.
Volume	2237.75(7) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	1.496 mm^{-1}	
F(000)	936	
Crystal size	0.46 x 0.13 x 0.11 mm^3	
Theta range for data collection	4.466 to 76.109°.	
Index ranges	-14<=h<=9, -22<=k<=21, -13<=l<=15	
Reflections collected	18237	
Independent reflections	4635 [R(int) = 0.0381]	
Completeness to theta = 74.587°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4632 / 0 / 298	
Goodness-of-fit on F^2	0.9991	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0963	
R indices (all data)	R1 = 0.0400, wR2 = 0.1006	
Largest diff. peak and hole	0.36 and -0.47 $e.Å^{-3}$	

Table S18 Crystal data and structure refinement for **60p**, PhTsYnPh*p*-F.

Identification code	083eaa17	
Empirical formula	C21 H16 F1 N1 O2 S1	
Formula weight	365.43	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.0977(2) Å	α= 90°.
	b = 9.8744(2) Å	β= 94.8026(19)°.
	c = 17.9598(4) Å	γ = 90°.
Volume	1784.46(6) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	1.826 mm^{-1}	
F(000)	760	
Crystal size	0.31 x 0.07 x 0.07 mm^3	
Theta range for data collection	4.394 to 76.074°.	
Index ranges	-8<=h<=12, -12<=k<=12, -21<=l<=22	
Reflections collected	9795	
Independent reflections	3703 [R(int) = 0.0320]	
Completeness to theta = 74.552°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.63	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3703 / 0 / 235	
Goodness-of-fit on F^2	1.0052	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0978	
R indices (all data)	R1 = 0.0431, wR2 = 0.1051	
Largest diff. peak and hole	0.31 and -0.40 $e.Å^{-3}$	

Table S19 Crystal data and structure refinement for **60q**, PhTsYnPh*o*-Br.

Identification code	011eaa18	
Empirical formula	C21 H16 Br1 N1 O2 S1	
Formula weight	426.33	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.2958(4) Å	α= 77.676(3)°.
	b = 13.3312(4) Å	β= 82.309(3)°.
	c = 13.4928(4) Å	γ = 70.428(3)°.
Volume	1866.03(11) $Å^3$	
Z	4	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	4.169 mm^{-1}	
F(000)	864	
Crystal size	0.47 x 0.13 x 0.04 mm^3	
Theta range for data collection	3.578 to 76.164°.	
Index ranges	-12<=h<=14, -16<=k<=16, -16<=l<=16	
Reflections collected	26610	
Independent reflections	7700 [R(int) = 0.0480]	
Completeness to theta = 73.879°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.43	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7699 / 677 / 639	
Goodness-of-fit on F^2	0.9979	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1296	
R indices (all data)	R1 = 0.0564, wR2 = 0.1402	
Largest diff. peak and hole	0.47 and -0.60 $e.Å^{-3}$	

Table S20 Crystal data and structure refinement for **60r**, PhTsYnPh*p*-CF_3.

Identification code	097eaa17	
Empirical formula	C22 H16 F3 N1 O2 S1	
Formula weight	415.43	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.9463(3) Å	α= 90°.
	b = 8.35330(10) Å	β= 110.087(3)°.
	c = 17.8295(5) Å	γ = 90°.
Volume	1950.75(8) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	1.893 mm^{-1}	
F(000)	856	
Crystal size	0.36 x 0.16 x 0.03 mm^3	
Theta range for data collection	4.950 to 76.149°.	
Index ranges	-16<=h<=17, -5<=k<=10, -22<=l<=22	
Reflections collected	10257	
Independent reflections	4045 [R(int) = 0.0269]	
Completeness to theta = 73.864°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.77	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4045 / 343 / 317	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1119	
R indices (all data)	R1 = 0.0513, wR2 = 0.1211	
Largest diff. peak and hole	0.42 and -0.40 e.$Å^{-3}$	

Table S21 Crystal data and structure refinement for **60s**, PhTsYnPh*m*-CO_2Me.

Identification code	092eaa17	
Empirical formula	C23 H19 N1 O4 S1	
Formula weight	405.47	
Temperature	30 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.20080(10) Å	α= 90°.
	b = 7.88030(10) Å	β= 93.8075(11)°.
	c = 39.7265(5) Å	γ = 90°.
Volume	1936.92(5) $Å^3$	
Z	4	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	848	
Crystal size	0.030 x 0.030 x 0.005 mm^3	
Theta range for data collection	1.992 to 27.330°.	
Index ranges	-8<=h<=8, -10<=k<=10, -52<=l<=52	
Reflections collected	31412	
Independent reflections	4823 [R(int) = 0.0834]	
Completeness to theta = 27.330°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4810 / 0 / 262	
Goodness-of-fit on F^2	0.9920	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1403	
R indices (all data)	R1 = 0.0528, wR2 = 0.1442	
Largest diff. peak and hole	0.62 and -0.72 e.$Å^{-3}$	

Table S22 Crystal data and structure refinement for **60t**, PhTsYnPh*p*-amide.

Identification code	016eaa18	
Empirical formula	C26 H24 N2 O4 S1	
Formula weight	460.55	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.6893(3) Å	α= 90°.
	b = 10.0520(2) Å	β= 90.862(2)°.
	c = 19.2599(5) Å	γ = 90°.
Volume	2262.80(9) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	1.571 mm^{-1}	
F(000)	968	
Crystal size	0.37 x 0.14 x 0.04 mm^3	
Theta range for data collection	4.395 to 76.116°.	
Index ranges	-13<=h<=14, -12<=k<=8, -24<=l<=23	
Reflections collected	18284	
Independent reflections	4689 [R(int) = 0.0483]	
Completeness to theta = 74.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.77	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4689 / 340 / 371	
Goodness-of-fit on F^2	1.0004	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1281	
R indices (all data)	R1 = 0.0610, wR2 = 0.1399	
Largest diff. peak and hole	0.48 and -0.46 $e.Å^{-3}$	

Table S23 Crystal data and structure refinement for **60u**, PhTsYnPh*p*-CN.

Identification code	095eaa17	
Empirical formula	C22 H16 N2 O2 S1	
Formula weight	372.45	
Temperature	200 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6947(3) Å	α= 92.377(3)°.
	b = 13.1700(5) Å	β= 99.257(3)°.
	c = 16.6557(6) Å	γ = 92.905(3)°.
Volume	1877.59(12) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	1.686 mm^{-1}	
F(000)	776	
Crystal size	0.25 x 0.06 x 0.04 mm^3	
Theta range for data collection	3.364 to 75.245°.	
Index ranges	-10<=h<=9, -16<=k<=16, -20<=l<=20	
Reflections collected	30846	
Independent reflections	7563 [R(int) = 0.0474]	
Completeness to theta = 69.225°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7559 / 0 / 487	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1039	
R indices (all data)	R1 = 0.0649, wR2 = 0.1214	
Largest diff. peak and hole	0.36 and -0.70 $e.Å^{-3}$	

Table S24 Crystal data and structure refinement for **60w**, PhTsYnThienyl.

Identification code	082eaa17	
Empirical formula	C19 H15 N1 O2 S2	
Formula weight	353.47	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 5.6358(2) Å	α= 90°.
	b = 17.1144(5) Å	β= 97.292(3)°.
	c = 17.2438(4) Å	γ = 90°.
Volume	1649.77(9) $Å^3$	
Z	4	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	3.016 mm^{-1}	
F(000)	736	
Crystal size	0.19 x 0.10 x 0.04 mm^3	
Theta range for data collection	3.653 to 76.311°.	
Index ranges	-7<=h<=4, -21<=k<=21, -21<=l<=21	
Reflections collected	8498	
Independent reflections	3407 [R(int) = 0.0353]	
Completeness to theta = 74.022°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.79	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3407 / 158 / 263	
Goodness-of-fit on F^2	1.0069	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0973	
R indices (all data)	R1 = 0.0430, wR2 = 0.1038	
Largest diff. peak and hole	0.37 and -0.34 e.$Å^{-3}$	

Table S25 Crystal data and structure refinement for **60x**, PhTsYnFuryl.

Identification code	035eaa18	
Empirical formula	C19 H15 N1 O3 S1	
Formula weight	337.40	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.49850(10) Å	α= 90°.
	b = 17.2869(2) Å	β= 98.6929(12)°.
	c = 17.0823(2) Å	γ = 90°.
Volume	1605.06(4) $Å^3$	
Z	4	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	1.937 mm^{-1}	
F(000)	704	
Crystal size	0.48 x 0.32 x 0.07 mm^3	
Theta range for data collection	3.659 to 76.151°.	
Index ranges	-6<=h<=6, -21<=k<=21, -21<=l<=20	
Reflections collected	18040	
Independent reflections	3340 [R(int) = 0.0276]	
Completeness to theta = 76.151°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.48	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3340 / 0 / 217	
Goodness-of-fit on F^2	1.0049	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0895	
R indices (all data)	R1 = 0.0334, wR2 = 0.0901	
Largest diff. peak and hole	0.31 and -0.32 $e.Å^{-3}$	

Table S26 Crystal data and structure refinement for **60y**, PhTsYnPyrrolyl.

Identification code	017eaa18	
Empirical formula	C24 H24 N2 O4 S1	
Formula weight	436.53	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.02070(10) Å	α= 90°.
	b = 15.6675(2) Å	β= 98.9018(9)°.
	c = 16.2703(2) Å	γ = 90°.
Volume	2271.81(5) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	1.533 mm^{-1}	
F(000)	920	
Crystal size	0.32 x 0.20 x 0.16 mm^3	
Theta range for data collection	3.940 to 76.080°.	
Index ranges	-6<=h<=11, -17<=k<=19, -20<=l<=20	
Reflections collected	11793	
Independent reflections	4696 [R(int) = 0.0212]	
Completeness to theta = 73.798°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.78 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4694 / 0 / 280	
Goodness-of-fit on F^2	0.9989	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0913	
R indices (all data)	R1 = 0.0369, wR2 = 0.0933	
Largest diff. peak and hole	0.31 and -0.43 e.$Å^{-3}$	

Table S27 Crystal data and structure refinement for **60z**, PhTsYnPyrazolyl.

Identification code	009eaa18	
Empirical formula	C19 H17 N3 O2 S1	
Formula weight	351.43	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 5.5451(2) Å	α= 90°.
	b = 17.0391(5) Å	β= 96.307(3)°.
	c = 18.4851(6) Å	γ = 90°.
Volume	1735.97(10) $Å^3$	
Z	4	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	1.801 mm^{-1}	
F(000)	736	
Crystal size	0.38 x 0.03 x 0.03 mm^3	
Theta range for data collection	3.538 to 76.470°.	
Index ranges	-6<=h<=6, -18<=k<=21, -23<=l<=23	
Reflections collected	18028	
Independent reflections	3599 [R(int) = 0.0534]	
Completeness to theta = 74.941°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3597 / 0 / 227	
Goodness-of-fit on F^2	1.0022	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0922	
R indices (all data)	R1 = 0.0476, wR2 = 0.0999	
Largest diff. peak and hole	0.45 and -0.37 $e.Å^{-3}$	

Table S28 Crystal data and structure refinement for **60ad**, PhTsYnBenzofuryl.

Identification code	015eaa18	
Empirical formula	C23 H17 N1 O3 S1	
Formula weight	387.46	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.9612(3) Å	α= 90°.
	b = 14.4372(2) Å	β= 107.7974(18)°.
	c = 17.4410(3) Å	γ = 90°.
Volume	3826.68(12) $Å^3$	
Z	8	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	1.700 mm^{-1}	
F(000)	1616	
Crystal size	0.31 x 0.16 x 0.08 mm^3	
Theta range for data collection	4.057 to 76.407°.	
Index ranges	-20<=h<=19, -14<=k<=18, -21<=l<=21	
Reflections collected	21698	
Independent reflections	7899 [R(int) = 0.0339]	
Completeness to theta = 74.115°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7897 / 0 / 505	
Goodness-of-fit on F^2	0.9971	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0973	
R indices (all data)	R1 = 0.0477, wR2 = 0.1071	
Largest diff. peak and hole	0.35 and -0.37 $e.Å^{-3}$	

Table S29 Crystal data and structure refinement for **60ae**, PhTsYnIndolyl.

Identification code	010eaa18	
Empirical formula	C24 H20 N2 O2 S1	
Formula weight	400.50	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P c c n	
Unit cell dimensions	a = 8.6295(2) Å	α= 90°.
	b = 34.4698(8) Å	β= 90°.
	c = 13.4832(3) Å	γ = 90°.
Volume	4010.67(16) $Å^3$	
Z	8	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	1.615 mm^{-1}	
F(000)	1680	
Crystal size	0.17 x 0.17 x 0.06 mm^3	
Theta range for data collection	5.133 to 75.953°.	
Index ranges	-9<=h<=10, -43<=k<=40, -16<=l<=16	
Reflections collected	19340	
Independent reflections	4171 [R(int) = 0.0413]	
Completeness to theta = 74.434°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.82	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4166 / 199 / 326	
Goodness-of-fit on F^2	1.0016	
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0850	
R indices (all data)	R1 = 0.0493, wR2 = 0.0951	
Largest diff. peak and hole	0.28 and -0.49 $e.Å^{-3}$	

Table S30 Crystal data and structure refinement for **60af**, PhTsYn2-pyridyl.

Identification code	021eaa18	
Empirical formula	C20 H16 N2 O2 S1	
Formula weight	348.42	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.15330(10) Å	α= 90°.
	b = 9.74980(10) Å	β= 98.4787(14)°.
	c = 19.5623(3) Å	γ = 90°.
Volume	1726.72(4) $Å^3$	
Z	4	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	1.791 mm^{-1}	
F(000)	728	
Crystal size	0.31 x 0.11 x 0.10 mm^3	
Theta range for data collection	4.571 to 76.257°.	
Index ranges	-11<=h<=11, -12<=k<=12, -24<=l<=20	
Reflections collected	19281	
Independent reflections	7154 [R(int) = 0.0239]	
Completeness to theta = 74.731°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7154 / 367 / 571	
Goodness-of-fit on F^2	1.0050	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0727	
R indices (all data)	R1 = 0.0292, wR2 = 0.0739	
Largest diff. peak and hole	0.24 and -0.19 $e.Å^{-3}$	
Absolute structure parameter	-0.004(8)	

Table S31 Crystal data and structure refinement for **60ag**, PhTsYn3-pyridyl.

Identification code	003eaa18	
Empirical formula	C20 H16 N2 O2 S1	
Formula weight	348.43	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.51080(10) Å	α= 90°.
	b = 17.4466(2) Å	β= 98.9439(13)°.
	c = 17.4797(2) Å	γ = 90°.
Volume	1660.15(4) $Å^3$	
Z	4	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	1.863 mm^{-1}	
F(000)	728	
Crystal size	0.26 x 0.08 x 0.07 mm^3	
Theta range for data collection	3.601 to 76.252°.	
Index ranges	-6<=h<=6, -21<=k<=19, -22<=l<=21	
Reflections collected	16981	
Independent reflections	3421 [R(int) = 0.0239]	
Completeness to theta = 73.965°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.72	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3420 / 0 / 226	
Goodness-of-fit on F^2	0.9968	
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0790	
R indices (all data)	R1 = 0.0325, wR2 = 0.0813	
Largest diff. peak and hole	0.39 and -0.36 $e.Å^{-3}$	

Table S32 Crystal data and structure refinement for **60ah**, PhTsYnQuin.

Identification code	004eaa18	
Empirical formula	C24 H17 Cl1 N2 O2 S1	
Formula weight	432.93	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 26.7389(7) Å	α= 90°.
	b = 9.28640(10) Å	β= 127.579(4)°.
	c = 20.9604(6) Å	γ = 90°.
Volume	4124.7(3) $Å^3$	
Z	8	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	2.780 mm^{-1}	
F(000)	1792	
Crystal size	0.20 x 0.19 x 0.14 mm^3	
Theta range for data collection	4.172 to 76.167°.	
Index ranges	-29<=h<=33, -11<=k<=9, -26<=l<=26	
Reflections collected	15829	
Independent reflections	4274 [R(int) = 0.0211]	
Completeness to theta = 74.643°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.68 and 0.59	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4266 / 0 / 271	
Goodness-of-fit on F^2	0.9980	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0909	
R indices (all data)	R1 = 0.0350, wR2 = 0.0928	
Largest diff. peak and hole	0.54 and -0.56 $e.Å^{-3}$	

Table S33 Crystal data and structure refinement for **60ai**, PhTsYnPyridazinyl.

Identification code	027eaa18	
Empirical formula	C19 H13 Cl2 N3 O2 S1	
Formula weight	418.30	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.8313(3) Å	α= 90°.
	b = 5.56320(10) Å	β= 103.847(2)°.
	c = 22.7015(5) Å	γ = 90°.
Volume	1818.65(7) $Å^3$	
Z	4	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.492 mm^{-1}	
F(000)	856	
Crystal size	0.040 x 0.005 x 0.005 mm^3	
Theta range for data collection	1.791 to 25.503°.	
Index ranges	-18<=h<=18, -6<=k<=6, -28<=l<=28	
Reflections collected	24602	
Independent reflections	3701 [R(int) = 0.0735]	
Completeness to theta = 25.503°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3690 / 0 / 244	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.0984	
R indices (all data)	R1 = 0.0714, wR2 = 0.1104	
Largest diff. peak and hole	0.57 and -0.61 $e.Å^{-3}$	

Table S34 Crystal data and structure refinement for **60aj**, PhTsYnPropenyl.

Identification code	096eaa17	
Empirical formula	C18 H17 N1 O2 S1	
Formula weight	311.40	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.8081(3) Å	α= 93.953(3)°.
	b = 9.8524(4) Å	β= 95.559(2)°.
	c = 16.8442(5) Å	γ = 97.707(3)°.
Volume	1599.87(10) $Å^3$	
Z	4	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	1.845 mm^{-1}	
F(000)	656	
Crystal size	0.34 x 0.13 x 0.06 mm^3	
Theta range for data collection	4.544 to 76.219°.	
Index ranges	-8<=h<=12, -12<=k<=12, -19<=l<=21	
Reflections collected	16088	
Independent reflections	6599 [R(int) = 0.0222]	
Completeness to theta = 73.932°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.74	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6599 / 0 / 397	
Goodness-of-fit on F^2	0.9987	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1046	
R indices (all data)	R1 = 0.0415, wR2 = 0.1083	
Largest diff. peak and hole	1.06 and -0.44 e.$Å^{-3}$	

Table S35 Crystal data and structure refinement for **60am**, PhYn*n*-Pr.

Identification code	002eaa18	
Empirical formula	C18 H19 N1 O2 S1	
Formula weight	313.42	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.1212(2) Å	α= 90°.
	b = 10.08280(10) Å	β= 98.1405(16)°.
	c = 17.7812(3) Å	γ = 90°.
Volume	1618.81(5) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	1.824 mm^{-1}	
F(000)	664	
Crystal size	0.32 x 0.07 x 0.06 mm^3	
Theta range for data collection	4.898 to 76.089°.	
Index ranges	-11<=h<=11, -12<=k<=12, -21<=l<=22	
Reflections collected	16927	
Independent reflections	3369 [R(int) = 0.0328]	
Completeness to theta = 74.567°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3369 / 0 / 199	
Goodness-of-fit on F^2	0.9985	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0916	
R indices (all data)	R1 = 0.0376, wR2 = 0.0957	
Largest diff. peak and hole	0.60 and -0.38 $e.Å^{-3}$	

Table S36 Crystal data and structure refinement for **60an**, PhTsYnCyclopropyl.

Identification code	075eaa17	
Empirical formula	C18 H17 N1 O2 S1	
Formula weight	311.40	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.6848(2) Å	α= 90°.
	b = 12.3717(2) Å	β= 90.2481(17)°.
	c = 14.9578(3) Å	γ = 90°.
Volume	1607.14(6) $Å^3$	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	1.837 mm^{-1}	
F(000)	656	
Crystal size	0.16 x 0.13 x 0.07 mm^3	
Theta range for data collection	4.638 to 76.233°.	
Index ranges	-10<=h<=10, -15<=k<=15, -18<=l<=18	
Reflections collected	35465	
Independent reflections	3348 [R(int) = 0.0377]	
Completeness to theta = 76.233°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3346 / 0 / 201	
Goodness-of-fit on F^2	1.0018	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0819	
R indices (all data)	R1 = 0.0351, wR2 = 0.0867	
Largest diff. peak and hole	0.18 and -0.36 $e.Å^{-3}$	

Table S37 Crystal data and structure refinement for **60ao**, PhTsYnBCP.

Identification code	034eaa18	
Empirical formula	C23 H23 N1 O2 S1	
Formula weight	377.51	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.81610(10) Å	α= 90°.
	b = 14.3934(3) Å	β= 96.2407(16)°.
	c = 16.0511(3) Å	γ = 90°.
Volume	2024.71(6) $Å^3$	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	1.548 mm^{-1}	
F(000)	800	
Crystal size	0.27 x 0.08 x 0.04 mm^3	
Theta range for data collection	4.136 to 76.183°.	
Index ranges	-11<=h<=10, -15<=k<=17, -20<=l<=19	
Reflections collected	15127	
Independent reflections	4185 [R(int) = 0.0291]	
Completeness to theta = 73.897°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.83	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4185 / 52 / 263	
Goodness-of-fit on F^2	0.9978	
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0879	
R indices (all data)	R1 = 0.0397, wR2 = 0.0942	
Largest diff. peak and hole	0.29 and -0.31 $e.Å^{-3}$	

Table S38 Crystal data and structure refinement for **60ap**, PhTsYnYn*i*-Pr.

Identification code	042eaa18	
Empirical formula	C20 H19 N1 O2 S1	
Formula weight	337.44	
Temperature	100 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.8528(2) Å	α= 90°.
	b = 12.4780(2) Å	β= 90°.
	c = 14.5448(2) Å	γ = 90°.
Volume	1788.18(5) $Å^3$	
Z	4	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	1.691 mm^{-1}	
F(000)	712	
Crystal size	0.27 x 0.19 x 0.19 mm^3	
Theta range for data collection	4.669 to 76.331°.	
Index ranges	-12<=h<=12, -15<=k<=15, -18<=l<=14	
Reflections collected	19547	
Independent reflections	3719 [R(int) = 0.0216]	
Completeness to theta = 76.331°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.73 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3719 / 0 / 218	
Goodness-of-fit on F^2	1.0039	
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0623	
R indices (all data)	R1 = 0.0235, wR2 = 0.0626	
Absolute structure parameter	-0.003(10)	
Largest diff. peak and hole	0.22 and -0.23 $e.Å^{-3}$	

Table S39 Crystal data and structure refinement for **66**, PhTsYnPh*o*-F,NHBn,*m*-NO_2.

Identification code	DIA0359	
Empirical formula	C28 H22 F1 N3 O4 S1	
Formula weight	515.56	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.07890(2) Å	α= 90°.
	b = 16.77420(6) Å	β= 90.3120(3)°.
	c = 23.40120(8) Å	γ = 90°.
Volume	2386.154(15) $Å^3$	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	1072	
Crystal size	0.16 x 0.01 x 0.005 mm^3	
Theta range for data collection	1.687 to 36.065°.	
Index ranges	-10<=h<=9, -28<=k<=27, -39<=l<=39	
Reflections collected	47994	
Independent reflections	11356 [R(int) = 0.089]	
Completeness to theta = 33.751°	98.2 %	
Absorption correction	Empirical	
Max. and min. transmission	1.0 and 0.99	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11356 / 0 / 334	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0690, wR2 = 0.1578	
R indices (all data)	R1 = 0.0738, wR2 = 0.1626	
Largest diff. peak and hole	0.68 and -0.46 e.$Å^{-3}$	

Table S40 Crystal data and structure refinement for **68a**, PhTsYnPh*p*-Cl.

Identification code	067eaa18	
Empirical formula	C21 H16 Cl1 N1 O2 S1	
Formula weight	381.88	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.18948(13) Å	α= 90°.
	b = 9.85221(12) Å	β= 91.5522(11)°.
	c = 17.8786(2) Å	γ = 90°.
Volume	1794.15(4) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	3.097 mm^{-1}	
F(000)	792	
Crystal size	0.57 x 0.10 x 0.03 mm^3	
Theta range for data collection	4.341 to 75.996°.	
Index ranges	-12<=h<=11, -12<=k<=11, -22<=l<=21	
Reflections collected	10532	
Independent reflections	3704 [R(int) = 0.025]	
Completeness to theta = 72.956°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.73	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3690 / 0 / 235	
Goodness-of-fit on F^2	0.9956	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0975	
R indices (all data)	R1 = 0.0385, wR2 = 0.1008	
Largest diff. peak and hole	0.43 and -0.39 $e.Å^{-3}$	

Table S41 Crystal data and structure refinement for **68b**, PhTfsYnPh*p*-Cl.

Identification code	068eaa18	
Empirical formula	C21 H13 Cl1 F3 N1 O2 S1	
Formula weight	435.85	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.1242(2) Å	α= 90°.
	b = 7.51200(9) Å	β= 95.1181(11)°.
	c = 13.11218(14) Å	γ = 90°.
Volume	1876.20(4) $Å^3$	
Z	4	
Density (calculated)	1.543 Mg/m^3	
Absorption coefficient	3.279 mm^{-1}	
F(000)	888	
Crystal size	0.32 x 0.23 x 0.08 mm^3	
Theta range for data collection	4.643 to 76.271°.	
Index ranges	-15<=h<=24, -9<=k<=9, -16<=l<=16	
Reflections collected	12739	
Independent reflections	3878 [R(int) = 0.0187]	
Completeness to theta = 73.982°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.55	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3864 / 0 / 262	
Goodness-of-fit on F^2	1.0142	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0829	
R indices (all data)	R1 = 0.0320, wR2 = 0.0836	
Largest diff. peak and hole	0.30 and -0.42 $e.Å^{-3}$	

Table S42 Crystal data and structure refinement for **68d**, PhNsYnPh*p*-Cl.

Identification code	066eaa18	
Empirical formula	C20 H13 Cl1 N2 O4 S1	
Formula weight	412.85	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.60760(10) Å	α= 90°.
	b = 13.4998(2) Å	β= 90°.
	c = 20.6985(3) Å	γ = 90°.
Volume	1846.33(5) $Å^3$	
Z	4	
Density (calculated)	1.485 Mg/m^3	
Absorption coefficient	3.158 mm^{-1}	
F(000)	848	
Crystal size	0.60 x 0.05 x 0.04 mm^3	
Theta range for data collection	3.909 to 76.501°.	
Index ranges	-8<=h<=8, -17<=k<=16, -25<=l<=25	
Reflections collected	42053	
Independent reflections	3852 [R(int) = 0.0758]	
Completeness to theta = 76.501°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.34	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3836 / 0 / 254	
Goodness-of-fit on F^2	1.0031	
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0779	
R indices (all data)	R1 = 0.0367, wR2 = 0.0836	
Largest diff. peak and hole	0.21 and -0.19 e.$Å^{-3}$	
Absolute structure parameter	-0.029(15)	

Table S43 Crystal data and structure refinement for **68e**, BnTrisYnMes.

Identification code	070eaa18	
Empirical formula	C33 H41 N1 O2 S1	
Formula weight	515.76	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 42.8168(10) Å	α= 90°.
	b = 12.7742(3) Å	β= 95.8320(19)°.
	c = 10.9525(2) Å	γ = 90°.
Volume	5959.5(2) $Å^3$	
Z	8	
Density (calculated)	1.150 Mg/m^3	
Absorption coefficient	1.174 mm^{-1}	
F(000)	2224	
Crystal size	0.41 x 0.41 x 0.08 mm^3	
Theta range for data collection	3.612 to 76.215°.	
Index ranges	-52<=h<=53, -15<=k<=15, -13<=l<=11	
Reflections collected	35819	
Independent reflections	9079 [R(int) = 0.0455]	
Completeness to theta = 74.690°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.55	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9047 / 2 / 668	
Goodness-of-fit on F^2	1.0083	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1476	
R indices (all data)	R1 = 0.0555, wR2 = 0.1479	
Largest diff. peak and hole	0.39 and -0.44 e.$Å^{-3}$	
Absolute structure parameter	0.177(18)	

Table S44 Crystal data and structure refinement for **68g**, Ph(*i*-Pr)$_2$TsYnMes.

Identification code	063eaa18	
Empirical formula	C30 H35 N1 O2 S1	
Formula weight	473.68	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.1992(3) Å	α= 78.677(3)°.
	b = 8.7627(3) Å	β= 78.151(3)°.
	c = 19.1910(6) Å	γ = 85.034(2)°.
Volume	1321.63(7) Å^3	
Z	2	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	1.282 mm^{-1}	
F(000)	508	
Crystal size	0.41 x 0.26 x 0.16 mm^3	
Theta range for data collection	4.790 to 76.165°.	
Index ranges	-10<=h<=10, -10<=k<=8, -24<=l<=23	
Reflections collected	13468	
Independent reflections	5424 [R(int) = 0.0192]	
Completeness to theta = 72.357°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.81 and 0.67	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5405 / 372 / 383	
Goodness-of-fit on F^2	1.0054	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1097	
R indices (all data)	R1 = 0.0409, wR2 = 0.1120	
Largest diff. peak and hole	0.42 and -0.38 e.Å^{-3}	

Table S45 Crystal data and structure refinement for **68o**, BPhTsYnMes.

Identification code	069eaa18	
Empirical formula	C34 H33 N1 O2 S1	
Formula weight	519.71	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7550(2) Å	α= 101.0960(16)°.
	b = 12.1458(3) Å	β= 93.1591(15)°.
	c = 12.9323(2) Å	γ = 108.6228(19)°.
Volume	1413.66(5) $Å^3$	
Z	2	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	1.249 mm^{-1}	
F(000)	552	
Crystal size	0.26 x 0.14 x 0.13 mm^3	
Theta range for data collection	3.510 to 76.403°.	
Index ranges	-12<=h<=11, -15<=k<=15, -16<=l<=16	
Reflections collected	31692	
Independent reflections	5868 [R(int) = 0.0213]	
Completeness to theta = 74.111°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5846 / 630 / 476	
Goodness-of-fit on F^2	0.9982	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1158	
R indices (all data)	R1 = 0.0446, wR2 = 0.1178	
Largest diff. peak and hole	1.06 and -0.61 e.$Å^{-3}$	

Table S46 Crystal data and structure refinement for **71a**, PhZYnPh.

Identification code	046eaa18	
Empirical formula	C22 H17 N1 O2	
Formula weight	327.38	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 23.2470(7) Å	α= 90°.
	b = 5.7960(1) Å	β= 110.538(3)°.
	c = 27.2800(8) Å	γ = 90°.
Volume	3442.07(17) $Å^3$	
Z	8	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	0.644 mm^{-1}	
F(000)	1376	
Crystal size	0.57 x 0.06 x 0.01 mm^3	
Theta range for data collection	4.061 to 76.180°.	
Index ranges	-26<=h<=29, -7<=k<=6, -34<=l<=33	
Reflections collected	24013	
Independent reflections	7151 [R(int) = 0.0511]	
Completeness to theta = 74.656°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7147 / 0 / 451	
Goodness-of-fit on F^2	1.0096	
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1017	
R indices (all data)	R1 = 0.0654, wR2 = 0.1183	
Largest diff. peak and hole	0.33 and -0.37 e.$Å^{-3}$	

Table S47 Crystal data and structure refinement for **71e**, PhEYnPh*p*-Cl.

Identification code	7103	
Empirical formula	C17 H14 Cl1 N1 O2	
Formula weight	299.76	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.0348(1) Å	α= 90°.
	b = 14.6892(2) Å	β= 94.8129(12)°.
	c = 16.4278(2) Å	γ = 90°.
Volume	1451.13(4) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	2.359 mm^{-1}	
F(000)	624	
Crystal size	0.18 x 0.06 x 0.03 mm^3	
Theta range for data collection	4.043 to 76.654°.	
Index ranges	-7<=h<=7, -18<=k<=18, -20<=l<=20	
Reflections collected	26317	
Independent reflections	3054 [R(int) = 0.032]	
Completeness to theta = 76.654°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3053 / 0 / 190	
Goodness-of-fit on F^2	0.9957	
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0782	
R indices (all data)	R1 = 0.0321, wR2 = 0.0805	
Largest diff. peak and hole	0.27 and -0.41 $e.Å^{-3}$	

Table S48 Crystal data and structure refinement for **71f**, PhIYnPh*p*-Cl.

Identification code	064eaa18	
Empirical formula	C18 H16 Cl1 N1 O2	
Formula weight	313.78	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.2161(3) Å	α= 90°.
	b = 6.18924(14) Å	β= 93.9383(19)°.
	c = 17.6025(4) Å	γ = 90°.
Volume	1545.13(6) $Å^3$	
Z	4	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	2.239 mm^{-1}	
F(000)	656	
Crystal size	0.57 x 0.07 x 0.02 mm^3	
Theta range for data collection	5.037 to 76.090°.	
Index ranges	-12<=h<=17, -7<=k<=7, -21<=l<=22	
Reflections collected	8048	
Independent reflections	3191 [R(int) = 0.0279]	
Completeness to theta = 73.807°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3180 / 0 / 199	
Goodness-of-fit on F^2	0.9989	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0965	
R indices (all data)	R1 = 0.0401, wR2 = 0.1012	
Largest diff. peak and hole	0.33 and -0.32 $e.Å^{-3}$	

Table S49 Crystal data and structure refinement for **71g**, PhBocYnPh*p*-Cl.

Identification code	065eaa18	
Empirical formula	C19 H18 Cl1 N1 O2	
Formula weight	327.81	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 5.93248(10) Å	α= 90°.
	b = 20.1321(3) Å	β= 97.4434(18)°.
	c = 14.4789(3) Å	γ = 90°.
Volume	1714.70(5) $Å^3$	
Z	4	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	2.039 mm^{-1}	
F(000)	688	
Crystal size	0.55 x 0.10 x 0.07 mm^3	
Theta range for data collection	4.392 to 76.066°.	
Index ranges	-6<=h<=7, -25<=k<=17, -17<=l<=18	
Reflections collected	5255	
Independent reflections	2836 [R(int) = 0.0254]	
Completeness to theta = 71.502°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.52	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2822 / 2 / 209	
Goodness-of-fit on F^2	1.0037	
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0967	
R indices (all data)	R1 = 0.0357, wR2 = 0.0986	
Largest diff. peak and hole	0.21 and -0.30 $e.Å^{-3}$	
Absolute structure parameter	-0.007(14)	

Table S50 Crystal data and structure refinement for **71h**, BrPhMocYnPh*p*-Cl.

Identification code	062eaa18	
Empirical formula	C16 H11 Br1 Cl1 N1 O2	
Formula weight	364.63	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I a	
Unit cell dimensions	a = 8.0586(3) Å	α= 90°.
	b = 21.5127(9) Å	β= 105.084(3)°.
	c = 9.0554(3) Å	γ = 90°.
Volume	1515.77(10) $Å^3$	
Z	4	
Density (calculated)	1.598 Mg/m^3	
Absorption coefficient	5.348 mm^{-1}	
F(000)	728	
Crystal size	0.13 x 0.06 x 0.01 mm^3	
Theta range for data collection	4.110 to 76.085°.	
Index ranges	-10<=h<=6, -26<=k<=26, -11<=l<=10	
Reflections collected	3771	
Independent reflections	2016 [R(int) = 0.0185]	
Completeness to theta = 72.280°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2006 / 2 / 191	
Goodness-of-fit on F^2	1.0130	
Final R indices [I>2sigma(I)]	R1 = 0.0302, wR2 = 0.0828	
R indices (all data)	R1 = 0.0314, wR2 = 0.0843	
Largest diff. peak and hole	0.72 and -0.37 $e.Å^{-3}$	
Absolute structure parameter	-0.02(3)	

Table S51 Crystal data and structure refinement for **85a**, MePhUreaPhYnPh*p*-Cl.

Identification code	076eaa18	
Empirical formula	C22 H17 Cl1 N2 O1	
Formula weight	360.84	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 31.8939(8) Å	α= 90°.
	b = 9.9151(3) Å	β= 90°.
	c = 5.73511(12) Å	γ = 90°.
Volume	1813.61(8) $Å^3$	
Z	4	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	1.958 mm^{-1}	
F(000)	752	
Crystal size	0.60 x 0.07 x 0.05 mm^3	
Theta range for data collection	2.771 to 76.282°.	
Index ranges	-39<=h<=38, -12<=k<=10, -7<=l<=5	
Reflections collected	10614	
Independent reflections	3321 [R(int) = 0.0383]	
Completeness to theta = 73.993°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.52	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3310 / 1 / 236	
Goodness-of-fit on F^2	0.9977	
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.1049	
R indices (all data)	R1 = 0.0444, wR2 = 0.1083	
Largest diff. peak and hole	0.34 and -0.21 $e.Å^{-3}$	
Absolute structure parameter	-0.014(17)	

Table S52 Crystal data and structure refinement for **85b**, Bn_2UreaPhYnPh*p*-Cl.

Identification code	098eaa18	
Empirical formula	C35 H29 Cl N2 O	
Formula weight	529.08	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.33163(12) Å	α= 90°.
	b = 15.13091(17) Å	β= 94.9283(11)°.
	c = 19.6848(2) Å	γ = 90°.
Volume	2769.14(5) $Å^3$	
Z	4	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	1.453 mm^{-1}	
F(000)	1112	
Crystal size	0.41 x 0.20 x 0.19 mm^3	
Theta range for data collection	3.690 to 76.596°.	
Index ranges	-11<=h<=10, -8<=k<=18, -24<=l<=24	
Reflections collected	19281	
Independent reflections	5762 [R(int) = 0.0224]	
Completeness to theta = 74.298°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.76 and 0.60	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5741 / 0 / 352	
Goodness-of-fit on F^2	1.0063	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0999	
R indices (all data)	R1 = 0.0406, wR2 = 0.1021	
Largest diff. peak and hole	0.35 and -0.39 $e.Å^{-3}$	

Table S53 Crystal data and structure refinement for **85c**, MorpholineUreaPhYnPh*p*-Cl.

Identification code	083eaa18	
Empirical formula	C19 H17 Cl1 N2 O2	
Formula weight	340.81	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.8692(3) Å	α= 90°.
	b = 11.0423(3) Å	β= 107.997(3)°.
	c = 15.7887(5) Å	γ = 90°.
Volume	1636.44(9) $Å^3$	
Z	4	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	2.179 mm^{-1}	
F(000)	712	
Crystal size	0.26 x 0.17 x 0.06 mm^3	
Theta range for data collection	4.971 to 76.452°.	
Index ranges	-12<=h<=12, -13<=k<=13, -13<=l<=19	
Reflections collected	13231	
Independent reflections	3419 [R(int) = 0.0234]	
Completeness to theta = 74.923°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.67	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3408 / 0 / 217	
Goodness-of-fit on F^2	1.0012	
Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0913	
R indices (all data)	R1 = 0.0359, wR2 = 0.0930	
Largest diff. peak and hole	0.24 and -0.42 $e.Å^{-3}$	

Table S54 Crystal data and structure refinement for **85d**, PyrrolidineUreaPhYnPh*p*-Cl.

Identification code	086eaa18	
Empirical formula	C19 H17 Cl1 N2 O1	
Formula weight	324.81	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.6364(3) Å	α= 90.194(4)°.
	b = 8.0673(4) Å	β= 95.692(4)°.
	c = 18.1207(8) Å	γ = 91.162(4)°.
Volume	819.71(8) $Å^3$	
Z	2	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	2.101 mm^{-1}	
F(000)	340	
Crystal size	0.25 x 0.23 x 0.04 mm^3	
Theta range for data collection	2.450 to 76.647°.	
Index ranges	-7<=h<=7, -10<=k<=9, -22<=l<=19	
Reflections collected	6413	
Independent reflections	3382 [R(int) = 0.0217]	
Completeness to theta = 74.348°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3371 / 0 / 208	
Goodness-of-fit on F^2	0.9943	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0966	
R indices (all data)	R1 = 0.0398, wR2 = 0.1001	
Largest diff. peak and hole	0.26 and -0.26 $e.Å^{-3}$	

Table S55 Crystal data and structure refinement for **85e**, Bn_3UreaYnPh*p*-Cl.

Identification code	7057	
Empirical formula	C30 H25 Cl1 N2 O1	
Formula weight	464.99	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.5510(1) Å	α= 94.3921(14)°.
	b = 10.1625(2) Å	β= 93.9897(14)°.
	c = 39.0314(6) Å	γ = 106.4572(17)°.
Volume	2473.38(8) $Å^3$	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	1.553 mm^{-1}	
F(000)	976	
Crystal size	0.18 x 0.16 x 0.04 mm^3	
Theta range for data collection	4.560 to 76.189°.	
Index ranges	-8<=h<=8, -12<=k<=12, -49<=l<=48	
Reflections collected	57251	
Independent reflections	10271 [R(int) = 0.029]	
Completeness to theta = 74.665°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10271 / 24 / 632	
Goodness-of-fit on F^2	0.9916	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0951	
R indices (all data)	R1 = 0.0420, wR2 = 0.1012	
Largest diff. peak and hole	0.30 and -0.40 $e.Å^{-3}$	

Table S56 Crystal data and structure refinement for **90d**, PhPivYnPh*p*-Cl.

Identification code	085eaa18	
Empirical formula	C19 H18 Cl1 N1 O1	
Formula weight	311.81	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	I -4	
Unit cell dimensions	a = 23.1825(3) Å	α= 90°.
	b = 23.1825(3) Å	β= 90°.
	c = 5.93331(12) Å	γ = 90°.
Volume	3188.72(10) $Å^3$	
Z	8	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	2.117 mm^{-1}	
F(000)	1312	
Crystal size	0.39 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.696 to 76.509°.	
Index ranges	-29<=h<=24, -29<=k<=28, -7<=l<=7	
Reflections collected	10568	
Independent reflections	3242 [R(int) = 0.0420]	
Completeness to theta = 76.509°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.56	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3228 / 0 / 200	
Goodness-of-fit on F^2	1.0027	
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0835	
R indices (all data)	R1 = 0.0356, wR2 = 0.0864	
Largest diff. peak and hole	0.29 and -0.20 $e.Å^{-3}$	
Absolute structure parameter	0.324(13)	

2.1b *Dichloroenamides and Miscellaneous.*

Table S57 Crystal data and structure refinement for **53a**, PhTsDCE.

Identification code	054eaa17	
Empirical formula	C15 H13 Cl2 N1 O2 S1	
Formula weight	342.25	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.7738(5) Å	α= 104.081(5)°.
	b = 9.1805(6) Å	β= 106.360(5)°.
	c = 12.3275(7) Å	γ = 104.268(5)°.
Volume	770.47(10) $Å^3$	
Z	2	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	5.085 mm^{-1}	
F(000)	352	
Crystal size	0.32 x 0.29 x 0.25 mm^3	
Theta range for data collection	3.968 to 75.985°.	
Index ranges	-9<=h<=9, -11<=k<=11, -15<=l<=14	
Reflections collected	6563	
Independent reflections	3159 [R(int) = 0.0209]	
Completeness to theta = 75.985°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.28 and 0.20	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3154 / 0 / 190	
Goodness-of-fit on F^2	1.0207	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0869	
R indices (all data)	R1 = 0.0342, wR2 = 0.0883	
Largest diff. peak and hole	0.28 and -0.44 $e.Å^{-3}$	

Table S58 Crystal data and structure refinement for **61**, PhTsPhCE.

Identification code	018eaa17b	
Empirical formula	C21 H18 Cl1 N1 O2 S1	
Formula weight	383.90	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0400(1) Å	α= 90°.
	b = 11.3138(1) Å	β= 102.4137(14)°.
	c = 16.9256(2) Å	γ = 90°.
Volume	1877.64(3) $Å^3$	
Z	4	
Density (calculated)	1.358 Mg/m^3	
Absorption coefficient	2.959 mm^{-1}	
F(000)	800	
Crystal size	0.32 x 0.32 x 0.30 mm^3	
Theta range for data collection	4.723 to 76.124°.	
Index ranges	-12<=h<=12, -14<=k<=12, -21<=l<=20	
Reflections collected	17368	
Independent reflections	3905 [R(int) = 0.0256]	
Completeness to theta = 74.601°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.41 and 0.30	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3903 / 0 / 235	
Goodness-of-fit on F^2	0.9981	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1000	
R indices (all data)	R1 = 0.0380, wR2 = 0.1006	
Largest diff. peak and hole	0.30 and -0.48 $e.Å^{-3}$	

Table S59 Crystal data and structure refinement for **62**, PhTsDPhE.

Identification code	056eaa17	
Empirical formula	C27 H23 N1 O2 S1	
Formula weight	425.55	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.8083(5) Å	α= 90°.
	b = 6.3994(1) Å	β= 99.273(2)°.
	c = 16.7452(3) Å	γ = 90°.
Volume	2200.66(8) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	1.489 mm^{-1}	
F(000)	896	
Crystal size	0.54 x 0.06 x 0.02 mm^3	
Theta range for data collection	5.353 to 76.224°.	
Index ranges	-26<=h<=26, -7<=k<=7, -17<=l<=20	
Reflections collected	17636	
Independent reflections	4535 [R(int) = 0.0461]	
Completeness to theta = 73.937°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.97 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4535 / 0 / 280	
Goodness-of-fit on F^2	1.0073	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1191	
R indices (all data)	R1 = 0.0539, wR2 = 0.1294	
Largest diff. peak and hole	0.39 and -0.42 $e.Å^{-3}$	

Table S60 Crystal data and structure refinement for **63**, Imine.

Identification code	046eaa17	
Empirical formula	C28 H20 N2	
Formula weight	384.48	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 8.2568(3) Å	α= 90°.
	b = 10.2424(3) Å	β= 90°.
	c = 23.9309(8) Å	γ = 90°.
Volume	2023.82(12) Å^3	
Z	4	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	0.568 mm^{-1}	
F(000)	808	
Crystal size	0.36 x 0.19 x 0.12 mm^3	
Theta range for data collection	6.513 to 76.074°.	
Index ranges	-10<=h<=9, -8<=k<=12, -29<=l<=28	
Reflections collected	6246	
Independent reflections	2096 [R(int) = 0.0211]	
Completeness to theta = 73.792°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.86	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2096 / 0 / 136	
Goodness-of-fit on F^2	0.9938	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0957	
R indices (all data)	R1 = 0.0418, wR2 = 0.1020	
Largest diff. peak and hole	0.22 and -0.21 e.Å^{-3}	

Table S61 Crystal data and structure refinement for **65a**, *p*-TolEnyne.

Identification code	032eaa18	
Empirical formula	C24 H20 Cl1 N1 O2 S1	
Formula weight	421.95	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3514(3) Å	α= 92.601(3)°.
	b = 10.3342(5) Å	β= 101.701(3)°.
	c = 12.9228(3) Å	γ = 105.438(4)°.
Volume	1046.87(7) $Å^3$	
Z	2	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	2.706 mm^{-1}	
F(000)	440	
Crystal size	0.51 x 0.13 x 0.06 mm^3	
Theta range for data collection	3.512 to 76.150°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=16	
Reflections collected	13662	
Independent reflections	4314 [R(int) = 0.0430]	
Completeness to theta = 73.104°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4308 / 0 / 262	
Goodness-of-fit on F^2	1.0320	
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.1383	
R indices (all data)	R1 = 0.0562, wR2 = 0.1409	
Largest diff. peak and hole	0.51 and -0.51 $e.Å^{-3}$	

Table S62 Crystal data and structure refinement for **65b**, TMSEnyne.

Identification code	031eaa18	
Empirical formula	C20 H22 Cl1 N1 O2 S1 Si1	
Formula weight	404.00	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.4303(3) Å	α= 90°.
	b = 13.7905(2) Å	β= 90°.
	c = 24.5388(5) Å	γ = 90°.
Volume	4206.44(15) $Å^3$	
Z	8	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	3.190 mm^{-1}	
F(000)	1696	
Crystal size	0.46 x 0.26 x 0.04 mm^3	
Theta range for data collection	5.065 to 76.201°.	
Index ranges	-12<=h<=15, -12<=k<=17, -30<=l<=29	
Reflections collected	15733	
Independent reflections	4364 [R(int) = 0.0370]	
Completeness to theta = 74.677°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.43	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4364 / 0 / 235	
Goodness-of-fit on F^2	1.0051	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0958	
R indices (all data)	R1 = 0.0433, wR2 = 0.1035	
Largest diff. peak and hole	0.42 and -0.24 $e.Å^{-3}$	

Table S63 Crystal data and structure refinement for **65c**, *i*-PrEnyne.

