Article

Adamantane-functionalized phthalimide scaffold: pathway to supramolecular interactions

Hamidou Keita[*]

Department of Chemistry, Clemson University, Clemson, SC 29634, United States
Email: hkeita@g.clemson.edu

Synthesis of AcidBr

1,2-dibromo O-xylene 200mg (0.757mmol) was dispersed in 3.6ml pyridine and 6ml water mixture. Then 473mg KMnO$_4$ (2.99mmol, 3.95eq) was added to it and reflux for 2hr. After which 945mg KMnO$_2$ was added several times (7x) and the reaction was kept refluxing overnight. After 16hrs, the mixture was filtered while hot and the residue washed with hot water. The filtrate was reduced under vacuum to remove the pyridine and the remaining solution was acidified with conc. HCl to form a white precipitate which was filtered and dried. Yield 208mg, 85%. Because of limited solubility of the product in organic solvent, a satisfactory NMR could not be obtained. ATR-IR: v 3091 (vw), 2904 (vw), 2791 (vw), 2616 (vw), 2516 (vw), 1700 (s), 1515 (w), 1408 (w), 1289 (m), 1239(s), 1158 (w), 1077 (m), 876 (m), 816 (w), 776 (m), 701(w), 607 (vw).

### Appendix A: NMR spectra of AdBr and its precursors.
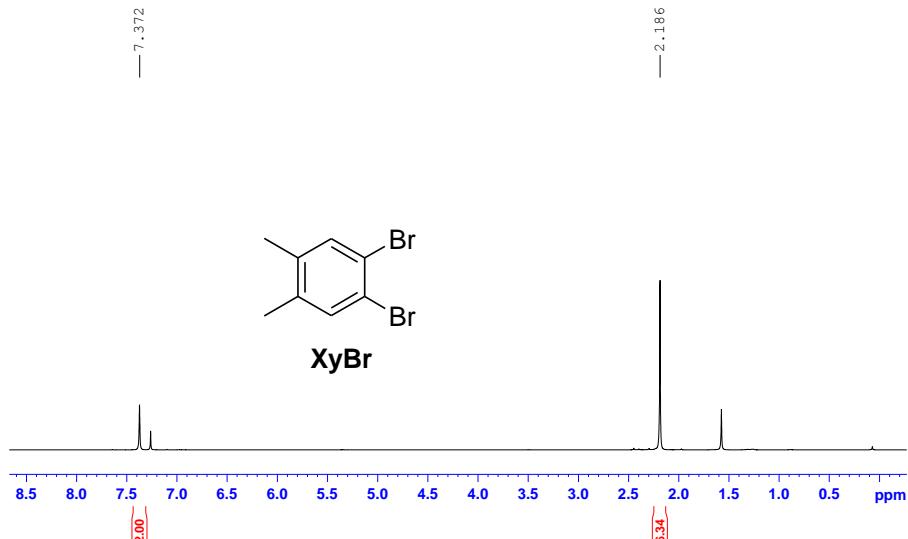
**Figure A1.** ^{1}H-NMR (CDCl$_3$) spectrum of XyBr.
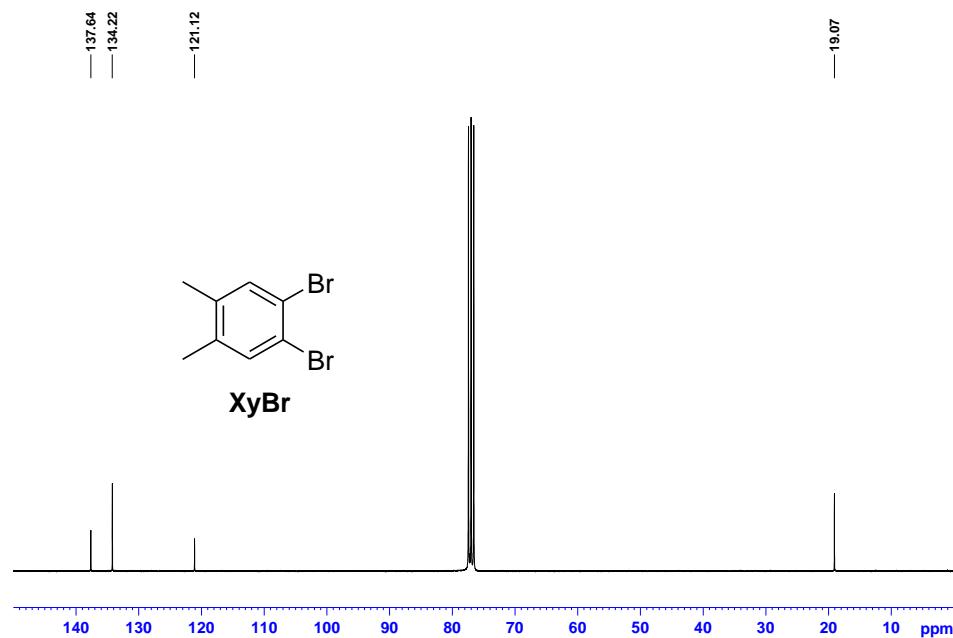
Figure A2. ^{13}C-NMR (CDCl$_3$) spectrum of XyBr.
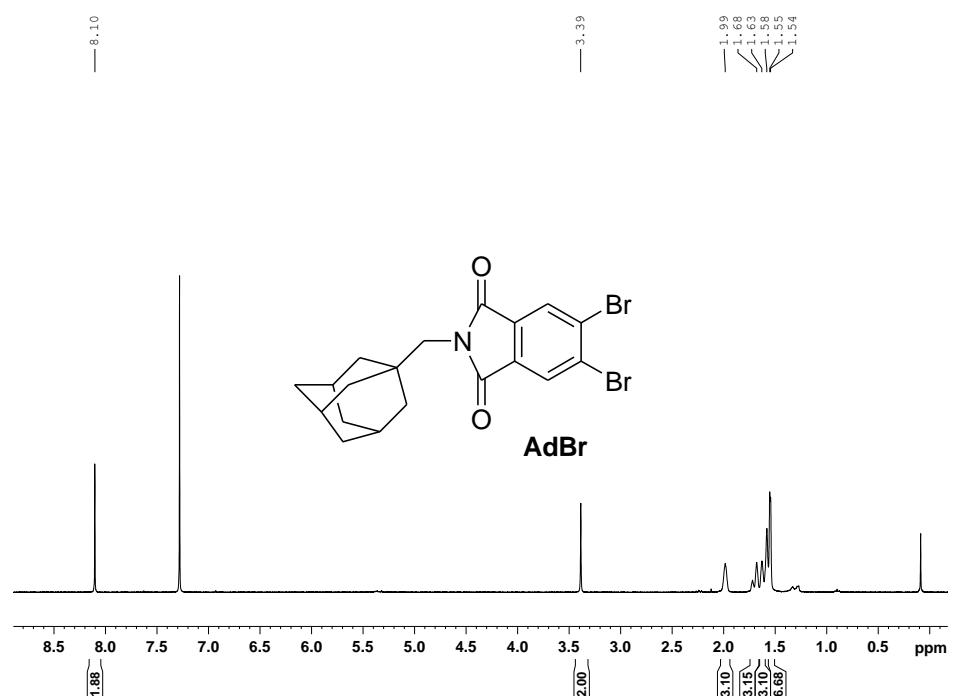
Figure A3. ^{1}H-NMR (CDCl$_3$) spectrum of AdBr.

