Electronic Supplementary Material (ESI) for CrystEngComm.

ELECTRONIC SUPPORTING INFORMATION

Shortening C≡N···Br-C_{sp3} halogen bonds via π-stacking

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1. General methods.

Solvents were purified with an MB SPS-800 purification system. All solvent used for catalytic experiment were dried with CaH_2 and distillated prior to use. $CDCl_3$ was filtered through alumina and stored under argon over molecular sieves. All the other employed chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques. ^1H and ^{13}C NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer. ^1H NMR spectra were referenced to residual protiated solvent (δ = 7.26 ppm for $CDCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (δ = 77.16 ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; hept, heptuplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, *J*, were reported in hertz unit (Hz).

2. Synthesis and characterization of 2-(dibromomethyl)benzonitrile (1).

To a solution of 2-methylbenzonitrile (5.05 mL, 43 mmol) in CCl_4 (50 mL) was added NBS (22.82 g, 128 mmol) successively. The reaction mixture was heated at 80°C in the presence of light for 24 h and monitored by TLC. After that the solvent was evaporated and the residue was dissolved in EtOAc and extracted with saturated $Na_2S_2O_3$. Organic layer was dried with Na2SO4, evaporated and purified by column chromatography on silica gel (petroleum ether/EtOAc 99:1 to 95:5) to give **1** as a white solid. NMR data match those reported in the literature.[1] The white single crystals suitable for X-ray diffraction studies were obtained by slow evaporation from a mixture of solvents (DCM/petroleum ether).

^1H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.69 (td, *J* = 7.8, 1.1 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.43 (td, *J* = 7.8, 1.1 Hz, 1H), 7.98 (s, 1H) ppm.

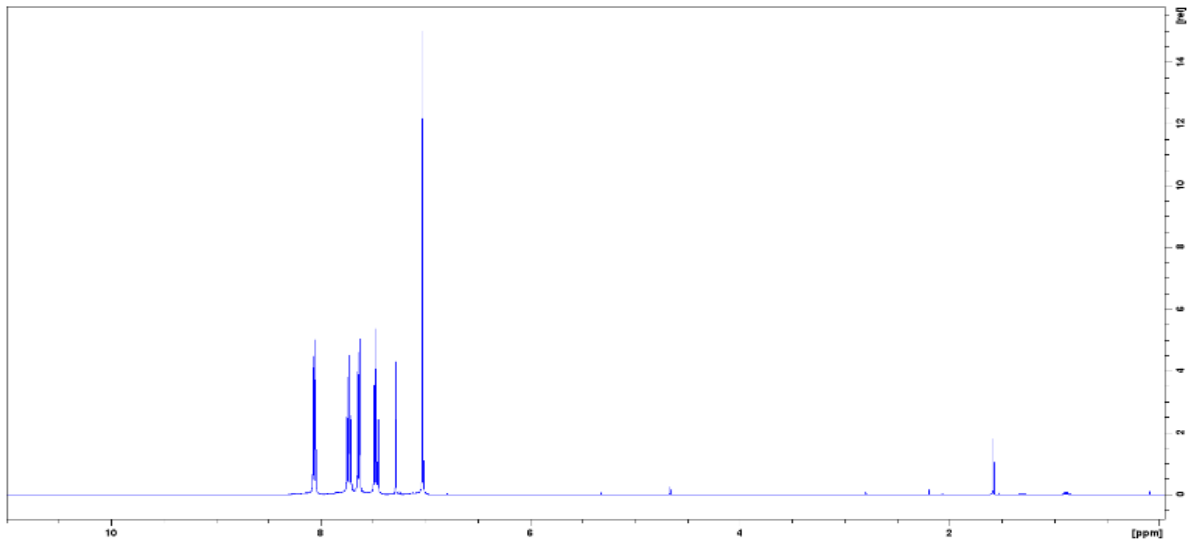


Figure S1. ^{1}H NMR spectra of **1** ($CDCl_3$, 400 MHz, 300 K).

