Supporting information

S1. Scorpionates found in the CSD

A search in the CSD, version 5.37 update November 2015, has been done using ConQuest program to retrieve the sample of tetrakis scorpionate derivatives. We have included only those structures that have 3D coordinates determined, no errors and R-factor ≤ 7.5% (171 hits corresponding to 164 different compounds).

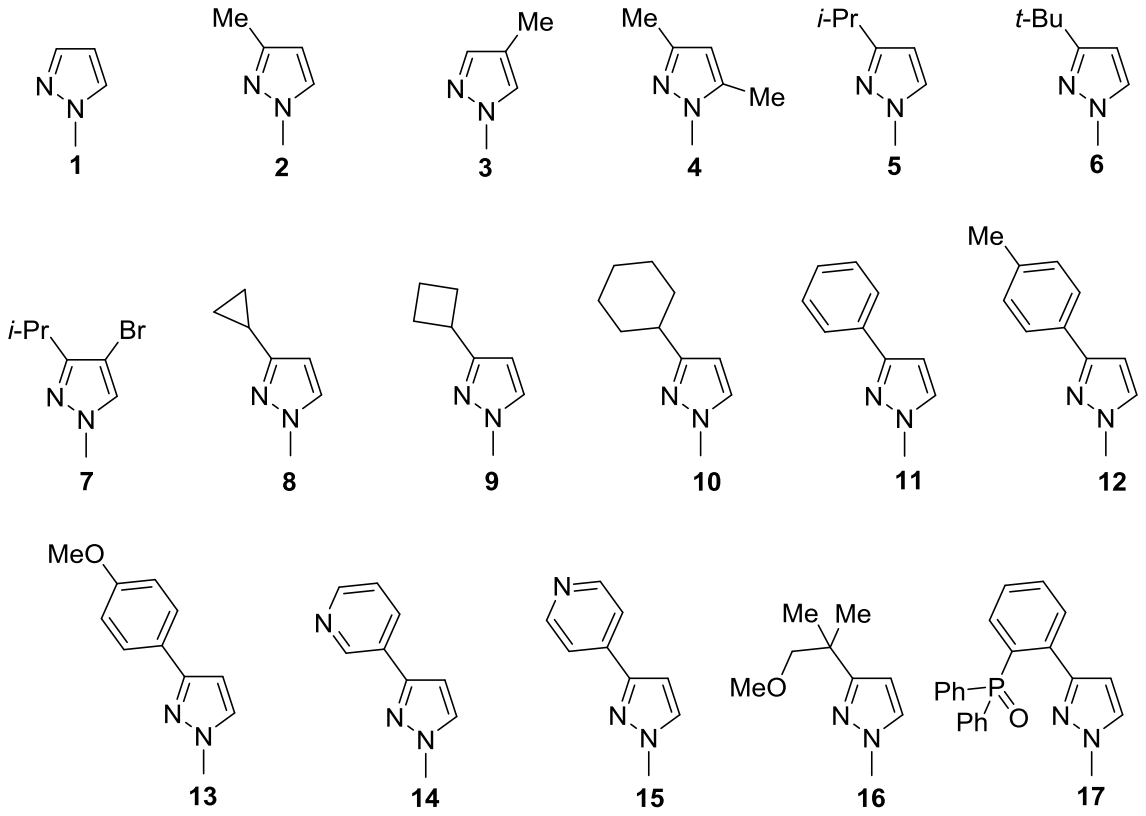


Figure S1 The seventeen pyrazoles used in the boron atom coordination; **16** and **17** use their O atoms in the coordination. Title compounds, **1** and **2**, contain pyrazoles **11** and **8** respectively.

