Electronic Supplementary Material (ESI) for Dalton Transactions.

Linear Cu(I) Chalocgenones: Synthesis and Application in Borylation of Unsymmetrical Alkynes

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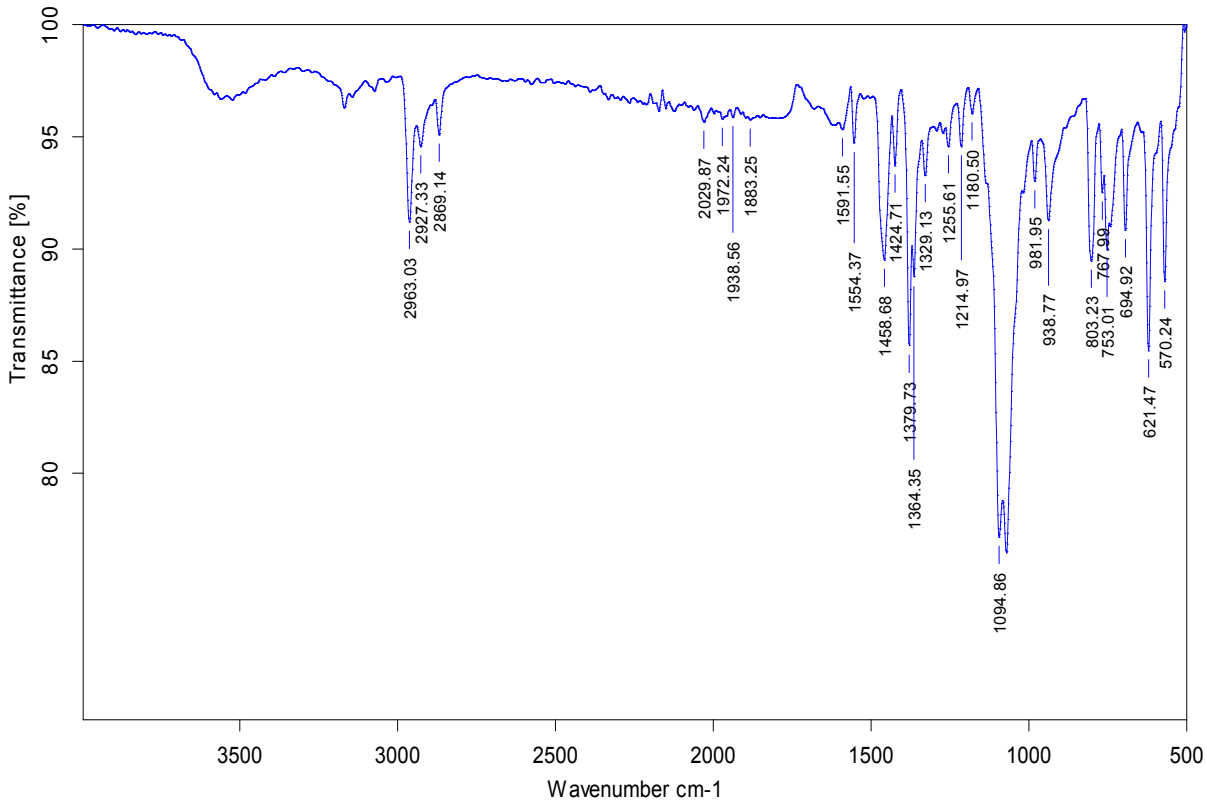


Fig. S1. Neat FT-IR spectrum of $[(IPrS)_2Cu]ClO_4$ (**1**).

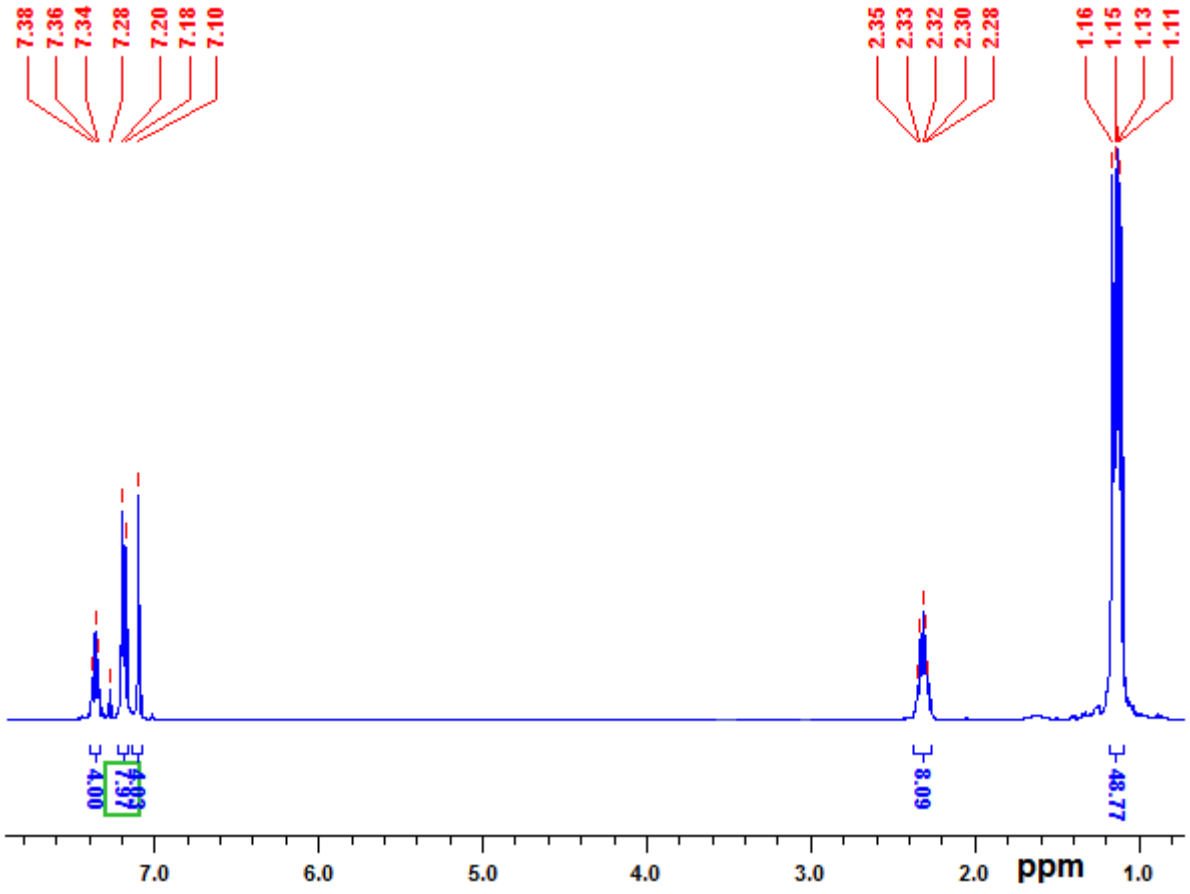


Fig. S2. ^{1}H NMR spectrum of $[(IPrS)_2Cu]ClO_4$ (**1**).

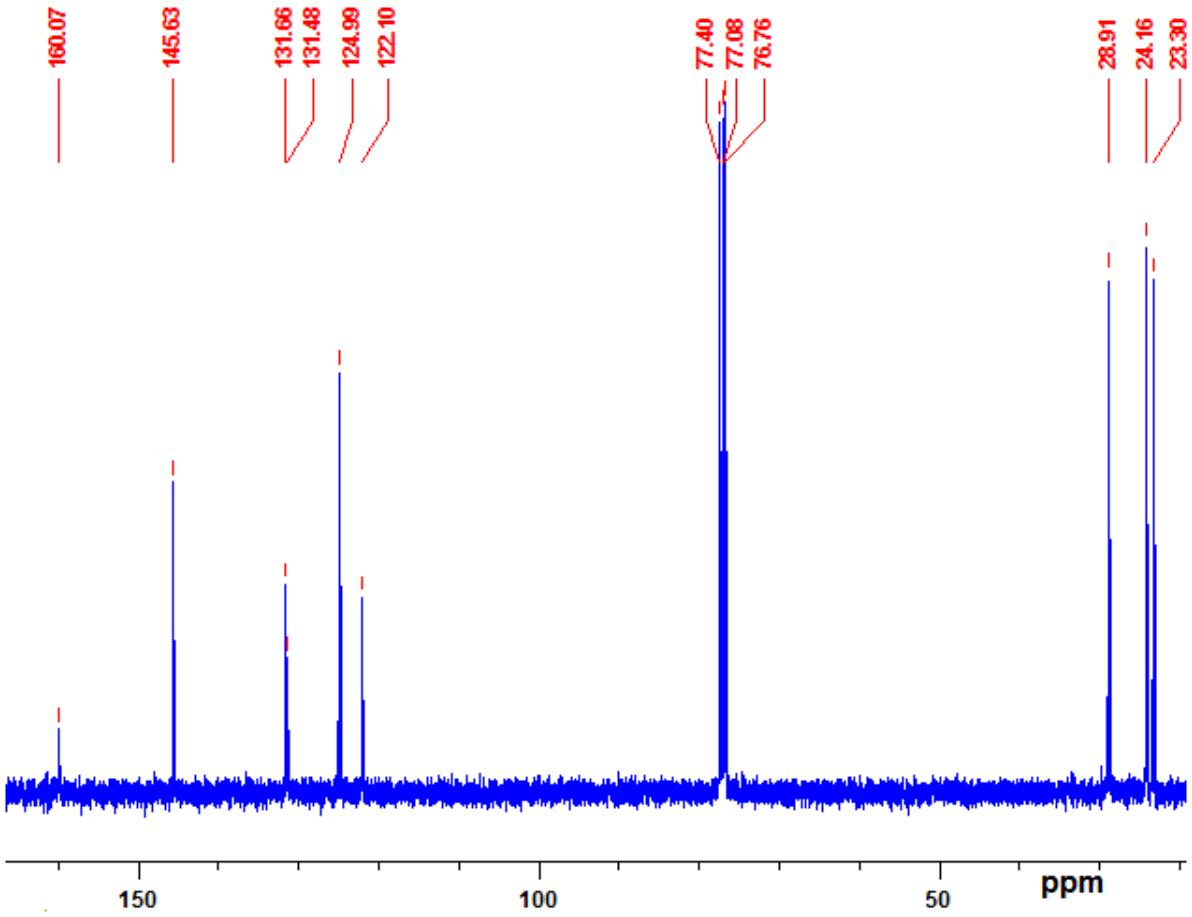


Fig. S3. ^{13}C NMR spectrum of $[(IPrS)_2Cu]ClO_4$ (**1**).

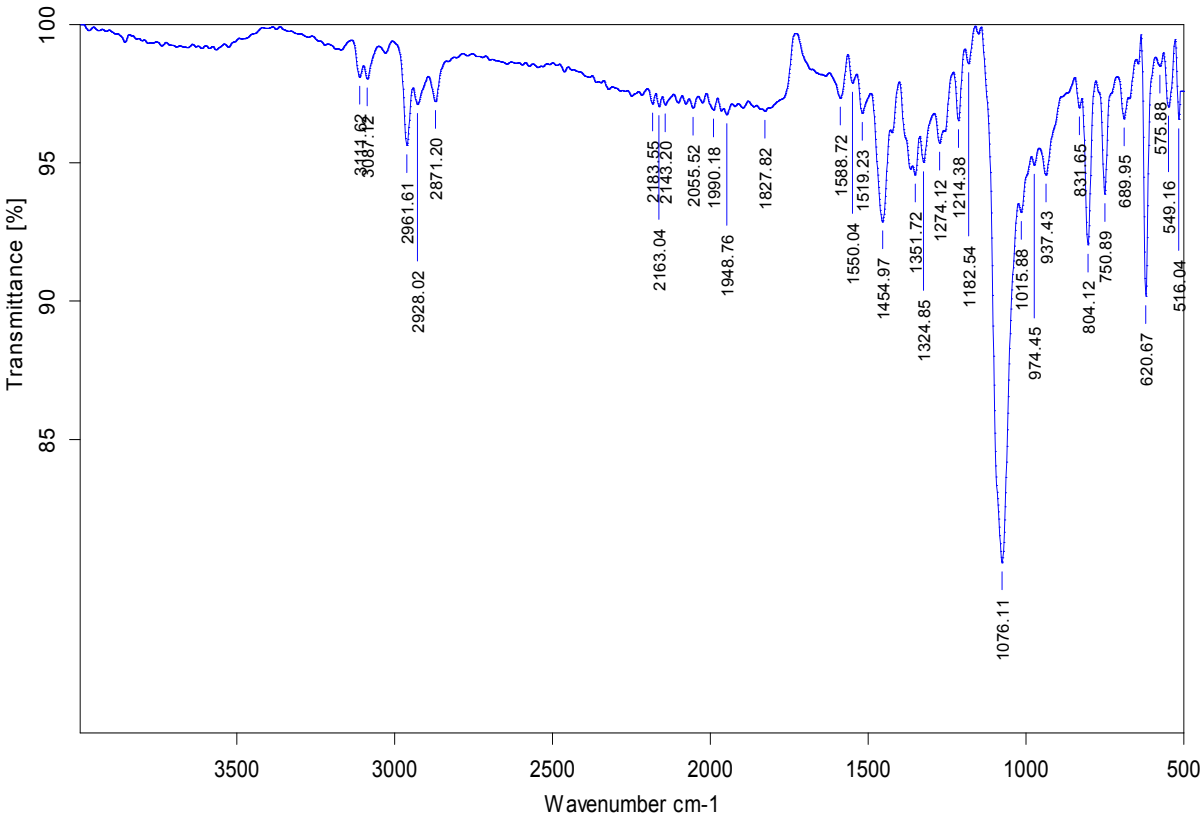


Fig. S4. Neat FT-IR spectrum of $[(IPrSe)_2Cu]ClO_4$ (**2**).

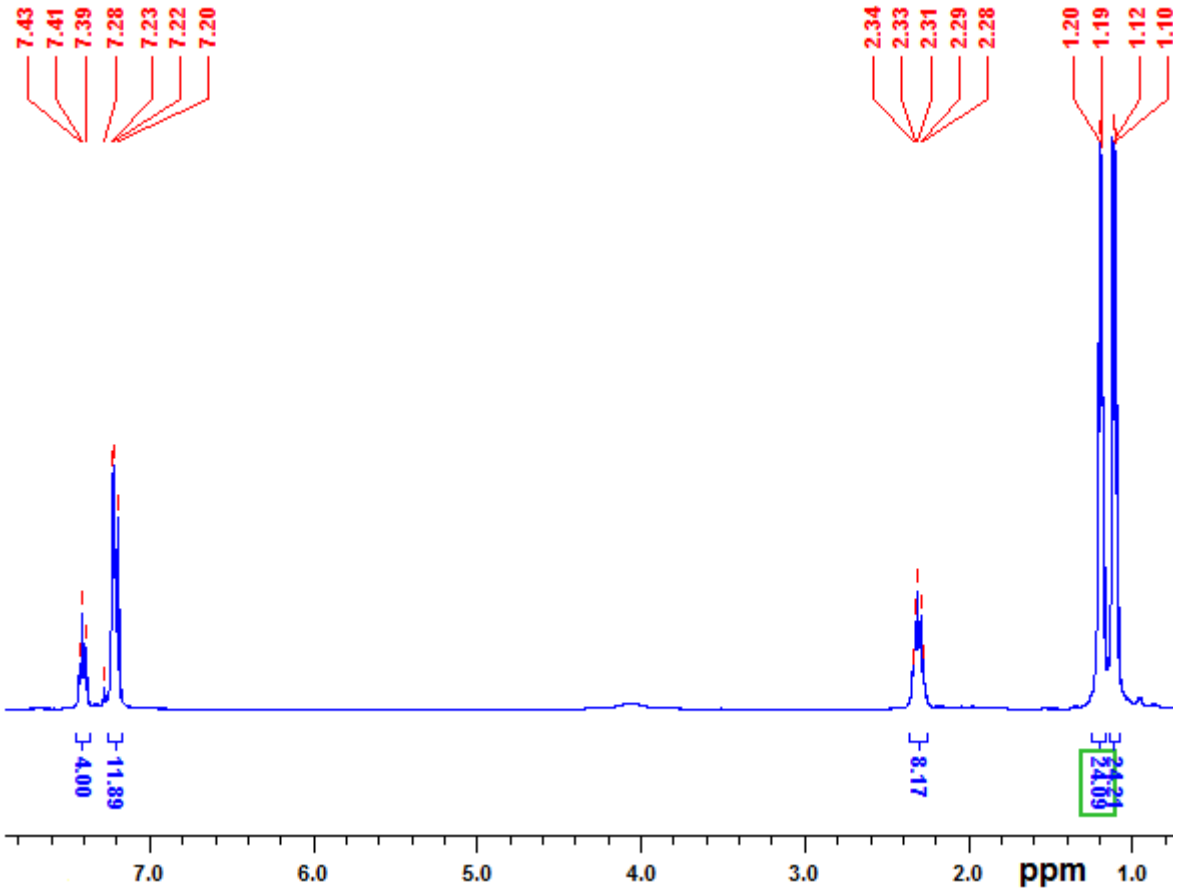


Fig. S5. ^{1}H NMR spectrum of $[(IPrSe)_2Cu]ClO_4$ (**2**).

