Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Iron(II)-Catalyzed Sulfur Directed C(sp^3)-H Bonds Amination/C-S Cross Coupling

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Contents

Experimental Details

General information

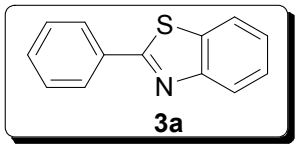
All reagents used in the experiment were obtained from commercial sources and used without further purification. Unless otherwise noted, all reactions were carried out at N_2 atmosphere. Analytical thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE DMX-500 spectrometry for ^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz, ^{19}F NMR at 470 MHz in $CDCl_3$, respectively. Unless otherwise noted, ^{1}H and ^{13}C chemical shifts are referenced to at $CDCl_3$ at 7.24 ppm and 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. The ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Mass spectras were performed on a Bruker Esquire 3000plus mass spectrometer equipped with ESI interface and ion trap analyzer. The ESI-HRMS were tested on Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

General procedure for preparation of 3 and 5

A mixture of phenyl-methanethiol **1a** (0.3 mmol, 37.2 mg), 2-Iodo-

phenylamine **2a** (0.3 mmol, 65.7 mg), $Fe(OAc)_2$ (5 mol%, 8.7 mg), 2-(2-Dimethylamino-vinyl)-inden-1-one **L5** (5 mol%, 10.0 mg) and Cs_2CO_3 (2 equiv, 195.6 mg) in DMSO (4 mL) was stirred under a N_2 atmosphere. After the reaction mixture was stirred at 100 °C for 24 h, it was allowed to cool to ambient temperature. Then the mixture was quenched with saturated salt water (10 mL), and the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried by sodium sulfate and concentrated in vacuo. The pure product 2-Phenyl-benzothiazole **5a** (54.4 mg, 86% yield) was obtained by flash column chromatography on silica gel.

Analytical Datas



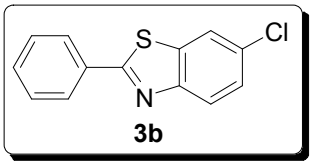
3a

2-phenylbenzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.09 (m, 3 H), 7.93-7.91 (d, *J* = 8.0 Hz, 1 H), 7.53-7.50 (m, 4 H), 7.42-7.39 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3, 154.4, 135.3, 133.9, 131.2, 129.3, 127.8, 126.6, 125.4, 123.5, 121.9;

ESI-HRMS *m/z*: Calcd for $C_{13}H_{10}NS^+$ $[M+H]^+$: 212.0534; Found 212.0537.



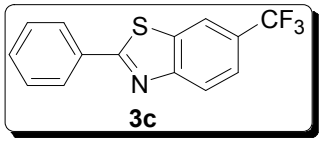
3b

5-chloro-2-phenylbenzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10-8.07 (m, 3 H), 7.82-7.81 (d, *J* = 8.5 Hz, 1 H), 7.54-7.49 (m, 3 H), 7.38-7.36 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 155.3, 133.5, 132.6, 131.6, 129.4, 127.9, 125.9, 123.3, 122.6;

ESI-HRMS *m/z*: Calcd for $C_{13}H_9ClNS^+$ $[M+H]^+$: 246.0144; Found 246.0147.



3c

5-(trifluoromethyl)-2-phenylbenzo[d]thiazole White solid;

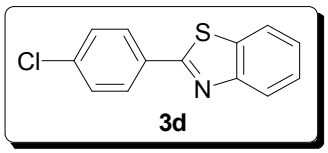
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 8.12-8.10 (m, 2 H), 8.02-8.00

(d, *J* = 8.5 Hz, 1 H), 7.64-7.62 (d, *J* = 8.0 Hz, 1 H), 7.56-7.51 (m, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 154.0, 138.7, 133.3, 131.9, 129.3 (*J* = 3.3 Hz), 128.0, 125.6, 123.4, 122.5, 121.8 (*J* = 3.3 Hz), 121.7 (*J* = 3.4 Hz), 120.7, 120.6 (*J* = 3.8 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -77.35;

ESI-HRMS *m/z*: Calcd for $C_{14}H_9F_3NS^+$ $[M+H]^+$: 280.0408; Found 280.0411.



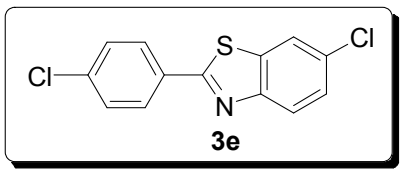
3d

2-(4-chlorophenyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09-8.07 (d, *J* = 8.0 Hz, 2 H), 7.92-7.90 (d, *J* = 8.0 Hz, 1 H), 7.53-7.47 (m, 3 H), 7.42-7.39 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 154.3, 137.3, 135.3, 132.4, 129.5, 129.0, 126.7, 125.7, 123.6, 121.9;

ESI-HRMS *m/z*: Calcd for $C_{13}H_9ClNS^+$ $[M+H]^+$: 246.0144; Found 246.0147.



3e

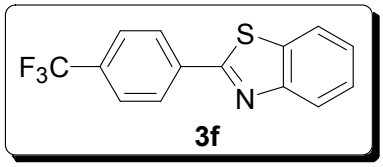
5-chloro-2-(4-chlorophenyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05-8.00 (m, 3 H), 7.81-7.80 (s, *J* = 8.5 Hz, 1 H), 7.49-7.47 (m, 2 H), 7.38-7.36 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 155.2, 137.7, 133.6, 132.8, 132.0, 129.6, 129.0, 126.1, 123.4, 122.6;

ESI-HRMS *m/z*: Calcd for $C_{13}H_8Cl_2NS^+$ $[M+H]^+$: 279.9754; Found

279.9757.



3f

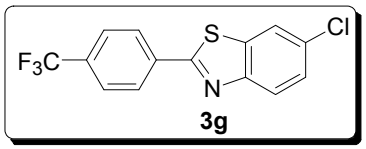
2-(4-(trifluoromethyl)phenyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22-8.20 (d, *J* = 8.5 Hz, 2 H), 8.13-8.11 (d, *J* = 8.5 Hz, 1 H), 7.95-7.93 (d, *J* = 8.5 Hz, 1 H), 7.76-7.75 (d, *J* = 8.5 Hz, 1 H), 7.46-7.43 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 137.0, 135.5, 132.9, 132.6, 128.0, 126.9, 126.3 (*J* = 3.5 Hz), 126.2 (*J* = 3.6 Hz), 126.0, 125.2, 123.9, 123.0, 122.0;

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.23;

ESI-HRMS *m/z*: Calcd for $C_{14}H_9F_3NS^+$ $[M+H]^+$: 280.0408; Found 280.0411.



3g

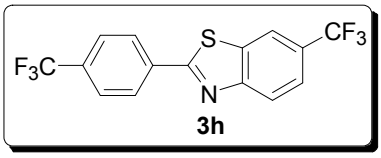
2-(4-chlorophenyl)-5-(trifluoromethyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1 H), 8.05-8.01 (m, 3 H), 7.65-7.63 (m, 1 H), 7.53-7.49 (m, 2 H), 7.28-7.27 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 153.9, 138.8, 136.4, 133.3 (*J* = 32.5 Hz), 129.7 (*J* = 32.4 Hz), 128.2, 126.5 (*J* = 3.8 Hz), 126.4 (*J* = 3.5), 125.2 (*J* = 48.3 Hz), 123.3, 122.8 (*J* = 25.4), 122.4 (*J* = 3.4 Hz), 121.1 (*J* = 4.0 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -65.11;

ESI-HRMS *m/z*: Calcd for $C_{14}H_8ClF_3NS^+$ $[M+H]^+$: 314.0018; Found 314.0021.



3h

5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)benzo[d]thiazole

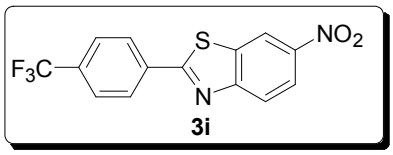
White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20-8.18 (d, *J* = 8.0 Hz, 2 H), 8.09 (s, 1 H), 7.85-7.83 (s, *J* = 8.5 Hz, 1 H), 7.77-7.56 (m, 2 H), 7.42-7.40 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2, 153.9, 149.6, 138.8, 138.7, 129.9 (*J* = 30.6 Hz), 128.7, 125.3, 124.6, 123.0 (*J* = 47.1 Hz), 122.7 (*J* = 3.4 Hz), 122.7, 121.4, 121.4, 121.3, 121.3;

^{19}F NMR (470 MHz, $CDCl_3$) δ -64.09, -80.94;

ESI-HRMS *m/z*: Calcd for $C_{15}H_8F_6NS^+$ $[M+H]^+$: 348.0282; Found 348.00285.



3i

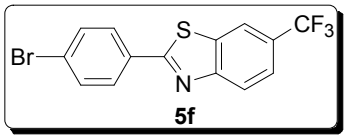
5-(trifluoromethyl)-2-(4-nitrophenyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38-8.36 (m, 3 H), 8.27-8.26 (m, 2 H), 8.08-8.06 (d, *J* = 8.5 Hz, 1 H), 7.70-7.68 (d, *J* = 8.5 Hz, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.1, 155.1, 136.7, 133.7, 133.0, 128.1, 126.6, 126.4, 126.3, 126.3, 123.3, 122.7;

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.58;

ESI-HRMS *m/z*: Calcd for $C_{14}H_8F_3N_2O_2S^+$ $[M+H]^+$: 325.0259; Found 325.0262.



5f

2-(4-bromophenyl)-5-(trifluoromethyl)benzo[d]thiazole White solid;

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37-8.35 (d, *J* = 8.5 Hz, 2 H), 8.26-8.24 (d, *J* = 9.0 Hz, 2 H), 8.11 (d, 1 H), 7.88-7.86 (d, *J* = 8.5 Hz, 1 H), 7.45-7.43 (m, 1 H);

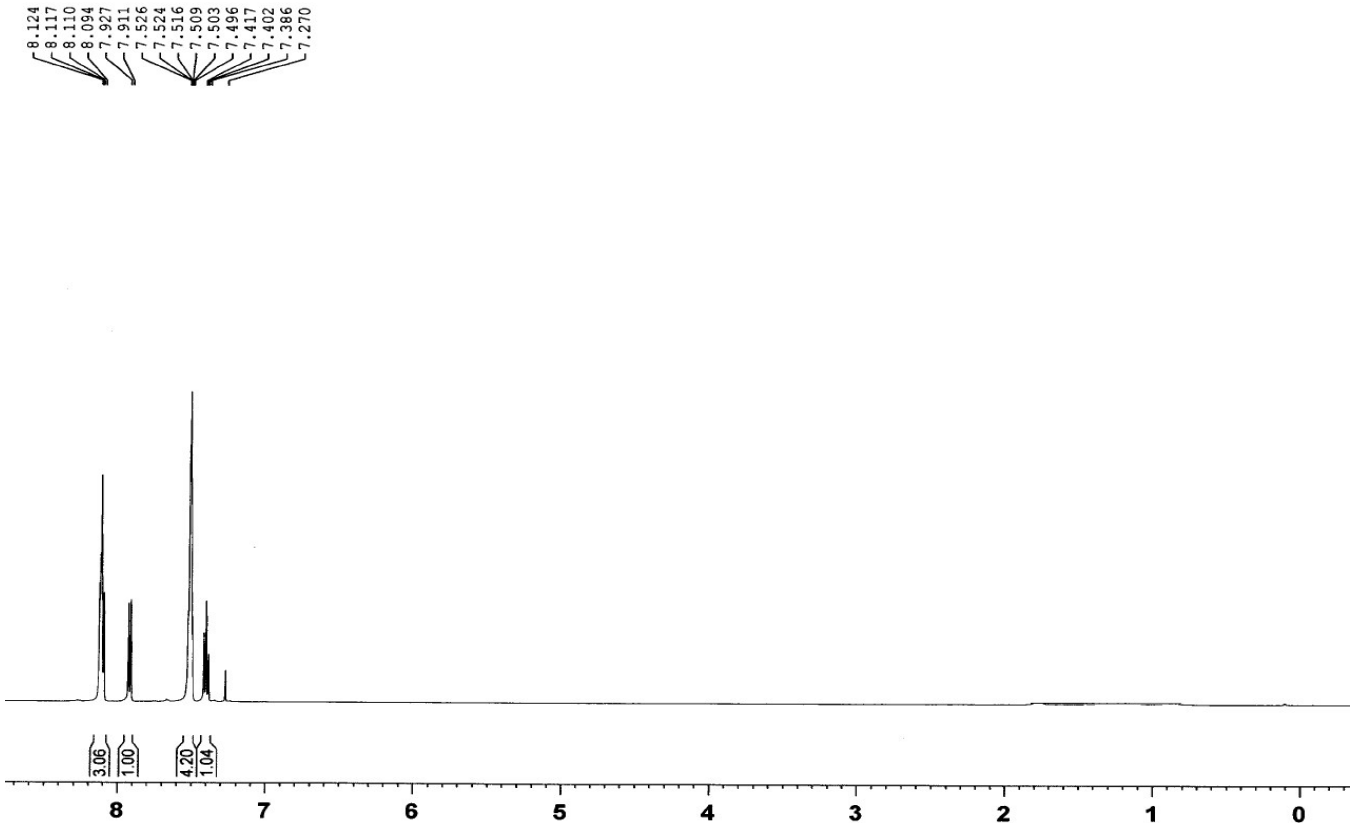
^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 155.1, 149.7, 139.0, 134.0, 133.3, 128.6, 127.0, 124.6, 123.9, 122.8;

