Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Ni-catalyzed direct iminoalkynylation of unactivated olefins with terminal alkynes: facile access to alkyne-labelled pyrrolines

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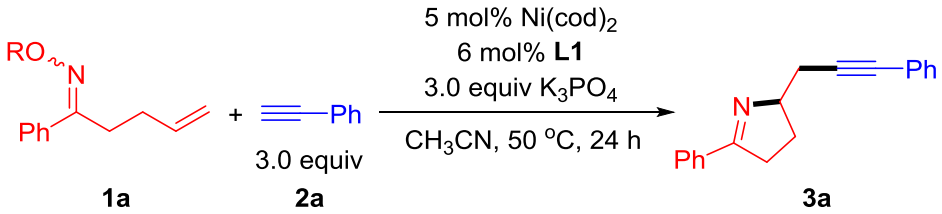
General information

Unless otherwise noted, commercially available reagents were used as received without further purification and all reactions were carried out using standard Schlenk technique or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and acetonitrile (CH_3CN) were dried using Eminex Solvent Purifier (EX-SPS5-800). Anhydrous *N, N*-dimethylformamide (DMF), *N, N*-dimethylacetamide (DMA) and 1-methyl-2-pyrrolidinone (NMP) were purchased from J&K Chemical Company. $Ni(cod)_2$, $NiCl_2$(glyme) and $NiBr_2$(glyme) were purchased from Strem. $Ni(OAc)_2 \cdot 4H_2O$ was purchased from J&K Chemical Company. NiI_2 was purchased from Alfa Aesar. $NiBr_2$(diglyme) was purchased from Sigma-Aldrich. Anhydrous K_3PO_4 was purchased from Acros. Flash column chromatography was performed on silica gel (200-300 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz and 600 MHz spectrometers at room temperature in $CDCl_3$ (containing 0.03% TMS) solution. ^1H NMR spectra was recorded with tetramethylsilane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) as internal reference. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectra were obtained by using Bruker UHR-ES-TOF MS or Thermo Scientific Q Exactive HF Orbitrap-FTMS. The IR spectra were measured on a PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrometer. Single crystal X-ray diffraction data was collected at 295 K for complex **3ac** on a SuperNova diffractometer. The corresponding ketones used in this work were prepared according to literature procedures.[1-5]

Optimization studies

Table S1. Effect of leaving group[a]

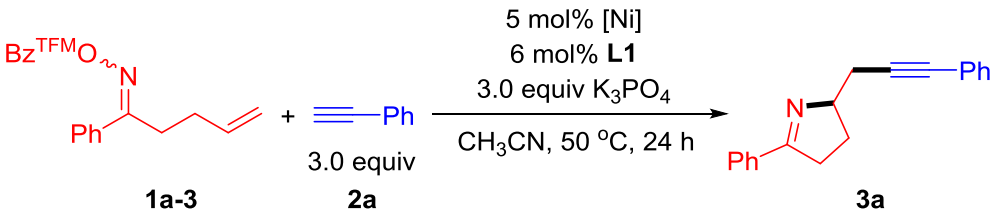


1a **2a** **3a**

Entry	R	Yield[b] (%)
1	Ac	33
2	Bz	54
3	$Bz^{p\text{-}OMe}$	44
4	$Bz^{p\text{-}CF_3}$	58
5	Bz^{TFM}	66
6	Bz^{F}	4

[a] Conditions: oxime **1a** (0.3 mmol), **2a** (0.9 mmol, 91.9 mg), $Ni(cod)_2$ (0.015 mmol, 4.1 mg), **L1** (0.018 mmol, 7.2 mg), K_3PO_4 (0.9 mmol, 191.0 mg), CH_3CN (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. $Bz^{p\text{-}OMe}$ = *p*-methoxybenzoyl, $Bz^{p\text{-}CF_3}$ = *p*-(trifluoromethyl)benzoyl, Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl, Bz^{F} = pentafluorobenzoyl.

Table S2. Effect of nickel source[a]

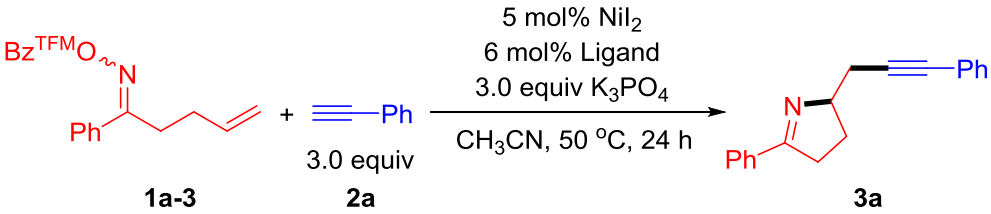


1a-3 **2a** **3a**

Entry	[Ni]	Yield[b] (%)
1	$Ni(cod)_2$	66
2	$NiCl_2(glyme)$	48
3	$NiBr_2(glyme)$	60
4	$Ni(OAc)_2{\cdot}4H_2O$	61
5	NiI_2	71
6	$NiBr_2(diglyme)$	57

[a] Conditions: oxime **1a-3** (0.3 mmol, 124.6 mg), **2a** (0.9 mmol, 91.9 mg), [Ni] (0.015 mmol), **L1** (0.018 mmol, 7.2 mg), K_3PO_4 (0.9 mmol, 191.0 mg), CH_3CN (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl.

Table S3. Effect of ligand[a]



Entry	Ligand	Yield[b] (%)
1	**L1**	71
2	**L2**	58
3	**L3**	46
4	**L4**	13
5	**L5**	23
6	**L6**	24
7	**L7**	58
8	**L8**	59
9	**L9**	2

[a] Conditions: oxime **1a-3** (0.3 mmol, 124.6 mg), **2a** (0.9 mmol, 91.9 mg), NiI_2 (0.015 mmol, 4.7 mg), **L** (0.018 mmol), K_3PO_4 (0.9 mmol, 191.0 mg), CH_3CN (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl.

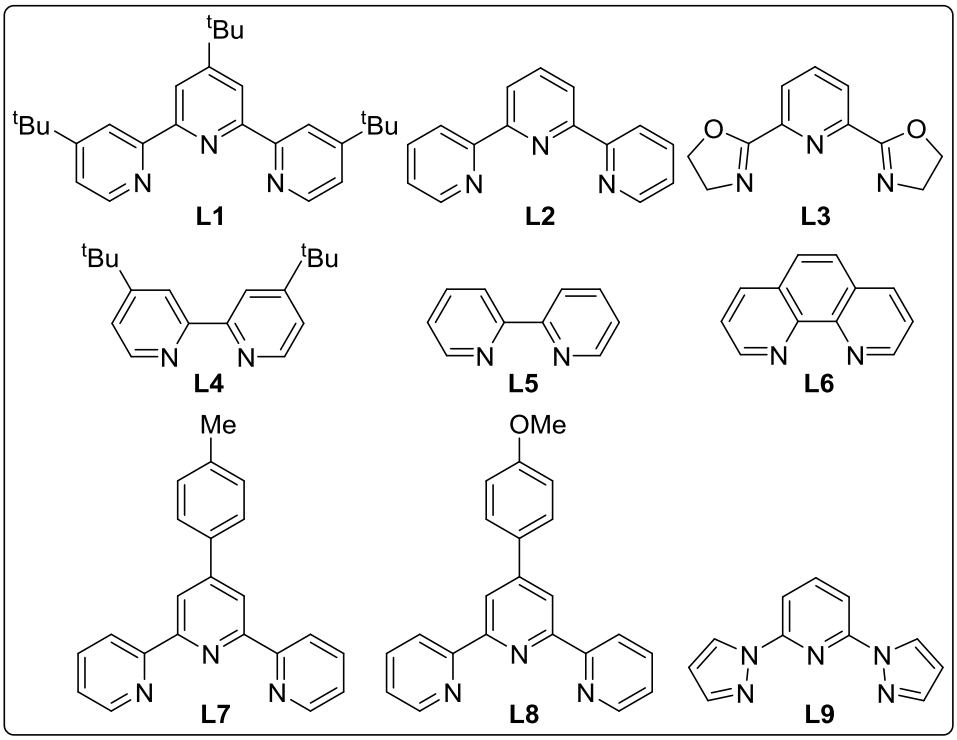
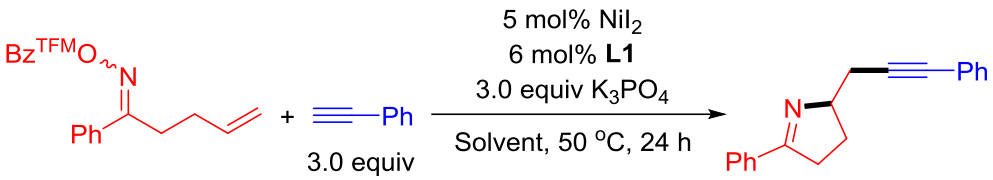


Table S4. Effect of solvent[a]

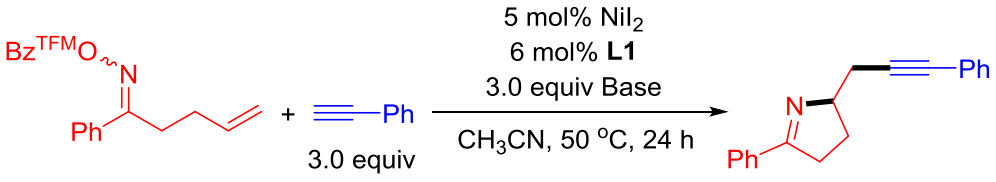


1a-3 **2a** **3a**

Entry	Solvent	Yield[b] (%)
1	CH_3CN	71
2	THF	55
3	DMF	56
4	DMA	58
5	NMP	46
6	DMSO	61

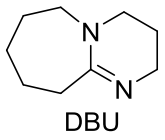
[a] Conditions: oxime **1a-3** (0.3 mmol, 124.6 mg), **2a** (0.9 mmol, 91.9 mg), NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), K_3PO_4 (0.9 mmol, 191.0 mg), solvent (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl.

Table S5. Effect of base[a]

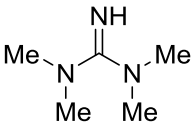


1a-3 **2a** **3a**

Entry	Base	Yield[b] (%)
1	K_3PO_4	71
2	Na_3PO_4	20
3	K_2CO_3	2
4	DBU	37
5	TMG	46
6	Et_3N	4



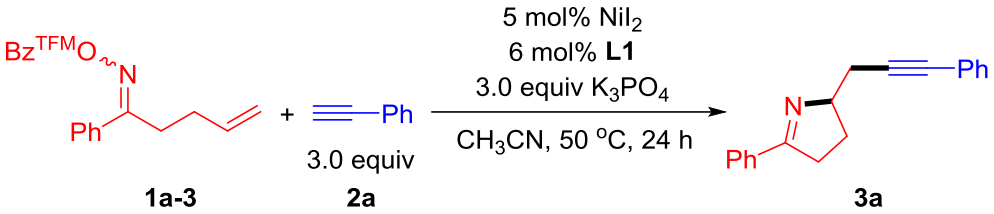
DBU



TMG

[a] Conditions: oxime **1a-3** (0.3 mmol, 124.6 mg), **2a** (0.9 mmol, 91.9 mg), NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), base (0.9 mmol), CH_3CN (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl.

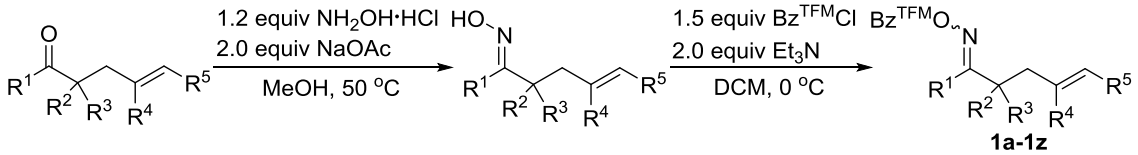
Table S6. Control experiment and the effects of other parameters[a]



Entry	NiI_2 (mol%)	**L1** (mol%)	Yield[b] (%)
1	-	6	0
2	5	-	2
3[c]	5	6	0
4[d]	5	6	62
5[e]	5	6	70
6[f]	5	6	39

[a] Conditions: oxime **1a-3** (0.3 mmol, 124.6 mg), **2a** (0.9 mmol, 91.9 mg), NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), K_3PO_4 (0.9 mmol, 191.0 mg), CH_3CN (3.0 mL), 50 °C, 24 h, in a sealed tube, under N_2 atmosphere. [b] Isolated yields. Bz^{TFM} = 3,5-bis(trifluoromethyl)benzoyl. [c] No K_3PO_4. [d] 30 °C. [e] **2a** (2.0 equiv), K_3PO_4 (2.0 equiv) were used. [f] **2a** (1.0 equiv), K_3PO_4 (1.0 equiv) were used.

General procedure for the synthesis of oxime esters 1a-1z

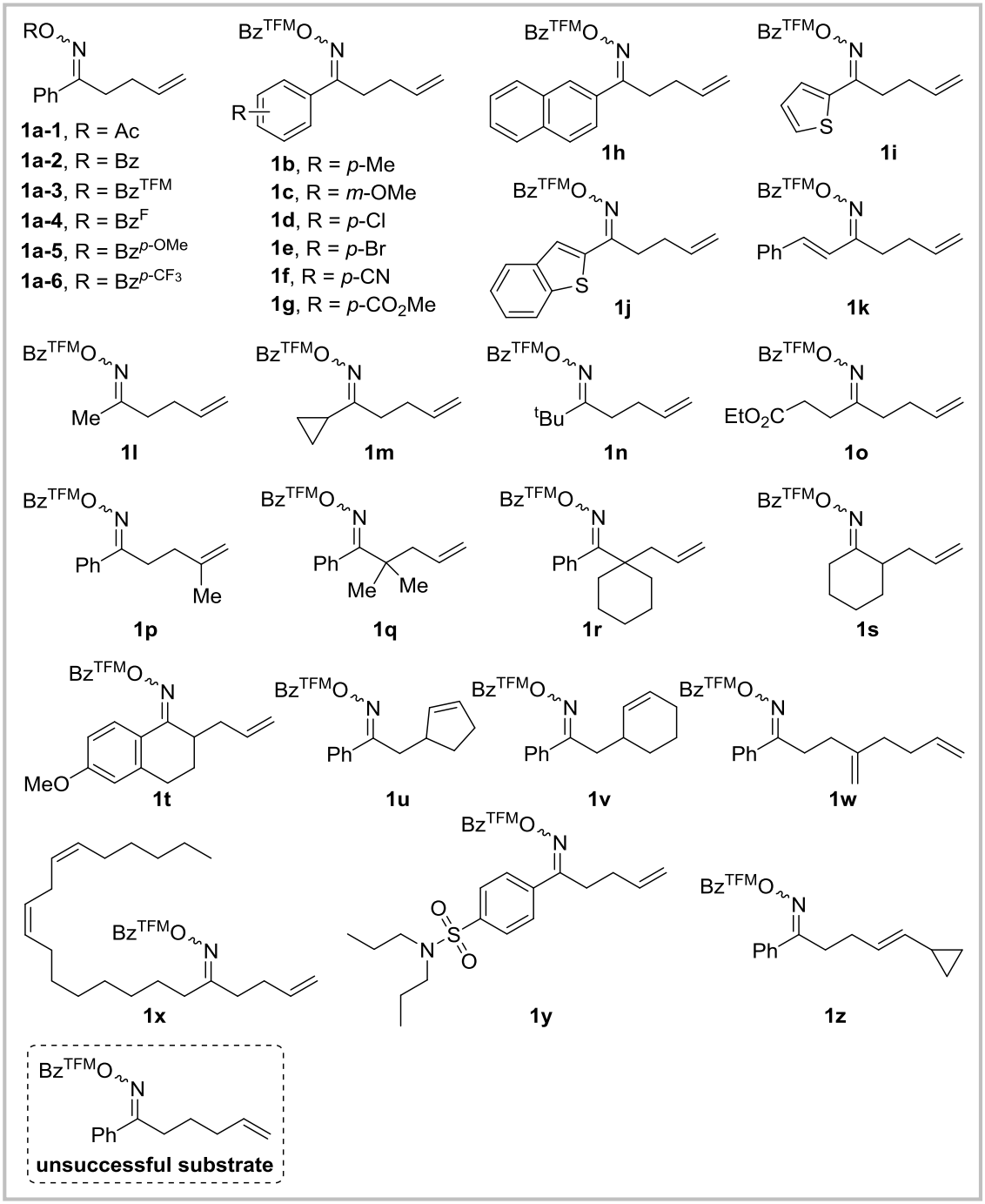


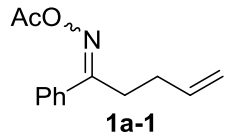
According to previous reported procedure, to a solution of the corresponding ketone (1.0 equiv) in methanol (1.0 M) was added sodium acetate (2.0 equiv) and hydroxylamine hydrochloride (1.2 equiv). The reaction mixture was stirred at 50 °C for 2 h and then cooled to room temperature. The excess methanol was removed under reduced pressure and the resulting mixture was extracted with ethyl acetate/water. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was concentrated under vacuum and the residue was used directly in the next step without further purification.

To a solution of the appropriate oxime (1.0 equiv) in anhydrous dichloromethane (0.5 M) at 0 °C was added Et_3N (2.0 equiv) and 3,5-bis(trifluoromethyl)benzoyl chloride (1.5 equiv) under nitrogen atmosphere. The reaction mixture was allowed to stir at the same temperature for hours until the oxime was consumed (determined by TLC). Then saturated

$NaHCO_3$ aqueous solution was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel to afford the corresponding oxime ester.

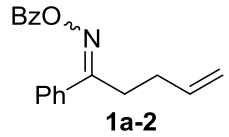
Table S7. γ,δ-unsaturated oxime esters used in this work.





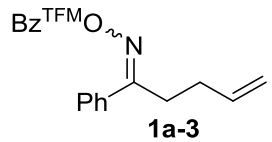
1a-1

1-Phenylpent-4-en-1-one *O*-acetyl oxime (1a-1). 10.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 86% overall yield (1.86 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.29-2.34 (m, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 5.00-5.07 (m, 2H), 5.78-5.85 (m, 2H), 7.38-7.44 (m, 3H), 7.69-7.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.82, 27.60, 30.59, 115.77, 127.24, 128.61, 130.50, 133.86, 136.46, 165.60, 168.97. The spectroscopic data are in agreement with that previously reported.[6]



1a-2

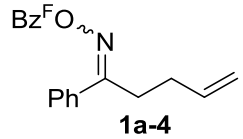
1-Phenylpent-4-en-1-one *O*-benzoyl oxime (1a-2). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 69% overall yield (0.96 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.46 (m, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 5.03-5.12 (m, 2H), 5.83-5.93 (m, 1H), 7.42-7.47 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 27.88, 30.62, 115.81, 127.20, 128.44, 128.49, 128.95, 129.39, 130.46, 133.17, 133.67, 136.27, 163.50, 166.51. The spectroscopic data are in agreement with that previously reported.[7]



1a-3

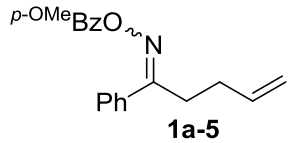
1-Phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1a-3). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) afforded the title product in 73% overall yield (1.52 g) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.42-2.45 (m, 2H), 3.08 (t, *J* = 7.8, 2H), 5.07-5.14 (m, 2H), 5.84-5.91 (m, 1H), 7.47 (t, *J* = 7.2, 2H), 7.51 (t, *J* = 7.2, 1H), 7.80 (d, *J*

= 7.2, 2H), 8.13 (s, 1H), 8.56 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 28.34, 30.84, 116.19, 122.75 (q, *J* = 273.0 Hz), 126.62 (q, *J* = 3.3 Hz), 127.38, 128.76, 129.60 (q, *J* = 2.1 Hz), 131.01, 131.46, 132.41 (q, *J* = 34.1 Hz), 133.16, 136.01, 161.04, 167.85. IR (neat): 3090, 3062, 2985, 2924, 2859, 1759, 1644, 1618, 1569, 1466, 1445, 1380, 1346, 1326, 1276, 1222, 1167, 1110, 1093, 1052, 994, 946, 911, 896, 843, 773, 752, 700, 689, 681, 664, 626, 609, 575, 526, 500, 468, 440 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{15}F_6NNaO_2$ $[M+Na]^+$: 438.0899, found 438.0899.



1a-4

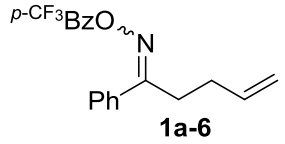
1-Phenylpent-4-en-1-one *O*-perfluorobenzoyl oxime (1a-4). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 76% overall yield (1.40 g) as a purple solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.32-2.36 (m, 2H), 3.00 (t, *J* = 7.8 Hz, 2H), 5.01-5.06 (m, 2H), 5.77-5.83 (m, 1H), 7.43-7.46 (m, 2H), 7.48-7.50 (m, 1H), 7.74-7.75 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): major signals: δ 28.20, 30.65, 116.11, 127.45, 128.80, 131.09, 133.02, 136.05, 156.52, 168.16. The spectroscopic data are in agreement with that previously reported.[8]



1a-5

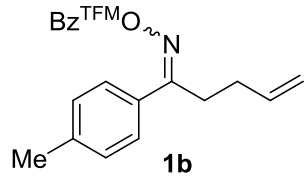
1-Phenylpent-4-en-1-one *O*-(4-methoxybenzoyl) oxime (1a-5). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 70% overall yield (1.08 g) as a purple solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.41-2.44 (m, 2H), 3.06 (t, *J* = 7.8 Hz, 2H), 3.89 (s, 3H), 5.04-5.12 (m, 2H), 5.85-5.90 (m, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.42-7.48 (m, 3H), 7.79 (d, *J* = 7.2 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.94, 30.70, 55.35, 113.81, 115.81, 121.19, 127.26, 128.53, 130.43, 131.55,

133.90, 136.45, 163.36, 163.57, 166.17. IR (neat): 3078, 3060, 2980, 2939, 2833, 1732, 1693, 1643, 1602, 1578, 1509, 1454, 1445, 1421, 1332, 1313, 1300, 1251, 1166, 1113, 1072, 1053, 1010, 910, 861, 844, 813, 756, 701, 690, 669, 636, 611, 549, 508, 488 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$: 332.1257, found 332.1257.



1a-6

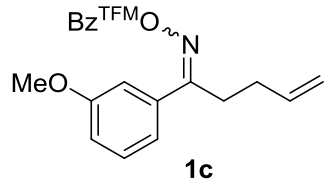
1-Phenylpent-4-en-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1a-6). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 87% overall yield (1.52 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.45 (m, 2H), 3.08 (t, J = 8.0 Hz, 2H), 5.04-5.12 (m, 2H), 5.82-5.92 (m, 1H), 7.43-7.51 (m, 3H), 7.77-7.80 (m, 4H), 8.23 (d, J = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 28.09, 30.75, 116.06, 123.49 (q, J = 273.2 Hz), 125.62 (q, J = 4.4 Hz), 127.37, 128.70, 129.94, 130.81, 132.43, 133.50, 134.71 (q, J = 33.1 Hz), 136.25, 162.49, 167.31. The spectroscopic data are in agreement with that previously reported.[9]



1b

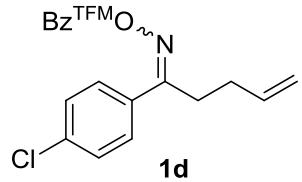
1-(*p*-Tolyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1b). 4.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 88% overall yield (1.52 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39-2.45 (m, 5H), 3.06 (t, J = 7.6 Hz, 2H), 5.06-5.15 (m, 2H), 5.82-5.92 (m, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 8.12 (s, 1H), 8.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.36, 28.27, 30.97, 116.19, 122.78 (q, J = 271.6 Hz), 126.64 (q, J = 3.6 Hz), 127.34, 129.52, 129.63 (q, J = 2.9 Hz), 130.22, 131.55, 132.45 (q, J = 33.9 Hz), 136.12, 141.54, 161.16, 167.76. IR (neat): 3088, 3068, 3009, 2983, 2928, 1842, 1758, 1640, 1621, 1598, 1561, 1513, 1462, 1438, 1384,

1334, 1280, 1216, 1193, 1168, 1128, 1114, 1059, 1013, 1002, 913, 896, 845, 830, 819, 756, 715, 698, 681, 647, 630, 563, 504, 437, 421, 404 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}F_6NNaO_2$ $[M+Na]^+$: 452.1056, found 452.1059.



1c

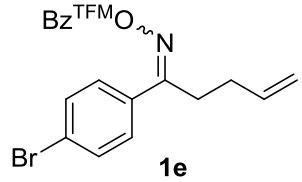
1-(3-Methoxyphenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1c). 10.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 65% overall yield (2.91 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.46 (m, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 3.87 (s, 3H), 5.06-5.16 (m, 2H), 5.82-5.92 (m, 1H), 7.05 (dt, *J* = 2.4, 7.2 Hz, 1H), 7.34-7.40 (m, 3H), 8.13 (s, 1H), 8.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.59, 30.90, 55.39, 112.82, 116.30, 116.82, 119.86, 122.76 (q, *J* = 271.5 Hz), 126.68 (q, *J* = 3.6 Hz), 129.65 (q, *J* = 3.7 Hz), 129.84, 131.45, 132.48 (q, *J* = 34.0 Hz), 134.54, 136.04, 159.84, 161.10, 167.94. IR (neat): 3092, 2986, 2934, 2837, 1756, 1640, 1619, 1598, 1579, 1492, 1465, 1422, 1384, 1330, 1275, 1216, 1173, 1122, 1065, 1038, 994, 908, 869, 845, 790, 754, 693, 681, 556, 520, 467, 438 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}F_6NNaO_3$ $[M+Na]^+$: 468.1005, found 468.1005.



1d

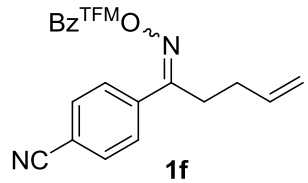
1-(4-Chlorophenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1d). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 85% overall yield (1.91 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.45 (m, 2H), 3.07 (t, *J* = 7.6 Hz, 2H), 5.07-5.16 (m, 2H), 5.81-5.91 (m, 1H), 7.42-7.45 (m, 2H), 7.74-7.78 (m, 2H), 8.14 (s, 1H), 8.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.20, 30.80, 116.49, 122.74 (q,

J = 270.9 Hz), 126.76 (q, J = 3.6 Hz), 128.74, 129.11, 129.64 (q, J = 3.6 Hz), 131.28, 131.61, 132.51 (q, J = 33.9 Hz), 135.77, 137.38, 160.99, 166.79. IR (neat): 3094, 3064, 2991, 2922, 1748, 1644, 1620, 1610, 1591, 1495, 1461, 1398, 1382, 1341, 1324, 1272, 1222, 1169, 1114, 1040, 1009, 995, 923, 911, 885, 844, 832, 816, 758, 717, 698, 680, 612, 578, 548, 497, 476, 438, 417 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{14}ClF_6NNaO_2$ $[M+Na]^+$: 472.0509, found 472.0505.



1e

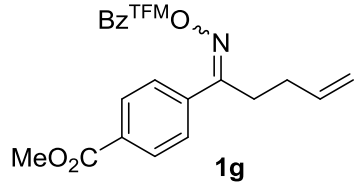
1-(4-Bromophenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1e). 4.5 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) afforded the title product in 48% overall yield (1.06 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39-2.44 (m, 2H), 3.06 (t, J = 7.6 Hz, 2H), 5.07-5.15 (m, 2H), 5.80-5.90 (m, 1H), 7.59-7.62 (m, 2H), 7.67-7.70 (m, 2H), 8.13 (s, 1H), 8.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.12, 30.79, 116.48, 122.72 (q, J = 271.6 Hz), 125.75, 126.78 (q, J = 3.6 Hz), 128.91, 129.63 (q, J = 2.9 Hz), 131.26, 132.06, 132.49 (q, J = 34.0 Hz), 135.75, 160.96, 166.86 *(1 aromatic carbon signal is not observed due to signal overlap).* IR (neat): 3103, 3070, 2987, 2922, 1749, 1643, 1620, 1588, 1492, 1460, 1382, 1324, 1272, 1222, 1169, 1115, 1071, 1039, 1007, 994, 965, 924, 911, 885, 844, 831, 813, 757, 713, 698, 680, 610, 578, 541, 517, 495, 482, 456, 438 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{15}BrF_6NO_2$ $[M+H]^+$: 494.0185, found 494.0188.



1f

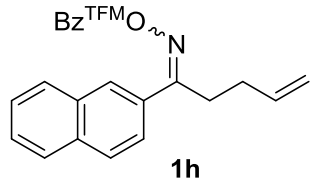
4-(1-(((3,5-Bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)benzonitrile (1f). 3.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: acetone = 10:1) afforded the title product in 49% overall yield

(0.65 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.46 (m, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 5.08-5.15 (m, 2H), 5.79-5.89 (m, 1H), 7.76-7.78 (m, 2H), 7.92-7.94 (m, 2H), 8.15 (s, 1H), 8.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.16, 30.62, 114.64, 116.81, 117.99, 122.67 (q, *J* = 270.9 Hz), 126.98 (q, *J* = 3.6 Hz), 128.07, 129.67 (q, *J* = 2.9 Hz), 130.95, 132.54, 132.58 (q, *J* = 33.9 Hz), 135.41, 137.57, 160.81, 166.28. IR (neat): 3054, 2981, 2938, 2227, 1750, 1620, 1468, 1382, 1275, 1224, 1173, 1124, 1093, 1040, 996, 927, 911, 892, 855, 846, 832, 825, 758, 698, 681, 661, 645, 616, 566, 549, 508, 441, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{14}F_6N_2NaO_2$ $[M+Na]^+$: 463.0852, found 463.0850.



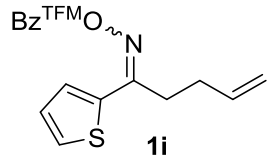
1g

Methyl 4-(1-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)benzoate (1g). 2.3 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 69% overall yield (0.75 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.46 (m, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 5.07-5.15 (m, 2H), 5.80-5.91 (m, 1H), 7.86-7.89 (m, 2H), 8.12-8.14 (m, 3H), 8.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.31, 30.71, 52.26, 116.49, 122.70 (q, *J* = 270.8 Hz), 126.81 (q, *J* = 3.6 Hz), 127.42, 129.63 (q, *J* = 2.9 Hz), 129.91, 131.18, 132.29, 132.48 (q, *J* = 34.0 Hz), 135.69, 137.35, 160.90, 166.19, 167.07. IR (neat): 3090, 2985, 2955, 1763, 1717, 1644, 1617, 1465, 1436, 1405, 1382, 1312, 1279, 1220, 1137, 1112, 1095, 1047, 1020, 1002, 954, 922, 914, 896, 861, 848, 835, 773, 758, 699, 682, 655, 612, 495, 467, 438, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{17}F_6NNaO_4$ $[M+Na]^+$: 496.0954, found 496.0953.



1h

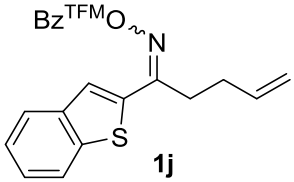
1-(Naphthalen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1h). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 82% overall yield (1.91 g) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.48-2.52 (m, 2H), 3.20 (t, *J* = 7.8 Hz, 2H), 5.09-5.17 (m, 2H), 5.88-5.95 (m, 1H), 7.54-7.59 (m, 2H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.91-7.95 (m, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 8.23 (s, 1H), 8.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.24, 31.09, 116.36, 122.79 (q, *J* = 271.6 Hz), 123.93, 126.74, 126.79 (q, *J* = 4.4 Hz), 127.63, 127.74, 127.99, 128.69, 128.82, 129.68 (q, *J* = 2.9 Hz), 130.46, 131.45, 132.50 (q, *J* = 33.9 Hz), 132.90, 134.53, 136.08, 161.17, 167.70. IR (neat): 3088, 3066, 3003, 2983, 2922, 1754, 1639, 1620, 1603, 1577, 1462, 1436, 1381, 1328, 1280, 1270, 1241, 1217, 1184, 1165, 1125, 1113, 1052, 1010, 996, 951, 907, 867, 843, 824, 756, 702, 693, 681, 668, 614, 556, 507, 476, 442, 429, 416 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{18}F_6NO_2$ $[M+H]^+$: 466.1236, found 466.1236.



1i

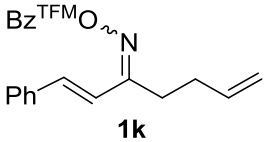
1-(Thiophen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1i). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 63% overall yield (1.32 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48-2.58 (m, 2H), 3.04-3.07 (m, 2H), 5.05-5.18 (m, 2H), 5.85-5.97 (m, 1H), 7.13 (dd, *J* = 4.0, 5.0 Hz, 0.6H, major), 7.21 (dd, *J* = 4.0, 5.2 Hz, 0.4H, minor), 7.51 (dd, *J* = 1.2, 5.2 Hz, 0.6H, major), 7.54 (dd, *J* = 0.8, 3.8 Hz, 0.6H, major), 7.63 (dd, *J* = 1.2, 4.0 Hz, 0.4H, minor), 7.71 (dd, *J* = 0.8, 5.2 Hz, 0.4H, minor), 8.12 (br, 1H), 8.53 (s, 1.2H, major), 8.71 (s, 0.8H, minor). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.98, 31.40, 32.25, 33.76, 115.94, 116.40, 122.74 (q, *J* = 271.6 Hz), 122.80 (q, *J* = 270.9 Hz), 126.67 (q, *J* = 3.6 Hz), 126.75, 175.54, 129.59 (q, *J* = 2.9 Hz), 129.81, 130.17, 130.27 (br), 131.21, 131.31, 132.37 (q, *J* = 34.0 Hz), 132.46 (q, *J* = 34.0 Hz), 132.49, 132.72, 135.92, 136.26, 136.39, 158.11, 160.73, 161.56, 162.98 *(2*

aromatic carbon signals of the isomers are not observed due to signal overlap). IR (neat): 3076, 1764, 1644, 1618, 1596, 1458, 1434, 1383, 1279, 1217, 1170, 1127, 1113, 1001, 909, 891, 845, 754, 740, 712, 697, 681, 663, 558, 507, 495, 438, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{13}F_6NNaO_2S$ $[M+Na]^+$: 444.0463, found 444.0463.



