Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

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

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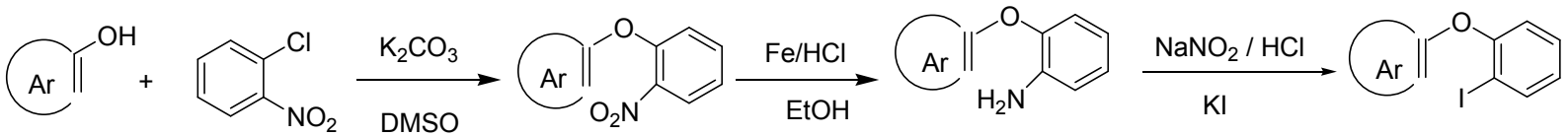
Synthesis of 2-iododiaryl ethers (1o-t)



Ar = C_6H_5-, 82%
Ar = 4-$CH_3C_6H_4$-, 95%
Ar = 4-ClC_6H_4-, 97%
Ar = 4-$OCH_3C_6H_4$-, 87%
Ar =1-naphthyl, 83%
Ar = 2-naphthyl, 87%

Ar = C_6H_5-, 80%
Ar = 4-$CH_3C_6H_4$-, 87%
Ar = 4-ClC_6H_4-, 92%
Ar = 4-$OCH_3C_6H_4$-, 92%
Ar =1-naphthyl, 89%
Ar = 2-naphthyl, 91%

1o, Ar = C_6H_5-, 88%
1p, Ar = 4-$CH_3C_6H_4$-, 86%
1q, Ar = 4-ClC_6H_4-, 83%
1r, Ar = 4-$OCH_3C_6H_4$-, 93%
1s, Ar =1-naphthyl, 85%
1t, Ar = 2-naphthyl, 81%

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 K_2CO_3 (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 acetae (3 x 20 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous Na_2SO_4, 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

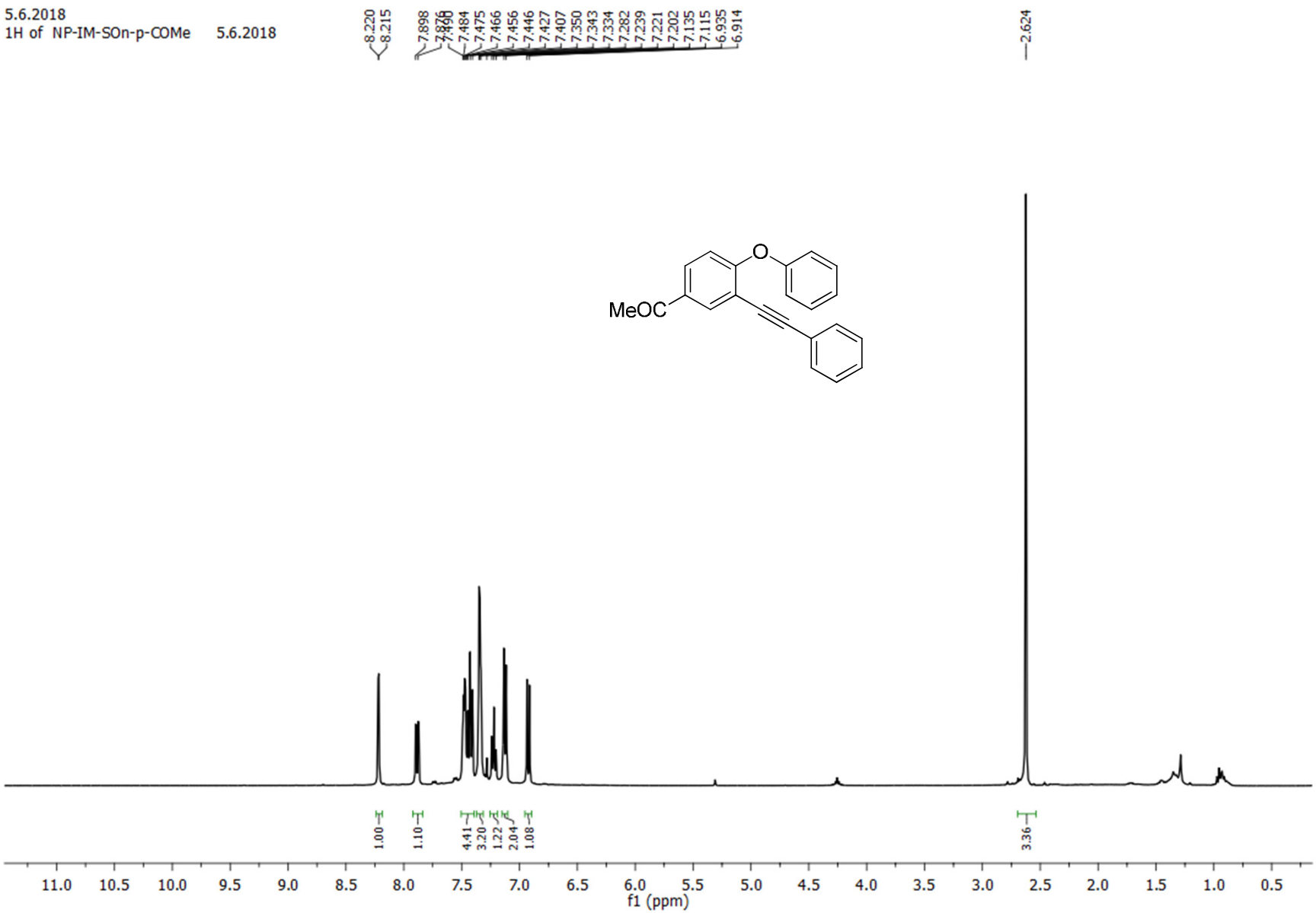
To a solution of 2-nitrodiaryl ether (4.0 mmol) in absolute ethanol (7 mL), iron power (10 eq.) was added at room temperature. Then, temperature of the reaction mixture was raised to 80°C and 1.0 mL of concentrated HCl was added dropwise over a period of 10 min. After 2h the reaction mixture was cooled 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

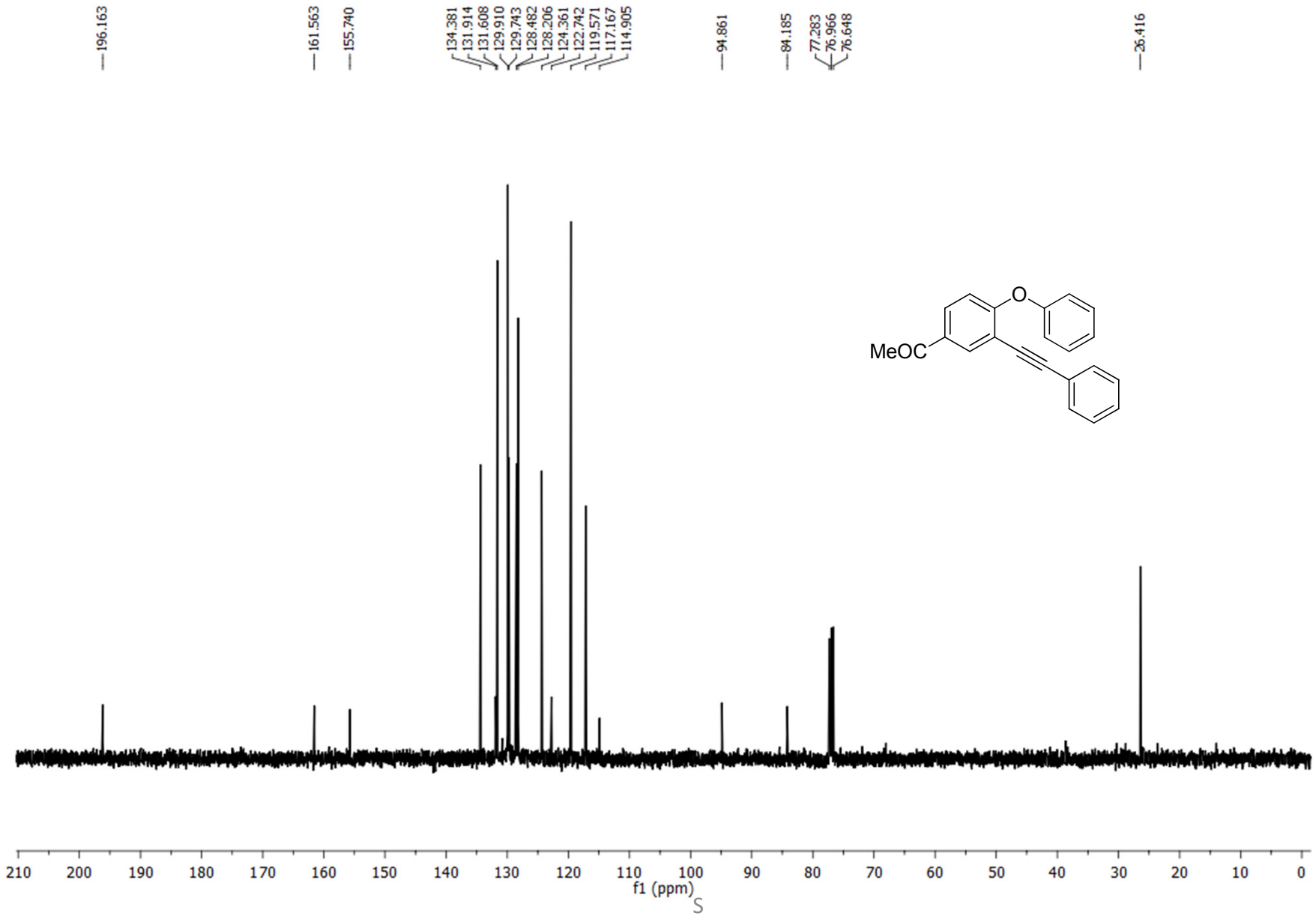
To a solution of 2-aminoodiaryl ether (4 mol) in 4.5 mL water, 1 mL of concentrated hydrochloric acid was added at 0°C and stirred for 10 min. To the reaction mixture an aqueous solution of sodium nitrite (4.8 mmol.) in 1 ml water was added at 0°C and stirred for 30 min. Then an aqueous solution of potassium iodide (6 mmol.) in 1 mL water was added to the reaction mixture at that temperature. The reaction mixture was allowed to come room temperature and stirred for 10 min and than 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 $Na_2S_2O_3$ 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 in under reduced pressure and the crude product purified by column chromatography to obtain the desired 2-iododiaryl ether.

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

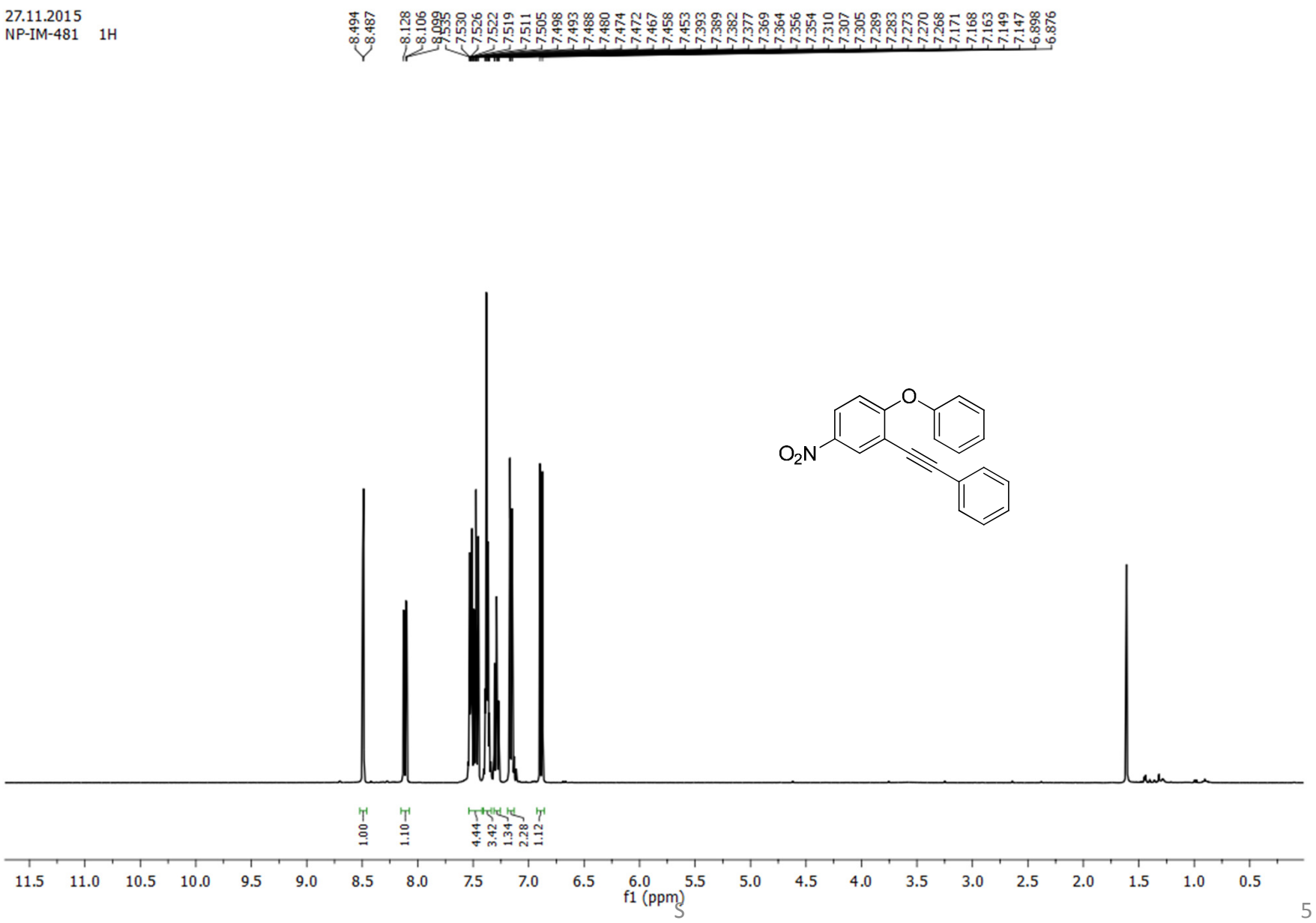
^{1}H NMR of 1-(4-phenoxy-3-(phenylethynyl)phenyl)ethanone (2a)



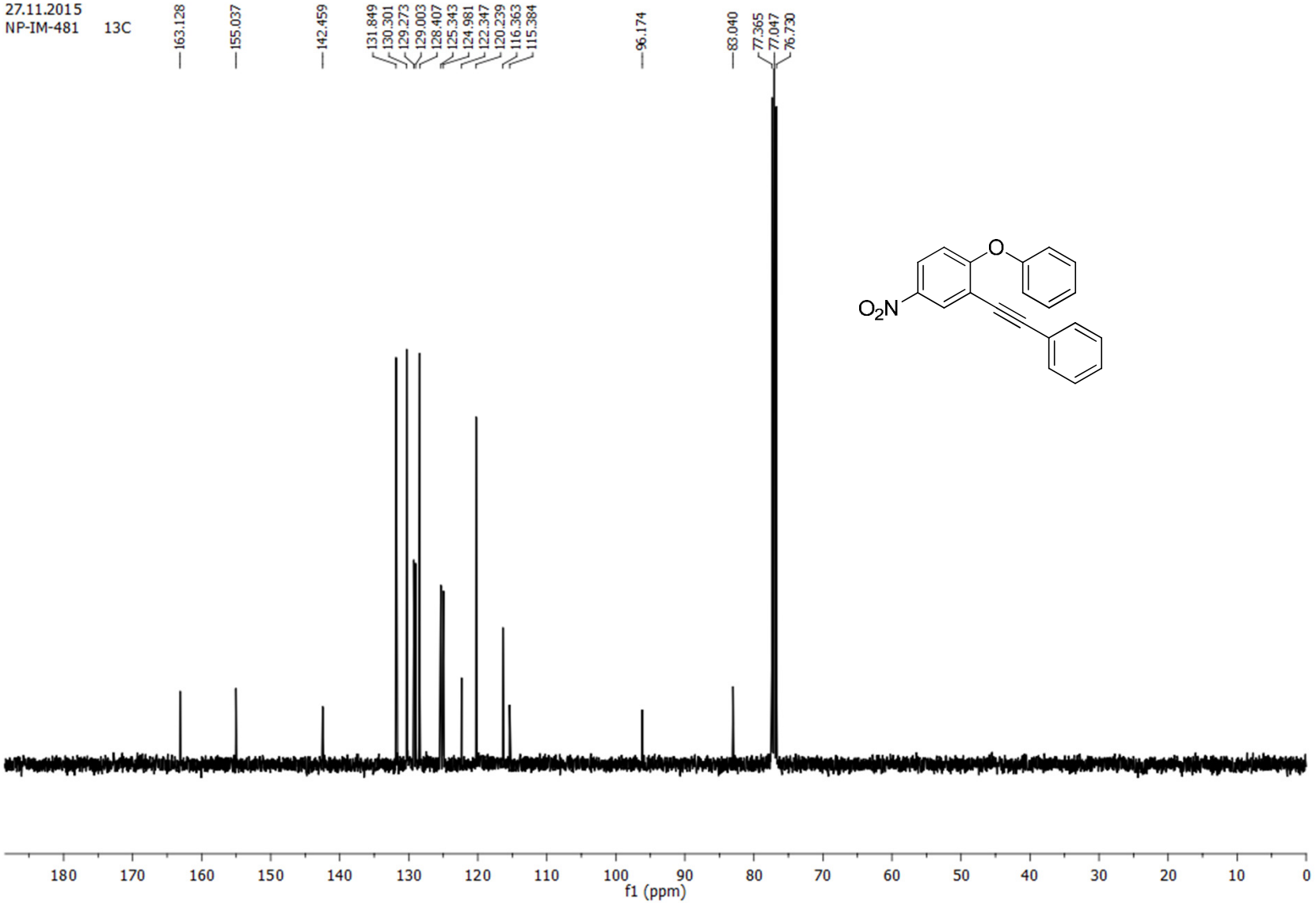
^{13}C NMR of 1-(4-phenoxy-3-(phenylethynyl)phenyl)ethanone (2a)



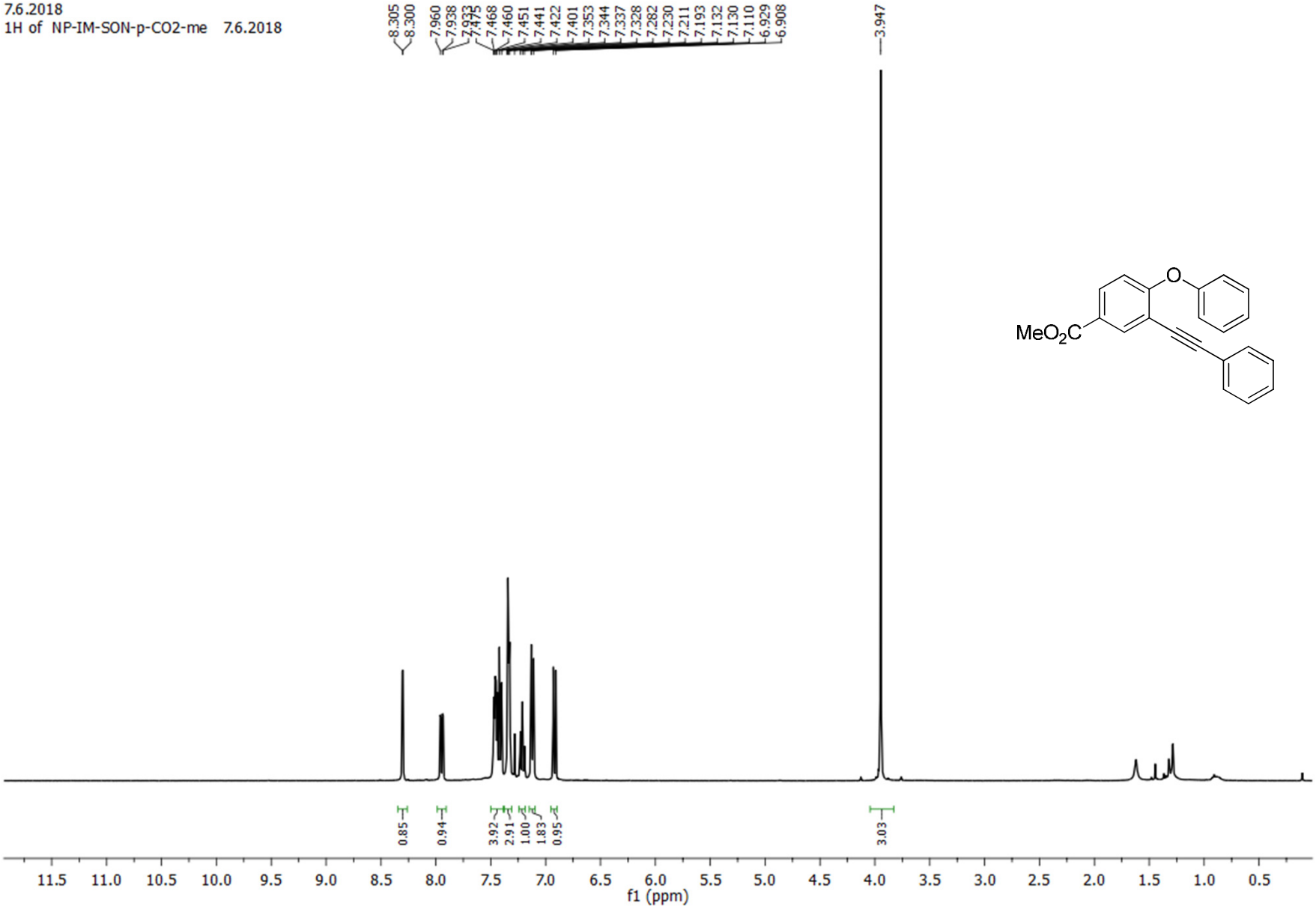
^{1}H NMR of 4-nitro-1-phenoxy-2-(phenylethynyl)benzene (2b)



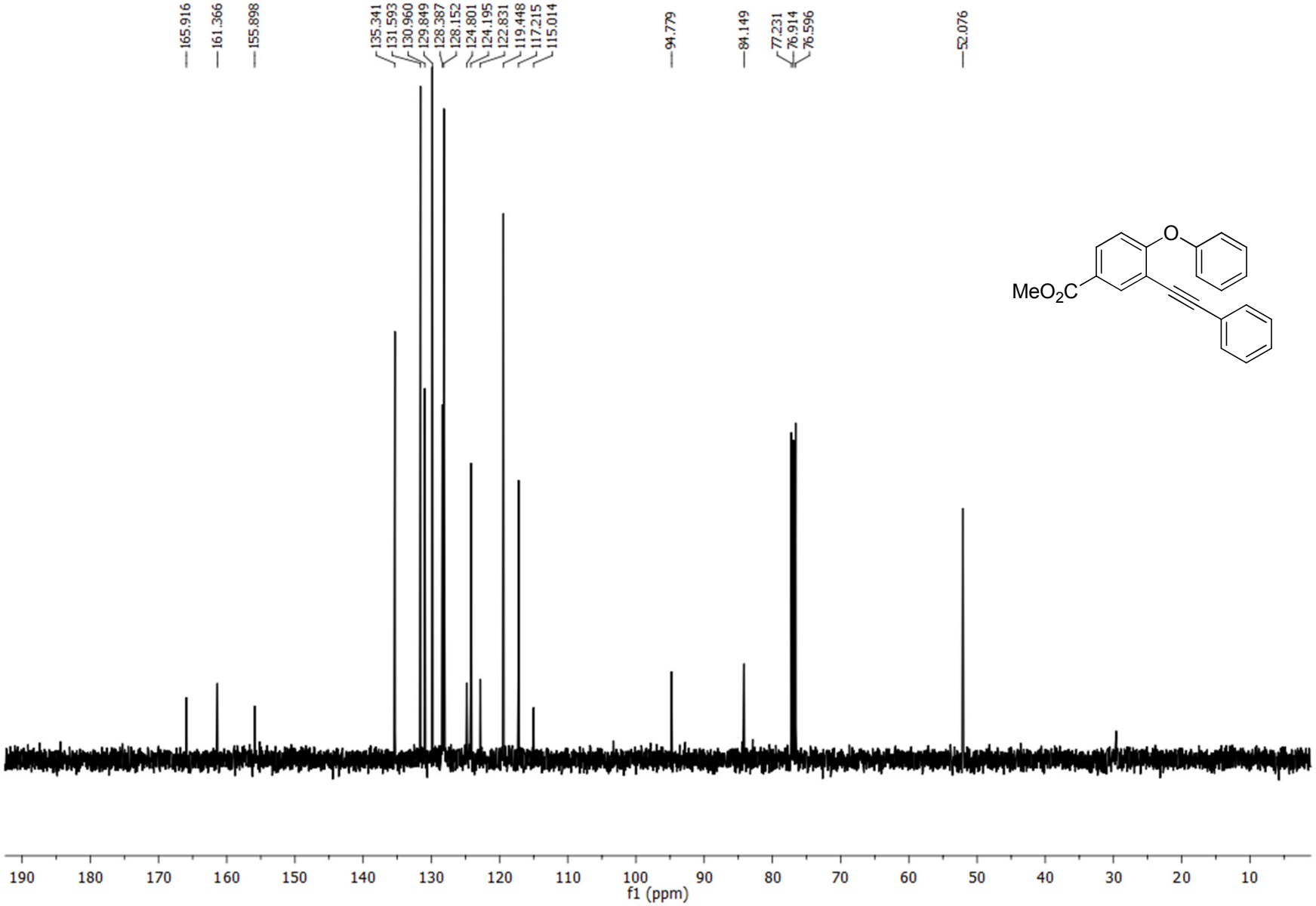
^{13}C NMR of 4-nitro-1-phenoxy-2-(phenylethynyl)benzene (2b)



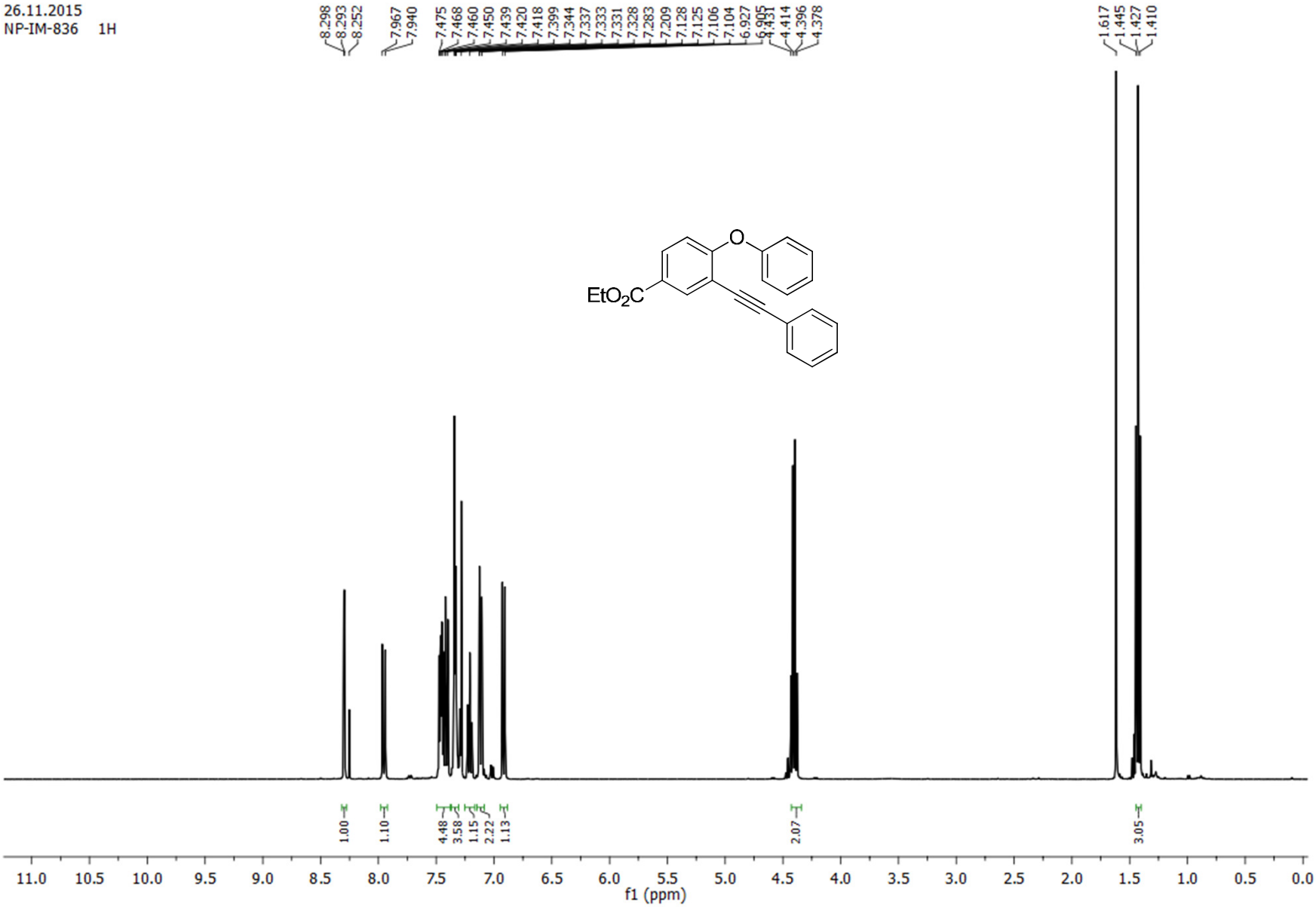
^{1}H NMR of methyl 4-phenoxy-3-(phenylethynyl)benzoate (2c)



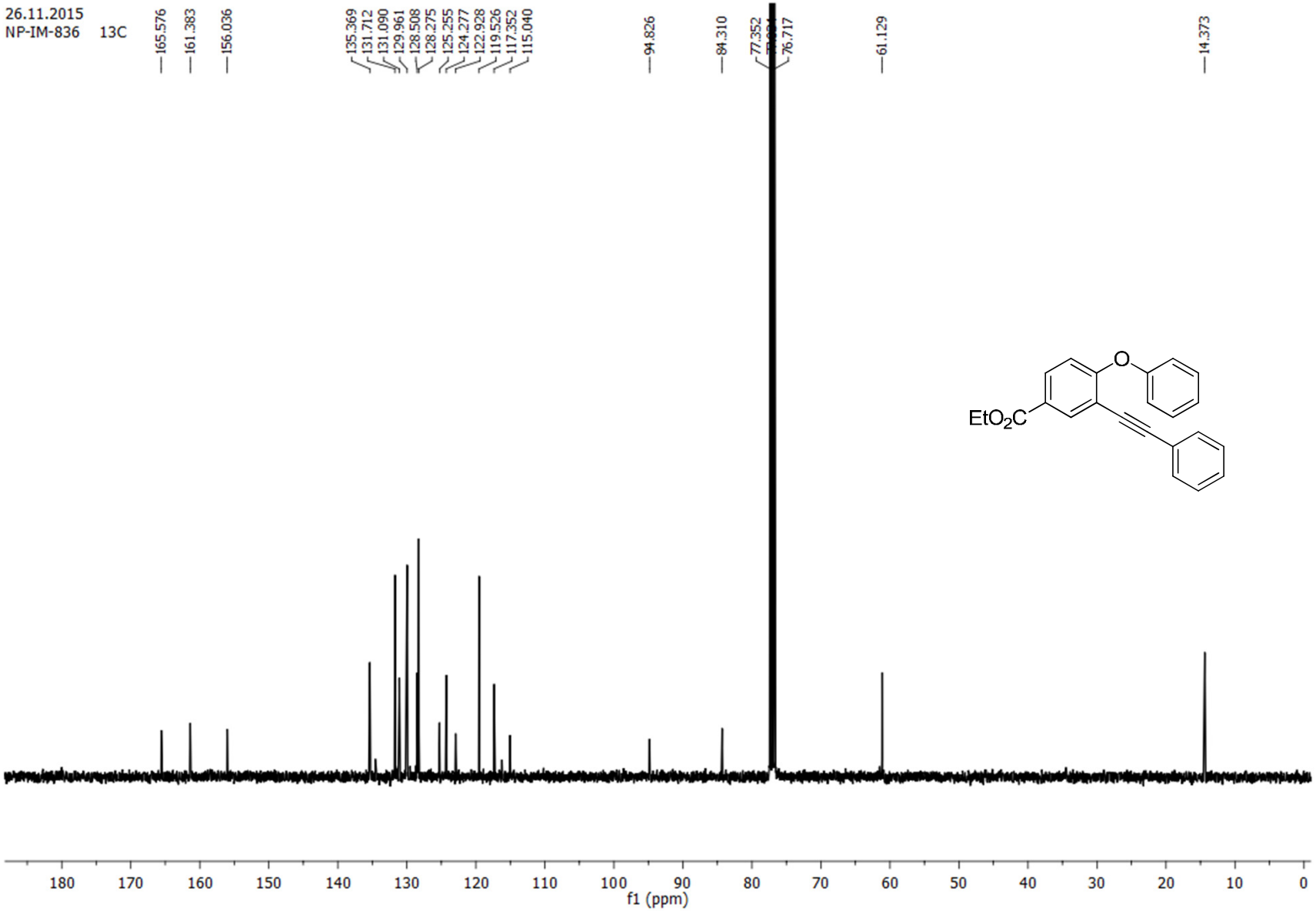
^{13}C NMR of methyl 4-phenoxy-3-(phenylethynyl)benzoate (2c)



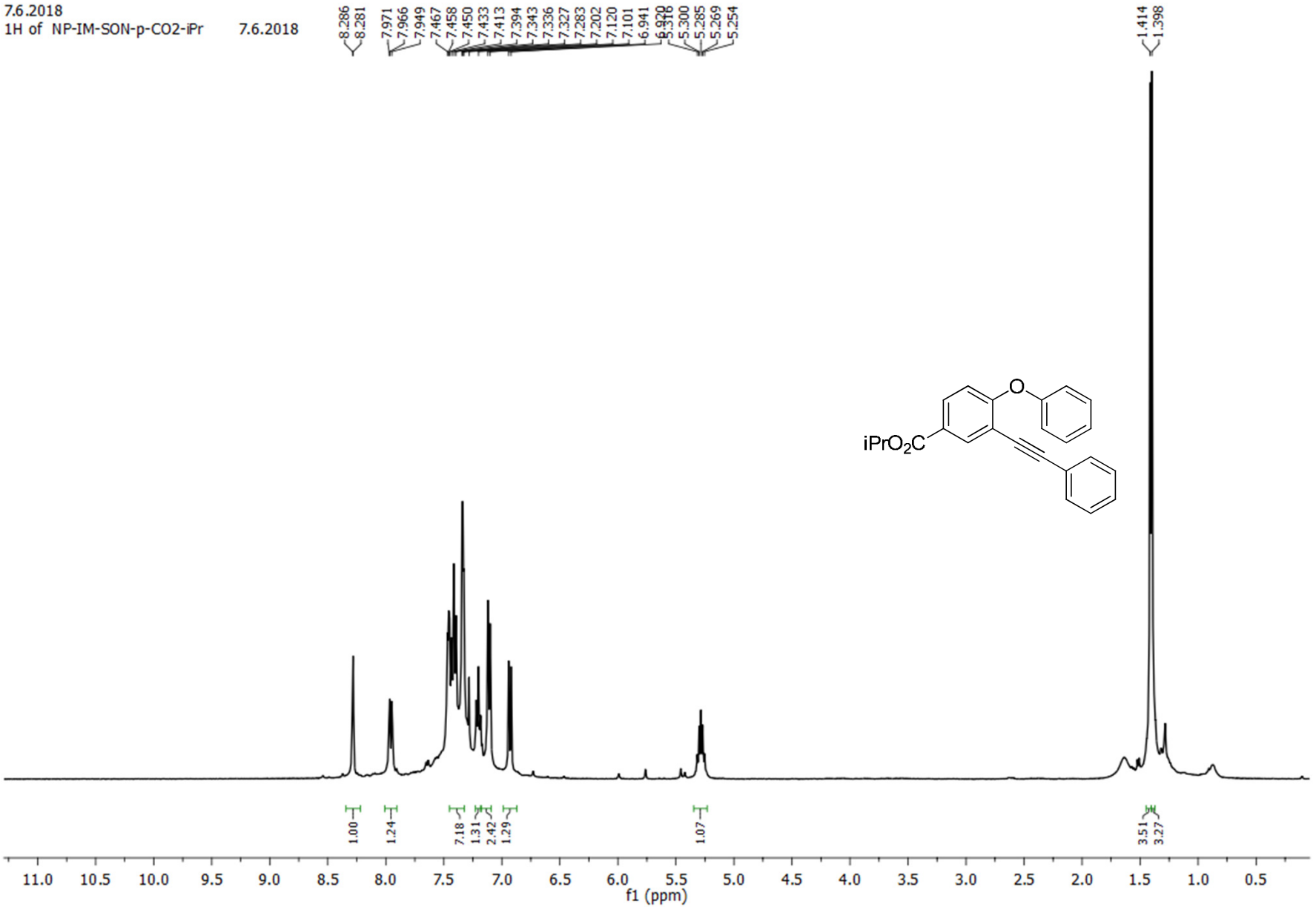
^{1}H NMR of ethyl 4-phenoxy-3-(phenylethynyl)benzoate (2d)



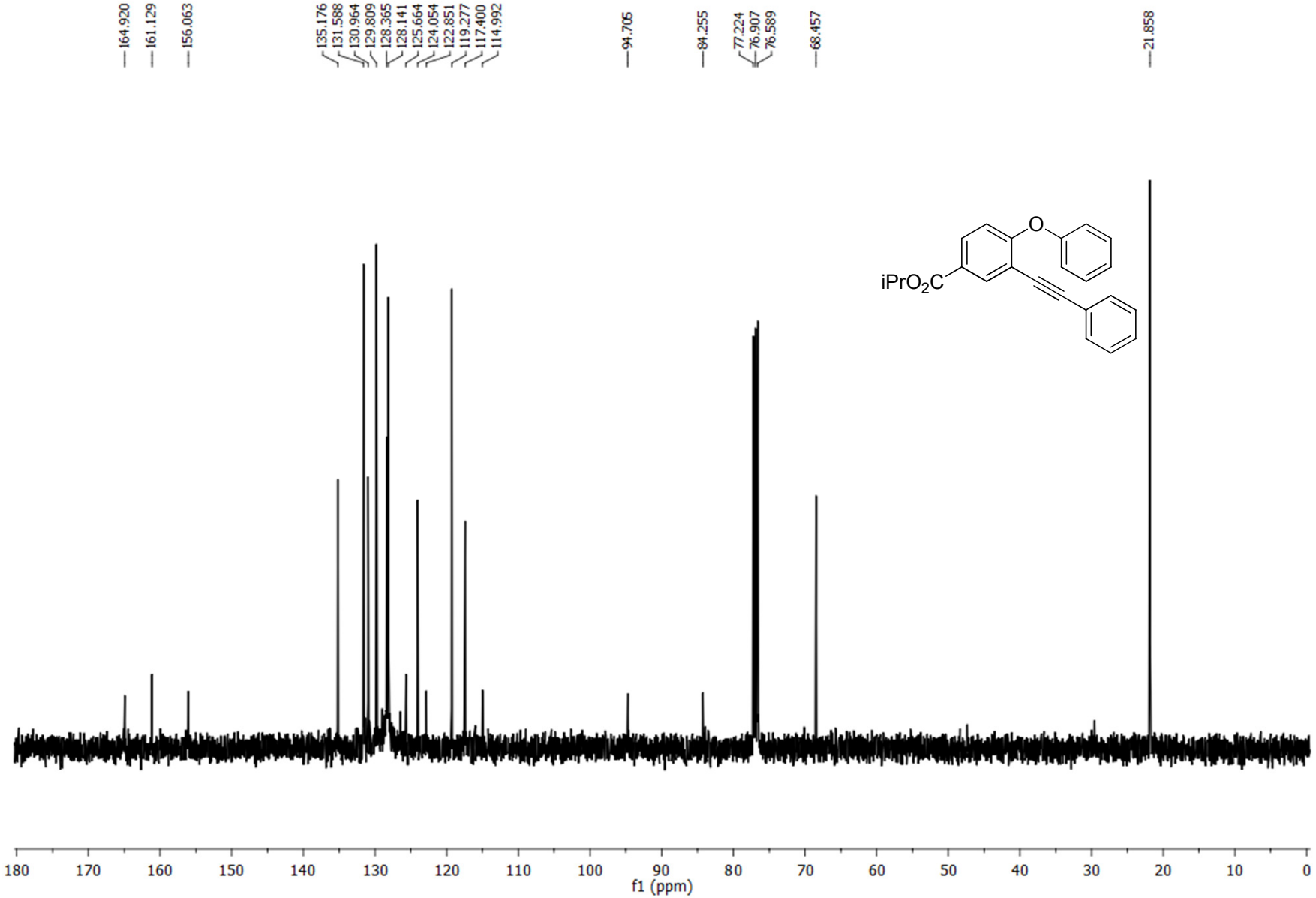
^{13}C NMR of ethyl 4-phenoxy-3-(phenylethynyl)benzoate (2d)



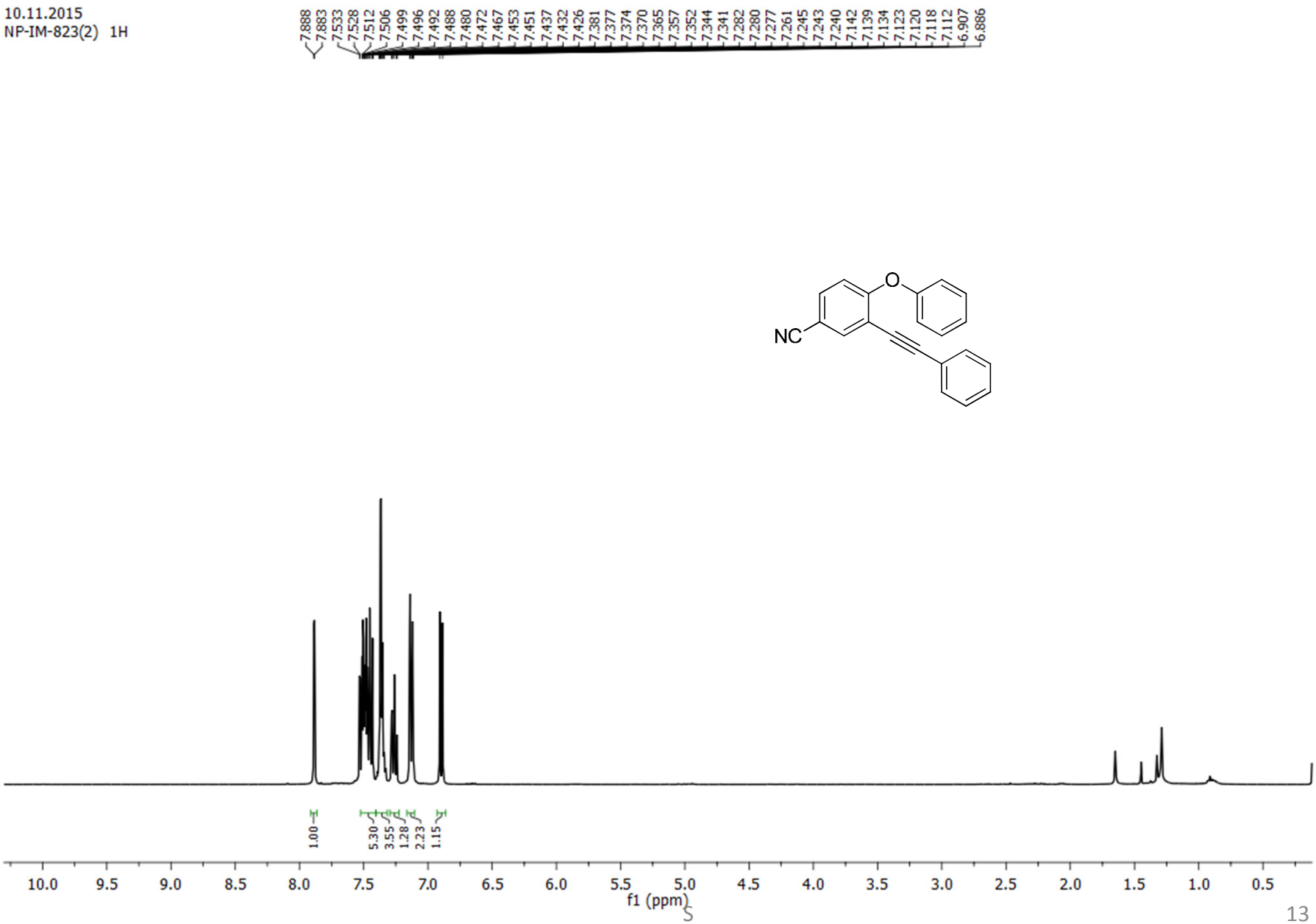
^{1}H NMR of isopropyl 4-phenoxy-3-(phenylethynyl)benzoate (2e)



