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Supporting Information

A Dialkylborenium Ion via Reaction of *N*-Heterocyclic Carbene-Organoboranes with Brønsted Acids - Synthesis and DOSY NMR Studies

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1. General remarks

Starting materials sourced from commercial suppliers were used as received unless otherwise stated. Dry solvents, where necessary, were obtained by distillation using standard procedures or by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering based on the Grubbs design.[1]

Petrol refers to the fraction of petroleum ether boiling in the range of 40-60 °C.

Reactions requiring anhydrous conditions were run under an atmosphere of dry nitrogen passed through two sequential drying columns – one packed with calcium chloride and one packed with phosphorous pentoxide; glassware and needles were either flame dried immediately prior to use or placed in an oven (160 °C) for at least 16 h and allowed to cool under an atmosphere of dry nitrogen; liquid reagents, solutions or solvents were added *via* syringe through rubber septa. The removal of solvents *in vacuo* was achieved using either a Büchi rotary evaporator (bath temperatures up to 40°C) at a pressure of either 15 mm Hg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, or a high vacuum line at room temperature.

Commercially available Merck Kieselgel $60F_{254}$ aluminium-backed plates and Macherey-Nagel Polygram Sil G/UV_{254} plastic-backed plates were used for TLC analysis. Visualisation was achieved by UV fluorescence, basic $KMnO_4$ solution and heat, ninhydrin stain and heat, ammonium molybdate solution and heat, dinitrophenylhydrazine and heat, anisaldehyde stain and heat or iodine vapour. Flash column chromatography was performed using Fluorochem 60 silica: 230-400 mesh (40-63 μm). The crude material was applied to the column as a solution or by pre-adsorption onto silica, as appropriate.

Melting points were determined using a Reichert melting point table and temperature controller and are uncorrected. Infra-red spectra were recorded in the range 4000-600 cm^{-1} on a Perkin Elmer Spectrum either as neat films or solids compressed onto a diamond window. Abbreviations used are: w (weak), m (medium), s (strong) and br (broad).

NMR spectra were recorded on a JEOL GX270, JEOL GX400, JEOL Lambda 300, JEOL Eclipse 400, JEOL Eclipse 300, Varian 400 or Varian 500 spectrometer. Chemical shifts are quoted in parts per million (ppm); ^{1}H NMR spectra are referenced to TMS or residual protons of the deuterated solvent as an internal standard;^{13}C NMR are referenced to TMS or the deuterated solvent as an internal standard; ^{19}F NMR spectra are referenced to CCl_3F as an external standard; ^{11}B NMR spectra are referenced to BF_3 as an external standard. Coupling constants (*J*) are quoted to the nearest 0.1 Hz.Unless otherwise noted, all coupling constants relate to $^{3}J_{H\text{-}H}$ couplings. Other abbreviations used are: s(singlet), d (doublet), t

(triplet), q (quartet), m (multiplet), br (broad) and app.(apparent). Assignments of ^{1}H NMR and ^{13}C NMR signals were made, where possible, using COSY, DEPT, HMQC and HMBC experiments.

Mass spectra were determined by the University of Bristol mass spectrometry service by either electron impact (EI+) or chemical ionisation (CI+) using a Fisons VG Analytical Autospec spectrometer, or by electrospray ionisation (ESI+) using a BrükerDaltonics Apex IV spectrometer or by nanospray ionisation using anApplied BiosystemsQStar XL (Quadrupole-QuadrupoleTime-of-flight) instrument with an Advion Biosciences Nanomate HD 'chip-based' nanospray source. Chiral HPLC was performed on an Agilent 1100 LC system equipped with a quaternary pump, diode array detector and column thermostat under the conditions specified in each case.Chiral GC was run on an Agilent 6890N network GC system with an FID detector under the conditions specified in each case. GCMS was run on an Agilent 6890 series GC system equipped with an Agilent 5973 network mass selective detector.

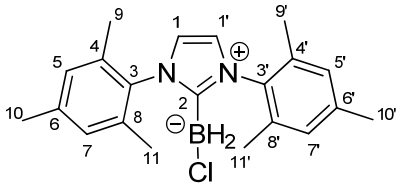
NHC-borane complexes IMes·BH_3 and IMes·9-BBN-H were prepared according to known literature procedures.[2]

2. Experimental details

2.1 Synthesis of IMes·BH$_3$ derivatives

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene-monochloroborane (8)

To a CH_2Cl_2 (3 mL) solution of IMes·BH$_3$**6** (100 mg, 0.32 mmol, 1.0 eq) was added a solution of hydrogen chloride (2 M in Et_2O, 0.16 mL, 0.32 mmol, 1.0 eq), resulting in the evolution of hydrogen gas, and the mixture was stirred for 1 h. The solvent was then removed *in vacuo*to yield **8** as a white solid (111 mg, 100 %).



8

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 12H, C-9, C-9', C-11 & C-11' C<u>H</u>$_3$), 2.24 (br s, 2H, B<u>H</u>$_2$Cl), 2.35 (s, C-10 & C-10' C<u>H</u>$_3$), 7.01 (s, 4H, C-5, C-5', C-7 & C-7' C<u>H</u>), 7.07 (s, 2H, C-1 & C-1' C<u>H</u>).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.6 (C-9, C-9', C-11 & C-11'), 21.0 (C-10 & C-10'), 121.9 (C-1 & C-1'), 129.0 (C-5, C-5', C-7 & C-7'), 133.6 (C-4, C-4', C-8 & C-8'), 134.7 (C-6 & C-6'), 139.4 (C-3 & C-3').No C-2 carbonsignal observed.

^{11}B NMR (96 MHz, $CDCl_3$): δ -19.4 (br s, <u>B</u>H$_2$Cl).

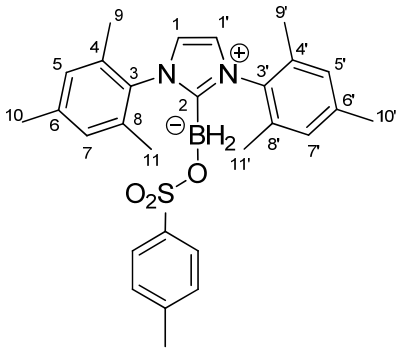
IR (u_{max} cm^{-1}, film): 2919 (w), 2404 (m), 2312 (w, BH_2Cl), 1485 (s), 1442 (m), 1375 (w), 1233 (s), 1179 (m), 1050 (s), 854 (s).

MS (ESI) *m/z*: 351 [M-H].$^+$

HRMS (ESI): calc. for $C_{21}H_{25}BClN_2^+$ 351.1794, found 351.1794.

1,3-Bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene-monotosylborane (9)

To a chloroform (1.4 mL) solution of IMes·BH_3 (**6**) (50 mg, 0.16 mmol, 1.0 eq) was added freshly dried (Dean-Stark) toluenesulfonic acid (27 mg, 0.16 mmol, 1.0 eq), resultingin the evolution of hydrogen gas, then the mixture was stirred for 1 h. The solvent was removed and the product dried *in vacuo*to yield **9** as a white solid (65 mg, 85 %).



9

$^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 12H, C-9, C-9', C-11 & C-11' C$\underline{H}_3$), 2.02 (s, 2H, B$\underline{H}_2$Ts), 2.24 (s, 3H, Ts-C$\underline{H}_3$), 2.26 (s, 6H, C-10 & C-10' C$\underline{H}_3$), 6.86 (s, 2H, C-1 & C-1 C$\underline{H}$), 6.92 (d, *J* = 8.1 Hz, 2H, Ts-C$\underline{H}$), 6.96 (s, 4H, C-5, C-5', C-7 & C-7' C$\underline{H}$), 7.20 (d, *J* = 8.1 Hz, 2H, Ts-C$\underline{H}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4 (C-9, C-9', C-11 & C-11'), 21.1 (C-10 & C-10'), 21.4 (Ts-$\underline{C}H_3$), 122.1 (C-1 & C-1'), 127.1 (Ts-$\underline{C}$H), 128.3 (Ts-$\underline{C}$H), 129.0 (C-5, C-5', C-7 & C-7'), 133.4 (C-4, C-4', C-8 & C-8'), 134.7 (C-6 & C-6'), 136.7 (Ts-$\underline{C}CH_3$), 139.4 (C-3 & C-3'), 141.1 (Ts-$\underline{C}SO_3$).No C-2 carbonsignal observed.

^{11}B NMR (128 MHz, $CDCl_3$): δ -12.4 (broad s, $\underline{B}H_2$OTs).

IR (υ_{max} cm^{-1}, film): 2980 (w), 2920 (w), 2424 (w), 2259 (w), 1535 (m), 1442 (m), 1211 (s), 1190 (s), 1009 (s), 912 (m).