Identification code	033eaa18	
Empirical formula	C20 H20 Cl1 N1 O2 S1	
Formula weight	373.90	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 14.6482(4) Å	α= 90°.
	b = 13.6946(3) Å	β= 90°.
	c = 18.6165(4) Å	γ = 90°.
Volume	3734.49(15) $Å^3$	
Z	8	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	2.957 mm^{-1}	
F(000)	1568	
Crystal size	0.29 x 0.11 x 0.04 mm^3	
Theta range for data collection	4.751 to 76.046°.	
Index ranges	-18<=h<=17, -17<=k<=11, -17<=l<=23	
Reflections collected	16349	
Independent reflections	3853 [R(int) = 0.0390]	
Completeness to theta = 71.484°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3851 / 0 / 226	
Goodness-of-fit on F^2	1.0033	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1032	
R indices (all data)	R1 = 0.0519, wR2 = 0.1152	
Largest diff. peak and hole	0.39 and -0.42 $e.Å^{-3}$	

Table S64 Crystal data and structure refinement for **67**, Indole.

Identification code	049eaa18	
Empirical formula	C28 H22 F1 N3 O4 S1	
Formula weight	515.56	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.9881(1) Å	α= 90°.
	b = 18.8011(4) Å	β= 96.7117(18)°.
	c = 21.7936(5) Å	γ = 90°.
Volume	2436.77(9) $Å^3$	
Z	4	
Density (calculated)	1.405 Mg/m^3	
Absorption coefficient	1.598 mm^{-1}	
F(000)	1072	
Crystal size	0.55 x 0.09 x 0.06 mm^3	
Theta range for data collection	4.085 to 76.347°.	
Index ranges	-7<=h<=6, -23<=k<=13, -22<=l<=27	
Reflections collected	16144	
Independent reflections	5052 [R(int) = 0.0394]	
Completeness to theta = 74.056°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.57	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5051 / 702 / 515	
Goodness-of-fit on F^2	1.0026	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1397	
R indices (all data)	R1 = 0.0606, wR2 = 0.1488	
Largest diff. peak and hole	0.67 and -0.56 $e.Å^{-3}$	

Table S65 Crystal data and structure refinement for **53d**, PhNsDCE.

Identification code	061eaa18	
Empirical formula	C14 H10 Cl2 N2 O4 S1	
Formula weight	373.22	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.0848(3) Å	α= 99.295(3)°.
	b = 7.8179(4) Å	β= 95.681(3)°.
	c = 15.6424(5) Å	γ = 114.639(4)°.
Volume	763.71(6) $Å^3$	
Z	2	
Density (calculated)	1.623 Mg/m^3	
Absorption coefficient	5.310 mm^{-1}	
F(000)	380	
Crystal size	0.39 x 0.32 x 0.13 mm^3	
Theta range for data collection	5.834 to 76.036°.	
Index ranges	-8<=h<=8, -9<=k<=9, -19<=l<=16	
Reflections collected	6551	
Independent reflections	3129 [R(int) = 0.0263]	
Completeness to theta = 69.953°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.50 and 0.18	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3116 / 90 / 245	
Goodness-of-fit on F^2	1.0186	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.1030	
R indices (all data)	R1 = 0.0378, wR2 = 0.1040	
Largest diff. peak and hole	0.40 and -0.46 $e.Å^{-3}$	

Table S66 Crystal data and structure refinement for **53f**, BrPhTsDCE.

Identification code	054eaa18	
Empirical formula	C15 H12 Br1 Cl2 N1 O2 S1	
Formula weight	421.14	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.2495(3) Å	α= 90°.
	b = 12.8062(3) Å	β= 107.912(3)°.
	c = 14.4524(5) Å	γ = 90°.
Volume	1628.92(9) $Å^3$	
Z	4	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	2.984 mm^{-1}	
F(000)	840	
Crystal size	0.23 x 0.23 x 0.19 mm^3	
Theta range for data collection	2.173 to 28.981°.	
Index ranges	-12<=h<=12, -16<=k<=17, -18<=l<=19	
Reflections collected	21091	
Independent reflections	3980 [R(int) = 0.0332]	
Completeness to theta = 25.214°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.57 and 0.47	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3967 / 90 / 230	
Goodness-of-fit on F^2	1.0057	
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0556	
R indices (all data)	R1 = 0.0338, wR2 = 0.0601	
Largest diff. peak and hole	0.72 and -0.51 $e.Å^{-3}$	

Table S67 Crystal data and structure refinement for **53g**, Ph(*i*-Pr)$_2$TsDCE.

Identification code	002eaa14	
Empirical formula	C21 H25 Cl2 N1 O2 S1	
Formula weight	426.41	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.6658(1) Å	α= 90°.
	b = 11.1469(1) Å	β= 107.7814(5)°.
	c = 15.5831(2) Å	γ = 90°.
Volume	2094.99(4) Å^3	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.426 mm^{-1}	
F(000)	896	
Crystal size	0.34 x 0.25 x 0.21 mm^3	
Theta range for data collection	5.166 to 27.486°.	
Index ranges	-15<=h<=15, -14<=k<=14, -20<=l<=20	
Reflections collected	36426	
Independent reflections	4775 [R(int) = 0.032]	
Completeness to theta = 26.937°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4775 / 0 / 244	
Goodness-of-fit on F^2	1.0025	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0806	
R indices (all data)	R1 = 0.0423, wR2 = 0.0864	
Largest diff. peak and hole	0.39 and -0.42 e.Å^{-3}	

Table S68 Crystal data and structure refinement for **53l**, BPhTsDCE.

Identification code	061eaa17	
Empirical formula	C25 H23 Cl2 N1 O2 S1	
Formula weight	472.43	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.6744(5) Å	α= 106.397(4)°.
	b = 13.5248(5) Å	β= 90.692(4)°.
	c = 13.9959(8) Å	γ = 97.377(3)°.
Volume	2279.59(19) $Å^3$	
Z	4	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	3.596 mm^{-1}	
F(000)	984	
Crystal size	0.20 x 0.20 x 0.11 mm^3	
Theta range for data collection	3.521 to 76.482°.	
Index ranges	-15<=h<=12, -16<=k<=17, -17<=l<=17	
Reflections collected	22404	
Independent reflections	9391 [R(int) = 0.0223]	
Completeness to theta = 73.423°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.67 and 0.47	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9388 / 106 / 615	
Goodness-of-fit on F^2	0.9967	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0837	
R indices (all data)	R1 = 0.0364, wR2 = 0.0868	
Largest diff. peak and hole	0.44 and -0.53 $e.Å^{-3}$	

Table S69 Crystal data and structure refinement for **53m**, *t*-BuTsDCE.

Identification code	055eaa18	
Empirical formula	C13 H17 Cl2 N1 O2 S1	
Formula weight	322.25	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.2882(2) Å	α= 90°.
	b = 10.2559(2) Å	β= 98.999(3)°.
	c = 17.9367(5) Å	γ = 90°.
Volume	1505.90(7) $Å^3$	
Z	4	
Density (calculated)	1.421 Mg/m^3	
Absorption coefficient	0.566 mm^{-1}	
F(000)	672	
Crystal size	0.27 x 0.24 x 0.17 mm^3	
Theta range for data collection	2.295 to 28.817°.	
Index ranges	-11<=h<=10, -13<=k<=13, -22<=l<=24	
Reflections collected	20214	
Independent reflections	3709 [R(int) = 0.0300]	
Completeness to theta = 25.071°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3692 / 90 / 218	
Goodness-of-fit on F^2	1.0031	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0731	
R indices (all data)	R1 = 0.0441, wR2 = 0.0812	
Largest diff. peak and hole	0.38 and -0.42 $e.Å^{-3}$	

Table S70 Crystal data and structure refinement for **69a**, PhZDCE.

Identification code	022eaa18	
Empirical formula	C16 H13 Cl2 N1 O2	
Formula weight	322.19	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.1755(3) Å	α= 90°.
	b = 7.9981(3) Å	β= 95.600(3)°.
	c = 18.6910(7) Å	γ = 90°.
Volume	1513.90(9) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	3.886 mm^{-1}	
F(000)	664	
Crystal size	0.18 x 0.16 x 0.11 mm^3	
Theta range for data collection	4.754 to 76.188°.	
Index ranges	-12<=h<=12, -9<=k<=7, -22<=l<=23	
Reflections collected	13487	
Independent reflections	3139 [R(int) = 0.0267]	
Completeness to theta = 74.664°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.65 and 0.58	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3139 / 81 / 227	
Goodness-of-fit on F^2	1.0015	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0946	
R indices (all data)	R1 = 0.0425, wR2 = 0.0983	
Largest diff. peak and hole	0.48 and -0.58 $e.Å^{-3}$	

Table S71 Crystal data and structure refinement for (*E*)-**72**, PhZPhCE.

Identification code	037eaa18	
Empirical formula	C22 H18 Cl1 N1 O2	
Formula weight	363.84	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1440(8) Å	α= 72.112(5)°.
	b = 9.4570(5) Å	β= 72.362(6)°.
	c = 12.3823(6) Å	γ = 65.173(7)°.
Volume	905.85(12) $Å^3$	
Z	2	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	1.989 mm^{-1}	
F(000)	380	
Crystal size	0.39 x 0.21 x 0.06 mm^3	
Theta range for data collection	3.830 to 76.185°.	
Index ranges	-10<=h<=11, -11<=k<=11, -15<=l<=15	
Reflections collected	18123	
Independent reflections	3751 [R(int) = 0.0322]	
Completeness to theta = 73.137°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3751 / 0 / 235	
Goodness-of-fit on F^2	0.9984	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1083	
R indices (all data)	R1 = 0.0446, wR2 = 0.1108	
Largest diff. peak and hole	0.78 and -0.43 $e.Å^{-3}$	

Table S72 Crystal data and structure refinement for **73**, (*E*)-Ester.

Identification code	036eaa18	
Empirical formula	C22 H18 Cl1 N1 O2	
Formula weight	363.84	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.0515(7) Å	α= 90°.
	b = 6.1296(1) Å	β= 98.229(2)°.
	c = 20.6331(5) Å	γ = 90°.
Volume	3636.39(14) $Å^3$	
Z	8	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	1.982 mm^{-1}	
F(000)	1520	
Crystal size	0.37 x 0.05 x 0.02 mm^3	
Theta range for data collection	4.941 to 76.229°.	
Index ranges	-36<=h<=32, -7<=k<=7, -25<=l<=25	
Reflections collected	19564	
Independent reflections	3794 [R(int) = 0.0285]	
Completeness to theta = 74.705°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3793 / 0 / 235	
Goodness-of-fit on F^2	1.0005	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0821	
R indices (all data)	R1 = 0.0348, wR2 = 0.0871	
Largest diff. peak and hole	0.27 and -0.21 $e.Å^{-3}$	

Table S73 Crystal data and structure refinement for **74**, Oxazolone.

Identification code	092eaa18	
Empirical formula	C15 H11 N1 O2	
Formula weight	237.26	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 6.0102(3) Å	α= 90°.
	b = 13.3092(6) Å	β= 104.129(5)°.
	c = 7.5133(3) Å	γ = 90°.
Volume	582.82(5) $Å^3$	
Z	2	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.733 mm^{-1}	
F(000)	248	
Crystal size	0.36 x 0.11 x 0.01 mm^3	
Theta range for data collection	6.653 to 76.036°.	
Index ranges	-7<=h<=7, -16<=k<=16, -9<=l<=8	
Reflections collected	5285	
Independent reflections	1797 [R(int) = 0.0385]	
Completeness to theta = 76.036°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1792 / 2 / 164	
Goodness-of-fit on F^2	1.0144	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0795	
R indices (all data)	R1 = 0.0358, wR2 = 0.0827	
Largest diff. peak and hole	0.15 and -0.16 e.$Å^{-3}$	
Absolute structure parameter (Flack)	-0.35(34)	
Absolute structure parameter (Flack)	-0.29(24)	
Hooft probability analysis	P2(correct) > 99.99%, P3(correct) 98.98%	

Table S74 Crystal data and structure refinement for **79**, $[Ph_2ZnBr][Mg_2Cl_3(THF)_6]$.

Identification code	040eaa18	
Empirical formula	C36 H58 Br1 Cl3 Mg2 O6 Zn	
Formula weight	887.10	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.6326(3) Å	α= 99.689(2)°.
	b = 12.3732(3) Å	β= 93.743(2)°.
	c = 15.3272(4) Å	γ = 105.281(2)°.
Volume	2083.74(10) $Å^3$	
Z	2	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	4.331 mm^{-1}	
F(000)	924	
Crystal size	0.54 x 0.13 x 0.06 mm^3	
Theta range for data collection	3.774 to 76.177°.	
Index ranges	-14<=h<=14, -15<=k<=15, -19<=l<=19	
Reflections collected	46942	
Independent reflections	8644 [R(int) = 0.0415]	
Completeness to theta = 74.653°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.27	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8644 / 660 / 547	
Goodness-of-fit on F^2	1.0066	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1261	
R indices (all data)	R1 = 0.0535, wR2 = 0.1344	
Largest diff. peak and hole	1.63 and -0.76 e.$Å^{-3}$	

Table S75 Crystal data and structure refinement for **69e**, PhBrMocDCE.

Identification code	060eaa18	
Empirical formula	C10 H8 Br1 Cl2 N1 O2	
Formula weight	324.99	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.51227(12) Å	α= 90°.
	b = 7.7799(1) Å	β= 100.5605(12)°.
	c = 14.88278(18) Å	γ = 90°.
Volume	1196.56(3) $Å^3$	
Z	4	
Density (calculated)	1.804 Mg/m^3	
Absorption coefficient	8.680 mm^{-1}	
F(000)	640	
Crystal size	0.53 x 0.26 x 0.14 mm^3	
Theta range for data collection	4.765 to 76.044°.	
Index ranges	-13<=h<=12, -9<=k<=9, -18<=l<=18	
Reflections collected	11556	
Independent reflections	2488 [R(int) = 0.0230]	
Completeness to theta = 74.523°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.30 and 0.01	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2477 / 0 / 145	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0678	
R indices (all data)	R1 = 0.0262, wR2 = 0.0681	
Largest diff. peak and hole	0.52 and -0.50 $e.Å^{-3}$	

Table S76 Crystal data and structure refinement for **83a**, PhMeUreaPhDCE.

Identification code	075eaa18	
Empirical formula	C16 H14 Cl2 N2 O1	
Formula weight	321.21	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 11.73302(18) Å	α= 90°.
	b = 15.08095(19) Å	β= 90°.
	c = 17.1489(3) Å	γ = 90°.
Volume	3034.42(8) $Å^3$	
Z	8	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	3.843 mm^{-1}	
F(000)	1328	
Crystal size	0.19 x 0.17 x 0.14 mm^3	
Theta range for data collection	5.158 to 76.518°.	
Index ranges	-14<=h<=14, -18<=k<=10, -21<=l<=21	
Reflections collected	22008	
Independent reflections	3182 [R(int) = 0.0254]	
Completeness to theta = 76.518°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.58 and 0.49	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3170 / 95 / 221	
Goodness-of-fit on F^2	1.0120	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0867	
R indices (all data)	R1 = 0.0348, wR2 = 0.0877	
Largest diff. peak and hole	0.28 and -0.44 $e.Å^{-3}$	

Table S77 Crystal data and structure refinement for $MgX_2(tmeda)_2$.

Identification code	079eaa18	
Empirical formula	C12 H32 Br1.33 Cl0.67 Mg1 N4	
Formula weight	386.72	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.9669(2) Å	α= 90°.
	b = 12.8026(4) Å	β= 99.455(3)°.
	c = 9.0901(3) Å	γ = 90°.
Volume	914.57(5) $Å^3$	
Z	2	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	5.089 mm^{-1}	
F(000)	403.858	
Crystal size	0.42 x 0.10 x 0.09 mm^3	
Theta range for data collection	6.025 to 76.339°.	
Index ranges	-8<=h<=9, -16<=k<=16, -10<=l<=11	
Reflections collected	7103	
Independent reflections	1896 [R(int) = 0.0222]	
Completeness to theta = 74.812°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.63 and 0.36	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1888 / 561 / 148	
Goodness-of-fit on F^2	0.9985	
Final R indices [I>2sigma(I)]	R1 = 0.0522, wR2 = 0.1200	
R indices (all data)	R1 = 0.0548, wR2 = 0.1223	
Largest diff. peak and hole	0.73 and -0.96 $e.Å^{-3}$	

Table S78 Crystal data and structure refinement for (*E*)-**88**, Cumulene.

Identification code	082eaa18	
Empirical formula	C44 H34 Cl2 N4 O2	
Formula weight	721.68	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3463(5) Å	α= 100.889(4)°.
	b = 9.9354(6) Å	β= 99.320(4)°.
	c = 11.7589(5) Å	γ = 105.992(5)°.
Volume	896.51(9) $Å^3$	
Z	1	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	1.981 mm^{-1}	
F(000)	376	
Crystal size	0.14 x 0.09 x 0.07 mm^3	
Theta range for data collection	3.931 to 76.247°.	
Index ranges	-10<=h<=10, -12<=k<=10, -11<=l<=14	
Reflections collected	7645	
Independent reflections	3705 [R(int) = 0.0212]	
Completeness to theta = 73.197°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3689 / 0 / 235	
Goodness-of-fit on F^2	1.0043	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0901	
R indices (all data)	R1 = 0.0420, wR2 = 0.0957	
Largest diff. peak and hole	0.31 and -0.33 $e.Å^{-3}$	

Table S79 Crystal data and structure refinement for **83b**, Bn_2UreaPhDCE.

Identification code	074eaa18	
Empirical formula	C23 H20 Cl2 N2 O1	
Formula weight	411.33	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 9.84297(19) Å	α= 90°.
	b = 22.6103(4) Å	β= 90°.
	c = 9.23830(15) Å	γ = 90°.
Volume	2056.00(7) $Å^3$	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	2.959 mm^{-1}	
F(000)	856	
Crystal size	0.36 x 0.09 x 0.06 mm^3	
Theta range for data collection	3.910 to 76.588°.	
Index ranges	-12<=h<=12, -28<=k<=24, -7<=l<=11	
Reflections collected	11200	
Independent reflections	3024 [R(int) = 0.0283]	
Completeness to theta = 75.056°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.60	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3007 / 451 / 400	
Goodness-of-fit on F^2	1.0050	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0998	
R indices (all data)	R1 = 0.0379, wR2 = 0.1021	
Largest diff. peak and hole	0.20 and -0.21 $e.Å^{-3}$	
Absolute structure parameter	-0.028(17)	

Table S80 Crystal data and structure refinement for **83c**, MorpholineUreaPhDCE.

Identification code	078eaa18	
Empirical formula	C13 H14 Cl2 N2 O2	
Formula weight	301.17	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.1344(2) Å	α= 90°.
	b = 10.0069(3) Å	β= 90°.
	c = 14.6736(4) Å	γ = 90°.
Volume	1341.26(6) $Å^3$	
Z	4	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	4.358 mm^{-1}	
F(000)	624	
Crystal size	0.16 x 0.13 x 0.04 mm^3	
Theta range for data collection	5.351 to 76.573°.	
Index ranges	-11<=h<=9, -8<=k<=12, -18<=l<=18	
Reflections collected	5899	
Independent reflections	2769 [R(int) = 0.0222]	
Completeness to theta = 74.276°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.63	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2760 / 0 / 173	
Goodness-of-fit on F^2	1.0065	
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0657	
R indices (all data)	R1 = 0.0260, wR2 = 0.0664	
Largest diff. peak and hole	0.16 and -0.22 $e.Å^{-3}$	
Absolute structure parameter	-0.002(11)	

Table S81 Crystal data and structure refinement for **83d**, PyrrolidineUreaPhDCE.

Identification code	059eaa18	
Empirical formula	C13 H14 Cl2 N2 O1	
Formula weight	285.17	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.49330(14) Å	α= 90°.
	b = 9.41442(10) Å	β= 114.5055(19)°.
	c = 9.19567(14) Å	γ = 90°.
Volume	669.048(19) $Å^3$	
Z	2	
Density (calculated)	1.415 Mg/m^3	
Absorption coefficient	4.277 mm^{-1}	
F(000)	296	
Crystal size	0.51 x 0.20 x 0.17 mm^3	
Theta range for data collection	5.286 to 76.156°.	
Index ranges	-10<=h<=10, -11<=k<=11, -11<=l<=11	
Reflections collected	14312	
Independent reflections	2764 [R(int) = 0.0322]	
Completeness to theta = 74.633°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.48 and 0.19	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2755 / 1 / 164	
Goodness-of-fit on F^2	1.0143	
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0656	
R indices (all data)	R1 = 0.0232, wR2 = 0.0656	
Largest diff. peak and hole	0.19 and -0.25 $e.Å^{-3}$	
Absolute structure parameter	0.009(9)	

Table S82 Crystal data and structure refinement for **83e**, Bn_3UreaDCE.

Identification code	097eaa18	
Empirical formula	C24 H22 Cl2 N2 O1	
Formula weight	425.36	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.1208(3) Å	α= 90°.
	b = 20.4726(4) Å	β= 114.189(3)°.
	c = 11.2885(3) Å	γ = 90°.
Volume	2133.6(1) $Å^3$	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	2.869 mm^{-1}	
F(000)	888	
Crystal size	0.34 x 0.27 x 0.21 mm^3	
Theta range for data collection	4.807 to 76.521°.	
Index ranges	-10<=h<=12, -25<=k<=23, -14<=l<=14	
Reflections collected	17158	
Independent reflections	4459 [R(int) = 0.0237]	
Completeness to theta = 74.990°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.55 and 0.45	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4443 / 146 / 308	
Goodness-of-fit on F^2	1.0063	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0806	
R indices (all data)	R1 = 0.0319, wR2 = 0.0817	
Largest diff. peak and hole	0.27 and -0.24 e.$Å^{-3}$	

Table S83 Crystal data and structure refinement for **89a**, PhBzDCE.

Identification code	084eaa18	
Empirical formula	C15 H11 Cl2 N1 O1	
Formula weight	292.16	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.4982(3) Å	α= 90°.
	b = 11.5732(3) Å	β= 90°.
	c = 15.7190(4) Å	γ = 90°.
Volume	1364.06(7) $Å^3$	
Z	4	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	4.197 mm^{-1}	
F(000)	600	
Crystal size	0.22 x 0.13 x 0.07 mm^3	
Theta range for data collection	4.745 to 76.173°.	
Index ranges	-9<=h<=9, -14<=k<=10, -19<=l<=18	
Reflections collected	11511	
Independent reflections	2853 [R(int) = 0.0255]	
Completeness to theta = 76.173°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2843 / 732 / 339	
Goodness-of-fit on F^2	1.0054	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0982	
R indices (all data)	R1 = 0.0373, wR2 = 0.0988	
Largest diff. peak and hole	0.58 and -0.32 e.$Å^{-3}$	
Absolute structure parameter	-0.004(19)	

Table S84 Crystal data and structure refinement for **89d**, PhPivDCE.

Identification code	088eaa18	
Empirical formula	C13 H15 Cl2 N1 O1	
Formula weight	272.17	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.45319(17) Å	α= 90°.
	b = 14.1247(3) Å	β= 104.585(2)°.
	c = 12.9871(3) Å	γ = 90°.
Volume	1323.14(5) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	4.273 mm^{-1}	
F(000)	568	
Crystal size	0.13 x 0.11 x 0.11 mm^3	
Theta range for data collection	4.709 to 76.679°.	
Index ranges	-9<=h<=9, -17<=k<=17, -16<=l<=16	
Reflections collected	22168	
Independent reflections	2781 [R(int) = 0.0326]	
Completeness to theta = 76.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.62 and 0.58	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2769 / 90 / 191	
Goodness-of-fit on F^2	1.0011	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0693	
R indices (all data)	R1 = 0.0291, wR2 = 0.0710	
Largest diff. peak and hole	0.31 and -0.19 $e.Å^{-3}$	

Table S85 Crystal data and structure refinement for **89e**, BnBzDCE.

Identification code	077eaa18	
Empirical formula	C16 H13 Cl2 N1 O1	
Formula weight	306.19	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.457(3) Å	α= 90°.
	b = 7.4463(12) Å	β= 90.176(16)°.
	c = 12.702(2) Å	γ = 90°.
Volume	1461.9(4) $Å^3$	
Z	4	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	3.941 mm^{-1}	
F(000)	632	
Crystal size	0.15 x 0.02 x 0.02 mm^3	
Theta range for data collection	5.725 to 76.733°.	
Index ranges	-8<=h<=19, -8<=k<=9, -15<=l<=15	
Reflections collected	7371	
Independent reflections	2837 [R(int) = 0.0921]	
Completeness to theta = 36.065°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.31	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2825 / 512 / 317	
Goodness-of-fit on F^2	1.0032	
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.2088	
R indices (all data)	R1 = 0.1298, wR2 = 0.2586	
Largest diff. peak and hole	0.77 and -0.61 $e.Å^{-3}$	

Table S86 Crystal data and structure refinement for **92**, Trichloroenamide.

Identification code	087eaa18	
Empirical formula	C30 H21 Cl3 N2 O2	
Formula weight	547.87	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.8532(3) Å	α= 90°.
	b = 10.5699(2) Å	β= 108.431(3)°.
	c = 20.2102(5) Å	γ = 90°.
Volume	2604.86(11) $Å^3$	
Z	4	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	3.437 mm^{-1}	
F(000)	1128	
Crystal size	0.21 x 0.09 x 0.07 mm^3	
Theta range for data collection	3.629 to 80.169°.	
Index ranges	-10<=h<=16, -13<=k<=12, -24<=l<=25	
Reflections collected	16898	
Independent reflections	5387 [R(int) = 0.0245]	
Completeness to theta = 72.954°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.79 and 0.48	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5360 / 0 / 334	
Goodness-of-fit on F^2	0.9949	
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0802	
R indices (all data)	R1 = 0.0343, wR2 = 0.0836	
Largest diff. peak and hole	0.32 and -0.24 $e.Å^{-3}$	

Table S87 Crystal data and structure refinement for **93a**, PhBzYnHydrate.

Identification code	089eaa18	
Empirical formula	C21 H16 Cl1 N1 O2	
Formula weight	349.82	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.9369(4) Å	α= 82.393(6)°.
	b = 11.1926(10) Å	β= 88.343(5)°.
	c = 13.0345(9) Å	γ = 79.980(6)°.
Volume	845.39(11) $Å^3$	
Z	2	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	2.110 mm^{-1}	
F(000)	364	
Crystal size	0.22 x 0.14 x 0.04 mm^3	
Theta range for data collection	3.421 to 76.591°.	
Index ranges	-7<=h<=7, -14<=k<=13, -12<=l<=16	
Reflections collected	9802	
Independent reflections	3480 [R(int) = 0.0424]	
Completeness to theta = 71.230°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3463 / 0 / 226	
Goodness-of-fit on F^2	0.9907	
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1382	
R indices (all data)	R1 = 0.0598, wR2 = 0.1485	
Largest diff. peak and hole	0.53 and -0.49 $e.Å^{-3}$	

Table S89 Crystal data and structure refinement for **89h**, $Me_2NBzPhDCE$.

Identification code	100eaa18	
Empirical formula	C17 H16 Cl2 N2 O1	
Formula weight	335.23	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.5526(2) Å	α= 90°.
	b = 11.5650(3) Å	β= 90°.
	c = 18.1770(5) Å	γ = 90°.
Volume	1587.69(7) $Å^3$	
Z	4	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	3.696 mm^{-1}	
F(000)	696	
Crystal size	0.34 x 0.13 x 0.09 mm^3	
Theta range for data collection	4.532 to 76.576°.	
Index ranges	-8<=h<=9, -13<=k<=14, -22<=l<=22	
Reflections collected	4889	
Independent reflections	2823 [R(int) = 0.0253]	
Completeness to theta = 75.044°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.72 and 0.46	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2809 / 414 / 318	
Goodness-of-fit on F^2	1.0047	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0929	
R indices (all data)	R1 = 0.0397, wR2 = 0.0957	
Largest diff. peak and hole	0.23 and -0.19 e.$Å^{-3}$	
Absolute structure parameter	0.043(19)	

Table S90 Crystal data and structure refinement for **89j**, MesCOPhDCE.

Identification code	101eaa18	
Empirical formula	C18 H17 Cl2 N1 O1	
Formula weight	334.24	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.09821(13) Å	α= 90°.
	b = 16.7201(3) Å	β= 91.0249(15)°.
	c = 12.1194(2) Å	γ = 90°.
Volume	1640.73(5) $Å^3$	
Z	4	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	3.556 mm^{-1}	
F(000)	696	
Crystal size	0.33 x 0.26 x 0.24 mm^3	
Theta range for data collection	4.506 to 76.573°.	
Index ranges	-10<=h<=10, -15<=k<=20, -15<=l<=15	
Reflections collected	13742	
Independent reflections	3419 [R(int) = 0.0276]	
Completeness to theta = 75.041°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.43 and 0.29	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3405 / 414 / 317	
Goodness-of-fit on F^2	0.9999	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0875	
R indices (all data)	R1 = 0.0337, wR2 = 0.0887	
Largest diff. peak and hole	0.21 and -0.28 $e.Å^{-3}$	

Table S91 Crystal data and structure refinement for **89k**, Cl_2BzPhDCE.

Identification code	107eaa18	
Empirical formula	C15 H9 Cl4 N1 O1	
Formula weight	361.05	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.75796(3) Å	α= 90°.
	b = 13.07348(7) Å	β= 94.9811(4)°.
	c = 30.22146(13) Å	γ = 90°.
Volume	3053.59(2) $Å^3$	
Z	8	
Density (calculated)	1.571 Mg/m^3	
Absorption coefficient	7.019 mm^{-1}	
F(000)	1456	
Crystal size	0.30 x 0.21 x 0.13 mm^3	
Theta range for data collection	3.686 to 76.229°.	
Index ranges	-9<=h<=9, -15<=k<=16, -38<=l<=38	
Reflections collected	167630	
Independent reflections	6373 [R(int) = 0.0378]	
Completeness to theta = 76.229°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.40 and 0.24	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6349 / 256 / 471	
Goodness-of-fit on F^2	1.0116	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0725	
R indices (all data)	R1 = 0.0309, wR2 = 0.0729	
Largest diff. peak and hole	0.36 and -0.30 $e.Å^{-3}$	

Table S92 Crystal data and structure refinement for **93h**, Me_2NBzPhYnHydrate.

Identification code	099eaa18	
Empirical formula	C23 H21 Cl1 N2 O2	
Formula weight	392.88	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.0920(3) Å	α= 76.239(4)°.
	b = 11.9892(6) Å	β= 79.136(3)°.
	c = 14.3204(5) Å	γ = 77.836(4)°.
Volume	982.50(8) $Å^3$	
Z	2	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	1.888 mm^{-1}	
F(000)	412	
Crystal size	0.50 x 0.17 x 0.14 mm^3	
Theta range for data collection	3.212 to 76.298°.	
Index ranges	-7<=h<=7, -15<=k<=14, -17<=l<=16	
Reflections collected	11731	
Independent reflections	4063 [R(int) = 0.0289]	
Completeness to theta = 74.009°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.41	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4046 / 0 / 253	
Goodness-of-fit on F^2	1.0059	
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1106	
R indices (all data)	R1 = 0.0435, wR2 = 0.1137	
Largest diff. peak and hole	0.27 and -0.36 e.$Å^{-3}$	

2.2 Synthesis and Applications of Yndiamides.

2.2a *Yndiamides*.

Table S93 Crystal data and structure refinement for **148a**, PhTsYndBnTs.

Identification code	032mwj13	
Empirical formula	C29 H26 N2 O4 S2	
Formula weight	530.67	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.9988(1) Å	α= 90°.
	b = 11.3400(2) Å	β= 92.2562(7)°.
	c = 28.9436(4) Å	γ = 90°.
Volume	2623.33(7) $Å^3$	
Z	4	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	1112	
Crystal size	0.37 x 0.25 x 0.16 mm^3	
Theta range for data collection	5.102 to 27.492°.	
Index ranges	-10<=h<=10, -13<=k<=14, -37<=l<=37	
Reflections collected	21448	
Independent reflections	5894 [R(int) = 0.0378]	
Completeness to theta = 25.017°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.86	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5894 / 0 / 334	
Goodness-of-fit on F^2	0.9978	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1301	
R indices (all data)	R1 = 0.0833, wR2 = 0.1564	
Largest diff. peak and hole	0.62 and -0.70 $e.Å^{-3}$	

Table S94 Crystal data and structure refinement for **148b**, BnTsYndBnTs.

Identification code	019eaa16	
Empirical formula	C30 H28 N2 O4 S2	
Formula weight	544.70	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/c	
Unit cell dimensions	a = 20.1948(14) Å	α= 90°.
	b = 5.4851(3) Å	β= 111.379(8)°.
	c = 25.6858(18) Å	γ = 90°.
Volume	2649.4(3) $Å^3$	
Z	4	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	1144	
Crystal size	0.32 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.811 to 30.431°.	
Index ranges	-28<=h<=27, -7<=k<=7, -36<=l<=36	
Reflections collected	14051	
Independent reflections	3668 [R(int) = 0.0498]	
Completeness to theta = 25.257°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3660 / 0 / 172	
Goodness-of-fit on F^2	1.0094	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1028	
R indices (all data)	R1 = 0.0590, wR2 = 0.1129	
Largest diff. peak and hole	0.55 and -0.43 $e.Å^{-3}$	

Table S95 Crystal data and structure refinement for **148c**, BnTsYndBnTfs.

Identification code	023eaa16	
Empirical formula	C30 H25 F3 N2 O4 S2	
Formula weight	598.67	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 2/c	
Unit cell dimensions	a = 20.2724(14) Å	α= 90°.
	b = 5.5029(3) Å	β= 110.727(8)°.
	c = 26.4849(19) Å	γ = 90°.
Volume	2763.3(3) $Å^3$	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	2.274 mm^{-1}	
F(000)	1240	
Crystal size	0.45 x 0.13 x 0.04 mm^3	
Theta range for data collection	4.664 to 76.548°.	
Index ranges	-25<=h<=25, -6<=k<=6, -31<=l<=33	
Reflections collected	13664	
Independent reflections	2867 [R(int) = 0.1061]	
Completeness to theta = 75.017°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.56	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2865 / 439 / 228	
Goodness-of-fit on F^2	1.0493	
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1516	
R indices (all data)	R1 = 0.0684, wR2 = 0.1557	
Largest diff. peak and hole	0.47 and -0.61 $e.Å^{-3}$	

Table S96 Crystal data and structure refinement for **148g**, BnTsYndBnPs.

Identification code	018eaa16	
Empirical formula	C28 H31 N2 O5 P1 S1	
Formula weight	538.60	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 22.7882(6) Å	α= 90°.
	b = 6.1234(2) Å	β= 98.699(3)°.
	c = 19.4319(6) Å	γ = 90°.
Volume	2680.36(14) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	1.978 mm^{-1}	
F(000)	1136	
Crystal size	0.51 x 0.11 x 0.04 mm^3	
Theta range for data collection	3.925 to 78.978°.	
Index ranges	-28<=h<=28, -7<=k<=7, -24<=l<=24	
Reflections collected	59413	
Independent reflections	5618 [R(int) = 0.0765]	
Completeness to theta = 75.819°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5616 / 0 / 334	
Goodness-of-fit on F^2	0.9996	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1108	
R indices (all data)	R1 = 0.0518, wR2 = 0.1223	
Largest diff. peak and hole	0.59 and -0.48 $e.Å^{-3}$	

Table S97 Crystal data and structure refinement for **148h**, BnTsYndHallPs.

Identification code	DIA0292	
Empirical formula	C25 H31 N2 O5 P1 S1	
Formula weight	502.57	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 5.8226(2) Å	α= 90°.
	b = 11.2280(5) Å	β= 92.151(3)°.
	c = 38.8063(13) Å	γ = 90°.
Volume	2535.22(17) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	1064	
Crystal size	0.07 x 0.06 x 0.02 mm^3	
Theta range for data collection	2.036 to 25.043°.	
Index ranges	-6<=h<=6, -13<=k<=11, -47<=l<=46	
Reflections collected	9611	
Independent reflections	3828 [R(int) = 0.0227]	
Completeness to theta = 25.043°	77.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.48	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3811 / 52 / 326	
Goodness-of-fit on F^2	1.0022	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1314	
R indices (all data)	R1 = 0.0542, wR2 = 0.1345	
Largest diff. peak and hole	0.60 and -0.60 $e.Å^{-3}$	

Table S98 Crystal data and structure refinement for **148i**, BnTsYndCyclohexenylPs.

Identification code	011eaa16b	
Empirical formula	C29 H37 N2 O5 P1 S1	
Formula weight	556.66	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 27.2661(11) Å	α= 90°.
	b = 10.2054(3) Å	β= 104.858(4)°.
	c = 20.9433(8) Å	γ = 90°.
Volume	5632.9(4) $Å^3$	
Z	8	
Density (calculated)	1.313 Mg/m^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	2368	
Crystal size	0.29 x 0.14 x 0.09 mm^3	
Theta range for data collection	3.439 to 29.709°.	
Index ranges	-37<=h<=36, -13<=k<=13, -28<=l<=29	
Reflections collected	68109	
Independent reflections	14348 [R(int) = 0.0545]	
Completeness to theta = 25.253°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14328 / 236 / 777	
Goodness-of-fit on F^2	1.0104	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1179	
R indices (all data)	R1 = 0.0845, wR2 = 0.1420	
Largest diff. peak and hole	0.60 and -0.57 $e.Å^{-3}$	

Table S99 Crystal data and structure refinement for **148j**, BnTsYndBuTs.

Identification code	DIA0271	
Empirical formula	C27 H30 N2 O4 S2	
Formula weight	510.68	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6002(1) Å	α= 110.059(3)°.
	b = 13.6554(5) Å	β= 97.834(2)°.
	c = 14.0300(6) Å	γ = 103.231(2)°.
Volume	1294.19(8) $Å^3$	
Z	2	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	540	
Crystal size	0.04 x 0.02 x 0.02 mm^3	
Theta range for data collection	1.611 to 36.314°.	
Index ranges	-12<=h<=12, -22<=k<=23, -24<=l<=24	
Reflections collected	27327	
Independent reflections	11896 [R(int) = 0.0351]	
Completeness to theta = 26.000°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11874 / 0 / 316	
Goodness-of-fit on F^2	1.0037	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0741	
R indices (all data)	R1 = 0.0420, wR2 = 0.0824	
Largest diff. peak and hole	0.49 and -0.51 $e.Å^{-3}$	

Table S100 Crystal data and structure refinement for **148k**, BnTsYndHallTs.

Identification code	DIA0272	
Empirical formula	C27 H28 N2 O4 S2	
Formula weight	508.66	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.6522(5) Å	α= 90°.
	b = 16.0100(11) Å	β= 92.266(7)°.
	c = 28.618(2) Å	γ = 90°.
Volume	2587.7(3) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	1072	
Crystal size	0.12 x 0.05 x 0.02 mm^3	
Theta range for data collection	1.851 to 27.444°.	
Index ranges	-7<=h<=6, -21<=k<=18, -33<=l<=36	
Reflections collected	17482	
Independent reflections	5876 [R(int) = 0.1029]	
Completeness to theta = 25.249°	91.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3579 / 0 / 316	
Goodness-of-fit on F^2	0.9822	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1336	
R indices (all data)	R1 = 0.0617, wR2 = 0.1503	
Largest diff. peak and hole	0.41 and -0.43 $e.Å^{-3}$	

Table S101 Crystal data and structure refinement for **148l**, BnTsYndHex-3-Ts.

Identification code	093eaa17	
Empirical formula	C29 H32 N2 O4 S2	
Formula weight	536.72	
Temperature	30 K	
Wavelength	0.68890 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.7168(13) Å	α= 109.871(9)°.
	b = 13.4950(13) Å	β= 99.916(11)°.
	c = 14.6953(15) Å	γ = 103.292(12)°.
Volume	1347.3(3) $Å^3$	
Z	2	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	568	
Crystal size	0.015 x 0.012 x 0.005 mm^3	
Theta range for data collection	1.485 to 25.565°.	
Index ranges	-8<=h<=8, -16<=k<=15, -18<=l<=17	
Reflections collected	8810	
Independent reflections	4098 [R(int) = 0.107]	
Completeness to theta = 25.054°	74.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.21	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4097 / 0 / 334	
Goodness-of-fit on F^2	1.0015	
Final R indices [I>2sigma(I)]	R1 = 0.0951, wR2 = 0.2488	
R indices (all data)	R1 = 0.1134, wR2 = 0.2875	
Largest diff. peak and hole	1.21 and -0.73 $e.Å^{-3}$	

Table S102 Crystal data and structure refinement for **148q**, BnTsYndCyTs.

Identification code	012eaa16	
Empirical formula	C29 H32 N2 O4 S2	
Formula weight	536.72	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.6540(2) Å	α= 90°.
	b = 28.8816(4) Å	β= 101.6142(18)°.
	c = 9.9460(2) Å	γ = 90°.
Volume	2716.39(9) $Å^3$	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	2.081 mm^{-1}	
F(000)	1136	
Crystal size	0.34 x 0.34 x 0.31 mm^3	
Theta range for data collection	4.790 to 76.552°.	
Index ranges	-12<=h<=12, -36<=k<=36, -12<=l<=12	
Reflections collected	65123	
Independent reflections	5678 [R(int) = 0.0644]	
Completeness to theta = 75.021°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.52 and 0.34	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5677 / 0 / 334	
Goodness-of-fit on F^2	1.0292	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1230	
R indices (all data)	R1 = 0.0475, wR2 = 0.1236	
Largest diff. peak and hole	0.47 and -0.52 $e.Å^{-3}$	

Table S103 Crystal data and structure refinement for **148s**, BnTsYndCyclohexenylTs.

Identification code	049eaa17	
Empirical formula	C31 H34 N2 O4 S2	
Formula weight	562.75	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0415(3) Å	α= 68.125(4)°.
	b = 14.0142(6) Å	β= 82.442(3)°.
	c = 14.2839(5) Å	γ = 74.060(3)°.
Volume	1435.62(11) $Å^3$	
Z	2	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	1.994 mm^{-1}	
F(000)	596	
Crystal size	0.50 x 0.49 x 0.38 mm^3	
Theta range for data collection	3.894 to 76.243°.	
Index ranges	-10<=h<=10, -17<=k<=16, -17<=l<=13	
Reflections collected	15685	
Independent reflections	5927 [R(int) = 0.0176]	
Completeness to theta = 73.956°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.47 and 0.27	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5927 / 855 / 407	
Goodness-of-fit on F^2	1.0049	
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0936	
R indices (all data)	R1 = 0.0375, wR2 = 0.0952	
Largest diff. peak and hole	0.30 and -0.41 $e.Å^{-3}$	

Table S104 Crystal data and structure refinement for **148w**, BnTsYndAcetalEsterTs.

Identification code	047eaa17	
Empirical formula	C37 H47 N2 O8.50 S2	
Formula weight	719.92	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 25.2091(9) Å	α= 90°.
	b = 5.7112(2) Å	β= 109.762(4)°.
	c = 27.7261(12) Å	γ = 90°.
Volume	3756.7(3) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	1.728 mm^{-1}	
F(000)	1532	
Crystal size	0.34 x 0.13 x 0.03 mm^3	
Theta range for data collection	3.387 to 76.391°.	
Index ranges	-29<=h<=31, -7<=k<=7, -34<=l<=33	
Reflections collected	26831	
Independent reflections	7612 [R(int) = 0.0536]	
Completeness to theta = 74.863°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7612 / 3 / 450	
Goodness-of-fit on F^2	1.0020	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1335	
R indices (all data)	R1 = 0.0537, wR2 = 0.1384	
Absolute structure parameter	-0.007(17)	
Largest diff. peak and hole	0.35 and -0.30 $e.Å^{-3}$	

Table S105 Crystal data and structure refinement for **148x,** BnTsYndMeMs.

Identification code	089eaa17	
Empirical formula	C18 H20 N2 O4 S2	
Formula weight	392.50	
Temperature	30 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.5543(1) Å	α= 90°.
	b = 27.4437(7) Å	β= 91.578(3)°.
	c = 12.2313(4) Å	γ = 90°.
Volume	1863.72(8) $Å^3$	
Z	4	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	0.312 mm^{-1}	
F(000)	824	
Crystal size	0.11 x 0.02 x 0.02 mm^3	
Theta range for data collection	1.767 to 27.470°.	
Index ranges	-7<=h<=7, -36<=k<=36, -16<=l<=16	
Reflections collected	21410	
Independent reflections	4621 [R(int) = 0.0957]	
Completeness to theta = 26.096°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4606 / 0 / 235	
Goodness-of-fit on F^2	1.0154	
Final R indices [I>2sigma(I)]	R1 = 0.0697, wR2 = 0.1788	
R indices (all data)	R1 = 0.0785, wR2 = 0.1846	
Largest diff. peak and hole	0.91 and -0.89 e.$Å^{-3}$	

Table S106 Crystal data and structure refinement for **160a**, HallTsYndBnTfs.

Identification code	027eaa17	
Empirical formula	C27 H25 F3 N2 O4 S2	
Formula weight	562.63	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.7175(2) Å	α= 90°.
	b = 15.7869(7) Å	β= 90.837(4)°.
	c = 29.4614(15) Å	γ = 90°.
Volume	2658.9(2) $Å^3$	
Z	4	
Density (calculated)	1.405 Mg/m^3	
Absorption coefficient	0.258 mm^{-1}	
F(000)	1168	
Crystal size	0.16 x 0.02 x 0.01 mm^3	
Theta range for data collection	1.833 to 29.522°.	
Index ranges	-8<=h<=6, -22<=k<=22, -38<=l<=37	
Reflections collected	19054	
Independent reflections	7105 [R(int) = 0.0990]	
Completeness to theta = 25.094°	89.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.27	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6081 / 1879 / 498	
Goodness-of-fit on F^2	1.0157	
Final R indices [I>2sigma(I)]	R1 = 0.0802, wR2 = 0.2050	
R indices (all data)	R1 = 0.1003, wR2 = 0.2214	
Largest diff. peak and hole	0.63 and -0.74 e.$Å^{-3}$	

Table S107 Crystal data and structure refinement for **160b**, HallTsYndBnPs.

Identification code	020eaa16	
Empirical formula	C25 H31 N2 O5 P1 S1	
Formula weight	502.57	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.9492(1) Å	α= 90°.
	b = 15.6540(5) Å	β= 90°.
	c = 27.5948(6) Å	γ = 90°.
Volume	2569.87(11) $Å^3$	
Z	4	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	2.021 mm^{-1}	
F(000)	1064	
Crystal size	0.34 x 0.12 x 0.07 mm^3	
Theta range for data collection	4.271 to 76.267°.	
Index ranges	-4<=h<=7, -19<=k<=19, -34<=l<=33	
Reflections collected	26121	
Independent reflections	5357 [R(int) = 0.0391]	
Completeness to theta = 76.267°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5357 / 70 / 336	
Goodness-of-fit on F^2	1.0331	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1325	
R indices (all data)	R1 = 0.0541, wR2 = 0.1357	
Absolute structure parameter	0.450(19)	
Largest diff. peak and hole	1.13 and -0.31 $e.Å^{-3}$	

Table S108 Crystal data and structure refinement for **160c**, HallTsYndHallTs.

Identification code	015eaa17	
Empirical formula	C24 H28 N2 O4 S2	
Formula weight	472.63	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 11.7327(5) Å	α= 90°.
	b = 13.9424(7) Å	β= 101.167(4)°.
	c = 15.5632(6) Å	γ = 90°.
Volume	2497.66(19) $Å^3$	
Z	4	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	1000	
Crystal size	0.36 x 0.32 x 0.25 mm^3	
Theta range for data collection	3.249 to 30.520°.	
Index ranges	-15<=h<=16, -19<=k<=19, -20<=l<=21	
Reflections collected	27618	
Independent reflections	3593 [R(int) = 0.0434]	
Completeness to theta = 26.247°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.83	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3270 / 28 / 164	
Goodness-of-fit on F^2	1.0092	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1057	
R indices (all data)	R1 = 0.0571, wR2 = 0.1198	
Largest diff. peak and hole	0.55 and -0.44 $e.Å^{-3}$	

Table S109 Crystal data and structure refinement for **160e**, MeYnTsYndHallTs.

