Electronic Supplementary Material (ESI) for CrystEngComm.

4-[4-(4-methoxyphenyl)-1,3-butadienyl]-1methylpyridinium 4-chlorobenzene sulphonate (MBMPCBS) – An efficient nonlinear optical crystal with superior thermal stability

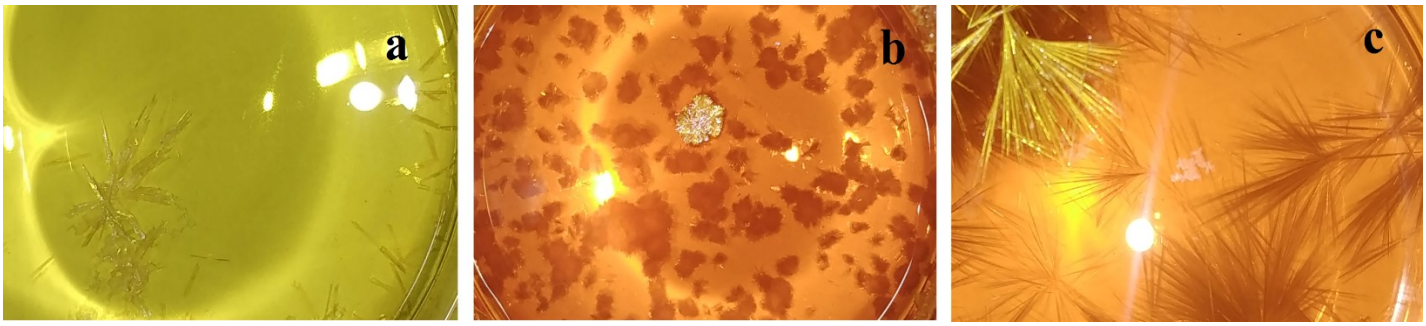

Fig. S1. MBMPCBS Crystals grown in (a) millipore water (b) methanol (c) methanol–acetonitrile solvent systems.

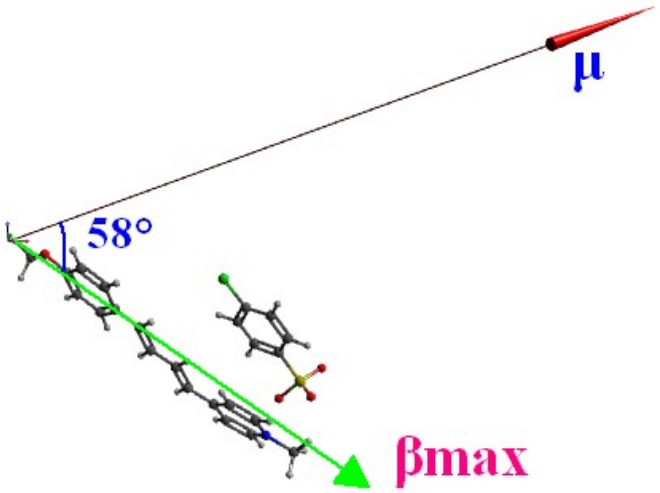

Fig. S2. Angle θ (μ, β_{max}) between the direction of the dipole moment μ and the main direction of the first hyperpolarizability $\beta_{max.}$ of MBMPCBS.

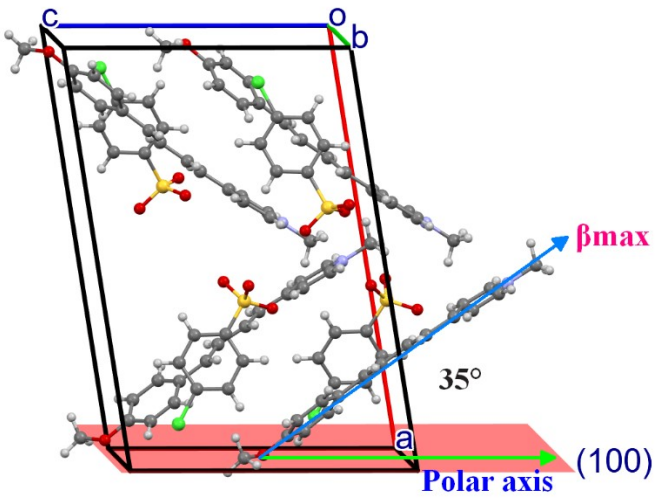

Fig. S3. Angle between the molecular hyperpolarizability β_{max} and the polar *c- axis* for MBMPCBS.

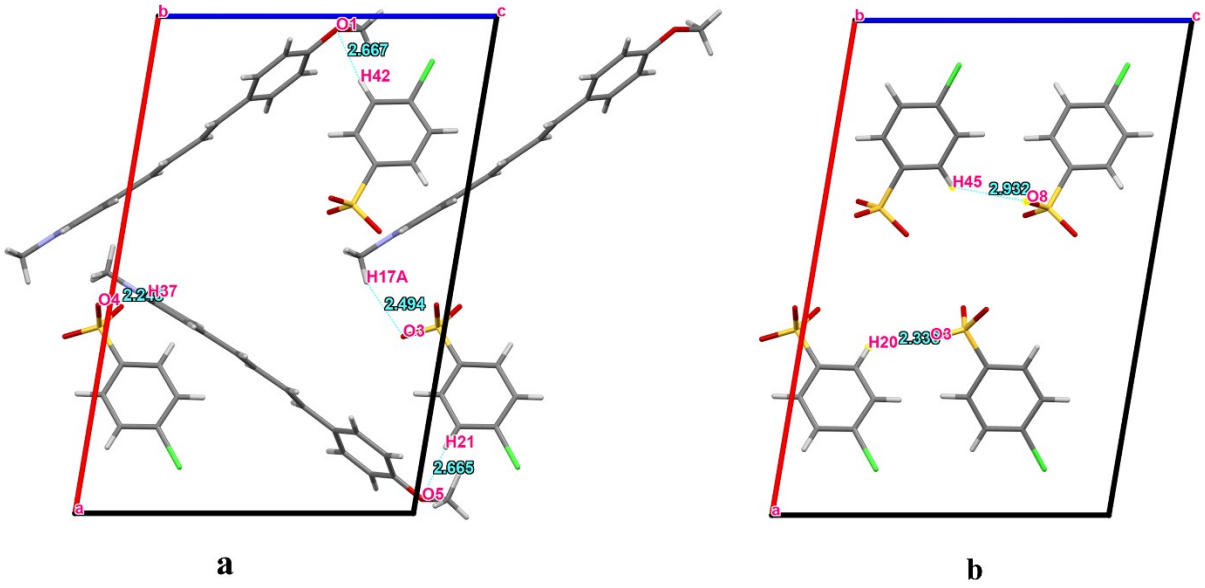

Fig. S4. Hydrogen bonding in MBMPCBS (a) between cations and anions and (b) between anions.

^{1}H NMR of MBMPCBS.