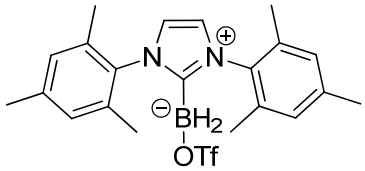
MS (ESI) *m/z*: 487 $[M-H]^+$.

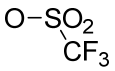
HRMS (ESI): calc. for $C_{28}H_{32}BN_2O_3S^+$ 487.2238, found 487.2221.

m.p. >130 °C (dec).

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene-borane-mono(trifluoromethanesulfonate) (10)

To a rapidly stirred CH_2Cl_2 (3 mL) solution of IMes·BH_3 (**6**) (62 mg, 0.20 mmol, 1.0 eq) at -40 °C, was added dropwisea solution of TfOH (0.47 M in DCM, 0.42 mL, 0.20 mmol,1.0 eq) over 30 minutes, resultingin the evolution of hydrogen gas. The mixture was stirred at -40 °C for 15minutes then warmed to ambient temperature andan aliquot was analysed by ^{11}B and ^{19}F NMR spectroscopy.



NB. OTf = 

10

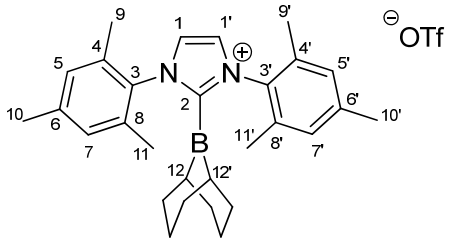
^{11}B NMR (96 MHz, DCM, unlocked): δ -10.4 (t, *J* = 98.8 Hz, $\underline{B}H_2OTf$).

^{19}F NMR (282 MHz, DCM, unlocked): δ -76.8 (s, $BH_2SO_3C\underline{F}_3$).

2.2 Synthesis of NHC-stabilised dialkylborenium ion

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane trifluoromethanesulfonate (11)

To a CD_2Cl_2 (2 mL) solution of IMes·9-BBN (**7**) (166 mg, 0.39 mmol, 1.0 eq) at-40 °C was added dropwisea solution of anhydrous TfOH (0.54 M in CD_2Cl_2, 0.72 mL, 0.39 mmol, 1.0 eq) over 30 minutes, resultingin the evolution of hydrogen gas. The reaction mixture was stirred at -40 °C for 20minutesand then warmed to ambient temperature. After 1h,fluorobenzene (0.76 mL, 0.78 mmol, 2.0 eq) was added and the mixture was transferred to a quartz NMR tube equipped, with a Young's tap, for DOSY NMR analysis.



11

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 – 1.83 (m, 14H, 9-BBN C<u>H</u>& C<u>H</u>$_2$), 2.11 (s, 12H, C-9, C-9', C-11 & C-11' C<u>H</u>$_3$), 2.37 (s, 6H, C-10 & C-10' C<u>H</u>$_3$), 7.09 (s, 4H, C-5, C-5', C-7 & C-7' C<u>H</u>), 7.84 (s, 2H, C-1 & C-1' C<u>H</u>).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 17.7, 18.3, 21.0, 21.9, 35.0, 36.0, 54.4 (C-9, C-9', C-11 & C-11'), 55.8 (C-10 & C-10'), 128.2 (C-1 & C-1'), 131.1 (C-4, C-4', C-8 & C-8'), 132.3 (C-6 & C-6'), 134.8 (C-5, C-5', C-7 & C-7'), 142.6 (C-3 & C-3') 163.1 (C-2).

^{11}B NMR (96 MHz, CD_2Cl_2): δ 81.4 (br s, peak width at ½ height = 715. 8 Hz).

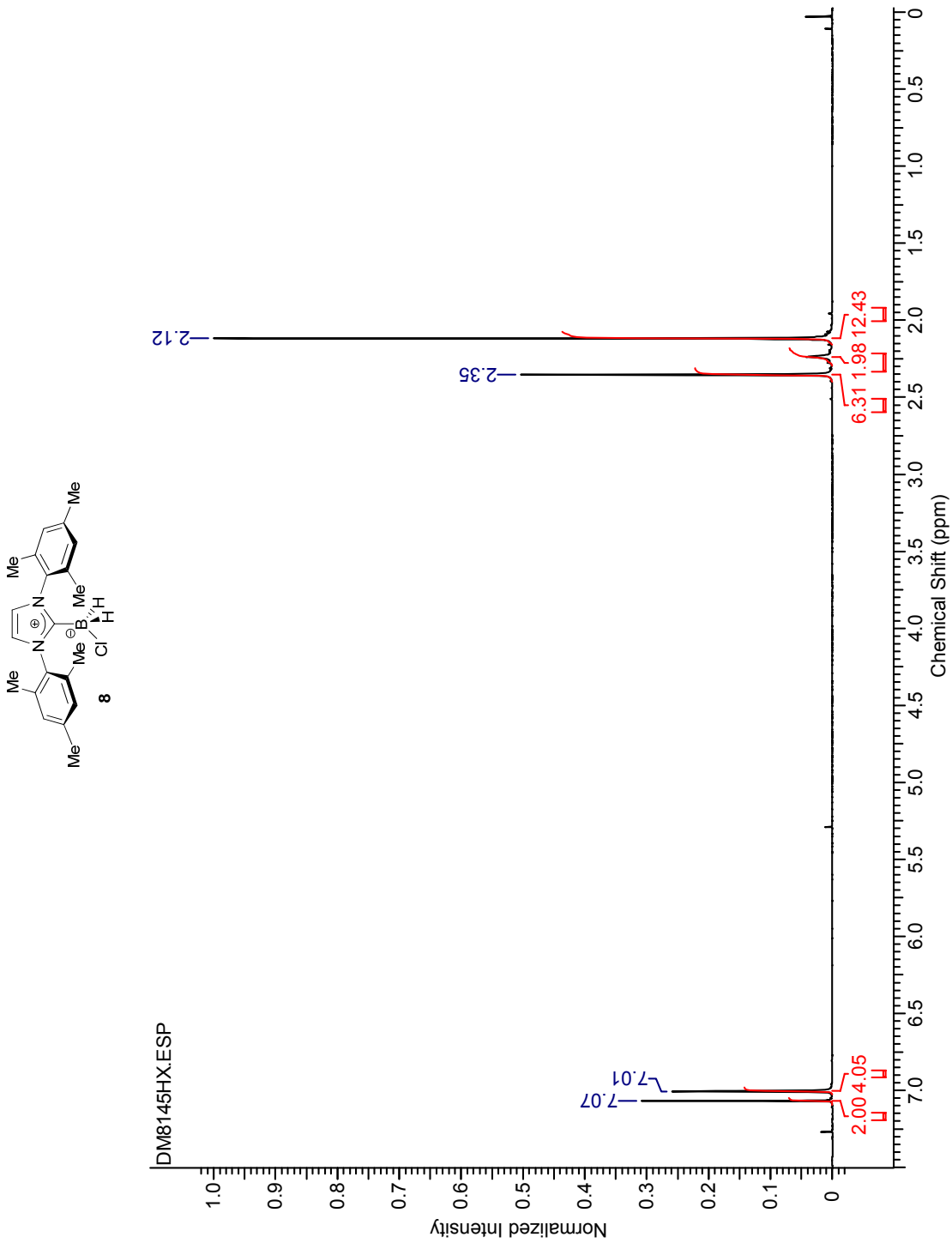
^{19}F NMR (470 MHz, CD_2Cl_2): δ -78.9 (s, $SO_3C\underline{F}_3$).