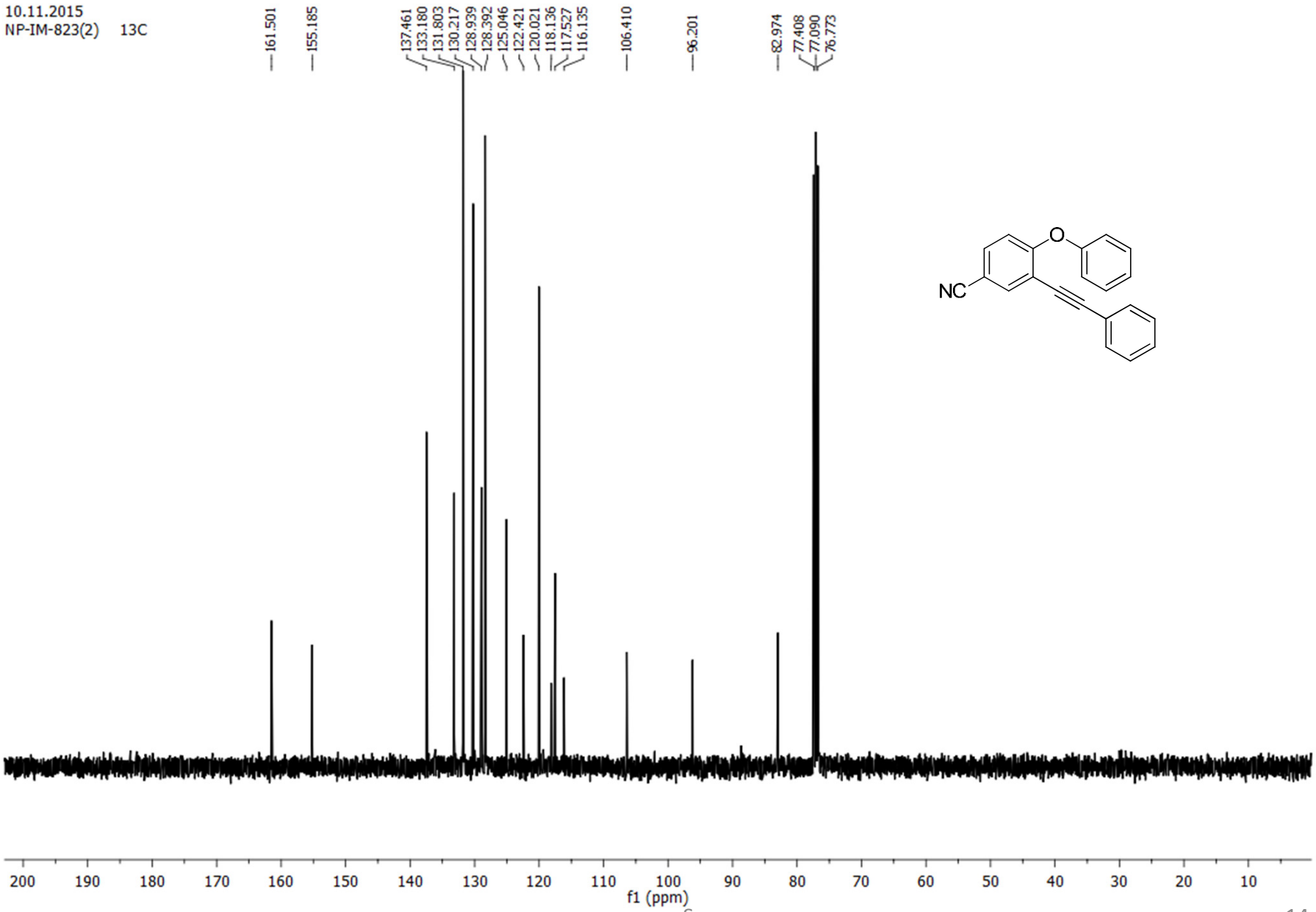
^{13}C NMR of isopropyl 4-phenoxy-3-(phenylethynyl)benzoate(2e)



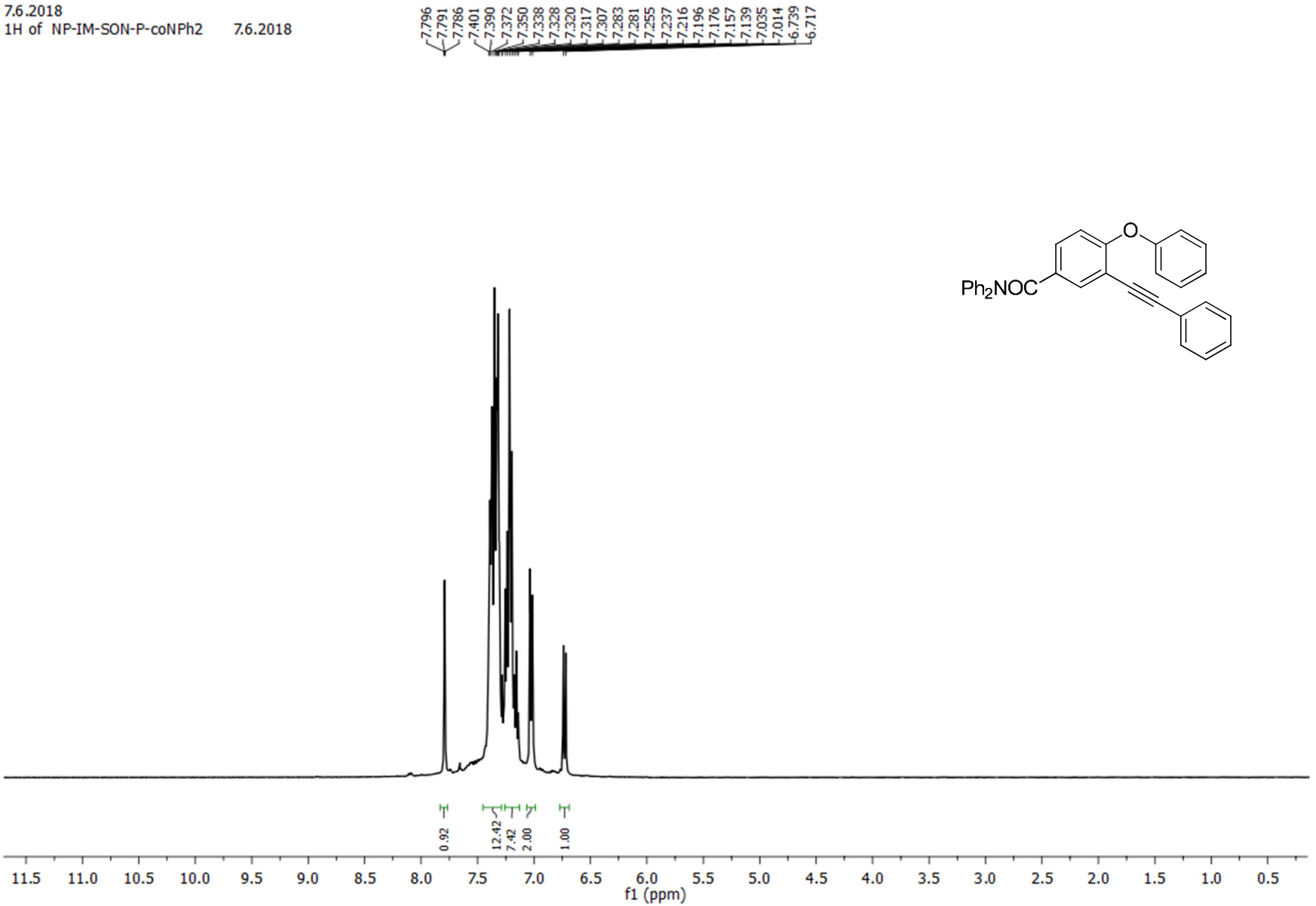
^{1}H NMR of 4-phenoxy-3-(phenylethynyl)benzonitrile (2f)



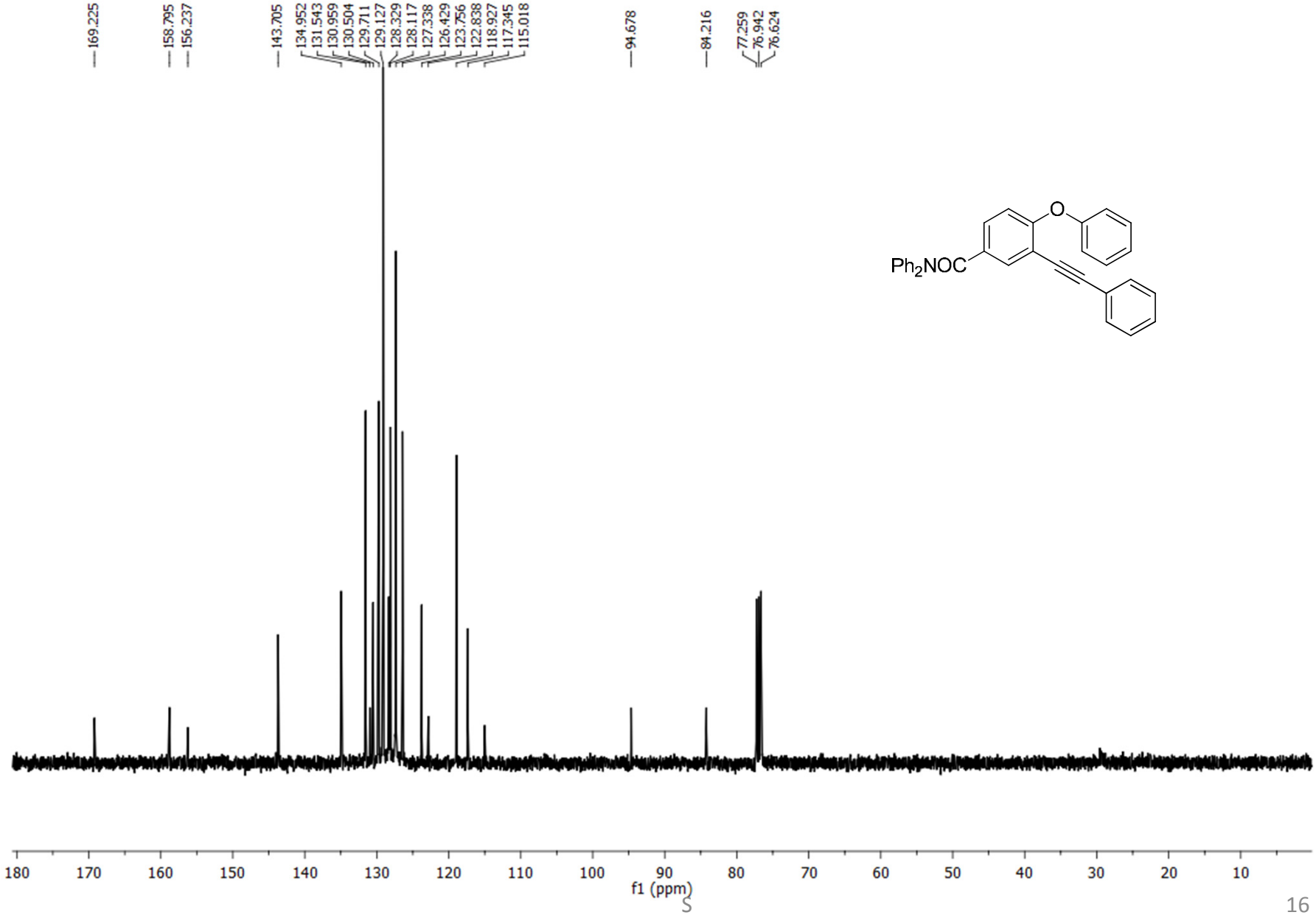
^{13}C NMR of 4-phenoxy-3-(phenylethynyl)benzonitrile (2f)



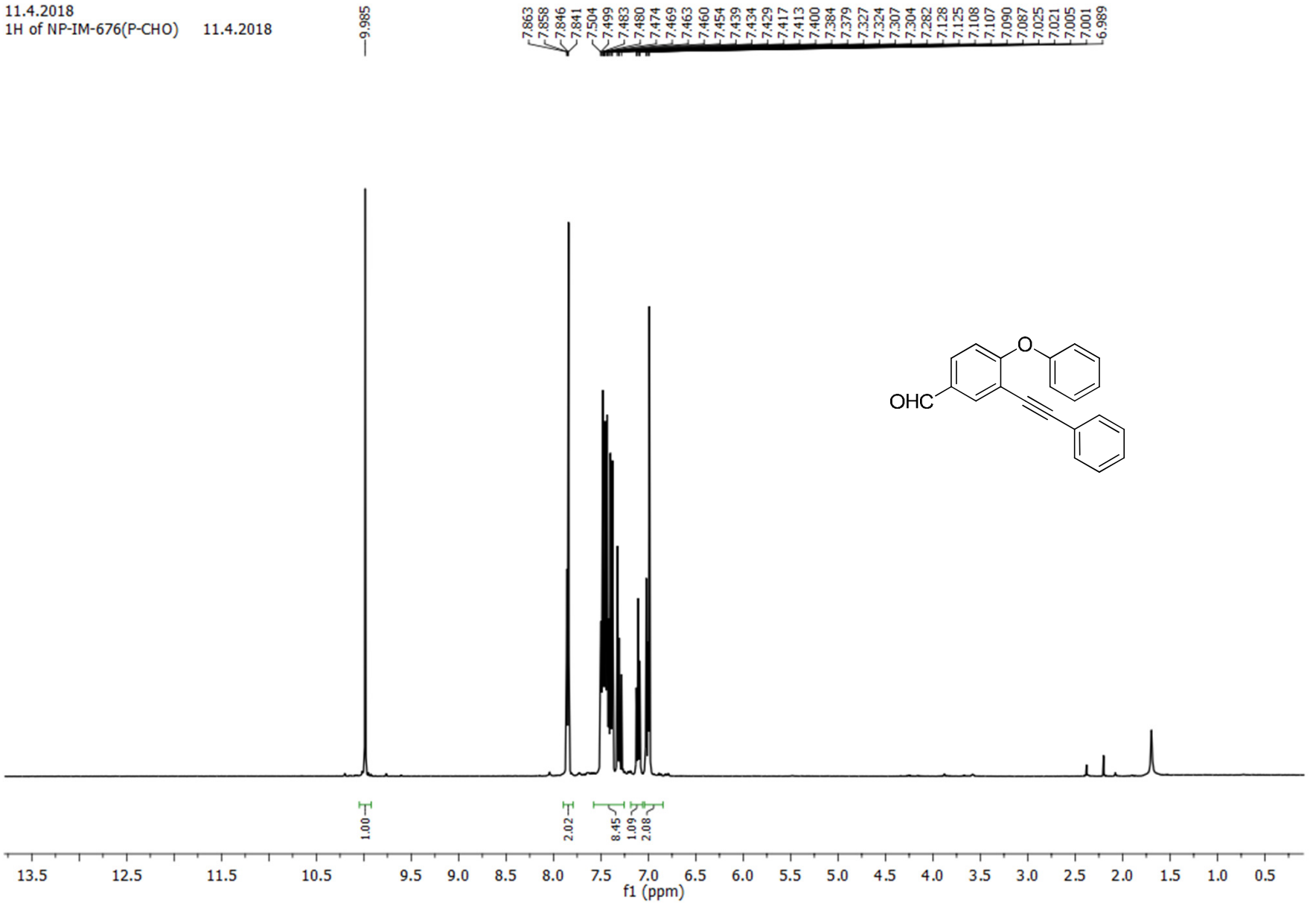
^{1}H NMR of 4-phenoxy-N,N-diphenyl-3-(phenylethynyl)benzamide (2g)



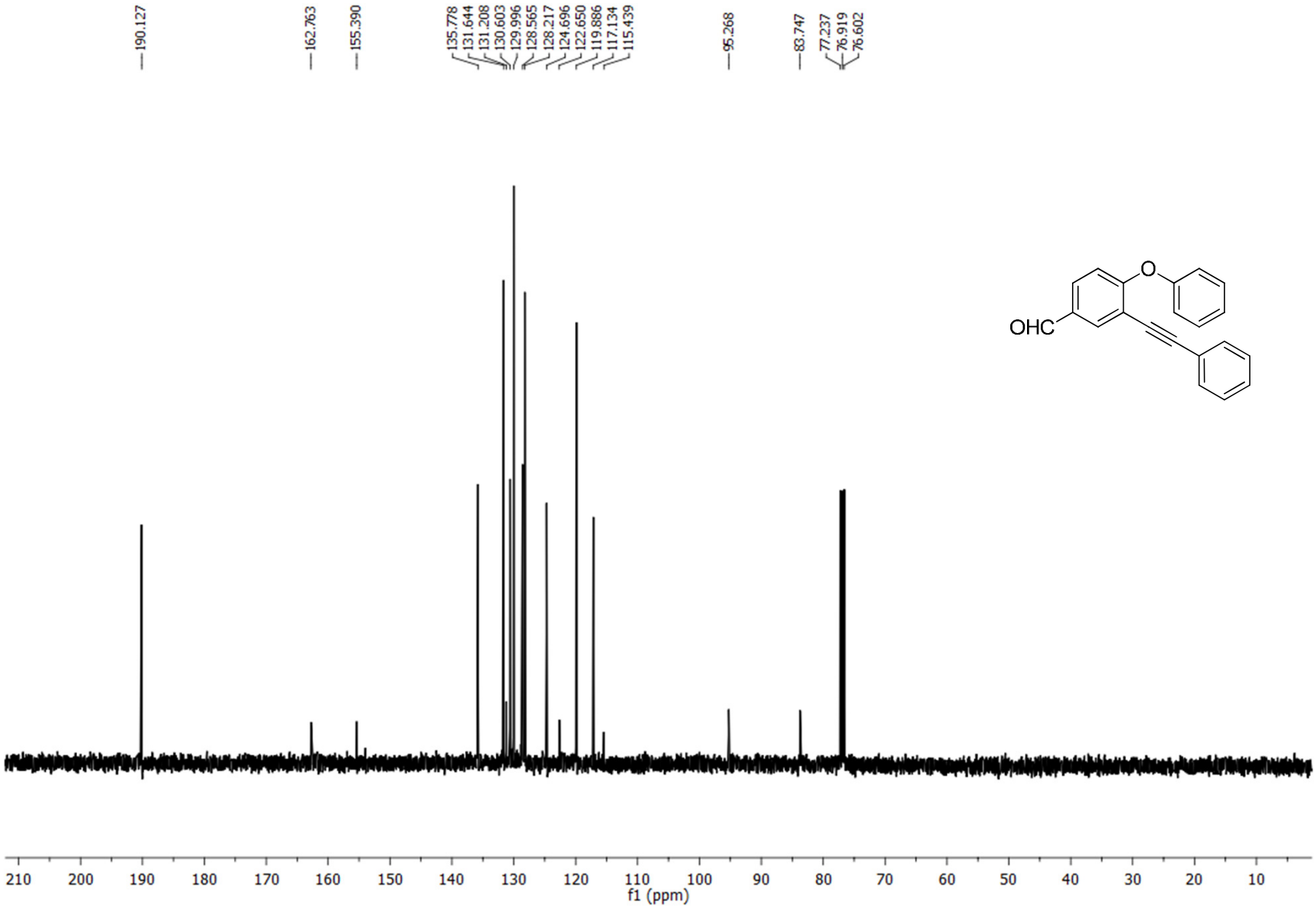
^{13}C NMR of 4-phenoxy-N,N-diphenyl-3-(phenylethynyl)benzamide (2g)



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



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



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

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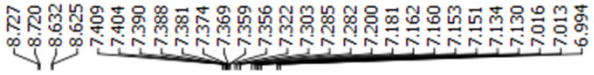
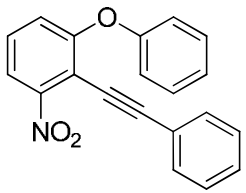
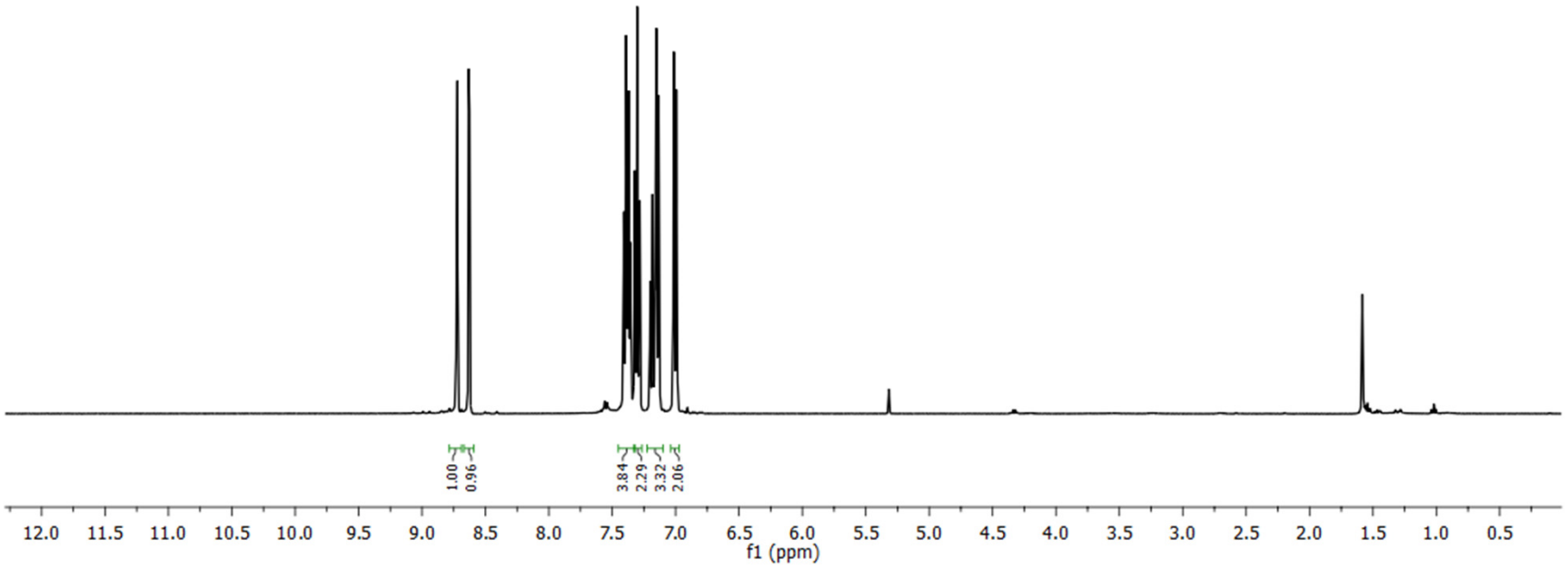
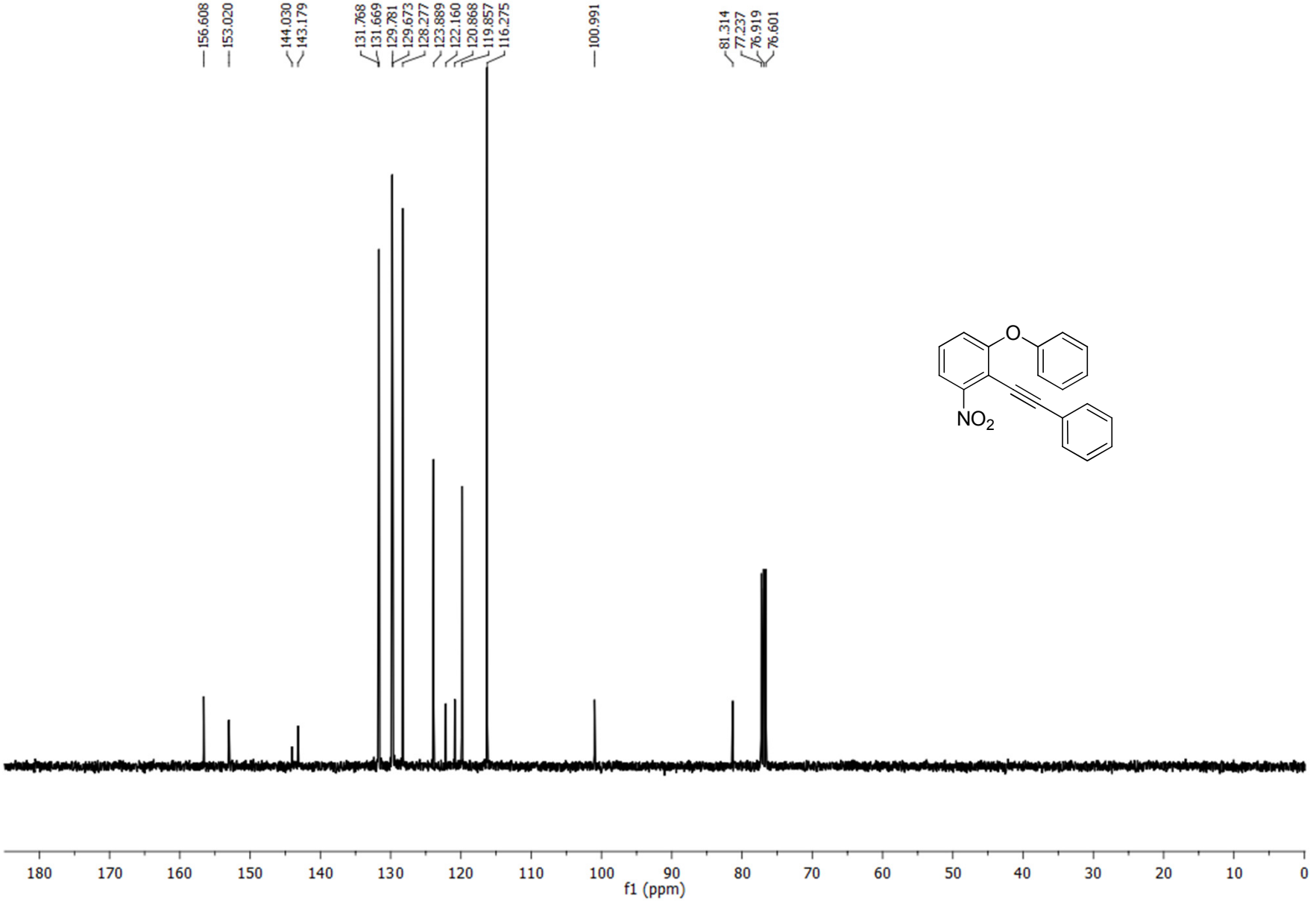


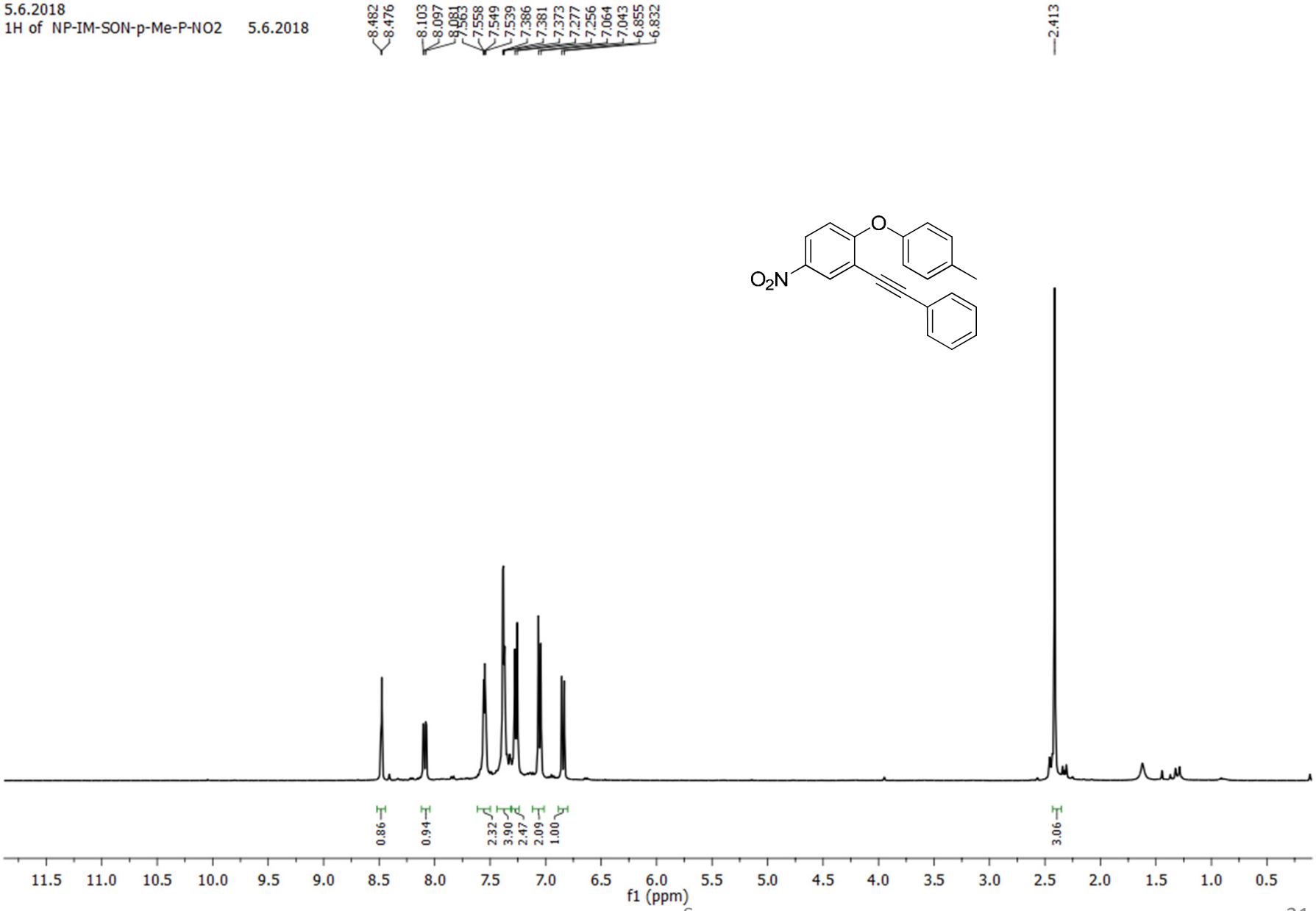




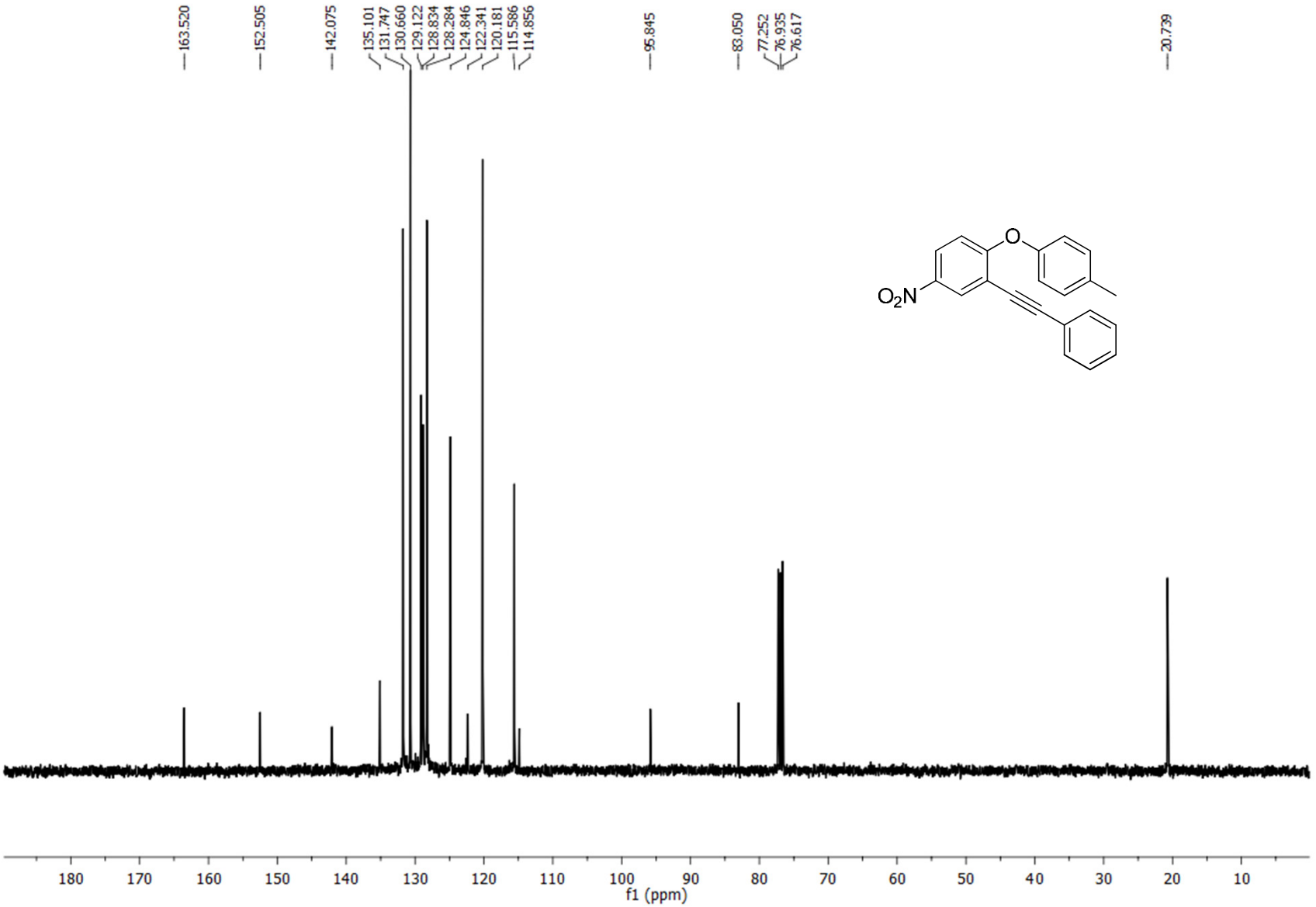
^{13}C NMR of 1-nitro-3-phenoxy-2-(phenylethynyl)benzene (2i)



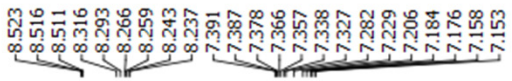
^{1}H NMR of 4-nitro-2-(phenylethynyl)-1-(p-tolyloxy)benzene (2k)

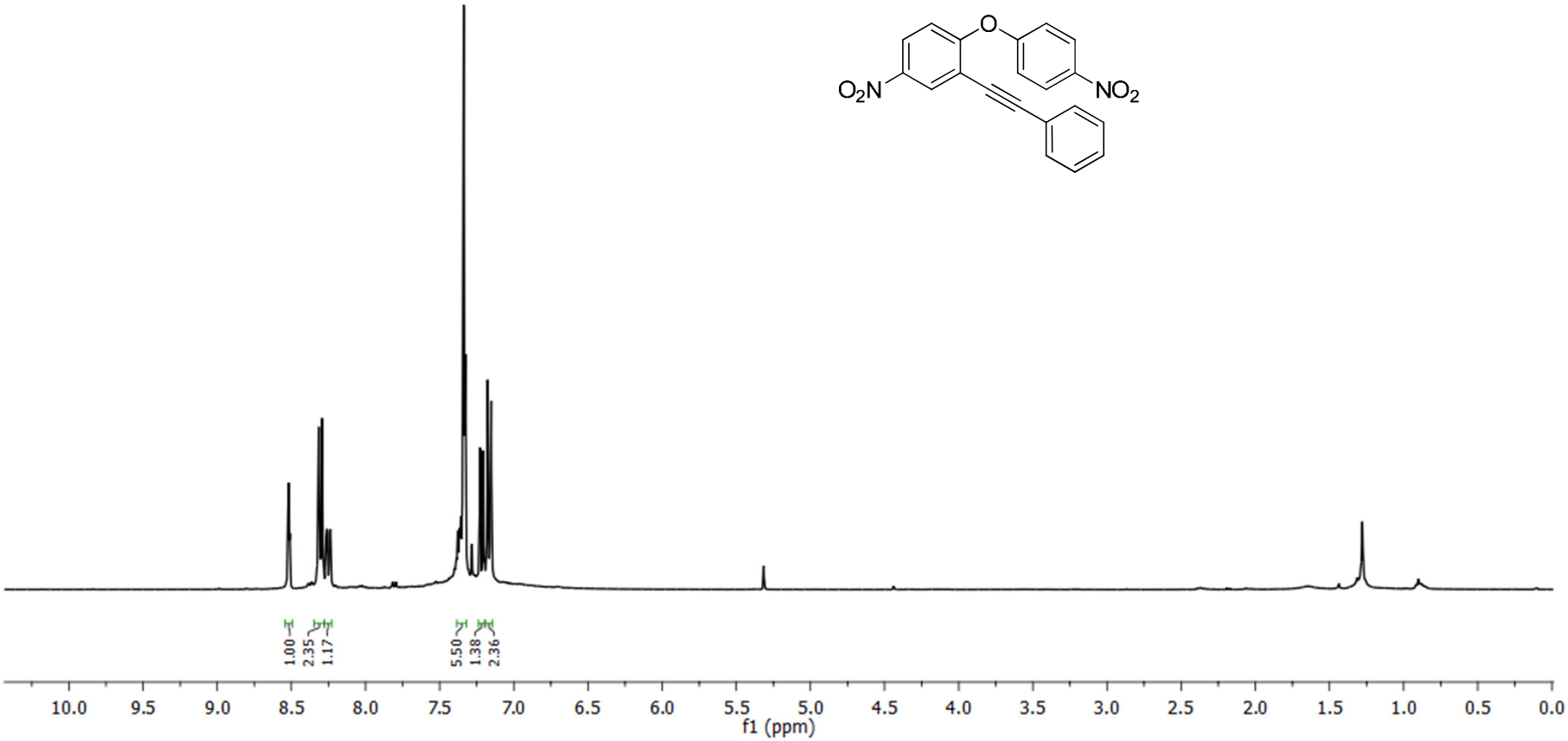


^{13}C NMR of 4-nitro-2-(phenylethynyl)-1-(p-tolyloxy)benzene (2k)

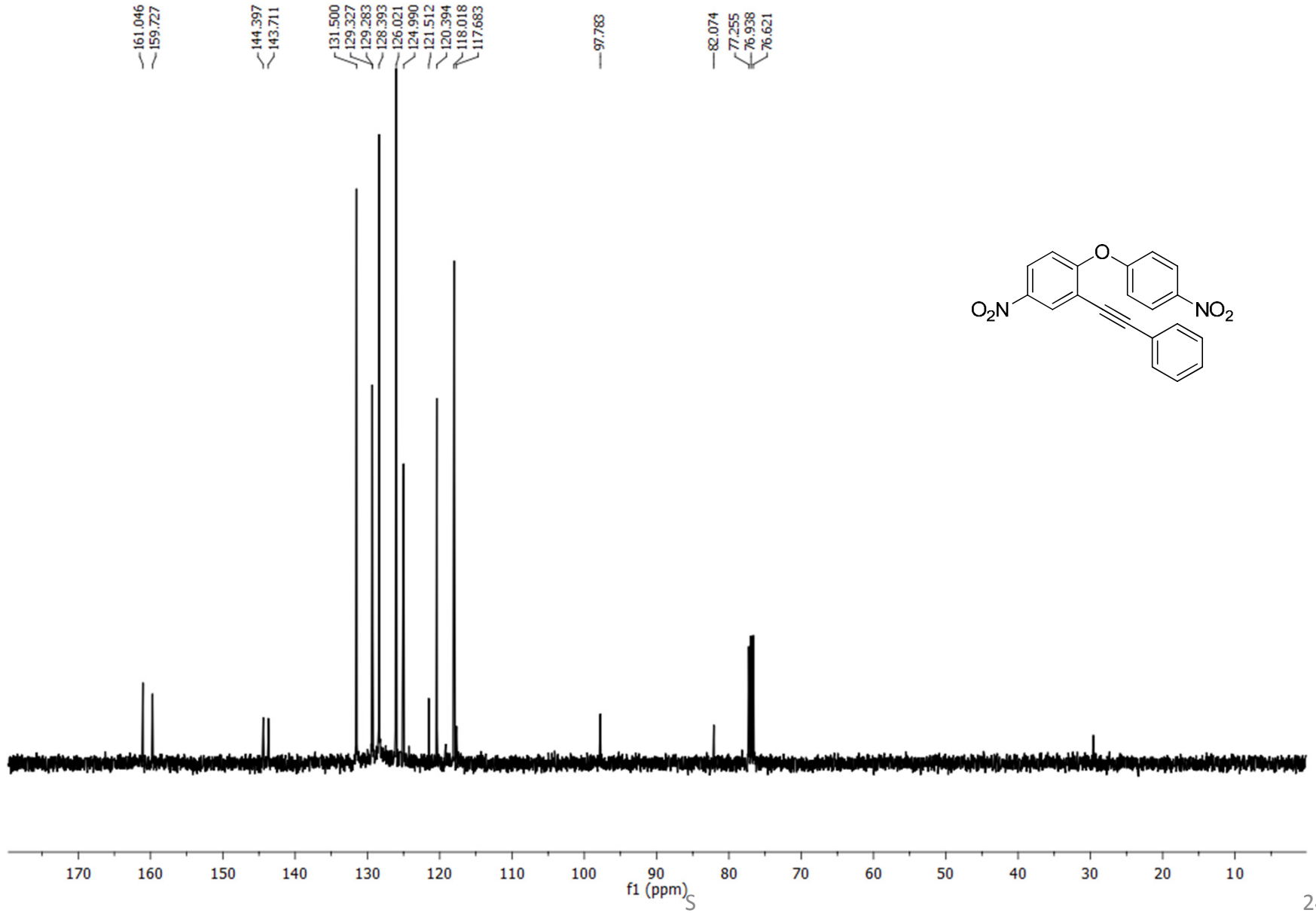


^{1}H NMR of 4-nitro-1-(4-nitrophenoxy)-2-(phenylethynyl)benzene (2l)

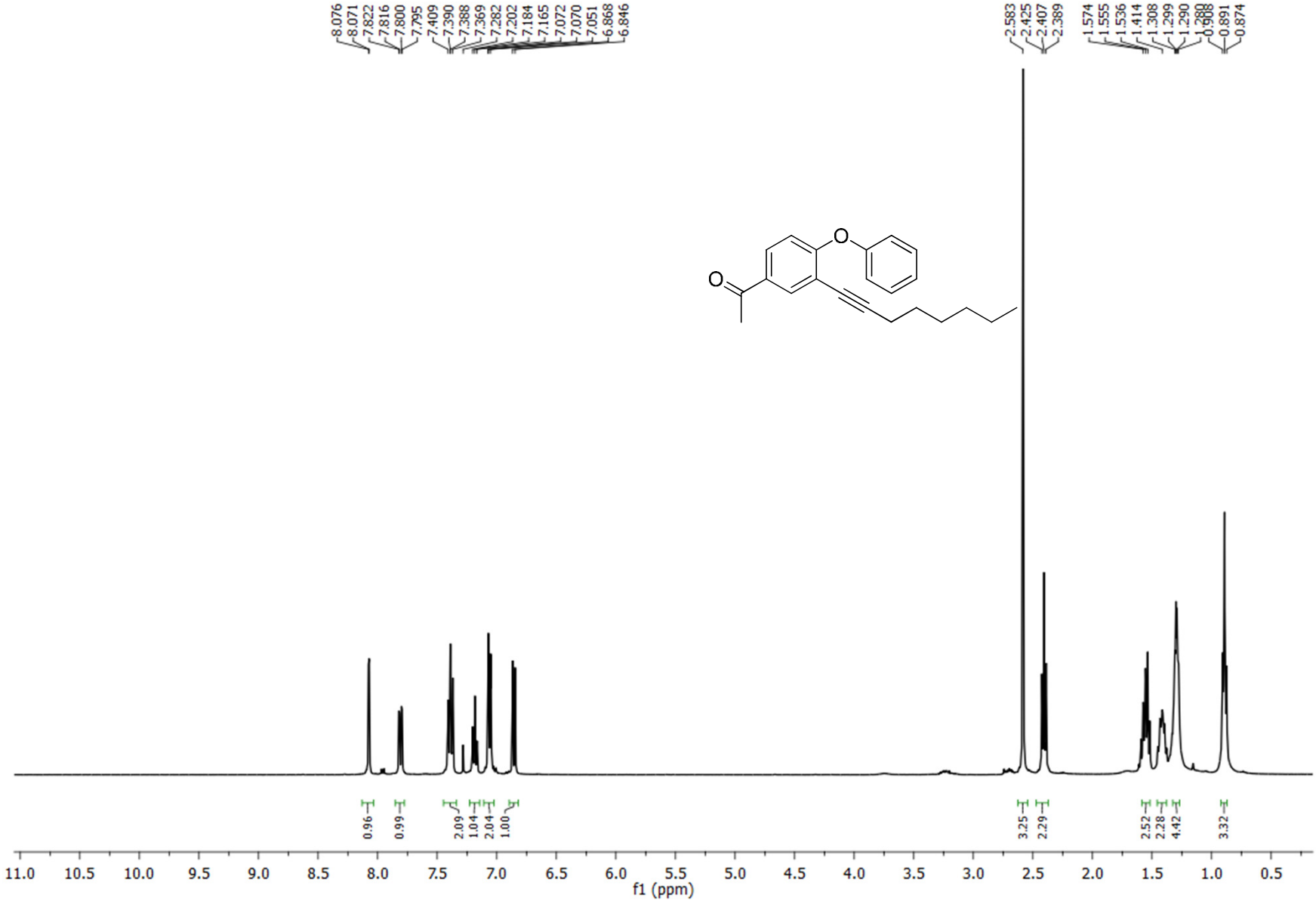




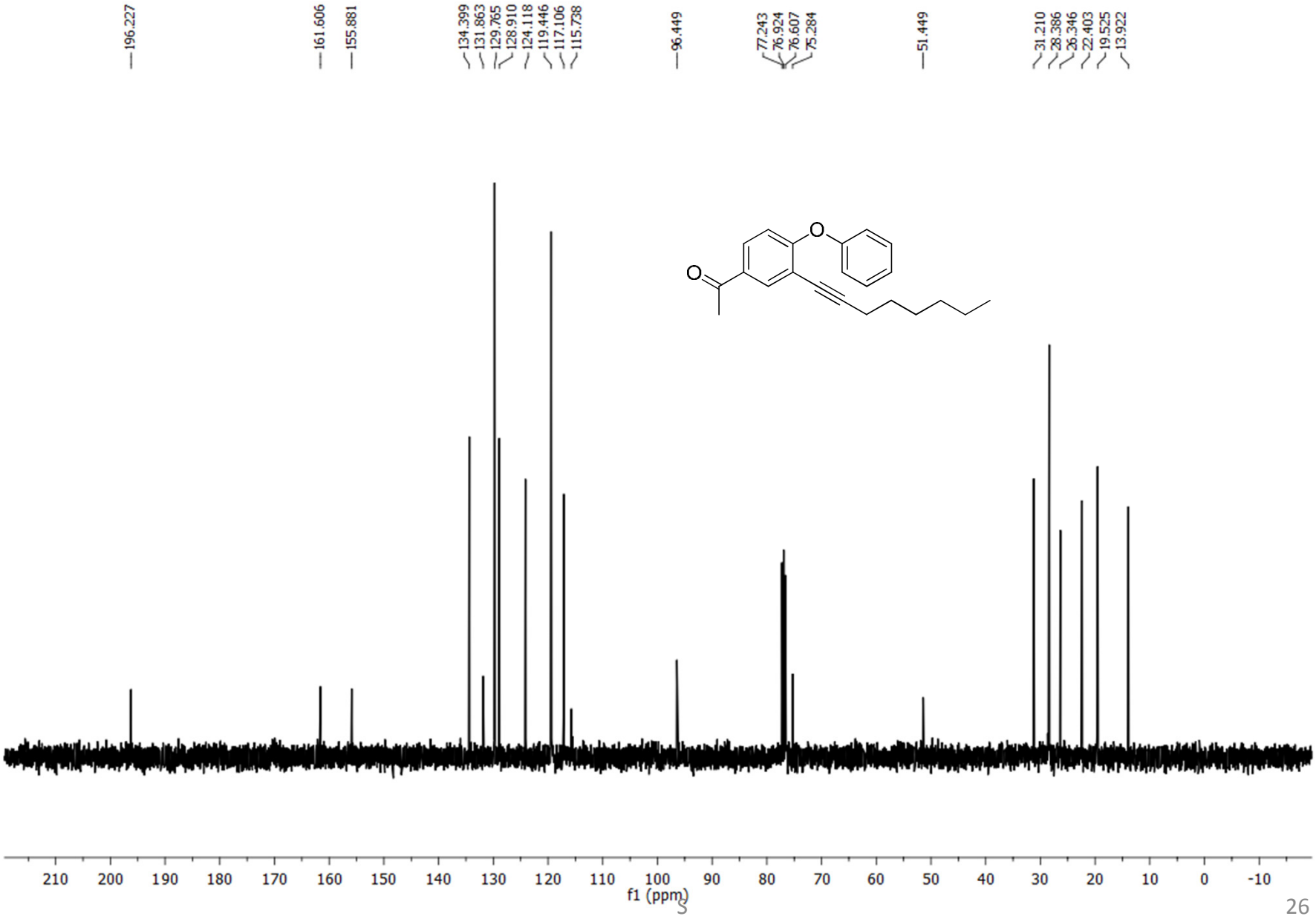
^{13}C NMR of 4-nitro-1-(4-nitrophenoxy)-2-(phenylethynyl)benzene (2l)