1j

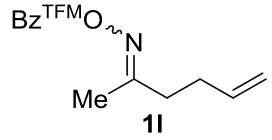
1-(Benzo[*b*]thiophen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1j). 3.0 mmol scale, purification of the crude product by recrystallization from a mixed solvent of dichloromethane and petroleum ether afforded the title product in 35% overall yield (0.49 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53-2.59 (m, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 5.10-5.21 (m, 2H), 5.88-5.98 (m, 1H), 7.37-7.46 (m, 2H), 7.77 (s, 1H), 7.82-7.87 (m, 2H), 8.13 (s, 1H), 8.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.54, 31.49, 116.60, 122.52, 122.75 (q, *J* = 270.9 Hz), 124.57, 124.78, 126.68, 126.78 (q, *J* = 3.6 Hz), 127.21, 129.65 (br), 131.17, 132.52 (q, *J* = 34.0 Hz), 135.87, 136.80, 138.86, 141.04, 160.58, 163.33. IR (neat): 3086, 2979, 1758, 1618, 1578, 1525, 1459, 1435, 1379, 1346, 1281, 1270, 1215, 1182, 1165, 1127, 1113, 1098, 998, 960, 908, 901, 838, 755, 729, 712, 701, 693, 681, 639, 559, 502, 439, 418, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{15}F_6NNaO_2S$ $[M+Na]^+$: 494.0620, found 494.0620



1k

(1*E*)-1-Phenylhepta-1,6-dien-3-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1k). 2.6 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 71% overall yield (0.82 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44-2.50 (m, 1.5H, major), 2.51-2.54 (m, 0.5H, minor), 2.85-2.89 (m, 0.5H, minor), 2.94 (t, *J* = 7.6 Hz, 1.5H, major), 5.07-5.20 (m, 2H), 5.87-5.97 (m, 1H), 7.05 (d, *J* = 16.4 Hz, 0.75H, major), 7.17-7.22 (m,

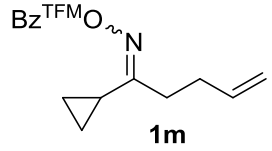
1H), 7.35-7.44 (m, 3.25H), 7.53-7.57 (m, 2H), 8.13 (s, 1H), 8.54 (s, 1.5H, major), 8.57 (s, 0.5H, minor). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.96 (major), 30.24 (minor), 31.21 (major), 31.80 (minor), 115.22 (minor), 115.79 (minor), 116.21 (major), 122.42 (major), 122.70 (q, *J* = 270.8 Hz, major), 122.75 (q, *J* = 271.6 Hz, minor), 126.55 (q, *J* = 3.6 Hz, minor), 126.67 (q, *J* = 3.6 Hz, major), 127.35 (major), 127.63 (minor), 128.87 (major), 129.01 (minor), 129.55 (br, major), 130.29 (minor), 131.24 (major), 131.58 (minor), 132.35 (q, *J* = 33.9 Hz, minor), 132.40 (q, *J* = 33.9 Hz, major), 134.93 (minor), 135.23 (major), 136.08 (major), 136.58 (minor), 138.45 (major), 140.43 (minor), 160.97 (major), 161.01 (minor), 164.30 (minor), 167.29 (major) *(2 aromatic carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3076, 2977, 2936, 2922, 1754, 1625, 1585, 1450, 1383, 1349, 1278, 1220, 1173, 1124, 1113, 999, 987, 964, 920, 905, 869, 845, 752, 702, 691, 681, 638, 614, 439, 430, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{18}F_6NO_2$ $[M+H]^+$: 442.1236, found 442.1236.



1l

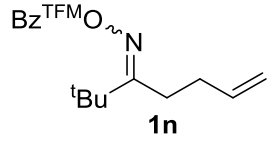
Hex-5-en-2-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1l). 10.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) afforded the title product in 59% overall yield (2.10 g) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.15 (s, 2.25H, major), 2.16 (s, 0.75H, minor), 2.37-2.44 (m, 2H), 2.56-2.58 (m, 1.5H, major), 2.66 (t, *J* = 7.8 Hz, 0.5H, minor), 5.05-5.15 (m, 2H), 5.80-5.89 (m, 1H), 8.10 (s, 1H), 8.50 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 15.59 (major), 20.09 (minor), 29.76 (minor), 30.14 (major), 30.50 (minor), 35.00 (major), 115.95 (major), 116.25 (minor), 122.71 (q, *J* = 273.2 Hz), 126.46 (q, *J* = 3.3 Hz), 129.51, 131.47 (minor), 131.57 (major), 132.28 (q, *J* = 34.1 Hz, major), 132.33 (q, *J* = 35.2 Hz, minor), 135.87 (minor), 136.18 (major), 161.18 (minor), 161.22 (major), 168.19 (major), 168.69 (minor) *(3 aromatic carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3084, 2985, 2926, 1754, 1644, 1618, 1382, 1277, 1222, 1175,

1130, 1113, 994, 911, 870, 845, 758, 698, 681, 668, 438 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{13}F_6NNaO_2$ $[M+Na]^+$: 376.0743, found 376.0743.



1m

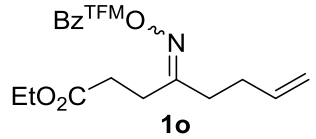
1-Cyclopropylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1m). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 45% overall yield (0.85 g) as a white solid. ^1H NMR (600 MHz, $CDCl_3$): δ 0.91-0.92 (m, 0.75H, minor), 0.96-0.97 (m, 2.5H, major), 1.07-1.08 (m, 0.75H, minor), 1.77-1.81 (m, 0.65H, major), 2.13-2.15 (m, 0.75H, minor), 2.27-2.29 (m, 0.35H, minor), 2.40-2.45 (m, 3.25H), 5.03-5.14 (m, 2H), 5.82-5.88 (m, 1H), 8.09 (s, 1H), 8.48 (s, 1.25H, major), 8.51 (s, 0.75H, minor). ^{13}C NMR (151 MHz, $CDCl_3$): δ 6.26 (minor), 6.49 (major), 10.14 (minor), 14.28 (major), 28.15 (major), 28.53 (minor), 30.64 (major), 30.88 (minor), 115.57 (minor), 115.97 (major), 122.71 (q, J = 273.0 Hz, major), 122.73 (q, J = 273.0 Hz, minor), 126.39 (q, J = 3.3 Hz), 129.45 (q, J = 3.3 Hz), 131.60 (major), 131.78 (minor), 132.23 (q, J = 34.1 Hz, minor), 132.30 (q, J = 34.1 Hz, major), 136.10 (major), 136.60 (minor), 160.98 (major), 161.47 (minor), 171.25 (minor), 172.44 (major) *(2 aromatic carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3090, 3013, 2947, 1752, 1642, 1611, 1462, 1382, 1279, 1271, 1249, 1222, 1168, 1114, 994, 912, 886, 865, 845, 829, 810, 759, 743, 698, 681, 614, 437 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{15}F_6NNaO_2$ $[M+Na]^+$: 402.0899, found 402.0899.



1n

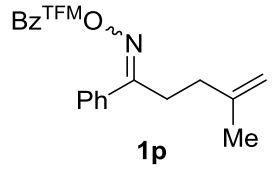
2,2-Dimethylhept-6-en-3-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1n). 6.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) afforded the title product in 83% overall

yield (1.97 g) as a light-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.29 (s, 9H), 2.36-2.40 (m, 2H), 2.57-2.60 (m, 2H), 5.07-5.12 (m, 2H), 5.85-5.91 (m, 1H), 8.10 (s, 1H), 8.49 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 27.02, 27.41, 31.26, 38.73, 115.63, 122.76 (q, J = 273.0 Hz), 126.47 (q, J = 3.3 Hz), 129.49 (q, J = 3.3 Hz), 131.79, 132.36 (q, J = 34.1 Hz), 136.47, 161.12, 176.48. IR (neat): 3090, 2974, 2936, 2874, 1757, 1644, 1616, 1480, 1382, 1278, 1224, 1177, 1132, 1112, 1034, 995, 911, 864, 846, 793, 758, 700, 681, 621, 499, 439 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{19}F_6NNaO_2$ $[M+Na]^+$: 418.1212, found 418.1211.



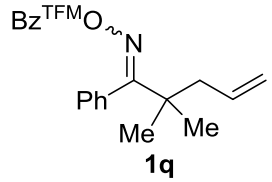
1o

Ethyl 4-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)oct-7-enoate (1o). 7.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) afforded the title product in 65% overall yield (2.01 g) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.24-1.30 (m, 3H), 2.39-2.44 (m, 2H), 2.58-2.64 (m, 3H), 2.73-2.79 (m, 2.1H), 2.85 (t, J = 7.8Hz, 0.9H, minor), 4.15-4.20 (m, 2H), 5.06-5.14 (m, 2H), 5.82-5.85 (m, 1H), 8.10-8.11 (m, 1H), 8.47 (s, 1.1H, major), 8.50 (s, 0.9H, minor). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.90 (minor), 14.02 (major), 25.07, 29.59 (minor), 29.90 (major), 29.96 (minor), 30.02 (major), 30.38 (major), 35.56 (minor), 60.64 (major), 60.98 (minor), 116.03 (minor), 116.27 (major), 122.68 (q, J = 273.0 Hz), 126.49 (q, J = 3.3 Hz, major), 126.57 (q, J = 3.3 Hz, minor), 129.48 (q, J = 3.3 Hz, major), 129.57 (q, J = 3.3 Hz, minor), 131.34 (minor), 131.45 (major), 132.32 (q, J = 34.1 Hz, major), 132.35 (q, J = 34.1 Hz, minor), 135.88 (major), 136.17 (minor), 160.89 (major), 161.05 (minor), 169.55 (major), 169.72 (minor), 171.39 (minor), 172.17 (major) *(1 aromatic carbon signal and 1 aliphatic carbon signal of the isomers are not observed due to signal overlap)*. IR (neat): 3088, 2985, 2934, 1759, 1735, 1642, 1620, 1457, 1381, 1348, 1278, 1222, 1176, 1131, 1113, 1095, 1039, 911, 867, 846, 758, 699, 681, 668, 438, 413 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{19}F_6NNaO_4$ $[M+Na]^+$: 462.1110, found 462.1109.



1p

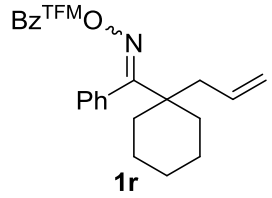
4-Methyl-1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1p). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) afforded the title product in 53% overall yield (1.13 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (s, 3H), 2.36 (t, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 4.79 (s, 1H), 4.84 (s, 1H), 7.45-7.53 (m, 3H), 7.80 (d, *J* = 7.6 Hz, 2H), 8.13 (s, 1H), 8.56 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.09, 27.73, 34.72, 111.44, 122.76 (q, *J* = 271.5 Hz), 126.68 (q, *J* = 3.6 Hz), 127.40, 128.84, 129.64 (q, *J* = 2.9 Hz), 131.08, 131.47, 132.49 (q, *J* = 34.0 Hz), 133.24, 143.59, 161.13, 168.29. IR (neat): 3092, 3052, 2977, 2934, 1755, 1650, 1620, 1571, 1498, 1458, 1384, 1324, 1286, 1269, 1224, 1170, 1129, 1069, 1032, 1019, 1001, 972, 945, 931, 915, 885, 843, 756, vc698, 681, 657, 634, 610, 577, 524, 500, 441, 414 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}F_6NNaO_2$ $[M+Na]^+$: 452.1056, found 452.1056.



1q

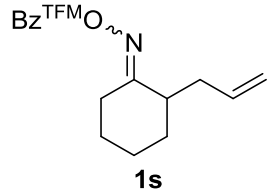
2,2-Dimethyl-1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1q). 13.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1) afforded the title product in 49% overall yield (2.80 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 6H), 2.42 (d, *J* = 7.2 Hz, 2H), 5.11-5.18 (m, 2H), 5.89-5.99 (m, 1H), 7.13-7.16 (m, 2H), 7.45-7.48 (m, 3H), 7.89 (s, 2H), 7.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.49, 41.46, 44.06, 118.51, 122.64 (q, *J* = 270.9 Hz), 126.26 (q, *J* = 3.6 Hz), 126.45, 128.18, 128.64, 129.42 (q, *J* = 2.9 Hz), 131.37, 132.05 (q, *J* = 33.9 Hz), 132.92, 133.87, 160.60, 176.11. IR (neat): 3090, 2979, 2934, 2874, 1759, 1622, 1492, 1468, 1444, 1382, 1278, 1218, 1177, 1132, 1044, 1022, 998, 912, 875, 846, 785, 757, 700, 681, 617, 580, 513, 432 cm^{-1}. HRMS (ESI) calcd. for

$C_{22}H_{19}F_6NNaO_2$ $[M+Na]^+$: 466.1212, found 466.1212.



1r

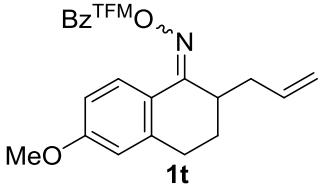
(1-Allylcyclohexyl)(phenyl)methanone *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1r). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 100:1) afforded the title product in 66% overall yield (1.59 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45-1.70 (m, 8H), 1.98-2.02 (m, 2H), 2.42 (d, J = 7.2 Hz, 2H), 5.14-5.20 (m, 2H), 5.90-6.01 (m, 1H), 7.18 (t, J = 4.0 Hz, 2H), 7.45-7.46 (m, 3H), 7.89 (s, 2H), 7.94 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 22.17, 25.88, 33.43, 41.10, 45.17, 118.25, 122.66 (q, J = 273.0 Hz), 126.21 (q, J = 3.3 Hz), 126.43, 128.15, 128.65, 129.43 (q, J = 3.3 Hz), 131.43, 132.03 (q, J = 33.1 Hz), 132.75, 133.50, 160.66, 174.59. IR (neat): 3084, 2933, 2853, 1759, 1638, 1619, 1591, 1492, 1455, 1377, 1274, 1247, 1215, 1175, 1134, 1116, 1076, 1050, 1023, 1001, 925, 913, 899, 866, 844, 797, 758, 714, 699, 680, 648, 613, 581, 549, 429 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{23}F_6NNaO_2$ $[M+Na]^+$: 506.1525, found 506.1531.



1s

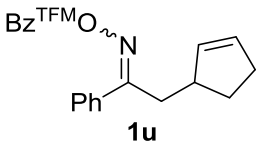
2-Allylcyclohexan-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1s). 7.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) afforded the title product in 45% overall yield (1.23 g) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.60-1.62 (m, 1H), 1.65-1.70 (m, 1H), 1.74-1.80 (m, 3H), 1.93-1.96 (m, 1H), 2.30-2.35 (m, 1H), 2.59-2.69 (m, 4H), 5.07-5.12 (m, 1H), 5.80-5.87 (m, 1H), 8.09 (s, 1H), 8.48 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 22.48, 25.72, 26.26, 31.51, 35.25, 41.73, 116.87, 122.79 (q, J = 273.2 Hz), 126.42 (q, J = 3.3 Hz),

129.56 (q, J = 3.3 Hz), 131.82, 132.29 (q, J = 34.1 Hz), 135.76, 161.66, 172.76. IR (neat): 3082, 2977, 2940, 2859, 1752, 1640, 1449, 1382, 1277, 1223, 1175, 1130, 1112, 1095, 996, 910, 846, 758, 699, 681, 668, 438, 415 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{17}F_6NNaO_2$ $[M+Na]^+$: 416.1056, found 416.1056.



1t

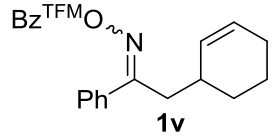
2-Allyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1t). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 58% overall yield (1.38 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97-2.08 (m, 2H), 2.32-2.39 (m, 1H), 2.42-2.49 (m, 1H), 2.73-2.77 (m, 1H), 2.96-3.05 (m, 1H), 3.63-3.68 (m, 1H), 3.84 (s, 3H), 5.11-5.18 (m, 2H), 5.82-5.92 (m, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 2.4, 9.0 Hz, 1H), 8.12 (s, 1H), 8.21 (d, J = 8.8 Hz, 1H), 8.56 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.64, 24.93, 33.97, 34.09, 55.26, 112.98, 113.48, 117.36, 120.06, 122.81 (q, J = 271.6 Hz), 126.50 (q, J = 3.6 Hz), 128.24, 129.64 (q, J = 2.9 Hz), 131.71, 132.38 (q, J = 33.9 Hz), 153.20, 141.82, 161.36, 162.00, 165.82. IR (neat): 3084, 3011, 2947, 2843, 1750, 1618, 1584, 1498, 1429, 1381, 1343, 1320, 1277, 1219, 1173, 1127, 1111, 1049, 1027, 998, 953, 911, 876, 861, 843, 816, 753, 713, 699, 681, 660, 617, 594, 540, 438, 416, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{20}F_6NO_3$ $[M+H]^+$: 472.1342, found 472.1342.



1u

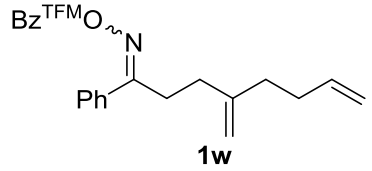
2-(Cyclopent-2-en-1-yl)-1-phenylethan-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1u). 2.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) afforded the title product in 90% overall yield (0.79 g) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.58-1.64 (m, 1H),

2.11-2.17 (m, 1H), 2.30-2.35 (m, 1H), 2.43-2.49 (m, 1H), 3.01-3.11 (m, 3H), 5.65-5.66 (m, 1H), 5.81-5.82 (m, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.49-7.52 (m, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 8.12 (s,1H), 8.55 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 30.09, 31.77, 34.80, 43.36, 122.81 (q, *J* = 273.0 Hz), 126.64 (q, *J* = 3.3 Hz), 127.63, 128.81, 129.76 (q, *J* = 3.3 Hz), 131.04, 131.52, 132.05, 132.44 (q, *J* = 34.1 Hz), 133.14, 133.53, 161.23, 167.80. IR (neat): 3090, 3060, 2958, 2851, 1857, 1749, 1618, 1565, 1449, 1382, 1325, 1277, 1269, 1223, 1172, 1127, 1024, 1001, 916, 877, 845, 780, 755, 730, 699, 693, 681, 669, 644, 625, 503, 439, 416 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{17}F_6NNaO_2$ $[M+Na]^+$: 464.1056, found 464.1051.



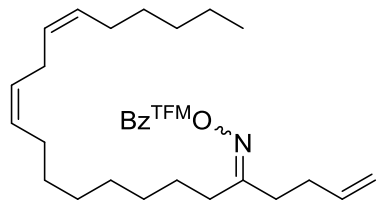
1v

2-(Cyclohex-2-en-1-yl)-1-phenylethan-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1v). 10.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1) afforded the title product in 57% overall yield (2.58 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38-1.46 (m, 1H), 1.49-1.59 (m, 1H), 1.71-1.79 (m, 1H), 1.81-1.88 (m, 1H), 1.97-2.03 (m, 2H), 2.46-2.53 (m, 1H), 2.96 (dd, *J* = 7.2, 12.8 Hz, 1H), 3.06 (dd, *J* = 8.0, 12.8 Hz, 1H), 5.55-5.58 (m, 1H), 5.74-5.77 (m, 1H), 7.44-7.52 (m, 3H), 7.80-7.83 (m, 2H), 8.12 (s, 1H), 8.56 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 20.82, 24.89, 29.40, 33.44, 34.98, 122.79 (q, *J* = 273.2 Hz), 126.63 (q, *J* = 3.3 Hz), 127.57, 128.81, 129.20, 129.74 (q, *J* = 3.3 Hz), 131.03, 131.53, 132.44 (q, *J* = 34.1 Hz), 133.53, 161.25, 167.64 *(1 aromatic carbon signal is not observed due to signal overlap)*. IR (neat): 3090, 3046, 3024, 2991, 2936, 2910, 2886, 2851, 1756, 1618, 1569, 1458, 1379, 1340, 1315, 1282, 1268, 1219, 1172, 1129, 1115, 1042, 1030, 1001, 912, 892, 843, 787, 766, 753, 726, 697, 688, 680, 649, 629, 578, 531, 502, 439, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}F_6NNaO_2$ $[M+ Na]^+$: 478.1212 found, 478.1212.



1w

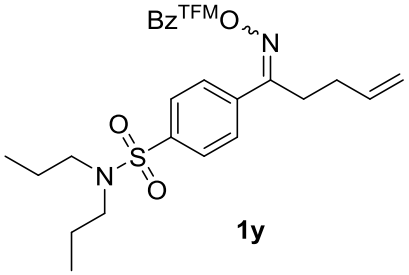
4-Methylene-1-phenyloct-7-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1w). 2.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 48% overall yield (0.45 g) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.14-2.18 (m, 4H), 2.36 (t, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 4.86 (s, 1H), 4.87 (s, 1H), 4.90-4.97 (m, 2H), 5.71-5.78 (m, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 8.13 (s, 1H), 8.55 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 27.68, 31.78, 33.05, 35.12, 110.51, 114.82, 122.76 (q, *J* = 273.0 Hz), 126.72 (q, *J* = 3.3 Hz), 127.42, 128.85, 129.64 (q, *J* = 3.3 Hz), 131.11, 131.46, 132.50 (q, *J* = 34.1 Hz), 133.21, 137.73, 146.95, 161.16, 168.35. IR (neat): 3088, 2983, 2926, 2849, 1753, 1642, 1619, 1569, 1460, 1443, 1382, 1330, 1277, 1221, 1193, 1174, 1127, 1060, 998, 906, 892, 845, 770, 755, 701, 693, 681, 661, 634, 562, 522, 439, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{21}F_6NNaO_2$ $[M+Na]^+$: 492.1369, found 492.1365.



1x

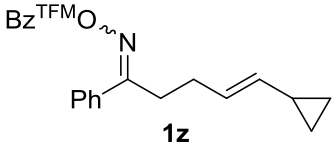
(13*Z*,16*Z*)-Docosa-1,13,16-trien-5-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1x). 6.6 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1) afforded the title product in 80% overall yield (3.02 g) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.87-0.90 (m, 3H), 1.26-1.40 (m, 14H), 1.61-1.65 (m, 2H), 2.02-2.06 (m, 4H), 2.35-2.39 (m, 1H), 2.41-2.46 (m, 2H), 2.50-2.56 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 1H), 2.74-2.79 (m, 2H), 5.06 (t, *J* = 10.2 Hz, 1H), 5.12 (dd, *J* = 2.4, 17.4 Hz, 1H), 5.30-5.39 (m, 4H), 5.80-5.90 (m, 1H), 8.10 (s, 1H), 8.49 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.97, 13.99, 22.50, 22.52, 25.54, 25.58, 26.16, 26.31,

27.06, 27.12, 27.15, 29.03, 29.07, 29.14, 29.17, 29.20, 29.28, 29.29, 29.44, 29.54, 29.84, 29.97, 30.18, 30.27, 31.46, 31.48, 33.60, 34.32, 115.92, 116.21, 122.76 (q, J = 273.0 Hz), 126.52 (q, J = 3.3 Hz), 127.80, 127.85, 128.06, 128.09, 129.55 (br), 129.81, 129.95, 130.17, 131.63, 131.67, 132.39 (q, J = 34.1 Hz), 136.07, 136.47, 161.24, 171.48, 171.52 *(some carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3088, 3010, 2928, 2857, 1758, 1642, 1620, 1458, 1382, 1278, 1222, 1178, 1136, 1113, 1095, 995, 911, 863, 846, 757, 699, 681, 438 cm^{-1}. HRMS (ESI) calcd. for $C_{31}H_{42}F_6NO_2$ $[M+H]^+$: 574.3114, found 574.3117.



1y

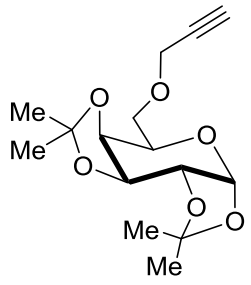
4-(1-(((3,5-Bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)-*N*,*N*-dipropylbenzenesulfonamide (1y). 5.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 68% overall yield (1.97 g) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.6 Hz, 6H), 1.52-1.62 (m, 4H), 2.43 (q, J = 7.6 Hz, 2H), 3.11 (t, J = 7.6 Hz, 6H), 5.08-5.15 (m, 2H), 5.80-5.90 (m, 1H), 7.88-7.93 (m, 4H), 8.15 (s, 1H), 8.55 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 11.05, 21.89, 28.37, 30.62, 49.92, 116.65, 122.66 (q, J = 273.0 Hz), 126.86 (q, J = 3.3 Hz), 127.39, 128.06, 129.64 (q, J = 3.3 Hz), 131.04, 132.52 (q, J = 34.1 Hz), 135.52, 136.96, 142.49, 160.90, 166.76. IR (neat): 3086, 3048, 2973, 2936, 2882, 1755, 1644, 1613, 1458, 1378, 1338, 1277, 1220, 1163, 1128, 1092, 1044, 1017, 986, 911, 887, 842, 799, 780, 756, 733, 699, 681, 616, 595, 568, 452, 435 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{29}F_6N_2O_4S$ $[M+H]^+$: 579.1747, found 579.1747.



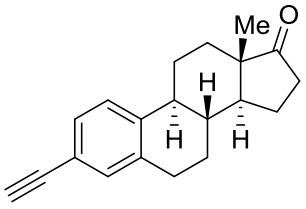
1z

(4*E*)-5-Cyclopropyl-1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime (1z). 2.0 mmol scale, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) afforded the title product in 68% overall yield (0.62 g) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.26-0.29 (m, 2H), 0.62-0.65 (m, 2H), 1.26-1.31 (m, 0.3H, minor), 1.32-1.38 (m, 0.7H, major), 2.33-2.37 (m, 0.6H, minor), 2.52-2.56 (m, 1.4H, major), 3.03 (t, *J* = 7.8 Hz, 0.6H, minor), 3.09 (t, *J* = 7.8 Hz, 1.4H, major), 4.80 (t, *J* = 10.2 Hz, 0.7H, major), 5.03-5.07 (m, 0.3H, minor), 5.31-5.35 (m, 0.7H, major), 5.49-5.54 (m, 0.3H, minor), 7.45-7.52 (m, 3H), 7.78-7.82 (m, 2H), 8.13 (s, 1H), 8.56 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 6.34, 6.85, 9.51, 13.29, 24.93, 28.87, 29.33, 29.69, 122.77 (q, *J* = 273.2 Hz), 124.75, 124.98, 126.67 (q, *J* = 3.3 Hz), 127.47, 127.53, 128.77, 129.63 (q, *J* = 2.3 Hz), 131.00, 131.56, 132.47 (q, *J* = 34.1 Hz), 133.34, 133.35, 136.14, 161.16, 161.29, 168.17, 168.38 *(some aromatic carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3088, 3007, 2983, 2857, 1755, 1621, 1569, 1460, 1443, 1384, 1328, 1284, 1274, 1217, 1171, 1115, 1061, 1048, 1020, 996, 939, 888, 844, 810, 768, 754, 693, 680, 642, 613, 590, 524, 493, 438 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}F_6NNaO_2$ $[M+Na]^+$: 478.1212, found 478.1215.

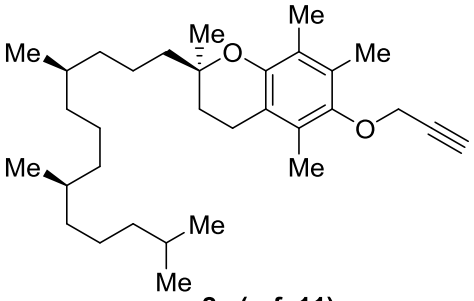
Synthesis of terminal alkynes



2w (ref. 10)

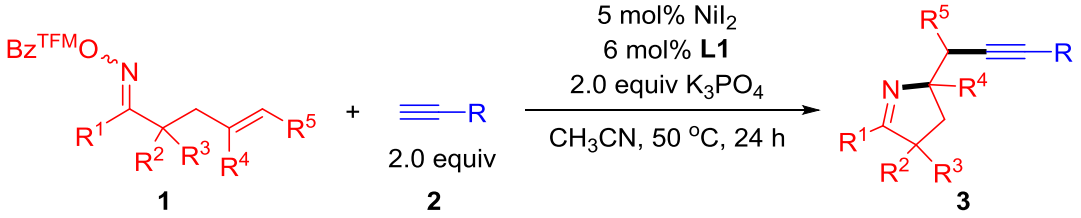


2x (ref. 11)

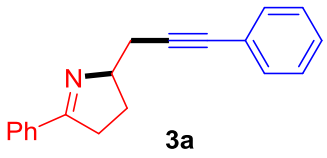


2y (ref. 11)

General procedure for nickel-catalyzed iminoalkynylation of unactivated alkenes



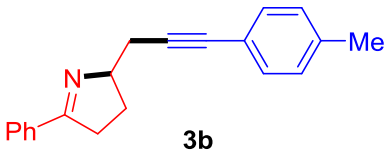
In a nitrogen-filled glovebox, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg) and acetonitrile (3.0 mL) were successively added to an oven-dried sealable Schlenk tube (15.0 mL). The mixture was stirred at room temperature for 5min. Then oxime ester **1** (0.3 mmol) and terminal alkyne (0.6 mmol) were added in sequence. The tube was securely sealed with parafilm, taken outside the glovebox and immersed into an oil bath preheated at 50 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and quenched with water. The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel to afford products **3**.



3a

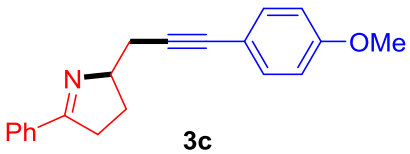
5-Phenyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3a). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 70% yield (54.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-1.94 (m, 2H), 2.17-2.26 (m, 1H), 2.61 (dd, *J* = 7.6, 16.4 Hz, 1H), 2.80-2.92 (m, 1H), 2.98-3.06 (m, 1H), 4.37-4.43 (m, 1H), 7.14-7.18 (m, 3H), 7.25-7.27 (m, 2H), 7.29-7.36 (m, 3H), 7.76-7.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.62, 27.71, 35.31, 71.66, 81.63, 87.38, 123.72, 127.54, 127.71, 128.09, 128.35, 130.46, 131.51, 134.33, 173.39. IR (neat): 3078, 3050, 2971, 2942, 2900, 2831, 2225, 1693, 1614, 1597, 1573, 1489, 1448, 1441, 1427, 1332, 1310, 1279, 1268, 1247, 1181, 1159, 1072, 1054, 1022, 992, 974, 928, 913, 762, 752, 690, 669, 649, 560, 537,

526, 514, 485, 428, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N$ $[M+H]^+$: 260.1434, found 260.1436.



3b

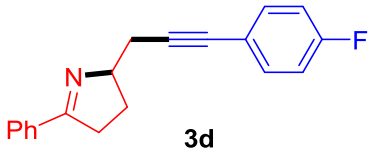
5-Phenyl-2-(3-(*p*-tolyl)prop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3b). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynyl-4-methylbenzene (0.6 mmol, 69.7 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 68% yield (55.9 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-1.93 (m, 1H), 2.22 (br, 4H), 2.59 (dd, *J* = 7.6, 16.6 Hz, 1H), 2.80-2.92 (m, 2H), 2.98-3.06 (m, 1H), 4.40 (br, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.31-7.33 (m, 3H), 7.77 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.30, 26.64, 27.71, 35.30, 71.72, 81.66, 86.53, 120.65, 127.73, 128.35, 128.85, 130.46, 131.40, 134.34, 137.52, 173.37. IR (neat): 3054, 3022, 2963, 2918, 2860, 2205, 2154, 1611, 1574, 1509, 1495, 1446, 1430, 1374, 1346, 1333, 1267, 1247, 1212, 1109, 1075, 1053, 1020, 913, 814, 754, 689, 641, 557, 530, 501, 430, 413 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590, found 274.1586.



3c

2-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3c). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynyl-4-methoxybenzene (0.6 mmol, 79.3 mg) and

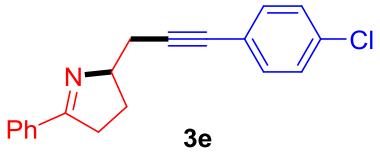
acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 75% yield (65.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-1.93 (m, 1H), 2.17-2.26 (m, 1H), 2.59 (dd, *J* = 7.6, 16.4 Hz, 1H), 2.79-2.91 (m, 2H), 2.98-3.06 (m, 1H), 3.67 (s, 3H), 4.39 (br, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.31-7.33 (m, 3H), 7.77 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.62, 27.71, 35.27, 55.12, 71.74, 81.35, 85.69, 113.70, 115.87, 127.73, 128.34, 130.46, 132.84, 134.31, 159.01, 173.35. IR (neat): 3062, 3034, 2999, 2959, 2923, 2851, 2837, 2205, 2173, 1606, 1571, 1507, 1454, 1444, 1348, 1330, 1291, 1264, 1243, 1183, 1172, 1106, 1054, 1034, 1022, 832, 816, 798, 761, 694, 661, 558, 537, 526, 507, 431, 412, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1539, found 290.1538.



