Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Catalytic Oxidation/C–H Functionalization of *N*-Arylpropiolamides by Means of Gold Carbenoid: Concise Route to 3-Acyloxindoles

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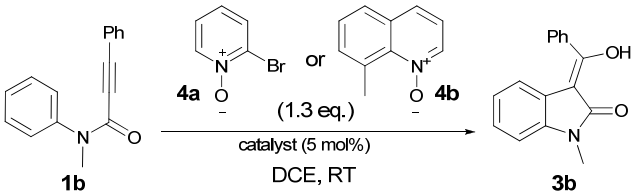
Contents:

General Remarks. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used without further purification. ^{1}H NMR spectra, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d_3. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. 1,2-Dichloroethane (DCE) and Dichloromethane (CH_2Cl_2) were freshly distilled from CaH_2; tetrahydrofuran was dried with sodium benzophenone and distilled before use; triethylamine (Et_3N) were stored over 4Å molecular sieves prior to use. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

2. Optimization of Reaction Conditions

Table S1 Screening of reaction conditions.[a]



Entry	Catalyst[b]	*N*-Oxide	*t* (h)	Yield (%)[c]
1	$[PPh_3AuCl]/AgNTf_2$	**4a**	12	69
2	$[IPrAuCl]/AgNTf_2$	**4a**	12	85
3	$[LAuCl]/AgNTf_2$	**4a**	12	94[d]
4	$[LAuCl]/AgNTf_2$	**4b**	24	93
5	$[LAuCl]/AgSbF_6$	**4a**	12	92
6	$[LAuCl]/AgNTf_2$	**4a**	0.03	41
7	$[LAuCl]/AgNTf_2$	**4a**	0.3	70
8	$[LAuCl]/AgNTf_2$	**4a**	6	85
9	$AgNTf_2$	**4a**	12	no reaction

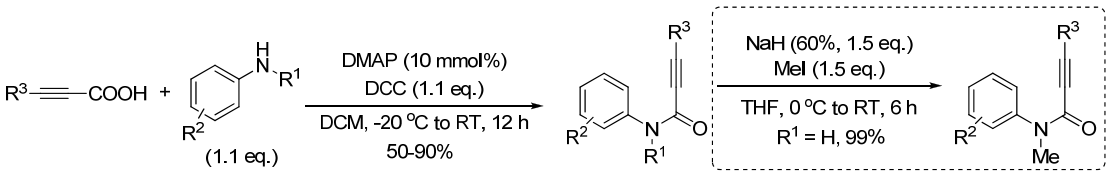
[a] [**1b**]=0.2 M, and 1.3 equiv of the oxidant **4**. [b] L = $(2,4\text{-}^{t}Bu_2PhO)_3P$, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, Tf = triflouoromethane-sulfonyl. [c] Estimated by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal reference. [d] Yield of isolated product: 91%. DCE = 1,2-dichloroethane.

The reaction in the presence of various gold catalysts and 2-bromopydine /8-methy-lisoquinoline *N*-oxide **4a** /**4b** (1.3 equiv) as the oxidant were investigated. To our delight, the desired 3-acyloxindole **3b** was produced in 69% yield, when [PPh_3AuCl]/ $AgNTf_2$ was used as the catalyst and the *N*-oxide **4a** as the oxidant (Table S1, entry 1). With the use of *N*-oxide **4a** as the oxidant, catalytic efficiency was improved with the more electrophilic [IPrAuCl]/$AgNTf_2$ and [(2,4-^{t}Bu$_2$PhO)$_3$PAuCl]/ $AgNTf_2$, both of which gave 85% and 94% yield, respectively (Table S1, entries 2-3). The combination of [(2,4-^{t}Bu$_2$PhO)$_3$P-AuCl]/$AgSbF_6$ afforded **3b** exclusively in 92% yield (entry 5). With an extended reaction time (24 h), the convesion was complete for the [(2,4-^{t}Bu$_2$PhO)$_3$P AuCl]/$AgNTf_2$ catalyst and 8-methylisoquino-line *N*-oxide as the oxidant led to 93% yield (entry 4). Moreover, the reaction became slower with the reaction proceeding, indicating the generated pyrridine derivatives rendered the reaction ineffective in some sense (entries 6-8). Further control experiment confirmed that no reaction occurred in the absence of a gold precatalyst (entry 10).

3. Typical Procedures for the Synthesis of Substrates 1

All of compounds in Table 1 and scheme 3 were synthesized according to the literature by a modification of the procedure, and the NMR spectroscopy were consisted with the those data.[S1]

Method A[S1a]**:**



***Scheme* S1**.

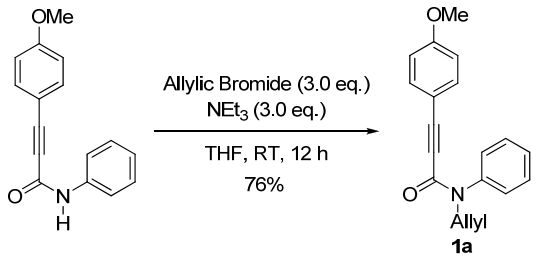
In a flame dried double Schlenk flask, a solution of the corresponding propynoic acid (5.5 mmol, 1.1 eq.) in CH_2Cl_2 (10 mL) was cooled to -20 °C and 4-dimethylaminopyridine (0.5 mmol, 0.1 eq.), dicyclohexylcarbodiimide (5.5 mmol, 1.1 eq.) in CH_2Cl_2 (5 mL) was added dropwise.

Then a solution of *N*-Methylaniline (or the relative aniline) (5.0 mmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred at room temperature for 12 hours. The crude mixture was filtered and washed with CH_2Cl_2. The filtrate was washed with 0.5 M aqueous HCl, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give **1** (50-90% yield) as a pale yellow solid or oil.

To a solution of 2-alkynamides (R^1 = H) of primary allylic amines (2.0 mmol) in THF (8 mL) was added NaH (120 mg, 60% in oil, 3.0 mmol) and CH_3I (1.9 mL, 3.0 mmol). The mixture was stirred for 30 min then poured into ice water (40 mL), extracted with CH_2Cl_2 (3 x 20 mL), washed (brine), dried (Na_2SO_4) and evaporated the solvent. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to afford corresponding products (quant. yield).

Note: All substrates **1** exist as a 6:1-10:1 mixture of rotamers and the spectroscopic datas of their major rotamers are reported.

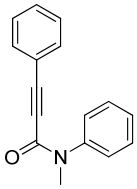
_N_-allyl-3-(4-methoxyphenyl)-_N_-phenylpropiolamide (1a)



1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 3H), 7.34-7.32 (m, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 6.02-5.84 (m, 1H), 5.28-5.14 (m, 2H), 4.18 (d, J = 6.0 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 160.9, 154.3, 141.9, 134.2, 132.4, 128.9, 128.5, 127.9, 118.2, 113.9, 112.2, 91.7, 81.9, 55.3, 51.3; MS (EI): m/z (%) = 291 (M^+, 14.14), 159 (100)； HRMS (EI): calculated for $[C_{19}H_{17}NO_2]^+$ 291.1259, found: 291.1260.

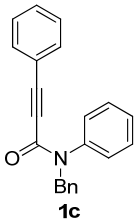
_N_-methyl-_N_,3-diphenylpropiolamide (1b)



1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.33 (m, 6H), 7.24 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 7.2 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.2, 132.4, 129.9, 129.1, 128.3, 127.9, 127.4, 120.4, 90.8, 82.5, 36.3.

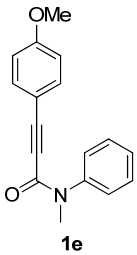
_N_-benzyl-_N_,3-diphenylpropiolamide (1c)



1c

^{1}HNMR (400 MHz, $CDCl_3$) δ 7.36-7.10 (m, 13H), 7.08 (d, J = 5.6 Hz, 2H), 5.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.6, 136.6, 132.4, 129.9, 129.0, 128.7, 128.6, 128.4, 128.2, 128.1, 127.5, 120.3, 91.4, 82.5, 52.2.

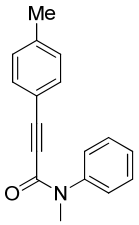
3-(4-methoxyphenyl)-_N_-methyl-_N_-phenylpropiolamide (1e)



1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 5H), 7.07(d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 154.5, 143.3, 134.2, 129.0, 127.7, 127.4 113.9, 112.2, 91.4, 81.9, 55.2, 36.2.

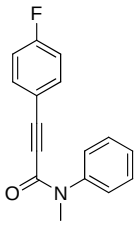
_N_-methyl-_N_-phenyl-3-p-tolylpropiolamide (1f)



1f

^{1}H (400 MHz, $CDCl_3$) δ 7.46-7.34 (m, 5H), 7.03 (s, 4H), 3.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.3, 140.4, 132.3, 129.05, 129.03, 127.8, 127.3, 117.3, 91.2, 82.2, 36.3, 21.5.

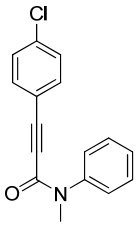
3-(4-fluorophenyl)-*N*-methyl-*N*-phenylpropiolamide (1g)



1g

^{1}H (400 MHz, $CDCl_3$) δ 7.46-7.28 (m, 5H), 7.13-7.06 (m, 2H), 6.94-6.89 (m, 2H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, $J_{C,F}$ = 251 Hz), 154.1, 143.1, 134.5 (d, $J_{C,F}$ = 9 Hz), 129.1, 127.9, 127.4, 125.4, 115.7 (d, $J_{C,F}$ = 22 Hz), 89.7, 82.3, 36.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -107.6.

3-(4-chlorophenyl)-*N*-methyl-*N*-phenylpropiolamide (1h)

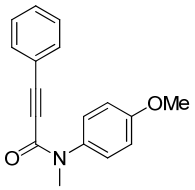


1h

^{1}H (400 MHz, $CDCl_3$) δ 7.47-7.34 (m, 5H), 7.21 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.1, 136.2, 133.6, 129.2, 128.7, 128.0, 127.4,

118.9, 89.5, 83.3, 36.4; MS (EI): m/z (%) = 269 (M^+, 34.80), 271 (12.15), 163 (100)；HRMS (EI): calculated for $[C_{16}H_{12}NO^{35}Cl]^+$ 269.0607, found: 269.0609.

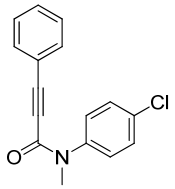
***N*-(4-Methoxyphenyl)-*N*-methyl-3-phenylpropiolamide (1j)**



1j

^{1}H (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 5H), 7.18 (d, J = 6.8 Hz, 2H), 6.95 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.5, 136.0, 132.4, 129.8, 128.2, 126.7, 120.4, 114.4, 114.2, 90.8, 82.6, 55.5, 36.5.

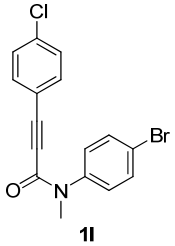
***N*-(4-chlorophenyl)-*N*-methyl-3-phenylpropiolamide (1k)**



1k

^{1}H (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 7H), 7.19 (d, J = 7.6 Hz, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 141.7, 133.6, 132.3, 130.1, 129.3, 128.7, 128.4, 126.7, 120.1, 91.2, 82.2, 36.3; MS (EI): m/z (%) = 269 (M^+, 6.83), 271 (2.60), 129 (100)；HRMS (EI): calculated for $[C_{16}H_{12}NO^{35}Cl]^+$ 269.0607, found: 269.0610.

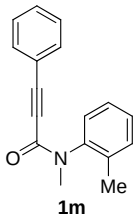
***N*-(4-bromophenyl)-3-(4-chlorophenyl)-*N*-methylpropiolamide (1l)**



1l

^{1}H (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.27-7.23 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.0, 136.4, 133.5, 132.3, 129.0, 128.8, 126.9, 121.6, 118.5, 90.0, 83.0, 36.3; MS (EI): m/z (%) = 374 (M^+, 3.49), 374 (3.87), 163 (100); HRMS (EI): calculated for $[C_{16}H_{11}NO^{35}Cl^{79}Br]^+$ 346.9713, found: 346.9714.

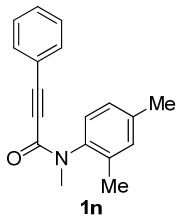
_N_-methyl-3-phenyl-_N_-_o_-tolylpropiolamide (1m)



1m

^{1}H (400 MHz, $CDCl_3$) δ 7.44-7.18 (m, 7H), 7.05 (d, J = 7.2 Hz, 2H), 3.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 141.8, 136.2, 132.4, 130.9, 129.8, 128.6, 128.5, 128.2, 126.9, 89.8, 82.2, 35.2, 17.4; MS (EI): m/z (%) = 249 (M^+, 32.18), 129 (100); HRMS (EI): calculated for $[C_{17}H_{15}NO]^+$ 249.1154, found: 249.1155.

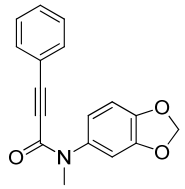
_N_-(2,4-dimethylphenyl)-_N_-methyl-3-phenylpropiolamide (1n)



1n

^{1}H (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.13-7.11 (m, 2H), 7.07 (d, J = 7.6 Hz, 3H), 3.28 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 139.3, 138.4, 135.8, 132.4, 129.7, 128.21, 128.18, 127.5, 120.4, 89.7, 82.4, 35.4, 21.0, 17.3; MS (EI): m/z (%) = 263 (M^+, 36.03), 129 (100); HRMS (EI): calculated for $[C_{18}H_{17}NO]^+$ 263.1310, found: 263.1312.

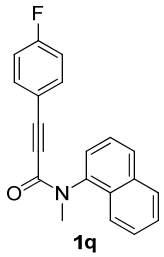
_N_-(benzo[_d_][1,3]dioxol-5-yl)-_N_-methyl-3-phenylpropiolamide (1o)



1o

^{1}H (400 MHz, $CDCl_3$) δ 7.47-7.34 (m, 1H), 7.30-7.23 (m, 4H), 6.85-6.83 (m, 3H), 6.04 (s, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.9, 147.2, 137.1, 132.4, 129.9, 128.3, 121.2, 120.5, 108.3, 108.1, 101.8, 90.9, 82.5, 36.6; MS (EI): m/z (%) = 279 (M^+, 34.41), 129 (100); HRMS (EI): calculated for $[C_{17}H_{13}NO_3]^+$ 279.0895, found: 279.0896.

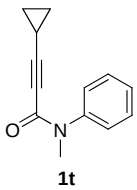
3-(4-fluorophenyl)-*N*-methyl-*N*-(naphthalen-1-yl)propiolamide (1q)



1q

^{1}H (400 MHz, $CDCl_3$) δ 7.95 (t, J = 7.2 Hz, 2H), 7.87 (d, J = 7.6 Hz, 1H), 7.60-7.49 (m, 4H), 6.81-6.71 (m, 4H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, $J_{C,F}$ = 250 Hz), 155.1, 139.5, 134.4 (d, $J_{C,F}$ = 9 Hz), 130.5, 129.0, 128.4, 127.9, 127.3, 126.6, 125.5, 122.5, 116.2, 115.6 (d, $J_{C,F}$ = 22 Hz), 89.5, 82.4, 36.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -107.7; m/z (%) = 303 (M^+, 30.36), 147 (100); HRMS (EI): calculated for $[C_{20}H_{14}NOF]^+$ 303.1059, found: 303.1060.

3-cyclopropyl-*N*-methyl-*N*-phenylpropiolamide (1t)

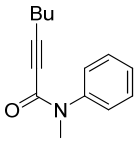


1t

^{1}H (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.27-7.24 (m, 2H), 3.30 (s,

3H), 1.13-1.07 (m, 1H), 0.73-0.68 (m, 2H), 0.46-0.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.4, 128.9, 127.6, 127.2, 97.5, 70.0, 36.2, 8.8, -0.6; MS (EI): m/z (%) = 199 (M^+, 11.25), 93 (100); HRMS (EI): calculated for $[C_{13}H_{13}NO]^+$ 199.0997, found: 199.0995.

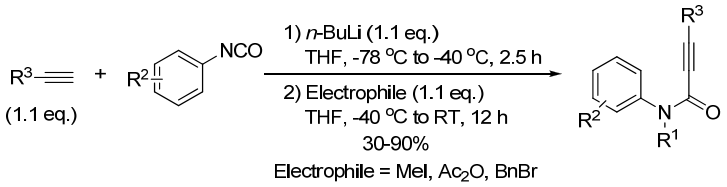
_N_-methyl-_N_-phenylhept-2-ynamide (1u)



1u

^{1}H (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.4 Hz, 2H), 7.34-7.26 (m, 3H), 3.32 (s, 3H), 2.09 (t, J = 6.8 Hz, 2H), 1.26-1.19 (m, 2H), 1.11-1.02 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.4, 129.0, 127.6, 127.3, 94.0, 74.9, 36.3, 29.3, 21.4, 18.3, 13.3; MS (EI): m/z (%) = 215 (M^+, 4.82), 147 (100); HRMS (EI): calculated for $[C_{14}H_{17}NO]^+$ 215.1310, found: 215.1313.

Method B[S1b]**:**



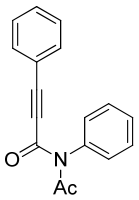
***Scheme* S2**.

In a heat gun dried and nitrogen filled Schlenk flask 1.1 equiv. of the corresponding terminal acetylene were dissolved in THF and cooled to –78 °C. At this temperature 1.0 equiv. of *n*-BuLi (2.5 *M* in hexane) were slowly added by syringe, then, the solution was stirred for 30 min and subsequently treated with 1.0 equiv. of the relative isocyanate, dissolved in a small amount of THF and allowed to warm up to –40 °C within 2 h. At this temperature 1.1 equiv. of the corresponding electrophile dissolved in a small amount of THF were added and the solution was allowed to warm to rt over night. For work up a saturated aqueous solution of NH4Cl was added, the organic layer was separated and the aqueous phases were extracted three times with diethyl ether. The combined organic phases were dried with MgSO4, filtered and, finally, the solvents were removed in vacuum. Column chromatography on silica (petroleum/ethyl acetate) afforded

the products **1** (30-90% yield).

Note: All substrates **1** exist as a 6:1-10:1 mixture of rotamers and the spectroscopic datas of their major rotamers are reported.

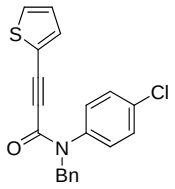
***N*-acetyl-*N*,3-diphenylpropiolamide (1d)**



1d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 3H), 7.40-7.35 (m, 1H), 7.32-7.24 (m, 4H), 7.10-7.08 (m, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 154.7, 138.4, 133.0, 130.8, 129.6, 129.4, 129.1, 128.4, 119.4, 96.2, 82.7, 27.4.

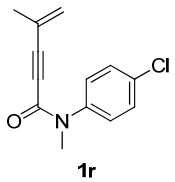
***N*-benzyl-*N*-(4-chlorophenyl)-3-(thiophen-2-yl)propiolamide (1i)**



1i

^{1}H (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 6H), 7.23-7.21 (m, 2H), 7.11-7.04 (m, 3H), 6.94-6.92 (m, 1H), 4.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 139.8, 136.2, 135.2, 134.0, 130.5, 130.0, 129.3, 128.7, 128.6, 127.8, 127.3, 119.8, 86.4, 85.8, 52.0; MS (EI): m/z (%) = 351 (M^+, 14.46), 353 (3.93), 91 (100)； HRMS (EI): calculated for $[C_{20}H_{14}NOS^{35}Cl]^+$ 351.0485, found: 351.0487.

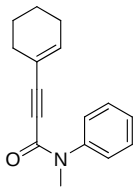
***N*-(4-chlorophenyl)-*N*,4-dimethylpent-4-en-2-ynamide (1r)**



1r

^{1}H (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 5.32 (s, 1H), 5.22 (s, 1H), 3.33 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 141.7, 133.6, 129.3, 128.6, 126.4, 124.7, 92.3, 81.1, 36.3, 22.1; MS (EI): m/z (%) = 233 (M^+, 11.25), 235 (3.87), 93 (100); HRMS (EI): calculated for $[C_{13}H_{12}NO^{35}Cl]^+$ 233.0607, found: 233.0606.

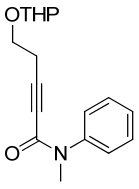
3-cyclohexenyl-*N*-methyl-*N*-phenylpropiolamide (1s)



1s

^{1}H (400 MHz, $CDCl_3$) δ 7.40 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 6.8 Hz, 1H), 7.29 (d, J = 7.2 Hz, 2H), 6.00 (s, 1H), 3.34 (s, 3H), 2.00 (s, 2H), 1.80 (s, 2H), 1.50-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.3, 140.2, 128.9, 127.6, 127.2, 118.9, 92.9, 80.4, 36.2, 27.8, 25.7, 21.8, 21.0; MS (EI): m/z (%) = 239 (M^+, 38.11), 77 (100); HRMS (EI): calculated for $[C_{16}H_{17}NO]^+$ 239.1310, found: 239.1308.

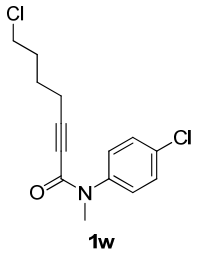
***N*-methyl-*N*-phenyl-5-(tetrahydro-2H-pyran-2-yloxy)pent-2-ynamide (1v)**



1v

^{1}H (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.34-7.32 (m, 1 H), 7.28-2.27(m, 2H), 4.47-4.46 (m, 1H), 3.78-3.72 (m, 1H), 3.58-3.52 (m, 2H), 3.47-3.44 (m, 1H), 3.32 (s, 3H), 2.39 (t, J = 7.2 Hz, 2H), 1.84-1.71 (m, 2H), 1.66-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.2, 129.0, 127.7, 127.1, 98.6, 90.6, 75.4, 64.5, 62.1, 36.3, 30.4, 25.3, 20.3, 19.2; MS (EI): m/z (%) = 287 (M^+, 0.49), 79 (100); HRMS (EI): calculated for $[C_{17}H_{21}NO_3]^+$ 287.1521, found: 287.1518.

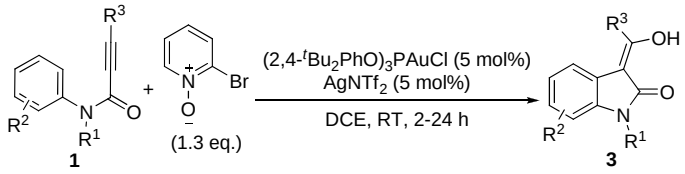
7-chloro-*N*-methyl-*N*-phenylhept-2-ynamide (1w)



1w

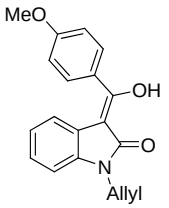
^{1}H (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 3.40 (t, J = 6.0 Hz, 2H), 3.29 (s, 3H), 2.18 (t, J = 6.4 Hz, 2H), 1.54-1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 141.8, 133.6, 129.3, 128.7, 126.6, 93.3, 75.2, 44.1, 36.3, 30.9, 24.5, 18.0; MS (EI): m/z (%) = 284 (M^+, 3.46), 286 (1.21), 77 (100); GCMS (EI): m/z (%) = 284 (M^+, 5.27), 286 (1.61), 147 (100).

4. General Procedures: Preparation of 3-Acyloxindoles



A sealed dry glass tube was charged with (2,4-^{t}Bu$_2$PhO)$_3$PAuCl (0.01 mmol, 5 mmol%) and $AgNTf_2$ (0.01 mmol, 5 mmol%), and to this mixture was added DCE (1 mL); the mixture was stirred for 10 minutes before it was added with a dichloroethane solution (1 mL) of compound **1** (0.2 mmol, 1.0 eq.) and 2-bromopydine *N*-oxide (0.26 mmol, 1.3 eq.). The reaction mixture was stirred at RT and the progress of the reaction was monitored by TLC. The reaction typically took 2-24 h. Upon completion, the mixture was concentrated and filtered over a short silica bed. The residue was purified by column chromatography on silica gel with a gradient eluant of petroleum ether (or hexane) and ethyl acetate (or dichloromethane) afforded the desired products **3**.

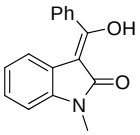
1-allyl-3-(hydroxy(4-methoxyphenyl)methylene)indolin-2-one (3a)



3a

Green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.79 (d, J = 8.8 Hz, 2H), 7.33-7.31 (m, 1H) 7.18-7.14 (m, 1H), 7.04 (d, J = 8.4 Hz, 2H), 6.96-6.90 (m, 2H), 5.97-5.88 (m, 1H), 5.26-5.22 (m, 2H), 4.54 (d, J = 5.2 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.3, 162.2, 138.1, 131.7, 130.4, 126.4, 125.5, 121.9, 121.8, 119.6, 117.5, 114.0, 109.2, 100.5, 55.5, 42.1; IR (neat): 2960, 1711, 1603, 1509, 1436, 1361, 1253, 1166, 1110, 1026, 925, 839, 749 ν cm^{-1}; MS (EI): m/z (%) = 307 (M^+, 38.09), 199 (100)；HRMS (EI): calculated for $[C_{19}H_{17}NO_3]^+$ 307.1208, found: 307.1210.

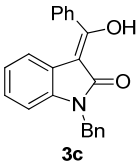
3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (3b)



3b

Yellow solid, m. p. 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.80-7.78 (m, 2H), 7.60-7.53 (m, 3H), 7.22-7.18 (m, 2H), 6.96-6.89 (m, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.0, 139.1, 134.1, 131.3, 128.6, 128.4, 125.9, 121.9, 121.6, 120.0, 108.3, 101.5, 25.9; IR (neat): 3051, 1641, 1599, 1487, 1335, 1109, 887, 769, 747, 704 ν cm^{-1}; MS (EI): m/z (%) = 251 (M^+, 53.68), 173 (100)；HRMS (EI): calculated for $[C_{16}H_{13}NO_2]^+$ 251.0946, found: 251.0947.

1-benzyl-3-(hydroxy(phenyl)methylene)indolin-2-one (3c)[S2]

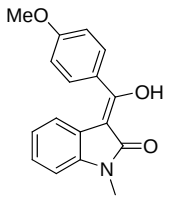


3c

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.82 (d, J = 6.4 Hz, 2H), 7.81-7.54 (m, 3H), 7.35-7.27 (m, 4H), 7.20 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.88 (t, J

= 7.6 Hz, 2H), 5.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.3, 138.2, 135.9, 134.1, 131.4, 128.8, 128.7, 128.4, 127.6, 127.3, 125.9, 121.9, 121.7, 119.7, 109.3, 101.3, 43.4.

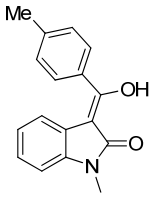
3-(hydroxy(4-methoxyphenyl)methylene)-1-methylindolin-2-one (3e)



3e

Yellow solid, m. p. 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 6.96-6.91 (m, 2H), 3.91 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.1, 162.1, 138.9, 130.3, 126.4, 125.6, 121.9, 121.8, 119.6, 114.0, 108.3, 100.7, 55.5, 25.9; IR (neat): 3334, 2973, 1643, 1454, 1380, 1258, 1089, 1048, 881, 804, 750 ν cm^{-1}; MS (EI): m/z (%) = 281 (M^+, 24.44), 173 (100)； HRMS (EI): calculated for $[C_{17}H_{15}NO_3]^+$ 281.1052, found: 281.1051.

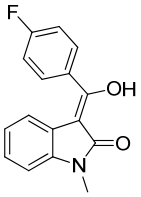
3-(hydroxy(p-tolyl)methylene)-1-methylindolin-2-one (3f)



3f

Yellow solid, m. p. 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 6.8 Hz, 1H),7.21 (t, J = 7.6 Hz, 1H), 6.98-6.91 (m, 2H), 3.42 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.3, 141.8, 139.0, 131.3, 129.3, 128.4, 125.7, 121.8, 121.7, 119.7, 108.3, 101.1, 25.8, 21.7; IR (neat): 3332, 2974, 1645, 1454, 1380, 1336, 1089, 1048, 881, 749 ν cm^{-1}; MS (EI): m/z (%) = 265 (M^+, 40.07), 173 (100)； HRMS (EI): calculated for $[C_{17}H_{15}NO_2]^+$ 265.1103, found: 265.1102.

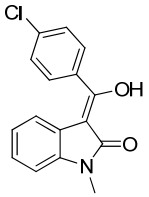
3-((4-fluorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (3g)



3g

Yellow solid, m. p. 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (q, J = 1.6 Hz, J = 5.6 Hz, 2H), 7.26-7.16 (m, 4H), 6.94 (q, J = 5.2 Hz, J = 8.0 Hz, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.7, 164.4 (d, $J_{C\text{-}F}$ = 251 Hz), 139.1, 138.8 (d, J = 9 Hz), 130.3, 126.0, 121.9, 121.4, 119.5, 115.9 (d, $J_{C\text{-}F}$ = 22 Hz), 108.5, 101.5, 25.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -107.5; IR (neat): 2986, 1648, 1603, 1508, 1469, 1338, 1231, 1157, 1111, 1072, 976, 848, 781, 748, 690 ν cm^{-1}; MS (EI): m/z (%) = 269 (M^+, 51.00), 173 (100)； HRMS (EI): calculated for $[C_{16}H_{12}NO_2F]^+$ 269.0852, found: 269.0850.

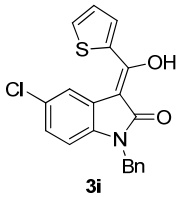
3-((4-chlorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (3h)



3h

Yellow solid, m. p. 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.00 (br s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.20 (q, J = 5.0 Hz, J = 7.6 Hz, 2H), 6.94 (q, J = 3.8 Hz, J = 8.0 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.4, 139.2, 137.4, 132.5, 129.9, 129.0, 126.2, 122.0, 121.2, 119.6, 108.5, 101.7, 25.9; IR (neat): 3060, 2969, 1637, 1607, 1486, 1222, 1162, 1089, 1049, 879, 780, 745, 727 ν cm^{-1}; MS (EI): m/z (%) = 285 (M^+, 37.17), 287 (11.98), 173 (100)； HRMS (EI): calculated for $[C_{16}H_{12}NO_2{}^{35}Cl]^+$ 285.0557, found: 285.0559.

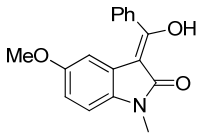
1-benzyl-5-chloro-3-(hydroxy(thiophen-2-yl)methylene)indolin-2-one (3i)



3i

Yellow solid, m. p. 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.00-13.50 (br s, 1H), 7.90 (s, 1H), 7.72-7.67 (m, 2H), 7.36-7.26 (m, 6H), 7.09-7.07 (m, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 165.7, 136.4, 135.9, 135.4, 131.5, 131.1, 128.9, 127.82, 127.78, 127.6, 127.2, 125.6, 123.0, 119.7, 110.2, 100.1, 43.6; IR (neat): 3104, 1641, 1615, 1412, 1354, 1278, 1189, 1081, 1026, 856, 808, 715, 698 v cm^{-1}; MS (EI): m/z (%) = 367 (M^+, 18.07), 369 (6.60), 91 (100)； HRMS (EI): calculated for $[C_{20}H_{14}NOS^{35}Cl]^+$ 367.0434, found: 367.0443.

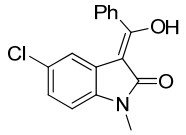
3-(hydroxoy(phenyl)methylene)-5-methoxy-1-methylindolin-2-one (3j)



3j

Yellow solid, m. p. 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.79-7.77 (m, 2H), 7.60-7.53 (m, 3H), 7.59-7.52 (m, 2H), 6.84 (d, J = 8.4 Hz, 1H), 6.77-6.73 (m, 2H), 3.65 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.2, 155.4, 134.0, 133.3, 131.4, 128.6, 128.3, 122.6, 111.0, 108.6, 106.6, 101.7, 55.63, 25.9; IR (neat): 3346, 2973, 1640, 1456, 1380, 1089, 1049, 881, 701 v cm^{-1}; MS (EI): m/z (%) = 281 (M^+, 97.26), 203 (100)； HRMS (EI): calculated for $[C_{17}H_{15}NO_3]^+$ 281.1052, found: 281.1053.

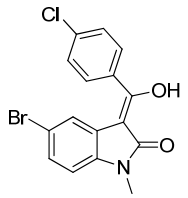
5-chloro-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (3k)



3k

Yellow solid, m. p. 169-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ1 5.00-13.50 (br s, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.63-7.55 (m, 3H), 7.16-7.14 (m, 2H), 6.85 (d, J = 8.8 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.7, 137.4, 133.6, 131.8, 128.8, 128.2, 127.3, 125.5, 123.0, 119.6, 109.1, 100.7, 26.0; IR (neat): 3055, 2937, 1637, 1481, 1447, 1342, 1275, 1178, 1075, 907, 877, 807, 768, 699 v cm^{-1}; MS (EI): m/z (%) = 285 (M^+, 60.82), 287 (20.98), 207 (100)； HRMS (EI): calculated for $[C_{16}H_{12}NO_2{}^{35}Cl]^+$ 285.0557, found: 285.0559.

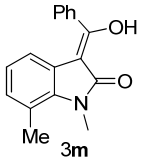
5-bromo-3-((4-chlorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (3l)



3l

Yellow solid, m. p. 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.33-7.30 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.9, 138.0, 137.9, 132.0, 129.8, 129.2, 128.6, 123.2, 122.4, 114.9, 109.8, 100.8, 26.0; IR (neat): 3057, 16634, 1632, 1600, 1483, 1326, 1272, 1092, 1048, 836, 798, 780 v cm^{-1}; MS (EI): m/z (%) = 363 (M^+, 41.76), 365 (49.86), 207 (100)；HRMS (EI): calculated for $[C_{16}H_{11}NO_2{}^{35}Cl^{79}Br]^+$ 362.9664, found: 362.9662.

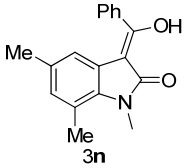
3-(hydroxy(phenyl)methylene)-1,7-dimethylindolin-2-one (3m)



3m

Yellow solid, m. p. 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.57-7.51 (m, 3H), 6.99 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.77-6.74 (m, 1H), 3.69 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.0, 137.1, 134.2, 131.2, 129.5, 128.6, 128.4, 122.2, 121.7, 120.1, 117.7, 101.3, 29.2, 19.3; IR (neat): 2923, 1633, 1592, 1575, 1448, 1344, 1279, 1123, 1082, 897, 741, 694 v cm^{-1}; MS (EI): m/z (%) = 265 (M^+, 53.33), 187 (100)；HRMS (EI): calculated for $[C_{17}H_{15}NO_2]^+$ 265.1103, found: 265.1103.

3-(hydroxy(phenyl)methylene)-1,5,7-trimethylindolin-2-one (3n)

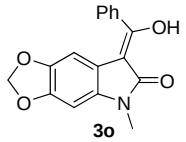


3n

Yellow solid, m. p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-14.00 (br s, 1H), 7.76-7.74 (m, 2H), 7.59-7.51 (m, 3H), 6.81 (s, 1H), 6.73 (s, 1H), 3.65 (s, 3H), 2.58 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 170.7, 134.9, 134.2, 131.2, 130.9, 130.3, 128.5, 128.4, 122.2,

119.7, 118.3, 101.3, 29.1, 21.0, 19.1; IR (neat): 2972, 2901, 1629, 1449, 1328, 1261, 1123, 1089, 1049, 864, 803, 741 ν cm^{-1}; MS (EI): m/z (%) = 279 (M^+, 64.41), 201 (100); HRMS (EI): calculated for $[C_{18}H_{17}NO_2]^+$ 279.1259, found: 279.1257.

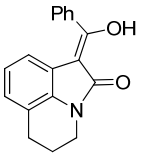
7-(hydroxy(phenyl)methylene)-5-methyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6(7*H*)-one (3o)



3o

Yellow solid, , m. p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.73-7.71 (m, 2H), 7.54-7.52 (m, 3H), 6.64 (s, 1H), 6.53 (s, 1H), 5.88 (s, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.3, 165.8, 163.3, 133.1, 132.9, 131.0, 130.9, 130.4, 129.3, 125.9, 124.7, 122.3, 121.6, 121.1, 118.3, 117.3, 116.0, 115.8, 101.7, 30.5; IR (neat): 3339, 2974, 1619, 1478, 1382, 1090, 1049, 881, 724 ν cm^{-1}; MS (EI): m/z (%) = 295 (M^+, 58.79), 217 (100); HRMS (EI): calculated for $[C_{17}H_{13}NO_4]^+$ 295.0845, found: 295.0847.

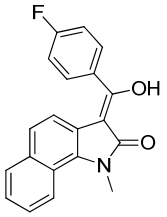
1-(hydroxy(phenyl)methylene)-5,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-2(4*H*)-one (3p)



3p

Yellow solid, m. p. 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.00 (br s, 1H), 7.83-7.81 (m, 2H), 7.59-7.51 (m, 3H), 7.05 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 3.90 (t, J = 6.0 Hz, 2H), 2.84 (t, J = 6.0 Hz, 2H), 2.12-2.06 (m, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 135.1, 134.2, 131.3, 128.5, 128.3, 124.5, 121.4, 120.4, 120.1, 117.6, 102.2, 38.6, 24.7, 21.2; IR (neat): 3034, 2955, 1722.1, 1619, 1444, 1325, 1261, 1109, 1021, 820, 767, 699 ν cm^{-1}; GCMS: m/z (%) = 277 (M^+, 67.48), 199 (100).

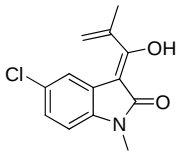
3-((4-fluorophenyl)(hydroxy)methylene)-1-methyl-1*H*-benzo[*g*]indol-2(3*H*)-one (3q)



3q

Bottlegreen solid, m. p. 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.4 Hz, 1H), 7.85-7.82 (m, 3H), 7.50-7.46 (m, 1H), 7.43-7.38 (m, 2H), 7.30-7.23 (m, 3H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.3, 164.5 (d, $J_{C\text{-}F}$ = 251 Hz), 133.1, 132.9, 131.0, 130.9, 130.4, 129.3, 125.9, 124.7, 122.3, 121.6, 121.1, 118.35, 117.3, 115.9 (d, $J_{C\text{-}F}$ = 22 Hz), 101.7, 30.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -107.3; IR (neat) 3050, 2906, 1642, 1509, 1466, 1322, 1230, 1105, 851, 805, 730 v cm^{-1}; MS (EI): m/z (%) = 319 (M^+, 64.86), 223 (100)； HRMS (EI): calculated for $[C_{20}H_{14}NO_2F]^+$ 319.1009, found: 319.1012.

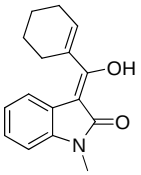
5-chloro-3-(1-hydroxy-2-methylallylidene)-1-methylindolin-2-one (3r)



3r

Yellow solid, , m. p. 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.35 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 171.8, 138.9, 137.5, 127.4, 125.3, 123.1, 121.4, 120.1, 109.1, 99.5, 25.9, 19.2; IR (neat): 3090, 2956, 1649, 1605, 1483, 1329, 1277, 1179, 1128, 932, 875, 806, 745, v cm^{-1}; MS (EI): m/z (%) = 249 (M^+, 100), 251 (32.52)； HRMS (EI): calculated for $[C_{13}H_{12}NO_2{}^{35}Cl]^+$ 249.0557, found: 249.0556.

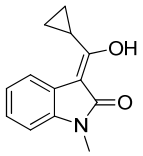
3-(cyclohexenyl(hydroxy)methylene)-1-methylindolin-2-one (3s)



3s

White solid, m. p. 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.21-7.18 (m, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.46-6.45 (m, 1H), 3.36 (s, 3H), 2.38-2.37 (m, 2H), 2.30-2.28 (m, 2H), 1.82-1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 172.0, 139.0, 134.2, 133.1, 125.3, 122.3, 121.8, 119.8, 108.3, 99.8, 25.8, 25.3, 24.8, 22.1, 21.7; IR (neat): 3335, 2972, 1638, 1605, 1491, 1467, 1325, 1262, 1088, 1050, 881, 806, 725 v cm^{-1}; MS (EI): m/z (%) = 255 (M^+, 61.74), 174 (100)；HRMS (EI): calculated for $[C_{16}H_{17}NO_2]^+$ 255.1259, found: 255.1259.

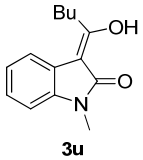
3-(cyclopropyl(hydroxy)methylene)-1-methylindolin-2-one (3t)



3t

White solid, , m. p. 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 3.36 (s, 3H), 2.31-2.25 (m, 1H), 1.40-1.36 (m, 2H), 1.16-1.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 170.8, 138.5, 124.6, 122.5, 121.9, 119.3, 108.3, 100.8, 25.7, 14.0, 9.3; IR (neat): 3012, 2970, 1645.71, 1603, 1490, 1370, 1050, 958, 889, 747, 699 v cm^{-1}; MS (EI): m/z (%) = 215 (M^+, 63.28), 173 (100)；HRMS (EI): calculated for $[C_{13}H_{13}NO_2]^+$ 215.0946, found: 215.0947.

3-(1-hydroxypentylidene)-1-methylindolin-2-one (3u)

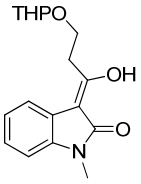


3u

Purple solid, m. p. 66-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 3.35 (s, 3H), 2.75 (t, J = 7.4 Hz, 2H), 1.81-1.73 (m, 2H), 1.54-1.46 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 171.3, 138.8, 125.0, 122.04, 121.99, 119.7, 108.3, 101.1, 33.5, 28.1, 25.6, 22.6, 13.8; IR (neat): 2967.0, 2901, 1654, 1438, 1381, 1242, 1066, 752 v cm^{-1}; MS (EI): m/z (%) = 231 (M^+, 48.26), 174 (100)；HRMS (EI): calculated for $[C_{14}H_{17}NO_2]^+$ 231.1259, found:

231.1259.

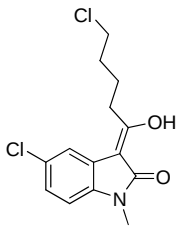
3-(1-hydroxy-3-(tetrahydro-2H-pyran-2-yloxy)propylidene)-1-methylindolin-2-one (3v)



3v

Purple oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 4.66-4.65 (m, 1H), 4.17-4.11 (m, 1H), 3.89-3.83 (m, 2H), 3.52-3.49 (m, 1H), 3.35 (s, 3H), 3.08 (t, J = 6.8 Hz, 2H), 1.76-1.64 (m, 2H), 1.58-1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 171.2, 138.9, 125.3, 122.1, 121.8, 120.1, 108.3, 102.4, 99.0, 63.5, 62.2, 34.5, 30.5, 25.7, 25.3, 19.3; IR (neat): 2940, 1655, 1608, 1468, 1343, 1260, 1199, 1120, 1076, 1031, 978, 870, 747, 705 v cm^{-1}; MS (EI): m/z (%) = 303 (M^+, 5.74), 201 (100)； HRMS (EI): calculated for $[C_{17}H_{21}NO_4]^+$ 303.1471, found: 303.1476.

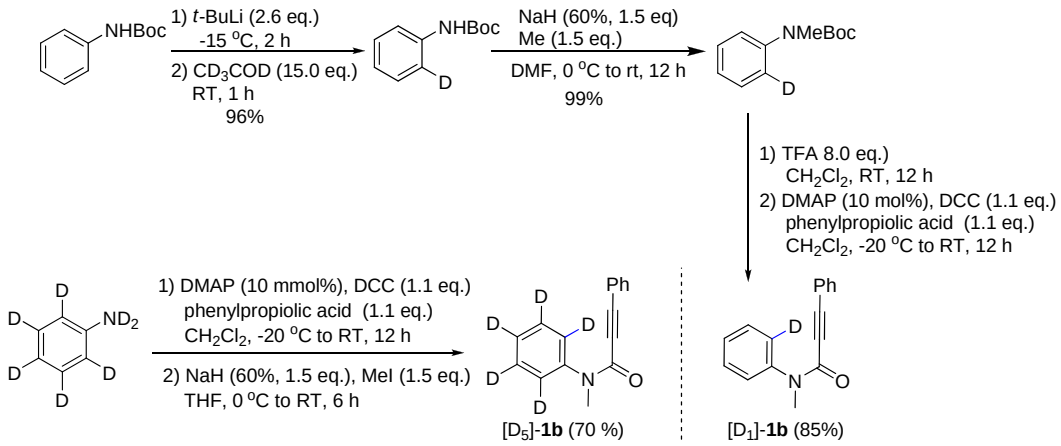
5-chloro-3-(5-chloro-1-hydroxypentylidene)-1-methylindolin-2-one (3w)



3w

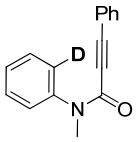
Purple solid, m. p. 42-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50-13.50 (br s, 1H), 7.29 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.60 (s, 2H), 3.32 (m, 1H), 3.89-3.83 (s, 3H), 2.76 (s, 2H), 1.95 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 171.0, 137.2, 127.6, 124.9, 123.2, 119.2, 109.2, 100.8, 44.4, 32.8, 31.8, 25.8, 22.9; IR (neat): 2967, 1653, 1485, 1326, 1260, 1148, 1087, 1049, 803, 716 v cm^{-1}; MS (EI): m/z (%) = 299 (M^+, 40.32), 264 (31.78), 266 (10.59), 208 (100)； HRMS (EI): calculated for $[C_{14}H_{15}NO_2{}^{35}Cl_2]^+$ 299.0480, found: 299.0486.

5. Mechanistic Studies: Kinetic Isotopic Effect (KIE) Studies



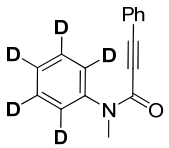
***Scheme* S4**.

Synthesis of [D_1]-**1b** involved 1) *ortho*-lithiation/deuteriation; 2) *N*-methylation; 3) Boc deprotection; 4) DCC-mediated amide formation provide [D_1]-**1b** aniline (Scheme S4). Steps 1), 2) and 3) follows a published procedure.[S3] Step 4) and the synthesis of [D_5]-**1b** follows the conditions described in Scheme S1.



[D_1]-**1b**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.41-7.30 (m, 3H), 7.23 (t, J = 7.6 Hz, 2H), 7.15-7.12 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.1, 132.4, 129.9, 129.1, 129.0, 128.3, 127.9, 127.3, 120.4, 90.8, 82.5, 36.3.



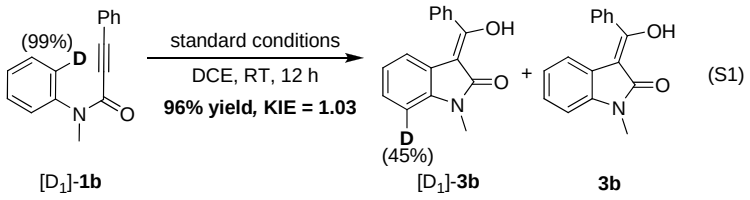
[D_5]-**1b**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.0, 132.4, 129.9, 128.6 (t, J = 25 Hz), 128.3, 127.4 (t, J = 24 Hz), 126.9 (t, J = 25 Hz), 120.4, 90.8, 82.5, 36.3.

4.1 Intramolecular KIE Experiment

A sealed dry glass tube was charged with (2,4-^{t}Bu$_2$PhO)$_3$PAuCl (0.01 mmol, 5 mmol%) and AgNTf$_2$ (0.01 mmol, 5 mmol%), and to this mixture was added DCE (1 mL); the mixture was stirred for 10 minutes before it was added with a dichloroethane solution (1 mL) of compound [D$_1$]-**1b** (0.2 mmol, 1.0 eq.) and 2-bromopydine *N*-oxide (0.26 mmol, 1.3 eq.). The reaction mixture was stirred at RT for 12 h. Then the mixture was concentrated and filtered over a short silica bed. The residue was purified by column chromatography on silica gel with a gradient eluant of petroleum ether (or hexane) and ethyl acetate afforded the desired products [D$_1$]-**3b**. The products were analyzed by ^{1}H NMR (Figure S1), and the results summarized in eq S1.

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.00-13.50 (br s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.60-7.52 (m, 3H), 7.22-7.18 (m, 2H), 6.96-6.89 (m, 1.54H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.0, 139.1, 139.0, 134.1, 131.3, 128.6, 128.4, 125.9, 125.8, 121.9, 121.6, 119.7, 108.3, 101.5, 25.9.



[D$_1$]-**1b** [D$_1$]-**3b** **3b**

The initial isotopic ratio of the reaction was determined to be KIE = k_H/k_D using the following protocols:[S3]

Because the *ortho*- and *para*-protons (*N*-aryl ring) overlap in the ^{1}H NMR spectrum, and because the *para*-proton is not deuteriumsubstituted, it is necessary to correct for this integral. The integral of a fully protonated position is:

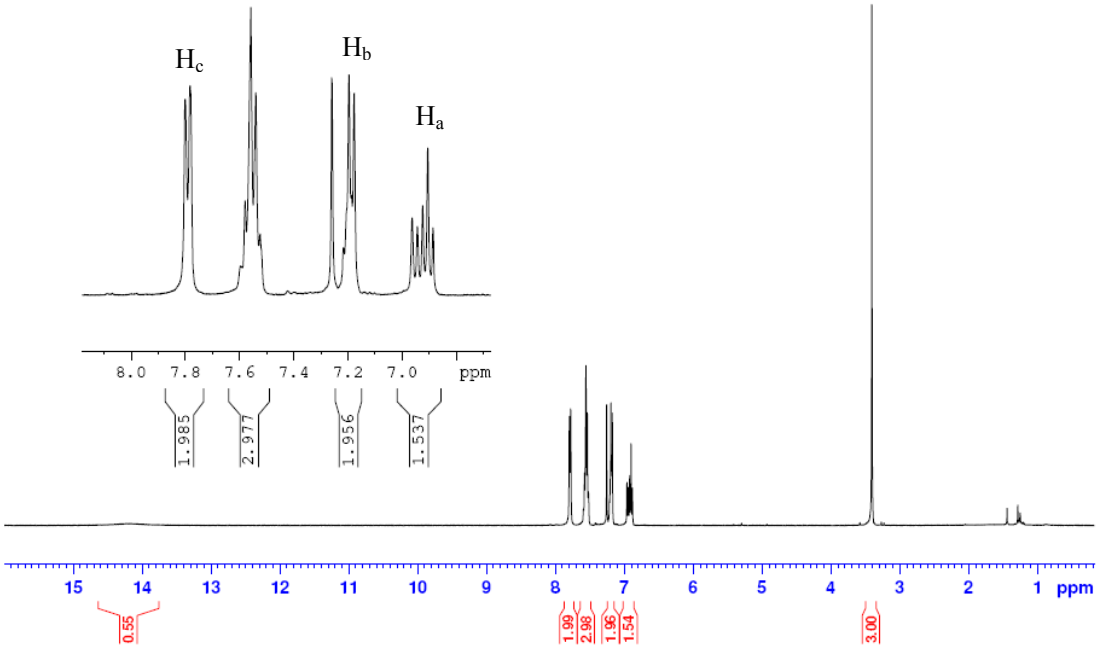
$H_{average} = (H_a + H_b) / 4 = (1.54+1.96) / 4 = 0.875$

The portion of the integral H_o that can be attributed to each *ortho*-proton is:

$H_o = (H_c - H_{average}) / 2 = (1.99 - 0.875) / 2 = 0.558$

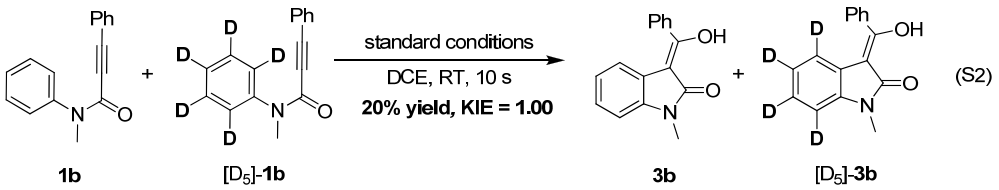
The initial proton/deuterium ratio at each *ortho*-position is:

KIE = k_H/k_D = 0.558 / (0.99-0.45) = 1.03



4.2 Intermolecular KIE Experiment

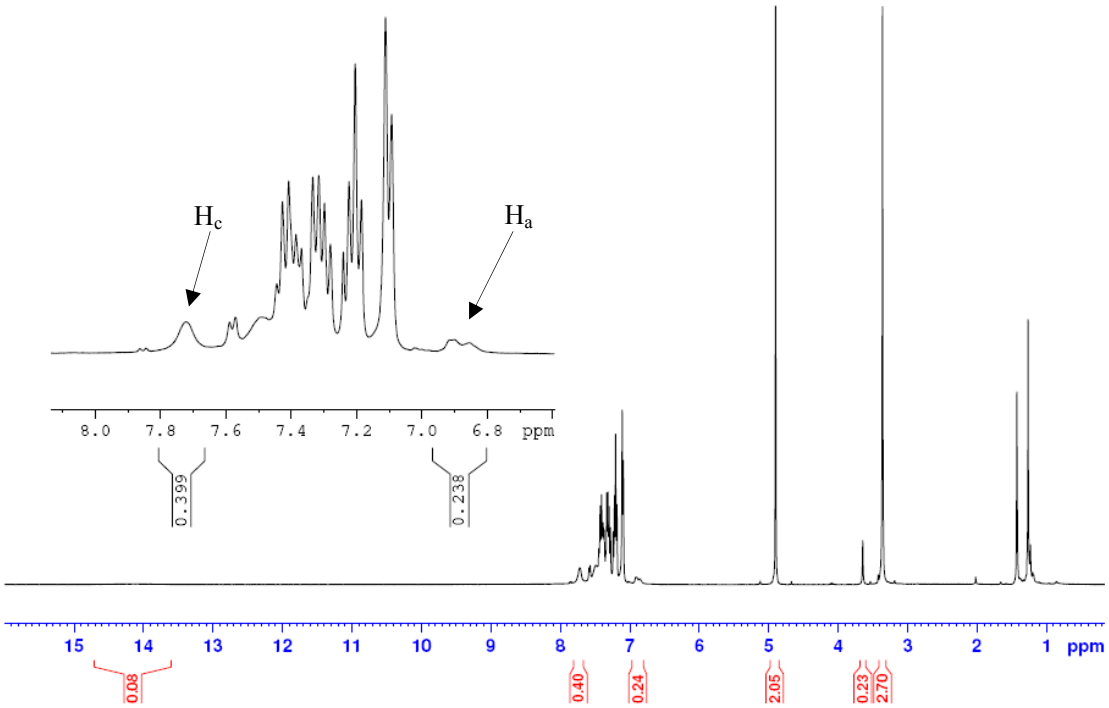
A sealed dry glass tube was charged with (2,4-^{t}Bu$_2$PhO)$_3$PAuCl (0.01 mmol, 5 mmol%) and $AgNTf_2$ (0.01 mmol, 5 mmol%), and to this mixture was added DCE (1 mL); the mixture was stirred for 10 minutes before it was added with a dichloroethane solution (1 mL) of compounds [D_5]-**1b** (0.1 mmol, 0.5 eq.), **1b** (0.1 mmol, 0.5 eq.) and 2-bromopydine *N*-oxide (0.26 mmol, 1.3 eq.). The reaction mixture was stirred at RT for 10 s. Then the mixture was concentrated and filtered over a short silica bed. The residue was directly analyzed by ^{1}H NMR using CH_2Br_2 (0.2 mmol, 1.0 eq.) as the internal reference. (Figure S2), and the results summarized in eq S2.