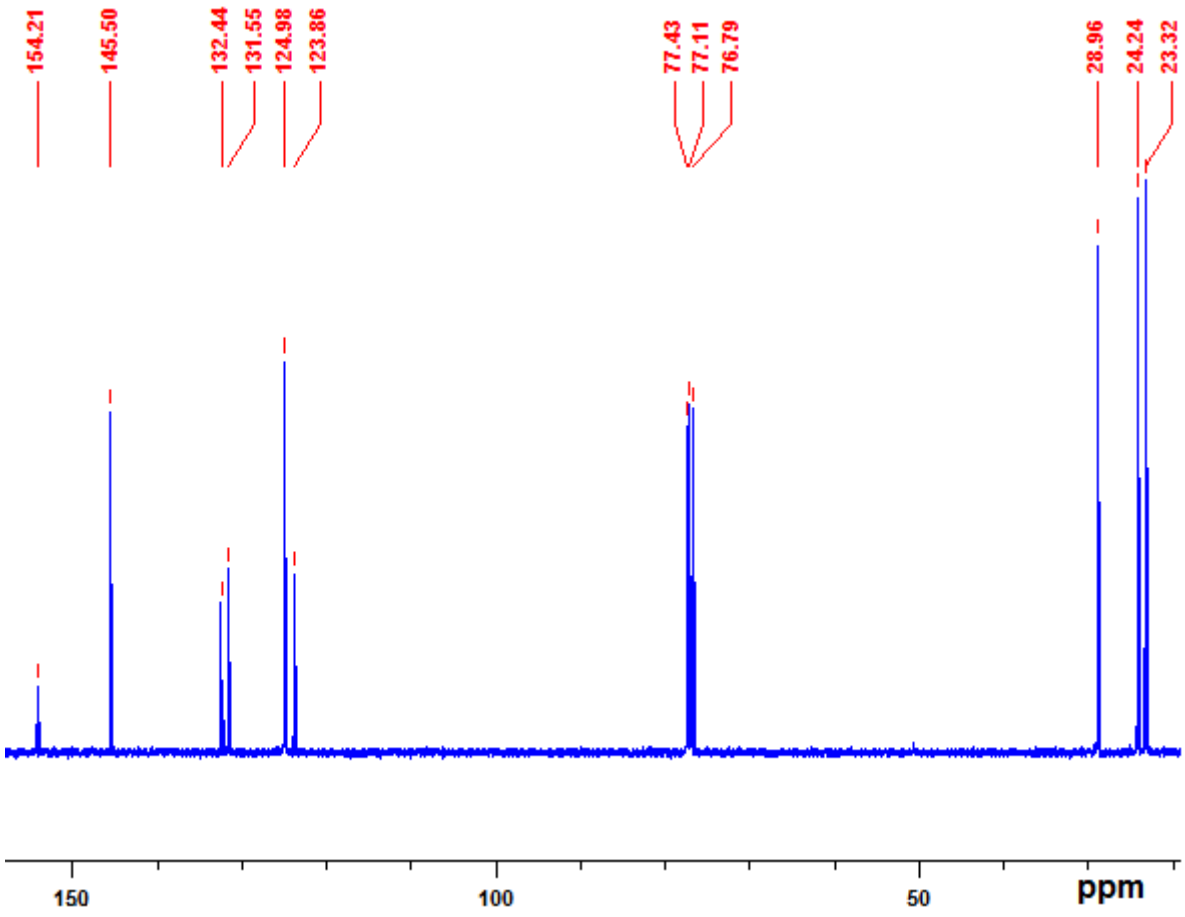


Fig. S6. ^{13}C NMR spectrum of $[(IPrSe)_2Cu]ClO_4$ (**2**).

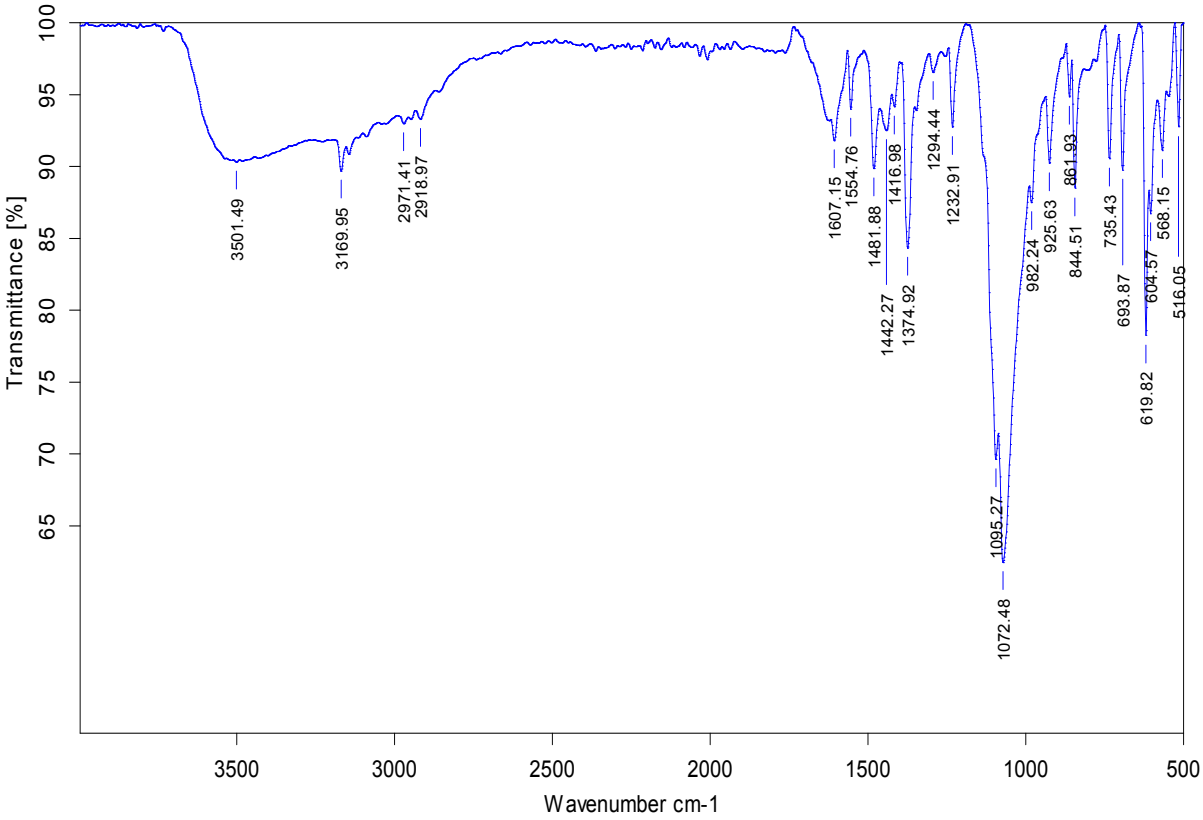


Fig. S7. Neat FT-IR spectrum of $[(IMesS)_2Cu]ClO_4$ (**3**).

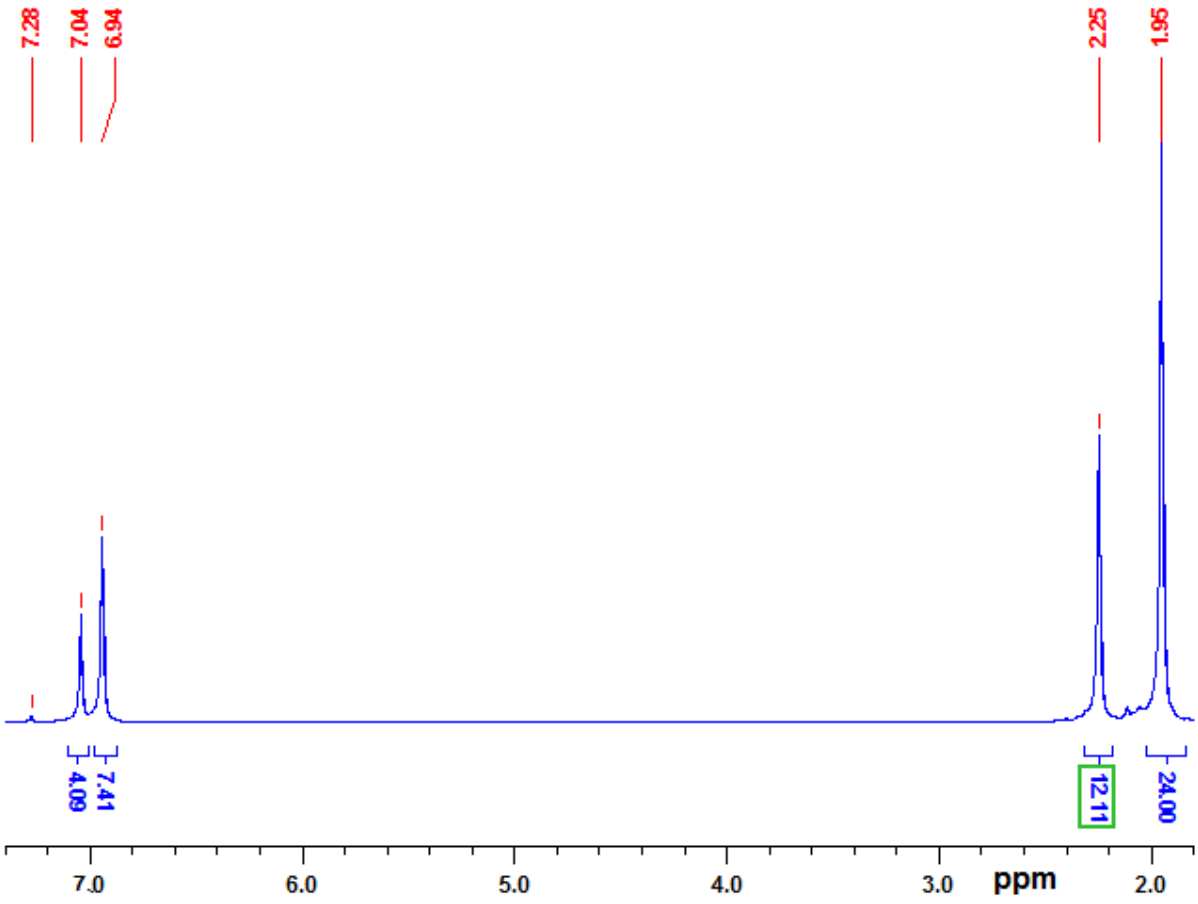


Fig. S8. ^{1}H NMR spectrum of $[(IMesS)_2Cu]ClO_4$ (**3**).

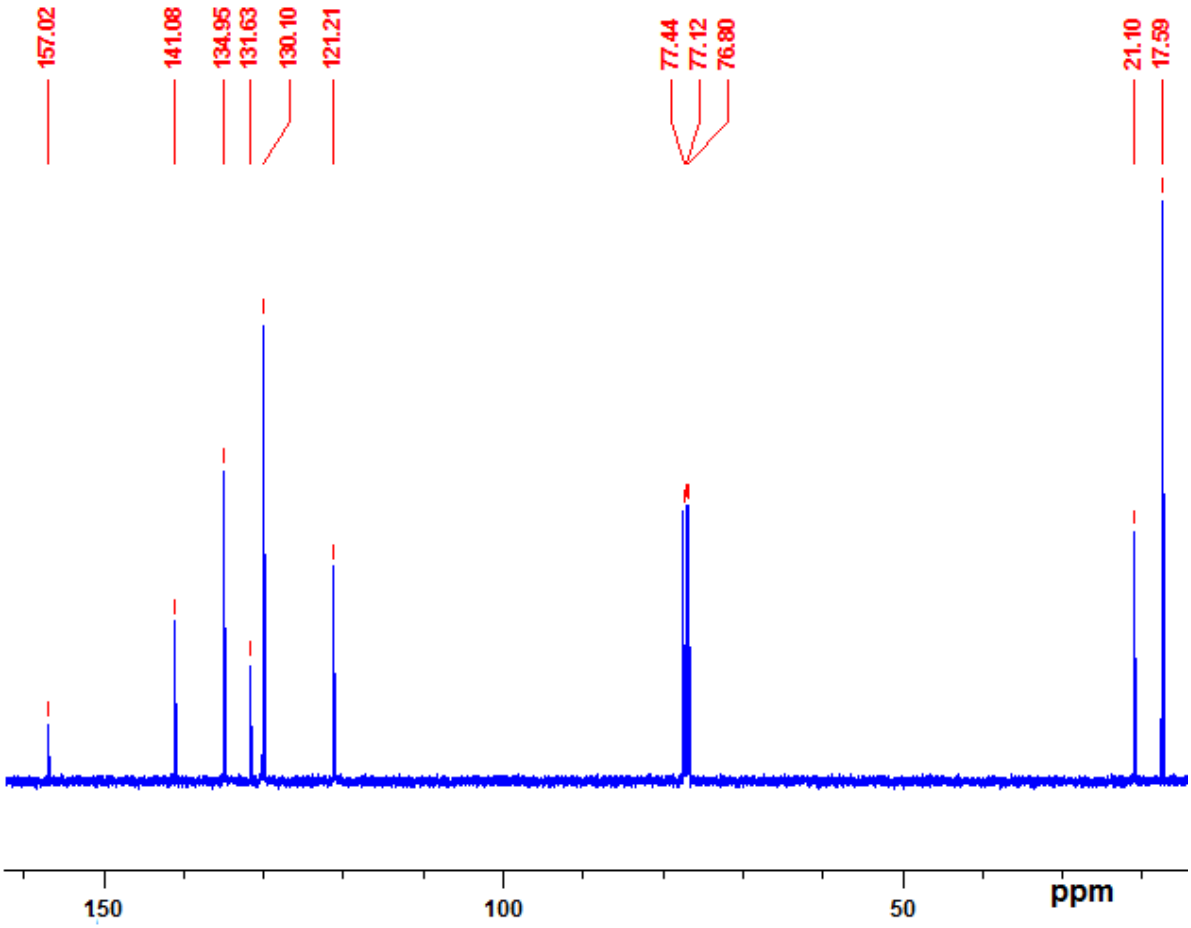


Fig. S9. ^{13}C NMR spectrum of $[(IMesS)_2Cu]ClO_4$ (**3**).

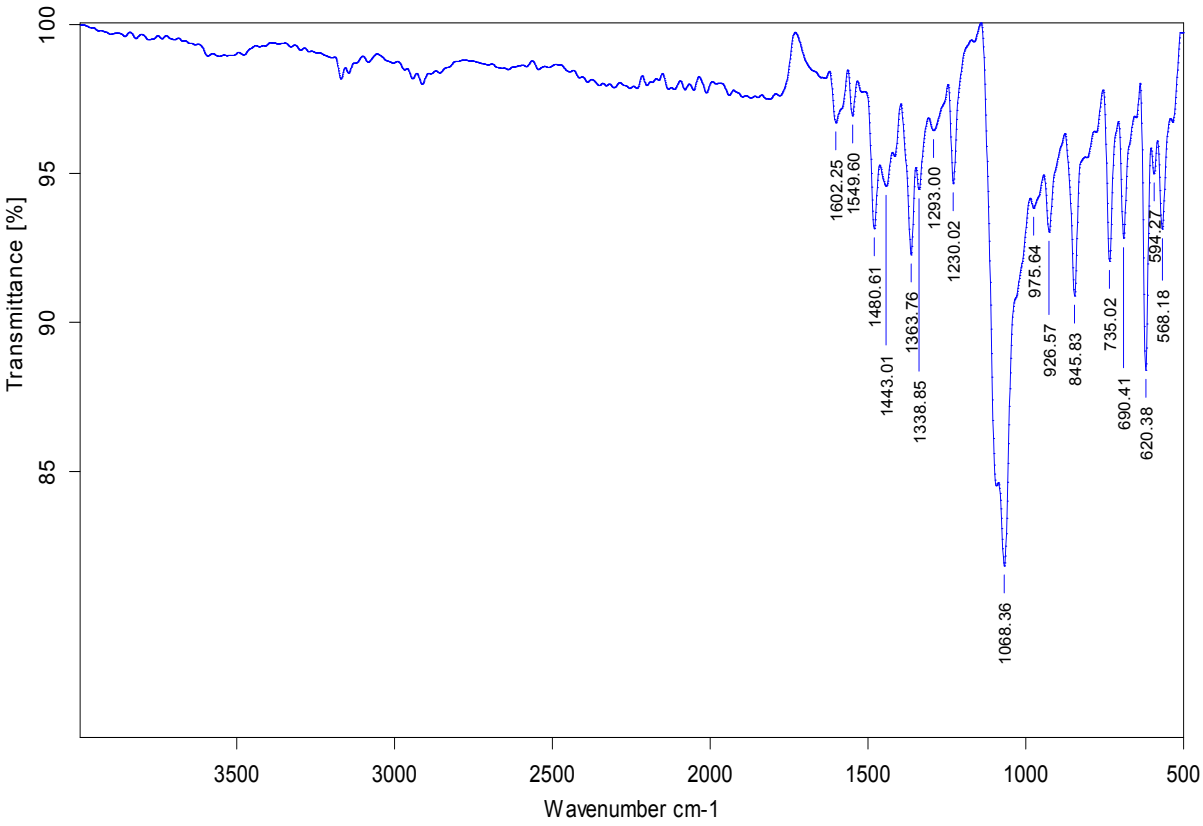


Fig. S10. Neat FT-IR spectrum of $[(IMesSe)_2Cu]ClO_4$ (**4**).

