Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

DBU-promoted Ring-opening Reactions of Multi-substituted Donor-Acceptor Cyclopropane: Access to Functionalized Chalcones With a Quaternary Carbon Group

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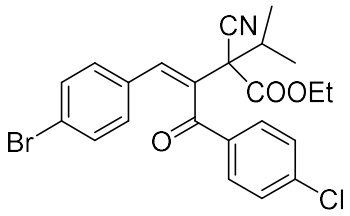
Ethyl (Z)-4-(4-bromophenyl)-3-(4-chlorobenzoyl)-2-cyano-2-isopropylbut-3-enoate (**3b**)



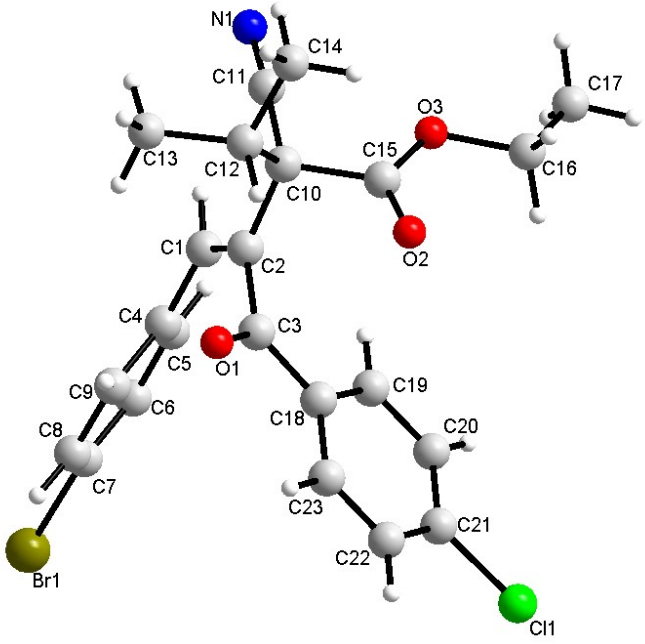


Table S1. Crystal data and structure refinement for **3b**.

Identification code	**3b**
Empirical formula	$C_{23}H_{21}BrClNO_3$
Formula weight	474.76
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.318(3) Å alpha = 90°.
	b = 9.2383(11) Å beta = 96.433(4)°.
	c = 20.240(3) Å gamma = 90°.
Volume	4518.5(9) $Å^3$
Z, Calculated density	8, 1.396 Mg/m^3
Absorption coefficient	1.960 mm^{-1}
F(000)	1936
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.69 to 27.57°.
Limiting indices	-31<=h<=31, -12<=k<=11, -26<=l<=26
Reflections collected / unique	32898 / 5163 [R(int) = 0.1008]
Completeness to theta = 27.57	99.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5163 / 0 / 265
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1245
R indices (all data)	R1 = 0.1794, wR2 = 0.1624
Largest diff. peak and hole	0.416 and -0.377 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3b**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	10891(1)	2837(1)	-6(1)	120(1)
Cl(1)	9444(1)	6625(2)	3036(1)	151(1)
O(3)	7119(1)	2673(3)	1250(1)	85(1)
C(18)	8891(2)	2462(5)	2028(2)	63(1)
O(1)	8800(1)	-66(4)	2034(1)	85(1)
C(3)	8685(1)	1055(5)	1743(2)	63(1)
C(15)	7474(2)	1791(5)	1562(2)	67(1)
O(2)	7622(1)	1833(4)	2146(2)	96(1)
C(11)	7401(2)	672(4)	442(2)	57(1)
C(1)	8525(1)	1360(4)	524(2)	58(1)
C(4)	9100(2)	1708(4)	430(2)	59(1)
C(2)	8319(1)	1050(4)	1088(2)	56(1)
C(19)	8735(2)	3778(6)	1743(2)	79(1)
C(10)	7708(1)	659(4)	1115(2)	55(1)
C(9)	9549(2)	964(5)	751(2)	71(1)
C(7)	10160(2)	2388(5)	181(2)	75(1)
C(12)	7622(2)	-859(5)	1423(2)	71(1)
C(6)	9725(2)	3130(5)	-143(2)	82(1)
C(21)	9245(2)	5010(6)	2637(2)	90(1)
N(1)	7169(1)	592(4)	-73(2)	73(1)
C(8)	10082(2)	1301(6)	623(2)	79(1)
C(5)	9200(2)	2773(5)	-19(2)	74(1)
C(23)	9240(2)	2461(6)	2616(2)	73(1)
C(22)	9415(2)	3731(7)	2916(2)	88(1)
C(14)	7011(2)	-1133(6)	1492(2)	95(2)
C(20)	8912(2)	5068(6)	2049(2)	90(1)
C(16)	6917(2)	3844(7)	1670(3)	125(2)
C(13)	7869(2)	-2049(5)	1037(3)	100(2)
C(17)	6584(3)	4756(7)	1283(3)	150(3)

Table S3. Bond lengths [Å] and angles [°] for **3b**.

Br(1)-C(7)	1.903(4)
Cl(1)-C(21)	1.741(5)
O(3)-C(15)	1.298(5)
O(3)-C(16)	1.493(5)
C(18)-C(19)	1.381(6)
C(18)-C(23)	1.383(5)
C(18)-C(3)	1.485(6)
O(1)-C(3)	1.209(4)
C(3)-C(2)	1.512(5)
C(15)-O(2)	1.197(4)
C(15)-C(10)	1.534(5)
C(11)-N(1)	1.131(4)
C(11)-C(10)	1.479(5)
C(1)-C(2)	1.328(5)
C(1)-C(4)	1.467(5)
C(4)-C(5)	1.379(5)
C(4)-C(9)	1.389(5)
C(2)-C(10)	1.535(5)
C(19)-C(20)	1.389(6)
C(10)-C(12)	1.558(5)
C(9)-C(8)	1.385(5)
C(7)-C(6)	1.366(6)
C(7)-C(8)	1.371(6)
C(12)-C(13)	1.511(6)
C(12)-C(14)	1.529(5)
C(6)-C(5)	1.368(5)
C(21)-C(22)	1.355(7)
C(21)-C(20)	1.362(6)
C(23)-C(22)	1.367(6)
C(16)-C(17)	1.356(7)
C(15)-O(3)-C(16)	114.9(4)
C(19)-C(18)-C(23)	118.3(4)
C(19)-C(18)-C(3)	122.9(4)
C(23)-C(18)-C(3)	118.8(4)
O(1)-C(3)-C(18)	120.7(3)
O(1)-C(3)-C(2)	120.4(4)
C(18)-C(3)-C(2)	118.9(4)
O(2)-C(15)-O(3)	124.7(4)
O(2)-C(15)-C(10)	120.9(4)
O(3)-C(15)-C(10)	114.4(4)