$H_o = H_{average} = [H_a + H_b (\approx H_c)] / 4 = (0.24 + 0.40) / 4 = 0.16$

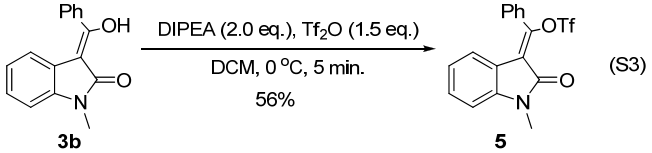
The initial proton/deuterium ratio at each *ortho*-position is:

$KIE = k_H/k_D = 0.16 / (0.40 - 0.24) = 1.00$



6. The Transformation of 3-Acyloxindoles

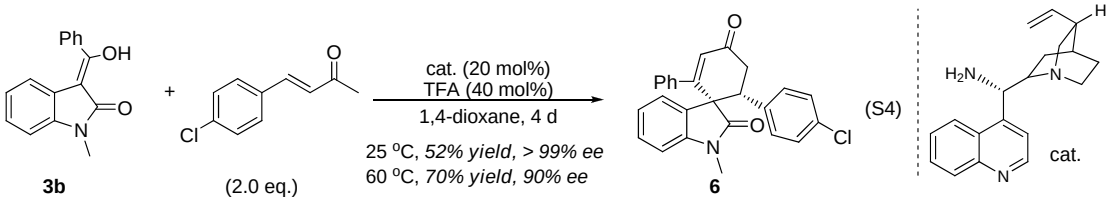
6.1 The Synthesis of Triflate 5[S4]



Compound **3b** (0.26 mmol, 67.0 mg) was dissolved in dichloromethane (1.3 mL) and then *N,N'*-diisopropylethylamine (0.52 mmol, 2.0 eq.) was added. The stirred reaction mixture was cooled

at 0 °C and a solution of trifluoromethanesulfonic anhydride (0.39 mmol, 1.5 eq) in dichloromethane (1.3 mL) was added. After 5 min. at 0 °C, the reaction mixture was washed with water (2 x 3 mL). The organic layer was dried (Na_2SO_4), filtered and evaporated. The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate, 5:1) to give pure compound **5.** White solid, m. p. 115-116 °C, 56% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.6 Hz, 2H), 7.66-7.58 (m, 2H), 7.50-7.46 (m, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.27-7.23 (m, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.6, 139.4, 139.0, 132.6, 132.4, 129.4, 128.4, 124.3, 124.1, 123.0, 122.0, 118.3 (q, $J_{C,F}$ = 320 Hz), 109.8, 105.1, 29.4 ; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -72.6; IR (neat): 3159, 2902, 1628, 1537, 1433, 1383, 1225, 1125, 1045, 947, 879, 818, 787, 699 ν cm^{-1}; MS (EI): m/z (%) = 383 (M^+, 20.72), 222 (100); HRMS (EI): calculated for $[C_{17}H_{12}F_3NO_4S]^+$ 383.0439, found: 383.0438.

6.2 The Enantioselective Synthesis of Six-membered Spirocyclic Oxindole 6[S5]

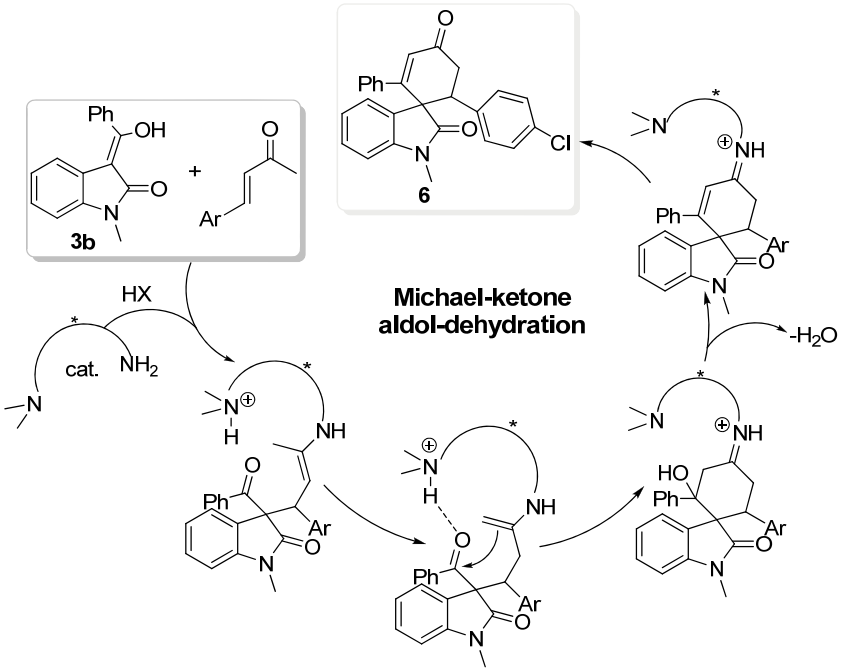


3-Acyloxindole **3b** (0.2 mmol, 1.0 eq.), *α,β*-unsaturated ketone (0.4 mmol, 2.0 eq.), cat. (20% mol), TFA (40% mol) were stirred in 1.0 mL 1, 4-dioxane at room temperature (or 60 °C) for four days. The reaction was monitored by TLC analysis. The reaction mixture was directly subjected to flash column chromatography on silica gel (dichloromethane) to furnish the corresponding products **6**.

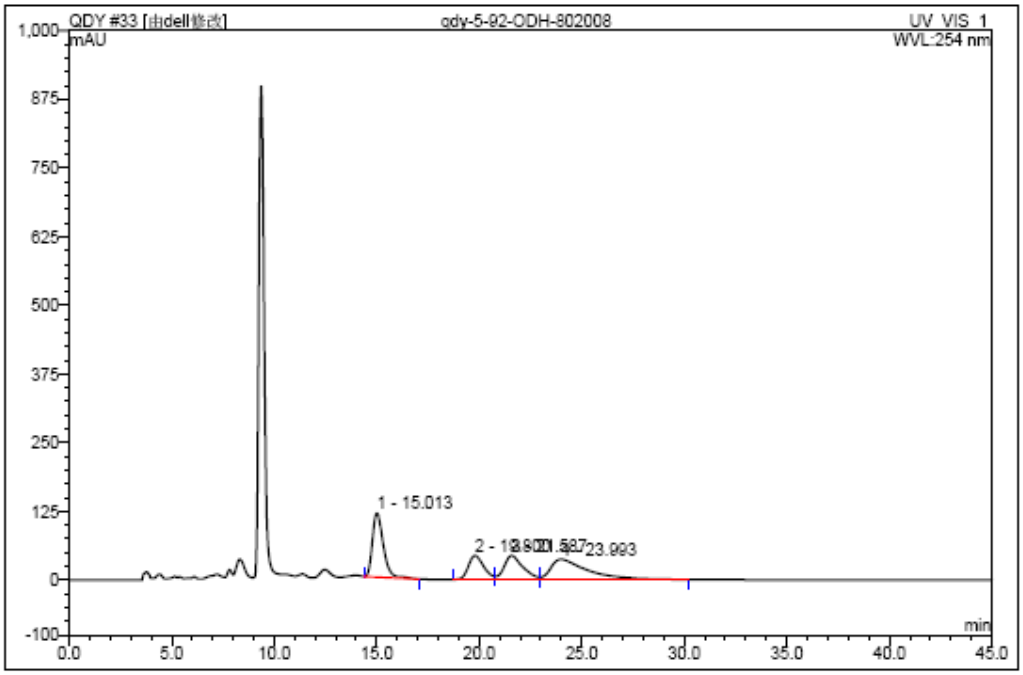
The diastereomeric ratio and enantiomeric excess was determined by chiral HPLC analysis. HPLC traces were compared to racemic samples prepared by performing the reactions using *N,N*-Dimethylethylenediamine as the catalyst for the synthesis of compound **6**.

White solid, m. p. 186-188 °C, 52% (or 70%) yield; >20:1 dr, Enantiomeric excess: >99% (or 90%), determined by HPLC (Chiralcel column OD-H, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, UV detection at 254 nm); T = RT, t_{major} = 14.87 min; T = 60 °C, t_{minor} = 21.63 min, t_{major}

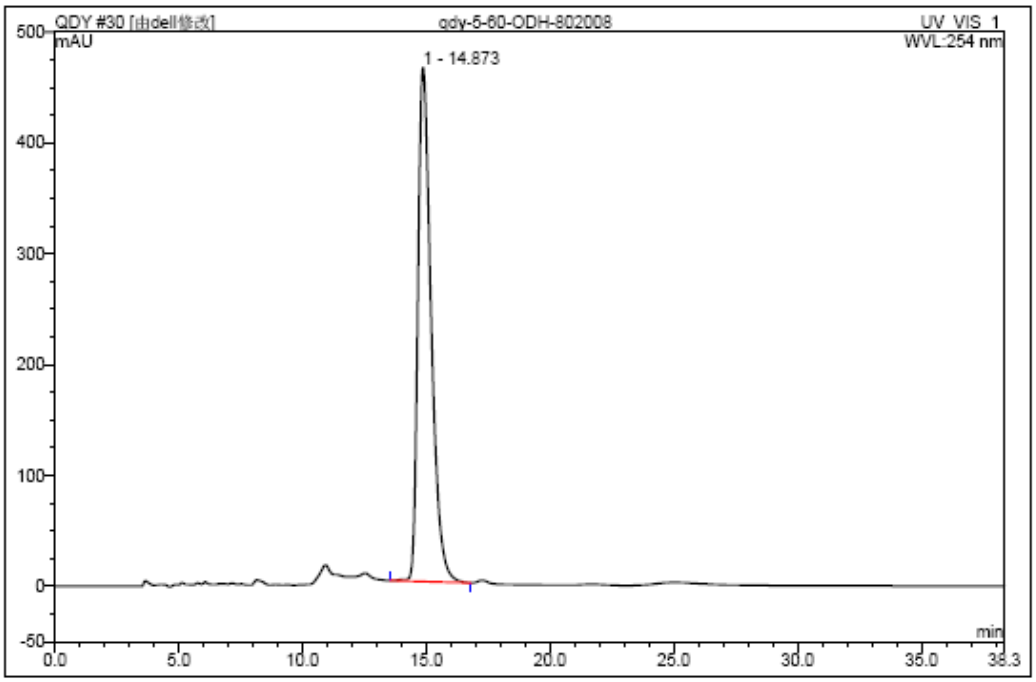
= 14.93 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14-6.87 (m, 10H), 6.75 (d, J = 8.0 Hz, 2H), 6.54 (s, 1H), 6.41 (d, J = 7.6 Hz, 1H), 3.97 (t, J = 15.4 Hz, 1H), 3.84 (dd, J = 15.4 Hz, 2.0 Hz, 1H), 2.94 (s, 3H), 2.56 (dd, J = 15.4 Hz, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.2, 173.9, 157.9, 143.1, 138.1, 135.3, 133.3, 131.4, 130.4, 129.5, 128.9, 128.6, 128.2, 127.6, 126.2, 123.9, 122.9, 108.1, 58.3, 50.3, 37.9, 26.3; IR (neat): 3396, 3011, 2913, 1704, 1643, 1573, 1493, 1372, 1086, 825, 751, 699 v cm^{-1}; MS (EI): m/z (%) = 413 (M^+, 20.95), 415 (8.61), 275 (100); HRMS (EI): calculated for $[C_{26}H_{20}NO_2{}^{35}Cl]^+$ 413.1183, found: 413.1178.



T = RT

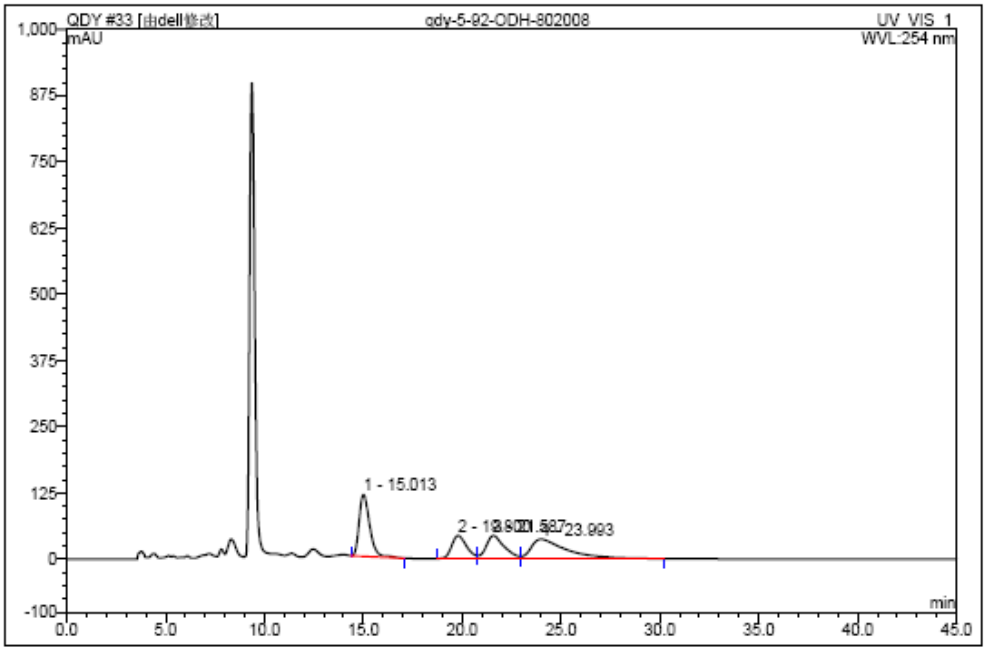


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.01	n.a.	116.514	71.794	31.38	n.a.	BMB
2	19.80	n.a.	43.027	37.246	16.28	n.a.	BM
3	21.59	n.a.	42.977	45.291	19.79	n.a.	M
4	23.99	n.a.	36.274	74.494	32.56	n.a.	MB
总和:			238.791	228.824	100.00	0.000	

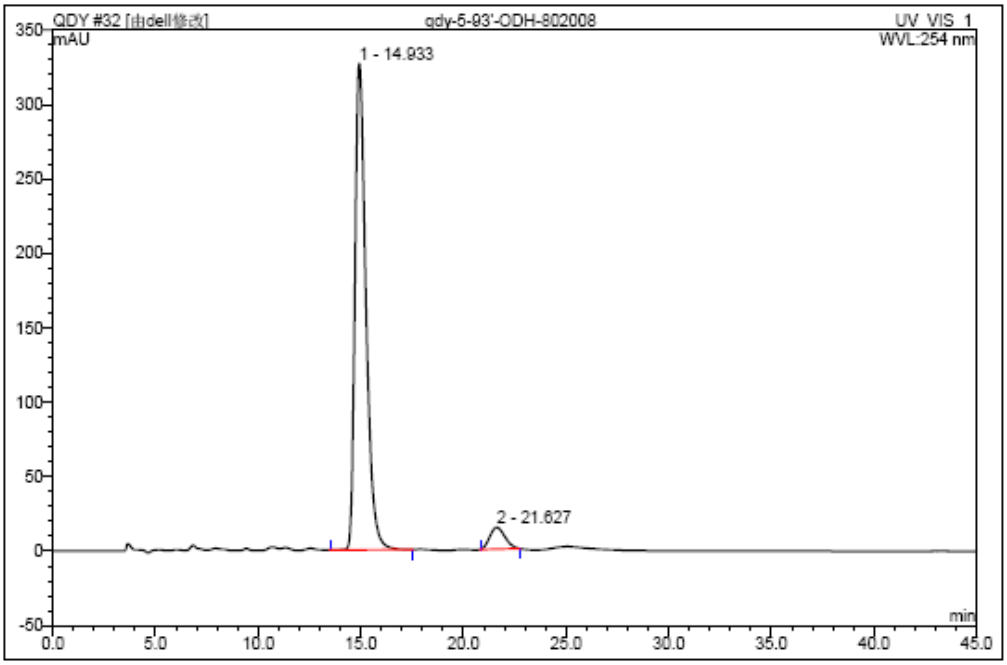


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	14.87	n.a.	463.613	287.182	100.00	n.a.	BMB
总和:			463.613	287.182	100.00	0.000	

T = 60 °C

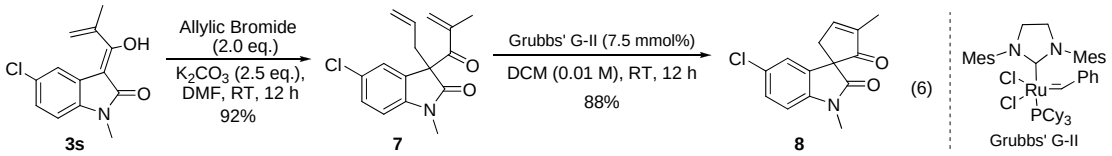


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.01	n.a.		116.514	71.794	31.38	n.a.	BMB
2	19.80	n.a.		43.027	37.246	16.28	n.a.	BM
3	21.59	n.a.		42.977	45.291	19.79	n.a.	M
4	23.99	n.a.		36.274	74.494	32.56	n.a.	MB
总和:				238.791	228.824	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	14.93	n.a.		326.740	202.769	94.23	n.a.	BMB
2	21.63	n.a.		14.532	12.425	5.77	n.a.	BMB*
总和:				341.271	215.194	100.00	0.000	

6.3 The Synthesis of Five-membered Spirocyclic Oxindole 8



A mixture of 3-acyloxindole **3s** (0.2 mmol, 1.0 eq.) and anhydrous potassium carbonate (0.5 mmol, 2.5 eq.) in DMF (2 mL) was stirred at RT for 10 min. Then allylic bromide (0.4 mmol, 2.0 eq.) was added slowly. The reaction was monitored by TLC and after completion (12 h) the mixture was diluted with ether (10 mL) and washed with water (3 x 5 mL), brine (1 x 5 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to afford the crude compound **7** as an pale orange oil. The product was nearly pure and could be used directly in the next step. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.29 (m, 1H), 7.07-7.06 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 5.393-5.390 (m, 1H), 5.27-5.16 (m, 1H), 5.03 (s, 1H), 4.96 (d, J = 17.2 Hz, 1H), 4.96 (d, J = 10.0 Hz, 1H), 3.22 (s, 1H), 2.98-2.93 (m, 1H), 2.85-2.80 (m, 1H), 1.78 (s, 3H).

The ring-closing olefin metathes.[S6] A solution of compound **7** (0.18 mmol) in CH_2Cl_2 (18 mL, 0.01 M) was treated with 7.5 mol% catalyst Grubbs' G-II (11.7 mg, 0.014 mmol) in one portion under nitrogen and stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography (petroleum ether/ ethyl acetate, 5:1) to spirocyclic oxindole **8.**

white solid, m. p. 167-169 °C, 88% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.29-7.26 (m, 1H), 6.952-6.948 (m, 1H), 6.80 (d, J = 8.0 Hz, 1H), 3.25-3.18 (m, 4H), 2.88-2.82 (m, 1H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.8, 174.1, 158.7, 143.4, 140.5, 131.3, 128.6, 128.2, 122.5, 109.5, 60.7, 38.0, 26.8, 10.7; IR (neat): 2930, 2863, 1726, 1696, 1608, 1490, 1325, 1038, 846, 770 ν cm^{-1}; MS (EI): m/z (%) = 261 (M^+, 79.18), 263 (29.66), 232 (100); HRMS (EI): calculated for $[C_{14}H_{12}NO_2{}^{35}Cl]^+$ 261.0557, found: 261.0556.

Reference:

[S1] a) A. Pinto, L. Neuville, P. Retailleau, J. Zhu, *Org. Lett*. **2006**, *21*, 4927; b) Daniel. M. D'Souza, A. Kiel, D.-Peter. Herten, F. Rominger, T. J. J. Müller, *Chem. Eur. J.* **2008**, *14*, 529; c) M.-B. Zhou, W.-T. Wei, Y.-X. Xie, Y. Lei, J.-H. Li, *J. Org. Chem.* **2010**, *75*, 5635.

[S2] B. Lu, D. Ma, *Org. Lett.* **2006**, *8*, 6115.

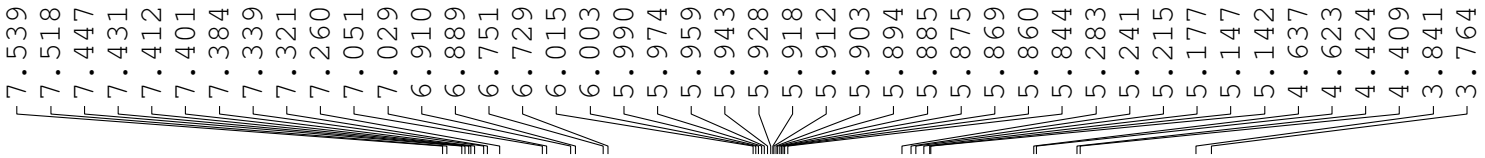
[S3] H. Xu, S. J. Zuend, M. G. Woll, Y. Tao, E. N. Jacobsen, *Science* **2010,***327*, 986.

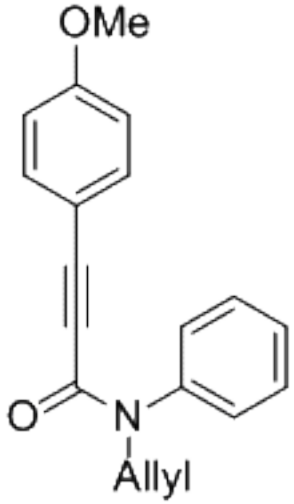
[S4] E. M. Beccalli, M. L. Gelmi, A. Marchesini, *Tetrahedron* **1998**, *54*, 6909.

[S5] L.-L. Wang, L. Peng, J.F. Bai, Q.-C.Huang, X.-Y. Xu, L.-X. Wang, *Chem. Commun.* **2010**, *46*, 8064.

[S6] K.Yoshida, T. Imamoto, *J. Am. Chem. Soc.* **2005**, *127*, 10470.

7. ^{1}H and ^{13}C spectra:





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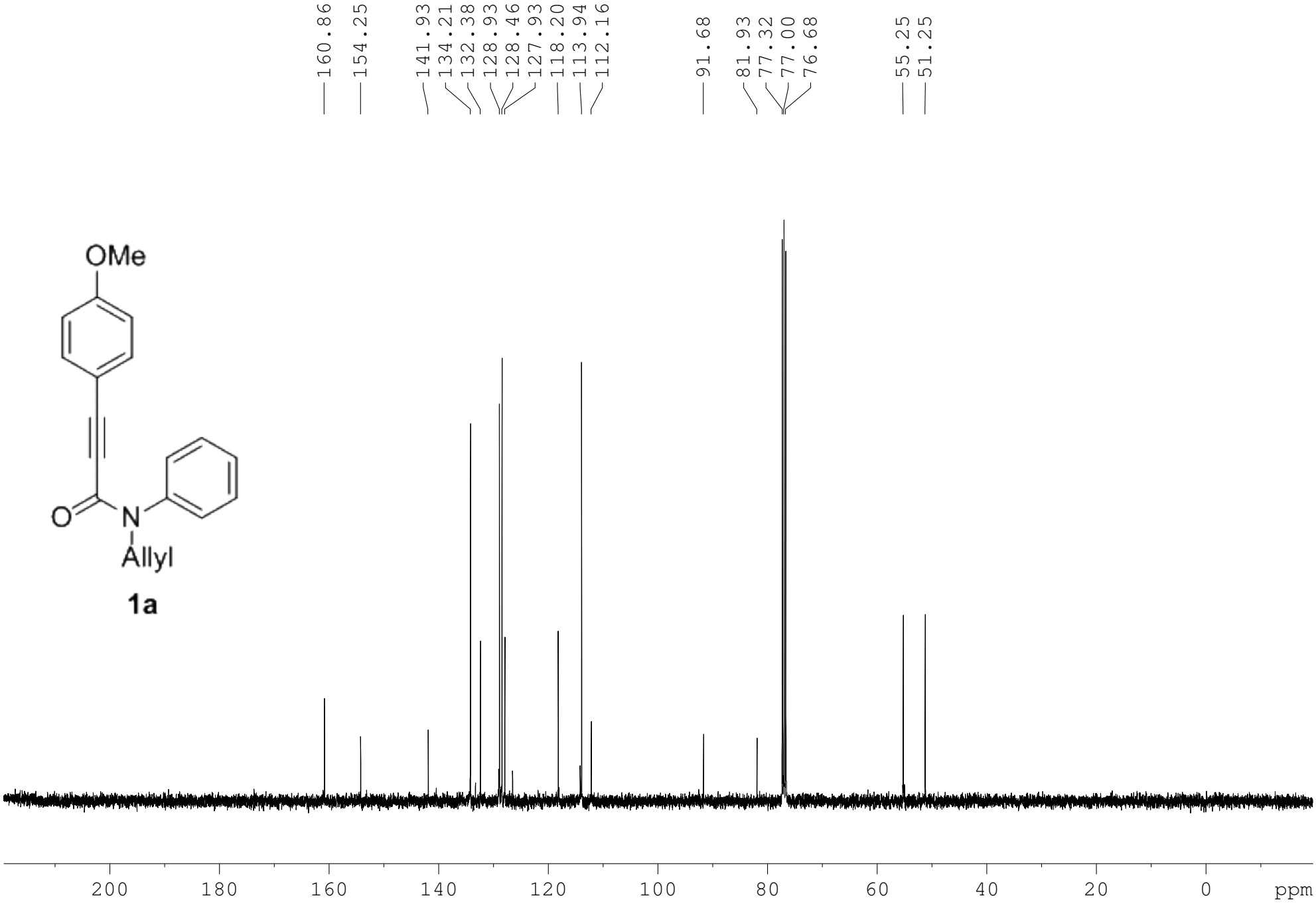