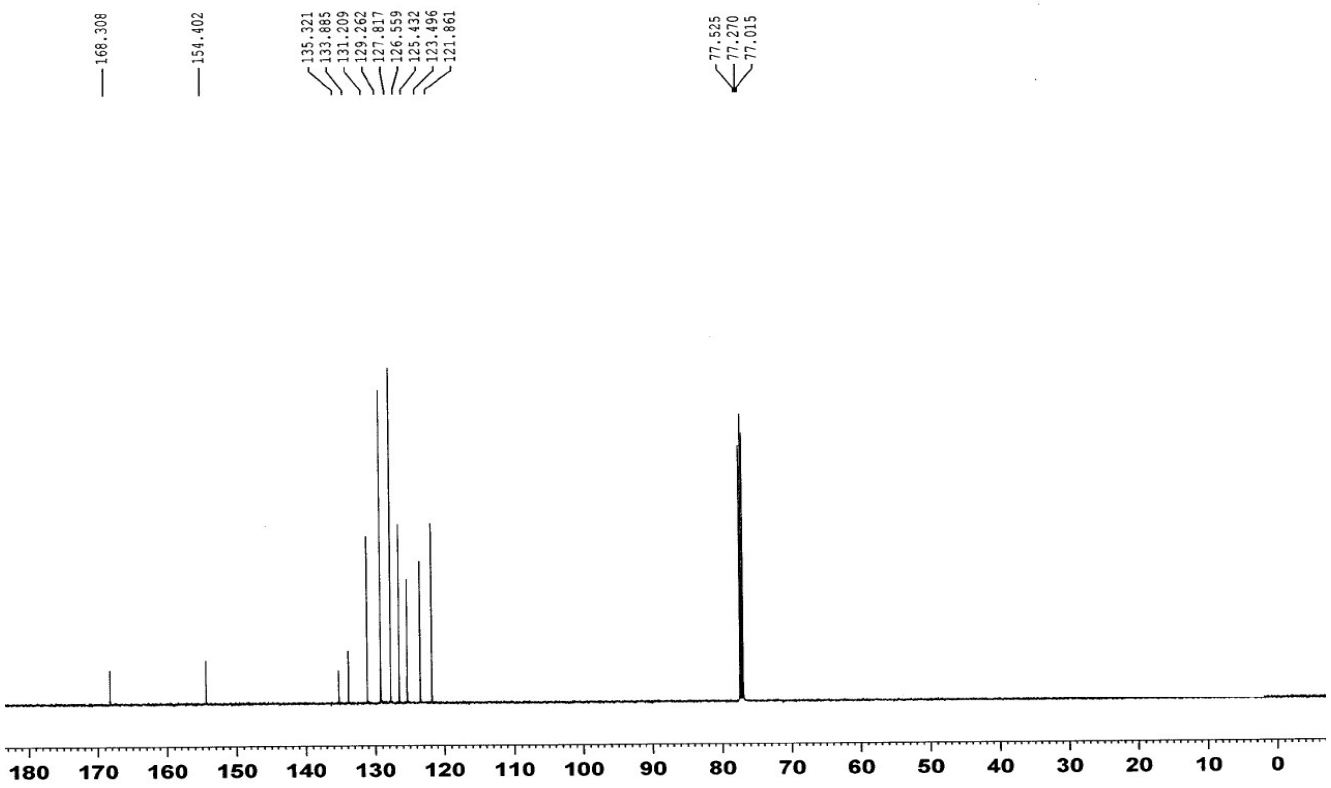
^{19}F NMR (470 MHz, $CDCl_3$) δ -79.64;

ESI-HRMS *m/z*: Calcd for $C_{14}H_8BrF_3NS^+$ $[M+H]^+$: 357.9513; Found 357.9516.

