

Supporting information

Synthesis of medium-sized (6-7-6) ring compounds by iron-catalyzed C-H activation/annulation

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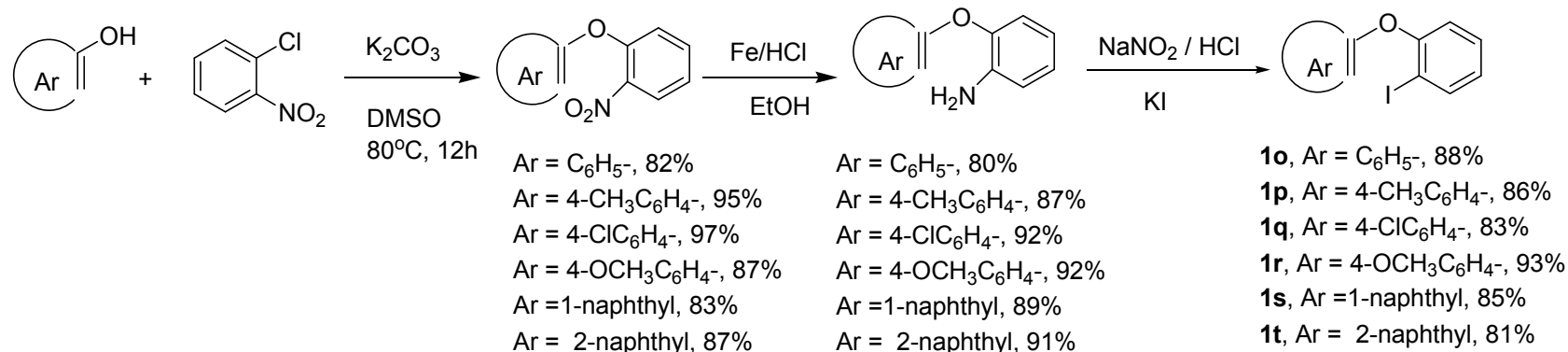
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Synthesis of 2-iododiaryl ethers (1o-t)



General procedure for the synthesis of 2-nitrodiaryl ether

A mixture of phenol (6.3 mmol), 2-chloro nitrobenzene 7.6 mmol (6.3 mmol) and K₂CO₃ (12.6 mmol) in DMSO (6 ml) was stirred at 80°C for 12h. After the completion of the reaction (as monitored by TLC) the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate and petroleum ether as eluent to afford the desired 2-nitrodiaryl ether.

General procedure for the synthesis of 2-aminodiaryl ether

To a solution of 2-nitrodiaryl ether (4.0 mmol) in absolute ethanol (7 mL), iron powder (10 eq.) was added at room temperature. Then, temperature of the reaction mixture was raised to 80°C and 1.0 mL of concentrated HCl was added dropwise over a period of 10 min. After 2h the reaction mixture was cooled to room temperature and then made alkaline using aq. NaOH solution. Then, solid mass was filtered and the amine was extracted from the filtrate using ethyl acetate (5 x 20 mL). Solvent was removed under reduced pressure and the prepared 2-aminodiaryl ether was subjected for the next step without further purification.

General procedure for the synthesis of 2-iododiaryl ether

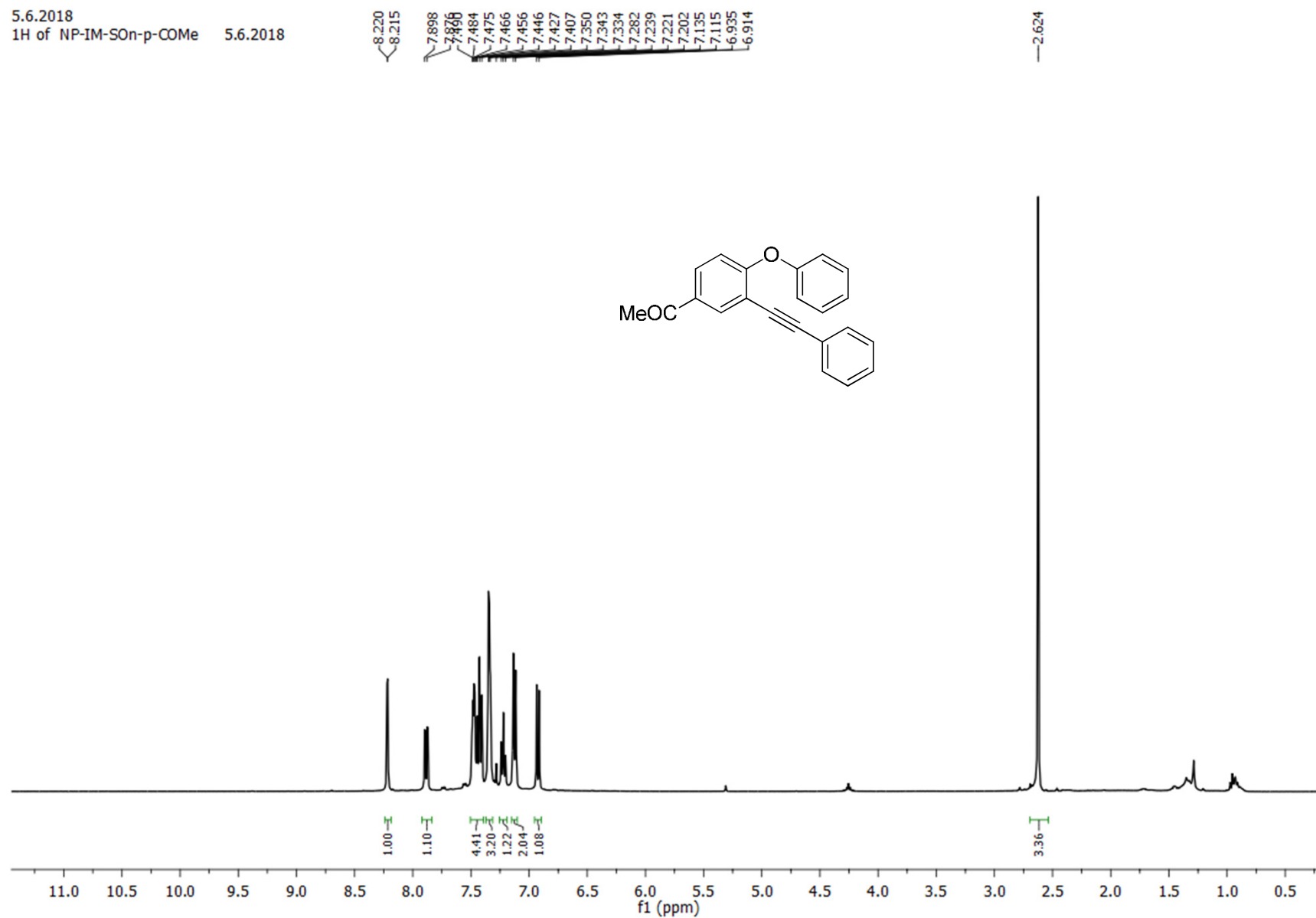
To a solution of 2-aminodiaryl ether (4 mmol) in 4.5 mL water, 1 mL of concentrated hydrochloric acid was added at 0°C and stirred for 10 min. To the reaction mixture an aqueous solution of sodium nitrite (4.8 mmol) in 1 mL water was added at 0°C and stirred for 30 min. Then an aqueous solution of potassium iodide (6 mmol) in 1 mL water was added to the reaction mixture at that temperature. The reaction mixture was allowed to come to room temperature and stirred for 10 min and then heated in a pre heated oil bath at 80°C for 30 min. Then, the reaction mixture was cooled to room temperature and 5 mL of saturated solution of Na₂S₂O₃ was added. The iodo-compound so formed was extracted with ethyl acetate (3 x 20 mL). The organic layer was washed with brine, the solvent removed under reduced pressure and the crude product purified by column chromatography to obtain the desired 2-iododiaryl ether.

Copies of ^1H and ^{13}C NMR spectra

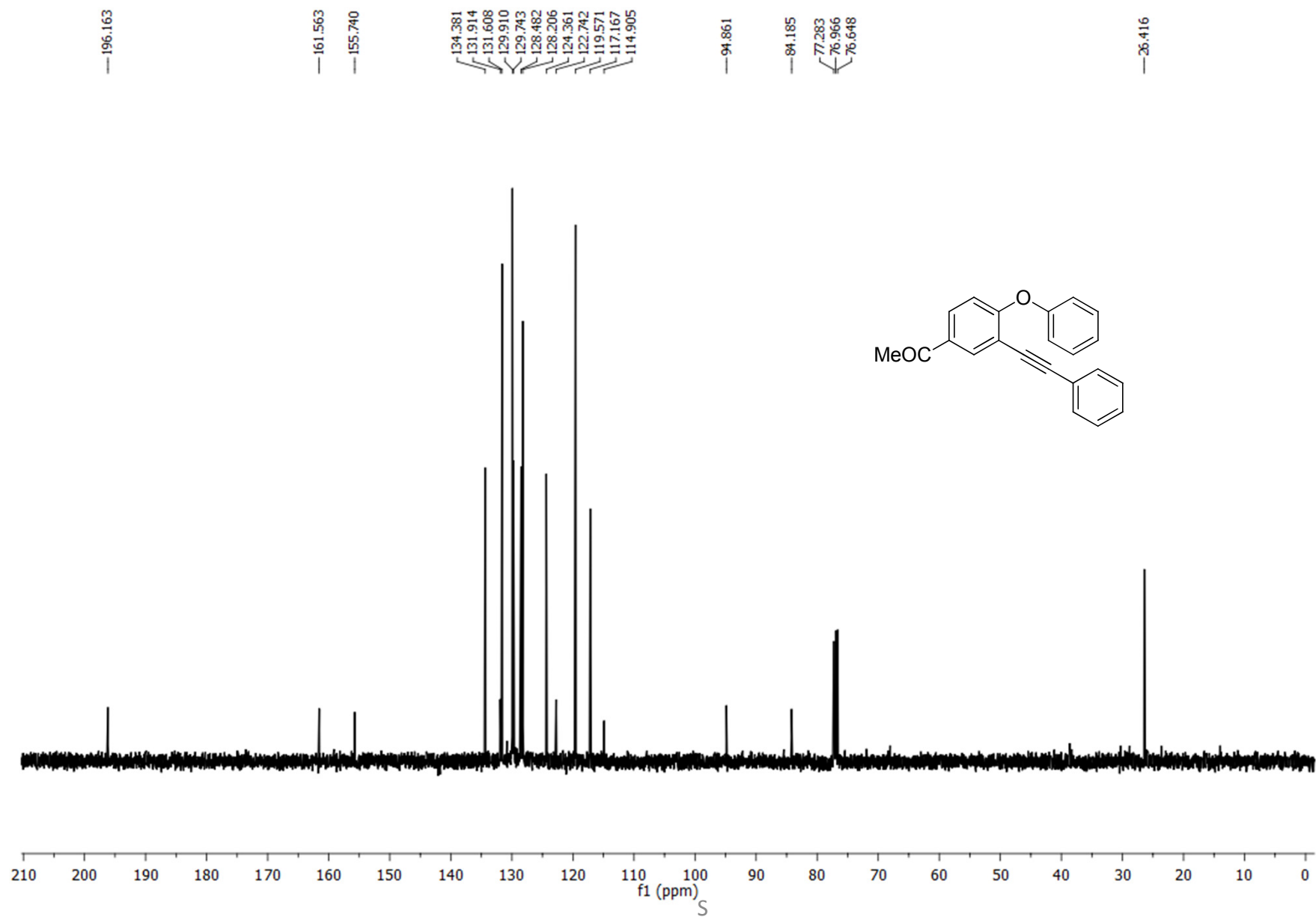
^1H NMR of 1-(4-phenoxy-3-(phenylethynyl)phenyl)ethanone (2a)

5.6.2018

^1H of NP-IM-SOn-p-COMe 5.6.2018

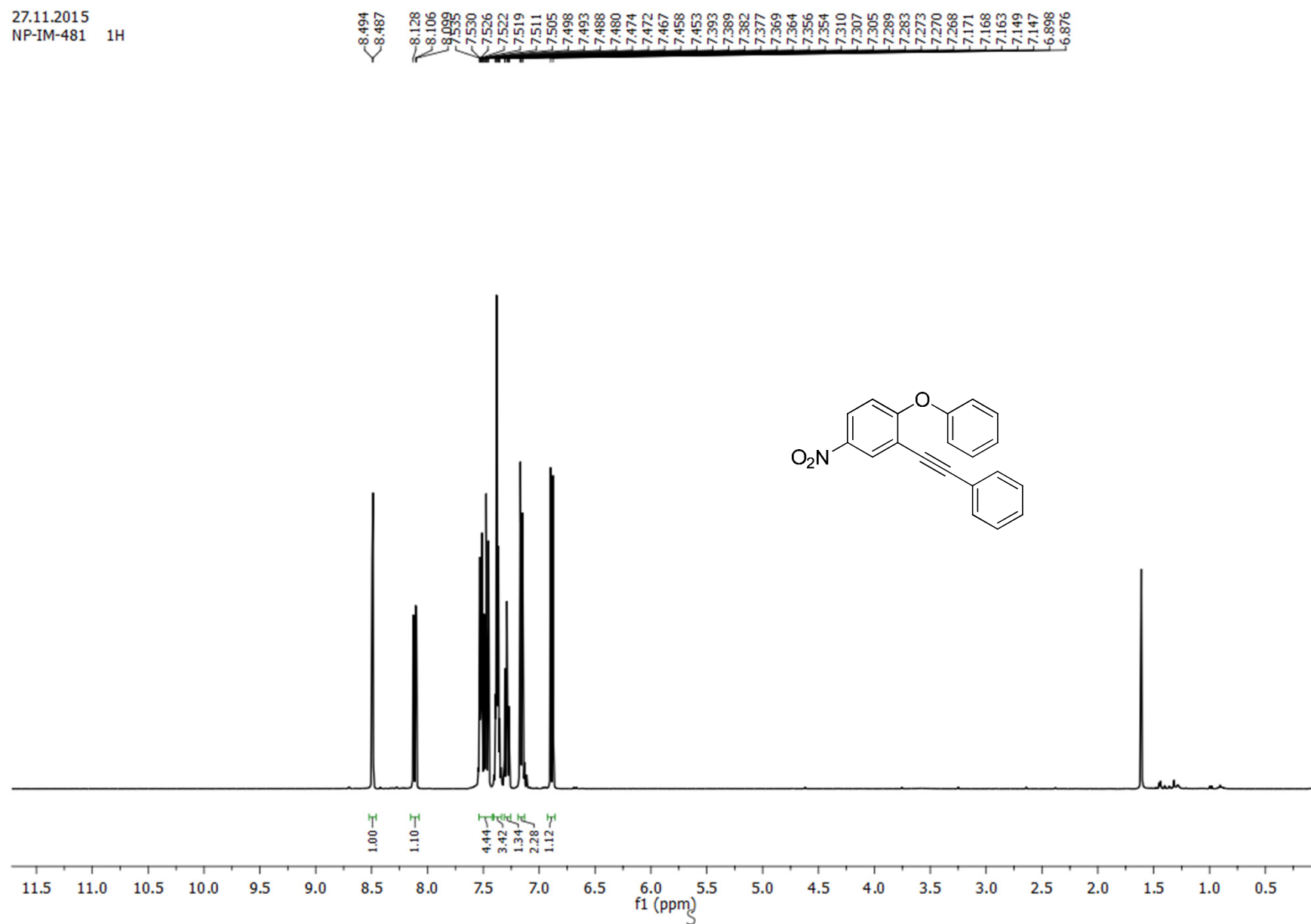


^{13}C NMR of 1-(4-phenoxy-3-(phenylethynyl)phenyl)ethanone (2a)

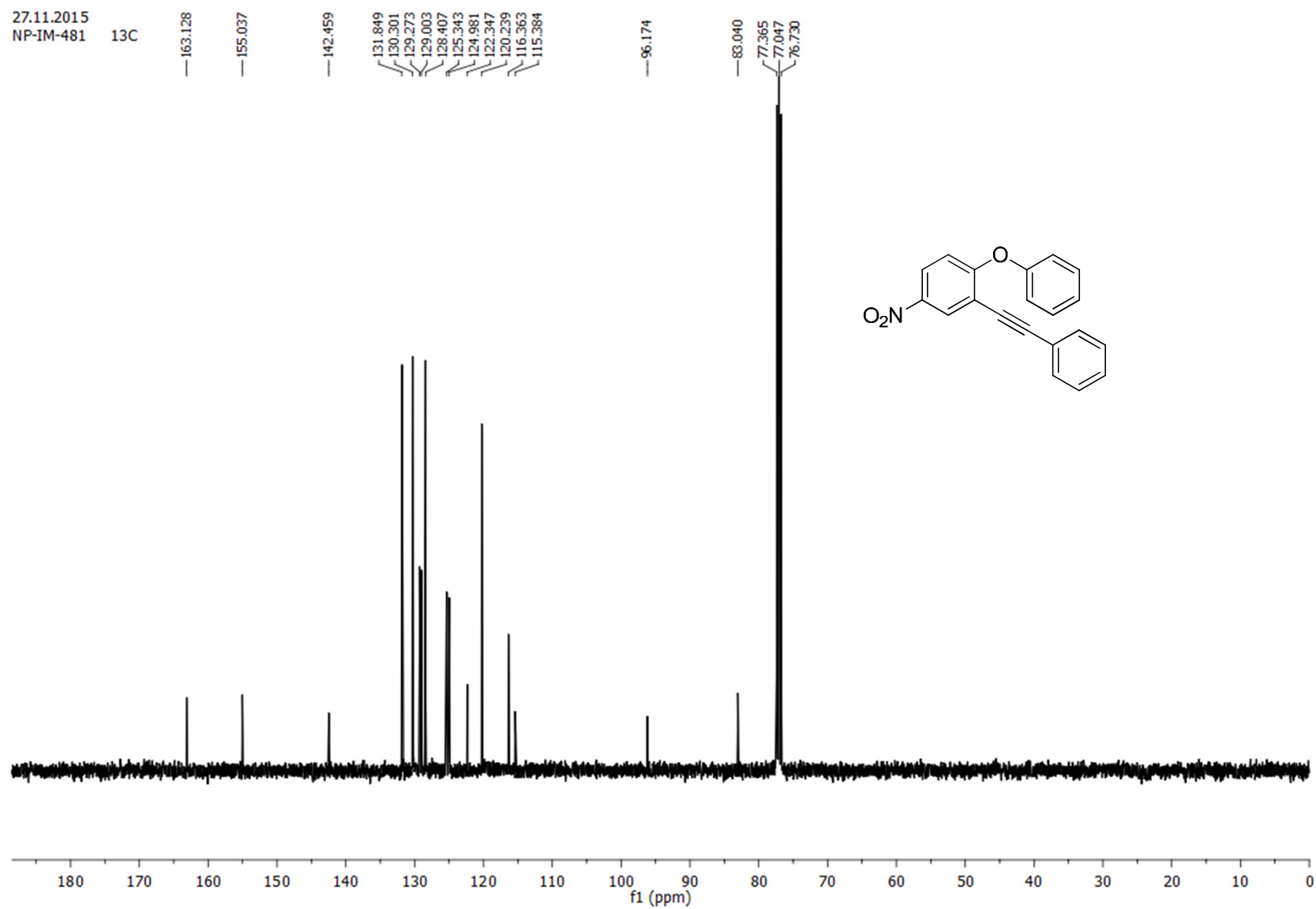


¹H NMR of 4-nitro-1-phenoxy-2-(phenylethynyl)benzene (2b)

27.11.2015
NP-IM-481 1H



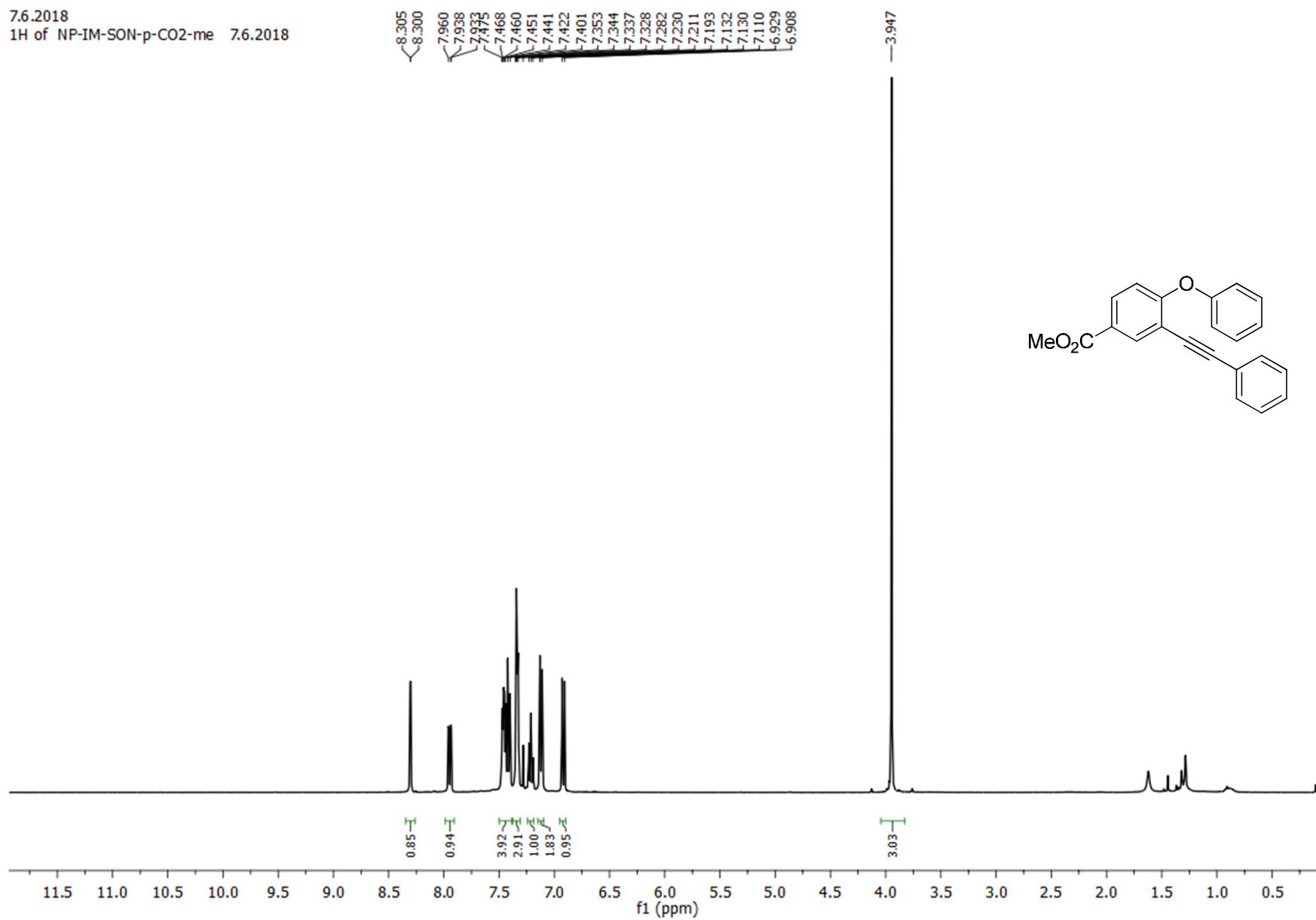
¹³C NMR of 4-nitro-1-phenoxy-2-(phenylethynyl)benzene (2b)



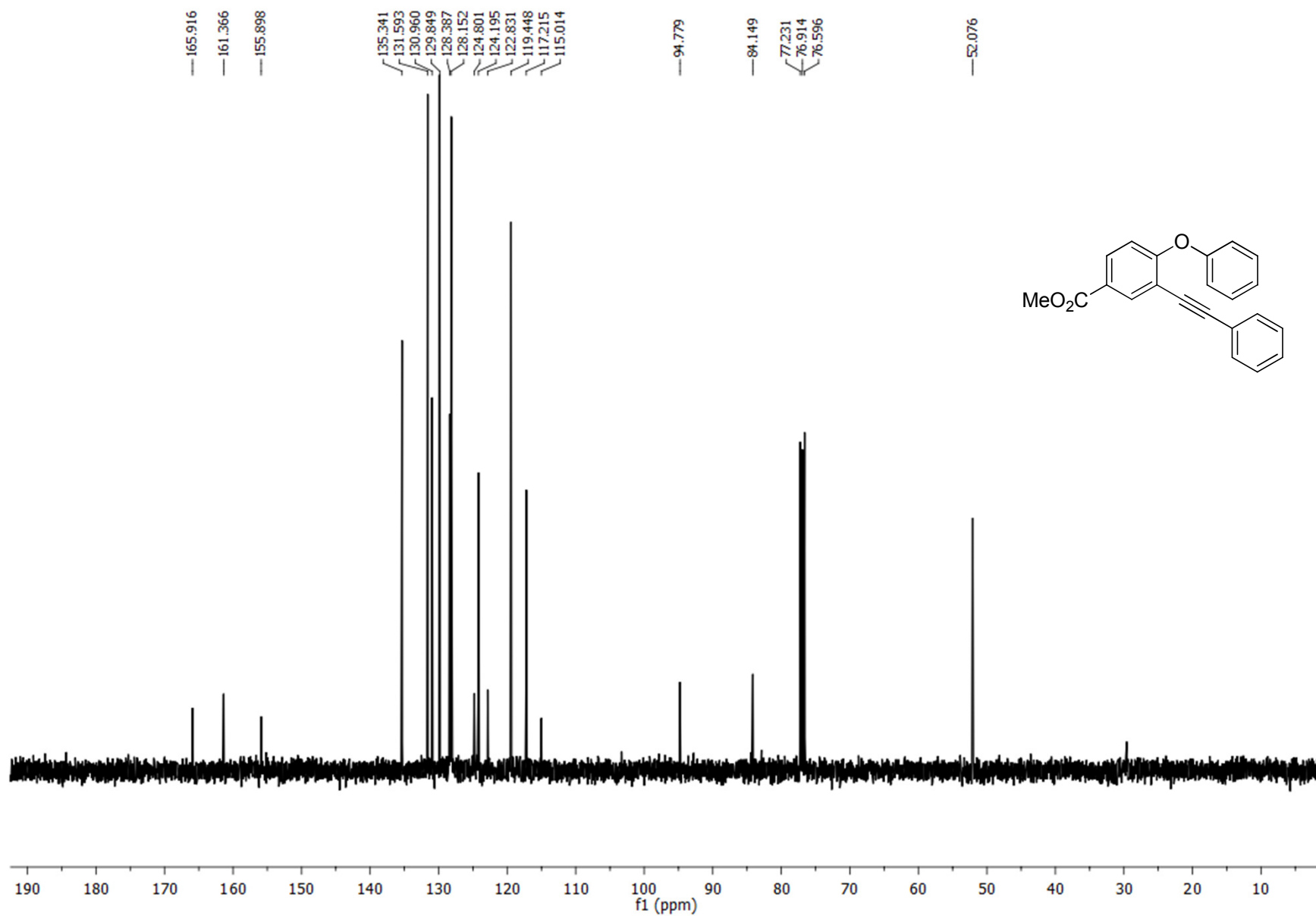
¹H NMR of methyl 4-phenoxy-3-(phenylethynyl)benzoate (2c)

7.6.2018

¹H of NP-IM-SON-p-CO2-me 7.6.2018

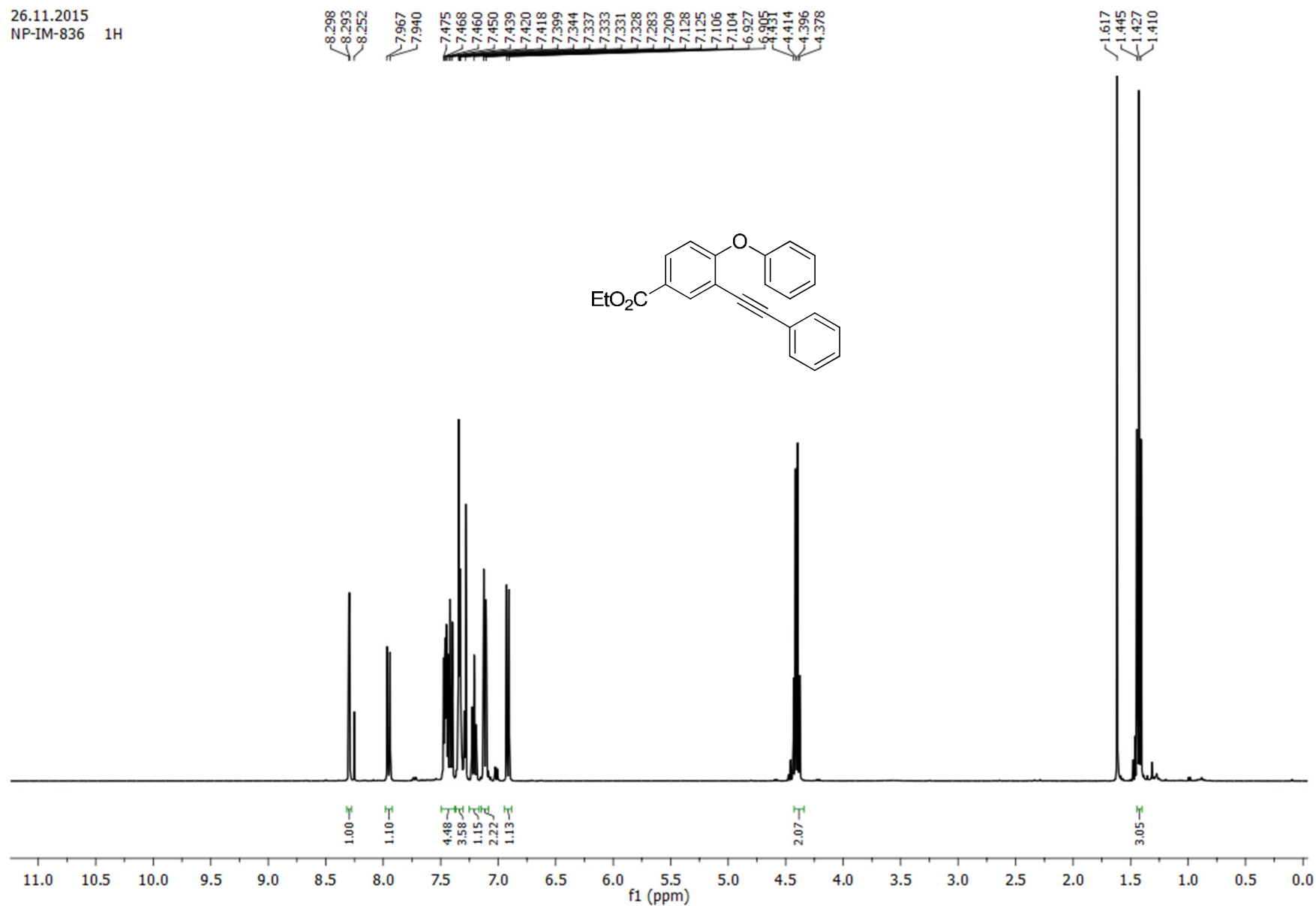


^{13}C NMR of methyl 4-phenoxy-3-(phenylethynyl)benzoate (2c)

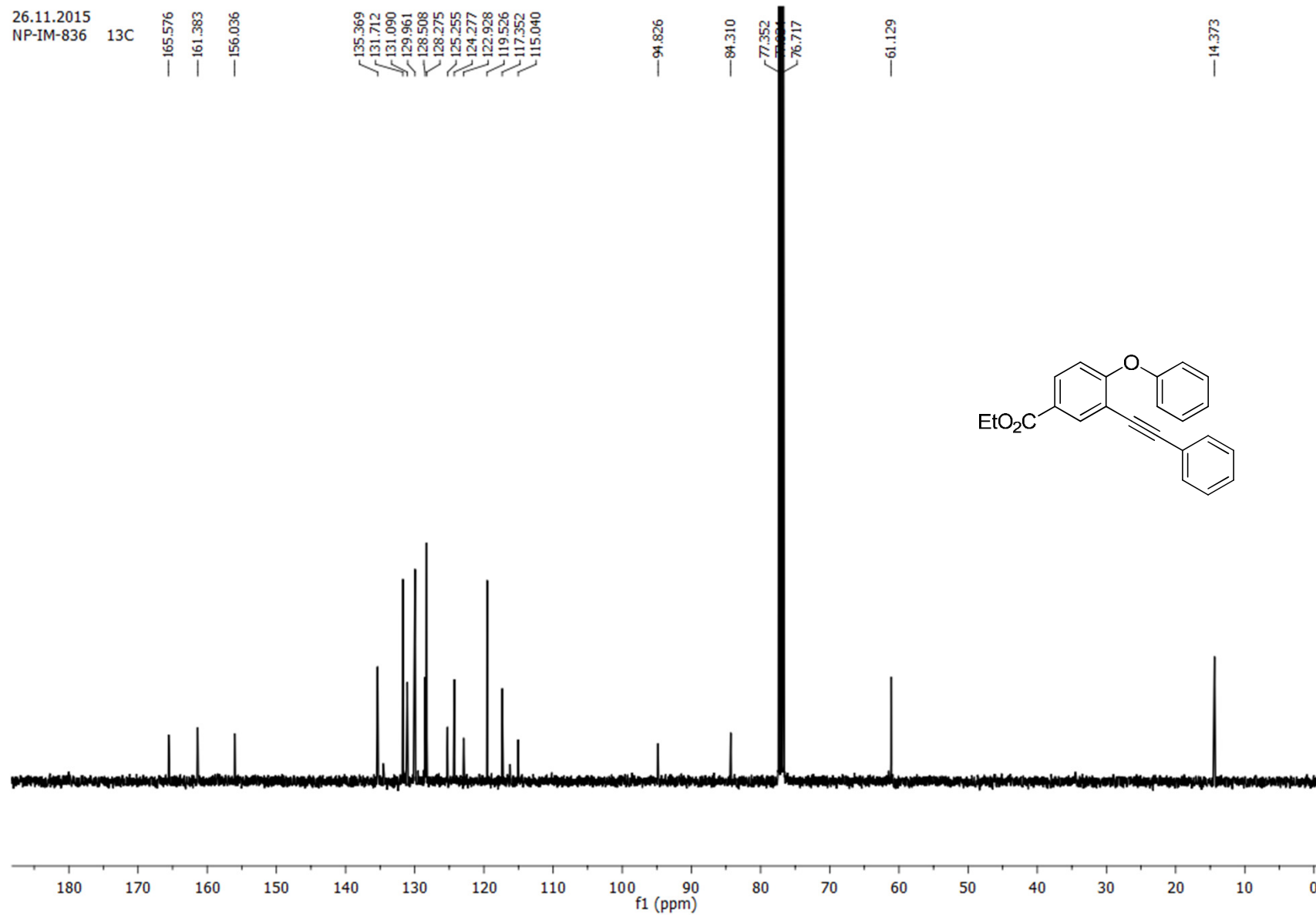


¹H NMR of ethyl 4-phenoxy-3-(phenylethynyl)benzoate (2d)

26.11.2015
NP-IM-836 1H



^{13}C NMR of ethyl 4-phenoxy-3-(phenylethynyl)benzoate (2d)



¹H NMR of isopropyl 4-phenoxy-3-(phenylethynyl)benzoate (2e)

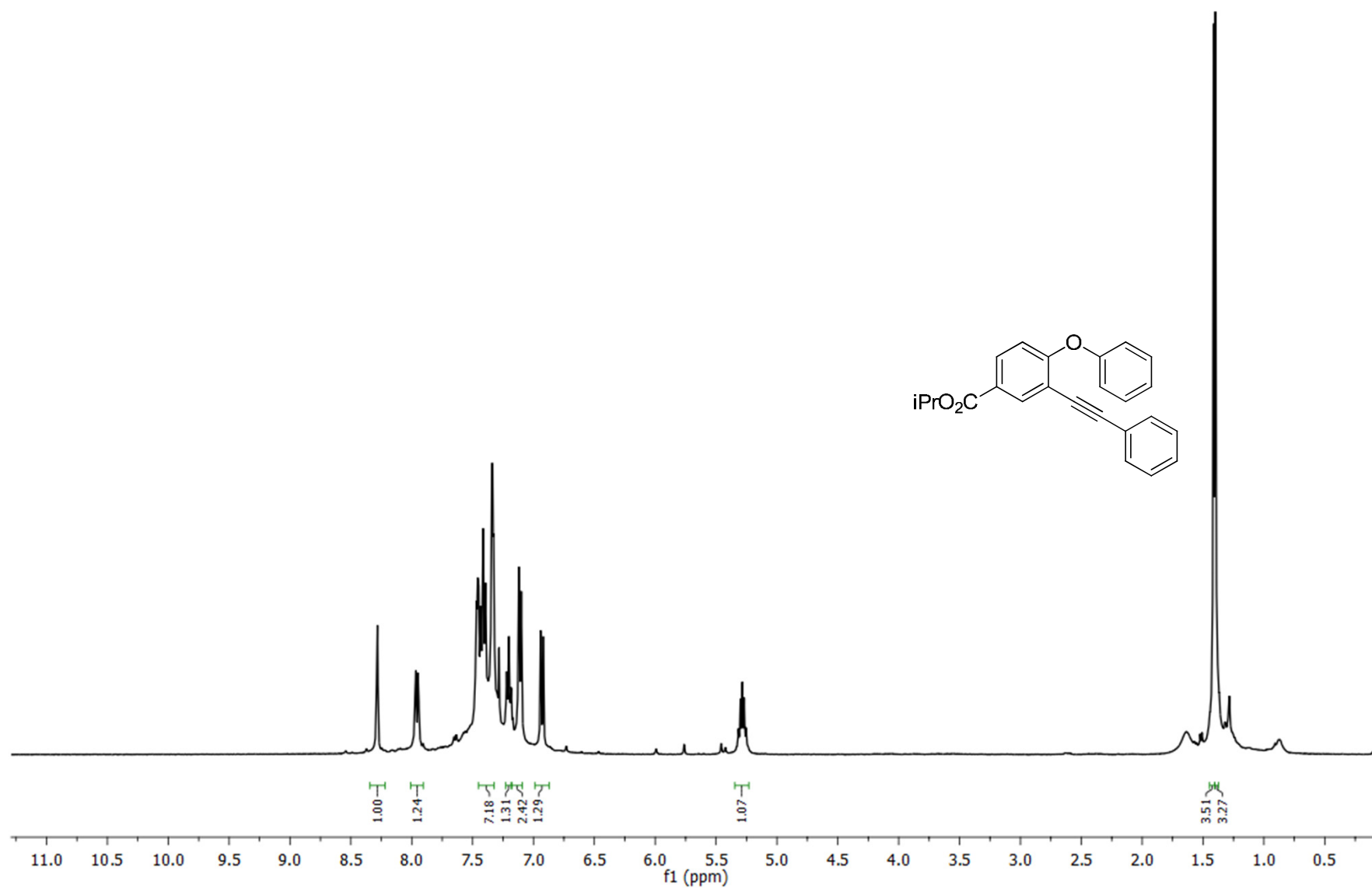
7.6.2018

1H of NP-IM-SON-p-CO2-iPr

7.6.2018

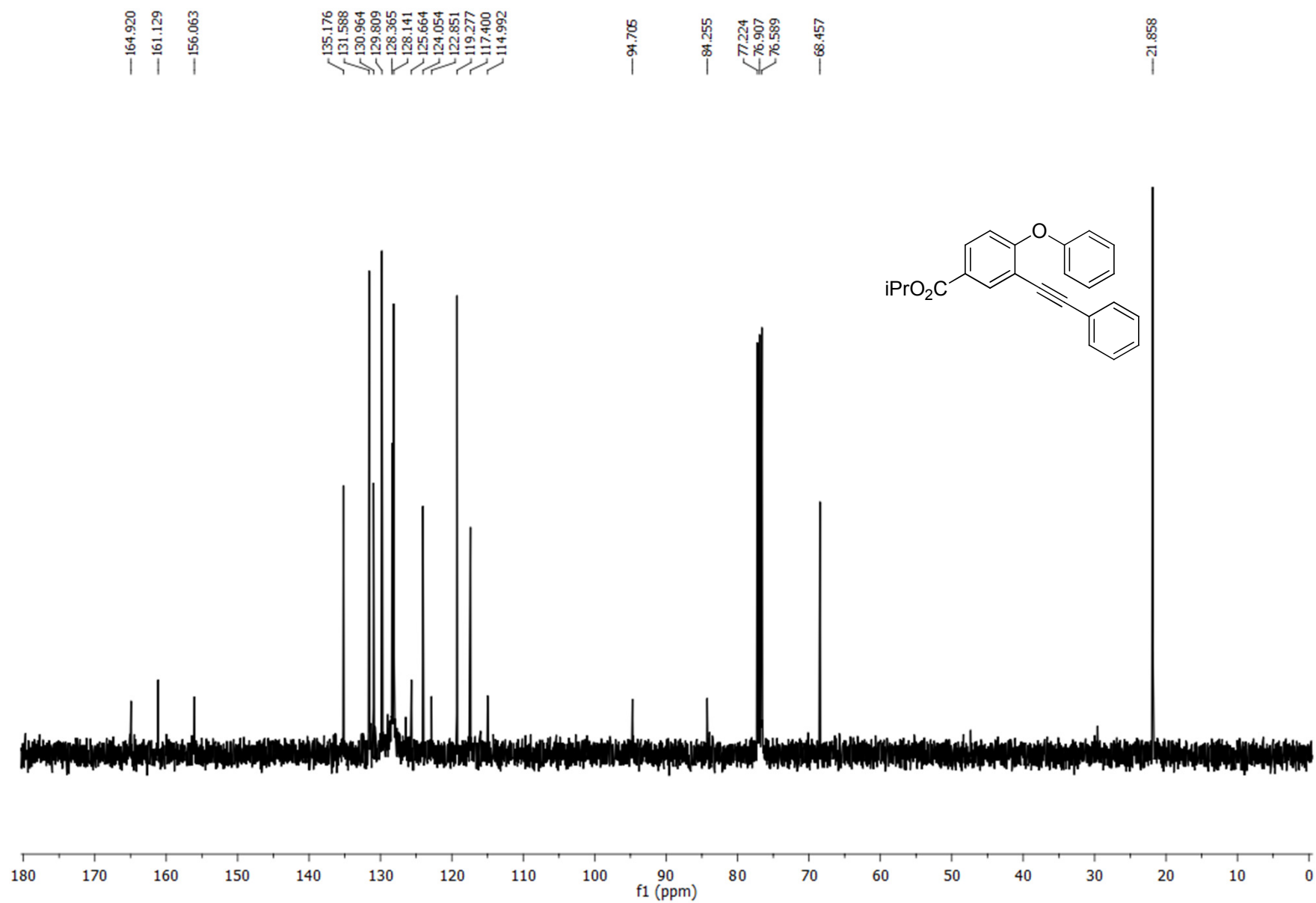
8.286
8.281
7.971
7.966
7.949
7.467
7.458
7.450
7.433
7.413
7.394
7.343
7.336
7.327
7.283
7.202
7.120
7.101
6.941
6.928
5.318
5.300
5.285
5.269
5.254

1.414
1.398



S

¹³C NMR of isopropyl 4-phenoxy-3-(phenylethynyl)benzoate(2e)

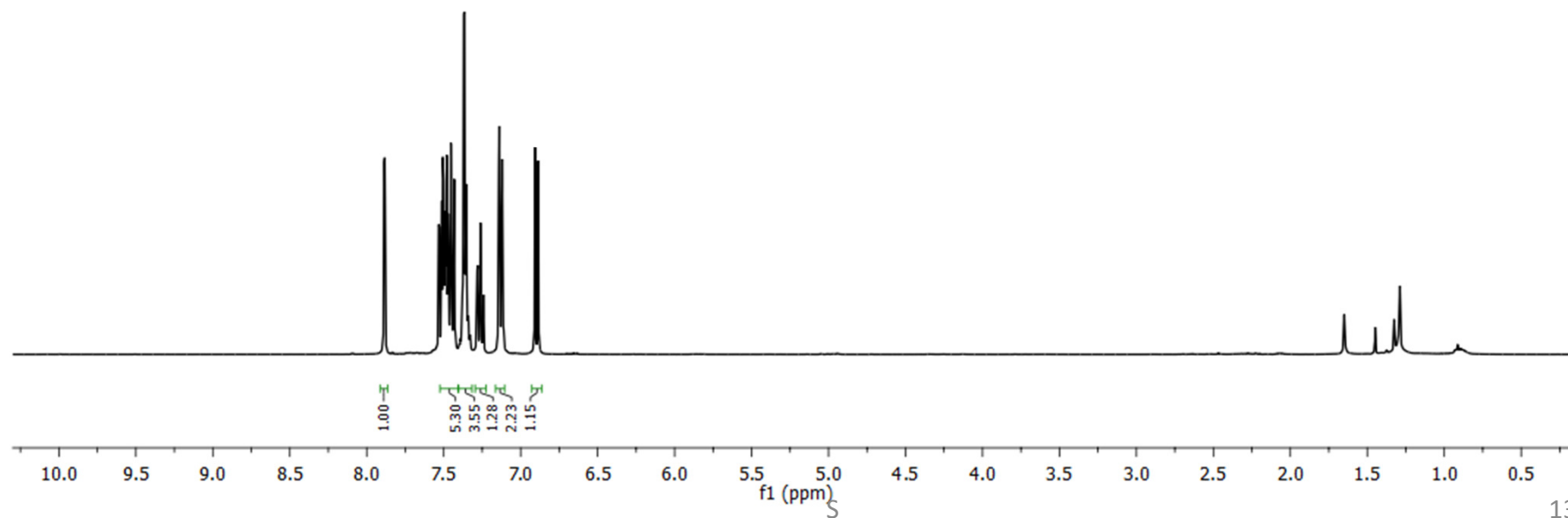
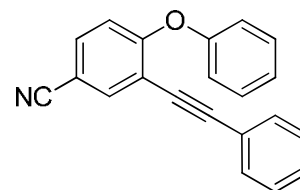


S

¹H NMR of 4-phenoxy-3-(phenylethynyl)benzonitrile (2f)

