–Supporting Information for–

Dynamic behavior of N-heterocyclic carbene boranes: boron–carbene bonds in *B,B*-disubstituted *N,N*-dimethylimidazol-2-ylidene boranes have substantial rotation barriers

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General information, synthesis:

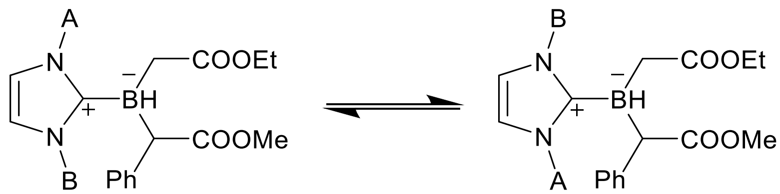
All reactions were performed in oven-dried glassware under an argon atmosphere, except where noted. Chemicals and solvents were purchased from commercial suppliers and used as received, excepting as follows. Dichloromethane, THF, ether, and toluene were dried by passing through an activated alumina column. All reactions were followed by TLC to completion, unless stated otherwise. TLC analysis was performed by illumination with a UV lamp (254 nm) or staining with PMA and heating. All flash chromatography was performed by automated flash chromatography with pre-packed silica gel columns. ^{1}H NMR spectra were measured on a 400 MHz and 500 MHz instruments in $CDCl_3$, and chemical shifts were measured relative to the TMS peak (δ 0.00). The following abbreviations were used to describe coupling: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{13}C NMR spectra were measured on 100 MHz, 125 MHz or 175 MHz with chemical shifts relative to residual solvent peak (δ 77.0 ($CDCl_3$) or 128.06 (C_6D_6)). The resonances for carbons bonded to boron in the ^{13}C-NMR spectrum are typically weak. The NHC-carbene carbon resonance was generally not observed. The resonance for CH_2 or CH adjacent to boron was observed in some but not all spectra. IR spectra were recorded as thin films (CH_2Cl_2) or neat on KBr plates on an FTIR spectrometer. HRMS experiments were conducted on a Q-tof instrument.

General information, NMR experiments:

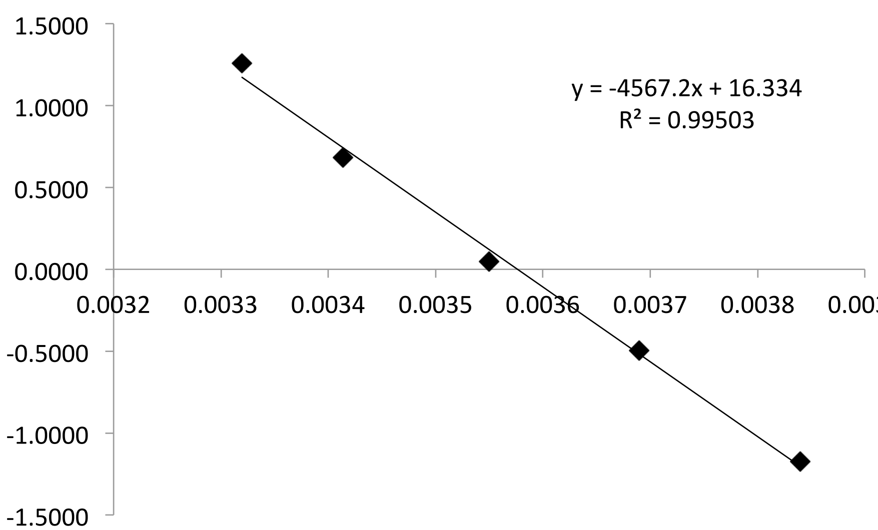
All the NMR experiments for rotational barrier calculations were performed on a 700 MHz NMR spectrometer. The sample temperature was varied from 260 to 333 K at a precision of ±0.1 K using a temperature controller. Samples were equilibrated for about 30 mins prior to acquisition. Temperatures were calibrated using 80% ethylene glycol in DMSO-d_6 and 4% methanol in methanol-d_4 for temperatures above and below 300 K, respectively.

For compound **7b**, 1D ^{1}H NMR spectra at various temperatures were collected to observe coalescence. The DNMR program in Bruker Topspin was used for line shape analysis of these 1H spectra to obtain k_{rot} values. For compounds **9**, **10**, **11** and **12**, since no coalescence was observed in variable temperature 1D ^{1}H spectra, either selective EXSY or 2D EXSY was used. For the selective EXSY experiment, a 180 degree Gaussian shaped selective pulse of 200-300 ms duration was used for excitation. For each temperature, four experiments with different mixing times (0, 200, 400, 800 ms) were collected. EXSY peaks were integrated and used for k_{rot} calculations. For 2D EXSY, three experiments with different mixing times (0, 200 and 500 ms) were collected at each temperature. EXSY volumes were then integrated and used for k_{rot} calculations. The EXSYCalc program from Mestrelab was used to calculate k_{rot} from EXSY integrals.

Rotational Barrier analysis 7b



Temperature (K)	k_{rot} (s^{-1})	1/T	ln(k_{rot}/T)
301.2	1060	0.0033	1.2581
292.9	580	0.0034	0.6831
281.7	295	0.0035	0.0460
271.0	165	0.0037	-0.4962
260.4	80.5	0.0038	-1.1741



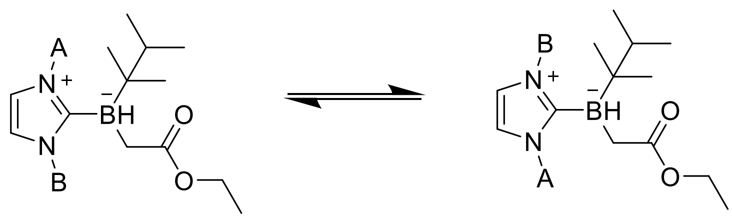
$\Delta H = -R * slope$ R = 8.3144621 J/K/mol

$\Delta S = R * \left(intercept - ln\left(\frac{k_b}{h}\right)\right)$ K_b = 1.38E-23 J/K

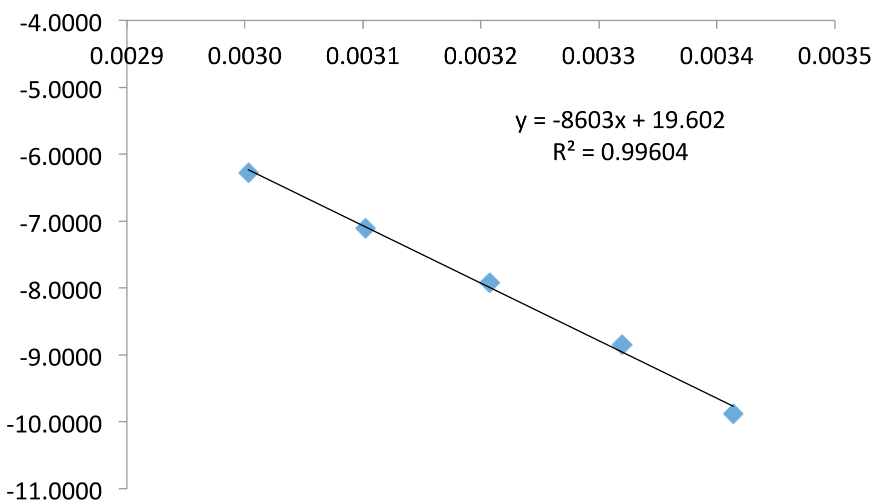
$\Delta G = \Delta H - T\Delta S$ h = 6.63E-34 J.s

ΔH = 37.97 kJmol^{-1}; ΔS = -61.74 Jmol^{-1}; ΔG$_{298}$ = 56.37 kJmol^{-1} (13.46 kcalmol^{-1})

Rotational Barrier analysis 9



Temperature (K)	k_{rot} (s^{-1})	1/T	$\ln(k_{rot}/T)$
292.93	0.015	0.0034	-9.8796
301.24	0.043	0.0033	-8.8467
311.78	0.113	0.0032	-7.9227
322.37	0.263	0.0031	-7.1100
333.02	0.629	0.0030	-6.2718



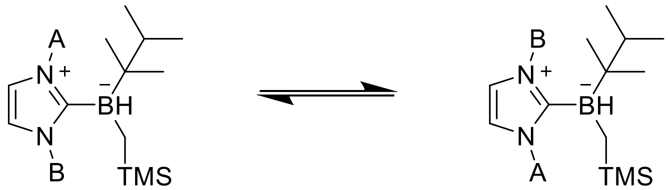
$\Delta H = -R * slope$ R = 8.3144621 J/K/mol

$\Delta S = R * \left(intercept - ln\left(\frac{k_b}{h}\right)\right)$ K_b = 1.38E-23 J/K

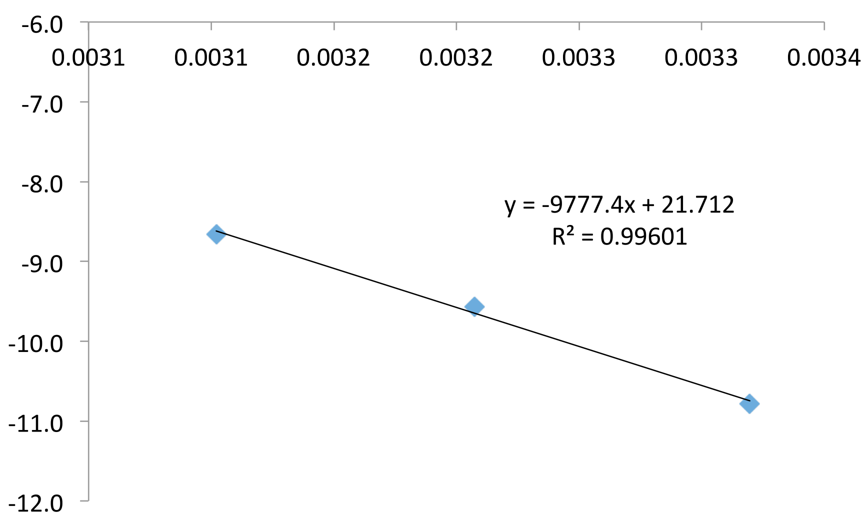
$\Delta G = \Delta H - T\Delta S$ h = 6.63E-34 J.s

ΔH = 71.53 kJmol^{-1}; ΔS = -34.57 Jmol^{-1}; ΔG_{298} = 81.83 kJmol^{-1} (19.55 kcalmol^{-1})

Rotational Barrier analysis 10



Temperature (K)	k_{rot} (s^{-1})	1/T	$ln(k_{rot}/T)$
301.24	0.00625	0.0033	-10.7831
311.78	0.02175	0.0032	-9.5704
322.37	0.056	0.0031	-8.6581



$\Delta H = -R * slope$

$\Delta S = R * \left(intercept - ln\left(\frac{k_b}{h}\right)\right)$

$\Delta G = \Delta H - T\Delta S$

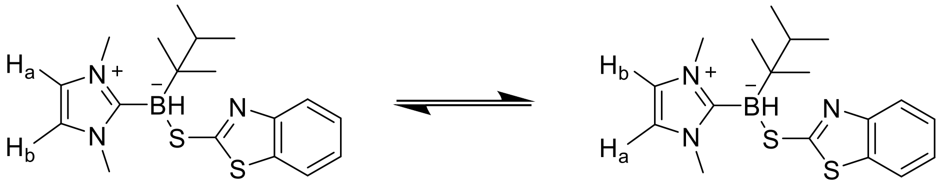
R = 8.3144621 J/K/mol

K_b = 1.38E-23 J/K

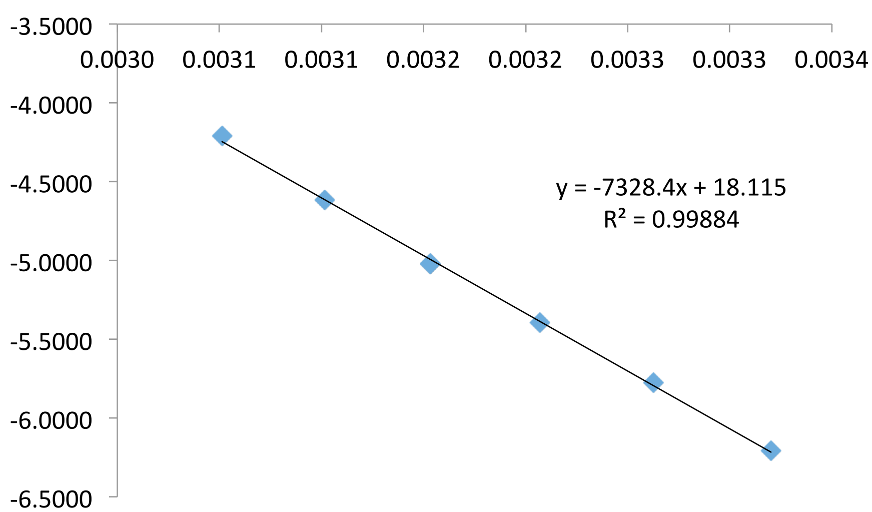
h = 6.63E-34 J.s

ΔH = 81.29 kJmol^{-1}; ΔS = -17.03 Jmol^{-1}; ΔG_{298} = 86.37 kJmol^{-1} (20.63 kcalmol^{-1})

Rotational Barrier analysis 11



Temperature (K)	k_{rot} (s^{-1})	1/T	$\ln(k_{rot}/T)$
301.2	0.6065	0.0033	-6.2078
306.5	0.9520	0.0033	-5.7744
311.8	1.4178	0.0032	-5.3933
317.1	2.0853	0.0032	-5.0244
322.4	3.1843	0.0031	-4.6176
327.7	4.8595	0.0031	-4.2113



