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Supporting Information

Synergic Effect of Copper-Based Metal–Organic Frameworks for Highly Efficient C-H Activation of Amidines

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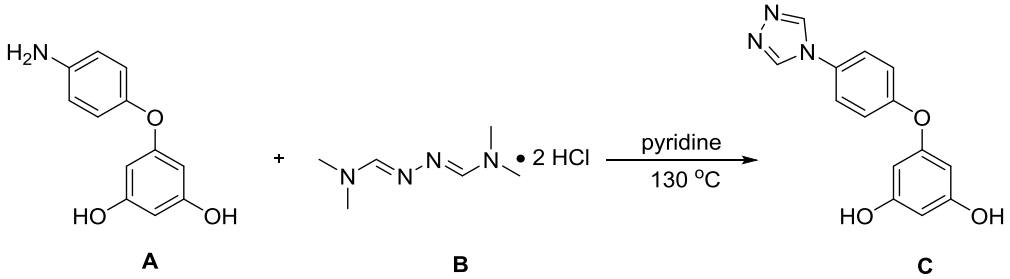
Contents

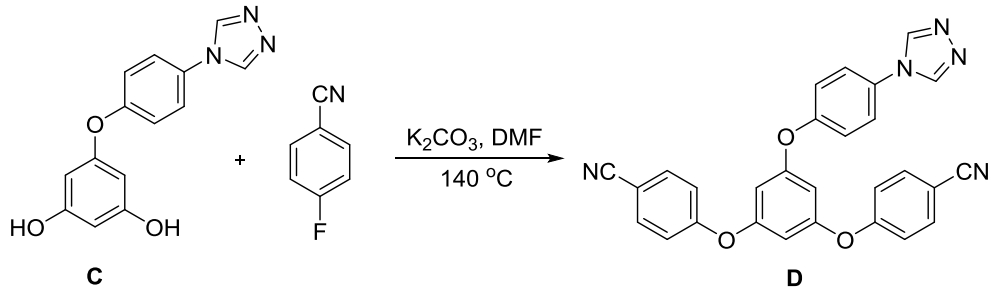
Section 1: General Materials and Methods

The TPPB ligand was prepared according to the literature method[S1-S2] and all other chemicals for the synthesis of **537-MOF** were obtained commercially. The DMSO and DMF were used without further purification and the amidine substrates were prepared according to the literature method.[S3] All reactions and manipulations were carried out under air atmosphere. The solvents were obtained commercially and used as received. Column chromatography was performed on silica gel (300–400 mesh). Elemental analysis (C, H and N) was performed on a Vario EL III Elementar analyzer. IR spectrum was measured on a Bruker Tensor 27 OPUS FT-IR spectrometer with KBr pellet in 4000–400 cm^{-1} region. Thermogravimetric analysis (TGA) curves were recorded on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 ℃ with a heating rate of 10 ℃ min^{-1} under nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku (model Ultima IV) diffractometer, equipped with a Rigaku D/teX ultrahigh-speed position sensitive detector and Cu-Kα X-ray (40 kV and 40mA). The intensity data were collected in the step-scan mode with the scan rate of 2 °/min and step size of 0.02 °. Inductively coupled plasma mass spectroscopy (ICP-MS) analysis was conducted using a Perkin-Elmer ELAN 9000 instrument after degradation of the sample in HNO_3. Gas adsorption isotherms were taken on a Belsorp-Max automatic volumetric sorption apparatus under ultrahigh vacuum in a clean system. Ultrahigh-purity-grade N_2, C_2H_2, and He gases (> 99.999%) were used in all measurements. The experimental temperatures were maintained by temperature-programmed water bath (at 273 and 298 K) and liquid nitrogen (at 77 K). ^1H, and ^{13}C were recorded on a 600 or 400 MHz Bruker NMR spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometer (HRMS) data were obtained with Micromass HPLC-Q-TOF mass spectrometer.

Section 2: Synthesis and Characterization for **TPPB**

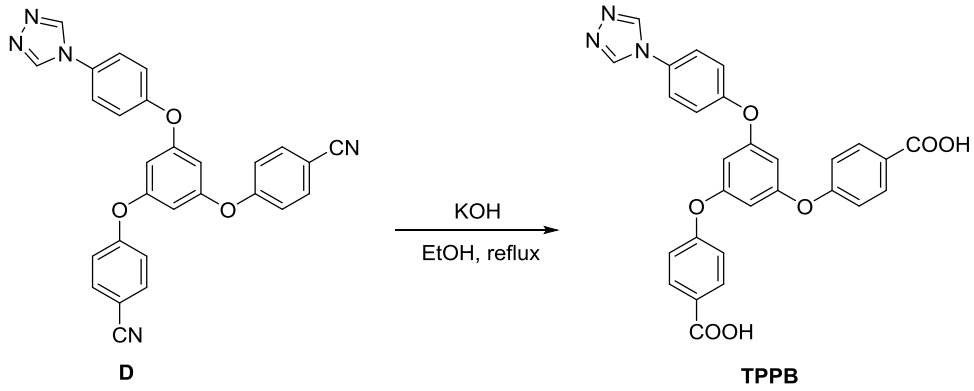


5-(4-aminophenoxy)benzene-1,3-diol **A** was prepared following published procedures or with appropriate modifications. **A** (21 g, 96.7 mmol) and (E)-N'-((E)-(dimethylamino) methylene)-N,N-dimethylformohydrazonamide **B** (63.0 g, 290.1 mmol) were dissolved in pyridine (60 mL). The mixture was heated at 130 ^{o}C with stirring for 18 h until the reaction was complete as determined by TLC. The excess pyridine was removed under reduced pressure, and then dumped into water (1000 mL). The mixture was stirred for 1 h and kept over night. Work-up was performed by filteration and subsequent washing with water. The target product **C** was achieved by recrystallization from EtOAc below 10 ^{o}C. **C** (21 g, yield: 81%).



The mixture of **C** (21 g, 78.0 mmol), 4-fluorobenzonitrile (19.8 g, 163.8 mmol) and K_2CO_3 (43.1 g, 312.0 mmol) in DMF (210 mL) was stirred for 12 h at 140 ^{o}C. After reaction completed, the mixture was diluted with water (6000 mL), and stirred for additional 1 h. The aqueous layer was extracted with ethyl acetate (200 mL × 3). The combined organic extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The residue

was obtained by concentration under reduced pressure and used without further purification. **D** (32.3 g, yield: 88%)



D **TPPB**

The mixture of **D** (32.3g, 68.5 mmol) and KOH (57.7g, 1.03 mol) in 1100 mL of EtOH was stirred at reflux for 24 h. After cooling to room temperature, the solvent was removed in vacuum and the residue was diluted with water (4000 mL). To this solution concentrated HCl was added at room until pH = 3. The mixture was filtered and washed with water until pH = 7. The crude product was dried to deliver **TPPB** 31.6 g (yield: 91%) as a solid. 1H NMR (300 MHz, DMSO) δ = 12.92 (s, 2H), 9.06 (s, 2H), 7.95 (d, J=8.7, 4H), 7.73 (d, J=8.9, 2H), 7.33 (d, J=8.9, 2H), 7.15 (d, J=8.7, 4H), 6.60 (s, 3H).

Section 3: Synthesis and Characterization for 537-MOF

A mixture of TPPB (0.028 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.042 mmol), N,N'-dimethylformamide (DMF) (1.0 mL) and methanol (0.5 mL) with 3 drops of acetic acid was added into a 20 mL Teflon-lined stainless steel vessel and then heated at 100 ^oC for 96 h in an oven. Green crystals were harvested and washed with fresh NMF (Yield: 40% based on TPPB). IR (KBr pellet, cm−1): 3438 (w, br), 3064 (w), 2927 (w), 1668 (s), 1592 (s), 1535 (m), 1504 (m), 1457 (m), 1401 (s), 1220 (vs), 1161 (m), 1120 (m), 1094 (m), 1007 (m), 839 (w), 785 (m), 710 (w), 656 (w), 527 (w) (Fig. S1).

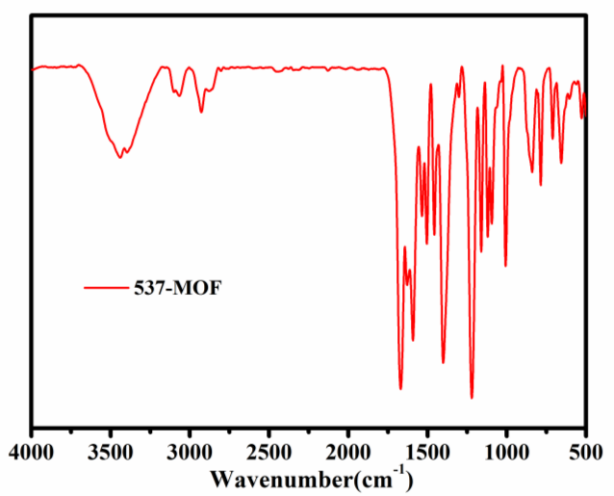


Fig. S1. IR spectra for **537-MOF**.

Section 4: Single-Crystal X-Ray Crystallography

Crystal data for **537-MOF** was collected on a SuperNova diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 294(2) K. Multi-scan absorption corrections were taken with the *CrysAlisPro* program.[S4] Empirical absorption corrections were performed with spherical harmonics implemented in *SCALE3 ABSPACK* scaling algorithm. The structures were solved by direct methods and all non-H atoms were refined anisotropically by the full-matrix least-squares method with the SHELXTL crystallographic software package.[S5-S6] All H atoms were located in calculated positions and treated in subsequent refinements as riding atoms. Attempts to locate and model the highly disordered solvent molecules in the void of **537-MOF** were unsuccessful. Thus, the SQUEEZE routine, a part of the PLATON software package [S7] was applied to calculate the disorder areas and remove the diffraction contribution to give a set of solvent free diffraction intensity. The chemical formula of **537-MOF** was determined based on crystal data combined with the results of elemental and thermogravimetric analysis. Crystallographic data and structural refinement details for **537-MOF** were summarized in Table S1. A comparison of the selected bond lengths and angles for **537-MOF** was listed in Table S2 and Table S3.

Table S1. Crystal data and structure refinement for 537-MOF.

Compound reference	537-MOF
Chemical formula	$C_{56}H_{34}Cu_2N_6O_{14}$
Formula weight	1142.98
Temperature (K)	293(2)
Crystal system	triclinic
Space group	*P*-1
a (Å)	12.1088(4)
b (Å)	16.9597(8)
c (Å)	19.1362(4)
Volume ($Å^3$)	3629.0(2)
Z	2
$\mu/(mm^{-1})$	1.173
Rint	0.0350
Goodness-of-fit on F^2	1.002
R_1 values [$I > 2\sigma(I)$]	0.0786
wR (F^2) values [$I > 2\sigma(I)$]	0.2250
R_1 values (all data)	0.0891
wR (F^2) values (all data)	0.2442
Completeness	99.94%
CCDC number	1547691

Table S2 Selected bond lengths (Å) for **537-MOF**.

537-MOF					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu1	Cu11	2.6796(9)	Cu2	O7	1.856(10)
Cu1	O132	1.991(3)	Cu2	N16	2.010(6)
Cu1	O143	1.977(3)	O13	Cu17	1.991(3)
Cu1	O1	1.946(3)	O14	Cu13	1.977(2)
Cu1	O21	1.978(3)	O2	Cu11	1.978(3)
Cu1	N54	2.168(3)	O9	Cu25	1.962(2)
Cu2	Cu25	2.7019(11)	N5	Cu14	2.168(3)
Cu2	O8	1.954(2)	O6	Cu25	2.010(5)
Cu2	O95	1.962(2)	N1	Cu26	2.010(6)
Cu2	O65	2.010(5)			

Symmetry transformations used to generate equivalent atoms. $^{1} -x, 2-y, -z$; $^{2} +x, 1+y, -1+z$; $^{3} -x, 1-y, 1-z$; $^{4} -x, 2-y, 1-z$; $^{5} 2-x, 1-y, 1-z$; $^{6} 2-x, 2-y, 1-z$; $^{7} +x, -1+y, 1+z$.

Table S3 Selected bond angles (°) for **537-MOF**.

537-MOF							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O131	Cu1	Cu12	84.49(9)	O65	Cu2	Cu25	89.09(17)
O131	Cu1	N53	96.16(11)	O7	Cu2	Cu25	76.6(2)
O144	Cu1	Cu12	82.67(8)	O7	Cu2	O8	88.81(18)
O144	Cu1	O131	167.16(12)	O7	Cu2	O95	87.51(18)
O144	Cu1	O22	89.53(13)	O7	Cu2	O65	165.7(3)
O144	Cu1	N53	96.61(12)	O7	Cu2	N16	85.0(5)
O1	Cu1	Cu12	83.41(9)	N16	Cu2	Cu25	161.6(5)
O1	Cu1	O131	89.44(13)	N16	Cu2	O65	109.3(5)
O1	Cu1	O144	89.31(14)	C54	O13	Cu17	122.3(3)
O1	Cu1	O22	167.11(12)	C27	O8	Cu2	123.1(2)
O1	Cu1	N53	101.42(12)	C54	O14	Cu14	124.6(2)
O22	Cu1	Cu12	83.71(9)	C1	O1	Cu1	123.7(3)
O22	Cu1	O131	88.85(13)	C1	O2	Cu12	122.7(2)
O22	Cu1	N53	91.47(12)	C27	O9	Cu25	123.9(2)
N53	Cu1	Cu12	175.13(8)	N4	N5	Cu13	127.3(2)
O8	Cu2	Cu25	83.98(8)	C47	N5	Cu13	124.5(2)
O8	Cu2	O95	166.85(12)	C26	O6	Cu25	105.0(6)
O8	Cu2	O65	89.90(15)	O6	C26	Cu25	50.5(5)

O8	Cu2	N16	95.1(2)	O7	C26	Cu25	94.0(6)
O95	Cu2	Cu25	82.89(8)	C23	C26	Cu25	156.7(5)
O95	Cu2	O65	90.56(16)	C26	O7	Cu2	124.8(6)
O95	Cu2	N16	97.1(2)	C56	N1	Cu26	153.5(14)

Symmetry transformations used to generate equivalent atoms. [1] $+x, 1+y, -1+z$; [2] $-x, 2-y, -z$; [3] $-x, 2-y, 1-z$; [4] $-x, 1-y, 1-z$; [5] $2-x, 1-y, 1-z$; [6] $2-x, 2-y, 1-z$; [7] $+x, -1+y, 1+z$.

Section 5: Gas Adsorption for **537-MOF** and Characterizations of the Reused Catalyst

The permanent porosity of **537-MOF** was elucidated by CO_2 adsorption at 195 K and 273K. The CH_2Cl_2-pretreated **537-MOF** was activated by heating in vacuum to afford the desolvated sample. Notably, **537-MOF** displays a type-I adsorption isotherm, as a typical microporous material. The CO_2 uptakes for **537-MOF** around 1 atm at 195 K and 273 K are 83.2 and 15.8 $cm^3 \cdot g^{-1}$, respectively. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas calculated from the CO_2 sorption isotherm at 195 K are 241.39 and 251.9 $m^2 \cdot g^{-1}$ (Fig. S2).

The thermogravimetry curves show that the as-synthesized samples lose the guest solvent molecules within the range 60–260 ^oC, above which pyrolysis of the host framework occurs (Fig. S3).

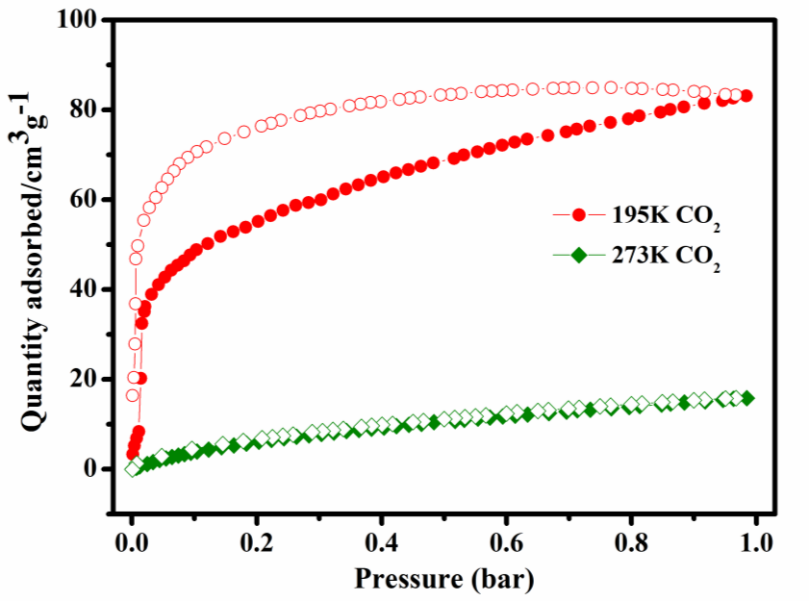


Fig. S2 The sorption isotherms of CO_2 for activated **537-MOF** at 195 K and 273 K.

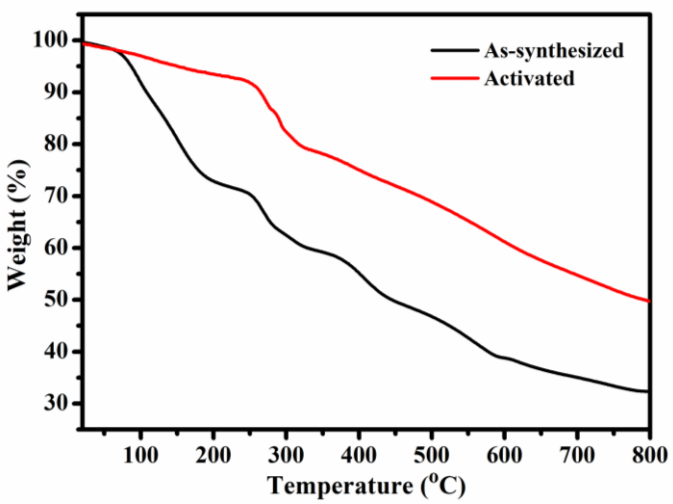


Fig. S3 TGA curves for as-synthesized **537-MOF** and activated **537-MOF**.