Identification code	057eaa17	
Empirical formula	C25 H28 N2 O4 S2	
Formula weight	484.64	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.0853(12) Å	α= 90°.
	b = 9.7620(6) Å	β= 109.440(9)°.
	c = 16.9652(15) Å	γ = 90°.
Volume	2512.1(4) $Å^3$	
Z	4	
Density (calculated)	1.281 Mg/m^3	
Absorption coefficient	2.192 mm^{-1}	
F(000)	1024	
Crystal size	0.11 x 0.10 x 0.07 mm^3	
Theta range for data collection	5.308 to 76.351°.	
Index ranges	-16<=h<=20, -12<=k<=8, -21<=l<=20	
Reflections collected	15681	
Independent reflections	5182 [R(int) = 0.0543]	
Completeness to theta = 72.533°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.86 and 0.66	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5178 / 1917 / 489	
Goodness-of-fit on F^2	0.9911	
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1300	
R indices (all data)	R1 = 0.0714, wR2 = 0.1521	
Largest diff. peak and hole	0.48 and -0.56 $e.Å^{-3}$	

Table S110 Crystal data and structure refinement for **160f**, MeYnTsYndMeYnTs.

Identification code	002eaa16	
Empirical formula	C26 H28 N2 O4 S2	
Formula weight	496.65	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 17.4465(2) Å	α= 90°.
	b = 10.0623(2) Å	β= 116.1040(6)°.
	c = 15.9615(3) Å	γ = 90°.
Volume	2516.25(5) $Å^3$	
Z	4	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.246 mm^{-1}	
F(000)	1048	
Crystal size	0.25 x 0.24 x 0.15 mm^3	
Theta range for data collection	5.110 to 27.502°.	
Index ranges	-22<=h<=22, -13<=k<=12, -20<=l<=20	
Reflections collected	22075	
Independent reflections	2866 [R(int) = 0.016]	
Completeness to theta = 26.952°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2864 / 0 / 154	
Goodness-of-fit on F^2	0.9750	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0958	
R indices (all data)	R1 = 0.0447, wR2 = 0.0995	
Largest diff. peak and hole	0.32 and -0.40 $e.Å^{-3}$	

Table S111 Crystal data and structure refinement for **160g**, MeYnTsYndPhYnTs.

Identification code	063eaa17	
Empirical formula	C31 H30 N2 O4 S2	
Formula weight	558.72	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6523(1) Å	α= 82.5389(9)°.
	b = 9.9930(1) Å	β= 77.1313(9)°.
	c = 16.8870(1) Å	γ = 62.2965(13)°.
Volume	1405.25(3) $Å^3$	
Z	2	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	588	
Crystal size	0.05 x 0.03 x 0.02 mm^3	
Theta range for data collection	2.232 to 29.483°.	
Index ranges	-13<=h<=13, -14<=k<=14, -24<=l<=24	
Reflections collected	23355	
Independent reflections	8415 [R(int) = 0.0439]	
Completeness to theta = 25.060°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8393 / 0 / 352	
Goodness-of-fit on F^2	0.9912	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1230	
R indices (all data)	R1 = 0.0489, wR2 = 0.1263	
Largest diff. peak and hole	0.48 and -0.51 $e.Å^{-3}$	

Table S112 Crystal data and structure refinement for **160h**, MeYnTsYndCyTs.

Identification code	039eaa17	
Empirical formula	C27 H32 N2 O4 S2	
Formula weight	512.69	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.8223(2) Å	α= 90°.
	b = 8.7283(2) Å	β= 90°.
	c = 44.7285(11) Å	γ = 90°.
Volume	2663.45(12) $Å^3$	
Z	4	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	2.095 mm^{-1}	
F(000)	1088	
Crystal size	0.29 x 0.16 x 0.11 mm^3	
Theta range for data collection	3.953 to 76.341°.	
Index ranges	-8<=h<=8, -11<=k<=10, -56<=l<=56	
Reflections collected	55246	
Independent reflections	5545 [R(int) = 0.0435]	
Completeness to theta = 76.341°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.79 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5540 / 0 / 317	
Goodness-of-fit on F^2	1.0546	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1102	
R indices (all data)	R1 = 0.0437, wR2 = 0.1109	
Absolute structure parameter	0.432(19)	
Largest diff. peak and hole	0.31 and -0.33 $e.Å^{-3}$	

Table S113 Crystal data and structure refinement for **160l**, BuTsYndBuTs.

Identification code	051eaa18	
Empirical formula	C24 H32 N2 O4 S2	
Formula weight	476.66	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.5473(3) Å	α= 90°.
	b = 13.0557(3) Å	β= 107.119(2)°.
	c = 12.4936(3) Å	γ = 90°.
Volume	2423.61(10) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	1016	
Crystal size	0.45 x 0.26 x 0.21 mm^3	
Theta range for data collection	2.076 to 28.977°.	
Index ranges	-20<=h<=20, -17<=k<=17, -16<=l<=16	
Reflections collected	52042	
Independent reflections	6101 [R(int) = 0.0410]	
Completeness to theta = 25.500°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.73	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6089 / 88 / 326	
Goodness-of-fit on F^2	1.0190	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0830	
R indices (all data)	R1 = 0.0570, wR2 = 0.0986	
Largest diff. peak and hole	0.52 and -0.53 e.$Å^{-3}$	

Table S114 Crystal data and structure refinement for **160m**, MeTsYndHallTs.

Identification code	042eaa17	
Empirical formula	C21 H24 N2 O4 S2	
Formula weight	432.56	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.9775(2) Å	α= 90°.
	b = 7.9596(3) Å	β= 90°.
	c = 45.7058(13) Å	γ = 90°.
Volume	2174.61(13) $Å^3$	
Z	4	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	2.466 mm^{-1}	
F(000)	912	
Crystal size	0.44 x 0.19 x 0.11 mm^3	
Theta range for data collection	3.869 to 76.264°.	
Index ranges	-7<=h<=6, -10<=k<=9, -57<=l<=57	
Reflections collected	22344	
Independent reflections	4536 [R(int) = 0.0383]	
Completeness to theta = 76.264°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.76 and 0.57	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4534 / 56 / 291	
Goodness-of-fit on F^2	1.0077	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1192	
R indices (all data)	R1 = 0.0431, wR2 = 0.1202	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	0.56 and -0.62 e.$Å^{-3}$	

2.2b *Bromoketene Aminals, Applications and Miscellaneous*.

Table S115 Crystal data and structure refinement for **155b**, BnBKA.

Identification code	024eaa17	
Empirical formula	C30 H29 Br1 N2 O4 S2	
Formula weight	625.61	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.7074(2) Å	α= 90°.
	b = 11.4666(2) Å	β= 95.3161(14)°.
	c = 33.2859(6) Å	γ = 90°.
Volume	5589.32(16) $Å^3$	
Z	8	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	1.660 mm^{-1}	
F(000)	2576	
Crystal size	0.09 x 0.07 x 0.07 mm^3	
Theta range for data collection	1.714 to 29.502°.	
Index ranges	-20<=h<=21, -16<=k<=16, -47<=l<=47	
Reflections collected	83946	
Independent reflections	16954 [R(int) = 0.0862]	
Completeness to theta = 25.077°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16908 / 2902 / 968	
Goodness-of-fit on F^2	0.9998	
Final R indices [I>2sigma(I)]	R1 = 0.1070, wR2 = 0.1905	
R indices (all data)	R1 = 0.1244, wR2 = 0.1951	
Largest diff. peak and hole	2.58 and -2.51 e.$Å^{-3}$.	

Table S116 Crystal data and structure refinement for **155c**, PhOBKA.

Identification code	DIA0388	
Empirical formula	C22 H20 Br1 N1 O3 S	
Formula weight	458.38	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 5.8441(2) Å	α= 90°.
	b = 18.4626(9) Å	β= 92.753(4)°.
	c = 18.0110(8) Å	γ = 90°.
Volume	1941.10(14) $Å^3$	
Z	4	
Density (calculated)	1.568 Mg/m^3	
Absorption coefficient	2.076 mm^{-1}	
F(000)	936	
Crystal size	0.18 x 0.01 x 0.007 mm^3	
Theta range for data collection	1.532 to 29.473°.	
Index ranges	-8<=h<=8, -26<=k<=26, -25<=l<=25	
Reflections collected	31679	
Independent reflections	5917 [R(int) = 0.113]	
Completeness to theta = 29.473°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.52	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4589 / 0 / 253	
Goodness-of-fit on F^2	1.0068	
Final R indices [I>2sigma(I)]	R1 = 0.0632, wR2 = 0.1475	
R indices (all data)	R1 = 0.0978, wR2 = 0.1674	
Largest diff. peak and hole	1.22 and -0.89 $e.Å^{-3}$	

Table S117 Crystal data and structure refinement for **155d**, BnTrisBKA.

Identification code	027eaa16	
Empirical formula	C38 H45 Br1 N2 O4 S2	
Formula weight	737.82	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.4224(6) Å	α= 67.042(4)°.
	b = 13.4700(5) Å	β= 74.084(4)°.
	c = 14.6435(7) Å	γ = 85.391(4)°.
Volume	2168.74(19) $Å^3$	
Z	2	
Density (calculated)	1.130 Mg/m^3	
Absorption coefficient	2.467 mm^{-1}	
F(000)	772	
Crystal size	0.31 x 0.24 x 0.21 mm^3	
Theta range for data collection	3.565 to 76.567°.	
Index ranges	-15<=h<=15, -16<=k<=15, -18<=l<=18	
Reflections collected	22149	
Independent reflections	8976 [R(int) = 0.0359]	
Completeness to theta = 73.504°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.60 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8975 / 356 / 560	
Goodness-of-fit on F^2	1.0032	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0953	
R indices (all data)	R1 = 0.0432, wR2 = 0.1020	
Largest diff. peak and hole	0.32 and -0.44 $e.Å^{-3}$	

Table S118 Crystal data and structure refinement for **155e**, PhTsBKA.

Identification code	033eaa17	
Empirical formula	C29 H27 Br1 N2 O4 S2	
Formula weight	611.58	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.5192(3) Å	α= 81.626(4)°.
	b = 9.7163(5) Å	β= 79.483(4)°.
	c = 16.8098(7) Å	γ = 89.429(4)°.
Volume	1353.28(10) $Å^3$	
Z	2	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	3.832 mm^{-1}	
F(000)	628	
Crystal size	0.36 x 0.29 x 0.27 mm^3	
Theta range for data collection	4.601 to 76.108°.	
Index ranges	-10<=h<=9, -9<=k<=12, -21<=l<=20	
Reflections collected	12044	
Independent reflections	5569 [R(int) = 0.0173]	
Completeness to theta = 73.064°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.36 and 0.29	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5566 / 14 / 353	
Goodness-of-fit on F^2	1.0084	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0795	
R indices (all data)	R1 = 0.0324, wR2 = 0.0803	
Largest diff. peak and hole	1.03 and -0.51 $e.Å^{-3}$	

Table S119 Crystal data and structure refinement for **159**, BnTsDiyne.

Identification code	DIA0292b	
Empirical formula	C32 H28 N2 O4 S2	
Formula weight	568.72	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.2558(2) Å	α= 90°.
	b = 15.3086(7) Å	β= 90°.
	c = 29.2087(14) Å	γ = 90°.
Volume	2797.2(2) $Å^3$	
Z	4	
Density (calculated)	1.350 Mg/m^3	
Absorption coefficient	0.231 mm^{-1}	
F(000)	1192	
Crystal size	0.07 x 0.02 x 0.02 mm^3	
Theta range for data collection	1.868 to 29.477°.	
Index ranges	-8<=h<=8, -21<=k<=21, -41<=l<=41	
Reflections collected	36478	
Independent reflections	8494 [R(int) = 0.0983]	
Completeness to theta = 29.477°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8475 / 0 / 362	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1574	
R indices (all data)	R1 = 0.0645, wR2 = 0.1610	
Largest diff. peak and hole	1.23 and -0.39 $e.Å^{-3}$	
Absolute structure parameter	0.03(7)	

Table S120 Crystal data and structure refinement for **162**, BnYnBrDimer.

Identification code	DIA0281	
Empirical formula	C71 H64 Br4 N4 O8 S4	
Formula weight	1549.19	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 24.9873(3) Å	α= 90°.
	b = 10.9675(1) Å	β= 101.7557(14)°.
	c = 25.7011(4) Å	γ = 90°.
Volume	6895.61(15) $Å^3$	
Z	4	
Density (calculated)	1.492 Mg/m^3	
Absorption coefficient	2.513 mm^{-1}	
F(000)	3144	
Crystal size	0.05 x 0.05 x 0.03 mm^3	
Theta range for data collection	1.972 to 25.334°.	
Index ranges	-28<=h<=28, -12<=k<=12, -28<=l<=28	
Reflections collected	27750	
Independent reflections	5597 [R(int) = 0.0768]	
Completeness to theta = 25.334°	81.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.42	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5570 / 476 / 510	
Goodness-of-fit on F^2	1.0069	
Final R indices [I>2sigma(I)]	R1 = 0.0678, wR2 = 0.1567	
R indices (all data)	R1 = 0.0867, wR2 = 0.1656	
Largest diff. peak and hole	1.40 and -1.21 $e.Å^{-3}$	

Table S121 Crystal data and structure refinement for **182**, MeHallCycloisomDA-PTAD.

Identification code	048eaa17	
Empirical formula	C29 H29 N5 O6 S2	
Formula weight	607.71	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.0900(1) Å	α= 90°.
	b = 13.9990(1) Å	β= 96.2470(8)°.
	c = 19.9396(2) Å	γ = 90°.
Volume	2799.74(4) $Å^3$	
Z	4	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	2.180 mm^{-1}	
F(000)	1272	
Crystal size	0.27 x 0.13 x 0.13 mm^3	
Theta range for data collection	3.866 to 76.267°.	
Index ranges	-12<=h<=12, -17<=k<=17, -25<=l<=25	
Reflections collected	59267	
Independent reflections	5845 [R(int) = 0.0444]	
Completeness to theta = 76.267°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5843 / 0 / 379	
Goodness-of-fit on F^2	1.0063	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1014	
R indices (all data)	R1 = 0.0390, wR2 = 0.1031	
Largest diff. peak and hole	0.33 and -0.45 $e.Å^{-3}$	

Table S122 Crystal data and structure refinement for **183**, BnHex3Cycloisom.

Identification code	058eaa17	
Empirical formula	C29 H32 N2 O4 S2	
Formula weight	536.72	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.0806(3) Å	α= 93.102(3)°.
	b = 10.2306(4) Å	β= 103.373(3)°.
	c = 14.6719(5) Å	γ = 108.248(3)°.
Volume	1384.89(9) $Å^3$	
Z	2	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	2.041 mm^{-1}	
F(000)	568	
Crystal size	0.26 x 0.24 x 0.14 mm^3	
Theta range for data collection	3.125 to 76.219°.	
Index ranges	-12<=h<=11, -12<=k<=12, -18<=l<=18	
Reflections collected	19416	
Independent reflections	5708 [R(int) = 0.0268]	
Completeness to theta = 73.932°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5708 / 0 / 334	
Goodness-of-fit on F^2	1.0033	
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0964	
R indices (all data)	R1 = 0.0367, wR2 = 0.0972	
Largest diff. peak and hole	0.31 and -0.38 $e.Å^{-3}$	

Table S123 Crystal data and structure refinement for **184**, MeHex3Cycloisom.

Identification code	073eaa17	
Empirical formula	C23 H28 N2 O4 S2	
Formula weight	460.62	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.6288(5) Å	α= 90°.
	b = 9.5506(3) Å	β= 105.377(4)°.
	c = 20.3317(7) Å	γ = 90°.
Volume	2364.47(15) $Å^3$	
Z	4	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	2.299 mm^{-1}	
F(000)	976	
Crystal size	0.21 x 0.14 x 0.11 mm^3	
Theta range for data collection	3.630 to 76.453°.	
Index ranges	-15<=h<=15, -11<=k<=12, -25<=l<=25	
Reflections collected	49277	
Independent reflections	4926 [R(int) = 0.0351]	
Completeness to theta = 74.924°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.78 and 0.67	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4926 / 0 / 280	
Goodness-of-fit on F^2	0.9981	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1240	
R indices (all data)	R1 = 0.0548, wR2 = 0.1304	
Largest diff. peak and hole	0.40 and -0.65 $e.Å^{-3}$	

Table S124 Crystal data and structure refinement for **185**, BnCyclohexCycloisom.

Identification code	017eaa17	
Empirical formula	C31 H34 N2 O4 S2	
Formula weight	562.75	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.9043(1) Å	α= 90°.
	b = 18.9435(2) Å	β= 91.5660(14)°.
	c = 14.9900(2) Å	γ = 90°.
Volume	2811.41(6) $Å^3$	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	2.036 mm^{-1}	
F(000)	1192	
Crystal size	0.40 x 0.29 x 0.16 mm^3	
Theta range for data collection	3.761 to 76.242°.	
Index ranges	-12<=h<=12, -17<=k<=23, -18<=l<=18	
Reflections collected	29295	
Independent reflections	5858 [R(int) = 0.0202]	
Completeness to theta = 74.717°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.72 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5857 / 243 / 404	
Goodness-of-fit on F^2	1.0007	
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0918	
R indices (all data)	R1 = 0.0374, wR2 = 0.0929	
Largest diff. peak and hole	0.44 and -0.36 $e.Å^{-3}$	

Table S125 Crystal data and structure refinement for **186**, BnHex4Cycloisom.

Identification code	044ea17	
Empirical formula	C29 H32 N2 O4 S2	
Formula weight	536.72	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.8117(2) Å	α= 73.376(2)°.
	b = 15.4377(4) Å	β= 89.763(2)°.
	c = 19.4068(4) Å	γ = 83.139(2)°.
Volume	2795.12(11) $Å^3$	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	2.022 mm^{-1}	
F(000)	1136	
Crystal size	0.20 x 0.13 x 0.07 mm^3	
Theta range for data collection	4.342 to 76.576°.	
Index ranges	-12<=h<=12, -19<=k<=19, -24<=l<=24	
Reflections collected	54031	
Independent reflections	11627 [R(int) = 0.0382]	
Completeness to theta = 74.279°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11626 / 1084 / 687	
Goodness-of-fit on F^2	0.9961	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0964	
R indices (all data)	R1 = 0.0441, wR2 = 0.1038	
Largest diff. peak and hole	0.34 and -0.41 $e.Å^{-3}$	

Table S126 Crystal data and structure refinement for **187**, BnCyclopropylCycloisom.

Identification code	069eaa17	
Empirical formula	C36.403 H37.806 N2 O4.50 S2	
Formula weight	639.48	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.2447(5) Å	α= 100.937(4)°.
	b = 12.6448(7) Å	β= 90.153(3)°.
	c = 14.1463(5) Å	γ = 110.185(5)°.
Volume	1684.13(15) $Å^3$	
Z	2	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	1.776 mm^{-1}	
F(000)	676.444	
Crystal size	0.21 x 0.17 x 0.09 mm^3	
Theta range for data collection	3.804 to 76.220°.	
Index ranges	-11<=h<=12, -15<=k<=15, -17<=l<=17	
Reflections collected	25895	
Independent reflections	6948 [R(int) = 0.0315]	
Completeness to theta = 73.933°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6947 / 7 / 456	
Goodness-of-fit on F^2	1.0021	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0972	
R indices (all data)	R1 = 0.0469, wR2 = 0.1046	
Largest diff. peak and hole	0.42 and -0.40 $e.Å^{-3}$	

Table S127 Crystal data and structure refinement for **188**, BnHallCycloisomDA-NPh.

Identification code	079eaa17	
Empirical formula	C37 H35 N3 O6 S2	
Formula weight	681.83	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.2943(1) Å	α= 76.5385(10)°.
	b = 26.7377(4) Å	β= 82.2339(8)°.
	c = 42.1538(5) Å	γ = 85.2381(9)°.
Volume	13333.4(3) $Å^3$	
Z	16	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	1.876 mm^{-1}	
F(000)	5728	
Crystal size	0.21 x 0.20 x 0.09 mm^3	
Theta range for data collection	3.604 to 76.910°.	
Index ranges	-15<=h<=13, -33<=k<=33, -53<=l<=52	
Reflections collected	251625	
Independent reflections	54950 [R(int) = 0.0577]	
Completeness to theta = 69.043°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.73	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	54734 / 978 / 3640	
Goodness-of-fit on F^2	1.0073	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1374	
R indices (all data)	R1 = 0.0620, wR2 = 0.1462	
Largest diff. peak and hole	1.34 and -1.43 $e.Å^{-3}$	

Table S128 Crystal data and structure refinement for **189**, BnHallCycloisomDA-DMAD.

Identification code	005eaa16b	
Empirical formula	C33 H34 N2 O8 S2	
Formula weight	650.77	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.3209(3) Å	α= 90°.
	b = 24.6386(5) Å	β= 111.167(3)°.
	c = 13.3435(3) Å	γ = 90°.
Volume	3164.22(7) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	1.986 mm^{-1}	
F(000)	1368	
Crystal size	0.23 x 0.21 x 0.20 mm^3	
Theta range for data collection	3.588 to 76.358°.	
Index ranges	-11<=h<=12, -30<=k<=30, -15<=l<=16	
Reflections collected	33543	
Independent reflections	6570 [R(int) = 0.0273]	
Completeness to theta = 74.831°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.67 and 0.62	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6565 / 0 / 406	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0839	
R indices (all data)	R1 = 0.0333, wR2 = 0.0852	
Largest diff. peak and hole	0.25 and -0.37 $e.Å^{-3}$	

Table S129 Crystal data and structure refinement for **191**, BnHallCycloisomDA-CHO.

Identification code	016eaa16	
Empirical formula	C34 H33 Br1 N2 O5 S2	
Formula weight	693.68	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.6807(3) Å	α= 90°.
	b = 9.8903(1) Å	β= 93.8761(15)°.
	c = 19.2705(3) Å	γ = 90°.
Volume	3171.92(5) $Å^3$	
Z	4	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	3.365 mm^{-1}	
F(000)	1432	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	4.600 to 76.507°.	
Index ranges	-20<=h<=20, -12<=k<=12, -23<=l<=24	
Reflections collected	77844	
Independent reflections	6653 [R(int) = 0.0403]	
Completeness to theta = 76.507°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.48	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6648 / 0 / 397	
Goodness-of-fit on F^2	0.9888	
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0728	
R indices (all data)	R1 = 0.0294, wR2 = 0.0750	
Largest diff. peak and hole	0.45 and -0.59 $e.Å^{-3}$	

Table S130 Crystal data and structure refinement for **192'**, BnHallCycloisomDNP.

Identification code	074eaa17	
Empirical formula	C19 H19 N5 O6 S1	
Formula weight	445.46	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6559(4) Å	α= 91.388(4)°.
	b = 9.3431(4) Å	β= 99.157(4)°.
	c = 13.8554(8) Å	γ = 94.171(4)°.
Volume	975.21(9) $Å^3$	
Z	2	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	1.924 mm^{-1}	
F(000)	464	
Crystal size	0.34 x 0.13 x 0.06 mm^3	
Theta range for data collection	4.749 to 75.786°.	
Index ranges	-7<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected	9167	
Independent reflections	4019 [R(int) = 0.0165]	
Completeness to theta = 72.754°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.70	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4019 / 0 / 280	
Goodness-of-fit on F^2	1.0007	
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0927	
R indices (all data)	R1 = 0.0367, wR2 = 0.0959	
Largest diff. peak and hole	0.28 and -0.37 $e.Å^{-3}$	

Table S131 Crystal data and structure refinement for **193**, Dihydrofuran.

Identification code	002eaa17b	
Empirical formula	C27 H28 N2 O5 S2	
Formula weight	524.66	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.9227(4) Å	α= 90°.
	b = 7.5283(1) Å	β= 90.023(2)°.
	c = 17.0066(4) Å	γ = 90°.
Volume	2550.72(9) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	2.235 mm^{-1}	
F(000)	1104	
Crystal size	0.20 x 0.13 x 0.13 mm^3	
Theta range for data collection	4.439 to 76.289°.	
Index ranges	-24<=h<=25, 0<=k<=9, 0<=l<=21	
Reflections collected	58503	
Independent reflections	5346 [R(int) = 0.0361]	
Completeness to theta = 76.289°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5327 / 2492 / 650	
Goodness-of-fit on F^2	0.9986	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1010	
R indices (all data)	R1 = 0.0453, wR2 = 0.1062	
Largest diff. peak and hole	0.22 and -0.19 e.$Å^{-3}$	

Table S132 Crystal data and structure refinement for **195**, Sugar.

Identification code	014eaa17b	
Empirical formula	C27 H32 N2 O7 S2	
Formula weight	560.69	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 20.2144(10) Å	α= 90°.
	b = 5.9150(3) Å	β= 108.569(6)°.
	c = 23.6559(13) Å	γ = 90°.
Volume	2681.2(3) $Å^3$	
Z	4	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	2.217 mm^{-1}	
F(000)	1184	
Crystal size	0.36 x 0.09 x 0.04 mm^3	
Theta range for data collection	3.943 to 76.260°.	
Index ranges	-25<=h<=25, -7<=k<=7, -29<=l<=28	
Reflections collected	15183	
Independent reflections	5568 [R(int) = 0.0360]	
Completeness to theta = 73.973°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.63	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5565 / 256 / 452	
Goodness-of-fit on F^2	1.0102	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1039	
R indices (all data)	R1 = 0.0544, wR2 = 0.1174	
Largest diff. peak and hole	0.49 and -0.55 $e.Å^{-3}$	

Table S133 Crystal data and structure refinement for (-)-**197**, [5+2].

Identification code	013eaa16	
Empirical formula	C36 H36 N2 O4 S2	
Formula weight	624.82	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 11.4886(2) Å	α= 90°.
	b = 15.5789(3) Å	β= 90°.
	c = 17.4504(3) Å	γ = 90°.
Volume	3123.26(9) $Å^3$	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	1.891 mm^{-1}	
F(000)	1320	
Crystal size	0.21 x 0.17 x 0.16 mm^3	
Theta range for data collection	3.804 to 76.292°.	
Index ranges	-14<=h<=14, -19<=k<=19, -16<=l<=21	
Reflections collected	39016	
Independent reflections	6507 [R(int) = 0.0524]	
Completeness to theta = 76.292°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.74 and 0.62	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6504 / 0 / 398	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0989	
R indices (all data)	R1 = 0.0396, wR2 = 0.1001	
Largest diff. peak and hole	0.18 and -0.33 $e.Å^{-3}$	
Absolute structure parameter (Flack)	-0.018(11) for 2853 Friedel pairs	
Absolute structure parameter (Hooft)	-0.011(4) for 2836 Friedel pairs	
Hooft probability analysis	P2(correct) > 99.9999%, P3 > 99.9999%	

Table S134 Crystal data and structure refinement for **198**, 2+2+2-Me.

Identification code	043eaa17	
Empirical formula	C26 H28 N2 O4 S2	
Formula weight	496.65	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.9371(4) Å	α= 90°.
	b = 12.0939(6) Å	β= 101.247(5)°.
	c = 20.5059(12) Å	γ = 90°.
Volume	2417.0(2) $Å^3$	
Z	4	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	2.293 mm^{-1}	
F(000)	1048	
Crystal size	0.29 x 0.19 x 0.01 mm^3	
Theta range for data collection	4.266 to 76.412°.	
Index ranges	-8<=h<=12, -14<=k<=15, -25<=l<=25	
Reflections collected	14020	
Independent reflections	5003 [R(int) = 0.0566]	
Completeness to theta = 74.120°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5003 / 0 / 307	
Goodness-of-fit on F^2	0.9971	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.0951	
R indices (all data)	R1 = 0.0668, wR2 = 0.1132	
Largest diff. peak and hole	0.50 and -0.52 $e.Å^{-3}$	

Table S135 Crystal data and structure refinement for **199**, 2+2+2-Ph.

Identification code	008eaa16	
Empirical formula	C31 H30 N2 O4 S2	
Formula weight	558.72	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.9202(2) Å	α= 90°.
	b = 10.9579(1) Å	β= 96.9937(6)°.
	c = 21.2577(3) Å	γ = 90°.
Volume	2756.03(7) $Å^3$	
Z	4	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	1176	
Crystal size	0.42 x 0.20 x 0.18 mm^3	
Theta range for data collection	3.056 to 27.504°.	
Index ranges	-15<=h<=15, -14<=k<=14, -27<=l<=27	
Reflections collected	60031	
Independent reflections	6315 [R(int) = 0.0289]	
Completeness to theta = 27.504°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.79	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6312 / 0 / 352	
Goodness-of-fit on F^2	0.9990	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1101	
R indices (all data)	R1 = 0.0683, wR2 = 0.1244	
Largest diff. peak and hole	0.64 and -0.80 $e.Å^{-3}$	

Table S136 Crystal data and structure refinement for **200**, GII-dipyrrole.

Identification code	076eaa17	
Empirical formula	C22 H24 N2 O4 S2	
Formula weight	444.58	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.4746(5) Å	α= 109.277(5)°.
	b = 12.1669(7) Å	β= 93.660(5)°.
	c = 12.8783(8) Å	γ = 100.828(5)°.
Volume	1075.79(12) $Å^3$	
Z	2	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	2.509 mm^{-1}	
F(000)	468	
Crystal size	0.24 x 0.10 x 0.02 mm^3	
Theta range for data collection	3.947 to 76.378°.	
Index ranges	-9<=h<=8, -12<=k<=15, -16<=l<=13	
Reflections collected	9488	
Independent reflections	4443 [R(int) = 0.0372]	
Completeness to theta = 74.087°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4442 / 0 / 271	
Goodness-of-fit on F^2	1.0068	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1020	
R indices (all data)	R1 = 0.0469, wR2 = 0.1097	
Largest diff. peak and hole	0.42 and -0.38 $e.Å^{-3}$	

Table S137 Crystal data and structure refinement for **203**, GII-endiamide.

Identification code	077eaa17	
Empirical formula	C24 H29 Cl1 N2 O4 S2	
Formula weight	509.09	
Temperature	295 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.0219(4) Å	α= 66.631(3)°.
	b = 14.2450(4) Å	β= 76.818(3)°.
	c = 14.6706(5) Å	γ = 85.344(2)°.
Volume	2618.94(15) $Å^3$	
Z	4	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	3.042 mm^{-1}	
F(000)	1072	
Crystal size	0.25 x 0.18 x 0.10 mm^3	
Theta range for data collection	3.380 to 76.612°.	
Index ranges	-15<=h<=17, -17<=k<=15, -18<=l<=18	
Reflections collected	26203	
Independent reflections	10843 [R(int) = 0.0255]	
Completeness to theta = 74.314°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.74 and 0.58	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10838 / 163 / 646	
Goodness-of-fit on F^2	1.0068	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1112	
R indices (all data)	R1 = 0.0502, wR2 = 0.1208	
Largest diff. peak and hole	0.46 and -0.40 $e.Å^{-3}$	

Table S138 Crystal data and structure refinement for **205**, PK.

Identification code	009eaa17	
Empirical formula	C28 H28 N2 O5 S2	
Formula weight	536.67	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 10.9365(7) Å	α= 90°.
	b = 20.4503(13) Å	β= 90°.
	c = 11.9294(8) Å	γ = 90°.
Volume	2668.1(3) $Å^3$	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	1128	
Crystal size	0.10 x 0.06 x 0.05 mm^3	
Theta range for data collection	1.916 to 29.623°.	
Index ranges	-15<=h<=15, -29<=k<=29, -17<=l<=17	
Reflections collected	40585	
Independent reflections	8176 [R(int) = 0.0879]	
Completeness to theta = 29.030°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.57	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5510 / 229 / 417	
Goodness-of-fit on F^2	1.0081	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1148	
R indices (all data)	R1 = 0.0488, wR2 = 0.1175	
Largest diff. peak and hole	0.31 and -0.27 $e.Å^{-3}$	
Absolute structure parameter (Flack)	-0.13(7)	

Table S139 Crystal data and structure refinement for **206**, Cyclobutene.

Identification code	DIA0274	
Empirical formula	C27 H28 N2 O4 S2	
Formula weight	508.66	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.9219(3) Å	α= 90°.
	b = 18.5816(5) Å	β= 99.437(3)°.
	c = 25.5671(9) Å	γ = 90°.
Volume	5118.5(3) $Å^3$	
Z	8	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	2144	
Crystal size	0.04 x 0.03 x 0.02 mm^3	
Theta range for data collection	1.871 to 36.412°.	
Index ranges	-18<=h<=18, -30<=k<=31, -43<=l<=43	
Reflections collected	82068	
Independent reflections	25377 [R(int) = 0.1286]	
Completeness to theta = 25.124°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.17	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25337 / 1904 / 852	
Goodness-of-fit on F^2	1.0000	
Final R indices [I>2sigma(I)]	R1 = 0.1078, wR2 = 0.1800	
R indices (all data)	R1 = 0.1748, wR2 = 0.2308	
Largest diff. peak and hole	1.24 and -1.20 $e.Å^{-3}$	

Table S140 Crystal data and structure refinement for **218**, BnYndHydrate.

Identification code	055eaa17	
Empirical formula	C30 H30 N2 O5 S2	
Formula weight	562.71	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 8.7988(2) Å	α= 90°.
	b = 20.7935(6) Å	β= 90°.
	c = 14.8405(4) Å	γ = 90°.
Volume	2715.19(12) $Å^3$	
Z	4	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	2.139 mm^{-1}	
F(000)	1184	
Crystal size	0.50 x 0.30 x 0.12 mm^3	
Theta range for data collection	4.252 to 76.049°.	
Index ranges	-7<=h<=10, -25<=k<=25, -18<=l<=16	
Reflections collected	12670	
Independent reflections	4942 [R(int) = 0.0252]	
Completeness to theta = 74.528°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77 and 0.39	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4940 / 1 / 353	
Goodness-of-fit on F^2	1.0053	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1079	
R indices (all data)	R1 = 0.0422, wR2 = 0.1134	
Largest diff. peak and hole	0.20 and -0.34 $e.Å^{-3}$	
Absolute structure parameter (Flack)	0.005(14)	

Table S141 Crystal data and structure refinement for **219**, Dihydroisoquinoline.

Identification code	017eaa16	
Empirical formula	C30 H28 N2 O4 S2	
Formula weight	544.70	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.5125(2) Å	α= 90°.
	b = 9.9079(2) Å	β= 90°.
	c = 27.9813(5) Å	γ = 90°.
Volume	2637.21(8) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	2.156 mm^{-1}	
F(000)	1144	
Crystal size	0.25 x 0.20 x 0.08 mm^3	
Theta range for data collection	4.735 to 76.340°.	
Index ranges	-11<=h<=11, -12<=k<=12, -35<=l<=31	
Reflections collected	24793	
Independent reflections	5488 [R(int) = 0.0256]	
Completeness to theta = 74.813°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.84 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5486 / 0 / 344	
Goodness-of-fit on F^2	1.0029	
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0627	
R indices (all data)	R1 = 0.0237, wR2 = 0.0632	
Largest diff. peak and hole	0.21 and -0.24 $e.Å^{-3}$	
Absolute structure parameter (Flack)	0.007(8)	

Table S142 Crystal data and structure refinement for **222**, Pyrrole.

Identification code	034eaa17	
Empirical formula	C28 H26 N2 O5 S2	
Formula weight	534.66	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.0538(1) Å	α= 90°.
	b = 9.9362(1) Å	β= 90.5177(13)°.
	c = 29.7321(4) Å	γ = 90°.
Volume	2674.60(5) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	2.145 mm^{-1}	
F(000)	1120	
Crystal size	0.32 x 0.14 x 0.04 mm^3	
Theta range for data collection	4.692 to 76.273°.	
Index ranges	-11<=h<=11, -12<=k<=12, -36<=l<=37	
Reflections collected	61691	
Independent reflections	5597 [R(int) = 0.045]	
Completeness to theta = 76.273°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.62	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5597 / 70 / 371	
Goodness-of-fit on F^2	1.0017	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.0815	
R indices (all data)	R1 = 0.0583, wR2 = 0.0819	
Largest diff. peak and hole	0.32 and -0.53 $e.Å^{-3}$	

Table S143 Crystal data and structure refinement for **228**, Spiroindolenine.

Identification code	073eaa18	
Empirical formula	C33 H31 N3 O4 S2	
Formula weight	597.76	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 22.8925(2) Å	α= 90°.
	b = 14.70582(13) Å	β= 90.2467(9)°.
	c = 17.12971(19) Å	γ = 90°.
Volume	5766.72(10) $Å^3$	
Z	8	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	2.034 mm^{-1}	
F(000)	2512	
Crystal size	0.43 x 0.11 x 0.06 mm^3	
Theta range for data collection	1.930 to 76.492°.	
Index ranges	-28<=h<=27, -10<=k<=18, -21<=l<=21	
Reflections collected	37791	
Independent reflections	11990 [R(int) = 0.325]	
Completeness to theta = 74.198°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.51	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11939 / 292 / 812	
Goodness-of-fit on F^2	0.9963	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1027	
R indices (all data)	R1 = 0.465, wR2 = 0.1109	
Largest diff. peak and hole	0.47 and -0.63 $e.Å^{-3}$	

Table S144 Crystal data and structure refinement for **229**, Pyrrolidinone.

Identification code	006eaa16	
Empirical formula	C26 H26 N2 O5 S2	
Formula weight	510.63	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.1922(2) Å	α= 90°.
	b = 10.2198(2) Å	β= 105.9816(8)°.
	c = 17.7600(3) Å	γ = 90°.
Volume	2476.38(7) $Å^3$	
Z	4	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	0.255 mm^{-1}	
F(000)	1072	
Crystal size	0.41 x 0.18 x 0.15 mm^3	
Theta range for data collection	1.493 to 27.500°.	
Index ranges	-18<=h<=18, -13<=k<=12, -23<=l<=22	
Reflections collected	48776	
Independent reflections	5683 [R(int) = 0.0261]	
Completeness to theta = 27.500°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5672 / 0 / 316	
Goodness-of-fit on F^2	0.9941	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.0981	
R indices (all data)	R1 = 0.0635, wR2 = 0.1112	
Largest diff. peak and hole	0.37 and -0.52 $e.Å^{-3}$	

Table S145 Crystal data and structure refinement for **231**, CyTsYndBzOH-adduct.

Identification code	018eaa18	
Empirical formula	C36 H37 I1 N2 O6 S2	
Formula weight	784.74	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.8872(4) Å	α= 77.728(3)°.
	b = 11.0195(5) Å	β= 84.814(3)°.
	c = 16.5916(6) Å	γ = 62.766(4)°.
Volume	1729.36(14) $Å^3$	
Z	2	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	8.798 mm^{-1}	
F(000)	800	
Crystal size	0.16 x 0.09 x 0.07 mm^3	
Theta range for data collection	4.568 to 76.250°.	
Index ranges	-13<=h<=9, -13<=k<=13, -20<=l<=19	
Reflections collected	19593	
Independent reflections	7138 [R(int) = 0.0290]	
Completeness to theta = 73.962°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.54 and 0.46	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7134 / 0 / 424	
Goodness-of-fit on F^2	0.9987	
Final R indices [I>2sigma(I)]	R1 = 0.0265, wR2 = 0.0667	
R indices (all data)	R1 = 0.0284, wR2 = 0.0686	
Largest diff. peak and hole	0.55 and -0.73 $e.Å^{-3}$	

Table S146 Crystal data and structure refinement for **232a**, BnPsYndBzOH-adduct.

Identification code	086eaa17	
Empirical formula	C35 H36 I1 N2 O7 P1 S1	
Formula weight	786.62	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 1 a 1	
Unit cell dimensions	a = 11.6448(2) Å	α= 90°.
	b = 16.6761(3) Å	β= 90.4861(17)°.
	c = 18.0003(4) Å	γ = 90°.
Volume	3495.35(12) $Å^3$	
Z	4	
Density (calculated)	1.495 Mg/m^3	
Absorption coefficient	8.605 mm^{-1}	
F(000)	1600	
Crystal size	0.21 x 0.07 x 0.07 mm^3	
Theta range for data collection	3.613 to 76.375°.	
Index ranges	-12<=h<=14, 0<=k<=20, -22<=l<=22	
Reflections collected	28661	
Independent reflections	6543 [R(int) = 0.0428]	
Completeness to theta = 74.848°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.55 and 0.30	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6514 / 2 / 425	
Goodness-of-fit on F^2	1.0025	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0671	
R indices (all data)	R1 = 0.0257, wR2 = 0.0674	
Largest diff. peak and hole	0.41 and -0.33 $e.Å^{-3}$	
Absolute structure parameter	0.308(3)	

2.3 Physical and Spectroscopic Properties of Ynamides and Yndiamides.

Table S147 Crystal data and structure refinement for Ph*o*-CyTsYnMe.

Identification code	001eaa17	
Empirical formula	C22 H23 N1 O2 S1	
Formula weight	365.50	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.6252(13) Å	α= 90°.
	b = 8.1283(6) Å	β= 114.188(10)°.
	c = 16.1996(14) Å	γ = 90°.
Volume	1876.8(3) $Å^3$	
Z	4	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	1.650 mm^{-1}	
F(000)	776	
Crystal size	0.23 x 0.09 x 0.05 mm^3	
Theta range for data collection	5.500 to 76.753°.	
Index ranges	-19<=h<=19, -9<=k<=10, -20<=l<=19	
Reflections collected	9581	
Independent reflections	3857 [R(int) = 0.044]	
Completeness to theta = 72.915°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.56	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3854 / 138 / 281	
Goodness-of-fit on F^2	0.9915	
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1323	
R indices (all data)	R1 = 0.0815, wR2 = 0.1539	
Largest diff. peak and hole	0.70 and -0.64 e.$Å^{-3}$	

Table S148 Crystal data and structure refinement for BnTsYnH.

Identification code	106eaa18	
Empirical formula	C16 H15 N1 O2 S1	
Formula weight	285.37	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 15.87014(11) Å	α= 90°.
	b = 5.93061(4) Å	β= 90°.
	c = 15.13527(9) Å	γ = 90°.
Volume	1424.527(15) $Å^3$	
Z	4	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	2.022 mm^{-1}	
F(000)	600	
Crystal size	0.26 x 0.19 x 0.14 mm^3	
Theta range for data collection	5.575 to 76.188°.	
Index ranges	-19<=h<=19, -7<=k<=7, -18<=l<=19	
Reflections collected	51903	
Independent reflections	2980 [R(int) = 0.0264]	
Completeness to theta = 76.188°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2969 / 1 / 182	
Goodness-of-fit on F^2	1.0040	
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0613	
R indices (all data)	R1 = 0.0230, wR2 = 0.0620	
Largest diff. peak and hole	0.14 and -0.21 $e.Å^{-3}$	
Absolute structure parameter	-0.002(12)	

Table S149 Crystal data and structure refinement for BnTsYnPh.

Identification code	005eaa17	
Empirical formula	C22 H19 N1 O2 S1	
Formula weight	361.46	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.7543(3) Å	α= 90°.
	b = 6.1763(1) Å	β= 109.3497(17)°.
	c = 15.9972(2) Å	γ = 90°.
Volume	1841.54(2) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	1.681 mm^{-1}	
F(000)	760	
Crystal size	0.20 x 0.18 x 0.08 mm^3	
Theta range for data collection	5.548 to 76.118°.	
Index ranges	-24<=h<=24, -7<=k<=7, -15<=l<=20	
Reflections collected	17346	
Independent reflections	3827 [R(int) = 0.0250]	
Completeness to theta = 74.596°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.75	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3810 / 0 / 235	
Goodness-of-fit on F^2	0.9909	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0849	
R indices (all data)	R1 = 0.0344, wR2 = 0.0871	
Largest diff. peak and hole	0.37 and -0.35 $e.Å^{-3}$	

Table S150 Crystal data and structure refinement for BnNsYnPh.

Identification code	038eaa17	
Empirical formula	C21 H16 N2 O4 S1	
Formula weight	392.43	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.7322(5) Å	α= 90°.
	b = 6.8506(1) Å	β= 90.608(2)°.
	c = 13.1415(3) Å	γ = 90°.
Volume	1866.36(7) $Å^3$	
Z	4	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	1.807 mm^{-1}	
F(000)	816	
Crystal size	0.35 x 0.32 x 0.06 mm^3	
Theta range for data collection	6.405 to 76.153°.	
Index ranges	-26<=h<=25, -6<=k<=8, -13<=l<=16	
Reflections collected	17591	
Independent reflections	3883 [R(int) = 0.0253]	
Completeness to theta = 74.630°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.69	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3882 / 0 / 253	
Goodness-of-fit on F^2	1.0010	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0870	
R indices (all data)	R1 = 0.0353, wR2 = 0.0912	
Largest diff. peak and hole	0.28 and -0.38 $e.Å^{-3}$	

Table S151 Crystal data and structure refinement for $BnTsYnSPhNO_2$.

Identification code	008eaa17	
Empirical formula	C22 H18 N2 O4 S1	
Formula weight	438.53	
Temperature	100 K	
Wavelength	0.68890 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.9529(7) Å	α= 85.750(4)°.
	b = 8.1722(4) Å	β= 83.644(7)°.
	c = 18.8754(8) Å	γ = 78.493(7)°.
Volume	1043.00(13) $Å^3$	
Z	2	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	0.287 mm^{-1}	
F(000)	456	
Crystal size	0.040 x 0.025 x 0.015 mm^3	
Theta range for data collection	2.108 to 26.376°.	
Index ranges	-8<=h<=8, -10<=k<=10, -24<=l<=24	
Reflections collected	11311	
Independent reflections	4486 [R(int) = 0.0543]	
Completeness to theta = 25.057°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.19	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4486 / 0 / 271	
Goodness-of-fit on F^2	0.9988	
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.2059	
R indices (all data)	R1 = 0.0738, wR2 = 0.2143	
Largest diff. peak and hole	0.76 and -0.50 $e.Å^{-3}$	

Table S152 Crystal data and structure refinement for IndoleTsYnPh.

Identification code	071eaa18	
Empirical formula	C25 H22 N2 O2 S1	
Formula weight	414.53	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.90521(9) Å	α= 90°.
	b = 10.26460(9) Å	β= 94.0451(8)°.
	c = 18.34822(17) Å	γ = 90°.
Volume	2048.74(3) $Å^3$	
Z	4	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	1.598 mm^{-1}	
F(000)	872	
Crystal size	0.37 x 0.13 x 0.07 mm^3	
Theta range for data collection	4.064 to 76.109°.	
Index ranges	-13<=h<=13, -12<=k<=12, -22<=l<=22	
Reflections collected	31752	
Independent reflections	4255 [R(int) = 0.0369]	
Completeness to theta = 74.587°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.89 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4239 / 0 / 271	
Goodness-of-fit on F^2	1.0001	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0860	
R indices (all data)	R1 = 0.0356, wR2 = 0.0884	
Largest diff. peak and hole	0.30 and -0.38 $e.Å^{-3}$	

Table S153 Crystal data and structure refinement for PhTsYnYnPhTs.

Identification code	024eaa18	
Empirical formula	C30 H24 N2 O4 S2	
Formula weight	540.66	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 14.2573(12) Å	α= 90°.
	b = 7.0276(5) Å	β= 99.054(8)°.
	c = 26.496(2) Å	γ = 90°.
Volume	2621.7(4) $Å^3$	
Z	4	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	2.169 mm^{-1}	
F(000)	1128	
Crystal size	0.10 x 0.04 x 0.02 mm^3	
Theta range for data collection	6.287 to 76.939°.	
Index ranges	-17<=h<=16, -8<=k<=8, -20<=l<=33	
Reflections collected	10057	
Independent reflections	2710 [R(int) = 0.0398]	
Completeness to theta = 73.861°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.88	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2709 / 0 / 172	
Goodness-of-fit on F^2	0.9956	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1353	
R indices (all data)	R1 = 0.0593, wR2 = 0.1453	
Largest diff. peak and hole	0.29 and -0.80 $e.Å^{-3}$	

3 Displacement Ellipsoid Plots.

3.1 Synthesis of Ynamides from 1,2-Dichloroenamides.

3.1a *Ynamides*.