— 8.10

AdBr

8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm

1.88

— 3.39

— 1.99

1.68
1.63
1.58
1.55
1.54

AdBr

3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 ppm

2.00   3.10   3.15 3.10 6.68
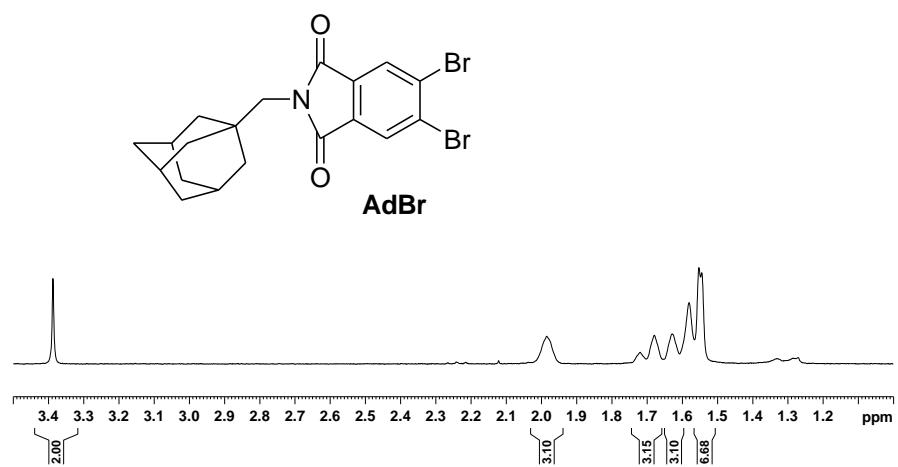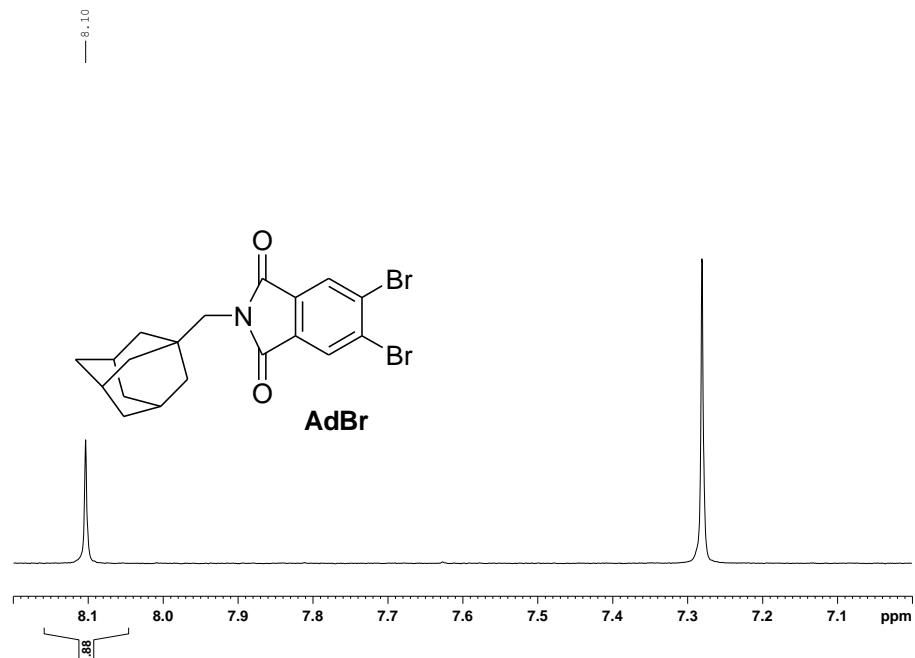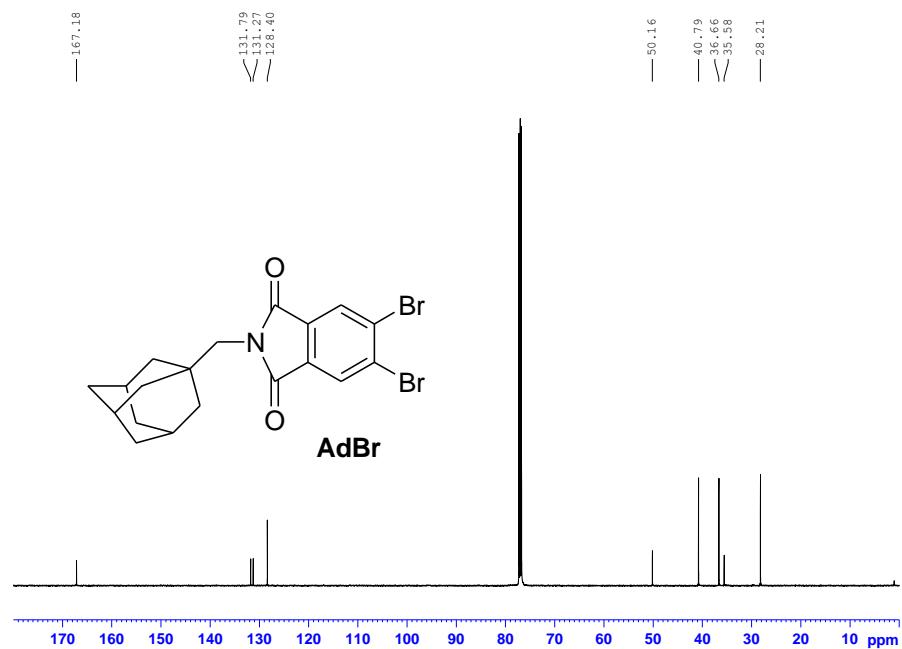
Figure A4. ^{13}C-NMR (CDCl$_3$) spectrum of AdBr.
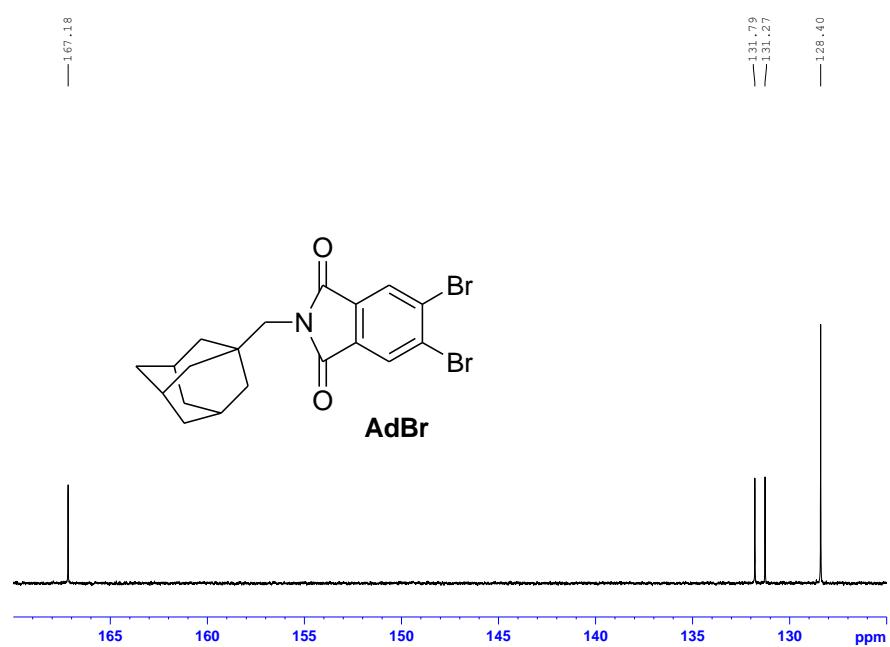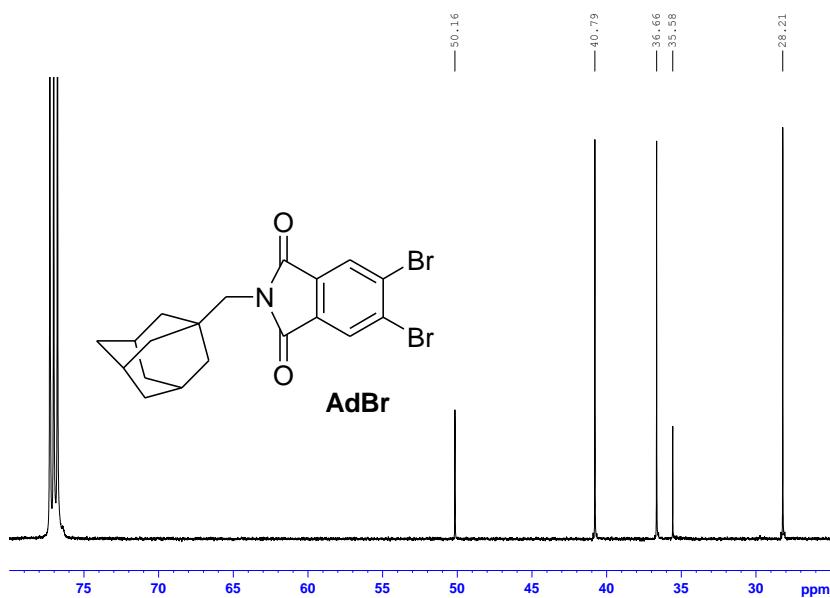
C₁₉H₁₉Br₂NO₂