3d

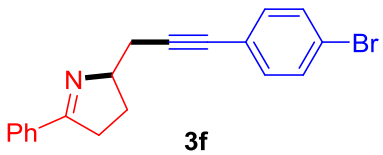
2-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3d). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynyl-4-fluorobenzene (0.6 mmol, 72.1 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:6) afforded the title product in 67% yield (55.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-1.91 (m, 1H), 2.18-2.27 (m, 1H), 2.60 (dd, *J* = 7.6, 16.4 Hz, 1H), 2.81-2.90 (m, 2H), 2.98-3.06 (m, 1H), 4.38-4.41 (m, 1H), 6.85 (t, *J* = 8.4 Hz, 2H), 7.21-7.25 (m, 2H), 7.30-7.37 (m, 3H), 7.76-7.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.60, 27.77, 35.33, 71.65, 80.58, 87.07, 115.31 (d, *J* = 21.7 Hz), 119.81 (d, *J* = 3.6 Hz), 127.73, 128.38, 130.51, 133.33 (d, *J*

= 8.0 Hz), 134.34, 162.03 (d, J = 247.0 Hz), 173.38. IR (neat): 3062, 3032, 2945, 2924, 2894, 2847, 2161, 1709, 1603, 1575, 1508, 1439, 1403, 1348, 1332, 1314, 1274, 1236, 1197, 1181, 1156, 1113, 1053, 1019, 969, 915, 858, 838, 769, 757, 691, 668, 657, 609, 549, 532, 498, 478, 452, 422, 410 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}FN$ $[M+H]^+$: 278.1340, found 278.1341.



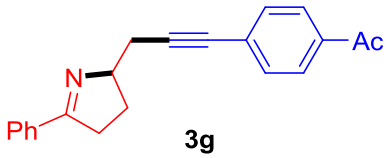
3e

2-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3e). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-chloro-4-ethynylbenzene (0.6 mmol, 81.9 mg) and acetonitrile (3.0 mL) were stirred at 50 ºC for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1) afforded the title product in 70% yield (61.8 mg) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.90-1.99 (m, 1H), 2.26-2.35 (m, 1H), 2.70 (dd, J = 7.6, 16.8 Hz, 1H), 2.89-2.99 (m, 2H), 3.06-3.15 (m, 1H), 4.47-4.49 (m, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.38-7.45 (m, 3H), 7.84-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.66, 27.78, 35.35, 71.58, 80.60, 88.54, 122.24, 127.73, 128.39, 128.42, 130.54, 132.77, 133.50, 134.31, 173.43. IR (neat): 3084, 3056, 3024, 2969, 2926, 2868, 2337, 2167, 1610, 1575, 1488, 1447, 1430, 1399, 1333, 1266, 1090, 1055, 1026, 1011, 970, 914, 827, 754, 690, 668, 583, 556, 526, 493, 473, 454, 423, 416, 407 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}ClN$ $[M+H]^+$: 294.1044, found 294.1044.



3f

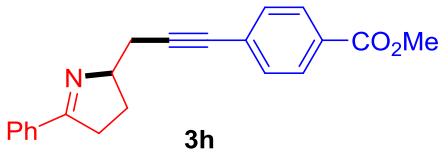
2-(3-(4-Bromophenyl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3f). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-bromo-4-ethynylbenzene (0.6 mmol, 108.6 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:6) afforded the title product in 66% yield (66.9 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91-1.99 (m, 1H), 2.26-2.35 (m, 1H), 2.69 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.90-2.98 (m, 2H), 3.06-3.15 (m, 1H), 4.47-4.49 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.39-7.46 (m, 3H), 7.84-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.70, 27.78, 35.37, 71.55, 80.68, 88.77, 121.70, 122.72, 127.75, 128.41, 130.56, 131.35, 133.03, 134.30, 173.48. IR (neat): 3107, 3080, 3056, 3026, 2969, 2930, 2890, 2866, 2161, 1978, 1905, 1611, 1586, 1575, 1485, 1447, 1428, 1393, 1346, 1340, 1266, 1214, 1097, 1072, 1054, 1024, 1009, 970, 916, 824, 758, 743, 690, 564, 549, 523, 488, 459 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}BrN$ $[M+H]^+$: 338.0539, found 338.0538.



3g

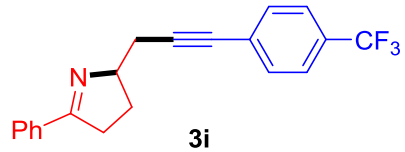
1-(4-(3-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)phenyl)ethan-1-one (3g). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-(4-ethynylphenyl)ethan-1-one (0.6 mmol, 86.5 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:4) afforded the title product in 69% yield (62.0 mg) as an orange solid. ^{1}H NMR (400

MHz, $CDCl_3$): δ 1.92-2.00 (m, 1H), 2.28-2.36 (m, 1H), 2.55 (s, 3H), 2.75 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.91-3.02 (m, 2H), 3.08-3.15 (m, 1H), 4.49-4.51 (m, 1H), 7.40-7.45 (m, 5H), 7.82-7.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.46, 26.77, 27.76, 35.33, 71.46, 81.12, 91.34, 127.68, 128.04, 128.35, 128.71, 130.51, 131.61, 134.23, 135.67, 173.43, 197.23. IR (neat): 3086, 3064, 3026, 2973, 2904, 2837, 2169, 1677, 1614, 1599, 1575, 1555, 1494, 1450, 1426, 1403, 1359, 1333, 1306, 1283, 1263, 1185, 1109, 1053, 1016, 956, 837, 762, 691, 630, 594, 550, 519, 497, 463, 444, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539, found 302.1539.



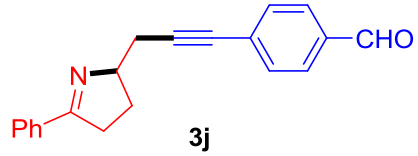
3h

Methyl 4-(3-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)benzoate (3h). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), methyl 4-ethynylbenzoate (0.6 mmol, 96.1 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:6) afforded the title product in 70% yield (66.7 mg) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.82-1.91 (m, 1H), 2.19-2.28 (m, 1H), 2.65 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.82-2.93 (m, 2H), 2.99-3.07 (m, 1H), 3.80 (s, 3H), 4.40-4.42 (m, 1H), 7.30-7.37 (m, 5H), 7.76-7.78 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.74, 27.76, 35.32, 52.03, 71.47, 81.13, 90.93, 127.70, 128.36, 128.51, 128.87, 129.28, 130.54, 131.43, 134.23, 166.49, 173.45. IR (neat): 3082, 3030, 2975, 2947, 2892, 2851, 2248, 2216, 1708, 1606, 1575, 1556, 1496, 1452, 1439, 1405, 1346, 1331, 1315, 1274, 1197, 1181, 1113, 1052, 1019, 969, 858, 845, 830, 769, 759, 692, 645, 572, 550, 533, 477 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489, found 318.1488.



3i

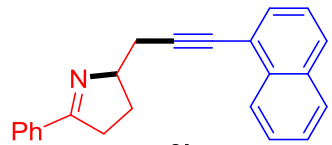
5-Phenyl-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3i). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynyl-4-(trifluoromethyl)benzene (0.6 mmol, 102.1 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 75% yield (73.5 mg) as a light-yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.92-1.98 (m, 1H), 2.29-2.35 (m, 1H), 2.75 (dd, *J* = 7.8, 17.1 Hz, 1H), 2.92-3.00 (m, 2H), 3.08-3.14 (m, 1H), 4.49-4.51 (m, 1H), 7.40-7.45 (m, 5H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 26.70, 27.79, 35.37, 71.50, 80.57, 90.35, 123.94 (q, *J* = 272.1 Hz), 125.04 (q, *J* = 3.3 Hz), 127.61, 127.73, 128.41, 129.32 (q, *J* = 33.1 Hz), 130.57, 131.78, 134.30, 173.48. IR (neat): 3086, 3056, 3032, 2928, 2902, 2223, 1928, 1612, 1574, 1512, 1495, 1448, 1432, 1404, 1322, 1270, 1214, 1162, 1151, 1121, 1103, 1066, 1017, 953, 916, 841, 761, 718, 690, 649, 596, 567, 550, 523, 495, 457, 414 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{17}F_3N$ $[M+H]^+$: 328.1308, found 328.1308.



3j

4-(3-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)benzaldehyde (3j). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 4-ethynylbenzaldehyde (0.6 mmol, 78.1 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with

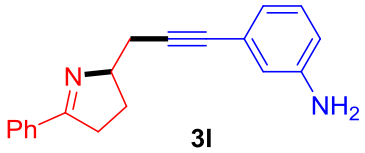
water and extracted with dichloromethane, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:5) afforded the title product in 47% yield (40.1 mg) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92-2.00 (m, 1H), 2.29-2.38 (m, 1H), 2.76 (dd, *J* = 7.6, 17.0 Hz, 1H), 2.92-3.03 (m, 2H), 3.08-3.17 (m, 1H), 4.49-4.52 (m, 1H), 7.39-7.44 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.85-7.87 (m, 2H), 9.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.82, 27.80, 35.38, 71.45, 81.14, 92.26, 127.72, 128.40, 129.39, 130.16, 130.58, 132.07, 134.25, 134.97, 173.50, 191.39. IR (neat): 3058, 3026, 2934, 2837, 2740, 2306, 2203, 1704, 1615, 1601, 1575, 1562, 1497, 1448, 1427, 1385, 1335, 1306, 1268, 1207, 1169, 1101, 1075, 1054, 1018, 915, 826, 760, 715, 691, 635, 555, 530, 489, 438, 413, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383, found 288.1381.



3k

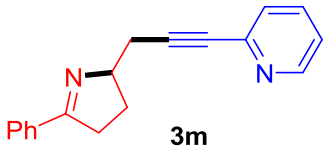
2-(3-(Naphthalen-1-yl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3k). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynylnaphthalene (0.6 mmol, 91.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 13:1:3) afforded the title product in 71% yield (66.2 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00-2.09 (m, 1H), 2.28-2.37 (m, 1H), 2.88-2.99 (m, 2H), 3.06-3.16 (m, 2H), 4.56-4.59 (m, 1H), 7.21-7.25 (m, 1H), 7.31-7.35 (m, 1H), 7.38-7.44 (m, 4H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.74 (dd, *J* = 8.0, 15.4 Hz, 2H), 7.89 (dd, J = 1.6, 7.4 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.95, 27.59, 35.51, 71.65, 79.77, 92.36, 121.42, 125.08,

126.10, 126.21, 126.35, 127.82, 127.94, 128.01, 128.38, 129.95, 130.49, 133.01, 133.40, 134.38, 173.42. IR (neat): 3103, 3054, 2973, 2916, 2898, 2870, 2831, 2219, 1808, 1735, 1612, 1586, 1575, 1494, 1447, 1427, 1394, 1344, 1330, 1277, 1251, 1207, 1174, 1074, 1055, 1025, 962, 919, 862, 846, 794, 771, 759, 690, 670, 632, 562, 543, 504, 480, 434 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{20}N$ $[M+H]^+$: 310.1590, found 310.1590.



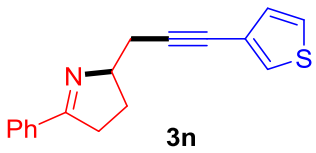
3l

3-(3-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)aniline (3l). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 3-ethynylaniline (0.6 mmol, 70.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:2:10) afforded the title product in 45% yield (37.3 mg) as a light-yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.92-2.04 (m, 1H), 2.25-2.34 (m, 1H), 2.68 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.88-2.98 (m, 2H), 3.06-3.15 (m, 1H), 3.50 (br, 2H), 4.47-4.50 (m, 1H), 6.56 (dd, *J* = 2.4, 7.8 Hz, 1H), 6.63-6.64 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.38-7.45 (m, 3H), 7.84-7.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.61, 27.68, 35.34, 71.66, 81.85, 86.72, 114.66, 117.92, 121.87, 124.38, 127.76, 128.36, 129.03, 130.47, 134.35, 146.11, 173.42. IR (neat): 3432, 3316, 3211, 3060, 2973, 2927, 2903, 2333, 2163, 1917, 1727, 1633, 1596, 1573, 1484, 1448, 1415, 1381, 1341, 1320, 1293, 1263, 1204, 1157, 1086, 1047, 993, 880, 782, 763, 689, 668, 650, 604, 559, 528, 456, 423 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{19}N_2$ $[M+H]^+$: 275.1543, found 275.1543.



3m

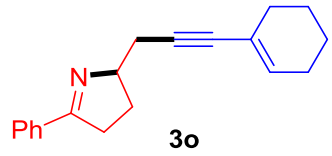
2-(3-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)pyridine (3m). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 2-ethynylpyridine (0.6 mmol, 61.9 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 1:1:5 to 1:3:5, gradient) afforded the title product in 63% yield (49.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95-2.02 (m, 1H), 2.31-2.38 (m, 1H), 2.69 (dd, *J* = 8.0, 16.8 Hz, 1H), 2.92-2.98 (m, 1H), 3.02-3.13 (m, 2H), 4.29-4.53 (m, 1H), 7.14-7.17 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.38-7.43 (m, 3H), 7.57 (td, *J* = 2.0, 7.6 Hz, 1H), 7.85 (dd, *J* = 2.0, 7.6 Hz, 2H), 8.53 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.52, 27.86, 35.20, 71.39, 81.28, 88.09, 122.27, 126.81, 127.68, 128.30, 130.45, 134.23, 135.89, 143.59, 149.68, 173.45. IR (neat): 3084, 3048, 3005, 2902, 2833, 2226, 1970, 1614, 1581, 1561, 1492, 1466, 1446, 1426, 1331, 1310, 1274, 1251, 1176, 1155, 1094, 1079, 1054, 1022, 1002, 979, 937, 902, 776, 765, 745, 698, 647, 628, 564, 549, 538, 531, 518, 498, 445, 405 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.1386, found 261.1387.



3n

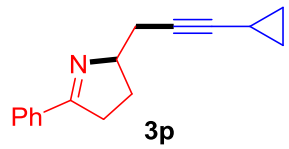
5-Phenyl-2-(3-(thiophen-3-yl)prop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3n). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 3-ethynylthiophene (0.6 mmol, 64.9 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 76%

yield (60.2 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-1.91 (m, 1H), 2.17-2.26 (m, 1H), 2.59 (dd, *J* = 7.6, 16.6 Hz, 1H), 2.80-2.91 (m, 2H), 2.98-3.05 (m, 1H), 4.37-4.41 (m, 1H), 6.93-6.94 (m, 1H), 7.10-7.12 (m, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.29-7.35 (m, 3H), 7.77 (dd, *J* = 2.0, 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.62, 27.76, 35.30, 71.64, 76.65, 86.91, 122.68, 124.90, 127.71, 127.75, 128.35, 129.91, 130.48, 134.33, 173.37. IR (neat): 3101, 3082, 2969, 2922, 2902, 2870, 2833, 2163, 1964, 1614, 1574, 1494, 1447, 1427, 1332, 1310, 1257, 1184, 1077, 1053, 1021, 1009, 988, 855, 801, 782, 761, 693, 628, 559, 510 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{16}NS$ $[M+H]^+$: 266.0998, found 266.0996.



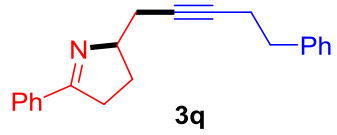
3o

2-(3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3o). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), 1-ethynylcyclohex-1-ene (0.6 mmol, 63.7 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 60% yield (47.4 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45-1.52 (m, 4H), 1.78-1.87 (m, 1H), 1.96-1.98 (m, 4H), 2.15-2.21 (m, 1H), 2.47 (dd, *J* = 8.0, 16.8 Hz, 1H), 2.78-2.87 (m, 2H), 2.96-3.05 (m, 1H), 4.31-4.35(m, 1H), 5.90 (br, 1H), 7.29-7.35 (m, 3H), 7.75-7.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.48, 22.27, 25.45, 26.52, 27.68, 29.40, 35.23, 71.87, 83.40, 84.33, 120.84, 127.70, 128.31, 130.38, 133.45, 134.44, 173.18. IR (neat): 3103, 3080, 3056, 3026, 2965, 2932, 2913, 2861, 2835, 2163, 1615, 1575, 1495, 1447, 1427, 1333, 1273, 1255, 1212, 1139, 1075, 1054, 1024, 917, 841, 802, 754, 689, 668, 646, 586, 555, 538, 525, 495, 455, 424 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{22}N$ $[M+H]^+$: 264.1747, found 264.1746.



3p

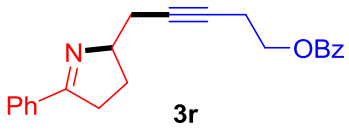
2-(3-Cyclopropylprop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3p). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), ethynylcyclopropane (0.6 mmol, 39.7 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 13:1:3) afforded the title product in 54% yield (35.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.54-0.58 (m, 2H), 0.65-0.69 (m, 2H), 1.15-1.19 (m, 1H), 1.83-1.89 (m, 1H), 2.20-2.25 (m, 1H), 2.35-2.42 (m, 1H), 2.67-2.73 (m, 1H), 2.90-2.94 (m, 1H), 3.01-3.06 (m, 1H), 4.33-4.36 (m, 1H), 7.37-7.43 (m, 3H), 7.82-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.47, 7.89, 7.90, 26.02, 27.66, 35.22, 71.97, 72.62, 84.40, 127.69, 128.33, 130.38, 134.45, 173.08. IR (neat): 3084, 3058, 3005, 2922, 2868, 2841, 2252, 1614, 1575, 1496, 1448, 1427, 1340, 1312, 1256, 1178, 1054, 1026, 923, 885, 812, 760, 692, 641, 557, 479, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{18}N$ $[M+H]^+$: 224.1434, found 224.1434.



3q

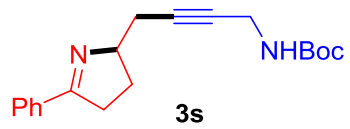
5-Phenyl-2-(5-phenylpent-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3q). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), but-3-yn-1-ylbenzene (0.6 mmol, 78.1 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent:

petroleum ether: ethyl acetate: dichloromethane = 10:1:3) afforded the title product in 54% yield (46.4 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76-1.85 (m, 1H), 2.13-2.22 (m, 1H), 2.38-2.45 (m, 3H), 2.69-2.78 (m, 3H), 2.81-2.90 (m, 1H), 2.95-3.04 (m, 1H), 4.30-4.36 (m, 1H), 7.16-7.19 (m, 3H), 7.23-7.26 (m, 2H), 7.37-7.44 (m, 3H), 7.82-7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.86, 25.96, 27.61, 35.19, 35.33, 71.89, 78.03, 80.66, 126.06, 127.70, 128.20, 128.32, 128.35, 130.38, 134.43. 140.85, 173.09. IR (neat): 3080, 3026, 2981, 2940, 2904, 2878, 2837, 2199, 1613, 1574, 1494, 1448, 1433, 1346, 1256, 1212, 1176, 1076, 1055, 1025, 913, 761, 739, 700, 690, 651, 590, 558, 499, 422 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{22}N$ $[M+H]^+$: 288.1747, found 288.1746.



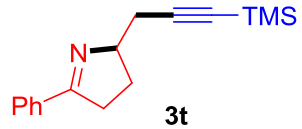
3r

5-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)pent-3-yn-1-yl benzoate (3r). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), but-3-yn-1-yl benzoate (0.6 mmol, 104.5 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:5) afforded the title product in 70% yield (69.8 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.89 (m, 1H), 2.16-2.25 (m, 1H), 2.41-2.48 (m, 1H), 2.59-2.63 (m, 2H), 2.70-2.76 (m, 1H), 2.82-2.90 (m, 1H), 2.99-3.07 (m, 1H), 4.32-4.37 (m, 3H), 7.35-7.44 (m, 5H), 7.52-7.56 (m, 1H), 7.80-7.84 (m, 2H), 8.03-8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.33, 25.87, 27.58, 35.17, 63.11, 71.67, 76.76, 79.16, 127.64, 128.23, 128.30, 129.52, 129.99, 130.40, 132.88, 134.26, 166.20, 173.19. IR (neat): 3066, 2963, 2932, 2900, 2868, 2205, 1719, 1616, 1600, 1575, 1494, 1451, 1391, 1330, 1313, 1286, 1268, 1257, 1234, 1178, 1158, 1107, 1100, 1071, 1053, 1023, 968, 921, 834, 761, 709, 690, 677, 659, 615, 559, 486, 406 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}NO_2$ $[M+H]^+$: 332.1645, found 332.1640.



3s

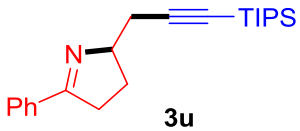
***tert*-Butyl (4-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)but-2-yn-1-yl)carbamate (3s).** 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), *tert*-butyl prop-2-yn-1-ylcarbamate (0.6 mmol, 93.1 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:15) afforded the title product in 58% yield (54.6 mg) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (m, 9H), 1.80-1.89 (m, 1H), 2.21-2.30 (m, 1H), 2.42-2.49 (m, 1H), 2.70-2.75 (m, 1H), 2.87-2.95 (m, 1H), 3.04-3.12 (m, 1H), 3.87 (br, 2H), 4.33-4.39 (m, 1H), 4.66 (br, 1H), 7.38-7.45 (m, 3H), 7.83-7.85 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 25.91, 27.72, 28.29, 30.77, 35.28, 71.55, 77.24, 79.64, 80.80, 127.72, 128.38, 130.50, 134.32, 155.25, 173.35. IR (neat): 3345, 3048, 2993, 2972, 2929, 2902, 2872, 2278, 1682, 1614, 1571, 1515, 1458, 1447, 1429, 1390, 1364, 1341, 1267, 1249, 1164, 1116, 1076, 1049, 1025, 964, 917, 875, 782, 758, 692, 668, 607, 558, 505, 462, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{25}N_2O_2$ $[M+H]^+$: 313.1911, found 313.1911.



3t

5-Phenyl-2-(3-(trimethylsilyl)prop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3t). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), ethynyltrimethylsilane (0.6 mmol, 58.9 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous

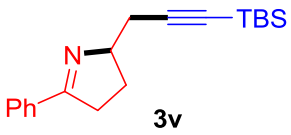
Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:1:10 to 15:1:3, gradient) afforded the title product in 50% yield (38.2 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.87-1.96 (m, 1H), 2.21-2.30 (m, 1H), 2.50 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.79 (dd, *J* = 4.4, 16.8 Hz, 1H), 2.87-2.96 (m, 1H), 3.03-3.12 (m, 1H), 4.38-4.44 (m, 1H), 7.37-7.44 (m, 3H), 7.82-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.02, 27.10, 27.57, 35.40, 71.51, 85.82, 104.48, 121.72, 128.34, 130.46, 134.37, 173.38. IR (neat): 3080, 3058, 3032, 2958, 2898, 2174, 1765, 1705, 1616, 1577, 1494, 1448, 1427, 1341, 1280, 1249, 1176, 1141, 1057, 1017, 972, 838, 758, 692, 643, 556, 445 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{22}NSi$ $[M+H]^+$: 256.1516, found 256.1516.



3u

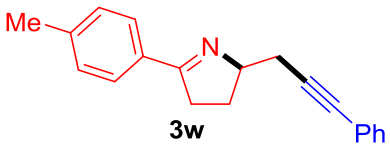
5-Phenyl-2-(3-(triisopropylsilyl)prop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3u). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), ethynyltriisopropylsilane (0.6 mmol, 109.4 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 69% yield (70.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93-1.05 (m, 21H), 1.92-2.01 (m, 1H), 2.21-2.30 (m, 1H), 2.61 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.82 (dd, *J* = 4.4, 16.8 Hz, 1H), 2.87-2.96 (m, 1H), 3.05-3.14 (m, 1H), 4.39-4.44 (m, 1H), 7.36-7.42 (m, 3H), 7.81-7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.17, 18.50, 27.07, 27.36, 35.43, 71.64, 81.68, 105.85, 127.73, 128.25, 130.36, 134.40, 173.12. IR (neat): 3080, 3060, 3028, 2942, 2894, 2864, 2172, 1617, 1576, 1494, 1462, 1383, 1341, 1310, 1252, 1210, 1176, 1074, 1058, 1017, 995, 971, 919, 883, 840, 760, 692, 676, 662, 632, 558, 460, 437, 411 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{34}NSi$ $[M+H]^+$:

340.2455, found 340.2455.



3v

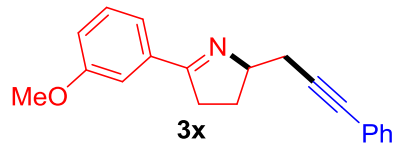
2-(3-(*tert*-Butyldimethylsilyl)prop-2-yn-1-yl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (3v). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), *tert*-butyl(ethynyl)dimethylsilane (0.6 mmol, 84.2 mg) and acetonitrile (3.0 mL) were stirred at 50 ºC for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 60% yield (53.3 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 6H), 0.86 (s, 9H), 1.89-1.98 (m, 1H), 2.21-2.30 (m, 1H), 2.56 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.80 (dd, *J* = 4.0, 16.8 Hz, 1H), 2.87-2.96 (m, 1H), 3.04-3.13 (m, 1H), 4.38-4.44 (m, 1H), 7.36-7.44 (m, 3H), 7.81-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.61, 16.39, 25.94, 27.08, 27.46, 35.40, 71.53, 83.98, 104.89, 127.73, 128.29, 130.41, 134.37, 173.21. IR (neat): 3068, 3024, 2952, 2927, 2886, 2855, 2172, 1611, 1575, 1494, 1461, 1448, 1360, 1345, 1250, 1210, 1182, 1077, 1054, 1018, 989, 941, 837, 824, 810, 775, 760, 695, 679, 600, 564, 550, 505, 457, 432, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{28}NSi$ $[M+H]^+$: 298.1986, found 298.1986.



3w

2-(3-Phenylprop-2-yn-1-yl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (3w). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(*p*-tolyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1b** (0.3 mmol, 128.8 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at

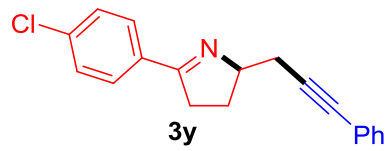
50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 72% yield (59.4 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91-2.00 (m, 1H), 2.45-2.34 (m, 1H), 2.37 (s, 3H), 2.67 (dd, *J* = 8.0, 16.6 Hz, 1H), 2.86-3.01 (m, 2H), 3.04-3.13 (m, 1H), 4.45-4.48 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.23-7.24 (m, 3H), 7.33-7.36 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.38, 26.67, 27.74, 35.25, 71.59, 81.58, 87.49, 123.77, 127.52, 127.70, 128.08, 129.06, 131.53, 131.65, 140.68, 173.23. IR (neat): 3058, 3030, 2965, 2919, 2894, 2863, 2221, 2161, 1741, 1613, 1567, 1512, 1489, 1454, 1442, 1430, 1401, 1329, 1266, 1248, 1215, 1180, 1111, 1072, 1054, 1027, 1017, 982, 949, 919, 862, 850, 820, 804, 750, 717, 692, 668, 597, 557, 535, 527, 513, 488, 475, 451, 432, 416, 408 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590, found 274.1590.



3x

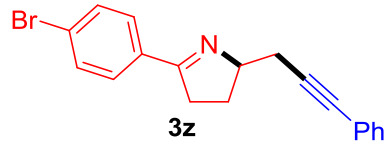
5-(3-Methoxyphenyl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3x). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol,127.4 mg), 1-(3-methoxyphenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1c** (0.3 mmol, 133.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 68% yield (58.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92-2.01 (m, 1H), 2.25-2.35 (m, 1H), 2.69 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.87-3.01 (m, 2H), 3.05-3.14 (m, 1H), 3.84 (s, 3H), 4.47-4.51 (m, 1H), 6.98 (dd, *J* = 2.4, 8.0 Hz, 1H), 7.23-7.25 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.34-7.39 (m, 3H), 7.45 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.63, 27.73, 35.43, 55.30, 71.68, 81.64, 87.39, 112.09, 116.92, 120.47, 123.73, 127.56,

128.10, 129.32, 131.52, 135.77, 159.58, 173.29. IR (neat): 3080, 3034, 2965, 2926, 2863, 2831, 2173, 1613, 1598, 1583, 1488, 1462, 1441, 1428, 1332, 1267, 1219, 1196, 1170, 1163, 1095, 1081, 1062, 1031, 1009, 994, 917, 865, 844, 815, 785, 756, 689, 619, 568, 523, 499, 475, 434, 406 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1539, found 290.1532.



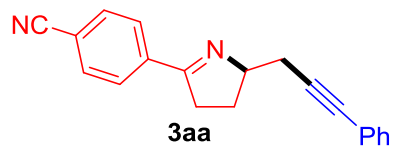
3y

5-(4-Chlorophenyl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3y). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(4-chlorophenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1d** (0.3 mmol, 134.9 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:3 to 15:1:3, gradient) afforded the title product in 64% yield (56.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93-2.02 (m, 1H), 2.26-2.35 (m, 1H), 2.70 (dd, *J* = 7.6, 16.6 Hz, 1H), 2.85-2.99 (m, 2H), 3.03-3.11 (m, 1H), 4.46-4.51 (m, 1H), 7.22-7.28 (m, 3H), 7.32-7.35 (m, 2H), 7.36-7.39 (m, 2H), 7.77-7.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.61, 27.78, 35.33, 71.78, 81.72, 87.21, 123.68, 127.62, 128.13, 128.61, 129.06, 131.52, 132.84, 136.52, 172.24. IR (neat): 3080, 3056, 3032, 2968, 2928, 2866, 2335, 2163, 1608, 1594, 1565, 1488, 1442, 1432, 1400, 1332, 1265, 1245, 1176, 1156, 1101, 1089, 1068, 1056, 1028, 1010, 973, 913, 837, 828, 806, 754, 734, 690, 668, 631, 562, 537, 527, 494, 453, 432, 416, 407 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}ClN$ $[M+H]^+$: 294.1044, found 294.1045.



3z

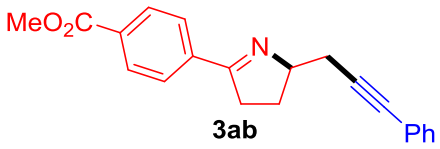
5-(4-Bromophenyl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3z). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(4-bromophenyl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1e** (0.3 mmol, 148.3 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:3 to 15:1:3, gradient) afforded the title product in 63% yield (63.9 mg) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95-2.02 (m, 1H), 2.27-2.36 (m, 1H), 2.71 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.86-2.99 (m, 2H), 3.03-3.11 (m, 1H), 4.48 (br, 1H), 7.24-7.25 (m, 3H), 7.33 (br, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.59, 27.77, 35.30, 71.81, 81.75, 87.18, 123.68, 125.00, 127.63, 128.14, 129.30, 131.53, 131.59, 133.27, 172.36. IR (neat): 3080, 3054, 3030, 2967, 2928, 2866, 2205, 2177, 1608, 1588, 1562, 1483, 1442, 1433, 1396, 1331, 1265, 1243, 1174, 1152, 1099, 1068, 1056, 1027, 1007, 914, 827, 806, 754, 726, 708, 690, 560, 535, 523, 516, 491, 450, 430, 406 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}BrN$ $[M+H]^+$: 338.0539, found 338.0538.



3aa

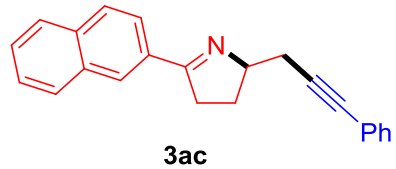
4-(2-(3-Phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzonitrile (3aa). 0.3 mmol scale, $Ni(cod)_2$ (0.03 mmol, 8.3 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6mmol,127.4mg),4-(1-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)ben zonitrile **1f** (0.3 mmol, 132.1 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1, gradient) afforded the title product in 52% yield (44.7 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98-2.07 (m,

1H), 2.31-2.40 (m, 1H), 2.76 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.90-2.99 (m, 2H), 3.07-3.16 (m, 1H), 4.54 (br, 1H), 7.25-7.26 (m, 3H), 7.32-7.33 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.51, 27.69, 35.42, 72.05, 81.90, 86.85, 113.84, 118.47, 123.57, 127.72, 128.17, 128.29, 131.51, 132.20, 138.32, 171.89. IR (neat): 3210, 3028, 2971, 2904, 2866, 2835, 2227, 1612, 1556, 1504, 1488, 1454, 1443, 1429, 1403, 1329, 1290, 1266, 1214, 1174, 1108, 1070, 1056, 1026, 1017, 963, 916, 848, 805, 755, 692, 668, 572, 527, 499, 482, 424, 416, 407 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{17}N_2$ $[M+H]^+$: 285.1386, found 285.1387.



