Table S1. Crystal data and structure refinement for **2, 3,** and **4**·2CH$_3$CN.

| Compound	**2**	**3**	**4**·2CH$_3$CN
Empirical formula	C$_{34}$H$_{51}$B$_{12}$CdN$_7$O$_3$	C$_{24}$H$_{32}$N$_6$O$_4$Zn	C$_{24}$H$_{46}$B$_{12}$N$_8$
Formula weight	847.93	533.92	576.41
Temperature/K	100.00	100.00	100.00
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	*P*2$_1$/*n*	*P*-1
a/Å	10.494(2)	13.8012(15)	8.036(2)
b/Å	12.322(4)	12.687(2)	10.416(4)
c/Å	18.644(6)	15.896(2)	10.700(4)
α/°	79.582(13)	90	106.211(14)
β/°	87.114(11)	115.116(5)	91.220(12)
γ/°	75.755(11)	90	109.216(10)
Volume/Å^3	2298.1(12)	2520.3(7)	805.8(4)
Z	2	4	1
ρ$_{calc}$g/cm^3	1.225	1.407	1.188
μ/mm^{-1}	0.515	1.016	0.067
F(000)	872.0	1120.0	306.0
Radiation	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 12, -24 ≤ l ≤ 18	-19 ≤ h ≤ 19, -17 ≤ k ≤ 13, -22 ≤ l ≤ 22	-11 ≤ h ≤ 11, -10 ≤ k ≤ 14, -15 ≤ l ≤ 14