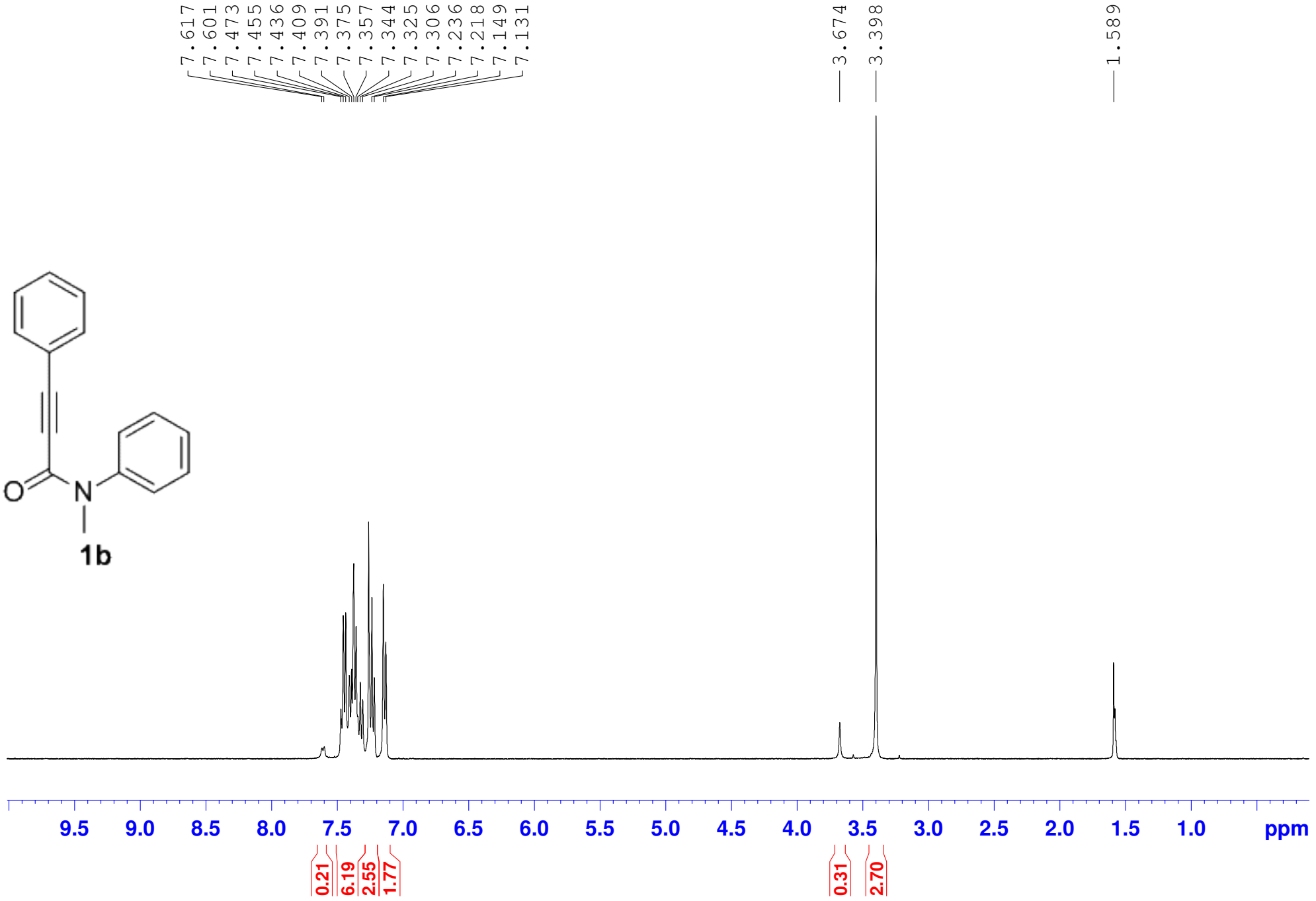

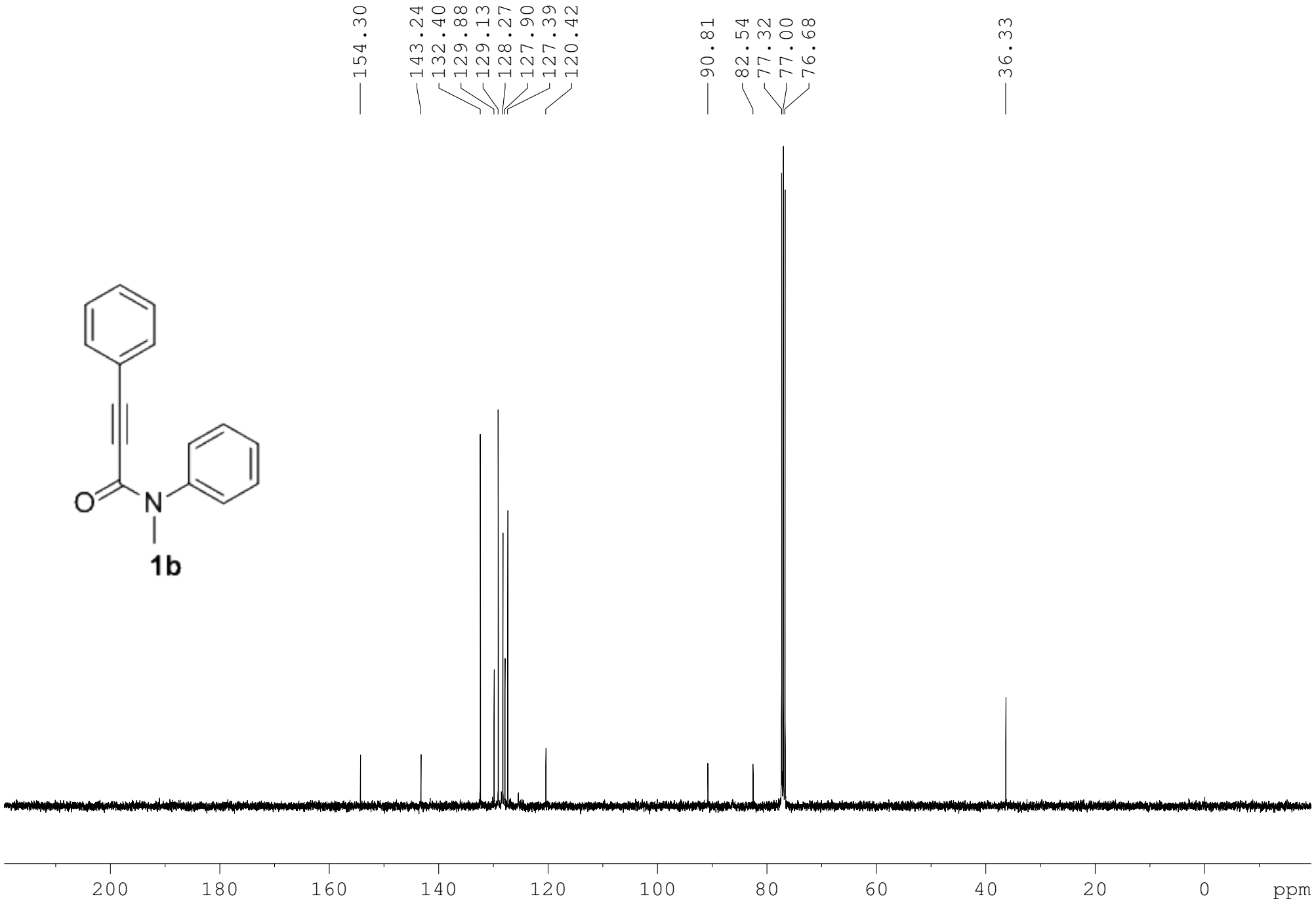

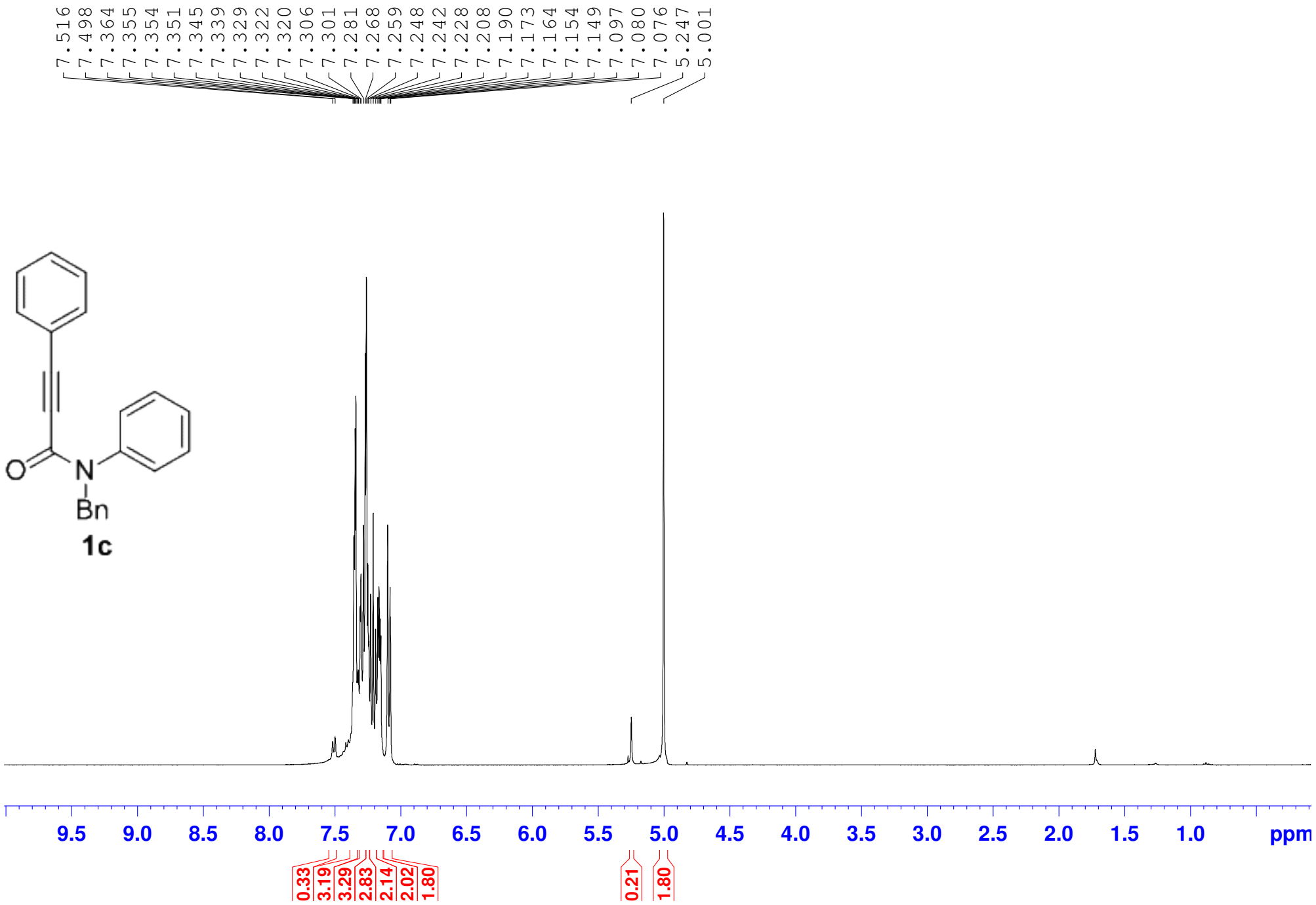

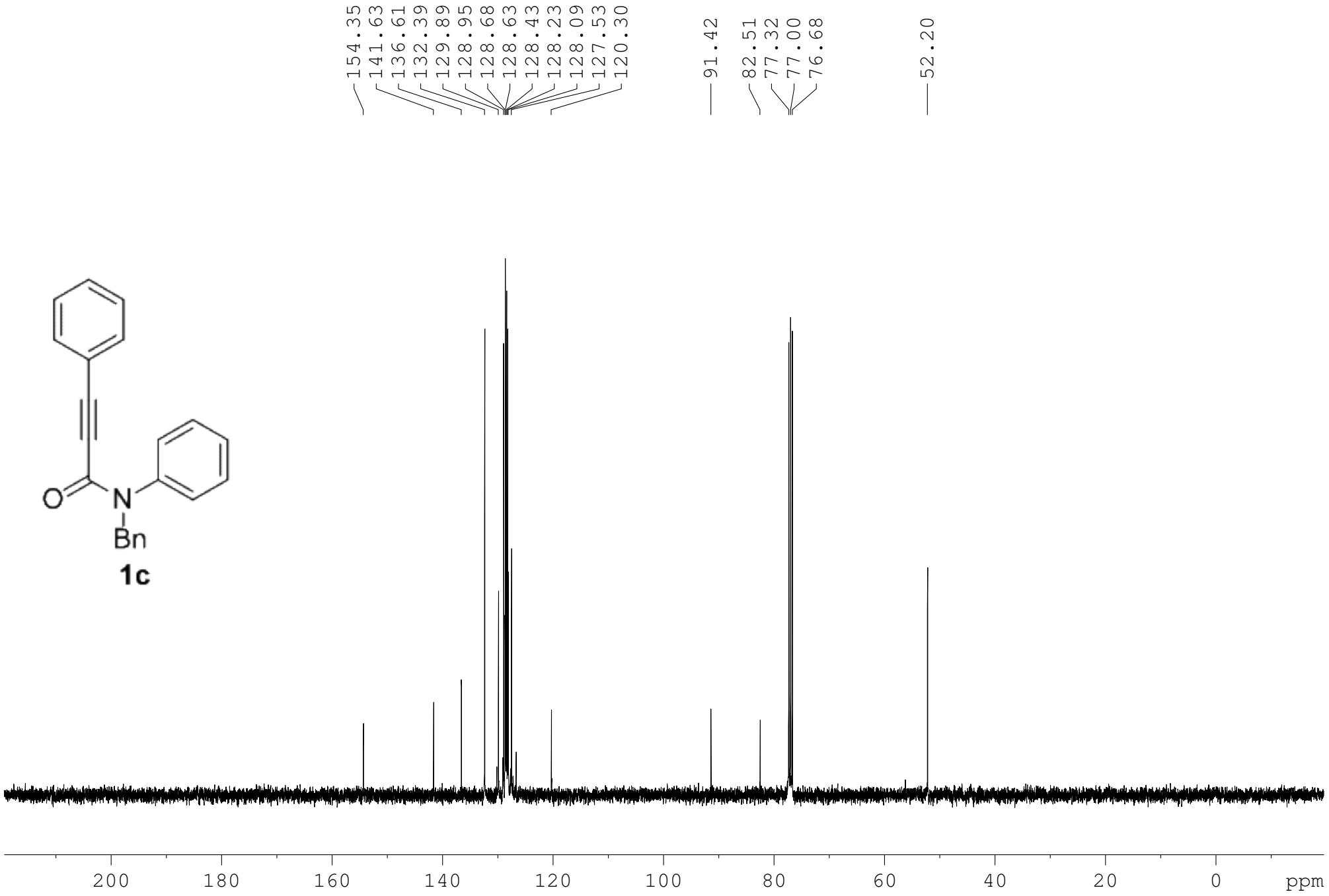

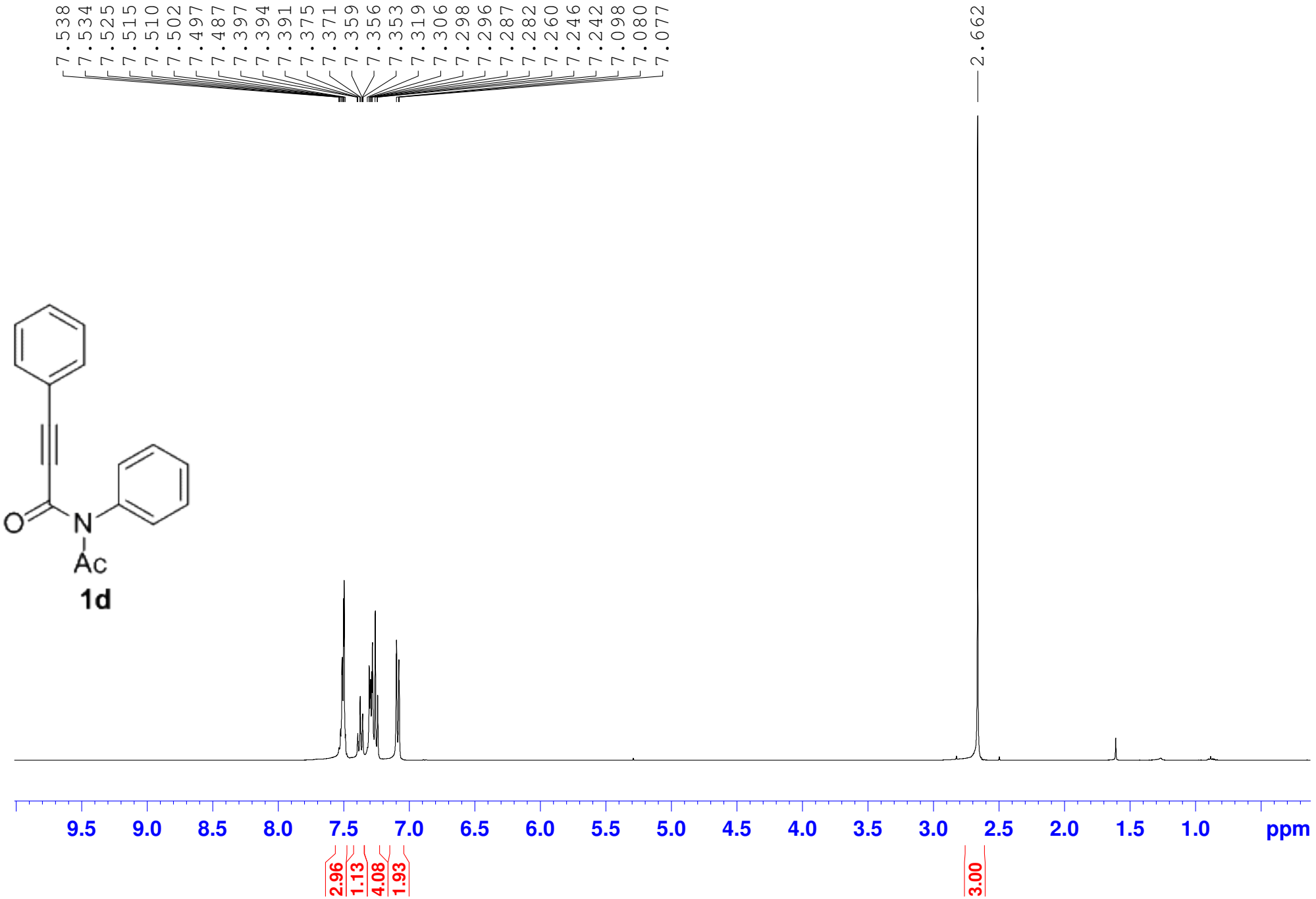

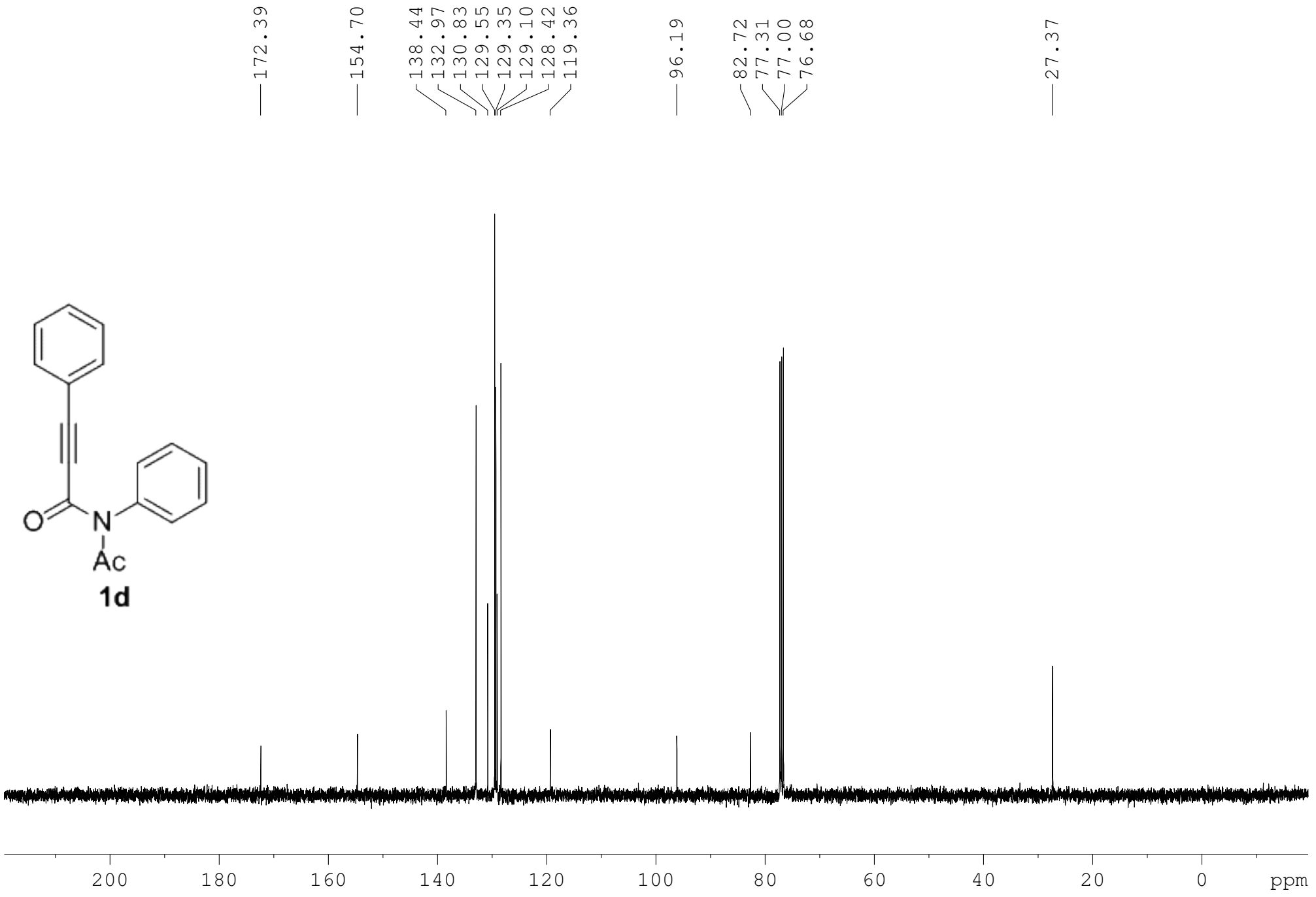

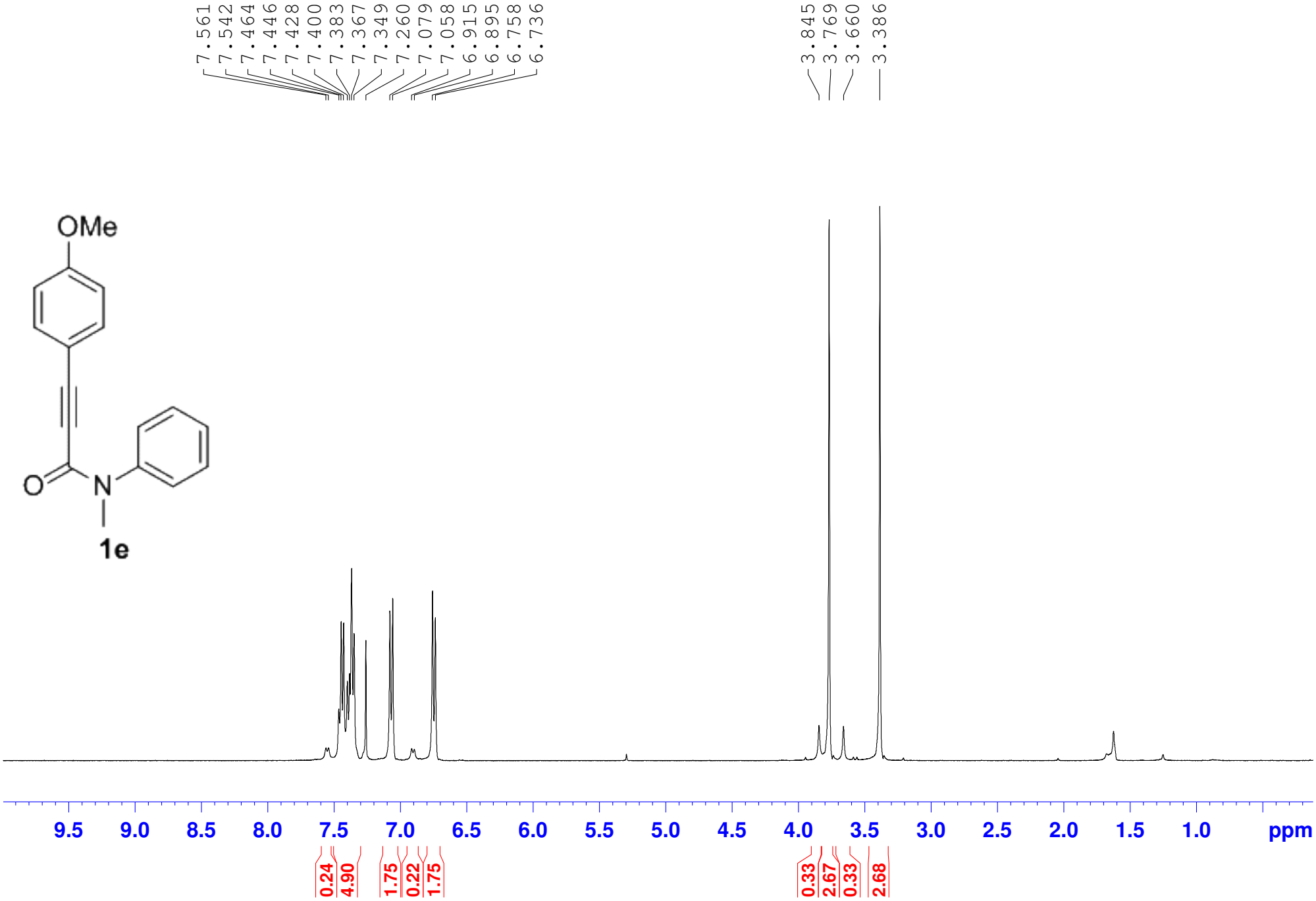

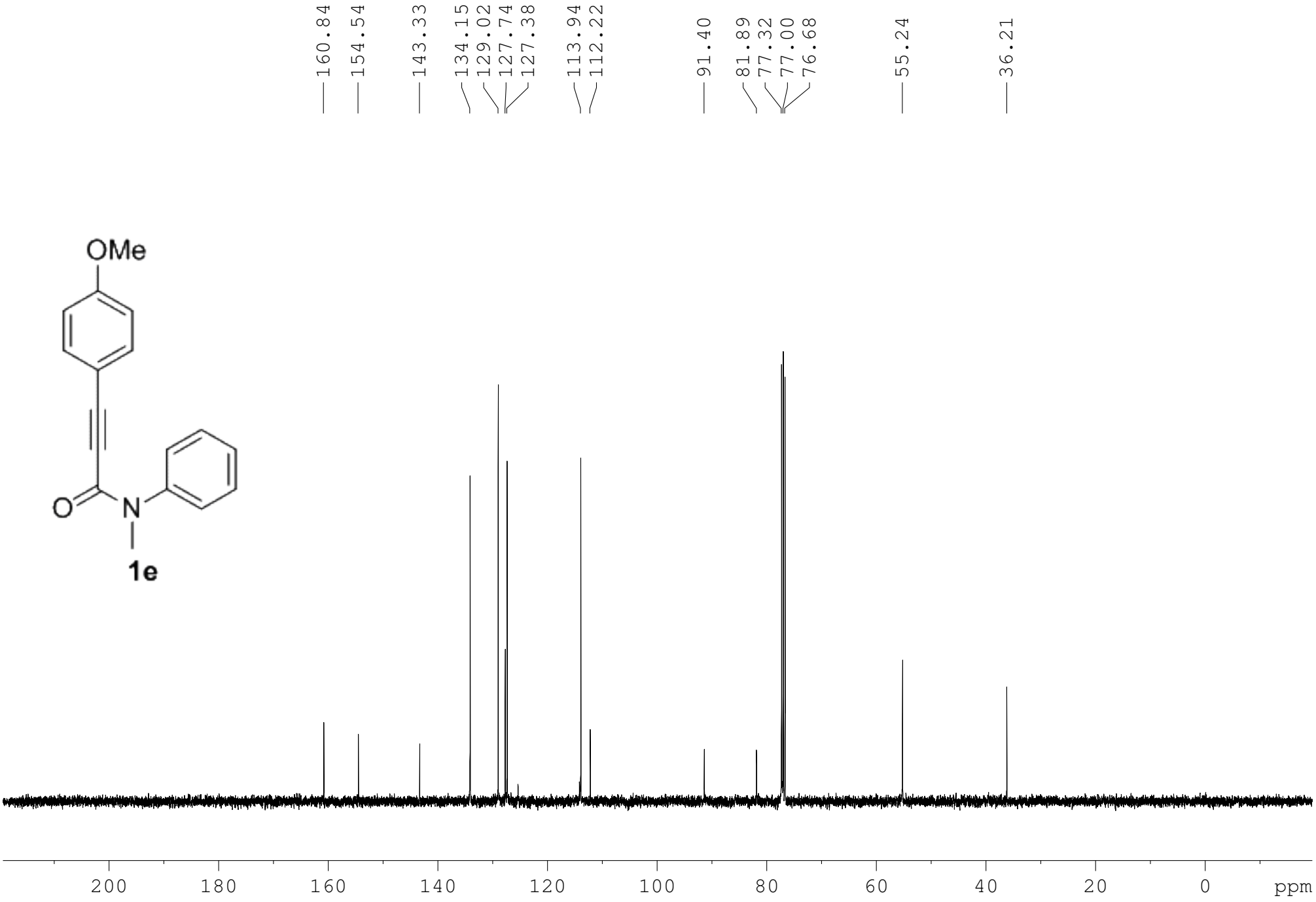

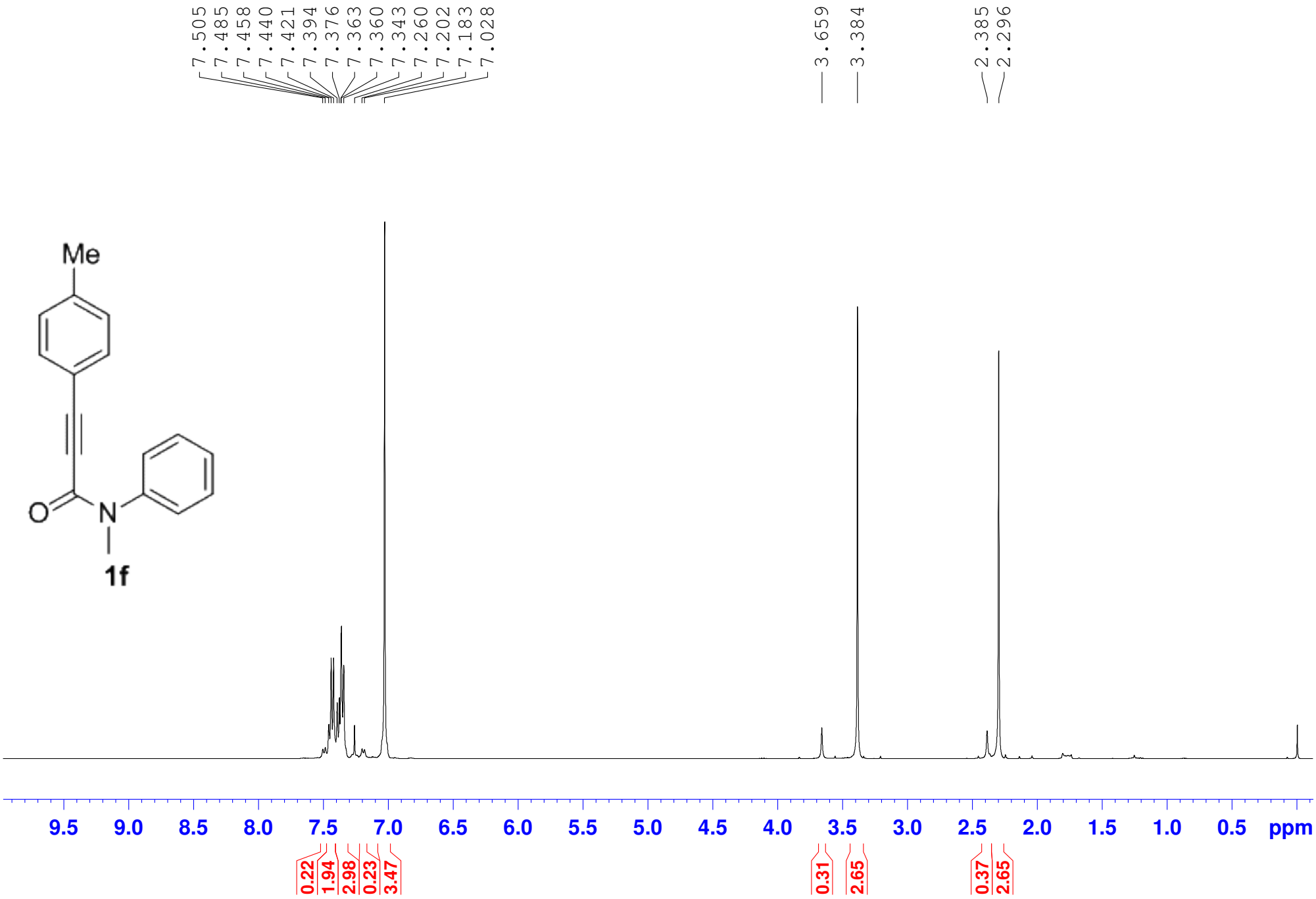

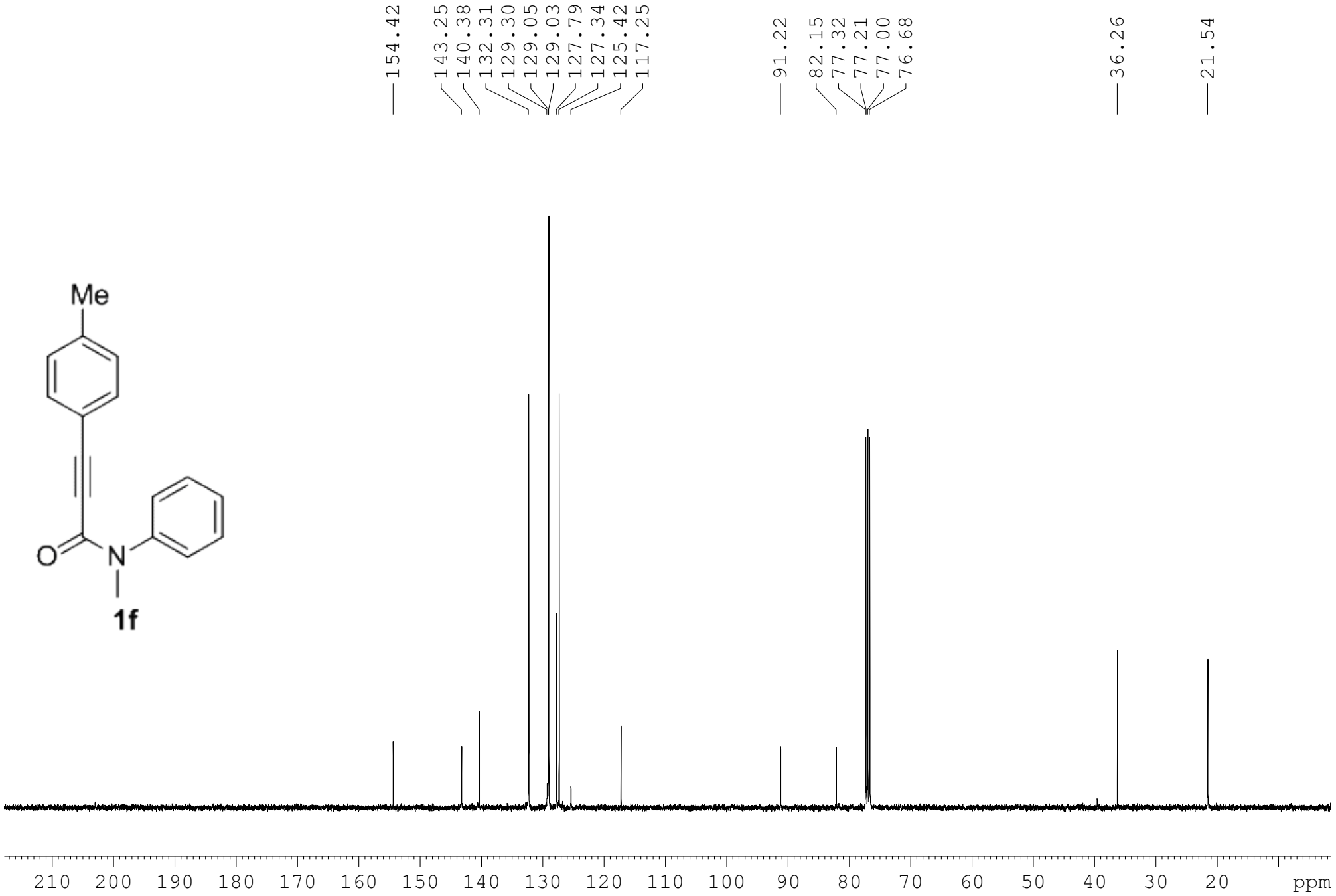

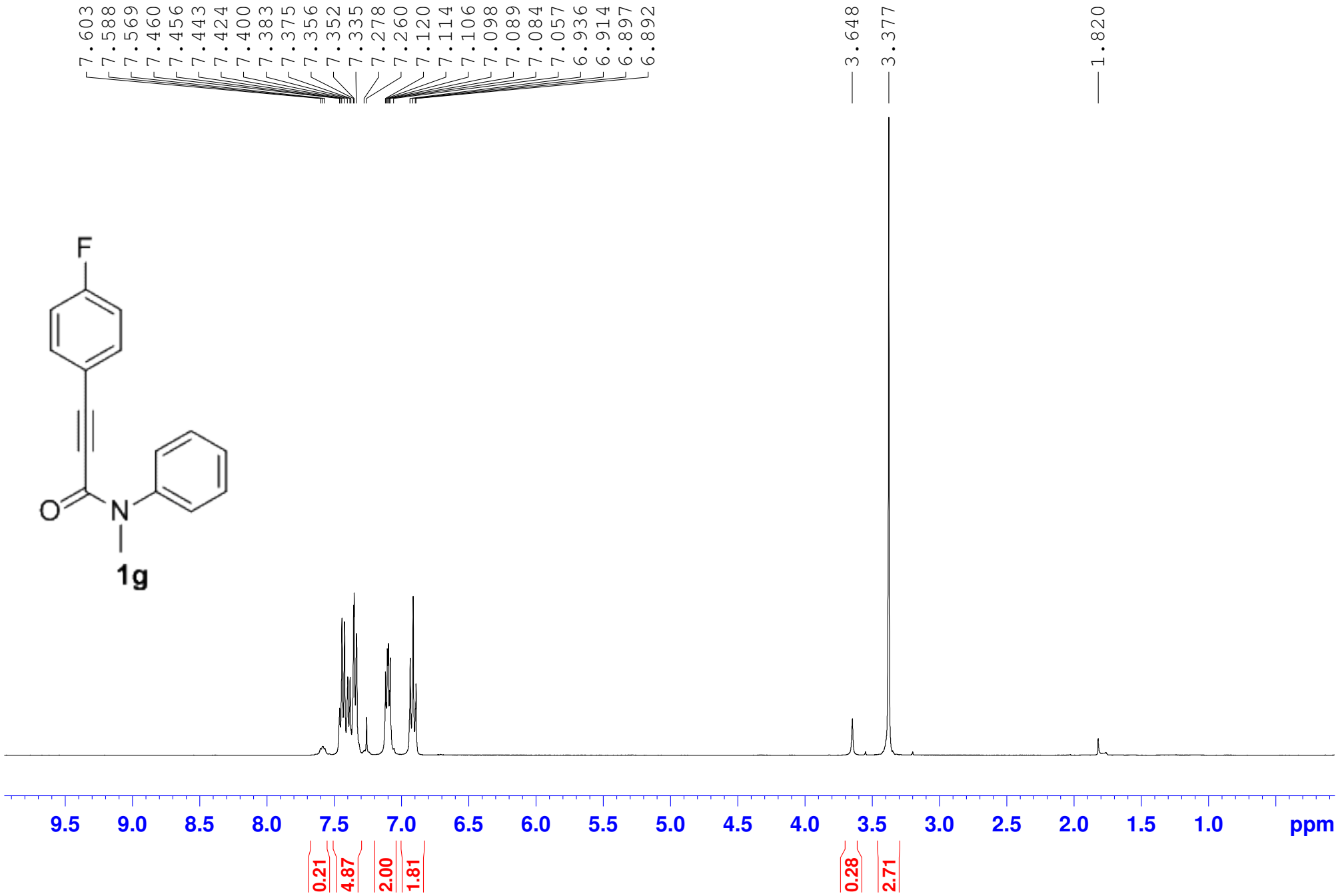

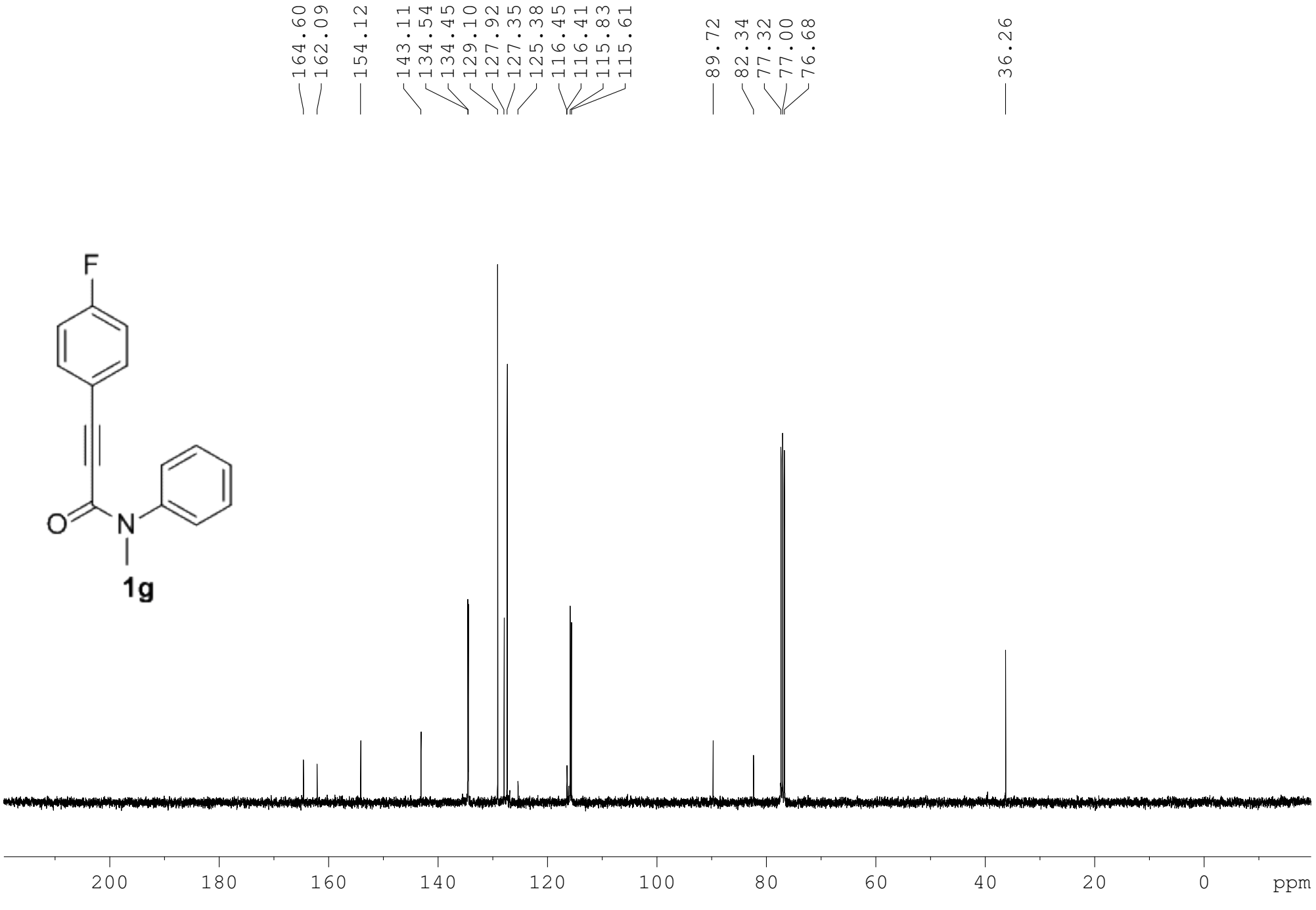

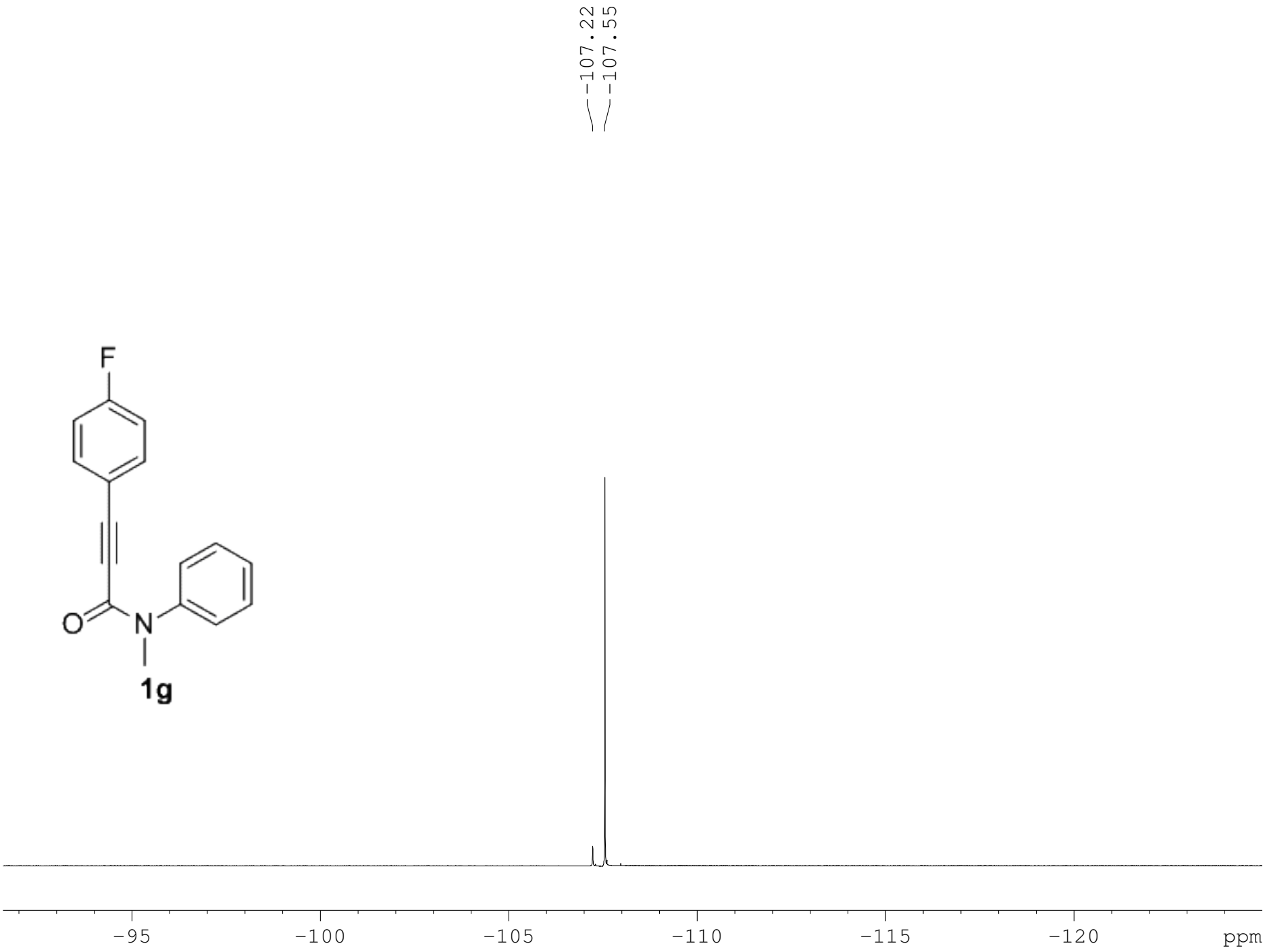

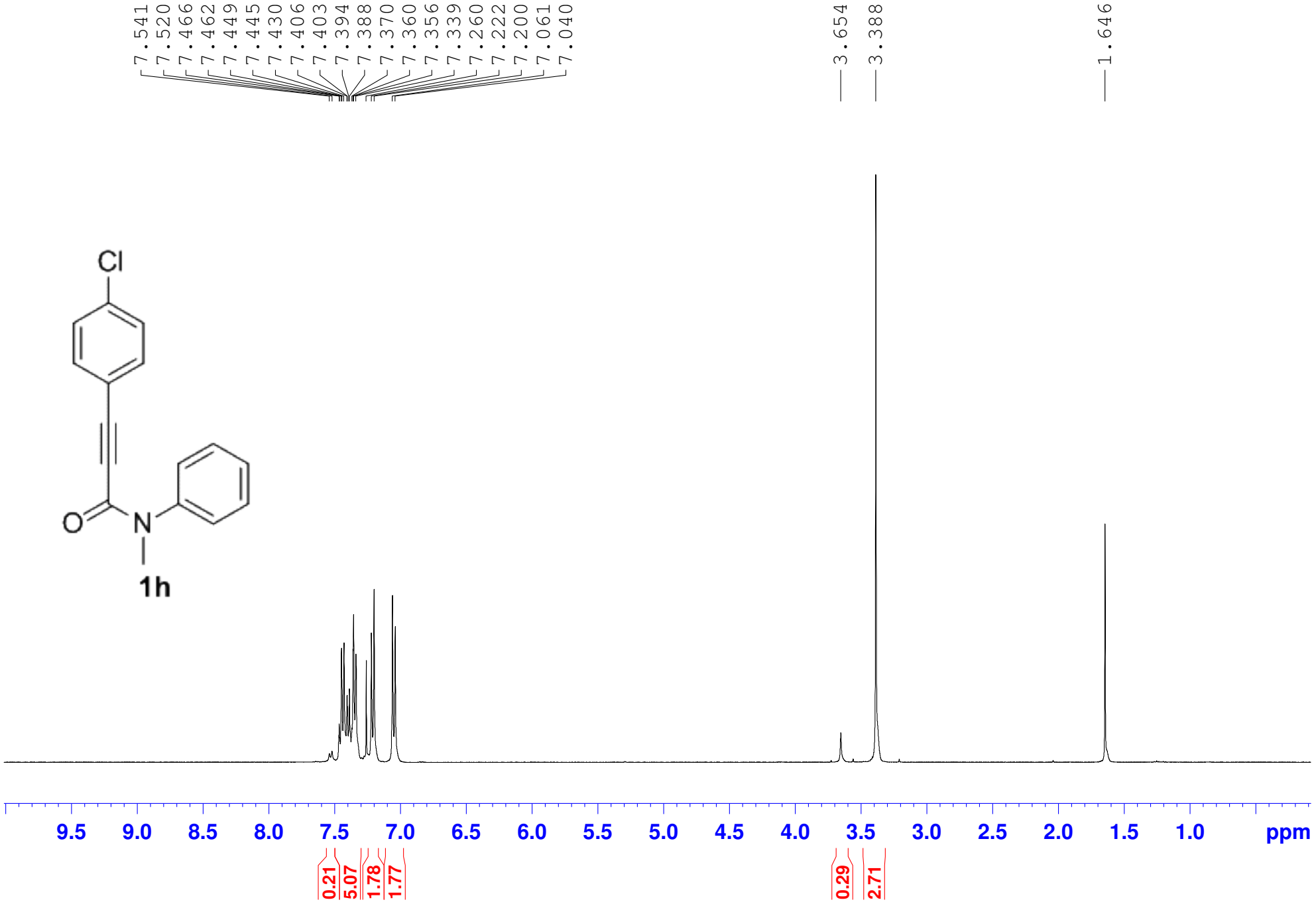

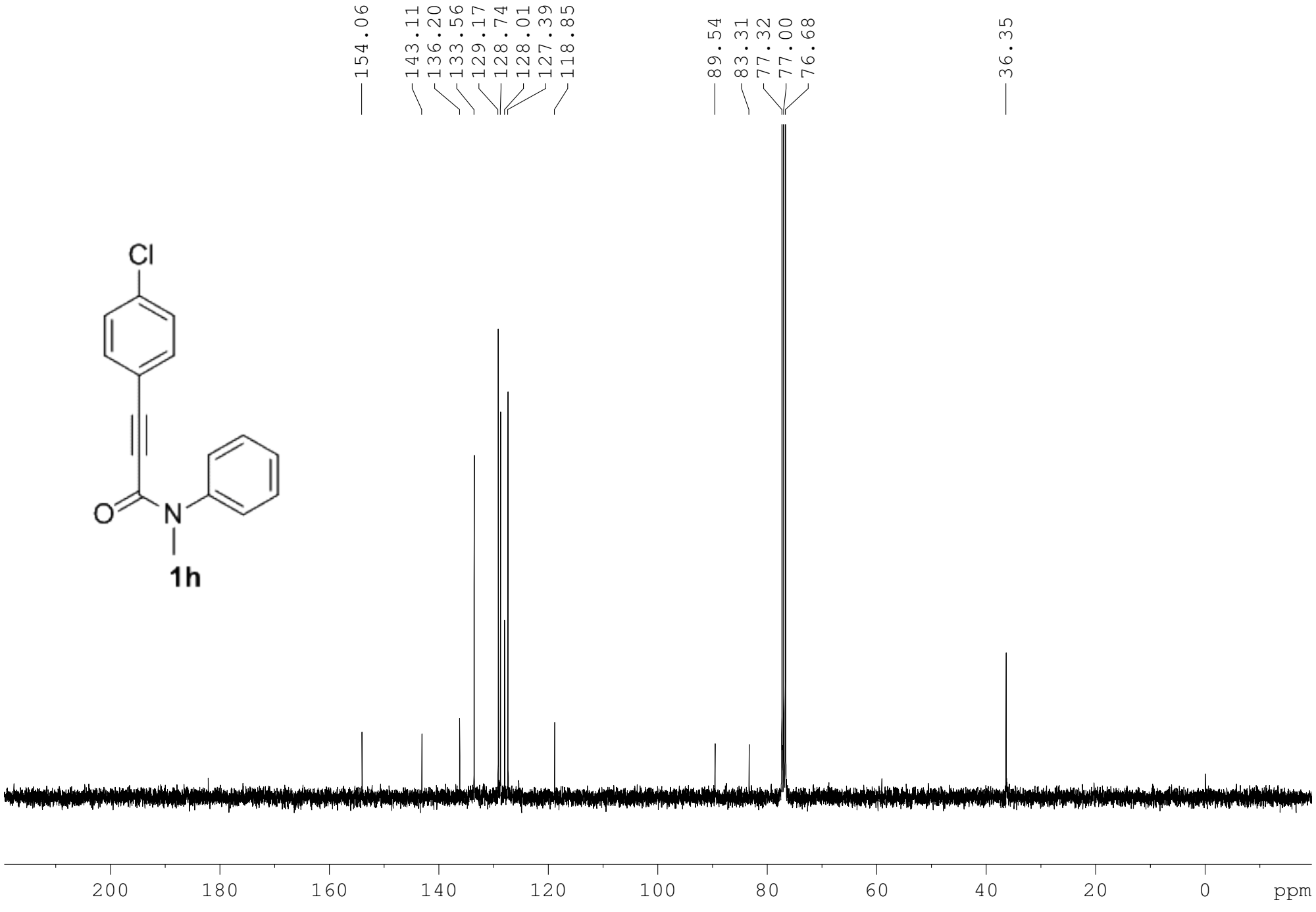

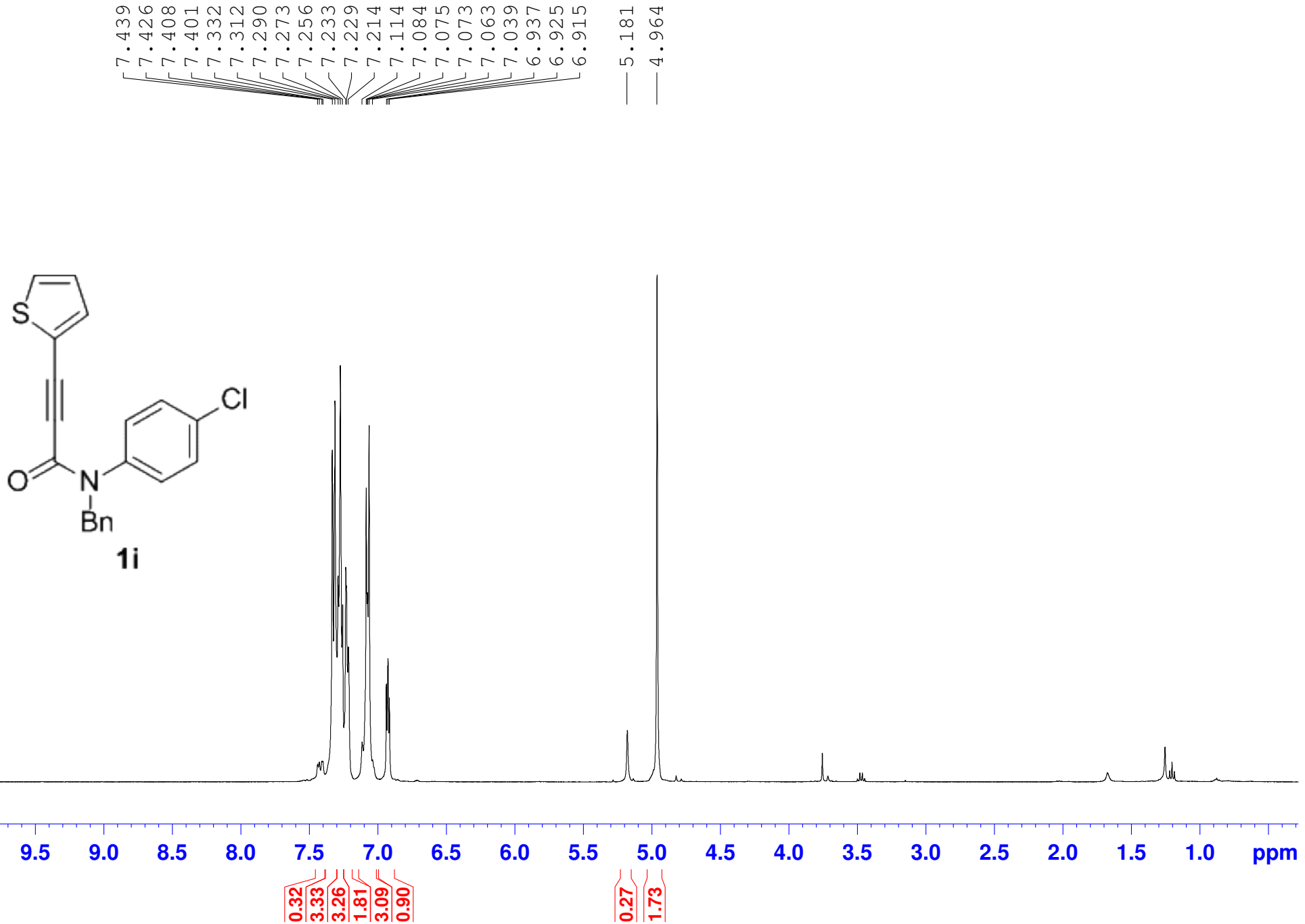

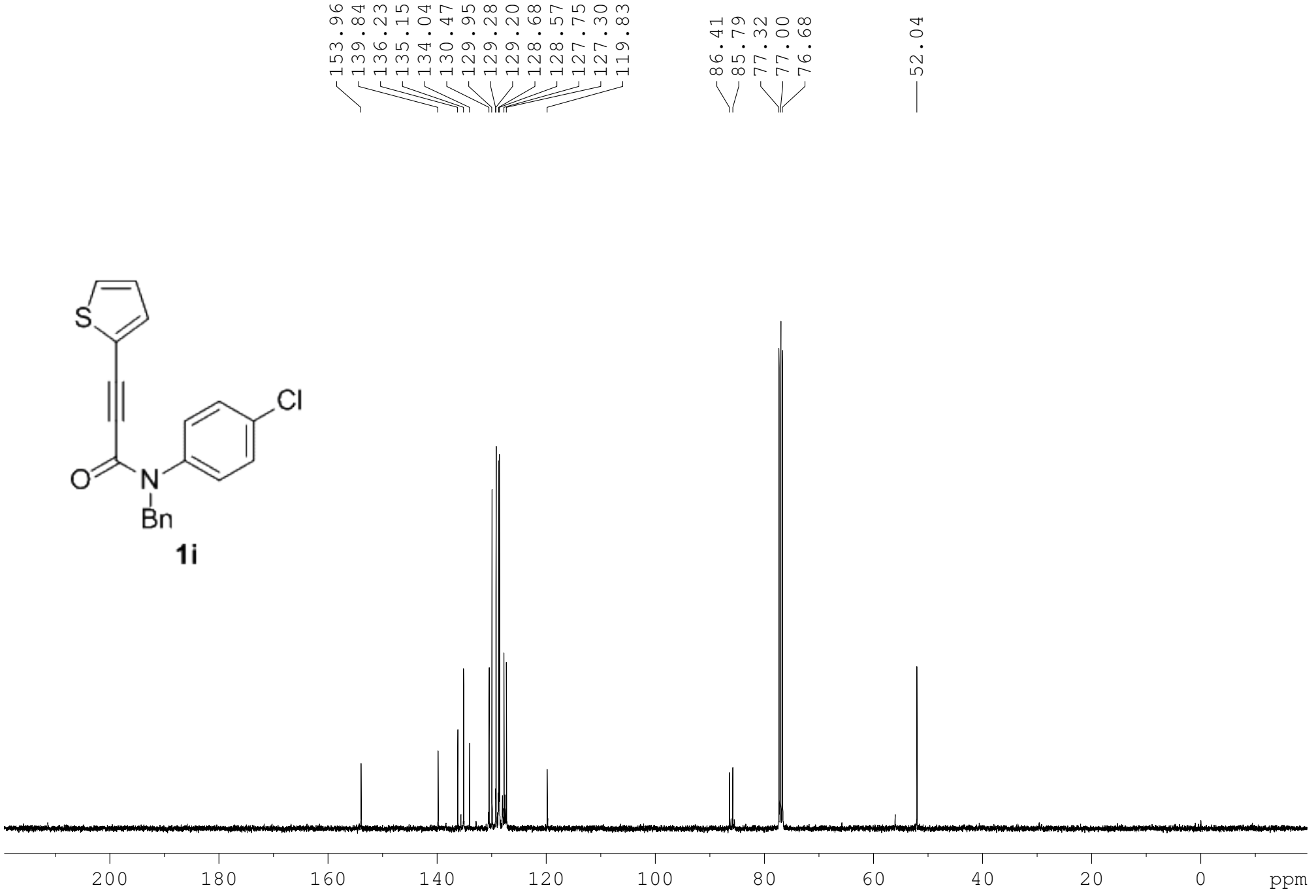

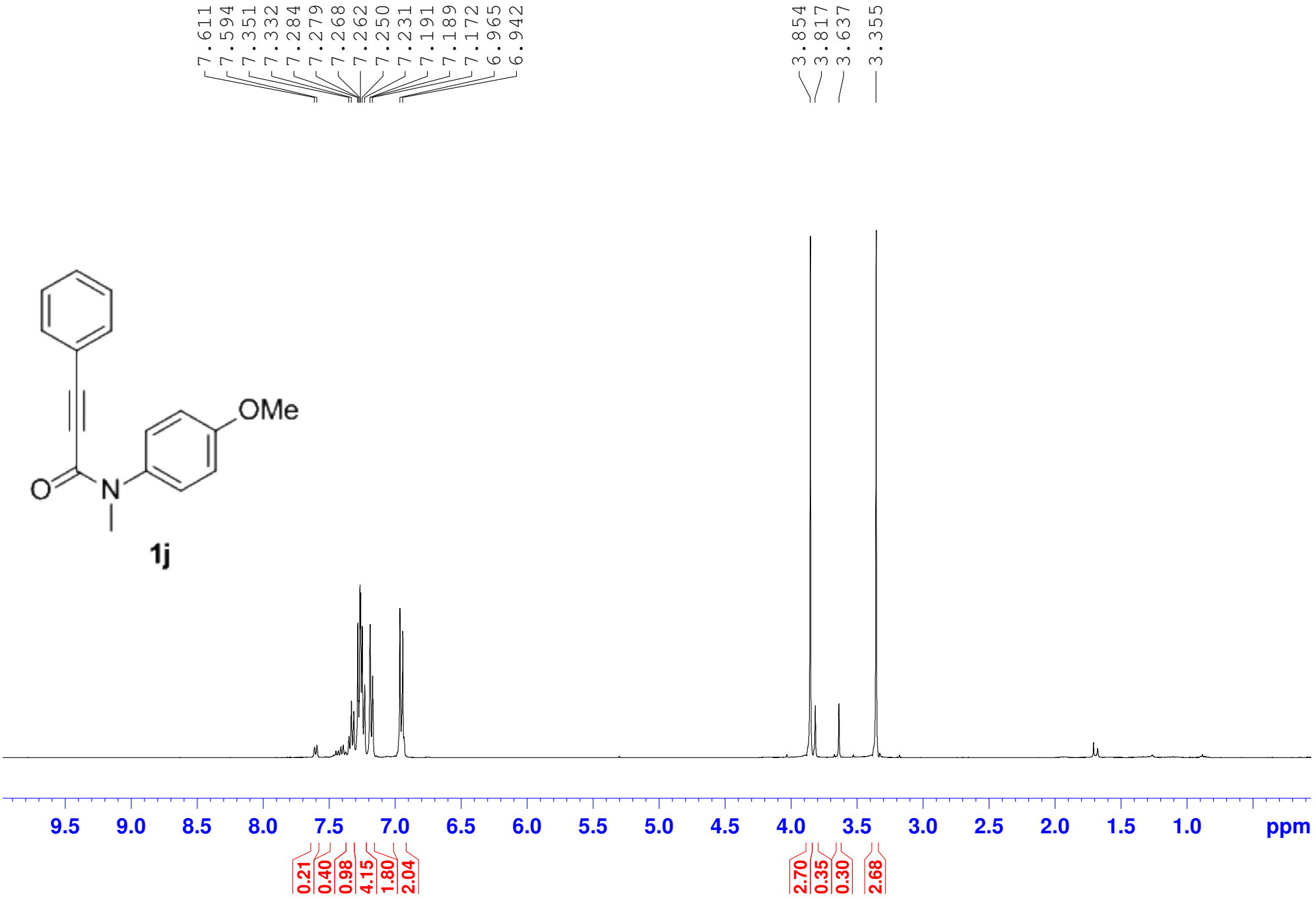

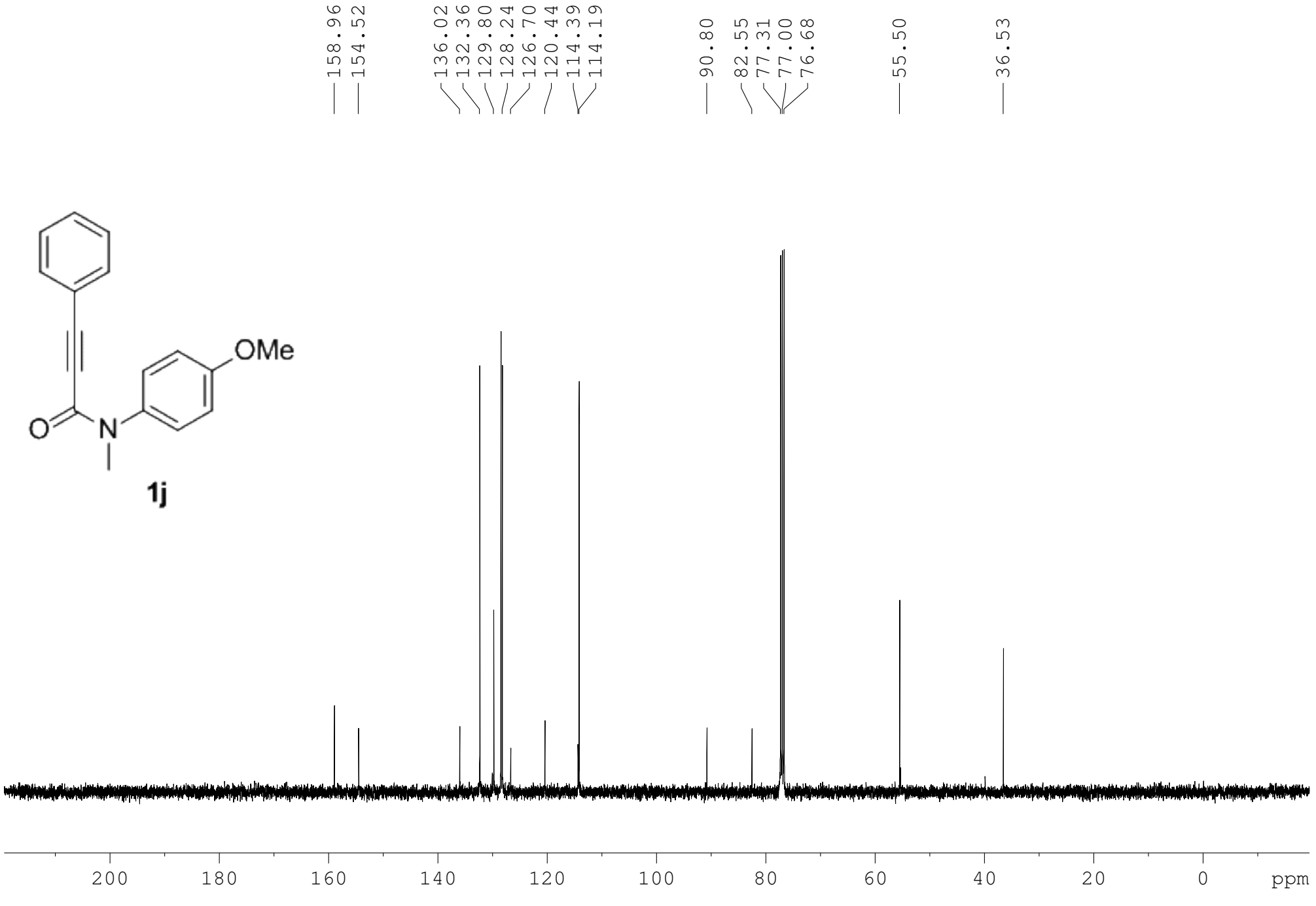

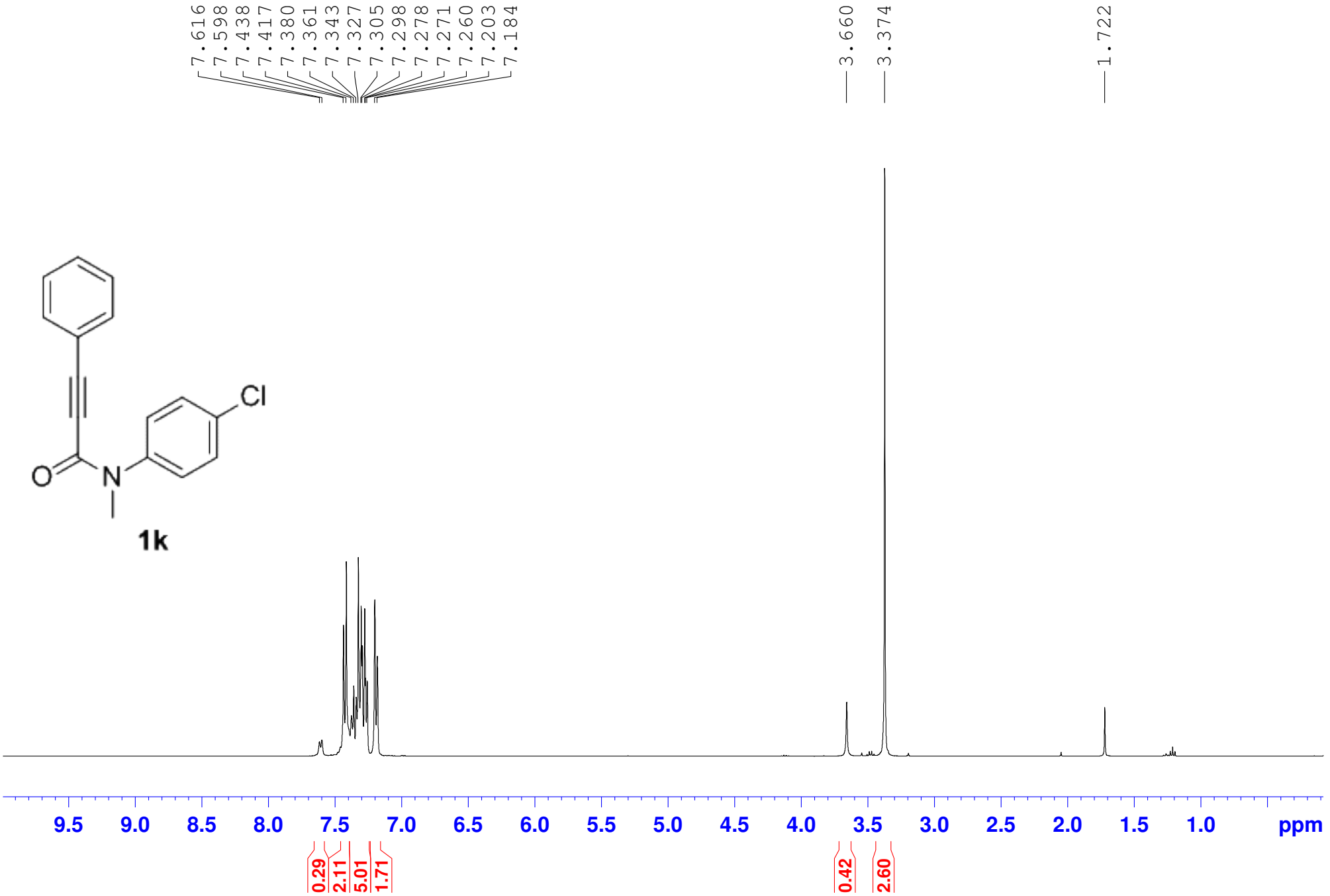

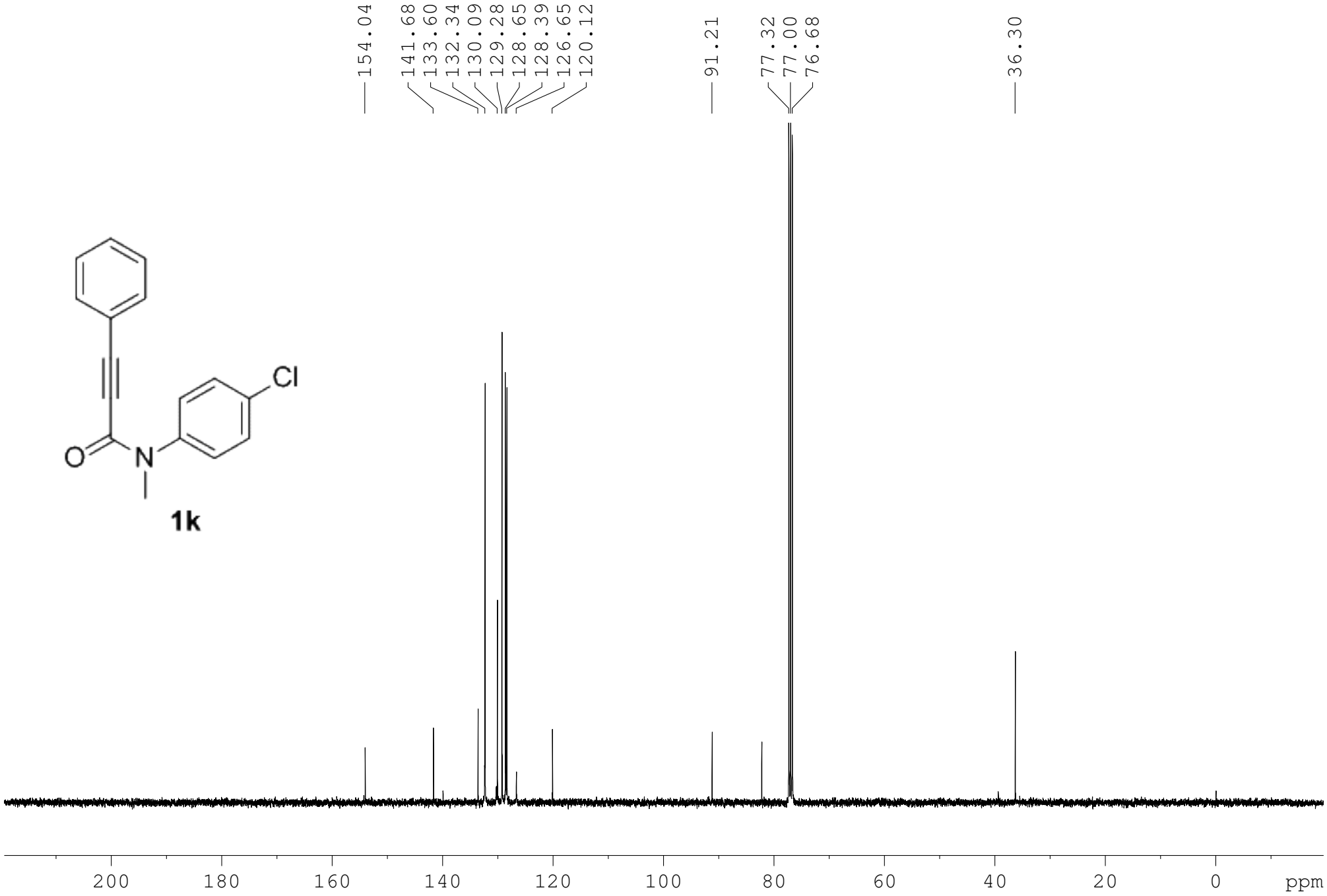

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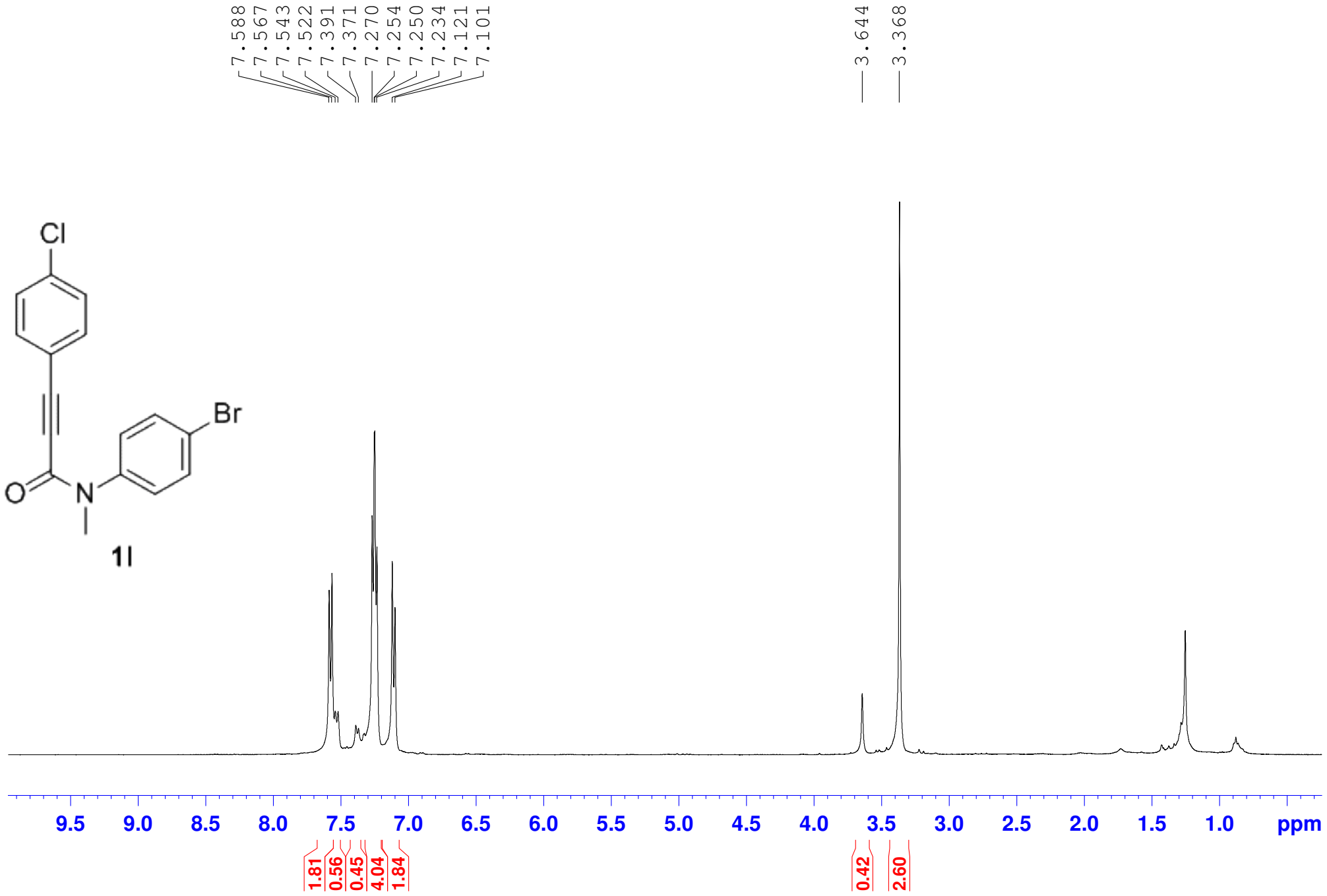

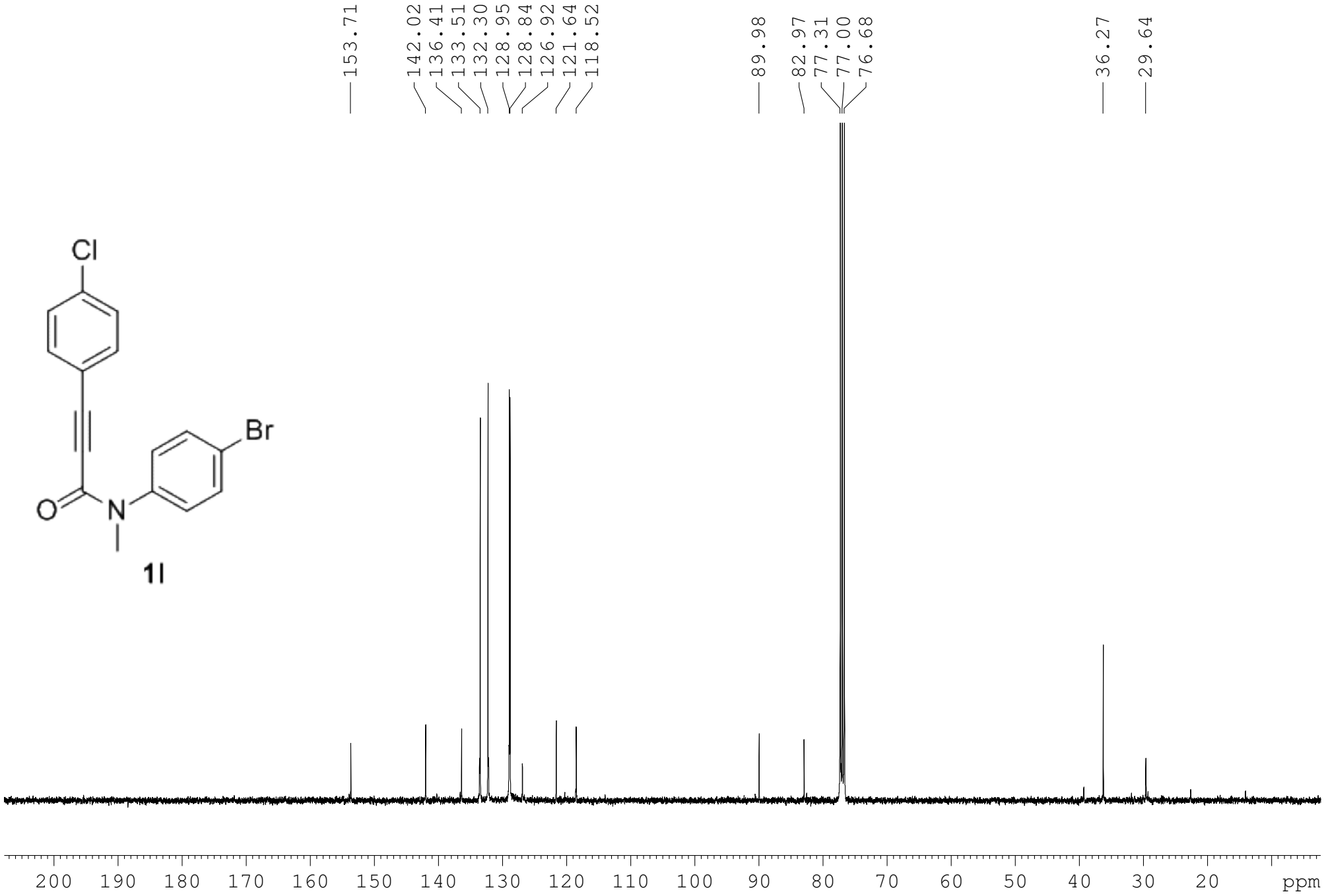

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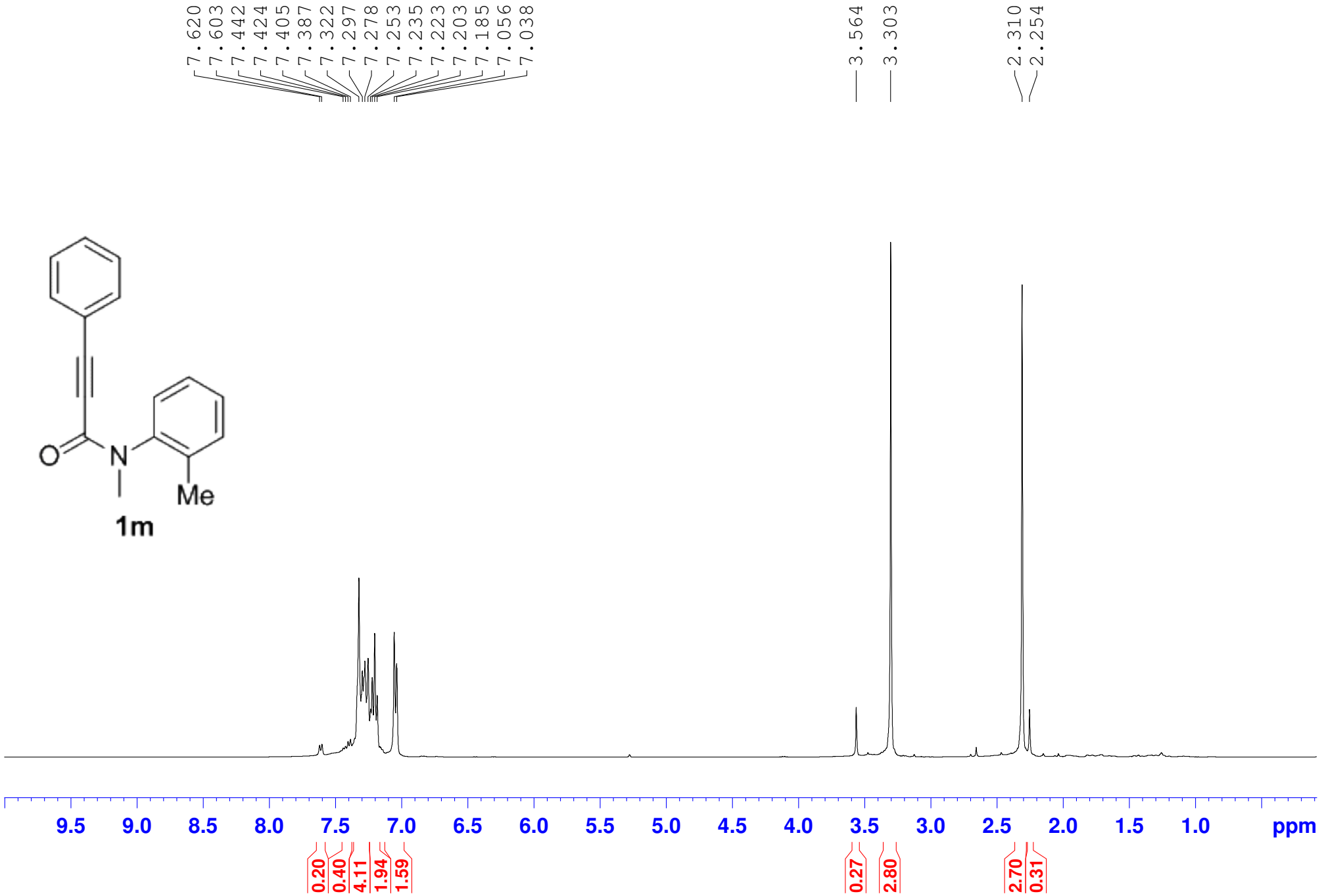