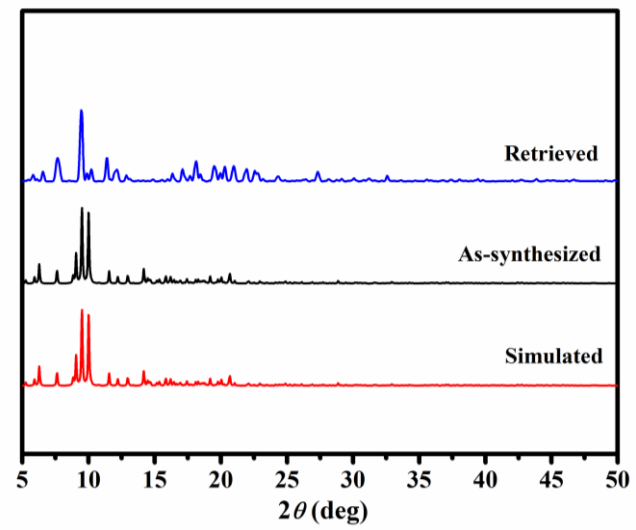


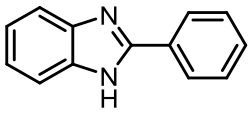
Fig. S4 PXRD patterns for 537-MOF catalyst after the reactions.

Section 6: General Procedure for C-H functionalization of amidines

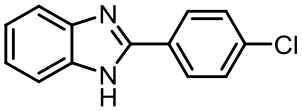
The activated **537-MOF** sample was carefully treated by grind and then used in catalytic reactions. A mixture of **537-MOF** (5 mg), Benzoic Acid (5 equiv) and DMSO/DMF (1:1, 2 mL) was stirred at room temperature for 5 min, to which amidine (0.25 mmol) was added. The mixture was stirred at 100°C under air atmosphere for 24. After cooling to room temperature, solvents were evaporated and the oily residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (polarity from 10:1 to 2:1).

Section 7 Characterization of Benzimidazoles

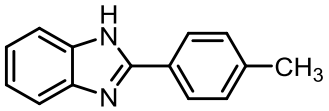
2-phenyl-1H-benzo[d]imidazole 2a. ^{1}H NMR (600 MHz, MeOD) δ = 8.15 – 8.06 (m, 2H), 7.61 (s, 2H), 7.56 – 7.47 (m, 3H), 7.30 – 7.21 (m, 2H). ^{13}C NMR (151 MHz, MeOD) δ 152.0, 130.0, 129.8, 129.6, 128.8, 126, 126.2, 122.5.



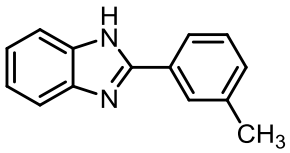
2-(4-chlorophenyl)-1H-benzo[d]imidazole 2b. ^{1}H NMR (600 MHz, MeOD) δ = 8.10 – 8.05 (m, 2H), 7.66 – 7.58 (m, 2H), 7.59 – 7.55 (m, 2H), 7.27 (dd, *J*=6.1, 3.1, 2H). ^{13}C NMR (151 MHz, MeOD) δ = 150.8, 135.9, 129.0, 129.0, 128.4, 127.90, 127.89, 122.7.



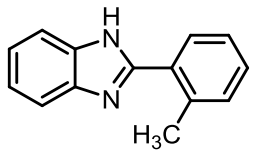
2-(p-tolyl)-1H-benzo[d]imidazole 2c. ^{1}H NMR (600 MHz, DMSO) δ = 12.85 (s, 1H), 8.07 (d, *J*=8.1, 2H), 7.67 – 7.62 (m, 1H), 7.51 (d, *J*=7.8, 1H), 7.36 (d, *J*=8.0, 2H), 7.20 (dd, *J*=17.6, 7.4, 2H), 2.38 (s, 3H).^{13}C NMR (151 MHz, DMSO) δ 151.8, 140.05, 130.0, 129.7, 129.1, 127.9, 126.8, 122.8, 122.1, 119.2, 111.7, 21.5.



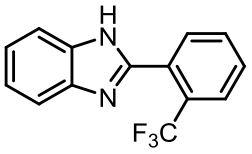
2-(m-tolyl)-1H-benzo[d]imidazole 2d. ^{1}H NMR (600 MHz, MeOD) δ 7.93 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.60 (dd, J = 5.9, 3.1 Hz, 2H), 7.43 (m, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.26 (dd, J = 6.0, 3.1 Hz, 2H), 5.49 (s, 1H), 2.46 (s, 3H).13C NMR (151 MHz, d-MeOH) δ 152.1, 138.8, 132.5, 130.9, 130.8, 129.4, 129.3, 128.7, 128.0, 127.0, 123.6, 122.6, 114.4, 20.2.



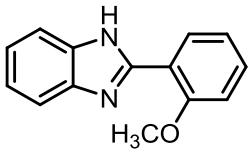
2-(o-tolyl)-1H-benzo[d]imidazole 2e. ^{1}H NMR (600 MHz, DMSO) δ 12.66 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.26 – 7.17 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 152.4, 144.1, 137.5, 134.8, 131.8, 130.5, 129.9, 129.8, 126.5, 122.9, 121.9, 119.4, 111.7, 21.5.



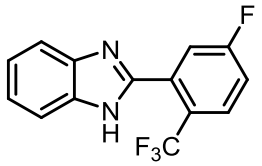
2-(2-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole 2f. ^{1}H NMR (600 MHz, CD_3OD) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.83 – 7.72 (m, 3H), 7.63 (s, 2H), 7.34 – 7.26 (m, 2H). ^{13}C NMR (151 MHz, CD_3OD) δ 149.8, 132.0, 131.9, 130.2, 129.7, 129.7, 129.3, 129.2, 129.0, 128.8, 128.0, 126.2 (q, *J* = 5.1 Hz) , 123.8 (d, *J* = 272.9 Hz), 122.7.



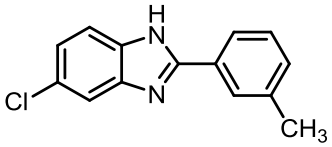
2-(2-methoxyphenyl)-1H-benzo[d]imidazole 2g. ^{1}H NMR (600 MHz, d-DMSO) δ 12.17 (s, 1H), 8.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.49 (ddd, *J* = 8.9, 7.4, 1.8 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.15 – 7.10 (m, 1H), 4.03 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 157.2, 149.4, 143.1, 135.1, 131.8, 130.2, 122.6, 122.0, 121.4, 118.9, 118.4, 112.6, 112.4, 56.2



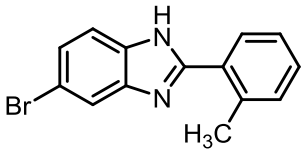
2-(5-fluoro-2-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole 2h. ^{1}H NMR (600 MHz, MeOD) δ = 7.76 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.29 (dd, J=6.0, 3.0, 2H), 7.17 (td, J=8.5, 2.8, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, MeOD) δ = 160.9 (d, J = 243.3 Hz), 151.28, 151.27, 133.08, 133.06, 132.6, 132.5, 131.6 (d, J = 7.8 Hz), 122.7, 122.1, 116.1 (J = 22.0 Hz).



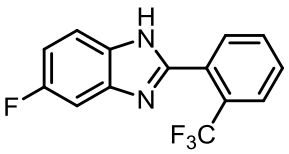
5-chloro-2-(m-tolyl)-1H-benzo[d]imidazole 2i. ^{1}H NMR (600 MHz, d-DMSO) δ 13.12 (d, J = 19.0 Hz, 1H), 8.00 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.75 – 7.64 (m, 1H), 7.60 – 7.50 (m, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.30 – 7.16 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 153.4, 138.8, 134.2, 131.4, 130.0, 129.5, 127.6, 124.2, 123.1, 122.5, 120.5, 118.6, 113.1, 111.5, 21.5.



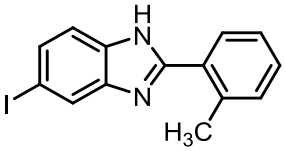
5-bromo-2-(o-tolyl)-1H-benzo[d]imidazole 2j. ^{1}H NMR (600 MHz, DMSO) δ = 12.92 (s, 1H), 8.05 – 7.94 (m, 1H), 7.79 (dd, *J*=11.3, 4.6, 1H), 7.54 (t, *J*=7.8, 1H), 7.48 – 7.36 (m, 4H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 167.9, 153.8, 137.6, 133.3, 131.8, 131.3, 130.1, 129.97, 129.96, 129.7, 129.0, 126.5, 125.1, 21.5.



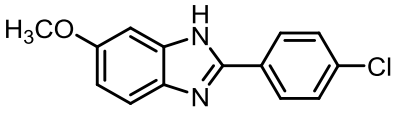
5-fluoro-2-(2-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole 2k. ^{1}H NMR (600 MHz, DMSO) δ 12.95 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.79 (dd, *J* = 16.8, 7.9 Hz, 2H), 7.76 – 7.30 (m, 2H), 7.12 (s, 1H). ^{13}C NMR (151 MHz, DMSO) δ159.2 (d, *J* = 206.3 Hz), 132.9, 132.6, 130.9, 130.3, 128.2 (q, *J* = 30.7 Hz), 127.1 (t, *J* = 5.2 Hz), 126.9, 125.1, 123.3, 121.5, 120.7, 111.4, 105.2.



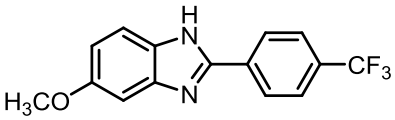
5-iodo-2-(o-tolyl)-1H-benzo[d]imidazole 2l. ^{1}H NMR (600 MHz, DMSO) δ 8.06 – 8.02 (m, 1H), 7.82 – 7.79 (m, 1H), 7.58 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49 (m, 4H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 167.81, 153.08, 137.61, 133.38, 131.82, 130.87, 130.19, 130.00, 129.78, 129.74, 129.14, 129.06, 126.53, 21.45.



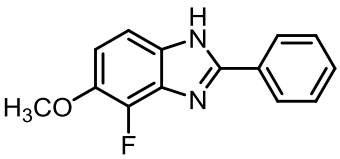
2-(4-chlorophenyl)-6-methoxy-1H-benzo[d]imidazole 2m. ^{1}H NMR (600 MHz, DMSO) δ 7.20 (s, 2H), 6.70 (d, *J* = 30.0 Hz, 3H), 6.27 (s, 1H), 6.10 (s, 1H), 4.13 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 158.0, 151.2, 146.2, 136.5, 129.9, 129.4, 128.5, 113.5, 109.8, 109.6, 101.4, 55.9.



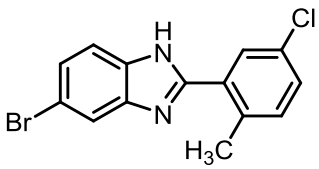
5-methoxy-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole 2n. 1H NMR (600 MHz, MeOD) δ 8.22 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.53 (s, 1H), 7.10 (s, 1H), 6.94 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, MeOD) δ 133.4, 131.3, 131.1, 130.9, 130.7, 129.2, 126.8, 126.6, 125.7 (q, *J* = 3.8 Hz), 125.0, 123.2, 121.4, 54.4.



4-fluoro-5-methoxy-2-phenyl-1H-benzo[d]imidazole 2o. ^{1}H NMR (600 MHz, DMSO) δ = 12.94 (s, 1H), 8.14 (d, *J*=7.4, 2H), 7.74 – 7.27 (m, 5H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 151.7, 149.8 (dd, *J* = 239.5, 56.7 Hz), 145.2, 140.4, 137.0, 130.6, 130.1, 129.4, 126.6, 105.7, 103.2, 99.0, 95



5-bromo-2-(5-chloro-2-methylphenyl)-1H-benzo[d]imidazole 2p. ^{1}H NMR (600 MHz, MeOD) δ 8.05 – 7.98 (m, 1H), 7.77 (d, J = 1.1 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.45 (dd, J = 18.0, 4.4 Hz, 1H), 7.40 (dd, J = 8.5, 1.7 Hz, 1H), 7.36 (dd, J = 8.2, 1.6 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, MeOD) δ 168.5, 152.6, 139.5, 135.7, 132.6, 131.0, 130.7, 129.3, 128.3, 128.1, 126.0, 125.7, 115.3, 26.6.

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8.10
8.09
8.09
8.08
8.08
8.08
7.61
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7.54
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7.52
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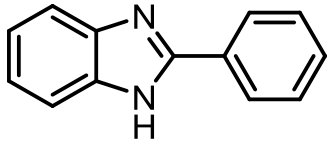
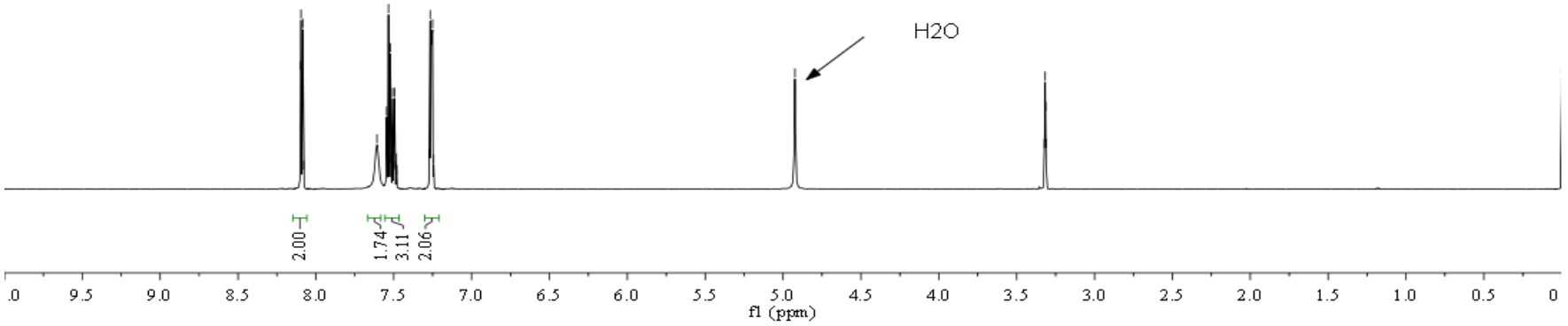
3.32
3.31
3.31