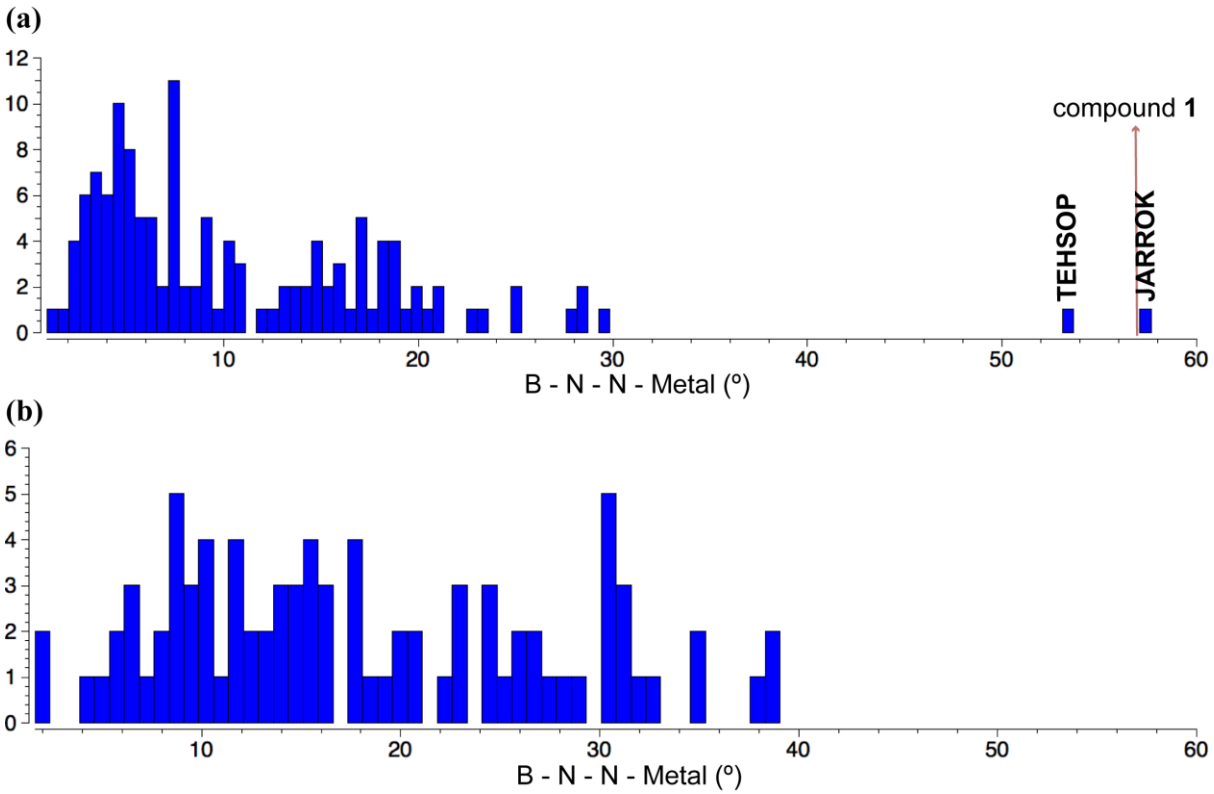


Figure S2 Distribution of the maximum absolute value observed for the dihedral angles B-N-N-Metal for the tetrakis scorpionates reported in the CSD. (a) Motifs where the metal cations are coordinated to three pyrazoles of the same tetrakis scorpionate. (b) Motifs where the metal cations are coordinated to two pyrazoles of the same tetrakis scorpionate. Compound **2** presents a dihedral angle (B-N-N-K) = 79.2(2) and 81.4(2) out of the range represented.

Table S1 Frequency of the pyrazoles used to form the tetrakis scorpionate derivatives. Compounds **1** and **2** are included and they contain the pyrazoles **11** and **8** respectively.

Pyrazole	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Frequency	123	18	2	1	5	1	1	3	1
Pyrazole	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	
Frequency	1	1	1	1	1	2	1	2	

Table S2 Analysis of the tetrakis scorpionate derivative motifs showing the pyrazole and the metal involved. Title compounds **1** and **2** are also included for comparison.

