Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Gold(I)-Catalyzed Intramolecular Oxidation-Cyclopropanation Sequence of Enynes: A Convenient Access to [*n*.1.0]Bicycloalkanes

Deyun Qian,[a] Junliang Zhang*[a,b]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N, Zhongshan Road, Shanghai 200062 (P. R. China), Fax: (+86) 21-6223-5039; E-mail: jlzhang@chem.ecnu.edu.cn*

[b] *State key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.*

Fax:(+86)-021-6223-5039; e-mail : jlzhang@chem.ecnu.edu.cn

Content

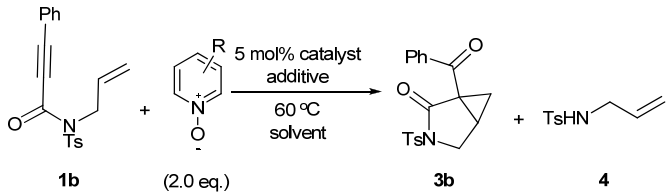
1. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H NMR, ^{13}C NMR spectra were measured at 400 MHz and 100 MHz in $CDCl_3$. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Tetrahydrofuran, benzene and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane (DCE) was distilled from CaH_2 prior to use.

2. Experimental Procedures and Characterization Data

2.1 Optimization of Reaction Conditions:

Table S1 Optimization of Reaction Conditions[a]



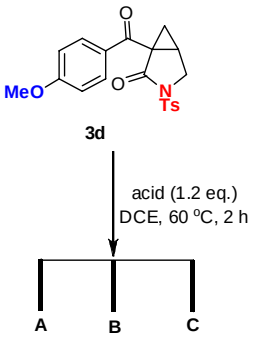
1b (2.0 eq.) **3b** **4**

Entry	Catalyst	R	Additive (eq.)	Solvent/ Time (h)	Yield (**3b**/**1b**/**4** %)[b]
1	[Ph_3PACl]/[$AgNTf_2$]	H	-	DCE/12	13/88/0
2	[Ph_3PACl]/[$AgNTf_2$]	H	MsOH (1.2)	DCE/12	22/83/0
3[c]	[IPrACl]/[$AgNTf_2$]	H	MsOH (1.2)	DCE/12	complicated mixture
4	[IPrACl]/[$AgNTf_2$]	2-Br	-	DCE/21	60/30/5
5	[IPrACl]/[$AgNTf_2$]	2-Br	MsOH (1.2)	DCE/21	67/14/5
6	[IPrACl]/[$AgNTf_2$]	2-Br	$HNTf_2$ (1.2)	DCE/21	68/11/10
7	[IPrACl]/[$AgNTf_2$]	2-Br	MsOH (1.2)	DCE/36	59/13/ 9
8[d]	[**L1**AuCl] /[$AgNTf_2$]	2-Br	MsOH (1.2)	DCE/21	35/19/30
9[e]	[**L2**AuCl] /[$AgNTf_2$]	2-Br	MsOH (1.2)	DCE/21	31/22/31
10	[IPrACl]/[$AgNTf_2$]	4-Ac	MsOH (1.2)	DCE/21	63/30/0
11	[IPrACl]/[$AgSbF_6$]	4-Ac	MsOH (1.2)	DCE/21	52/24/0
12	[IPrACl]/[$AgNTf_2$]	4-Ac	$HNTf_2$ (1.2)	DCE/21	64/32/0
13	[IPrACl]/[$AgNTf_2$]	4-Ac	HOAc (1 mL)	DCE/28	63/29/0
14[f]	[IPrACl]/[$AgNTf_2$]	4-Ac	$HNTf_2$ (1.2)	DCE/21	62/20/0
15[g]	[IPrACl]/[$AgNTf_2$]	4-Ac	$HNTf_2$ (1.2)	DCE/36	73/26/0
16[h]	[IPrACl]/[$AgNTf_2$]	4-Ac	$HNTf_2$ (1.2)	DCE/36	81/12/0
17[i]	[IPrACl]/[$AgNTf_2$]	4-Ac	$HNTf_2$ (1.2)	DCE/36	66/31/0
18	[IPrACl]/[$AgNTf_2$]	4-Ac	MsOH (1.2)	THF/21	41/53/0
19	[IPrACl]/[$AgNTf_2$]	4-Ac	MsOH (1.2)	CH_3CN/21	45/51/0
20	-	4-Ac	MsOH (1.2)	DCE/21	nr
21	[$AgNTf_2$]	4-Ac	MsOH (1.2)	DCE/21	23/74/0
22	$Rh_2(OAc)_4$	2-Br	-	toluene/21	12/53/32
23	$PtCl_2$	2-Br	-	DCE/21	nr
24	$Pd(OAc)_2$	4-Ac	MsOH (1.2)	DCE/21	nr

[a] The reaction was performed with 0.2 mmol of **1a** and 5 mol% of catalyst in 2.0 mL DCE at 60 °C, Au/$AgNTf_2$ = 1:1. [b] Determined by ^{1}H NMR analysis using CH_2Br_2 as the internal reference. [c] IPr = *N*,*N*'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. [d] **L1** = X-phos. [e] **L2** = P(*t*Bu)$_2$(*o*-biphenyl). [f] 1.2 eq. of oxidant. [g] 71% isolated yield. [h] 10 mol% of catalyst. [i] 3.0 eq. of oxidant.

2.2 The Control Experiments Regarding Acid Stability:

(1)

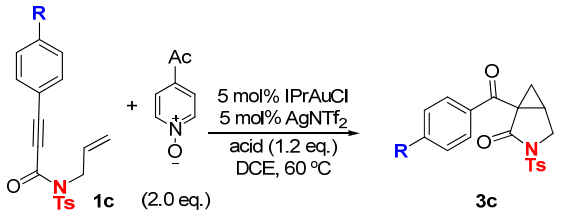


Entry	Acid	**3d** (mmol) t = 0 h	The yield of **3d** (%)[a] t = 2 h
A	-	0.1	96
B	MsOH	0.1	46
C	$HNTf_2$	0.1	0

[a] Determined by ^1H NMR analysis using CH_2Br_2 as the internal reference.

In three dried glass tube, the corresponding acid (1.2 eq.) in DCE (0.5 mL) was added respectively to a solution of **3d** (0.1 mmol) in DCE (o.5 mL) at room temperature under nitrogen. The reaction mixture was stirred at 60 °C in the same oil and the progress of the reaction was monitored by TLC. After 2h, the reaction was treated with saturated aqueous $NaHCO_3$ (5 mL), and the resulting mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4. The mixture was concentrated and the crude yield was determined by ^1H NMR.

(2)

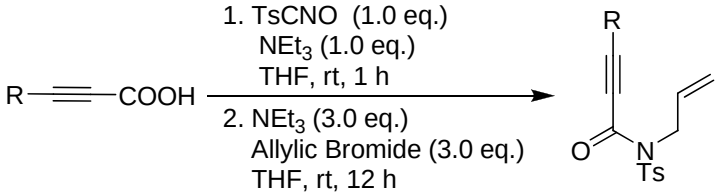


Entry	R	Acid	Time (h)	Yield (%)[a]
1	Me	MsOH	38	62
2	Me	$HNTf_2$	38	41
3	MeO	MsOH	48	81
4	MeO	$HNTf_2$	48	65

[a] Determined by ^1H NMR analysis using CH_2Br_2 as the internal reference.

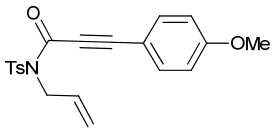
2. 3 General Procedure for Synthesis of Enyne Substrates 1:

2.3.1 Preparation of Enyne Substrates 1b to 1i:



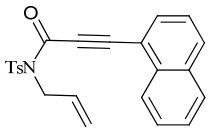
In a flame dried round-bottom flask, the corresponding carboxylic acid (5.0 mmol) was dissolved in dry THF (0.5 M) under argon and tosyl isocyanate (1.0 equiv) was added to the solution. After being stirred at rt for 10 mins under the inter N_2 was disconnected and Et_3N (1.0 equiv) was added drop-wise to the open flask, allowing the release of the formed CO_2. After being stirredg for 1h at rt, allyl bromide (3.0 equiv) and extra Et_3N (3.0 equiv) were sequentially added and the mixture was stirred overnight. After the starting material was consumpted completely, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc = 5:1) to afford the corresponding enyne products. The spectra of **1b**[1], **1c**[3], **1f**[4] and **1i**[1] are consistened with the literatures.

Substrate 1d



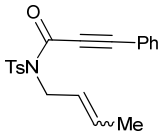
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.48-7.46 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.00-5.94 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.69 (d, *J* = 3.6 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 152.8, 145.0, 136.0, 134.7, 132.6, 129.4, 128.7, 118.8, 114.4, 111.1, 94.0, 81.2, 55.4, 49.4, 21.6; MS (EI): m/z (%) = 369 (M^+, 6.54), 159 (100)； HRMS (EI): calculated for $[C_{20}H_{19}NO_4S]^+$ 369.1035, found: 369.1033.

Substrate 1e



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 6.4 Hz, 3H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.59 (t, *J* = 8.8 Hz, 2H), 7.47-7.44 (m, 1H), 7.28 (d, J = 7.6 Hz, 2H), 6.04-6.00 (m, 1H), 5.46 (d, *J* = 16.8 Hz, 1H), 5.35 (d, *J* = 10.0 Hz, 1H), 4.77 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 145.1, 135.9, 133.5, 133.0, 132.9, 131.7, 129.5, 128.7, 128.5, 127.8, 127.0, 127.9, 125.7, 125.1, 118.9, 117.0, 91.8, 86.0, 49.4, 21.6; MS (EI): m/z (%) = 389 (M^+, 2.44), 179 (100); HRMS (EI): calculated for $[C_{23}H_{19}NO_3S]^+$ 389.1086, found: 389.1086.

Substrate 1g



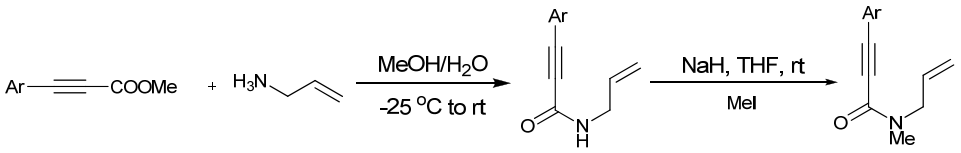
E/*Z* = 4.2:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.8 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.48-7.45 (m, 1H), 7.40-7.37 (m, 2H), 7.30-7.27 (m, 2H), 5.90-5.88 (m, 0.8H), 5.75-5.72 (m, 0.2H), 5.64-5.60 (m, 0.8H), 5.55-5.49 (m, 0.2H), 4.76 (d, *J* = 6.0 Hz, 0.3H), 4.63 (d, *J* = 6.0 Hz, 1.6H), 2.42 (s, 3H), 1.82 (d, *J* = 6.8 Hz, 0.5H), 1.74 (d, *J* = 6.0 Hz, 2.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 144.9, 136.1, 134.7, 132.6, 131.0, 130.9, 129.4, 129.3, 128.6, 128.5, 125.3, 125.0, 119.5, 92.8, 81.6, 48.9, 44.2, 21.6, 17.6, 13.1. The spectroscopic data match well with those in the literature.[4]

Substrate 1h

The enyne substrate **1h** was synthesized according to literature procedure reported by Lu.[5] The spectrum of substrate **1h** was consistened with the literature.[3]

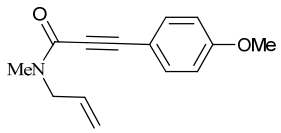
2.3.2 Preparation of Enyne Substrates 1j and 1k:

Substrates **1j** and **1k** were synthesized following a published literature procedure.[6]



To a solution of allylamine (1.8 mL, 24.0 mmol) in a solvent mixture[MeOH (2 mL) + H_2O (2 mL)] was slowly added the corresponding propynoate (1.68 g, 20.0 mmol) at -20 °C to -30 °C with stirring. After addition of the propynoate, the stirring was continued for 5 minutes. The solvent was evaporated and column chromatography on silica gel (hexanes/EtOAc = 3:1) afforded the 2-alkynamides of primary allylic amines. To a solution of 2-alkynamides of primary allylic amines (2.0 mmol) in THF (8 mL) was added NaH (128 mg, 60% in oil, 3.2 mmol) and CH_3I (0.2 mL, 3.2 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 (hexanes) to afford corresponding enyne products. The spectrum of substrates **1j** was consistened with the literature.[2]

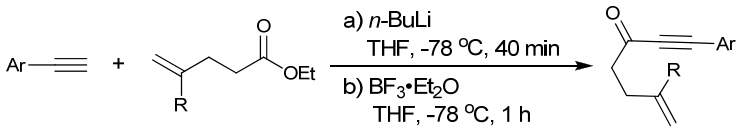
Substrate 1k



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 6.88-6.86 (m, 2H), 5.87-5.71 (m, 1H), 5.27-5.18 (m, 2H), 4.25-4.23 (m, 1.2H), 4.07-4.06 (m, 0.8H), 3.82 (m, 3H), 3.21 (s, 1.2H), 2.97 (m, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 154.9, 154.7, 134.1, 132.7, 132.1, 118.0, 117.8, 114.2, 112.4, 90.9, 90.3, 80.9, 80.7, 55.3, 53.7, 48.9, 35.8, 32.0; IR (neat): ν 3405, 3324, 3050, 2991, 2204, 1668, 1353, 1324, 1169, 1139, 1083, 928, 770 cm^{-1}; HRMS (EI): calculated for $[C_{14}H_{15N}O_2]^+$ 229.1103, found: 229.1102.

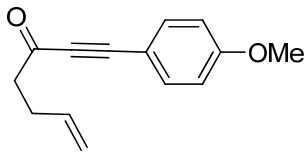
2.3.3 Preparation of Enyne Substrates 1l to 1n:

Substrates **1l**, **1m** and **1n** were synthesized following a published literature procedure.[7]



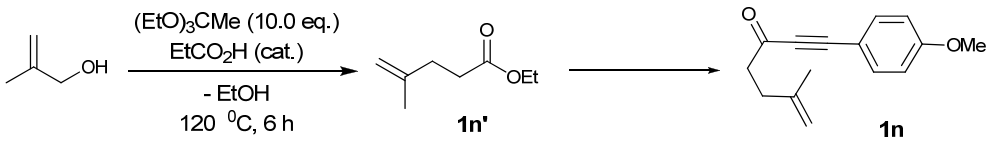
In a flame dried double Schlenk flask, a solution of the corresponding alkyne (20.0 mmol) in anhydrous THF (20 mL) was cooled to -78 °C under an argon atmosphere and n-BuLi (2.5 M in hexane, 8.0 mL, 20.0 mmol) was added dropwise. The solution was stirred for 40 min, and then a solution of boron trifluoride diethyl etherate (3.1 mL, 25.0 mmol) and ethyl pent-4-enoate (10.0 mmol) in anhydrous THF (5.0 mL) was added. The slightly yellow reaction mixture was stirred for 30 min and the cooling device was removed. A saturated aqueous solution of ammonium chloride (30 mL) was added and the aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic phases were washed with brine (50 mL) and dried over Na_2SO_4. Removal of the solvent under reduced pressure led to a brown oil, which was subjected to flash column chromatography on silica (hexanes/EtOAc = 50:1 to 20: 1). The spectrum of substrates **1l** was consistened with the literature.[7]

Substrate 1m



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 5.90-5.80 (m, 1H), 5.11-5.01(m, 2H), 3.83 (s, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.50-2.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 161.6, 136.4, 135.4, 135.1, 115.6, 114.3, 111.7, 92.1, 87.6, 55.4, 44.4, 28.1; MS (EI): m/z (%) = 214 (M^+, 14.08), 159 (100); HRMS (EI): calculated for $[C_{14}H_{14}O_2]^+$ 214.0994, found: 214.0945.

Substrate 1n

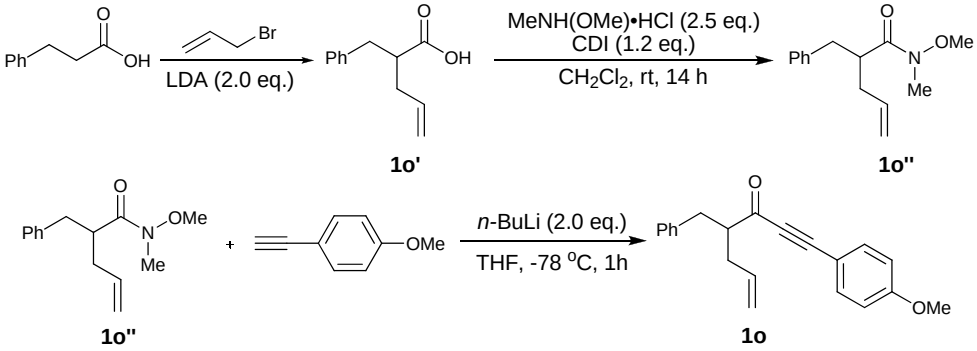


1n' was synthesized following the procedure of the literature 8.

1n, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 1H), 4.73 (s, 1H), 3.84 (s, 3H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.77 (m, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 187.4, 161.6, 143.8, 135.1, 114.3, 111.7, 110.6, 92.1, 87.6, 55.4, 43.5, 31.8, 22.6; MS (EI): m/z (%) = 228 (M^+, 6.76), 159 (100); HRMS (EI): calculated for $[C_{15}H_{16}O_2]^+$ 228.1150, found: 228.1149.

2.3.4 Preparation of Enyne Substrates 1o to 1q:

Substrate 1o

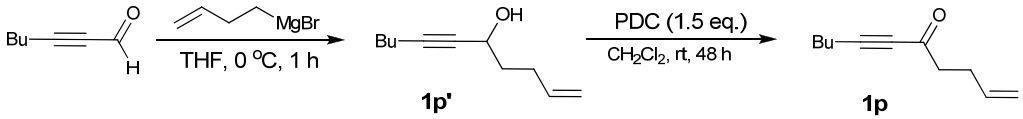


1o', prepared by a procedure reported by Kim.[9] Weinreb amide **1o''**, prepared according to the literature.[10]

n-BuLi (2.5 M in hexane, 7.2 mL, 18.0 mmol) was added dropwise to a solution of 4-Ethynylanisole (2.4 g, 18.0 mmol) in THF (10 mL) at –78 °C. The mixture was stirred for 30 min. The above solution was transferred via cannula to the Weinreb amide **1o''** (2.1 g, 9.0 mmol) in THF (10 mL) at –78 °C, stirred for 1 h and let warm up to room temperature. Then, 1 N HCl was added dropwise until disappearance of the white precipitate. The reaction mixture was extracted with Et_2O (3 x 20 mL) and

the combined organic layers were washed with brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by FC (hexanes/EtOAc = 20:1) to afford **1o** (1.9 g, 70%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.20-7.18 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.84-5.74 (m, 1H), 5.13-5.06 (m, 2H), 3.84 (s, 3H), 3.16-3.11 (m, 1H), 3.05-2.99 (m, 1H), 2.88-2.83 (m, 1H), 2.57-2.50 (m, 1H), 2.43-2.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 161.7, 138.9, 135.1, 134.8, 129.1, 128.5, 128.4, 128.3, 126.4, 117.5, 114.3, 111.7, 93.3, 87.3, 55.6, 55.4, 36.7, 35.1; MS (EI): m/z (%) = 304 (M^+, 3.42), 159 (100); HRMS (EI): calculated for $[C_{21}H_{20}O_2]^+$ 304.1463, found: 304.1461.

Substrate 1p



1p, prepared by a modification of a produce reported by Narasaka.[11]

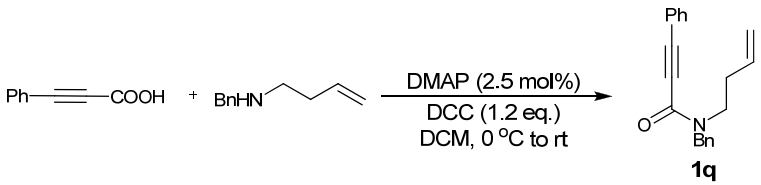
1p', prepared according to the literature.[12] A solution of 2-heptynal[13] (1.10 g, 10.0 mmol) in THF was added to a solution of but-3-enylmagnesium bromide (1M in THF, 15.0 mmol) at 0 °C and stirring was continued for 1 h. The reaction was carefully quenched with water at 0 °C and the aqueous layer was extracted with methyl *tert*-butyl ether. The combined organic phases were dried over Na_2SO_4 before they were filtered and evaporated. This material was not purified, but rather used as a mixture in the subsequent step.

In a dry flask under argon, to a dichloromethane solution (100 ml) of **1p'** was added pyridinium dichromate (5.6 g, 15.0 mmol). The reaction mixture was stirred at rt for 48 h and filtered through Celite. The filtrate was concentrated in vacuo and purification by flash column chromatography gave the title compound **1p** (1.10 g; 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85-5.75 (m, 1H), 5.06-4.98 (m, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.42-2.34 (m, 4H), 1.59-1.52 (m, 2H), 1.45-1.40 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz,

CDCl3): δ 187.4, 136.4, 115.5, 94.6, 80.7, 44.5, 29.7, 28.0, 21.9, 18.6, 13.4; HRMS (EI): calculated for $[C_{11}H_{16}O]^+$ 164.1201, found: 164.1199.

Substrate 1q



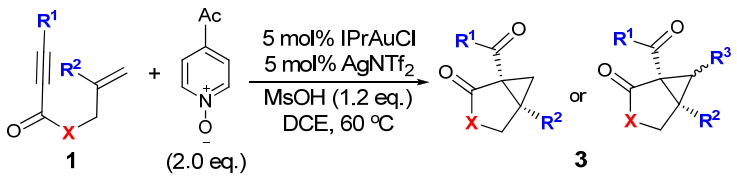
1q

To a solution of 3-phenylpropiolic acid (0.75 g, 5.0 mmol) in CH_2Cl_2 (10 mL), was added dropwise a solution of DCC (1.03 g, 5.0 mmol) and DMAP (61.1 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) at -20 °C. N-benzylbut-3-en-1-amine[14] (0.74 g, 4.6 mmol) in CH_2C1_2 (5 mL) was then added and the mixture was stirred for 20 h at room temperature. The solid was filtered off and the filtrate was washed with 0.1 N HCI (10 mL) and dried (Na_2SO_4). After removal of the solvent, column chromatograph (hexanes/EtOAc = 5: 1) gave the oily product **1q** (1.20 g, 90 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.35-7.24 (m, 8H), 5.82-5.73 (m, 1H), 5.11-5.03 (m, 2H), 4.87 (s, 1H), 4.69 (s, 1H), 3.65 (t, *J* = 7.2 Hz, 1H), 3.45 (t, *J* = 7.2 Hz, 1H), 2.42-2.37 (m, 1H), 2.33-2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 154.9, 154.7, 136.6, 136.4, 134.9, 134.3, 132.38, 132.35, 130.04, 130.00, 128.8, 128.7, 128.5, 128.4, 128.1, 127.9, 127.6, 127.5, 110.5, 120.4, 117.5, 117.0, 90.3, 90.1, 81.8, 81.7, 52.9, 47.8, 47.6, 43.8, 33.0, 31.6; MS (EI): m/z (%) = 289 (M^+, 1.43), 129 (100)； HRMS (EI): calculated for $[C_{20}H_{19}NO]^+$ 289.1467, found: 289.1467.

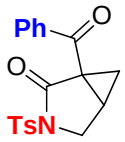
2.4 General Procedure for Gold(I)-Catalyzed Intramolecular Oxidation-Cyclopropanation Sequence of Enynes 1:

General Procedure A:



In a dried glass tube, a mixture of IPrAuCl (6.2 mg, 0.01 mmol, 5 mol %) and $AgNTf_2$ (3.8 mg, 0.01 mmol, 5 mol %) in DCE (1 mL) was stirred at room temperature under nitrogen for 30 min to generate the gold catalyst. 4-acetylpyridine *N*-oxide (54.8 mg, 0.4 mmol), MsOH (0.24 mmol) and the premixed catalyst solution was added sequentially to a solution of enynes **1** (0.2 mmol) in DCE (1 mL) at room temperature under nitrogen. After stirring at 60 °C for 1 – 72 h, the reaction was treated with saturated aqueous $NaHCO_3$ (5 mL), and the resulting mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4. The mixture was concentrated and the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 5:1 to 7:3) to afford the desired product **3**.

1-benzoyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3b).

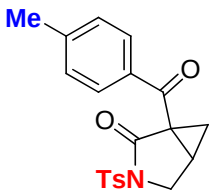


3b

White solid, m. p. = 159-161 °C, 71% yield (hexanes/ethyl acetate = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.55-7.52 (m, 1H), 7.34-7.33 (m, 4H), 4.09-4.02 (m, 2H), 2.55-2.53 (m, 1H), 2.46 (s, 3H), 2.00-1.97 (m, 1H), 1.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 192.2, 169.3, 145.4, 135.5, 134.5, 133.6, 129.8, 129.2, 128.3, 128.2, 47.3, 38.6, 21.7, 21.4, 19.2. The spectroscopic data match well with those in the literature.[1]

1-(4-methylbenzoyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3c).

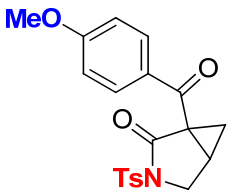


3c

White solid, m. p. = 128-137 °C, 73% yield (hexanes/ethyl acetate = 7:3).

m. p. = ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.08-4.05 (m, 2H), 2.51 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 1.95 (s, 1H), 1.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 169.4, 145.4, 144.5, 134.4, 132.9, 129.7, 129.4, 129.0, 128.1, 47.3, 38.5, 21.7, 21.6, 21.2, 19.0; IR (neat): ν 3091, 2960, 2855, 1731, 1672, 1604, 1357, 1171, 1105, 1084, 1002, 960, 810, 763, 713 cm^{-1}; HRMS (ESI): calculated for $[C_{20}H_{19}NNaO_4S]^+$ 392.09270, found:392.09233.

1-(4-methoxybenzoyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3d).

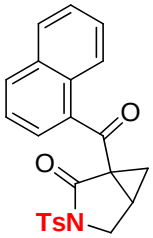


3d

White solid, m. p. = 168-170 °C, 81% yield (hexanes/ethyl acetate = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 4.08-3.99 (m, 2H), 3.86 (s, 3H), 2.53-2.50 (m, 1H), 2.45 (s, 3H), 1.90 (t, *J* = 5.8 Hz, 1H), 1.35-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.1, 169.5, 164.0, 145.4, 134.5, 131.8, 129.8, 128.3, 128.2, 113.7, 55.5, 47.3, 38.4, 21.7, 20.6, 19.2; IR (neat): ν 3101, 3017, 2935, 2903, 2838, 1723, 1670, 1596, 1379, 1350, 1258, 1162, 1115, 1094, 1028, 838, 808, 755 cm^{-1}; HRMS (ESI): calculated for $[C_{20}H_{19}NNaO_5S]^+$ 386.10567, found: 386.10567.