N
N
H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9.0
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6.5
6.0
5.5
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4.0
3.5
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1.5
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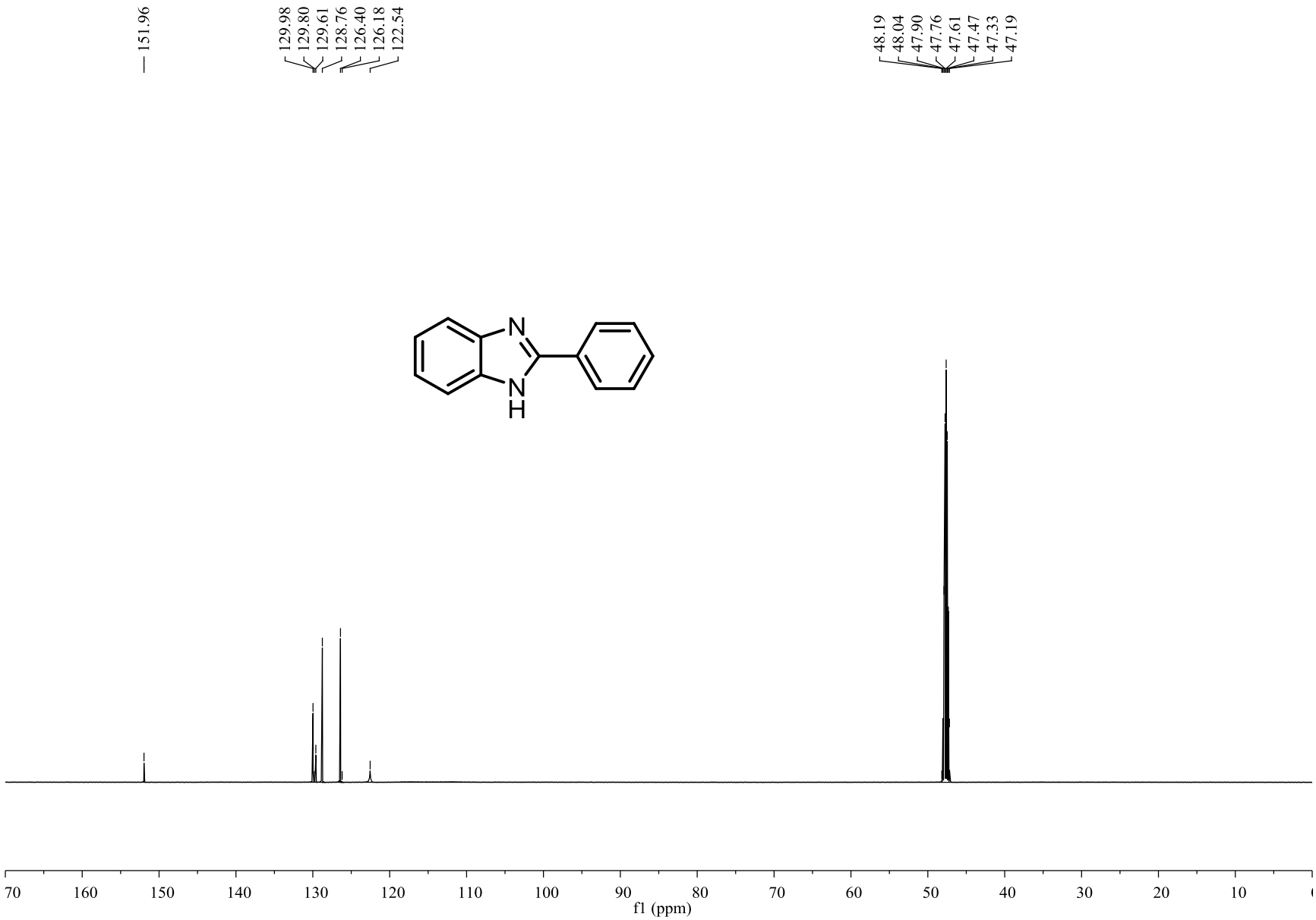
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47.61
47.47
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47.19
N
N
H
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60
50
40
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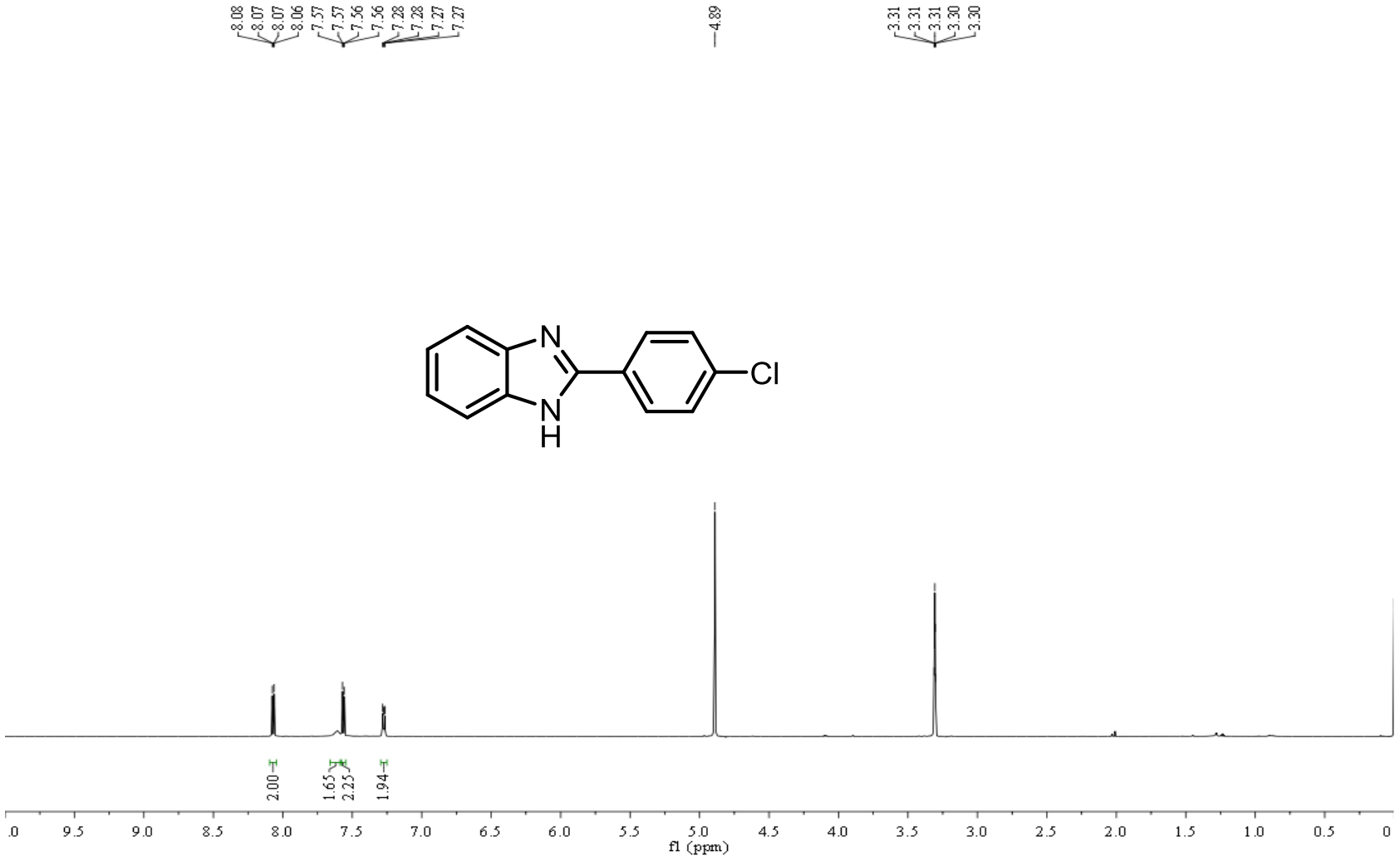
10
f1 (ppm)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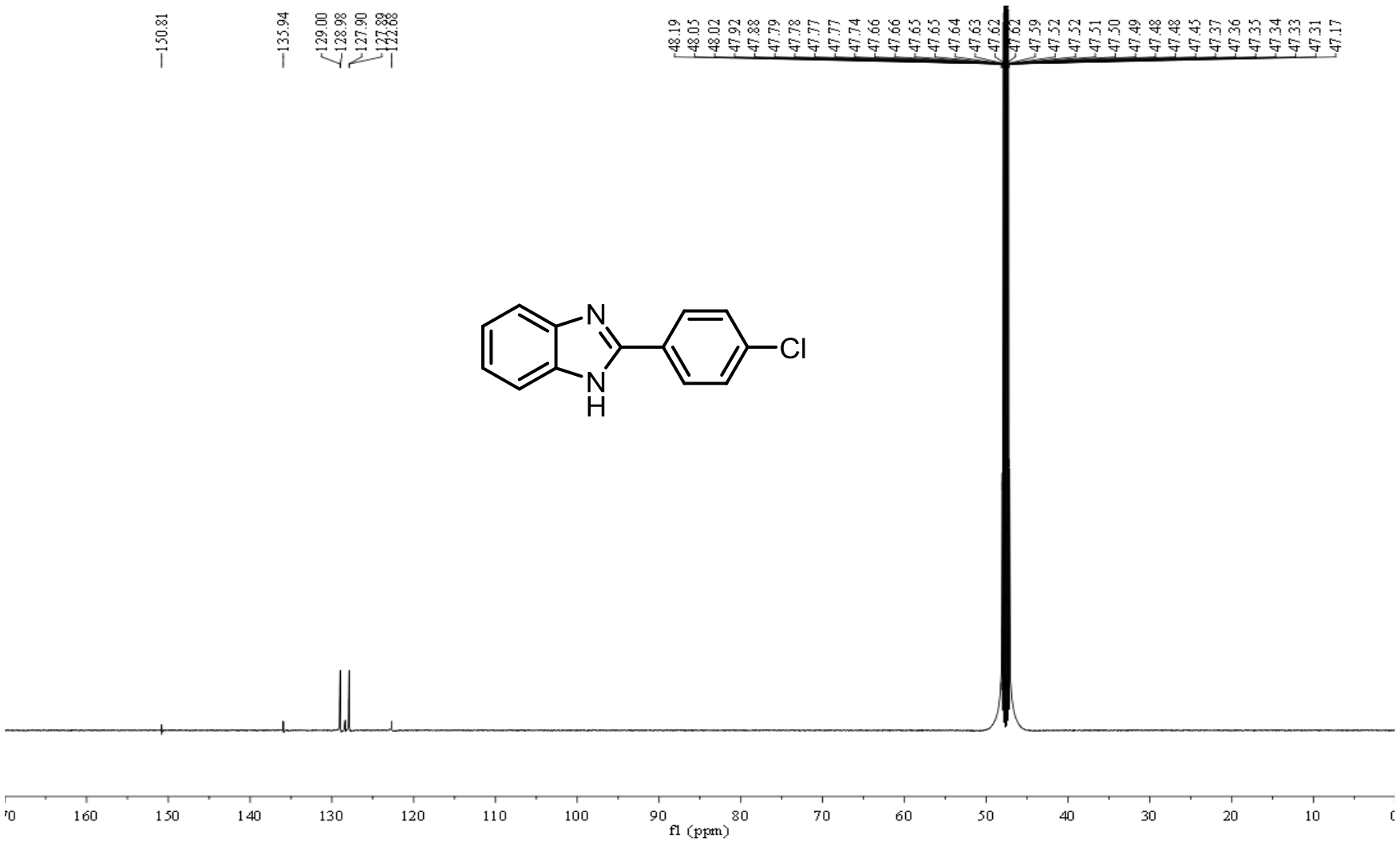
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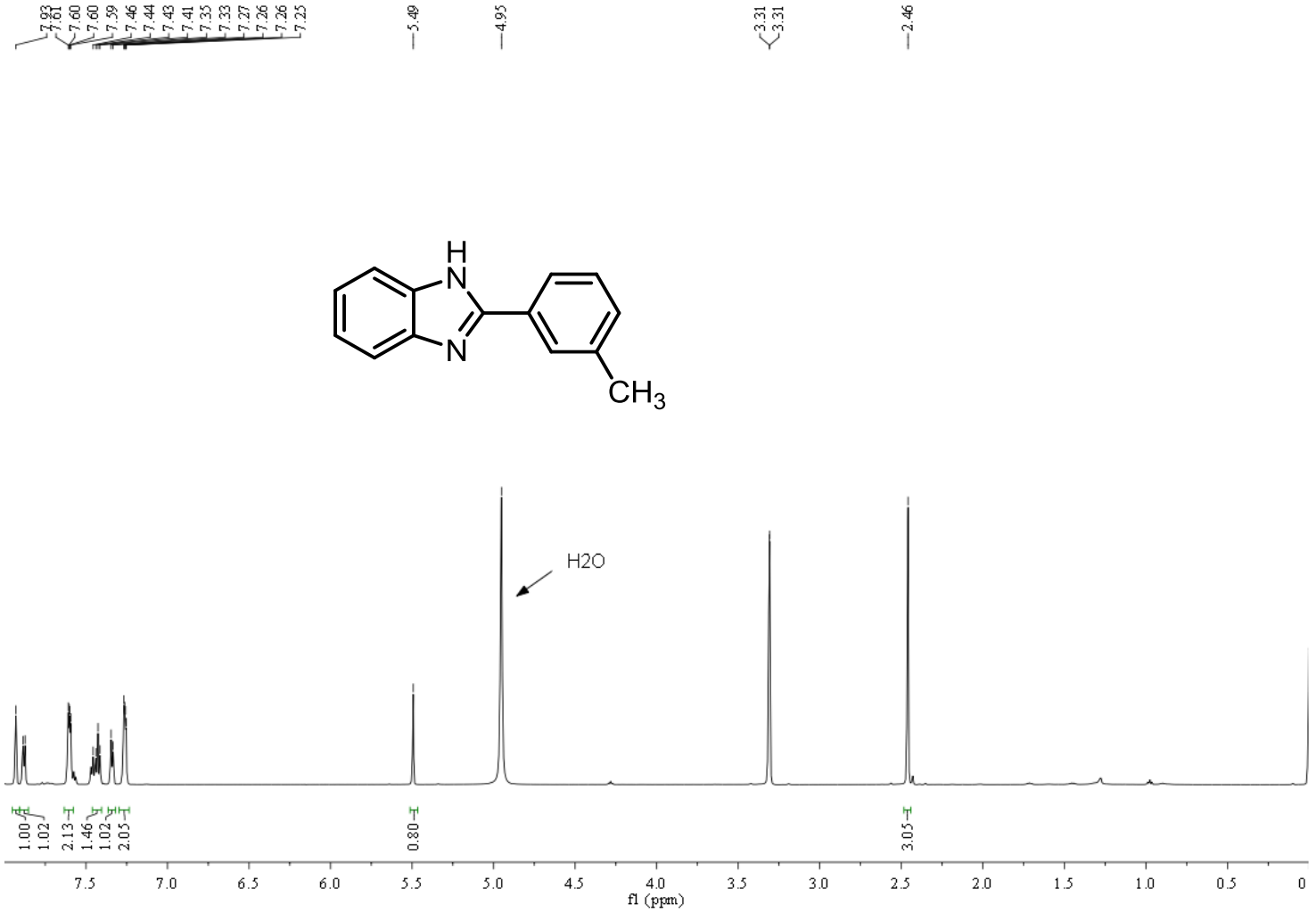
f1 (ppm)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3.31
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1.02
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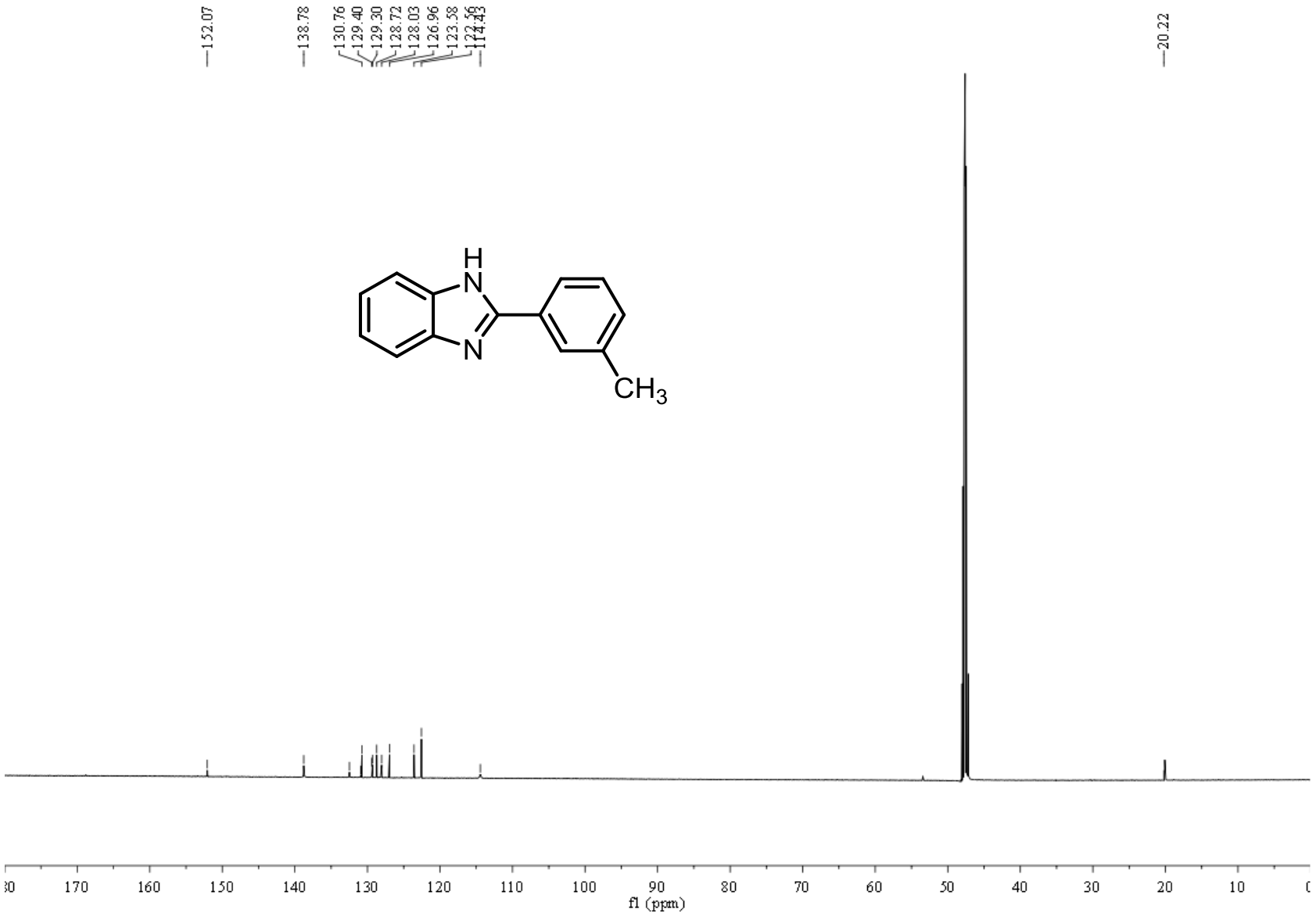
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CH3
170
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


