Supporting information

Synthesis and theoretical studies of aromatic azaborines

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Initial tests for method and basis sets

Since the final idea is to use the synthesized azaborines as ligands in metal complexes, the selection of the method is limited to quantum chemical DFT methods. Although our previous computational studies have shown the best performance/computational cost ratio can be obtained by the PBE0 functional, we also tested the very often used B3LYP in optimizing the geometry of the compound **1** (Figure S1). In addition, three standard basis sets were tested, DZ-level 6-31G(d), and TZ-levels 6-311G(d,p) and 6-311++G(d,p). The results showed, that expectedly, PBE0/6-31G(d) produced reasonable geometrical parameters for the test molecule compared to available experimental data (not exactly the same molecules were found from the crystal structure data base). As a conclusion, the limited DZ basis set can be used for geometry optimization, and can also give reliable relative energies.

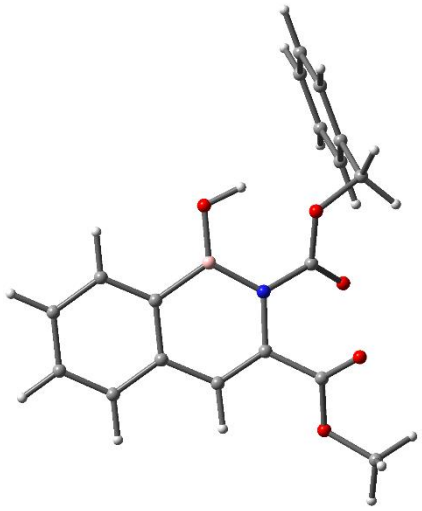

Figure S1. The parent compound **1**. The color code of the atoms: C = gray, B = pink, O = red, N = blue, H = white.

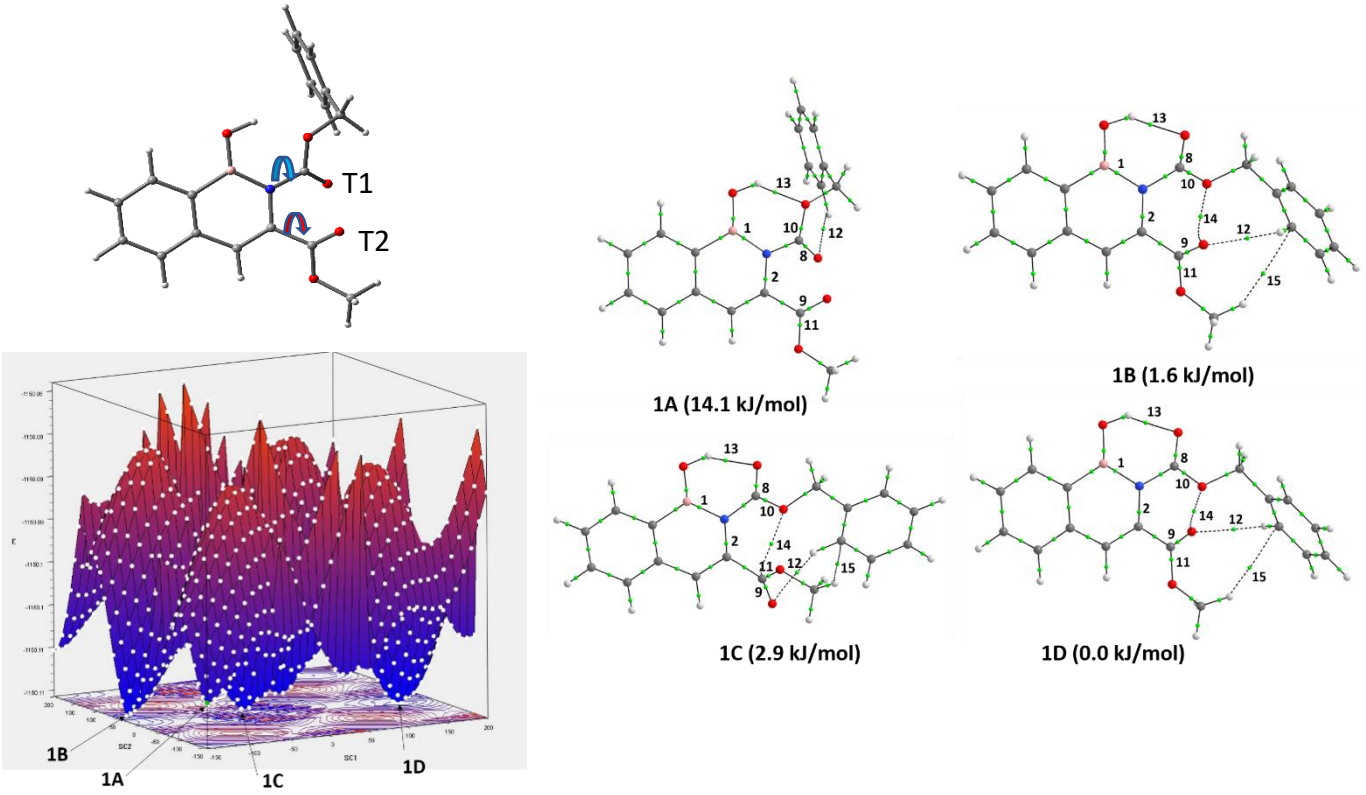

Figure S2. 2D conformational analysis of two rotations (T1, T2) of the DBZ and COOMe substituents in the BN ring. The numbers in the structures on the right refer to the different bond critical points, which are used in the topological charge density analysis according to the QTAIM (Quantum Theory of Atoms in Molecules) method.

Optimized geometries

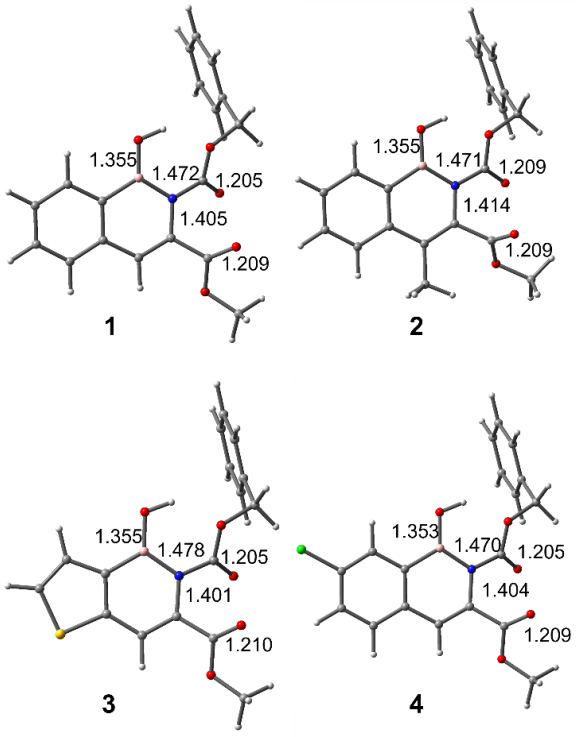

Figure S3. Selected optimized bond distances (Å) for compounds **1**-**4**. The selected parameters are: d(B-N), d(N-C), d(B-O) and d(C=O). The colour code of the atoms: The color code of the atoms: C = gray, B = pink, O = red, N = blue, H = white.