1-(1-naphthoyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3e).

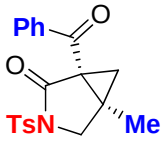


3e

White solid, m. p. = 143-145 °C, 40% yield (hexanes/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27-8.26 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 3H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.47-4.45 (m, 2H), 7.33-7.25 (m, 3H), 4.07 (s, 1H), 2.70 (s, 1H), 2.42 (s, 3H), 2.22 (s, 1H), 1.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 195.5, 168.8, 145.3, 134.5, 133.84, 133.78, 133.0, 130.2, 129.8, 128.60, 128.55, 128.0, 127.9, 126.5, 125.0, 124.1, 47.1, 40.1, 24.1, 21.7, 21.1; IR (neat): ν 3096, 2919, 1727, 1672, 1623, 1357, 1303, 1172, 1118, 1099, 900, 813, 801, 768, 662 cm^{-1}; HRMS (ESI): calculated for $[C_{23}H_{19}NNaO_4S]^+$ 428.09270, found: 428.09245.

1-benzoyl-5-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3f).

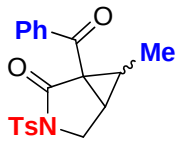


3f

White solid, m. p. = 147-150 °C, 59% yield (hexanes/ethyl acetate = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.51-7.48 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.27-7.23 (m, 2H), 4.16 (d, *J* = 10.4 Hz, 2H), 3.92 (d, *J* = 10.4 Hz, 2H), 2.48 (s, 3H), 2.08 (s, 1H), 1.24 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 191.8, 170.5, 145.5, 136.4, 134.6, 133.3, 129.8, 128.6, 128.5, 128.2, 52.9, 43.4, 31.4, 22.7, 21.8, 15.7; IR (neat): ν 3077, 2956, 2927, 1727, 1678, 1597, 1484, 1450, 1353, 1171, 1105, 1084, 1002, 960, 810, 763, 713 cm^{-1}; HRMS (ESI): calculated for $[C_{20}H_{19}NNaO_4S]^+$ 392.09270, found:392.09162.

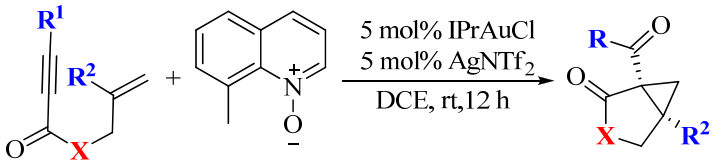
1-benzoyl-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3g).



3g

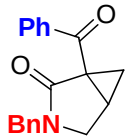
1:4.2 mixture of two isomers, 67% ^{1}H NMR yield. *Minor isomer*, white solid, 11% isolated yield (hexanes/ethyl acetate = 1:3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.2 Hz, 2H), δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.56-7.52 (m, 1H), 7.40-7.31 (m, 4H), 4.12-4.08 (m, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 4.12-4.08 (m, 1H), 2.44 (s, 3H), 2.10-2.03 (m, 1H), 1.22 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 193.1, 167.4, 145.4, 135.7, 134.9, 133.5, 129.7, 129.4, 128.3, 128.2, 44.0, 43.6, 25.5, 25.3, 21.7, 7.0; *Major isomer*, white solid, 50% isolated yield (hexanes/ethyl acetate = 1:3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.2 Hz, 2H), δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.61-7.57 (m, 1H), 7.48-7.45 (m, 2H), 7.30-7.28 (m, 2H), 4.06 (d, *J* = 10.4 Hz, 1H), 3.84-3.80 (m, 1H), 2.44 (s, 3H), 2.41 (s, 4H), 1.97-1.94 (m, 1H), 1.04 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 191.9, 168.7, 145.3, 136.2, 134.6, 134.0, 130.2, 129.7, 128.4, 128.2, 47.0, 43.9, 29.2, 23.5, 21.6, 12.5; MS (EI): m/z (%) = 369 (M^+, 1.73), 135 (100)； HRMS (EI): calculated for $[C_{20}H_{19}NO_4S]^+$ 369.1035, found: 369.1036.

General Procedure B:



In a dried glass tube, a mixture of IPrAuCl (6.2 mg, 0.01 mmol, 5 mol %) and $AgNTf_2$ (3.8 mg, 0.01 mmol, 5 mol %) in DCE (1 mL) was stirred at room temperature under nitrogen for 30 min to generate the gold catalyst. 8-methylquinoline *N*-oxide (63.7 mg, 0.4 mmol) and the premixed catalyst solution was added sequentially to a solution of enynes **1** (0.2 mmol) in DCE (1 mL) at room temperature under nitrogen. After stirred at rt for 12 h, the mixture was concentrated and the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10:1 to 3:7) to afford the desired product **3**.

1-benzoyl-3-benzyl-3-azabicyclo[3.1.0]hexan-2-one (3h).

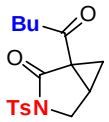


3h

White solid, m. p. = 100-102 °C, 53% yield (hexanes/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.58-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.37-7.32 (m, 3H),7.27-7.26 (m, 2H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 3.66-3.62 (m, 1H), 3.30 (d, *J* = 10.8 Hz, 1H), 2.36-2.35 (m, 1H), 2.03-2.02 (m, 1H), 1.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 194.7, 171.3, 136.6, 136.4, 133.1, 129.0, 128.8, 128.4, 128.3, 127.9, 47.1, 46.6, 38.6, 22.3, 18.7; IR (neat): ν 3068, 3028, 2926, 2884, 1599, 1580, 1489, 1446, 1423, 1355, 1296, 1269, 1225, 1065, 1026, 1001, 783, 756, 712, 697 cm^{-1}; MS (EI): m/z (%) = 291 (M^+, 11.08), 91 (100); HRMS (EI): calculated for $[C_{19}H_{17}NO_2]^+$ 291.1259, found: 291.1255.

1-pentanoyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-one (3i).

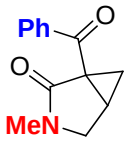


3i

Yellow oil, 65% yield (hexanes/ethyl acetate = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.89 (d, *J* = 7.8 Hz, 2H), 7.35(d, *J* = 7.8 Hz, 2H), 3.89 (s, 2H), 3.02-2.94 (m, 1H), 2.79-2.71 (m, 1H), 2.48-2.47 (m, 1H), 2.44 (s, 3H), 1.91-1.89 (m, 1H), 1.51-1.41 (m, 2H), 1.28-1.22 (m, 2H), 1.12 (s, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 203.1, 169.4, 145.4, 134.6, 129.8, 128.0, 46.8, 41.5, 38.7, 25.4, 24.0, 23.7, 22.1, 21.7, 13.8. The spectroscopic data match well with those in the literature.[1]

1-benzoyl-3-methyl-3-azabicyclo[3.1.0]hexan-2-one (3j).

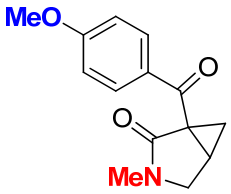


3j

Yellow oil, 56% yield (hexanes/ethyl acetate = 3:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 2H, *J* = 7.6 Hz), 7.54-7.52 (m, 1H), 7.46-7.42 (m, 2H), 3.80-3.76 (m, 1H), 3.39 (d, 1H, *J* = 10.4 Hz), 2.84 (s, 3H), 2.43-2.41 (m, 1H), 2.01-1.99 (m, 1H), 1.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 171.4, 136.5, 133.1, 129.0, 128.3, 49.9, 38.5, 29.7, 22.1, 19.3. The spectroscopic data match well with those in the literature.[2]

1-(4-methoxybenzoyl)-3-methyl-3-azabicyclo[3.1.0]hexan-2-one (3k).

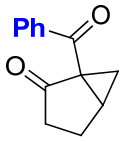


3k

White solid, m. p. = 115-118 °C, 62% yield (hexanes/ethyl acetate = 3:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H, *J* = 8.0 Hz), 6.91 (d, 2H, *J* = 8.0 Hz), 3.83 (s, 3H), 3.76-3.72 (m, 1H), 3.37 (d, 1H, *J* = 10.8 Hz), 2.82 (s, 3H), 2.37-2.36 (m, 1H), 1.92-1.90 (m, 1H), 1.09-1.08 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): δ 192.6, 171.6, 163.5, 131.5, 129.3, 113.5, 55.4, 49.9, 38.3, 29.7, 21.3, 19.0; IR (neat): ν 3086, 3060, 3014, 2964, 2922, 2841, 1676, 1657, 1600, 1576, 1510, 1454, 1428, 1400, 1366, 1315, 1287, 1255, 1175, 1020, 836; MS (EI): m/z (%) = 245 (M^+, 6.82), 42 (100); HRMS (EI): calculated for $[C_{14}H_{15}NO_3]^+$ 245.1052, found:245.1051.

1-benzoylbicyclo[3.1.0]hexan-2-one (3l).

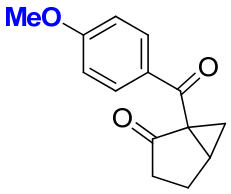


3l

Yellow oil, 75% yield (hexanes/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 2H, *J* = 7.2 Hz), 7.57 (m, 1H), 7.44 (t, 2H, *J* = 7.2 Hz), 2.68-2.63 (m, 1H), 2.50-2.30 (m, 3H), 2.20-2.12 (m, 1H), 2.07-2.06 (m, 1H), 1.48-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.7, 195.1, 136.3, 133.1, 129.0, 128.3, 45.1, 33.1, 31.7, 21.6, 19.9; IR (neat): ν 3061, 2947, 2881, 1720, 1666, 1598, 1580, 1449, 1415, 1370, 1318, 1297, 1266, 1208, 1176, 1096, 1066, 1031, 770, 696 cm^{-1}; MS (EI): m/z (%) = 200 (M^+, 4.53), 105 (100); HRMS (EI): calculated for $[C_{13}H_{12}O_2]^+$ 200.0837, found: 200.0838.

1-(4-methoxybenzoyl)bicyclo[3.1.0]hexan-2-one (3m).

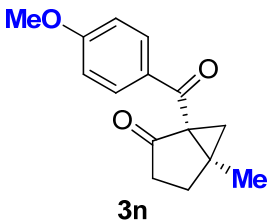


3m

Yellow oil, 85% yield (hexanes/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2H, *J* = 8.4 Hz), 6.92 (d, 1H, *J* = 8.4 Hz), 3.86 (s, 3H), 2.65-2.60 (m, 1H), 2.45-2.32 (m, 3H), 2.20-2.10 (m, 1H), 2.05-1.95 (m, 1H), 1.48-1.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 193.0, 163.6, 131.5, 129.1, 113.6, 55.4, 44.9, 33.1, 30.8, 21.5, 19.7; IR (neat): ν 3006, 2943, 2841, 1720, 1658, 1597, 1575, 1510, 1458, 1419, 1369, 1309, 1255, 1213, 1166, 1095, 1028, 839, 811, 737 cm^{-1}; MS (EI): m/z (%) = 230 (M^+, 22.06), 135 (100); HRMS (EI): calculated for $[C_{13}H_{12}O_2]^+$ 230.0943, found: 230.0944.

1-(4-methoxybenzoyl)-5-methylbicyclo[3.1.0]hexan-2-one (3n).



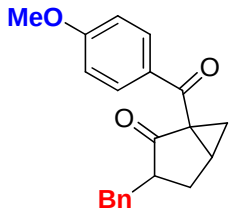
3n

Yellow oil, 60% yield (hexanes/ethyl acetate = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 2H, *J* = 8.4 Hz), 6.92 (d, 2H, *J* = 8.0 Hz), 3.85 (s, 3H), 2.44-2.18 (m, 4H), 2.07-2.03 (m, 1H), 1.48-1.45 (m, 1H), 1.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

210.8, 193.2, 163.5, 131.1, 129.9, 113.8, 55.4, 50.7, 40.8, 34.2, 28.9, 23.8, 18.5; IR (neat): ν 3075, 3004, 2954, 2935, 2871, 1721, 1657, 1598, 1574, 1510, 1449, 1419, 1357, 1341, 1310, 1252, 1210, 1167, 1114, 1064, 1026, 843, 823 cm^{-1}; MS (EI): m/z (%) = 244 (M^+, 11.84), 135 (100); HRMS (EI): calculated for $[C_{15}H_{10}O_3]^+$ 244.1099, found: 244.1100.

3-benzyl-1-(4-methoxybenzoyl)bicyclo[3.1.0]hexan-2-one (3o).

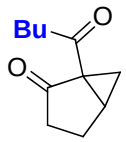


3o

Yellow oil, a mixture of diastereomer (1: 1.5), 78% yield (hexanes/ethyl acetate = 10:1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 1.2H, J = 7.2 Hz), 7.69 (d, 0.8H, J = 7.2 Hz), 7.31-7.15 (m, 5H), 6.93 (d, 1.2H, J = 7.6 Hz), 6.89 (d, 0.8H, J = 7.6 Hz), 3.86 (s, 3H), 3.19-2.99 (m, 1.6H), 2.742.45 (m, 3.2H), 2.22-2.14 (m, 0.8H), 1.92-1.85 (m, 1.6H), 1.52-1.51 (m, 0.4H), 1.35 (s, 0.4H), 1.26-1.22 (m, 0.8H), 0.88-0.87 (m, 0.8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 209.6, 193.3, 192.9, 163.58, 163.56, 139.1, 139.0, 131.54, 131.52, 129.3, 129.20, 129.15, 128.5, 126.6, 126.4, 113.63, 113.59, 55.5, 49.7, 46.4, 44.9, 44.4, 38.4, 35.5, 29.3, 29.0, 28.4, 26.9, 21.2, 19.4; IR (neat): ν 3028, 3005, 2934, 2873, 1718, 1658, 1598, 1575, 1510, 1454, 1420, 1310, 1254, 1211, 1165, 1115, 1023, 839, 746, 702 cm^{-1}; MS (EI): m/z (%) = 320 (M^+, 15.51), 135 (100); HRMS (EI): calculated for $[C_{21}H_{20}O_3]^+$ 320.1412, found: 320.1413.

1-pentanoylbicyclo[3.1.0]hexan-2-one (3p).



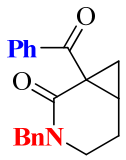
3p

Yellow oil, hexanes/ethyl acetate = 10:1, 78% yield.

^1H NMR (300 MHz, $CDCl_3$) δ : 3.08-2.97 (m, 1H), 2.85-2.74 (m, 1H), 2.64-2.58 (m, 1H), 2.30-2.24 (m, 2H), 2.20-1.95 (m, 3H), 1.59-1.48 (m, 2H), 1.43-1.40 (m, 1H), 1.35-1.33 (m, 2H), 0.90 (t, J = 9.6 Hz,

3H); ^{13}C NMR (CDCl3, 75 MHz) δ: 209.6, 204.7, 45.2, 41.8, 35.6, 34.2, 25.7, 25.2, 20.9, 13.9; IR (neat): ν 2958, 2935, 2874, 1723, 1689, 1458, 1382, 1304, 1257, 1091, 1034 cm^{-1}; MS (EI): m/z (%) = 180 (M^+, 1.77), 55 (100); HRMS (EI): calculated for $[C_{11}H_{16}O_2]^+$ 180.1150, found: 180.1151.

1-benzoyl-3-benzyl-3-azabicyclo[4.1.0]heptan-2-one (3q).

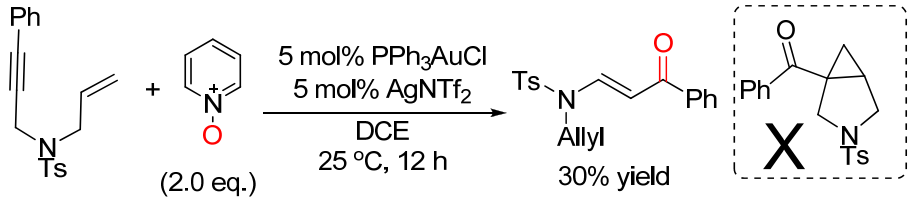


3q

White solid, m. p. = 126-128 °C, 41% yield (hexanes/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35-7.24 (m, 5H), 4.69 (d, *J* = 14.4 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H), 3.27-3.23 (m, 1H), 3.19-3.12 (m, 1H), 2.31-2.24 (m, 1H), 2.14-2.06 (m, 2H), 2.04 (s, 1H), 1.50 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 168.7, 137.12, 137.06, 132.6, 128.7, 128.3, 128.2, 128.1, 127.6, 50.1, 42.2, 34.6, 24.7, 20.4, 12.2; IR (neat): ν 3086, 3029, 2927, 2863, 1679, 1622, 1496, 1444, 1393, 1324, 1278, 1216, 1186, 1108, 1073, 1002, 740, 695 cm^{-1}; MS (EI): m/z (%) = 305 (M^+, 32.29), 91 (100); HRMS (EI): calculated for $[C_{20}H_{19}NO_2]^+$ 305.1416, found: 305.1417.

2.5 Gold(I)-Catalyzed Reaction of Enyne 1a:



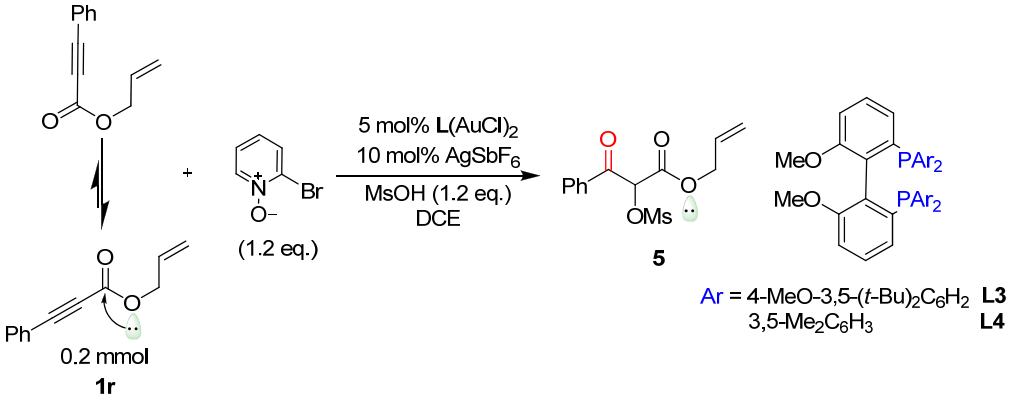
1a **2a** **3a**

In a dried glass tube, a mixture of IPrAuCl (6.2 mg, 0.01 mmol, 5 mol %) and $AgNTf_2$ (3.8 mg, 0.01 mmol, 5 mol %) in DCE (1 mL) was stirred at room temperature under nitrogen for 30 min to generate the gold catalyst. The mixture of 2-4 equiv. of pyridine *N*-oxide and **1a** in DCE (1 mL) was treated with the premixed gold catalyst and stirred at room temperature for 12 h. The mixture was concentrated and

the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 3:1) to afford **2a** in 30% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 13.2 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.55-7.51 (m, 1H), 7.46-7.42 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 13.6 Hz, 1H), 5.71-5.63 (m, 1H), 5.26-5.22 (m, 2H), 4.22-4.21 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 145.0, 142.5, 138.5, 135.3, 134.2, 134.1, 132.4, 130.2, 129.3, 129.2, 128.5, 128.0, 127.4, 118.7, 103.6, 48.8, 21.6..

2.6 Gold(I)-Catalyzed Reaction of Enyne 1r:



Entry	L	T (℃)	Time (h)	Yield (%)[a]
1	**L3**	rt	24	53[b]
2	**L4**	rt	24	34
3[c]	**L4**	60	24	51

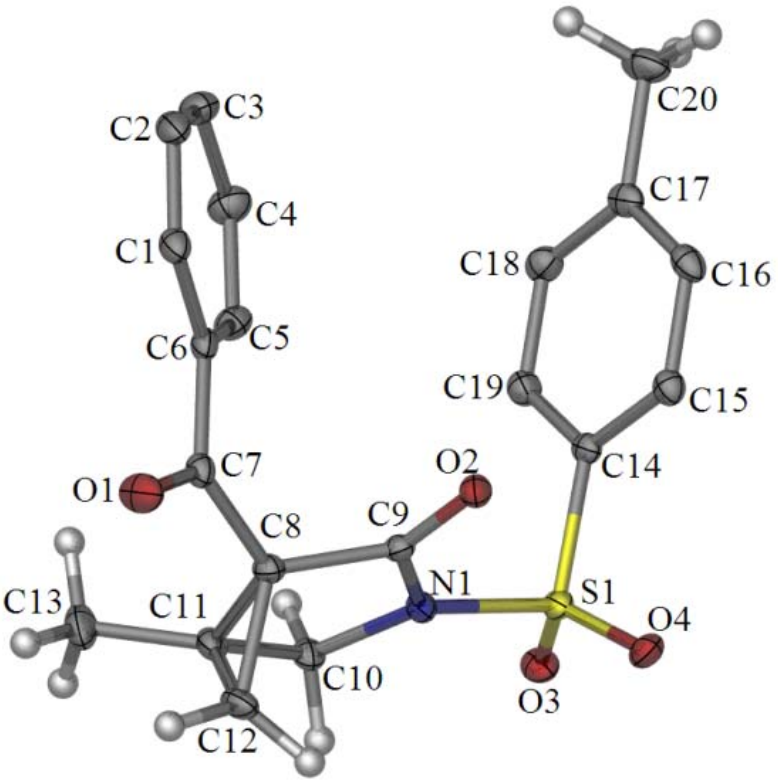
[a] ^{1}H NMR yield. [b] Isolated yield. [c] 2-bromopydine *N*-oxide (2.0 eq.).

MeO-DTBM-BIPHEP$(AuCl)_2$ (15.6 mg, 0.010 mmol) was added to a suspension of $AgSbF_6$ (6.8 mg, 0.020 mmol) in DCM (1 mL) at room temperature under nitrogen for 30 min to generate the gold catalyst. 2-bromopydine *N*-oxide (41.8 mg, 0.24 mmol), MsOH (0.12 mmol) and the premixed catalyst solution was added sequentially to a solution of enynes **1r** (0.2 mmol) in DCE (1 mL) at room temperature under nitrogen. After stirred for 24 h, the reaction was treated with saturated aqueous $NaHCO_3$ (5 mL), and the resulting solution was extracted with DCM (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4. The mixture was concentrated and the residue was

purified by column chromatography on silica gel (hexanes/EtOAc = 5:1) to afford **5** in 53% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.67-7.65 (m, 1H), 7.53-7.50 (m, 2H), 6.26 (s, 1H), 5.87-5.77 (m, 1H), 5.29-5.22 (m, 2H), 4.72-4.71 (m, 2H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 164.3, 134.7, 134.4, 130.4, 129.4, 129.0, 119.6, 67.2, 39.7.

2.7 Crystal Structure of Bicyclo [3.1.0]hexan-2one 3f:



Bond precision:	C-C = 0.0035 A		Wavelength=0.71073
Cell:	a=7.0007(8)	b=10.4842(8)	c=12.8845(12)
	alpha=103.453(8)	beta=95.091(3)	gamma=95.585(3)
Temperature: 173 K			
	Calculated		Reported
Volume	909.29(15)		909.29(15)
Space group	P -1		P-1
Hall group	-P 1		?
Moiety formula	C20 H19 N O4 S		?
Sum formula	C20 H19 N O4 S		C20 H19 N O4 S
Mr	369.43		369.42
Dx,g cm-3	1.349		1.349
Z	2		2
Mu (mm-1)	0.203		0.203
F000	388.0		388.0
F000'	388.43		
h,k,lmax	8,12,15		8,12,15
Nref	3221		3187
Tmin,Tmax	0.943,0.964		0.900,0.964
Tmin'	0.898		
Correction method= MULTI-SCAN			
Data completeness= 0.989		Theta(max)= 25.000	
R(reflections)= 0.0471(2919)		wR2(reflections)= 0.1329(3187)	
S = 1.088	Npar= 235		

3. References:

1. X. Tong,M. Beller and M. K. Tse, *J. Am. Chem. Soc.* 2007, **129**, 4906.

2. L. L. Welbes, T. W. Lyons, K. A. Cychosz and M. S. Sanford, *J. Am. Chem. Soc.* 2007, **129**, 5836.

3. H. Peng and G. Liu, *Org. Lett.*, **2011**, *13*, 772.

4. T. L.Young, K. C. Young and K. K. Youn, *J. Org. Chem.* 2009, **74,** 7922.

5. H. Jiang, S. Ma, G. Zhu and X. Lu, *Tetrahedron* 1996, **52**, 10945.

6. X. Xie, X. Lu and Y. Liu, *J. Org. Chem.* 2001, **66**, 6545.

7. M. Schelwies, R. Moser, A. L. Dempwolff, F. Rominger and G. Helmchen, *Chem. Eur. J.* 2009, **15**, 10888.

8. P. Kraft, and A. Bruneau, *Eur. J. Org. Chem.* 2007, 2257.

9. D. H. Kim and S. Chung, *Tetrahedron: Asymmetry* 1999, **10**, 3769.

10. W. E. Brenzovich, D. Jr. Benitez , A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A., III Goddard, and F. D. Toste, *Angew. Chem., Int. Ed.* 2010, **49**, 5519

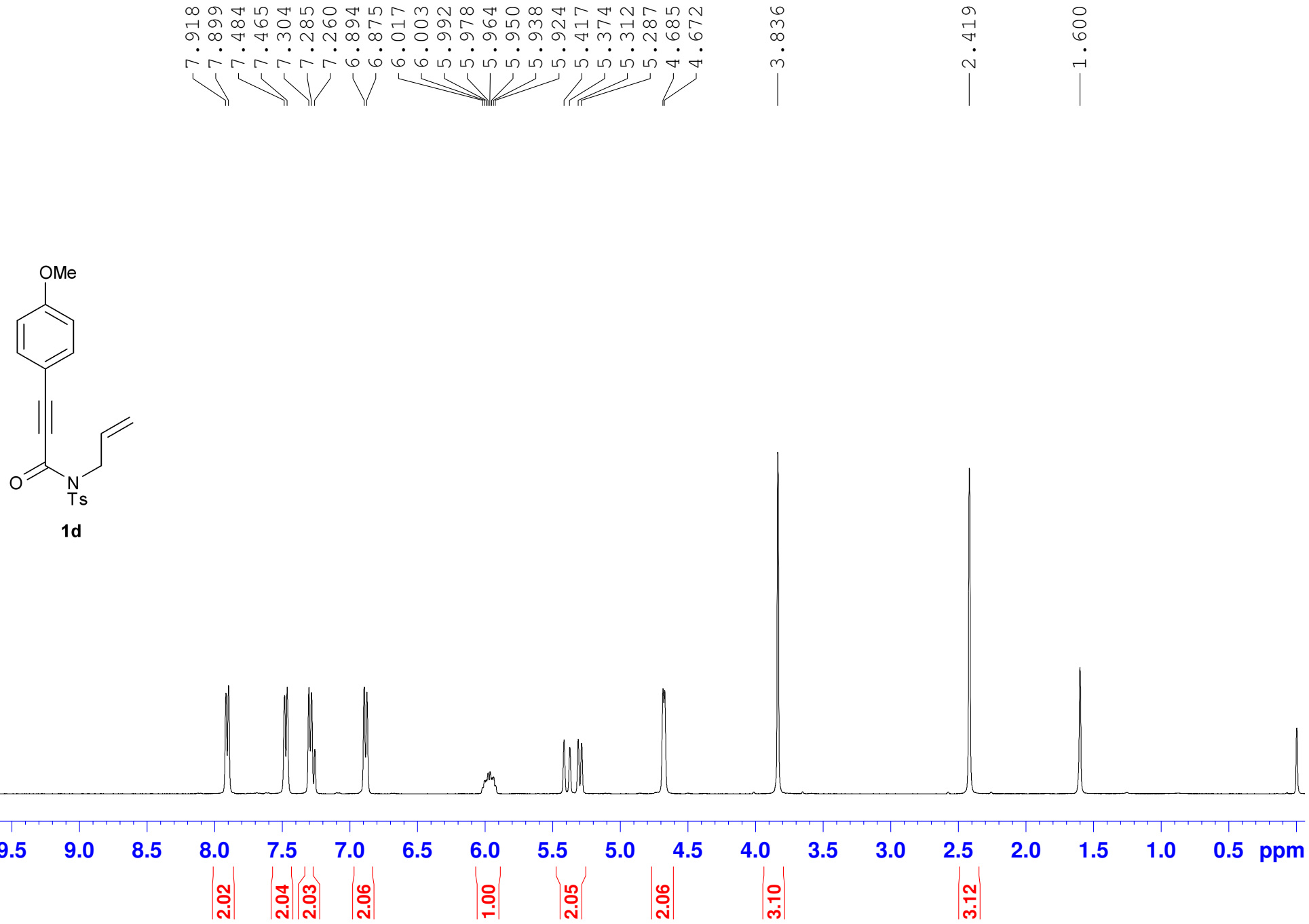
11. T. Kobayashi, Y. Koga and K. Narasaka, *J. Organomet. Chem.* 2001, **624**, 73.

