Supplementary Material (ESI) for PCCP

SUPPORTING INFORMATION

On the Nature of the B…N Interaction and the Conformational Flexibility of Arylboronic Azaesters

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1. Methods – additional information

The ellipticity. The ellipticity of the bond is examined by the analyses of the eigenvalues of Hessian matrix (Hessian matrix is formed by nine second derivatives of electron densities).

$$\varepsilon = \frac{|\lambda_1|}{|\lambda_2|} - 1$$

λ_1, λ_2 are the eigenvalues of the Hessian matrix, perpendicular to the bond axis. In the case of the ideal sigma bond, ellipticity is equal to zero. The larger values of it indicate multiple bond character. However, in the case of triple bond this value is again equal to zero. Ellipticity is often examined at the BCP, but it could be also analysis along the whole bond path, which provides important information about curvature of the bond.

Source function. It has been shown that electron density $\rho(\boldsymbol{r})$ at the point $\boldsymbol{r}$ within the atomic basin is regarded to consist of contributions from a local source ($LS(\boldsymbol{r}, \boldsymbol{r'})$)operating at all other points $\boldsymbol{r'}$:

$$\rho(r) = \int LS(r,r')dr' = -\frac{1}{4\pi}\int \frac{\nabla^2\rho(r')}{|r-r'|}dr'$$

The integration of the local source over the atomic basin Ω has been called source function contribution $S(\boldsymbol{r}, \Omega)$ from that atom to electron density $\rho(\boldsymbol{r})$:

$$S(r,\Omega) = \int_\Omega LS(r,r')dr'$$

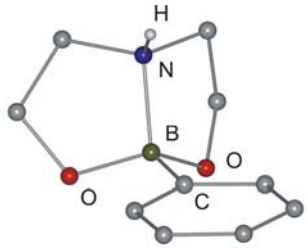
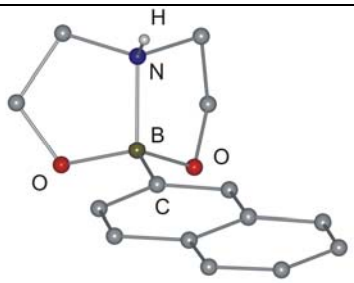
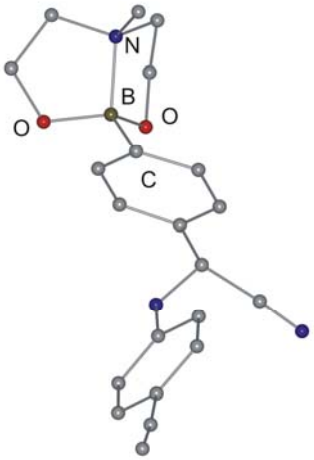
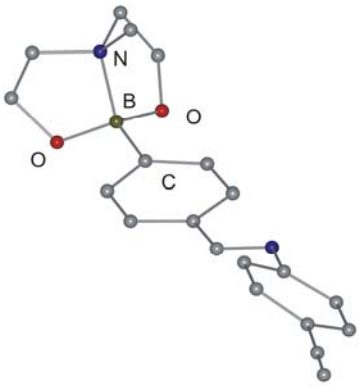
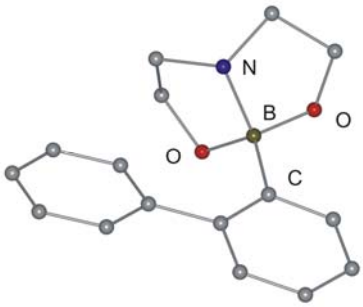
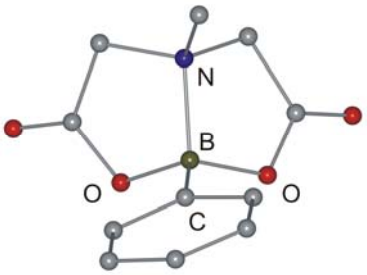
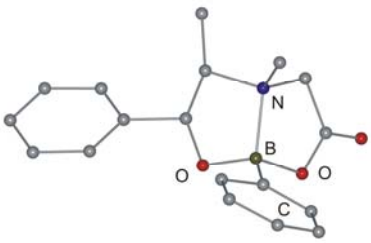
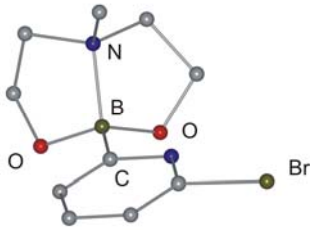
According to this electron density can be viewed as determined solely by internal source function self-contribution and by external source function contribution from other atoms:

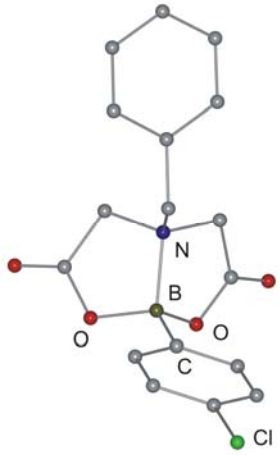
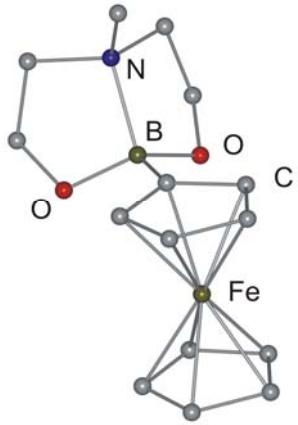
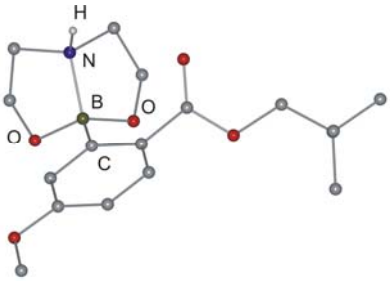
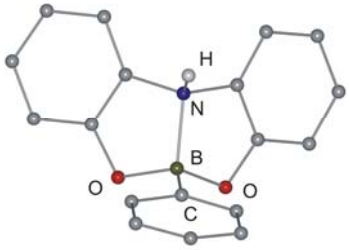
$$\rho(r) = S(r,\Omega) + \sum\nolimits_{\Omega'\neq\Omega} S(r,\Omega')$$

Source function provides many chemical information as it shows the contribution from the atom to the whole density at any point within the molecule. For more details see ref 35.

2. Azaesters of arylboronic acids – literature report

Table 1S. Molecular structures of arylboronic azaesters previously reported in the literature together with B–N bond lengths.

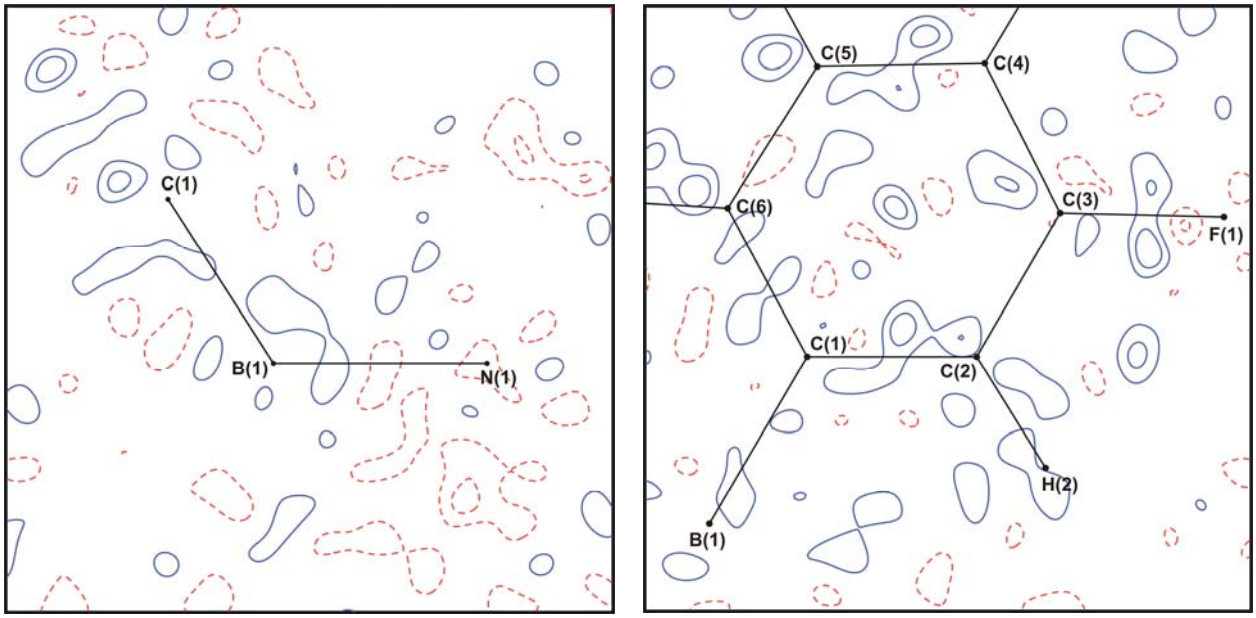
Molecular structure	d_{B-N}/Å	Ref.	Molecular structure	d_{B-N}/Å	Ref.
 PBORXZ	1.660	[13]	 COQRAB	1.672	[14]
 GEDTOZ	1.690	[15]	 GEDTIT	1.684	[15]
 GEDTEP	1.712	[16]	 NIVYEW	1.661	[16]
 SIBGIT	1.714	[17]	 EYIWUE	1.696	[18]

 SEBPIZ	1.684	[19]	 PAPVEI	1.735	[20]
 PUTBUB	1.657	[21]	 GEKCUU	1.698	[22]

3. Structural and multipole refinement details for 1

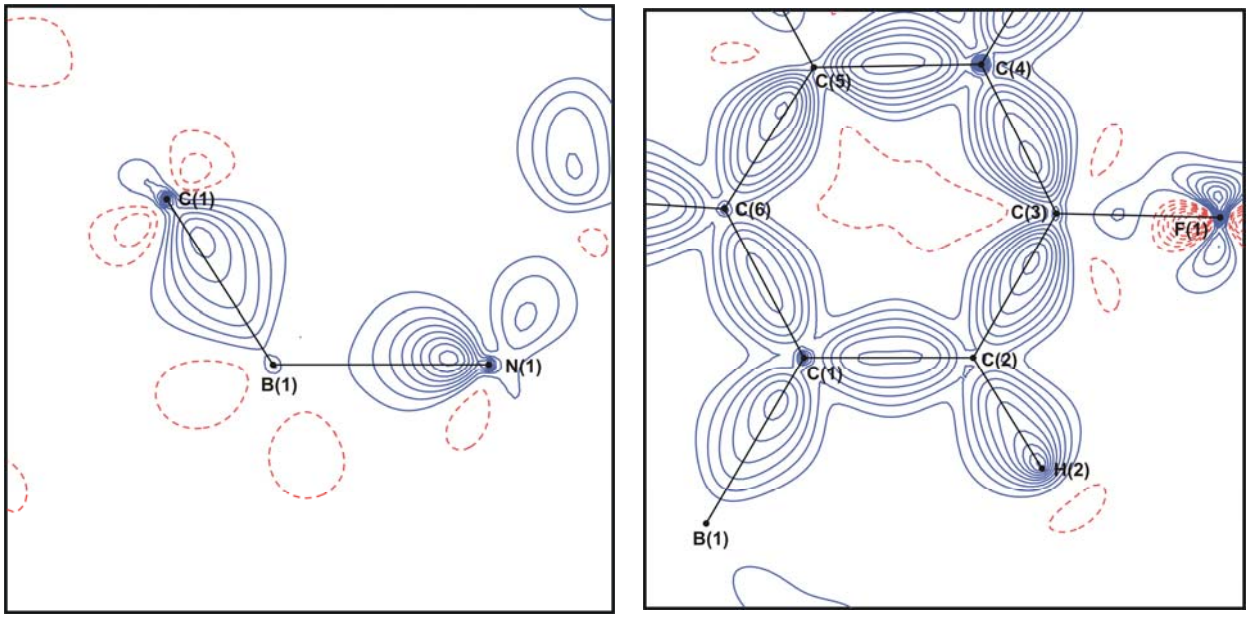
Table 2S. Crystal data for compound **1**.

Formula	$C_{14}H_{20}BF_2NO_2$
Molecular mass	283.12 a.u.
Measurement temperature (*T*)	90(2) K
Crystal system	orthorhombic
Space group	$P2_1/n$
Unit cell parameters:	
a	6.6681(2) Å
b	21.4324(6) Å
c	9.8980(3) Å
α	90°
β	102.551(2)°
γ	90°
Volume (*V*)	1380.75(7) Å^3
Z	4
Calculated density	1.362 g·cm^{-3}
F(000)	600
Crystal size	0.38 × 0.37 × 0.10 mm^3
θ range for data collection	2.312° ÷ 52.324°
Absorption coefficient (μ_{abs})	0.107 mm^{-1}
(sin θ_{max}) / λ	1.12 Å^{-1}
Index ranges	$-14 < h < 14$
	$-47 < k < 47$
	$-19 < l < 22$
No. of reflections collected / unique	123017 / 15927
Completeness	> 99%
R_{int}	4.4 %
Absorption correction	multi-scan
IAM refinement	
No. reflections / restrains / parameters	15927 / 0 / 181
GooF	1.110
*R*1 / *wR*2 (for $I > 3\sigma(I)$)	3.84% / 11.38%
*R*1 / *wR*2 (for all data)	5.64% / 13.04%
Largest residual density peak and hole	+0.637 *e*·Å^{-3} / –0.628 *e*·Å^{-3}
Multipole refinement	
No. of reflections (for $I > 3\sigma(I)$) / parameters	11742 / 870 = 13.50
*R*1 / *wR*1 (for $I > 3\sigma(I)$)	1.97% / 2.57%
*R*2 / *wR*2 (for $I > 3\sigma(I)$)	2.21% / 4.79%
GooF (for $I > 3\sigma(I)$)	1.191
Largest residual density peak and hole	+0.164 *e*·Å^{-3} / –0.145 *e*·Å^{-3}



(*a*) (*b*)

Figure 1S. Residual density maps in (*a*) B(1)N(1)C(1) and (*b*) C(1)C(2)C(3) planes. Blue solid lines denote positive values and red dashed lines to the negative ones. Contours at $\pm 0.05 \cdot n$ *e*·Å^{-5} (n = 1, 2, …).



(*a*) (*b*)

Figure 2S. Experimental static deformation density maps in (*a*) B(1)N(1)C(1) and (*b*) C(1)C(2)C(3) planes calculated by taking into account neighbouring molecules in the crystal lattice. Blue solid lines denote positive values and red dashed lines to the negative ones. Contours at $\pm 0.1 \cdot n$ *e*·Å^{-5} (n = 1, 2, …). Note that there is positive deformation density along the C(3)–F(1) bond.

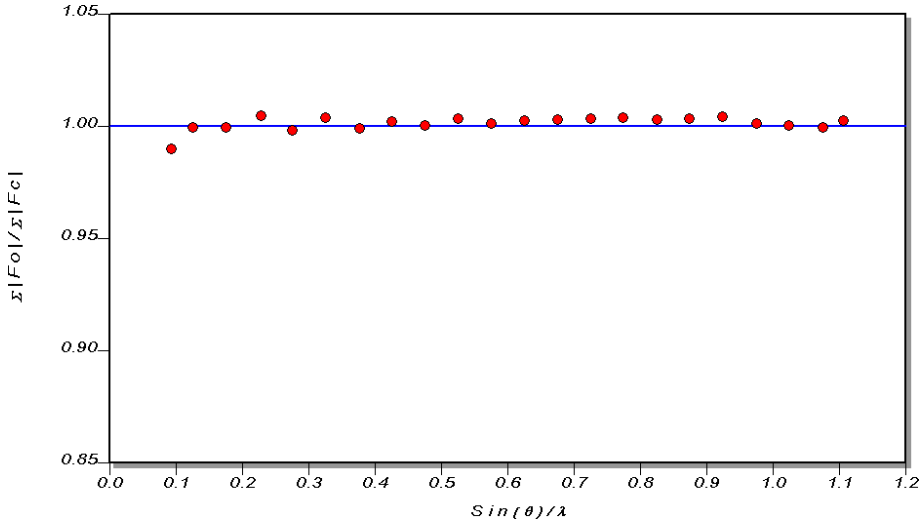


Figure 3S. Averaged plot showing the $|F_o|$ / $|F_c|$ *versus* resolution. F_o and F_c stand for observed and calculated structure factors, respectively.

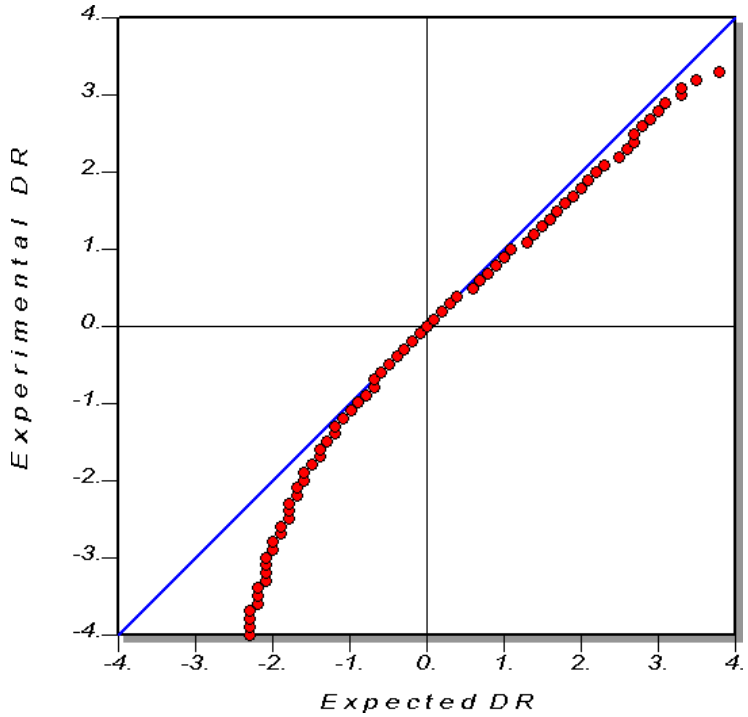


Figure 4S. Normal probability plot.

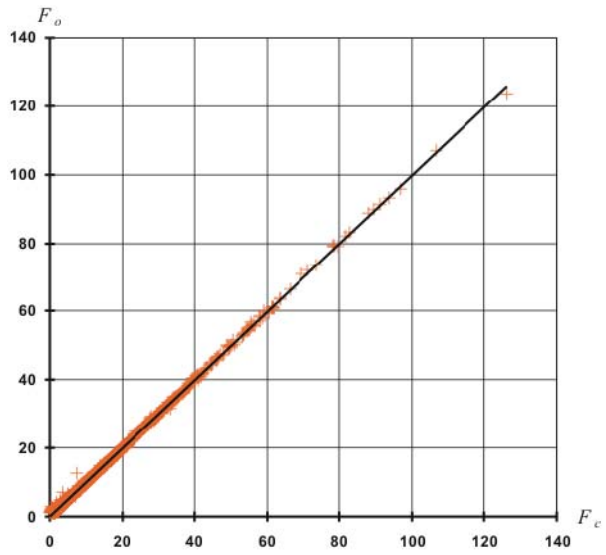


Figure 5S. The plot of F_o *versus* F_c. The straight line represents the fitted linear function ($R^2 = 0.9992$; $F_o = 0.9976 \cdot F_c + 0.0329$).

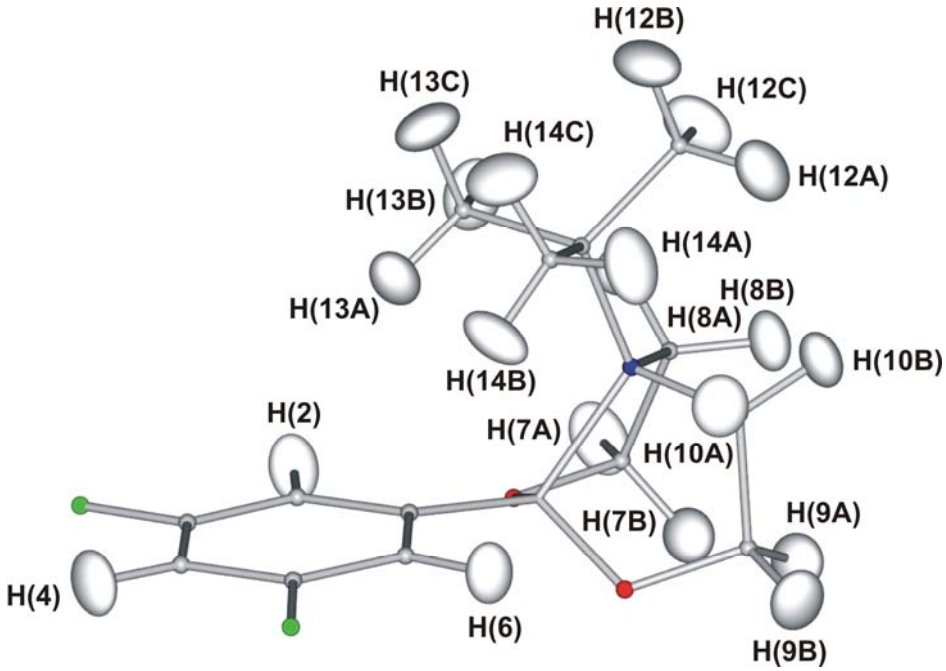


Figure 6S. Estimated (SHADE2) ADPs for hydrogen atoms (ellipsoids are drawn at 60% probability).

Table 3S. Minima and maxima of residual electron density.

Highest peaks	*Height* / $e \cdot Å^{-3}$	*Remarks*
1	+0.16	0.51 Å from C(14)
2	+0.13	0.37 Å from C(5)
3	+0.13	Random position
4	+0.13	0.64 Å from C(2)
5	+0.13	0.74 Å from C(6)
6	+0.13	Random position
7	+0.13	Random position
8	+0.12	Random position
9	+0.12	Random position
10	+0.12	Random position
Deepest holes	*Height* / $e \cdot Å^{-3}$	*Remarks*
1	–0.15	Random position
2	–0.14	0.48 Å from C(8)
3	–0.13	0.39 Å from C(14)
4	–0.13	Random position
5	–0.12	0.45 Å from C(13)
6	–0.12	Random position
7	–0.12	Random position
8	–0.12	0.36 Å from F(2)
9	–0.11	Random position
10	–0.11	Random position

Table 4S. Geometrical (d – distance) and topological parameters (ρ – electron density, L – negative Laplacian of electron density, ε – ellipticity) in BCPs for (*a*) isolated molecule with electron density constructed from monopole populations, (*b*) theoretical for isolated molecule with experimental geometry and (*c*) theoretically optimised structure. The values for crystalline state are the same as for (*a*) in respect do experimental error. Values in square brackets stand for RCPs.

Bond	(*a*) *Closed form*				(*b*) *Closed form*			(*c*) *Open form*			
	d / Å	$\rho(\boldsymbol{r}_{BCP})$ / $e{\cdot}$Å^{-3}	$L(\boldsymbol{r}_{BCP})$ / $e{\cdot}$Å^{-5}	ε	$\rho(\boldsymbol{r}_{BCP})$ / $e{\cdot}$Å^{-3}	$L(r_{CP})$ / $e{\cdot}$Å^{-5}	ε	d / Å	$\rho(\boldsymbol{r}_{BCP})$ / $e{\cdot}$Å^{-3}	$L(\boldsymbol{r}_{BCP})$ / $e{\cdot}$Å^{-5}	ε
B(1)…N(1)	1.7646(3)	0.76(2)	4.36(8)	0.07	0.658	0.853	0.18	[2.7870]	[0.110]	[1.147]	–
B(1)–C(1)	1.6134(3)	1.16(2)	6.2(1)	0.05	1.150	3.758	0.05	1.5800	1.234	4.103	0.04
B(1)–O(1)	1.4428(3)	1.26(2)	–6.6(1)	0.11	1.131	–18.252	0.08	1.3750	1.296	–25.932	0.07
B(1)–O(2)	1.4544(3)	1.21(2)	–5.7(1)	0.05	1.090	–17.067	0.13	1.3761	1.289	–25.794	0.08
N(1)–C(8)	1.5099(3)	1.60(2)	8.06(9)	0.06	1.616	12.334	0.03	1.4586	1.804	15.996	0.06
N(1)–C(10)	1.4963(3)	1.69(2)	11.14(9)	0.11	1.661	13.306	0.03	1.4568	1.808	16.152	0.06
N(1)–C(11)	1.5374(3)	1.55(2)	8.14(8)	0.08	1.521	10.719	0.02	1.5007	1.645	12.925	0.05
C(3)–F(1)	1.3567(4)	1.93(3)	16.8(1)	0.12	1.645	–0.753	0.09	1.3627	1.629	0.371	0.07
C(5)–F(2)	1.3502(4)	1.98(3)	22.6(2)	0.20	1.666	–1.655	0.08	1.3627	1.629	0.370	0.07
C(1)–C(2)	1.4027(3)	2.08(2)	17.07(8)	0.06	2.025	17.174	0.17	1.4078	2.008	16.995	0.16
C(2)–C(3)	1.3826(3)	2.24(3)	21.88(9)	0.22	2.142	19.698	0.26	1.3886	2.116	19.187	0.26
C(3)–C(4)	1.3842(3)	2.30(3)	23.15(9)	0.19	2.129	19.294	0.28	1.3918	2.099	18.758	0.27
C(4)–C(5)	1.3870(3)	2.24(3)	21.26(9)	0.10	2.119	19.104	0.28	1.3917	2.099	18.761	0.27
C(5)–C(6)	1.3853(3)	2.22(3)	20.47(9)	0.25	2.129	19.409	0.27	1.3887	2.116	19.183	0.26
C(6)–C(1)	1.4018(3)	2.10(2)	18.14(8)	0.08	2.028	17.267	0.17	1.4077	2.009	17.003	0.16
C(7)–C(8)	1.5304(4)	1.76(2)	13.39(7)	0.03	1.676	13.404	0.05	1.5502	1.615	12.631	0.07
C(9)–C(10)	1.5159(4)	1.79(2)	14.26(8)	0.12	1.723	14.098	0.05	1.5411	1.643	13.019	0.07
O(1)–C(7)	1.4101(3)	1.93(3)	16.85(12)	0.11	1.783	13.918	0.02	1.4204	1.663	10.416	0.01
O(2)–C(9)	1.4121(3)	1.91(3)	15.37(12)	0.04	1.768	13.624	0.01	1.4225	1.653	10.265	0.01
C(11)–C(12)	1.5353(3)	1.69(3)	10.65(7)	0.03	1.645	12.835	0.02	1.5437	1.621	12.502	0.02
C(11)–C(13)	1.5341(4)	1.64(2)	10.55(7)	0.19	1.644	12.896	0.02	1.5429	1.622	12.623	0.02
C(11)–C(14)	1.5328(3)	1.67(2)	10.61(7)	0.02	1.642	12.826	0.02	1.5423	1.622	12.616	0.02
C(2)–H(2)	0.950	1.94(5)	21.50(20)	0.05	1.907	25.751	0.02	1.088	1.889	25.381	0.02
C(4)–H(4)	0.950	1.90(5)	19.79(22)	0.03	1.887	25.399	0.02	1.086	1.874	25.150	0.02
C(6)–H(6)	0.950	1.94(5)	20.88(20)	0.04	1.900	25.356	0.02	1.088	1.888	25.366	0.02
C(7)–H(7A)	0.990	1.92(5)	22.86(20)	0.10	1.908	25.261	0.03	1.098	1.897	24.998	0.04
C(7)–H(7B)	0.990	1.87(5)	17.80(21)	0.02	1.915	25.071	0.04	1.096	1.903	24.787	0.04
C(8)–H(8A)	0.990	1.89(5)	18.62(22)	0.09	1.891	24.469	0.03	1.109	1.816	22.203	0.03
C(8)–H(8B)	0.990	1.87(5)	19.30(22)	0.04	1.910	25.026	0.03	1.091	1.908	24.916	0.02
C(9)–H(9A)	0.990	1.87(5)	18.79(20)	0.03	1.910	25.318	0.04	1.098	1.896	25.021	0.04
C(9)–H(9B)	0.990	1.86(5)	17.56(21)	0.09	1.908	24.766	0.03	1.096	1.903	24.822	0.05
C(10)–H(10A)	0.990	1.93(5)	20.55(21)	0.04	1.910	25.120	0.03	1.102	1.912	25.098	0.02
C(10)–H(10B)	0.990	1.88(5)	18.25(23)	0.02	1.893	24.543	0.03	1.110	1.808	22.012	0.03
C(12)–H(12A)	0.980	1.84(6)	15.36(28)	0.06	1.983	26.719	0.01	1.099	1.828	22.634	0.01
C(12)–H(12B)	0.980	1.88(6)	19.31(21)	0.05	1.980	26.805	0.01	1.099	1.824	22.624	0.01
C(12)–H(12C)	0.980	1.84(6)	15.95(26)	0.03	1.985	26.793	0.01	1.099	1.825	22.581	0.01
C(13)–H(13A)	0.980	1.83(5)	17.45(26)	0.12	2.001	27.657	0.01	1.096	1.842	23.350	0.01
C(13)–H(13B)	0.980	1.81(6)	14.75(30)	0.14	1.978	26.473	0.02	1.096	1.838	22.807	0.01
C(13)–H(13C)	0.980	1.88(6)	20.35(23)	0.08	1.977	26.605	0.02	1.097	1.834	22.833	0.01
C(14)–H(14A)	0.980	1.85(6)	17.70(25)	0.06	1.983	26.619	0.01	1.096	1.838	22.812	0.01
C(14)–H(14B)	0.980	1.77(6)	14.31(28)	0.08	2.000	27.686	0.01	1.098	1.839	23.221	0.01
C(14)–H(14C)	0.980	1.85(6)	18.26(22)	0.07	1.983	26.844	0.01	1.097	1.837	22.949	0.01

4. Quantum-chemical calculations

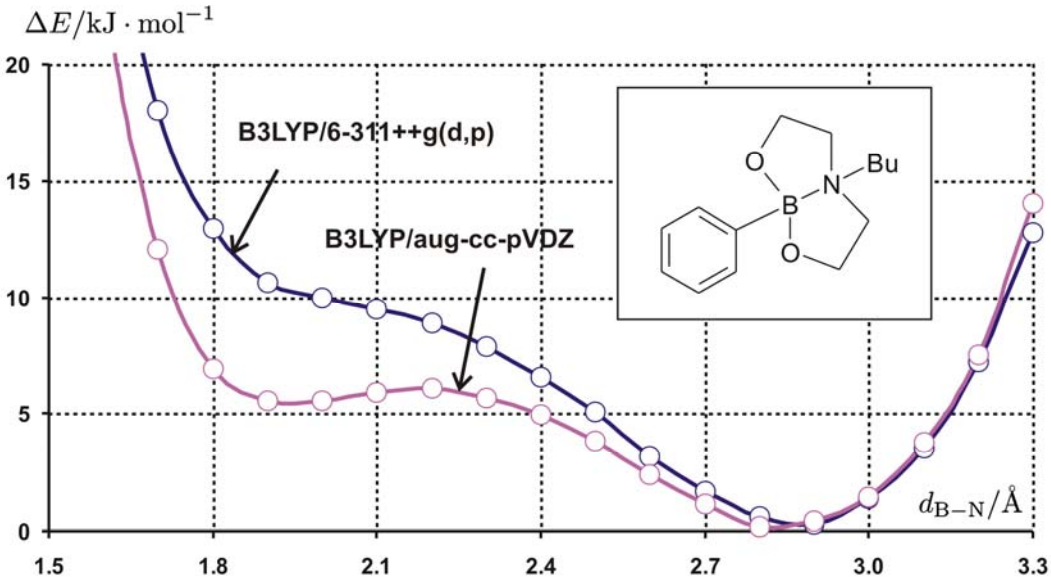


Figure 7S. Energy scan performed at DFT level of theory (B3LYP) with 6-311++G(*d*,*p*) and aug-cc-pVDZ basis sets for 6-butyl-2-phenyl-(*N*–*B*)-1,3,6,2-dioxazaborocane.

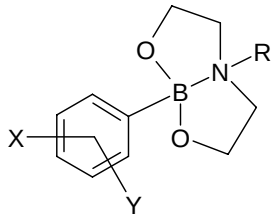
Table 5S. Integrated atomic charges (Q), dipole moments (μ) for (*a*) the isolated molecule with experimental geometry and (*b*) theoretically optimised structure. I stands for the integrated Lagrangian (compound **1**).