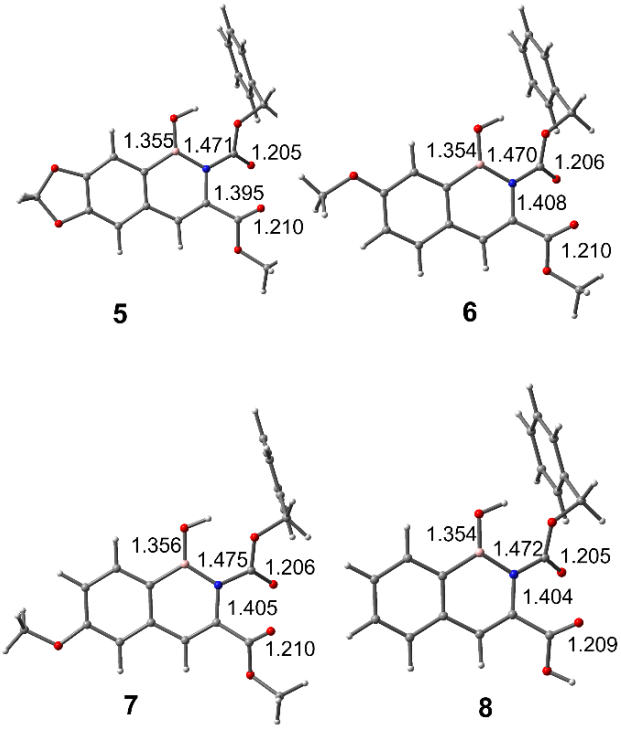

Figure S4. Selected optimized bond distances (Å) for compounds **5**-**8**. The selected parameters are: d(B-N), d(N-C), d(B-O) and d(C=O). The colour code of the atoms: The color code of the atoms: C = gray, B = pink, O = red, N = blue, H = white.

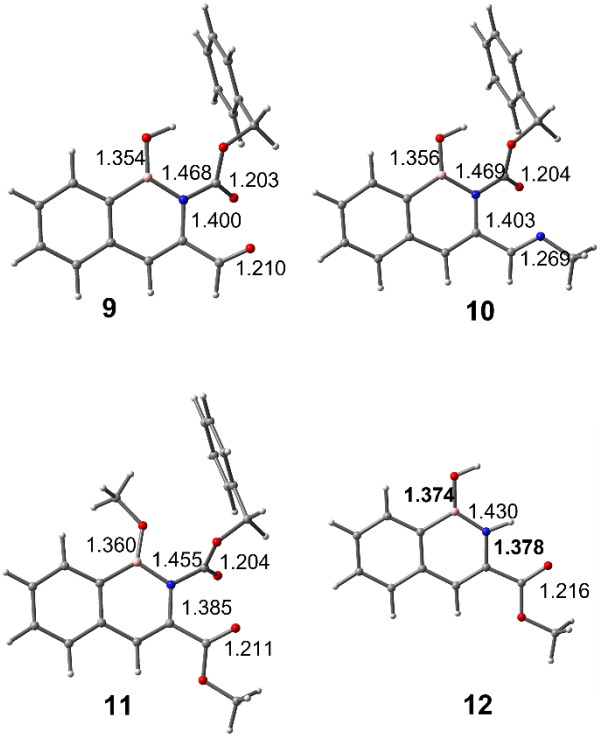

Figure S5. Selected optimized bond distances (Å) for compounds **9**-**12**. The selected parameters are: d(B-N), d(N-C), d(B-O) and d(C=O). The colour code of the atoms: The color code of the atoms: C = gray, B = pink, O = red, N = blue, H = white.

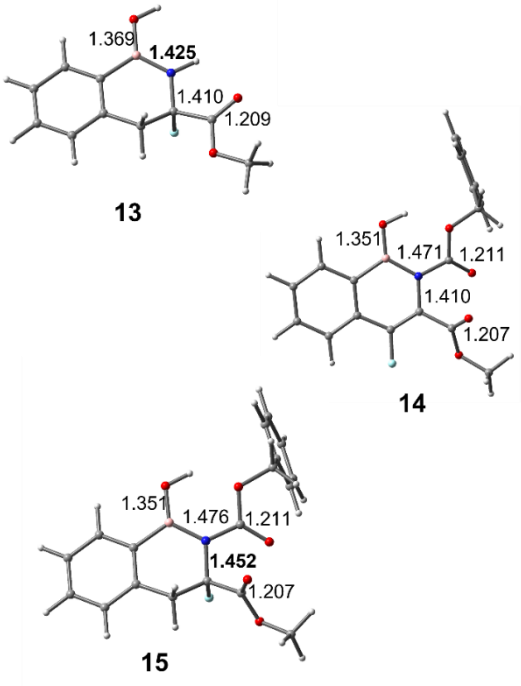

Figure S6. Selected optimized bond distances (Å) for compounds **13**-**15**. The selected parameters are: d(B-N), d(N-C), d(B-O) and d(C=O). The colour code of the atoms: The color code of the atoms: C = gray, B = pink, O = red, N = blue, H = white.