12.85
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8.06
7.96
7.96
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7.64
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7.62
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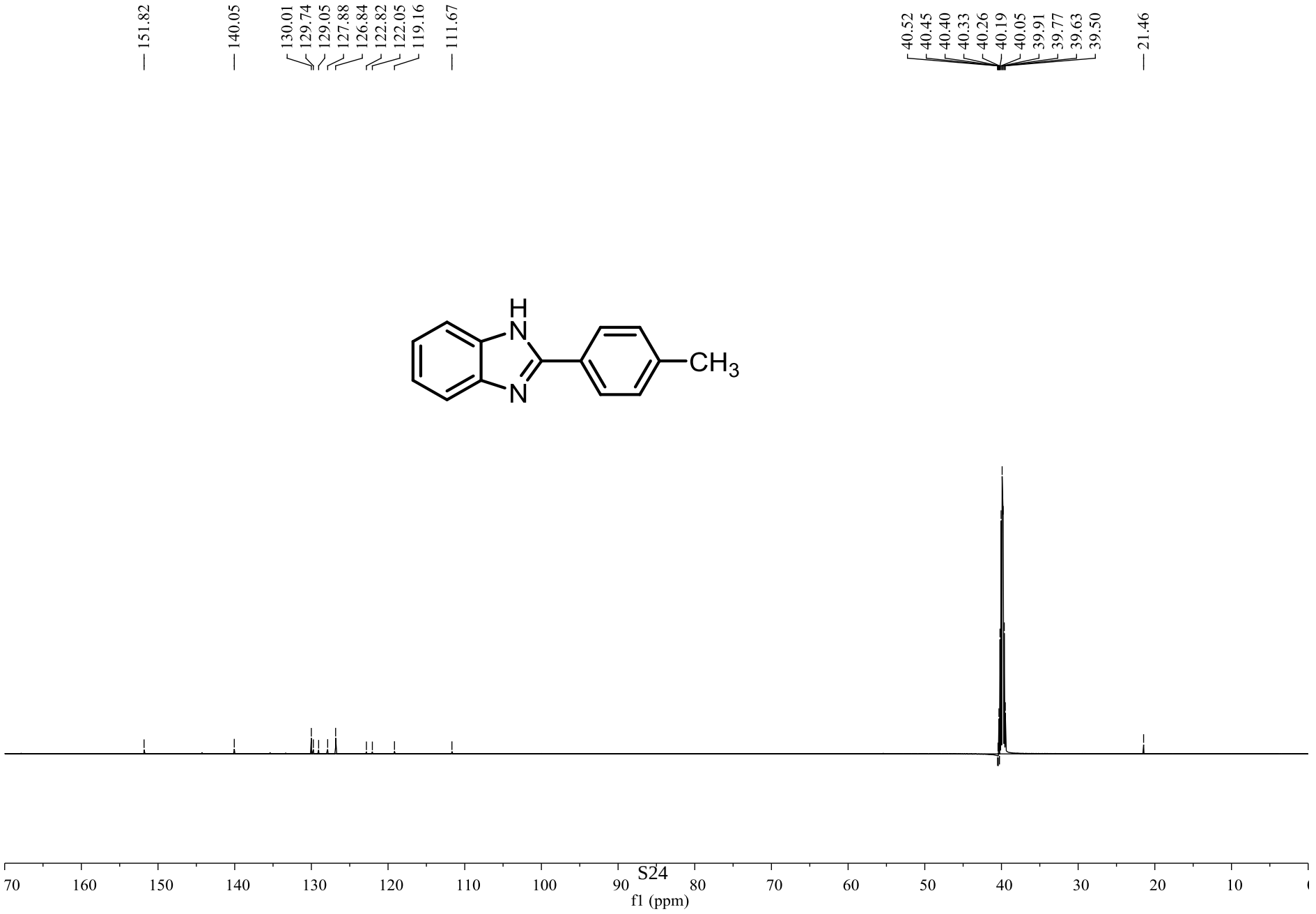
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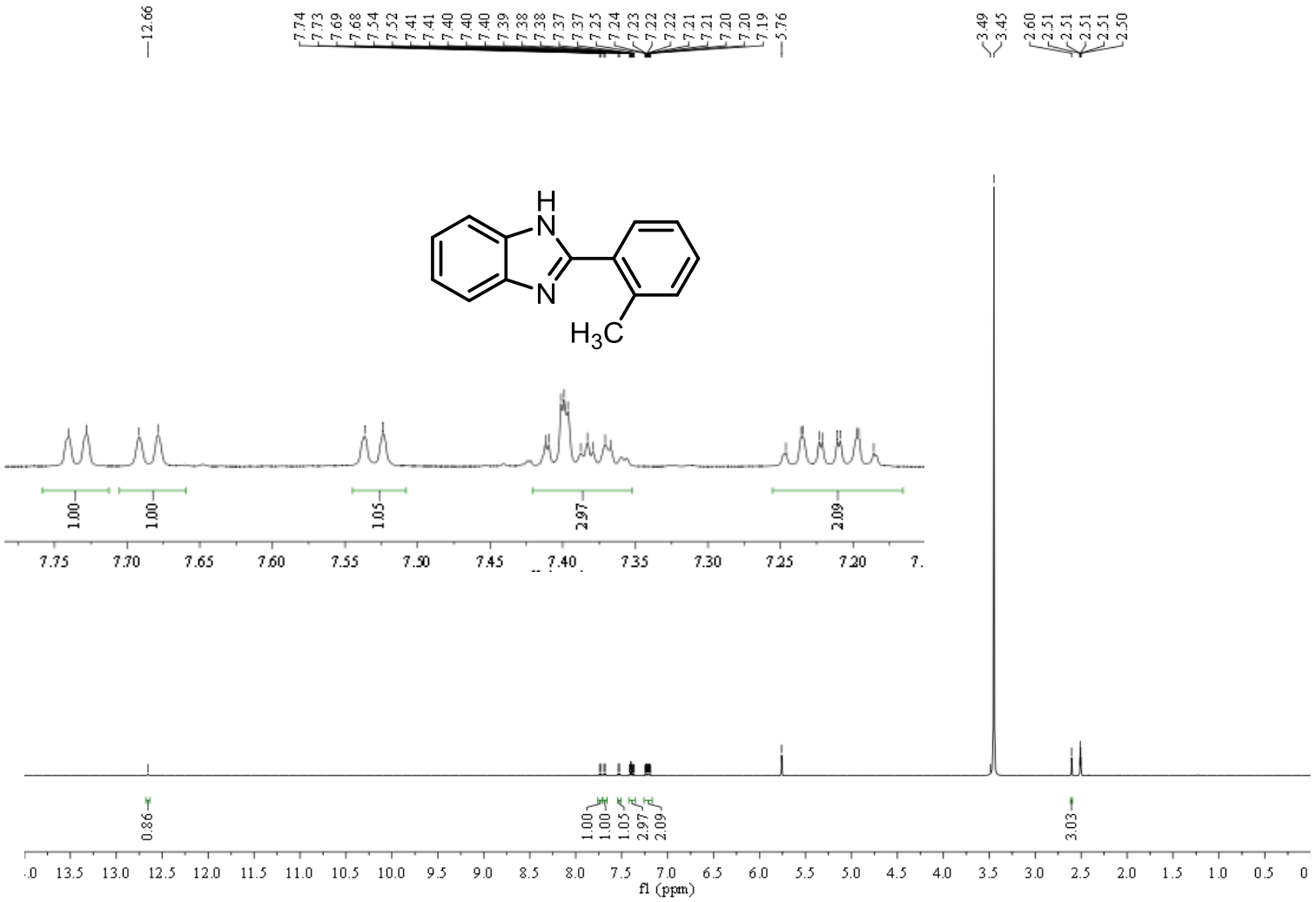
f1 (ppm)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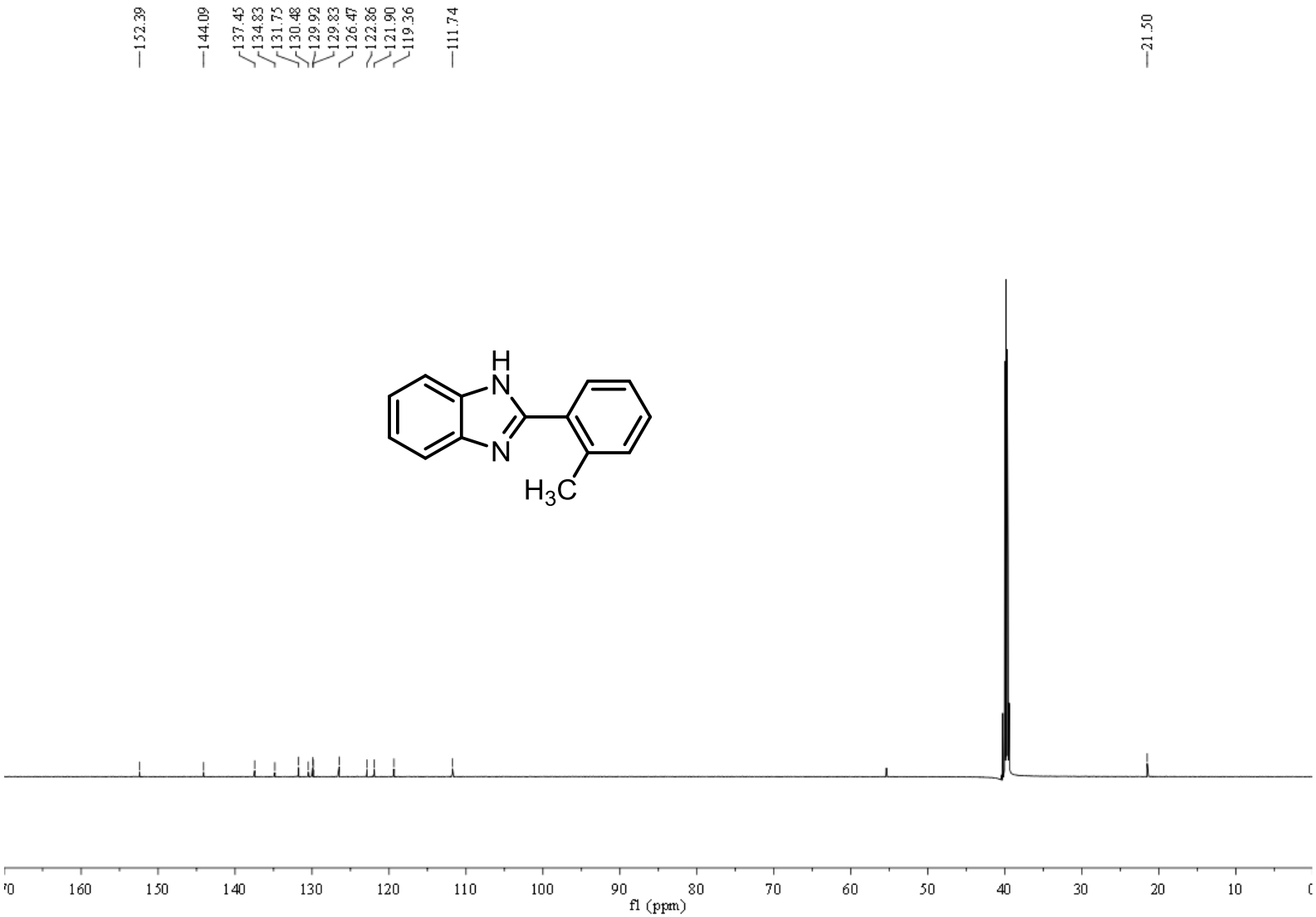
3.03
f1 (ppm)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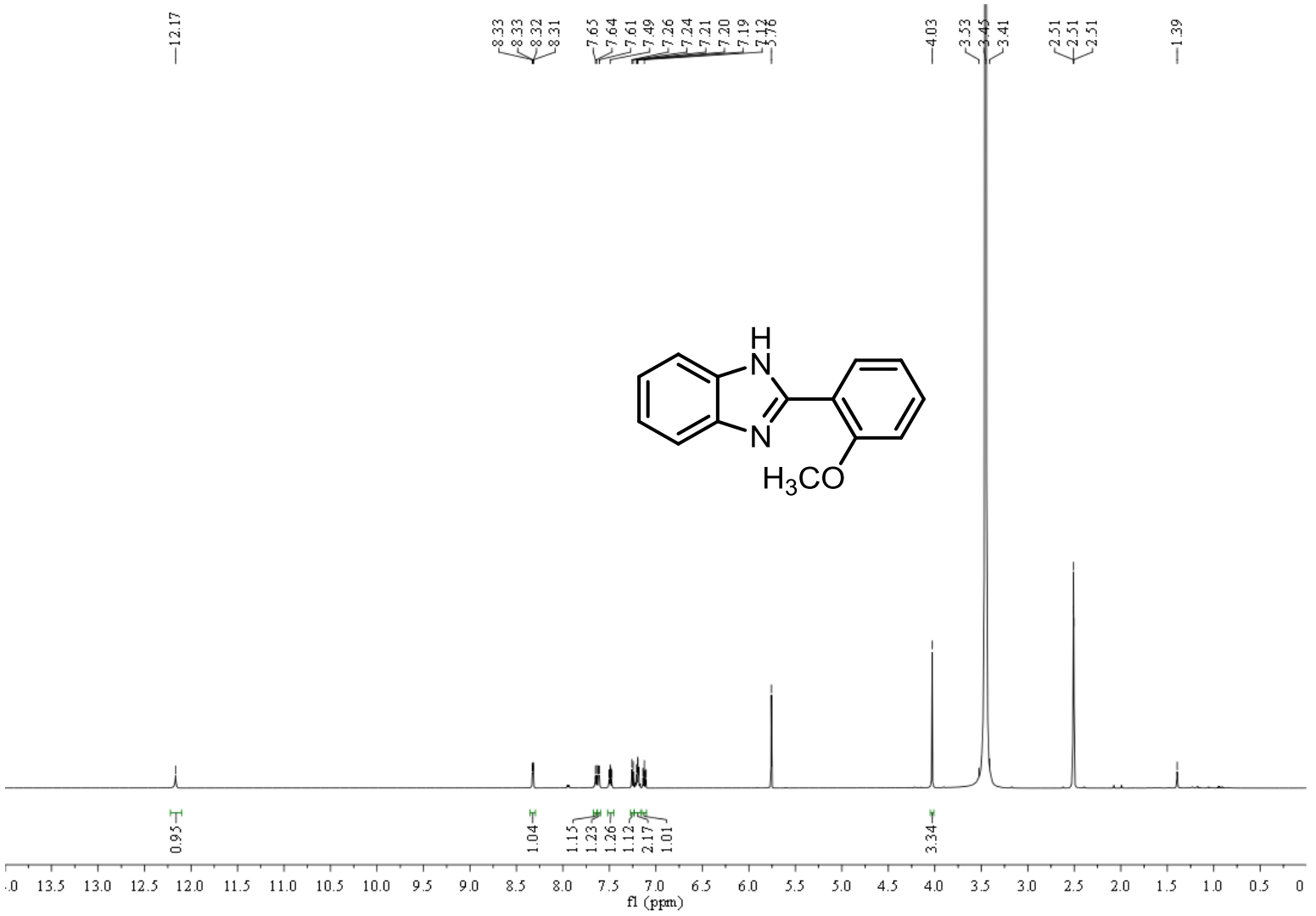
f1 (ppm)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3.45
3.41
2.51
2.51
2.51
1.39
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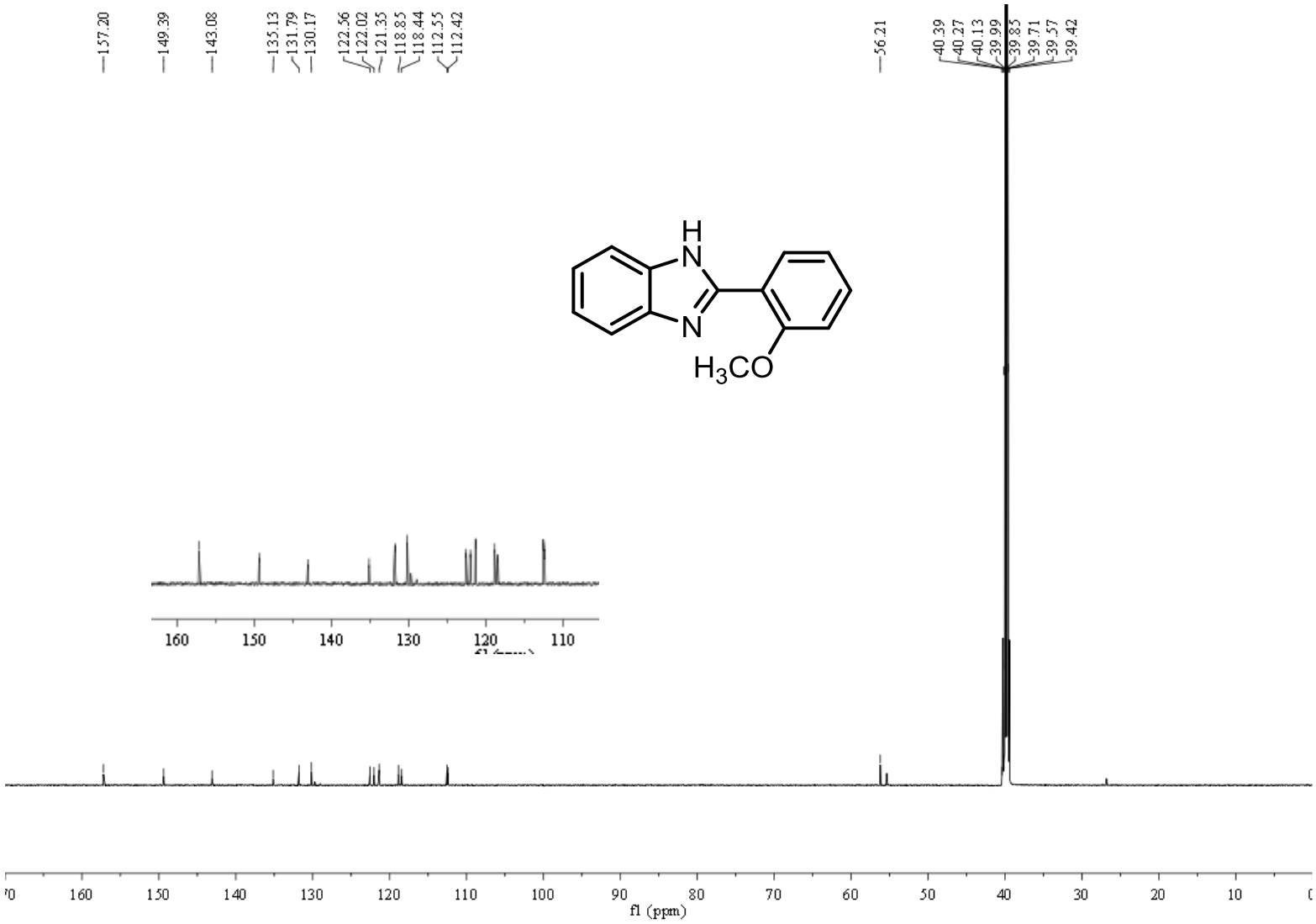
f1 (ppm)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40.13
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fl (ppm)