Spectrums

3a

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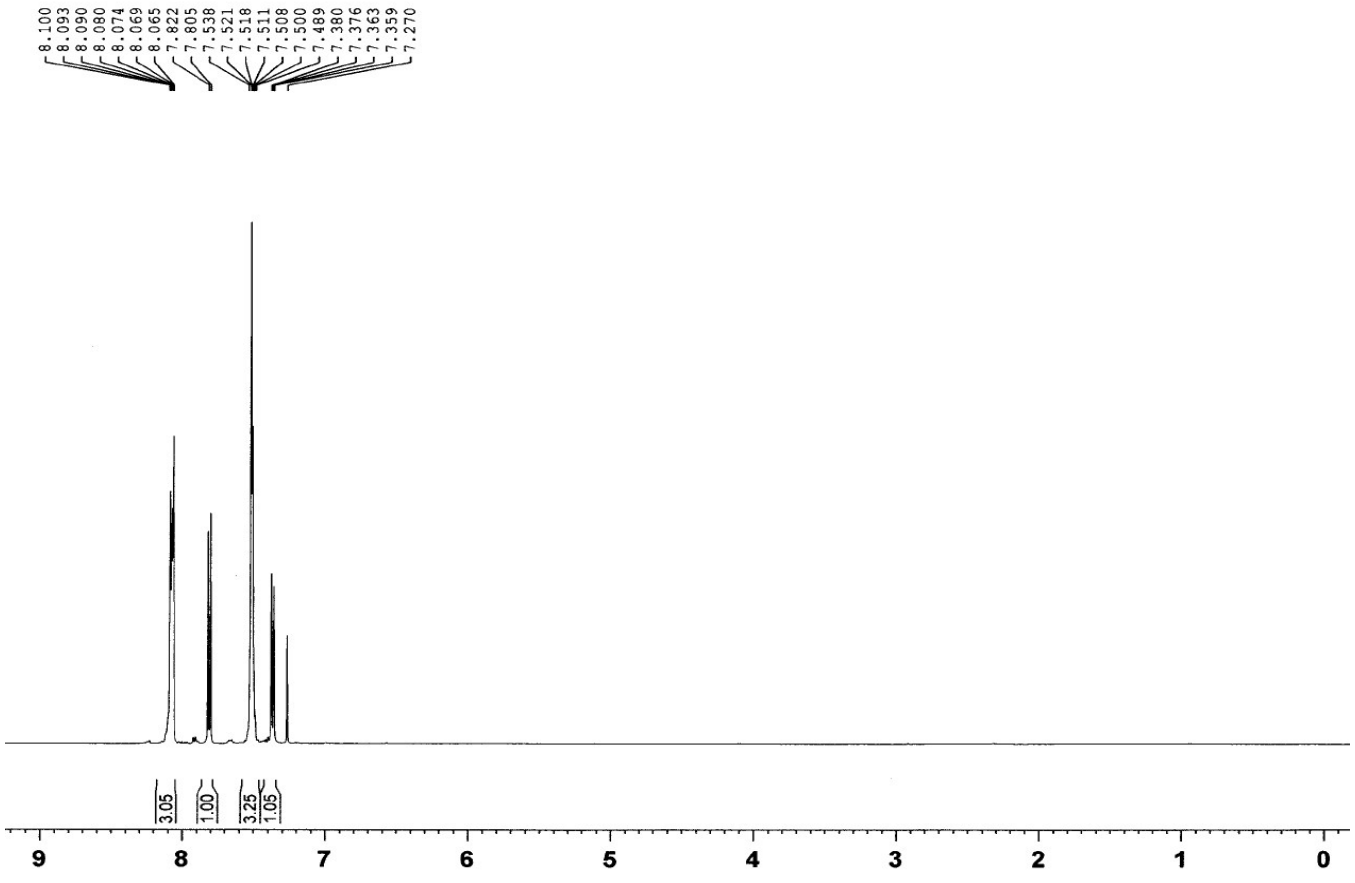
135.321
133.885
131.209
129.262
127.817
126.559
125.432
123.496
121.861
77.525
77.270
77.015
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3b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7.508
7.500
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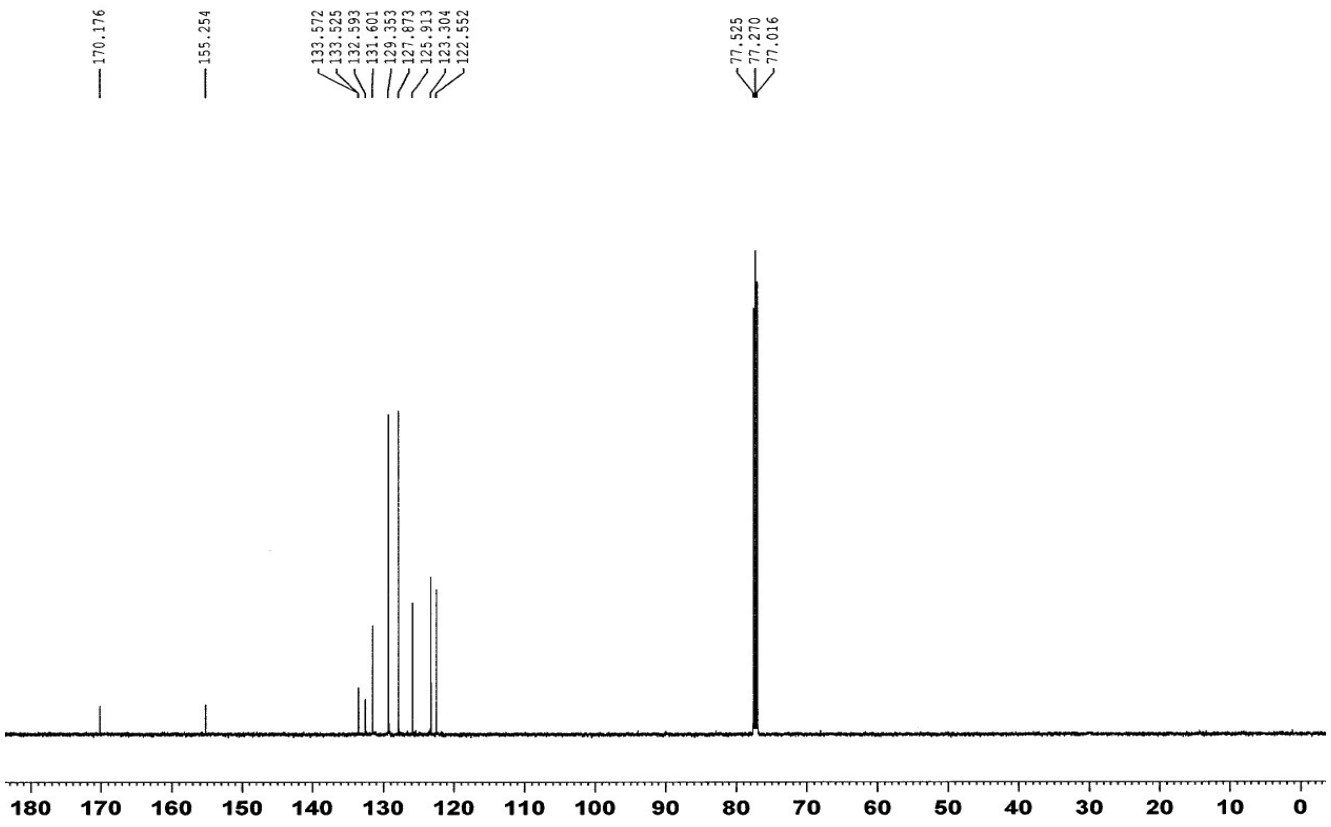
1.00
3.25
1.05
9 8 7 6 5 4 3 2 1 0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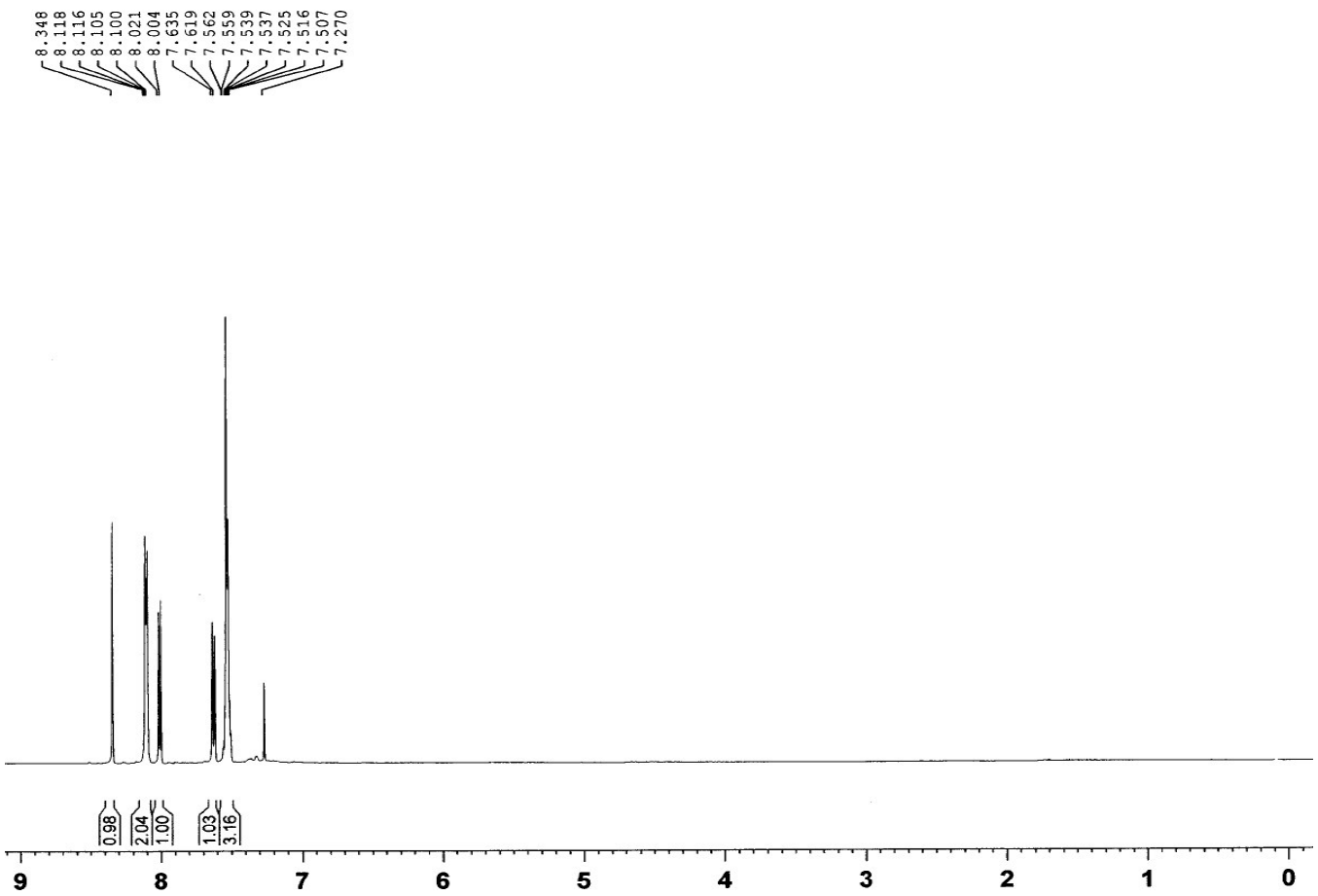
132.593
131.601
129.353
127.873
125.913
123.304
122.552
77.525
77.270
77.016
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3c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8.105
8.100
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7.619
7.562
7.559
7.539
7.537
7.525
7.516
7.507
7.270
