Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Selective CO_2 adsorption by a new metal-organic framework: synergy between open metal sites and a charged imidazolinium backbone

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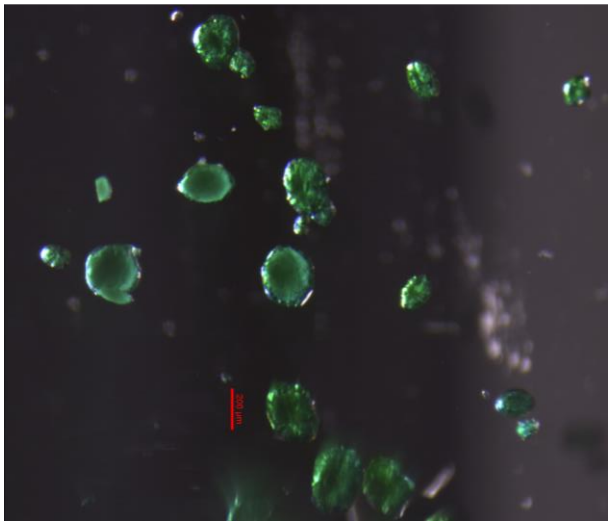

Figure S1.Light microscope image of **Cu-Sp5-EtOH** single crystals. Scale bar (in red): 200 µm

Table S1. Crystallographic data for **Cu-Sp5-EtOH** and **Cu-Sp5-MeOH**

	Cu-Sp5-EtOH	**Cu-Sp5-EtOH**	**Cu-Sp5-MeOH**
Formula	$C_{19}H_{19}CuN_3O_8$	$C_{19}H_{19}CuN_3O_8$	$C_{17}H_{13}CuN_3O_{8.88}$
Molecular weight	480.91	480.91	464.84
T, K	100(2)	293(2)	100(2)
λ, Å	0.71073	0.67522	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca
a, Å	17.705(2)	17.8332(4)	16.610(4)
b, Å	9.2515(9)	9.2678(1)	8.957(2)
c, Å	24.566(2)	24.5582(2)	25.681(6)
α, °	90	90	90
β, °	90	90	90
γ, °	90	90	90
V, Å^3	4023.9(6)	4058.8(1)	3821(2)
Z	8	8	8
D_{calc}, g/cm^3	1.588	1.571	1.616
μ, mm^{-1}	1.14	0.99	1.20
Absorption correction	Multi-scan	Multi-scan	Multi-scan
F_{000}	1976	1968	1888
θ range for data collection, °	2.3–23.3	1.6-25.5	2.7-24.9
index ranges	−19 ≤ h ≤ 19	−13 ≤ h ≤ 13	−15 ≤ h ≤ 15
	−10 ≤ k ≤ 10	−11 ≤ k ≤ 11	−8 ≤ k ≤ 8
	−27 ≤ k ≤ 27	−30 ≤ k ≤ 30	−23 ≤ k ≤ 23
Reflections collected	23222	17084	23016
Independent reflections (R_{int})	2890 (0.100)	3204 (0.020)	1494 (0.149)
reflections with I > 2σ(I)	2188	3014	1142
data/restraints/parameters	2890/19/284	3204/4/284	1494/0/212
S	1.06	1.08	1.20
R [(F^2 > 2σ(F^2)]	R_1 = 0.065	R_1 = 0.069	R_1 = 0.087
	wR_2 = 0.1494	wR_2 = 0.192	wR_2 = 0.183
R (all data)	R_1 = 0.091	R_1 = 0.071	R_1 = 0.118
	wR_2 = 0.163	wR_2 = 0.195	wR_2 = 0.202
weighting Scheme*, x/y	0.0556/24.6838	0.1107/8.3969	0/73.2275
largest diff. peak and hole, e/Å^3	1.08 and –0.63	0.83 and –0.73	0.52 and –0.38

*$w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$

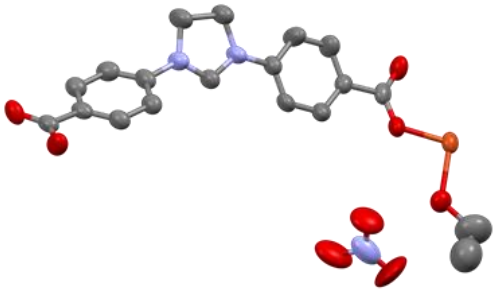

Figure S2. Thermal ellipsoid plot of asymmetric unit of **Cu-Sp5-EtOH** structure obtained at 293K. Nitrate anion is clearly positioned. Hydrogen atoms are omitted for clarity.

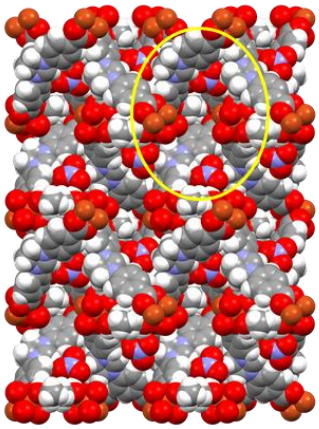

Figure S3.The space-filling model of **Cu-Sp5-EtOH** structure. View along *b* axis. Highlighted is single channel in the structure.

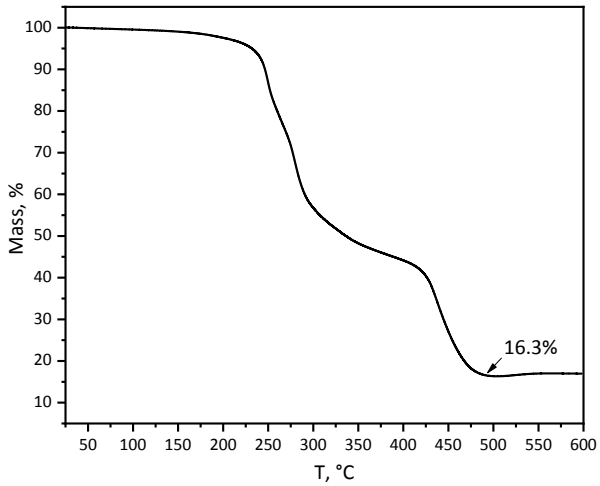

Figure S4. TGA curve for **Cu-Sp5-EtOH** in air. Heating rate: 5 °C/min.

