Table S01. Summary of the X-ray diffraction analyses of compounds **2b** and **6**.

Crystal data	**2b**	**6**
Chemical formula	$NbON_7C_{26}BH_{33}$. 1.5 C_6H_6	$NbFON_6C_{34}BH_{39}$
Molecular weight	706.52	670.44
ρ_{calcd} ($g.cm^{-3}$)	1.34	1.33
Crystal system	triclinic	monoclinic
Space group	P 1 bar	P $2_1/c$
a (Å)	11.738(2)	13.314(4)
b (Å)	12.607(2)	16.800(4)
c (Å)	13.073(2)	16.101(5)
α (°)	67.03(2)	90.0
β (°)	85.25(2)	111.79(3)
γ (°)	80.31(2)	90.0
V ($Å^3$)	1755(1)	3344(2)
Z	2	4
μ (cm^{-1})	0.37	0.38
F(000)	734	1383
Crystal Size (mm)	0.60 × 0.40 × 0.10	0.20 × 0.10 × 0.10
Crystal shape	block	plate
Crystal Color	orange	orange
Data collection		
Diffractometer	STOE IPDS	STOE IPDS
Radiation type	MoKα	MoKα
Wavelength (Å)	0.71073 (graphite monoch.)	0.71073 (graphite monoch.)
Tube power (kW)	1.50	1.50
Collimator size (mm)	0.5	0.5
Temperature (K)	160	293
Detector distance (mm)	80	80

2θ range (°)	3.5-48.5	3.6-48.1
h k l range	$-13 \le h \le 13$	$-15 \le h \le 14$
	$-12 \le k \le 14$	$0 \le k \le 18$
	$0 \le l \le 14$	$0 \le l \le 18$
Phi movement mode	rotation	rotation
Phi start (°)	0.0	0.0
Phi end (°)	249.6	200
Phi incr (°)	1.6	2
No of exposures	156	100
Measurement duration (h)	19	12
Irradiation/exposures (min)	3	3
Refls for cell refinement	5000	2000
No of measured reflections	10226	20785
No of independent reflections	5219	5201
Merging R value	0.0246	0.051
<u>Refinement</u>		
Refinement on	F	F
R[a]	0.0261	0.0390
Rw[b]	0.0322	0.0279
G.O.F (S)[c]	1.155	1.10
Weighting scheme	Chebychev[d]	Chebychev[d]
Coefs Ar[d]	1.39, -0.0294, 1.11	0.245, -1.57, 0.246, -0.672
No of reflections used	4225 [$I>3\sigma(I)$]	3137 [$I>2\sigma(I)$]
No of parameters used	416	400
Residual elec density ($e.Å^{-3}$)	-0.34/0.40	-0.47/0.36
Rms shift/esd	0.0066	0.0123

[a] $R=\Sigma(||Fo|-||Fc||)/\Sigma|Fo|$.
[b] $Rw=[\Sigma w(||Fo|-||Fc||)^2/\Sigma(|Fo|)^2]^{1/2}$.
[c] Goodness of Fit$=[\Sigma(|Fo-Fc|)^2/(Nobs-Nparameters)]^{1/2}$.
[d] $w = w'[1-(\Delta F/6\sigma(F))^2]^2$. $w' = 1/\Sigma(r=1,3)ArTr(x)$ where Ar are the coefficients for the Chebyshev polynomial Tr(x) with x = Fc/Fc(max).

Table S11. Fractional atomic coordinates for $NbON_7C_{26}BH_{33}$. 1.5 C_6H_6 (**2b**) with their esd in parentheses.

Atom	x/a	y/b	z/c	U(eq)
Nb(1)	0.22512(2)	0.49912(2)	0.27732(2)	0.0142
O(4)	0.3271(2)	0.2300(1)	0.3991(1)	0.0308
N(1)	0.2925(2)	0.5444(2)	0.4148(2)	0.0192
N(2)	0.3420(2)	0.6434(2)	0.3878(2)	0.0198
N(3)	0.1663(2)	0.7014(2)	0.2054(1)	0.0170
N(4)	0.2368(2)	0.7747(2)	0.2127(2)	0.0182
N(5)	0.4022(2)	0.5535(2)	0.2089(2)	0.0195
N(6)	0.4302(2)	0.6575(2)	0.2032(2)	0.0201
N(7)	0.0527(2)	0.5052(2)	0.3486(2)	0.0193
C(1)	0.2108(2)	0.3949(2)	0.1818(2)	0.0198
C(2)	0.1905(2)	0.5054(2)	0.1182(2)	0.0177
C(3)	0.0942(2)	0.4024(2)	0.3872(2)	0.0188
C(4)	0.2950(2)	0.3299(2)	0.3563(2)	0.0224
C(5)	0.2973(2)	0.4908(2)	0.5263(2)	0.0229
C(6)	0.3501(2)	0.5539(2)	0.5696(2)	0.0293
C(7)	0.3767(2)	0.6499(2)	0.4809(2)	0.0267
C(8)	0.0686(2)	0.7688(2)	0.1595(2)	0.0186
C(9)	0.0757(2)	0.8848(2)	0.1373(2)	0.0239
C(10)	0.1830(2)	0.8862(2)	0.1712(2)	0.0229
C(11)	0.4906(2)	0.5061(2)	0.1612(2)	0.0231
C(12)	0.5739(2)	0.5792(2)	0.1247(2)	0.0276
C(13)	0.5344(2)	0.6738(2)	0.1522(2)	0.0251
C(21)	0.1707(2)	0.5711(2)	0.0001(2)	0.0176
C(22)	0.1270(2)	0.5216(2)	-0.0652(2)	0.0206
C(23)	0.1169(2)	0.5801(2)	-0.1786(2)	0.0283
C(24)	0.1506(2)	0.6893(2)	-0.2304(2)	0.0327
C(25)	0.1920(2)	0.7400(2)	-0.1670(2)	0.0322
C(26)	0.2014(2)	0.6825(2)	-0.0534(2)	0.0239
C(31)	0.0600(2)	0.2873(2)	0.4587(2)	0.0238
C(32)	-0.0507(2)	0.2972(2)	0.5248(2)	0.0322
C(51)	0.2451(2)	0.3832(2)	0.5904(2)	0.0307
C(71)	0.4322(3)	0.7487(3)	0.4798(3)	0.0450
C(81)	-0.0300(2)	0.7217(2)	-0.1355(2)	0.0250
C(100)	0.2375(3)	0.9872(2)	0.1647(3)	0.0372
C(110)	0.2143(2)	0.2796(2)	0.1759(2)	0.0308
C(111)	0.4949(2)	0.3909(2)	0.1529(2)	0.0323
C(131)	0.5898(2)	0.7778(2)	0.1331(2)	0.0331
C(201)	0.2649(2)	-0.0047(2)	0.8657(2)	0.0363
C(202)	0.3608(3)	-0.0837(2)	0.9108(2)	0.0346
C(203)	0.4521(3)	-0.1018(2)	0.8435(3)	0.0416
C(204)	0.4465(3)	-0.0402(3)	0.7302(3)	0.0510
C(205)	0.3483(3)	0.0399(3)	0.6852(2)	0.0483
C(206)	0.2586(3)	0.0567(2)	0.7532(3)	0.0398
C(211)	0.8959(4)	-0.0007(3)	0.5564(3)	0.0648
C(212)	0.8980(4)	0.0241(3)	0.4447(3)	0.0623
C(213)	1.0021(5)	0.0244(3)	0.3881(3)	0.0686
B(1)	0.3556	0.7260	0.2659	0.0213