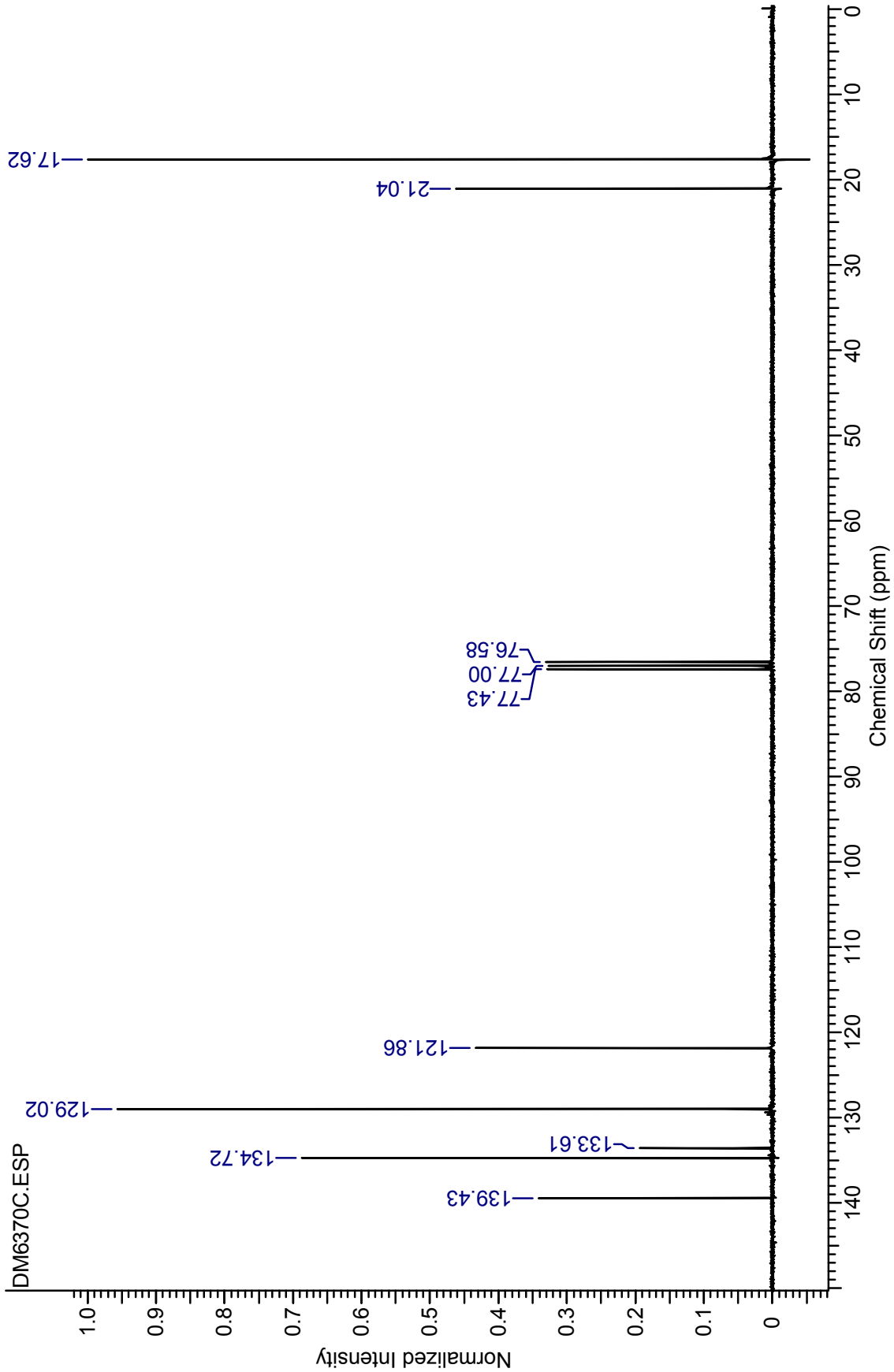
MS (ESI) *m/z*: 425[M].$^+$

HRMS (ESI): calc. for $C_{29}H_{38}BN_2^+$425.3123, found 425.3134.

Diffusion coefficients: ^{1}H (IMes) = 5.84 x 10^{-10} m^2s^{-1}, ^{19}F(OTf) = 6.83 x $10^{-10}m^2s^{-1}$.