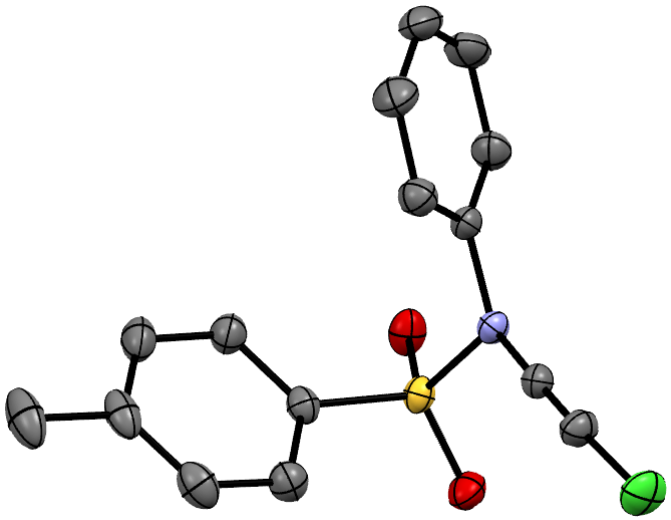

Figure S1: Solid state structure of **56a**, PhTsYnCl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

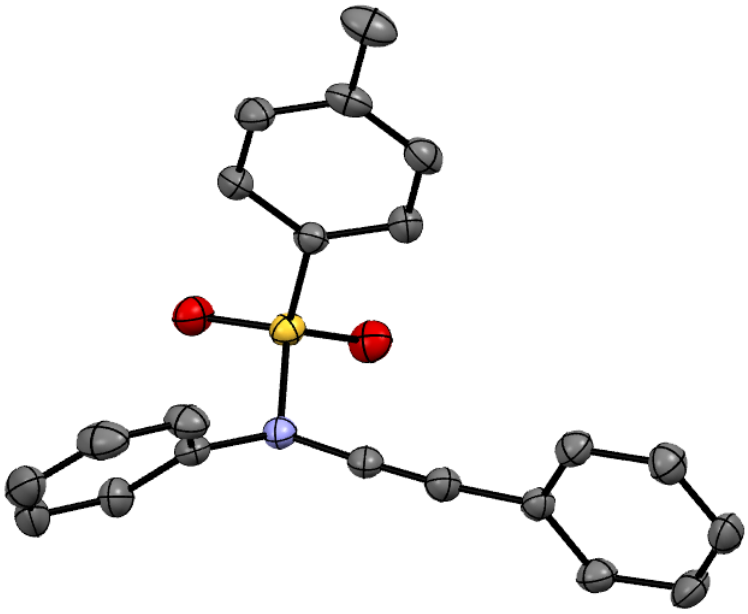

Figure S2: Solid state structure of **60a**, PhTsYnPh(P1). Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

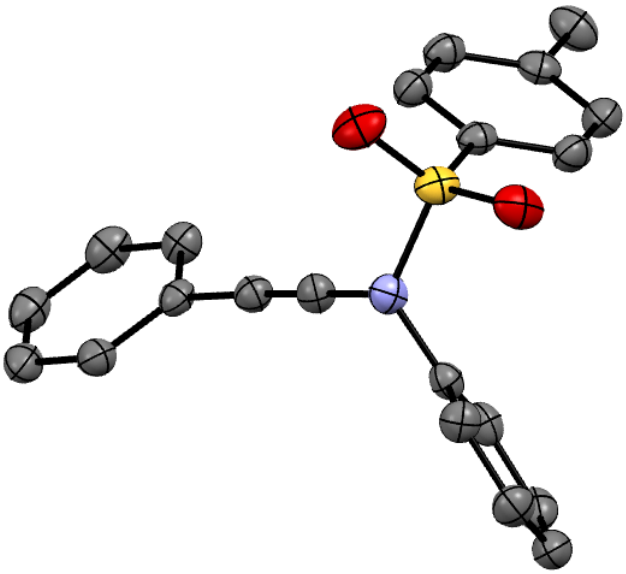

Figure S3: Solid state structure of **60a**, PhTsYnPh(P2). Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

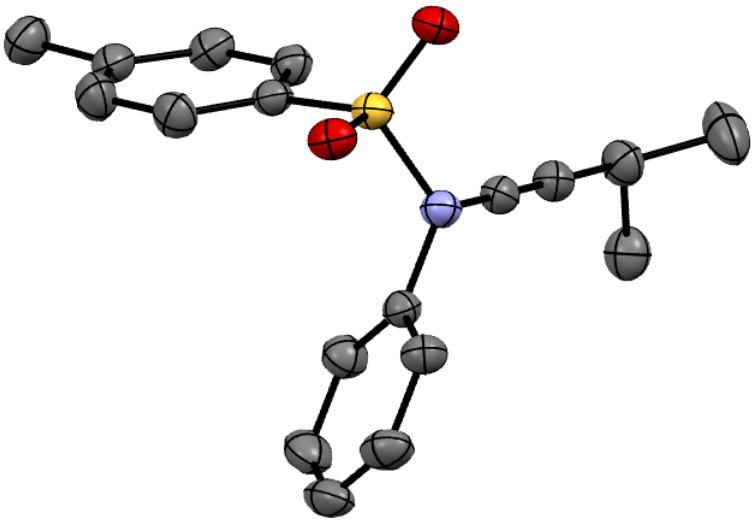

Figure S4: Solid state structure of **60b**, PhTsYn*i*-Pr. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

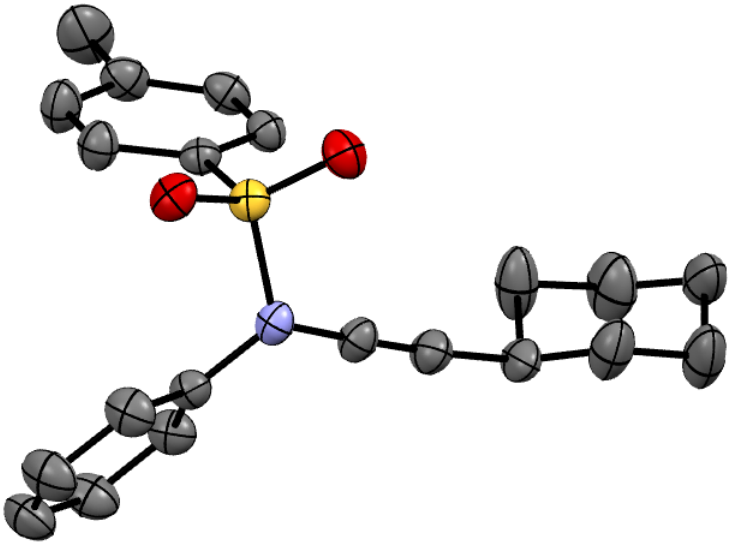

Figure S5: Solid state structure of **60c**, PhTsYnCy. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

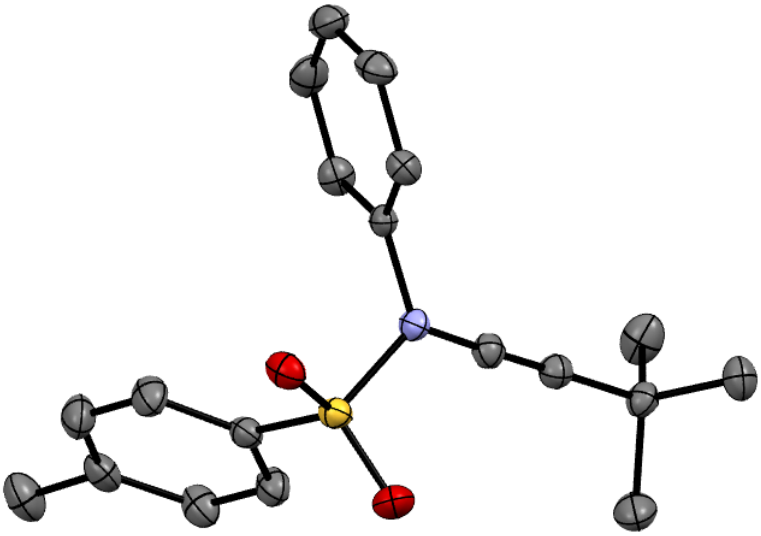

Figure S6: Solid state structure of **60d**, PhTsYn*t*-Bu. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

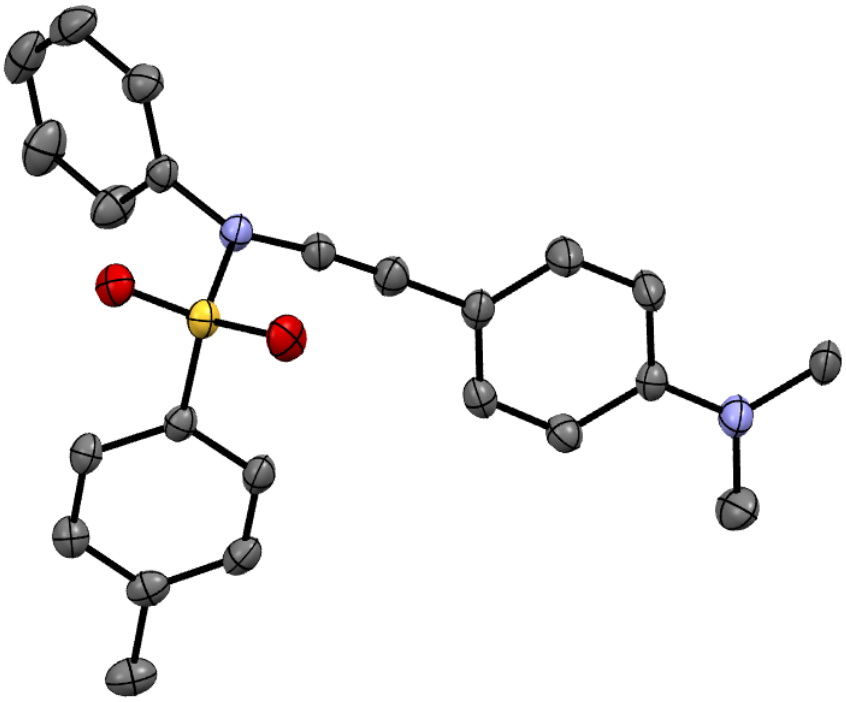

Figure S7: Solid state structure of **60e**, PhTsYnPh*p*-NMe_2. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

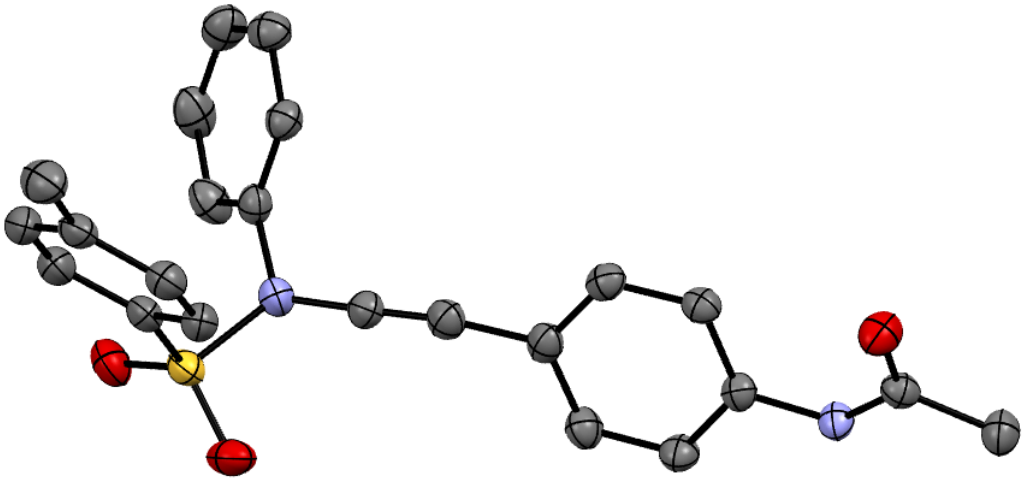

Figure S8: Solid state structure of **60f**, PhTsYnPh*p*-NHAc. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

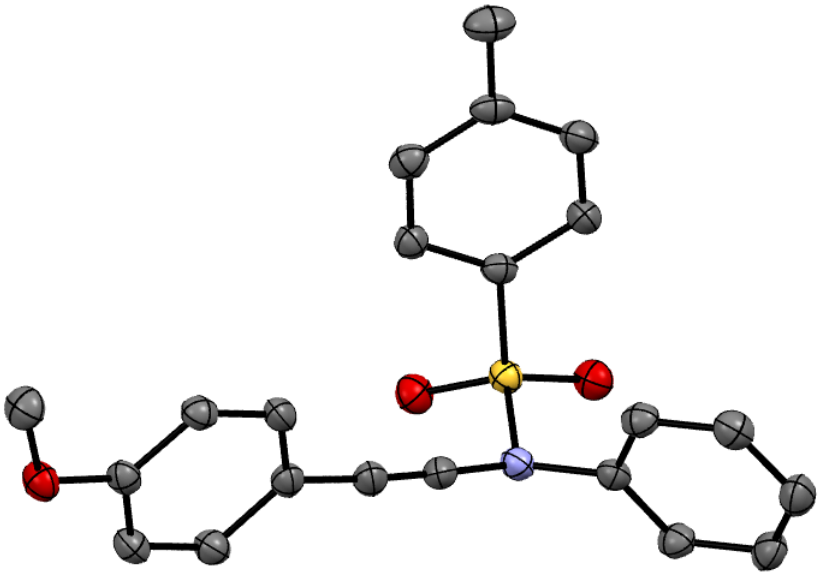

Figure S9: Solid state structure of **60g**, PhTsYnPh*p*-OMe. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

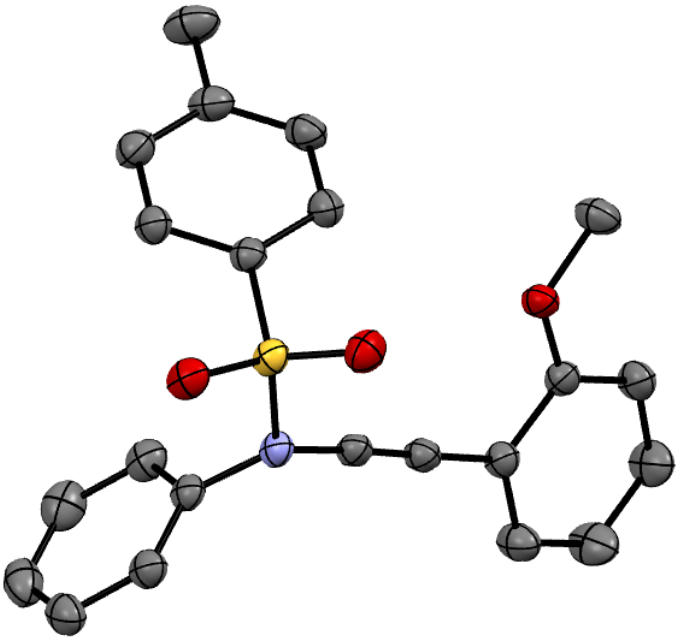

Figure S10: Solid state structure of **60h**, PhTsYnPh*o*-OMe. Displacement ellipsoid plots are drawn at 50% probability. Co-crystallised solvent and hydrogen atoms have been omitted for clarity.

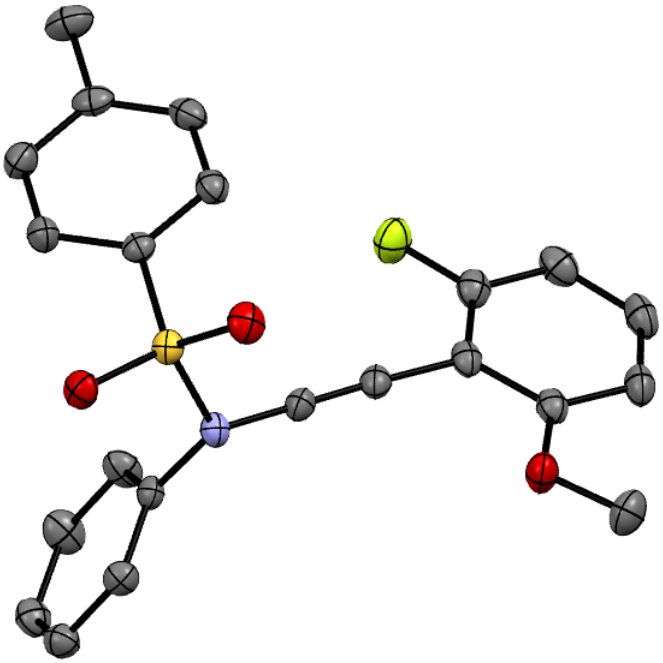

Figure S11: Solid state structure of **60i**, PhTsYnPh*o*-F,OMe. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

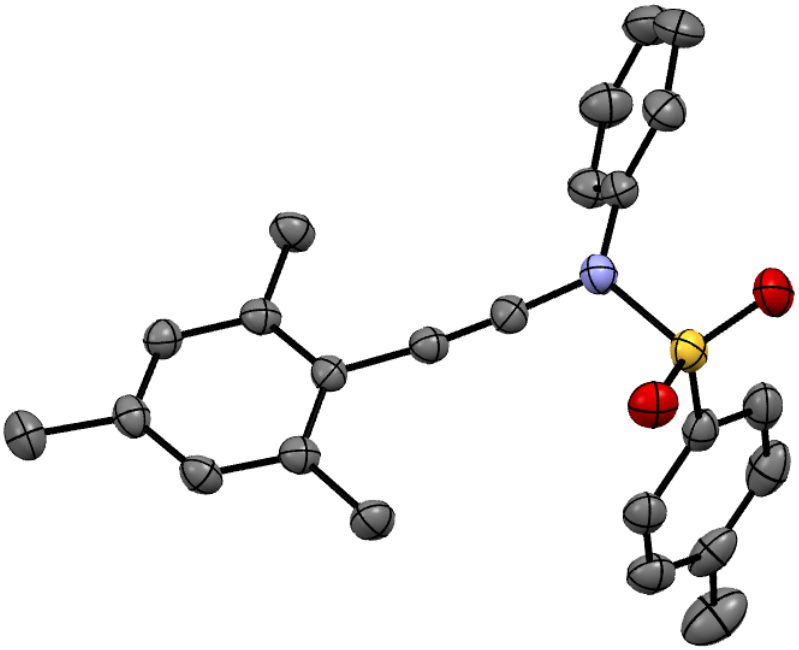

Figure S12: Solid state structure of **60j**, PhTsYnMes. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

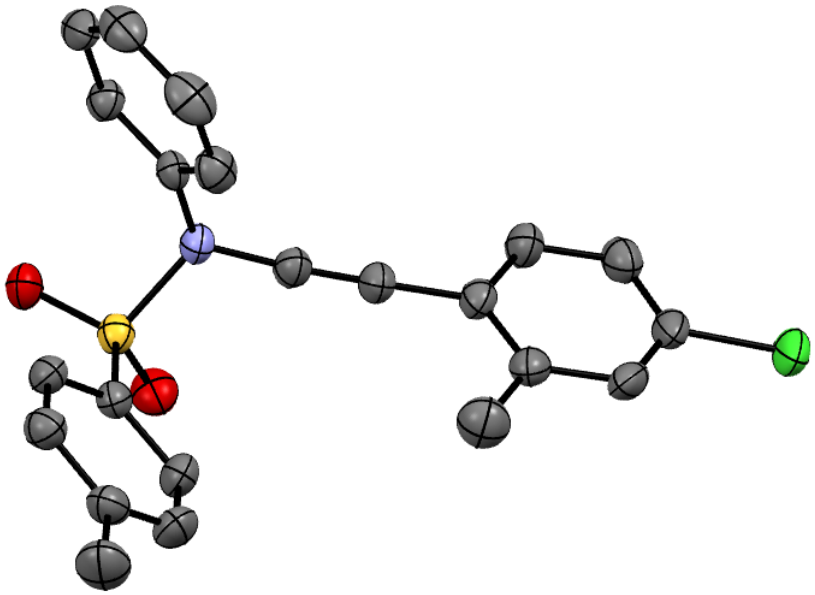

Figure S13: Solid state structure of **60k**, PhTsYnPh*o*-Me,*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

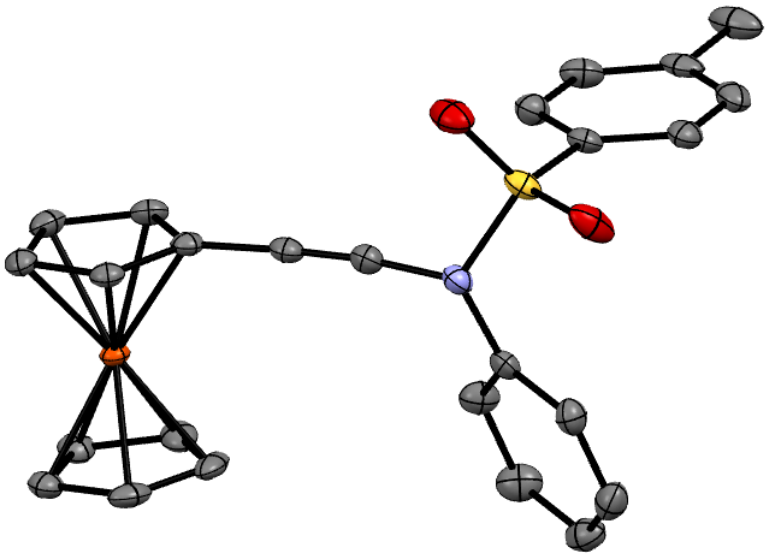

Figure S14: Solid state structure of **60l**, PhTsYnFc. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

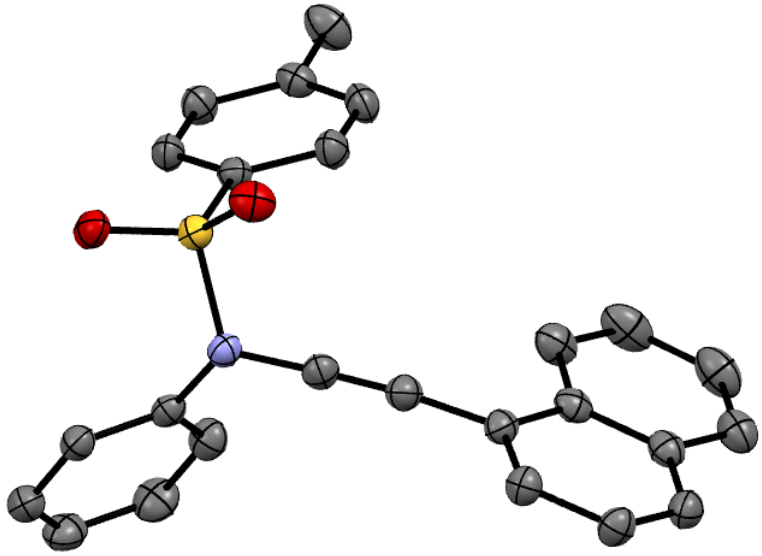

Figure S15: Solid state structure of **60m**, PhTsYn1-Np. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

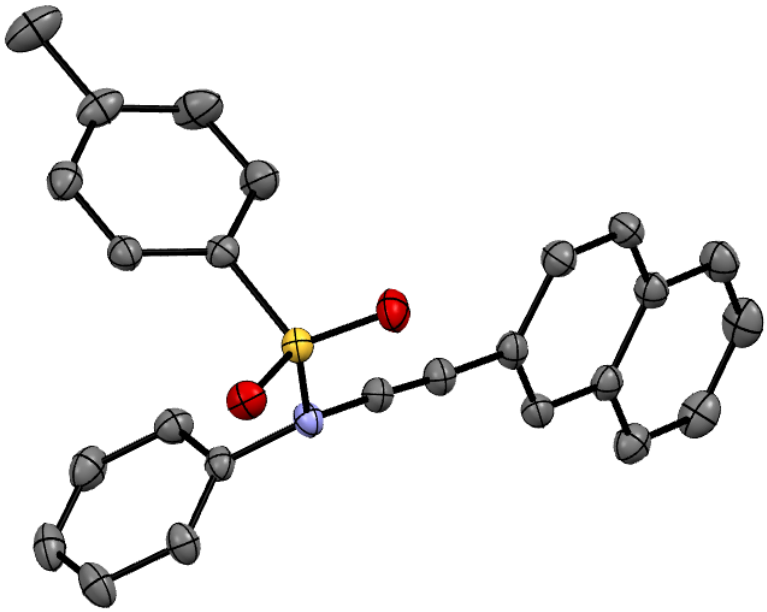

Figure S16: Solid state structure of **60n**, PhTsYn2-Np. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

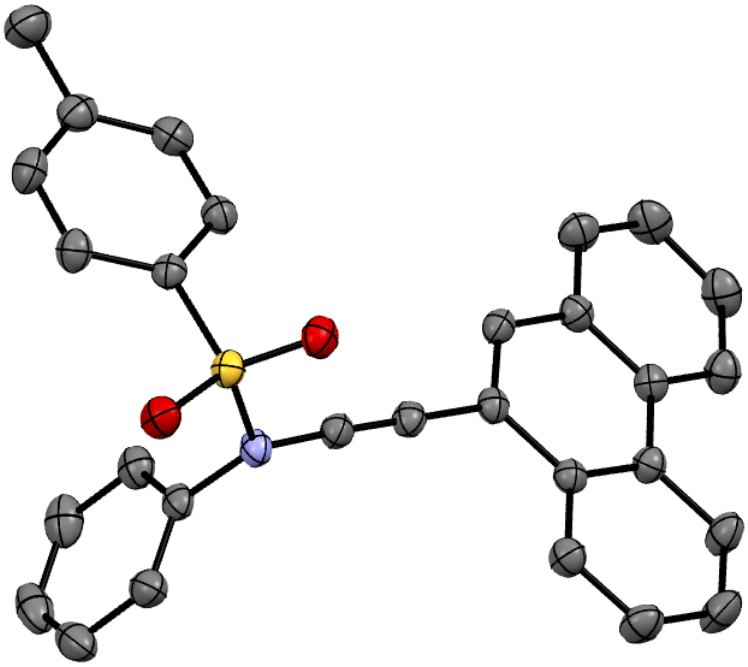

Figure S17: Solid state structure of **60o**, PhTsYnPhen. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

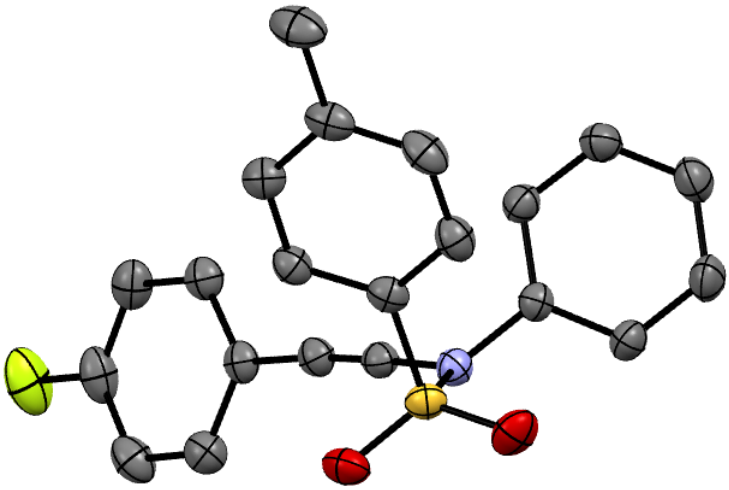

Figure S18: Solid state structure of **60p**, PhTsYnPh*p*-F. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

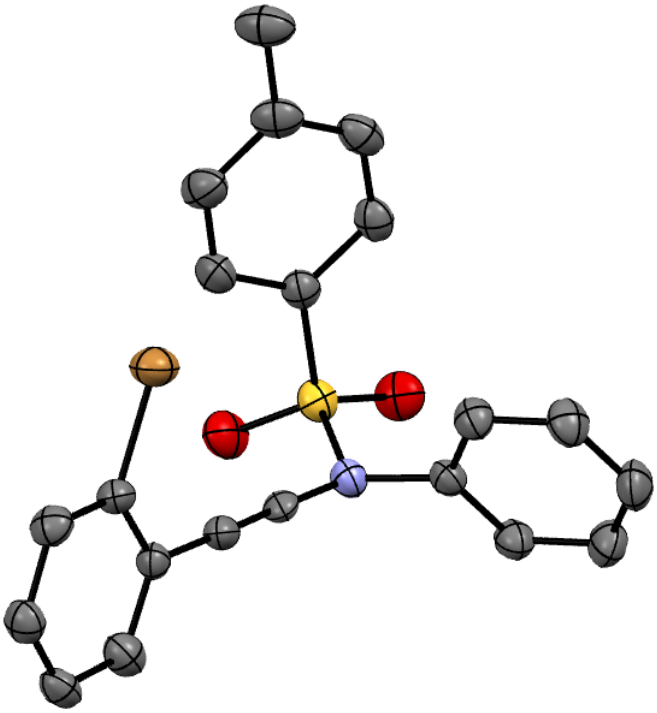

Figure S19: Solid state structure of **60q**, PhTsYnPh*o*-Br. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

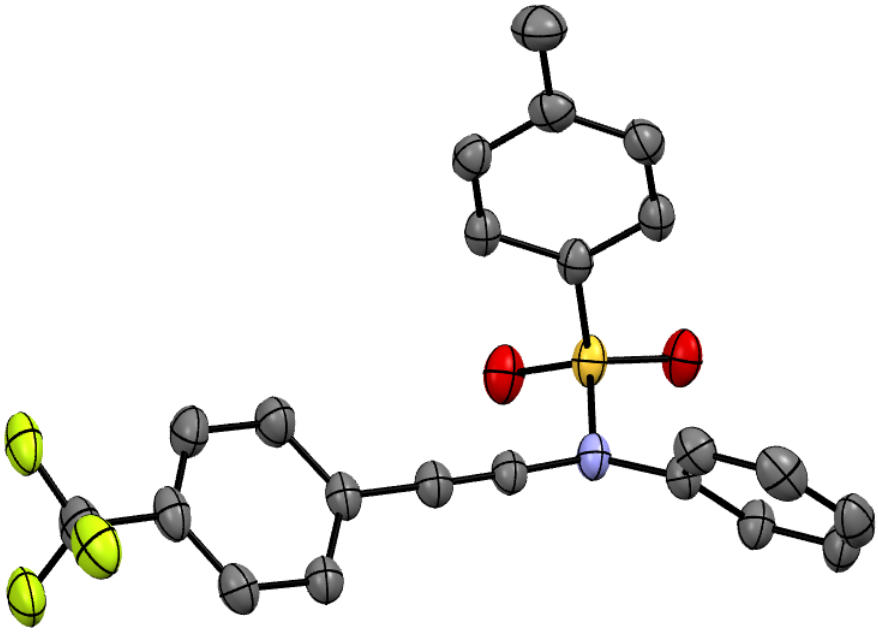

Figure S20: Solid state structure of **60r**, PhTsYnPh*p*-CF_3. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

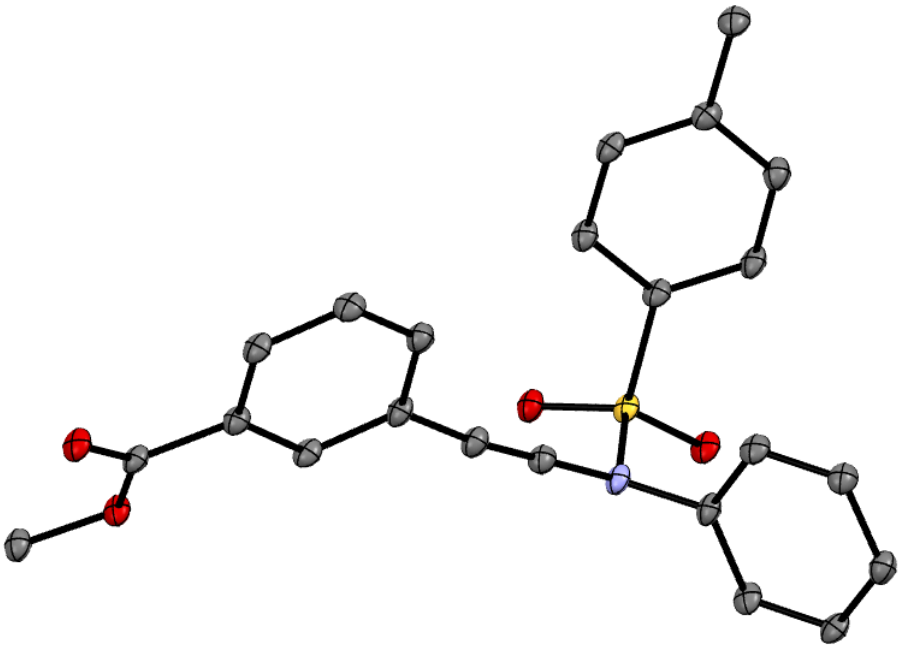

Figure S21: Solid state structure of **60s**, PhTsYnPh*m*-CO_2Me. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

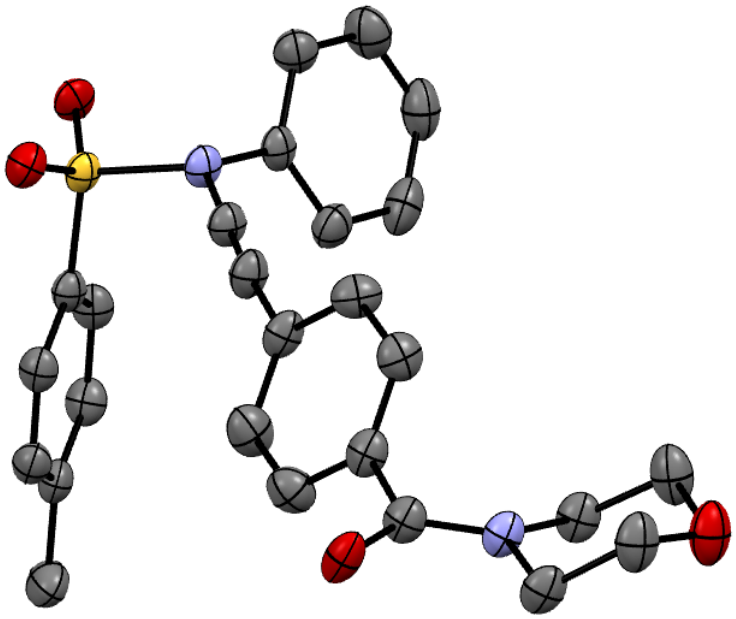

Figure S22: Solid state structure of **60t**, PhTsYnPh*p*-amide. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

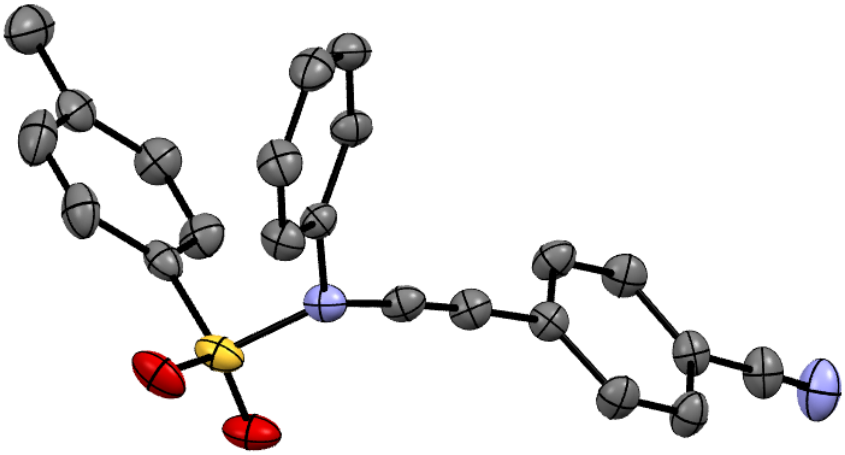

Figure S23: Solid state structure of **60u**, PhTsYnPh*p*-CN. Displacement ellipsoid plots are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

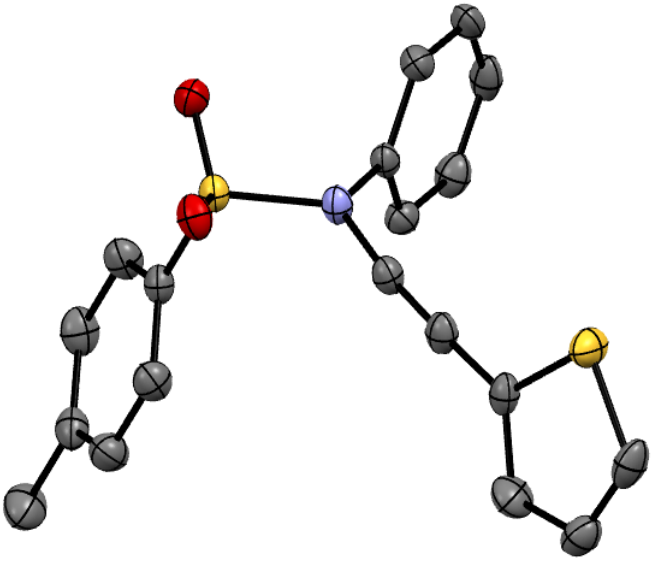

Figure S24: Solid state structure of **60w**, PhTsYnThienyl. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

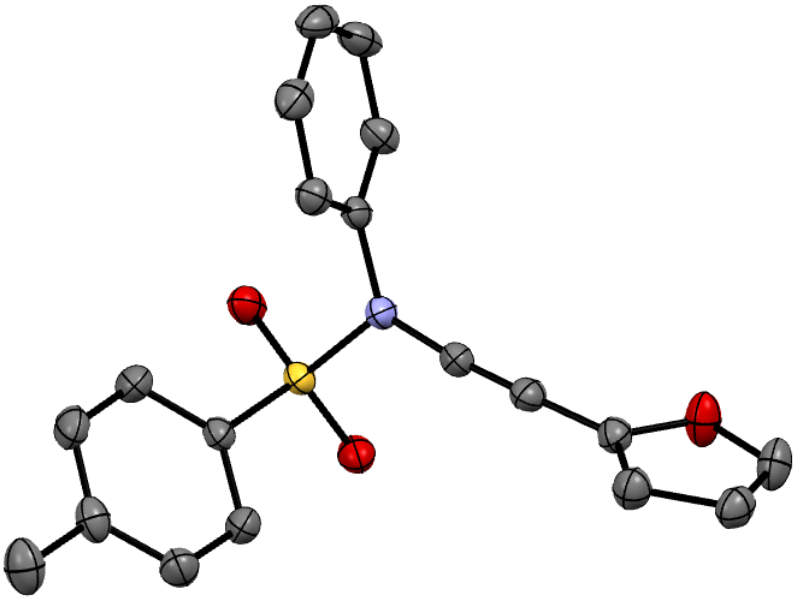

Figure S25: Solid state structure of **60x**, PhTsYnFuryl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

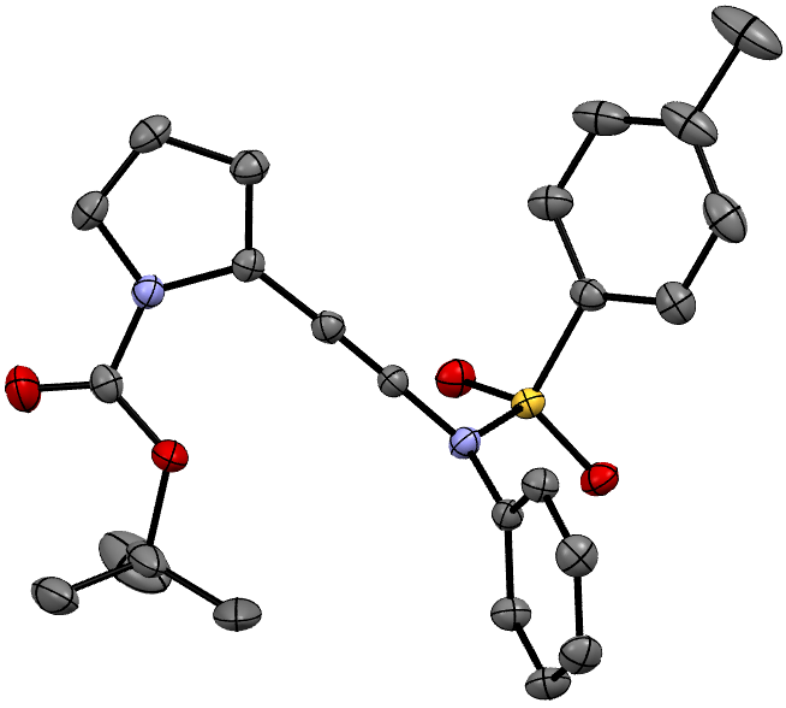

Figure S26: Solid state structure of **60y**, PhTsYnPyrrolyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

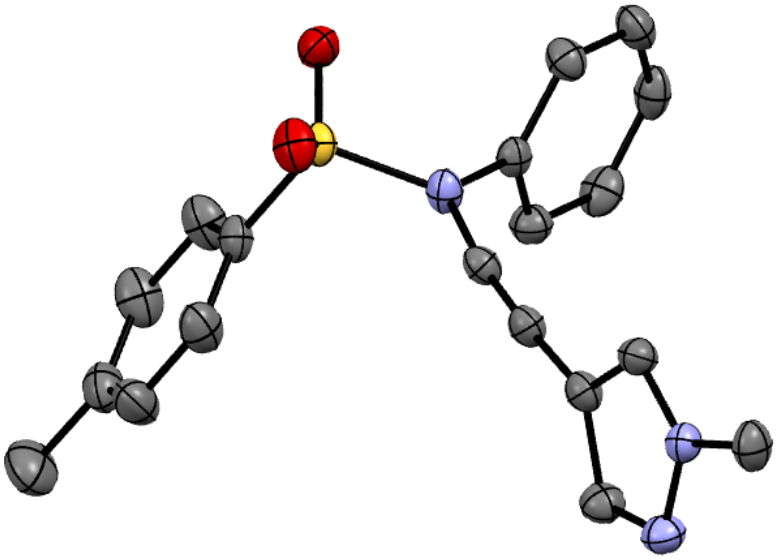

Figure S27: Solid state structure of **60z**, PhTsYnPyrazolyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

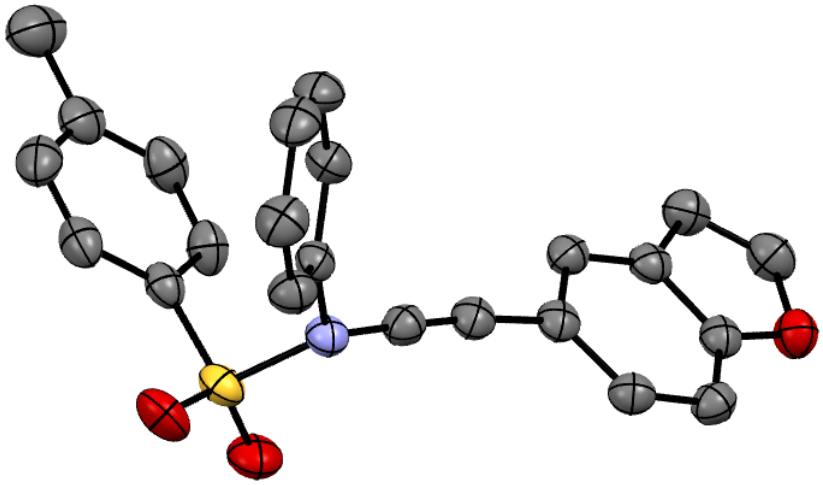

Figure S28: Solid state structure of **60ad**, PhTsYnBenzofuryl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

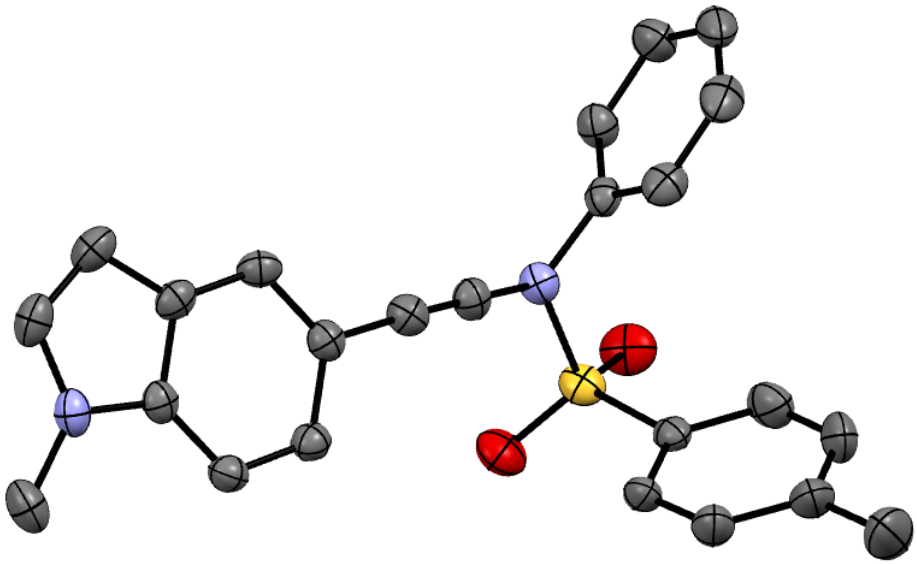

Figure S29: Solid state structure of **60ae**, PhTsYnIndolyl. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

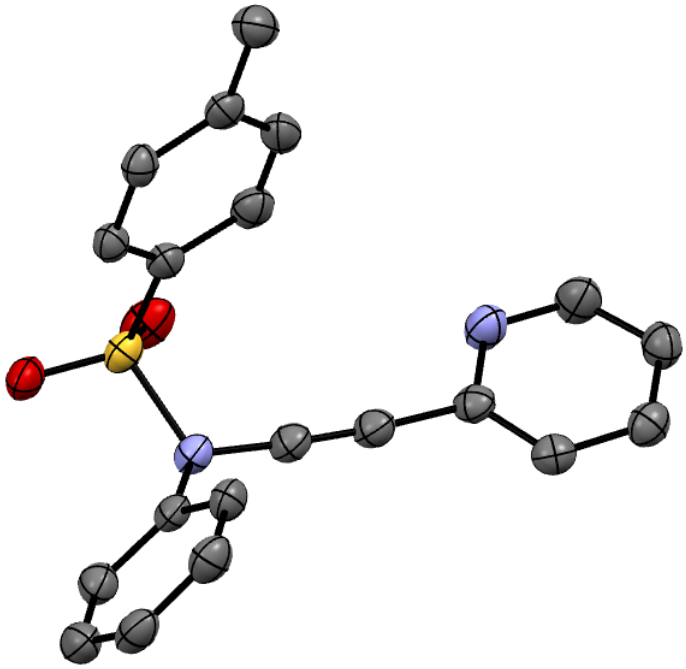

Figure S30: Solid state structure of **60af**, PhTsYn2-pyridyl. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

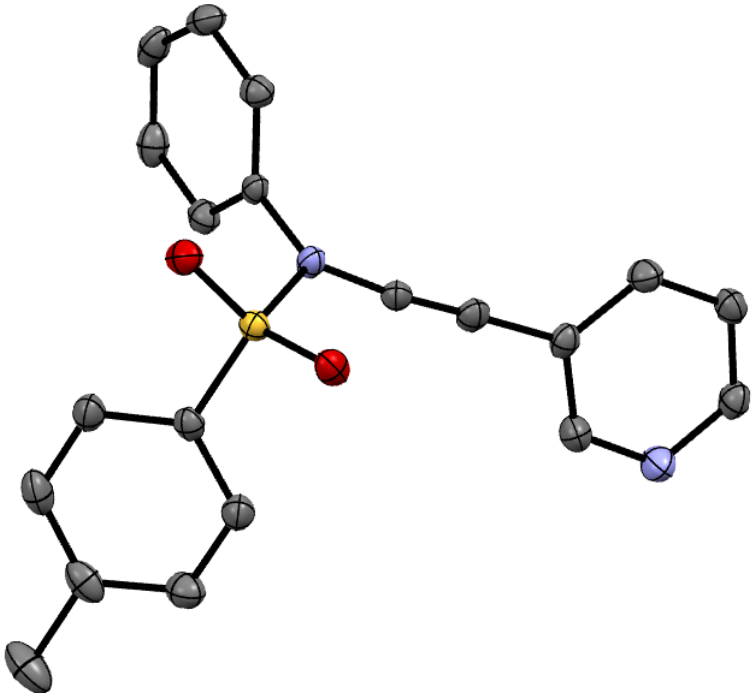

Figure S31: Solid state structure of **60ag**, PhTsYn3-pyridyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