Table S12. Calculated hydrogen fractional atomic coordinates for $NbON_7C_{26}BH_{33}$. 1.5 C_6H_6 (**2b**).

Atom	x/a	y/b	z/c	U(iso)
H(1)	0.3921	0.7901	0.2624	0.0267
H(61)	0.3651	0.5344	0.6464	0.0328
H(91)	0.0173	0.9507	0.1049	0.0271
H(121)	0.6456	0.5663	0.0873	0.0288
H(221)	0.1040	0.4458	-0.0303	0.0254
H(231)	0.0863	0.5451	-0.2217	0.0356
H(241)	0.1454	0.7293	-0.3096	0.0360
H(251)	0.2144	0.8161	-0.2025	0.0363
H(261)	0.2295	0.7193	-0.0107	0.0293
H(311)	0.1210	0.2434	0.5097	0.0275
H(312)	0.0493	0.2469	0.4121	0.0275
H(321)	-0.0684	0.2207	0.5692	0.0386
H(322)	-0.0410	0.3368	0.5723	0.0386
H(323)	-0.1127	0.3403	0.4748	0.0386
H(511)	0.2584	0.3597	0.6682	0.0322
H(512)	0.1635	0.3986	0.5779	0.0322
H(513)	0.2799	0.3220	0.5664	0.0322
H(711)	0.4499	0.7362	0.5544	0.0580
H(712)	0.3801	0.8202	0.4487	0.0580
H(713)	0.5021	0.7532	0.4356	0.0580
H(811)	-0.0116	0.6386	0.1594	0.0288
H(812)	-0.0980	0.7409	0.1745	0.0288
H(813)	-0.0436	0.7553	0.0571	0.0288
H(1001)	0.1845	1.0578	0.1326	0.0436
H(1002)	0.2569	0.9777	0.2380	0.0436
H(1003)	0.3065	0.9911	0.1192	0.0436
H(1101)	0.1994	0.2897	0.1013	0.0364
H(1102)	0.2893	0.2347	0.1971	0.0364
H(1103)	0.1566	0.2395	0.2254	0.0364
H(1111)	0.5654	0.3738	0.1159	0.0390
H(1112)	0.4917	0.3316	0.2262	0.0390
H(1113)	0.4302	0.3932	0.1114	0.0390
H(1311)	0.6631	0.7718	0.0957	0.0374
H(1312)	0.6013	0.7821	0.2032	0.0374
H(1313)	0.5408	0.8468	0.0881	0.0374
H(2011)	0.2018	0.0077	0.9133	0.0447
H(2021)	0.3641	-0.1266	0.9897	0.0413
H(2031)	0.5194	-0.1568	0.8753	0.0497
H(2041)	0.5096	-0.0525	0.6826	0.0635
H(2051)	0.3440	0.0833	0.6065	0.0520
H(2061)	0.1909	0.1114	0.7223	0.0452
H(2111)	0.8233	-0.0016	0.5962	0.0705
H(2121)	0.8271	0.0413	0.4059	0.0665
H(2131)	1.0039	0.0412	0.3098	0.0689