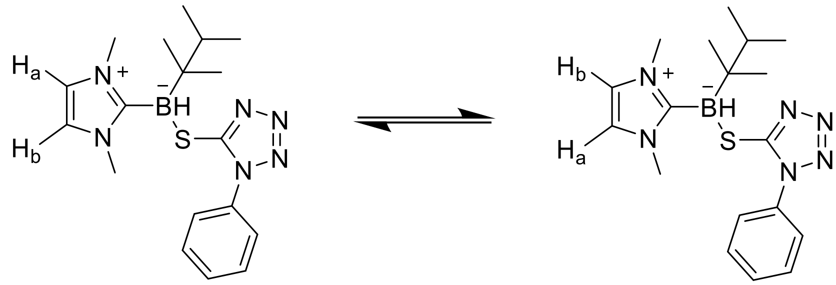
$\Delta H = -R * slope$ R = 8.3144621 J/K/mol

$\Delta S = R * \left(intercept - ln\left(\frac{k_b}{h}\right)\right)$ K_b = 1.38E-23 J/K

$\Delta G = \Delta H - T\Delta S$ h = 6.63E-34 J.s

ΔH = 60.93 kJmol^{-1}; ΔS = -46.93 Jmol^{-1}; ΔG_{298} = 74.92 kJmol^{-1} (17.89 kcalmol^{-1})

Rotational Barrier analysis of 12



Temperature (K)	k_{rot} (s^{-1})	1/T	$ln(k_{rot}/T)$
301.2	0.1845	0.0033	-7.3978
306.5	0.3485	0.0033	-6.7793
311.8	0.4785	0.0032	-6.4795
317.1	0.7380	0.0032	-6.0631
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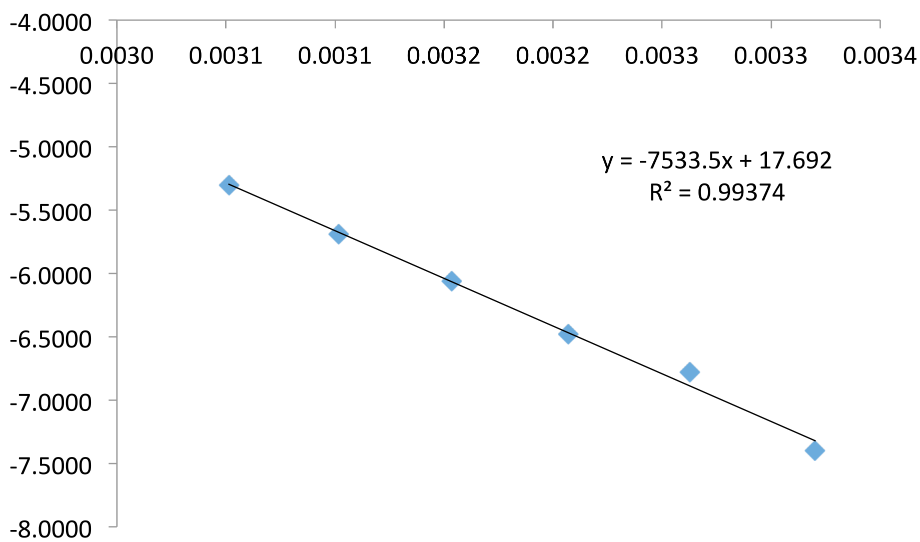
327.7	1.6325	0.0031	-5.3021



$\Delta H = -R * slope$ R = 8.3144621 J/K/mol

$\Delta S = R * \left(intercept - ln\left(\frac{k_b}{h}\right)\right)$ K_b = 1.38E-23 J/K

$\Delta G = \Delta H - T\Delta S$ h = 6.63E-34 J.s

ΔH = 62.64 kJmol^{-1}; ΔS = -50.45 Jmol^{-1}; ΔG_{298} = 77.67 kJmol^{-1} (18.55 kcalmol^{-1})

Figure S1. HPLC analysis of compound 13, on next page. Conditions: (*S*,*S*)-Whelk-O 1 column (Pirkle, 250 mm x 4.6 mm ID) eluting with hexanes:iPrOH at 1.0 mL/min, 10-20 μg per injection. Preparatory HPLC resolutions were performed on an (*S*,*S*)-Whelk-O 1 column (Pirkle, 25 cm x 21.1 mm ID) eluting with hexanes:iPrOH at 7.0 mL/min, 40 mg per injection. All HPLC injections were monitored with a Waters model 440 UV detector at wavelength 254 nm.

Reported by User: System   Project Name: Defaults

SAMPLE INFORMATION

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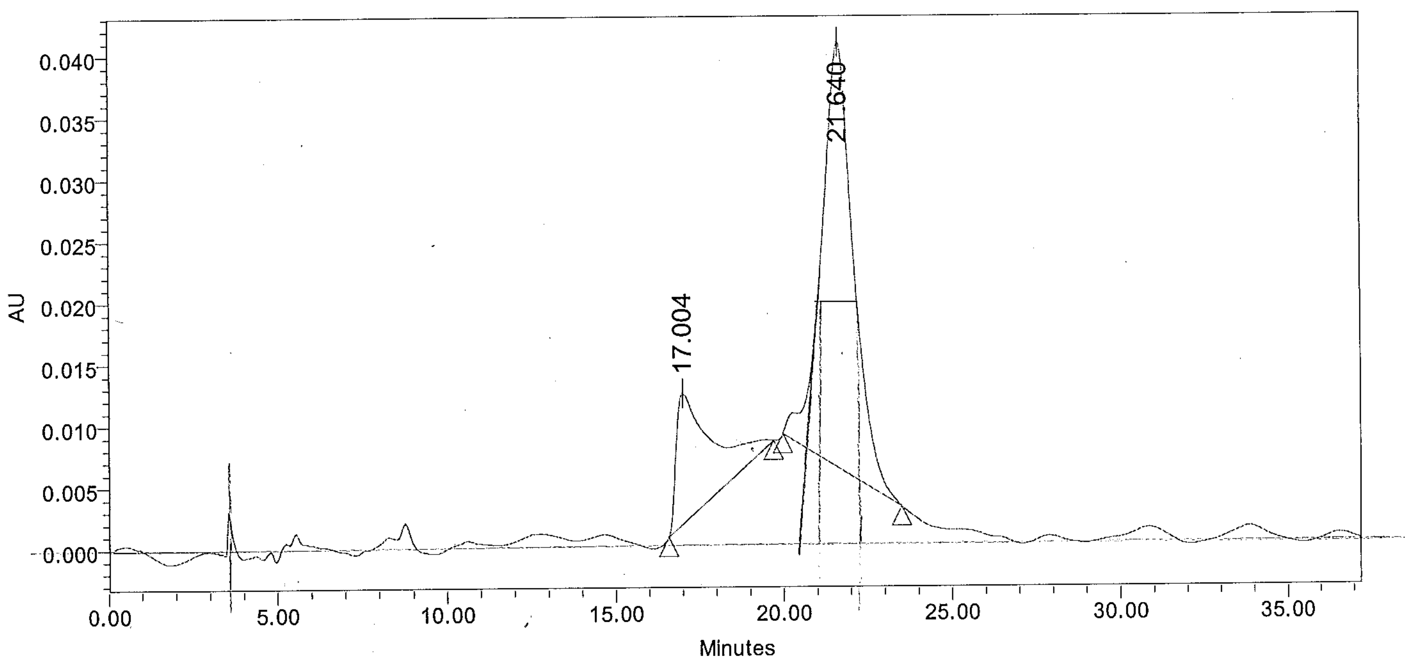
Injection #:	1	Date Processed:	1/8/2014 4:04:18 PM
Injection Volume:	10.00 ul	Processing Method:	xl13067
Run Time:	60.0 Minutes	Channel Name:	2487Channel 1
Sample Set Name:		Proc. Chnl. Descr.:	254

Auto-Scaled Chromatogram



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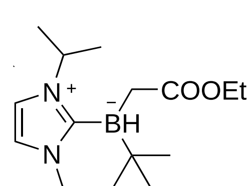

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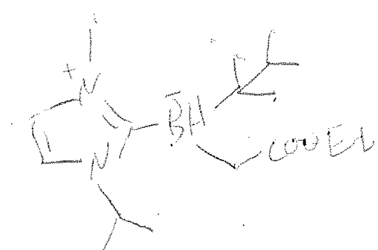

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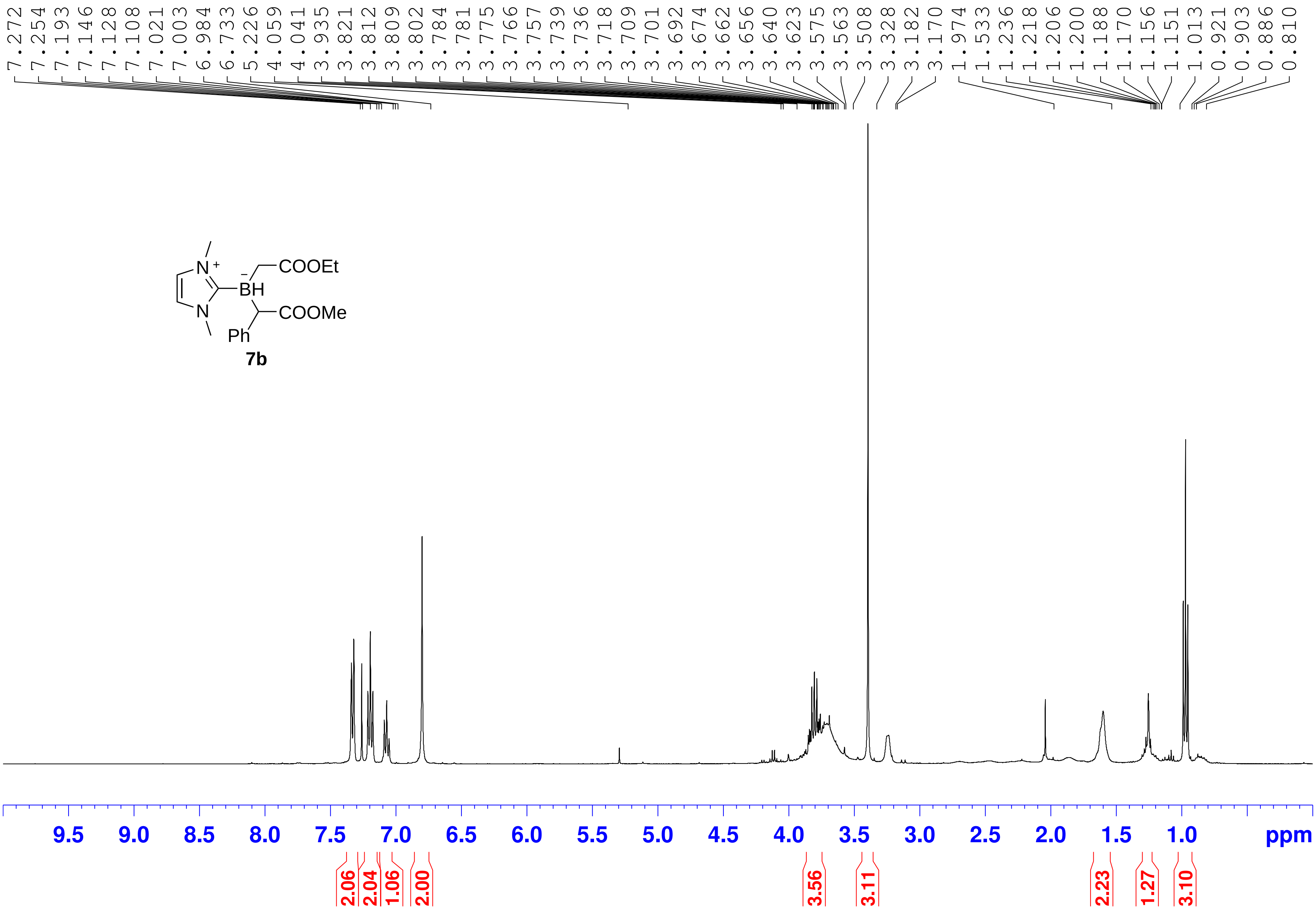

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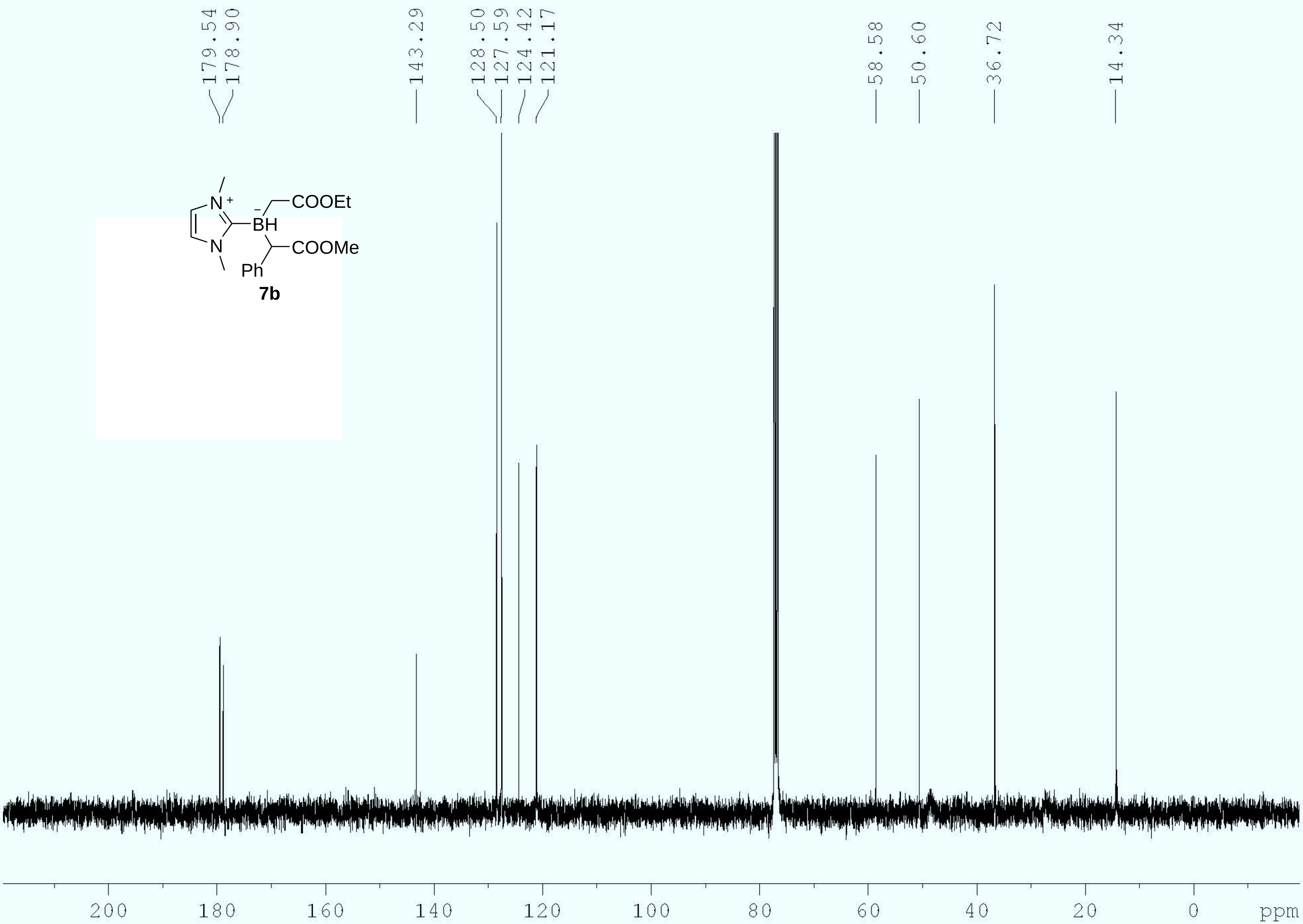

