Electronic Supplementary Information

Synthesis of non-proteinogenic phenylalanine derivatives by rhodium-catalyzed [2+2+2] cycloaddition reactions

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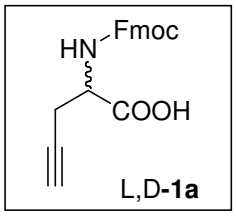
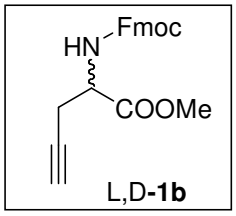
Contents

- Preparation of propargylglycine aminoacids L,D-**1a** and **1b** and characterization data S2-S3
- Preparation of diynes **2h**, **12a**-**b**, and **7b** and characterization data S3-S5
- Preparation of phenylalanine derivatives (*S*)-**4a** and (*S*)-**4b** by methylation reactions and characterization data S5
- Characterization data of homocoupled product **6** S6
- ^{1}H and ^{13}C NMR spectra of all new compounds S7-S35

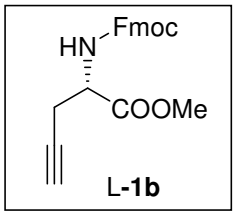
Preparation of propargylglycine amino acids L,D-1a and 1b and characterization data



***N*-α-(((9*H*-Fluoren-9-yl)methoxy)carbonyl)-L,D-propargylglycine,** L,D-**1a.** In a two-necked 100 mL flask, L,D-propargylglycine (0.50 g, 4.42 mmols) and sodium bicarbonate (0.74 g, 8.84 mmols) were taken in a water:dioxane (1:3 (v:v)) mixture (16 mL) and cooled to 0ºC with an ice-water bath. *N*-(9-Fluorenylmethoxycarbonyloxy)succinimide (1.51 g, 4.46 mmols) in dioxane (16 mL) was added dropwise to this solution and the resulting mixture was warmed to room temperature and stirred for 1h30m (TLC monitoring). The mixture was transferred to a decantation funnel and ethyl acetate (20 mL) and water (10 mL) were added. The resulting organic phase was washed with 1N hydrochloric acid (2 x 25 mL), water (2 x 25 mL), and brine (2 x 25 mL), then dried with anhydrous sodium sulfate, filtered, and the solvent was removed by vacuum evaporation to yield *N*-α-(((9*H*-fluoren-9-yl)methoxy)carbonyl)-L,D-propargylglycine, L,D-**1a** (1.46 g, 99% yield) as a colourless solid; mp 173-174ºC; ^{1}H NMR (400 MHz, CD_3COOD) δ 2.31 (t, *J* = 2.6 Hz, 1H), 2.81-2.87 (m, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 4.49 (d, *J* = 6.8 Hz, 2H), 4.65 (t, *J* = 5.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H).

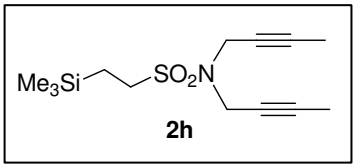


***N*-α-(((9*H*-Fluoren-9-yl)methoxy)carbonyl)-L,D-propargylglycine methyl ester,** L,D-**1b.** In a 10 mL flask, trimethylsilyl chloride (0.15 mL, 1.15 mmols) was added dropwise over *N*-α-(((9*H*-fluoren-9-yl)methoxy)carbonyl)-L,D-propargylglycine, L,D-**1a** (0.19 g, 0.56 mmols). Methanol was then added (2 mL) and the reaction was stirred at room temperature for 2 hours (TLC monitoring). The solvent was removed by vacuum evaporation to yield *N*-α-(((9*H*-Fluoren-9-yl)methoxy)carbonyl)-L,D-propargylglycine methyl ester, L,D-**1b** (0.18 g, 95% yield) as a colourless solid; mp 118-119 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (t, *J* = 2.2 Hz, 1H), 2.82 (dd, *J* = 4.4 / 2.2 Hz, 2H), 3.84 (s, 3H), 4.28 (t, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 4.59 (dt, *J* = 7.6 / 2.2 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 7.31-7.38 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.62-7.66 (m, 2H), 7.79 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 47.1, 52.4, 52.9, 67.3, 71.9, 78.3, 120.0, 125.1, 127.1, 127.8, 141.3, 143.7, 143.8, 155.6, 170.8; ESI-MS (*m*/*z*) 350 $[M+H]^+$, 372 $[M+Na]^+$.

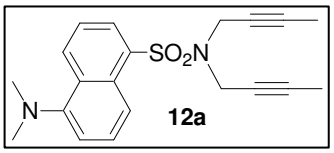


***N*-α-(((9*H*-Fluoren-9-yl)methoxy)carbonyl)-L-propargylglycine methyl ester,** L-**1b.** L-**1b** was prepared according to the method described above for L,D-**1b**. Colourless solid (0.16 g, 96% yield, >99% ee) $[\alpha]^{20}_{D}$ +25.84 (*c* 0.02, CH_2Cl_2). The ee was determined with HPLC analysis using a chiral column (Kromasil 100 TBB column, 4.6 x 250 mm, 5 μm, r.t.; eluent: 99 % hexanes / 1 % THF, flow rate: 1.0 mL/min. over 40 min.; λ = 254 nm; retention time 24.8 min. and 27.0 min. for L,D-**1b**; retention time 24.8 min for L-**1b** (>99% ee)).

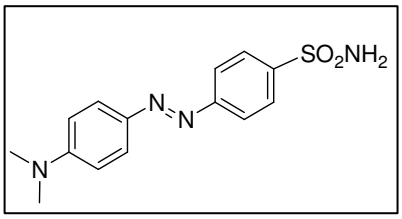
Preparation of diynes 2h, **12a-b, and 7b and characterization data**



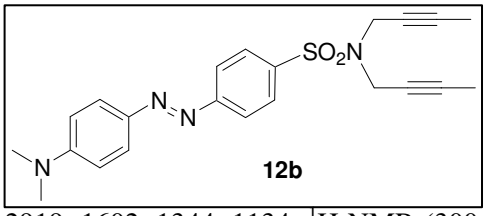
***N*,*N*-bis(2-butynyl)-(2-trimethylsilyl)etansulfonamide, 2h.** In a two-necked 100 mL flask, a mixture of 2-(trimethylsilyl)etansulfonamide (1.00 g, 5.51 mmols), potassium carbonate (3.83 g, 27.68 mmols) and 50 mL of acetonitrile was heated to reflux. 1-Bromo-2-butyne (1.00 mL, 11.08 mmols) was added to this solution and the resulting mixture was stirred for 2h (TLC monitoring). The mixture was cooled to room temperature, salts were filtered off and the solvent was removed by vacuum evaporation to yield *N*,*N*-bis(2-butynyl)-(2-trimethylsilyl)etansulfonamide, **2h** (0.98 g, 62% yield) as a colourless solid; mp 49-50 ºC; IR (ATR) ν (cm^{-1}): 2955, 1323, 1144; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.00-1.07 (m, 2H), 1.82 (t, *J* = 2.4 Hz, 6H), 2.97-3.04 (m, 2H), 4.11 (q, *J* = 2.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -2.0, 3.5, 9.8, 36.8, 48.6, 72.9, 81.3; ESI-MS (*m*/*z*) 308 $[M+Na]^+$; HRMS calcd. for $[C_{13}H_{23}NO_2SSi + H]^+$: 308.1111. Found: 308.1123.



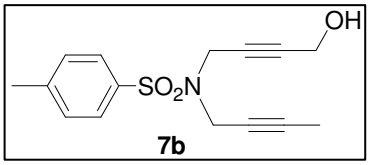
***N*,*N*-bis(2-butynyl)-5-(dimethylamino)naphtalene-1-sulfonamide, 12a. 12a** was prepared according to the method described above for **2h**. Yellow solid (0.42 g, 100% yield); mp 94-95 ºC; IR (ATR) ν (cm^{-1}): 2919, 1340, 1144; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (t, *J* = 2.4 Hz, 6H), 2.87 (s, 6H), 4.17 (q, *J* = 2.4 Hz, 4H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.46-7.58 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.4, 36.3, 45.4, 72.2, 81.3, 115.2, 119.8, 123.1, 128.0, 130.0, 130.3, 130.5, 134.6, 151.6; ESI-MS (*m*/*z*) 355 $[M+H]^+$; HRMS calcd. for $[C_{20}H_{22}N_2O_2S + H]^+$: 355.1475. Found: 355.1481.



4-Dimethylaminoazobenzene-4'-sulfonamide. A degassed solution of 4-dimethylaminoazobenzene-4'-sulfonyl chloride (0.99 g, 2.98 mmols), 28 mL of ammonium hydroxide (25%) and 60 mL of dichloromethane was stirred at room temperature for 2h (TLC monitoring). The solid obtained was then filtered and washed with ethyl ether (2 x 20 mL) to afford 4-dimethylaminoazobenzene-4'-sulfonamide (0.91 g, 99% yield) as an orange solid; mp 228-229 ºC; IR (ATR) ν (cm^{-1}): 3343, 3247, 1604, 1301, 1140; ^{1}H NMR (400 MHz, acetone-d_6) δ 3.14 (s, 6H), 3.50-3.54 (m, 1H), 3.59-3.63 (m, 1H), 6.87 (d, *J* = 9.2 Hz, 2H), 7.87 (d, *J* = 9.2 Hz, 2H), 7.92 (d, *J* = 9.2 Hz, 2H), 8.02 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 40.4, 62.0, 73.5, 112.5, 123.1, 126.4, 128.1, 144.3, 145.1, 154.4, 155.9; ESI-MS (*m/z*) 276 $[M+H]^+$, 298 $[M+Na]^+$.



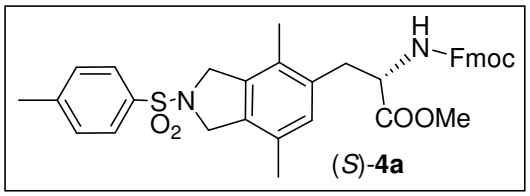
***N*,*N*-bis(2-butynyl)-4-dimethylaminoazobenzene-4'-sulfonamide, 12b. 12b** was prepared according to the method described above for **2h**. Red solid (0.41 g, 99% yield); mp 165-166 ºC; IR (ATR) ν (cm^{-1}): 2919, 1602, 1344, 1134; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (t, *J* = 2.4 Hz, 6H), 3.11 (s, 6H), 4.12 (q, *J* = 2.4 Hz, 4H), 6.75 (d, *J* = 9.3 Hz, 2H), 7.86-7.92 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.4, 36.7, 40.2, 71.5, 81.9, 111.4, 122.1, 125.7, 128.9, 137.9, 143.6, 153.1, 155.7; ESI-MS (*m/z*) 409 $[M+H]^+$; HRMS calcd. for $[C_{22}H_{24}N_4O_2S + H]^+$: 409.1693. Found: 409.1679.



***N*-(2-butynyl)-*N*-(2-propynyl-4-ol)-(4-methyphenyl)sulfonamide, 7b.** In a two-necked 25 mL flask, 1.7 mL (2.72 mmols) of 1.6 M solution *n*-BuLi in hexanes was added dropwise to a solution of *N*-(2-butynyl)-*N*-(2-propinil)-(4-methylphenyl)sulfonamide (1.00 g, 5.51 mmols) in 2 mL of anhydrous THF at -78 ºC under a nitrogen atmosphere. The mixture was stirred for 1h and then a solution of *p*-formaldehyde (0.42 g, 12.68 mmols) in 1 mL of anhydrous THF at -78 ºC was added and allowed to warm to room temperature overnight. The reaction was quenched with saturated ammonium chloride (10 mL) and the aqueous layer was extracted with ethyl acetate (3 x 10 mL), dried over sodium sulfate, filtered and concentrated. The product was purified by column chromatography on silica gel using mixtures of hexanes/ethyl acetate of increasing polarity (8/2 to 7/3) as the

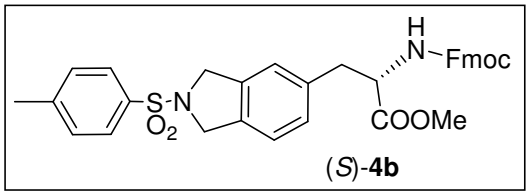
eluent to afford **7b** (0.24 g, 39% yield) as a yellow oil; IR (ATR) ν (cm^{-1}): 3525, 2920, 1345, 1157; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (t, *J* = 2.4 Hz, 3H), 1.97 (br abs, 1H), 2.42 (s, 3H), 4.06-4.10 (m, 4H), 4.14-4.18 (m, 2H), 7.30 (AA' part, AA'BB' syst., *J* = 8.4 Hz, 2H), 7.72 (BB' part, AA'BB' syst., *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.3, 21.4, 36.3, 36.8, 50.6, 71.2, 78.2, 82.0, 83.7, 127.9, 129.3, 135.1, 143.7; HRMS calcd. for $[C_{15}H_{17}NO_3S + H]^+$: 292.1002. Found: 292.1016.

Preparation of phenylalanine derivatives (*S*)-4a and (*S*)-4b by methylation reactions and characterization data



(*S*)-**4a**

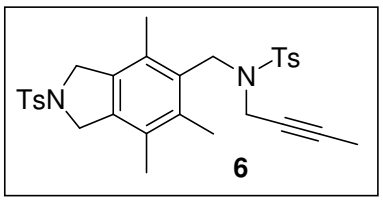
(*S*)-2-(((9*H*-Fluoren-9-yl)methoxy)carbonylamino)-3-(4,7-dimethyl-2-tosylisoindolin-5-yl)propanoic acid methyl ester, (*S*)-**4a**. In a 25 mL flask, trimethylsilyl chloride (0.01 mL, 0.06 mmols) was added dropwise over (*S*)-**3a** (0.020 g, 0.03 mmols). Methanol was then added (1 mL) and the reaction mixture was stirred at room temperature for 1 hour (TLC monitoring). The solvent was removed by vacuum evaporation, the residue was taken in dichloromethane, filtered, and the solvent removed to yield (*S*)-**4a** (0.020 g, 96% yield, >99% ee) as a colourless solid $[\alpha]^{20}_D$ +19.05 (*c* 0.01, CH_2Cl_2). The ee was determined with HPLC analysis using a chiral column (Kromasil 100 TBB column, 4.6 x 250 mm, 5 µm, r.t.; eluent: 90 % hexanes / 10 % THF, flow rate: 1.0 mL/min. over 40 min.; λ = 254 nm; retention time 23.8 min. and 27.5 min. for (*R*,*S*)-**4a**; retention time 27.5 min for (*S*)-**4a** (>99% ee)).



(*S*)-**4b**

(*S*)-2-(((9*H*-Fluoren-9-yl)methoxy)carbonylamino)-3-(2-tosylisoindolin-5-yl)propanoic acid methyl ester, (*S*)-**4b** was prepared according to the methylation method described above. Colourless solid (95% yield, >99% ee) $[\alpha]^{20}_D$ +16.0 (*c* 0.01, CH_2Cl_2). The ee was determined with HPLC analysis using a chiral column (Kromasil 100 TBB column, 4.6 x 250 mm, 5 µm, r.t.; eluent: 90 % hexanes / 10 % THF, flow rate: 1.0 mL/min. over 40 min.; λ = 254 nm; retention time 36.2 min. and 41.4 min. for (*R*,*S*)-**4b**; retention time 41.4 min for (*S*)-**4b** (>99% ee)).

Characterization data of homocoupled product 6



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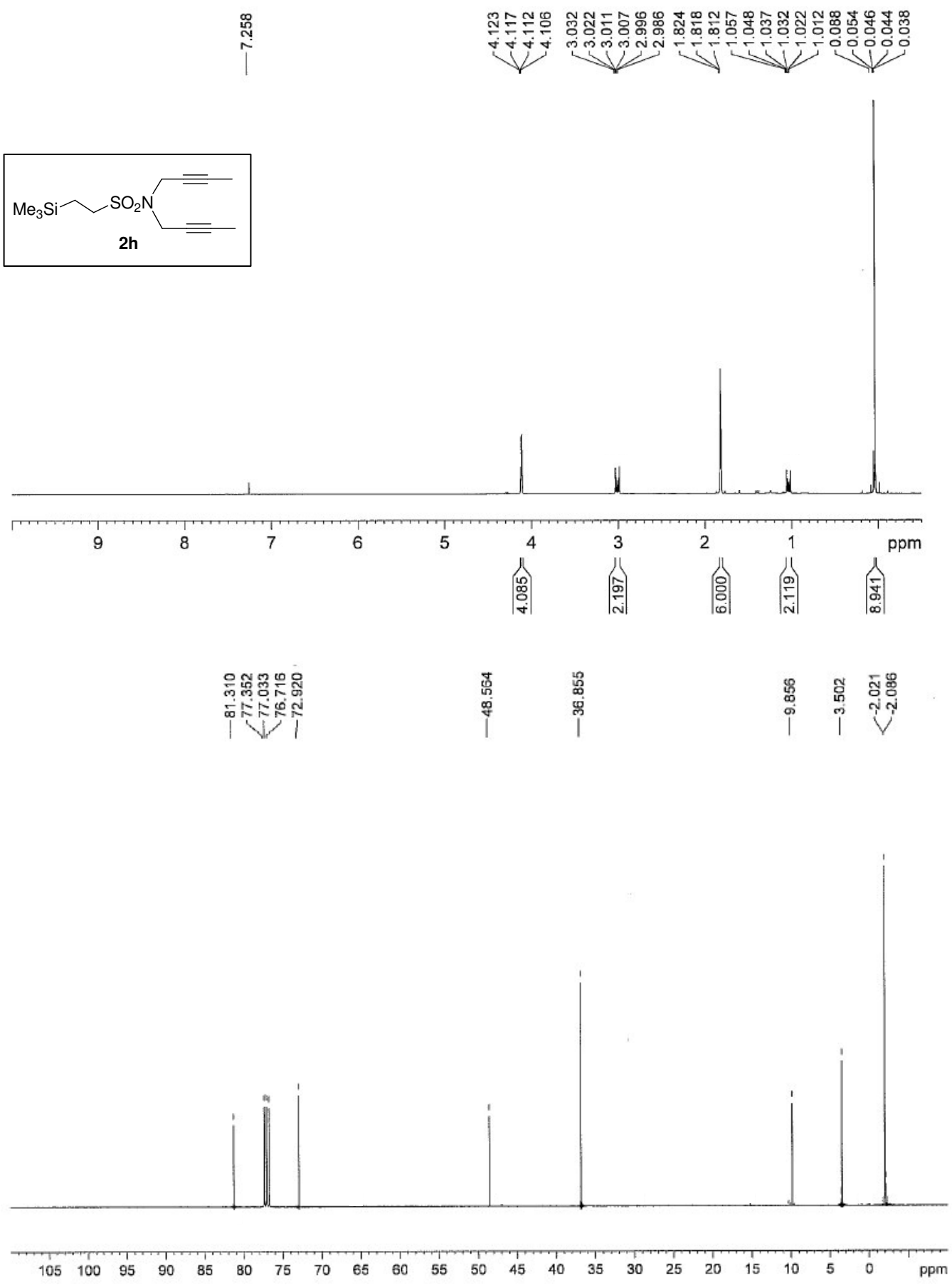
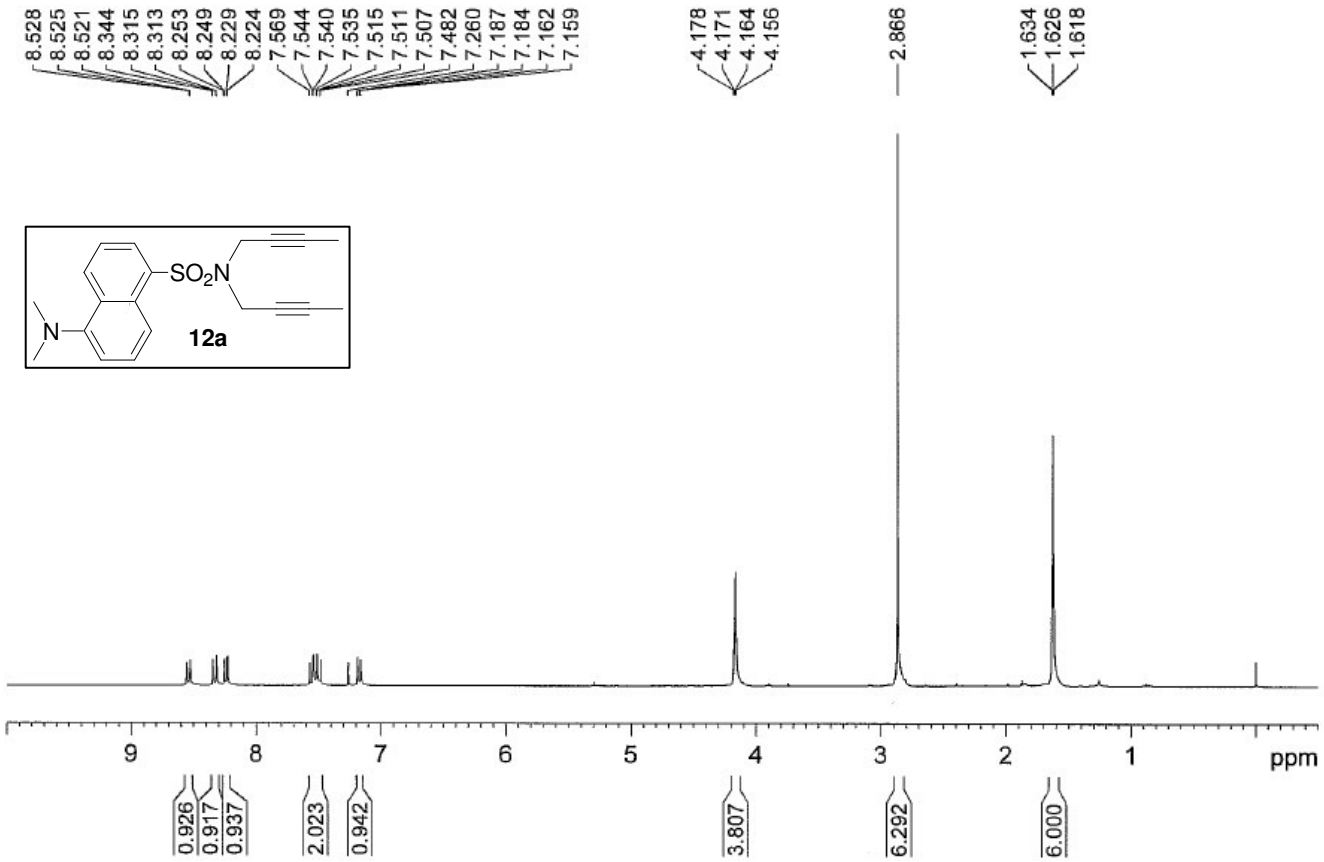
Colourless solid; mp 188-189 ºC; IR (ATR) ν (cm^{-1}): 2918, 1342, 1158; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, *J* = 2.4 Hz, 3H), 2.07 (s, 3H), 2.20 (s, 3H), 2.27 (s, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 3.61 (q, *J* = 2.4 Hz, 2H), 4.42 (s, 2H), 4.55 (br abs, 2H), 4.58 (br abs, 2H), 7.32 (d, *J* = 7.6 Hz, 4H), 7.75-7.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.4, 15.9, 16.4, 16.7, 21.7, 35.3, 44.9, 54.2, 54.3, 72.8, 82.3, 127.8, 128.6, 129.3, 129.4, 130.1, 130.5, 131.0, 133.2, 134.2, 135.3, 135.8, 137.8, 143.6, 143.9; ESI-MS (*m*/*z*) 551 $[M+H]^+$.