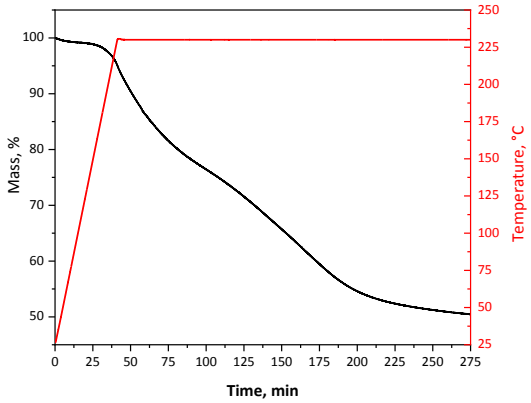

Figure S5. TGA curve for **Cu-Sp5-EtOH** in nitrogen atmosphere with the following program: 5°C/min until 230 °C, hold at 230 C. *The abscissa represents time in minutes*.

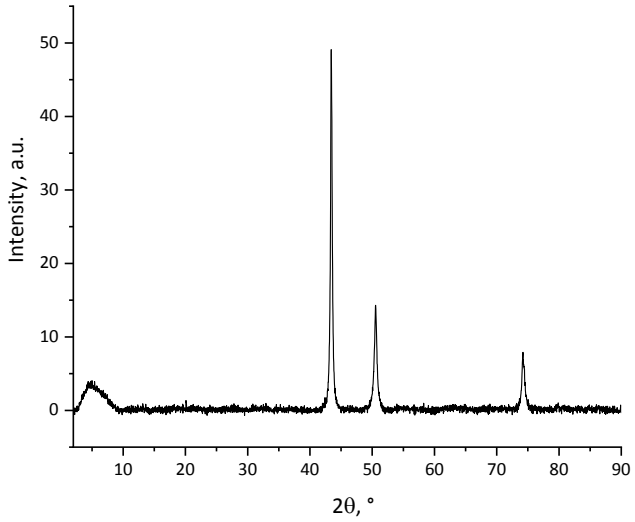

Figure S6. Powder pattern of the final product after **Cu-Sp5-EtOH** treatment at 230 °C in nitrogen atmosphere. The feature below 10 ° is due to the sample holder specifics.

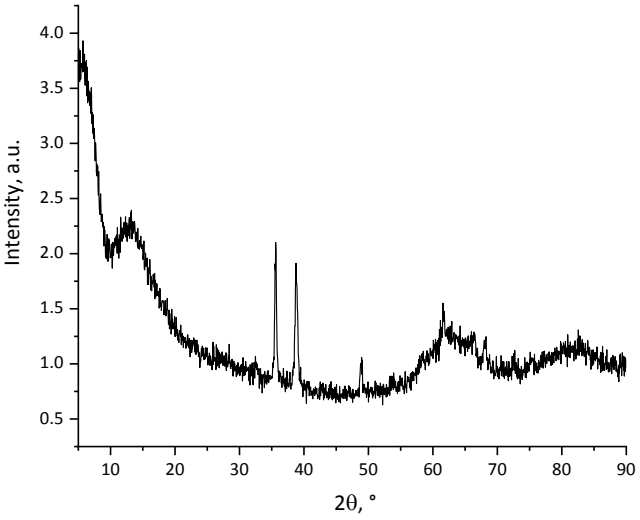

Figure S7. Powder pattern of the final product after **Cu-Sp5-EtOH** thermal decomposition in air. The broad peaks arise from the sample holder, while all the narrow peaks correspond to the copper (II) oxide.

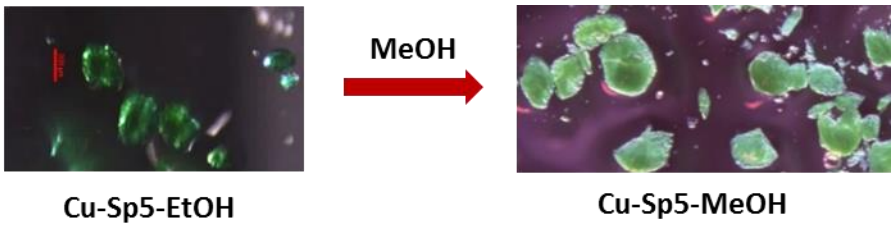

Figure S8. Light microscope images indicating the change in crystal size during transformation of **Cu-Sp5-EtOH** to **Cu-Sp5-MeOH** upon methanol soaking