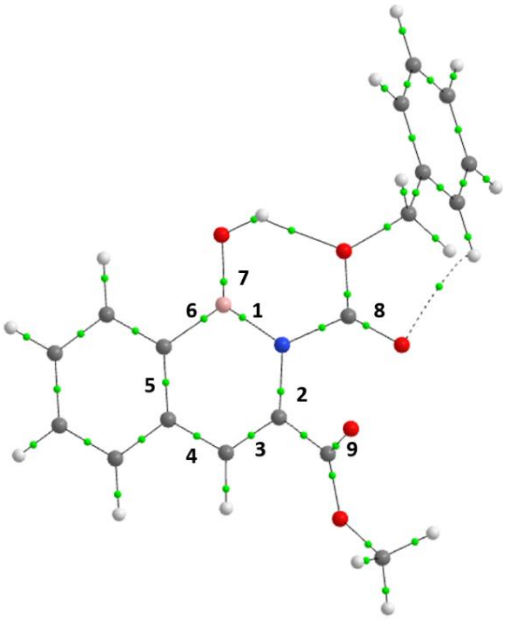

Figure S7. Numbering of the selected BCPs

Table S1. Properties of the electron density at the selected bond critical points (BCPs, see Figure 3) of the compound **1.** The parameters are ρ = electron density, $|V|/G$ = ratio between potential and kinetic energy densities, DI = delocalization index, E = total energy at the BCP.

BCP #	Type	ρ[e/Å^3]	$\lvert V\rvert/G$	DI	E[kJ/mol]
1	B-N	1.191	1.51	0.41	-532
2	N-C	1.973	3.01	0.99	-839
3	C-C	2.260	3.87	1.56	-650
4	C-C	1.929	4.43	1.14	-446
5	C-C	2.041	4.12	1.32	-512
6	B-C	1.299	2.19	0.46	-483
7	B-O	1.417	1.34	0.46	-725
8	C=O	2.840	1.93	1.15	-1973
9	C=O	2.801	1.92	1.21	-1940

Table S2. Properties of the electron density at the B-N bond critical point (BCP #1, see Figure S7) of the compounds **1**-**15**. ρ = electron density, |V|/G = ratio between potential energy density and kinetic energy density, DI = delocalization index, E_{BCP} = total energy at the BCP.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ρ	1.191	1.193	1.173	1.198	1.193	1.197	1.182	1.191	1.201	1.200	1.239	1.305	1.328	1.192	1.187
|V|/G	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.49	1.51	1.51	1.53
DI	0.41	0.40	0.41	0.41	0.41	0.41	0.40	0.41	0.41	0.41	0.42	0.44	0.44	0.41	0.40
E_{BCP}	-532	-534	-523	-537	-534	-536	-527	-532	-538	-538	-566	-610	-618	-533	-524

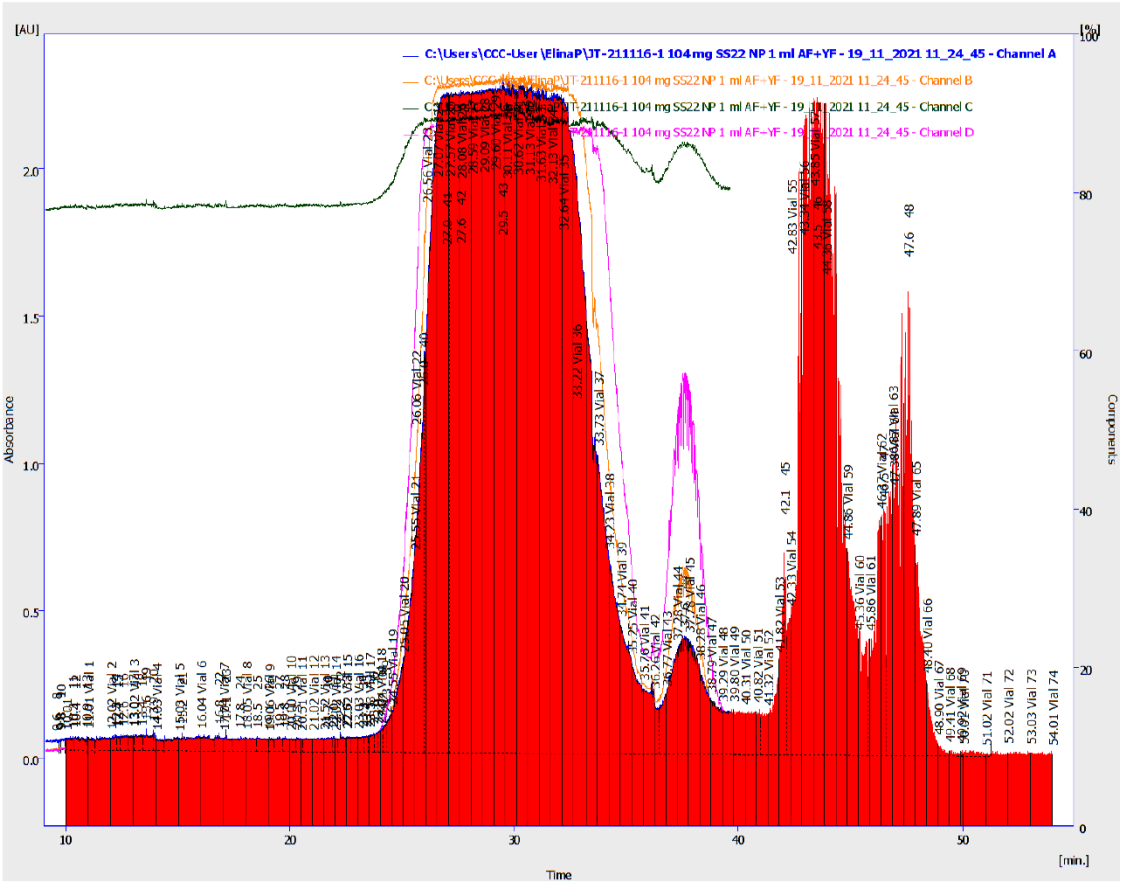

Figure S8. An example of HPCCC chromatogram of Key Compound **1**.