^{1}H and ^{13}C NMR spectra of diynes 2h, 12a-b, and 7b

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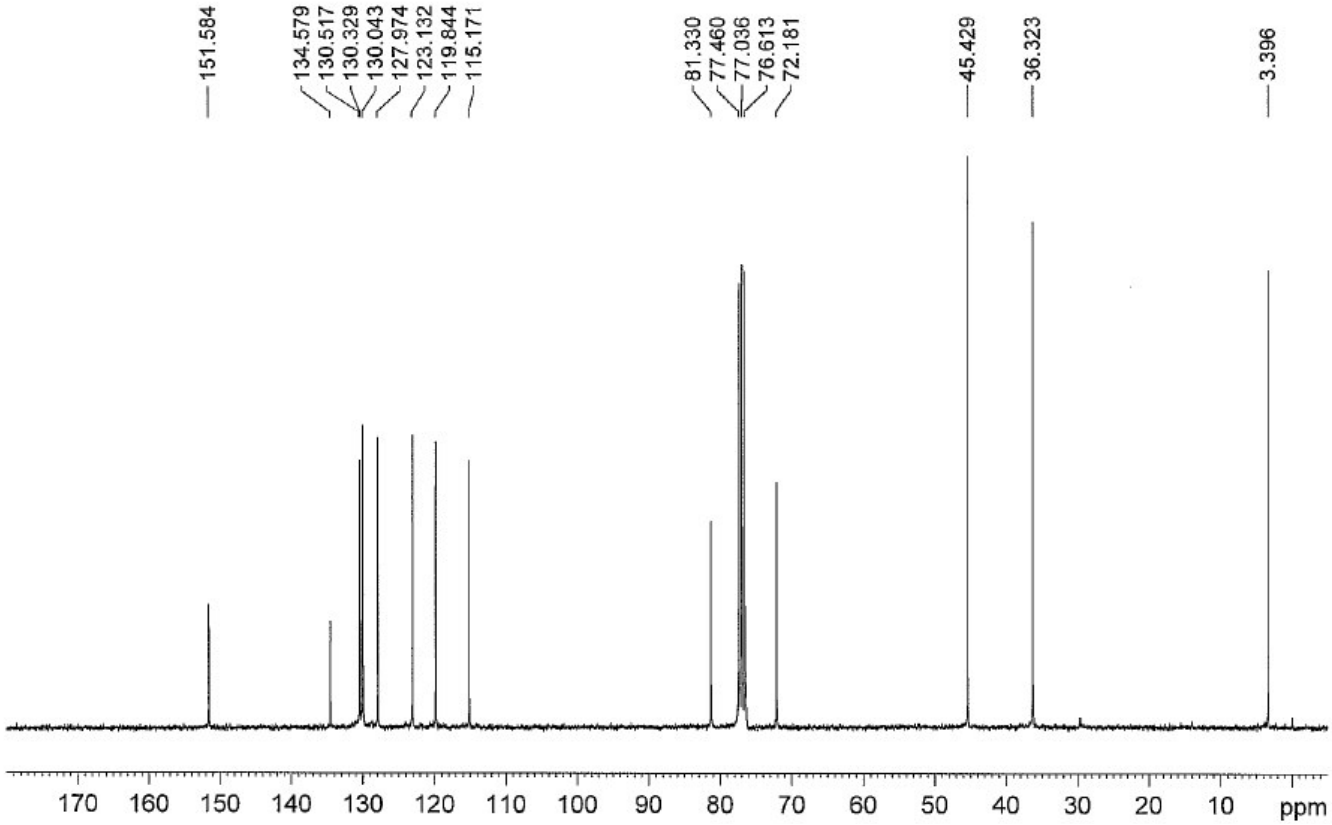
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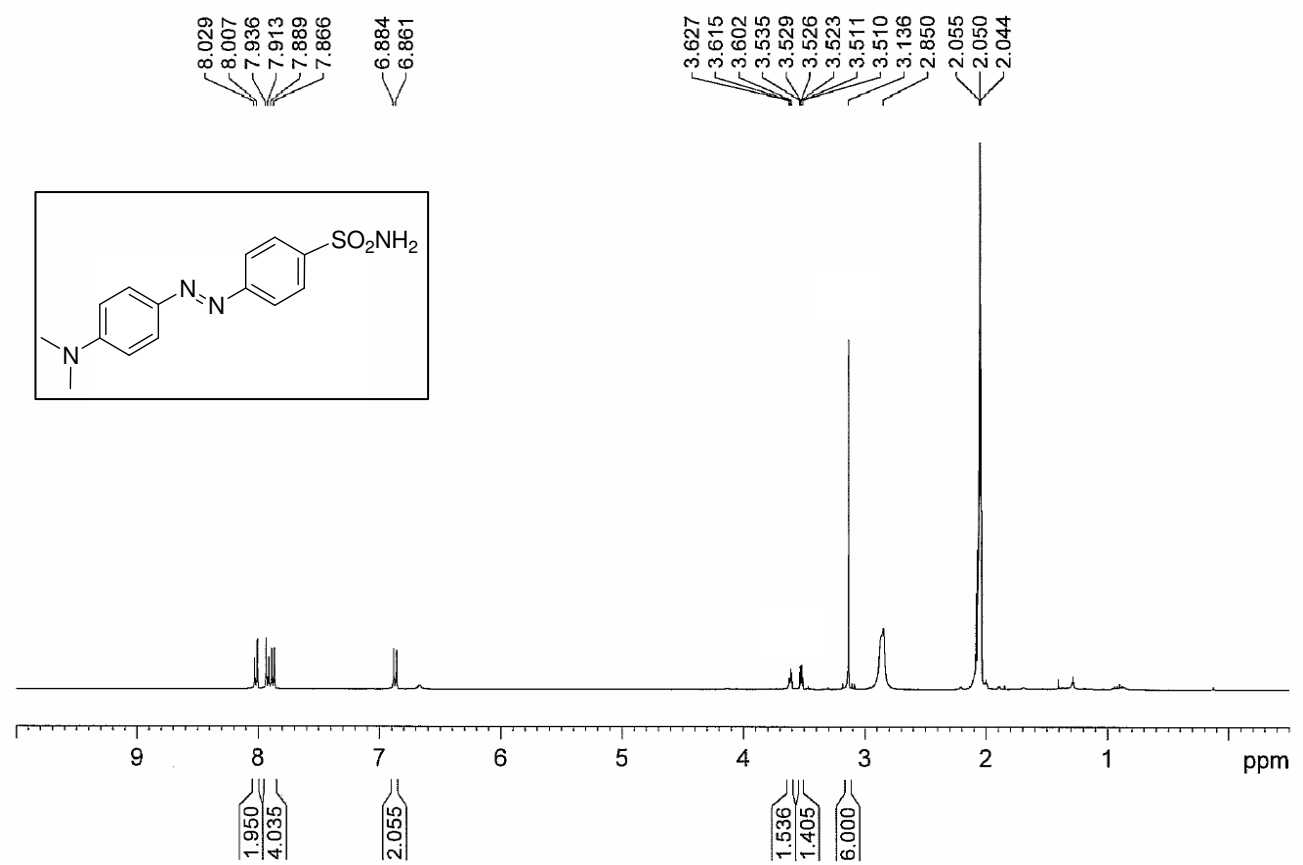
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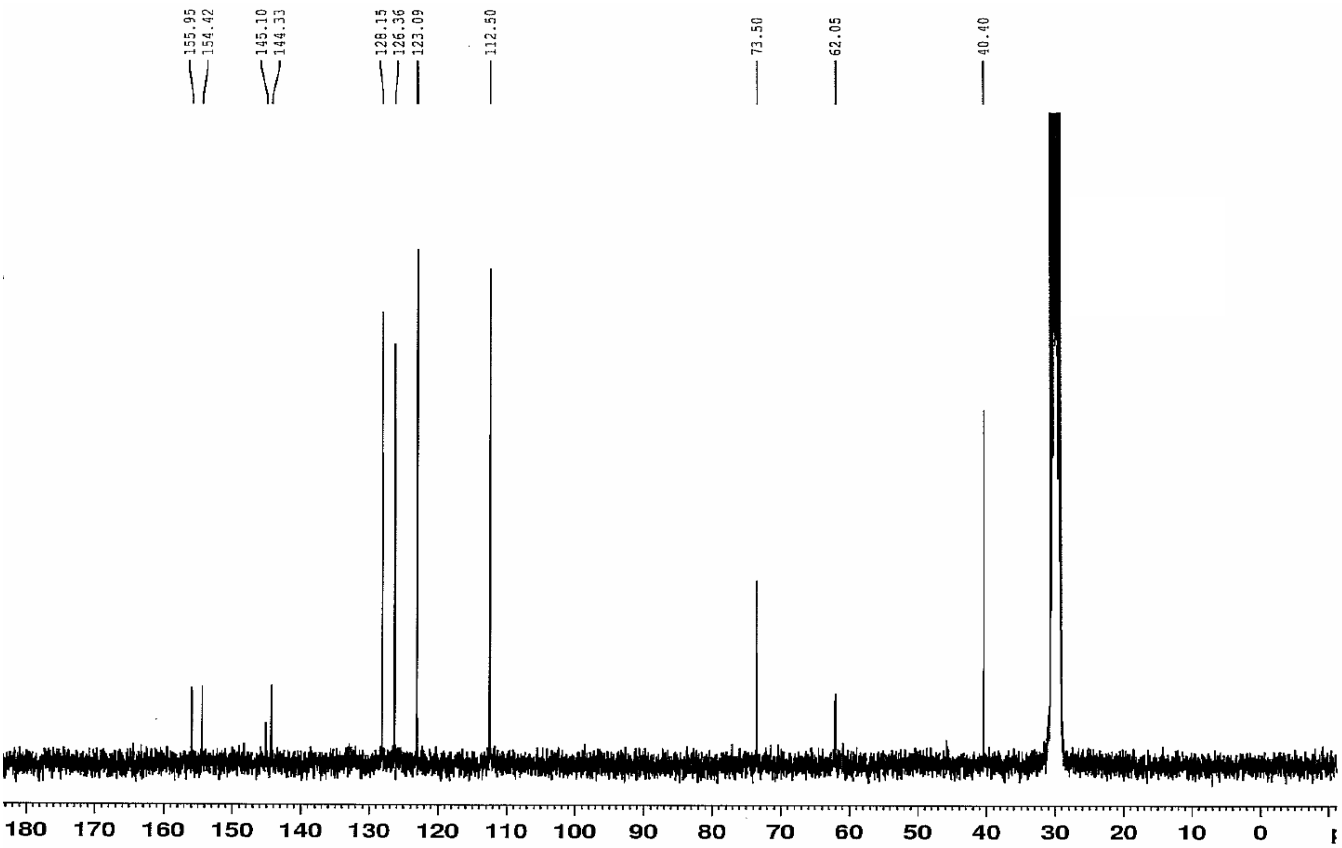
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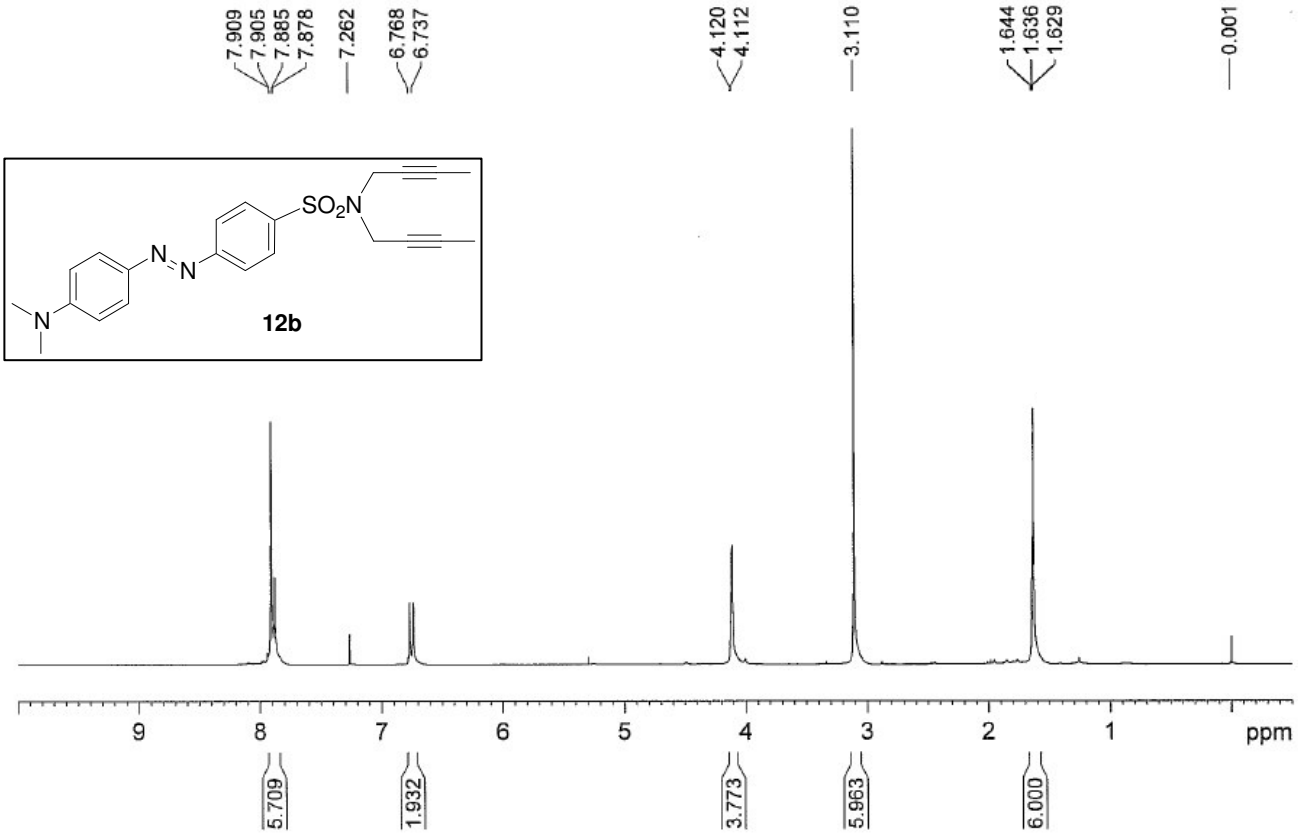
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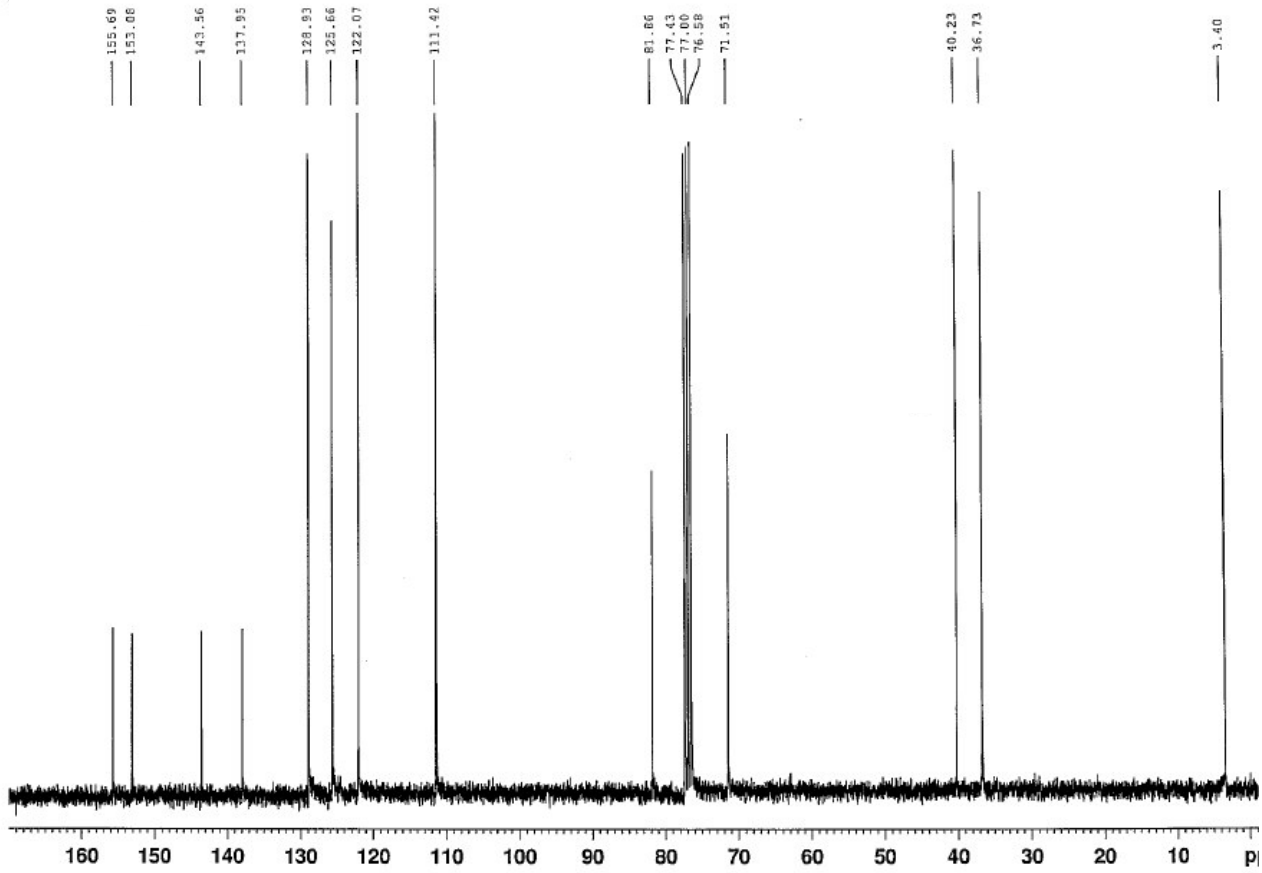
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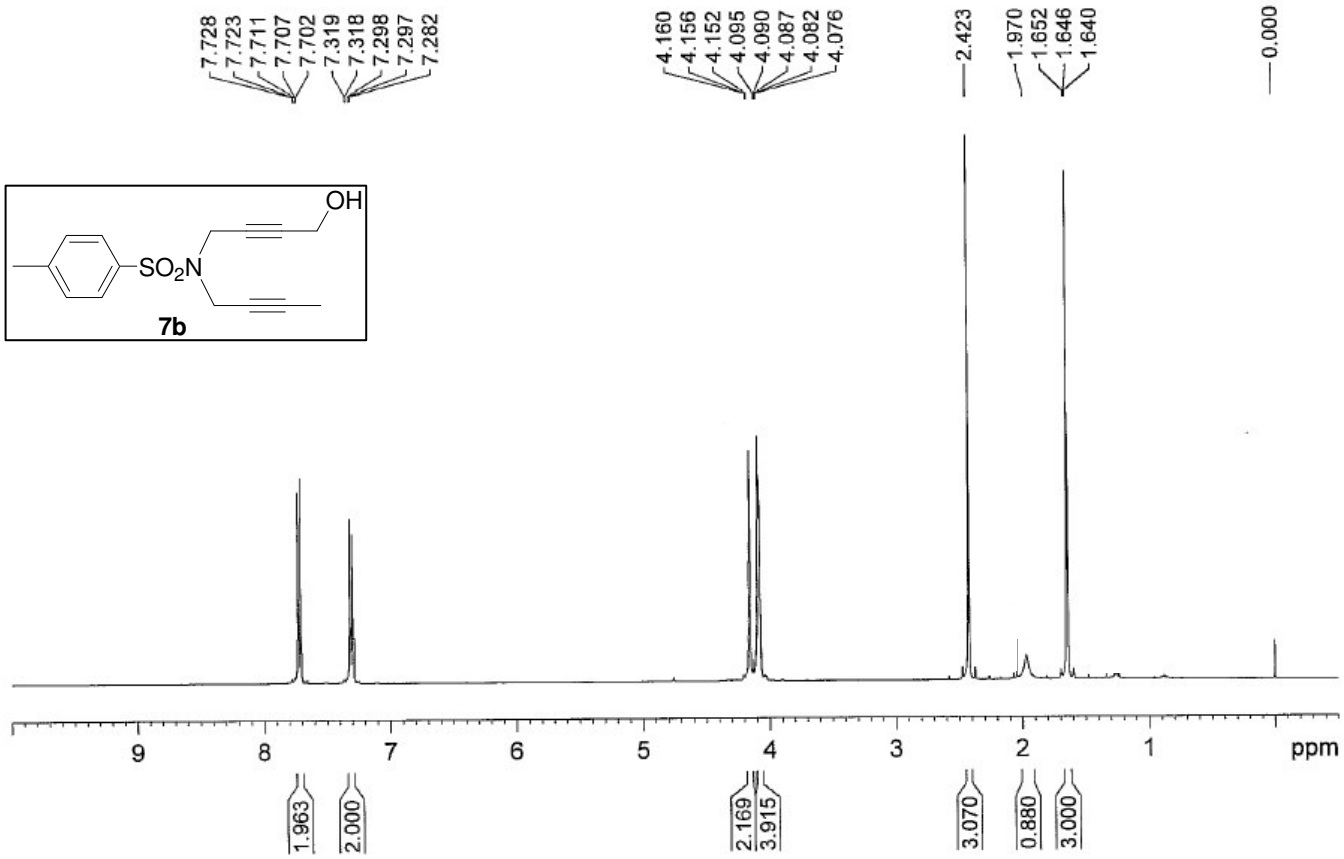
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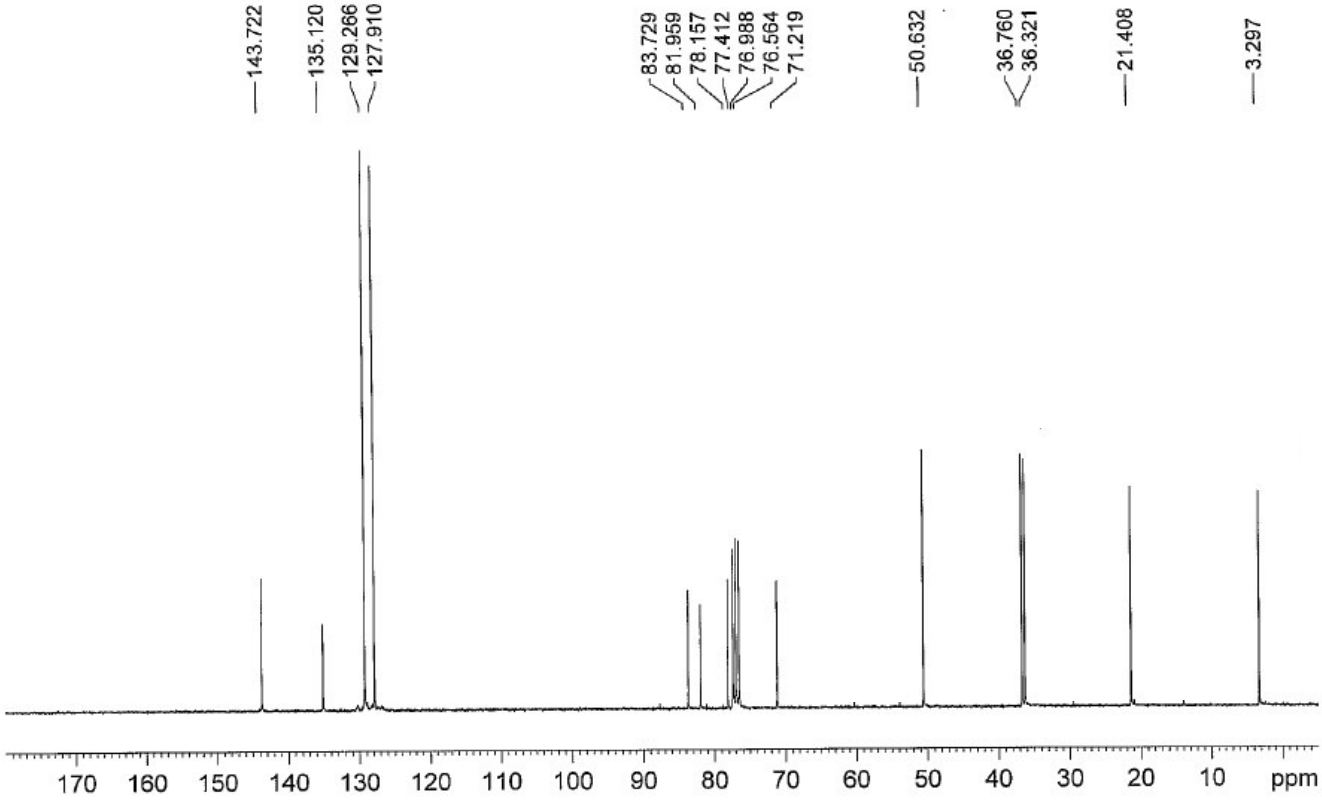
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129.266
127.910
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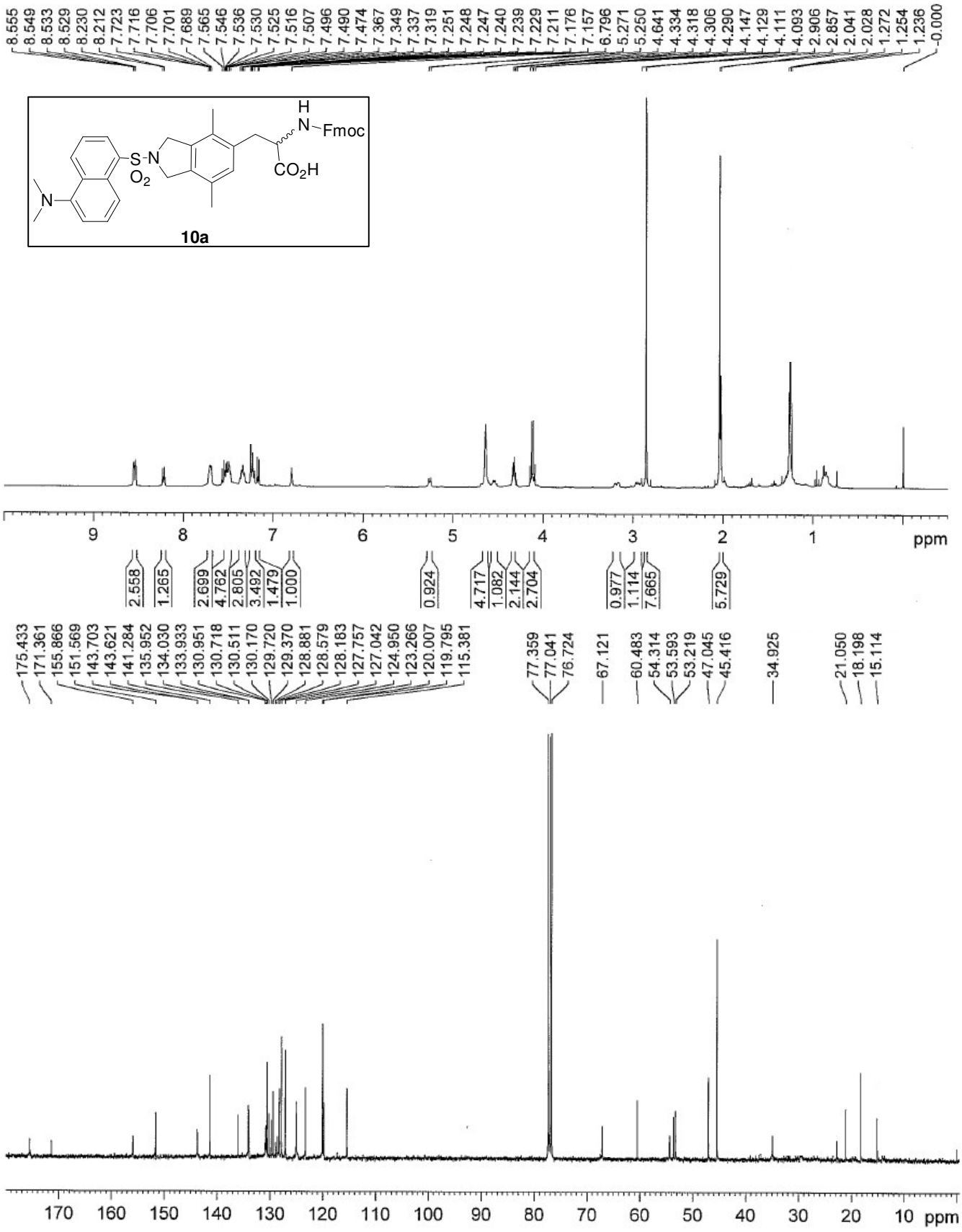
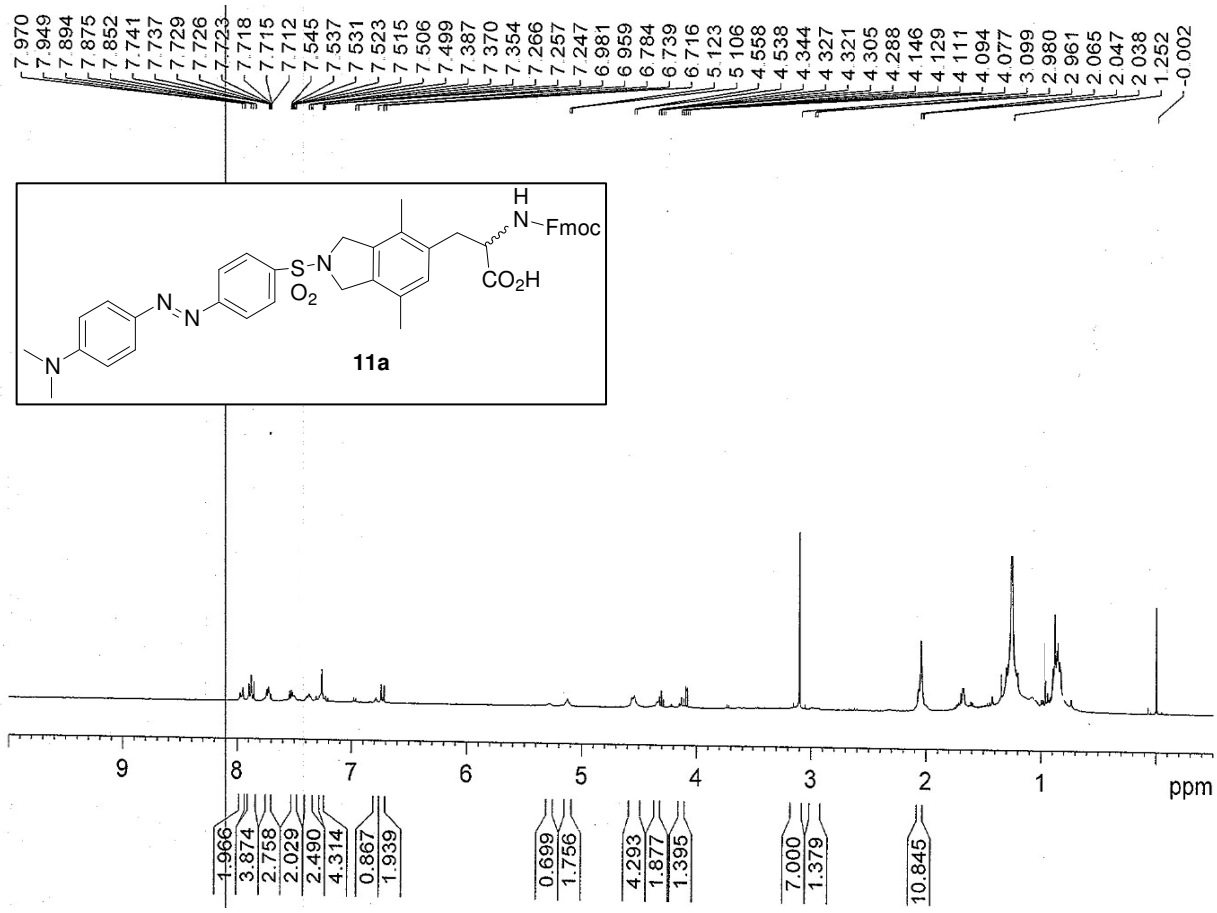
78.157
77.412
76.988
76.564
71.219
50.632
36.760
36.321
21.408
3.297
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H and ^{13}C NMR spectra of phenylalanine derivatives 10a, 11a, 4a-h, 10b, 11b, 8c/9c, 8a/9a, 8b, 9b, and 5a-f