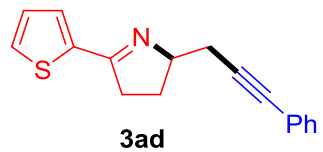
3ab

Methyl 4-(2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrol-5-yl)benzoate (3ab). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), methyl 4-(1-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)benzoate **1g** (0.3 mmol, 142.0 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 72% yield (68.5 mg) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95-2.04 (m, 1H), 2.29-2.38 (m, 1H), 2.73 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.91-3.01 (m, 2H), 3.08-3.17 (m, 1H), 3.93 (s, 3H), 4.51-4.53 (m, 1H), 7.23-7.26 (m, 3H), 7.32-7.35 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.56, 27.72, 35.48, 52.17, 71.94, 81.77, 87.09, 123.64, 127.62, 127.68, 128.12, 129.61, 131.50, 131.63, 138.34, 166.58, 172.66. IR (neat): 3032, 2995, 2942, 2920, 2843, 2205, 1713, 1610, 1504, 1490, 1434, 1409, 1313, 1272, 1193, 1178, 1111, 1103, 1056, 1016, 963, 917, 868, 819, 773, 763, 703, 694, 635, 561, 528, 509, 481, 432, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489, found 318.1482.



3ac

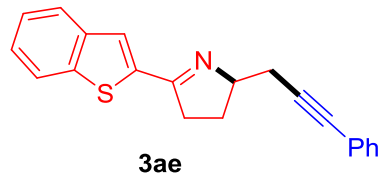
5-(Naphthalen-2-yl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ac). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(naphthalen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1h** (0.3 mmol, 139.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:10) afforded the title product in 76% yield (70.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96-2.05 (m, 1H), 2.29-2.38 (m, 1H), 2.74 (dd, *J* = 7.6, 16.8 Hz, 1H), 2.98-3.06 (m, 2H), 3.17-3.26 (m, 1H), 4.52-4.55 (m, 1H), 7.22 (t, *J* = 3.2 Hz, 3H), 7.34-7.36 (m, 2H), 7.46-7.52 (m, 2H), 7.81-7.88 (m, 3H), 8.10 (dd, *J* = 1.6, 8.8 Hz, 1H), 8.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.70, 27.81, 35.30, 71.81, 81.69, 87.42, 123.73, 124.61, 126.30, 127.03, 127.55, 127.68, 128.05, 128.09, 128.27, 128.65, 131.53, 131.85, 132.89, 134.37, 173.31. IR (neat): 3058, 3028, 2963, 2898, 2205, 2150, 1612, 1594, 1571, 1489, 1470, 1443, 1428, 1385, 1349, 1322, 1267, 1188, 1160, 1127, 1071, 1051, 1018, 994, 948, 919, 898, 862, 827, 802, 758, 742, 695, 663, 586, 535, 474, 444, 409 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{20}N$ $[M+H]^+$: 310.1590, found 310.1592.



3ad

2-(3-Phenylprop-2-yn-1-yl)-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole (3ad). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(thiophen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1i** (0.3 mmol, 126.4 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and

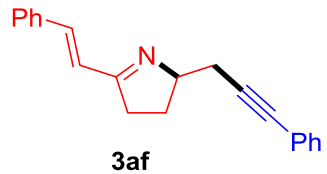
extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: acetone = 20:1) afforded the title product in 57% yield (45.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95-2.04 (m, 1H), 2.27-2.36 (m, 1H), 2.66 (dd, *J* = 8.0, 16.8 Hz, 1H), 2.88-3.01 (m, 2H), 3.06-3.14 (m, 1H), 4.43-4.49 (m, 1H), 7.06 (dd, J = 3.6, 5.0 Hz, 1H), 7.23-7.25 (m, 3H), 7.34-7.37 (m, 3H), 7.42 (dd, *J* = 0.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.55, 28.04, 35.94, 71.56, 81.68, 87.32, 123.73, 127.41, 127.58, 128.12, 129.24, 129.47, 131.54, 139.15, 167.83. IR (neat): 3074, 2967, 2916, 2264, 2053, 2017, 1606, 1524, 1487, 1433, 1328, 1265, 1230, 1071, 1053, 1009, 973, 926, 851, 839, 819, 767, 711, 697, 662, 637, 586, 535, 508, 485, 446, 439, 430, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{16}NS$ $[M+H]^+$: 266.0998, found 266.0999.



3ae

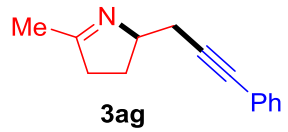
5-(Benzo[*b*]thiophen-2-yl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ae). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-(benzo[*b*]thiophen-2-yl)pent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1j** (0.3 mmol, 141.4 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 56% yield (53.0 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98-2.07 (m, 1H), 2.30-2.39 (m, 1H), 2.70 (dd, *J* = 8.0, 16.6 Hz, 1H), 2.94-3.04 (m, 2H), 3.12-3.20 (m, 1H), 4.49-4.52 (m, 1H), 7.22-7.24 (m, 3H), 7.32-7.38 (m, 4H), 7.53 (s, 1H), 7.76-7.79 (m, 1H), 7.81-7.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.48, 28.08, 35.72, 71.81, 81.75, 87.16, 122.56, 123.67, 124.40, 124.45, 125.88, 126.61, 127.59, 128.12, 131.53, 139.20, 139.45, 141.01, 168.50. IR (neat): 3072, 3056, 3013, 2959,

2920, 2863, 2205, 1604, 1522, 1489, 1428, 1338, 1325, 1267, 1241, 1198, 1177, 1154, 1050, 1013, 973, 942, 912, 862, 838, 797, 754, 746, 729, 689, 648, 592, 575, 534, 508, 453, 425, 410 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{18}NS$ $[M+H]^+$: 316.1154, found 316.1154.



3af

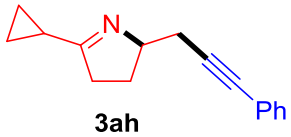
(*E*)-2-(3-Phenylprop-2-yn-1-yl)-5-styryl-3,4-dihydro-2*H*-pyrrole (3af). 0.3 mmol scale, $Ni(cod)_2$ (0.03 mmol, 8.3 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), (1*E*)-1-phenylhepta-1,6-dien-3-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1k** (0.3 mmol, 132.4 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product in 34% yield (28.8 mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.84-1.93 (m, 1H), 2.21-2.30 (m, 1H), 2.68 (dd, *J* = 7.6, 16.6 Hz, 1H), 2.73-2.81 (m, 1H), 2.89-3.01 (m, 2H), 4.38-4.44 (m, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 7.12 (d, *J* = 16.4 Hz, 1H), 7.24-7.26 (m, 3H), 7.29-7.35 (m, 2H), 7.37-7.39 (m, 3H), 7.49 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 26.63, 27.61, 34.03, 71.39, 81.72, 87.30, 123.78, 124.77, 127.25, 127.62, 128.15, 128.82, 129.09, 131.62, 135.86, 139.25, 173.98. IR (neat): 3078, 3056, 3026, 2928, 2859, 2244, 2219, 1954, 1883, 1814, 1686, 1633, 1588, 1490, 1450, 1442, 1429, 1348, 1278, 1264, 1239, 1177, 1136, 1071, 1048, 1015, 961, 912, 842, 749, 689, 586, 532, 506, 494, 468, 449, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}N$ $[M+H]^+$: 286.1590, found 286.1593.



3ag

5-Methyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ag). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4

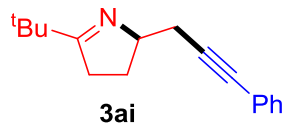
mg), hex-5-en-2-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1l** (0.3 mmol, 106.0 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: dichloromethane: methanol = 50:1) afforded the title product in 69% yield (40.6 mg) as a light-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.77-1.83 (m, 1H), 2.06 (s, 3H), 2.13-2.19 (m, 1H), 2.46-2.52 (m, 1H), 2.58-2.65 (m, 2H), 2.83 (dd, *J* = 7.2, 16.8 Hz, 1H), 4.22-4.24 (m, 1H), 7.26-7.29 (m, 3H), 7.37-7.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.67, 26.56, 28.09, 39.21, 71.23, 81.47, 87.44, 123.82, 127.56, 128.12, 131.54, 175.48. IR (neat): 3076, 3054, 3036, 2947, 2917, 2233, 1647, 1598, 1571, 1490, 1455, 1445, 1429, 1378, 1345, 1316, 1278, 1227, 1208, 1172, 1138, 1070, 1039, 1004, 949, 914, 842, 755, 691, 668, 603, 527, 507, 424 cm^{-1}. HRMS (ESI) calcd. for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277, found 198.1278.



3ah

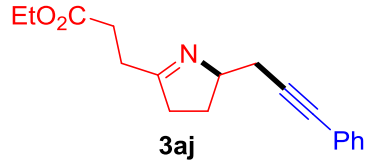
5-Cyclopropyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ah). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-cyclopropylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1m** (0.3 mmol, 113.8 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 63% yield (42.4 mg) as a light-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.82-0.88 (m, 4H), 1.75-1.82 (m, 2H), 2.12-2.16 (m, 1H), 2.32-2.37 (m, 1H), 2.46-2.50 (m, 1H) 2.57 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 4.22 (br, 1H), 7.27 (br, 3H), 7.38-7.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 7.05, 7.48, 14.14, 26.62, 27.47, 34.82, 70.74, 81.46, 87.54, 123.86, 127.55, 128.13, 131.55, 180.02. IR (neat): 3080, 3056, 3005, 2909, 2837,

2237, 1699, 1631, 1598, 1569, 1490, 1454, 1442, 1427, 1402, 1377, 1348, 1315, 1267, 1198, 1098, 1070, 1053, 1026, 981, 913, 862, 818, 755, 721, 691, 668, 526, 513, 475, 418 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{18}N$ $[M+H]^+$: 224.1434, found 224.1438.



3ai

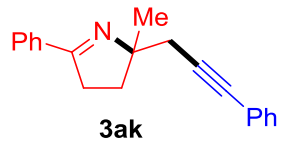
5-(*tert*-Butyl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ai). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2,2-dimethylhept-6-en-3-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1n** (0.3 mmol, 118.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 65% yield (46.4 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.17 (s, 9H), 1.80-1.86 (m, 1H), 2.07-2.13 (m, 1H), 2.50-2.56 (m, 1H), 2.63 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.69-2.75 (m, 1H), 2.83 (dd, *J* = 4.2, 16.8 Hz, 1H), 4.24-4.28 (m, 1H), 7.25-7.28 (m, 3H), 7.35-7.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.45, 27.55, 28.23, 33.71, 35.71, 70.49, 81.34, 87.45, 123.86, 127.48, 128.10, 131.47, 185.34. IR (neat): 3080, 3050, 2967, 2924, 2900, 2867, 2833, 2339, 2246, 2161, 1893, 1808, 1627, 1598, 1572, 1490, 1475, 1457, 1442, 1427, 1389, 1363, 1339, 1318, 1263, 1223, 1206, 1160, 1109, 1072, 1016, 994, 973, 924, 767, 697, 668, 534, 522, 504, 477, 419 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{22}N$ $[M+H]^+$: 240.1747, found 240.1747.



3aj

Ethyl 3-(2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrol-5-yl)propanoate (3aj). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6

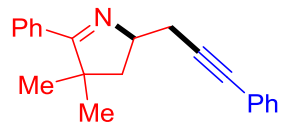
mmol, 127.4 mg), ethyl 4-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)oct-7-enoate **1o** (0.3 mmol, 131.8 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with dichloromethane, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 2:1:5) afforded the title product in 70% yield (59.4 mg) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.79-1.85 (m, 1H), 2.11-2.17 (m, 1H), 2.47-2.58 (m, 2H), 2.61-2.65 (m, 3H), 2.66-2.69 (m, 2H), 2.82 (dd, *J* = 4.8, 16.8 Hz, 1H), 4,10-4.14 (m, 2H), 4.24 (br, 1H), 7.26-7.29 (m, 3H), 7.37-7.38 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 14.14, 26.46, 27.61, 28.39, 30.82, 38.06, 60.39, 71.00, 81.43, 87.35, 123.78, 127.56, 128.12, 131.53, 172.92, 176.83. IR (neat): 3443, 3398, 3080, 3054, 3030, 2979, 2924, 2866, 2849, 2827, 2231, 1982, 1899, 1733, 1690, 1640, 1596, 1571, 1493, 1478, 1431, 1417, 1391, 1369, 1328, 1269, 1241, 1208, 1190, 1177, 1167, 1144, 1113, 1087, 1074, 1055, 1025, 972, 948, 922, 868, 838, 810, 777, 754, 694, 669, 614, 580, 531, 510, 478, 425 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1645, found 284.1646.



3ak

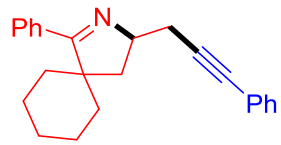
2-Methyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ak). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 4-methyl-1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1p** (0.3 mmol, 128.8 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:3) afforded the title product in 65% yield (53.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (s, 3H), 1.86-1.93 (m, 1H), 2.23-2.30 (m, 1H), 2.68 (d, *J* = 16.4 Hz, 1H), 2.80 (d, *J* = 16.4 Hz,

1H), 3.01-3.15 (m, 2H), 7.23-7.25 (m, 3H), 7.32-7.34 (m, 2H), 7.37-7.44 (m, 3H), 7.83-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.21, 32.73, 33.71, 35.70, 76.10, 81.76, 87.58, 123.84, 127.55, 127.74, 128.13, 128.35, 130.38, 131.53, 134.62, 171.26. IR (neat): 3074, 3060, 3026, 2963, 2933, 2899, 2866, 2215, 1950, 1611, 1573, 1489, 1455, 1443, 1371, 1340, 1314, 1257, 1220, 1158, 1136, 1116, 1090, 1070, 1019, 1002, 913, 858, 827, 771, 755, 689, 670, 634, 562, 547, 526, 512, 445, 414 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590, found 274.1589.



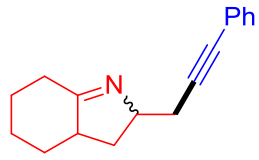
3al

4,4-Dimethyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3al). 0.3 mmol scale, $Ni(cod)_2$ (0.03 mmol, 8.3 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2,2-dimethyl-1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)-benzoyl) oxime **1q** (0.3 mmol, 133.0 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:6) afforded the title product in 56% yield (48.3 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.38 (s, 3H), 1.87 (dd, *J* = 8.4, 12.6 Hz, 1H), 2.21 (dd, *J* = 7.2, 12.6 Hz, 1H), 2.74 (dd, *J* = 8.0, 16.4 Hz, 1H), 3.03 (dd, *J* = 4.8, 16.6 Hz, 1H), 4.26-4.33 (m, 1H), 7.24-7.28 (m, 3H), 7.34-7.41 (m, 5H), 7.69-7.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.24, 26.72, 27.19, 46.91, 50.85, 66.75, 82.02, 87.44, 123.80, 127.57, 127.88, 128.12, 128.13, 129.43, 131.55, 134.71, 180.45. IR (neat): 3048, 2976, 2956, 2923, 2869, 2835, 2158, 1903, 1820, 1770, 1596, 1569, 1489, 1461, 1441, 1428, 1390, 1370, 1343, 1317, 1265, 1236, 1201, 1172, 1152, 1089, 1070, 1043, 1020, 979, 953, 927, 767, 714, 691, 621, 538, 529, 499, 479, 458, 416 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{22}N$ $[M+H]^+$: 288.1747, found 288.1746.



3am

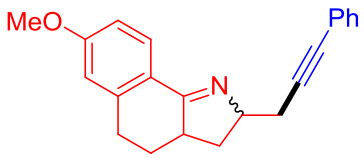
1-Phenyl-3-(3-phenylprop-2-yn-1-yl)-2-azaspiro[4.5]dec-1-ene (3am). 0.3 mmol scale, $Ni(cod)_2$ (0.03 mmol, 8.3 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), (1-allylcyclohexyl)(phenyl)methanone *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1r** (0.3 mmol, 145.0 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) afforded the title product in 43% yield (42.7 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.13-1.19 (m, 1H), 1.31-1.40 (m, 1H), 1.46-1.52 (m, 1H), 1.56-1.58 (m, 2H), 1.66-1.79 (m, 6H), 2.44-2.47 (m, 1H), 2.77 (dd, *J* = 7.8, 16.5 Hz, 1H), 3.01 (d, *J* = 16.2 Hz, 1H), 4.30-4.31 (m, 1H), 7.25-7.27 (m, 3H), 7.37 (br, 3H), 77.40-7.41 (m, 2H), 7.54-7.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 23.13, 23.29, 25.53, 27.01, 32.21, 35.60, 39.91, 56.90, 67.48, 82.07, 87.51, 123.84, 127.59, 127.98, 128.04, 128.15, 128.93, 131.58, 135.72, 181.46. IR (neat): 3078, 3050, 3022, 2926, 2854, 2335, 2221, 1810, 1599, 1570, 1490, 1442, 1348, 1293, 1263, 1247, 1204, 1156, 1069, 1029, 1002, 911, 843, 755, 691, 669, 603, 591, 526, 511, 441, 417 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{26}N$ $[M+H]^+$: 328.2060, found 328.2063.



3an

2-(3-Phenylprop-2-yn-1-yl)-3,3a,4,5,6,7-hexahydro-2*H*-indole (3an). 0.3 mmol scale, $Ni(cod)_2$ (0.03 mmol, 8.3 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2-allylcyclohexan-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1s** (0.3 mmol, 118.0 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted

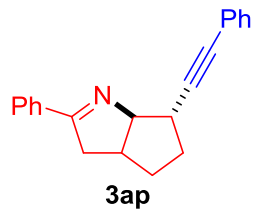
with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: acetone: dichloromethane = 5:1:10) afforded a mixture of diastereoisomers (d.r. 3:2) in 67% yield (47.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07-1.25 (m, 1H), 1.30-1.35 (m, 0.6H, major), 1.37-1.51 (m, 2H), 1.65-1.73 (m, 0.4H, minor), 1.75-1.81 (m, 1H), 1.98-2.00 (m, 1H), 2.10-2.21 (m, 2H), 2.34-2.41 (m, 1H), 2.53 (dd, *J* = 7.2, 16.6 Hz, 0.4H, minor), 2.59-2.79 (m, 3H), 2.89 (dd, *J* = 7.2, 16.8 Hz, 0.6H, major), 4.10 (br, 0.6H, major), 4.30 (br, 0.4H, minor), 7.26-7.27 (m, 3H), 7.36-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.14 (major), 25.27 (minor), 26.53 (minor), 26.64 (major), 26.88 (minor), 27.07 (major), 31.68 (major), 31.79 (minor), 34.22 (minor), 34.73 (major), 34.92 (minor), 35.27 (major), 48.05 (minor), 48.77 (major), 69.34, 81.24 (minor), 81.84 (major), 87.54 (minor), 87.63 (major), 123.79 (minor), 123.84 (major), 127.49 (major), 127.53 (minor), 128.07 (major), 128.12 (minor), 131.47 (minor), 131.51 (major), 179.92 (major), 180.39 (minor) *(1 aliphatic carbon signal of the isomers is not observed due to signal overlap)*. IR (neat): 3078, 3050, 2928, 2857, 2353, 2158, 1713, 1651, 1598, 1571, 1490, 1443, 1347, 1278, 1176, 1148, 1070, 1023, 965, 913, 805, 755, 691, 668, 526, 509, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{20}N$ $[M+H]^+$: 238.1590, found 238.1592.



3ao

7-Methoxy-2-(3-phenylprop-2-yn-1-yl)-3,3a,4,5-tetrahydro-2*H*-benzo[*g*]indole (3ao). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2-allyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1t** (0.3 mmol, 141.4 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column

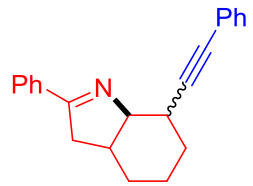
chromatography on silica gel (eluent: petroleum ether: ethyl acetate: acetone = 5:1) afforded a mixture of diastereoisomers (d.r. 7:3) in 72% yield (68.2 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41-1.49 (m, 0.7H, major), 1.54-1.70 (m, 1H), 1.77-1.85 (m, 0.3H, minor), 2.21-2.27 (m, 1H), 2.35-2.41 (m, 0.3H, minor), 2.46-2.57 (m, 1H), 2.70-2.77 (m, 1H), 2.81-2.96 (m, 2H), 2.97-3.03 (m, 0.7H, major), 3.13 (dd, *J* = 4.8, 16.8 Hz, 1H), 3.80 (m, 3H), 4.15-4.18 (m, 0.7H, major), 4.51-4.56 (m, 0.3H, minor), 6.68 (br, 1H), 6.78-6.82 (m, 1H), 7.22-7.28 (m, 3H), 7.33-7.39 (m, 2H), 8.04-8.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.34 (minor). 26.99 (major), 29.69 (major), 29.94 (minor), 30.21 (major), 30.41 (minor), 34.43 (minor), 36.70 (major), 45.80 (minor), 47.58 (major), 55.16, 69.58 (minor), 69.68 (major), 81.13 (minor), 81.87 (major), 87.70 (major), 88.00 (minor), 112.80 (major), 112.82 (minor), 112.93 (minor), 112.97 (major), 122.94 (major), 122.97 (minor), 123.72 (minor), 123.83 (major), 127.48 (major), 127.52 (minor), 127.74 (major), 127.83 (minor), 128.06 (major), 128.10 (minor), 131.45 (minor), 131.52 (major), 142.98 (major), 143.04 (minor), 161.53 (major), 161.55 (minor), 173.51 (major), 173.82 (minor) *(1 aliphatic carbon signal of the isomers is not observed due to signal overlap)*. IR (neat): 3080, 3048, 3019, 2957, 2932, 2912, 2851, 2248, 2209, 1625, 1602, 1568, 1491, 1464, 1456, 1442, 1428, 1359, 1338, 1308, 1270, 1236, 1214, 1150, 1140, 1122, 1103, 1069, 1027, 968, 919, 872, 853, 824, 777, 754, 723, 694, 657, 616, 586, 568, 530, 497, 453, 441, 424 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}NO$ $[M+H]^+$: 316.1696, found 316.1696.



3ap

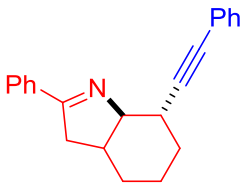
2-Phenyl-6-(phenylethynyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*b*]pyrrole (3ap). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2-(cyclopent-2-en-1-yl)-1-phenylethan-1-one *O*-(3,5-bis(trifluoro-methyl)benzoyl) oxime **1u** (0.3 mmol, 132.4 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and

dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) afforded the title product in 72% yield (61.6 mg) as a yellow oil. The relative stereochemistry of **3ap** was determined by 2D NOESY and 1D differential NOESY experiments. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.40-1.45 (m, 1H), 1.76-1.80 (m, 2H), 2.20-2.26 (m, 1H), 2.78 (dt, *J* = 2.4, 18.0 Hz, 1H), 2.97-3.02 (m, 1H), 3.16-3.18 (m, 1H), 3.21-3.25 (m, 1H), 4.89-4.90 (m, 1H), 7.25-7.30 (m, 3H), 7.39-7.44 (m, 5H), 7.83-7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.43, 33.49, 37.69, 38.65, 43.62, 81.46, 85.87, 92.52, 123.96, 127.52, 127.86, 128.13, 128.40, 130.54, 131.59, 134.23, 172.36. IR (neat): 3101, 3080, 3058, 3032, 2861, 2379, 2231, 1950, 1735, 1615, 1598, 1574, 1489, 1443, 1427, 1338, 1303, 1288, 1269, 1246, 1230, 1177, 1103, 1072, 1054, 1024, 915, 902, 887, 846, 813, 754, 689, 591, 554, 537, 525, 465, 439 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{20}N$ $[M+H]^+$: 286.1590, found 286.1589.



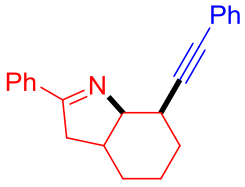
3aq

2-Phenyl-7-(phenylethynyl)-3a,4,5,6,7,7a-hexahydro-3*H*-indole (3aq). 0.3 mmol scale, NiI_2 (0.03 mmol, 9.4 mg), **L1** (0.036 mmol, 14.5 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 2-(cyclohex-2-en-1-yl)-1-phenylethan-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1v** (0.3 mmol, 136.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 ºC for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: acetone = 20:1) afforded a mixture of diastereoisomers (d.r. 3:1) in 46% yield (41.4 mg) as a yellow solid.



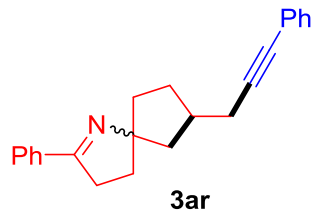
3aq-major

3aq-major (35% yield, 31.4 mg); The relative stereochemistry of **3aq-major** was determined by 2D NOESY experiment. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.15-1.21 (m, 1H), 1.41-1.46 (m, 1H), 1.63-1.68 (m, 1H), 1.70-1.81 (m, 3H), 2.61-2.66 (m, 1H), 2.71 (dd, *J* = 2.4, 16.2 Hz, 1H), 2.88-2.92 (m, 1H), 3.39 (q, *J* = 4.2 Hz, 1H), 4.10 (br, 1H), 7.25-7.30 (m, 3H), 7.39-7.43 (m, 3H), 7.44-7.48 (m, 2H), 7.83-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.64, 27.14, 27.23, 31.66, 35.17, 42.14, 74.23, 81.72, 92.89, 124.00, 127.51, 128.08, 128.12, 128.38, 130.48, 131.64, 134.99, 174.25. IR (neat): 3060, 3026, 2932, 2918, 2855, 2331, 2219, 1678, 1599, 1572, 1489, 1446, 1426,1333, 1267, 1198, 1180, 1115, 1071, 1055, 1016, 917, 885, 858, 754, 739, 689, 573, 556, 536, 524, 490, 410 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747, found 300.1747.



3aq-minor

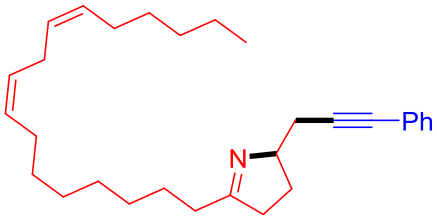
3aq-minor (11% yield, 10.0 mg); The relative stereochemistry of **3aq-minor** was determined by 2D NOESY experiment. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36-1.43 (m, 2H), 1.62-1.68 (m, 1H), 1.71-1.82 (m, 3H), 2.45-2.49 (m, 1H), 2.82-2.94 (m, 2H), 3.19-3.23 (m, 1H), 4.19 (t, *J* = 5.6 Hz, 1H), 7.16-7.22 (m, 3H), 7.25-7.29 (m, 2H), 7.37-7.45 (m, 3H), 7.90-7.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.09, 26.49, 28.05, 32.52, 37.06, 41.90, 72.06, 82.16, 92.43, 124.10, 127.28, 127.75, 127.93, 128.30, 130.42, 131.62, 135.05, 174.98. IR (neat): 3052, 3030, 2928, 2855, 2199, 1671, 1599, 1573, 1490, 1447, 1338, 1264, 1176, 1156, 1070, 1017, 910, 853, 756, 732, 690, 669, 647, 605, 566, 533 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747, found 300.1745.



3ar

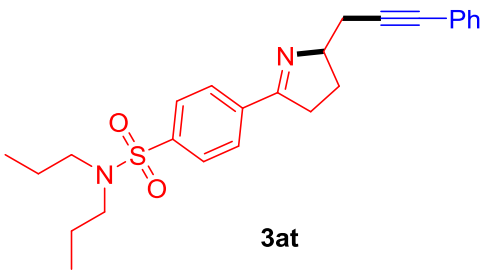
2-Phenyl-7-(3-phenylprop-2-yn-1-yl)-1-azaspiro[4.4]non-1-ene (3ar). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 4-methylene-1-phenyloct-7-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1w** (0.3 mmol, 140.8 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:3) afforded a mixture of diastereoisomers (d.r. 7:3) in 60% yield (56.4 mg) as a brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.57-1.61 (m, 1H), 1.65-1.69 (m, 0.3H, minor), 1.74-1.80 (m, 1H), 1.83-1.84 (m, 0.3H, minor), 1.86-1.88 (m, 0.3H, minor), 1.89-1.94 (m, 1H), 1.95-2.05 (m, 2H), 2.12-2.18 (m, 1H), 2.19-2.22 (m, 0.7H, major), 2.34-2.37 (m, 0.7H, major), 2.50-2.55 (m, 2H), 2.63-2.67 (m, 0.7H, major), 2.90-2.97 (m, 2H), 7.23-7.26 (m, 3H), 7.37-7.43 (m, 5H), 7.82 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 25.18 (major), 25.59 (minor), 30.70 (minor), 31.38 (major), 34.75 (minor), 34.90 (major), 36.15 (minor), 36.33 (major), 38.06 (major), 38.24 (minor), 39.02 (minor), 39.47 (major), 45.43 (minor), 45.71 (major), 80.69 (minor), 81.00 (major), 83.22 (minor), 83.34 (major), 89.31 (major), 89.61 (minor), 124.01, 127.37 (minor), 127.40 (major), 127.55, 128.07 (minor), 128.11 (major), 128.26, 130.05 (major), 130.09 (minor), 131.48 (major), 131.52 (minor), 134.76 (minor), 134.88 (major), 169.64 (major), 170.00 (minor) *(3 aromatic carbon signals of the isomers are not observed due to signal overlap)*. IR (neat): 3084, 3056, 3026, 2942, 2862, 2237, 1948, 1613, 1575, 1490, 1447, 1341, 1308, 1243, 1178, 1154, 1070, 1024, 990, 913, 842, 754, 690, 559, 526, 511, 410 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{24}N$ $[M+H]^+$: 314.1903, found 314.1902.

Late-stage modification of natural products and medicinally relevant molecules



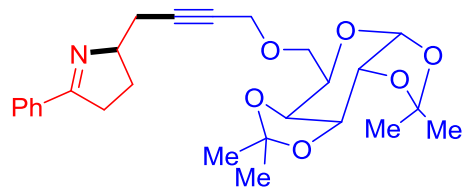
3as

5-((8*Z*,11*Z*)-heptadeca-8,11-dien-1-yl)-2-(3-phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3as). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), (13*Z*,16*Z*)-docosa-1,13,16-trien-5-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1x** (0.3 mmol, 172.1 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with dichloromethane, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 8:1:10) afforded the title product in 60% yield (75.2 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.27-1.38 (m, 14H), 1.55-1.61 (m, 2H), 1.79-1.83 (m, 1H), 2.01-2.07 (m, 4H), 2.10-2.16 (m, 1H), 2.35 (t, *J* = 7.8 Hz, 2H), 2.44-2.49 (m, 1H), 2.59-2.66 (m, 2H), 2.77 (t, *J* = 6.6 Hz, 2H), 2.84 (dd, *J* = 4.2, 16.8 Hz, 1H), 4.24 (br, 1H), 5.31-5.40 (m, 4H), 7.25-7.28 (m, 3H), 7.36-7.38 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 14.01, 22.51, 25.56, 26.52, 26.58, 27.14, 27.55, 29.08, 29.25, 29.28, 29.40, 29.57, 31.46, 33.81, 37.45, 70.84, 81.46, 87.45, 123.85, 127.51, 127.87, 127.93, 128.09, 130.03, 130.14, 131.52, 179.05 *(1 aliphatic carbon signal is not observed due to signal overlap).* IR (neat): 3082, 3056, 3009, 2926, 2854, 2377, 2329, 2197, 1711, 1643, 1598, 1490, 1456, 1427, 1352, 1312, 1267, 1176, 1070, 1028, 984, 947, 913, 880, 846, 755, 725, 691, 668, 526, 411 cm^{-1}. HRMS (ESI) calcd. for $C_{30}H_{44}N$ $[M+H]^+$: 418.3468, found 418.3468.



3at

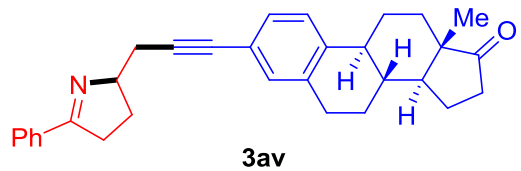
4-(2-(3-Phenylprop-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrol-5-yl)-*N*,*N*-dipropylbenzenesulfonamide (3at). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 4-(1-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)-*N*,*N*-dipropylbenzenesulfonamide **1y** (0.3 mmol, 173.6 mg), phenylacetylene (0.6 mmol, 61.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product in 50% yield (62.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 6H), 1.50-1.59 (m, 4H), 1.99-2.05 (m, 1H), 2.32-2.37 (m, 1H), 2.75 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.92-3.00 (m, 2H), 3.07-3.16 (m, 5H), 4.53 (br, 1H), 7.25-7.26 (m, 3H), 7.33-7.35 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.12, 21.86, 26.56, 27.74, 35.52, 49.86, 72.00, 81.85, 86.98, 123.62, 127.09, 127.69, 128.16, 128.27, 131.52, 137.85, 141.72, 172.18. IR (neat): 3052, 2965, 2928, 2873, 2377, 2333, 2163, 1616, 1597, 1565, 1490, 1468, 1442, 1427, 1398, 1339, 1291, 1268, 1188, 1153, 1088, 1071, 1054, 1035, 1024, 1015, 989, 917, 850, 835, 798, 775, 755, 721, 694, 668, 601, 572, 546, 527, 516, 490, 445, 426 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{31}N_2O_2S$ $[M+H]^+$: 423.2101, found 423.2101.