	(*a*) *Theoretical closed form*			(*b*) *Theoretical open form*		
Atom	Q / e	$\|\|\boldsymbol{\mu}\|\|$ / D	I / $10^{-3}\cdot e\cdot$Å^{-2}	Q / e	$\|\|\boldsymbol{\mu}\|\|$ / D	I / $10^{-3}\cdot e\cdot$Å^{-2}
F(1)	–0.610	0.367	–0.24	–0.604	0.427	–0.17
F(2)	–0.619	0.430	–0.24	–0.603	0.415	–0.20
O(1)	–1.233	0.793	0.88	–1.284	1.137	–0.47
O(2)	–1.227	0.708	1.03	–1.283	1.136	–0.45
N(1)	–1.001	0.887	0.78	–0.948	0.506	–0.25
B(1)	+2.124	0.332	–1.03	+2.196	0.171	–0.33
C(1)	–0.482	2 597	0.96	–0.555	2.894	0.80
C(2)	+0.077	0.580	0.65	+0.091	0.390	0.70
C(3)	+0.308	1.222	0.41	+0.302	1.599	0.72
C(4)	+0.072	0.528	0.20	+0.076	0.292	0.67
C(5)	+0.356	1.604	0.20	+0.416	1.578	0.72
C(6)	+0.098	0.467	0.62	+0.176	0.440	0.68
C(7)	+0.487	1.022	0.59	+0.508	1.341	0.55
C(8)	+0.195	0.726	0.69	+0.195	0.952	0.61
C(9)	+0.490	0.830	0.47	+0.512	1.316	0.58
C(10)	+0.071	0.728	0.22	+0.091	0.957	0.65
C(11)	+0.389	0.764	0.71	+0.436	0.879	0.67
C(12)	–0.098	0.180	0.59	–0.077	0.073	0.70
C(13)	–0.072	0.288	0.44	–0.085	0.054	0.74
C(14)	–0.056	0.187	0.61	–0.061	0.052	0.75
H(2)	+0.015	0.457	0.04	+0.054	0.333	0.05
H(4)	+0.016	0.437	0.03	+0.063	0.322	0.05
H(6)	+0.081	0.401	0.06	+0.057	0.339	0.04
H(7A)	+0.011	0.524	0.06	+0.004	0.365	0.03
H(7B)	+0.060	0.477	0.08	+0.019	0.341	0.04
H(8A)	+0.062	0.445	0.02	+0.041	0.402	0.04
H(8B)	+0.071	0.383	0.06	+0.002	0.326	0.03
H(9A)	+0.012	0.447	0.08	+0.018	0.340	0.04
H(9B)	+0.008	0.484	0.07	+0.004	0.359	0.04
H(10A)	+0.060	0.444	0.03	+0.000	0.312	0.03
H(10B)	+0.074	0.412	0.20	+0.042	0.415	0.03
H(12A)	+0.071	0.457	0.03	+0.033	0.359	0.04
H(12B)	+0.023	0.485	0.03	+0.023	0.370	0.05
H(12C)	+0.028	0.414	0.06	+0.028	0.360	0.04
H(13A)	+0.070	0.450	0.05	+0.001	0.353	0.03
H(13B)	+0.035	0.452	0.07	+0.034	0.353	0.03
H(13C)	+0.044	0.442	0.08	+0.025	0.361	0.05
H(14A)	+0.044	0.467	0.05	+0.028	0.217	0.05
H(14B)	+0.010	0.435	0.06	–0.004	0.354	0.03
H(14C)	+0.013	0.432	0.06	+0.013	0.375	0.02

Table 6S. Cartesian coordinates for **1** used in theoretical calculations for (*a*) open and (*b*) closed form (the same as in XDPROP module).

Atom	*Open form* (*a*)			*Closed form* (*b*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	6.238983	1.007025	3.137831	-7.982254	-3.708353	0.010446
F(2)	1.878625	1.580265	4.764697	-8.080506	1.009569	0.011567
O(1)	4.492944	4.539768	0.160444	-3.042755	-2.485699	0.067207
O(2)	2.319277	5.101138	1.188576	-3.091441	-0.007598	0.077206
N(1)	2.395003	3.726228	-0.847620	-1.898744	-1.237344	-2.154470
B(1)	3.221638	4.085508	0 .669366	-3.660116	-1.258650	0.005227
C(1)	3.477322	2.970305	1.807066	-5.239803	-1.291213	0.010452
C(2)	4.748807	2.397766	1.958548	-5.931594	-2.517300	0.010450
C(3)	5.003198	1.555163	3.024748	-7.320229	-2.517300	0.010449
C(4)	4.059203	1.239195	3.986564	-8.078722	-1.350392	0.010519
C(5)	2.813718	1.827133	3.822481	-7.369527	-0.152972	0.010934
C(6)	2.502327	2.670738	2.768783	-5.982024	-0.095108	0.010564
C(7)	4.265549	5.302170	-1.003755	-1.652506	-2.704322	-0.125156
C(8)	3.250211	4.500698	-1.821636	-1.206118	-2.382381	-1.574325
C(9)	1.417077	5.612862	0.230288	-1.731362	0.302931	-0.200518
C(10)	1.092127	4.441768	-0.675602	-1.382392	0.038833	-1.678127
C(11)	2.194251	2.282932	-1.337311	-2.216737	-1.338516	-3.617629
C(12)	1.575529	2.296745	-2.741802	-0.937207	-1.424560	-4.476841
C(13)	3.541029	1.550991	-1.355730	-3.100211	-2.580407	-3.858058
C(14)	1.249642	1.515264	-0.403793	-3.046749	-0.116015	-4.059608
H(2)	5.559803	2.622539	1.276835	-5.392579	-3.462299	0.013353
H(4)	4.270995	0.560892	4.803863	-9.166082	-1.373055	0.011066
H(6)	1.513240	3.109769	2.725997	-5.482963	0.871612	0.013983
H(7A)	5.207445	5.445339	-1.537471	-1.473734	-3.770690	0.067071
H(7B)	3.890483	6.295683	-0.749353	-1.069538	-2.147216	0.617493
H(8A)	2.622121	5.132015	-2.453729	-0.105579	-2.249051	-1.564523
H(8B)	3.788980	3.777779	-2.437742	-1.411194	-3.262733	-2.185398
H(9A)	1.829394	6.453747	-0.331322	-1.606069	1.375118	0.001312
H(9B)	0.524196	5.974991	0.744201	-1.059995	-0.228963	0.483148
H(10A)	0.379515	3.792292	-0.162889	-1.829203	0.842366	-2.265146
H(10B)	0.682220	4.714077	-1.650397	-0.280557	0.126528	-1.782326
H(12A)	0.653745	2.818074	-2.746289	-0.299957	-0.542187	-4.326492
H(12B)	1.384894	1.303250	-3.055195	-1.190157	-1.474649	-5.544951
H(12C)	2.238031	2.721622	-3.450314	-0.347698	-2.318700	-4.233480
H(13A)	3.974743	1.529981	-0.389936	-3.985467	-2.551626	-3.210809
H(13B)	4.280531	1.962165	-1.992443	-2.575311	-3.526830	-3.684344
H(13C)	3.414993	0.550293	-1.678824	-3.434444	-2.592637	-4.903273
H(14A)	0.246750	1.841095	-0.500979	-2.451322	0.801923	-4.133004
H(14B)	1.527061	1.616060	0.613202	-3.883237	0.058547	-3.370985
H(14C)	1.297707	0.495862	-0.686690	-3.459742	-0.304854	-5.058137

Table 7S. Calculated relative energies of the B–N energy scans for the azaesters derivatives. Values in brackets stand for the B…N optimal distances of the open and closed forms of boronic azaesters. The energy of the most stable form is chosen as a reference point.



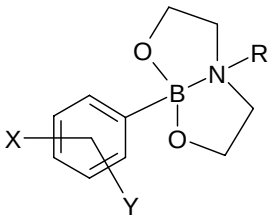
d(B–N) / Å	ΔE/kJ·mol^{-1}						
	X,*Y*=H			*X*,*Y*=F	*R*=Bu, *Y*=H		
	R=Bu	*R*=Bu*	*R*=H	*R*=^{t}Bu	*X*=2-Br	*X*=3-Br	*X*=4-Br
1.5	53.13	57.89	38.46	74.22	40.24	47.73	45.99
1.6	24.06	30.48	15.97	48.41	14.36	21.00	19.42
1.7	11.86	17.87	7.04	39.01	3.28	8.31	9.12
1.8	6.68	12.78	4.83	29.71	0.07	4.16	5.08
1.9	5.32	10.43	5.54	23.35	0.42	3.61	4.13
2.0	5.31	9.77	6.86	18.81	2.02	3.61	4.52
2.1	5.70	9.34	7.72	16.45	3.70	4.47	5.06
2.2	5.85	8.74	7.79	12.46	4.76	4.73	5.33
2.3	5.48	7.71	7.06	9.03	5.19	4.62	5.05
2.4	4.75	6.40	5.78	5.92	5.02	4.10	4.40
2.5	3.62	4.88	4.17	3.90	4.38	3.14	3.33
2.6	2.17	3.00	2.46	1.57	3.45	1.84	1.96
2.7	0.91	1.47	0.88	0.39	2.66	0.72	0.77
2.8	0.01	0.40	0.10	0.20	2.55	-0.07	0.00
2.9	0.19	0.12	0.97	1.06	3.17	0.10	0.06
3.0	1.20	1.21	2.55	3.06	4.87	1.52	1.40
3.1	3.57	3.37	5.54	5.93	7.69	4.04	3.90
3.2	7.33	7.02	10.07	10.43	12.07	8.02	7.80
3.3	13.82	12.57	16.39	16.82	18.08	13.96	13.64

*B3LYP/6-311++G(d,p)

Table 8S. Topological parameters (ρ – electron density, L – negative Laplacian of electron density) at BCPs of boron-nitrogen dative bonds in **1** for all computed scan steps.

d(B–N) / Å	$\rho(\boldsymbol{r}_{BCP})$ / e·Å^{-3}	$L(\boldsymbol{r}_{BCP})$ / e·Å^{-5}	CP
1.5	1.103	14.755	(3,–1)
1.6	0.895	7.946	(3,–1)
1.7	0.738	2.942	(3,–1)
1.8	0.619	0.067	(3,–1)
1.9	0.521	–0.269	(3,–1)
2.0	0.436	0.494	(3,–1)
2.1	0.364	1.035	(3,–1)
2.2	0.303	1.304	(3,–1)
2.3	0.253	1.389	(3,–1)
2.4	0.211	1.380	(3,–1)
2.5	0.178	1.329	(3,–1)
2.6	0.150	1.271	(3,–1)
2.7	0.127	1.202	(3,–1)
2.8	0.107	1.118	(3,–1)
2.9	0.091	1.039	(3,+1)
3.0	0.078	0.967	(3,+1)
3.1	0.067	0.902	(3,+1)
3.2	0.058	0.849	(3,+1)
3.3	0.051	0.839	(3,+1)

Table 9S. Topological parameters (ρ – electron density, L – negative Laplacian of electron density) at the BCPs of boron-nitrogen dative bonds for the closed forms of halide-substituted azaesters used in theoretical calculations together with associated B–N bond lengths.



R	X,Y	$d_{B–N}$ / Å	$\rho(\boldsymbol{r}_{BCP})$ / e·Å^{-3}	$L(\boldsymbol{r}_{BCP})$ / e·Å^{-5}
Bu	4-Br, H	1.911	0.513	0.190
Bu	3-Br, H	1.888	0.534	0.315
Bu	2-Br, H	1.834	0.590	0.352
Bu	4-F, H	1.907	0.515	0.188
Bu	2-F, 3-F	1.809	0.617	0.087
Bu	3-F, 4-F	1.876	0.545	0.341
Bu	2-F, 5-F	1.804	0.622	0.011
Bu	2-F, 4-F	1.815	0.610	0.160
Bu	3-F, 5-F	1.864	0.558	0.376
Bu	3-Cl, 5-Cl	1.882	0.541	0.367
Bu	2-Cl, 3-Cl	1.821	0.604	0.271
Bu	H, H	1.930	0.495	–0.037
H	H, H	1.814	0.593	0.340

Table 10S. The B–O and B–C bond lengths in **1,** as a function of the B…N distances for different scan steps – numerical values.

	d(B–N) / Å	*d*(B–O)* / Å	*d*(B–C) / Å
	1.500	1.487	1.626
	1.600	1.474	1.624
	1.700	1.462	1.621
	1.800	1.449	1.614
	1.900	1.436	1.608
	2.000	1.425	1.601
	2.100	1.414	1.596
	2.200	1.405	1.592
	2.300	1.397	1.588
	2.400	1.391	1.585
	2.500	1.385	1.583
	2.600	1.381	1.582
	2.700	1.378	1.581
	2.800	1.375	1.580
	2.900	1.374	1.578
	3.000	1.373	1.577
	3.100	1.373	1.576
	3.200	1.374	1.575
	3.300	1.375	1.573
Closed form:	1.764	1.449	1.614
Open form:	2.787	1.376	1.580

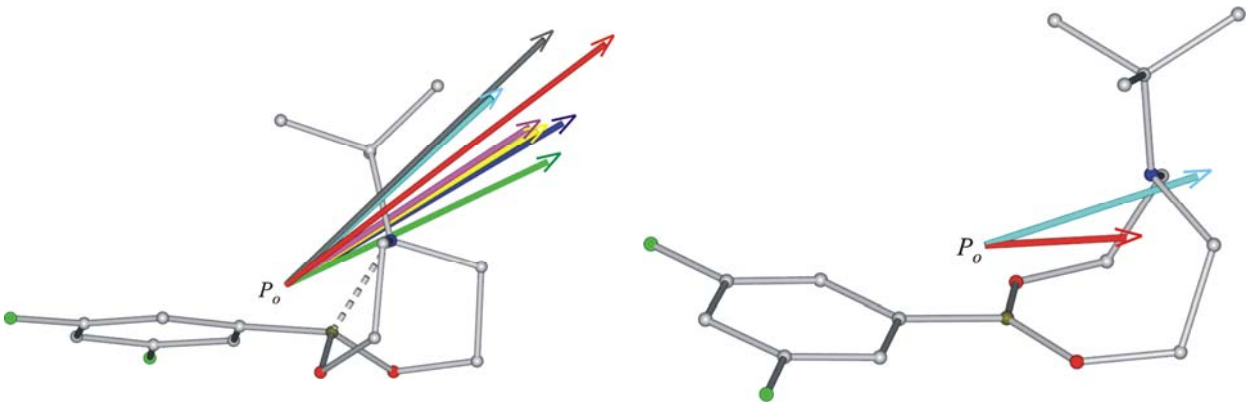
* mean value of B(1)–O(1) and B(1)–O(2)

Table 11S. Second-order perturbation theory analyses of the Kohn-Sham equations on NBO basis for compound **1** (ED – electron density together with the description of natural orbital hybrid of which NBO is composed, E_2 energy of hyperconjugative interaction, $E_j - E_i$ – energy difference between donor and acceptor i and j NBO orbitals, $F_{i,j}$ – Fock matrix element between i-th and j-th NBO orbitals, LP – lone electron pair, LP* unfilled p-type orbital).

	Donor	ED / e Hybride	Acceptor	ED / e Hybride	E_2 / kJ·mol^{-1}	E_j-E_i / a.u	$F_{i,j}$ / a.u
Closed form	O(1) LP2	1.875 s (0.01%) p (99.78%)	B(1) LP1*	0.352 s (1.13%) p (98.67%)	14.75	0.40	0.073
	O(2) LP2	1.886 s (0.01%) p (99.78%)			15.58	0.40	0.075
	N(1) LP1	1.701 s (16.26%) p (83.70%)			54.3	0.50	0.149
Open form	O(1) LP2	1.822 s (0.70%) p (99.14%)	B(1) LP1*	0.372 s (5.29%) p (94.69%)	46.09	0.35	0.119
	O(2) LP2	1.819 s (0.49%) p (99.35%)			46.68	0.35	0.120
	N(1) LP1	1.843 s (9.93%) p (90.02%)			2.96	0.30	0.028

Table 12S. Different dipole moments for the closed and open forms of **1** ($||\boldsymbol{\mu}||$ denotes the magnitude of the dipole moment). Values in square brackets next to the dipole moment magnitudes denote the dipole moment enhancements in crystalline state in respect to the dipole moment for the isolated molecule ($[x]_A = (\mu - \mu_A) \cdot 100\% / \mu_A$). given in subscript.

Dipole moment	$\|\|\boldsymbol{\mu}\|\|$ / D *Closed form*	*Open form*	*Remarks*
B1	8.64	–	Integrated dipole moment over the whole molecule (sum over atomic contributions) – experimental data (isolated molecule)
B2	8.83 $[2.2\%]_{\mathbf{B1}}$	–	Integrated dipole moment over the whole molecule (sum over atomic contributions) – experimental data (molecule in a crystal)
B3	13.26	3.75	Integrated dipole moment over the whole molecule (sum over atomic contributions) – theoretical data from DFT calculations (isolated molecule)
M1	8.71	–	Dipole moment calculated directly from the multipole populations (isolated molecule)
M2	9.59 $[10.1\%]_{\mathbf{M1}}$	–	Dipole moment calculated directly from the multipole populations (molecule in a crystal)
E1	8.99	5.98	Theoretically calculated dipole moment at Hartree-Fock level (isolated molecule)
E2	11.55 $[28.5\%]_{\mathbf{E1}}$	–	Estimated dipole moment at Hartree-Fock level using Spackman's iterative approach[20] (molecule in a crystal)



(*a*) (*b*)

Figure 8S. Total dipole moments of **1** anchored approximately at the geometric centre of the molecule for (*a*) closed and (*b*) open forms of **1**. Colour coding for the values from Table 13S: **B1** – green, **B2** - yellow, **B3** – red, **M1** – magenta, **M2** – blue , **E1** – cyan, **E2** – grey (P_o – geometric centre); atomic colours are the same as in Figure 1.

5. VT NMR studies

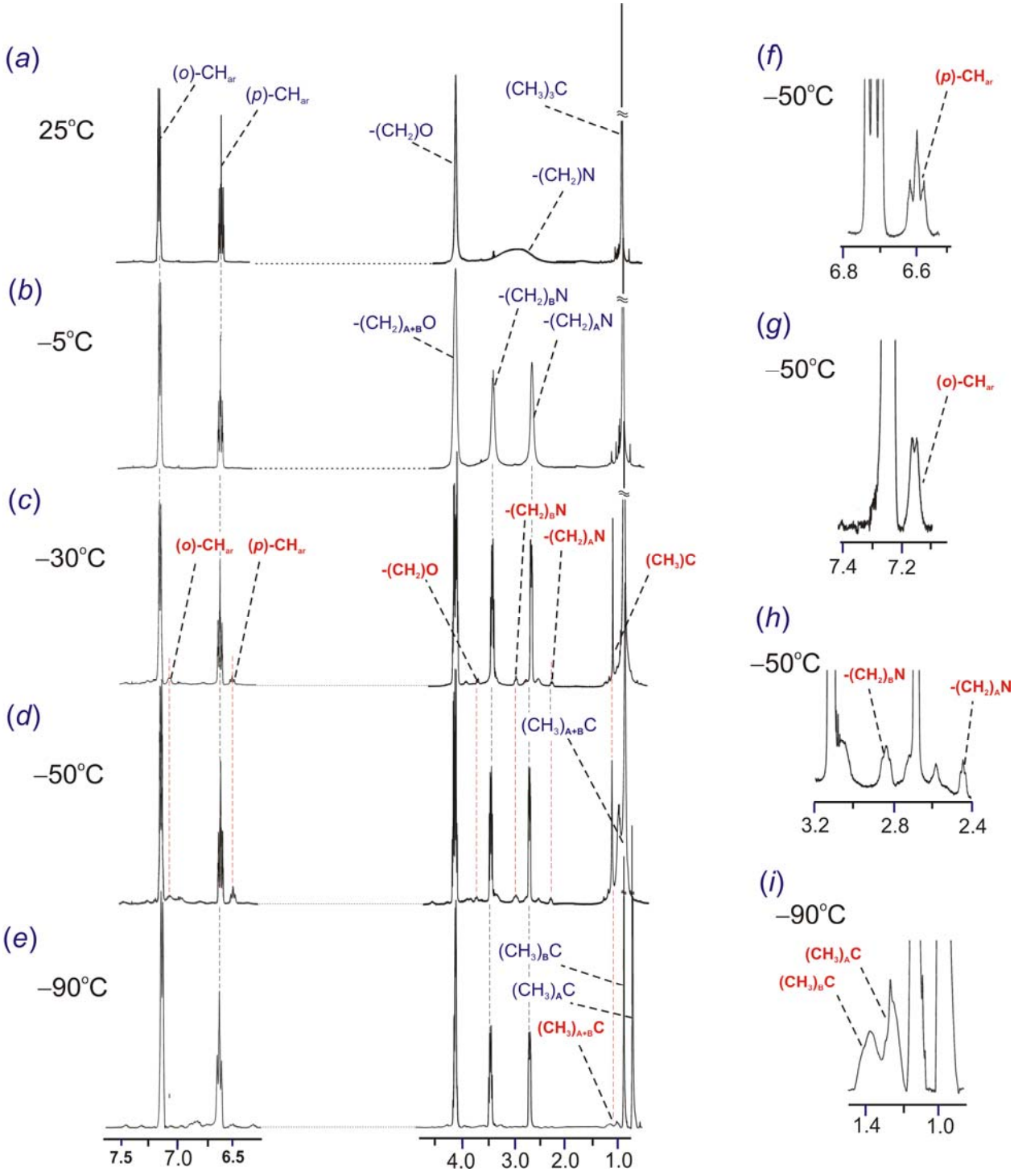


Figure 9S. ^{1}H NMR spectra (500 MHz) for a solution of **1** in CD_2Cl_2 taken at five different temperatures: (*a*) 25°C, (*b*) –5°C, (*c*) –30°C, (*d*) –50°C and (*e*) –90°C; (*f* – *i*) more detailed view of some selected parts of the NMR spectra. Peaks of the closed and open forms have been assigned in blue and red colours, respectively.

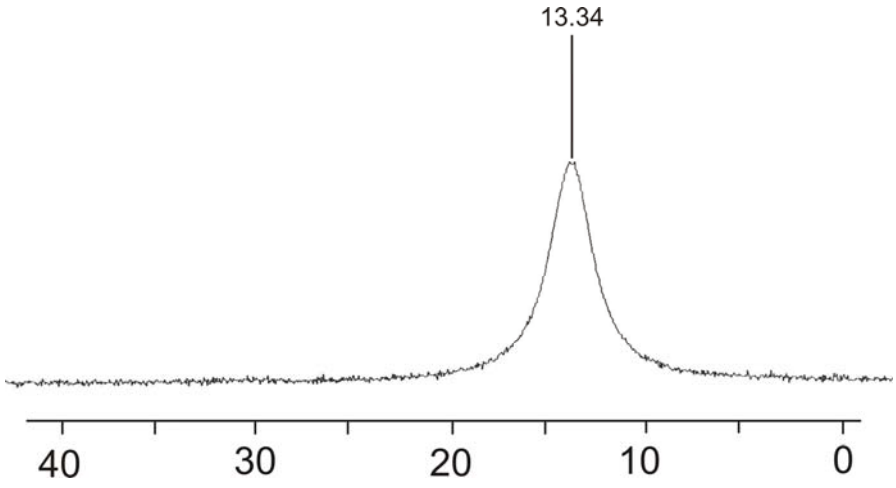


Figure 10S. ^{11}B NMR spectrum of **1** in the solution of CD2Cl$_2$ recorded at room temperature (T = 25^{o}C).

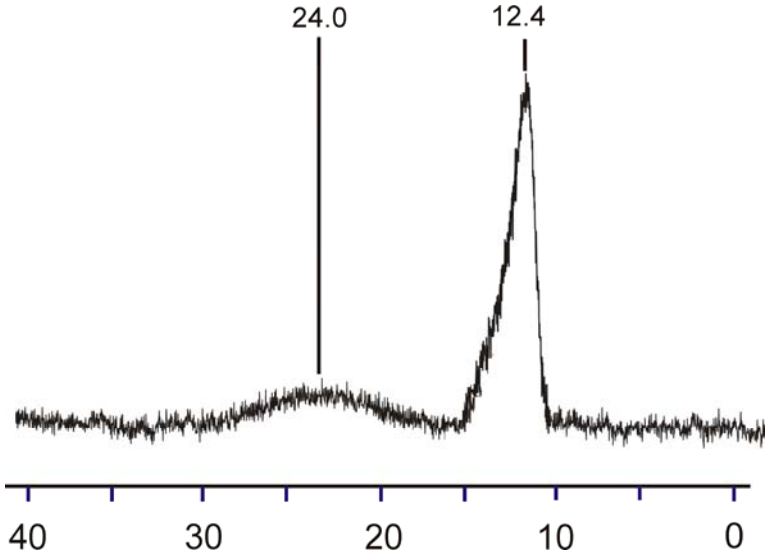


Figure 11S. ^{11}B NMR spectrum of the closed (12.41 ppm) and open (24.07 ppm) forms of **1** in the solution of CD_2Cl_2 recorded at –50^{o}C.

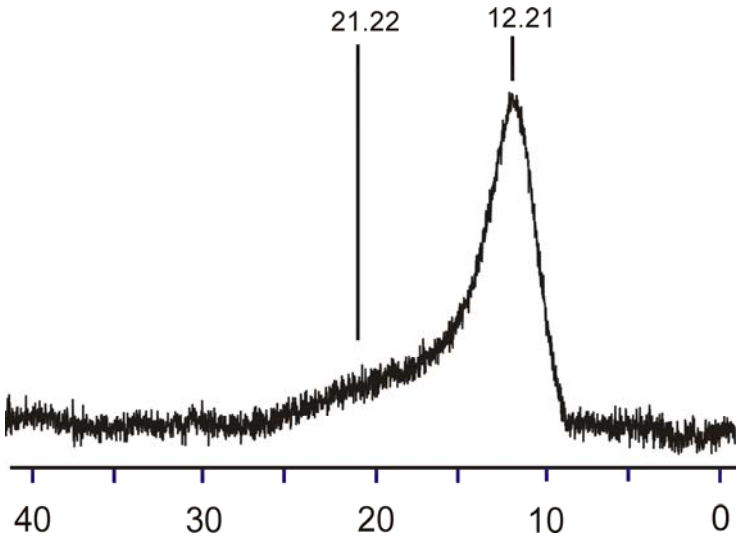


Figure 12S. ^{11}B NMR spectrum of the closed (12.24 ppm) and open (23.89 ppm) forms of **1** in the solution of CD_2Cl_2 recorded at –90^{o}C.

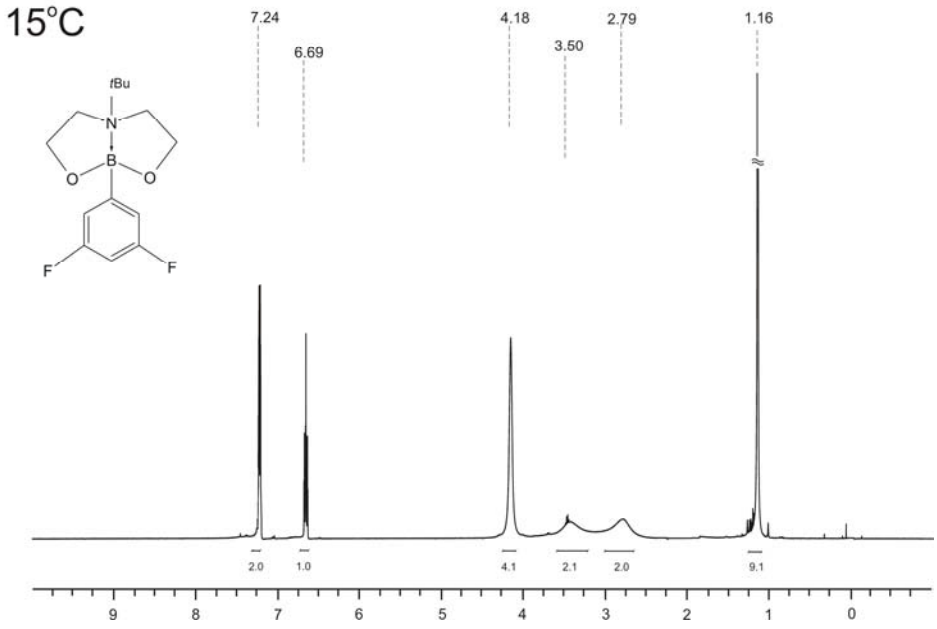


Figure 13S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at 15°C.

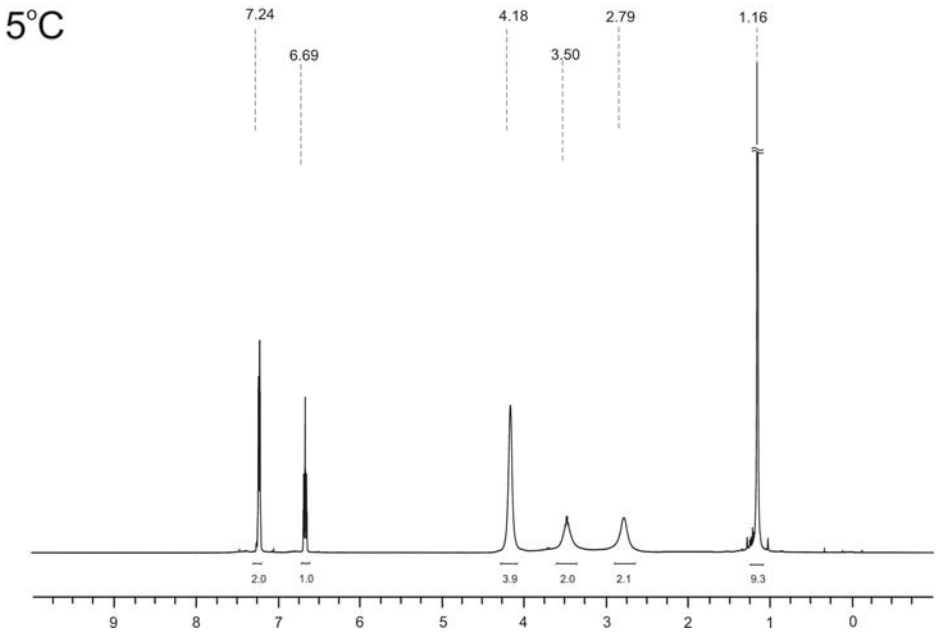


Figure 14S. ^{1}H NMR spectrum of **1** in the solution of CD_2Cl_2 recorded at 5°C.

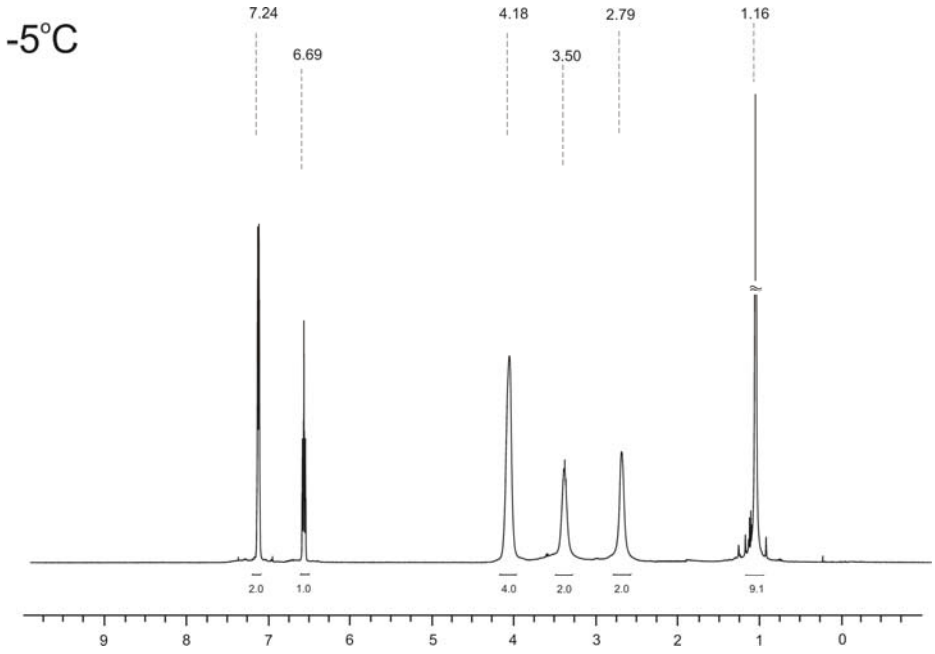


Figure 15S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at –5°C.