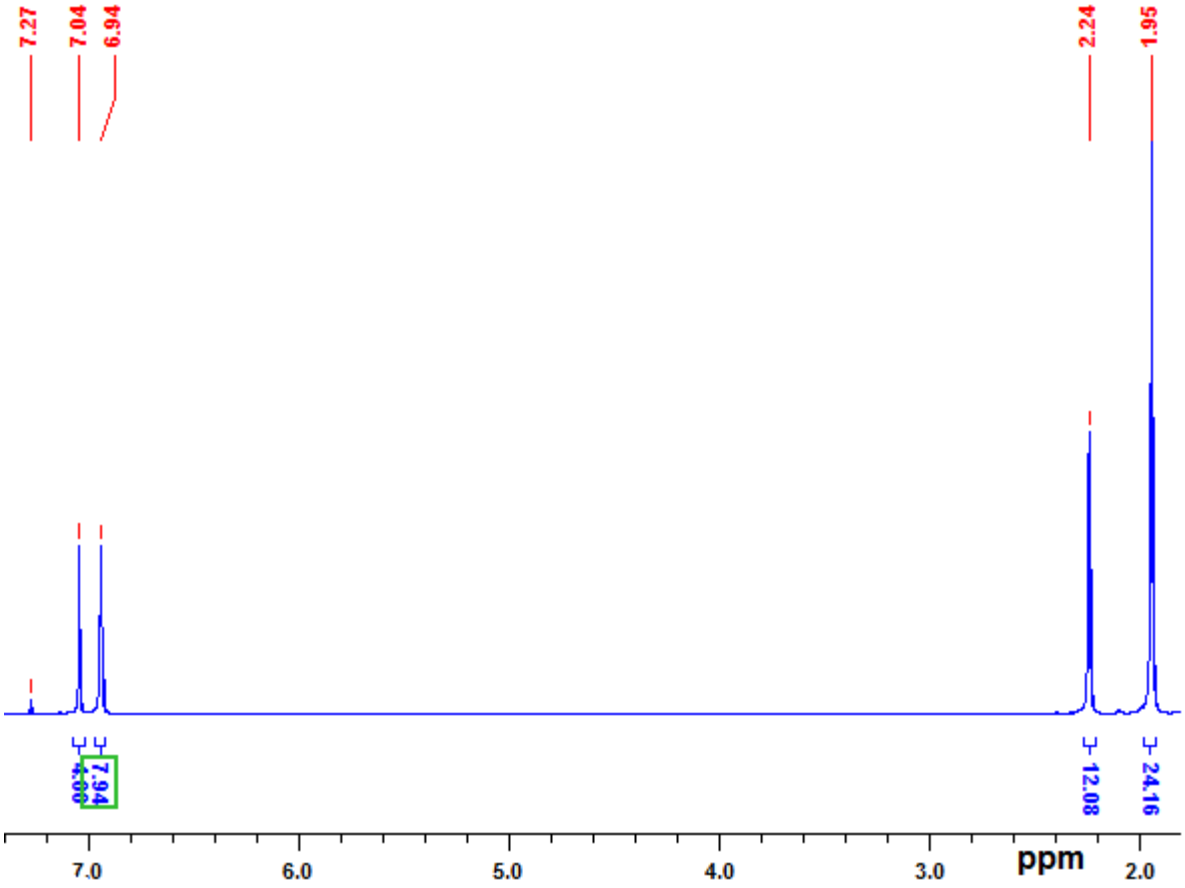


Fig. S11. ^{1}H NMR spectrum of $[(IMesSe)_2Cu]ClO_4$ (**4**).

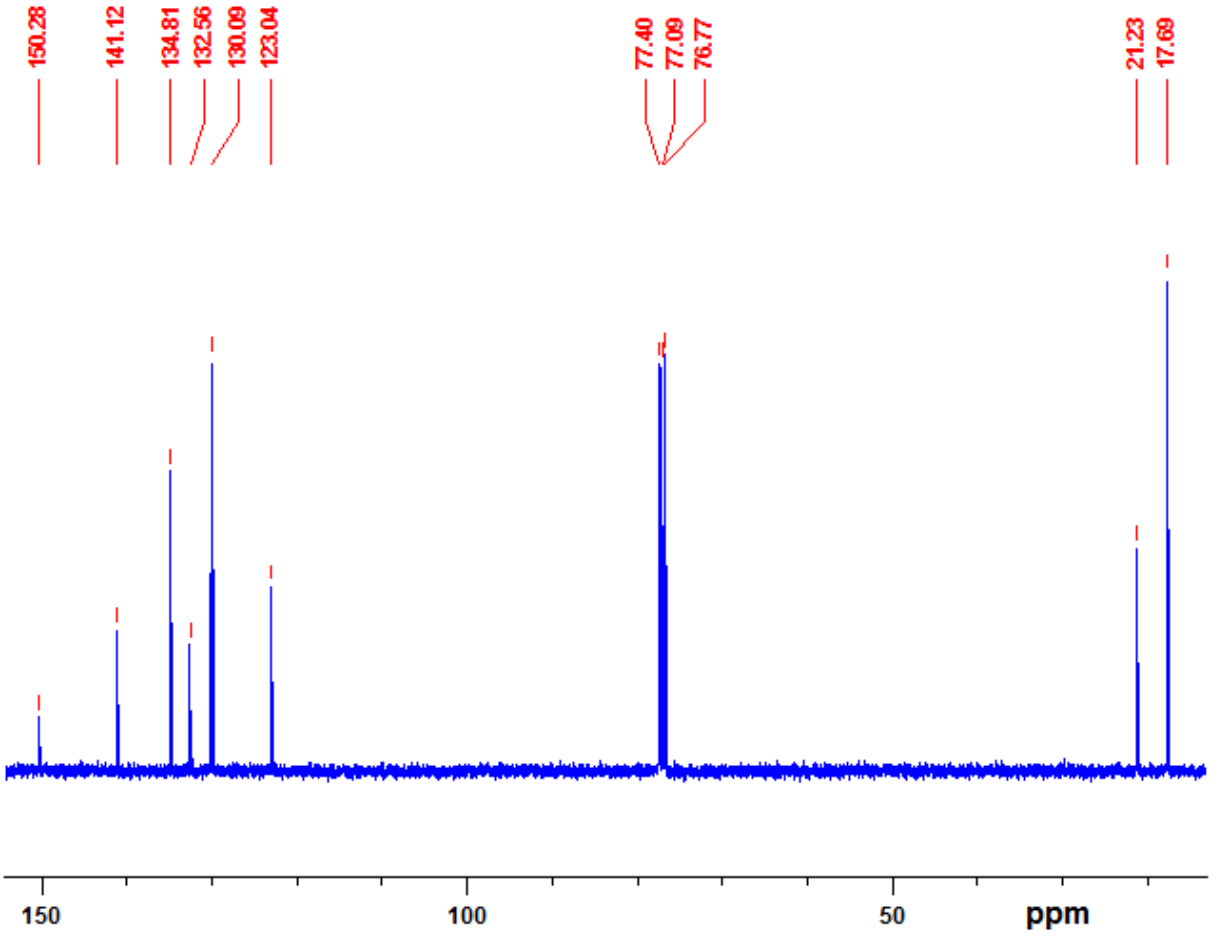


Fig. S12. ^{13}C NMR spectrum of $[(IMesSe)_2Cu]ClO_4$ (**4**).

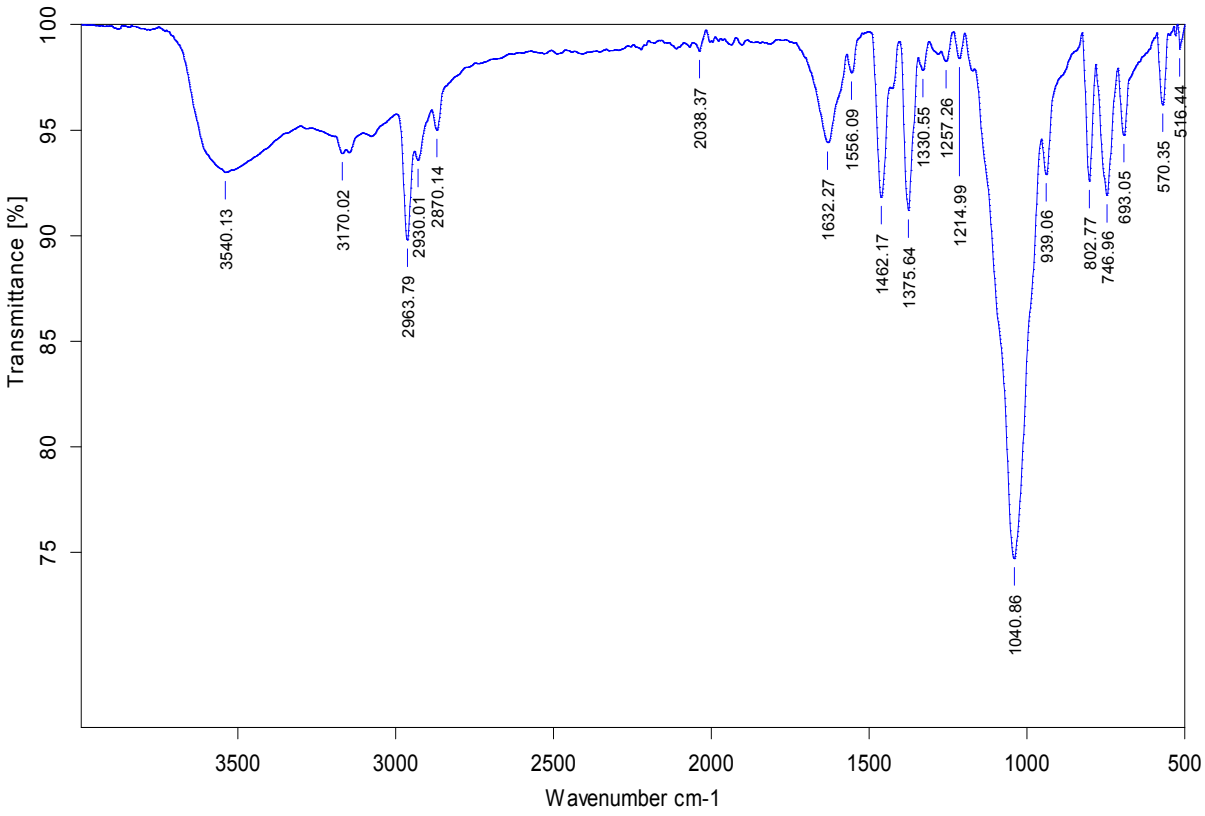


Fig. S13. Neat FT-IR spectrum of $[(IPrS)_2Cu]BF_4$ (**5**).

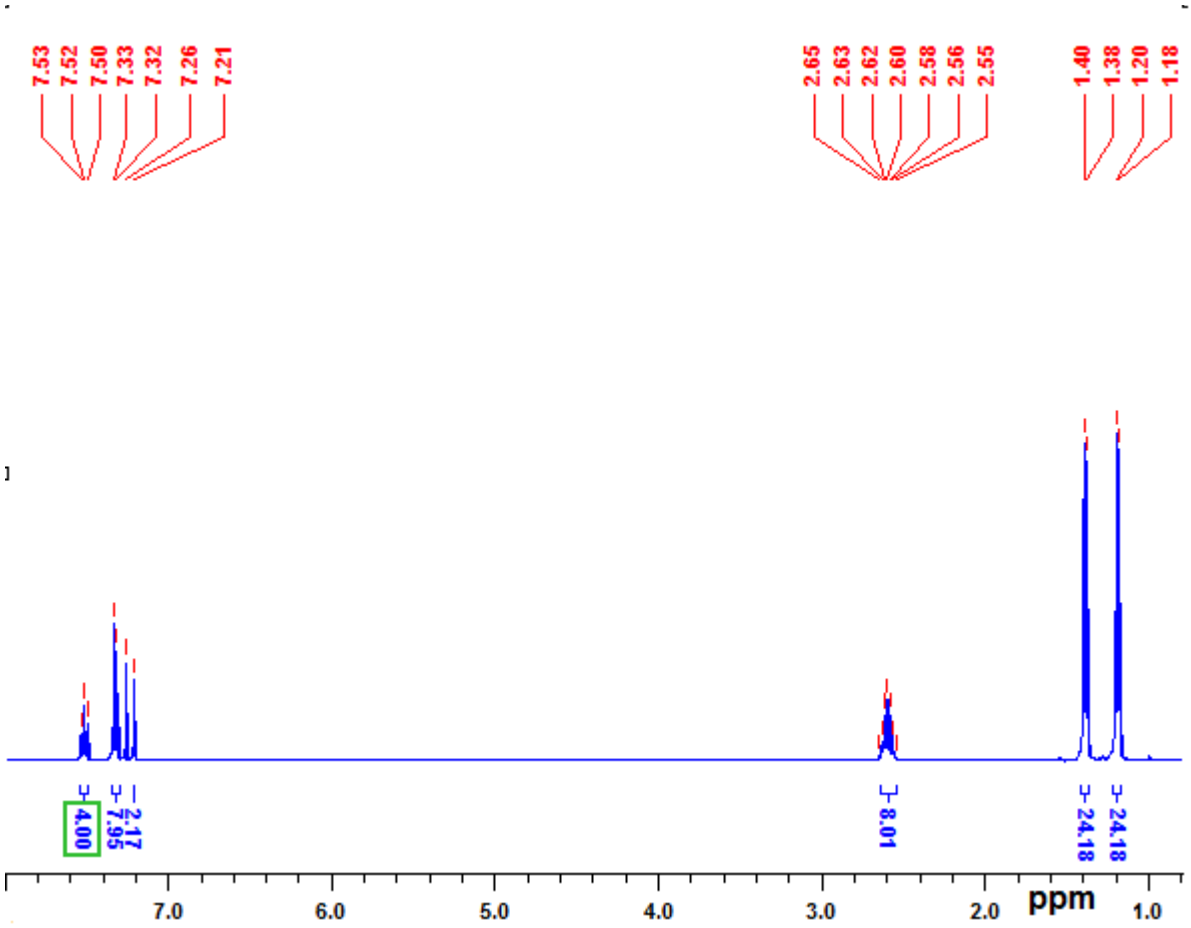


Fig. S14. ^{1}H NMR spectrum of $[(IPrS)_2Cu]BF_4$ (**5**).

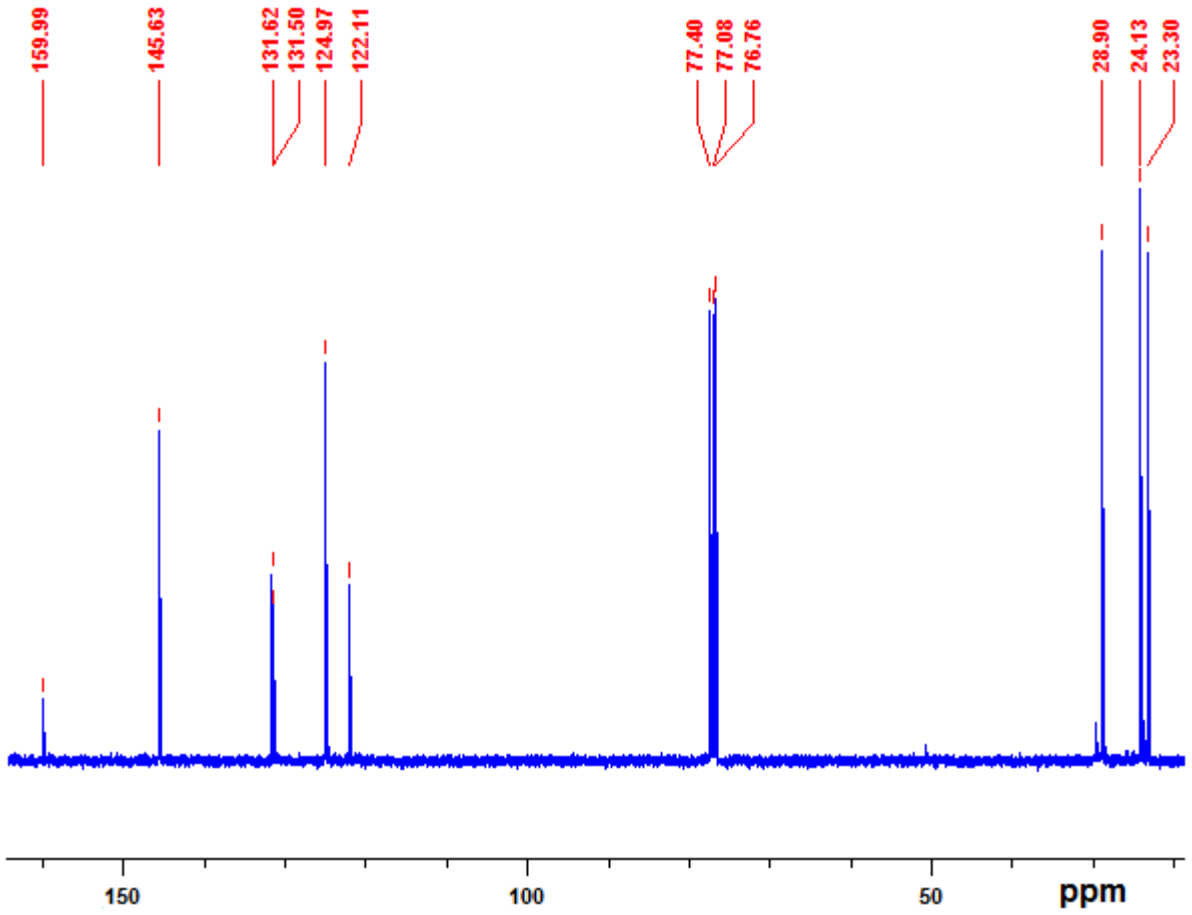


Fig. S15. ^{13}C NMR spectrum of $[(IPrS)_2Cu]BF_4$ (**5**).