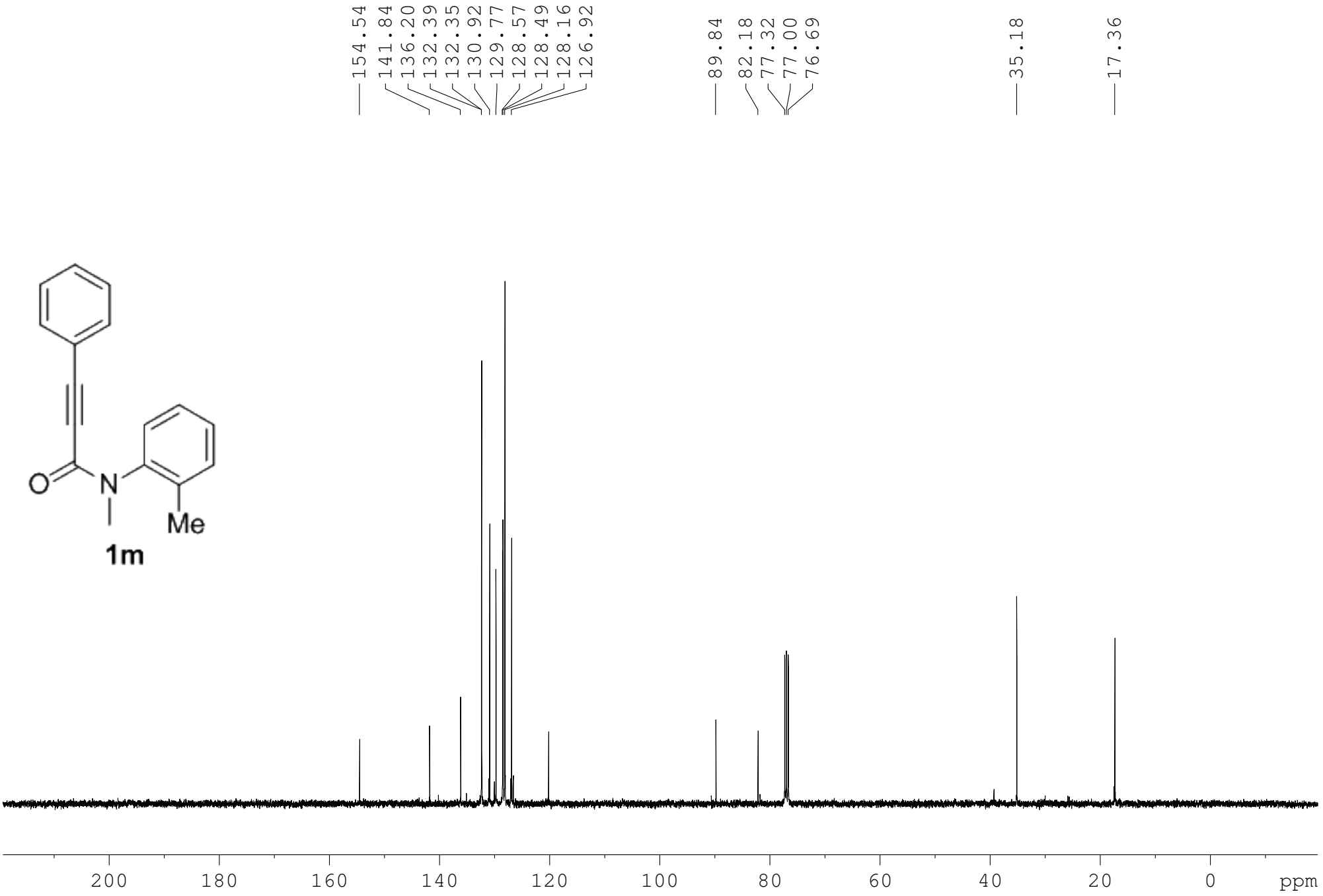

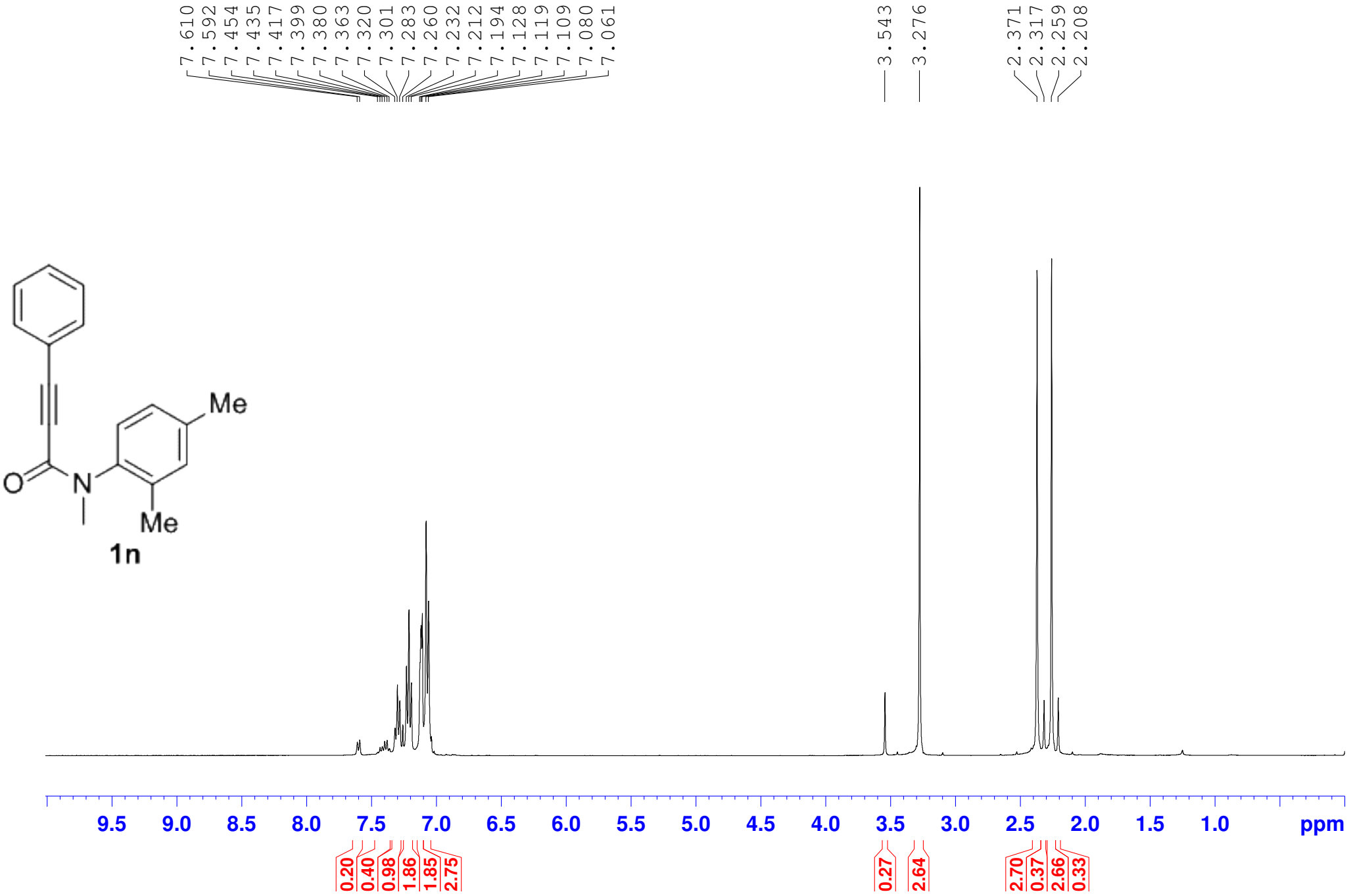

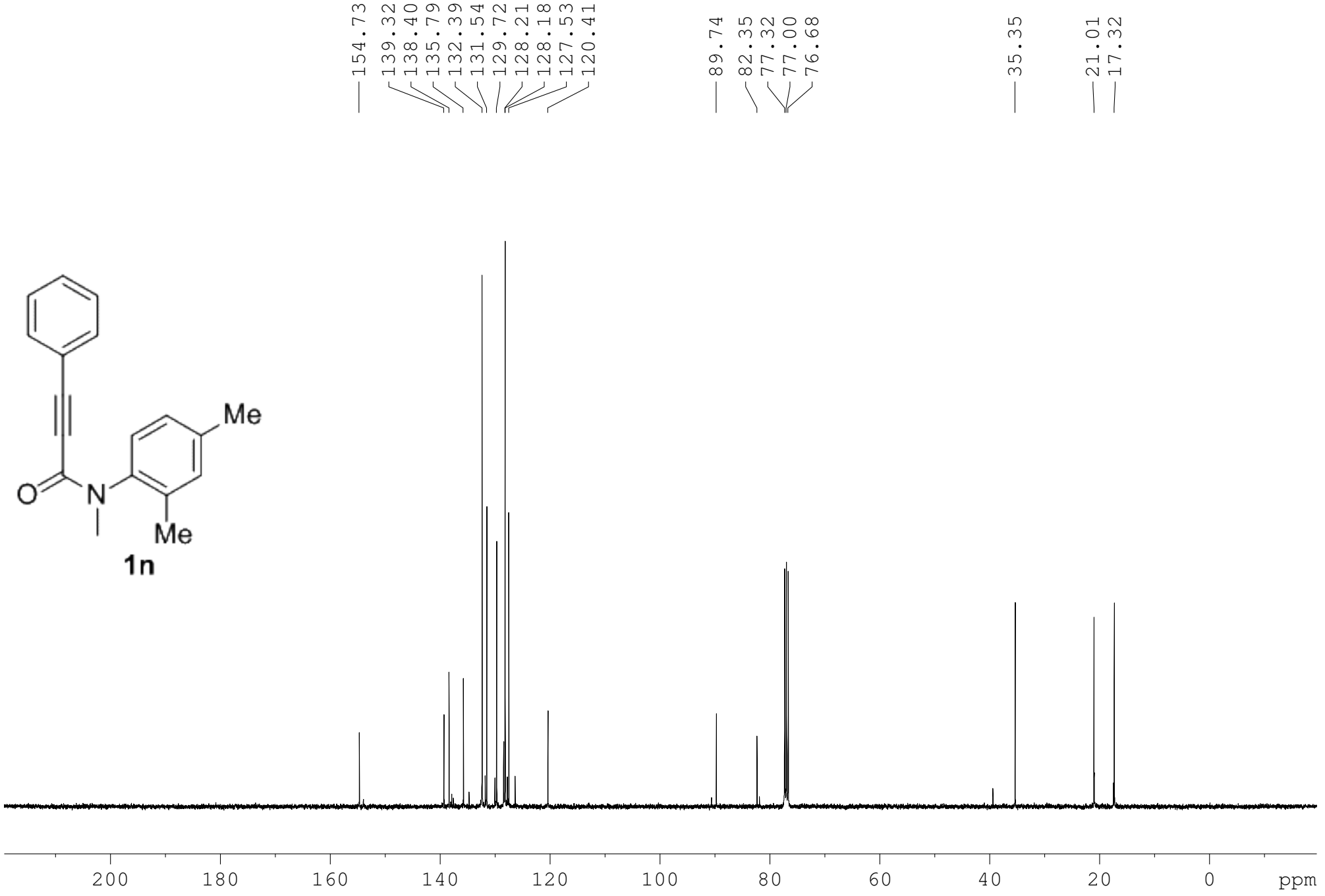

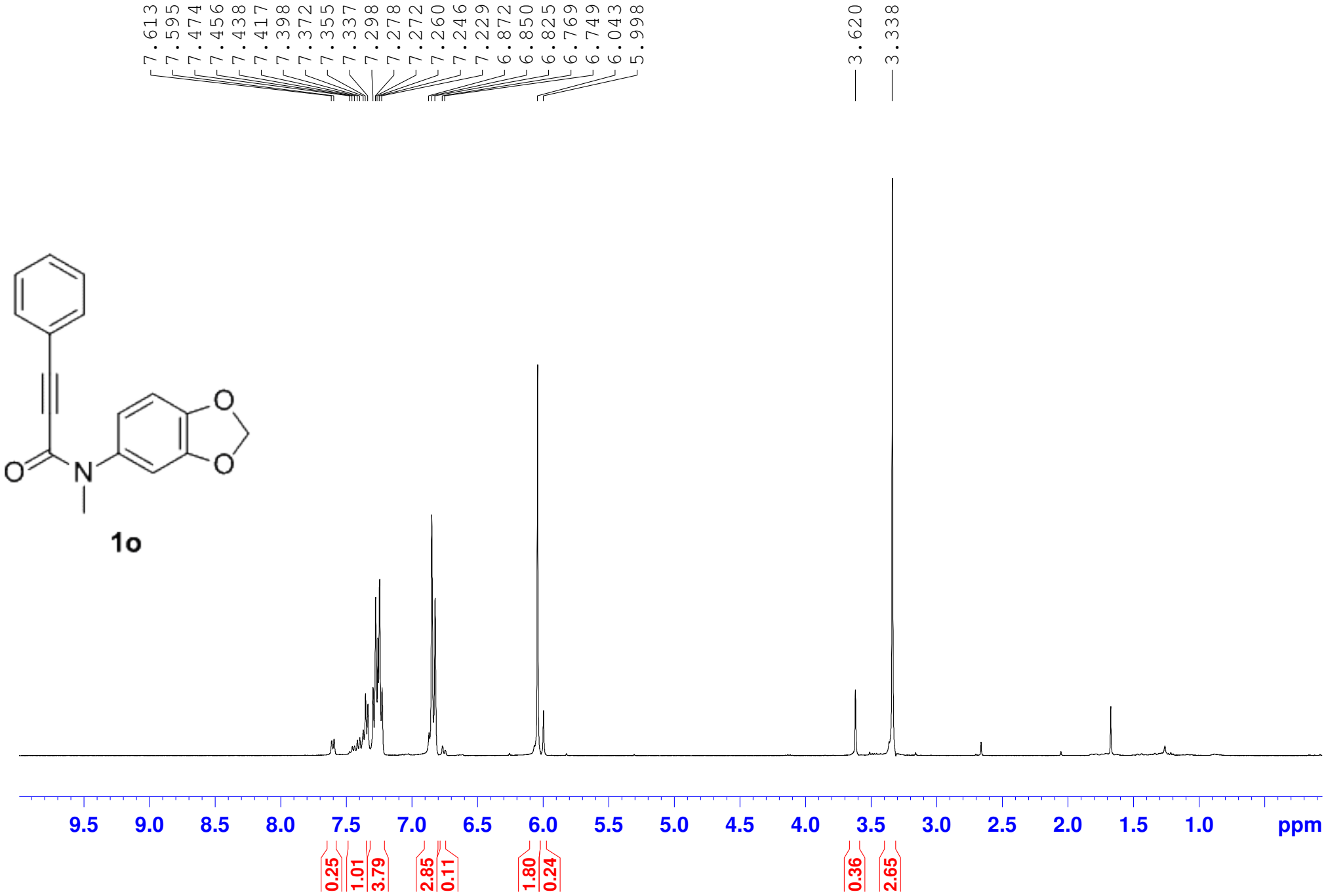

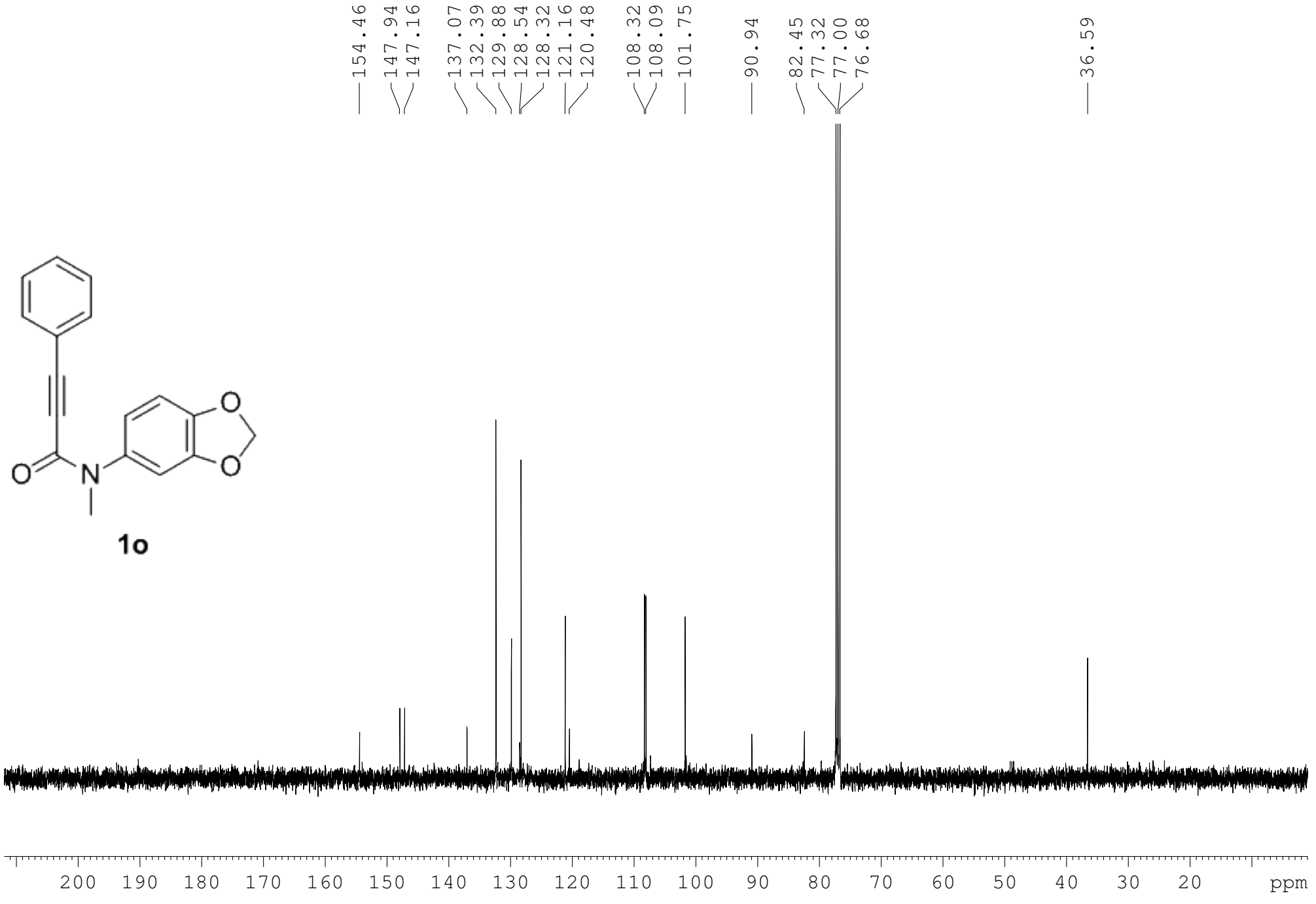

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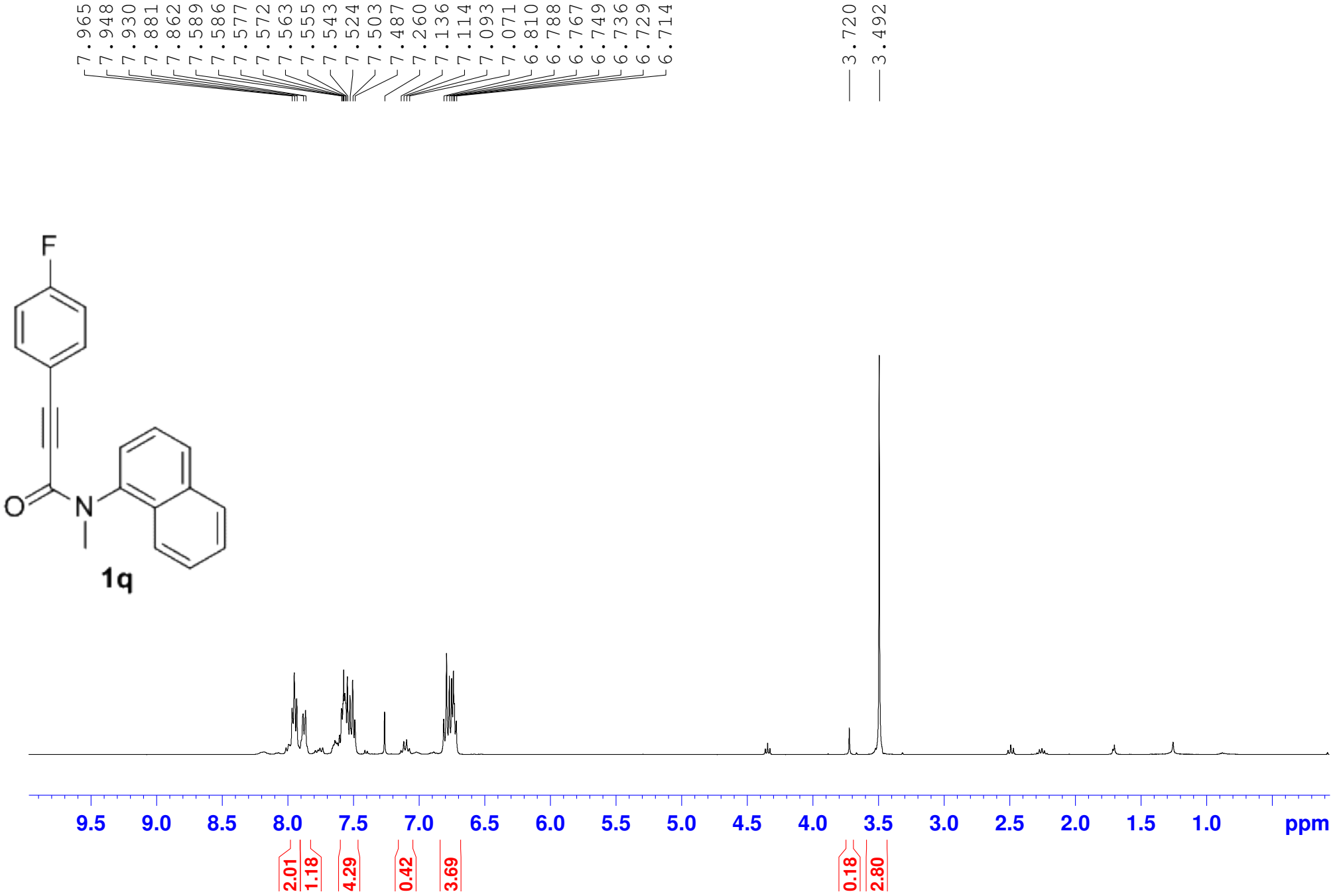

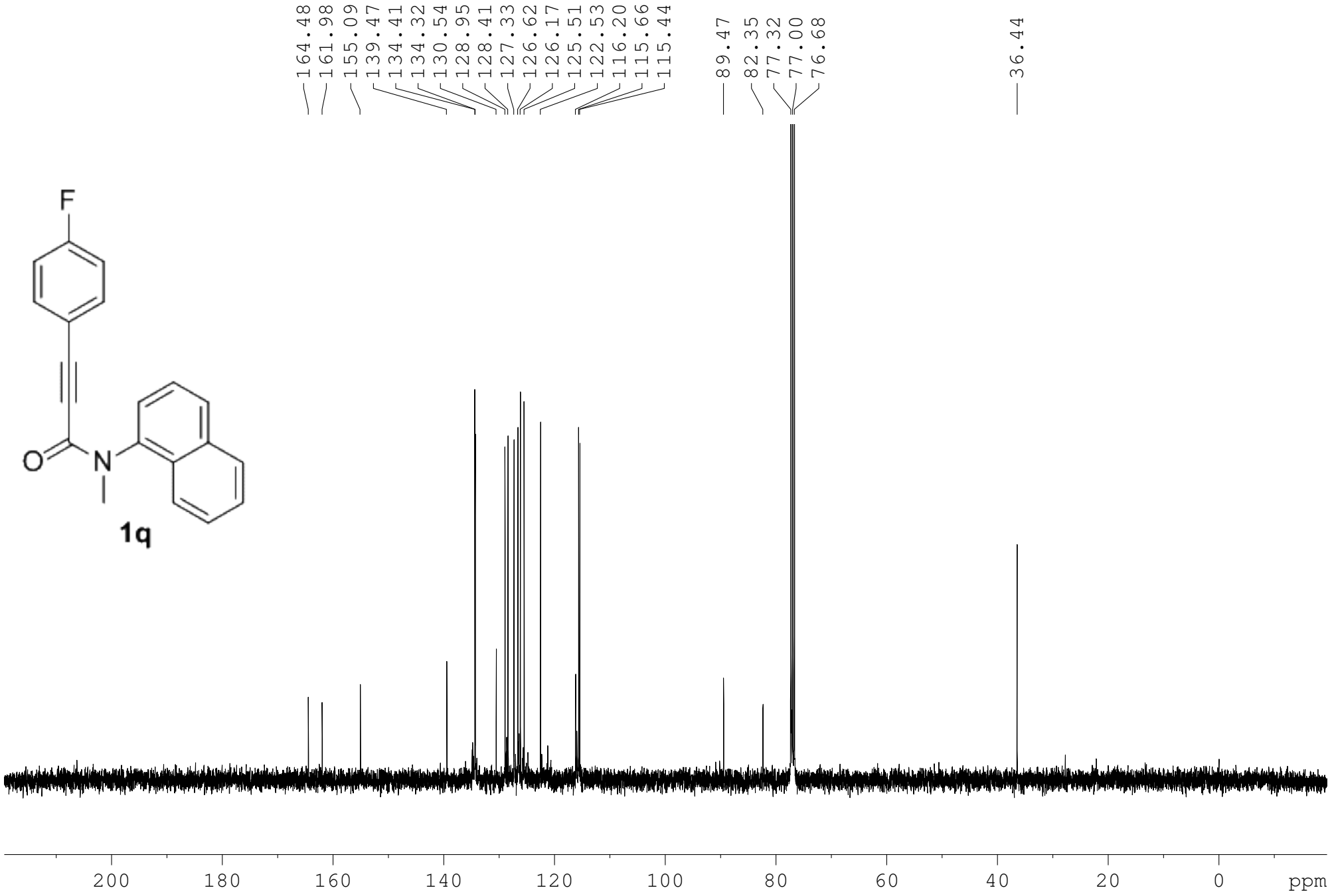

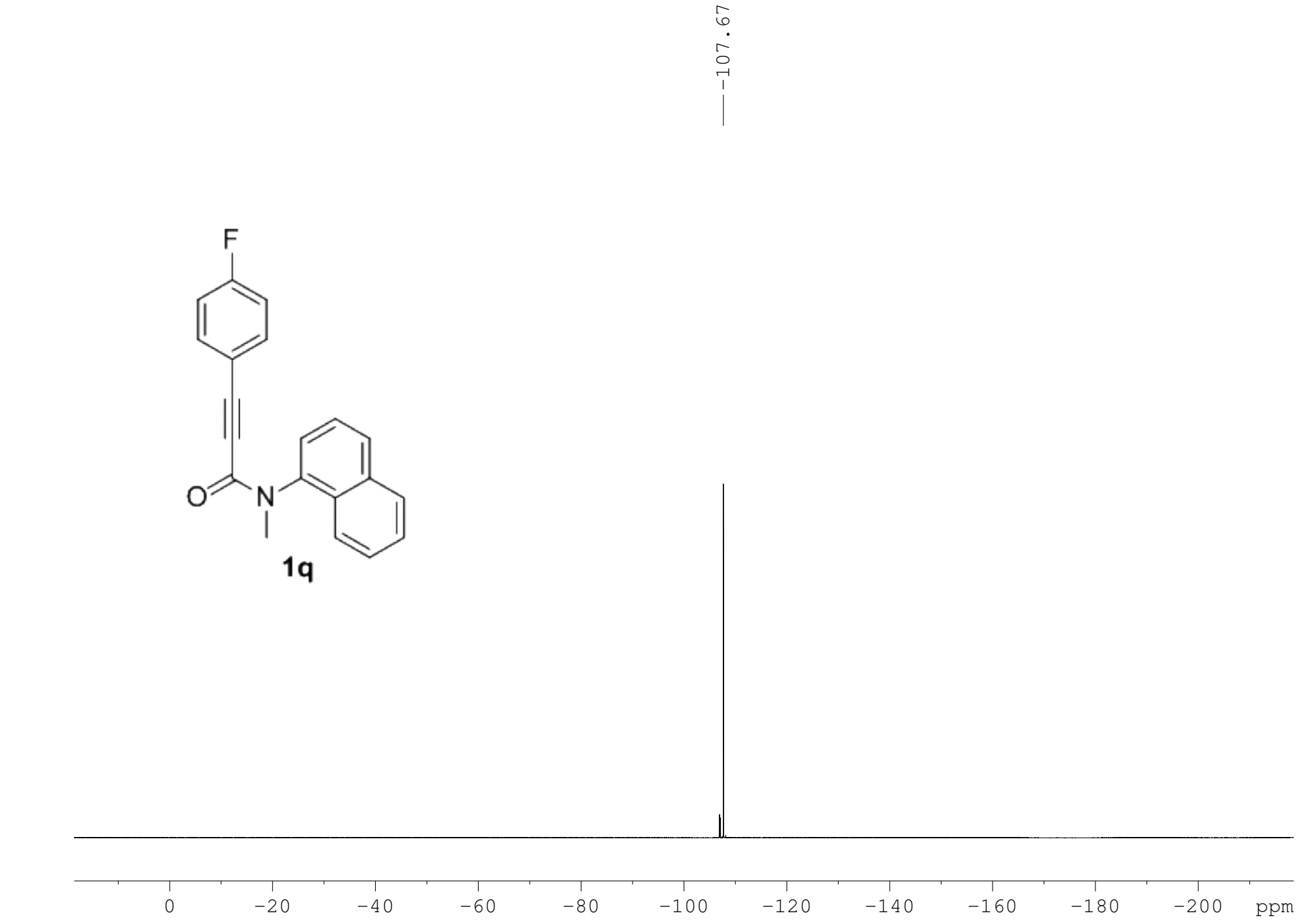

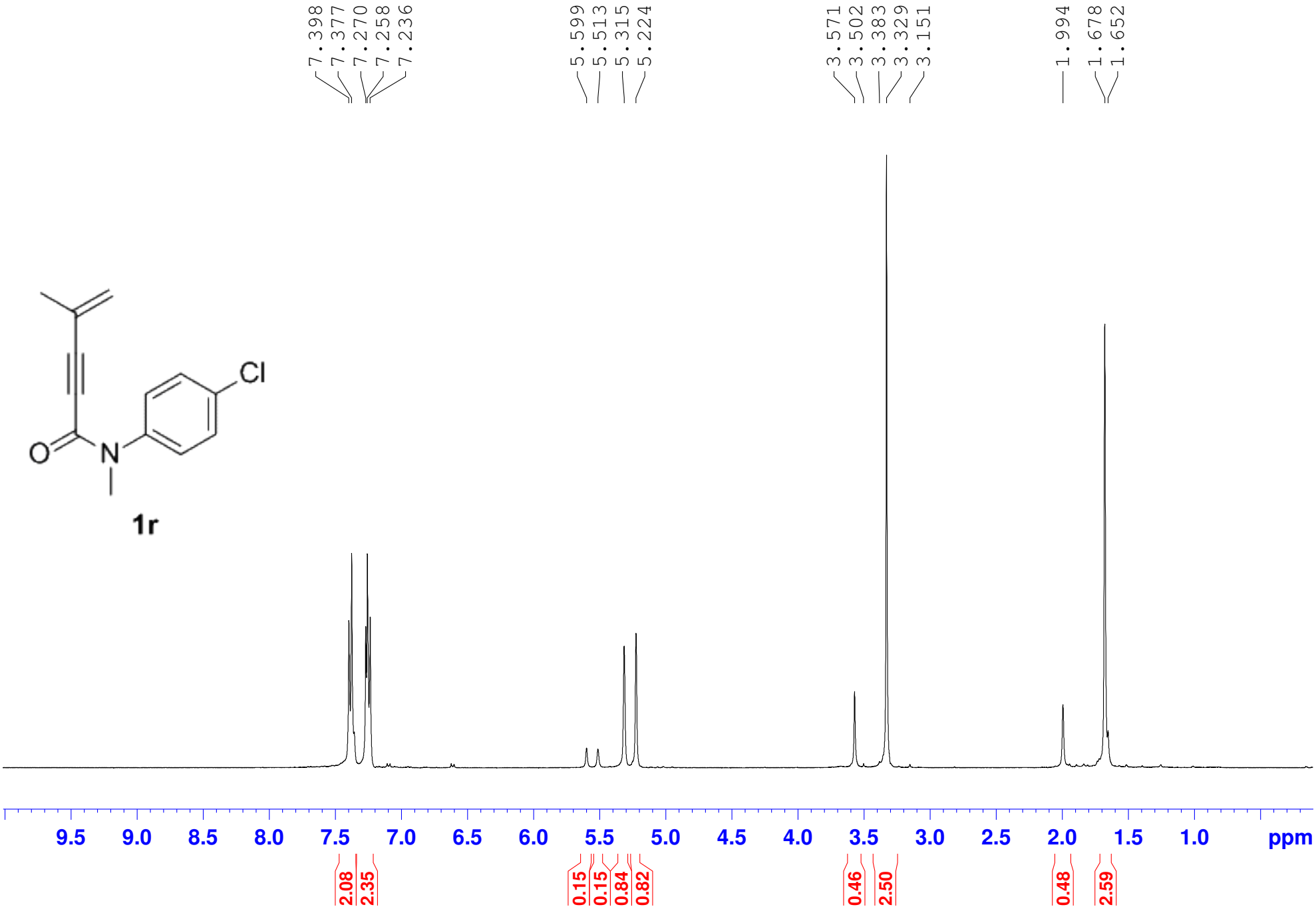

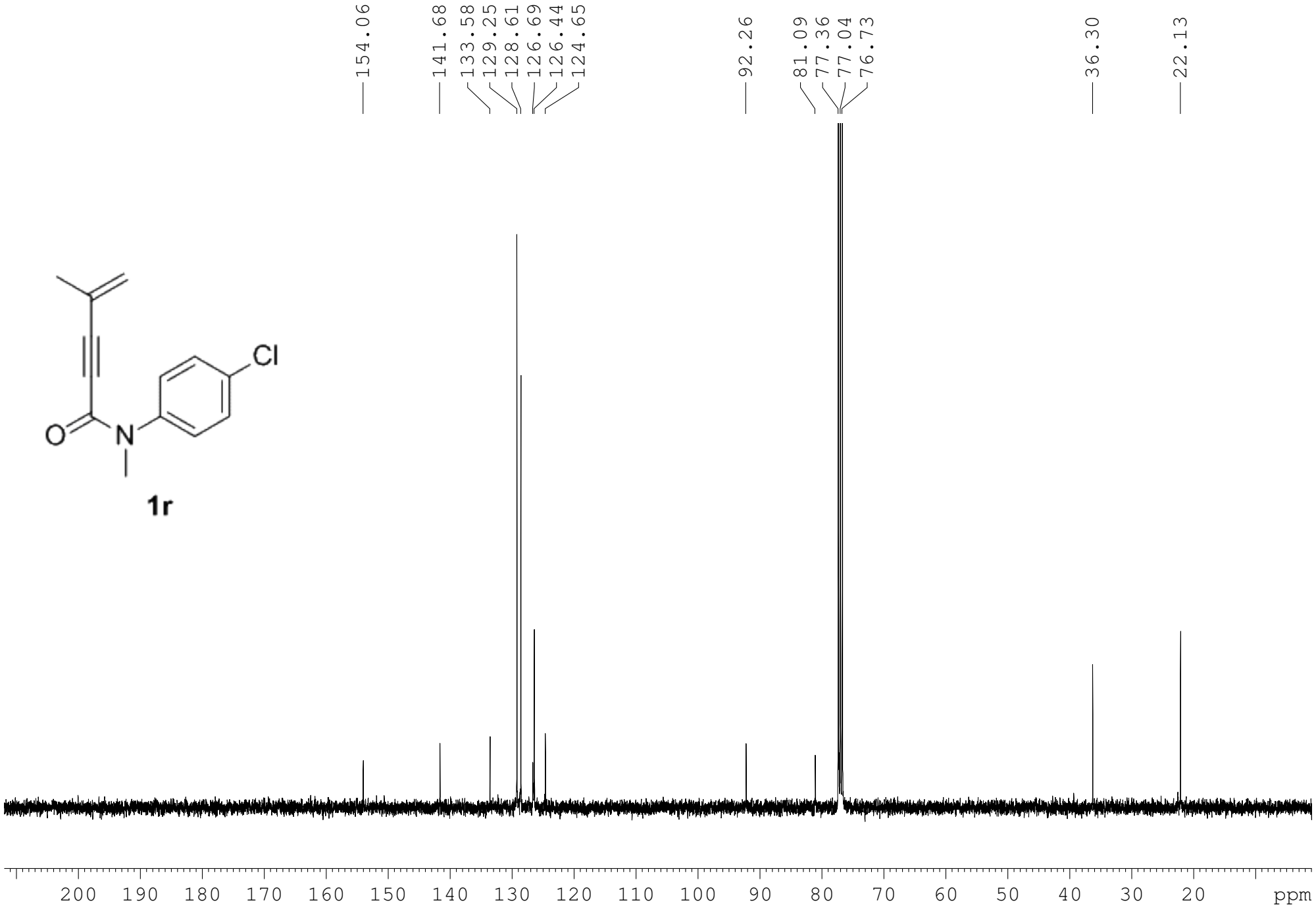

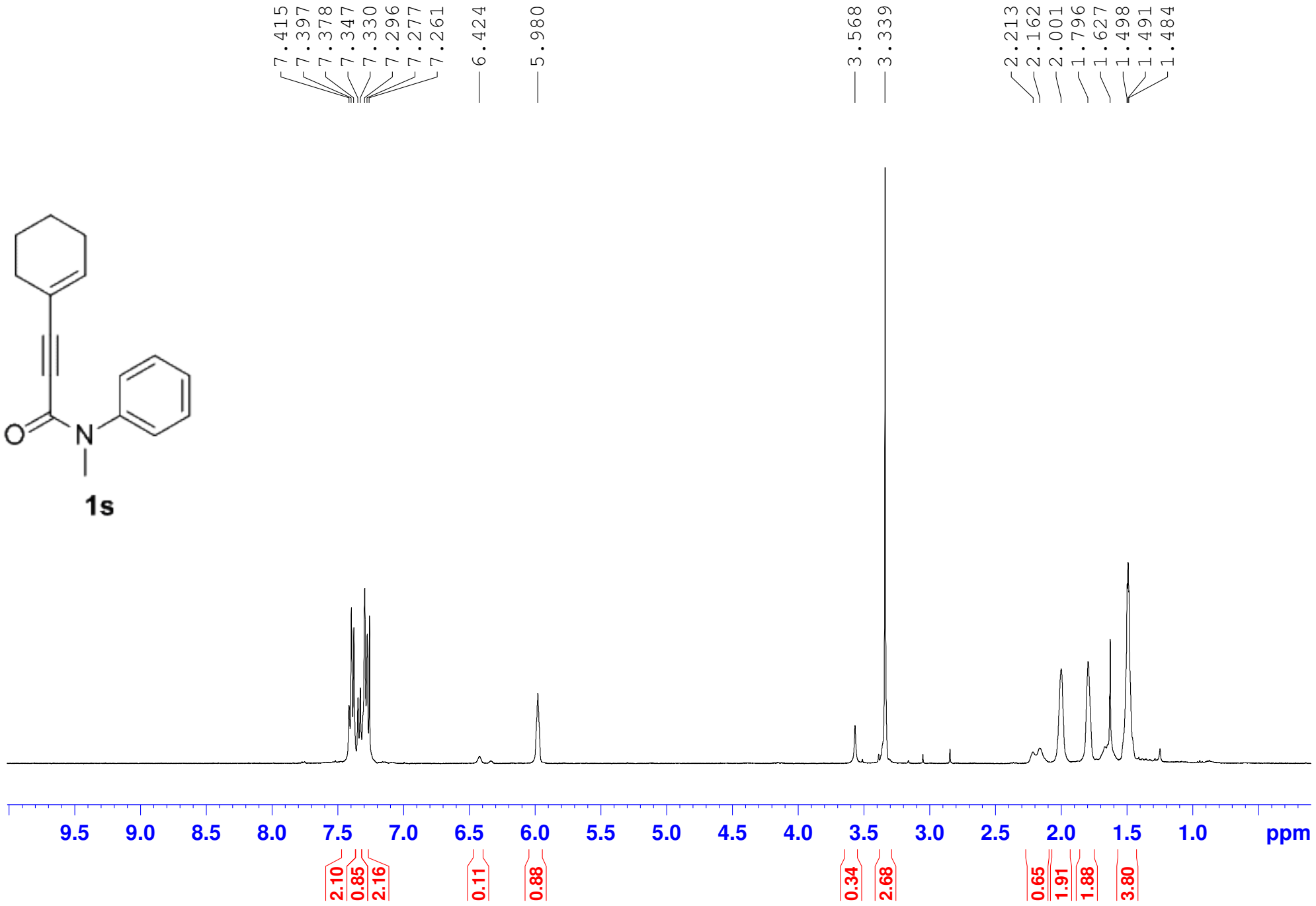

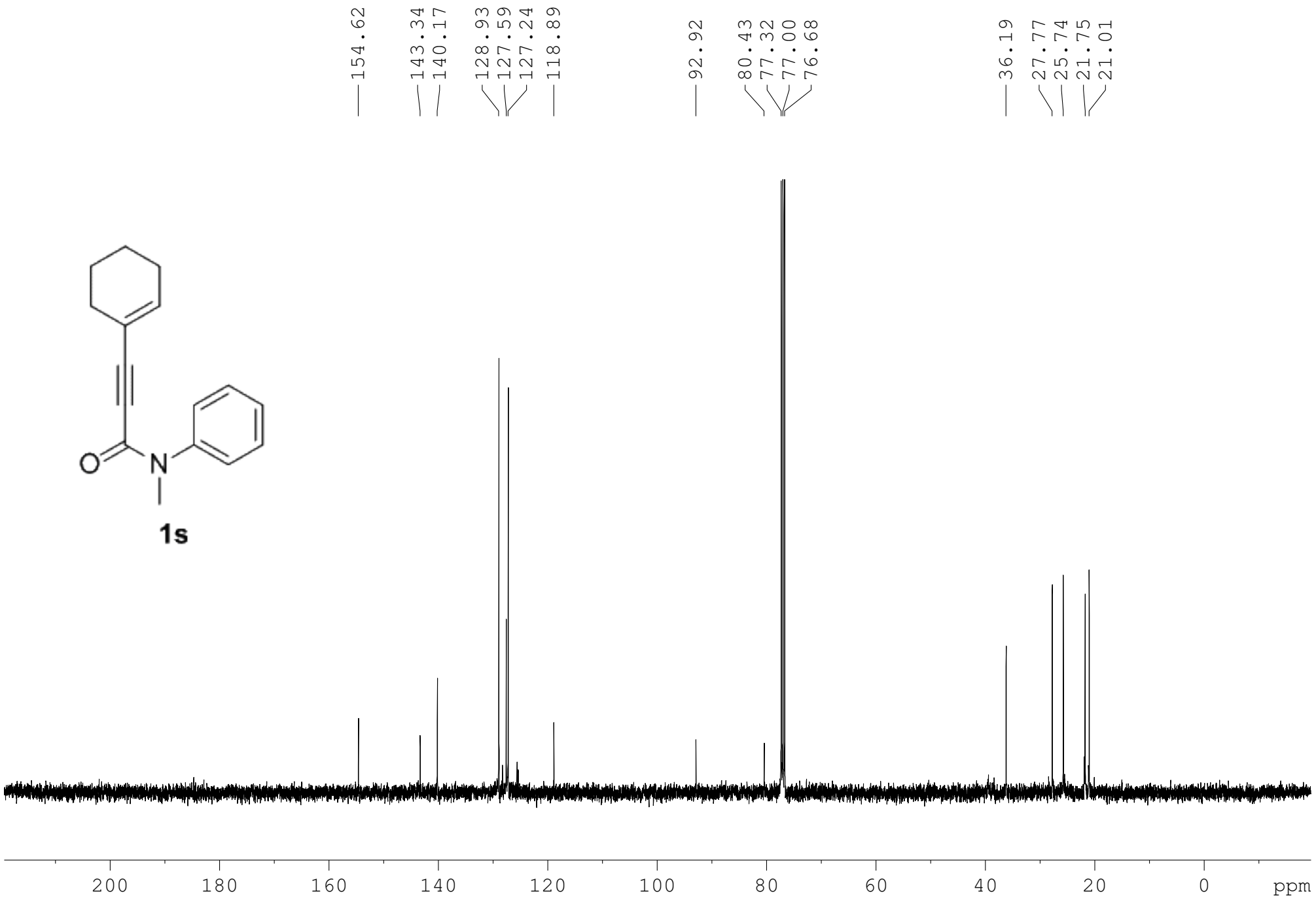

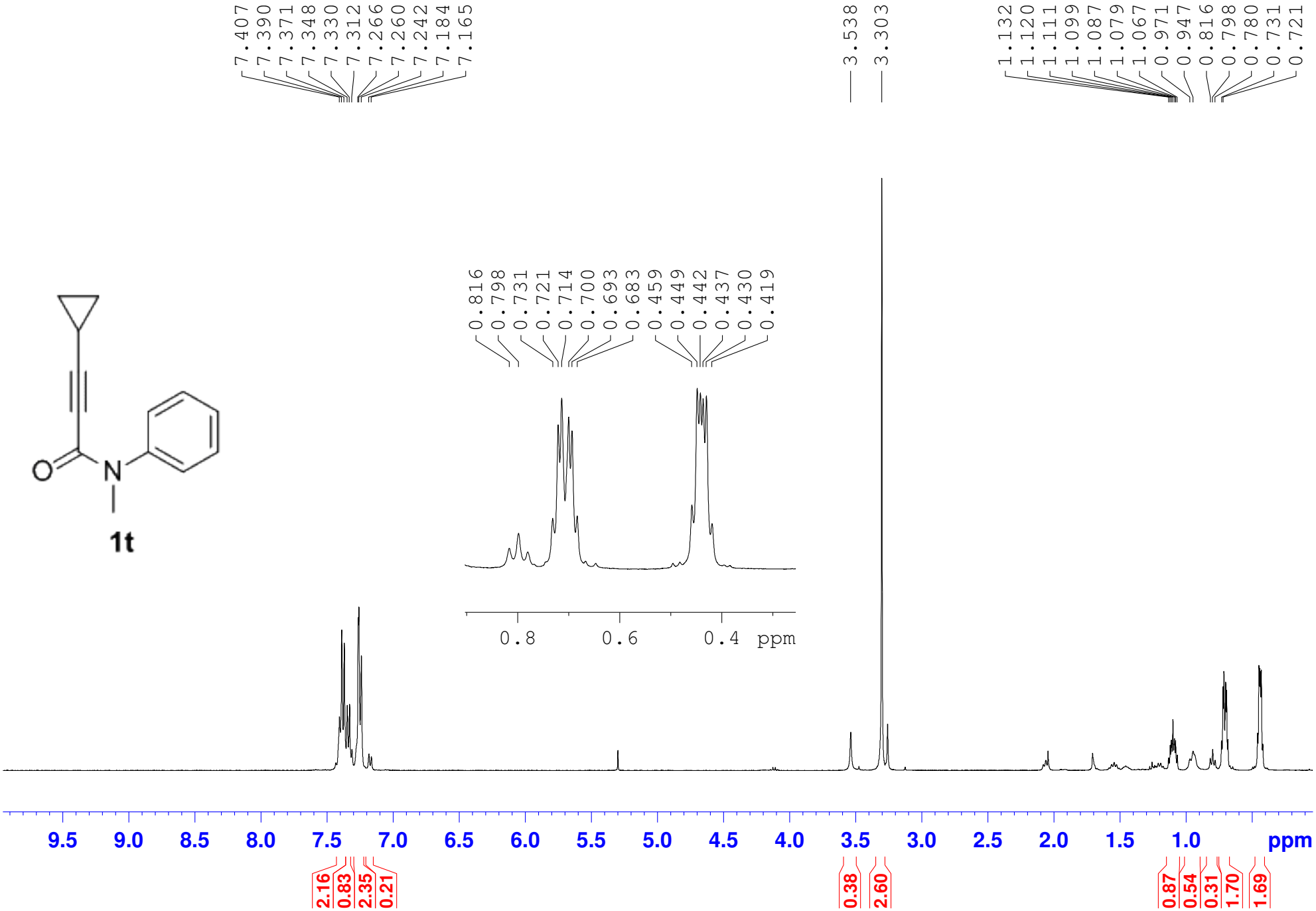

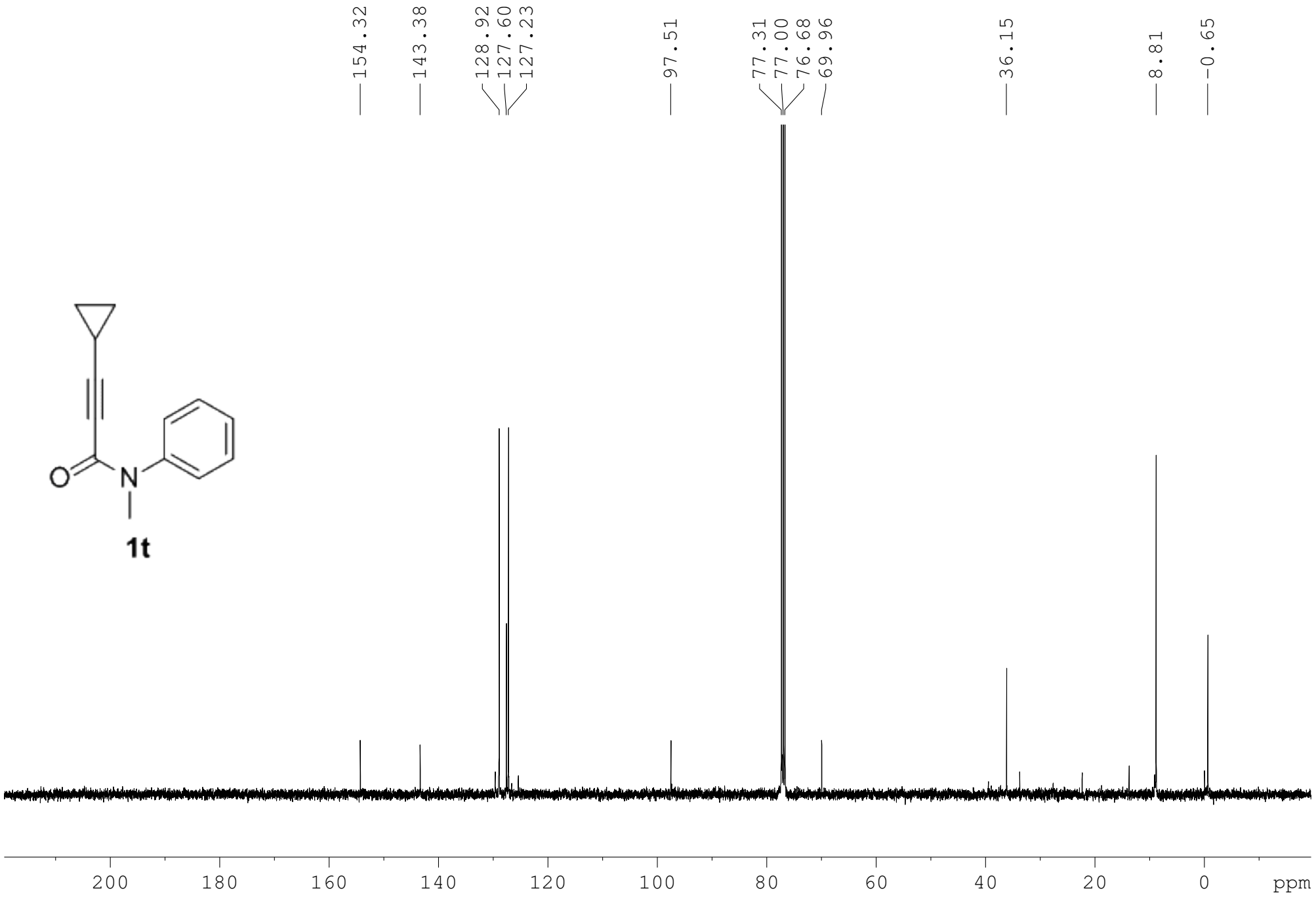

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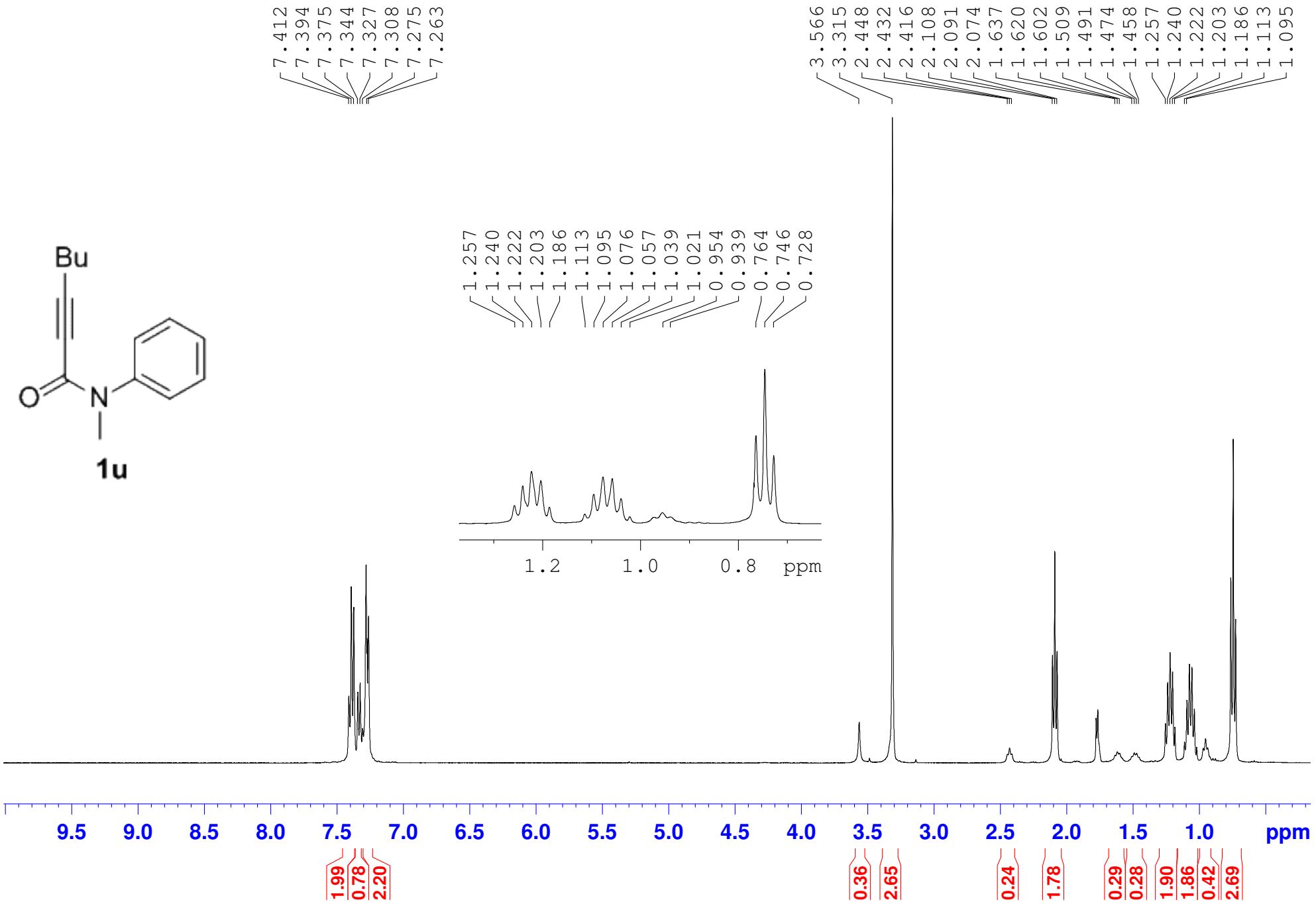