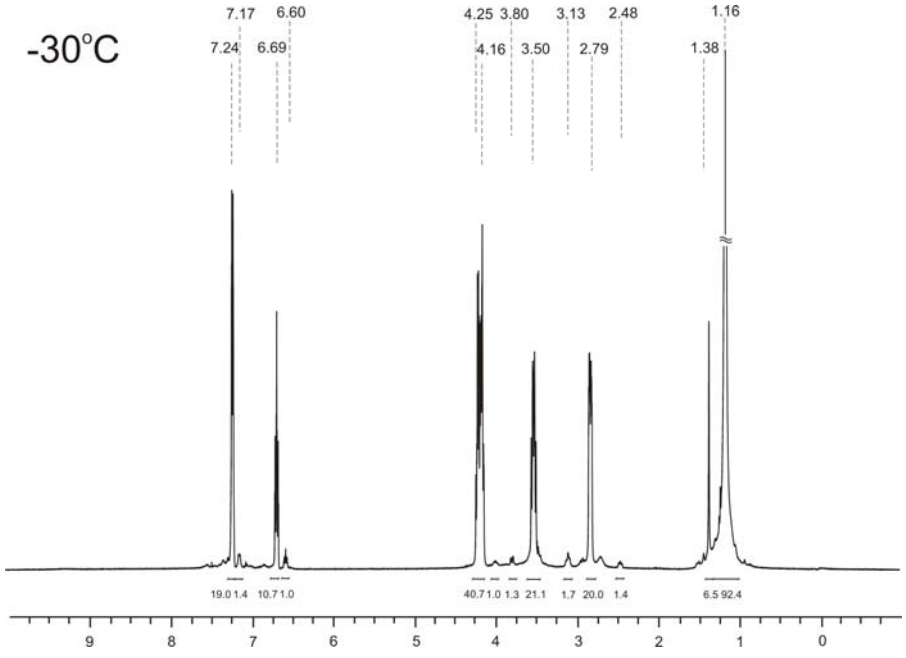


Figure 16S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at –30°C.

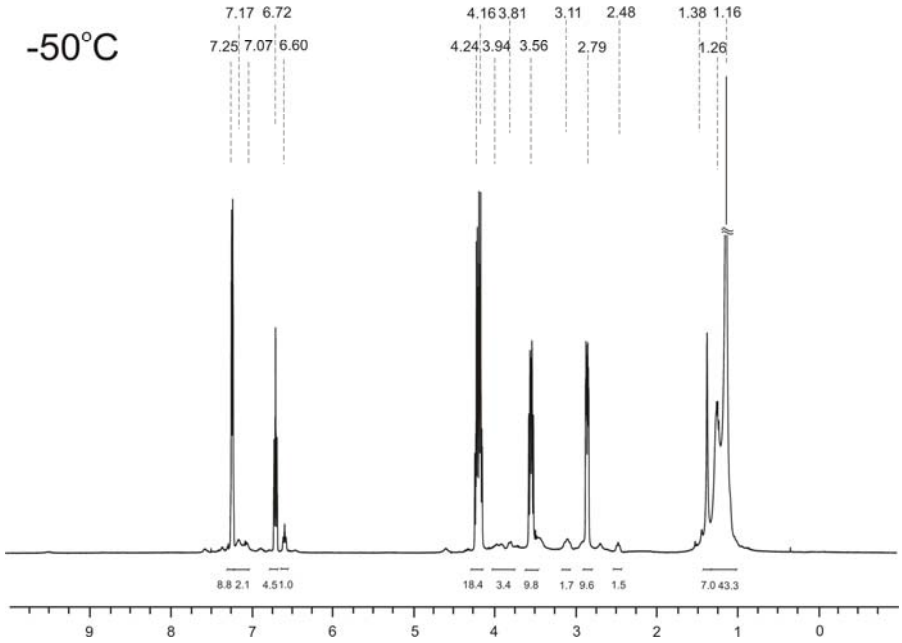


Figure 17S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at –50°C.

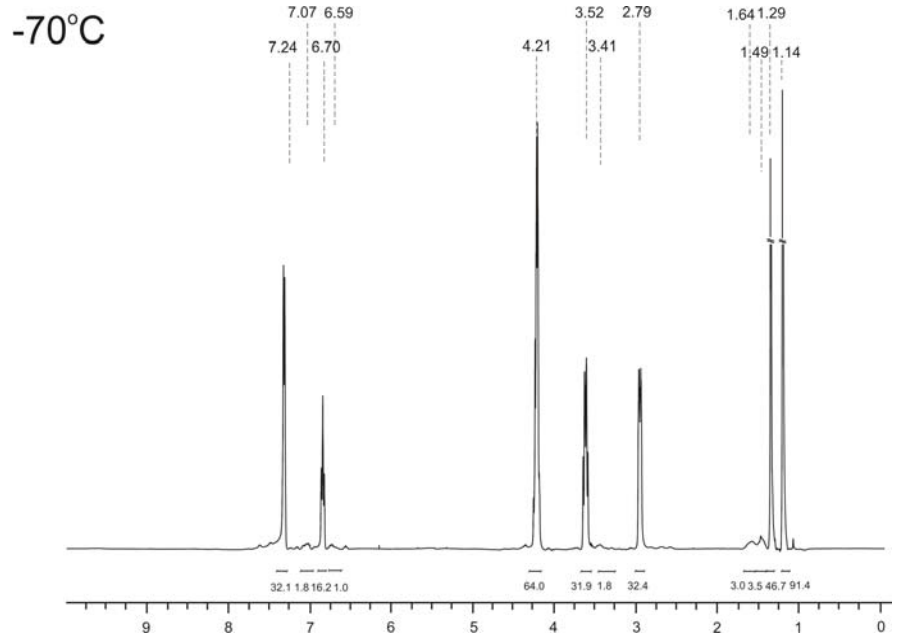


Figure 18S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at –70°C.

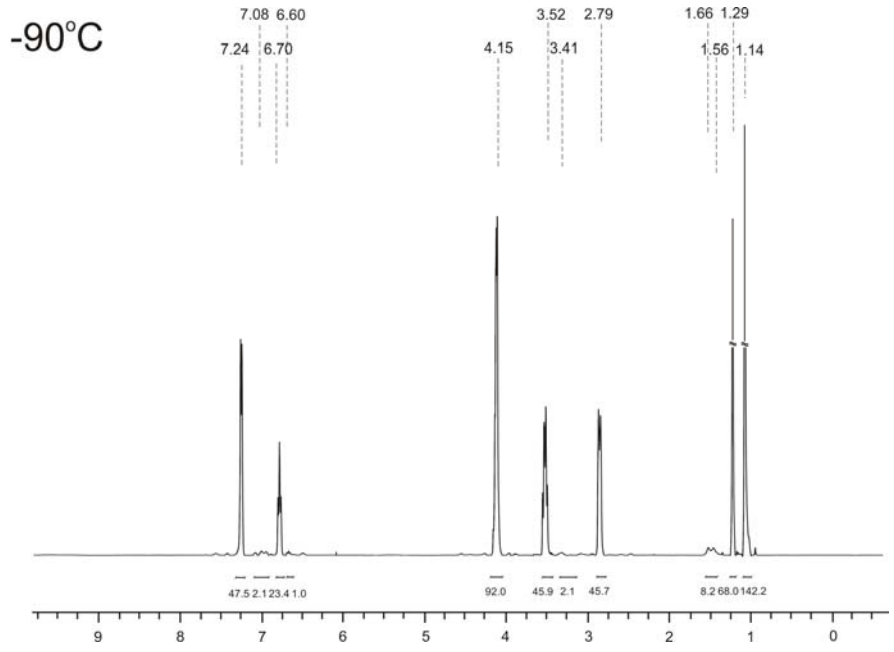


Figure 19S. ^{1}H NMR spectra of **1** in the solution of CD_2Cl_2 recorded at –90°C.

6. Scan coordinates

Table 13S. Cartesian coordinates for **1** with B–N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*). All others parameters were fully optimised at B3LYP/aug-cc-pVDZ level.

Atom	$d_{B–N}$ = 1.5 Å (*a*)			$d_{B–N}$ = 1.6 Å (*b*)			$d_{B–N}$ = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.193528	–0.004740	–0.661939	–1.193614	–0.006383	–0.662203	–1.195953	0.000526	–0.660662
F(2)	3.526796	0.067019	–0.743908	3.525826	0.072207	–0.747109	3.525901	0.059576	–0.747185
O(1)	0.147795	0.999484	4.158497	0.036682	0.841742	4.158901	–0.006971	0.767632	4.131085
O(2)	2.561412	0.497504	4.162543	2.498367	0.654567	4.153681	2.478545	0.793798	4.103057
N(1)	0.950253	–1.164402	4.547088	1.112284	–1.236697	4.617073	1.266122	–1.222938	4.749981
B(1)	1.232598	0.056504	3.722667	1.231650	0.078293	3.713440	1.237210	0.125150	3.714693
C(1)	1.216936	0.000000	2.095873	1.217824	0.000000	2.093416	1.217531	0.000000	2.094815
C(2)	0.000000	0.000000	1.388693	0.000000	0.000000	1.388631	0.000000	0.000000	1.388743
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.167476	0.009323	–0.758217	1.166049	0.011826	–0.759244	1.164339	0.009031	–0.761440
C(5)	2.358543	0.032919	–0.040247	2.358036	0.035876	–0.042298	2.355271	0.029820	–0.042549
C(6)	2.408834	0.028821	1.349201	2.409896	0.031350	1.346424	2.408293	0.032505	1.345439
C(7)	–0.768525	0.401943	5.035443	–0.702065	0.204336	5.165819	–0.321897	0.480241	5.467131
C(8)	–0.535913	–1.100294	4.848436	–0.342431	–1.273613	5.032662	0.052183	–0.994518	5.628326
C(9)	2.556080	0.392788	5.562614	2.539126	0.535285	5.550489	2.854890	0.491456	5.420962
C(10)	1.719447	–0.872991	5.855204	1.944800	–0.850348	5.847366	2.516676	–0.991312	5.576673
C(11)	1.368195	–2.594481	4.032226	1.612878	–2.623030	4.072068	1.237360	–2.685753	4.191906
C(12)	1.012196	–3.654143	5.095253	1.362704	–3.712345	5.136511	1.236464	–3.692805	5.354879
C(13)	0.663251	–2.989323	2.720211	0.918793	–3.047317	2.761765	–0.038066	–2.905106	3.363783
C(14)	2.882593	–2.597139	3.766320	3.118807	–2.535325	3.775155	2.463951	–2.948289	3.295602
H(2)	–0.954268	0.036075	1.911301	–0.950910	0.030684	1.917117	–0.949521	0.038872	1.918884
H(4)	1.148163	0.019502	–1.845374	1.146360	0.021237	–1.846450	1.144914	0.014901	–1.848340
H(6)	3.375076	0.082329	1.847203	3.376935	0.090821	1.841953	3.376169	0.102305	1.838338
H(7A)	–1.803349	0.680259	4.781291	–1.781477	0.362390	5.018255	–1.398268	0.626286	5.640424
H(7B)	–0.597285	0.708170	6.085793	–0.449216	0.588069	6.172945	0.218387	1.130698	6.175335
H(8A)	–0.791108	–1.728955	5.705766	–0.478747	–1.860753	5.945354	0.257905	–1.301006	6.658946
H(8B)	–1.071956	–1.450036	3.964968	–0.925221	–1.719857	4.226887	–0.764153	–1.600279	5.234623
H(9A)	1.003411	–0.749330	6.671429	1.306479	–0.859924	6.734800	2.362114	–1.315013	6.611043
H(9B)	2.355802	–1.724301	6.085095	2.733681	–1.586380	5.988419	3.326688	–1.573845	5.141462
H(10A)	3.583419	0.291117	5.940864	3.576482	0.606357	5.906471	3.934543	0.656923	5.551974
H(10B)	2.097965	1.279129	6.032046	1.948277	1.326266	6.042006	2.332545	1.119805	6.162064
H(12A)	1.488205	–4.599231	4.811474	1.869196	–4.630923	4.816979	2.130846	–3.608877	5.983161
H(12B)	–0.067534	–3.834070	5.141771	0.297641	–3.949300	5.241239	1.231856	–4.705719	4.930989
H(12C)	1.364247	–3.403831	6.101074	1.759431	–3.449036	6.123904	0.346986	–3.603361	5.990571
H(13A)	0.917343	–4.037645	2.525039	1.208867	–4.086157	2.562041	–0.146665	–2.163229	2.570536
H(13B)	0.995544	–2.397799	1.870053	1.236090	–2.439937	1.914414	–0.947015	–2.916307	3.975300
H(13C)	–0.428641	–2.934722	2.781163	–0.174451	–3.022816	2.806248	0.030309	–3.893748	2.893663
H(14A)	3.483776	–2.447217	4.668702	3.738047	–2.403536	4.668812	3.385462	–3.095145	3.870251
H(14B)	3.158399	–1.837390	3.033545	3.341484	–1.731149	3.070468	2.620112	–2.153578	2.563477
H(14C)	3.148889	–3.579304	3.358910	3.421355	–3.484076	3.313865	2.294466	–3.877532	2.738555

Table 14S. Cartesian coordinates for **1** with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	$d_{B–N}$ = 1.8 Å (*a*)			$d_{B–N}$ = 1.9 Å (*b*)			$d_{B–N}$ = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.193711	–0.008248	–0.662259	–1.193521	–0.004683	–0.661648	–1.192087	–0.002854	–0.662656
F(2)	3.526884	0.074580	–0.748909	3.525890	0.058402	–0.753372	3.527145	0.049335	–0.750952
O(1)	–0.021251	0.626696	4.182766	–0.004747	0.556642	4.208373	–0.002924	0.534004	4.221447
O(2)	2.469174	0.649056	4.170517	2.485701	0.629855	4.160715	2.483904	0.526303	4.197653
N(1)	1.247366	–1.436737	4.693061	1.314112	–1.516184	4.736368	1.246247	–1.620898	4.756395
B(1)	1.232056	0.067034	3.703901	1.248127	0.072011	3.695560	1.240397	0.069502	3.687511
C(1)	1.219270	0.000000	2.091770	1.221059	0.000000	2.088947	1.220888	0.000000	2.088564
C(2)	0.000000	0.000000	1.388498	0.000000	0.000000	1.388880	0.000000	0.000000	1.388758
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.166393	0.013573	–0.759600	1.165335	0.010222	–0.760598	1.166858	0.007056	–0.758357
C(5)	2.358568	0.039265	–0.043367	2.359021	0.031187	–0.046271	2.361087	0.025542	–0.044053
C(6)	2.410991	0.037225	1.345124	2.413009	0.031646	1.341773	2.414671	0.027372	1.344035
C(7)	–0.460168	0.113129	5.414988	–0.329023	0.115292	5.503231	–0.447118	–0.021007	5.437236
C(8)	–0.083625	–1.370214	5.379648	0.060187	–1.365629	5.543182	–0.097092	–1.512799	5.383302
C(9)	2.707624	0.361054	5.523661	2.812515	0.278460	5.481395	2.670428	0.237977	5.561488
C(10)	2.337604	–1.129090	5.696715	2.506358	–1.223153	5.601392	2.301754	–1.250380	5.753083
C(11)	1.447129	–2.829964	4.034076	1.409403	–2.915892	4.082591	1.482227	–2.997297	4.112390
C(12)	1.289434	–3.923133	5.106146	1.406424	–4.006493	5.170129	1.424623	–4.105082	5.183079
C(13)	0.393626	–3.057059	2.936213	0.220712	–3.146353	3.131473	0.405863	–3.272444	3.046497
C(14)	2.842802	–2.939622	3.386987	2.703740	–3.029280	3.253745	2.854131	–3.035761	3.411403
H(2)	–0.947595	0.015910	1.922672	–0.946916	0.020233	1.924502	–0.946703	0.021545	1.924682
H(4)	1.146500	0.018884	–1.846769	1.144148	0.013973	–1.847754	1.146648	0.009797	–1.845650
H(6)	3.378211	0.098081	1.840301	3.379698	0.085210	1.838651	3.380891	0.076228	1.842296
H(7A)	–1.549273	0.237038	5.503441	–1.409933	0.231539	5.667404	–1.534688	0.116462	5.517873
H(7B)	0.000109	0.629678	6.274127	0.185395	0.699937	6.282838	0.010511	0.474351	6.309123
H(8A)	–0.045471	–1.843925	6.367048	0.194817	–1.743929	6.563884	–0.123494	–1.979979	6.377301
H(8B)	–0.811888	–1.900342	4.761609	–0.731889	–1.940146	5.062916	–0.822785	–2.017356	4.742756
H(9A)	2.009316	–1.383490	6.710826	2.328050	–1.538667	6.636462	1.962475	–1.457779	6.776373
H(9B)	3.212268	–1.728654	5.459057	3.360652	–1.778391	5.216224	3.190280	–1.850218	5.569167
H(10A)	3.769889	0.524310	5.755711	3.882273	0.464864	5.653005	3.724582	0.406197	5.821695
H(10B)	2.118656	1.010230	6.191735	2.252128	0.876076	6.217791	2.061862	0.896932	6.199427
H(12A)	1.951730	–3.762995	5.965705	2.240928	–3.892130	5.873491	2.176602	–3.960414	5.969414
H(12B)	1.555636	–4.891689	4.665031	1.514976	–4.988190	4.691039	1.626955	–5.075413	4.710871
H(12C)	0.256779	–3.999407	5.467212	0.468669	–4.022299	5.739016	0.435934	–4.169701	5.654750
H(13A)	0.556616	–2.406498	2.075802	0.173357	–2.383723	2.350339	0.370608	–2.481158	2.292831
H(13B)	–0.634568	–2.919565	3.286009	–0.745400	–3.185892	3.645911	–0.595324	–3.397384	3.474514
H(13C)	0.476952	–4.097530	2.598458	0.356122	–4.120595	2.646062	0.652778	–4.213587	2.540501
H(14A)	3.640813	–3.116576	4.116853	3.601452	–3.142593	3.871876	3.699064	–2.977513	4.105972
H(14B)	3.086619	–2.050802	2.800506	2.835111	–2.170732	2.589863	2.946187	–2.231990	2.675486
H(14C)	2.842616	–3.798342	2.705819	2.638335	–3.928262	2.629304	2.949637	–3.992717	2.884653

Table 15S. Cartesian coordinates for **1** with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	$d_{B–N}$ = 2.1 Å (*a*)			$d_{B–N}$ = 2.2 Å (*b*)			$d_{B–N}$ = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.193533	–0.004293	–0.661056	–1.192409	–0.003947	–0.661750	–1.191838	–0.004050	–0.662110
F(2)	3.525577	0.042254	–0.758703	3.526227	0.037283	–0.757051	3.526763	0.031556	–0.756882
O(1)	0.022720	0.427597	4.251896	0.023103	0.334613	4.270016	0.013523	0.207242	4.276095
O(2)	2.515826	0.423715	4.192994	2.514602	0.321552	4.216507	2.503464	0.290191	4.226906
N(1)	1.281524	–1.768988	4.752127	1.271719	–1.911697	4.744357	1.343252	–2.023382	4.769010
B(1)	1.257538	0.036504	3.679922	1.256025	0.011485	3.676121	1.255231	–0.004033	3.671520
C(1)	1.223600	0.000000	2.084457	1.223476	0.000000	2.084868	1.223879	0.000000	2.084098
C(2)	0.000000	0.000000	1.388740	0.000000	0.000000	1.388937	0.000000	0.000000	1.388762
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.164872	0.008157	–0.761275	1.165947	0.008218	–0.759688	1.166512	0.006679	–0.759090
C(5)	2.360268	0.023043	–0.049227	2.361638	0.020521	–0.047725	2.362451	0.017812	– 0.047435
C(6)	2.416744	0.022146	1.338339	2.417616	0.017083	1.339882	2.418676	0.015621	1.340215
C(7)	–0.287708	–0.057396	5.538192	–0.271812	–0.176129	5.552073	–0.231680	–0.292947	5.574104
C(8)	0.038908	–1.557088	5.537293	0.042467	–1.681551	5.533350	0.145831	–1.788644	5.595672
C(9)	2.819451	0.007937	5.503799	2.815340	–0.143287	5.513898	2.844429	–0.206520	5.504965
C(10)	2.478582	–1.494018	5.590686	2.476872	–1.646966	5.561621	2.576581	–1.724443	5.517051
C(11)	1.325975	–3.133486	4.054676	1.302924	–3.256423	4.023856	1.352044	–3.359849	4.047281
C(12)	1.325755	–4.281113	5.083513	1.341626	–4.420681	5.032442	1.380625	–4.531537	5.048716
C(13)	0.111567	–3.279430	3.117877	0.059749	–3.398610	3.123820	0.103401	–3.471728	3.150478
C(14)	2.590824	–3.229654	3.180737	2.537063	–3.326988	3.103564	2.581874	–3.442804	3.121077
H(2)	–0.946180	0.019212	1.925915	–0.946145	0.012765	1.926234	–0.945702	0.007456	1.926818
H(4)	1.142438	0.011193	–1.848399	1.143787	0.011719	–1.846905	1.144821	0.008772	–1.846346
H(6)	3.383767	0.059501	1.835894	3.384192	0.042095	1.838902	3.385280	0.037976	1.839297
H(7A)	–1.360299	0.095699	5.721567	–1.341582	–0.019404	5.747266	–1.303886	–0.177802	5.783366
H(7B)	0.258665	0.484716	6.324511	0.283452	0.353871	6.339273	0.310675	0.282634	6.336535
H(8A)	0.129117	–1.948668	6.560870	0.128361	–2.075486	6.558161	0.286470	–2.128681	6.635093
H(8B)	–0.781783	–2.078612	5.044515	–0.789676	–2.189574	5.045825	–0.689232	–2.349571	5.174680
H(9A)	2.322657	–1.809575	6.632297	2.348451	–1.984904	6.601592	2.534673	–2.094575	6.555065
H(9B)	3.323775	–2.055098	5.193162	3.318609	–2.193691	5.136181	3.416744	–2.213079	5.022774
H(10A)	3.893004	0.162272	5.680012	3.889331	0.004525	5.691914	3.914269	–0.017261	5.666979
H(10B)	2.276236	0.601128	6.254127	2.276171	0.428197	6.282696	2.298490	0.318196	6.300771
H(12A)	2.196957	–4.237121	5.750068	2.243175	–4.388820	5.657876	2.273874	–4.495644	5.686403
H(12B)	1.364561	–5.244677	4.557547	1.346871	–5.378313	4.494822	1.398413	–5.487811	4.508631
H(12C)	0.416829	–4.279743	5.698816	0.462767	–4.416803	5.690109	0.493790	–4.534012	5.695901
H(13A)	0.022024	–2.422871	2.442331	–0.068960	–2.519055	2.484524	0.017511	–2.604514	2.486974
H(13B)	–0.834010	–3.407812	3.657061	–0.864462	–3.565793	3.688412	–0.829219	–3.574737	3.716533
H(13C)	0.246248	–4.180048	2.506436	0.191562	–4.273159	2.475131	0.192586	–4.370671	2.528137
H(14A)	3.515541	–3.304320	3.763978	3.483769	–3.389776	3.651352	3.524130	–3.569682	3.666450
H(14B)	2.668684	–2.375665	2.500111	2.576456	–2.464939	2.430153	2.657743	–2.553777	2.485367
H(14C)	2.530484	–4.142517	2.575628	2.469554	–4.234754	2.491434	2.477644	–4.318923	2.469399

Table 16S. Cartesian coordinates for **1** with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	$d_{B–N}$ = 2.4 Å (*a*)			$d_{B–N}$ = 2.5 Å (*b*)			$d_{B–N}$ = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.191111	–0.004917	–0.662248	–1.191496	0.000901	–0.662034	–1.190851	0.007570	–0.662434
F(2)	3.527139	0.027349	–0.756561	3.526902	0.001855	–0.758777	3.527531	–0.025286	–0.756738
O(1)	0.020114	0.173062	4.278918	0.025988	0.136981	4.280724	0.020990	0.171310	4.269905
O(2)	2.510564	0.174291	4.232548	2.513077	0.151327	4.228203	2.507686	0.151299	4.227547
N(1)	1.276906	–2.125822	4.819254	1.298323	–2.160784	4.939565	1.259547	–2.093635	5.171591
B(1)	1.254705	–0.020050	3.668067	1.258295	–0.010534	3.664880	1.253188	0.024849	3.664280
C(1)	1.224204	0.000000	2.083550	1.225020	0.000000	2.082204	1.224721	0.000000	2.082617
C(2)	0.000000	0.000000	1.388779	0.000000	0.000000	1.388734	0.000000	0.000000	1.388606
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.167154	0.006391	–0.758211	1.166672	–0.001347	–0.758828	1.167506	–0.010113	–0.757653
C(5)	2.363498	0.015771	–0.047030	2.363553	0.000716	–0.048498	2.364124	–0.016165	–0.046860
C(6)	2.419700	0.012298	1.340605	2.420583	0.001606	1.339029	2.420963	–0.010434	1.340712
C(7)	–0.240422	–0.321017	5.578749	–0.224586	–0.312667	5.600358	–0.229011	–0.148402	5.628214
C(8)	0.075947	–1.831307	5.611447	0.095931	–1.819768	5.703065	0.071555	–1.641766	5.892894
C(9)	2.821516	–0.320731	5.520678	2.817898	–0.289860	5.539105	2.805057	–0.187540	5.571883
C(10)	2.506556	–1.831248	5.565256	2.524357	–1.801834	5.655631	2.498489	–1.680007	5.825873
C(11)	1.268514	–3.459787	4.106689	1.286667	–3.522483	4.289344	1.216734	–3.504383	4.650885
C(12)	1.293043	–4.629552	5.111398	1.257070	–4.649833	5.341468	1.172849	–4.533196	5.799505
C(13)	0.010608	–3.562722	3.221157	0.058228	–3.637828	3.364394	–0.019959	–3.676509	3.744938
C(14)	2.489147	–3.550530	3.167996	2.531747	–3.682438	3.393647	2.453077	–3.767391	3.766186
H(2)	–0.945589	0.005639	1.927041	–0.945391	0.008546	1.927121	–0.945451	0.015666	1.926679
H(4)	1.145623	0.007866	–1.845542	1.144482	–0.001295	–1.846123	1.146163	–0.011342	–1.845017
H(6)	3.385952	0.027465	1.840555	3.387180	0.011653	1.838323	3.387444	–0.003735	1.840239
H(7A)	–1.307538	–0.164109	5.786159	–1.292153	–0.153323	5.802997	–1.294455	0.042658	5.813498
H(7B)	0.321685	0.237229	6.338896	0.334160	0.280530	6.335373	0.335891	0.511436	6.298064
H(8A)	0.173150	–2.164733	6.659654	0.180289	–2.097232	6.770042	0.157049	–1.794283	6.985834
H(8B)	–0.774396	–2.358142	5.176899	–0.752716	–2.367023	5.290207	–0.789860	–2.218515	5.553388
H(9A)	2.448872	–2.165035	6.616190	2.486951	–2.080244	6.725225	2.480962	–1.853726	6.919284
H(9B)	3.339337	–2.358949	5.098023	3.364510	–2.334155	5.208760	3.326887	–2.260753	5.418243
H(10A)	3.896016	–0.164565	5.686163	3.889706	–0.114915	5.702651	3.878832	–0.010834	5.719217
H(10B)	2.289996	0.237419	6.302514	2.277332	0.298041	6.291551	2.273164	0.468715	6.271473
H(12A)	1.289018	–5.590064	4.578367	2.138890	–4.610625	5.995211	1.159521	–5.556944	5.400745
H(12B)	0.414200	–4.612201	5.769905	1.251810	–5.632328	4.849974	0.273740	–4.405906	6.417582
H(12C)	2.194134	–4.602344	5.738595	0.359204	–4.589710	5.970994	2.053040	–4.441750	6.450512
H(13A)	–0.077579	–2.690406	2.563353	0.009533	–2.787020	2.674836	–0.049011	–2.893382	2.977624
H(13B)	–0.917031	–3.665110	3.796003	–0.889915	–3.701751	3.910427	–0.966868	–3.660158	4.296884
H(13C)	0.090082	–4.458561	2.593232	0.140336	–4.557105	2.771395	0.033630	–4.650261	3.242434
H(14A)	3.439354	–3.657791	3.703861	3.462146	–3.792856	3.962067	3.379886	–3.873509	4.342334
H(14B)	2.549955	–2.670496	2.517668	2.633474	–2.829426	2.711646	2.585595	–2.964300	3.030845
H(14C)	2.385993	–4.438705	2.532545	2.424145	–4.592747	2.791299	2.312230	–4.709878	3.222917

Table 17S. Cartesian coordinates for **1** with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	$d_{B–N}$ = 2.7 Å (*a*)			$d_{B–N}$ = 2.8 Å (*b*)			$d_{B–N}$ = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.191164	0.004325	–0.662373	–1.189668	0.002317	–0.662282	–1.188099	0.000630	–0.662554
F(2)	3.527472	–0.014667	–0.757534	3.527708	–0.008601	–0.756350	3.528292	–0.000819	–0.754636
O(1)	0.022186	0.110035	4.271869	0.029720	0.105566	4.277218	0.028545	–0.028507	4.279165
O(2)	2.506017	0.104076	4.229803	2.505055	0.032524	4.232497	2.498347	0.073374	4.236384
N(1)	1.275004	–2.139798	5.295609	1.221856	–2.155279	5.447972	1.370618	–2.180255	5.583725
B(1)	1.253976	0.010160	3.662441	1.254651	0.000067	3.660961	1.254592	–0.013849	3.659349
C(1)	1.225063	0.000000	2.081973	1.225305	0.000000	2.081564	1.225145	0.000000	2.081615
C(2)	0.000000	0.000000	1.388548	0.000000	0.000000	1.388673	0.000000	0.000000	1.388775
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.167353	–0.005894	–0.757861	1.168324	–0.003082	–0.756437	1.169562	–0.000801	–0.754838
C(5)	2.364051	–0.009353	–0.047278	2.365519	–0.005474	–0.046825	2.367160	0.000083	–0.045968
C(6)	2.421349	–0.006247	1.340200	2.422189	–0.004430	1.340748	2.422456	0.002004	1.341774
C(7)	–0.224948	–0.171363	5.641405	–0.211949	–0.107993	5.661413	–0.197461	–0.206236	5.672488
C(8)	0.074361	–1.652367	5.967477	0.036735	–1.576484	6.071028	0.144239	–1.633105	6.154964
C(9)	2.798840	–0.181899	5.589455	2.786161	–0.200607	5.605942	2.787453	–0.094641	5.619612
C(10)	2.503672	–1.661903	5.921400	2.464685	–1.652762	6.022198	2.578809	–1.545904	6.101256
C(11)	1.264508	–3.582576	4.875210	1.172920	–3.633442	5.188006	1.425690	–3.675248	5.471444
C(12)	1.323230	–4.529113	6.091911	1.182995	–4.448252	6.499215	1.484079	–4.354948	6.857645
C(13)	–0.007500	–3.871084	4.050670	–0.095295	–3.971980	4.373592	0.187508	–4.184007	4.697328
C(14)	2.463179	–3.854080	3.942918	2.380637	–4.039965	4.315397	2.666027	–4.084033	4.642822
H(2)	–0.945488	0.009698	1.926688	–0.945249	0.006497	1.927386	–0.945294	–0.001604	1.927733
H(4)	1.145803	–0.006424	–1.845225	1.146307	–0.003129	–1.843966	1.148018	–0.001436	–1.842621
H(6)	3.387844	–0.001735	1.839671	3.388568	–0.003306	1.840568	3.388305	0.003239	1.842962
H(7A)	–1.291320	0.022220	5.818583	–1.271678	0.123306	5.833549	–1.271029	–0.041309	5.835244
H(7B)	0.334676	0.514099	6.288470	0.367455	0.596443	6.269175	0.327197	0.562489	6.249953
H(8A)	0.131314	–1.755319	7.069517	0.077121	–1.609812	7.179218	0.162614	–1.605318	7.264821
H(8B)	–0.780962	–2.240664	5.633206	–0.836814	–2.153061	5.764062	–0.687997	–2.275891	5.865631
H(9A)	2.490582	–1.768990	7.024523	2.468277	–1.688588	7.131042	2.612402	–1.527029	7.211099
H(9B)	3.341753	–2.253755	5.550788	3.287572	–2.280797	5.677700	3.442044	–2.121990	5.764988
H(10A)	3.871495	0.006615	5.730416	3.863897	–0.035274	5.737276	3.849869	0.153658	5.745749
H(10B)	2.264769	0.503928	6.257208	2.274824	0.535149	6.237061	2.225057	0.626969	6.221873
H(12A)	1.298410	–5.578701	5.768276	1.152764	–5.525678	6.284409	1.541984	–5.446500	6.745878
H(12B)	0.468750	–4.366797	6.762974	0.312140	–4.209730	7.125237	0.589158	–4.128257	7.453453
H(12C)	2.246287	–4.379428	6.668152	2.091765	–4.251187	7.084514	2.366719	–4.031063	7.426250
H(13A)	–0.141527	–3.116831	3.265309	–0.185138	–3.308162	3.504176	0.054289	–3.616928	3.766863
H(13B)	–0.917599	–3.908344	4.660863	–1.018035	–3.906268	4.962743	–0.740227	–4.127943	5.279421
H(13C)	0.088110	–4.852864	3.570695	–0.027275	–5.005611	4.012161	0.333058	–5.240392	4.440024
H(14A)	3.429825	–3.821973	4.458574	3.331375	–4.031243	4.862067	3.611636	–3.939268	5.179350
H(14B)	2.483206	–3.131761	3.117344	2.469328	–3.376752	3.445350	2.704566	–3.519138	3.702403
H(14C)	2.368685	–4.860968	3.517561	2.236016	–5.065699	3.953955	2.601745	–5.152226	4.401760