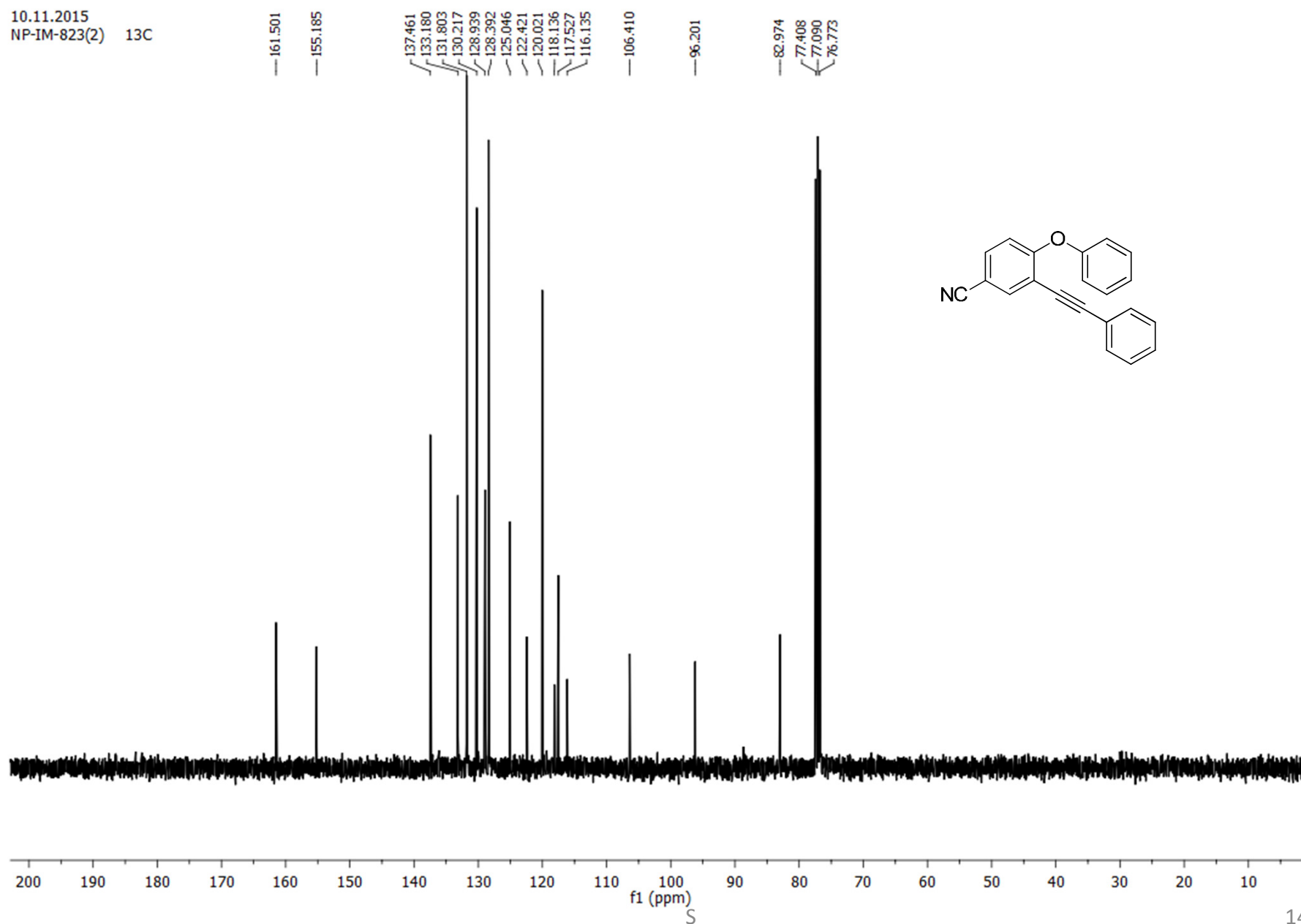
10.11.2015
NP-IM-823(2) 1H

7.888
7.883
7.533
7.528
7.512
7.506
7.499
7.496
7.492
7.488
7.480
7.472
7.467
7.453
7.451
7.437
7.432
7.426
7.381
7.377
7.374
7.370
7.365
7.357
7.352
7.344
7.341
7.282
7.280
7.277
7.261
7.245
7.243
7.240
7.142
7.139
7.134
7.123
7.120
7.118
7.112
6.907
6.886



¹³C NMR of 4-phenoxy-3-(phenylethynyl)benzonitrile (2f)

10.11.2015
NP-IM-823(2) 13C

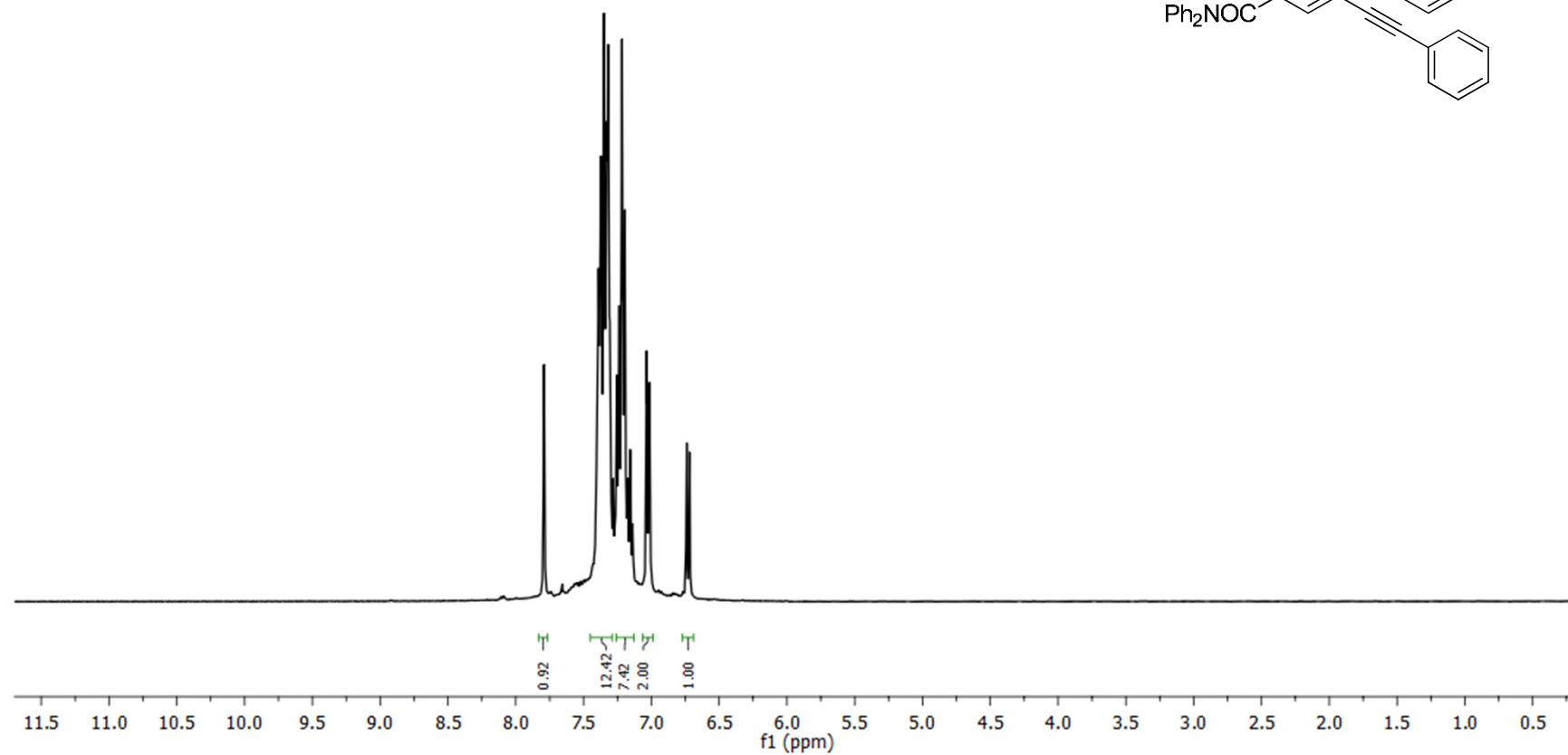
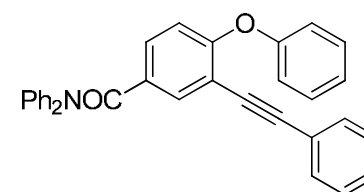


¹H NMR of 4-phenoxy-N,N-diphenyl-3-(phenylethynyl)benzamide (2g)

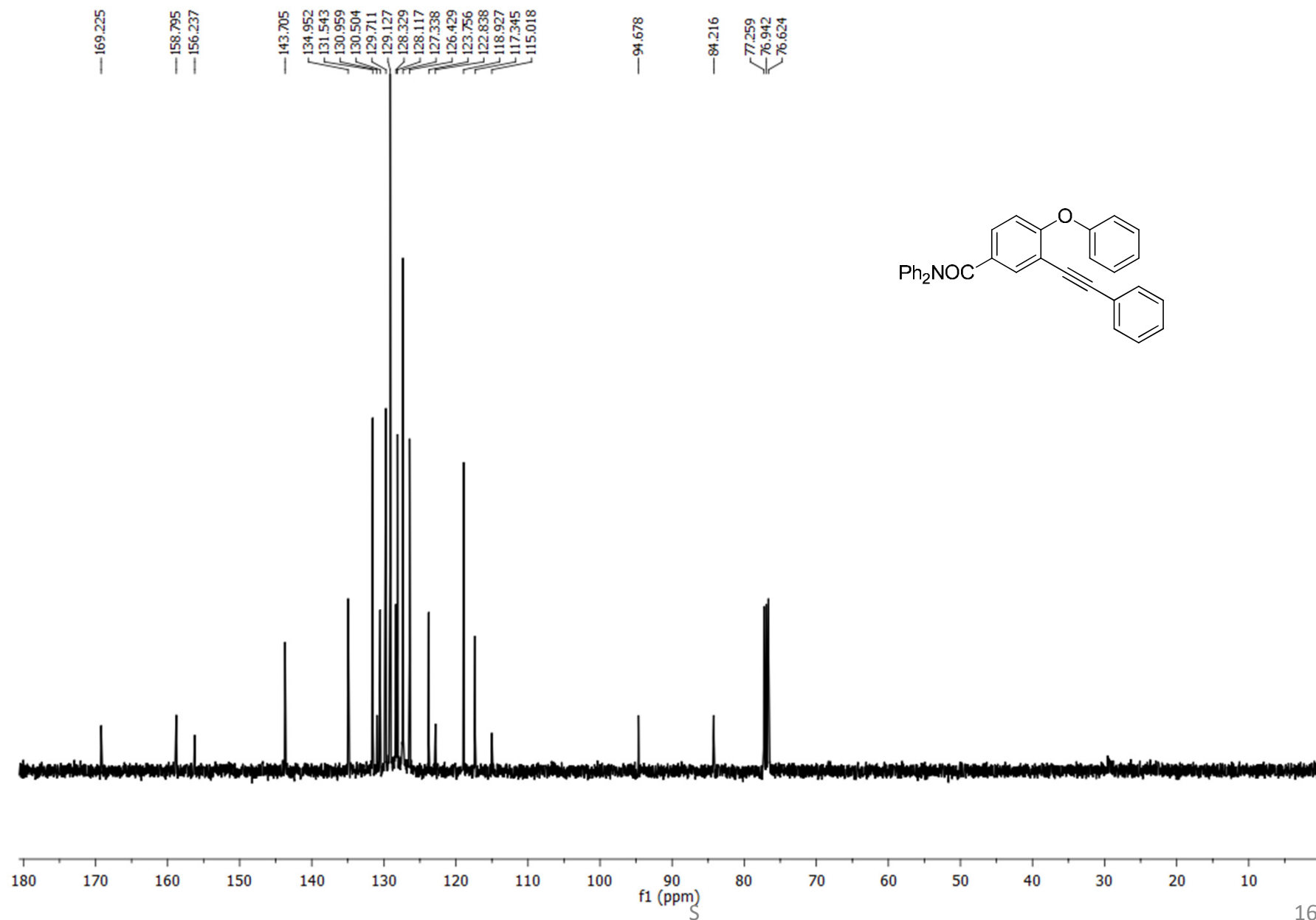
7.6.2018

1H of NP-IM-SON-P-coNPh2 7.6.2018

7.796
7.791
7.786
7.401
7.390
7.372
7.350
7.338
7.328
7.320
7.317
7.307
7.283
7.281
7.255
7.237
7.216
7.196
7.176
7.157
7.139
7.035
7.014
6.739
6.717



^{13}C NMR of 4-phenoxy-N,N-diphenyl-3-(phenylethynyl)benzamide (2g)

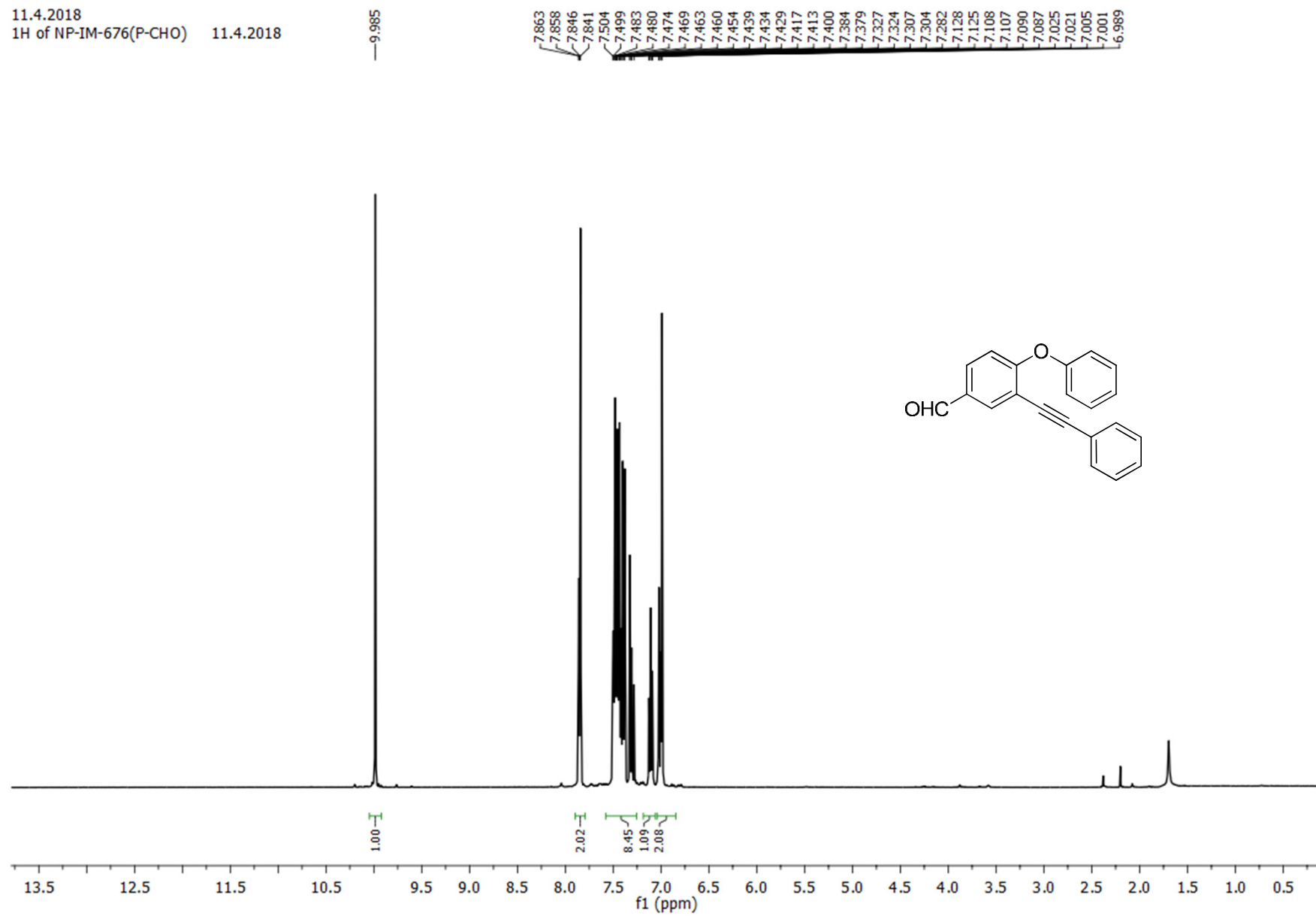


¹H NMR of 4-phenoxy-3-(phenylethynyl)benzaldehyde (2h)

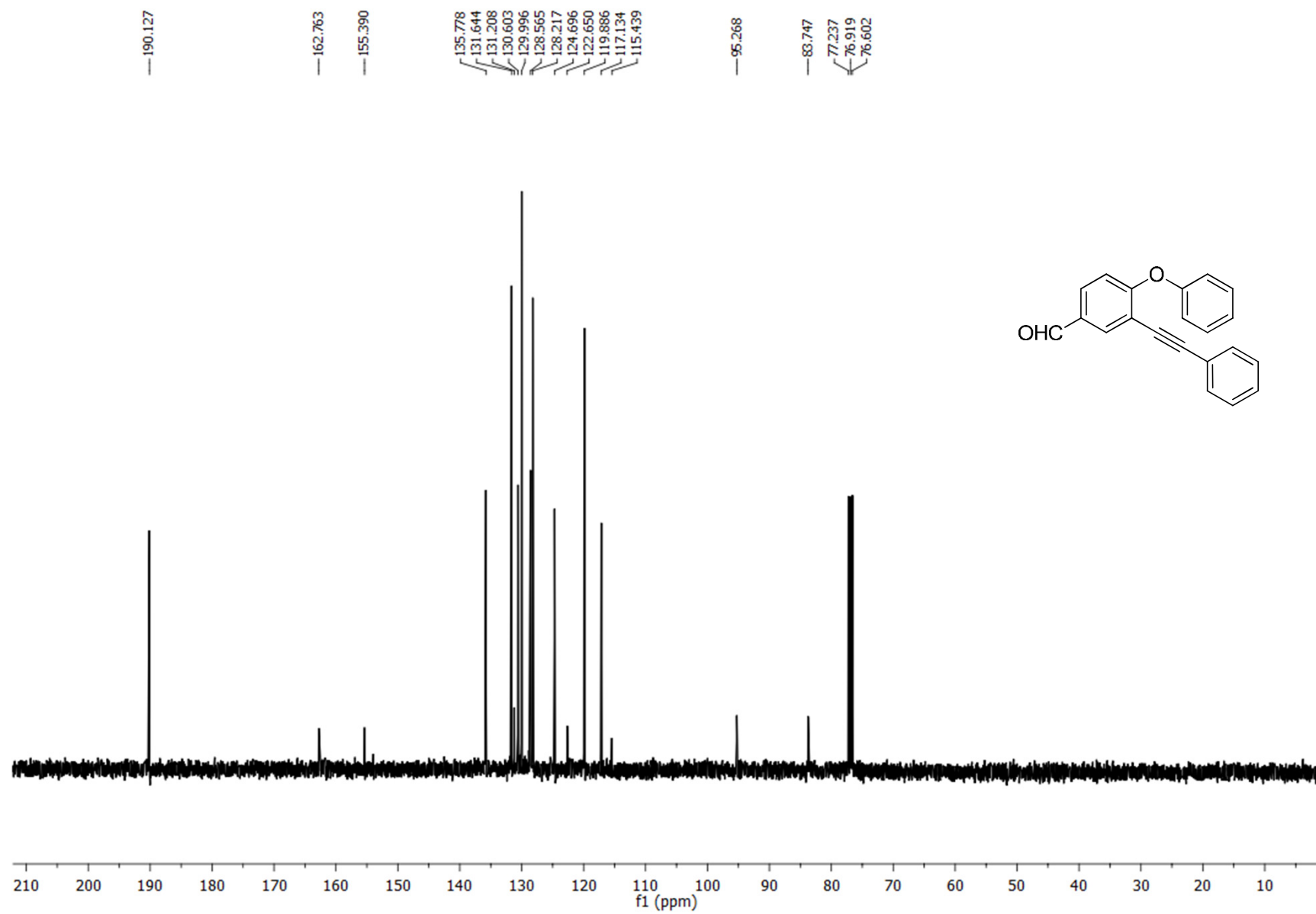
11.4.2018

¹H of NP-IM-676(P-CHO)

11.4.2018



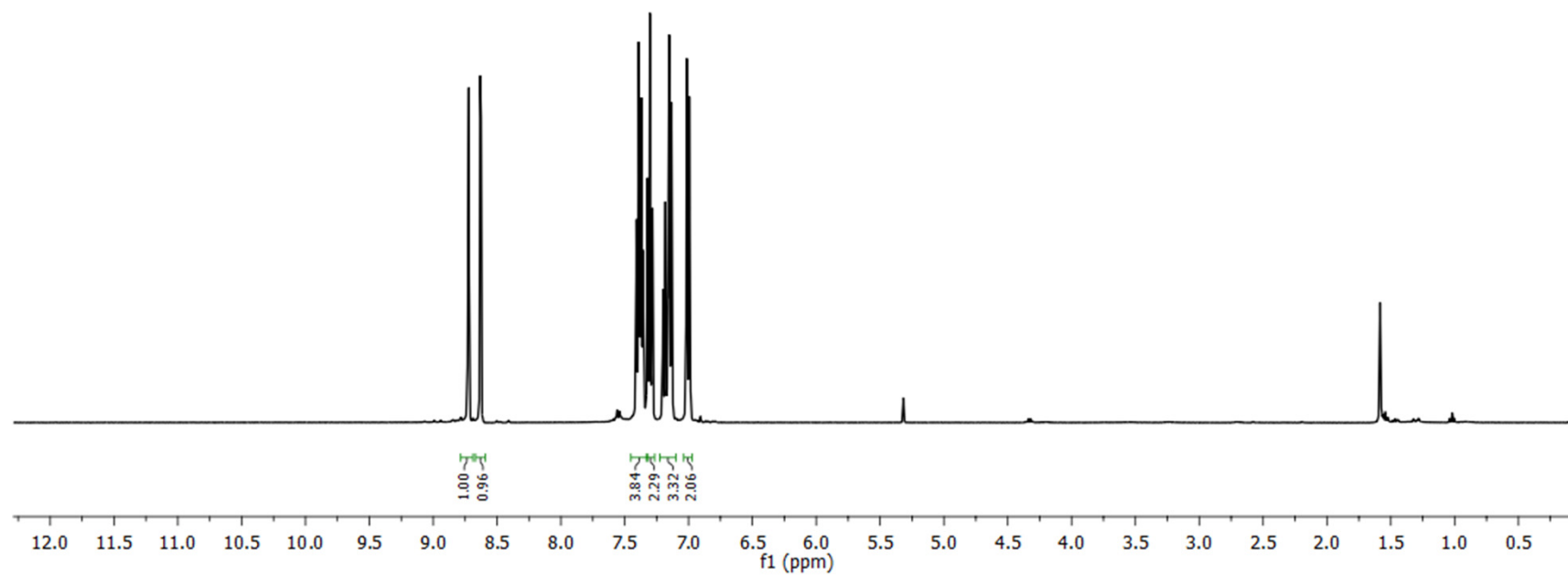
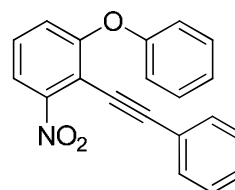
¹³C NMR of 4-phenoxy-3-(phenylethynyl)benzaldehyde (2h)



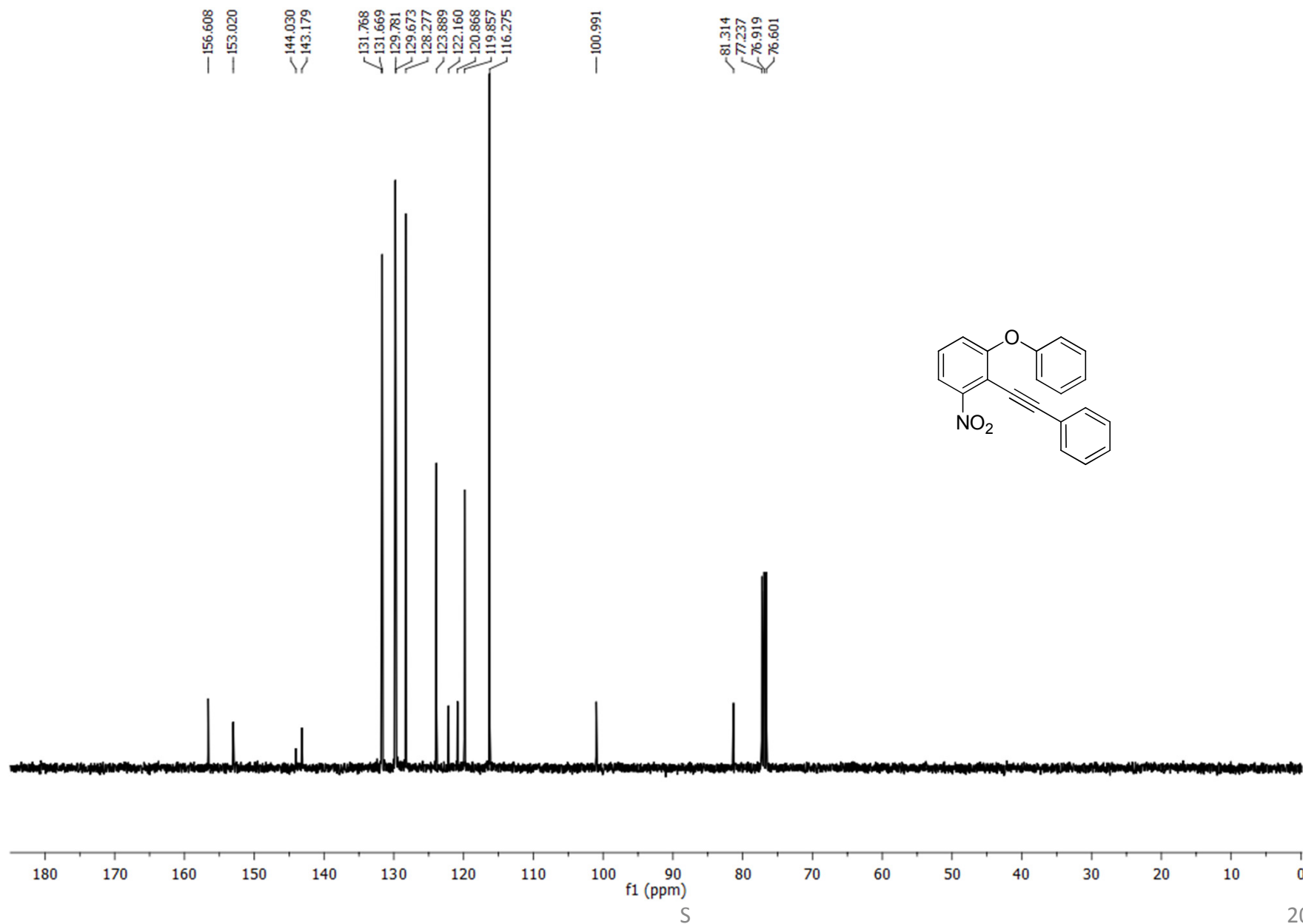
¹H NMR of 1-nitro-3-phenoxy-2-(phenylethynyl)benzene (2i)

7.6.2018
1H of NP-IM-SON-3-NO2 7.6.2018

8.727
8.720
8.632
8.625
7.409
7.404
7.390
7.388
7.381
7.374
7.369
7.359
7.356
7.322
7.303
7.285
7.282
7.200
7.181
7.162
7.160
7.153
7.151
7.134
7.130
7.016
7.013
6.994



^{13}C NMR of 1-nitro-3-phenoxy-2-(phenylethynyl)benzene (2i)



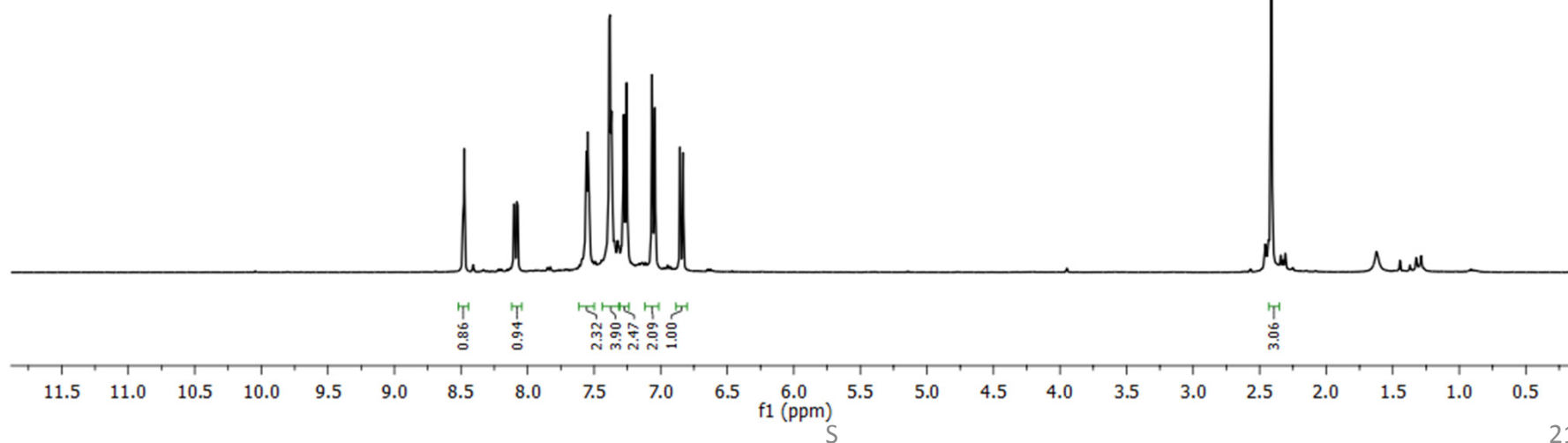
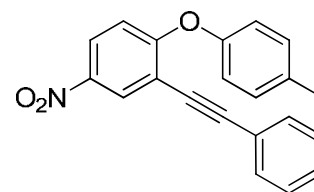
¹H NMR of 4-nitro-2-(phenylethynyl)-1-(p-tolyloxy)benzene (2k)

5.6.2018

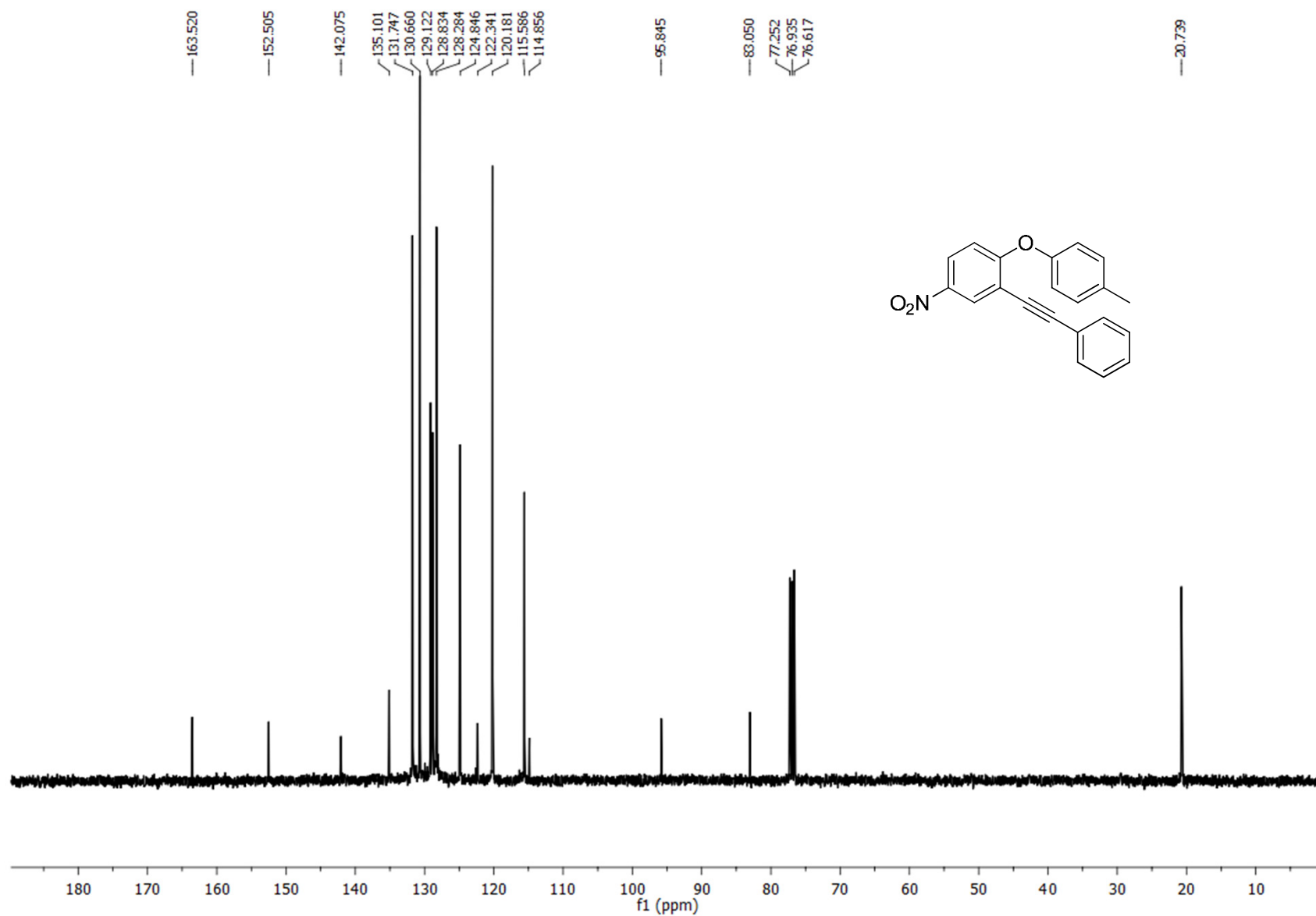
¹H of NP-IM-SON-p-Me-P-NO₂ 5.6.2018

8.482
8.476
8.103
8.097
8.081
8.063
7.558
7.549
7.539
7.386
7.381
7.373
7.277
7.256
7.064
7.043
6.855
6.832

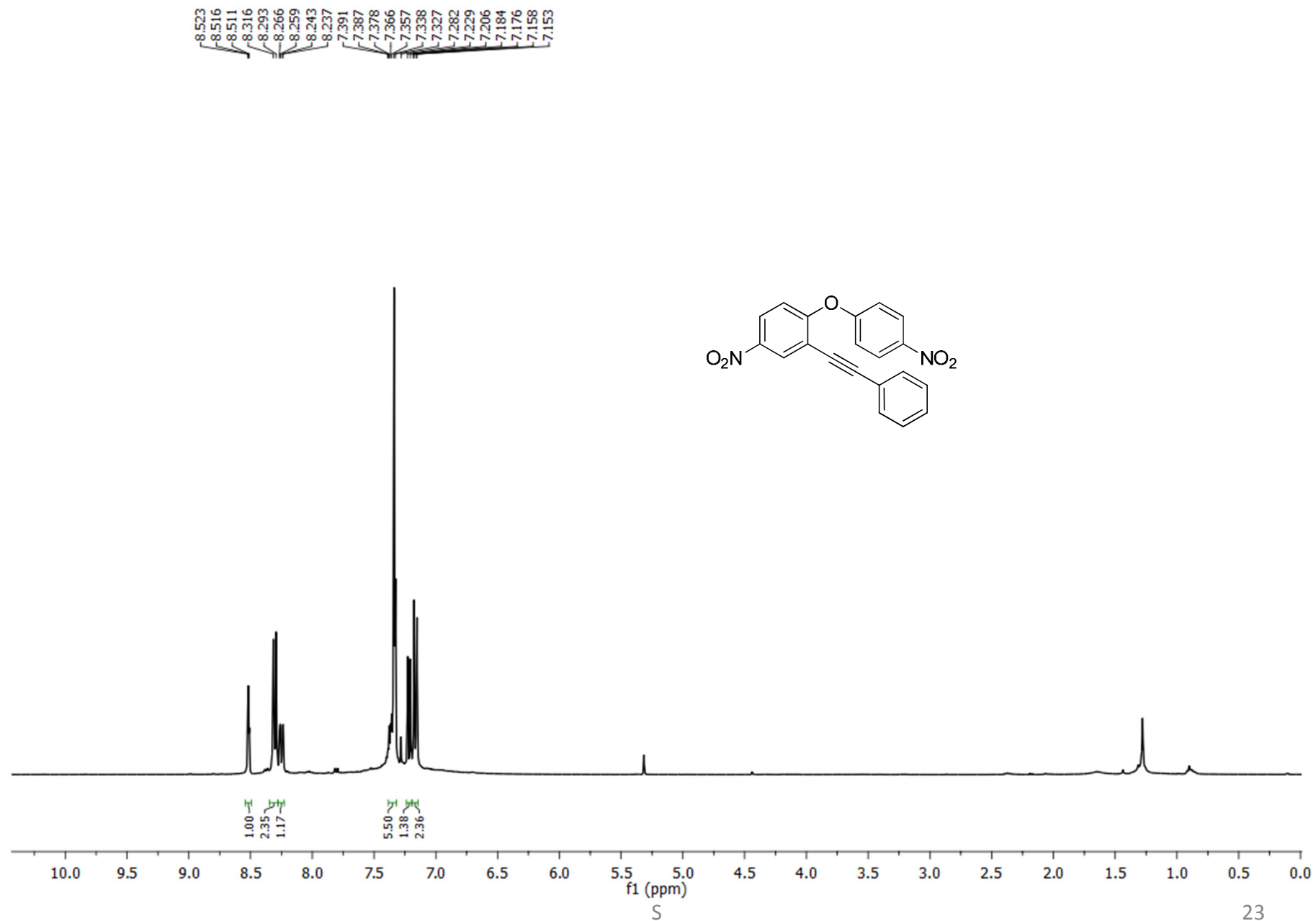
2.413



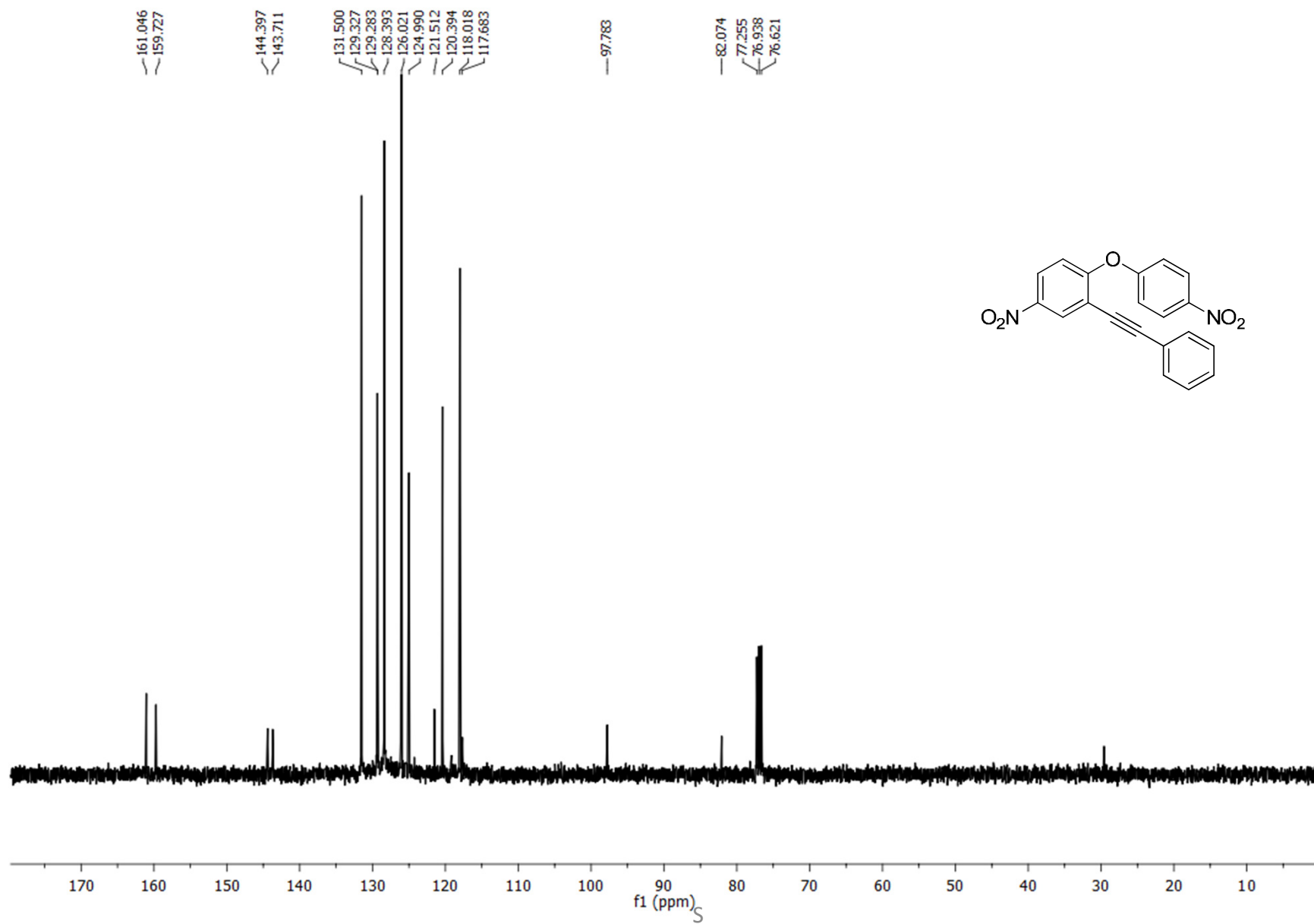
^{13}C NMR of 4-nitro-2-(phenylethynyl)-1-(p-tolyloxy)benzene (2k)



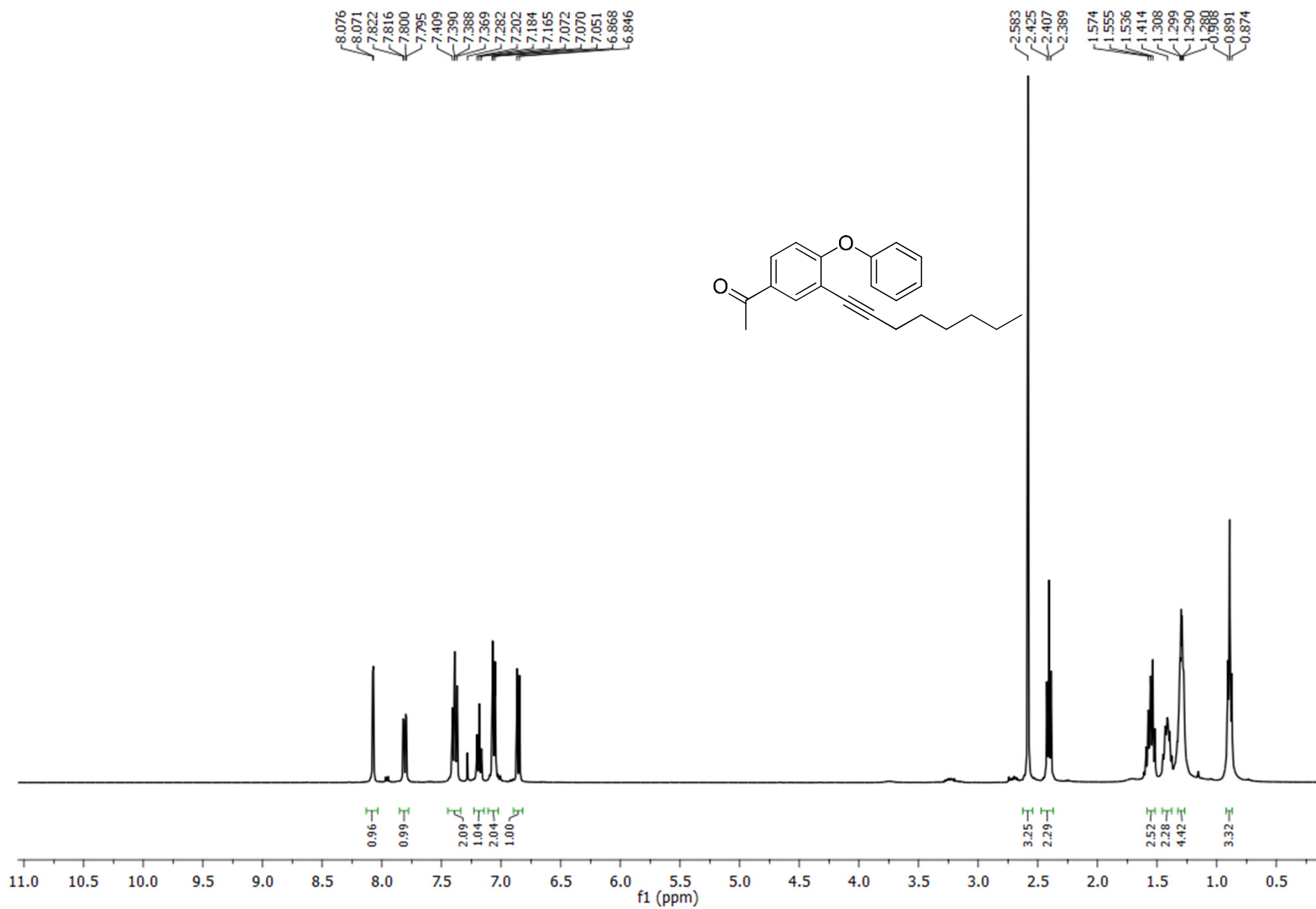
¹H NMR of 4-nitro-1-(4-nitrophenoxy)-2-(phenylethynyl)benzene (2l)



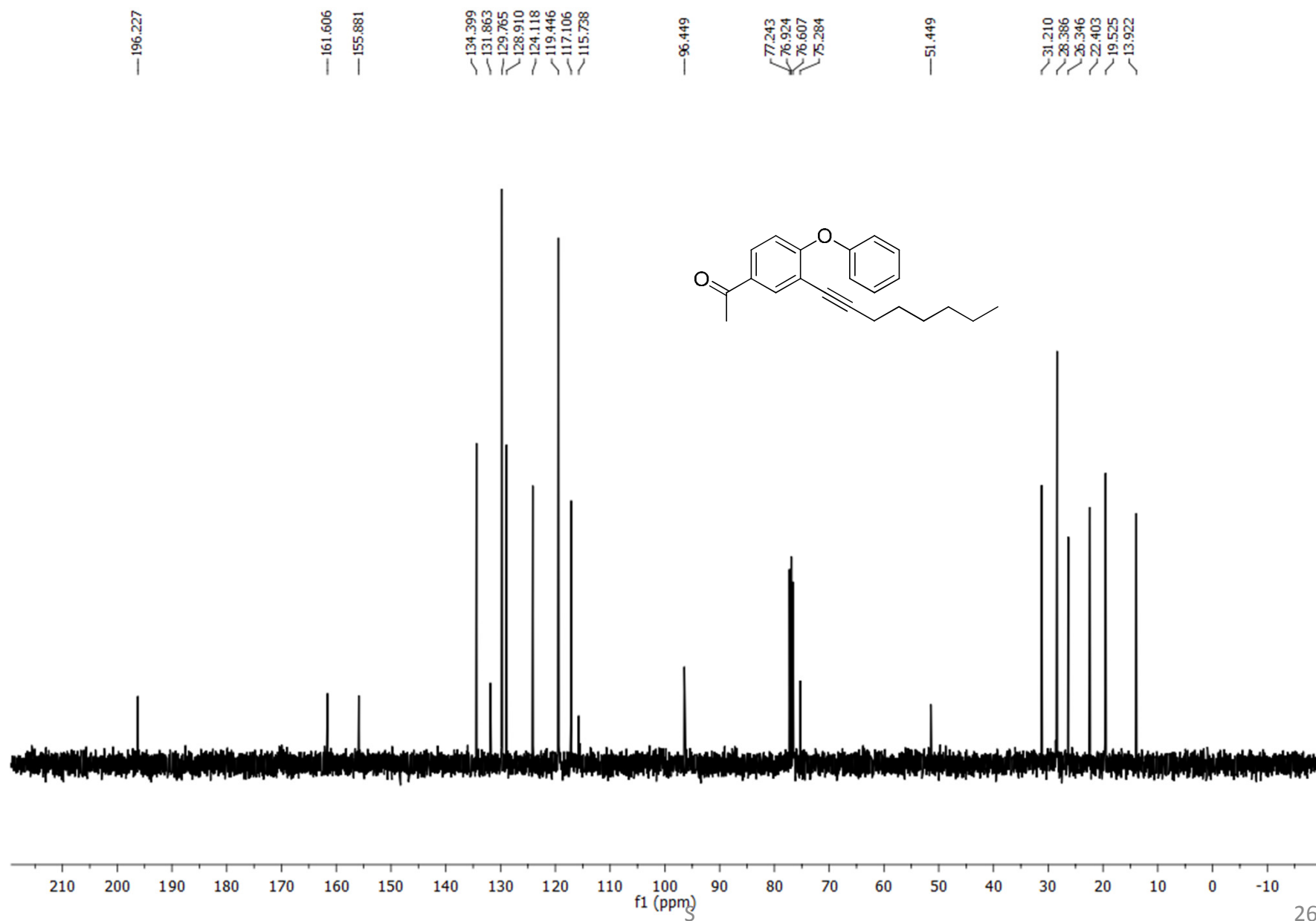
^{13}C NMR of 4-nitro-1-(4-nitrophenoxy)-2-(phenylethynyl)benzene (2I)