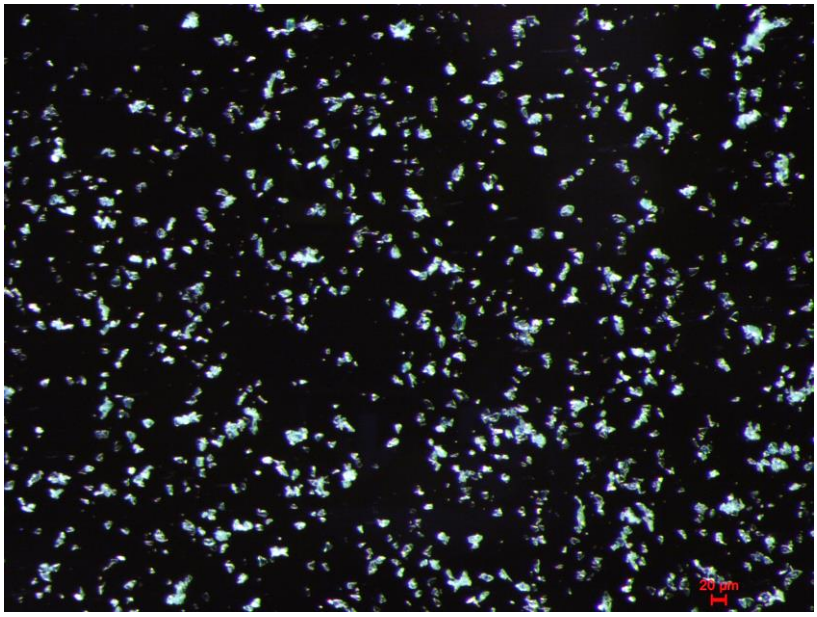

Figure S9. Light microscope image of **Cu-Sp5-MeOH**. Scale bar (in red): 20 µm

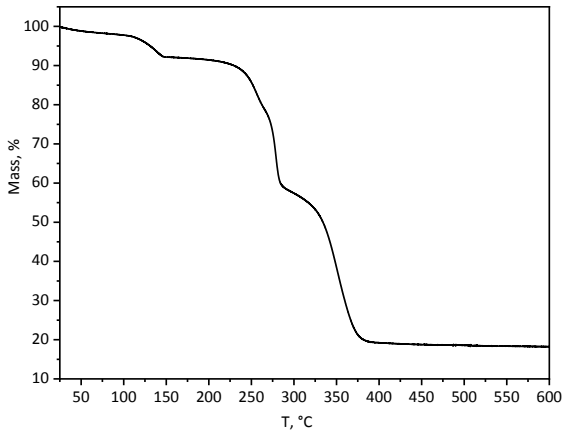

Figure S10. TGA curve for **Cu-Sp5-MeOH** in air. Heating rate: 5 °C/min.

Isosteric heat of adsorption calculation

The calculation was performed via a custom-written Matlab script. Isotherms for a particular gas were fitted using double-site Langmuir model. Then, for each loading point, the pressure was extracted from the fits and the isosteric heat of adsorption was calculated via Clausius-Clapeyron equation:

$$-Q_{st} = R\frac{\partial lnP}{\partial\left(\frac{1}{T}\right)}$$

Where $\frac{\partial lnP}{\partial\left(\frac{1}{T}\right)}$ was extracted from linear fit of lnP vs. 1/T.

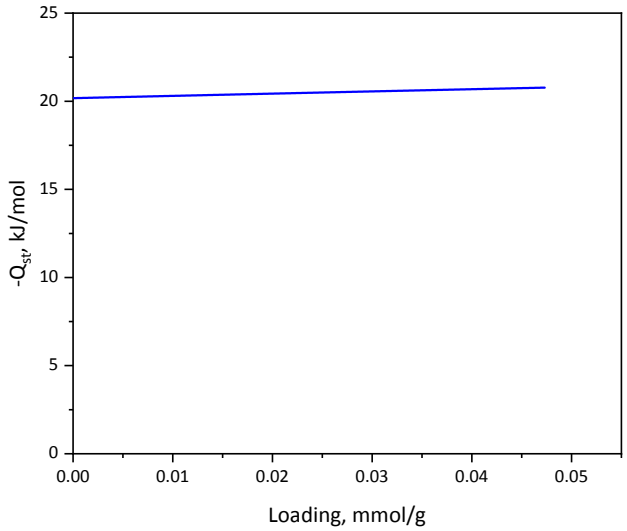

Figure S11. Isosteric heat of N_2 adsorption for **Cu-Sp5.**

IAST calculations

The calculations were performed using pyIAST software[1]. Each isotherm was fitted with a double-site Langmuir model and the IAST calculation was performed for 15% CO_2/ 85% N_2 mixture at 1 bar.

Table S2. Overview of metal-organic frameworks for CO_2 separation

MOF	Functional sites[e]	BET (m^2/g)	mmol/g(wt%)at 0.15 bar (CO_2)	S[f]	T	$-Q_{st}$ (kJ/mol)	Reference
				175 (IAST, 50 °C)			[2]
Mg-MOF-74	OMS	1800	5.87 (25.83)	44.4	303	47	
Ni-MOF-74	OMS	1312	3.84 (16.9)	30	298	42	[2]
CuBTTri	OMS	1770	0.69 (3.08)	18.4	298	24	[2]
en-CuBTTri	OMS/LBS	345	0.51 (2.24)	42.5	298	86.7	[2]
CG-9	OMS + GO	1532	2.09(9.2)	31.3	273	–	[2]
$[NH_2(CH_3)_2][Zn_3(bta)(btc)_2]$[a]	OMS	697	1.37(6.03)	84.9	273	–	[2]
FeBTT	OMS	2010	1.19(5.24)	16.9	298	–	[2]
$[NH_2(CH_3)_2]_2[Cd_3(bta)(btc)_2]_2$	OMS	508	1.14(5.02)	23	273	–	[2]
Cu-btc	OMS	1400	1.04(4.56)	34.4	293	25.9	[2]
Cu-TDPAT	OMS	1938	1.67(6.85)	79(IAST)	298	42.2	[3]
PCN-88	OMS	3308	0.69(3.04)	29.8	296	27	[2]
$[(CH_3)_2NH_2]_2[Tb_6(\mu^3\text{-}OH)_8(FTZB)_6(H_2O)_6](H_2O)_{22}$[b]	OMS + ion pairs + F + N + OH	1220	1.35(5.61)	15(IAST, 10%CO_2)	298	58.1	[4]
$[Zn_3L_2(HCOO)_{1.5}][(CH_3)_2NH_2]_{1.5}\cdot xDMF$[c]	Ion pairs	569.5	1.12(4.70)	24 (IAST)	273	–	[5]
$[Zn_2(L)(bpb)_2](NO_3)(DMF)_3(H_2O)_4$[d]	Ion pairs	425	0.89(3.77)	181	273	23.5	[6]
Cu-Sp5-MeOH	OMS + ion pairs	204	0.64(2.73)	**207 (IAST) 80**	298	**43.1**	**This work**
Cu-Sp5-MeOH	OMS + ion pairs	204	1.10(4.60)	**253 (IAST) 80**	278	**43.1**	**This work**

[a] bta = benzotriazolate, btc = 1,3,5-benzenetricarboxylate

[b] H_2FTZB = 2-fluoro-4-(1H-tetrazol-5- yl)benzoic acid

[c] H_3L =9-(4-carboxy- phenyl)-9H-carbazole-3,6-dicarboxylic acid

[d] $H_4L^+Cl^-$ = 1,3-Bis(3,5-dicarboxyphenyl)imidazolium chloride, bpb = 1,4-bis(4-pyridyl)benzene