3. NMR Spectra

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0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Chemical Shift (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
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21.04
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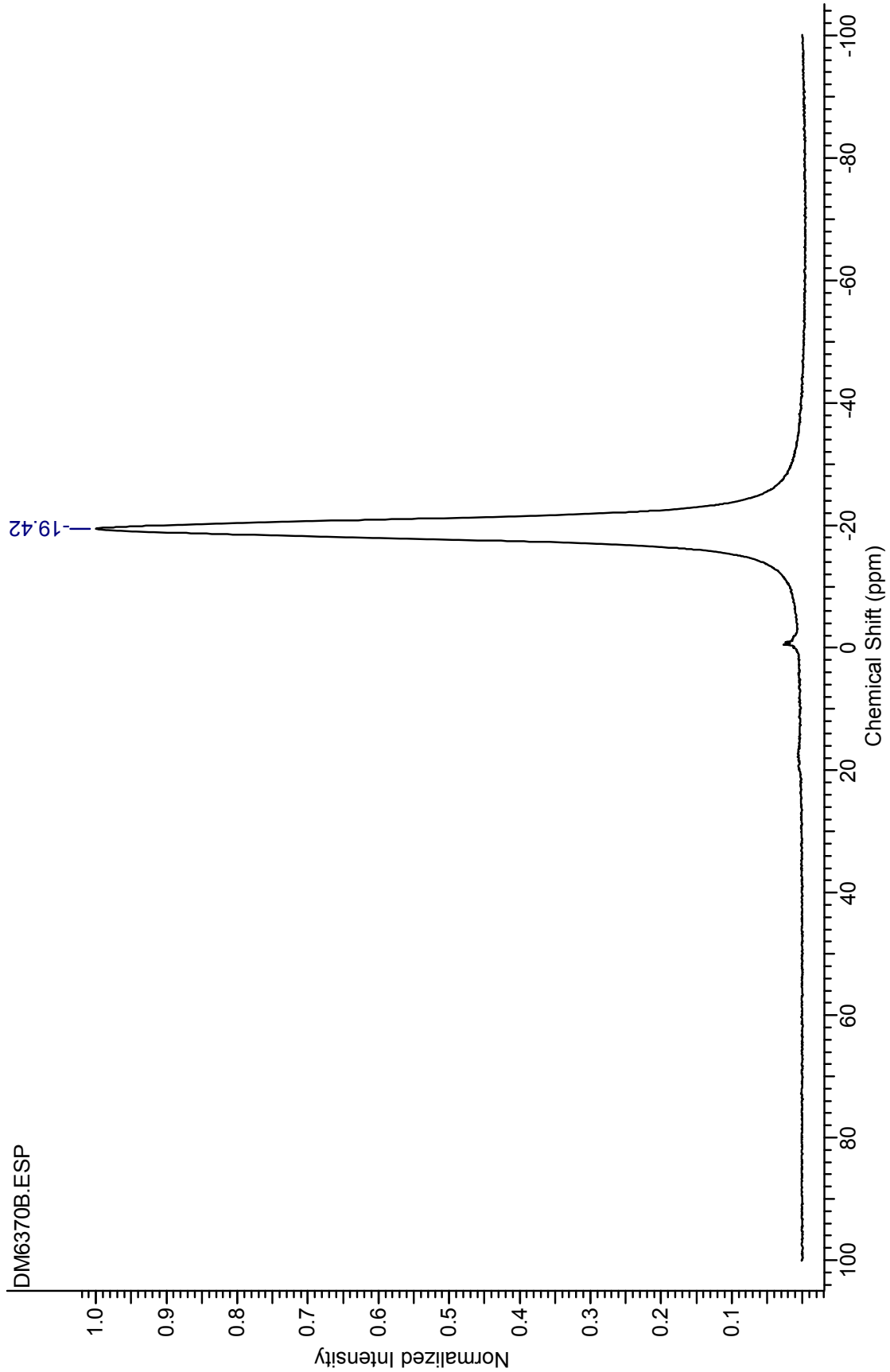
77.00
77.43
121.86
129.02
133.61
134.72
139.43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0.7
0.6
0.5
0.4
0.3
0.2
0.1
100
80
60
40
20
0
-20
-40
-60
-80
-100
Chemical Shift (ppm)
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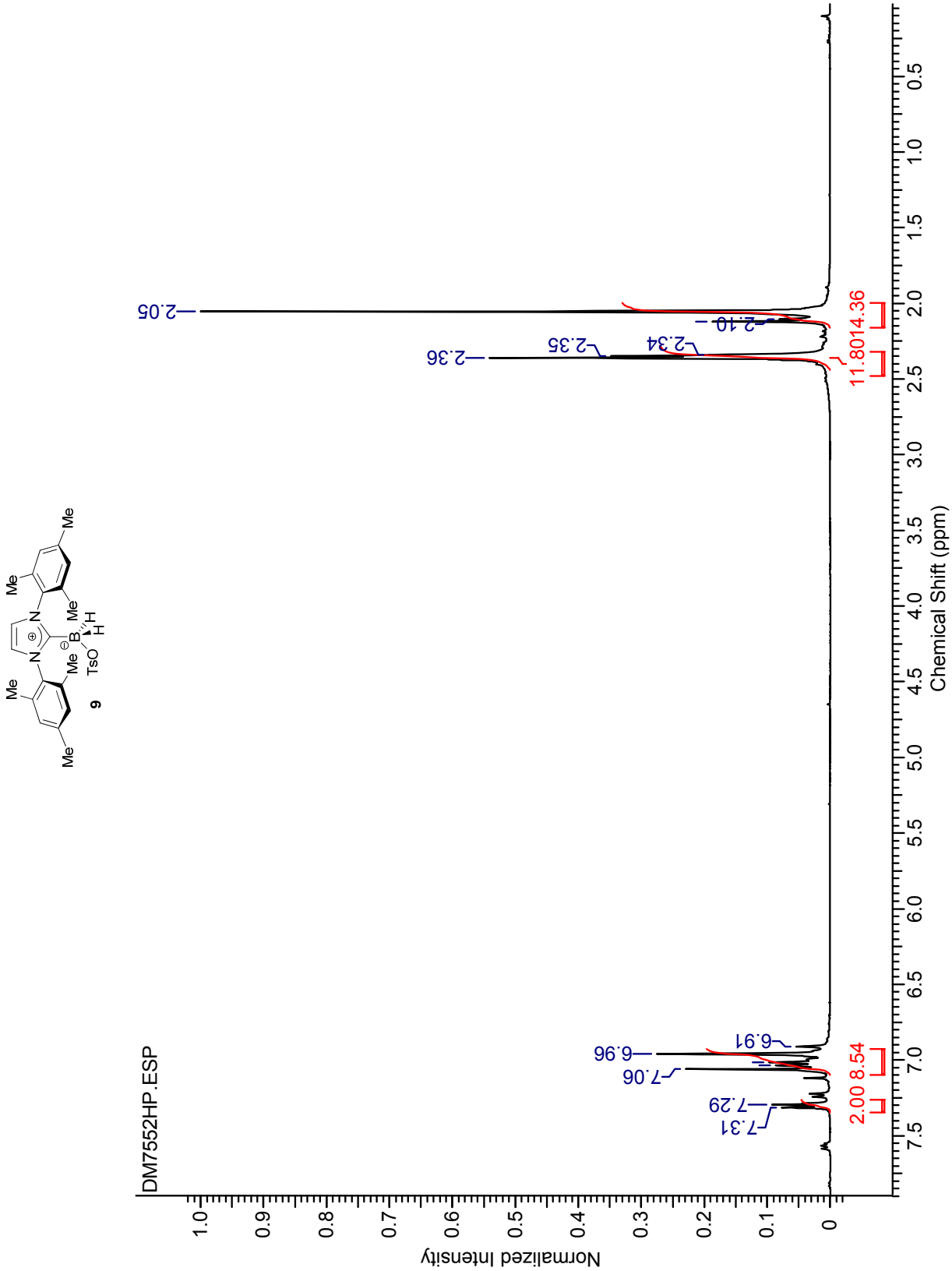
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Chemical Shift (ppm)
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2.34
2.35
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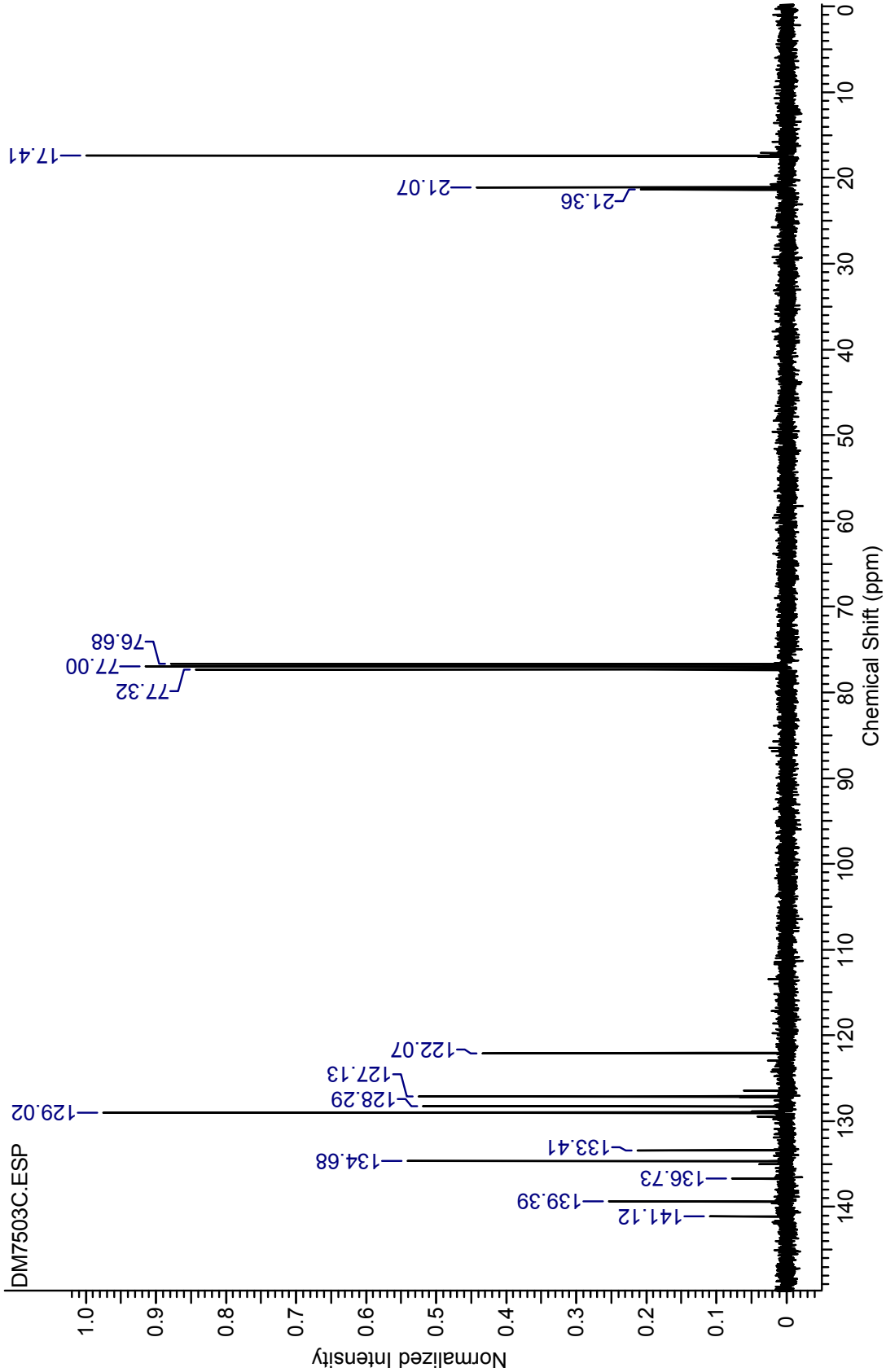
6.91
6.96
7.06