3au

5-Phenyl-2-(4-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)but-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3au). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-((prop-2-yn-1-yloxy)methyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran **2w** (0.6

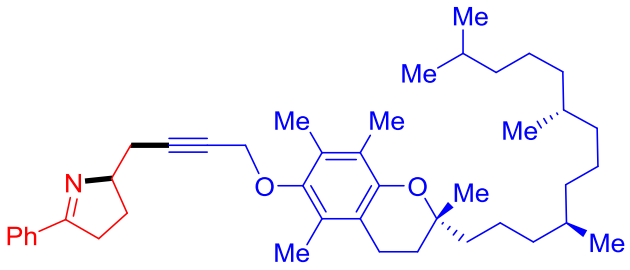
mmol, 179.0 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the title product in 66% yield (90.7 mg) as a light-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.32 (s, 6H), 1.44 (s, 3H), 1.54 (s, 3H), 1.87-1.90 (m, 1H), 2.26-2.27 (m, 1H), 2.50 (dd, *J* = 7.2, 16.5 Hz, 1H), 2.80 (d, *J* = 16.2 Hz, 1H), 2.88-2.94 (m, 1H), 3.07-3.11 (m, 1H), 3.60-3.63 (m, 1H), 3.70-3.73 (m, 1H), 3.93-3.98 (m, 1H), 4.12-4.23 (m, 3H), 4.29-4.30 (m, 1H), 4.39 (br, 1H), 4.57 (t, *J* = 7.2 Hz, 1H), 5.53 (d, *J* = 3.6 Hz, 1H), 7.39-7.43 (m, 3H), 7.84 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 24.36, 24.40, 24.82, 25.87, 25.88, 25.96, 27.61, 27.67, 35.20, 58.86, 58.87, 66.53, 66.56, 68.18, 68.21, 70.39, 70.56, 71.02, 71.04, 71.48, 76.96, 84.24, 96.24, 108.42, 108.44, 109.12, 109.14, 127.69, 128.31, 128.33, 130.41, 130.43, 134.26, 173.26, 173.27. IR (neat): 3060, 3026, 2986, 2934, 2379, 2333, 2237, 1715, 1615, 1575, 1494, 1449, 1372, 1343, 1308, 1254, 1210, 1167, 1097, 1066, 1000, 917, 890, 863, 824, 804, 761, 733, 693, 668, 649, 557, 511 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{34}N$ $[M+H]^+$: 456.2381, found 456.2380.



3av

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(3-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)prop-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3av). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), (8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one **2x** (0.6 mmol, 167.0 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification

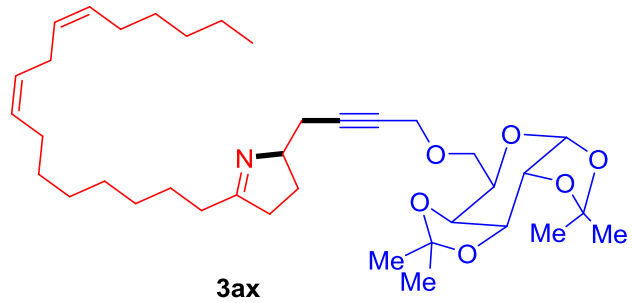
of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) afforded the title product in 60% yield (79.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.36-1.66 (m, 6H), 1.94-2.18 (m, 5H), 2.23-2.32 (m, 2H), 2.36-2.40 (m, 1H), 2.49 (dd, *J* = 8.4, 18.8 Hz, 1H), 2.69 (dd, *J* = 7.6, 16.4 Hz, 1H), 2.81-2.84 (m, 2H), 2.89-2.99 (m, 2H), 3.08-3.16 (m, 1H), 4.49 (br, 1H), 7.08 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.39-7.45 (m, 3H), 7.86 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.72, 21.47, 25.48, 26.23, 26.64, 27.68, 28.94, 31.44, 35.31, 35.73, 37.87, 44.27, 47.83, 50.37, 71.70, 81.59, 86.60, 121.04, 125.13, 127.72, 128.33, 128.79, 130.44, 132.00, 134.34, 136.31, 139.43, 173.35, 220.64. IR (neat): 3072, 3024, 2965, 2951, 2931, 2903, 2870, 2851, 2379, 2329, 2163, 1736, 1690, 1605, 1572, 1493, 1447, 1406, 1373, 1340, 1277, 1253, 1214, 1186, 1136, 1082, 1053, 1022, 1007, 965, 909, 890, 845, 824, 781, 761, 731, 691, 668, 641, 616, 577, 560, 514, 499,472, 445, 413 cm^{-1}. HRMS (ESI) calcd. for $C_{31}H_{34}NO$ $[M+H]^+$: 436.2635, found 436.2635.



3aw

5-Phenyl-2-(4-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)but-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3aw). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 1-phenylpent-4-en-1-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1a-3** (0.3 mmol, 124.6 mg), (*R*)-2,5,7,8-tetramethyl-6-(prop-2-yn-1-yloxy)-2-((4*R*,8*R*)-4,8,12-trimethyl-tridecyl)chromane **2y** (0.6 mmol, 281.3 mg) and acetonitrile (3.0 mL) were stirred at 50 °C for 24 h. Then the reaction mixture was quenched with water and extracted with dichloromethane, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:1:20) afforded the title product in 53%

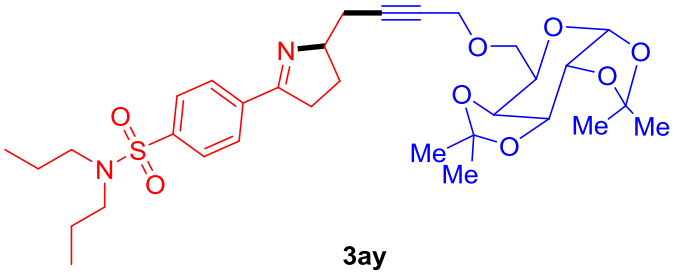
yield (98.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76-0.79 (m, 12H), 0.97-1.08 (m, 6H), 1.14-1.24 (m, 11H), 1.26-1.38 (m, 4H), 1.41-1.47 (m, 3H), 1.63-1.74 (m, 2H), 1.75-1.81 (m, 1H), 1.98 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 2.14-2.18 (m, 1H), 2.41-2.46 (m, 3H), 2.71-2.85 (m, 2H), 2.93-2.97 (m, 1H), 4.24 (s, 2H), 4.30-4.32 (m, 1H), 7.29-7.34 (m, 3H), 7.75 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.72, 12.15, 12.99, 19.59, 19.69, 20.56, 20.95, 22.57, 22.66, 23.80, 24.37, 24.73, 26.11, 27.68, 27.90, 31.19, 32.62, 32.72, 35.24, 37.21, 37.35, 37.38, 37.40, 39.30, 40.03, 61.02, 71.44, 74.73, 77.25, 84.19, 117.35, 122.74, 126.06, 127.76, 127.97, 128.33, 130.51, 134.23, 147.85, 148.00, 173.46. IR (neat): 3084, 3054, 3032, 2924, 2866, 2724, 2375, 2329, 2231, 1616, 1576, 1496, 1456, 1412, 1376, 1365, 1340, 1312, 1252, 1156, 1084, 1060, 983, 917, 864, 844, 807, 759, 737, 692, 668, 609, 557, 473, 412 cm^{-1}. HRMS (ESI) calcd. for $C_{43}H_{64}NO_2$ $[M+H]^+$: 626.4932, found 626.4939.



3ax

5-((8*Z*,11*Z*)-Heptadeca-8,11-dien-1-yl)-2-(4-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)but-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ax). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), (13*Z*,16*Z*)-docosa-1,13,16-trien-5-one *O*-(3,5-bis(trifluoromethyl)benzoyl) oxime **1x** (0.3 mmol, 172.1 mg), (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-((prop-2-yn-1-yloxy)methyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran **2w** (0.6 mmol, 179.0 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 2:1) afforded the title product in 52% yield (95.8 mg) as a

yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.26-1.39 (m, 21H), 1.45 (s, 3H), 1.54 (s, 3H), 1.57 (br, 1H), 1.64-1.73 (m, 1H), 2.00-2.14 (m, 5H), 2.31-2.48 (m, 4H), 2.56-2.57 (m, 1H), 2.67 (dd, *J* = 2.0, 16.6 Hz, 1H), 2.77 (t, *J* = 6.4 Hz, 2H), 3.61-3.65 (m, 1H), 3.73 (dd, *J* = 5.6, 10.0 Hz, 1H), 3.96-4.00 (m, 1H), 4.14 (br, 1H), 4.18-4.20 (m, 2H), 4.26 (dd, *J* = 2.0, 7.8 Hz, 1H), 4.31 (dd, *J* = 2.4, 5.2 Hz, 1H), 4.60 (dd, *J* = 2.4, 8.0 Hz, 1H), 5.29-5.42 (m, 4H), 5.54 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 14.04, 22.53, 24.45, 24.89, 25.59, 25.96, 25.99, 26.03, 26.55, 27.17, 27.72, 29.14, 29.26, 29.30, 29.44, 29.48, 29.60, 31.49, 33.83, 37.33, 59.01, 66.65, 68.25, 68.27, 70.49, 70.65, 70.82, 71.15, 71.17, 84.46, 96.33, 108.53, 109.24, 127.89, 127.98, 130.06, 130.18, 179.02. IR (neat): 2981, 2926, 2855, 2351, 2329, 2169, 1713, 1642, 1457, 1380, 1306, 1254, 1210, 1168, 1099, 1068, 1001, 917, 891, 865, 823, 805, 771, 725, 668, 650, 511, 423, 416 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{60}NO_6$ $[M+H]^+$: 614.4415, found 614.4419.

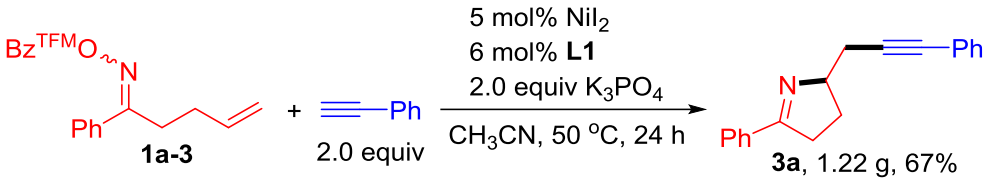


3ay

5-(4-(Heptan-4-ylsulfonyl)phenyl)-2-(4-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)but-2-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (3ay). 0.3 mmol scale, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg), 4-(1-(((3,5-bis(trifluoromethyl)benzoyl)oxy)imino)pent-4-en-1-yl)-*N*,*N*-dipropylbenzenesulfonamide **1y** (0.3 mmol, 173.6 mg), (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-((prop-2-yn-1-yloxy)methyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran **2w** (0.6 mmol, 179.0 mg) and acetonitrile (3.0 mL) were stirred at 80 °C for 24 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 8:1) afforded the title

product in 58% yield (107.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 6H), 1.33 (s, 3H), 1.34 (s, 3H), 1.45 (s, 3H) 1.50-1.59 (m, 7H), 1.89-1.94 (m, 1H), 2.29-2.33 (m, 1H), 2.50-2.56 (m, 1H), 2.77-2.83 (m, 1H), 2.91-2.97 (m, 1H), 3.07-3.13 (m, 5H), 3.63 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.71 (dd, *J* = 5.6, 10.2 Hz, 1H), 3.95-3.98 (m, 1H), 4.13-4.24 (m, 3H), 4.31 (dd, *J* = 2.4, 5.0 Hz, 1H), 4.40-4.43 (m, 1H), 4.60 (dd, *J* = 2.4, 7.8 Hz, 1H), 5.53 (d, *J* = 5.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.10, 21.86, 24.43, 24.44, 24.85, 25.91, 25.93, 26.00, 27.73, 35.40, 49.86, 58.93, 66.60, 66.61, 68.27, 68.30, 70.43, 70.59, 71.11, 71.87, 77.24, 83.93, 96.29, 108.50, 109.21, 127.05, 128.26, 137.78, 141.68, 172.12. IR (neat): 3054, 2968, 2934, 2876, 2379, 2349, 2158, 1733, 1616, 1565, 1458, 1381, 1339, 1255, 1211, 1156, 1090, 1067, 996, 918, 890, 866, 798, 774, 735, 701, 668, 651, 598, 574, 542, 511, 417 cm^{-1}. HRMS (ESI) calcd. for $C_{32}H_{47}N_2O_8S$ $[M+H]^+$: 619.3048, found 619.3048.

Gram scale study

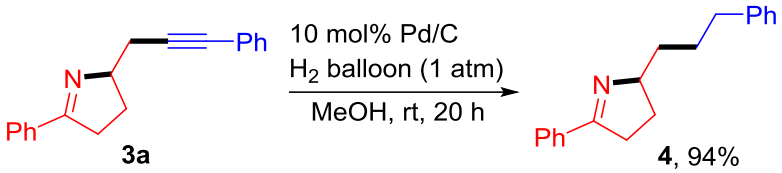


To an oven-dried sealable Schlenk tube (150.0 mL) equipped with a stir bar was added NiI_2 (0.35 mmol, 109.4 mg), **L1** (0.42 mmol, 168.7 mg), anhydrous K_3PO_4 (14.0 mmol, 2.97 g) and acetonitrile (70.0 mL) using standard Schlenk technique under nitrogen atmosphere. The mixture was stirred at room temperature for 5min. Then oxime ester **1a-3** (7.0 mmol, 2.91 g) and phenylacetylene (14.0 mmol, 1.43 g) were added in sequence. The tube was securely sealed with parafilm and immersed into an oil bath preheated at 50 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and quenched with water. The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:3) to afford product **3a** in 67% yield (1.22 g) as a yellow oil. *This result highlights the*

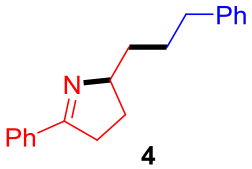
robustness and scalability of this process, as no significant loss in yield was observed when it was scaled up to 7.0 mmol scale.

Synthetic transformations of 3a

Synthesis of compound 4

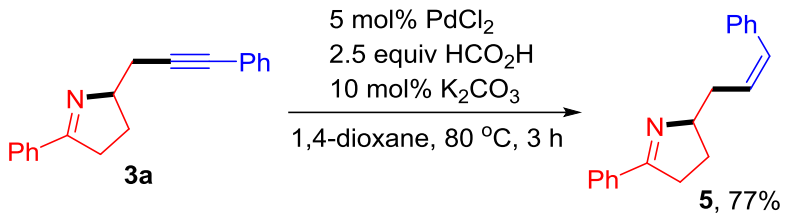


The reaction was performed according to a literature procedure.[12] To an oven-dried round-bottom flask (25.0 mL) equipped with a stir bar was added **3a** (0.3 mmol, 77.8 mg), Pd/C (10% w, 12.0 mg) and methanol (4.0 mL). Then the reaction mixture was stirred at room temperature for 20 h under a H_2 balloon (1 atm). After the indicated time, the mixture was filtered through a celite pad and washed with additional methanol. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the title product **4** in 94% yield (74.5 mg) as a yellow oil.

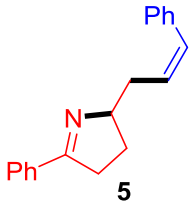


5-Phenyl-2-(3-phenylpropyl)-3,4-dihydro-2*H*-pyrrole (4). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.52-1.60 (m, 2H), 1.76-1.81 (m, 1H), 1.82-1.91 (m, 2H), 2.14-2.19 (m, 1H), 2.65-2.73 (m, 2H), 2.81-2.87 (m, 1H), 2.95-3.00 (m, 1H), 4.16-4.20 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.19-7.22 (m, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.36-7.40 (m, 3H), 7.82-7.83 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 28.44, 34.86, 36.00, 36.25, 73.05, 125.57, 127.56, 128.17, 128.27, 128.37, 130.16, 134.65, 142.49, 171.74 *(1 aliphatic carbon signal is not observed due to signal overlap)*. IR (neat): 3086, 3062, 3026, 2929, 2857, 1614, 1575, 1495, 1449, 1336, 1180, 1085, 1075, 1022, 921, 844, 759, 692, 668, 592, 557, 494 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{22}N$ $[M+H]^+$: 264.1746, found 264.1746.

Synthesis of compound 5

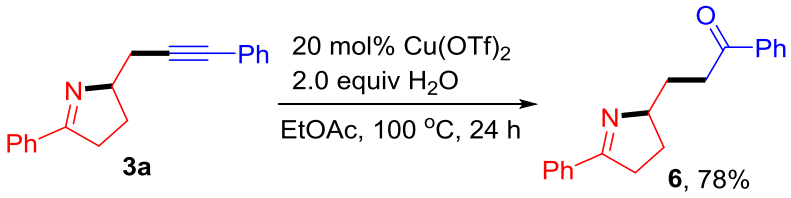


This reaction was performed according to an adapted version of a literature procedure.[13] **3a** (0.3 mmol, 77.8 mg), $PdCl_2$ (0.015 mmol, 2.7 mg), K_2CO_3 (0.03 mmol, 4.1 mg) and 1,4-dioxane (3.0 mL) were successively added to an oven-dried sealable Schlenk tube (15.0 mL) under nitrogen atmosphere. Then formic acid (0.75 mmol, 34.5 mg) was added at once within a minute, and the tube was immersed into an oil bath preheated at 80 °C. After stirring for 3 h, the reaction mixture was cooled to room temperature and quenched with water. The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford the title product **5** in 77% yield (60.6 mg) as a white solid.

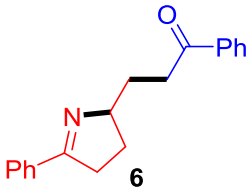


(*Z*)-5-Phenyl-2-(3-phenylallyl)-3,4-dihydro-2*H*-pyrrole (5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58-1.68 (m, 1H), 2.15-2.23 (m, 1H), 2.57-2.65 (m, 1H), 2.83-2.92 (m, 2H), 2.95-3.03 (m, 1H), 4.32-4.36 (m, 1H), 5.81 (dt, *J* = 7.2, 12.0 Hz, 1H), 6.55 (dt, *J* = 2.0, 11.6 Hz, 1H), 7.18-7.23 (m, 1H), 7.27-7.34 (m, 4H), 7.36-7.42 (m, 3H), 7.81-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.05, 35.04, 35.27, 73.07, 126.54, 127.67, 128.10, 128.35, 128.79, 129.34, 130.34, 130.46, 134.52, 137.53, 172.53. IR (neat): 3086, 3054, 3023, 2939, 1614, 1574, 1494, 1447, 1335, 1307, 1261, 1178, 1076, 1057, 1027, 915, 804, 759, 691, 668, 618, 557, 507, 416, 407 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{20}N$ $[M+H]^+$: 262.1590, found 262.1589.

Synthesis of compound 6

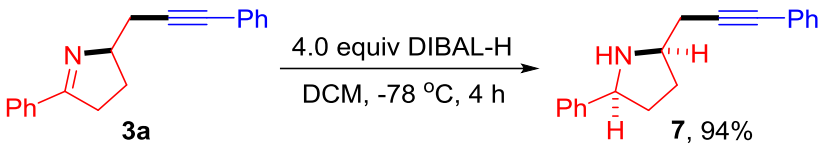


The reaction was performed according to a literature procedure.[14] $Cu(OTf)_2$ (0.2 mmol, 72.3 mg) and water (2.0 mmol, 36.0 mg) were added to a solution of **3a** (1.0 mmol, 259.4 mg) in EtOAc (2.0 mL). The reaction mixture was stirred at 100 °C for 24 h. After completion of the reaction, the mixture was cooled to room temperature, and water was added. The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) to afford the title product **6** in 78% yield (215.9 mg) as a yellow solid.

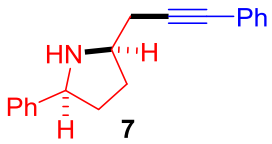


1-Phenyl-3-(5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-1-one (6). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.63-1.70 (m, 1H), 1.98-2.04 (m, 1H), 2.12-2.17 (m, 1H), 2.25-2.31 (m, 1H), 2.90-2.95 (m, 1H), 3.03-3.08 (m, 1H), 3.22-3.27 (m, 1H), 3.32-3.37 (m, 1H), 4.27-4.29 (m, 1H), 7.39-7.44 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 6.6 Hz, 2H), 8.01-8.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 28.88, 31.32, 35.04, 36.17, 72.50, 127.65, 128.15, 128.39, 128.52, 130.36, 132.88, 134.63, 137.05, 172.41, 200.42. IR (neat): 3056, 3019, 2975, 2937, 2902, 2866, 2847, 1683, 1610, 1596, 1573, 1494, 1448, 1409, 1370, 1338, 1307, 1254, 1203, 1183, 1070, 1058, 1036, 1024, 996, 968, 923, 880, 754, 740, 686, 625, 615, 560, 539, 414 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1539.

Synthesis of compound 7

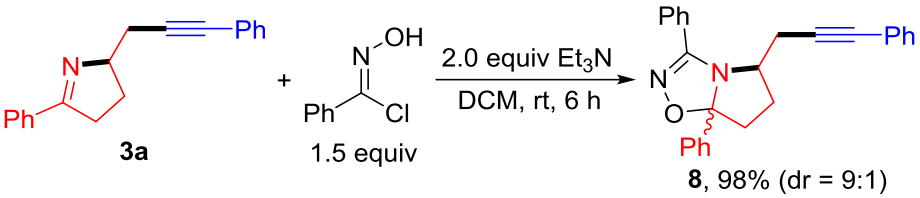


The reaction was performed according to a literature procedure.[15] To a solution of **3a** (0.3 mmol, 77.8 mg) in dichloromethane (3.0 mL) was added dropwise DIBAL-H (1.5 M in toluene) (1.2 mmol, 0.8 mL) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 4 h. Then it was quenched with saturated NH_4Cl aqueous solution. The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel which was pretreated with triethylamine before loading the sample (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1, gradient) to afford the title product **7** in 94% yield (73.4 mg) as a yellow oil. The relative stereochemistry of **7** was determined by 1D differential NOESY experiment.

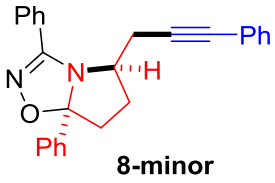


2-Phenyl-5-(3-phenylprop-2-yn-1-yl)pyrrolidine (7). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.63-1.71 (m, 2H), 1.91-1.97 (m, 1H), 2.04-2.09 (m, 1H), 2.37 (br, 1H), 2.52- 2.59 (m, 2H), 3.37-3.41 (m, 1H), 4.10 (t, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.14-7.18 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.30-7.33 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 26.84, 30.76, 34.18, 57.53, 62.57, 81.65, 87.95, 123.69, 126.54, 126.75, 127.56, 128.10, 128.21, 131.50, 144.68. IR (neat): 3082, 3058, 3028, 2933, 2375, 2331, 2233, 1952, 1875, 1814, 1729, 1599, 1573, 1545, 1490, 1442, 1399, 1345, 1271, 1172, 1105, 1070, 1027, 912, 844, 754, 690, 668, 629, 558, 526 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{20}N$ $[M+H]^+$: 262.1590, found 262.1589.

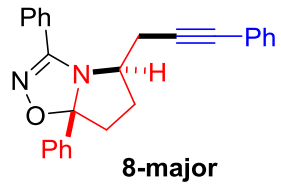
Synthesis of compound 8



This reaction was performed according to a literature procedure.[15] To a round-bottom flask (25.0 mL) equipped with a stir bar was added **3a** (0.3 mmol, 77.8 mg), *N*-hydroxybenzimidoyl chloride (0.45 mmol, 70.0 mg), Et_3N (0.6 mmol, 60.7 mg) and dichloromethane (6.0 mL). The reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the solvent was removed in vacuo, and the residue was purified directly by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) to afford a mixture of diastereoisomers (d.r. 9:1) in 98% yield (110.8 mg) as a white solid.



3,7a-Diphenyl-5-(3-phenylprop-2-yn-1-yl)-5,6,7,7a-tetrahydropyrrolo[1,2-*d*][1,2,4]oxadiazole (8). 8-minor (10% yield, 11 mg); The relative stereochemistry of **8-minor** was determined by 1D differential NOESY experiment. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30-2.43 (m, 3H), 2.47-2.55 (m, 2H), 2.74-2.78 (m, 1H), 4.06-4.09 (m, 1H), 7.25-7.31 (m, 4H), 7.35-7.38 (m, 4H), 7.40-7.44 (m, 3H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.85-7.86 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 23.22, 32.65, 36.92, 62.83, 83.02, 85.82, 110.08, 123.20, 124.92, 127.44, 127.61, 127.96, 128.12, 128.16, 128.25, 128.85, 130.81, 131.51, 143.61, 157.04. IR (neat): 3062, 3030, 2991, 2969, 2929, 2379, 2331, 2161, 1958, 1814, 1717, 1682, 1589, 1557, 1489, 1443, 1431, 1366, 1350, 1329, 1293, 1265, 1202, 1170, 1146, 1072, 1026, 990, 963, 942, 919, 864, 852, 767, 759, 727, 692, 668, 654, 552, 527, 493, 469, 434, 411 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1805, found 379.1805.

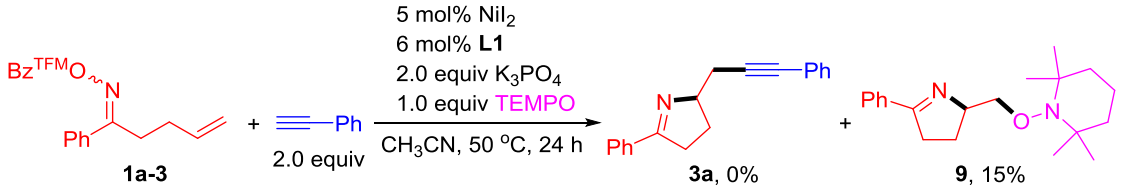


8-major

8-major (88% yield, 99.8 mg); The relative stereochemistry of **8-major** was determined by 1D differential NOESY experiment. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.08 (dd, *J* = 6.6, 12.6 Hz, 1H), 2.20-2.27 (m, 1H), 2.49-2.55 (m, 1H), 2.65-2.75 (m, 2H), 2.82 (dd, *J* = 6.0, 16.8 Hz, 1H), 3.88-3.92 (m, 1H), 7.25-7.31 (m, 4H), 7.33-7.38 (m, 6H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 25.72, 29.47, 38.26, 64.15, 82.72, 86.71, 109.59, 123.14, 125.16, 126.73, 127.98, 128.01, 128.18, 128.25, 128.71, 130.72, 131.47, 142.69, 159.12 *(1 aromatic carbon signal is not observed due to signal overlap)*. IR (neat): 3058, 3030, 2924, 2872, 2853, 2375, 2333, 1956, 1594, 1559, 1490, 1445, 1355, 1321, 1248, 1222, 1176, 1109, 1090, 1071, 1026, 1002, 985, 914, 880, 755, 690, 646, 526, 480, 436 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1805, found 379.1805.

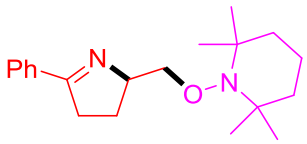
Mechanistic studies:

Radical trap experiment



In a nitrogen-filled glovebox, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg) and acetonitrile (3.0 mL) were successively added to an oven-dried sealable Schlenk tube (15.0 mL). The mixture was stirred at room temperature for 5min. Then oxime ester **1a-3** (0.3 mmol, 124.6 mg), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 0.3 mmol, 46.9 mg) and phenylacetylene (0.6 mmol, 61.3 mg) were added in sequence. The tube was securely sealed with parafilm, taken outside the glovebox and immersed into an oil bath preheated at 50 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and quenched with water. The organic phase was extracted with ethyl acetate. The combined organic layers were

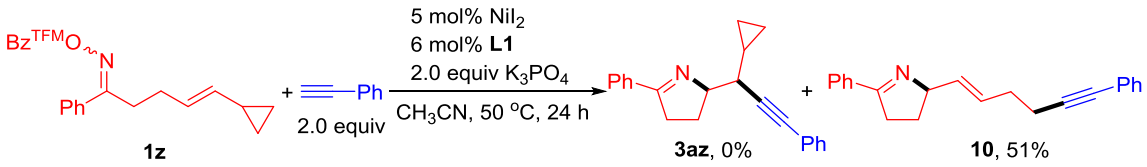
washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by preparative TLC on silica gel (eluent: petroleum ether: ethyl acetate = 8:1) to afford TEMPO-trapped adduct **9** in 15% yield (14.0 mg) as a white solid. While the desired transformation was seriously inhibited, and no product **3a** was detected in the reaction mixture. *This result indicates that the reaction might proceed via the corresponding carbon-centered radical.*



9

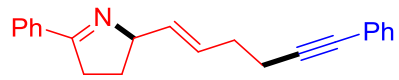
2,2,6,6-Tetramethyl-1-((5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)methoxy)piperidine (9). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.95 (s, 3H), 1.10 (s, 3H), 1.16 (s, 3H), 1.21 (s, 3H), 1.26-1.30 (m, 2H), 1.39-1.46 (m, 4H), 2.04-2.05 (m, 1H), 2.11-2.18 (m, 1H), 2.96-3.03 (m, 2H), 3.96 (br, 1H), 4.07-4.09 (m, 1H), 4.44 (br, 1H), 7.41 (br, 3H), 7.85-7.86 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 17.05, 19.99, 20.23, 25.87, 32.99, 33.19, 35.38, 39.60, 59.87, 127.71, 128.33, 130.26, 134.72, 173.43. The spectroscopic data are in agreement with that previously reported.[15]

Radical clock experiment



In a nitrogen-filled glovebox, NiI_2 (0.015 mmol, 4.7 mg), **L1** (0.018 mmol, 7.2 mg), anhydrous K_3PO_4 (0.6 mmol, 127.4 mg) and acetonitrile (3.0 mL) were successively added to an oven-dried sealable Schlenk tube (15.0 mL). The mixture was stirred at room temperature for 5min. Then oxime ester **1z** (0.3 mmol, 136.6 mg) and phenylacetylene (0.6 mmol, 61.3 mg) were added in sequence. The tube was securely sealed with parafilm, taken outside the glovebox and immersed into an oil bath preheated at 50 °C. After stirring for 24 h, the reaction mixture was cooled to room temperature and quenched with water.

The organic phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 25:1) to afford the ring-opened product **10** in 51% yield (46.2 mg) as a yellow oil, while the normal cross-coupling product **3az** was not observed. *This result further supports that a radical pathway might be involved in this process, and it is probably generated through an iminyl radical triggered 5-exo-trig cyclization of γ,δ-unsaturated oxime esters.*



10

(*E*)-5-Phenyl-2-(6-phenylhex-1-en-5-yn-1-yl)-3,4-dihydro-2*H*-pyrrole (10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.80 (m, 1H), 2.23-2.32 (m, 1H), 2.34-2.39 (m, 2H), 2.48-2.52 (m, 2H), 2.83-2.92 (m, 1H), 2.99-3.08 (m, 1H), 4.69-4.74 (m, 1H), 5.68 (dd, *J* = 7.2, 15.2 Hz, 1H), 5.77-5.84 (m, 1H), 7.23-7.28 (m, 3H), 7.37-7.44 (m, 5H), 7.85-7.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.47, 29.63, 31.64, 34.99, 74.24, 80.98, 89.65, 123.88, 127.44, 127.72, 128.09, 128.31, 129.05, 130.41, 131.47, 133.29, 134.40, 173.00. IR (neat): 3103, 3054, 3028, 2967, 2917, 1952, 1895, 1806, 1684, 1607, 1573, 1489, 1443, 1425, 1340, 1259, 1233, 1176, 1071, 1052, 1026, 966, 912, 842, 752, 688, 561, 525, 481, 418 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747, found 300.1747.

References:

[1] H.-B. Yang and N. Selander, *Chem. Eur. J.*, 2017, **23**, 1779-1783.

[2] Z. C. Litman, A. Sharma and J. F. Hartwig, *ACS Catal.*, 2017, **7**, 1998-2001.

[3] R.-H. Liu, D. Wei, B. Han and W. Yu, *ACS Catal.*, 2016, **6**, 6525-6530.

[4] A. Faulkner and J. F. Bower, *Angew. Chem. Int. Ed.*, 2012, **51**, 1675-1679.

[5] J. Davies, N. S. Sheikh and D. Leonori, *Angew. Chem. Int. Ed.*, 2017, **56**, 13361-13365.

[6] F. Portela-Cubillo, R. Alonso-Ruiz, D. Sampedro and J. C. Walton, *J. Phys. Chem. A*, 2009, **113**, 10005-10012.

[7] L. Wang and C. Wang, *Org. Chem. Front.*, 2018, **5**, 3476-3482.

[8] S.-H. Cai, J.-H. Xie, S. Song, L. Ye, C. Feng and T.-P. Loh, *ACS Catal.*, 2016, **6**, 5571-5574.

[9] X. Shen, C. Huang, X.-A. Yuan and S. Yu, *Angew. Chem. Int. Ed.*, 2021, **60**, 9672-9679.

[10] H. Ito, T. Kamachi and E. Yashima, *Chem. Commun.*, 2012, **48**, 5650-5652.

[11] E.-C. Liu and J. J. Topczewski, *J. Am. Chem. Soc.*, 2019, **141**, 5135-5138.

[12] L. Zhou, S. Li, B. Xu, D. Ji, L. Wu, Y. Liu, Z.-M. Zhang and J. Zhang, *Angew. Chem. Int. Ed.*, 2020, **59**, 2769-2775.