N(1)-C(11)-C(10)	175.8(4)
C(2)-C(1)-C(4)	128.0(3)
C(5)-C(4)-C(9)	118.3(4)
C(5)-C(4)-C(1)	118.9(3)
C(9)-C(4)-C(1)	122.8(4)
C(1)-C(2)-C(3)	120.7(3)
C(1)-C(2)-C(10)	122.7(3)
C(3)-C(2)-C(10)	116.5(3)
C(18)-C(19)-C(20)	120.8(4)
C(11)-C(10)-C(15)	110.8(3)
C(11)-C(10)-C(2)	110.8(3)
C(15)-C(10)-C(2)	106.6(3)
C(11)-C(10)-C(12)	107.4(3)
C(15)-C(10)-C(12)	107.7(3)
C(2)-C(10)-C(12)	113.6(3)
C(8)-C(9)-C(4)	120.3(4)
C(6)-C(7)-C(8)	121.6(4)
C(6)-C(7)-Br(1)	119.1(4)
C(8)-C(7)-Br(1)	119.3(4)
C(13)-C(12)-C(14)	111.9(4)
C(13)-C(12)-C(10)	111.6(3)
C(14)-C(12)-C(10)	111.1(3)
C(7)-C(6)-C(5)	118.6(4)
C(22)-C(21)-C(20)	121.5(5)
C(22)-C(21)-Cl(1)	119.8(4)
C(20)-C(21)-Cl(1)	118.6(5)
C(7)-C(8)-C(9)	119.2(4)
C(6)-C(5)-C(4)	122.0(4)
C(22)-C(23)-C(18)	120.8(4)
C(21)-C(22)-C(23)	119.9(4)
C(21)-C(20)-C(19)	118.7(5)
C(17)-C(16)-O(3)	109.6(4)

Symmetry transformations used to generate equivalent atoms:

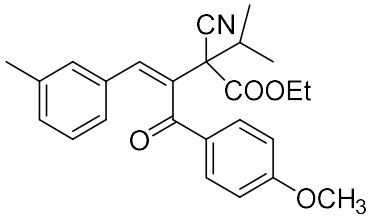
Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **3b**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	65(1)	157(1)	141(1)	-26(1)	25(1)	-23(1)
Cl(1)	181(2)	146(1)	120(1)	-53(1)	-9(1)	-16(1)
O(3)	100(2)	96(2)	57(2)	-5(2)	9(2)	39(2)
C(18)	48(2)	99(4)	42(2)	10(2)	4(2)	8(2)
O(1)	81(2)	99(2)	70(2)	29(2)	-14(2)	10(2)
C(3)	48(2)	94(4)	47(2)	13(2)	3(2)	9(2)
C(15)	56(2)	95(3)	49(3)	-4(2)	11(2)	1(2)
O(2)	89(2)	146(3)	52(2)	-21(2)	2(2)	24(2)
C(11)	51(2)	72(3)	48(2)	3(2)	7(2)	14(2)
C(1)	52(2)	77(3)	44(2)	1(2)	0(2)	8(2)
C(4)	55(2)	78(3)	44(2)	-8(2)	5(2)	4(2)
C(2)	52(2)	71(3)	44(2)	3(2)	3(2)	11(2)
C(19)	74(3)	108(4)	52(3)	-2(3)	-4(2)	10(3)
C(10)	50(2)	73(3)	41(2)	4(2)	6(2)	9(2)
C(9)	61(3)	93(3)	58(3)	-4(2)	10(2)	16(2)
C(7)	58(3)	96(4)	71(3)	-24(3)	9(2)	-12(2)
C(12)	61(3)	91(3)	58(3)	17(2)	-1(2)	3(2)
C(6)	75(3)	100(4)	69(3)	6(2)	3(2)	-15(3)
C(21)	89(3)	116(4)	64(3)	-25(3)	4(3)	-6(3)
N(1)	71(2)	93(3)	52(2)	0(2)	-5(2)	11(2)
C(8)	57(3)	104(4)	74(3)	-17(3)	3(2)	18(2)
C(5)	59(3)	95(3)	66(3)	6(2)	1(2)	-5(2)
C(23)	55(2)	114(4)	50(3)	9(3)	0(2)	1(2)
C(22)	73(3)	136(5)	53(3)	1(3)	-8(2)	-5(3)
C(14)	80(3)	115(4)	88(3)	25(3)	6(2)	-19(3)
C(20)	102(4)	94(4)	72(3)	-3(3)	-1(3)	11(3)
C(16)	153(5)	147(5)	77(4)	-32(4)	17(3)	77(4)
C(13)	108(4)	78(3)	113(4)	12(3)	11(3)	16(3)
C(17)	208(7)	127(5)	116(5)	-23(4)	26(5)	71(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3b**.

	x	y	z	U(eq)
H(1)	8269	1355	134	70
H(19)	8504	3803	1332	94
H(9)	9491	220	1059	85
H(12)	7825	-860	1881	85
H(6)	9785	3879	-448	98
H(8)	10389	786	838	94
H(5)	8895	3274	-249	88
H(23)	9361	1566	2814	88
H(22)	9654	3716	3321	106
H(14A)	6801	-1153	1050	142
H(14B)	6870	-358	1757	142
H(14C)	6972	-2065	1713	142
H(20)	8804	5972	1853	108
H(16A)	6710	3415	2015	151
H(16B)	7236	4386	1895	151
H(13A)	7813	-2984	1248	150
H(13B)	8266	-1874	1032	150
H(13C)	7687	-2059	579	150
H(17A)	6788	5158	934	224
H(17B)	6464	5546	1557	224
H(17C)	6260	4226	1079	224

Ethyl (Z)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)-4-(m-tolyl)but-3-enoate (**3h**)