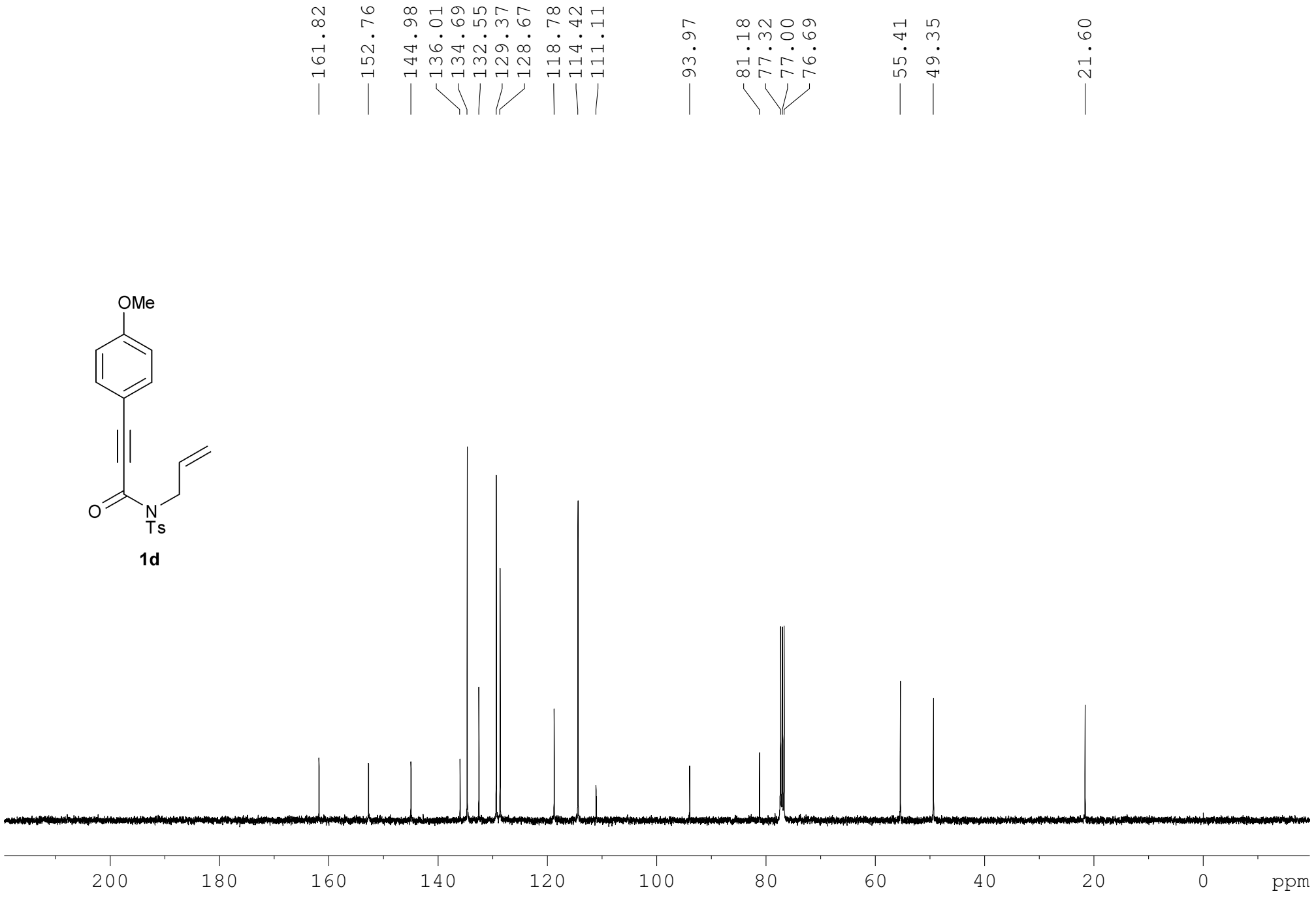
12. V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* 2004, **126**, 8654

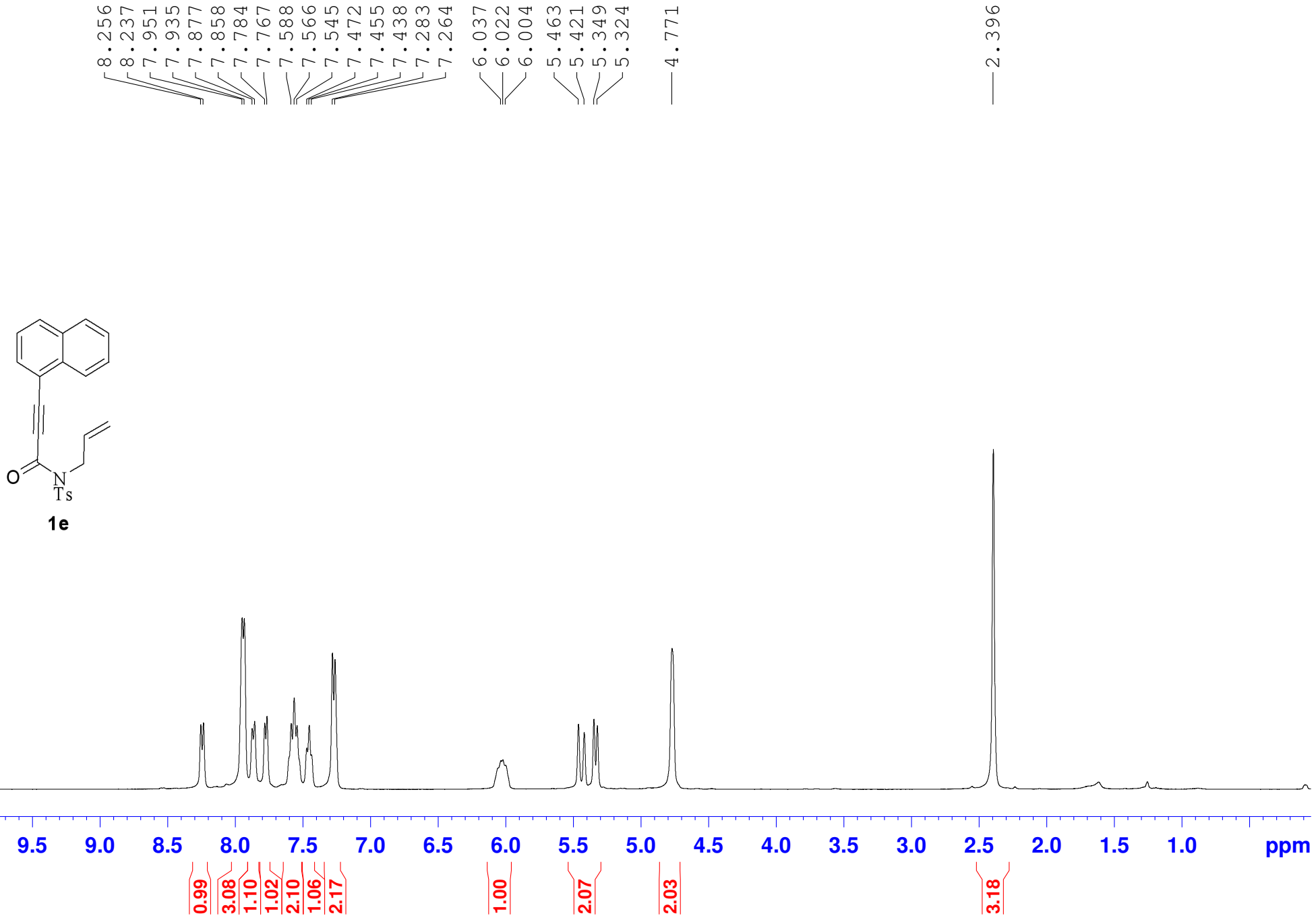
13. H. Kuroda, E. Hanakia, H. Izawaa, M. Kanoa and H. Itahashia, *Tetrahedron* 2004, **60**, 1913.

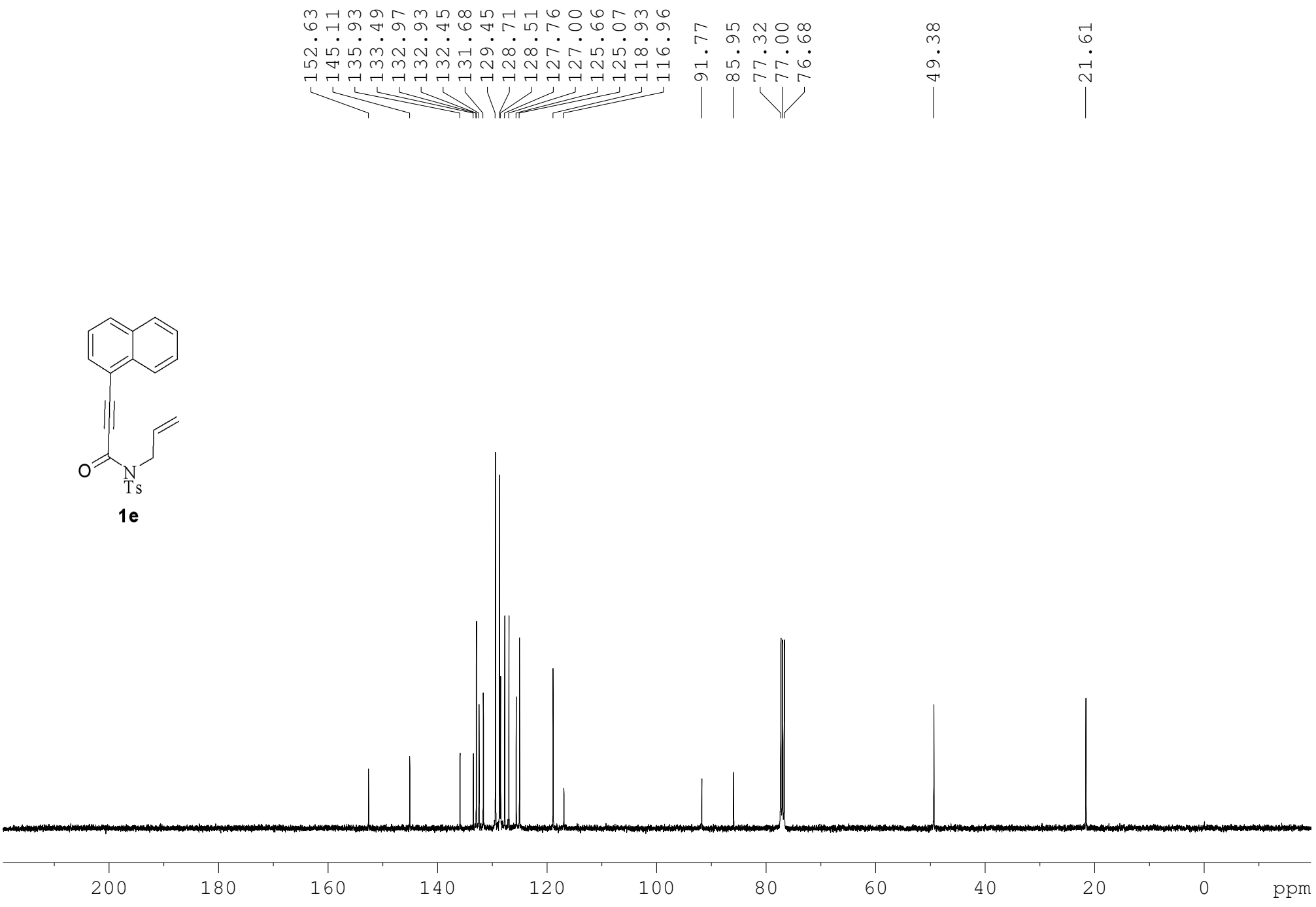
14. C. Taillier, T. Hameury, V. Bellosta and J. Cossy *Tetrahedron* 2007, **63**, 4472.

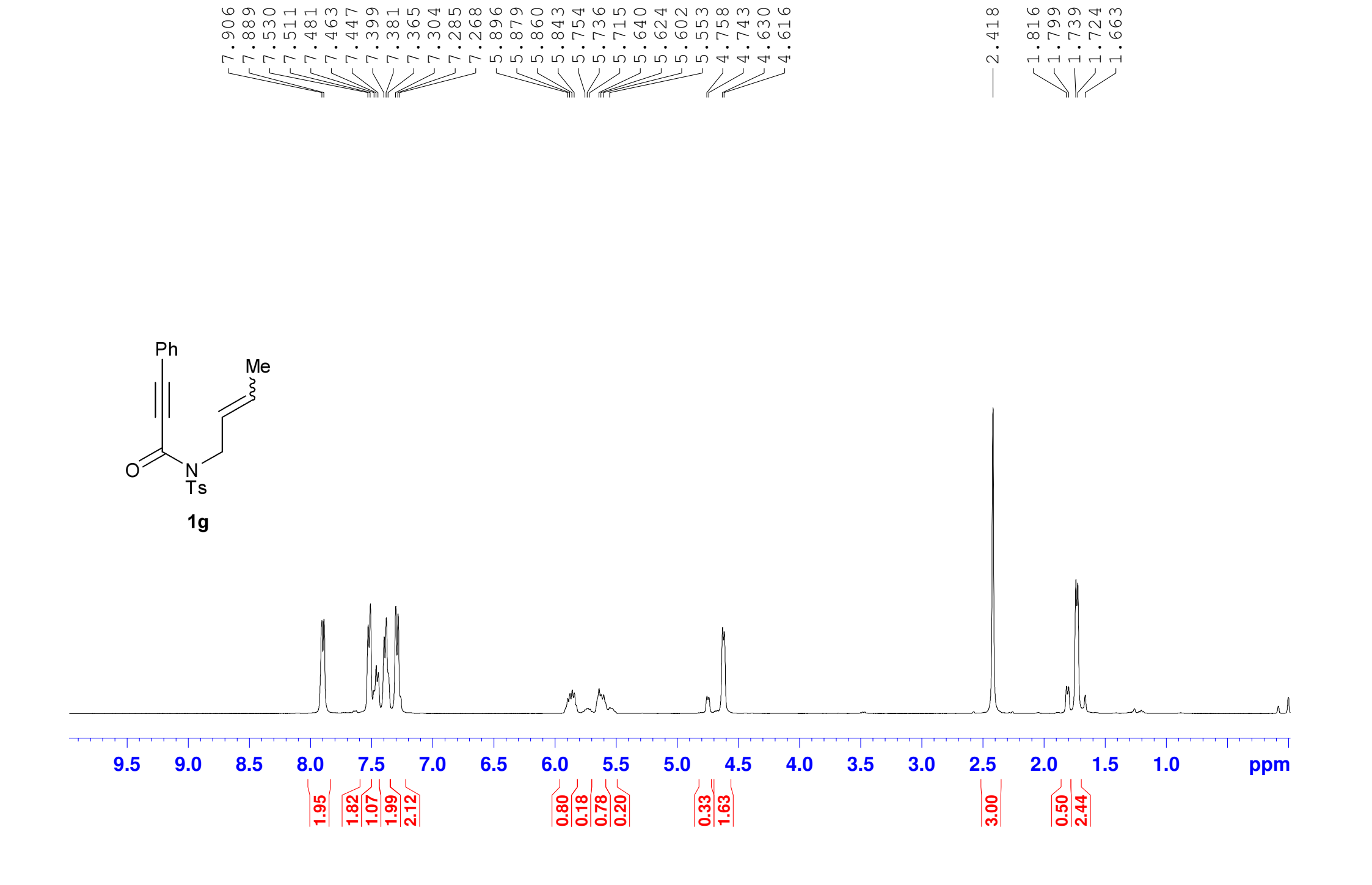
4. ^{1}H and ^{13}C NMR Spectra for New Compounds