Crystal Structure Report for Q_0098_HK_AdBr

A specimen of $C_{19}H_{19}Br_2NO_2$, approximate dimensions 0.256 mm x 0.312 mm x 0.452 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a triclinic unit cell yielded a total of 40110 reflections to a maximum θ angle of 33.18° (0.65 Å resolution), of which 6439 were independent (average redundancy 6.229, completeness = 98.7%, R_{int} = 1.69%, R_{sig} = 1.07%) and 6143 (95.40%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 7.3485(3) Å, $\underline{b}$ = 8.0912(4) Å, $\underline{c}$ = 15.0118(7) Å, α = 100.7690(10)°, β = 102.3410(10)°, γ = 93.5710(10)°, volume = 851.72(7) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7672 and 1.0000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{19}H_{19}Br_2NO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 217 variables converged at R1 = 1.61%, for the observed data and wR2 = 4.13% for all data. The goodness-of-fit was 1.088. The largest peak in the final difference electron density synthesis was 0.663 e⁻/Å³ and the largest hole was -0.346 e⁻/Å³ with an RMS deviation of 0.057 e⁻/Å³. On the basis of the final model, the calculated density was 1.767 g/cm³ and F(000), 452 e⁻.
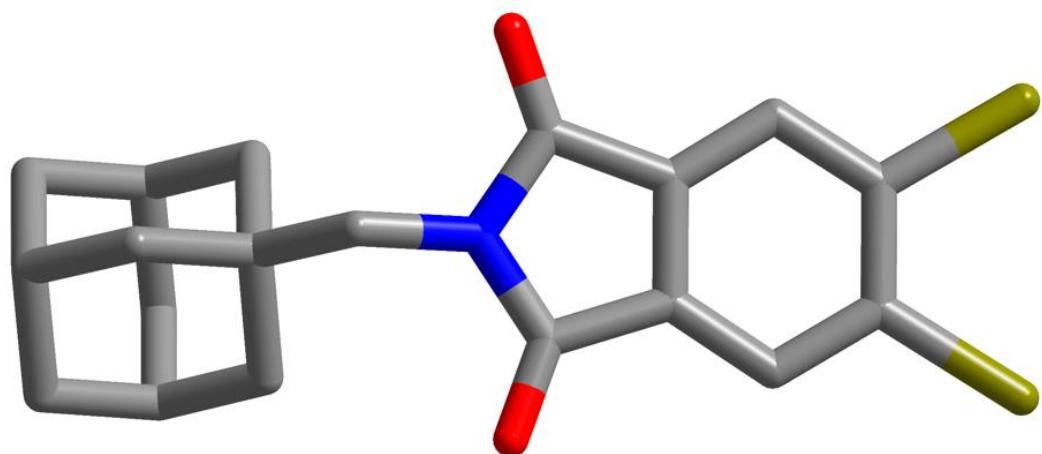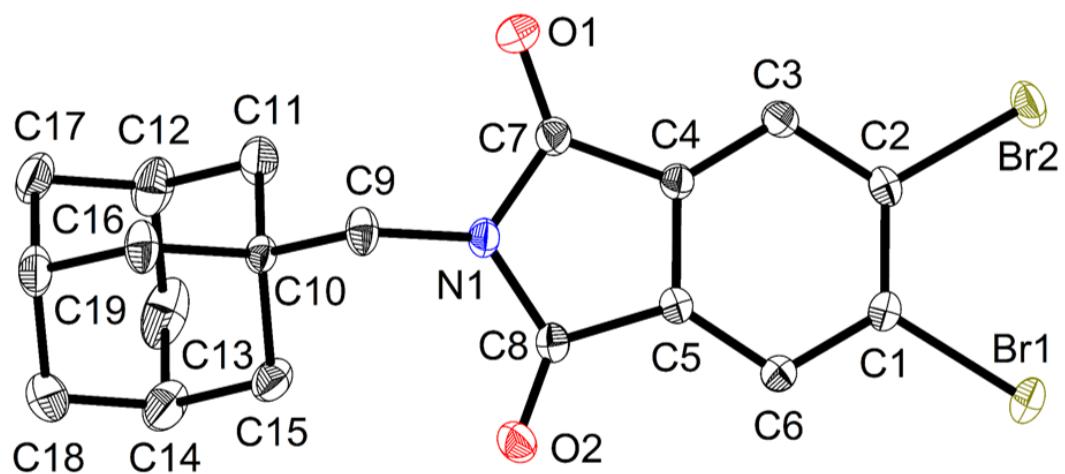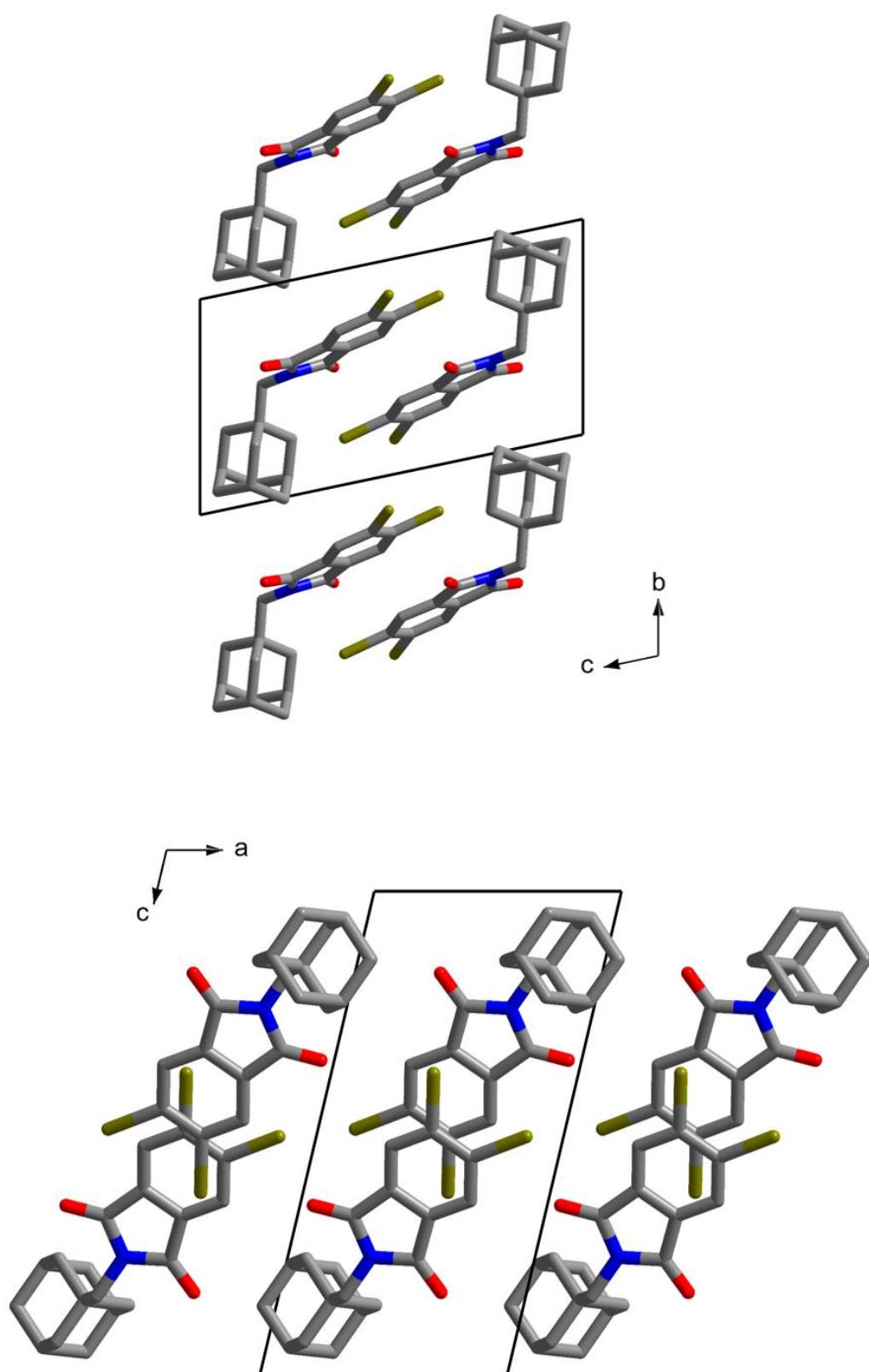
Table 1. Sample and crystal data for Q_0098_HK_AdBr.