Reflections collected	14162	20891	6246
Independent reflections	10200 [R_{int} = 0.0263, R_{sigma} = 0.0803]	7064 [R_{int} = 0.0333, R_{sigma} = 0.0422]	4553 [R_{int} = 0.0221, R_{sigma} = 0.0549]
Data/restraints/parameters	10200/0/520	7064/0/339	4553/0/201
Goodness-of-fit on F^2	1.021	1.028	1.037
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1050	R_1 = 0.0336, wR_2 = 0.0728	R_1 = 0.0483, wR_2 = 0.1084
Final *R* indexes [all data]	R_1 = 0.0727, wR_2 = 0.1149	R_1 = 0.0506, wR_2 = 0.0784	R_1 = 0.0656, wR_2 = 0.1171
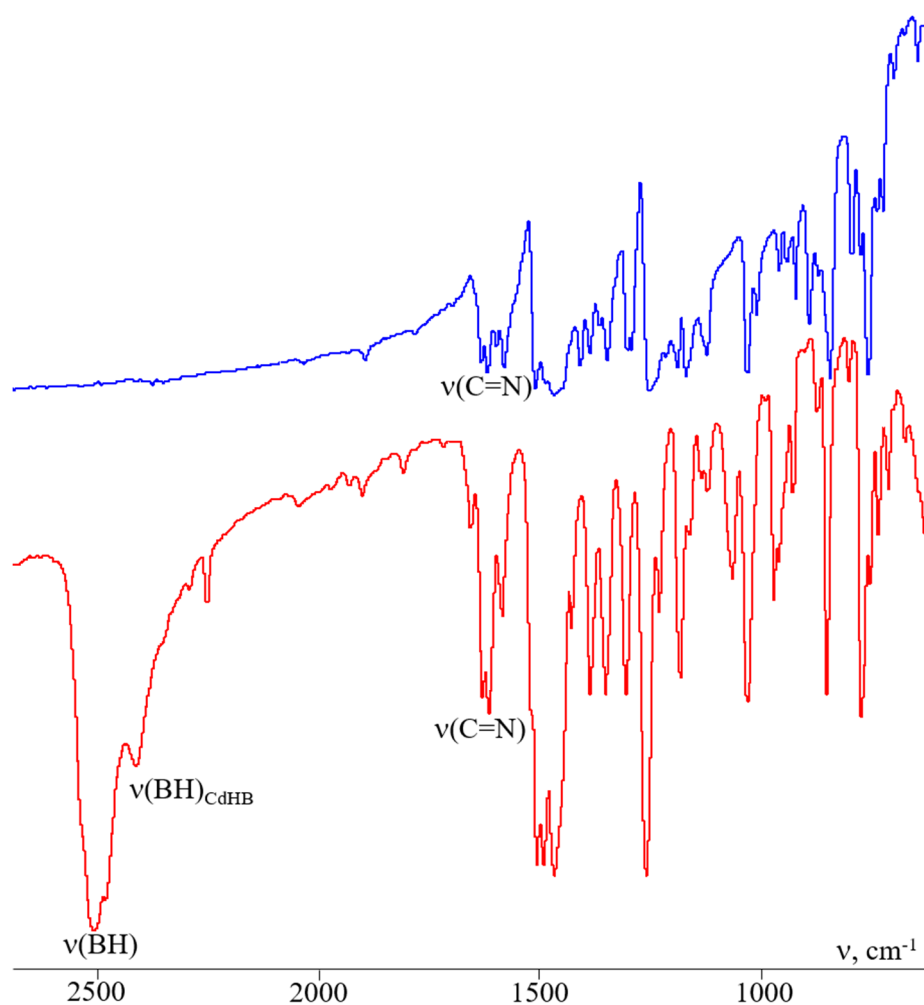
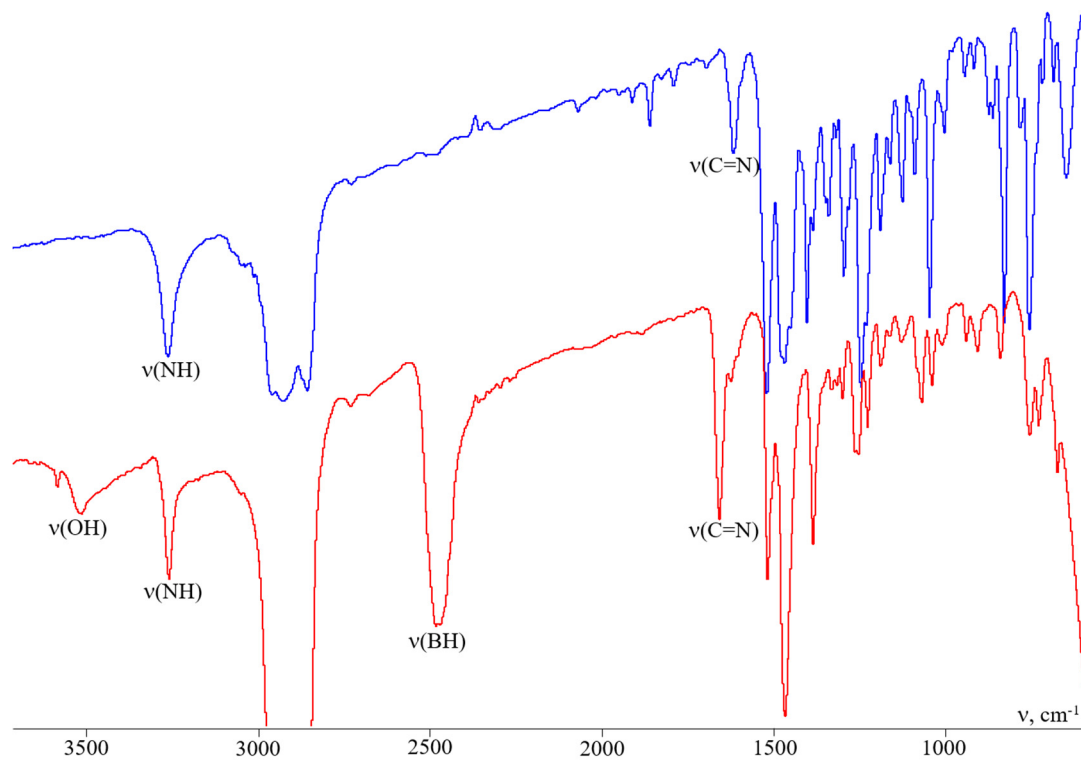**Figure S1**. IR spectra of ligand L^1 (blue) and complex **1** (red).

Figure S2. IR spectra of ligand L^2 (blue) and complex 2 (red).
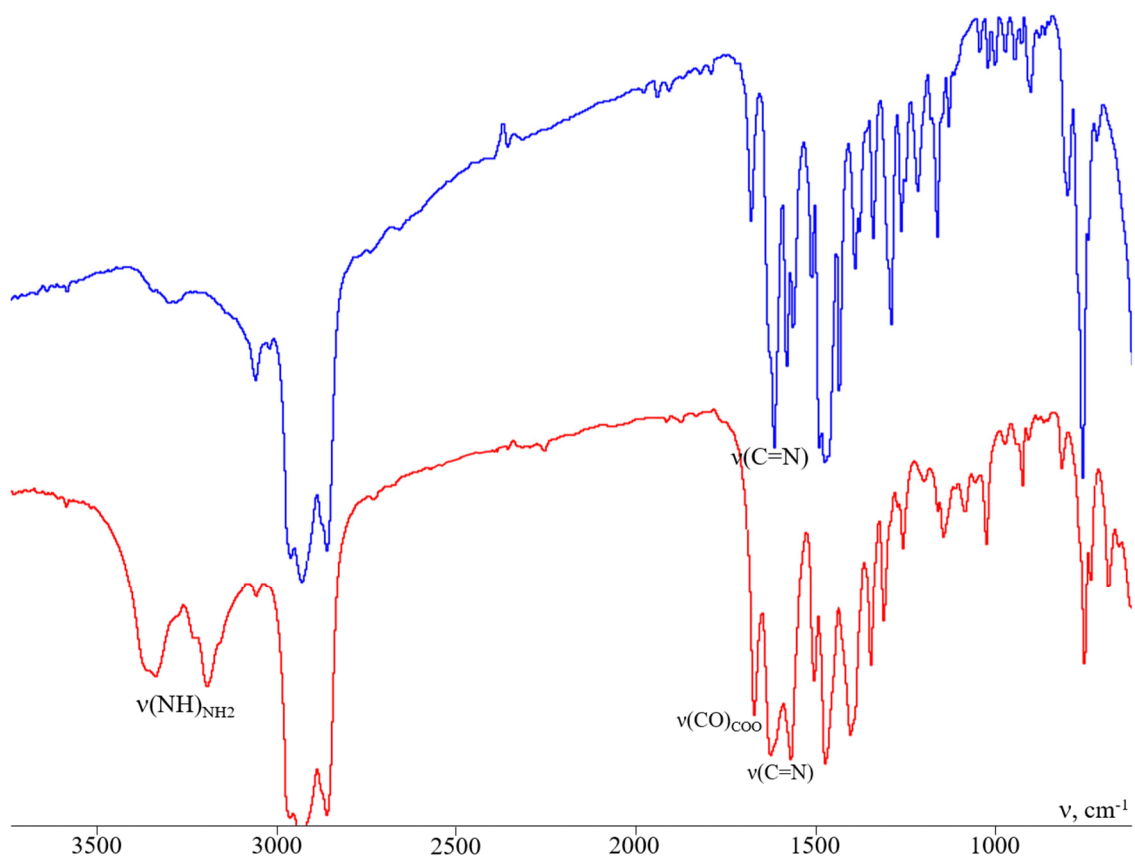
Figure S3. IR spectra of ligand L^3 (blue) and complex 3 (red).