[e] OMS = open metal site, LBS = Lewis basic site, GO = graphene oxide, F = fluorine atoms, N = uncoordinated tetrazole atoms, OH = hydroxy ions

[f] Unless otherwise mentioned, S = $[q(CO_2)/q(N_2)]:[p(CO_2)/p(N_2)]$ where q are loadings for $p(CO_2)$ = 0.15 bar, $p(N_2)$ = 0.85 bar from single component isotherm data

Table S3. Physicochemical properties of CO_2 and N_2 molecules[7]

Molecule	Normal boiling point (K)	Kinetic diameter, Å	Quadrupole moment, 10^{-27} esu^{-1} cm^{-1}	Dipole moment, 10^{-27} esu^{-1} cm^{-1}	Polarizability, 10^{-25} cm^3
CO_2	194.65*	3.3	43.0	0	29.1
N_2	77.35	3.64	15.2	0	17.4

*sublimes

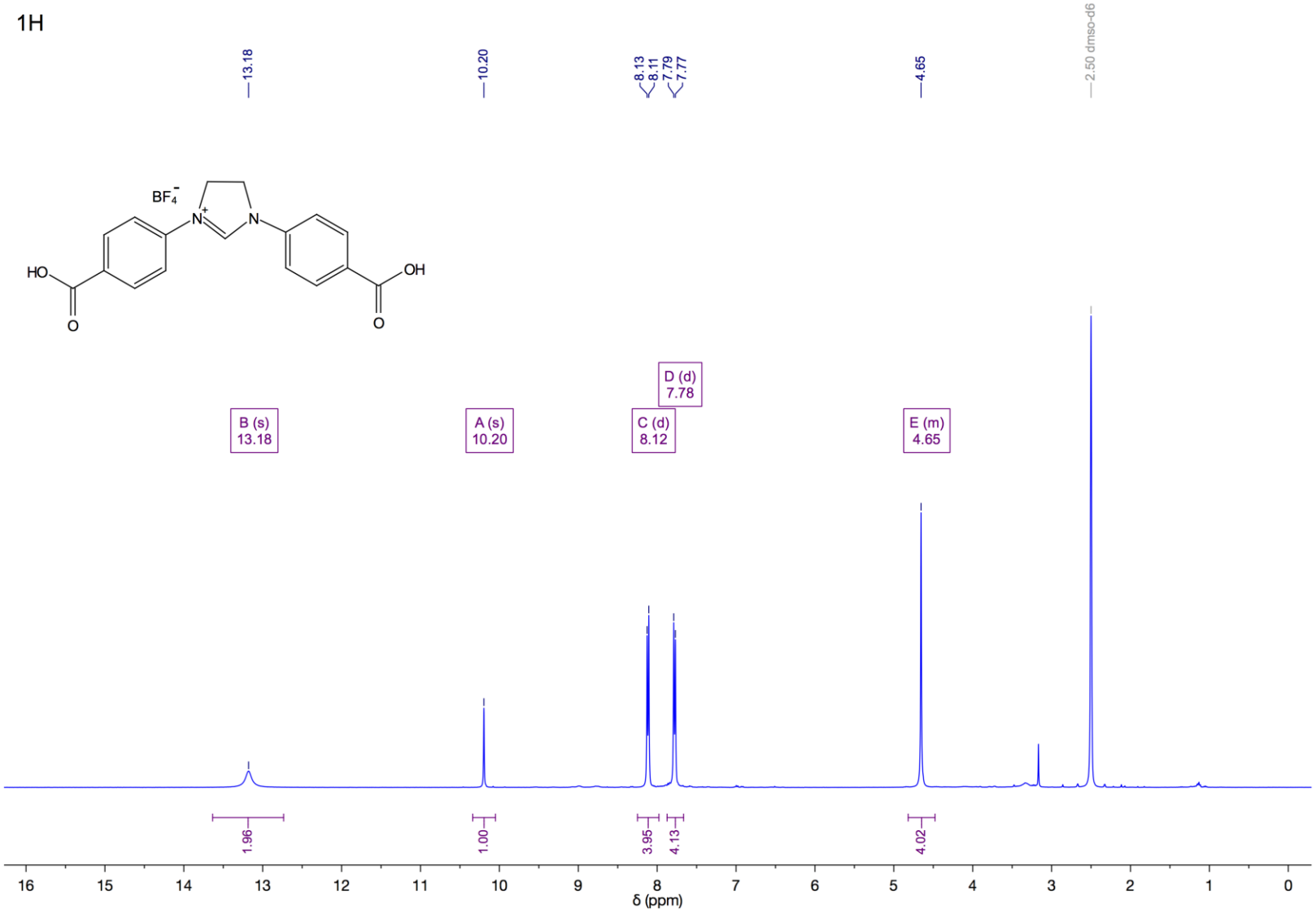

Figure S12. ^{1}H NMR spectrum of the ligand **H_2Sp5-BF_4**.