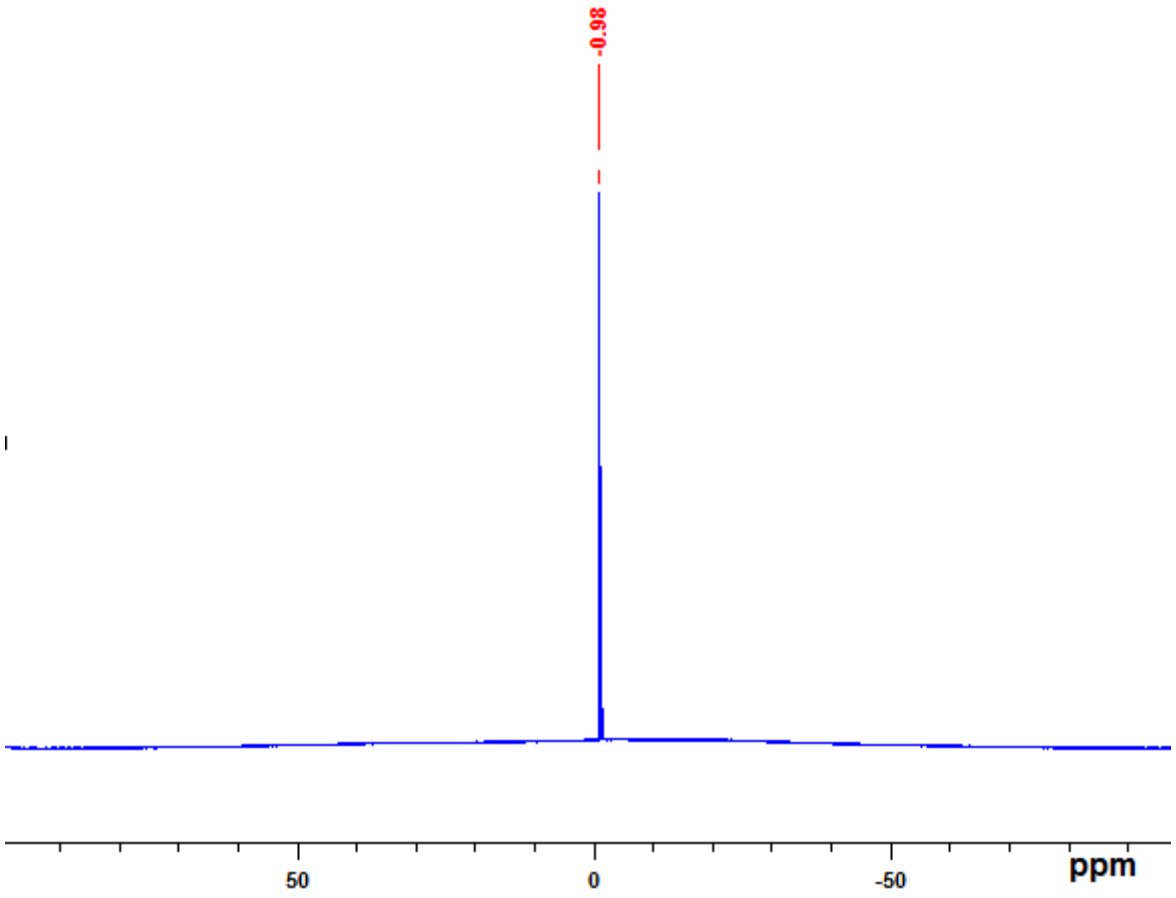


Fig. S16. ^{11}B NMR spectrum of $[(IPrS)_2Cu]BF_4$ (**5**).

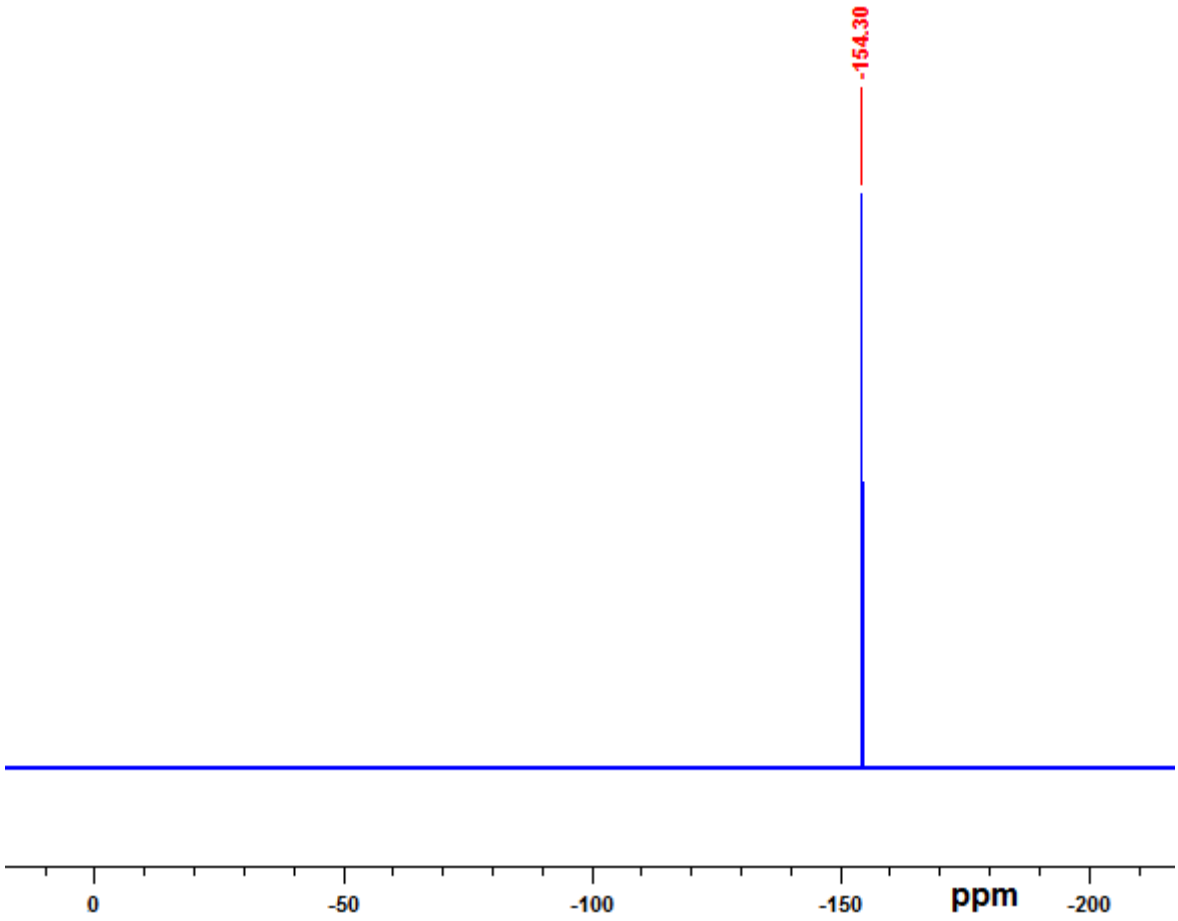


Fig. S17. ^{19}F NMR spectrum of $[(IPrS)_2Cu]BF_4$ (**5**).

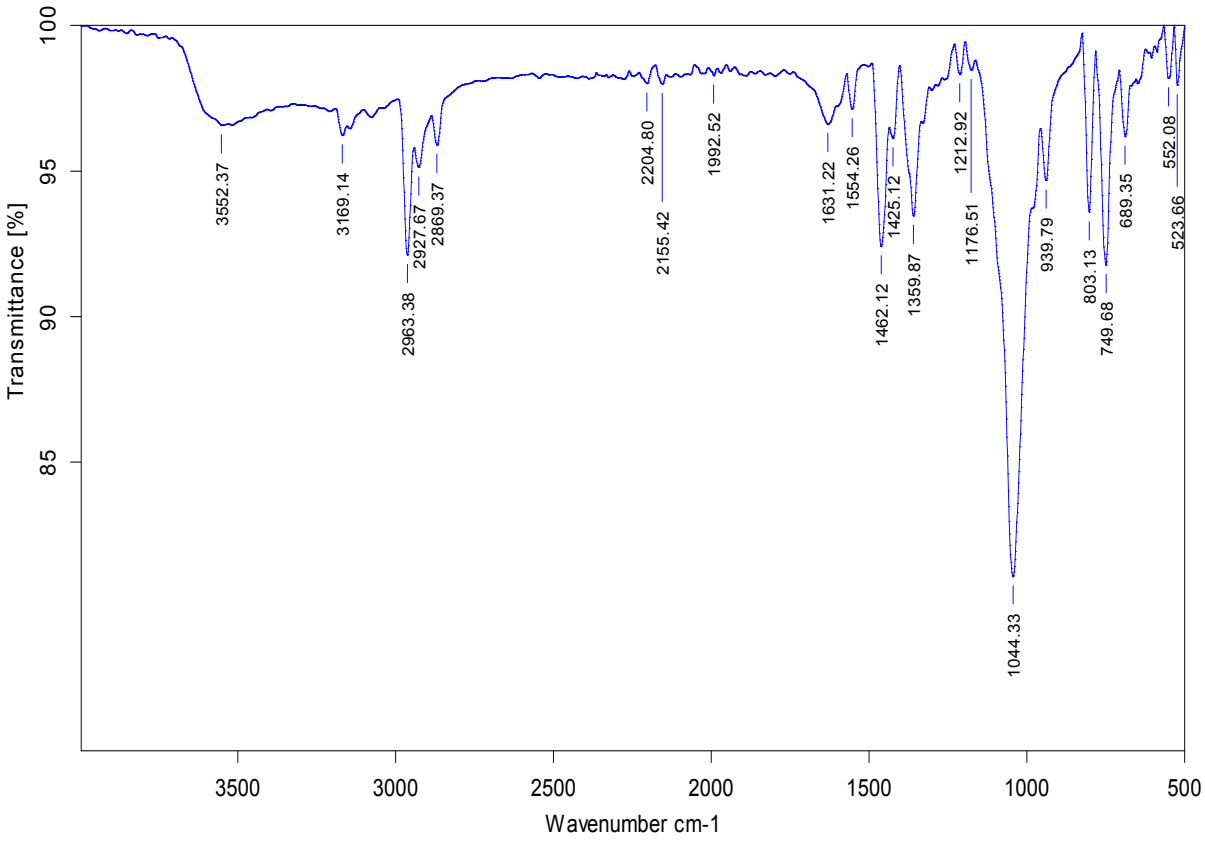


Fig. S18. Neat FT-IR spectrum of $[(IPrSe)_2Cu]BF_4$ (**6**).

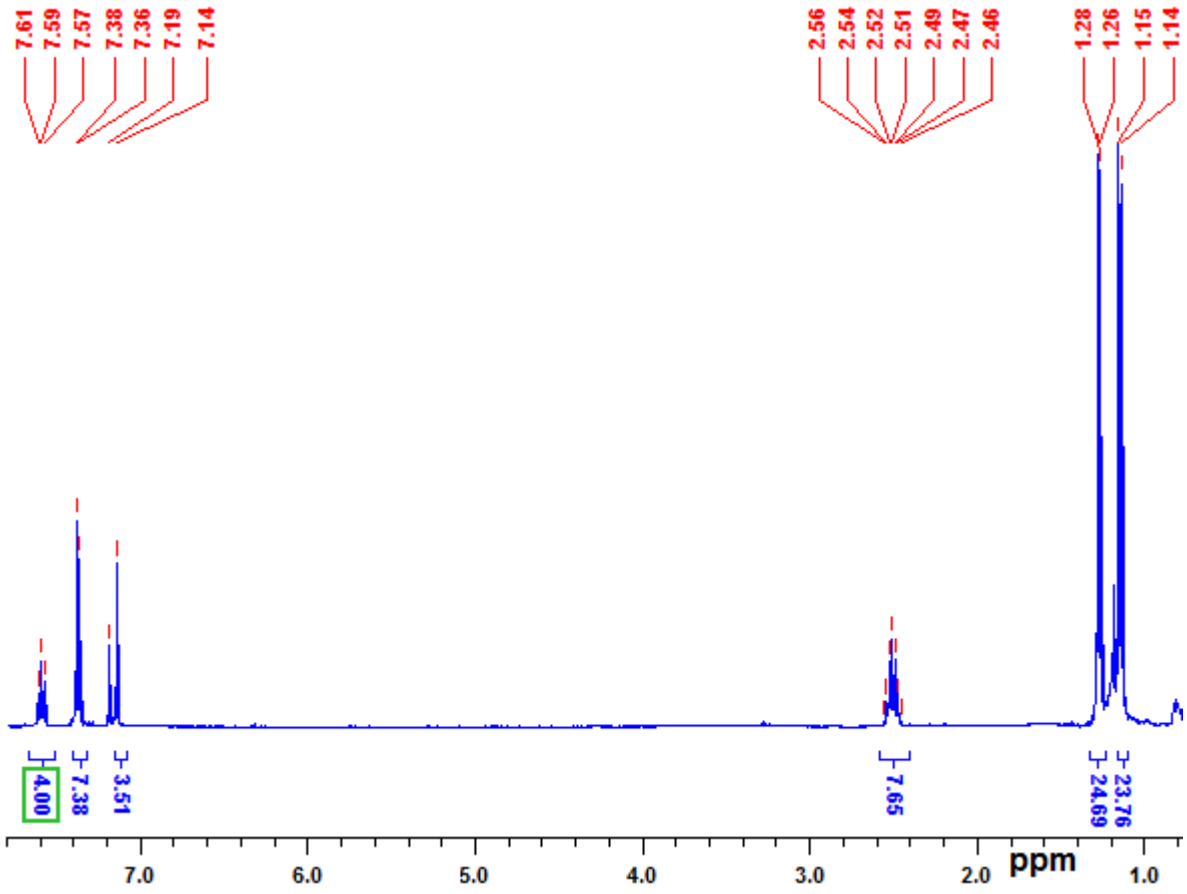


Fig. S19. ^{1}H NMR spectrum of $[(IPrSe)_2Cu]BF_4$ (**6**).

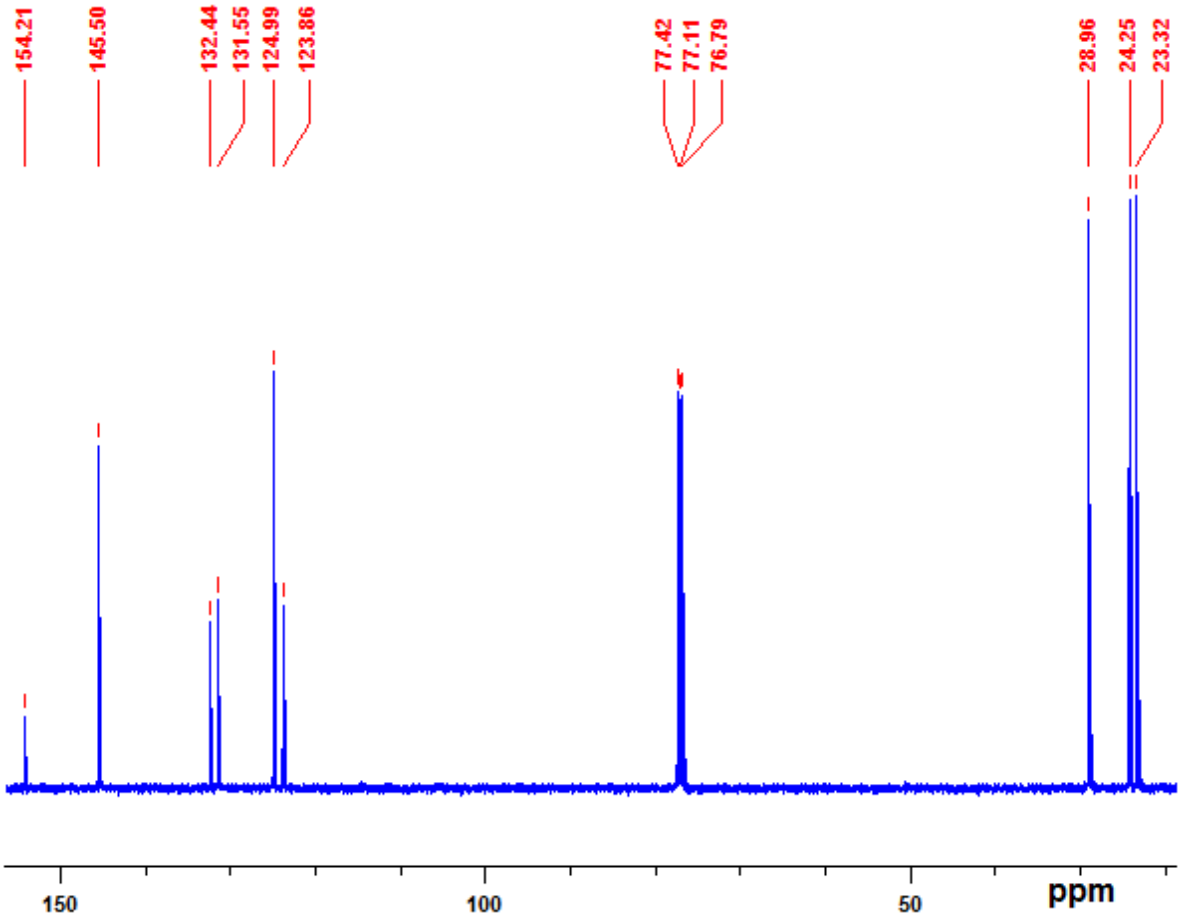


Fig. S20. ^{13}C NMR spectrum of $[(IPrSe)_2Cu]BF_4$ (**6**).