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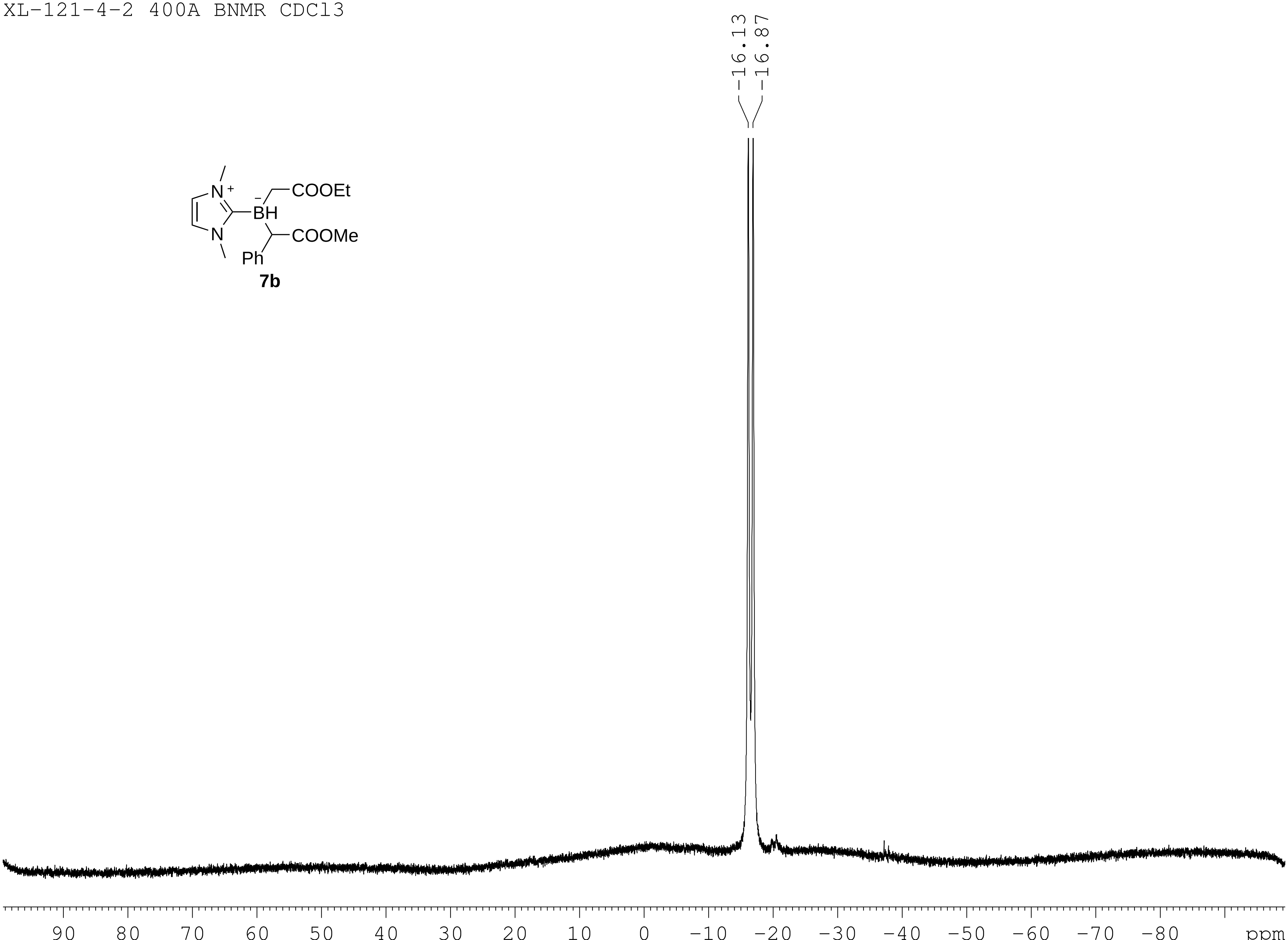
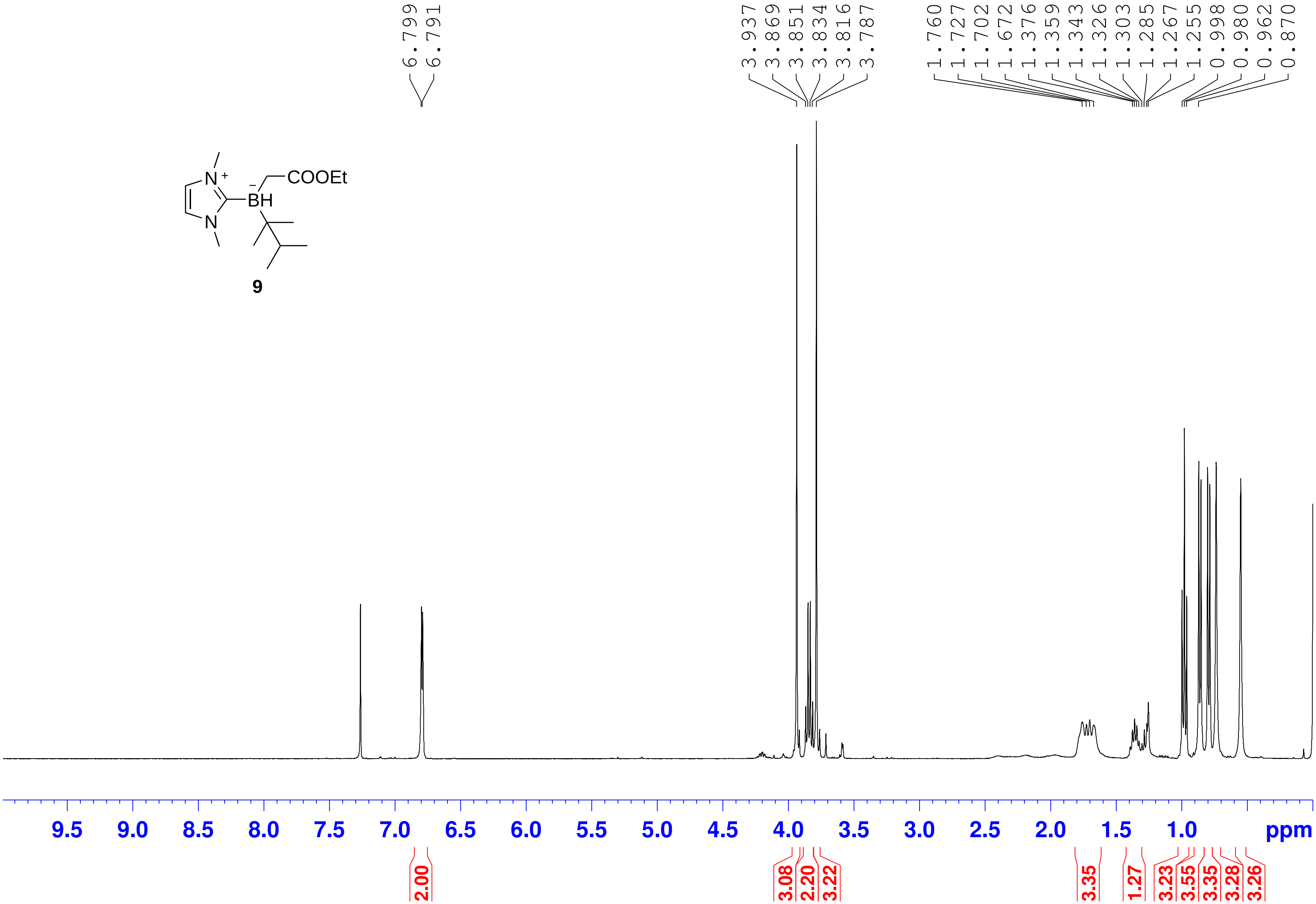
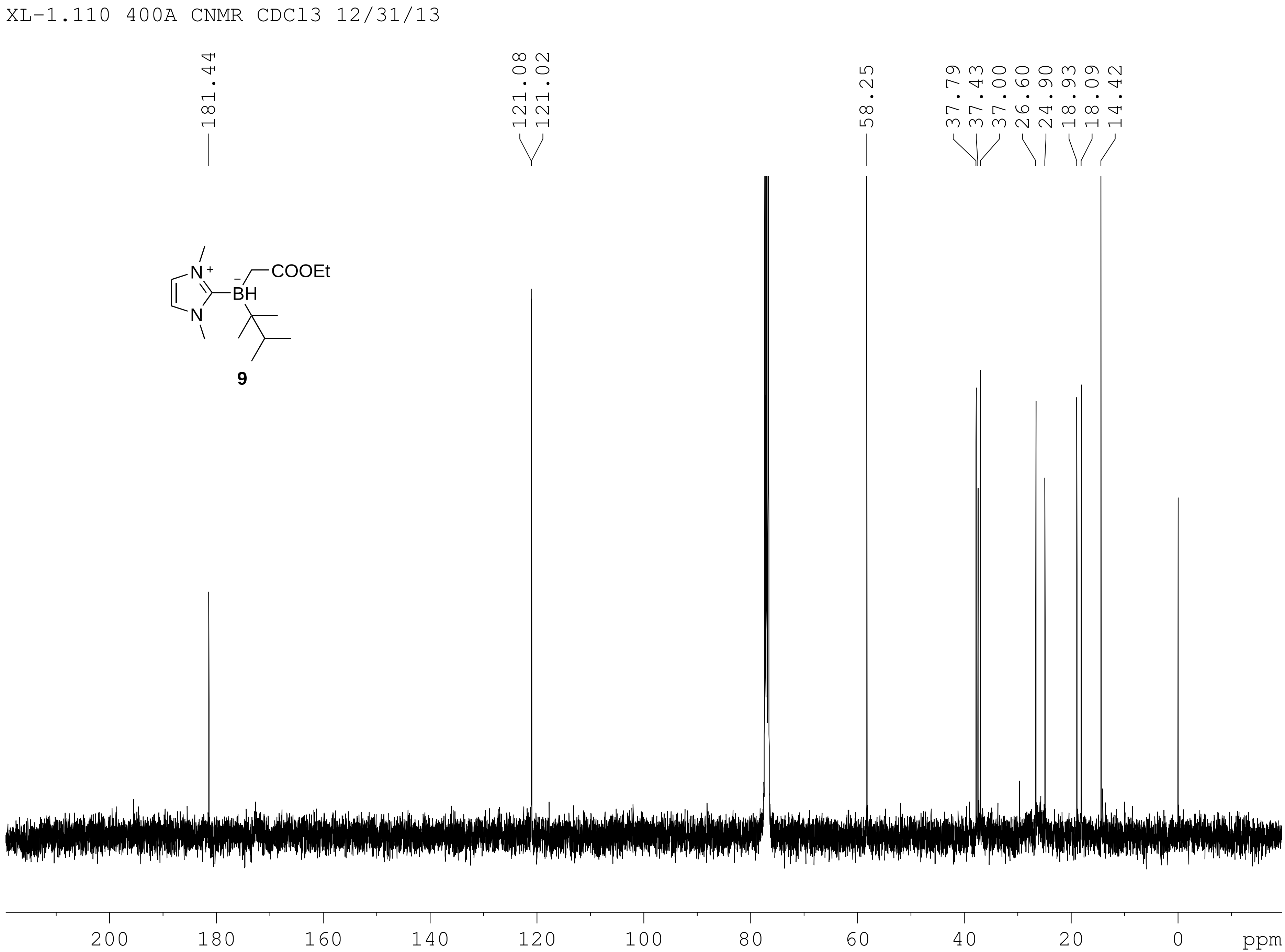


XL-RB-2 400A HNMR CDCl3 05/28/13

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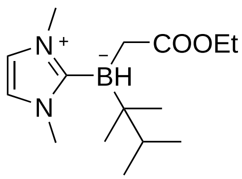
XL-RB-2 400A BNMR CDCl3 05/28/13