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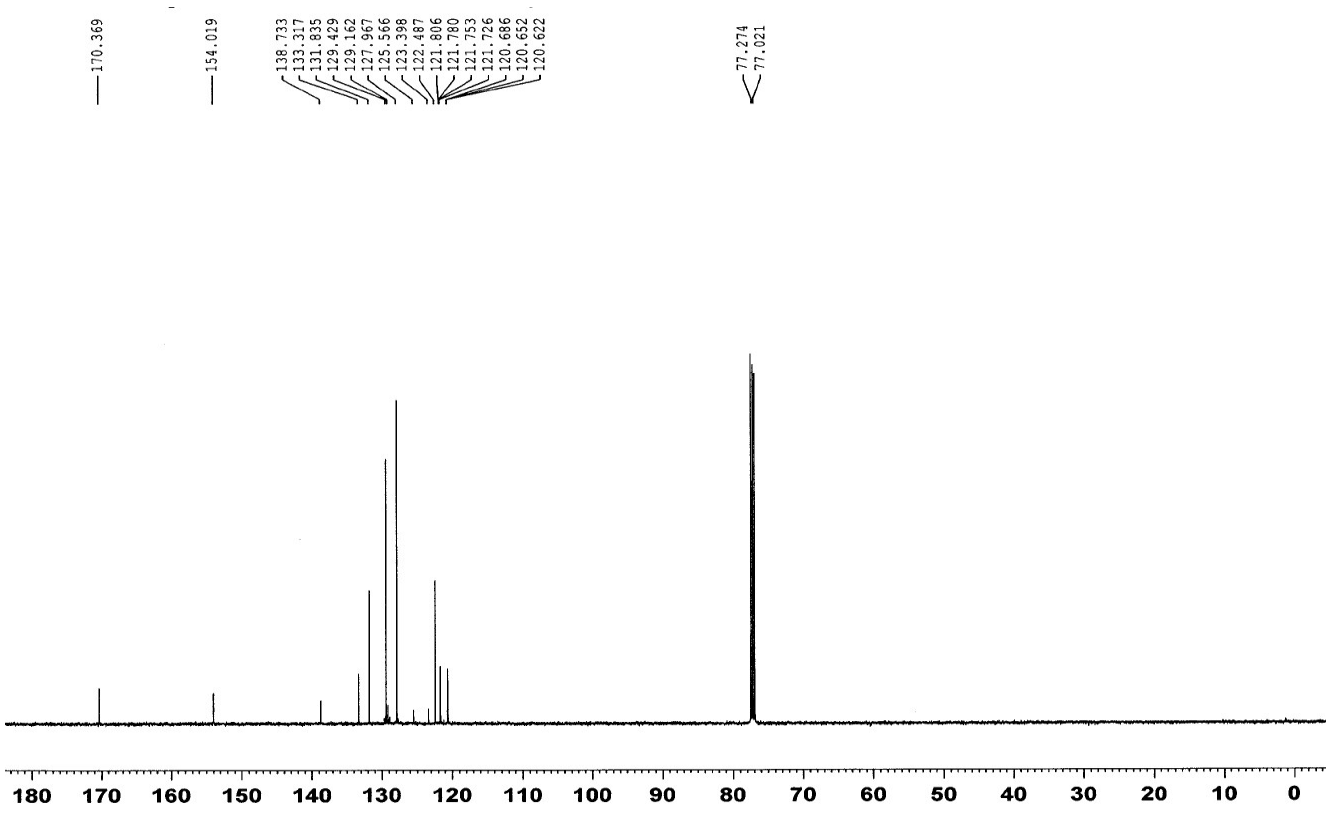
2.04
1.00
1.03
3.16
9 8 7 6 5 4 3 2 1 0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121.753
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77.021
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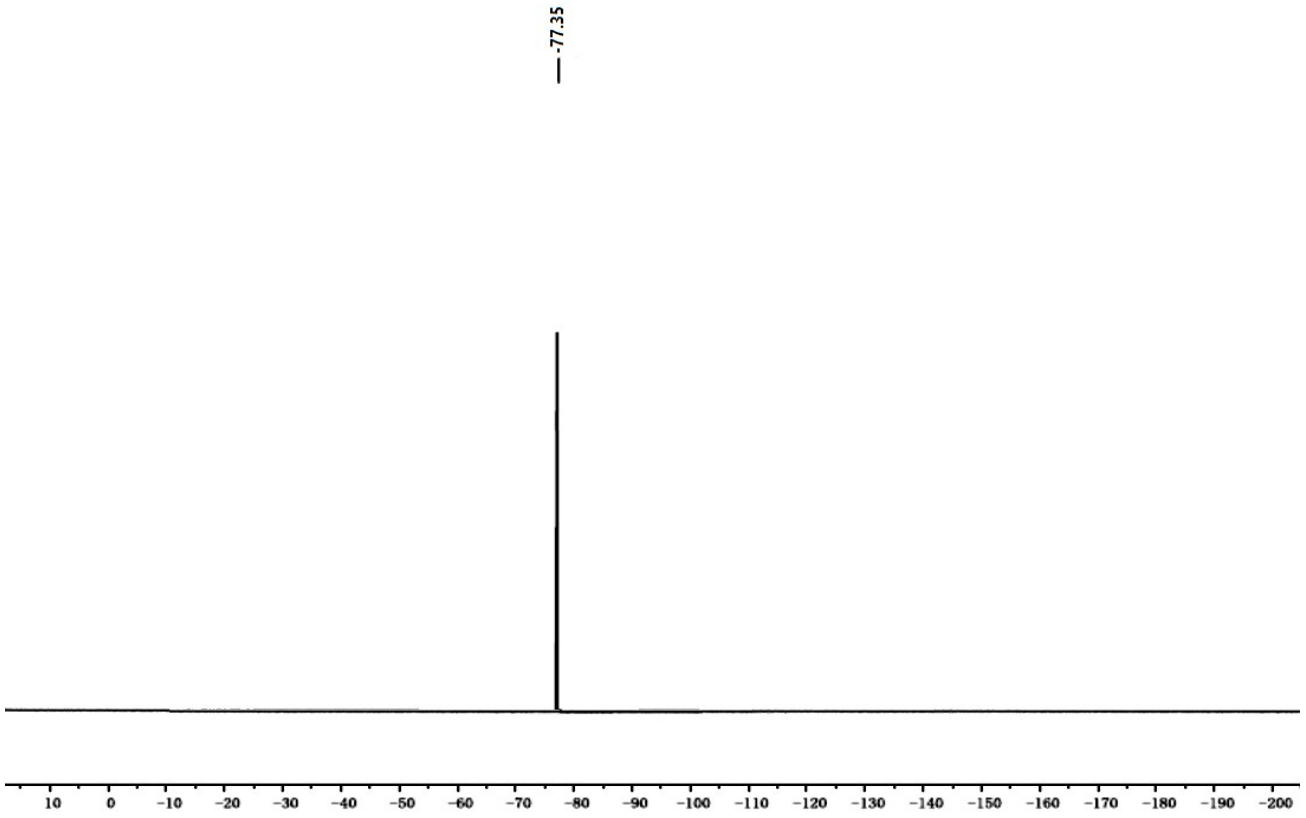
3c ^{19}F NMR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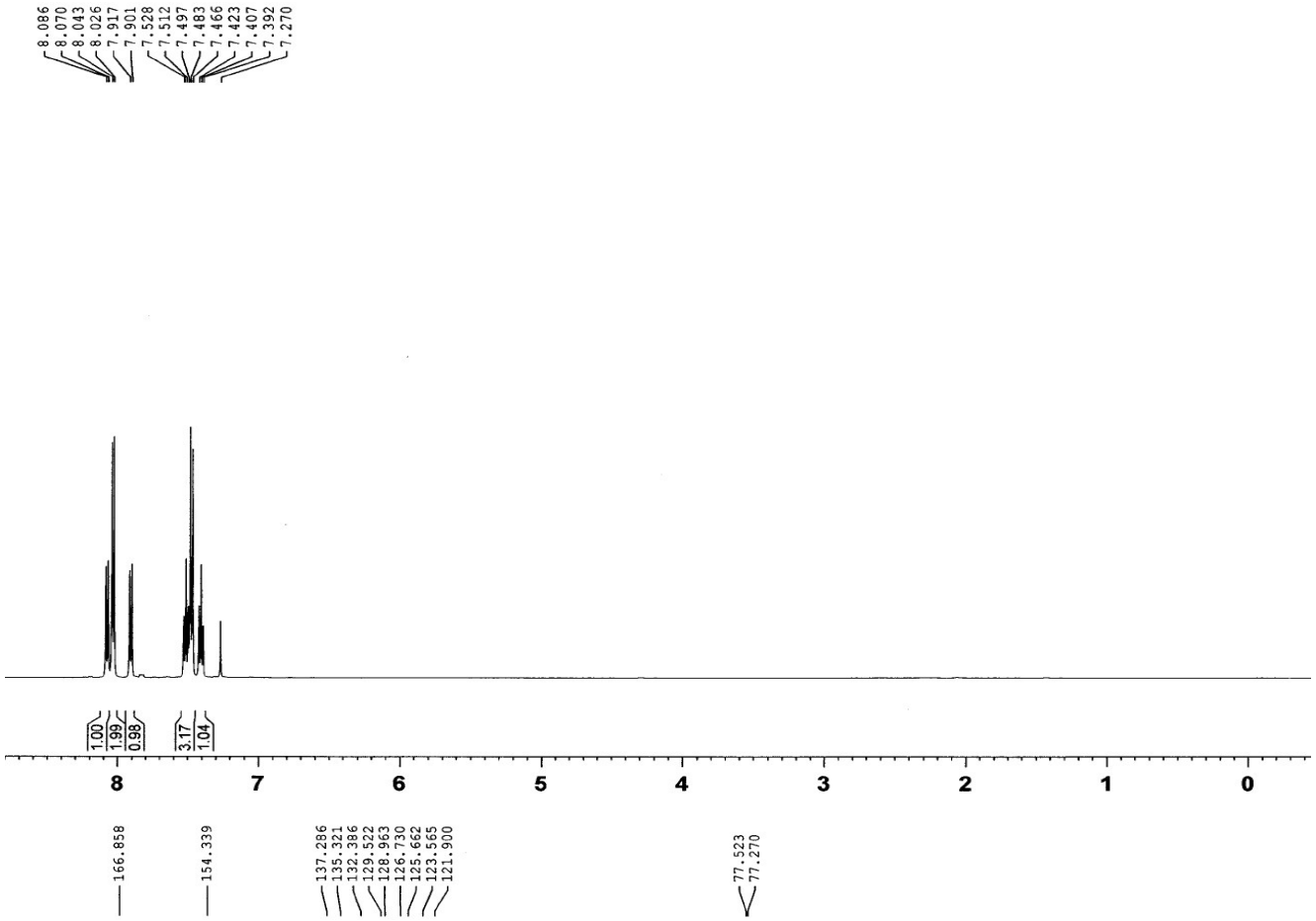
3d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4
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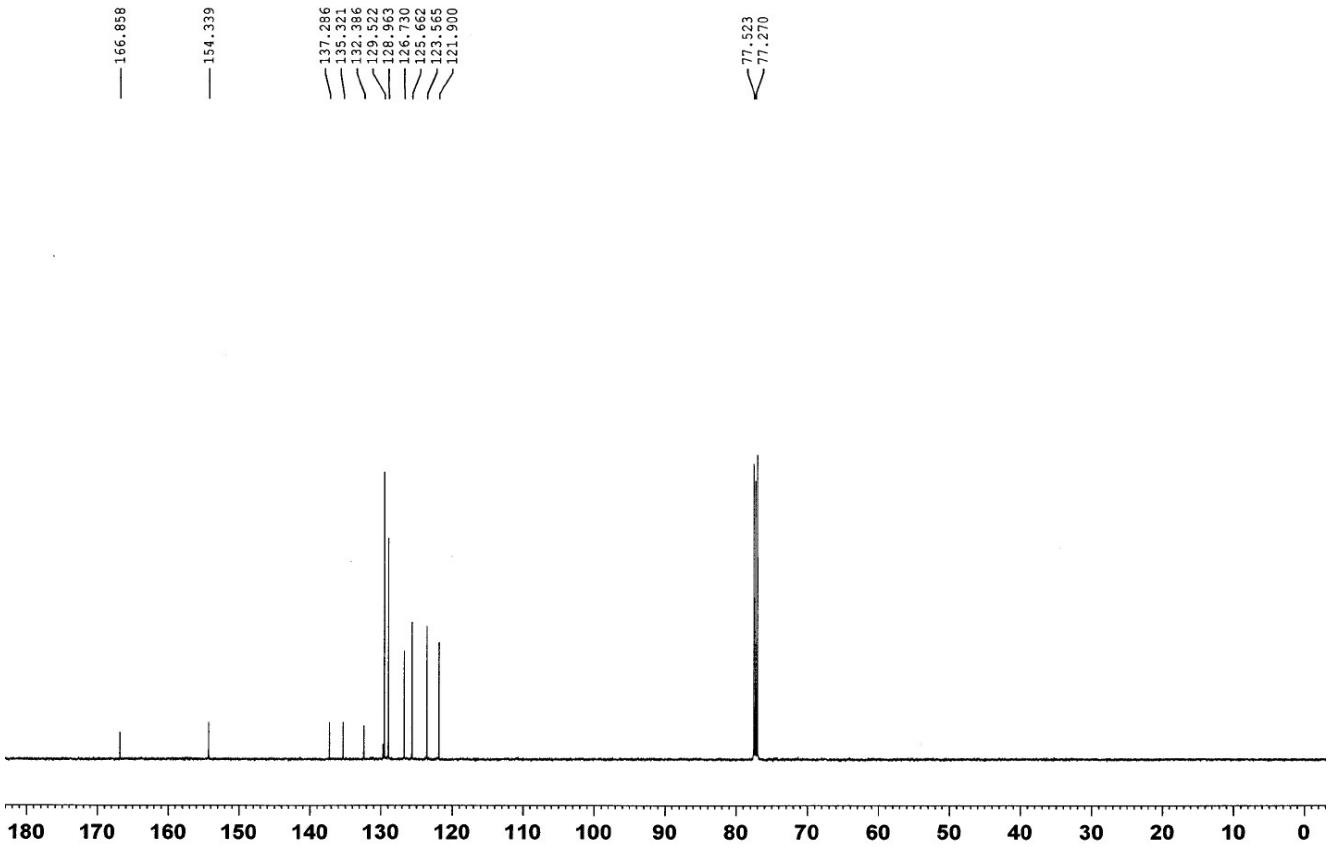
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77.270
180
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50
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30
20
10
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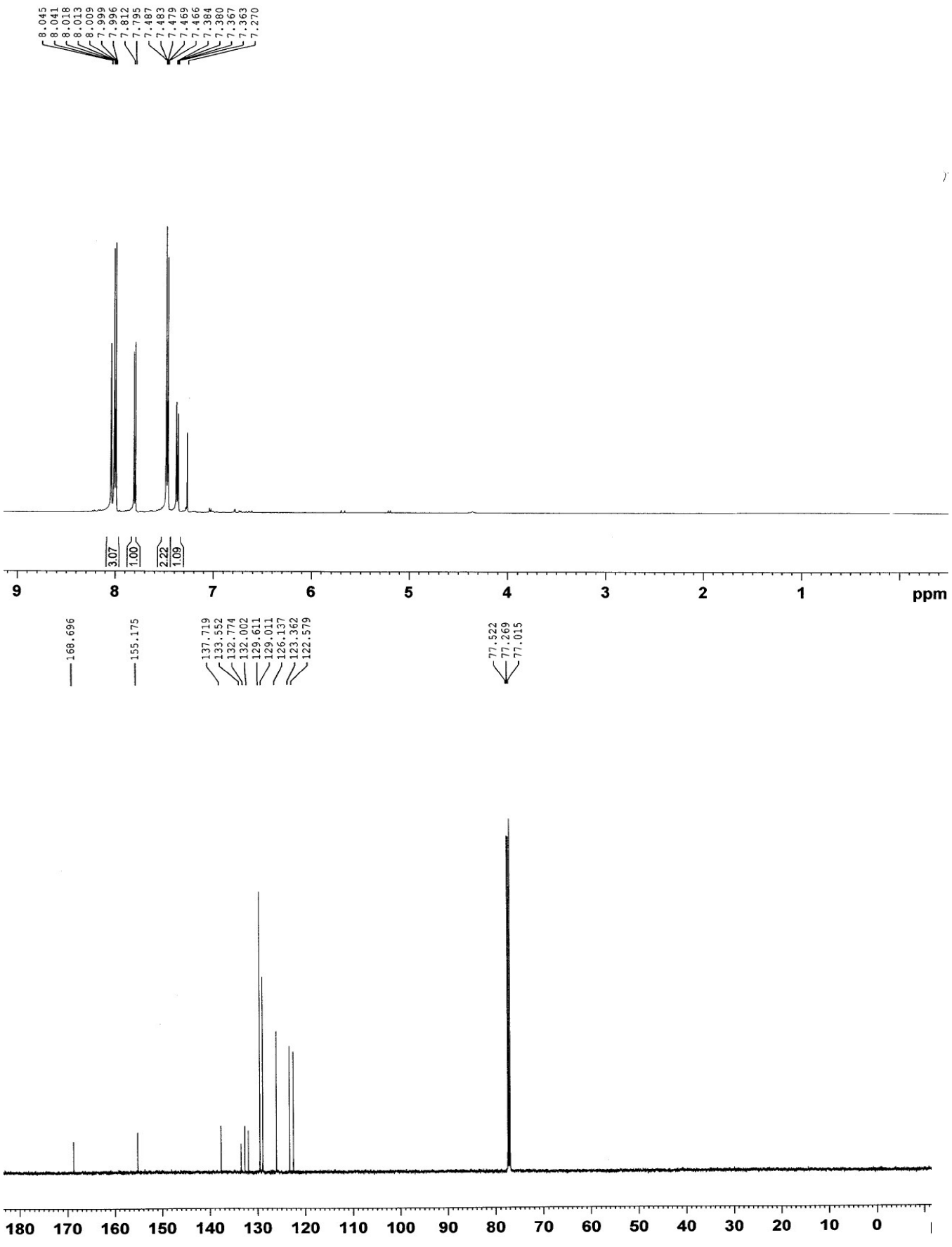
3e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7.469