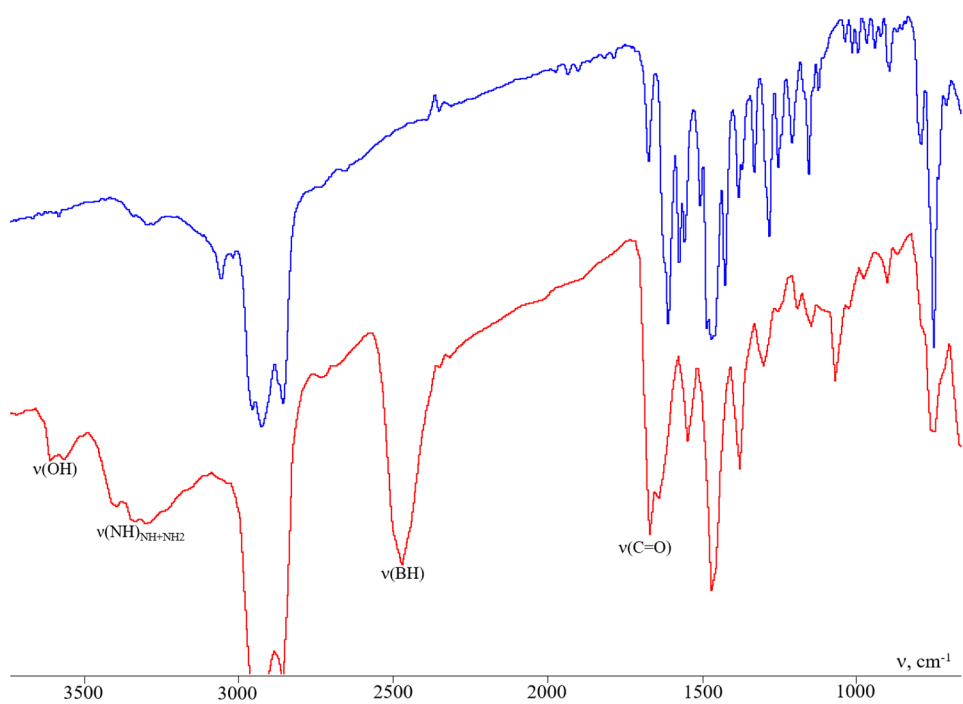

Figure S4. IR spectra of ligand L^3 (blue) and a precipitate containing $(HBz\text{-}NH_2)_2[B_{12}H_{12}]$ (**4**) and a cadmium(II) complex with salicylaldehyde (red).
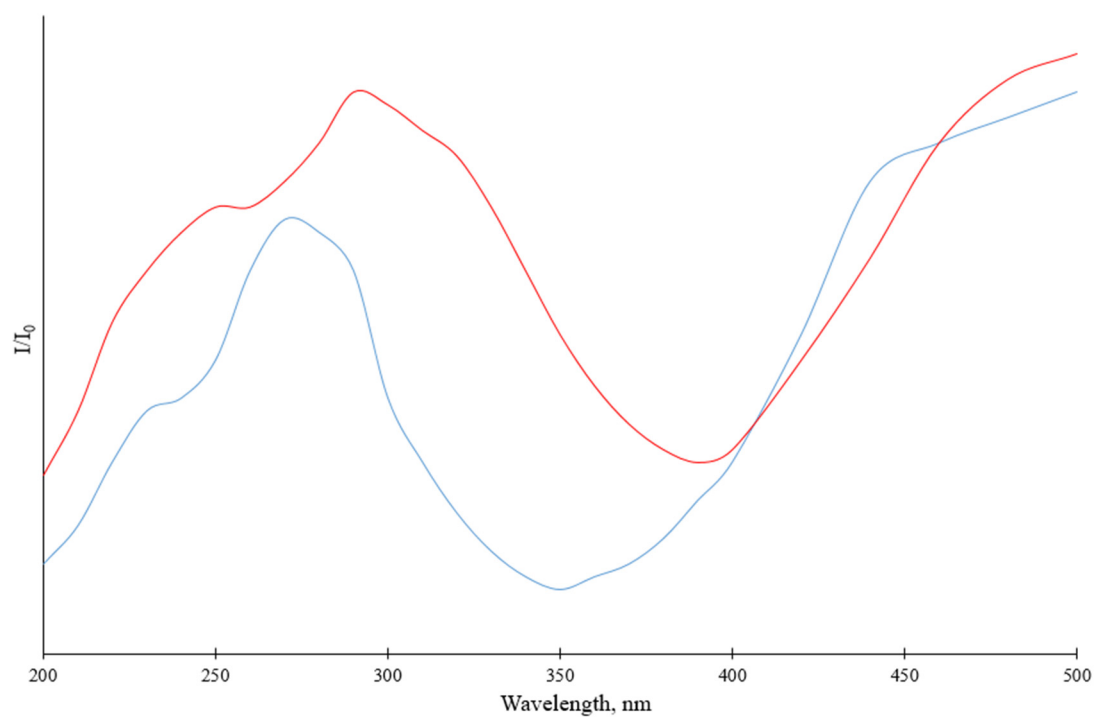
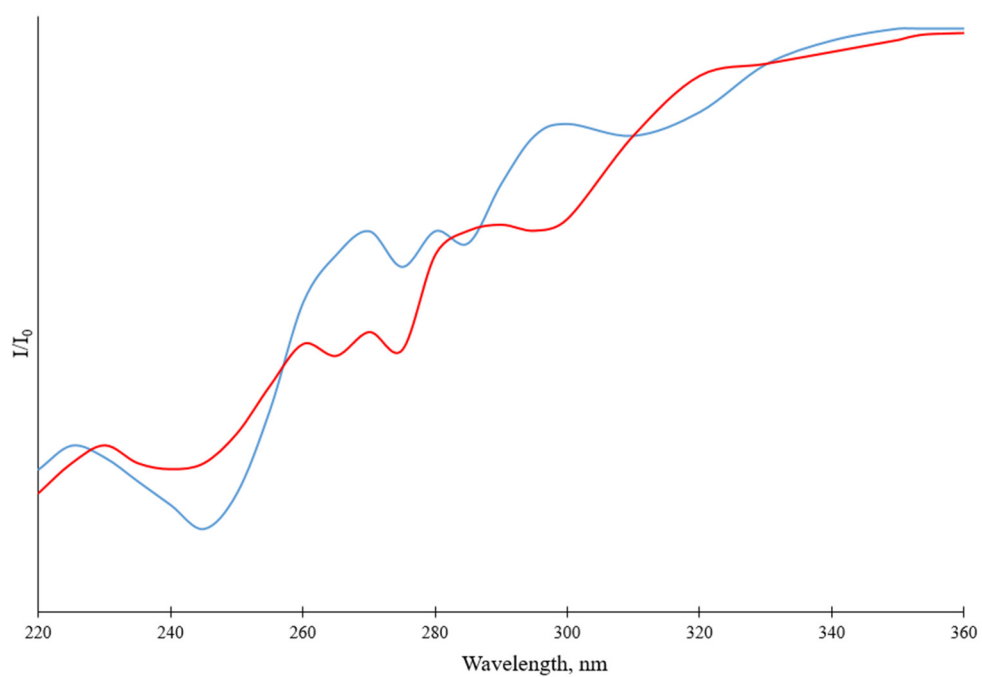**Figure S5**. UV-vis absorption spectra of ligand L^1 (blue) and complex **1** (red).