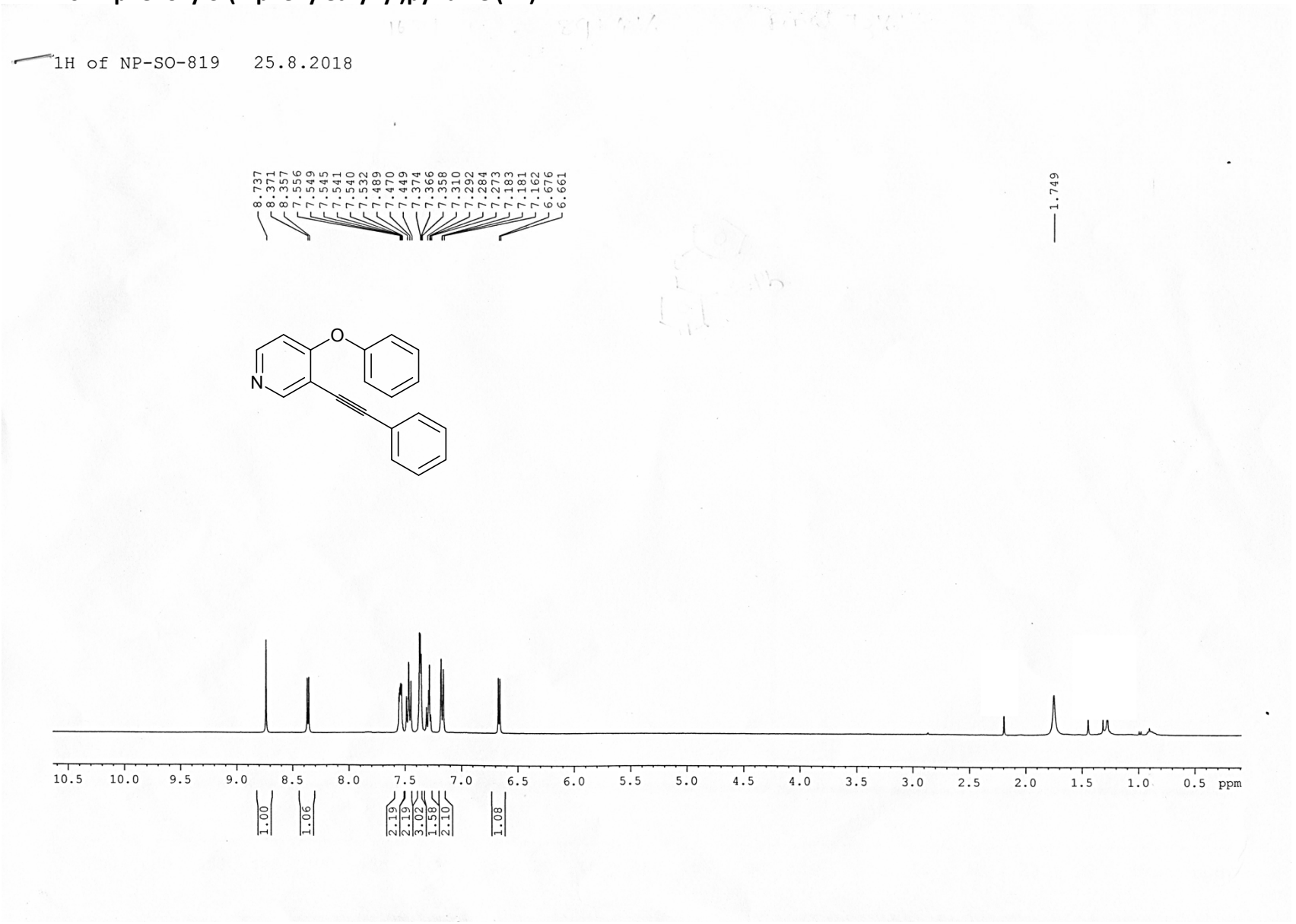
^{1}H NMR of 1-(3-(oct-1-yn-1-yl)-4-phenoxyphenyl)ethanone (2m)



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



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



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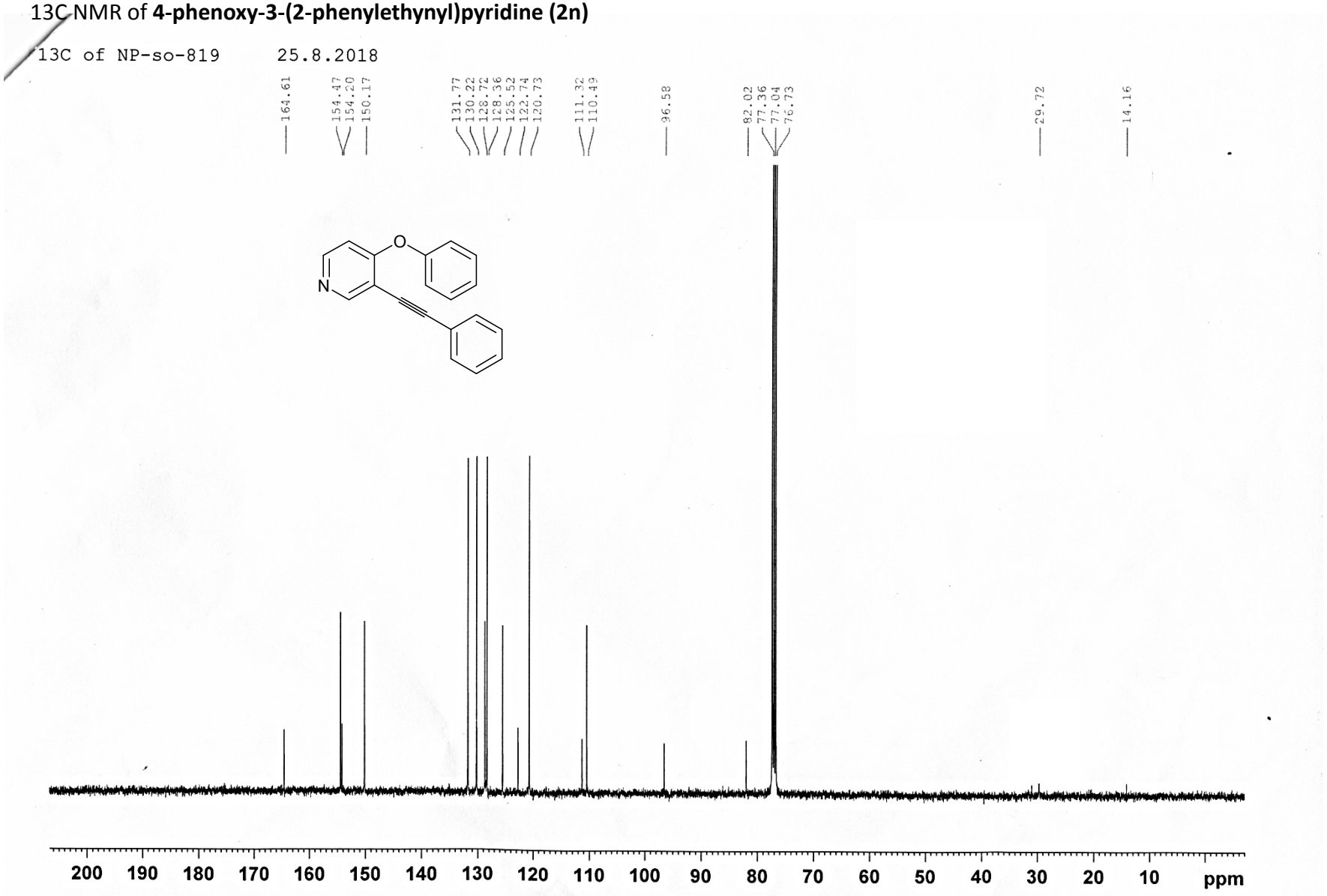
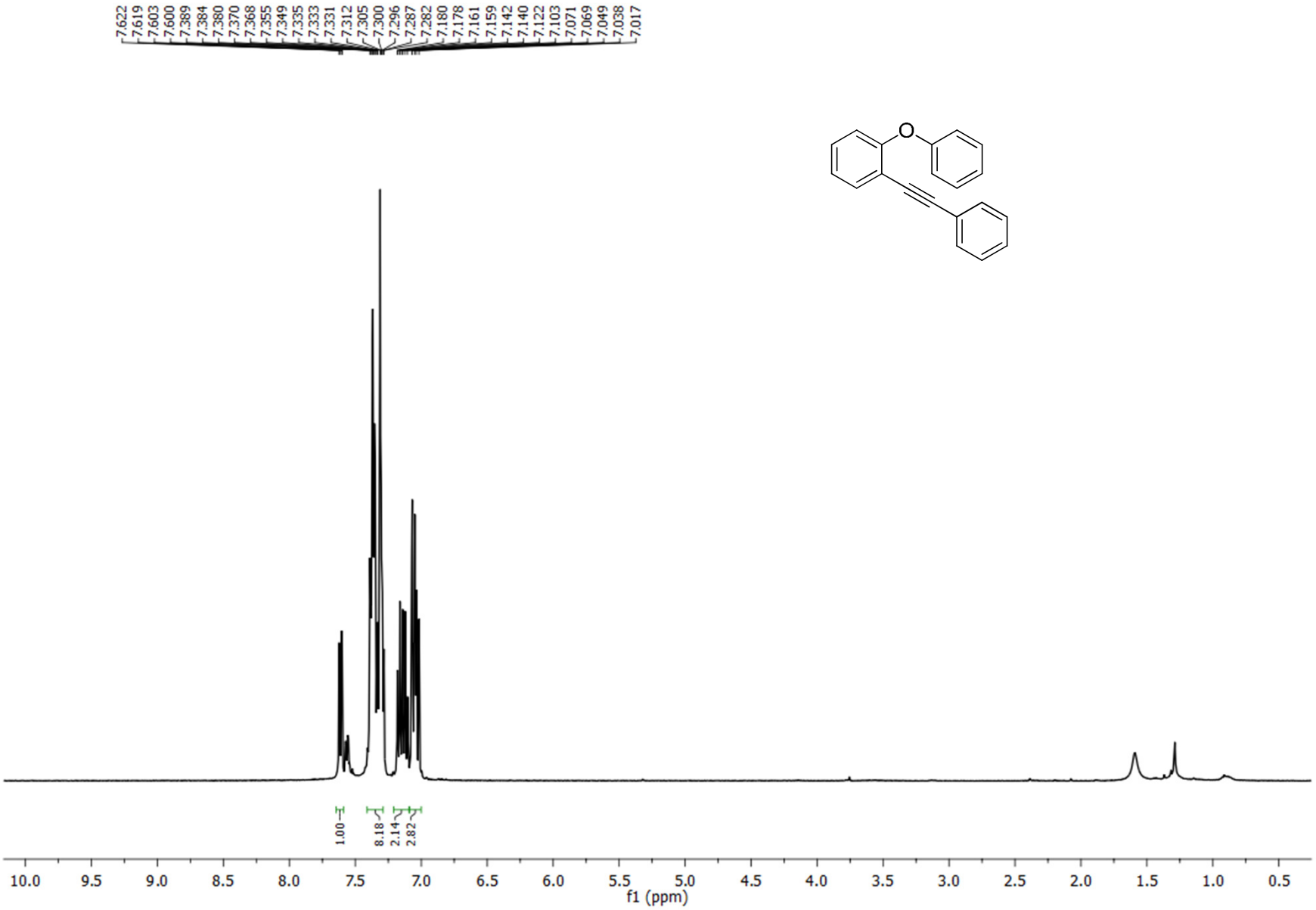
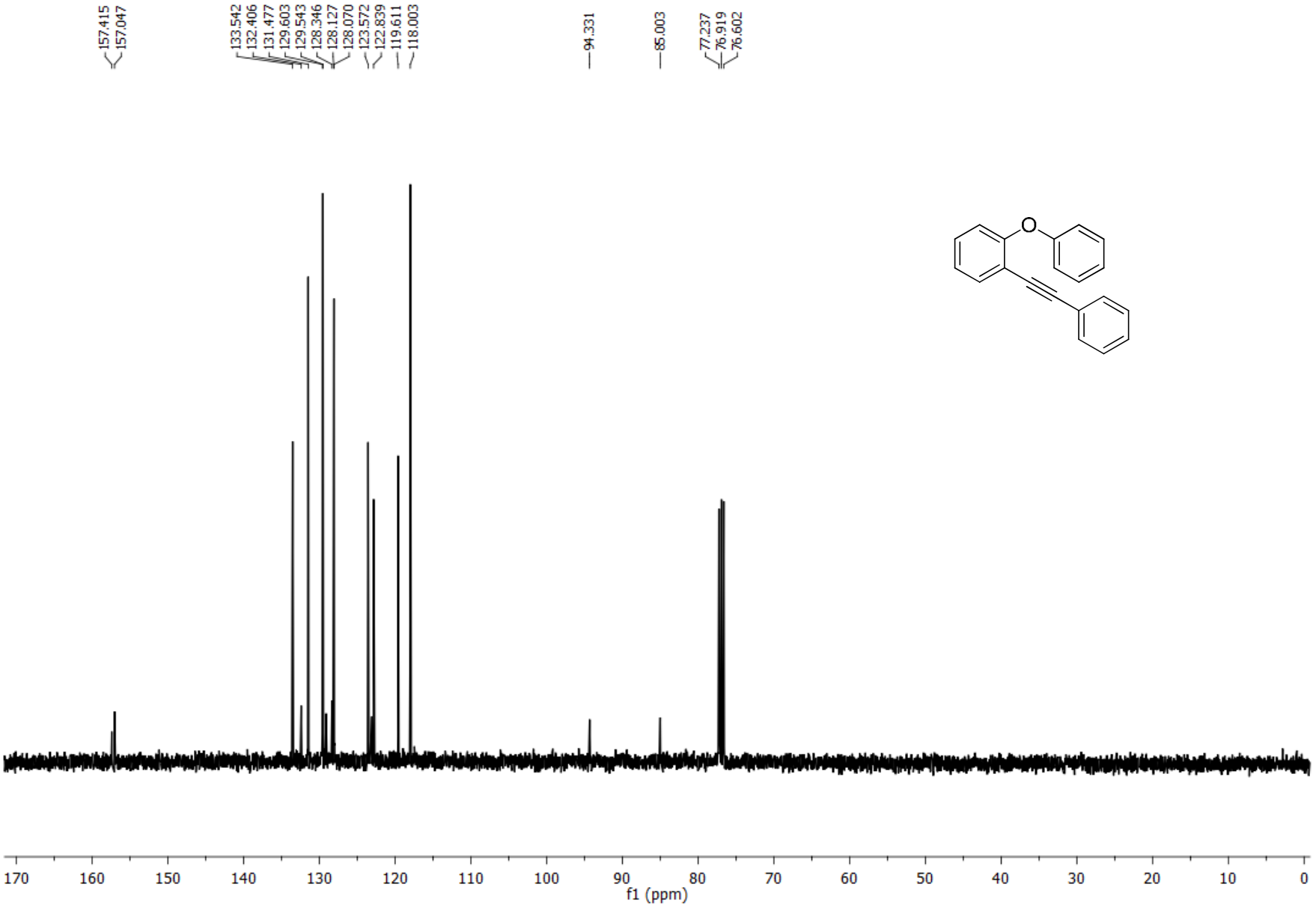


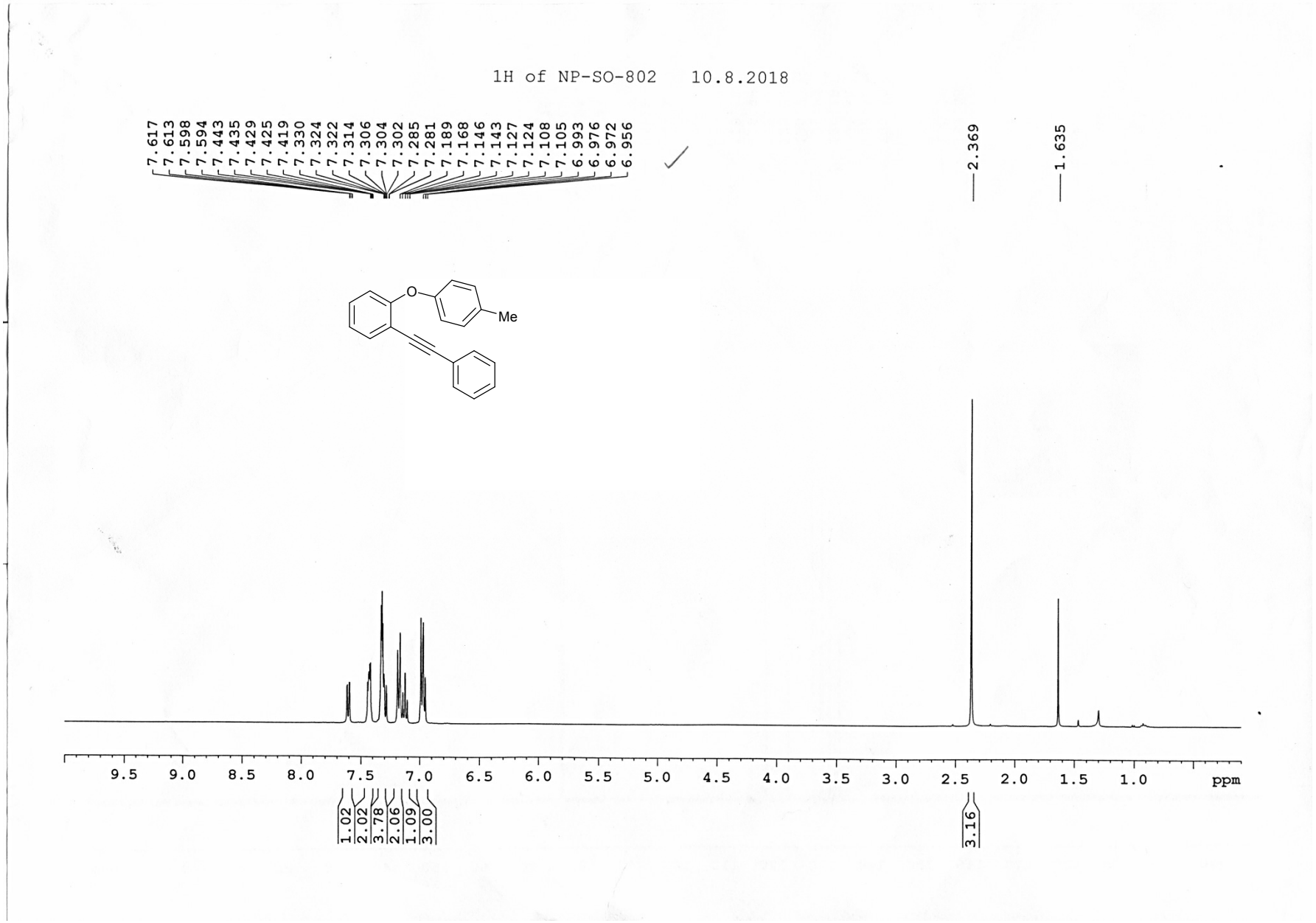
^{1}H NMR of 1-phenoxy-2-(phenylethynyl)benzene (2o)



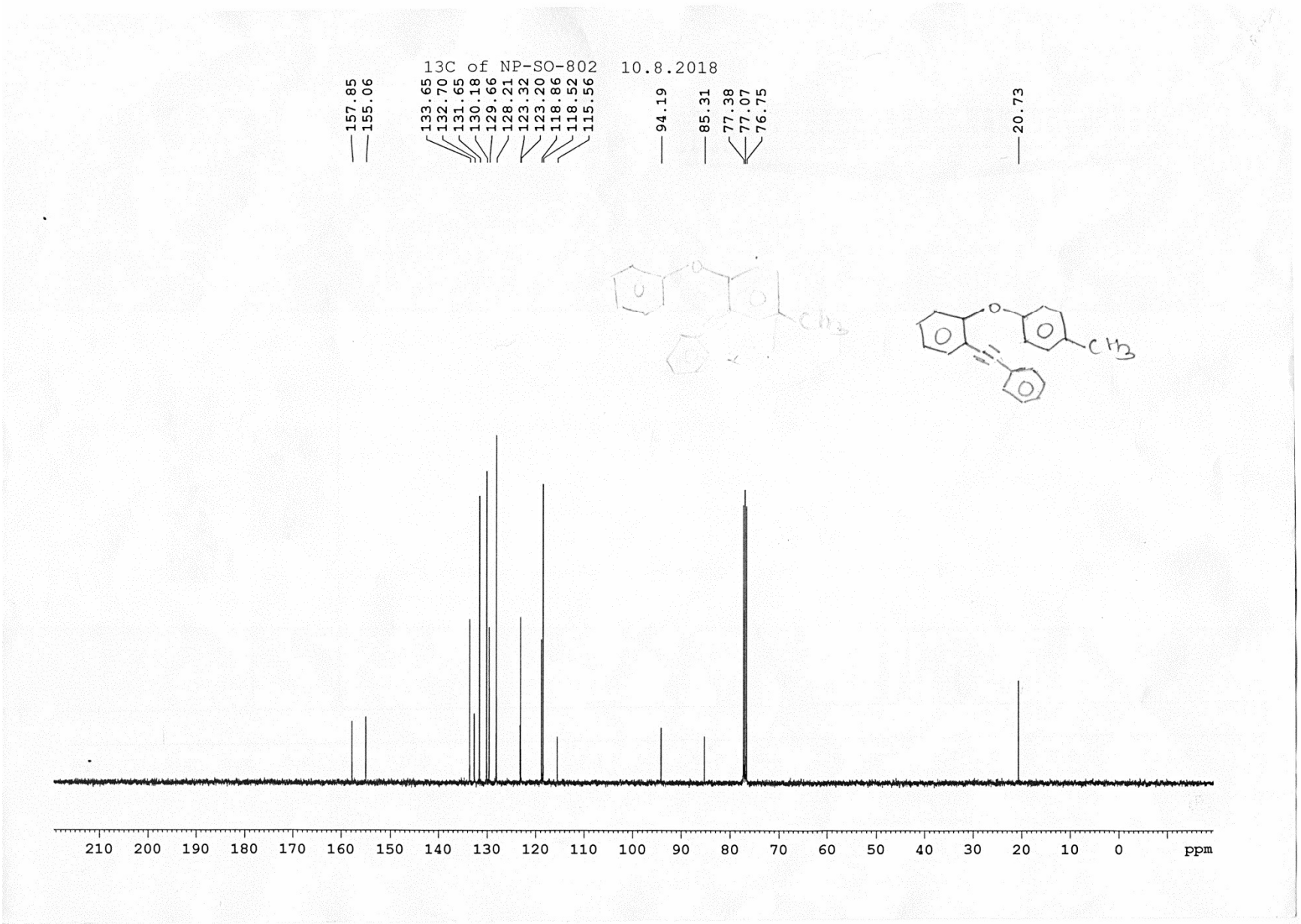
^{13}C NMR of 1-phenoxy-2-(phenylethynyl)benzene (2o)



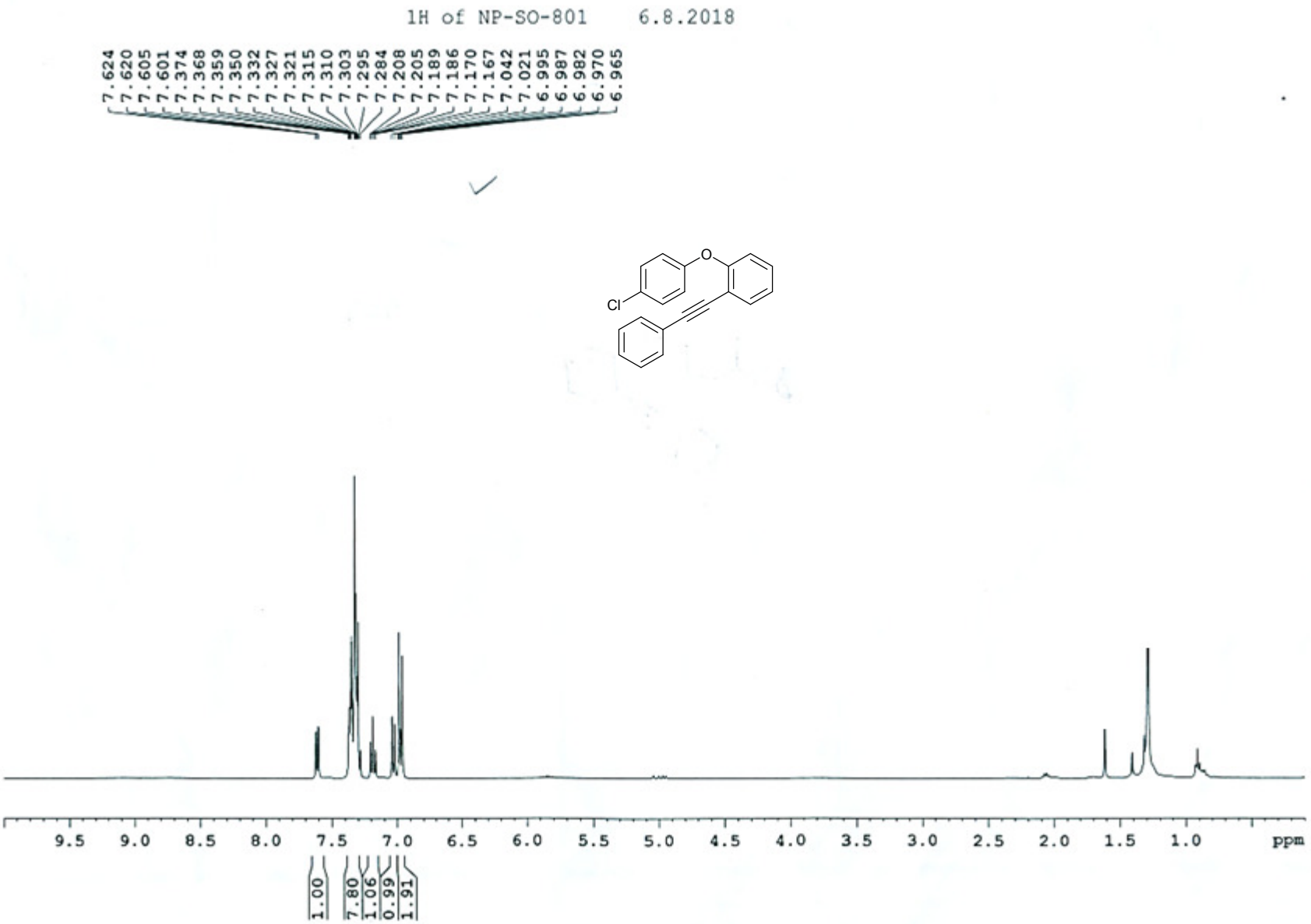
1H NMR of 1-(*p*-tolyloxy)-2-(2-phenylethynyl)benzene (2p)



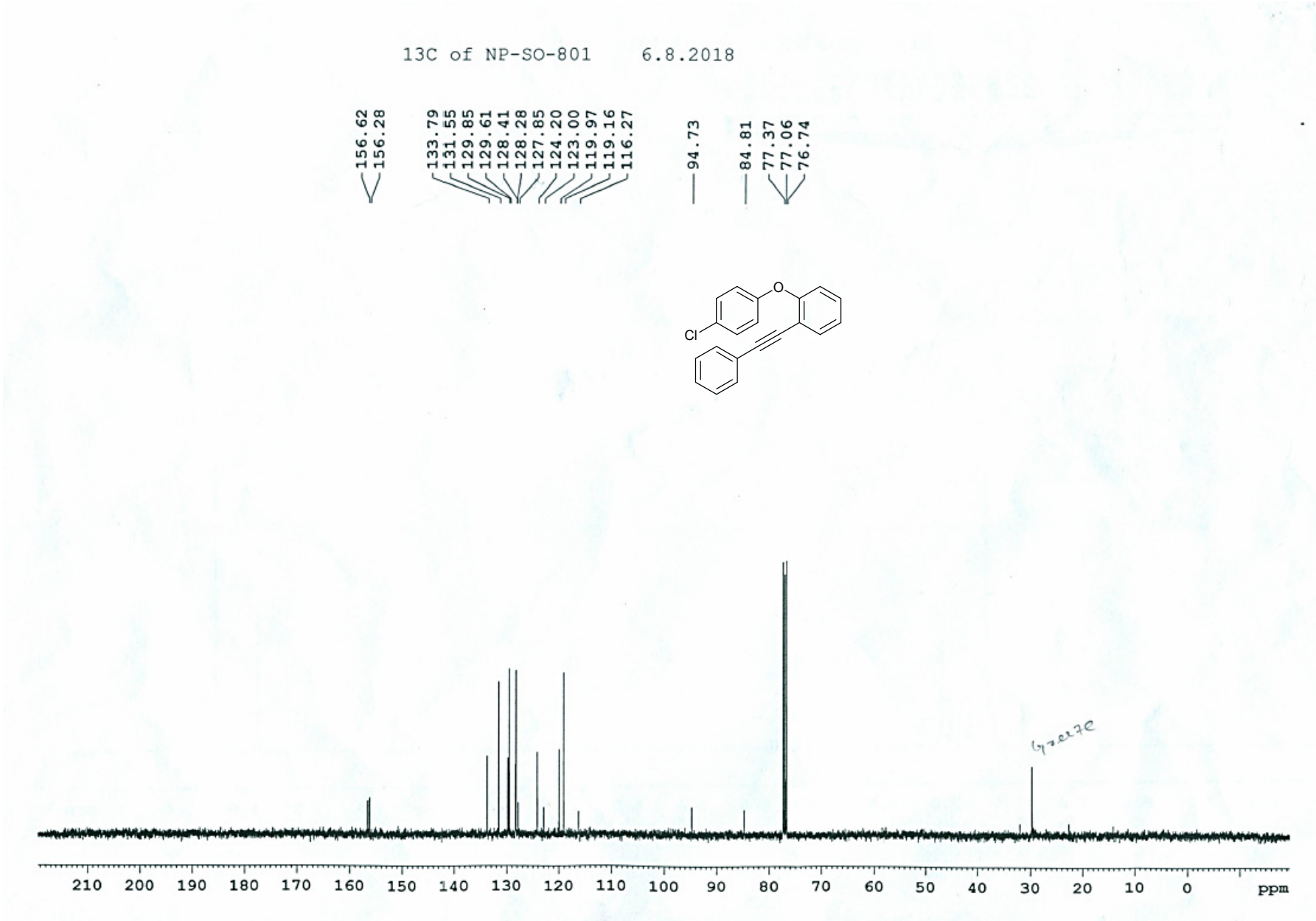
13C NMR of 1-(*p*-tolyloxy)-2-(2-phenylethynyl)benzene (2p)



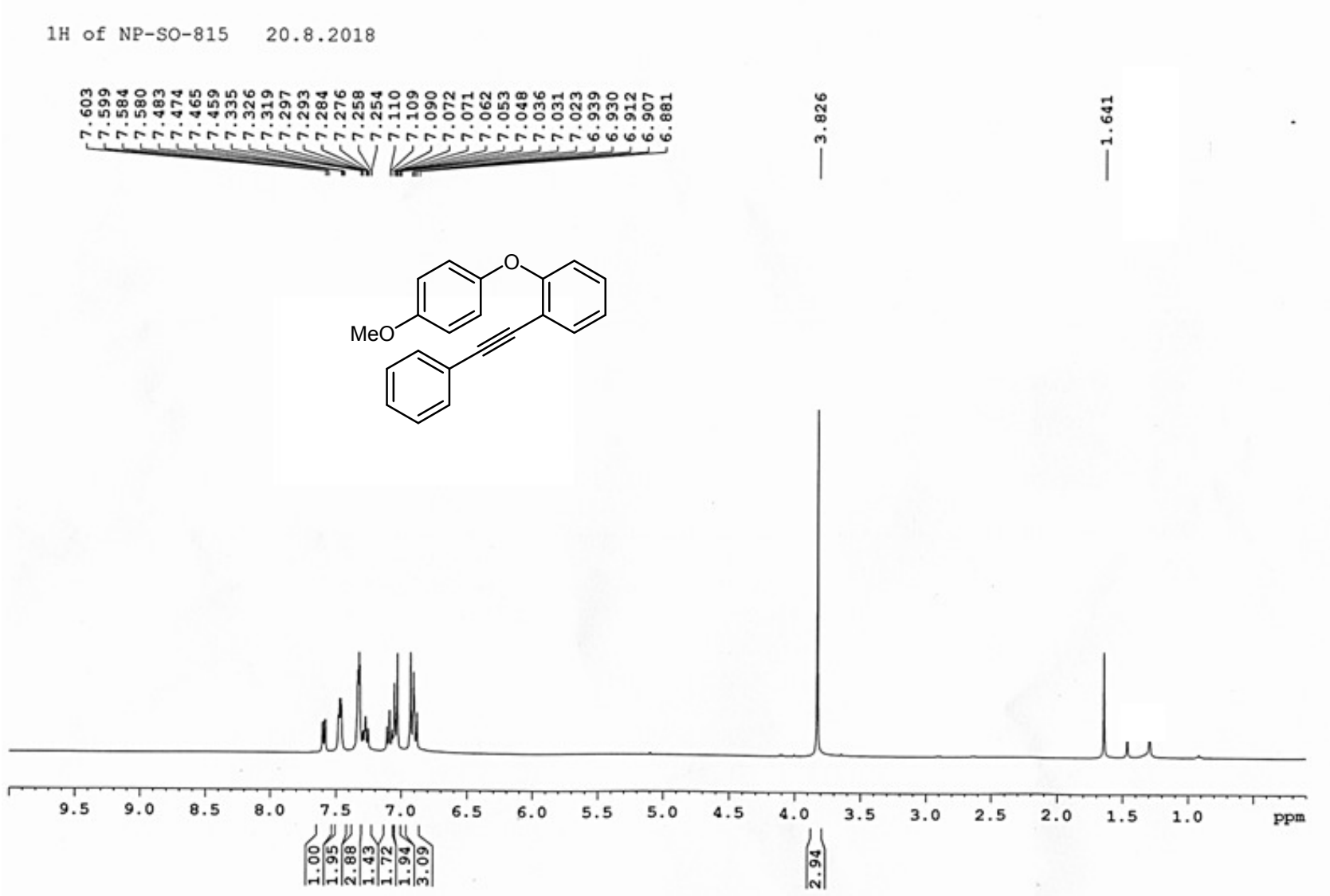
1H NMR of **1-(4-Chlorophenoxy)-2-(2-phenylethynyl)benzene (2q)**



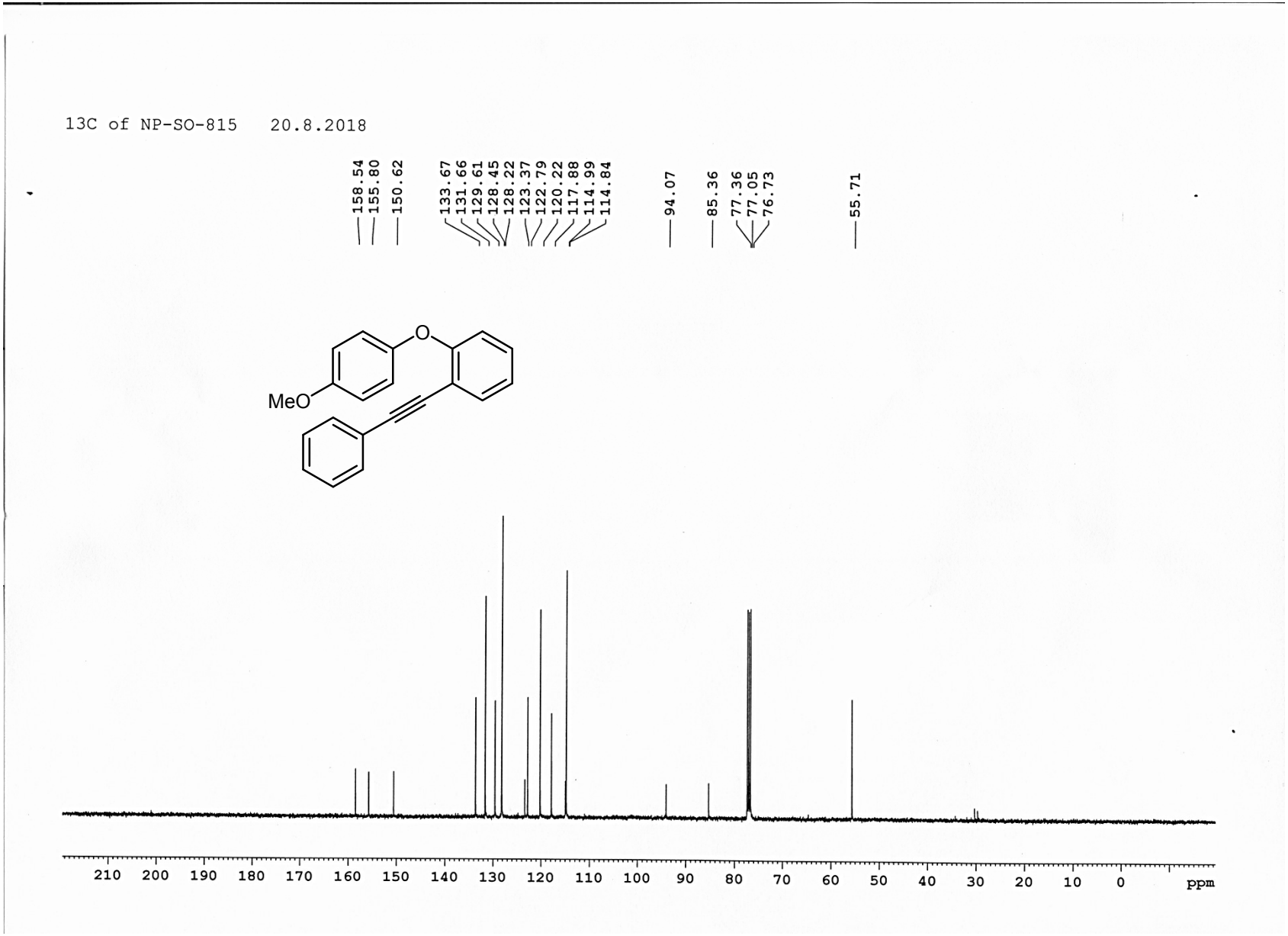
13C NMR of **1-(4-Chlorophenoxy)-2-(2-phenylethynyl)benzene (2q)**



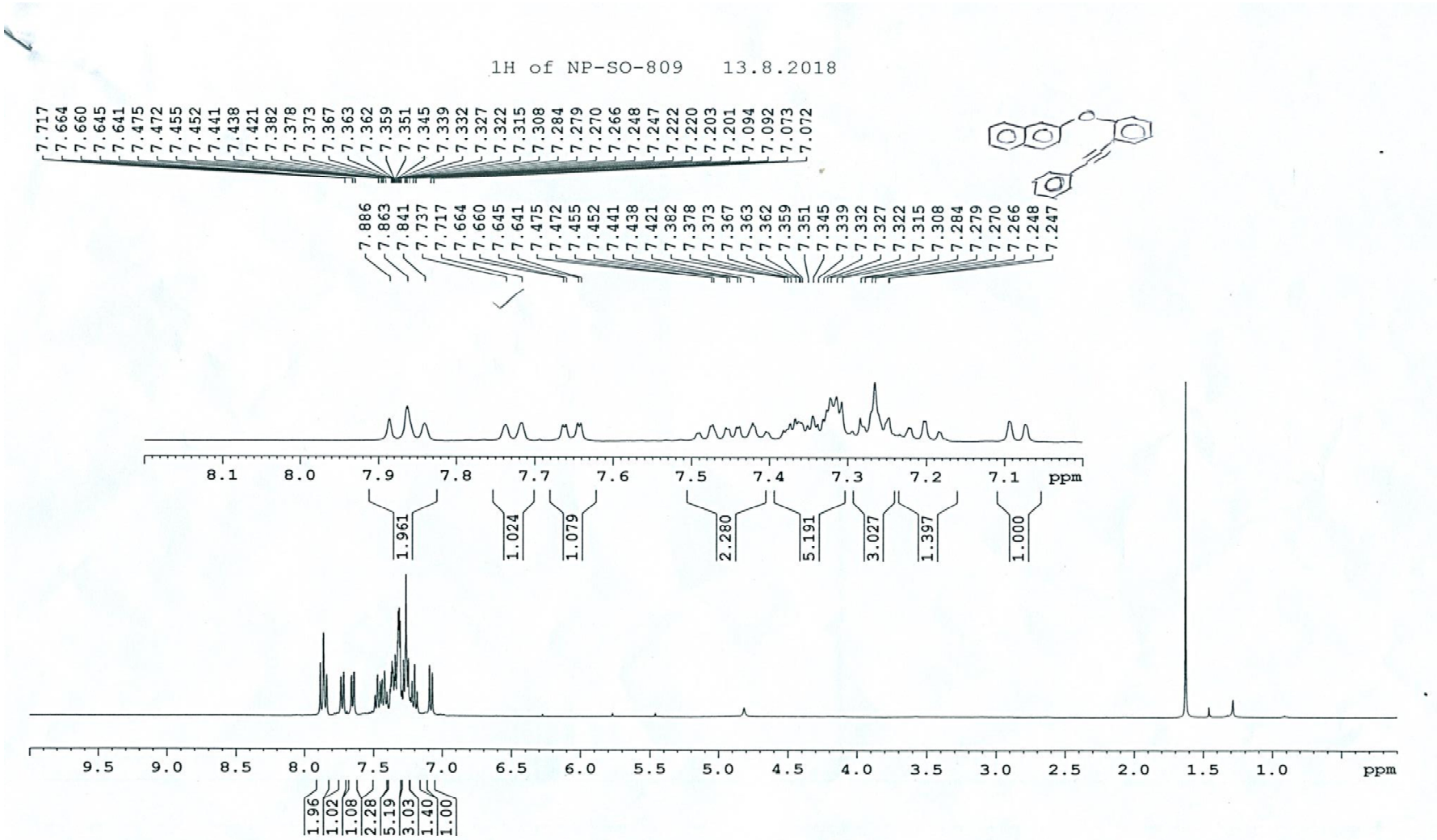
^{1}H NMR of **1-(4-Methoxyphenoxy)-2-(2-phenylethynyl)benzene (2r)**



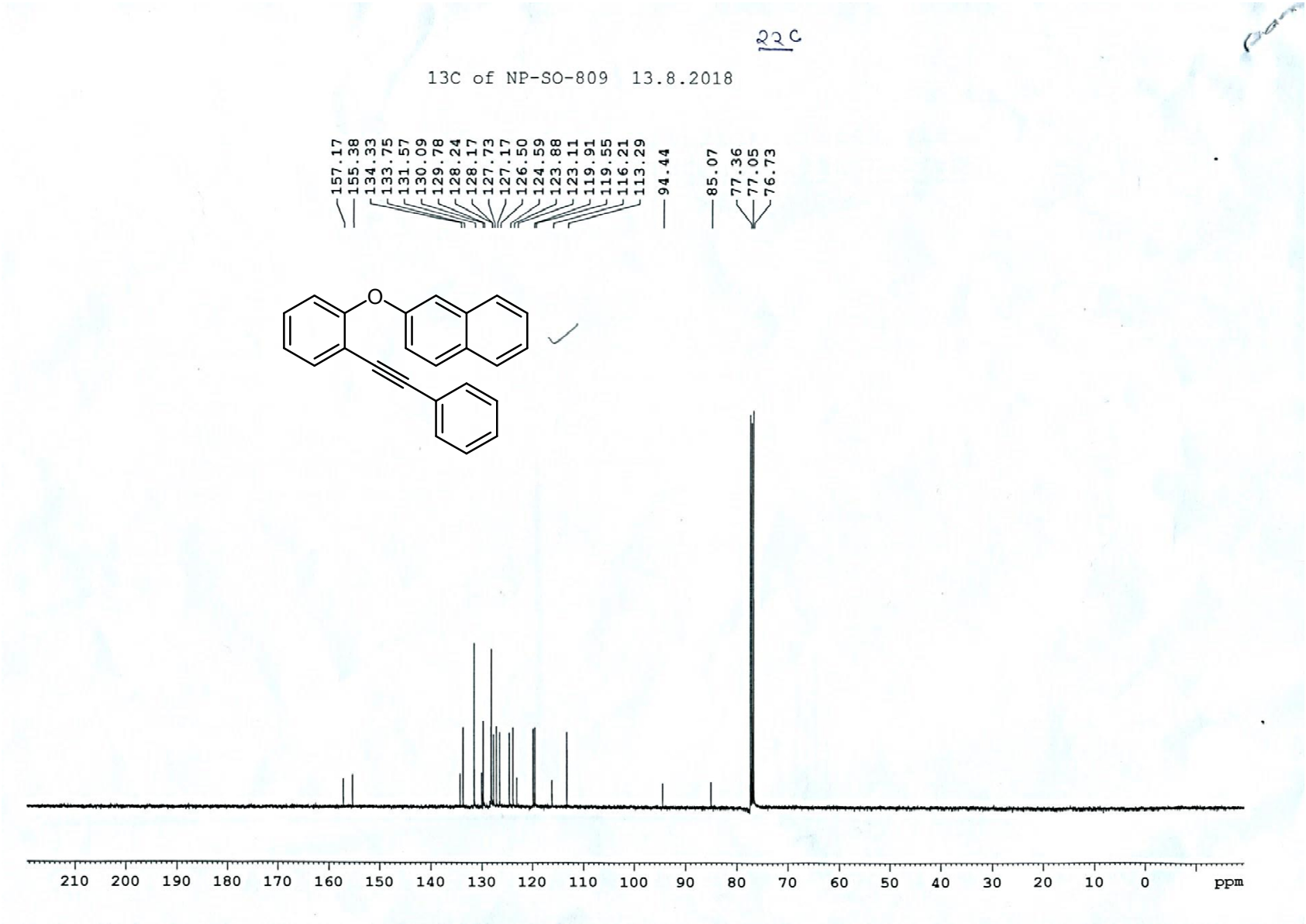
13C NMR of **1-(4-Methoxyphenoxy)-2-(2-phenylethynyl)benzene (2r)**