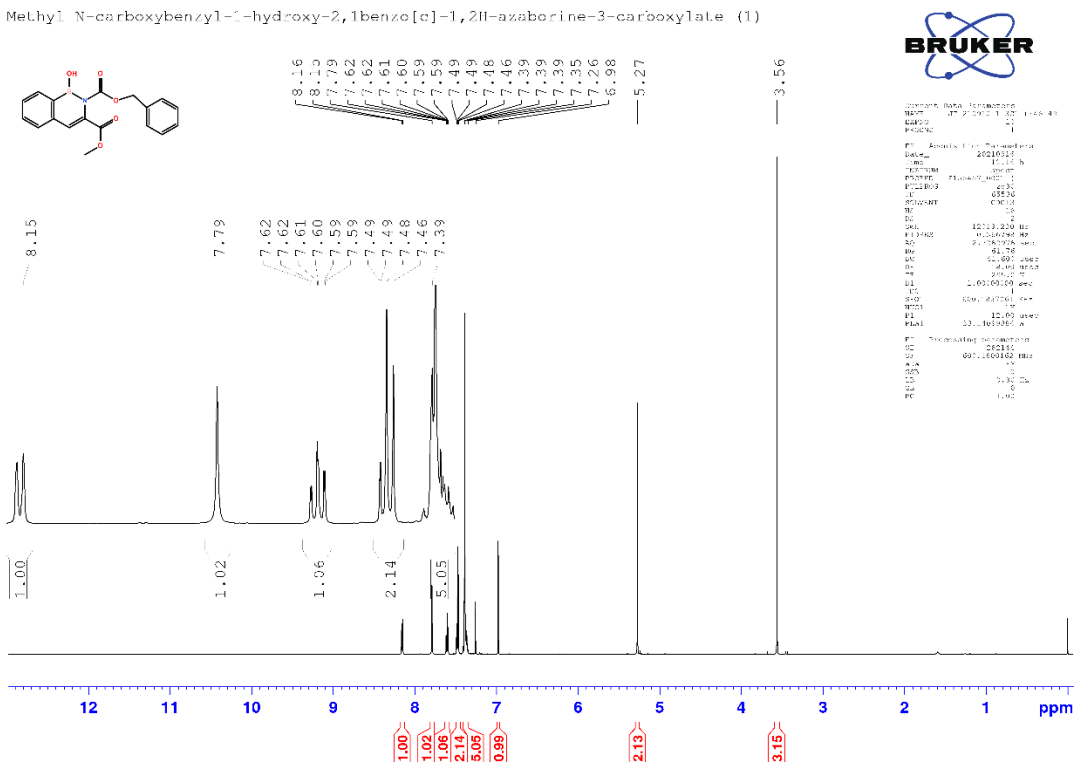

Figure S9 ^{1}H NMR of **1**

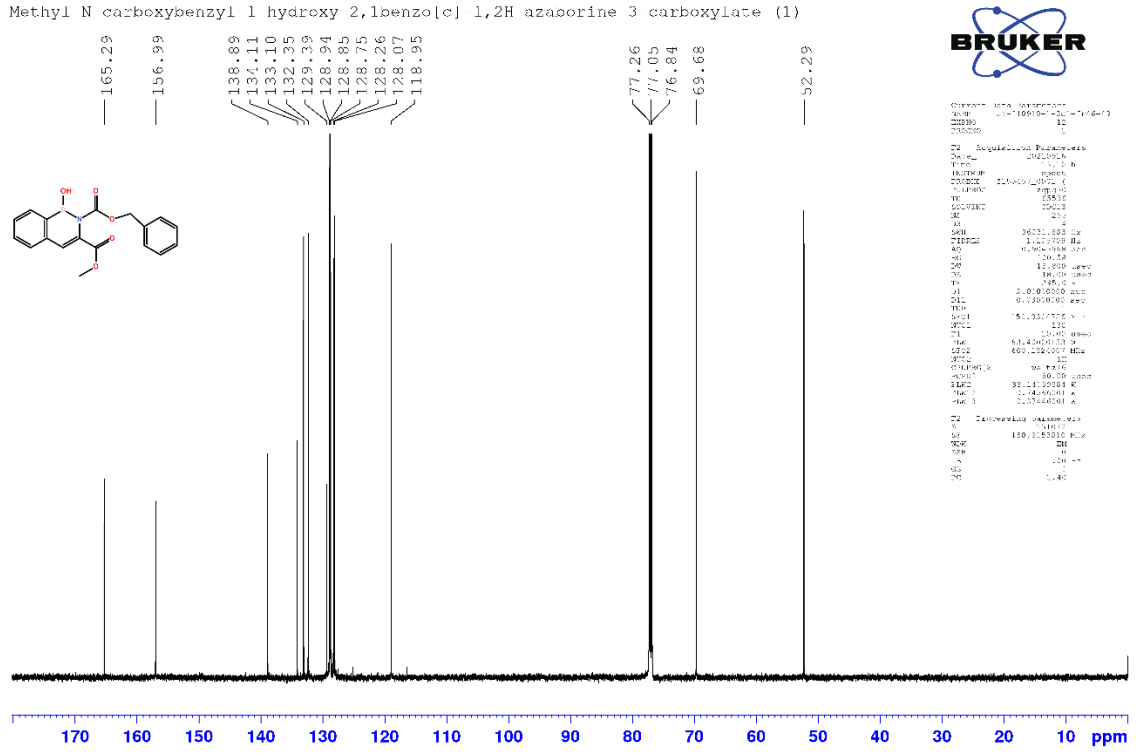

Figure S10 ^{13}C NMR of **1**

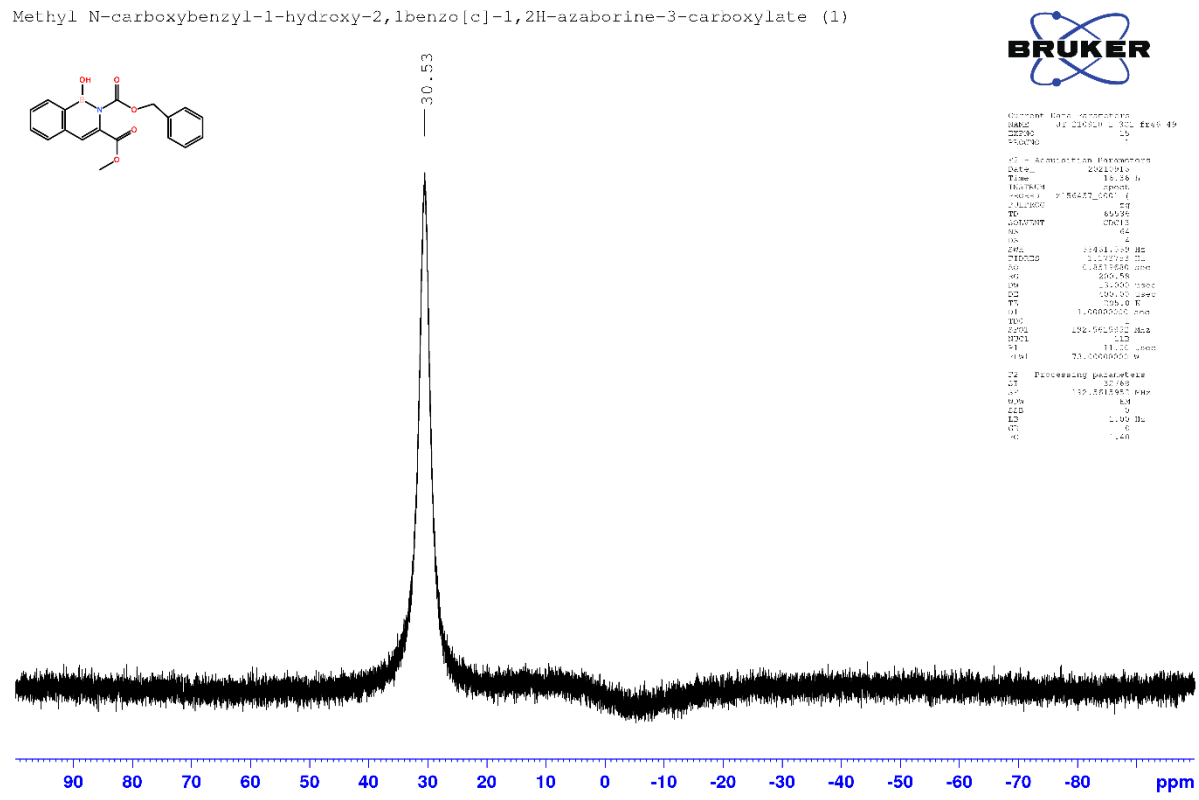