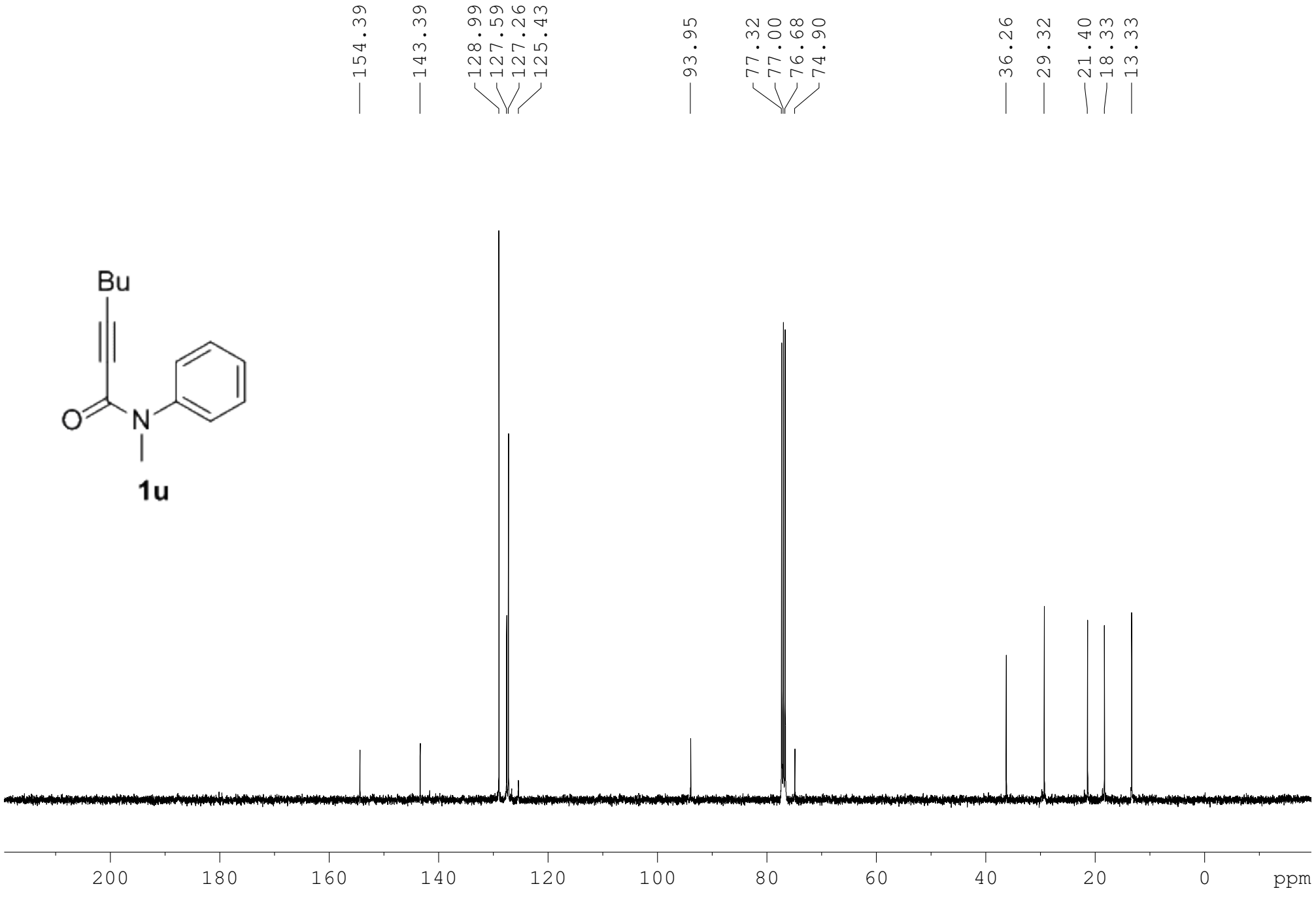

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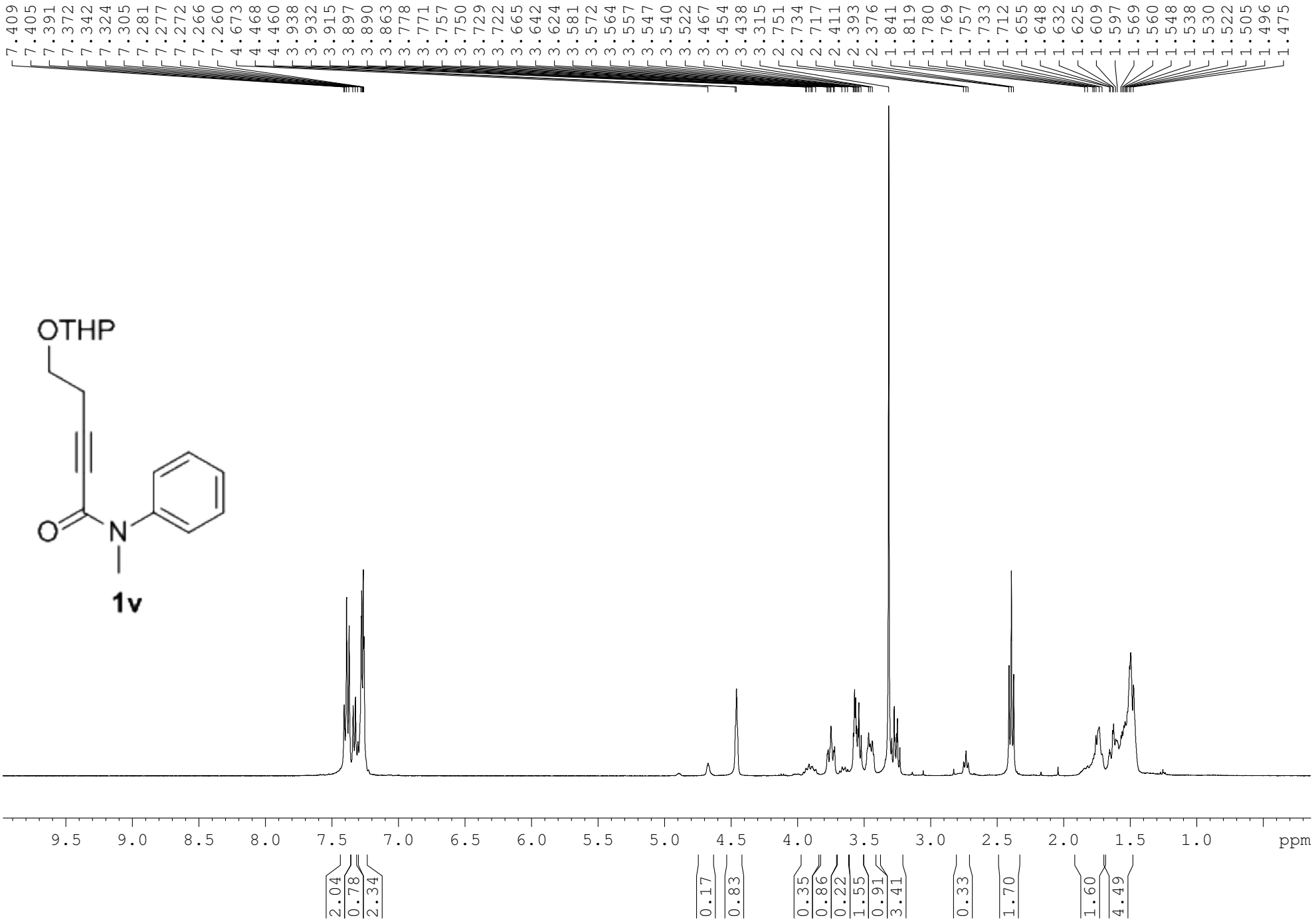