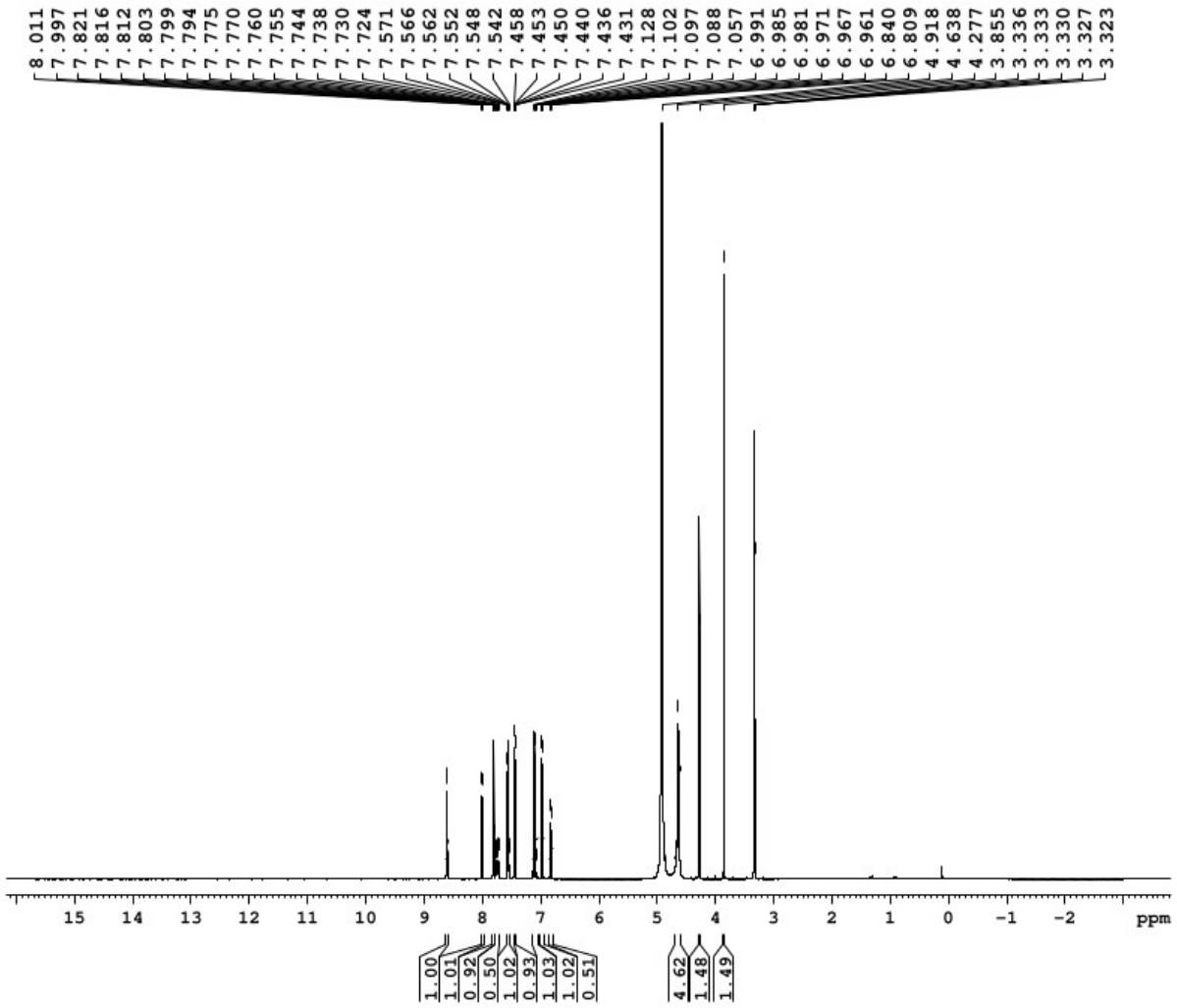

Fig. S5. ^{1}H NMR of MBMPCBS.

MBMPCBS, ^{1}H NMR (500 MHz, CD_3OD, δ): 8.616 (2H, d, J=7.0Hz, $C_5H_4N^+$), 8.011(2H,d, J=7.0 Hz, $C_5H_4N^+$), 7.821 (2H, d, J = 13.5 Hz, $C_6H_4Cl\text{-}SO_3^-$), 7.775 (2H, d, J = 22.5 Hz, C_6H_4Cl-SO3), 7.571 (2H, d, J = 14.5Hz, $C_6H_4\text{-}OCH_3$), 7.458 (2H, d, J = 13.5 Hz $C_6H_4\text{-}OCH_3$), 7.102 (1H, d, J = 7Hz, $C_6H_4\text{-}OCH_3{=}C_5H_4\ N^+$), 6.840 (1H, d, J = 15.5 Hz, $C_6H_4\text{-}OCH_3{=}C_5H_4\ N^+$), 4.277 (3H, s, $C_6H_4\text{-}OCH_3$), 3.855 (3H,s, $C_5H_4N^+{-}CH_3$).

[1]H NMR of MBMPI.

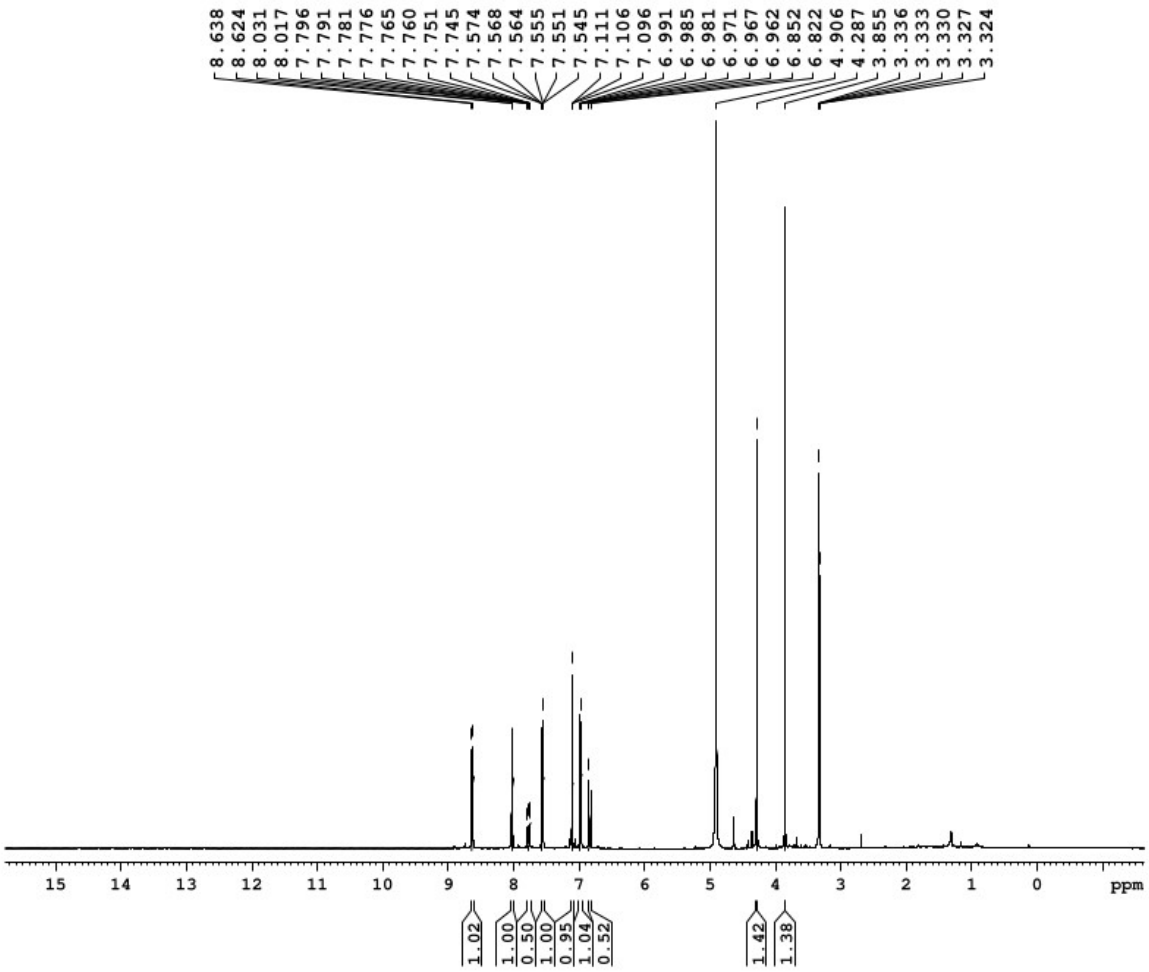

Fig. S6. [1]H NMR of MBMPI.