7.29
7.31
2.00
8.54
9
Me
TsO
H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Chemical Shift (ppm)
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127.13
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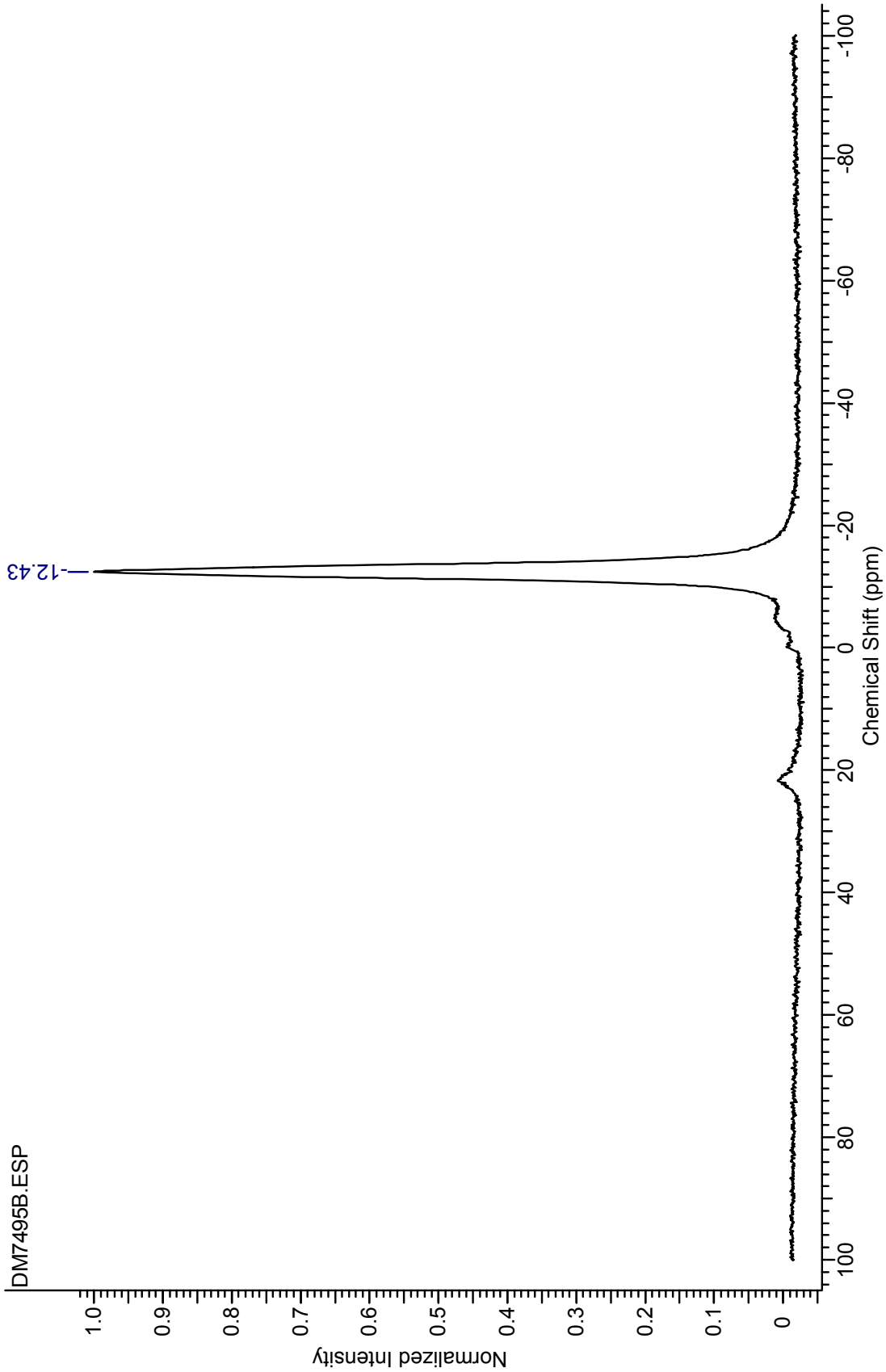
77.32
77.00
76.68
21.36
21.07
17.41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40
20
0
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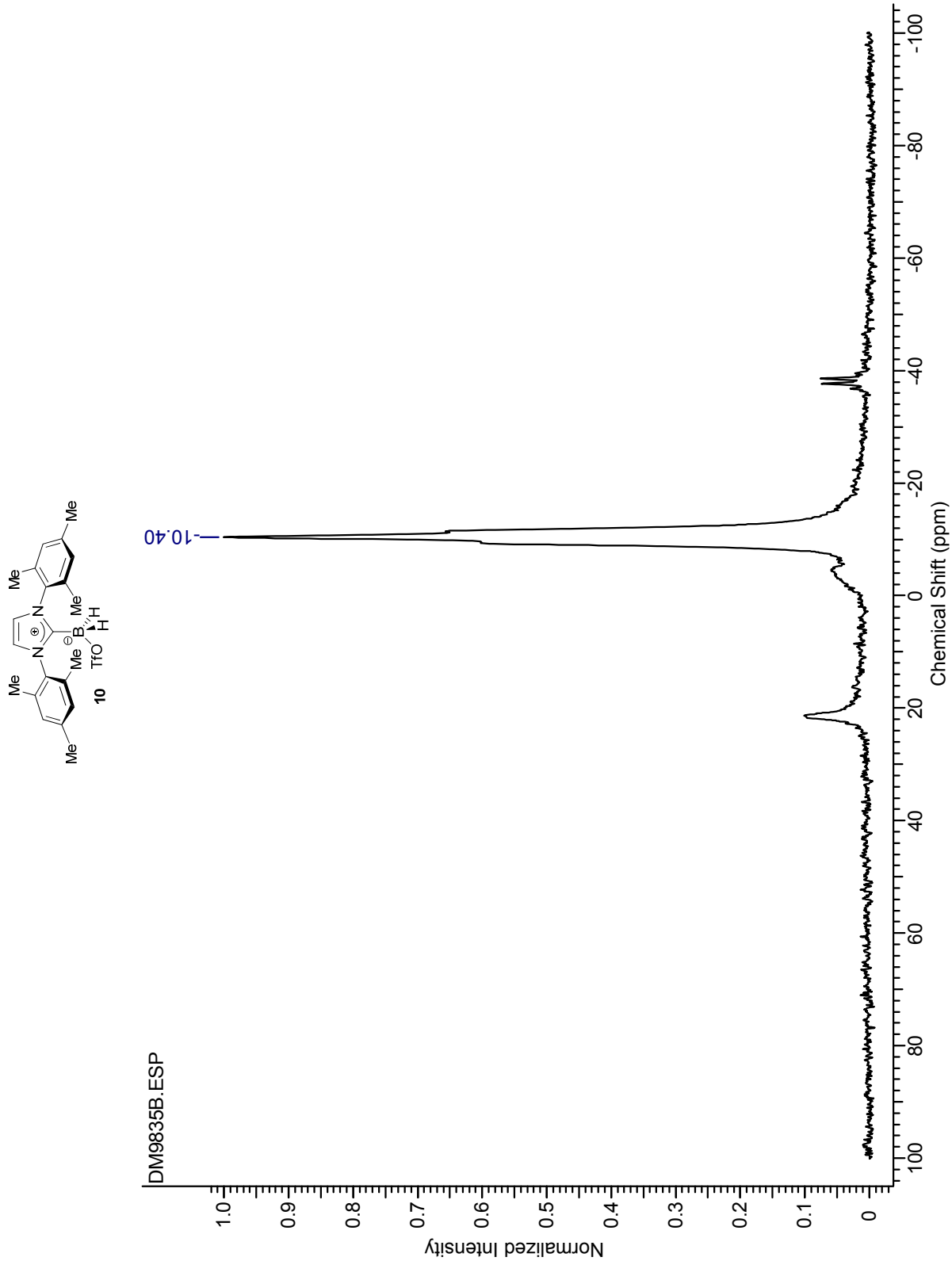
-40
-60
-80
-100
Chemical Shift (ppm)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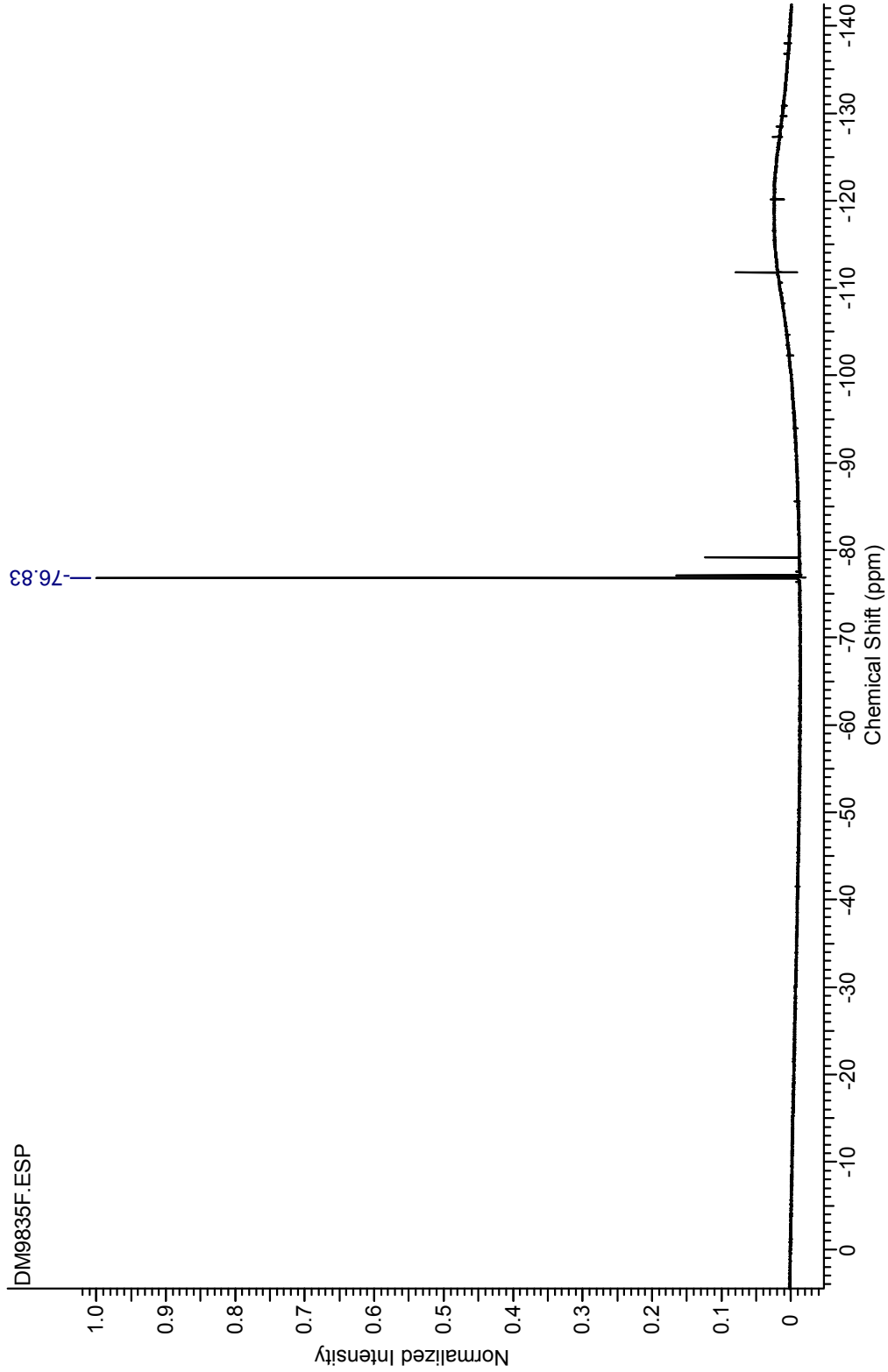
TfO
H
B
N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Normalized Intensity
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0.7
0.6
0.5
0.4
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0.2
0.1
0
Chemical Shift (ppm)
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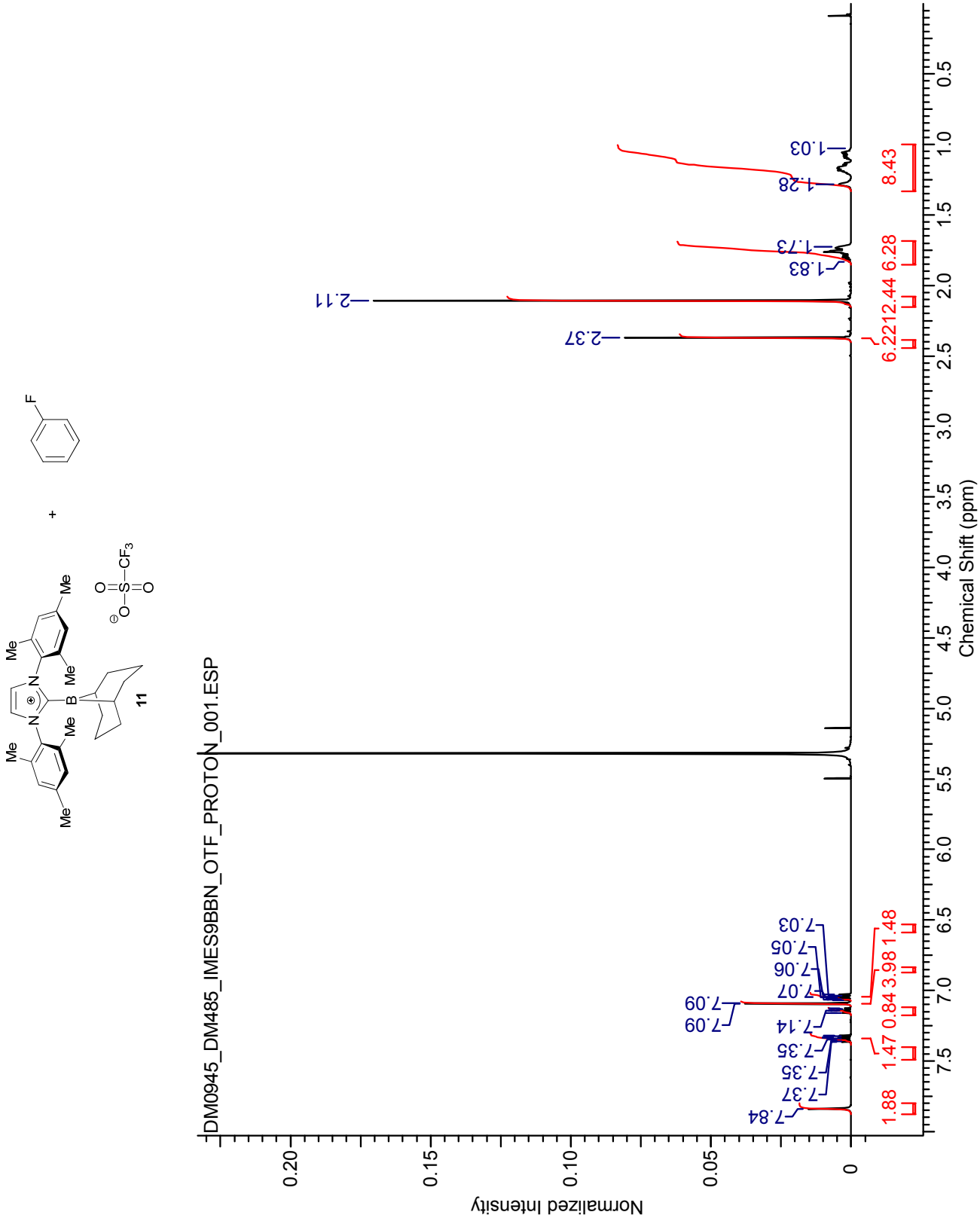