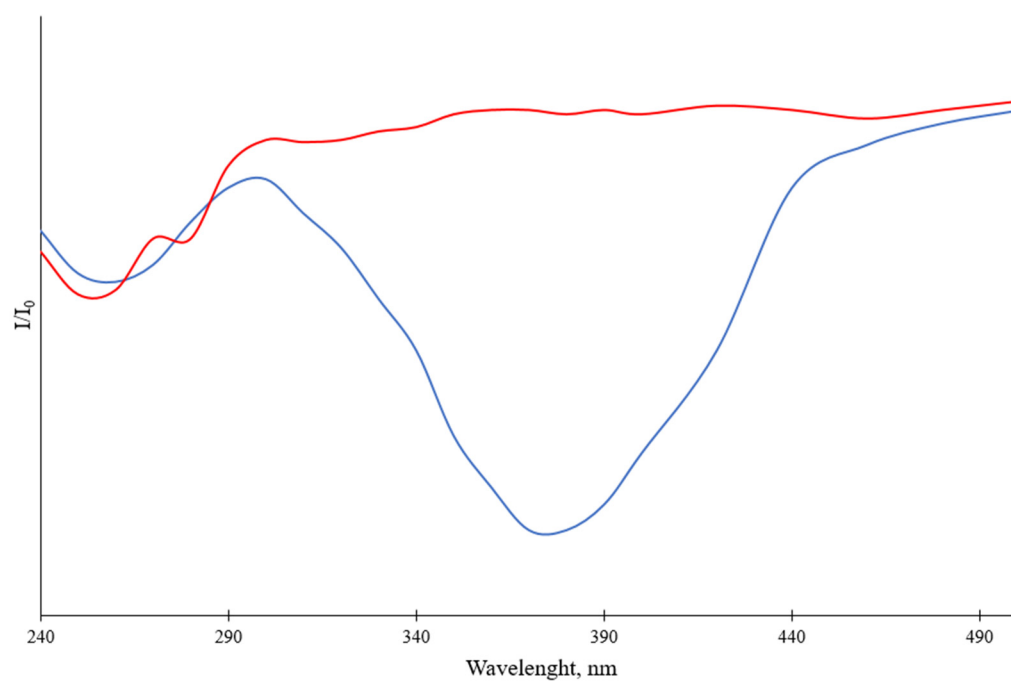**Figure S6**. UV-vis absorption spectra of ligand L^2 (blue) and complex **2** (red).

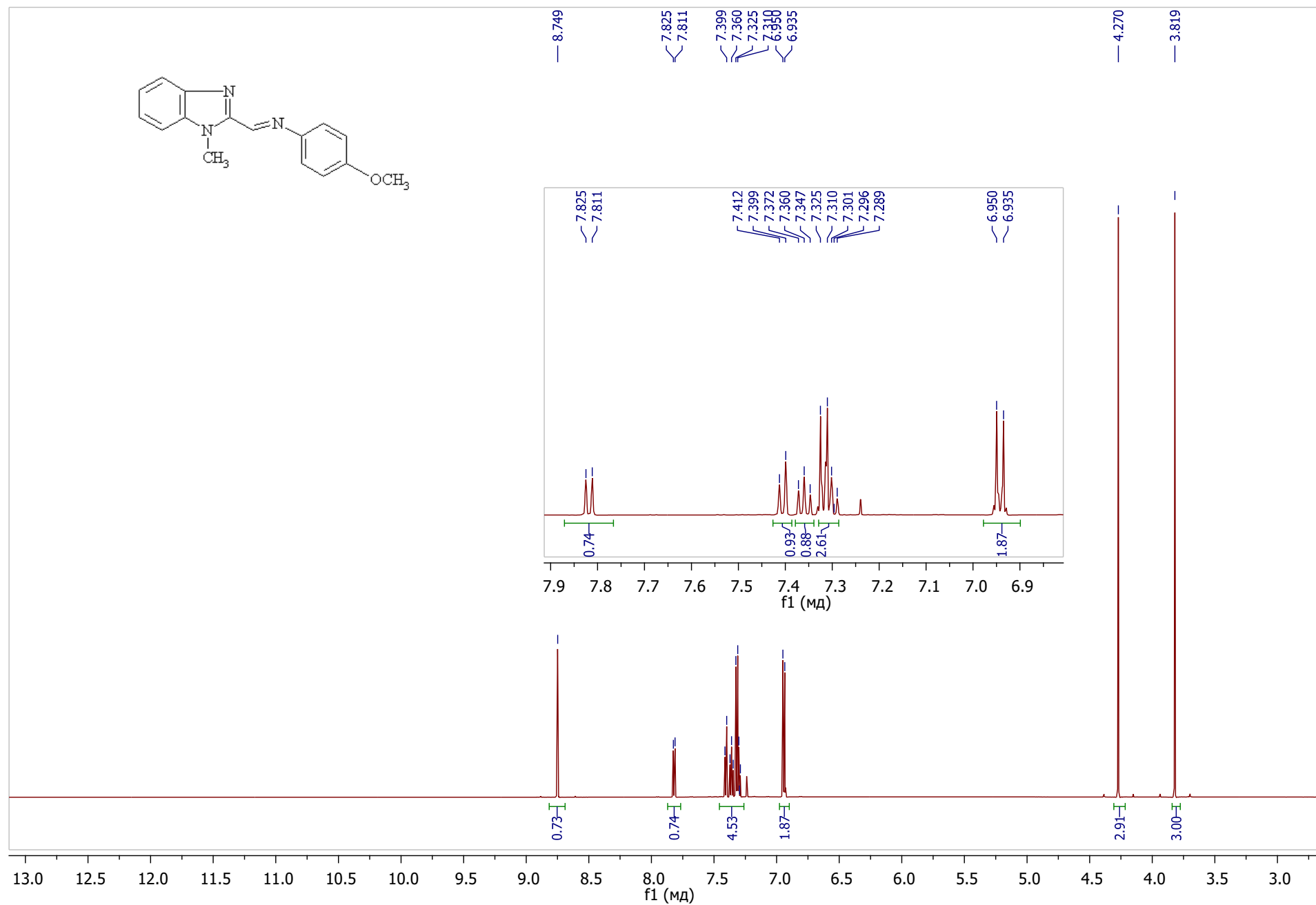**Figure S7**. UV-vis absorption spectra of ligand L^3 (blue) and complex **3** (red).