Identification code	Q_0098_HK_XyBrAd	
Chemical formula	$C_{19}H_{19}Br_2NO_2$	
Formula weight	453.17 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.256 x 0.312 x 0.452 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.3485(3) Å	α = 100.7690(10)°
	b = 8.0912(4) Å	β = 102.3410(10)°
	c = 15.0118(7) Å	γ = 93.5710(10)°
Volume	851.72(7) Å³	
Z	2	
Density (calculated)	1.767 g/cm³	
Absorption coefficient	4.770 mm⁻¹	
F(000)	452	

Table 2. Data collection and structure refinement for Q_0098_HK_AdBr.

Theta range for data collection	3.42 to 33.18°	
Index ranges	-11<=h<=11, -12<=k<=12, -23<=l<=23	
Reflections collected	40110	
Independent reflections	6439 [R(int) = 0.0169]	
Max. and min. transmission	1.0000 and 0.7672	
Structure solution technique	direct methods	
Structure solution program	SHELXT-2014 (Sheldrick 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick 2014)	
Function minimized	$\Sigma \ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6439 / 0 / 217	
Goodness-of-fit on F^2	1.088	
Δ/σ_{max}	0.002	
Final R indices	6143 data; I>2σ(I)	R1 = 0.0161, wR2 = 0.0406
	all data	R1 = 0.0174, wR2 = 0.0413
Weighting scheme	w=1/[σ²(F_o^2)+(0.0158P)²+0.4101P] where P=(F_o^2+2F_c^2)/3	
Largest diff. peak and hole	0.663 and -0.346 eÅ⁻³	
R.M.S. deviation from mean	0.057 eÅ⁻³	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for Q_0098_HK_AdBr. (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.)

	x/a	y/b	z/c	U(eq)
Br1	0.58591(2)	0.21447(2)	0.62299(2)	0.01510(2)
Br2	0.15127(2)	0.16213(2)	0.49231(2)	0.01569(3)
O1	0.34660(10)	0.37497(10)	0.16986(5)	0.01932(13)
O2	0.94584(9)	0.44529(9)	0.34972(5)	0.01524(12)
N1	0.66304(11)	0.43117(9)	0.24250(5)	0.01154(12)
C1	0.53605(12)	0.26853(10)	0.50404(6)	0.01088(13)
C2	0.35343(12)	0.24502(10)	0.44869(6)	0.01099(13)
C3	0.31537(12)	0.28185(11)	0.35965(6)	0.01171(13)
C4	0.46674(12)	0.33939(10)	0.32879(6)	0.01065(13)
C5	0.64773(11)	0.36354(10)	0.38372(6)	0.01024(13)
C6	0.68727(12)	0.33123(11)	0.47268(6)	0.01144(13)
C7	0.47374(12)	0.38227(11)	0.23718(6)	0.01229(14)
C8	0.77659(12)	0.41934(10)	0.32834(6)	0.01095(13)
C9	0.73566(13)	0.45557(11)	0.16189(6)	0.01323(14)

	x/a	y/b	z/c	U(eq)
C10	0.77602(12)	0.63953(10)	0.15439(6)	0.01047(13)
C11	0.59891(13)	0.73175(12)	0.14371(7)	0.01691(16)
C12	0.64795(16)	0.91420(13)	0.13359(7)	0.02065(18)
C13	0.7971(2)	0.00774(13)	0.21929(8)	0.0260(2)
C14	0.97364(17)	0.91590(13)	0.22834(7)	0.0227(2)
C15	0.92349(14)	0.73548(12)	0.23955(6)	0.01692(16)
C16	0.85540(14)	0.63737(12)	0.06731(6)	0.01619(15)
C17	0.72568(15)	0.90948(13)	0.04614(7)	0.01939(17)
C18	0.05144(16)	0.91158(14)	0.14127(8)	0.0243(2)
C19	0.90302(15)	0.81863(13)	0.05578(7)	0.01812(16)

Table 4. Bond lengths (Å) for Q_0098_HK_AdBr.