MBMPI, [1]HNMR (500 MHz, CD_3OD, δ) 3.855 (3H, s), 4.287 (3H, s), 6.852 (1H, d, J = 15 Hz), 6.981, (2H, d, J = 5 Hz), 7.0–7.1 (2H, m), 7.551 (2H, d, J = 3 Hz), 7.776 (1H, dm, J = 5.5 Hz), 8.031 (2H, d, J = 7 Hz), and 8.638 (2H, d, J = 7 Hz).

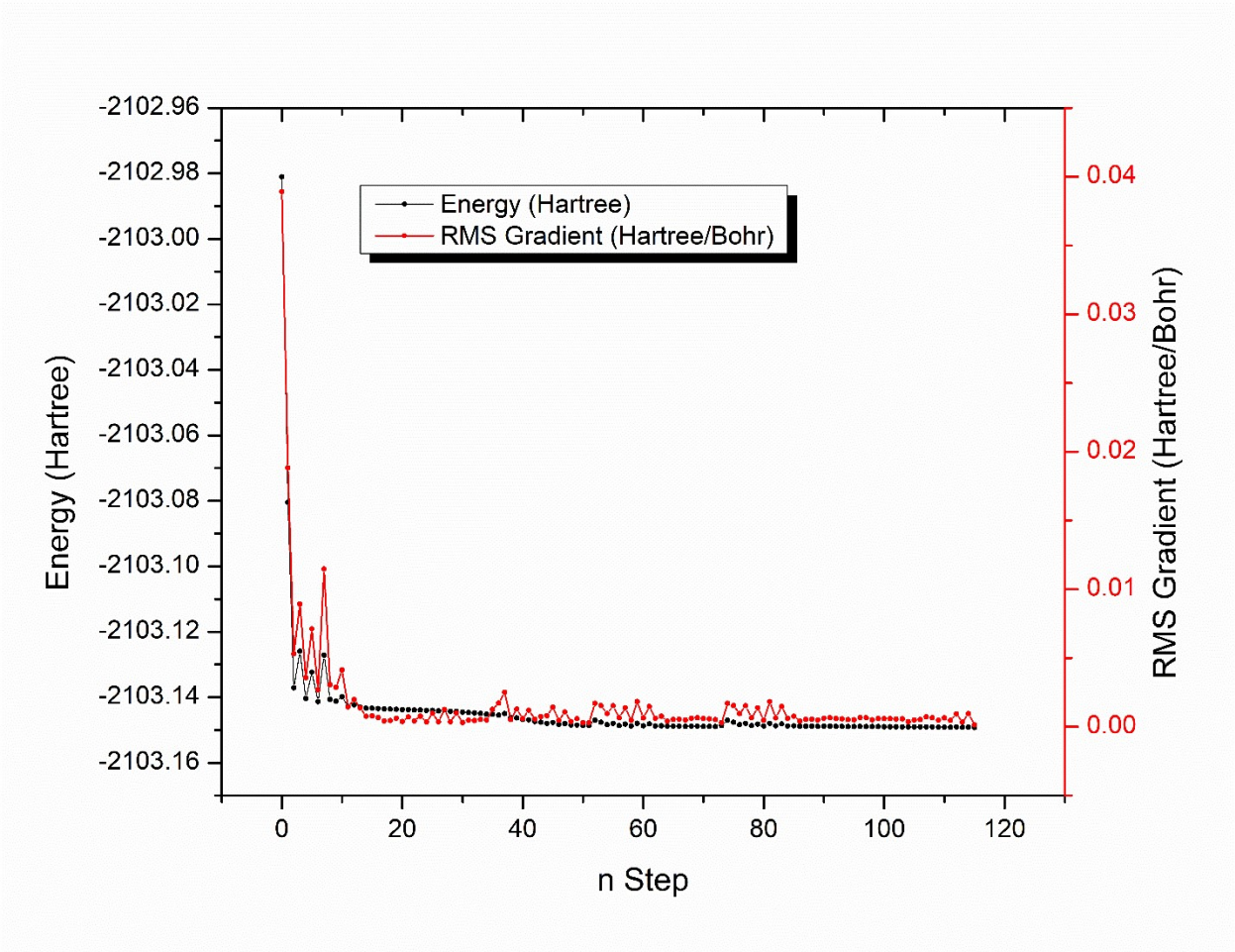

Fig. S7. Energy convergence plot depicting a global minimum.

Table S1. NLO results from DFT calculations.

B3LYP/6–311+G (d,p)	**Average polarizability**		**Polarizability anisotropy**		**1st hyperpolarizability**		**2nd hyperpolarizability**	
	AU	10^{-24} Esu	AU	10^{-24} Esu	AU	10^{-30} Esu	AU	10^{-34} Esu
Urea	28.28878	4.192	17.845397	2.645	90.456874	0.7815	8017.4222	0.04038
MBSC	323.14854	47.89	221.95955	32.89	8603.2476	74.32	294995.66	1.486
DAST	367.3717326	54.4445	180.9794424	26.8212	14128.03362	122.052	374932.556	1.88842
MBMPCBS (Present work)	402.10166	59.59	234.68301	34.78	16880.376	145.8	1015960.7	5.117

Table S2. Crystallography data of MBMPCBS

Identification code	Shelx	
Empirical formula	C_{23} H_{22} Cl N O_4 S	
Formula weight	443.92	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 18.8216(2) Å	α= 90°
	b = 9.2134(2) Å	β= 99.552°
	c = 12.6540(4) Å	γ= 90°
Volume	2163.92(10) $Å^3$	
Z	4	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	0.303 mm^{-1}	
F(000)	928	
Crystal size	0.300 x 0.250 x 0.250 mm^3	
Theta range for data collection	3.116 to 24.997°.	
Index ranges	-22<=h<=22, -10<=k<=10, -15<=l<=14	
Reflections collected	36832	
Independent reflections	36832 [R(int) = ?]	
Completeness to theta = 24.997°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6354	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	36832 / 176 / 602	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1462	
R indices (all data)	R1 = 0.0726, wR2 = 0.1582	
Absolute structure parameter	-0.07(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.388 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for MBMPCBS. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	X	*Y*	*Z*	U(eq)
C(1)	734(5)	3484(10)	4600(7)	42(2)
C(2)	1156(6)	4685(10)	4473(8)	42(2)
C(3)	1616(6)	4665(11)	3727(9)	46(2)
C(4)	1665(4)	3461(9)	3078(6)	38(2)
C(5)	1234(5)	2260(10)	3220(7)	44(2)
C(6)	780(5)	2283(10)	3939(8)	52(2)
C(7)	2134(5)	3398(10)	2265(7)	45(2)
C(8)	2477(5)	4495(11)	1871(7)	45(2)
C(9)	2911(5)	4295(12)	1036(7)	48(2)
C(10)	3211(6)	5380(13)	567(9)	50(3)
C(11)	3632(7)	5231(12)	-300(9)	48(3)
C(12)	3852(7)	6444(16)	-812(9)	58(3)
C(13)	4235(7)	6308(18)	-1618(9)	69(4)
N(1)	4408(6)	5005(12)	-1979(9)	63(4)
C(15)	4217(6)	3773(15)	-1507(9)	59(3)
C(16)	3831(7)	3890(15)	-672(9)	55(3)
C(17)	262(7)	4545(13)	6069(10)	65(3)
C(18)	7006(4)	5636(8)	-4353(6)	31(2)
C(19)	7031(5)	5607(9)	-3254(7)	40(2)
C(20)	7660(5)	5990(10)	-2558(8)	49(2)
C(21)	8262(5)	6351(10)	-2998(9)	50(2)
C(22)	8255(5)	6398(10)	-4090(9)	55(3)
C(23)	7619(5)	6048(10)	-4770(7)	43(2)
C(14)	4835(9)	4911(15)	-2854(12)	81(5)
O(1)	273(4)	3378(7)	5322(5)	58(2)
Cl(1)	9075(2)	6711(3)	-2145(3)	81(1)
S(1)	6194(1)	5192(2)	-5236(2)	31(1)