Table S13. Anisotropic thermal parameters for $NbON_7C_{26}BH_{33}$. 1.5 C_6H_6 (**2b**) with their esd in parentheses.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Nb(1)	0.0149(1)	0.0147(1)	0.0128(1)	-0.00493(7)	-0.00189(7)	-0.00123(7)
O(4)	0.034(1)	0.0214(9)	0.029(1)	-0.0040(7)	-0.0066(8)	0.0056(7)
N(1)	0.0181(9)	0.022(1)	0.016(1)	-0.0065(8)	-0.0028(8)	-0.0016(7)
N(2)	0.0172(9)	0.026(1)	0.019(1)	-0.0106(8)	-0.0042(8)	-0.0038(8)
N(3)	0.0190(9)	0.0181(9)	0.0153(9)	-0.0071(7)	0.0001(8)	-0.0049(7)
N(4)	0.0203(9)	0.0189(9)	0.017(1)	-0.0083(7)	-0.0008(8)	-0.0051(7)
N(5)	0.0180(9)	0.025(1)	0.0166(9)	-0.0090(8)	-0.0006(8)	-0.0023(8)
N(6)	0.0165(9)	0.025(1)	0.018(1)	-0.0064(8)	-0.0010(8)	-0.0063(8)
N(7)	0.019(1)	0.022(1)	0.018(1)	-0.0081(8)	0.0003(8)	-0.0039(8)
C(1)	0.019(1)	0.022(1)	0.021(1)	-0.0107(9)	0.001(1)	-0.0031(9)
C(2)	0.013(1)	0.023(1)	0.020(1)	-0.0103(9)	0.0009(9)	-0.0044(8)
C(3)	0.019(1)	0.024(1)	0.015(1)	-0.0097(9)	-0.001(1)	-0.0041(9)
C(4)	0.019(1)	0.030(1)	0.017(1)	-0.009(1)	-0.001(1)	-0.0023(9)
C(5)	0.020(1)	0.030(1)	0.016(1)	-0.007(1)	-0.006(1)	0.0027(9)
C(6)	0.028(1)	0.045(2)	0.016(1)	-0.013(1)	-0.008(1)	-0.003(1)
C(7)	0.021(1)	0.039(1)	0.025(1)	-0.016(1)	-0.005(1)	-0.007(1)
C(8)	0.018(1)	0.020(1)	0.016(1)	-0.0062(9)	-0.0016(9)	-0.0005(9)
C(9)	0.025(1)	0.019(1)	0.024(1)	-0.0060(9)	-0.003(1)	0.0017(9)
C(10)	0.029(1)	0.019(1)	0.020(1)	-0.0076(9)	0.001(1)	-0.0037(9)
C(11)	0.018(1)	0.034(1)	0.016(1)	-0.009(1)	-0.003(1)	0.003(1)
C(12)	0.017(1)	0.042(1)	0.019(1)	-0.009(1)	0.002(1)	-0.001(1)
C(13)	0.018(1)	0.036(1)	0.016(1)	-0.002(1)	-0.002(1)	-0.007(1)
C(21)	0.014(1)	0.022(1)	0.019(1)	-0.0099(9)	0.0011(9)	-0.0019(8)
C(22)	0.020(1)	0.022(1)	0.022(1)	-0.0089(9)	-0.001(1)	-0.0055(9)
C(23)	0.029(1)	0.036(1)	0.025(1)	-0.016(1)	-0.006(1)	-0.003(1)
C(24)	0.041(2)	0.036(1)	0.018(1)	-0.006(1)	-0.004(1)	-0.007(1)
C(25)	0.046(2)	0.027(1)	0.022(1)	-0.004(1)	-0.002(1)	-0.014(1)
C(26)	0.029(1)	0.026(1)	0.019(1)	-0.010(1)	0.000(1)	-0.009(1)
C(31)	0.028(1)	0.019(1)	0.022(1)	-0.0054(9)	-0.002(1)	-0.0044(9)
C(32)	0.038(1)	0.026(1)	0.034(1)	-0.013(1)	0.012(1)	-0.011(1)
C(51)	0.041(2)	0.031(1)	0.015(1)	-0.003(1)	-0.003(1)	-0.005(1)
C(71)	0.053(2)	0.059(2)	0.036(2)	-0.025(1)	-0.010(2)	-0.024(2)
C(81)	0.018(1)	0.026(1)	0.029(1)	-0.009(1)	-0.007(1)	-0.0002(9)
C(100)	0.045(2)	0.024(1)	0.045(2)	-0.013(1)	-0.005(1)	-0.009(1)
C(110)	0.046(2)	0.024(1)	0.025(1)	-0.013(1)	-0.001(1)	-0.004(1)
C(111)	0.027(1)	0.039(1)	0.033(1)	-0.020(1)	0.004(1)	0.003(1)
C(131)	0.024(1)	0.046(2)	0.028(1)	-0.008(1)	-0.001(1)	-0.015(1)
C(201)	0.035(1)	0.037(1)	0.041(2)	-0.016(1)	-0.003(1)	-0.010(1)
C(202)	0.043(2)	0.032(1)	0.030(1)	-0.008(1)	-0.008(1)	-0.013(1)
C(203)	0.040(2)	0.035(1)	0.051(2)	-0.017(1)	-0.011(1)	-0.001(1)
C(204)	0.053(2)	0.060(2)	0.047(2)	-0.025(2)	0.014(2)	-0.021(2)
C(205)	0.075(2)	0.039(2)	0.028(2)	-0.001(1)	-0.006(2)	-0.025(2)
C(206)	0.046(2)	0.027(1)	0.043(2)	-0.007(1)	-0.014(1)	-0.006(1)
C(211)	0.094(3)	0.038(2)	0.057(2)	-0.013(2)	-0.014(2)	-0.002(2)
C(212)	0.095(3)	0.032(2)	0.056(2)	-0.008(1)	-0.034(2)	-0.006(2)
C(213)	0.128(4)	0.036(2)	0.041(2)	-0.012(1)	-0.027(3)	-0.006(2)
B(1)	0.0245	0.0178	0.0253	-0.0095	-0.0035	-0.0084

Table S14. Bond lengths (Å) and angles (°) for $NbON_7C_{26}BH_{33}$. 1.5 C_6H_6 (**2b**) with their esd in parentheses.

Nb(1) - N(1)	2.318(2)
Nb(1) - N(3)	2.347(2)
Nb(1) - N(5)	2.299(2)
Nb(1) - N(7)	2.159(2)
Nb(1) - C(1)	2.169(2)
Nb(1) - C(2)	2.121(2)
Nb(1) - C(3)	2.194(2)
Nb(1) - C(4)	2.030(2)
O(4) - C(4)	1.169(3)
N(1) - N(2)	1.373(3)
N(1) - C(5)	1.348(3)
N(2) - C(7)	1.351(3)
N(2) - B(1)	1.539(2)
N(3) - N(4)	1.373(3)
N(3) - C(8)	1.336(3)
N(4) - C(10)	1.354(3)
N(4) - B(1)	1.531(2)
N(5) - N(6)	1.377(3)
N(5) - C(11)	1.341(3)
N(6) - C(13)	1.352(3)
N(6) - B(1)	1.538(2)
N(7) - C(3)	1.220(3)
C(1) - C(2)	1.307(3)
C(1) - C(110)	1.479(3)
C(2) - C(21)	1.456(3)
C(3) - C(31)	1.488(3)
C(5) - C(6)	1.383(4)
C(5) - C(51)	1.492(4)
C(6) - C(7)	1.370(4)
C(7) - C(71)	1.495(4)
C(8) - C(9)	1.392(3)
C(8) - C(81)	1.492(3)
C(9) - C(10)	1.374(4)
C(10) - C(100)	1.489(3)
C(11) - C(12)	1.385(4)
C(11) - C(111)	1.489(4)
C(12) - C(13)	1.373(4)
C(13) - C(131)	1.487(4)
C(21) - C(22)	1.406(3)
C(21) - C(26)	1.398(3)
C(22) - C(23)	1.379(4)
C(23) - C(24)	1.387(4)
C(24) - C(25)	1.385(4)
C(25) - C(26)	1.379(4)
C(31) - C(32)	1.514(3)
C(201) - C(202)	1.371(4)
C(201) - C(206)	1.370(4)
C(202) - C(203)	1.376(4)
C(203) - C(204)	1.379(5)
C(204) - C(205)	1.397(5)
C(205) - C(206)	1.364(5)
C(211) - C(212)	1.368(6)
C(211) - C(213)	1.379(6)
C(212) - C(213)	1.375(7)