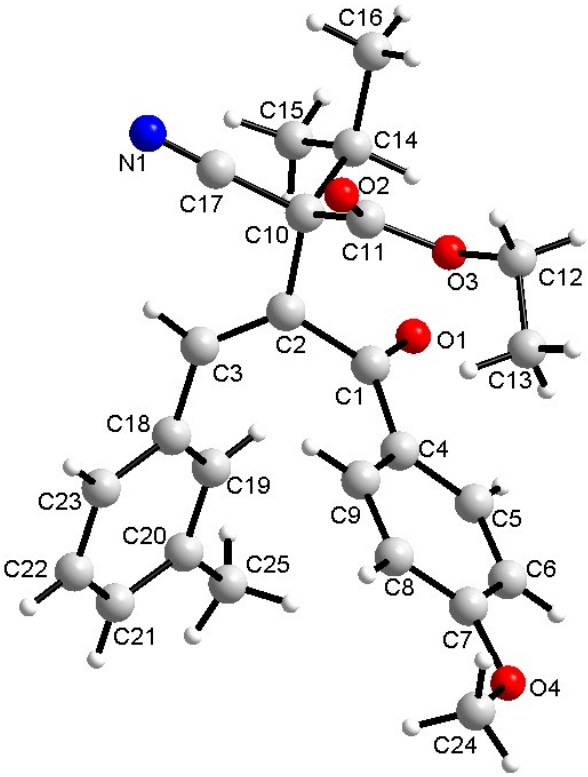


Table S6. Crystal data and structure refinement for **3h**.

Identification code	**3h**
Empirical formula	$C_{25}H_{27}NO_4$
Formula weight	405.48
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.129(6) Å alpha = 90°.
	b = 15.539(9) Å beta = 105.482(17)°.
	c = 15.252(9) Å gamma = 90°.
Volume	2313(2) $Å^3$
Z, Calculated density	4, 1.164 Mg/m^3
Absorption coefficient	0.078 mm^{-1}
F(000)	864
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.91 to 25.00°.
Limiting indices	-11<=h<=12, -16<=k<=18, -18<=l<=18
Reflections collected / unique	18808 / 4069 [R(int) = 0.0761]
Completeness to theta = 25.00	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4054 / 13 / 276
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1954
R indices (all data)	R1 = 0.1042, wR2 = 0.2262
Largest diff. peak and hole	0.636 and -0.447 $e.Å^{-3}$

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3h**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-611(2)	1976(1)	7030(1)	58(1)
C(2)	-832(3)	562(2)	7569(2)	45(1)
C(4)	1323(3)	1514(2)	8190(2)	45(1)
C(1)	-63(3)	1403(2)	7559(2)	45(1)
O(4)	5109(2)	2066(2)	10008(2)	78(1)
O(3)	-1293(2)	1694(2)	9006(1)	72(1)
C(9)	1911(3)	929(2)	8878(2)	52(1)
C(3)	-420(3)	-175(2)	7274(2)	49(1)
C(7)	3863(3)	1839(2)	9433(2)	56(1)
C(5)	2061(3)	2269(2)	8133(2)	53(1)
C(19)	1058(3)	280(2)	6266(2)	54(1)
C(8)	3170(3)	1083(2)	9500(2)	57(1)
C(10)	-2150(3)	620(2)	7896(2)	51(1)
C(18)	754(3)	-306(2)	6882(2)	49(1)
C(6)	3305(3)	2427(2)	8740(2)	58(1)
C(20)	2161(3)	149(2)	5891(2)	59(1)
C(17)	-2791(3)	-242(2)	7852(2)	65(1)
N(1)	-3324(3)	-896(2)	7793(3)	92(1)
C(23)	1555(3)	-1044(2)	7095(2)	64(1)
O(2)	-1993(4)	479(2)	9498(2)	122(1)
C(14)	-3242(3)	1255(2)	7288(2)	61(1)
C(21)	2945(3)	-585(3)	6146(3)	73(1)
C(11)	-1800(3)	906(2)	8898(2)	64(1)
C(22)	2652(4)	-1173(3)	6736(3)	78(1)
C(25)	2449(4)	793(3)	5225(3)	85(1)
C(15)	-3605(4)	996(3)	6278(2)	77(1)
C(24)	5700(4)	1524(3)	10770(3)	92(1)
C(16)	-4520(4)	1321(3)	7635(3)	91(1)
C(13)	434(7)	2057(6)	10358(5)	199(3)
C(12)	-965(5)	2073(3)	9919(3)	99(1)

Table S8. Bond lengths [Å] and angles [°] for **3h**.

O(1)-C(1)	1.230(3)
C(2)-C(3)	1.337(4)
C(2)-C(1)	1.524(4)
C(2)-C(10)	1.547(4)
C(4)-C(9)	1.397(4)
C(4)-C(5)	1.406(4)
C(4)-C(1)	1.484(4)
O(4)-C(7)	1.377(4)
O(4)-C(24)	1.430(5)
O(3)-C(11)	1.321(4)
O(3)-C(12)	1.466(4)
C(9)-C(8)	1.393(4)
C(3)-C(18)	1.481(4)
C(7)-C(8)	1.386(4)
C(7)-C(6)	1.396(4)
C(5)-C(6)	1.372(4)
C(19)-C(20)	1.400(4)
C(19)-C(18)	1.399(4)
C(10)-C(17)	1.483(4)
C(10)-C(11)	1.539(5)
C(10)-C(14)	1.585(4)
C(18)-C(23)	1.393(4)
C(20)-C(21)	1.385(5)
C(20)-C(25)	1.508(5)
C(17)-N(1)	1.142(4)
C(23)-C(22)	1.378(5)
O(2)-C(11)	1.188(4)
C(14)-C(16)	1.527(5)
C(14)-C(15)	1.539(5)
C(21)-C(22)	1.369(5)
C(13)-C(12)	1.397(6)
C(3)-C(2)-C(1)	121.6(2)
C(3)-C(2)-C(10)	122.1(2)
C(1)-C(2)-C(10)	116.2(2)
C(9)-C(4)-C(5)	117.5(3)
C(9)-C(4)-C(1)	123.4(2)
C(5)-C(4)-C(1)	118.9(2)
O(1)-C(1)-C(4)	121.6(2)
O(1)-C(1)-C(2)	119.0(2)
C(4)-C(1)-C(2)	119.4(2)