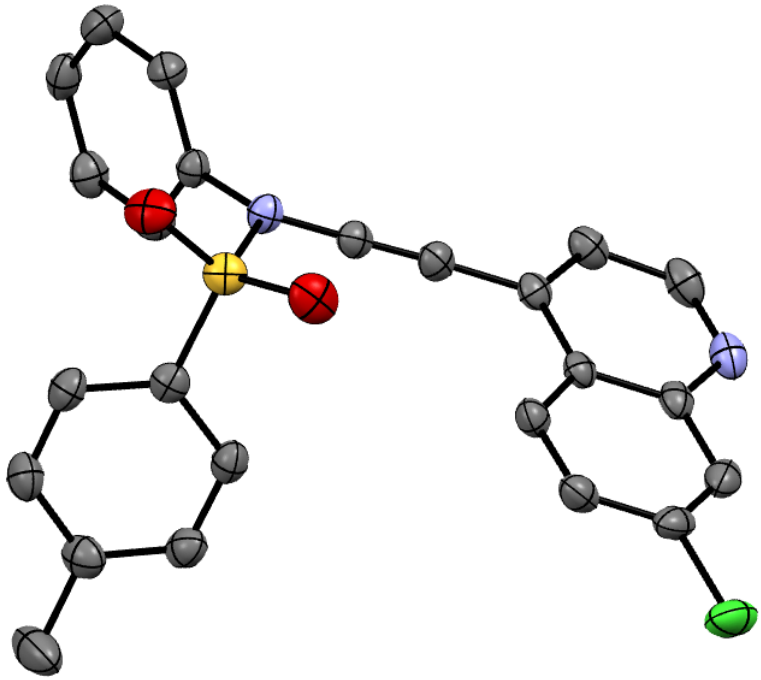

Figure S32: Solid state structure of **60ah**, PhTsYnQuin. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

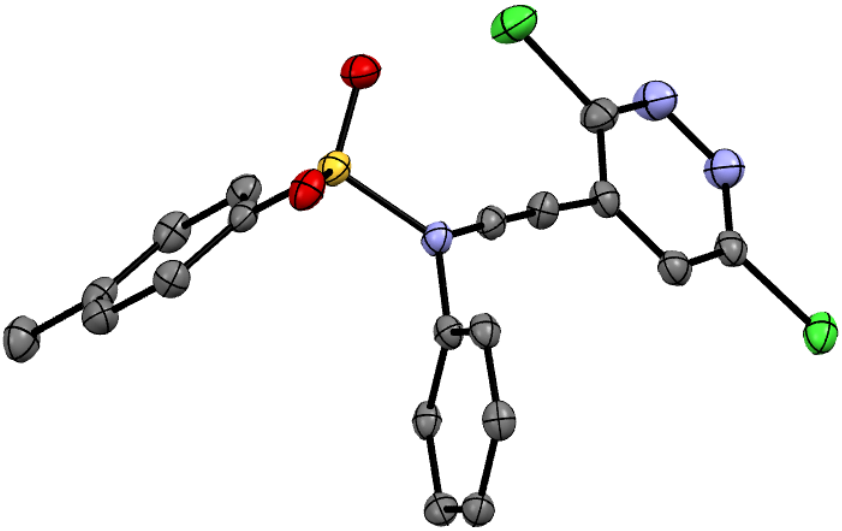

Figure S33: Solid state structure of **60ai**, PhTsYnPyridazinyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

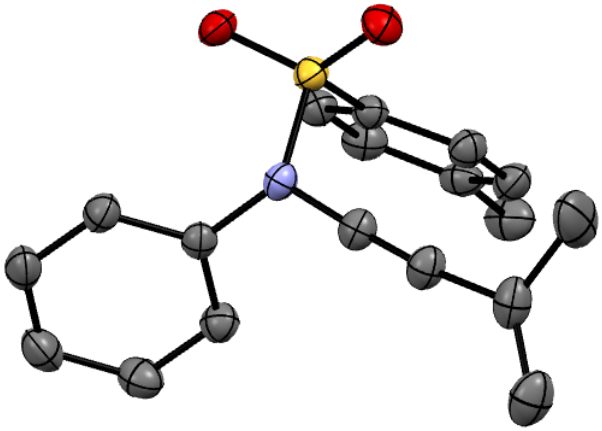

Figure S34: Solid state structure of **60aj**, PhTsYnPropenyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

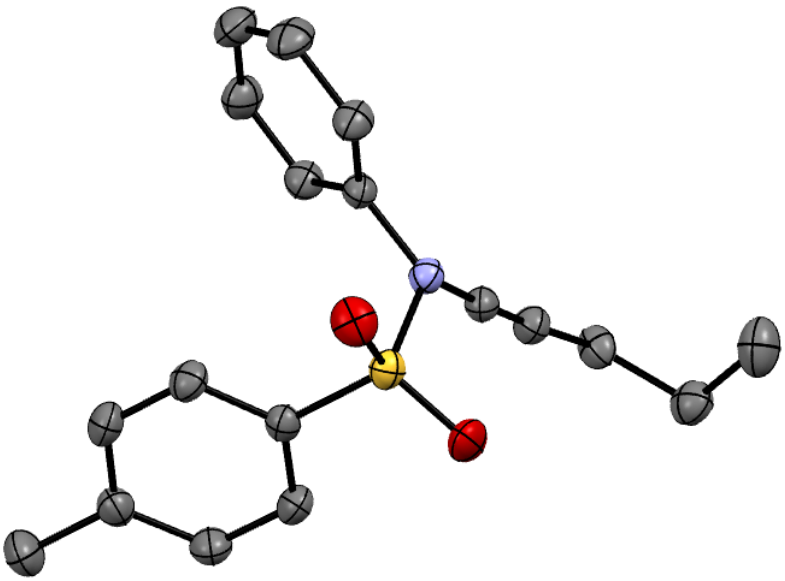

Figure S35: Solid state structure of **60am**, PhYn*n*-Pr. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

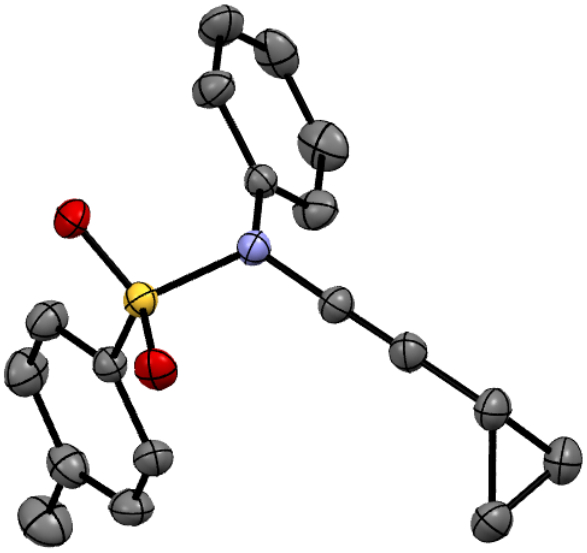

Figure S36: Solid state structure of **60an**, PhTsYnCyclopropyl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

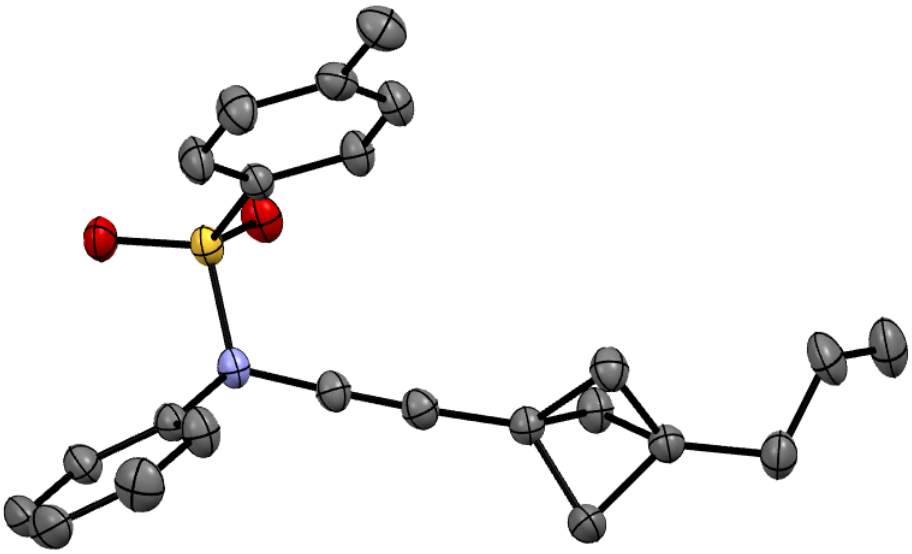

Figure S37: Solid state structure of **60ao**, PhTsYnBCP. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

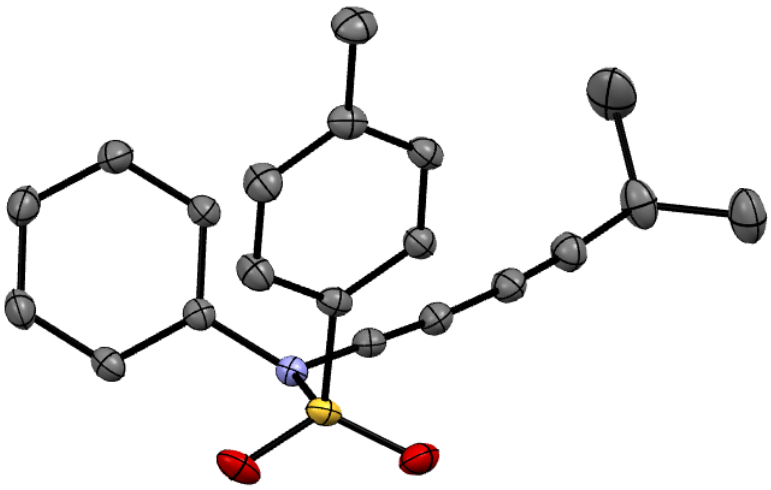

Figure S38: Solid state structure of **60ap**, PhTsYnYn*i*-Pr. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

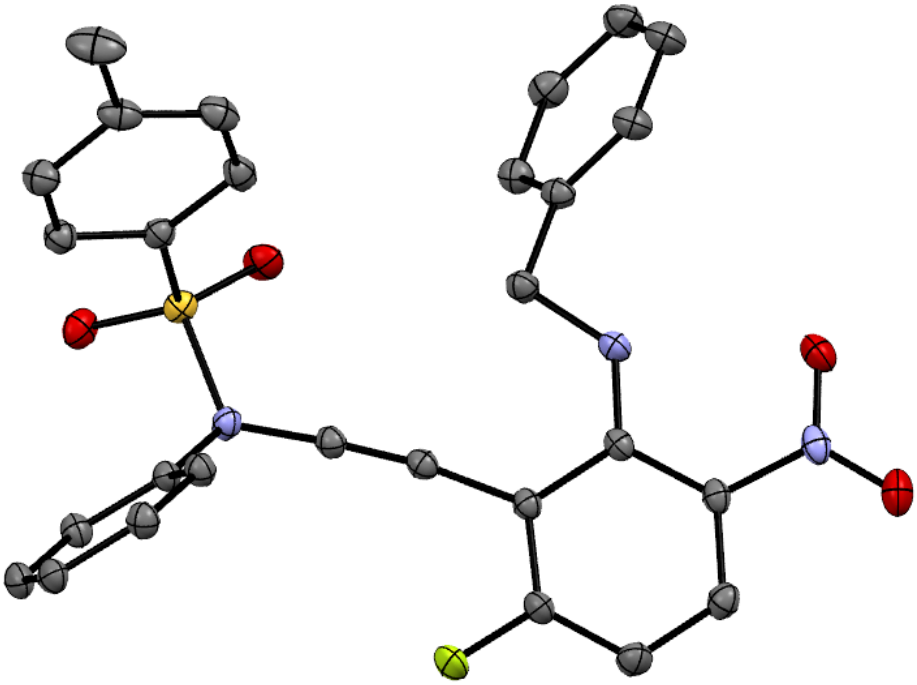

Figure S39: Solid state structure of **66**, PhTsYnPh*o*-F,NHBn,*m*-NO_2. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

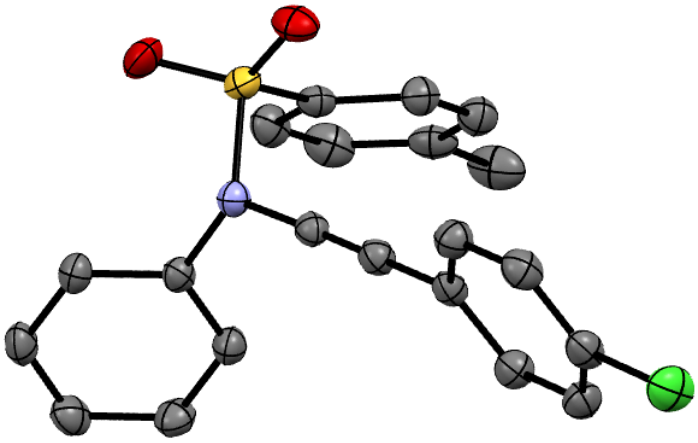

Figure S40: Solid state structure of **68a**, PhTsYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

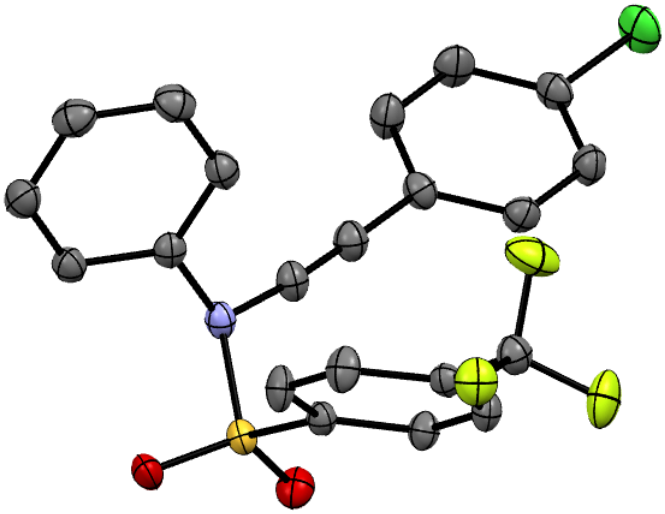

Figure S41: Solid state structure of **68b**, PhTfsYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

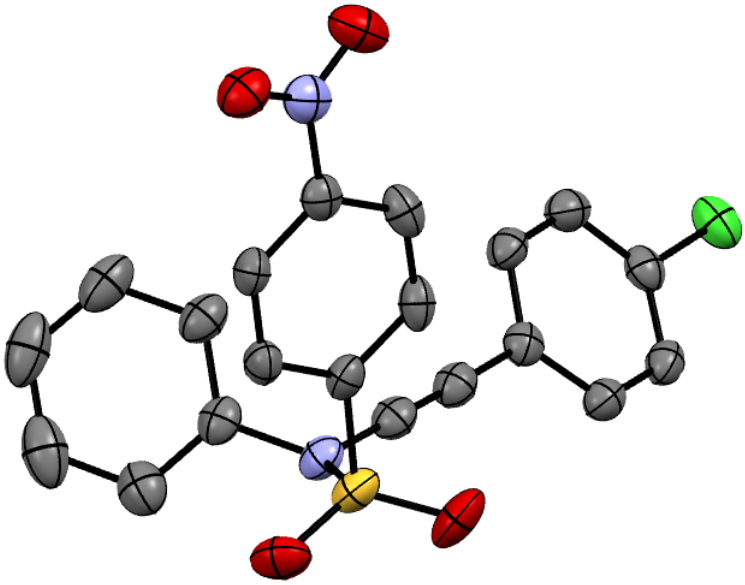

Figure S42: Solid state structure of **68d**, PhNsYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

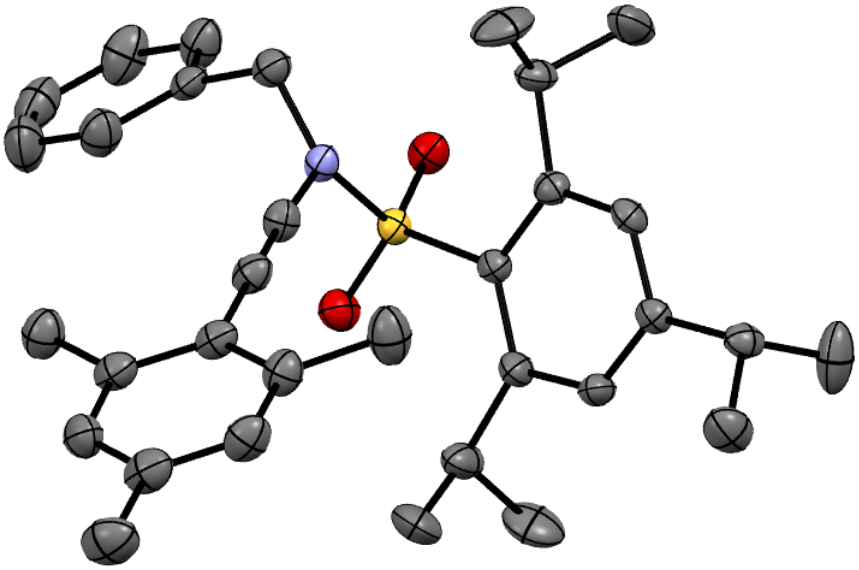

Figure S43: Solid state structure of **68e**, BnTrisYnMes. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

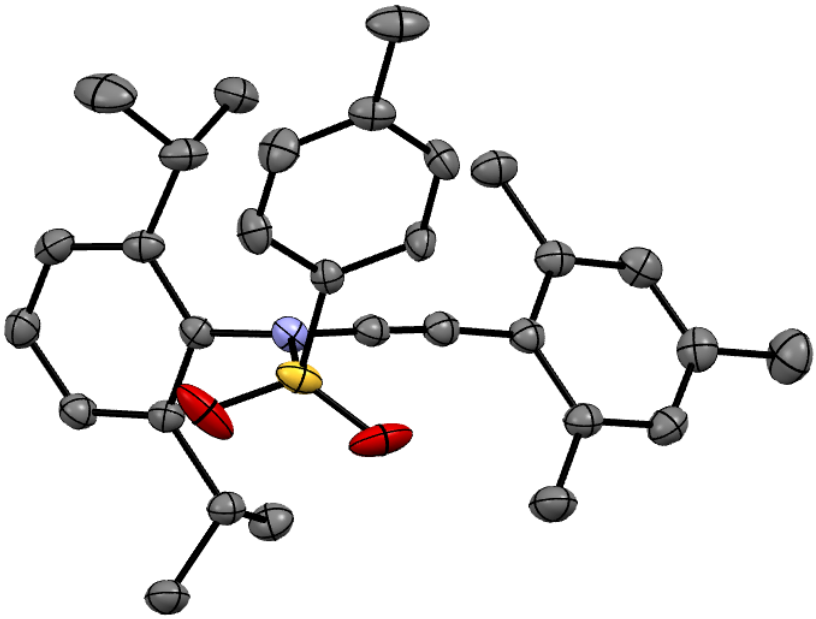

Figure S44: Solid state structure of **68g**, Ph(*i*-Pr)$_2$TsYnMes. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

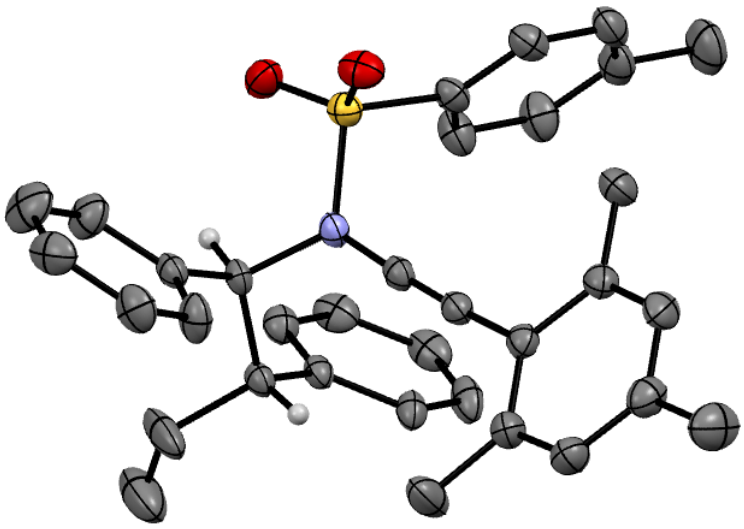

Figure S45: Solid state structure of **68o**, BPhTsYnMes. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms, except at the stereocentres, have been omitted for clarity.

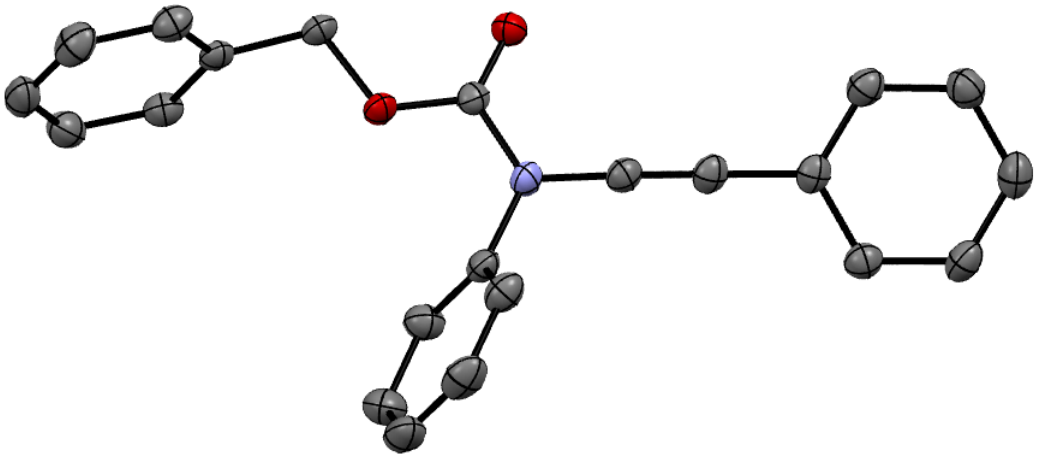

Figure S46: Solid state structure of **71a**, PhZYnPh. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

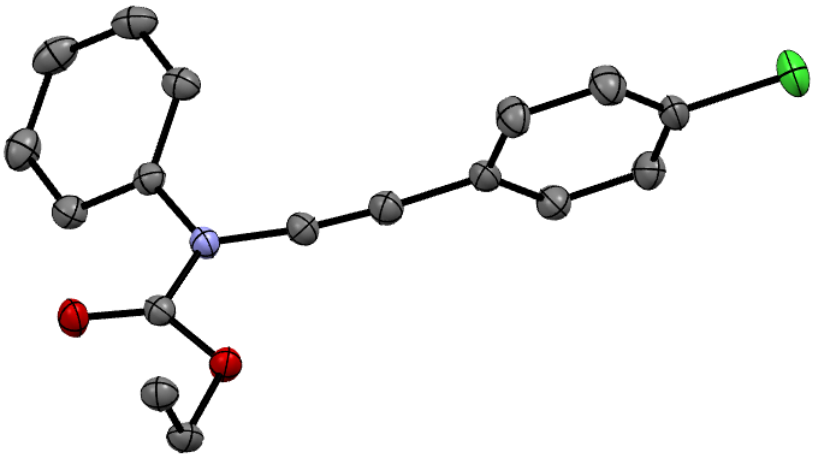

Figure S47: Solid state structure of **71e**, PhEYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

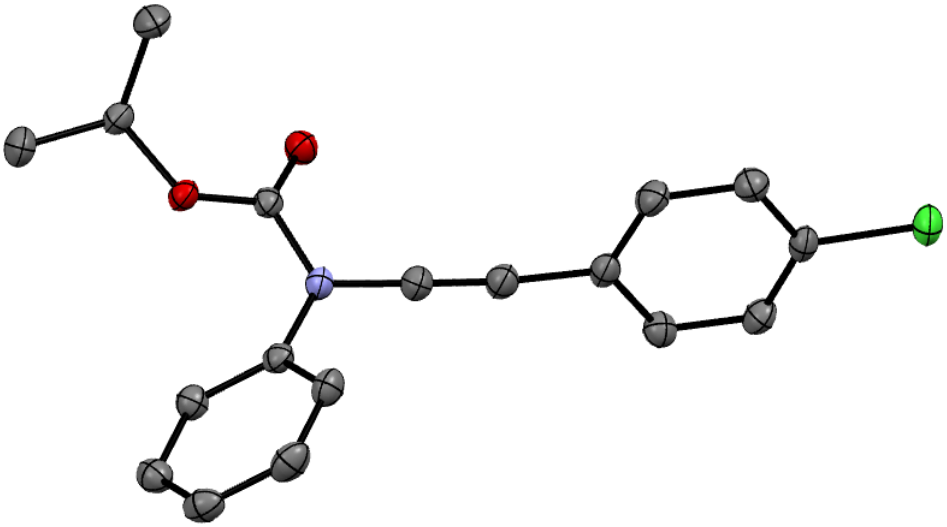

Figure S48: Solid state structure of **71f**, PhIYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

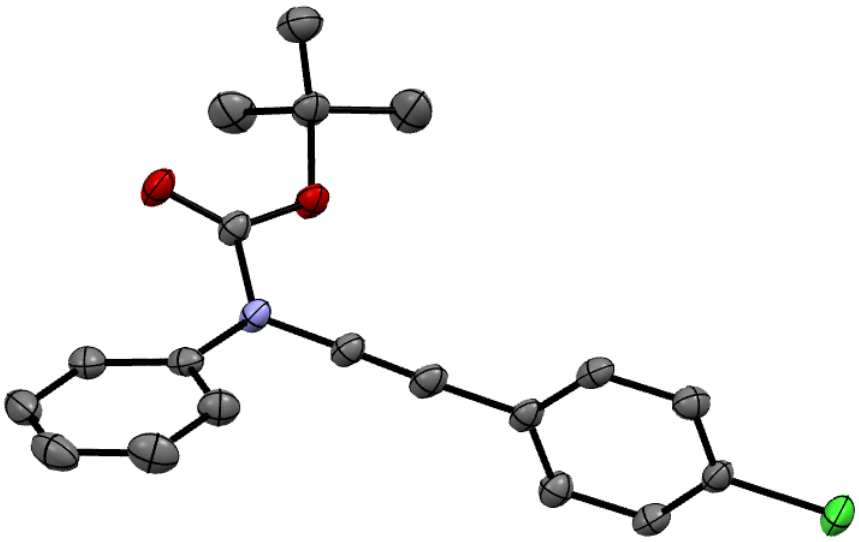

Figure S49: Solid state structure of **71g**, PhBocYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

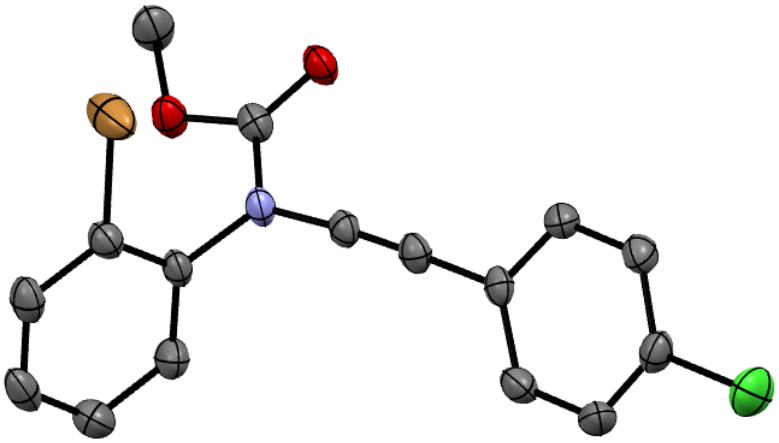

Figure S50: Solid state structure of **71h**, BrPhMocYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

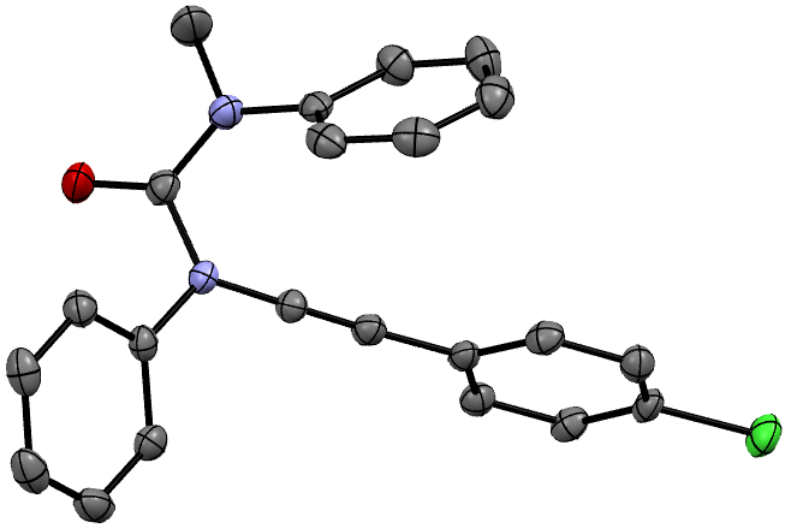

Figure S51: Solid state structure of **85a**, MePhUreaPhYnPh*p*-Cl.Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

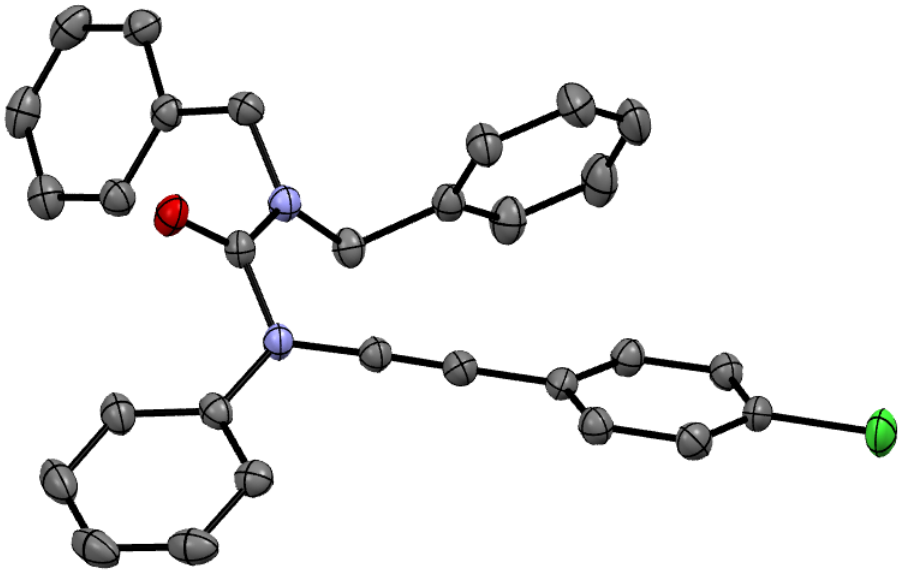

Figure S52: Solid state structure of **85b**, Bn_2UreaPhYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Co-crystallised solvent and hydrogen atoms have been omitted for clarity.

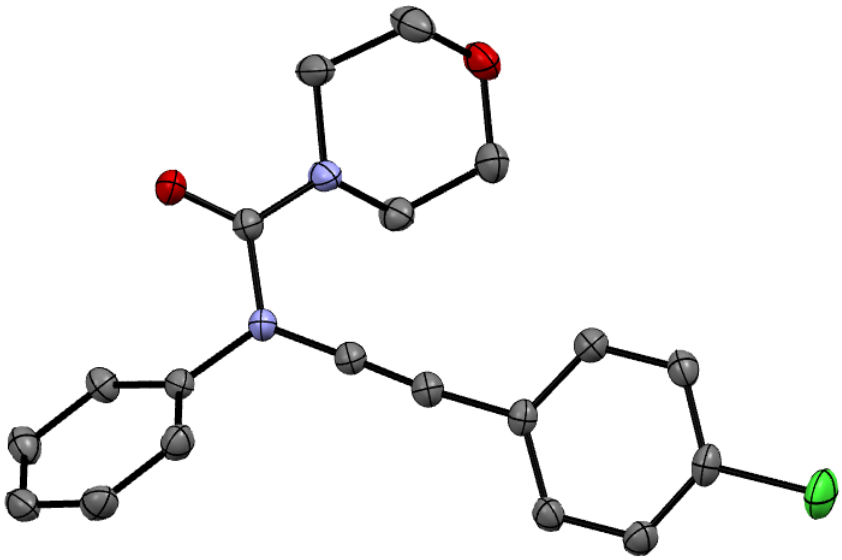

Figure S53: Solid state structure of **85c**, MorpholineUreaPhYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

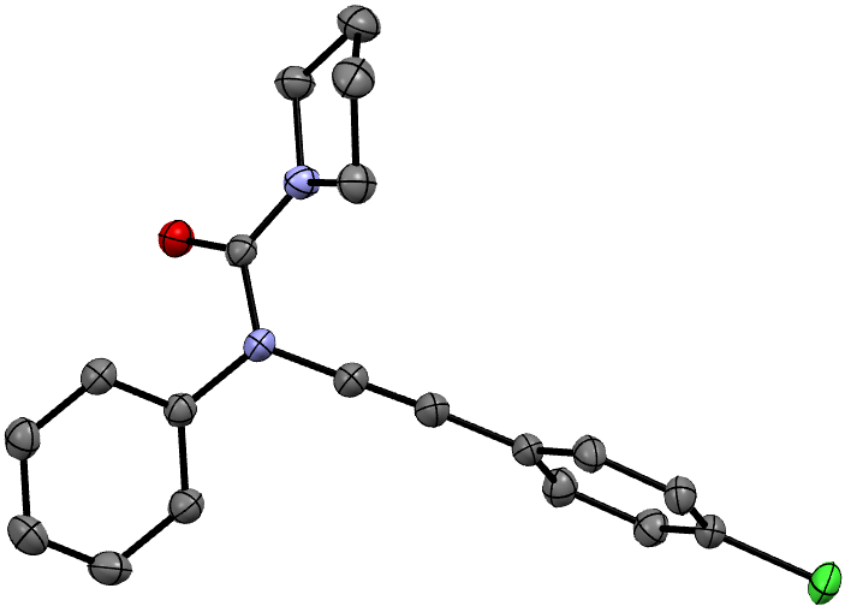

Figure S54: Solid state structure of **85d**, PyrrolidineUreaPhYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Co-crystallised solvent and hydrogen atoms have been omitted for clarity.

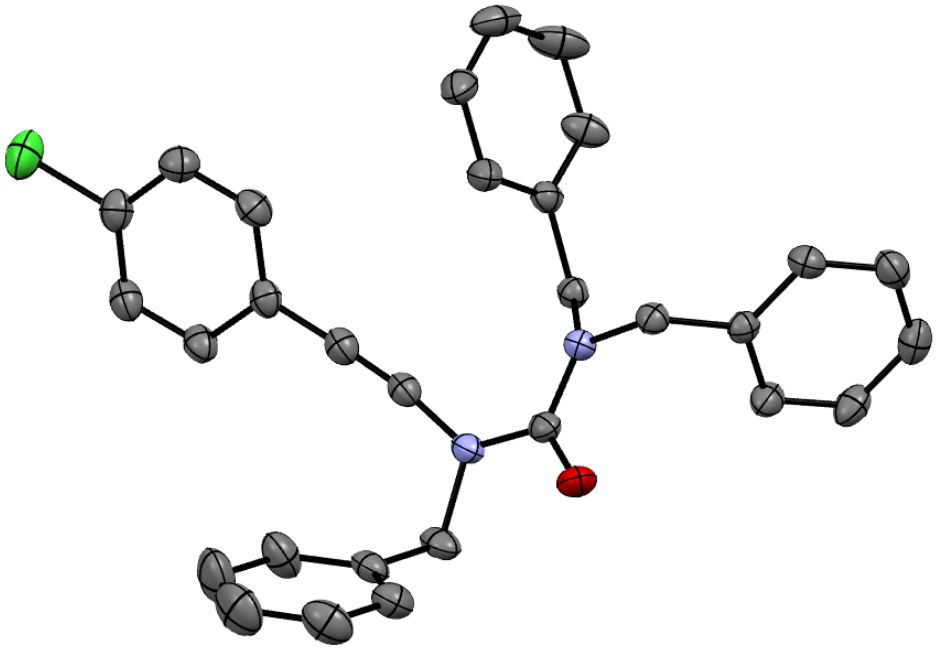

Figure S55: Solid state structure of **85e**, Bn_3UreaYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

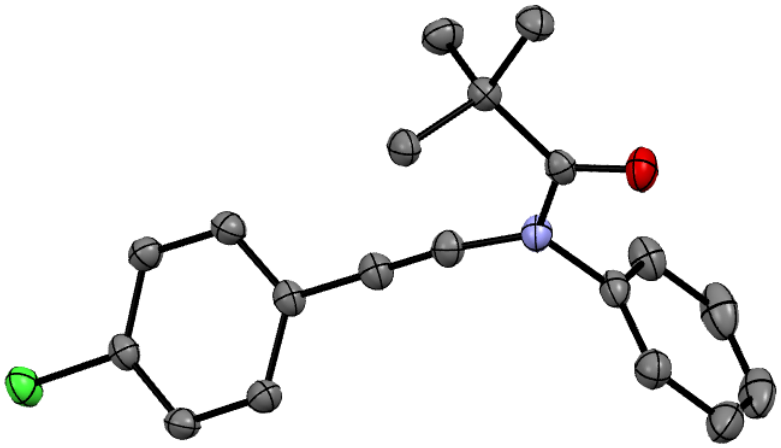

Figure S56: Solid state structure of **90d**, PhPivYnPh*p*-Cl. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

3.1b *Dichloroenamides and Miscellaneous*.

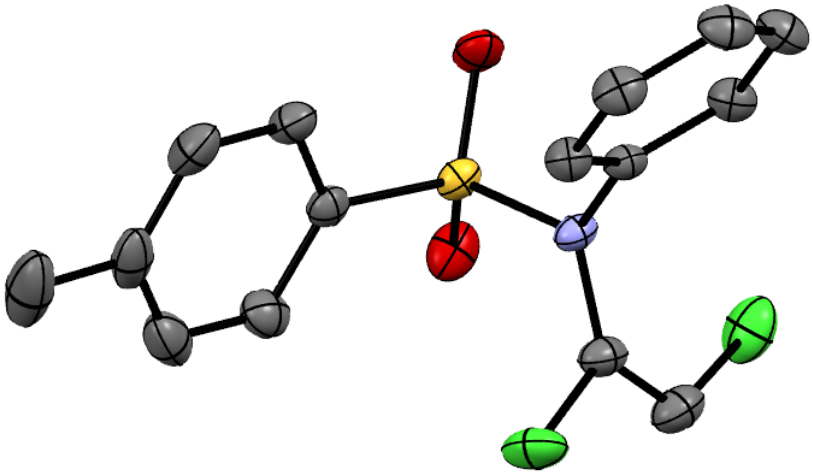

Figure S57: Solid state structure of **53a**, PhTsDCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

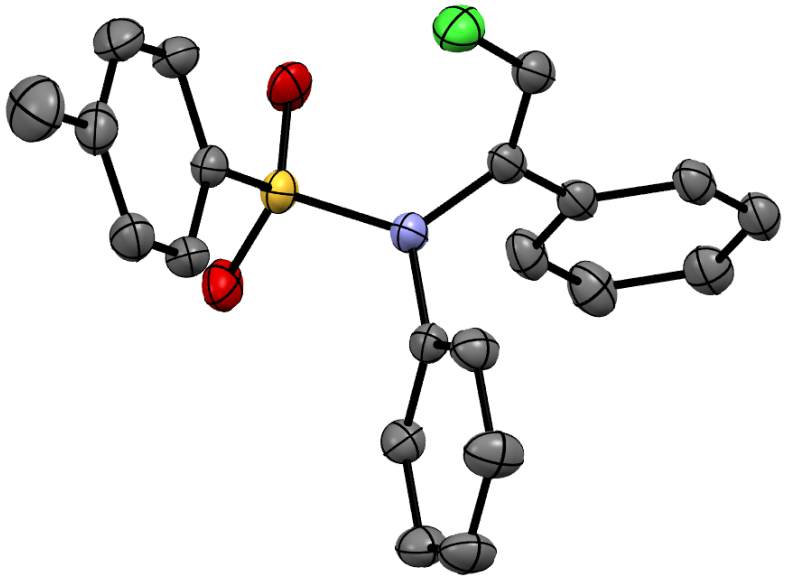

Figure S58: Solid state structure of **61**, PhTsPhCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

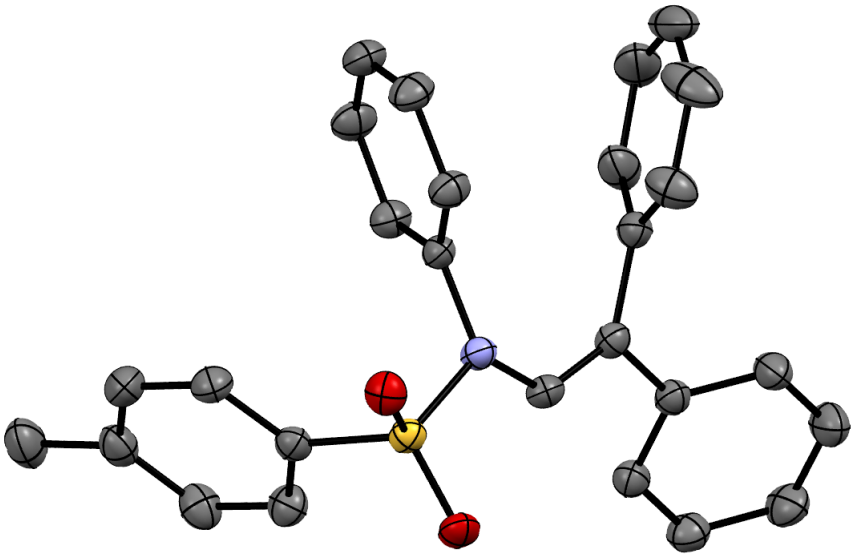

Figure S59: Solid state structure of **62**, PhTsDPhE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

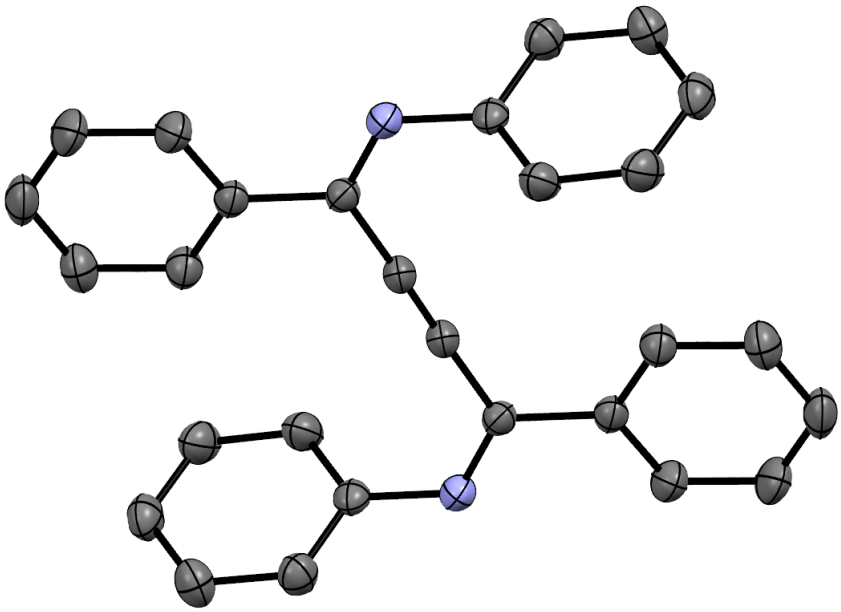

Figure S60: Solid state structure of **63**, Imine. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

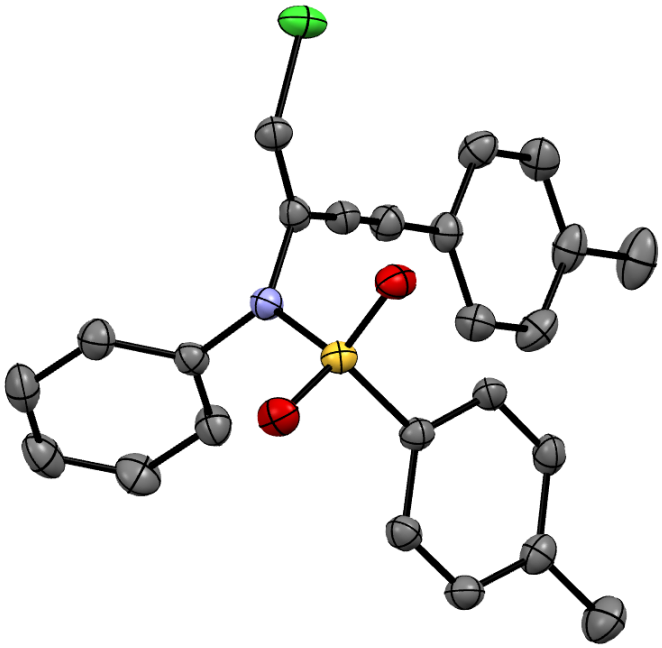

Figure S61: Solid state structure of **65a**, *p*-TolEnyne. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

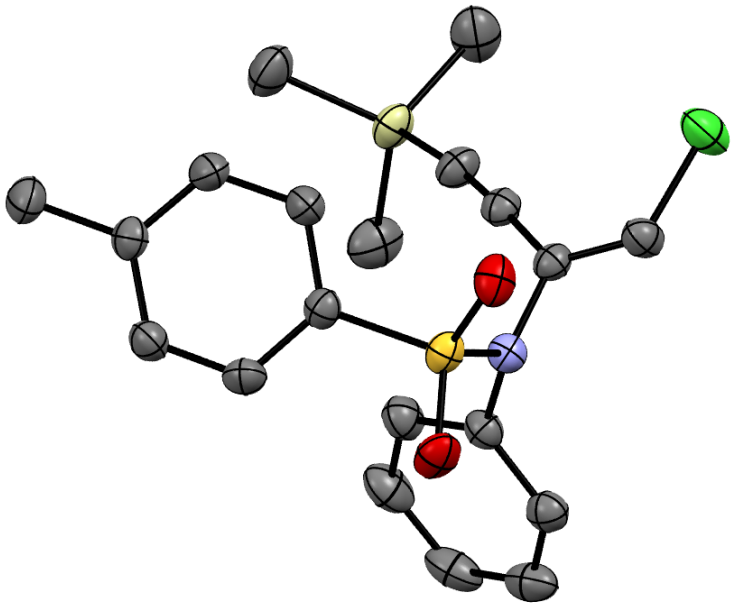

Figure S62: Solid state structure of **65b**, TMSEnyne. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

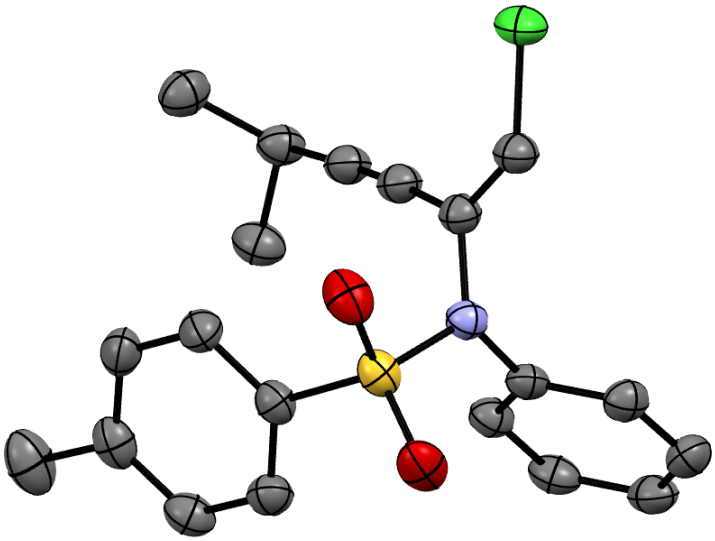

Figure S63: Solid state structure of **65c**, *i*-PrEnyne. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

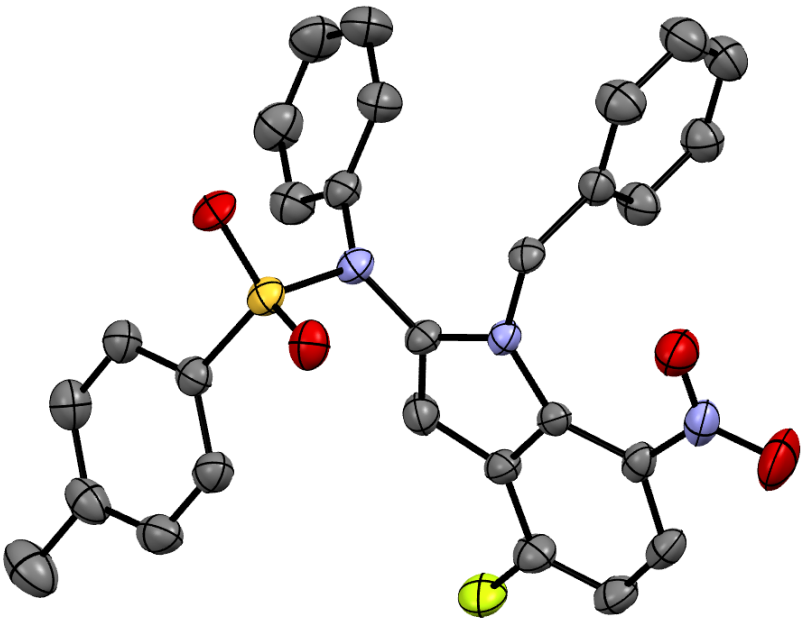

Figure S64: Solid state structure of **66**, Indole. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms and disordered components have been omitted for clarity.