Figure S11 ^{11}B NMR of **1**

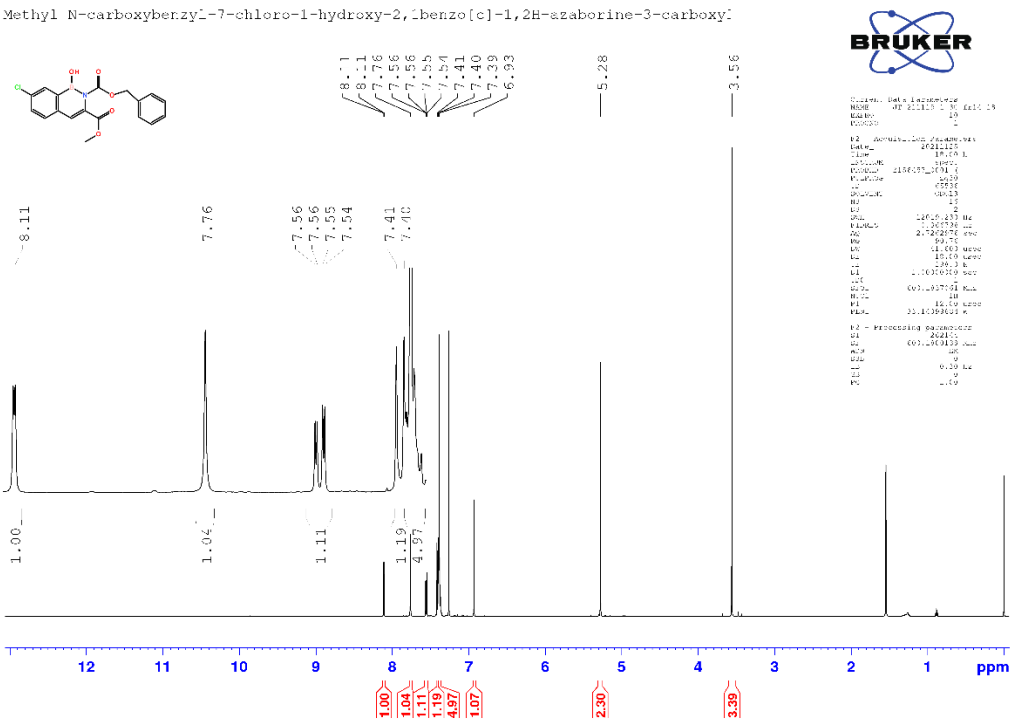

Figure S12 ^{1}H NMR of **4**

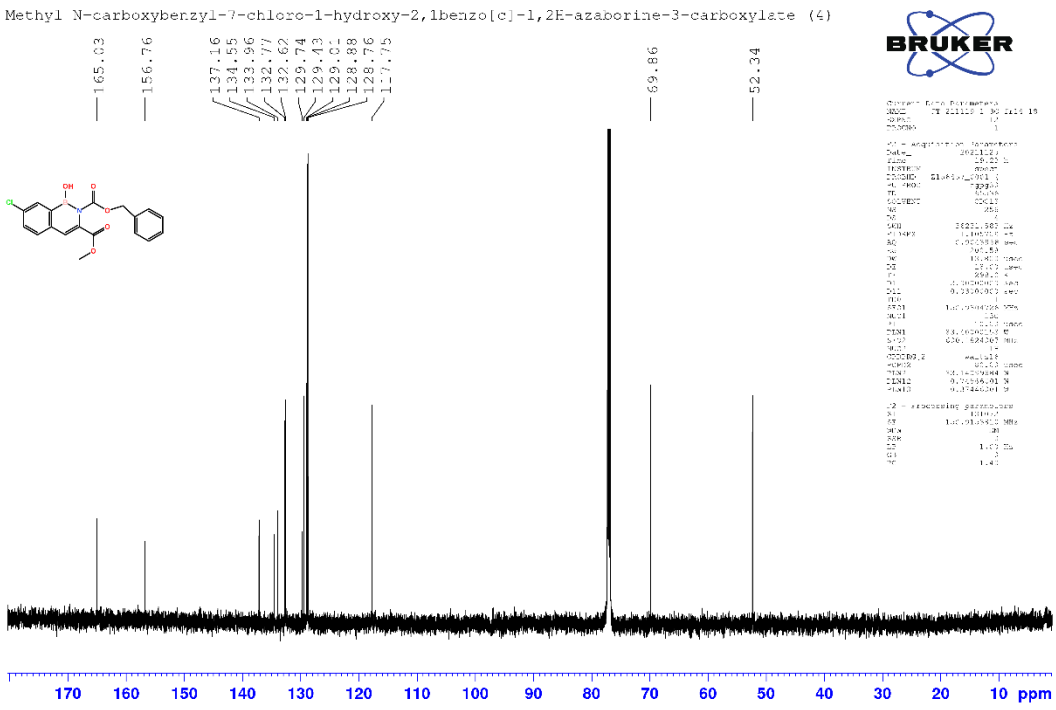

Figure S13 ^{13}C NMR of **4**