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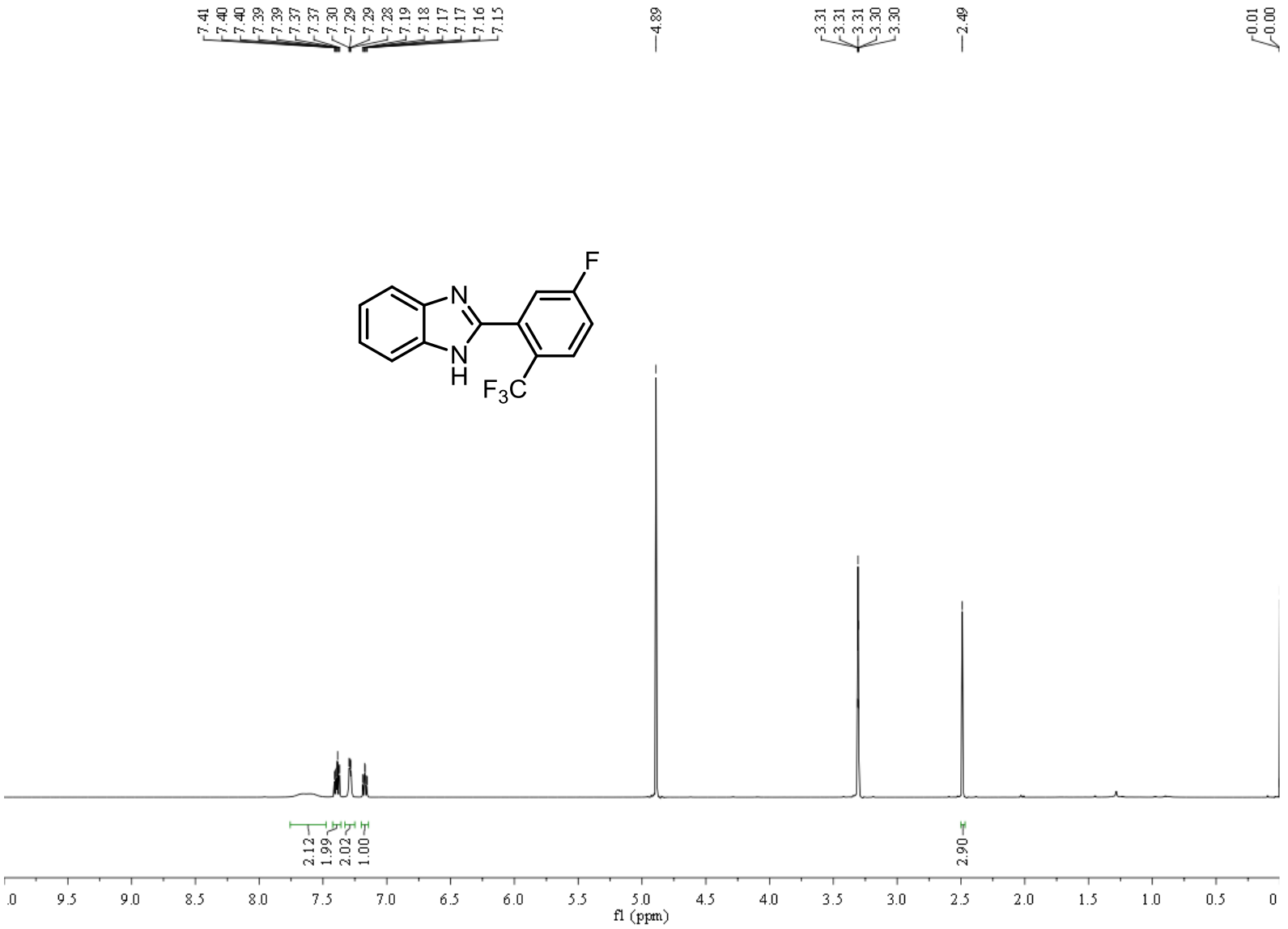
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3.31
3.30
3.30
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N
H
F3C
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2.02
1.00
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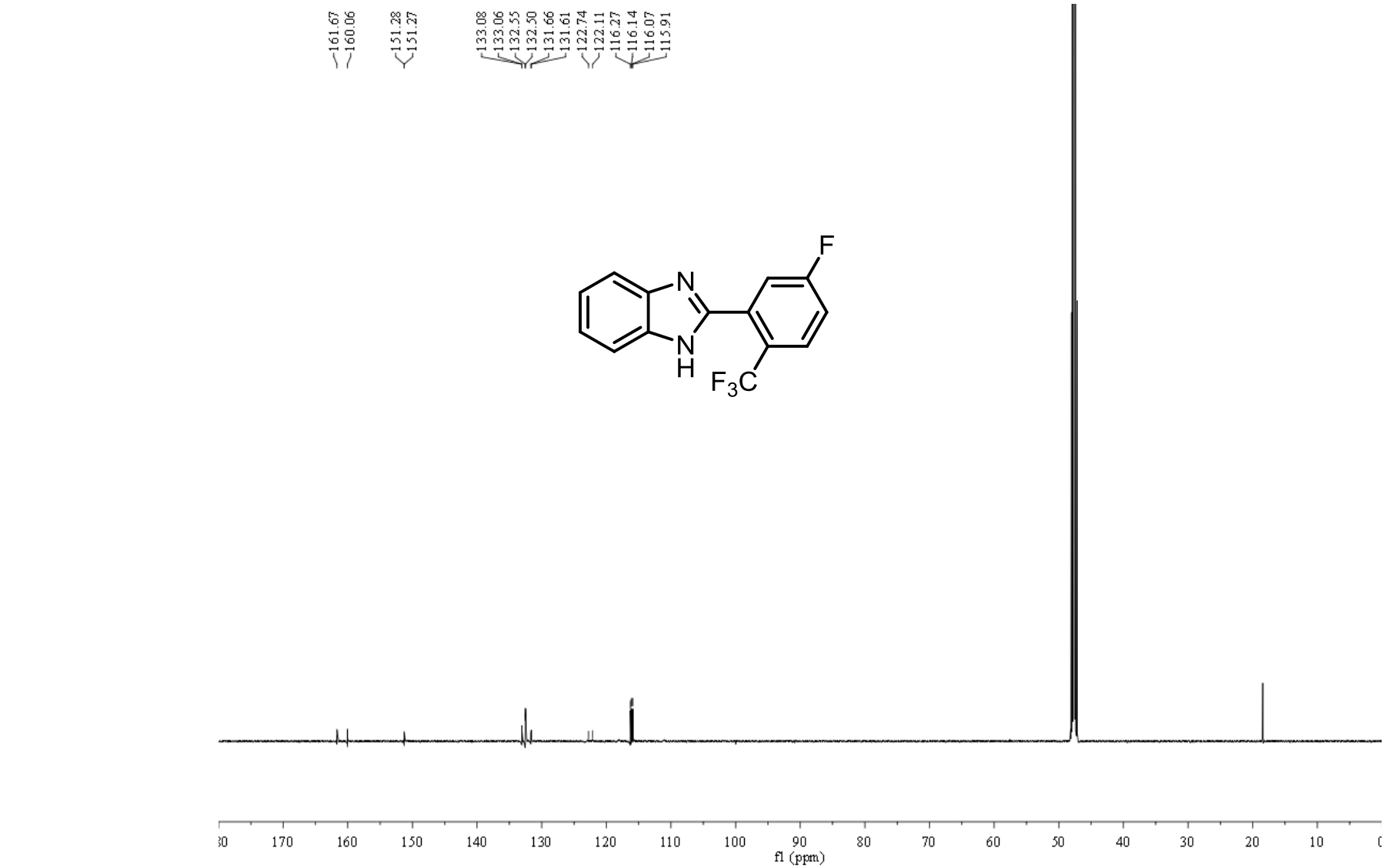
fl (ppm)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F
N
N
H
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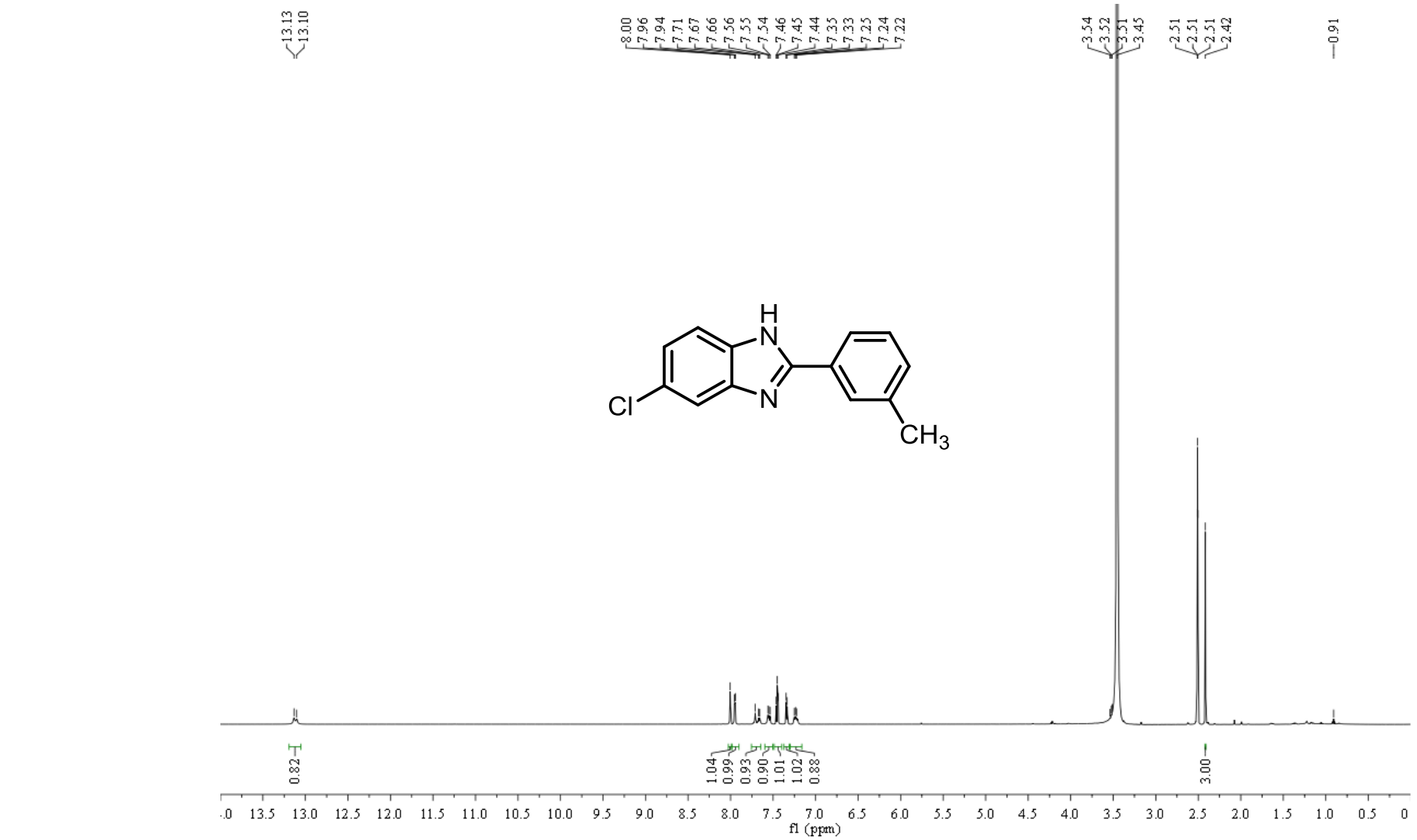
f1 (ppm)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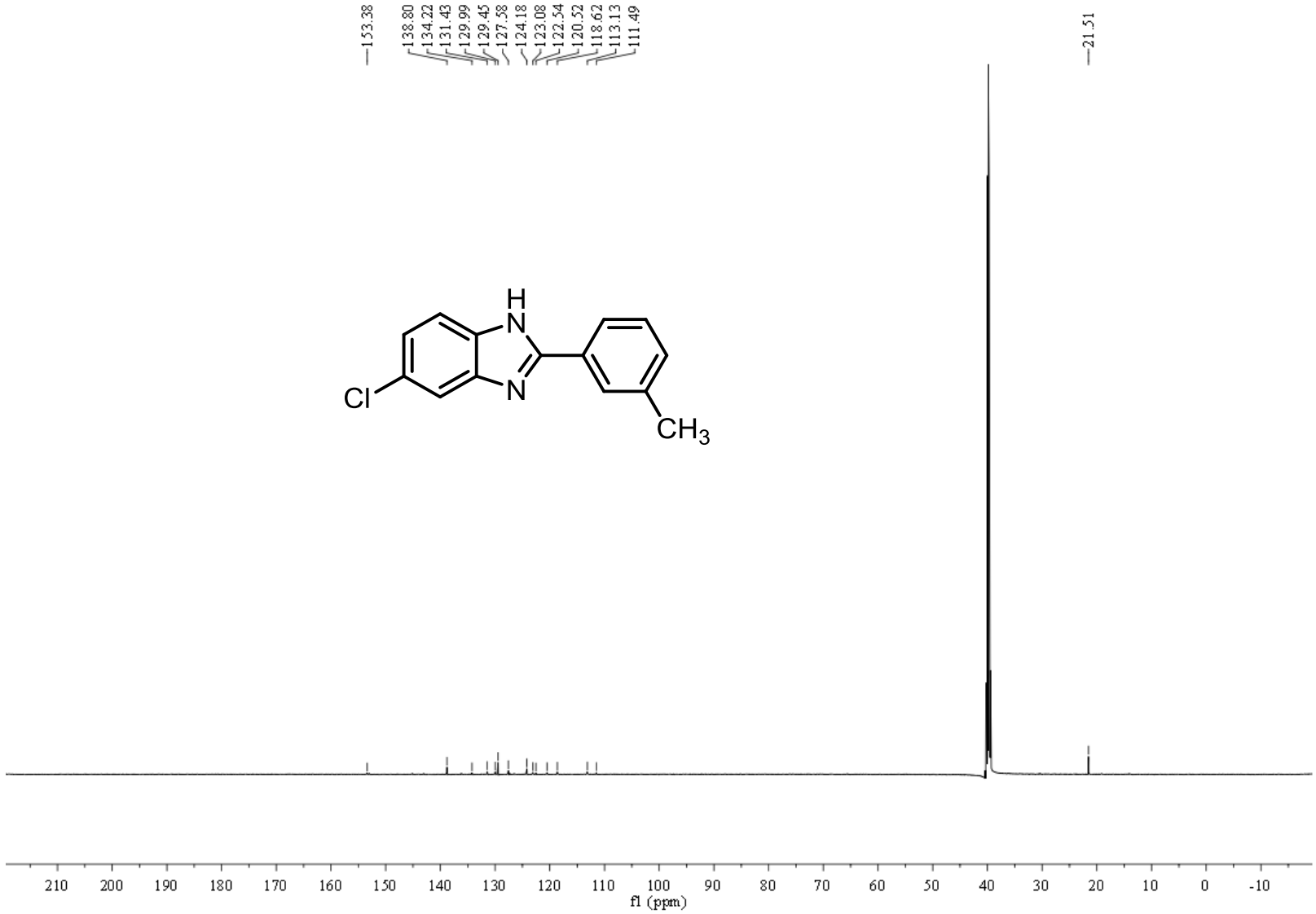
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N
Cl
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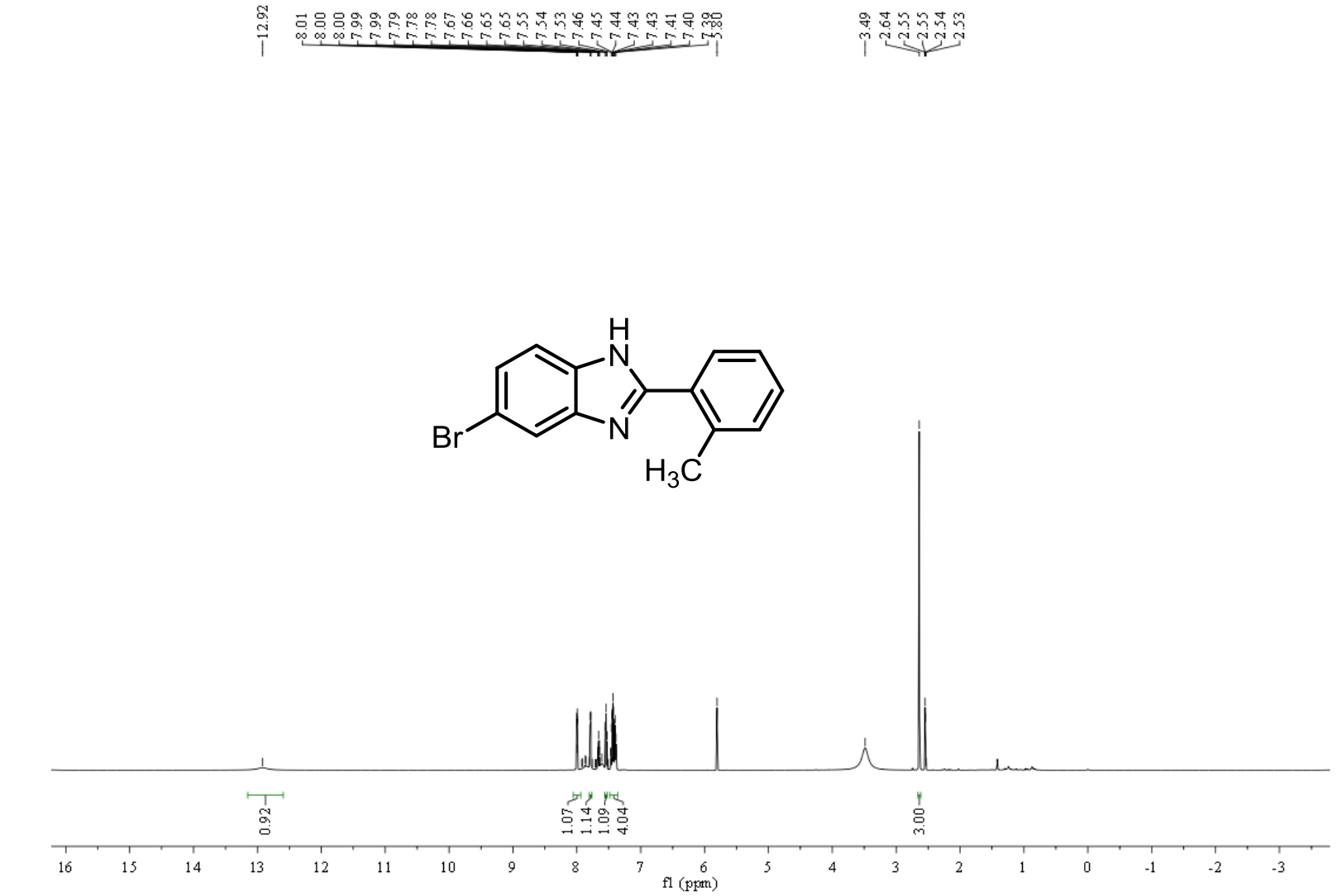
f1 (ppm)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2.54
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N
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Br
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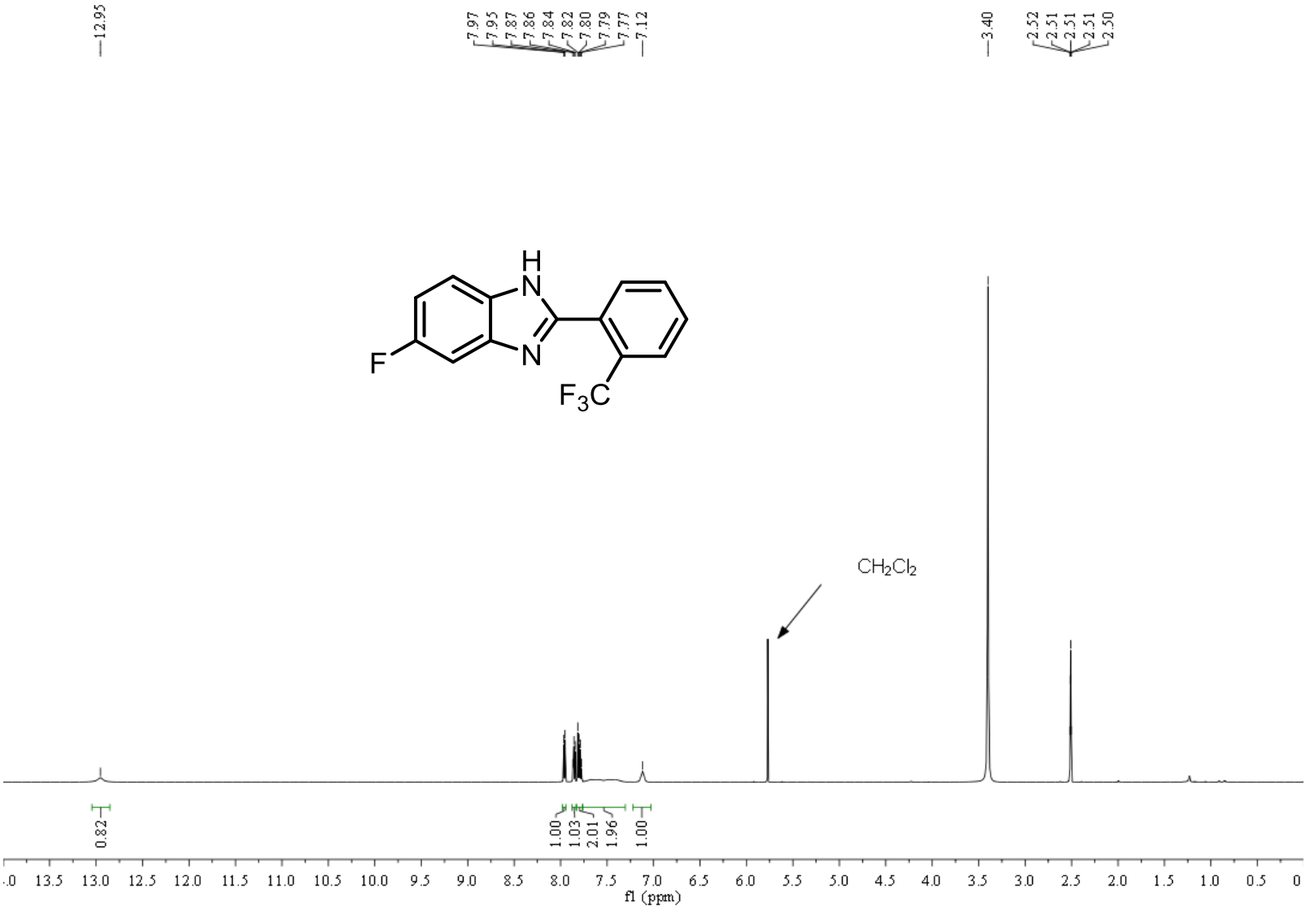
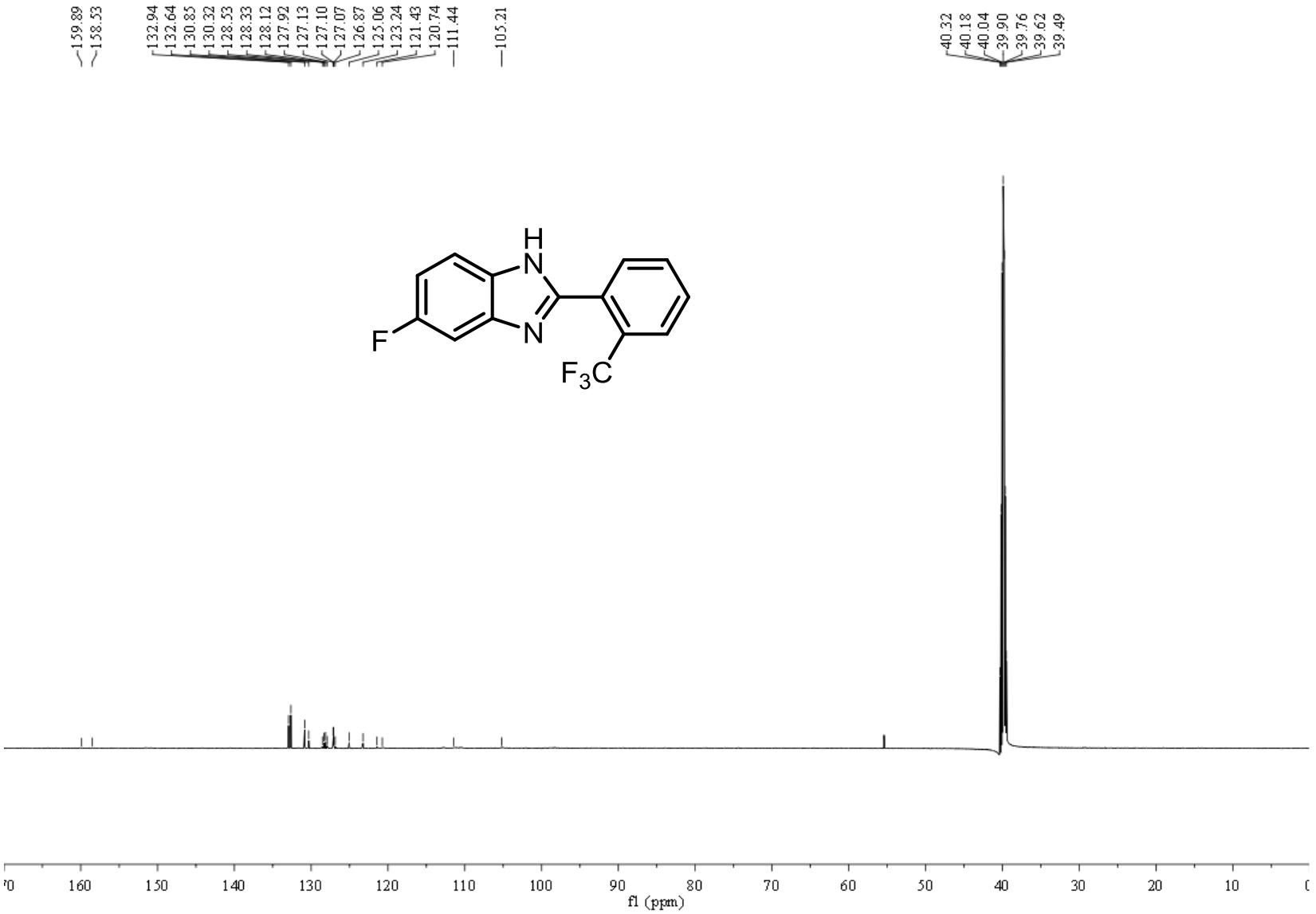
1.09
4.04
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