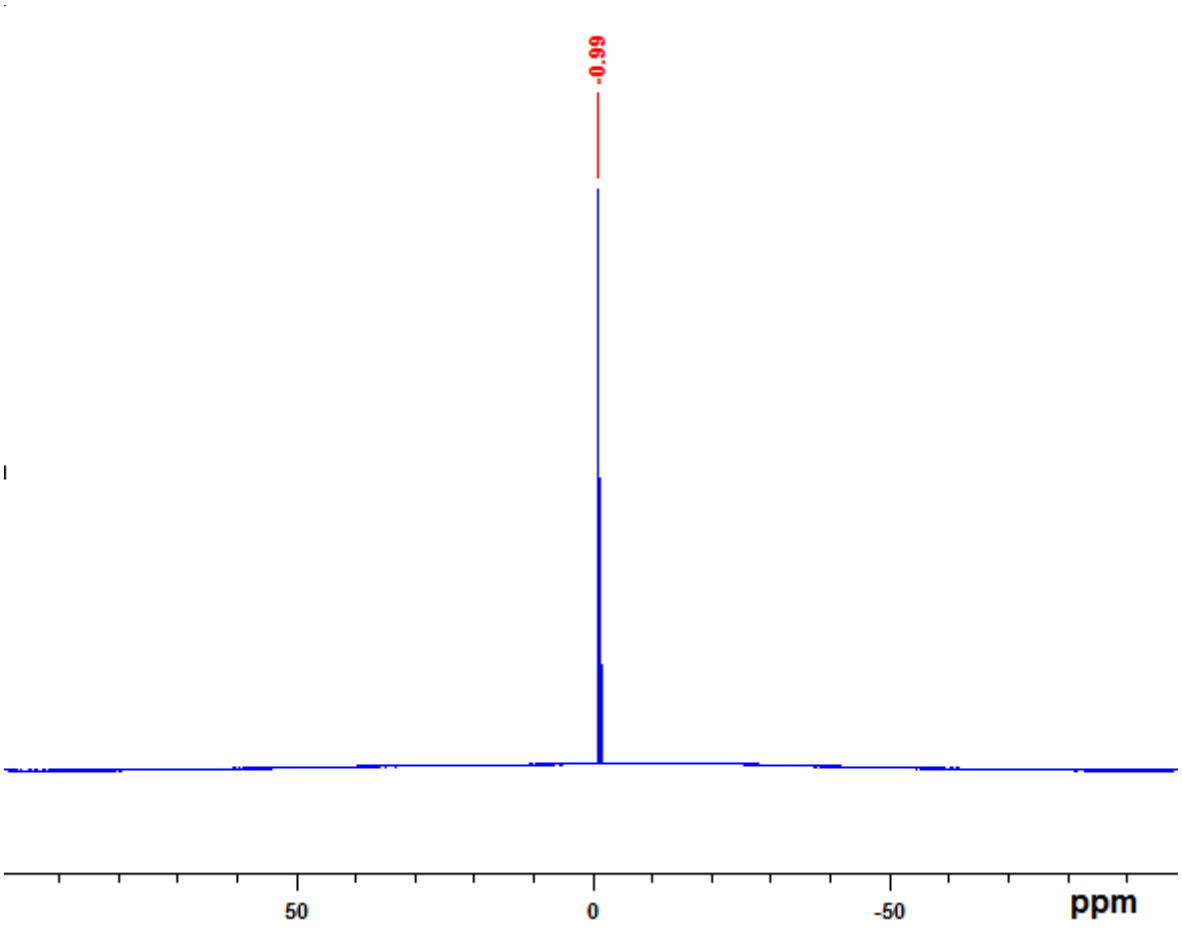


Fig. S21. ^{11}B NMR spectrum of $[(IPrSe)_2Cu]BF_4$ (**6**).

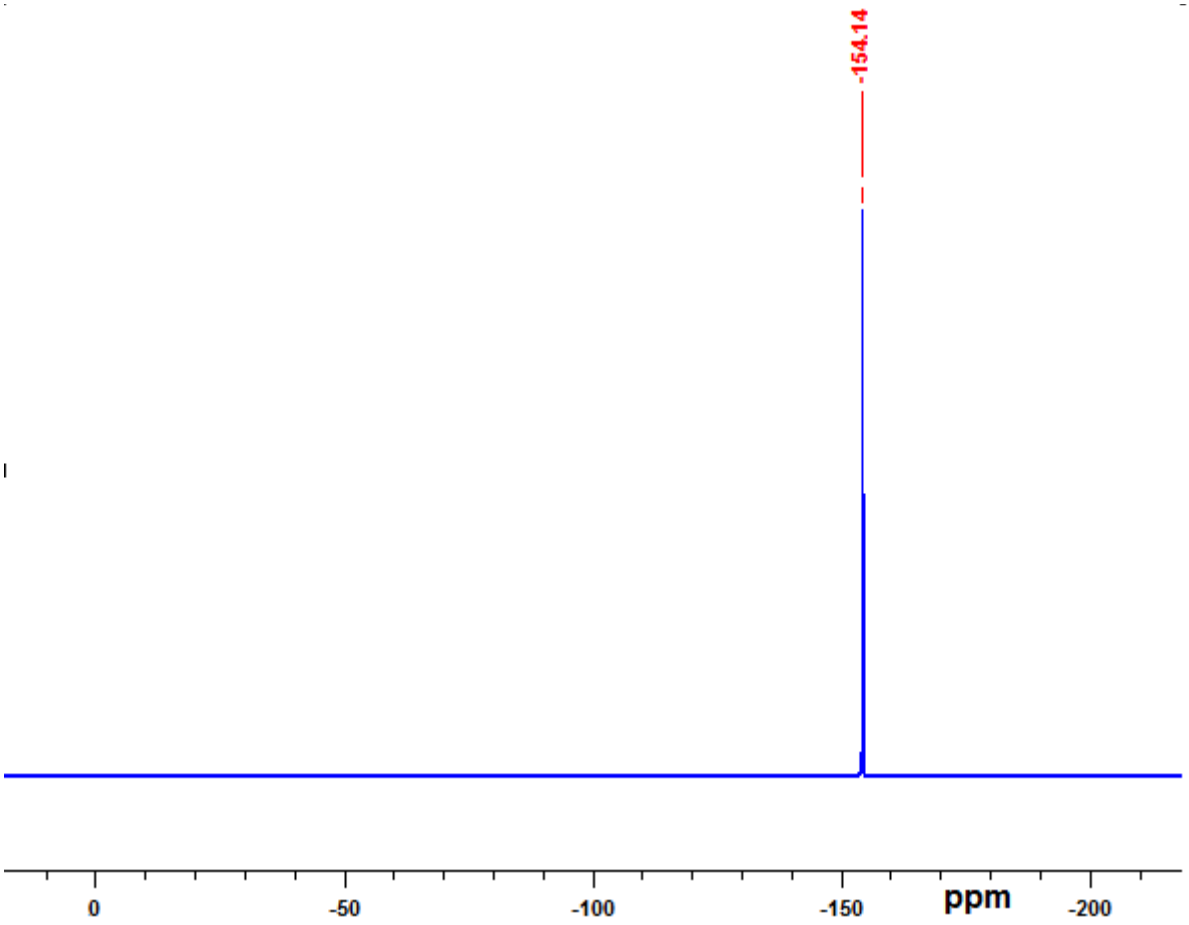
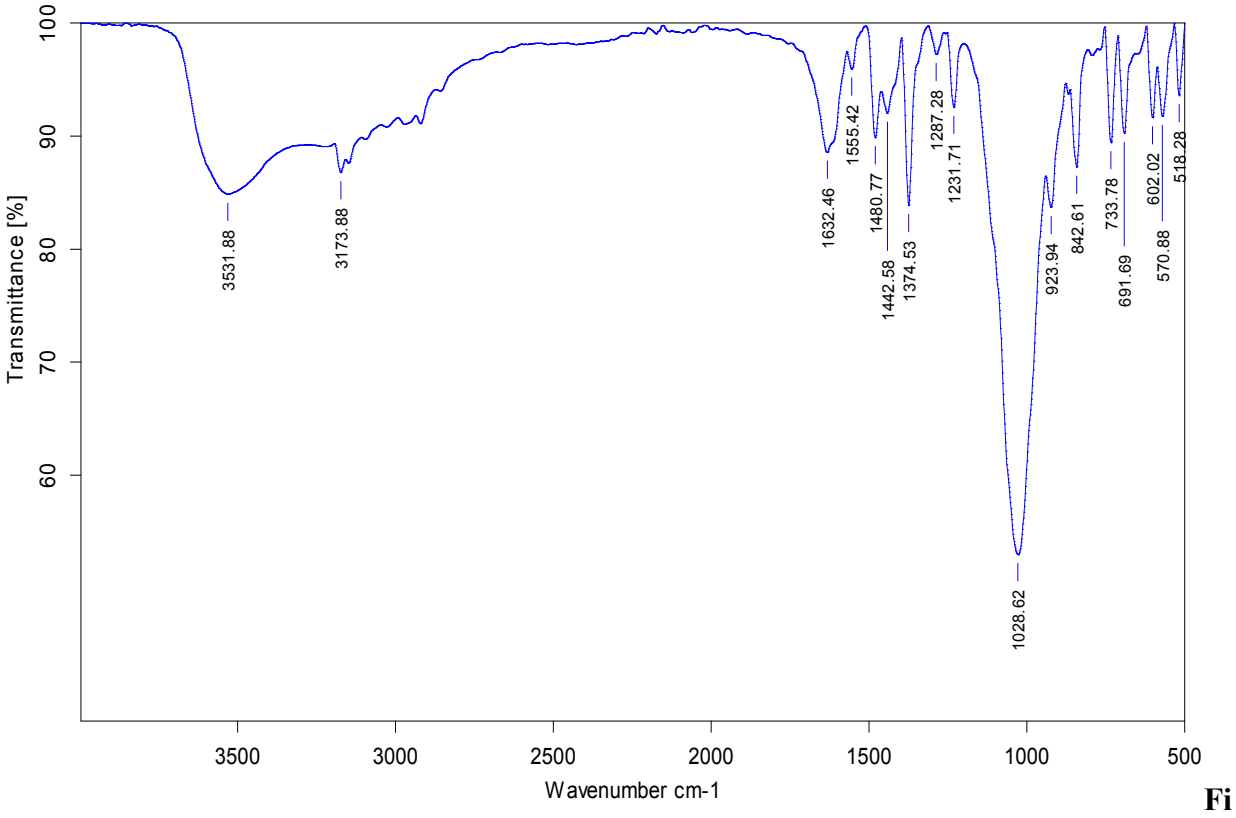


Fig. S22. ^{19}F NMR spectrum of $[(IPrSe)_2Cu]BF_4$ (**6**).



Fi

g. S23. Neat FT-IR spectrum of $[(IMesS)_2Cu]BF_4$ (**7**).

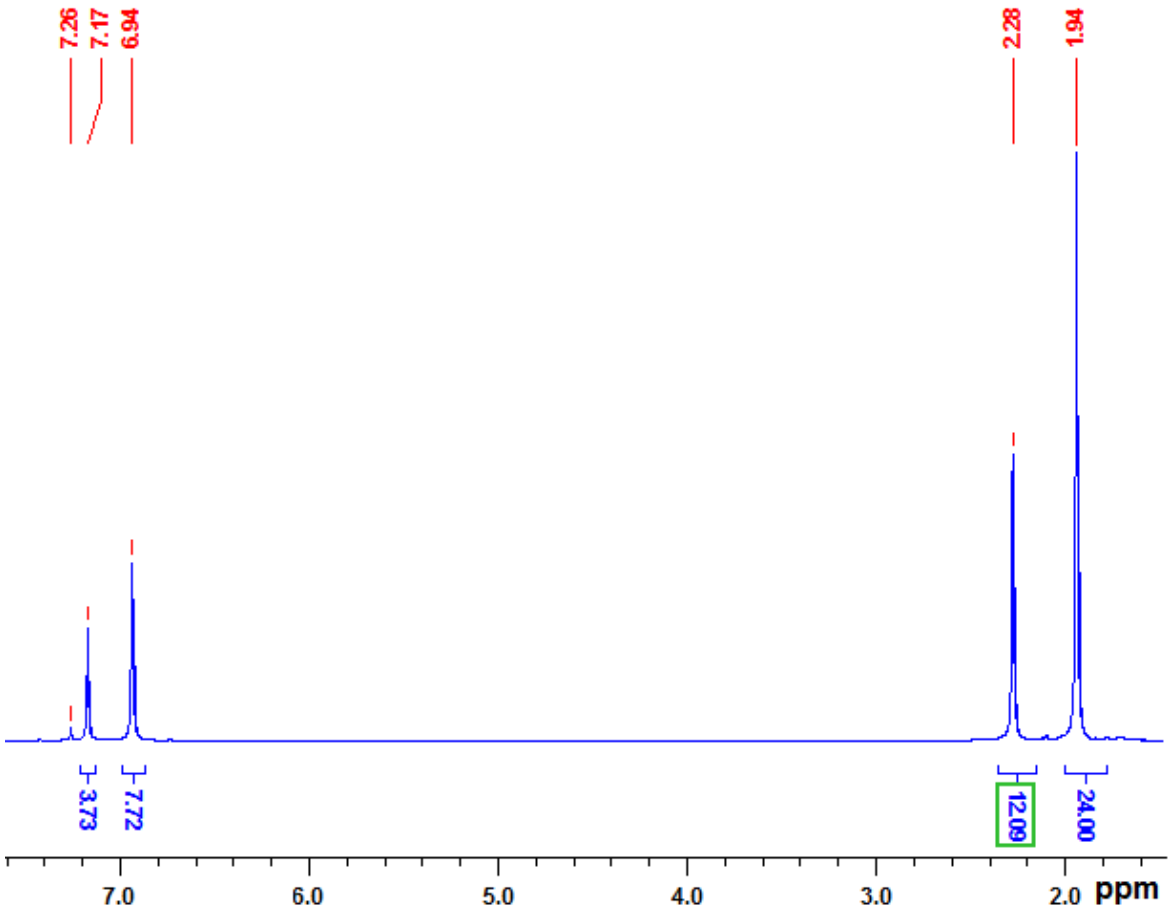


Fig. S24. ^{1}H NMR spectrum of $[(IMesS)_2Cu]BF_4$ (**7**).

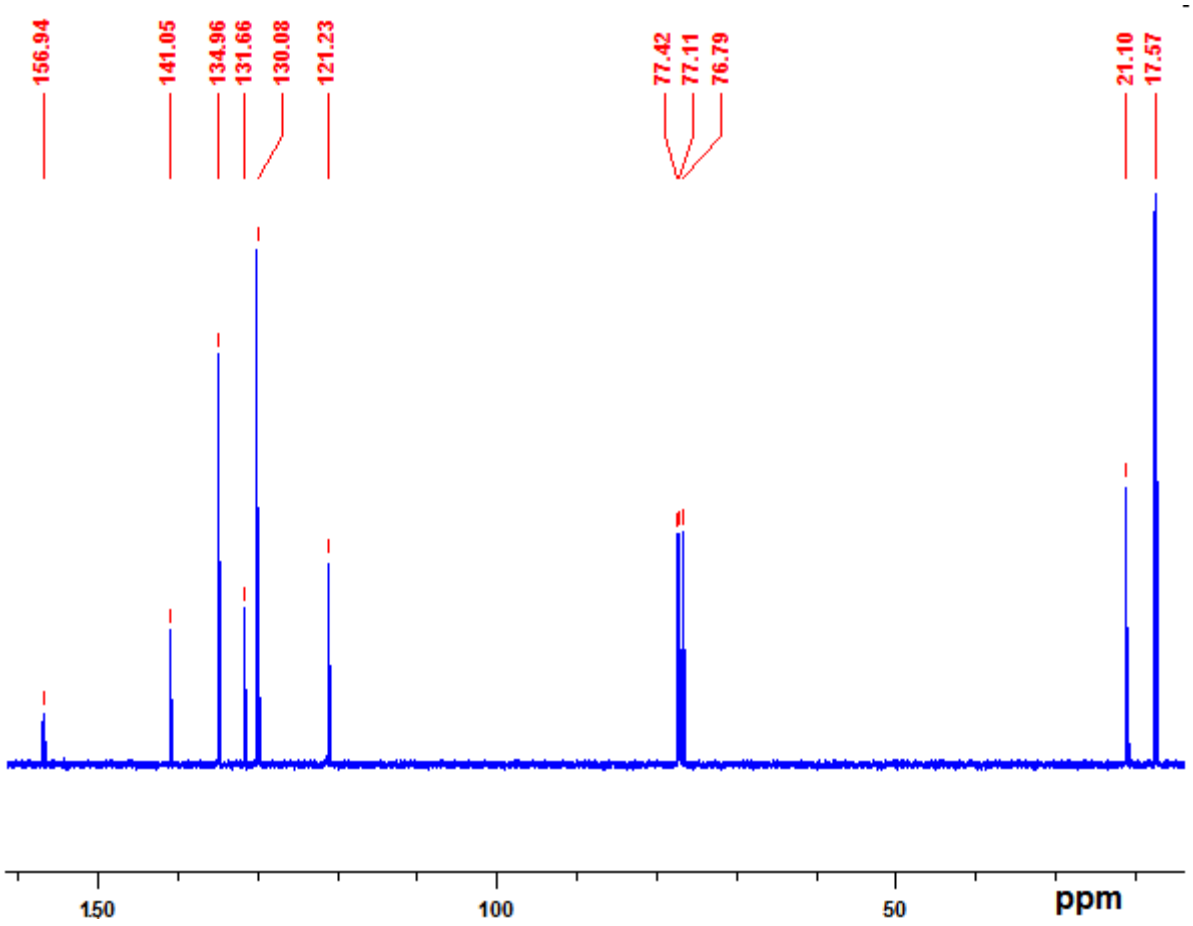


Fig. S25. ^{13}C NMR spectrum of $[(IMesS)_2Cu]BF_4$ (**7**).