C(7)-O(4)-C(24)	118.7(3)
C(11)-O(3)-C(12)	118.3(3)
C(8)-C(9)-C(4)	122.0(3)
C(2)-C(3)-C(18)	127.6(2)
O(4)-C(7)-C(8)	124.4(3)
O(4)-C(7)-C(6)	115.6(3)
C(8)-C(7)-C(6)	120.0(3)
C(6)-C(5)-C(4)	121.0(3)
C(20)-C(19)-C(18)	121.5(3)
C(7)-C(8)-C(9)	119.0(3)
C(17)-C(10)-C(11)	106.7(3)
C(17)-C(10)-C(2)	109.8(2)
C(11)-C(10)-C(2)	110.3(2)
C(17)-C(10)-C(14)	107.9(3)
C(11)-C(10)-C(14)	109.9(2)
C(2)-C(10)-C(14)	112.1(2)
C(23)-C(18)-C(19)	118.2(3)
C(23)-C(18)-C(3)	120.0(3)
C(19)-C(18)-C(3)	121.7(3)
C(5)-C(6)-C(7)	120.5(3)
C(21)-C(20)-C(19)	117.7(3)
C(21)-C(20)-C(25)	122.4(3)
C(19)-C(20)-C(25)	119.9(3)
N(1)-C(17)-C(10)	177.5(4)
C(22)-C(23)-C(18)	120.5(3)
C(16)-C(14)-C(15)	111.4(3)
C(16)-C(14)-C(10)	111.3(3)
C(15)-C(14)-C(10)	111.4(3)
C(22)-C(21)-C(20)	121.7(3)
O(2)-C(11)-O(3)	124.0(3)
O(2)-C(11)-C(10)	124.2(3)
O(3)-C(11)-C(10)	111.7(3)
C(21)-C(22)-C(23)	120.2(3)
C(13)-C(12)-O(3)	113.0(4)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters (Å^2 x 10^3) for **3h**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

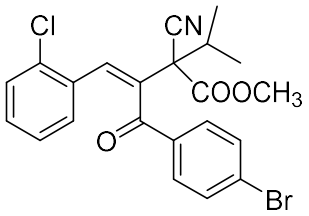
	U11	U22	U33	U23	U13	U12
O(1)	66(1)	49(1)	60(1)	13(1)	17(1)	1(1)
C(2)	53(2)	43(2)	41(2)	1(1)	15(1)	-4(1)
C(4)	57(2)	39(1)	41(2)	-1(1)	20(1)	-4(1)
C(1)	60(2)	40(2)	40(2)	2(1)	22(1)	2(1)
O(4)	70(1)	83(2)	72(2)	-2(1)	3(1)	-19(1)
O(3)	97(2)	75(2)	51(1)	-17(1)	28(1)	-18(1)
C(9)	66(2)	42(2)	50(2)	2(1)	18(2)	-7(1)
C(3)	57(2)	44(2)	49(2)	-2(1)	18(1)	-8(1)
C(7)	59(2)	60(2)	52(2)	-10(2)	18(1)	-6(1)
C(5)	66(2)	40(2)	56(2)	4(1)	22(2)	-4(1)
C(19)	60(2)	52(2)	52(2)	-6(1)	17(1)	-1(1)
C(8)	67(2)	52(2)	50(2)	3(1)	12(2)	-3(2)
C(10)	60(2)	46(2)	53(2)	-4(1)	24(1)	-7(1)
C(18)	55(2)	46(2)	48(2)	-8(1)	15(1)	-7(1)
C(6)	68(2)	45(2)	64(2)	-2(2)	20(2)	-13(1)
C(20)	60(2)	71(2)	48(2)	-11(2)	18(1)	-14(2)
C(17)	68(2)	56(2)	83(2)	-10(2)	42(2)	-10(2)
N(1)	96(2)	65(2)	133(3)	-17(2)	64(2)	-20(2)
C(23)	68(2)	53(2)	73(2)	2(2)	22(2)	2(2)
O(2)	210(4)	104(2)	68(2)	3(2)	63(2)	-50(2)
C(14)	59(2)	62(2)	66(2)	-8(2)	21(2)	1(2)
C(21)	58(2)	88(3)	78(2)	-15(2)	26(2)	4(2)
C(11)	81(2)	63(2)	58(2)	0(2)	35(2)	-10(2)
C(22)	73(2)	72(2)	93(3)	-1(2)	30(2)	14(2)
C(25)	86(2)	104(3)	73(2)	1(2)	37(2)	-16(2)
C(15)	74(2)	88(3)	63(2)	-4(2)	9(2)	9(2)
C(24)	73(2)	121(3)	72(3)	4(2)	1(2)	-11(2)
C(16)	73(2)	102(3)	106(3)	-14(3)	38(2)	14(2)
C(13)	162(5)	296(8)	136(5)	-129(5)	36(4)	2(5)
C(12)	116(3)	124(3)	63(2)	-36(2)	31(2)	-27(3)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3h**.

	x	y	z	U(eq)
H(9)	1447	421	8922	63
H(3)	-932	-662	7319	59
H(5)	1701	2668	7678	63
H(19)	514	767	6103	65
H(8)	3541	685	9955	69
H(6)	3781	2928	8690	70
H(23)	1349	-1453	7483	77
H(14)	-2825	1828	7339	74
H(21)	3690	-681	5911	88
H(22)	3195	-1660	6895	94
H(25A)	3105	557	4939	127
H(25B)	2810	1311	5542	127
H(25C)	1615	921	4770	127
H(15A)	-3930	413	6214	116
H(15B)	-2806	1043	6057	116
H(15C)	-4308	1371	5934	116
H(24A)	5079	1473	11145	138
H(24B)	6547	1770	11118	138
H(24C)	5871	964	10557	138
H(16A)	-5154	1719	7263	136
H(16B)	-4268	1520	8253	136
H(16C)	-4943	765	7606	136
H(13A)	748	1471	10425	298
H(13B)	591	2318	10947	298
H(13C)	926	2369	10002	298
H(12A)	-1281	2665	9872	119
H(12B)	-1456	1763	10285	119

Methyl

(Z)-3-(4-bromobenzoyl)-4-(2-chlorophenyl)-2-cyano-2-isopropylbut-3-enoate (**3m**)