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7.729
7.726
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7.718
7.715
7.712
7.545
7.537
7.531
7.523
7.515
7.506
7.499
7.387
7.370
7.354
7.266
7.257
7.247
6.981
6.959
6.784
6.739
6.716
5.123
5.106
4.558
4.538
4.344
4.327
4.321
4.305
4.288
4.146
4.129
4.111
4.094
4.077
3.099
2.980
2.961
2.065
2.047
2.038
1.252
-0.002
H
N
Fmoc
S
N
O2
CO2H
N
N
N
11a
9
8
7
6
5
4
3
2
1
ppm
1.966
3.874
2.758
2.029
2.490
4.314
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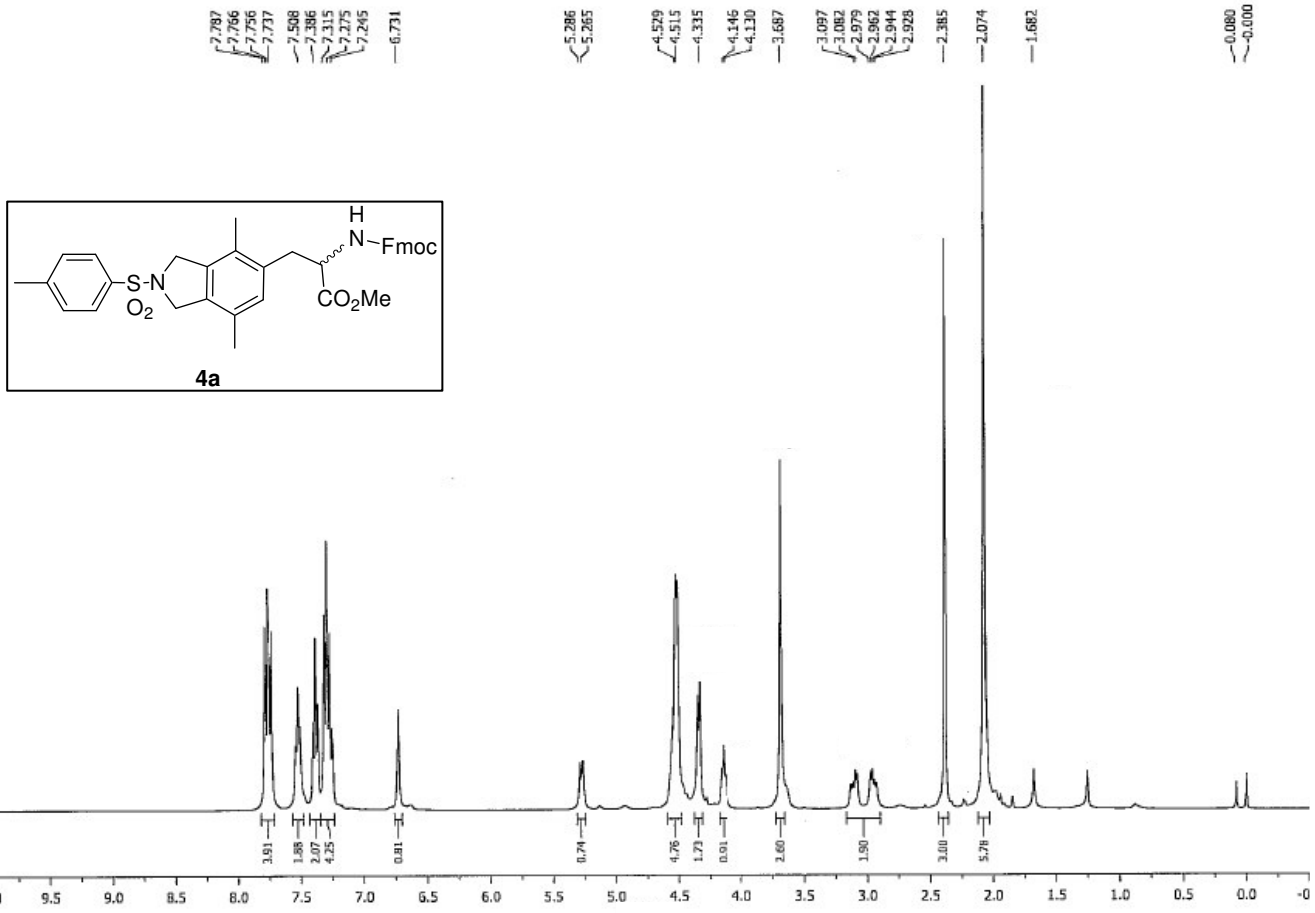
1.939
0.699
1.756
4.293
1.877
1.395
7.000
1.379
10.845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7.756
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7.386
7.315
7.275
7.245
6.731
5.286
5.265
4.529
4.515
4.335
4.146
4.130
3.687
3.097
3.082
2.979
2.962
2.944
2.928
2.385
2.074
1.682
0.080
-0.000
H
N
Fmoc
S-N
O2
CO2Me
4a
3.91
1.88
2.07
4.25
0.81
0.74
4.76
1.73
0.91
2.60
1.90
3.00
5.78
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
1.0
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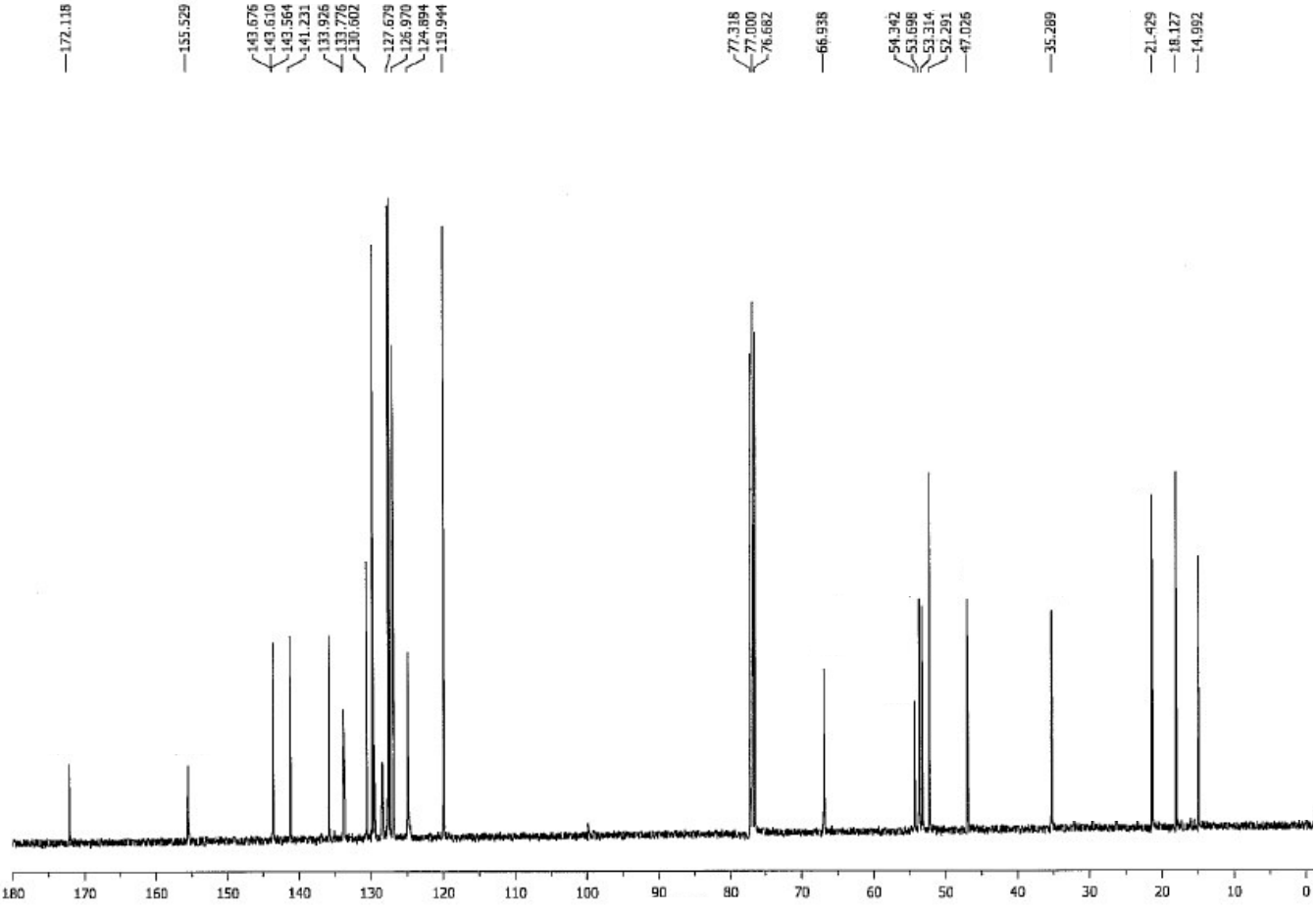
0.0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143.676
143.610
143.564
141.231
133.926
133.776
130.602
127.679
126.970
124.894
119.944
77.318
77.000
76.682
66.938
54.342
53.698
53.314
52.291
47.026
35.289
21.429
18.127
14.992
180
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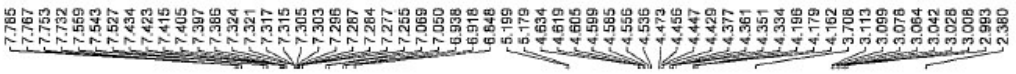
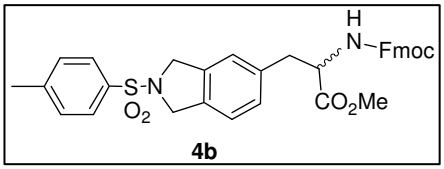
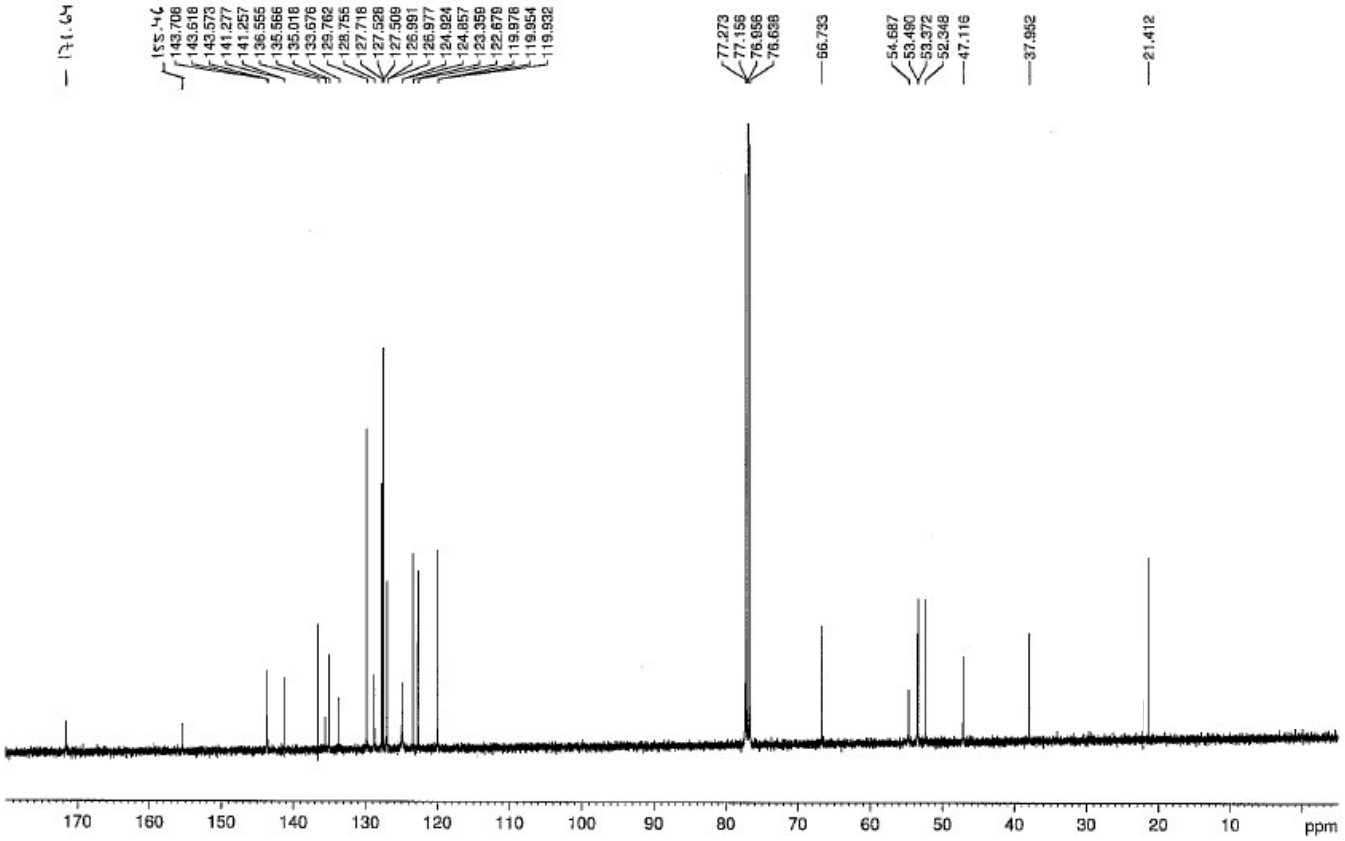
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