¹H NMR of 1-(3-(oct-1-yn-1-yl)-4-phenoxyphenyl)ethanone (2m)



¹³C NMR of 1-(3-(oct-1-yn-1-yl)-4-phenoxyphenyl)ethanone (2m)

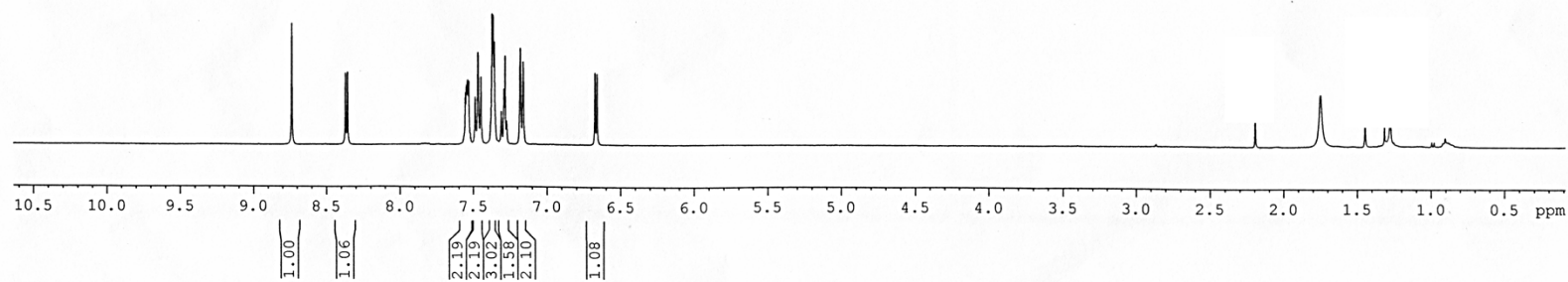
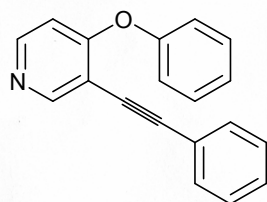


¹H NMR of 4-phenoxy-3-(2-phenylethynyl)pyridine (2n)

¹H of NP-SO-819 25.8.2018

8.737
8.371
8.357
7.556
7.549
7.545
7.541
7.540
7.532
7.489
7.470
7.449
7.374
7.366
7.358
7.310
7.292
7.284
7.273
7.183
7.181
7.162
6.676
6.661

— 1.749

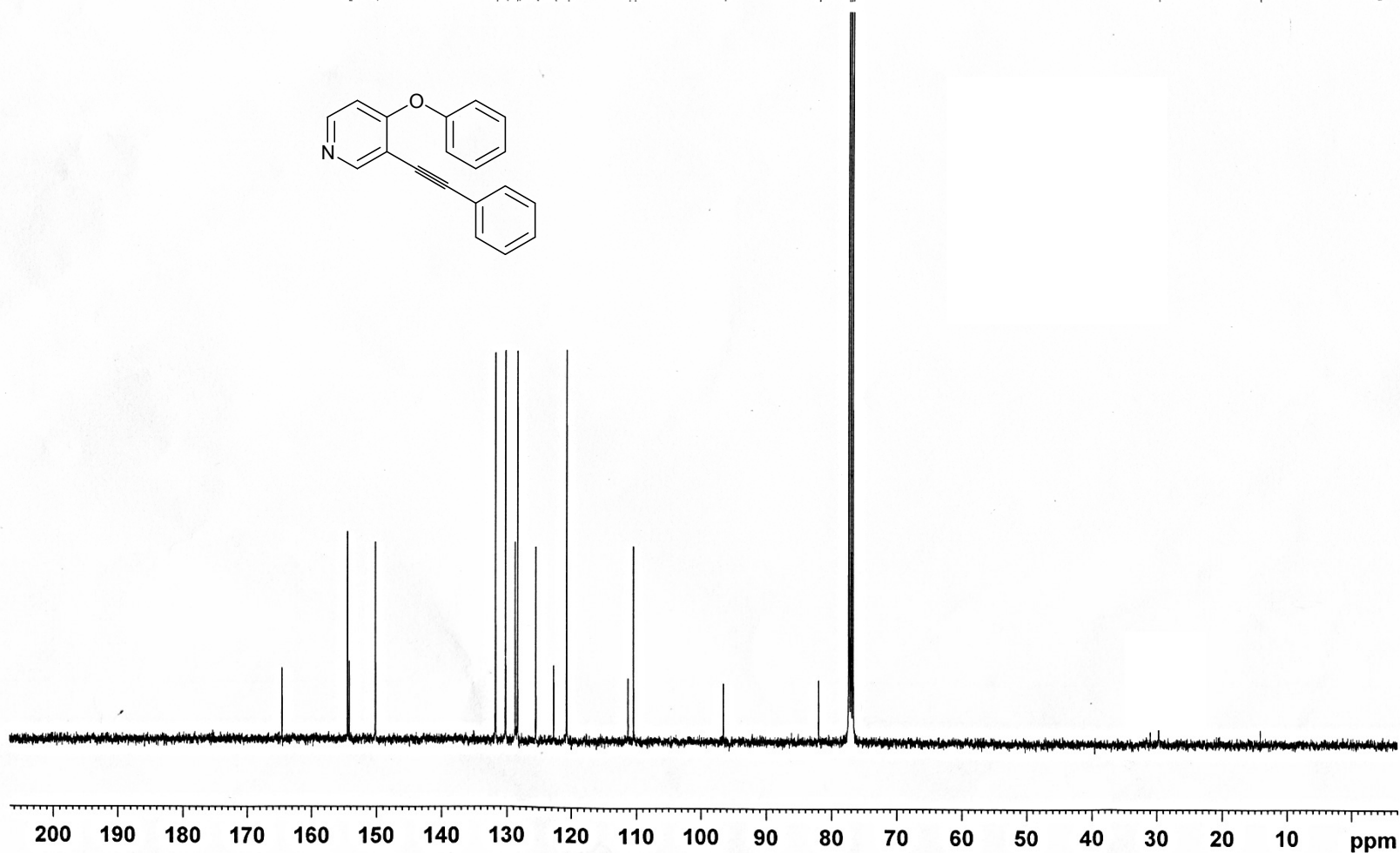
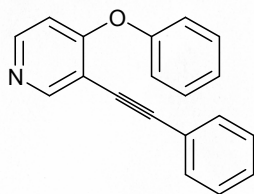


¹³C NMR of 4-phenoxy-3-(2-phenylethynyl)pyridine (2n)

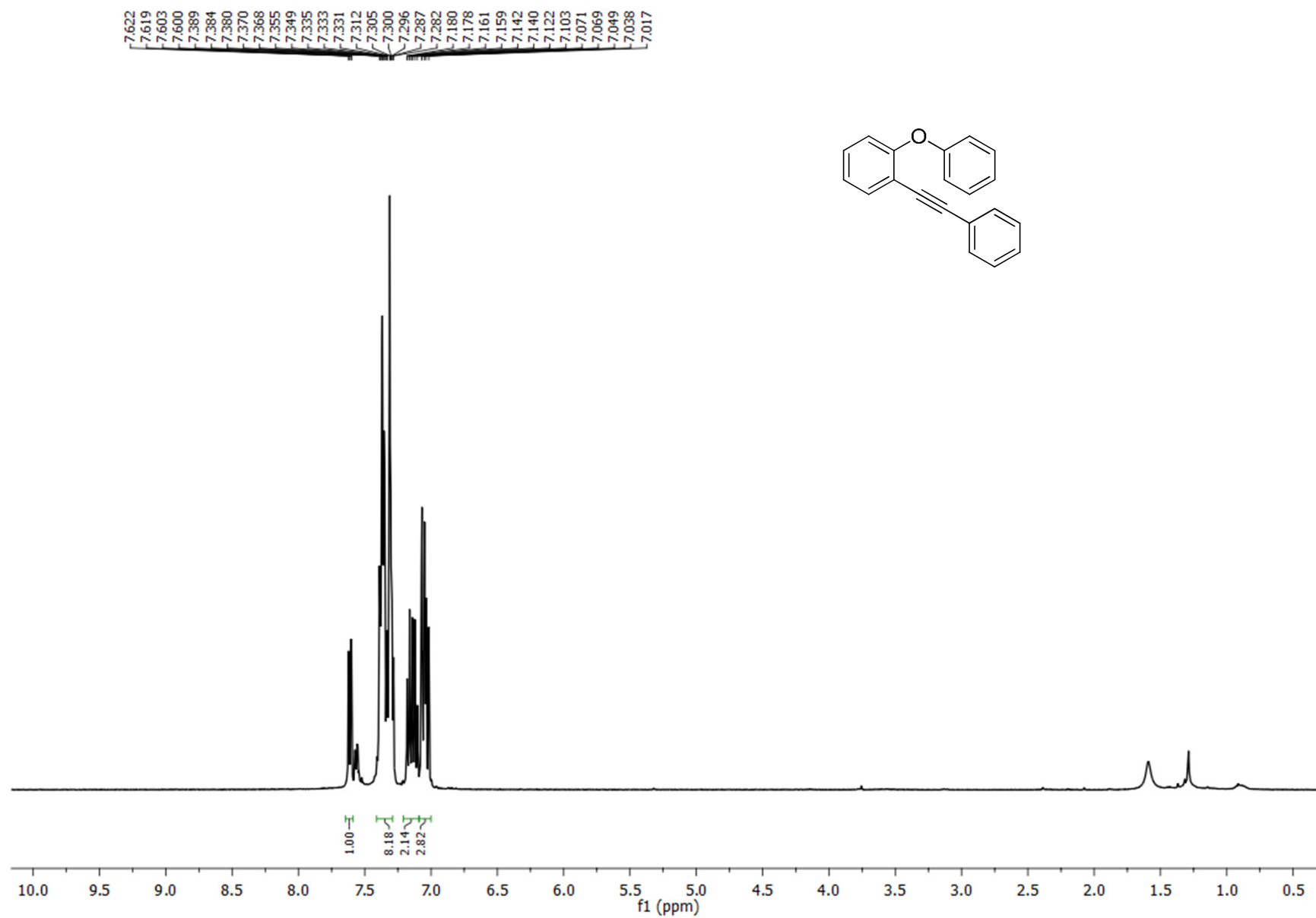
¹³C of NP-so-819

25.8.2018

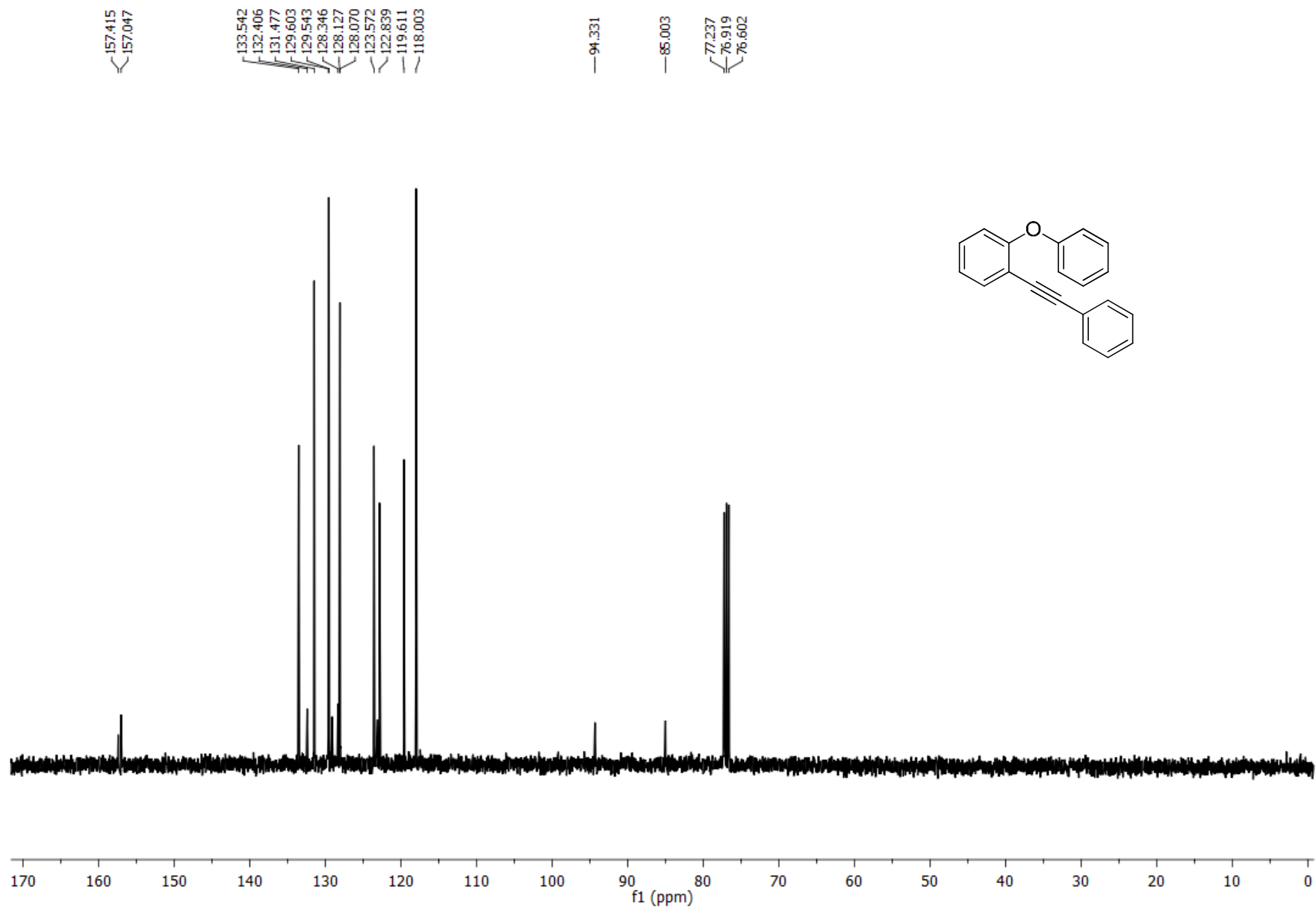
164.61
154.47
154.20
150.17
131.77
130.22
128.72
128.36
125.52
122.74
120.73
111.32
110.49
96.58
82.02
77.36
77.04
76.73
29.72
14.16



¹H NMR of 1-phenoxy-2-(phenylethynyl)benzene (2o)

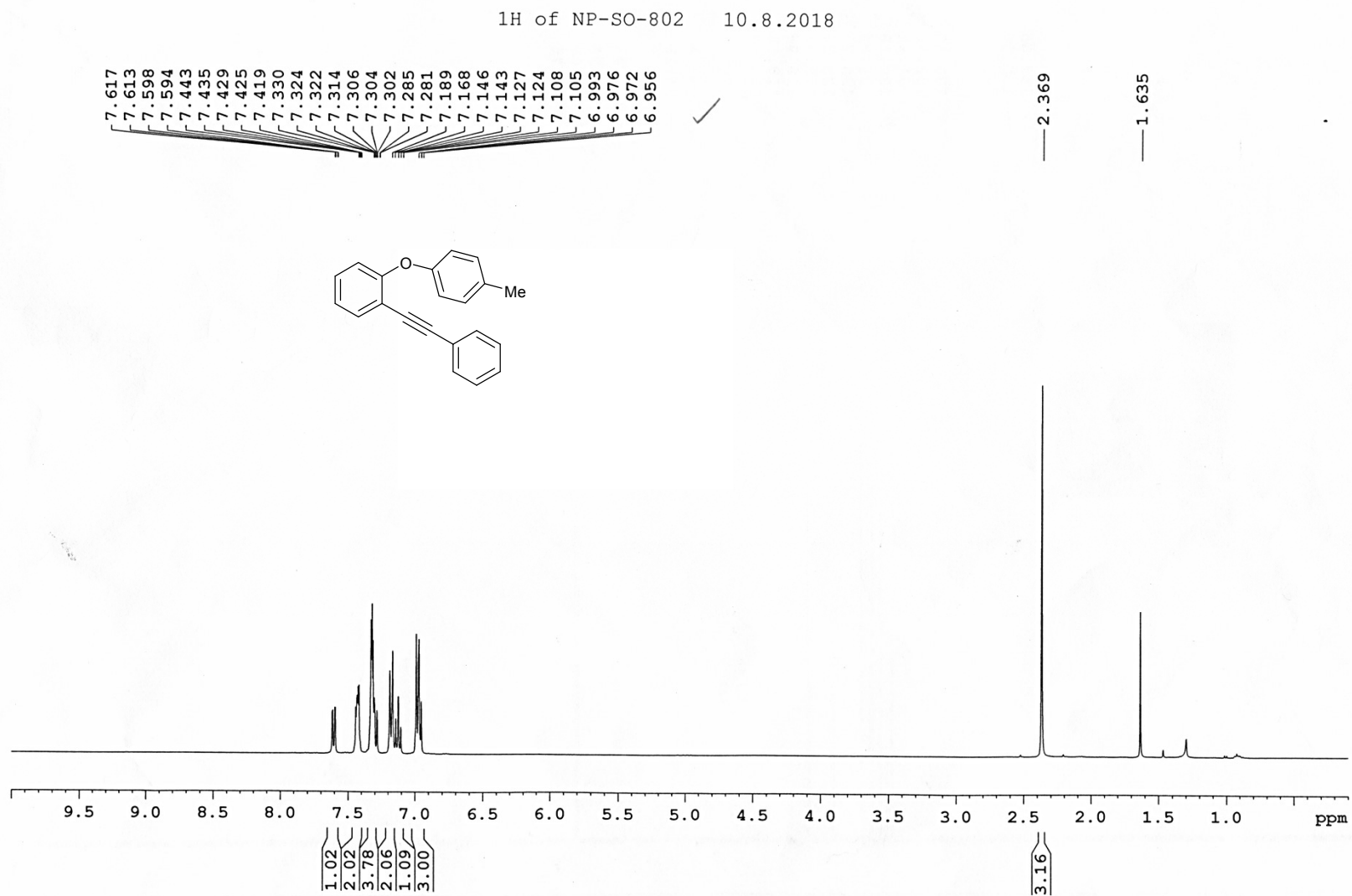


^{13}C NMR of 1-phenoxy-2-(phenylethynyl)benzene (2o)

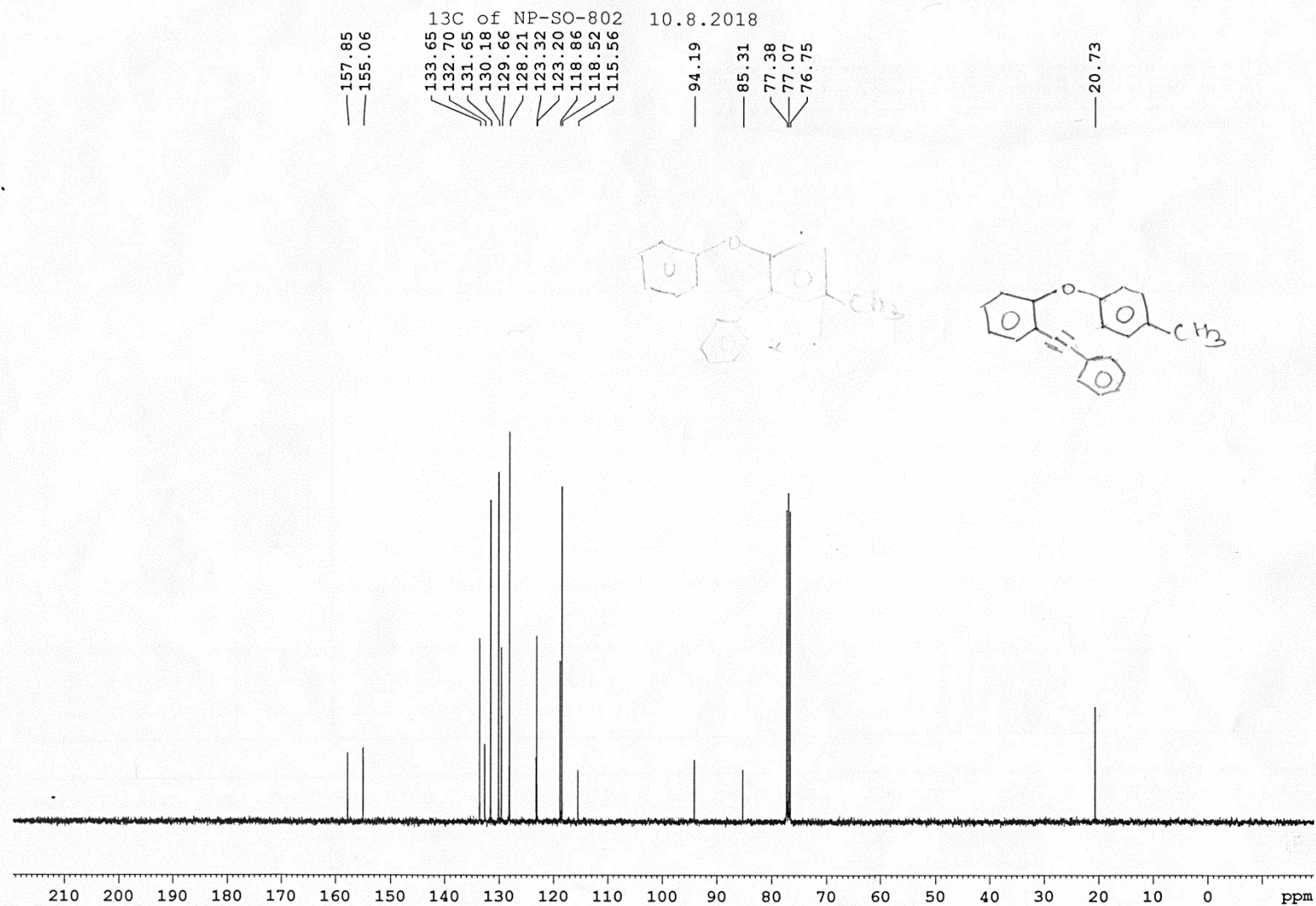


S

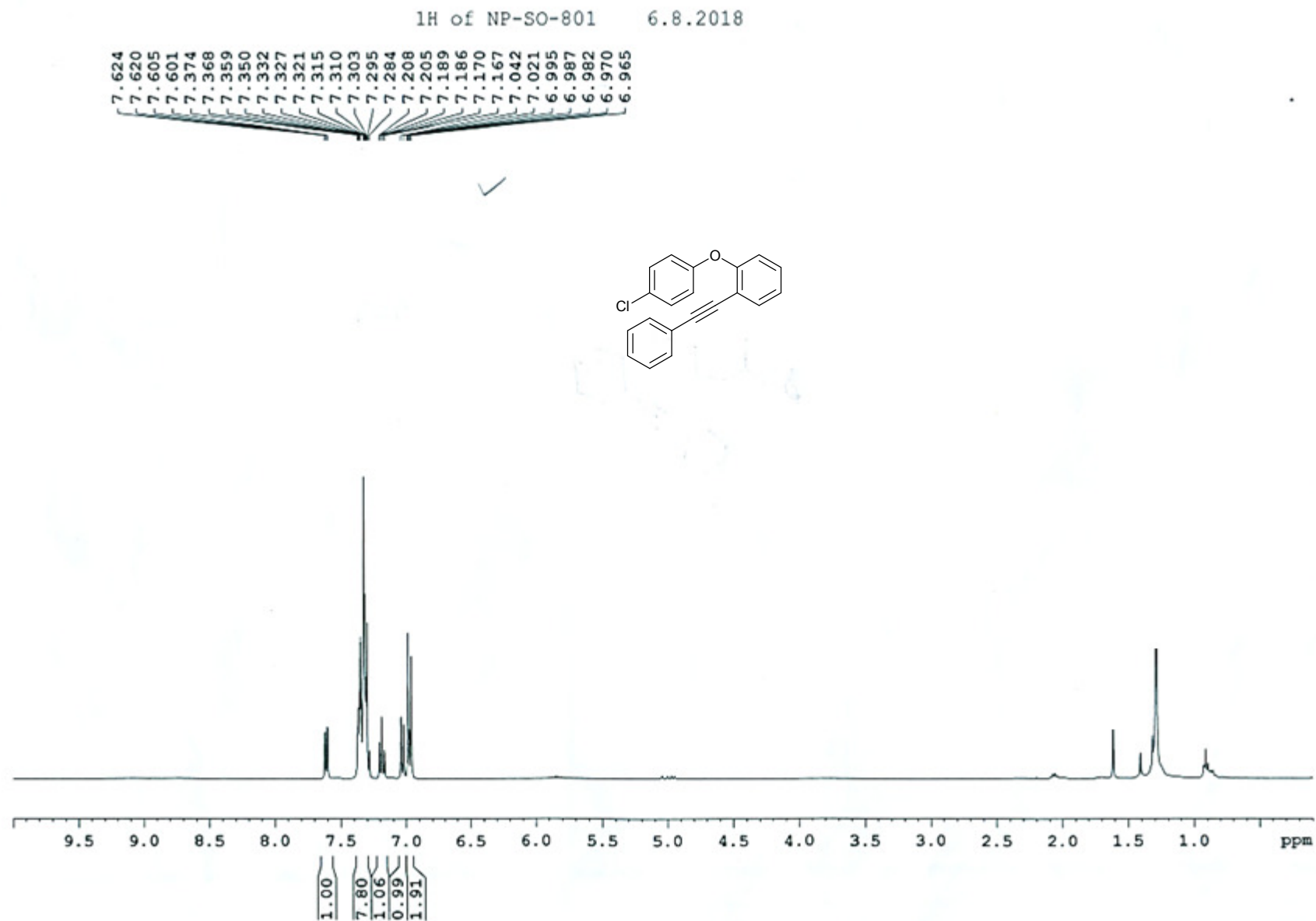
¹H NMR of 1-(*p*-toloxy)-2-(2-phenylethynyl)benzene (2p)



¹³C NMR of 1-(*p*-toloxy)-2-(2-phenylethynyl)benzene (2p)



¹H NMR of 1-(4-Chlorophenoxy)-2-(2-phenylethynyl)benzene (2q)



¹³C NMR of 1-(4-Chlorophenoxy)-2-(2-phenylethynyl)benzene (2q)

¹³C of NP-SO-801

6.8.2018

156.62
156.28

133.79
131.55
129.85
129.61
128.41
128.28
127.85
124.20
123.00
119.97
119.16
116.27

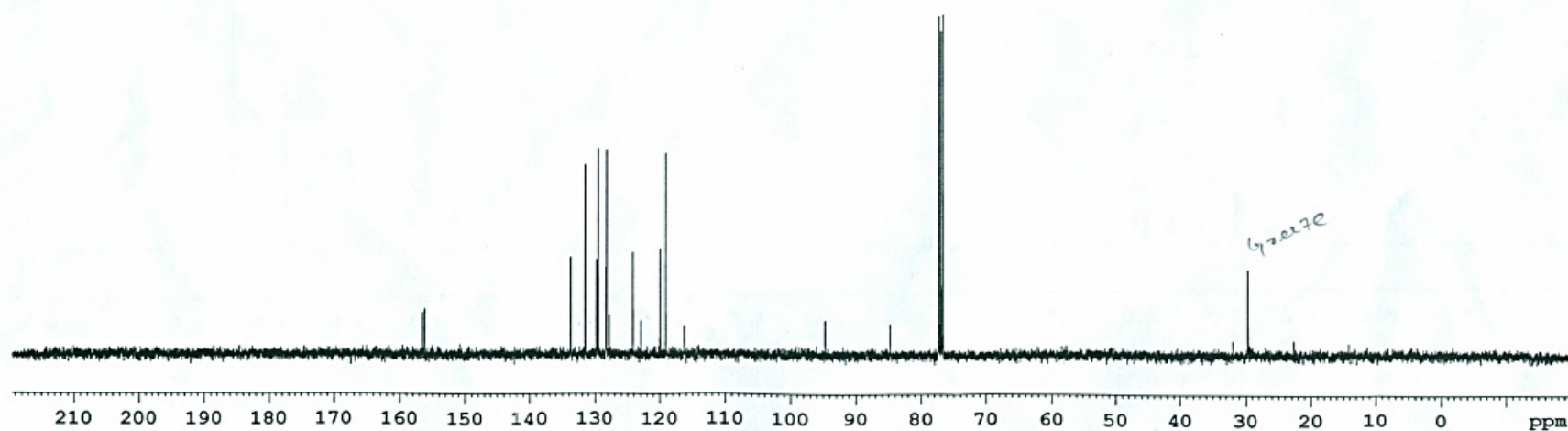
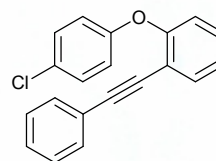
94.73

84.81

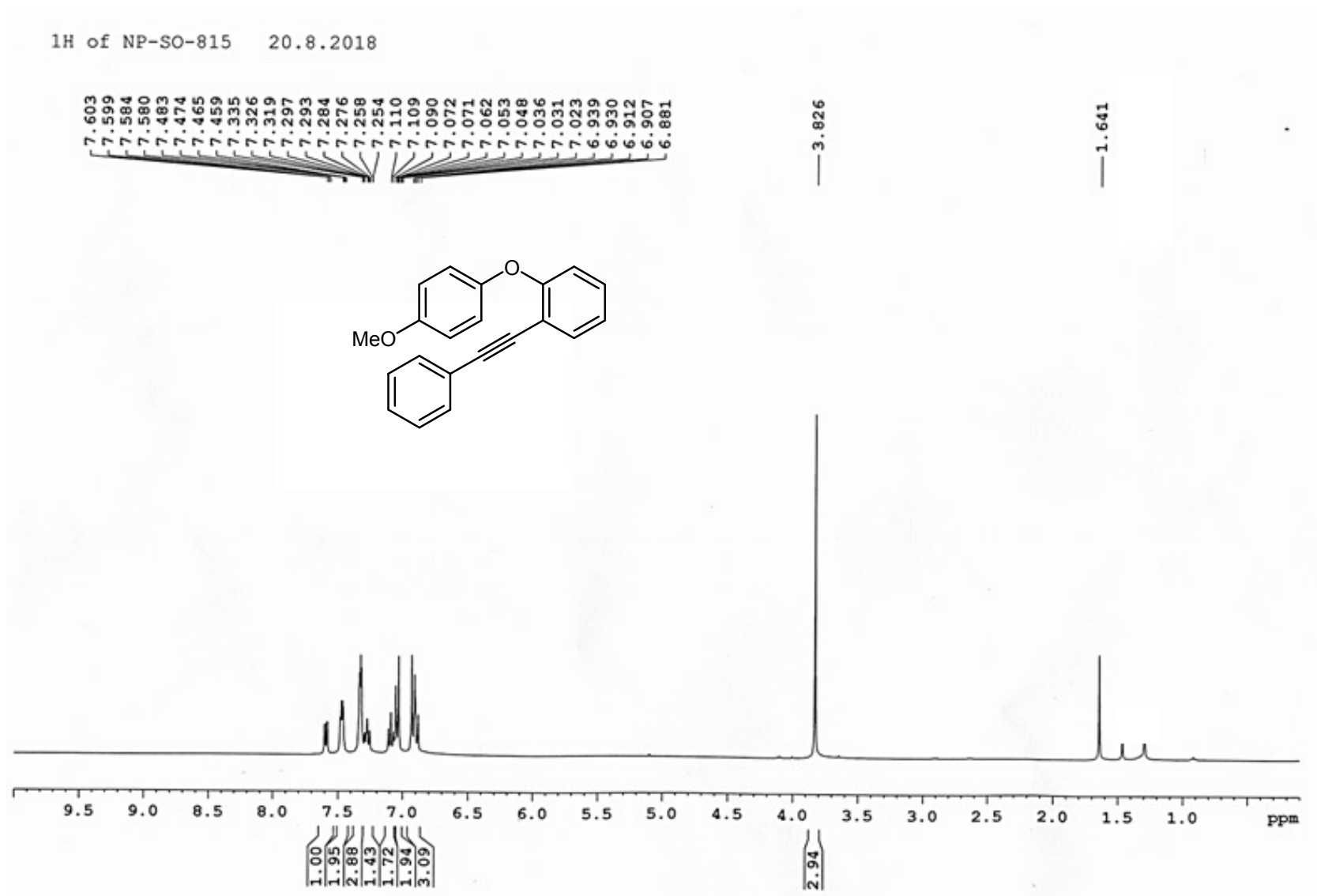
77.37

77.06

76.74

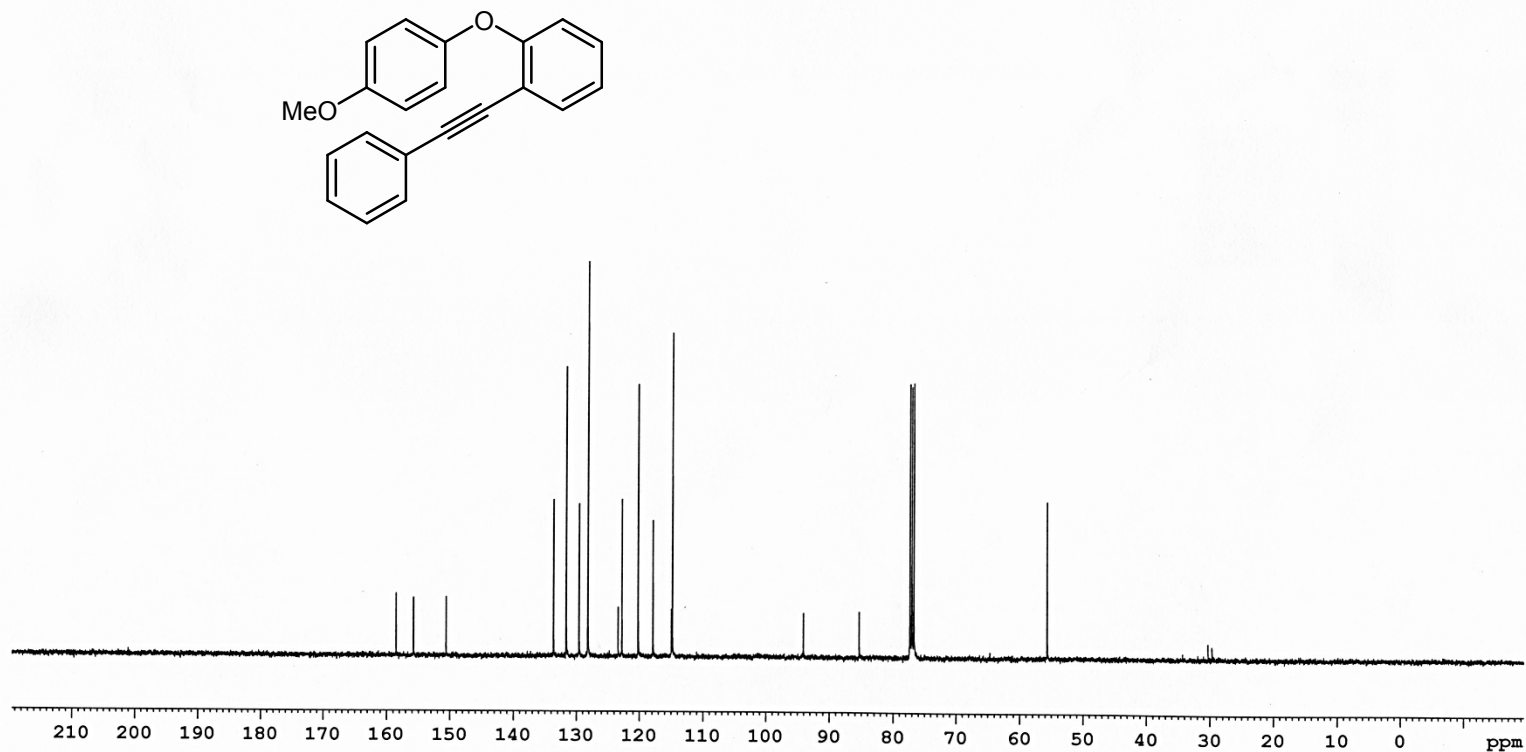


¹H NMR of 1-(4-Methoxyphenoxy)-2-(2-phenylethynyl)benzene (2r)

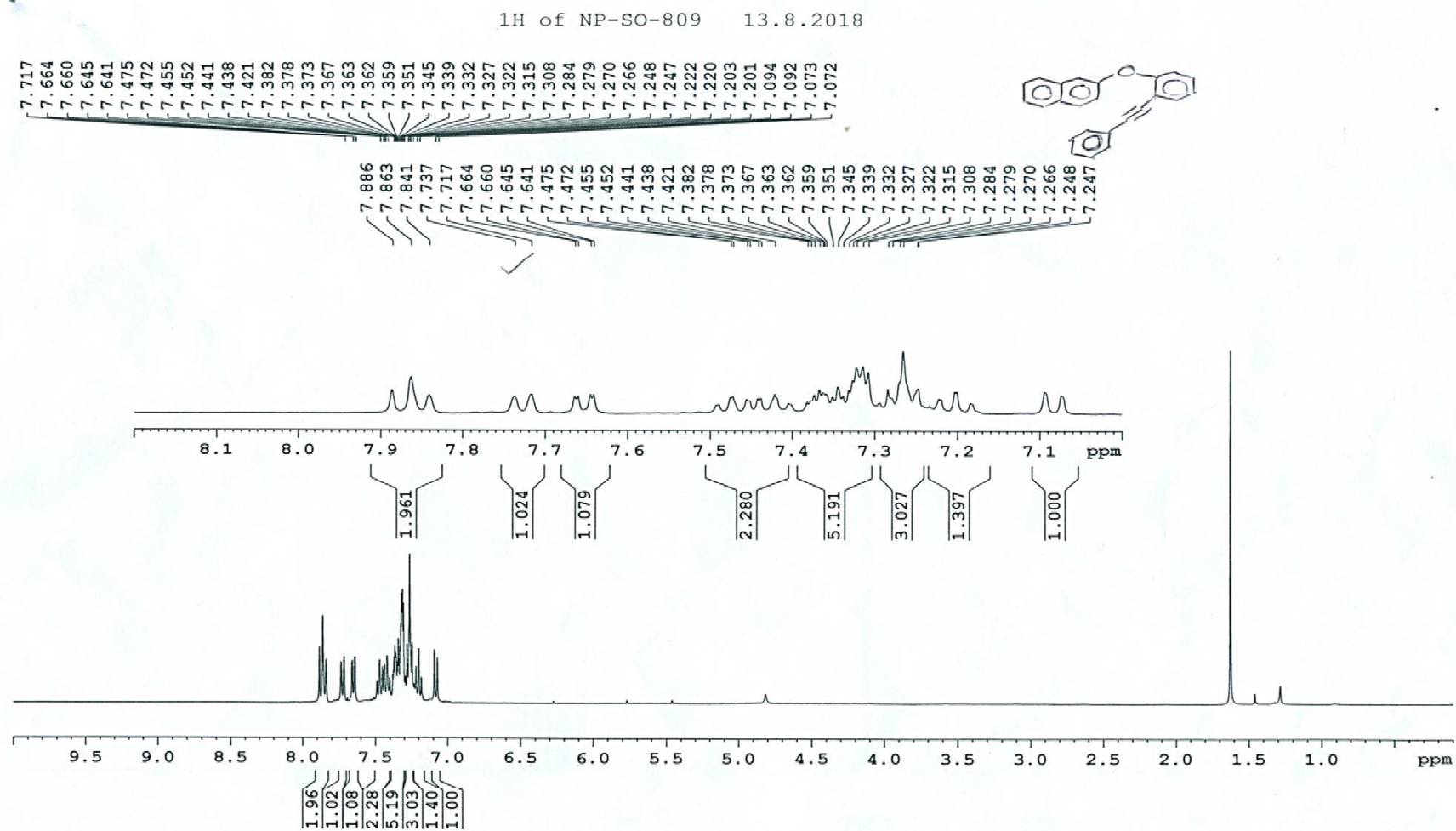


¹³C NMR of 1-(4-Methoxyphenoxy)-2-(2-phenylethynyl)benzene (2r)

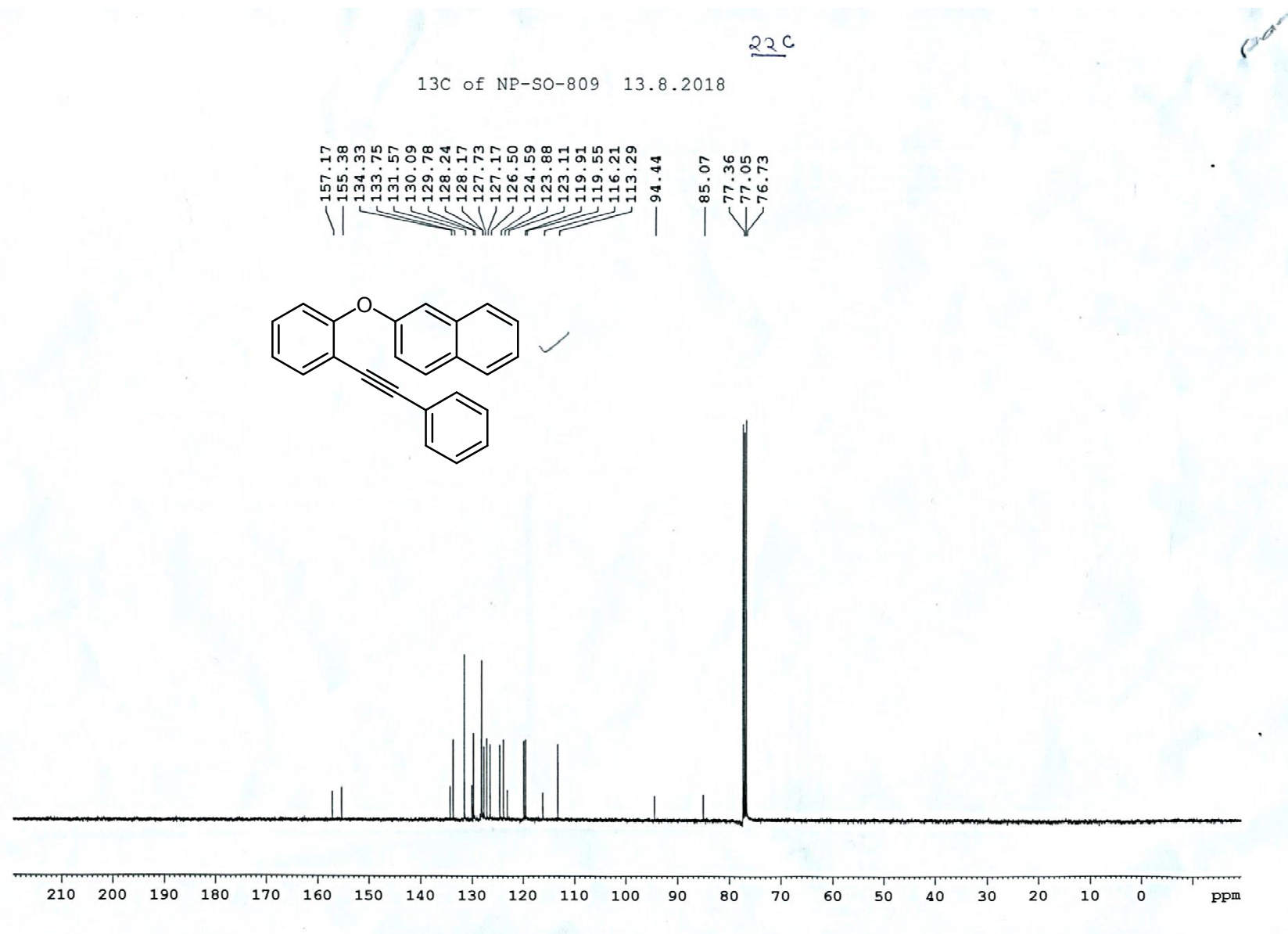
¹³C of NP-SO-815 20.8.2018



¹H NMR of 2-(2-(2-phenylethynyl)phenoxy)naphthalene (2s)