N(1)	- Nb(1) -	N(3)	80.37(6)
N(1)	- Nb(1) -	N(5)	76.42(6)
N(3)	- Nb(1) -	N(5)	82.37(6)
N(1)	- Nb(1) -	N(7)	90.52(7)
N(3)	- Nb(1) -	N(7)	80.44(7)
N(5)	- Nb(1) -	N(7)	159.94(7)
N(1)	- Nb(1) -	C(1)	156.98(8)
N(3)	- Nb(1) -	C(1)	121.47(8)
N(5)	- Nb(1) -	C(1)	97.97(7)
N(7)	- Nb(1) -	C(1)	99.79(8)
N(1)	- Nb(1) -	C(2)	161.00(7)
N(3)	- Nb(1) -	C(2)	86.47(7)
N(5)	- Nb(1) -	C(2)	88.36(7)
N(7)	- Nb(1) -	C(2)	100.80(8)
C(1)	- Nb(1) -	C(2)	35.44(9)
N(1)	- Nb(1) -	C(3)	93.50(7)
N(3)	- Nb(1) -	C(3)	112.91(7)
N(5)	- Nb(1) -	C(3)	160.36(8)
N(7)	- Nb(1) -	C(3)	32.56(8)
C(1)	- Nb(1) -	C(3)	84.71(8)
N(1)	- Nb(1) -	C(4)	89.96(8)
N(3)	- Nb(1) -	C(4)	169.85(8)
N(5)	- Nb(1) -	C(4)	92.41(8)
N(7)	- Nb(1) -	C(4)	102.89(8)
C(1)	- Nb(1) -	C(4)	67.76(9)
C(2)	- Nb(1) -	C(3)	104.27(8)
C(2)	- Nb(1) -	C(4)	102.14(9)
C(3)	- Nb(1) -	C(4)	70.49(9)
Nb(1)	- N(1) -	N(2)	120.6(1)
Nb(1)	- N(1) -	C(5)	133.5(2)
N(2)	- N(1) -	C(5)	105.9(2)
N(1)	- N(2) -	C(7)	109.9(2)
N(1)	- N(2) -	B(1)	121.0(2)
C(7)	- N(2) -	B(1)	129.0(2)
Nb(1)	- N(3) -	N(4)	120.4(1)
Nb(1)	- N(3) -	C(8)	133.2(1)
N(4)	- N(3) -	C(8)	106.3(2)
N(3)	- N(4) -	C(10)	110.0(2)
N(3)	- N(4) -	B(1)	120.7(1)
C(10)	- N(4) -	B(1)	129.3(2)
Nb(1)	- N(5) -	N(6)	121.0(1)
Nb(1)	- N(5) -	C(11)	132.2(2)
N(6)	- N(5) -	C(11)	106.6(2)
N(5)	- N(6) -	C(13)	109.7(2)
N(5)	- N(6) -	B(1)	120.1(1)
C(13)	- N(6) -	B(1)	129.5(2)
Nb(1)	- N(7) -	C(3)	75.3(1)
Nb(1)	- C(1) -	C(2)	70.3(1)
Nb(1)	- C(1) -	C(110)	149.9(2)
C(2)	- C(1) -	C(110)	139.7(2)
Nb(1)	- C(2) -	C(1)	74.3(1)
Nb(1)	- C(2) -	C(21)	150.4(2)
C(1)	- C(2) -	C(21)	134.9(2)
Nb(1)	- C(3) -	N(7)	72.1(1)
Nb(1)	- C(3) -	C(31)	147.8(2)
N(7)	- C(3) -	C(31)	139.8(2)
Nb(1)	- C(4) -	O(4)	174.3(2)
N(1)	- C(5) -	C(6)	110.1(2)

N(1)	- C(5)	- C(51)	123.1(2)
C(6)	- C(5)	- C(51)	126.7(2)
C(5)	- C(6)	- C(7)	106.3(2)
N(2)	- C(7)	- C(6)	107.8(2)
N(2)	- C(7)	- C(71)	123.0(2)
C(6)	- C(7)	- C(71)	129.1(3)
N(3)	- C(8)	- C(9)	110.0(2)
N(3)	- C(8)	- C(81)	122.9(2)
C(9)	- C(8)	- C(81)	127.1(2)
C(8)	- C(9)	- C(10)	106.3(2)
N(4)	- C(10)	- C(9)	107.4(2)
N(4)	- C(10)	- C(100)	123.3(2)
C(9)	- C(10)	- C(100)	129.3(2)
N(5)	- C(11)	- C(12)	109.4(2)
N(5)	- C(11)	- C(111)	123.3(2)
C(12)	- C(11)	- C(111)	127.3(2)
C(11)	- C(12)	- C(13)	106.9(2)
N(6)	- C(13)	- C(12)	107.3(2)
N(6)	- C(13)	- C(131)	123.2(2)
C(12)	- C(13)	- C(131)	129.5(2)
C(2)	- C(21)	- C(22)	121.0(2)
C(2)	- C(21)	- C(26)	121.0(2)
C(22)	- C(21)	- C(26)	117.8(2)
C(21)	- C(22)	- C(23)	121.1(2)
C(22)	- C(23)	- C(24)	120.2(2)
C(23)	- C(24)	- C(25)	119.4(2)
C(24)	- C(25)	- C(26)	120.8(2)
C(21)	- C(26)	- C(25)	120.7(2)
C(3)	- C(31)	- C(32)	113.1(2)
C(202)	- C(201)	- C(206)	120.5(3)
C(201)	- C(202)	- C(203)	120.3(3)
C(202)	- C(203)	- C(204)	119.6(3)
C(203)	- C(204)	- C(205)	119.6(3)
C(204)	- C(205)	- C(206)	120.0(3)
C(201)	- C(206)	- C(205)	120.0(3)
C(212)	- C(211)	- C(213)	120.0(4)
C(211)	- C(212)	- C(213)	119.8(4)
C(211)	- C(213)	- C(212)	120.1(4)
N(2)	- B(1)	- N(4)	110.0(1)
N(2)	- B(1)	- N(6)	108.6(1)
N(4)	- B(1)	- N(6)	110.0(1)

Table S21. Fractional atomic coordinates for $NbFON_6C_{34}BH_{39}$ (**6**) with their esd in parentheses.