Br1-C1	**1.8832(8)**	**Br2-C2**	**1.8819(8)**
O1-C7	1.2104(11)	O2-C8	1.2107(10)
N1-C8	1.4009(11)	N1-C7	1.4036(11)
N1-C9	1.4629(11)	C1-C6	1.3987(12)
C1-C2	1.4000(12)	C2-C3	1.3975(12)
C3-C4	1.3802(12)	C3-H3	0.95
C4-C5	1.3877(11)	C4-C7	1.4902(12)
C5-C6	1.3820(12)	C5-C8	1.4884(12)
C6-H6	0.95	C9-C10	1.5291(12)
C9-H9A	0.99	C9-H9B	0.99
C10-C15	1.5309(12)	C10-C11	1.5339(13)
C10-C16	1.5389(12)	C11-C12	1.5406(14)
C11-H11A	0.99	C11-H11B	0.99
C12-C17	1.5348(14)	C12-C13	1.5359(17)
C12-H12	1.0	C13-C14	1.5285(18)
C13-H13A	0.99	C13-H13B	0.99
C14-C18	1.5303(16)	C14-C15	1.5318(13)
C14-H14	1.0	C15-H15A	0.99
C15-H15B	0.99	C16-C19	1.5363(13)
C16-H16A	0.99	C16-H16B	0.99
C17-C19	1.5291(15)	C17-H17A	0.99
C17-H17B	0.99	C18-C19	1.5300(15)
C18-H18A	0.99	C18-H18B	0.99
C19-H19	1.0		

Table 5. Bond angles (°) for Q_0098_HK_AdBr.

C8-N1-C7	**111.55(7)**	**C8-N1-C9**	**123.81(7)**
C7-N1-C9	123.41(7)	C6-C1-C2	121.28(8)
C6-C1-Br1	117.88(6)	C2-C1-Br1	120.84(6)
C3-C2-C1	121.31(8)	C3-C2-Br2	117.96(6)
C1-C2-Br2	120.74(6)	C4-C3-C2	116.69(8)
C4-C3-H3	121.7	C2-C3-H3	121.7
C3-C4-C5	122.07(8)	C3-C4-C7	129.64(8)
C5-C4-C7	108.28(7)	C6-C5-C4	121.97(8)
C6-C5-C8	129.84(8)	C4-C5-C8	108.15(7)
C5-C6-C1	116.65(8)	C5-C6-H6	121.7
C1-C6-H6	121.7	O1-C7-N1	125.38(8)
O1-C7-C4	128.73(8)	N1-C7-C4	105.88(7)
O2-C8-N1	125.43(8)	O2-C8-C5	128.43(8)
N1-C8-C5	106.11(7)	N1-C9-C10	115.57(7)
N1-C9-H9A	108.4	C10-C9-H9A	108.4
N1-C9-H9B	108.4	C10-C9-H9B	108.4

H9A-C9-H9B	107.4	C9-C10-C15	110.61(7)
C9-C10-C11	112.26(7)	C15-C10-C11	109.55(7)
C9-C10-C16	107.32(7)	C15-C10-C16	108.37(7)
C11-C10-C16	108.61(7)	C10-C11-C12	109.66(8)
C10-C11-H11A	109.7	C12-C11-H11A	109.7
C10-C11-H11B	109.7	C12-C11-H11B	109.7
H11A-C11-H11B	108.2	C17-C12-C13	109.09(9)
C17-C12-C11	109.21(8)	C13-C12-C11	109.81(8)
C17-C12-H12	109.6	C13-C12-H12	109.6
C11-C12-H12	109.6	C14-C13-C12	109.78(8)
C14-C13-H13A	109.7	C12-C13-H13A	109.7
C14-C13-H13B	109.7	C12-C13-H13B	109.7
H13A-C13-H13B	108.2	C13-C14-C18	109.60(9)
C13-C14-C15	108.81(9)	C18-C14-C15	110.15(9)
C13-C14-H14	109.4	C18-C14-H14	109.4
C15-C14-H14	109.4	C10-C15-C14	110.34(7)
C10-C15-H15A	109.6	C14-C15-H15A	109.6
C10-C15-H15B	109.6	C14-C15-H15B	109.6
H15A-C15-H15B	108.1	C19-C16-C10	110.52(7)
C19-C16-H16A	109.5	C10-C16-H16A	109.5
C19-C16-H16B	109.5	C10-C16-H16B	109.5
H16A-C16-H16B	108.1	C19-C17-C12	109.42(8)
C19-C17-H17A	109.8	C12-C17-H17A	109.8
C19-C17-H17B	109.8	C12-C17-H17B	109.8
H17A-C17-H17B	108.2	C19-C18-C14	109.06(8)
C19-C18-H18A	109.9	C14-C18-H18A	109.9
C19-C18-H18B	109.9	C14-C18-H18B	109.9
H18A-C18-H18B	108.3	C17-C19-C18	110.21(9)
C17-C19-C16	109.30(8)	C18-C19-C16	108.96(8)
C17-C19-H19	109.5	C18-C19-H19	109.5
C16-C19-H19	109.5		