H
N
Fmoc
S-N
O2
CO2Me

4b

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 0.0 ppm
4.046 2.040 1.981 4.092 0.946 0.835 0.839 0.764 1.031 4.210 2.018 1.074 2.631 1.801 3.000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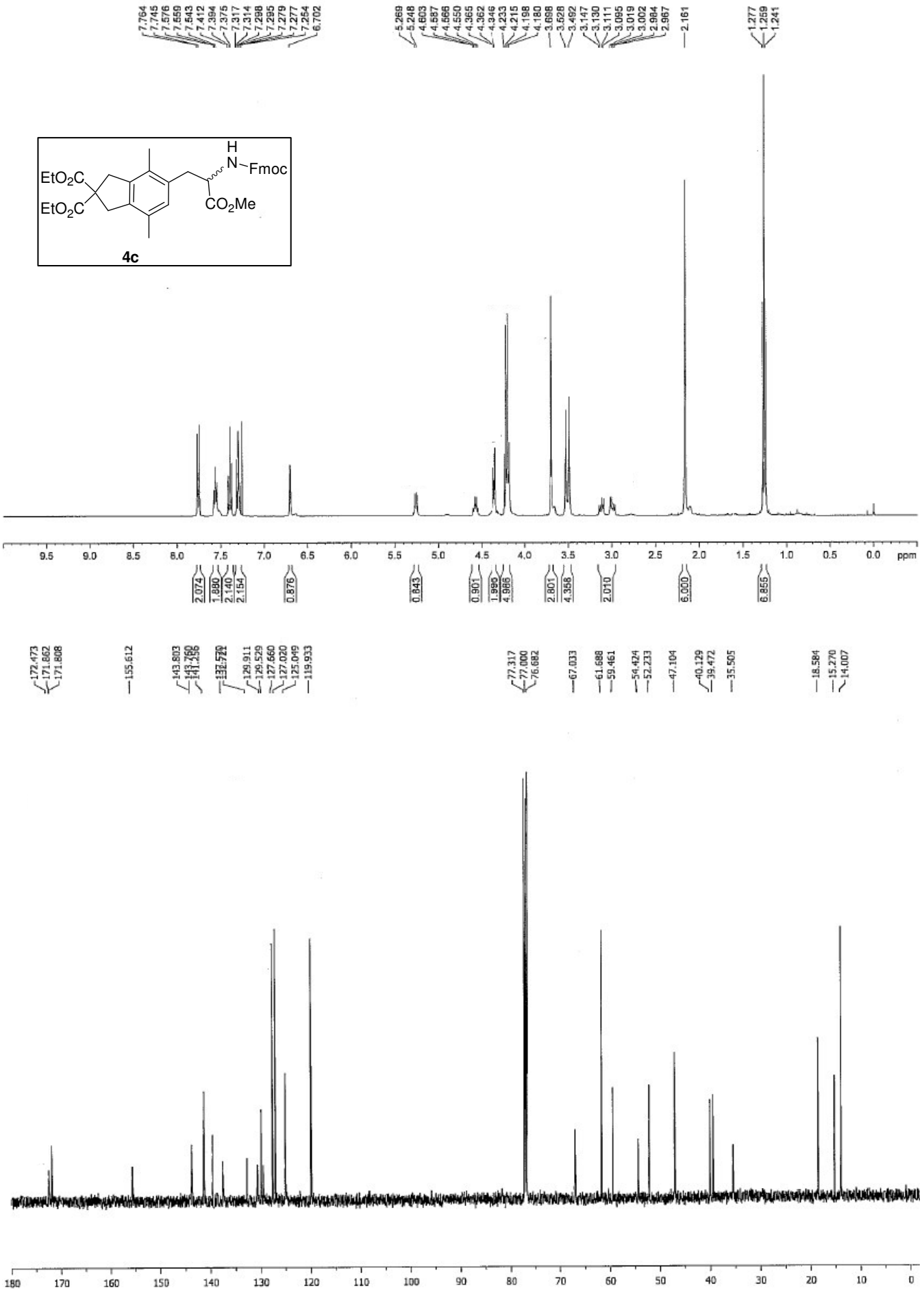
77.156
76.956
76.638
66.733
54.687
53.480
53.372
52.348
47.116
37.952
21.412
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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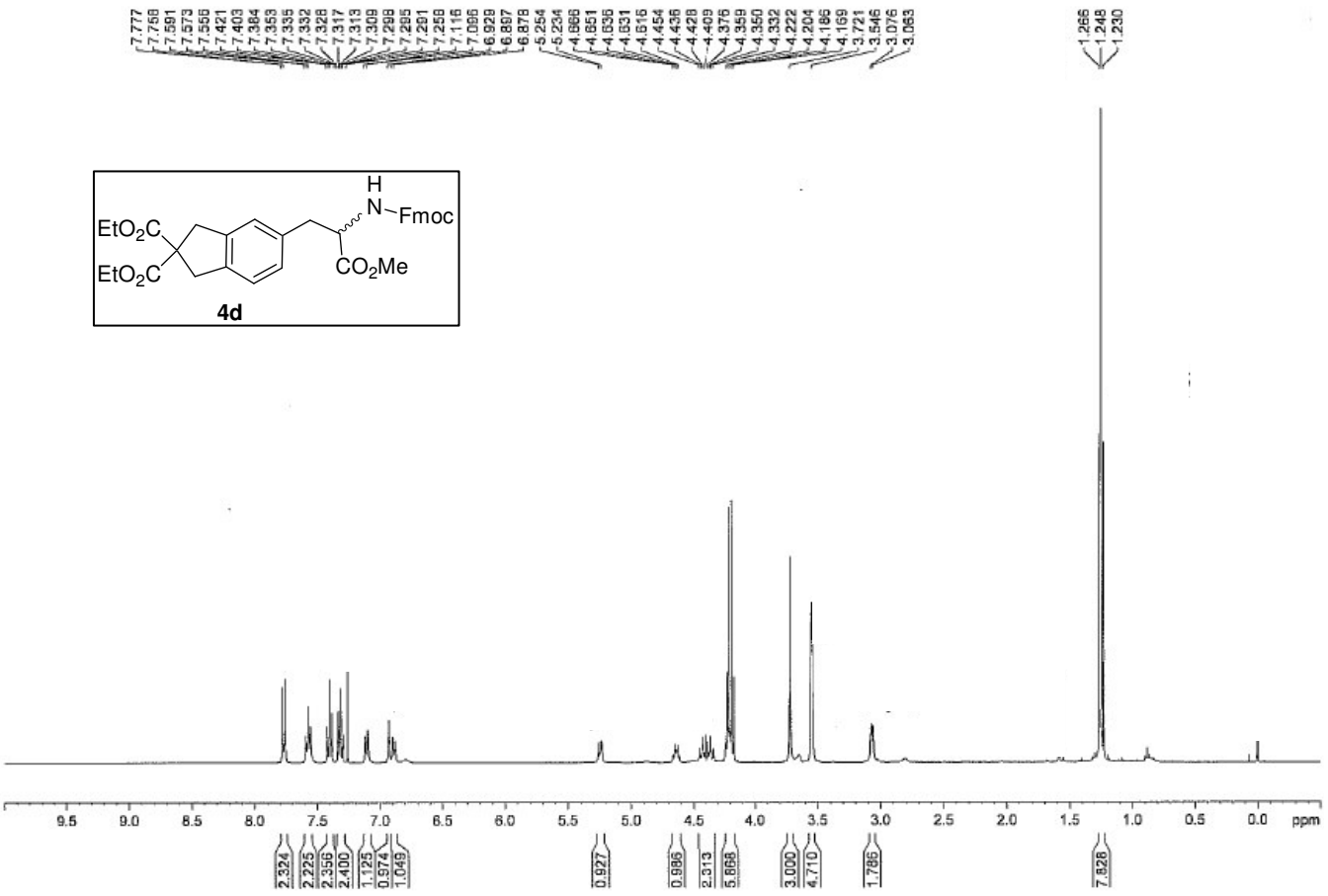
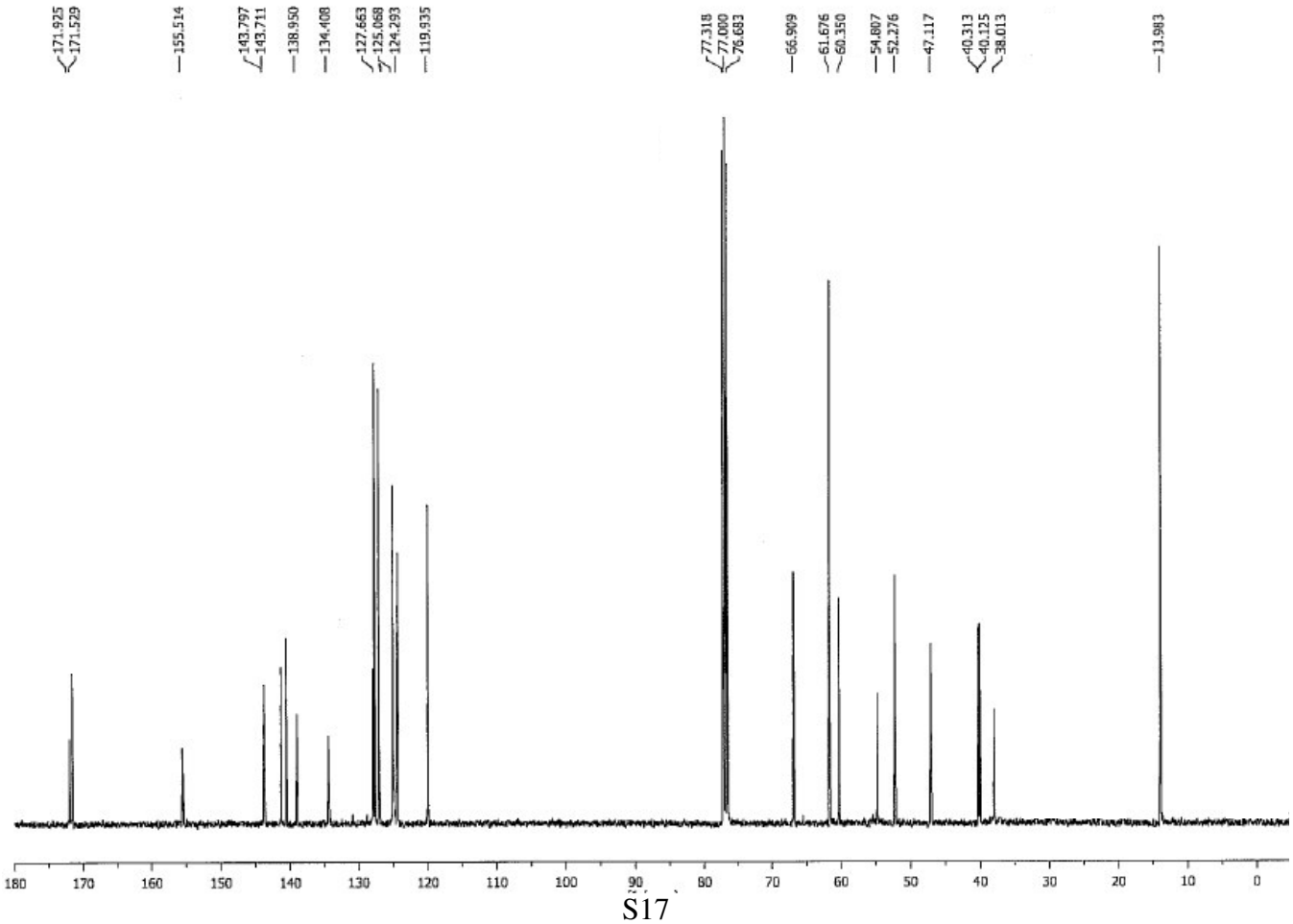
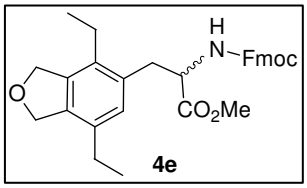
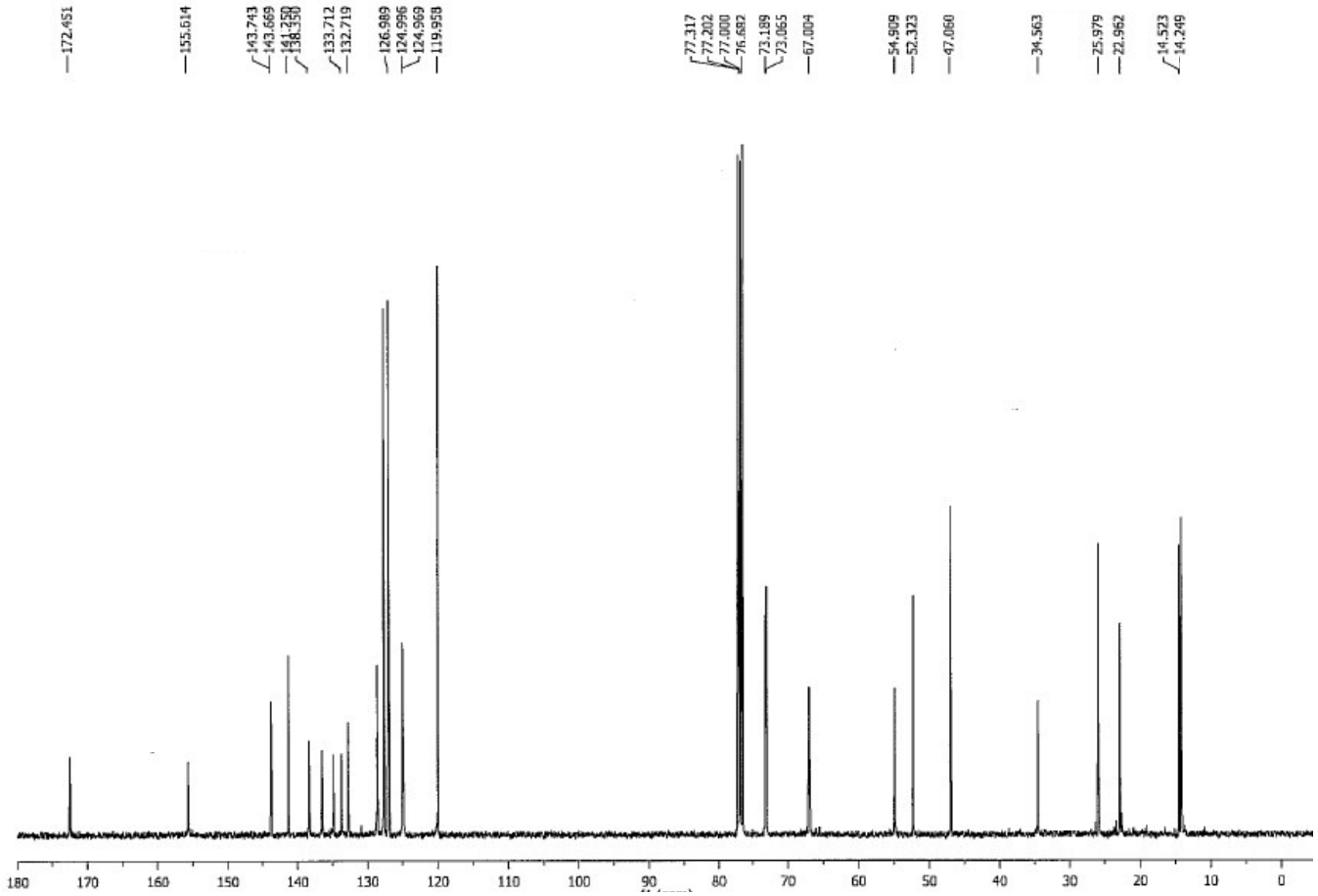
7.576
7.559
7.543
7.412
7.394
7.375
7.317
7.314
7.298
7.295
7.279
7.277
7.254
6.702
5.269
5.248
4.603
4.587
4.566
4.550
4.365
4.362
4.346
4.233
4.215
4.198
4.180
3.698
3.528
3.492
3.147
3.130
3.111
3.095
3.019
3.002
2.984
2.967
2.161
1.277
1.259
1.241
H
N
Fmoc
EtO2C
EtO2C
CO2Me
4c
ppm
2.074
1.890
2.140
2.154
0.876
0.843
0.901
1.999
4.986
2.801
4.358
2.010
6.000
6.855
172.473
171.862
171.808
155.612
143.803
143.760
141.356
137.570
137.521
129.911
129.529
127.660
127.020
125.049
119.933
77.317
77.000
76.682
67.033
61.688
59.461
54.424
52.233
47.104
40.129
39.472
35.505
18.584
15.270
14.007