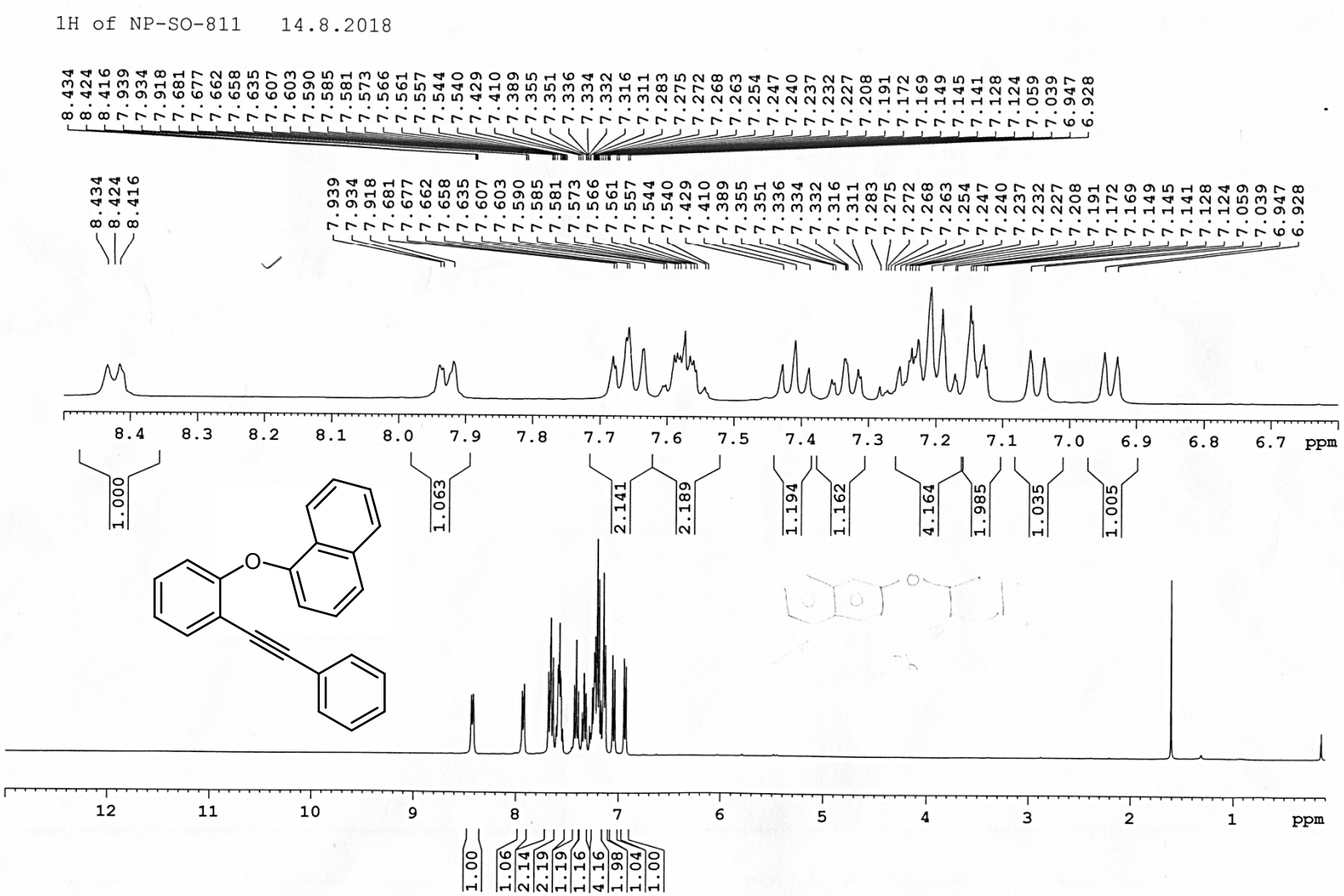
^{1}H NMR of 2-(2-(2-phenylethynyl)phenoxy)naphthalene (2s)



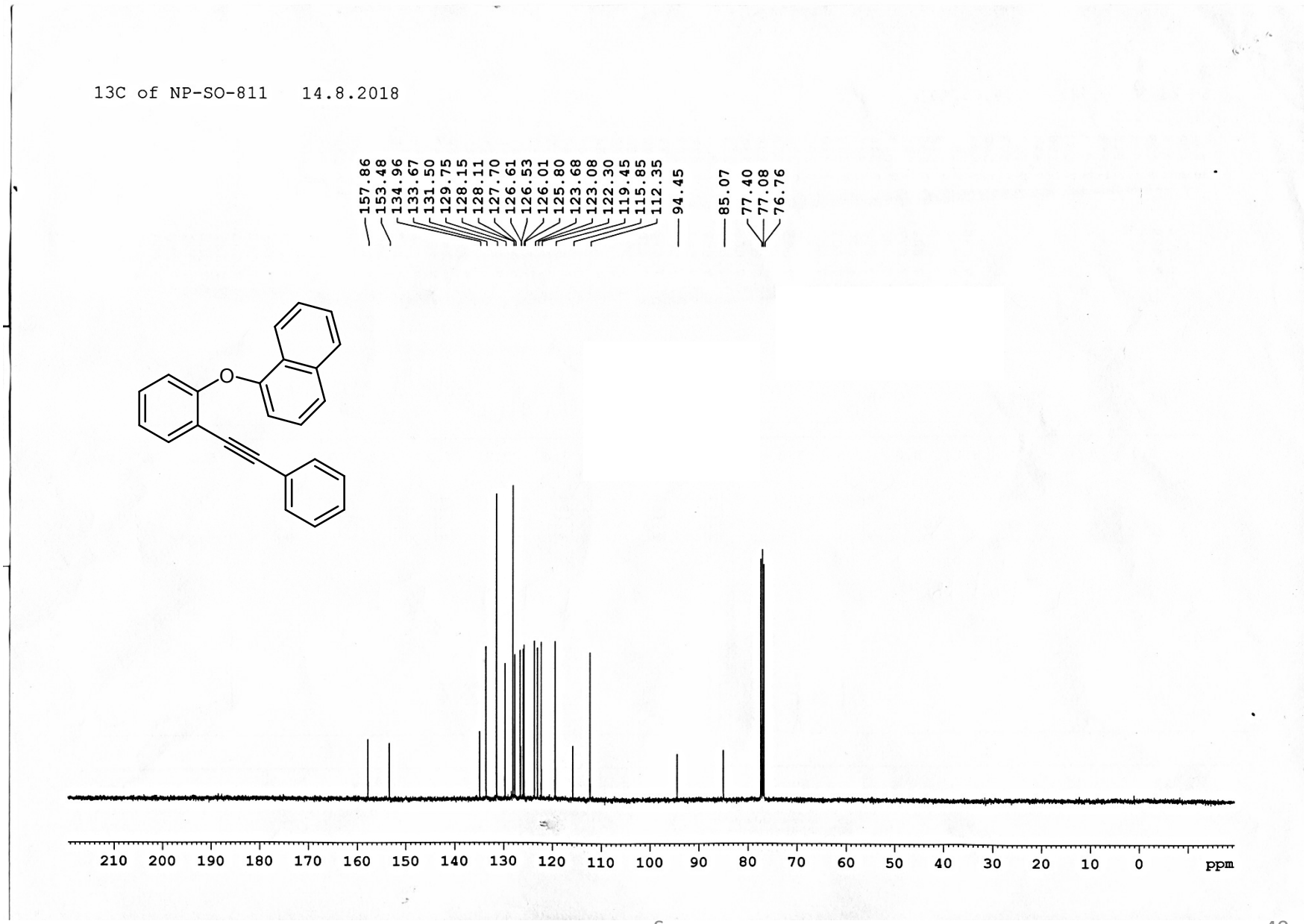
^{13}C NMR of 2-(2-(2-phenylethynyl)phenoxy)naphthalene (2s)



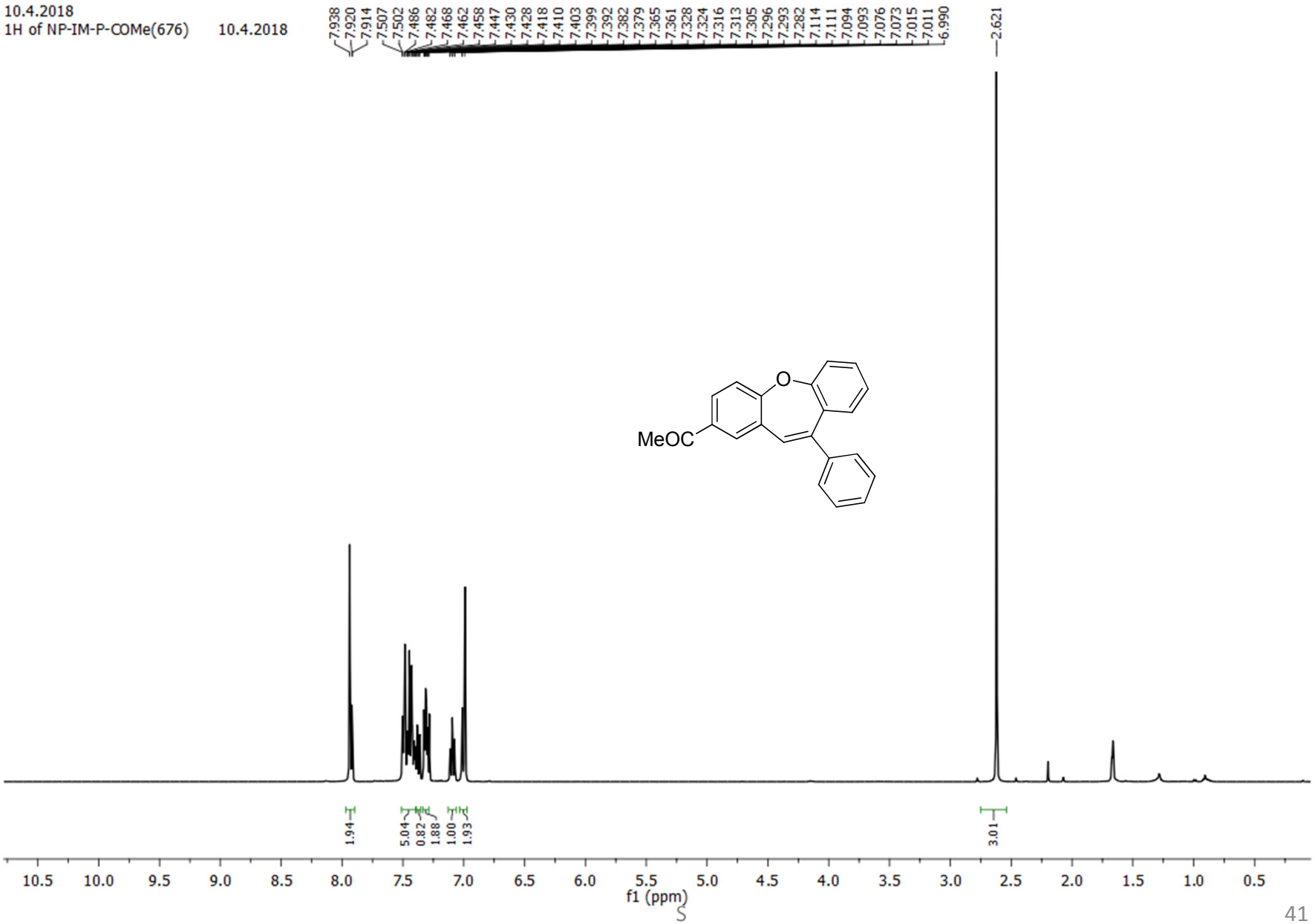
1H NMR of **1-(2-(2-phenylethynyl)phenoxy)naphthalene (2t)**



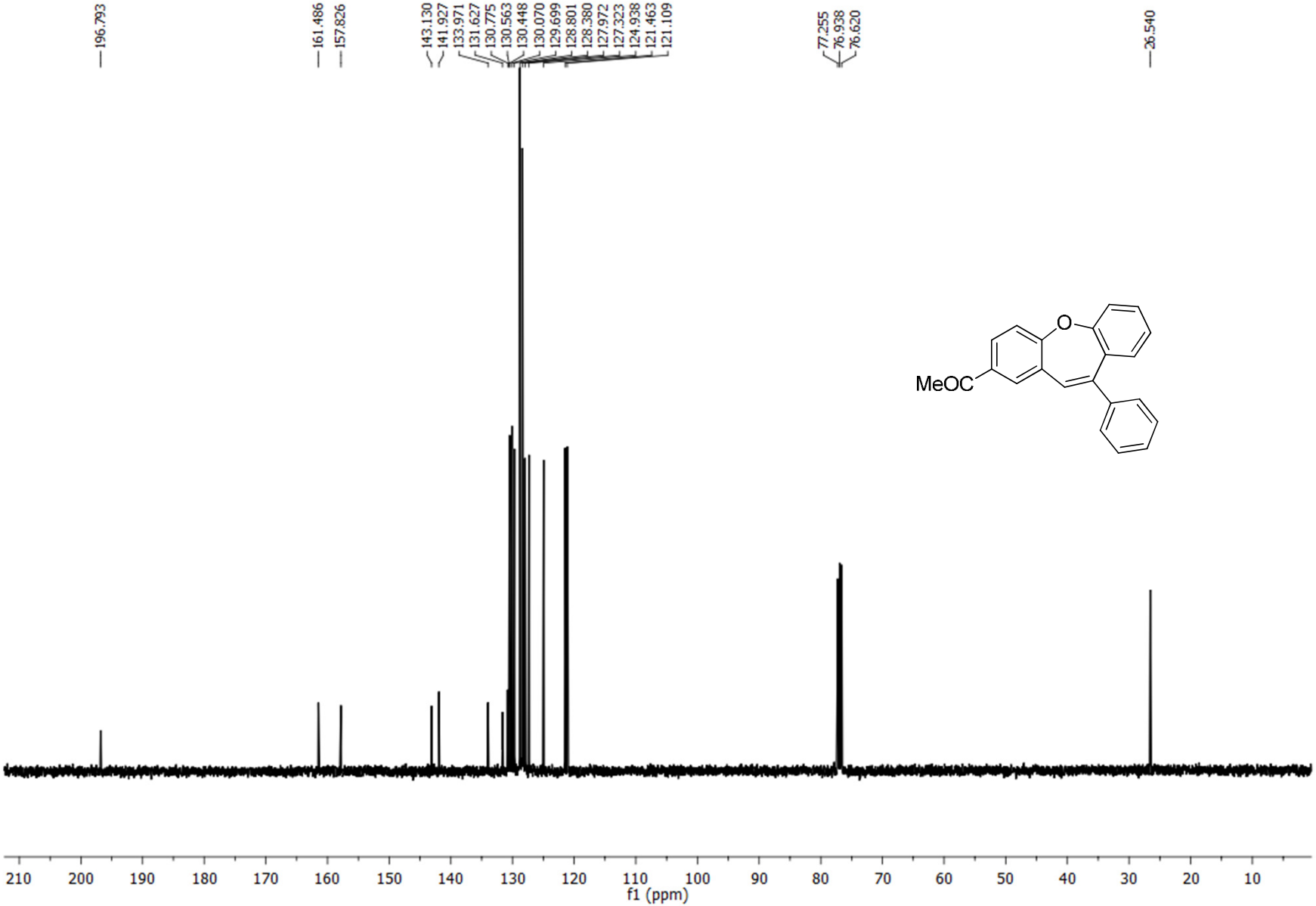
13C NMR of **1-(2-(2-phenylethynyl)phenoxy)naphthalene (2t)**



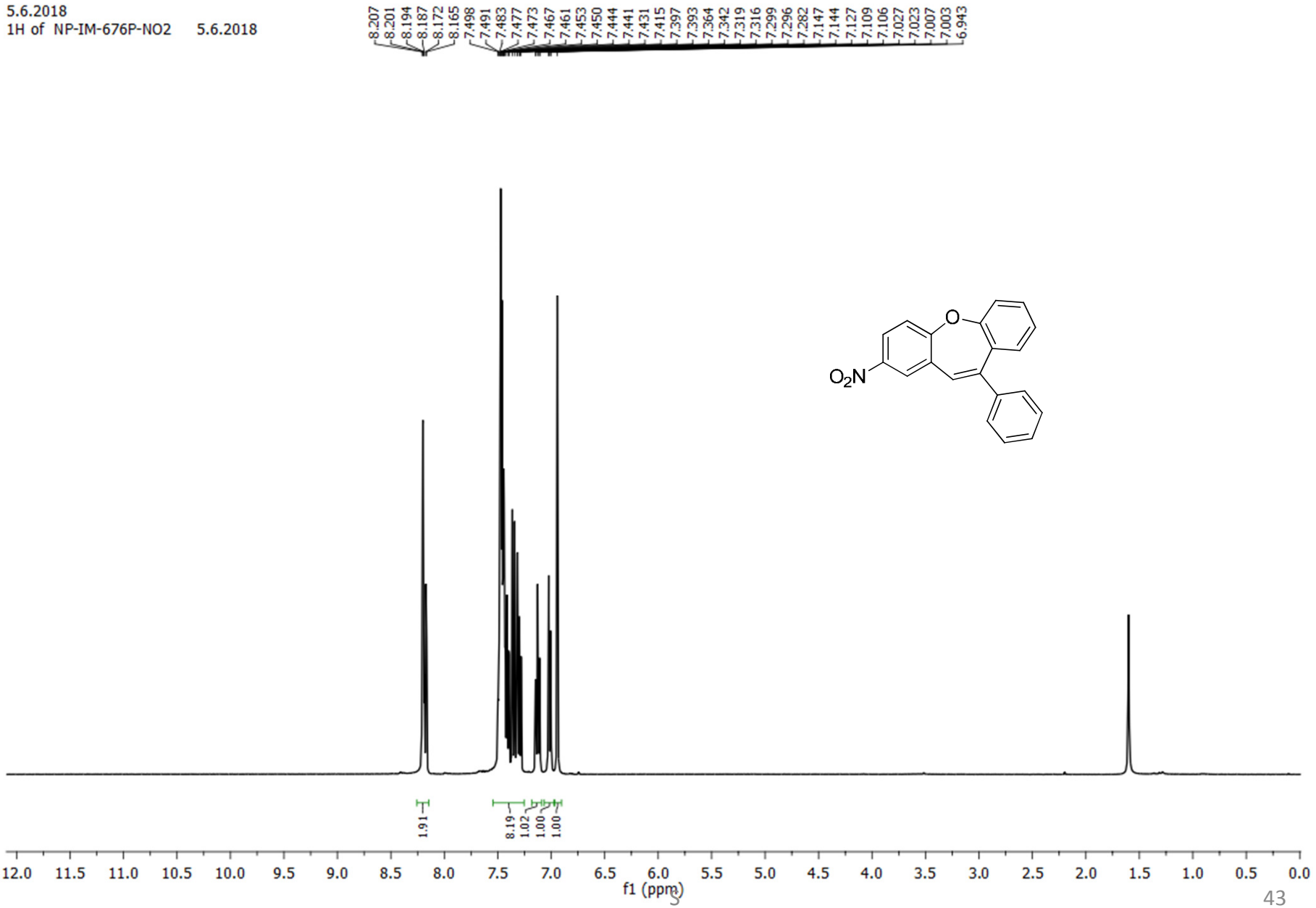
^{1}H NMR of 1-(10-phenyldibenzo[b,f]oxepin-2-yl)ethanone (3a)



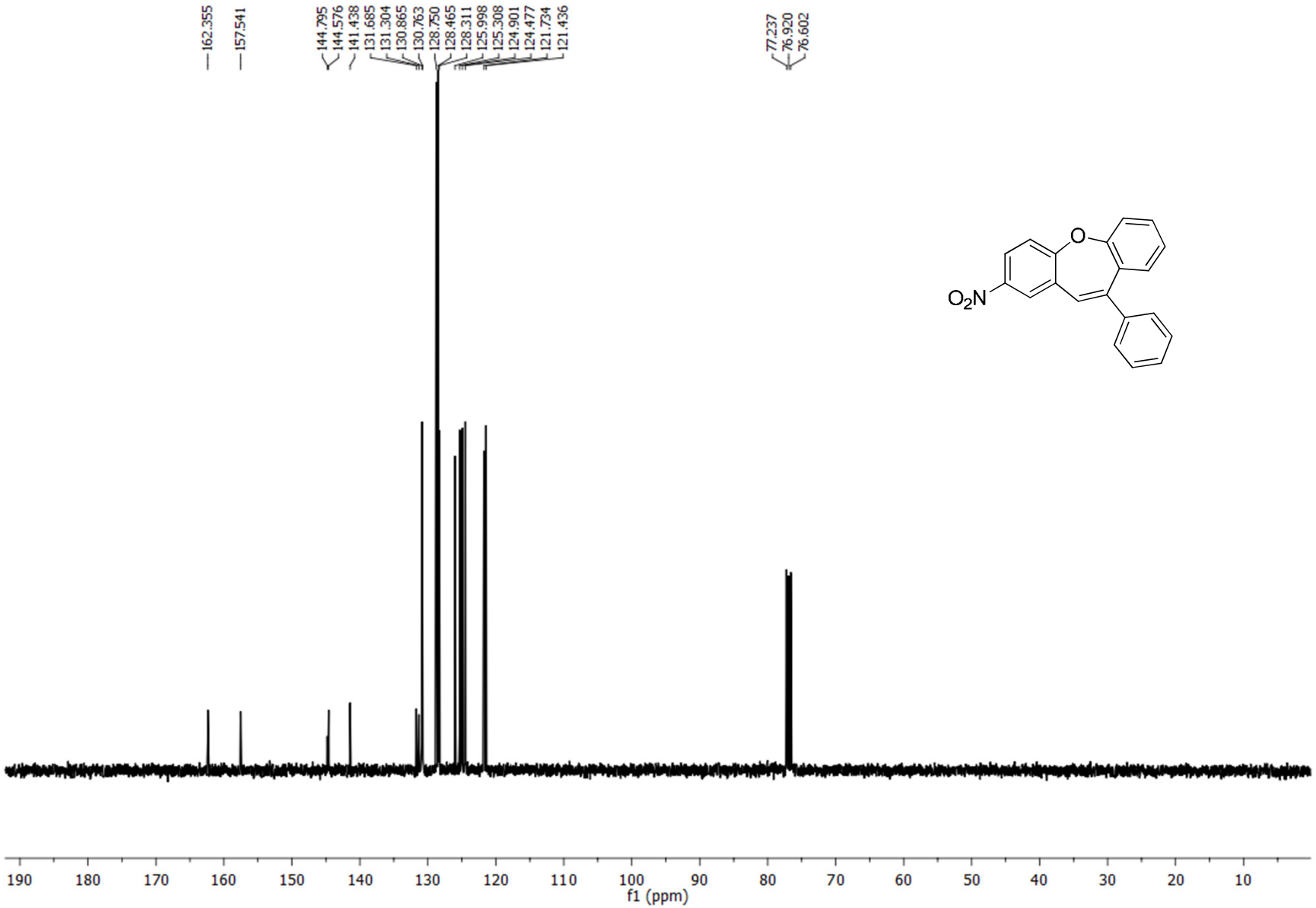
^{13}C NMR of 1-(10-phenyldibenzo[b,f]oxepin-2-yl)ethanone (3a)



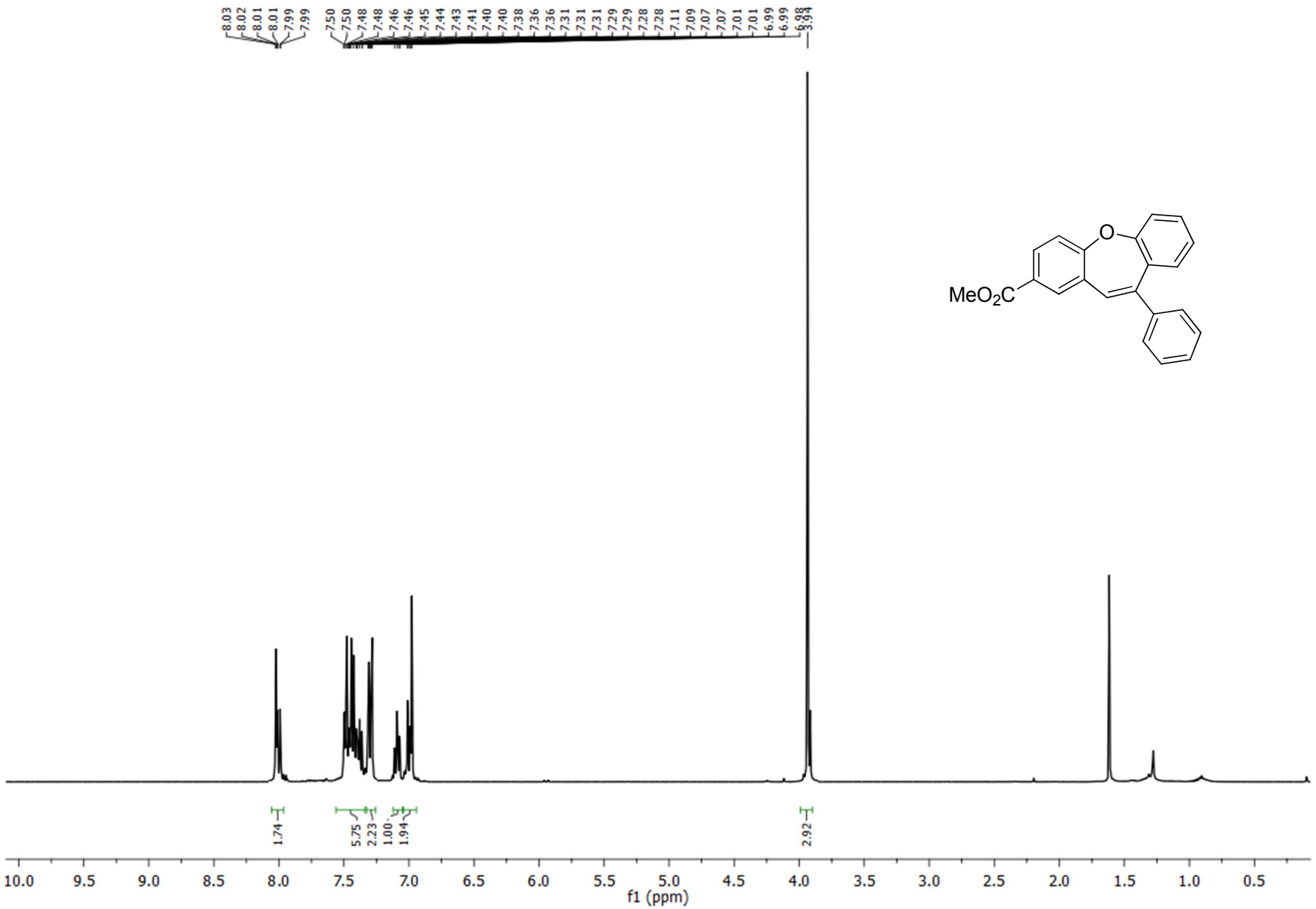
^{1}H NMR of 2-nitro-10-phenyldibenzo[b,f]oxepine (3b)



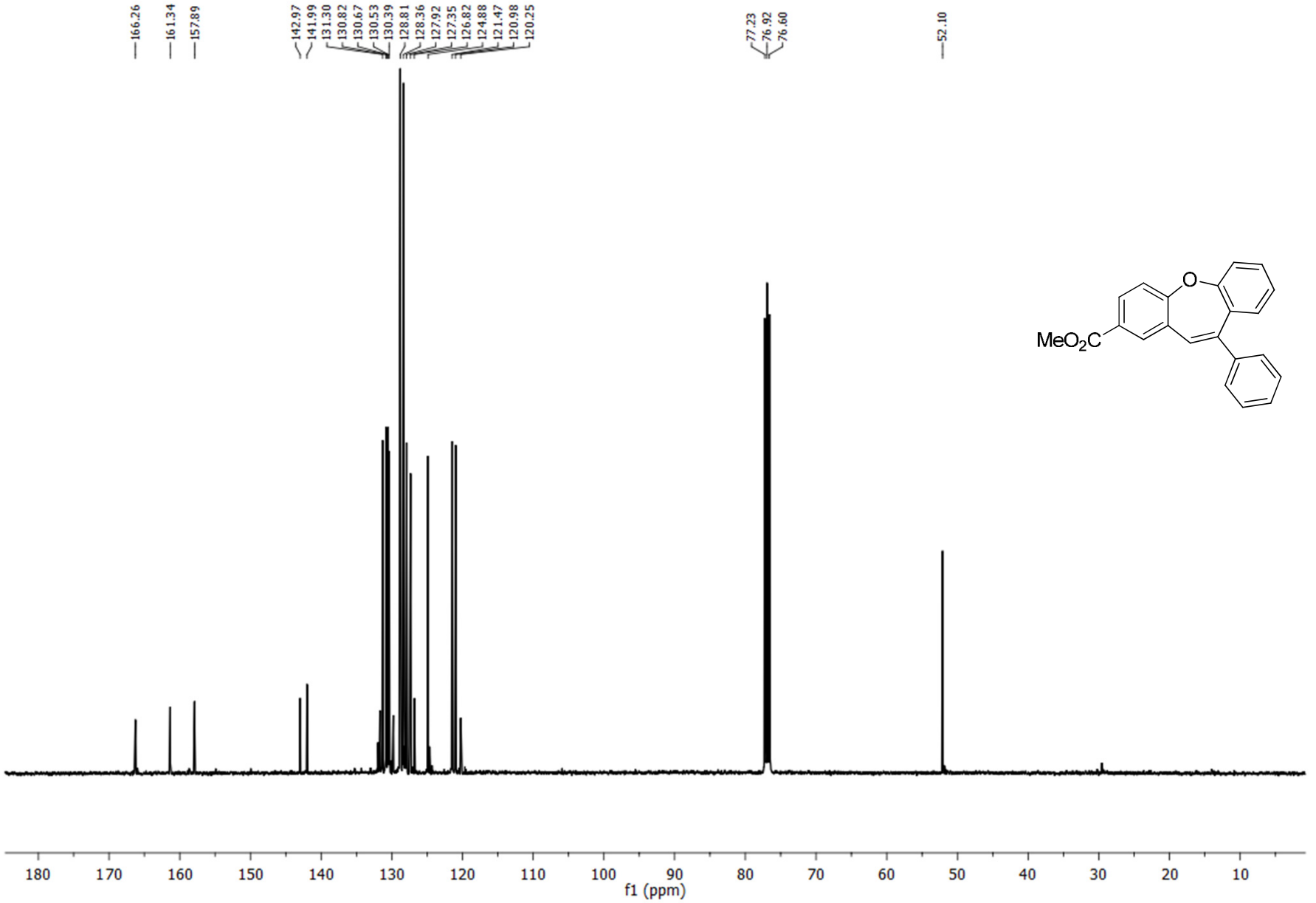
^{13}C NMR of 2-nitro-10-phenyldibenzo[b,f]oxepine (3b)



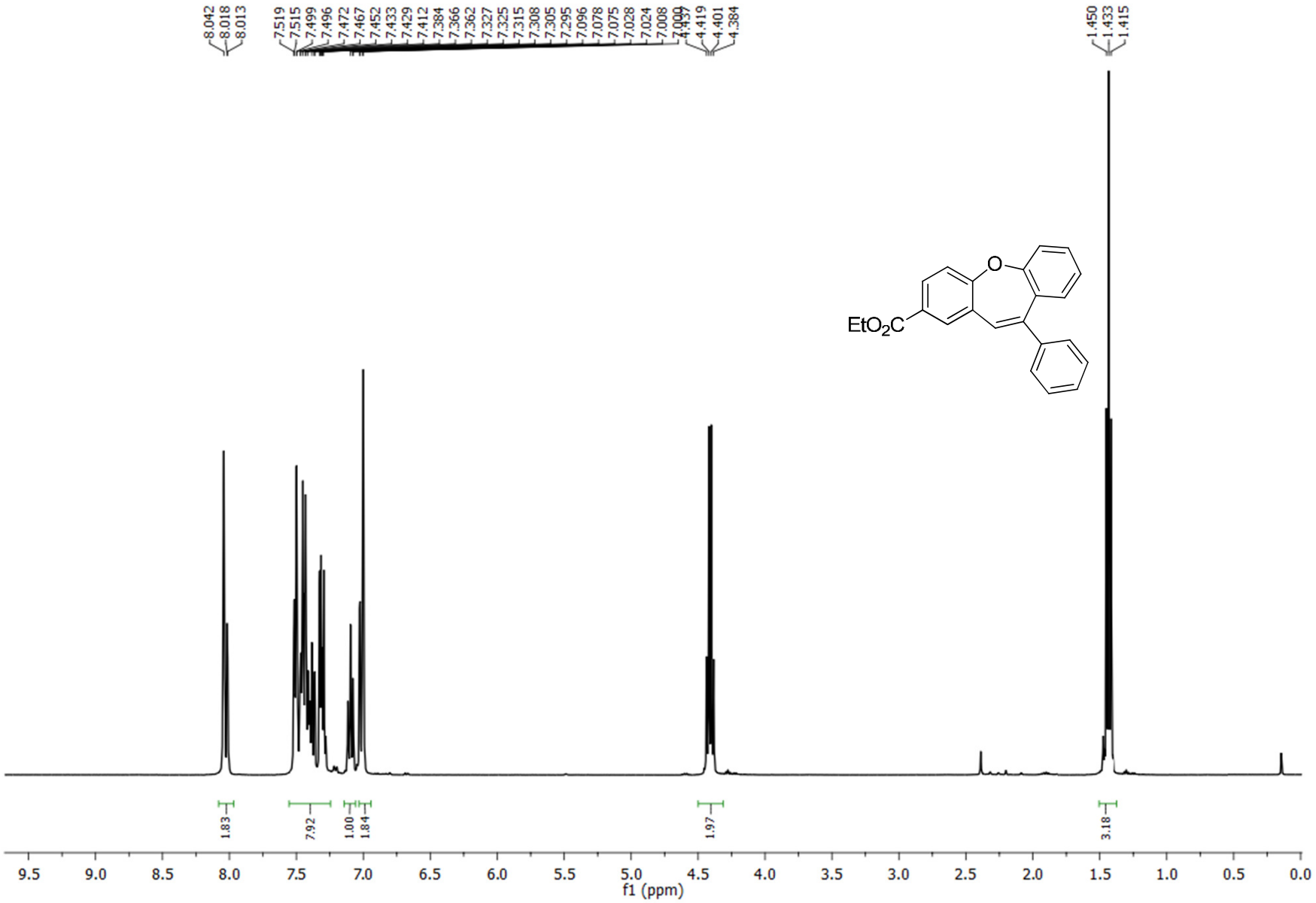
^{1}H NMR of methyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3c)



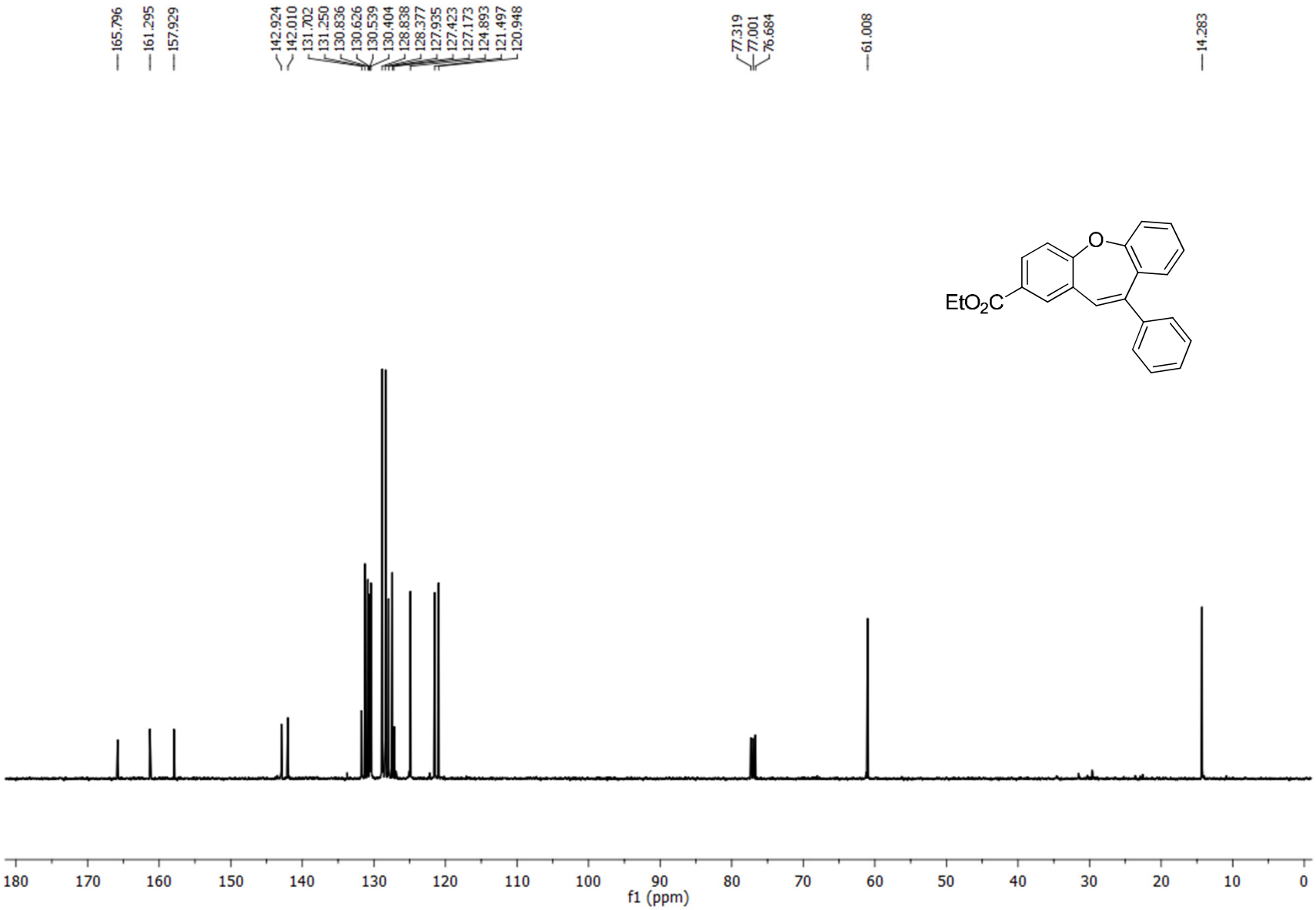
^{13}C NMR of methyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3c)



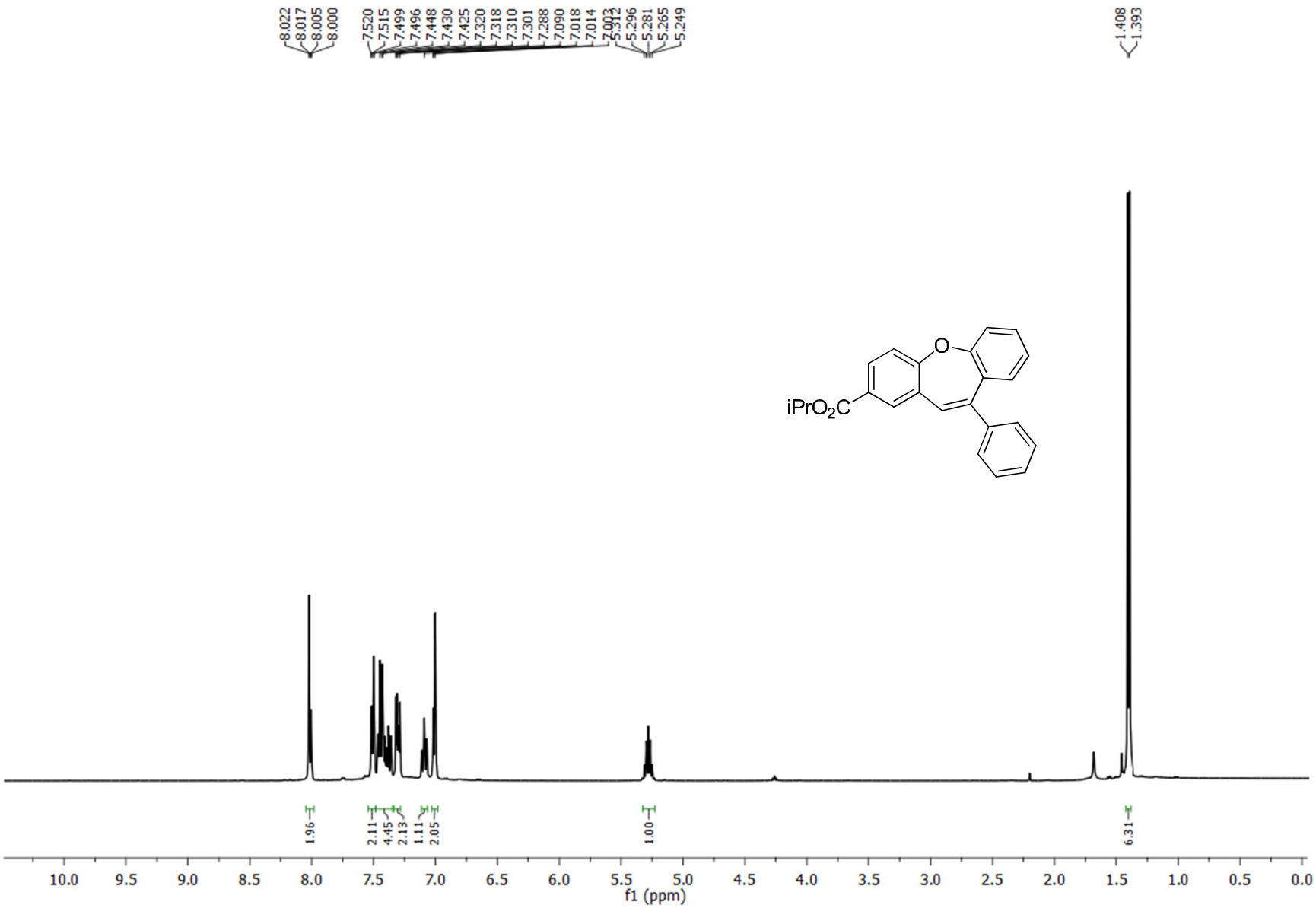
^{1}H NMR of ethyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3d)



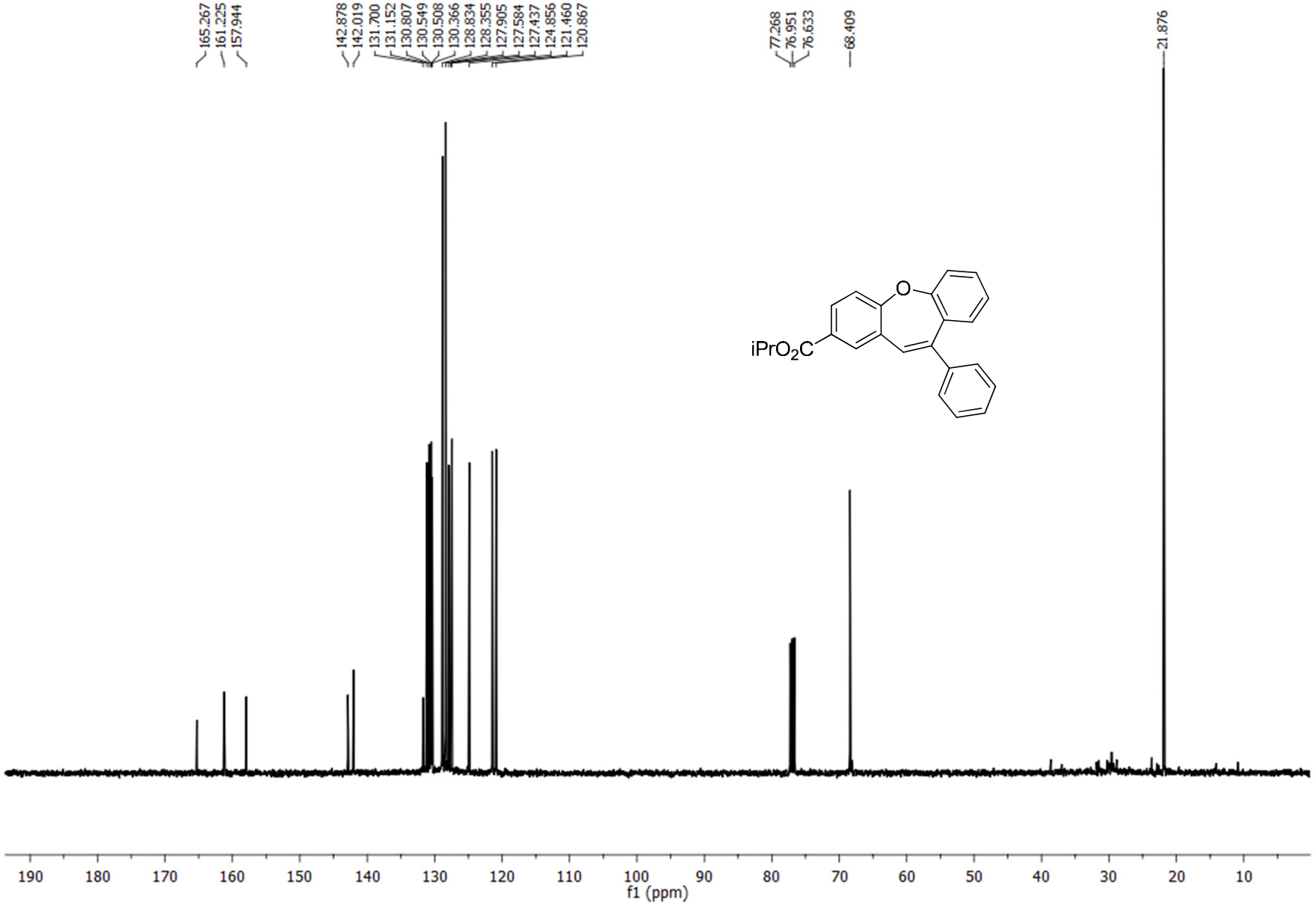
^{13}C NMR of ethyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3d)