[13] R. Iwasaki, E. Tanaka, T. Ichihashi, Y. Idemoto and K. Endo, *J. Org. Chem.*, 2018, **83**, 13574-13579.

[14] M. Hassam and W.-S. Li, *Tetrahedron*., 2015, **71**, 2719-2723.

[15] H.-B. Yang, S. R. Pathipati and N. Selander, *ACS Catal.*, 2017, **7**, 8441-8445.

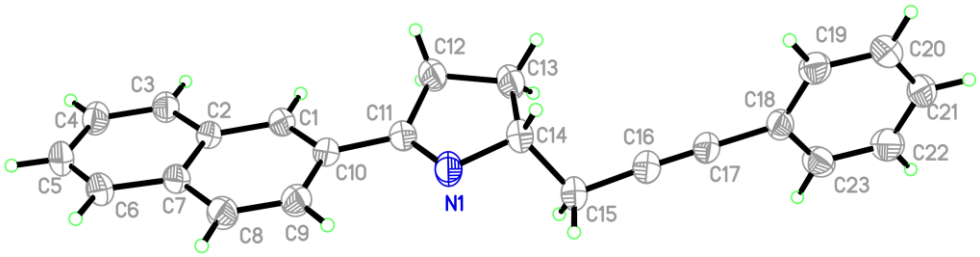
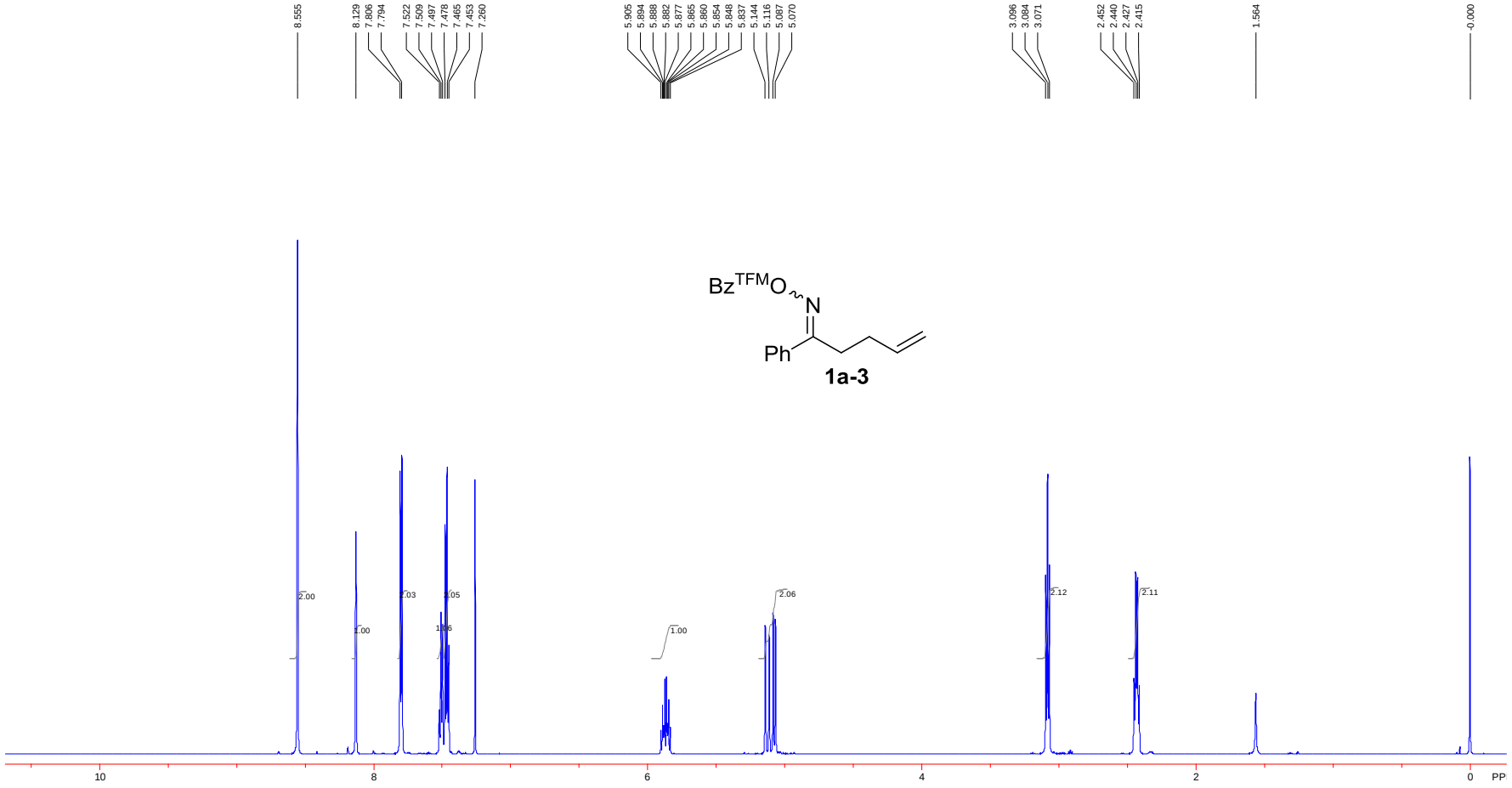


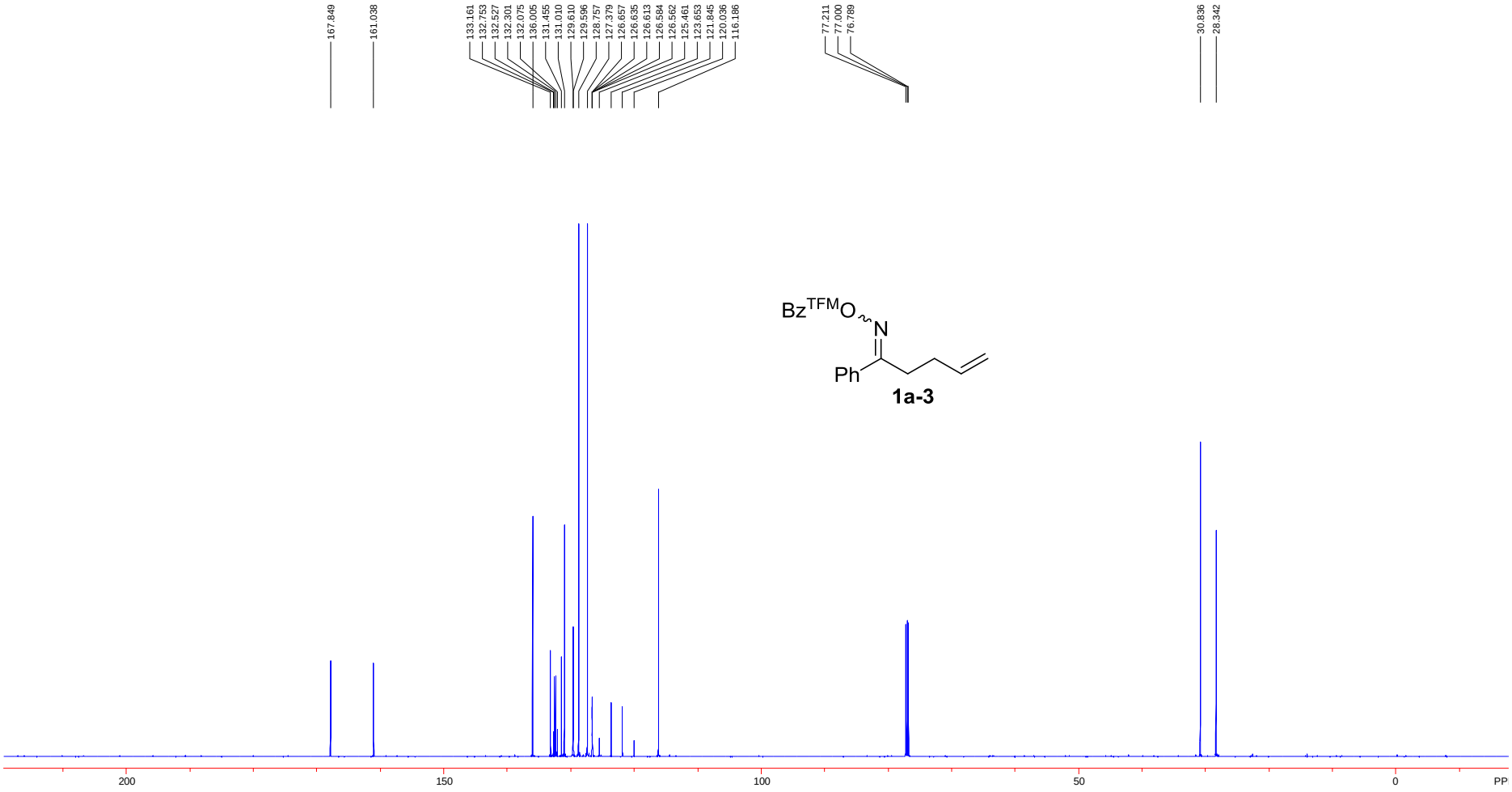
Figure S1. X-ray crystal structure of complex **3ac**

NMR spectra of all new compounds

^{1}H NMR(600 MHz, $CDCl_3$)



^{13}C NMR(151 MHz, $CDCl_3$)



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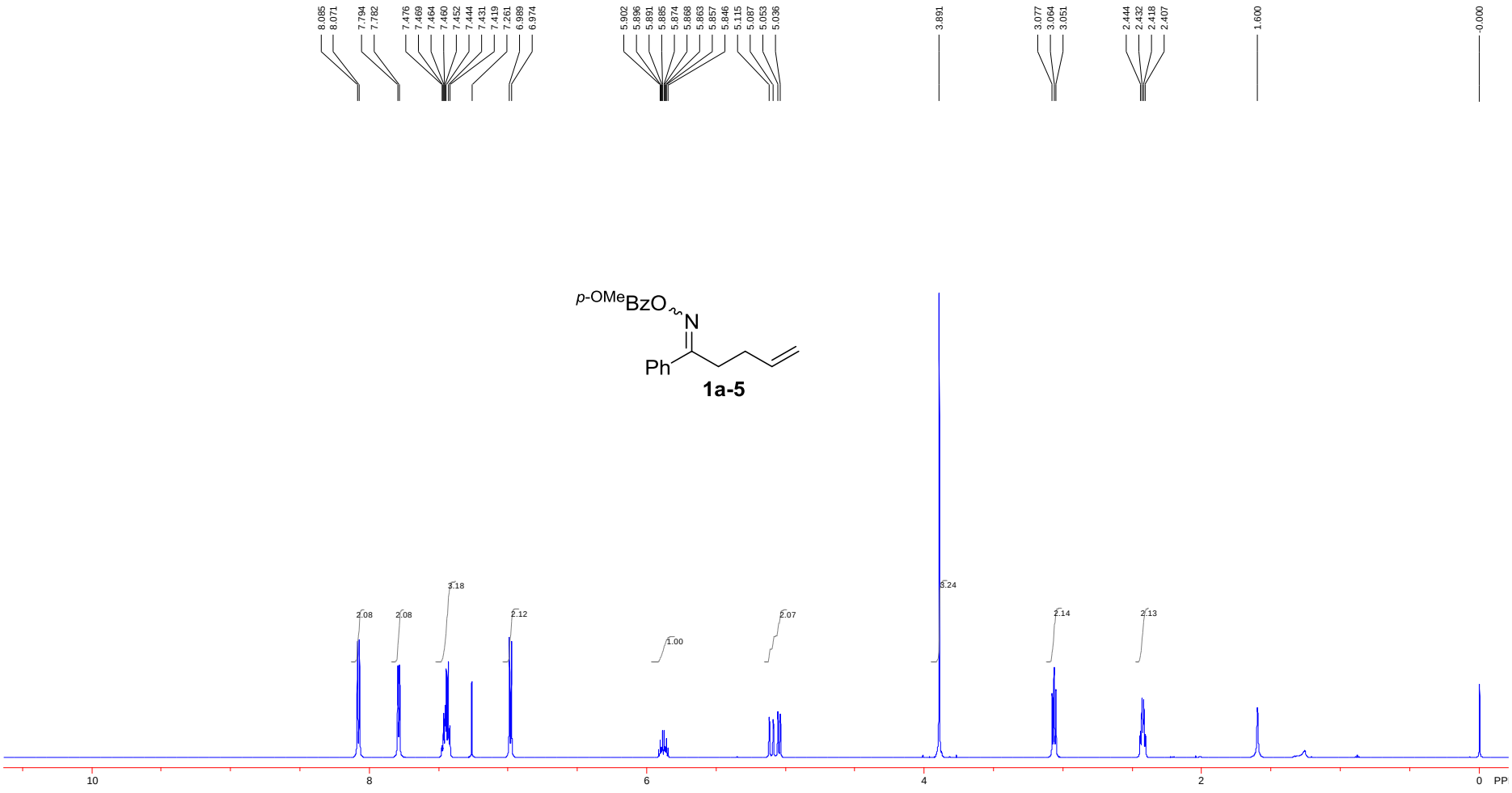

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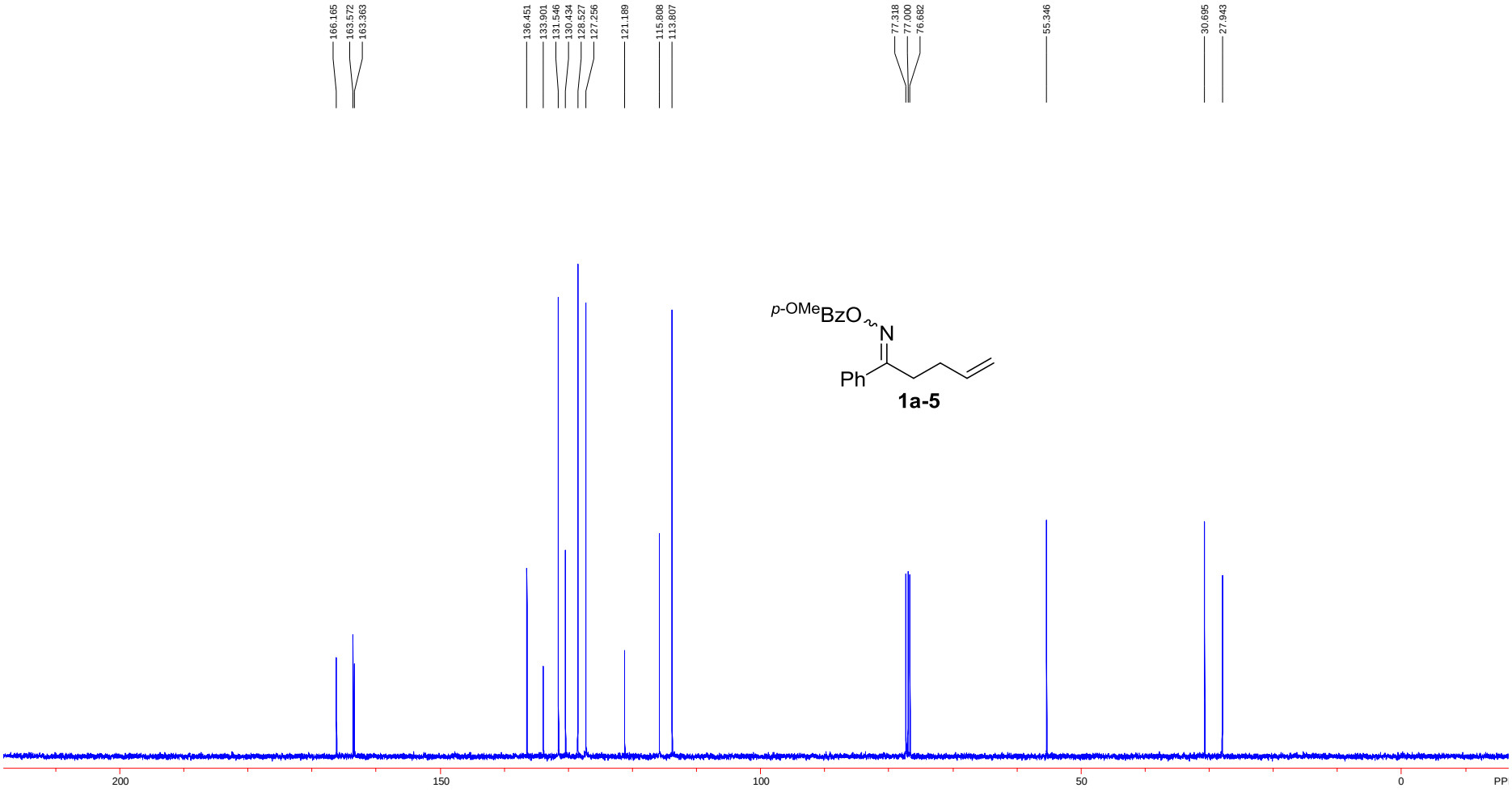

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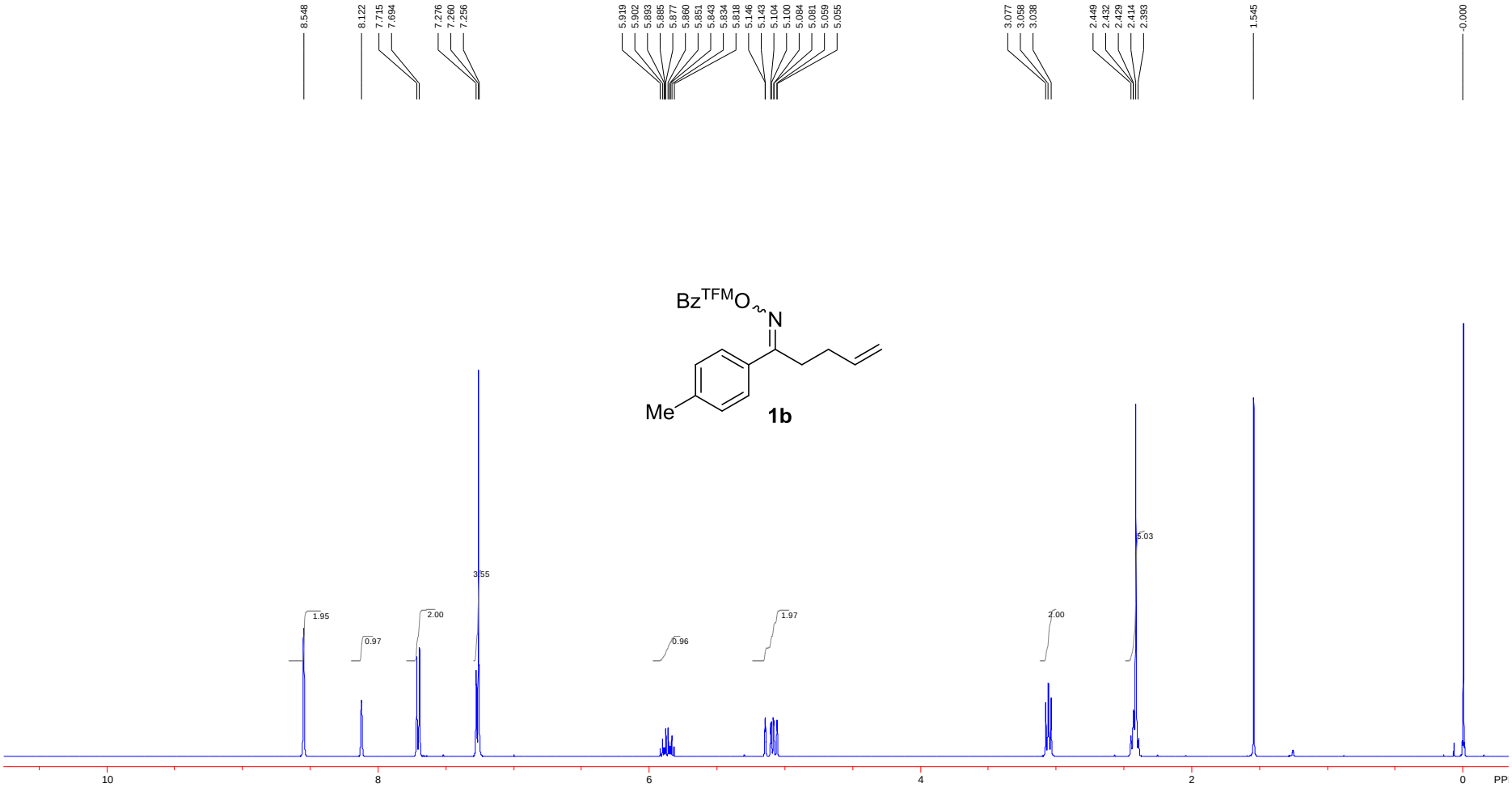

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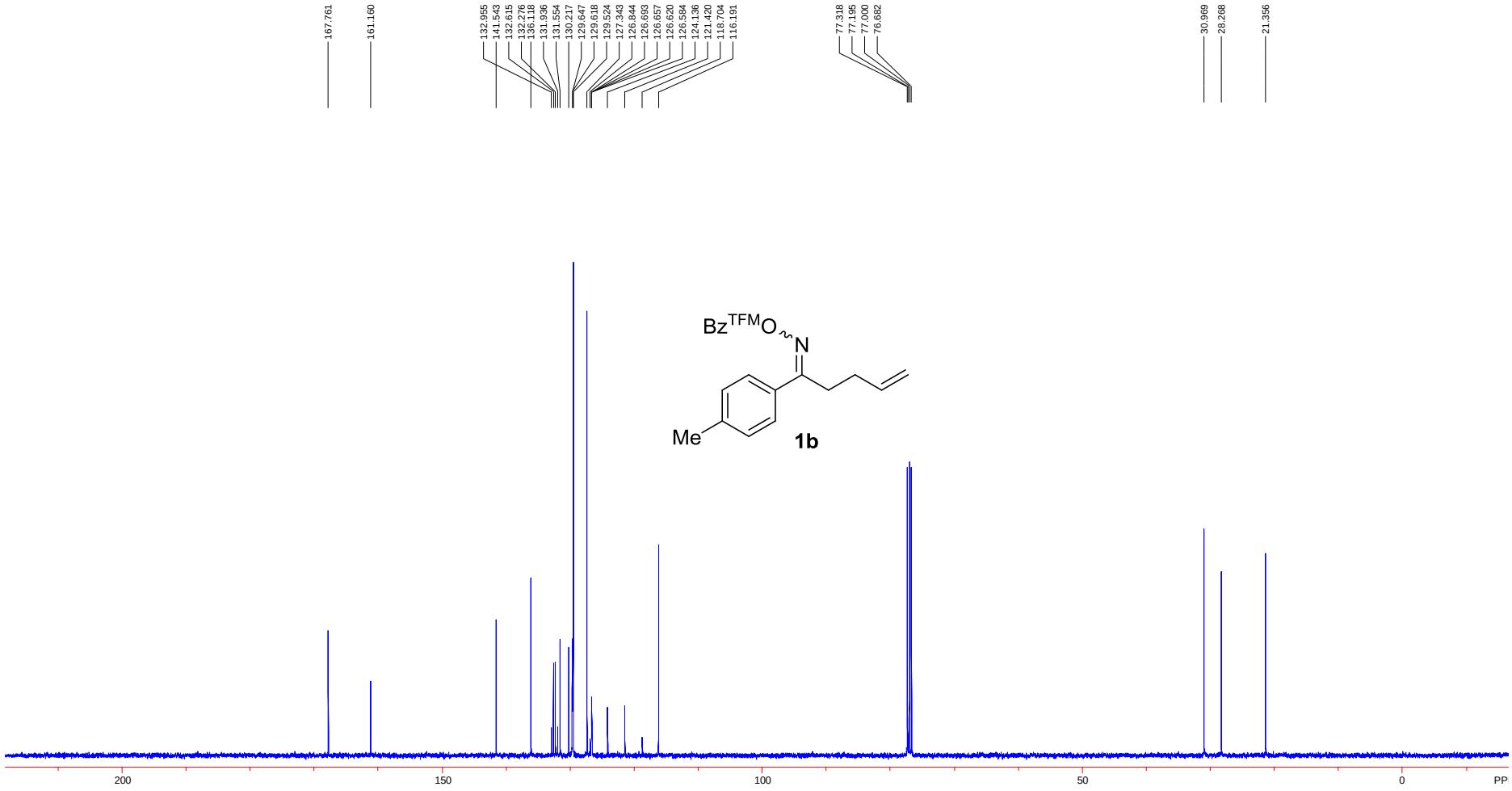

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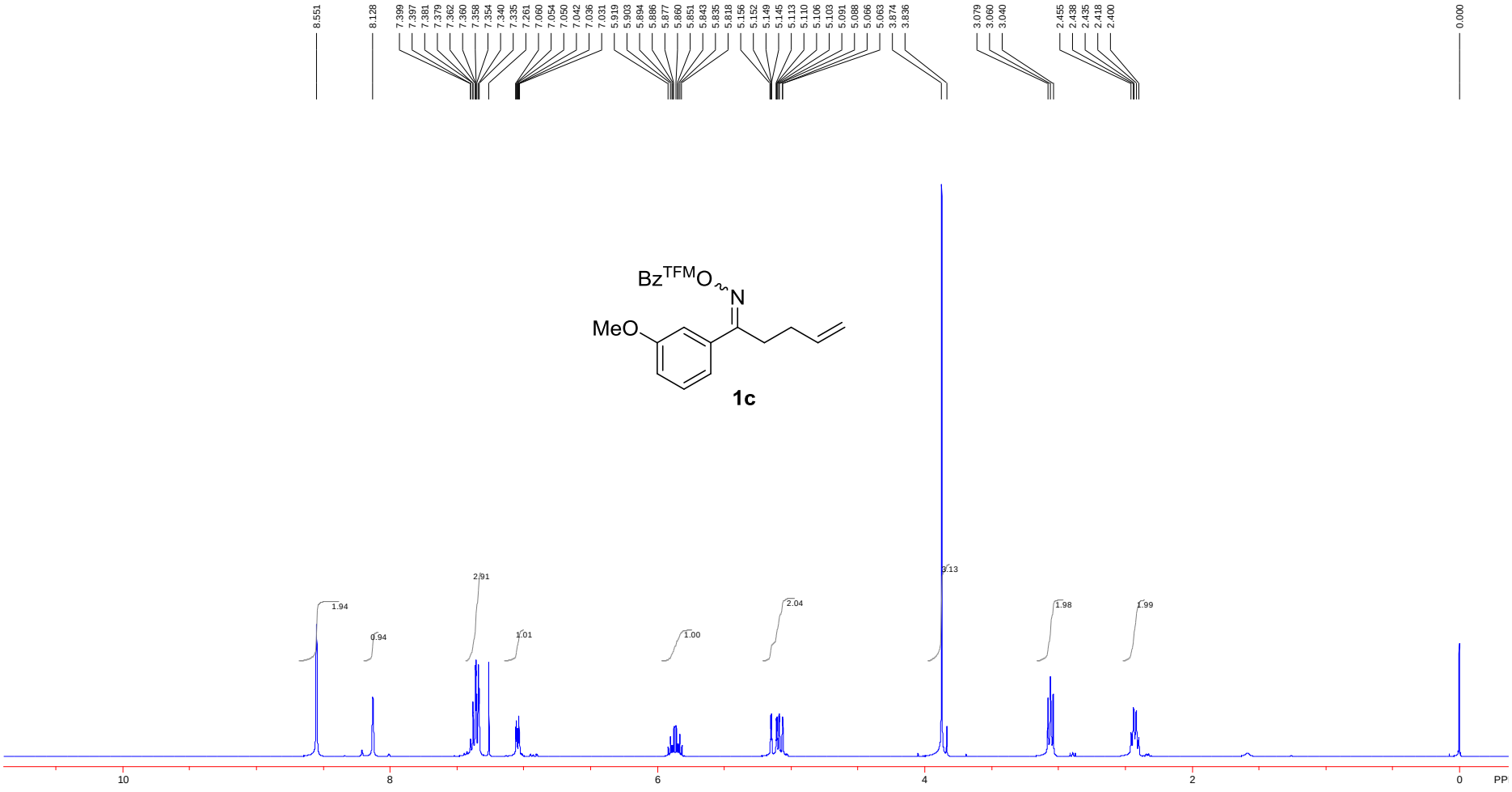

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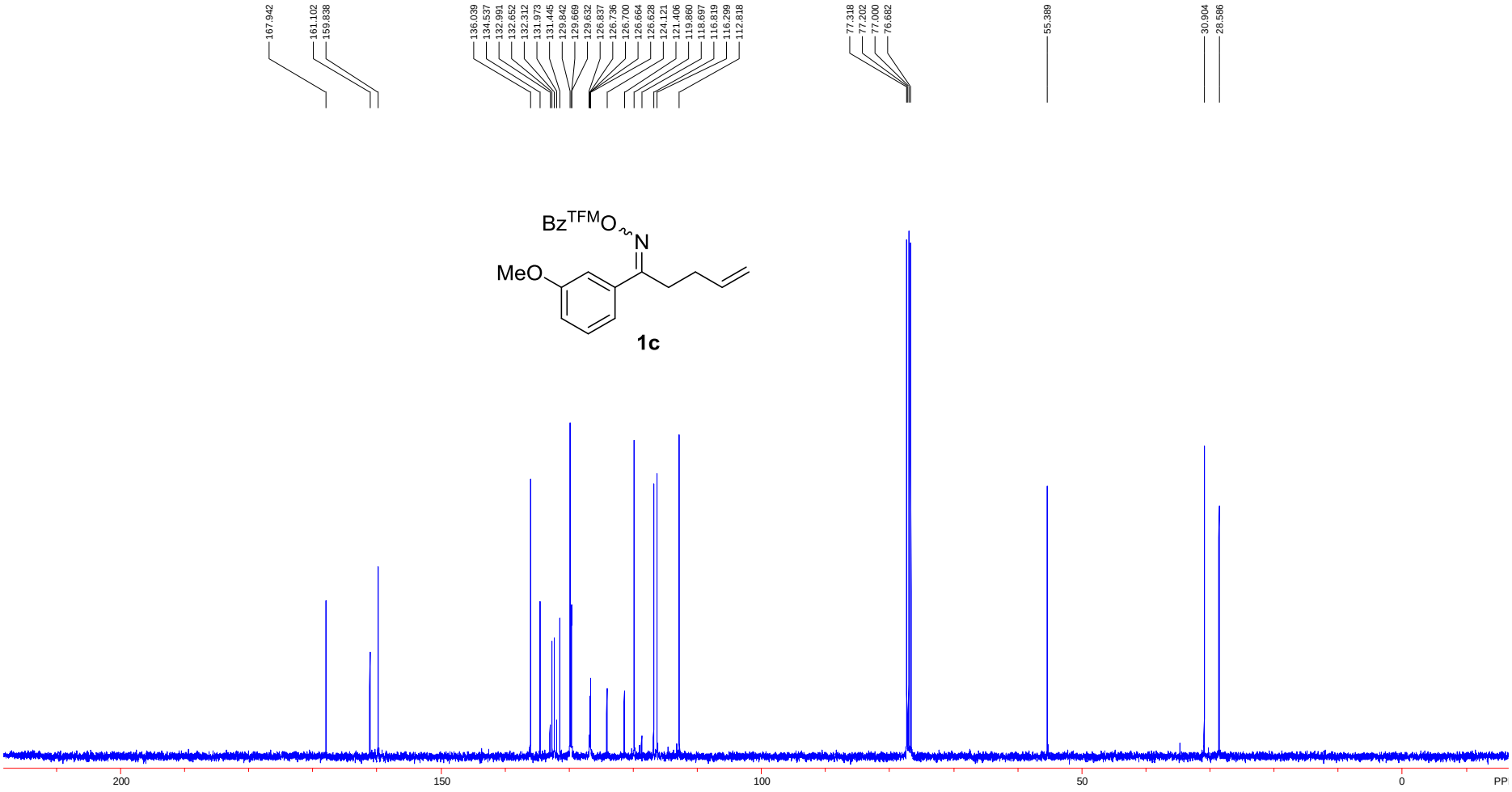