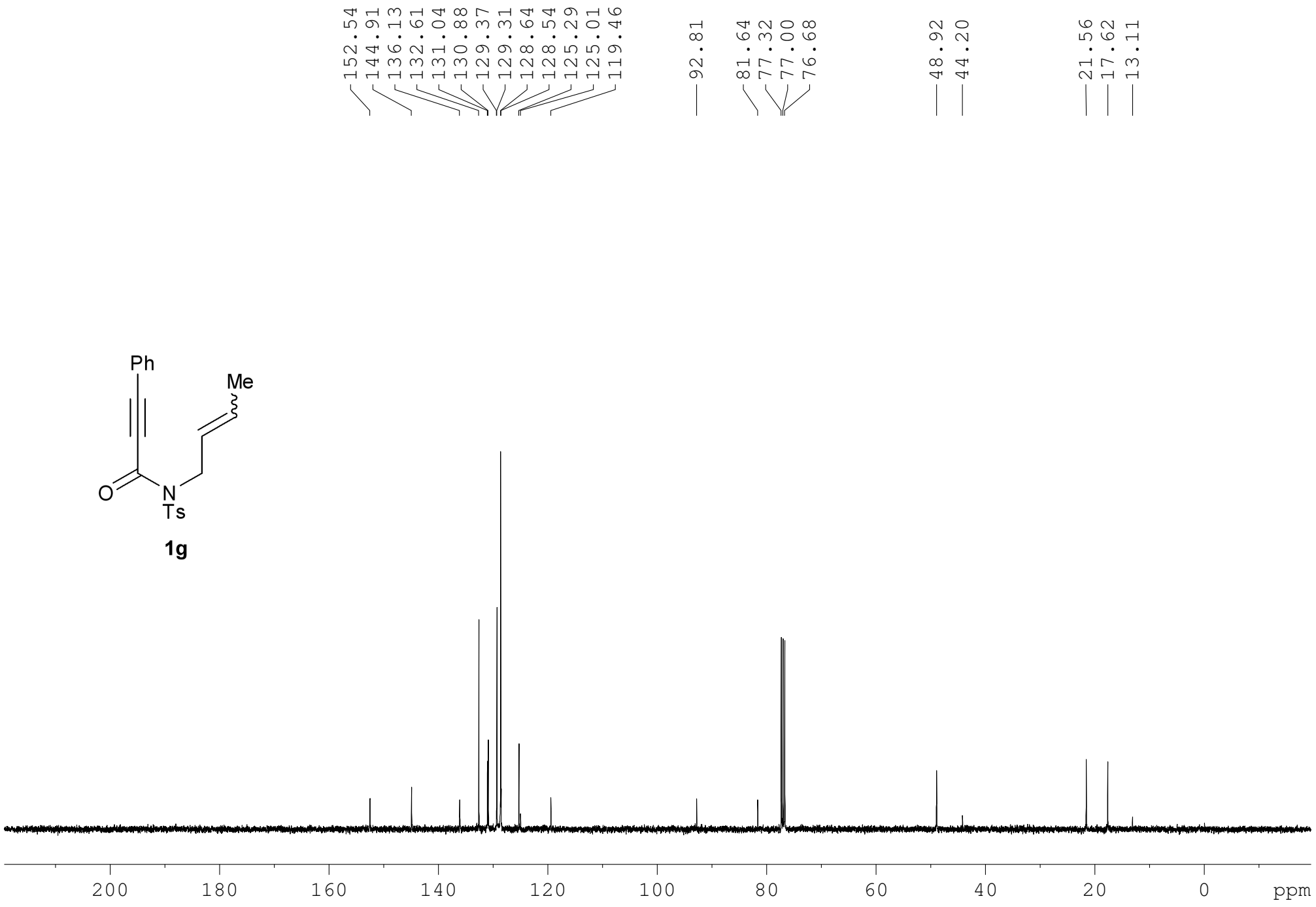


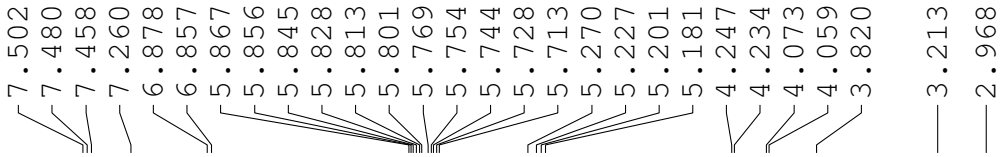


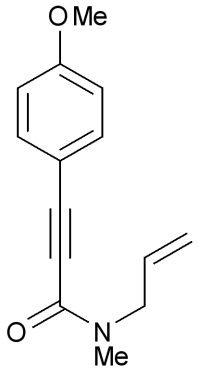




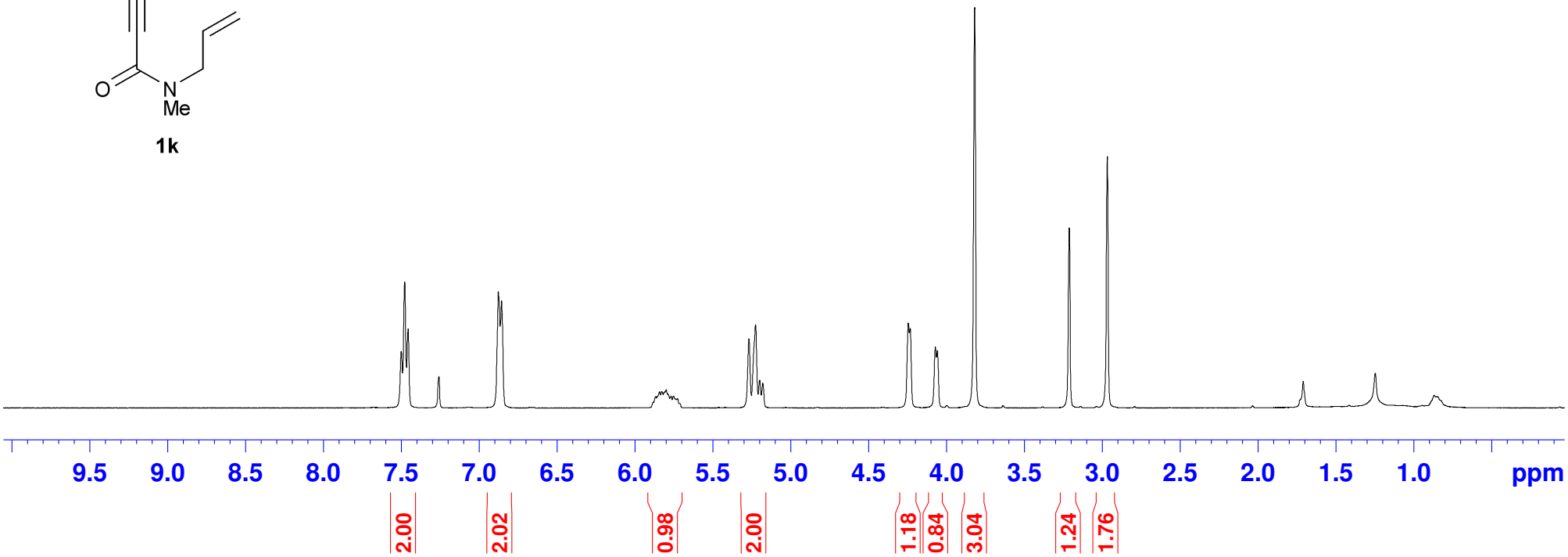


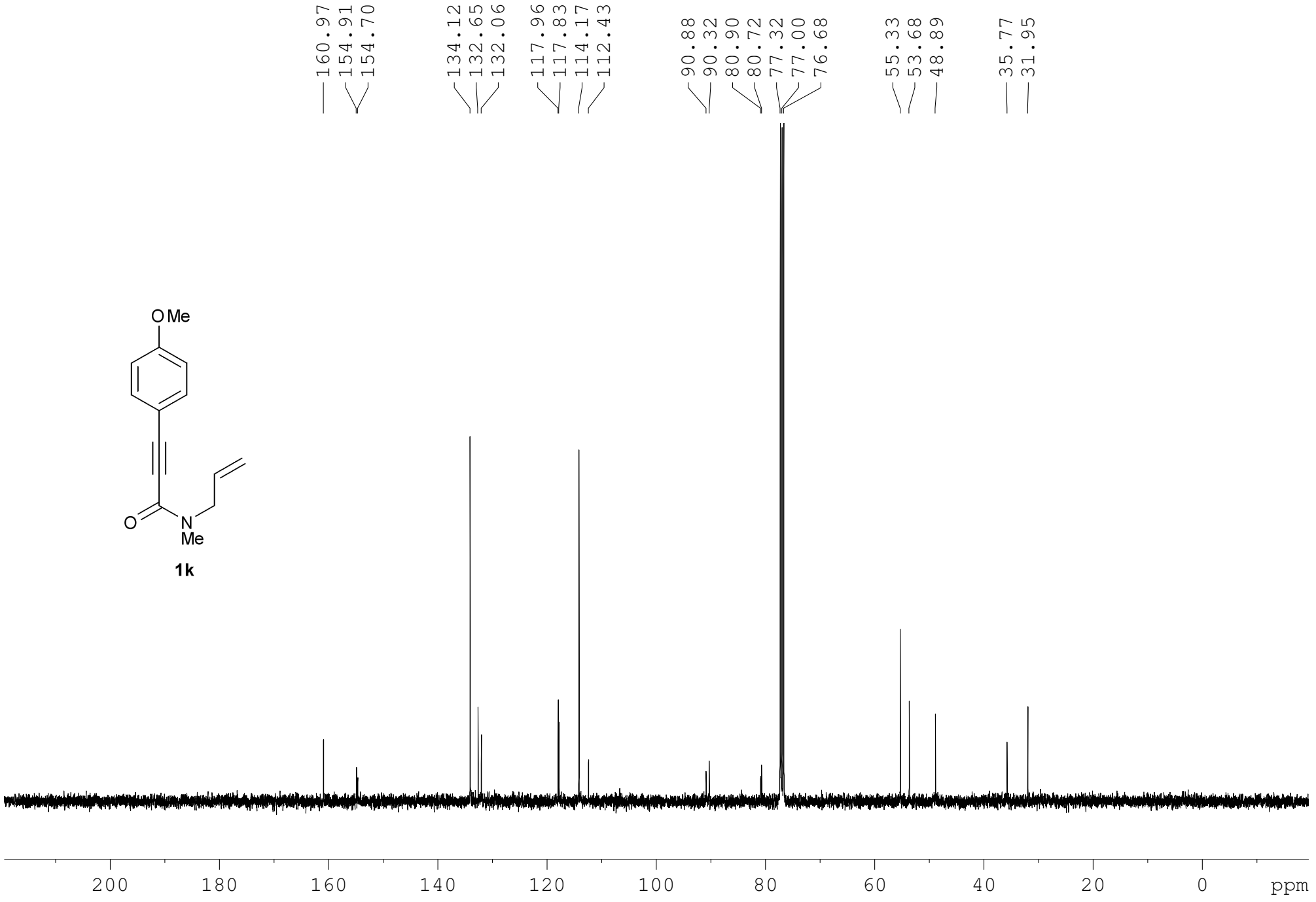




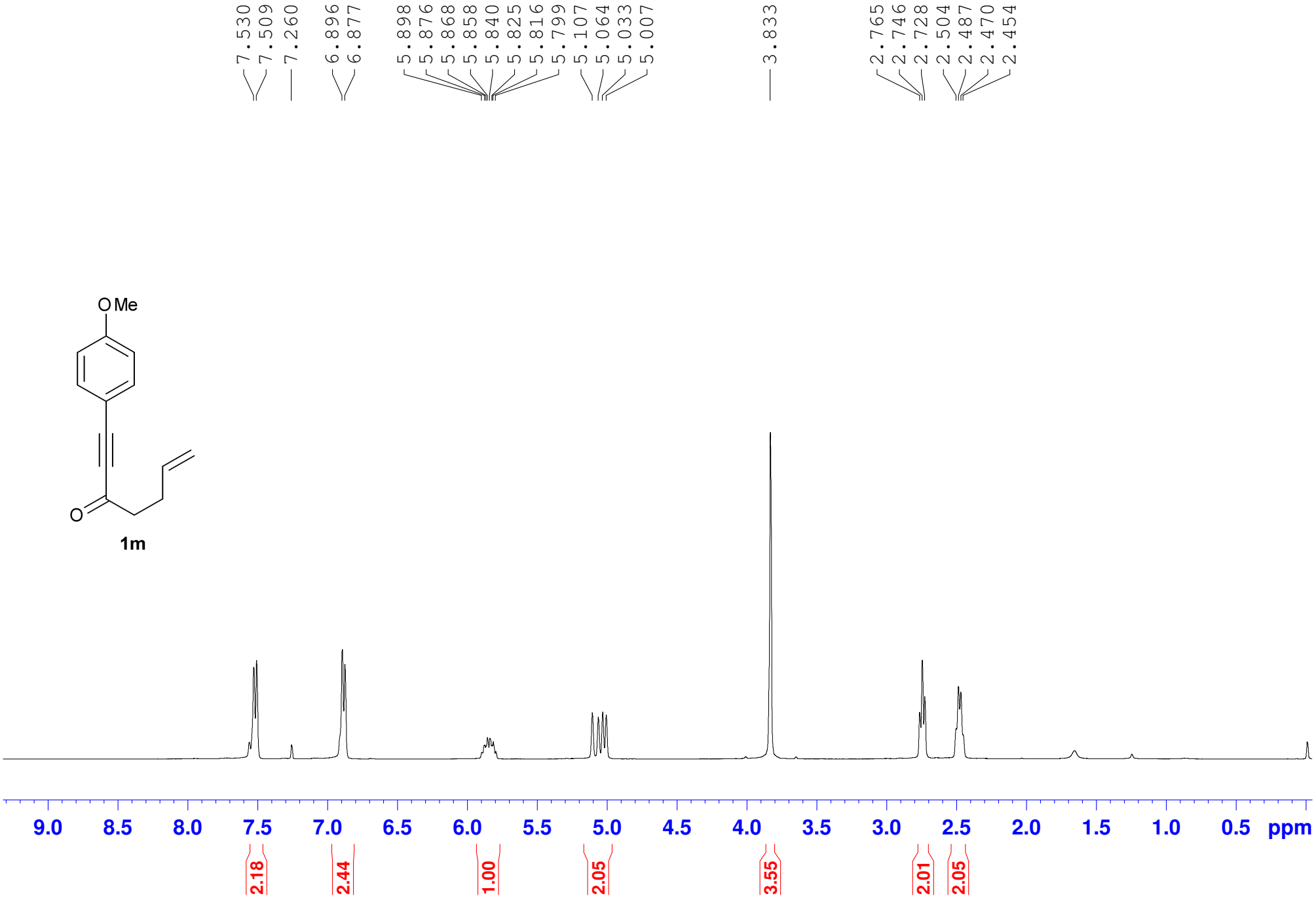


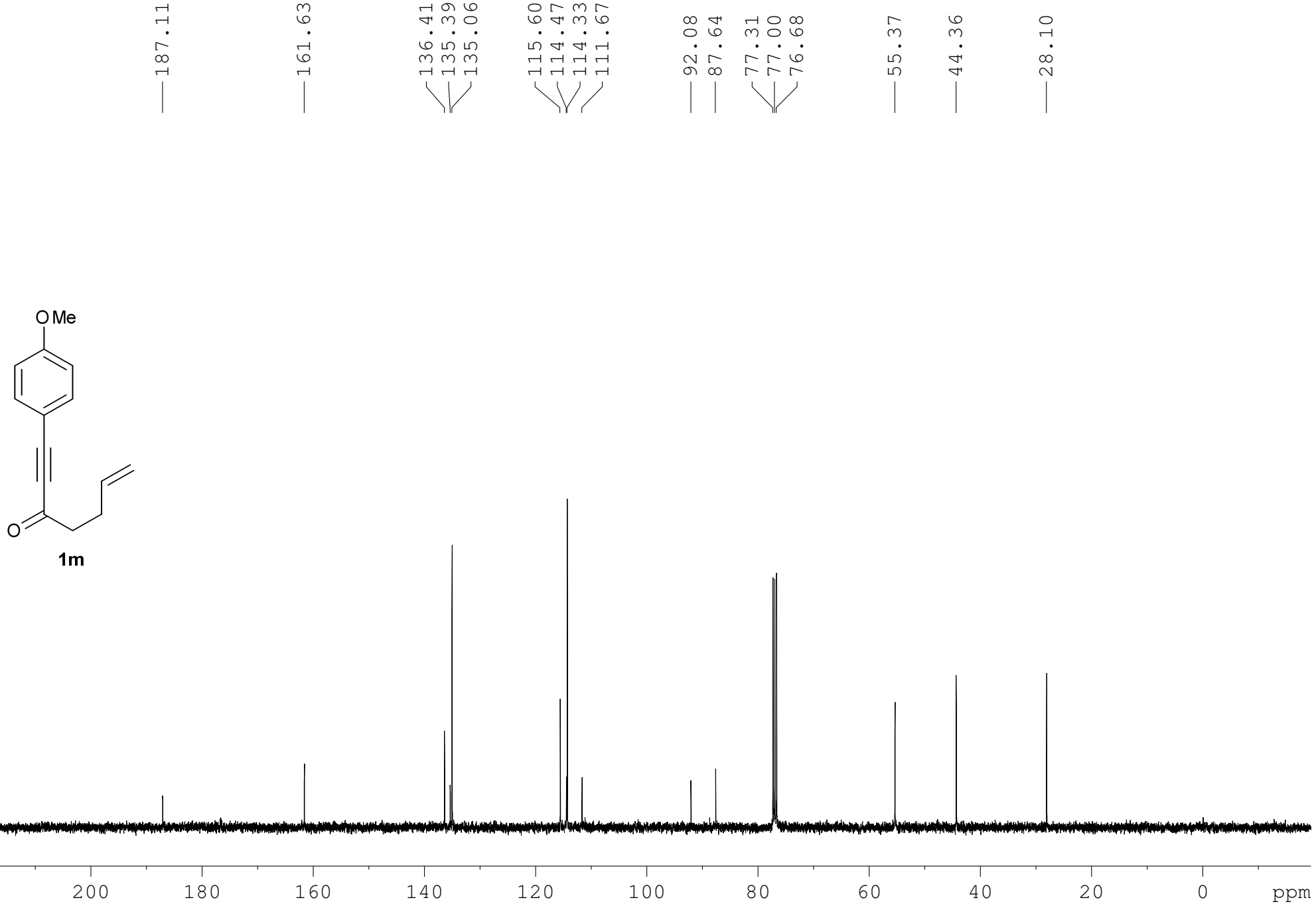
1k

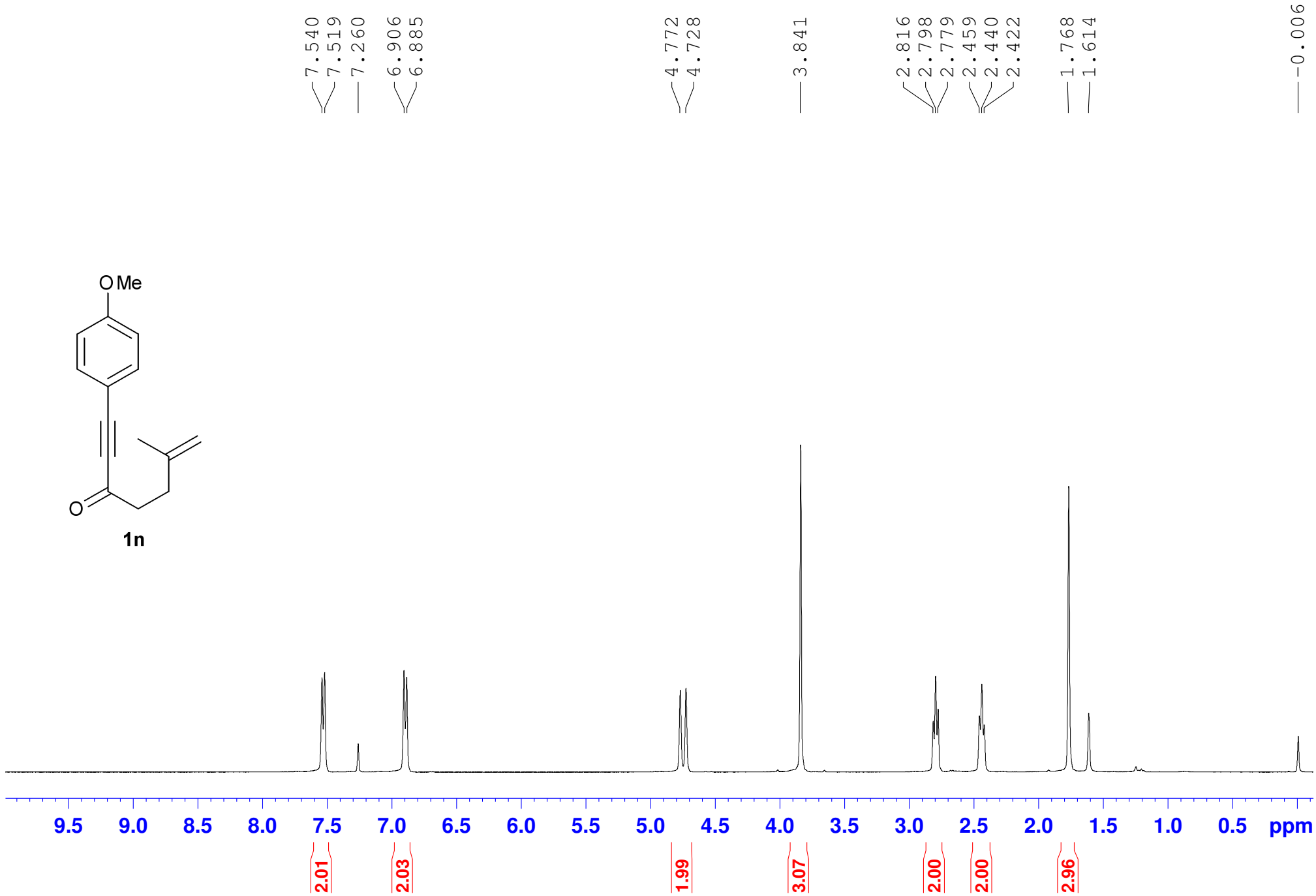


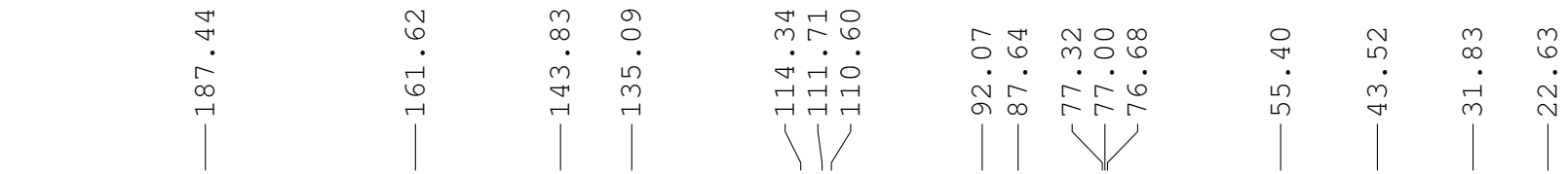