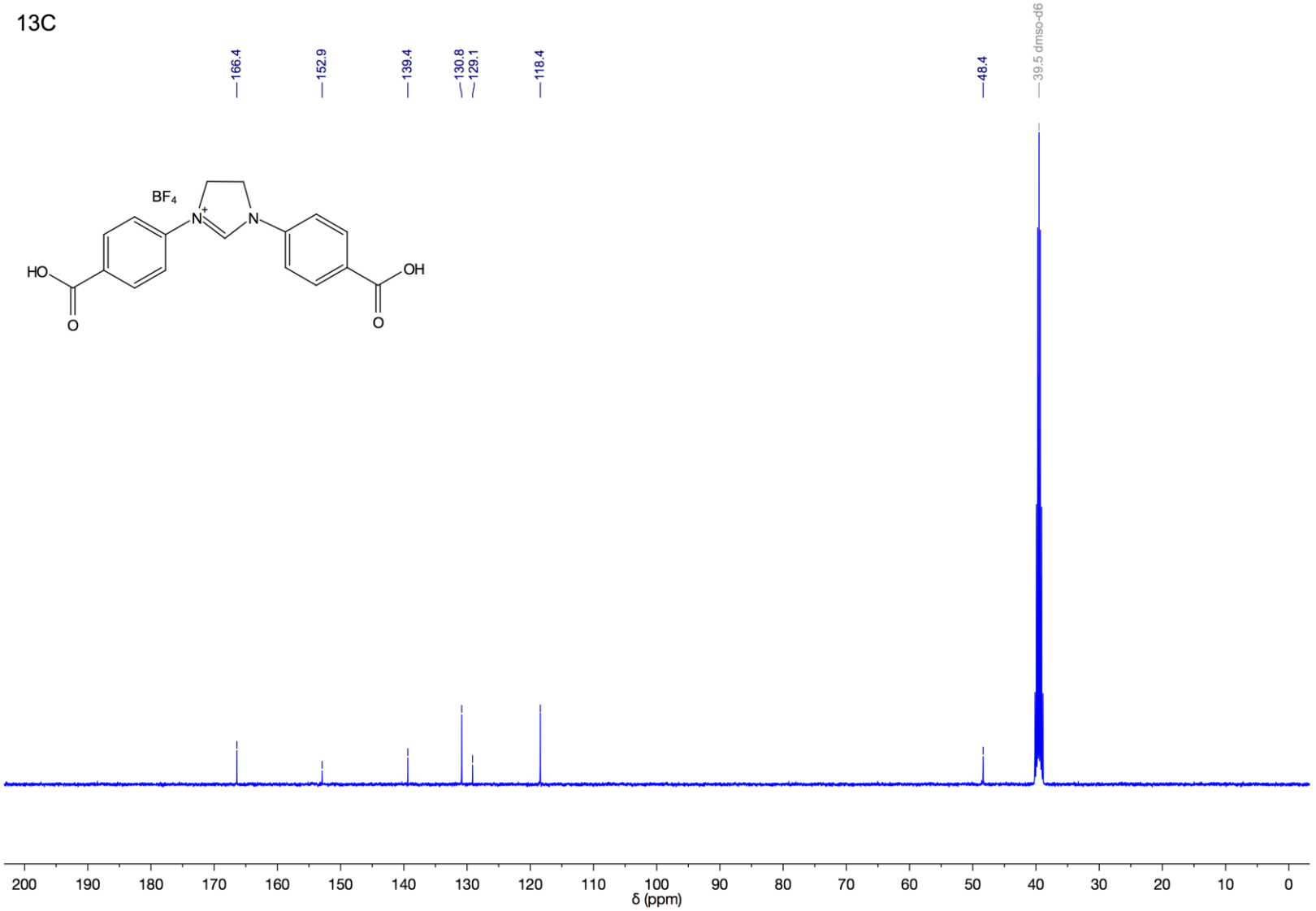

Figure S13. ^{13}C NMR spectrum of the ligand **H_2Sp5-BF_4**.

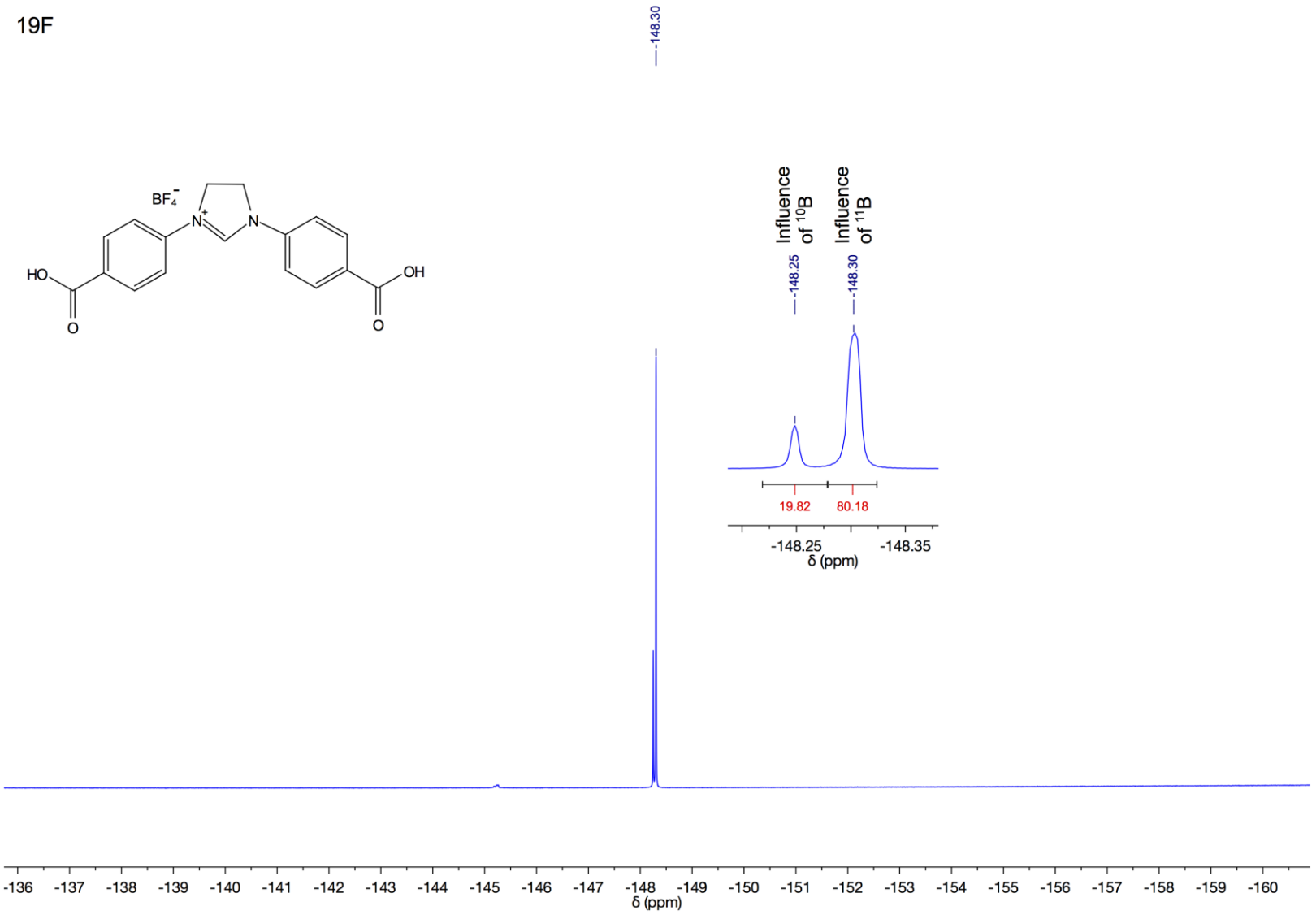

Figure S14. ^{19}F NMR spectrum of the ligand **H_2Sp5-BF_4**.