-140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Normalized Intensity
Chemical Shift (ppm)
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7.84
7.37
7.35
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7.09
7.09
7.07
7.06
7.05
7.03
2.37
2.11
1.83
1.73
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1.88
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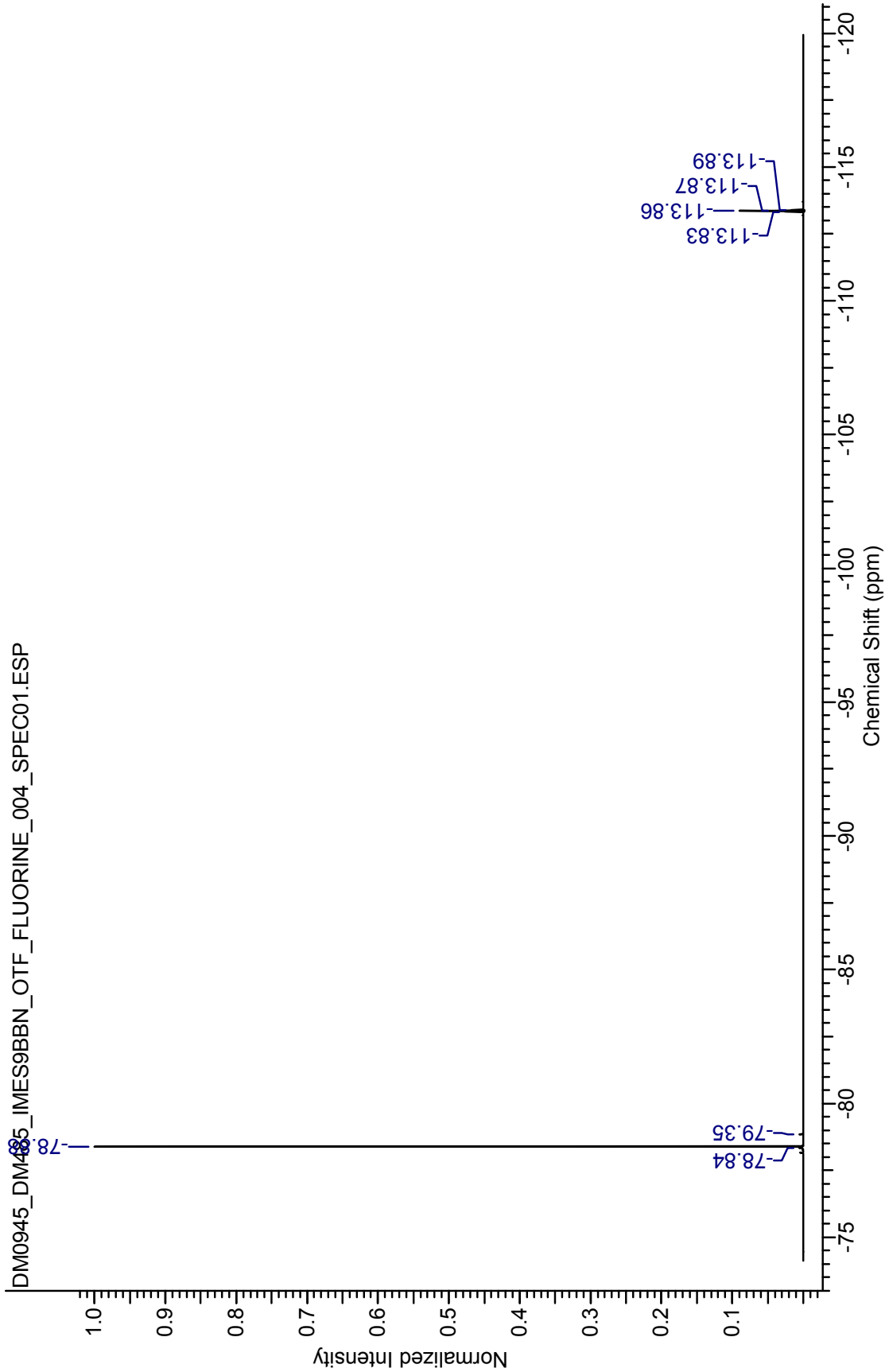
1.48
6.22
12.44
6.28
8.43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-78.84
-79.35
-113.83
-113.86
-113.87
-113.89
Normalized Intensity
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0.7
0.6
0.5
0.4
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0.2
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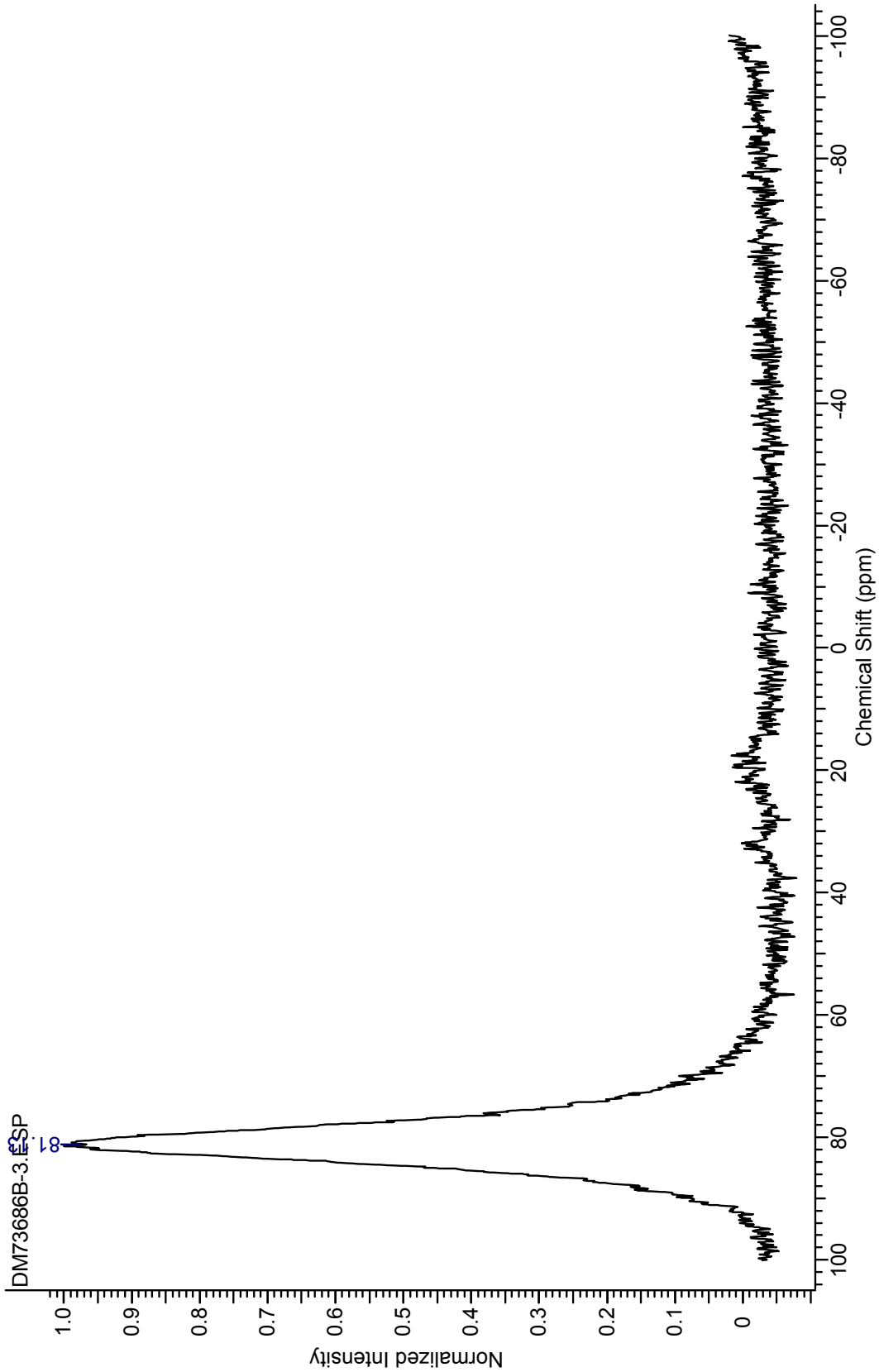
-90
-95
-100
-105
-110
-115
-120
Chemical Shift (ppm)