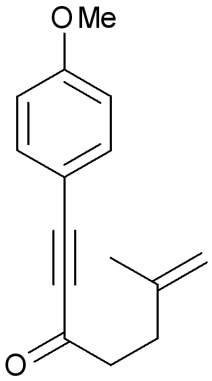
1k



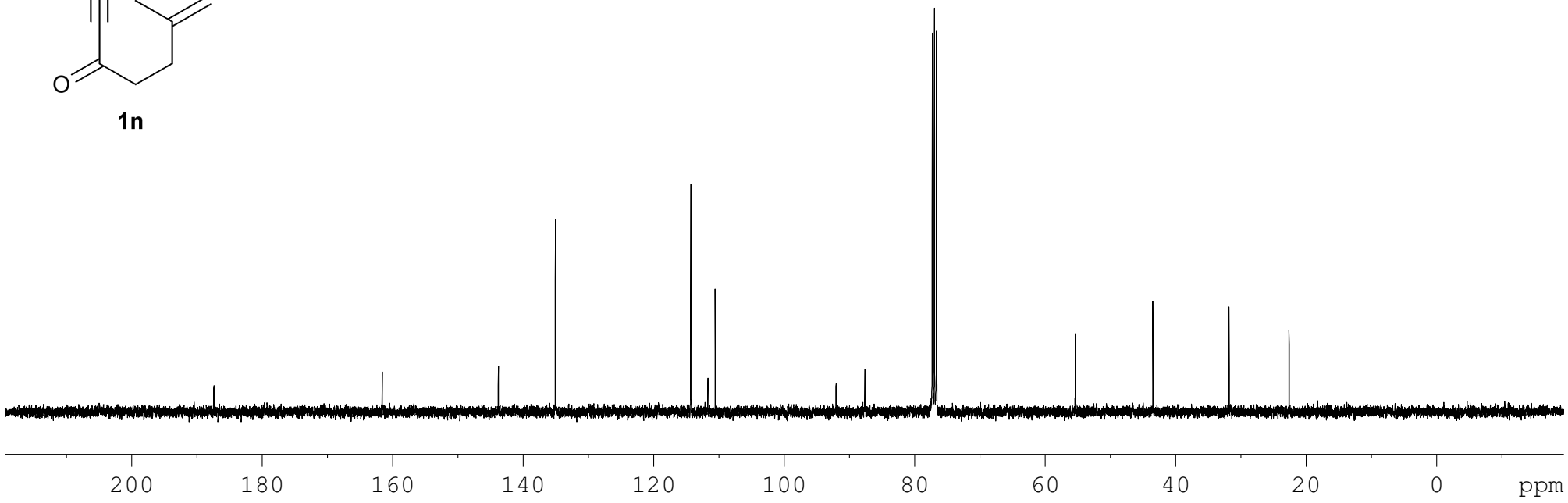


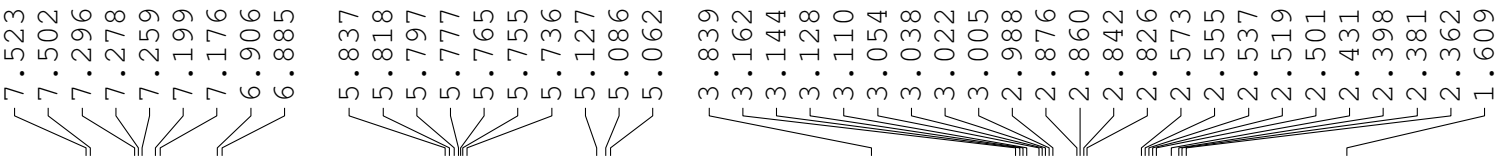


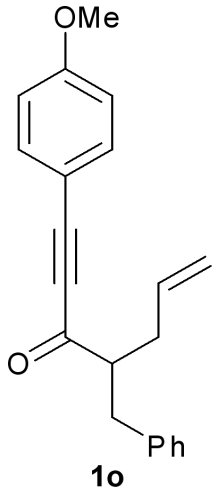




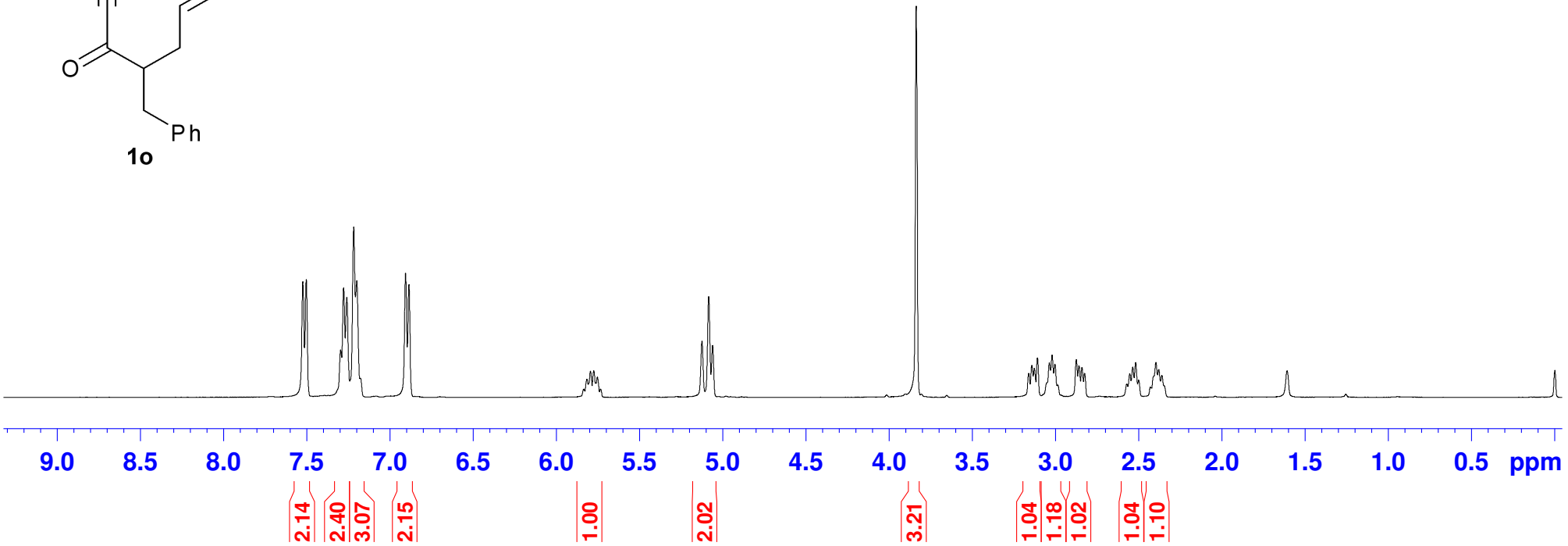
1n

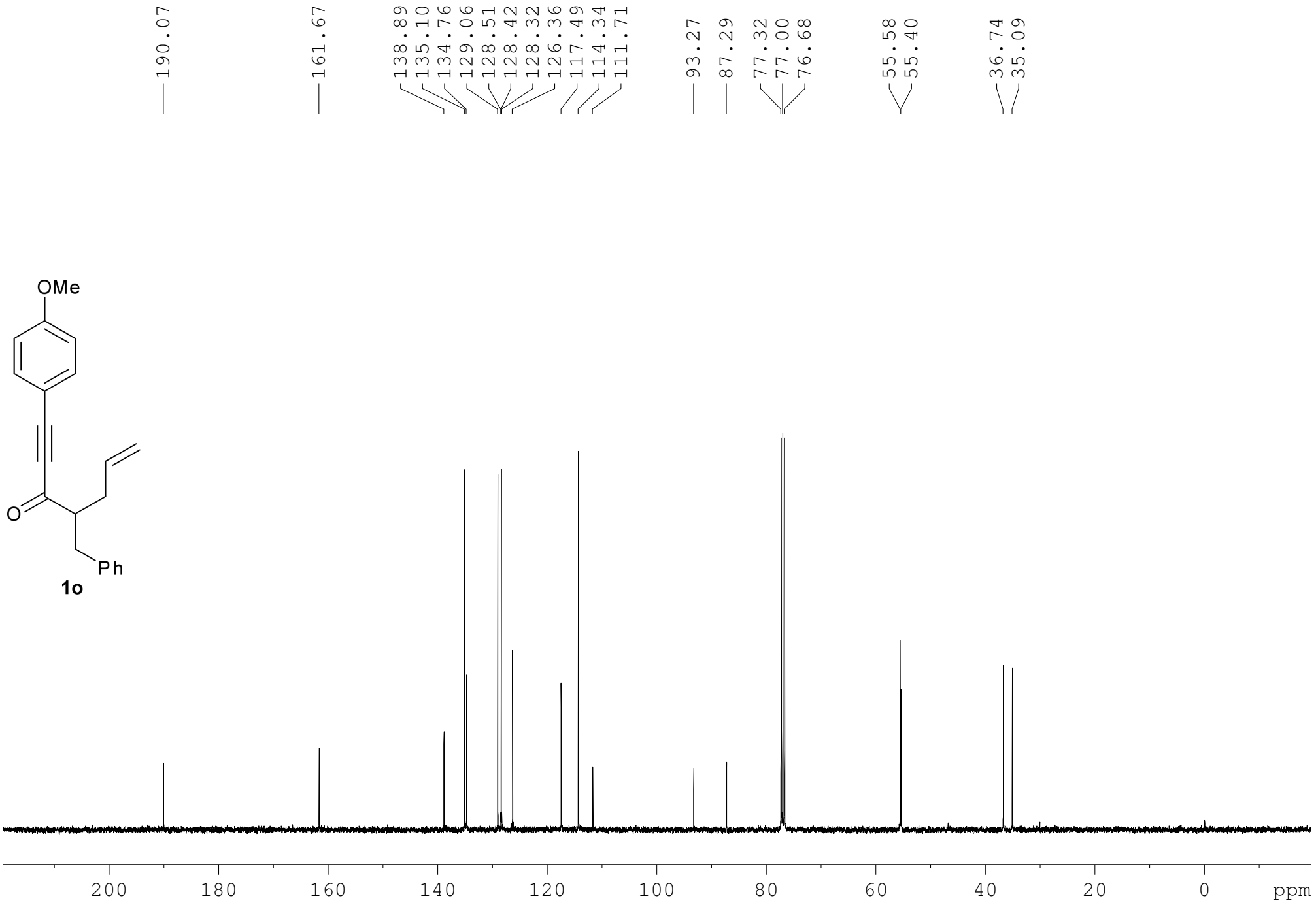


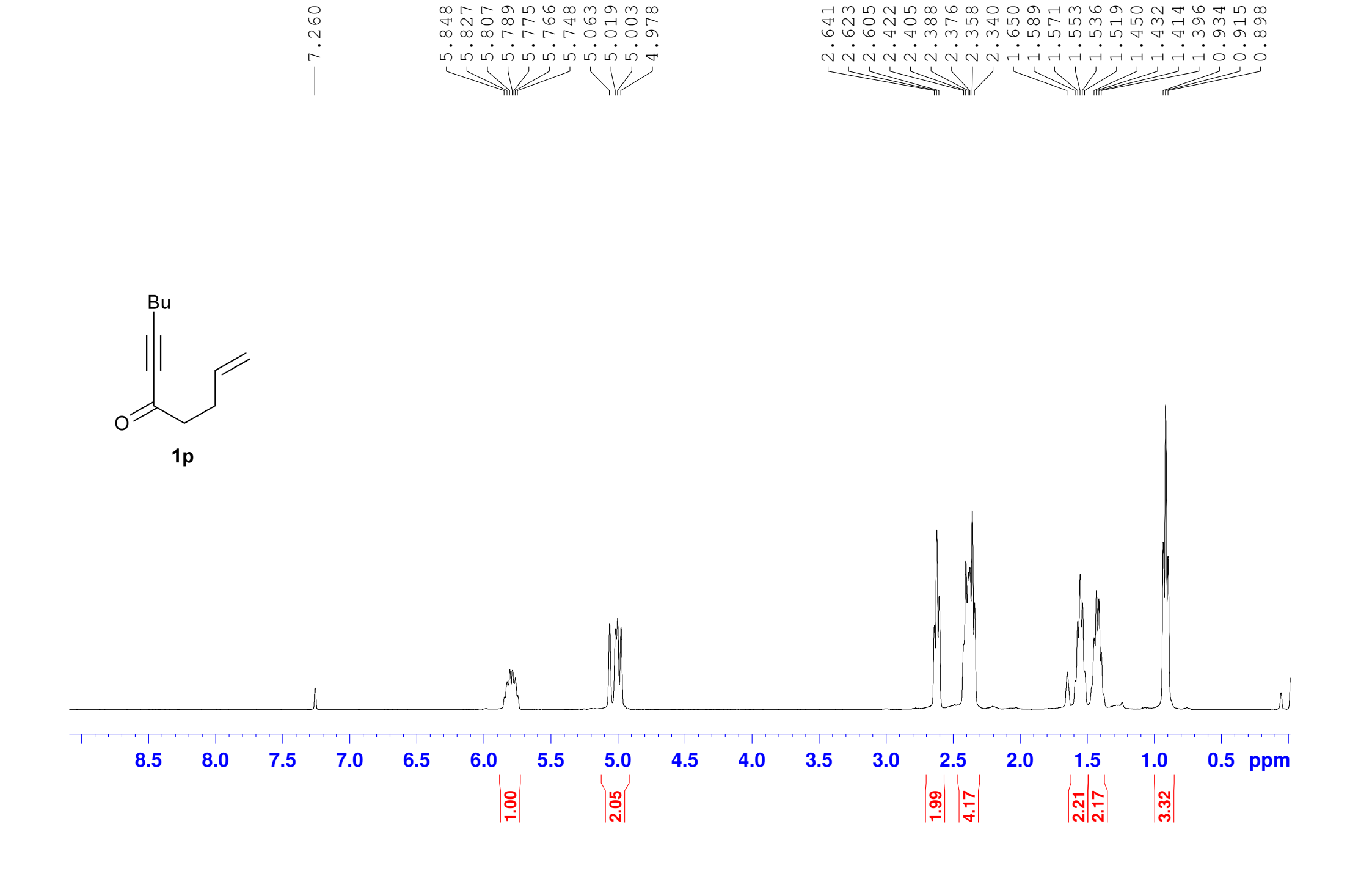


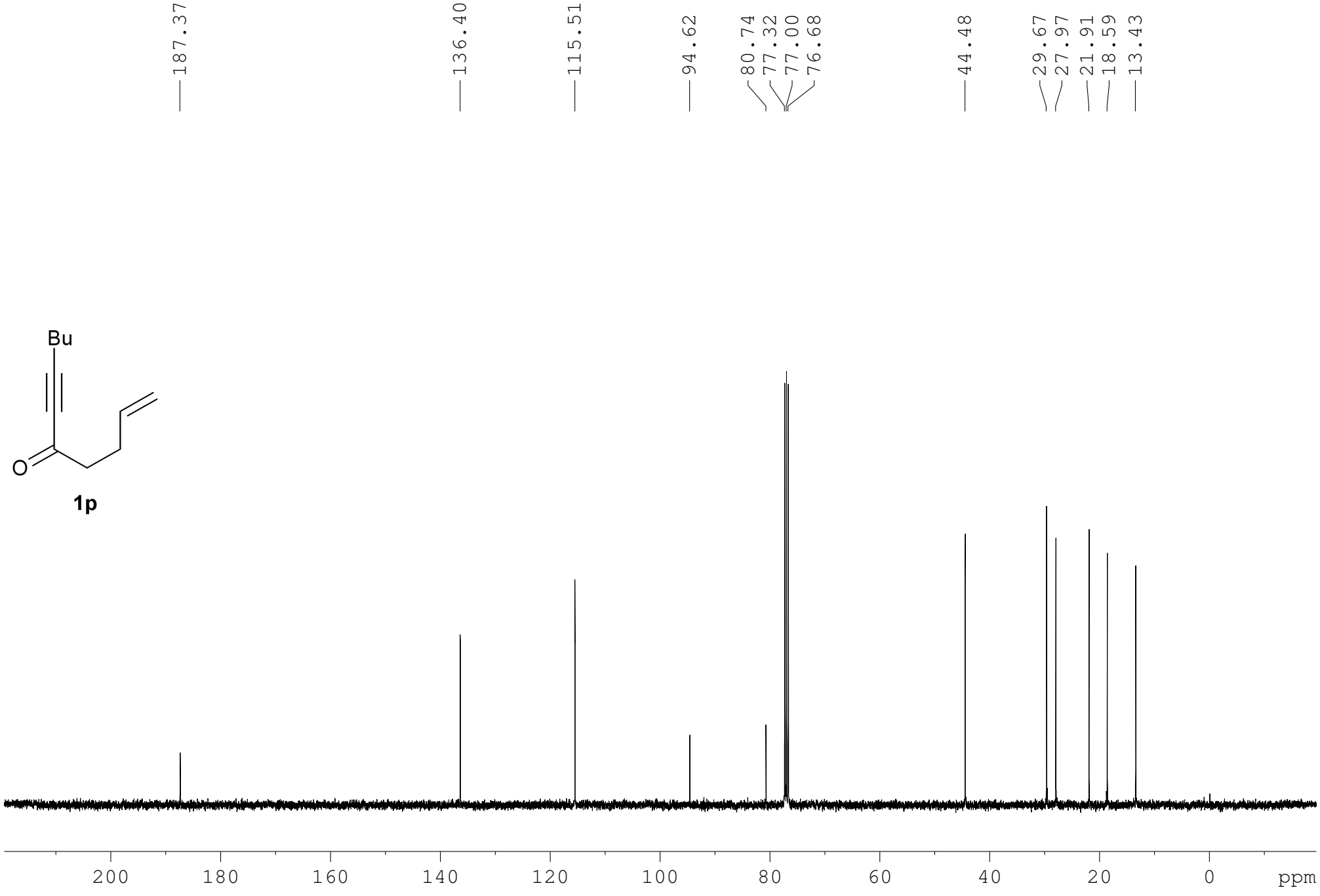


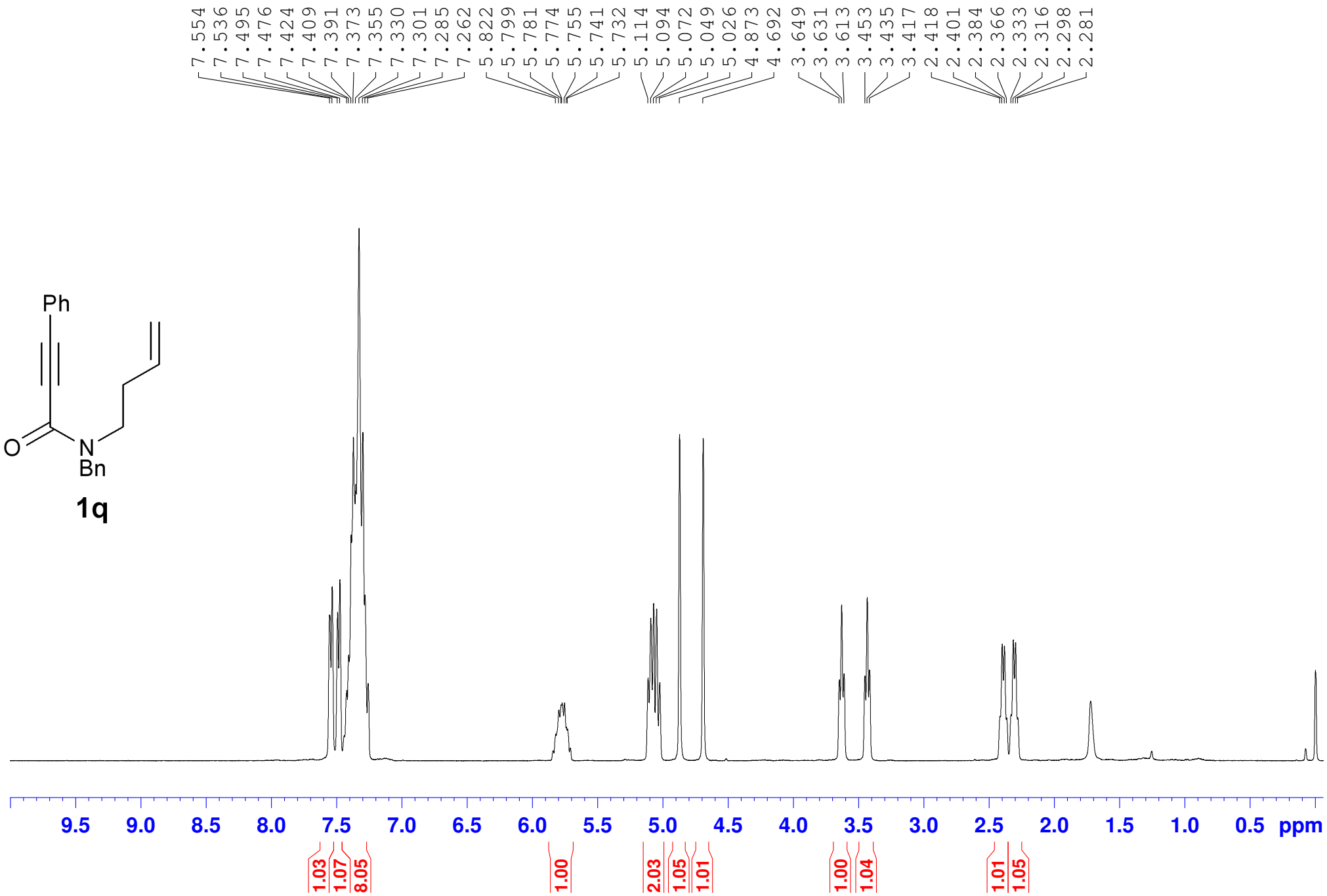
1o

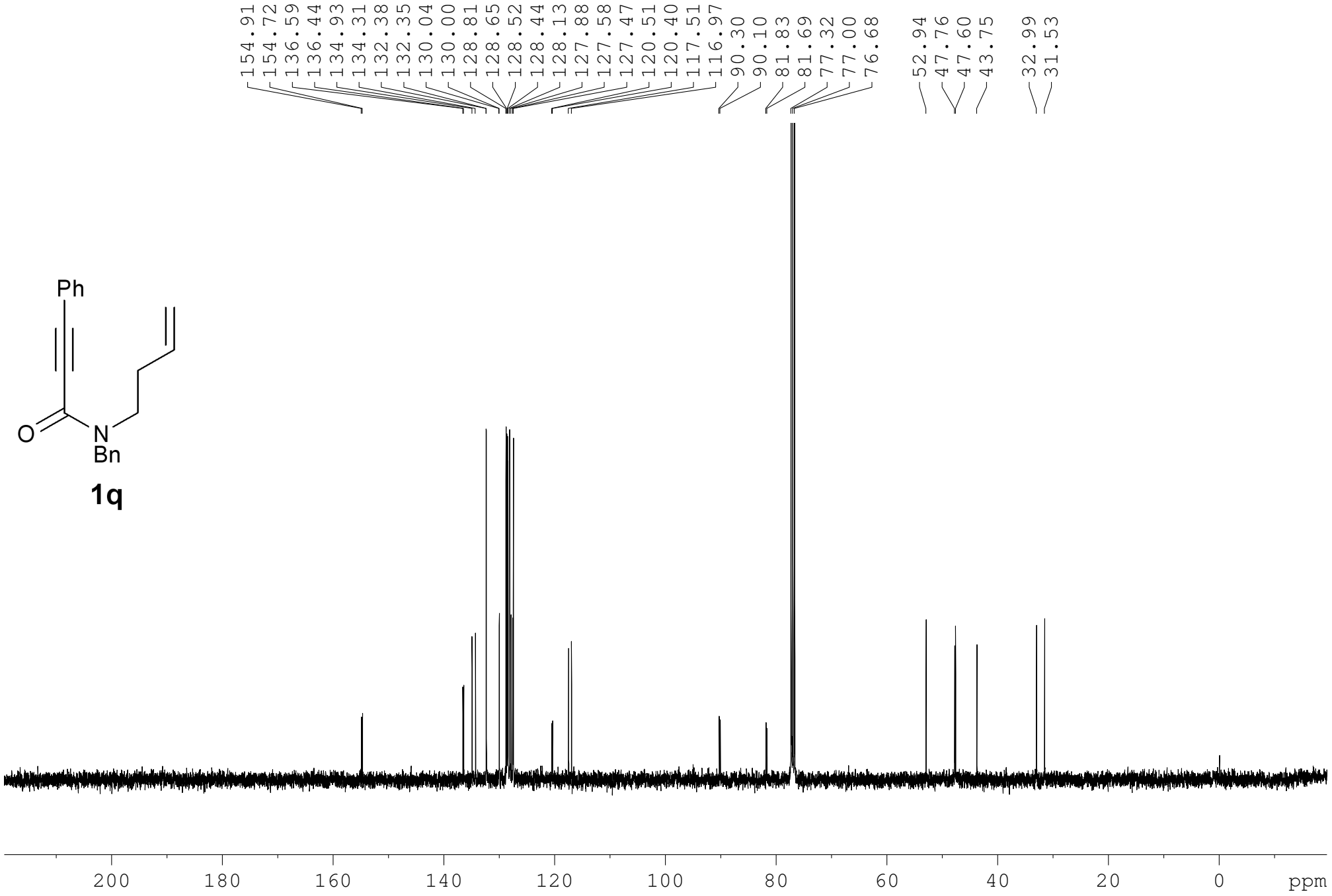