O(2)	6343(12)	3910(30)	-5833(19)	59(6)
O(3)	5653(10)	4930(30)	-4584(13)	48(7)
O(4)	6015(12)	6430(20)	-5950(20)	66(8)
O(2')	6446(13)	4690(40)	-6158(19)	59(8)
O(3')	5857(15)	4090(30)	-4675(19)	59(8)
O(4')	5807(11)	6530(20)	-5320(30)	53(8)
C(24)	2372(5)	8956(10)	1418(7)	43(2)
C(25)	1738(5)	8615(10)	1789(9)	52(2)
C(26)	1720(5)	8655(10)	2860(9)	49(2)
C(27)	2323(5)	9020(10)	3602(8)	50(2)
C(28)	2962(5)	9399(10)	3232(7)	40(2)
C(29)	2985(4)	9369(8)	2151(6)	31(2)
N(2)	5582(7)	9970(13)	5843(9)	73(4)
C(31)	5777(7)	8781(17)	6412(10)	69(4)
C(32)	6158(7)	8853(16)	7432(9)	62(4)
C(33)	6366(7)	10196(12)	7910(10)	53(3)
C(34)	6147(8)	11413(17)	7300(10)	65(4)
C(35)	5764(7)	11273(19)	6290(11)	75(5)
C(36)	6784(6)	10340(13)	8976(9)	50(3)
C(37)	7081(5)	9285(11)	9609(7)	46(2)
C(38)	7520(5)	9470(11)	10641(8)	46(2)
C(39)	7859(5)	8380(10)	11214(7)	46(2)
C(40)	8331(5)	8446(9)	12258(7)	38(2)
C(41)	8384(6)	9667(10)	12917(8)	43(2)
C(42)	8838(6)	9705(10)	13901(8)	44(2)
C(43)	9258(5)	8489(10)	14232(7)	42(2)
C(44)	9223(5)	7285(11)	13564(8)	52(2)
C(45)	8767(5)	7262(10)	12612(7)	41(2)
C(46)	9733(8)	9577(13)	15935(10)	66(3)
C(30)	5161(9)	9885(16)	4752(12)	92(6)
O(5)	9724(4)	8384(8)	15187(5)	57(2)
Cl(2)	915(2)	8290(3)	3320(3)	81(1)
S(2)	3797(1)	9814(2)	1667(2)	31(1)
O(6)	3970(13)	8580(20)	1050(30)	67(8)
O(7)	3646(13)	11080(30)	980(30)	67(7)
O(8)	4322(11)	10090(40)	2597(14)	62(8)

O(6')	4168(16)	8440(30)	1700(40)	50(10)
O(7')	3550(20)	10330(80)	610(30)	71(13)
O(8')	4160(20)	10850(50)	2400(40)	65(11)

Table S4. Bond lengths [Å] and angles [°] for MBMPCBS.

C(1)-O(1)	1.364(10)
C(1)-C(2)	1.387(12)
C(1)-C(6)	1.399(12)
C(2)-C(3)	1.383(15)
C(2)-H(2)	0.9500
C(3)-C(4)	1.393(13)
C(3)-H(3)	0.9500
C(4)-C(5)	1.402(12)
C(4)-C(7)	1.464(12)
C(5)-C(6)	1.348(13)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.339(13)
C(7)-H(7)	0.9500
C(8)-C(9)	1.450(13)
C(8)-H(8)	0.9500
C(9)-C(10)	1.335(14)
C(9)-H(9)	0.9500
C(10)-C(11)	1.464(16)
C(10)-H(10)	0.9500
C(11)-C(12)	1.389(16)
C(11)-C(16)	1.395(17)
C(12)-C(13)	1.349(18)
C(12)-H(12)	0.9500
C(13)-N(1)	1.343(17)
C(13)-H(13)	0.9500
N(1)-C(15)	1.358(15)
N(1)-C(14)	1.476(19)

C(15)-C(16)	1.382(16)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-O(1)	1.434(12)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.383(11)
C(18)-C(23)	1.398(11)
C(18)-S(1)	1.785(8)
C(19)-C(20)	1.399(12)
C(19)-H(19)	0.9500
C(20)-C(21)	1.385(13)
C(20)-H(20)	0.9500
C(21)-C(22)	1.380(14)
C(21)-Cl(1)	1.750(9)
C(22)-C(23)	1.392(13)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(14)-H(1A)	0.9800
C(14)-H(1B)	0.9800
C(14)-H(1C)	0.9800
S(1)-O(2')	1.408(18)
S(1)-O(4')	1.425(16)
S(1)-O(3)	1.433(15)
S(1)-O(3')	1.443(16)
S(1)-O(2)	1.453(16)
S(1)-O(4)	1.461(14)
C(24)-C(25)	1.389(12)
C(24)-C(29)	1.407(11)
C(24)-H(24)	0.9500
C(25)-C(26)	1.362(14)
C(25)-H(25)	0.9500
C(26)-C(27)	1.389(14)
C(26)-Cl(2)	1.743(9)
C(27)-C(28)	1.405(12)

C(27)-H(27)	0.9500
C(28)-C(29)	1.376(11)
C(28)-H(28)	0.9500
C(29)-S(2)	1.786(8)
N(2)-C(31)	1.328(16)
N(2)-C(35)	1.346(19)
N(2)-C(30)	1.476(19)
C(31)-C(32)	1.371(17)
C(31)-H(31)	0.9500
C(32)-C(33)	1.404(18)
C(32)-H(32)	0.9500
C(33)-C(34)	1.384(16)
C(33)-C(36)	1.451(17)
C(34)-C(35)	1.37(2)
C(34)-H(34)	0.9500
C(35)-H(35)	0.9500
C(36)-C(37)	1.323(14)
C(36)-H(36)	0.9500
C(37)-C(38)	1.434(13)
C(37)-H(37)	0.9500
C(38)-C(39)	1.337(13)
C(38)-H(38)	0.9500
C(39)-C(40)	1.466(12)
C(39)-H(39)	0.9500
C(40)-C(45)	1.393(12)
C(40)-C(41)	1.394(12)
C(41)-C(42)	1.389(15)
C(41)-H(41)	0.9500
C(42)-C(43)	1.395(13)
C(42)-H(42)	0.9500
C(43)-O(5)	1.373(11)
C(43)-C(44)	1.390(12)
C(44)-C(45)	1.359(13)
C(44)-H(44)	0.9500
C(45)-H(45)	0.9500
C(46)-O(5)	1.449(12)