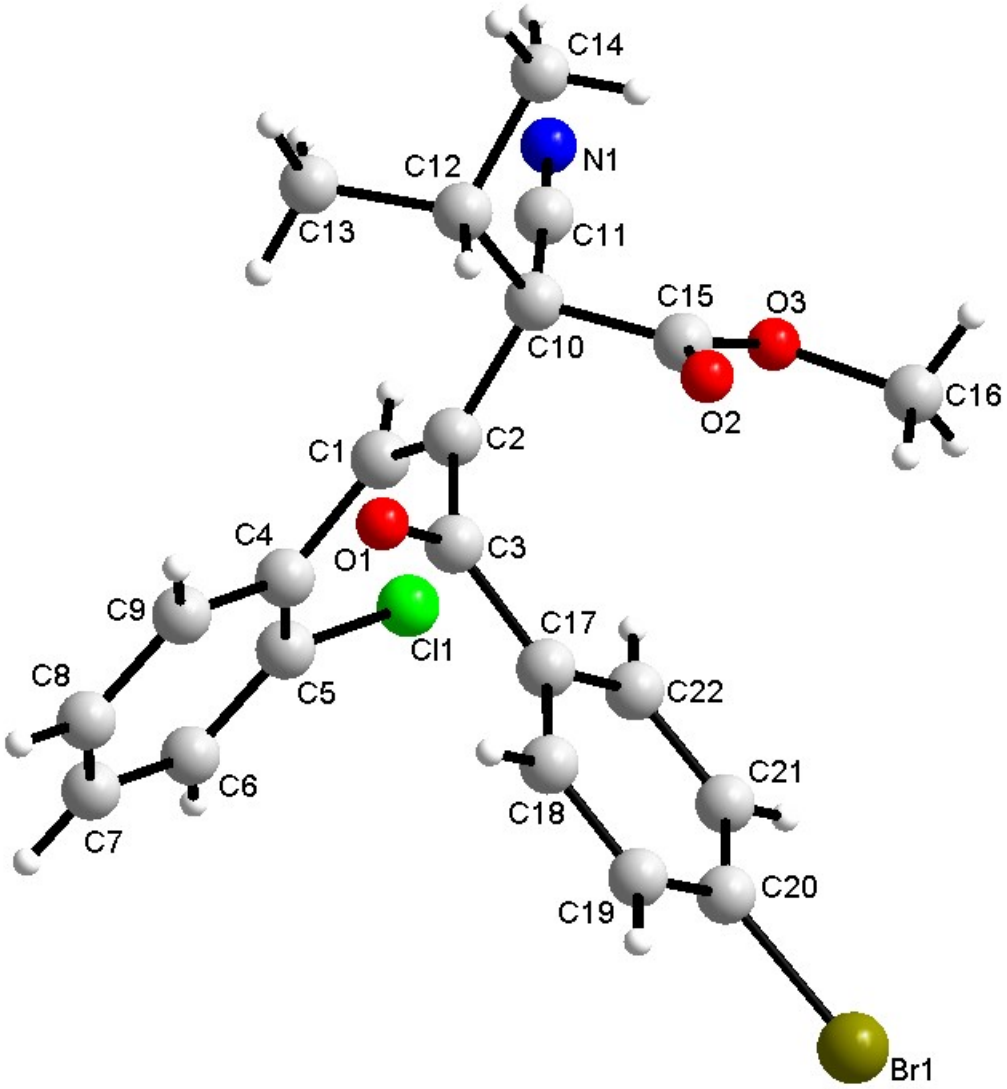


Table S11. Crystal data and structure refinement for **3m**.

Identification code	**3m**
Empirical formula	$C_{22}H_{19}BrClNO_3$
Formula weight	460.73
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.6584(17) Å alpha = 90°.
	b = 7.2134(7) Å beta = 102.956(3)°.
	c = 19.131(2) Å gamma = 90°.
Volume	2105.8(4) $Å^3$
Z, Calculated density	4, 1.453 Mg/m^3
Absorption coefficient	2.101 mm^{-1}
F(000)	936
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.52 to 27.49°.
Limiting indices	-20<=h<=19, -9<=k<=9, -24<=l<=22
Reflections collected / unique	22317 / 4841 [R(int) = 0.0459]
Completeness to theta = 27.49	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4822 / 0 / 256
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1014
R indices (all data)	R1 = 0.0864, wR2 = 0.1269
Largest diff. peak and hole	0.215 and -0.327 $e.Å^{-3}$

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3m**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4594(1)	4534(1)	1121(1)	87(1)
Cl(1)	8210(1)	5296(1)	-955(1)	77(1)
C(2)	8198(1)	9537(3)	499(1)	39(1)
C(1)	8337(1)	8883(3)	-114(1)	41(1)
C(5)	7603(2)	7271(3)	-1246(1)	45(1)
C(4)	7699(1)	8814(3)	-805(1)	40(1)
O(1)	7129(1)	11797(2)	554(1)	71(1)
C(9)	7210(2)	10378(4)	-1076(1)	54(1)
O(3)	8895(2)	7231(3)	1937(1)	83(1)
C(17)	6647(1)	8749(3)	657(1)	42(1)
C(19)	5215(2)	8086(4)	855(2)	62(1)
C(18)	5824(2)	9325(4)	729(1)	53(1)
C(20)	5426(2)	6243(4)	917(1)	57(1)
C(10)	8926(2)	9813(3)	1175(1)	45(1)
C(22)	6831(2)	6860(3)	704(1)	54(1)
O(2)	8146(2)	9686(4)	2111(1)	100(1)
C(8)	6648(2)	10361(4)	-1743(2)	68(1)
C(3)	7295(2)	10160(3)	564(1)	44(1)
C(7)	6560(2)	8804(5)	-2160(1)	66(1)
C(21)	6221(2)	5615(4)	840(2)	61(1)
C(12)	9123(2)	11902(4)	1340(1)	60(1)
N(1)	10383(2)	8263(4)	1022(1)	76(1)
C(11)	9741(2)	8898(4)	1087(1)	52(1)
C(6)	7039(2)	7244(4)	-1915(1)	59(1)
C(15)	8624(2)	8917(4)	1809(1)	60(1)
C(16)	8559(4)	6285(6)	2498(2)	129(2)
C(13)	9304(2)	12935(4)	698(2)	78(1)
C(14)	9887(2)	12153(5)	1988(2)	100(1)

Table S13. Bond lengths [Å] and angles [°] for **3m**.