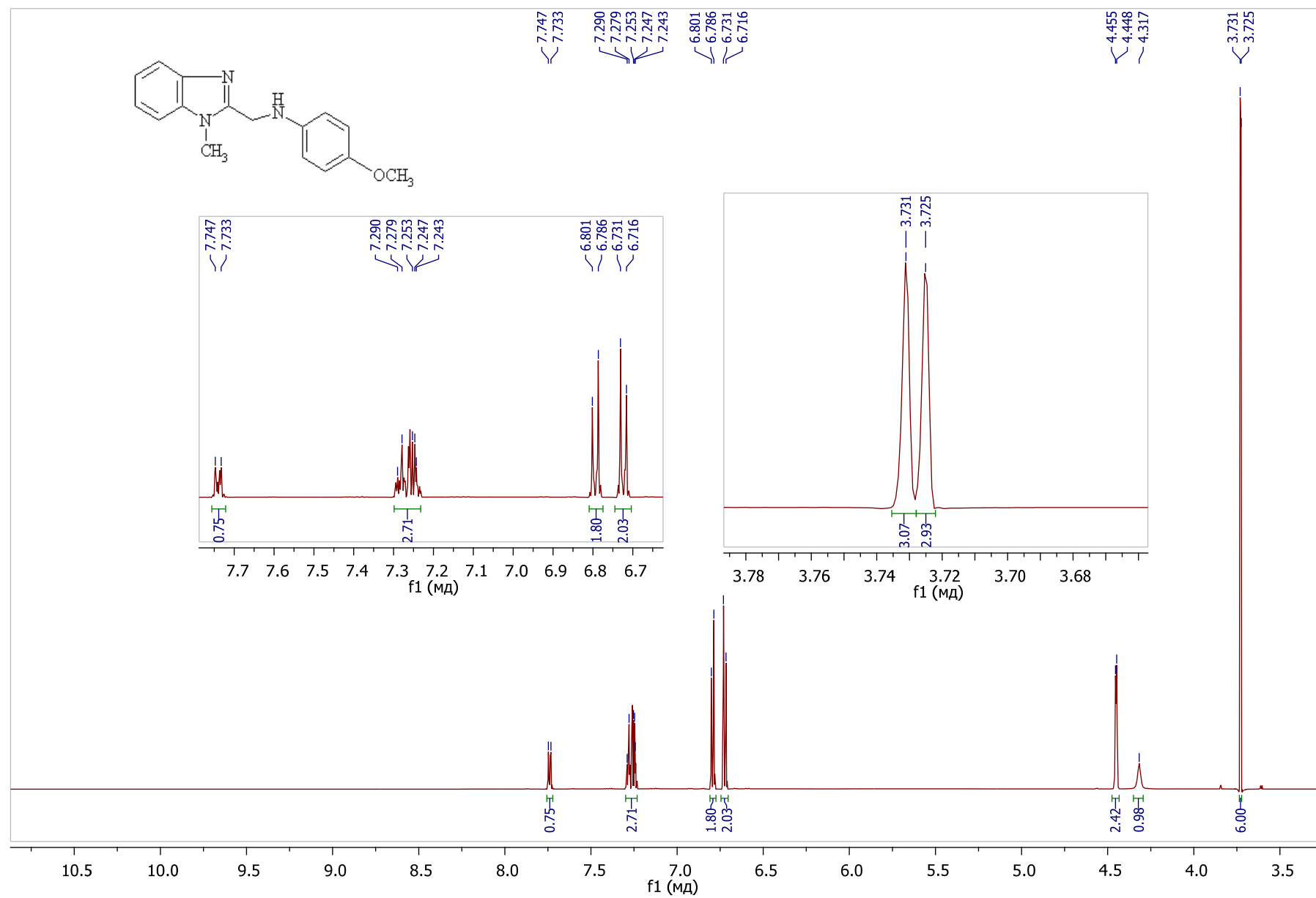**Figure S8**. ^1H NMR spectrum of *N*-(4-methoxyphenyl)-1-(1-methylbenzimidazol-2-yl)methanimine (L^1).

Figure S9. ^{1}H NMR spectrum of 4-methoxy-*N*-[(1-methylbenzimidazol-2-yl)methyl]aniline (L^2).