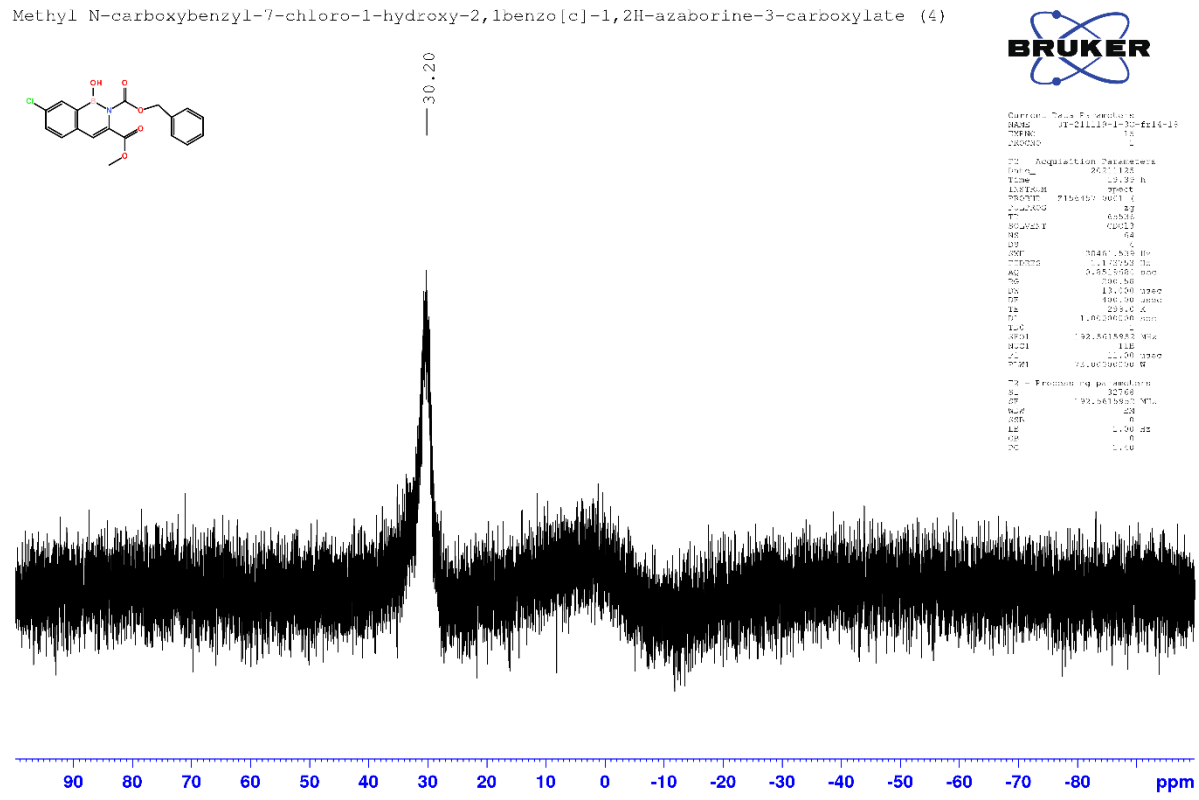

Figure S14 ^{11}B NMR of **4**

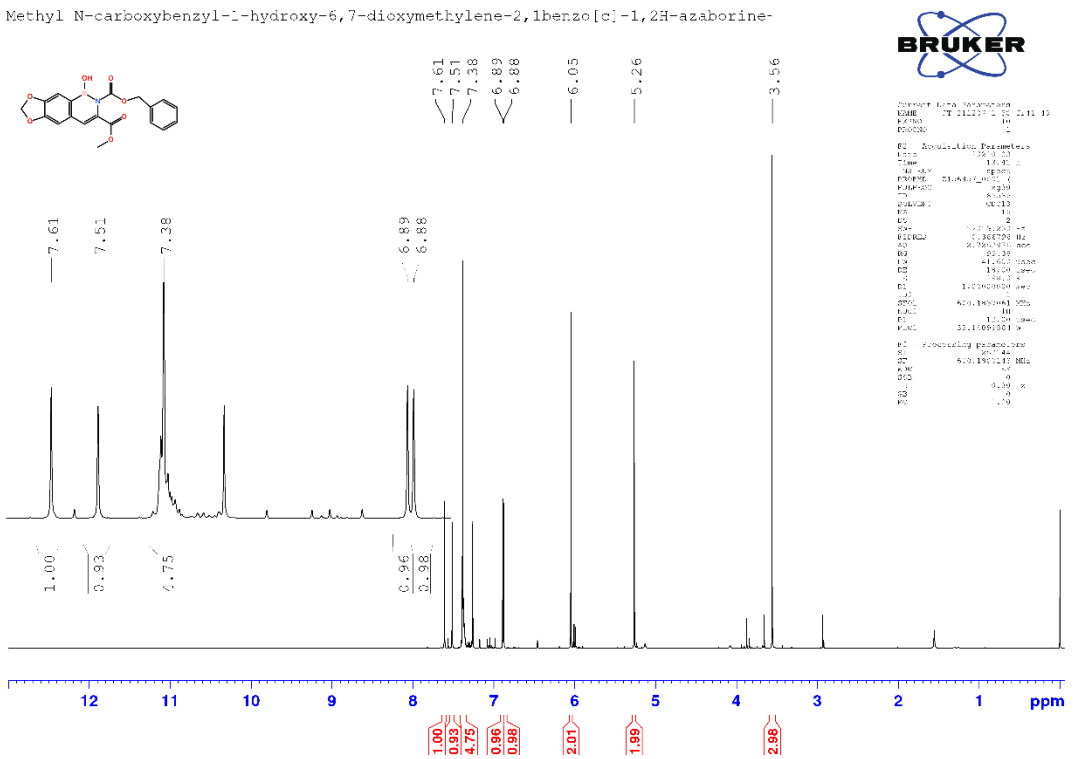

Figure S15 ^{1}H NMR of **5**