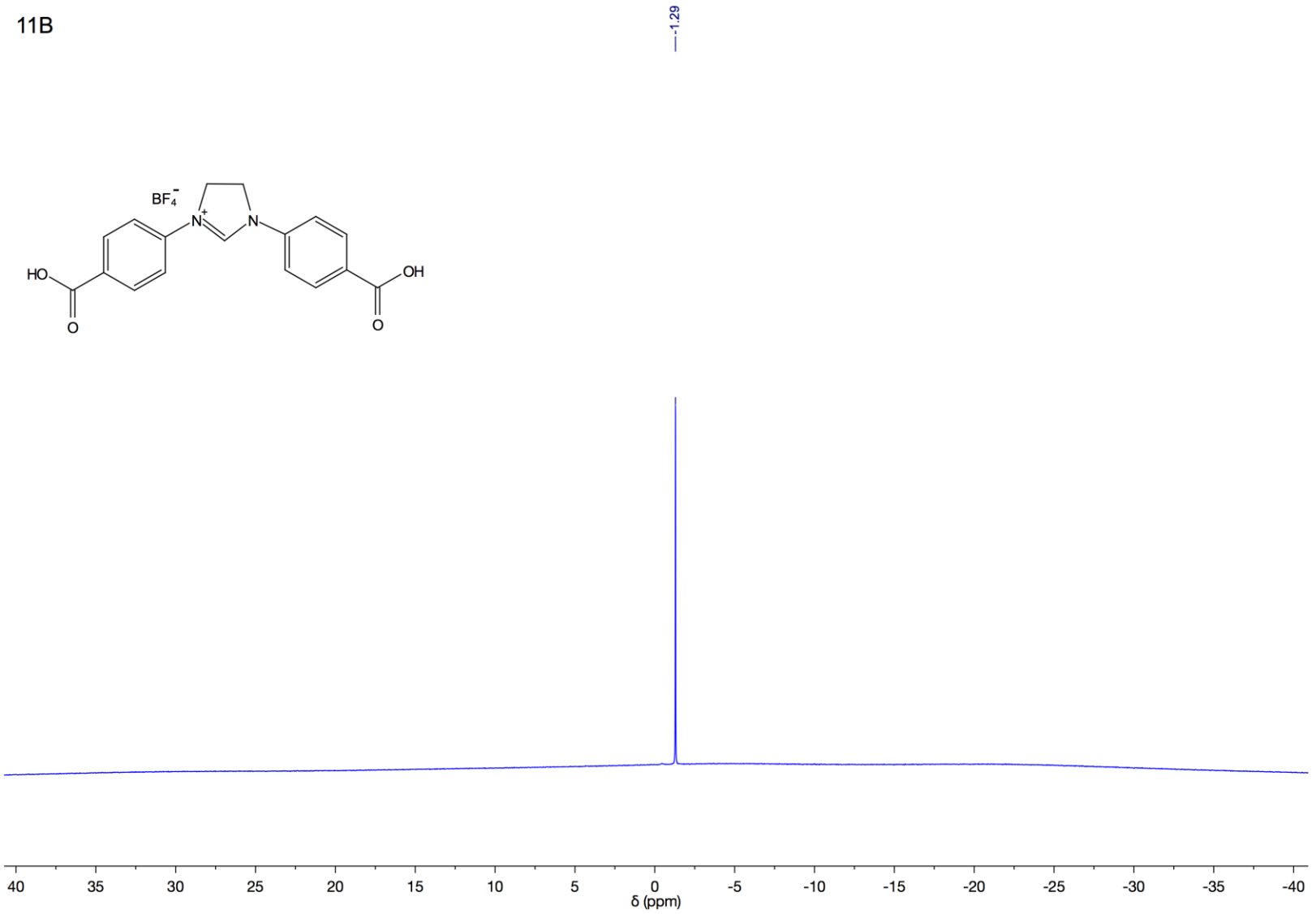

Figure S15. ^{11}B NMR spectrum of the ligand **H_2Sp5-BF_4**.