7.466
7.384
7.380
7.367
7.363
7.270
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2.22
1.09
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8
7
6
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77.269
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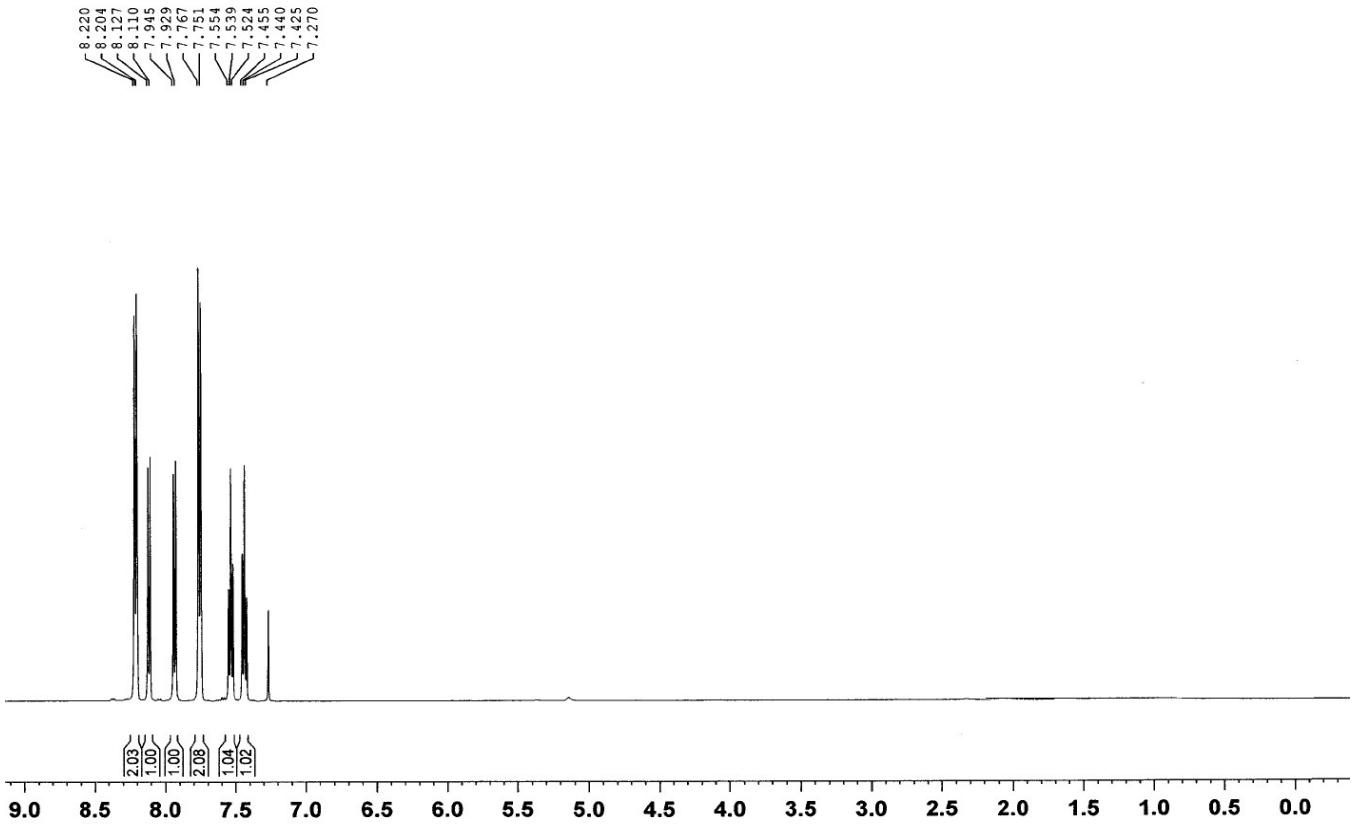
3f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7.524
7.455
7.440
7.425
7.270
2.03
1.00
1.00
2.08
1.04
1.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
1.0
0.5
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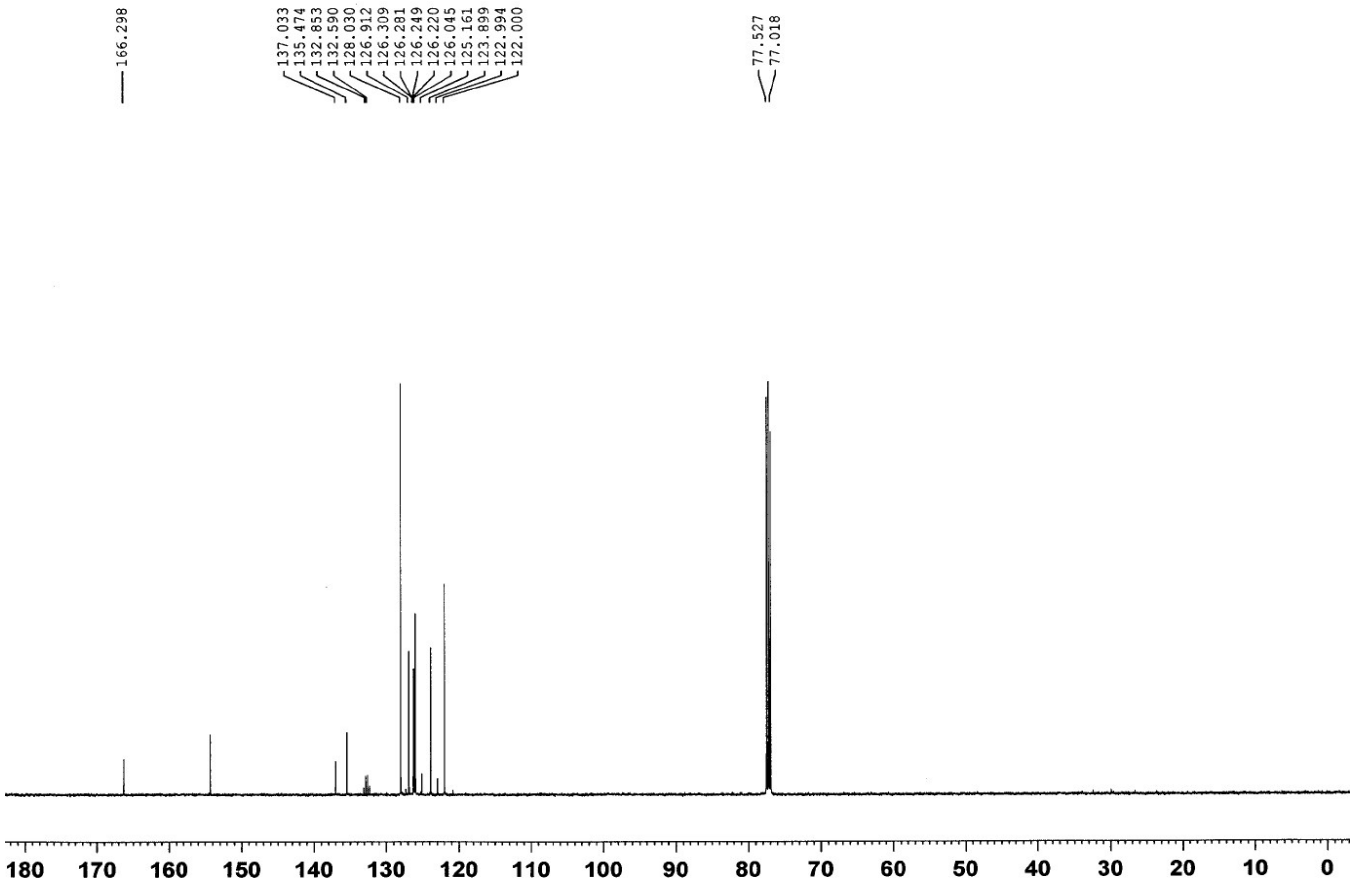
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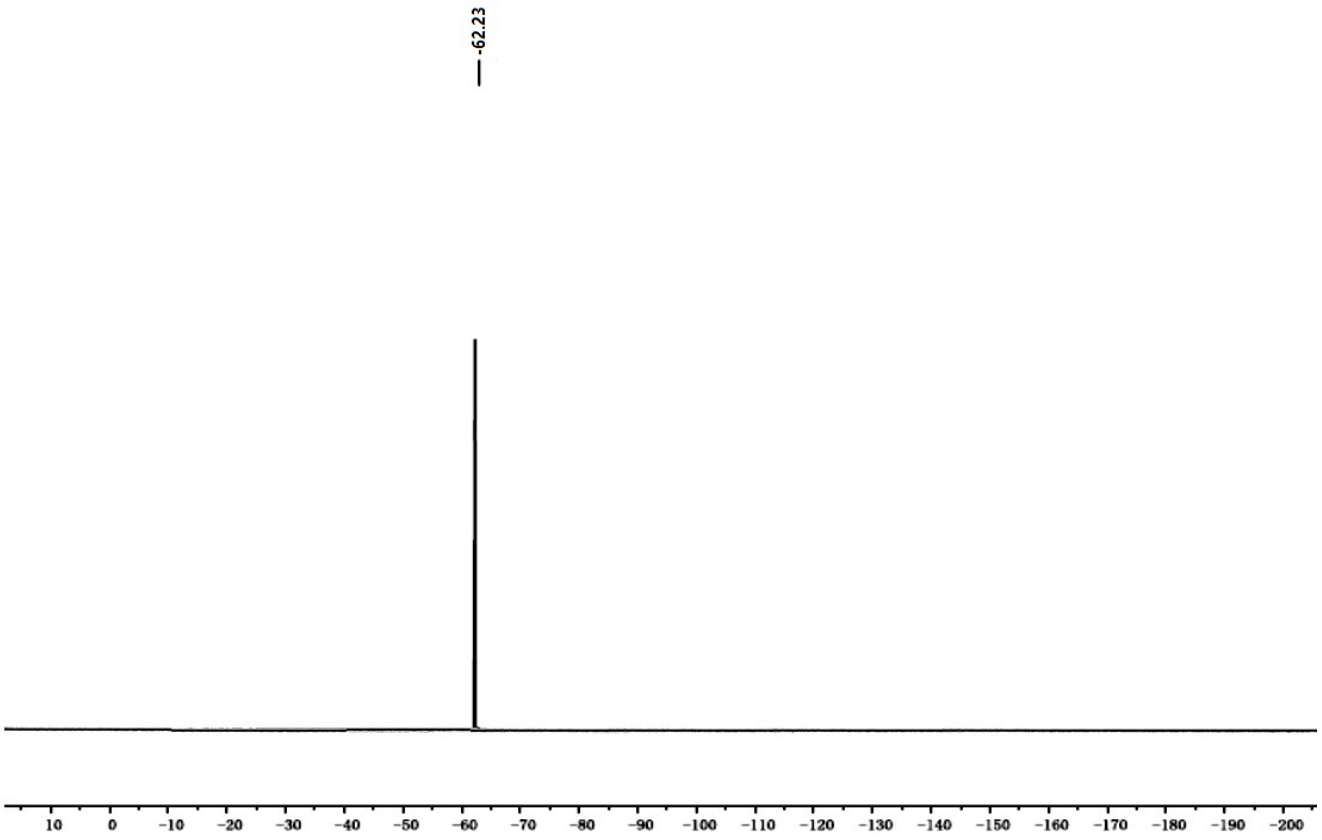
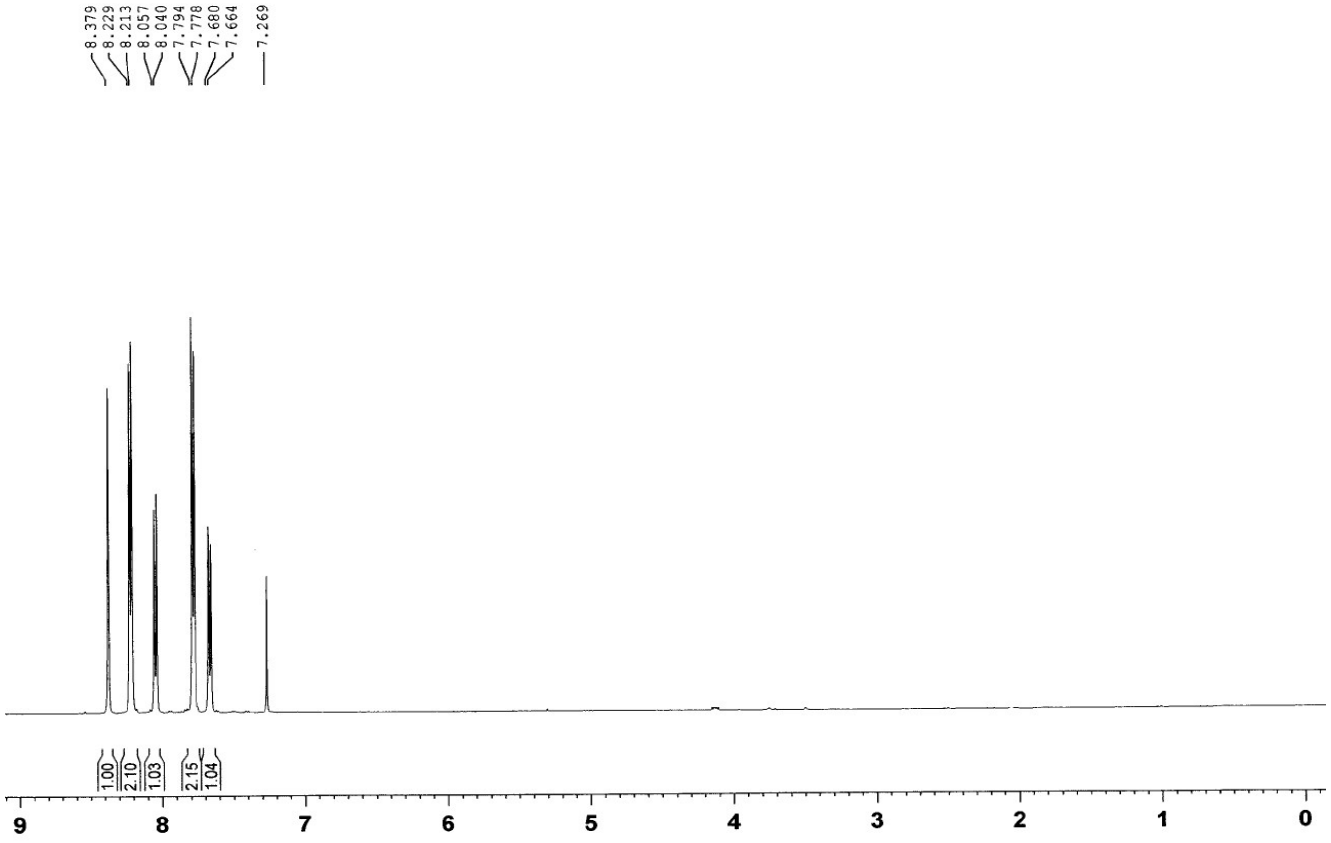
126.249
126.220
126.045
125.161
123.899
122.994
122.000
77.527
77.018
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3f ^{19}F NMR