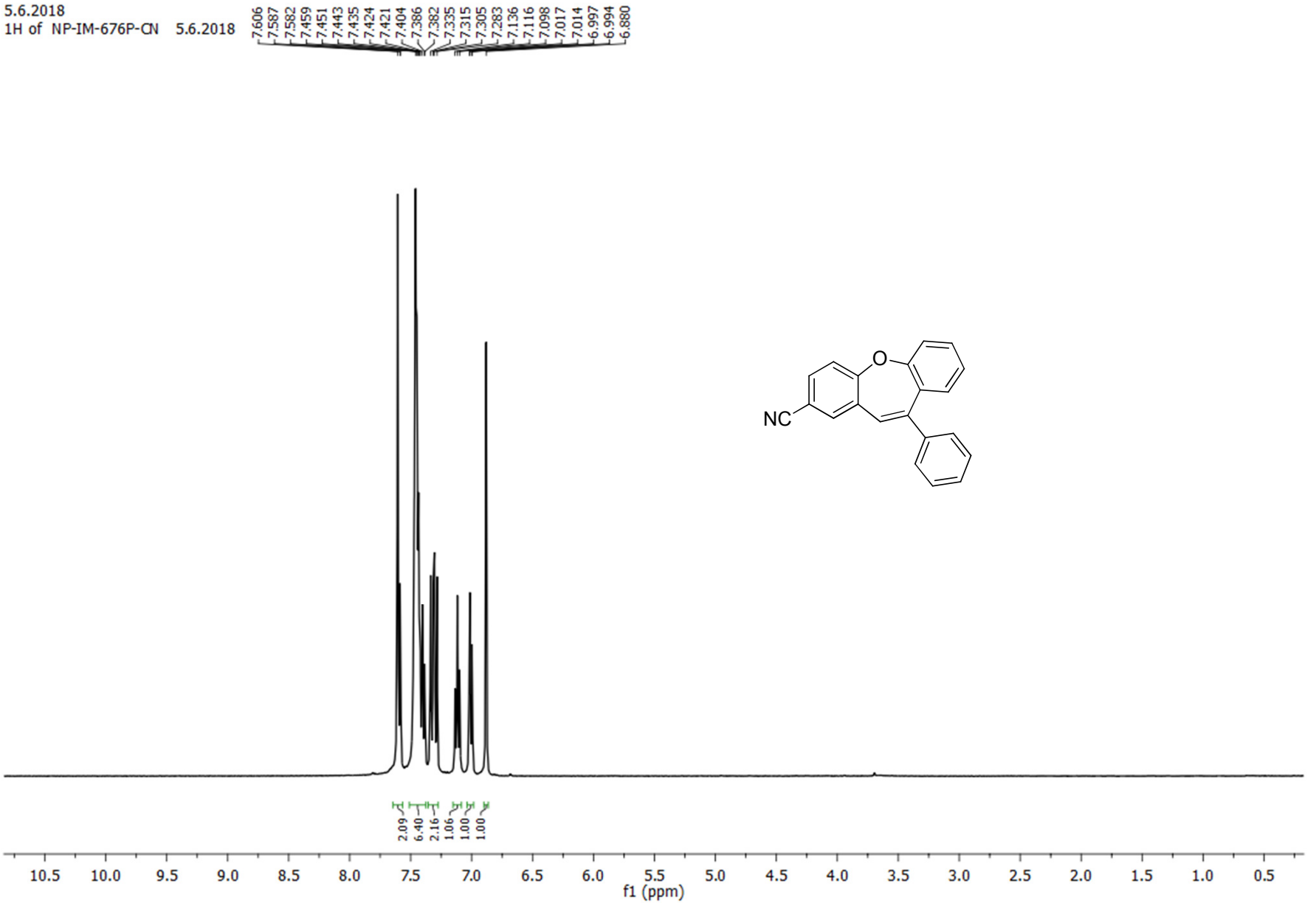
^{1}H NMR of isopropyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3e)



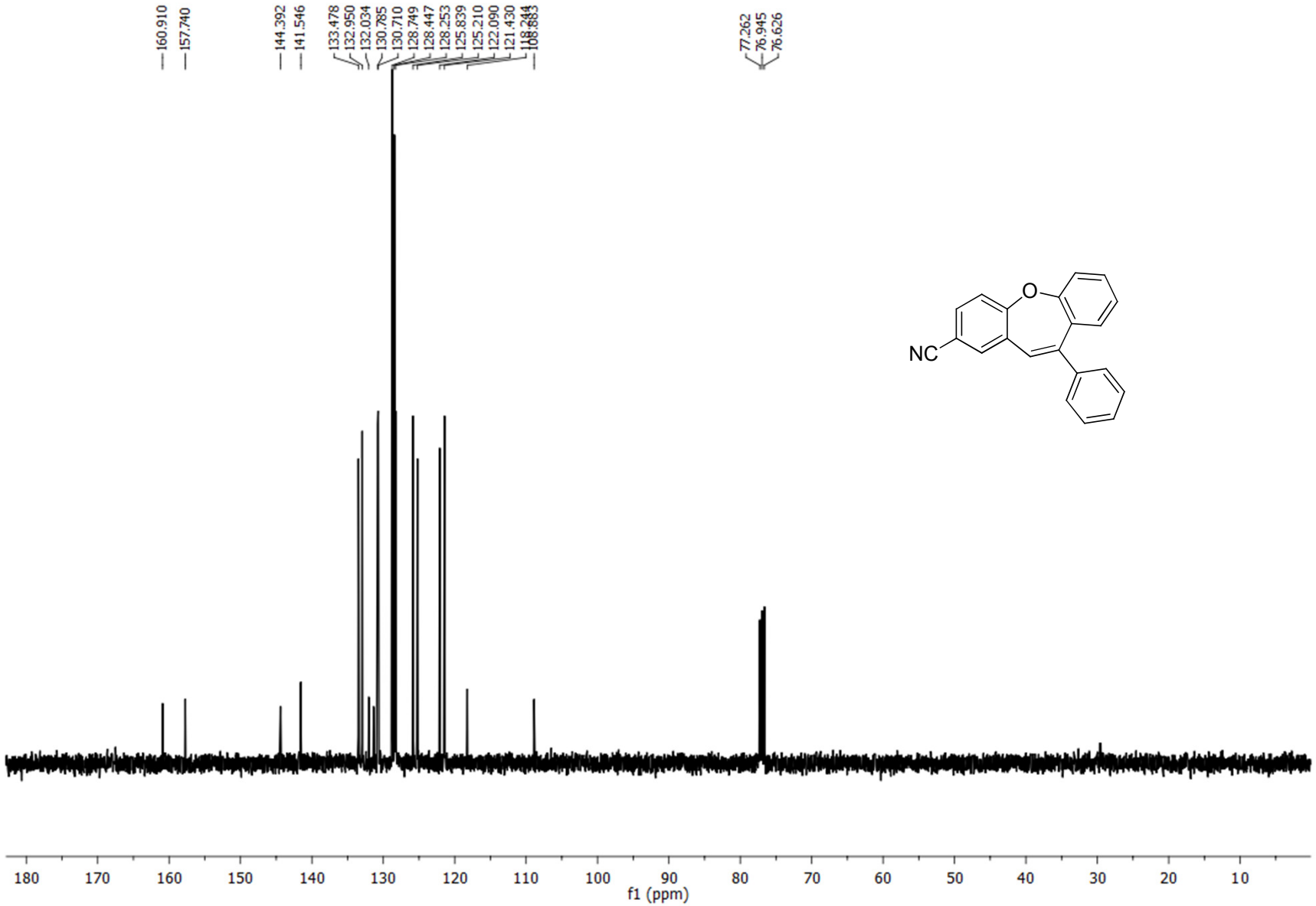
^{13}C NMR of isopropyl 10-phenyldibenzo[b,f]oxepine-2-carboxylate (3e)



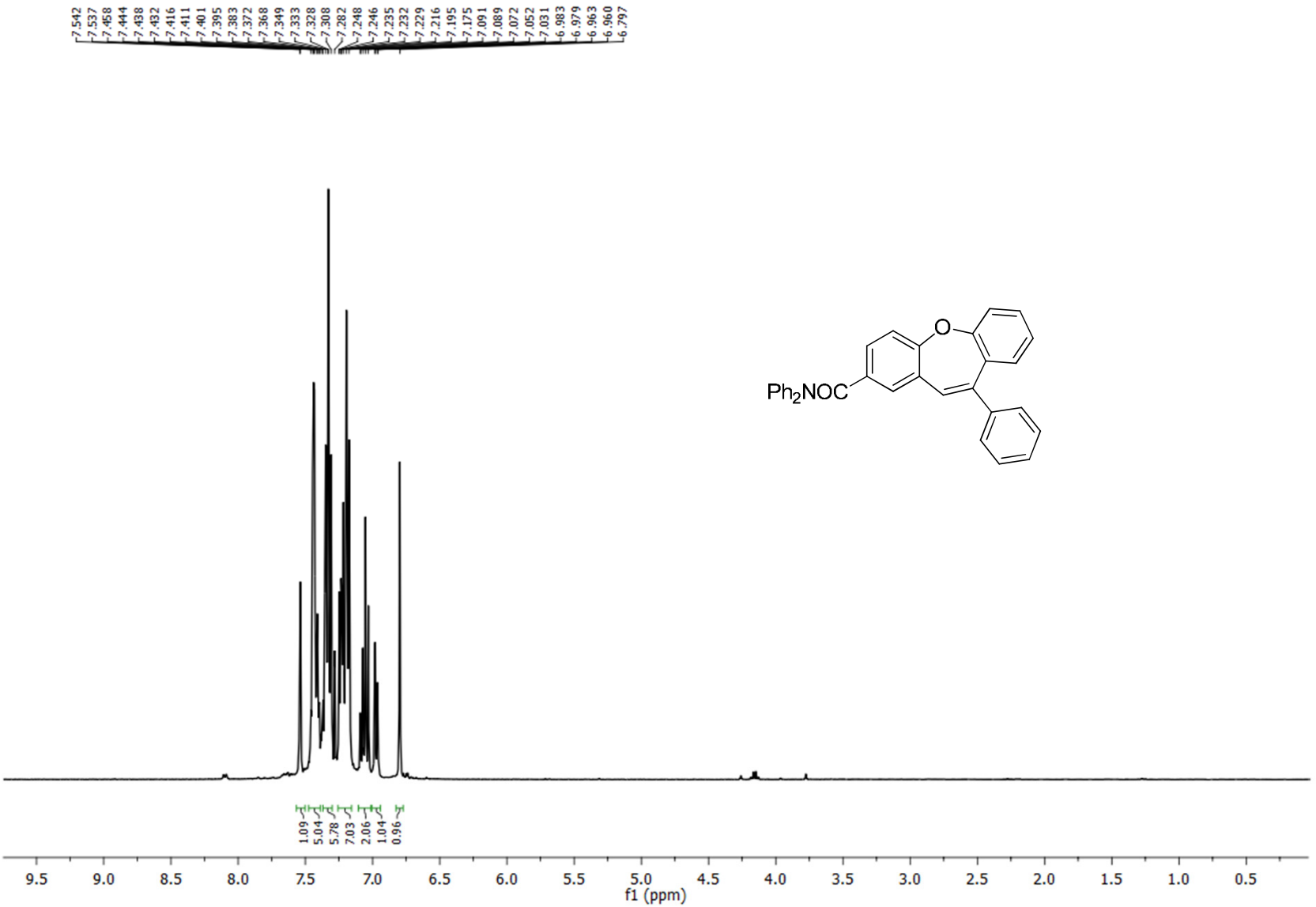
^{1}H NMR of 10-phenyldibenzo[b,f]oxepine-2-carbonitrile (3f)



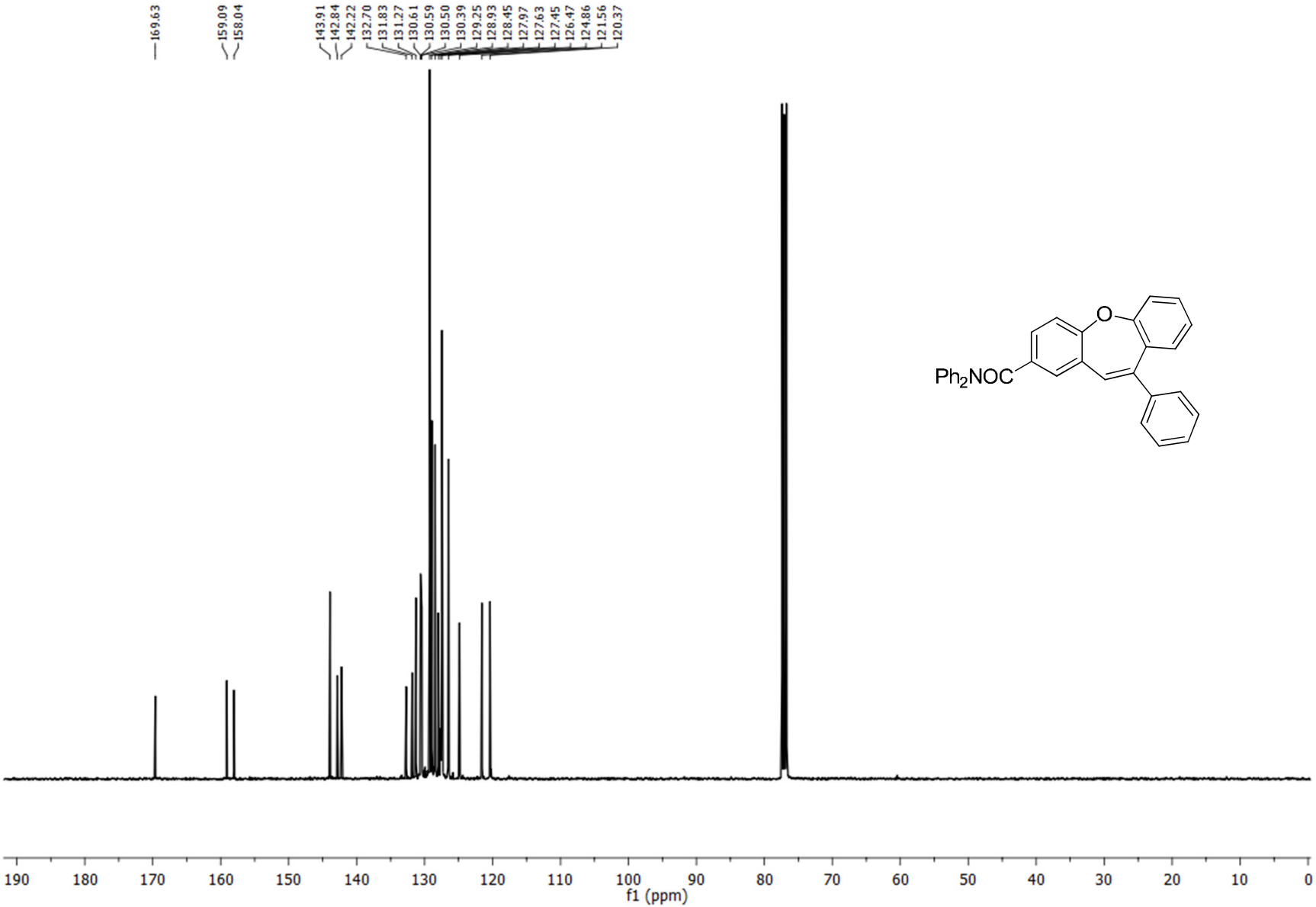
^{13}C NMR of 10-phenyldibenzo[b,f]oxepine-2-carbonitrile (3f)



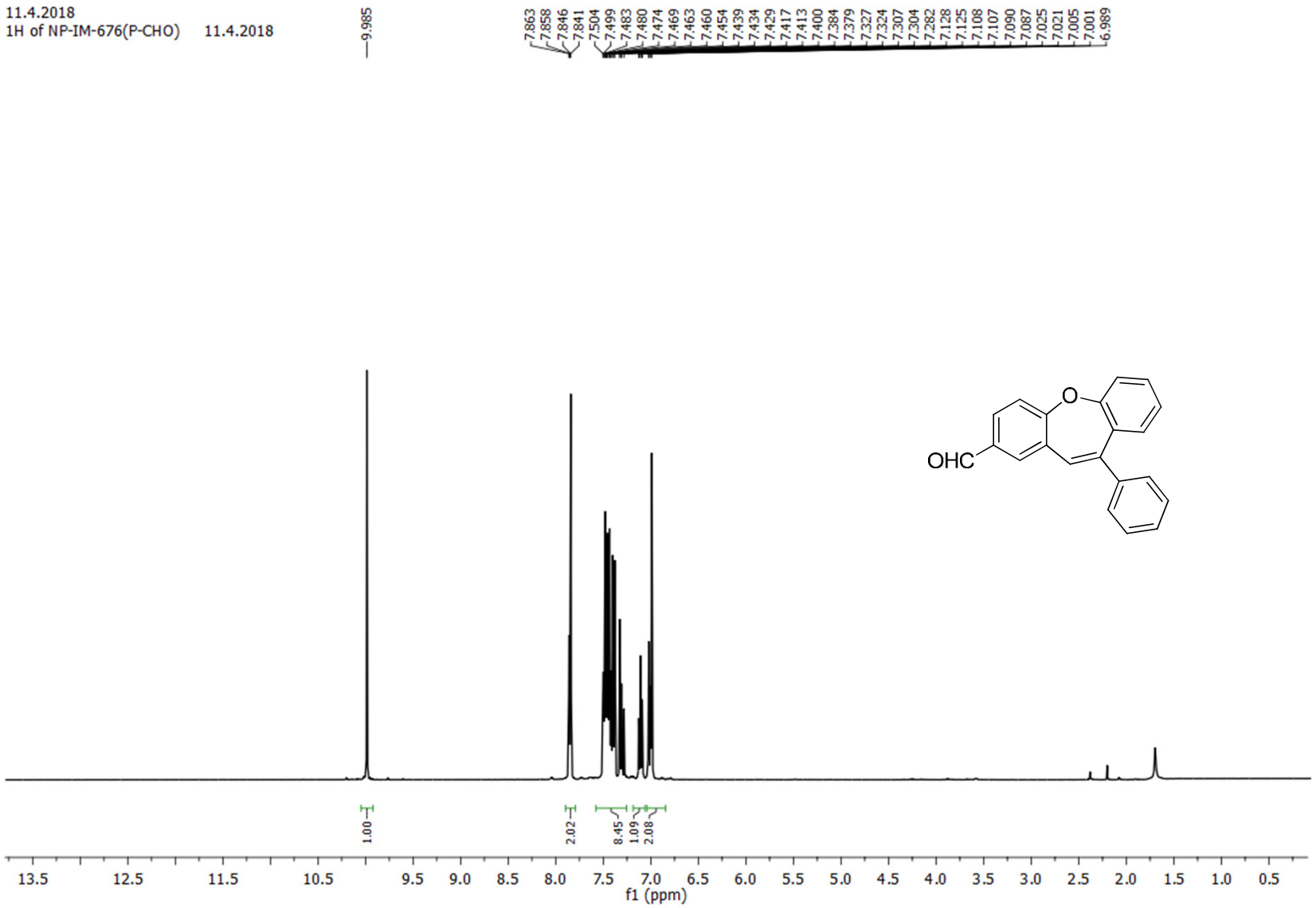
^{1}H NMR of N,N,10-triphenyldibenzo[b,f]oxepine-2-carboxamide (3g)



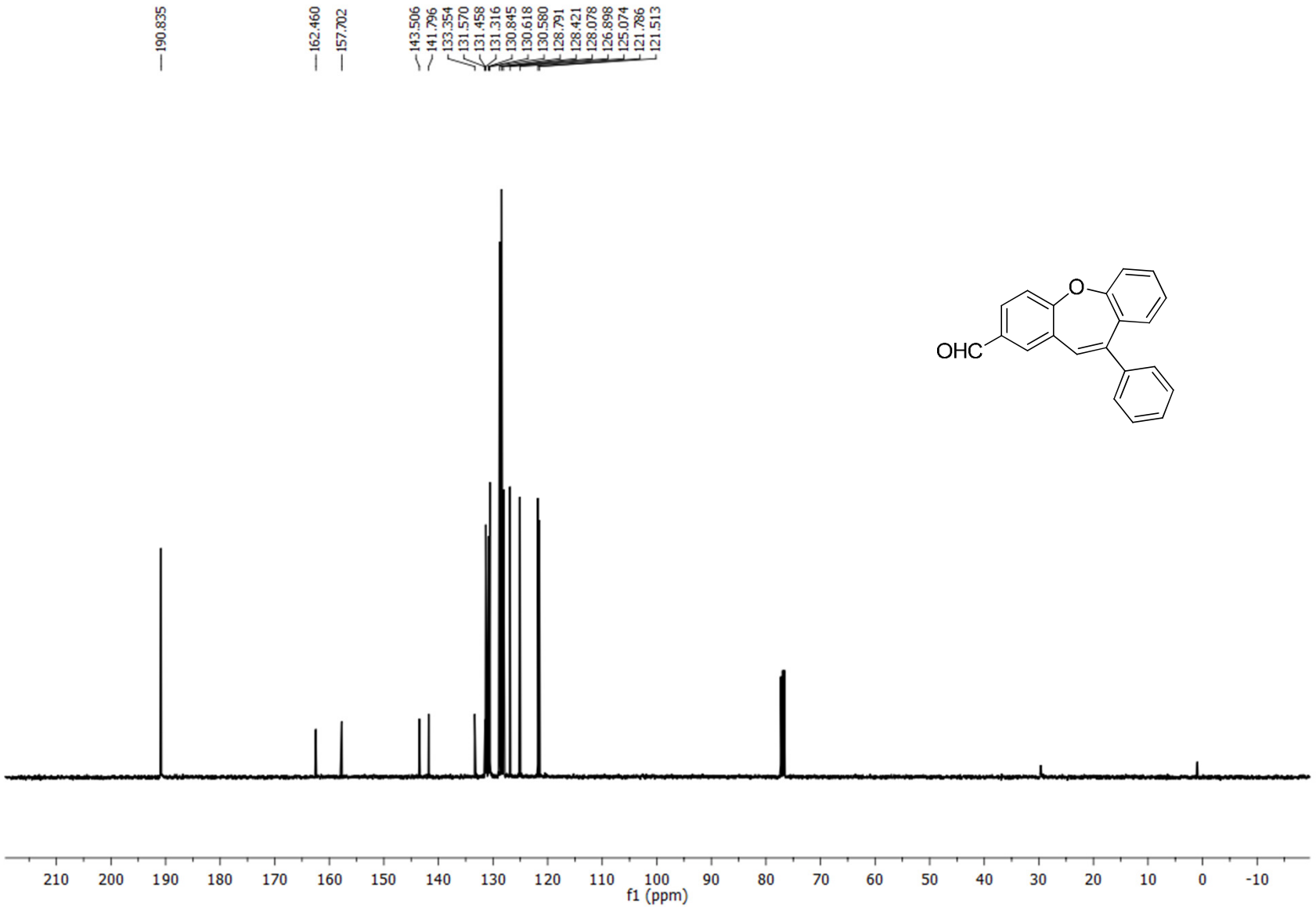
^{13}C NMR of N,N,10-triphenyldibenzo[b,f]oxepine-2-carboxamide (3g)



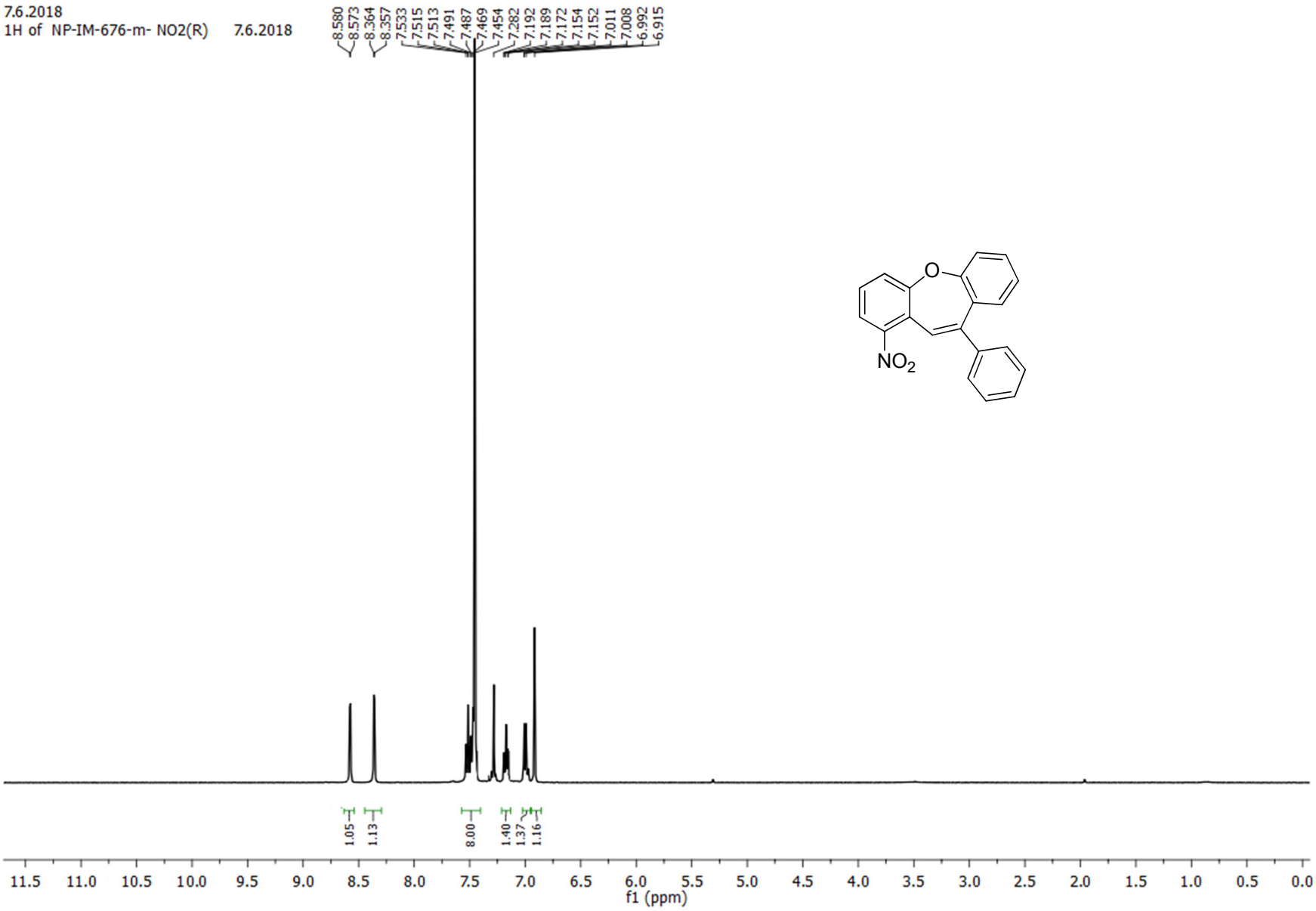
^{1}H NMR of 10-phenyldibenzo[b,f]oxepine-2-carbaldehyde (3h)



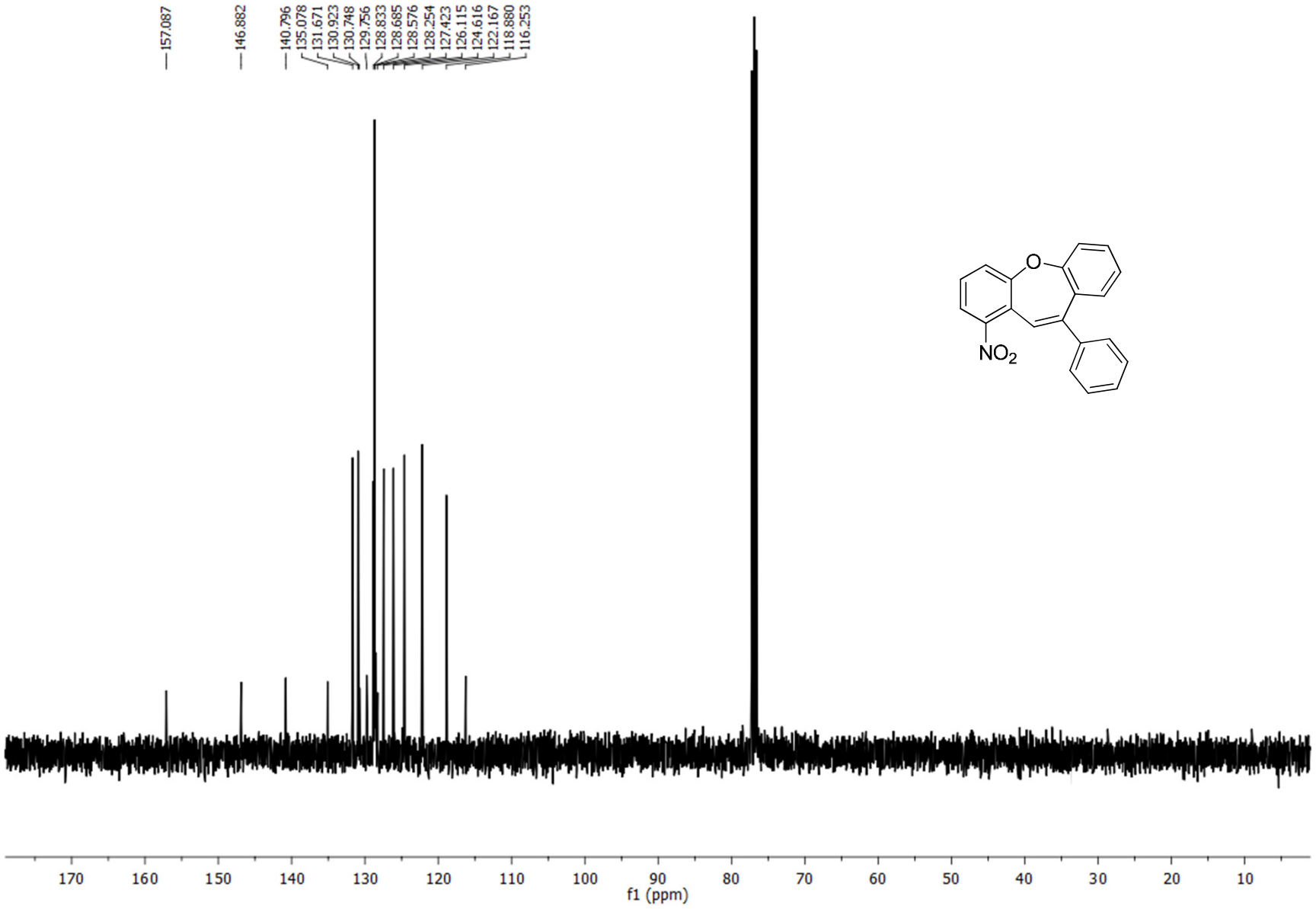
^{13}C NMR of 10-phenyldibenzo[b,f]oxepine-2-carbaldehyde (3h)



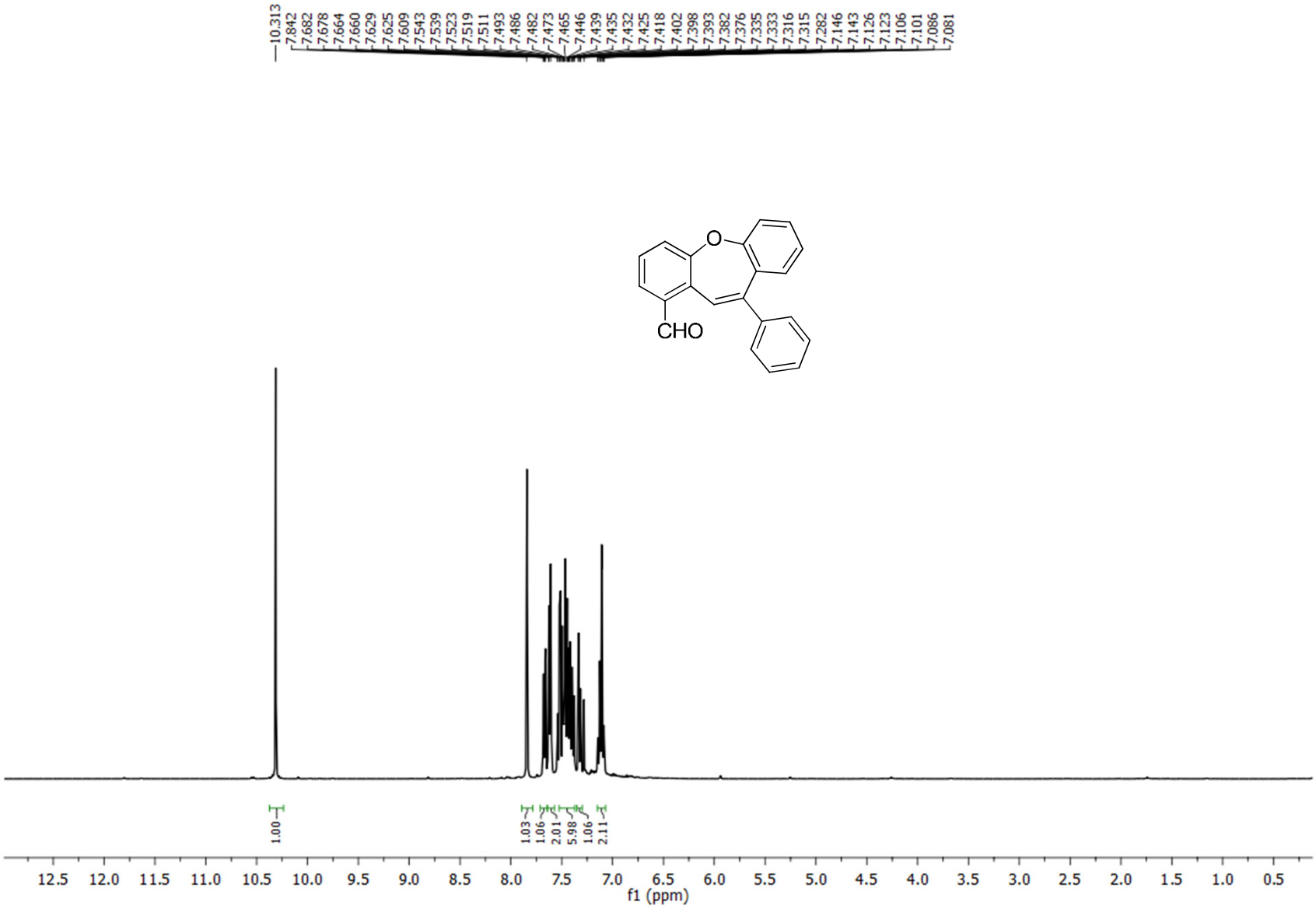
^{1}H NMR of 1-nitro-10-phenyldibenzo[b,f]oxepine (3i)



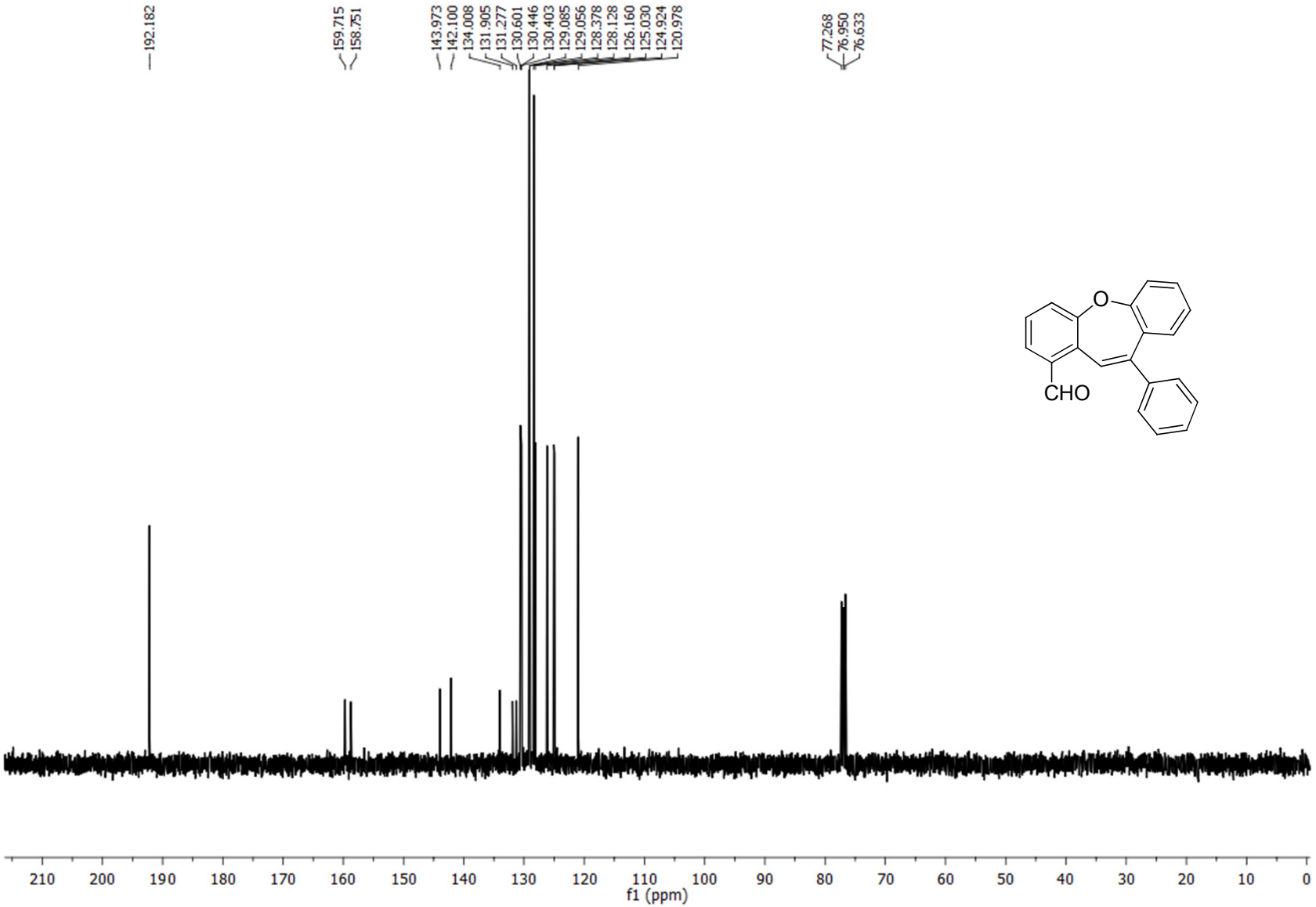
^{13}C NMR of 1-nitro-10-phenyldibenzo[b,f]oxepine (3i)



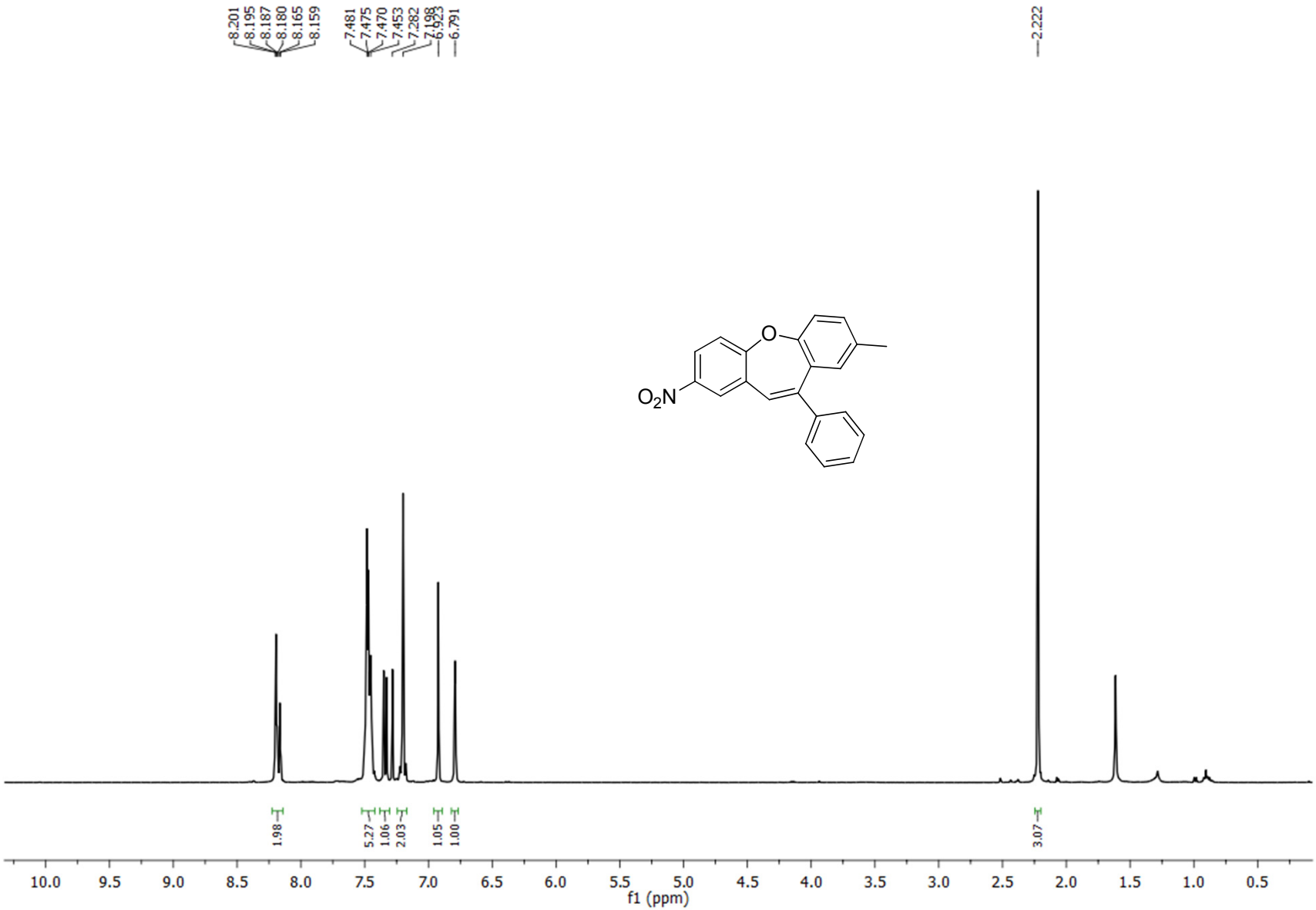
^{1}H NMR of 10-phenyldibenzo[b,f]oxepine-1-carbaldehyde (3j)



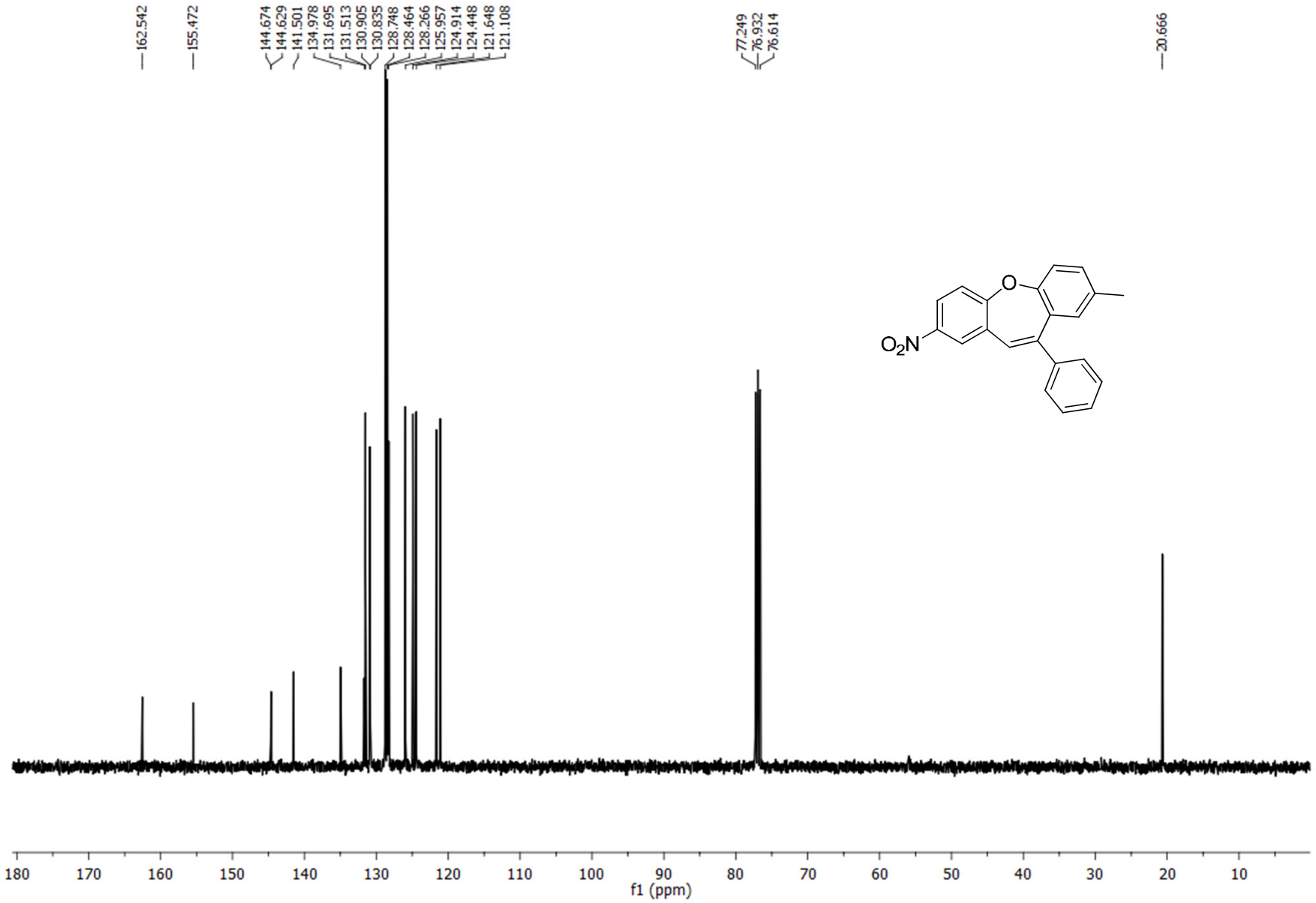
^{13}C NMR of 10-phenyldibenzo[b,f]oxepine-1-carbaldehyde (3j)