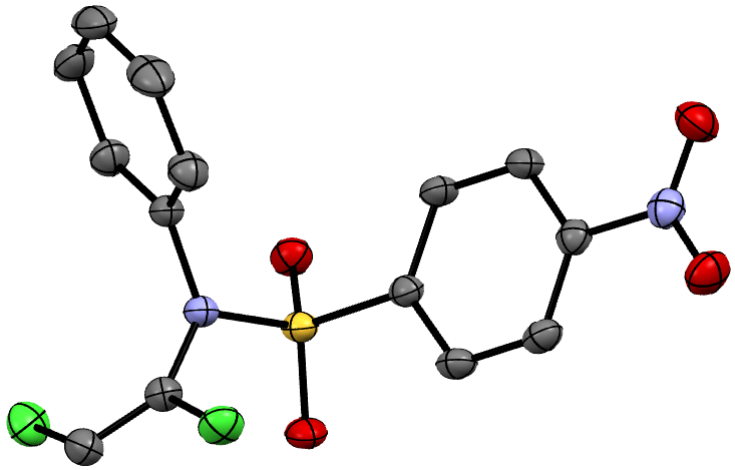

Figure S65: Solid state structure of **53d**, PhNsDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

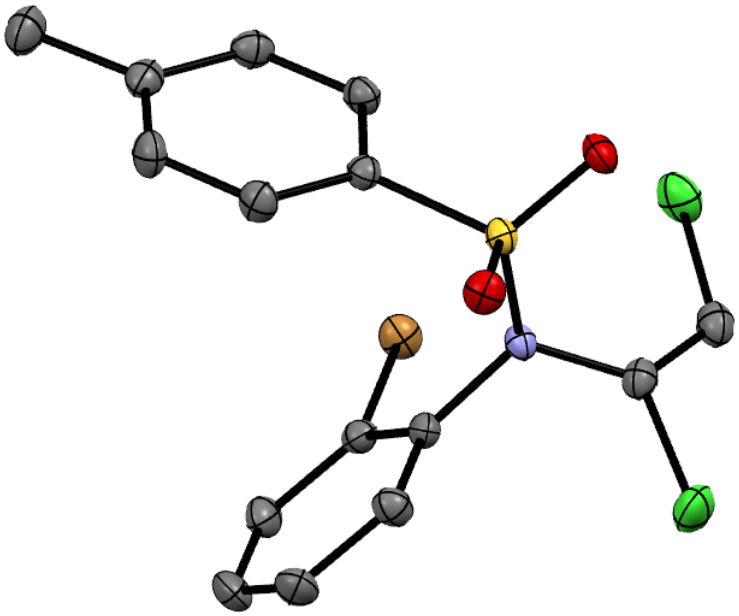

Figure S66: Solid state structure of **53f**, BrPhTsDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

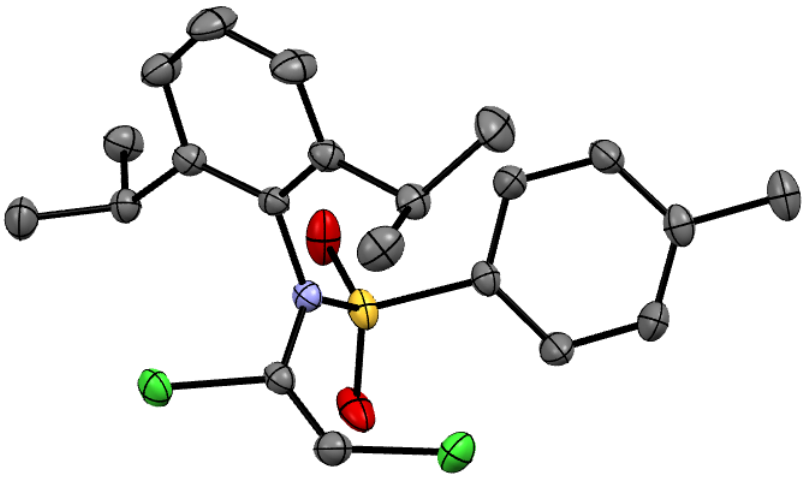

Figure S67: Solid state structure of **53g**, Ph(*i*-Pr)$_2$TsDCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

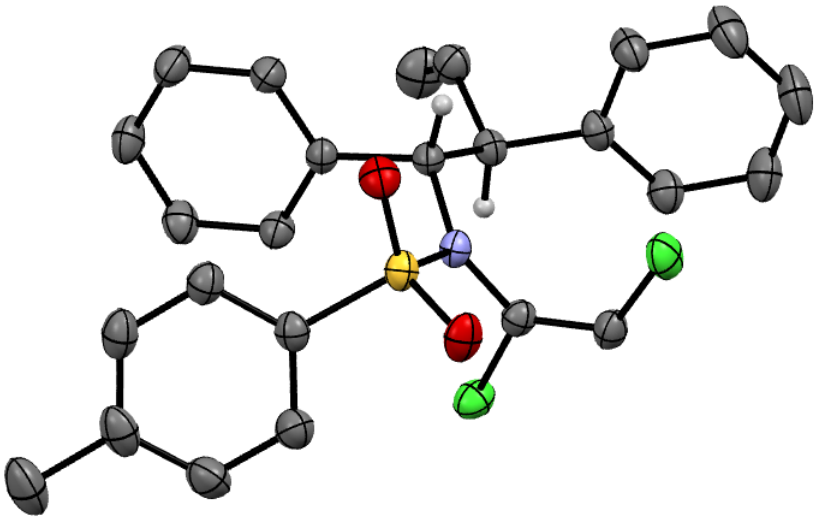

Figure S68: Solid state structure of **53l**, BPhTsDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms, except at the stereocentres, have been omitted for clarity.

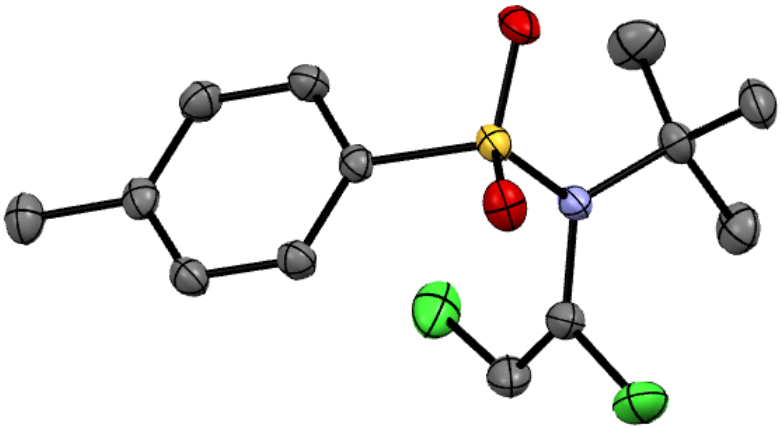

Figure S69: Solid state structure of **53m**, *t*-BuTsDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

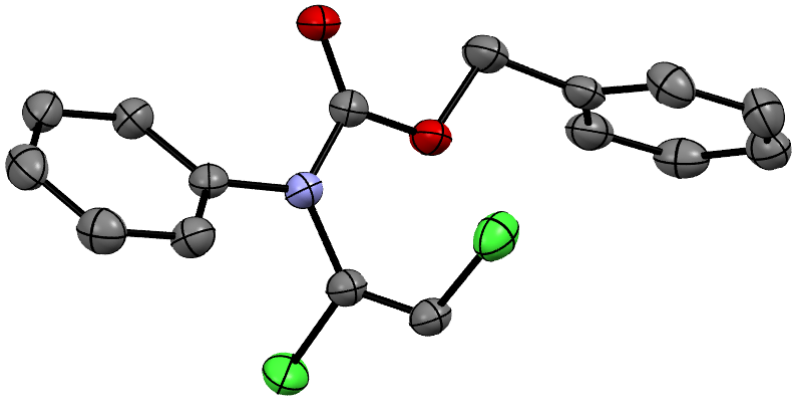

Figure S70: Solid state structure of **69a**, PhZDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

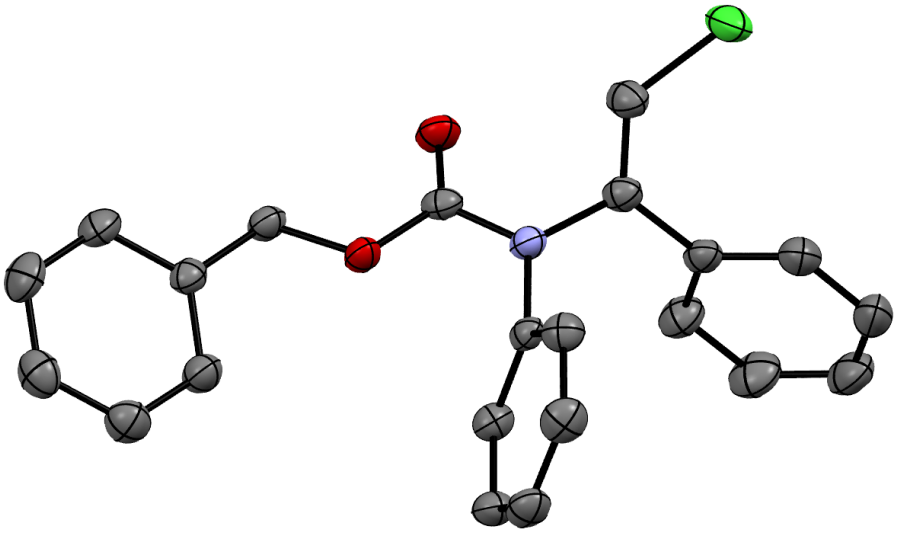

Figure S71: Solid state structure of (*E*)-**72**, PhZPhCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

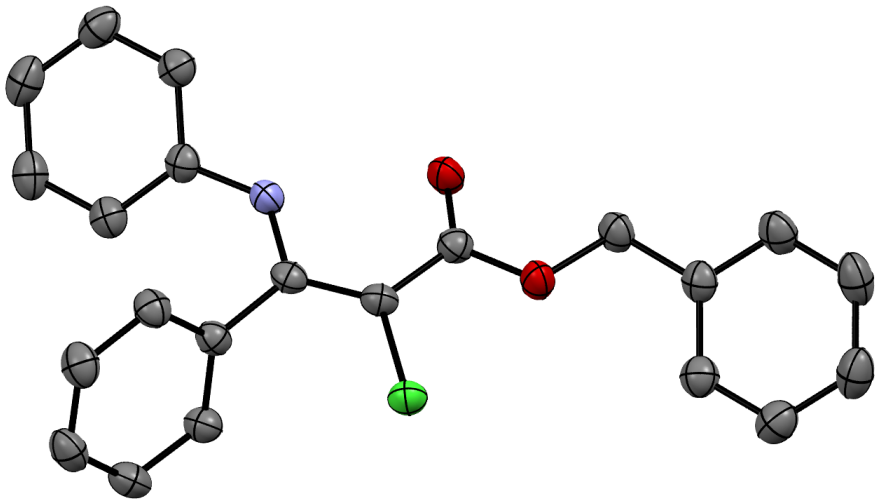

Figure S72: Solid state structure of **73**, (*E*)-Ester. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

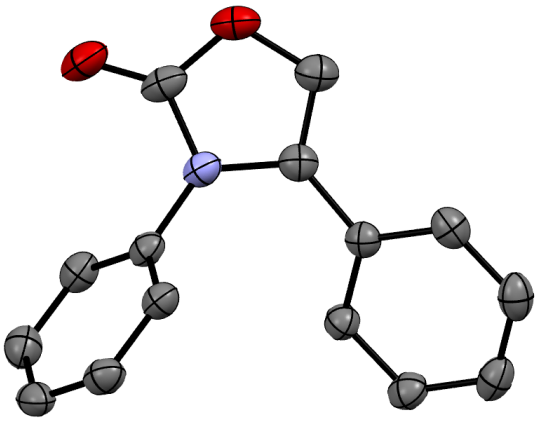

Figure S73: Solid state structure of **74**, Oxazolone. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

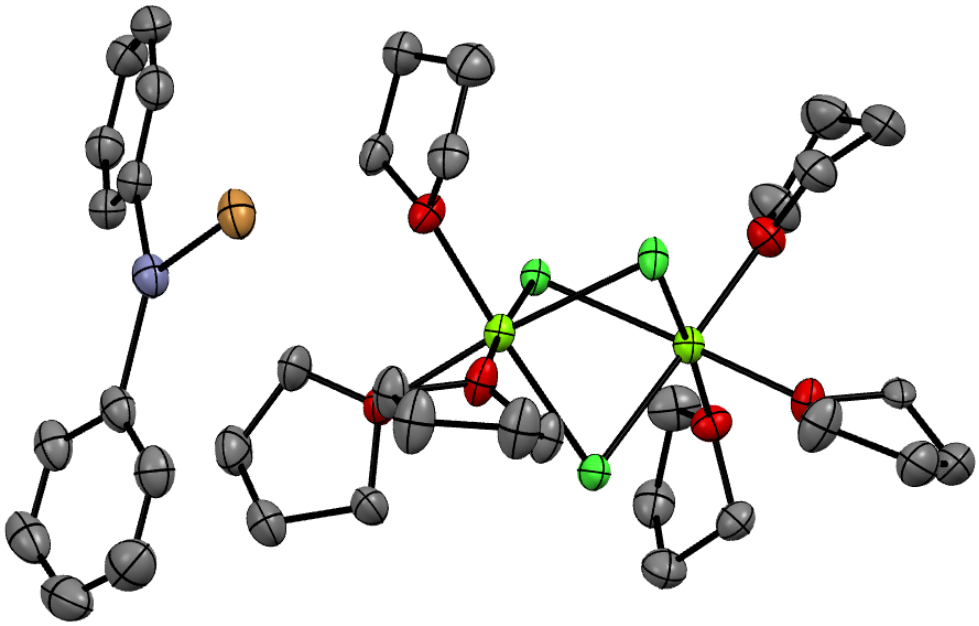

Figure S74: Solid state structure of **79**, $[Ph_2ZnBr][Mg_2Cl_3(THF)_6]$. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms and disordered components have been omitted for clarity.

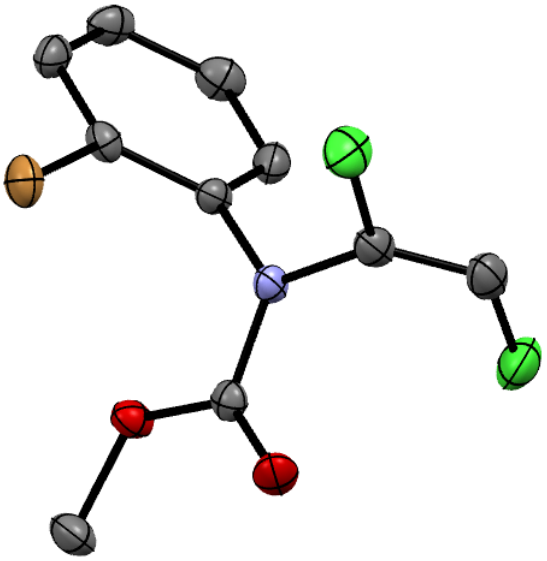

Figure S75: Solid state structure of **69e**, PhBrMocDCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

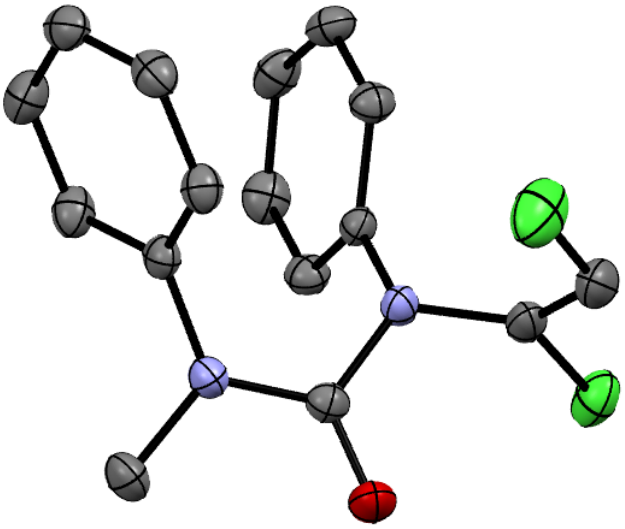

Figure S76: Solid state structure of **83a**, PhMeUreaPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

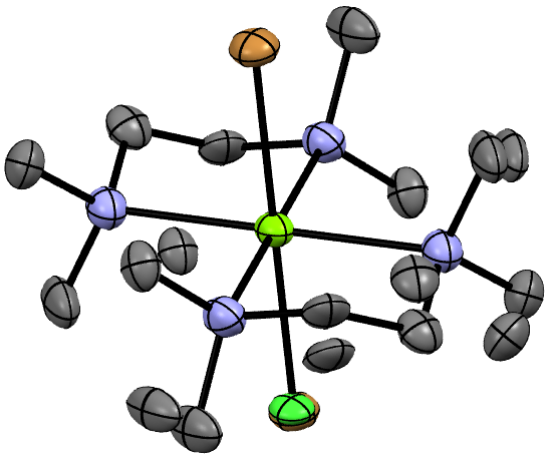

Figure S77: Solid state structure of $MgX_2(TMEDA)_2$. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

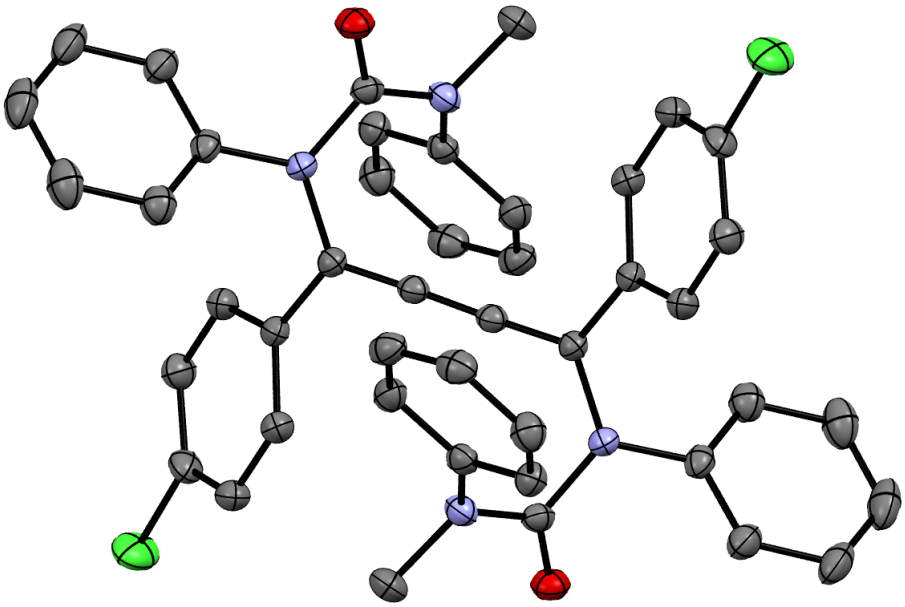

Figure S78: Solid state structure of (*E*)-**88**, Cumulene. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

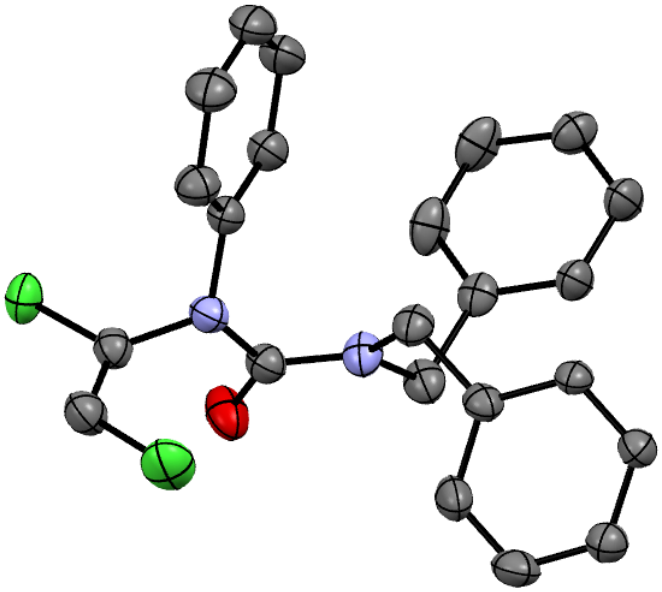

Figure S79: Solid state structure of **83b**, Bn_2UreaPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

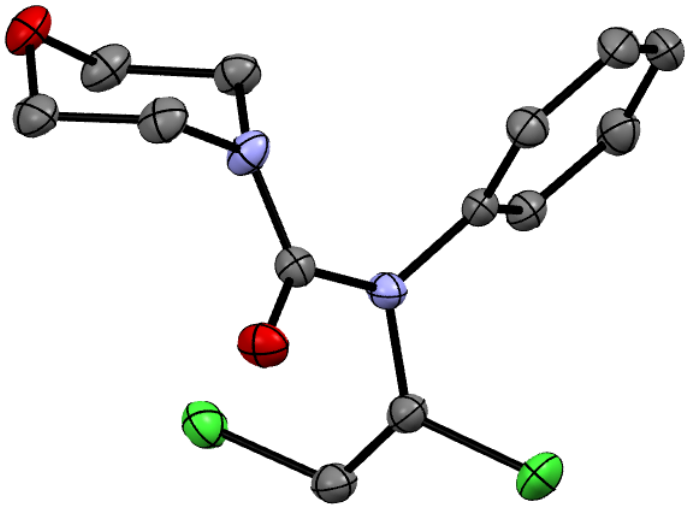

Figure S80: Solid state structure of **83c**, MorpholineUreaPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

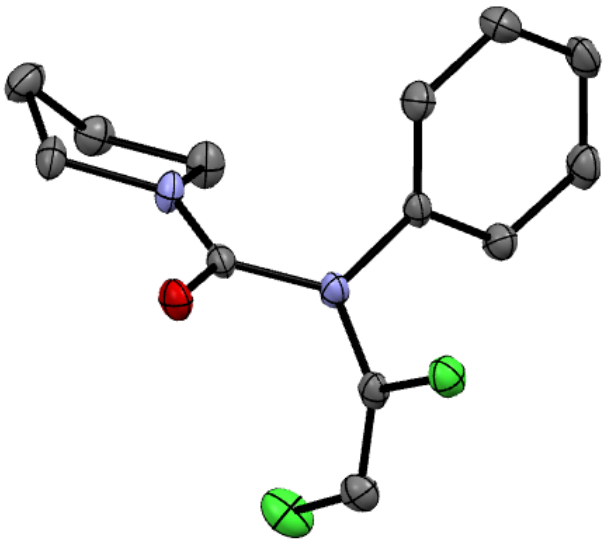

Figure S81: Solid state structure of **83d**, PyrrolidineUreaPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

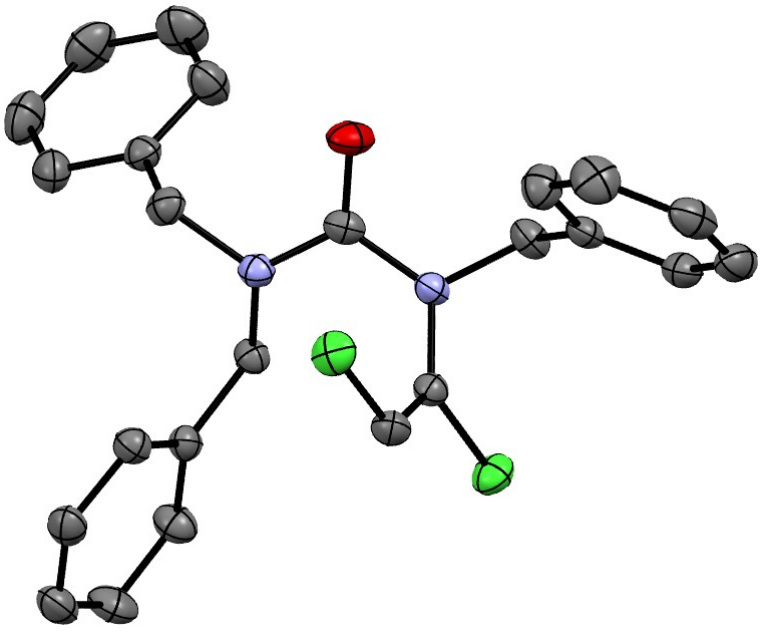

Figure S81: Solid state structure of **83e**, Bn_3UreaDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

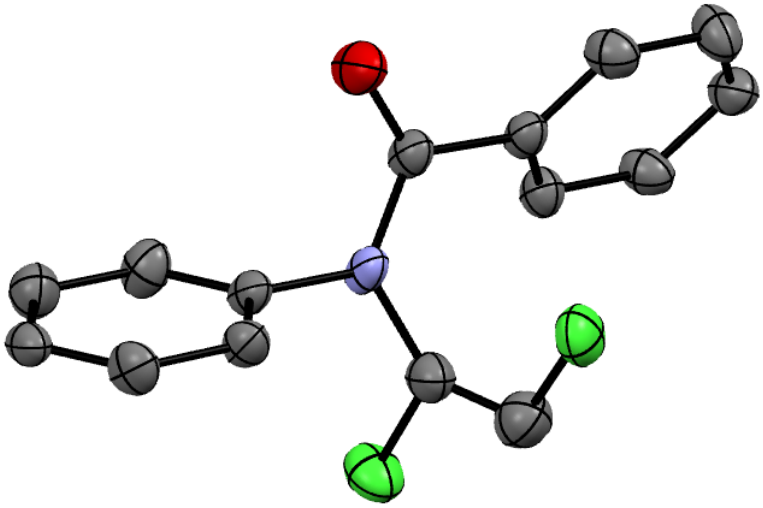

Figure S83: Solid state structure of **89a**, PhBzDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

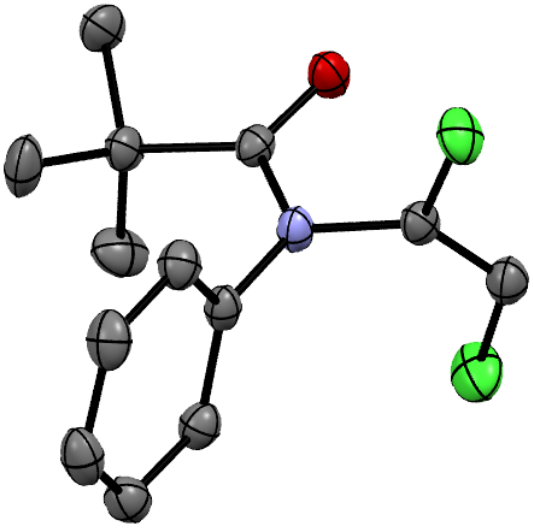

Figure S84: Solid state structure of **89d**, PhPivDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

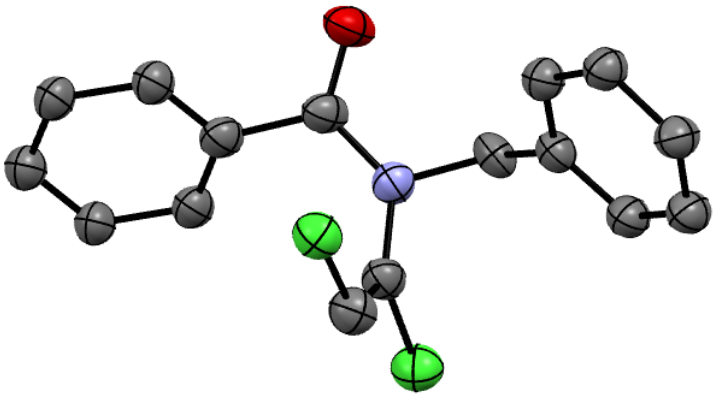

Figure S85: Solid state structure of **89e**, BnBzDCE. Displacement ellipsoid plots are drawn at 30% probability. Disordered components and hydrogen atoms have been omitted for clarity.

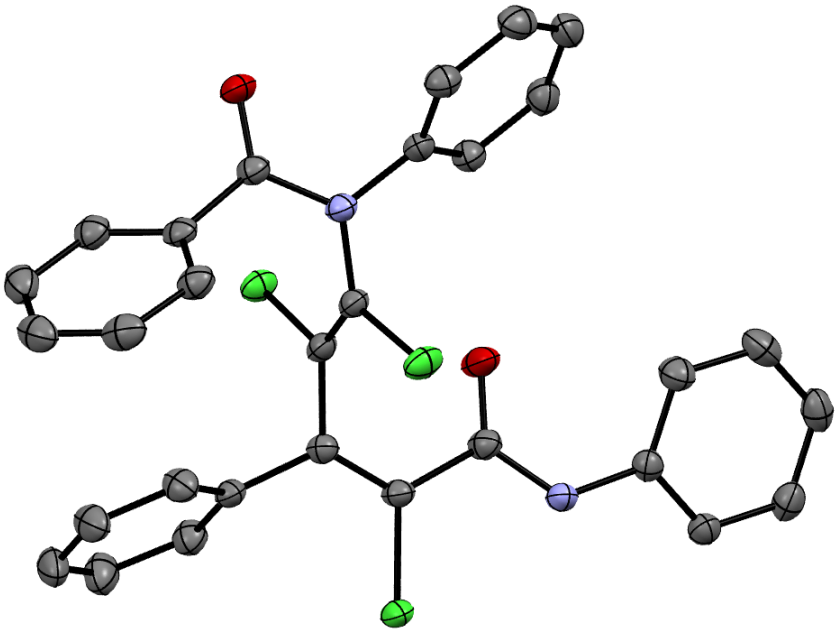

Figure S86: Solid state structure of **92**, Trichloroenamide. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

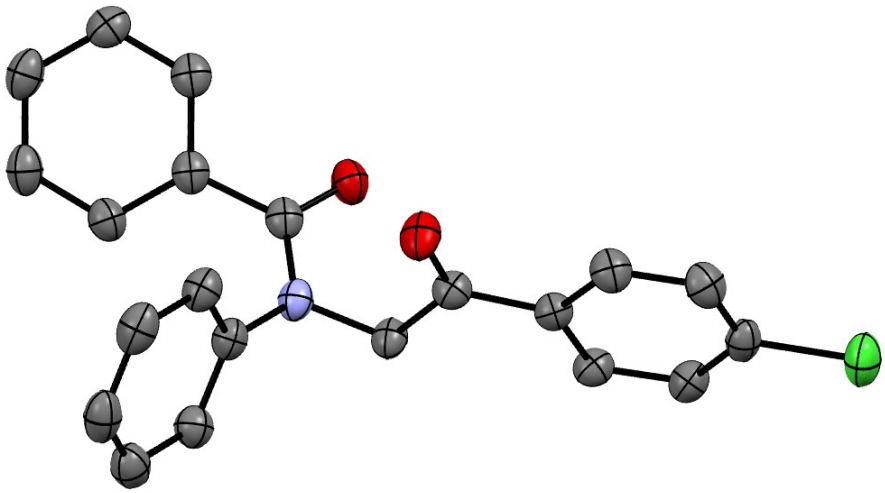

Figure S87: Solid state structure of **93a**, PhBzYnHydrate. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

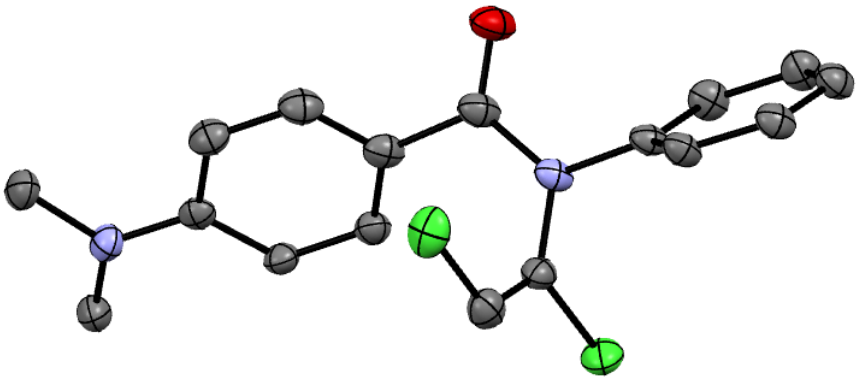

Figure S89: Solid state structure of **89h**, Me_2NBzPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

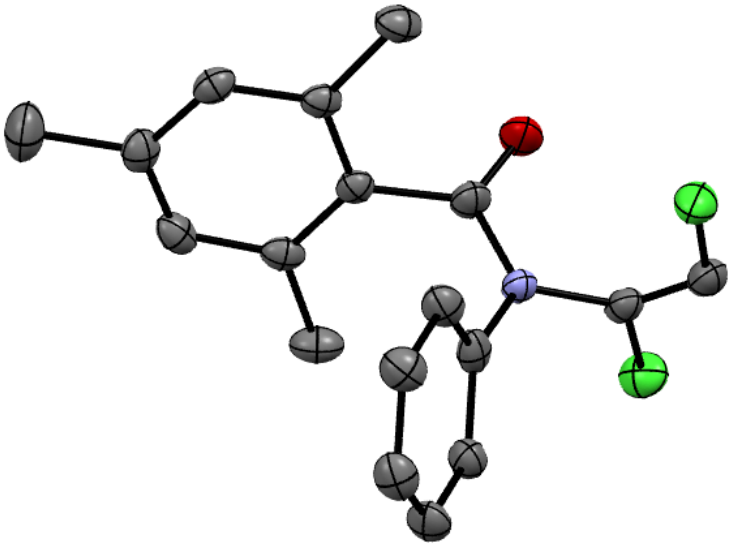

Figure S90: Solid state structure of **89j**, MesCOPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

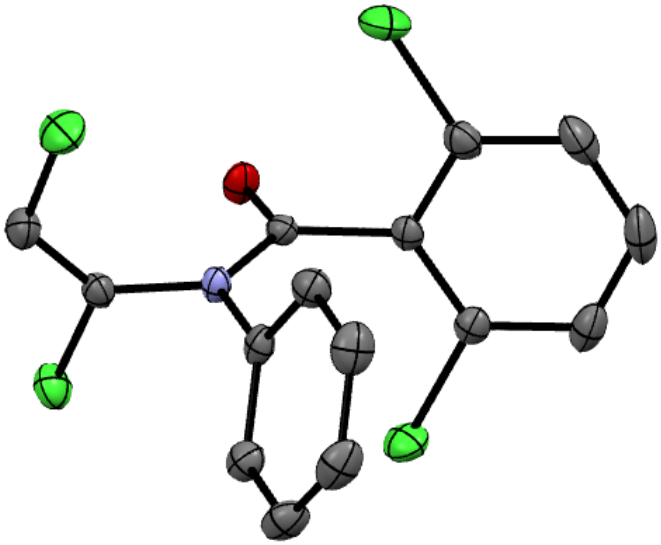

Figure S91: Solid state structure of **89k**, Cl_2BzPhDCE. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

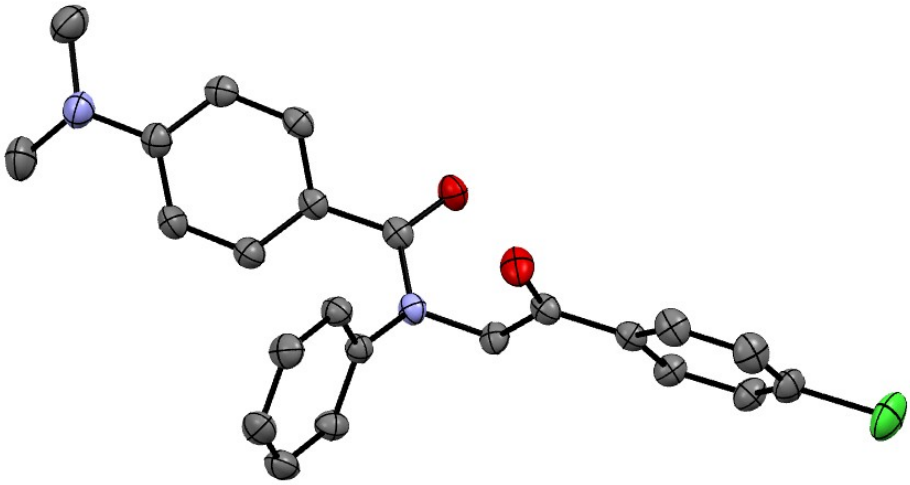

Figure S92: Solid state structure of **93h**, Me_2NBzPhYnHydrate. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

3.2 Synthesis and Applications of Yndiamides.

3.2a *Yndiamides*.

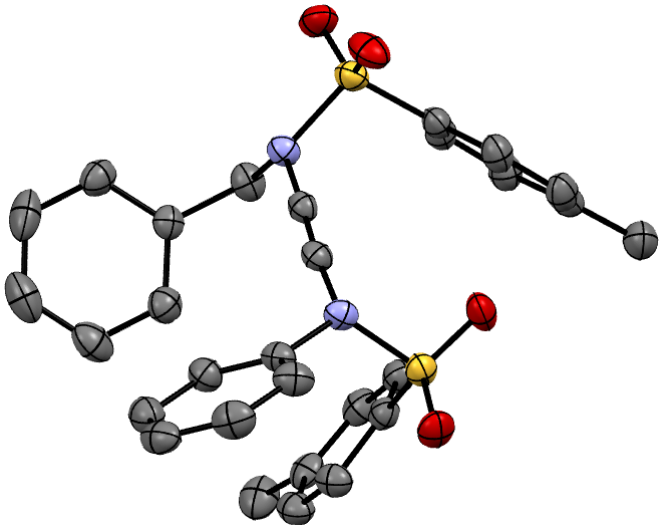

Figure S93: Solid state structure of **148a**, PhTsYndBnTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

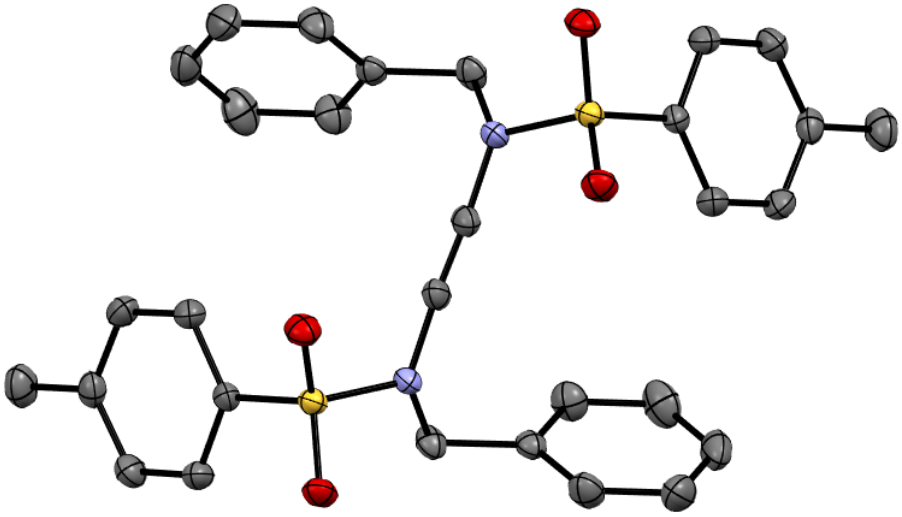

Figure S94: Solid state structure of **148b**, BnTsYndBnTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

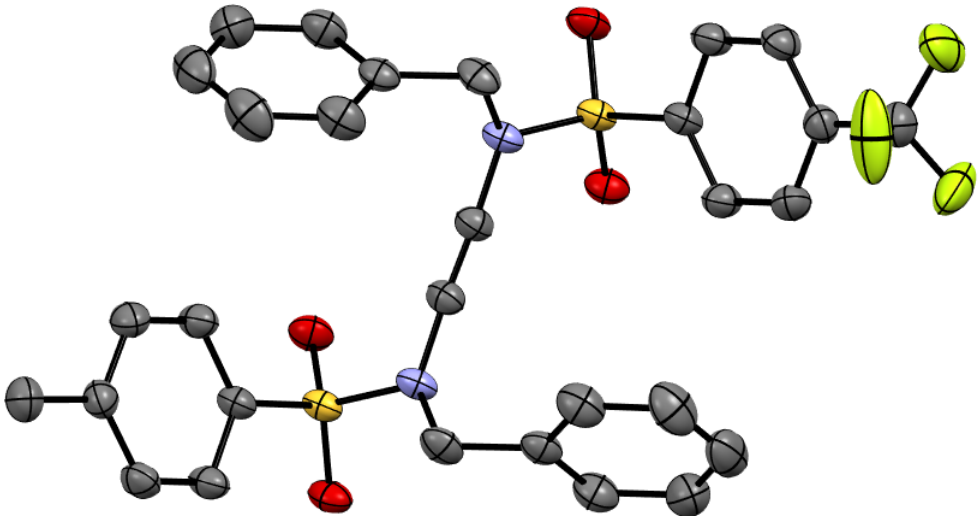

Figure S95: Solid state structure of **148c**, BnTsYndBnTfs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

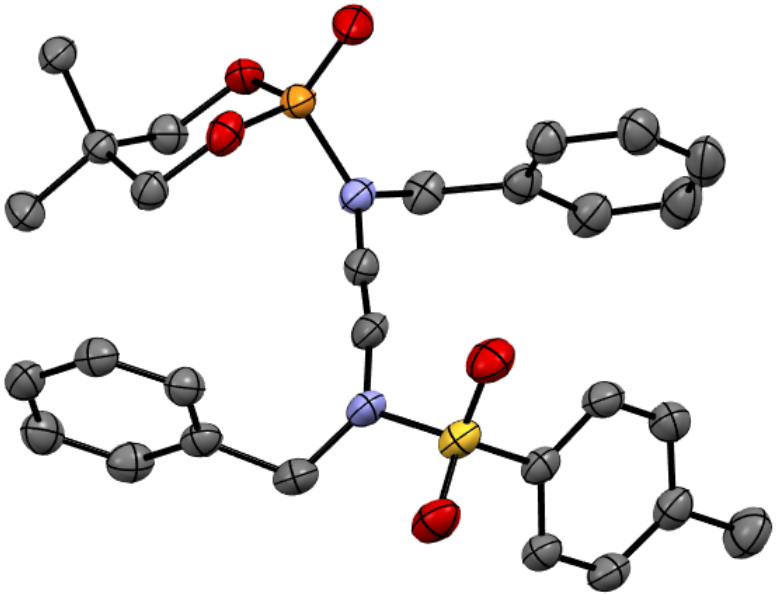

Figure S96: Solid state structure of **148g**, BnTsYndBnPs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

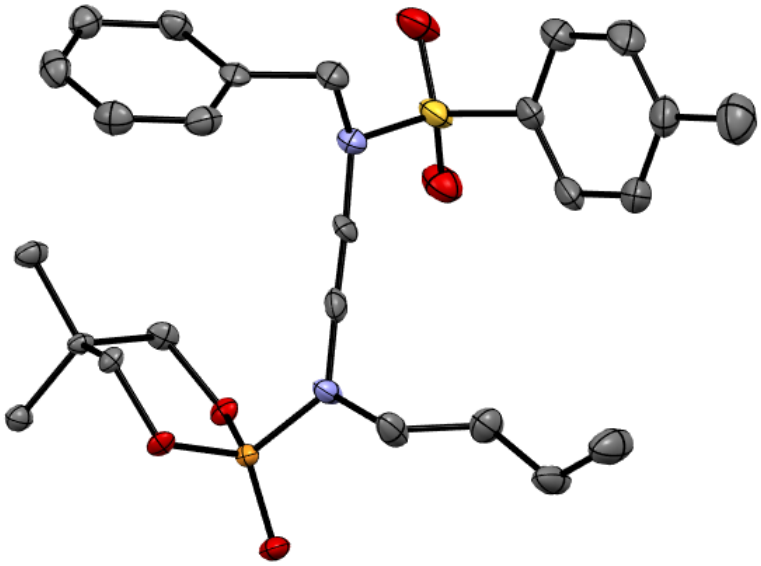

Figure S97: Solid state structure of **148h**, BnTsYndHallPs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

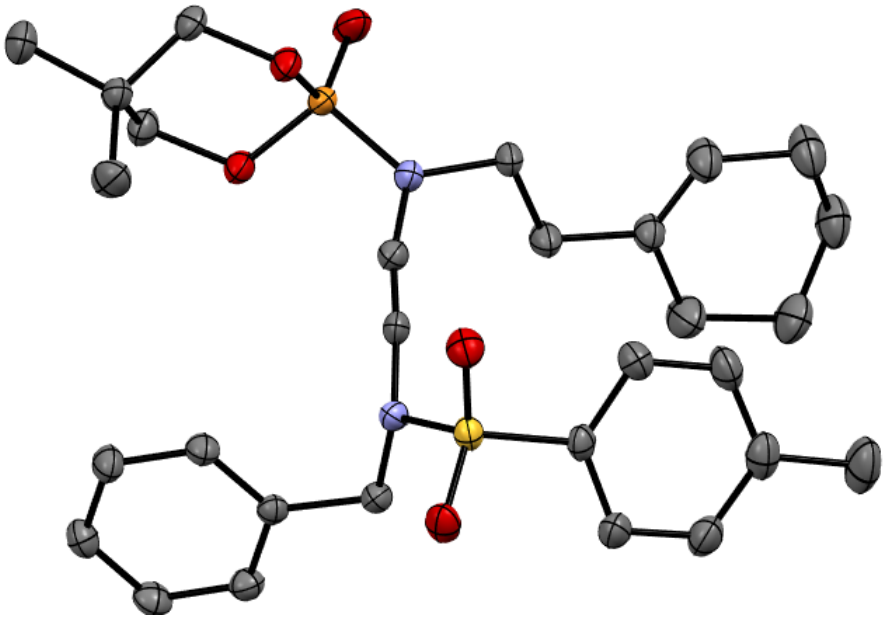

Figure S98: Solid state structure of **148i**, BnTsYndCyclohexenylPs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

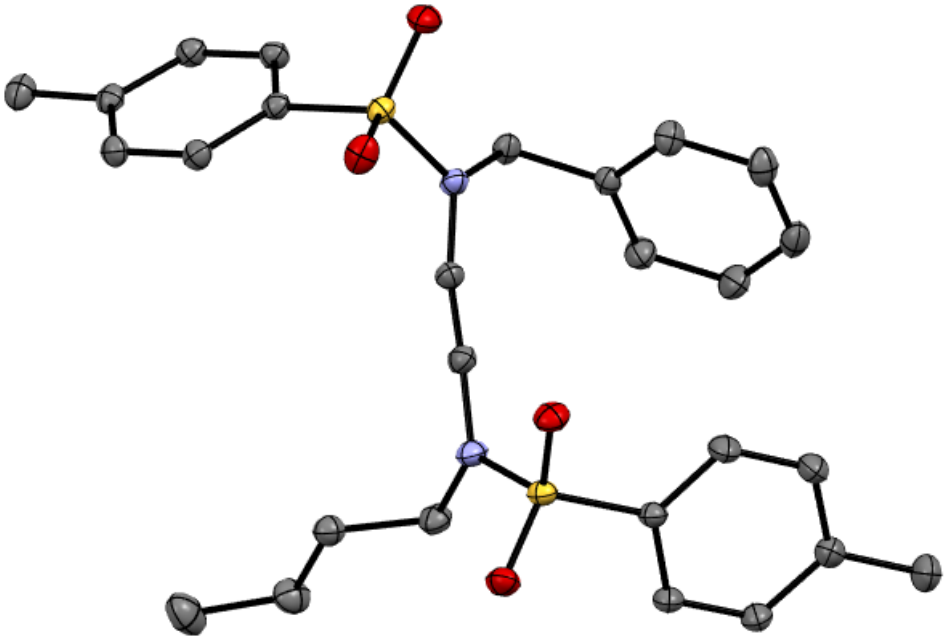

Figure S99: Solid state structure of **148j**, BnTsYndBuTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