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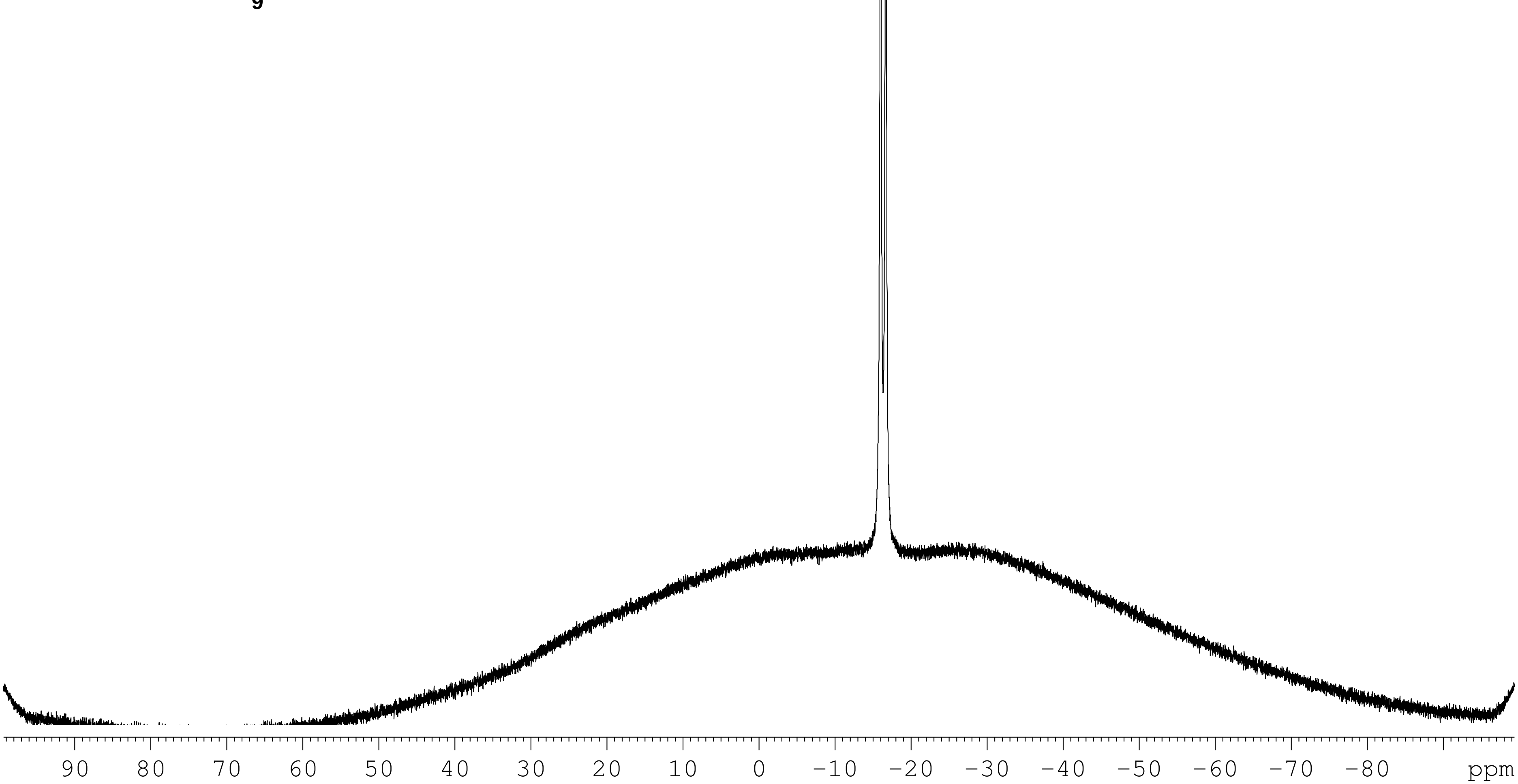

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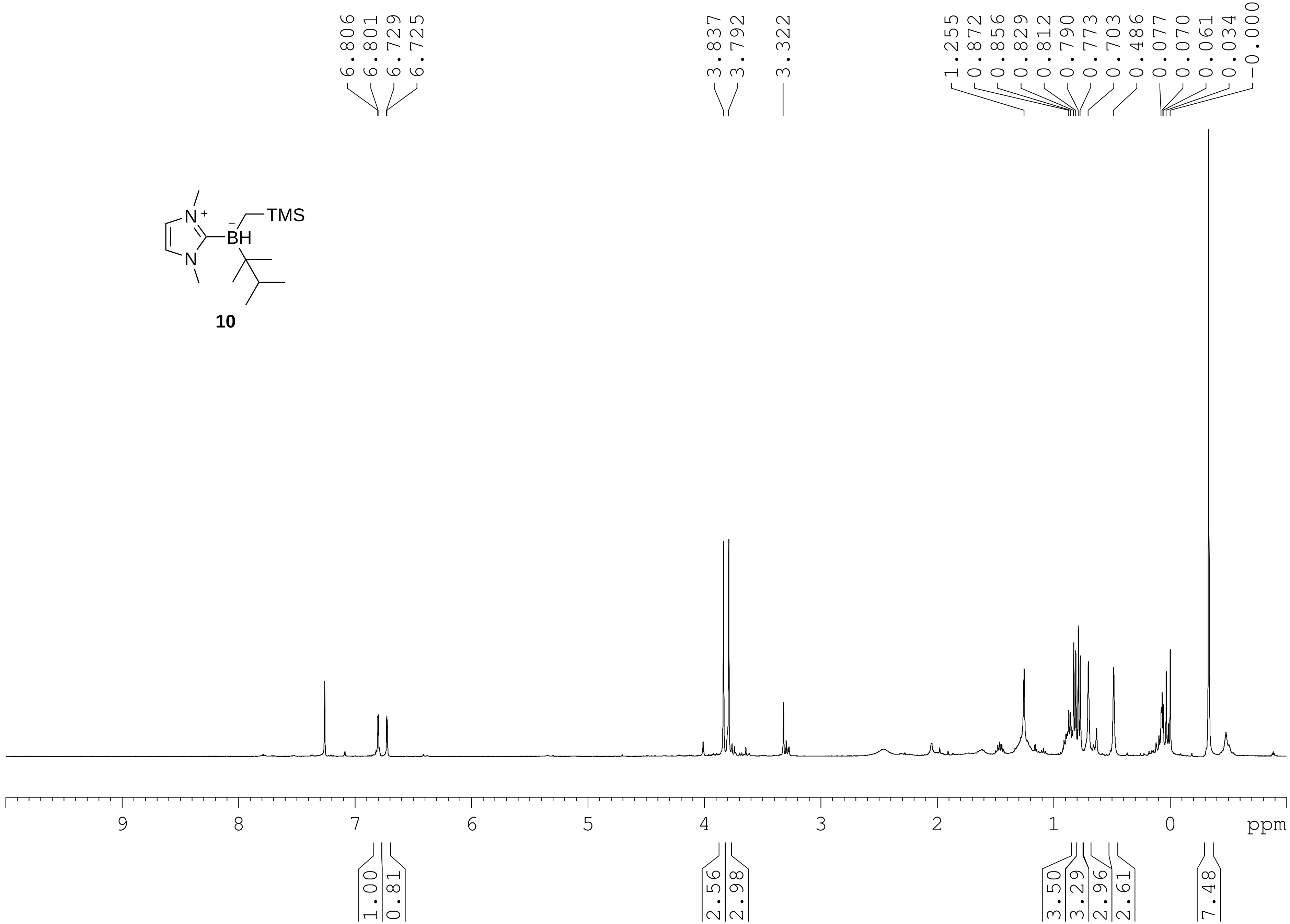

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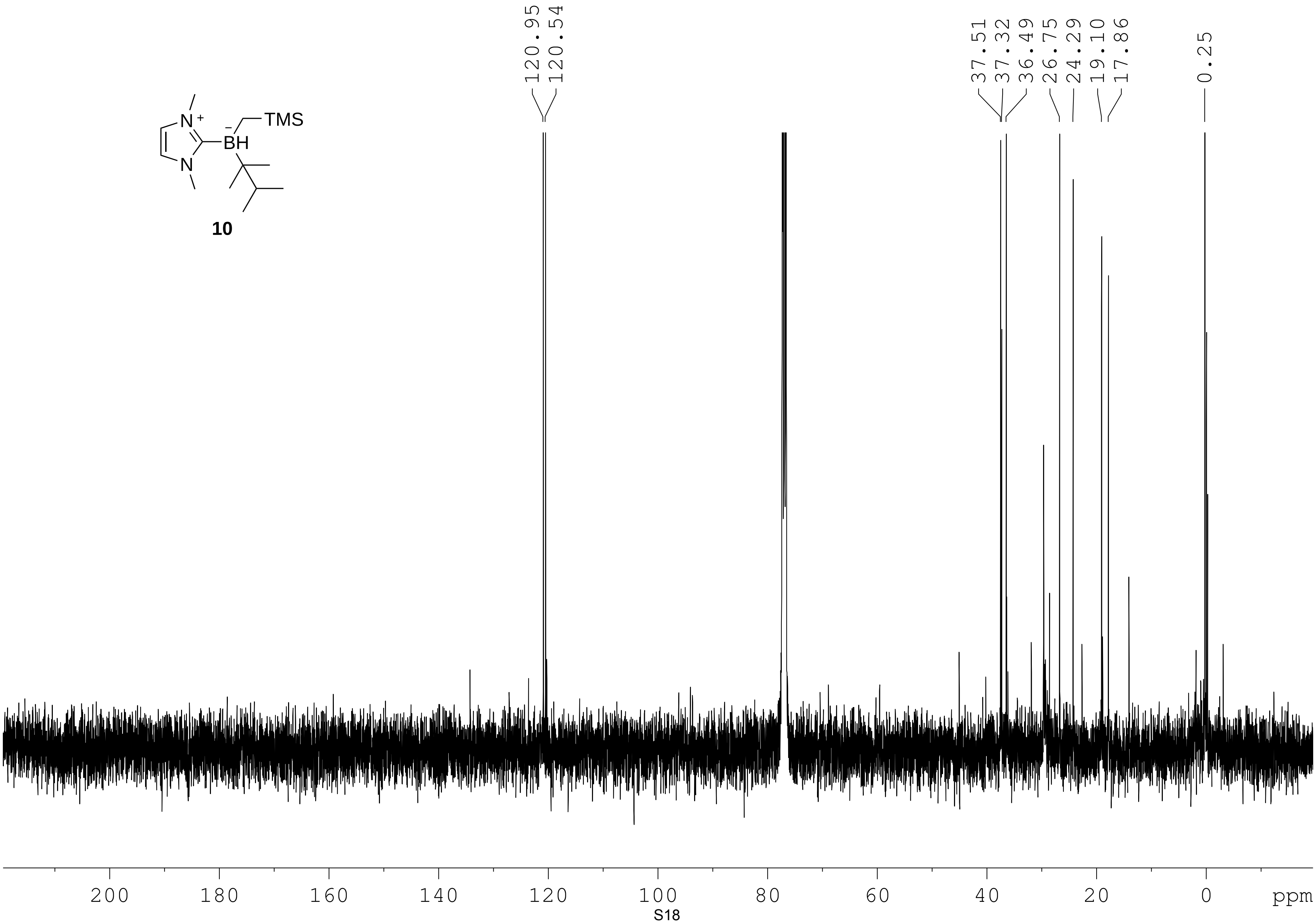

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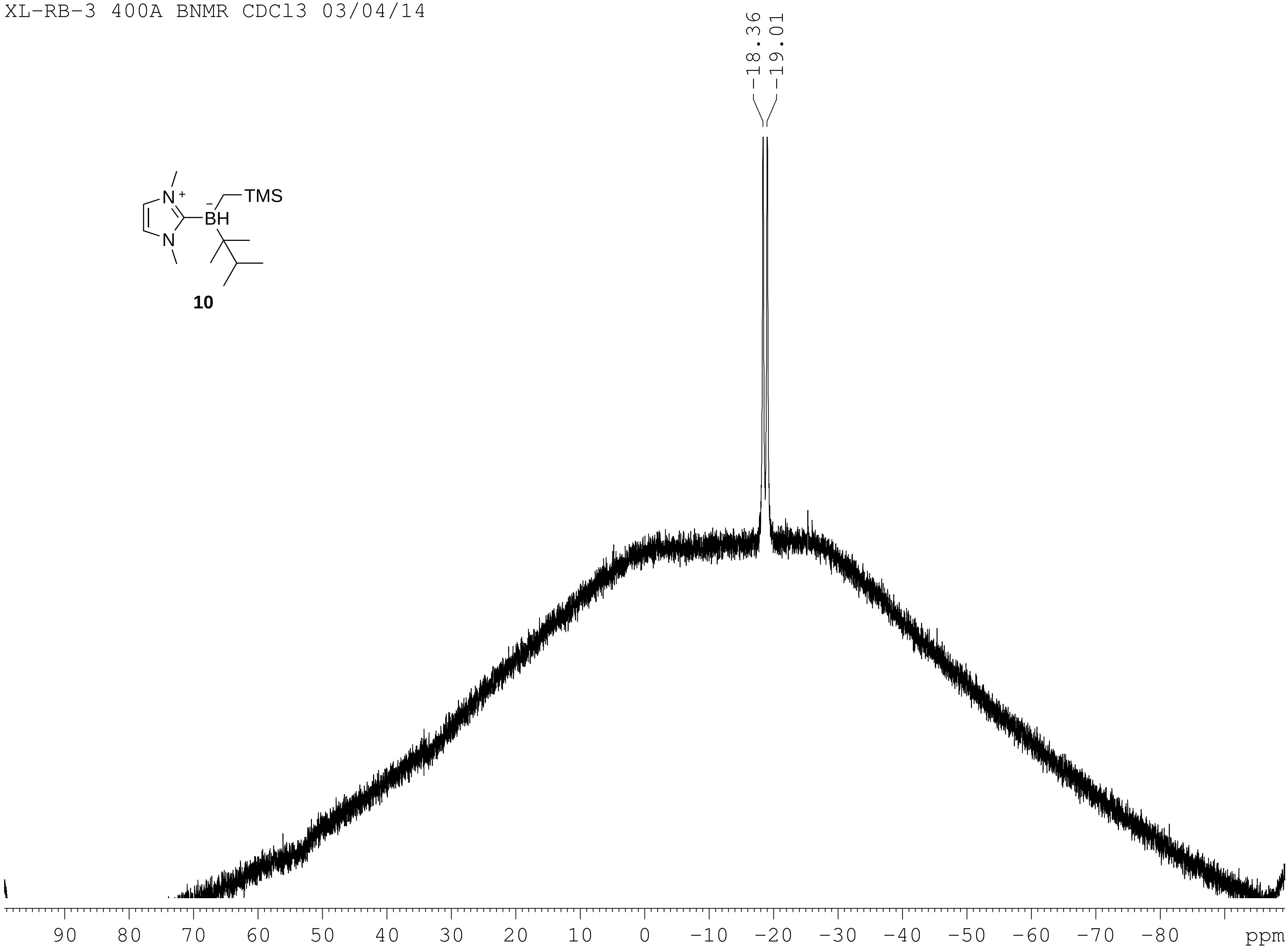