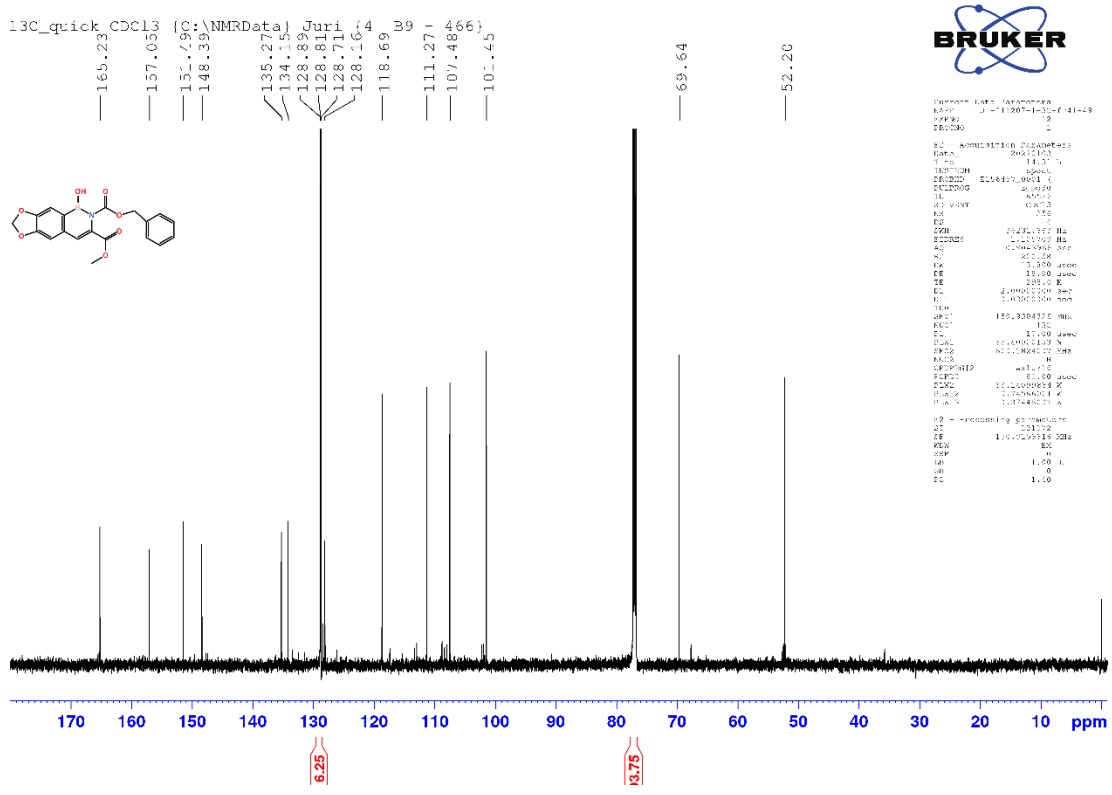

Figure S16 ^{13}C NMR of **5**

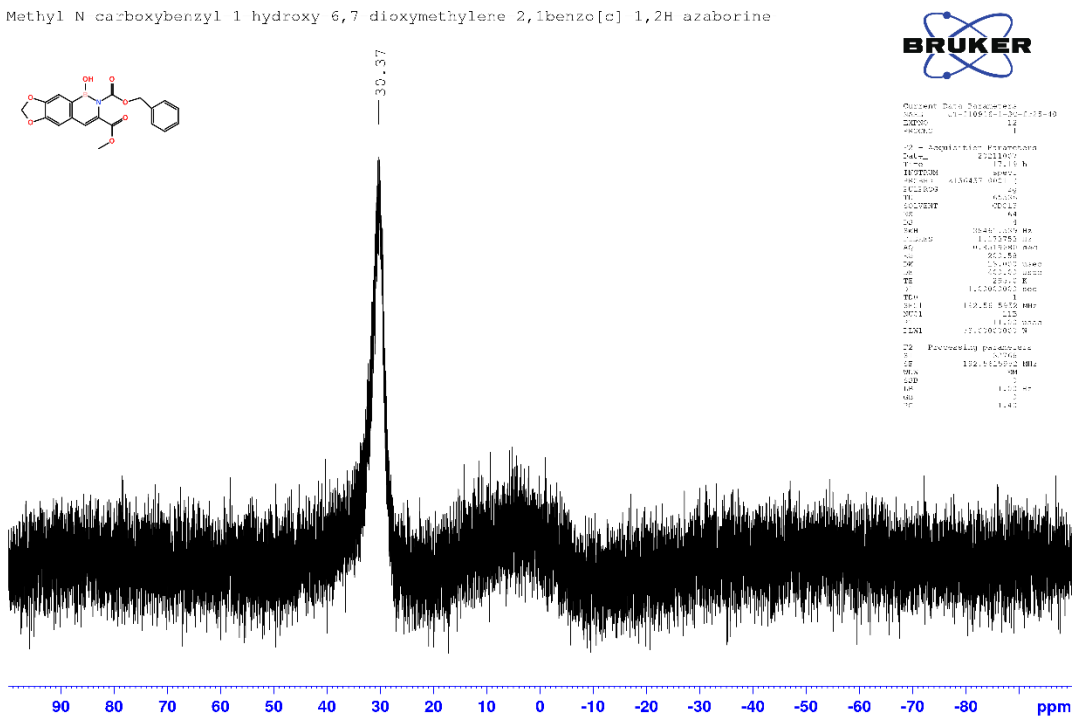

Figure S17 ^{11}B NMR of **5**

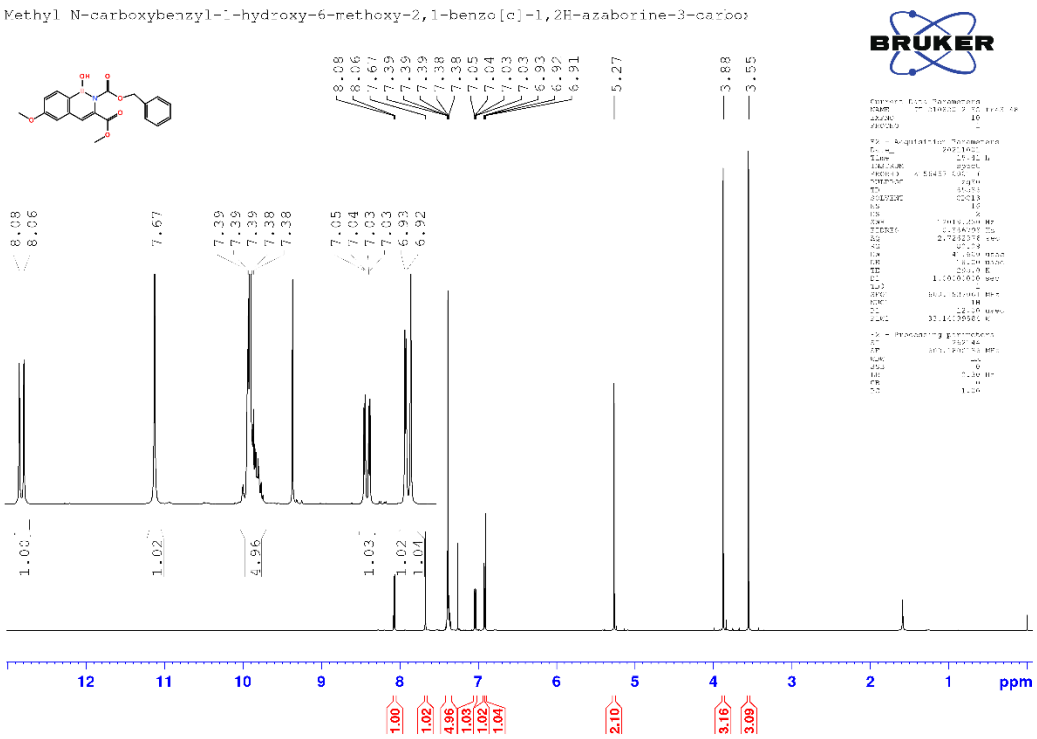