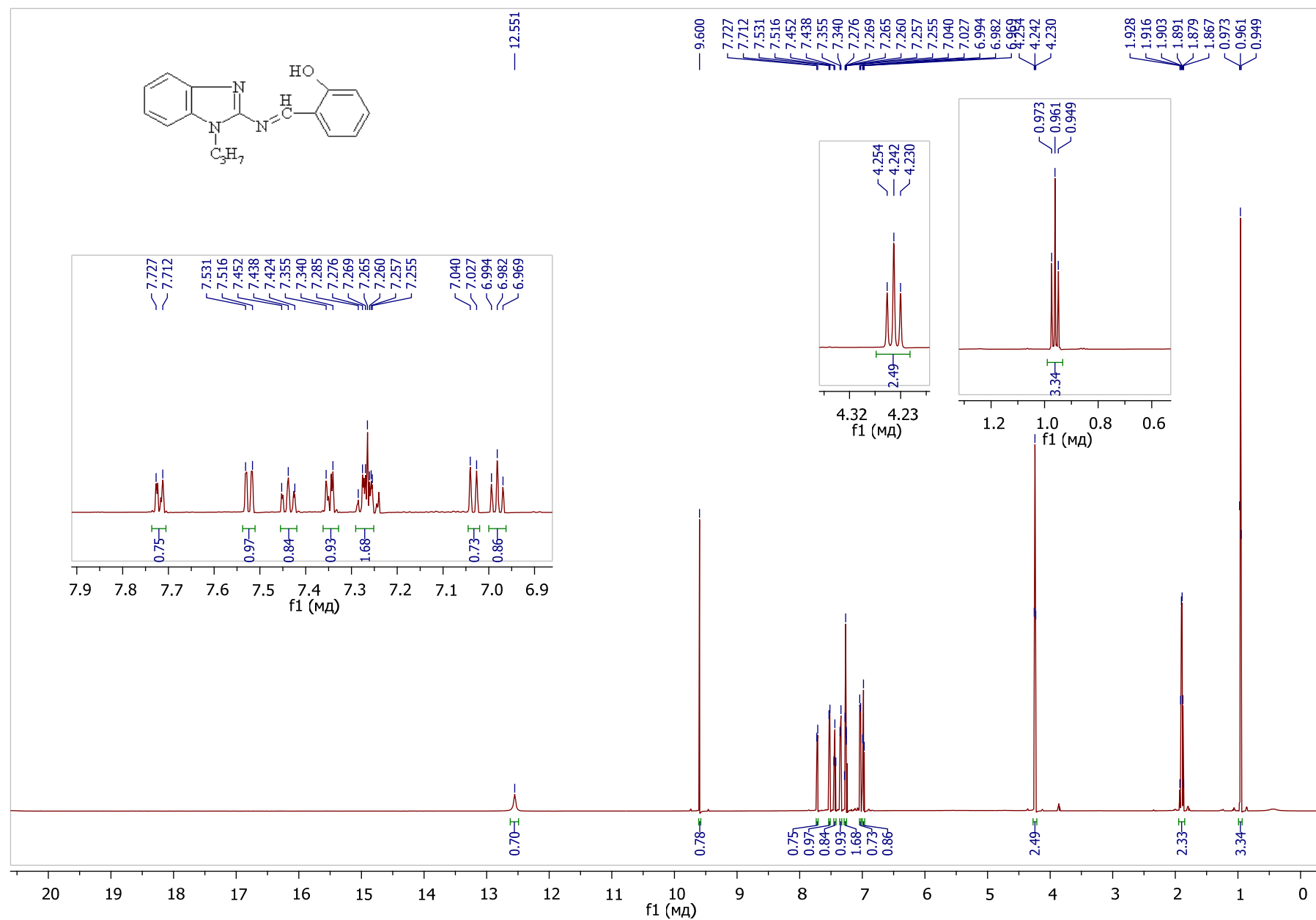
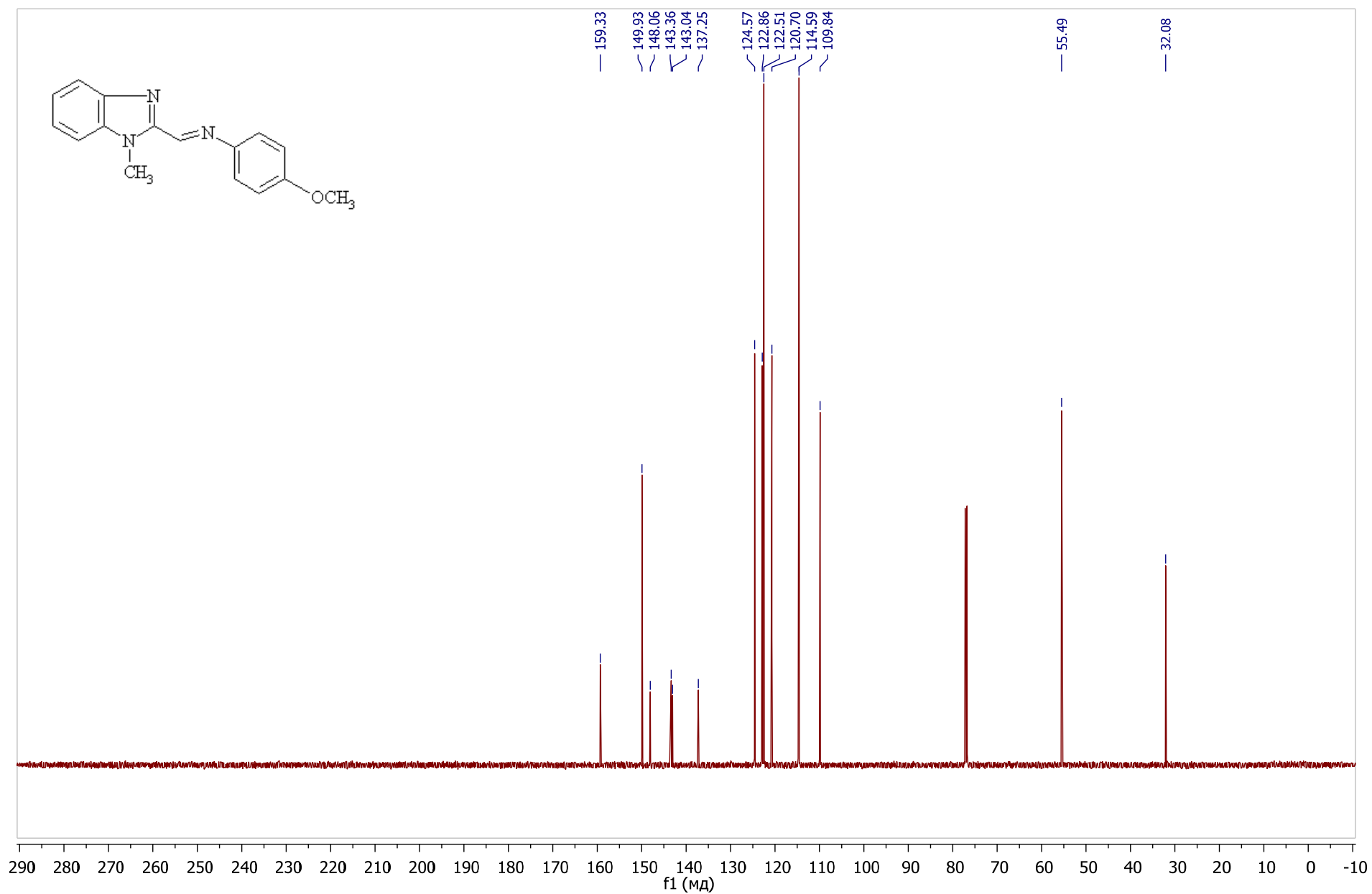**Figure S10**. ^{1}H NMR spectrum of 2-[(*E*)-(1-propylbenzimidazol-2-yl)iminomethyl]phenol (L^3).