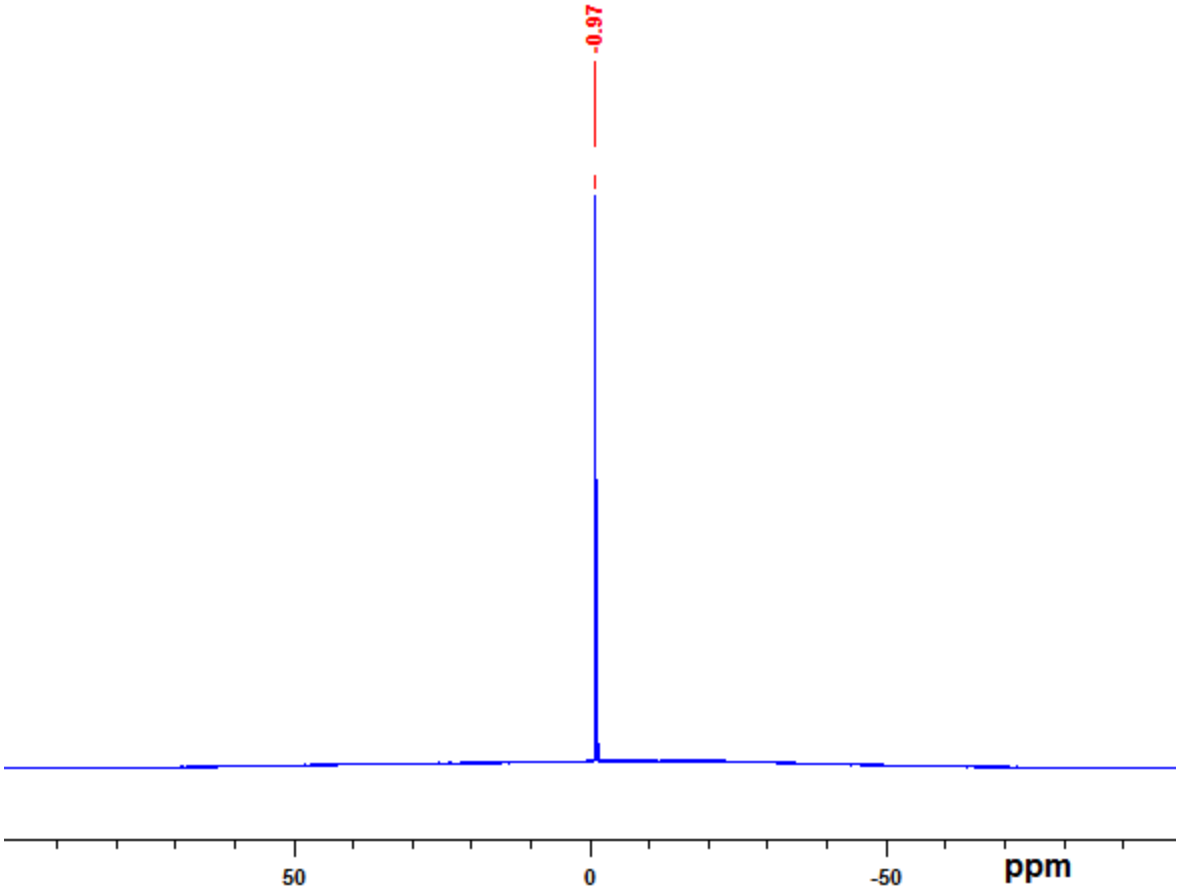


Fig. S26. ^{11}B NMR spectrum of $[(IMesS)_2Cu]BF_4$ (**7**).

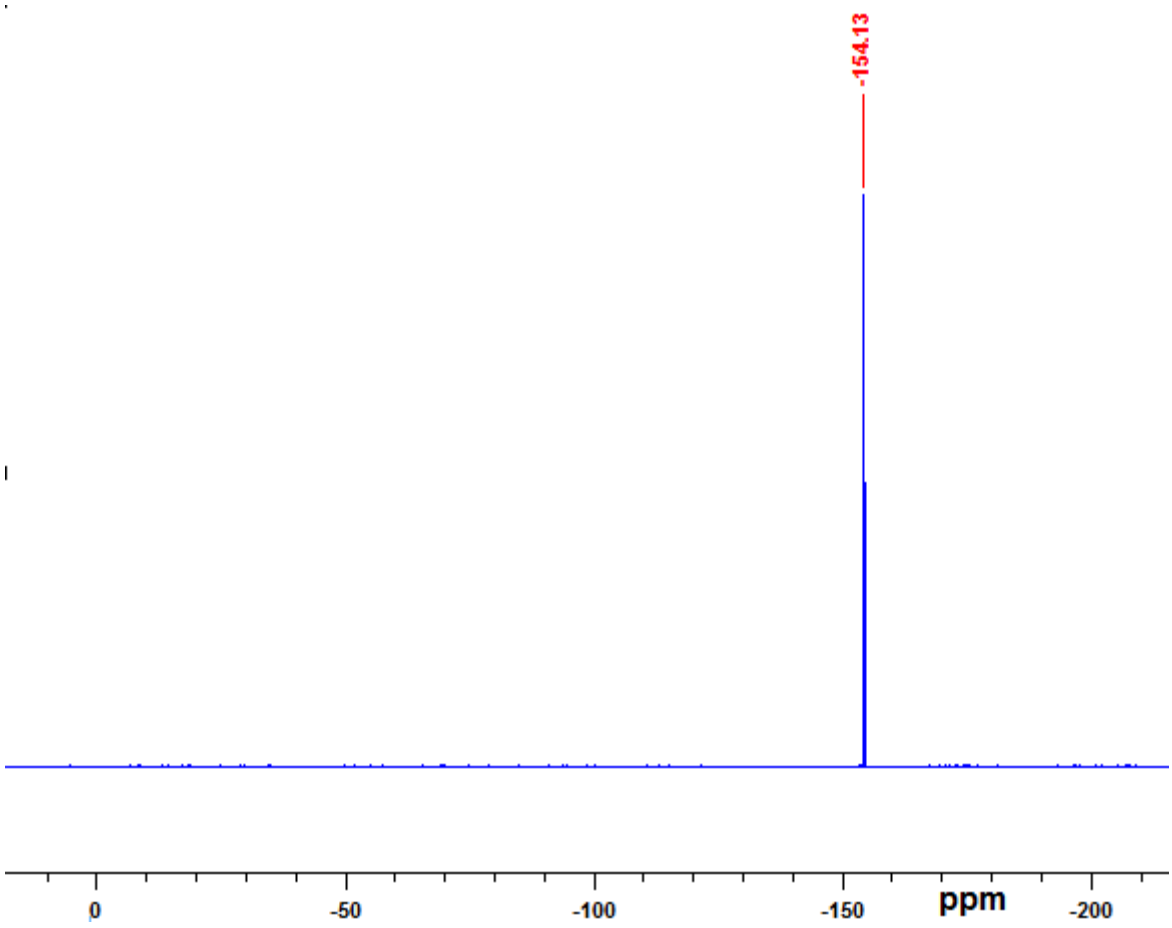


Fig. S27. ^{19}F NMR spectrum of $[(IMesS)_2Cu]BF_4$ (**7**).

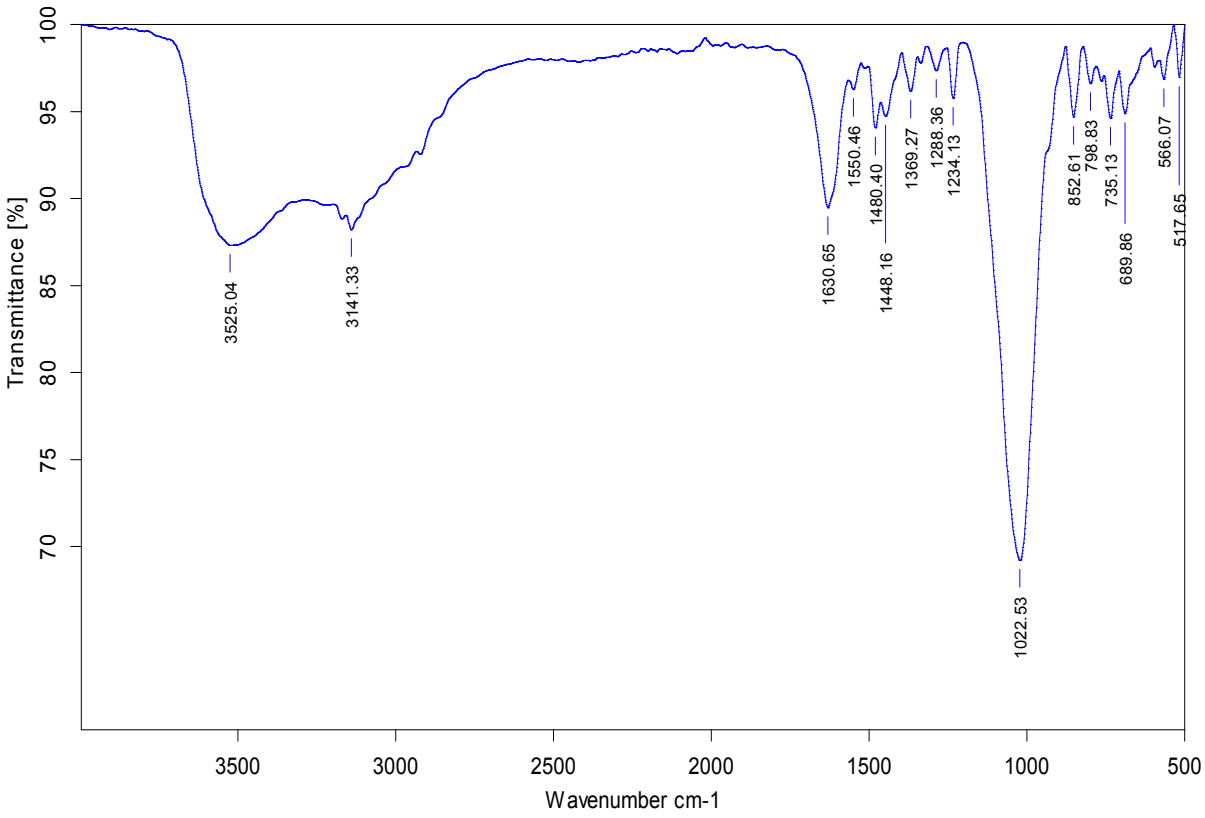


Fig. S28. Neat FT-IR spectrum of $[(IMesSe)_2Cu]BF_4$ (**8**).

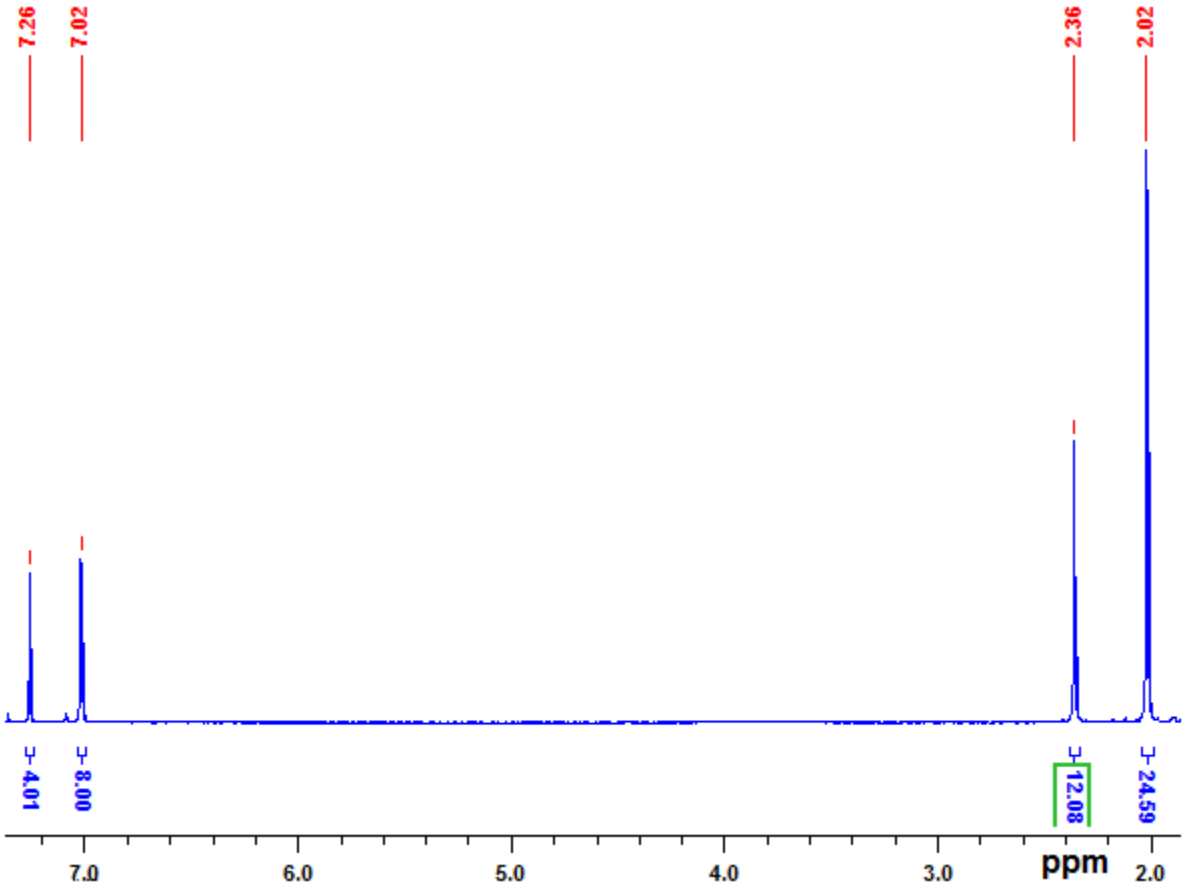


Fig. S29. ^{1}H NMR spectrum of $[(IMesSe)_2Cu]BF_4$ (**8**).

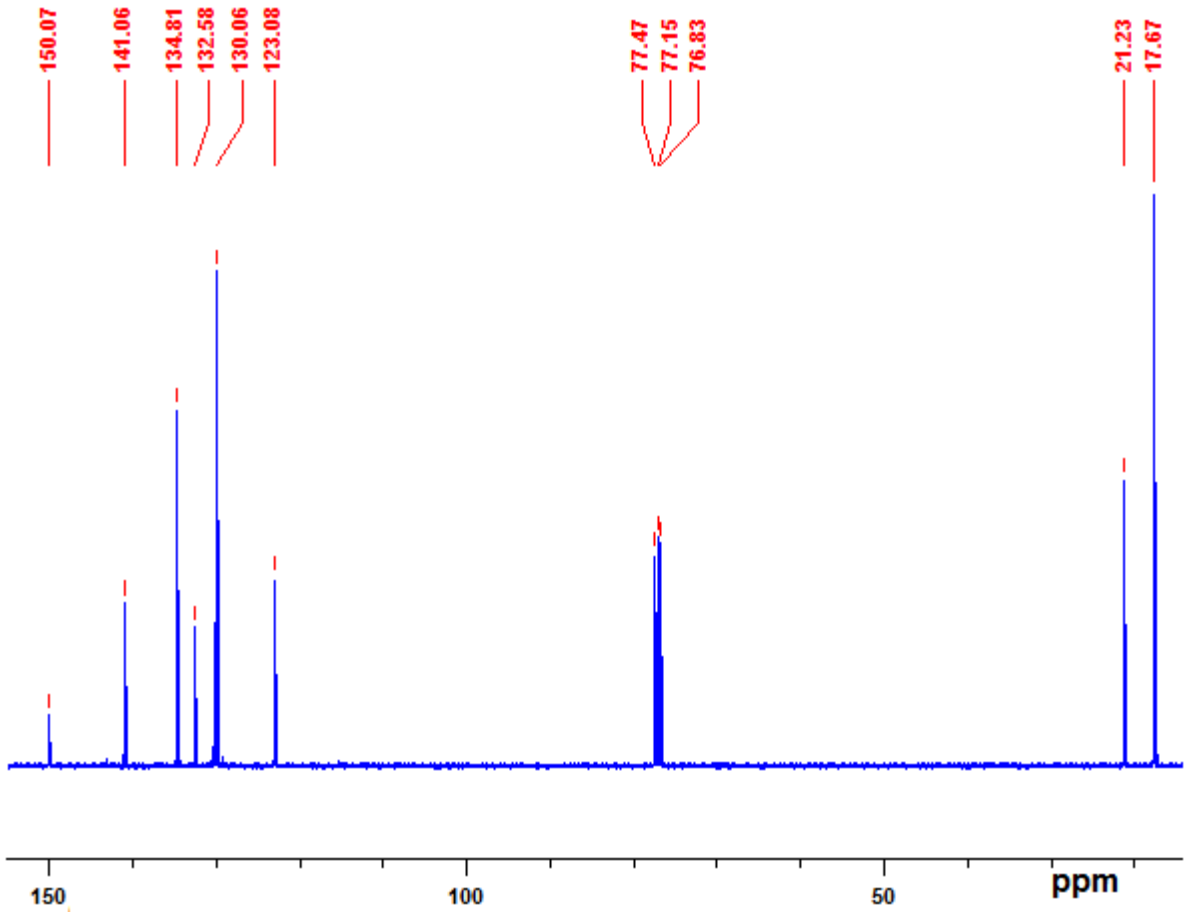


Fig. S30. ^{13}C NMR spectrum of $[(IMesSe)_2Cu]BF_4$ (**8**).