Figure S18 ^{1}H NMR of **7**

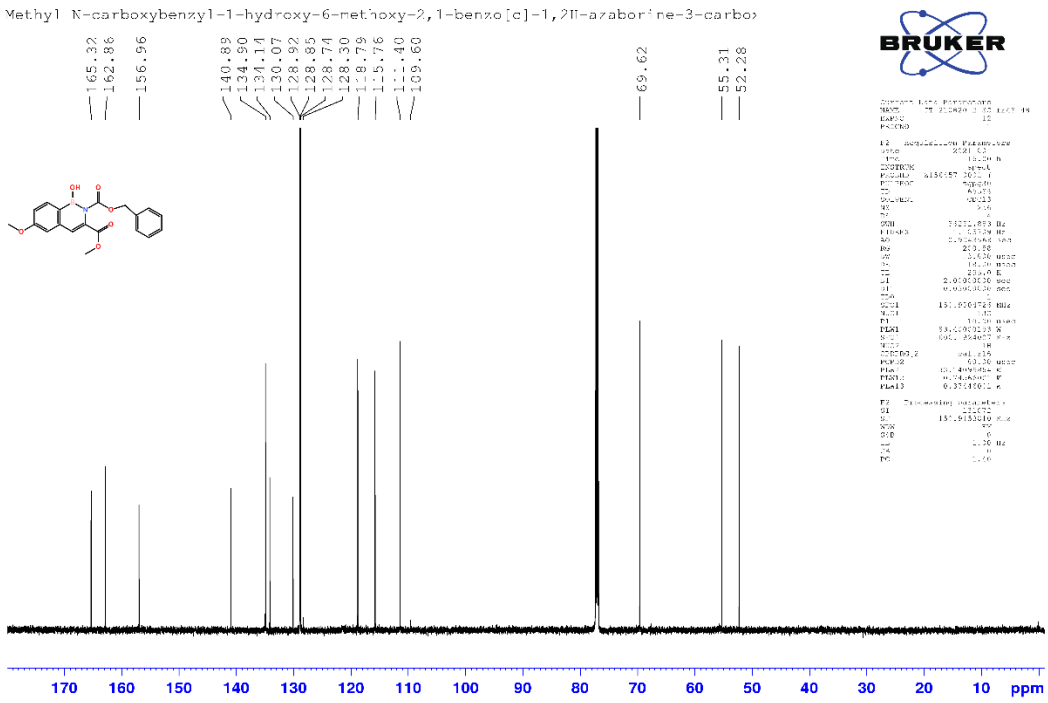

Figure S19 ^{13}C NMR of **7**

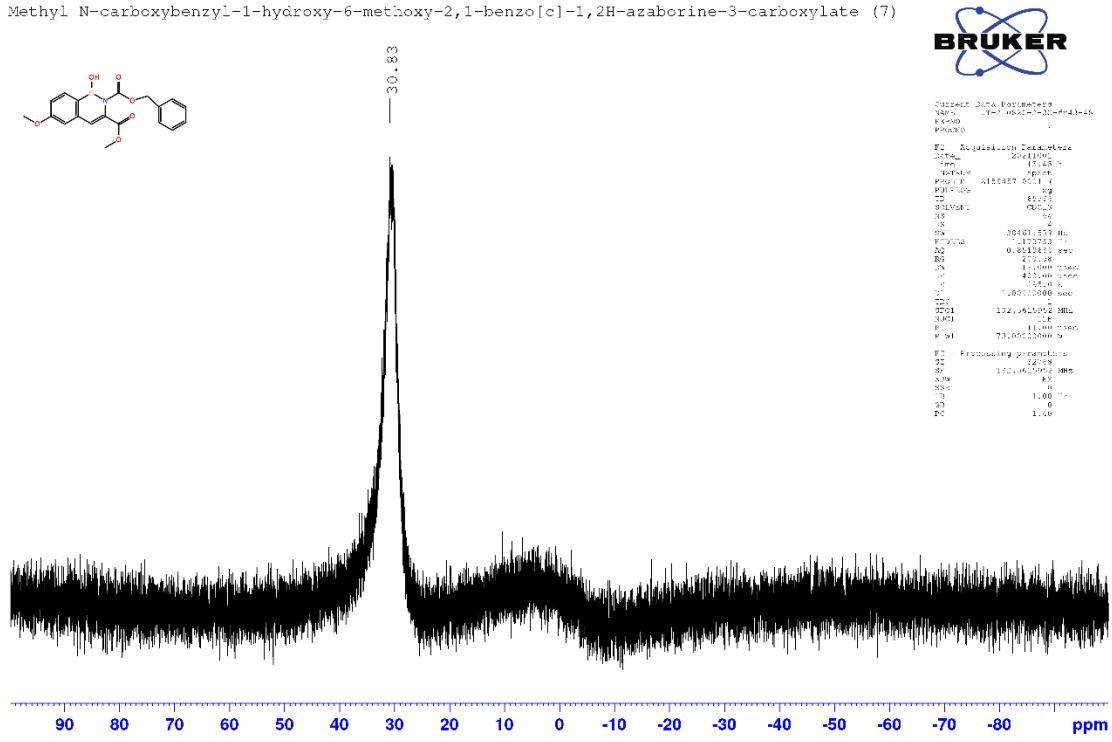

Figure S20 ^{11}B NMR of **7**