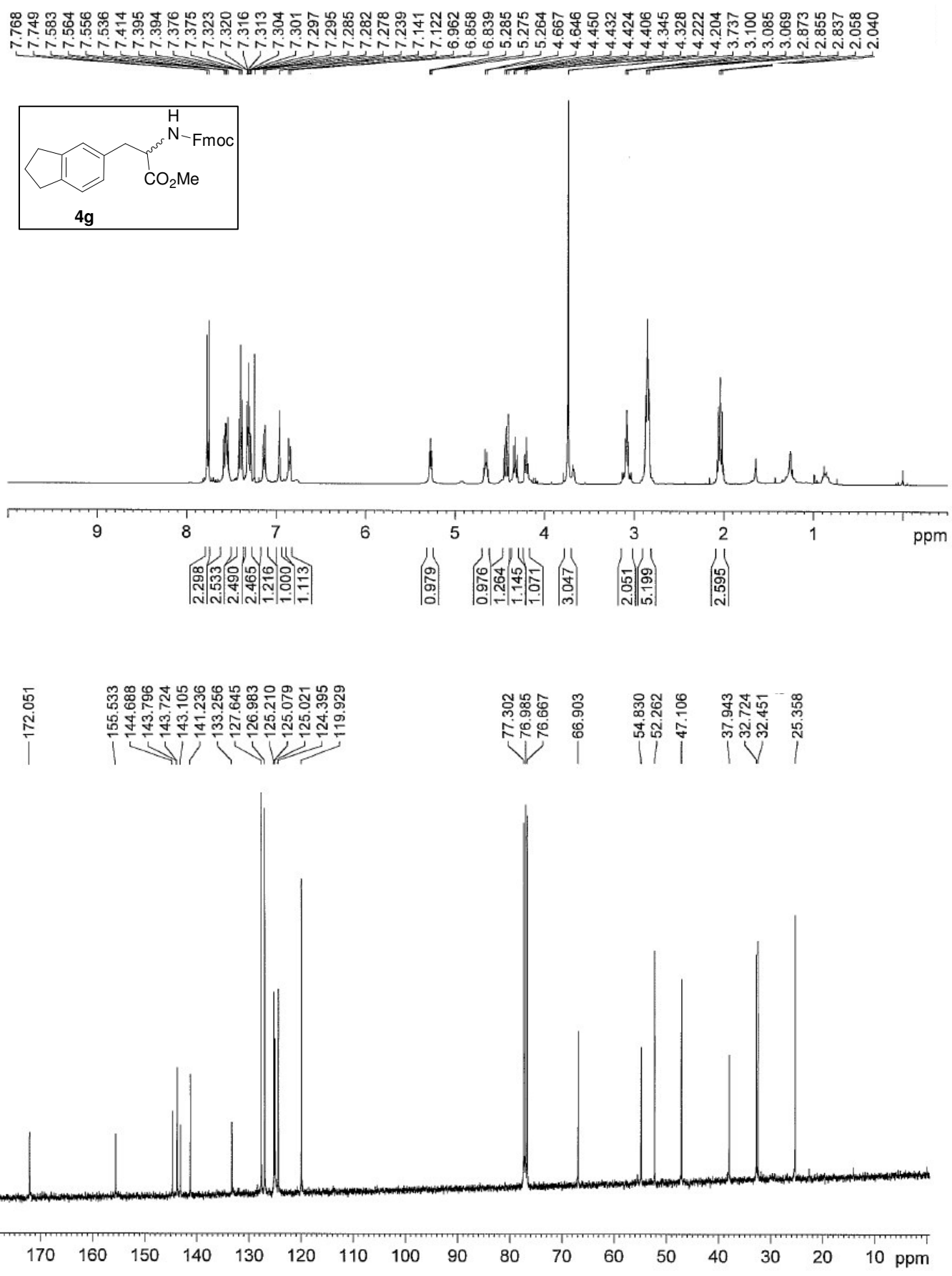

EtO2C
EtO2C
H
N
Fmoc
CO2Me
4d





4e

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7.556
7.536
7.414
7.395
7.394
7.376
7.375
7.323
7.320
7.316
7.313
7.304
7.301
7.297
7.295
7.285
7.282
7.278
7.239
7.141
7.122
6.962
6.858
6.839
5.285
5.275
5.264
4.667
4.646
4.450
4.432
4.424
4.406
4.345
4.328
4.222
4.204
3.737
3.100
3.085
3.069
2.873
2.855
2.837
2.058
2.040
H
N
Fmoc
CO2Me
4g
9
8
7
6
5
4
3
2
1
ppm
2.298
2.533
2.490
2.465
1.216
1.000
1.113
0.979
0.976
1.264
1.145
1.071
3.047
2.051
5.199
2.595
172.051
155.533
144.688
143.796
143.724
143.105
141.236
133.256
127.645
126.983
125.210
125.079
125.021
124.395
119.929
77.302
76.985
76.667
66.903
54.830
52.262
47.106
37.943
32.724
32.451
25.358
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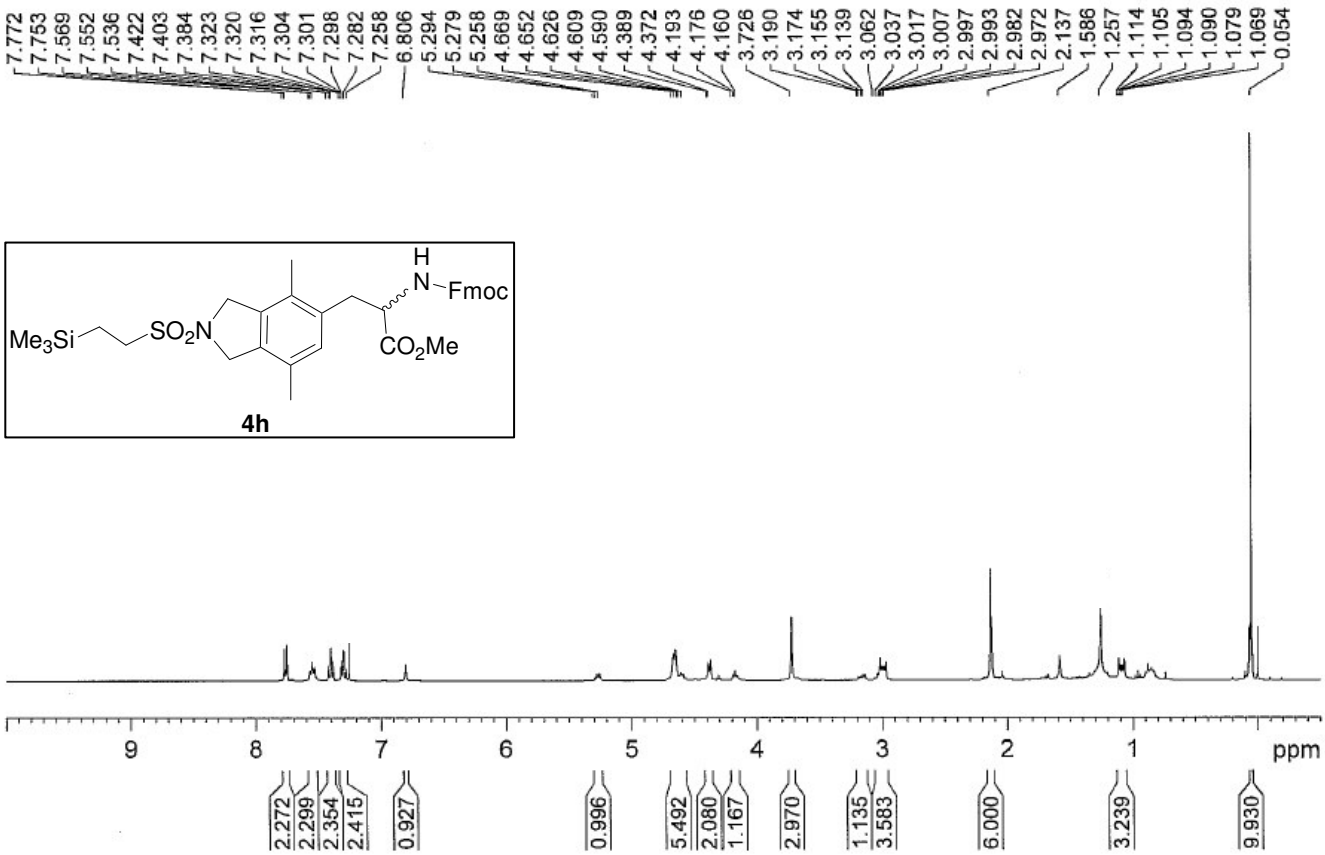
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.384
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7.320
7.316
7.304
7.301
7.298
7.282
7.258
6.806
5.294
5.279
5.258
4.669
4.652
4.626
4.609
4.590
4.389
4.372
4.193
4.176
4.160
3.726
3.190
3.174
3.155
3.139
3.062
3.037
3.017
3.007
2.997
2.993
2.982
2.972
2.137
1.586
1.257
1.114
1.105
1.094
1.090
1.079
1.069
0.054
H
N
Fmoc
Me3Si
SO2N
CO2Me
4h
9
8
7
6
5
4
3
2
1
ppm
2.272
2.299
2.354
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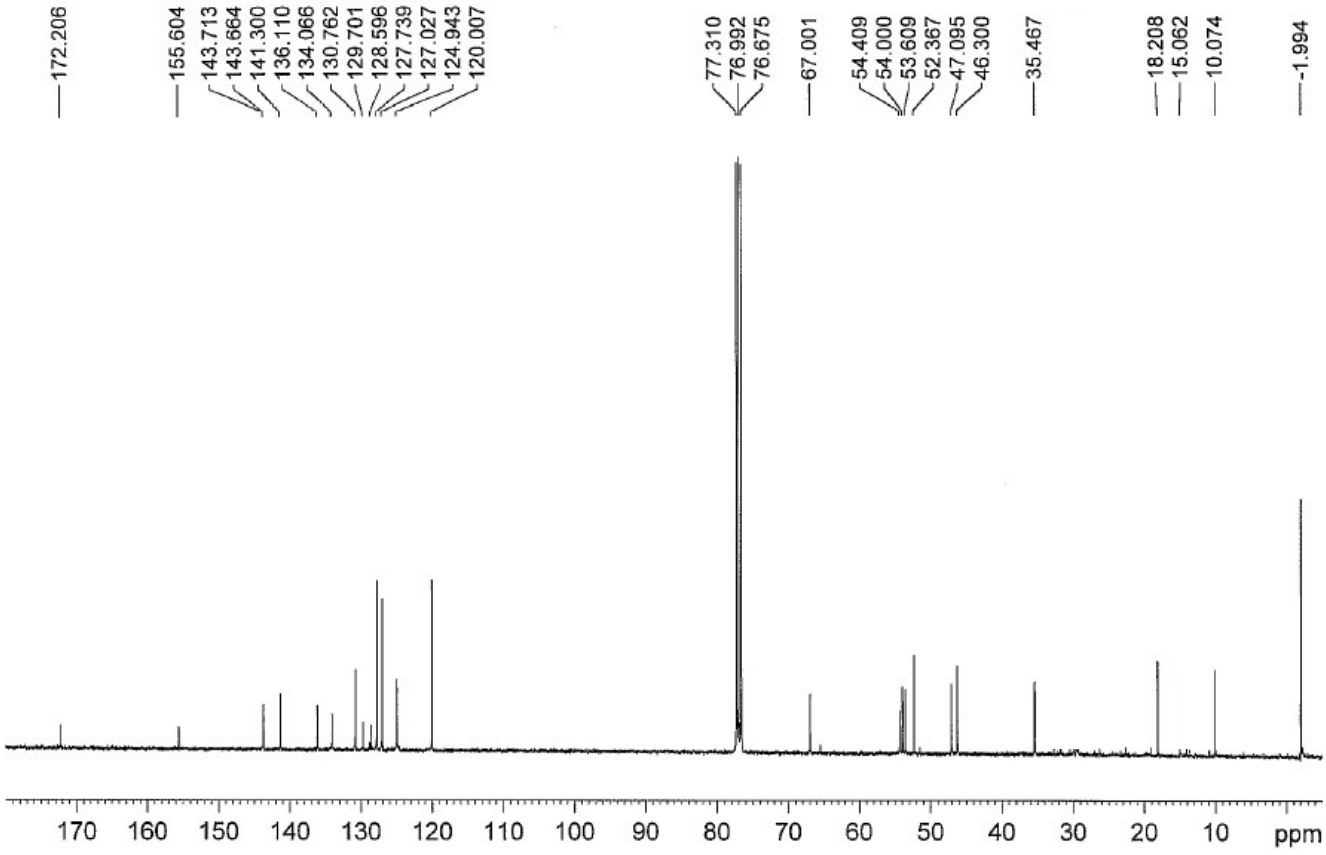
3.239
9.930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143.664
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124.943
120.007
77.310
76.992
76.675
67.001
54.409
54.000
53.609
52.367
47.095
46.300
35.467
18.208
15.062
10.074
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150
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30
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10
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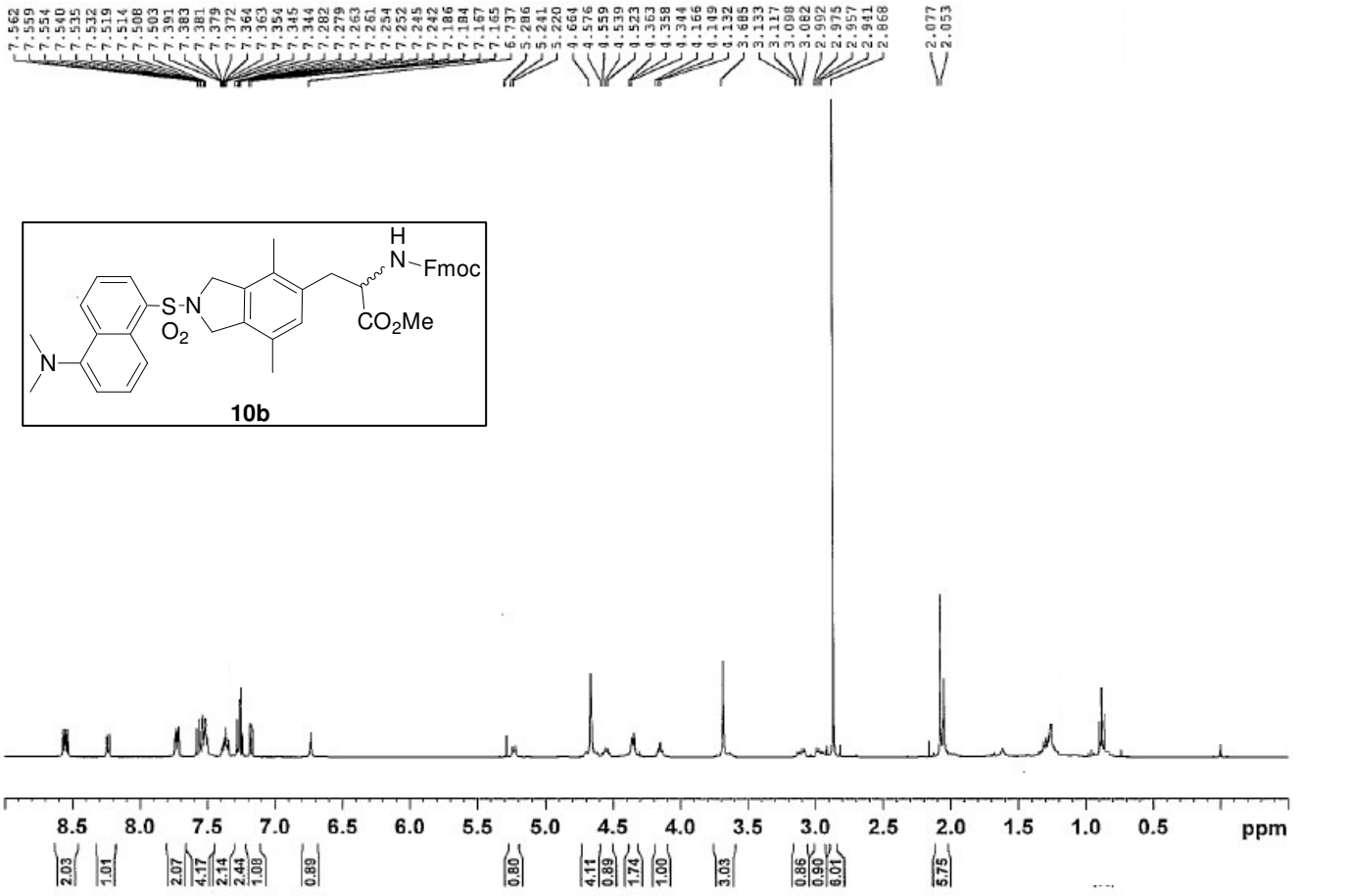
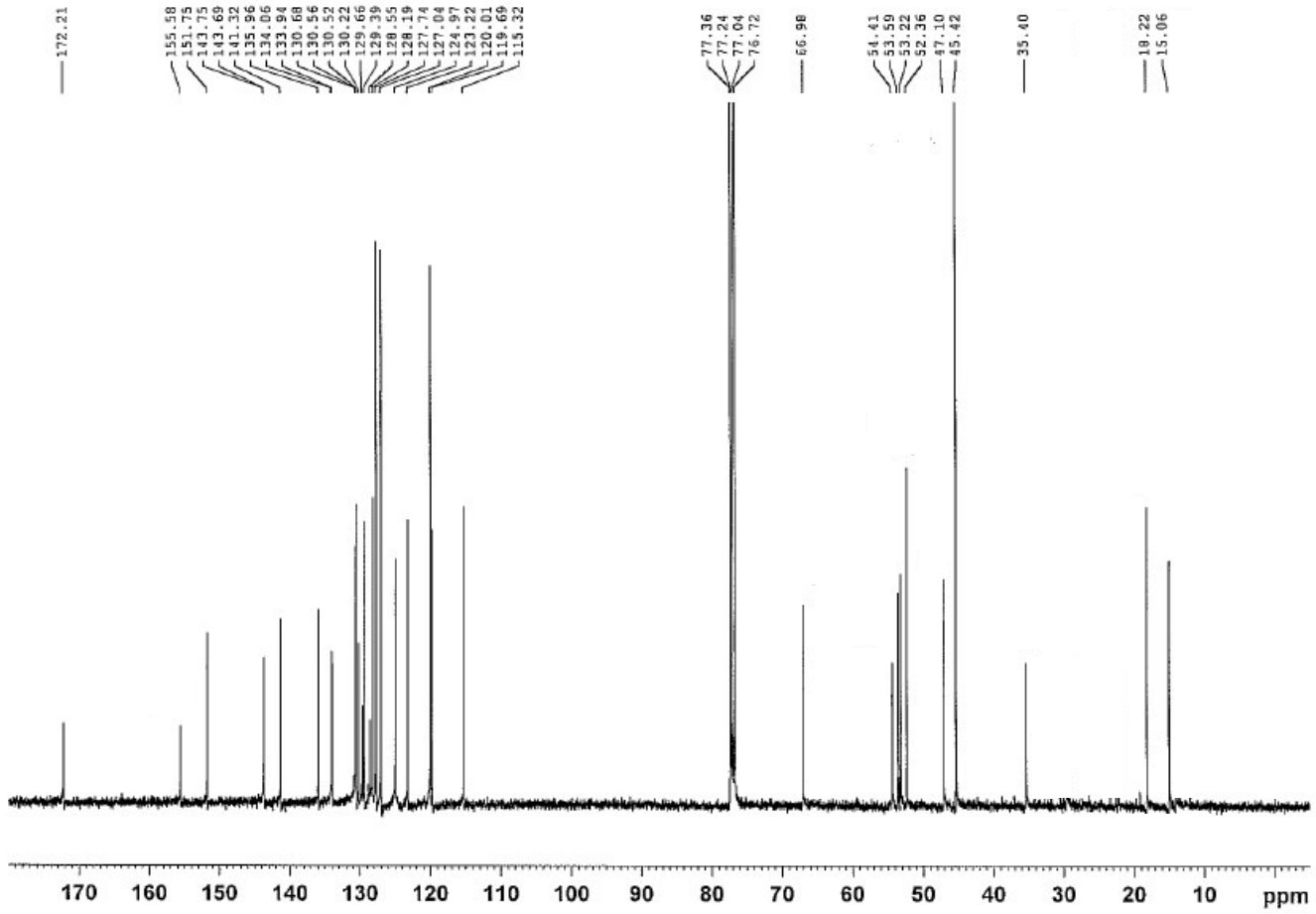
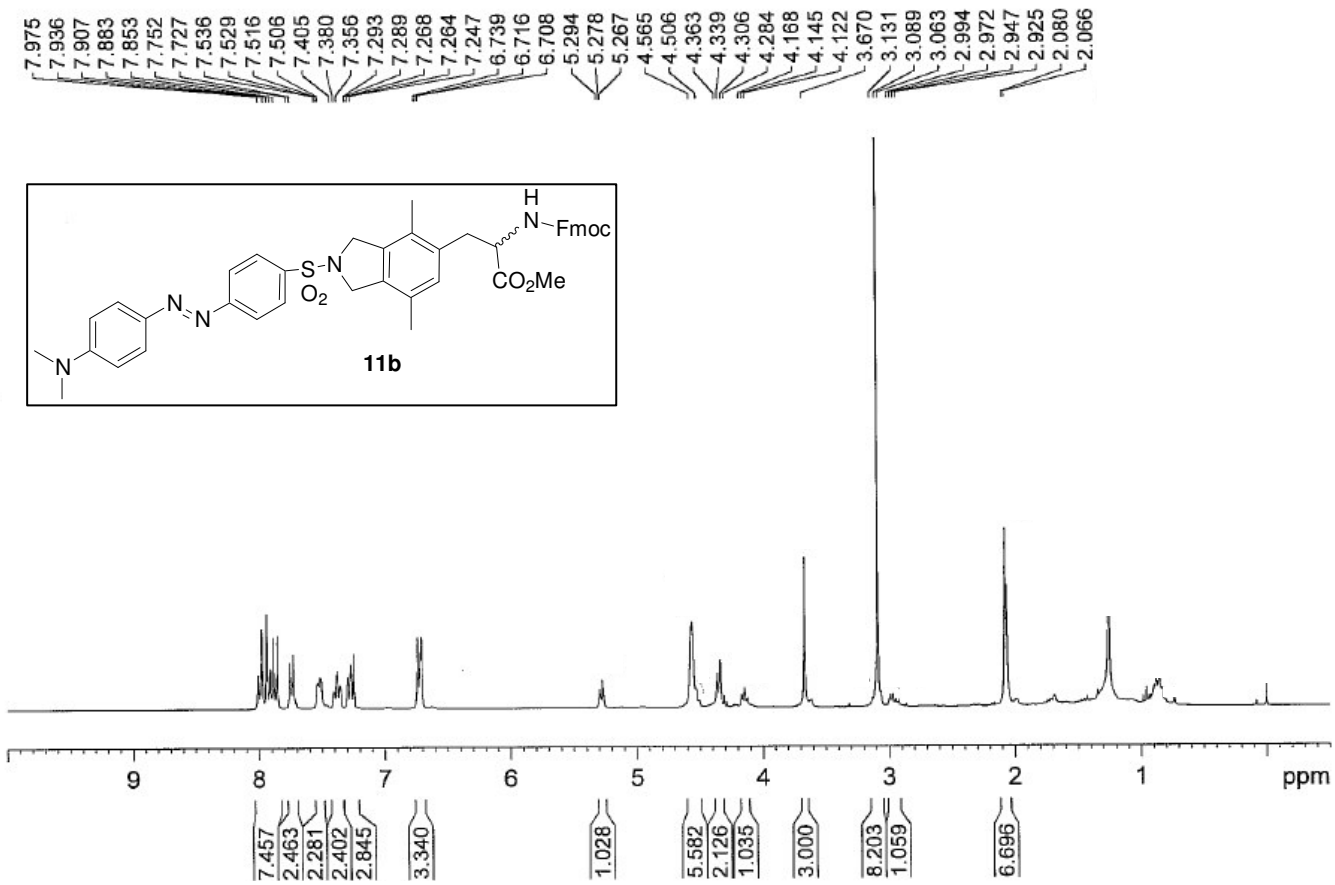