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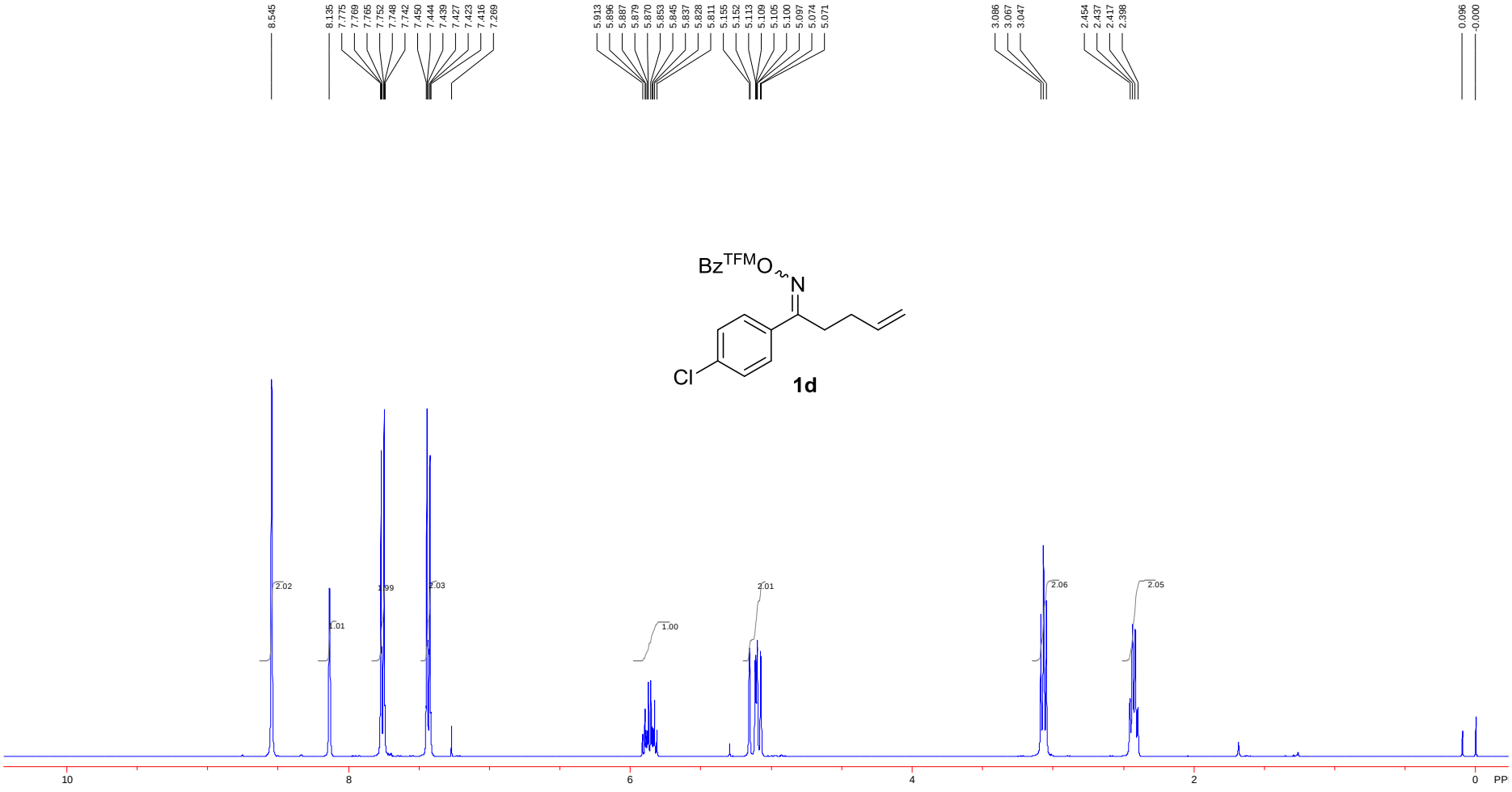

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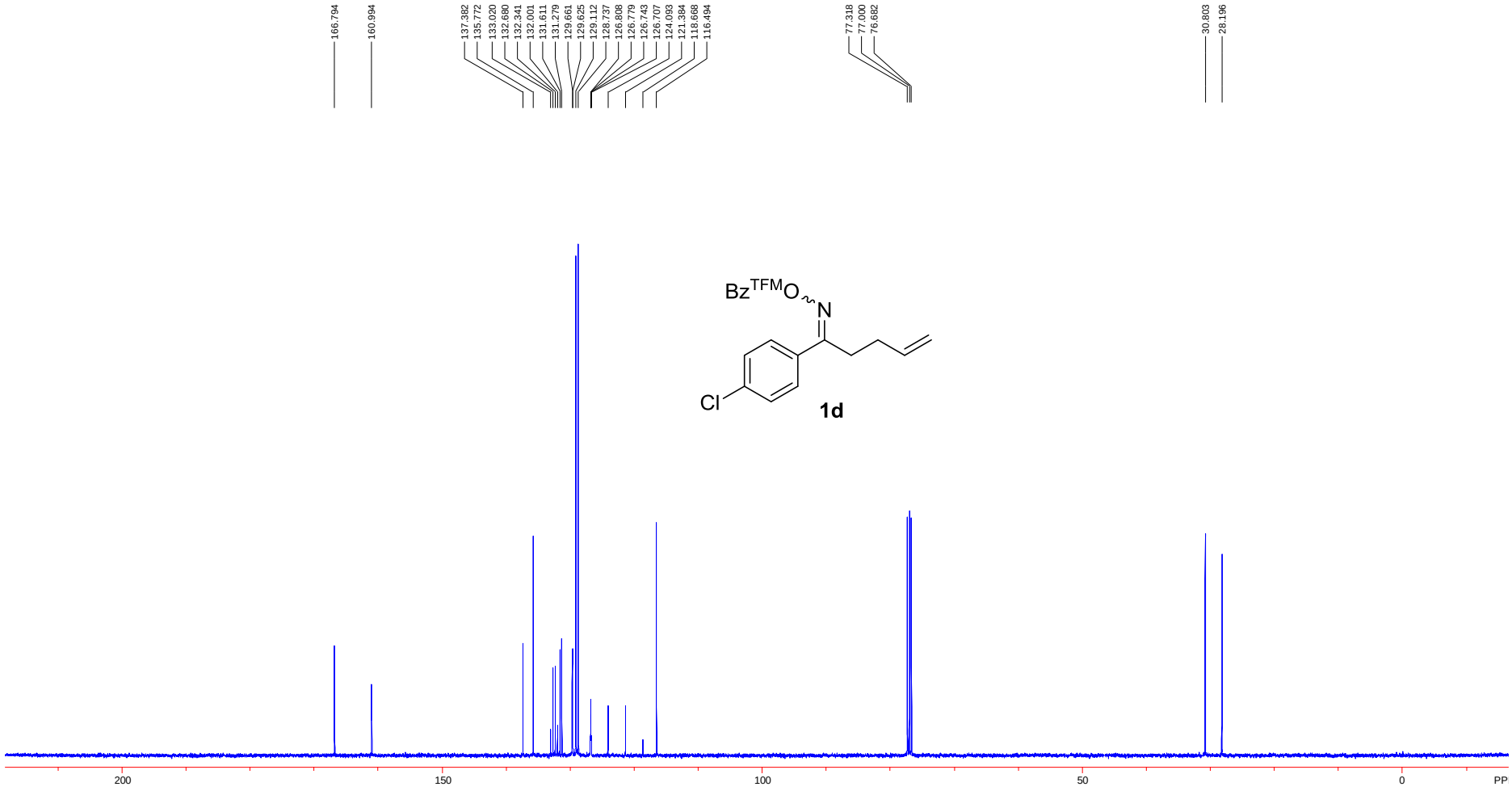

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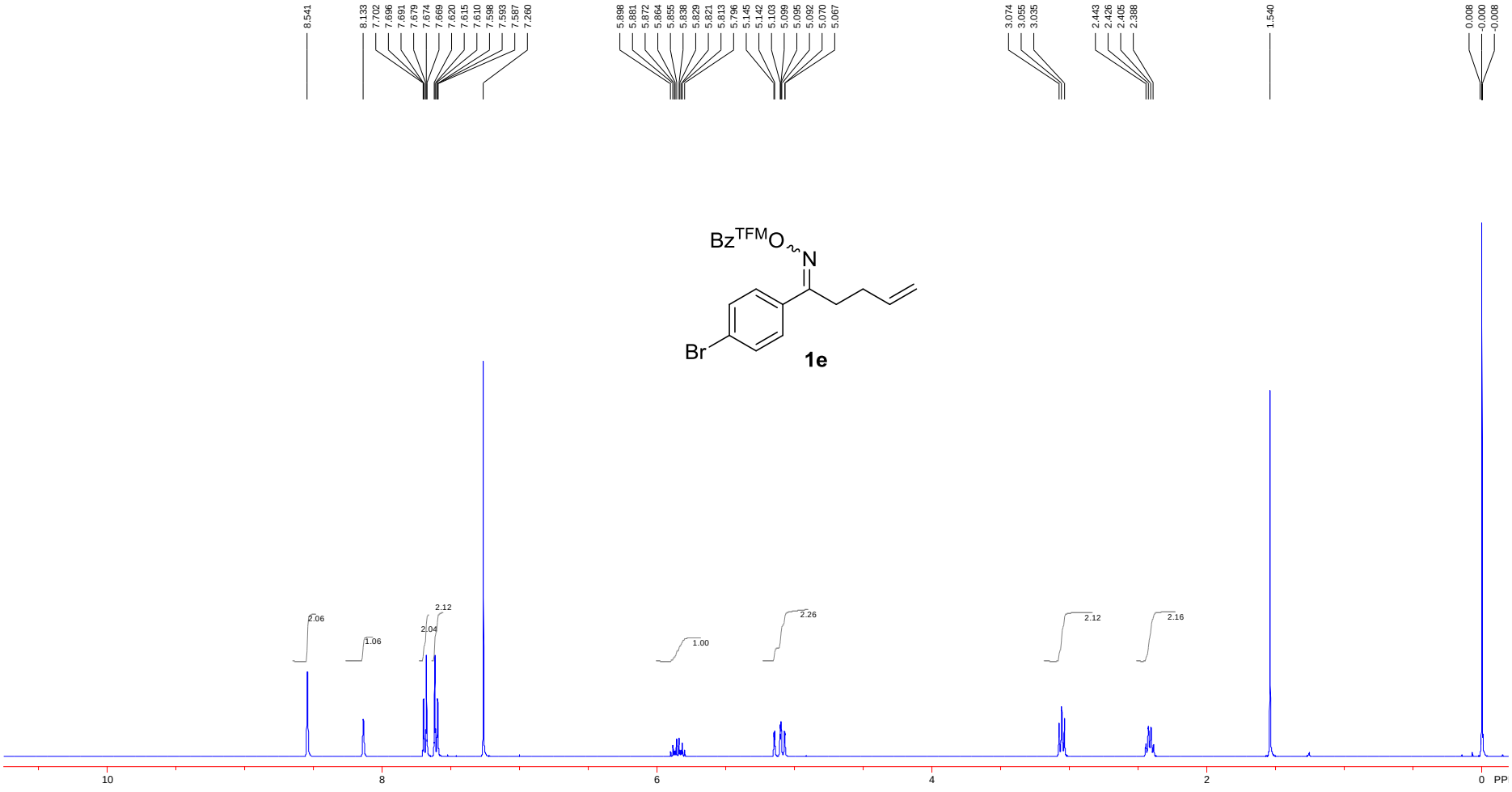

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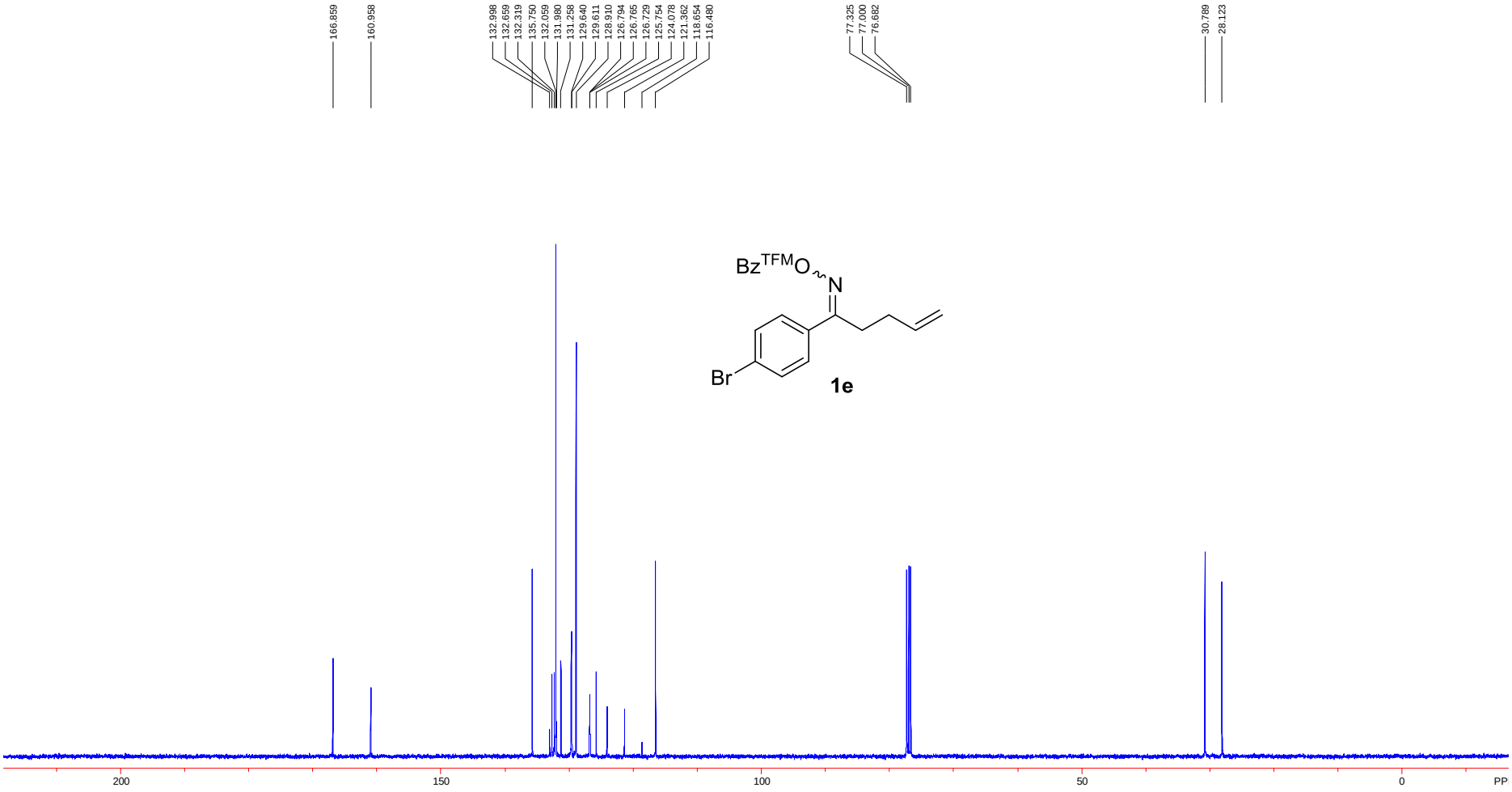

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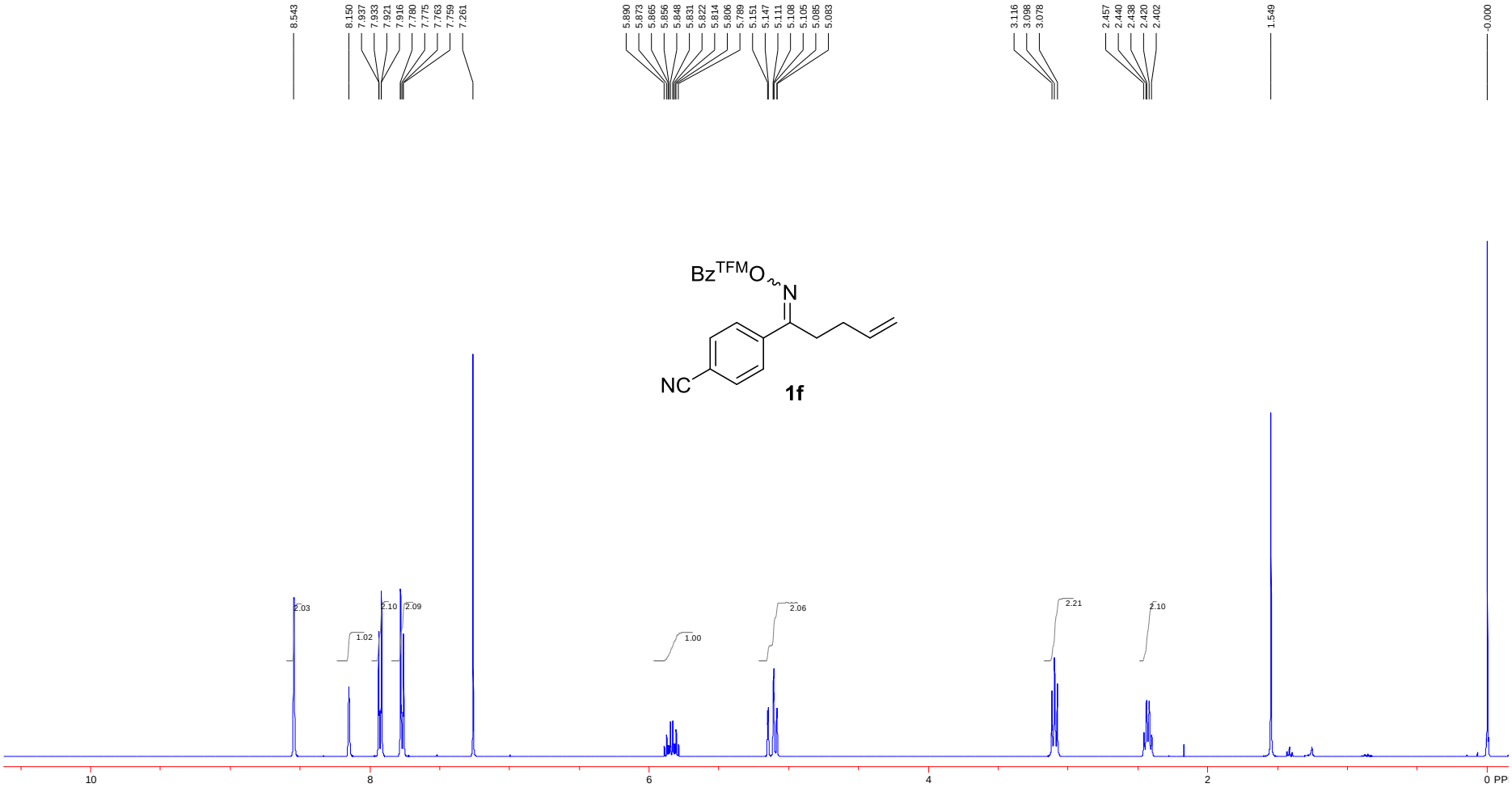

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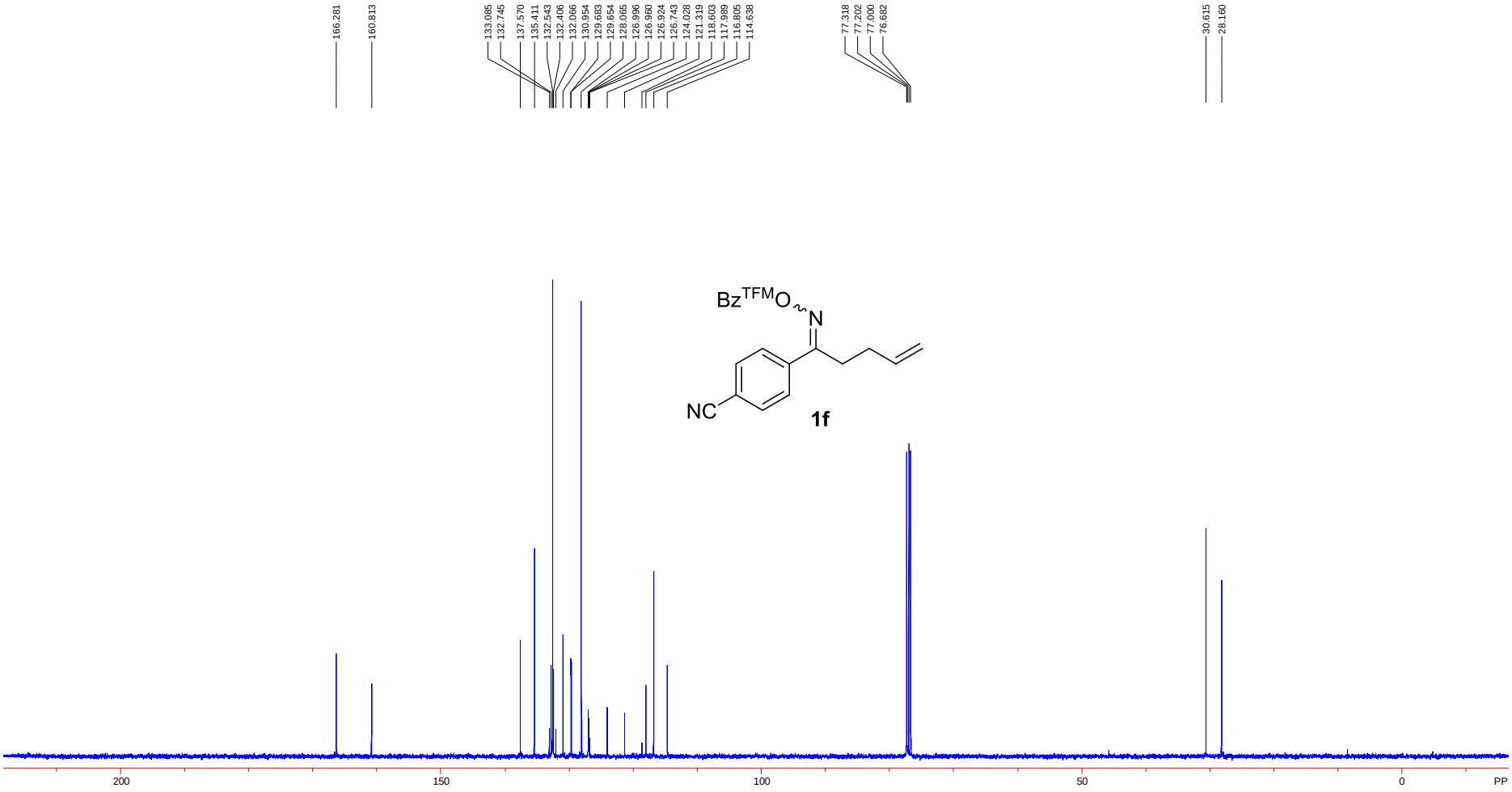

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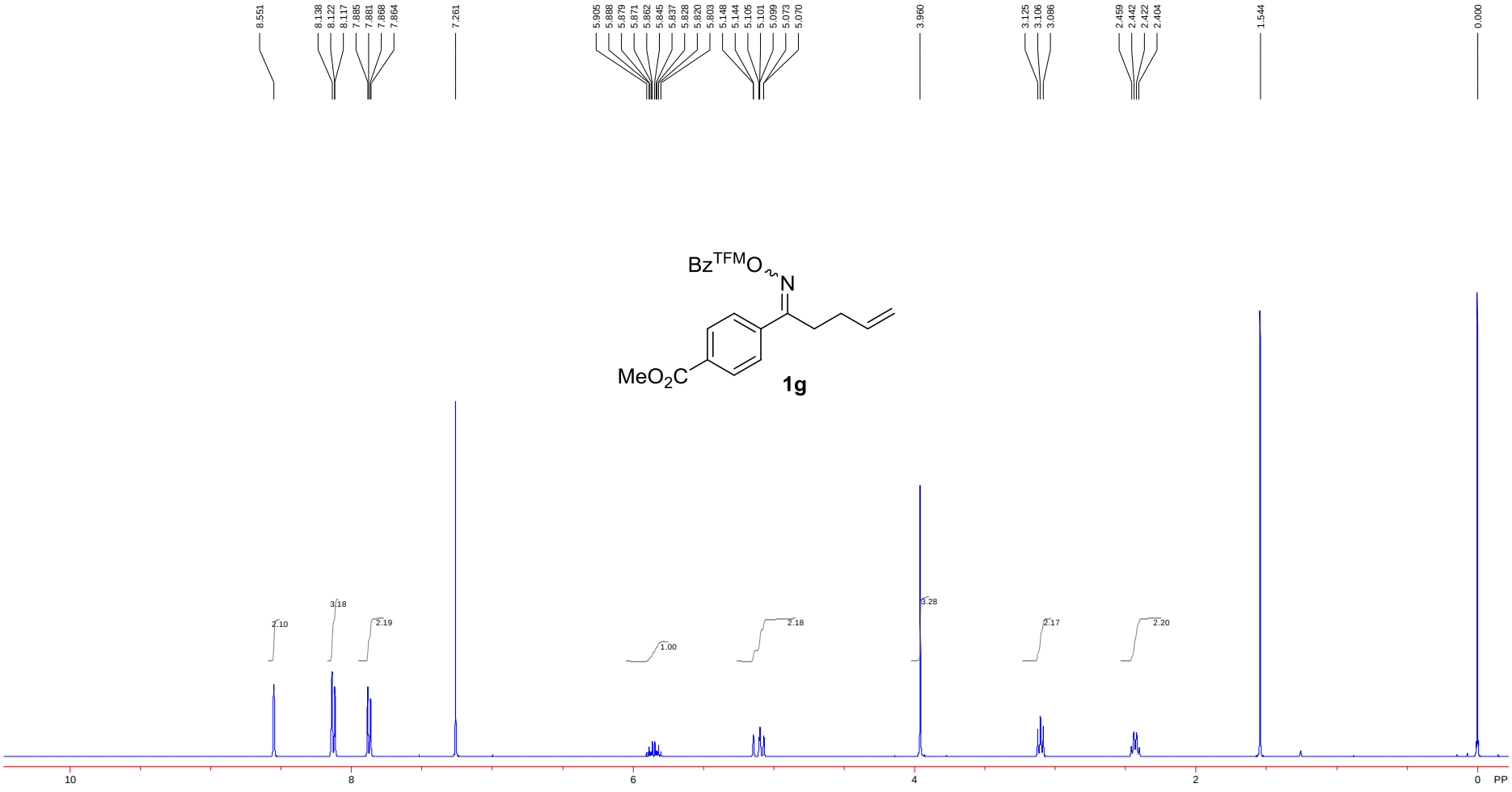

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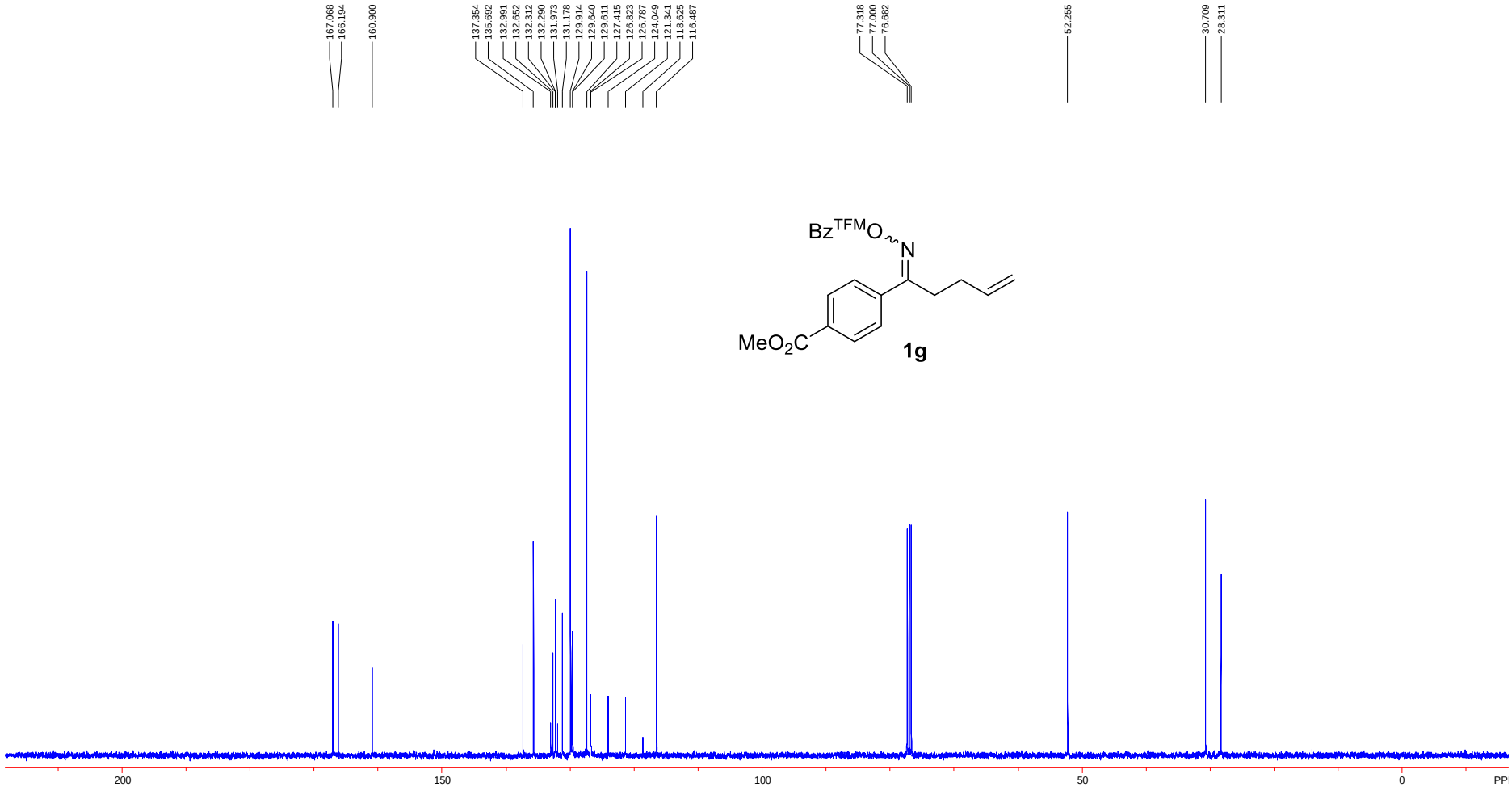

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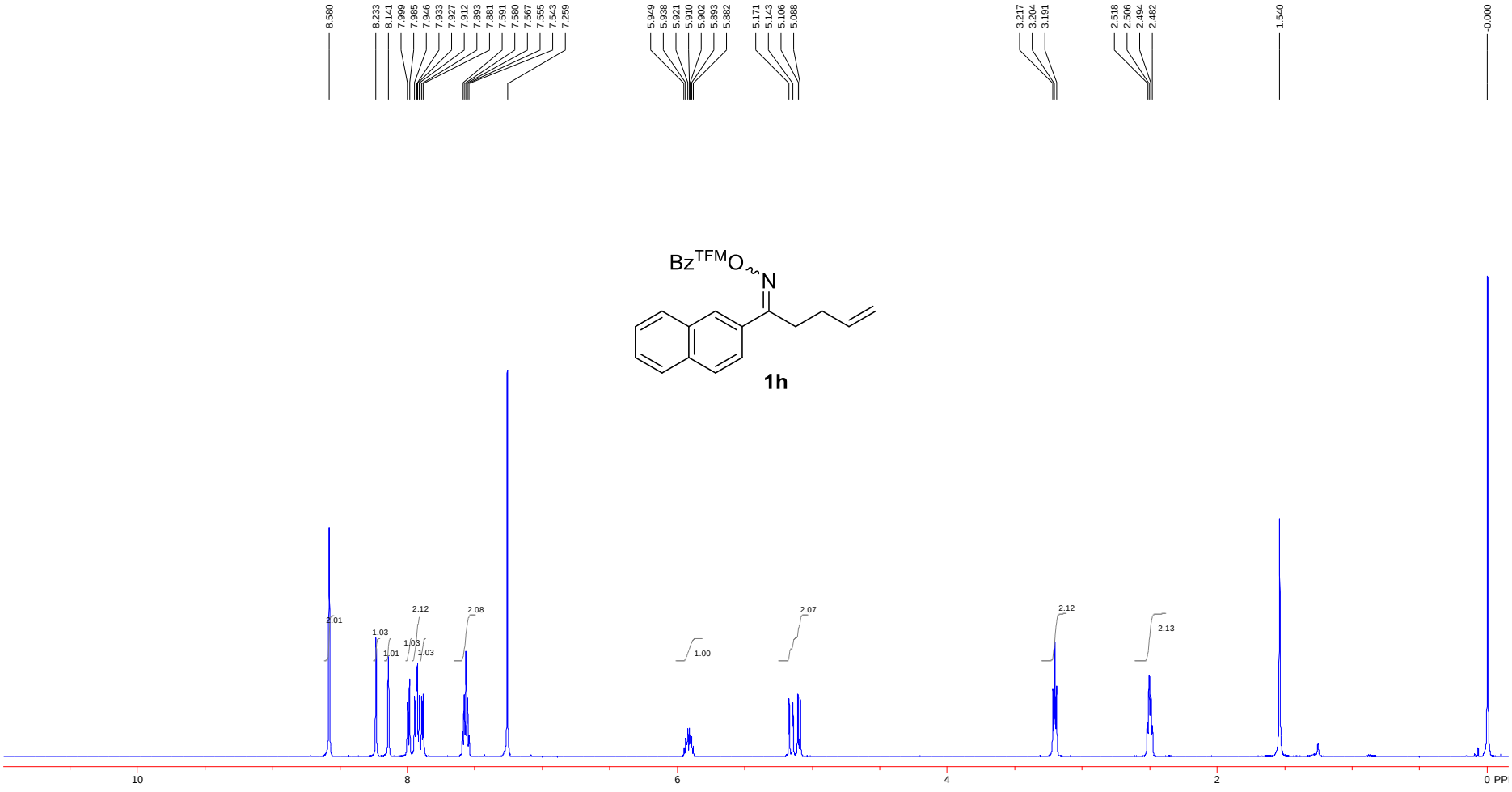