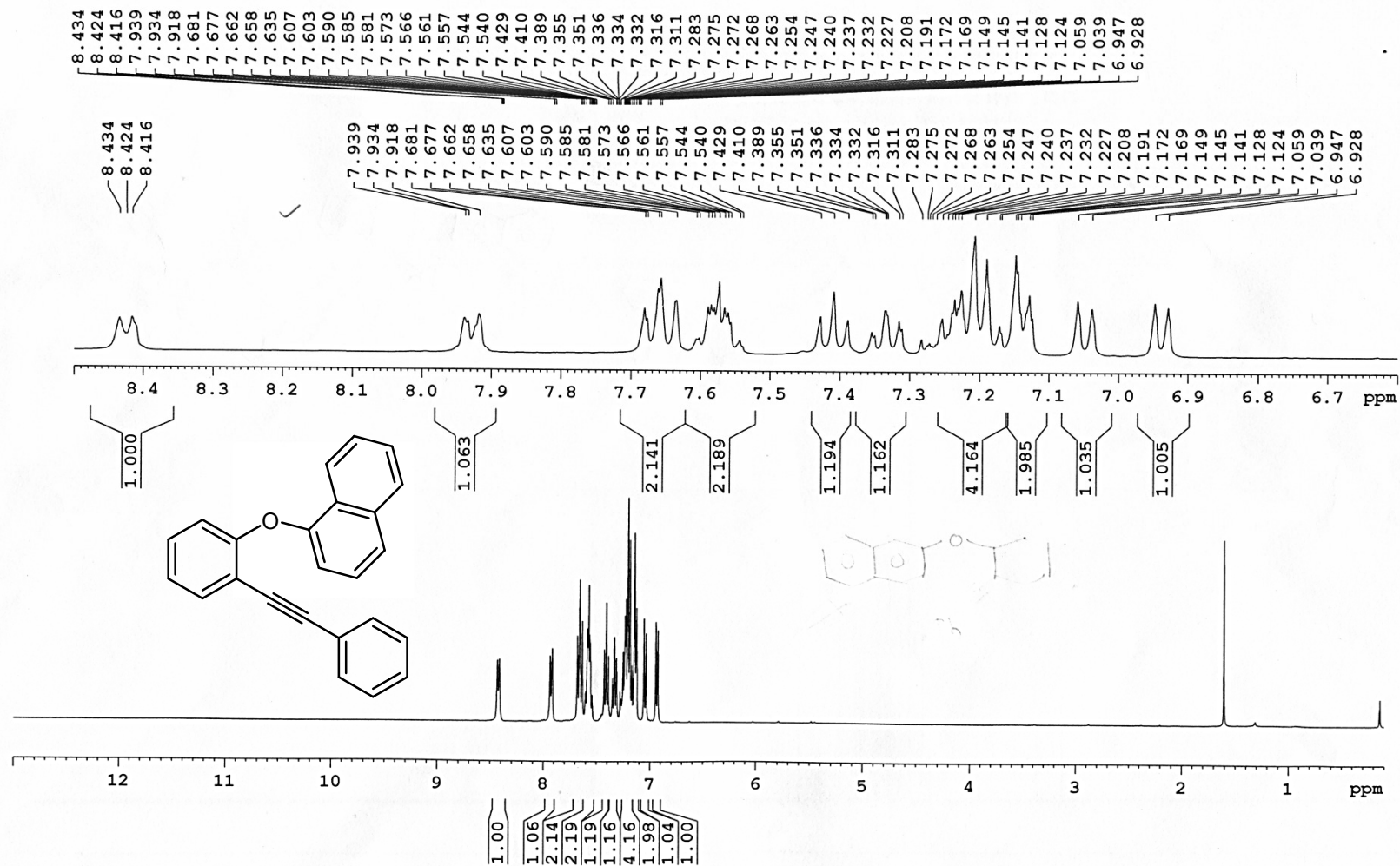


^{13}C NMR of 2-(2-(2-phenylethynyl)phenoxy)naphthalene (2s)



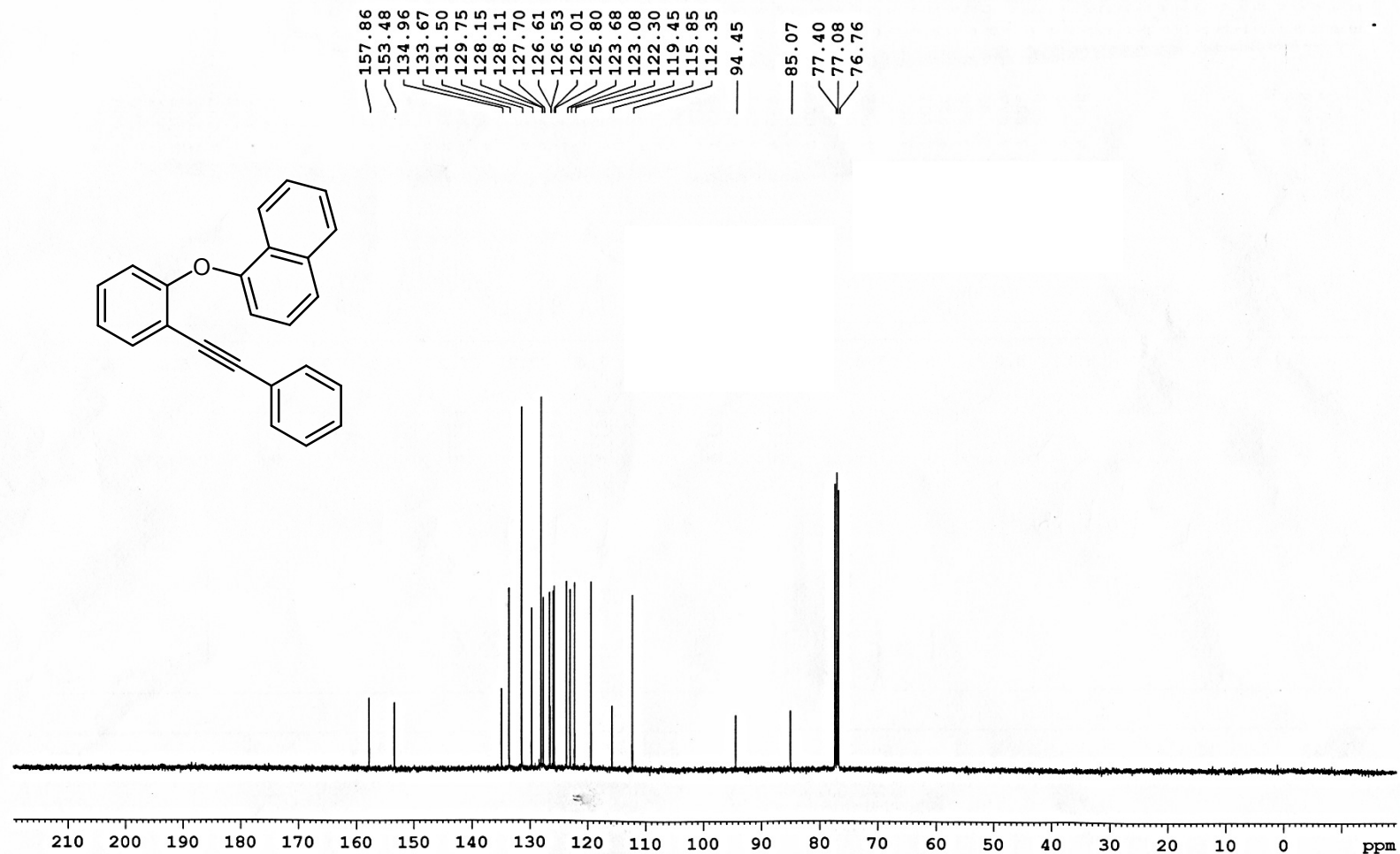
¹H NMR of 1-(2-(2-phenylethynyl)phenoxy)naphthalene (2t)

¹H of NP-SO-811 14.8.2018



¹³C NMR of 1-(2-(2-phenylethynyl)phenoxy)naphthalene (2t)

¹³C of NP-SO-811 14.8.2018

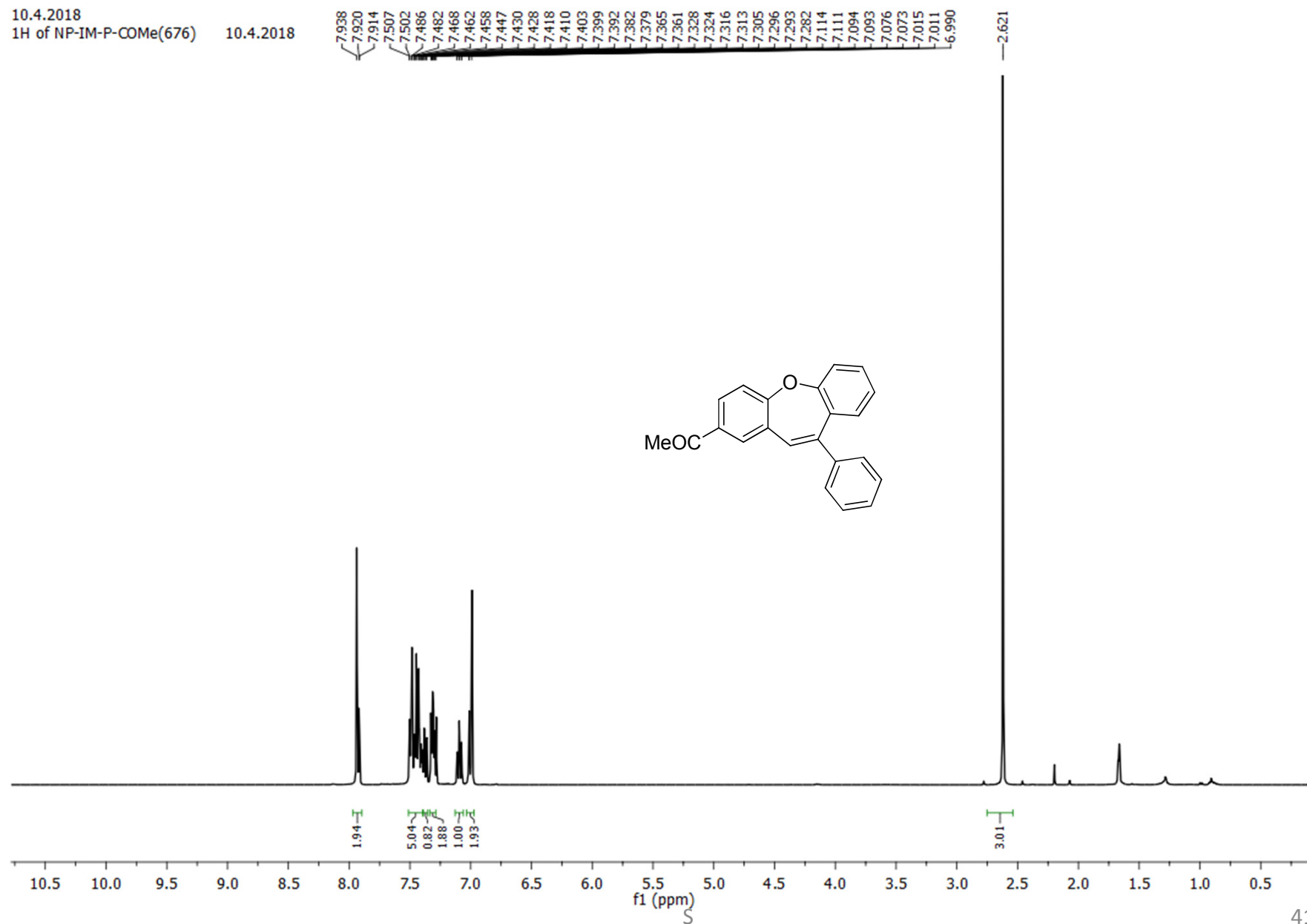


¹H NMR of 1-(10-phenyldibenzo[b,f]oxepin-2-yl)ethanone (3a)

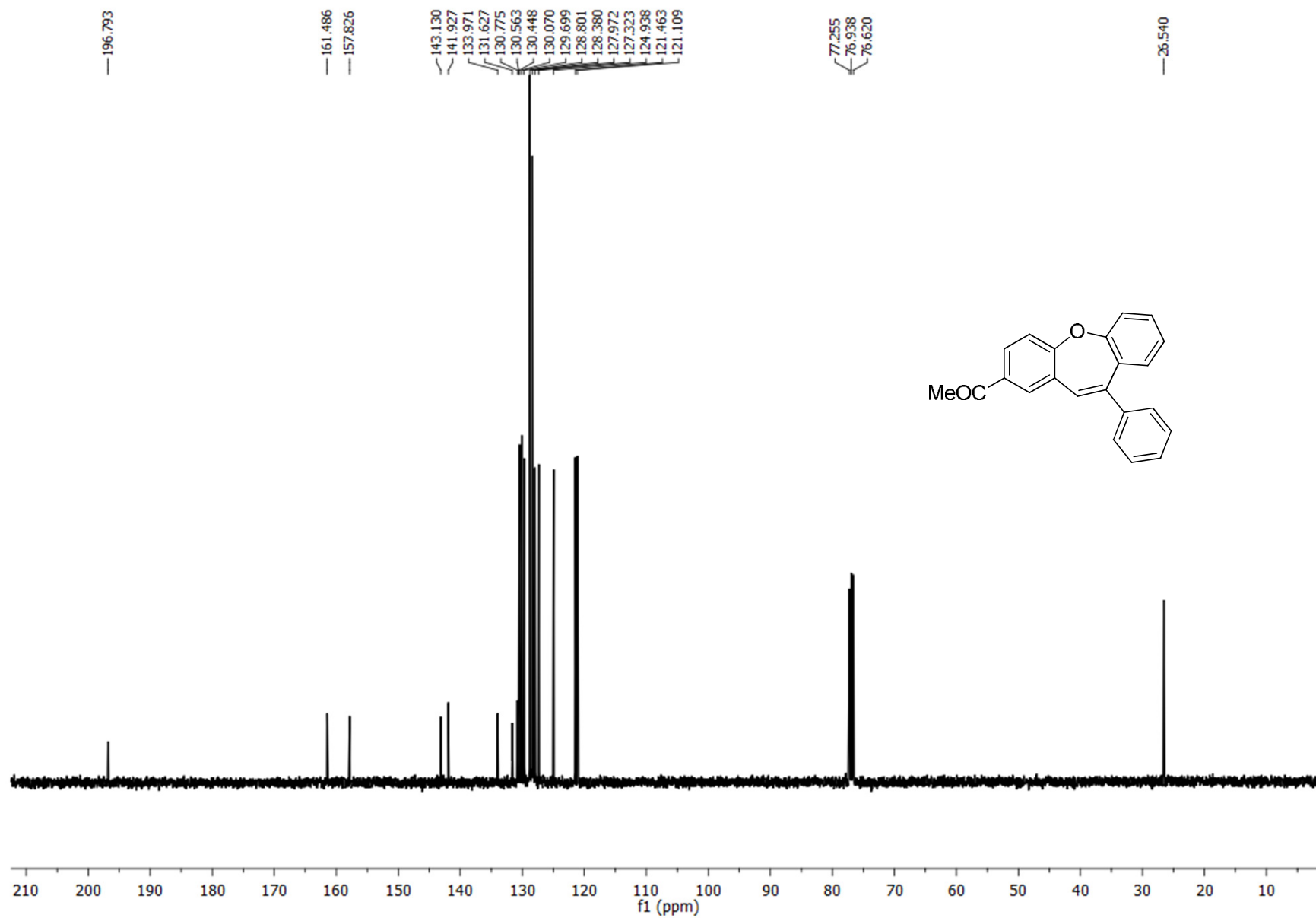
10.4.2018

1H of NP-IM-P-COMe(676)

10.4.2018



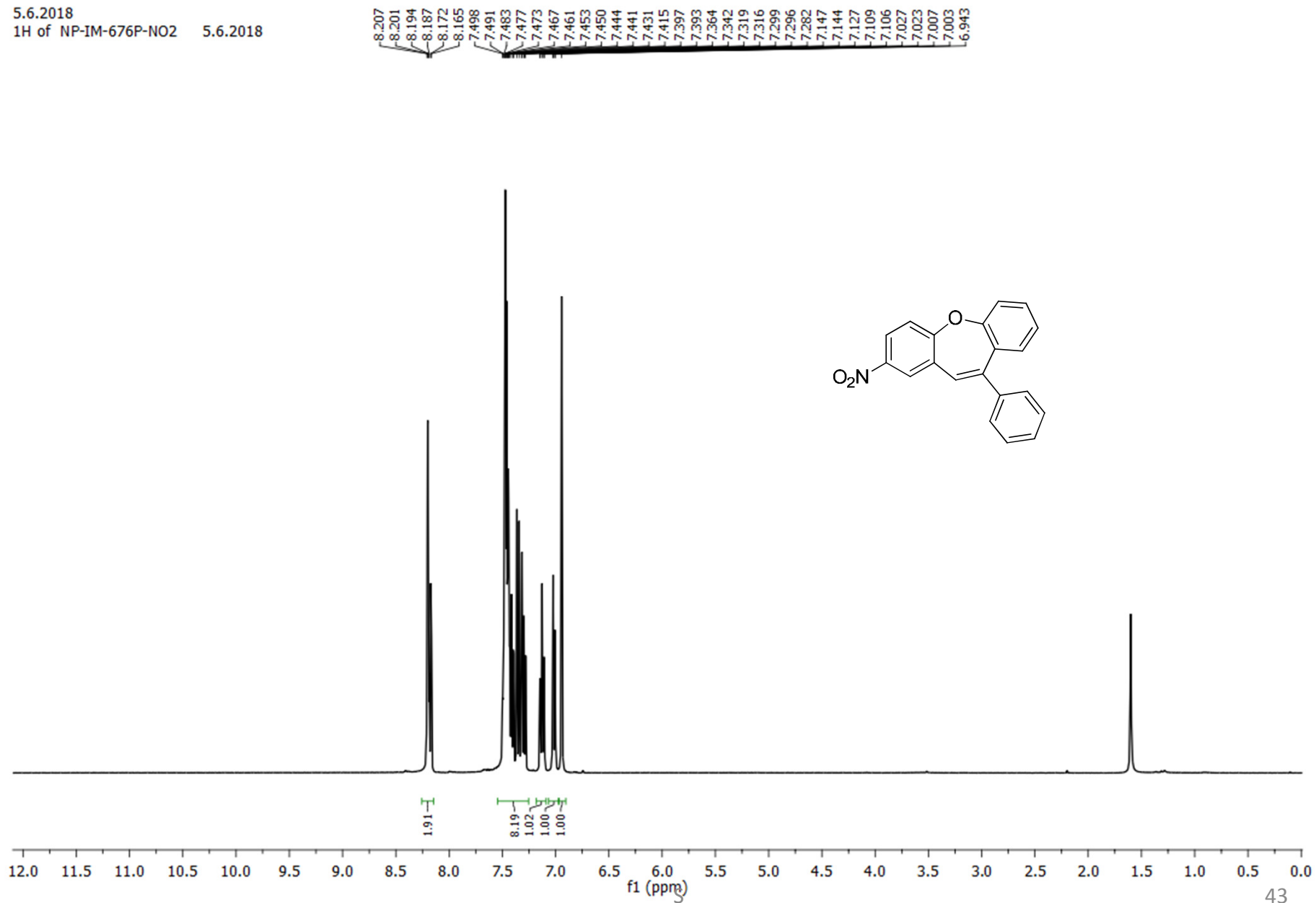
^{13}C NMR of 1-(10-phenyldibenzo[b,f]oxepin-2-yl)ethanone (3a)



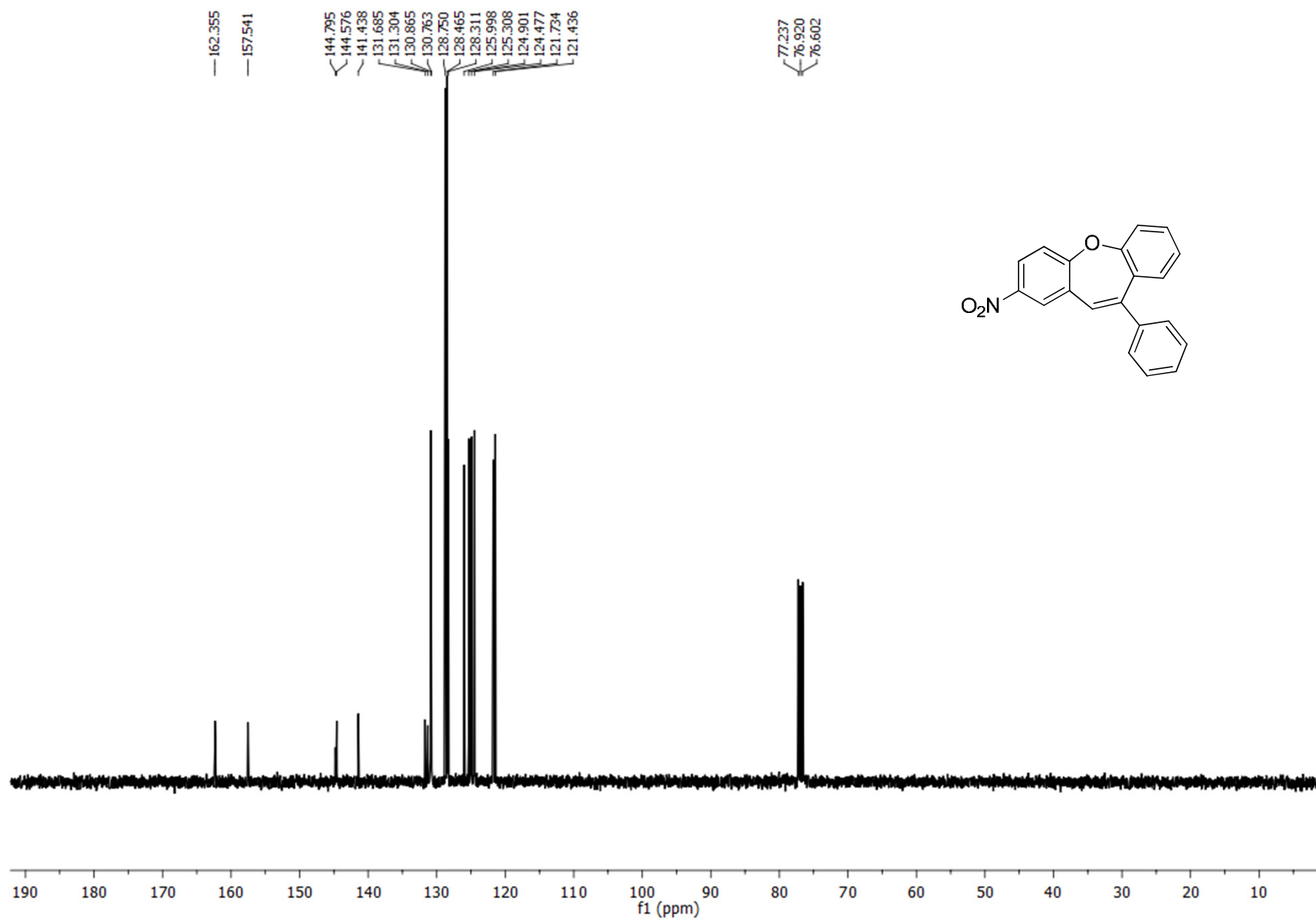
¹H NMR of 2-nitro-10-phenyldibenzo[b,f]oxepine (3b)

5.6.2018

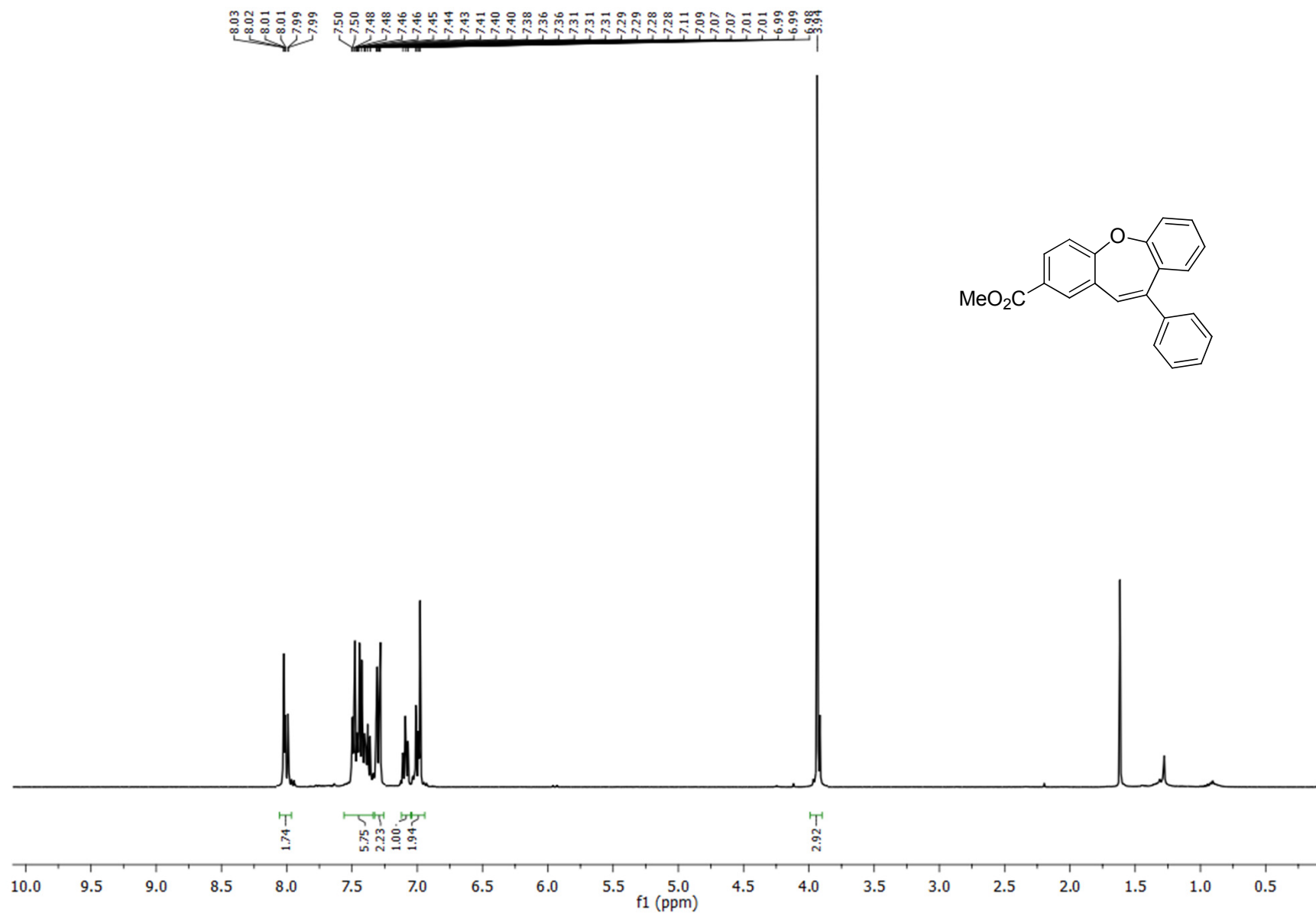
1H of NP-IM-676P-NO2 5.6.2018



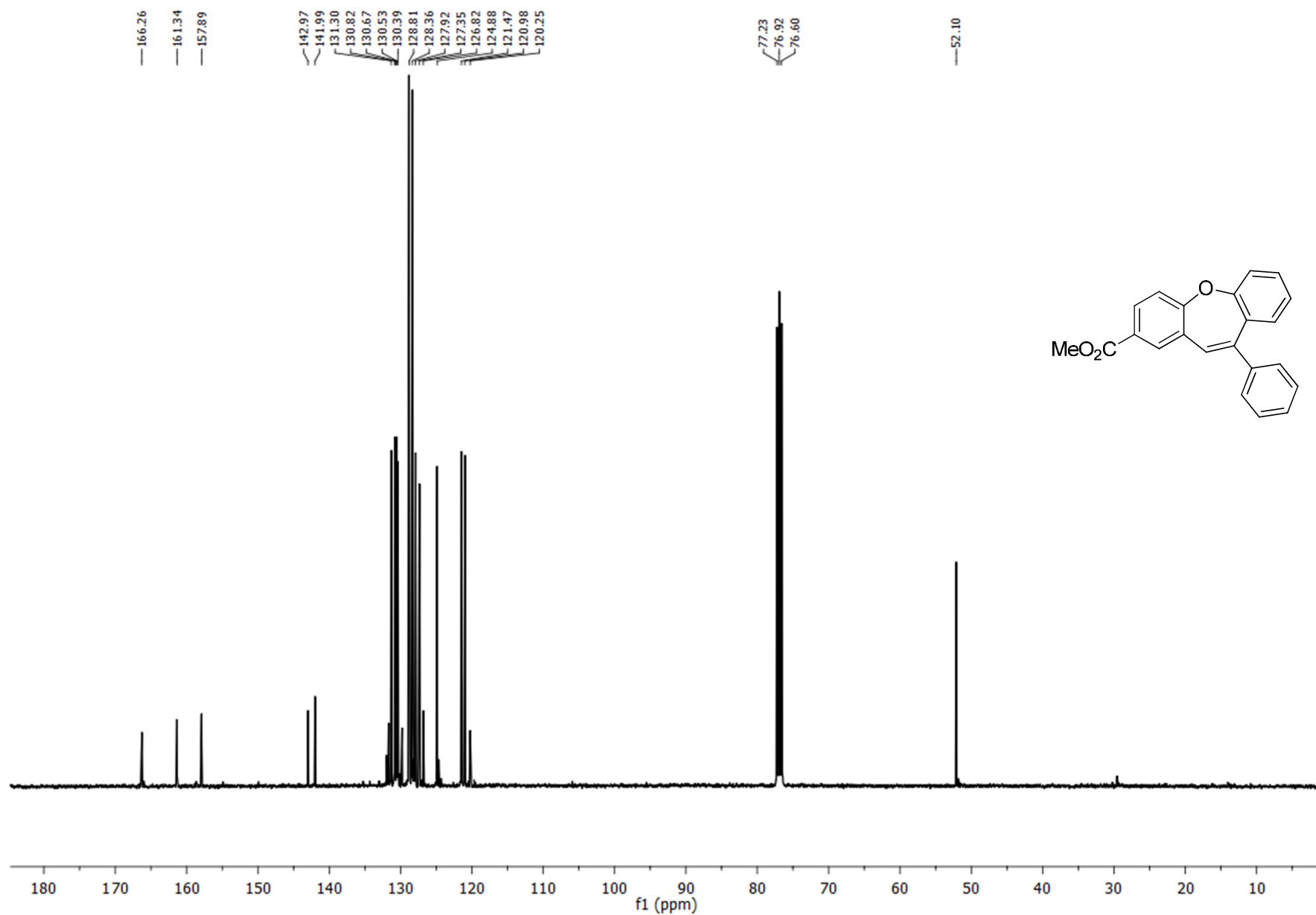
^{13}C NMR of 2-nitro-10-phenyldibenzo[b,f]oxepine (3b)



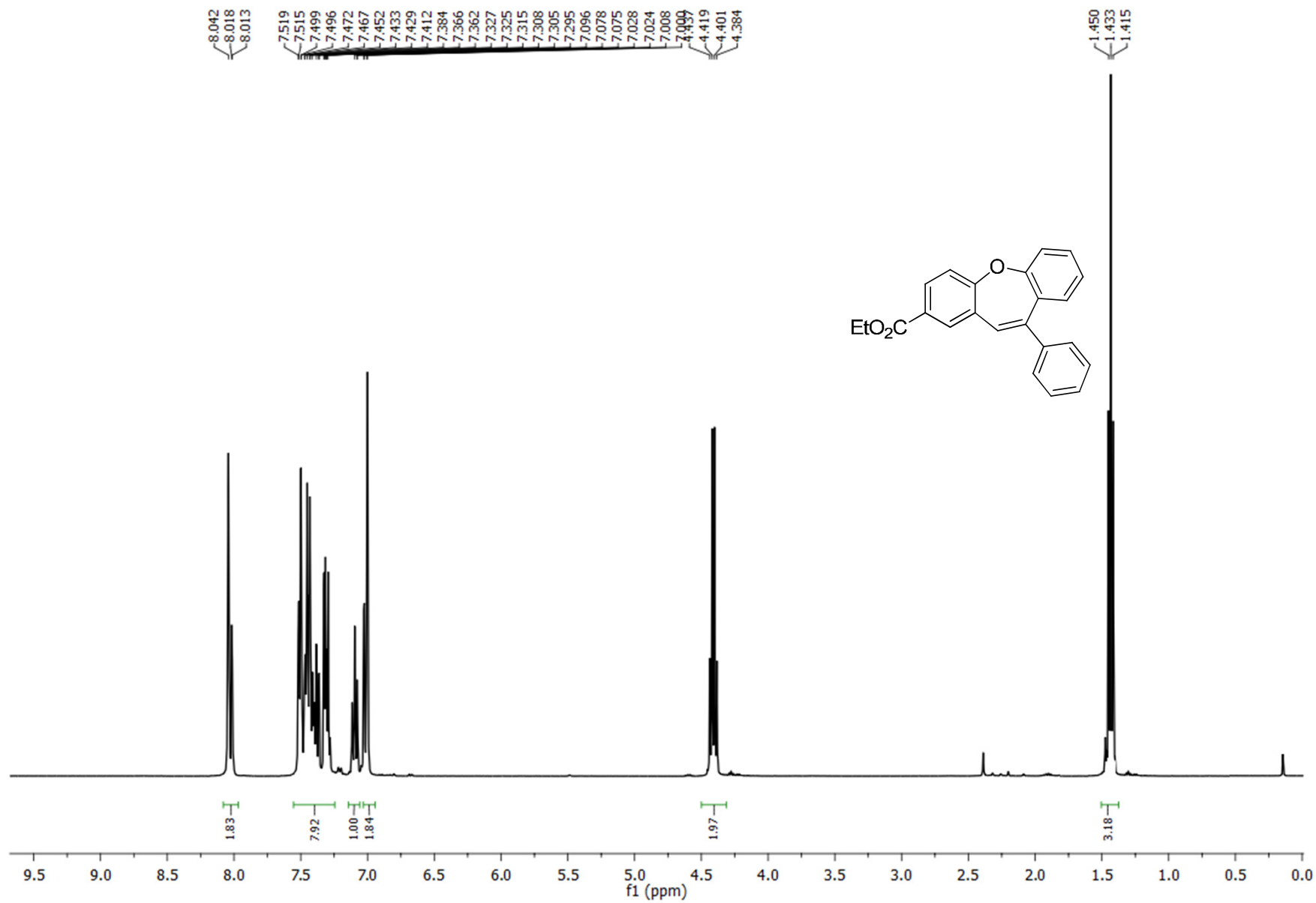
¹H NMR of methyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3c)



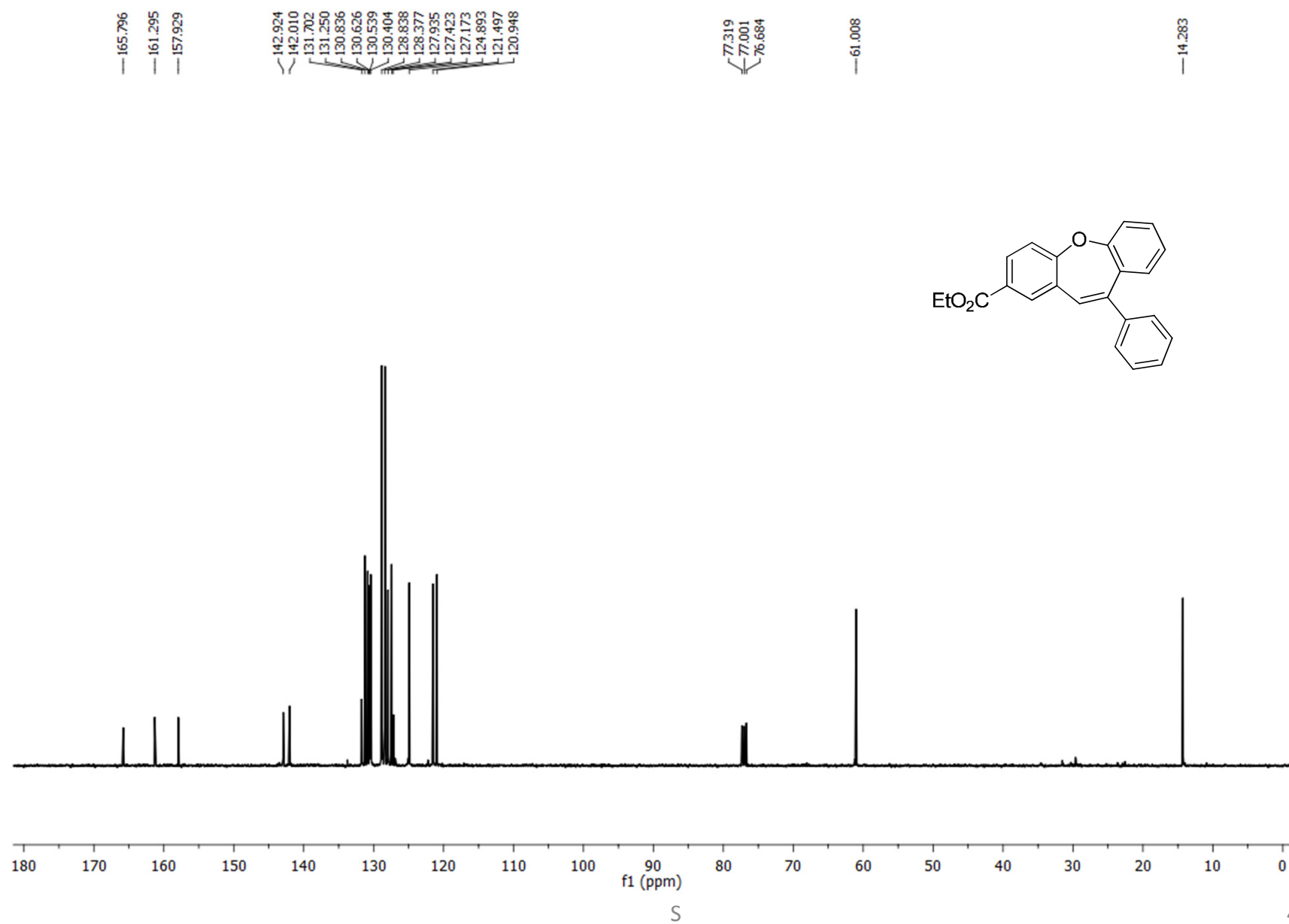
^{13}C NMR of methyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3c)



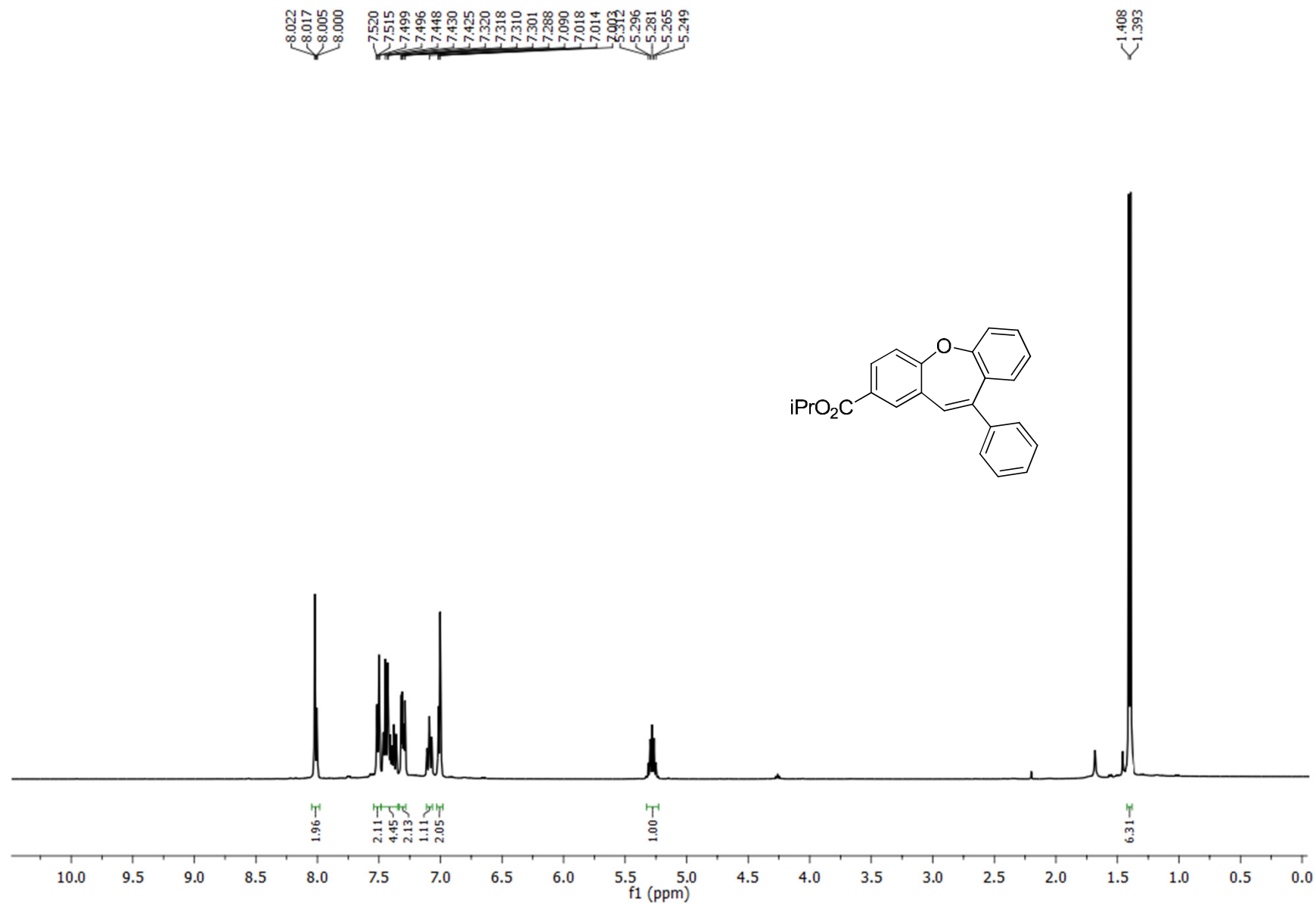
¹H NMR of ethyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3d)



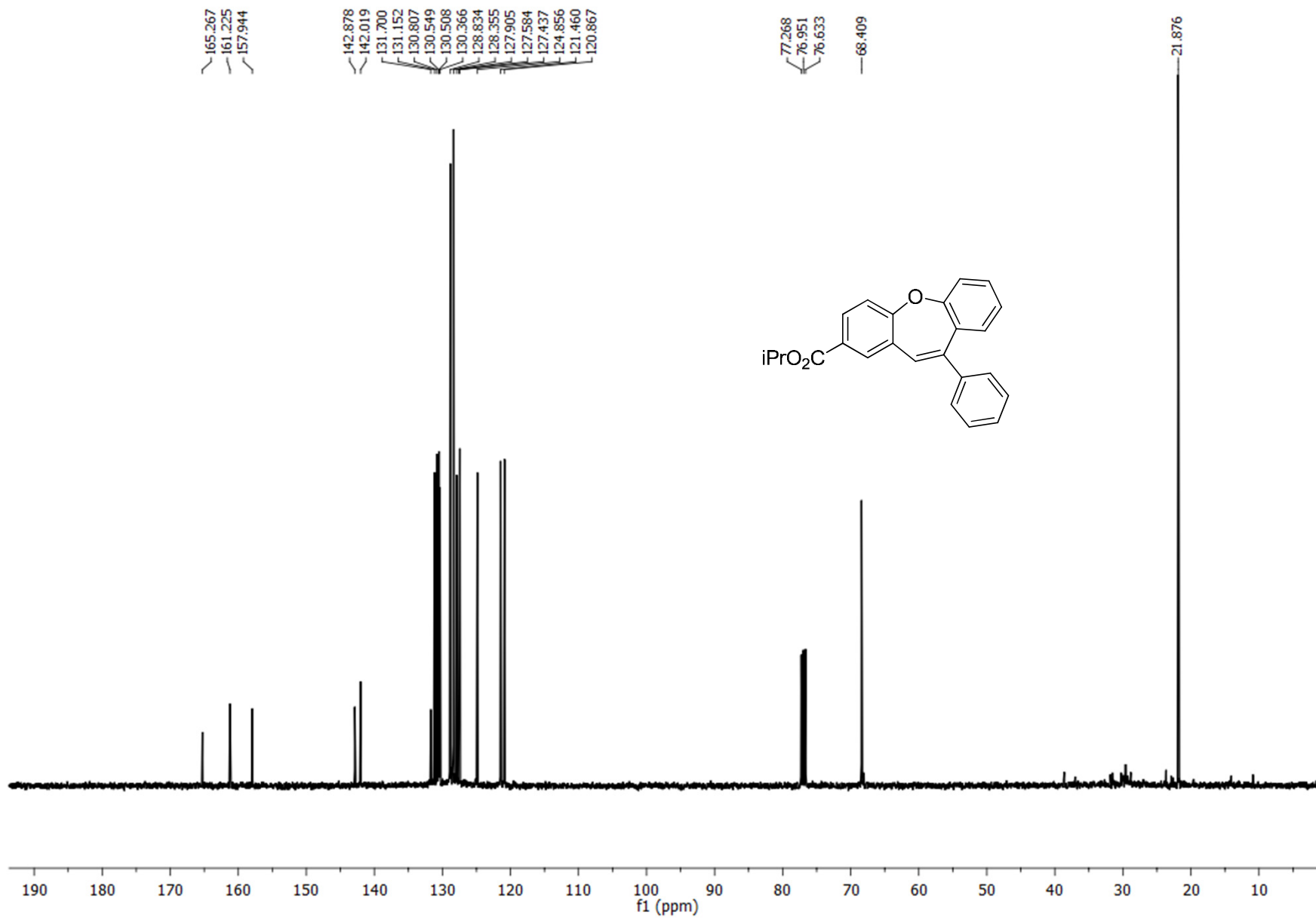
¹³C NMR of ethyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3d)



¹H NMR of isopropyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3e)