Table 18S. Cartesian coordinates for **1** with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	$d_{B–N}$ = 3.0 Å (*a*)			$d_{B–N}$ = 3.1 Å (*b*)			$d_{B–N}$ = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
F(1)	–1.188457	–0.002651	–0.662540	–1.190093	0.003121	–0.661941	–1.190038	–0.000941	–0.662067
F(2)	3.528629	0.005866	–0.754377	3.527408	–0.012419	–0.759108	3.527562	0.003851	–0.758907
O(1)	0.029104	0.083048	4.280218	0.039922	0.060417	4.288196	0.041195	–0.010610	4.293993
O(2)	2.489467	–0.084295	4.245423	2.499092	0.000464	4.241719	2.494076	–0.010314	4.249365
N(1)	1.126282	–2.141820	5.771331	1.263151	–1.996279	6.015727	1.291461	–2.002024	6.151892
B(1)	1.249619	–0.015856	3.658261	1.257668	0.013238	3.655258	1.256346	–0.002751	3.653557
C(1)	1.225040	0.000000	2.081544	1.226353	0.000000	2.079434	1.226448	0.000000	2.079184
C(2)	0.000000	0.000000	1.388667	0.000000	0.000000	1.388670	0.000000	0.000000	1.388656
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.169305	0.003023	–0.754830	1.167716	–0.004005	–0.757227	1.167888	0.001782	–0.756998
C(5)	2.367040	0.003533	–0.045486	2.365661	–0.007724	–0.048565	2.365824	0.002334	–0.048278
C(6)	2.422766	–0.000027	1.342328	2.423348	–0.005665	1.338958	2.423692	0.001335	1.339255
C(7)	–0.211842	0.006230	5.682207	–0.187718	0.068785	5.696801	–0.176445	0.050589	5.704939
C(8)	–0.033436	–1.412308	6.268461	0.049553	–1.285971	6.398892	0.083626	–1.258850	6.487870
C(9)	2.759133	–0.209262	5.639315	2.772729	0.022279	5.641815	2.770191	0.026780	5.651015
C(10)	2.398805	–1.594060	6.223293	2.494981	–1.307859	6.380618	2.537261	–1.294312	6.418684
C(11)	1.014575	–3.636853	5.784973	1.255500	–3.477387	6.245842	1.281235	–3.455959	6.515014
C(12)	1.015310	–4.204621	7.221646	1.276381	–3.830537	7.749539	1.317153	–3.670508	8.044537
C(13)	–0.284102	–4.064061	5.065037	0.003857	–4.099002	5.589640	0.018588	–4.126896	5.933293
C(14)	2.183870	–4.250802	4.984000	2.479025	–4.112018	5.551286	2.494764	–4.159370	5.870595
H(2)	–0.945183	0.000832	1.927660	–0.944894	0.003800	1.927977	–0.944852	–0.001986	1.928064
H(4)	1.149266	0.004649	–1.842508	1.145796	–0.004082	–1.844669	1.146164	0.002778	–1.844445
H(6)	3.388759	–0.003852	1.843136	3.389849	–0.007281	1.838526	3.390127	0.000439	1.838997
H(7A)	–1.261647	0.294363	5.828928	–1.249629	0.316739	5.829123	–1.242783	0.282060	5.831798
H(7B)	0.390398	0.750198	6.213882	0.378607	0.878068	6 168571	0.372579	0.895104	6.132860
H(8A)	–0.027137	–1.296419	7.373867	0.001288	–1.071316	7.489434	0.038937	–0.967599	7.561554
H(8B)	–0.930257	–1.979153	6.014320	–0.805951	–1.920541	6.162907	–0.771706	–1.911002	6.304872
H(9A)	2.455263	–1.492242	7.328902	2.548850	–1.067847	7.465439	2.663905	–1.029563	7.492769
H(9B)	3.192168	–2.281986	5.927710	3.331815	–1.973430	6.163316	3.363105	–1.959165	6.159939
H(10A)	3.843412	–0.075853	5.754022	3.848582	0.223131	5.735606	3.842142	0.250923	5.737304
H(10B)	2.286241	0.607476	6.194442	2.259691	0.866410	6.113751	2.243699	0.865449	6.116907
H(12A)	1.952024	–3.970064	7.745645	1.251782	–4.920204	7.889368	2.224996	–3.240435	8.488585
H(12B)	0.908565	–5.298245	7.204012	0.406535	–3.409993	8.272307	1.307724	–4.743067	8.283394
H(12C)	0.181292	–3.798319	7.810226	2.185760	–3.454073	8.237541	0.445804	–3.214810	8.534012
H(13A)	–0.375034	–3.553318	4.097733	–0.105499	–3.747780	4.555432	–0.103331	–3.868975	4.873331
H(13B)	–1.186935	–3.865800	5.655437	–0.921560	–3.879819	6.135281	–0.898052	–3.853830	6.469603
H(13C)	–0.258061	–5.145732	4.883550	0.107926	–5.191144	5.574454	0.117014	–5.216652	6.014107
H(14A)	3.146168	–4.182973	5.505235	3.425229	–3.891069	6.059392	3.444814	–3.906102	6.355916
H(14B)	2.277951	–3.762477	4.005288	2.551009	–3.771490	4.510288	2.566008	–3.908748	4.804277
H(14C)	1.989229	–5.318188	4.821157	2.369897	–5.203783	5.551551	2.374659	–5.246046	5.962362

Table 19S. Cartesian coordinates for **1** with B-N distance constrained to 3.3 Å.

Atom	d_{B-N} = 3.3 Å		
	x / Å	*y* / Å	*z* / Å
F(1)	–1.190015	–0.001280	–0.662032
F(2)	3.527550	0.005691	–0.759615
O(1)	0.046935	–0.053229	4.301482
O(2)	2.490848	0.008035	4.256718
N(1)	1.326206	–1.921763	6.333069
B(1)	1.256489	0.000022	3.651301
C(1)	1.226843	0.000000	2.078550
C(2)	0.000000	0.000000	1.388623
C(3)	0.000000	0.000000	0.000000
C(4)	1.167874	0.002092	–0.757166
C(5)	2.365891	0.003504	–0.048668
C(6)	2.424205	0.003060	1.338773
C(7)	–0.167285	0.094917	5.708682
C(8)	0.136054	–1.130917	6.616670
C(9)	2.769291	0.086200	5.659285
C(10)	2.591338	–1.215055	6.473081
C(11)	1.291344	–3.334956	6.823830
C(12)	1.256839	–3.405969	8.367172
C(13)	0.055426	–4.050929	6.237546
C(14)	2.532420	–4.094933	6.310307
H(2)	–0.944730	–0.003045	1.928264
H(4)	1.145616	0.002775	–1.844571
H(6)	3.390627	0.003566	1.838551
H(7A)	–1.241269	0.295999	5.821465
H(7B)	0.348912	0.992063	6.065687
H(8A)	0.129717	–0.717669	7.650573
H(8B)	–0.725081	–1.798040	6.547310
H(9A)	2.809263	–0.915511	7.524544
H(9B)	3.393086	–1.889533	6.166340
H(10A)	3.834686	0.343490	5.732348
H(10B)	2.221652	0.920762	6.107408
H(12A)	0.343194	–2.949495	8.770873
H(12B)	2.120989	–2.888742	8.806174
H(12C)	1.285511	–4.450339	8.707279
H(13A)	–0.011106	–3.873824	5.156698
H(13B)	–0.886475	–3.736334	6.702694
H(13C)	0.142590	–5.131389	6.408485
H(14A)	2.667124	–3.940463	5.231653
H(14B)	3.453882	–3.801538	6.827702
H(14C)	2.396228	–5.168723	6.487633

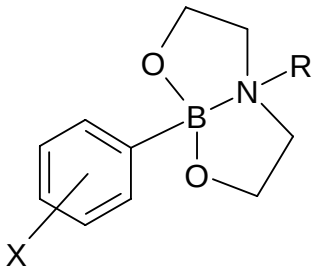


Table 20S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*).

Atom	$d_{B–N}$ = 1.5 Å (*a*)			$d_{B–N}$ = 1.6 Å (*b*)			$d_{B–N}$ = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.186229	0.000000	2.155051	1.196508	0.000000	2.137391	1.188600	0.000000	2.151238
C(2)	0.000000	0.000000	1.400509	0.000000	0.000000	1.398797	0.000000	0.000000	1.400032
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.223797	0.012498	–0.667631	1.206492	0.007633	–0.707791	1.223916	0.014121	–0.668441
C(5)	2.429433	0.036407	0.034352	2.395745	0.022568	0.021983	2.430800	0.037331	0.031635
C(6)	2.394216	0.029622	1.433279	2.406010	0.020588	1.416328	2.396902	0.029774	1.430580
H(2)	–0.960102	0.033309	1.917110	–0.951224	0.030390	1.930950	–0.957490	0.021256	1.921600
H(3)	–0.933958	0.005130	–0.559960	–0.941410	0.006398	–0.551673	–0.933784	0.002284	–0.560292
H(5)	3.377289	0.069112	–0.500952	1.220945	0.012535	–1.796019	3.378010	0.068291	–0.504763
H(6)	3.337868	0.072210	1.978342	3.352514	0.054616	1.952734	3.340086	0.066853	1.976836
B(1)	1.155887	0.010029	3.776742	1.192665	–0.021840	3.753455	1.163362	–0.025742	3.758130
O(1)	–0.101281	0.654613	4.279013	–0.037182	0.601274	4.302561	–0.102551	0.487327	4.304785
O(2)	2.368680	0.656175	4.292144	2.437603	0.528308	4.280586	2.379635	0.522029	4.328053
N(1)	1.135753	–1.319555	4.470861	1.146957	–1.470516	4.431133	1.173337	–1.579524	4.447812
C(7)	–0.884566	–0.226256	5.039703	–0.721096	–0.226247	5.206953	–0.702622	–0.349607	5.259991
C(8)	–0.321239	–1.613298	4.726396	–0.287914	–1.644997	4.842685	–0.240530	–1.763662	4.901781
C(9)	2.386792	0.388139	5.673470	2.518011	0.144011	5.631190	2.492280	0.077182	5.657352
C(10)	1.890999	–1.068392	5.783453	2.071335	–1.330182	5.634602	2.136983	–1.422119	5.603935
C(11)	1.789295	–2.442288	3.699907	1.601421	–2.592890	3.537693	1.608351	–2.667466	3.514561
H(11A)	1.294876	–2.474837	2.724655	0.976723	–2.549501	2.640074	0.946943	–2.617412	2.643107
H(11B)	2.824522	–2.126252	3.527784	2.623728	–2.345513	3.229471	2.612195	–2.395735	3.167624
C(12)	1.739334	–3.818398	4.361900	1.542687	–3.988935	4.156736	1.602957	–4.078076	4.104530
H(11A)	2.160582	–3.785548	5.377291	2.124691	–4.026757	5.089370	2.224421	–4.119769	5.011586
H(11B)	0.696489	–4.151415	4.464109	0.505619	–4.241766	4.421562	0.582820	–4.355537	4.408520
C(13)	2.514059	–4.853072	3.532675	2.083024	–5.047667	3.184991	2.121672	–5.108249	3.091725
H(13A)	2.101014	–4.883500	2.512836	1.505376	–5.008948	2.248719	1.505905	–5.062677	2.180309
H(13B)	3.560284	–4.525789	3.431314	3.120789	–4.797233	2.916443	3.143058	–4.833072	2.786497
C(14)	2.472963	–6.255661	4.145180	2.030563	–6.465173	3.761379	2.119525	–6.537321	3.641351
H(14A)	2.912112	–6.262285	5.153509	2.628598	–6.542808	4.681124	2.755154	–6.620535	4.535086
H(14B)	3.035516	–6.971210	3.530821	2.423925	–7.197876	3.044147	2.497505	–7.248730	2.894917
H(14C)	1.440010	–6.624268	4.226645	0.998943	–6.757215	4.006523	1.104251	–6.854035	3.921552
H(7A)	–0.816767	–0.002384	6.122188	–0.466070	0.010384	6.258325	–0.405310	–0.082333	6.291757
H(7B)	–1.948544	–0.162629	4.760131	–1.810341	–0.107302	5.099820	–1.798771	–0.269848	5.204287
H(8A)	–0.443051	–2.360712	5.516751	–0.388391	–2.382841	5.645979	–0.313685	–2.489504	5.720030
H(8B)	–0.736306	–2.001325	3.789271	–0.833615	–1.993308	3.958262	–0.809220	–2.132163	4.040154
H(9A)	1.723743	1.072924	6.227623	1.864481	0.762542	6.269498	1.812718	0.627152	6.330165
H(9B)	3.406845	0.494249	6.068372	3.550150	0.246637	5.993794	3.520052	0.225941	6.016628
H(10A)	1.226626	–1.254909	6.632761	1.554340	–1.644771	6.547308	1.692669	–1.805648	6.529287
H(10B)	2.726374	–1.770026	5.832021	2.929507	–1.987339	5.473744	3.031347	–2.009221	5.377850
Br(1)	1.250912	0.012971	–2.593101	4.071858	0.050979	–0.933420	1.249019	0.015096	–2.593556

Table 21S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	$d_{B–N}$ = 1.8 Å (*a*)			$d_{B–N}$ = 1.9 Å (*b*)			$d_{B–N}$ = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.189473	0.000000	2.149924	1.190510	0.000000	2.148755	1.191456	0.000000	2.147405
C(2)	0.000000	0.000000	1.399793	0.000000	0.000000	1.399253	0.000000	0.000000	1.399045
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.223896	0.003594	–0.668840	1.224472	0.000311	–0.668668	1.224408	0.003479	–0.668956
C(5)	2.431333	0.016082	0.030619	2.432067	0.008164	0.030091	2.432649	0.013467	0.029004
C(6)	2.398234	0.013619	1.429309	2.399417	0.006849	1.428982	2.400623	0.010700	1.427589
H(2)	–0.957616	0.025584	1.921063	–0.956433	0.024014	1.922365	–0.955723	0.016457	1.923389
H(3)	–0.934123	0.006992	–0.559626	–0.933725	0.007923	–0.560187	–0.933742	0.005319	–0.560143
H(5)	3.378219	0.034873	–0.506888	3.379007	0.021827	–0.507412	3.379131	0.028748	–0.509185
H(6)	3.341306	0.041301	1.975820	3.342224	0.028207	1.976089	3.343465	0.031670	1.974556
B(1)	1.168756	–0.015505	3.750117	1.167303	–0.023078	3.743549	1.170317	–0.036001	3.736546
O(1)	–0.070938	0.498202	4.317577	–0.067387	0.456729	4.313194	–0.079496	0.337184	4.322906
O(2)	2.413037	0.430245	4.327071	2.421788	0.335244	4.339759	2.412777	0.300235	4.348486
N(1)	1.118969	–1.665432	4.467936	1.074022	–1.777021	4.468105	1.136748	–1.899429	4.462155
C(7)	–0.642824	–0.288983	5.332510	–0.552804	–0.263316	5.420554	–0.500480	–0.400384	5.446680
C(8)	–0.272536	–1.736164	4.996283	–0.255596	–1.740228	5.130429	–0.169712	–1.872338	5.156174
C(9)	2.543625	–0.062994	5.637817	2.629418	–0.270536	5.592665	2.661595	–0.345832	5.575113
C(10)	2.156234	–1.554272	5.550501	2.221899	–1.746501	5.420161	2.311109	–1.832713	5.365870
C(11)	1.420694	–2.767285	3.508092	1.188078	–2.867940	3.463082	1.239530	–2.968160	3.439725
H(11A)	0.705563	–2.671861	2.683360	0.397804	–2.701562	2.721372	0.419738	–2.810102	2.727777
H(11B)	2.412910	–2.557640	3.090783	2.142011	–2.720461	2.941997	2.170577	–2.791707	2.886321
C(12)	1.370298	–4.179772	4.093629	1.099978	–4.289335	4.024394	1.205195	–4.401689	3.978208
H(11A)	2.078569	–4.272100	4.930970	1.876112	–4.442225	4.789864	2.015479	–4.547246	4.709297
H(11B)	0.369431	–4.381291	4.504144	0.131284	–4.435263	4.526183	0.261451	–4.576423	4.517426
C(13)	1.700526	–5.238740	3.033029	1.261941	–5.345301	2.923201	1.345922	–5.437455	2.855528
H(13A)	0.996640	–5.139704	2.192368	0.490668	–5.187442	2.153336	0.539153	–5.288142	2.120993
H(13B)	2.701586	–5.038651	2.620490	2.230826	–5.198817	2.421036	2.288770	–5.259242	2.315313
C(14)	1.648125	–6.668226	3.579083	1.170839	–6.779504	3.451739	1.313017	–6.881225	3.364558
H(14A)	2.368654	–6.808106	4.398154	1.955336	–6.979441	4.196286	2.131969	–7.071284	4.073800
H(14B)	1.886611	–7.400137	2.795677	1.287198	–7.509456	2.639305	1.414860	–7.596222	2.536924
H(14C)	0.647865	–6.908613	3.968196	0.198773	–6.965105	3.931720	0.366413	–7.099153	3.880514
H(7A)	–0.271023	–0.008028	6.334861	–0.085211	0.062806	6.365481	–0.015262	–0.053480	6.373798
H(7B)	–1.734881	–0.157071	5.338799	–1.635818	–0.099421	5.516688	–1.584325	–0.269542	5.575655
H(8A)	–0.354065	–2.424754	5.846817	–0.286032	–2.372251	6.028213	–0.170827	–2.490117	6.065942
H(8B)	–0.910382	–2.098742	4.181691	–0.989834	–2.118720	4.410032	–0.917631	–2.274176	4.462844
H(9A)	1.897118	0.482308	6.345198	2.046792	0.221568	6.388349	2.078312	0.097976	6.397410
H(9B)	3.583115	0.051683	5.975236	3.691812	–0.192732	5.863299	3.725238	–0.235293	5.828530
H(10A)	1.781575	–1.966140	6.495457	1.969862	–2.236169	6.370043	2.127332	–2.356179	6.314884
H(10B)	3.028177	–2.137732	5.239662	3.050872	–2.293301	4.958690	3.148378	–2.325121	4.859318
Br(1)	1.247393	0.001544	–2.593541	1.248031	–0.001608	–2.593089	1.247277	0.001440	–2.593026

Table 22S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	d_{B-N} = 2.1 Å (*a*)			d_{B-N} = 2.2 Å (*b*)			d_{B-N} = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.192625	0.000000	2.145879	1.193266	0.000000	2.144962	1.194051	0.000000	2.143885
C(2)	0.000000	0.000000	1.398757	0.000000	0.000000	1.398508	0.000000	0.000000	1.398254
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.224131	0.002941	–0.669747	1.224233	0.001826	–0.669695	1.224043	–0.001462	–0.670222
C(5)	2.432981	0.012132	0.027287	2.433480	0.008946	0.026813	2.433674	0.001468	0.025679
C(6)	2.401746	0.010557	1.425586	2.402775	0.008209	1.424882	2.403591	0.002478	1.423578
H(2)	–0.955103	0.012108	1.924004	–0.954757	0.009866	1.924237	–0.954479	0.010300	1.924308
H(3)	–0.933868	0.004482	–0.559917	–0.933881	0.004324	–0.559843	–0.934002	0.004981	–0.559611
H(5)	3.379033	0.025762	–0.511651	3.379350	0.019849	–0.512453	3.379377	0.007565	–0.513895
H(6)	3.344777	0.030904	1.972043	3.345813	0.025403	1.971266	3.346657	0.014990	1.969801
B(1)	1.175096	–0.034934	3.730681	1.176049	–0.030733	3.726449	1.178489	–0.019358	3.723141
O(1)	–0.081995	0.247711	4.323895	–0.081866	0.192303	4.322331	–0.074603	0.180908	4.317671
O(2)	2.410155	0.280399	4.349876	2.409130	0.245864	4.348061	2.416444	0.201764	4.341297
N(1)	1.194103	–1.992047	4.491831	1.213770	–2.068729	4.554189	1.187650	–2.118944	4.662104
C(7)	–0.427998	–0.464864	5.490186	–0.414314	–0.504854	5.503626	–0.389398	–0.449921	5.542001
C(8)	–0.074680	–1.942632	5.240970	–0.055129	–1.987726	5.289515	–0.061100	–1.950842	5.409433
C(9)	2.713776	–0.392733	5.550757	2.707216	–0.403546	5.565057	2.714960	–0.420486	5.574042
C(10)	2.408065	–1.886648	5.323724	2.423085	–1.907928	5.374036	2.415437	–1.927363	5.438150
C(11)	1.252459	–3.063131	3.474796	1.282746	–3.166398	3.572247	1.209109	–3.275783	3.752499
H(11A)	0.394399	–2.918386	2.805456	0.424407	–3.050692	2.896776	0.337027	–3.184777	3.090152
H(11B)	2.150931	–2.882437	2.870327	2.181066	–2.998381	2.962996	2.096372	–3.169656	3.112968
C(12)	1.261935	–4.495638	4.019665	1.303123	–4.584507	4.156435	1.212286	–4.655846	4.424199
H(11A)	2.111044	–4.626836	4.708435	2.153515	–4.688823	4.848490	2.084573	–4.740706	5.091334
H(11B)	0.349617	–4.676467	4.609044	0.392435	–4.754123	4.751947	0.320114	–4.758888	5.061830
C(13)	1.355613	–5.537006	2.897529	1.403348	–5.657253	3.065296	1.240888	–5.799903	3.404038
H(13A)	0.512288	–5.398811	2.202812	0.558482	–5.545055	2.367590	0.370993	–5.710165	2.734286
H(13B)	2.269087	–5.353936	2.310401	2.315050	–5.484921	2.472002	2.131414	–5.693088	2.764618
C(14)	1.360579	–6.978233	3.414912	1.418777	–7.083408	3.622897	1.243171	–7.186648	4.053793
H(14A)	2.215015	–7.157013	4.084149	2.276079	–7.238128	4.294459	2.122004	–7.320264	4.701635
H(14B)	1.427954	–7.697411	2.587293	1.488326	–7.825387	2.815740	1.262953	–7.981520	3.295640
H(14C)	0.442510	–7.201107	3.978202	0.503662	–7.295873	4.195001	0.346232	–7.336731	4.672583
H(7A)	0.086473	–0.069626	6.380004	0.098148	–0.085864	6.382588	0.144421	0.011714	6.385003
H(7B)	–1.508137	–0.356113	5.661362	–1.494626	–0.399557	5.674762	–1.464407	–0.317597	5.726160
H(8A)	–0.028765	–2.514038	6.180977	–0.024495	–2.529898	6.248935	–0.030744	–2.427894	6.404249
H(8B)	–0.850250	–2.388165	4.607221	–0.829248	–2.448231	4.664369	–0.859751	–2.430632	4.831185
H(9A)	2.146408	0.013943	6.402200	2.131344	0.017455	6.402654	2.154961	0.034120	6.403820
H(9B)	3.781149	–0.253180	5.771943	3.771435	–0.246857	5.789063	3.783235	–0.269392	5.781433
H(10A)	2.309251	–2.430081	6.275931	2.345102	–2.421886	6.345979	2.369750	–2.402205	6.433431
H(10B)	3.235696	–2.333330	4.760968	3.259429	–2.353208	4.822735	3.235794	–2.394718	4.880485
Br(1)	1.245526	–0.000019	–2.593373	1.245313	–0.001006	–2.592981	1.244302	–0.004113	–2.593309

Table 23S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	d_{B-N} = 2.4 Å (*a*)			d_{B-N} = 2.5 Å (*b*)			d_{B-N} = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.194473	0.000000	2.143228	1.194672	0.000000	2.142652	1.194885	0.000000	2.142250
C(2)	0.000000	0.000000	1.398030	0.000000	0.000000	1.397853	0.000000	0.000000	1.397818
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.224022	0.002863	–0.670463	1.224136	–0.003177	–0.670300	1.224094	0.000552	–0.670345
C(5)	2.433844	0.008663	0.025221	2.434102	–0.003533	0.025196	2.434097	0.002442	0.025059
C(6)	2.404098	0.006891	1.422925	2.404508	–0.001532	1.422751	2.404857	0.001900	1.422574
H(2)	–0.954574	0.004917	1.923942	–0.954550	0.007187	1.923719	–0.954517	0.002803	1.923713
H(3)	–0.933997	0.002061	–0.559614	–0.933973	0.004185	–0.559626	–0.934111	0.001667	–0.559385
H(5)	3.379373	0.017286	–0.514589	3.379618	–0.002007	–0.514686	3.379629	0.005985	–0.514777
H(6)	3.347333	0.017548	1.968840	3.347801	0.004634	1.968581	3.348255	0.006156	1.968171
B(1)	1.179388	–0.031616	3.720591	1.179150	–0.006446	3.719483	1.179129	–0.016422	3.718485
O(1)	–0.071958	0.128405	4.315505	–0.070349	0.144977	4.307088	–0.069783	0.097147	4.304756
O(2)	2.418059	0.139949	4.338567	2.418153	0.138380	4.330782	2.416588	0.094846	4.329176
N(1)	1.179700	–2.196916	4.755712	1.161155	–2.175522	4.962375	1.162739	–2.211732	5.111447
C(7)	–0.378073	–0.463311	5.563033	–0.373384	–0.342517	5.600902	–0.366326	–0.325863	5.624004
C(8)	–0.064261	–1.971845	5.488353	–0.080014	–1.854859	5.659470	–0.078864	–1.833081	5.772932
C(9)	2.708717	–0.450906	5.590223	2.694960	–0.352472	5.629328	2.686966	–0.330823	5.653349
C(10)	2.409881	–1.962029	5.508244	2.392386	–1.863144	5.680429	2.394100	–1.837548	5.794116
C(11)	1.191299	–3.397322	3.908434	1.162665	–3.476505	4.280772	1.165328	–3.559462	4.532252
H(11A)	0.316610	–3.337247	3.245376	0.287187	–3.498802	3.615918	0.290015	–3.633540	3.870383
H(11B)	2.076168	–3.330321	3.259702	2.047876	–3.503947	3.629107	2.050829	–3.636056	3.884344
C(12)	1.190645	–4.744211	4.646395	1.152287	–4.717384	5.186932	1.155879	–4.731761	5.526244
H(11A)	2.068270	–4.802601	5.309490	2.031219	–4.697903	5.850482	2.032494	–4.661838	6.189521
H(11B)	0.303397	–4.809264	5.295921	0.266338	–4.690404	5.840819	0.267637	–4.660798	6.173773
C(13)	1.202485	–5.936240	3.682476	1.151244	–6.024059	4.385031	1.161331	–6.092555	4.820289
H(13A)	0.325524	–5.873891	3.018772	0.273865	–6.039193	3.719054	0.286433	–6.157838	4.153927
H(13B)	2.086221	–5.864736	3.028735	2.034732	–6.045568	3.727336	2.047218	–6.158439	4.168668
C(14)	1.205464	–7.290623	4.397306	1.142626	–7.274654	5.269002	1.152800	–7.277599	5.790276
H(14A)	2.090549	–7.397512	5.041609	2.027030	–7.304470	5.922370	2.035661	–7.259761	6.446228
H(14B)	1.213585	–8.120885	3.677779	1.143035	–8.191444	4.663463	1.156203	–8.234918	5.251019
H(14C)	0.314567	–7.406576	5.031968	0.251124	–7.298996	5.912886	0.259887	–7.258332	6.432445
H(7A)	0.161822	0.026731	6.384946	0.171540	0.212104	6.376185	0.178593	0.271787	6.365839
H(7B)	–1.451119	–0.317957	5.748203	–1.444442	–0.171847	5.775250	–1.436998	–0.145444	5.790396
H(8A)	–0.048828	–2.402316	6.505997	–0.084618	–2.187979	6.714481	–0.099311	–2.096436	6.848589
H(8B)	–0.869964	–2.464102	4.930334	–0.891828	–2.380810	5.142007	–0.890723	–2.385616	5.283518
H(9A)	2.150865	0.032940	6.403868	2.138944	0.203944	6.395461	2.128757	0.266351	6.385673
H(9B)	3.777175	–0.296154	5.793463	3.763558	–0.187780	5.823403	3.754521	–0.152486	5.840675
H(10A)	2.382393	–2.394320	6.524887	2.377750	–2.198031	6.734806	2.396449	–2.103244	6.869419
H(10B)	3.228664	–2.446026	4.962139	3.209652	–2.392813	5.175478	3.212707	–2.390667	5.316707
Br(1)	1.244084	0.001197	–2.593236	1.244266	–0.005440	–2.592861	1.244037	–0.000481	–2.592709

Table 24S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	$d_{B–N}$ = 2.7 Å (*a*)			$d_{B–N}$ = 2.8 Å (*b*)			$d_{B–N}$ = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.194384	0.000000	2.142683	1.195386	0.000000	2.141229	1.195608	0.000000	2.140767
C(2)	0.000000	0.000000	1.397771	0.000000	0.000000	1.397743	0.000000	0.000000	1.397707
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.224601	–0.003995	–0.669423	1.223921	–0.005625	–0.670614	1.224006	0.005155	–0.670503
C(5)	2.434296	–0.007402	0.026683	2.434129	–0.009419	0.024464	2.434278	0.009836	0.024467
C(6)	2.404945	–0.006217	1.424217	2.405451	–0.005734	1.421889	2.405883	0.006854	1.421873
H(2)	–0.954602	0.006529	1.923464	–0.954463	0.005180	1.923733	–0.954332	–0.005405	1.923948
H(3)	–0.933991	0.003212	–0.559507	–0.934268	0.003678	–0.559095	–0.934322	–0.001859	–0.558999
H(5)	3.380097	–0.009307	–0.512688	3.379571	–0.012932	–0.515491	3.379706	0.014929	–0.515503
H(6)	3.348167	–0.006836	1.970171	3.349027	–0.004543	1.967184	3.349410	0.008311	1.967260
B(1)	1.174100	0.000754	3.718557	1.180619	0.014881	3.716457	1.180669	–0.023185	3.714831
O(1)	–0.070468	0.154603	4.296135	–0.065504	0.084809	4.300886	–0.063125	–0.022208	4.305282
O(2)	2.410681	0.037095	4.331571	2.414905	0.105436	4.322755	2.410760	0.047733	4.329051
N(1)	1.049594	–2.161878	5.330240	1.182668	–2.101750	5.549452	1.228843	–2.189895	5.641757
C(7)	–0.384294	–0.151809	5.644881	–0.350063	–0.131828	5.674985	–0.344222	–0.233809	5.682864
C(8)	–0.176438	–1.651749	5.926151	–0.065692	–1.586935	6.090390	–0.036965	–1.673969	6.135129
C(9)	2.653252	–0.291099	5.690048	2.677575	–0.105052	5.702127	2.668284	–0.135742	5.715288
C(10)	2.294987	–1.763701	5.970280	2.411412	–1.564719	6.113416	2.443233	–1.590266	6.169562
C(11)	0.989733	–3.570840	4.928990	1.197779	–3.553840	5.346336	1.279754	–3.647532	5.510595
H(11A)	0.126161	–3.684391	4.256745	0.324194	–3.808515	4.727951	0.417618	–3.953498	4.898958
H(11B)	1.883709	–3.778693	4.322996	2.086285	–3.792628	4.743030	2.178768	–3.894676	4.926153
C(12)	0.889563	–4.603525	6.063974	1.194513	–4.423707	6.614820	1.285921	–4.458070	6.818215
H(11A)	1.753929	–4.498587	6.738721	2.070422	–4.176438	7.235063	2.149932	–4.162190	7.433965
H(11B)	–0.006879	–4.399152	6.670404	0.305619	–4.189257	7.221428	0.386134	–4.218475	7.406512
C(13)	0.827999	–6.042383	5.538769	1.207953	–5.923139	6.295987	1.337957	–5.969177	6.566171
H(13A)	–0.025520	–6.139245	4.848833	0.334399	–6.168543	5.671109	0.478179	–6.261745	5.942398
H(13B)	1.729730	–6.248315	4.940300	2.095534	–6.155823	5.686169	2.238138	–6.206977	5.977102
C(14)	0.703931	–7.087654	6.651191	1.203669	–6.806233	7.547403	1.338350	–6.798234	7.853920
H(14A)	1.558821	–7.036635	7.341607	2.084242	–6.606963	8.175763	2.206457	–6.552732	8.483352
H(14B)	0.666607	–8.105938	6.240048	1.214921	–7.872962	7.284129	1.376808	–7.874599	7.636296
H(14C)	–0.211079	–6.931116	7.241246	0.308467	–6.621643	8.159350	0.431822	–6.608805	8.447496
H(7A)	0.186692	0.479172	6.336985	0.187693	0.586726	6.304802	0.170970	0.508077	6.303857
H(7B)	–1.444991	0.093470	5.791190	–1.421746	0.066880	5.811736	–1.421029	–0.058845	5.812141
H(8A)	–0.233244	–1.812581	7.021647	–0.123925	–1.640945	7.197292	–0.123701	–1.695626	7.242407
H(8B)	–1.010454	–2.201435	5.471423	–0.871341	–2.216956	5.691685	–0.823477	–2.328884	5.737633
H(9A)	2.124730	0.395311	6.362852	2.115413	0.604253	6.321064	2.088602	0.574569	6.315982
H(9B)	3.727669	–0.147636	5.867854	3.742803	0.112854	5.858702	3.727328	0.110827	5.871749
H(10A)	2.295177	–1.920391	7.067937	2.449719	–1.617318	7.221240	2.497587	–1.601776	7.278992
H(10B)	3.090047	–2.392896	5.550463	3.235478	–2.180497	5.730373	3.282459	–2.194097	5.800030
Br(1)	1.245674	–0.004427	–2.591769	1.243265	–0.007252	–2.592798	1.243265	0.005619	–2.592519