DM73686B-3.ESP
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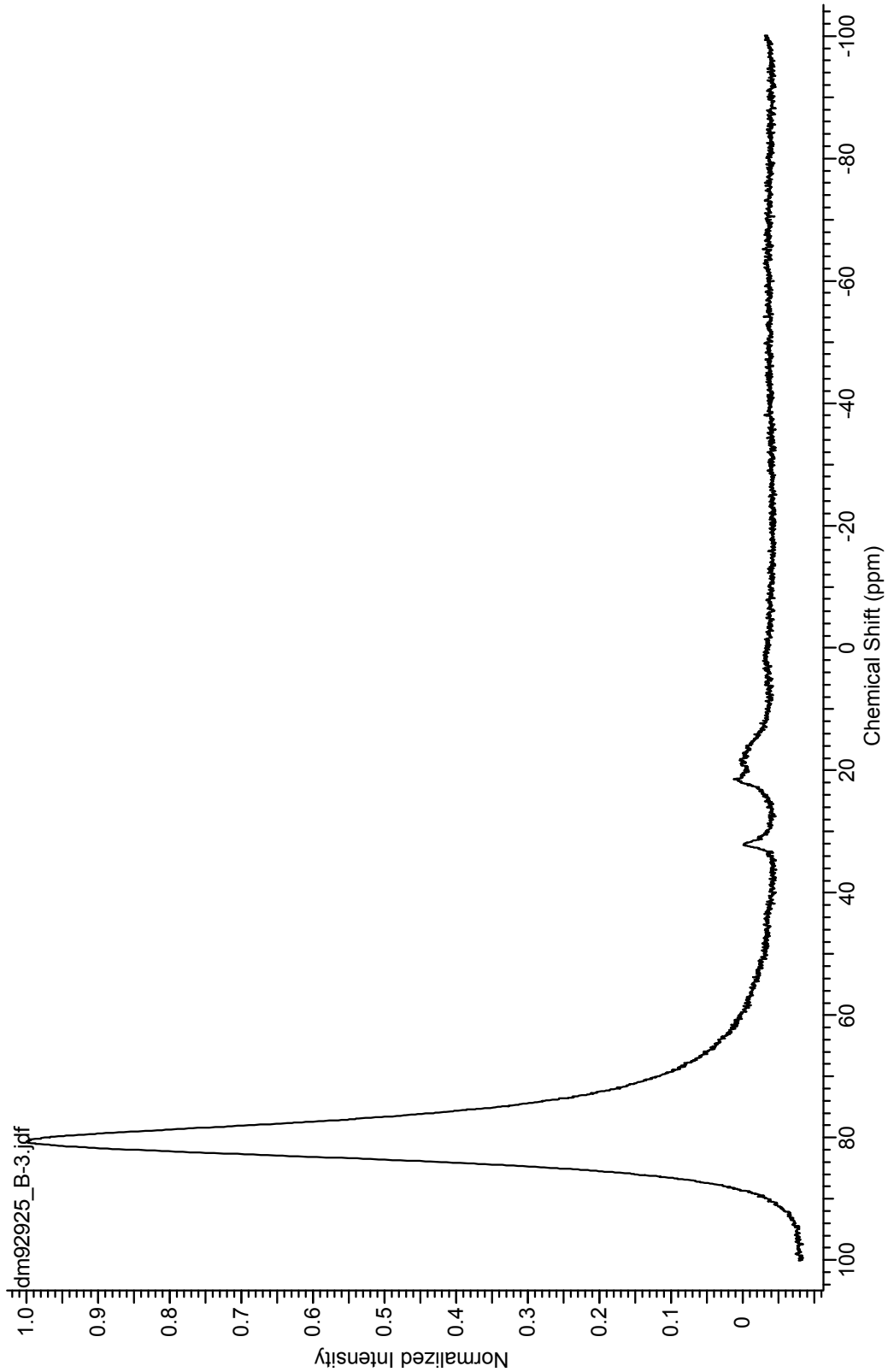
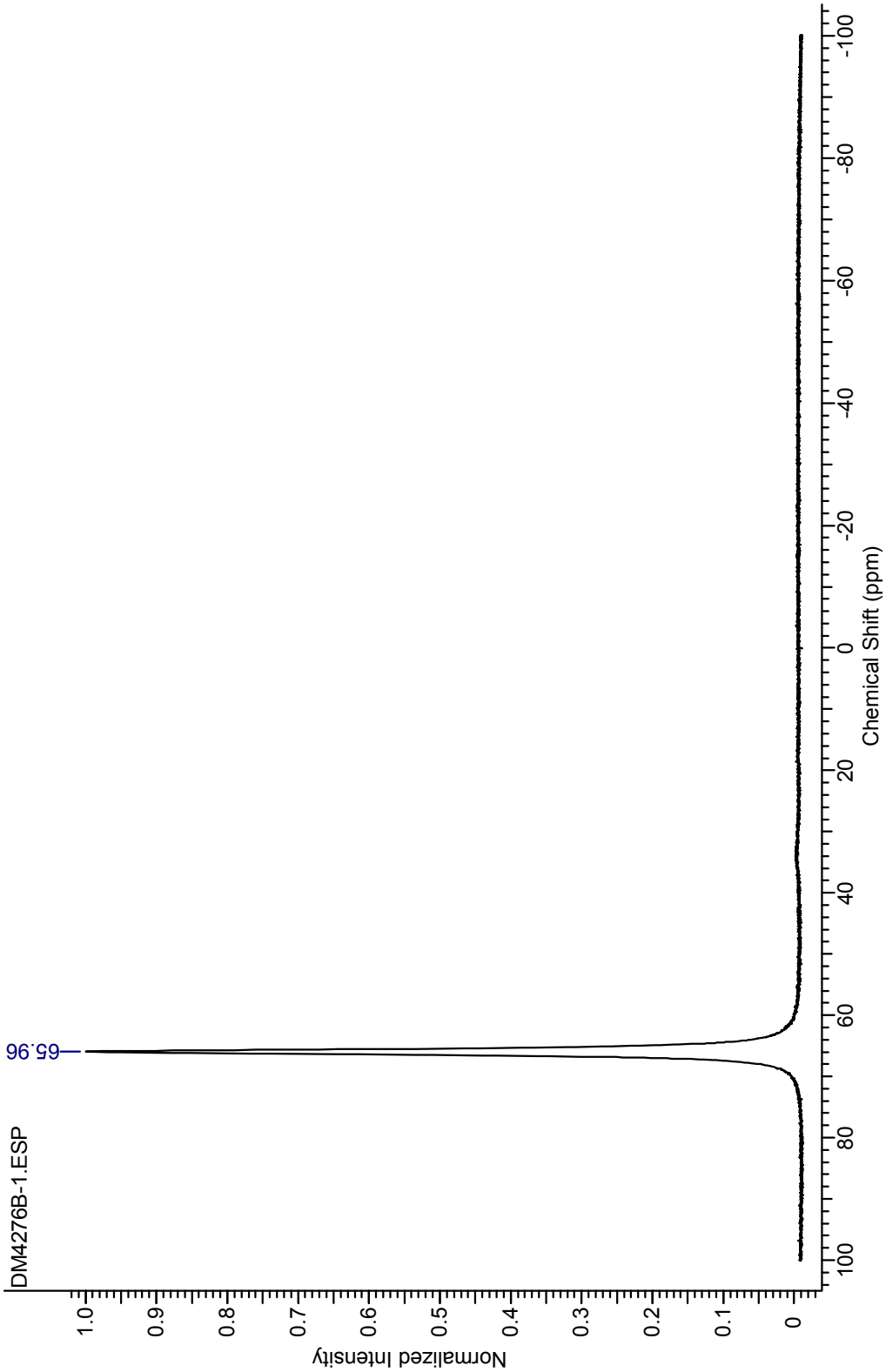
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
80
60
40
20
0
-20
-40
-60
-80
-100
Chemical Shift (ppm)