Br(1)-C(20)	1.896(3)
Cl(1)-C(5)	1.734(2)
C(2)-C(1)	1.327(3)
C(2)-C(3)	1.515(3)
C(2)-C(10)	1.533(3)
C(1)-C(4)	1.469(3)
C(5)-C(4)	1.384(3)
C(5)-C(6)	1.384(3)
C(4)-C(9)	1.396(3)
O(1)-C(3)	1.209(3)
C(9)-C(8)	1.378(4)
O(3)-C(15)	1.293(4)
O(3)-C(16)	1.465(4)
C(17)-C(18)	1.389(3)
C(17)-C(22)	1.392(3)
C(17)-C(3)	1.476(3)
C(19)-C(18)	1.367(4)
C(19)-C(20)	1.369(4)
C(20)-C(21)	1.364(4)
C(10)-C(11)	1.479(4)
C(10)-C(15)	1.540(4)
C(10)-C(12)	1.556(3)
C(22)-C(21)	1.377(4)
O(2)-C(15)	1.182(3)
C(8)-C(7)	1.366(4)
C(7)-C(6)	1.375(4)
C(12)-C(13)	1.515(4)
C(12)-C(14)	1.528(4)
N(1)-C(11)	1.137(3)
C(1)-C(2)-C(3)	121.3(2)
C(1)-C(2)-C(10)	123.5(2)
C(3)-C(2)-C(10)	115.10(19)
C(2)-C(1)-C(4)	126.5(2)
C(4)-C(5)-C(6)	122.3(2)
C(4)-C(5)-Cl(1)	119.26(17)
C(6)-C(5)-Cl(1)	118.43(19)
C(5)-C(4)-C(9)	116.7(2)
C(5)-C(4)-C(1)	122.3(2)
C(9)-C(4)-C(1)	120.8(2)
C(8)-C(9)-C(4)	121.2(3)

C(15)-O(3)-C(16)	114.9(3)
C(18)-C(17)-C(22)	118.0(2)
C(18)-C(17)-C(3)	119.0(2)
C(22)-C(17)-C(3)	123.0(2)
C(18)-C(19)-C(20)	119.1(2)
C(19)-C(18)-C(17)	121.4(2)
C(21)-C(20)-C(19)	121.4(2)
C(21)-C(20)-Br(1)	119.5(2)
C(19)-C(20)-Br(1)	119.0(2)
C(11)-C(10)-C(2)	110.15(19)
C(11)-C(10)-C(15)	109.1(2)
C(2)-C(10)-C(15)	107.90(19)
C(11)-C(10)-C(12)	108.6(2)
C(2)-C(10)-C(12)	111.89(19)
C(15)-C(10)-C(12)	109.2(2)
C(21)-C(22)-C(17)	120.5(2)
C(7)-C(8)-C(9)	120.5(3)
O(1)-C(3)-C(17)	121.6(2)
O(1)-C(3)-C(2)	119.3(2)
C(17)-C(3)-C(2)	119.01(19)
C(8)-C(7)-C(6)	119.9(2)
C(20)-C(21)-C(22)	119.5(2)
C(13)-C(12)-C(14)	110.1(3)
C(13)-C(12)-C(10)	112.1(2)
C(14)-C(12)-C(10)	111.2(2)
N(1)-C(11)-C(10)	177.2(3)
C(7)-C(6)-C(5)	119.3(2)
O(2)-C(15)-O(3)	124.5(3)
O(2)-C(15)-C(10)	121.9(3)
O(3)-C(15)-C(10)	113.5(2)

Symmetry transformations used to generate equivalent atoms:

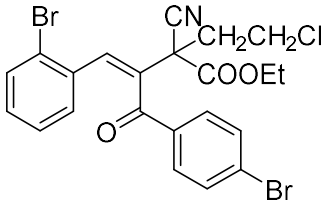
Table S14. Anisotropic displacement parameters (Å^2 x 10^3) for **3m**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	76(1)	108(1)	87(1)	-13(1)	35(1)	-39(1)
Cl(1)	93(1)	54(1)	75(1)	-4(1)	4(1)	15(1)
C(2)	35(1)	41(1)	40(1)	1(1)	8(1)	1(1)
C(1)	32(1)	48(1)	42(1)	3(1)	8(1)	3(1)
C(5)	41(1)	52(1)	44(1)	0(1)	10(1)	-3(1)
C(4)	33(1)	49(1)	37(1)	0(1)	8(1)	-2(1)
O(1)	61(1)	48(1)	109(2)	-5(1)	31(1)	9(1)
C(9)	51(2)	57(2)	50(2)	0(1)	3(1)	7(1)
O(3)	113(2)	76(1)	70(1)	19(1)	43(1)	3(1)
C(17)	34(1)	52(1)	40(1)	-7(1)	8(1)	3(1)
C(19)	40(1)	84(2)	67(2)	-4(2)	20(1)	3(1)
C(18)	43(1)	61(2)	56(2)	-1(1)	14(1)	12(1)
C(20)	51(2)	72(2)	52(2)	-11(1)	17(1)	-13(1)
C(10)	42(1)	56(1)	35(1)	2(1)	6(1)	1(1)
C(22)	45(1)	54(1)	67(2)	-6(1)	22(1)	4(1)
O(2)	116(2)	125(2)	79(2)	16(1)	61(2)	29(2)
C(8)	62(2)	80(2)	56(2)	13(2)	0(2)	16(2)
C(3)	43(1)	46(1)	43(1)	-6(1)	8(1)	5(1)
C(7)	53(2)	99(2)	40(1)	6(2)	-1(1)	0(2)
C(21)	61(2)	50(1)	78(2)	-7(1)	27(2)	-6(1)
C(12)	56(2)	65(2)	55(2)	-7(1)	1(1)	-4(1)
N(1)	50(1)	103(2)	73(2)	5(2)	9(1)	16(1)
C(11)	44(1)	69(2)	41(1)	8(1)	3(1)	3(1)
C(6)	55(2)	76(2)	43(2)	-13(1)	8(1)	-14(1)
C(15)	58(2)	81(2)	41(1)	2(1)	9(1)	-1(2)
C(16)	192(5)	114(3)	103(3)	39(3)	82(3)	-10(3)
C(13)	86(2)	64(2)	81(2)	6(2)	10(2)	-17(2)
C(14)	97(3)	105(3)	76(2)	-19(2)	-24(2)	-17(2)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3m**.