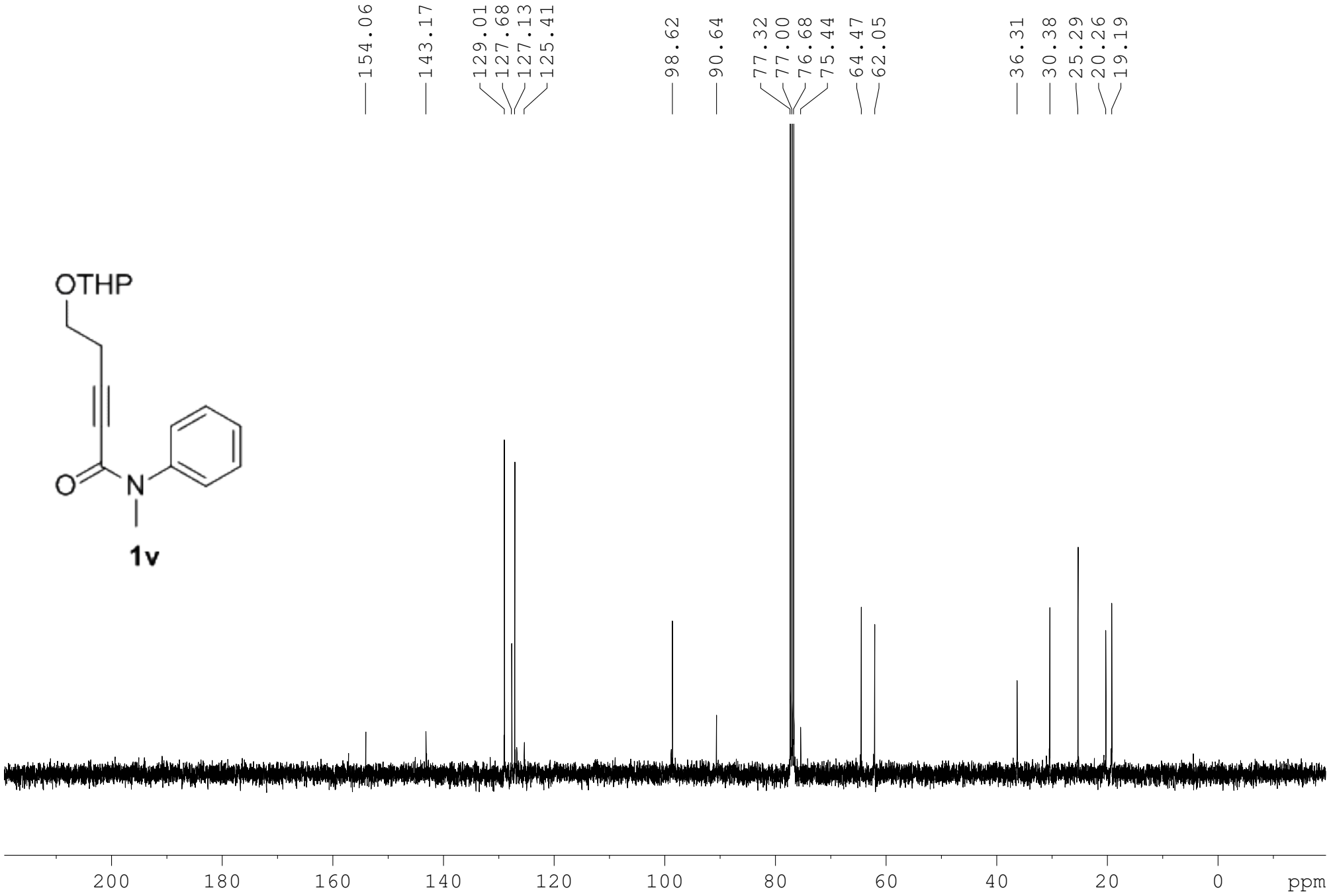

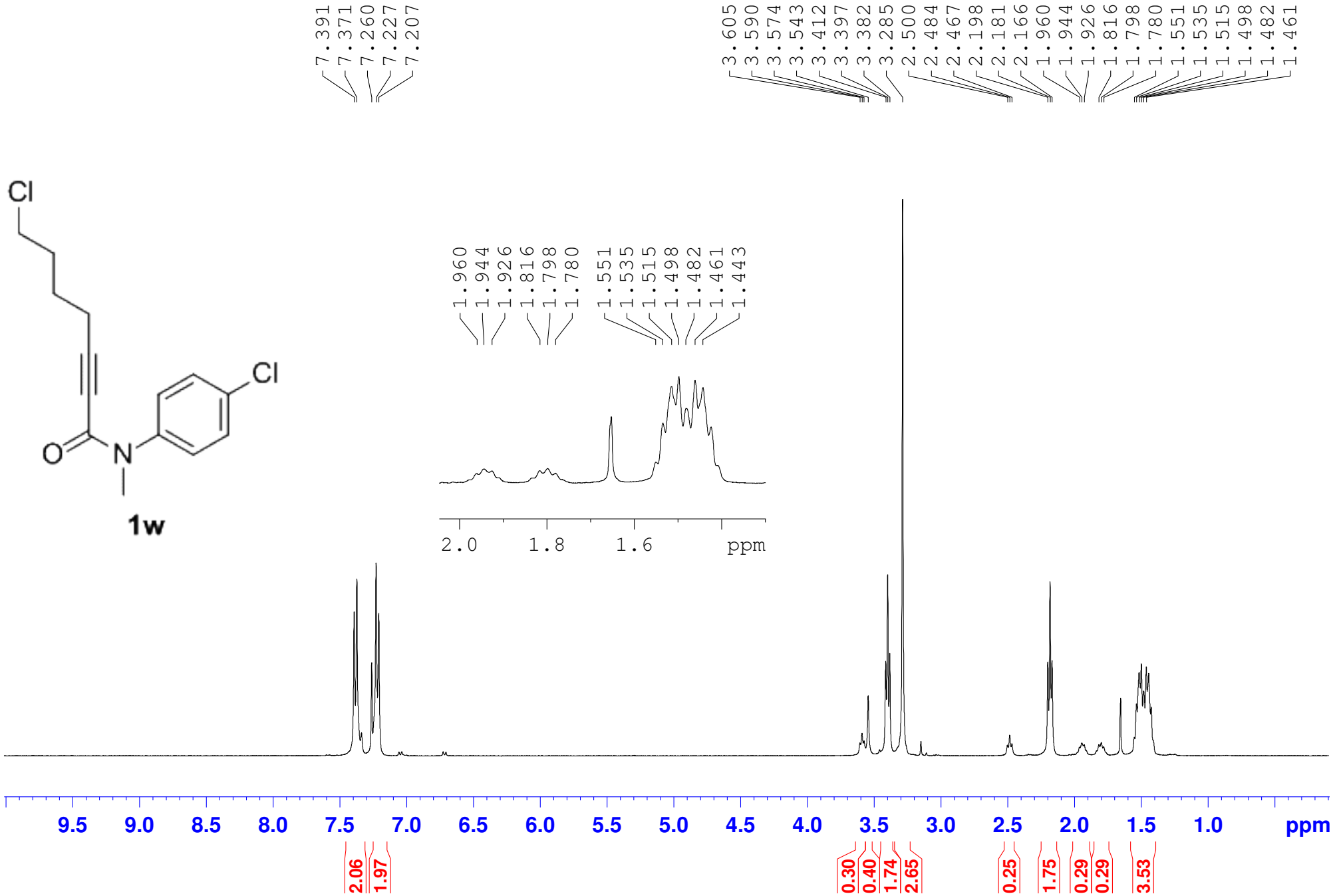

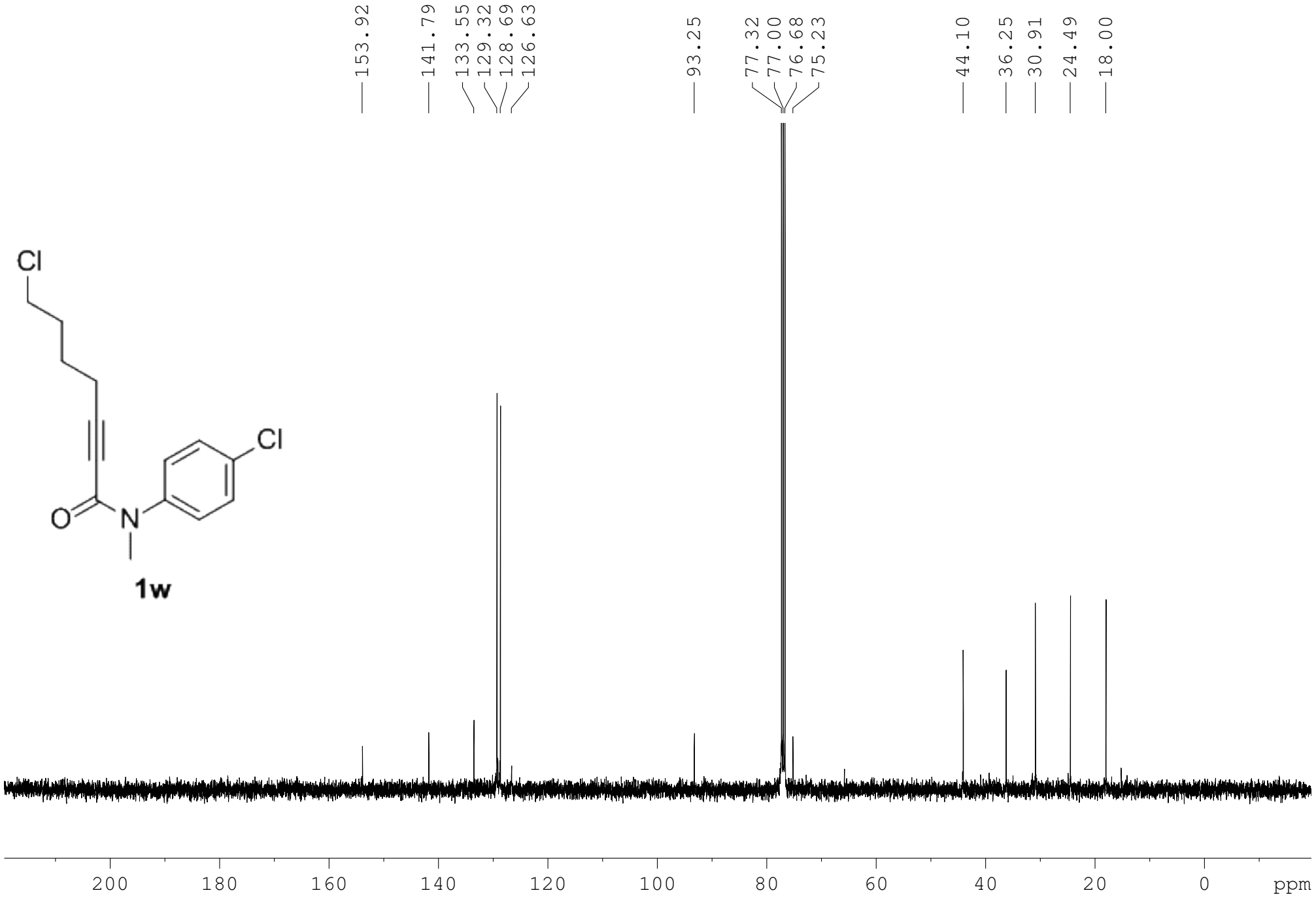

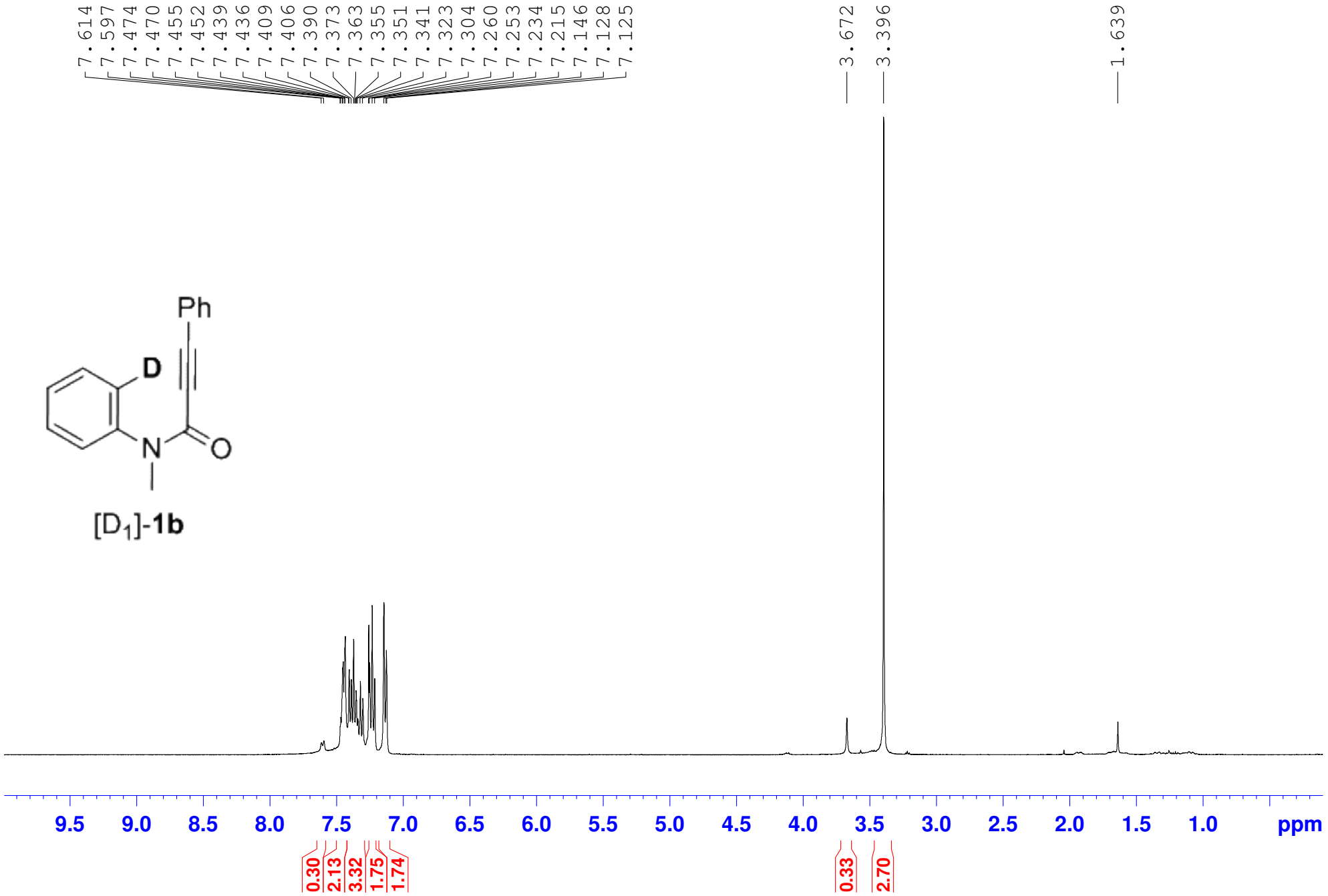

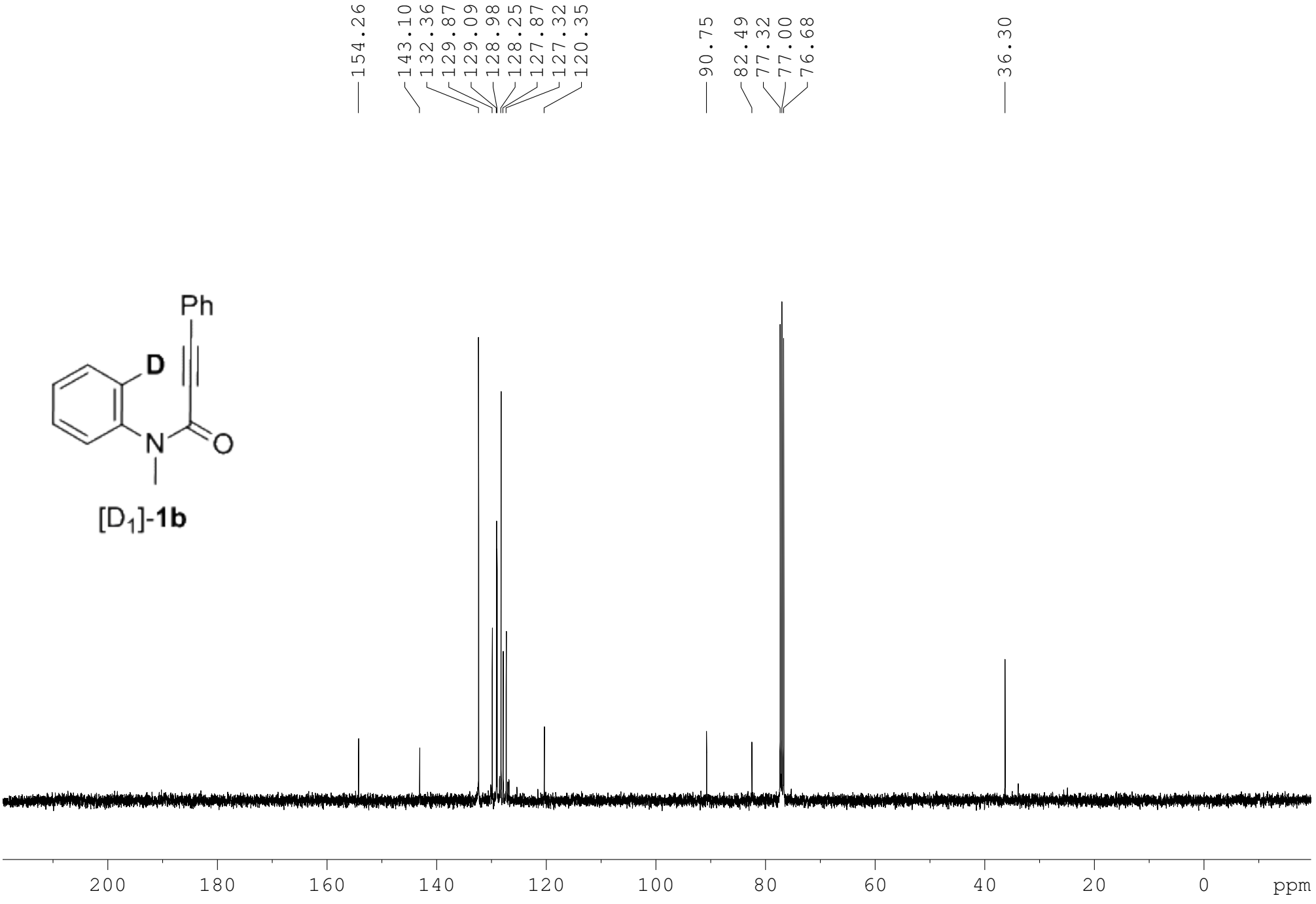

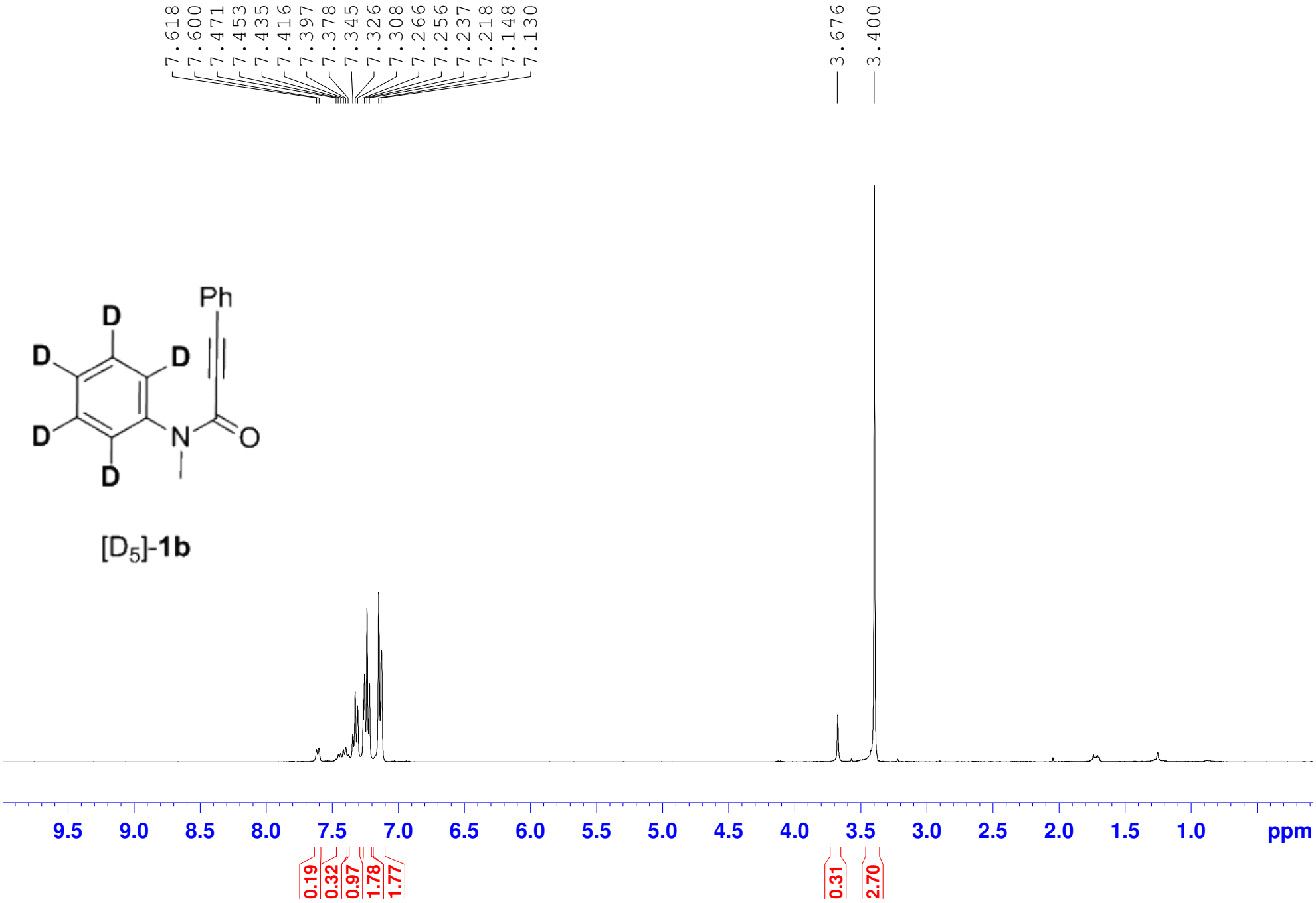

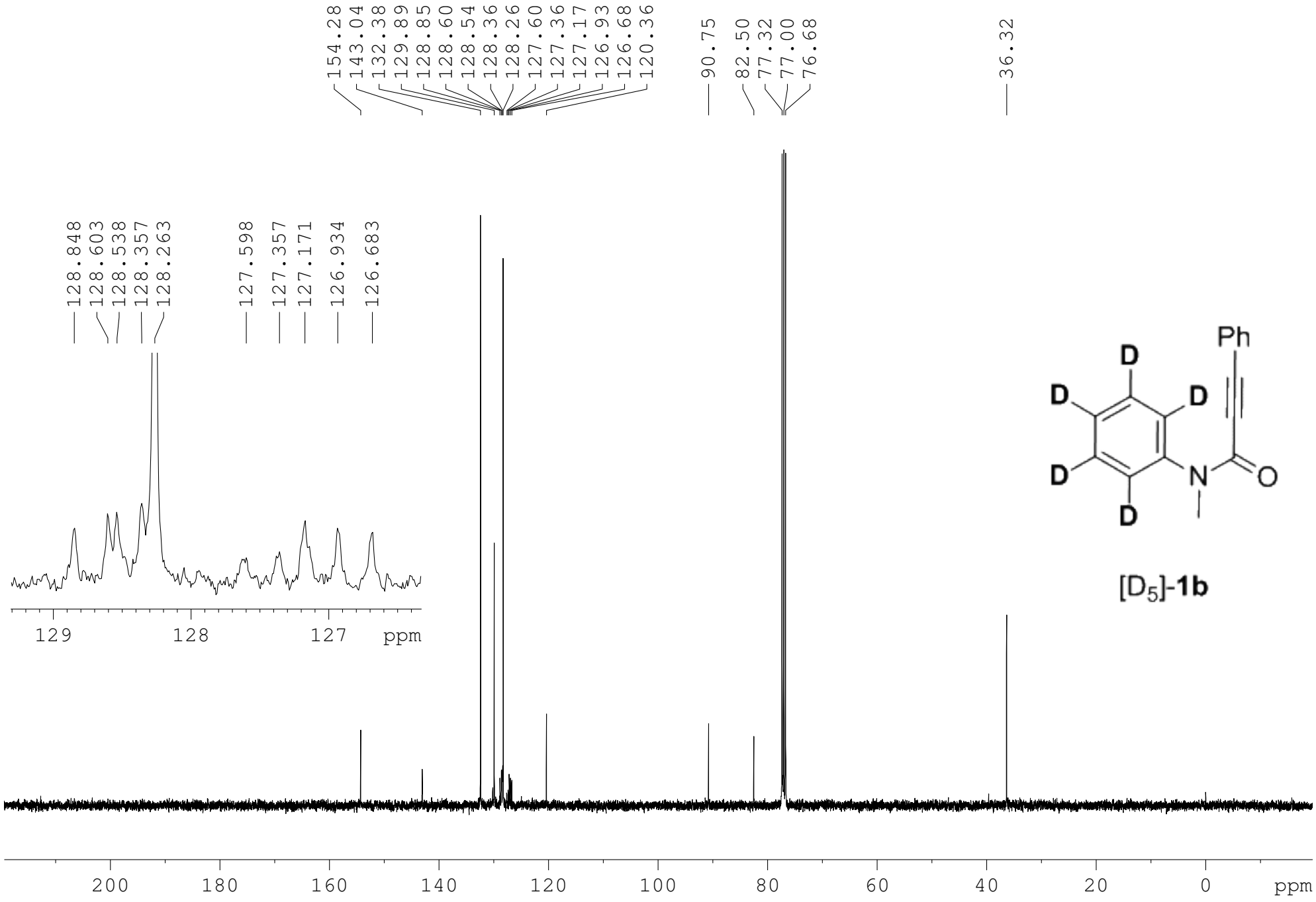

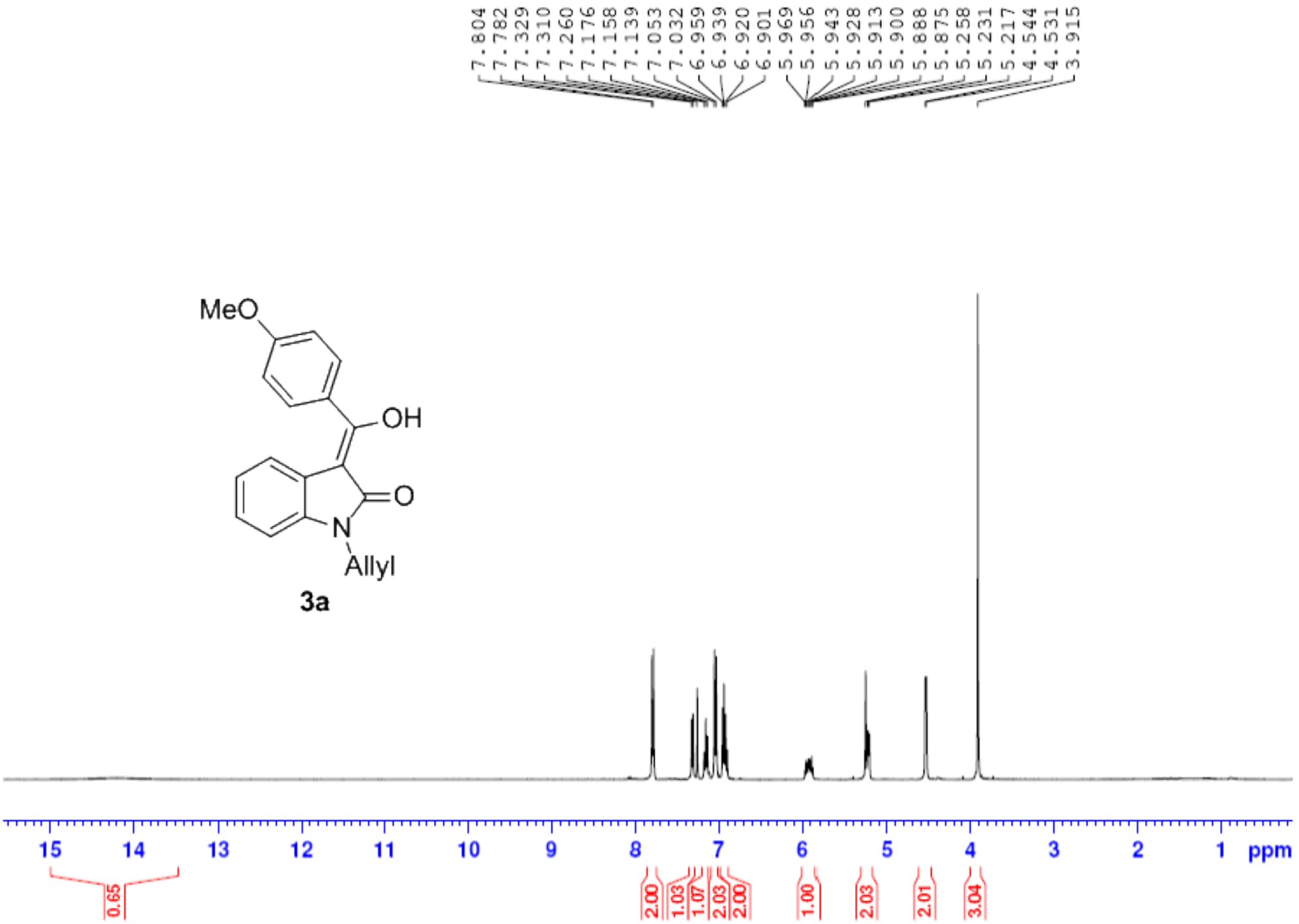

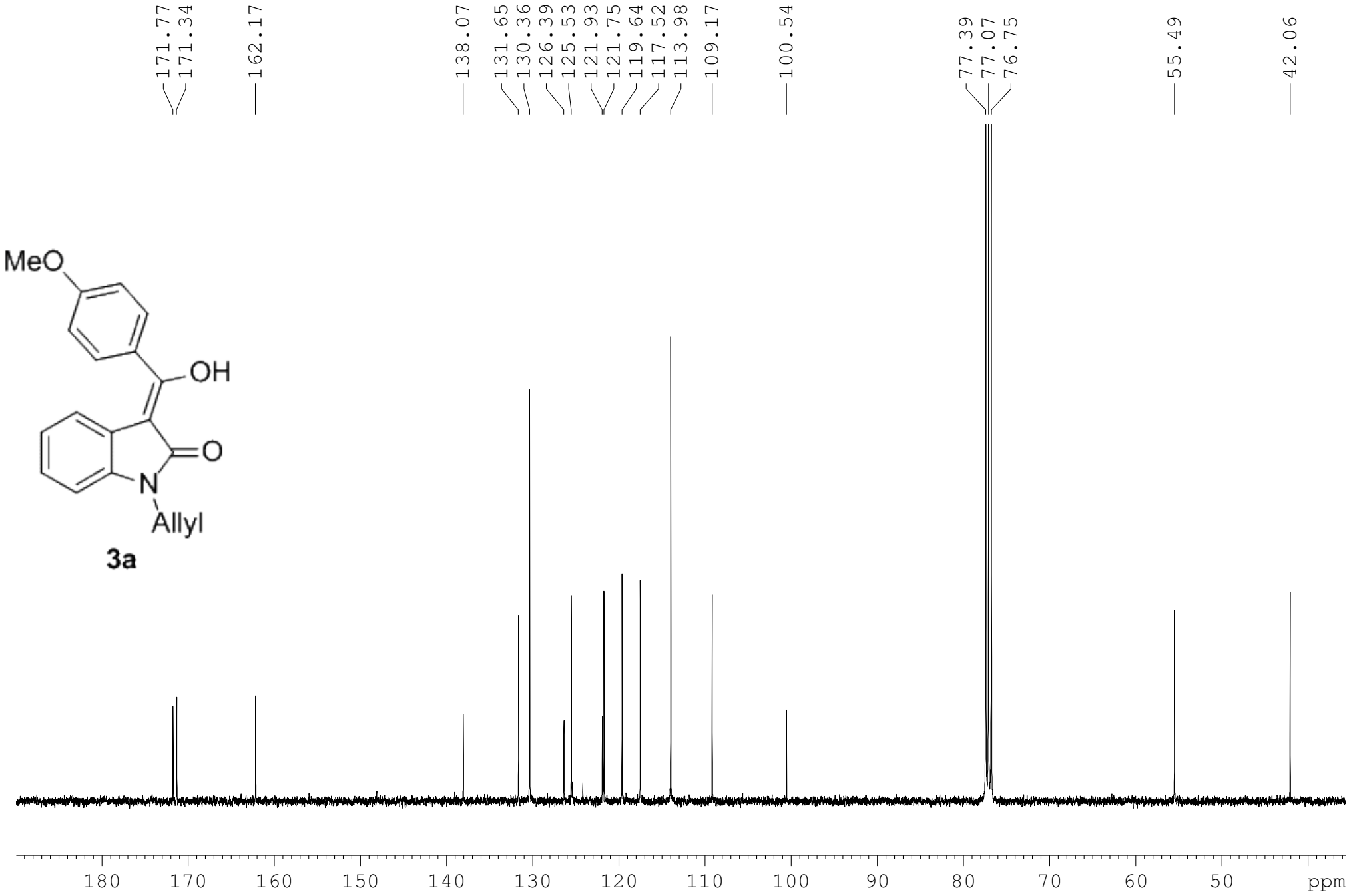

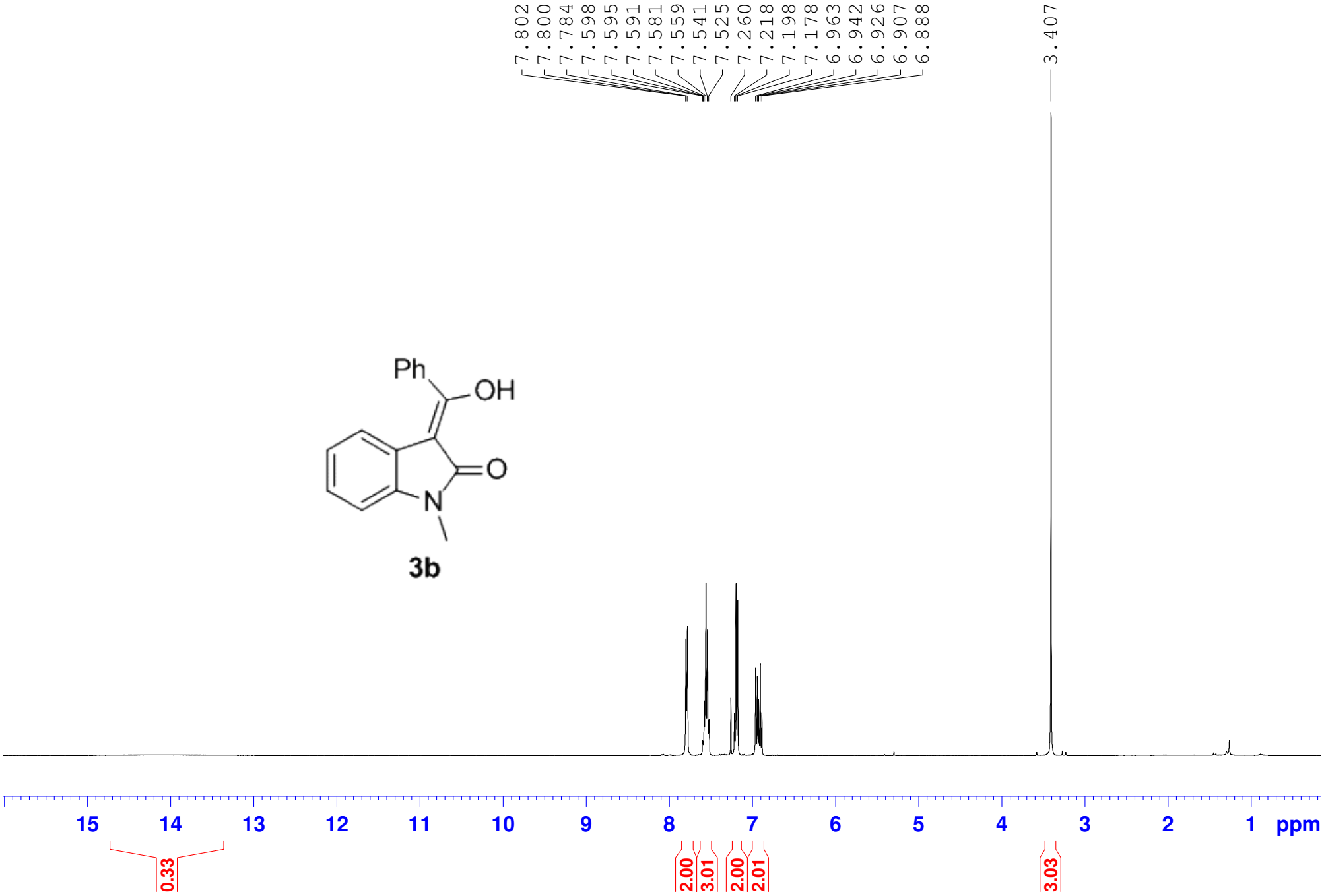

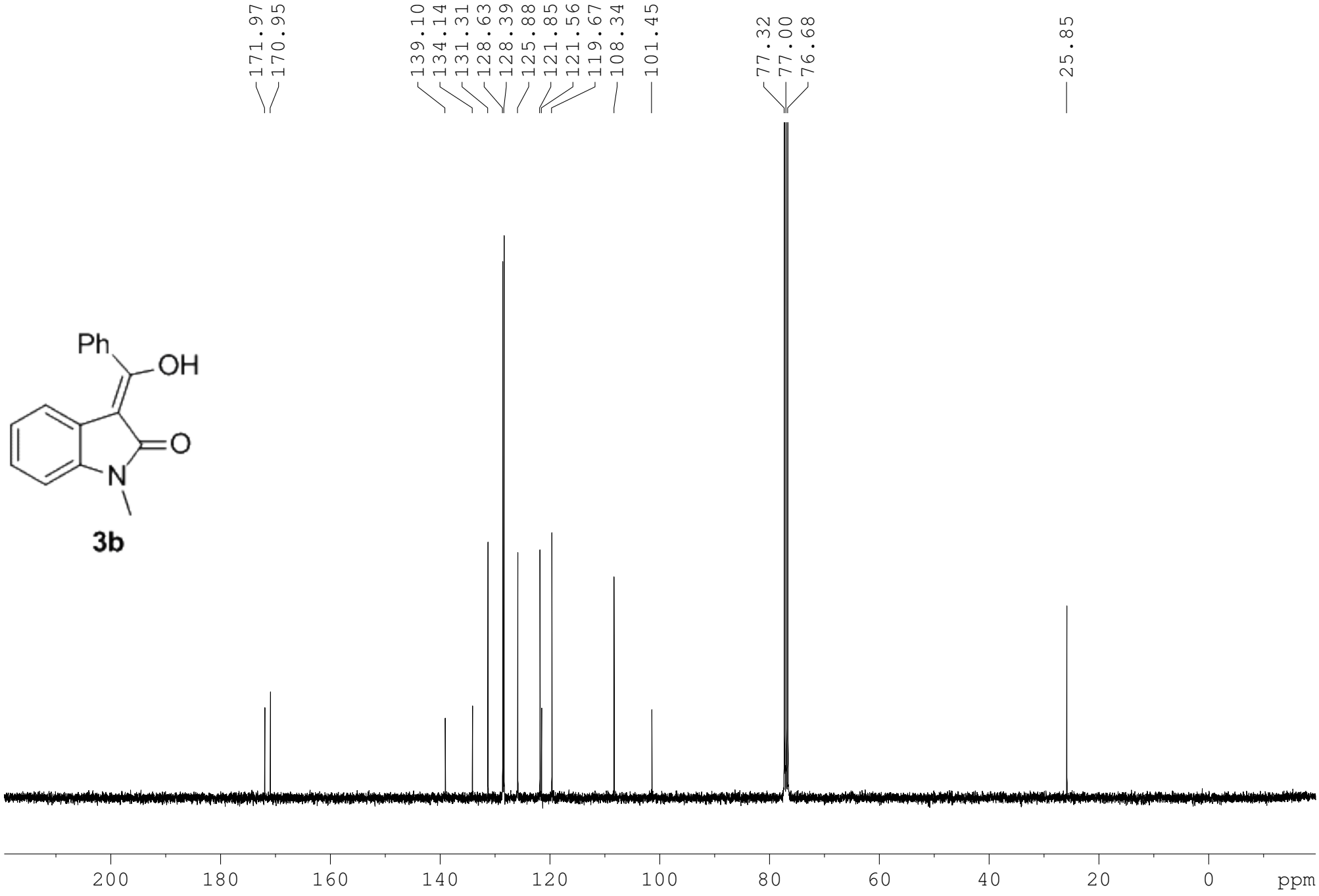

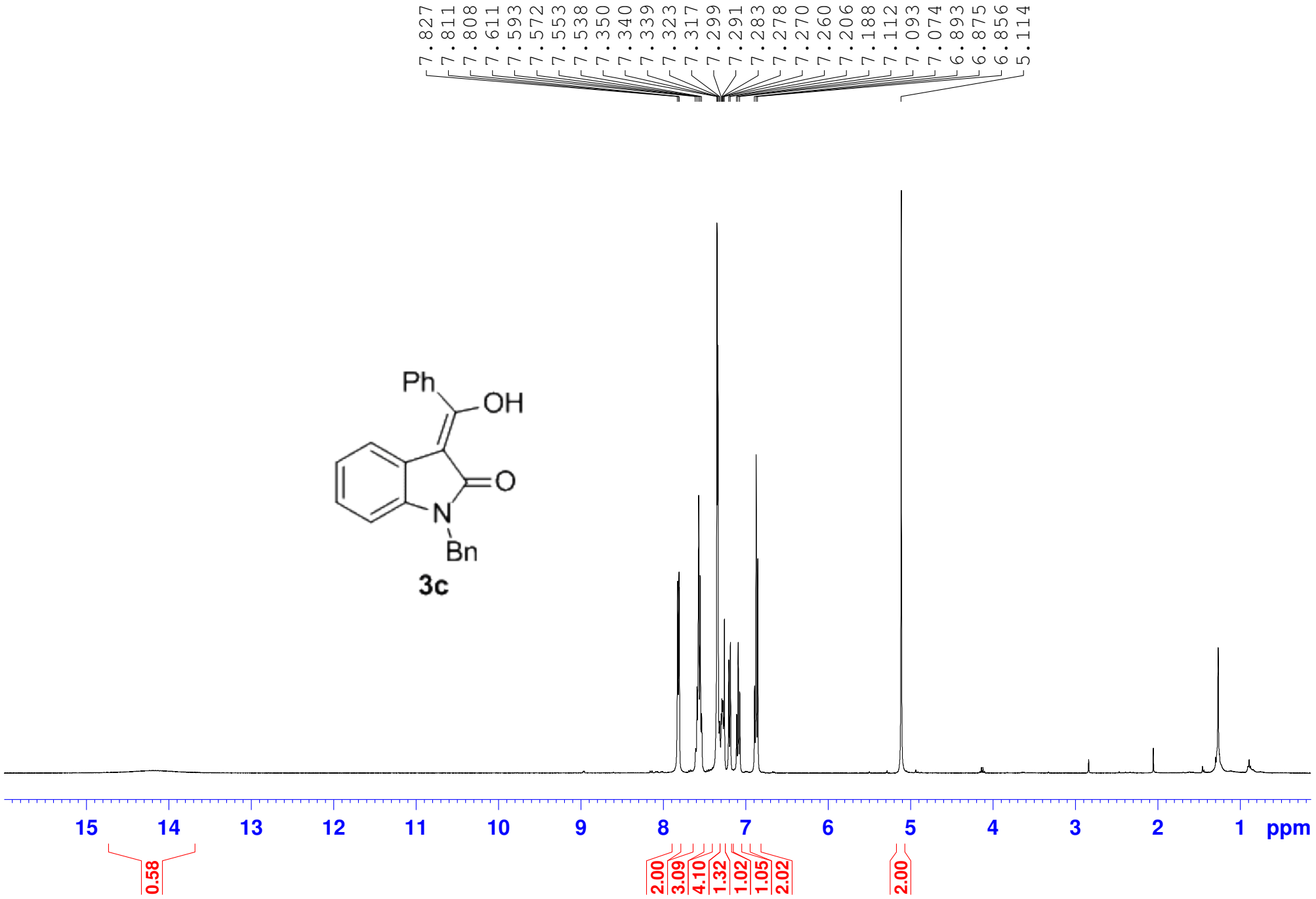

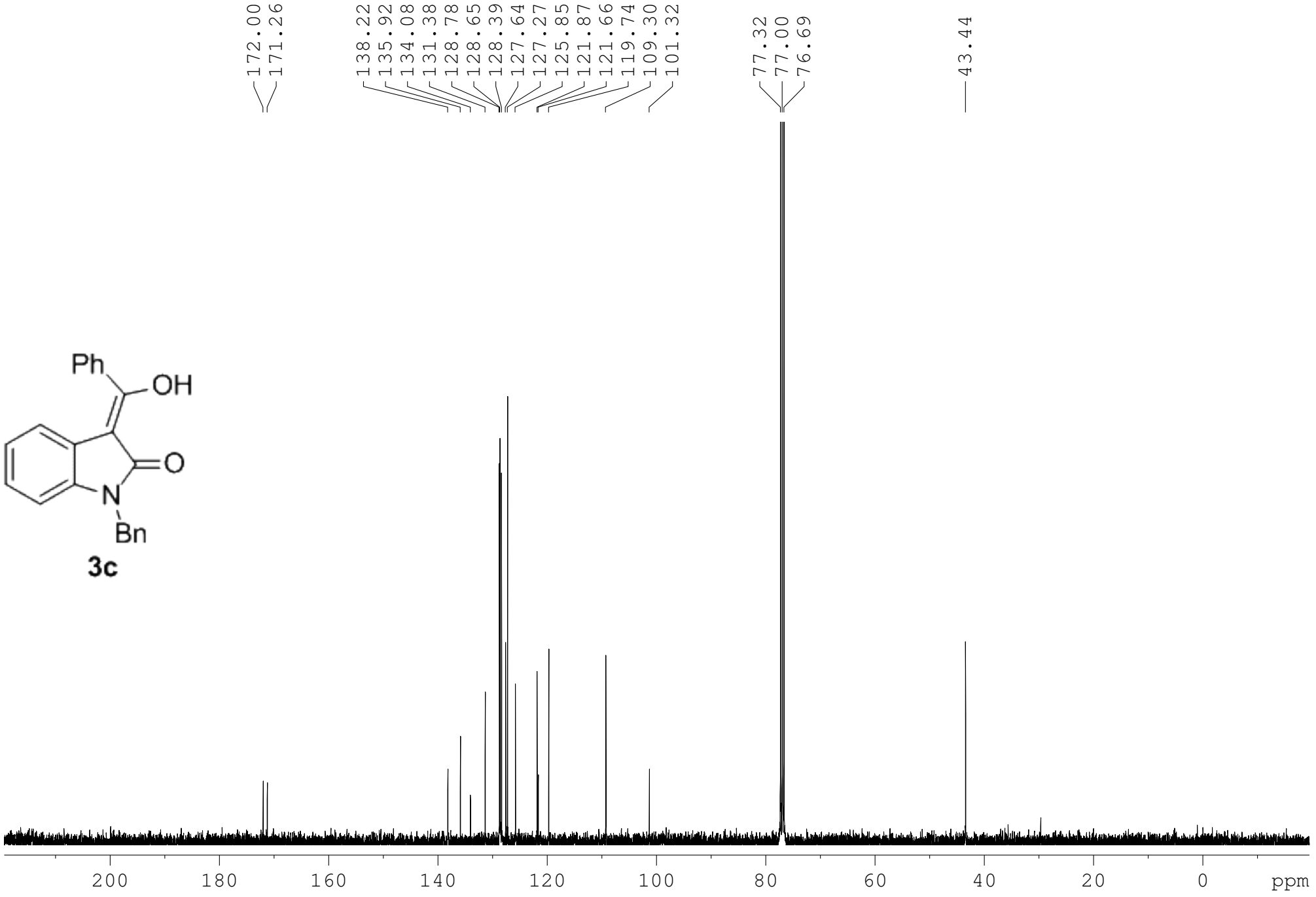

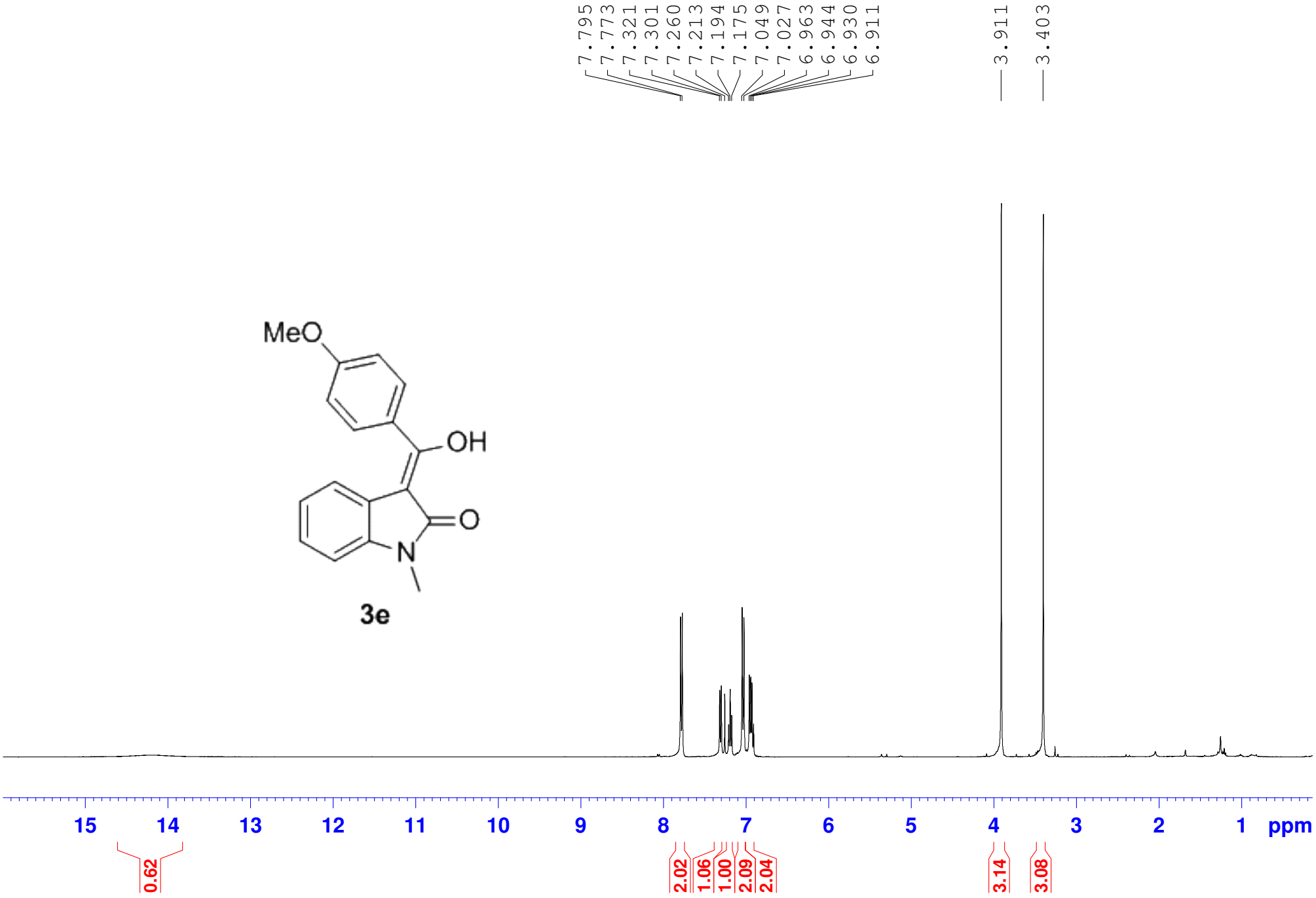

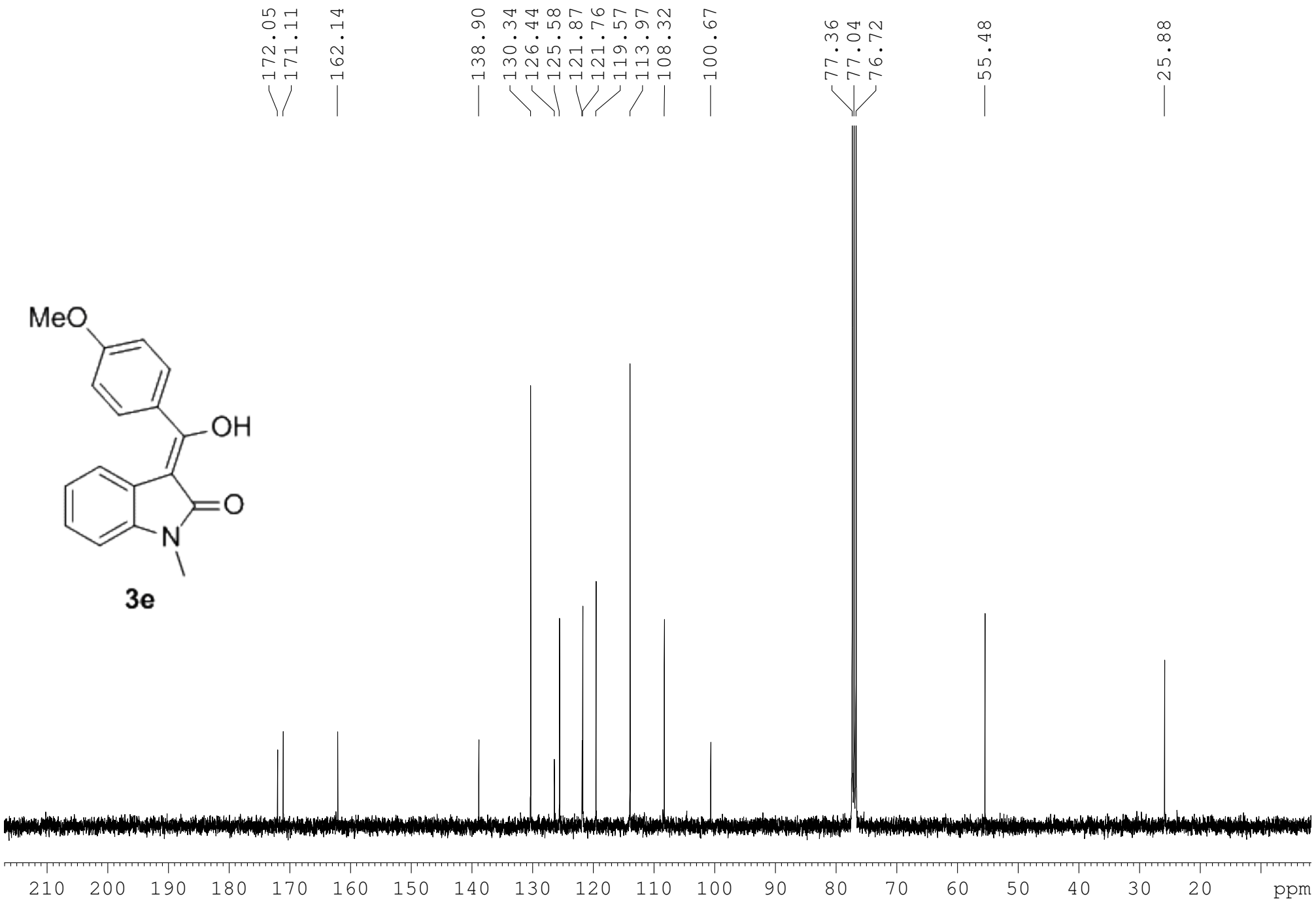

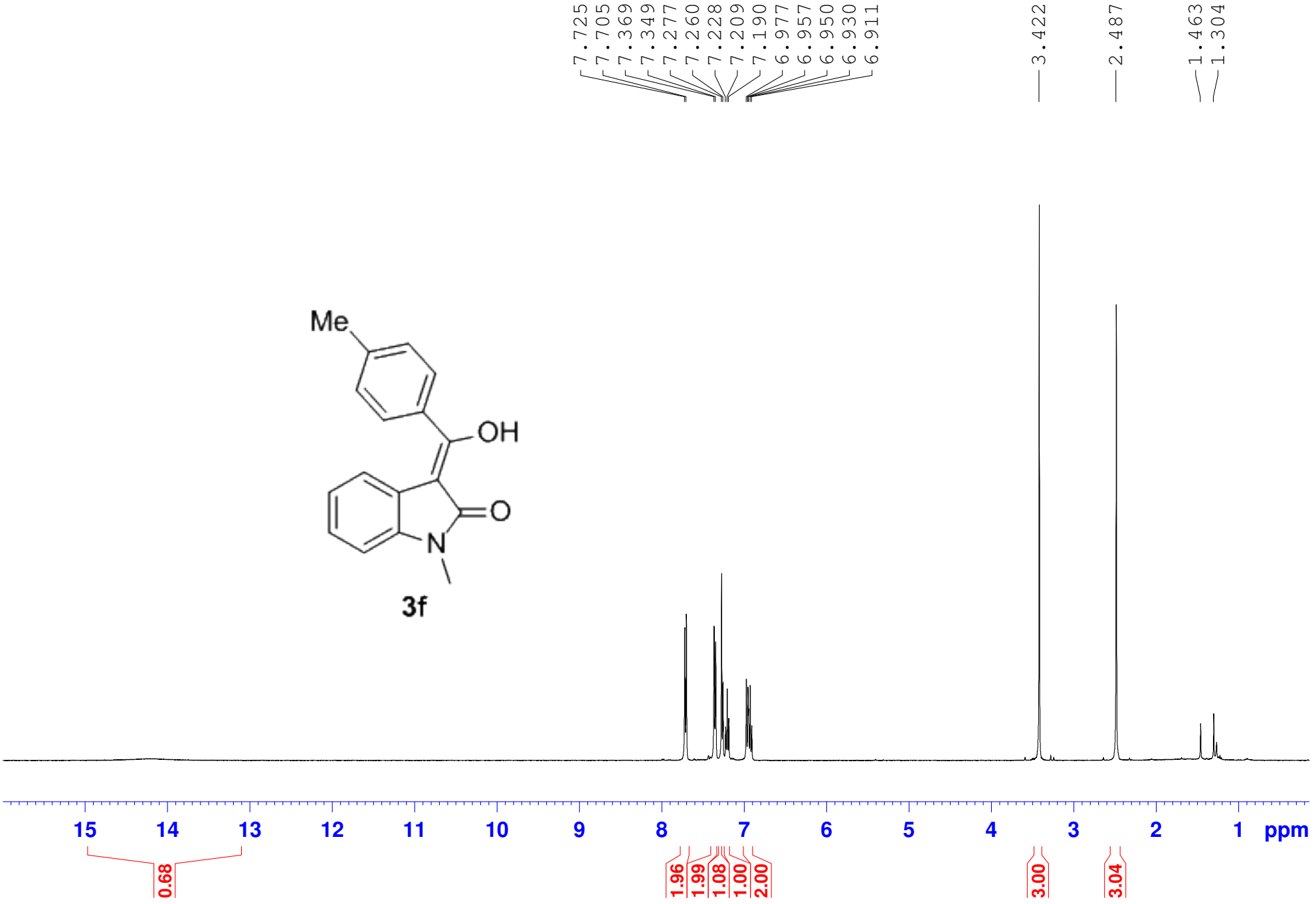

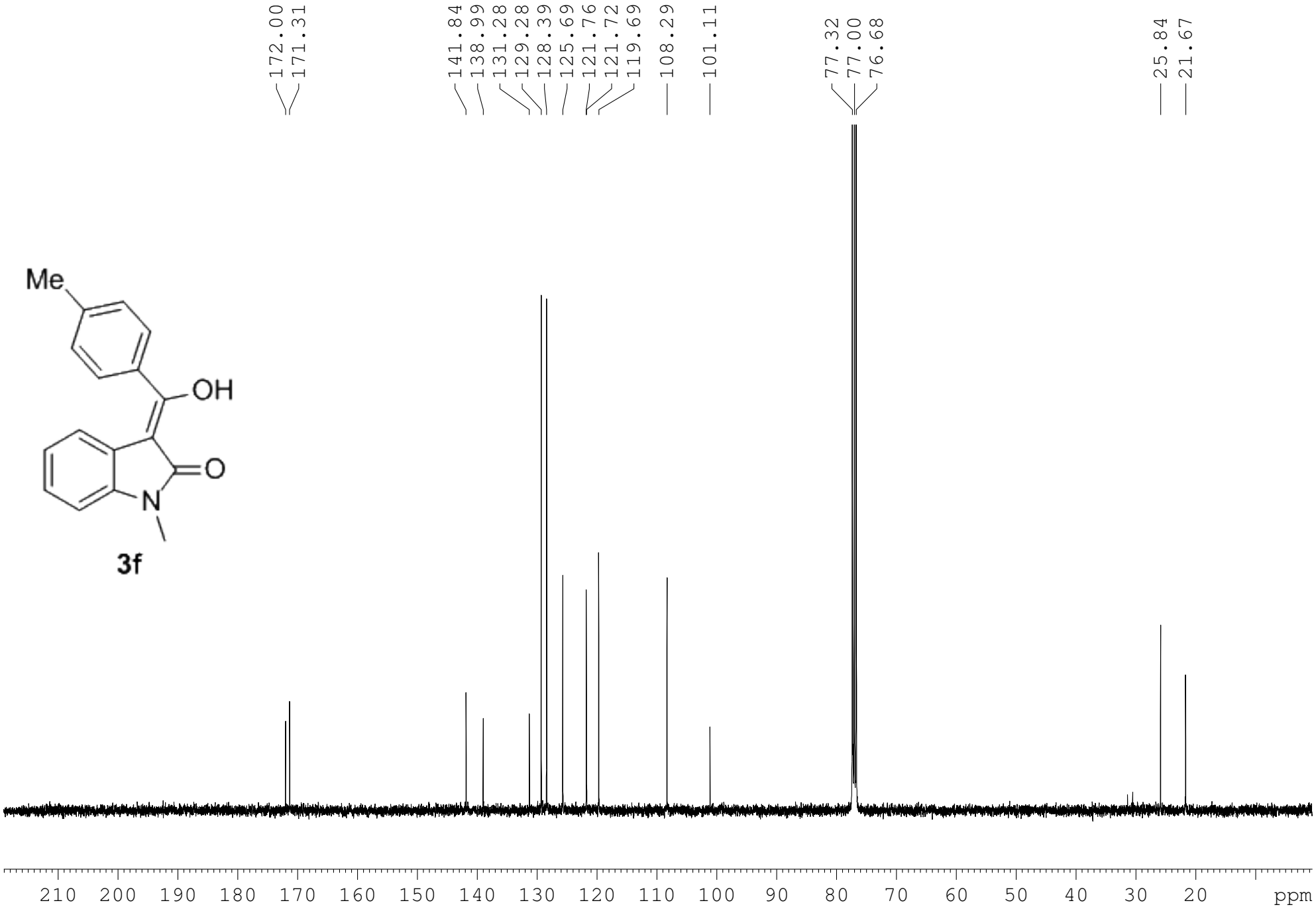

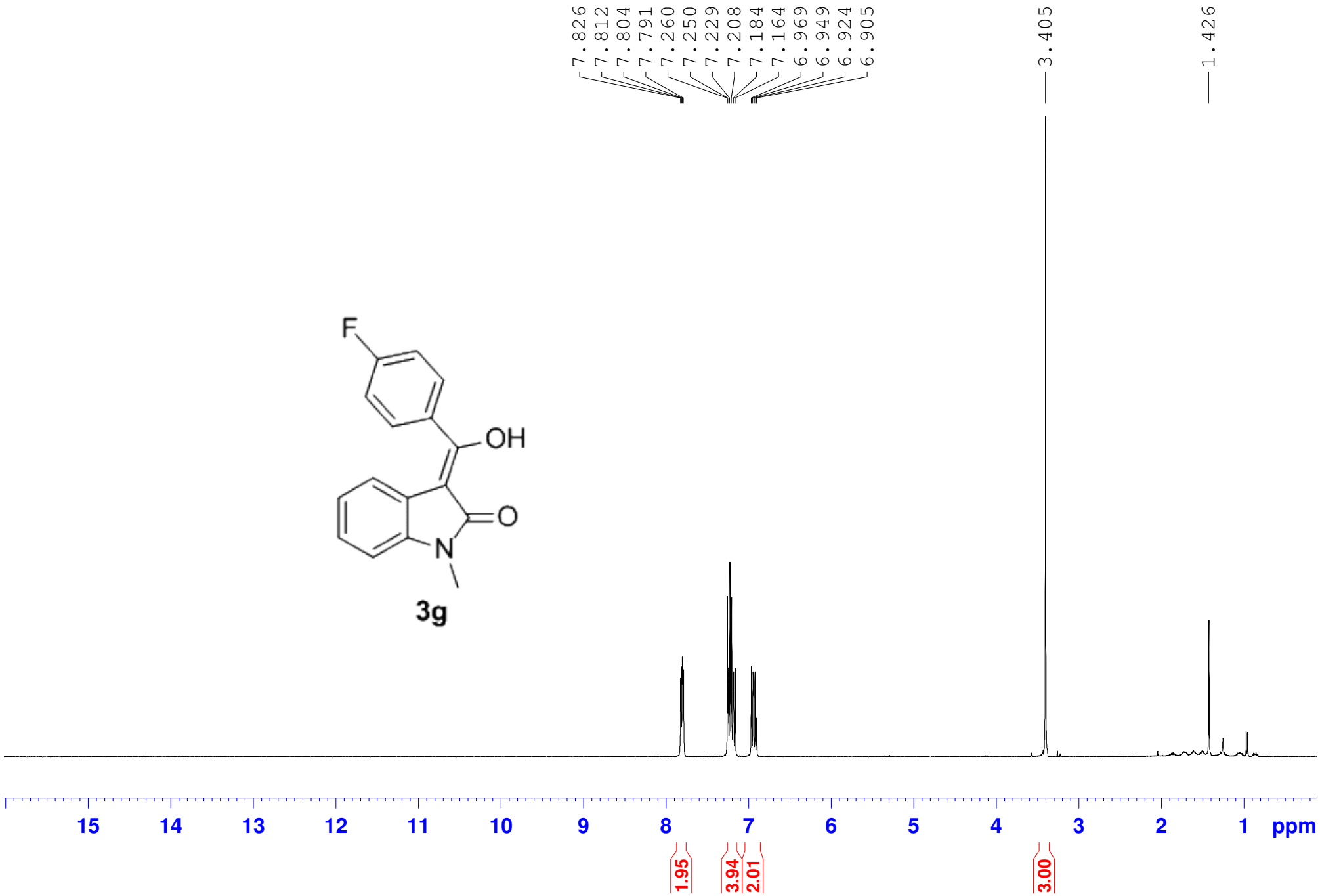

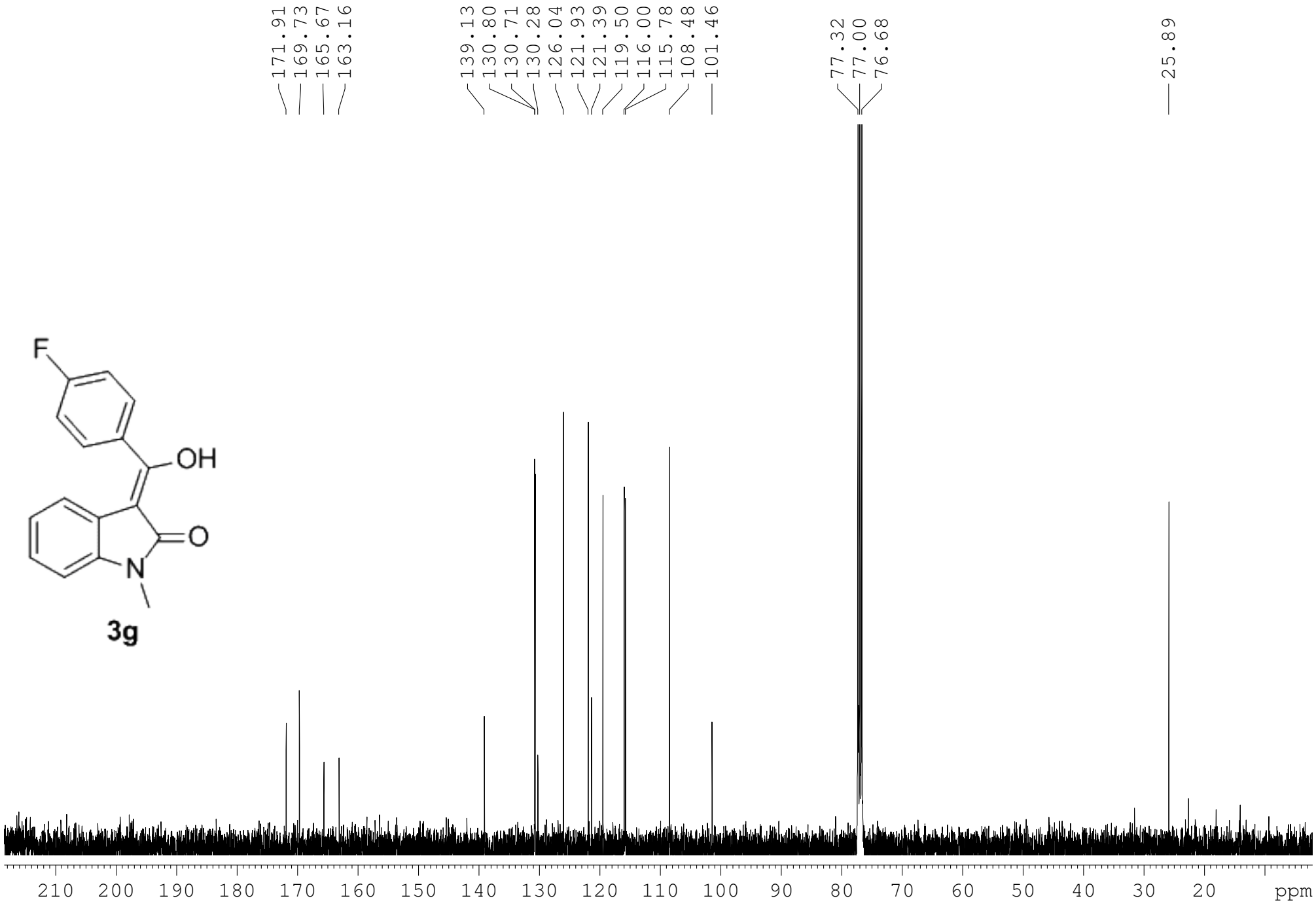

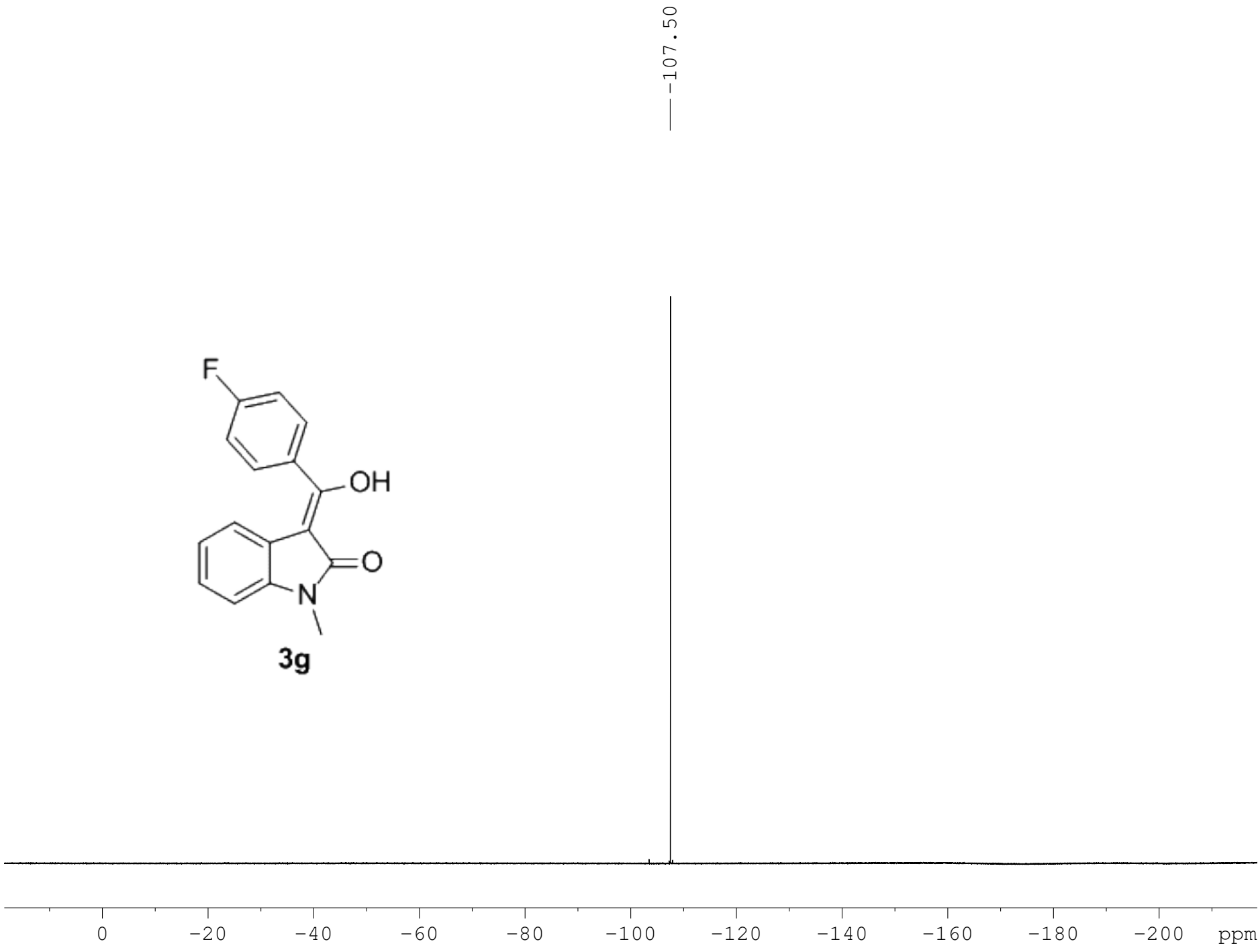

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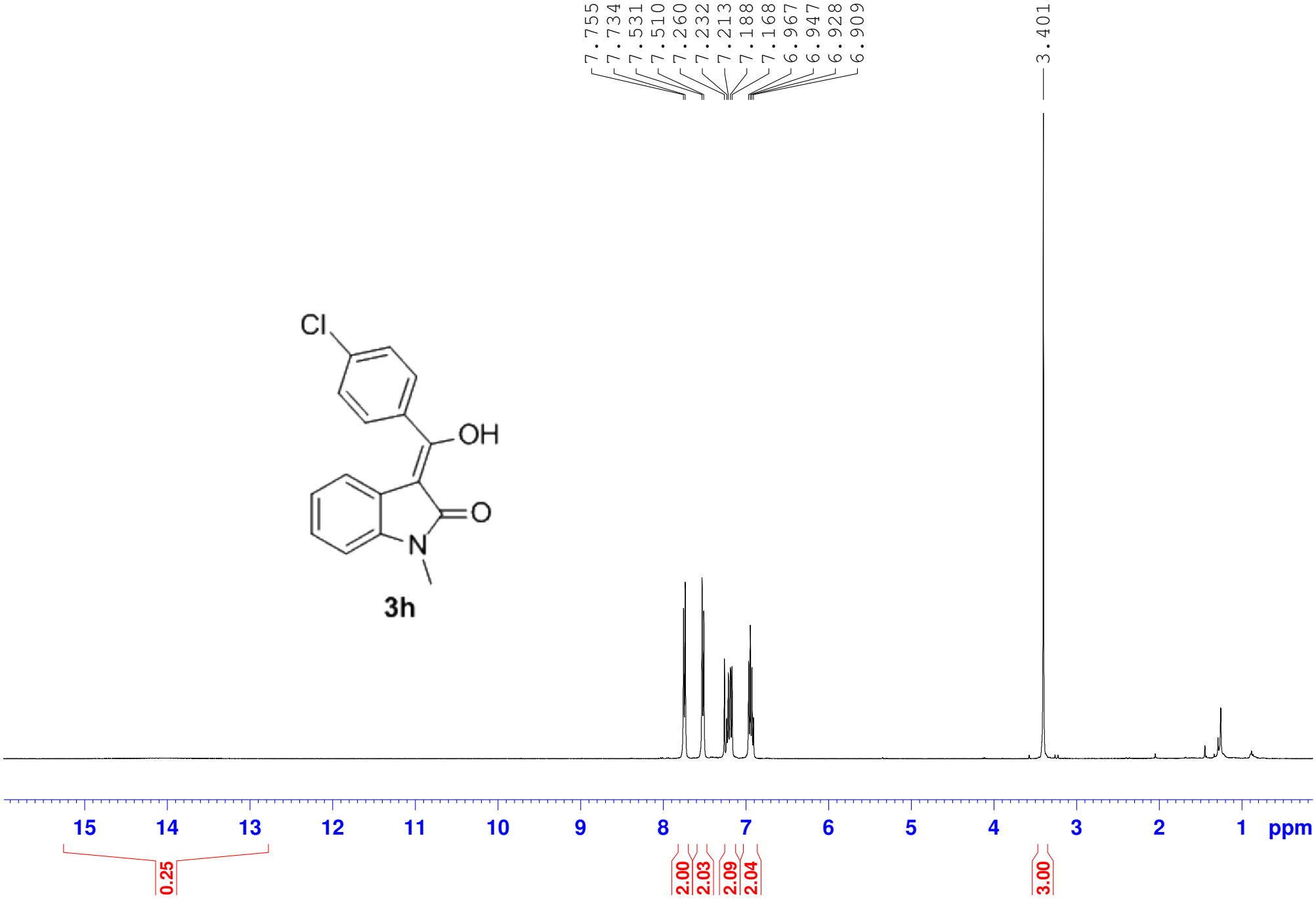