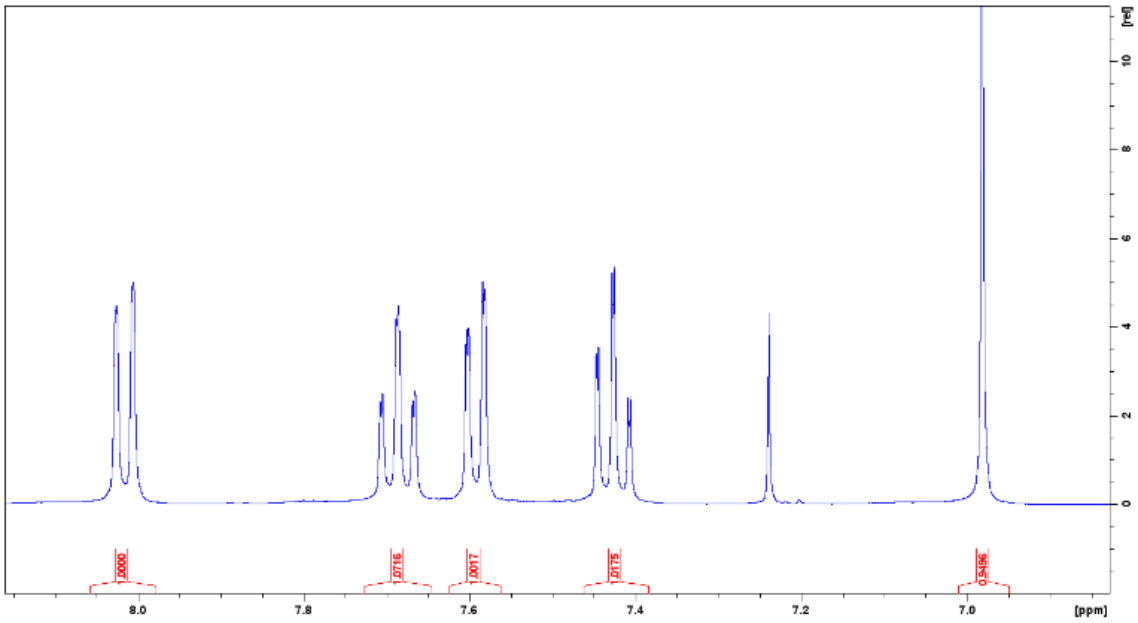


Figure S2. ^{1}H NMR spectra of **1** - aromatic region ($CDCl_3$, 400 MHz, 300 K).

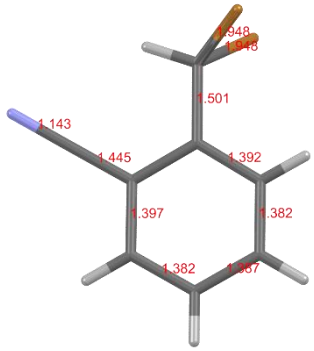


Figure S3. X-ray structure of **1** with bond length (Å).

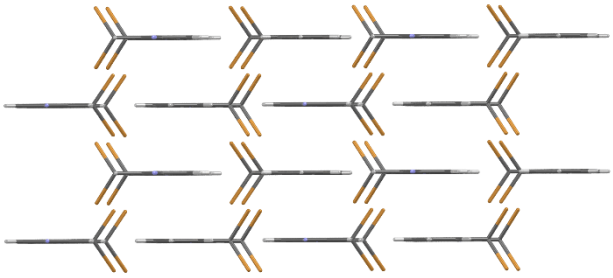


Figure S4. Molecular packing in the 1 crystal from X-ray diffraction analysis.

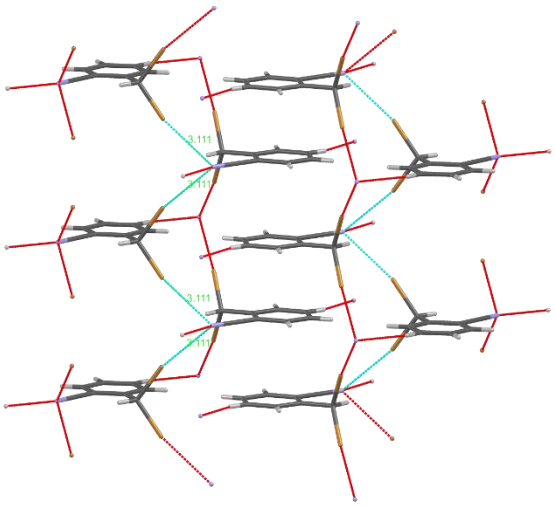
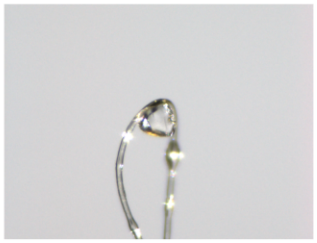
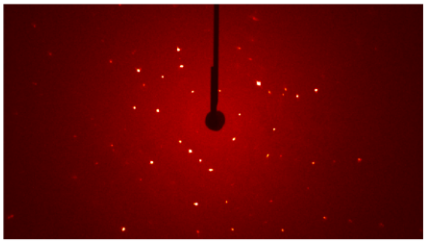
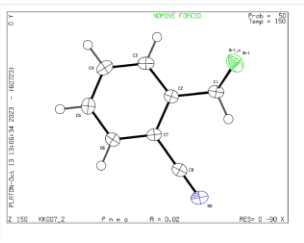