C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(30)-H(2A)	0.9800
C(30)-H(2B)	0.9800
C(30)-H(2C)	0.9800
S(2)-O(8')	1.42(3)
S(2)-O(7')	1.42(3)
S(2)-O(8)	1.429(17)
S(2)-O(6')	1.44(2)
S(2)-O(6)	1.450(14)
S(2)-O(7)	1.452(16)

O(1)-C(1)-C(2)	125.2(8)
O(1)-C(1)-C(6)	117.0(8)
C(2)-C(1)-C(6)	117.9(9)
C(3)-C(2)-C(1)	120.3(9)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	121.5(9)
C(2)-C(3)-H(3)	119.2
C(4)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	117.2(8)
C(3)-C(4)-C(7)	123.6(8)
C(5)-C(4)-C(7)	119.2(8)
C(6)-C(5)-C(4)	121.3(9)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	121.7(9)
C(5)-C(6)-H(6)	119.2
C(1)-C(6)-H(6)	119.2
C(8)-C(7)-C(4)	128.0(9)
C(8)-C(7)-H(7)	116.0
C(4)-C(7)-H(7)	116.0
C(7)-C(8)-C(9)	122.7(9)
C(7)-C(8)-H(8)	118.7

C(9)-C(8)-H(8)	118.7
C(10)-C(9)-C(8)	124.0(11)
C(10)-C(9)-H(9)	118.0
C(8)-C(9)-H(9)	118.0
C(9)-C(10)-C(11)	125.8(11)
C(9)-C(10)-H(10)	117.1
C(11)-C(10)-H(10)	117.1
C(12)-C(11)-C(16)	116.0(13)
C(12)-C(11)-C(10)	121.0(11)
C(16)-C(11)-C(10)	123.1(10)
C(13)-C(12)-C(11)	121.1(14)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
N(1)-C(13)-C(12)	122.0(13)
N(1)-C(13)-H(13)	119.0
C(12)-C(13)-H(13)	119.0
C(13)-N(1)-C(15)	120.1(12)
C(13)-N(1)-C(14)	120.0(10)
C(15)-N(1)-C(14)	119.8(11)
N(1)-C(15)-C(16)	118.8(13)
N(1)-C(15)-H(15)	120.6
C(16)-C(15)-H(15)	120.6
C(15)-C(16)-C(11)	122.1(12)
C(15)-C(16)-H(16)	119.0
C(11)-C(16)-H(16)	119.0
O(1)-C(17)-H(17A)	109.5
O(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(23)	119.6(8)
C(19)-C(18)-S(1)	120.5(6)
C(23)-C(18)-S(1)	120.0(6)
C(18)-C(19)-C(20)	120.8(9)
C(18)-C(19)-H(19)	119.6

C(20)-C(19)-H(19)	119.6
C(21)-C(20)-C(19)	118.1(9)
C(21)-C(20)-H(20)	120.9
C(19)-C(20)-H(20)	120.9
C(22)-C(21)-C(20)	122.5(9)
C(22)-C(21)-Cl(1)	118.3(8)
C(20)-C(21)-Cl(1)	119.2(8)
C(21)-C(22)-C(23)	118.4(9)
C(21)-C(22)-H(22)	120.8
C(23)-C(22)-H(22)	120.8
C(22)-C(23)-C(18)	120.6(9)
C(22)-C(23)-H(23)	119.7
C(18)-C(23)-H(23)	119.7
N(1)-C(14)-H(1A)	109.5
N(1)-C(14)-H(1B)	109.5
H(1A)-C(14)-H(1B)	109.5
N(1)-C(14)-H(1C)	109.5
H(1A)-C(14)-H(1C)	109.5
H(1B)-C(14)-H(1C)	109.5
C(1)-O(1)-C(17)	117.9(8)
O(2')-S(1)-O(4')	117.3(13)
O(2')-S(1)-O(3')	114.4(15)
O(4')-S(1)-O(3')	112.5(13)
O(3)-S(1)-O(2)	112.3(10)
O(3)-S(1)-O(4)	112.1(11)
O(2)-S(1)-O(4)	110.7(13)
O(2')-S(1)-C(18)	102.9(10)
O(4')-S(1)-C(18)	102.9(7)
O(3)-S(1)-C(18)	107.1(7)
O(3')-S(1)-C(18)	104.7(8)
O(2)-S(1)-C(18)	107.1(8)
O(4)-S(1)-C(18)	107.2(7)
C(25)-C(24)-C(29)	119.6(8)
C(25)-C(24)-H(24)	120.2
C(29)-C(24)-H(24)	120.2
C(26)-C(25)-C(24)	119.7(9)

C(26)-C(25)-H(25)	120.2
C(24)-C(25)-H(25)	120.2
C(25)-C(26)-C(27)	121.8(9)
C(25)-C(26)-Cl(2)	119.6(8)
C(27)-C(26)-Cl(2)	118.6(8)
C(26)-C(27)-C(28)	118.9(9)
C(26)-C(27)-H(27)	120.5
C(28)-C(27)-H(27)	120.5
C(29)-C(28)-C(27)	119.7(8)
C(29)-C(28)-H(28)	120.1
C(27)-C(28)-H(28)	120.1
C(28)-C(29)-C(24)	120.2(8)
C(28)-C(29)-S(2)	120.4(6)
C(24)-C(29)-S(2)	119.4(6)
C(31)-N(2)-C(35)	118.7(13)
C(31)-N(2)-C(30)	121.3(13)
C(35)-N(2)-C(30)	120.0(11)
N(2)-C(31)-C(32)	121.6(14)
N(2)-C(31)-H(31)	119.2
C(32)-C(31)-H(31)	119.2
C(31)-C(32)-C(33)	120.8(13)
C(31)-C(32)-H(32)	119.6
C(33)-C(32)-H(32)	119.6
C(34)-C(33)-C(32)	116.0(14)
C(34)-C(33)-C(36)	120.7(12)
C(32)-C(33)-C(36)	123.3(11)
C(35)-C(34)-C(33)	120.5(15)
C(35)-C(34)-H(34)	119.7
C(33)-C(34)-H(34)	119.7
N(2)-C(35)-C(34)	122.3(13)
N(2)-C(35)-H(35)	118.8
C(34)-C(35)-H(35)	118.8
C(37)-C(36)-C(33)	127.3(12)
C(37)-C(36)-H(36)	116.3
C(33)-C(36)-H(36)	116.3
C(36)-C(37)-C(38)	125.9(11)

C(36)-C(37)-H(37)	117.1
C(38)-C(37)-H(37)	117.1
C(39)-C(38)-C(37)	123.8(10)
C(39)-C(38)-H(38)	118.1
C(37)-C(38)-H(38)	118.1
C(38)-C(39)-C(40)	128.4(9)
C(38)-C(39)-H(39)	115.8
C(40)-C(39)-H(39)	115.8
C(45)-C(40)-C(41)	117.3(8)
C(45)-C(40)-C(39)	119.6(8)
C(41)-C(40)-C(39)	123.0(8)
C(42)-C(41)-C(40)	122.0(9)
C(42)-C(41)-H(41)	119.0
C(40)-C(41)-H(41)	119.0
C(41)-C(42)-C(43)	118.9(9)
C(41)-C(42)-H(42)	120.6
C(43)-C(42)-H(42)	120.6
O(5)-C(43)-C(44)	116.0(8)
O(5)-C(43)-C(42)	124.6(8)
C(44)-C(43)-C(42)	119.4(9)
C(45)-C(44)-C(43)	120.7(9)
C(45)-C(44)-H(44)	119.6
C(43)-C(44)-H(44)	119.6
C(44)-C(45)-C(40)	121.7(9)
C(44)-C(45)-H(45)	119.2
C(40)-C(45)-H(45)	119.2
O(5)-C(46)-H(46A)	109.5
O(5)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
O(5)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
N(2)-C(30)-H(2A)	109.5
N(2)-C(30)-H(2B)	109.5
H(2A)-C(30)-H(2B)	109.5
N(2)-C(30)-H(2C)	109.5