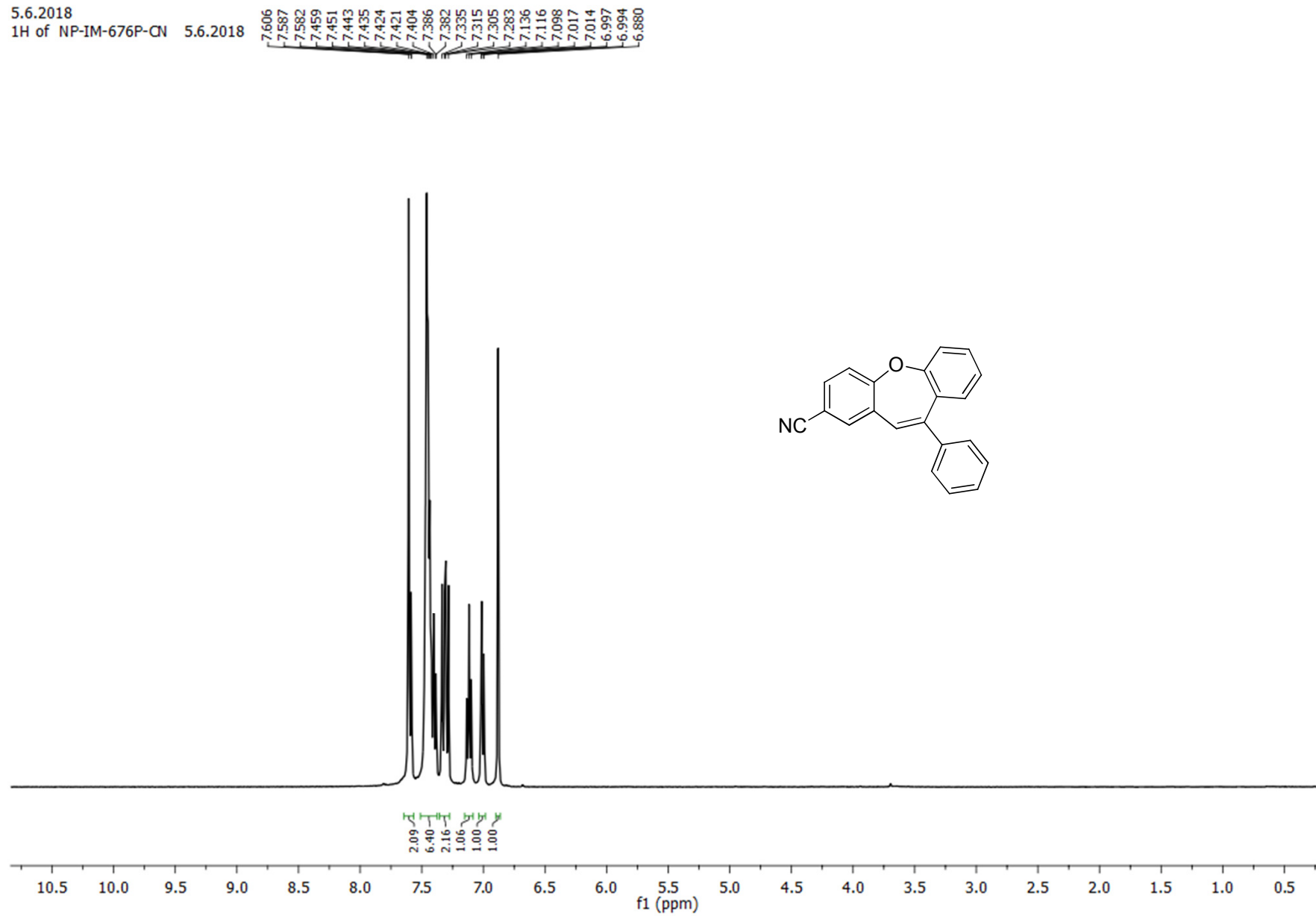
^{13}C NMR of isopropyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3e)



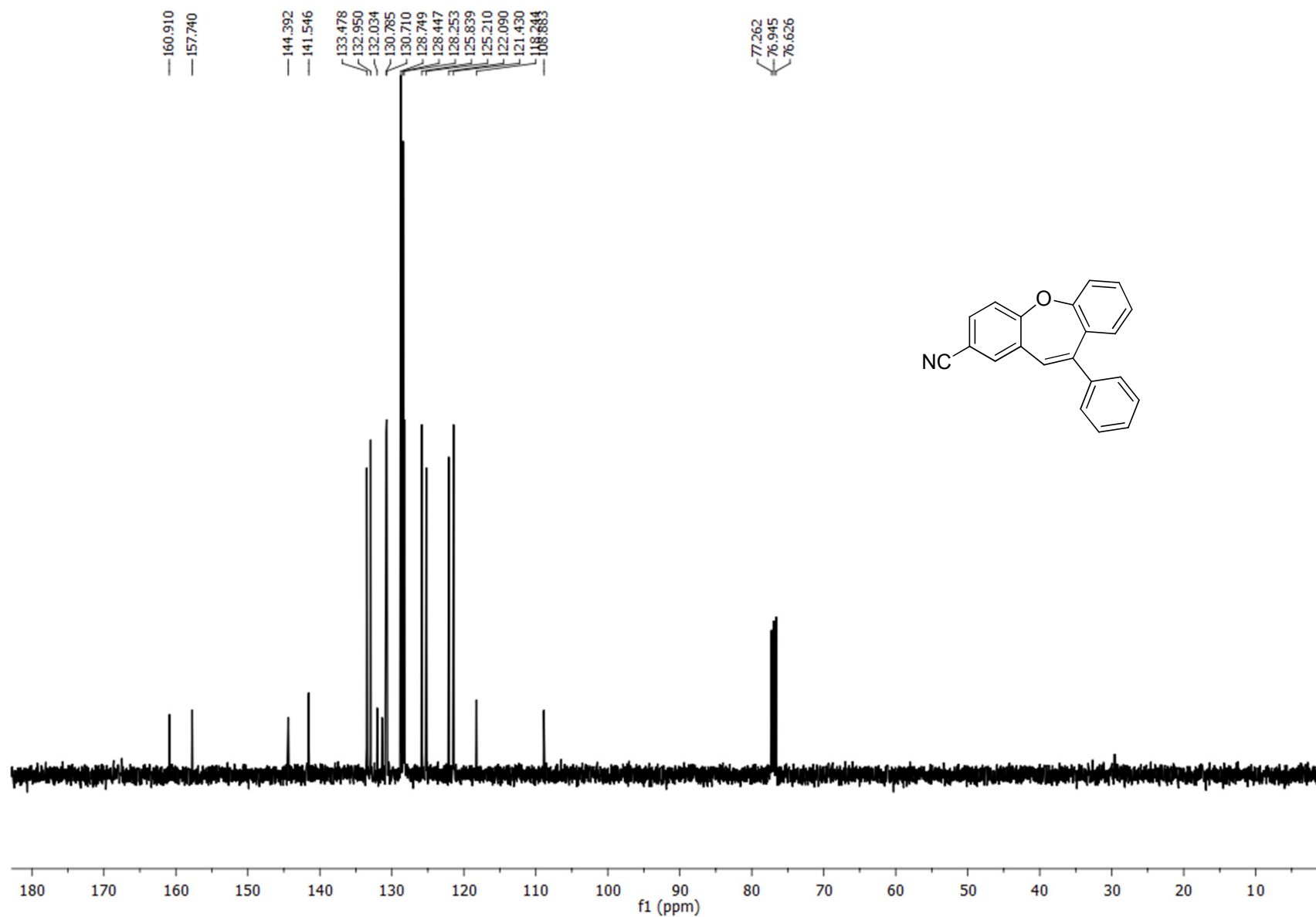
¹H NMR of 10-phenyldibenzo[b,f]oxepine-2-carbonitrile (3f)

5.6.2018

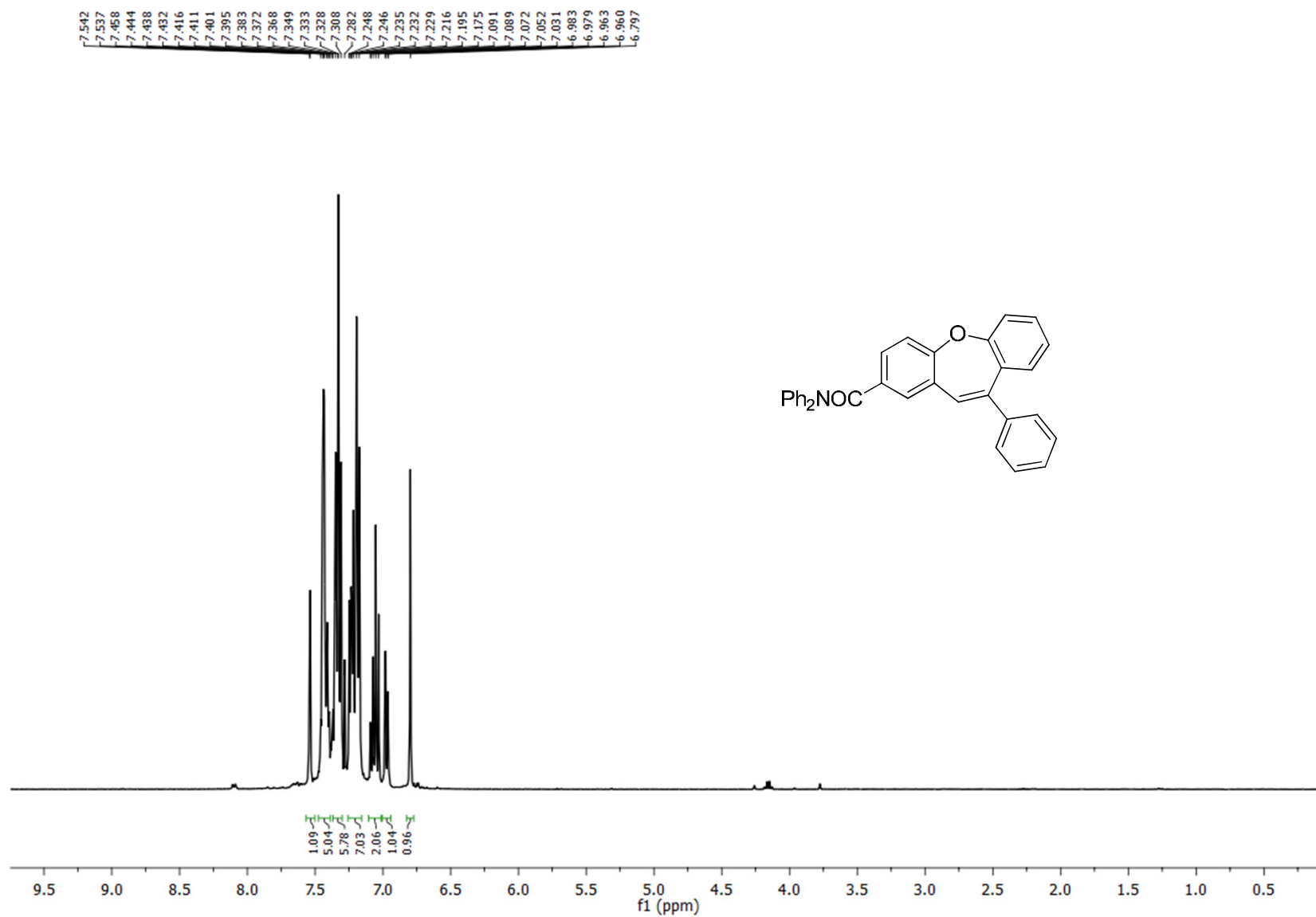
1H of NP-IM-676P-CN 5.6.2018



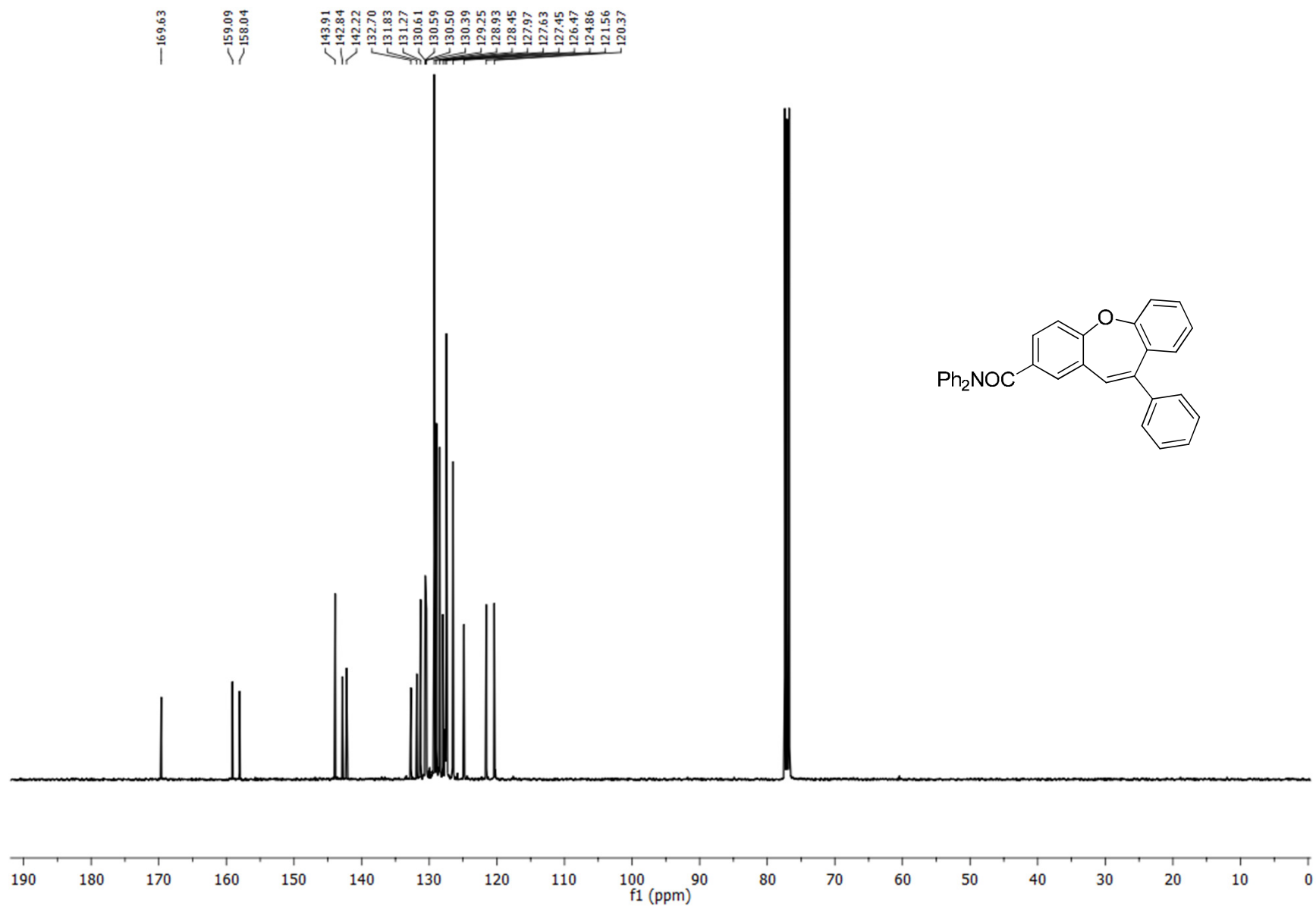
^{13}C NMR of 10-phenyldibenzo[b,f]oxepine-2-carbonitrile (3f)



¹H NMR of N,N,10-triphenyldibenzo[b,f]oxepine-2-carboxamide (3g)



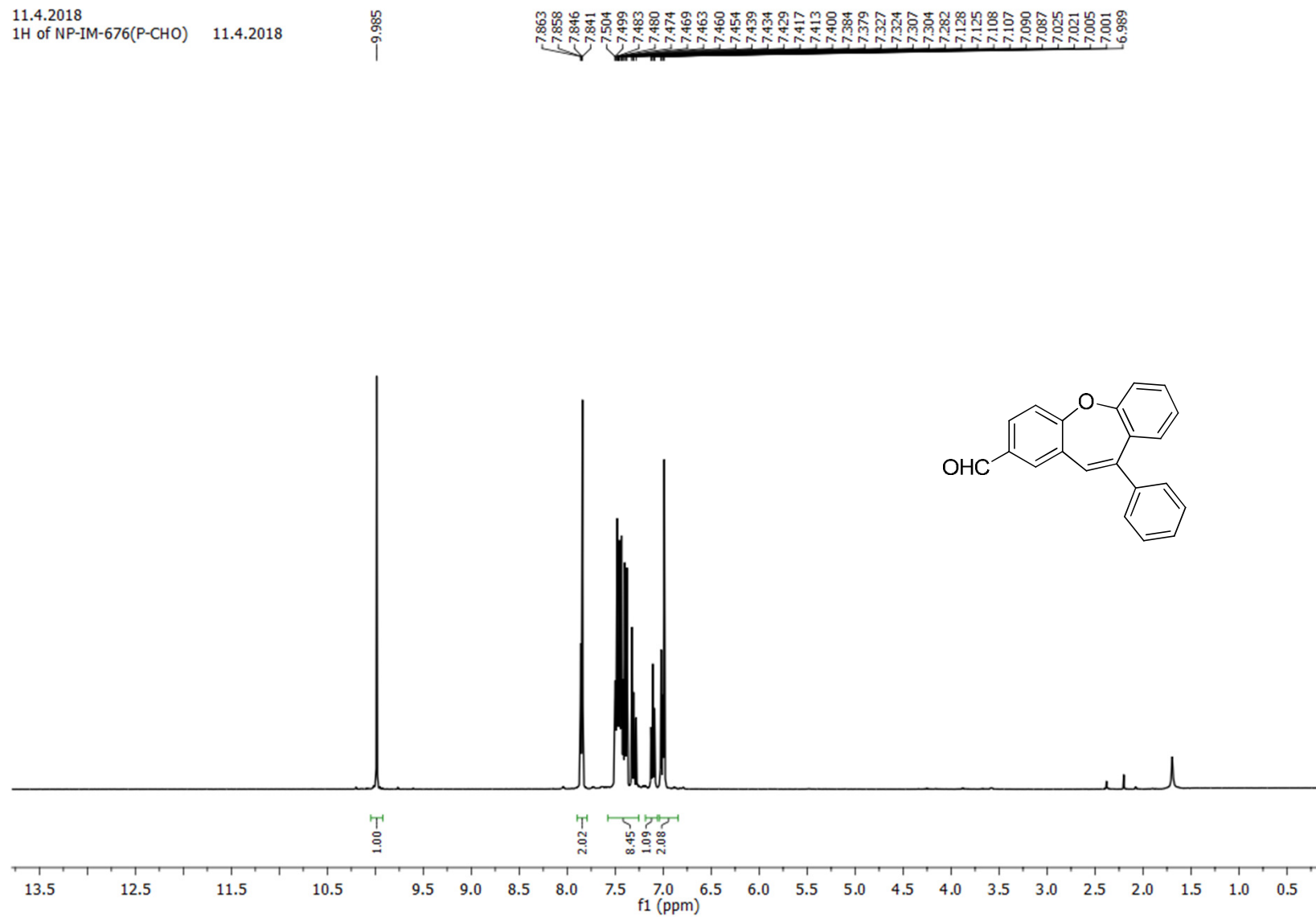
^{13}C NMR of N,N,10-triphenyldibenzo[b,f]oxepine-2-carboxamide (3g)



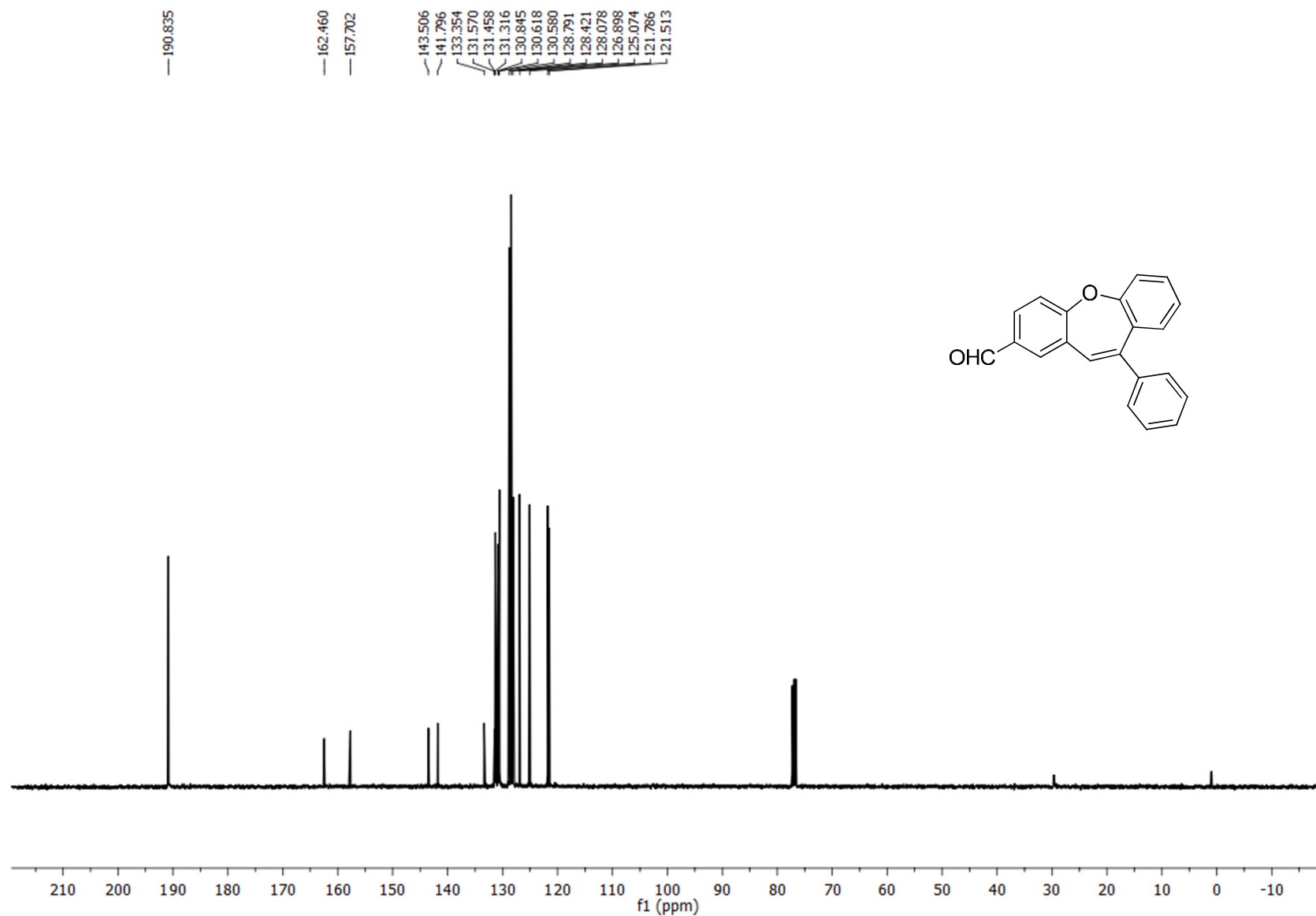
¹H NMR of 10-phenyldibenzo[b,f]oxepine-2-carbaldehyde (3h)

11.4.2018

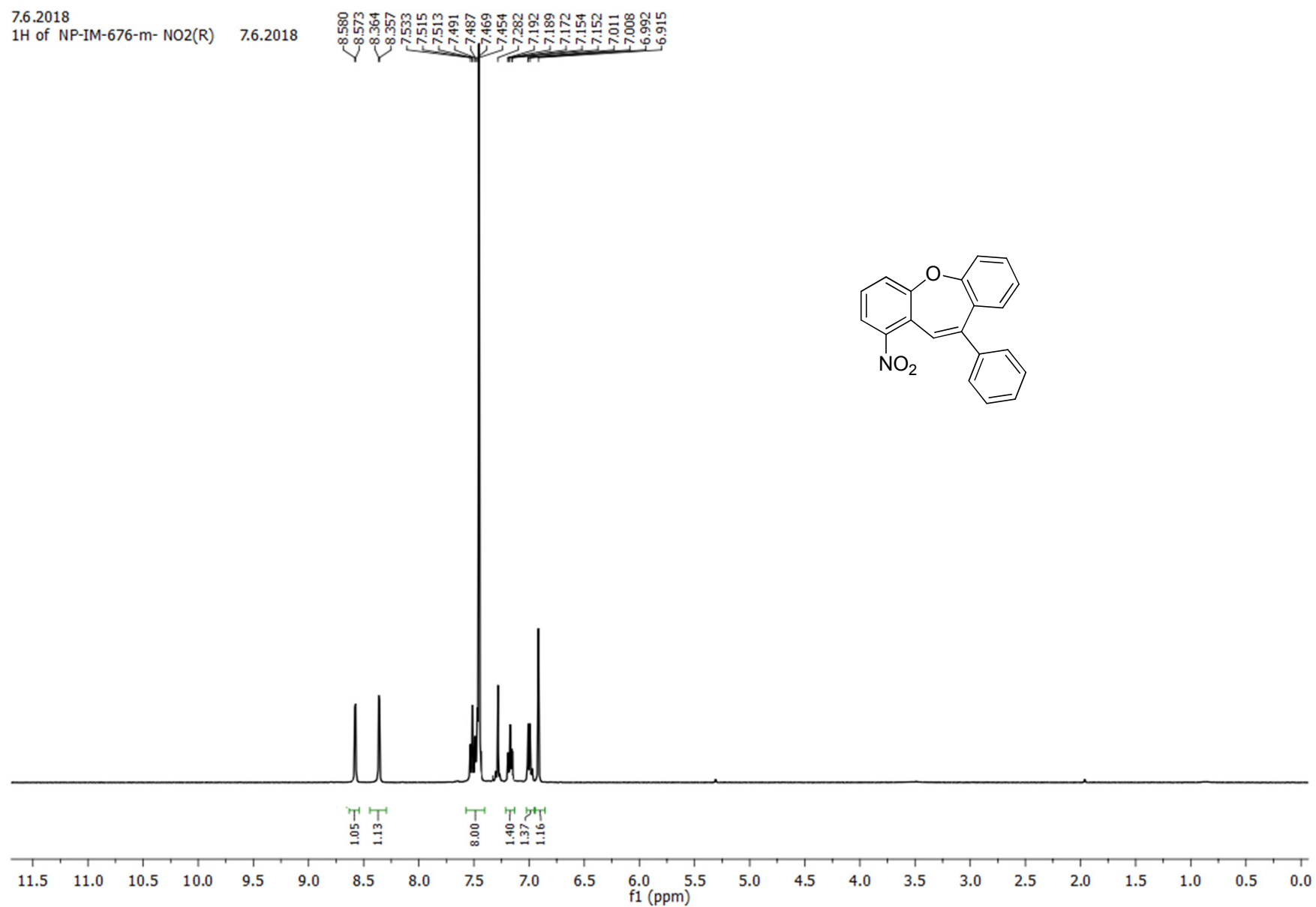
¹H of NP-IM-676(P-CHO) 11.4.2018



¹³C NMR of 10-phenyldibenzo[b,f]oxepine-2-carbaldehyde (3h)

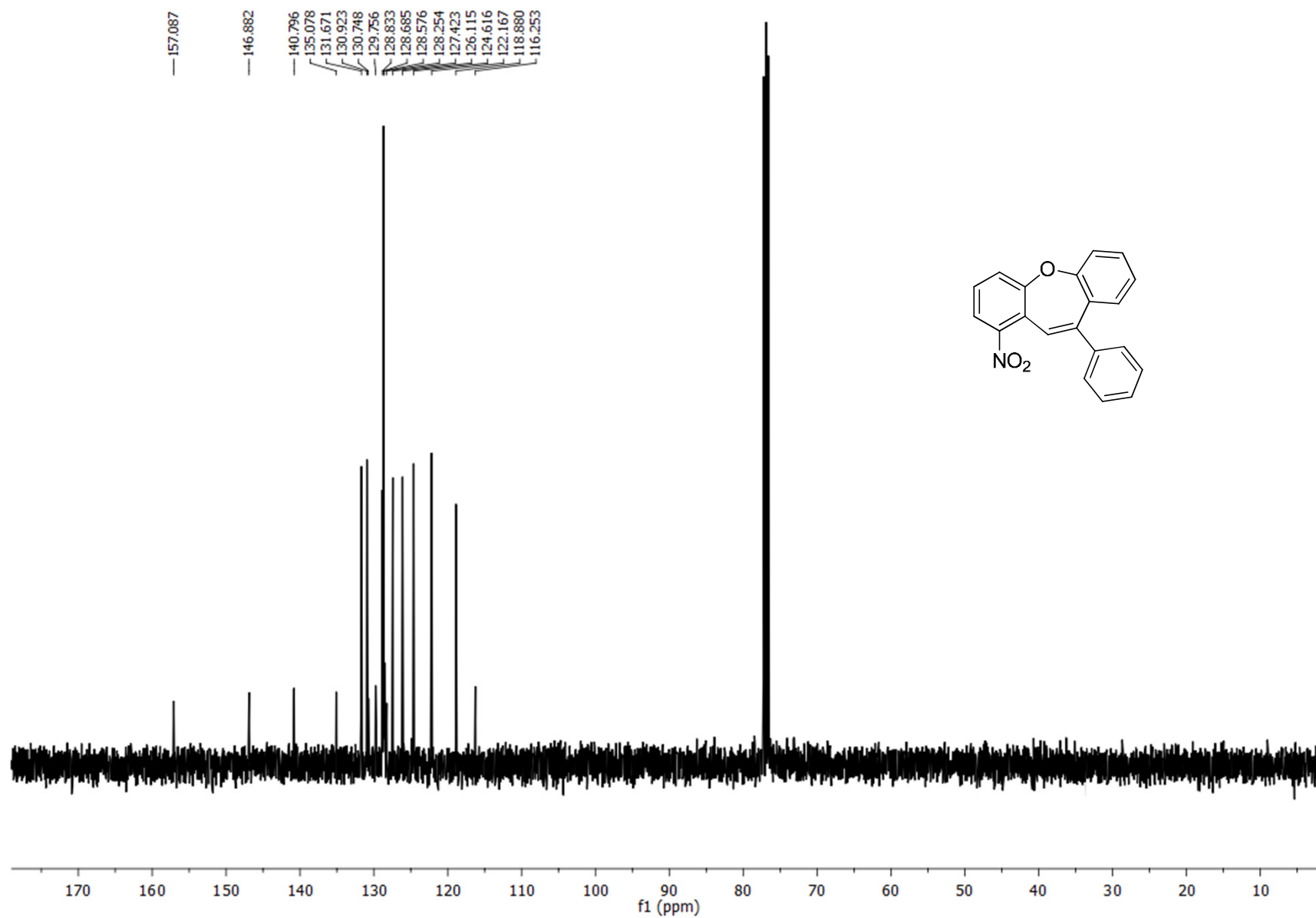


¹H NMR of 1-nitro-10-phenyldibenzo[b,f]oxepine (3i)

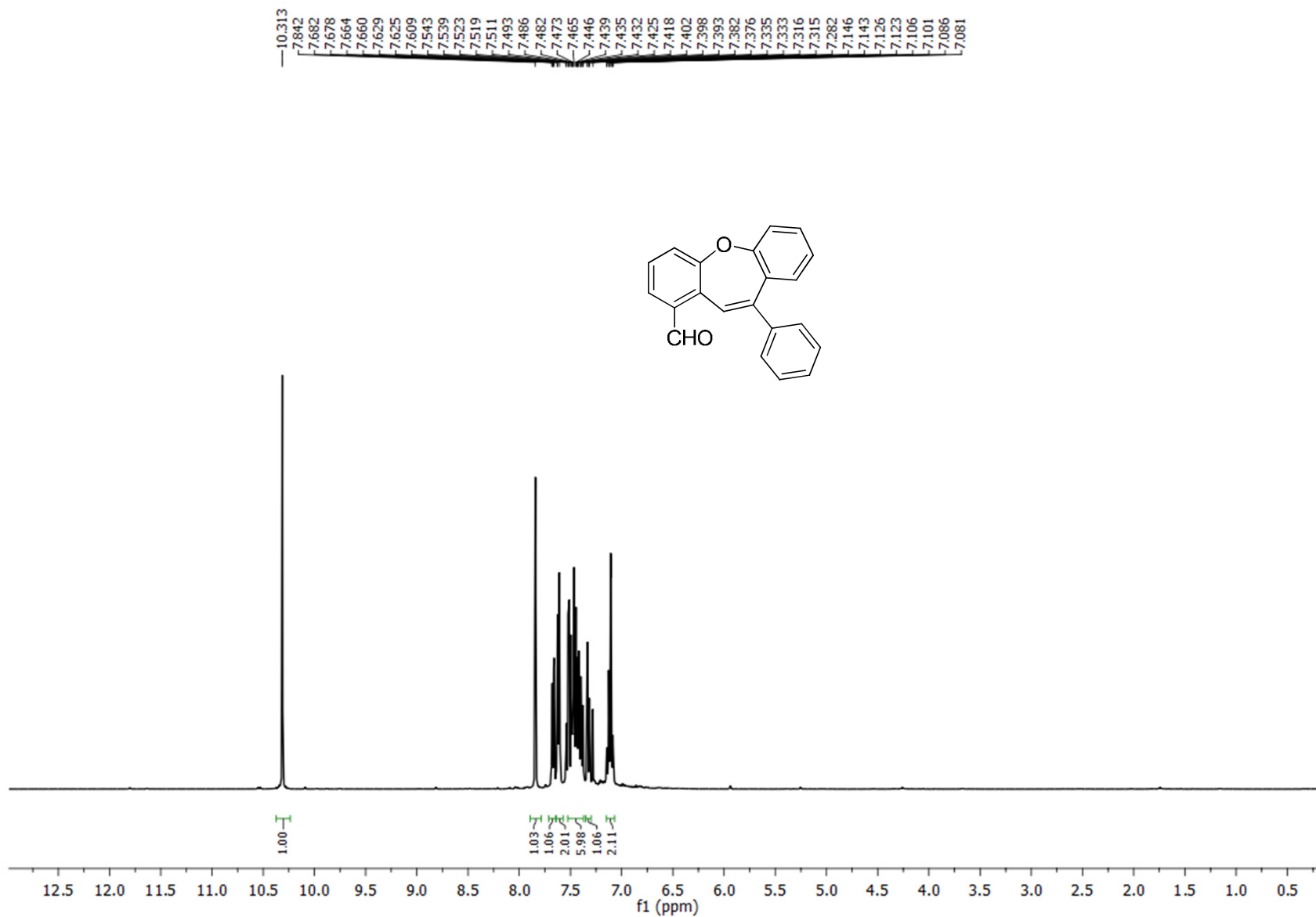


S

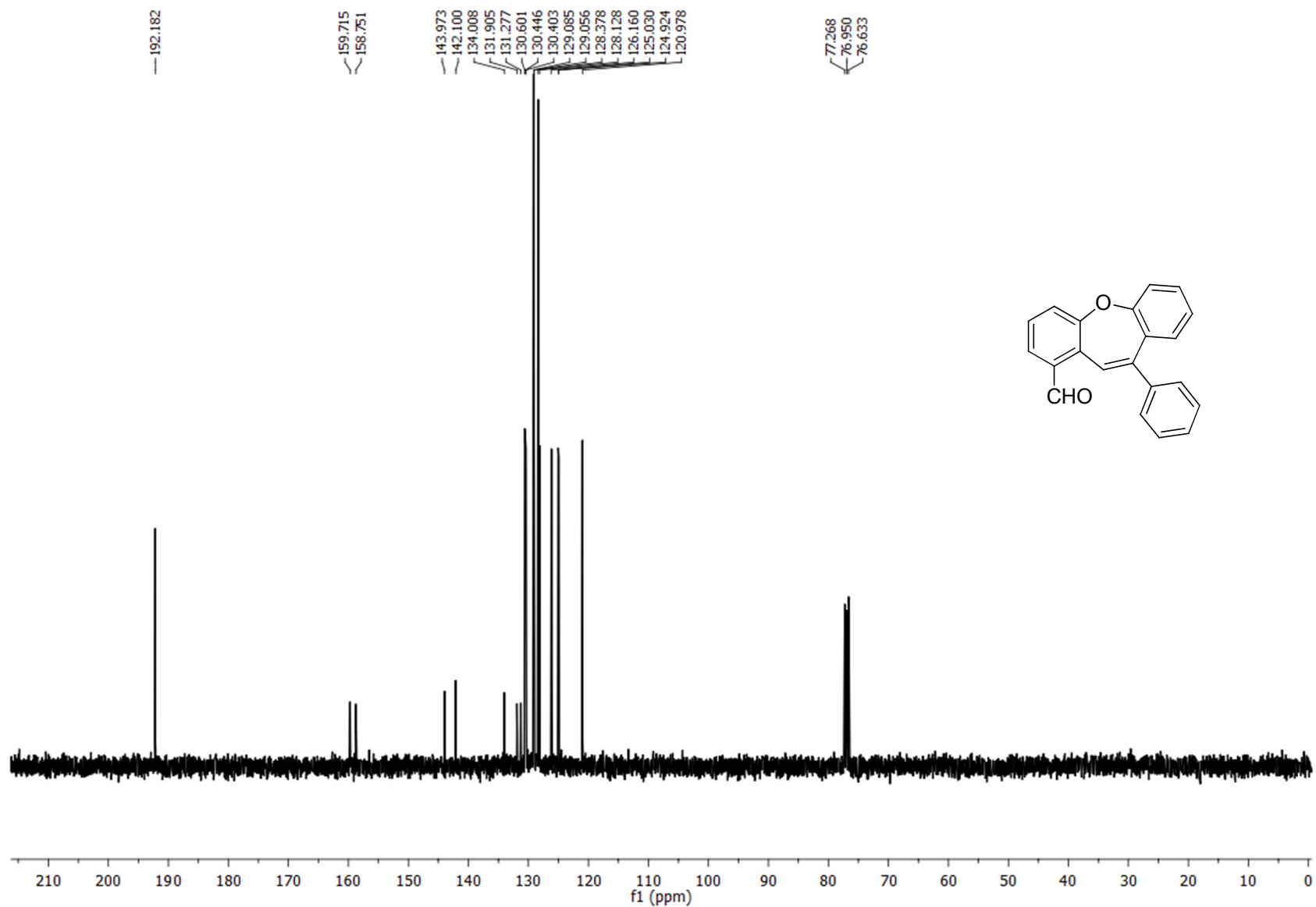
¹³C NMR of 1-nitro-10-phenyldibenzo[b,f]oxepine (3i)



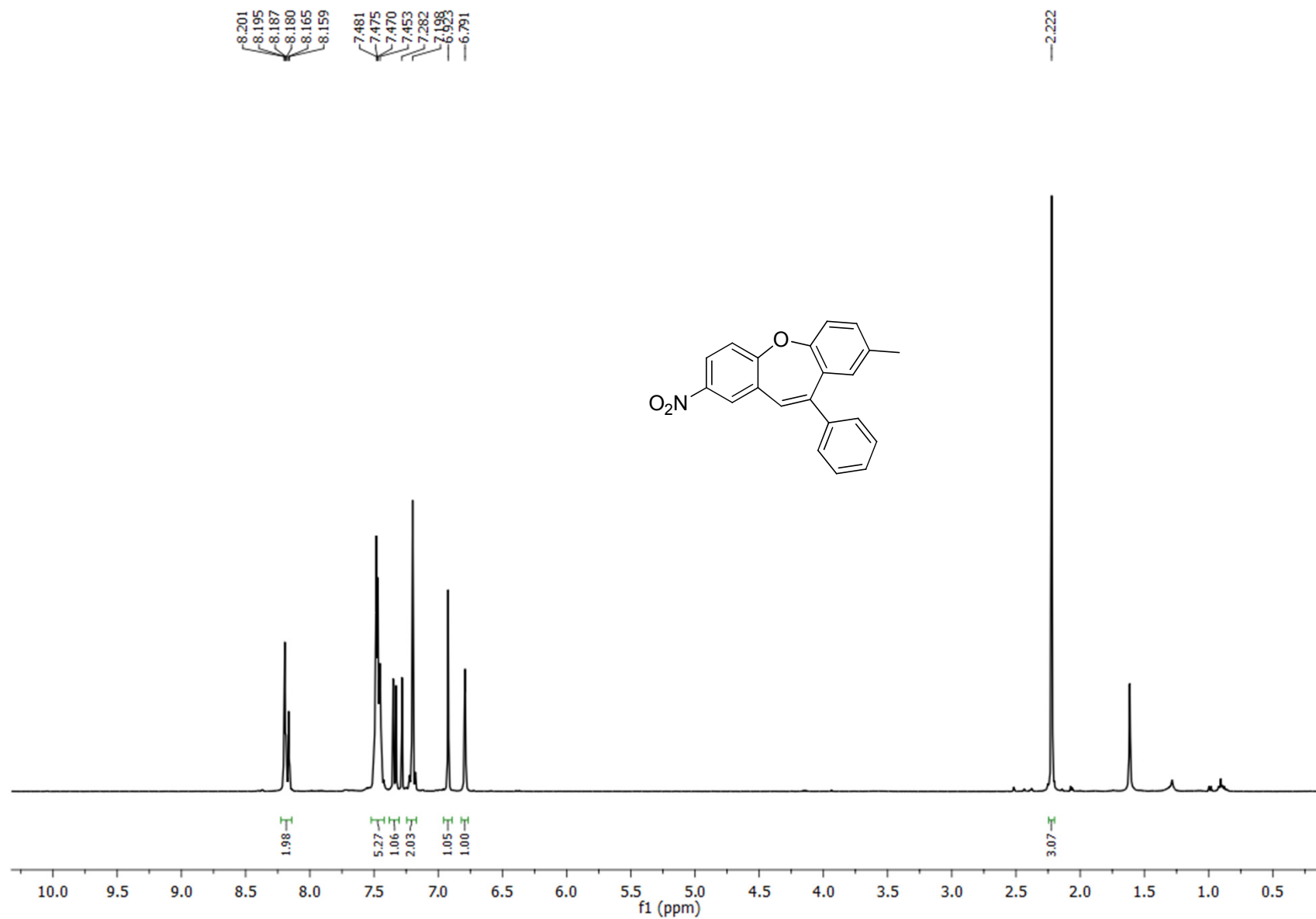
¹H NMR of 10-phenyldibenzo[b,f]oxepine-1-carbaldehyde (3j)



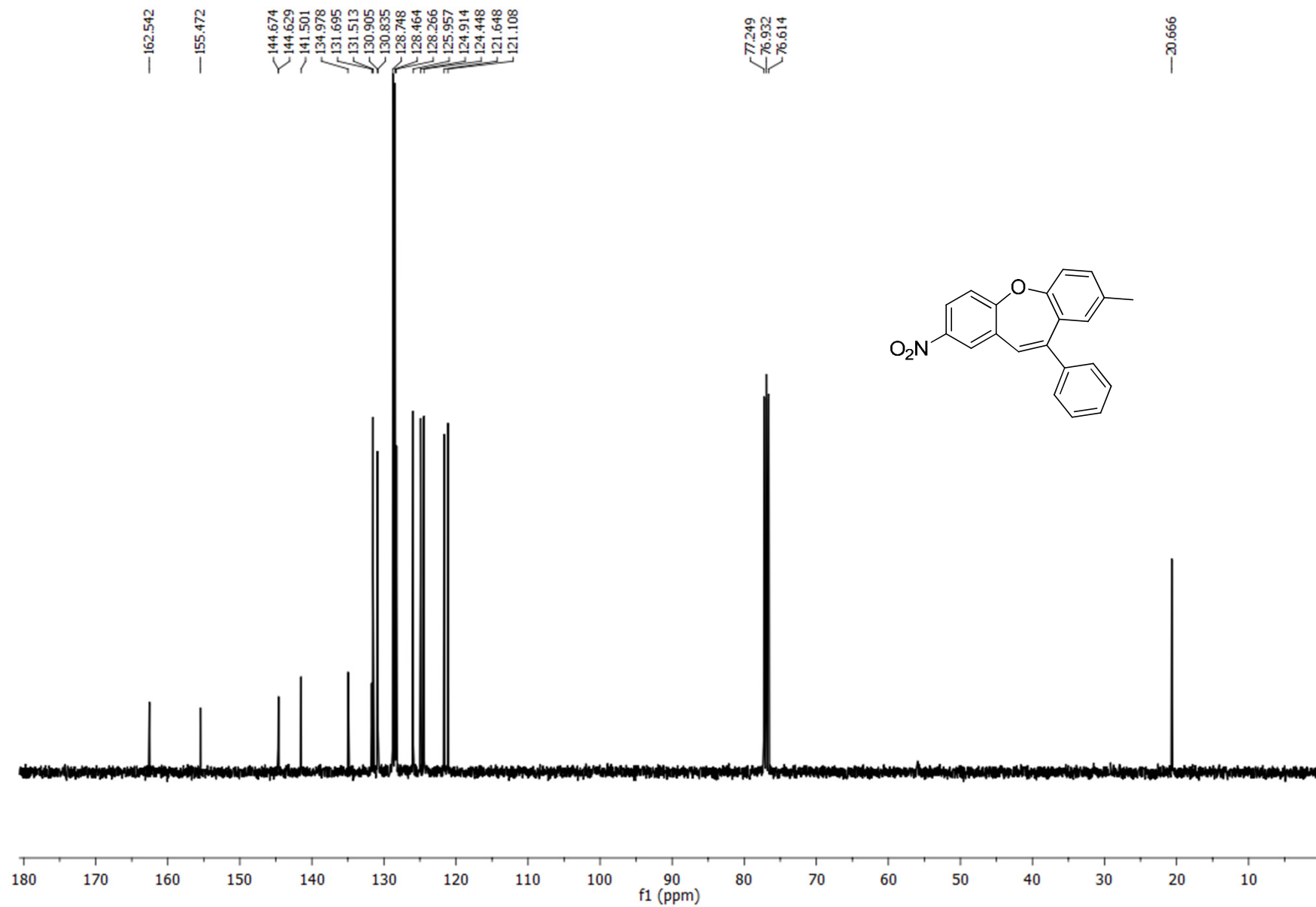
¹³C NMR of 10-phenyldibenzo[b,f]oxepine-1-carbaldehyde (3j)



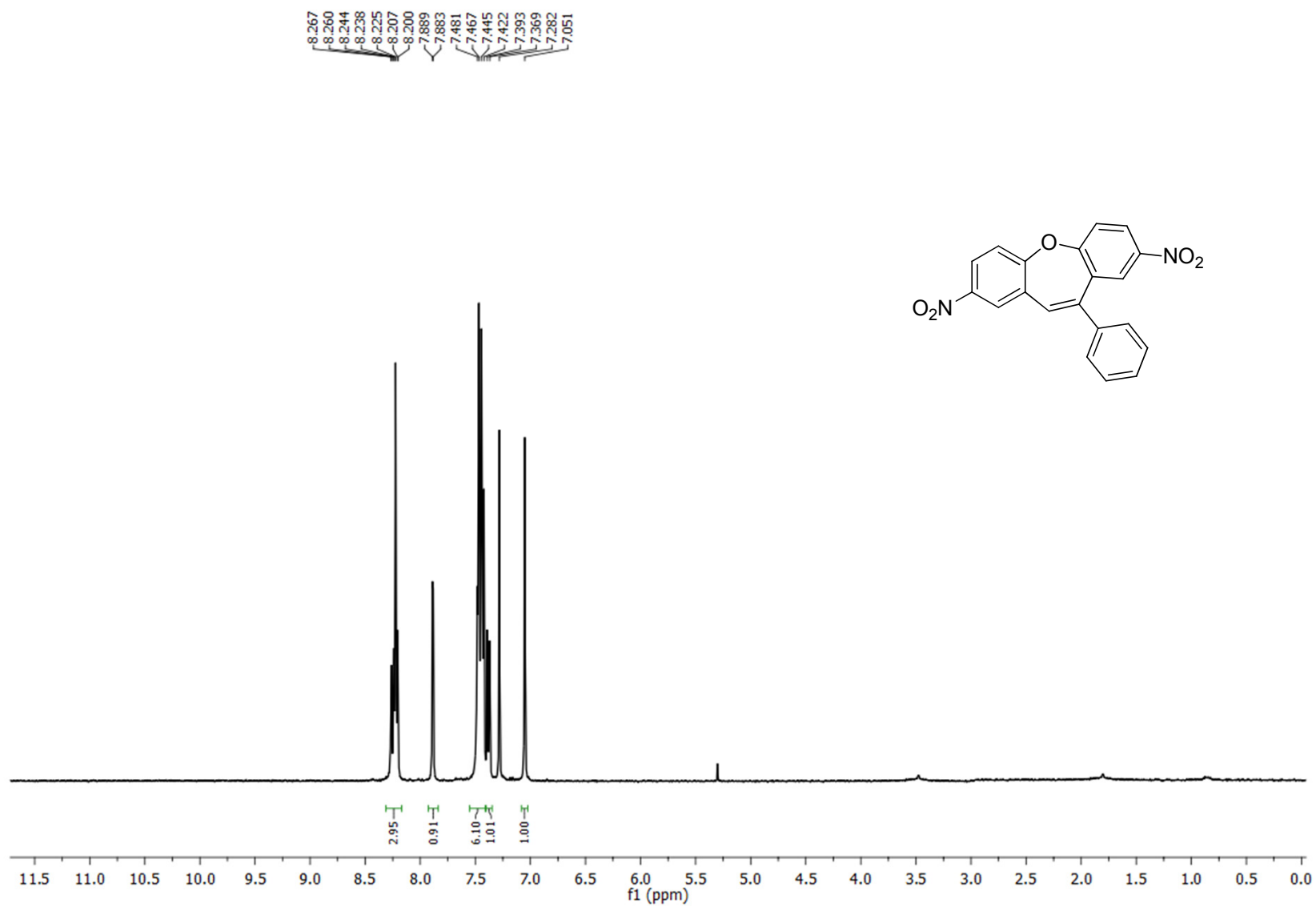
¹H NMR of 8-methyl-2-nitro-10-phenyldibenzo[b,f]oxepine (3k)