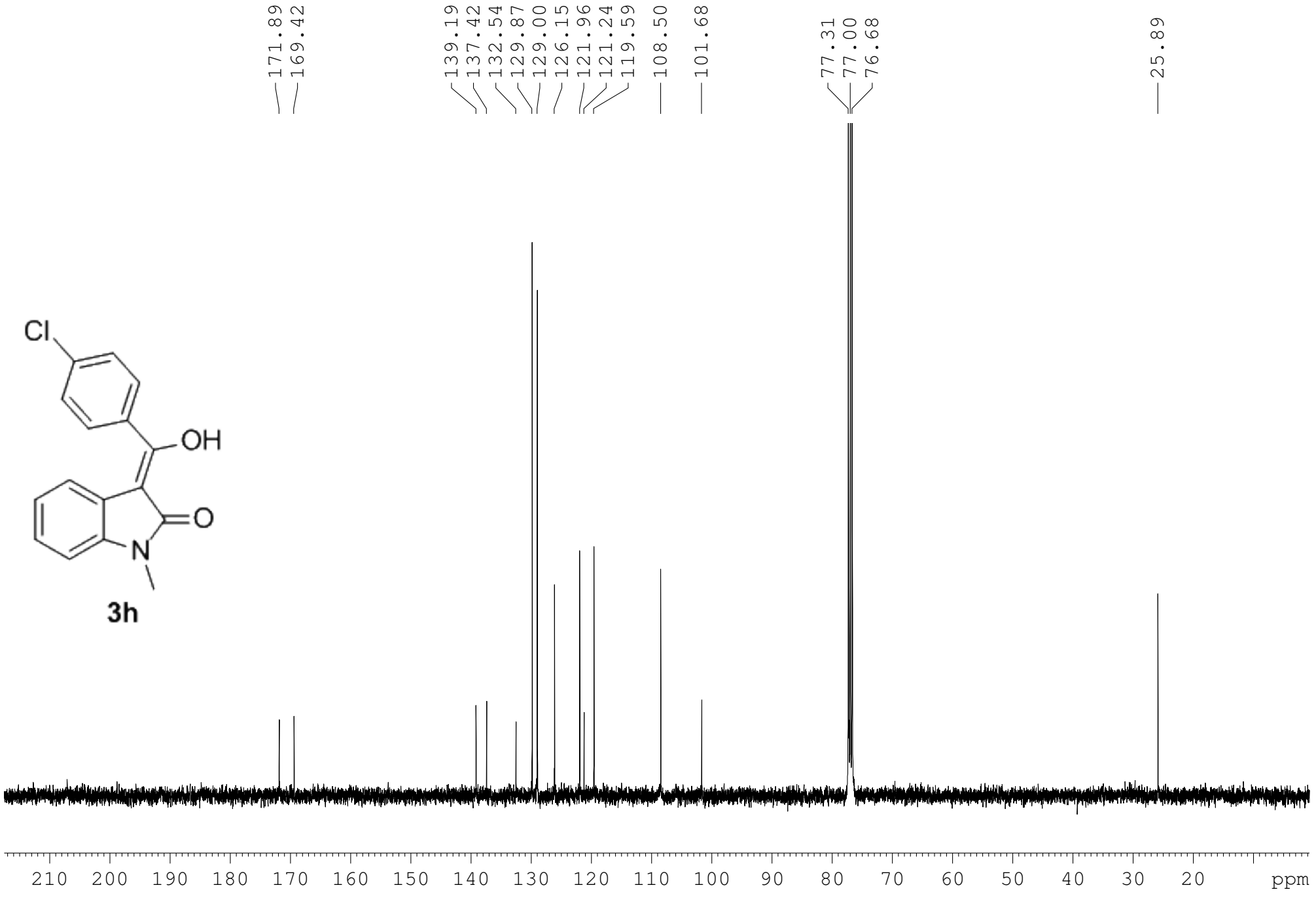

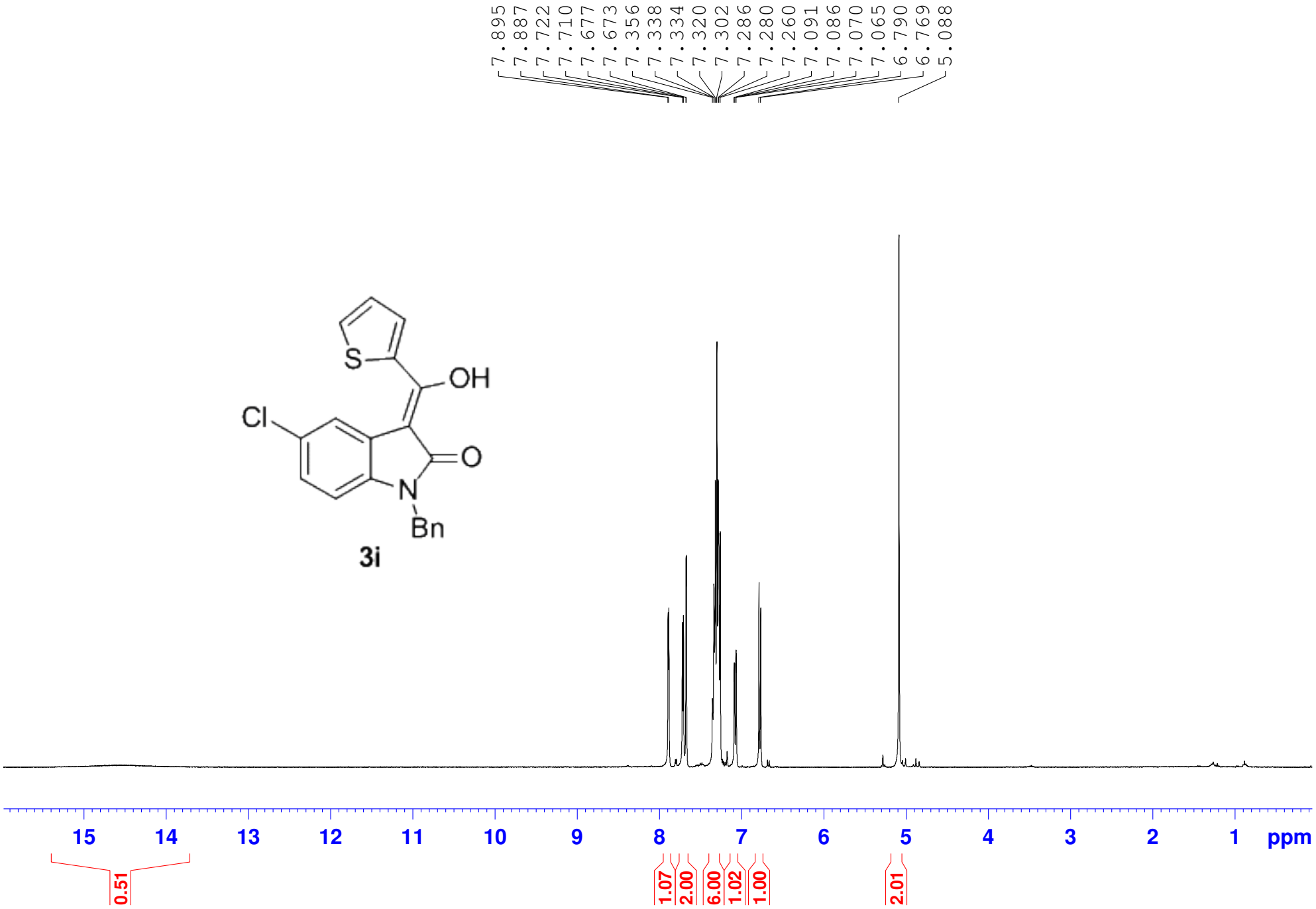

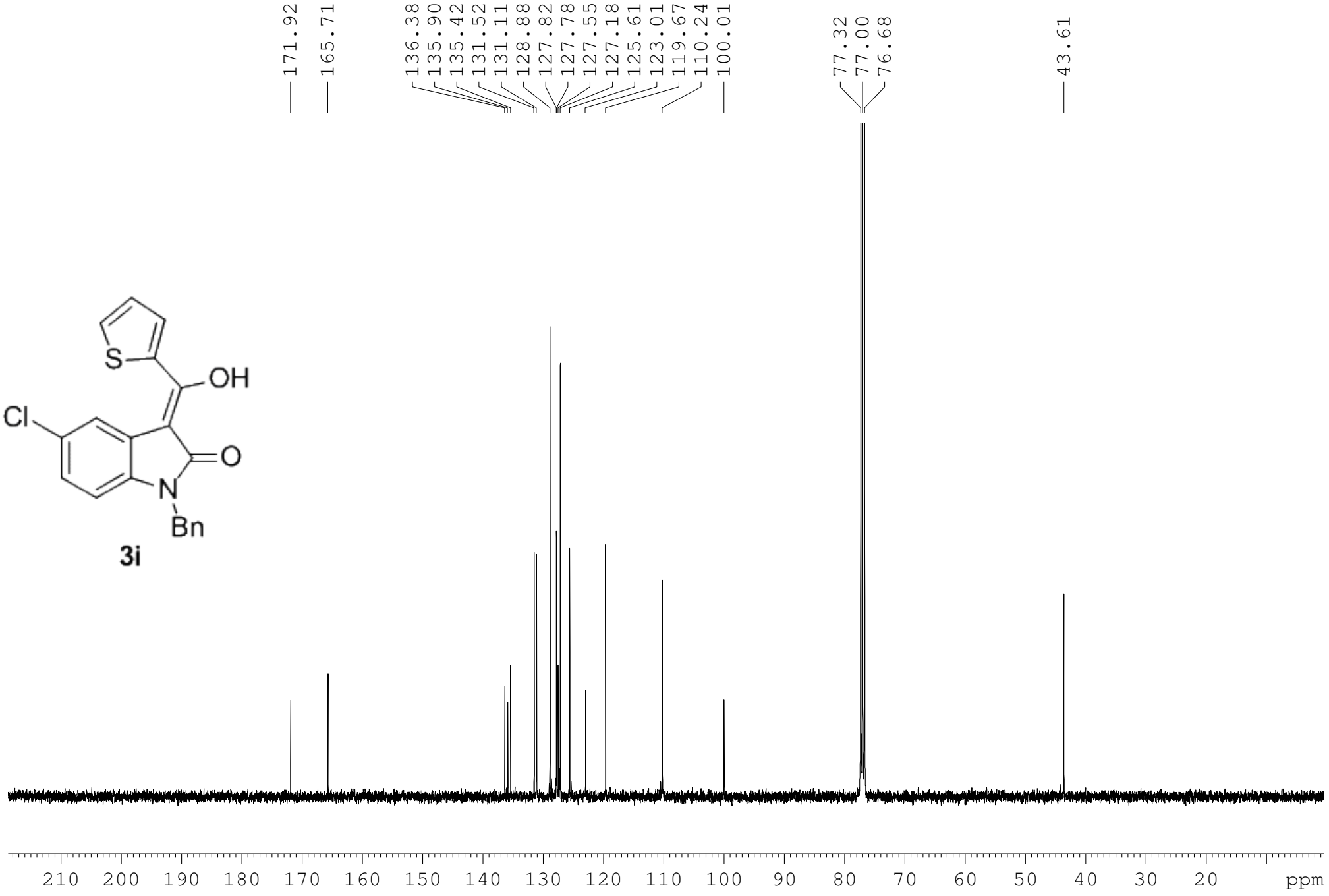

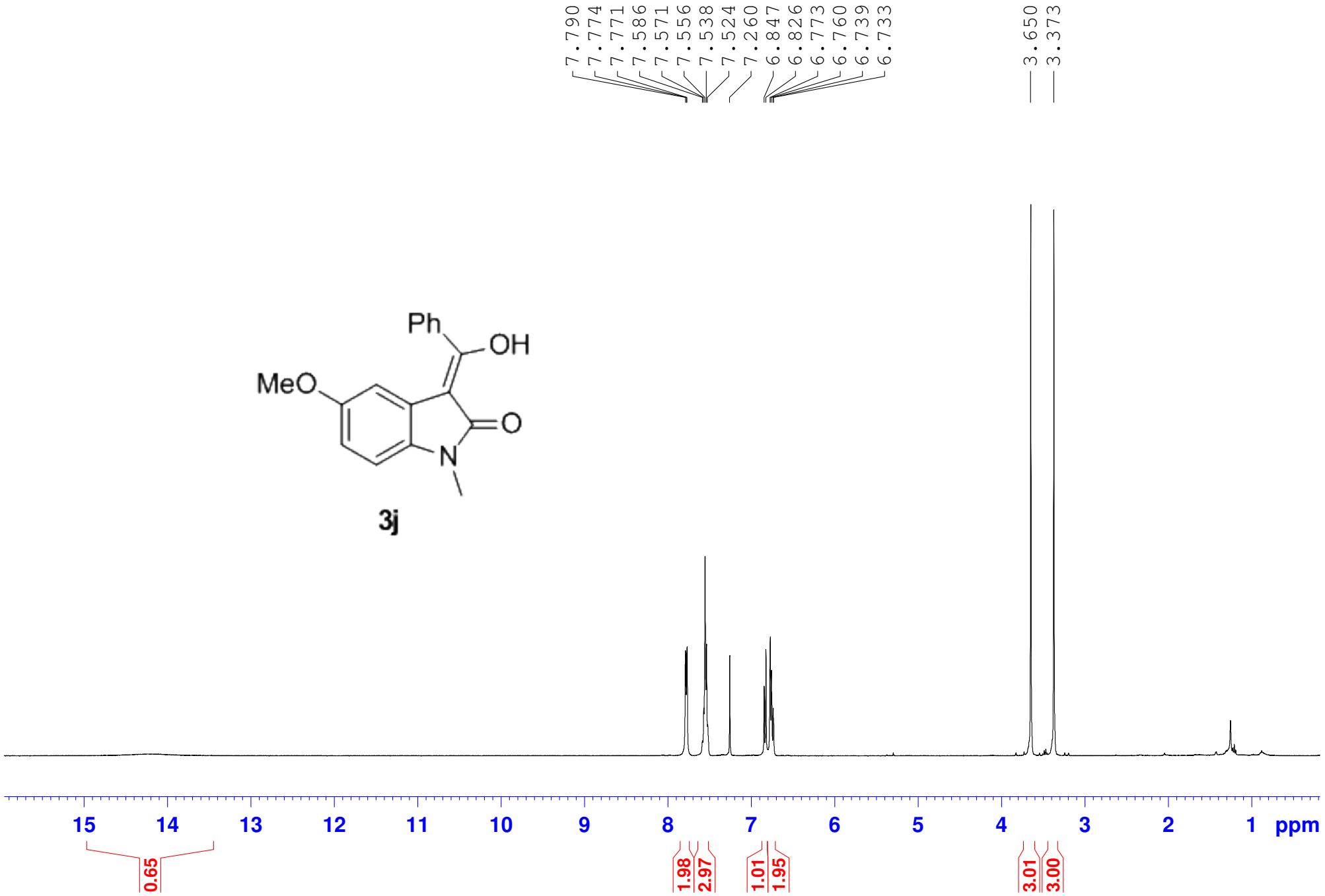

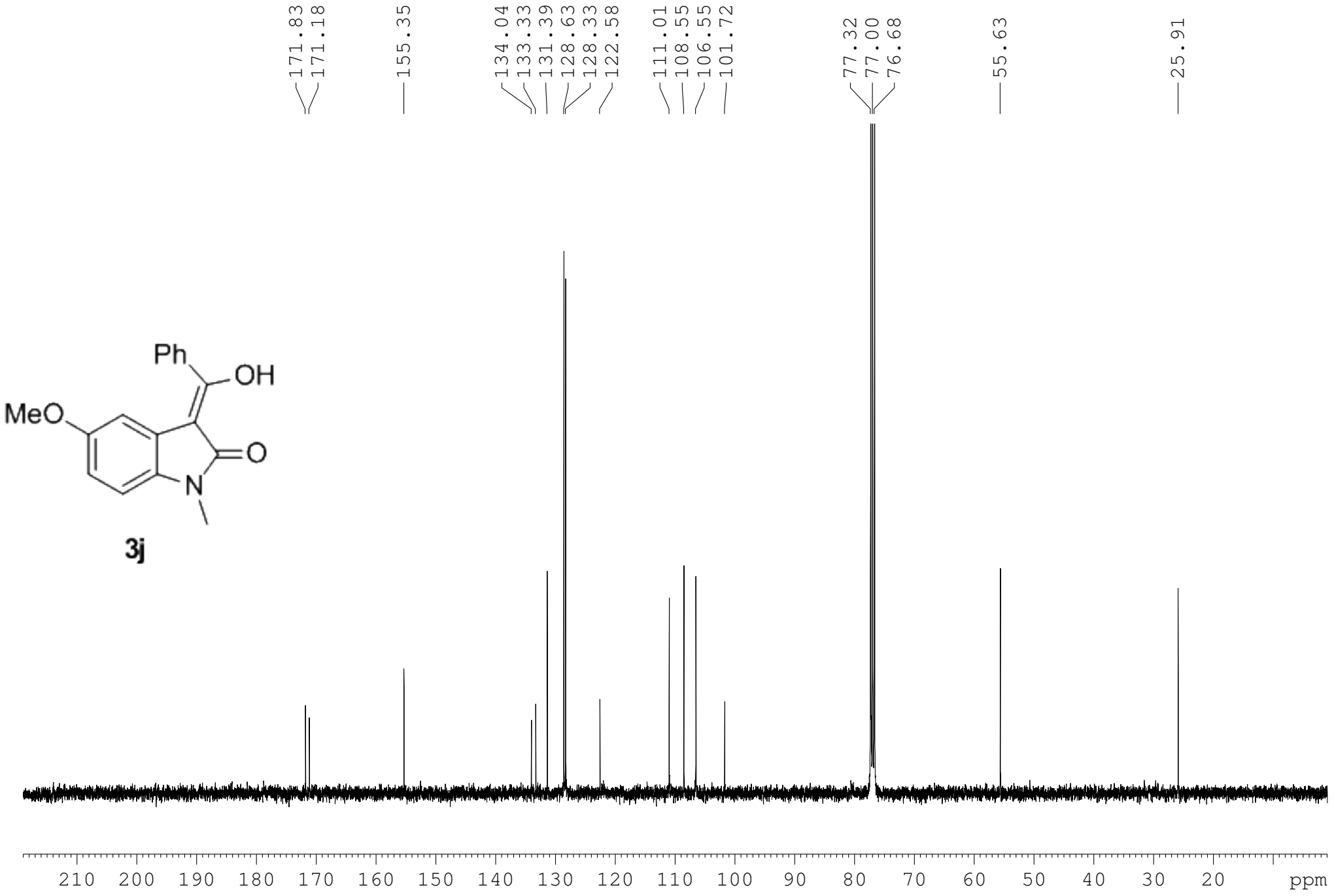

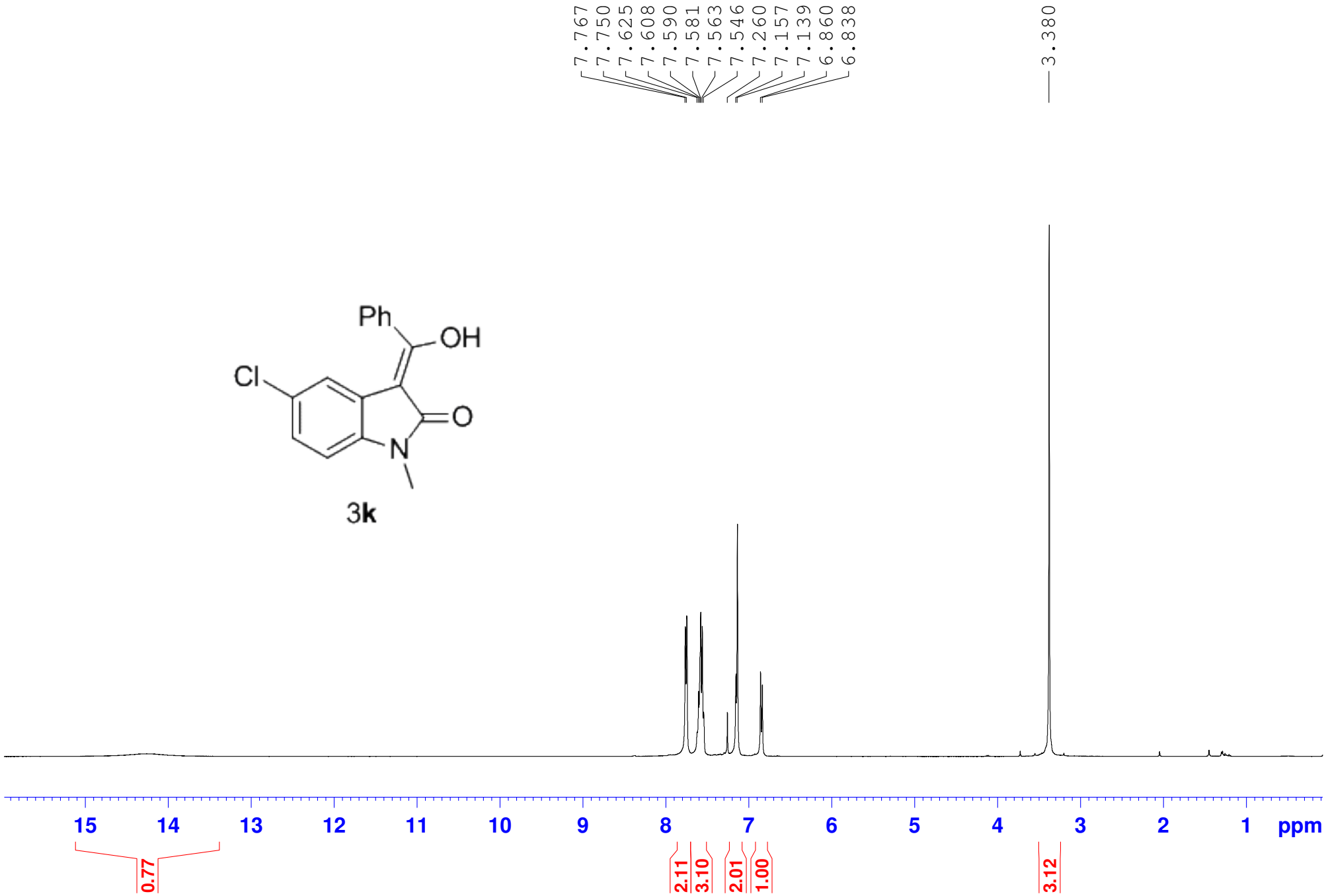

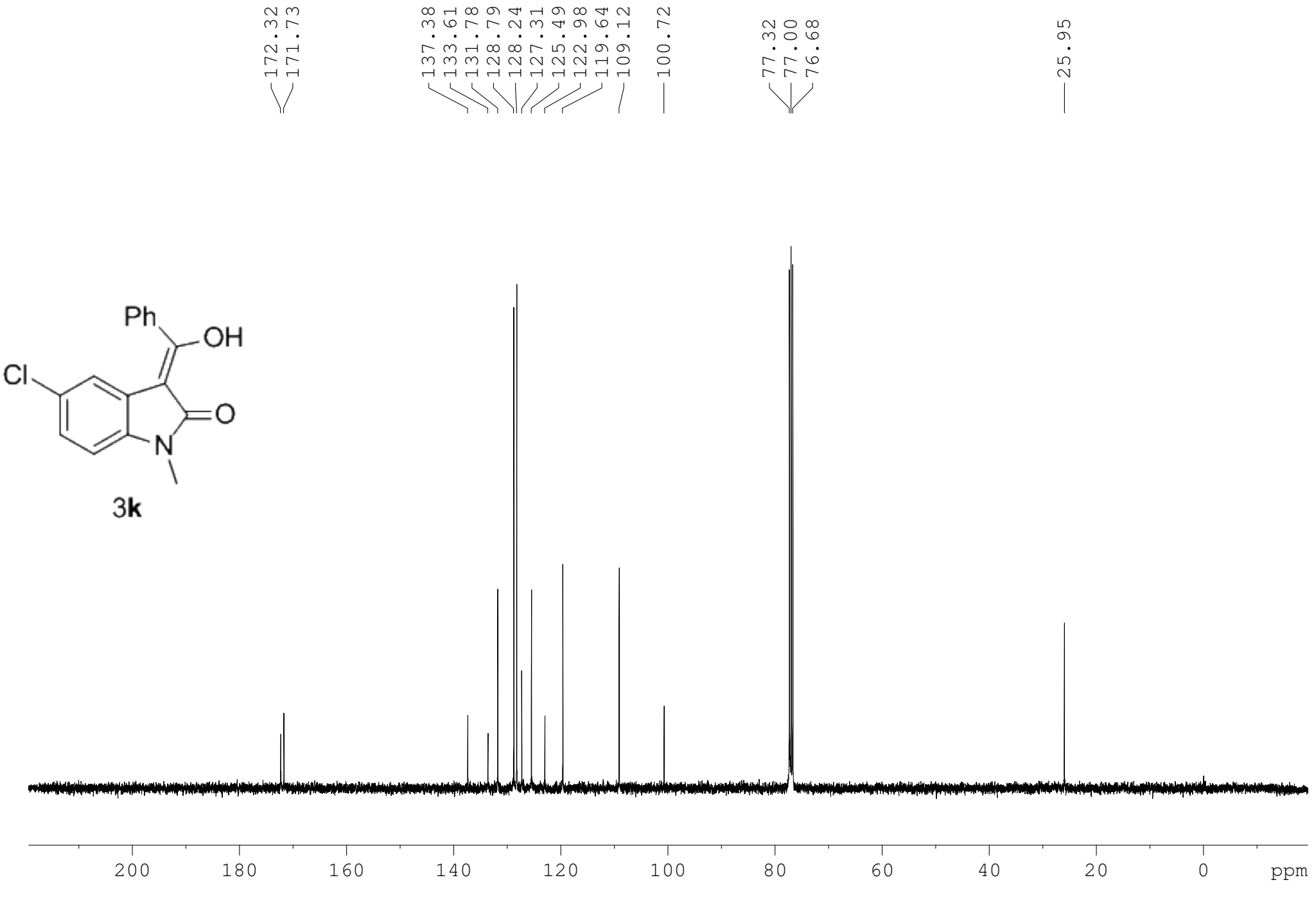

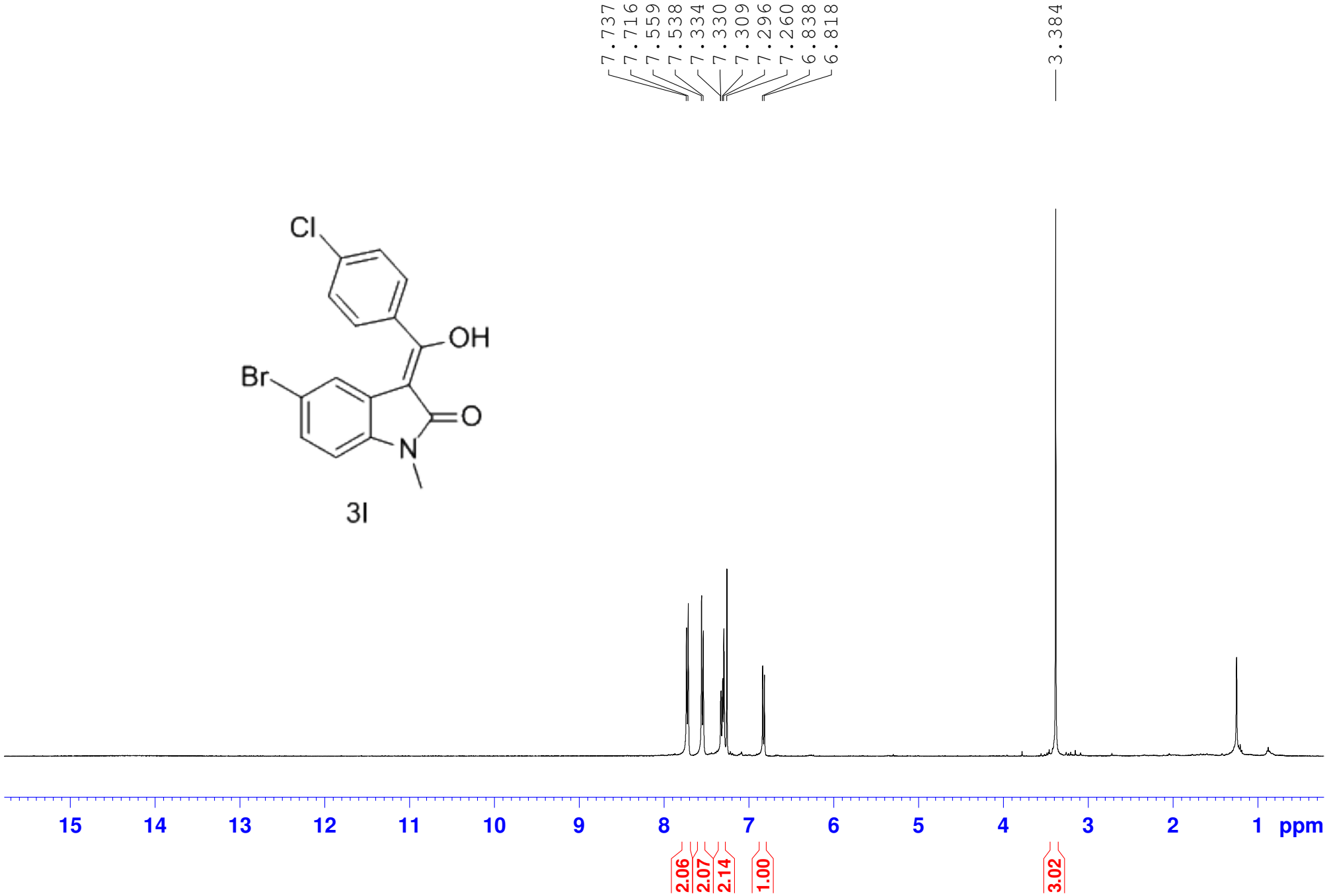

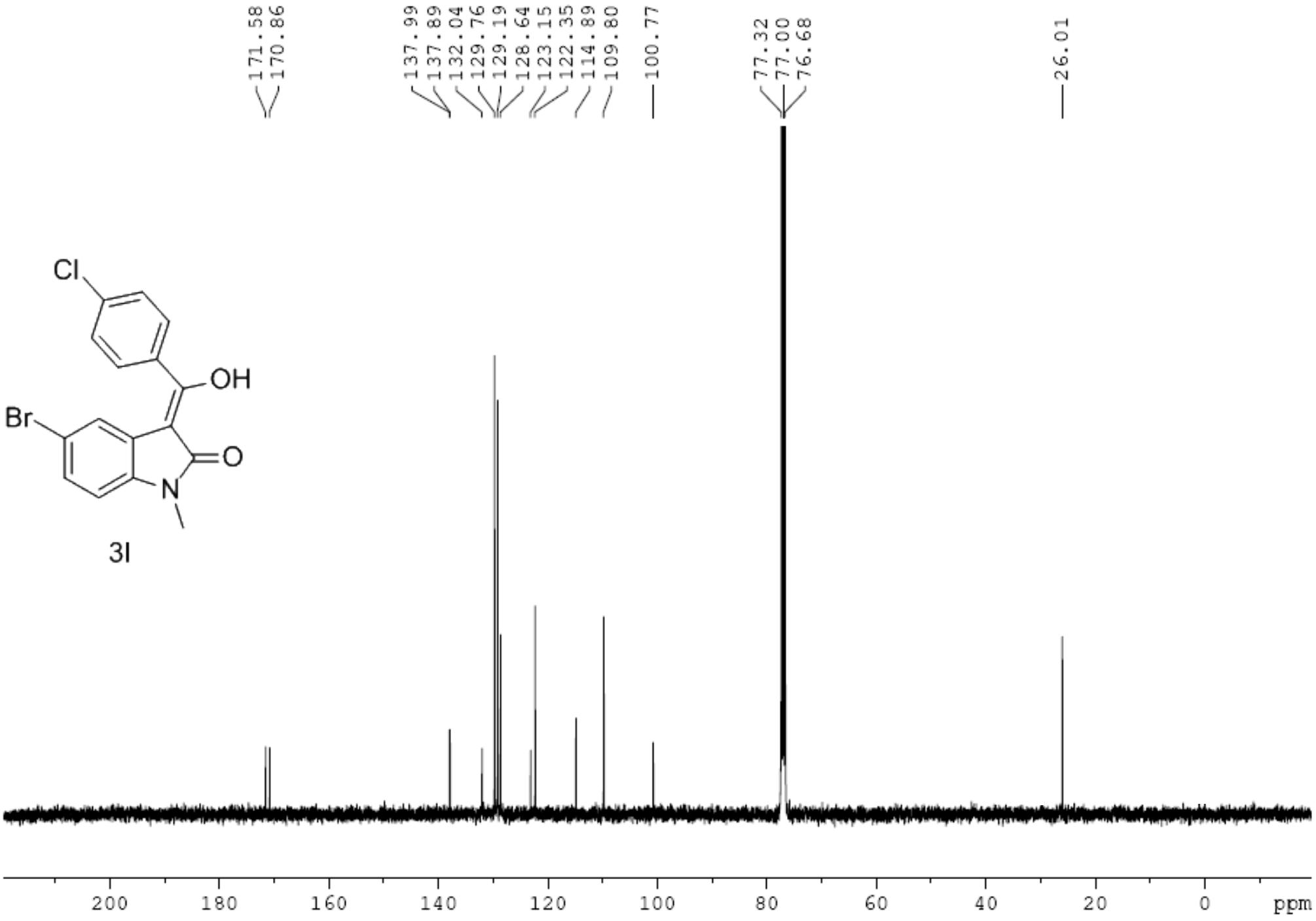

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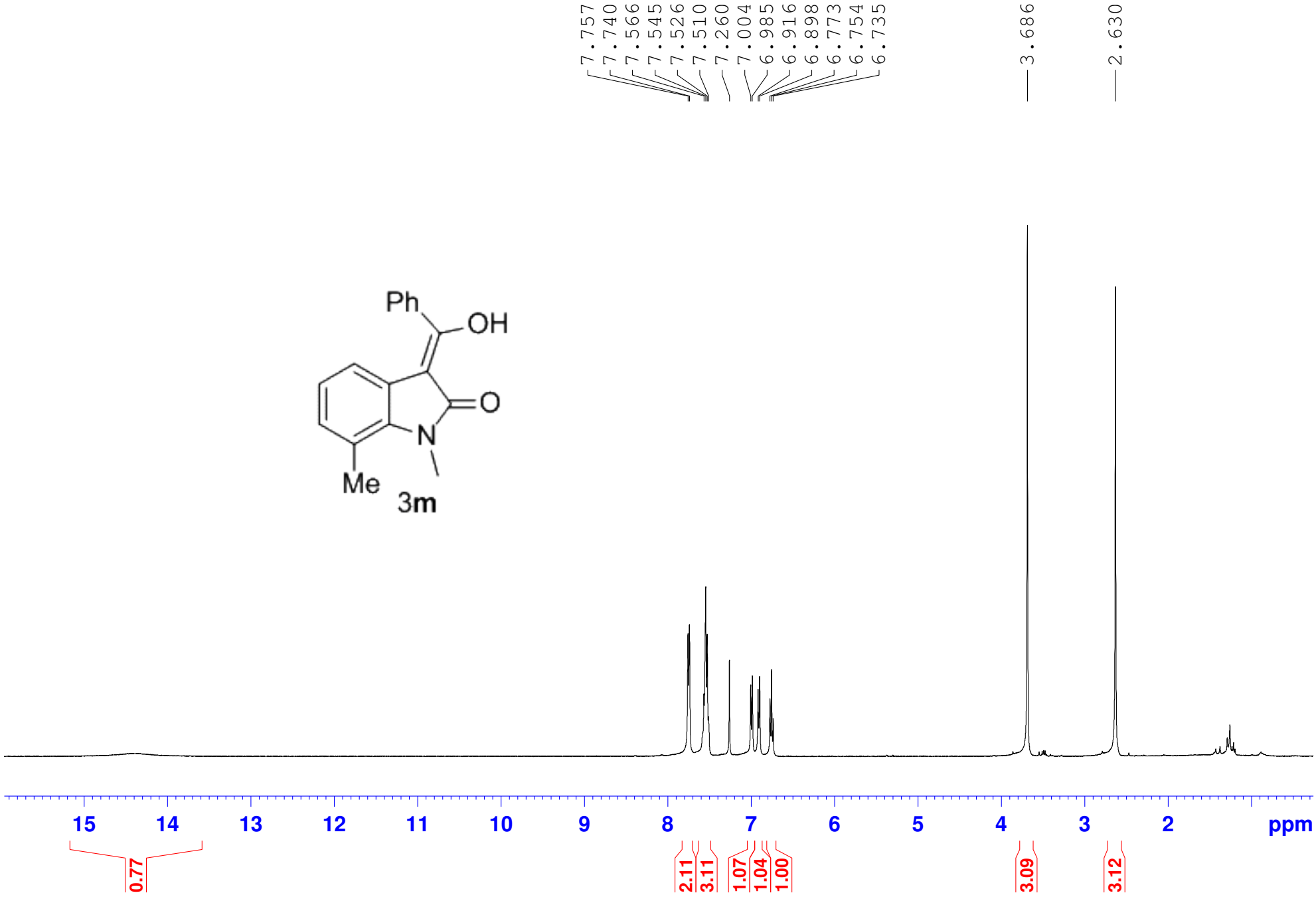

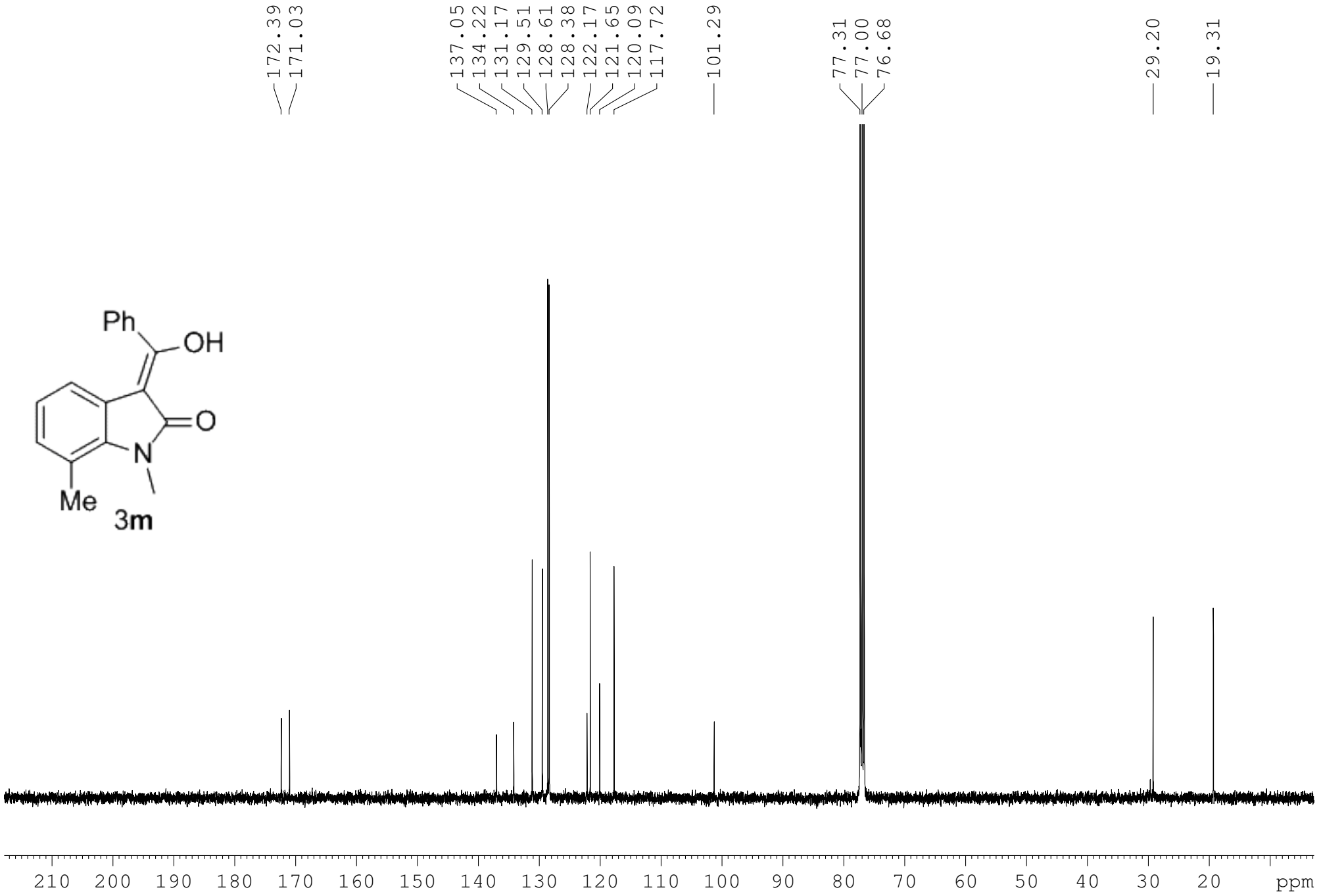

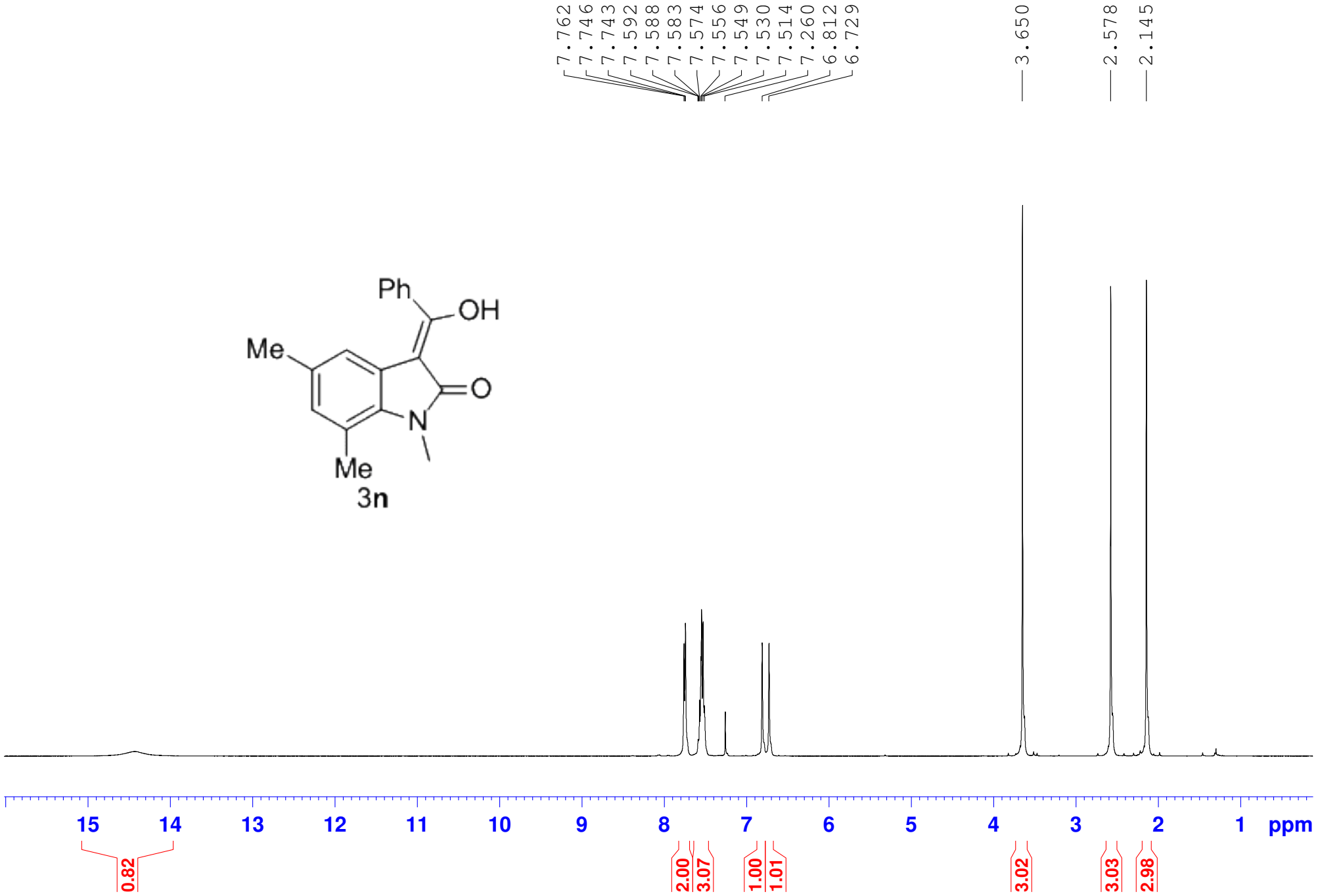

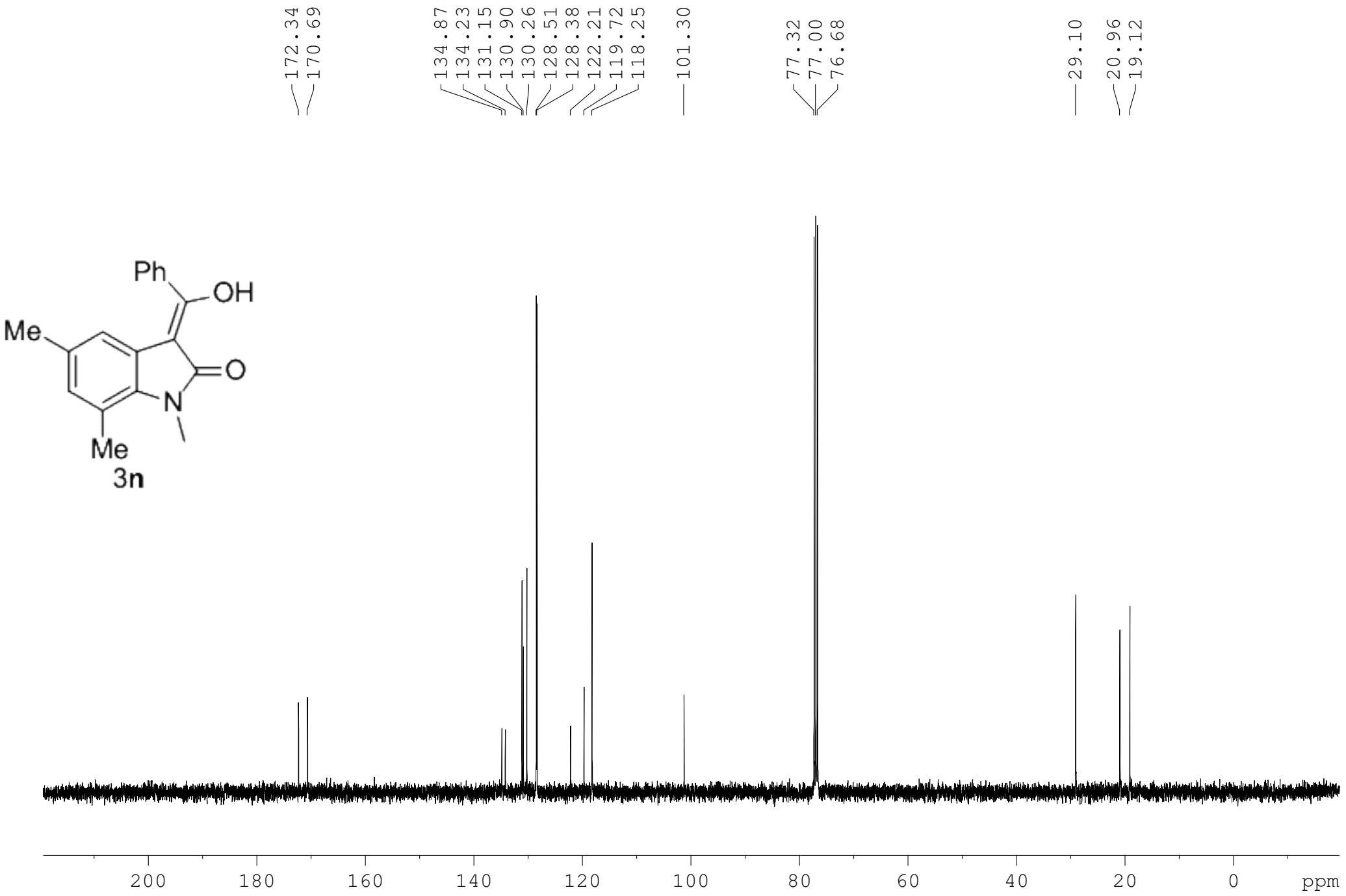

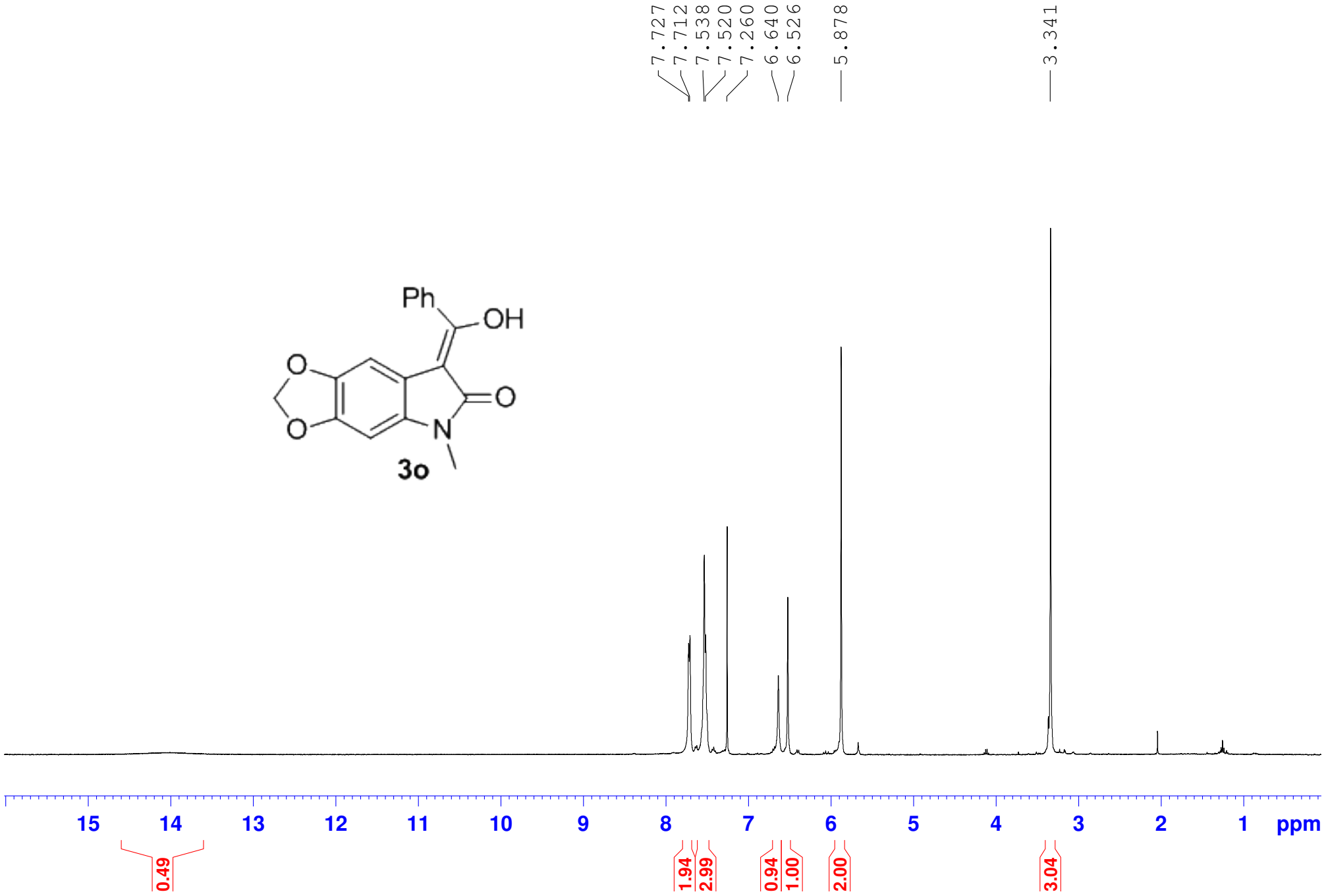

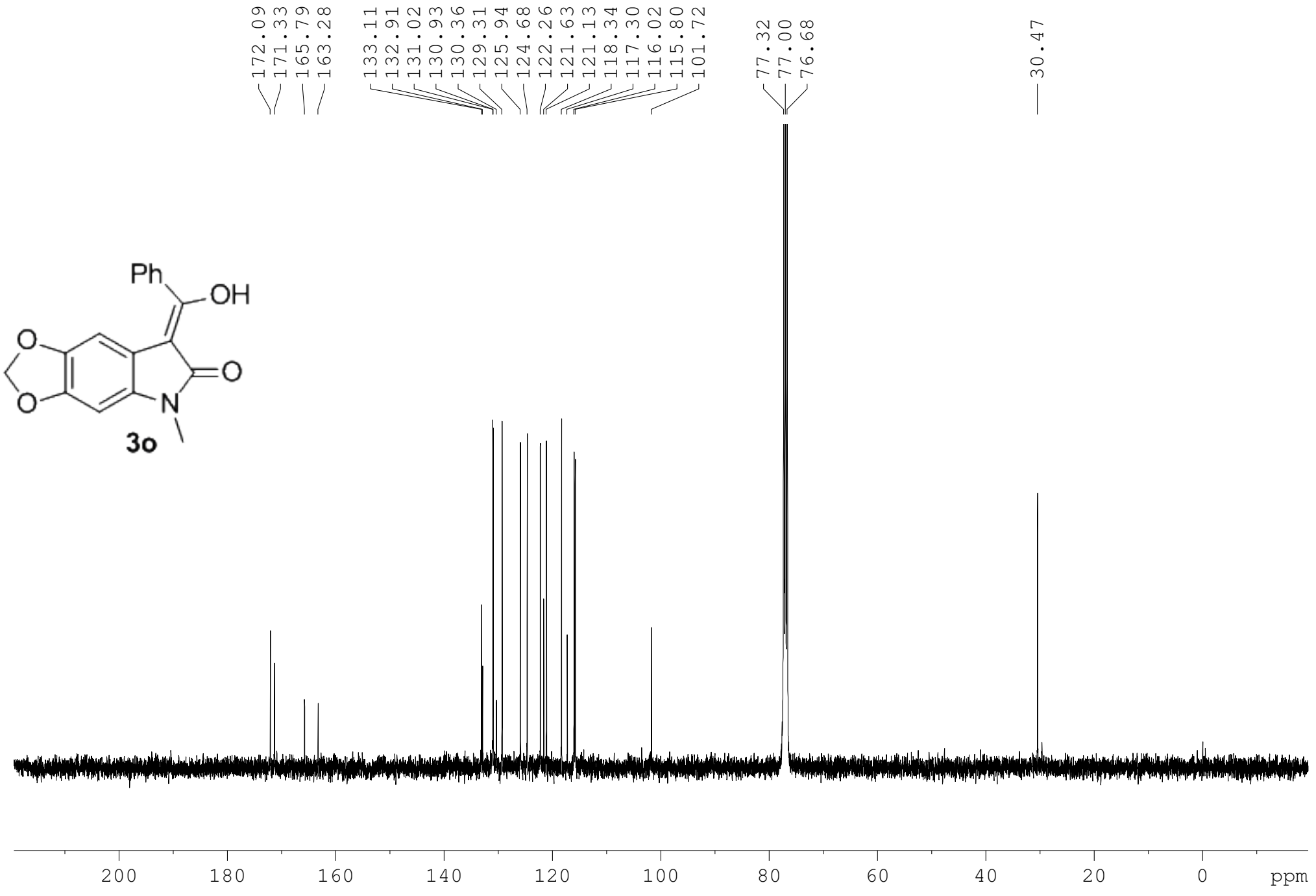

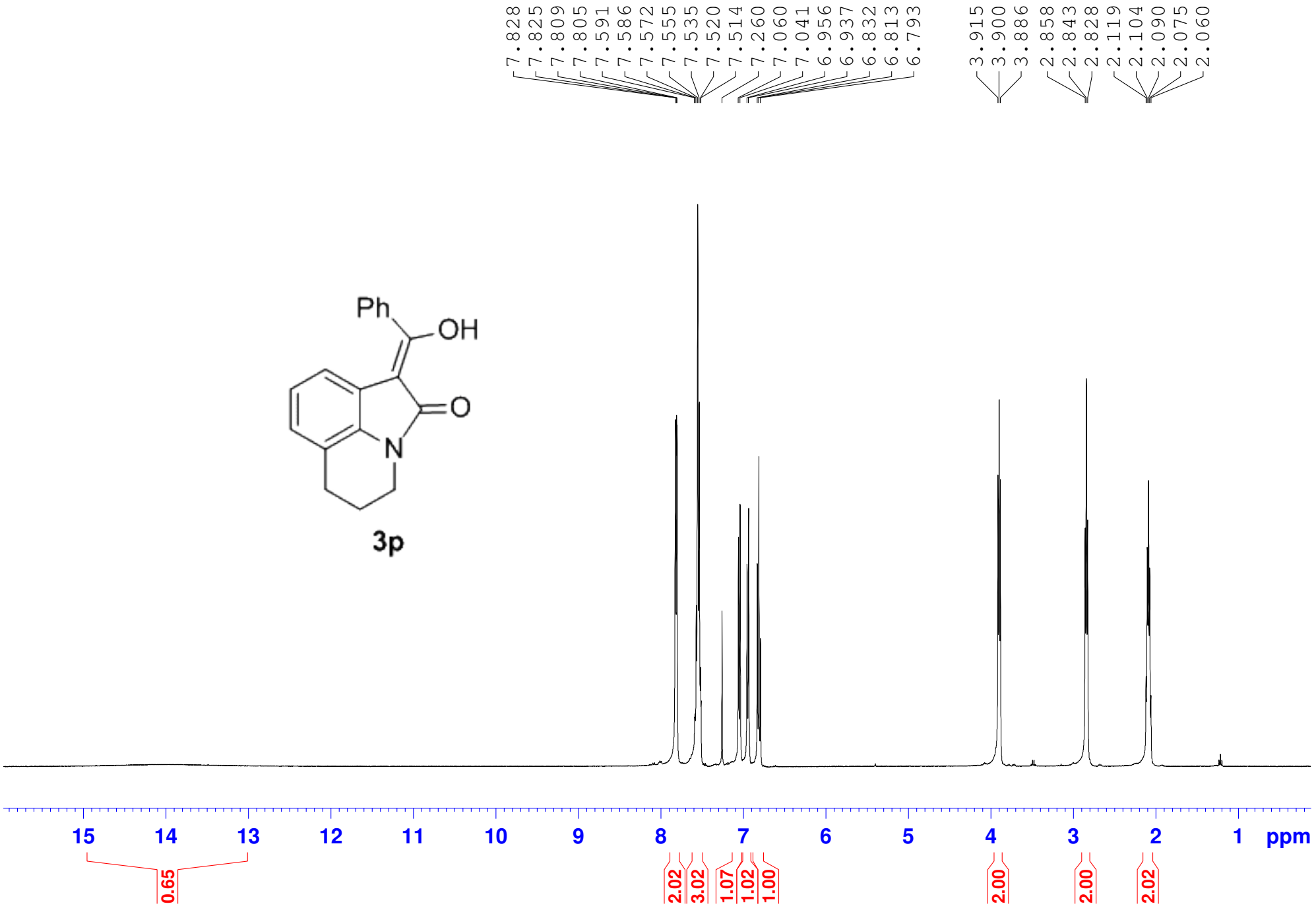

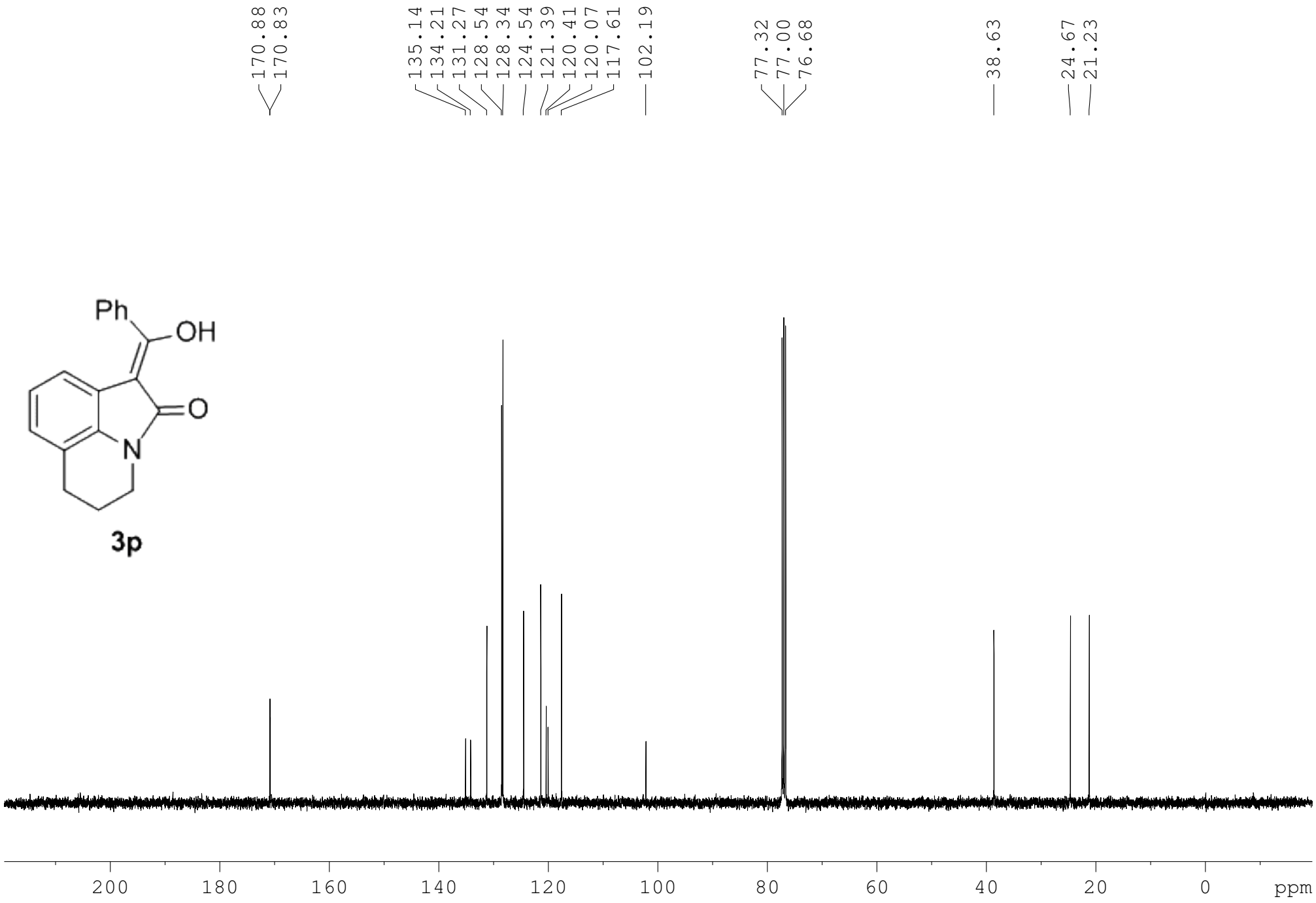

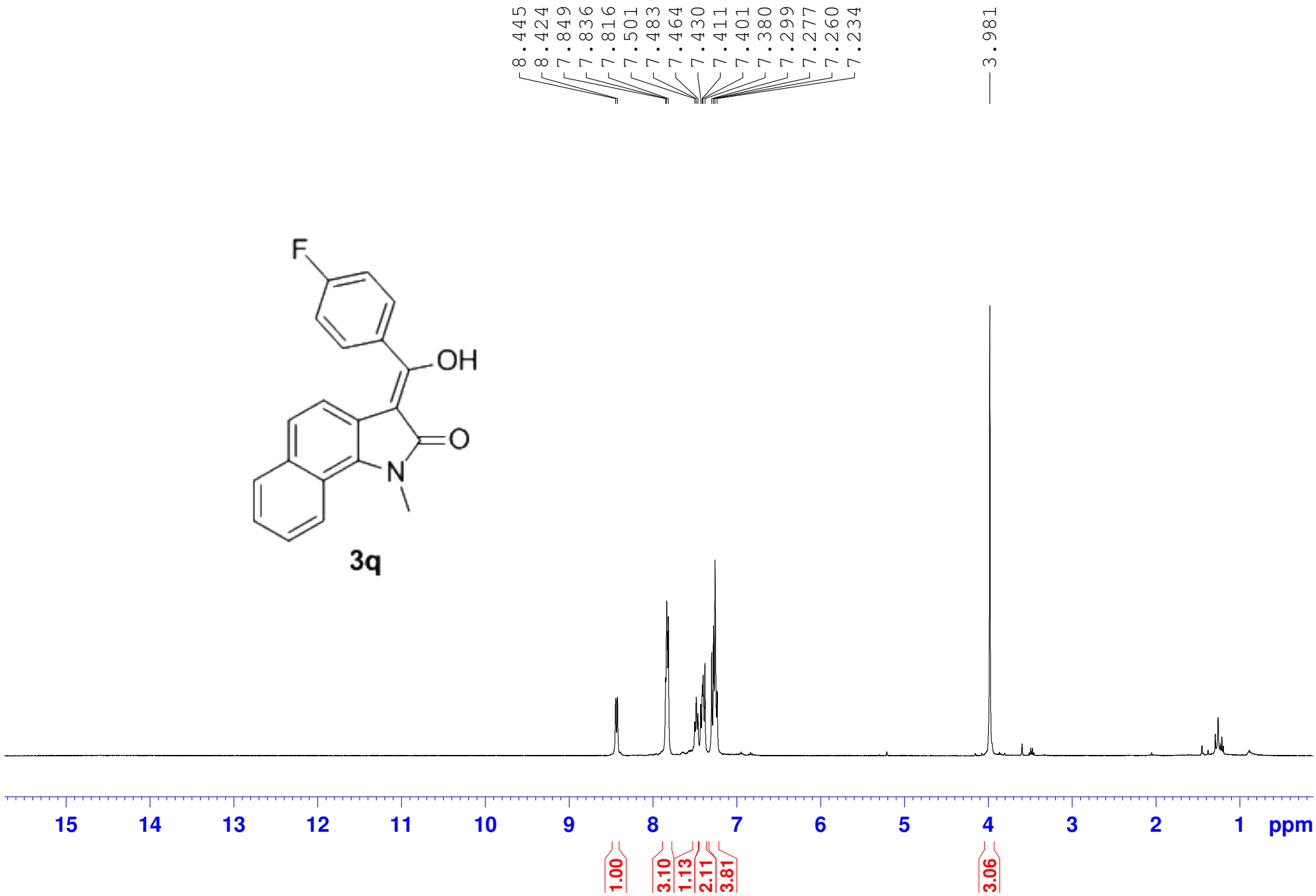

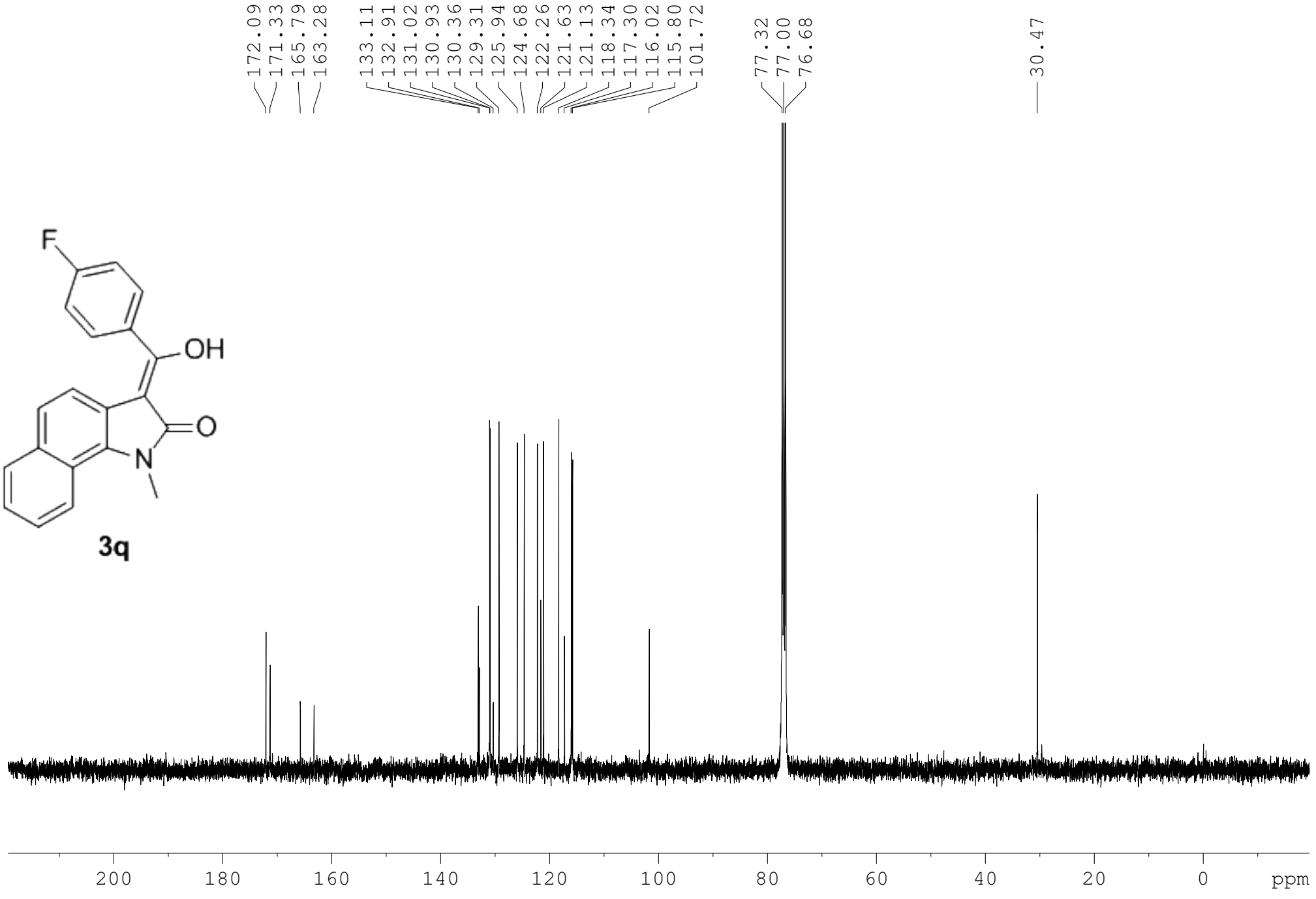

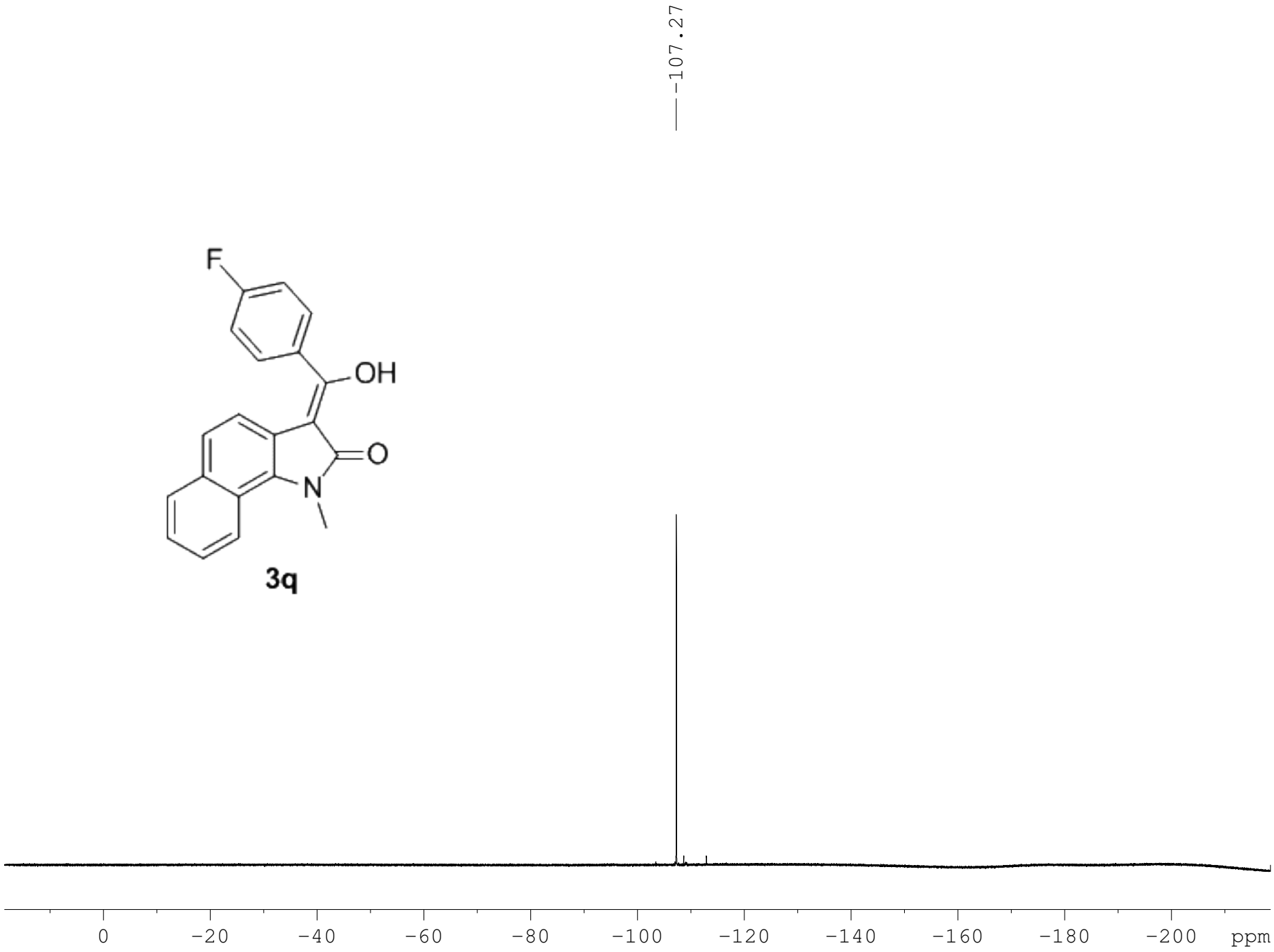

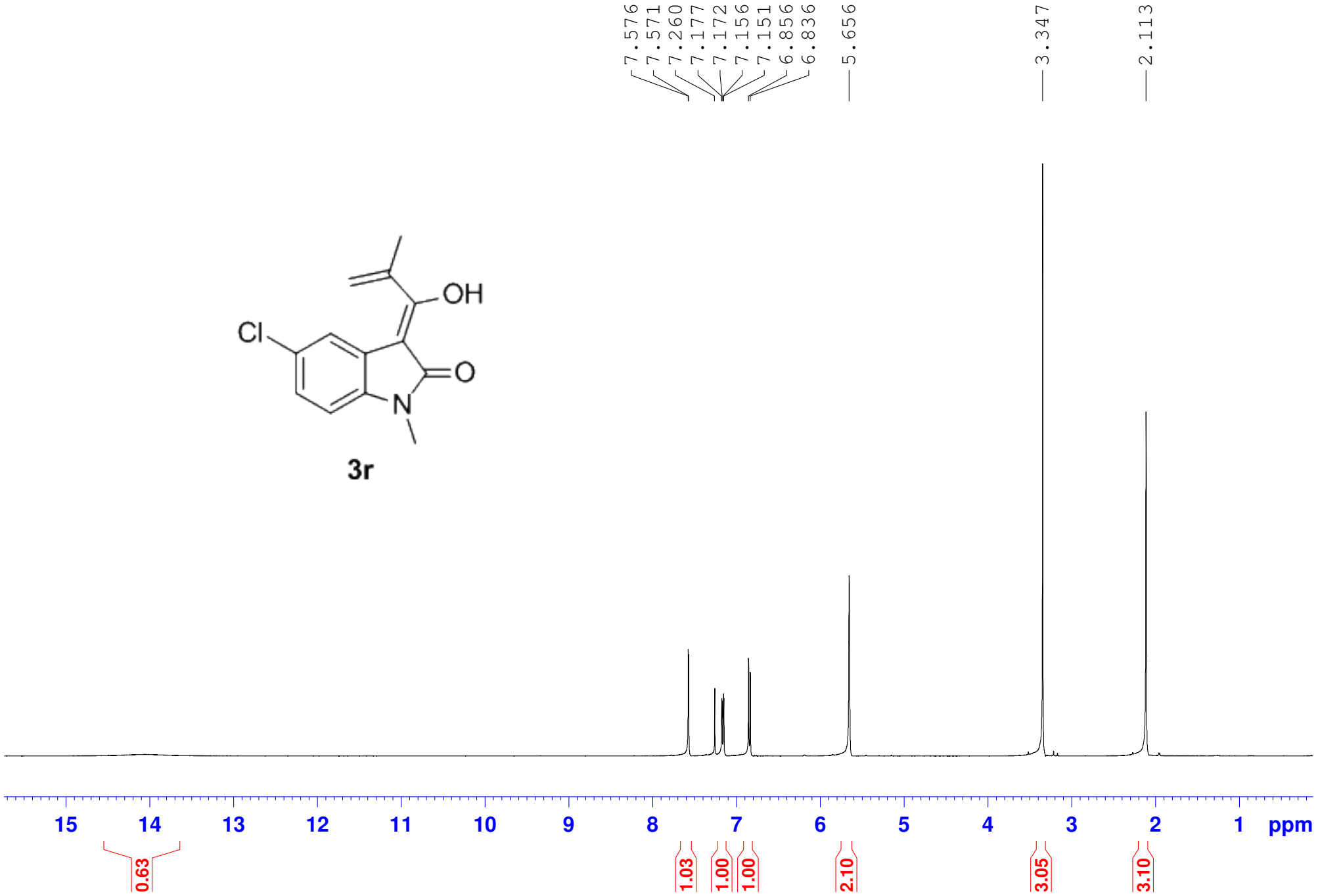

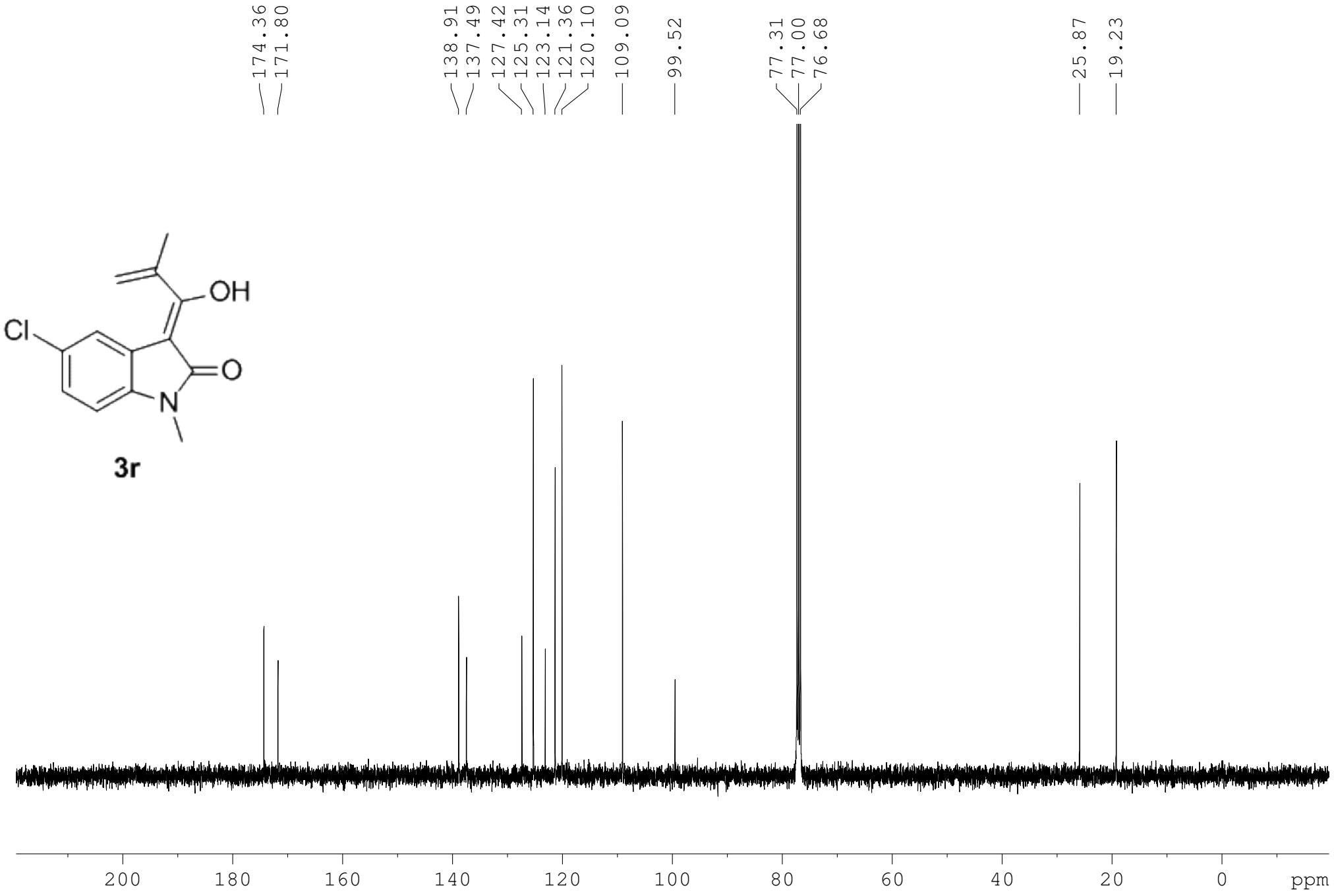

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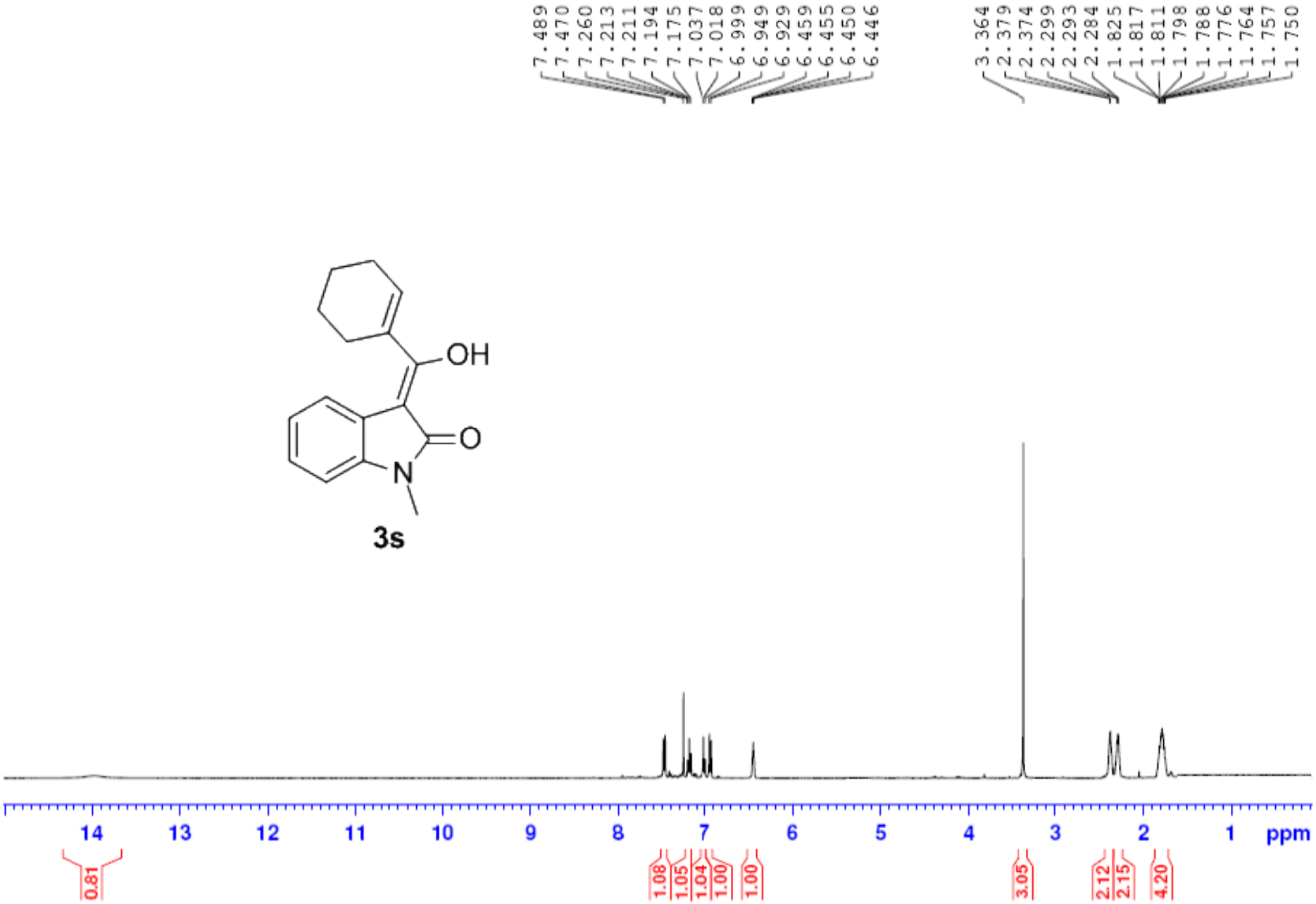