-62.23
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

3g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8.040
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7.778
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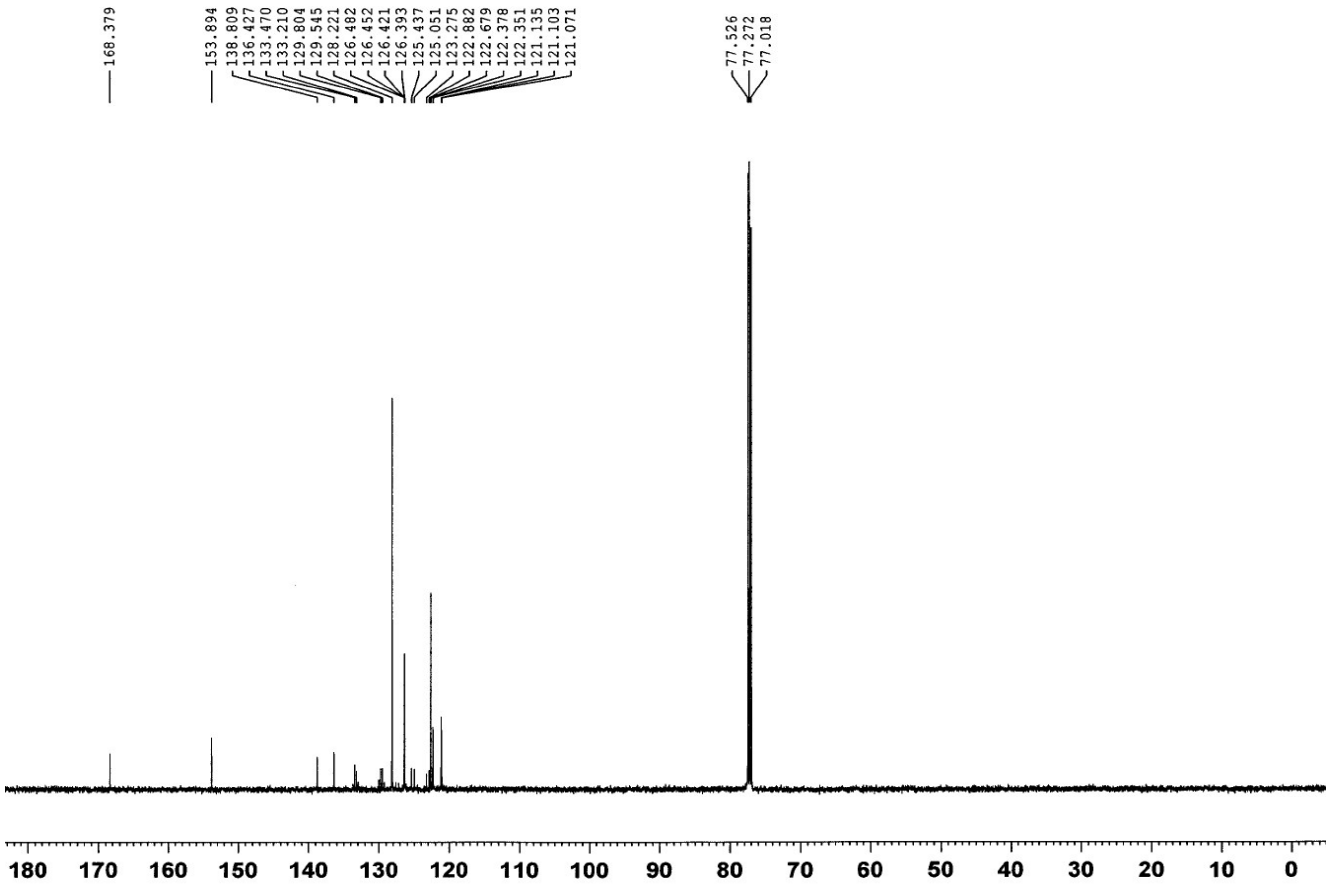
7.664
7.269
1.00
2.10
1.03
2.15
1.04
9 8 7 6 5 4 3 2 1 0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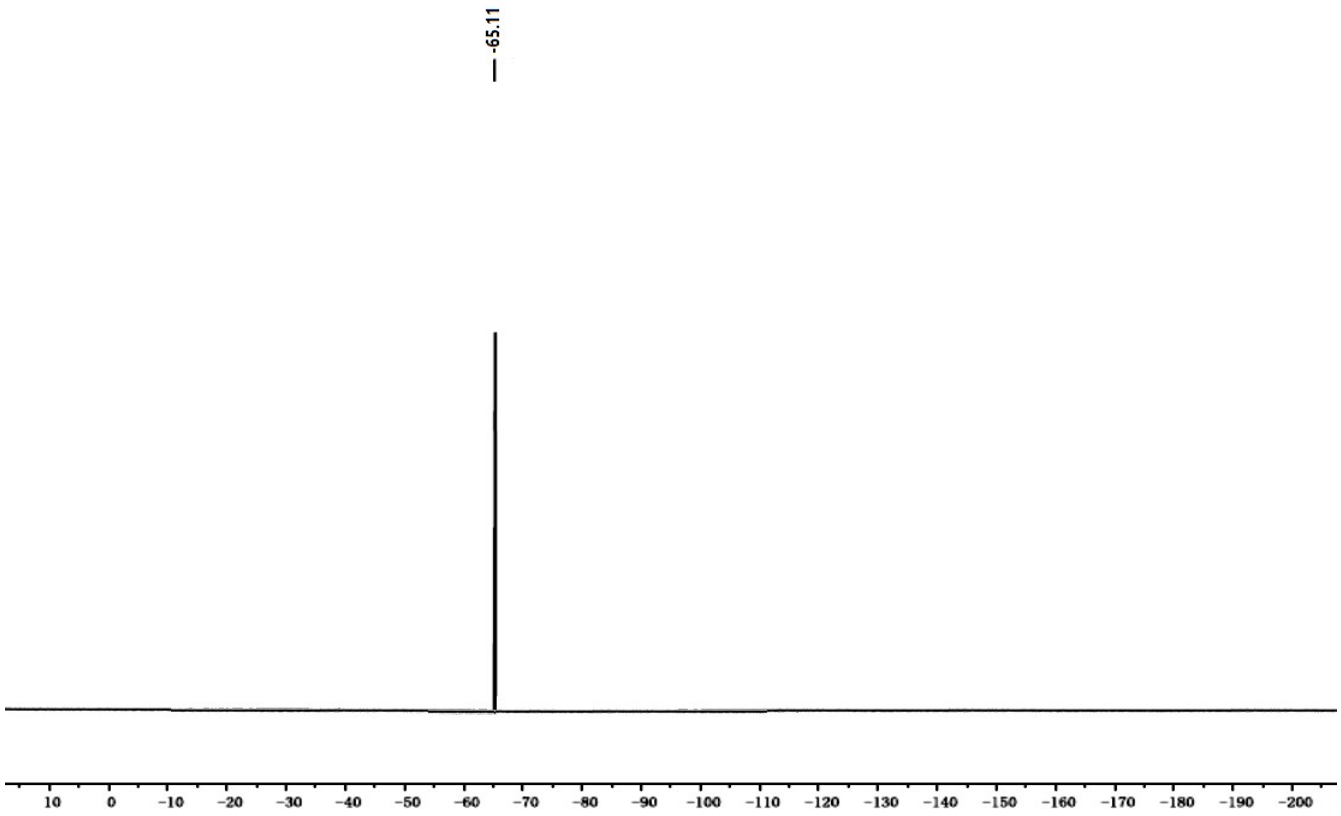
138.809
136.427
133.470
133.210
129.804
129.545
128.221
126.482
126.452
126.421
126.393
125.437
125.051
123.275
122.882
122.679
122.378
122.351
121.135
121.103
121.071
77.526
77.272
77.018
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3g ^{19}F NMR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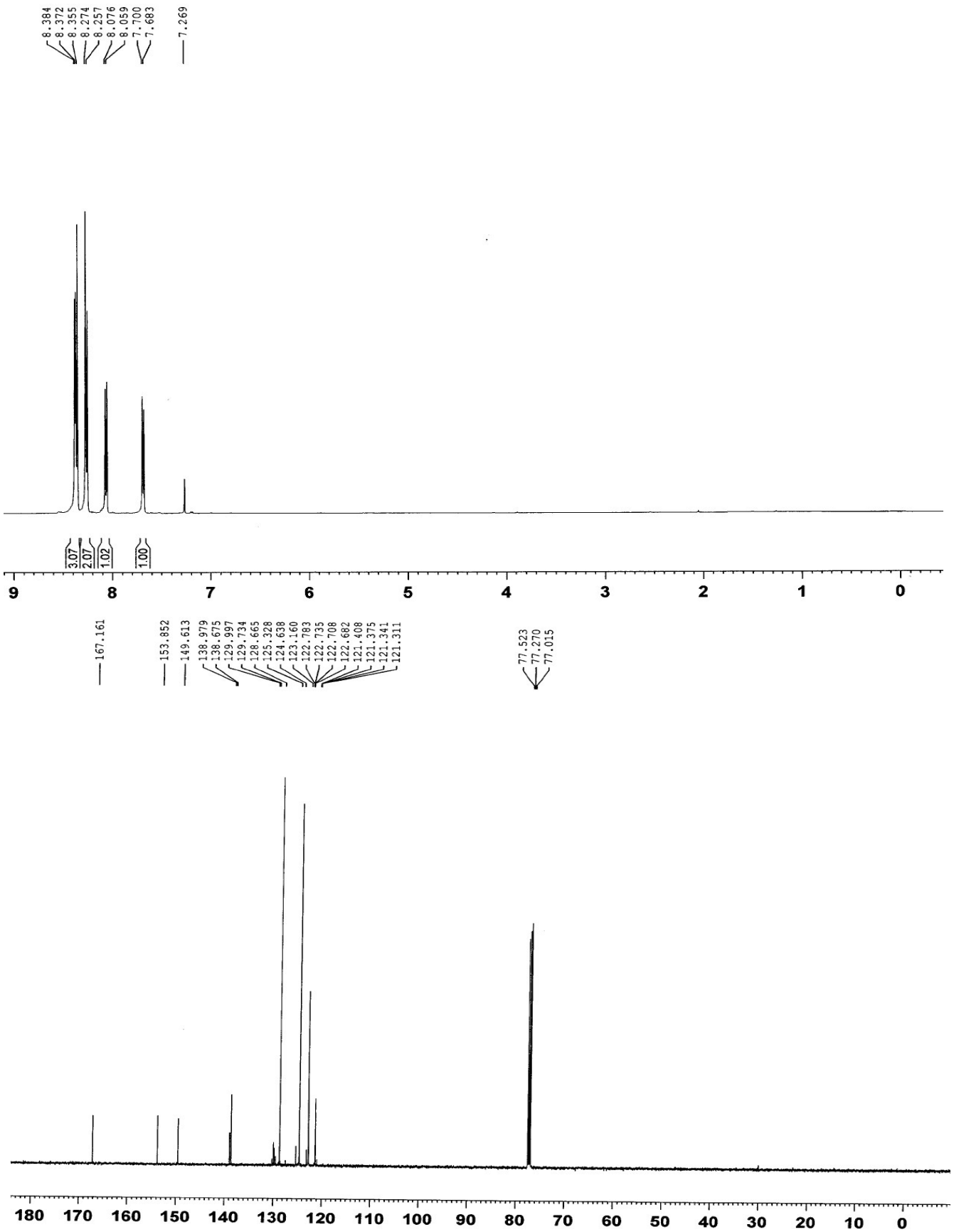
3h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8.372
8.355
8.274
8.257
8.076
8.059
7.700
7.683
7.269
3.07
2.07
1.02
1.00
9
8
7
6
5
4
3
2
1
0
167.161
153.852
149.613
138.979
138.675
129.997
129.734
128.665
125.328
124.638
123.160
122.783
122.735
122.708
122.682
121.408
121.375
121.341
121.311
77.523
77.270
77.015
180
170
160
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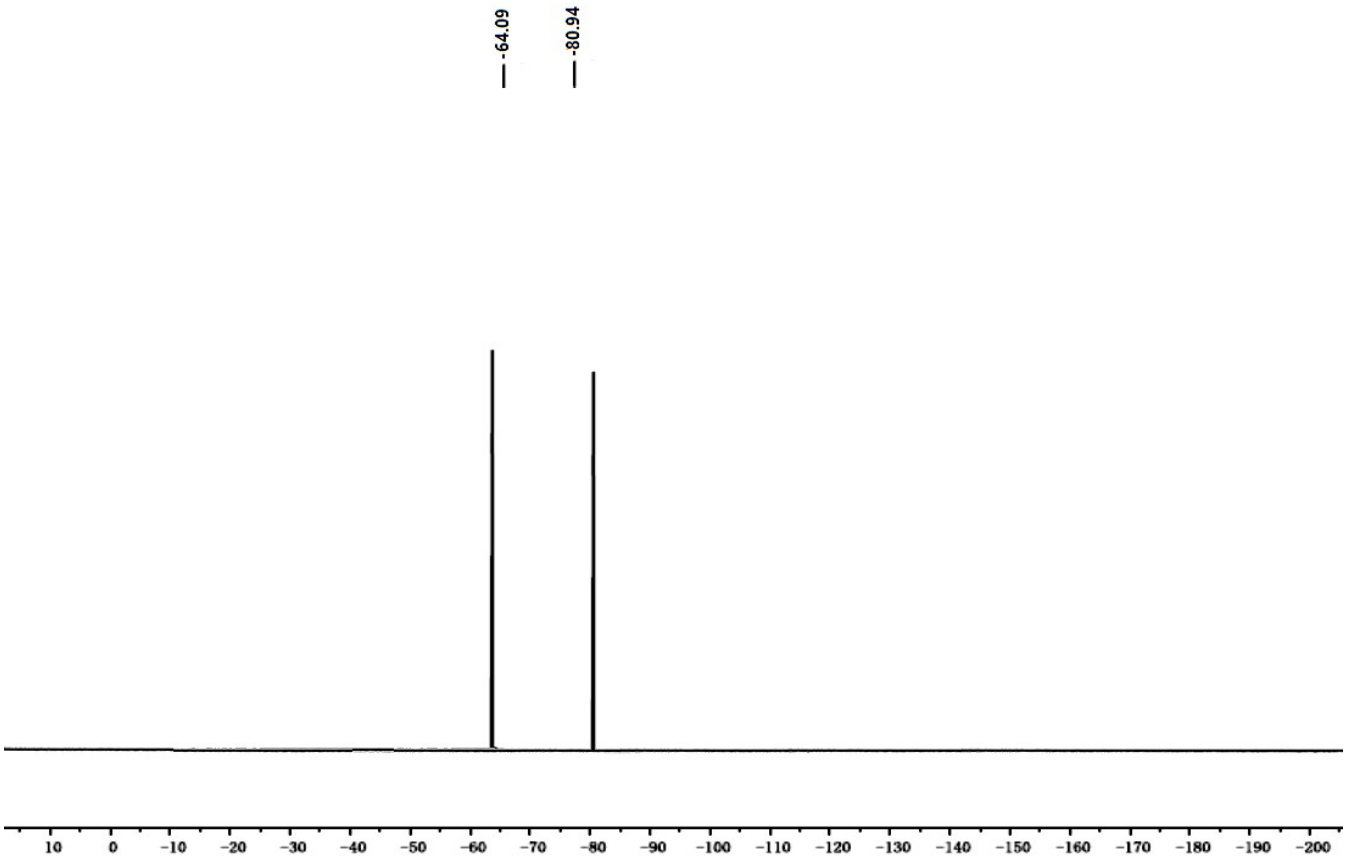
0