167.86
153.77
137.60
133.32
131.82
131.29
130.13
129.97
129.96
129.74
129.04
126.51
125.10
40.44
40.32
40.18
40.03
39.89
39.75
39.61
39.47
21.48
H
N
N
Br
H3C
f1 (ppm)


12.95
7.97
7.95
7.87
7.86
7.84
7.82
7.80
7.79
7.77
7.12
3.40
2.52
2.51
2.51
2.51
2.50
H
N
N
F
F3C
CH2Cl2
0.82
1.00
1.03
2.01
1.96
1.00
f1 (ppm)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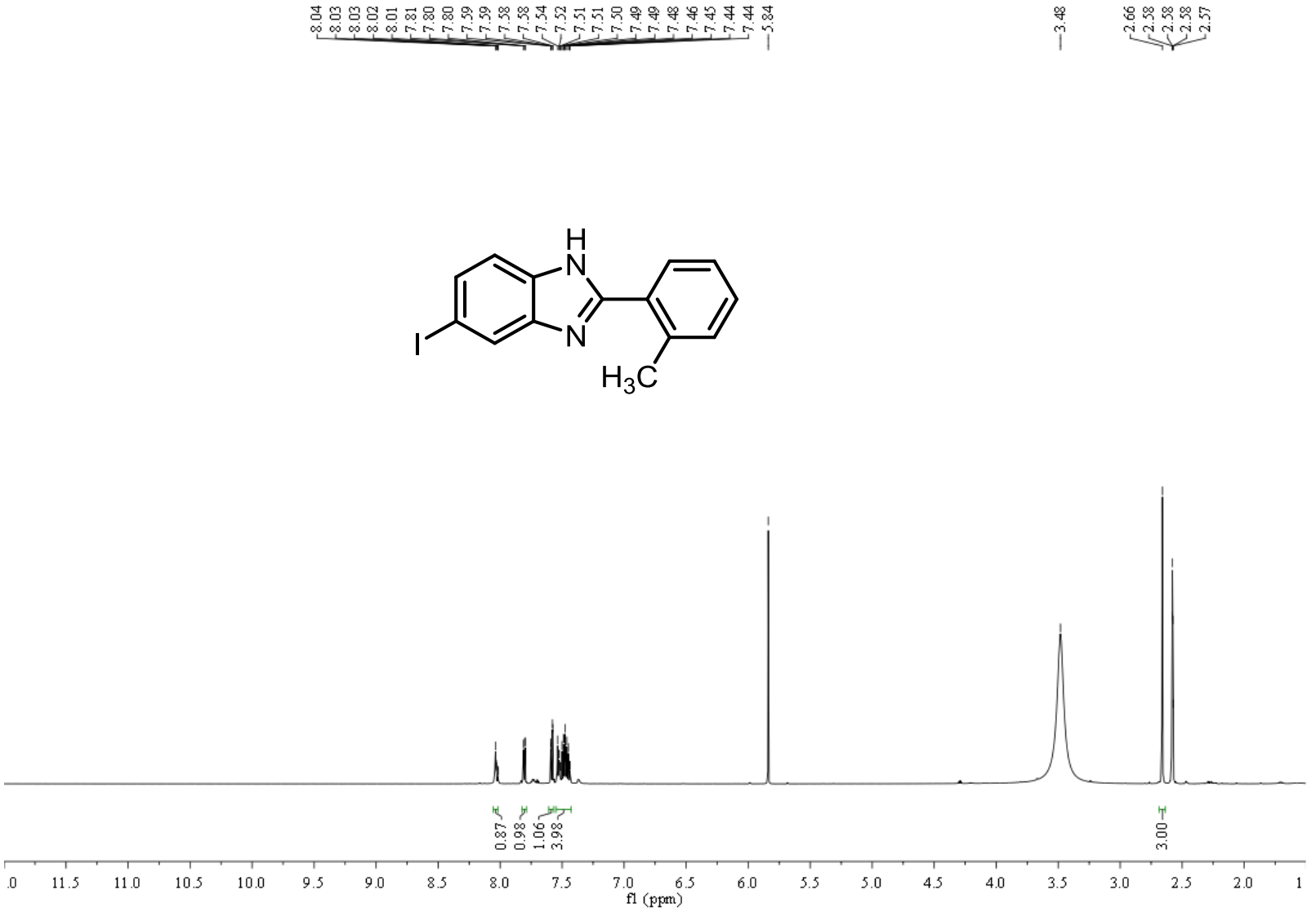
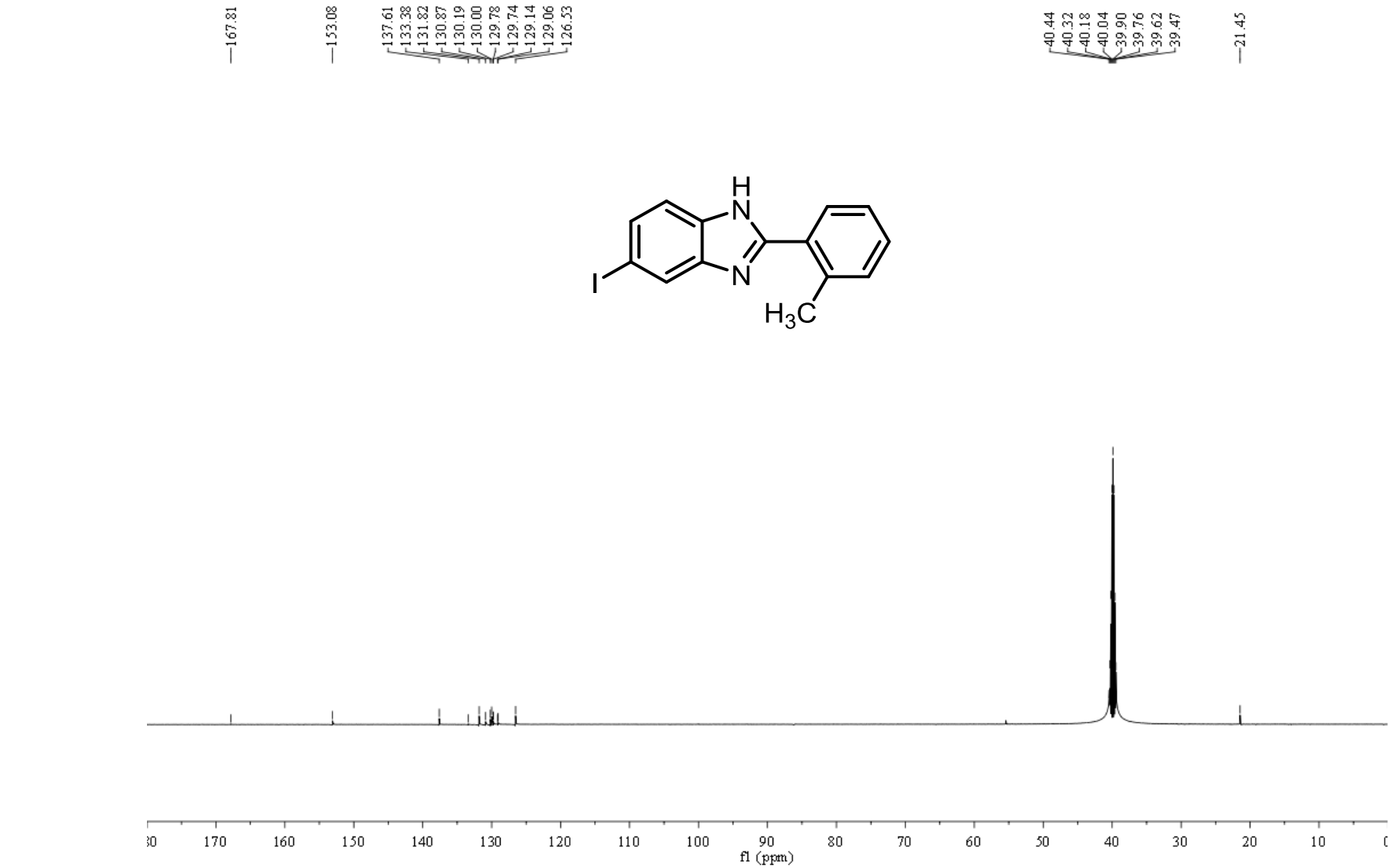
132.64
130.85
130.32
128.53
128.33
128.12
127.92
127.13
127.10
127.07
126.87
125.06
123.24
121.43
120.74
111.44
105.21
40.32
40.18
40.04
39.90
39.76
39.62
39.49
H
N
N
F
F3C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.04
8.03
8.03
8.02
8.01
7.81
7.80
7.80
7.59
7.59