Table 25S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	d_{B-N} = 3.0 Å (*a*)			d_{B-N} = 3.1 Å (*b*)			d_{B-N} = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.194567	0.000000	2.141925	1.196032	0.000000	2.139935	1.196472	0.000000	2.139208
C(2)	0.000000	0.000000	1.397543	0.000000	0.000000	1.397609	0.000000	0.000000	1.397553
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.225042	–0.004199	–0.668902	1.224079	–0.003674	–0.670503	1.224002	0.003170	–0.670745
C(5)	2.434763	–0.009436	0.027374	2.434584	–0.006725	0.024227	2.434729	0.005439	0.023699
C(6)	2.405721	–0.008887	1.424823	2.406593	–0.003974	1.421519	2.407119	0.003752	1.420911
H(2)	–0.954703	0.005545	1.923088	–0.954283	0.002499	1.924026	–0.954123	–0.003218	1.924277
H(3)	–0.933826	0.002247	–0.559689	–0.934274	0.002162	–0.559015	–0.934319	–0.001401	–0.558938
H(5)	3.380454	–0.013311	–0.512120	3.379827	–0.009695	–0.516035	3.379825	0.008143	–0.516810
H(6)	3.348997	–0.014174	1.970766	3.350188	–0.004490	1.966859	3.350731	0.003540	1.966239
B(1)	1.172110	0.006799	3.715212	1.180932	0.015703	3.712086	1.182219	–0.006808	3.709940
O(1)	–0.066315	0.140220	4.299009	–0.056868	0.034341	4.311770	–0.051679	–0.019098	4.318959
O(2)	2.395035	–0.062384	4.341450	2.407045	0.039795	4.334922	2.405468	–0.009544	4.340194
N(1)	0.956135	–2.038516	5.899254	1.164450	–1.962780	6.098576	1.168098	–1.986110	6.224331
C(7)	–0.360555	0.101055	5.690363	–0.333089	0.044225	5.709588	–0.324625	0.017358	5.719224
C(8)	–0.230395	–1.305242	6.305688	–0.088256	–1.300304	6.419910	–0.087741	–1.302373	6.480558
C(9)	2.631811	–0.161664	5.741834	2.656386	0.053392	5.737831	2.653773	0.028831	5.744936
C(10)	2.244795	–1.529397	6.336023	2.405114	–1.291282	6.446192	2.414084	–1.292745	6.501944
C(11)	0.822244	–3.494080	5.982412	1.166108	–3.403534	6.350772	1.170738	–3.402290	6.584055
H(11A)	–0.076791	–3.776044	5.413706	0.295200	–3.830780	5.830567	0.294710	–3.867293	6.106337
H(11B)	1.678467	–3.934902	5.450002	2.058132	–3.823226	5.861250	2.058404	–3.860261	6.121224
C(12)	0.737465	–4.098881	7.394794	1.142559	–3.849703	7.823748	1.159251	–3.733112	8.087656
H(11A)	1.635898	–3.825014	7.970096	2.013820	–3.432243	8.352642	2.035726	–3.277574	8.574837
H(11B)	–0.121478	–3.666515	7.931741	0.248905	–3.441786	8.321736	0.270806	–3.284724	8.559547
C(13)	0.599981	–5.625448	7.368591	1.147979	–5.375825	7.967376	1.163110	–5.243108	8.352310
H(13A)	–0.298302	–5.898173	6.791714	0.279319	–5.792461	7.432674	0.288508	–5.699140	7.861176
H(13B)	1.455460	–6.056899	6.824579	2.040052	–5.783512	7.465366	2.049650	–5.692034	7.876248
C(14)	0.517022	–6.249363	8.764760	1.123161	–5.847491	9.424323	1.151785	–5.596174	9.842440
H(14A)	1.419948	–6.027450	9.352561	1.999411	–5.476466	9.976271	2.033885	–5.183821	10.354208
H(14B)	0.414533	–7.341988	8.708954	1.126587	–6.944396	9.489854	1.154473	–6.684287	9.995682
H(14C)	–0.347700	–5.860090	9.322219	0.223960	–5.483956	9.943352	0.258144	–5.190345	10.339190
H(7A)	0.239533	0.840201	6.232986	0.203003	0.863942	6.200471	0.207654	0.851836	6.188369
H(7B)	–1.408642	0.413855	5.793383	–1.403626	0.271351	5.806986	–1.395712	0.244641	5.810711
H(8A)	–0.320097	–1.180887	7.406504	–0.219273	–1.100371	7.506279	–0.247867	–1.053884	7.553832
H(8B)	–1.094596	–1.898974	5.979236	–0.890500	–1.990425	6.125316	–0.884907	–2.004122	6.198720
H(9A)	2.148729	0.665036	6.274904	2.106601	0.871273	6.216519	2.106954	0.858992	6.204929
H(9B)	3.713911	–0.032979	5.881134	3.723591	0.286657	5.855203	3.721296	0.264498	5.855026
H(10A)	2.333565	–1.433559	7.440176	2.510462	–1.087788	7.534756	2.553911	–1.043163	7.577767
H(10B)	2.997741	–2.262691	6.017518	3.218168	–1.976854	6.171416	3.221270	–1.988311	6.233647
Br(1)	1.246544	–0.003198	–2.590886	1.242984	–0.004008	–2.592232	1.242470	0.004397	–2.592226

Table 26S. Cartesian coordinates for azaester derivative (X = 4-Br, R = Bu) with B-N distance constrained to 3.3 Å (*a*).

Atom	d_{B-N} = 3.3 Å (*a*)		
	x / Å	*y* / Å	*z* / Å
C(1)	1.196721	0.000000	2.138727
C(2)	0.000000	0.000000	1.397496
C(3)	0.000000	0.000000	0.000000
C(4)	1.224101	0.007926	–0.670629
C(5)	2.434983	0.013768	0.023603
C(6)	2.407554	0.008852	1.420768
H(2)	–0.954018	–0.007050	1.924405
H(3)	–0.934218	–0.003868	–0.559040
H(5)	3.379919	0.020347	–0.517098
H(6)	3.351125	0.008448	1.966202
B(1)	1.182795	–0.023261	3.707823
O(1)	–0.047720	–0.052410	4.325062
O(2)	2.402335	–0.057969	4.346063
N(1)	1.155418	–1.986220	6.360377
C(7)	–0.320592	0.013205	5.726342
C(8)	–0.102479	–1.280807	6.538686
C(9)	2.646891	0.011206	5.752415
C(10)	2.408997	–1.279920	6.564344
C(11)	1.151267	–3.362830	6.847262
H(11A)	0.273687	–3.866143	6.412585
H(11B)	2.037907	–3.864895	6.429842
C(12)	1.136426	–3.557434	8.374950
H(11A)	2.007823	–3.053948	8.821967
H(11B)	0.243234	–3.074777	8.801598
C(13)	1.149311	–5.038082	8.769592
H(13A)	0.283346	–5.542250	8.311217
H(13B)	2.044057	–5.518151	8.341735
C(14)	1.126253	–5.263503	10.284333
H(14A)	1.997732	–4.798132	10.768155
H(14B)	1.140569	–6.334653	10.529327
H(14C)	0.222483	–4.829097	10.736644
H(7A)	0.212027	0.858134	6.175444
H(7B)	–1.391088	0.246664	5.808893
H(8A)	–0.299188	–0.983982	7.594070
H(8B)	–0.894783	–1.990902	6.262372
H(9A)	2.107595	0.859192	6.187612
H(9B)	3.716060	0.242363	5.856053
H(10A)	2.581719	–0.978937	7.622702
H(10B)	3.206952	–1.991627	6.309329
Br(1)	1.242406	0.010364	–2.592028

Table 27S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*).

Atom	d_{B-N} = 1.5 Å (*a*)			d_{B-N} = 1.6 Å (*b*)			d_{B-N} = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.212955	0.000000	2.109568	1.212509	0.000000	2.109133	1.215965	0.000000	2.105162
C(2)	0.000000	0.000000	1.394616	0.000000	0.000000	1.395065	0.000000	0.000000	1.394311
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.183124	0.027761	–0.737564	1.184635	0.019489	–0.736049	1.183850	0.006130	–0.738333
C(5)	2.392913	0.058528	–0.035511	2.395391	0.043814	–0.034119	2.395760	0.017624	–0.040050
C(6)	2.404217	0.042726	1.363045	2.405276	0.036134	1.363768	2.407583	0.014429	1.358527
H(2)	–0.946754	0.026873	1.931589	–0.943305	0.020413	1.937384	–0.942972	0.019969	1.937812
H(3)	1.161886	0.036383	–1.825630	1.164902	0.026746	–1.824240	1.160928	0.010807	–1.826439
H(5)	3.330329	0.100299	–0.592604	3.332821	0.079348	–0.591527	3.332513	0.037972	–0.599237
H(6)	3.356157	0.083863	1.892066	3.358459	0.083457	1.891122	3.360867	0.049768	1.885927
B(1)	1.221914	–0.028778	3.735323	1.214672	0.011176	3.727541	1.233862	–0.025149	3.714142
O(1)	0.011391	0.696605	4.235187	–0.075227	0.528722	4.236750	0.015482	0.525547	4.275167
O(2)	2.493206	0.541134	4.223266	2.407624	0.704092	4.221873	2.498541	0.492280	4.256509
N(1)	1.129694	–1.367093	4.406447	1.311455	–1.414287	4.447740	1.226566	–1.577508	4.407056
C(7)	–0.612519	–0.016225	5.273963	–0.579929	–0.231988	5.305143	–0.135494	0.062751	5.592977
C(8)	–0.293284	–1.470014	4.932865	–0.060777	–1.647649	5.031985	0.214855	–1.441053	5.523725
C(9)	2.653215	0.142493	5.559349	2.641671	0.307006	5.548234	3.066236	–0.311205	5.258387
C(10)	2.141519	–1.318265	5.560307	2.360833	–1.216159	5.533739	2.624339	–1.738284	4.918033
C(11)	1.440368	–2.544440	3.508125	1.703029	–2.545810	3.534543	0.850359	–2.678286	3.461788
H(11A)	0.757522	–2.470637	2.656914	0.987177	–2.541318	2.706021	–0.143625	–2.427687	3.073549
H(11B)	2.451155	–2.375460	3.119695	2.677376	–2.276928	3.111462	1.545164	–2.619968	2.617205
C(12)	1.328486	–3.923294	4.156862	1.762296	–3.928662	4.183685	0.857320	–4.085233	4.060176
H(11A)	1.997735	–4.004136	5.025595	2.447748	–3.925055	5.044151	1.874597	–4.352302	4.383178
H(11B)	0.307052	–4.089066	4.527547	0.771912	–4.208945	4.569909	0.221074	–4.126684	4.957005
C(13)	1.678478	–5.029112	3.150631	2.223219	–4.992446	3.177241	0.364516	–5.125072	3.044254
H(13A)	1.034276	–4.930047	2.263774	1.534538	–4.998799	2.318457	–0.659343	–4.868407	2.731671
H(13B)	2.711300	–4.883736	2.798459	3.209900	–4.711317	2.777986	0.985588	–5.068011	2.136975
C(14)	1.530352	–6.434665	3.738755	2.296717	–6.395626	3.785486	0.389491	–6.553942	3.593474
H(14A)	2.179629	–6.569798	4.616138	3.009698	–6.429610	4.622229	1.408295	–6.851769	3.881547
H(14B)	1.801535	–7.201734	3.001190	2.621115	–7.133964	3.039924	0.030738	–7.272020	2.843936
H(14C)	0.494660	–6.626083	4.055185	1.316129	–6.715089	4.167535	–0.251579	–6.649689	4.482080
H(7A)	–0.216615	0.250395	6.271910	–0.233949	0.138992	6.287933	0.528863	0.597016	6.293330
H(7B)	–1.696445	0.174365	5.284486	–1.679874	–0.202692	5.309449	–1.171467	0.212721	5.927357
H(8A)	–0.361477	–2.200703	5.744895	–0.014330	–2.317709	5.896622	0.612952	–1.850393	6.459055
H(8B)	–0.919314	–1.792226	4.093889	–0.669544	–2.110580	4.247365	–0.673196	–2.013228	5.241197
H(9A)	2.066812	0.772801	6.249833	1.982096	0.833373	6.259666	2.728850	–0.018105	6.270346
H(9B)	3.709949	0.202847	5.857981	3.682645	0.520110	5.830657	4.162958	–0.225483	5.240041
H(10A)	1.670017	–1.653425	6.489298	2.010610	–1.632553	6.483822	2.670462	–2.445801	5.753634
H(10B)	2.960130	–1.997538	5.311857	3.262836	–1.751426	5.224607	3.227986	–2.121737	4.087253
Br(1)	–1.685198	–0.021210	–0.941815	–1.683253	–0.012186	–0.943335	–1.683557	–0.004170	–0.942670

Table 28S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	d_{B-N} = 1.8 Å (*a*)			d_{B-N} = 1.9 Å (*b*)			d_{B-N} = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.213887	0.000000	2.107448	1.214949	0.000000	2.105917	1.216137	0.000000	2.104260
C(2)	0.000000	0.000000	1.394169	0.000000	0.000000	1.394150	0.000000	0.000000	1.394104
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.186059	0.003768	–0.734966	1.185963	0.006488	–0.735150	1.185716	0.008146	–0.735576
C(5)	2.397078	0.010891	–0.034091	2.397688	0.015303	–0.035412	2.398164	0.018026	–0.037123
C(6)	2.407841	0.007324	1.364359	2.409173	0.010284	1.362727	2.410463	0.012362	1.360702
H(2)	–0.943301	0.026783	1.936599	–0.942535	0.019950	1.937953	–0.941814	0.014213	1.939087
H(3)	1.166264	0.008562	–1.823176	1.165485	0.011117	–1.823361	1.164383	0.012310	–1.823786
H(5)	3.334478	0.026880	–0.592308	3.334609	0.032463	–0.594295	3.334581	0.035414	–0.596753
H(6)	3.359603	0.032312	1.894821	3.361006	0.033585	1.893045	3.362416	0.034006	1.890715
B(1)	1.215247	–0.012585	3.711282	1.219202	–0.027166	3.703278	1.224472	–0.037076	3.695983
O(1)	–0.001412	0.545180	4.264245	–0.010119	0.437433	4.284725	–0.014368	0.332177	4.299003
O(2)	2.488047	0.398378	4.268747	2.482231	0.345469	4.279977	2.478917	0.303164	4.284725
N(1)	1.116337	–1.657246	4.436061	1.155119	–1.784330	4.423188	1.206478	–1.901098	4.420619
C(7)	–0.393782	–0.065965	5.467979	–0.381522	–0.219778	5.472237	–0.354269	–0.356678	5.479708
C(8)	–0.126355	–1.564374	5.267438	–0.088335	–1.710878	5.239782	–0.033320	–1.841160	5.229833
C(9)	2.810648	–0.265928	5.465029	2.804731	–0.338144	5.466962	2.811741	–0.392770	5.463325
C(10)	2.369497	–1.720479	5.252815	2.404947	–1.803620	5.232253	2.456124	–1.869656	5.215652
C(11)	1.041032	–2.767286	3.439174	1.111343	–2.868167	3.404447	1.187890	–2.968916	3.391751
H(11A)	0.165509	–2.568405	2.810683	0.234487	–2.676512	2.774468	0.306278	–2.791341	2.763151
H(11B)	1.920764	–2.670923	2.792272	1.991777	–2.737454	2.763652	2.064550	–2.810366	2.751087
C(12)	0.962904	–4.174916	4.032711	1.063539	–4.292453	3.962802	1.175250	–4.402955	3.929328
H(11A)	1.851992	–4.376541	4.648883	1.952041	–4.484441	4.583378	2.063677	–4.576670	4.555840
H(11B)	0.091738	–4.256004	4.700273	0.188862	–4.409209	4.620783	0.298789	–4.551713	4.578698
C(13)	0.856808	–5.242328	2.935193	0.993760	–5.338385	2.842311	1.145037	–5.436869	2.796270
H(13A)	–0.032999	–5.040255	2.319336	0.105539	–5.144075	2.221508	0.258049	–5.259292	2.168521
H(13B)	1.722921	–5.156566	2.260690	1.864263	–5.217907	2.178752	2.018563	–5.284346	2.143287
C(14)	0.781442	–6.666447	3.492530	0.946505	–6.775639	3.368276	1.131900	–6.881351	3.304164
H(14A)	1.673768	–6.907999	4.088461	1.838665	–7.009061	3.967733	2.025488	–7.098401	3.907688
H(14B)	0.710127	–7.405064	2.682810	0.899764	–7.498587	2.542702	1.110208	–7.595484	2.469839
H(14C)	–0.098413	–6.794024	4.140011	0.064055	–6.936991	4.004662	0.249506	–7.073381	3.932111
H(7A)	0.157510	0.332678	6.336753	0.163160	0.169364	6.348453	0.188650	0.034527	6.355063
H(7B)	–1.463673	0.116282	5.644118	–1.454038	–0.062349	5.654941	–1.428060	–0.225083	5.673634
H(8A)	–0.024575	–2.125785	6.204343	0.004023	–2.282066	6.173125	0.056830	–2.412578	6.164785
H(8B)	–0.944031	–2.000763	4.683973	–0.898926	–2.145843	4.644900	–0.839222	–2.282468	4.632736
H(9A)	2.312575	0.186236	6.339731	2.288323	0.087743	6.343140	2.283407	0.009959	6.342347
H(9B)	3.895153	–0.211286	5.638090	3.885650	–0.258303	5.650750	3.889500	–0.284858	5.650011
H(10A)	2.212791	–2.278587	6.183988	2.277122	–2.370899	6.163741	2.364227	–2.440617	6.150732
H(10B)	3.124984	–2.240828	4.654273	3.179355	–2.292251	4.630702	3.245582	–2.327051	4.608653
Br(1)	–1.681841	–0.000834	–0.944474	–1.681559	–0.004046	–0.944269	–1.681403	–0.006242	–0.943905

Table 29S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	d_{B-N} = 2.1 Å (*a*)			d_{B-N} = 2.2 Å (*b*)			d_{B-N} = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.212333	0.000000	2.111614	1.217585	0.000000	2.102388	1.217842	0.000000	2.101990
C(2)	0.000000	0.000000	1.396417	0.000000	0.000000	1.393761	0.000000	0.000000	1.393592
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.194462	0.006986	–0.725285	1.185983	0.004190	–0.735464	1.186302	0.001527	–0.735062
C(5)	2.403814	0.016307	–0.021806	2.399193	0.008978	–0.038373	2.399663	0.003865	–0.038176
C(6)	2.410673	0.010298	1.375043	2.412530	0.004974	1.359021	2.413208	0.002179	1.359044
H(2)	–0.943844	0.014637	1.937934	–0.941280	0.012119	1.939390	–0.941073	0.010716	1.939412
H(3)	1.179518	0.011372	–1.813636	1.164070	0.007000	–1.823694	1.164550	0.003385	–1.823319
H(5)	3.342151	0.031111	–0.577955	3.335182	0.019727	–0.598733	3.335585	0.011007	–0.598657
H(6)	3.356691	0.023688	1.907845	3.364440	0.018033	1.888945	3.365144	0.012929	1.888874
B(1)	1.213080	–0.063224	3.696743	1.228255	–0.032844	3.686312	1.227879	–0.021427	3.683693
O(1)	–0.010270	0.283742	4.327483	–0.003886	0.253396	4.303170	–0.008079	0.212006	4.298019
O(2)	2.470425	0.143363	4.307862	2.486491	0.177266	4.283961	2.481587	0.162058	4.280730
N(1)	1.114680	–2.046081	4.381281	1.169857	–2.072853	4.507865	1.190227	–2.125283	4.612335
C(7)	–0.461640	–0.499222	5.409454	–0.319996	–0.401427	5.513069	–0.314275	–0.408295	5.530116
C(8)	–0.197846	–1.972875	5.042634	–0.047200	–1.906616	5.315245	–0.033508	–1.918778	5.391431
C(9)	2.671356	–0.531982	5.528334	2.802371	–0.519539	5.470325	2.789154	–0.481667	5.500532
C(10)	2.273321	–2.010366	5.293423	2.431719	–2.000076	5.256448	2.442815	–1.977254	5.357600
C(11)	1.202450	–3.082152	3.331450	1.104416	–3.168783	3.523413	1.149843	–3.280802	3.701284
H(11A)	0.407915	–2.874843	2.603260	0.214500	–2.993355	2.904112	0.262932	–3.161202	3.063688
H(11B)	2.152917	–2.923067	2.805233	1.971598	–3.058410	2.858391	2.022003	–3.201490	3.037546
C(12)	1.107572	–4.531077	3.821256	1.066486	–4.587395	4.105383	1.128577	–4.661537	4.371156
H(11A)	1.853652	–4.708589	4.611336	1.968325	–4.764826	4.711992	2.019368	–4.777684	5.008480
H(11B)	0.120925	–4.704694	4.278726	0.206597	–4.686086	4.786403	0.255231	–4.735871	5.038089
C(13)	1.321209	–5.538565	2.685800	0.971301	–5.657754	3.011420	1.084359	–5.803251	3.348850
H(13A)	0.592455	–5.341795	1.883885	0.070916	–5.474595	2.404366	0.195489	–5.682944	2.709621
H(13B)	2.315750	–5.375679	2.241631	1.828209	–5.554189	2.327137	1.955594	–5.724110	2.679434
C(14)	1.198138	–6.994480	3.142556	0.931475	–7.084237	3.566994	1.063004	–7.190990	3.996076
H(14A)	1.923730	–7.224414	3.936714	1.834913	–7.307361	4.153455	1.957492	–7.354328	4.615085
H(14B)	1.381504	–7.688919	2.311402	0.866633	–7.824562	2.757927	1.032792	–7.984155	3.236469
H(14C)	0.193284	–7.204036	3.537542	0.061831	–7.230157	4.224468	0.182074	–7.313895	4.643167
H(7A)	0.035685	–0.220621	6.352044	0.251144	0.009196	6.358964	0.251480	0.038764	6.360057
H(7B)	–1.538346	–0.326612	5.544579	–1.384921	–0.236446	5.727037	–1.380551	–0.244293	5.737255
H(8A)	–0.266404	–2.630713	5.923009	0.015337	–2.427398	6.284628	0.008651	–2.395405	6.385898
H(8B)	–0.949749	–2.295395	4.312704	–0.881079	–2.340783	4.751537	–0.860852	–2.375086	4.835033
H(9A)	2.088676	–0.077656	6.343969	2.285638	–0.093376	6.343152	2.261516	–0.019363	6.347061
H(9B)	3.732664	–0.458767	5.801137	3.881966	–0.423158	5.650559	3.865821	–0.363965	5.684696
H(10A)	2.070436	–2.530373	6.241867	2.386004	–2.538887	6.217100	2.409934	–2.461152	6.349024
H(10B)	3.102957	–2.524616	4.795646	3.208605	–2.469169	4.641273	3.234048	–2.461927	4.773206
Br(1)	–1.659795	–0.001931	–0.943582	–1.680820	–0.003839	–0.943750	–1.680405	–0.001493	–0.943929

Table 30S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	d_{B-N} = 2.4 Å (*a*)			d_{B-N} = 2.5 Å (*b*)			d_{B-N} = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.217922	0.000000	2.101801	1.218157	0.000000	2.101252	1.218368	0.000000	2.100859
C(2)	0.000000	0.000000	1.393479	0.000000	0.000000	1.393397	0.000000	0.000000	1.393362
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.186632	0.006497	–0.734603	1.186740	0.000453	–0.734469	1.186781	0.002935	–0.734401
C(5)	2.400002	0.012407	–0.037729	2.400237	0.000904	–0.037853	2.400342	0.005106	–0.037975
C(6)	2.413661	0.007829	1.359356	2.414073	0.000340	1.359130	2.414392	0.003063	1.358948
H(2)	–0.941143	0.004354	1.939190	–0.941036	0.006314	1.939202	–0.941099	0.002063	1.939067
H(3)	1.165150	0.008518	–1.822882	1.165260	0.001359	–1.822755	1.165261	0.003886	–1.822689
H(5)	3.335890	0.022737	–0.598171	3.336115	0.004553	–0.598361	3.336187	0.009914	–0.598498
H(6)	3.365583	0.016872	1.889179	3.366060	0.005798	1.888812	3.366499	0.006854	1.888385
B(1)	1.227451	–0.035425	3.681779	1.227919	–0.009897	3.680859	1.228621	–0.018321	3.679731
O(1)	–0.011723	0.140005	4.294682	–0.010989	0.146931	4.286454	–0.009946	0.097319	4.284713
O(2)	2.477906	0.116851	4.278584	2.477121	0.126435	4.270486	2.476364	0.088149	4.267703
N(1)	1.213319	–2.203279	4.711443	1.218282	–2.180006	4.922042	1.230967	–2.214307	5.071722
C(7)	–0.310086	–0.451404	5.544624	–0.301497	–0.343323	5.582578	–0.291704	–0.329966	5.606346
C(8)	–0.018173	–1.963750	5.460748	–0.015100	–1.856925	5.632047	–0.004571	–1.837661	5.745912
C(9)	2.776615	–0.478128	5.526733	2.766224	–0.360516	5.568103	2.762750	–0.331732	5.590593
C(10)	2.456104	–1.985048	5.448294	2.457415	–1.869822	5.627747	2.468922	–1.837649	5.741431
C(11)	1.198616	–3.404004	3.864233	1.210158	–3.483077	4.243865	1.229734	–3.563306	4.494916
H(11A)	0.315837	–3.333179	3.213151	0.328472	–3.504966	3.587312	0.348226	–3.639547	3.841634
H(11B)	2.075551	–3.347997	3.203775	2.089309	–3.514227	3.584216	2.109173	–3.639877	3.838787
C(12)	1.191188	–4.750654	4.602527	1.205304	–4.721515	5.153306	1.231292	–4.733821	5.490974
H(11A)	2.076715	–4.819892	5.254004	2.089565	–4.701736	5.809763	2.114099	–4.661513	6.145785
H(11B)	0.311806	–4.804901	5.263571	0.324630	–4.691924	5.814099	0.349138	–4.663281	6.146736
C(13)	1.175980	–5.942634	3.638566	1.196004	–6.030094	4.354529	1.232169	–6.095754	4.787144
H(13A)	0.292426	–5.868687	2.984936	0.311798	–6.046499	3.697735	0.348981	–6.164906	4.132265
H(13B)	2.053171	–5.882626	2.974886	2.072712	–6.053441	3.687841	2.109856	–6.159836	4.124303
C(14)	1.169391	–7.296966	4.353463	1.195998	–7.278504	5.241616	1.239795	–7.279234	5.759048
H(14A)	2.059458	–7.414872	4.988953	2.088503	–7.308647	5.883877	2.131382	–7.258215	6.403018
H(14B)	1.160014	–8.127224	3.633946	1.186763	–8.196746	4.638355	1.238206	–8.237414	5.221302
H(14C)	0.283470	–7.401875	4.996912	0.312617	–7.299382	5.896699	0.355565	–7.261101	6.413139
H(7A)	0.247163	0.028847	6.360722	0.255511	0.206070	6.352985	0.263243	0.264035	6.343592
H(7B)	–1.378494	–0.291701	5.743491	–1.369481	–0.167622	5.769473	–1.359945	–0.148157	5.785660
H(8A)	0.004376	–2.397766	6.476699	–0.011454	–2.194346	6.685649	–0.016031	–2.105615	6.820556
H(8B)	–0.837551	–2.442861	4.911359	–0.833921	–2.376908	5.119678	–0.821196	–2.386917	5.260818
H(9A)	2.235759	0.013430	6.347030	2.220998	0.201796	6.337497	2.214301	0.270006	6.326302
H(9B)	3.849581	–0.337860	5.715842	3.837587	–0.199824	5.749412	3.832754	–0.153987	5.763673
H(10A)	2.435675	–2.417146	6.465118	2.450847	–2.200553	6.683436	2.480723	–2.098222	6.817851
H(10B)	3.261191	–2.479958	4.891724	3.267860	–2.404861	5.117521	3.282696	–2.393854	5.259418
Br(1)	–1.679973	–0.006746	–0.944079	–1.679832	–0.000963	–0.944013	–1.679700	–0.003498	–0.943876

Table 31S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	d_{B-N} = 2.7 Å (*a*)			d_{B-N} = 2.8 Å (*b*)			d_{B-N} = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.217734	0.000000	2.101525	1.218655	0.000000	2.100180	2.415315	0.005387	1.359079
C(2)	0.000000	0.000000	1.393296	0.000000	0.000000	1.393334	1.218760	0.000000	2.099877
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	1.393326
C(4)	1.187538	–0.002602	–0.733283	1.186965	–0.004735	–0.734132	–1.679058	–0.006536	–0.943765
C(5)	2.400723	–0.006139	–0.036061	2.400590	–0.009098	–0.037956	1.187183	0.006421	–0.733840
C(6)	2.414420	–0.006267	1.360886	2.414944	–0.006699	1.358898	2.400863	0.010175	–0.037738
H(2)	–0.941324	0.007100	1.938524	–0.941116	0.005846	1.938965	3.367428	0.004064	1.888502
H(3)	1.167076	–0.001931	–1.821595	1.165487	–0.004802	–1.822415	1.228926	–0.026589	3.676525
H(5)	3.336861	–0.007315	–0.596098	3.336421	–0.012498	–0.598464	1.165813	0.007949	–1.822127
H(6)	3.366338	–0.007780	1.890712	3.367138	–0.007049	1.888157	3.336663	0.015614	–0.598253
B(1)	1.223032	0.000705	3.680163	1.229065	0.013445	3.678114	2.470723	–0.011560	4.268887
O(1)	–0.009727	0.170605	4.275604	–0.005283	0.112544	4.280077	1.209711	–2.197455	5.599276
O(2)	2.469386	0.020980	4.271661	2.474209	0.073185	4.263700	–0.003374	0.026357	4.285601
N(1)	1.096135	–2.158073	5.296818	1.206615	–2.103240	5.510909	–0.022493	–1.624573	6.115376
C(7)	–0.310181	–0.131818	5.628638	–0.274524	–0.096494	5.658818	2.459640	–1.655490	6.105484
C(8)	–0.116722	–1.634032	5.907318	–0.021024	–1.558266	6.069754	–0.270249	–0.171679	5.668420
C(9)	2.726232	–0.304534	5.628463	2.752977	–0.143561	5.639308	1.190792	–3.655810	5.466682
C(10)	2.353786	–1.771664	5.919707	2.455985	–1.595878	6.056375	2.744112	–0.211481	5.650184
C(11)	1.016527	–3.566880	4.898216	1.183363	–3.555443	5.308653	0.304141	–3.920993	4.871412
H(11A)	0.142409	–3.672426	4.238542	0.294907	–3.789135	4.703389	2.066297	–3.943080	4.865065
H(11B)	1.899726	–3.784385	4.279943	2.056899	–3.815847	4.692560	1.185728	–4.467422	6.773601
C(12)	0.921820	–4.596976	6.036025	1.178383	–4.424365	6.577746	2.072366	–4.208845	7.373763
H(11A)	1.796873	–4.500315	6.698144	2.070208	–4.198645	7.183423	0.307537	–4.191061	7.378207
H(11B)	0.036388	–4.382300	6.654900	0.305633	–4.167749	7.198585	1.169730	–5.979085	6.519962
C(13)	0.837523	–6.035772	5.513825	1.149307	–5.923793	6.259905	0.284835	–6.235216	5.915653
H(13A)	–0.027368	–6.124585	4.837158	0.255101	–6.148694	5.656959	2.045898	–6.252943	5.910659
H(13B)	1.727870	–6.251798	4.902006	2.015891	–6.177445	5.628608	1.165098	–6.809061	7.807110
C(14)	0.719442	–7.078300	6.629489	1.154919	–6.806204	7.511790	2.056929	–6.600606	8.416399
H(14A)	1.585675	–7.036187	7.306243	2.057759	–6.631623	8.115395	1.153653	–7.885822	7.588363
H(14B)	0.664069	–8.096547	6.220317	1.128919	–7.872863	7.249286	0.281139	–6.582859	8.421503
H(14C)	–0.184281	–6.910752	7.233710	0.282489	–6.596512	8.148067	0.290685	0.545199	6.279018
H(7A)	0.277031	0.492682	6.313013	0.291074	0.608459	6.279547	–1.335085	0.054024	5.815934
H(7B)	–1.365898	0.126113	5.787642	–1.338545	0.129506	5.811128	–0.090377	–1.643629	7.223939
H(8A)	–0.162192	–1.793975	7.003436	–0.064742	–1.611414	7.177314	–0.845192	–2.242122	5.731690
H(8B)	–0.962428	–2.173905	5.462670	–0.847584	–2.167817	5.682292	2.533950	–1.671536	7.213707
H(9A)	2.215071	0.391478	6.304710	2.219238	0.580783	6.265856	3.816092	–0.015049	5.787859
H(9B)	3.804561	–0.173380	5.790958	3.825843	0.046570	5.778440	3.825843	0.046570	5.778440
H(10A)	2.365512	–1.923174	7.017966	2.508720	–1.647583	7.163630	3.263169	–2.296581	5.719726
H(10B)	3.136210	–2.412231	5.493450	3.258940	–2.232653	5.663044	2.208701	0.523173	6.262460
Br(1)	–1.679028	0.001454	–0.944393	–1.679356	0.004252	–0.943728	–0.941105	–0.004820	1.939011