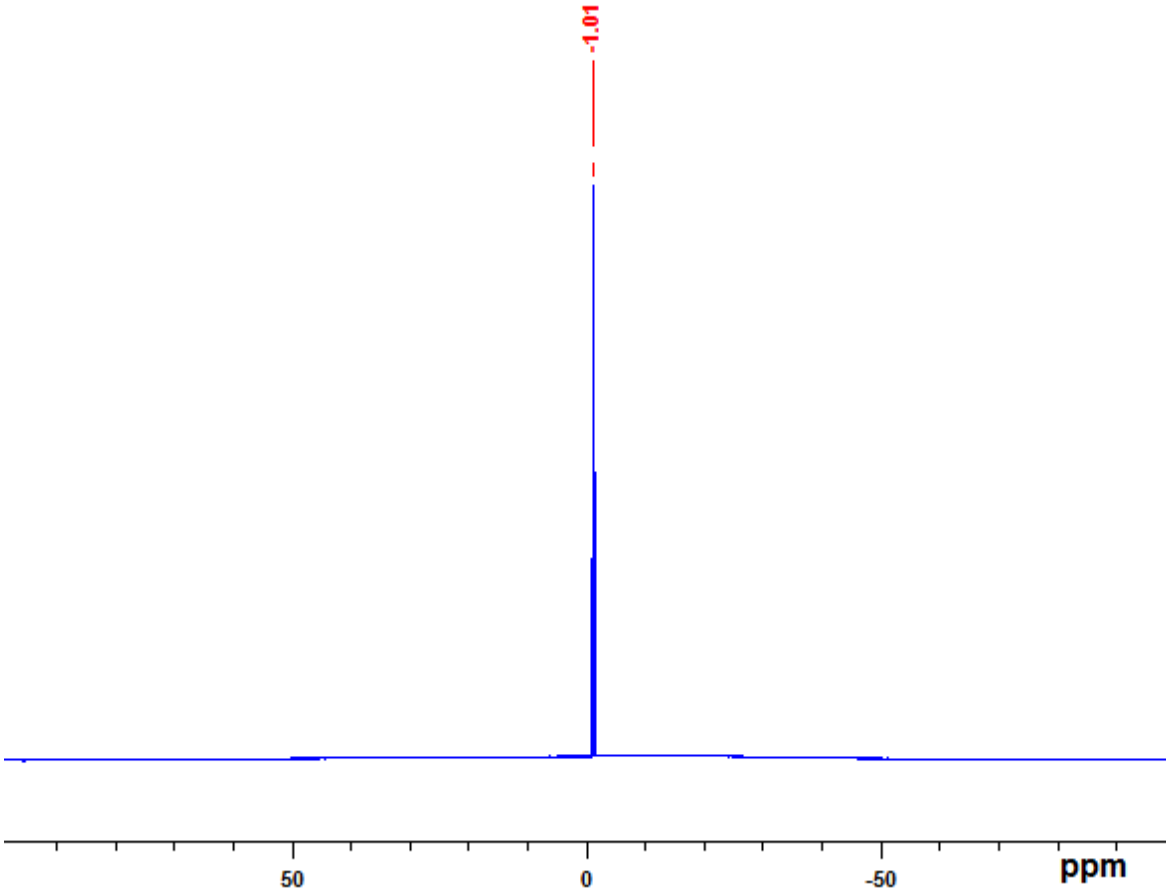


Fig. S31. ^{11}B NMR spectrum of $[(IMesSe)_2Cu]BF_4$ (**8**).

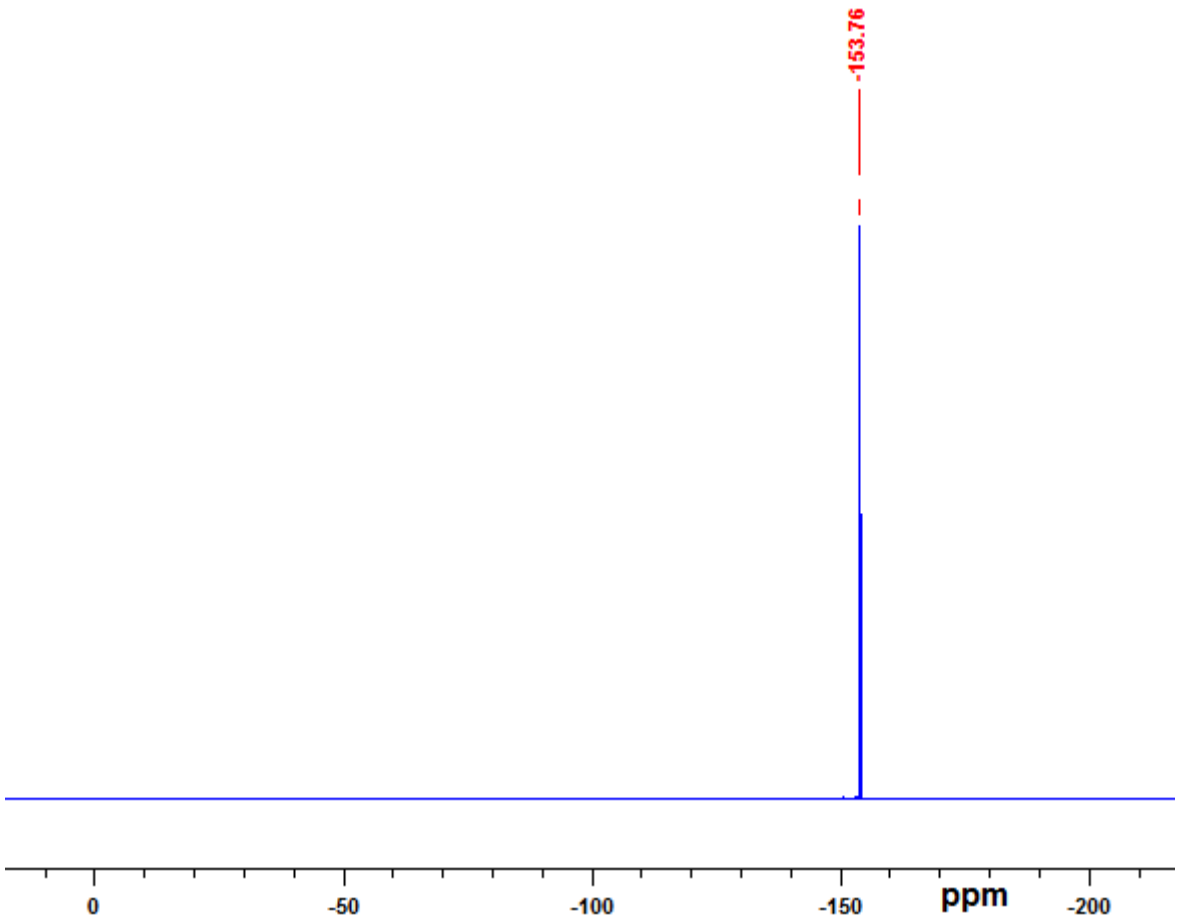


Fig. S32. ^{19}F NMR spectrum of $[(IMesSe)_2Cu]BF_4$ (**8**).

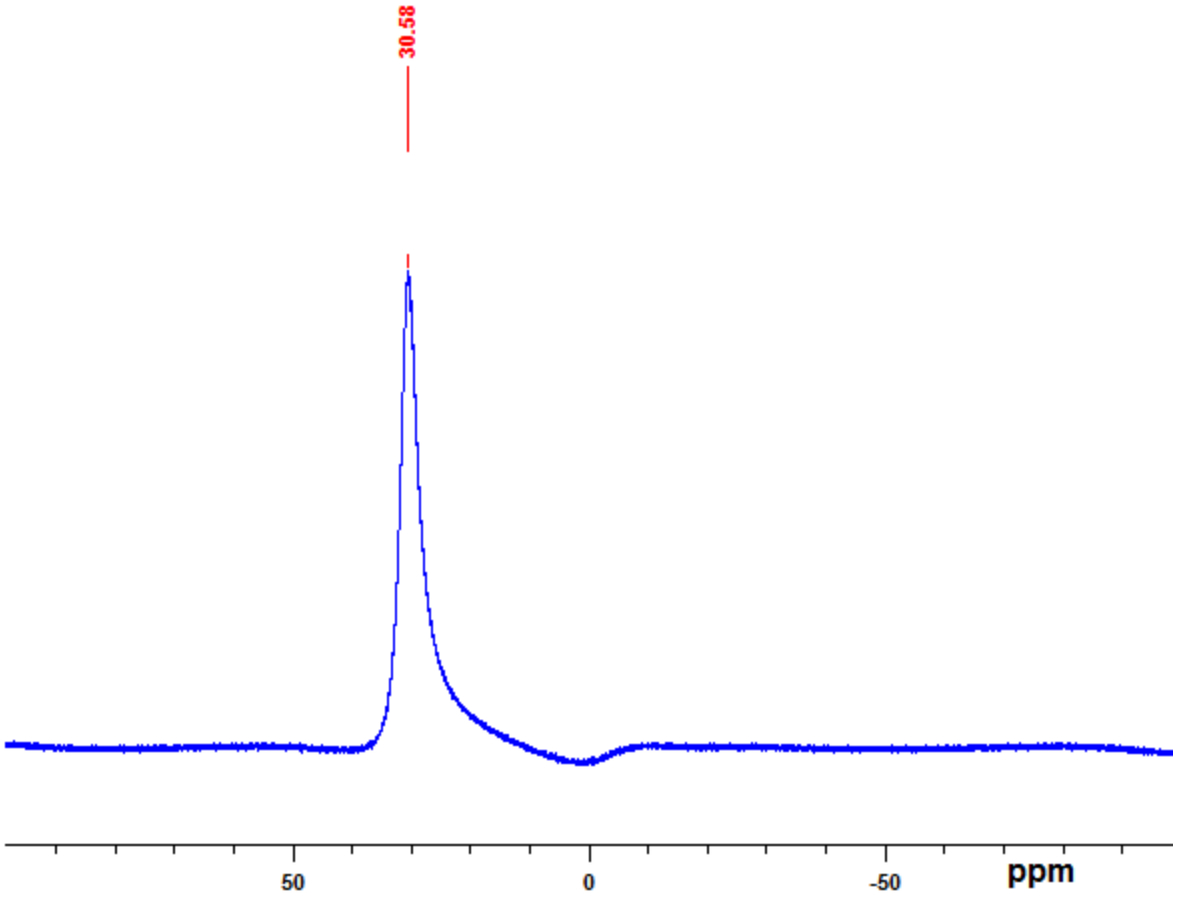


Fig. S33. ^{11}B NMR spectrum of (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane.

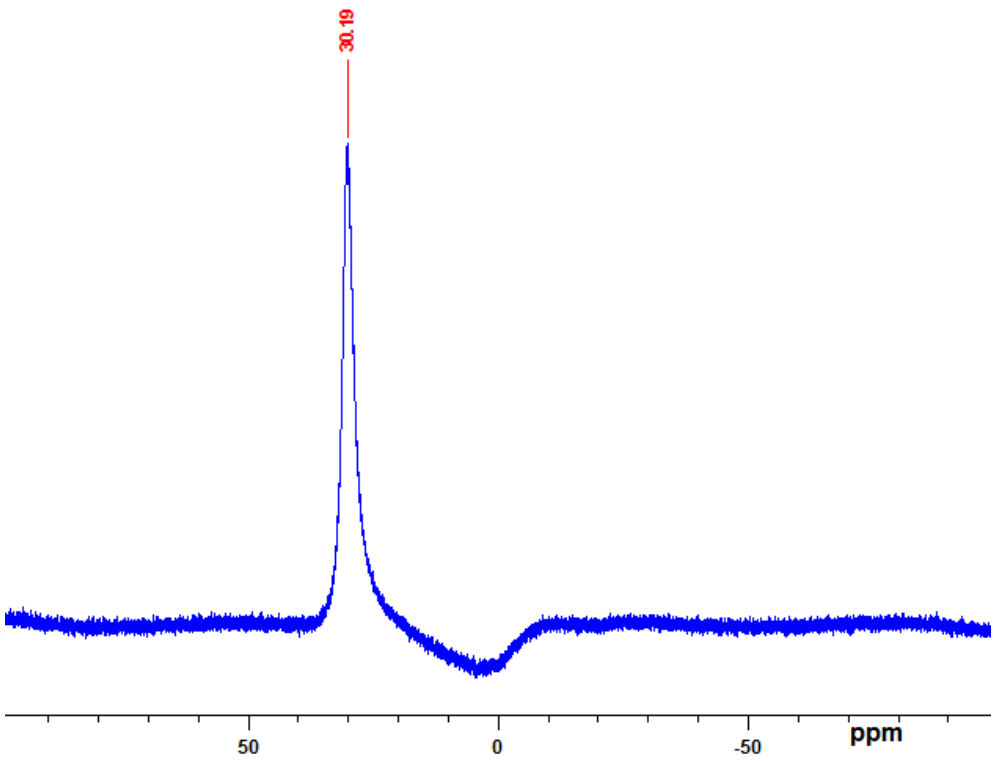


Fig. S34. ^{11}B NMR spectrum of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane.

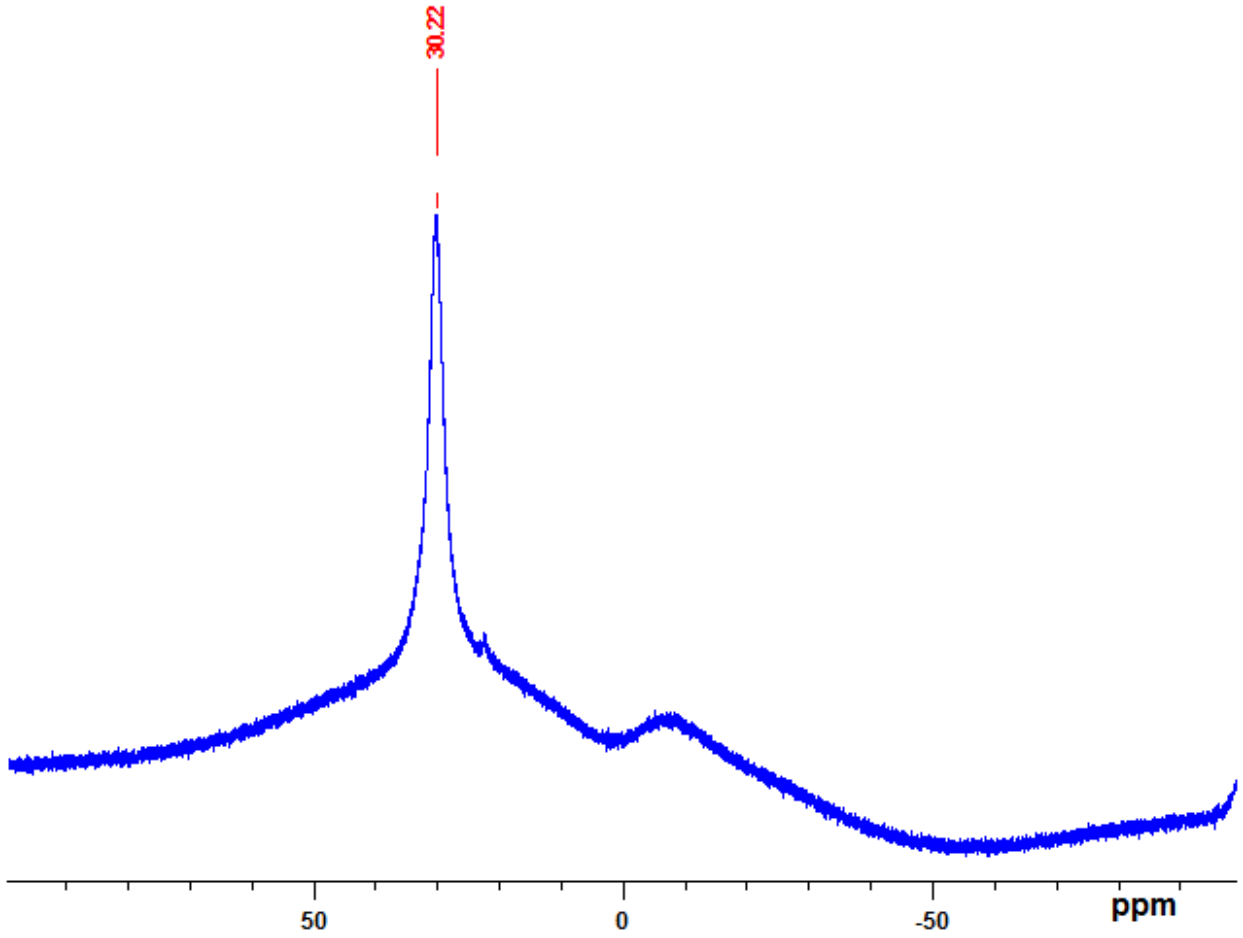


Fig. S35. ^{11}B NMR spectrum of (Z)-4,4,5,5-tetramethyl-2-(1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane.

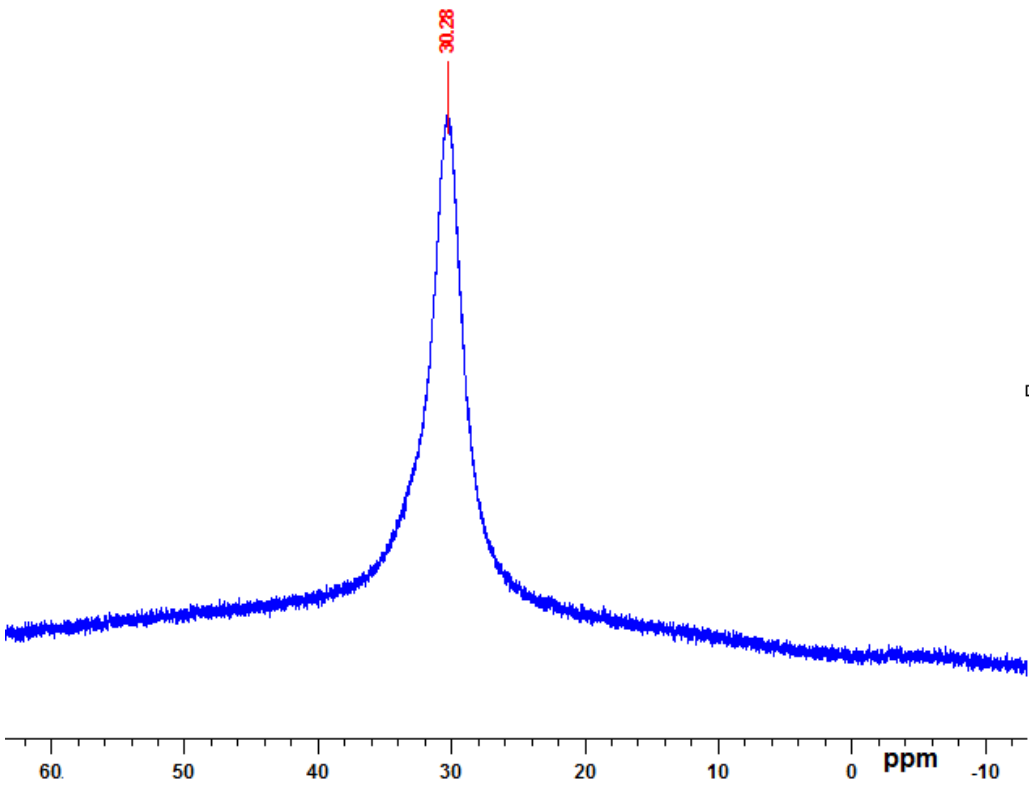


Fig. S36. ^{11}B NMR spectrum of (Z) ethyl -3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate.