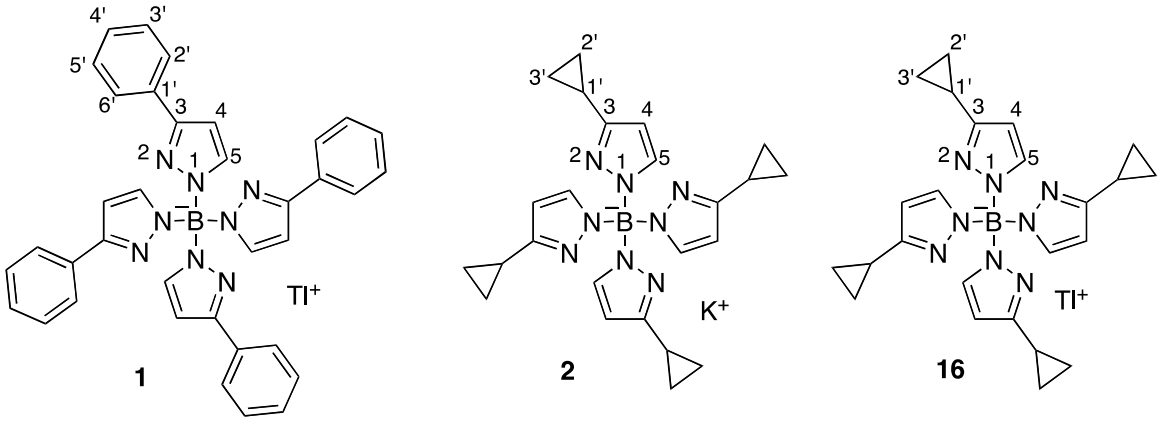
refcode	Motif	Pz	Metal	refcode	Motif	Pz	Metal
JAJQOB	A	1	-	CODGIL	A	4	-

GOGGUG	B	2	Ir	KILZAG	B	1	K
KILZEK	B	1	Na	MIBVOJ/01	C	1	Ag
QUGGII	C	1	Ag	SIQQUE	C	1	Ag
SIQREP	C	1	Ag	SIQRIT	C	1	Ag
SIQROZ	C	1	Ag	SIQRUF	C	1	Ag
SIQSOA	C	2	Ag	SIQSUG	C	2	Ag
SIQTAN	C	2	Ag	SIQTER	C	2	Ag
JARTAY	C	15	Ag	DAYCEL	C	1	Au
FAGKUU	C	1	Au	DEGCEX	C	1	B
ASBCUA	C	1	Cu	YACMEW	C	1	Cu
ZEJQOU	C	1	Cu	XAJHOF	C	2	Cu
HESMAT	C	1	Hg	TITBUT	C	1	Hg
ESODAR	C	1	Ir	JOBMAP	C	1	Ir
YUMXUZ	C	1	Pd	YUMYEK	C	1	Pd
GUVNOA	C	6	Pd	NIDCOU	C	1	Pt
BOKPUM	C	1	Re	GUCXEH	C	1	Re
GUDRUS	C	1	Re	GUFTOQ	C	1	Re
ZURNAB	C	1	Re	ZURNEF	C	1	Re
ZURNIJ	C	1	Re	BIZTUZ	C	1	Rh
BIZVAH	C	1	Rh	RIQNOV	C	17	Tl
SIQRAL	D	1	Ag	SIQSAM	D	2	Ag
SIQSEQ	D	2	Ag	SIQSIU	D	2	Ag
ZIHXAP	D	1	Cd	LOGXIP	D	1	Co
HARTOJ	D	1	Cr	KELGIT	D	1	Cr
XAJHEV	D	2	Cu	XAJHIZ	D	2	Cu
OKELIZ	D	5	Cu	TUHKEN	D	12	Cu
TUHKIR	D	12	Cu	RIQNUB	D	17	Eu
AMEHAC	D	1	Fe	AMOFIS	D	1	Fe
DEBTIP/01	D	1	Fe	IXIQUC	D	1	Fe