H
N
Fmoc
S
N
O2
CO2Me
N
10b
ppm


ppm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7.536
7.529
7.516
7.506
7.405
7.380
7.356
7.293
7.289
7.268
7.264
7.247
6.739
6.716
6.708
5.294
5.278
5.267
4.565
4.506
4.363
4.339
4.306
4.284
4.168
4.145
4.122
3.670
3.131
3.089
3.063
2.994
2.972
2.947
2.925
2.080
2.066
H
N
Fmoc
S
N
O2
CO2Me
N
N
N
11b
9
8
7
6
5
4
3
2
1
ppm
7.457
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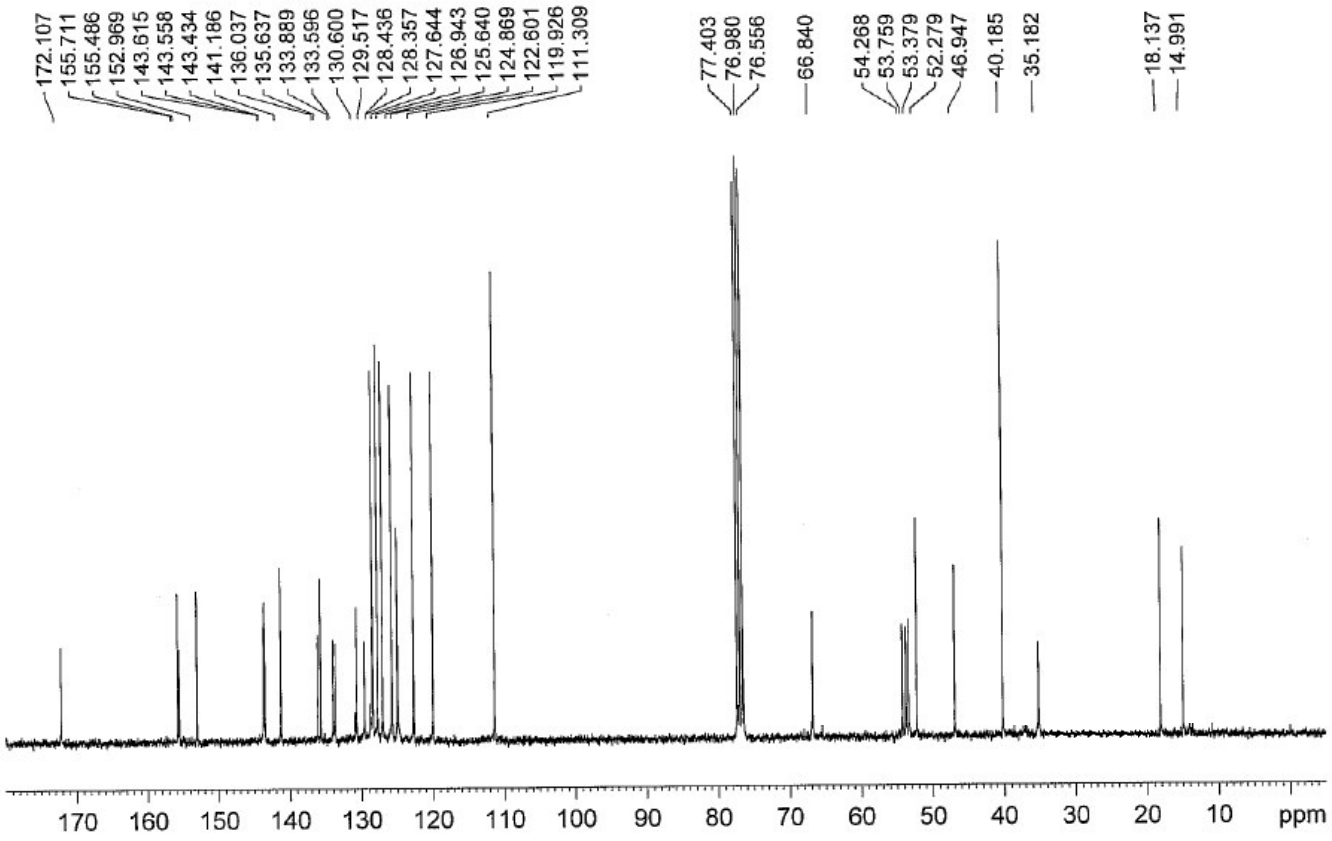
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130.600
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128.436
128.357
127.644
126.943
125.640
124.869
122.601
119.926
111.309
77.403
76.980
76.556
66.840
54.268
53.759
53.379
52.279
46.947
40.185
35.182
18.137
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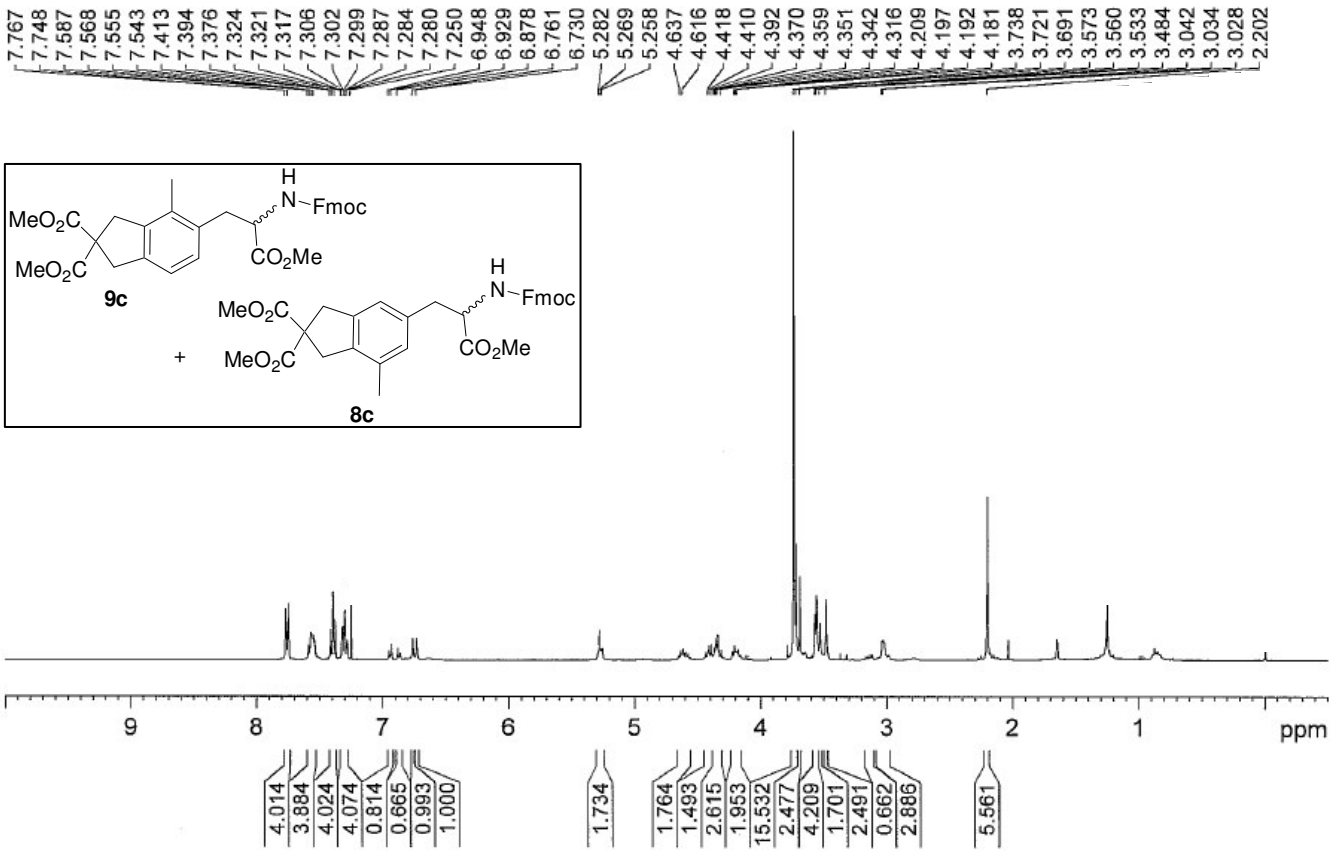
10
ppm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7.302
7.299
7.287
7.284
7.280
7.250
6.948
6.929
6.878
6.761
6.730
5.282
5.269
5.258
4.637
4.616
4.418
4.410
4.392
4.370
4.359
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4.342
4.316
4.209
4.197
4.192
4.181
3.738
3.721
3.691
3.573
3.560
3.533
3.484
3.042
3.034
3.028
2.202
MeO2C
MeO2C
H
N
Fmoc
CO2Me
9c
+
8c
9
8
7
6
5
4
3
2
1
ppm
4.014
3.884
4.024
4.074
0.814
0.665
0.993
1.000
1.734
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1.953
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1.701
2.491
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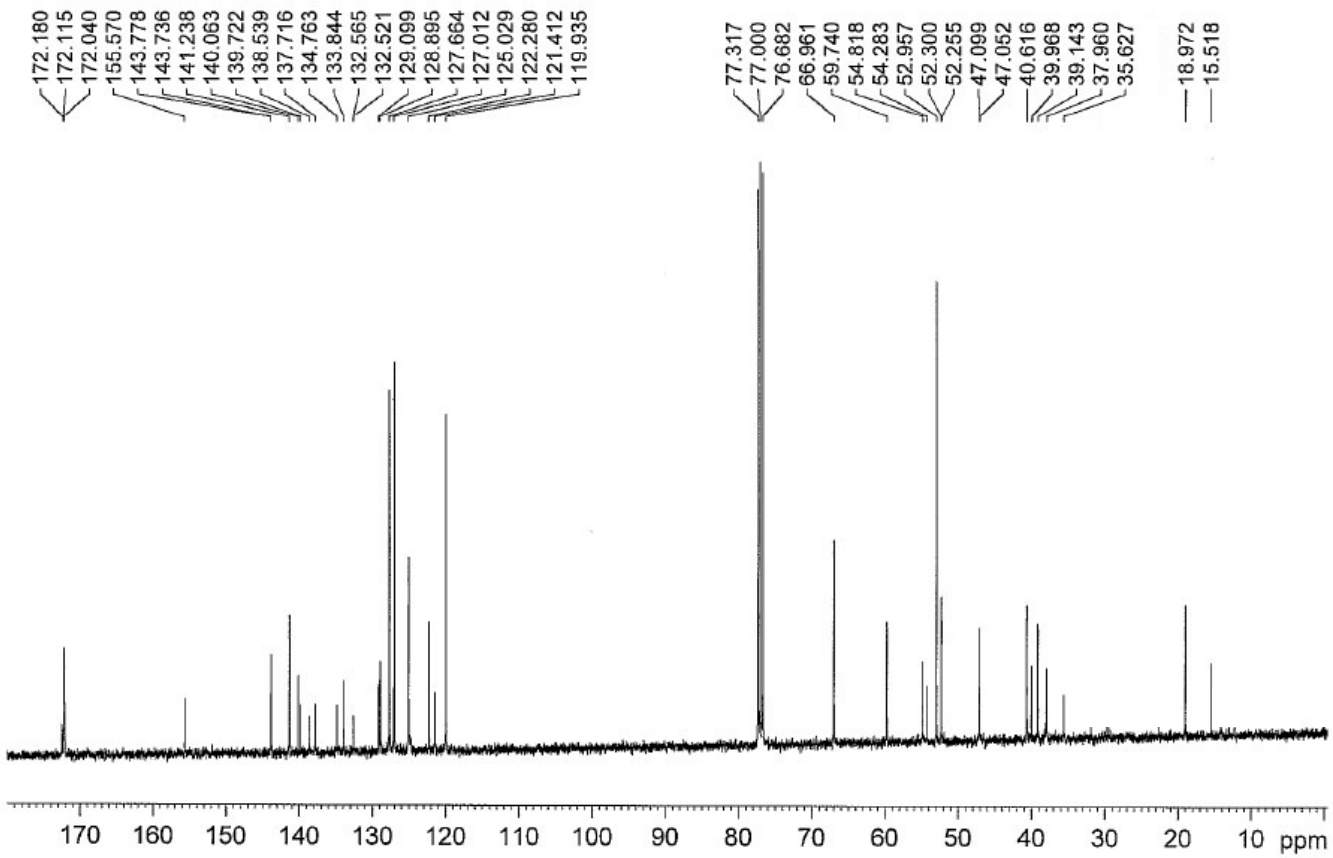
5.561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143.736
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137.716
134.763
133.844
132.565
132.521
129.099
128.895
127.664
127.012
125.029
122.280
121.412
119.935
77.317
77.000
76.682
66.961
59.740
54.818
54.283
52.957
52.300
52.255
47.099
47.052
40.616
39.968
39.143
37.960
35.627
18.972
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150
140
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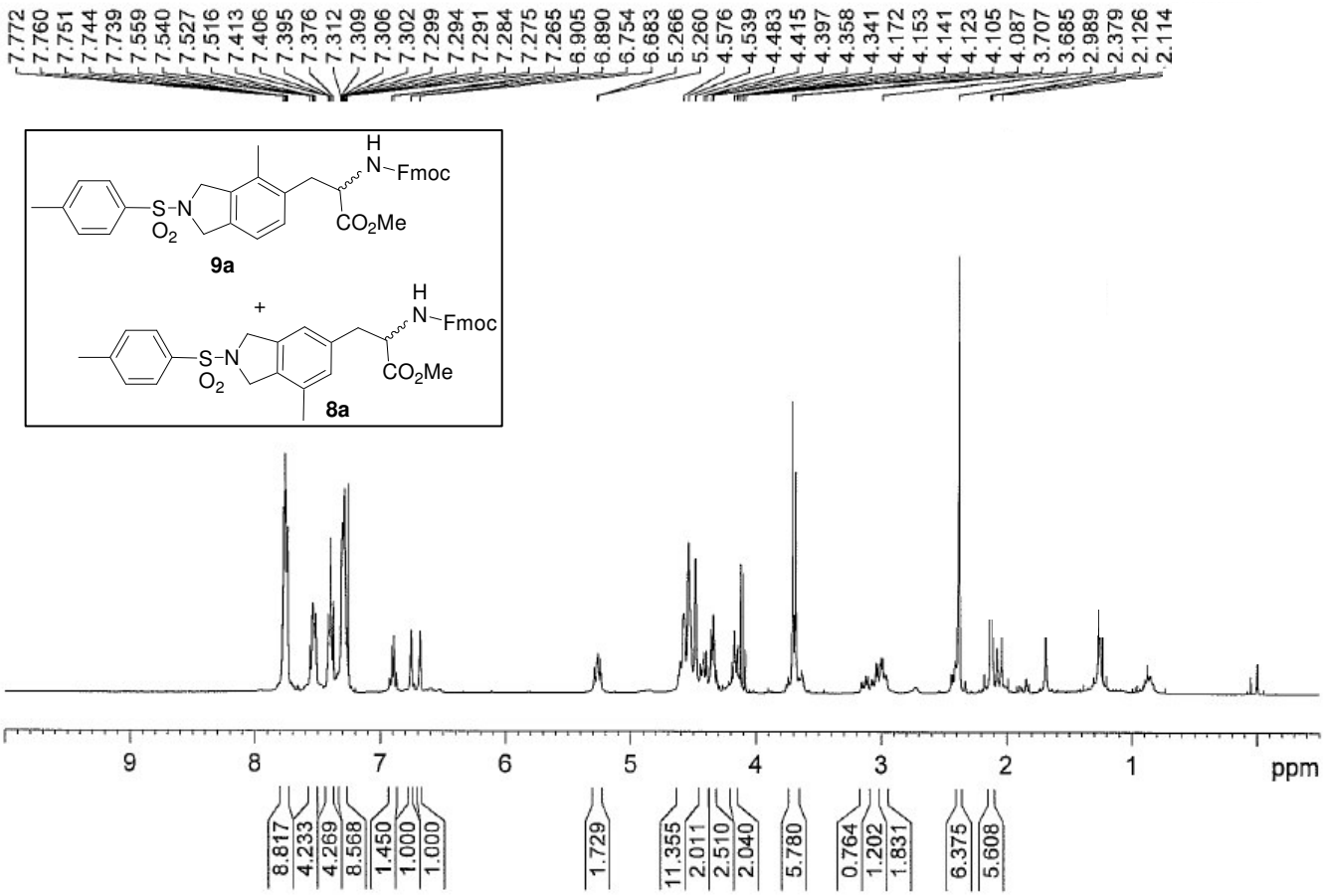
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.376
7.312
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7.299
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7.291
7.284
7.275
7.265
6.905
6.890
6.754
6.683
5.266
5.260
4.576
4.539
4.483
4.415
4.397
4.358
4.341
4.172
4.153
4.141
4.123
4.105
4.087
3.707
3.685
2.989
2.379
2.126
2.114
H
N
Fmoc
S-N
O2
CO2Me
9a
+
8a
ppm
8.817
4.233
4.269
8.568
1.450
1.000
1.000
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2.040
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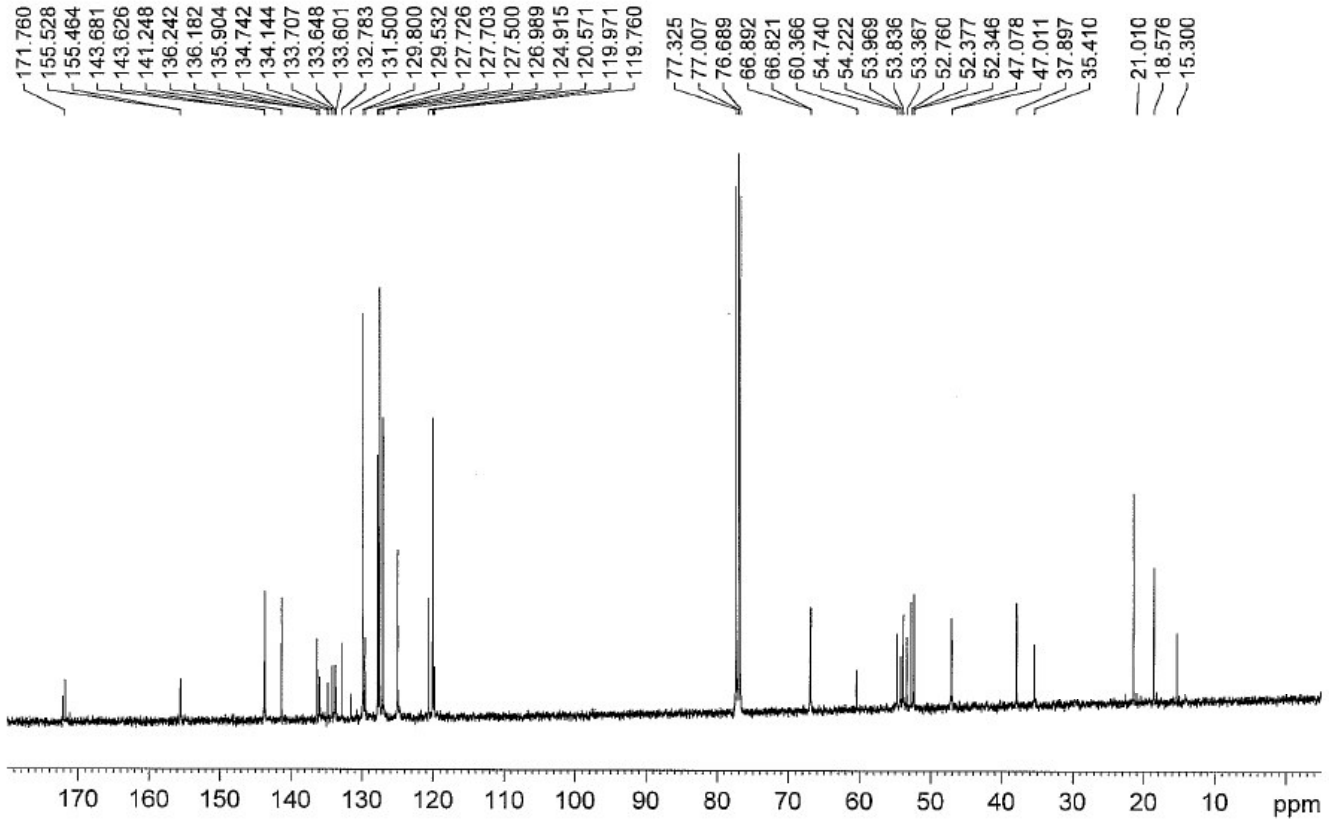
5.608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133.648
133.601
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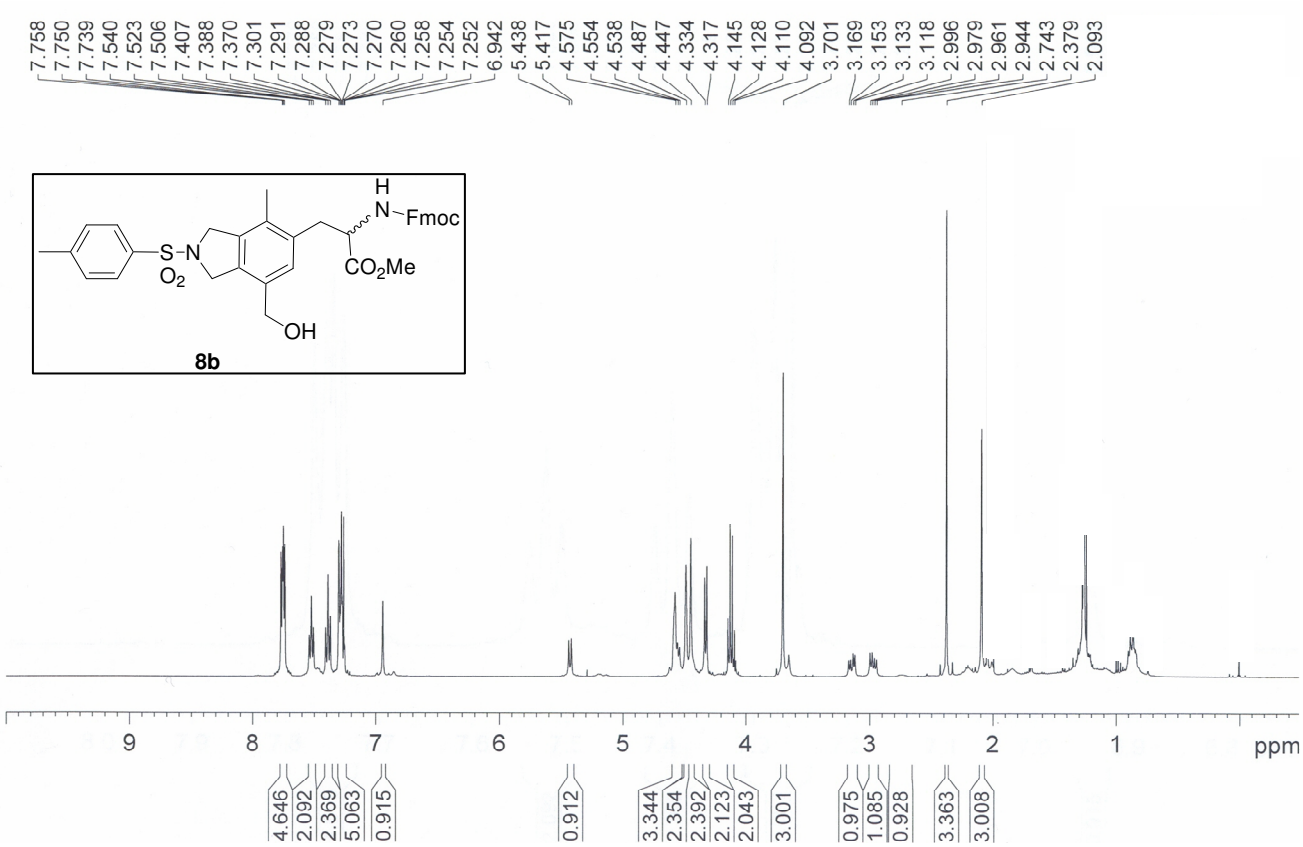
131.500
129.800
129.532
127.726
127.703
127.500
126.989
124.915
120.571
119.971
119.760
77.325
77.007
76.689
66.892
66.821
60.366
54.740
54.222
53.969
53.836
53.367
52.760
52.377
52.346
47.078
47.011
37.897
35.410
21.010
18.576
15.300
ppm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7.750
7.739
7.540
7.523
7.506
7.407
7.388
7.370
7.301
7.291
7.288
7.279
7.273
7.270
7.260
7.258
7.254
7.252
6.942
5.438
5.417
4.575
4.554
4.538
4.487
4.447
4.334
4.317
4.145
4.128
4.110
4.092
3.701
3.169
3.153
3.133
3.118
2.996
2.979
2.961
2.944
2.743
2.379
2.093
H
N
Fmoc
S
N
O2
CO2Me
OH
8b
9
8
7
6
5
4
3
2
1
ppm
4.646
2.092
2.369
5.063
0.915
0.912
3.344
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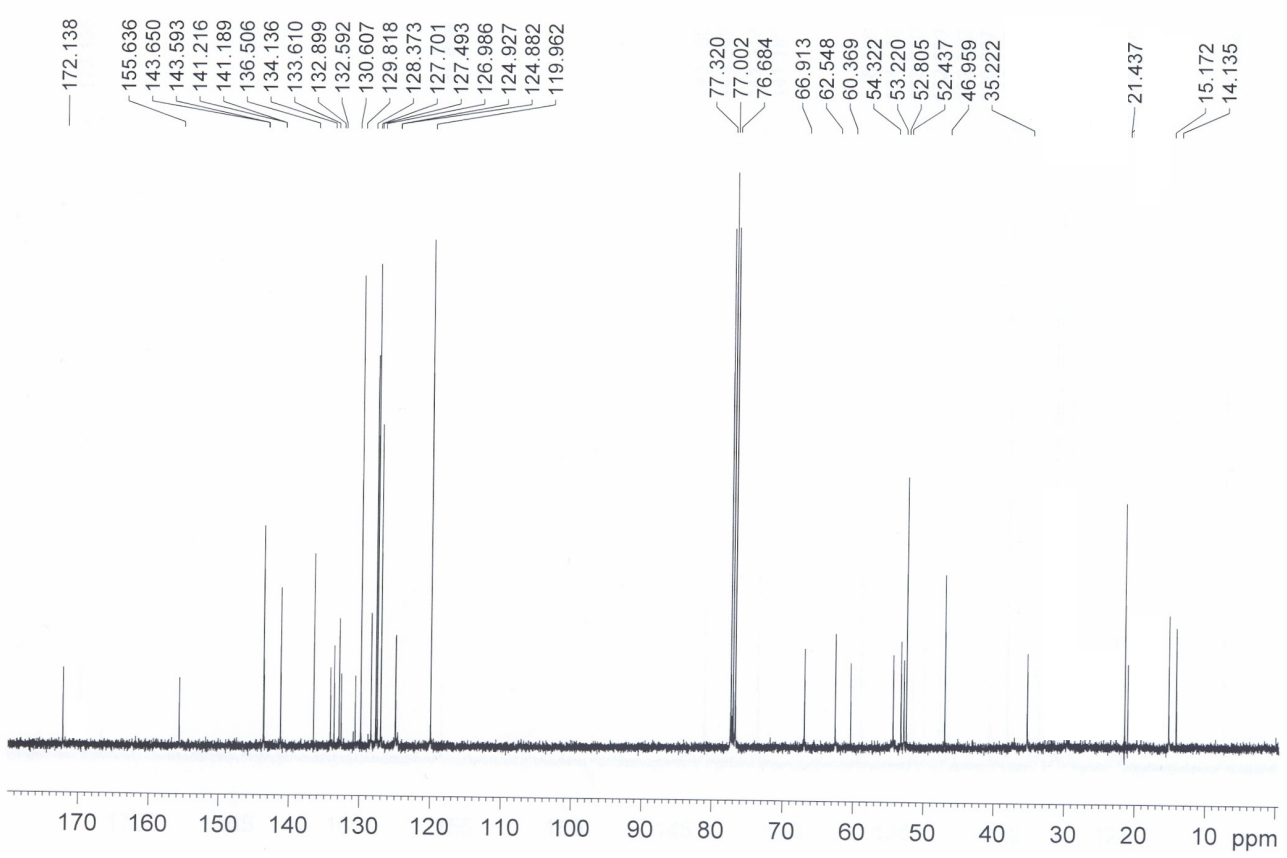
2.392
2.123
2.043
3.001
0.975
1.085
0.928
3.363
3.008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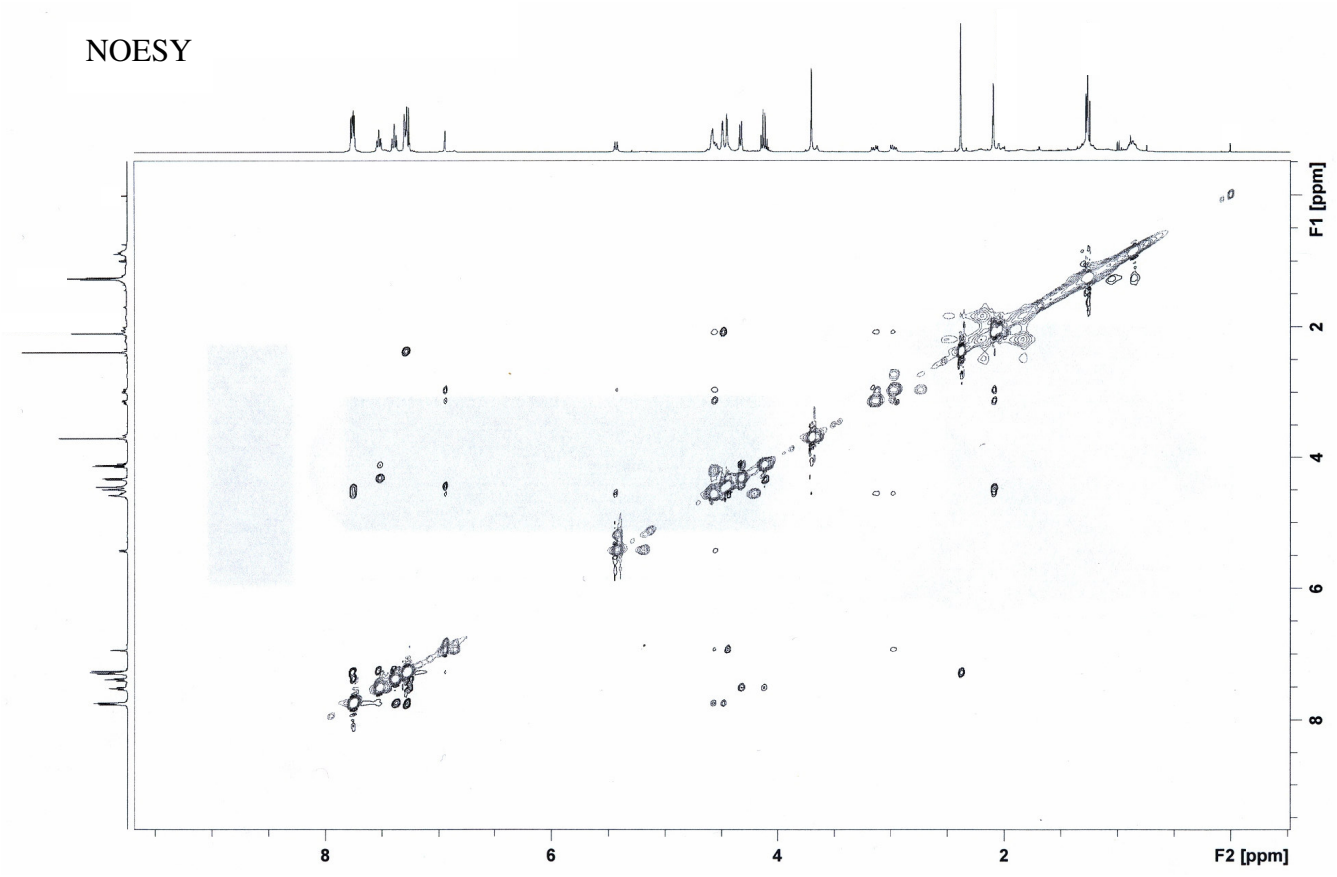
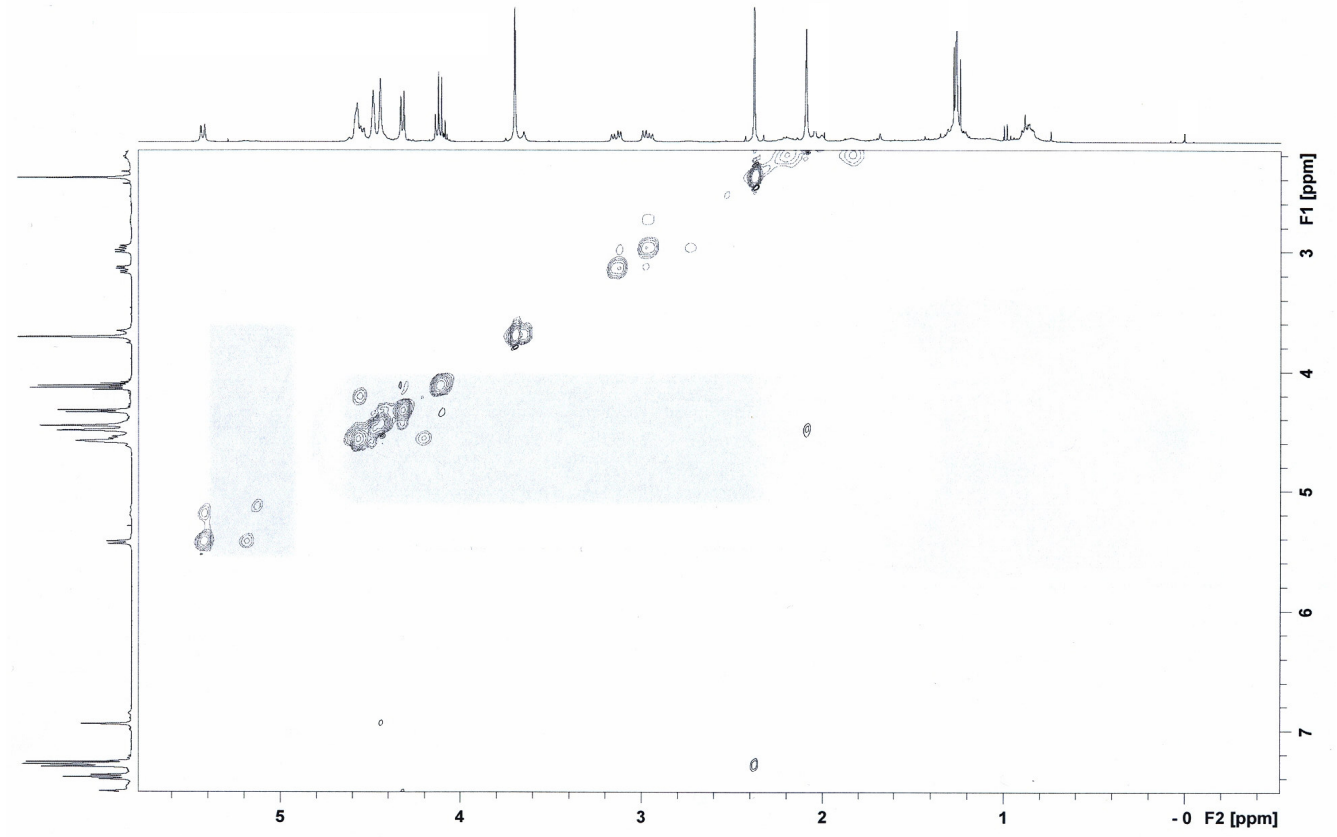
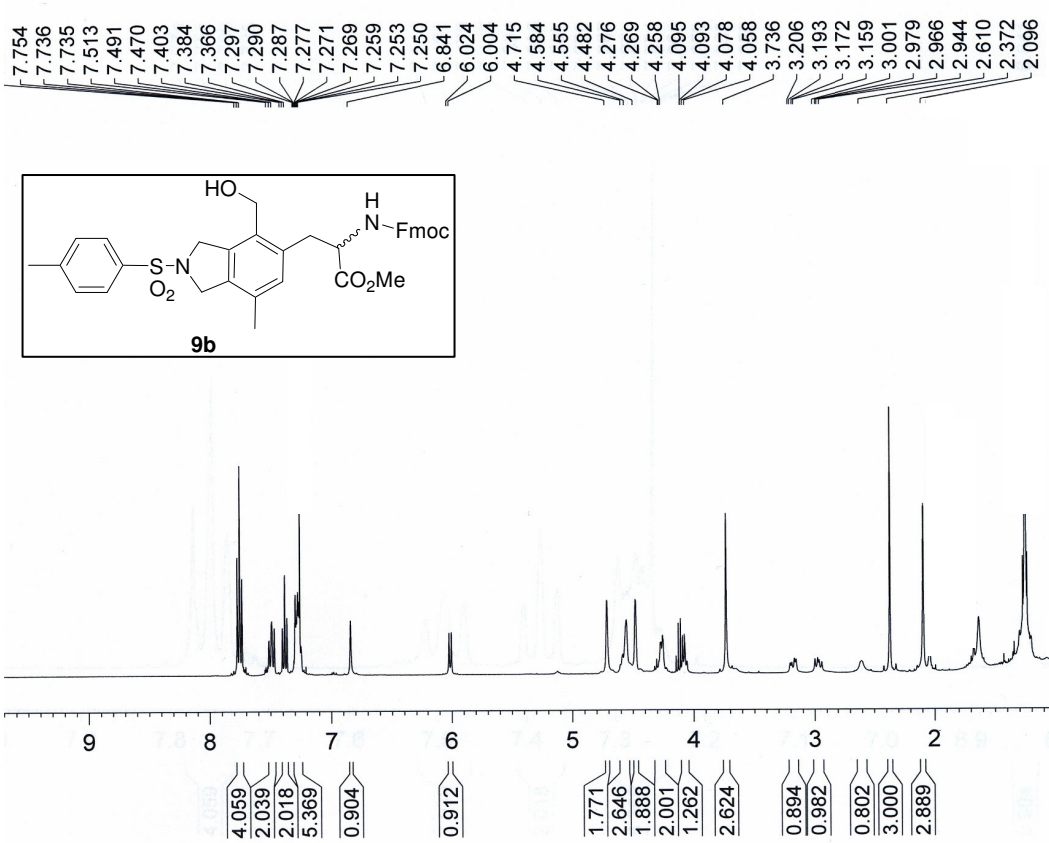
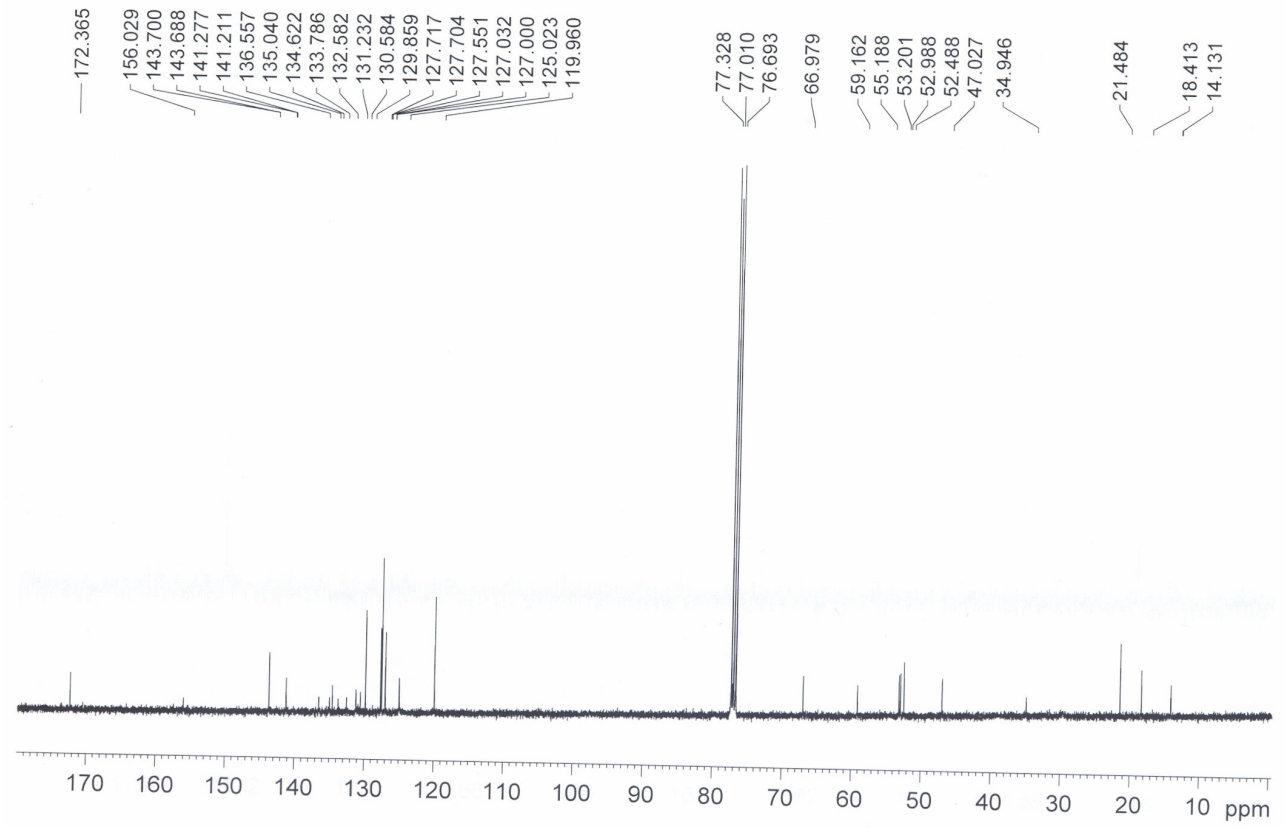
155.636
143.650
143.593
141.216
141.189
136.506
134.136
133.610
132.899
132.592
130.607
129.818
128.373
127.701
127.493
126.986
124.927
124.882
119.962
77.320
77.002
76.684
66.913
62.548
60.369
54.322
53.220
52.805
52.437
46.959
35.222
21.437
15.172
14.135
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NOESY