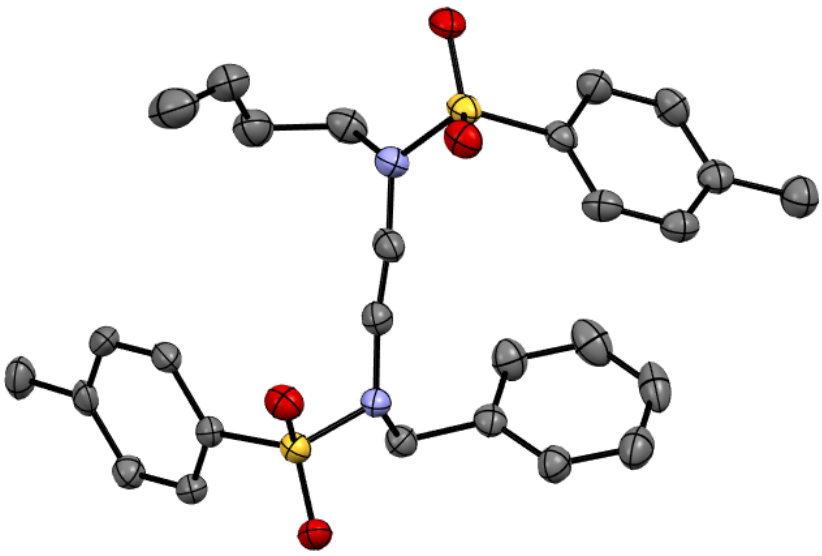

Figure S100: Solid state structure of **148k**, BnTsYndHallTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

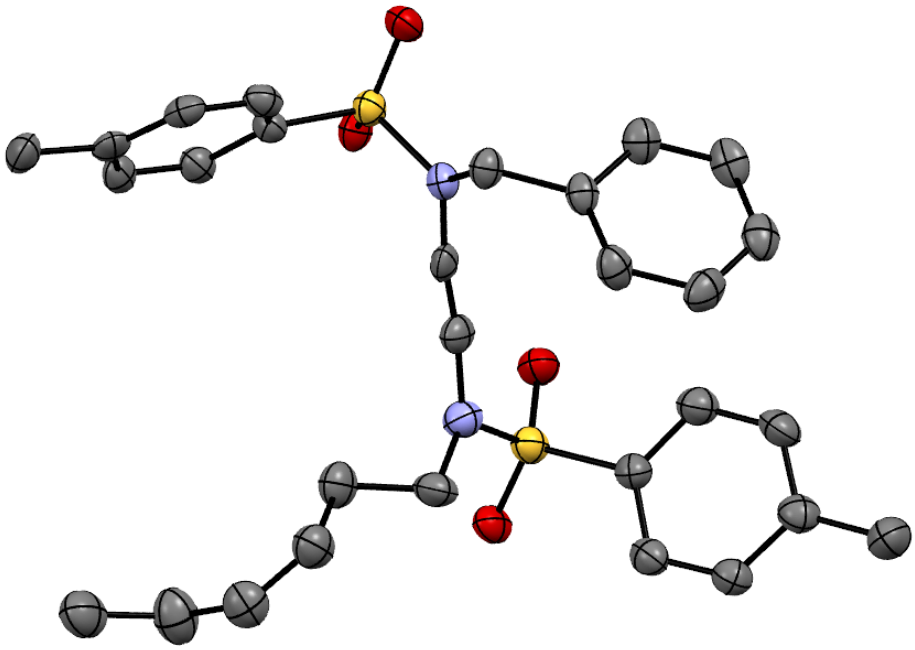

Figure S101: Solid state structure of **148l**, BnTsYndHex-3-Ts. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

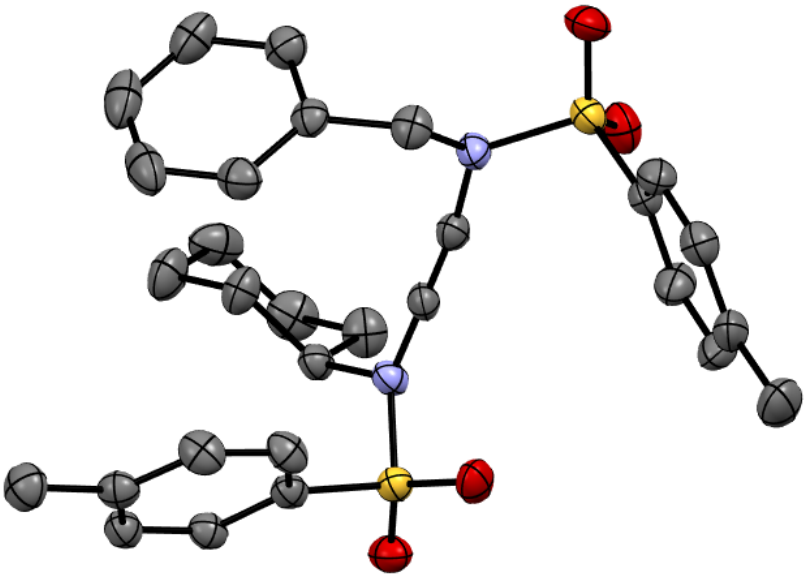

Figure S102: Solid state structure of **148q**, BnTsYndCyTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

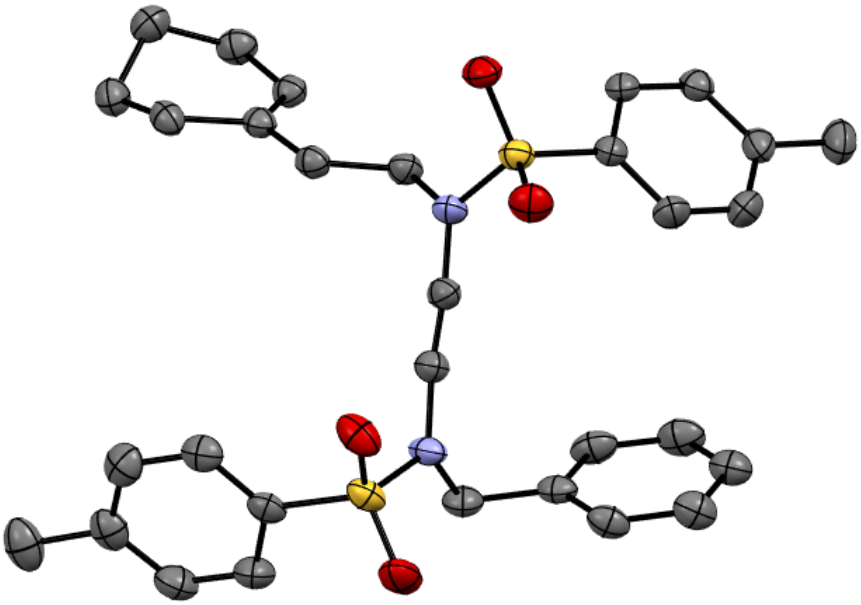

Figure S103: Solid state structure of **148s**, BnTsYndCyclohexenylTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

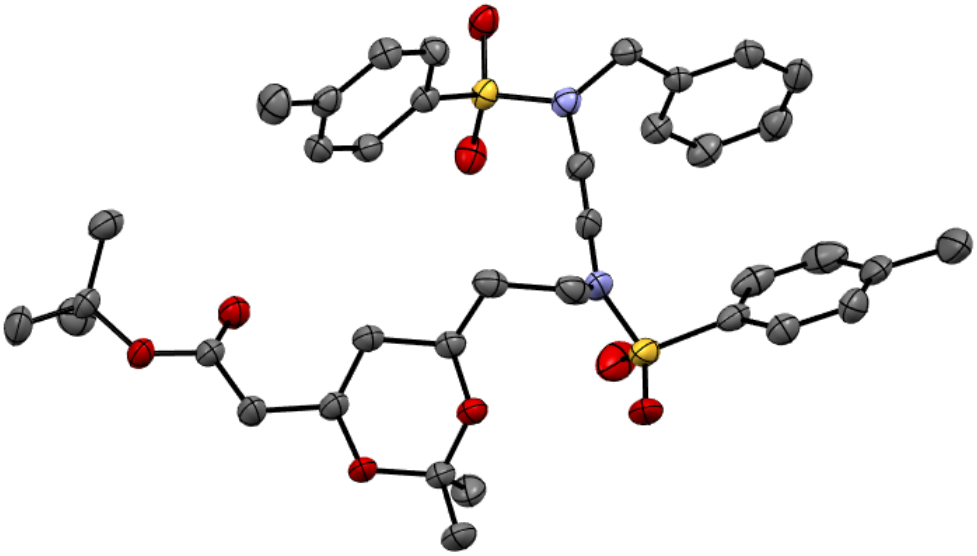

Figure S104: Solid state structure of **148w**, BnTsYndAcetalEsterTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms and co crystallised water molecule have been omitted for clarity.

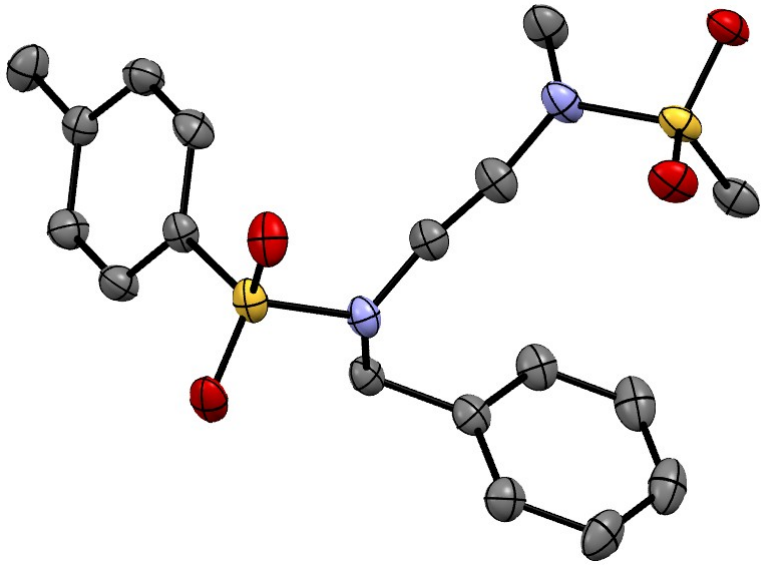

Figure S105: Solid state structure of **148x,** BnTsYndMeMs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

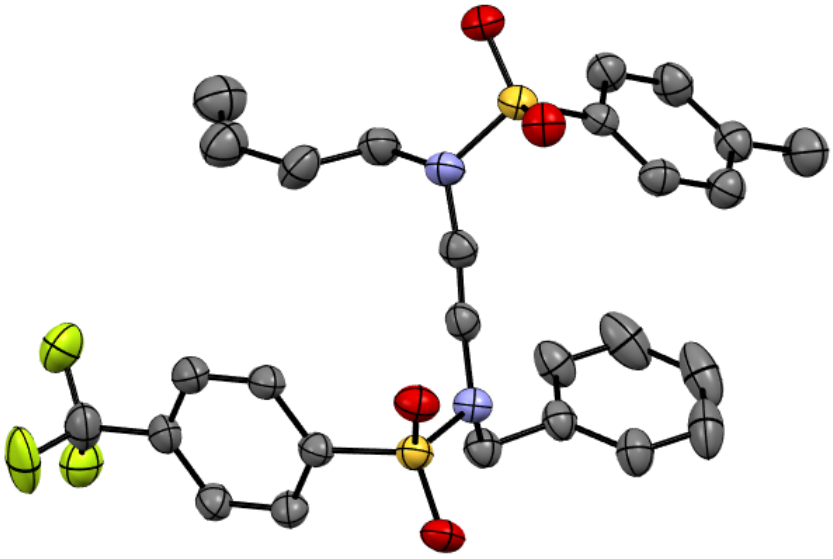

Figure S106: Solid state structure of **160a**, HallTsYndBnTfs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

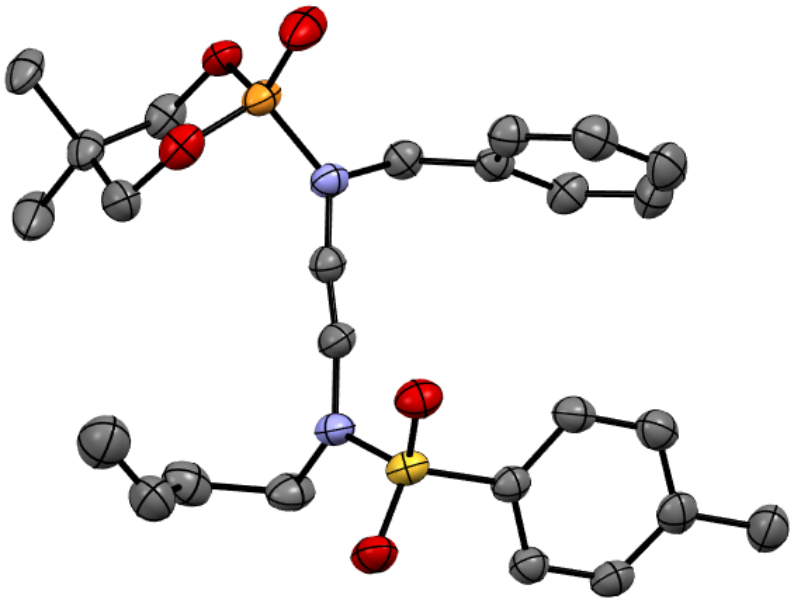

Figure S107: Solid state structure of **160b**, HallTsYndBnPs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

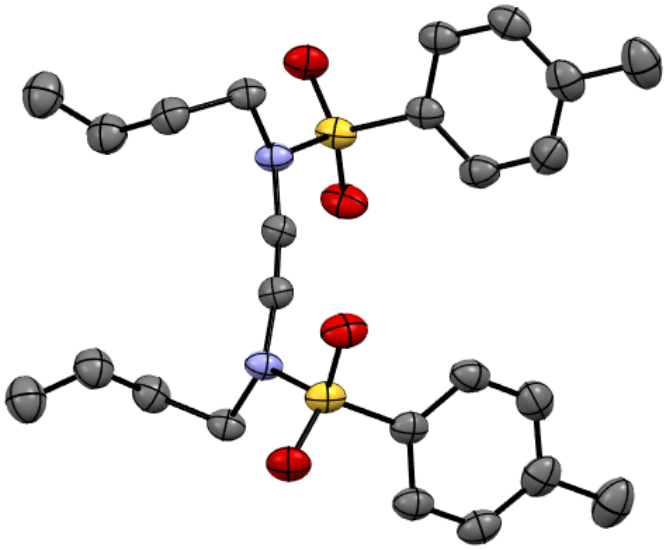

Figure S108: Solid state structure of **160c**, HallTsYndHallTs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

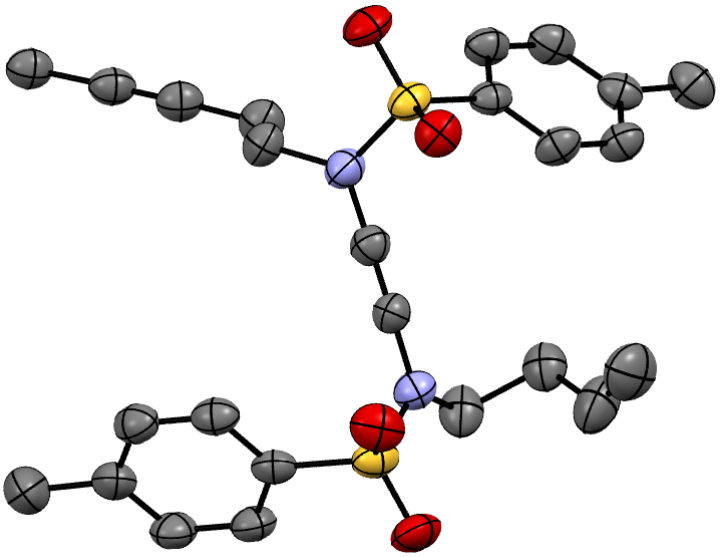

Figure S109: Solid state structure of **160e**, MeYnTsYndHallTs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

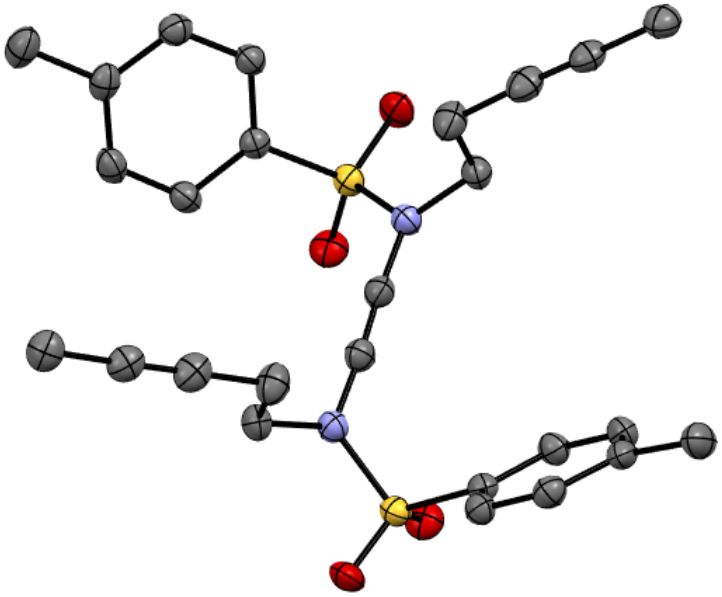

Figure S110: Solid state structure of **160f**, MeYnTsYndMeYnTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

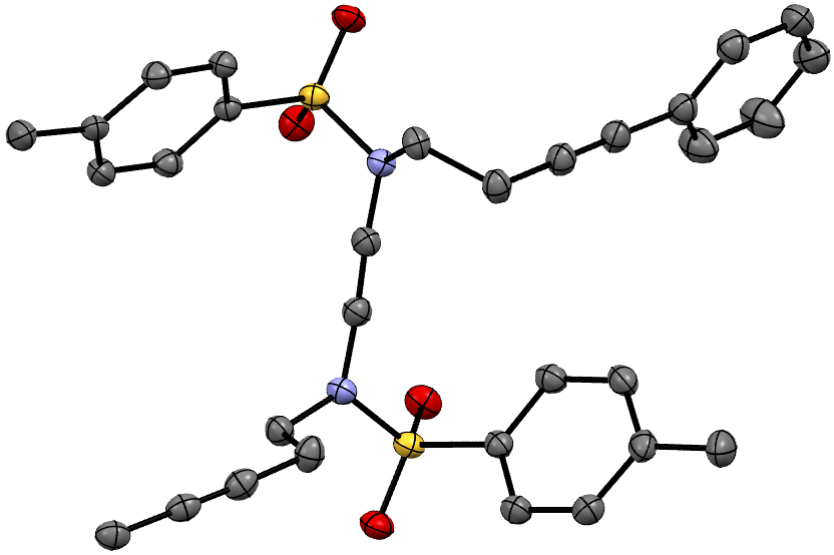

Figure S111: Solid state structure of **160g**, MeYnTsYndPhYnTs.. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

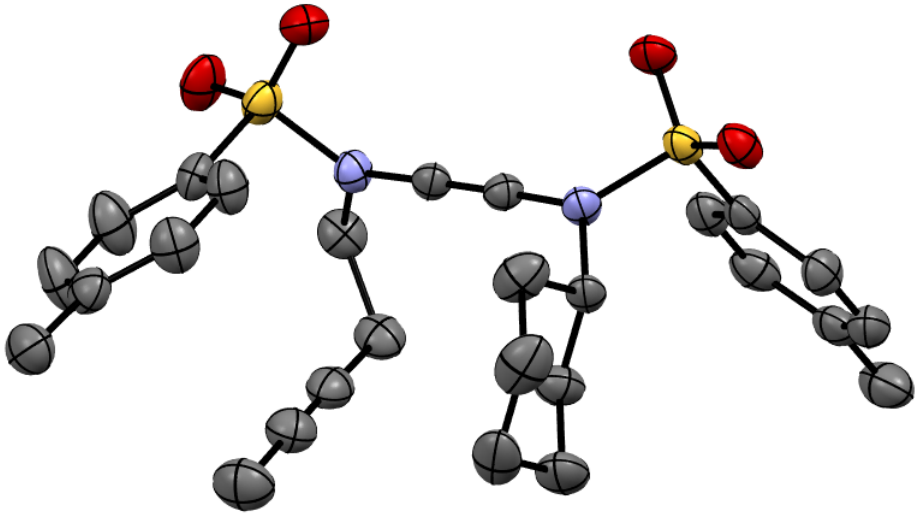

Figure S112: Solid state structure of **160h**, MeYnTsYndCyTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

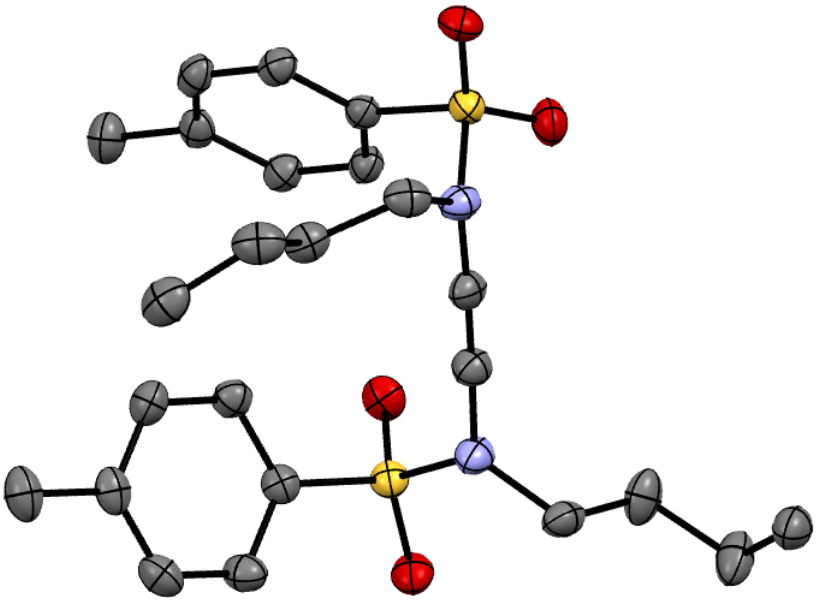

Figure S113: Solid state structure of **160l**, BuTsYndBuTs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

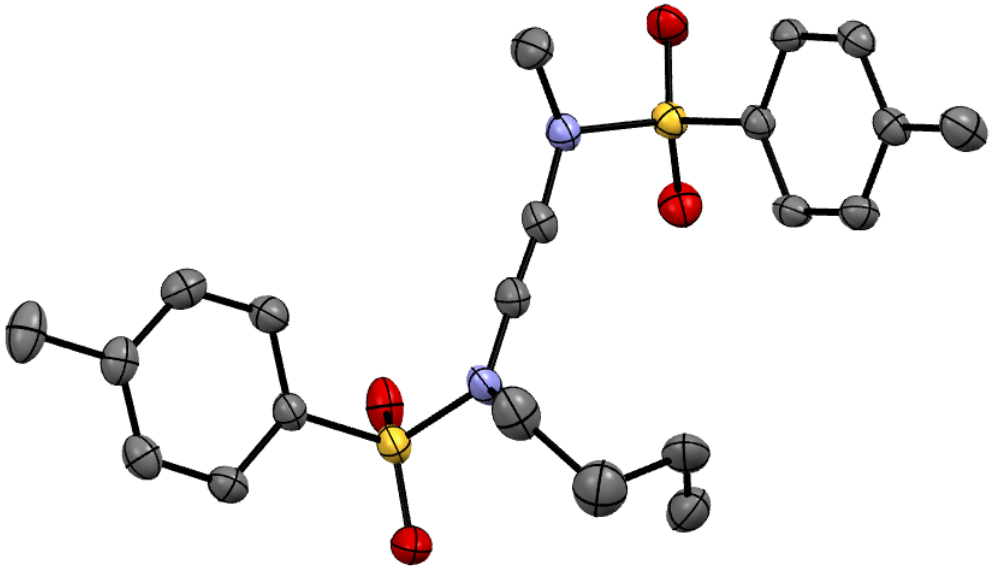

Figure S114: Solid state structure of **160m**, MeTsYndHallTs. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms have been omitted for clarity.

3.2b *Bromoketene Aminals, Applications and Miscellaneous.*

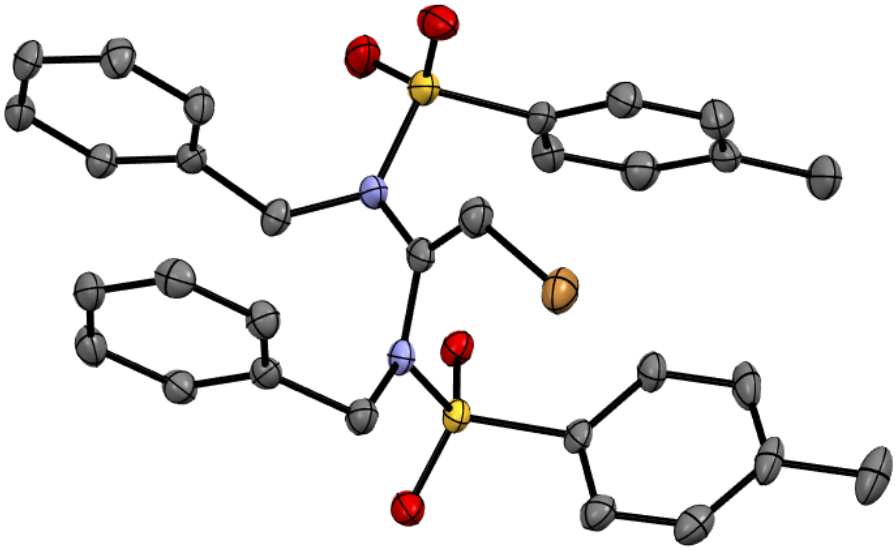

Figure S115: Solid state structure of **155b**, BnBKA. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

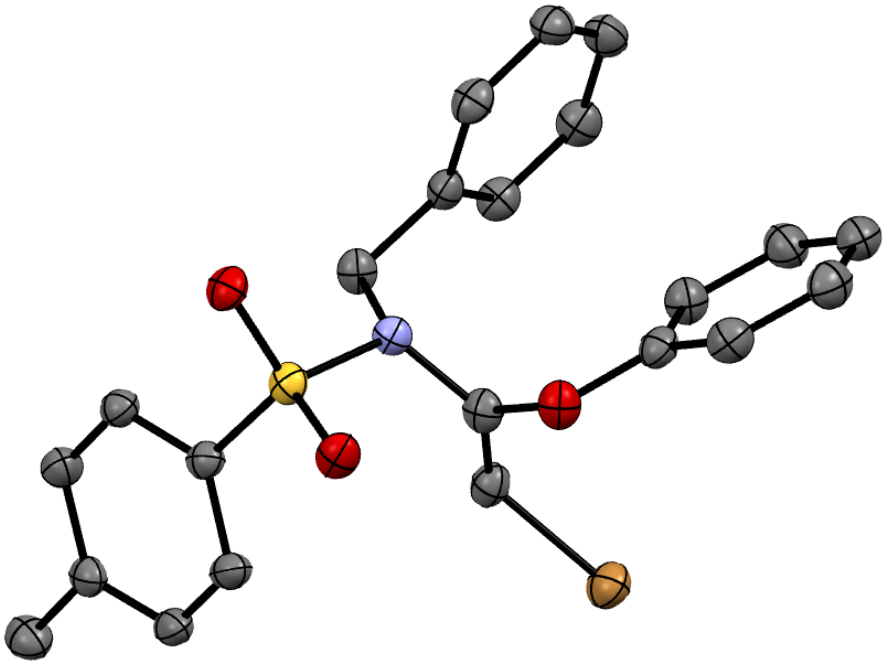

Figure S116: Solid state structure of **155c**, PhOBKA. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

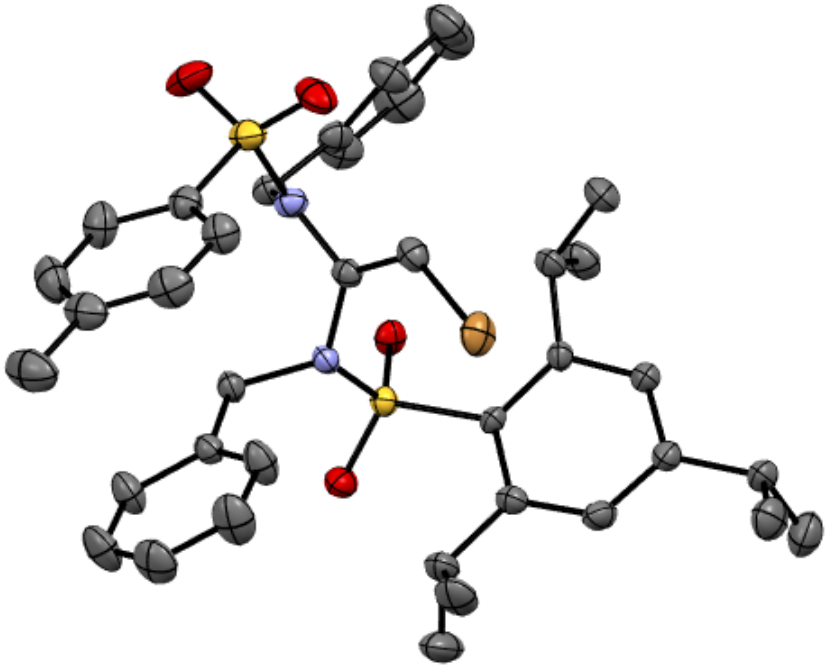

Figure S117: Solid state structure of **155d**, BnTrisBKA. Displacement ellipsoid plots are drawn at 30% probability. Disordered components and hydrogen atoms are omitted for clarity.

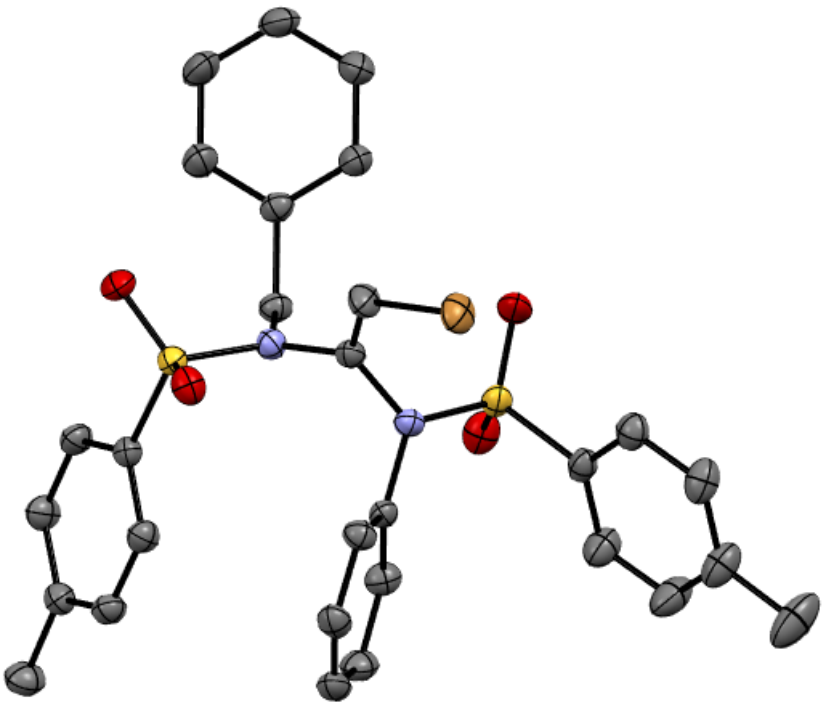

Figure S118: Solid state structure of **155e**, PhTsBKA. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

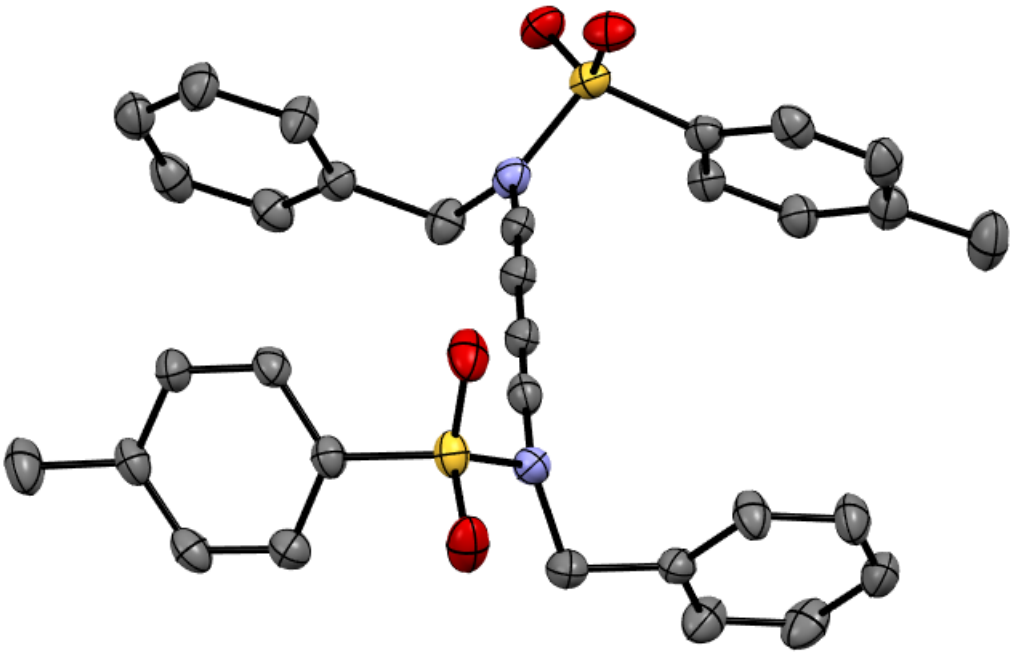

Figure S119: Solid state structure of **159**, BnTsDiyne. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

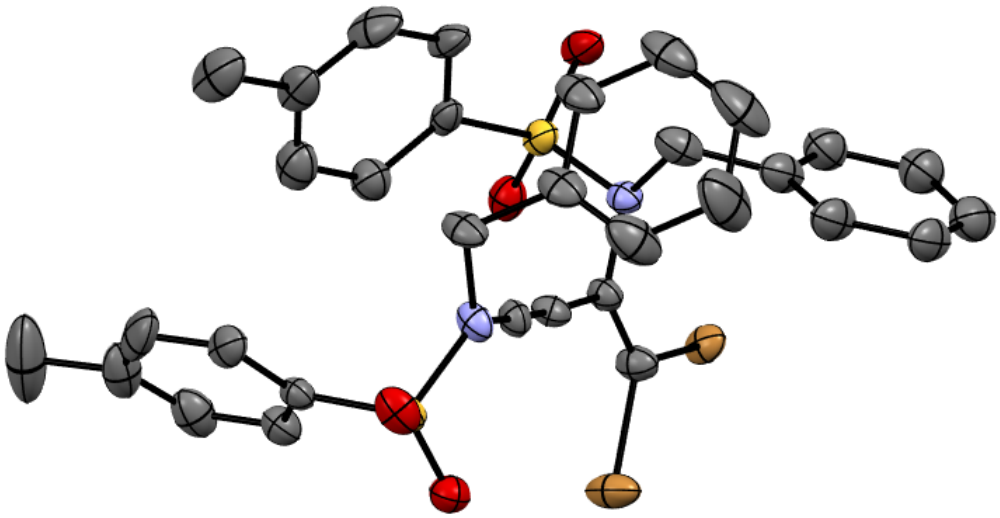

Figure S120: Solid state structure of **162**, BnYnBrDimer. Displacement ellipsoid plots are drawn at 50% probability. Disordered components, solvent molecule and hydrogen atoms are omitted for clarity.

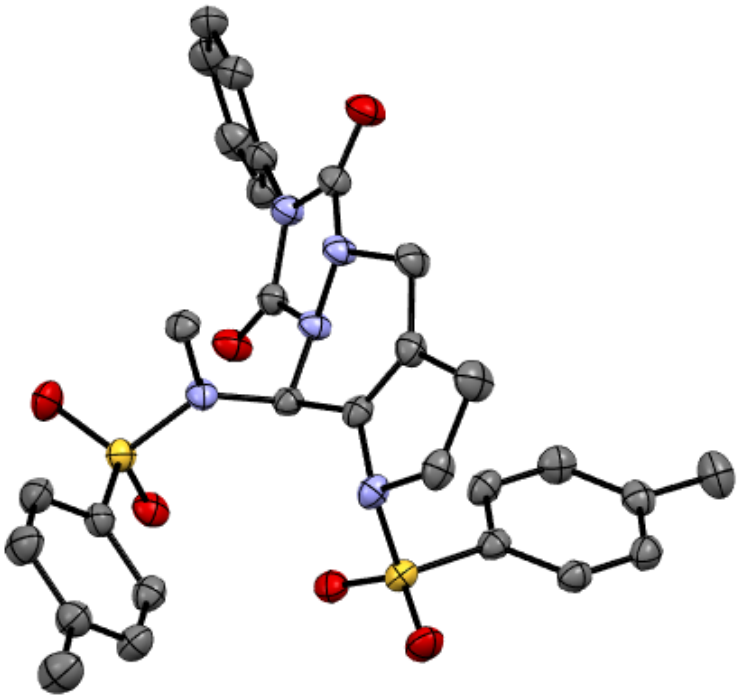

Figure S121: Solid state structure of **182**, MeHallCycloisomDA-PTAD. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

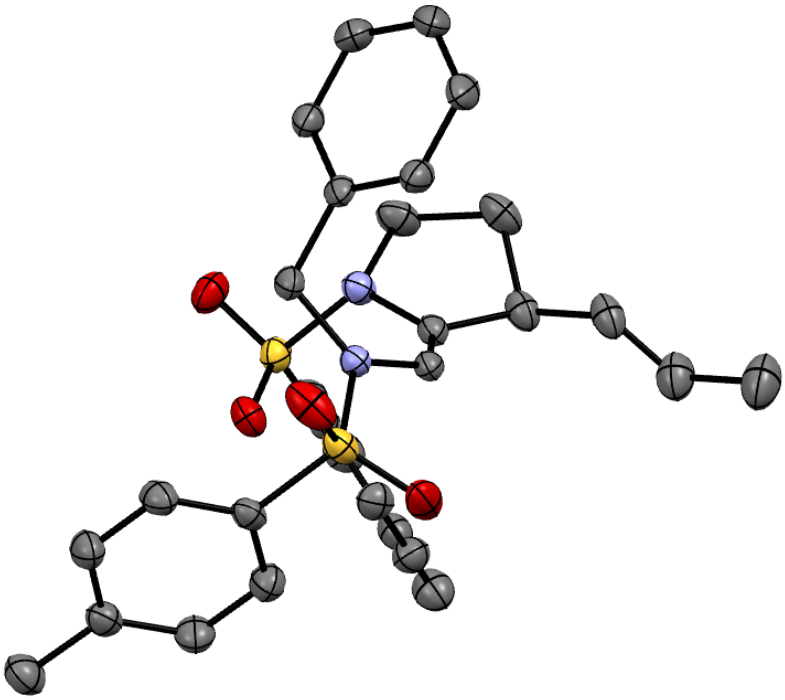

Figure S122: Solid state structure of **183**, BnHex3Cycloisom. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

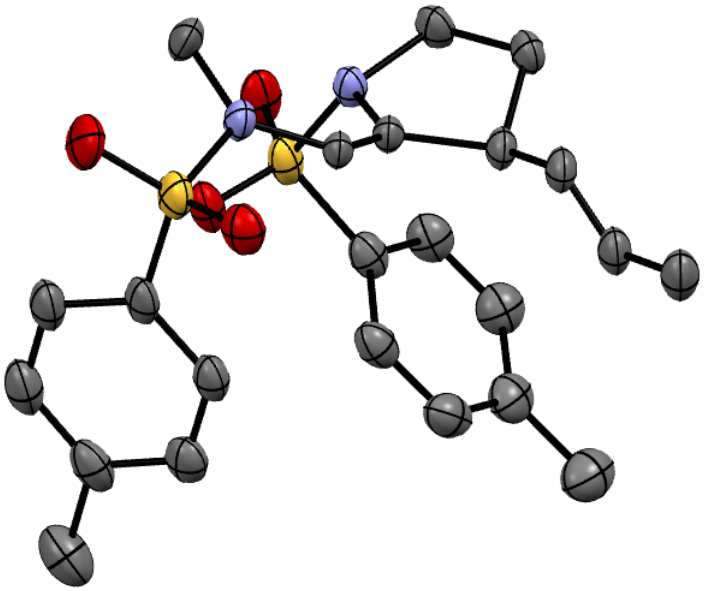

Figure S123: Solid state structure of **184**, MeHex3Cycloisom. Displacement ellipsoid plots are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

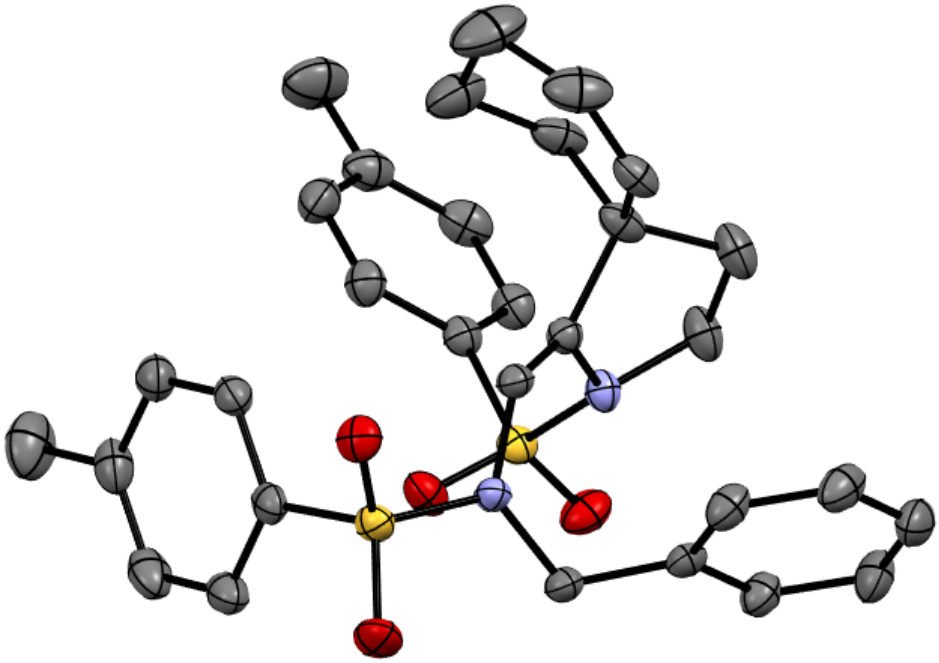

Figure S124: Solid state structure of **185**, BnCyclohexCycloisom. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

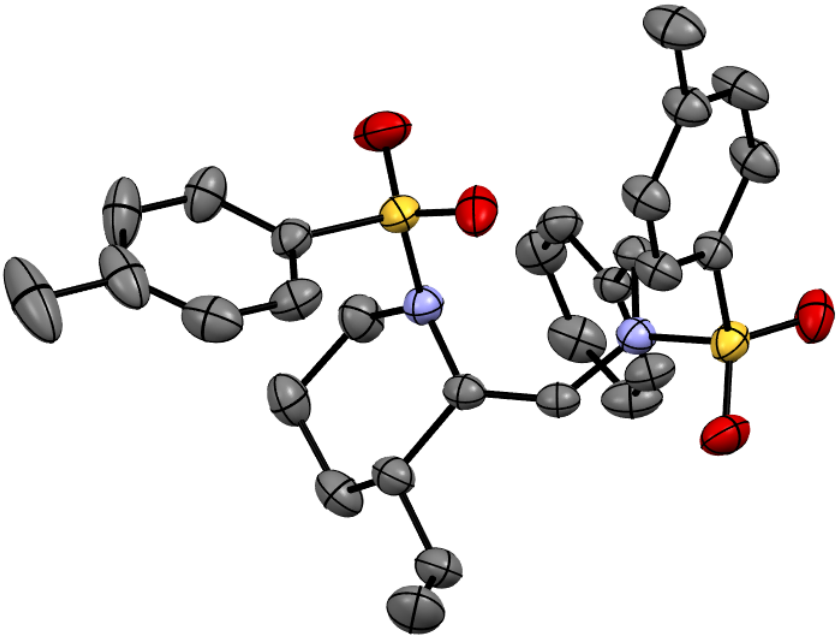

Figure S125: Solid state structure of **186**, BnHex4Cycloisom. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

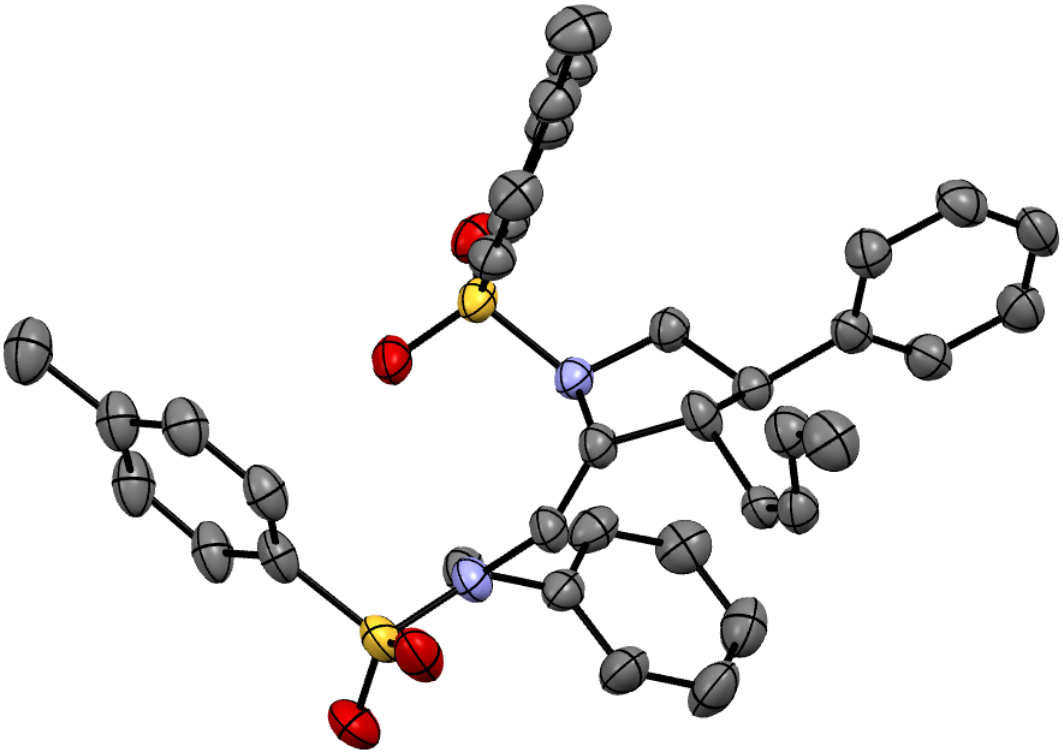

Figure S126: Solid state structure of **187**, BnCyclopropylCycloisom. Displacement ellipsoid plots are drawn at 50% probability. Disordered components corresponding to (*E*)-**57**, solvent molecules and hydrogen atoms are omitted for clarity.