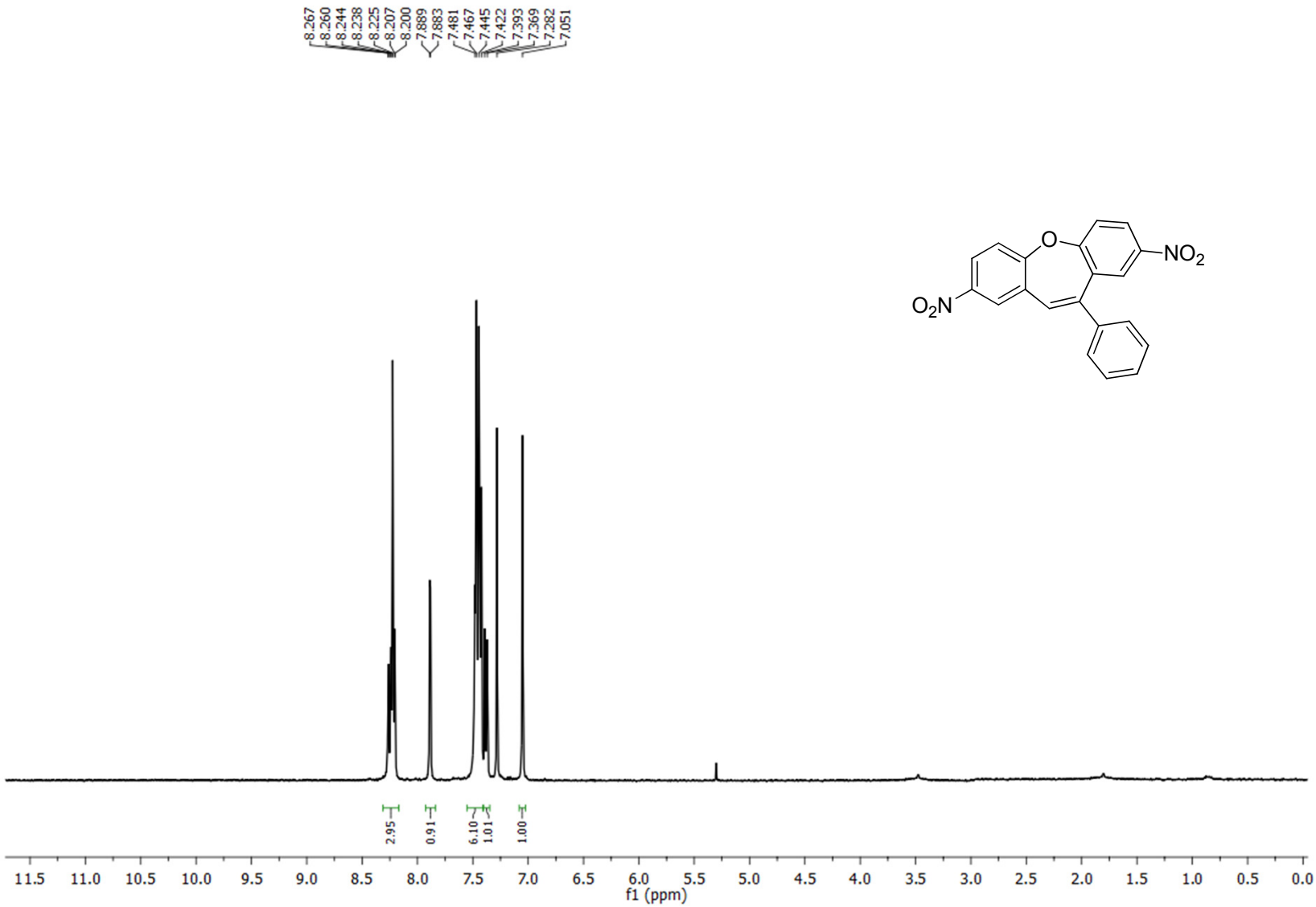
^{1}H NMR of 8-methyl-2-nitro-10-phenyldibenzo[b,f]oxepine (3k)



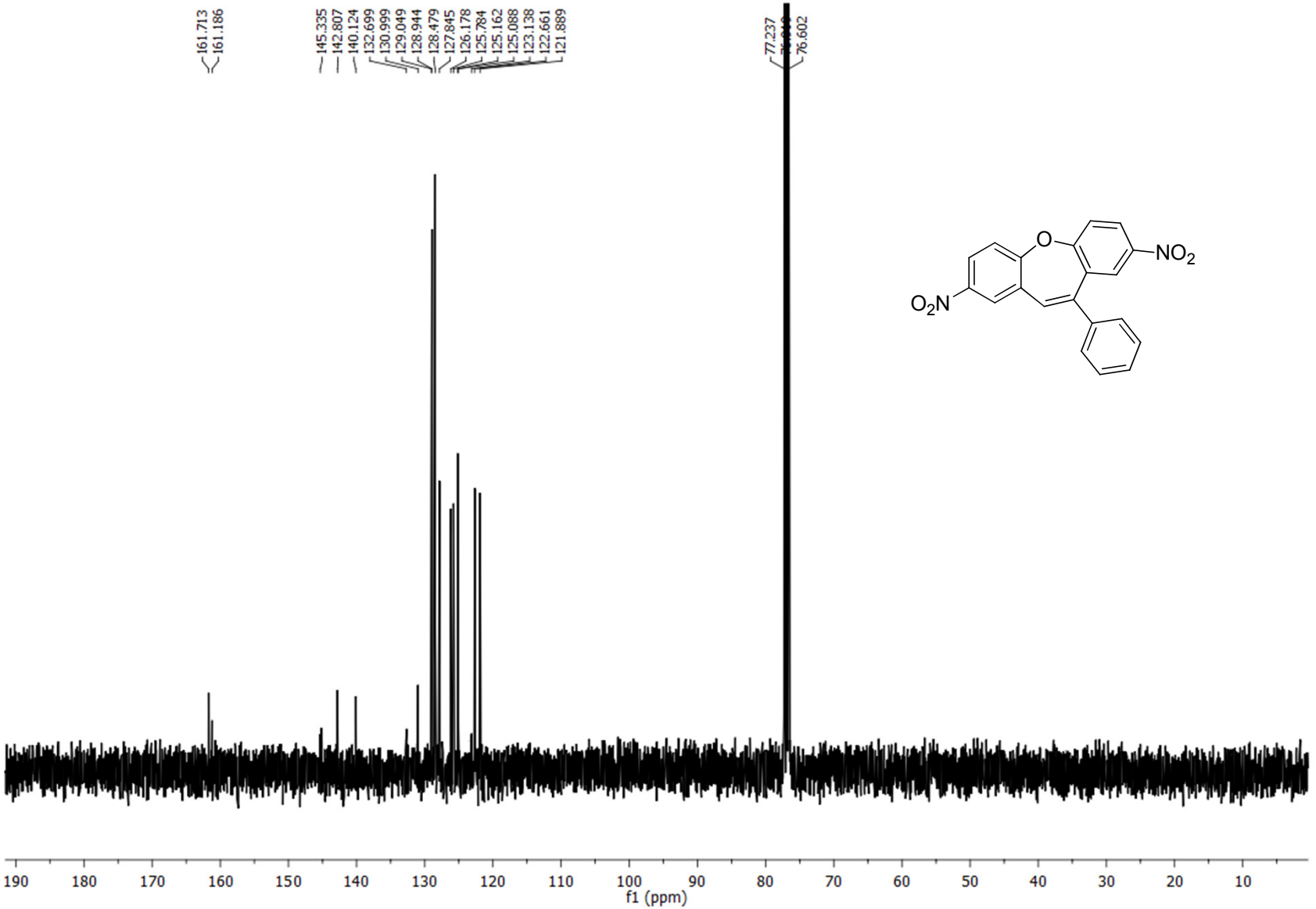
^{13}C NMR of 8-methyl-2-nitro-10-phenyldibenzo[b,f]oxepine (3k)



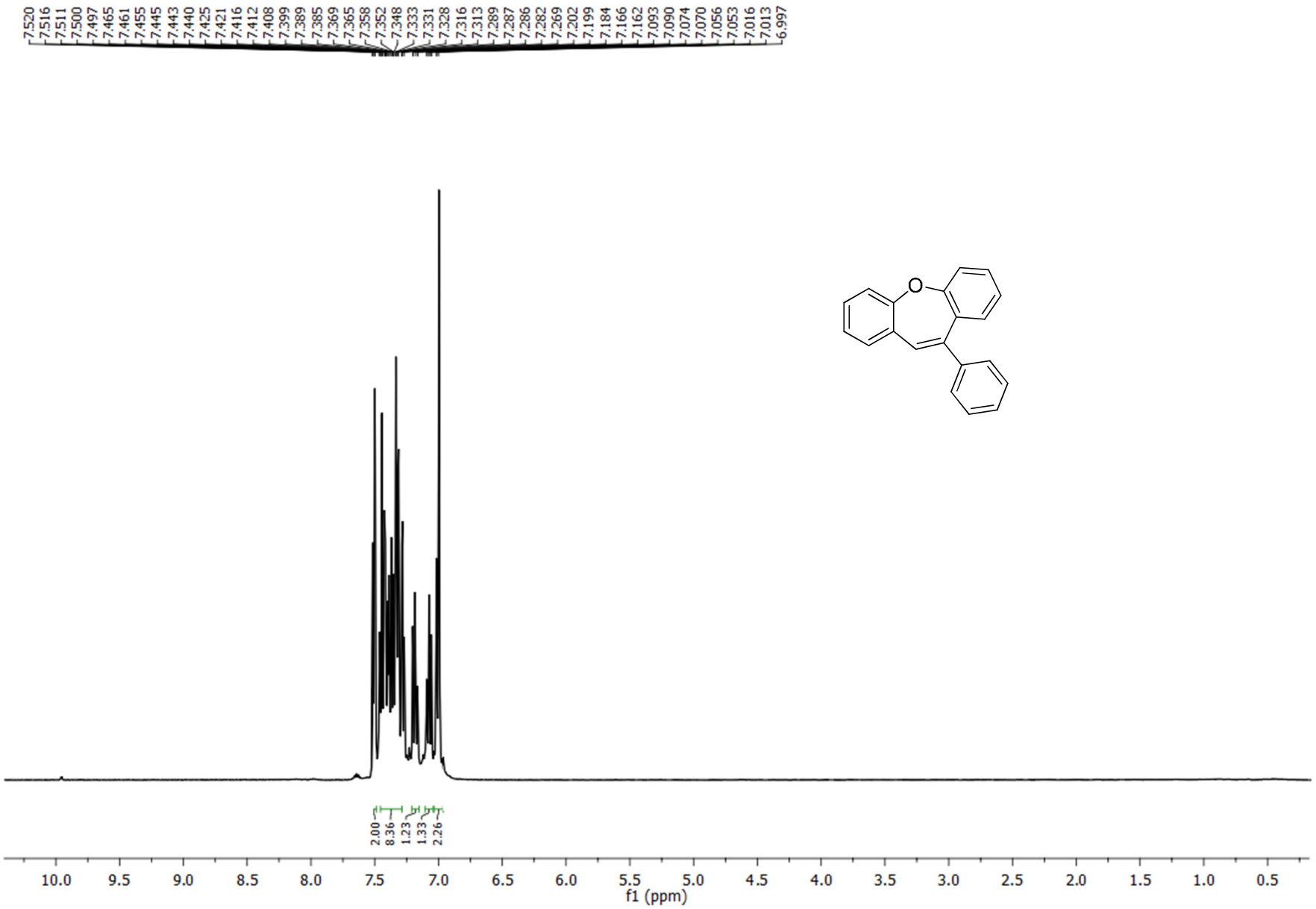
^{1}H NMR of 2,8-dinitro-10-phenyldibenzo[b,f]oxepine (3l)



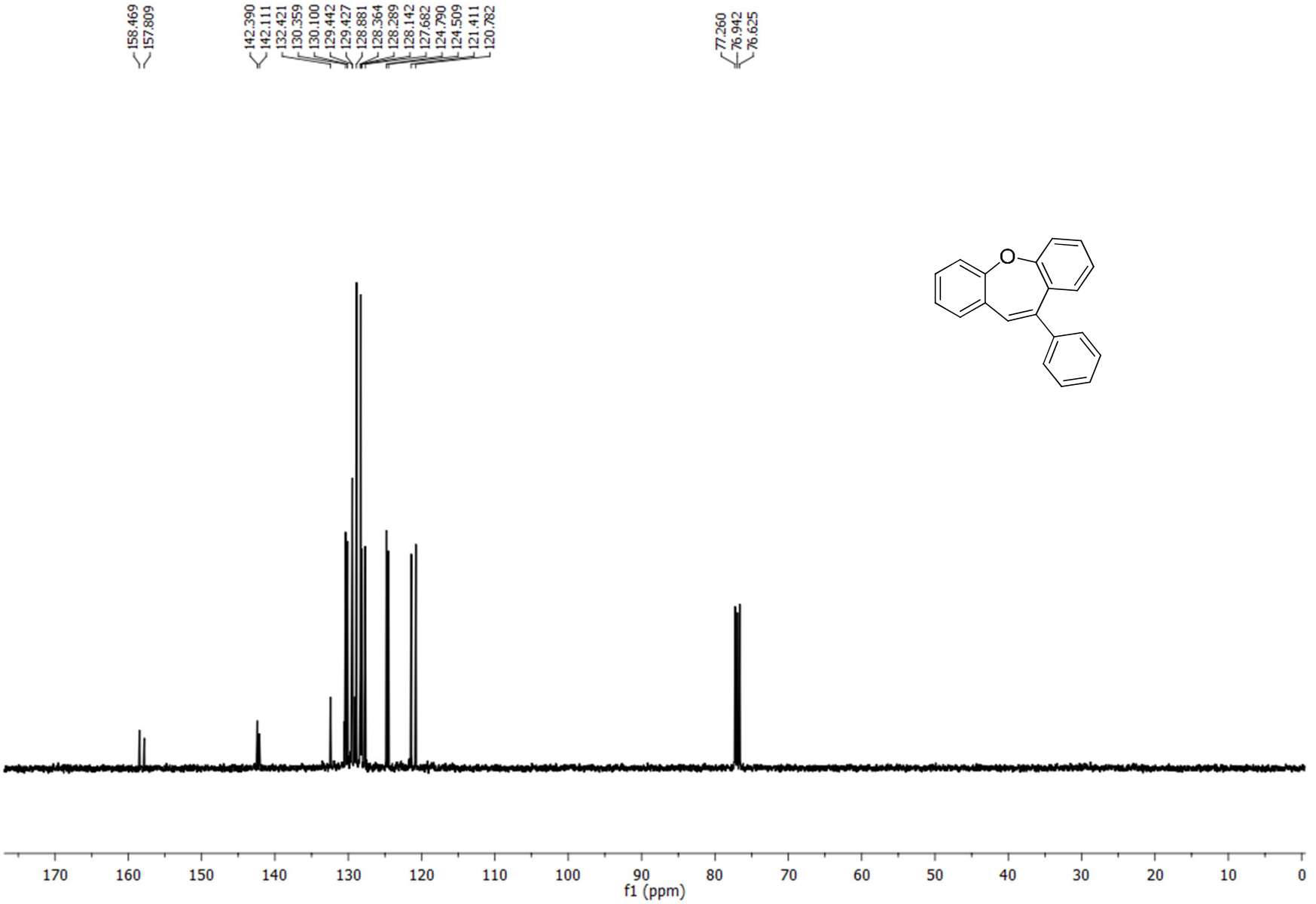
^{13}C NMR of 2,8-dinitro-10-phenyldibenzo[b,f]oxepine (3l)



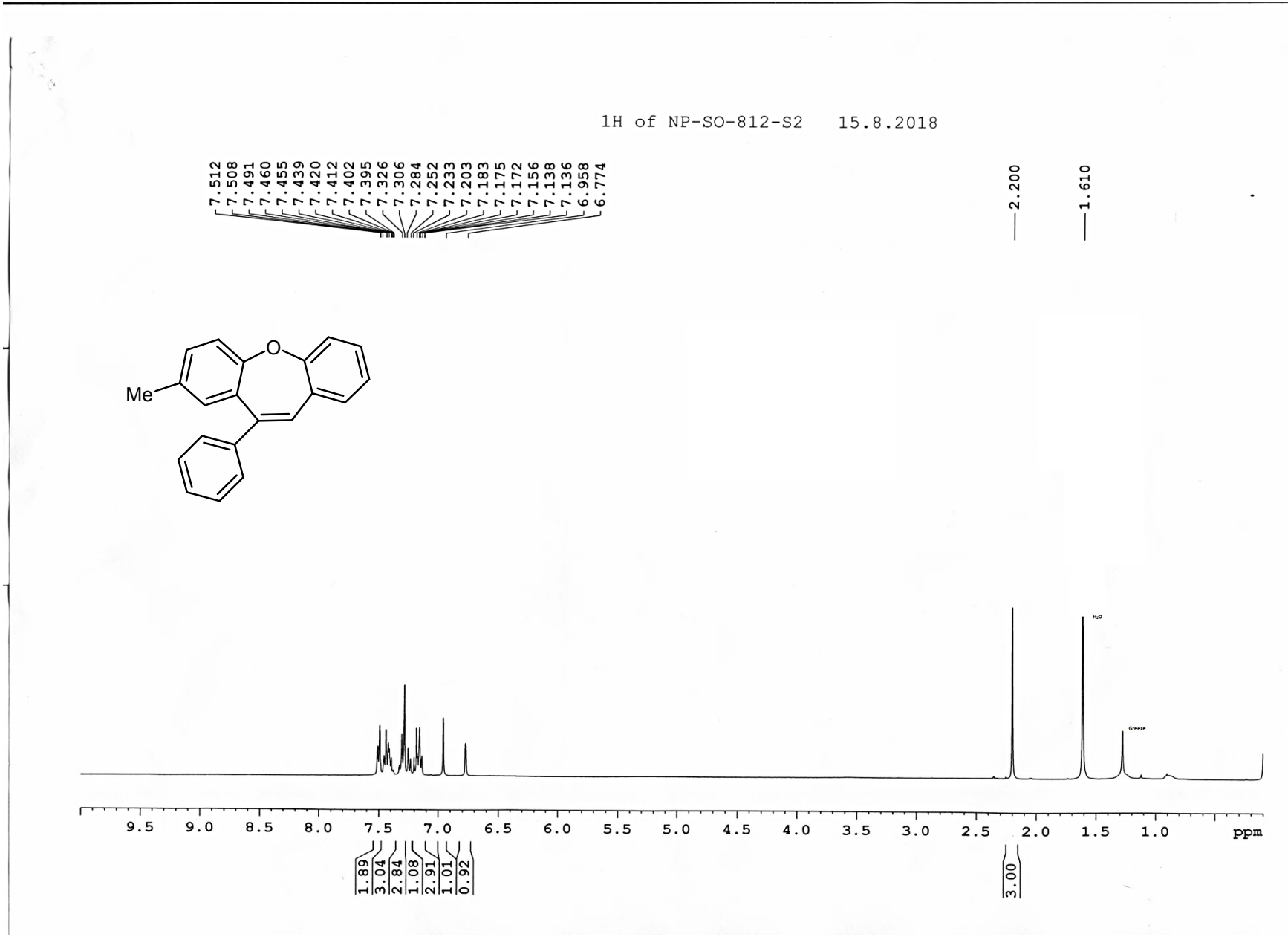
^{1}H NMR of 10-phenyldibenzo[b,f]oxepine (3o)



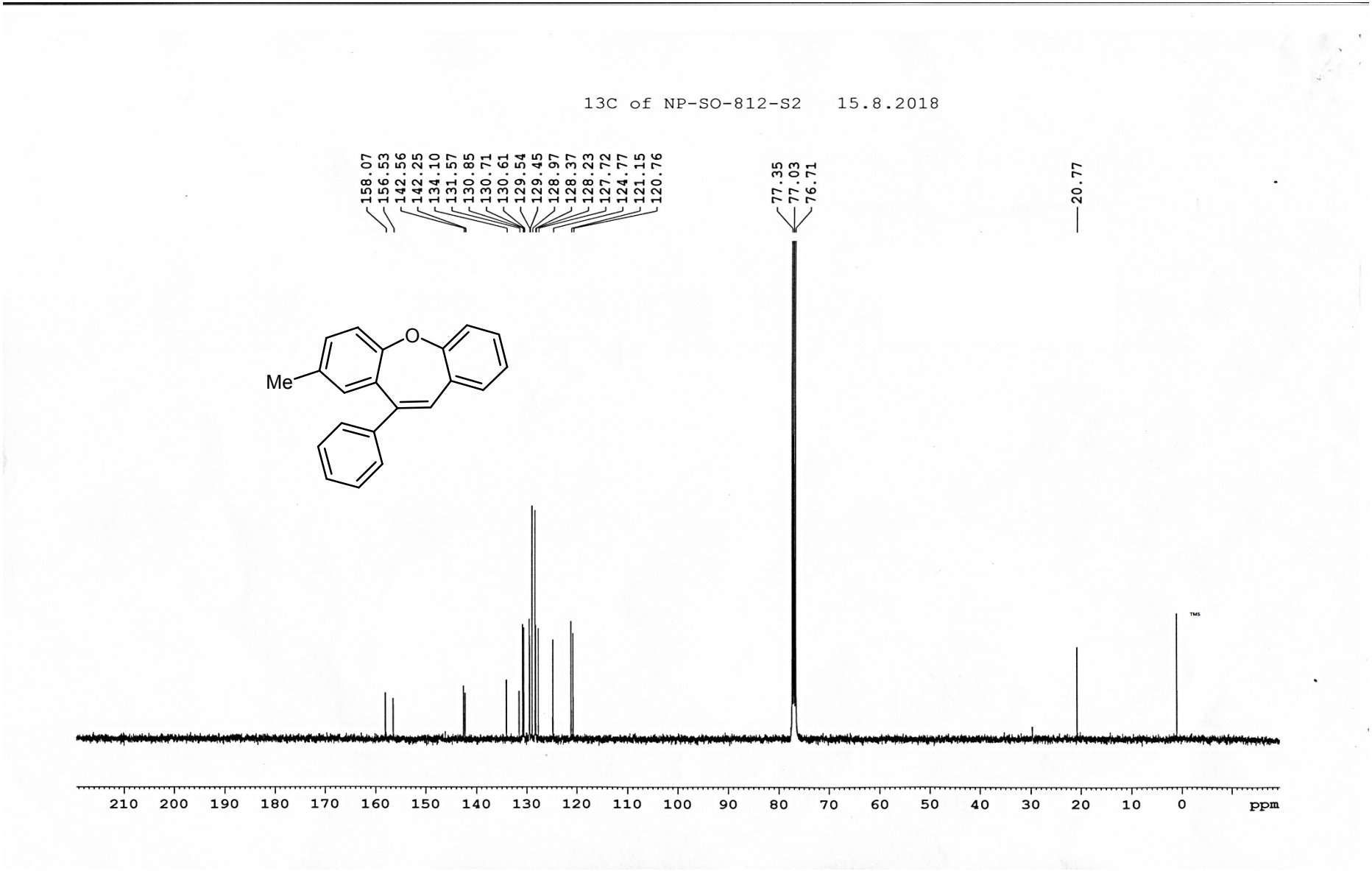
^{13}C NMR of 10-phenyldibenzo[b,f]oxepine (3o)



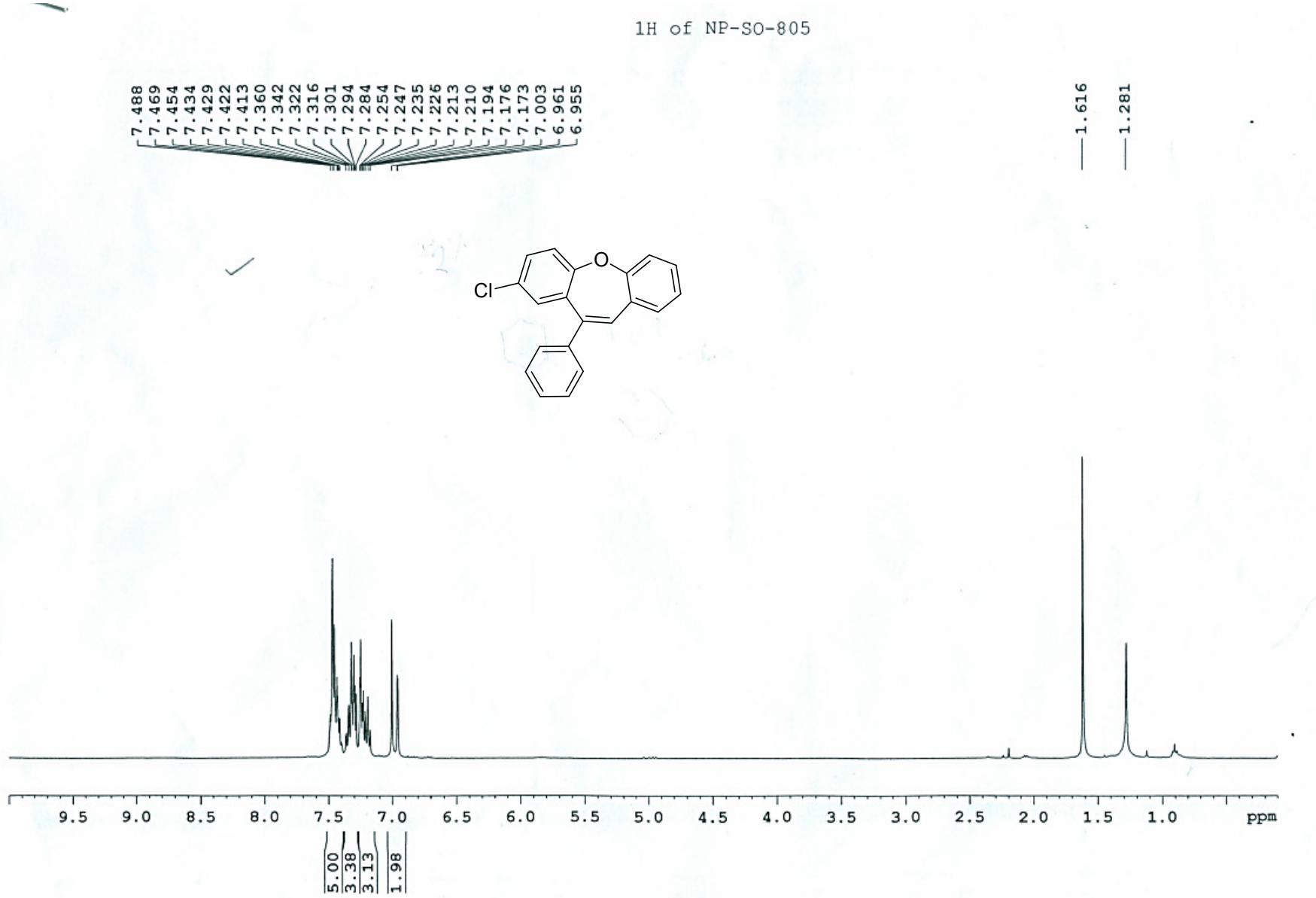
^{1}H NMR of 2-Methyl-10-phenyldibenzo[*b,f*]oxepine (3p)



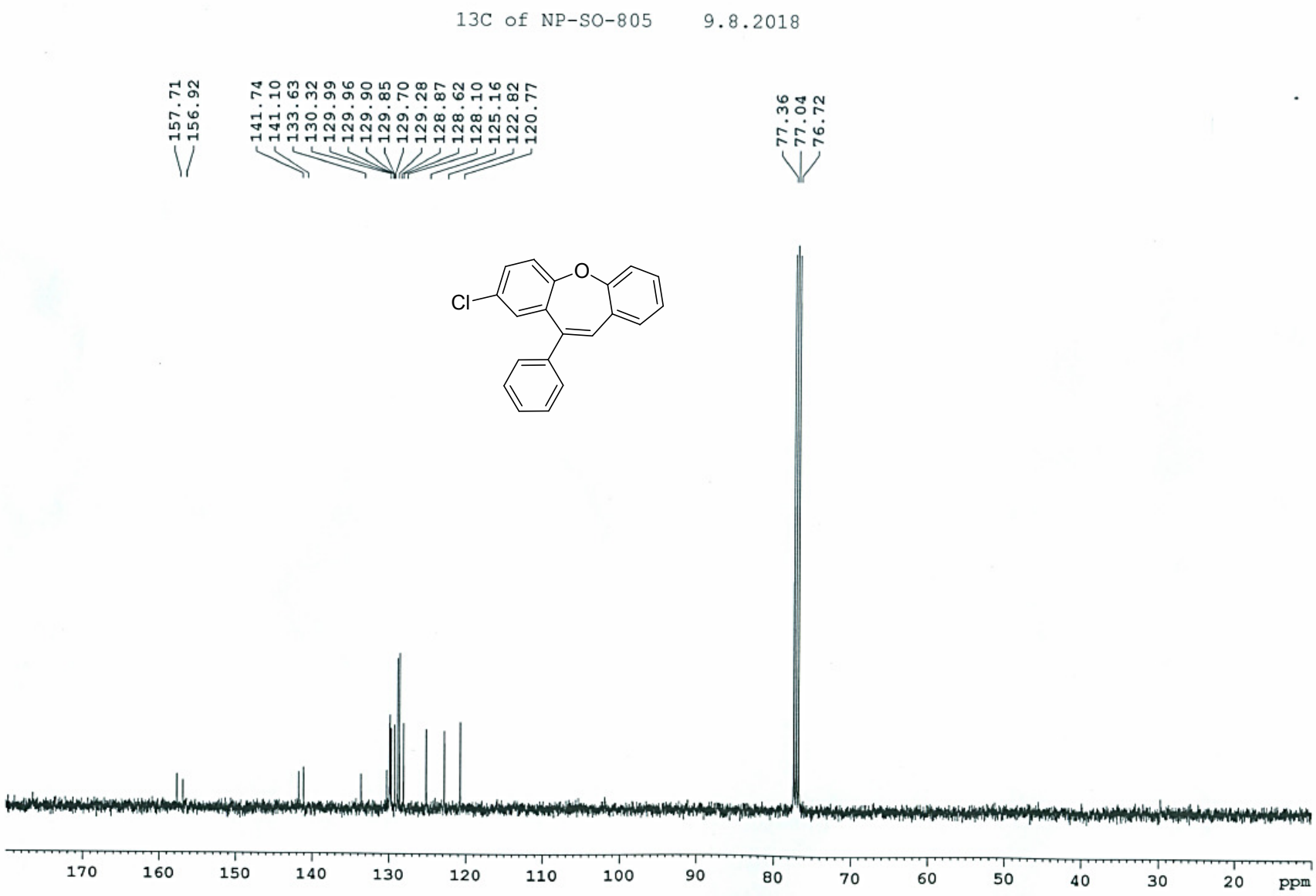
^{13}C NMR of **2-Methyl-10-phenyldibenzo[*b,f*]oxepine (3p)**



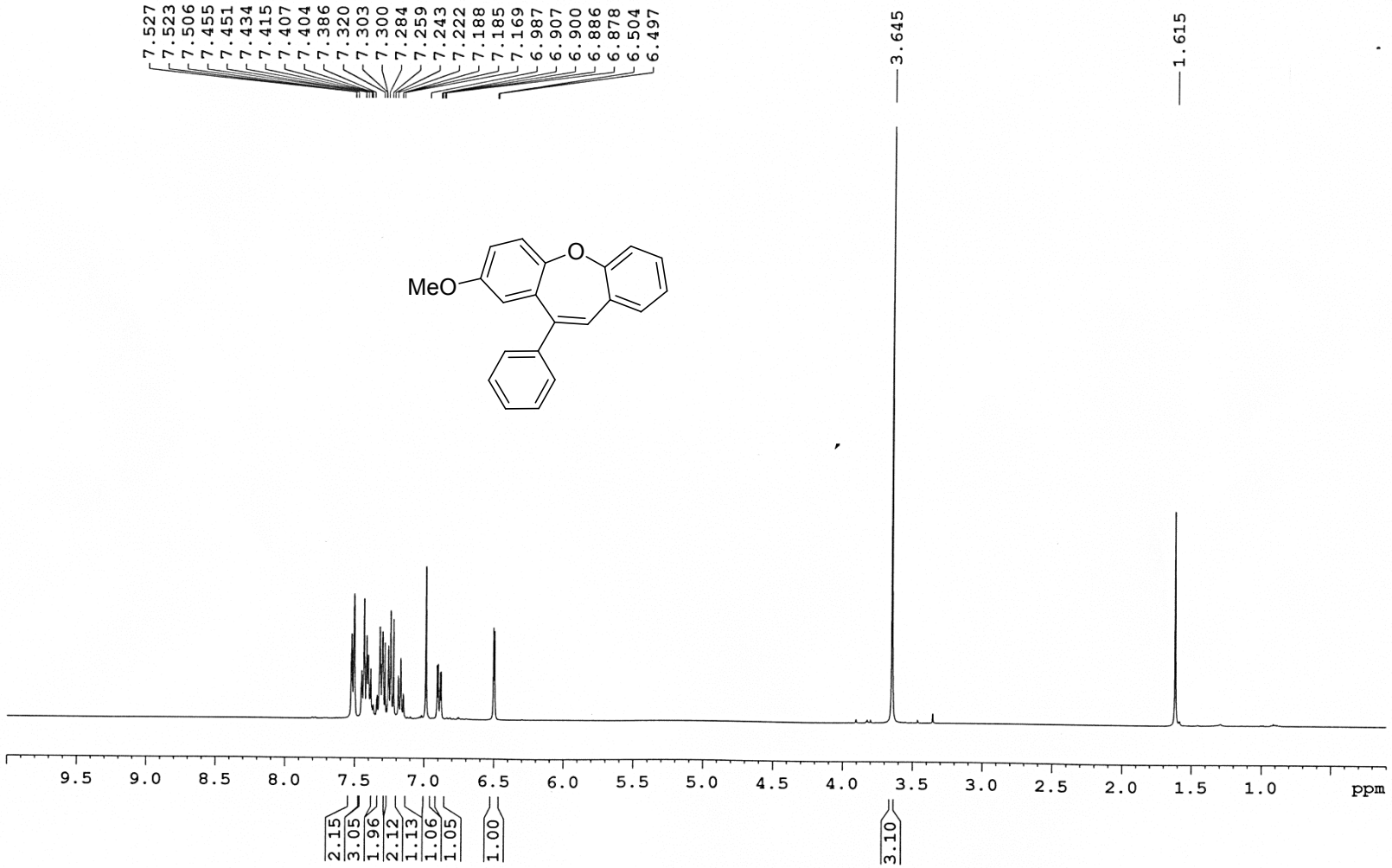
^{1}H NMR of **2-Chloro-10-phenyldibenzo[*b,f*]oxepine (3q)**



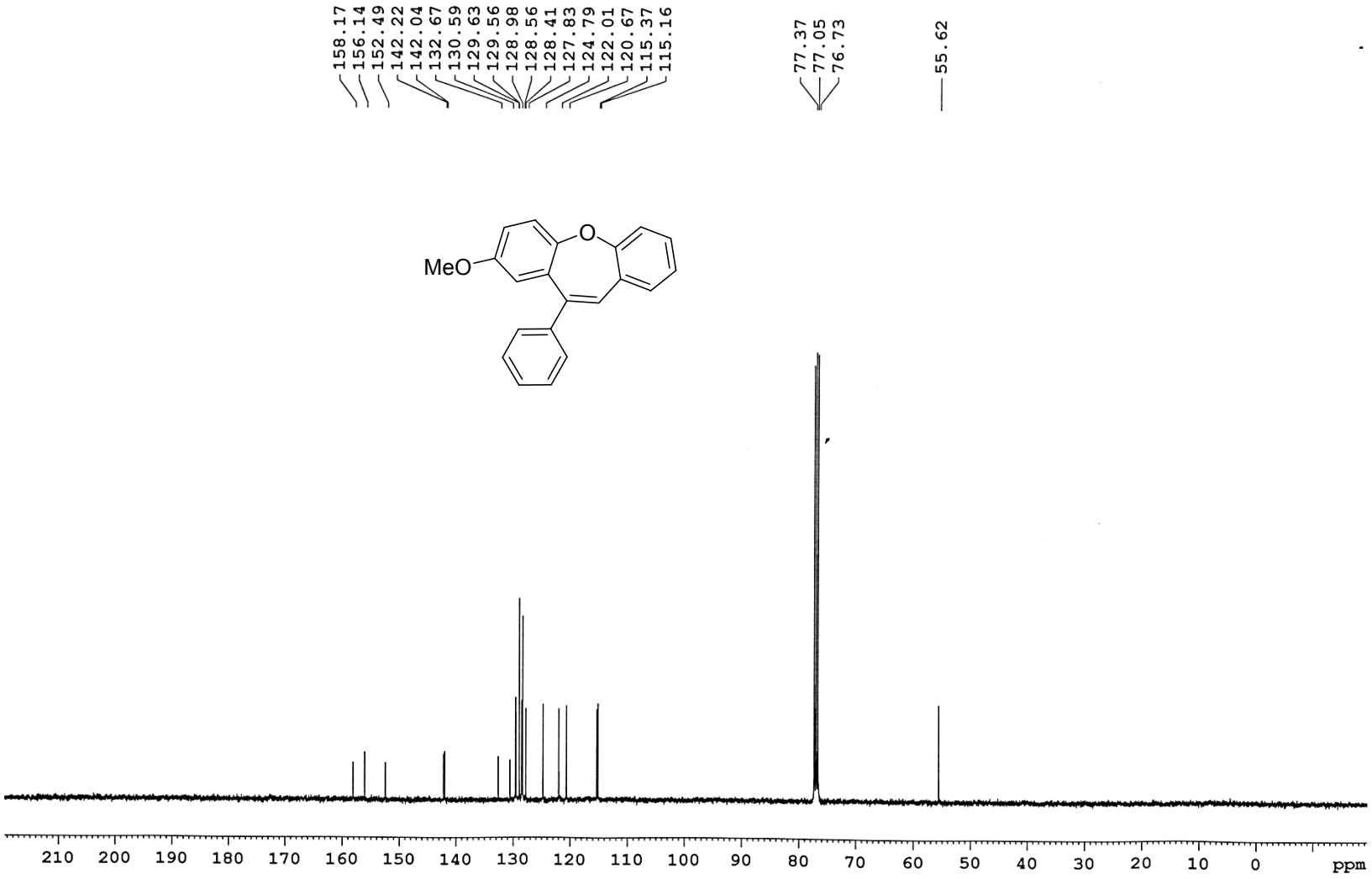
^{13}C NMR of **2-Chloro-10-phenyldibenzo[*b,f*]oxepine (3q)**



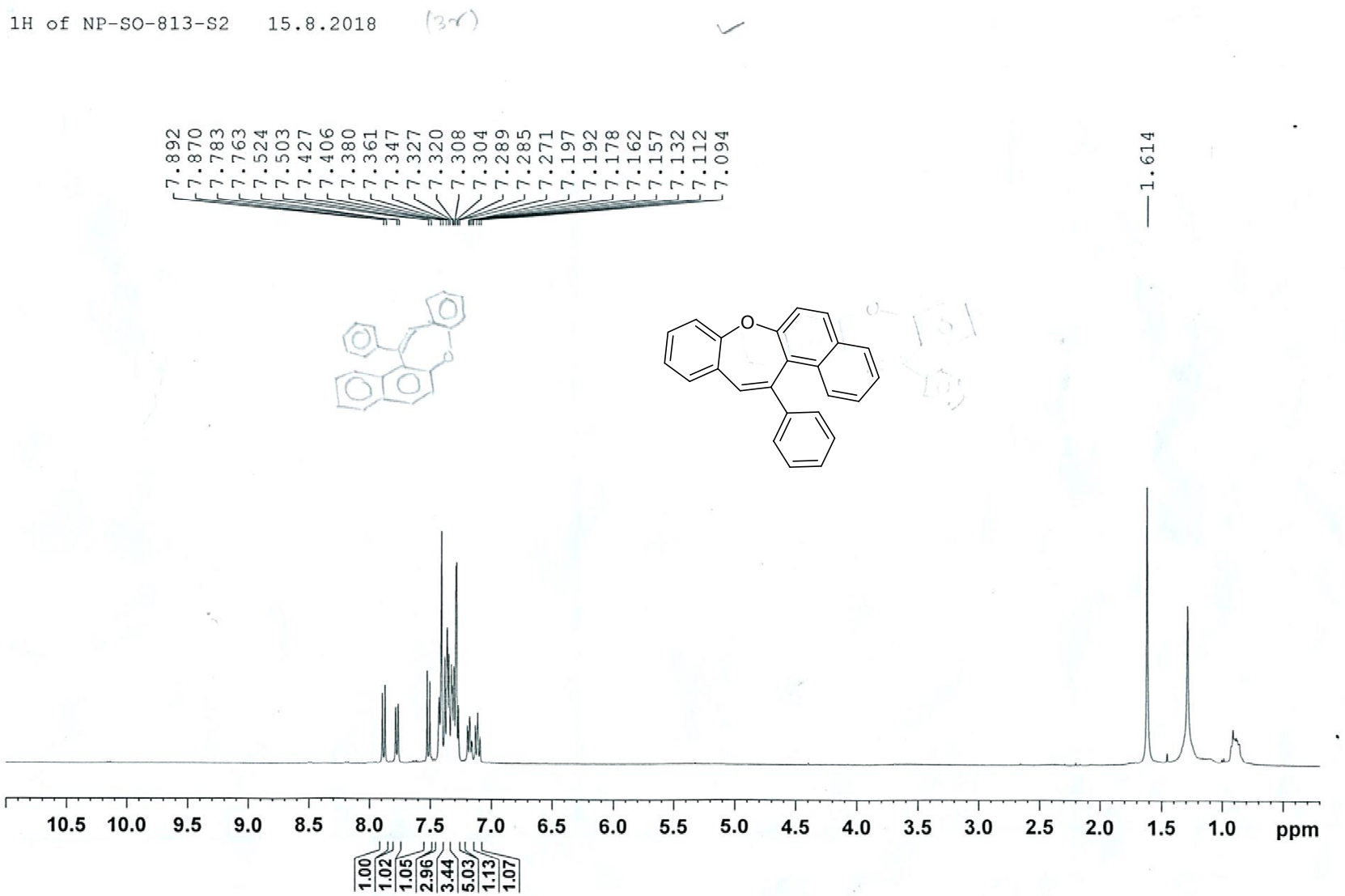
^{1}H NMR of 2-Methoxy-10-phenyldibenzo[*b,f*]oxepine (3r)



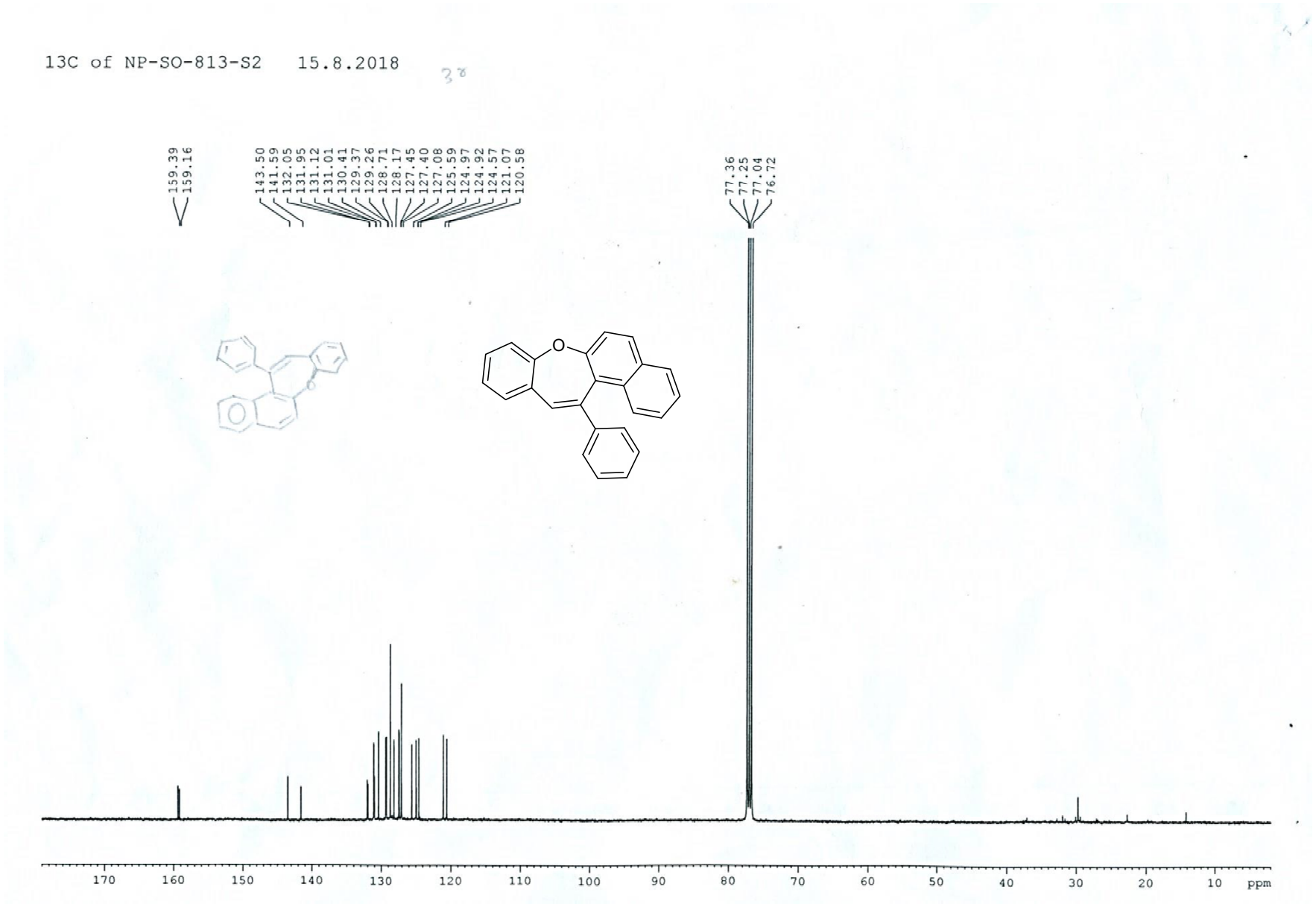
^{13}C NMR of 2-Methoxy-10-phenyldibenzo[*b,f*]oxepine (3r)