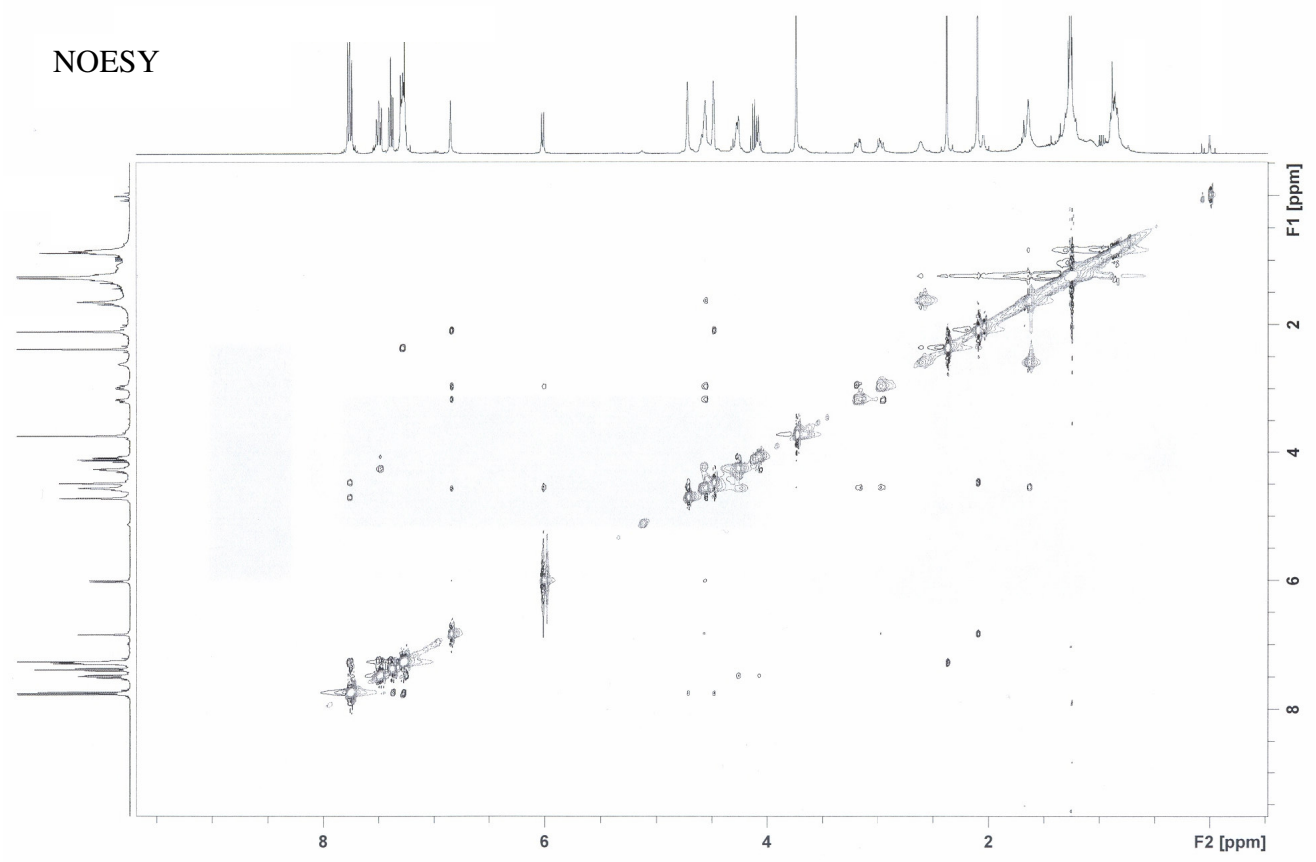


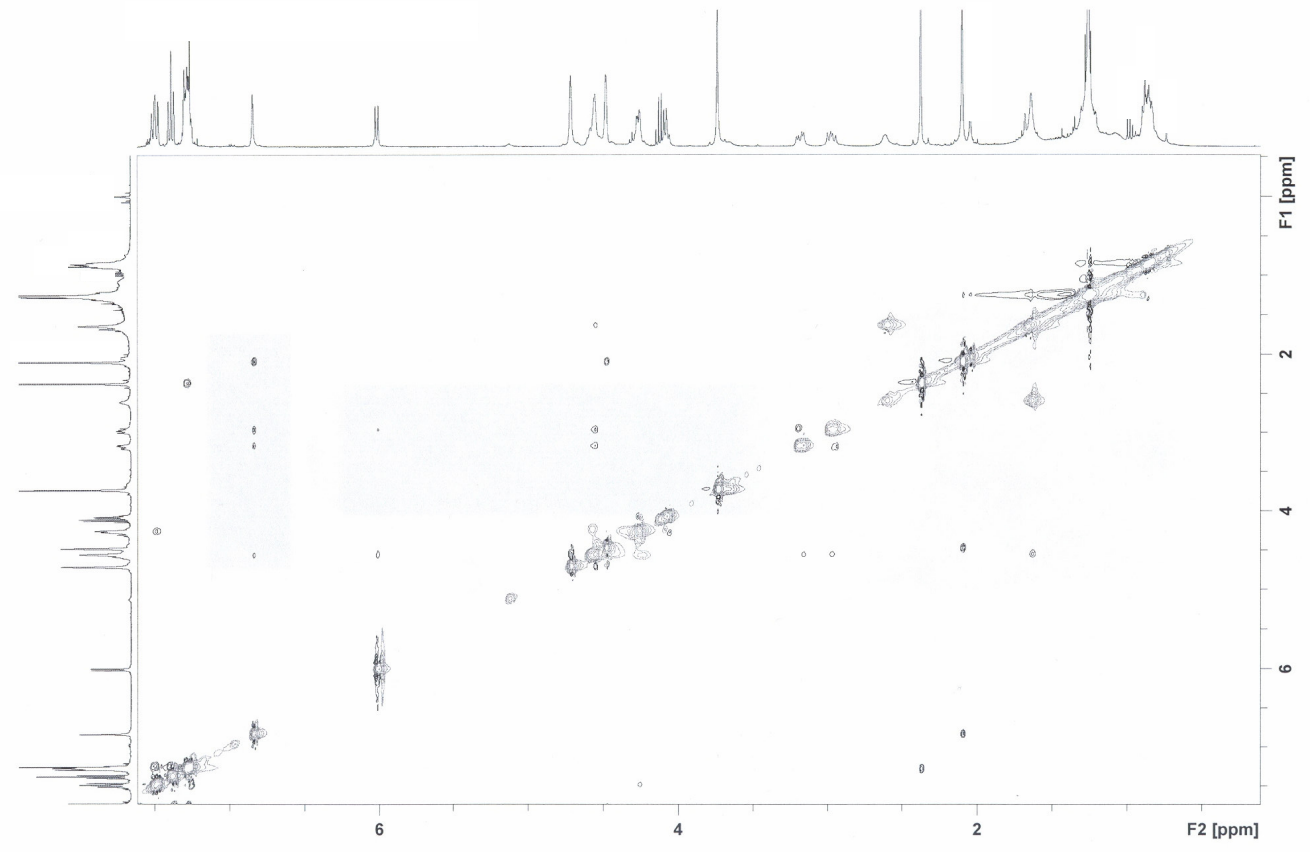


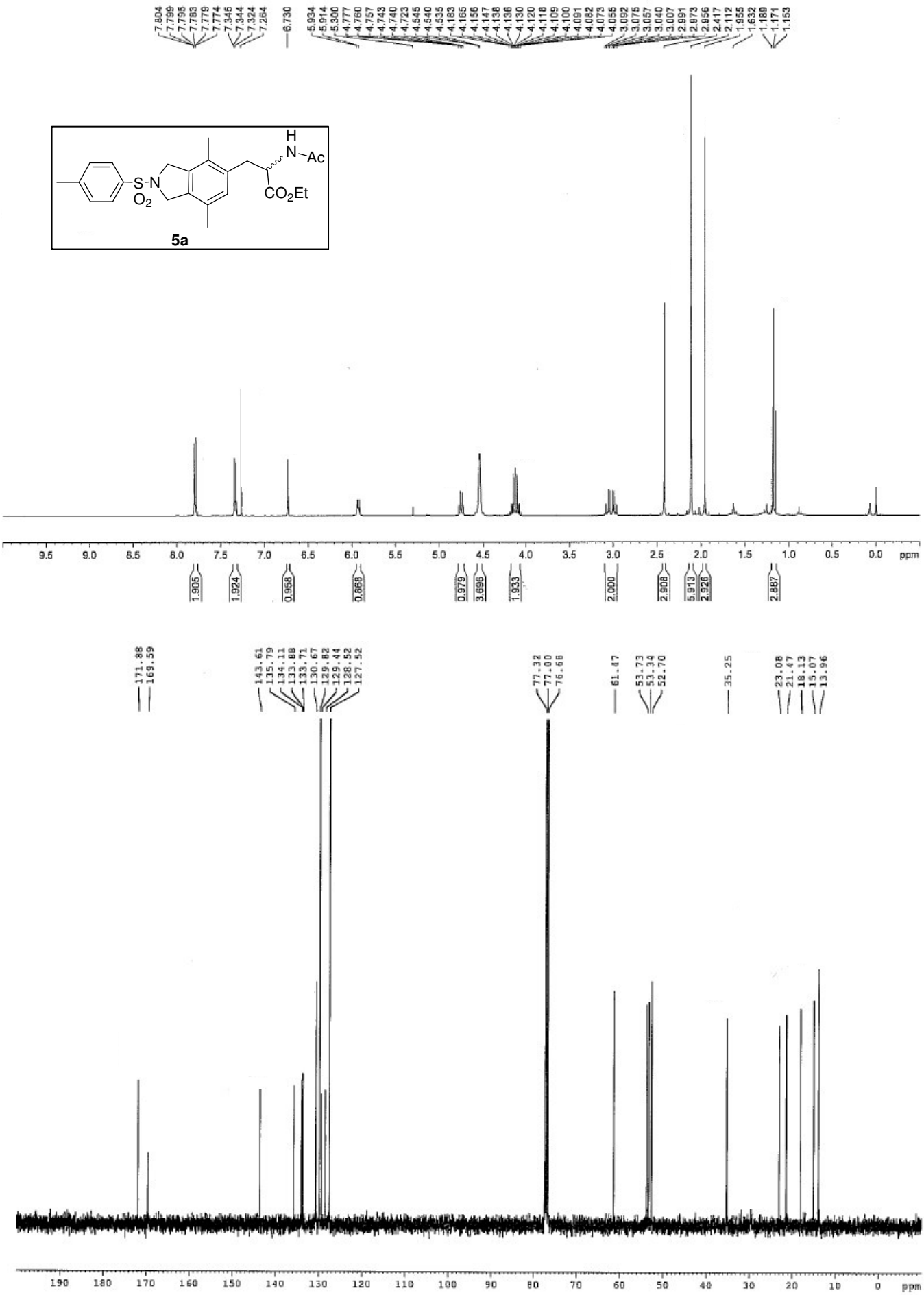

7.754
7.736
7.735
7.513
7.491
7.470
7.403
7.384
7.366
7.297
7.290
7.287
7.277
7.271
7.269
7.259
7.253
7.250
6.841
6.024
6.004
4.715
4.584
4.555
4.482
4.276
4.269
4.258
4.095
4.093
4.078
4.058
3.736
3.206
3.193
3.172
3.159
3.001
2.979
2.966
2.944
2.610
2.372
2.096
HO
H
N
Fmoc
S
N
O2
CO2Me
9b
9
8
7
6
5
4
3
2
1
ppm
4.059
2.039
2.018
5.369
0.904
0.912
1.771
2.646
1.888
2.001
1.262
2.624
0.894
0.982
0.802
3.000
2.889


172.365
156.029
143.700
143.688
141.277
141.211
136.557
135.040
134.622
133.786
132.582
131.232
130.584
129.859
127.717
127.704
127.551
127.032
127.000
125.023
119.960
77.328
77.010
76.693
66.979
59.162
55.188
53.201
52.988
52.488
47.027
34.946
21.484
18.413
14.131
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NOESY



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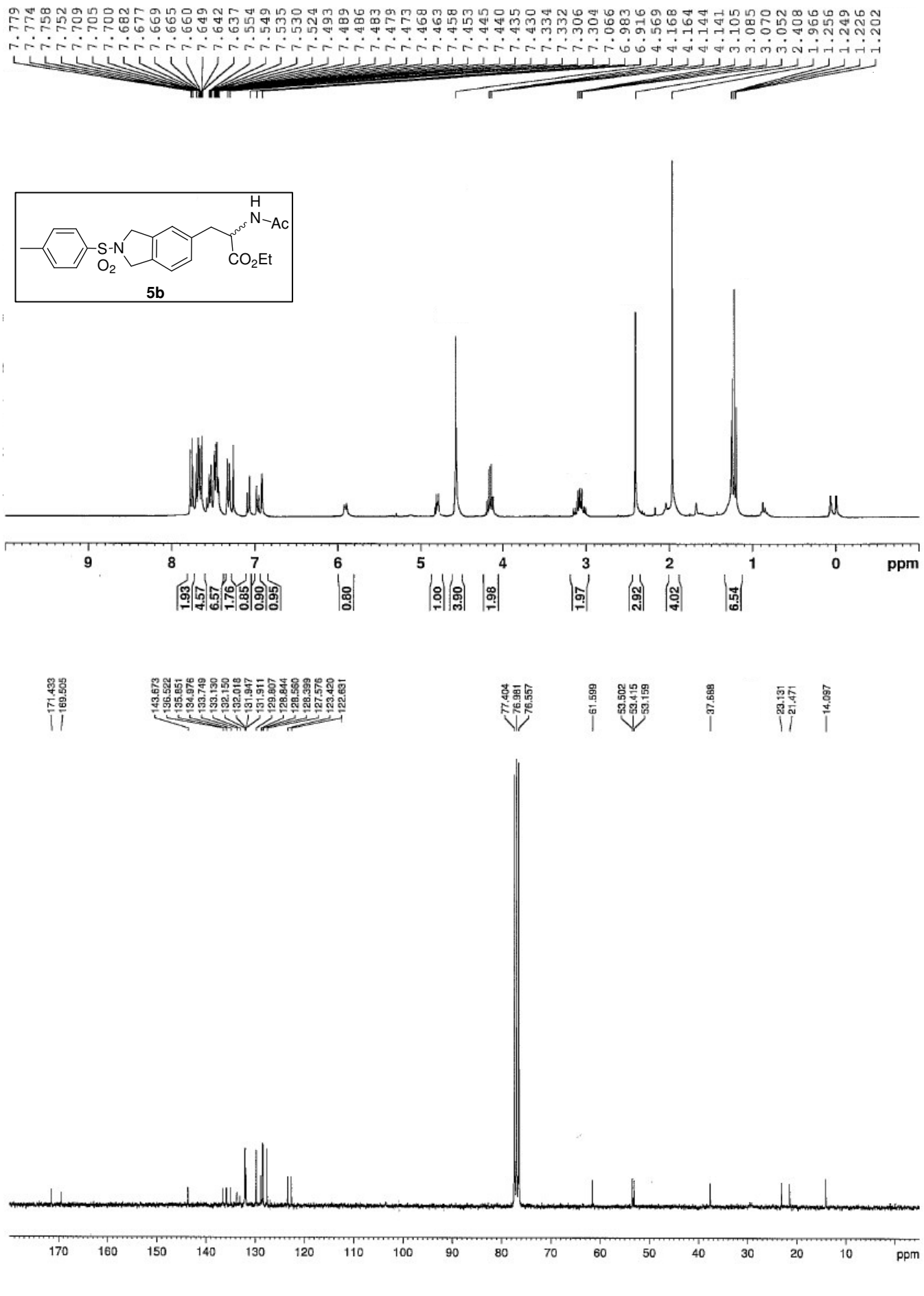
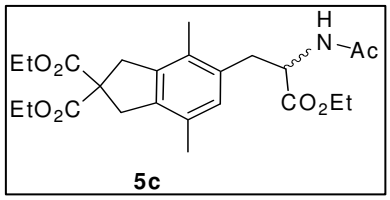
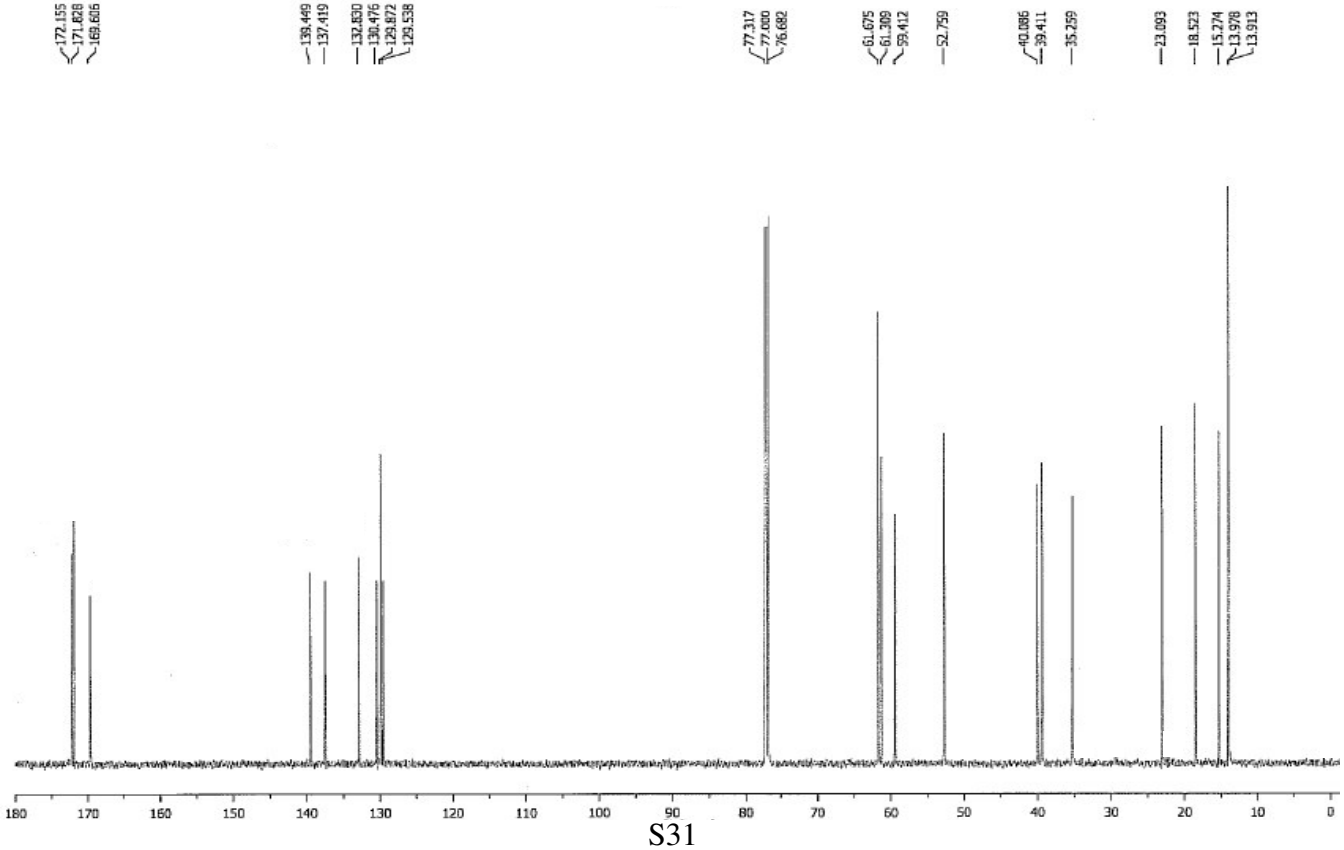
7.799
7.795
7.783
7.779
7.774
7.345
7.344
7.324
7.264
6.730
5.934
5.914
5.300
4.777
4.760
4.757
4.743
4.740
4.723
4.545
4.540
4.535
4.183
4.165
4.156
4.147
4.136
4.136
4.130
4.120
4.118
4.109
4.100
4.091
4.082
4.073
4.055
3.092
3.075
3.057
3.040
3.007
2.991
2.873
2.856
2.417
2.112
1.955
1.632
1.189
1.171
1.153
H
N
Ac
S
N
O2
CO2Et
5a
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
0.0
ppm
1.905
1.924
0.958
0.668
0.979
3.696
1.933
2.000
2.908
5.913
2.926
2.887
171.88
169.59
143.61
135.79
134.11
133.88
133.71
130.67
129.82
129.44
128.52
127.52
77.32
77.00
76.68
61.47
53.73
53.34
52.70
35.25
23.08
21.47
18.13
15.07
13.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