Figure S11. ^{13}C NMR spectrum of *N*-(4-methoxyphenyl)-1-(1-methylbenzimidazol-2-yl)methanimine (L^1).
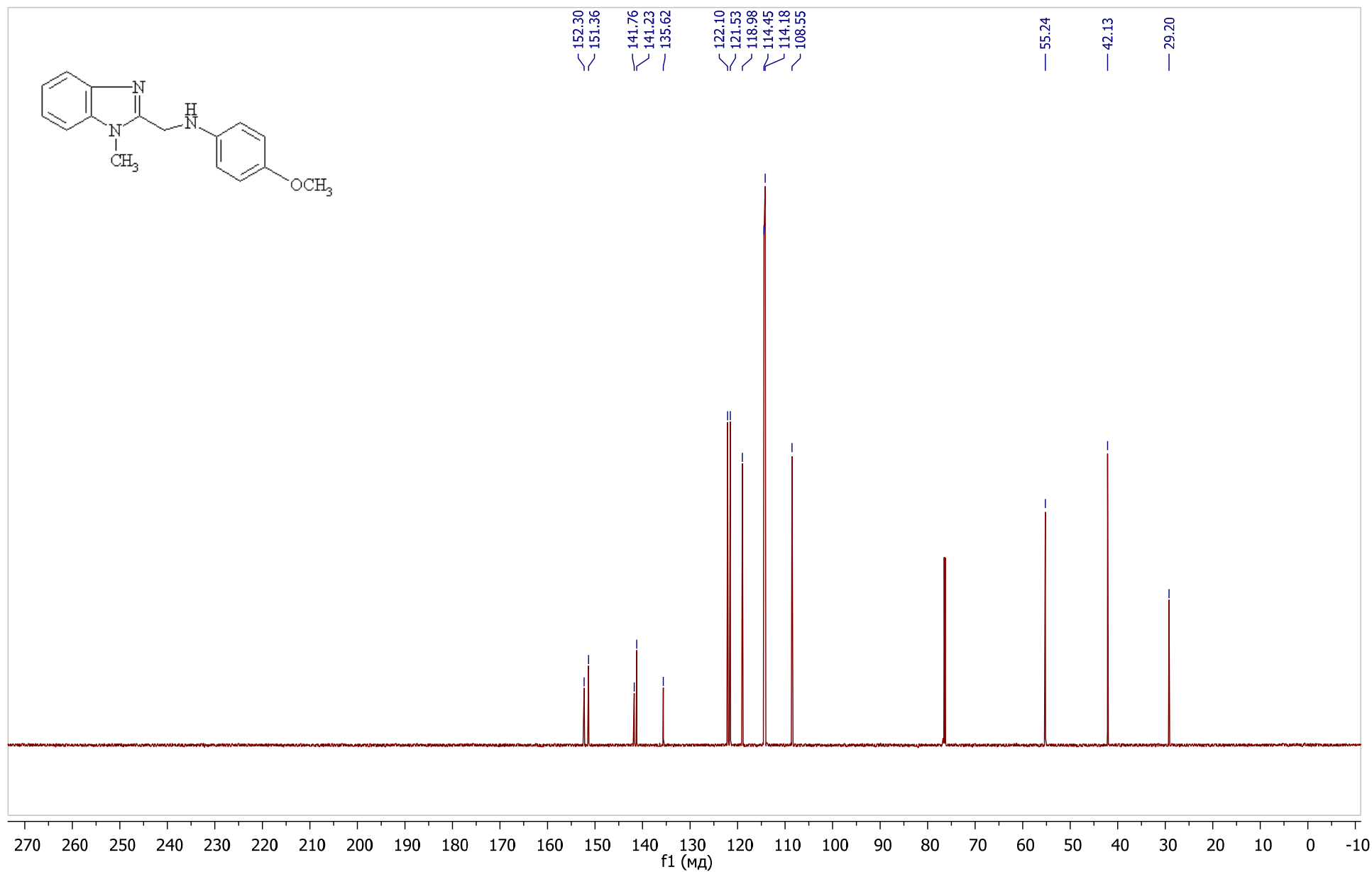
Figure S12. ^{13}C NMR spectrum of 4-methoxy-*N*-[(1-methylbenzimidazol-2-yl)methyl]aniline (L^2).