Table 32S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	d_{B-N} = 3.0 Å (*a*)			d_{B-N} = 3.1 Å (*b*)			d_{B-N} = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.217889	0.000000	2.100921	1.219241	0.000000	2.099013	1.219330	0.000000	2.098786
C(2)	0.000000	0.000000	1.393214	0.000000	0.000000	1.393331	0.000000	0.000000	1.393295
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.188337	–0.003498	–0.732290	1.187406	–0.003532	–0.733629	1.187755	0.002481	–0.733188
C(5)	2.401494	–0.008382	–0.035060	2.401310	–0.006794	–0.037997	2.401691	0.003627	–0.037556
C(6)	2.415332	–0.008497	1.361881	2.416097	–0.004434	1.358756	2.416543	0.002251	1.359182
H(2)	–0.941423	0.005699	1.938370	–0.941015	0.002367	1.939299	–0.940969	–0.003018	1.939392
H(3)	1.168446	–0.002849	–1.820613	1.165924	–0.003689	–1.821909	1.166495	0.003168	–1.821474
H(5)	3.337675	–0.011706	–0.594959	3.336979	–0.009894	–0.598696	3.337342	0.005390	–0.598263
H(6)	3.367179	–0.014015	1.891926	3.368222	–0.005533	1.888222	3.368524	0.001167	1.888942
B(1)	1.221363	0.006447	3.676889	1.230335	0.014930	3.673755	1.229125	–0.007142	3.672073
O(1)	–0.005636	0.150637	4.279398	0.003406	0.041958	4.292282	0.005196	–0.011786	4.298259
O(2)	2.453464	–0.074018	4.281761	2.466718	0.029409	4.274519	2.461818	–0.018791	4.281892
N(1)	1.027428	–2.043951	5.858232	1.236370	–1.963469	6.060364	1.243658	–1.988474	6.184862
C(7)	–0.283221	0.101987	5.674539	–0.252881	0.053556	5.694428	–0.246117	0.025369	5.702934
C(8)	–0.153962	–1.309250	6.277115	–0.006468	–1.292623	6.401270	–0.003877	–1.296260	6.459771
C(9)	2.709114	–0.172973	5.679197	2.737890	0.041582	5.673857	2.733512	0.017442	5.682788
C(10)	2.321860	–1.537645	6.281011	2.487721	–1.301046	6.386190	2.498414	–1.303722	6.443175
C(11)	0.892309	–3.499477	5.940123	1.234152	–3.404839	6.307977	1.240388	–3.404403	6.546100
H(11A)	–0.014497	–3.778635	5.382593	0.344066	–3.823122	5.813836	0.357878	–3.864456	6.075543
H(11B)	1.740730	–3.940829	5.395756	2.107112	–3.830380	5.789785	2.121620	–3.868156	6.076877
C(12)	0.824238	–4.106862	7.352295	1.252188	–3.855125	7.779775	1.238955	–3.733754	8.050063
H(11A)	1.730905	–3.837000	7.916446	2.143837	–3.448132	8.282171	2.124750	–3.287592	8.529081
H(11B)	–0.026289	–3.672817	7.901147	0.378789	–3.439381	8.306482	0.359788	–3.275323	8.529506
C(13)	0.681636	–5.632944	7.324887	1.246764	–5.381613	7.919124	1.228158	–5.243524	8.315915
H(13A)	–0.221871	–5.902024	6.754557	0.355410	–5.787822	7.414687	0.345277	–5.690375	7.831256
H(13B)	1.531594	–6.066130	6.773615	2.116181	–5.796756	7.384469	2.106481	–5.702364	7.834066
C(14)	0.607677	–6.258781	8.720695	1.269415	–5.857382	9.374773	1.223670	–5.595304	9.806389
H(14A)	1.512906	–6.034794	9.304189	2.169273	–5.497768	9.895394	2.113896	–5.192236	10.311457
H(14B)	0.508286	–7.351650	8.664075	1.262893	–6.954449	9.437240	1.215556	–6.683272	9.960484
H(14C)	–0.255376	–5.872897	9.283033	0.393826	–5.485503	9.927191	0.338107	–5.179375	10.309199
H(7A)	0.327701	0.833682	6.215017	0.296176	0.869682	6.176723	0.297162	0.857372	6.163656
H(7B)	–1.328085	0.420065	5.792135	–1.320173	0.288409	5.806639	–1.314552	0.257577	5.810304
H(8A)	–0.236889	–1.192875	7.379376	–0.119192	–1.091468	7.489520	–0.146069	–1.047071	7.535287
H(8B)	–1.022316	–1.897129	5.951094	–0.817923	–1.977098	6.119308	–0.809505	–1.992965	6.189912
H(9A)	2.238043	0.657506	6.216936	2.201088	0.863442	6.160146	2.197999	0.849761	6.151844
H(9B)	3.793740	–0.050353	5.803203	3.808346	0.267442	5.774515	3.803788	0.247854	5.775195
H(10A)	2.422040	–1.439156	7.383940	2.613742	–1.098486	7.472710	2.657014	–1.055264	7.516704
H(10B)	3.069132	–2.274417	5.957360	3.290898	–1.992555	6.097479	3.296963	–2.004031	6.161722
Br(1)	–1.678041	0.002797	–0.944725	–1.678668	0.003896	–0.943669	–1.678289	–0.001579	–0.943887

Table 33S. Cartesian coordinates for azaester derivative (X = 3-Br, R = Bu) with B-N distance constrained to 3.3 Å.

Atom	d_{B-N} = 3.3 Å (*a*)		
	x / Å	*y* / Å	*z* / Å
C(1)	1.219774	0.000000	2.098074
C(2)	0.000000	0.000000	1.393350
C(3)	0.000000	0.000000	0.000000
C(4)	1.187714	0.000656	–0.733248
C(5)	2.401909	0.001082	–0.038052
C(6)	2.417100	0.001722	1.358593
H(2)	–0.940820	–0.002824	1.939764
H(3)	1.166216	0.000802	–1.821523
H(5)	3.337379	0.001285	–0.599030
H(6)	3.369036	0.002145	1.888419
B(1)	1.230536	0.001129	3.669913
O(1)	0.013540	–0.053858	4.308174
O(2)	2.461680	0.021482	4.284593
N(1)	1.318754	–1.889236	6.373382
C(7)	–0.233346	0.048658	5.712265
C(8)	0.048670	–1.207915	6.563961
C(9)	2.736454	0.130202	5.682965
C(10)	2.560341	–1.148694	6.525695
C(11)	1.357706	–3.245201	6.915891
H(11A)	0.493010	–3.791730	6.508470
H(11B)	2.256724	–3.736915	6.513250
C(12)	1.358362	–3.375121	8.450267
H(11A)	2.214844	–2.824199	8.869325
H(11B)	0.452026	–2.904790	8.862444
C(13)	1.423438	–4.835781	8.909824
H(13A)	0.573250	–5.389203	8.479628
H(13B)	2.332302	–5.303896	8.498773
C(14)	1.414779	–4.992760	10.433306
H(14A)	2.272166	–4.476491	10.889901
H(14B)	1.466533	–6.050503	10.726660
H(14C)	0.498900	–4.568766	10.870856
H(7A)	0.276483	0.927668	6.120545
H(7B)	–1.309710	0.246694	5.809258
H(8A)	–0.123843	–0.877469	7.613345
H(8B)	–0.731732	–1.948684	6.339415
H(9A)	2.178570	0.968155	6.113879
H(9B)	3.799173	0.399173	5.755355
H(10A)	2.755980	–0.821773	7.572291
H(10B)	3.368865	–1.844475	6.260051
Br(1)	–1.678190	0.000462	–0.943706

Table 34S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*).

Atom	d_{B-N} = 1.5 Å (*a*)			d_{B-N} = 1.6 Å (*b*)			d_{B-N} = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.188148	1.161788	0.000000	2.184327	1.163836	0.000000	2.181435	1.166158	0.000000
C(2)	1.399634	0.000000	0.000000	1.398673	0.000000	0.000000	1.398536	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.684403	1.215471	0.006651	–0.683020	1.217076	0.001948	–0.683490	1.217010	0.003263
C(5)	0.045602	2.406581	0.010337	0.045600	2.408522	0.000495	0.043338	2.409617	0.001059
C(6)	1.440621	2.364409	0.010820	1.440919	2.367679	–0.001357	1.438612	2.370084	–0.001884
H(2)	–0.545108	–0.941923	–0.001211	–0.546303	–0.941215	0.002051	–0.546147	–0.941295	0.000473
H(3)	–1.774928	1.223529	0.013574	–1.773612	1.225511	0.007614	–1.774097	1.224547	0.009278
H(5)	–0.470230	3.367547	0.025298	–0.471664	3.368738	0.008788	–0.475295	3.369050	0.008855
H(6)	1.996319	3.299749	0.046481	2.000718	3.300906	0.015588	1.998561	3.303400	0.012405
B(1)	3.834869	1.292561	0.094668	3.813796	1.282546	0.066721	3.802350	1.283290	0.063763
O(1)	4.129217	2.656030	0.573680	4.161206	2.686590	0.322848	4.180940	2.676256	0.269122
O(2)	4.436937	0.265641	0.981548	4.417553	0.347148	1.025824	4.432888	0.332847	0.970147
N(1)	4.648239	1.169495	–1.159638	4.628554	0.970897	–1.274563	4.637011	0.947321	–1.378619
C(7)	5.410939	–0.516904	0.344762	5.510991	–0.363666	0.506460	5.546655	–0.337792	0.439048
C(8)	5.191774	–0.236812	–1.148640	5.325788	–0.340499	–1.012243	5.357786	–0.334450	–1.081446
C(9)	5.510956	2.837457	0.403850	5.508101	2.857892	–0.034788	5.511249	2.848918	–0.148702
C(10)	5.777046	2.194316	–0.967521	5.622975	2.119673	–1.374448	5.580784	2.121724	–1.499844
C(11)	3.890497	1.449697	–2.445362	3.779695	0.895041	–2.515761	3.759792	0.824958	–2.588141
H(11A)	3.034895	0.768668	–2.448312	3.029544	0.119402	–2.334573	3.035567	0.032838	–2.373215
H(11B)	3.495274	2.466623	–2.345110	3.249258	1.851828	–2.584564	3.200329	1.764959	–2.662193
C(12)	4.693228	1.293601	–3.735154	4.539855	0.599719	–3.808323	4.493238	0.526984	–3.896277
H(11A)	5.617131	1.888788	–3.702916	5.324437	1.351753	–3.978086	5.246513	1.302408	–4.100839
H(11B)	4.997856	0.245285	–3.864200	5.045392	–0.374023	–3.734030	5.035434	–0.426511	–3.814169
C(13)	3.859238	1.725290	–4.950170	3.592270	0.581704	–5.015997	3.517823	0.450210	–5.078805
H(13A)	2.901622	1.182530	–4.945392	2.806305	–0.170493	–4.848388	2.761569	–0.323320	–4.875081
H(13B)	3.608487	2.793038	–4.855429	3.078774	1.552939	–5.088683	2.970502	1.402224	–5.159440
C(14)	4.579621	1.483540	–6.279340	4.314374	0.284415	–6.333034	4.216229	0.146980	–6.407249
H(14A)	5.534268	2.028229	–6.319351	5.082777	1.042214	–6.544978	4.954070	0.924107	–6.654980
H(14B)	3.967483	1.819178	–7.126952	3.611083	0.276396	–7.176534	3.493136	0.097312	–7.232452
H(14C)	4.796398	0.415376	–6.424667	4.810484	–0.696603	–6.301577	4.744969	–0.816553	–6.367050
H(7A)	6.432844	–0.238780	0.668101	6.473881	0.093943	0.802839	6.494323	0.152859	0.729089
H(7B)	5.270600	–1.587429	0.561815	5.507181	–1.399652	0.878527	5.579564	–1.370696	0.817372
H(8A)	6.080372	–0.276660	–1.784562	6.253128	–0.412554	–1.589969	6.292367	–0.404200	–1.649528
H(8B)	4.414168	–0.889164	–1.553040	4.641186	–1.135320	–1.317346	4.693684	–1.152209	–1.372188
H(9A)	6.090593	2.340497	1.200159	6.191715	2.436156	0.721743	6.227985	2.428526	0.576821
H(9B)	5.764682	3.906806	0.402276	5.740402	3.926182	–0.148144	5.734020	3.918895	–0.264525
H(10A)	6.738076	1.682105	–1.069079	6.622736	1.740273	–1.609999	6.584344	1.785503	–1.783436
H(10B)	5.675202	2.926835	–1.771353	5.291484	2.774271	–2.185298	5.194328	2.778695	–2.284862
Br(1)	2.170338	–1.791486	–0.047105	2.182360	–1.785607	–0.018694	2.184990	–1.782944	–0.029113

Table 35S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	d_{B-N} = 1.8 Å (*a*)			d_{B-N} = 1.9 Å (*b*)			d_{B-N} = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.178726	1.168466	0.000000	2.176774	1.170148	0.000000	2.174351	1.172389	0.000000
C(2)	1.398442	0.000000	0.000000	1.398426	0.000000	0.000000	1.398443	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.684257	1.216708	0.002483	–0.684484	1.216706	0.005350	–0.685329	1.216251	0.007867
C(5)	0.040739	2.410462	–0.001500	0.039265	2.411380	0.003359	0.036662	2.412097	0.007090
C(6)	1.435921	2.372316	–0.005056	1.434336	2.374240	–0.003021	1.431529	2.376356	–0.001523
H(2)	–0.545849	–0.941460	0.000617	–0.545688	–0.941505	–0.001041	–0.545233	–0.941746	–0.002643
H(3)	–1.774881	1.223133	0.008403	–1.775123	1.222639	0.011544	–1.775981	1.221109	0.014367
H(5)	–0.479199	3.369156	0.004390	–0.481645	3.369488	0.011281	–0.485490	3.369472	0.016366
H(6)	1.995579	3.305929	0.004664	1.993791	3.308103	0.003792	1.990186	3.310763	0.002658
B(1)	3.792225	1.285857	0.056860	3.784083	1.285829	0.036218	3.775799	1.288611	0.022596
O(1)	4.196716	2.669023	0.190682	4.213643	2.654794	0.103799	4.221615	2.643578	0.031293
O(2)	4.446322	0.330335	0.920252	4.467112	0.314925	0.837887	4.481207	0.301258	0.761870
N(1)	4.644753	0.906144	–1.482300	4.635652	0.873318	–1.611406	4.640054	0.852909	–1.727611
C(7)	5.585626	–0.297872	0.389165	5.616363	–0.278142	0.284584	5.644198	–0.253628	0.193970
C(8)	5.396796	–0.335432	–1.133085	5.406755	–0.340136	–1.236181	5.427172	–0.333777	–1.326905
C(9)	5.506074	2.843545	–0.290424	5.500336	2.827846	–0.437795	5.490623	2.820645	–0.552508
C(10)	5.532232	2.106755	–1.640037	5.482305	2.089298	–1.789035	5.446922	2.085625	–1.906892
C(11)	3.746405	0.715142	–2.660152	3.712195	0.645060	–2.756052	3.706192	0.594427	–2.850858
H(11A)	3.056432	–0.095699	–2.403918	3.045613	–0.175478	–2.468173	3.059446	–0.235852	–2.543884
H(11B)	3.150174	1.631170	–2.751015	3.092993	1.546280	–2.846924	3.066066	1.481427	–2.942527
C(12)	4.457556	0.403778	–3.978441	4.391201	0.326828	–4.090666	4.367484	0.275777	–4.195368
H(11A)	5.170921	1.204049	–4.226673	5.077541	1.140207	–4.371441	5.033224	1.100333	–4.493621
H(11B)	5.043590	–0.522020	–3.878495	5.003436	–0.582212	–3.990916	5.000151	–0.619537	–4.096251
C(13)	3.458374	0.244307	–5.132382	3.365081	0.122345	–5.213078	3.328910	0.040178	–5.299629
H(13A)	2.743721	–0.555268	–4.883945	2.676726	–0.688804	–4.929996	2.662528	–0.783196	–4.999318
H(13B)	2.866170	1.167638	–5.228754	2.748485	1.029675	–5.309304	2.691249	0.933231	–5.392969
C(14)	4.136175	–0.071202	–6.468643	4.011949	–0.202309	–6.562455	3.960370	–0.281544	–6.657038
H(14A)	4.832650	0.728750	–6.759783	4.680111	0.608343	–6.888351	4.604306	0.541244	–7.000870
H(14B)	3.396028	–0.179245	–7.272987	3.252262	–0.343603	–7.343182	3.191448	–0.447133	–7.423926
H(14C)	4.708128	–1.008924	–6.411994	4.608292	–1.124705	–6.505018	4.578810	–1.189451	–6.601782
H(7A)	6.512160	0.235818	0.667871	6.529541	0.285952	0.543231	6.540129	0.340140	0.442689
H(7B)	5.661627	–1.320637	0.787362	5.730345	–1.293456	0.691708	5.793250	–1.261891	0.606281
H(8A)	6.340721	–0.402562	–1.687964	6.351332	–0.409971	–1.792096	6.377484	–0.402685	–1.875875
H(8B)	4.760775	–1.183553	–1.399954	4.785141	–1.206548	–1.478701	4.823101	–1.216943	–1.554937
H(9A)	6.257942	2.440795	0.408430	6.282666	2.433855	0.230937	6.294486	2.435137	0.094093
H(9B)	5.712073	3.914587	–0.425369	5.693920	3.899667	–0.583753	5.670315	3.894201	–0.702689
H(10A)	6.537333	1.814429	–1.967327	6.485057	1.829424	–2.152719	6.450469	1.861612	–2.295172
H(10B)	5.087956	2.749955	–2.406422	4.996678	2.727031	–2.535193	4.929446	2.719829	–2.634955
Br(1)	2.187175	–1.780579	–0.027087	2.187595	–1.778814	–0.026328	2.188342	–1.776609	–0.028545

Table 36S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	d_{B-N} = 2.1 Å (*a*)			d_{B-N} = 2.2 Å (*b*)			d_{B-N} = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.171467	1.174733	0.000000	2.169073	1.176540	0.000000	2.164578	1.179540	0.000000
C(2)	1.398414	0.000000	0.000000	1.398418	0.000000	0.000000	1.398218	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.686795	1.215379	0.001443	–0.687611	1.214906	0.004804	–0.688510	1.214519	0.007083
C(5)	0.033082	2.412450	–0.005267	0.030703	2.413016	–0.000620	0.027256	2.414205	–0.001273
C(6)	1.427734	2.378322	–0.011187	1.425172	2.380094	–0.009540	1.421574	2.383223	–0.011943
H(2)	–0.544598	–0.942145	0.000194	–0.544238	–0.942354	–0.002395	–0.543916	–0.942557	–0.006880
H(3)	–1.777460	1.218580	0.006893	–1.778280	1.217060	0.010706	–1.779180	1.215284	0.013777
H(5)	–0.490407	3.369095	–0.002726	–0.493833	3.369049	0.003300	–0.499069	3.369209	0.000040
H(6)	1.985014	3.313519	–0.012951	1.981586	3.315816	–0.015323	1.976576	3.319989	–0.023334
B(1)	3.767631	1.294451	0.035227	3.761293	1.296374	0.023959	3.750527	1.298257	0.043712
O(1)	4.220402	2.635231	–0.050069	4.222047	2.617915	–0.143473	4.227348	2.570877	–0.272539
O(2)	4.470002	0.318485	0.772530	4.470532	0.319950	0.735461	4.441162	0.331101	0.757054
N(1)	4.716954	0.774453	–1.764325	4.771719	0.711291	–1.840636	5.021154	0.566028	–1.856116
C(7)	5.679869	–0.192941	0.260639	5.708196	–0.155588	0.251846	5.746142	–0.089870	0.411181
C(8)	5.518218	–0.355967	–1.261722	5.581320	–0.372877	–1.267999	5.792711	–0.415063	–1.094911
C(9)	5.487885	2.811565	–0.639812	5.485525	2.792210	–0.745493	5.530502	2.737266	–0.794497
C(10)	5.476092	2.025290	–1.966800	5.490248	1.976890	–2.055514	5.669614	1.861701	–2.056828
C(11)	3.828102	0.428317	–2.895399	3.920343	0.301830	–2.974970	4.357750	0.025264	–3.053583
H(11A)	3.198980	–0.407316	–2.565686	3.305152	–0.539045	–2.630824	3.750950	–0.831473	–2.730950
H(11B)	3.161158	1.286526	–3.051803	3.233388	1.134592	–3.178408	3.654343	0.791712	–3.409037
C(12)	4.537153	0.065579	–4.205147	4.664909	–0.087725	–4.258553	5.285048	–0.397707	–4.202279
H(11A)	5.177686	0.900480	–4.529538	5.292247	0.751675	–4.597283	5.893839	0.461687	–4.524855
H(11B)	5.203256	–0.795335	–4.039473	5.348173	–0.925559	–4.049410	5.990284	–1.164283	–3.844366
C(13)	3.542965	–0.272740	–5.322772	3.703382	–0.487416	–5.384089	4.507534	–0.947250	–5.404033
H(13A)	2.901067	–1.105662	–4.996171	3.070975	–1.321087	–5.040912	3.898461	–1.805422	–5.078902
H(13B)	2.872581	0.586316	–5.483695	3.019472	0.351038	–5.590607	3.796170	–0.182841	–5.755295
C(14)	4.225967	–0.640910	–6.642973	4.421837	–0.889279	–6.675422	5.412149	–1.372656	–6.564201
H(14A)	4.848600	0.187031	–7.012793	5.035449	–0.062527	–7.062652	6.011286	–0.526223	–6.930929
H(14B)	3.486751	–0.876429	–7.420791	3.704613	–1.168759	–7.459322	4.823640	–1.756644	–7.408865
H(14C)	4.875962	–1.519956	–6.522139	5.086890	–1.749280	–6.508464	6.108939	–2.165278	–6.254086
H(7A)	6.533673	0.458562	0.508872	6.531326	0.534025	0.495963	6.498981	0.660676	0.691063
H(7B)	5.868171	–1.171112	0.725047	5.924884	–1.111358	0.748726	5.964317	–0.998335	0.988848
H(8A)	6.495723	–0.430985	–1.762938	6.576671	–0.449014	–1.735790	6.844768	–0.486161	–1.425889
H(8B)	4.952455	–1.271645	–1.460285	5.043754	–1.310629	–1.442877	5.321600	–1.391798	–1.250939
H(9A)	6.297082	2.476164	0.026687	6.301088	2.490092	–0.071942	6.297557	2.501689	–0.044259
H(9B)	5.641256	3.882338	–0.832771	5.620009	3.860208	–0.965543	5.651821	3.795405	–1.063402
H(10A)	6.494952	1.834982	–2.336541	6.518415	1.819062	–2.419234	6.735001	1.771032	–2.335288
H(10B)	4.945160	2.618895	–2.719486	4.944553	2.543725	–2.818650	5.150433	2.365773	–2.881029
Br(1)	2.192268	–1.773161	–0.015762	2.195409	–1.770156	–0.021808	2.202875	–1.763393	–0.053948

Table 37S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	d_{B-N} = 2.4 Å (*a*)			d_{B-N} = 2.5 Å (*b*)			d_{B-N} = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.167311	1.177934	0.000000	2.163075	1.180517	0.000000	2.161701	1.180560	0.000000
C(2)	1.398362	0.000000	0.000000	1.398226	0.000000	0.000000	1.397964	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.687900	1.214750	0.009558	–0.688521	1.214512	0.011687	–0.687755	1.215236	0.002537
C(5)	0.029321	2.413607	0.006215	0.026518	2.414770	0.005740	0.027274	2.415416	–0.012039
C(6)	1.423616	2.381589	–0.005947	1.420715	2.384435	–0.008063	1.421770	2.385172	–0.020922
H(2)	–0.544064	–0.942429	–0.006204	–0.543838	–0.942556	–0.010260	–0.544296	–0.942363	–0.006619
H(3)	–1.778575	1.216401	0.016205	–1.779188	1.215075	0.018906	–1.778411	1.216383	0.008750
H(5)	–0.495996	3.369171	0.012534	–0.500355	3.369442	0.009460	–0.499822	3.369946	–0.017909
H(6)	1.979294	3.317878	–0.013933	1.975258	3.321637	–0.021495	1.976438	3.322466	–0.039059
B(1)	3.756297	1.297595	0.016898	3.747533	1.297841	0.033423	3.744126	1.294046	0.067003
O(1)	4.222177	2.597299	–0.226035	4.226533	2.544190	–0.351011	4.241772	2.488814	–0.424026
O(2)	4.469869	0.319957	0.706327	4.438835	0.330148	0.734243	4.399322	0.369686	0.847668
N(1)	4.847494	0.651481	–1.901910	5.146031	0.514164	–1.884924	5.403061	0.377815	–1.713011
C(7)	5.729091	–0.135238	0.255090	5.767605	–0.061884	0.442190	5.764377	0.011465	0.715740
C(8)	5.646352	–0.396303	–1.261589	5.888928	–0.424846	–1.051473	6.058629	–0.462767	–0.719816
C(9)	5.495145	2.765139	–0.813427	5.546676	2.719280	–0.830497	5.601913	2.669534	–0.777643
C(10)	5.537317	1.928342	–2.109893	5.759298	1.825531	–2.070046	5.981217	1.699990	–1.915958
C(11)	4.046615	0.195963	–3.051399	4.566983	–0.069707	–3.102410	5.025013	–0.321131	–2.947300
H(11A)	3.431936	–0.645236	–2.705257	3.965312	–0.936041	–2.794621	4.410365	–1.184931	–2.657335
H(11B)	3.352690	1.009531	–3.305105	3.863167	0.668050	–3.514468	4.367464	0.351846	–3.516775
C(12)	4.840317	–0.217611	–4.298744	5.563821	–0.493465	–4.192087	6.181350	–0.787701	–3.845888
H(11A)	5.467967	0.621945	–4.637057	6.171409	0.372868	–4.498102	6.800827	0.076940	–4.132831
H(11B)	5.527111	–1.039750	–4.043716	6.264523	–1.238081	–3.782449	6.837256	–1.468323	–3.280522
C(13)	3.924127	–0.659318	–5.446074	4.861559	–1.080631	–5.421845	5.686162	–1.497278	–5.111506
H(13A)	3.291703	–1.493442	–5.103688	4.253441	–1.945148	–5.111875	5.063245	–2.358780	–4.823056
H(13B)	3.236279	0.163784	–5.696576	4.153944	–0.337508	–5.823011	5.026073	–0.816929	–5.672976
C(14)	4.691991	–1.082801	–6.701678	5.832089	–1.508244	–6.526582	6.822278	–1.971807	–6.022224
H(14A)	5.307014	–0.256916	–7.088556	6.431472	–0.656160	–6.879714	7.445142	–1.127236	–6.352285
H(14B)	4.006598	–1.392829	–7.502480	5.294950	–1.920597	–7.391914	6.432473	–2.470957	–6.920169
H(14C)	5.363168	–1.928044	–6.489652	6.528728	–2.279676	–6.166598	7.477094	–2.685158	–5.500403
H(7A)	6.529449	0.578094	0.502346	6.487825	0.714058	0.735484	6.423360	0.835551	1.018909
H(7B)	5.955526	–1.073112	0.780514	5.985320	–0.950423	1.049994	5.946714	–0.818336	1.411654
H(8A)	6.660662	–0.480288	–1.688925	6.960043	–0.491087	–1.321085	7.156613	–0.522492	–0.853851
H(8B)	5.126945	–1.347316	–1.421209	5.443595	–1.415018	–1.200661	5.654443	–1.475378	–0.834942
H(9A)	6.300372	2.486301	–0.119037	6.287198	2.517146	–0.045506	6.257121	2.556655	0.095445
H(9B)	5.622951	3.829930	–1.051812	5.657096	3.773939	–1.116920	5.711753	3.703244	–1.132329
H(10A)	6.579132	1.798192	–2.449499	6.839720	1.770607	–2.301539	7.083712	1.683786	–2.019679
H(10B)	4.995307	2.475303	–2.890376	5.261635	2.303075	–2.923085	5.569066	2.096944	–2.852036
Br(1)	2.196415	–1.768378	–0.037791	2.204739	–1.761293	–0.068212	2.213381	–1.756121	–0.061637

Table 38S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	d_{B-N} = 2.7 Å (*a*)			d_{B-N} = 2.8 Å (*b*)			d_{B-N} = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.160847	1.181040	0.000000	2.098452	1.208495	0.000000	2.097660	1.208839	0.000000
C(2)	1.398030	0.000000	0.000000	1.394976	0.000000	0.000000	1.394975	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.687668	1.215228	0.009591	–0.698411	1.207229	0.003449	–0.698487	1.207236	0.003162
C(5)	0.026998	2.415760	0.000916	–0.000885	2.415176	0.005485	–0.001253	2.415366	0.004472
C(6)	1.421445	2.385898	–0.013283	1.393915	2.416517	0.002176	1.393567	2.416953	0.001093
H(2)	–0.544201	–0.942366	–0.010161	–0.548835	–0.952572	–0.000777	–0.548775	–0.952623	–0.000950
H(3)	–1.778315	1.216347	0.016667	–1.798001	1.206887	0.004821	–1.798087	1.206718	0.004498
H(5)	–0.500407	3.370117	0.000891	–0.550636	3.367236	0.008485	–0.551168	3.367339	0.006437
H(6)	1.975522	3.323632	–0.033290	1.946064	3.369020	–0.002788	1.945798	3.369306	–0.006249
B(1)	3.743319	1.292973	0.032546	3.596522	1.203228	–0.013837	3.595184	1.204917	–0.010211
O(1)	4.233551	2.455271	–0.529569	4.148879	2.363803	–0.335440	4.146718	2.341622	–0.404393
O(2)	4.419115	0.374777	0.796464	4.144830	0.092793	0.455824	4.144209	0.104569	0.478404
N(1)	5.518204	0.338154	–1.764146	5.383066	0.485023	–2.046678	5.588892	0.423417	–1.965815
C(7)	5.798470	0.056344	0.694383	5.514143	–0.235531	0.334584	5.527443	–0.185278	0.460267
C(8)	6.149058	–0.450375	–0.716880	5.950375	–0.473033	–1.116874	6.081085	–0.474808	–0.940045
C(9)	5.597827	2.658937	–0.861573	5.516950	2.538820	–0.643238	5.529313	2.534601	–0.624806
C(10)	6.039740	1.680699	–1.969808	5.938725	1.819970	–1.930868	6.067979	1.786635	–1.849874
C(11)	5.222425	–0.404037	–2.993140	5.303473	0.000409	–3.412419	5.686892	–0.116194	–3.309706
H(11A)	4.628983	–1.284561	–2.707684	4.712851	–0.959801	–3.394647	5.136098	–1.099934	–3.317762
H(11B)	4.564494	0.227160	–3.608634	4.705173	0.752695	–4.001745	5.131741	0.585933	–3.995268
C(12)	6.432505	–0.848161	–3.831699	6.627386	–0.250111	–4.135083	7.093698	–0.336574	–3.866640
H(11A)	7.026346	0.033287	–4.122210	7.225534	0.697889	–4.174407	7.655327	0.634172	–3.879538
H(11B)	7.093209	–1.482499	–3.219982	7.234461	–1.004016	–3.568416	7.660801	–1.041029	–3.203247
C(13)	6.017616	–1.616294	–5.091803	6.375376	–0.751605	–5.540024	7.023802	–0.902469	–5.268015
H(13A)	5.421538	–2.495510	–4.799882	5.775110	–1.698975	–5.497293	6.459594	–1.872561	–5.252279
H(13B)	5.351034	–0.982766	–5.698608	5.762407	0.001965	–6.102214	6.450676	–0.198436	–5.927945
C(14)	7.207313	–2.067242	–5.944292	7.666187	–1.003609	–6.275585	8.399116	–1.126690	–5.841592
H(14A)	7.803680	–1.205946	–6.280038	8.267274	–0.065291	–6.351001	8.968188	–0.166845	–5.889449
H(14B)	6.874541	–2.612573	–6.838342	7.457606	–1.372786	–7.308692	8.324654	–1.544395	–6.874589
H(14C)	7.873475	–2.732327	–5.375136	8.280144	–1.770511	–5.744219	8.977341	–1.845052	–5.211479
H(7A)	6.423891	0.907832	0.991105	6.157680	0.520182	0.849796	6.113169	0.606988	0.989202
H(7B)	5.991134	–0.748515	1.416270	5.598873	–1.209362	0.896274	5.598261	–1.133511	1.067484
H(8A)	7.253920	–0.491403	–0.802838	7.079648	–0.476229	–1.139429	7.208698	–0.462075	–0.865882
H(8B)	5.772919	–1.475951	–0.814166	5.600554	–1.501019	–1.419263	5.770080	–1.521308	–1.222209
H(9A)	6.234725	2.587843	0.028582	6.165807	2.263936	0.225102	6.121612	2.314206	0.297668
H(9B)	5.686791	3.686654	–1.238839	5.606090	3.650203	–0.810333	5.603982	3.641386	–0.830503
H(10A)	7.145281	1.716444	–2.045247	7.067577	1.820015	–1.969517	7.196035	1.841277	–1.808752
H(10B)	5.635984	2.043775	–2.923330	5.566632	2.428049	–2.804037	5.731849	2.346910	–2.768928
Br(1)	2.215398	–1.754188	–0.063748	2.355312	–1.651095	0.008741	2.356107	–1.650635	0.008162