Figure S5. Short halogen bond (Br···NC, 3.111 Å) between aliphatic and aromatic part in the crystal structure of **1**.

3. X-ray data of 1.

X-ray crystallographic study

($C_8H_5Br_2N$); $M = 274.95$. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.170 x 0.120 x 0.090 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-K_α radiation (λ = 0.71073 Å, multilayer monochromator) at T = 150(2) K. Crystal structure has been described in orthorhombic symmetry and *P n m a* (I.T.#62) centric space group (R_{int} = 0.0304). Cell parameters have been refined as follows: a = 13.7185(18), b = 7.2021(9), c = 8.8003(12) Å, V = 869.5(2) Å^3. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 2.100 g.cm^{-3} and 9.254 mm^{-1} respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program [1], and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program [2]). All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 1074 unique intensities and 64 parameters converged at $\omega R(F^2)$ = 0.0523 (R_F = 0.0238) for 883 observed reflections with $I > 2\sigma$.
In the CHECKCIF procedure, no A-type, B-type and C-type meaningfull alerts has remained.

1. G. M. Sheldrick, *Acta Cryst.* 2015, A**71**, 3-8
2. Sheldrick G.M., *Acta Cryst.* C**71** 2015 3-8

Data collection strategy details

```
Software                    : BIS V6.2.15/2021-03-15 && APEX4 2022.10-0
Number of scans             :         5
Total length of scans  [*]  :    291.00 (deg.)
Total exposition time  [*]  :       1 h 37 min.

 [*] fast scan not included
```

Scan	Time(s)	Width	DX(mm)	Frames	Range	2Theta	Omega	Phi	Chi	T(K)
1 Fast	2.0	1.00	34.0	180	180.0	0.0	0.0	0.0	54.7	150.0
2 Fast@	2.0	1.00	34.0	180	180.0	0.0	0.0	180.0	54.7	150.0
3 Omega	20.0	1.00	34.0	97	97.0	0.1	2.7	144.0	-44.5	150.0
4 Omega	20.0	1.00	34.0	97	97.0	0.1	2.7	216.0	-44.5	150.0
5 Omega	20.0	1.00	34.0	97	97.0	0.1	2.7	0.0	-44.5	150.0

@: attenuated beam

Structural data

... Crystal data ...

Empirical formula	$C_8H_5Br_2N$
Formula weight	274.95 g/mol
Temperature	150(2) K
Radiation type	Mo-Kα
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P* n m a (I.T.#62)
Unit cell dimensions	a = 13.7185(18) Å
	b = 7.2021(9) Å
	c = 8.8003(12) Å
	α = 90 °
	β = 90 °
	γ = 90 °
Volume	869.5(2) $Å^3$
Z, Calculated density	4, 2.100 $g.cm^{-3}$
Absorption coefficient	9.254 mm^{-1}
F(000)	520
Crystal size	0.170 x 0.120 x 0.090 mm
Crystal color	colourless
Crystal description	prism

... Data collection and data reduction ...

Diffractometer	D8 Venture (Bruker-AXS)
Detector	CMOS-PHOTON70
θ range for data collection	2.750 to 27.468°
$(\sin\theta/\lambda)_{max}$ $Å^{-1}$	0.649
h_{min}, h_{max}	-17, 17
k_{min}, k_{max}	-9, 8
l_{min}, l_{max}	-11, 11
Reflections collected / unique	7270 / 1074 [^{a}R(int) = 0.0304]
Reflections [$I > 2\sigma$]	883
Completeness to θ_{max}	0.999
Absorption correction type	multi-scan
Max. and min. transmission	0.435, 0.312

... Refinement ...

Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	1074 / 0 / 64
^{b}Goodness-of-fit	1.045
Final R indices [$I > 2\sigma$]	^{c}R_1 = 0.0238, ^{d}wR_2 = 0.0523
Final R indices [all data]	^{c}R_1 = 0.0316, ^{d}wR_2 = 0.0563
^{e}Shelxl weighting scheme parameters	a = 0.0155, b = 1.6587
$\Delta\rho_{min}$, $\Delta\rho_{max}$	-0.604, 0.721 $e.Å^{-3}$

$^a R_{int} = \frac{\sum|F_o^2 - \langle F_o^2\rangle|}{\sum F_o^2}$

$^b S = \left\{\frac{\sum[w(F_o^2 - F_c^2)^2]}{n-p}\right\}^{1/2}$

$^c R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$

$^d wR_2 = \left\{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}\right\}^{1/2}$

$^e w = 1./[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [2F_c^2 + Max(F_o^2, 0)]/3$

Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)	adp
Br1	0.20624(2)	0.53161(4)	0.49716(3)	1	0.03419(11)	Uani
C1	0.2813(3)	0.750000	0.4390(4)	1	0.0270(8)	Uani
H1	0.288738	0.749999	0.325936	1	0.032	Uiso
C2	0.3811(2)	0.750000	0.5090(4)	1	0.0220(6)	Uani
C3	0.3941(3)	0.750000	0.6659(4)	1	0.0272(8)	Uani
H3	0.338674	0.750000	0.730562	1	0.033	Uiso
C4	0.4862(3)	0.750000	0.7295(4)	1	0.0284(8)	Uani
H4	0.493816	0.750000	0.836794	1	0.034	Uiso
C5	0.5675(3)	0.750000	0.6359(4)	1	0.0268(8)	Uani
H5	0.630802	0.750000	0.679584	1	0.032	Uiso
C6	0.5572(3)	0.750000	0.4797(4)	1	0.0247(7)	Uani
H6	0.613112	0.750000	0.416034	1	0.030	Uiso
C7	0.4639(3)	0.750000	0.4161(4)	1	0.0202(7)	Uani
C8	0.4538(2)	0.750000	0.2527(4)	1	0.0234(7)	Uani
N9	0.4454(2)	0.750000	0.1235(3)	1	0.0310(7)	Uani

Anisotropic displacement parameters ($Å^2$)

The anisotropic displacement factor exponent takes the form: $-2\pi[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Br1	0.02691(15)	0.03073(16)	0.04492(17)	-0.00872(12)	0.00188(12)	-0.00423(10)
C1	0.0242(18)	0.035(2)	0.0221(16)	0.000	0.0056(14)	0.000
C2	0.0218(15)	0.0215(16)	0.0226(15)	0.000	0.0026(14)	0.000
C3	0.0276(18)	0.0324(19)	0.0215(16)	0.000	0.0058(14)	0.000
C4	0.036(2)	0.031(2)	0.0191(16)	0.000	-0.0004(14)	0.000
C5	0.0251(18)	0.0271(18)	0.0282(18)	0.000	-0.0051(14)	0.000
C6	0.0213(16)	0.0272(18)	0.0255(17)	0.000	0.0030(14)	0.000
C7	0.0247(17)	0.0170(15)	0.0188(15)	0.000	0.0031(13)	0.000
C8	0.0217(16)	0.0229(17)	0.0254(17)	0.000	0.0041(13)	0.000
N9	0.0335(17)	0.0378(18)	0.0218(15)	0.000	0.0048(13)	0.000

Bond length [Å]

Br1	- C1	=	1.948(2)
C1	- C2	=	1.501(5)
C1	- H1	=	1.0000
C2	- C3	=	1.393(5)
C2	- C7	=	1.401(5)
C3	- C4	=	1.381(5)
C3	- H3	=	0.9500
C4	- C5	=	1.385(5)
C4	- H4	=	0.9500
C5	- C6	=	1.383(5)
C5	- H5	=	0.9500
C6	- C7	=	1.396(5)
C6	- H6	=	0.9500
C7	- C8	=	1.445(5)
C8	- N9	=	1.143(4)