Atom	x/a	y/b	z/c	U(eq)
Nb(1)	0.20294(3)	0.21542(2)	0.25756(3)	0.0337
F(1)	0.0848(2)	0.1627(1)	0.2764(2)	0.0484
O(1)	0.2258(2)	0.1406(2)	0.1706(2)	0.0437
B(1)	0.1927(4)	0.4178(3)	0.2312(4)	0.0414
N(1)	0.1959(3)	0.3159(2)	0.3464(2)	0.0393
N(2)	0.2045(3)	0.3951(2)	0.3261(2)	0.0419
N(3)	0.0789(3)	0.2996(2)	0.1579(2)	0.0406
N(4)	0.0881(3)	0.3812(2)	0.1659(2)	0.0394
N(5)	0.3082(3)	0.3019(2)	0.2169(2)	0.0410
N(6)	0.2873(3)	0.3832(2)	0.2103(2)	0.0416
C(1)	0.1883(5)	0.2378(3)	0.4751(3)	0.0622
C(2)	0.1968(4)	0.3144(3)	0.4311(3)	0.0504
C(3)	0.2053(4)	0.3908(3)	0.4631(3)	0.0547
C(4)	0.2105(4)	0.4397(3)	0.3973(3)	0.0495
C(5)	0.2211(5)	0.5289(3)	0.3968(4)	0.0741
C(6)	-0.0564(4)	0.2026(3)	0.0662(4)	0.0668
C(7)	-0.0186(3)	0.2849(3)	0.0949(3)	0.0426
C(8)	-0.0723(4)	0.3557(3)	0.0648(3)	0.0513
C(9)	-0.0038(4)	0.4159(3)	0.1098(3)	0.0430
C(10)	-0.0190(4)	0.5044(3)	0.1041(4)	0.0605
C(11)	0.4418(4)	0.2105(3)	0.1904(3)	0.0569
C(12)	0.3941(3)	0.2901(3)	0.1926(3)	0.0432
C(13)	0.4260(4)	0.3623(3)	0.1699(4)	0.0556
C(14)	0.3596(4)	0.4190(3)	0.1819(4)	0.0546
C(15)	0.3610(6)	0.5079(4)	0.1686(5)	0.0940
C(16)	0.3424(4)	0.1825(3)	0.3472(3)	0.0378
C(17)	0.3077(3)	0.1014(3)	0.3236(3)	0.0390
C(18)	0.2502(4)	0.0826(3)	0.2341(3)	0.0419
C(19)	0.1999(4)	0.0033(3)	0.2029(3)	0.0455
C(20)	0.2640(4)	-0.0596(3)	0.2216(3)	0.0483
C(21)	0.3115(4)	0.0422(3)	0.3962(3)	0.0548
C(22)	0.0820(4)	0.0022(3)	0.1472(4)	0.0706
C(30)	0.2346(4)	-0.1448(3)	0.2028(3)	0.0470
C(31)	0.1489(4)	-0.1777(3)	0.2180(4)	0.0571
C(32)	0.1261(5)	-0.2589(3)	0.2030(4)	0.0678
C(33)	0.1900(5)	-0.3051(3)	0.1735(4)	0.0689
C(34)	0.2751(5)	-0.2731(3)	0.1575(4)	0.0649
C(35)	0.2982(4)	-0.1934(3)	0.1728(3)	0.0514
C(40)	0.4424(3)	0.2077(3)	0.4187(3)	0.0398
C(41)	0.5249(4)	0.1555(3)	0.4665(3)	0.0500
C(42)	0.6181(4)	0.1820(4)	0.5336(4)	0.0664
C(43)	0.6322(4)	0.2613(4)	0.5542(4)	0.0681
C(44)	0.5534(4)	0.3146(3)	0.5064(4)	0.0680
C(45)	0.4602(4)	0.2883(3)	0.4402(3)	0.0547

Table S22. Hydrogen fractional atomic coordinates for $NbFON_6C_{34}BH_{39}$ (**6**) with their esd in parentheses when appropriate.

Atom	x/a	y/b	z/c	U(iso)
H(1)	0.193(3)	0.483(3)	0.224(3)	0.0500
H(11)	0.1904	0.2483	0.5343	0.0747
H(12)	0.2477	0.2038	0.4785	0.0747
H(13)	0.1214	0.2120	0.4407	0.0747
H(31)	0.2071	0.4068	0.5210	0.0643
H(51)	0.2241	0.5500	0.4530	0.0827
H(52)	0.2862	0.5427	0.3875	0.0827
H(53)	0.1599	0.5509	0.3494	0.0827
H(61)	-0.1277	0.2044	0.0208	0.0683
H(62)	-0.0579	0.1729	0.1166	0.0683
H(63)	-0.0079	0.1775	0.0426	0.0683
H(81)	-0.1440	0.3618	0.0208	0.0550
H(101)	-0.0892	0.5168	0.0606	0.0711
H(102)	-0.0131	0.5247	0.1615	0.0711
H(103)	0.0356	0.5283	0.0866	0.0711
H(111)	0.5018	0.2161	0.1713	0.0676
H(112)	0.4665	0.1874	0.2491	0.0676
H(113)	0.3881	0.1766	0.1494	0.0676
H(131)	0.4842	0.3711	0.1494	0.0698
H(151)	0.4182	0.5213	0.1483	0.1082
H(152)	0.3727	0.5344	0.2242	0.1082
H(153)	0.2929	0.5244	0.1247	0.1082
H(201)	0.3398	-0.0488	0.2513	0.0551
H(211)	0.3539	0.0639	0.4537	0.0624
H(212)	0.3436	-0.0067	0.3873	0.0624
H(213)	0.2394	0.0320	0.3934	0.0624
H(221)	0.0590	-0.0517	0.1312	0.0714
H(222)	0.0424	0.0246	0.1807	0.0714
H(223)	0.0688	0.0330	0.0940	0.0714
H(311)	0.1042	-0.1449	0.2390	0.0696
H(321)	0.0659	-0.2818	0.2135	0.0782
H(331)	0.1749	-0.3609	0.1638	0.0726
H(341)	0.3187	-0.3061	0.1356	0.0727
H(351)	0.3591	-0.1712	0.1627	0.0576
H(411)	0.5168	0.0997	0.4525	0.0581
H(421)	0.6732	0.1446	0.5660	0.0729
H(431)	0.6964	0.2796	0.6015	0.0715
H(441)	0.5636	0.3705	0.5193	0.0752
H(451)	0.4059	0.3263	0.4079	0.0599

Table S23. Anisotropic thermal parameters for $NbFON_6C_{34}BH_{39}$ (**6**) with their esd in parentheses.