Table 39S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	d_{B-N} = 3.0 Å (*a*)			d_{B-N} = 3.1 Å (*b*)			d_{B-N} = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	2.097502	1.209006	0.000000	2.096824	1.209256	0.000000	2.096958	1.209498	0.000000
C(2)	1.394944	0.000000	0.000000	1.394872	0.000000	0.000000	1.394899	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	–0.698589	1.207210	0.002492	–0.698577	1.207179	0.002513	–0.698780	1.207153	0.002112
C(5)	–0.001509	2.415395	0.003073	–0.001823	2.415445	0.002434	–0.002117	2.415583	0.001600
C(6)	1.393324	2.417111	0.000237	1.392945	2.417363	–0.000708	1.392701	2.417615	–0.001673
H(2)	–0.548709	–0.952681	–0.000914	–0.548698	–0.952694	–0.001188	–0.548584	–0.952805	–0.001404
H(3)	–1.798215	1.206570	0.003536	–1.798199	1.206422	0.004004	–1.798453	1.206241	0.003327
H(5)	–0.551471	3.367351	0.003918	–0.551968	3.367283	0.002634	–0.552328	3.367412	0.001420
H(6)	1.945388	3.369572	–0.007803	1.945164	3.369641	–0.010584	1.944736	3.370132	–0.010969
B(1)	3.593990	1.207213	–0.004708	3.591872	1.208733	–0.003657	3.589805	1.208527	0.000700
O(1)	4.149656	2.345573	–0.386210	4.152599	2.325818	–0.436735	4.160838	2.349680	–0.349632
O(2)	4.147559	0.085557	0.425880	4.153540	0.092825	0.431417	4.164101	0.059743	0.323598
N(1)	5.792662	0.506277	–1.921614	5.979929	0.525556	–1.858503	6.164574	0.495137	–1.760447
C(7)	5.537156	–0.165299	0.487526	5.543352	–0.117285	0.579644	5.535365	–0.088719	0.632746
C(8)	6.201450	–0.405430	–0.872995	6.322875	–0.343359	–0.752701	6.497695	–0.232267	–0.555493
C(9)	5.539158	2.571889	–0.512069	5.542768	2.573548	–0.501781	5.552494	2.580701	–0.454908
C(10)	6.185249	1.885926	–1.720753	6.257458	1.932548	–1.660310	6.222742	1.939191	–1.670994
C(11)	6.065971	0.013197	–3.259191	6.426504	0.026046	–3.146150	6.800676	–0.030852	–2.954005
H(11A)	5.559078	–0.989130	–3.357425	5.997810	–1.009237	–3.271311	6.459409	–1.099755	–3.067263
H(11B)	5.566095	0.715779	–3.985608	5.963967	0.680388	–3.939290	6.399313	0.547677	–3.834323
C(12)	7.534765	–0.139315	–3.656173	7.935719	–0.037747	–3.382982	8.328814	0.000323	–3.003857
H(11A)	8.058423	0.848816	–3.571381	8.384009	0.984540	–3.275123	8.696784	1.055173	–2.907853
H(11B)	8.047644	–0.849615	–2.955946	8.416191	–0.695587	–2.612180	8.750723	–0.579536	–2.141483
C(13)	7.646887	–0.653944	–5.074533	8.229308	–0.577528	–4.765779	8.824398	–0.591932	–4.305146
H(13A)	7.120340	–1.641675	–5.157004	7.775745	–1.598489	–4.873298	8.455267	–1.647487	–4.400835
H(13B)	7.128066	0.055503	–5.772490	7.745460	0.080845	–5.535276	8.396482	–0.013627	–5.166599
C(14)	9.086206	–0.811824	–5.491914	9.711839	–0.653097	–5.025201	10.329244	–0.573665	–4.381745
H(14A)	9.620140	0.168114	–5.446452	10.177955	0.359047	–4.949411	10.715329	0.472171	–4.313916
H(14B)	9.146093	–1.197858	–6.538096	9.906051	–1.055017	–6.048848	10.673365	–1.014620	–5.348307
H(14C)	9.615598	–1.530042	–4.820093	10.208878	–1.323481	–4.282920	10.774278	–1.165651	–3.545725
H(7A)	6.064059	0.623309	1.079893	6.012606	0.698977	1.183155	5.868465	0.712917	1.340276
H(7B)	5.593671	–1.130002	1.071437	5.587010	–1.064186	1.194312	5.556266	–1.068072	1.196382
H(8A)	7.319207	–0.384617	–0.703164	7.423984	–0.289412	–0.498573	7.525277	0.042840	–0.169348
H(8B)	5.927140	–1.447653	–1.206249	6.101109	–1.400075	–1.081015	6.524781	–1.327346	–0.828884
H(9A)	6.075945	2.339579	0.440825	6.036290	2.381311	0.482681	6.085342	2.335497	0.496339
H(9B)	5.599157	3.686910	–0.679178	5.588586	3.685488	–0.696643	5.603393	3.700435	–0.600823
H(10A)	7.304484	1.997191	–1.604102	7.360792	2.128056	–1.503740	7.290180	2.316055	–1.675735
H(10B)	5.878874	2.460518	–2.641905	5.946354	2.465785	–2.604850	5.711700	2.338001	–2.595123
Br(1)	2.356085	–1.650649	0.006057	2.356772	–1.650208	0.006067	2.356830	–1.650221	0.002064

Table 40S. Cartesian coordinates for azaester derivative (X = 2-Br, R = Bu) with B-N distance constrained to 3.3 Å (*a*).

Atom	d_{B-N} = 3.3 Å (*a*)		
	x / Å	*y* / Å	*z* / Å
C(1)	2.097405	1.209458	0.000000
C(2)	1.394859	0.000000	0.000000
C(3)	0.000000	0.000000	0.000000
C(4)	–0.698714	1.207201	0.002727
C(5)	–0.002009	2.415625	0.002555
C(6)	1.392768	2.417592	–0.001006
H(2)	–0.548598	–0.952816	–0.002170
H(3)	–1.798435	1.206328	0.004051
H(5)	–0.552208	3.367481	0.003036
H(6)	1.944795	3.370271	–0.008120
B(1)	3.587836	1.207139	0.001403
O(1)	4.171418	2.374909	–0.216119
O(2)	4.177020	0.029434	0.164262
N(1)	6.336488	0.605753	–1.722908
C(7)	5.518970	–0.118868	0.584273
C(8)	6.603507	–0.126294	–0.505536
C(9)	5.565201	2.595774	–0.330041
C(10)	6.208456	2.044291	–1.602742
C(11)	7.162015	0.198186	–2.844103
H(11A)	6.932079	–0.887572	–3.044735
H(11B)	6.825489	0.788692	–3.743410
C(12)	8.675986	0.354113	–2.694786
H(11A)	8.938257	1.426159	–2.497116
H(11B)	9.036102	–0.243947	–1.816912
C(13)	9.378372	–0.114591	–3.950554
H(13A)	9.112369	–1.186444	–4.150561
H(13B)	9.016054	0.484277	–4.827875
C(14)	10.874249	0.020973	–3.829149
H(14A)	11.161415	1.086549	–3.657347
H(14B)	11.372437	–0.332161	–4.764142
H(14C)	11.257631	–0.586754	–2.974092
H(7A)	5.758898	0.621222	1.391182
H(7B)	5.517427	–1.146452	1.054779
H(8A)	7.556791	0.224733	–0.005964
H(8B)	6.762433	–1.203946	–0.803634
H(9A)	6.110582	2.276426	0.591973
H(9B)	5.622949	3.723306	–0.393439
H(10A)	7.215872	2.554948	–1.683518
H(10B)	5.582060	2.378089	–2.480815
Br(1)	2.356322	–1.650508	–0.003226

Table 41S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*).

Atom	d_{B-N} = 1.5 Å (*a*)			d_{B-N} = 1.6 Å (*b*)			d_{B-N} = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.194590	0.000000	2.144456	1.195362	0.000000	2.142725	1.197001	0.000000	2.140302
C(2)	0.000000	0.000000	1.399726	0.000000	0.000000	1.399827	0.000000	0.000000	1.399488
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.211126	0.017271	–0.699073	1.211419	0.013317	–0.699356	1.211412	–0.000938	–0.699799
C(5)	2.413648	0.037764	0.015737	2.414713	0.037080	0.014451	2.415730	0.006397	0.012134
C(6)	2.398725	0.023567	1.415223	2.399488	0.035083	1.413670	2.401370	0.008747	1.411489
H(2)	–0.954978	0.031739	1.927377	–0.952099	0.023822	1.931760	–0.950826	0.025818	1.933561
H(3)	–0.944851	0.000912	–0.546774	–0.944818	0.004176	–0.546710	–0.944428	0.010658	–0.547116
H(4)	1.217444	0.028289	–1.790098	1.217887	0.020118	–1.790495	1.216870	0.002998	–1.790932
H(5)	3.364276	0.070666	–0.519815	3.365010	0.068956	–0.521733	3.365575	0.022262	–0.525385
H(6)	3.343613	0.052456	1.959299	3.344471	0.084410	1.956713	3.346625	0.041847	1.955062
B(1)	1.183269	–0.039605	3.766401	1.183187	0.009417	3.759025	1.189546	–0.000773	3.747770
O(1)	–0.011116	0.720003	4.270996	–0.088241	0.594120	4.252844	–0.063763	0.536530	4.277074
O(2)	2.460405	0.481570	4.290723	2.402068	0.640822	4.280261	2.428030	0.559823	4.288300
N(1)	1.033118	–1.380765	4.421188	1.193532	–1.417627	4.482515	1.200725	–1.538488	4.472549
C(7)	–0.726210	–0.019578	5.228392	–0.637791	–0.137348	5.320898	–0.430373	–0.072958	5.486453
C(8)	–0.420101	–1.472210	4.847723	–0.198949	–1.579525	5.044157	–0.054175	–1.547937	5.306069
C(9)	2.543162	0.098388	5.637704	2.602570	0.224860	5.606028	2.798561	–0.045428	5.498564
C(10)	1.960583	–1.341001	5.645603	2.234598	–1.277474	5.586092	2.450941	–1.526679	5.312846
C(11)	1.400294	–2.552495	3.539907	1.542935	–2.562295	3.571175	1.213286	–2.679577	3.498737
H(11A)	0.797947	–2.459108	2.632258	0.830257	–2.525528	2.740637	0.336290	–2.551941	2.854936
H(11B)	2.444010	–2.392892	3.244610	2.527602	–2.332441	3.148257	2.093230	–2.537866	2.861977
C(12)	1.211266	–3.936811	4.159712	1.539494	–3.949011	4.215817	1.222334	–4.072523	4.128553
H(11A)	1.723667	–4.014520	5.129200	2.256283	–3.992518	5.049049	2.099130	–4.189233	4.782916
H(11B)	0.143910	–4.119594	4.351238	0.549064	–4.167974	4.640177	0.334252	–4.209266	4.763447
C(13)	1.739685	–5.030944	3.220256	1.893399	–5.035914	3.191125	1.246756	–5.170437	3.056199
H(13A)	1.323350	–4.875971	2.213103	1.204401	–4.964961	2.335600	0.373067	–5.052774	2.396732
H(13B)	2.830897	–4.925823	3.120679	2.900473	–4.841370	2.791083	2.133534	–5.034073	2.418235
C(14)	1.402876	–6.443674	3.703638	1.840023	–6.448754	3.778488	1.254401	–6.582246	3.648922
H(14A)	1.830418	–6.637990	4.698367	2.538414	–6.556209	4.621357	2.137566	–6.741885	4.284724
H(14B)	1.800321	–7.202032	3.015831	2.107980	–7.201626	3.024941	1.270342	–7.343626	2.857538
H(14C)	0.315140	–6.590850	3.772013	0.831590	–6.688111	4.146566	0.361218	–6.759358	4.265826
H(7A)	–0.393507	0.190733	6.263262	–0.271911	0.208826	6.305215	0.085268	0.371684	6.355968
H(7B)	–1.802682	0.204878	5.175593	–1.734609	–0.042592	5.325436	–1.512298	0.036648	5.652510
H(8A)	–0.555720	–2.232317	5.623497	–0.204565	–2.261774	5.900964	0.095532	–2.100702	6.240507
H(8B)	–0.994815	–1.747034	3.956337	–0.820467	–1.996893	4.244115	–0.831441	–2.047714	4.718678
H(9A)	1.955397	0.766792	6.290714	1.969790	0.785992	6.314891	2.269516	0.387566	6.365943
H(9B)	3.587705	0.116568	5.981423	3.652044	0.375630	5.898151	3.877226	0.083849	5.671593
H(10A)	1.400702	–1.609015	6.547166	1.844690	–1.673228	6.529714	2.306783	–2.084282	6.245288
H(10B)	2.754360	–2.075017	5.491580	3.110371	–1.862549	5.292708	3.240403	–2.010430	4.728272

Table 42S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	d_{B-N} = 1.8 Å (*a*)			d_{B-N} = 1.9 Å (*b*)			d_{B-N} = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.198728	0.000000	2.137919	1.198350	0.000000	2.138452	1.198727	0.000000	2.137881
C(2)	0.000000	0.000000	1.399529	0.000000	0.000000	1.399056	0.000000	0.000000	1.398902
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.210533	0.007205	–0.700991	1.211929	0.003837	–0.699191	1.212295	0.005090	–0.698563
C(5)	2.415968	0.021443	0.009036	2.417022	0.013027	0.011650	2.417676	0.013764	0.012046
C(6)	2.402770	0.019764	1.407992	2.403739	0.011261	1.410666	2.404891	0.010303	1.410774
H(2)	–0.949798	0.015215	1.935471	–0.950037	0.016962	1.934554	–0.949856	0.015217	1.934575
H(3)	–0.944738	0.005320	–0.546649	–0.944152	0.006465	–0.547453	–0.943970	0.005105	–0.547672
H(4)	1.214362	0.011509	–1.792130	1.217174	0.007613	–1.790334	1.217790	0.009023	–1.789708
H(5)	3.364971	0.043750	–0.529640	3.366256	0.029506	–0.526732	3.366690	0.029362	–0.526660
H(6)	3.348275	0.054390	1.950992	3.348391	0.036774	1.955275	3.349300	0.030144	1.955862
B(1)	1.198427	–0.021992	3.738474	1.190408	–0.032653	3.732547	1.188936	–0.042742	3.726159
O(1)	–0.070802	0.391363	4.307991	–0.059452	0.381709	4.314944	–0.058497	0.319257	4.328735
O(2)	2.418220	0.525160	4.302214	2.433030	0.384343	4.328133	2.432007	0.295259	4.338309
N(1)	1.289204	–1.673292	4.449086	1.188444	–1.795676	4.440887	1.171760	–1.913070	4.434383
C(7)	–0.394389	–0.284189	5.496383	–0.412196	–0.301530	5.492185	–0.471789	–0.437044	5.441736
C(8)	0.037115	–1.739025	5.266643	–0.064441	–1.778199	5.244734	–0.135423	–1.903882	5.126063
C(9)	2.807266	–0.101664	5.497498	2.771714	–0.295524	5.511370	2.687665	–0.358558	5.558277
C(10)	2.532508	–1.596561	5.280010	2.429157	–1.773617	5.263435	2.344082	–1.846023	5.340202
C(11)	1.357221	–2.771893	3.439808	1.198289	–2.870399	3.412396	1.284975	–2.968450	3.399971
H(11A)	0.477005	–2.663753	2.795675	0.324775	–2.703528	2.770788	0.465157	–2.808767	2.688495
H(11B)	2.231368	–2.568254	2.810958	2.081829	–2.701042	2.785312	2.214754	–2.776811	2.849665
C(12)	1.430549	–4.186551	4.017271	1.195723	–4.300797	3.957167	1.263159	–4.408075	3.922879
H(11A)	2.301850	–4.279012	4.683316	2.071512	–4.459329	4.604833	2.073960	–4.553594	4.653567
H(11B)	0.541180	–4.391874	4.631910	0.306487	–4.463529	4.585135	0.320611	–4.598025	4.459124
C(13)	1.531550	–5.242194	2.908049	1.211078	–5.338024	2.826447	1.416028	–5.430729	2.789903
H(13A)	0.665782	–5.145086	2.234694	0.338481	–5.176084	2.174746	0.601757	–5.289315	2.062071
H(13B)	2.422041	–5.036940	2.294094	2.099053	–5.173270	2.196629	2.351786	–5.230129	2.245144
C(14)	1.601102	–6.672864	3.449214	1.206988	–6.781033	3.338639	1.412697	–6.879543	3.285461
H(14A)	2.479931	–6.811091	4.096011	2.088153	–6.982576	3.965371	2.244729	–7.063329	3.981069
H(14B)	1.669958	–7.402959	2.631480	1.217613	–7.497888	2.506418	1.513479	–7.585469	2.449836
H(14C)	0.707490	–6.917504	4.041977	0.311983	–6.984856	3.944669	0.477279	–7.117043	3.813127
H(7A)	0.108321	0.153572	6.376122	0.113402	0.095728	6.376756	0.014589	–0.102977	6.373307
H(7B)	–1.478334	–0.225508	5.673369	–1.490883	–0.185790	5.671704	–1.556046	–0.313749	5.576745
H(8A)	0.191430	–2.309520	6.190900	0.038741	–2.358486	6.171515	–0.136373	–2.538280	6.024499
H(8B)	–0.722440	–2.247032	4.662593	–0.853036	–2.233180	4.635211	–0.880488	–2.294889	4.423372
H(9A)	2.258712	0.288408	6.372287	2.234414	0.103447	6.388051	2.104702	0.075454	6.386441
H(9B)	3.878432	0.072463	5.676431	3.847867	–0.177803	5.704302	3.751633	–0.244889	5.809985
H(10A)	2.429235	–2.168756	6.210405	2.312766	–2.350941	6.190465	2.160969	–2.375048	6.286467
H(10B)	3.347628	–2.029545	4.690293	3.227485	–2.229618	4.667526	3.184162	–2.332645	4.832631

Table 43S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	d_{B-N} = 2.1 Å (*a*)			d_{B-N} = 2.2 Å (*b*)			d_{B-N} = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.199839	0.000000	2.136316	1.200267	0.000000	2.135735	1.201096	0.000000	2.134601
C(2)	0.000000	0.000000	1.398612	0.000000	0.000000	1.398375	0.000000	0.000000	1.398140
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.212102	0.002658	–0.699008	1.212352	0.002099	–0.698677	1.212203	–0.002523	–0.698963
C(5)	2.418129	0.009076	0.010491	2.418665	0.006916	0.010506	2.418930	–0.002977	0.009414
C(6)	2.406068	0.007700	1.408983	2.406991	0.006331	1.408787	2.407893	–0.000926	1.407493
H(2)	–0.949201	0.012247	1.935192	–0.948957	0.010188	1.935211	–0.948679	0.011695	1.935299
H(3)	–0.944015	0.005303	–0.547490	–0.943923	0.004768	–0.547589	–0.943979	0.006428	–0.547436
H(4)	1.216848	0.005238	–1.790144	1.217147	0.004427	–1.789835	1.216452	–0.000856	–1.790129
H(5)	3.366761	0.021211	–0.528847	3.367146	0.016798	–0.529091	3.367176	0.000934	–0.530616
H(6)	3.350589	0.026041	1.953686	3.351419	0.022214	1.953543	3.352388	0.010223	1.952017
B(1)	1.193047	–0.038442	3.720311	1.192893	–0.031862	3.716470	1.195277	–0.016058	3.713131
O(1)	–0.058925	0.242333	4.328286	–0.060841	0.189211	4.325207	–0.052645	0.188723	4.320115
O(2)	2.431881	0.271030	4.338190	2.428675	0.242528	4.336605	2.436504	0.200352	4.329309
N(1)	1.214390	–2.001805	4.465129	1.235570	–2.074034	4.533606	1.202190	–2.118640	4.645387
C(7)	–0.396705	–0.479718	5.490147	–0.387381	–0.517182	5.501643	–0.362716	–0.447565	5.541783
C(8)	–0.048028	–1.956871	5.224662	–0.030123	–1.998707	5.274174	–0.042197	–1.949282	5.399249
C(9)	2.744490	–0.415661	5.528076	2.732466	–0.414119	5.547292	2.739278	–0.428840	5.556401
C(10)	2.435121	–1.906610	5.287590	2.448151	–1.917628	5.348860	2.434339	–1.934217	5.415713
C(11)	1.262749	–3.061273	3.436076	1.301578	–3.161490	3.540965	1.215408	–3.270249	3.729802
H(11A)	0.398428	–2.908308	2.776868	0.439660	–3.040617	2.871070	0.340704	–3.172407	3.072006
H(11B)	2.154636	–2.873268	2.824289	2.195693	–2.984777	2.928103	2.099629	–3.163313	3.086225
C(12)	1.277114	–4.499602	3.965253	1.328517	–4.585113	4.111518	1.217093	–4.653993	4.394182
H(11A)	2.138224	–4.641107	4.636873	2.183822	–4.694120	4.796872	2.090964	–4.744689	5.058504
H(11B)	0.375038	–4.684349	4.569042	0.422268	–4.762417	4.711604	0.326418	–4.758260	5.033785
C(13)	1.347038	–5.529171	2.830400	1.424063	–5.647504	3.009935	1.239983	–5.792804	3.368087
H(13A)	0.488296	–5.384176	2.156328	0.571824	–5.533738	2.321488	0.370924	–5.694836	2.698342
H(13B)	2.247074	–5.338661	2.225175	2.328948	–5.464478	2.409415	2.131388	–5.687148	2.729669
C(14)	1.364786	–6.975801	3.332250	1.452994	–7.078609	3.554270	1.234685	–7.183144	4.010177
H(14A)	2.234308	–7.160427	3.980166	2.317859	–7.234396	4.215858	2.111235	–7.323986	4.659637
H(14B)	1.413835	–7.686743	2.496162	1.518487	–7.813194	2.739934	1.253029	–7.974232	3.247924
H(14C)	0.460001	–7.205224	3.914160	0.544956	–7.301296	4.133772	0.335569	–7.332650	4.625973
H(7A)	0.124994	–0.094038	6.380101	0.129305	–0.106466	6.382322	0.177718	0.006036	6.385266
H(7B)	–1.475421	–0.371010	5.671164	–1.466985	–0.413359	5.679458	–1.436248	–0.312168	5.733544
H(8A)	0.004415	–2.536576	6.159403	0.003522	–2.548979	6.229118	–0.009875	–2.432676	6.391172
H(8B)	–0.829161	–2.395607	4.593005	–0.806879	–2.453104	4.647773	–0.845719	–2.421365	4.821336
H(9A)	2.184884	–0.019062	6.389544	2.160736	0.000654	6.391090	2.185609	0.022822	6.392321
H(9B)	3.813924	–0.280044	5.742603	3.797872	–0.258833	5.767670	3.809374	–0.282792	5.759215
H(10A)	2.344158	–2.460304	6.234871	2.374812	–2.437619	6.318165	2.392422	–2.413445	6.409269
H(10B)	3.257132	–2.347947	4.712448	3.282247	–2.359069	4.791045	3.250305	–2.401473	4.851501

Table 44S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	d_{B-N} = 2.4 Å (*a*)			d_{B-N} = 2.5 Å (*b*)			d_{B-N} = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.201526	0.000000	2.133967	1.201791	0.000000	2.133321	1.202005	0.000000	2.132892
C(2)	0.000000	0.000000	1.397987	0.000000	0.000000	1.397863	0.000000	0.000000	1.397794
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.212190	0.003838	–0.698974	1.212227	–0.002310	–0.698896	1.212204	0.001515	–0.698897
C(5)	2.419112	0.007955	0.009039	2.419307	–0.004048	0.008850	2.419363	0.002463	0.008678
C(6)	2.408484	0.005921	1.406971	2.408926	–0.002228	1.406664	2.409249	0.001727	1.406426
H(2)	–0.948666	0.004968	1.935181	–0.948562	0.007255	1.935132	–0.948631	0.002715	1.934939
H(3)	–0.944025	0.002038	–0.547353	–0.944042	0.004378	–0.547280	–0.944100	0.001649	–0.547158
H(4)	1.216237	0.005800	–1.790144	1.216204	–0.001446	–1.790069	1.216109	0.002636	–1.790069
H(5)	3.367206	0.016330	–0.531168	3.367366	–0.002741	–0.531451	3.367376	0.006123	–0.531658
H(6)	3.353049	0.015565	1.951277	3.353535	0.003262	1.950878	3.353992	0.005601	1.950369
B(1)	1.196049	–0.030996	3.710788	1.196274	–0.005506	3.709629	1.196459	–0.015623	3.708494
O(1)	–0.050704	0.132113	4.317260	–0.049269	0.144683	4.308914	–0.048139	0.099362	4.306781
O(2)	2.438083	0.137734	4.325686	2.438083	0.141885	4.317458	2.437405	0.095085	4.315307
N(1)	1.197234	–2.196797	4.744860	1.189204	–2.174758	4.952325	1.187732	–2.212643	5.098828
C(7)	–0.349365	–0.460237	5.565269	–0.342443	–0.344792	5.603252	–0.335737	–0.326896	5.625928
C(8)	–0.041216	–1.969738	5.485877	–0.048204	–1.857094	5.657055	–0.049746	–1.834963	5.768287
C(9)	2.734027	–0.456123	5.573653	2.722253	–0.349714	5.613064	2.715717	–0.333681	5.635658
C(10)	2.432526	–1.966610	5.489940	2.423881	–1.861214	5.663576	2.423193	–1.840751	5.774896
C(11)	1.200052	–3.394744	3.894890	1.188947	–3.474099	4.268561	1.186283	–3.557621	4.514513
H(11A)	0.322178	–3.329886	3.236554	0.310021	–3.496547	3.608279	0.308293	–3.628145	3.855805
H(11B)	2.081375	–3.328719	3.241260	2.070482	–3.498758	3.611818	2.068958	–3.632652	3.862546
C(12)	1.199010	–4.743551	4.629600	1.185643	–4.716908	5.172392	1.179696	–4.734032	5.503950
H(11A)	2.077802	–4.805118	5.290875	2.066719	–4.695867	5.833081	2.057551	–4.666159	6.165815
H(11B)	0.312907	–4.808798	5.280762	0.301819	–4.694081	5.829343	0.292683	–4.666038	6.153532
C(13)	1.206647	–5.933312	3.662943	1.186041	–6.022113	4.368166	1.184351	–6.092148	4.792924
H(13A)	0.332191	–5.864142	2.996553	0.306656	–6.038467	3.704820	0.311672	–6.152981	4.123191
H(13B)	2.092882	–5.865362	3.012184	2.067551	–6.039797	3.707684	2.072390	–6.157362	4.144135
C(14)	1.199500	–7.289532	4.374314	1.183624	–7.274554	5.249620	1.170238	–7.281061	5.758153
H(14A)	2.082815	–7.403973	5.019788	2.070796	–7.303824	5.899288	2.048992	–7.265287	6.419694
H(14B)	1.203138	–8.118233	3.652849	1.183275	–8.190350	4.642452	1.177417	–8.236466	5.215403
H(14C)	0.306890	–7.400971	5.007415	0.294924	–7.301816	5.897286	0.273396	–7.264543	6.394931
H(7A)	0.197492	0.026095	6.385050	0.207518	0.208006	6.376569	0.215223	0.266642	6.366846
H(7B)	–1.420799	–0.312447	5.758802	–1.412492	–0.175369	5.786143	–1.405069	–0.145557	5.801270
H(8A)	–0.020652	–2.402780	6.502547	–0.046830	–2.193335	6.711285	–0.064956	–2.102733	6.843147
H(8B)	–0.851935	–2.458036	4.931584	–0.862493	–2.381938	5.142269	–0.865043	–2.384107	5.280675
H(9A)	2.181854	0.026097	6.392349	2.169093	0.203614	6.383750	2.162891	0.261173	6.374161
H(9B)	3.804041	–0.304303	5.771915	3.791617	–0.183186	5.802518	3.784739	–0.156719	5.817247
H(10A)	2.410938	–2.401989	6.505617	2.416441	–2.198679	6.717400	2.431986	–2.109617	6.849576
H(10B)	3.246785	–2.450271	4.936732	3.239337	–2.387558	5.152161	3.238713	–2.392619	5.290710

Table 45S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	d_{B-N} = 2.7 Å (*a*)			d_{B-N} = 2.8 Å (*b*)			d_{B-N} = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.201526	0.000000	2.133967	1.201791	0.000000	2.133321	1.202005	0.000000	2.132892
C(2)	0.000000	0.000000	1.397987	0.000000	0.000000	1.397863	0.000000	0.000000	1.397794
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.212190	0.003838	–0.698974	1.212227	–0.002310	–0.698896	1.212204	0.001515	–0.698897
C(5)	2.419112	0.007955	0.009039	2.419307	–0.004048	0.008850	2.419363	0.002463	0.008678
C(6)	2.408484	0.005921	1.406971	2.408926	–0.002228	1.406664	2.409249	0.001727	1.406426
H(2)	–0.948666	0.004968	1.935181	–0.948562	0.007255	1.935132	–0.948631	0.002715	1.934939
H(3)	–0.944025	0.002038	–0.547353	–0.944042	0.004378	–0.547280	–0.944100	0.001649	–0.547158
H(4)	1.216237	0.005800	–1.790144	1.216204	–0.001446	–1.790069	1.216109	0.002636	–1.790069
H(5)	3.367206	0.016330	–0.531168	3.367366	–0.002741	–0.531451	3.367376	0.006123	–0.531658
H(6)	3.353049	0.015565	1.951277	3.353535	0.003262	1.950878	3.353992	0.005601	1.950369
B(1)	1.196049	–0.030996	3.710788	1.196274	–0.005506	3.709629	1.196459	–0.015623	3.708494
O(1)	–0.050704	0.132113	4.317260	–0.049269	0.144683	4.308914	–0.048139	0.099362	4.306781
O(2)	2.438083	0.137734	4.325686	2.438083	0.141885	4.317458	2.437405	0.095085	4.315307
N(1)	1.197234	–2.196797	4.744860	1.189204	–2.174758	4.952325	1.187732	–2.212643	5.098828
C(7)	–0.349365	–0.460237	5.565269	–0.342443	–0.344792	5.603252	–0.335737	–0.326896	5.625928
C(8)	–0.041216	–1.969738	5.485877	–0.048204	–1.857094	5.657055	–0.049746	–1.834963	5.768287
C(9)	2.734027	–0.456123	5.573653	2.722253	–0.349714	5.613064	2.715717	–0.333681	5.635658
C(10)	2.432526	–1.966610	5.489940	2.423881	–1.861214	5.663576	2.423193	–1.840751	5.774896
C(11)	1.200052	–3.394744	3.894890	1.188947	–3.474099	4.268561	1.186283	–3.557621	4.514513
H(11A)	0.322178	–3.329886	3.236554	0.310021	–3.496547	3.608279	0.308293	–3.628145	3.855805
H(11B)	2.081375	–3.328719	3.241260	2.070482	–3.498758	3.611818	2.068958	–3.632652	3.862546
C(12)	1.199010	–4.743551	4.629600	1.185643	–4.716908	5.172392	1.179696	–4.734032	5.503950
H(11A)	2.077802	–4.805118	5.290875	2.066719	–4.695867	5.833081	2.057551	–4.666159	6.165815
H(11B)	0.312907	–4.808798	5.280762	0.301819	–4.694081	5.829343	0.292683	–4.666038	6.153532
C(13)	1.206647	–5.933312	3.662943	1.186041	–6.022113	4.368166	1.184351	–6.092148	4.792924
H(13A)	0.332191	–5.864142	2.996553	0.306656	–6.038467	3.704820	0.311672	–6.152981	4.123191
H(13B)	2.092882	–5.865362	3.012184	2.067551	–6.039797	3.707684	2.072390	–6.157362	4.144135
C(14)	1.199500	–7.289532	4.374314	1.183624	–7.274554	5.249620	1.170238	–7.281061	5.758153
H(14A)	2.082815	–7.403973	5.019788	2.070796	–7.303824	5.899288	2.048992	–7.265287	6.419694
H(14B)	1.203138	–8.118233	3.652849	1.183275	–8.190350	4.642452	1.177417	–8.236466	5.215403
H(14C)	0.306890	–7.400971	5.007415	0.294924	–7.301816	5.897286	0.273396	–7.264543	6.394931
H(7A)	0.197492	0.026095	6.385050	0.207518	0.208006	6.376569	0.215223	0.266642	6.366846
H(7B)	–1.420799	–0.312447	5.758802	–1.412492	–0.175369	5.786143	–1.405069	–0.145557	5.801270
H(8A)	–0.020652	–2.402780	6.502547	–0.046830	–2.193335	6.711285	–0.064956	–2.102733	6.843147
H(8B)	–0.851935	–2.458036	4.931584	–0.862493	–2.381938	5.142269	–0.865043	–2.384107	5.280675
H(9A)	2.181854	0.026097	6.392349	2.169093	0.203614	6.383750	2.162891	0.261173	6.374161
H(9B)	3.804041	–0.304303	5.771915	3.791617	–0.183186	5.802518	3.784739	–0.156719	5.817247
H(10A)	2.410938	–2.401989	6.505617	2.416441	–2.198679	6.717400	2.431986	–2.109617	6.849576
H(10B)	3.246785	–2.450271	4.936732	3.239337	–2.387558	5.152161	3.238713	–2.392619	5.290710