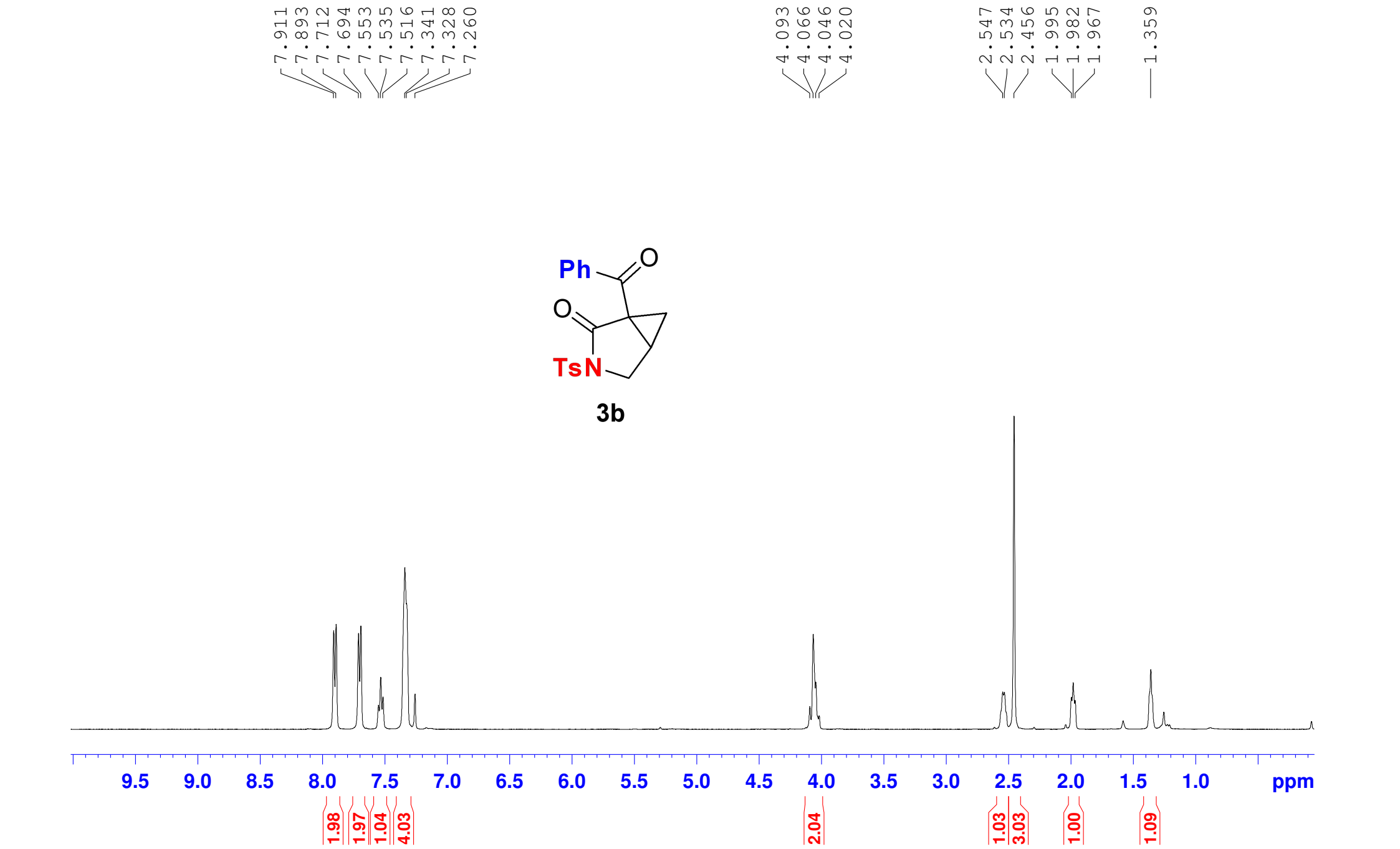


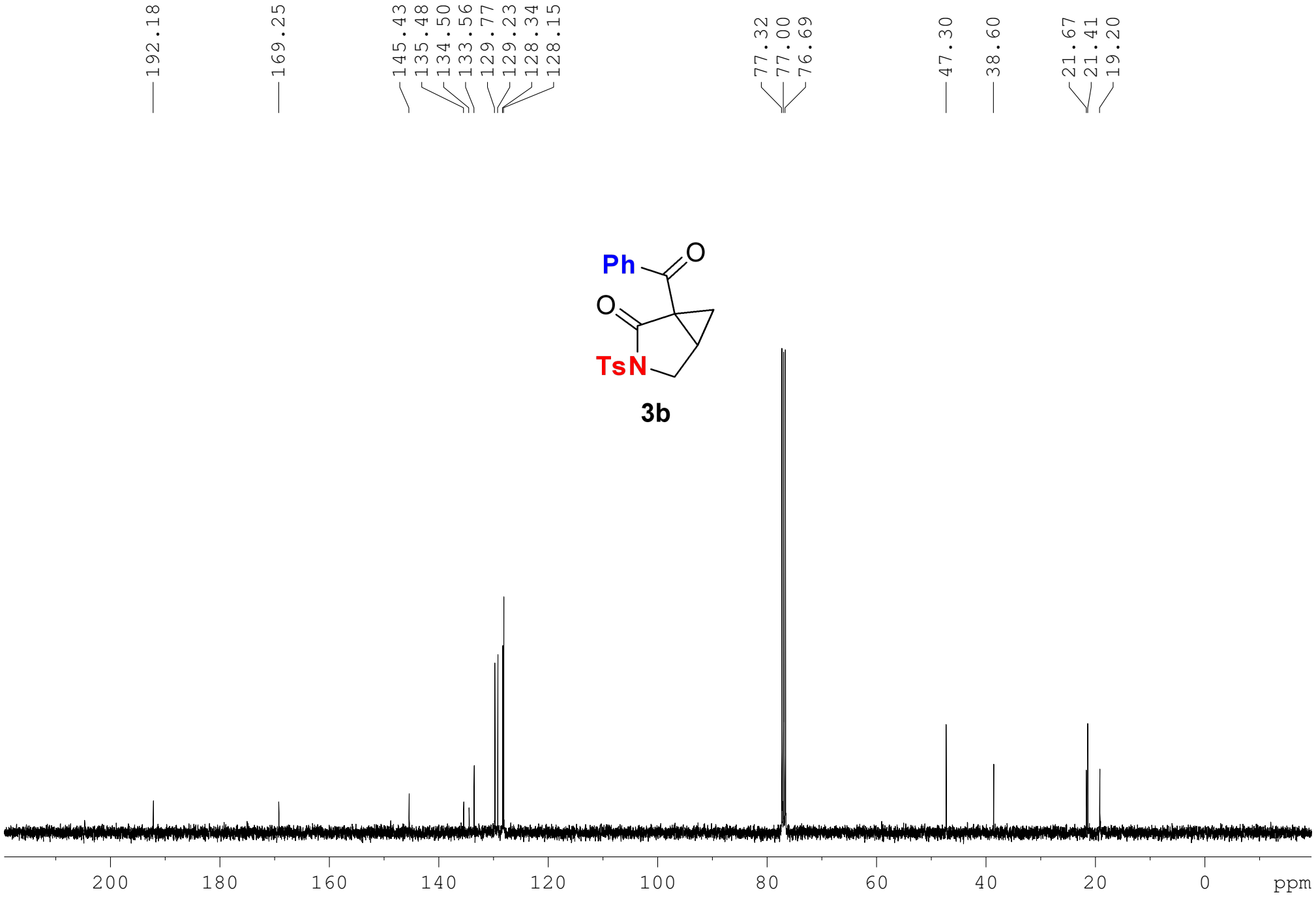


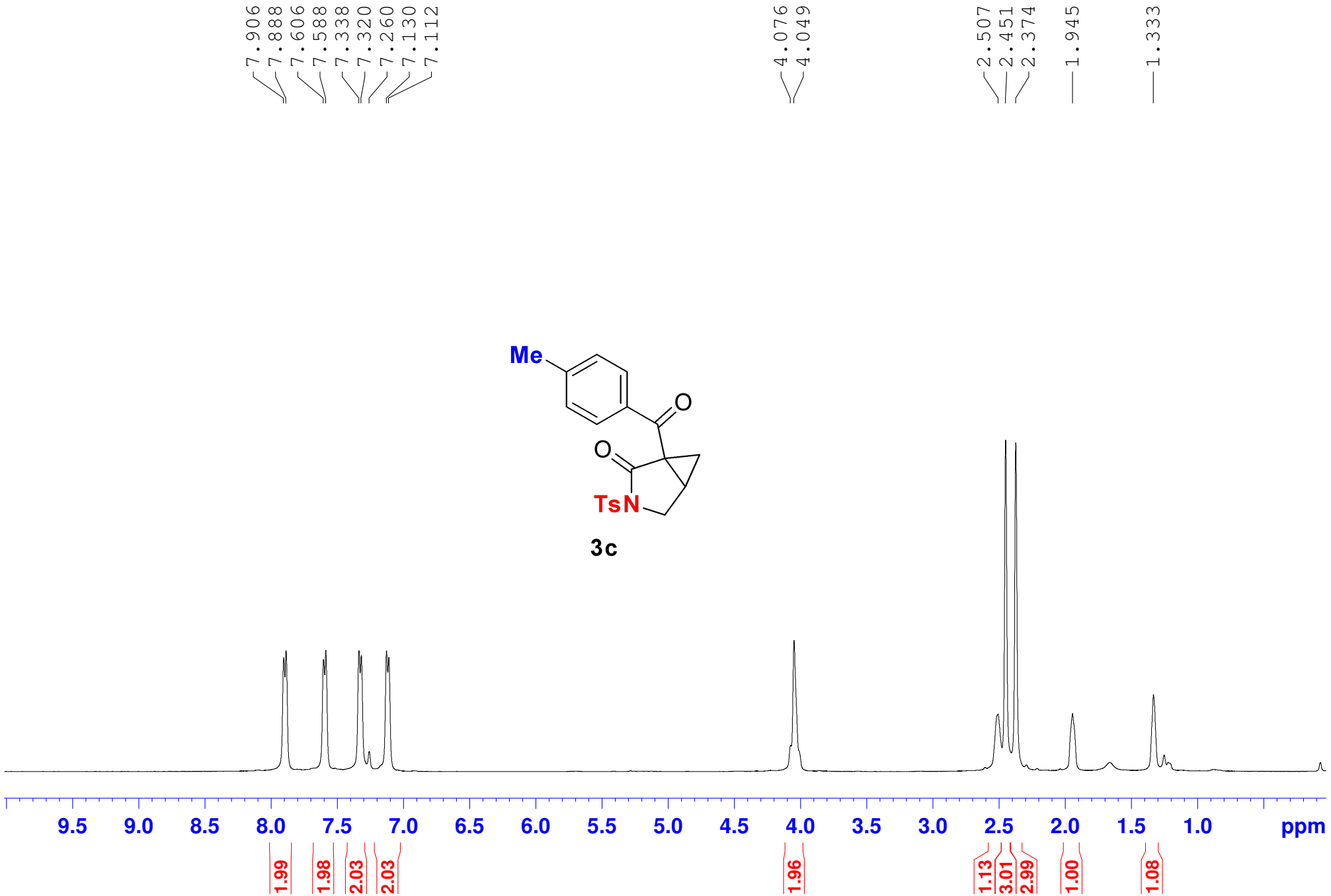


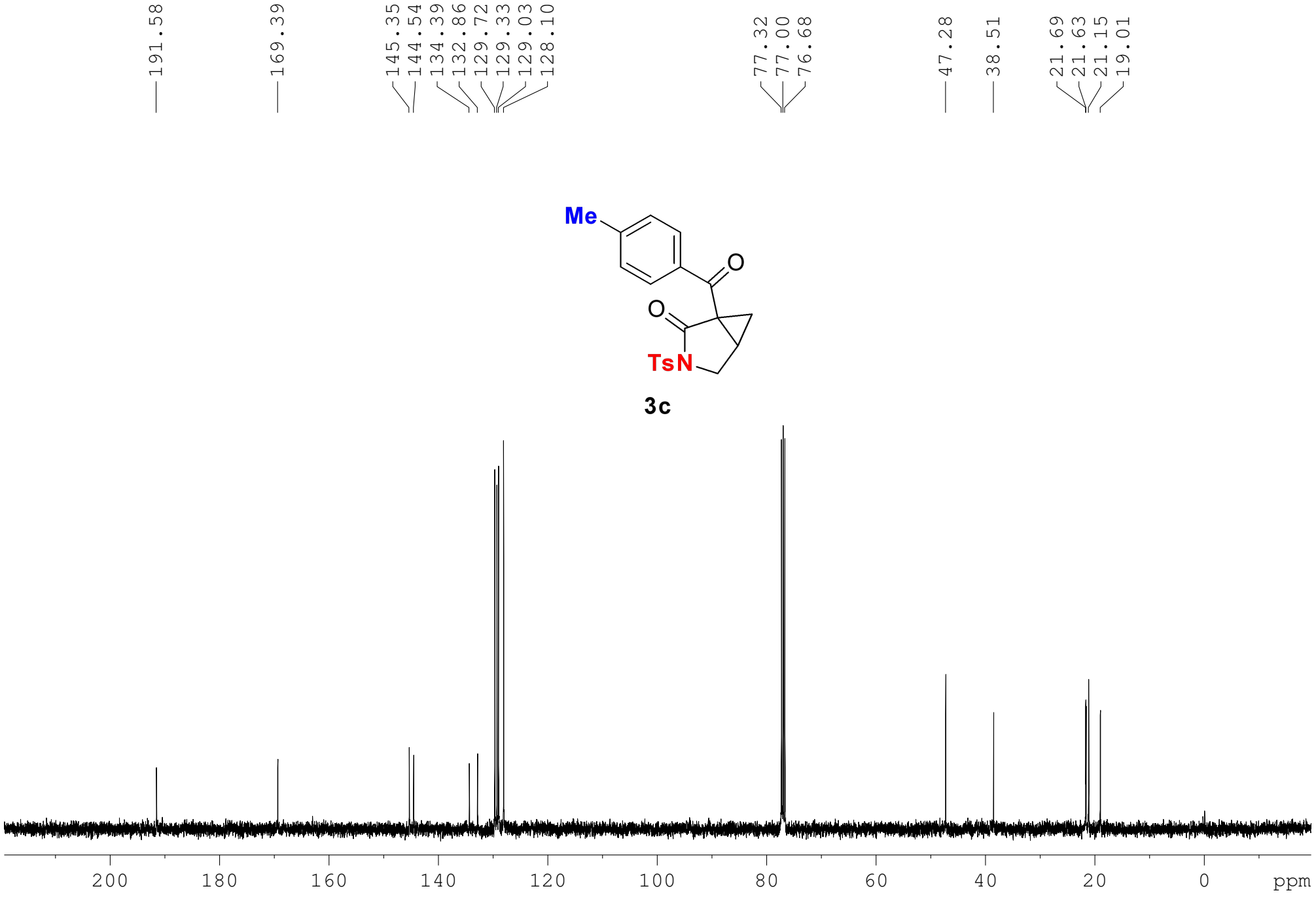


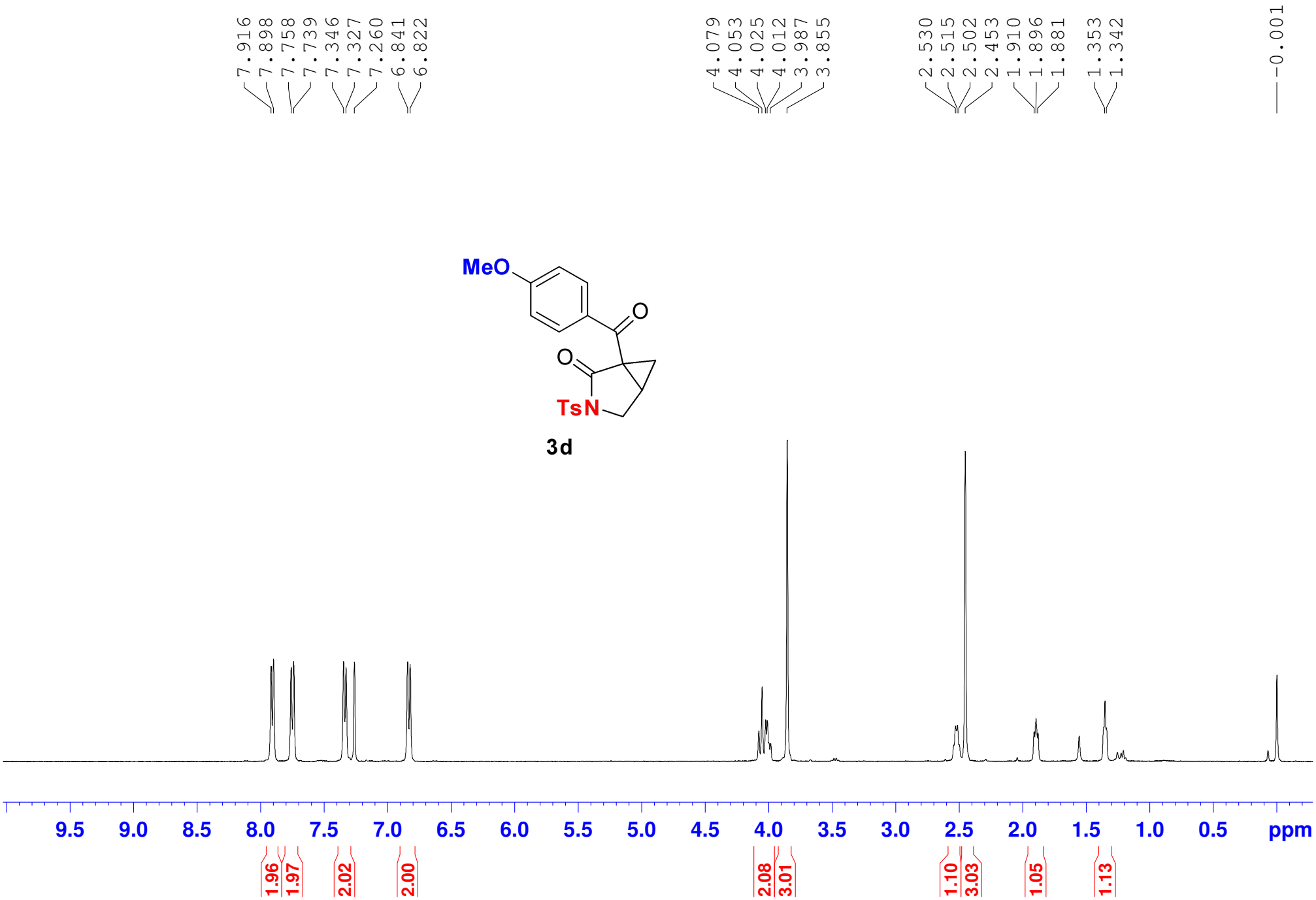


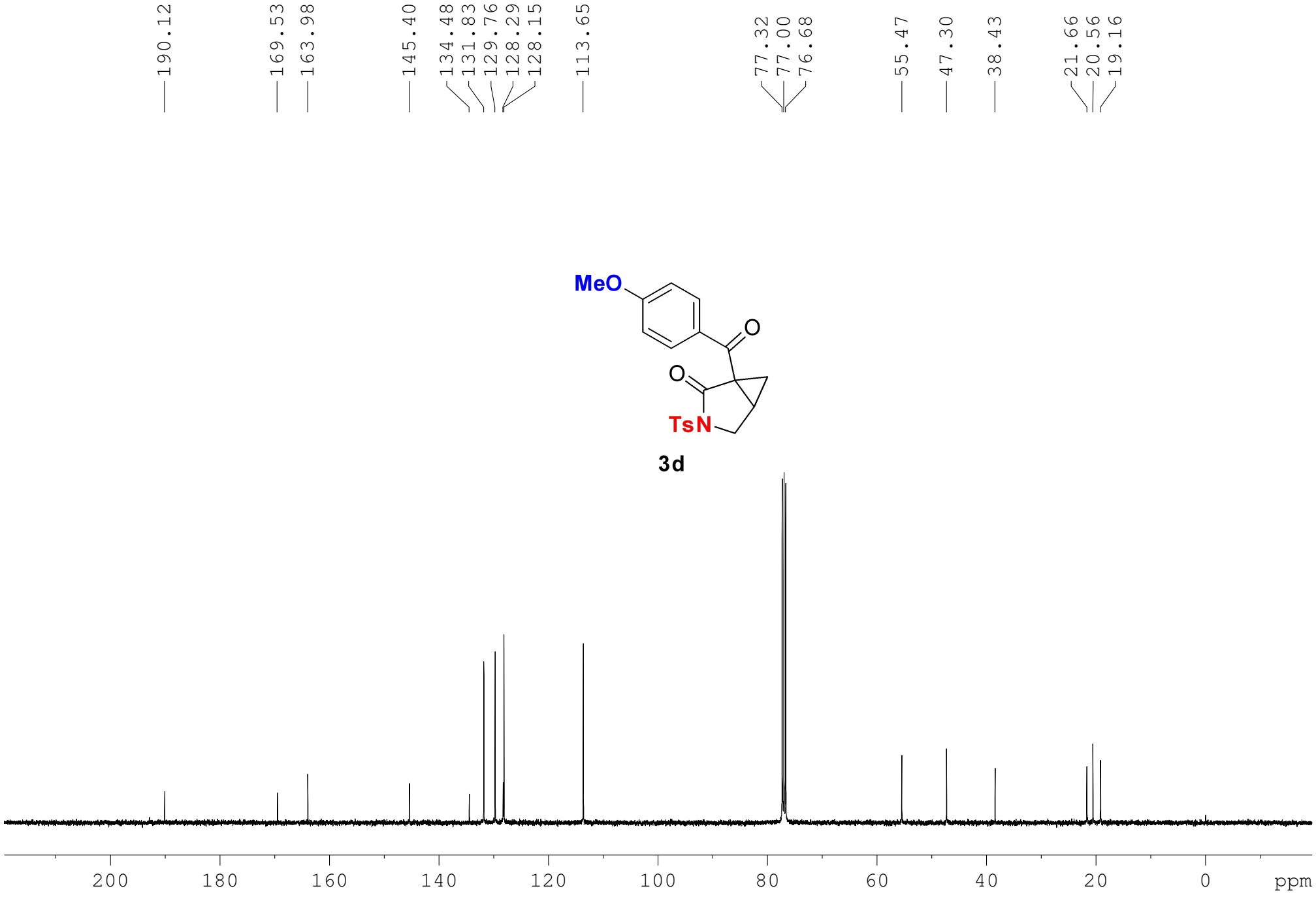


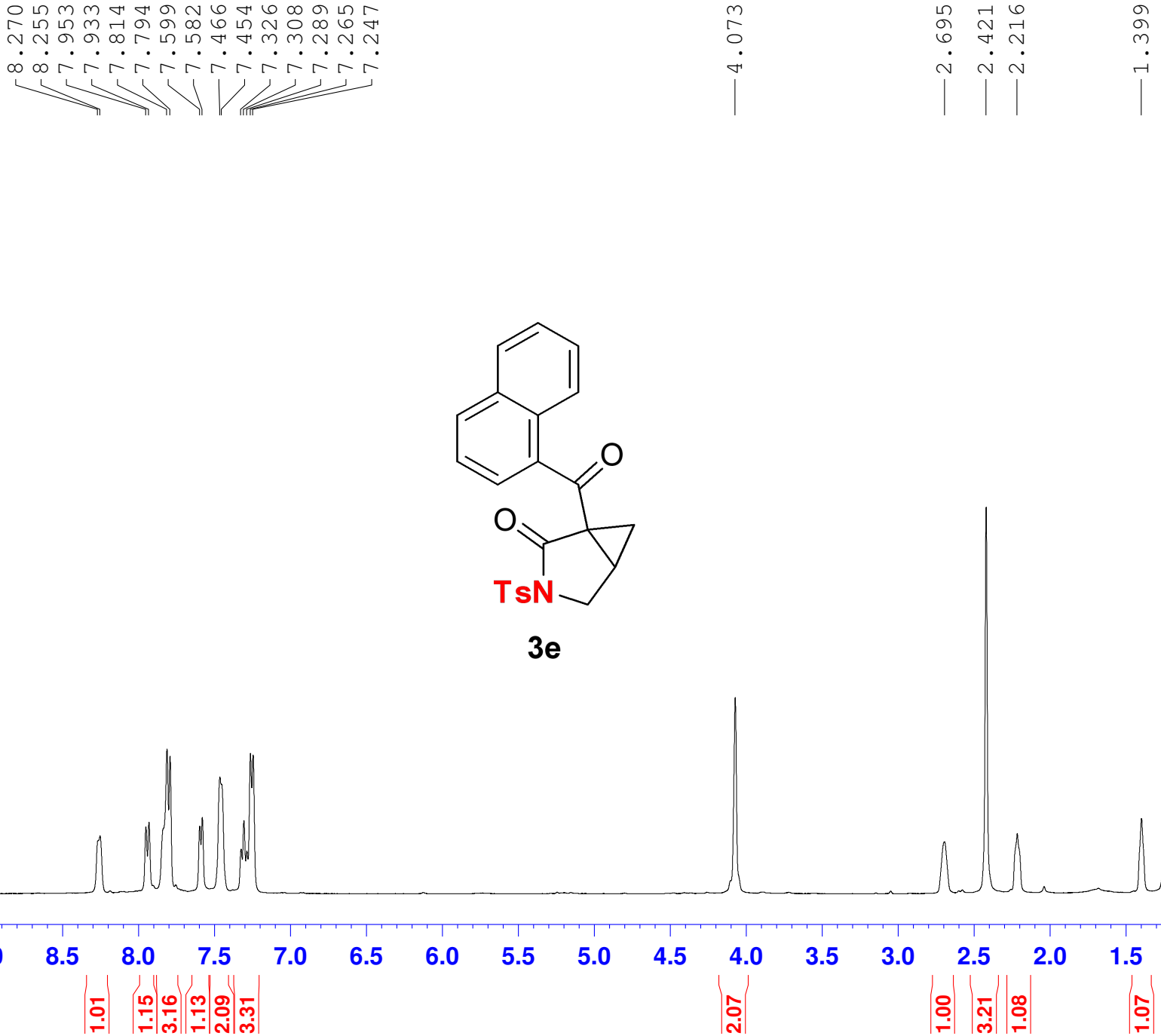


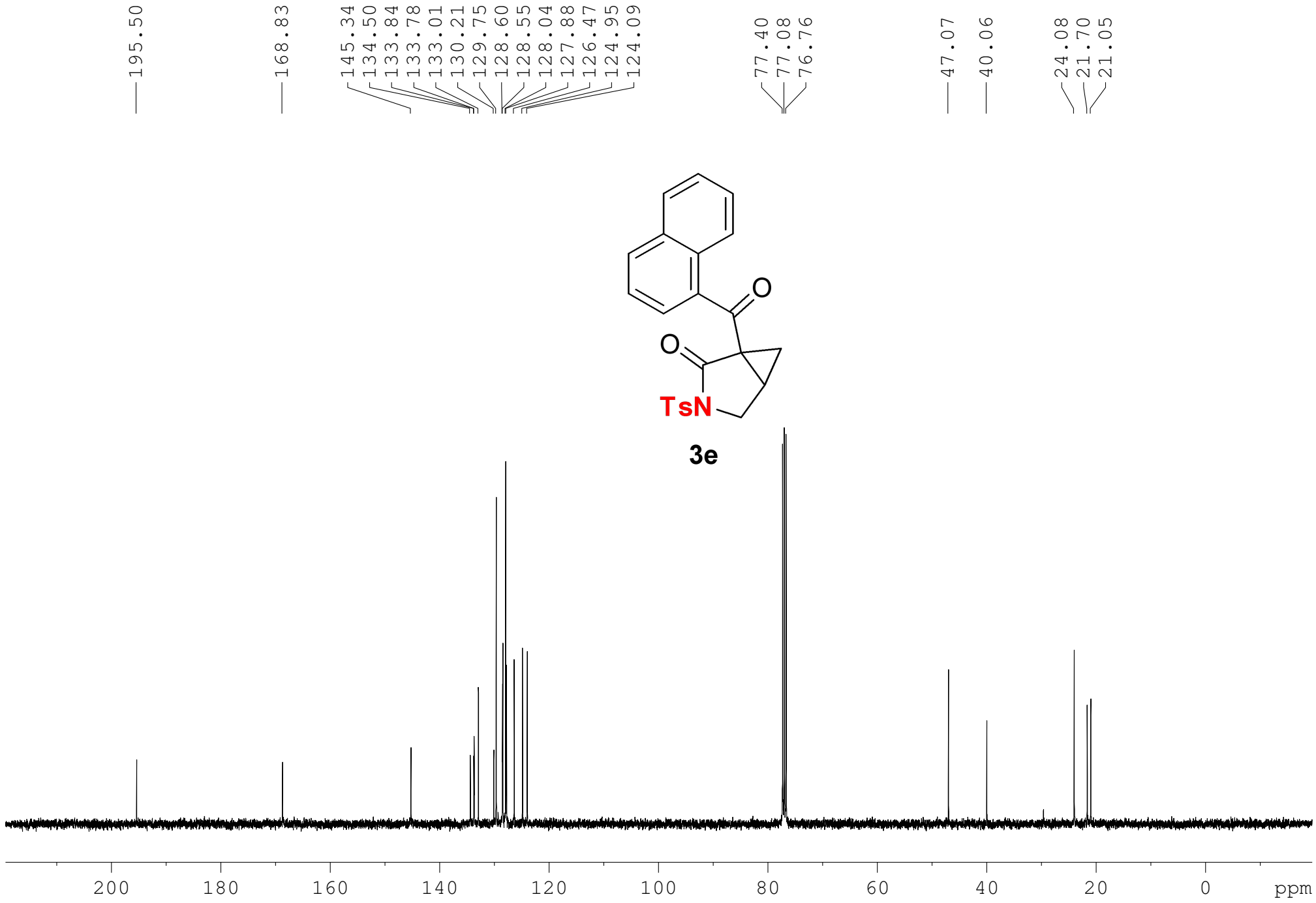


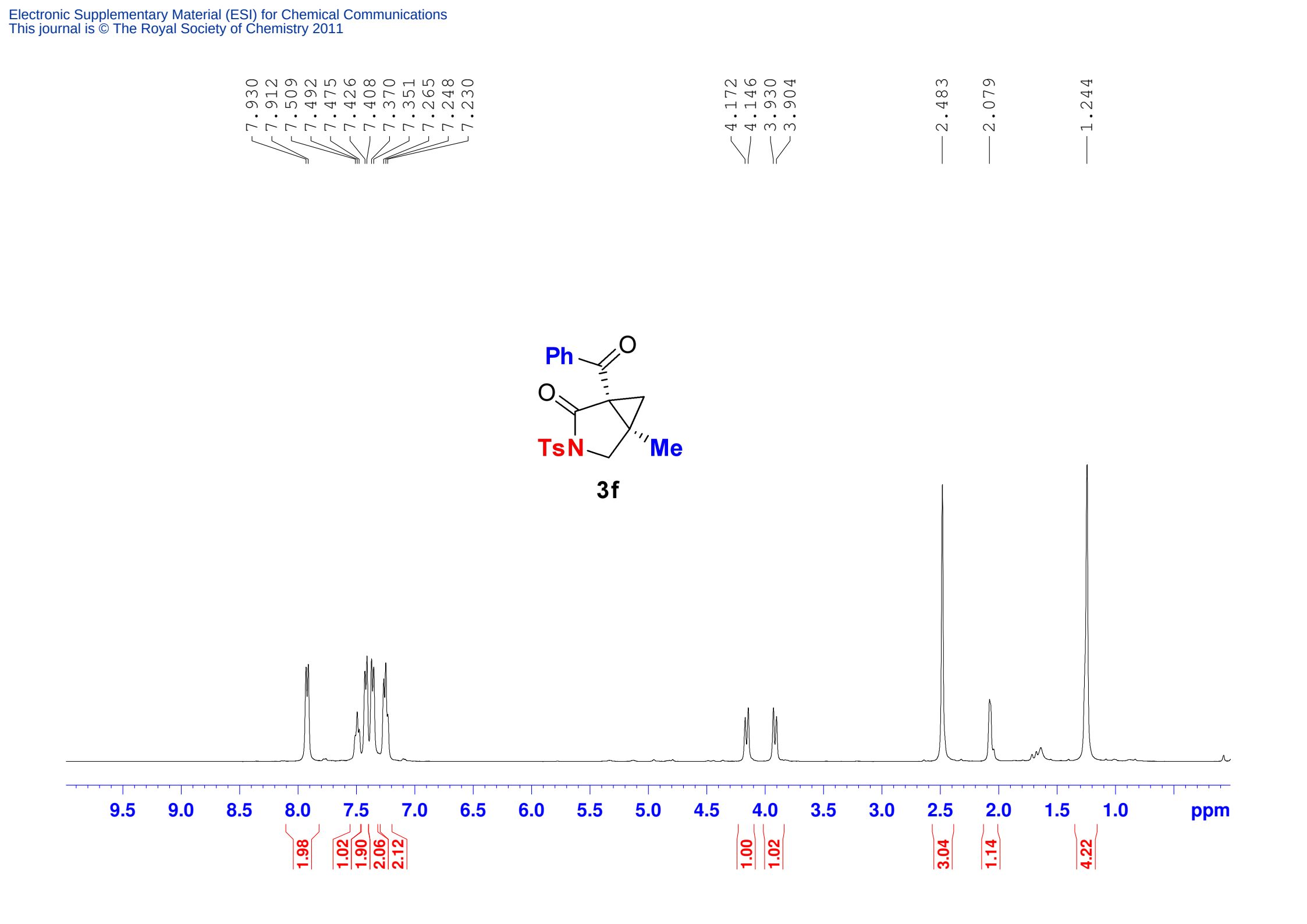