Angles [°]

C2	- C1	- Br1_#1	=	111.96(15)
C2	- C1	- Br1	=	111.96(15)
Br1_#1	- C1	- Br1	=	107.66(16)
C2	- C1	- H1	=	108.4
Br1_#1	- C1	- H1	=	108.4
Br1	- C1	- H1	=	108.4
C3	- C2	- C7	=	118.3(3)
C3	- C2	- C1	=	121.7(3)
C7	- C2	- C1	=	120.0(3)
C4	- C3	- C2	=	121.3(3)
C4	- C3	- H3	=	119.4
C2	- C3	- H3	=	119.4
C3	- C4	- C5	=	119.7(3)
C3	- C4	- H4	=	120.2
C5	- C4	- H4	=	120.2
C6	- C5	- C4	=	120.6(3)
C6	- C5	- H5	=	119.7
C4	- C5	- H5	=	119.7
C5	- C6	- C7	=	119.5(3)
C5	- C6	- H6	=	120.3
C7	- C6	- H6	=	120.3
C6	- C7	- C2	=	120.6(3)
C6	- C7	- C8	=	119.1(3)
C2	- C7	- C8	=	120.2(3)
N9	- C8	- C7	=	179.7(4)

Symmetry transformations used to generate equivalent atoms:

#1	x, -y-1/2, z	+ T = [0, 2, 0] :	(+x, -y+3/2, +z)

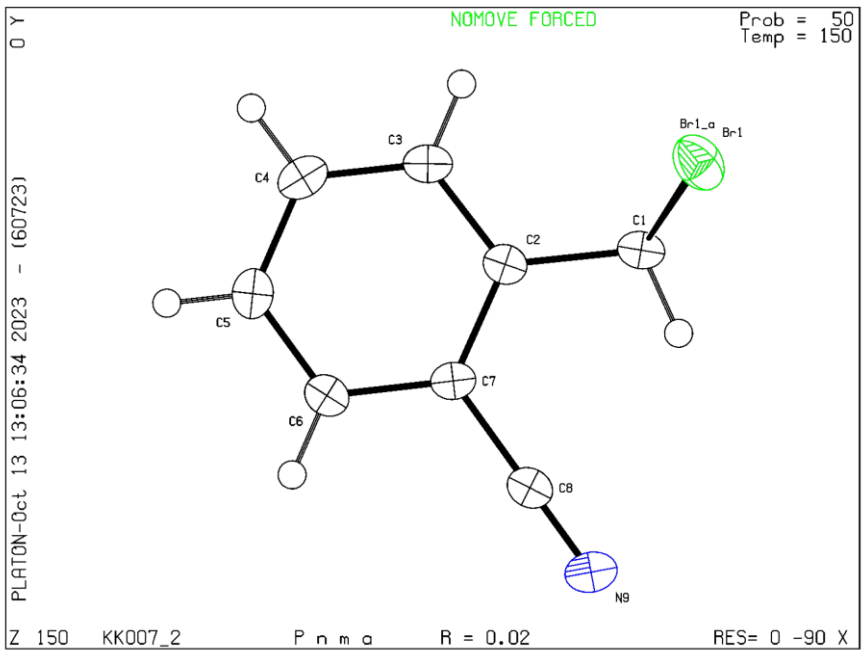
Torsion angles [°]

Br1_#1	- C1	- C2	- C3	=	60.50(15)
Br1	- C1	- C2	- C3	=	-60.50(15)
Br1_#1	- C1	- C2	- C7	=	-119.50(15)
Br1	- C1	- C2	- C7	=	119.50(15)
C7	- C2	- C3	- C4	=	0.000(1)
C1	- C2	- C3	- C4	=	180.000(1)
C2	- C3	- C4	- C5	=	0.000(1)
C3	- C4	- C5	- C6	=	0.000(1)
C4	- C5	- C6	- C7	=	0.000(1)
C5	- C6	- C7	- C2	=	0.000(0)
C5	- C6	- C7	- C8	=	180.000(1)
C3	- C2	- C7	- C6	=	0.000(0)
C1	- C2	- C7	- C6	=	180.000(0)
C3	- C2	- C7	- C8	=	180.000(0)
C1	- C2	- C7	- C8	=	0.000(0)

Symmetry transformations used to generate equivalent atoms:

#1	x, -y-1/2, z	+ T = [0, 2, 0] :	(+x, -y+3/2, +z)

Structure visualization



4. Theoretical methods.

The optimization using periodic boundary conditions were performed at the BP86-D3/def2-TZVP level of theory. This geometry was used to analyze the energetic features of the adducts analyzed in this work, that were calculated at the PBE0[2]-D3[3]/def2-TZVP[4] level of theory using the fully optimized geometries. The Turbomole 7.7 program[5] has been used for the optimizations and energetic calculations. The NBO analysis[6] was performed using the NBO 7.0 program.[7] Molecular electrostatic potential (MEP) surfaces have been computed at the same level of theory and represented using 0.001 a.u. isovalue of electron density to map the electrostatic potential. The NCIplot analysis[8] has been performed using the AIMAll program at the same level of theory.[9] For the NCIplot analysis, the following setting were used, S = 0.5, ρ cut-off = 0.04 a.u., color scale $-0.035 \leq \text{sign}(\lambda_2)\rho \leq -0.035$ a.u. For the evaluation of the HB and HaBs energies using the QTAIM analysis, the equations proposed in the literature were used.[10,11]

5. XYZ cartesian coordinates

```
C   -1.050349 -1.425625  0.892267
H   -2.119915 -1.300764  0.724412
C   -0.328165 -2.376227  0.176833
H   -0.838682 -3.000140 -0.557191
C    1.044435 -2.532318  0.396210
H    1.613380 -3.276716 -0.163116
C    1.692635 -1.731029  1.336911
H    2.762603 -1.851219  1.509343
C    0.993051 -0.768263  2.070056
C   -0.397918 -0.617247  1.840890
C   -1.151745  0.352075  2.565735
N   -1.755315  1.149234  3.166235
C    1.675890  0.096791  3.081070
H    0.993393  0.798796  3.569348
Br   2.495070 -0.938935  4.544420
Br   3.099002  1.212027  2.296101
N    5.745711  2.591694  1.484535
C    6.553357  1.885862  1.026223
C    7.527313  1.015228  0.454920
C    8.862060  1.096800  0.891498
H    9.133286  1.822116  1.658254
C    9.824139  0.253682  0.343330
H   10.857117  0.320981  0.685192
C    9.470500 -0.675588 -0.640684
H   10.222473 -1.338025 -1.072434
C    8.146742 -0.757378 -1.074517
H    7.869184 -1.481220 -1.841563
C    7.159414  0.076501 -0.541972
C    5.737221 -0.001235 -0.998369
H    5.087623  0.715627 -0.487063
Br   4.925300 -1.767420 -0.671899
Br   5.529271  0.383578 -2.920318
C    0.397918  0.617247 -1.840890
C    1.050349  1.425625 -0.892267
H    2.119915  1.300764 -0.724412
C    0.328165  2.376227 -0.176833
H    0.838682  3.000140  0.557191
C   -1.044435  2.532318 -0.396210
H   -1.613380  3.276716  0.163116
C   -1.692635  1.731029 -1.336911
H   -2.762603  1.851219 -1.509343
C   -0.993051  0.768263 -2.070056
C    1.151745 -0.352075 -2.565735
N    1.755315 -1.149234 -3.166235
C   -1.675890 -0.096791 -3.081070
H   -0.993393 -0.798796 -3.569348
Br  -3.099002 -1.212027 -2.296101
Br  -2.495070  0.938935 -4.544420
N   -5.745711 -2.591694 -1.484535
C   -6.553357 -1.885862 -1.026223
C   -7.527313 -1.015228 -0.454920
C   -8.862060 -1.096800 -0.891498
H   -9.133286 -1.822116 -1.658254
C   -9.824139 -0.253682 -0.343330
H  -10.857117 -0.320981 -0.685192
C   -9.470500  0.675588  0.640684
H  -10.222473  1.338025  1.072434
C   -8.146742  0.757378  1.074517
H   -7.869184  1.481220  1.841563
C   -7.159414 -0.076501  0.541972
C   -5.737221  0.001235  0.998369
H   -5.087623 -0.715627  0.487063
Br  -5.529271 -0.383578  2.920318
Br  -4.925300  1.767420  0.671899
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6. References.

1. C. Sun and B. Xu, *J. Org. Chem.,* 2008, **73**, 7361–7364.

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