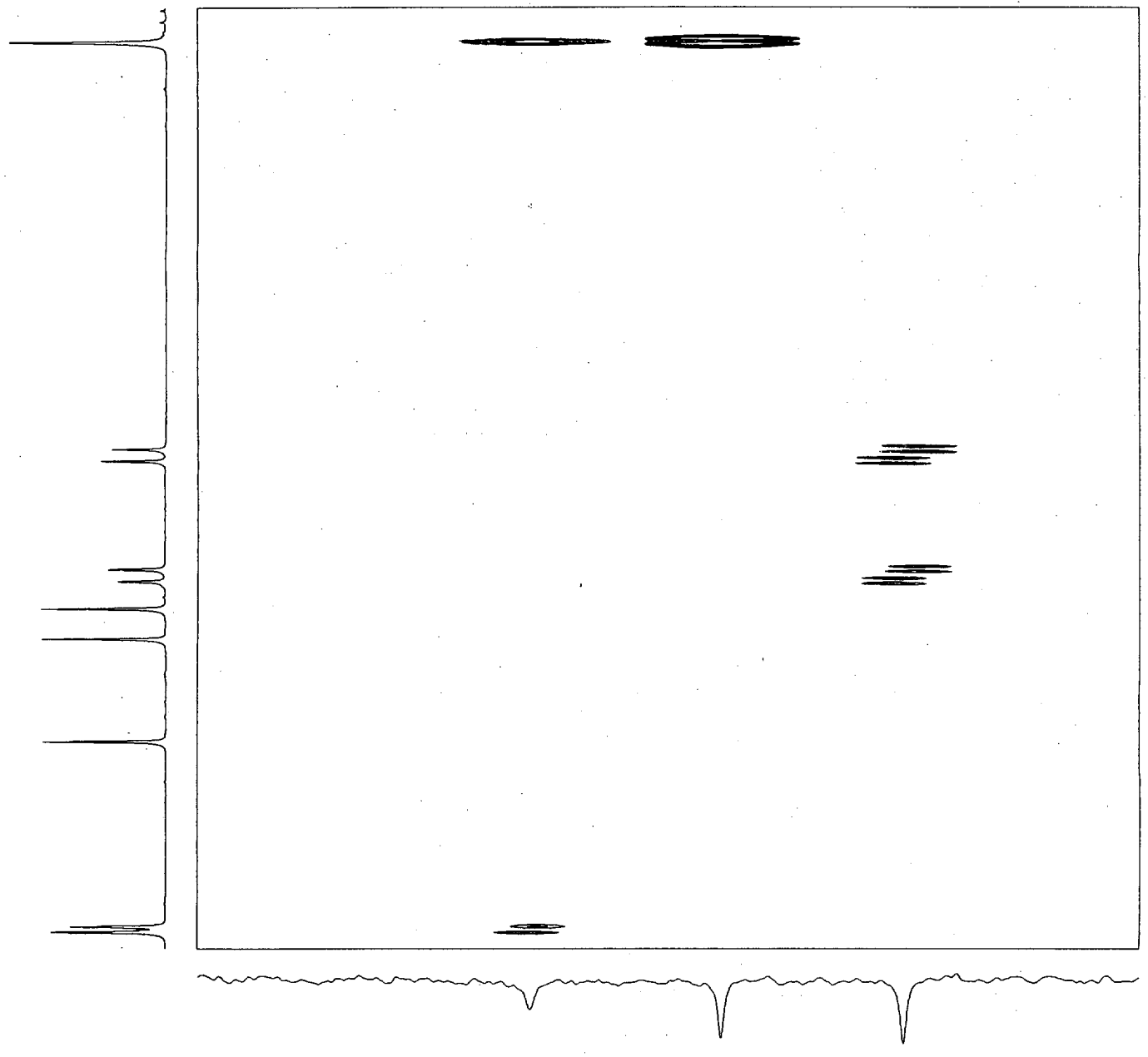
Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Nb(1)	0.0355(2)	0.0305(2)	0.0323(2)	0.0003(2)	0.0092(2)	-0.0007(2)
F(1)	0.043(2)	0.047(2)	0.057(2)	0.010(1)	0.020(1)	-0.001(1)
O(1)	0.051(2)	0.039(2)	0.040(2)	-0.004(1)	0.015(2)	-0.003(2)
B(1)	0.046(3)	0.033(3)	0.043(3)	0.001(2)	0.015(3)	0.001(3)
N(1)	0.041(2)	0.042(2)	0.033(2)	0.002(2)	0.011(2)	0.002(2)
N(2)	0.050(2)	0.036(2)	0.036(2)	-0.004(2)	0.012(2)	0.002(2)
N(3)	0.043(2)	0.036(2)	0.041(2)	0.002(2)	0.014(2)	-0.002(2)
N(4)	0.043(2)	0.031(2)	0.042(2)	0.001(2)	0.013(2)	-0.001(2)
N(5)	0.042(2)	0.041(3)	0.036(2)	-0.001(2)	0.011(2)	-0.001(2)
N(6)	0.045(2)	0.037(2)	0.042(2)	0.000(2)	0.016(2)	-0.000(2)
C(1)	0.078(4)	0.073(4)	0.042(3)	0.008(3)	0.030(3)	0.005(3)
C(2)	0.052(3)	0.063(4)	0.036(3)	0.002(2)	0.016(2)	0.005(2)
C(3)	0.064(4)	0.061(4)	0.039(3)	-0.013(3)	0.020(3)	0.008(3)
C(4)	0.050(3)	0.043(3)	0.048(3)	-0.016(3)	0.009(2)	0.006(2)
C(5)	0.087(5)	0.051(4)	0.073(4)	-0.023(3)	0.017(3)	-0.002(3)
C(6)	0.059(3)	0.048(3)	0.065(4)	0.005(3)	-0.010(3)	-0.010(3)
C(7)	0.036(2)	0.046(3)	0.040(3)	0.007(2)	0.006(2)	-0.008(2)
C(8)	0.039(3)	0.051(3)	0.048(3)	0.010(3)	-0.002(2)	0.002(2)
C(9)	0.044(3)	0.043(3)	0.044(3)	0.015(2)	0.018(2)	0.013(2)
C(10)	0.066(4)	0.049(3)	0.064(4)	0.007(3)	0.022(3)	0.017(3)
C(11)	0.044(3)	0.061(3)	0.067(3)	-0.008(3)	0.022(3)	0.002(3)
C(12)	0.039(3)	0.051(3)	0.042(3)	-0.004(2)	0.018(2)	-0.002(2)
C(13)	0.050(3)	0.060(4)	0.066(4)	-0.000(3)	0.032(3)	-0.009(3)
C(14)	0.058(3)	0.047(3)	0.066(4)	0.008(3)	0.031(3)	-0.012(3)
C(15)	0.094(5)	0.052(4)	0.150(7)	0.022(4)	0.062(5)	-0.009(4)
C(16)	0.043(3)	0.033(2)	0.034(3)	-0.000(2)	0.011(2)	0.004(2)
C(17)	0.041(3)	0.035(3)	0.039(3)	0.002(2)	0.013(2)	0.005(2)
C(18)	0.042(3)	0.037(3)	0.043(3)	-0.004(2)	0.011(2)	0.003(2)
C(19)	0.043(3)	0.034(3)	0.051(3)	-0.006(2)	0.007(2)	0.000(2)
C(20)	0.041(3)	0.042(3)	0.057(3)	-0.008(2)	0.012(2)	-0.005(2)
C(21)	0.058(3)	0.045(3)	0.054(3)	0.014(2)	0.012(3)	-0.002(2)
C(22)	0.048(3)	0.049(4)	0.088(4)	-0.010(3)	-0.005(3)	-0.003(3)
C(30)	0.041(3)	0.039(3)	0.051(3)	-0.007(2)	0.005(2)	-0.006(2)
C(31)	0.063(4)	0.050(3)	0.062(4)	-0.003(3)	0.027(3)	-0.002(3)
C(32)	0.061(4)	0.057(4)	0.079(4)	-0.000(3)	0.019(3)	-0.022(3)
C(33)	0.078(4)	0.038(3)	0.074(4)	-0.010(3)	0.010(3)	-0.008(3)
C(34)	0.062(4)	0.047(3)	0.077(4)	-0.017(3)	0.015(3)	0.005(3)
C(35)	0.039(3)	0.045(3)	0.064(3)	-0.010(2)	0.011(3)	0.002(2)
C(40)	0.034(2)	0.043(3)	0.040(3)	-0.004(2)	0.011(2)	-0.001(2)
C(41)	0.042(3)	0.051(3)	0.053(3)	0.003(3)	0.013(3)	0.005(2)
C(42)	0.045(3)	0.078(4)	0.063(4)	0.010(3)	0.006(3)	0.003(3)
C(43)	0.045(3)	0.094(5)	0.050(3)	-0.009(3)	-0.000(3)	-0.017(3)
C(44)	0.051(3)	0.063(4)	0.077(4)	-0.019(3)	0.008(3)	-0.020(3)
C(45)	0.044(3)	0.051(3)	0.056(3)	-0.007(3)	0.003(2)	-0.005(3)