H(2A)-C(30)-H(2C)	109.5
H(2B)-C(30)-H(2C)	109.5
C(43)-O(5)-C(46)	117.2(8)
O(8')-S(2)-O(7')	116(2)
O(8')-S(2)-O(6')	113.1(17)
O(7')-S(2)-O(6')	113.9(18)
O(8)-S(2)-O(6)	113.5(11)
O(8)-S(2)-O(7)	113.0(11)
O(6)-S(2)-O(7)	110.2(12)
O(8')-S(2)-C(29)	106.1(15)
O(7')-S(2)-C(29)	103.1(15)
O(8)-S(2)-C(29)	105.8(8)
O(6')-S(2)-C(29)	103.1(10)
O(6)-S(2)-C(29)	106.7(7)
O(7)-S(2)-C(29)	107.2(9)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for MBMPCBS. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(5)	49(5)	41(5)	1(4)	0(4)	1(4)
C(2)	48(6)	39(5)	35(5)	-3(4)	-2(5)	-2(5)
C(3)	48(6)	42(5)	46(6)	4(5)	1(5)	-7(5)
C(4)	38(5)	43(5)	30(4)	5(4)	0(4)	10(4)
C(5)	53(6)	26(5)	53(6)	3(4)	10(5)	-4(4)
C(6)	56(6)	41(6)	57(6)	1(5)	6(5)	-13(5)
C(7)	48(5)	40(5)	46(5)	1(4)	4(4)	6(4)
C(8)	44(6)	51(6)	38(5)	-1(5)	2(4)	1(5)
C(9)	44(5)	56(6)	42(6)	-1(5)	3(4)	-3(5)
C(10)	45(6)	59(6)	46(6)	-3(5)	3(5)	-6(5)
C(11)	42(6)	65(7)	33(6)	1(5)	-2(5)	-13(5)
C(12)	54(7)	69(8)	48(7)	12(5)	0(5)	-15(6)
C(13)	52(7)	106(12)	43(7)	23(7)	-5(5)	-33(7)
N(1)	39(6)	111(11)	36(6)	5(5)	-1(5)	-16(5)
C(15)	45(6)	82(9)	48(7)	-7(6)	2(5)	-17(6)
C(16)	43(6)	75(9)	46(6)	0(6)	6(5)	-21(6)
C(17)	64(8)	74(7)	61(7)	-5(7)	25(6)	10(7)
C(18)	36(5)	23(4)	35(4)	-4(3)	6(3)	2(3)
C(19)	43(5)	39(5)	37(5)	6(4)	5(4)	6(4)
C(20)	52(6)	39(5)	50(6)	1(4)	-8(4)	8(4)
C(21)	39(5)	34(5)	72(7)	-3(5)	-9(5)	3(4)
C(22)	38(5)	44(6)	82(8)	-9(5)	10(5)	-8(4)
C(23)	47(5)	36(5)	50(6)	-1(4)	16(4)	1(4)
C(14)	49(9)	157(17)	37(7)	13(6)	5(7)	-25(7)
O(1)	46(4)	76(5)	56(4)	-1(3)	17(3)	-3(3)
Cl(1)	56(2)	50(2)	121(3)	-16(2)	-32(2)	1(1)
S(1)	38(2)	25(1)	30(1)	2(1)	7(1)	1(1)
O(2)	70(12)	61(13)	45(10)	-21(9)	10(8)	13(10)
O(3)	34(9)	78(18)	35(8)	-5(7)	12(7)	-6(8)
O(4)	63(12)	41(9)	83(16)	35(10)	-22(11)	-12(8)
O(2')	51(12)	100(20)	30(12)	-26(12)	11(9)	8(13)

O(3')	55(13)	52(16)	66(12)	24(11)	-1(10)	-23(11)
O(4')	45(10)	31(9)	75(18)	-11(9)	-12(10)	9(7)
C(24)	45(5)	41(6)	44(5)	2(4)	5(4)	-1(4)
C(25)	43(5)	41(6)	70(7)	2(5)	-1(5)	-4(4)
C(26)	41(5)	33(5)	78(7)	11(5)	22(5)	5(4)
C(27)	57(6)	40(5)	59(6)	3(4)	30(5)	5(5)
C(28)	40(5)	44(5)	36(5)	-2(4)	11(4)	4(4)
C(29)	36(5)	26(4)	33(4)	1(3)	9(4)	2(3)
N(2)	52(7)	139(14)	32(6)	11(5)	18(5)	48(6)
C(31)	58(8)	103(11)	48(7)	-7(7)	12(6)	41(7)
C(32)	62(8)	91(10)	34(6)	8(6)	12(5)	38(7)
C(33)	44(7)	80(8)	40(7)	5(5)	19(5)	28(6)
C(34)	56(8)	85(9)	57(7)	24(6)	24(6)	26(7)
C(35)	58(8)	118(13)	57(8)	41(8)	30(7)	52(8)
C(36)	50(6)	58(6)	42(6)	3(5)	11(5)	16(5)
C(37)	44(5)	54(6)	40(5)	0(4)	14(4)	8(5)
C(38)	45(6)	55(6)	40(5)	1(5)	10(4)	5(5)
C(39)	47(5)	47(6)	44(5)	-2(4)	9(4)	-4(4)
C(40)	37(5)	40(5)	38(5)	3(4)	10(4)	-10(4)
C(41)	62(7)	26(4)	43(6)	4(4)	16(5)	8(5)
C(42)	62(7)	35(5)	35(5)	0(4)	11(5)	-9(5)
C(43)	34(5)	53(6)	40(5)	2(4)	13(4)	-8(4)
C(44)	55(6)	44(6)	58(6)	2(5)	8(5)	11(5)
C(45)	46(6)	31(5)	47(5)	2(4)	6(4)	4(4)
C(46)	78(9)	77(8)	40(6)	-1(6)	0(6)	-25(7)
C(30)	54(10)	190(20)	32(7)	13(7)	11(7)	47(8)
O(5)	46(4)	77(5)	46(4)	-2(3)	-1(3)	3(3)
Cl(2)	60(2)	50(2)	146(3)	15(2)	57(2)	3(1)
S(2)	38(2)	27(1)	30(1)	0(1)	10(1)	-2(1)
O(6)	78(12)	38(8)	99(19)	-28(10)	50(13)	-12(8)
O(7)	65(11)	67(13)	72(14)	43(10)	25(10)	11(10)
O(8)	43(10)	110(20)	31(8)	-2(8)	1(7)	-24(10)
O(6')	45(14)	36(12)	80(20)	8(12)	39(15)	13(9)
O(7')	53(17)	120(40)	39(18)	37(18)	13(14)	10(20)
O(8')	70(20)	60(20)	70(20)	-18(16)	19(16)	-30(17)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for MBMPCBS.