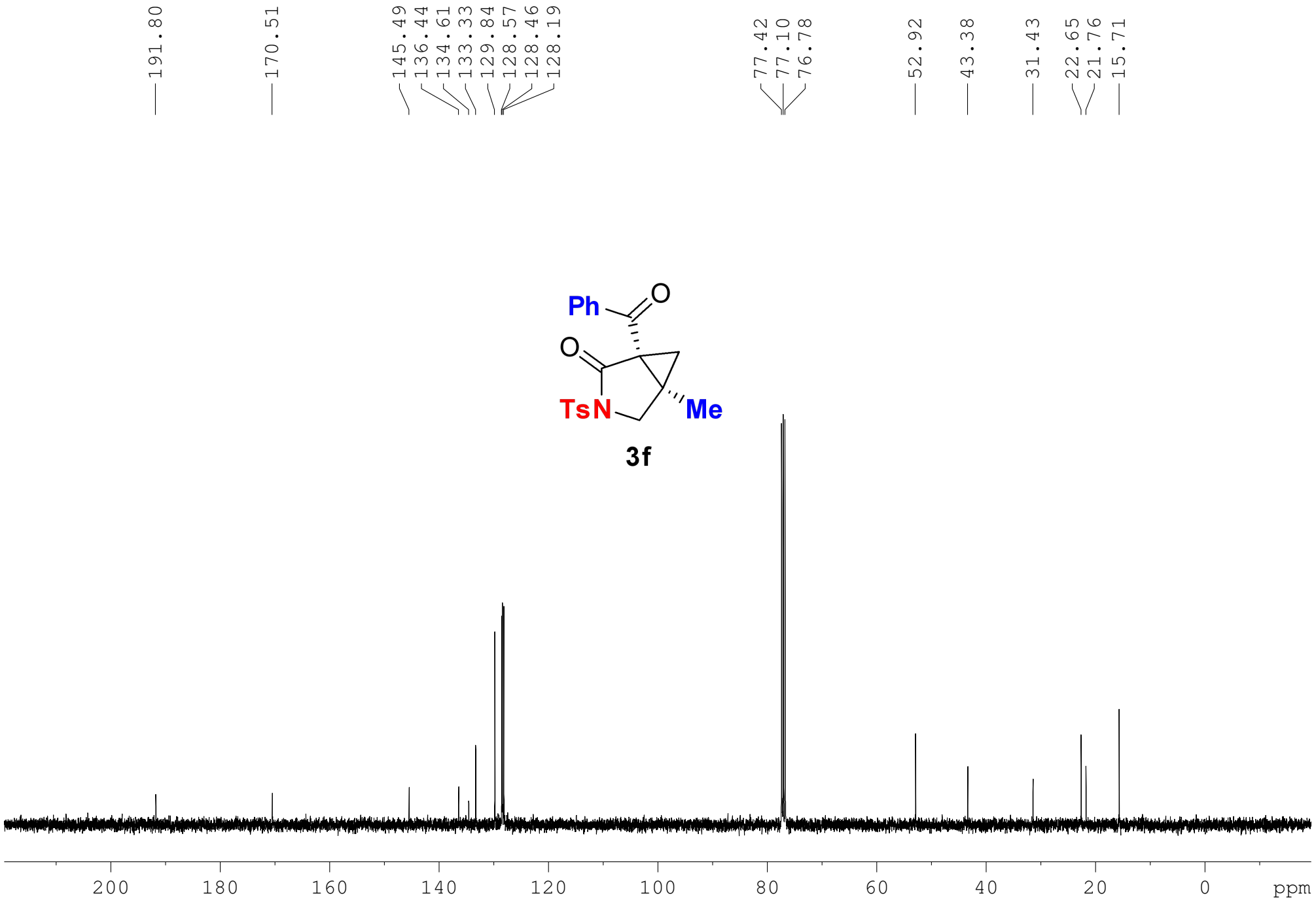


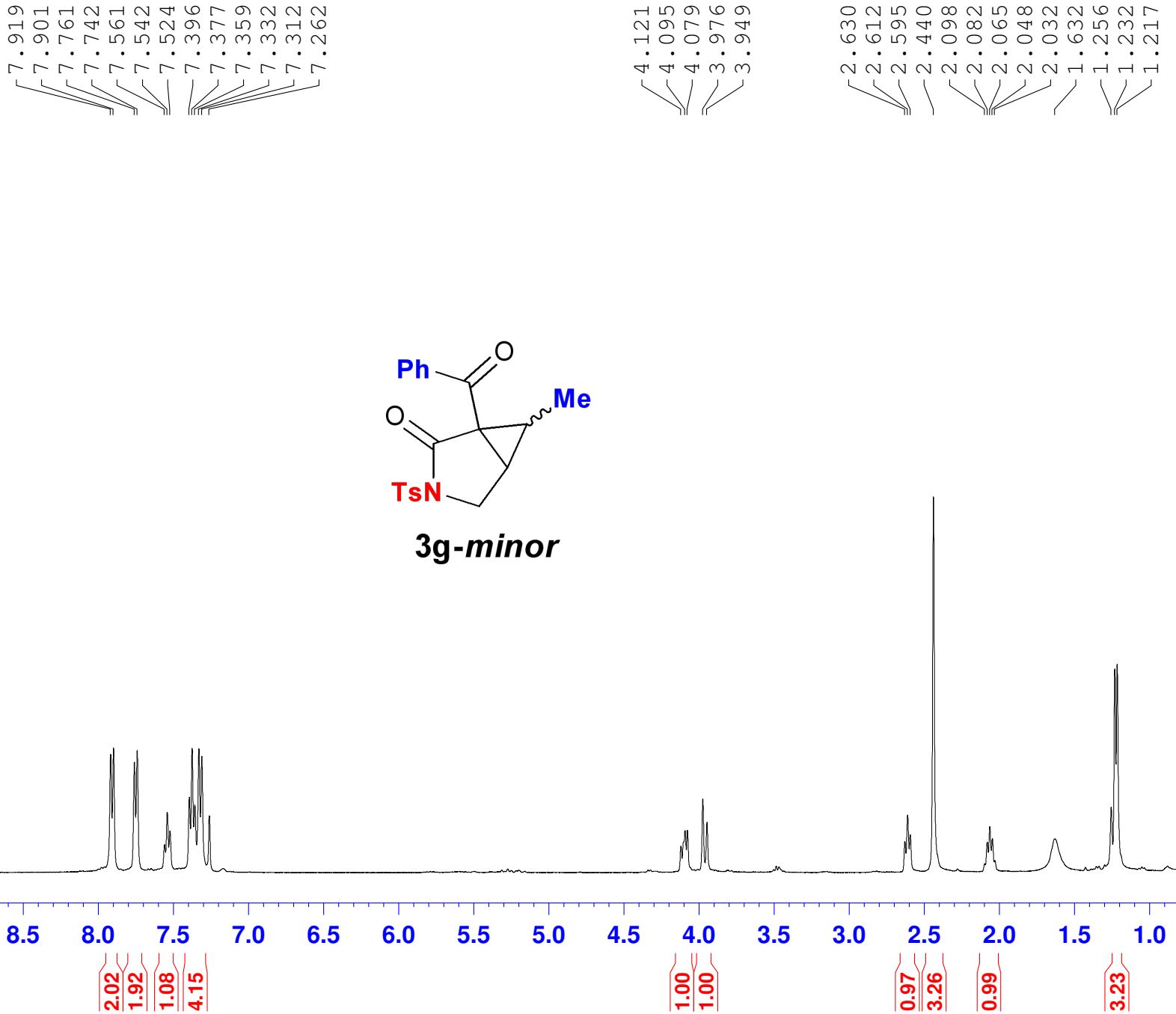


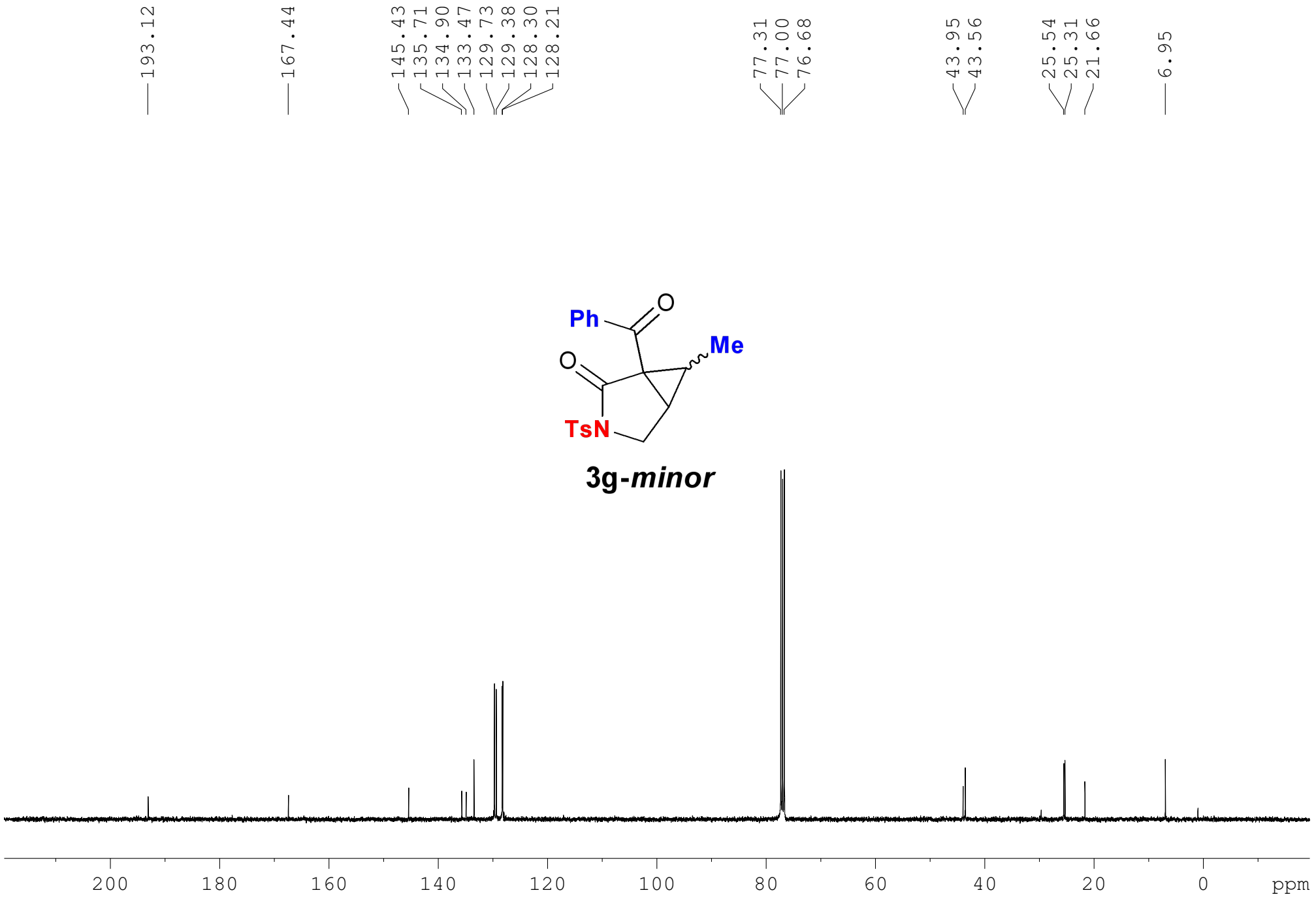


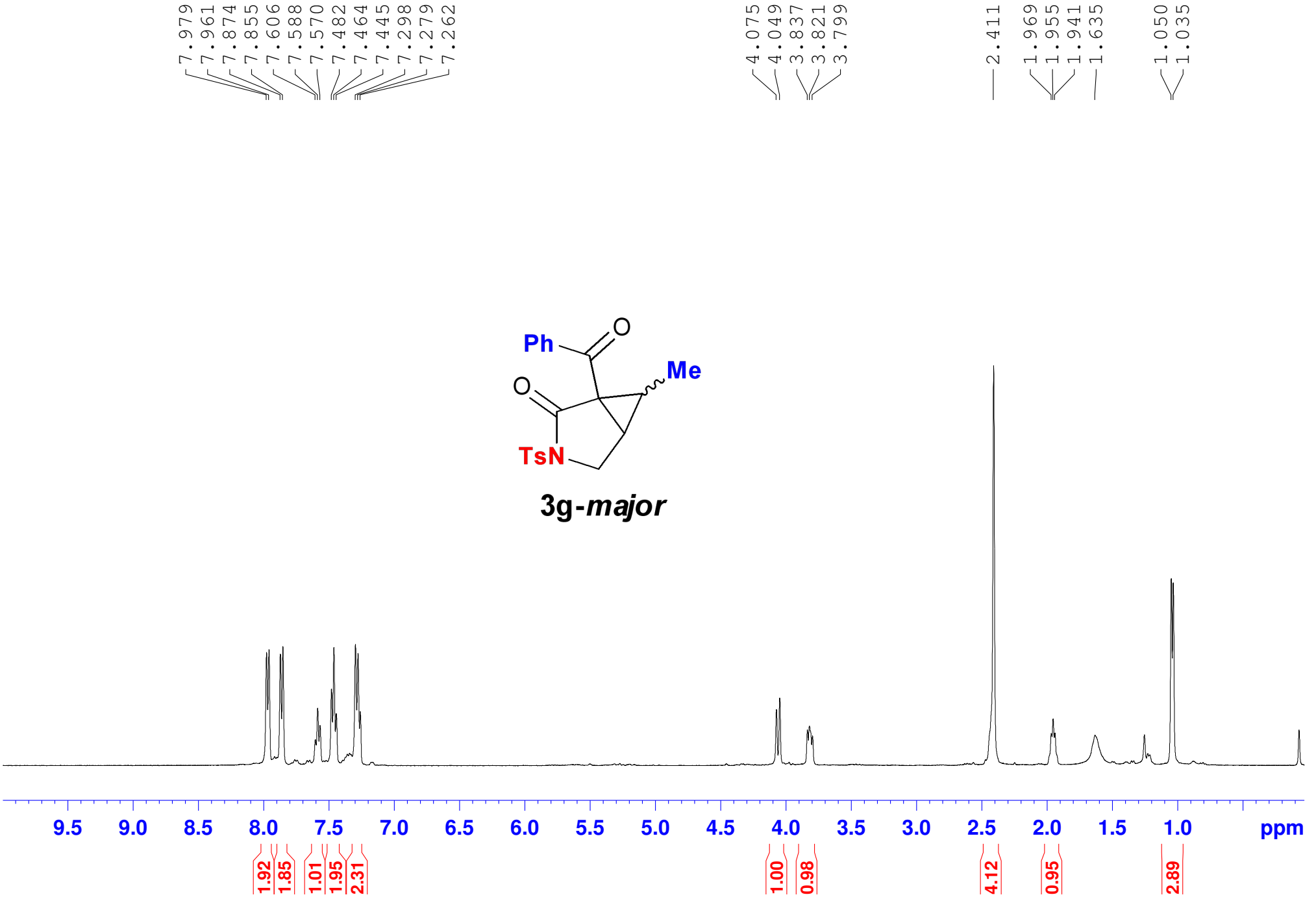


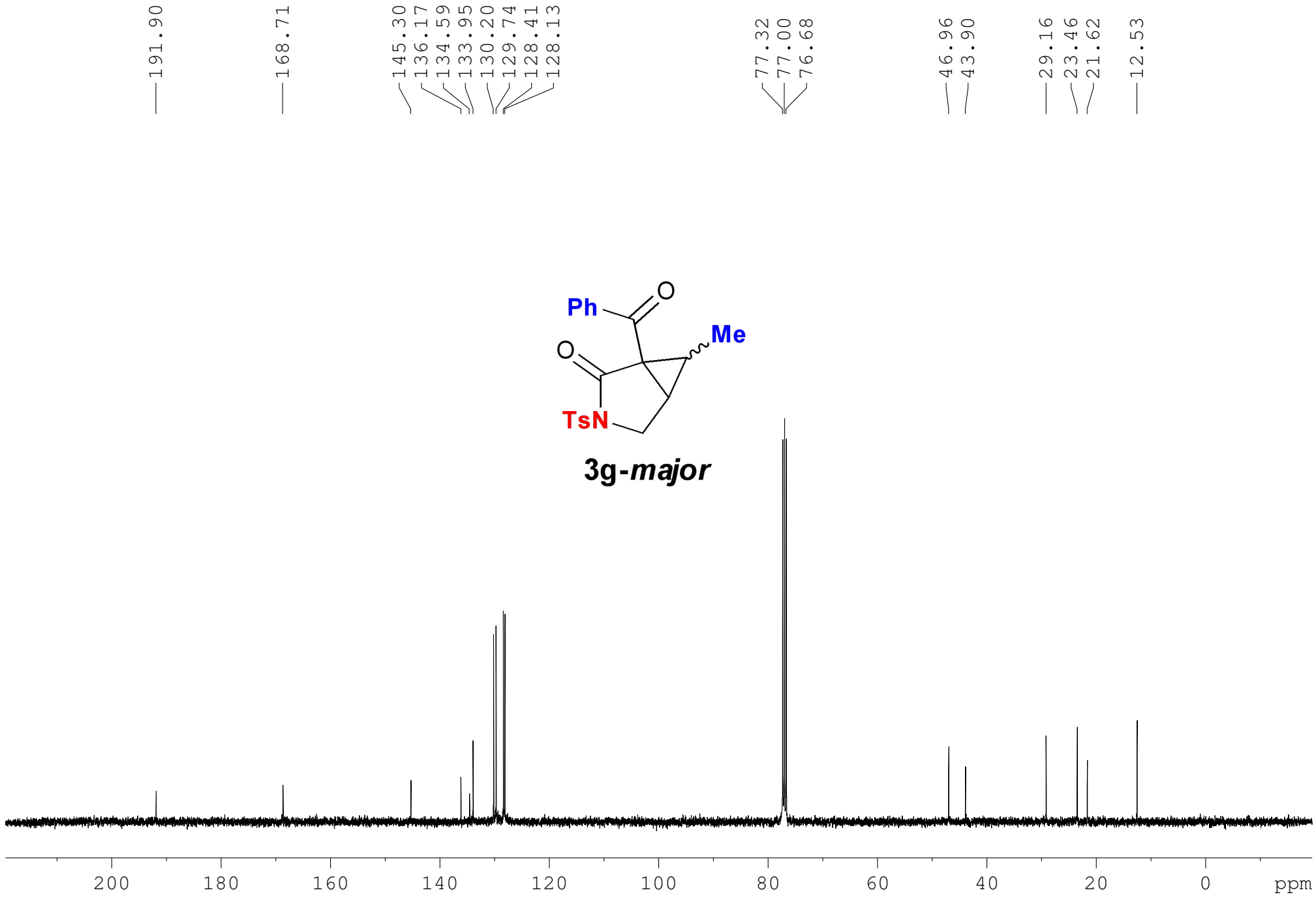


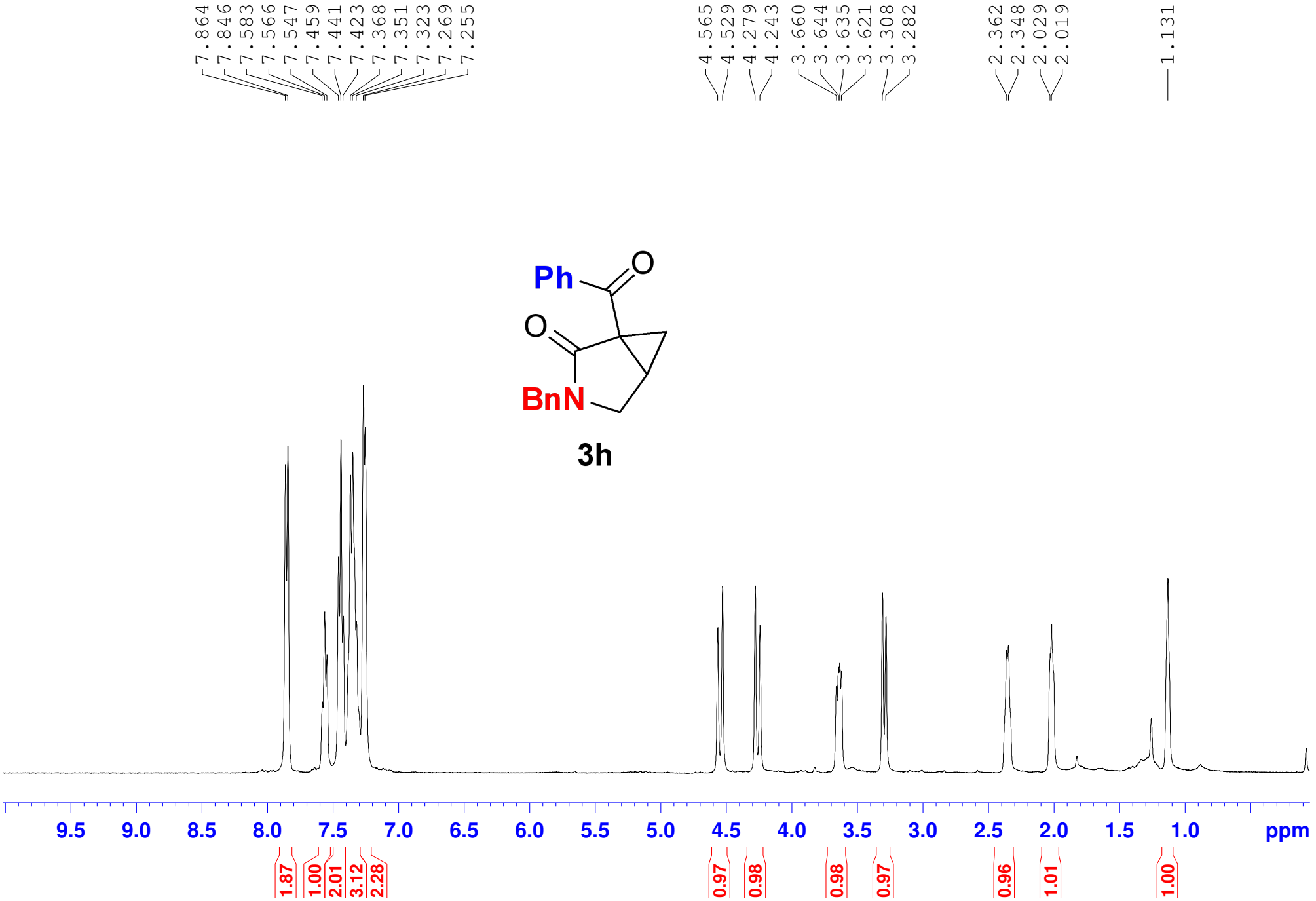


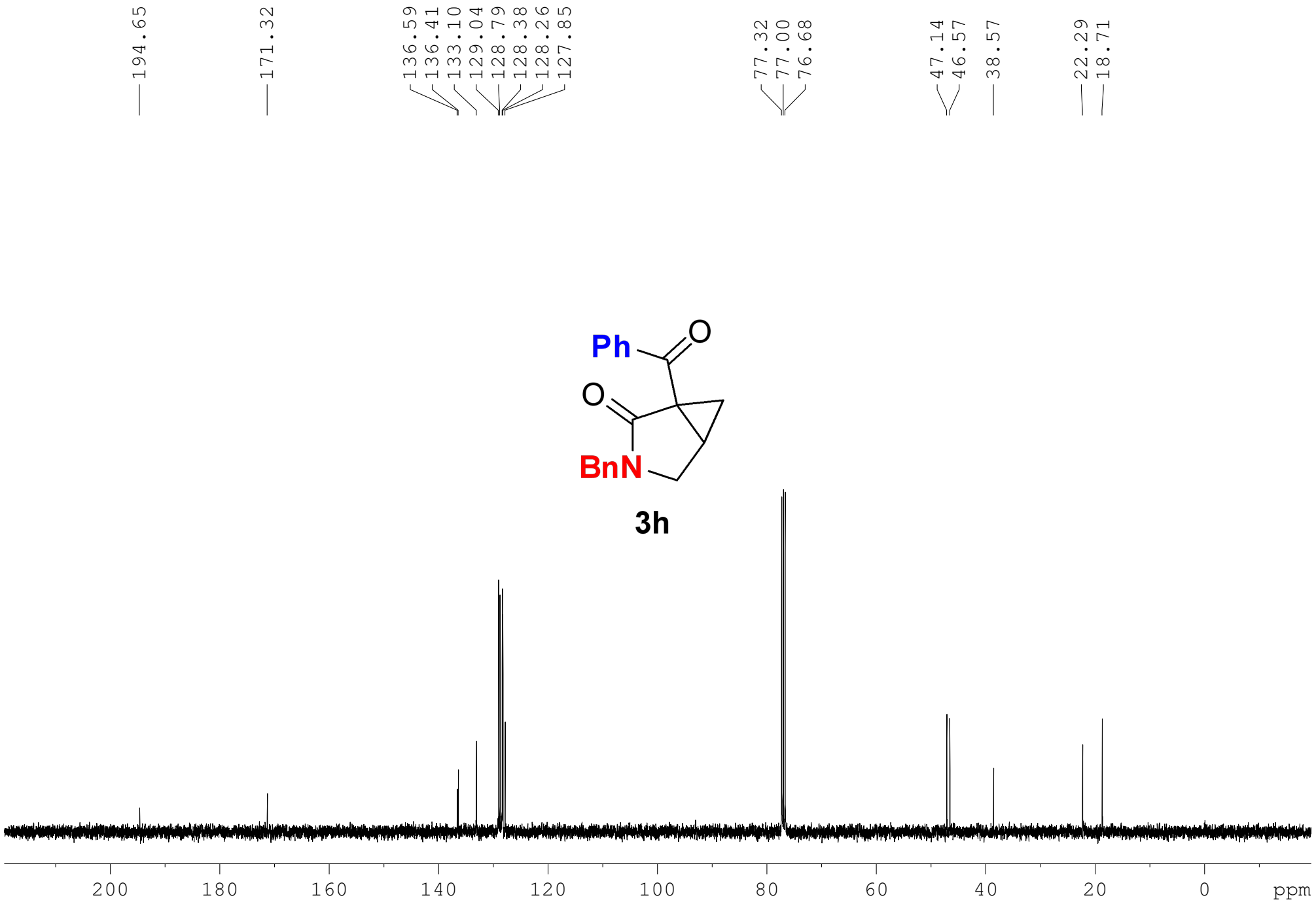


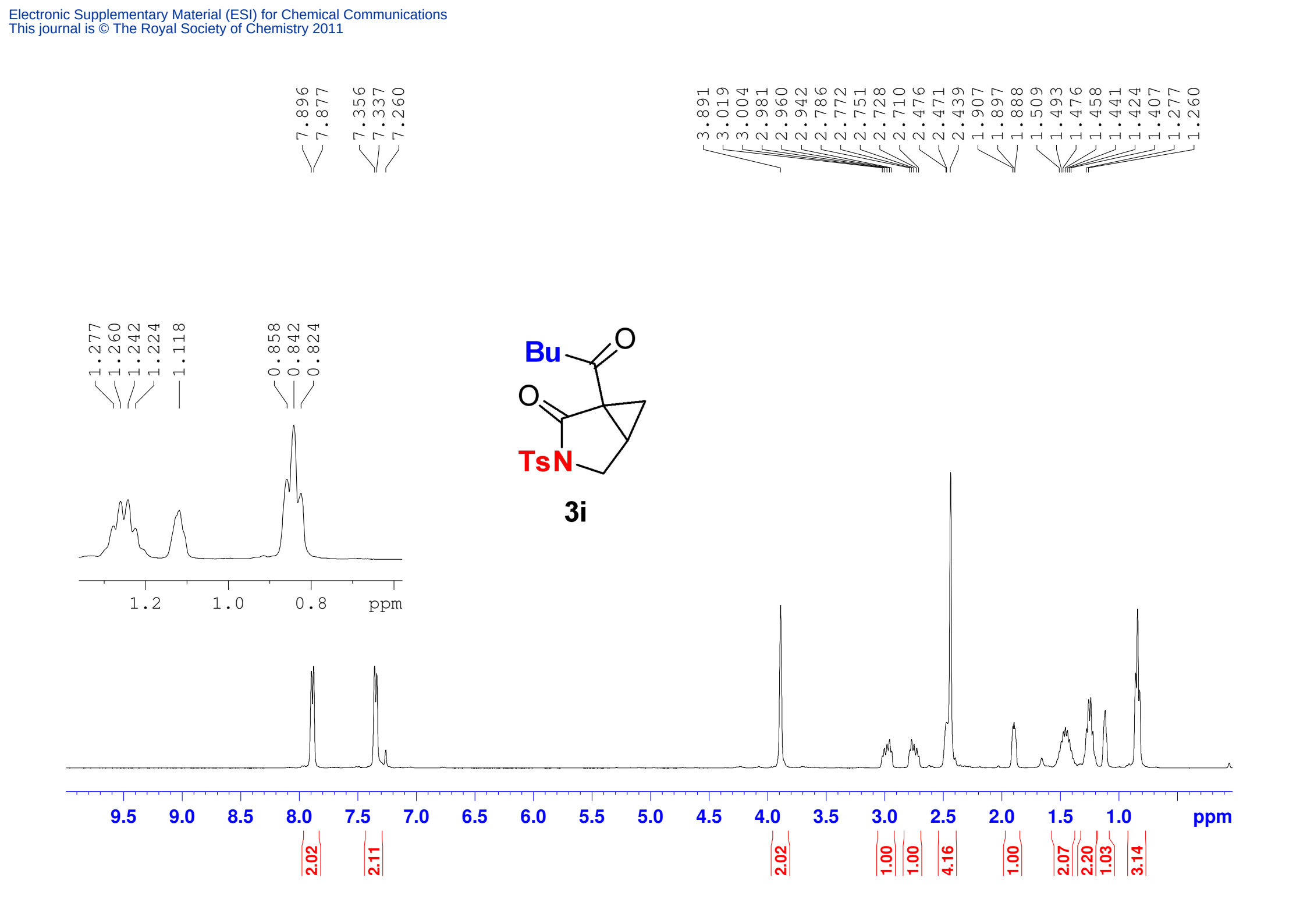


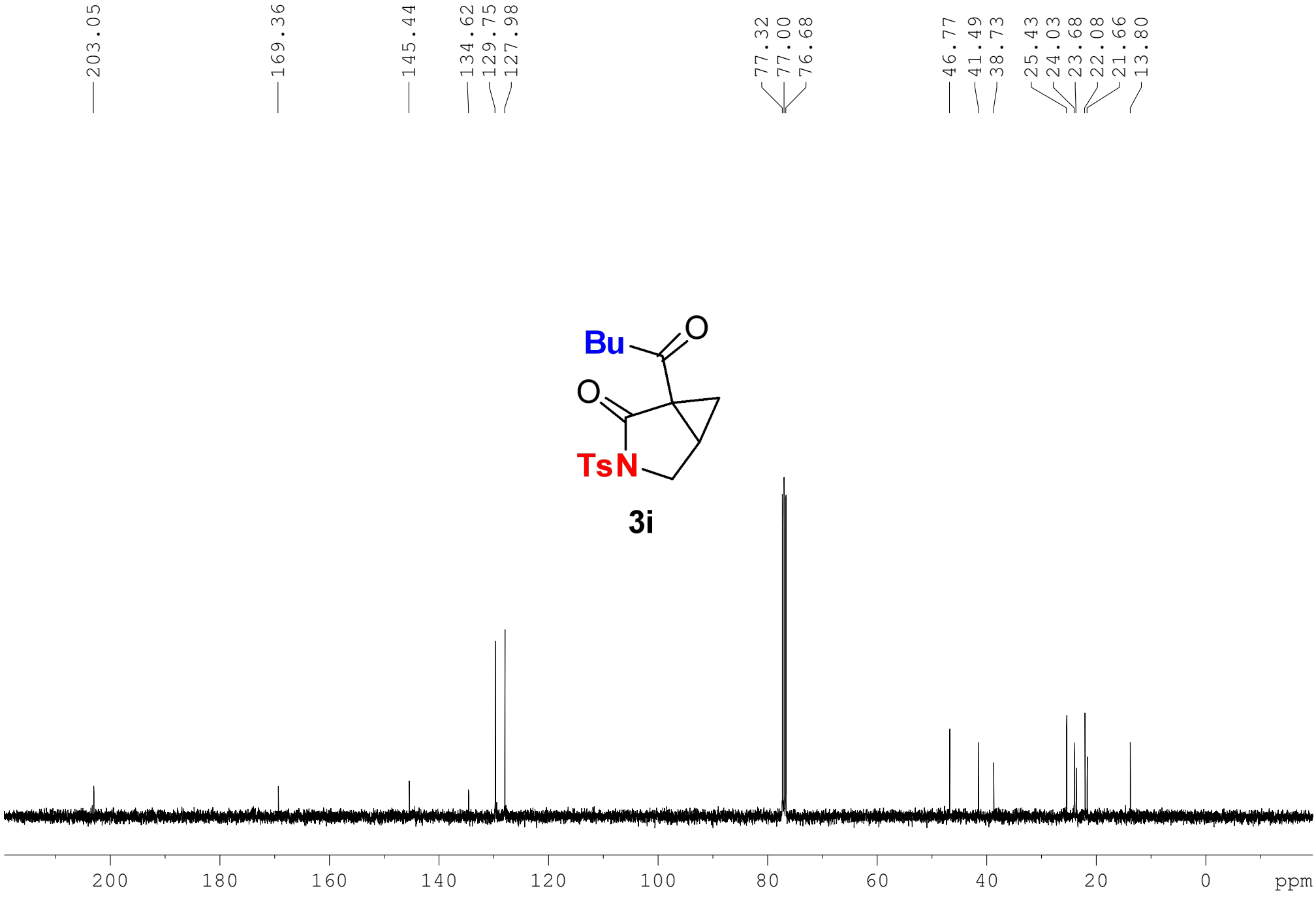


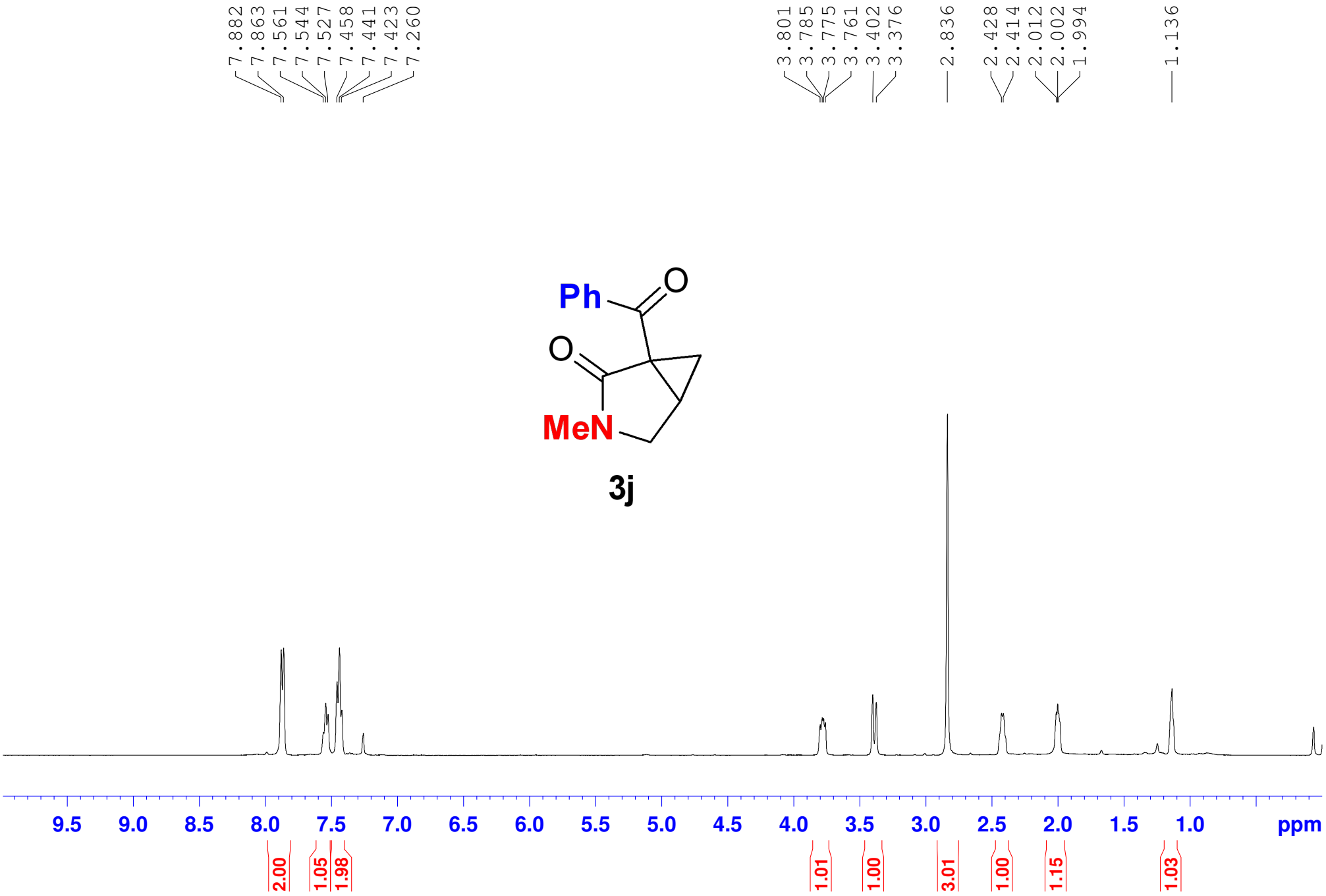