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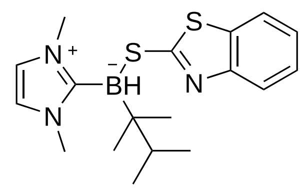

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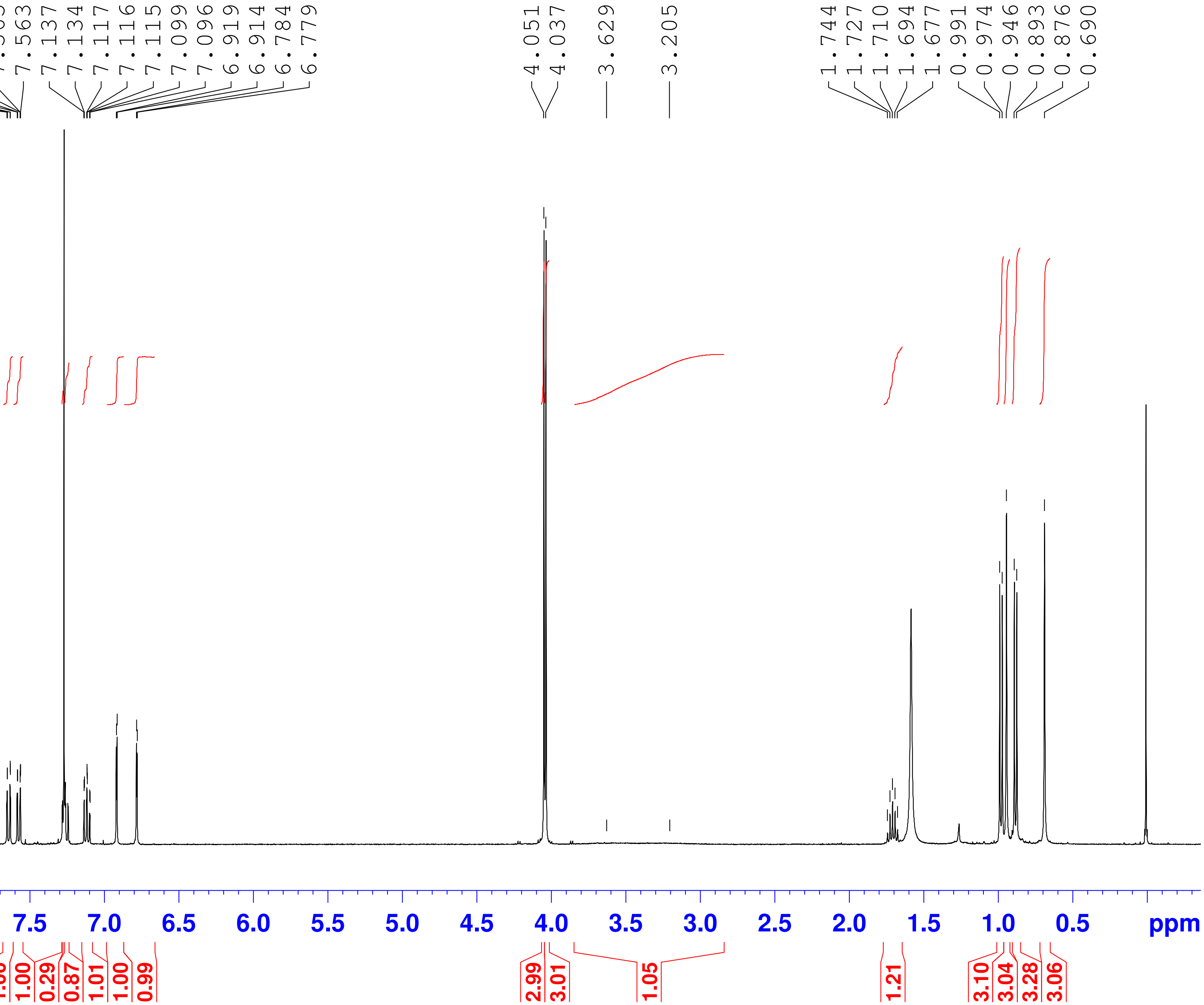

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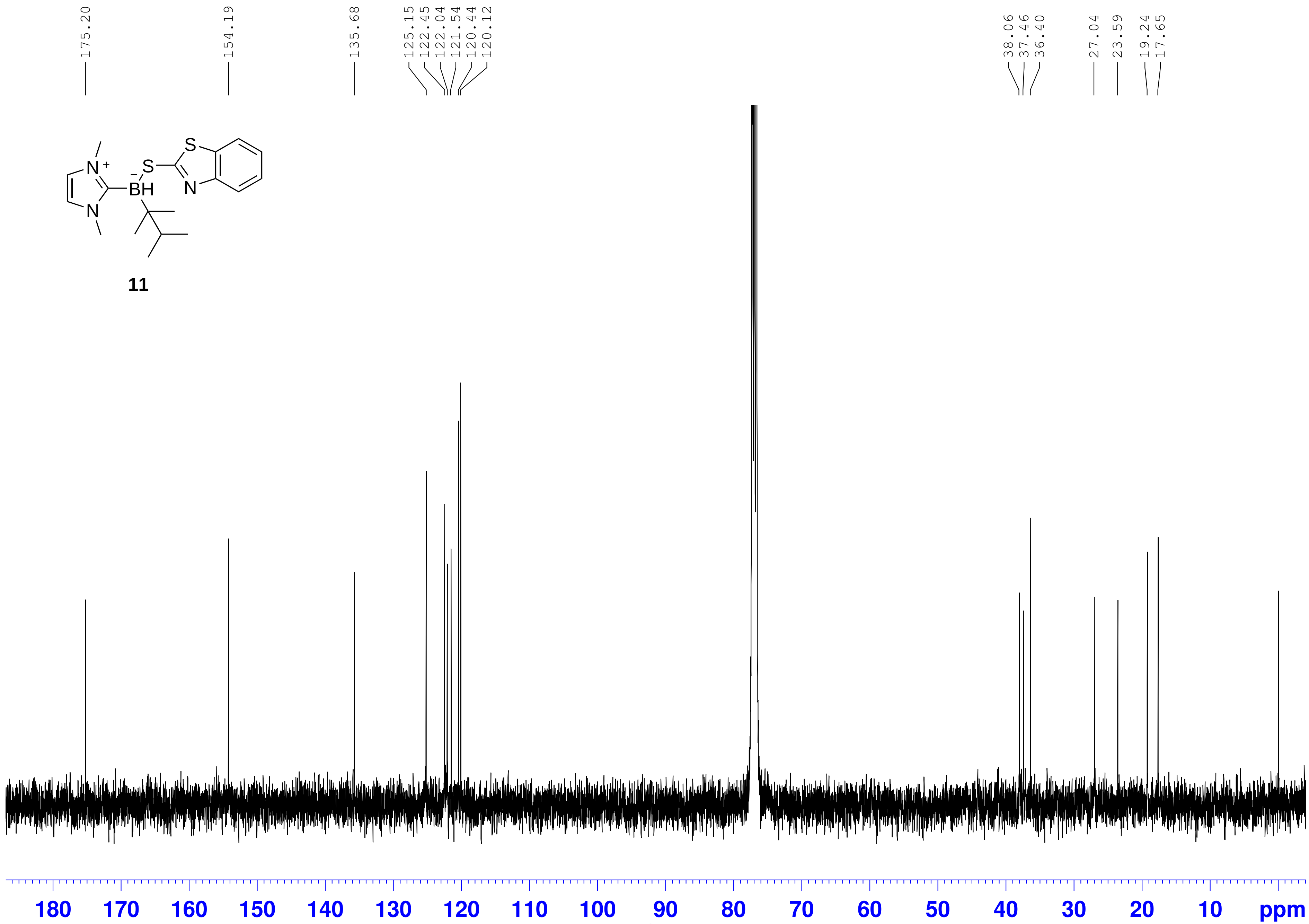

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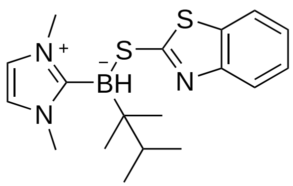

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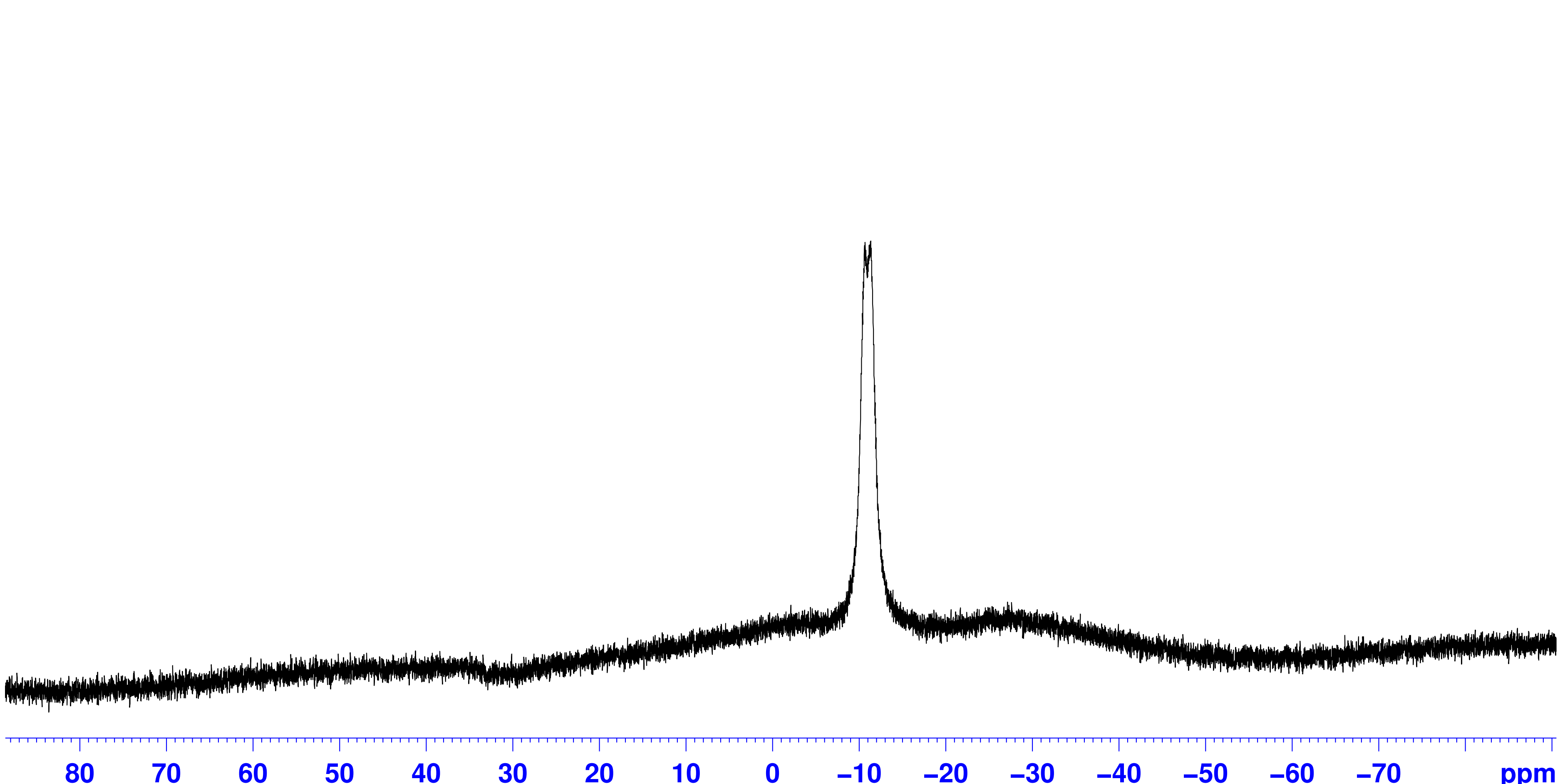