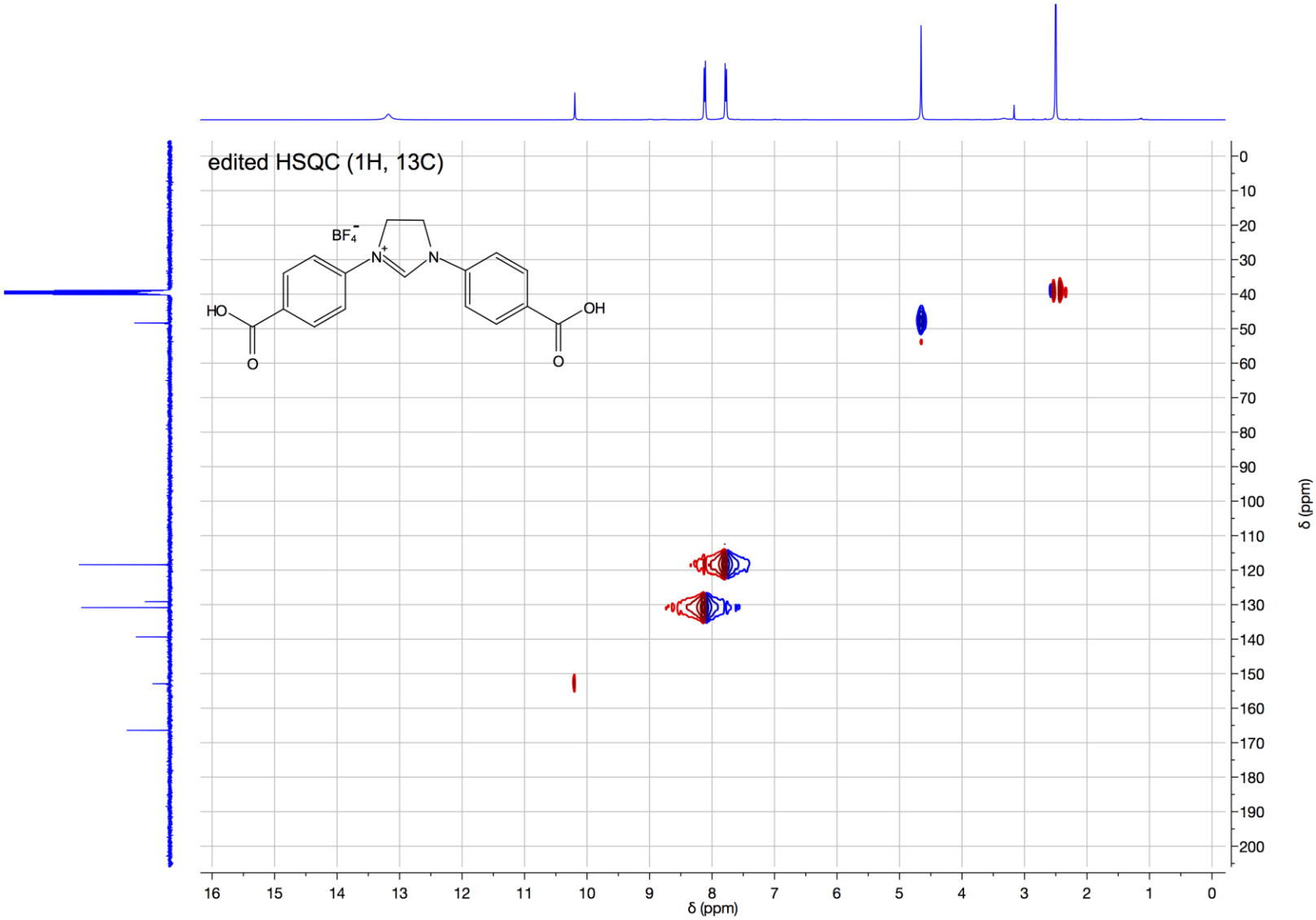

Figure S16. ^{1}H-^{13}C HSQC NMR spectrum of the ligand **H_2Sp5-BF_4**.

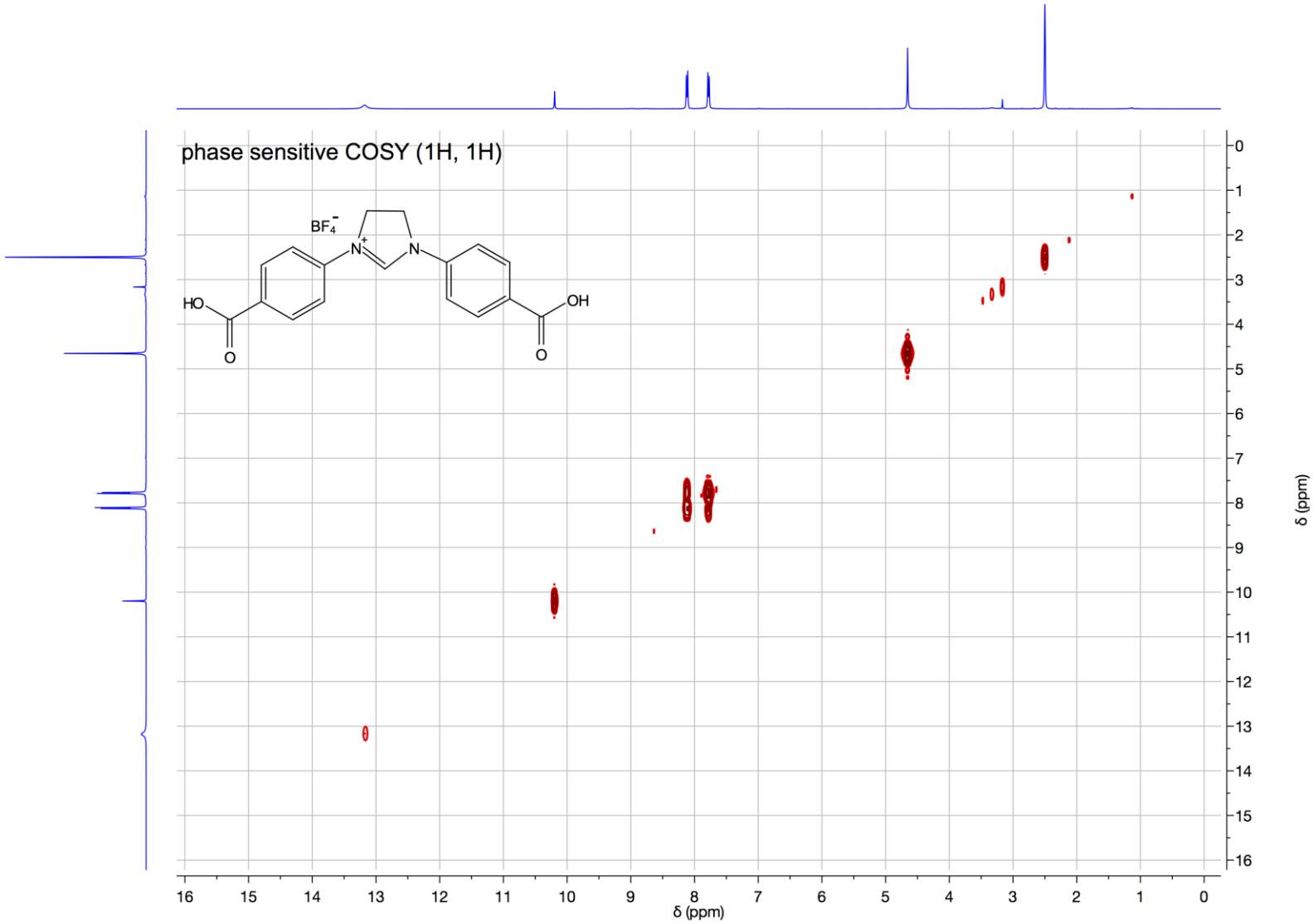

Figure S17. ^{1}H-^{1}H COSY NMR spectrum of the ligand **H_2Sp5-BF_4**.