	X	*Y*	*Z*	U(eq)
H(2)	1129	5525	4899	50
H(3)	1905	5493	3656	55
H(5)	1263	1412	2802	53
H(6)	483	1462	3997	62
H(7)	2205	2463	1983	54
H(8)	2433	5443	2149	54
H(9)	2986	3333	810	57
H(10)	3144	6334	819	60
H(12)	3732	7385	-590	70
H(13)	4386	7159	-1941	82
H(15)	4346	2848	-1747	71
H(16)	3697	3029	-341	66
H(17A)	745	4679	6483	97
H(17B)	-76	4314	6556	97
H(17C)	109	5440	5678	97
H(19)	6615	5324	-2970	48
H(20)	7673	6002	-1804	59
H(22)	8675	6663	-4371	65
H(23)	7600	6088	-5524	52
H(1A)	4665	4090	-3321	122
H(1B)	5344	4770	-2551	122
H(1C)	4780	5811	-3273	122
H(24)	2391	8912	673	52
H(25)	1319	8355	1299	63
H(27)	2304	9013	4348	60
H(28)	3376	9676	3726	48
H(31)	5649	7858	6103	83
H(32)	6283	7982	7821	74

H(34)	6264	12352	7586	77
H(35)	5621	12125	5887	90
H(36)	6851	11298	9251	59
H(37)	6997	8319	9358	55
H(38)	7572	10420	10934	56
H(39)	7783	7442	10905	55
H(41)	8101	10497	12686	52
H(42)	8862	10545	14341	52
H(44)	9522	6468	13775	63
H(45)	8744	6418	12176	50
H(46A)	9870	10472	15603	99
H(46B)	10082	9371	16583	99
H(46C)	9252	9693	16125	99
H(2A)	5256	10747	4344	138
H(2B)	4646	9839	4795	138
H(2C)	5300	9013	4393	138

Table S7. Crystal data and structure refinement for MBMPI.

Identification code	MBMPI
Empirical formula	$C_{17}H_{18}NOI$
Formula weight	379.22
Temperature/K	173(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	6.3116(12)
b/Å	7.6593(13)
c/Å	33.650(6)
α/°	90
β/°	91.663(6)
γ/°	90
Volume/Å^3	1626.0(5)
Z	4
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	1.965
F(000)	752.0
Crystal size/mm^3	0.358 × 0.228 × 0.097
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.844 to 54.982
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-43 \leq l \leq 43$
Reflections collected	25101
Independent reflections	3685 [R_{int} = 0.0508, R_{sigma} = 0.0297]
Data/restraints/parameters	3685/0/183
Goodness-of-fit on F^2	1.176
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.1191
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1203
Largest diff. peak/hole / e Å^{-3}	0.48/-0.85

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for MBMPI. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*Y*	*Z*	U(eq)
C1	11952(6)	8226(4)	7986.3(11)	28.9(7)
C2	12635(6)	9054(5)	7640.3(12)	31.9(7)
C3	11293(6)	9159(5)	7313.6(11)	31.7(7)
C4	9254(6)	8451(4)	7310.9(11)	28.8(7)
C5	8571(6)	7708(5)	7666.1(11)	32.2(7)
C6	9897(6)	7608(5)	8000.8(11)	32.2(7)
C7	12757(8)	7332(6)	8651.6(13)	46.7(10)
C8	7954(6)	8501(5)	6944.4(12)	33.7(8)
C9	6107(6)	7676(5)	6872.8(11)	32.6(7)
C10	4925(6)	7801(5)	6502.0(11)	32.6(7)
C11	3023(6)	7045(5)	6442.4(11)	33.9(8)
C12	-1417(7)	6180(5)	5718.4(15)	42.2(10)
C13	-203(7)	6187(5)	6061.9(14)	38.5(9)
C14	1733(6)	7090(5)	6080.1(11)	31.7(7)
C15	2316(6)	7976(6)	5735.6(12)	36.7(8)
C16	1030(7)	7924(6)	5401.4(12)	41.0(9)
C17	-2181(9)	7023(8)	5030.3(16)	58.9(13)
N1	-797(5)	7021(5)	5395.3(11)	38.7(7)
O1	13423(4)	8112(4)	8289.9(9)	36.5(6)
I1	-3058.1(4)	1456.5(4)	5650.7(2)	42.14(13)

Table S9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for MBMPI. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	33.9(17)	21.3(15)	31.5(17)	-3.7(13)	-0.6(14)	1.8(13)
C2	31.5(17)	26.8(17)	37.7(19)	-4.3(14)	3.9(14)	-3.5(14)

Table S9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for MBMPI. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	37.6(18)	27.5(17)	30.1(17)	-0.5(14)	4.6(14)	-2.9(14)
C4	30.1(17)	24.0(16)	32.3(18)	-1.3(13)	0.0(14)	2.7(13)
C5	27.6(16)	33.4(18)	35.7(19)	3.8(15)	1.9(14)	-3.4(14)
C6	35.3(18)	31.5(18)	29.9(17)	3.9(14)	-0.1(14)	-3.6(14)
C7	56(3)	44(2)	39(2)	6.4(18)	-15.7(19)	-12(2)
C8	39(2)	29.2(18)	32.6(18)	0.9(14)	0.4(15)	2.4(14)
C9	37.5(18)	28.1(17)	32.1(18)	2.5(14)	0.0(14)	0.9(14)
C10	38.2(19)	28.2(17)	31.2(18)	0.5(14)	0.3(14)	3.9(14)
C11	42(2)	29.2(17)	30.6(18)	4.0(14)	-3.5(15)	-1.1(15)
C12	35(2)	31.0(19)	60(3)	1.2(18)	-5.8(18)	-6.1(16)
C13	40(2)	28.7(18)	47(2)	7.2(16)	-1.2(17)	-3.3(15)
C14	35.4(18)	25.2(16)	34.4(18)	-1.5(14)	-1.8(14)	1.3(14)
C15	34.7(18)	43(2)	31.9(18)	1.5(16)	-3.7(15)	-6.6(16)
C16	44(2)	47(2)	31.9(19)	1.1(17)	-3.9(16)	-0.5(18)
C17	55(3)	72(3)	49(3)	-10(2)	-24(2)	-4(3)
N1	37.2(17)	38.3(18)	40.1(18)	-6.2(14)	-8.3(14)	1.9(14)
O1	35.9(14)	34.1(14)	39.1(15)	1.0(11)	-7.3(11)	-2.7(11)
I1	39.70(18)	45.08(19)	41.53(18)	-2.91(11)	-0.73(11)	-9.11(11)

Table S10. Bond Lengths for MBMPI.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.405(5)	C9	C10	1.438(5)

Table S10. Bond Lengths for MBMPI.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C6	1.383(5)	C10	C11	1.343(6)
C1	O1	1.363(5)	C11	C14	1.446(5)
C2	C3	1.371(6)	C12	C13	1.369(6)
C3	C4	1.396(5)	C12	N1	1.332(6)
C4	C5	1.403(5)	C13	C14	1.403(6)
C4	C8	1.462(5)	C14	C15	1.402(6)
C5	C6	1.386(5)	C15	C16	1.368(6)
C7	O1	1.430(5)	C16	N1	1.344(6)
C8	C9	1.342(6)	C17	N1	1.487(6)