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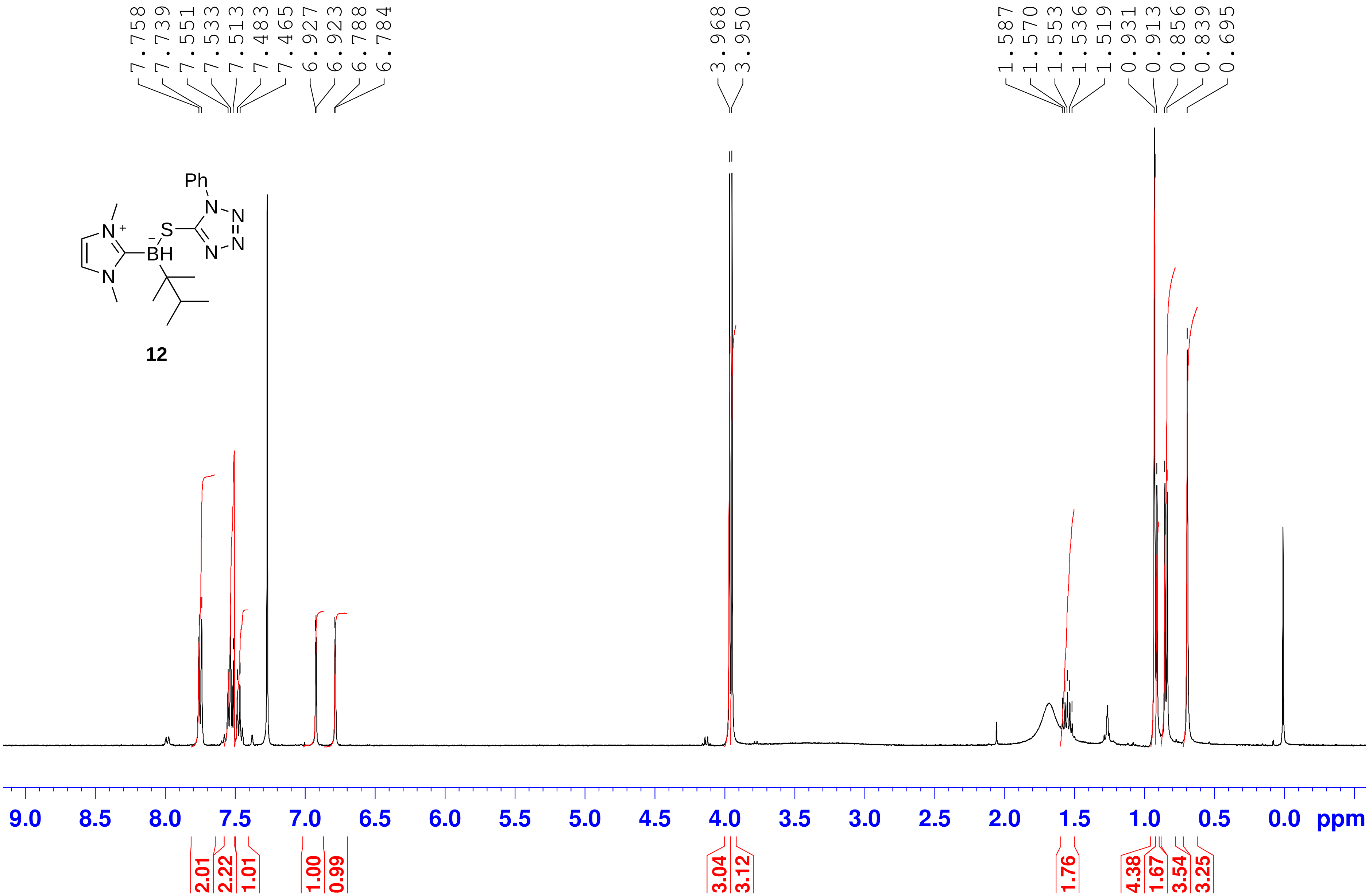

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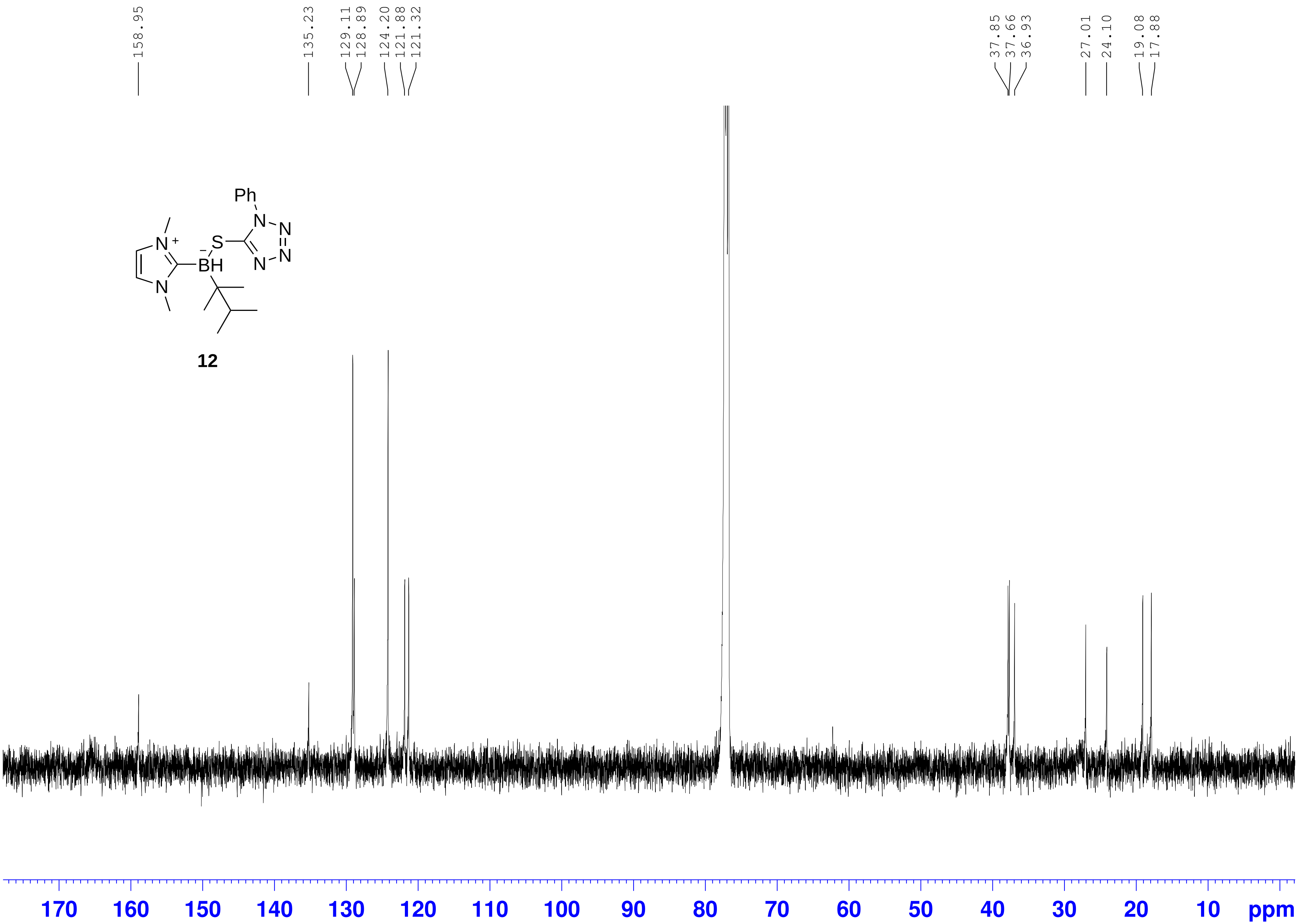

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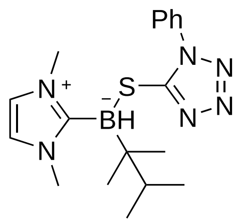

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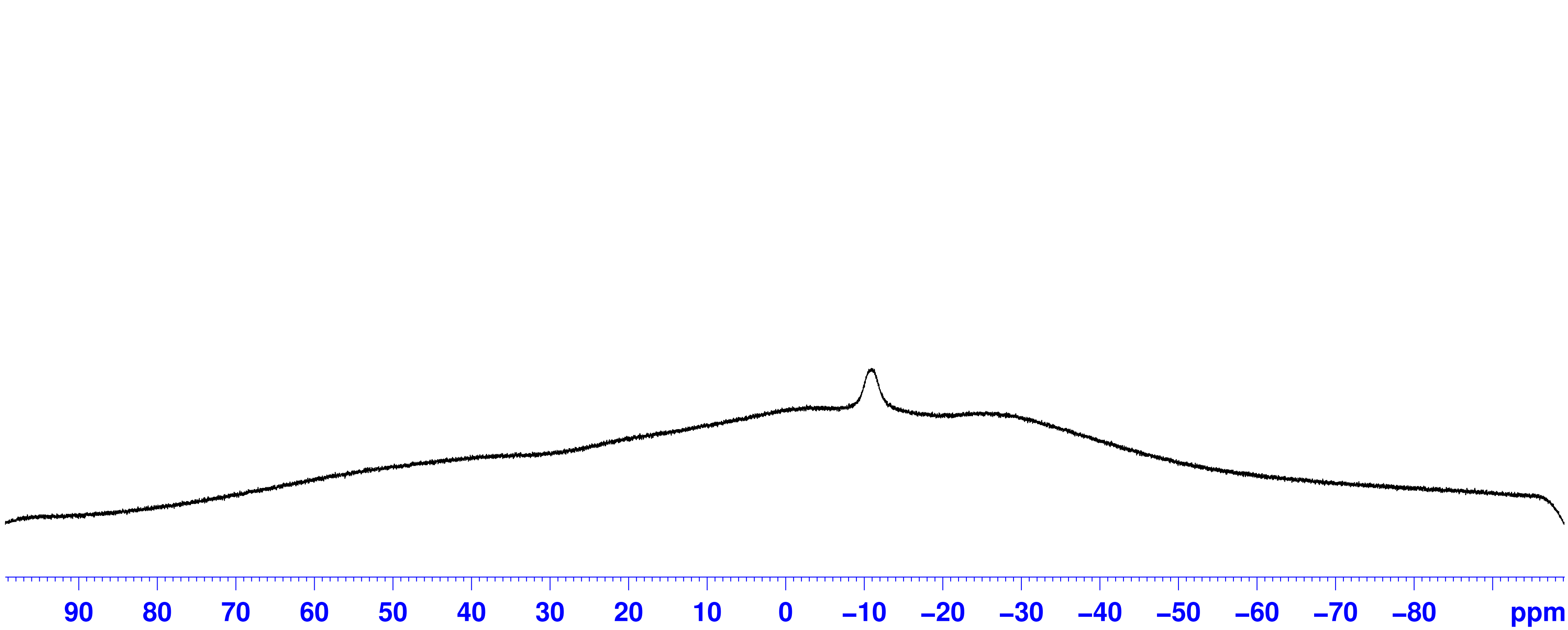
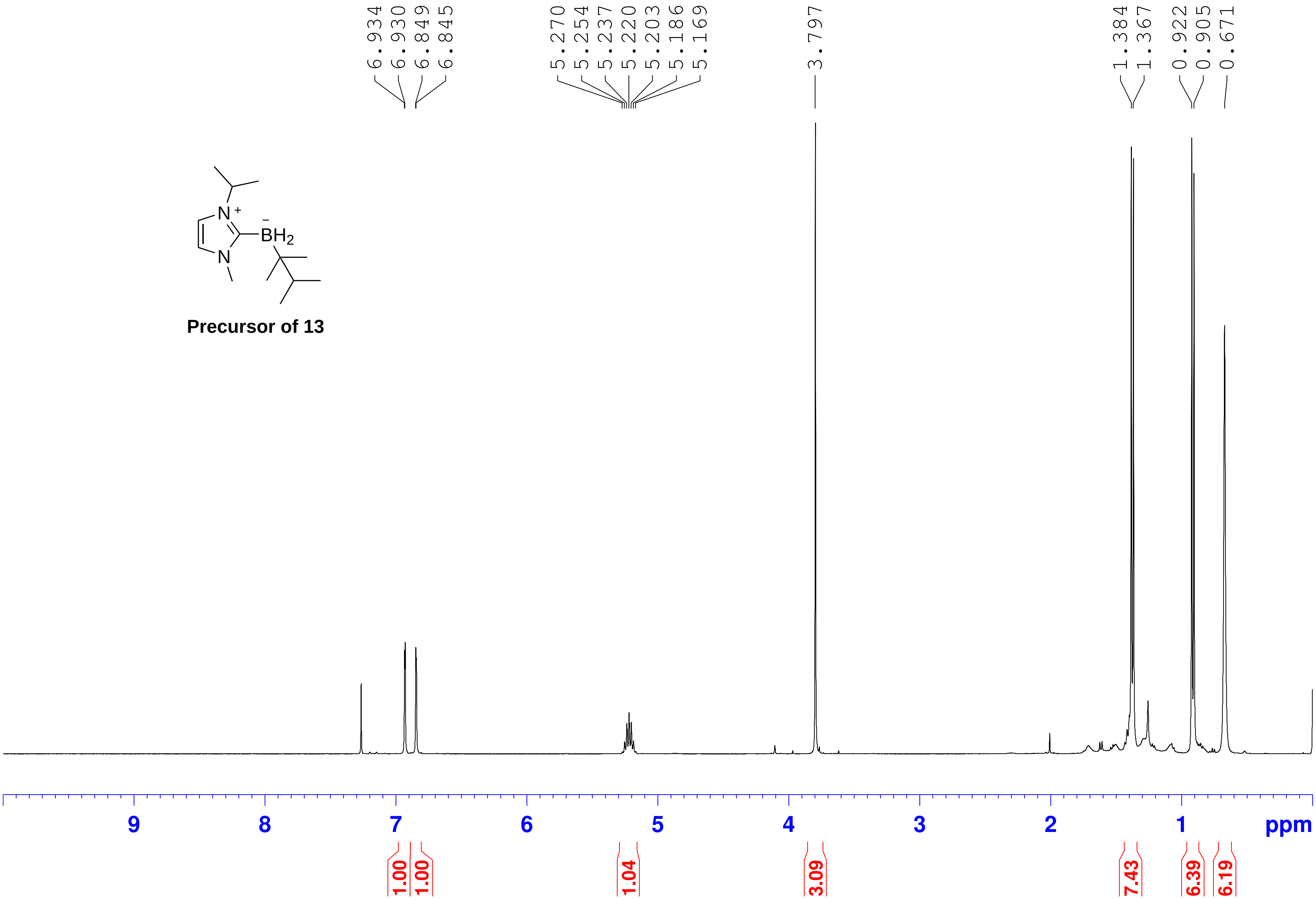