^{11}B NMR of IMes·9-BBN OTfafter 5 days at room temperature:



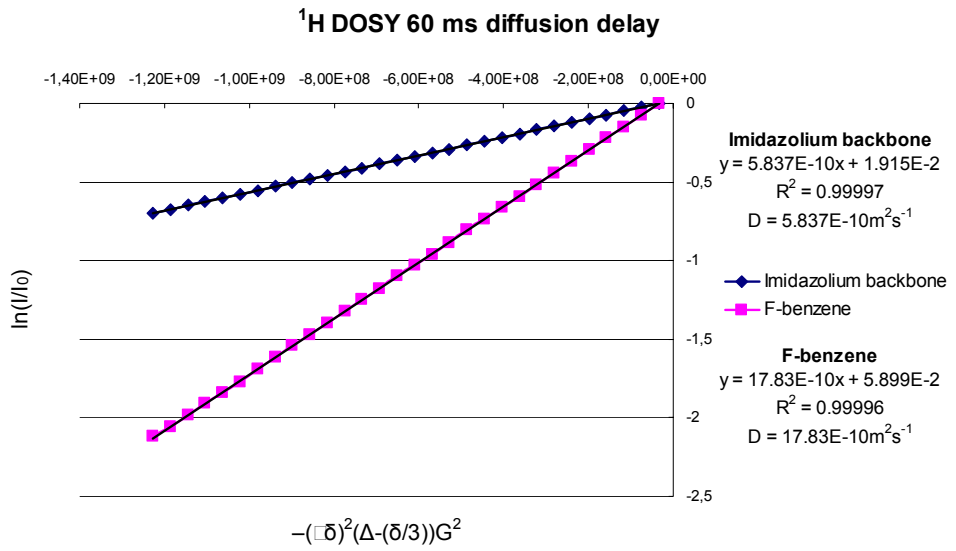
^{11}B NMR of 9-BBN-OTf in hexanes

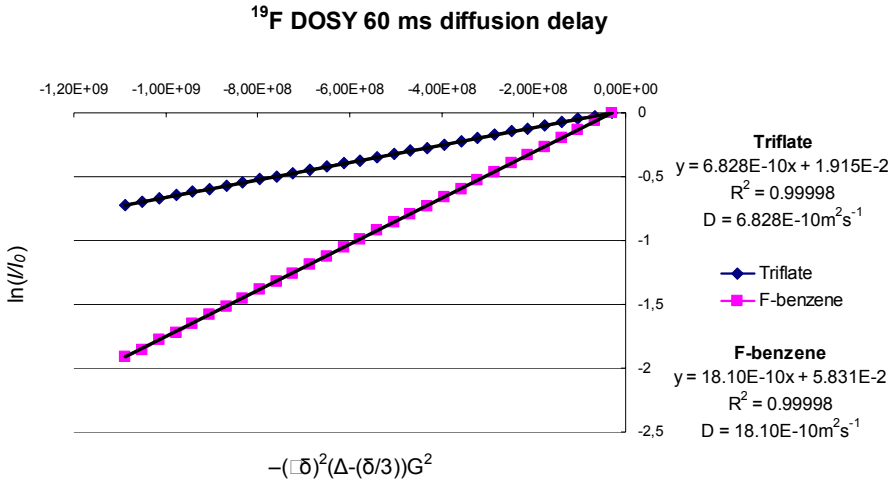


4. Diffusion Ordered NMR Spectroscopy

Diffusion co-efficients were established by NMR spectroscopy, using the PGSE-based DOneshot sequence[3]which is based on the BPPSTE sequence, but includes a purge pulse in the diffusion delay, unbalanced gradient pulses in the BPPs and incrementing heating compensation gradients. The sequence was derived directly from the Varian VNMRJ 3 sequence library, and employed a 60ms diffusion delay (Δ), gradient length (δ) of 2 ms, and 30 field gradient strength increments, each collected with 64 scans.Data were collected on a VNMRS500 NMR spectrometer equipped with 60G/cm gradients and a broadband tuneable probe. The temperature was equilibrated at 25 °C for at least 10 minutes prior to the start of data collection, using the spectrometers temperature controller, but the exact absolute temperature was not calibrated for this particular study. Diffusion co-efficients were determined by plotting the intensity of peaks (I/I_o) versus $-(\delta\gamma)^2(\Delta-(\delta/3))G^2$ and fitting with linear regression analysis leading to values of D with R^2 values of >0.999. The experiments were carried out using a sample of **11**(concentration 0.54 mM, see experimental procedure for preparation of **11**) and fluorobenzene(1.08 mM) dissolved in CD_2Cl_2.

The data fits are presented below for the ^1H and ^{19}F experiments, and compare the diffusion co-efficients of the imidazolium (^1H) and triflate (^{19}F) ions against a fluorobenzene internal standard.





5. References

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