	x	y	z	U(eq)
H(1)	8895	8424	-105	49
H(9)	7265	11453	-800	64
H(19)	4665	8490	897	75
H(18)	5685	10579	692	64
H(22)	7371	6435	644	64
H(8)	6327	11417	-1910	81
H(7)	6177	8800	-2608	79
H(21)	6351	4356	878	74
H(12)	8602	12455	1459	72
H(6)	6984	6181	-2197	70
H(16A)	8966	6434	2951	193
H(16B)	8486	4989	2385	193
H(16C)	8004	6810	2525	193
H(13A)	9457	14196	831	118
H(13B)	8789	12915	315	118
H(13C)	9780	12349	543	118
H(14A)	10413	11673	1877	150
H(14B)	9765	11496	2391	150
H(14C)	9962	13447	2102	150

Ethyl (Z)-3-(4-bromobenzoyl)-4-(2-bromophenyl)-2-(2-chloroethyl)-2-cyanobut-3-enoate (**3p**)



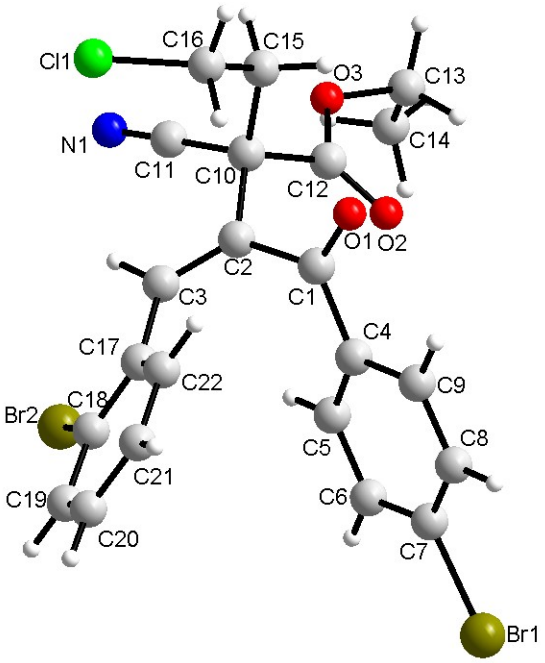


Table S16. Crystal data and structure refinement for **3p**.

Identification code	**3p**
Empirical formula	$C_{22}H_{18}Br_2ClNO_3$
Formula weight	539.62
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.1923(11) Å alpha = 75.123(4)°.
	b = 10.0872(14) Å beta = 88.610(4)°.
	c = 13.952(2) Å gamma = 78.866(4)°.
Volume	1093.0(3) $Å^3$
Z, Calculated density	2, 1.640 Mg/m^3
Absorption coefficient	3.853 mm^{-1}
F(000)	536
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.51 to 27.53°.
Limiting indices	-10<=h<=10, -13<=k<=13, -18<=l<=17
Reflections collected / unique	12899 / 5034 [R(int) = 0.0545]
Completeness to theta = 27.53	96.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4873 / 1 / 263
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1377
R indices (all data)	R1 = 0.1293, wR2 = 0.1730
Largest diff. peak and hole	0.686 and -0.484 $e.Å^{-3}$

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3p**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(2)	3405(1)	-746(1)	9366(1)	67(1)
Br(1)	6157(1)	5987(1)	8917(1)	70(1)
Cl(1)	-3090(2)	1280(2)	6752(2)	102(1)
C(3)	845(6)	1515(5)	7925(4)	40(1)
O(1)	-309(5)	4851(4)	6507(3)	71(1)
C(2)	793(6)	2454(5)	7059(4)	39(1)
C(1)	801(6)	3971(5)	6969(4)	44(1)
C(5)	3611(6)	3509(5)	7832(4)	46(1)
C(4)	2137(6)	4396(5)	7461(3)	42(1)
C(22)	-129(6)	2834(6)	9173(4)	52(1)
C(6)	4800(6)	3950(5)	8274(4)	51(1)
C(17)	899(6)	1723(5)	8915(3)	40(1)
C(7)	4531(6)	5317(5)	8319(4)	47(1)
N(1)	989(7)	-606(5)	6383(4)	72(1)
C(11)	810(7)	560(6)	6245(4)	51(1)
C(18)	1911(6)	782(5)	9664(4)	49(1)
C(10)	606(7)	2079(5)	6077(4)	47(1)
O(2)	2753(6)	3420(5)	5488(3)	77(1)
C(9)	1918(6)	5785(5)	7504(4)	47(1)
C(8)	3077(7)	6246(5)	7949(4)	53(1)
C(15)	-1087(7)	2802(6)	5492(4)	59(2)
C(20)	887(8)	2014(8)	10850(4)	67(2)
C(12)	1992(8)	2566(6)	5384(4)	59(2)
C(16)	-2645(8)	2903(7)	6147(6)	81(2)
C(21)	-134(8)	2995(7)	10124(5)	67(2)
C(19)	1910(7)	911(6)	10621(4)	57(2)
O(3)	2120(6)	1985(5)	4640(3)	88(1)
C(13)	3204(12)	2489(8)	3830(6)	120(3)
C(14)	4740(11)	1514(11)	3932(9)	190(6)

Table S18. Bond lengths [Å] and angles [°] for **3p**.