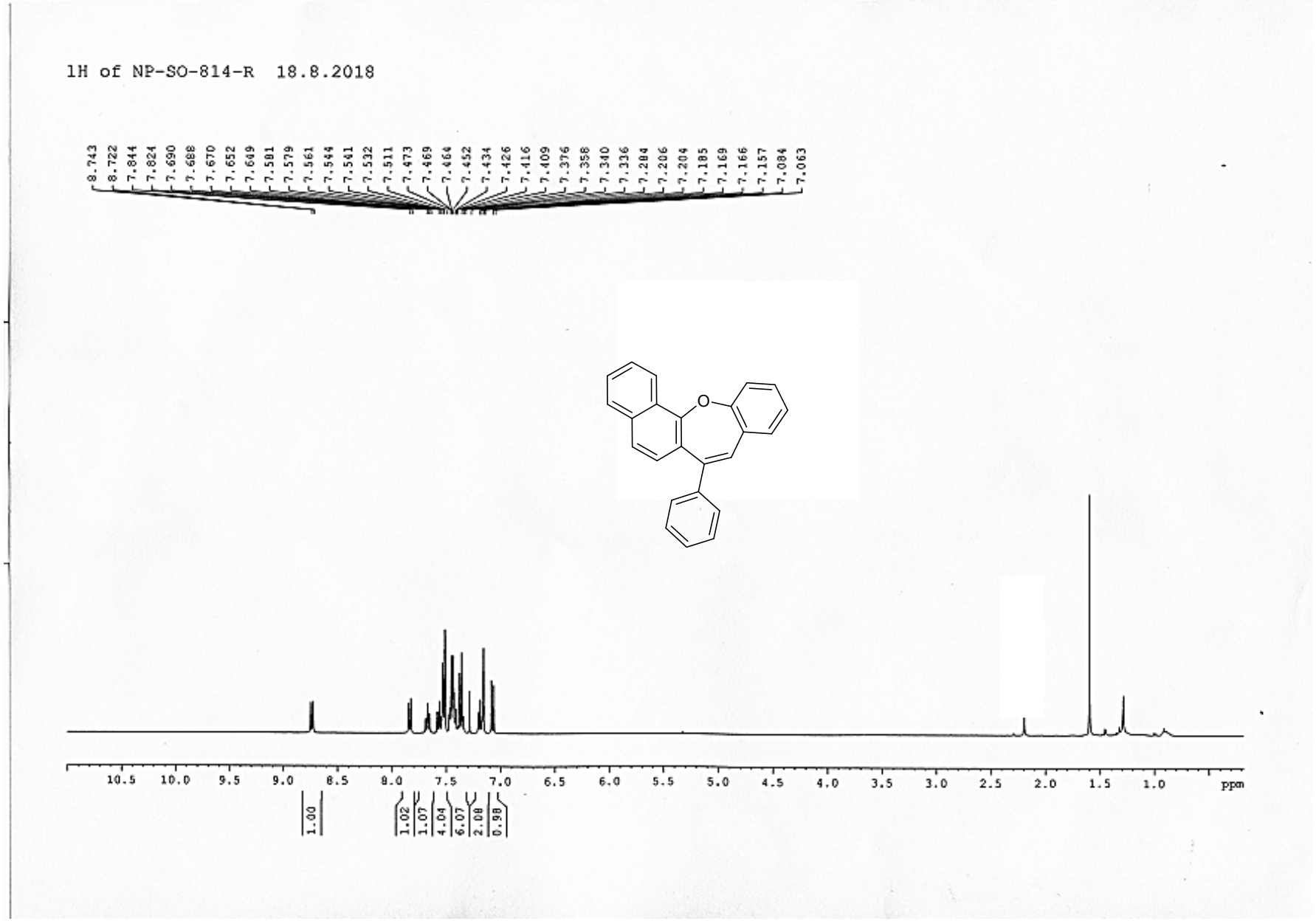
^{1}H NMR of 11-Phenyl benzo[*b*]naphth[1,2-*f*]oxepin (3s)



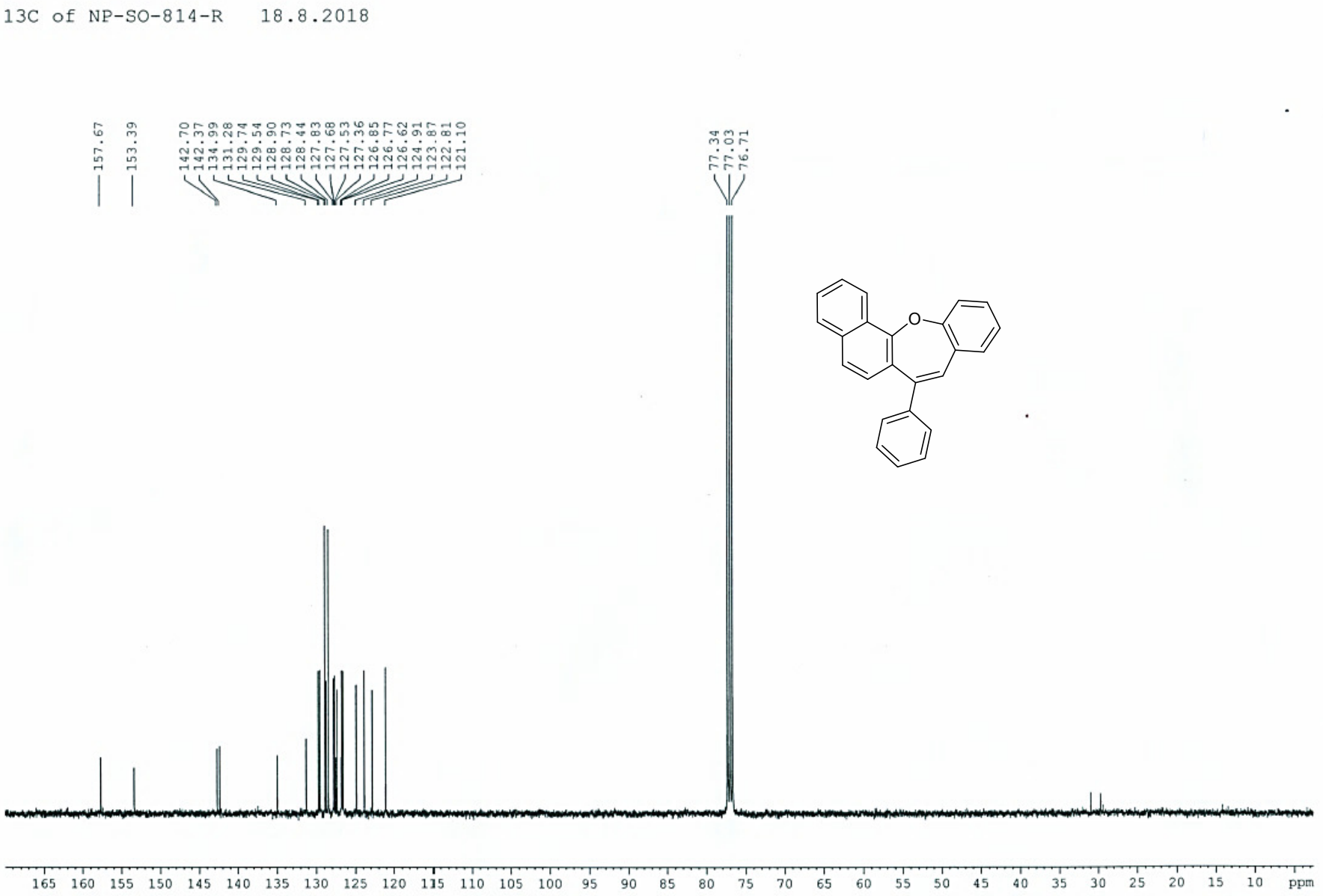
^{13}C NMR of 11-Phenyl benzo[*b*]naphth[1,2-*f*]oxepin (3s)



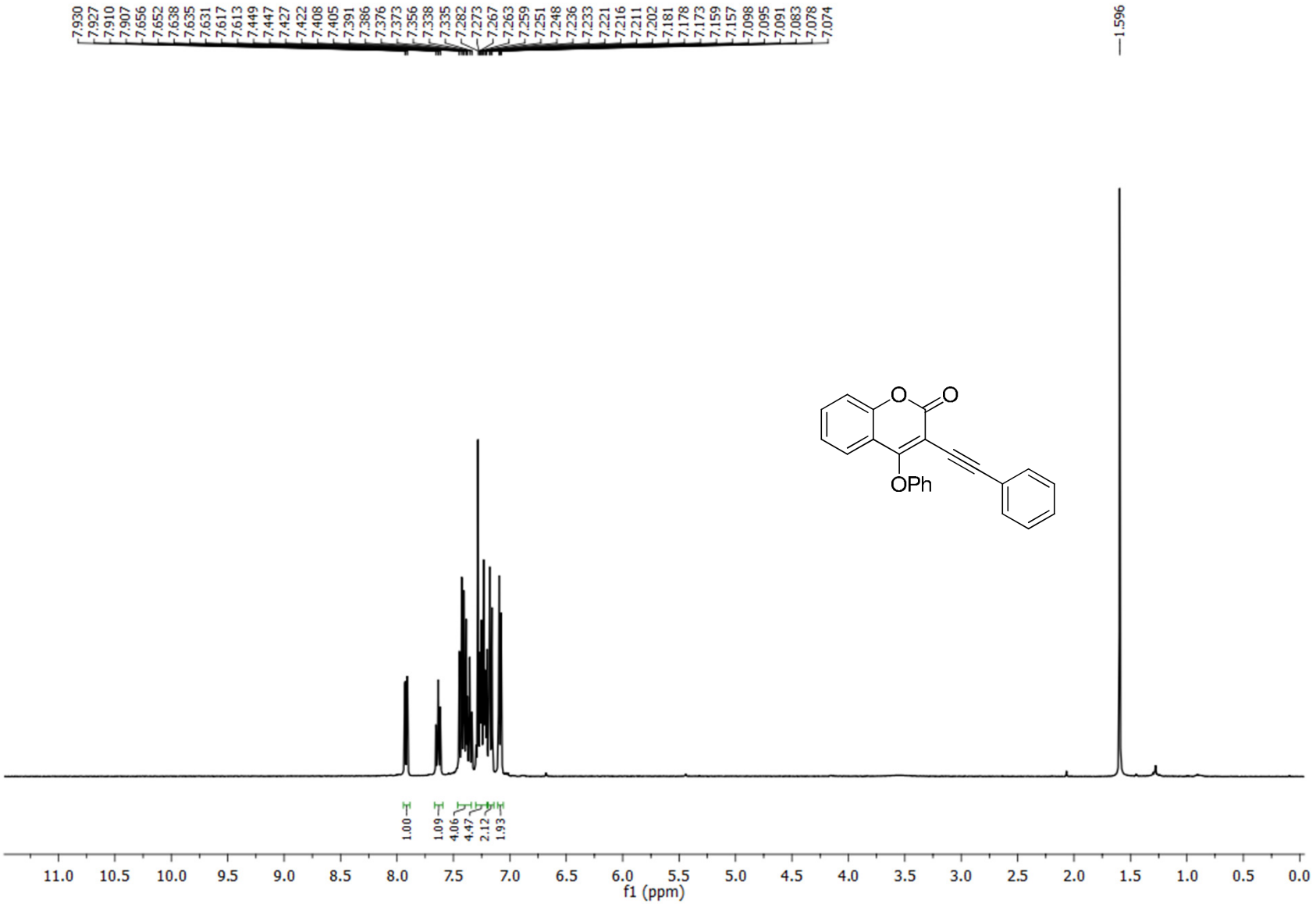
1H NMR of **12-Phenyl benzo[*b*]naphth[2,1-*f*]oxepin (3t)**



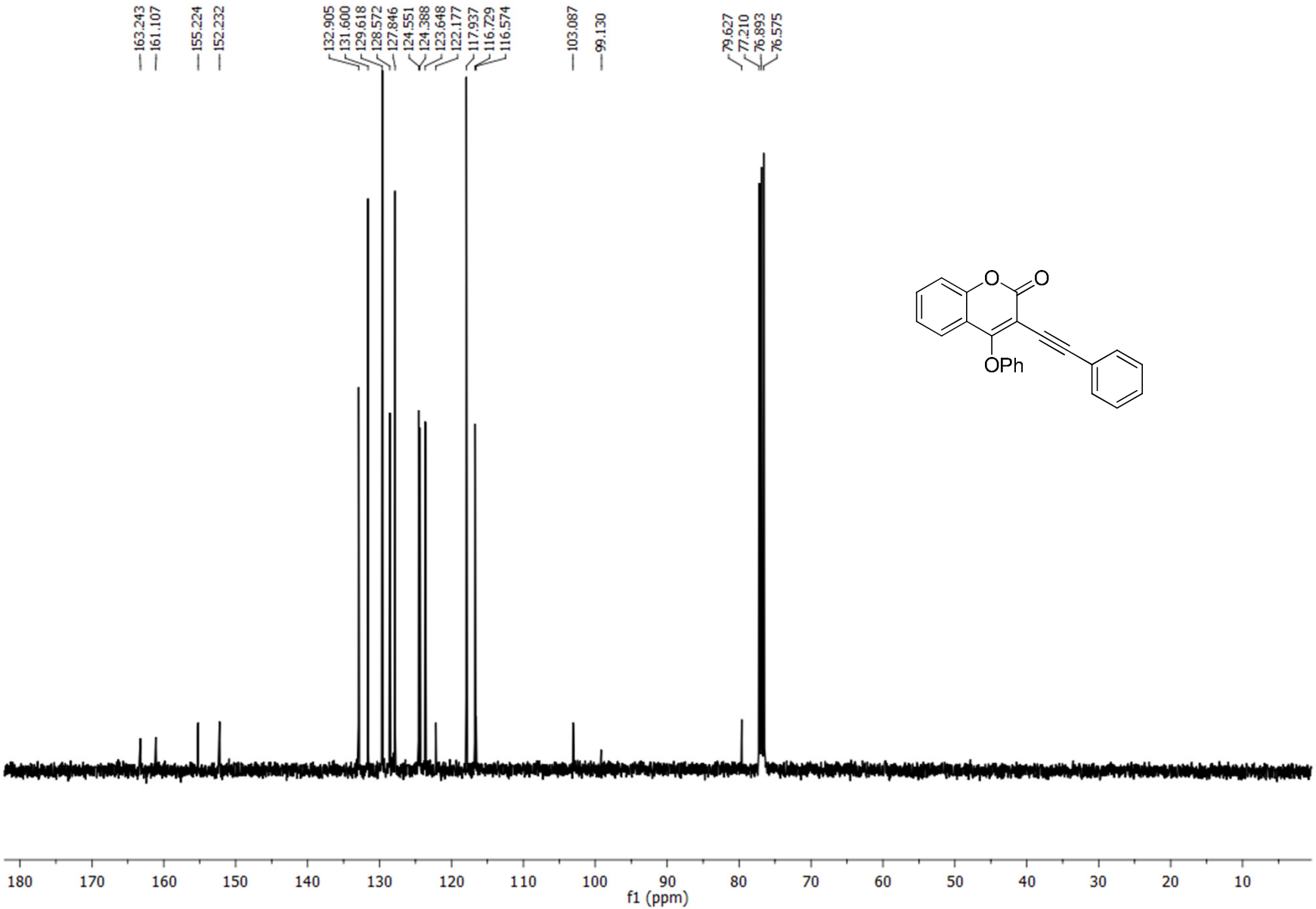
13 NMR of **12-Phenyl benzo[*b*]naphth[2,1-*f*]oxepin (3t)**



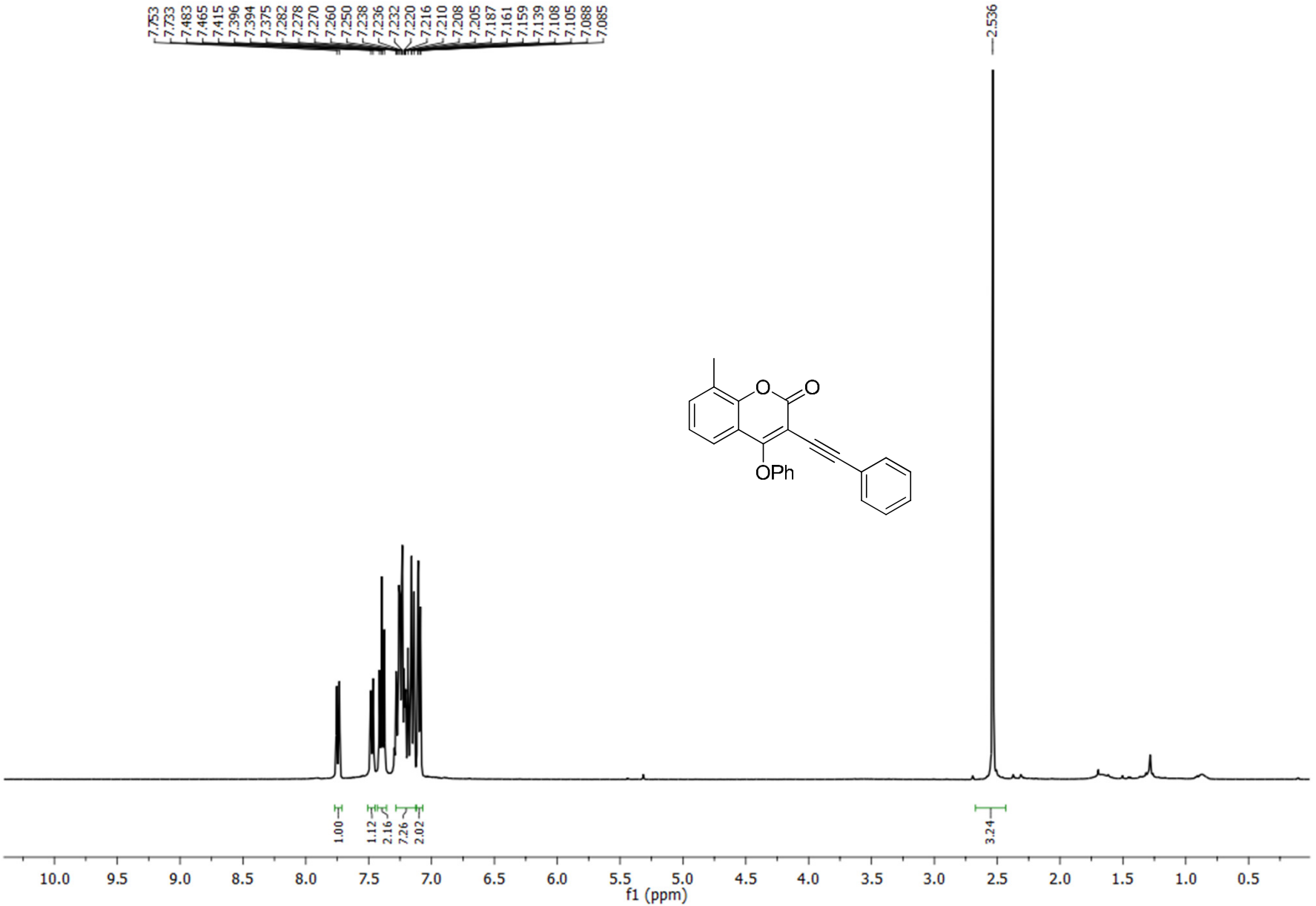
^{1}H NMR of 4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5a)



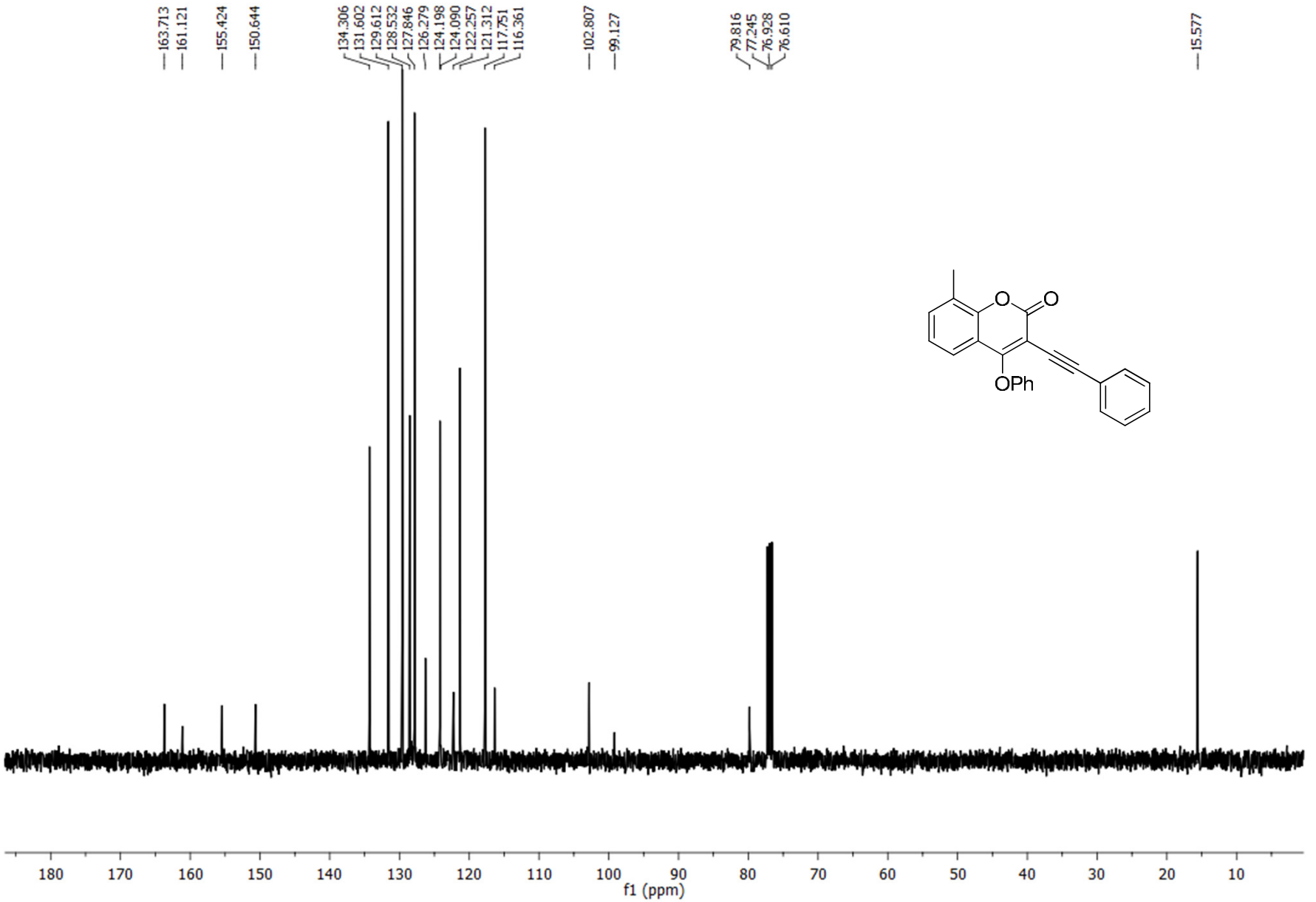
^{13}C NMR of 4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5a)



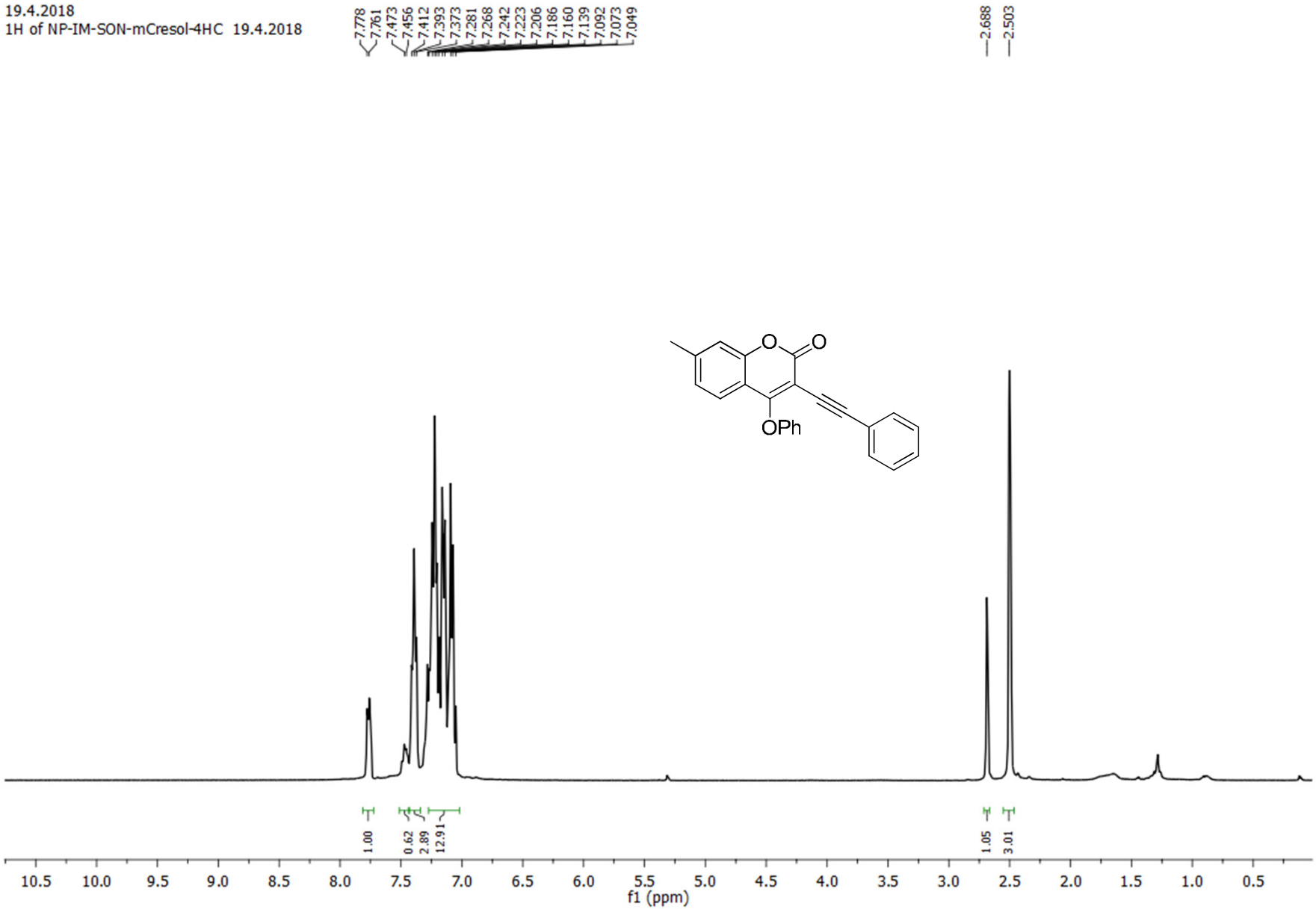
^{1}H NMR of 8-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5b)



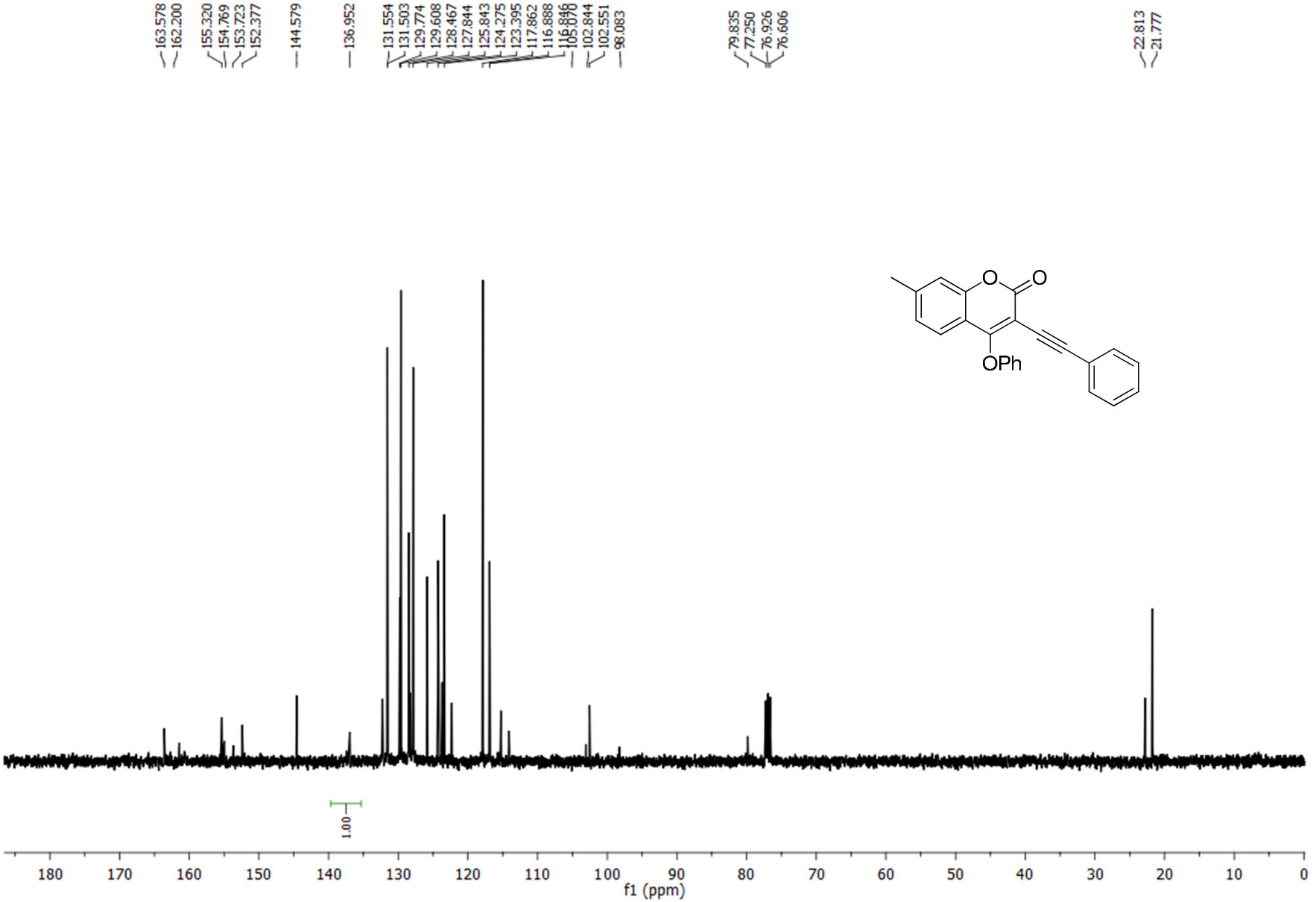
^{13}C NMR of 8-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5b)



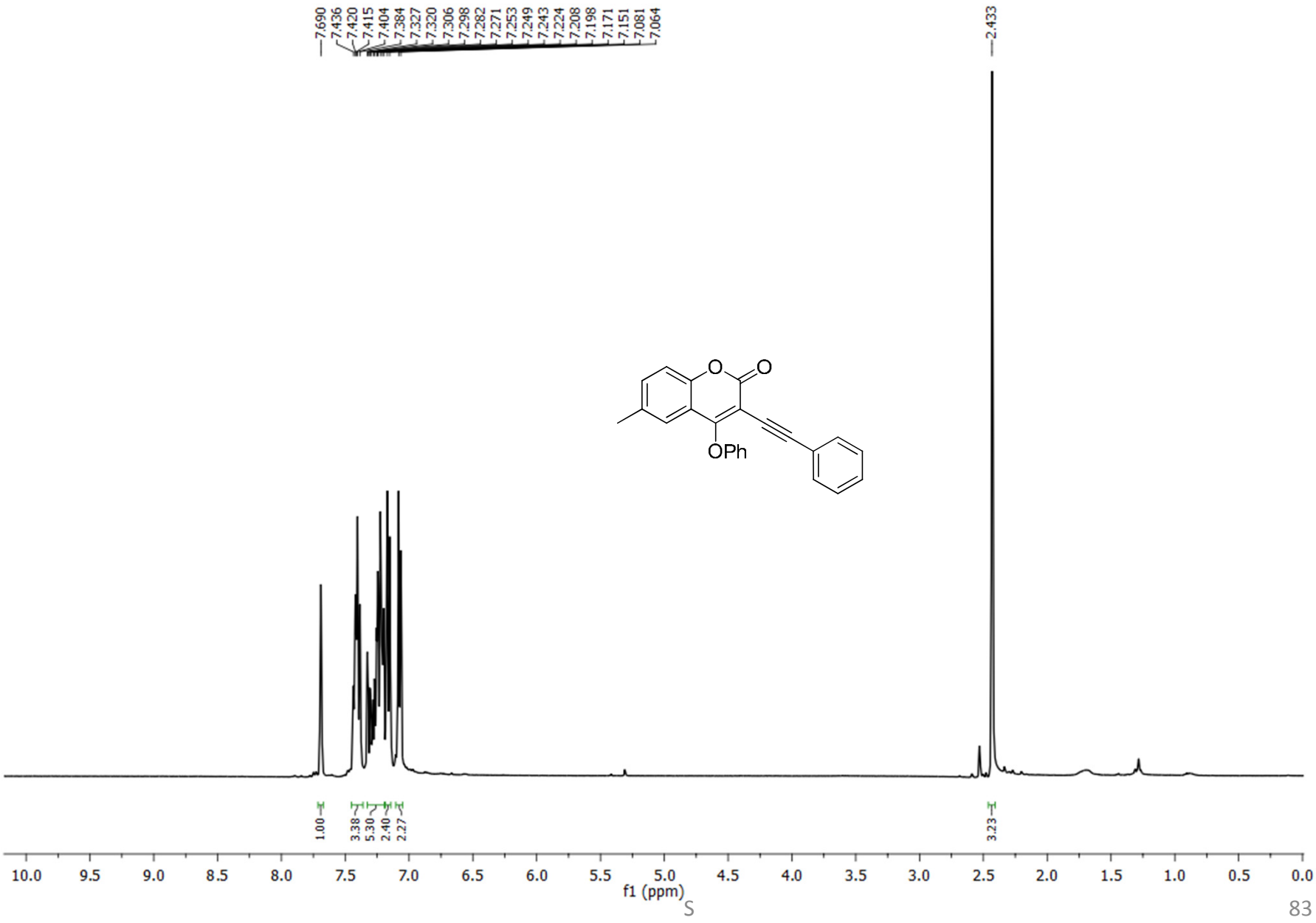
^{1}H NMR of 7-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5c)



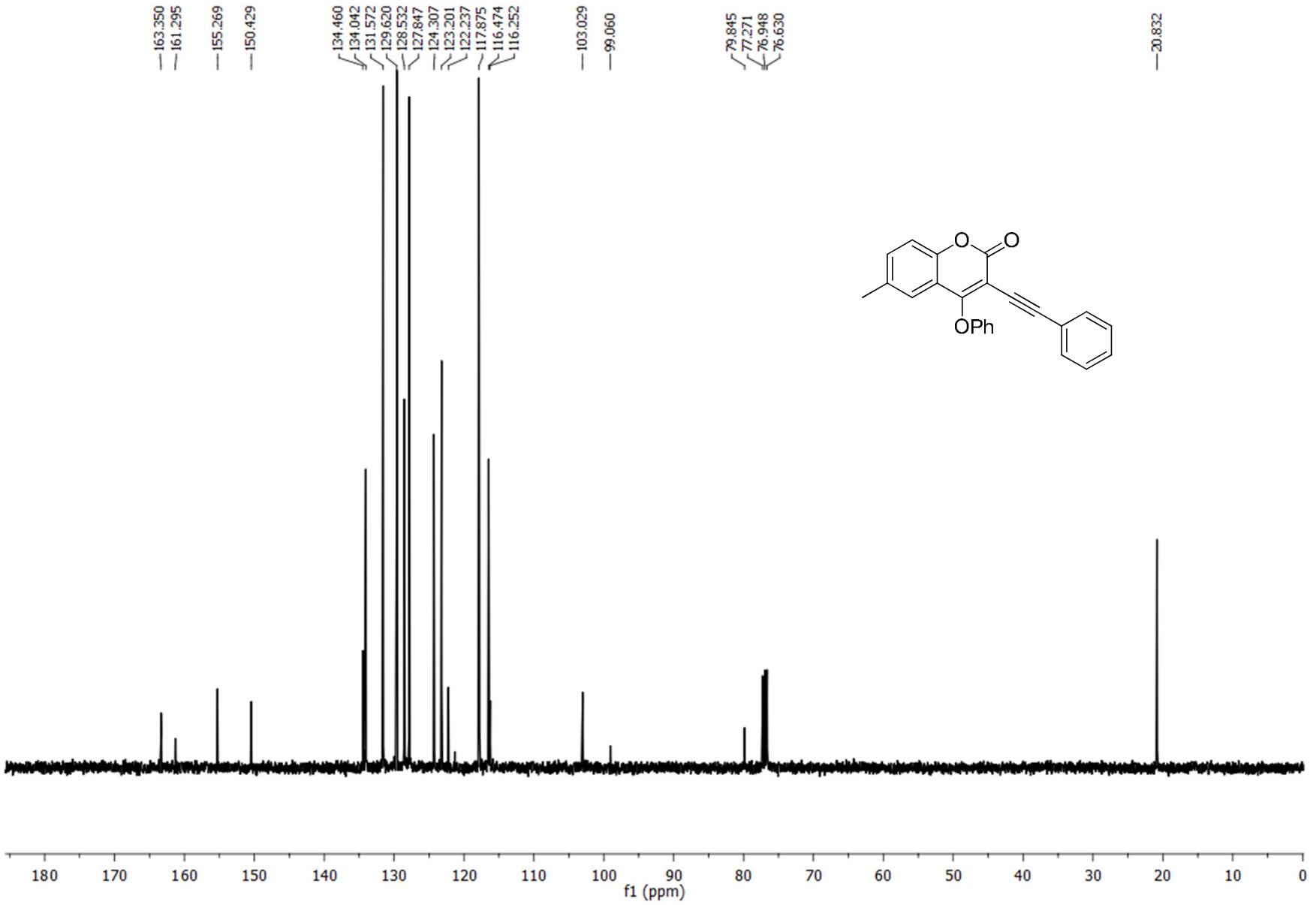
^{13}C NMR of 7-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5c)



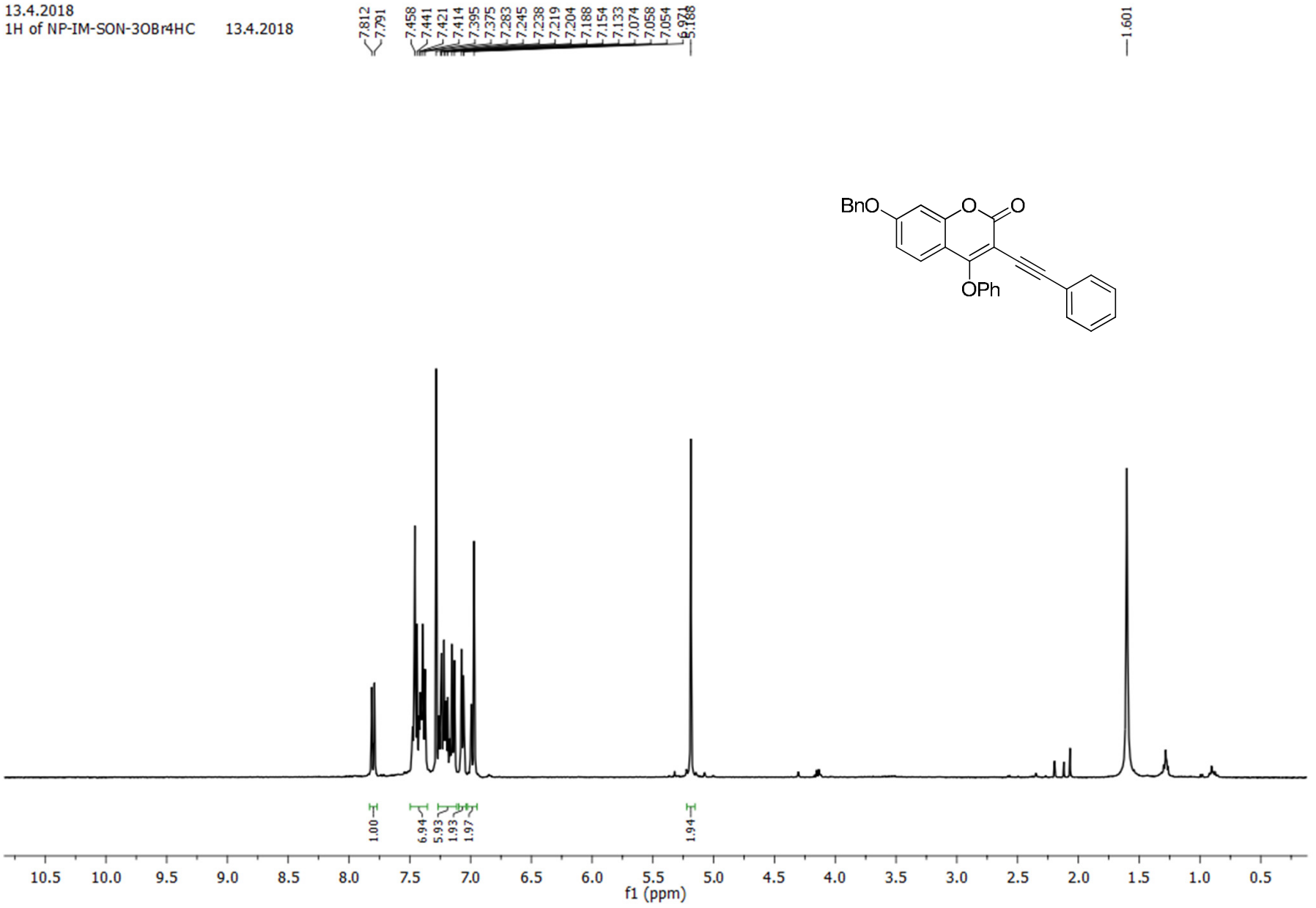
^{1}H NMR of 6-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5d)



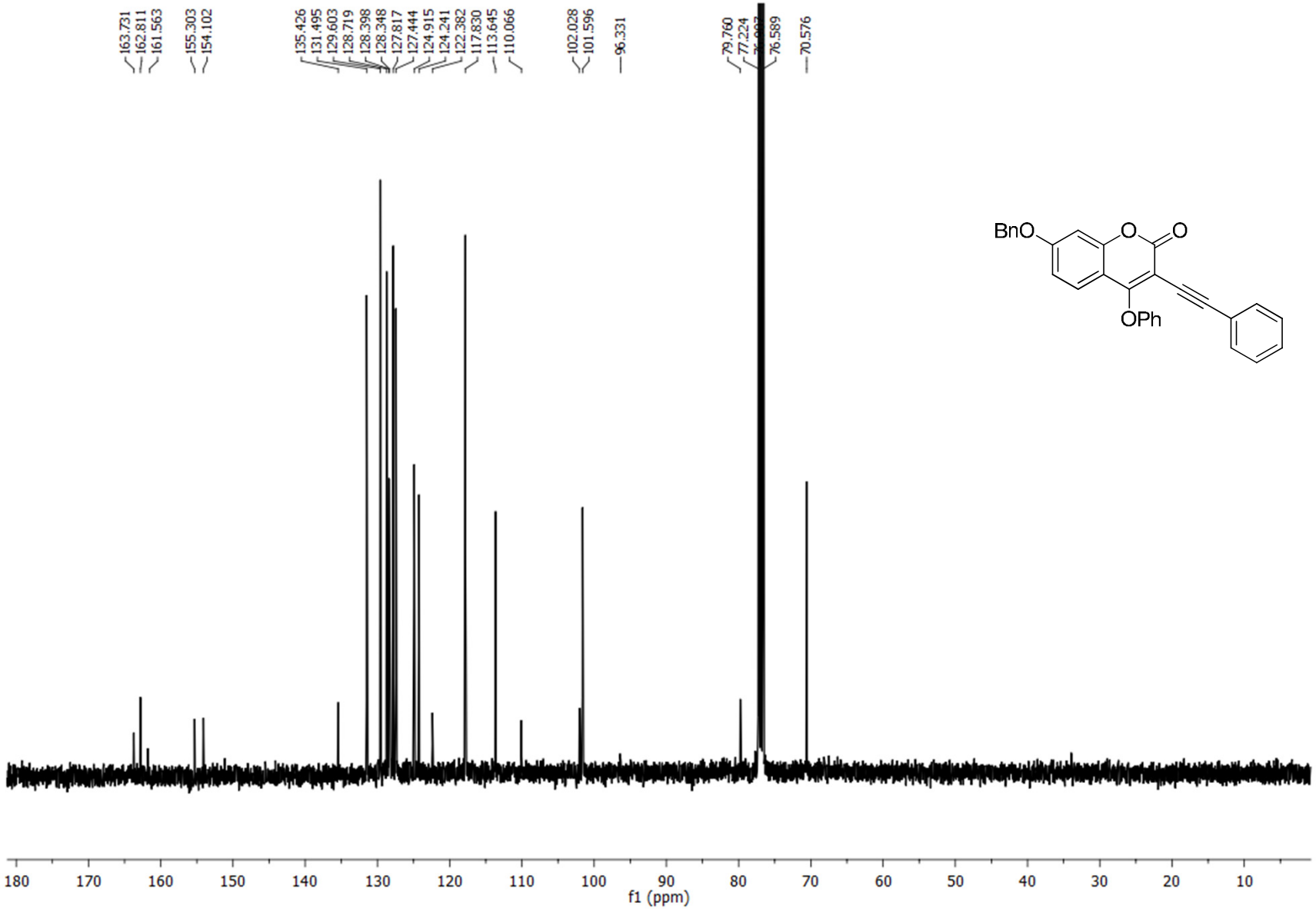
^{13}C NMR of 6-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5d)



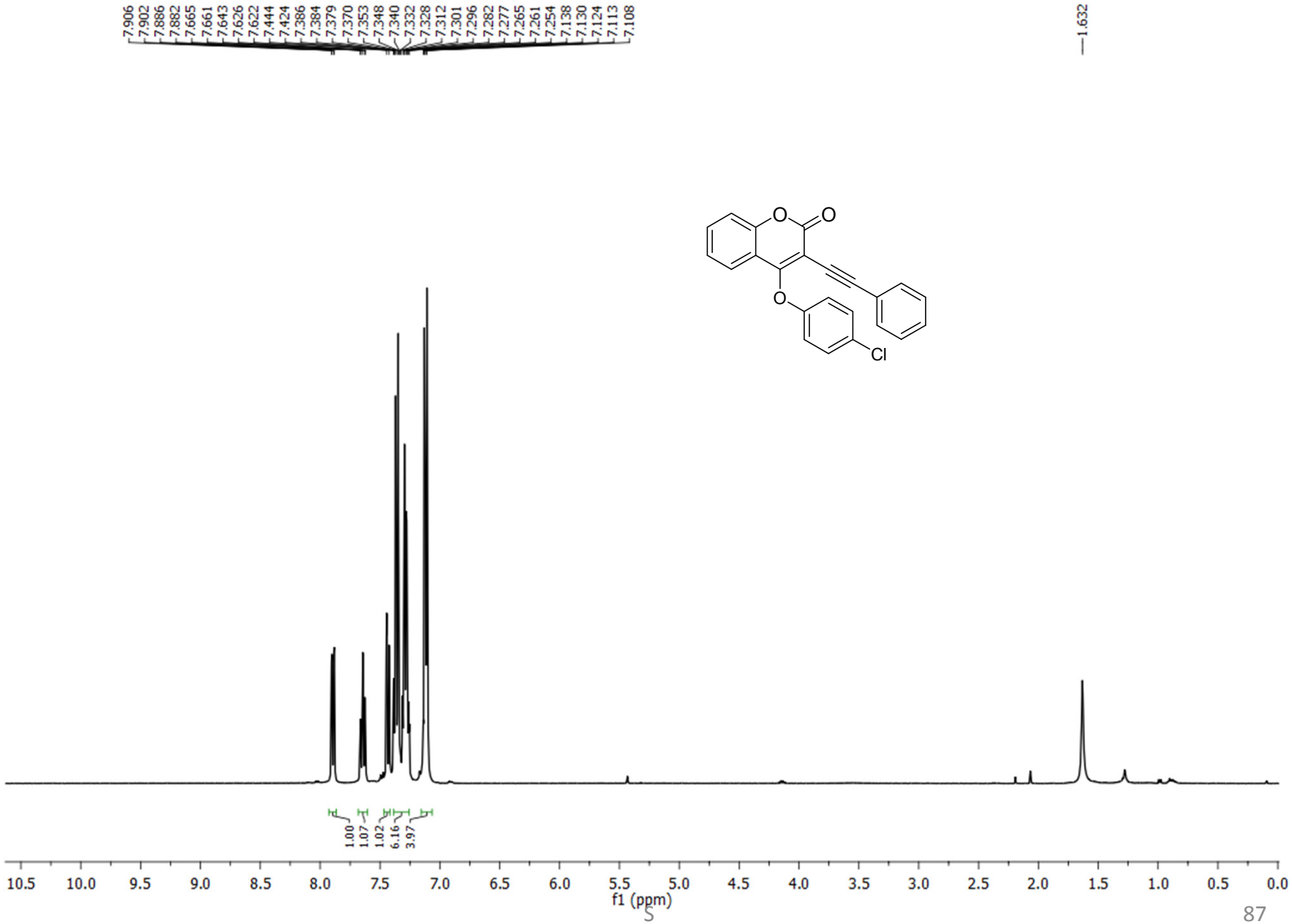
^{1}H NMR of 7-(benzyloxy)-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5e)