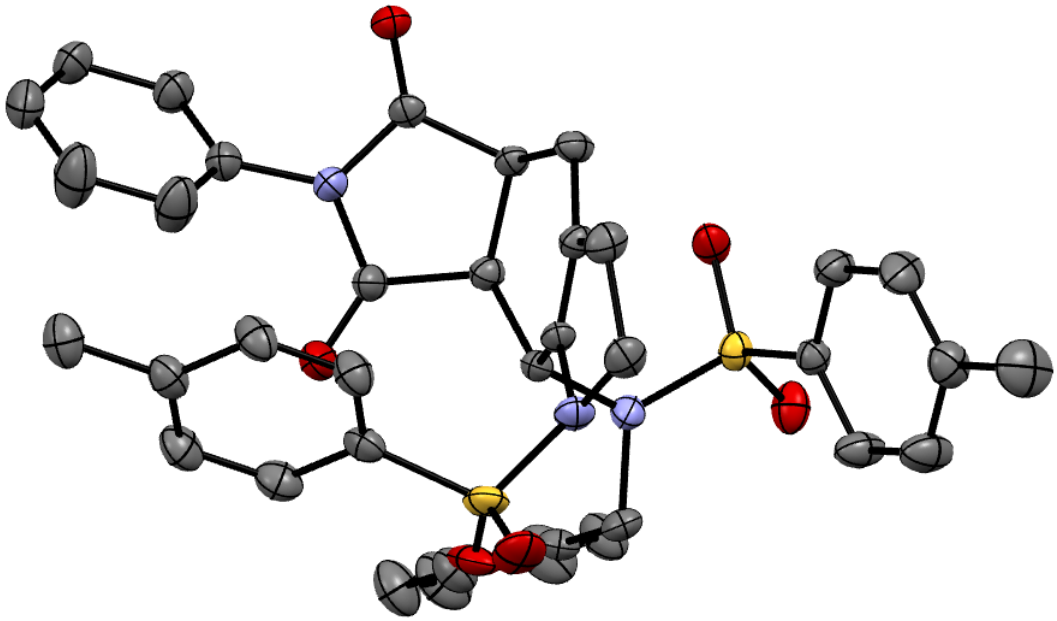

Figure S127: Solid state structure of **188**, BnHallCycloisomDA-NPh. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

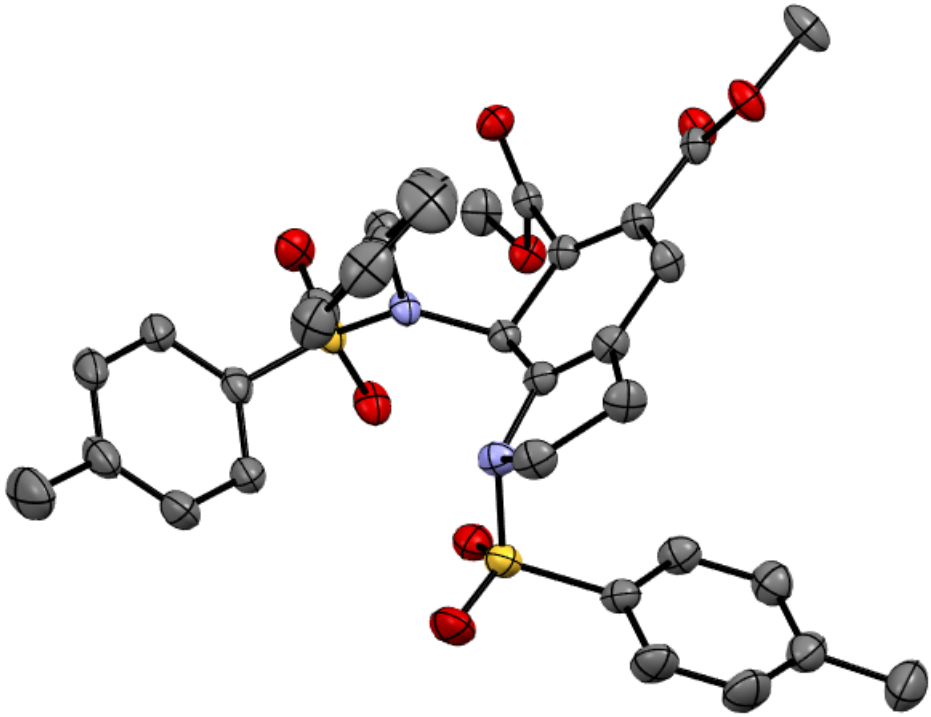

Figure S128: Solid state structure of **189**, BnHallCycloisomDA-DMAD. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

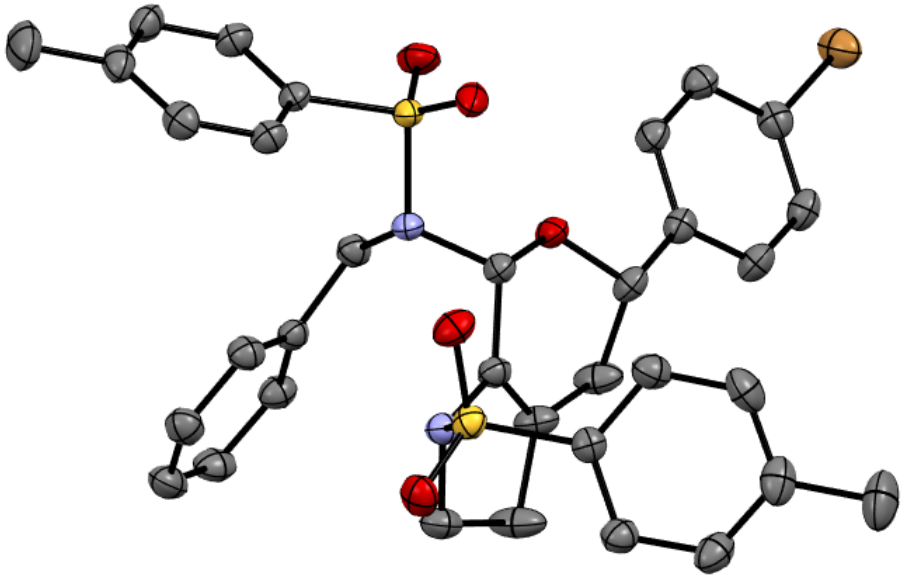

Figure S129: Solid state structure of **191**, BnHallCycloisomDA-CHO. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

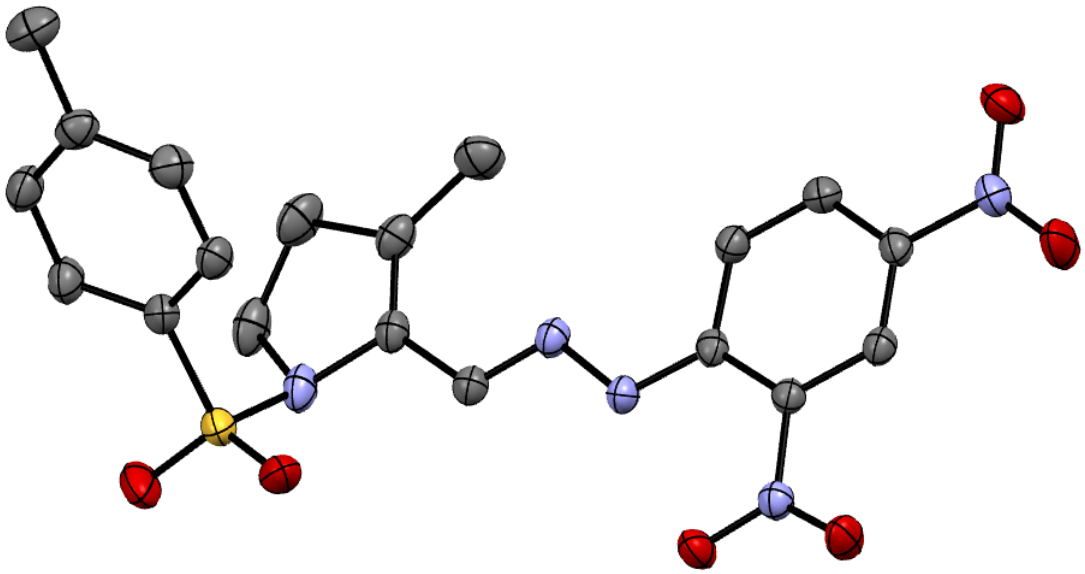

Figure S130: Solid state structure of **192'**, BnHallCycloisomDNP. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

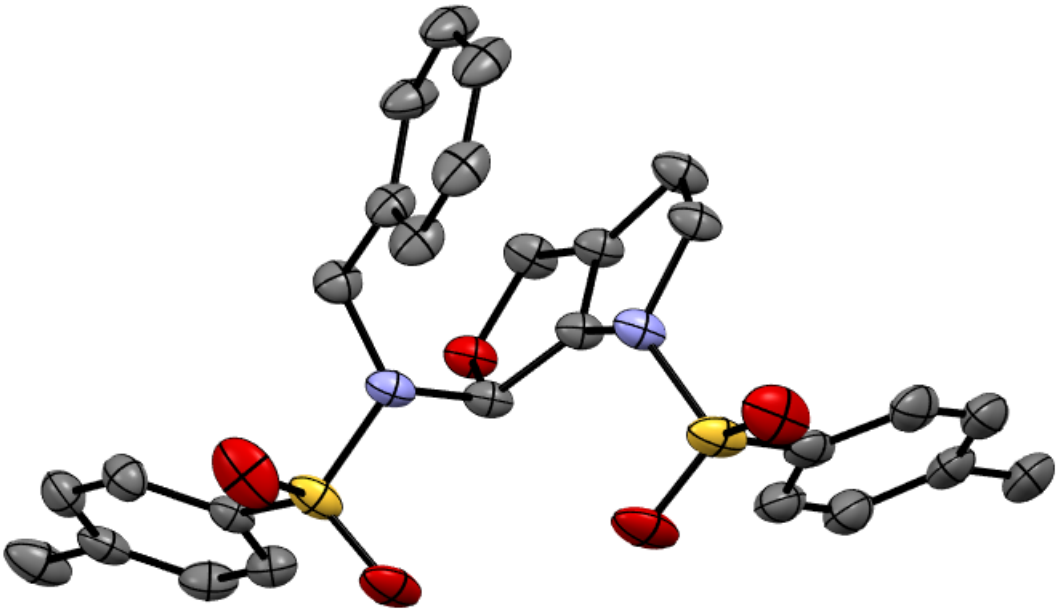

Figure S131: Solid state structure of **193**, Dihydrofuran. Displacement ellipsoid plots are drawn at 30% probability. Disordered components and hydrogen atoms are omitted for clarity.

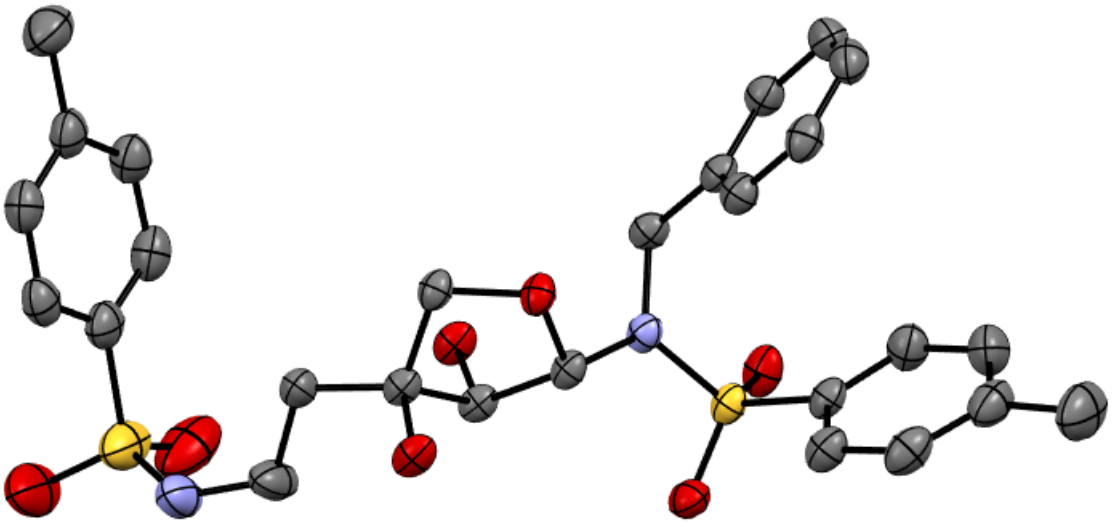

Figure S132: Solid state structure of **195**, Sugar. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

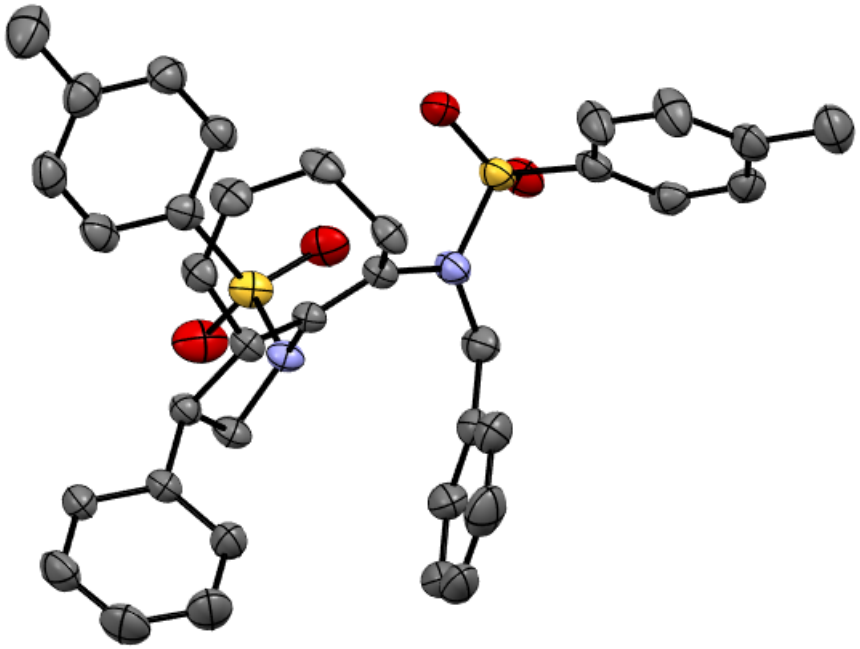

Figure S133: Solid state structure of (-)-**197**, [5+2]. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

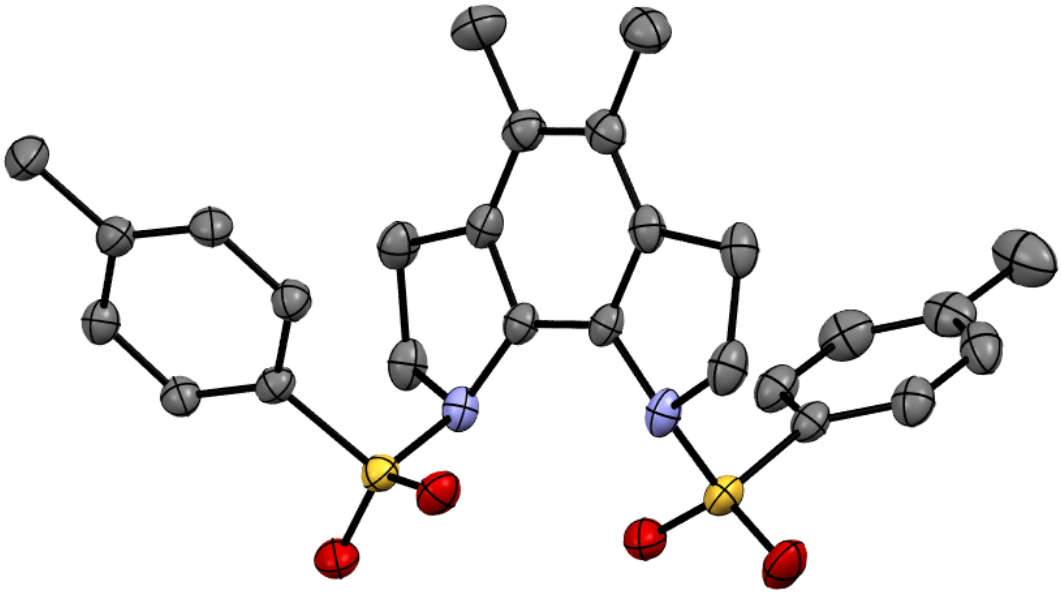

Figure S134: Solid state structure of **198**, 2+2+2-Me. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

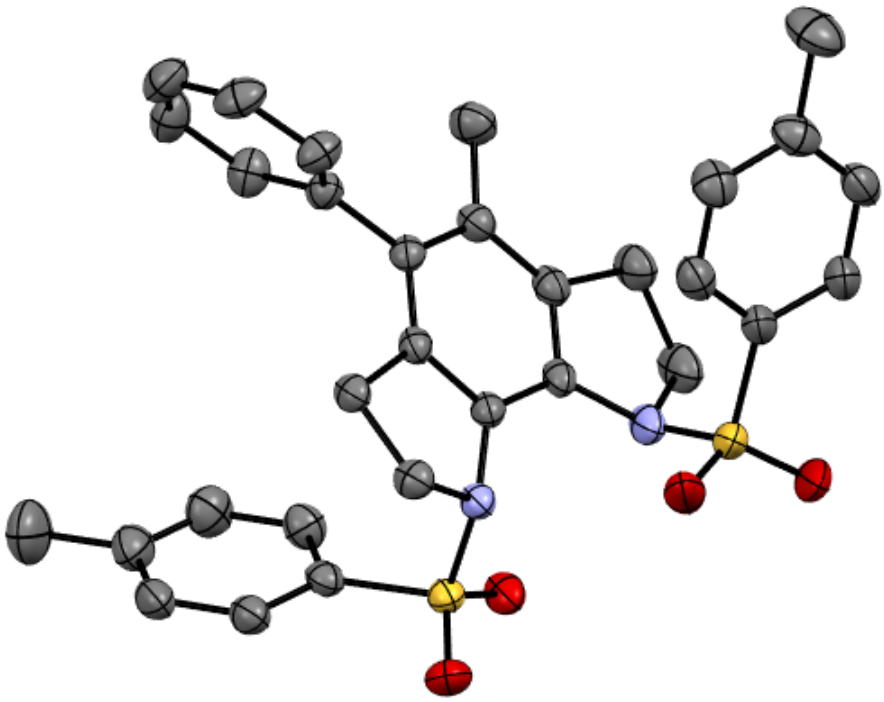

Figure S135: Solid state structure of **199**, 2+2+2-Ph. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

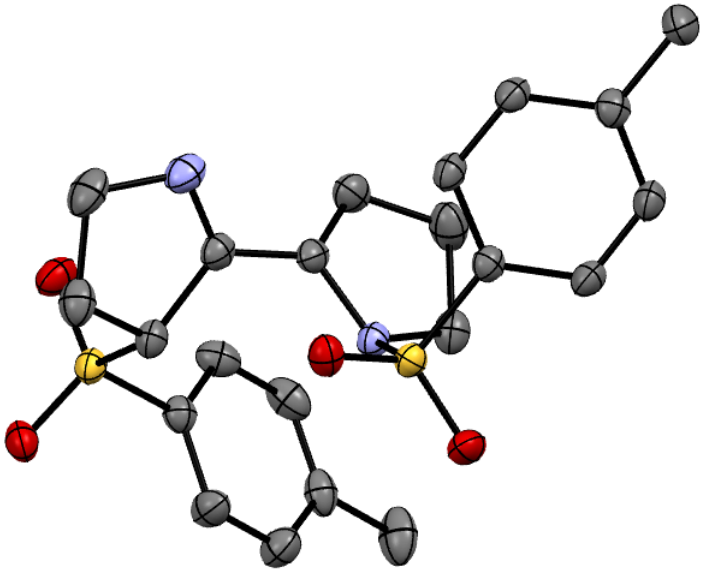

Figure S136: Solid state structure of **200**, GII-dipyrrole. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

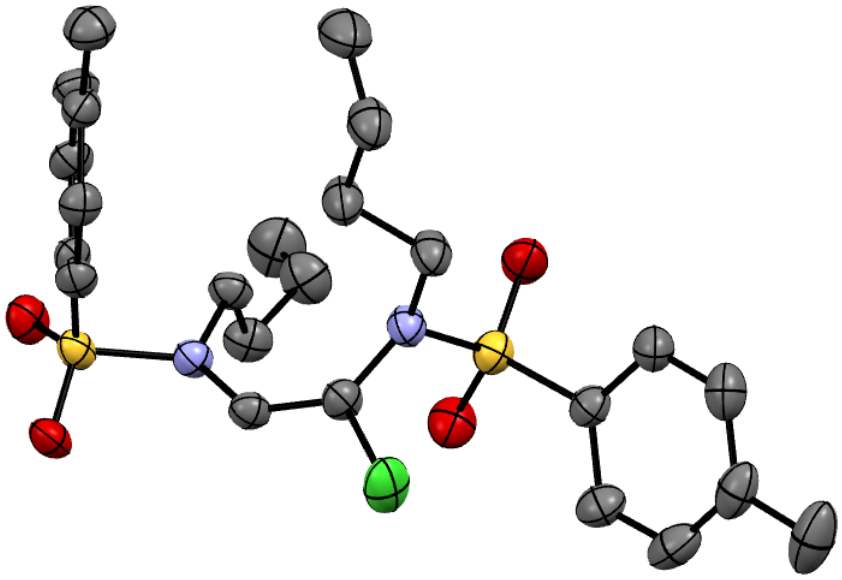

Figure S137: Solid state structure of **203**, GII-endiamide. Displacement ellipsoid plots are drawn at 30% probability. Disordered components and hydrogen atoms are omitted for clarity.

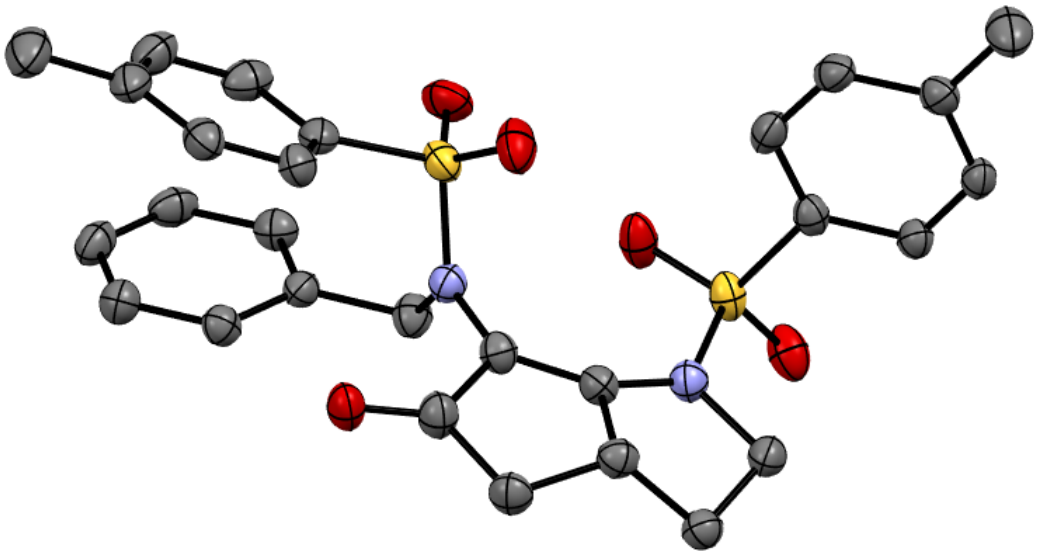

Figure S138: Solid state structure of **205**, PK. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

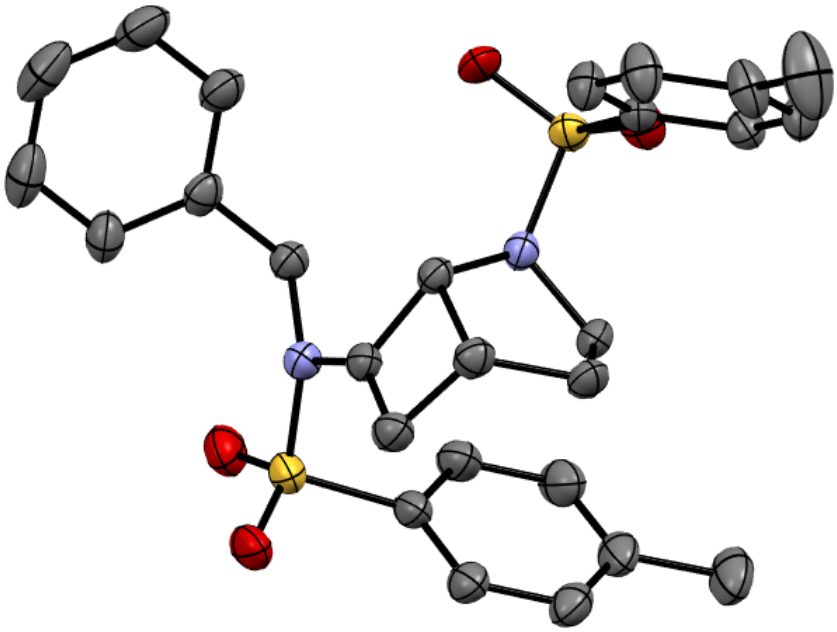

Figure S139: Solid state structure of **206**, Cyclobutene. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

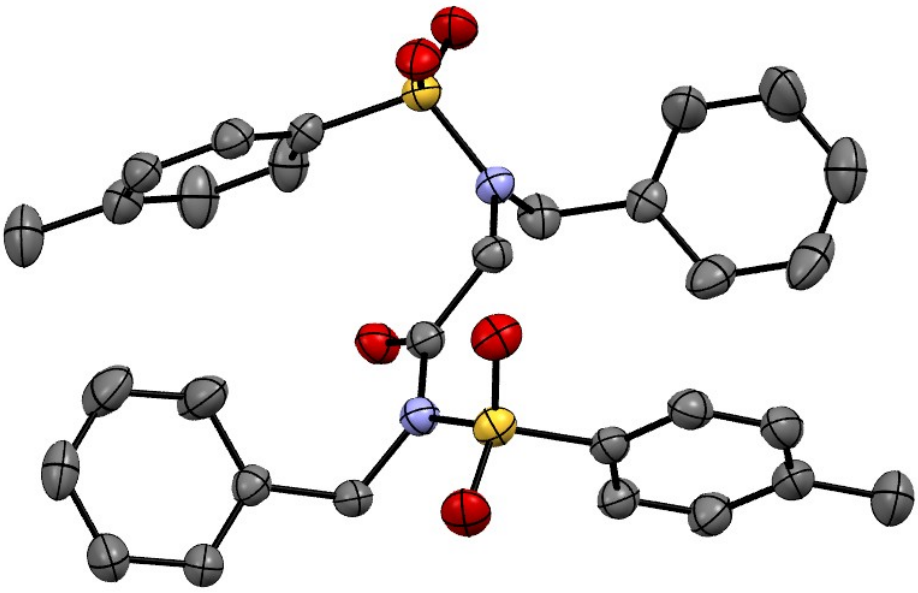

Figure S140: Solid state structure of **218**, BnYndHydrate. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

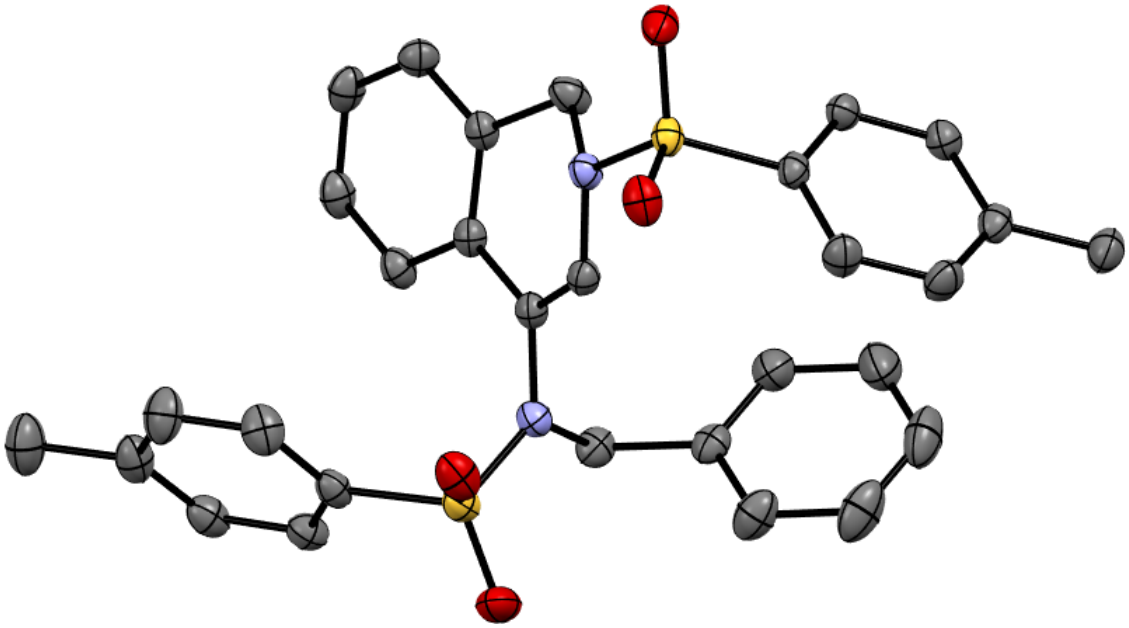

Figure S141: Solid state structure of **219**, Dihydroisoquinoline. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

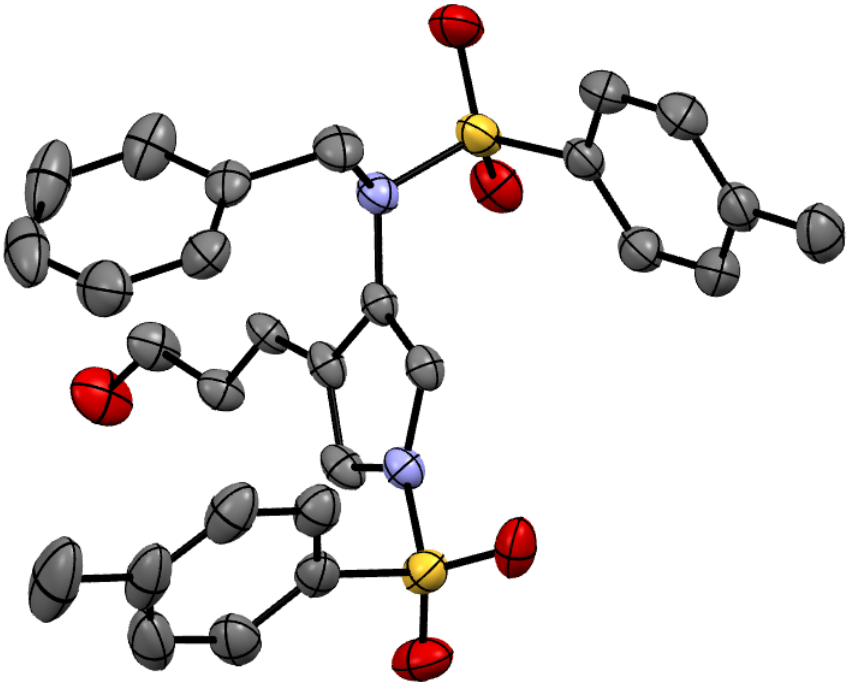

Figure S142: Solid state structure of **222**, Pyrrole. Displacement ellipsoid plots are drawn at 50% probability. Disordered components corresponding to (*Z*)-**222** and hydrogen atoms are omitted for clarity.

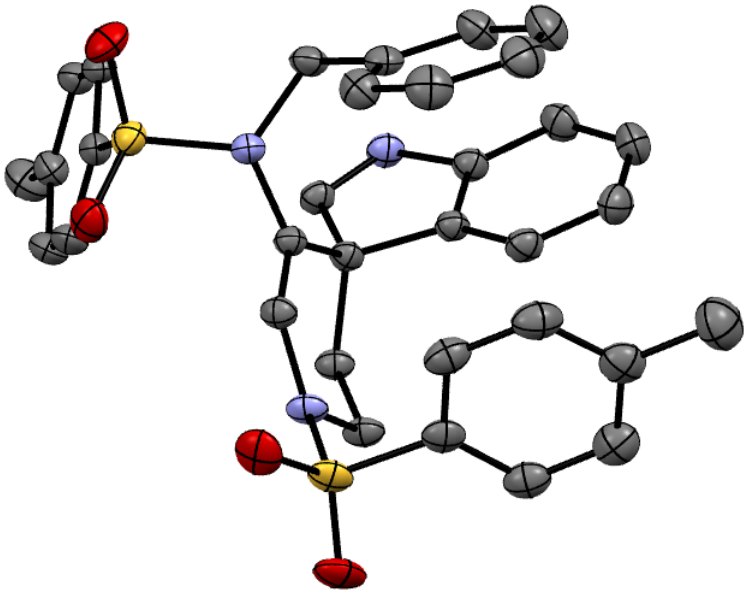

Figure S143: Solid state structure of **228**, Spiroindolenine. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

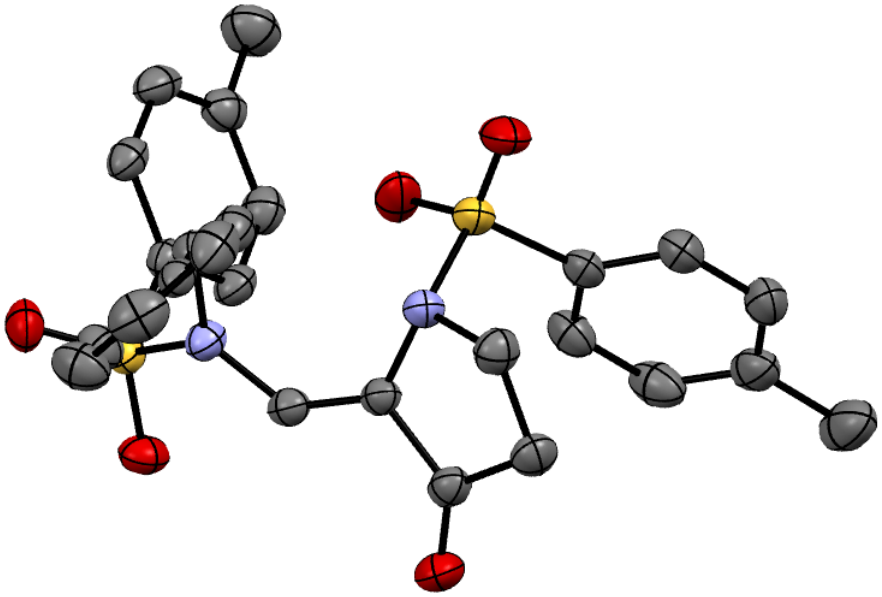

Figure S144: Solid state structure of **229**, Pyrrolidinone. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

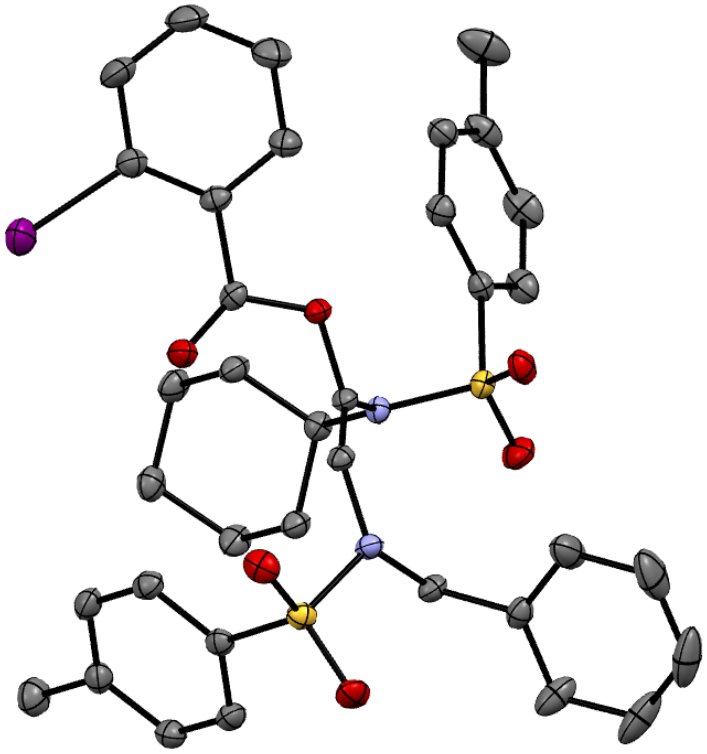

Figure S145: Solid state structure of **231**, CyTsYndBzOH-adduct. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

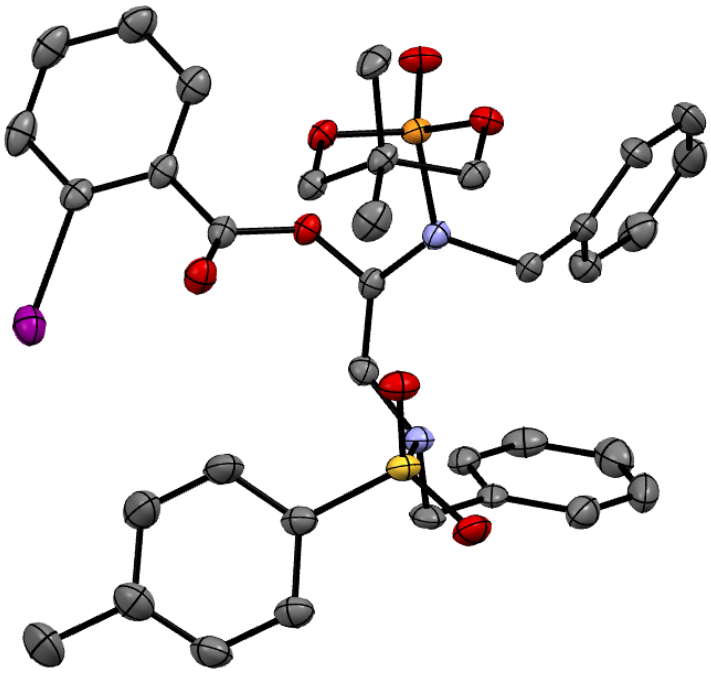

Figure S146: Solid state structure of **232a**, BnPsYndBzOH-adduct. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

3.3 Physical and Spectroscopic Properties of Ynamides and Yndiamides.

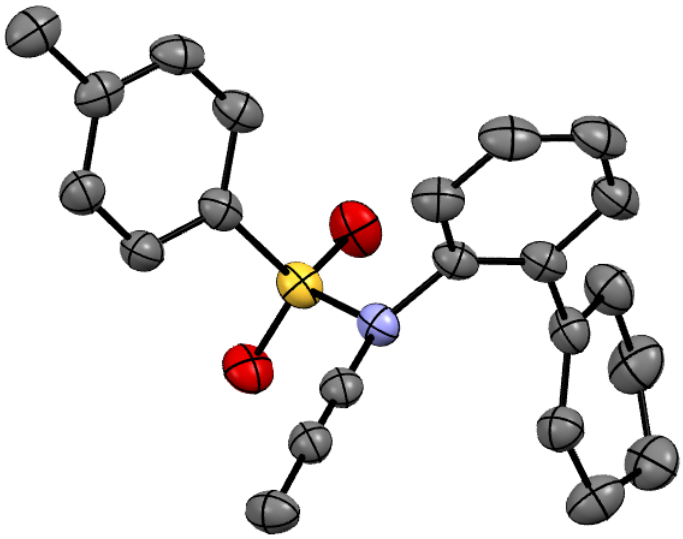

Figure S147: Solid state structure of Ph*o*-CyTsYnMe. Displacement ellipsoid plots are drawn at 50% probability. Disordered components and hydrogen atoms are omitted for clarity.

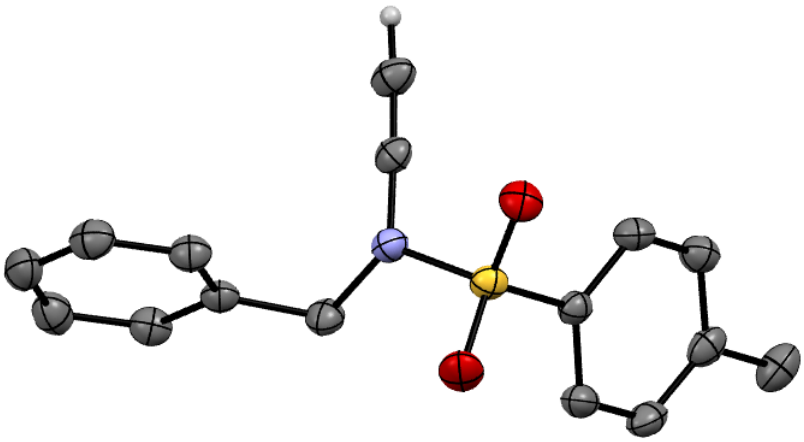

Figure S148: Solid state structure of BnTsYnH. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms, except on the alkyne, are omitted for clarity.

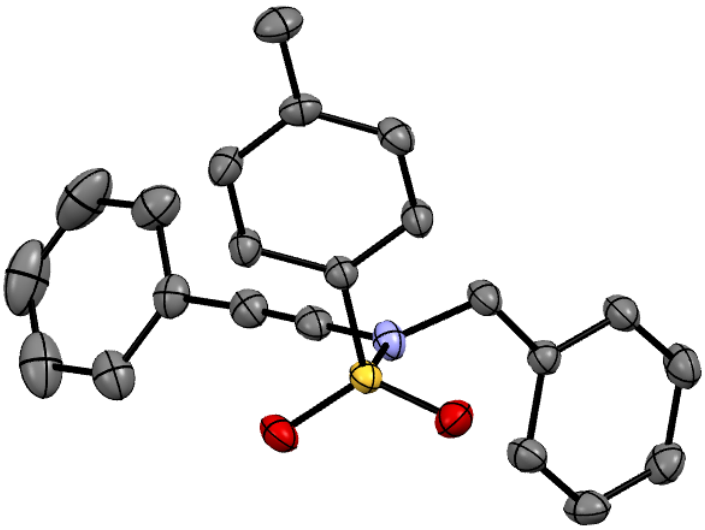

Figure S149: Solid state structure of BnTsYnPh. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

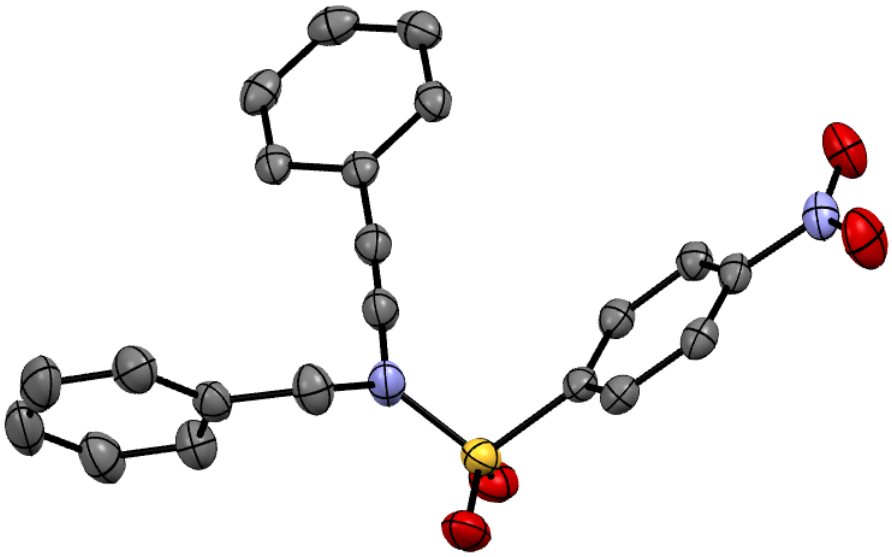

Figure S150: Solid state structure of BnNsYnPh. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

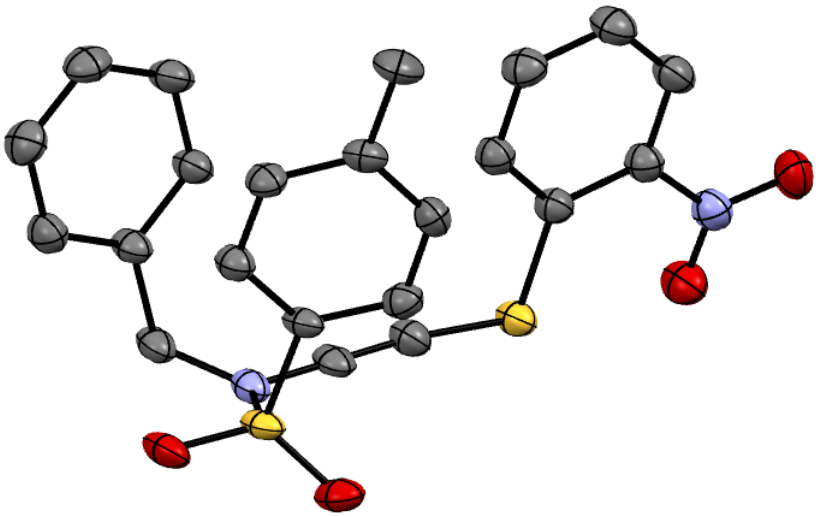

Figure S151: Solid state structure of $BnTsYnSPhNO_2$. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

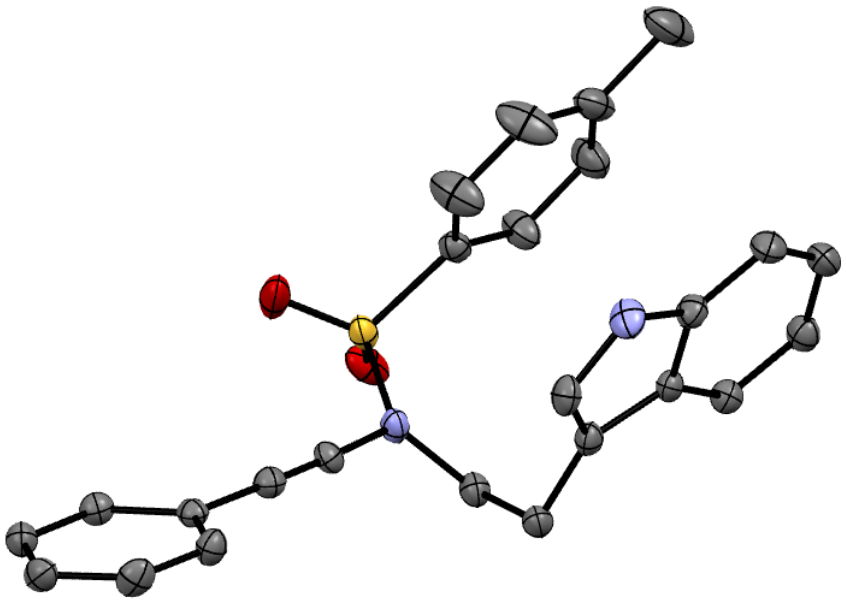

Figure S152: Solid state structure of IndoleTsYnPh. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

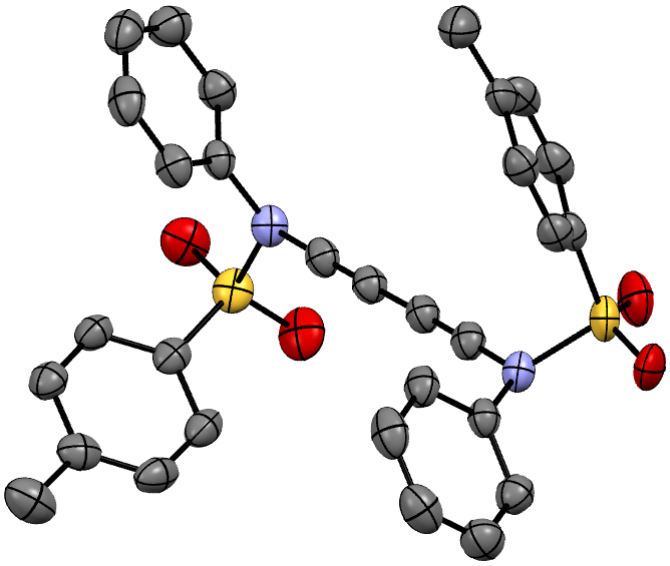

Figure S153: Solid state structure of PhTsYnYnPhTs. Displacement ellipsoid plots are drawn at 50% probability. Hydrogen atoms are omitted for clarity.