Table S24. Bond lengths (Å) and angles (°) for $NbFON_6C_{34}BH_{39}$ (**6**) with their esd in parentheses.

Nb(1) - F(1)	1.925(2)
Nb(1) - O(1)	1.988(3)
Nb(1) - N(1)	2.238(4)
Nb(1) - N(3)	2.310(4)
Nb(1) - N(5)	2.277(4)
Nb(1) - C(16)	1.962(4)
Nb(1) - C(17)	2.376(4)
Nb(1) - C(18)	2.387(4)
O(1) - C(18)	1.362(5)
B(1) - N(2)	1.526(6)
B(1) - N(4)	1.529(6)
B(1) - N(6)	1.534(7)
N(1) - N(2)	1.384(5)
N(1) - C(2)	1.359(6)
N(2) - C(4)	1.347(6)
N(3) - N(4)	1.378(5)
N(3) - C(7)	1.341(5)
N(4) - C(9)	1.353(5)
N(5) - N(6)	1.390(5)
N(5) - C(12)	1.354(5)
N(6) - C(14)	1.350(6)
C(1) - C(2)	1.493(7)
C(2) - C(3)	1.373(7)
C(3) - C(4)	1.363(7)
C(4) - C(5)	1.505(7)
C(6) - C(7)	1.484(7)
C(7) - C(8)	1.380(6)
C(8) - C(9)	1.374(6)
C(9) - C(10)	1.499(7)
C(11) - C(12)	1.486(7)
C(12) - C(13)	1.380(7)
C(13) - C(14)	1.361(7)
C(14) - C(15)	1.510(7)
C(16) - C(17)	1.444(6)
C(16) - C(40)	1.462(6)
C(17) - C(18)	1.394(6)
C(17) - C(21)	1.521(6)
C(18) - C(19)	1.492(6)
C(19) - C(20)	1.321(6)
C(19) - C(22)	1.491(7)
C(20) - C(30)	1.484(6)
C(30) - C(31)	1.369(7)
C(30) - C(35)	1.386(7)
C(31) - C(32)	1.399(7)
C(32) - C(33)	1.361(8)
C(33) - C(34)	1.361(8)
C(34) - C(35)	1.376(7)
C(40) - C(41)	1.393(6)
C(40) - C(45)	1.396(7)
C(41) - C(42)	1.382(7)
C(42) - C(43)	1.369(8)
C(43) - C(44)	1.376(8)
C(44) - C(45)	1.375(6)