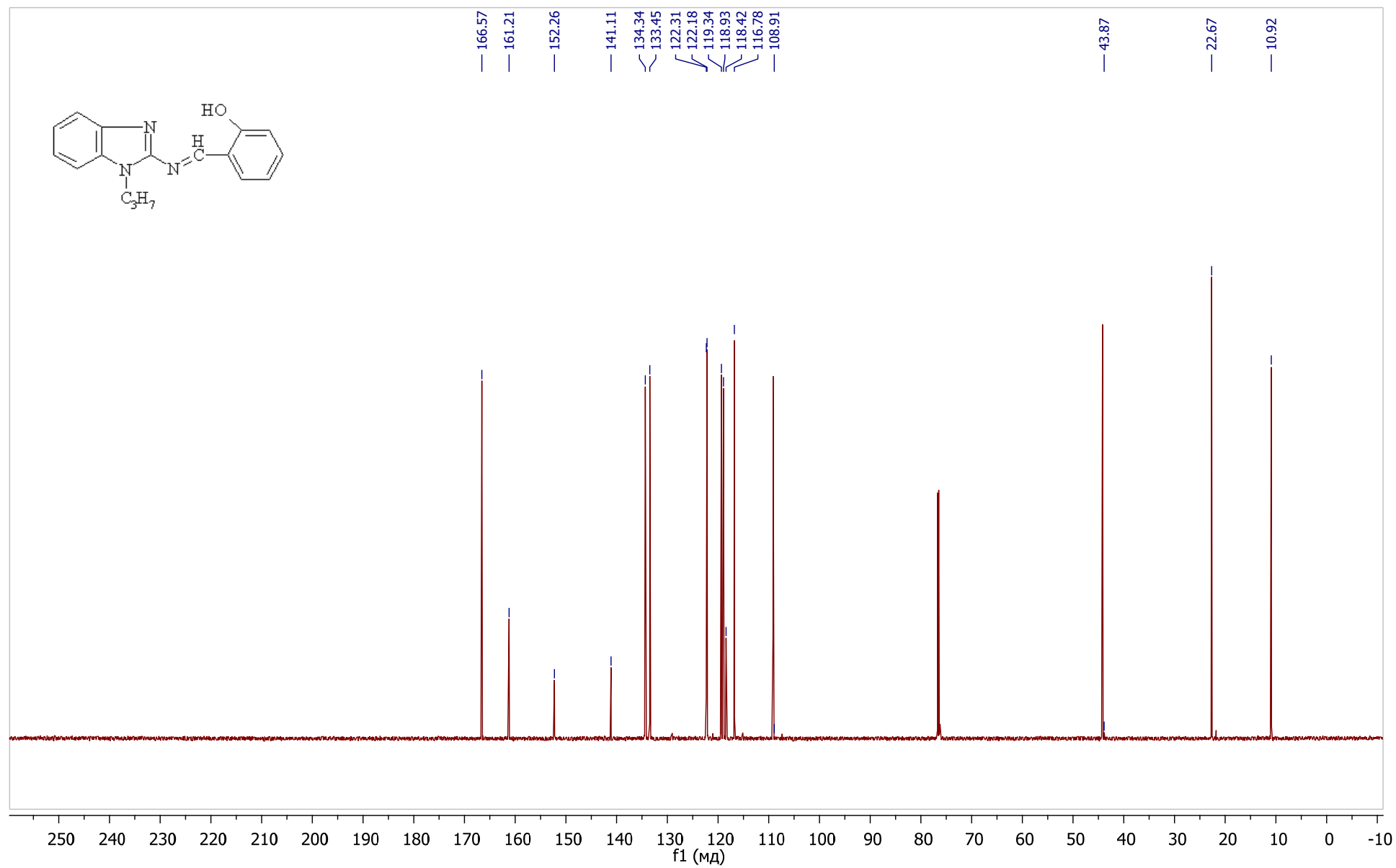
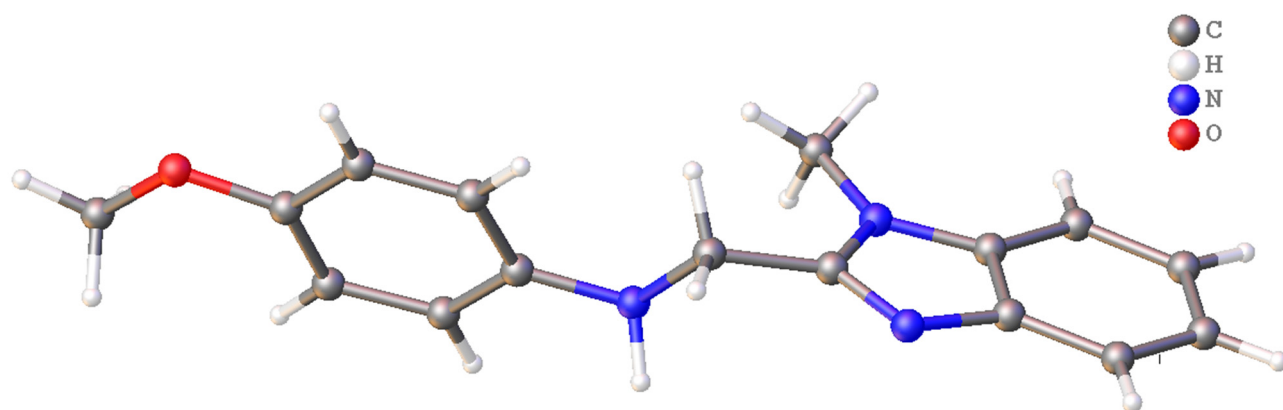**Figure S13**. ^{13}C NMR spectrum of 2-[(*E*)-(1-propylbenzimidazol-2-yl)iminomethyl]phenol (L^3).

Figure S14. Structure of ligand L^2.