IXIRAJ	D	1	Fe	IXIRIR	D	1	Fe
PERYUI	D	1	Fe	REFDOX	D	1	Fe
REJMUP	D	1	Fe	REJNEA	D	1	Fe
RERRUD/01	D	1	Fe	RIDXOS	D	1	Fe
RIDYAF	D	1	Fe	RIDYIN	D	1	Fe
RIFREF	D	1	Fe	SOQJIS	D	1	Fe
TEFKOG/01	D	1	Fe	TIZPUO	D	1	Fe
UDURUI	D	1	Fe	WOXVEM	D	1	Fe
XUGPIA	D	1	Fe	XUHBAF	D	1	Fe
YUMFUI	D	1	Fe	PZBCMO	D	1	Mb
VOGGAZ	D	1	Mb	HARTUP	D	1	Mn
BOXZAP	D	1	Mo	KEYKII	D	1	Mo
JIQLOK	D	10	Mo	JIQLIE	D	13	Mo
TEHSOP	D	16	Na	OKELOF	D	5	Ni
OKELUL	D	5	Ni	FOBNUH	D	1	P
CAMSEQ	D	1	Pd	CAMSIU	D	1	Pd
YIPLAK	D	1	Pd	RUNHAJ	D	1	Pt
GUFTUW	D	1	Re	GUFVAE	D	1	Re
LIJFEP	D	1	Re	LIJFIT	D	1	Re
NUGJEE	D	1	Re	WAYWEY	D	1	Re
YOZTUC	D	1	Re	YOZVAK	D	1	Re
BIZVEL	D	1	Rh	BODNAJ	D	1	Rh
HEDFEC	D	1	Ru	HEDFOM	D	1	Ru
HEDFUS	D	1	Ru	PZBZRU10	D	1	Ru
KOSTOB	D	1	Sn	NUJGOO	D	3	Sn
TERHED	D	3	Sn	**1**	D	11	Tl
JARRUQ	D	14	Tl	JARROK	D	15	Tl
COVCIZ/10	D	1	W	GABMED	E	1	Co/Rh
GABMIH	E	1	Co/Rh	OGOZOZ	E	1	Pd

OGOZUF	E	1	Pd	OGUBAT	E	1	Pd
GABMUT	E	1	Pd/Rh	GABLIG	E	1	Rh
GABLOM	E	1	Rh	GABLUS	E	1	Rh
GABMAZ	E	1	Rh	GABMON	E	1	Zn/Rh
DAPPIU	E(pol)	1	Cu	DAPPUG	E(pol)	1	Cu
2	E(pol)	8	K	DEGCIB	F	1	-
SUTZAI	F	1	-	KUWWUU	G	1	Be
JAJTUJ	G	5	Co	AQIHOY	G	7	Co
OKEMAS	G	2	Ni	VOTVOP	G	1	Pb
KIVXES	G	1	Sn	ESIZAH	G	5	Zn
WECFEP	H	1	Cd	MESNUT	H	1	Co
AKEQIQ	H	2	Co	XUHYOO	H	9	Co
MESPEF	H	1	Cu	HOKJOG	H	2	Cu
AVICIR	H	1	Fe	ZAWHUA	H	1	Fe
AKEQEM	H	2	Fe	PIVQOA	H	8	Fe
RESWIW/01	H	8	Fe	WAMFAR	H	1	Mg
MESNON	H	1	Mn	PIBNEU	H	1	Mn
AKEQAI	H	2	Mn	MESPAB	H	1	Ni
AKEQOW	H	2	Ni	MESPIJ	H	1	Zn
AKEQUC	H	2	Zn	ZESRIY	I	1	Eu
QIDGAL/01	I	1	Sm	WOLQIX	I	1	U
WOLQOD	I	1	U	WOLQUJ	I	1	U
HASSUP	J	1	Ga	VIHWEP	J	1	V
JAJQIV	K	1	Sm	ZESROE	K	1	Yb

S2. NMR properties for compounds 1, 2 and 16



1 2 16

NMR parameters: solution and solid state

Solution NMR spectra were recorded on a Bruker DRX 400 (9.4 Tesla, 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 40.56 MHz for ^{15}N) spectrometer with a 5-mm inverse detection H-X probe equipped with a z-gradient coil, at 300 K. Chemical shifts (δ in ppm) are given from internal solvents: DMSO-d_6 2.49 for ^{1}H and 39.5 for ^{13}C, and for ^{15}N NMR nitromethane (0.00) was used as external standard. 2D (^{1}H-^{13}C) gs-HMQC, (^{1}H-^{13}C), (^{1}H-^{15}N) gs-HMQC and (^{1}H-^{15}N) gs-HMBC were acquired and processed using standard Bruker NMR software and in non-phase-sensitive mode [1]. Gradient selection was achieved through a 5% sine truncated shaped pulse gradient of 1 ms. The FIDs were processed using zero filling in the F1 domain and a sine-bell window function in both dimensions was applied prior to Fourier transformation.