Br(2)-C(18)	1.903(5)
Br(1)-C(7)	1.902(5)
Cl(1)-C(16)	1.741(7)
C(3)-C(2)	1.327(6)
C(3)-C(17)	1.451(7)
O(1)-C(1)	1.206(5)
C(2)-C(1)	1.504(6)
C(2)-C(10)	1.530(7)
C(1)-C(4)	1.490(7)
C(5)-C(6)	1.366(7)
C(5)-C(4)	1.379(7)
C(4)-C(9)	1.394(6)
C(22)-C(21)	1.377(7)
C(22)-C(17)	1.387(7)
C(6)-C(7)	1.371(7)
C(17)-C(18)	1.382(7)
C(7)-C(8)	1.384(7)
N(1)-C(11)	1.122(6)
C(11)-C(10)	1.466(7)
C(18)-C(19)	1.375(7)
C(10)-C(12)	1.544(8)
C(10)-C(15)	1.575(7)
O(2)-C(12)	1.195(7)
C(9)-C(8)	1.361(7)
C(15)-C(16)	1.555(9)
C(20)-C(19)	1.360(8)
C(20)-C(21)	1.383(9)
C(12)-O(3)	1.310(7)
O(3)-C(13)	1.468(8)
C(13)-C(14)	1.425(8)
C(2)-C(3)-C(17)	128.5(4)
C(3)-C(2)-C(1)	122.9(4)
C(3)-C(2)-C(10)	121.8(4)
C(1)-C(2)-C(10)	115.2(4)
O(1)-C(1)-C(4)	119.7(4)
O(1)-C(1)-C(2)	119.2(4)
C(4)-C(1)-C(2)	121.0(4)
C(6)-C(5)-C(4)	121.4(5)
C(5)-C(4)-C(9)	118.2(5)
C(5)-C(4)-C(1)	123.6(4)

C(9)-C(4)-C(1)	118.1(4)
C(21)-C(22)-C(17)	121.8(5)
C(5)-C(6)-C(7)	118.8(5)
C(18)-C(17)-C(22)	116.4(5)
C(18)-C(17)-C(3)	121.7(5)
C(22)-C(17)-C(3)	121.8(4)
C(8)-C(7)-C(6)	121.7(5)
C(8)-C(7)-Br(1)	117.8(4)
C(6)-C(7)-Br(1)	120.4(4)
N(1)-C(11)-C(10)	178.9(6)
C(19)-C(18)-C(17)	122.8(5)
C(19)-C(18)-Br(2)	118.0(4)
C(17)-C(18)-Br(2)	119.2(4)
C(11)-C(10)-C(2)	110.2(4)
C(11)-C(10)-C(12)	108.0(4)
C(2)-C(10)-C(12)	108.6(4)
C(11)-C(10)-C(15)	109.0(4)
C(2)-C(10)-C(15)	114.7(4)
C(12)-C(10)-C(15)	106.1(4)
C(8)-C(9)-C(4)	121.4(5)
C(9)-C(8)-C(7)	118.3(5)
C(16)-C(15)-C(10)	115.0(5)
C(19)-C(20)-C(21)	120.1(5)
O(2)-C(12)-O(3)	125.5(6)
O(2)-C(12)-C(10)	124.0(5)
O(3)-C(12)-C(10)	110.3(5)
C(15)-C(16)-Cl(1)	113.2(4)
C(22)-C(21)-C(20)	119.6(6)
C(20)-C(19)-C(18)	119.3(5)
C(12)-O(3)-C(13)	117.5(6)
C(14)-C(13)-O(3)	109.1(7)

Symmetry transformations used to generate equivalent atoms:

Table S19. Anisotropic displacement parameters (Å^2 x 10^3) for **3p**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(2)	72(1)	51(1)	72(1)	-13(1)	-16(1)	-1(1)
Br(1)	67(1)	72(1)	77(1)	-25(1)	-7(1)	-24(1)
Cl(1)	84(1)	108(2)	101(2)	-7(1)	11(1)	-14(1)
C(3)	43(3)	32(3)	46(3)	-11(2)	0(2)	-6(2)
O(1)	77(3)	37(2)	90(3)	-10(2)	-34(2)	3(2)
C(2)	43(3)	34(3)	39(3)	-10(2)	-4(2)	-4(2)
C(1)	53(3)	34(3)	39(3)	-5(2)	-3(2)	-1(2)
C(5)	49(3)	30(3)	54(3)	-7(2)	-1(3)	-3(2)
C(4)	56(3)	35(3)	33(3)	-7(2)	6(2)	-6(2)
C(22)	56(3)	54(3)	47(3)	-15(3)	6(3)	-11(3)
C(6)	48(3)	39(3)	60(4)	-6(3)	-6(3)	-5(2)
C(17)	44(3)	38(3)	39(3)	-5(2)	3(2)	-16(2)
C(7)	48(3)	48(3)	49(3)	-13(3)	8(2)	-16(3)
N(1)	94(4)	50(3)	71(4)	-21(3)	-11(3)	-4(3)
C(11)	66(4)	40(3)	45(3)	-13(3)	-9(3)	0(3)
C(18)	49(3)	46(3)	54(3)	-13(3)	4(3)	-16(2)
C(10)	65(3)	31(3)	41(3)	-9(2)	-3(3)	-3(2)
O(2)	90(3)	90(3)	60(3)	-22(2)	10(2)	-35(3)
C(9)	51(3)	32(3)	52(3)	-11(2)	-2(3)	4(2)
C(8)	67(4)	40(3)	57(4)	-18(3)	7(3)	-14(3)
C(15)	71(4)	51(3)	48(3)	-10(3)	-18(3)	4(3)
C(20)	70(4)	103(5)	42(3)	-32(4)	14(3)	-36(4)
C(12)	77(4)	51(4)	41(3)	-10(3)	3(3)	0(3)
C(16)	72(4)	69(4)	100(5)	-23(4)	-21(4)	-6(3)
C(21)	63(4)	84(5)	66(4)	-35(4)	19(3)	-23(3)
C(19)	63(4)	69(4)	38(3)	-3(3)	-5(3)	-25(3)
O(3)	124(4)	78(3)	67(3)	-30(3)	35(3)	-20(3)
C(13)	165(9)	101(6)	77(5)	-14(5)	61(6)	-4(6)
C(14)	122(8)	152(10)	214(13)	66(9)	83(8)	10(7)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3p**.

	x	y	z	U(eq)
H(3)	848	585	7894	48
H(5)	3802	2572	7780	55
H(22)	-849	3502	8681	63
H(6)	5796	3322	8545	61
H(9)	939	6422	7216	56
H(8)	2893	7182	8004	64
H(15A)	-992	3757	5113	71
H(15B)	-1260	2275	5007	71
H(20)	874	2110	11510	80
H(16A)	-3618	3463	5725	97
H(16B)	-2464	3402	6649	97
H(21)	-834	3774	10280	81
H(19)	2616	237	11118	68
H(13A)	2658	2591	3183	144
H(13B)	3411	3416	3854	144
H(14A)	5501	1729	4376	285
H(14B)	5238	1576	3280	285
H(14C)	4538	565	4209	285