3h ^{19}F NMR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-80.94
10
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-10
-20
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-40
-50
-60
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-80
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-100
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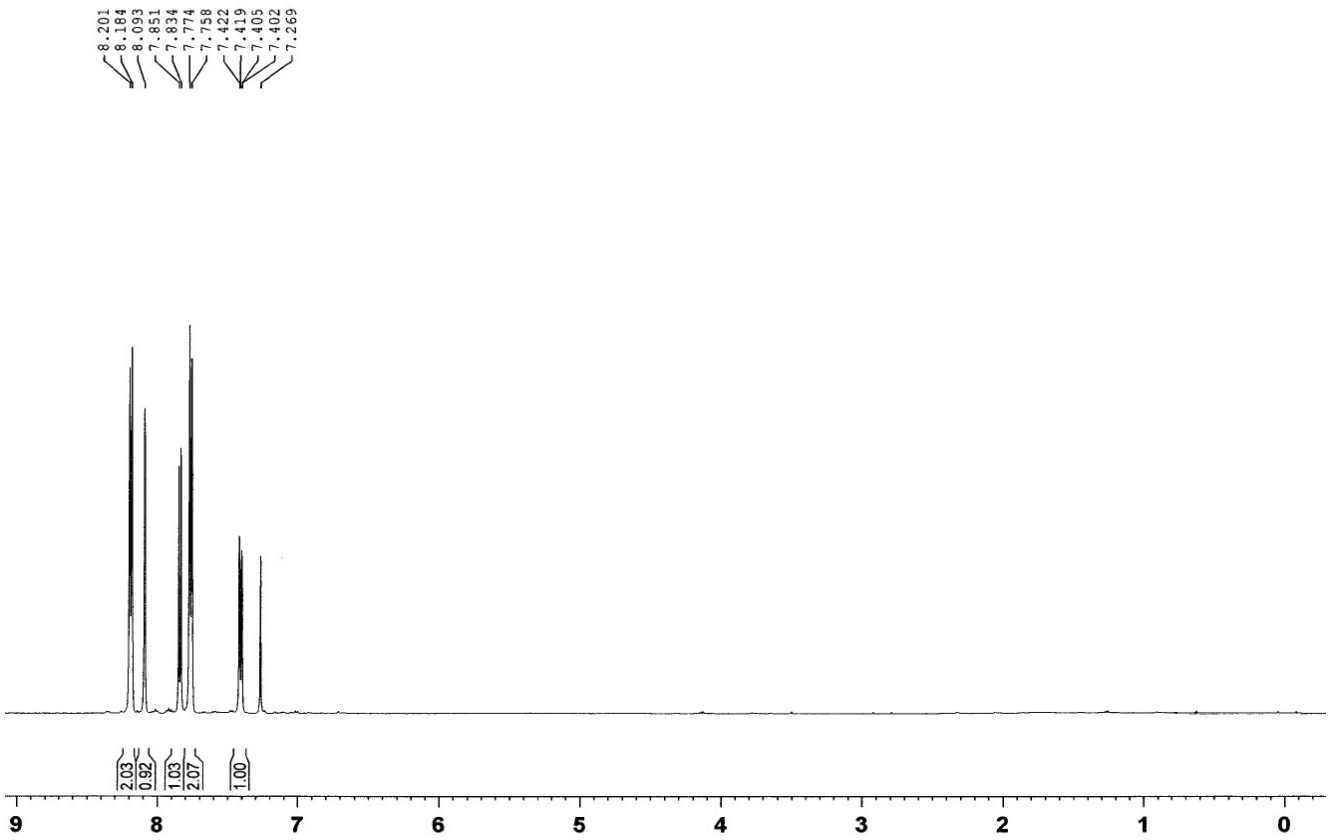
-130
-140
-150
-160
-170
-180
-190
-200

3i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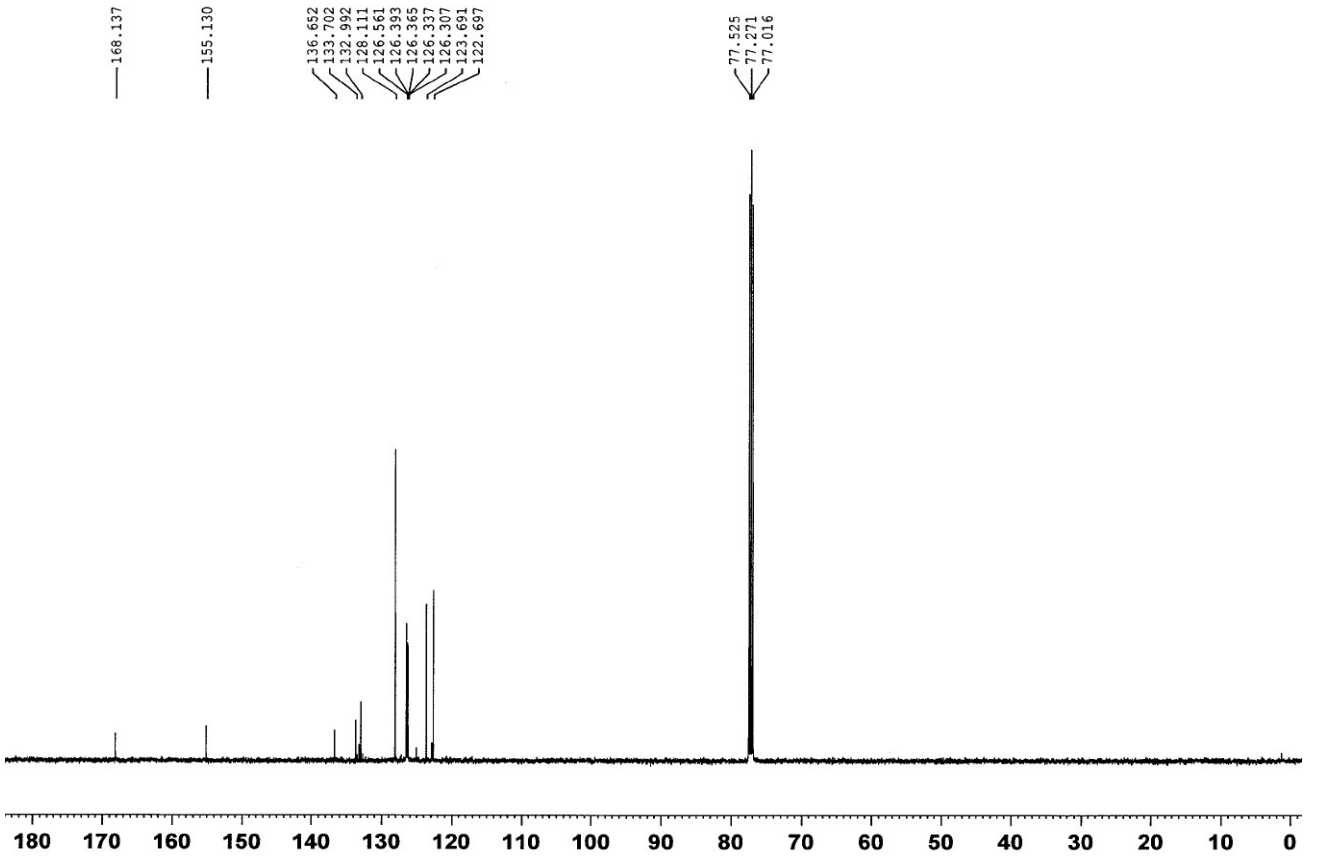
8.184
8.093
7.851
7.834
7.774
7.758
7.422
7.419
7.405
7.402
7.269
2.03
0.92
1.03
2.07
1.00
9
8
7
6
5
4
3
2
1
0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133.702
132.992
128.111
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126.393
126.365
126.337
126.307
123.691
122.697
77.525
77.271
77.016
180
170
160
150
140
130
120
110
100
90
80
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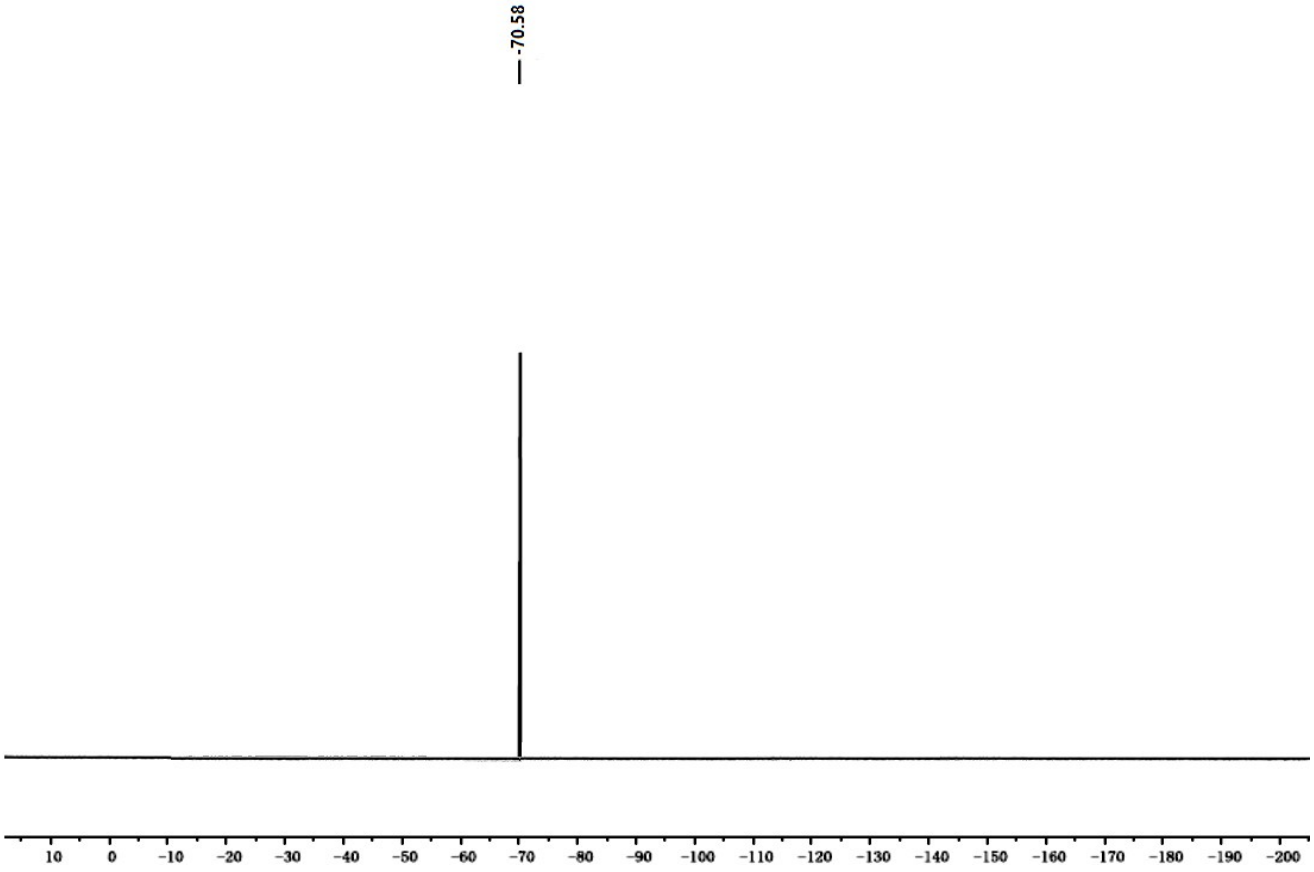
60
50
40
30
20
10
0