Solid state NMR spectra were recorded on a Bruker WB 400 (9.4 Tesla, 100.73 MHz for ^{13}C and 40.60 MHz for ^{15}N) at 300 K using a 4 mm DVT probehead. Samples were carefully packed in a 4-mm diameter cylindrical zirconia rotors with Kel-F end-caps. Operating conditions involved 2.9 μs 90° ^{1}H pulses and decoupling field strength of 86.2 kHz by SPINAL 64 sequence. ^{13}C spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to the Me4Si (for the carbonyl atom δ (glycine) = 176.1 ppm) and ^{15}N spectra to $^{15}NH_4Cl$ and then converted to nitromethane scale using the relationship: δ ^{15}N(nitromethane) = δ ^{15}N(ammonium chloride) – 338.1 ppm. In order to distinguish protonated and unprotonated carbon and nitrogen atoms, the NQS (Non-Quaternary Suppression) experiment by conventional cross-polarization was recorded; before the acquisition the decoupler is switched off for a very short time of 25 μs for ^{13}C and 80 μs for ^{15}N [2-4].

[1] Berger, S.; Braun, S. 200 and more NMR experiments, Wiley-VCH, Weinheim, 2004.

[2] Du Bois Murphy P. D. (1983). *J. Magn. Reson.* **52**, 343–345.

[3] Du Bois Murphy P. D. (1985). *J. Magn. Reson.* **62**, 303–308.

[4] Alemany, L. B.; Grant, D.M.; Alger, T. D.: Pugmire, R. J. (1983). *J. Am. Chem. Soc.* **105**, 6697–6704.

Comp.	Atom	Solvent or state	Chemical shifts (ppm) and some coupling constants (Hz)	Calc. S_4	Calc. D_2
1[a] Tl^+	N1	---	---		
	N2	---	---		
	C3	DMSO-d_6	151.5, $^3J(^{11}B\text{-}^{13}C)$ = 4.7		
	C4	DMSO-d_6	101.9		
	C5	DMSO-d_6	136.3		
	C1'	DMSO-d_6	134.5		
	C2', C6'	DMSO-d_6	125.4		
	C3', C5'	DMSO-d_6	128.5		
	C4'	DMSO-d_6	126.9		
	H4	DMSO-d_6	6.59		
	H5	DMSO-d_6	7.53		
	H2', H6'	DMSO-d_6	7.76		
	H3', H5'	DMSO-d_6	7.34		
	H4'	DMSO-d_6	7.20		
16[b] Tl^+	N1	DMSO-d_6	–155.1, $^1J(^{11}B\text{-}^{15}N)$ = 35.3		
	N2	DMSO-d_6	–71.8		
	C3	DMSO-d_6	155.8		
	C4	DMSO-d_6	99.6		
	C5	DMSO-d_6	135.1		
	C1'	DMSO-d_6	9.2		
	C2', C3'	DMSO-d_6	8.3		
	H4	DMSO-d_6	5.79		
	H5	DMSO-d_6	6.88		
	H1'	DMSO-d_6	2.02		
	H2', H3'	DMSO-d_6	0.59; 0.86		
16[b] Tl^+	N1	CPMAS	–152.8		
	N2	CPMAS	–68.2 (m)		
	C3	CPMAS	156.3; 158.4; 160.4		
	C4	CPMAS	97.4; 98.1; 100.1; 105.4, $^3J(^{13}C\text{-}^{205}Tl)$ = 58, direct J = 263		
	C5	CPMAS	133.8, 135.1, 135.9, 136.6, 138.0, 139.3		
	C1'	CPMAS	7.27-12.9		
	C2'	CPMAS	7.27-12.9		