7.58
7.58
7.54
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.46
7.45
7.44
7.44
5.84
3.48
2.66
2.58
2.58
2.58
2.57
H
N
N
I
H3C
0.87
0.98
1.06
3.98
3.00
f1 (ppm)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137.61
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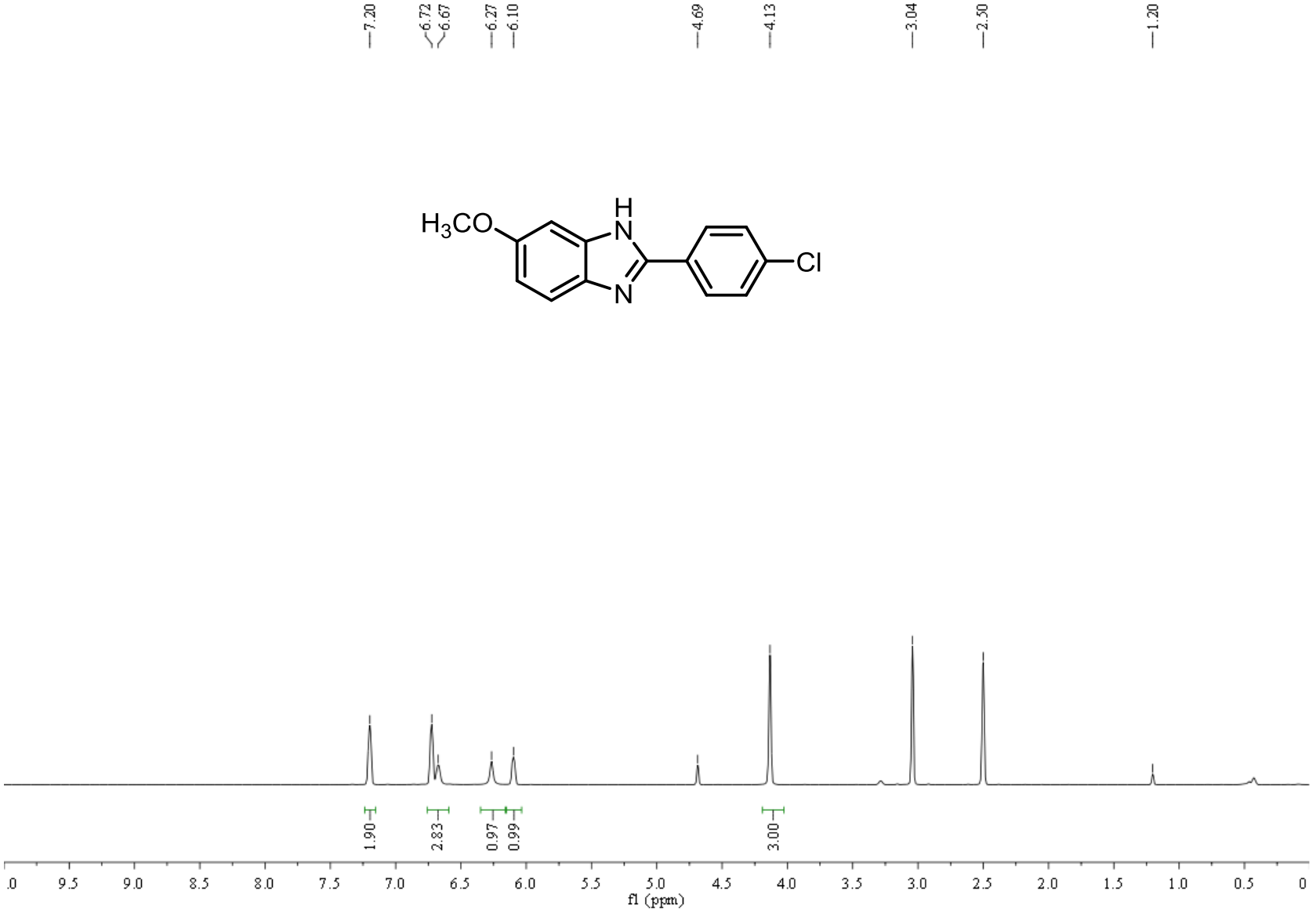
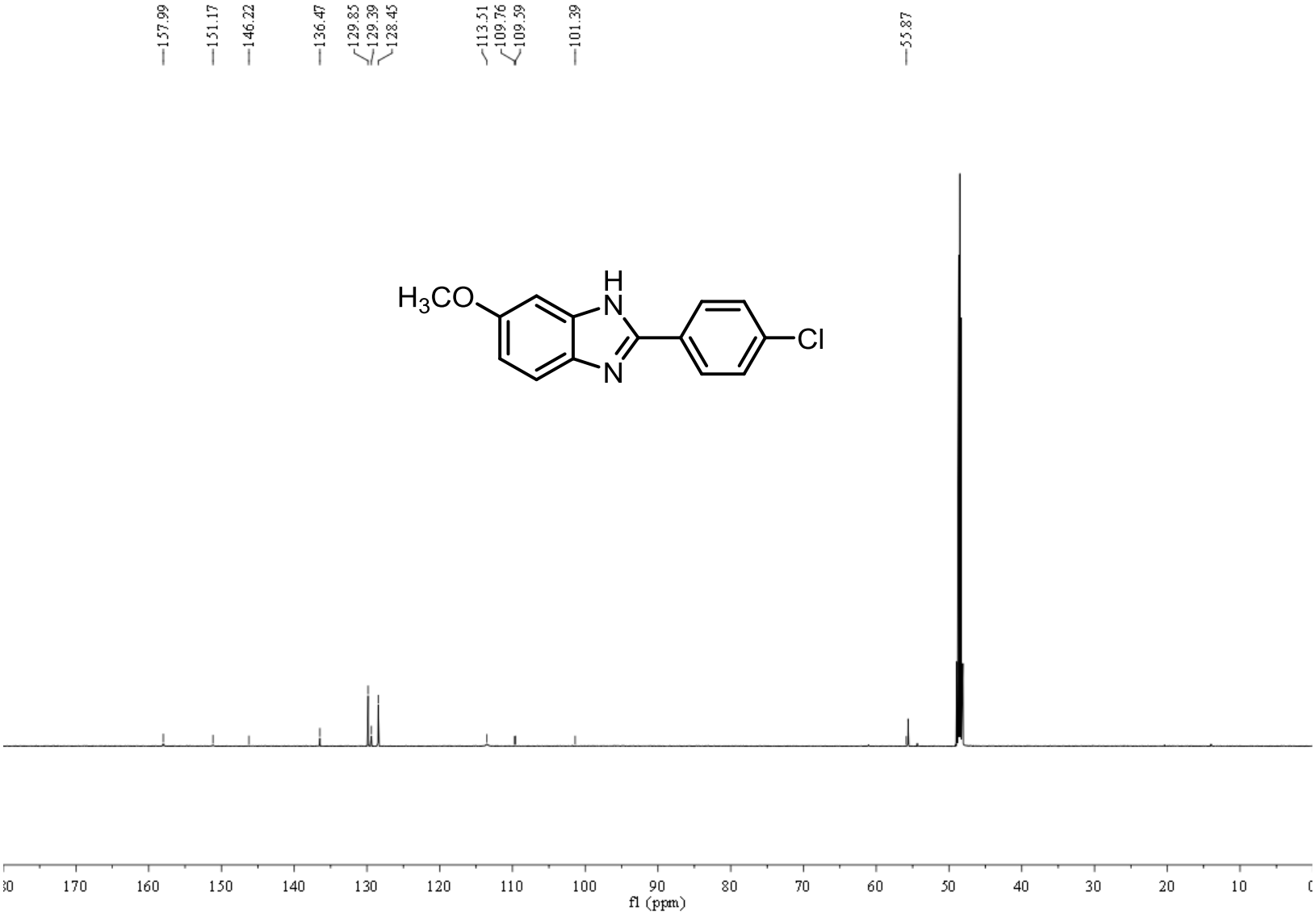
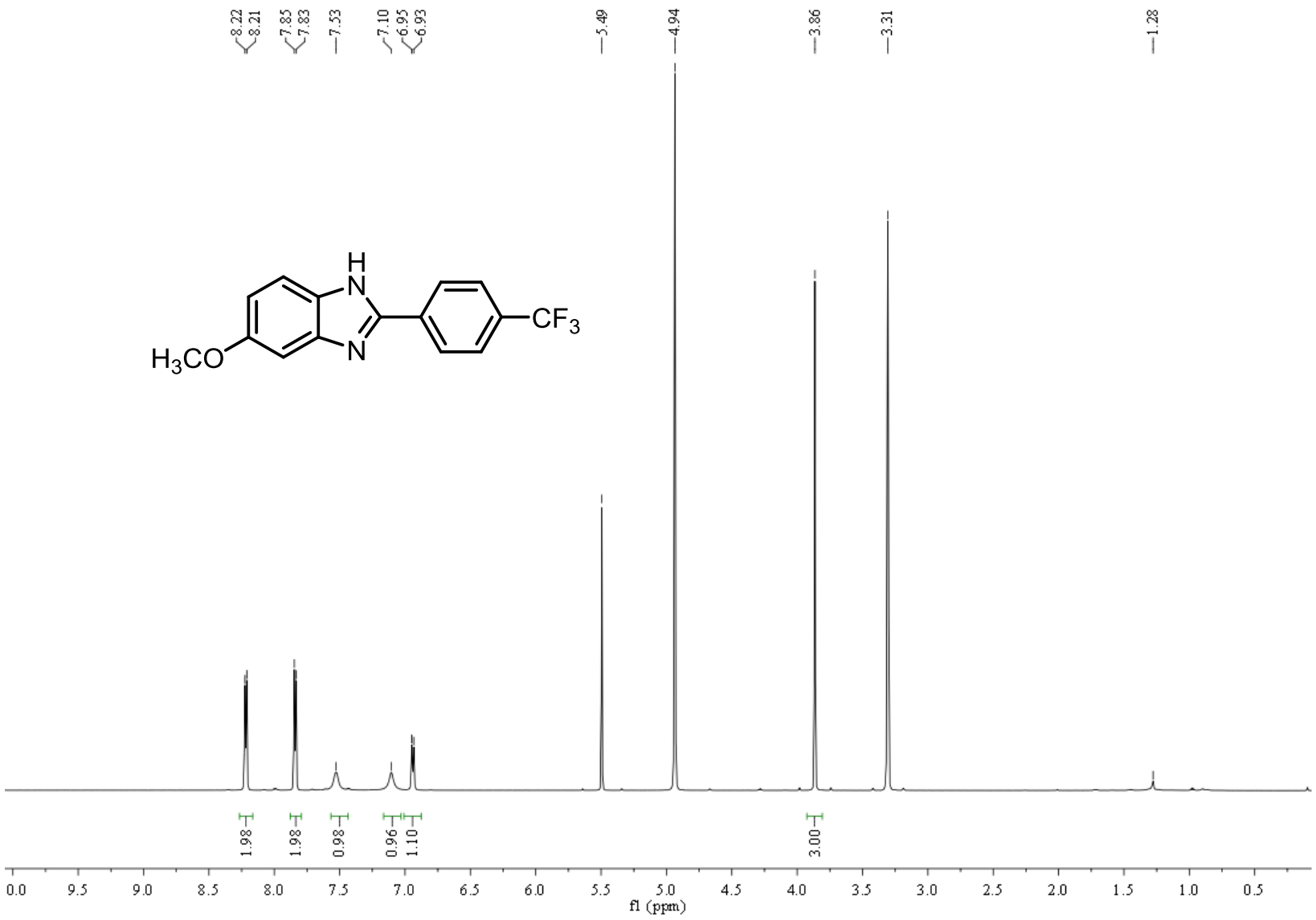
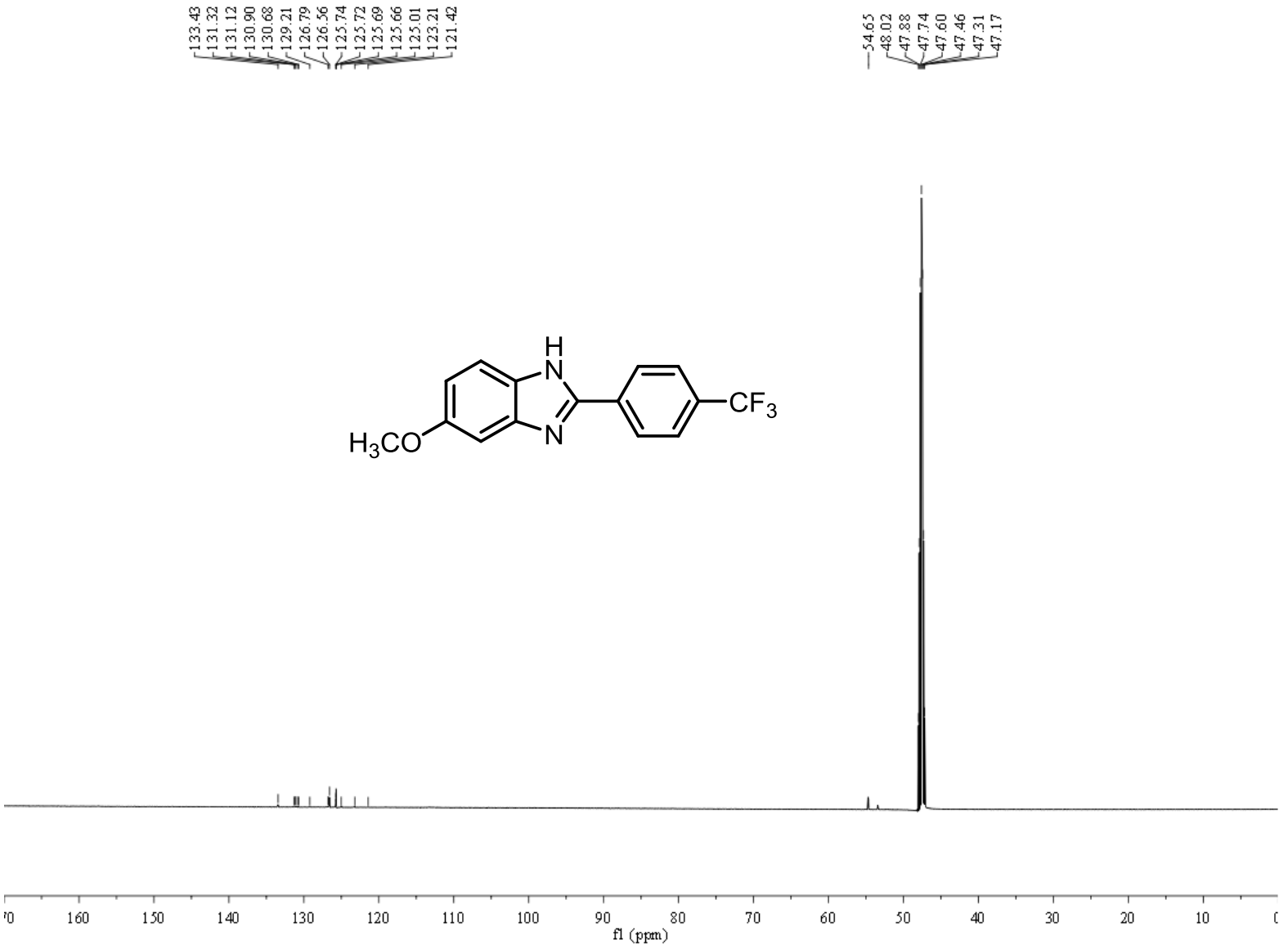
131.82
130.87
130.19
130.00
129.78
129.74
129.14
129.06
126.53
40.44
40.32
40.18
40.04
39.90
39.76
39.62
39.47
21.45
H
N
N
I
H3C
f1 (ppm)

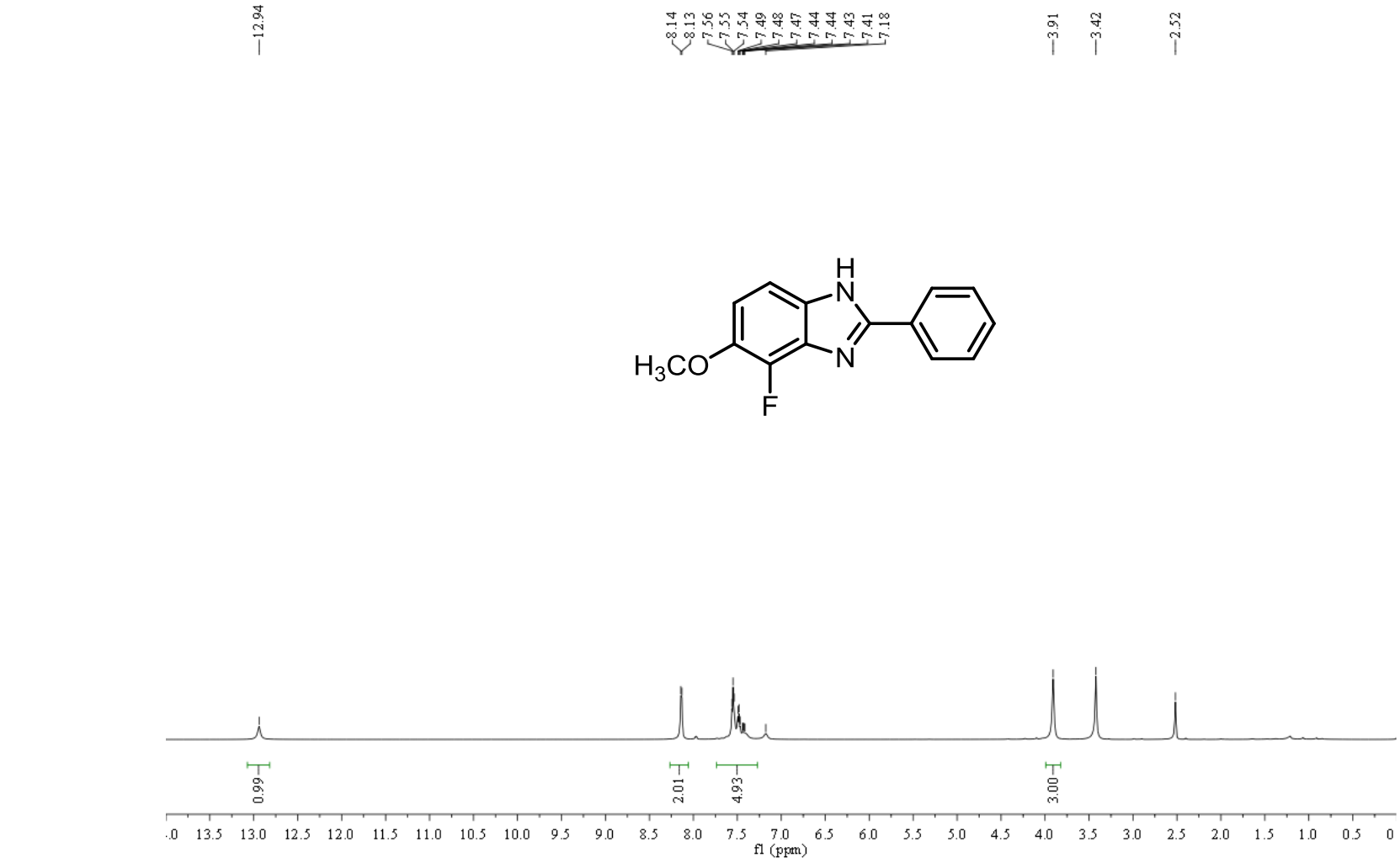

7.20
6.72
6.67
6.27
6.10
4.69
4.13
3.04
2.30
1.20
H3CO
H
N
N
Cl
1.90
2.83
0.97
0.99
3.00
f1 (ppm)