3i ^{19}F NMR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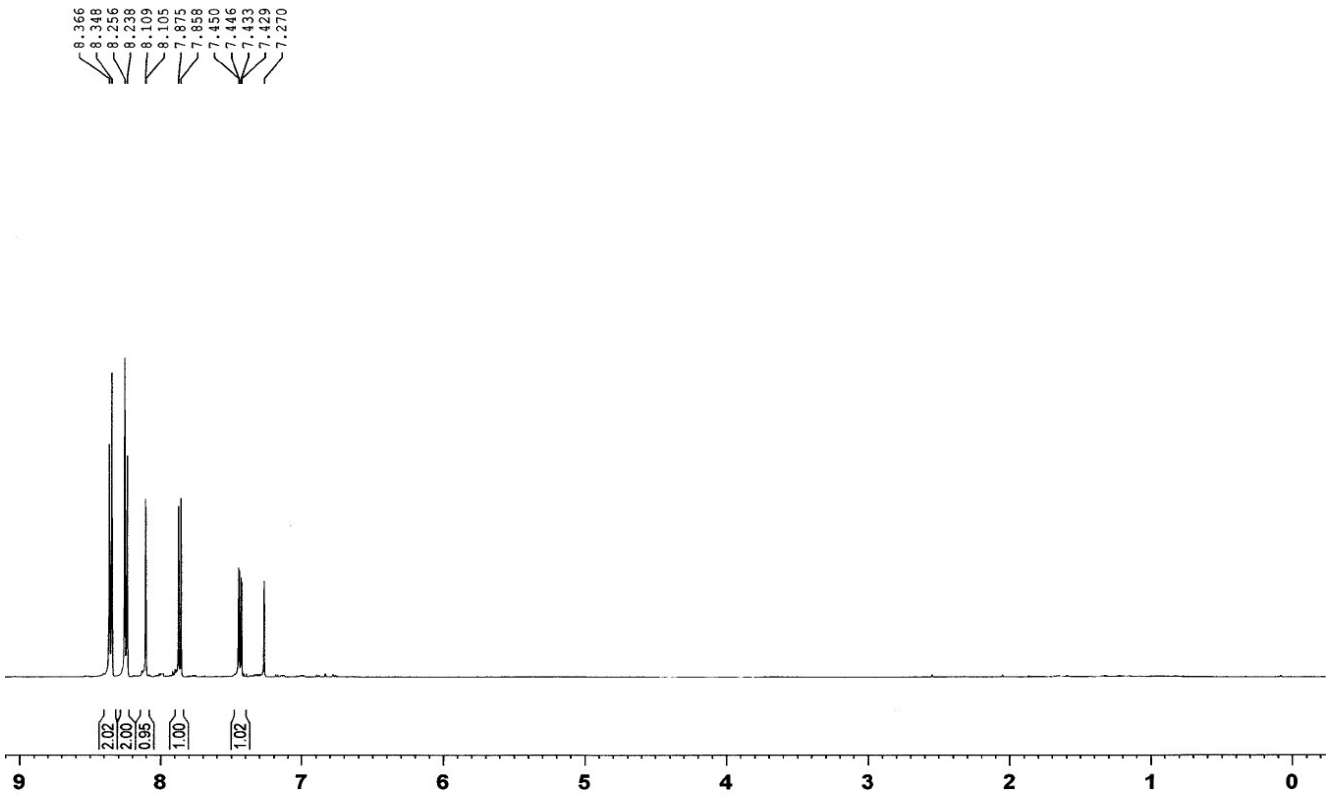
5f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8.256
8.238
8.109
8.105
7.875
7.858
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7.446
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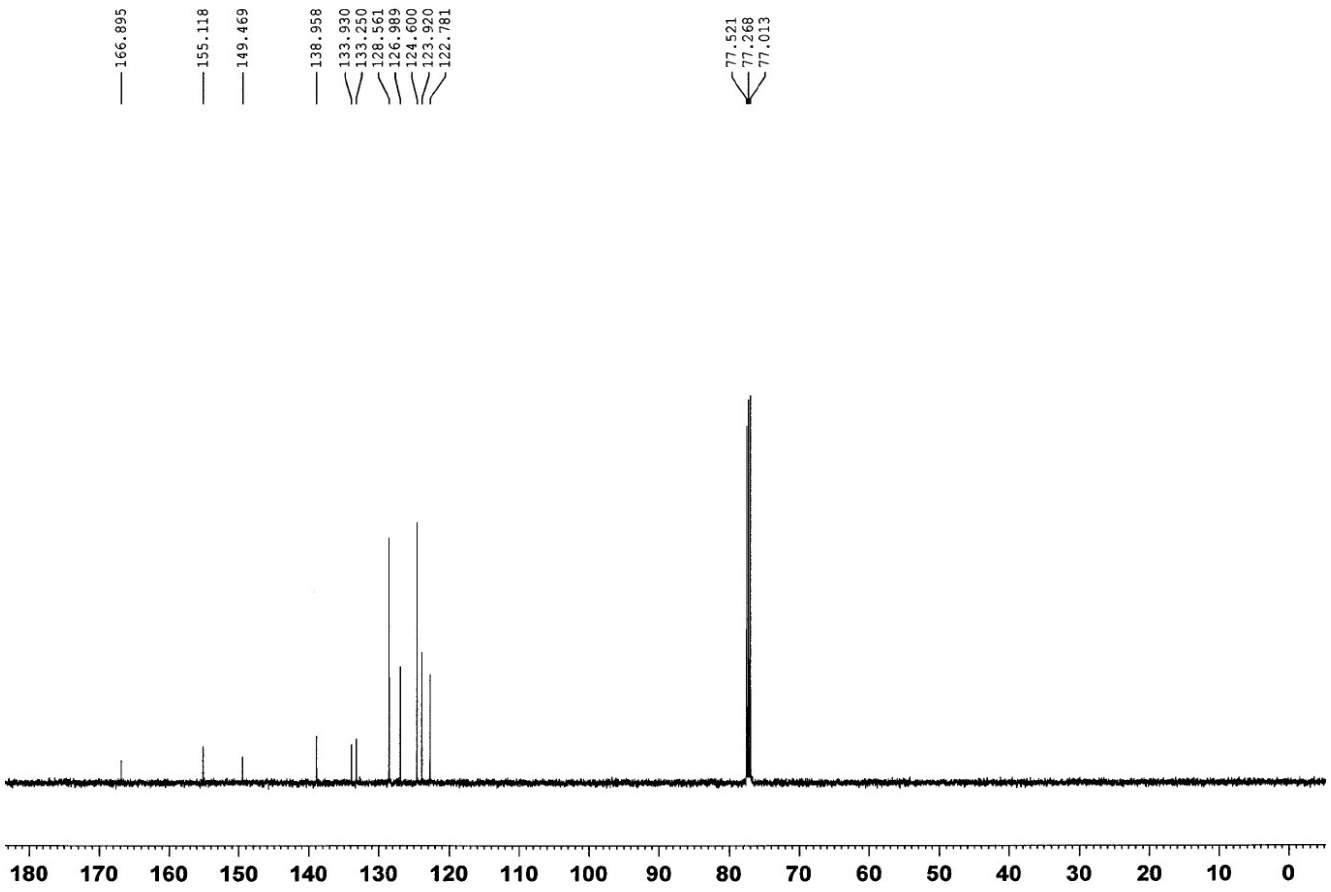
7.429
7.270
2.02
2.00
0.95
1.00
1.02
9 8 7 6 5 4 3 2 1 0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149.469
138.958
133.930
133.250
128.561
126.989
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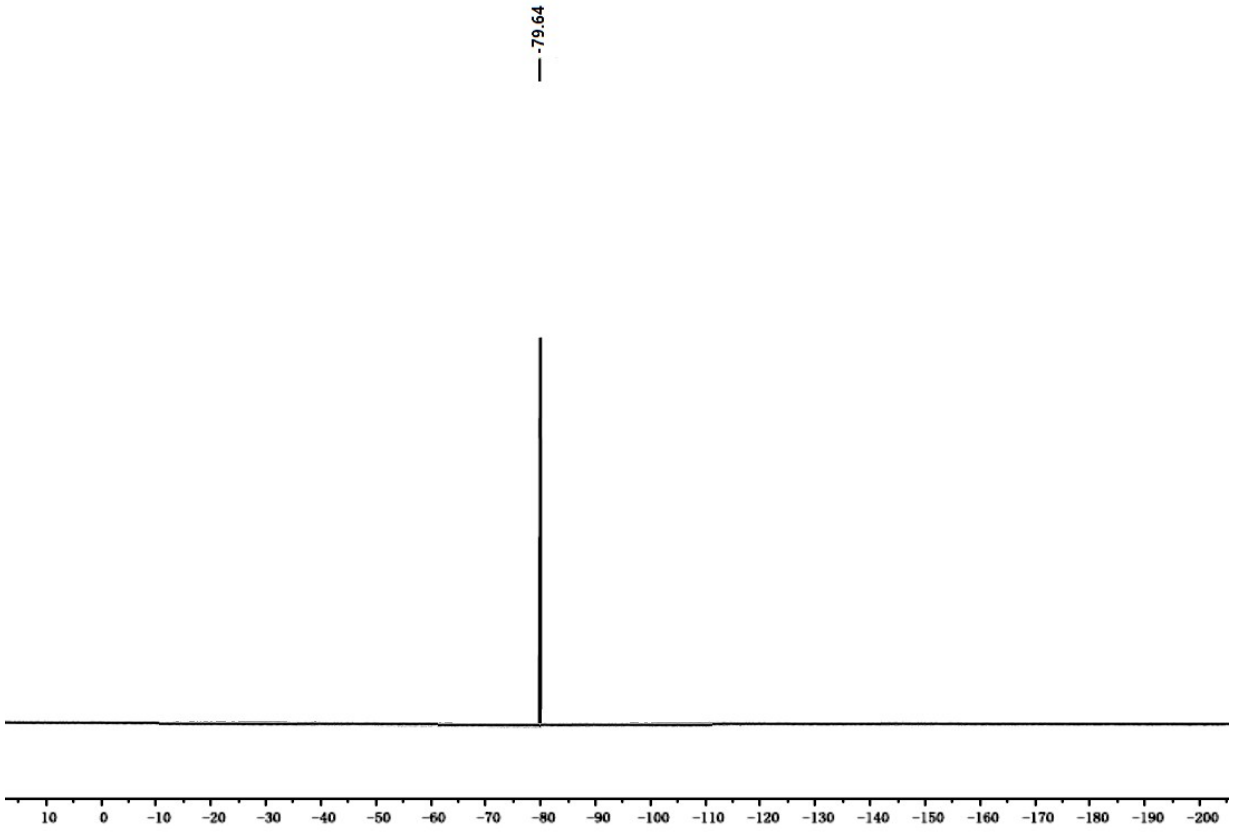
122.781
77.521
77.268
77.013
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

5f ^{19}F NMR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