Table S11. Bond Angles for MBMPI.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	119.6(3)	C10	C11	C14	126.5(4)
O1	C1	C2	115.5(3)	N1	C12	C13	121.1(4)
O1	C1	C6	124.8(3)	C12	C13	C14	120.3(4)
C3	C2	C1	119.6(3)	C13	C14	C11	119.5(4)
C2	C3	C4	122.0(4)	C15	C14	C11	123.6(4)
C3	C4	C5	117.3(3)	C15	C14	C13	116.8(4)
C3	C4	C8	119.3(3)	C16	C15	C14	120.1(4)
C5	C4	C8	123.4(3)	N1	C16	C15	121.0(4)
C6	C5	C4	121.4(3)	C12	N1	C16	120.6(4)
C1	C6	C5	119.8(3)	C12	N1	C17	119.7(4)
C9	C8	C4	127.1(4)	C16	N1	C17	119.7(4)
C8	C9	C10	123.4(4)	C1	O1	C7	117.0(3)
C11	C10	C9	122.7(4)				

Table S12. Hydrogen Bonds for MBMPI.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C7	H7A	I1[1]	0.98	3.28	3.894(5)	122.6
C7	H7B	I1[2]	0.98	3.12	4.087(5)	170.7
C12	H12	I1	0.95	3.16	3.768(4)	123.5
C15	H15	I1[3]	0.95	3.05	3.970(4)	164.3
C16	H16	I1[4]	0.95	2.97	3.829(4)	150.5
C17	H17C	I1[5]	0.98	3.30	3.904(5)	121.5

Table S13. Torsion Angles for MBMPI.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.6(6)	C10	C11	C14	C13	178.2(4)
C2	C1	C6	C5	4.2(6)	C10	C11	C14	C15	-0.8(7)
C2	C1	O1	C7	177.8(4)	C11	C14	C15	C16	178.5(4)
C2	C3	C4	C5	3.7(5)	C12	C13	C14	C11	-178.4(4)
C2	C3	C4	C8	-175.8(3)	C12	C13	C14	C15	0.7(6)
C3	C4	C5	C6	-2.8(6)	C13	C12	N1	C16	-1.0(7)
C3	C4	C8	C9	169.9(4)	C13	C12	N1	C17	-178.5(4)
C4	C5	C6	C1	-1.0(6)	C13	C14	C15	C16	-0.6(6)
C4	C8	C9	C10	179.9(4)	C14	C15	C16	N1	-0.4(7)
C5	C4	C8	C9	-9.6(6)	C15	C16	N1	C12	1.2(7)
C6	C1	C2	C3	-3.4(5)	C15	C16	N1	C17	178.7(5)
C6	C1	O1	C7	-1.6(5)	N1	C12	C13	C14	0.0(7)
C8	C4	C5	C6	176.6(4)	O1	C1	C2	C3	177.1(3)
C8	C9	C10	C11	-176.3(4)	O1	C1	C6	C5	-176.4(3)
C9	C10	C11	C14	-179.5(4)					

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for MBMPI.

Atom	*X*	*Y*	*Z*	U(eq)
H2	14018.99	9538.28	7632.81	38
H3	11764.59	9731.39	7081.85	38
H5	7168.74	7262.77	7677.31	39
H6	9394.99	7117.39	8239.66	39
H7A	11653.63	8055.68	8767.73	70
H7B	13969.65	7243.34	8838.99	70
H7C	12190.43	6163.48	8595.87	70
H8	8474.65	9191.47	6733.98	40
H9	5550.31	6973.97	7077.7	39
H10	5514.02	8443.8	6290.56	39
H11	2468.51	6418.69	6659.78	41
H12	-2724.7	5564.31	5710.12	51
H13	-671.73	5579.13	6289.17	46
H15	3606.11	8614.1	5734.12	44
H16	1435.14	8535.07	5169.94	49
H17A	-2931.52	5905.26	5008.17	88
H17B	-1310.88	7188.65	4796.72	88
H17C	-3212.51	7974.84	5045.29	88

Table S15. The coordinates of the equilibrium structure

EQUILIBRIUM GEOMETRY

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
C	6.0	11.2318359722	-4.2676809228	-8.2080909332
C	6.0	10.0455479791	-3.7956590977	-7.6884936839
C	6.0	9.4663452975	-4.3858081050	-6.5551471073
C	6.0	10.1374627206	-5.5168859048	-6.0254090332
C	6.0	11.2955448608	-5.9666107108	-6.5984518227
N	7.0	11.8325279986	-5.3576499343	-7.6866427495
C	6.0	13.0864368741	-5.8577080156	-8.2826081576
C	6.0	8.2765012842	-3.8052854916	-5.9733450920
C	6.0	7.7428630497	-4.1118160572	-4.7633788063
C	6.0	6.6033111214	-3.4536381246	-4.1998845076
C	6.0	6.1239430071	-3.7264267281	-2.9606874933
C	6.0	5.0039166625	-3.0933047077	-2.2857830105
C	6.0	4.6114838774	-3.5571431959	-1.0126096823
C	6.0	3.5537593995	-2.9891093294	-0.3286952431
C	6.0	2.8407827561	-1.9224316310	-0.8943086826
C	6.0	3.2144749532	-1.4381899042	-2.1564716778
C	6.0	4.2783409046	-2.0206968803	-2.8312159955
O	8.0	1.8207973483	-1.4323484154	-0.1486456350
C	6.0	1.0665947151	-0.3318799855	-0.6494059141
C	6.0	12.6318960551	-2.5952043449	-4.7226263265
C	6.0	12.9030600431	-3.4485376906	-3.6543216786
C	6.0	12.1118013618	-3.4142595578	-2.5084490535
C	6.0	11.0523450258	-2.5138769090	-2.4477576235
C	6.0	10.7786089690	-1.6434940481	-3.4981201023
C	6.0	11.5783927711	-1.6873086534	-4.6388178338
S	16.0	13.6780499458	-2.6616925419	-6.2119973459
O	8.0	14.7645107172	-1.6995250117	-5.9894990583
O	8.0	12.7489274644	-2.3010682118	-7.3293547300
O	8.0	14.0998335420	-4.0915529320	-6.2788352566
CL	17.0	10.0294408167	-2.4789174168	-1.0057384845
H	1.0	11.7330066823	-3.7884254476	-9.0331856219
H	1.0	9.6142028954	-2.9054278759	-8.1253789837
H	1.0	9.7608182463	-6.0384883373	-5.1566231260
H	1.0	11.8469105869	-6.8109997894	-6.2097761151
H	1.0	13.6793657005	-5.0036988753	-8.5980557797

H	1.0	13.6550274676	-6.3780169305	-7.5176900759
H	1.0	12.8512852977	-6.5194872069	-9.1202828758
H	1.0	7.8166117990	-3.0062226332	-6.5491946900
H	1.0	8.2113196118	-4.8762632172	-4.1477684070
H	1.0	6.1295718000	-2.6897561026	-4.8108536546
H	1.0	6.6299175570	-4.5013712336	-2.3879554870
H	1.0	5.1527788198	-4.3810998261	-0.5592180730
H	1.0	3.2539752329	-3.3500918509	0.6476962223
H	1.0	2.6879601445	-0.6114832043	-2.6142105308
H	1.0	4.5498717355	-1.6222614250	-3.8017728193
H	1.0	0.3262682478	-0.1098772470	0.1169296702
H	1.0	1.7013011740	0.5464726036	-0.8062646303
H	1.0	0.5558220849	-0.5890640464	-1.5836521796
H	1.0	13.7260553347	-4.1480352707	-3.7348449950
H	1.0	12.3172955263	-4.0696677665	-1.6709470735
H	1.0	9.9525803160	-0.9470767788	-3.4244279131
H	1.0	11.3770862454	-1.0325870784	-5.4780701405