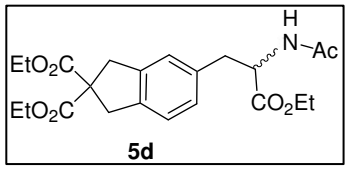

7.779
7.774
7.758
7.752
7.709
7.705
7.700
7.682
7.677
7.669
7.665
7.660
7.649
7.642
7.637
7.554
7.549
7.535
7.530
7.524
7.493
7.489
7.486
7.483
7.479
7.473
7.468
7.463
7.458
7.453
7.445
7.440
7.435
7.430
7.334
7.332
7.306
7.304
7.066
6.983
6.916
4.569
4.168
4.164
4.144
4.141
3.105
3.085
3.070
3.052
2.408
1.966
1.256
1.249
1.226
1.202
H
N
Ac
S-N
O2
CO2Et
5b
9
8
7
6
5
4
3
2
1
0
ppm
1.93
4.57
6.57
1.76
0.85
0.90
0.95
0.80
1.00
3.90
1.98
1.97
2.92
4.02
6.54
171.433
169.505
143.673
136.522
135.851
134.976
133.749
133.130
132.150
132.018
131.947
131.911
129.807
128.844
128.560
128.399
127.576
123.420
122.631
77.404
76.981
76.557
61.599
53.502
53.415
53.159
37.688
23.131
21.471
14.097
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H
N
Ac
EtO2C
EtO2C
CO2Et

5c

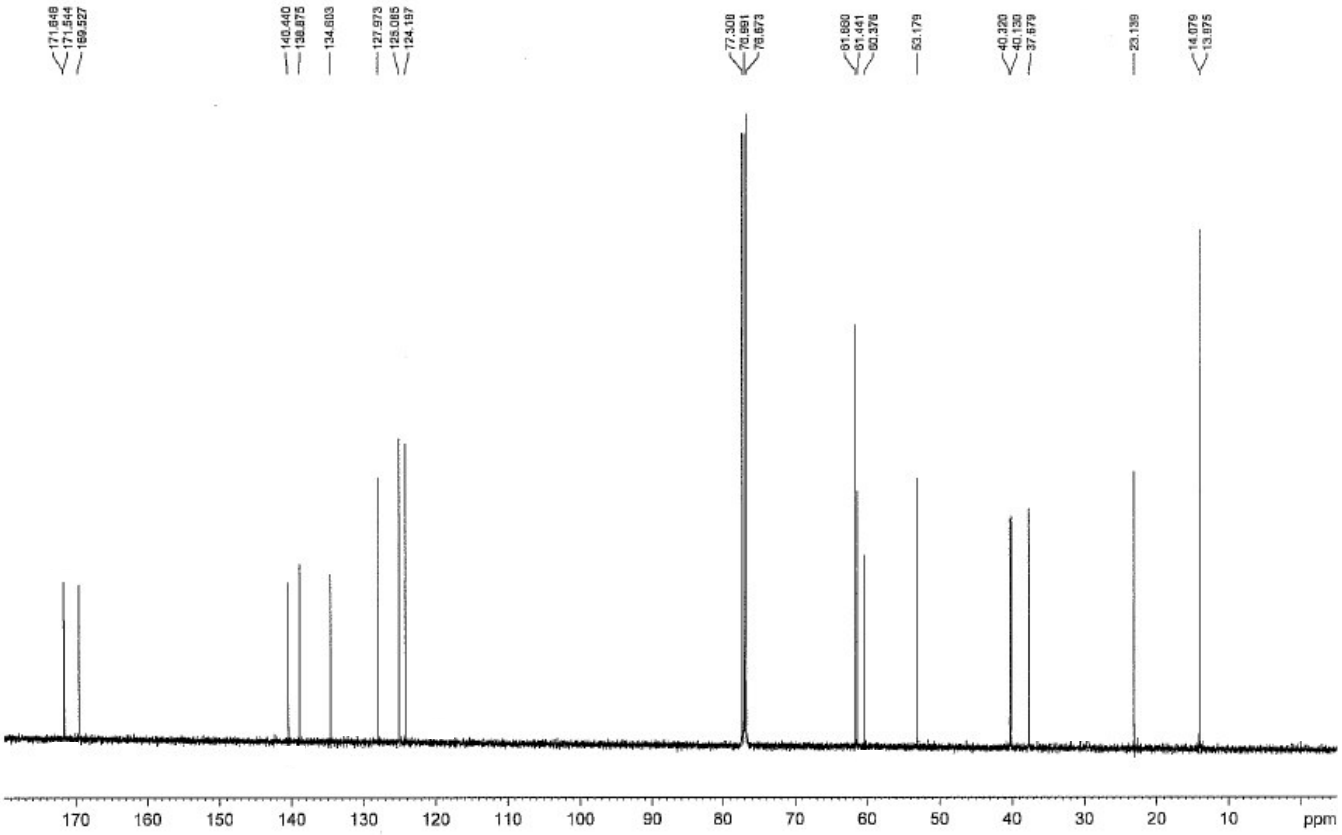
7.273
6.690
6.002
5.983
4.787
4.770
4.751
4.161
4.134
4.106
4.079
3.527
3.497
3.042
3.036
3.019
3.001
2.984
2.178
2.169
1.974
1.271
1.253
1.190
1.154
0.94
0.88
0.97
4.01
1.98
1.95
1.91
2.00
5.85
2.88
6.47
3.00

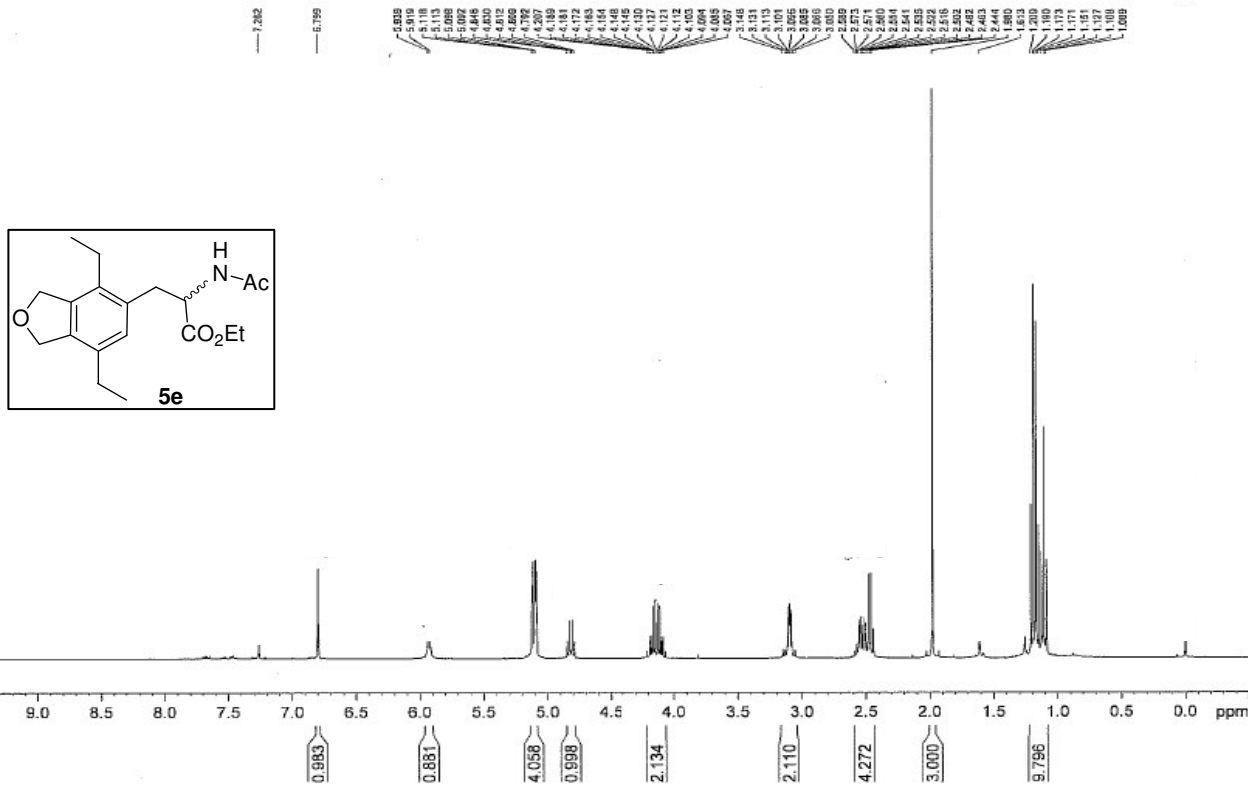

172.155
171.826
169.686
138.449
137.419
132.630
130.476
129.672
129.538
77.317
77.000
76.682
61.675
61.309
59.412
52.759
40.086
39.411
35.259
23.093
18.523
15.274
13.978
13.913

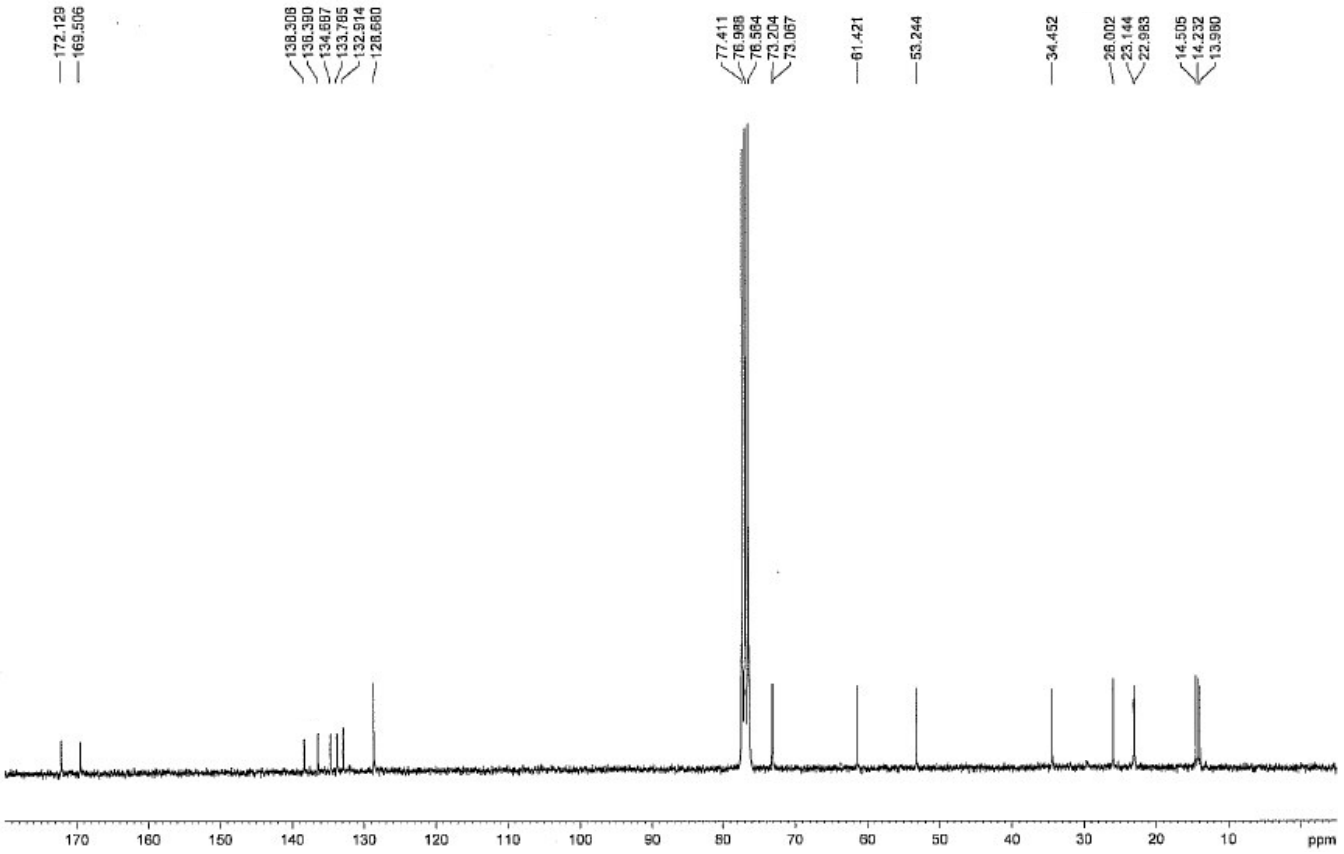

H
N
Ac
EtO2C
EtO2C
CO2Et

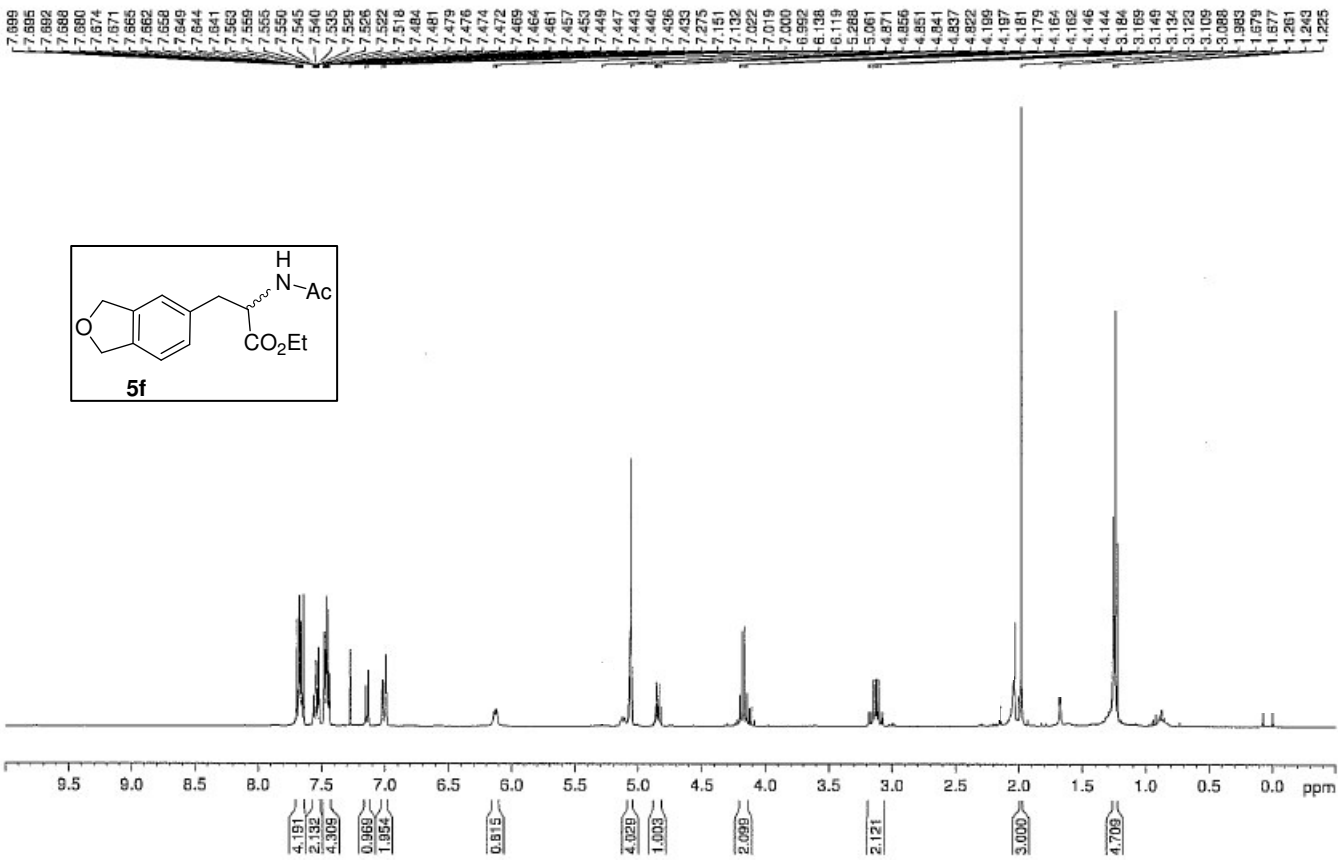
5d

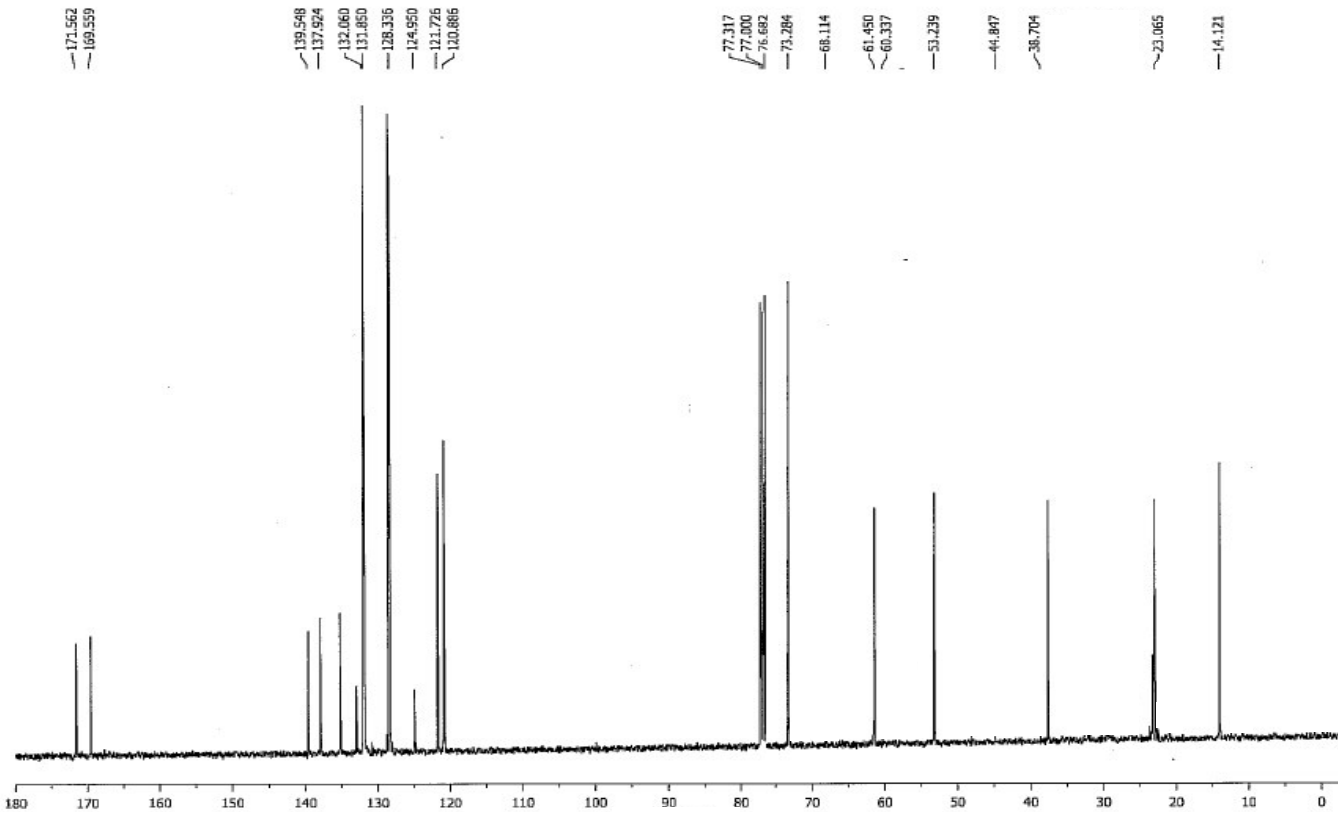
7.267
7.109
7.090
6.933
6.910
6.891
5.922
5.902
5.297
4.842
4.827
4.823
4.813
4.808
4.793
4.227
4.225
4.210
4.207
4.192
4.189
4.171
4.154
4.136
3.549
3.542
3.077
3.062
1.984
1.271
1.269
1.253
1.251
1.235
1.217
1.010
0.980
1.035
0.914
0.994
6.280
4.017
1.934
3.000
10.273


171.848
171.544
169.527
140.440
138.875
134.803
127.973
126.085
124.197
77.308
76.991
76.673
61.660
61.441
60.376
53.179
40.320
40.130
37.679
23.139
14.079
13.975
ppm


H
N
Ac
O
CO2Et
5e
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 0.0 ppm
0.983
0.881
4.058
0.998
2.134
2.110
4.272
3.000
9.796


172.129
169.506
138.308
136.390
134.697
133.765
132.914
128.660
77.411
76.988
76.564
73.204
73.067
61.421
53.244
34.452
26.002
23.144
22.983
14.505
14.232
13.980
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H
N
Ac
O
CO2Et
5f
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 0.0 ppm
4.191
2.132
4.309
0.969
1.954
0.815
4.029
1.003
2.099
2.121
3.000
4.709


171.562
169.559
139.548
137.924
132.060
131.850
128.336
124.950
121.726
120.866
77.317
77.000
76.682
73.284
68.114
61.450
60.337
53.239
44.847
38.704
23.065
14.121
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

^{1}H and ^{13}C NMR spectra of homocoupled product 6