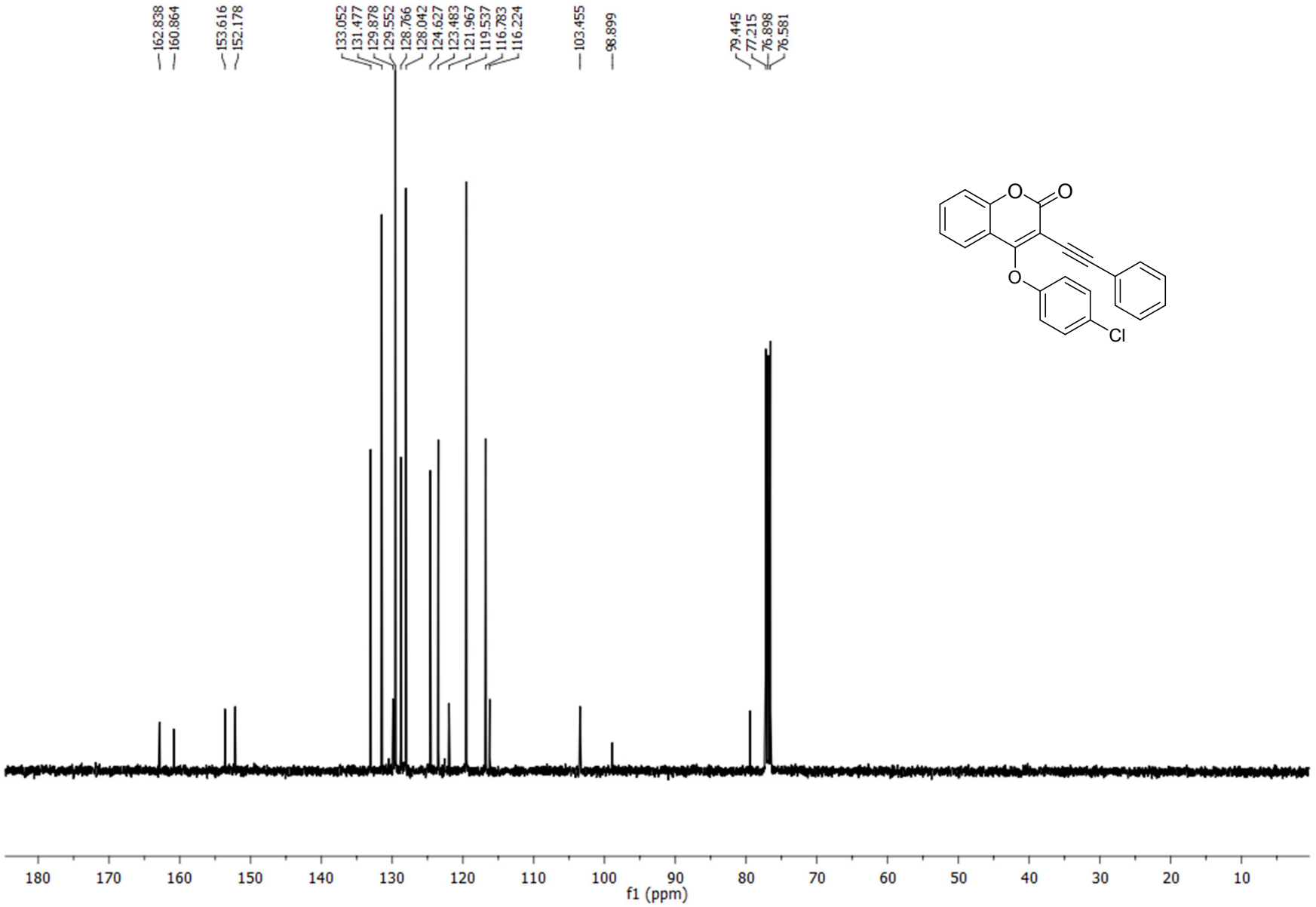
^{13}C NMR of 7-(benzyloxy)-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5e)



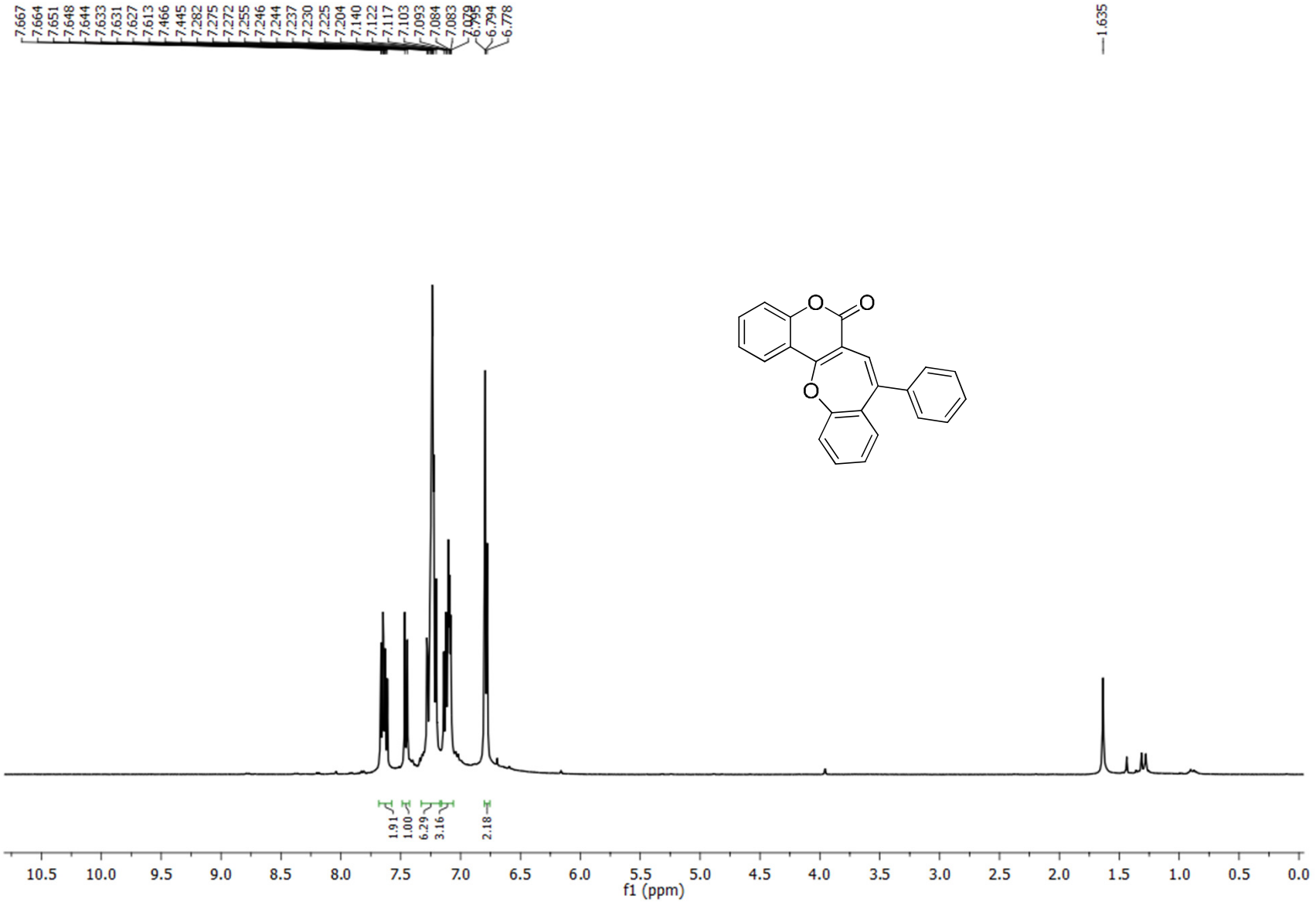
^{1}H NMR of 4-(4-chlorophenoxy)-3-(2-phenylethynyl)-2H-chromen-2-one (5f)



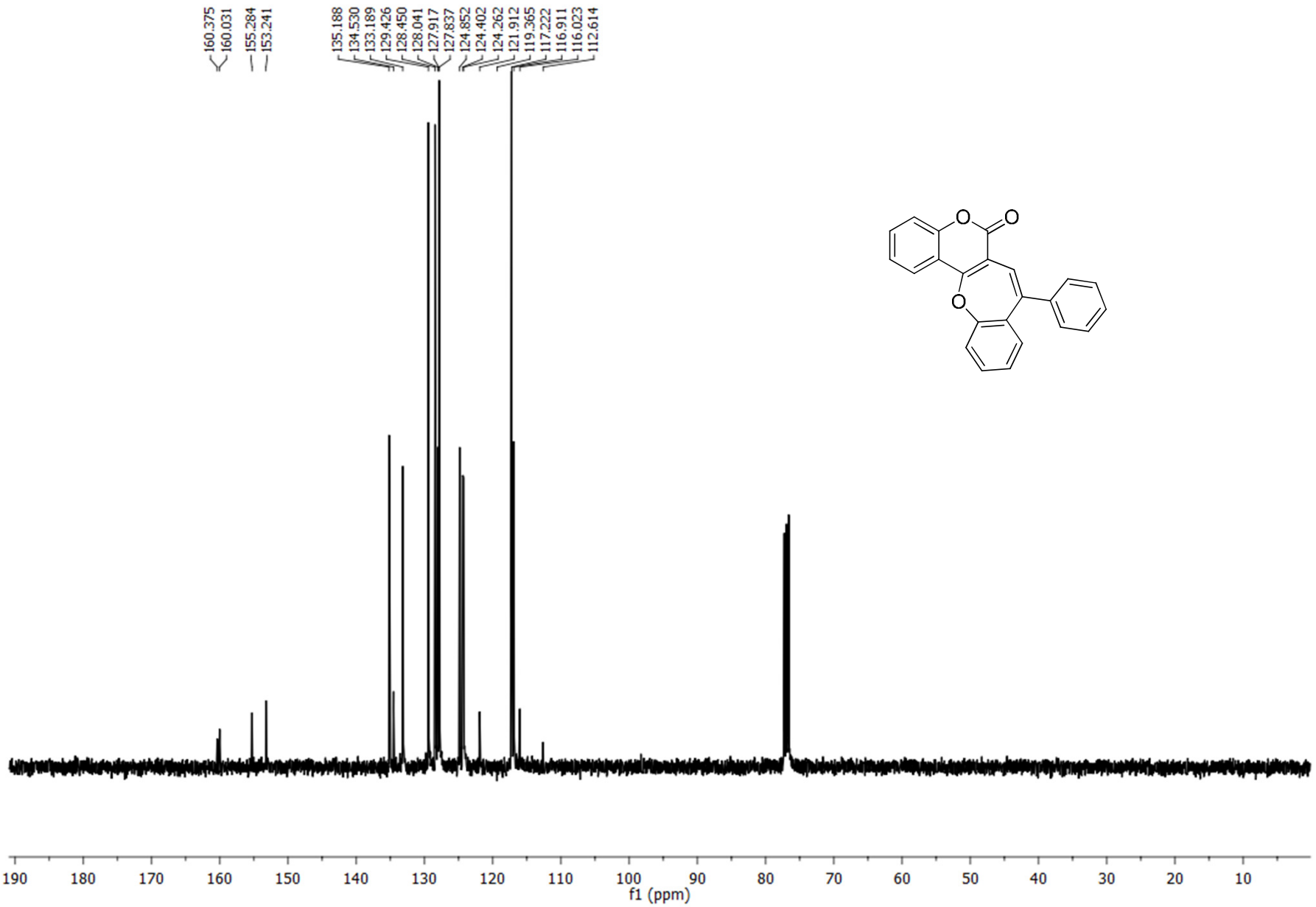
^{13}C NMR of 4-(4-chlorophenoxy)-3-(2-phenylethynyl)-2H-chromen-2-one (5f)



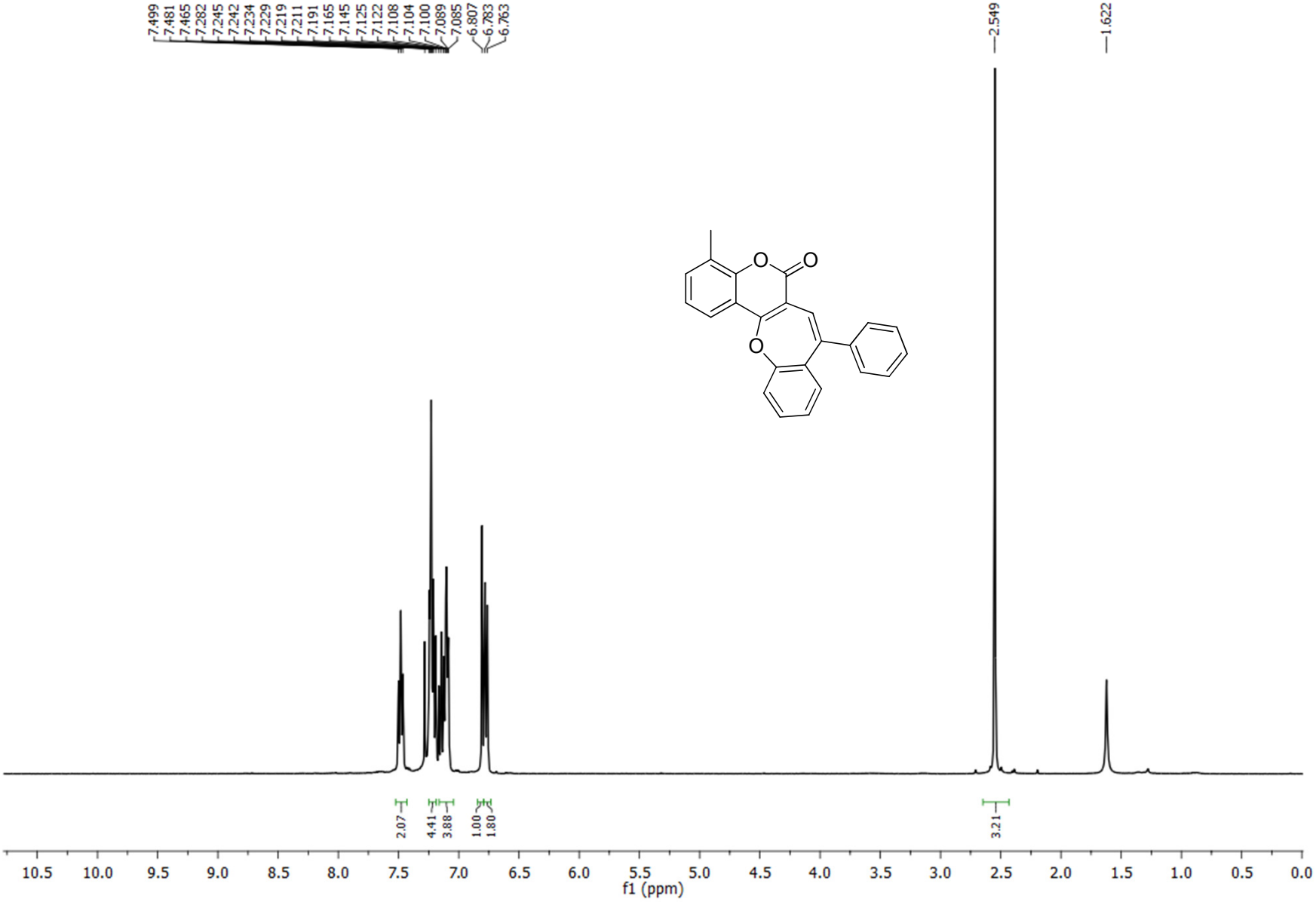
^{1}H NMR of 8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6a)



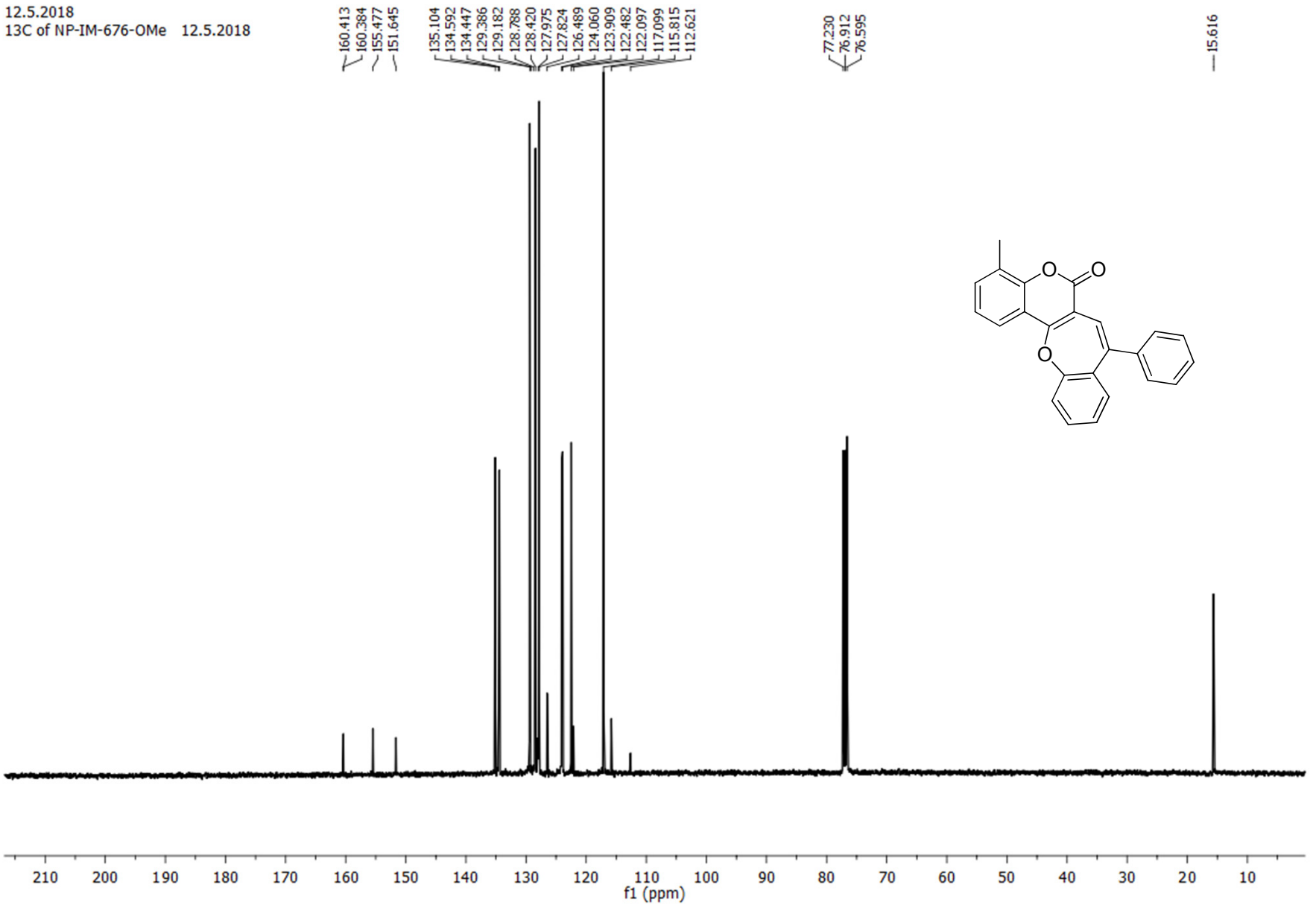
^{13}C NMR of 8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6a)



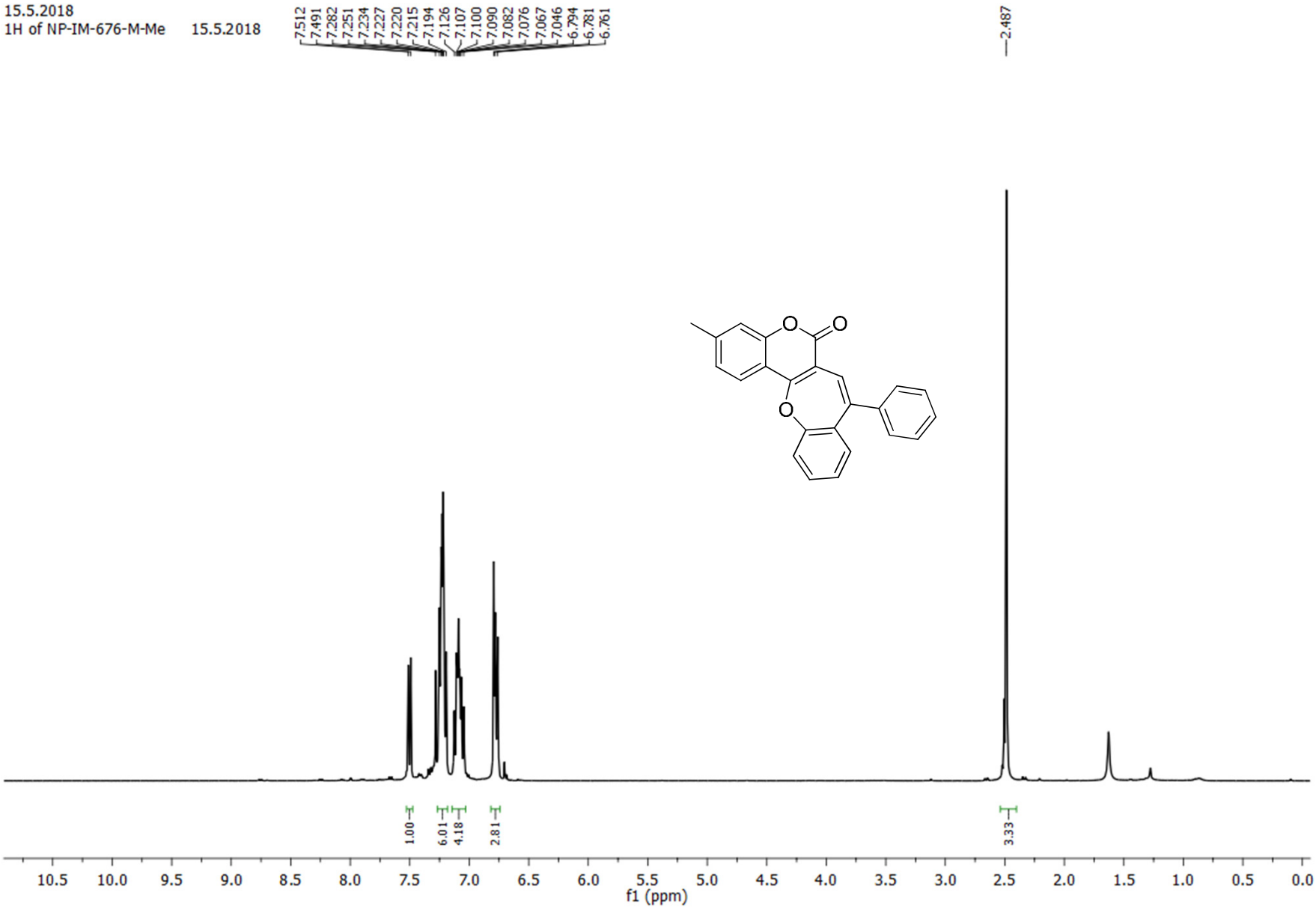
^{1}H NMR of 4-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6b)



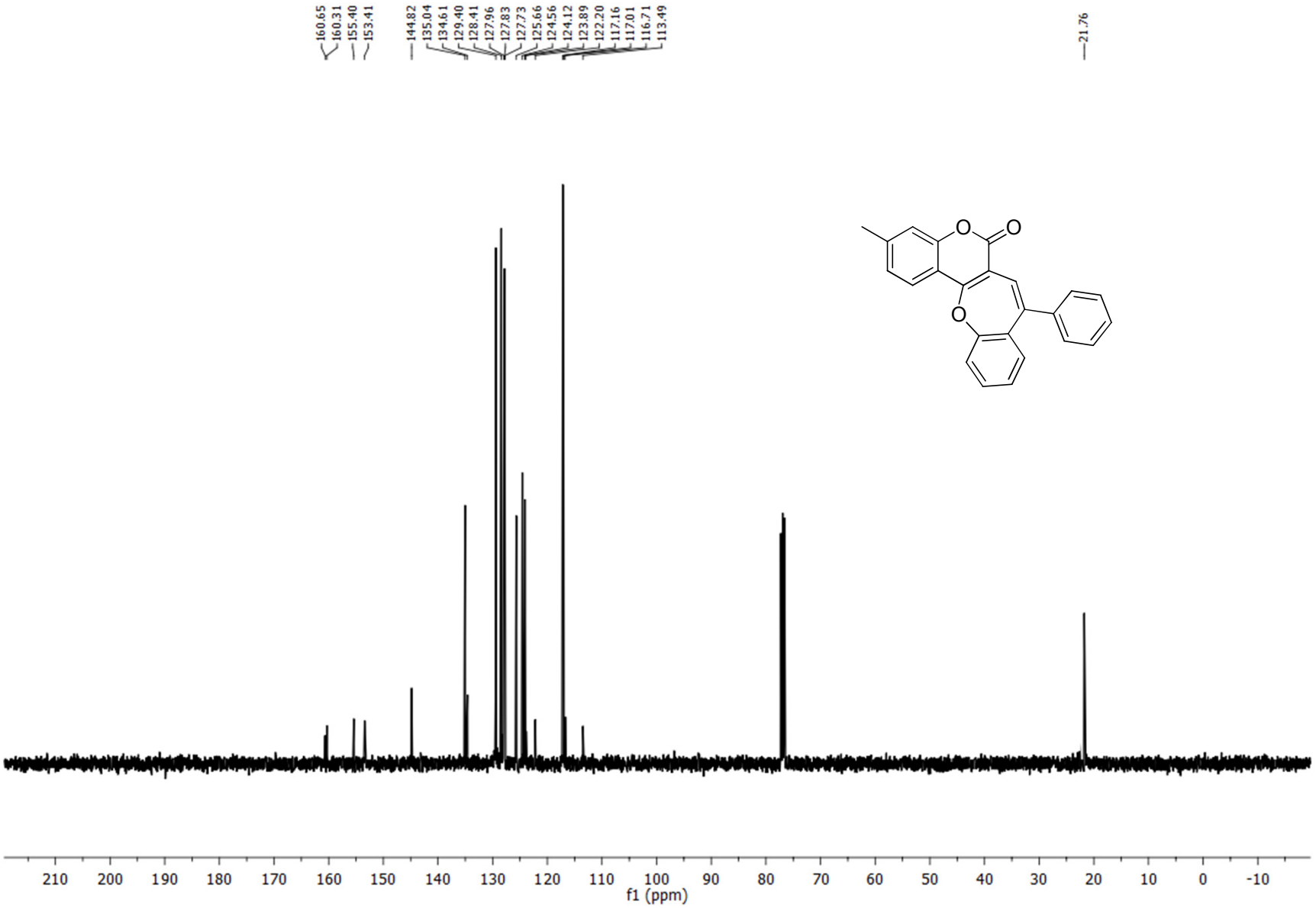
^{13}C NMR of 4-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6b)



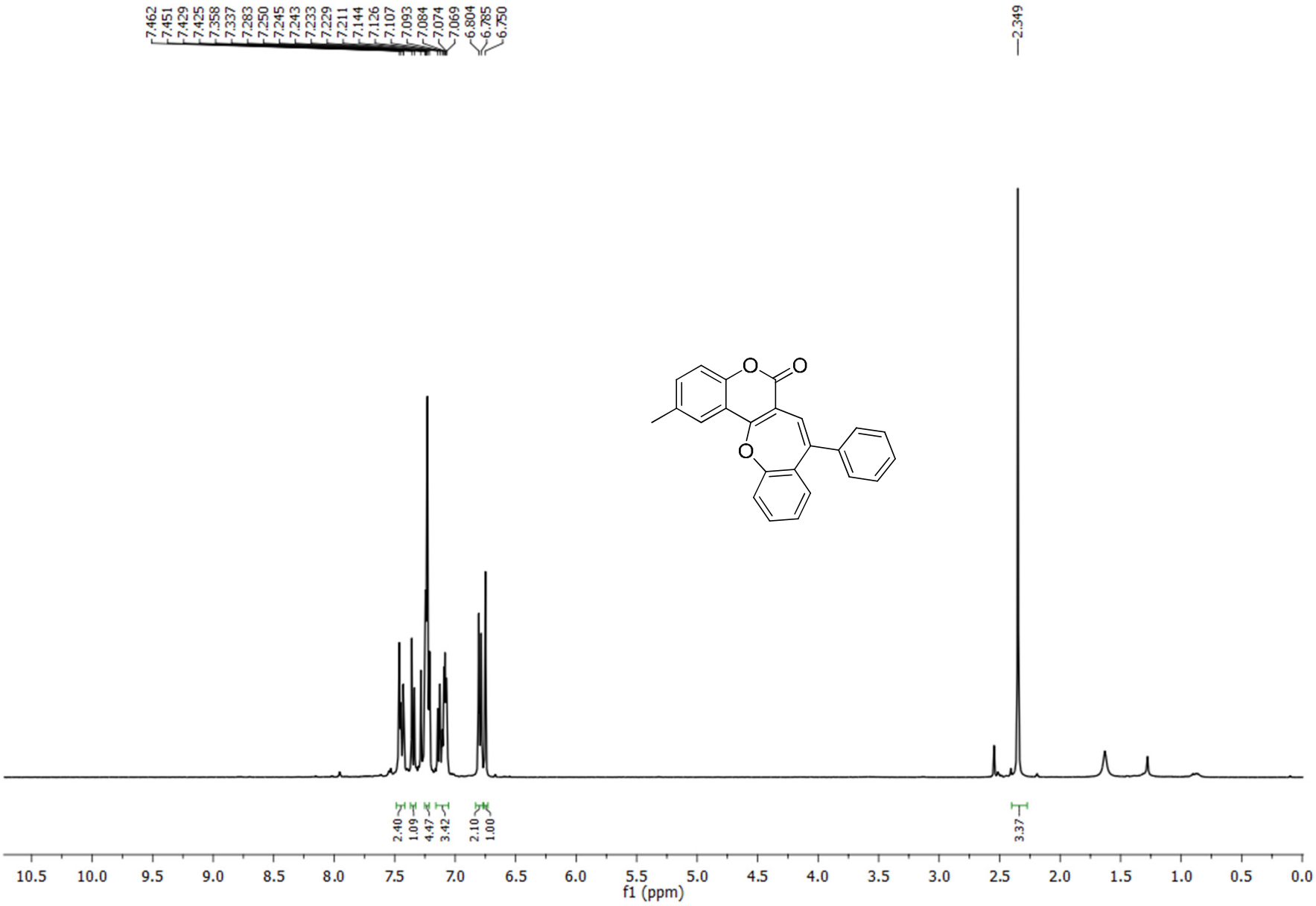
^{1}H NMR of 3-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6c)



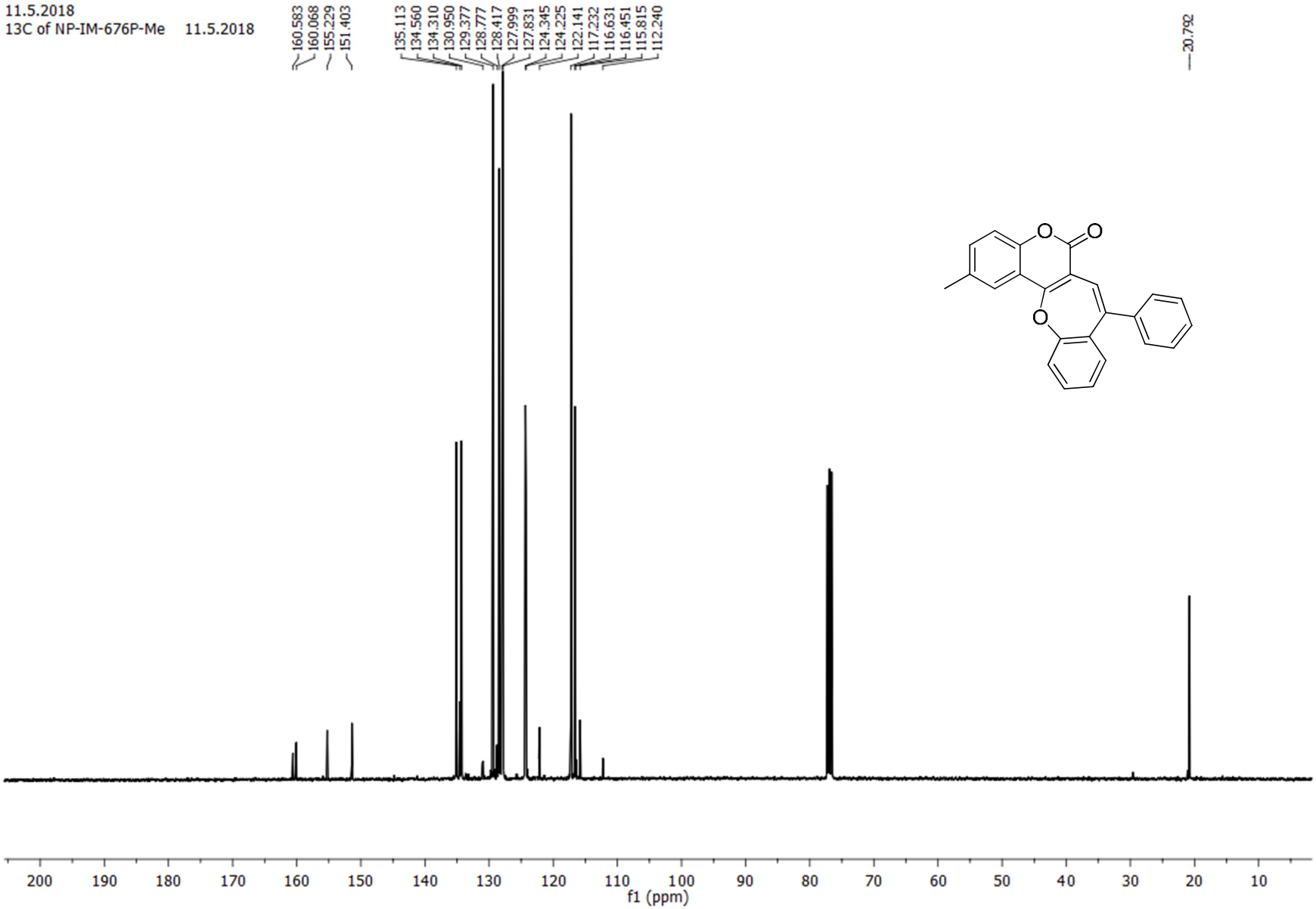
^{13}C NMR of 3-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6c)



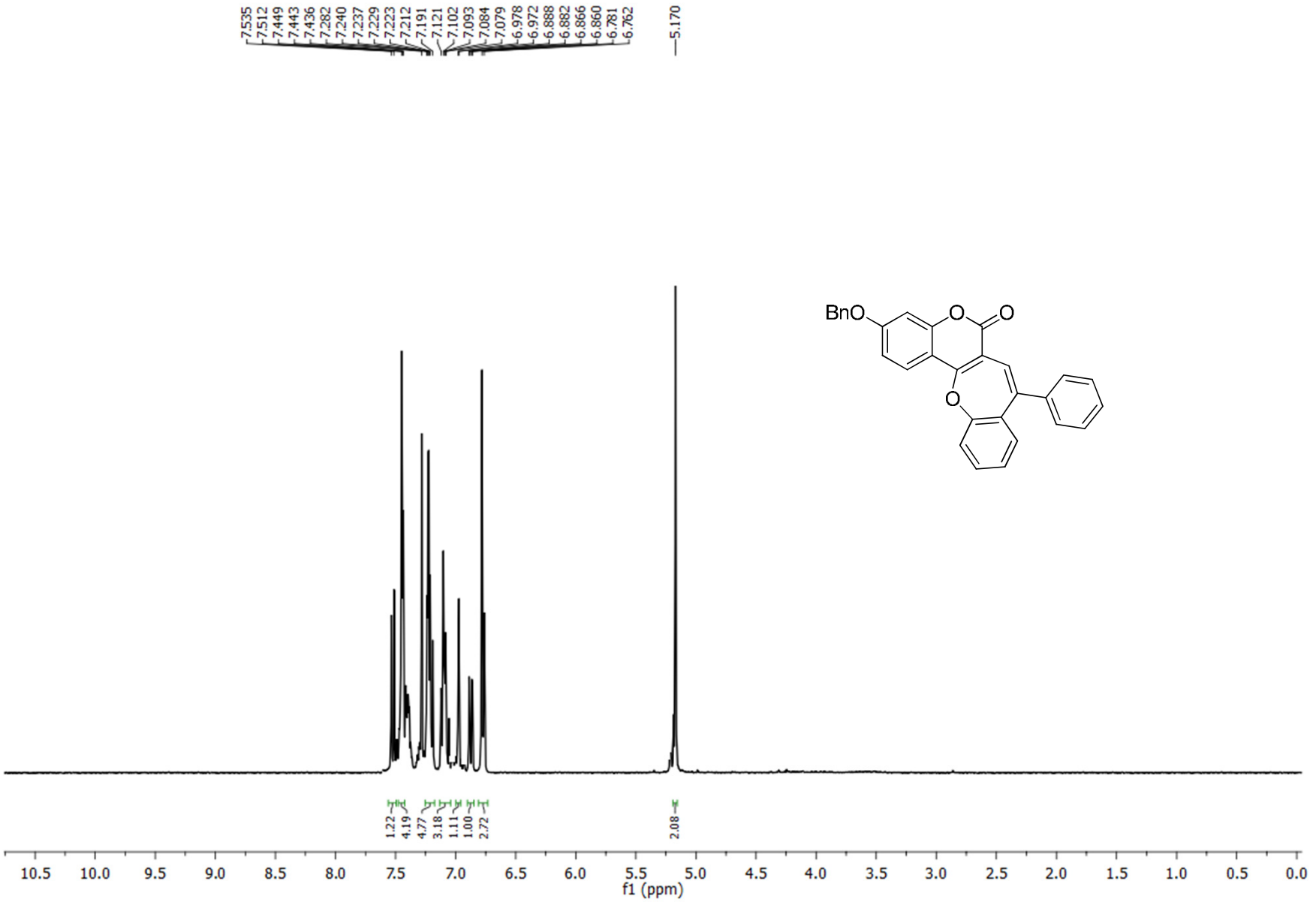
^{1}H NMR of 2-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6d)



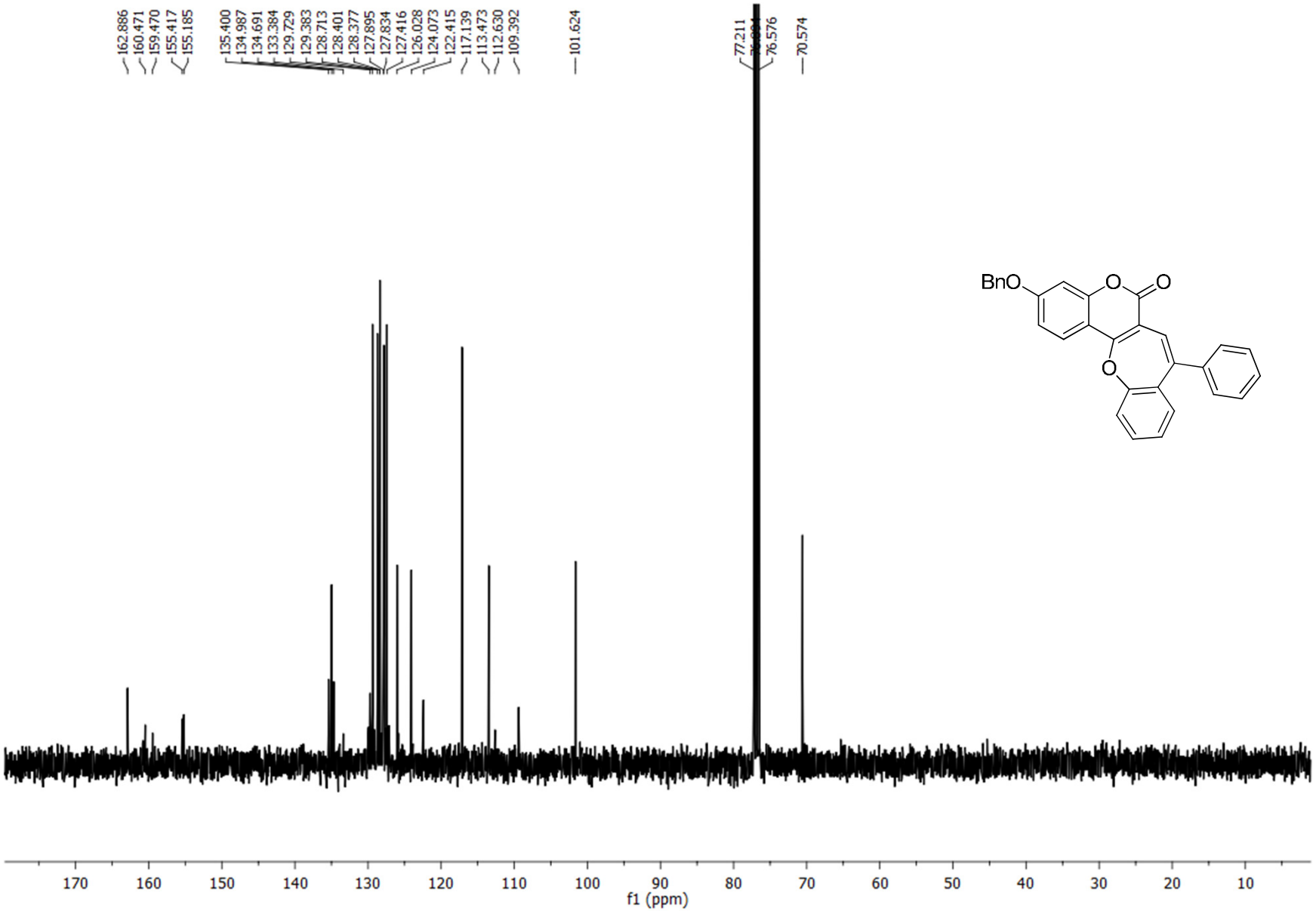
^{13}C NMR of 2-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6d)



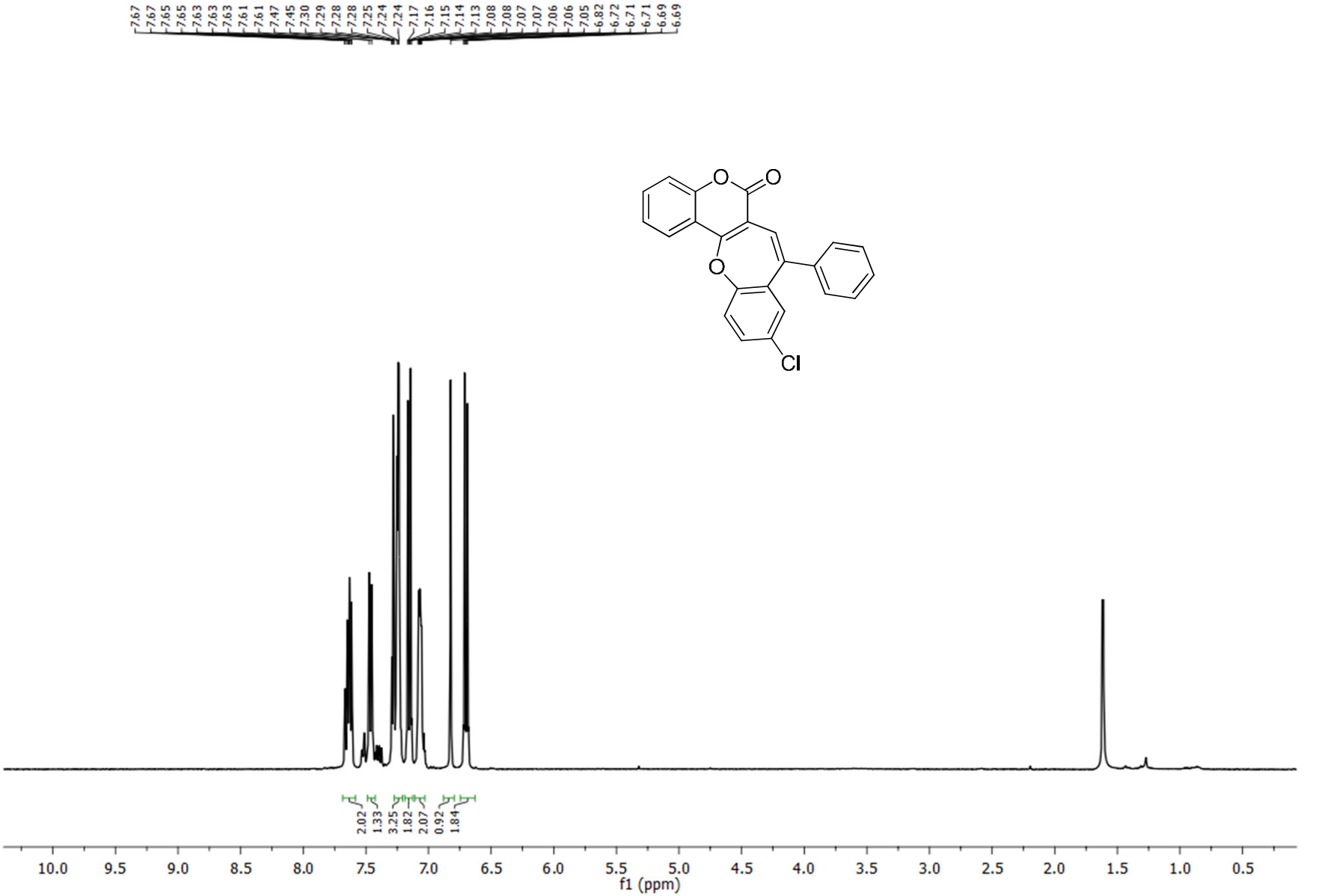
^{1}H NMR of 3-(benzyloxy)-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6e)



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



^{1}H 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)