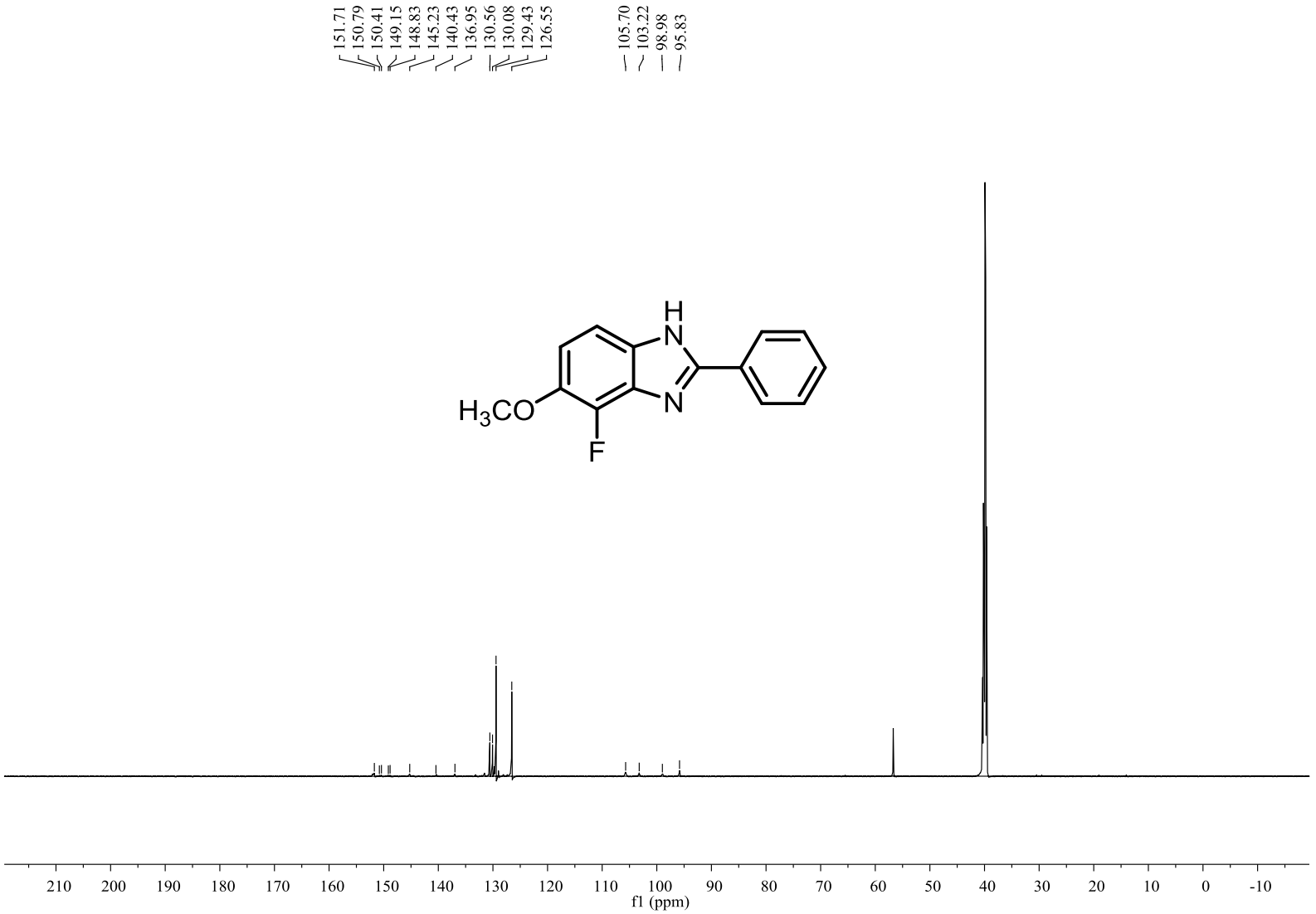

157.99
151.17
146.22
136.47
129.85
129.39
128.45
113.51
109.76
109.59
101.39
55.87
H3CO
H
N
N
Cl
f1 (ppm)


8.22
8.21
7.85
7.83
7.53
7.10
6.95
6.93
5.49
4.94
3.86
3.31
1.28
H
N
N
CF_3
H_3CO
1.98
1.98
0.98
0.96
1.10
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

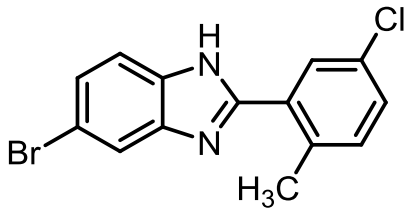

133.43
131.32
131.12
130.90
130.68
129.21
126.79
126.56
125.74
125.72
125.69
125.66
125.01
123.21
121.42
54.65
48.02
47.88
47.74
47.60
47.46
47.31
47.17
H
N
N
CF3
H3CO
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

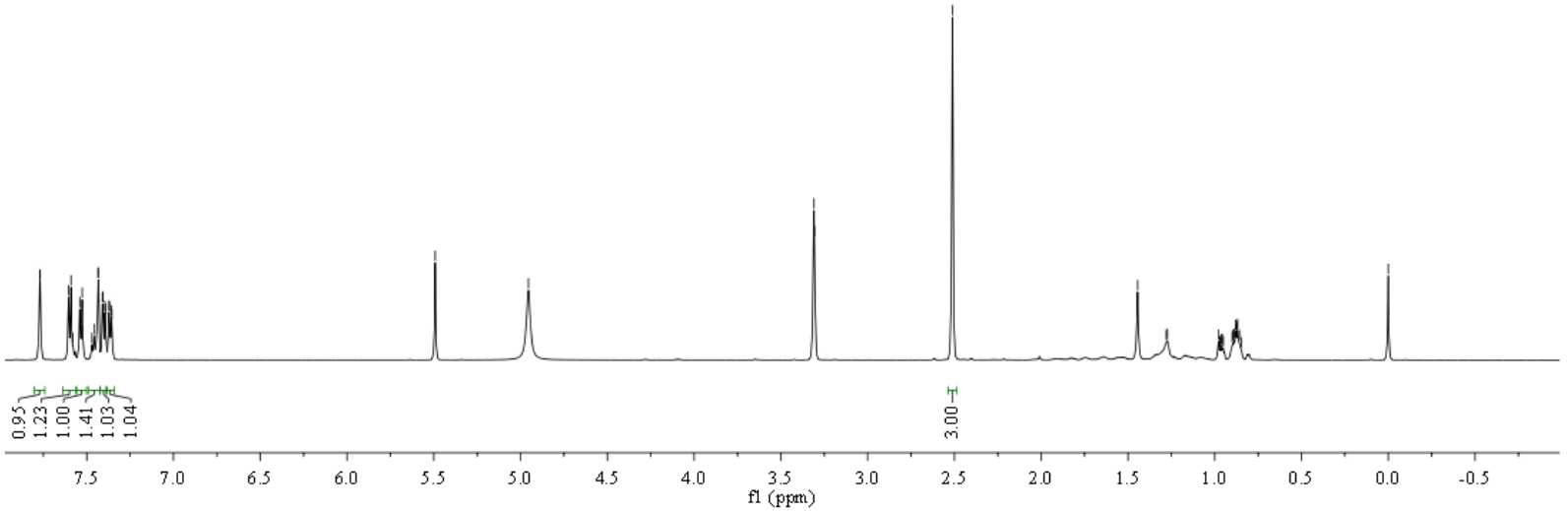
.8.

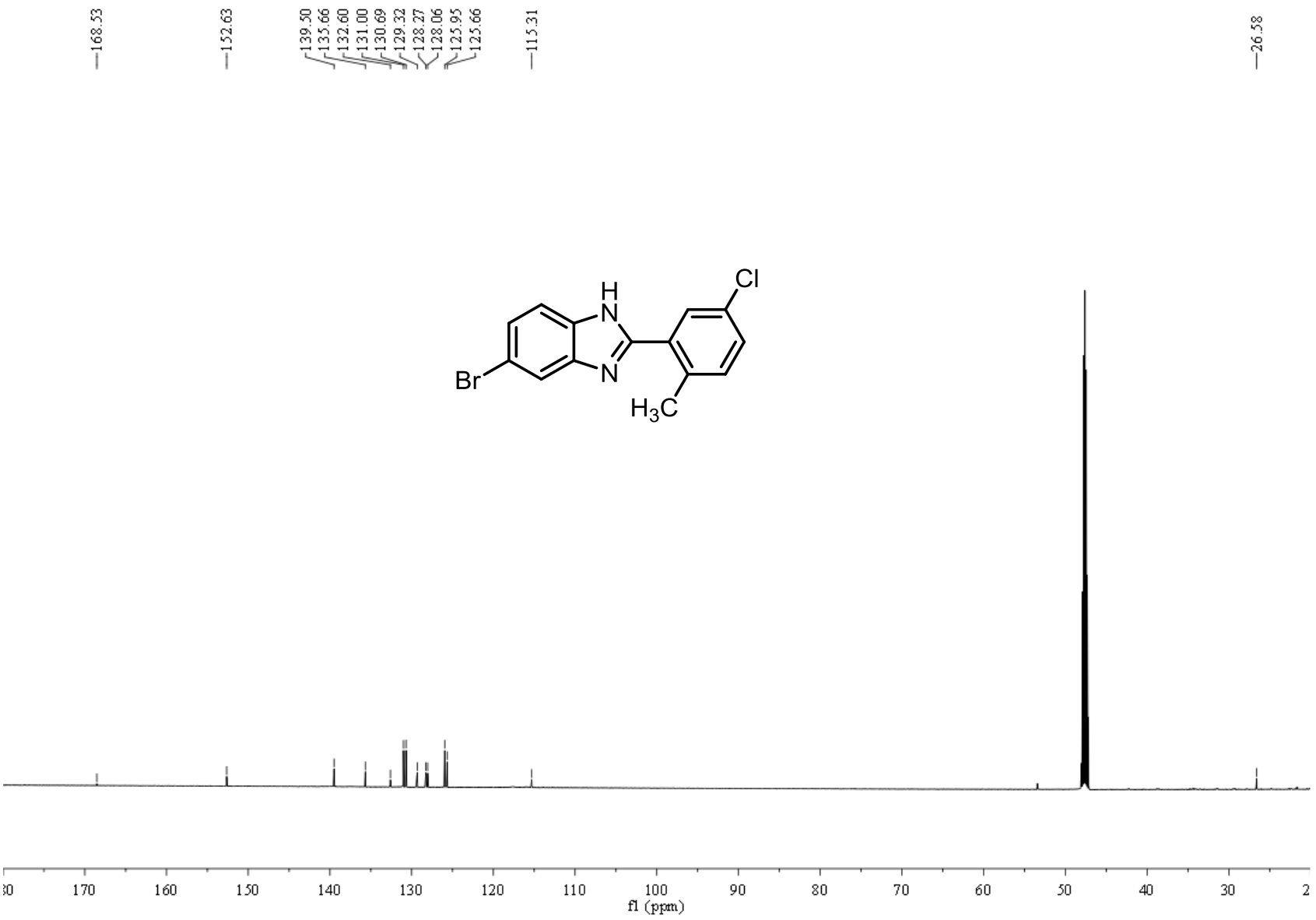

12.94
8.14
8.13
7.56
7.55
7.54
7.49
7.48
7.47
7.44
7.44
7.43
7.41
7.18
3.91
3.42
2.52
H
N
N
H3CO
F
0.99
2.01
4.93
3.00
fl (ppm)

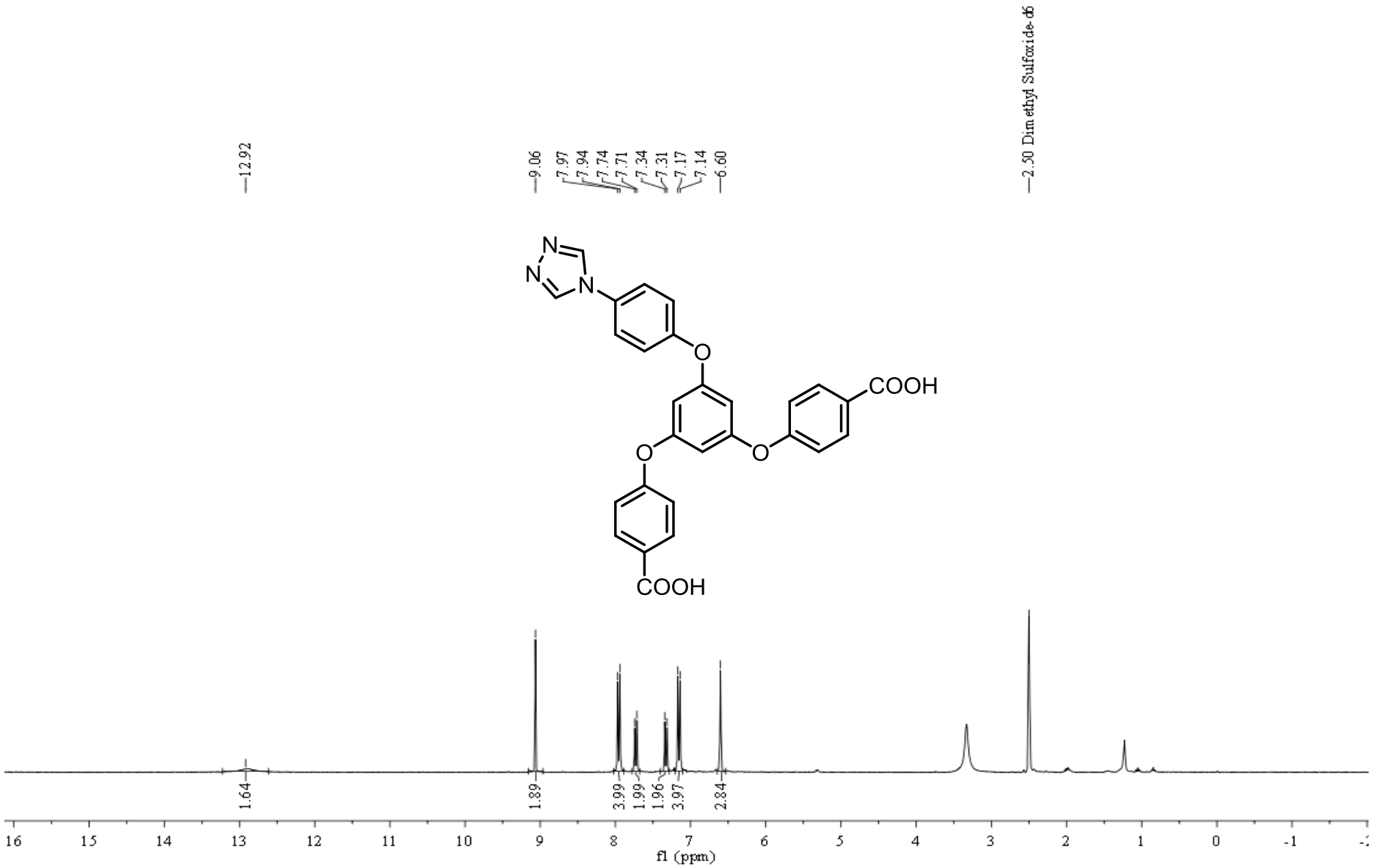

151.71
150.79
150.41
149.15
148.83
145.23
140.43
136.95
130.56
130.08
129.43
126.55
105.70
103.22
98.98
95.83
H
N
N
H3CO
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.77
7.77
7.60
7.59
7.54
7.53
7.47
7.46
7.43
7.43
7.41
7.41
7.40
7.39
7.37
7.37
7.36
4.96
3.31
3.31
3.31
2.51
1.44
1.28
1.27
0.98
0.89
0.89
0.88
0.87
0.87
0.87
0.86


H
N
N
Cl
Br
H3C


0.95
1.23
1.00
1.41
1.03
1.04
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.53
152.63
139.50
135.66
132.60
131.00
130.69
129.32
128.27
128.06
125.95
125.66
115.31
26.58
H
N
N
Cl
Br
H3C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


12.92
9.06
7.97
7.94
7.74
7.71
7.34
7.31
7.17
7.14
6.60
2.50 Dimethyl Sulfoxide-d6
N
N
N
O
O
O
COOH
COOH
1.64
1.89
3.99
1.99
1.96
3.97
2.84
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

References

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