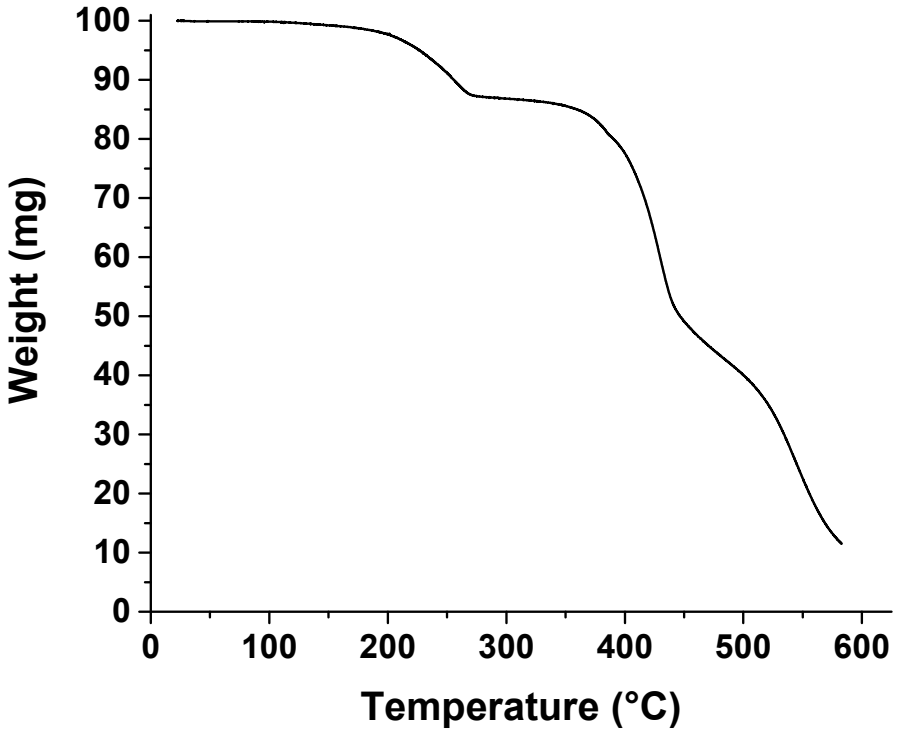

Figure S18. TGA curve of the ligand **H_2Sp5-BF_4**.

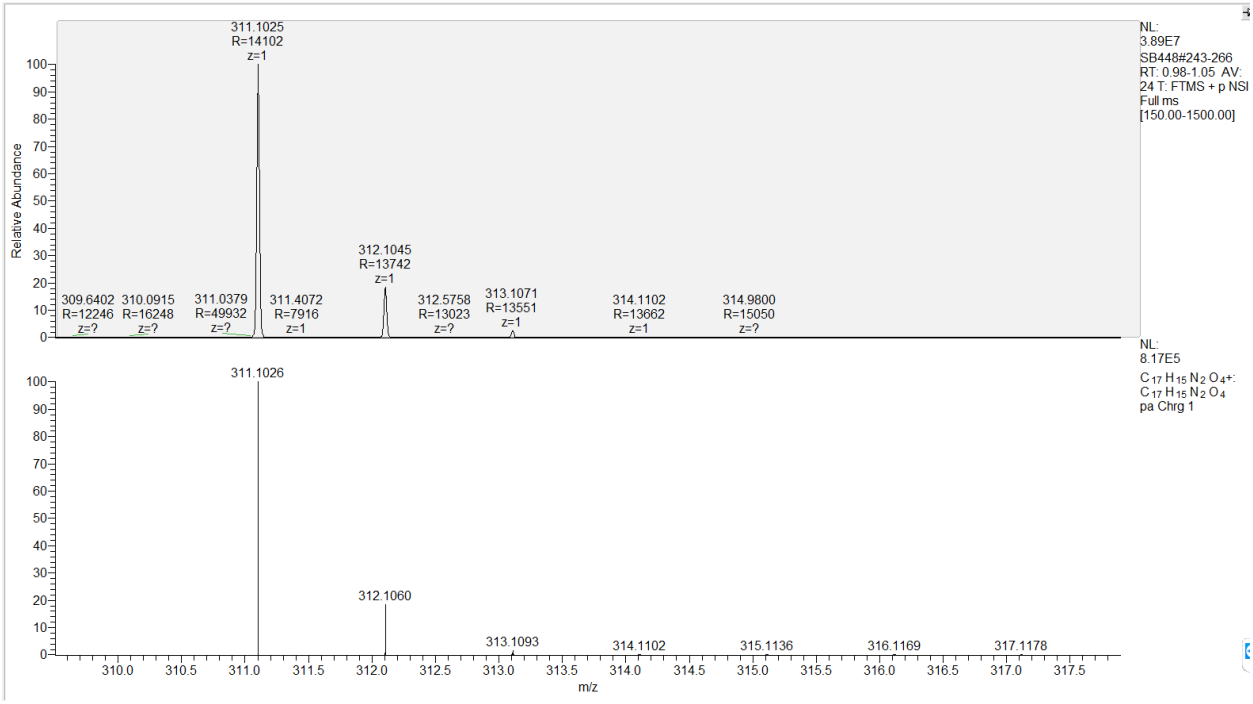

Figure S19. Theoretical (below) and experimental (above) HRMS spectra of the ligand **H_2Sp5-BF_4**.

References:

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