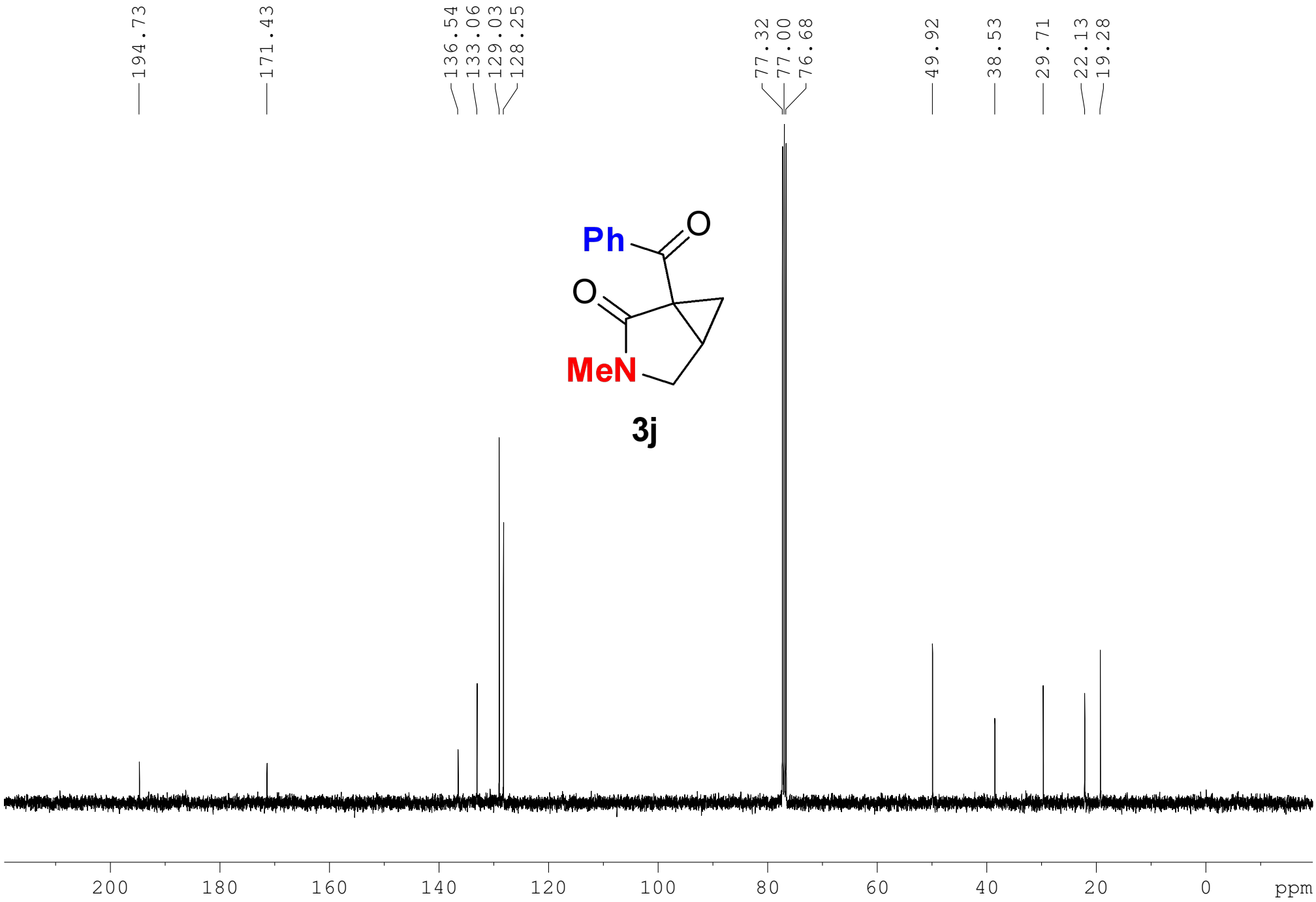


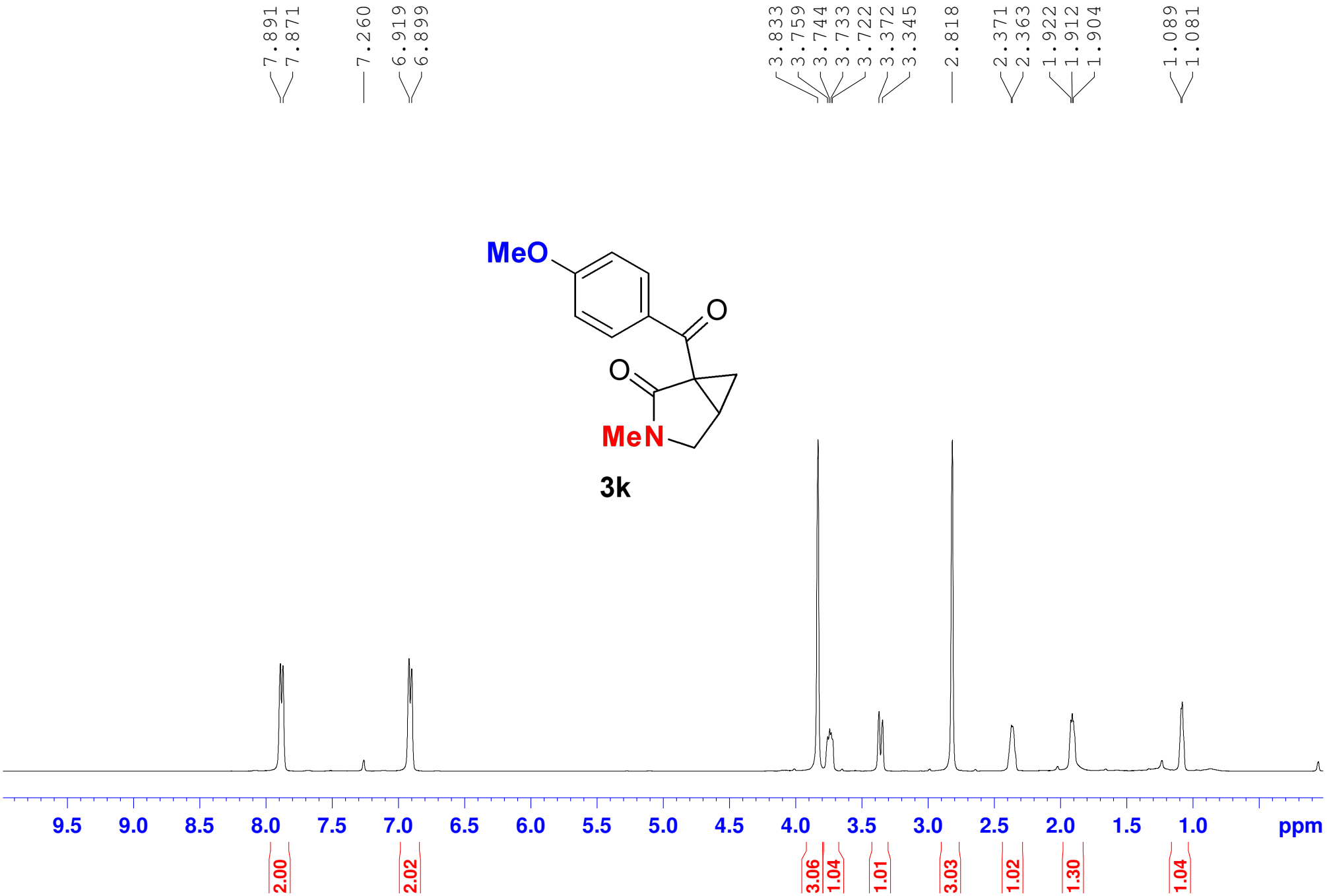


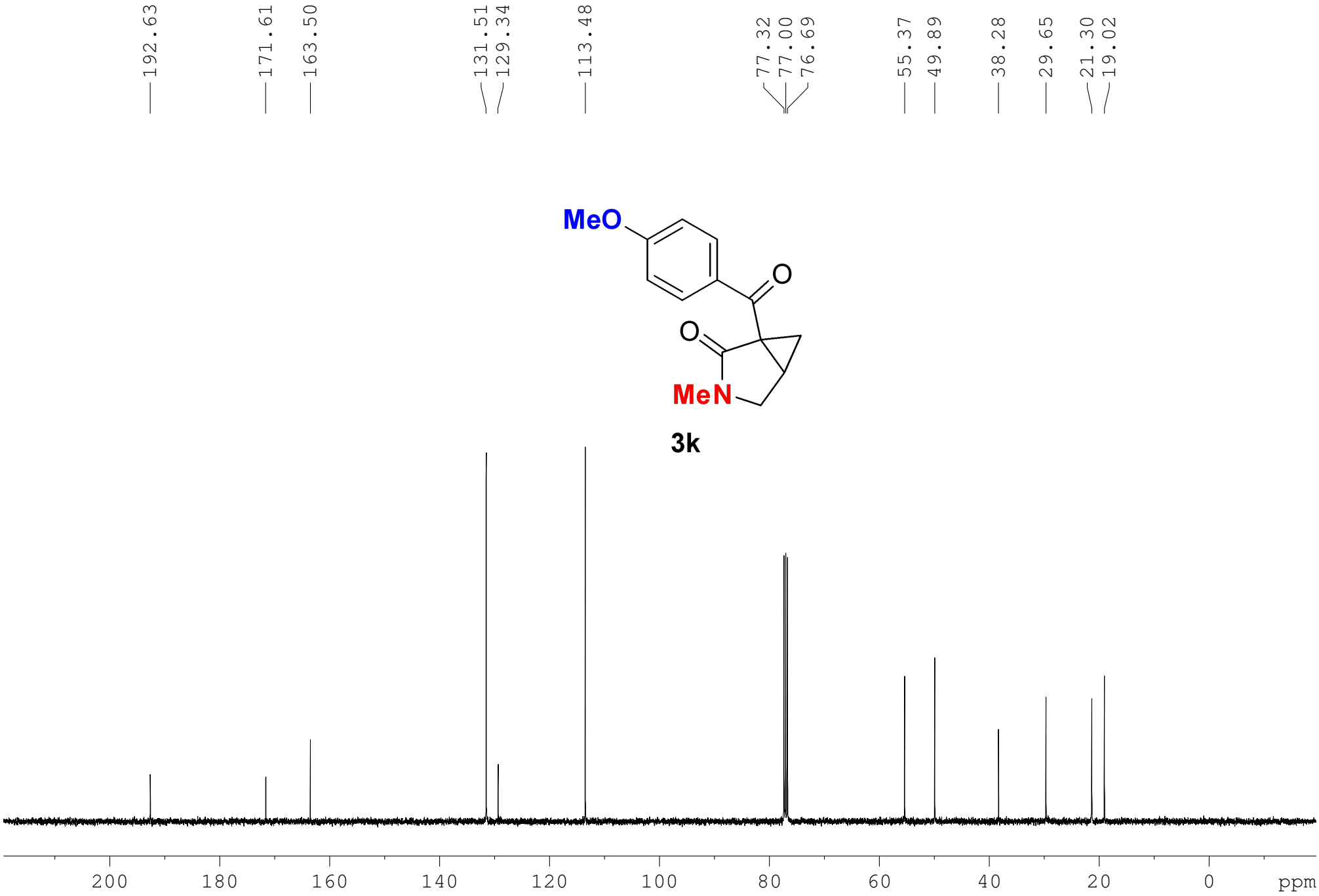


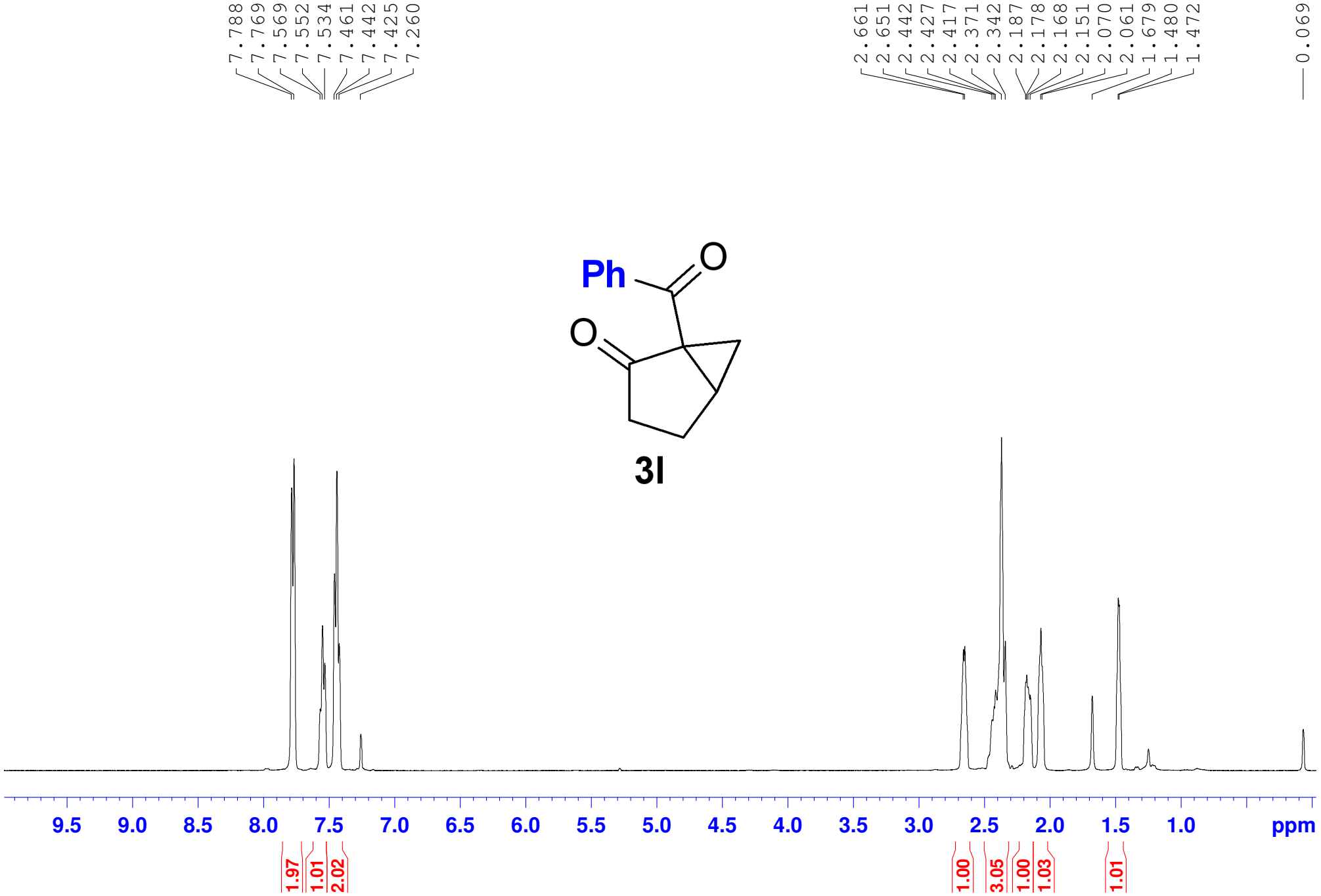


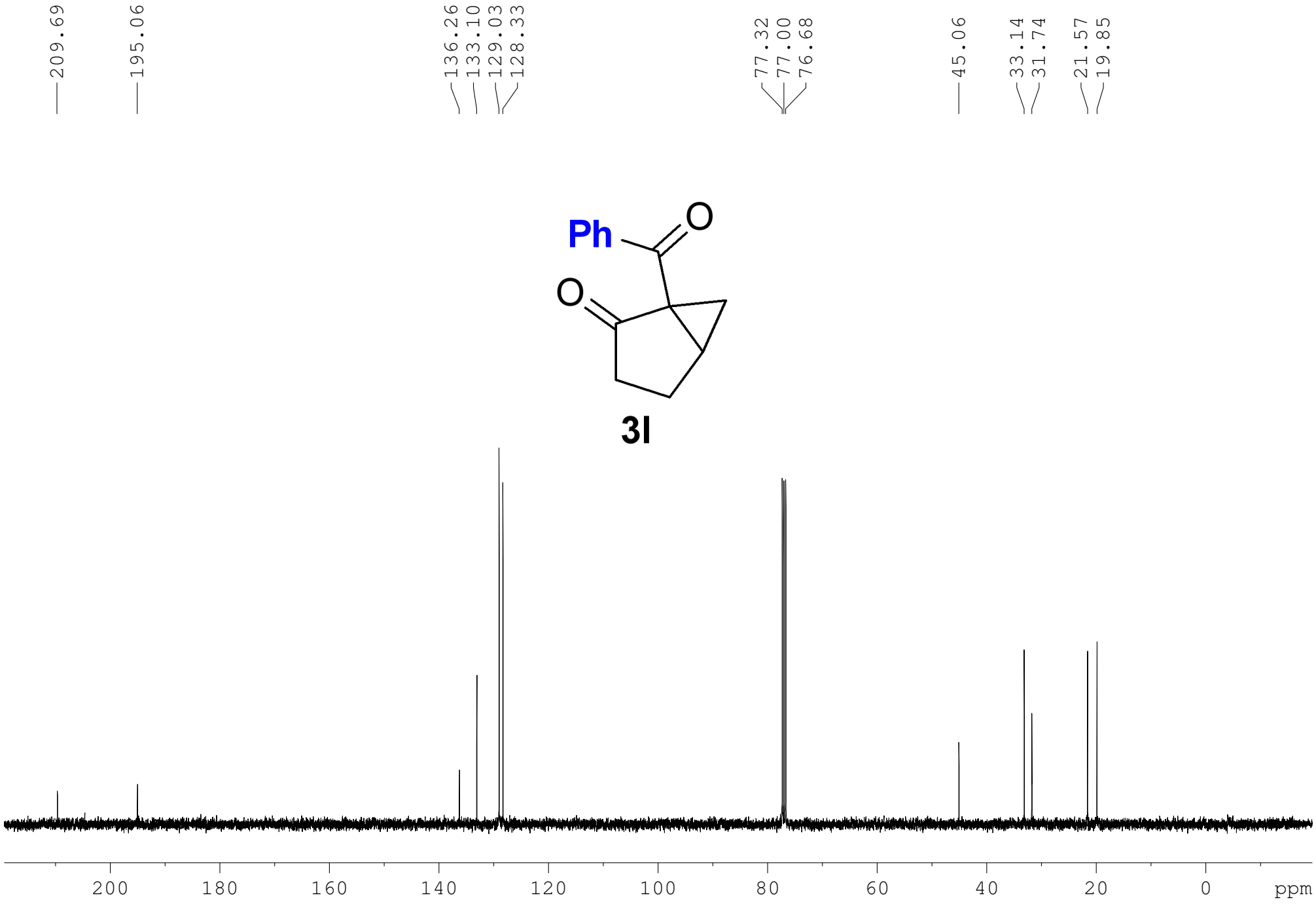




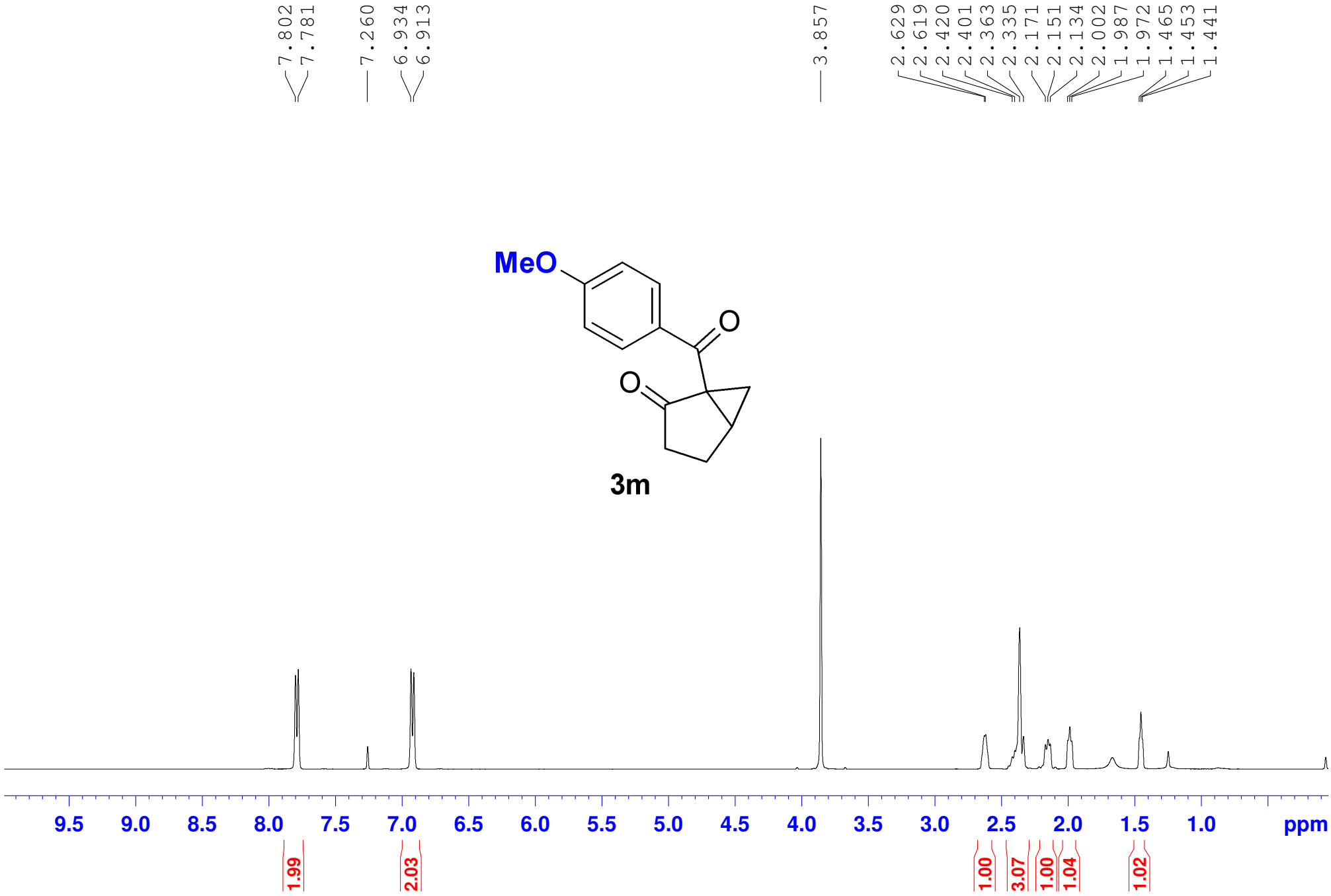




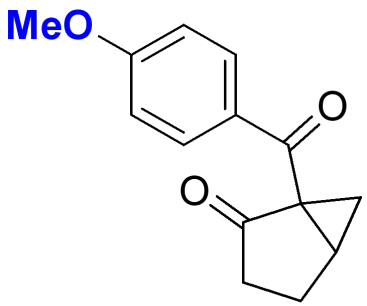




3l



209.94
193.03
163.56
131.50
129.09
113.58
77.32
77.00
76.68
55.41
44.88
33.10
30.83
21.49
19.74



3m