XL-RB-4’ 400A HNMR CDCl3 02/27/14



Precursor of 13

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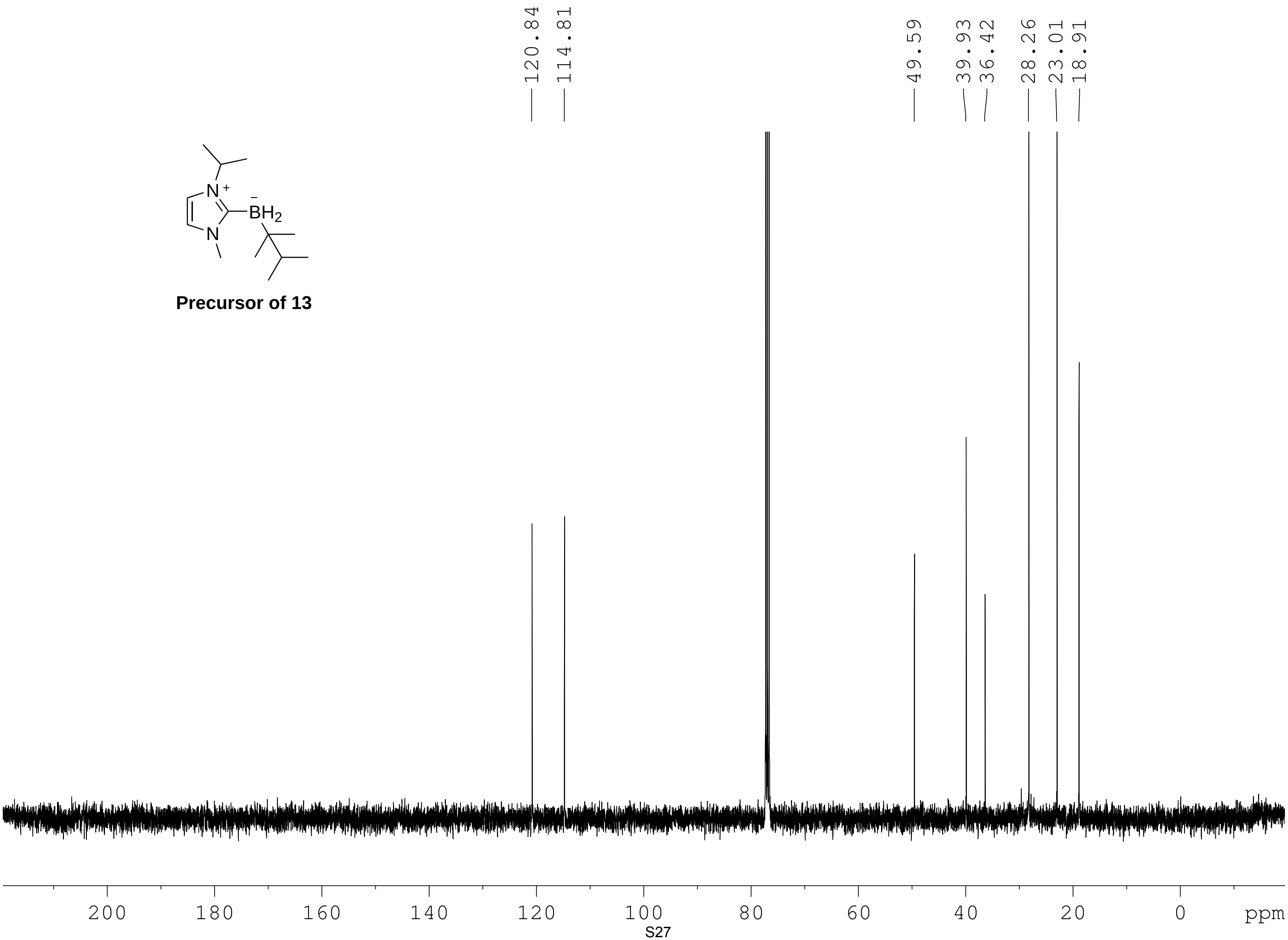

Precursor of 13

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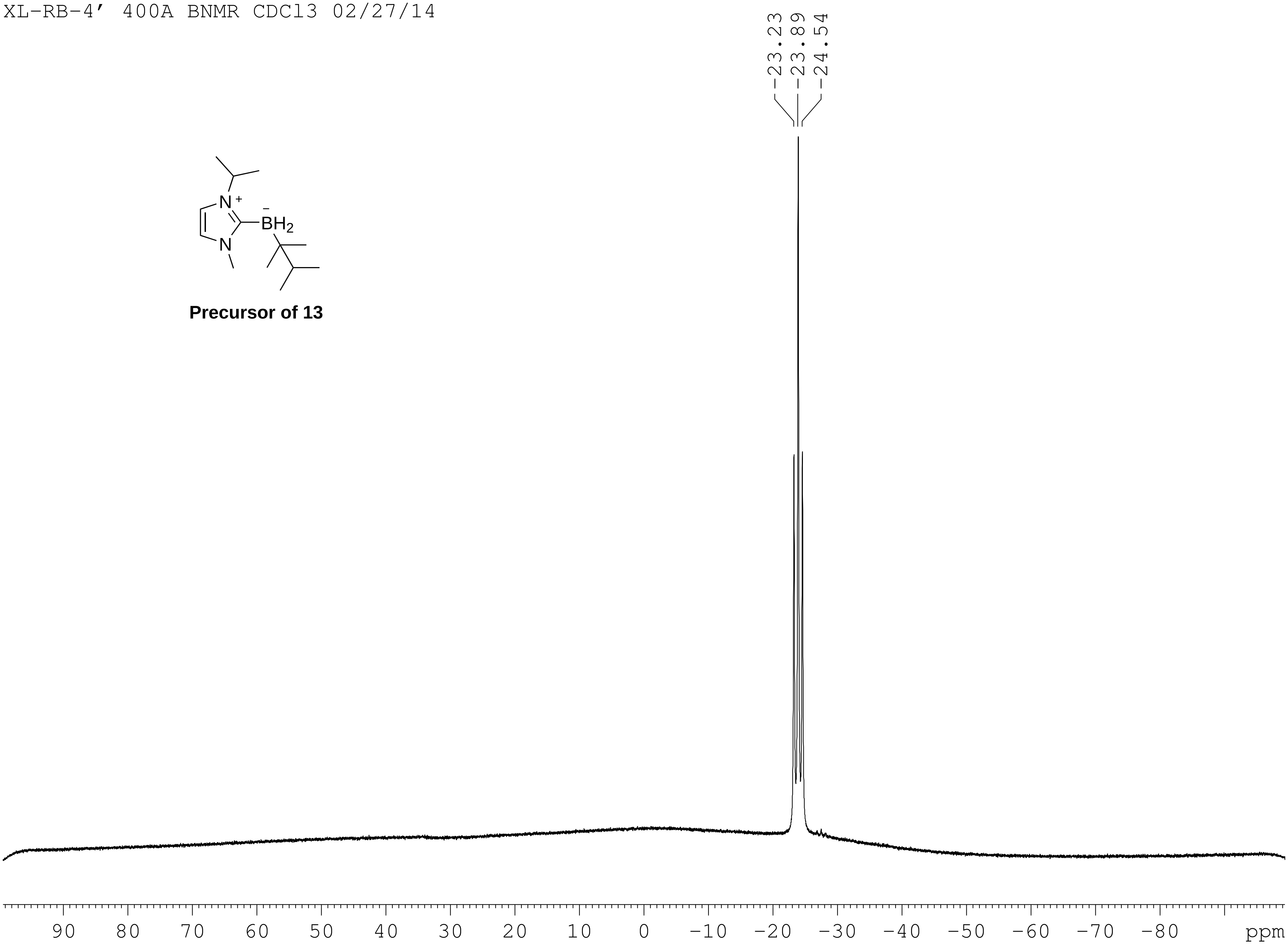

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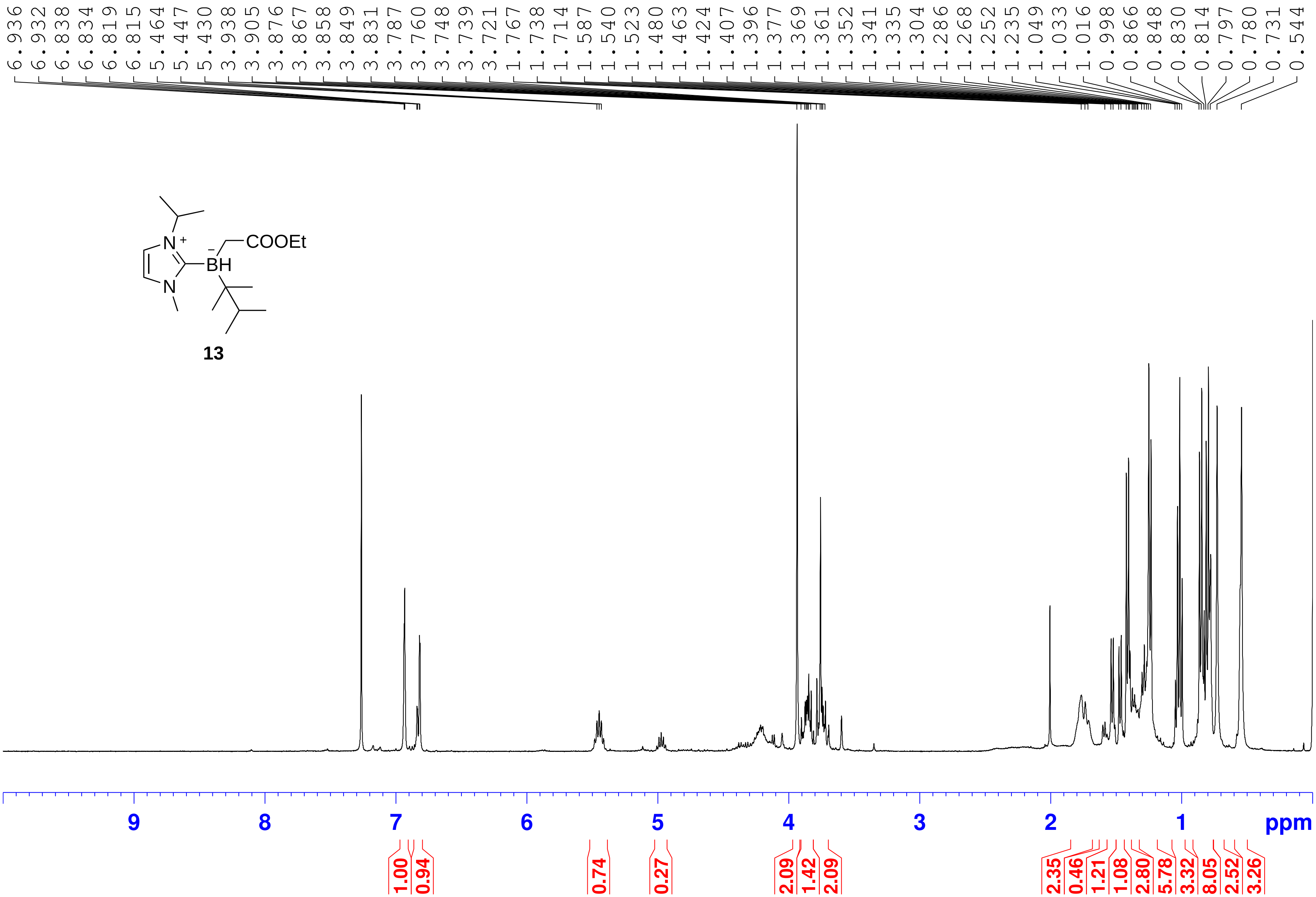