	C3'	CPMAS	7.27-12.9		
This work					
1 Tl^+	N1	DMSO-d_6	–148.4, $^1J(^{11}B\text{-}^{15}N)$ = 30.4	–145.6[c]	–146.8[d]
	N2	DMSO-d_6	–71.0	–65.2	–59.1
	C3	DMSO-d_6	150.8, $^3J(^{11}B\text{-}^{13}C)$ = 3.4	150.0	150.2
	C4	DMSO-d_6	101.2, $^1J(^1H\text{-}^{13}C)$ = 173.0, $^3J(^{11}B\text{-}^{13}C)$ = 1.5	98.5	98.7
	C5	DMSO-d_6	136.2, $^2J(^{11}B\text{-}^{13}C)$ = 3.1	136.8	135.0
	C1'	DMSO-d_6	134.8	139.6	139.9
	C2', C6'	DMSO-d_6	125.2, $^1J(^1H\text{-}^{13}C)$ = 160.6	124.8	124.8
	C3', C5'	DMSO-d_6	128.4	126.4	126.5
	C4'	DMSO-d_6	126.6, 125.2, $^1J(^1H\text{-}^{13}C)$ = 161.6	122.2	122.2
	H4	DMSO-d_6	6.61, $^3J_{HH}$ = 2.2	6.32	6.21
	H5	DMSO-d_6	7.53, $^3J_{HH}$ = 2.2	7.57	7.78
	H2', H6'	DMSO-d_6	7.76	7.89	7.92
	H3', H5'	DMSO-d_6	7.34	7.08	7.07
	H4'	DMSO-d_6	7.20	6.76	6.84
1 Tl^+	N1	CPMAS	–144.8, –148.3, –157.7 (intensity 1:2:1)		
	N2	CPMAS	–61.0, –70.2, –80.4 (intensity 1:2:1)		
	C3	CPMAS	153.0, 154.6 (intensity 1:3)		
	C4	CPMAS	109.0, 102.1 (intensity 1:3)		
	C5	CPMAS	139.6, 137.2 (intensity 1:3)		
	C1'	CPMAS	133.6, 132.9, 132.0 (intensity 1:2:1)		
	C2'	CPMAS	122.5, 124.8, 127.6, 129,0, 130,9		
	C3'	CPMAS	122.5, 124.8, 127.6, 129,0, 130,9		
	C4'	CPMAS	122.5, 124.8, 127.6, 129,0, 130,9		
	C5'	CPMAS	122.5, 124.8, 127.6, 129,0, 130,9		
	C6'	CPMAS	122.5, 124.8, 127.6, 129,0, 130,9		
2 K^+	N1	DMSO-d_6	–152.3, $^1J(^{11}B\text{-}^{15}N)$ = 33.6	–149.0[e]	–150.2[f]
	N2	DMSO-d_6	–73.7	–68.1	–62.1
	C3	DMSO-d_6	153.6, $^3J(^{11}B\text{-}^{13}C)$ = 3.2	153.2	152.5
	C4	DMSO-d_6	98.0, $^1J(^1H\text{-}^{13}C)$ = 170.1, $^2J(^1H\text{-}^{13}C)$ = 10.1; $^3J(^{11}B\text{-}^{13}C)$ = 2.5	91.1	91.8
	C5	DMSO-d_6	134.7, $^1J(^1H\text{-}^{13}C)$ = 181.9, $^2J(^{11}B\text{-}^{13}C)$ = 3.1	136.2	134.3

	C1'	DMSO-d_6	9.61, $^1J(^1H\text{-}^{13}C)$ = 160.7	14.1	14.0
	C2', C3'	DMSO-d_6	7.87, $^1J(^1H\text{-}^{13}C)$ = 161.3	9.5	9.4
	H4	DMSO-d_6	5.61, $^3J_{HH}$ = 2.3	5.25	5.21
	H5	DMSO-d_6	7.03, $^3J_{HH}$ = 2.3	7.46	7.64
	H1'	DMSO-d_6	1.82, $^3J_{HH}$ (*cis*) = 8.4; $^3J_{HH}$ (*trans*) = 5.3	1.91	1.90
	H2', H3'	DMSO-d_6	0.51, 0.77	0.35, 0.46	0.26, 0.46
2 K^+	N1	CPMAS	–151.2 [d, $^1J(^{11}B\text{-}^{15}N)$ = 25.5], –155.8 [d, $^1J(^{11}B\text{-}^{15}N)$ = 28.3], –164.7 (s), –173.0 (s)		
	N2	CPMAS	–83.4, –85.2, –89.6 (intensity 2:1:1)		
	C3	CPMAS	156.9 (m)[g]		
	C4	CPMAS	96.6 (m)[g]		
	C5	CPMAS	136.4 (m)[g]		
	C1'	CPMAS	8.7 (m)[g]		
	C2'	CPMAS	8.7 (br)[g]		
	C3'	CPMAS	8.7 (br)[g]		

[a] From (López *et al*. 1995).

[b] From (Claramunt *et al*. 2004a).

[c] ^{11}B = 1.13.

[d] ^{11}B = 1.21.

[e] ^{11}B = 0.29.

[f] ^{11}B = 0.87.

[g] Several lines (up to eight) of different intensities.