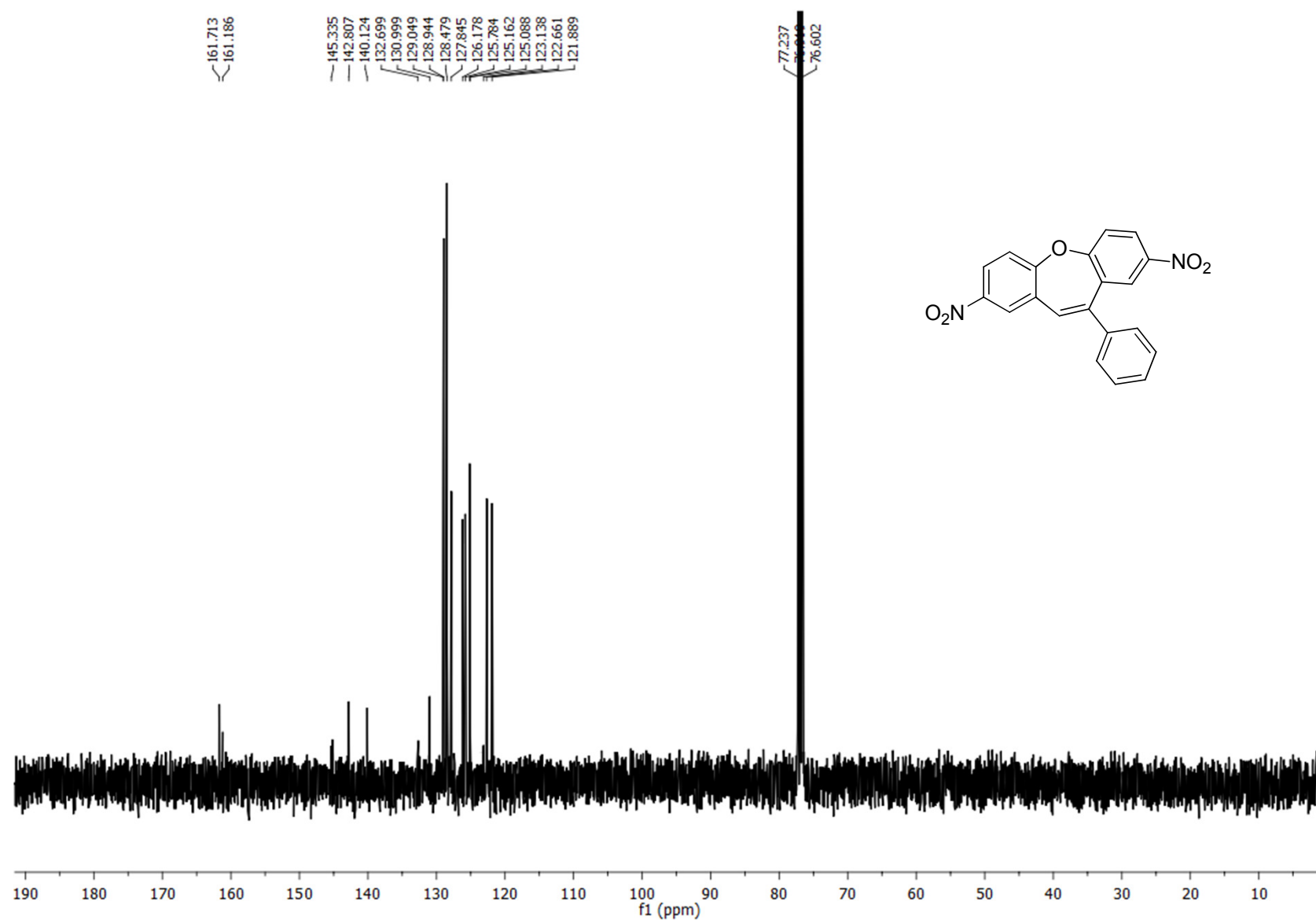
^{13}C NMR of 8-methyl-2-nitro-10-phenyldibenzo[b,f]oxepine (3k)



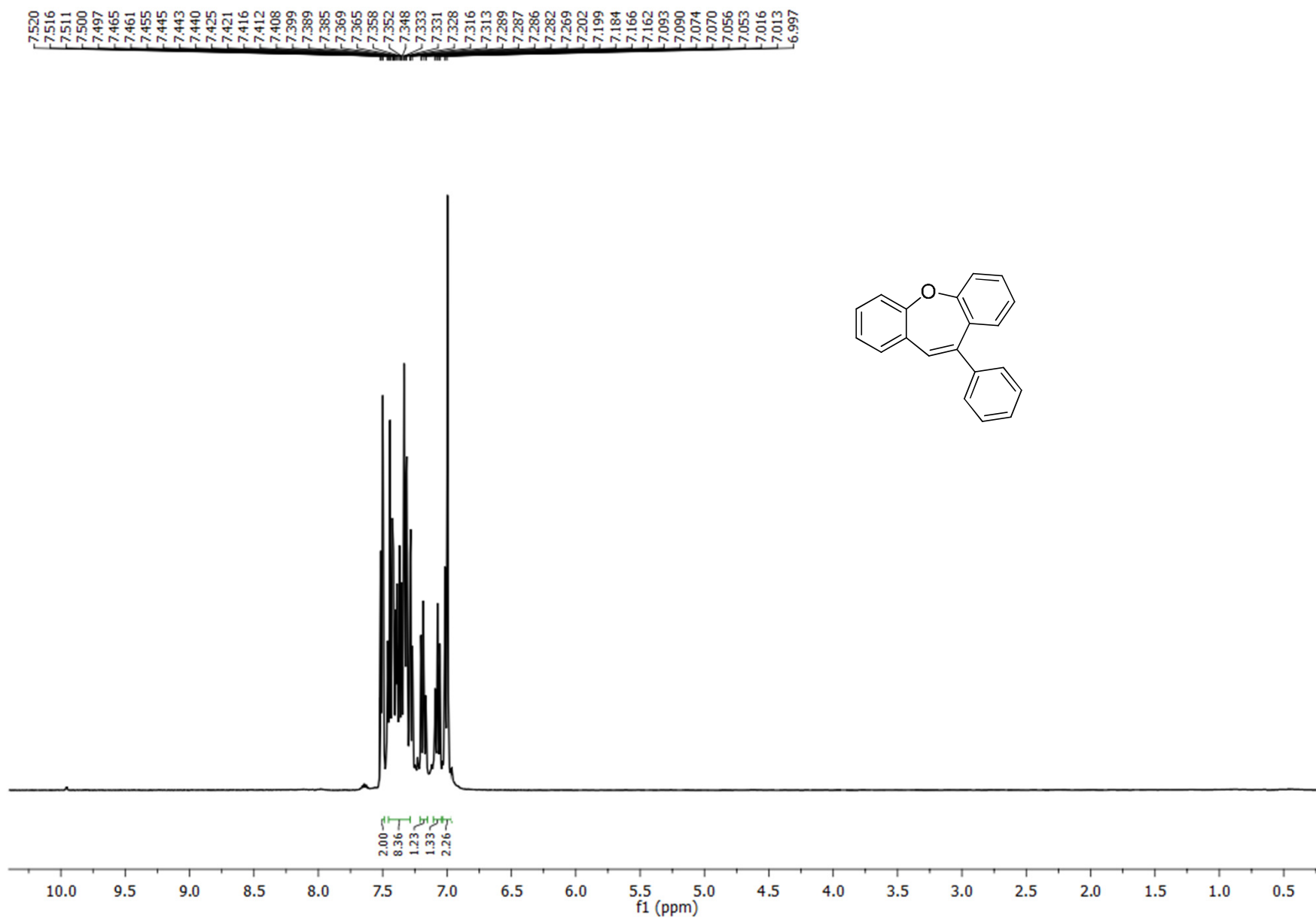
¹H NMR of 2,8-dinitro-10-phenyldibenzo[b,f]oxepine (3l)



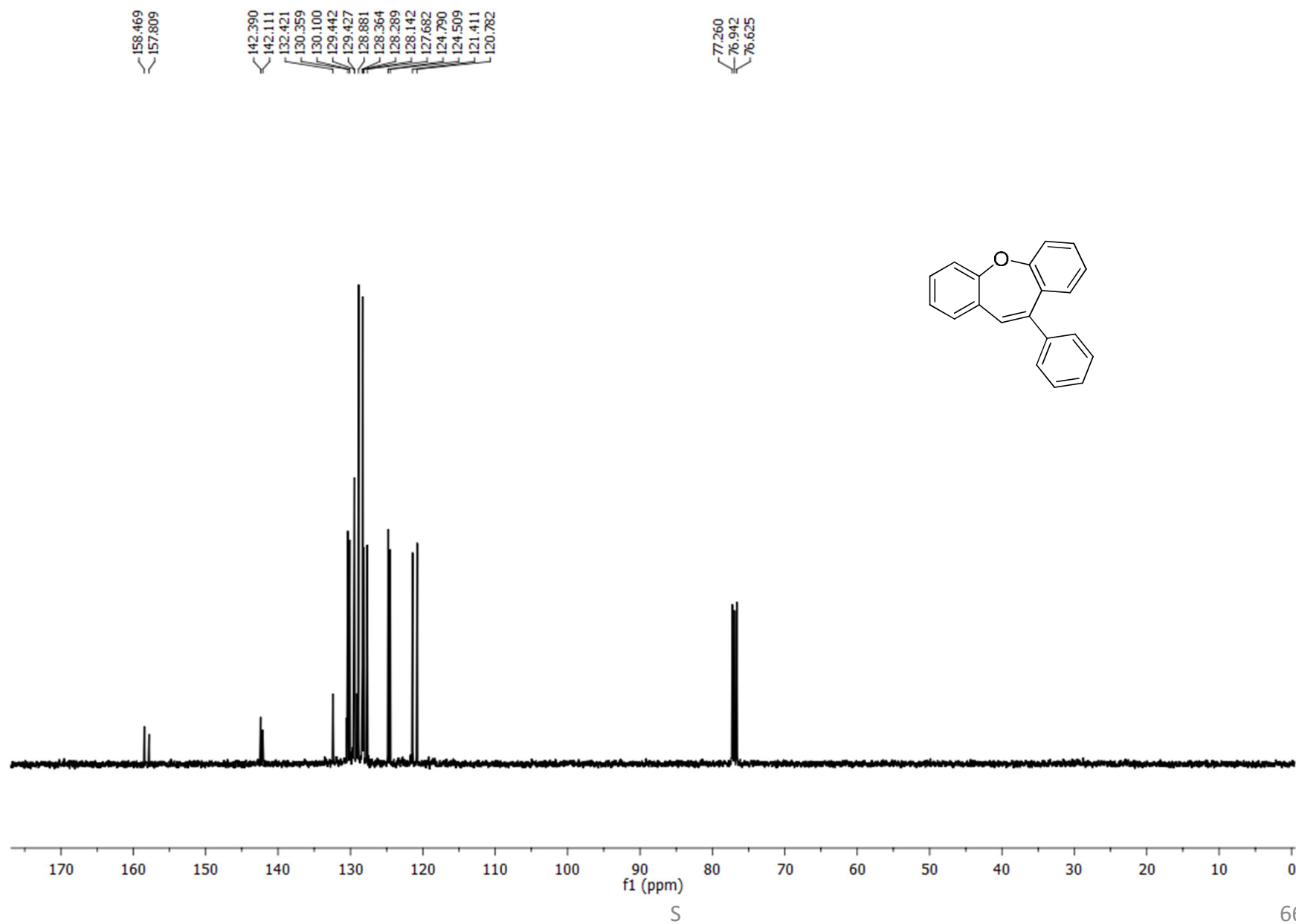
^{13}C NMR of 2,8-dinitro-10-phenyldibenzo[b,f]oxepine (3l)



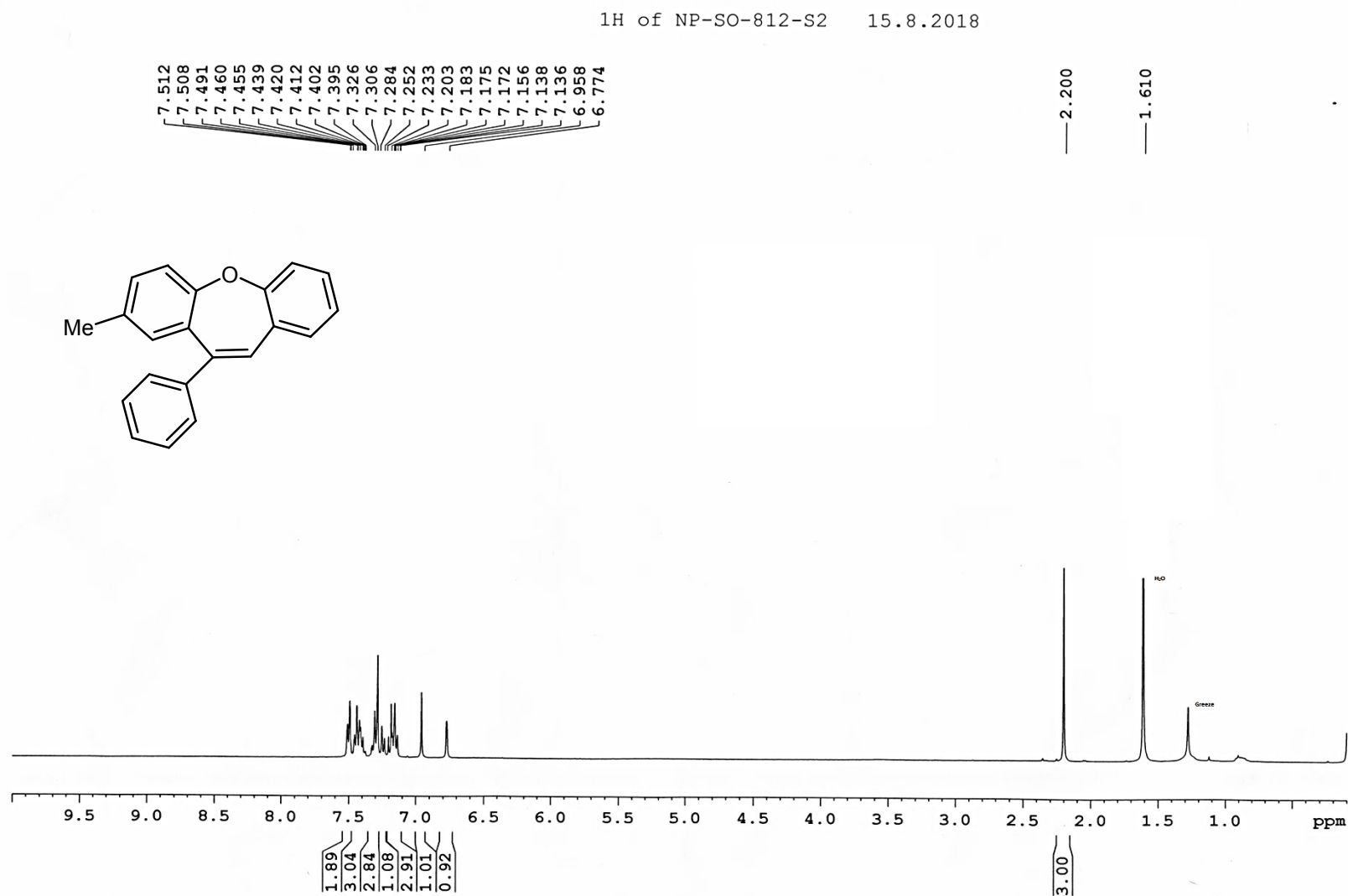
¹H NMR of 10-phenyldibenzo[b,f]oxepine (3o)



^{13}C NMR of 10-phenyldibenzo[b,f]oxepine (3o)

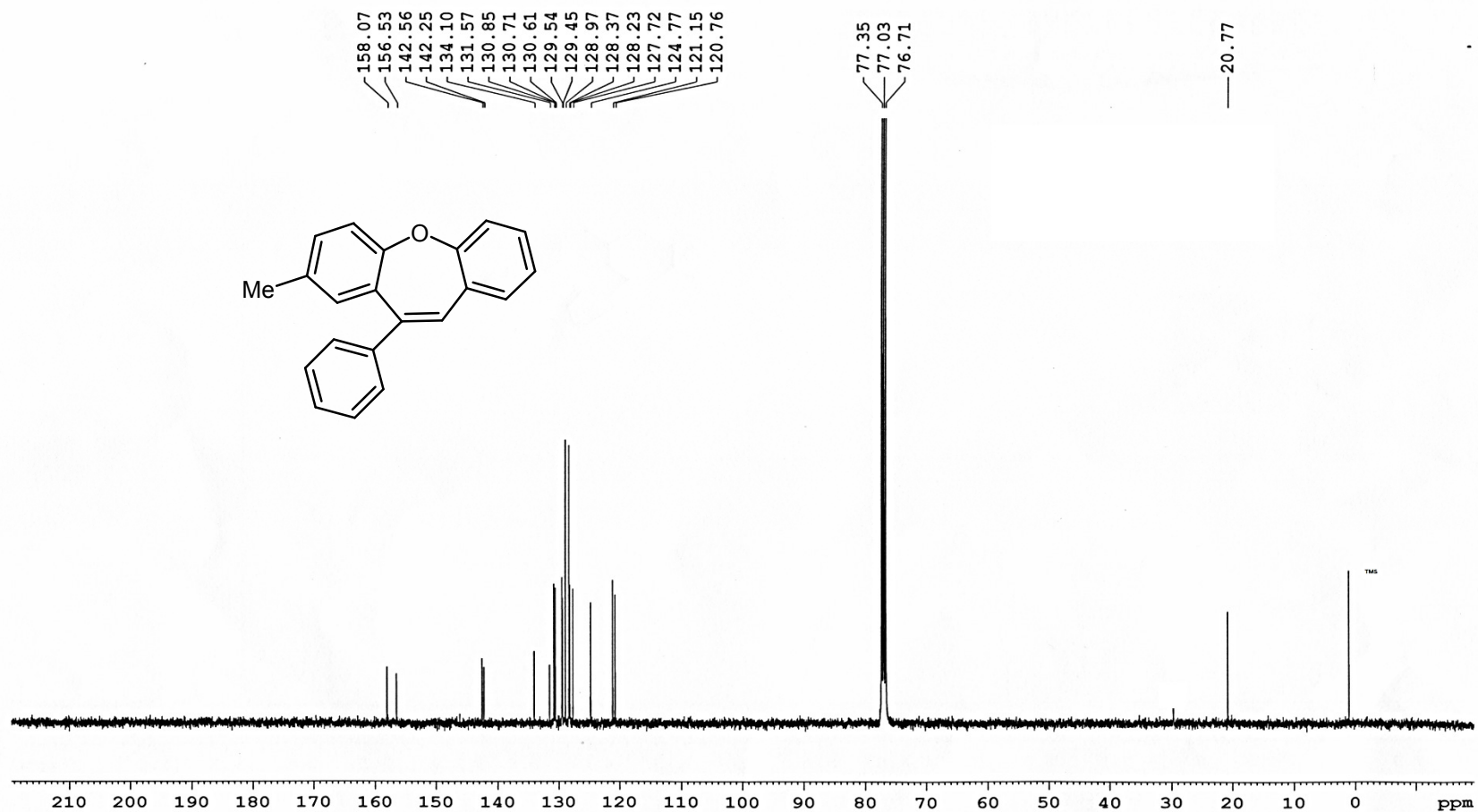


¹H NMR of 2-Methyl-10-phenyldibenzo[*b,f*]oxepine (3p)



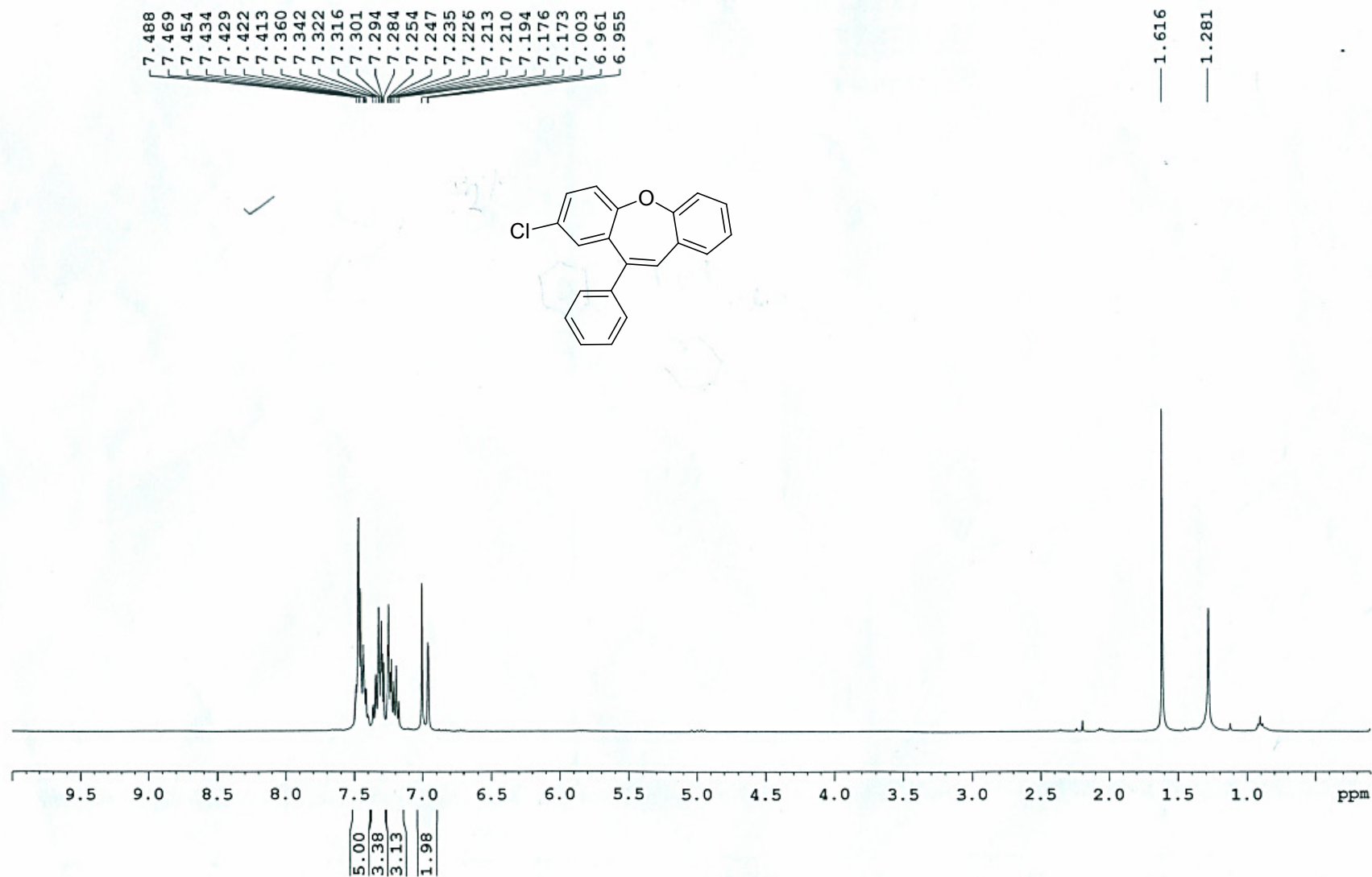
¹³C NMR of 2-Methyl-10-phenyldibenzo[*b,f*]oxepine (3p)

13C of NP-SO-812-S2 15.8.2018



¹H NMR of 2-Chloro-10-phenyldibenzo[*b,f*]oxepine (3q)

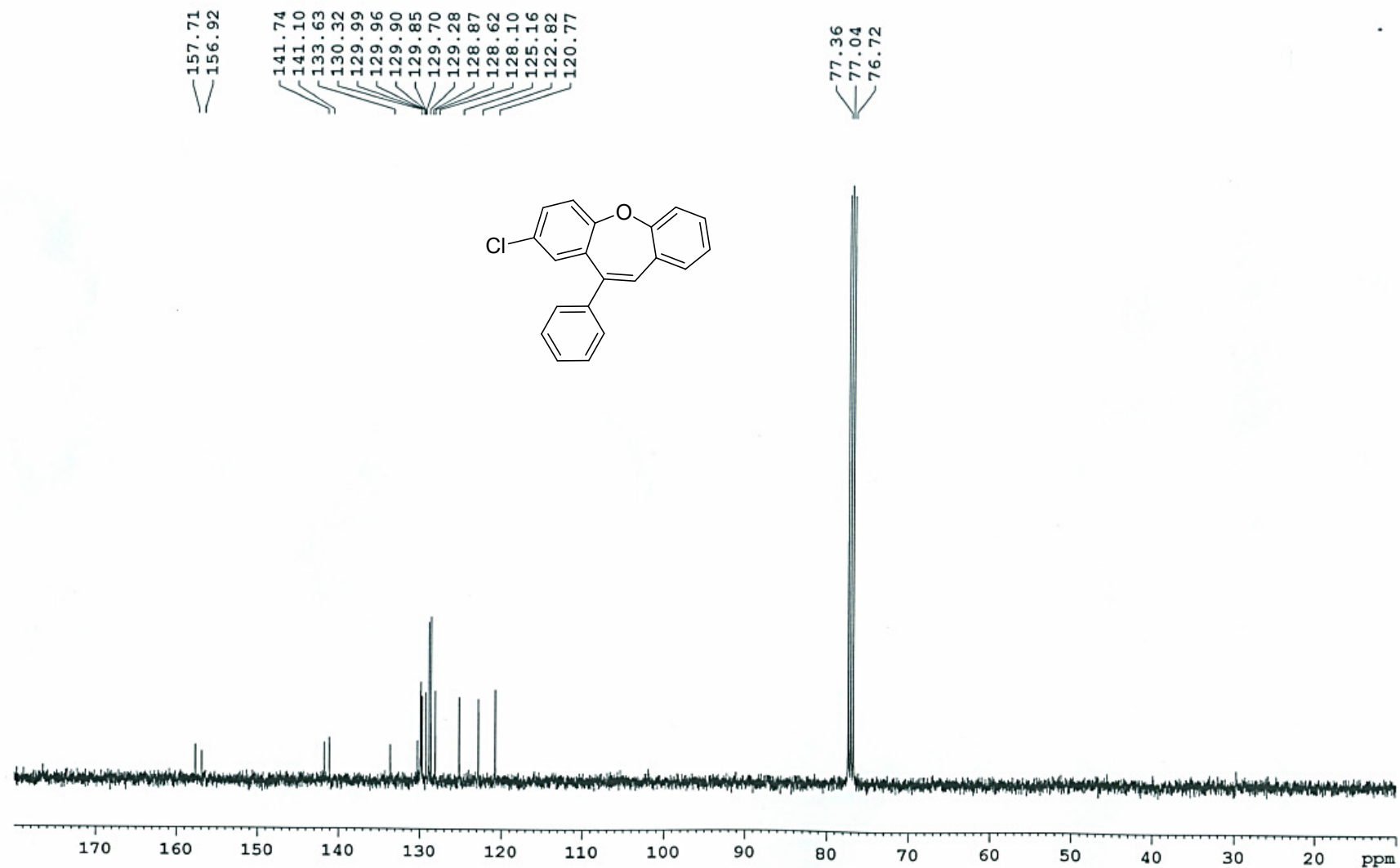
¹H of NP-SO-805



¹³C NMR of 2-Chloro-10-phenyldibenzo[*b,f*]oxepine (3q)

¹³C of NP-SO-805

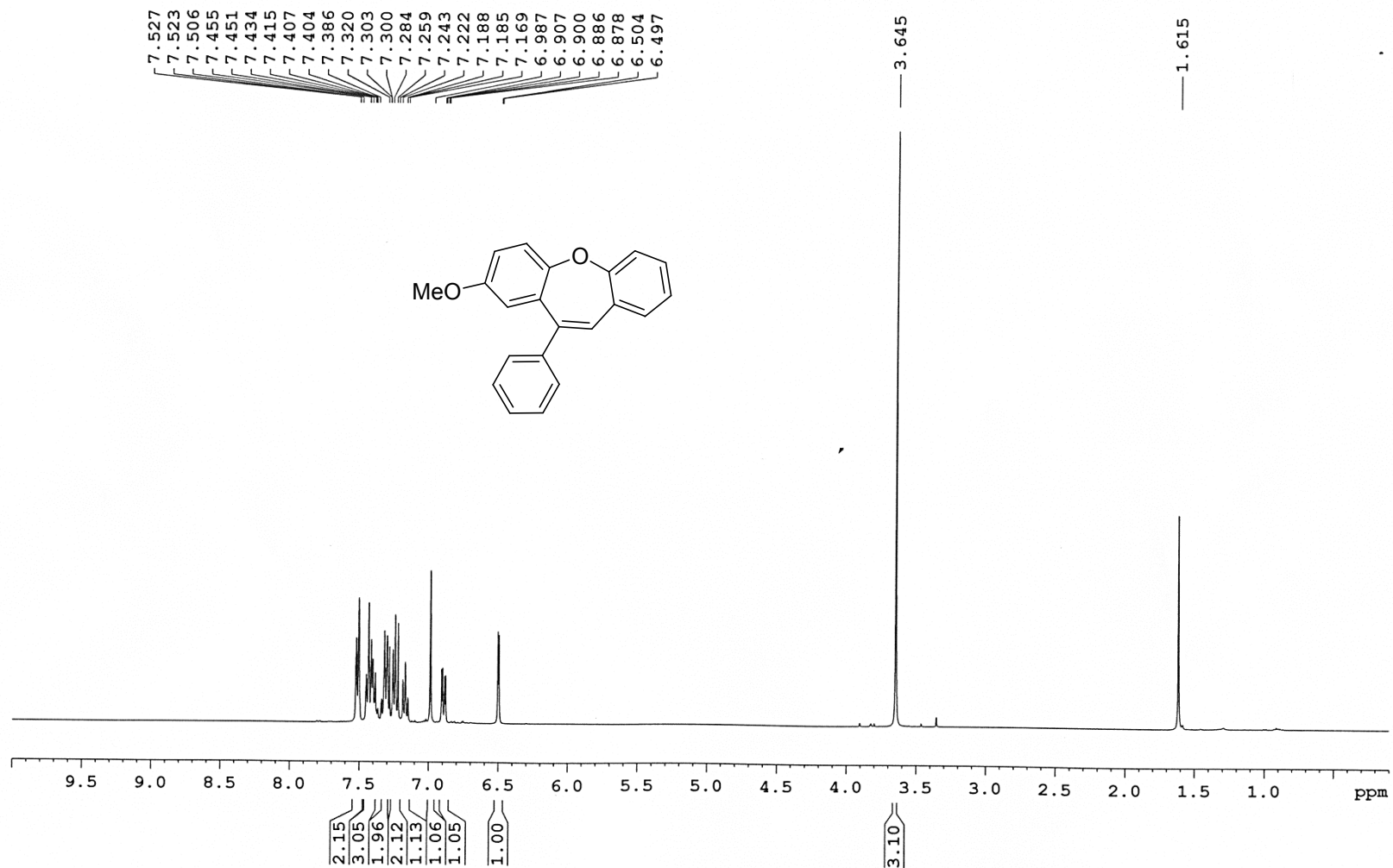
9.8.2018



¹H NMR of 2-Methoxy-10-phenyldibenzo[*b,f*]oxepine (3r)

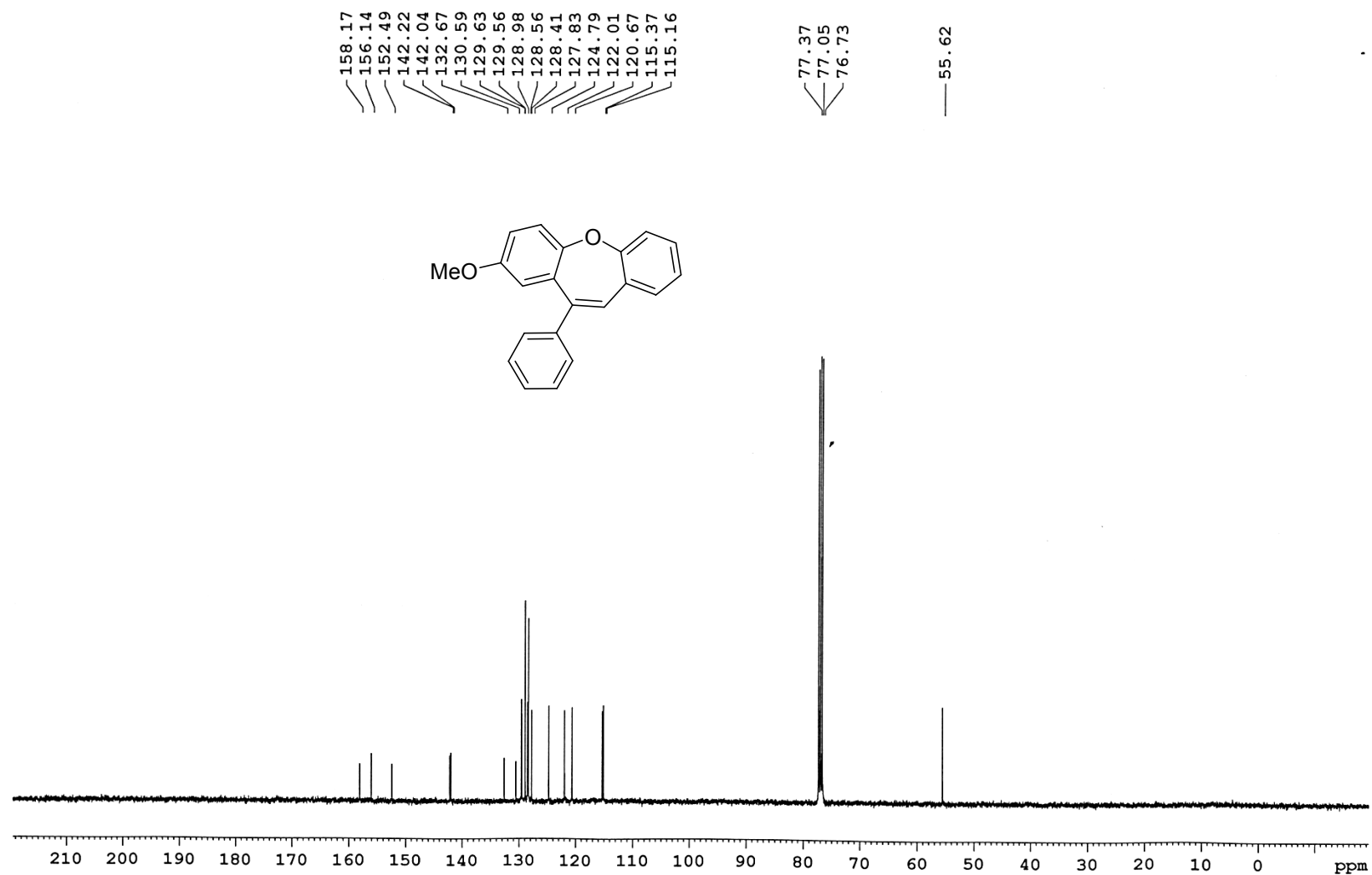
¹H of NP-SO-816 (R2)

23.8.2018



^{13}C NMR of 2-Methoxy-10-phenyldibenzo[*b,f*]oxepine (3r)

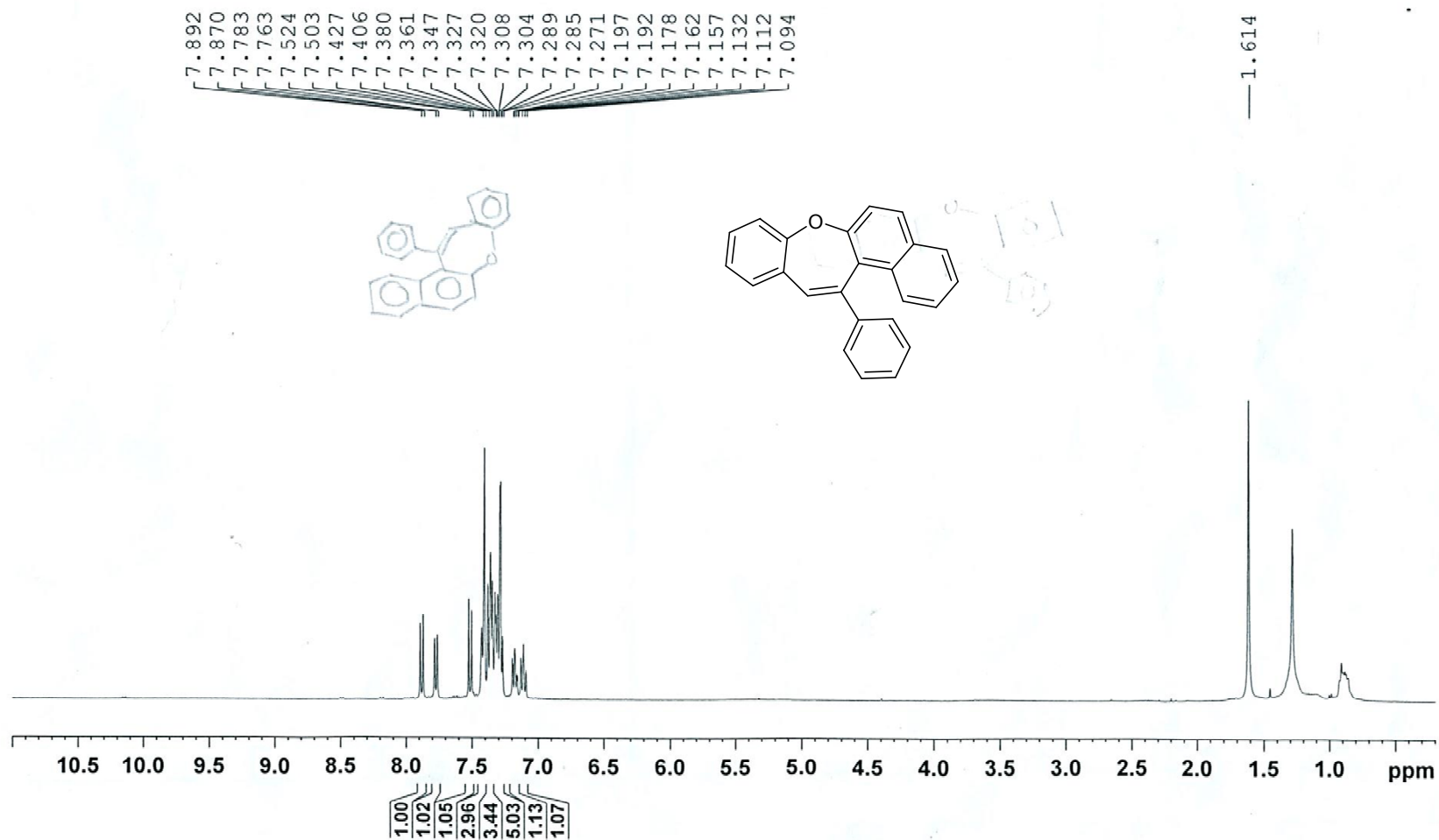
^{13}C of NP-SO-816(R2) 24.8.2018



^1H NMR of 11-Phenyl benzo[*b*]naphth[1,2-*f*]oxepin (3s)

^1H of NP-SO-813-S2 15.8.2018

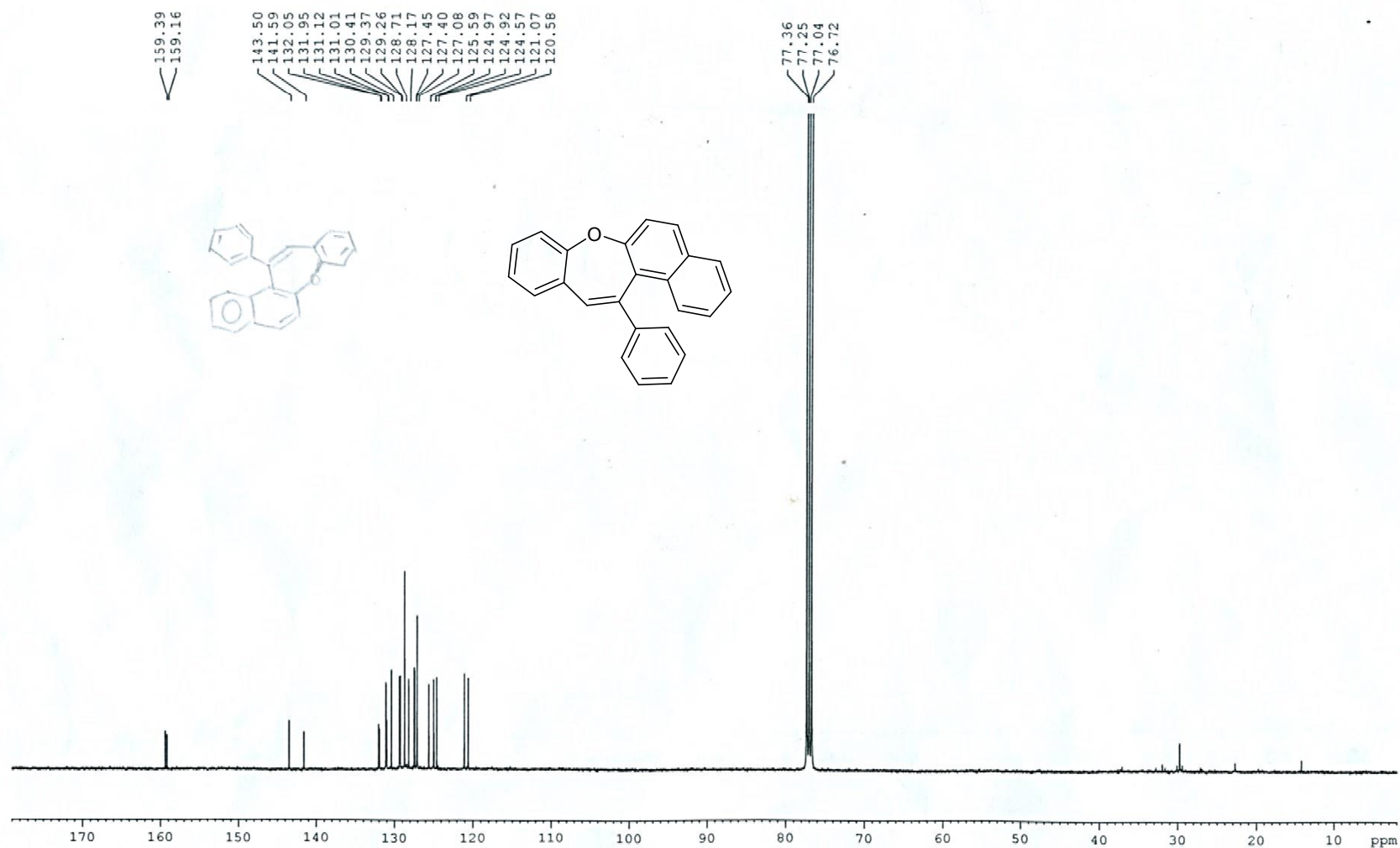
(3s)



^{13}C NMR of 11-Phenyl benzo[*b*]naphth[1,2-*f*]oxepin (3s)