Table 46S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	d_{B-N} = 3.0 Å (*a*)			d_{B-N} = 3.1 Å (*b*)			d_{B-N} = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.201844	0.000000	2.132286	1.203246	0.000000	2.130365	1.203536	0.000000	2.129843
C(2)	0.000000	0.000000	1.397502	0.000000	0.000000	1.397577	0.000000	0.000000	1.397525
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.213107	–0.004248	–0.697515	1.212155	–0.003461	–0.698934	1.212262	0.002443	–0.698774
C(5)	2.420085	–0.009971	0.010556	2.419922	–0.006715	0.007558	2.420192	0.004066	0.007483
C(6)	2.410207	–0.009501	1.408265	2.411028	–0.004242	1.405092	2.411545	0.002800	1.404965
H(2)	–0.948742	0.005857	1.934358	–0.948321	0.002303	1.935262	–0.948194	–0.003054	1.935470
H(3)	–0.943850	0.002313	–0.547378	–0.944204	0.002071	–0.546829	–0.944146	–0.001061	–0.546891
H(4)	1.218143	–0.003515	–1.788650	1.215548	–0.003565	–1.790053	1.215614	0.002874	–1.789888
H(5)	3.368212	–0.014052	–0.529478	3.367551	–0.009782	–0.533296	3.367702	0.006065	–0.533546
H(6)	3.354826	–0.015140	1.952503	3.355950	–0.005159	1.948728	3.356374	0.002101	1.948769
B(1)	1.190043	0.008056	3.705064	1.198721	0.015226	3.702028	1.198677	–0.005512	3.699991
O(1)	–0.043215	0.151237	4.300601	–0.034673	0.036501	4.313336	–0.031425	–0.017534	4.319522
O(2)	2.416299	–0.067797	4.326966	2.428894	0.037061	4.319946	2.425496	–0.006559	4.326469
N(1)	0.979677	–2.041267	5.885894	1.191125	–1.964184	6.087793	1.200564	–1.982116	6.216543
C(7)	–0.330866	0.102875	5.692067	–0.301780	0.047119	5.711754	–0.293593	0.022913	5.720325
C(8)	–0.205557	–1.308305	6.296051	–0.056600	–1.298674	6.420213	–0.052756	–1.297038	6.481246
C(9)	2.658961	–0.167670	5.724956	2.686511	0.047771	5.720148	2.684059	0.031813	5.727942
C(10)	2.269707	–1.534278	6.320923	2.437063	–1.298151	6.426511	2.448660	–1.290228	6.487492
C(11)	0.845620	–3.496606	5.963682	1.192277	–3.406165	6.328690	1.202835	–3.398488	6.574130
H(11A)	–0.056786	–3.775829	5.398932	0.307792	–3.825767	5.825494	0.326105	–3.862582	6.096627
H(11B)	1.698572	–3.936088	5.424848	2.071025	–3.826165	5.815704	2.089882	–3.856253	6.109889
C(12)	0.767564	–4.107325	7.374103	1.200177	–3.863922	7.798501	1.192546	–3.731936	8.077326
H(11A)	1.669532	–3.837386	7.945664	2.085291	–3.454533	8.310394	2.069301	–3.277298	8.564870
H(11B)	–0.087669	–3.675397	7.917334	0.320097	–3.455344	8.319696	0.304402	–3.284064	8.550277
C(13)	0.627291	–5.633503	7.342621	1.201808	–5.391019	7.930057	1.195908	–5.242316	8.339578
H(13A)	–0.271178	–5.902847	6.764433	0.315720	–5.799138	7.417859	0.325514	–5.698577	7.841168
H(13B)	1.482303	–6.064426	6.797409	2.076636	–5.798941	7.398665	2.086494	–5.689433	7.869363
C(14)	0.542958	–6.262331	8.736540	1.217681	–5.874584	9.383262	1.174184	–5.598061	9.828987
H(14A)	1.442841	–6.037499	9.327935	2.112928	–5.514101	9.911195	2.051062	–5.183849	10.348232
H(14B)	0.446309	–7.355347	8.677166	1.215236	–6.972029	9.439978	1.178987	–6.686450	9.980569
H(14C)	–0.325483	–5.879173	9.292448	0.337354	–5.509101	9.932464	0.275554	–5.195656	10.319500
H(7A)	0.274539	0.834672	6.238980	0.239795	0.864591	6.200617	0.243570	0.856800	6.185194
H(7B)	–1.377196	0.419683	5.802973	–1.371061	0.277802	5.816861	–1.363688	0.252426	5.820460
H(8A)	–0.297234	–1.193155	7.397947	–0.178325	–1.099852	7.508103	–0.205001	–1.048766	7.555794
H(8B)	–1.070714	–1.896875	5.962551	–0.863393	–1.985750	6.130883	–0.852587	–1.997874	6.204485
H(9A)	2.181734	0.660357	6.261491	2.141445	0.865096	6.205366	2.141561	0.861872	6.193544
H(9B)	3.742310	–0.043311	5.860244	3.755001	0.278702	5.832558	3.752703	0.266801	5.830883
H(10A)	2.360150	–1.439076	7.425123	2.553006	–1.099712	7.515059	2.594679	–1.041194	7.562838
H(10B)	3.020791	–2.268958	6.001158	3.245430	–1.985128	6.141328	3.253609	–1.986442	6.214142

Table 47S. Cartesian coordinates for azaester derivative (X = H, R = Bu) with B-N distance constrained to 3.3 Å.

Atom	d_{B-N} = 3.3 Å (*a*)		
	x / Å	*y* / Å	*z* / Å
C(1)	1.204378	0.000000	2.128969
C(2)	0.000000	0.000000	1.397580
C(3)	0.000000	0.000000	0.000000
C(4)	1.212103	0.004439	–0.699039
C(5)	2.420287	0.009896	0.006645
C(6)	2.412160	0.009804	1.403971
H(2)	–0.947965	–0.005454	1.935988
H(3)	–0.944170	–0.002020	–0.546722
H(4)	1.215332	0.004820	–1.790134
H(5)	3.367532	0.014619	–0.534761
H(6)	3.357143	0.014877	1.947566
B(1)	1.199621	0.008868	3.697760
O(1)	–0.018447	–0.088871	4.334241
O(2)	2.423527	0.084852	4.326901
N(1)	1.337836	–1.849602	6.421174
C(7)	–0.275191	0.022041	5.734902
C(8)	0.043071	–1.218924	6.599383
C(9)	2.686981	0.213824	5.722804
C(10)	2.547216	–1.063419	6.579923
C(11)	1.431745	–3.219333	6.914004
H(11A)	0.571016	–3.776714	6.513200
H(11B)	2.331828	–3.672343	6.469701
C(12)	1.479596	–3.400883	8.442846
H(11A)	2.343440	–2.854377	8.852673
H(11B)	0.581997	–2.952992	8.897430
C(13)	1.574840	–4.875079	8.849484
H(13A)	0.699015	–5.416226	8.456813
H(13B)	2.455316	–5.326915	8.364752
C(14)	1.664890	–5.083475	10.364134
H(14A)	2.550164	–4.581167	10.781355
H(14B)	1.735327	–6.150415	10.617763
H(14C)	0.779532	–4.676305	10.874564
H(7A)	0.202609	0.921231	6.138267
H(7B)	–1.358214	0.183925	5.825770
H(8A)	–0.151910	–0.891201	7.646325
H(8B)	–0.708804	–1.986998	6.369422
H(9A)	2.098142	1.035148	6.145581
H(9B)	3.739532	0.519706	5.800879
H(10A)	2.716272	–0.715246	7.624736
H(10B)	3.385785	–1.730882	6.335659

Table 48S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 1.5 Å (*a*), 1.6 Å (*b*) and 1.7 Å (*c*).

Atom	d_{B-N} = 1.5 Å (*a*)			d_{B-N} = 1.6 Å (*b*)			d_{B-N} = 1.7 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.196789	0.000000	2.139632	1.199383	0.000000	2.139079	1.199640	0.000000	2.137987
C(2)	0.000000	0.000000	1.400077	0.000000	0.000000	1.399264	0.000000	0.000000	1.399321
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.210629	–0.004992	–0.700170	1.211518	–0.005273	–0.699974	1.210998	0.006766	–0.700645
C(5)	2.416026	–0.001501	0.010432	2.416117	–0.004456	0.010521	2.416259	0.018640	0.008994
C(6)	2.402330	0.003221	1.409691	2.403337	–0.000969	1.410277	2.403850	0.015755	1.408448
H(2)	–0.949989	0.028910	1.935880	–0.952252	0.034024	1.931881	–0.950533	0.015962	1.934784
H(3)	–0.944651	0.011642	–0.546822	–0.944474	0.013935	–0.547104	–0.944744	0.005106	–0.546759
H(4)	1.215575	–0.002284	–1.791269	1.216063	–0.000572	–1.791087	1.214863	0.011073	–1.791780
H(5)	3.365562	0.010240	–0.527899	3.365599	0.004886	–0.527865	3.365291	0.038689	–0.529862
H(6)	3.351116	0.041014	1.949274	3.348853	0.029010	1.953835	3.349789	0.048865	1.951192
B(1)	1.200229	–0.041607	3.756166	1.187732	–0.028824	3.749262	1.195604	–0.073754	3.741188
O(1)	–0.133776	0.284087	4.349612	0.027716	0.669619	4.303071	–0.040242	0.418475	4.331012
O(2)	2.304258	0.758923	4.306781	2.490991	0.335212	4.354726	2.453841	0.366259	4.355183
N(1)	1.463498	–1.412532	4.305031	0.984225	–1.502869	4.337290	1.161134	–1.681546	4.292382
H(1)	1.928821	–1.991636	3.608674	0.625092	–2.124129	3.616535	0.985060	–2.313950	3.516882
C(7)	0.124210	–2.011340	4.627935	–0.039381	–1.366487	5.439397	0.020035	–1.725292	5.263296
C(8)	–0.653531	–0.778325	5.106119	–0.220815	0.158276	5.589041	–0.306489	–0.244296	5.541473
C(9)	2.395651	–1.241748	5.494587	2.343449	–1.957732	4.765479	2.521687	–1.918356	4.853426
C(10)	2.539856	0.289991	5.611776	3.004906	–0.648588	5.214589	2.971028	–0.523534	5.311054
H(7A)	0.217922	–2.831143	5.349349	0.303842	–1.878067	6.346040	0.286054	–2.305833	6.155204
H(7B)	–0.290734	–2.392685	3.688115	–0.966875	–1.835226	5.093300	–0.825213	–2.209161	4.761324
H(8A)	–0.508862	–0.617879	6.192619	0.483218	0.565938	6.335902	0.308443	0.147148	6.371283
H(8B)	–1.733797	–0.901664	4.931507	–1.242335	0.409527	5.906879	–1.363285	–0.116118	5.815243
H(9A)	1.972517	–1.733445	6.377276	2.282766	–2.740540	5.531100	2.506850	–2.679171	5.644107
H(9B)	3.349245	–1.716926	5.241698	2.845205	–2.355241	3.875735	3.155916	–2.264885	4.029371
H(10A)	1.807379	0.696265	6.331287	2.769263	–0.432217	6.274773	2.597244	–0.304036	6.328950
H(10B)	3.547770	0.574881	5.944274	4.100442	–0.711047	5.126680	4.068717	–0.454448	5.340515

Table 49S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 1.8 Å (*a*), 1.9 Å (*b*) and 2.0 Å (*c*).

Atom	d_{B-N} = 1.8 Å (*a*)			d_{B-N} = 1.9 Å (*b*)			d_{B-N} = 2.0 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.199949	0.000000	2.137135	1.200056	0.000000	2.136669	1.199786	0.000000	2.136732
C(2)	0.000000	0.000000	1.399166	0.000000	0.000000	1.398947	0.000000	0.000000	1.398698
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.211082	0.007769	–0.700496	1.211363	0.008968	–0.700074	1.211932	0.003168	–0.699176
C(5)	2.416679	0.019566	0.008807	2.417136	0.020914	0.009164	2.417752	0.009815	0.010409
C(6)	2.404607	0.015734	1.408015	2.405221	0.016192	1.408111	2.405794	0.008328	1.409083
H(2)	–0.950085	0.013026	1.935149	–0.949892	0.010182	1.935074	–0.949804	0.013572	1.934639
H(3)	–0.944648	0.003974	–0.546863	–0.944511	0.002622	–0.547009	–0.944268	0.004607	–0.547291
H(4)	1.214875	0.012028	–1.791644	1.215348	0.013073	–1.791233	1.216629	0.006117	–1.790352
H(5)	3.365534	0.039069	–0.530315	3.365903	0.039998	–0.530050	3.366630	0.022167	–0.528725
H(6)	3.350191	0.044622	1.951270	3.350453	0.041044	1.951889	3.350847	0.028147	1.953152
B(1)	1.196714	–0.073909	3.734361	1.196304	–0.069417	3.728429	1.192591	–0.045013	3.724453
O(1)	–0.047686	0.349222	4.337222	–0.050579	0.298178	4.339828	–0.057190	0.284209	4.332625
O(2)	2.448897	0.330813	4.353079	2.445571	0.290186	4.350906	2.438643	0.279380	4.343577
N(1)	1.182601	–1.780372	4.306888	1.188517	–1.870039	4.334811	1.185578	–1.921722	4.415765
H(1)	1.075148	–2.419758	3.525871	1.124422	–2.524966	3.563211	1.183435	–2.619511	3.681071
C(7)	–0.006452	–1.833397	5.202379	–0.029484	–1.906280	5.177155	–0.075661	–1.926454	5.178670
C(8)	–0.344127	–0.360999	5.513768	–0.367243	–0.435424	5.497673	–0.414923	–0.452332	5.477459
C(9)	2.513670	–1.940760	4.944190	2.494000	–1.969396	5.021683	2.446404	–1.934727	5.179041
C(10)	2.910287	–0.518963	5.373207	2.861467	–0.528029	5.416809	2.788264	–0.463651	5.486908
H(7A)	0.192705	–2.440624	6.095118	0.116024	–2.521589	6.076068	–0.005652	–2.534468	6.093129
H(7B)	–0.827405	–2.290570	4.638209	–0.835234	–2.344483	4.576639	–0.851279	–2.353545	4.531702
H(8A)	0.239717	0.005369	6.376196	0.196540	–0.081359	6.377637	0.114264	–0.097701	6.377786
H(8B)	–1.409660	–0.244926	5.757645	–1.437471	–0.320237	5.720452	–1.492337	–0.331863	5.659131
H(9A)	2.487604	–2.665474	5.768940	2.459372	–2.658197	5.877716	2.375038	–2.548780	6.089391
H(9B)	3.203801	–2.300385	4.172056	3.220601	–2.345263	4.291654	3.221156	–2.358734	4.528999
H(10A)	2.469627	–0.267199	6.355162	2.379097	–0.245103	6.368992	2.254959	–0.112151	6.386030
H(10B)	4.002322	–0.428632	5.467875	3.947694	–0.426035	5.553622	3.864944	–0.346866	5.675237

Table 50S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 2.1 Å (*a*), 2.2 Å (*b*) and 2.3 Å (*c*).

Atom	d_{B-N} = 2.1 Å (*a*)			d_{B-N} = 2.2 Å (*b*)			d_{B-N} = 2.3 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.199261	0.000000	2.137639	1.200737	0.000000	2.135044	1.201157	0.000000	2.134315
C(2)	0.000000	0.000000	1.398588	0.000000	0.000000	1.398271	0.000000	0.000000	1.398083
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.206762	0.017574	–0.696377	1.212084	0.002054	–0.699053	1.212112	0.003046	–0.699046
C(5)	2.414126	0.020601	0.010854	2.418565	0.006710	0.009634	2.418830	0.007606	0.009250
C(6)	2.404620	0.012411	1.409209	2.407289	0.005931	1.407835	2.407908	0.005649	1.407276
H(2)	–0.949514	–0.001228	1.935002	–0.949196	0.008491	1.934926	–0.949019	0.005928	1.934926
H(3)	–0.944257	0.004153	–0.547269	–0.944187	0.003355	–0.547292	–0.944181	0.001986	–0.547244
H(4)	1.209502	0.025393	–1.787544	1.216417	0.003877	–1.790246	1.216251	0.004892	–1.790240
H(5)	3.361953	0.035047	–0.529981	3.367067	0.015118	–0.530085	3.367184	0.015538	–0.530666
H(6)	3.350089	0.028616	1.952508	3.352149	0.019515	1.952023	3.352705	0.015907	1.951439
B(1)	1.288861	–0.244434	3.334336	1.194878	–0.030626	3.716030	1.195716	–0.029314	3.712976
O(1)	0.049958	0.169393	4.420712	–0.056401	0.199086	4.324035	–0.052367	0.171483	4.319722
O(2)	2.539451	0.211252	4.285242	2.436647	0.223538	4.333445	2.439341	0.173138	4.328345
N(1)	1.073207	–1.987120	4.486091	1.211854	–2.056349	4.574028	1.193740	–2.117820	4.676375
H(1)	1.091027	–2.720330	3.788081	1.223888	–2.833988	3.926611	1.193829	–2.943351	4.091751
C(7)	–0.220166	–1.911172	5.178500	–0.048663	–1.970864	5.314553	–0.059711	–1.960522	5.410598
C(8)	–0.223317	–0.592344	5.574632	–0.386644	–0.479405	5.515143	–0.374161	–0.456268	5.542295
C(9)	2.287016	–1.925195	5.311114	2.461366	–1.944107	5.329492	2.445624	–1.962016	5.413352
C(10)	2.928887	–0.516095	5.425316	2.767867	–0.445549	5.529572	2.757983	–0.457758	5.550074
H(7A)	–0.233431	–2.492360	6.114306	–0.012438	–2.501853	6.280653	–0.038534	–2.438383	6.405919
H(7B)	–0.979949	–2.321822	4.502285	–0.826811	–2.433776	4.695045	–0.850087	–2.437912	4.817800
H(8A)	0.349404	–0.235867	6.446106	0.146568	–0.062247	6.383631	0.169854	–0.005045	6.385599
H(8B)	–1.290280	–0.492938	5.819119	–1.462630	–0.353044	5.699537	–1.446832	–0.308939	5.729662
H(9A)	2.183060	–2.484321	6.254663	2.423440	–2.472796	6.296765	2.423122	–2.442736	6.407283
H(9B)	3.104412	–2.370375	4.731006	3.256119	–2.393677	4.721360	3.237480	–2.436878	4.820479
H(10A)	2.417239	–0.160200	6.334039	2.217753	–0.036765	6.391457	2.210740	–0.009788	6.393071
H(10B)	4.008264	–0.378138	5.580008	3.839189	–0.297508	5.724685	3.829847	–0.309537	5.741291

Table 51S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 2.4 Å (*a*), 2.5 Å (*b*) and 2.6 Å (*c*).

Atom	d_{B-N} = 2.4 Å (*a*)			d_{B-N} = 2.5 Å (*b*)			d_{B-N} = 2.6 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.201415	0.000000	2.133802	1.201683	0.000000	2.133280	1.201876	0.000000	2.132890
C(2)	0.000000	0.000000	1.397937	0.000000	0.000000	1.397838	0.000000	0.000000	1.397783
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.212234	0.002377	–0.698868	1.212216	0.002494	–0.698870	1.212209	–0.002794	–0.698838
C(5)	2.419088	0.005868	0.009241	2.419211	0.005377	0.008979	2.419262	–0.004672	0.008886
C(6)	2.408374	0.004232	1.407131	2.408788	0.003176	1.406772	2.409105	–0.003892	1.406621
H(2)	–0.948824	0.003676	1.934977	–0.948735	0.001884	1.934959	–0.948767	0.005251	1.934772
H(3)	–0.944139	0.001413	–0.547254	–0.944163	0.000522	–0.547165	–0.944192	0.002642	–0.547062
H(4)	1.216402	0.003620	–1.790065	1.216256	0.003583	–1.790066	1.216233	–0.002481	–1.790030
H(5)	3.367374	0.011730	–0.530759	3.367408	0.010082	–0.531139	3.367430	–0.005508	–0.531265
H(6)	3.353073	0.011441	1.951397	3.353503	0.007413	1.950922	3.353952	–0.002306	1.950499
B(1)	1.195208	–0.026751	3.710839	1.195947	–0.025380	3.709418	1.195658	–0.003752	3.708889
O(1)	–0.053770	0.131423	4.313473	–0.050995	0.108821	4.308883	–0.049822	0.126075	4.301272
O(2)	2.436997	0.147066	4.323568	2.438671	0.108003	4.317881	2.438678	0.100805	4.311239
N(1)	1.204587	–2.162764	4.805077	1.190300	–2.191466	4.957632	1.168846	–2.141666	5.188282
H(1)	1.215549	–3.039286	4.300544	1.191290	–3.115209	4.545904	1.162356	–3.113117	4.907087
C(7)	–0.053121	–1.952704	5.513250	–0.061523	–1.903044	5.644890	–0.081005	–1.757212	5.828276
C(8)	–0.368360	–0.444402	5.564866	–0.358045	–0.391128	5.595756	–0.355378	–0.254170	5.629916
C(9)	2.448035	–1.932334	5.532031	2.437634	–1.904232	5.653493	2.417011	–1.778437	5.843880
C(10)	2.743040	–0.419388	5.581308	2.735543	–0.392539	5.607007	2.723513	–0.281607	5.643858
H(7A)	–0.050913	–2.370691	6.536770	–0.071861	–2.243110	6.698064	–0.110271	–1.985538	6.912038
H(7B)	–0.840154	–2.458893	4.939840	–0.857695	–2.435670	5.108930	–0.883313	–2.327601	5.342222
H(8A)	0.171625	0.051455	6.384435	0.189525	0.152571	6.378207	0.198654	0.355709	6.356110
H(8B)	–1.441630	–0.292179	5.744263	–1.428782	–0.218250	5.771122	–1.423597	–0.053000	5.789497
H(9A)	2.434849	–2.345448	6.557408	2.440622	–2.244813	6.706557	2.426867	–2.003102	6.928738
H(9B)	3.250878	–2.430831	4.974026	3.237063	–2.437118	5.122659	3.214571	–2.366503	5.371257
H(10A)	2.186199	0.073001	6.391634	2.182394	0.151335	6.385415	2.175197	0.341902	6.362827
H(10B)	3.811863	–0.252571	5.773723	3.805030	–0.220450	5.790581	3.794061	–0.101964	5.813191

Table 52S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 2.7 Å (*a*), 2.8 Å (*b*) and 2.9 Å (*c*).

Atom	d_{B-N} = 2.7 Å (*a*)			d_{B-N} = 2.8 Å (*b*)			d_{B-N} = 2.9 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.202193	0.000000	2.132342	1.202402	0.000000	2.131902	1.204057	0.000000	2.129255
C(2)	0.000000	0.000000	1.397732	0.000000	0.000000	1.397688	0.000000	0.000000	1.397802
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.212078	–0.004851	–0.699008	1.212085	–0.001155	–0.698991	1.212491	–0.002214	–0.699652
C(5)	2.419271	–0.008328	0.008406	2.419373	–0.002083	0.008262	2.420486	–0.002760	0.006693
C(6)	2.409429	–0.005785	1.406090	2.409789	–0.002123	1.405901	2.411457	0.000514	1.404324
H(2)	–0.948719	0.005600	1.934736	–0.948694	0.001520	1.934783	–0.948053	–0.001427	1.935629
H(3)	–0.944256	0.003346	–0.546908	–0.944286	0.001012	–0.546829	–0.944213	0.001083	–0.546701
H(4)	1.215856	–0.005048	–1.790184	1.215807	–0.000979	–1.790158	1.215767	–0.002482	–1.790671
H(5)	3.367334	–0.011465	–0.531869	3.367385	–0.002688	–0.532081	3.368016	–0.004281	–0.534162
H(6)	3.354409	–0.004649	1.949673	3.354812	–0.002264	1.949380	3.356363	0.003559	1.948037
B(1)	1.196878	0.008931	3.707740	1.197581	–0.004971	3.706473	1.196799	–0.015129	3.690706
O(1)	–0.047768	0.107126	4.299900	–0.044782	0.065888	4.302635	–0.047126	–0.032457	4.303480
O(2)	2.438035	0.104849	4.307748	2.437667	0.053425	4.308622	2.422752	0.109540	4.327097
N(1)	1.189353	–2.100803	5.392663	1.185106	–2.112462	5.549927	1.292670	–2.070402	5.734394
H(1)	1.188667	–3.100712	5.239566	1.183567	–3.122452	5.493405	1.356928	–3.078801	5.790465
C(7)	–0.061161	–1.652832	5.986313	–0.067329	–1.610116	6.091306	–0.001662	–1.601422	6.201705
C(8)	–0.342042	–0.174642	5.657032	–0.335213	–0.152246	5.674268	–0.332079	–0.185077	5.687429
C(9)	2.437572	–1.655691	5.993363	2.433536	–1.614583	6.104654	2.499334	–1.437424	6.240753
C(10)	2.723103	–0.177951	5.666636	2.715811	–0.160223	5.683353	2.692016	–0.009024	5.717632
H(7A)	–0.098959	–1.777006	7.087652	–0.126785	–1.661483	7.198484	–0.098998	–1.580378	7.307435
H(7B)	–0.861731	–2.266612	5.552786	–0.868170	–2.242564	5.685573	–0.751039	–2.305039	5.816138
H(8A)	0.207387	0.498550	6.327950	0.215389	0.554166	6.308284	0.166636	0.594532	6.276192
H(8B)	–1.411380	0.030210	5.803858	–1.403638	0.064395	5.810875	–1.412206	–0.026874	5.806502
H(9A)	2.469196	–1.780732	7.094802	2.478590	–1.660978	7.212693	2.542525	–1.384921	7.348879
H(9B)	3.239239	–2.270738	5.563661	3.235624	–2.253810	5.712312	3.348415	–2.046111	5.904411
H(10A)	2.170505	0.495827	6.334361	2.165630	0.553379	6.309642	2.086861	0.701009	6.294008
H(10B)	3.791821	0.024990	5.820478	3.784759	0.048883	5.827486	3.741093	0.282649	5.860182

Table 53S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 3.0 Å (*a*), 3.1 Å (*b*) and 3.2 Å (*c*).

Atom	d_{B-N} = 3.0 Å (*a*)			d_{B-N} = 3.1 Å (*b*)			d_{B-N} = 3.2 Å (*c*)		
	x / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å	*x* / Å	*y* / Å	*z* / Å
C(1)	1.203519	0.000000	2.129981	1.203354	0.000000	2.130209	1.202733	0.000000	2.130902
C(2)	0.000000	0.000000	1.397666	0.000000	0.000000	1.397557	0.000000	0.000000	1.397447
C(3)	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C(4)	1.211564	–0.001659	–0.699706	1.212194	–0.007926	–0.698815	1.212346	–0.011266	–0.698410
C(5)	2.419532	–0.001934	0.006261	2.419970	–0.013265	0.007635	2.419890	–0.020982	0.008472
C(6)	2.410864	0.001829	1.403766	2.411199	–0.005436	1.405126	2.410885	–0.012668	1.405870
H(2)	–0.948393	–0.001628	1.935455	–0.948416	0.001298	1.935184	–0.948735	0.003855	1.934676
H(3)	–0.944465	0.001456	–0.546458	–0.944119	0.007100	–0.546910	–0.944051	0.009905	–0.546884
H(4)	1.214213	–0.001915	–1.790837	1.215689	–0.007808	–1.789941	1.216252	–0.010579	–1.789526
H(5)	3.367028	–0.003259	–0.534873	3.367564	–0.020896	–0.533234	3.367655	–0.032218	–0.531995
H(6)	3.355947	0.006731	1.946980	3.356170	–0.003770	1.948747	3.355828	–0.014820	1.949549
B(1)	1.206748	0.012693	3.701499	1.198594	0.018797	3.700025	1.201539	0.018544	3.698211
O(1)	–0.017114	–0.106865	4.323154	–0.026267	–0.113100	4.316245	–0.021634	–0.097628	4.326400
O(2)	2.432800	0.194075	4.305007	2.419422	0.181031	4.318371	2.422945	0.144725	4.323145
N(1)	1.430098	–2.022412	5.894320	1.387123	–1.972286	6.068579	1.348275	–1.875040	6.273634
H(1)	1.505215	–3.020454	6.038784	1.465893	–2.947105	6.326285	1.407694	–2.809418	6.656087
C(7)	0.155362	–1.507880	6.365105	0.093538	–1.424000	6.440092	0.060674	–1.261917	6.558624
C(8)	–0.245078	–0.162412	5.725808	–0.279866	–0.112689	5.717163	–0.280579	–0.007745	5.725727
C(9)	2.655917	–1.333128	6.258508	2.602738	–1.239129	6.379724	2.581542	–1.131332	6.484957
C(10)	2.769784	0.090912	5.683110	2.722432	0.144450	5.709962	2.706510	0.199651	5.719917
H(7A)	0.110878	–1.363724	7.466352	–0.009661	–1.214877	7.527572	–0.066032	–0.954038	7.620407
H(7B)	–0.603298	–2.257618	6.103122	–0.654367	–2.186741	6.183877	–0.698220	–2.029647	6.353902
H(8A)	0.247482	0.678950	6.228072	0.200645	0.751218	6.191463	0.202073	0.883649	6.142413
H(8B)	–1.325481	–0.025604	5.871714	–1.363093	0.030516	5.833969	–1.363272	0.154368	5.823252
H(9A)	2.805761	–1.237152	7.356058	2.748773	–1.056249	7.467355	2.771309	–0.874212	7.550854
H(9B)	3.486718	–1.935252	5.865932	3.440879	–1.863411	6.040414	3.400768	–1.788852	6.161226
H(10A)	2.188489	0.807452	6.276741	2.131569	0.895472	6.248299	2.114756	0.988308	6.198846
H(10B)	3.821575	0.398333	5.765145	3.772802	0.454978	5.798593	3.757847	0.509052	5.800307

Table 54S. Cartesian coordinates for azaester derivative (X = H, R = H) with B-N distance constrained to 3.3 Å.

Atom	$d_{B–N}$ = 3.3 Å (*a*)		
	x / Å	*y* / Å	*z* / Å
C(1)	1.203972	0.000000	2.128967
C(2)	0.000000	0.000000	1.397537
C(3)	0.000000	0.000000	0.000000
C(4)	1.211446	–0.005507	–0.699782
C(5)	2.419950	–0.007531	0.005437
C(6)	2.411823	–0.001713	1.402610
H(2)	–0.948309	0.000376	1.935674
H(3)	–0.944561	0.002640	–0.546122
H(4)	1.213628	–0.007650	–1.790884
H(5)	3.367192	–0.011880	–0.536002
H(6)	3.356839	0.002491	1.945972
B(1)	1.213557	0.014718	3.693972
O(1)	0.000921	–0.123966	4.343027
O(2)	2.437083	0.137264	4.318252
N(1)	1.440129	–1.767853	6.461843
H(1)	1.550311	–2.647608	6.948055
C(7)	0.100643	–1.223126	6.625635
C(8)	–0.258914	–0.009983	5.743302
C(9)	2.611234	–0.914570	6.618462
C(10)	2.708516	0.329901	5.705816
H(7A)	–0.121945	–0.887658	7.663572
H(7B)	–0.599275	–2.038652	6.395094
H(8A)	0.199752	0.903647	6.138014
H(8B)	–1.345408	0.127992	5.834011
H(9A)	2.734945	–0.513494	7.649645
H(9B)	3.482930	–1.553422	6.419351
H(10A)	2.098843	1.152250	6.097292
H(10B)	3.752809	0.667915	5.761537