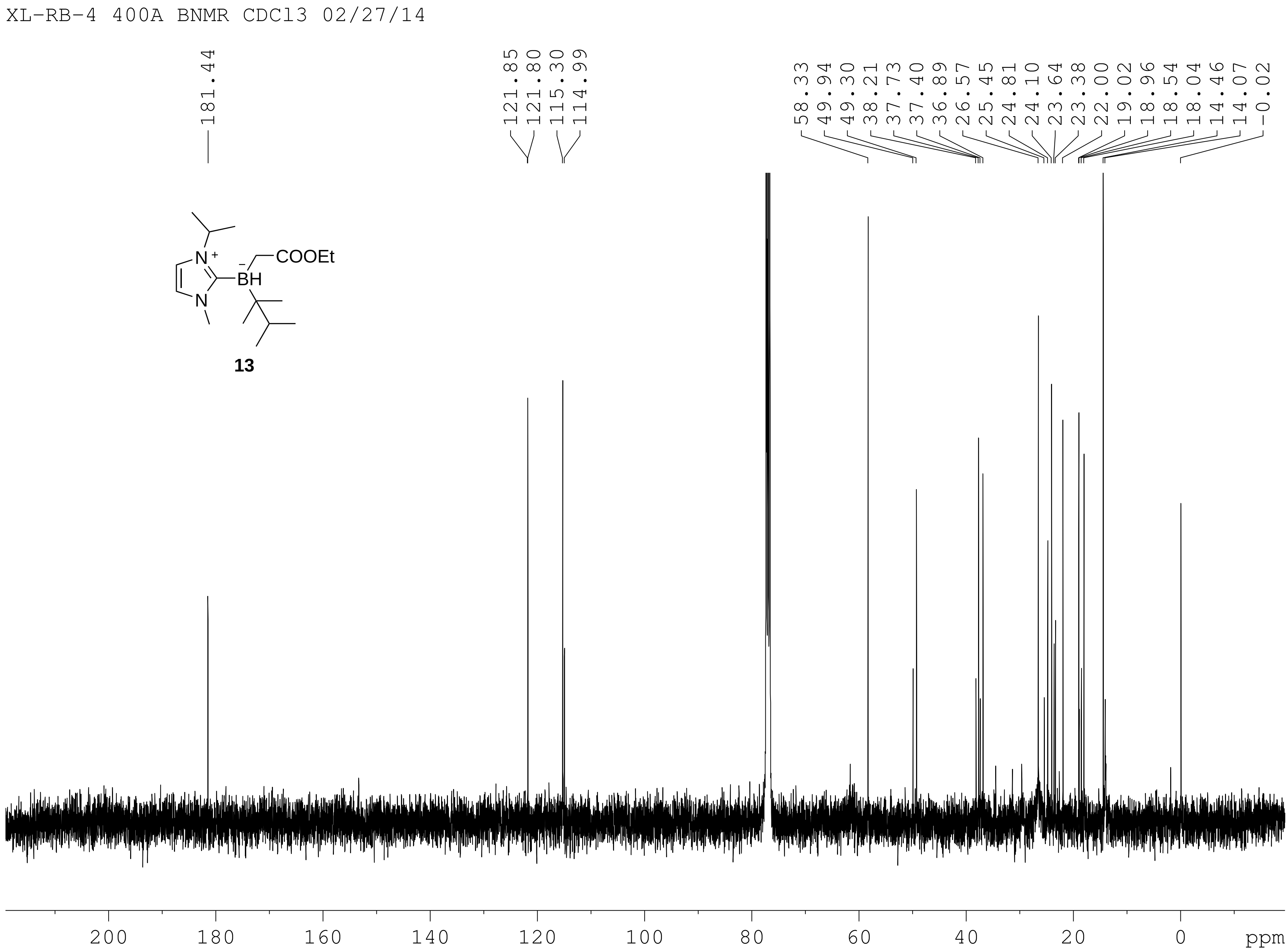
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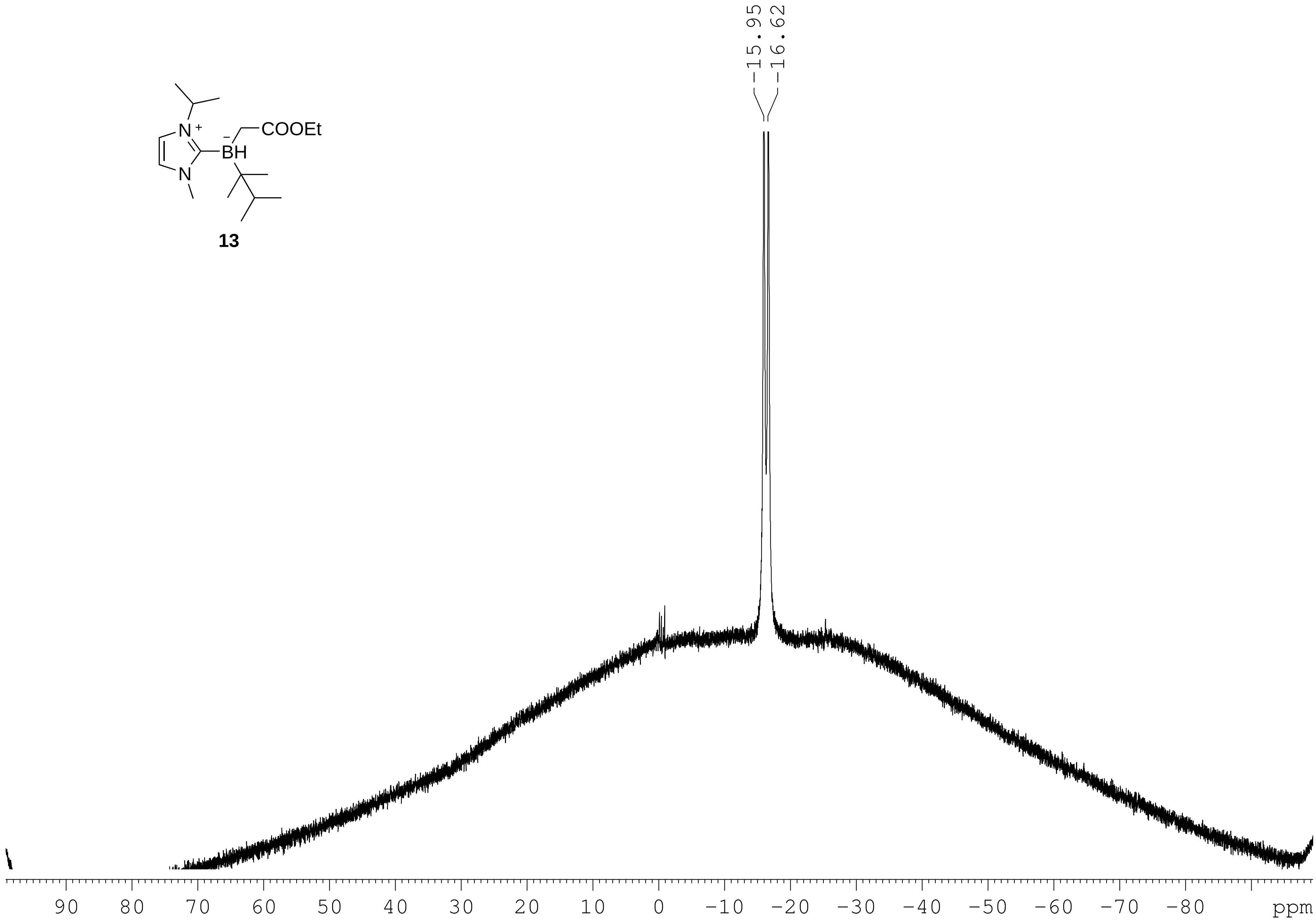

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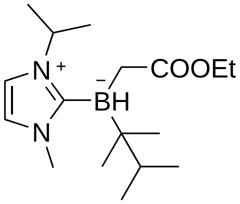

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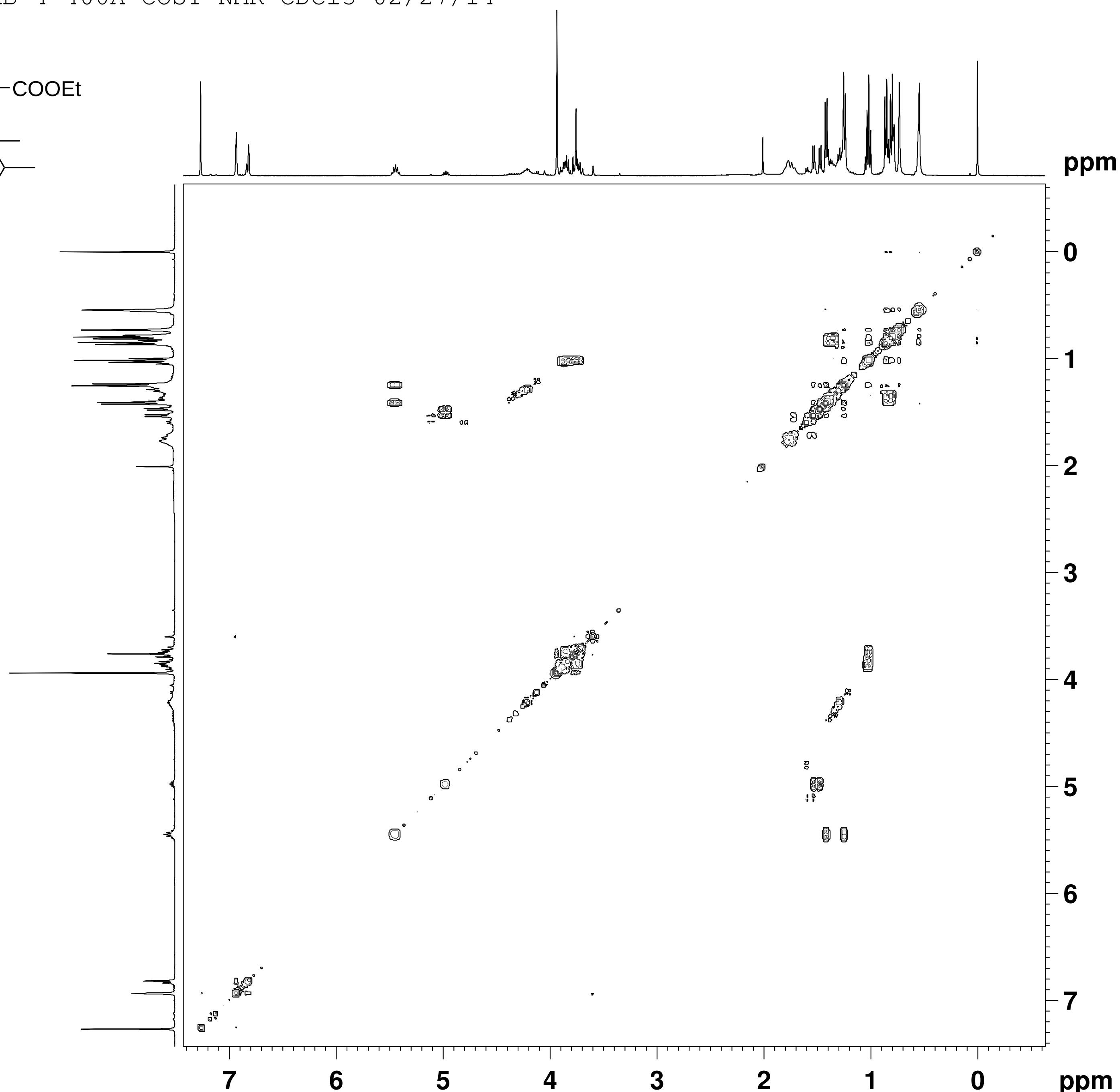

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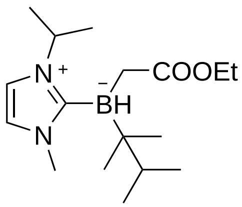

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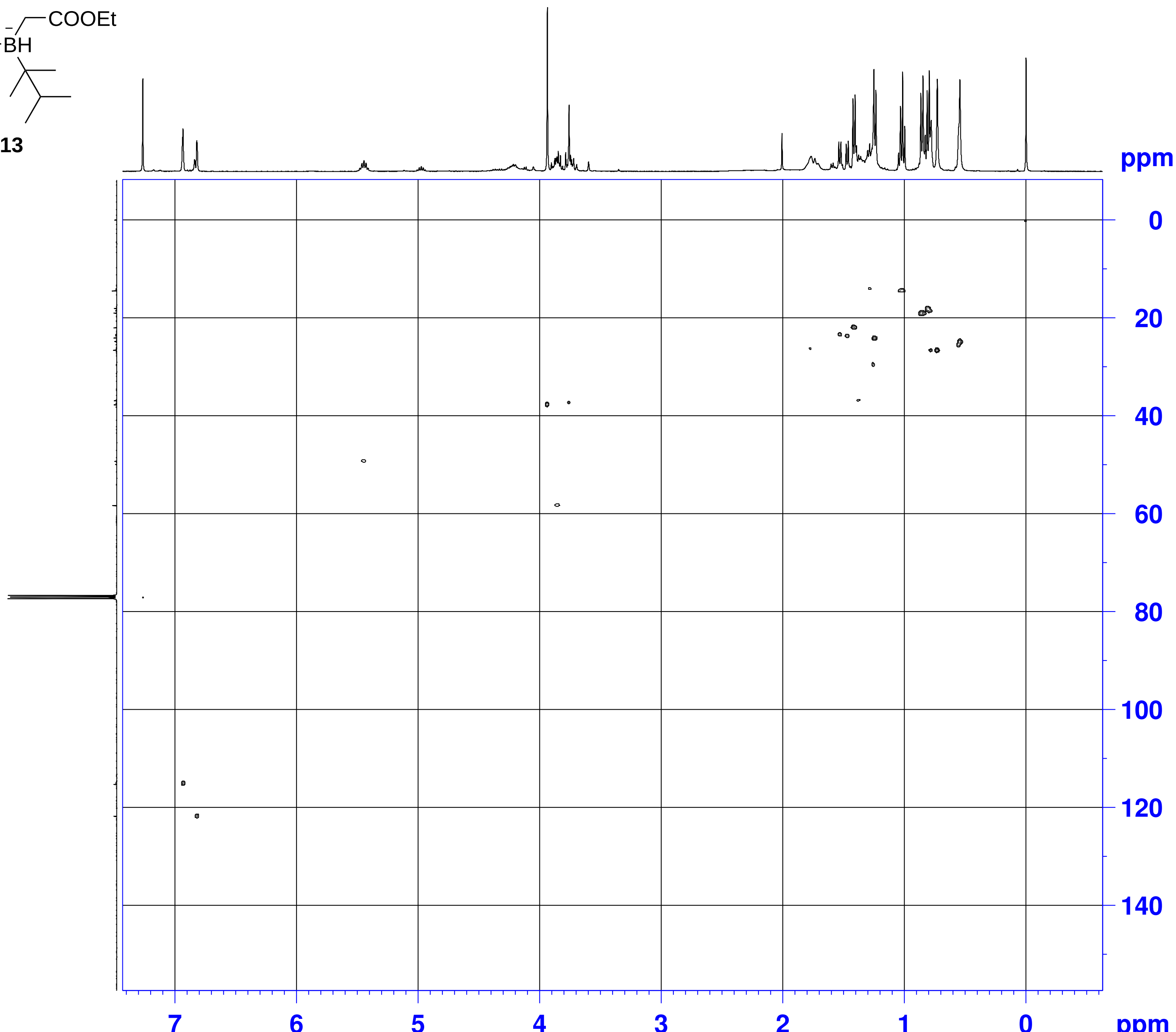

BRUKER

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EXPNO	15	
PROCNO	1	
Date_	20140227	
Time	17.55	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	hsqcetgpsi	
TD	1024	
SOLVENT	CDCl3	
NS	2	
DS	16	
SWH	3225.806	Hz
FIDRES	3.150202	Hz
AQ	0.1587700	sec
RG	203	
DW	155.000	usec
DE	6.50	usec
TE	555.0	K
CNST2	145.0000000	
D0	0.00000300	sec
D1	1.43712604	sec
D4	0.00172414	sec
D11	0.03000000	sec
D13	0.00000400	sec
D16	0.00020000	sec
D24	0.00110000	sec
IN0	0.00003000	sec
ZGOPTNS		

======== CHANNEL f1 ========

NUC1	1H	
P1	13.75	usec
P2	27.50	usec
P28	1000.00	usec
ND0	2	
TD	256	
SFO1	100.6203	MHz
FIDRES	65.104164	Hz
SW	165.639	ppm
FnMODE	Echo-Antiecho	
SI	1024	
SF	400.1300084	MHz
WDW	QSINE	
SSB	2	
LB	0.00	Hz
GB	0	
PC	1.40	
SI	1024	
MC2	echo-antiecho	
SF	100.6127690	MHz
WDW	QSINE	
SSB	2	
LB	0.00	Hz
GB	0	