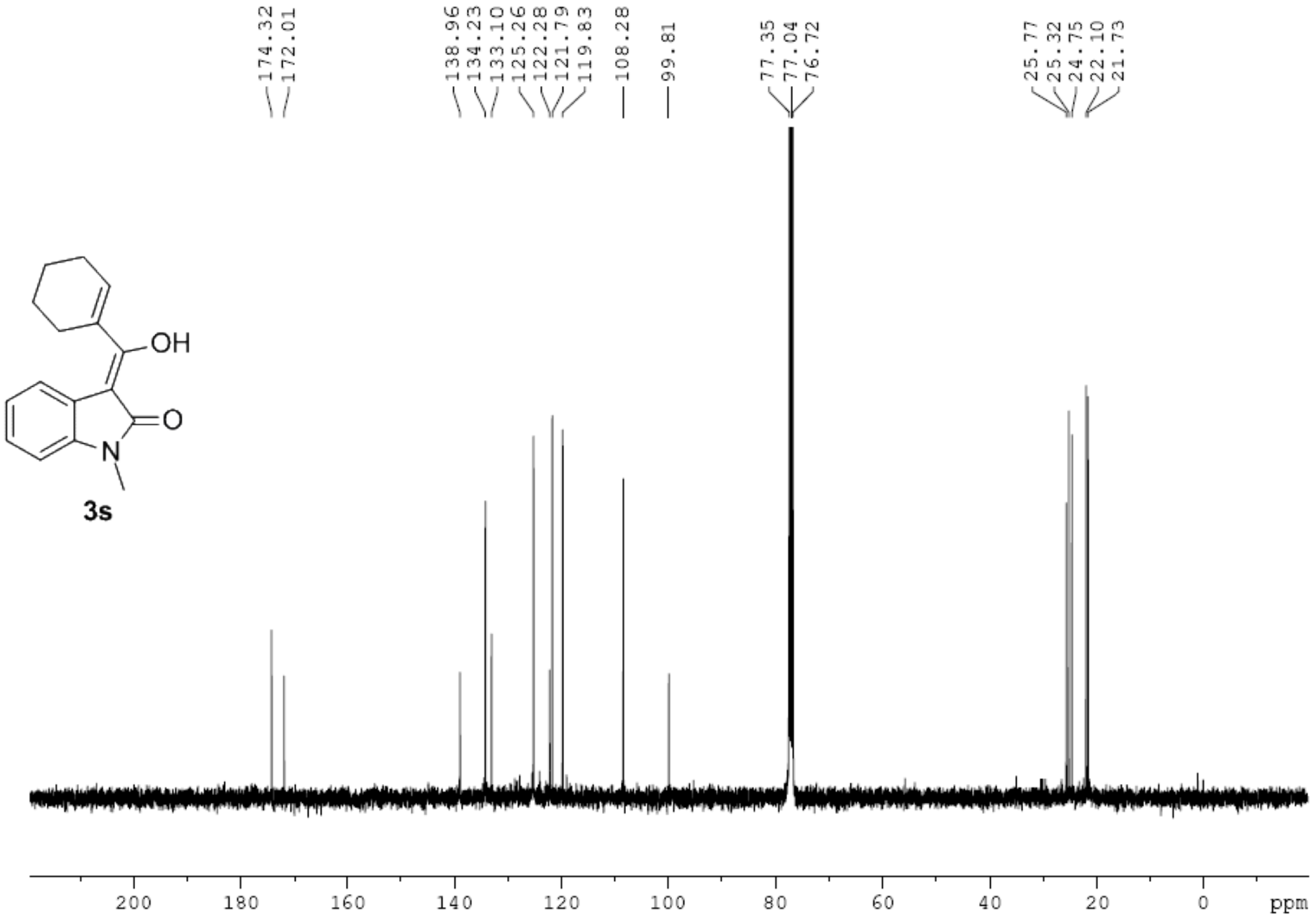

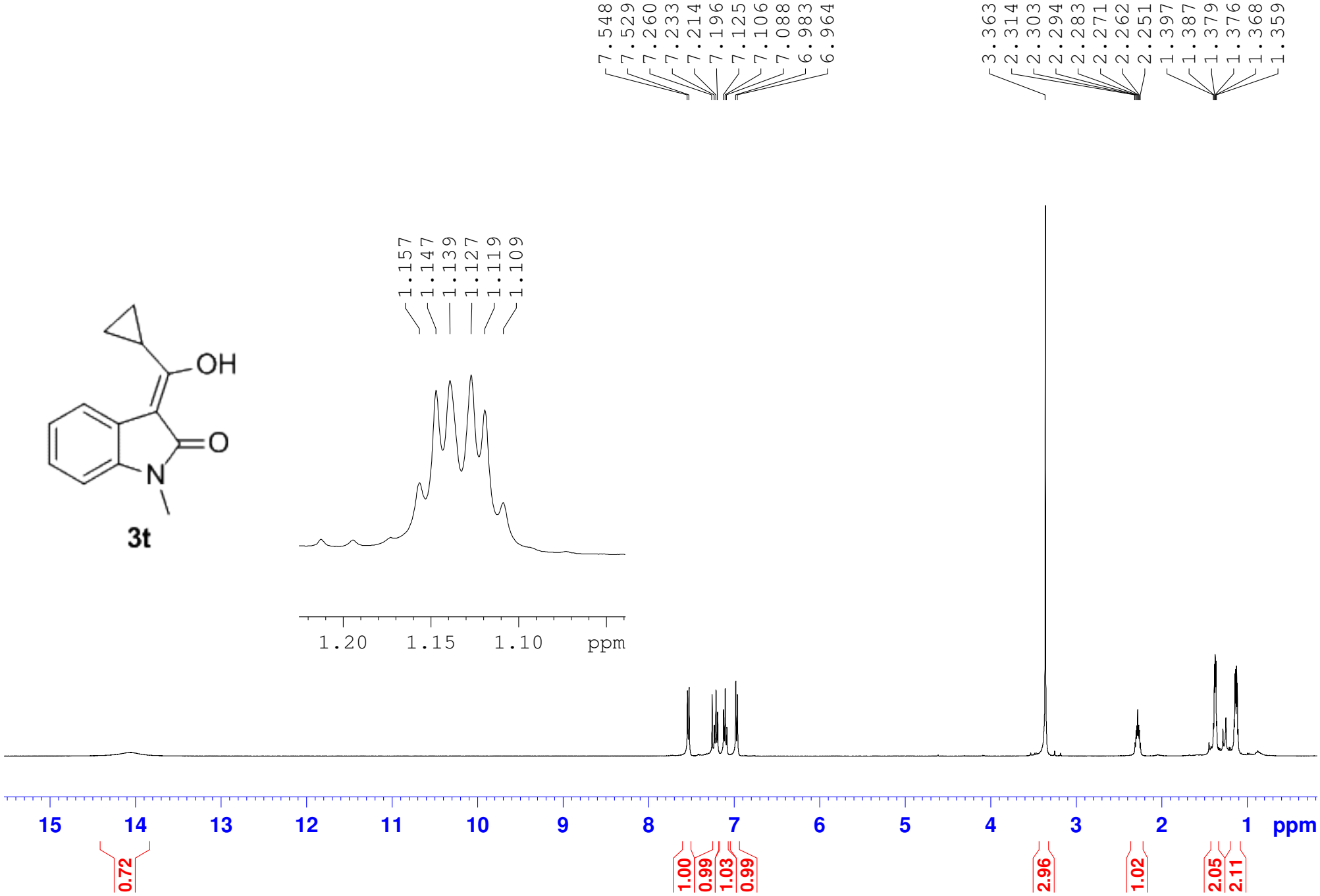

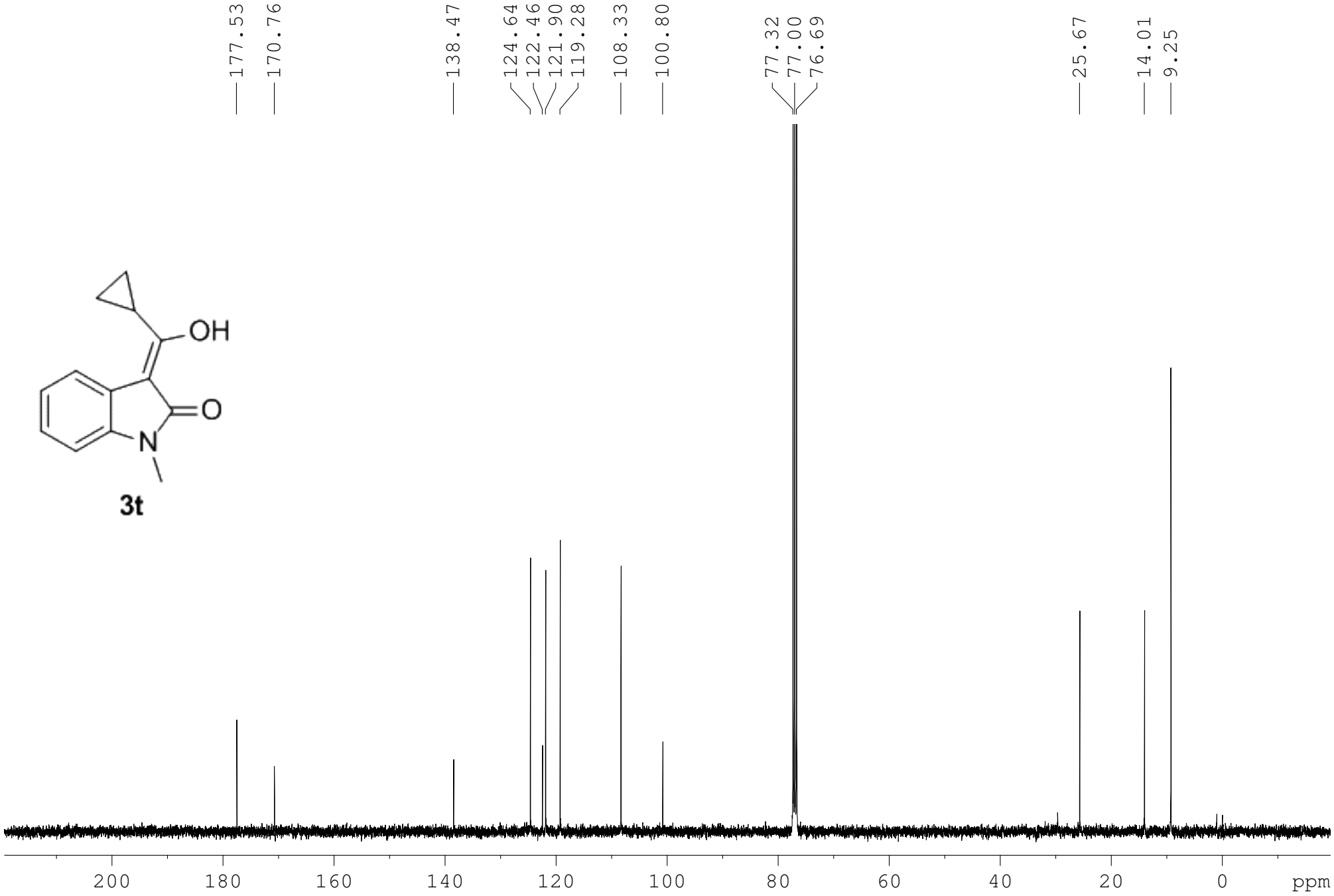

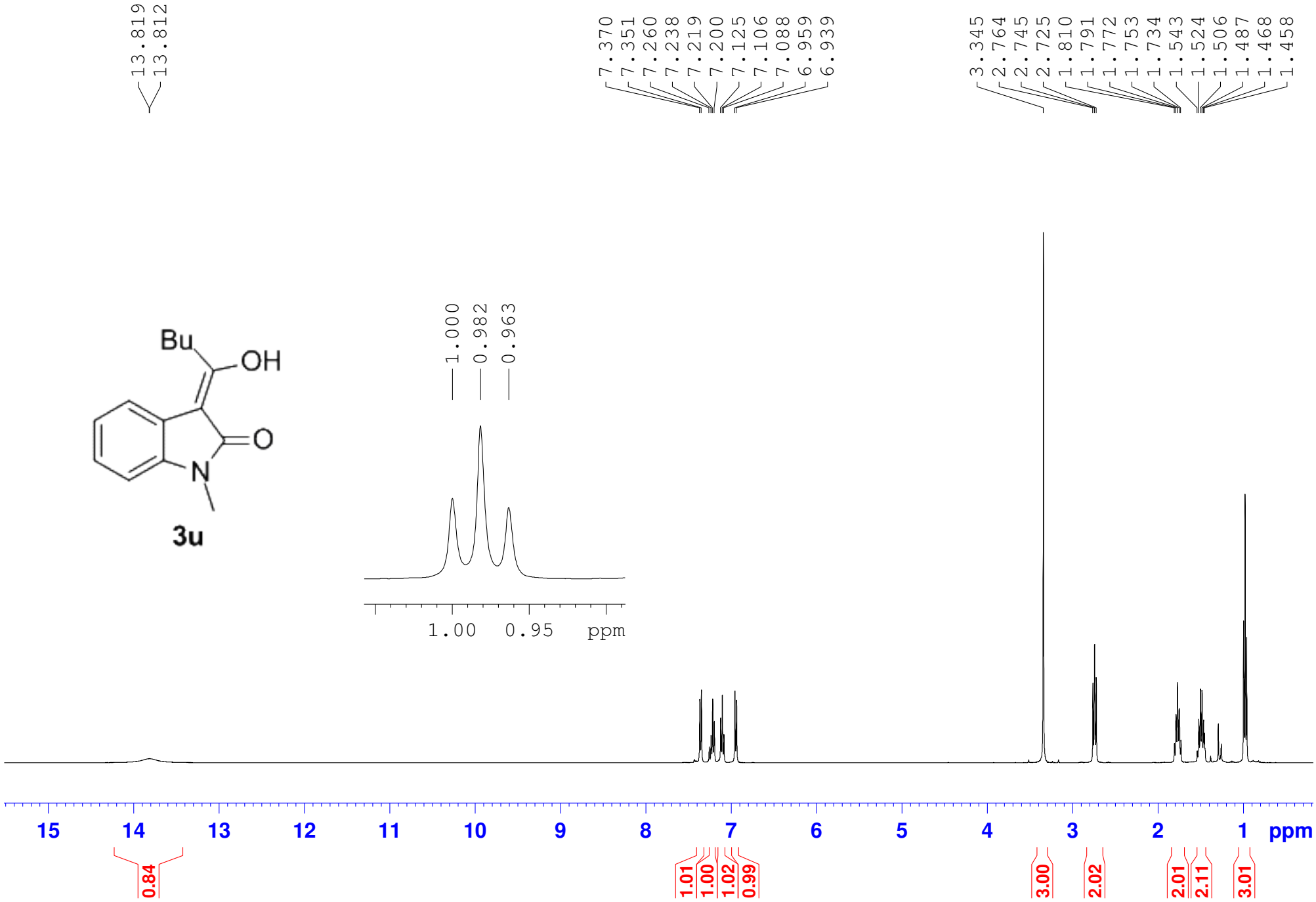

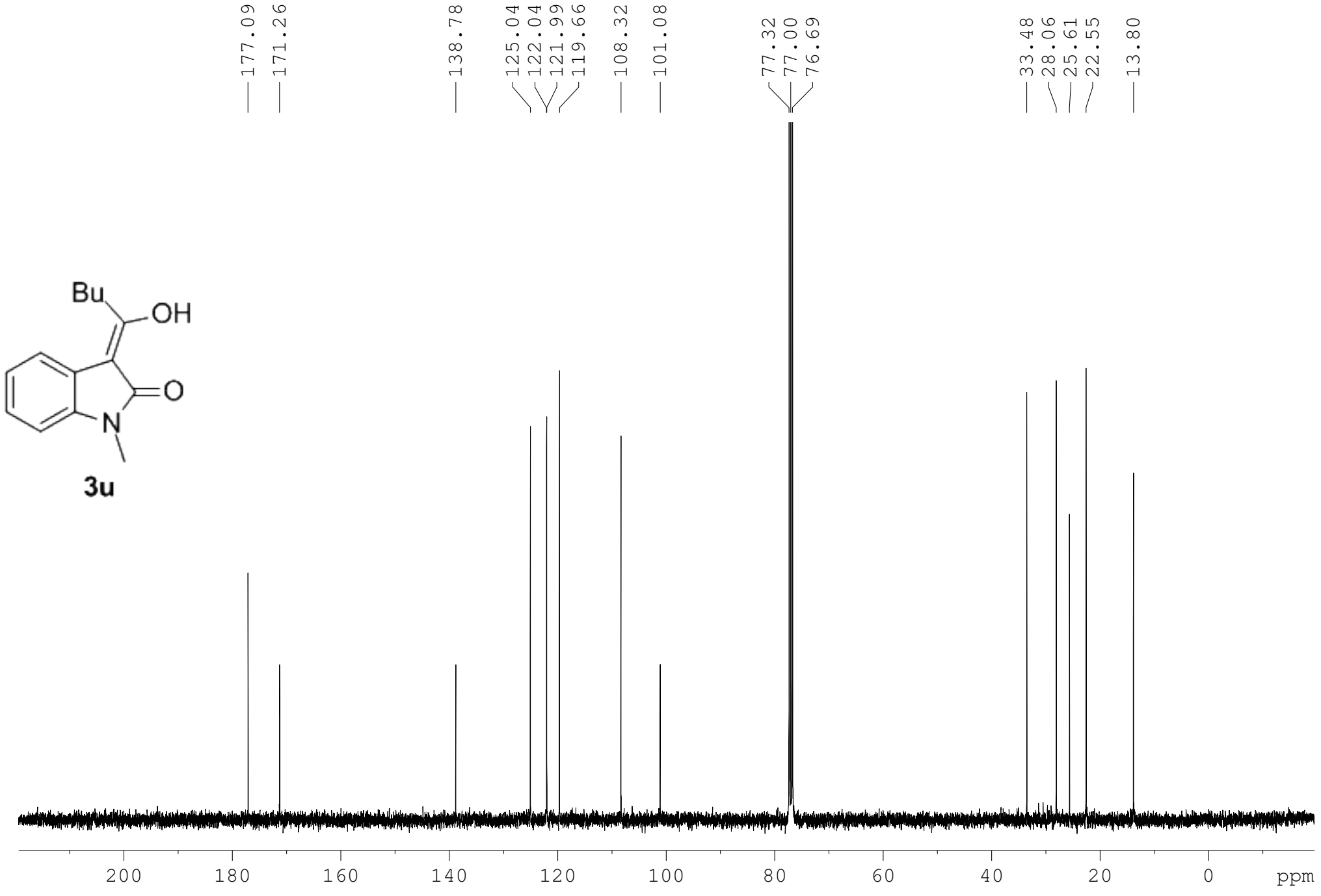

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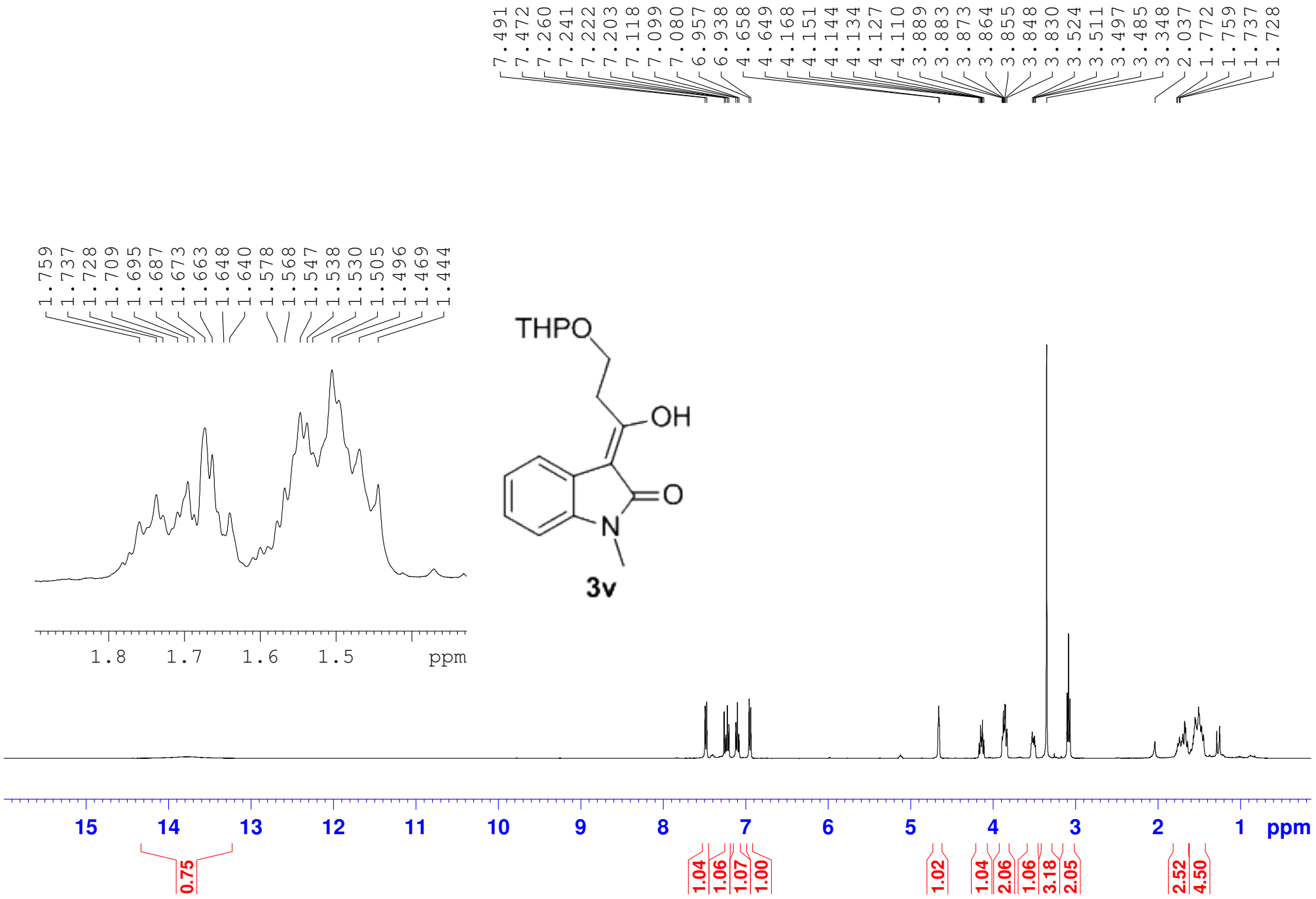

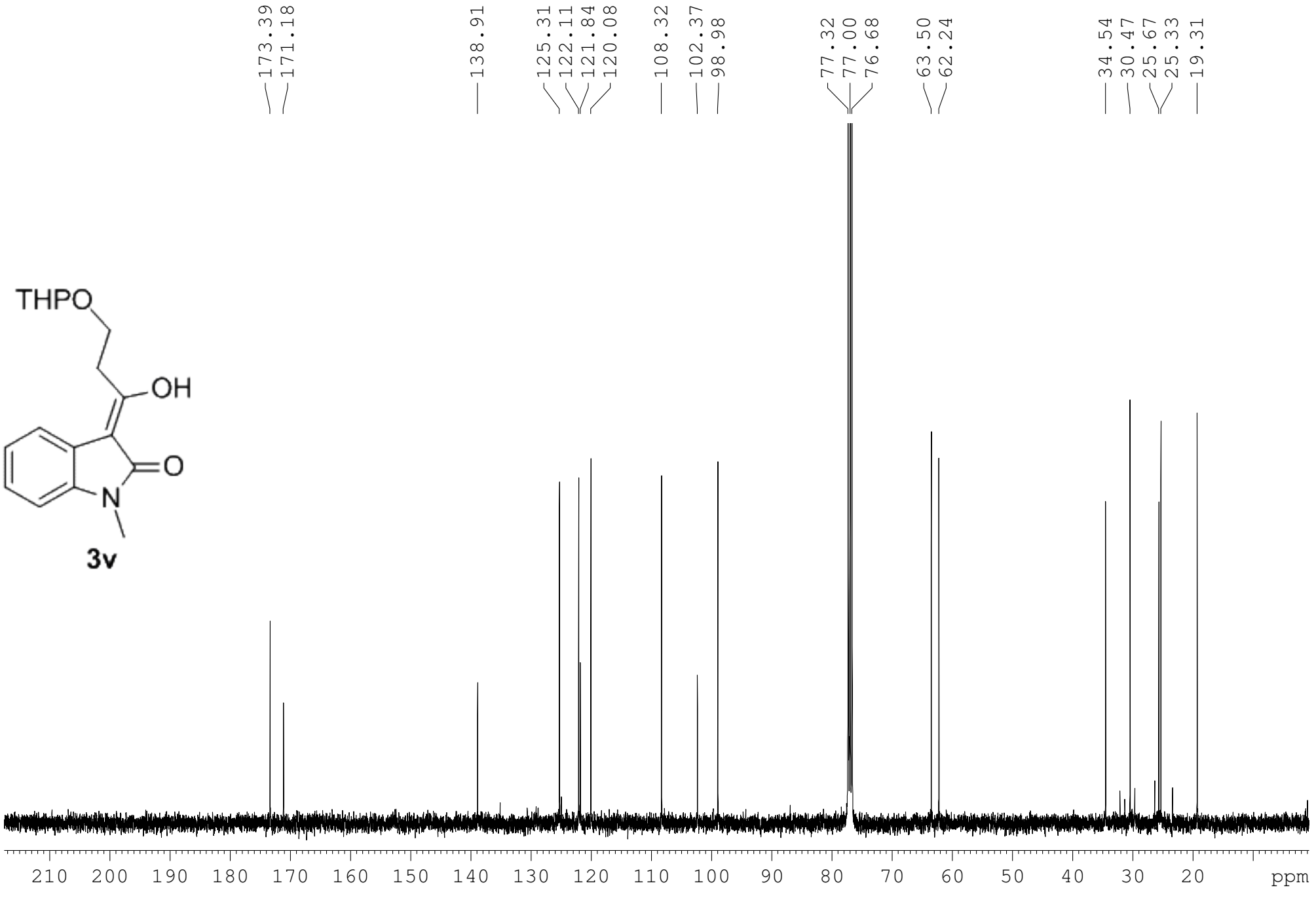

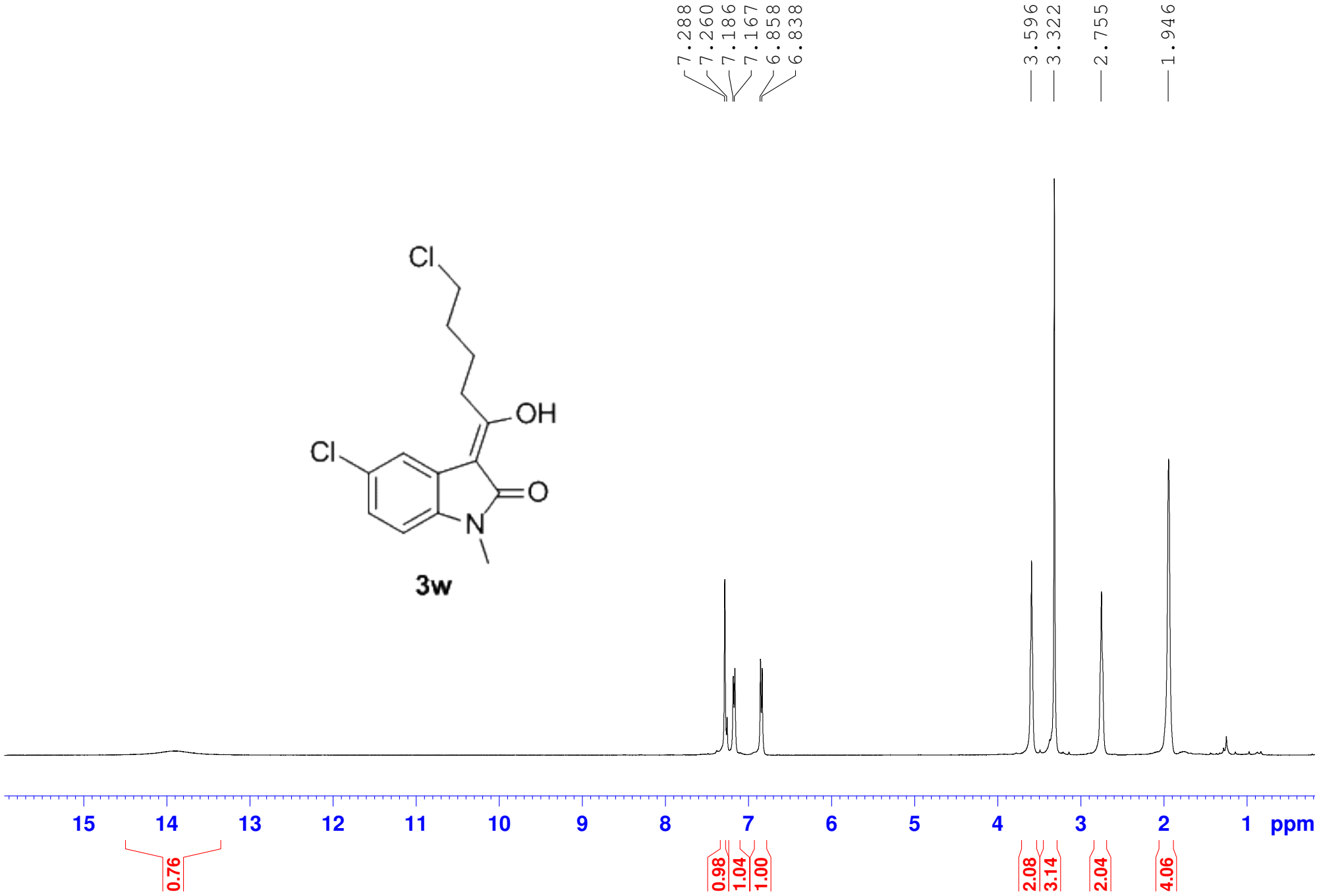

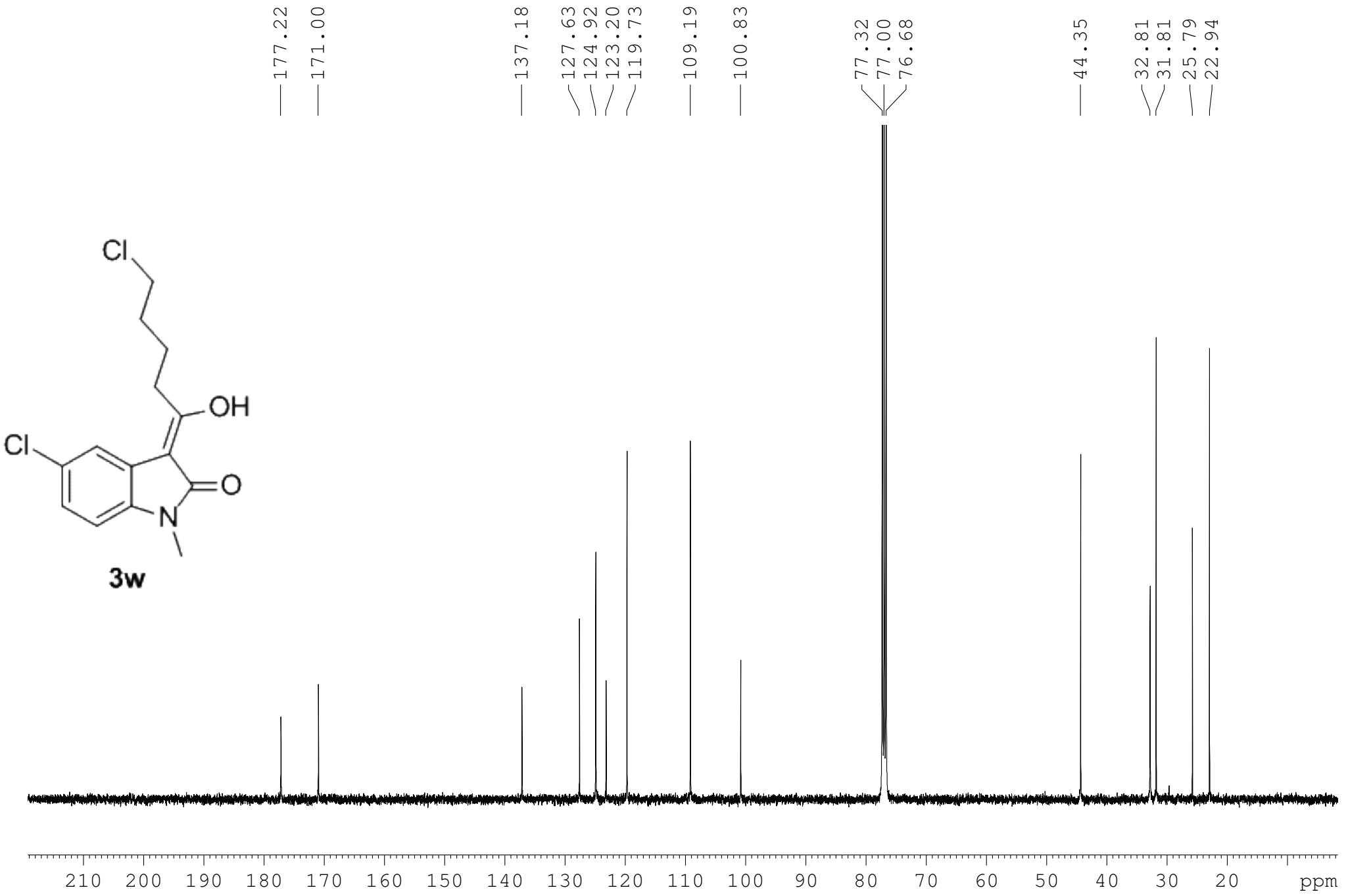

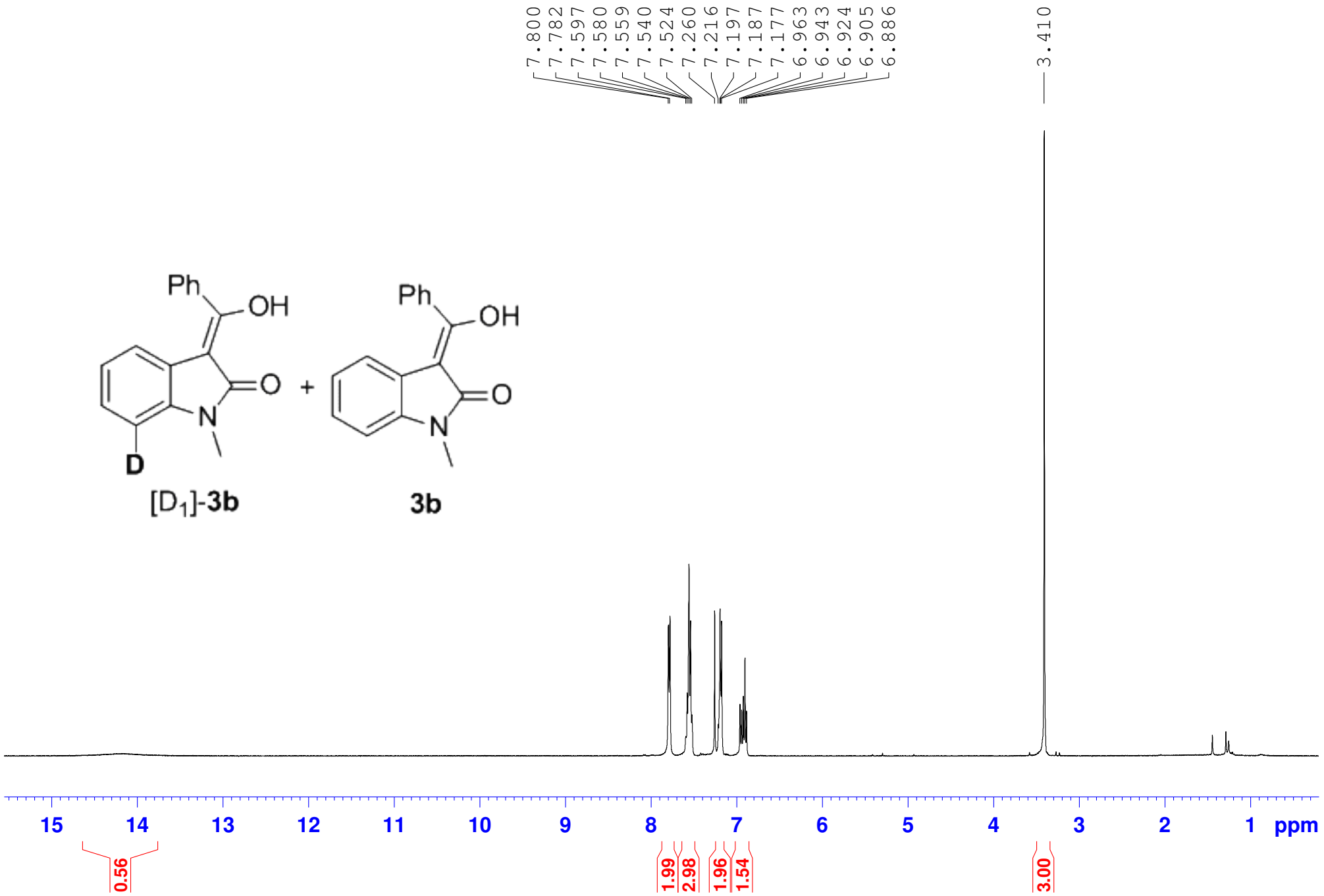

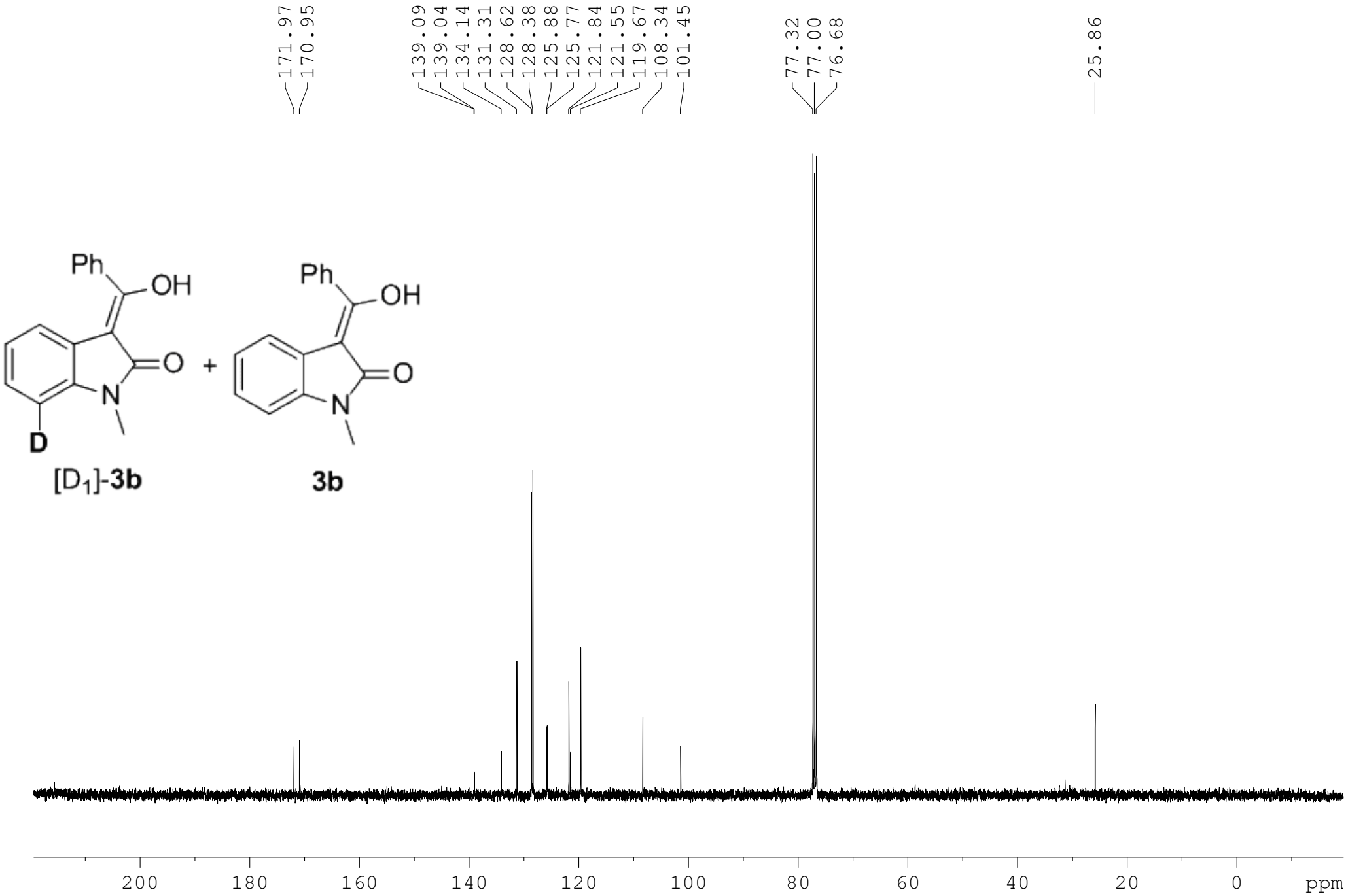

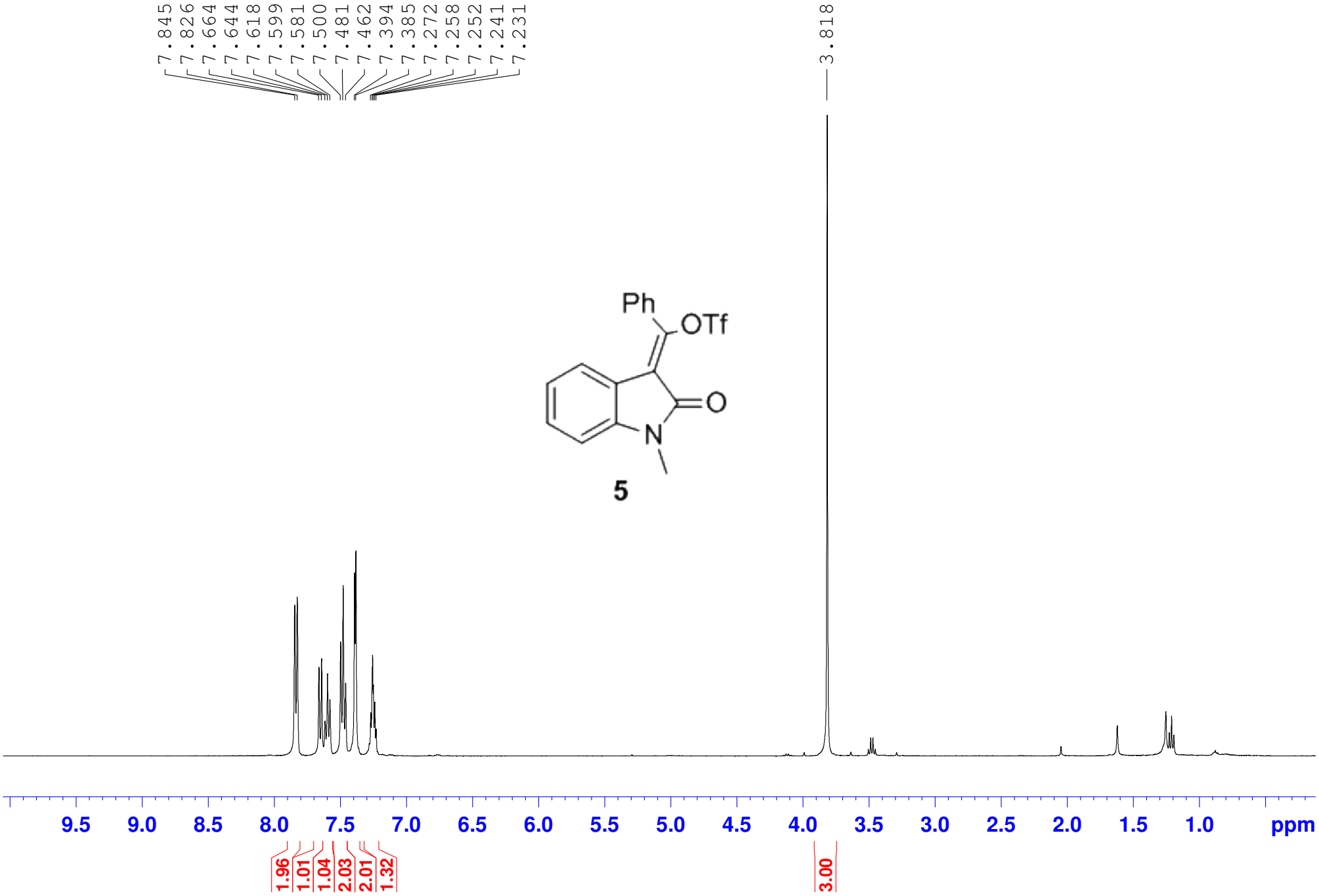

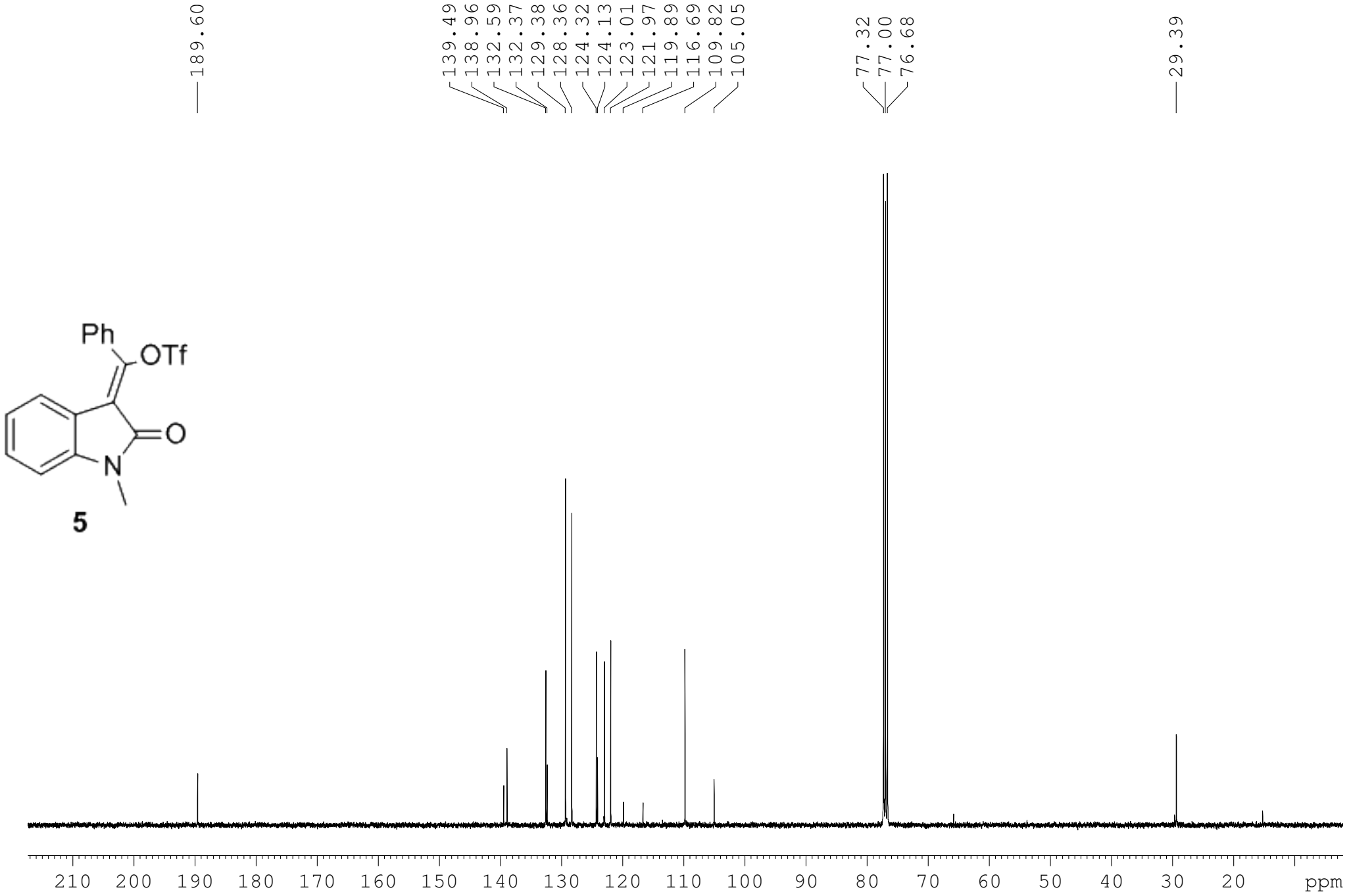

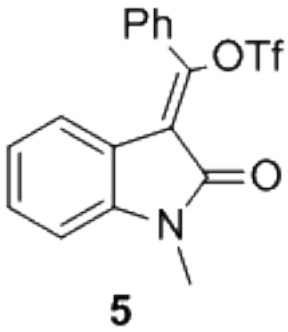

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