F(1)	- Nb(1)	- O(1)	99.7(1)
F(1)	- Nb(1)	- N(1)	90.9(1)
O(1)	- Nb(1)	- N(1)	169.0(1)
F(1)	- Nb(1)	- N(3)	88.6(1)
O(1)	- Nb(1)	- N(3)	98.9(1)
N(1)	- Nb(1)	- N(3)	78.1(1)
F(1)	- Nb(1)	- N(5)	164.8(1)
O(1)	- Nb(1)	- N(5)	85.9(1)
N(1)	- Nb(1)	- N(5)	83.0(1)
N(3)	- Nb(1)	- N(5)	76.5(1)
F(1)	- Nb(1)	- C(16)	111.1(2)
O(1)	- Nb(1)	- C(16)	89.4(2)
N(1)	- Nb(1)	- C(16)	89.7(2)
N(3)	- Nb(1)	- C(16)	157.1(2)
N(5)	- Nb(1)	- C(16)	82.9(2)
F(1)	- Nb(1)	- C(17)	86.4(1)
O(1)	- Nb(1)	- C(17)	65.6(1)
N(1)	- Nb(1)	- C(17)	118.7(1)
N(3)	- Nb(1)	- C(17)	162.6(1)
N(5)	- Nb(1)	- C(17)	108.8(1)
F(1)	- Nb(1)	- C(18)	82.7(1)
O(1)	- Nb(1)	- C(18)	34.8(1)
N(1)	- Nb(1)	- C(18)	152.0(1)
N(3)	- Nb(1)	- C(18)	128.7(1)
N(5)	- Nb(1)	- C(18)	108.9(1)
C(16)	- Nb(1)	- C(17)	37.4(2)
C(16)	- Nb(1)	- C(18)	67.6(2)
C(17)	- Nb(1)	- C(18)	34.0(1)
Nb(1)	- O(1)	- C(18)	88.8(2)
N(2)	- B(1)	- N(4)	108.5(4)
N(2)	- B(1)	- N(6)	109.7(4)
N(4)	- B(1)	- N(6)	108.0(4)
Nb(1)	- N(1)	- N(2)	123.2(3)
Nb(1)	- N(1)	- C(2)	129.8(3)
N(2)	- N(1)	- C(2)	106.5(4)
B(1)	- N(2)	- N(1)	119.3(4)
B(1)	- N(2)	- C(4)	131.6(4)
N(1)	- N(2)	- C(4)	108.6(4)
Nb(1)	- N(3)	- N(4)	121.9(3)
Nb(1)	- N(3)	- C(7)	130.8(3)
N(4)	- N(3)	- C(7)	106.4(4)
B(1)	- N(4)	- N(3)	119.4(4)
B(1)	- N(4)	- C(9)	130.8(4)
N(3)	- N(4)	- C(9)	109.8(4)
Nb(1)	- N(5)	- N(6)	121.5(3)
Nb(1)	- N(5)	- C(12)	131.7(3)
N(6)	- N(5)	- C(12)	106.8(4)
B(1)	- N(6)	- N(5)	120.8(4)
B(1)	- N(6)	- C(14)	130.7(4)
N(5)	- N(6)	- C(14)	108.4(4)
N(1)	- C(2)	- C(1)	121.3(4)
N(1)	- C(2)	- C(3)	109.1(4)
C(1)	- C(2)	- C(3)	129.6(5)
C(2)	- C(3)	- C(4)	107.0(4)
N(2)	- C(4)	- C(3)	108.8(4)
N(2)	- C(4)	- C(5)	121.7(5)
C(3)	- C(4)	- C(5)	129.6(5)
N(3)	- C(7)	- C(6)	121.9(4)

N(3)	- C(7)	- C(8)	109.6(4)
C(6)	- C(7)	- C(8)	128.5(4)
C(7)	- C(8)	- C(9)	107.0(4)
N(4)	- C(9)	- C(8)	107.1(4)
N(4)	- C(9)	- C(10)	122.4(4)
C(8)	- C(9)	- C(10)	130.5(4)
N(5)	- C(12)	- C(11)	123.6(4)
N(5)	- C(12)	- C(13)	108.9(4)
C(11)	- C(12)	- C(13)	127.5(4)
C(12)	- C(13)	- C(14)	107.3(4)
N(6)	- C(14)	- C(13)	108.6(4)
N(6)	- C(14)	- C(15)	122.4(5)
C(13)	- C(14)	- C(15)	129.0(5)
Nb(1)	- C(16)	- C(17)	87.1(3)
Nb(1)	- C(16)	- C(40)	146.5(3)
C(17)	- C(16)	- C(40)	126.2(4)
Nb(1)	- C(17)	- C(16)	55.6(2)
Nb(1)	- C(17)	- C(18)	73.4(3)
C(16)	- C(17)	- C(18)	119.1(4)
Nb(1)	- C(17)	- C(21)	135.9(3)
C(16)	- C(17)	- C(21)	119.9(4)
C(18)	- C(17)	- C(21)	119.7(4)
Nb(1)	- C(18)	- O(1)	56.4(2)
Nb(1)	- C(18)	- C(17)	72.6(3)
O(1)	- C(18)	- C(17)	120.0(4)
Nb(1)	- C(18)	- C(19)	140.9(3)
O(1)	- C(18)	- C(19)	115.7(4)
C(17)	- C(18)	- C(19)	123.8(4)
C(18)	- C(19)	- C(20)	117.8(4)
C(18)	- C(19)	- C(22)	117.0(4)
C(20)	- C(19)	- C(22)	125.1(4)
C(19)	- C(20)	- C(30)	128.6(4)
C(20)	- C(30)	- C(31)	121.9(5)
C(20)	- C(30)	- C(35)	119.3(5)
C(31)	- C(30)	- C(35)	118.8(5)
C(30)	- C(31)	- C(32)	120.4(5)
C(31)	- C(32)	- C(33)	119.5(5)
C(32)	- C(33)	- C(34)	120.8(5)
C(33)	- C(34)	- C(35)	119.8(5)
C(30)	- C(35)	- C(34)	120.7(5)
C(16)	- C(40)	- C(41)	123.6(4)
C(16)	- C(40)	- C(45)	119.8(4)
C(41)	- C(40)	- C(45)	116.6(4)
C(40)	- C(41)	- C(42)	121.6(5)
C(41)	- C(42)	- C(43)	120.4(5)
C(42)	- C(43)	- C(44)	119.3(5)
C(43)	- C(44)	- C(45)	120.4(5)
C(40)	- C(45)	- C(44)	121.7(5)



Expanded region of the ^{1}H-^{13}C HMBC NMR spectrum of **2c**