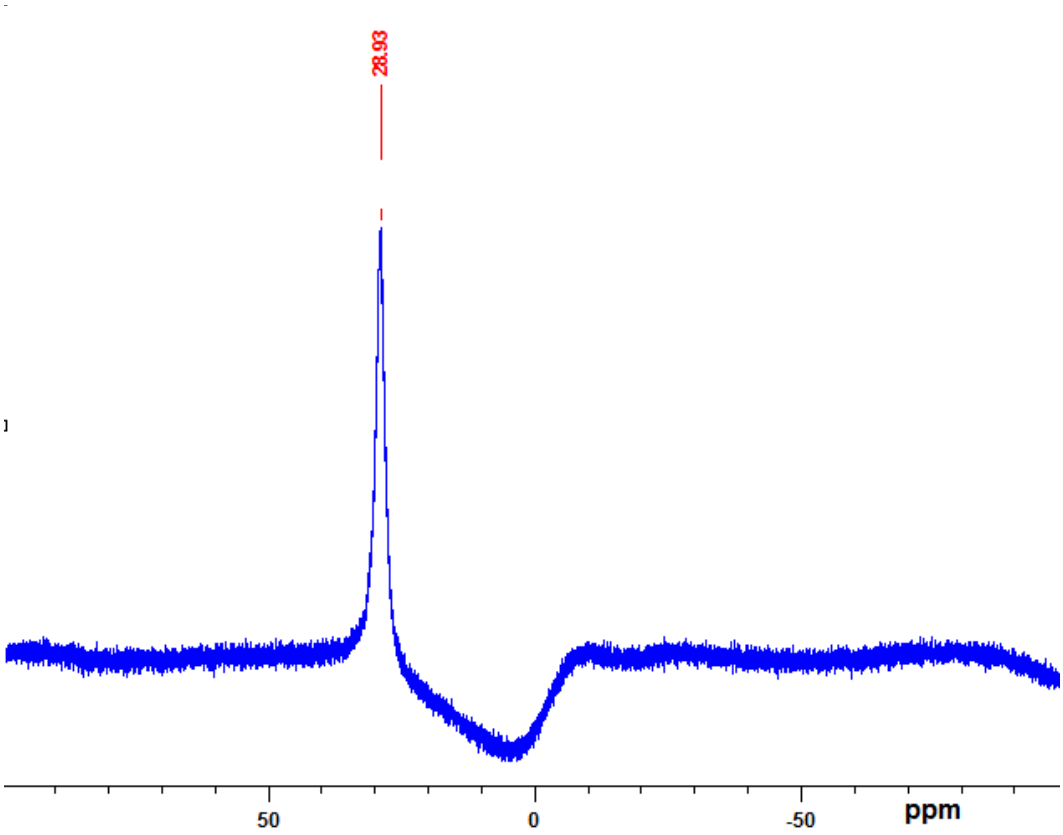


Fig. S38. ^{11}B NMR spectrum of (Z)-2-(hex-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

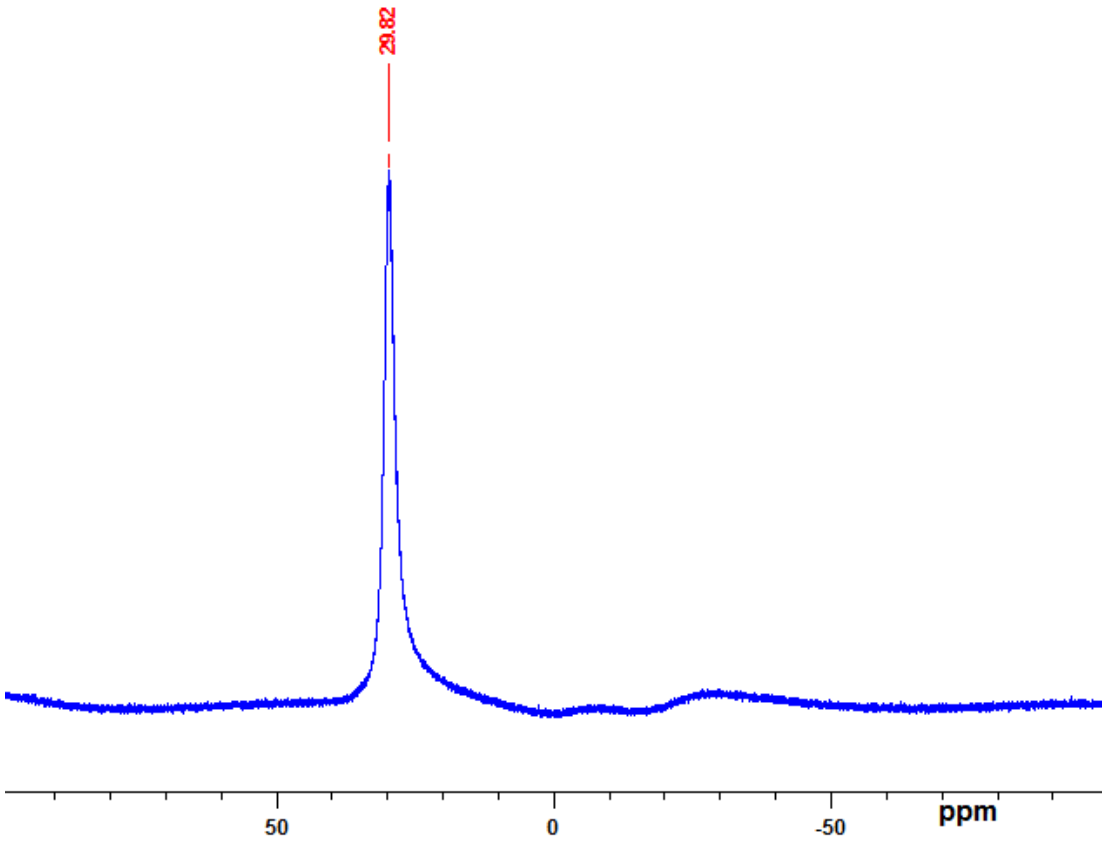


Fig. S39. ^{11}B NMR spectrum of (E)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane.

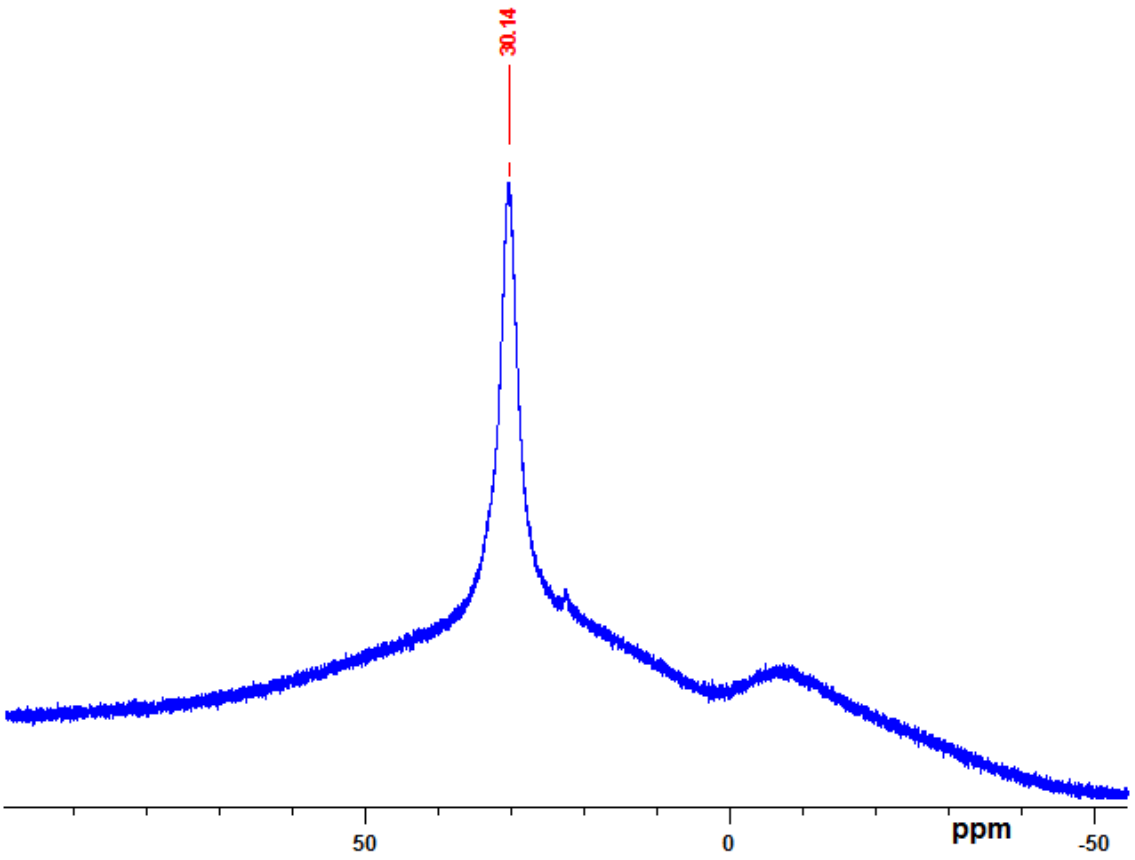


Fig. S40. ^{11}B NMR spectrum of (Z)-4,4,5,5-Tetramethyl-2-(oct-2-en-2-yl)-1,3,2-dioxaborolane.

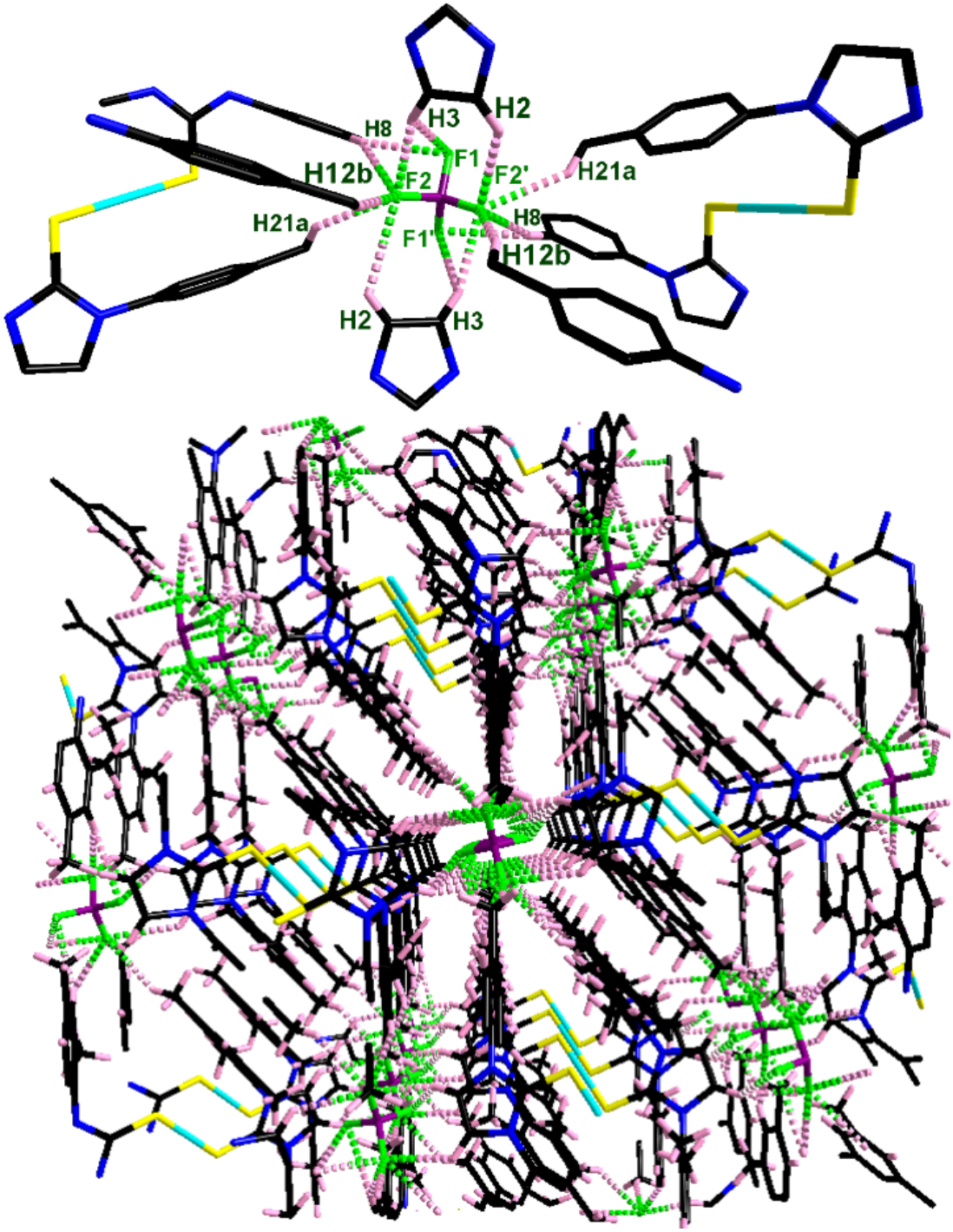


Fig. S41. Top; Intermolecular H-bonding interaction between the CH group (of aromatic ring and imidazole ring) with the F atom of tetra fluoro borate unit in **7**; D···A distances [Å]; F(1)···C(3)H, 2.6235(1); F(1)···C(8)H, 2.7145(1); F(2)···C(2)H, 2.8304(1); F(2)···C(12B)H, 2.7798(1); F(2)···C(21A)H, 2.5720(1). C–D···A angles [^{0}]; B(1)–F(1)

···H(3), 81.54; B(1)–F(1) ···H(8), 94.64; B(1)–F(2) ···H(2), 111.76; B(1)–F(2) ···H(3), 95.22; B(1)–F(2) ···H(8), 88.70; B(1)–F(2) ···H(12b), 137.55; B(1)–F(2) ···H(21a), 127.29. Non interacting hydrogen atoms and methyl groups have been omitted for the clarity. Bottom; Molecular association of **7** in solid state through extensive H···F bonding.

Table S1. Structural parameters of compounds **1**-**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{54}H_{69}ClCuN_4O_4S_2$	$C_{54}H_{72}N_4O_4ClCuSe_2$	$C_{42}H_{48}N_4O_4ClCuS_2$	$C_{42}H_{48}N_4CuSe_2ClO_4$
Formula weight	1001.25	1098.12	835.96	929.79
Temperature (K)	298	150	298	150
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c	C2/c	C2/c	$P2_12_12_1$
a/Å	19.8863(14)	19.5343(15)	21.1509(9)	8.3174(3)
b/Å	15.9337(4)	16.1976(6)	8.2603(3)	17.8053(5)
c/Å	20.405(3)	21.4008(15)	24.586(1)	28.9437(7)
α/°	90	90	90	90
β/°	114.235(8)	121.691(10)	101.678(4)	90
γ/°	90	90	90	90
Volume (Å^3)	5895.8(10)	5761.7(9)	4206.5(3)	4286.4(2)
Z	4	4	4	4
ρ_{calc}/mg mm^{-3}	1.128	1.2658	1.3200	1.4407
Absorption coefficient (μ/mm^{-1})	1.931	2.744	2.602	3.586
F(000)	2124.0	2272.4	1752.6	1887.5
Reflections collected	12751	10957	8849	11109
R_{int}	0.0308	0.0354	0.0277	0.0363
GOF on F^2	1.650	1.039	1.030	1.035
R_1 ($I>2\sigma(I)$)	0.0868	0.0766	0.0481	0.0480
wR_2 ($I>2\sigma(I)$)	0.2510	0.233171	0.145660	0.140271
R_1 values (all data)	0.1097	0.0866	0.0642	0.0551
R_2 values (all data)	0.2710	0.2332	0.1457	0.1403

Table S2. Structural parameters of compounds **5**-**8**.

	5	**6**	**7**	**8**
Empirical formula	$C_{54}H_{72}N_4S_2CuBF_4$	$C_{54}H_{72}BN_4F_4CuSe_2$	$C_{42}H_{48}BN_4F_4S_2Cu$	$C_{42}H_{48}BCuF_4N_4Se_2$
Formula weight	991.70	1085.44	823.32	917.16
Temperature (K)	298	150	150	150
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
a/Å	19.9289(11)	19.6185(8)	20.0772(7)	19.9268(8)
b/Å	15.8882(5)	16.1577(3)	8.2488(3)	8.3983(3)
c/Å	20.3741(16)	21.2244(9)	24.7461(10)	24.7922(10)
α/°	90	90	90	90
β/°	114.824(8)	121.810(6)	101.745(4)	100.413(4)
γ/°	90	90	90	90
Volume (Å^3)	5855.1(7)	5717.4(5)	4012.5(3)	4080.6(3)
Z	4	4	4	4
ρ_{calc}/mg mm^{-3}	1.1249	1.2609	1.3629	1.4928
Absorption coefficient (μ/mm^{-1})	1.574	2.385	2.188	3.235
F(000)	2104.4	2239.3	1719.5	1854.4
Reflections collected	11826	10507	6872	6844
R_{int}	0.0346	0.0221	0.0220	0.0240
GOF on F^2	1.067	1.031	1.049	1.052
R_1 ($I>2\sigma(I)$)	0.0865	0.0736	0.0383	0.0391
wR_2 ($I>2\sigma(I)$)	0.295348	0.235445	0.108046	0.106102
R_1 values (all data)	0.1127	0.0763	0.0442	0.0433
R_2 values (all data)	0.2953	0.2354	0.1080	0.1061