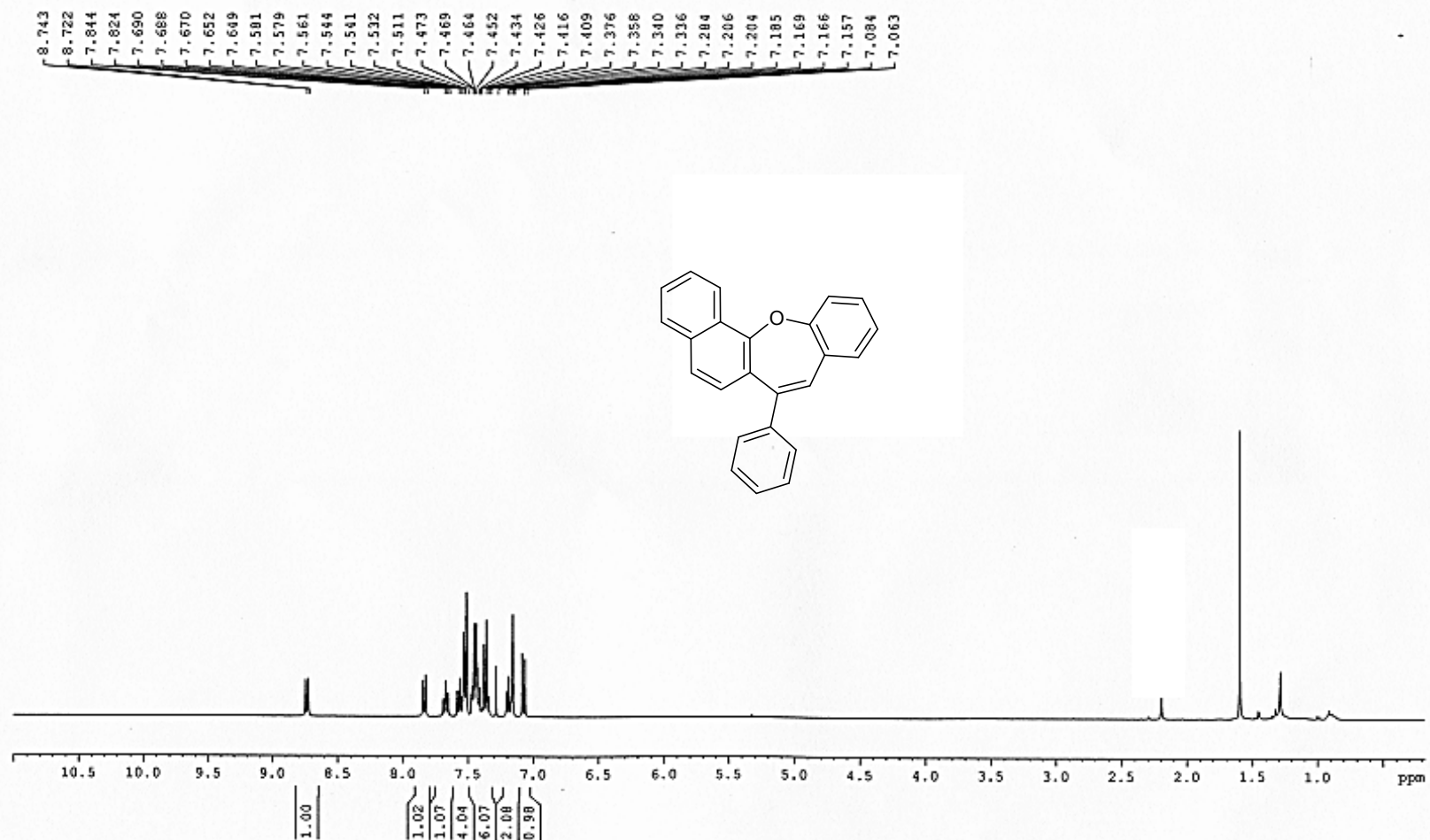
^{13}C of NP-SO-813-S2 15.8.2018

38



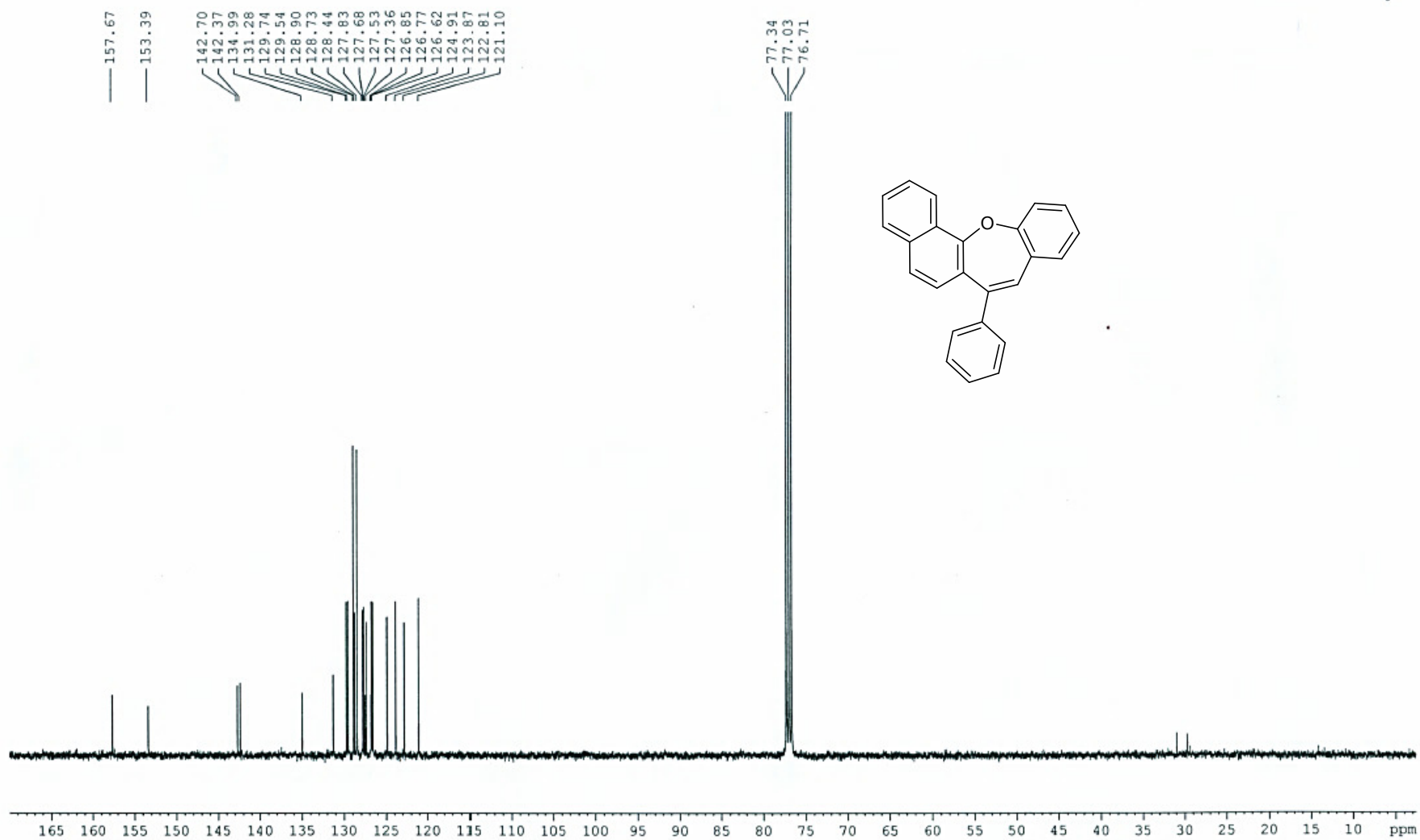
¹H NMR of 12-Phenyl benzo[*b*]naphth[2,1-*f*]oxepin (3t)

¹H of NP-SO-814-R 18.8.2018

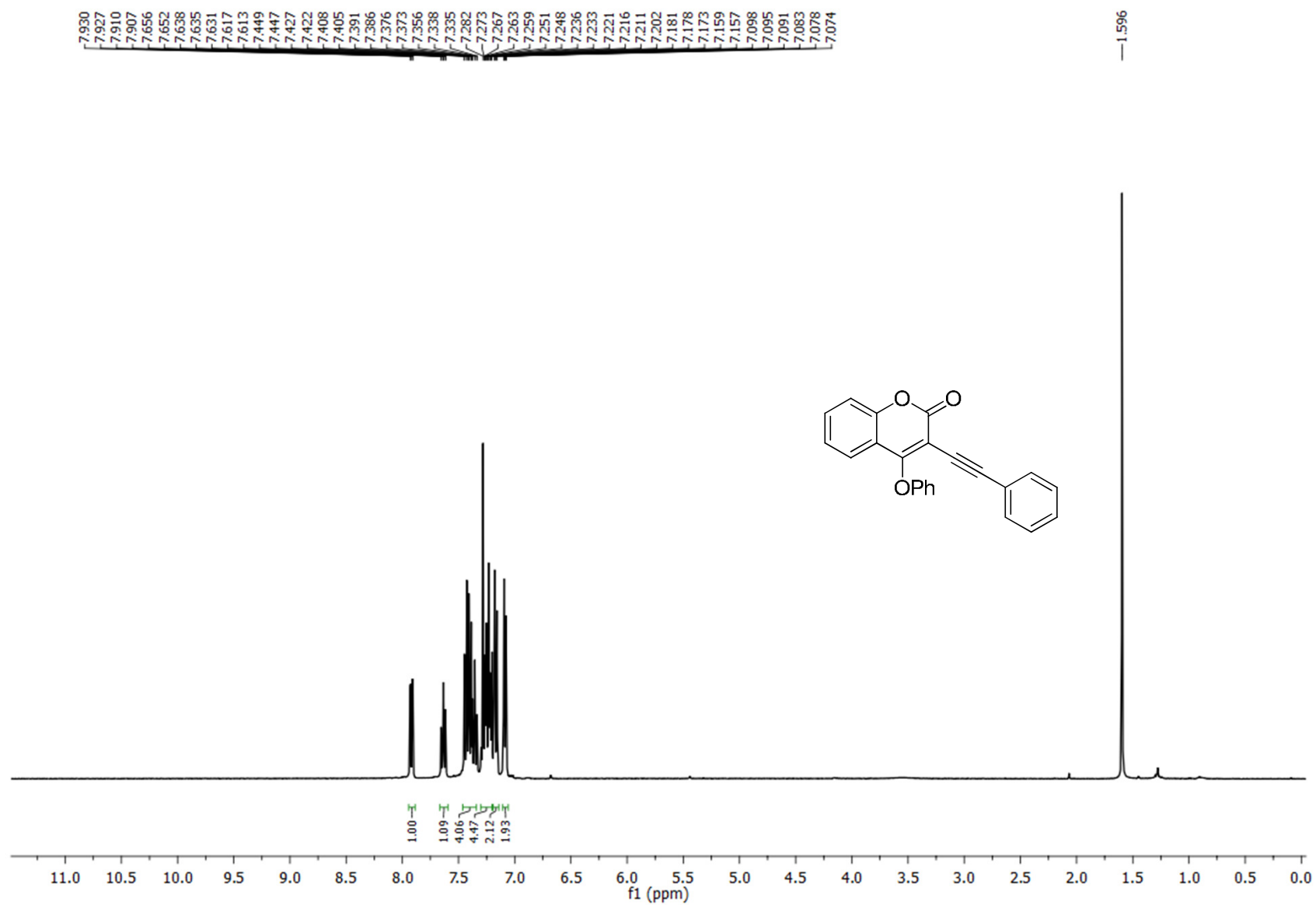


13 NMR of 12-Phenyl benzo[*b*]naphth[2,1-*f*]oxepin (3t)

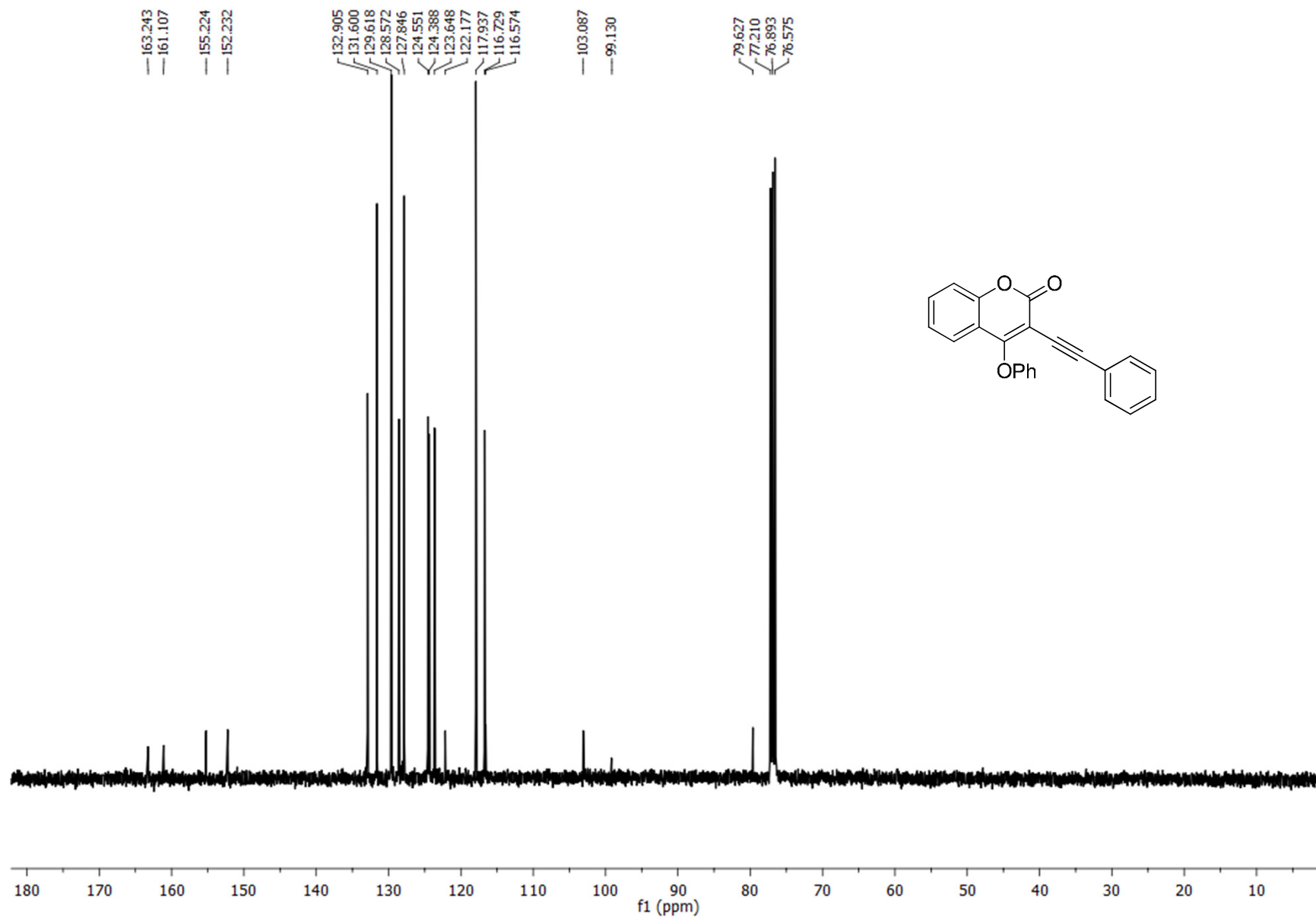
13C of NP-SO-814-R 18.8.2018



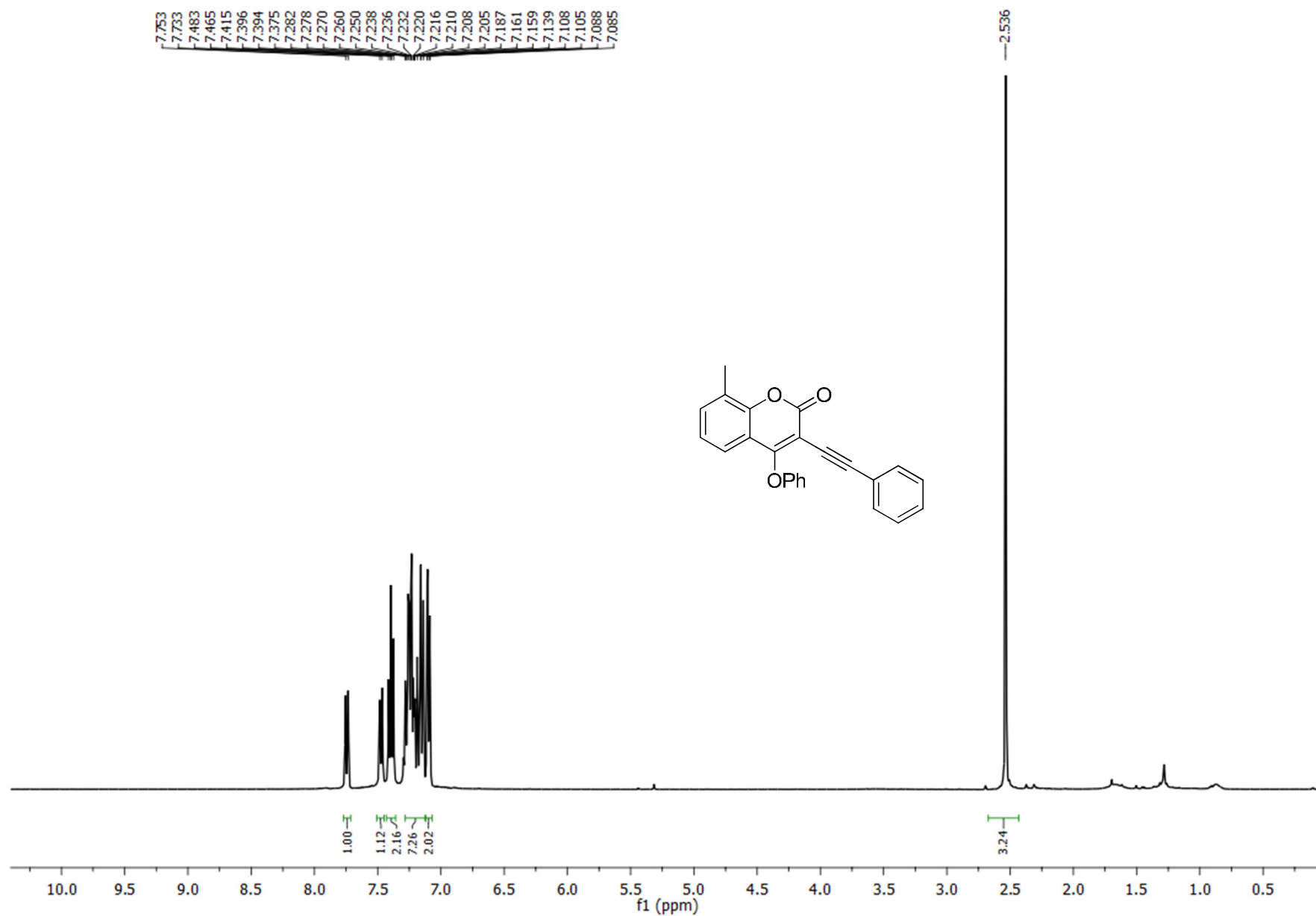
¹H NMR of 4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5a)



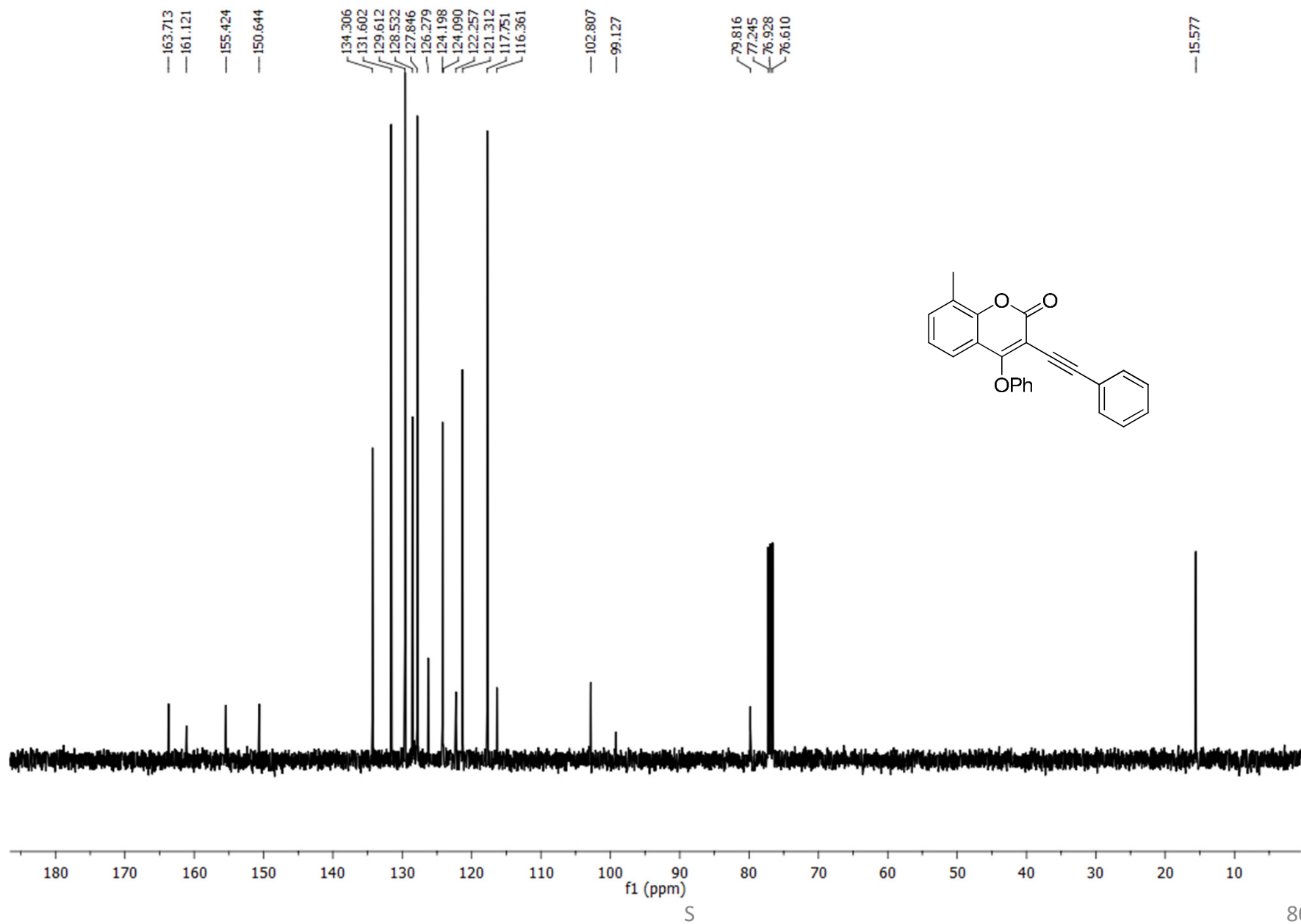
¹³C NMR of 4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5a)



¹H NMR of 8-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5b)



¹³C NMR of 8-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5b)



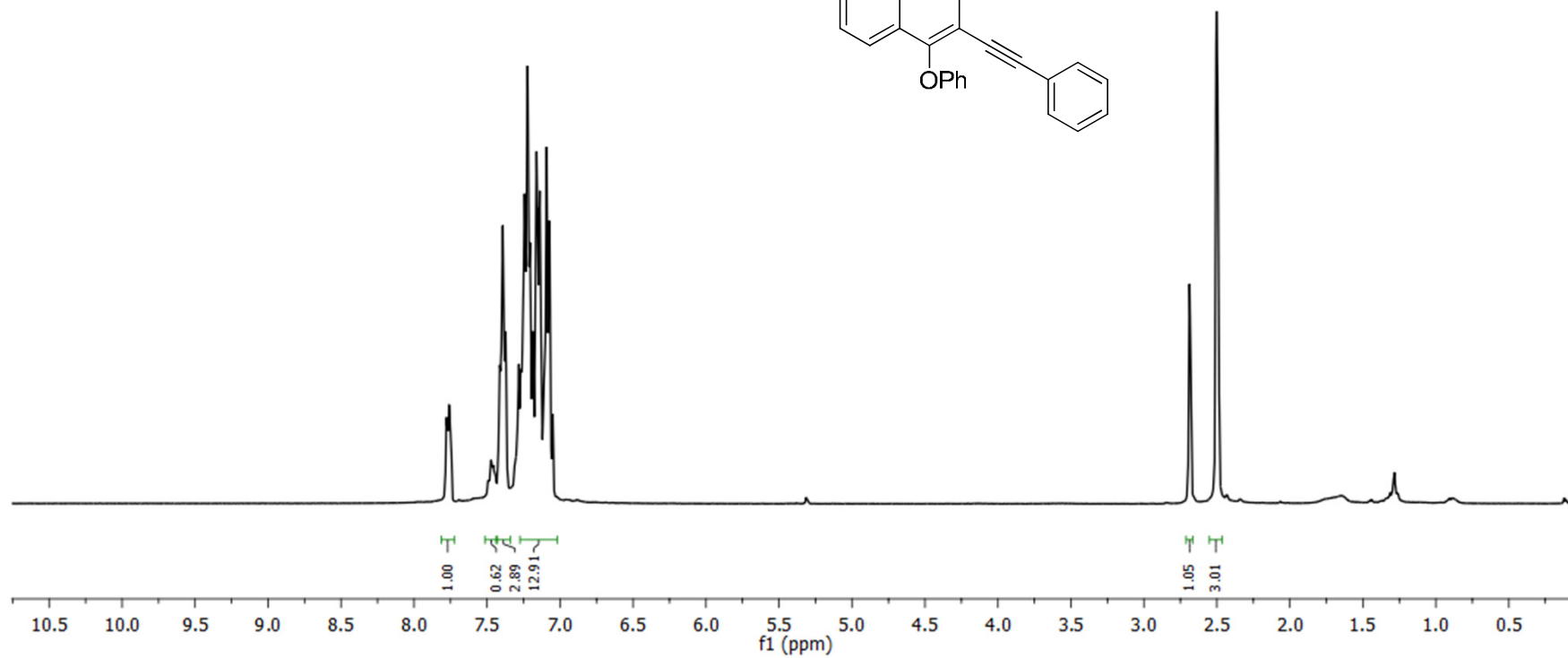
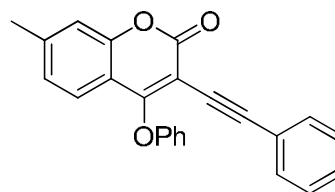
^1H NMR of 7-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5c)

19.4.2018

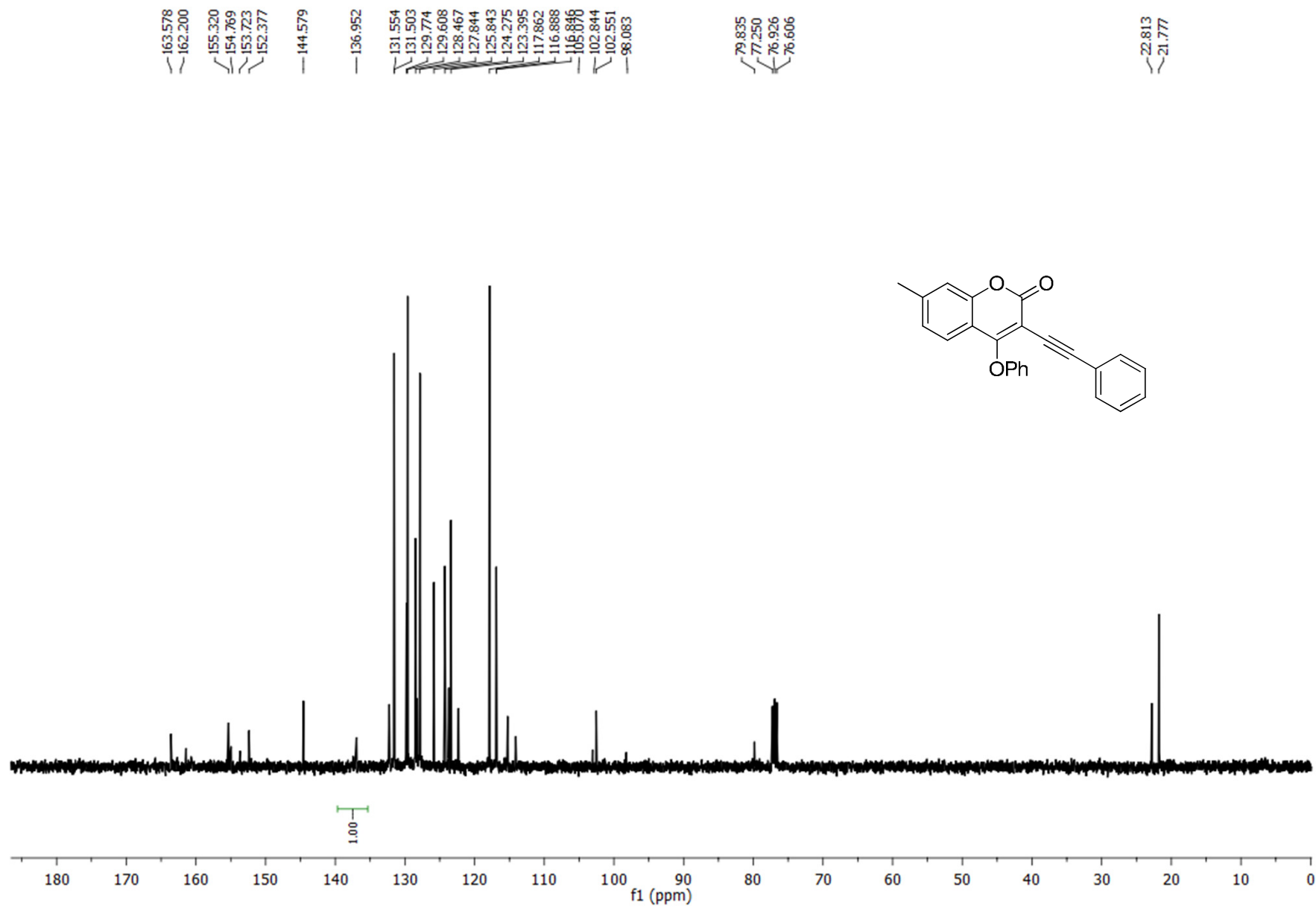
^1H of NP-IM-SON-mCresol-4HC 19.4.2018

7.778
7.761
7.473
7.456
7.412
7.393
7.373
7.281
7.268
7.242
7.223
7.206
7.186
7.160
7.139
7.092
7.073
7.049

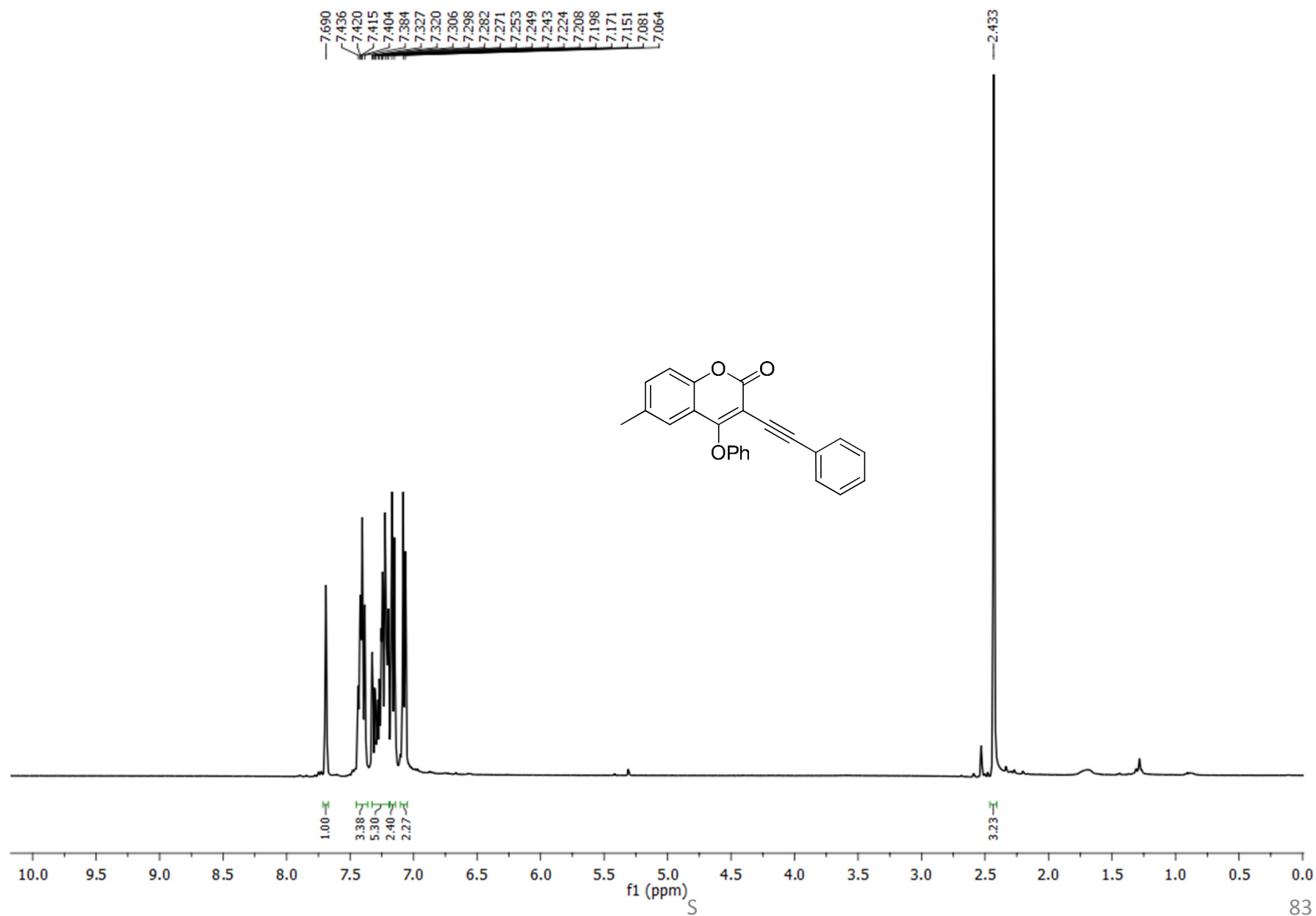
2.688
2.503



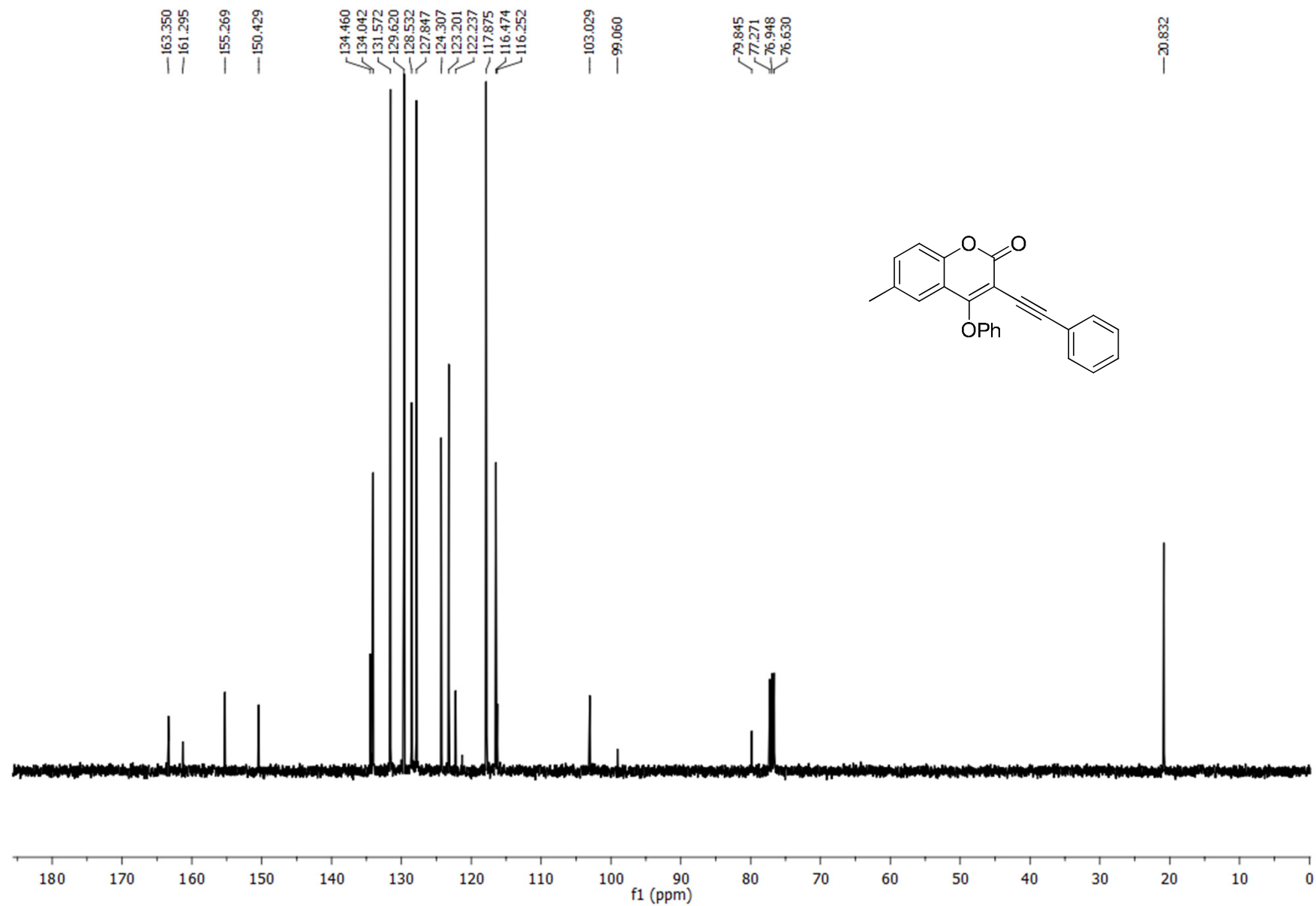
¹³C NMR of 7-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5c)



¹H NMR of 6-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5d)



¹³C NMR of 6-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5d)

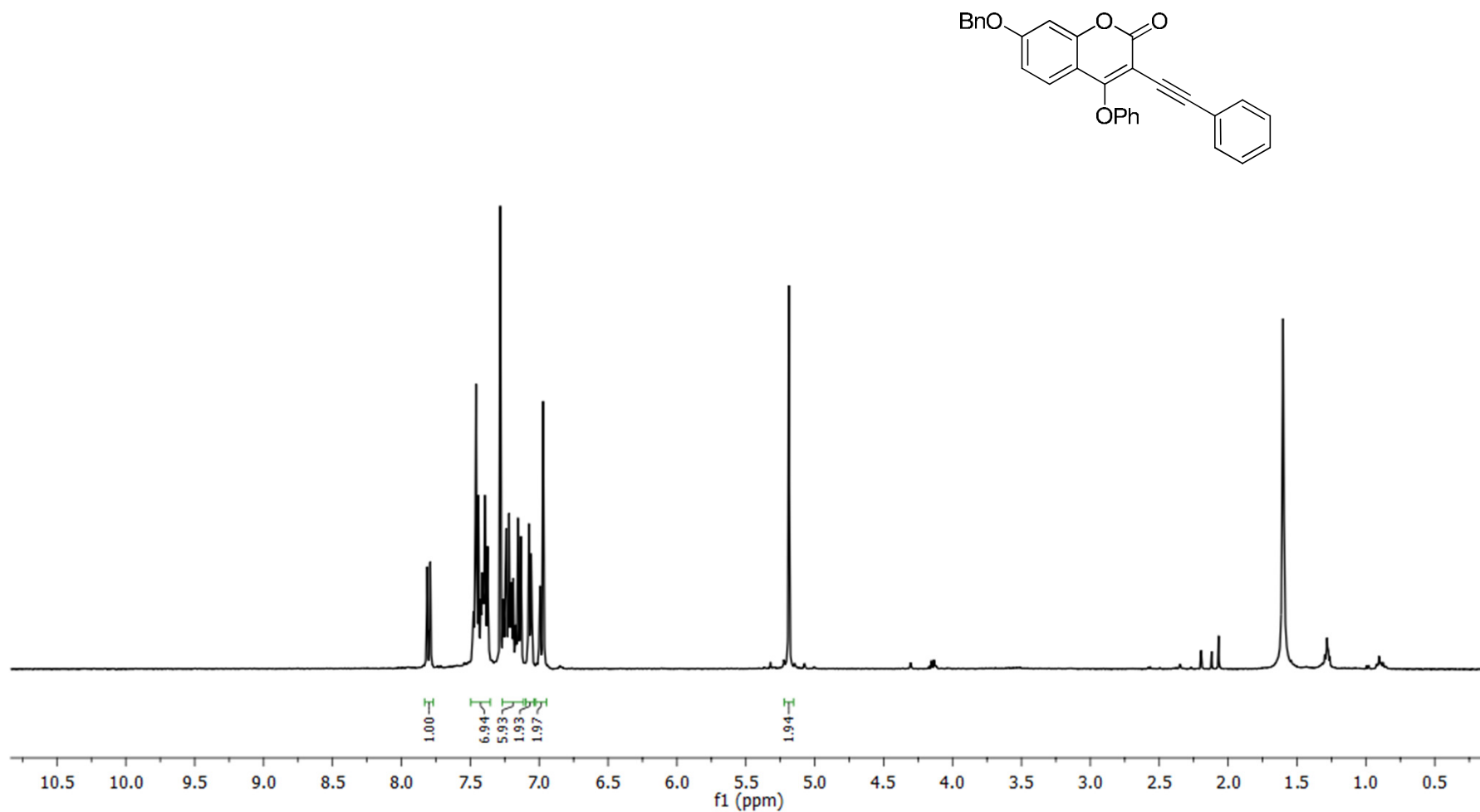


¹H NMR of 7-(benzyloxy)-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5e)

13.4.2018

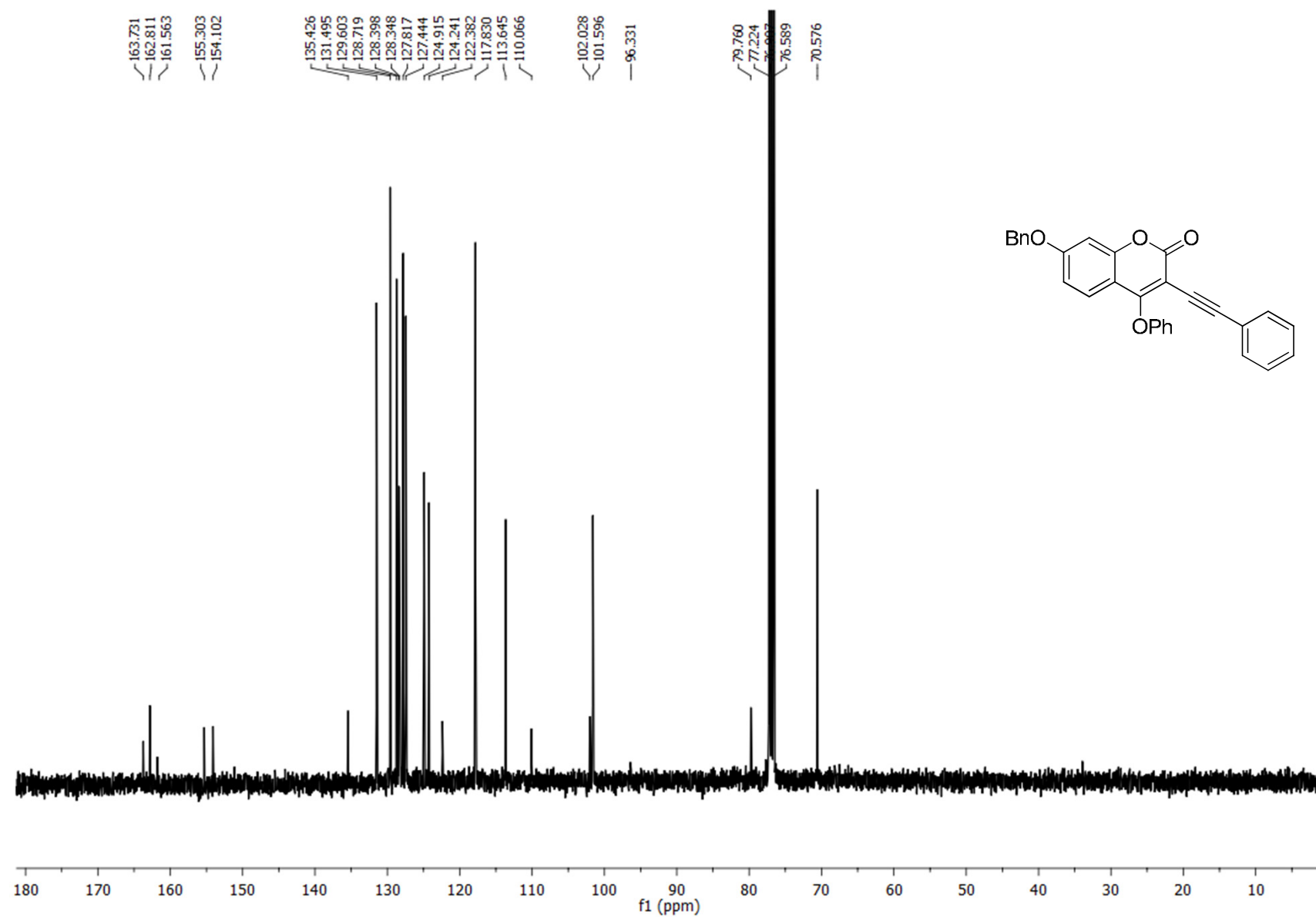
1H of NP-IM-SON-3OBr4HC

13.4.2018

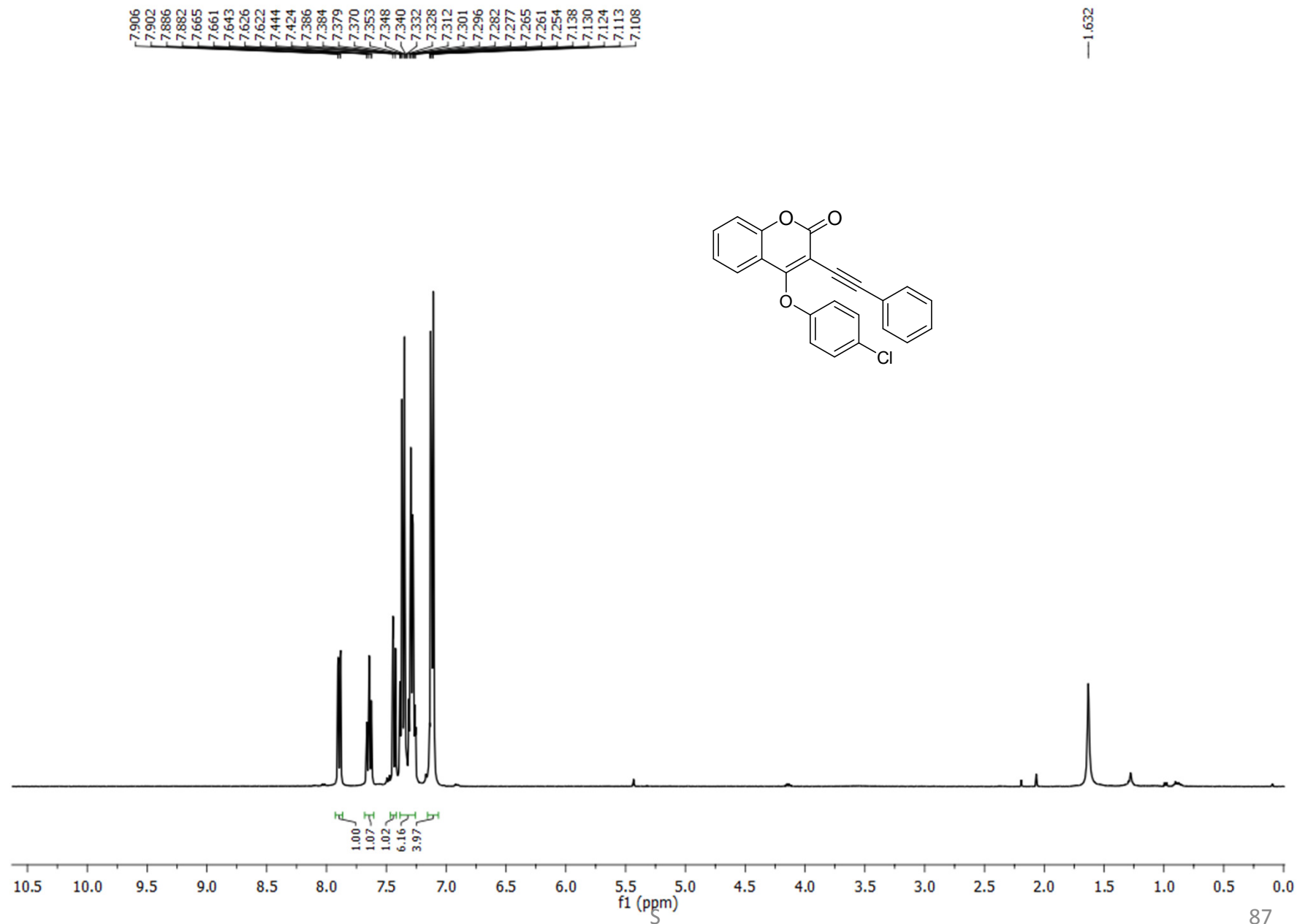


S

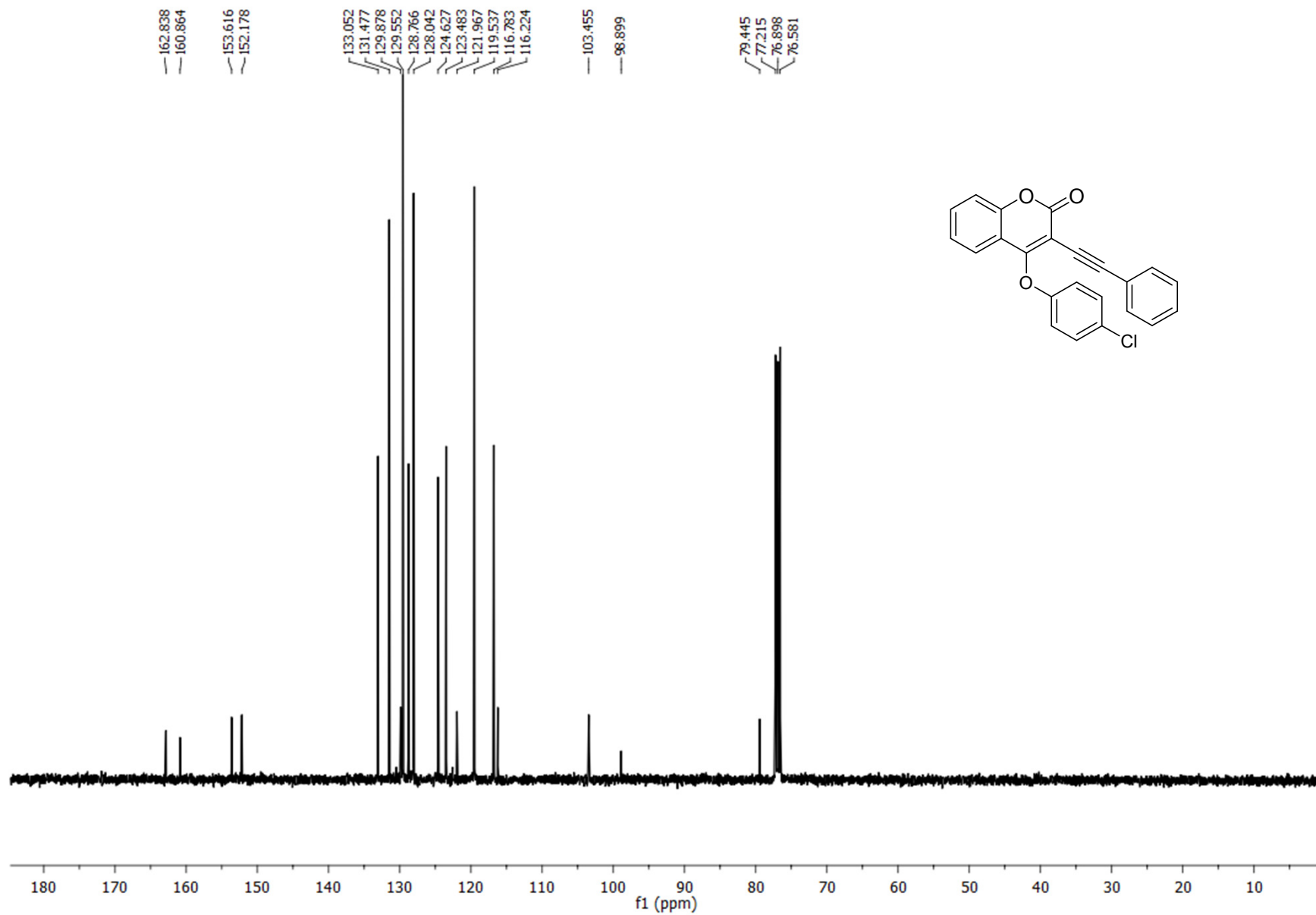
^{13}C NMR of 7-(benzyloxy)-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5e)