Table 6. Anisotropic atomic displacement parameters (Å^2) for Q_0098_HK_AdBr. (The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.01884(4)	0.01741(4)	0.01094(4)	0.00628(3)	0.00424(3)	0.00313(3)
Br2	0.01350(4)	0.01853(4)	0.01773(4)	0.00578(3)	0.00822(3)	-0.00029(3)
O1	0.0169(3)	0.0264(4)	0.0123(3)	0.0059(3)	-0.0014(2)	-0.0039(3)
O2	0.0107(3)	0.0177(3)	0.0193(3)	0.0075(2)	0.0045(2)	0.0018(2)
N1	0.0133(3)	0.0125(3)	0.0095(3)	0.0034(2)	0.0036(2)	-0.0004(2)
C1	0.0133(3)	0.0106(3)	0.0098(3)	0.0031(2)	0.0038(3)	0.0020(3)
C2	0.0114(3)	0.0103(3)	0.0124(3)	0.0023(3)	0.0053(3)	0.0004(2)
C3	0.0107(3)	0.0123(3)	0.0118(3)	0.0022(3)	0.0026(3)	-0.0001(3)
C4	0.0112(3)	0.0110(3)	0.0097(3)	0.0022(2)	0.0025(3)	0.0001(3)
C5	0.0104(3)	0.0101(3)	0.0106(3)	0.0024(2)	0.0032(2)	0.0008(2)
C6	0.0109(3)	0.0123(3)	0.0114(3)	0.0034(3)	0.0024(3)	0.0013(3)
C7	0.0136(3)	0.0121(3)	0.0106(3)	0.0022(3)	0.0024(3)	-0.0012(3)
C8	0.0121(3)	0.0100(3)	0.0118(3)	0.0033(3)	0.0042(3)	0.0014(3)
C9	0.0193(4)	0.0107(3)	0.0110(3)	0.0015(3)	0.0074(3)	0.0002(3)
C10	0.0130(3)	0.0104(3)	0.0084(3)	0.0020(2)	0.0036(3)	0.0003(3)
C11	0.0164(4)	0.0194(4)	0.0191(4)	0.0093(3)	0.0073(3)	0.0051(3)
C12	0.0271(5)	0.0179(4)	0.0223(4)	0.0104(3)	0.0098(4)	0.0096(4)
C13	0.0498(7)	0.0118(4)	0.0179(4)	0.0032(3)	0.0105(4)	0.0050(4)
C14	0.0336(5)	0.0138(4)	0.0156(4)	0.0045(3)	-0.0035(4)	-0.0077(4)
C15	0.0231(4)	0.0127(3)	0.0121(3)	0.0038(3)	-0.0017(3)	-0.0035(3)
C16	0.0225(4)	0.0154(4)	0.0135(4)	0.0035(3)	0.0099(3)	0.0015(3)

	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
C17	0.0253(4)	0.0192(4)	0.0151(4)	0.0094(3)	0.0028(3)	0.0013(3)
C18	0.0220(5)	0.0227(5)	0.0278(5)	0.0128(4)	0.0011(4)	-0.0074(4)
C19	0.0223(4)	0.0189(4)	0.0161(4)	0.0077(3)	0.0079(3)	-0.0006(3)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Q_0098_HK_AdBr.

	x/a	y/b	z/c	U(eq)
H3	0.1914	0.2680	0.3222	0.014
H6	0.8109	0.3506	0.5106	0.014
H9A	0.6440	0.3964	0.1047	0.016
H9B	0.8529	0.4009	0.1640	0.016
H11A	0.5453	0.7336	0.1990	0.02
H11B	0.5041	0.6711	0.0880	0.02
H12	0.5328	0.9748	0.1278	0.025
H13A	0.8278	1.1252	0.2129	0.031
H13B	0.7478	1.0124	0.2760	0.031
H14	1.0699	0.9770	0.2844	0.027
H15A	1.0374	0.6754	0.2468	0.02
H15B	0.8743	0.7395	0.2963	0.02
H16A	0.9697	0.5778	0.0731	0.019
H16B	0.7621	0.5751	0.0115	0.019
H17A	0.6307	0.8493	-0.0096	0.023
H17B	0.7551	1.0263	0.0383	0.023
H18A	1.0845	1.0284	0.1345	0.029
H18B	1.1662	0.8526	0.1470	0.029
H19	0.9533	0.8149	-0.0014	0.022

Table 8. Hydrogen bond distances (Å) and angles (°) for Q_0098_HK_AdBr.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C3-H3···O2	0.95	2.43	3.0810(11)	125.5
C6-H6···Br2	0.95	3.04	3.7265(8)	130.0
C6-H6···O2	0.95	2.66	3.4879(11)	146.5