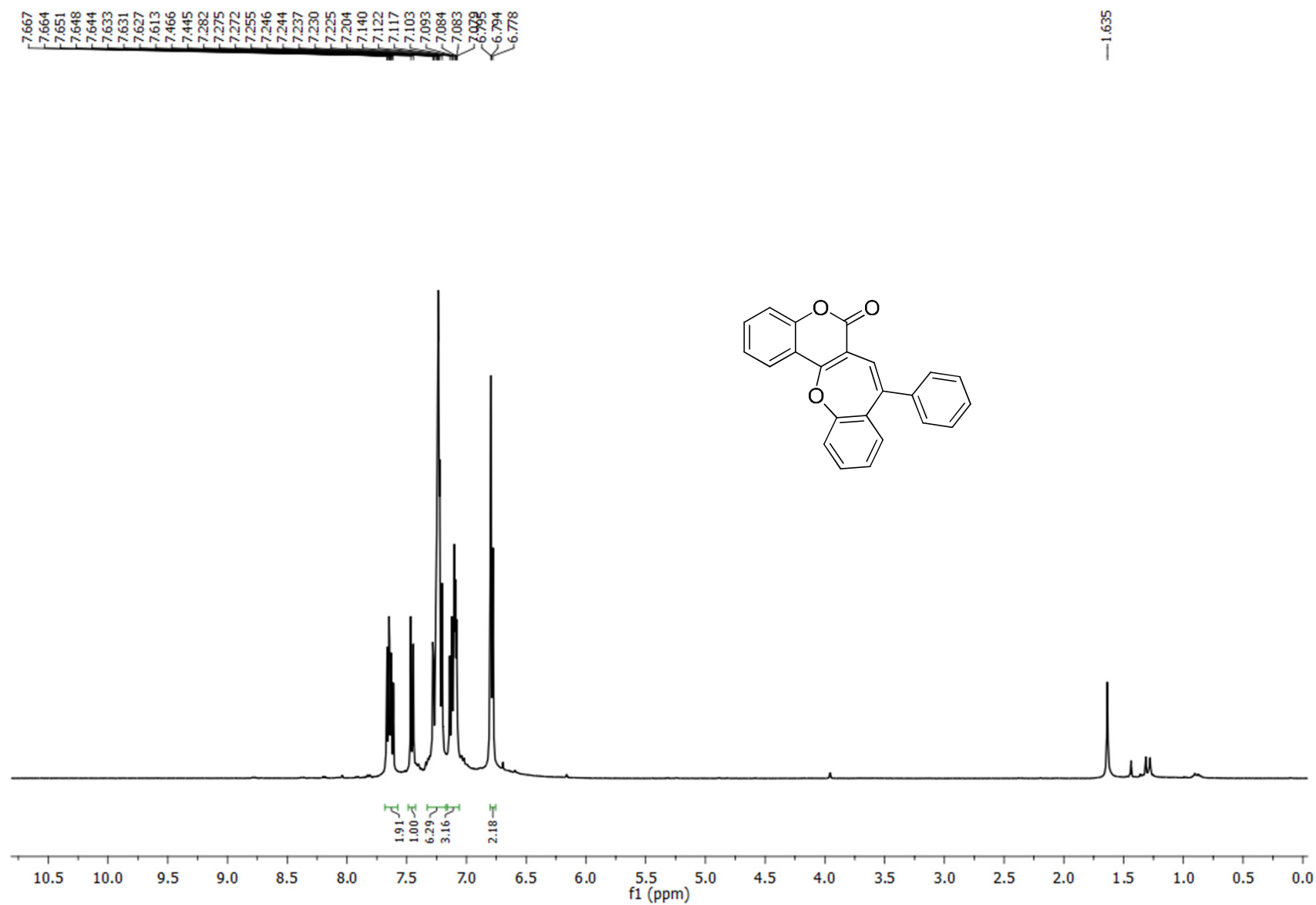
¹H NMR of 4-(4-chlorophenoxy)-3-(2-phenylethynyl)-2H-chromen-2-one (5f)



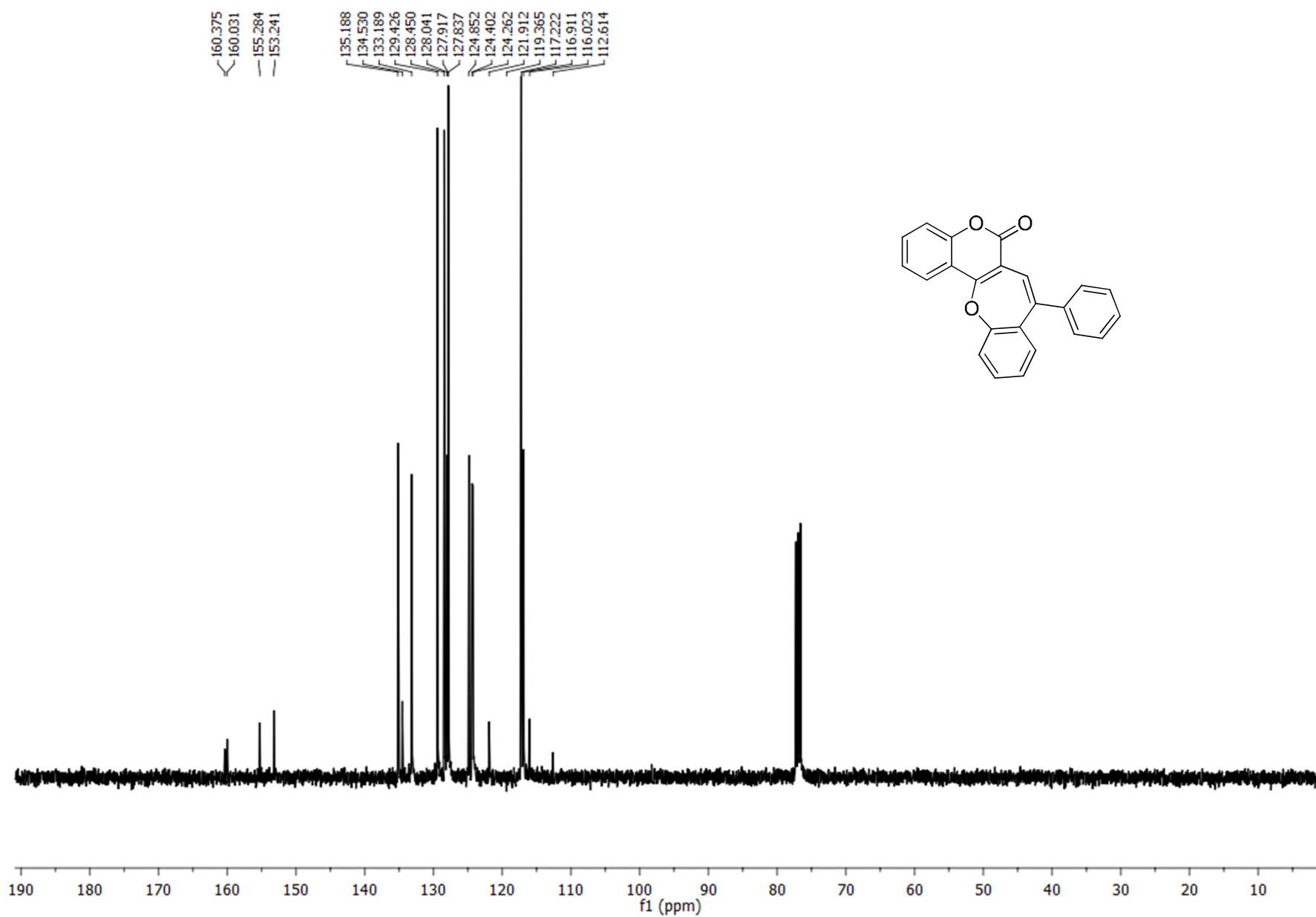
^{13}C NMR of 4-(4-chlorophenoxy)-3-(2-phenylethynyl)-2H-chromen-2-one (5f)



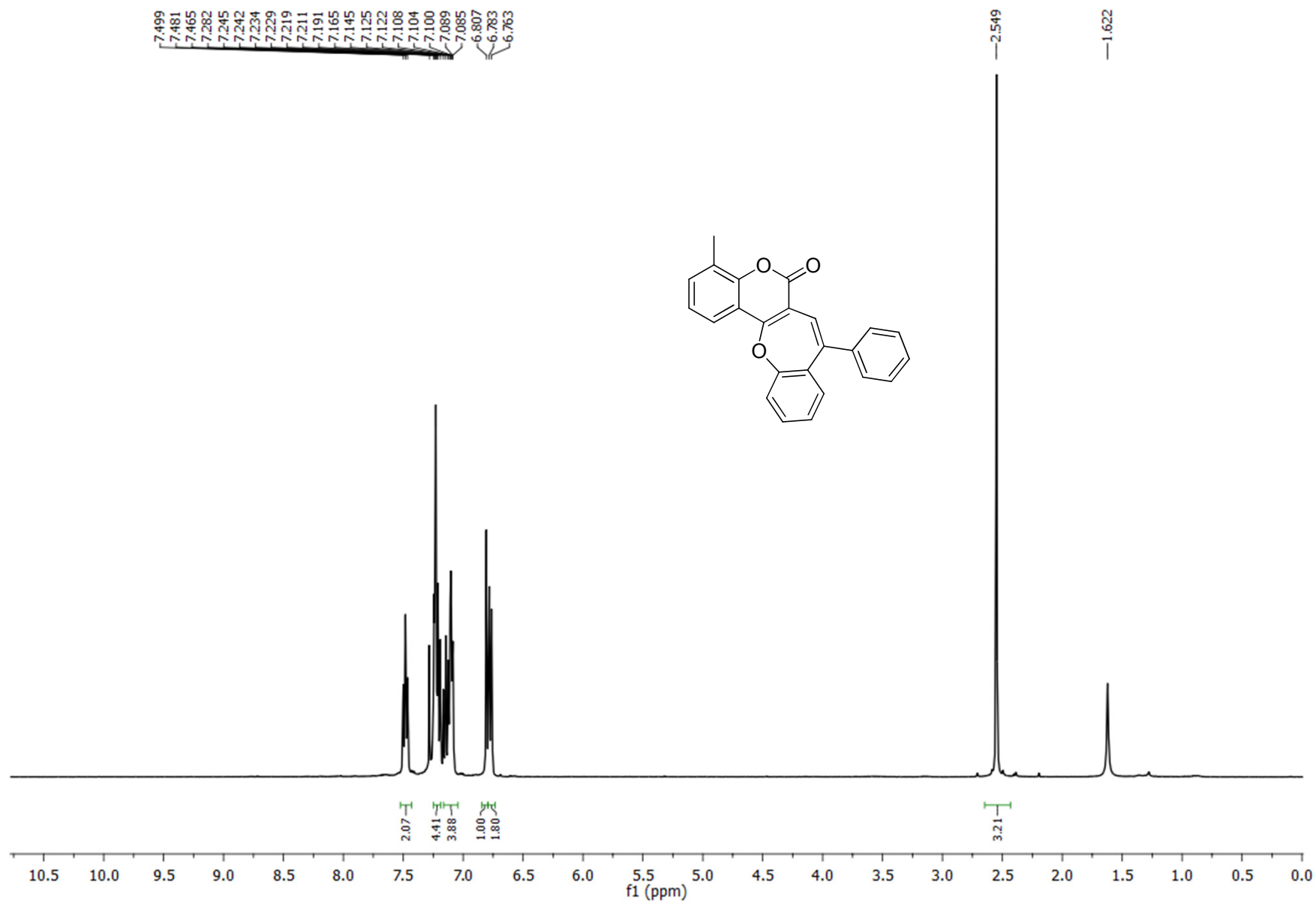
¹H NMR of 8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6a)



¹³C NMR of 8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6a)



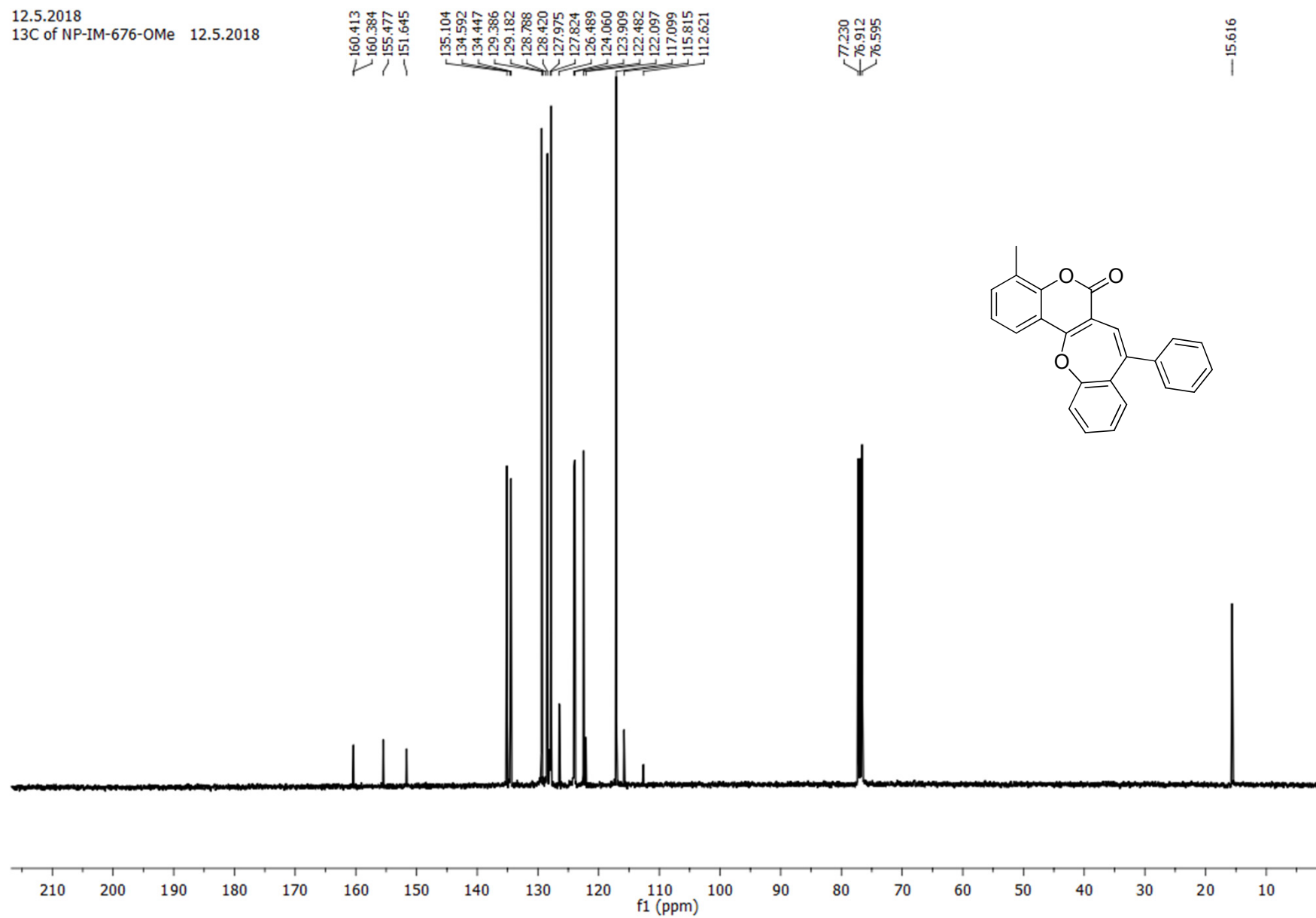
¹H NMR of 4-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6b)



¹³C NMR of 4-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6b)

12.5.2018

13C of NP-IM-676-OMe 12.5.2018



S

^1H NMR of 3-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6c)

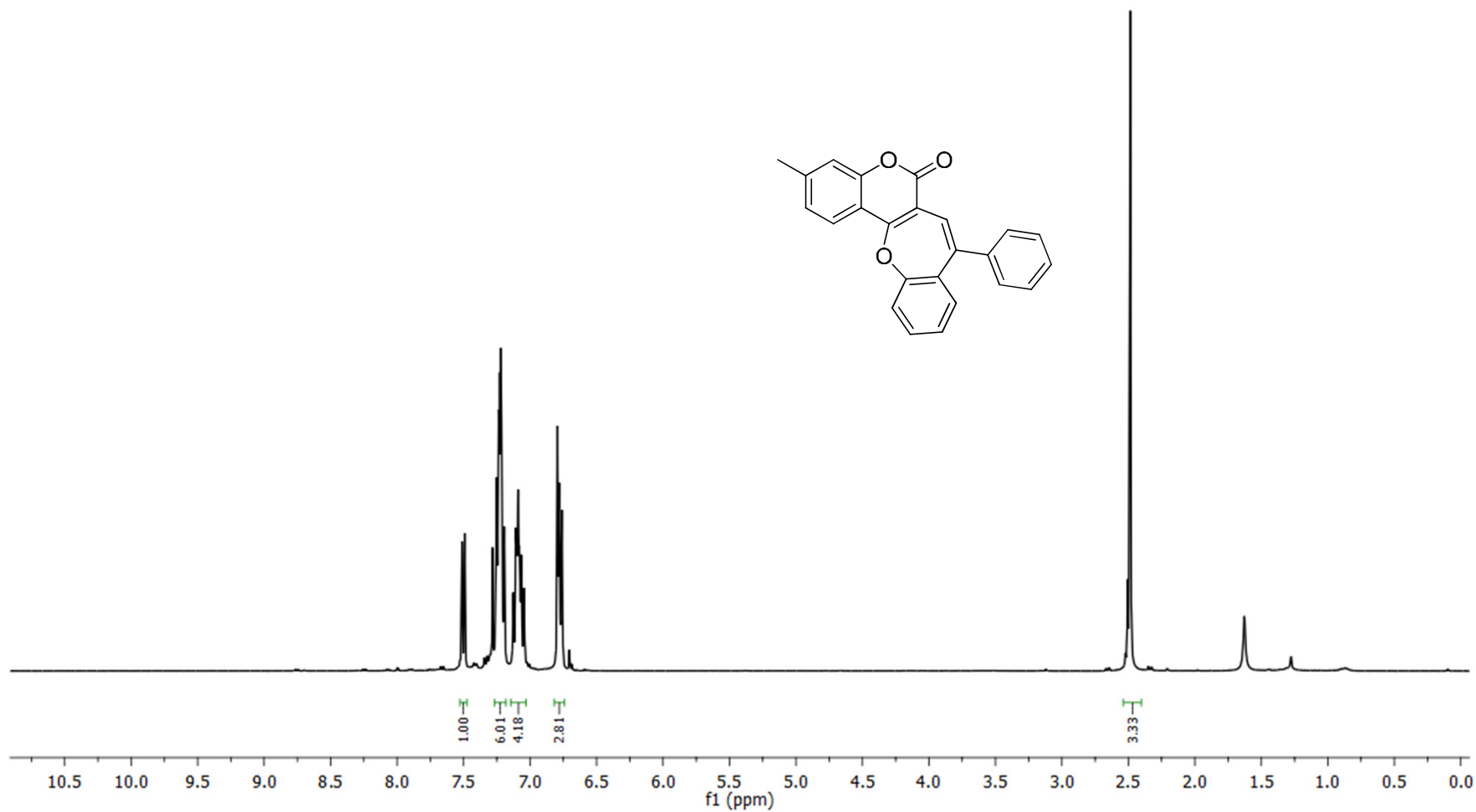
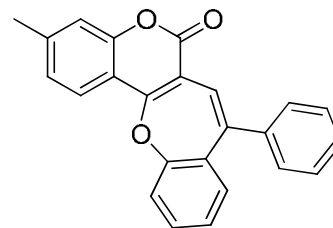
15.5.2018

1H of NP-IM-676-M-Me

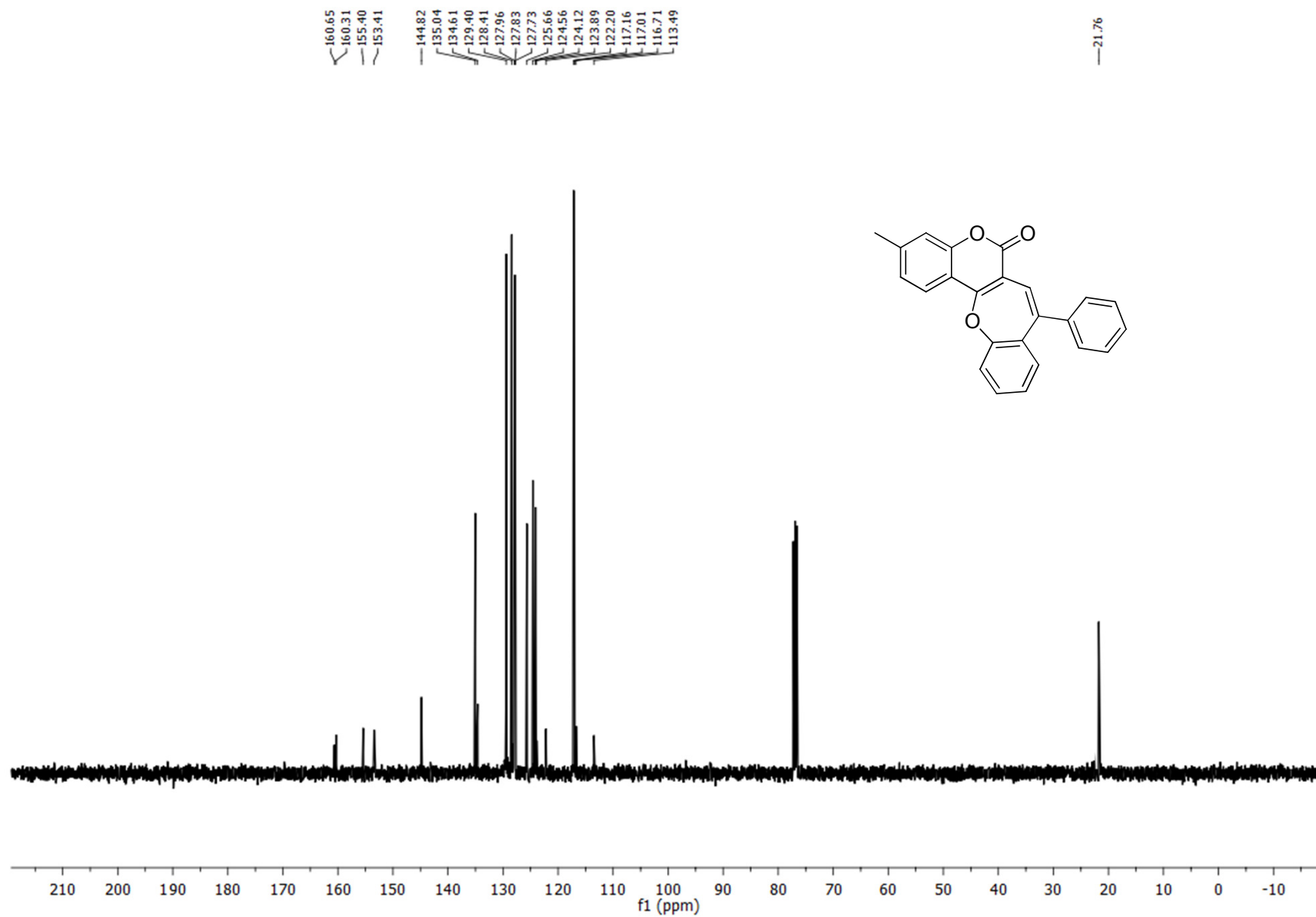
15.5.2018

7.512
7.491
7.282
7.251
7.234
7.227
7.220
7.215
7.194
7.126
7.107
7.100
7.090
7.082
7.076
7.067
7.046
6.794
6.781
6.761

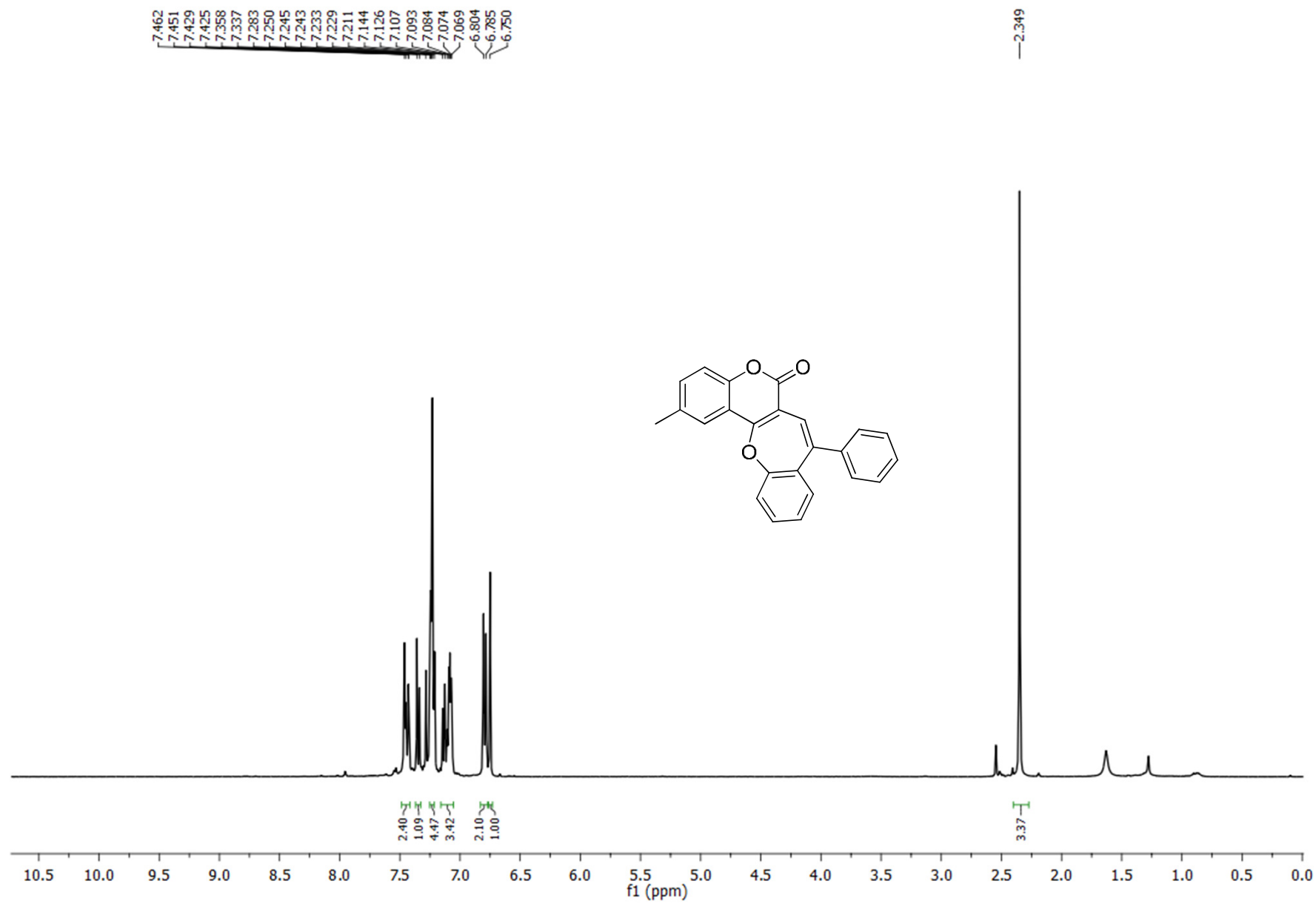
2.487



^{13}C NMR of 3-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6c)



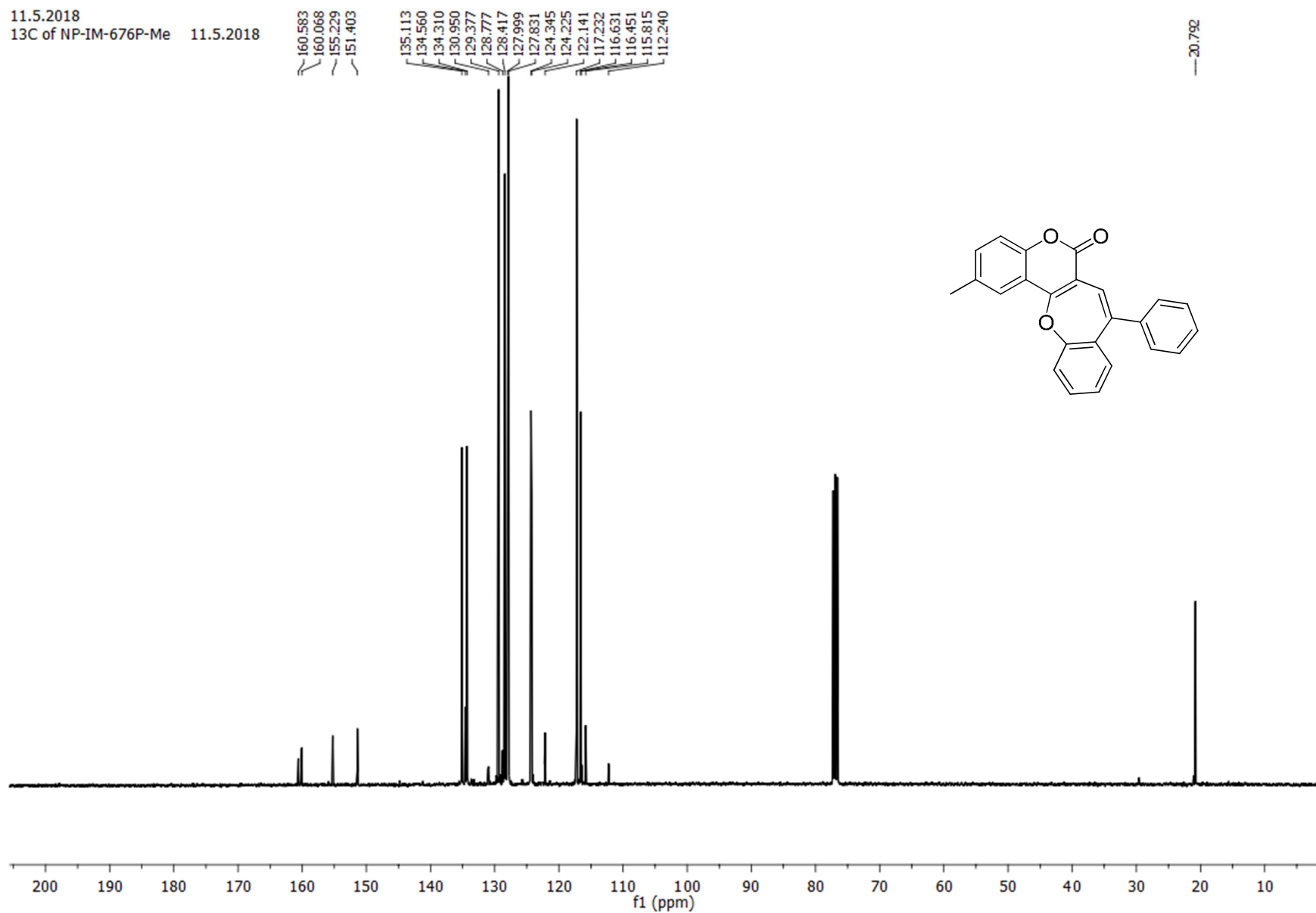
¹H NMR of 2-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6d)



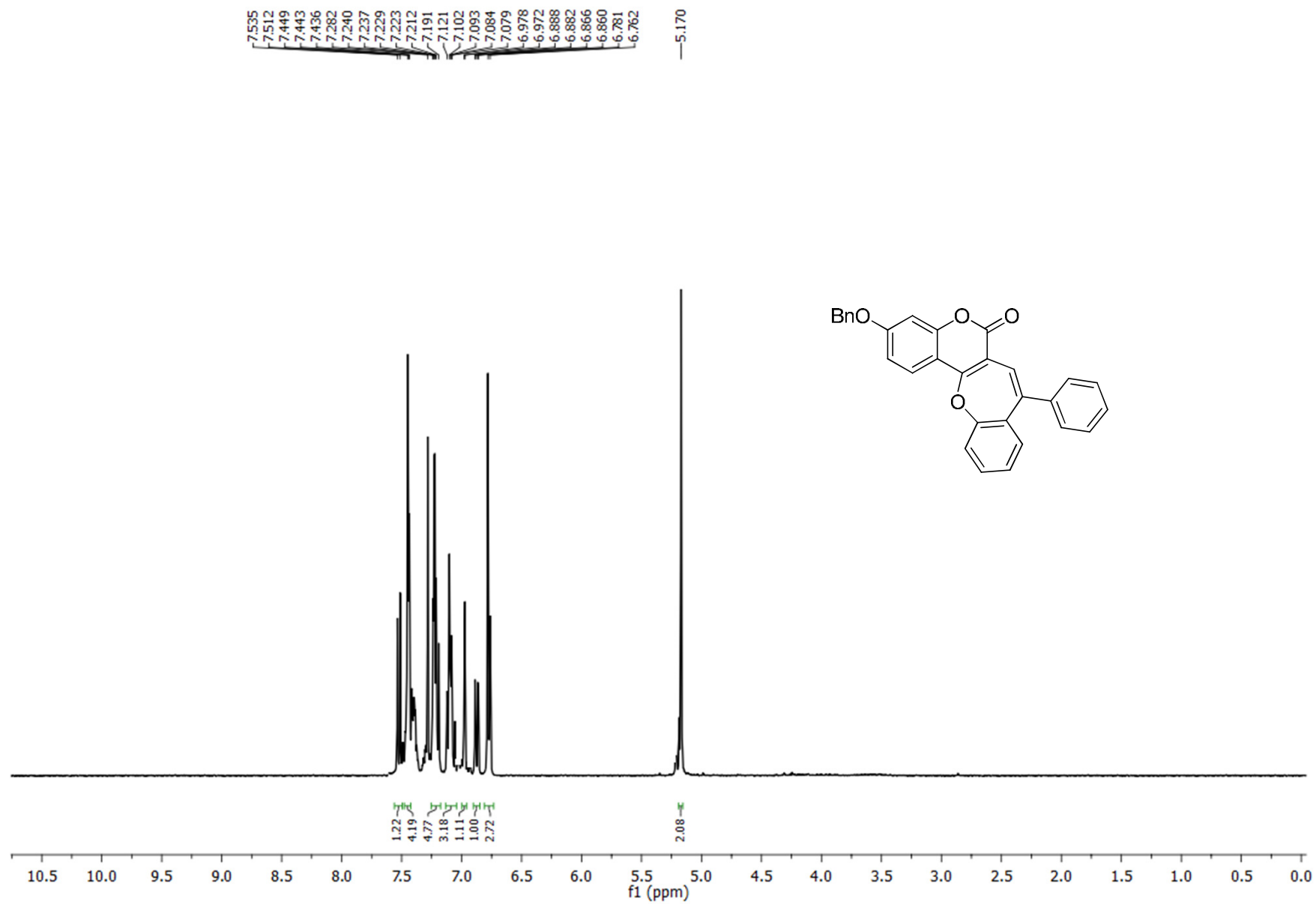
¹³C NMR of 2-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6d)

11.5.2018

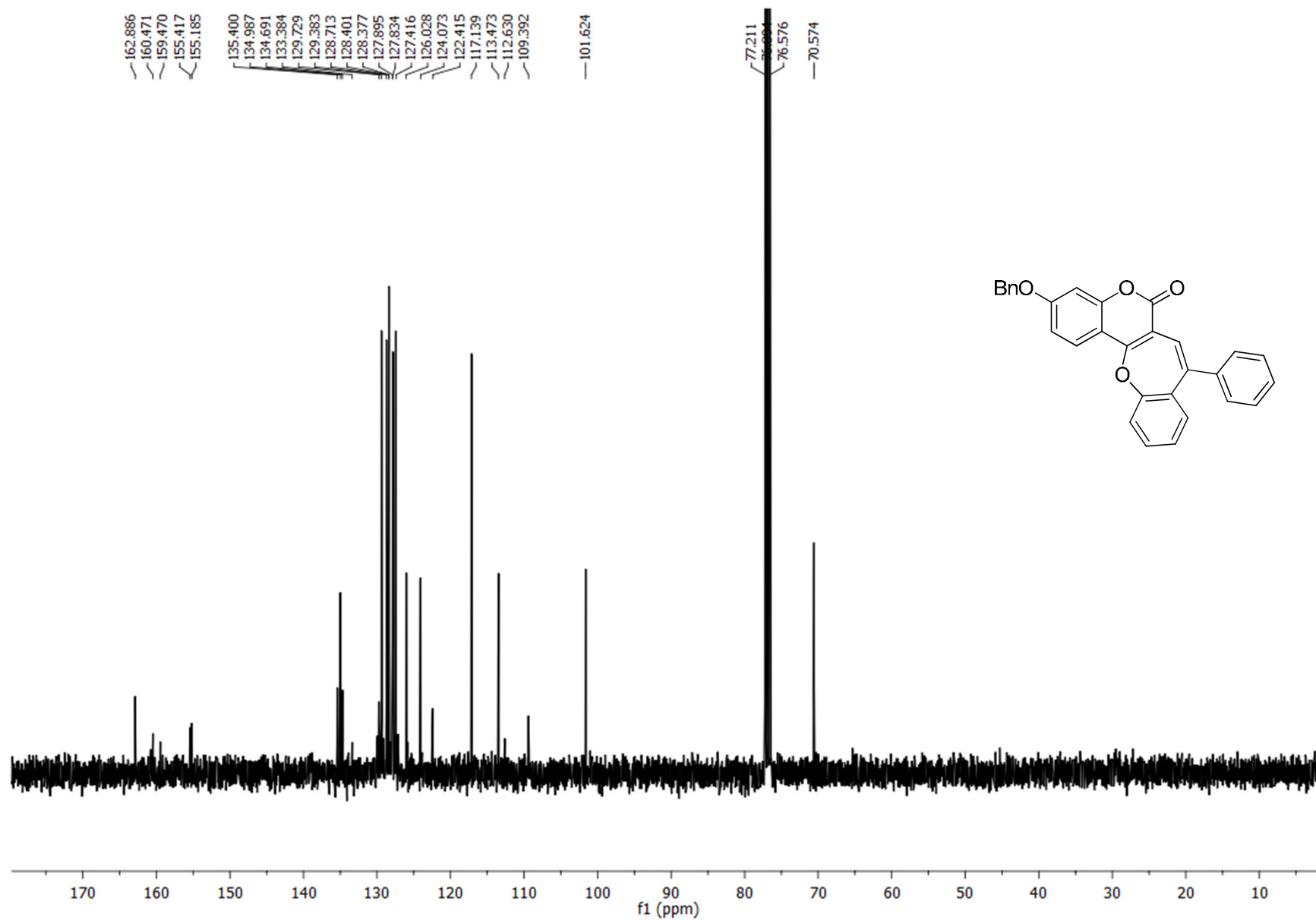
¹³C of NP-IM-676P-Me 11.5.2018



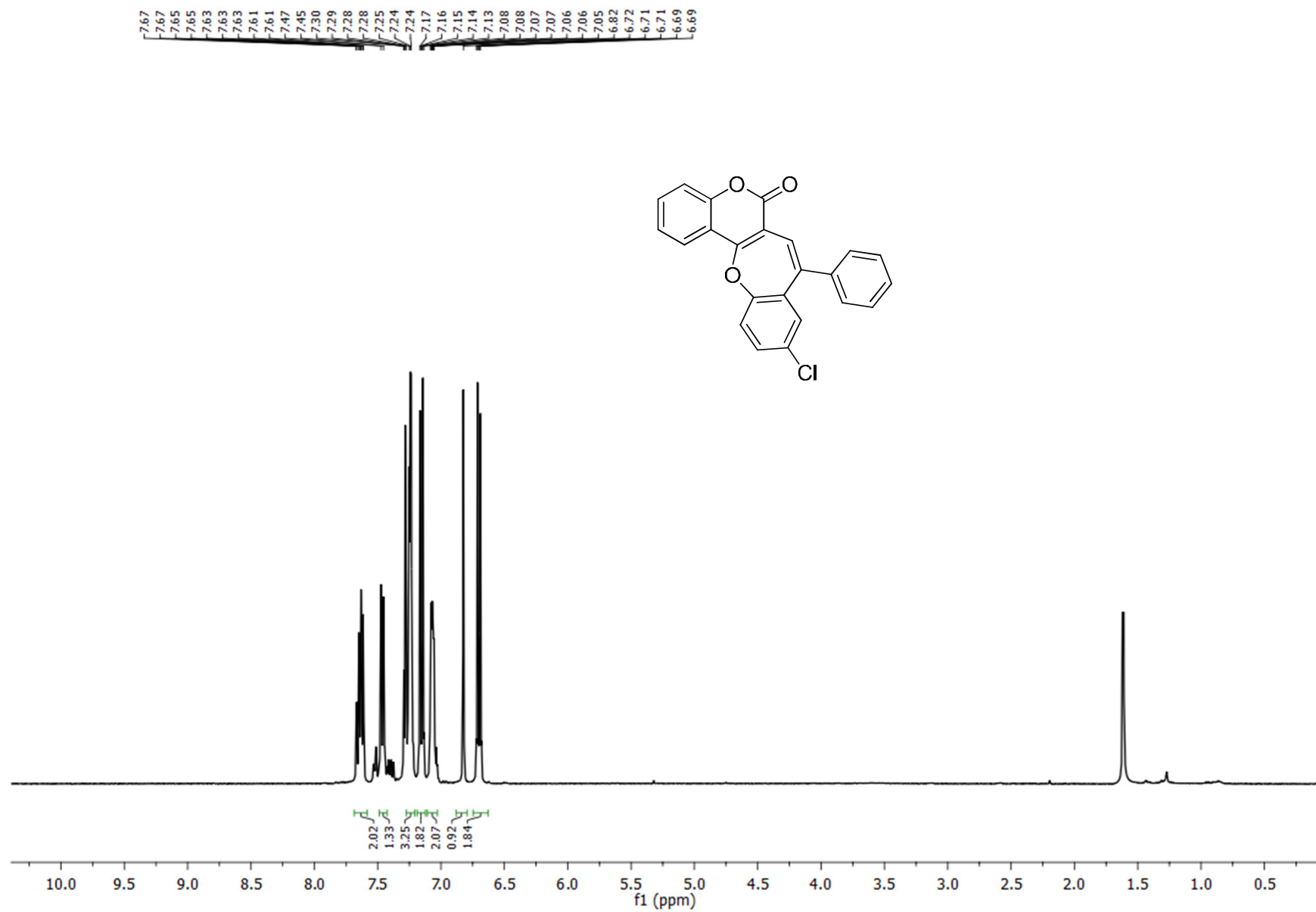
¹H NMR of 3-(benzyloxy)-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6e)



¹³C NMR of 3-(benzyloxy)-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6e)



¹H NMR of 10-chloro-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6f)



^{13}C NMR of 10-chloro-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6f)