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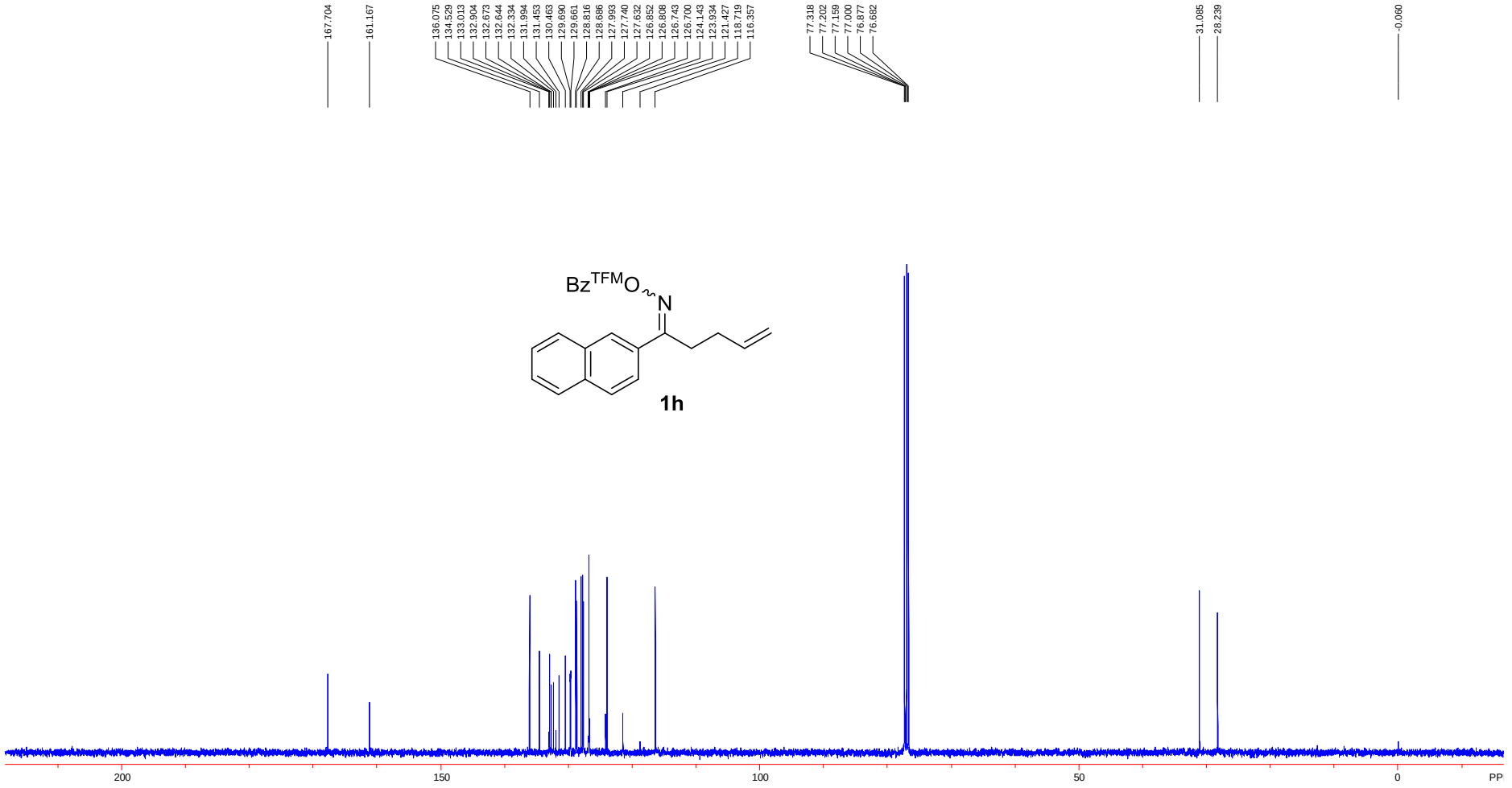

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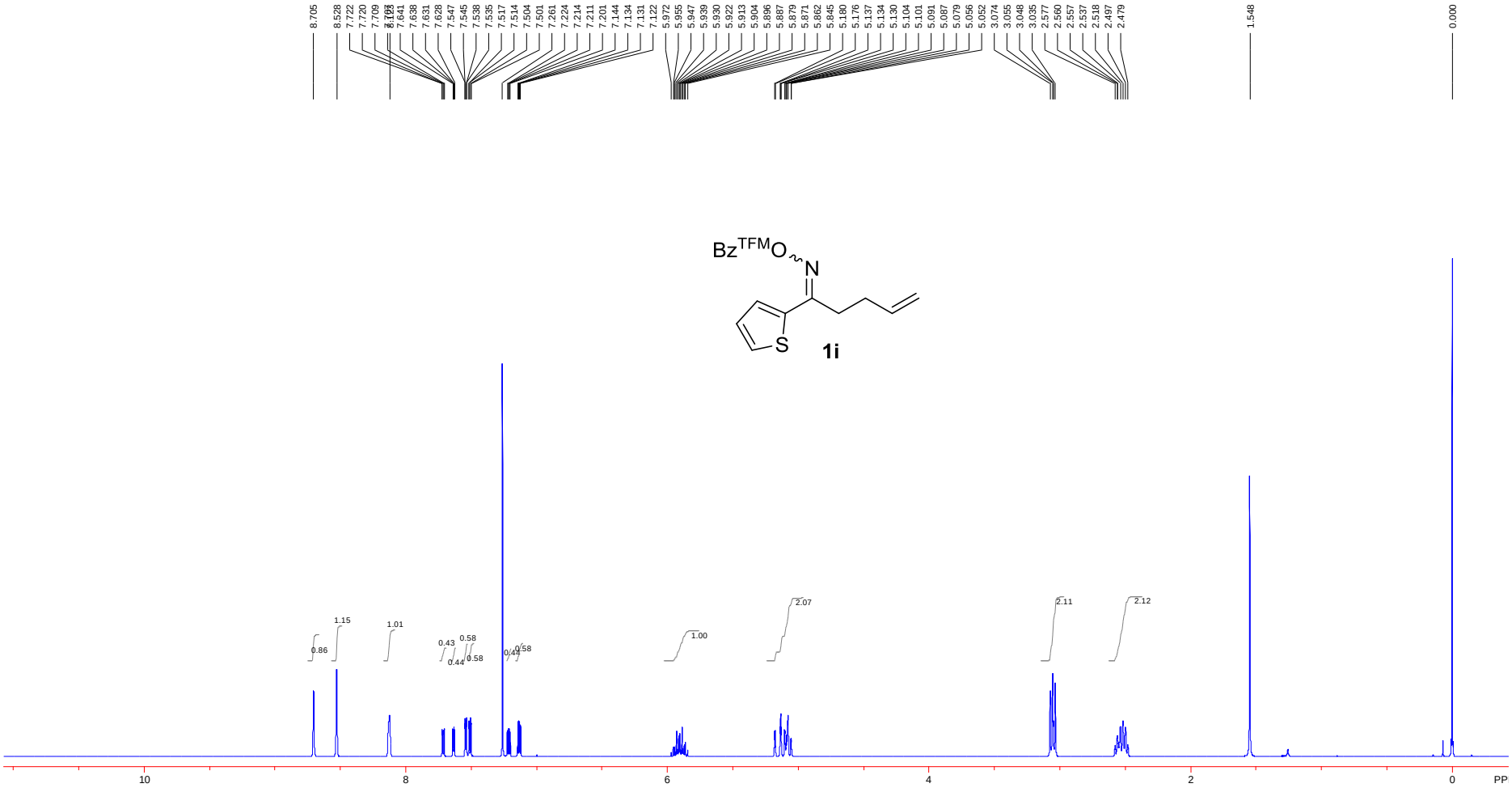

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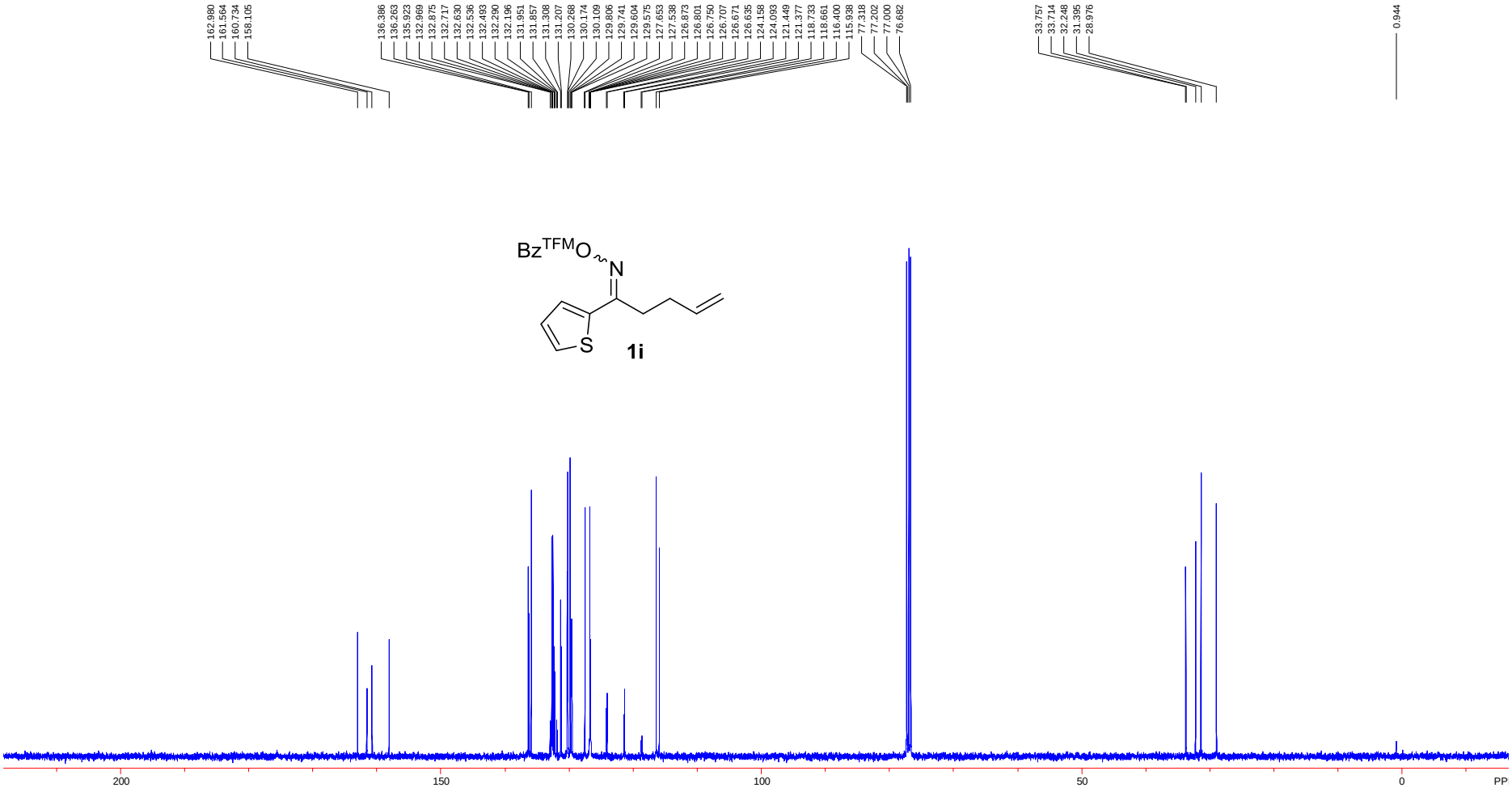

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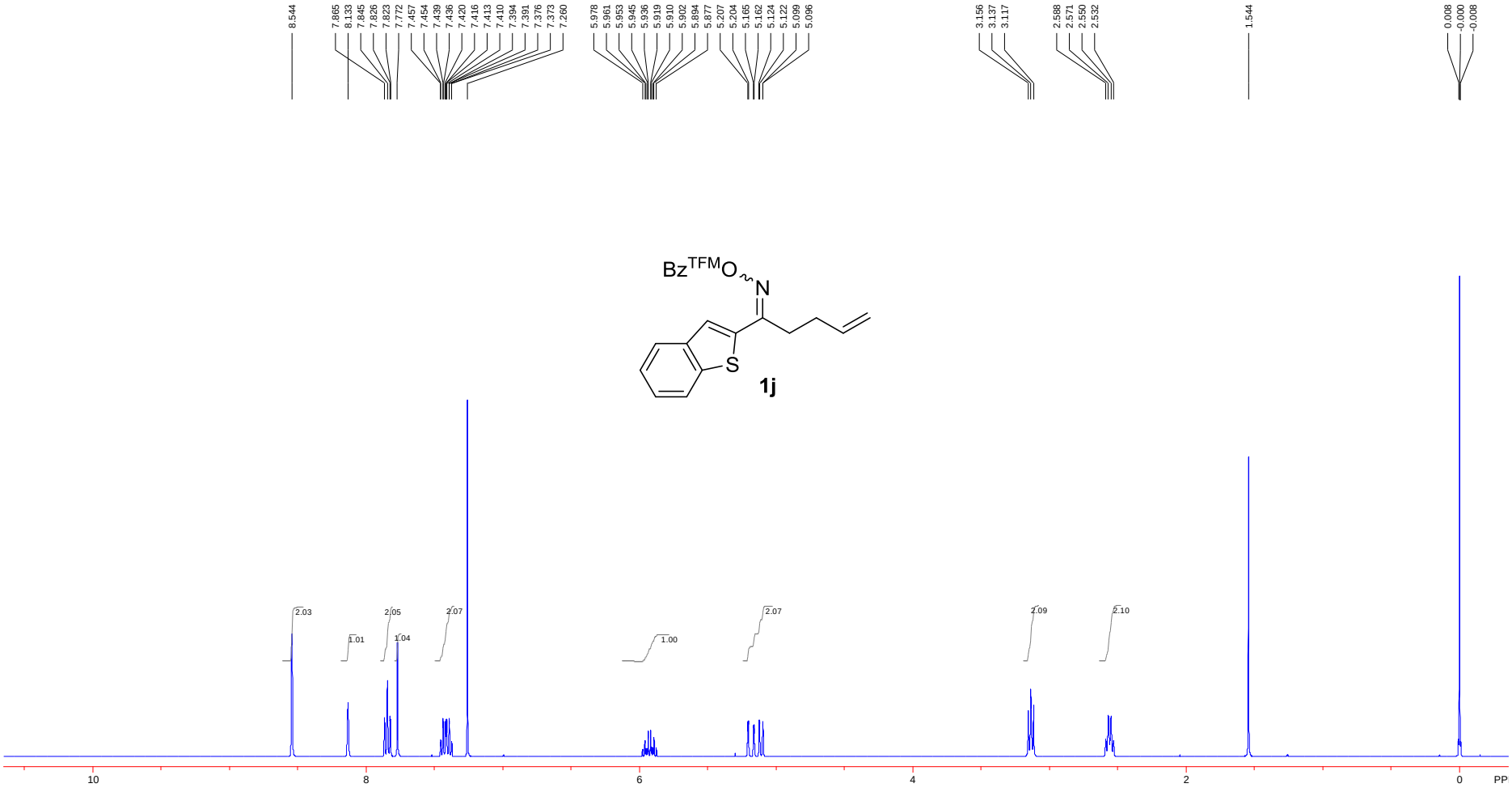

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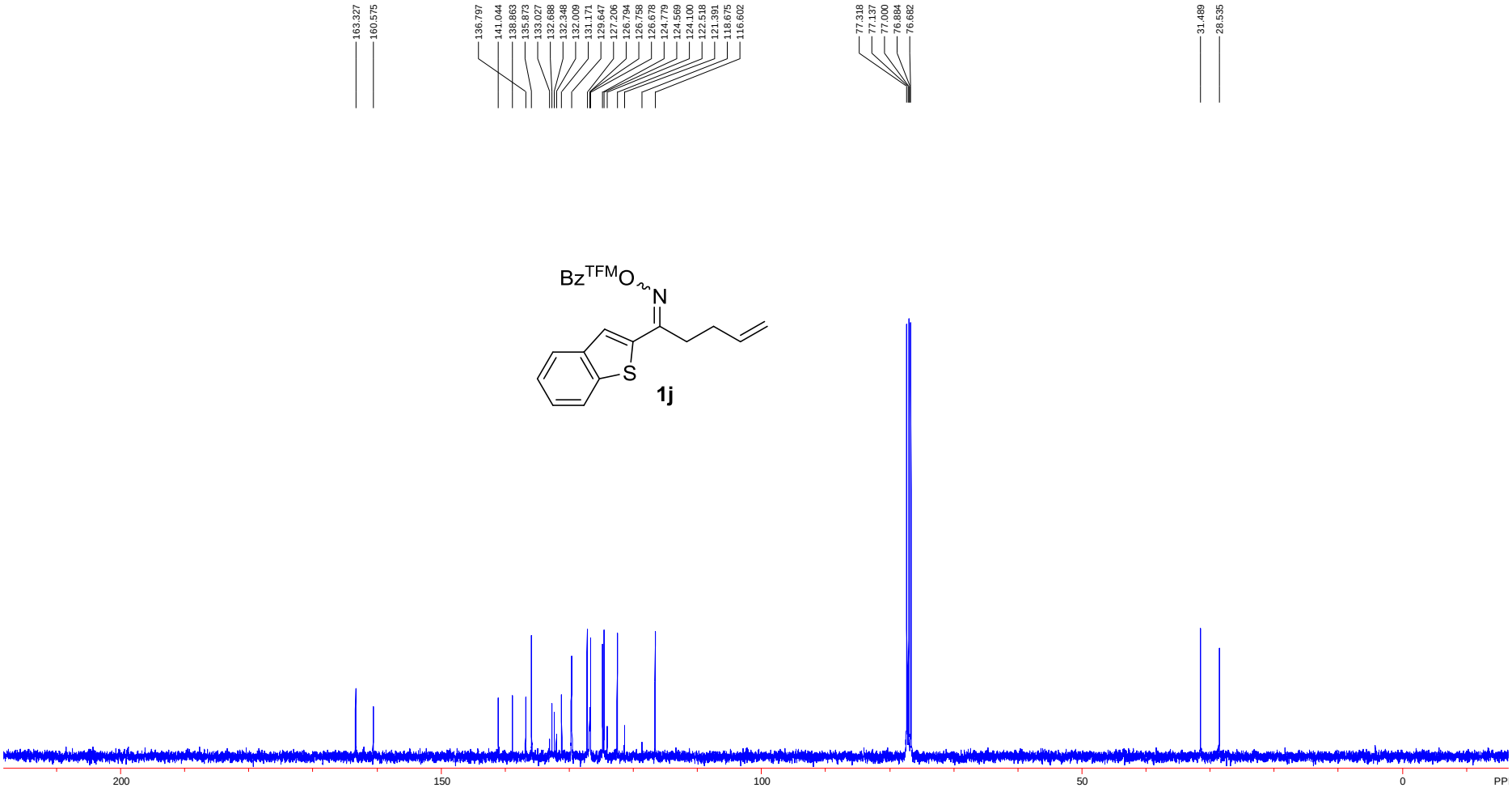

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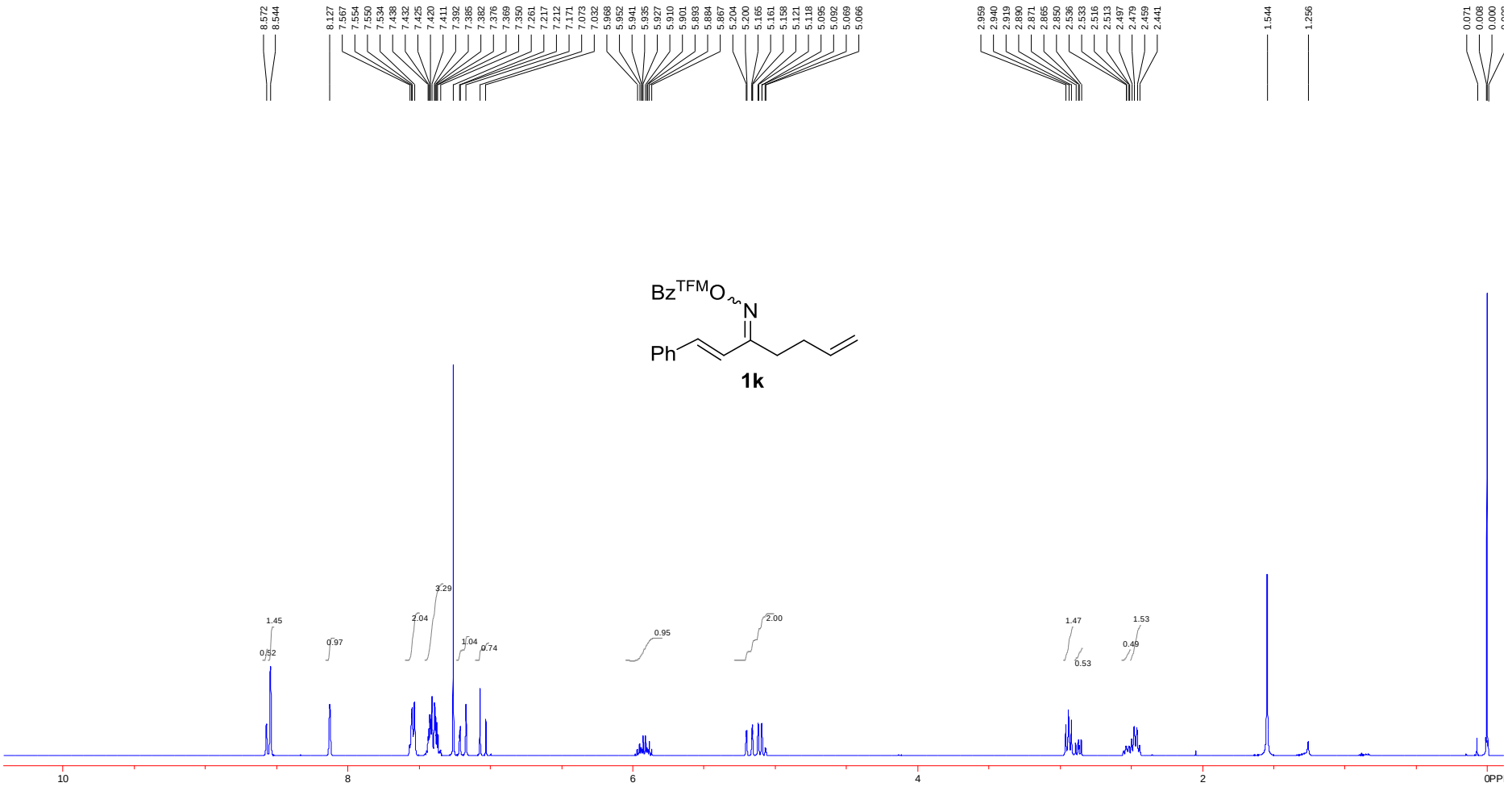

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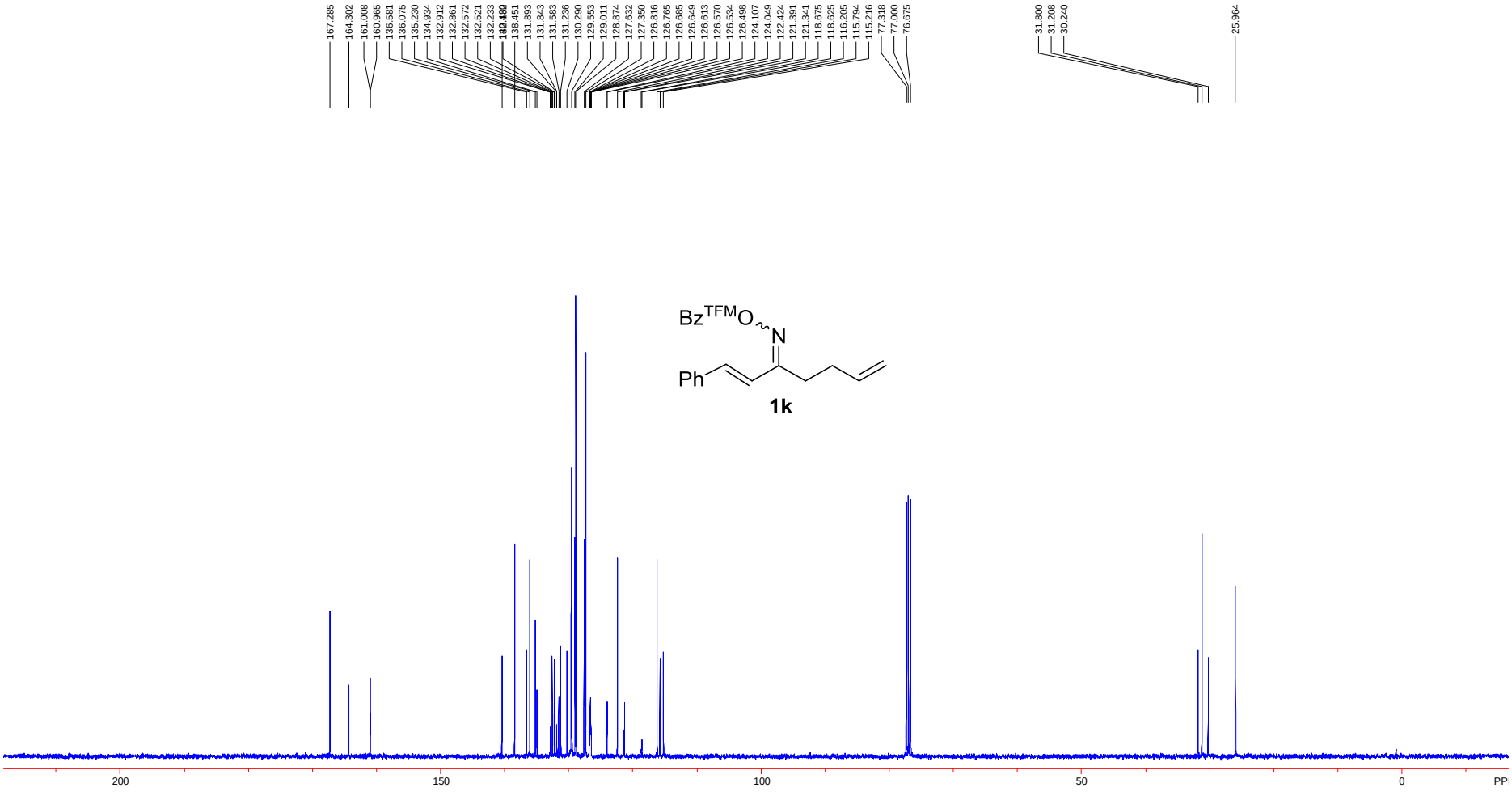

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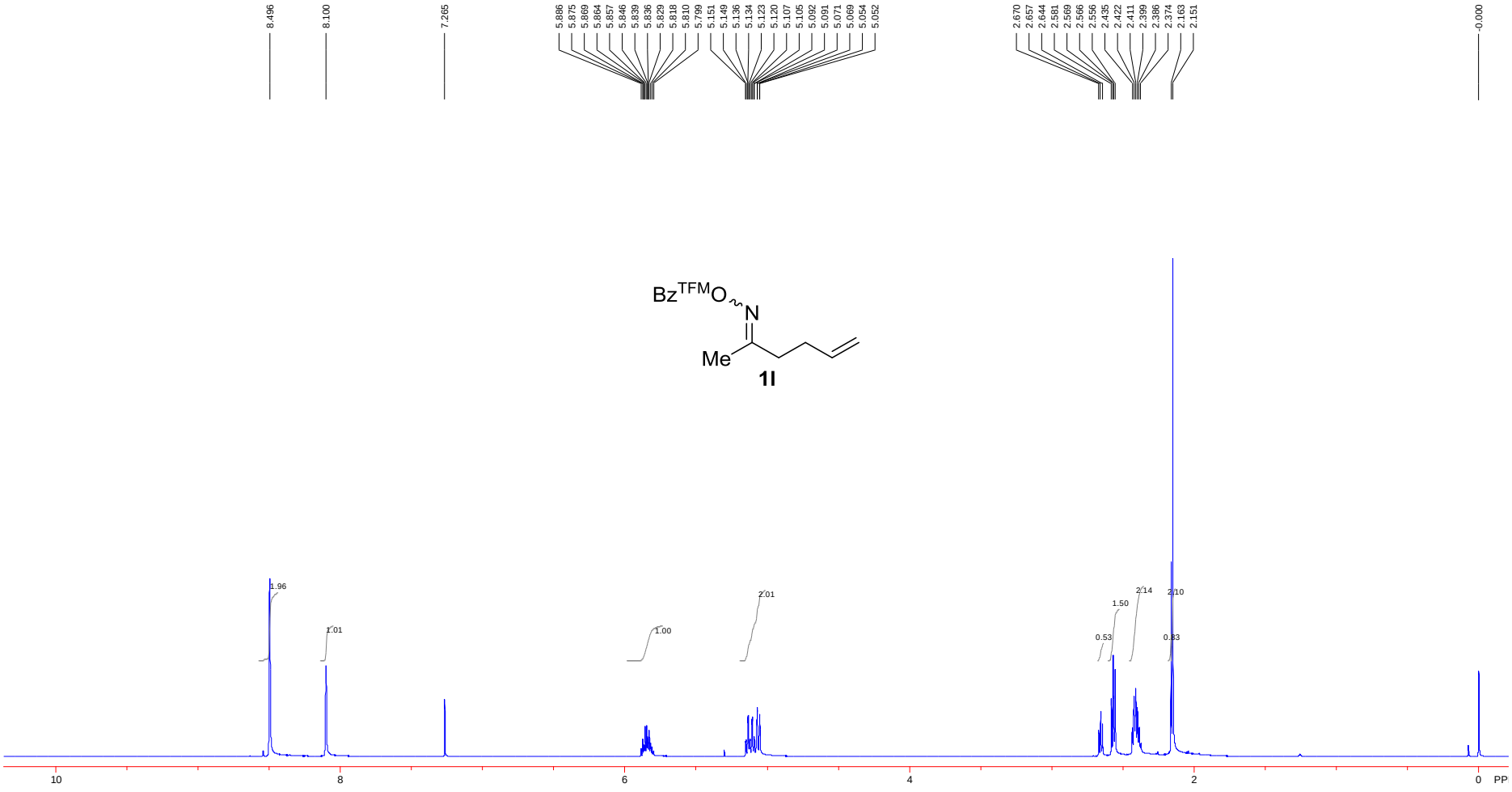

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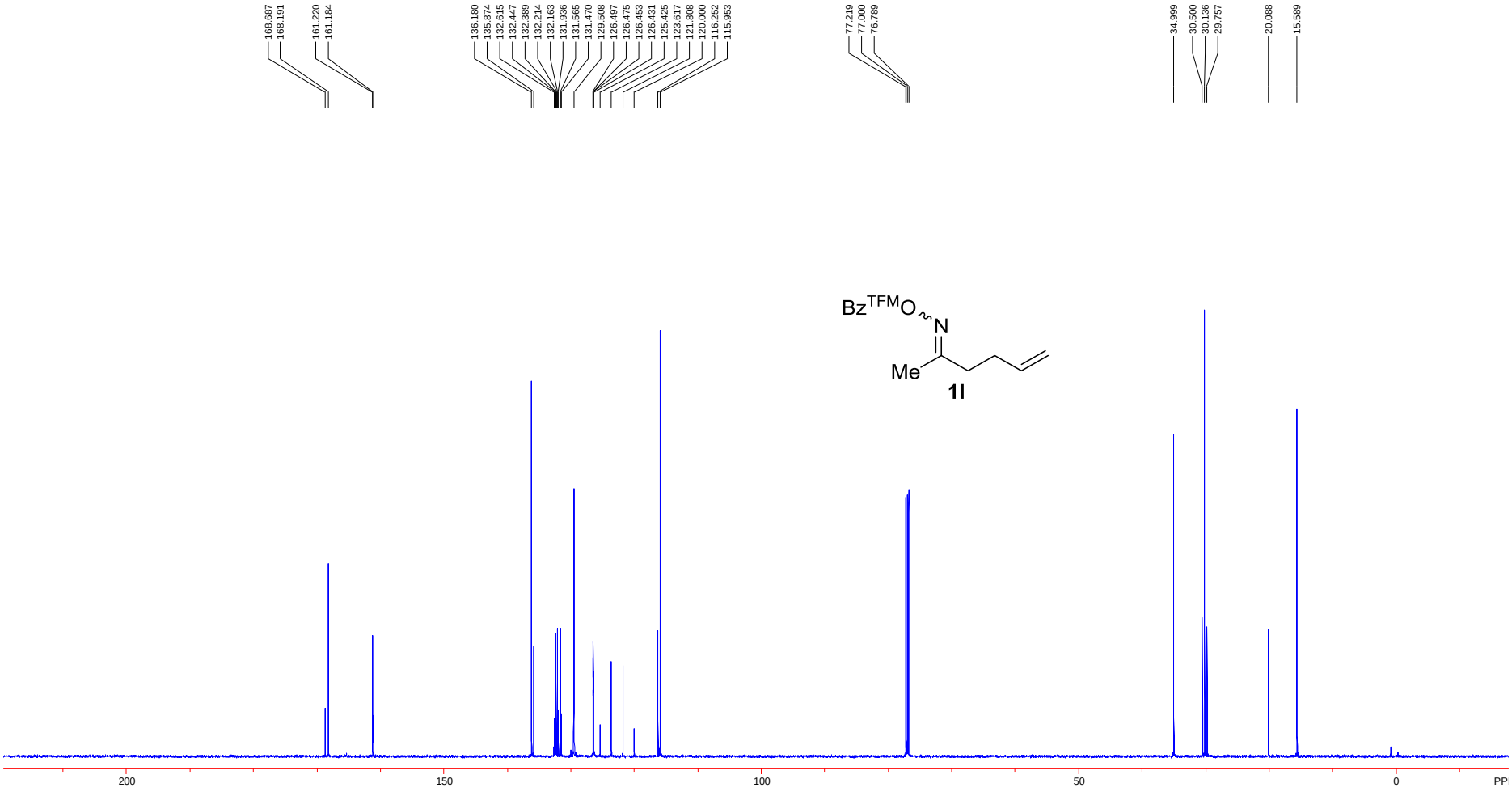

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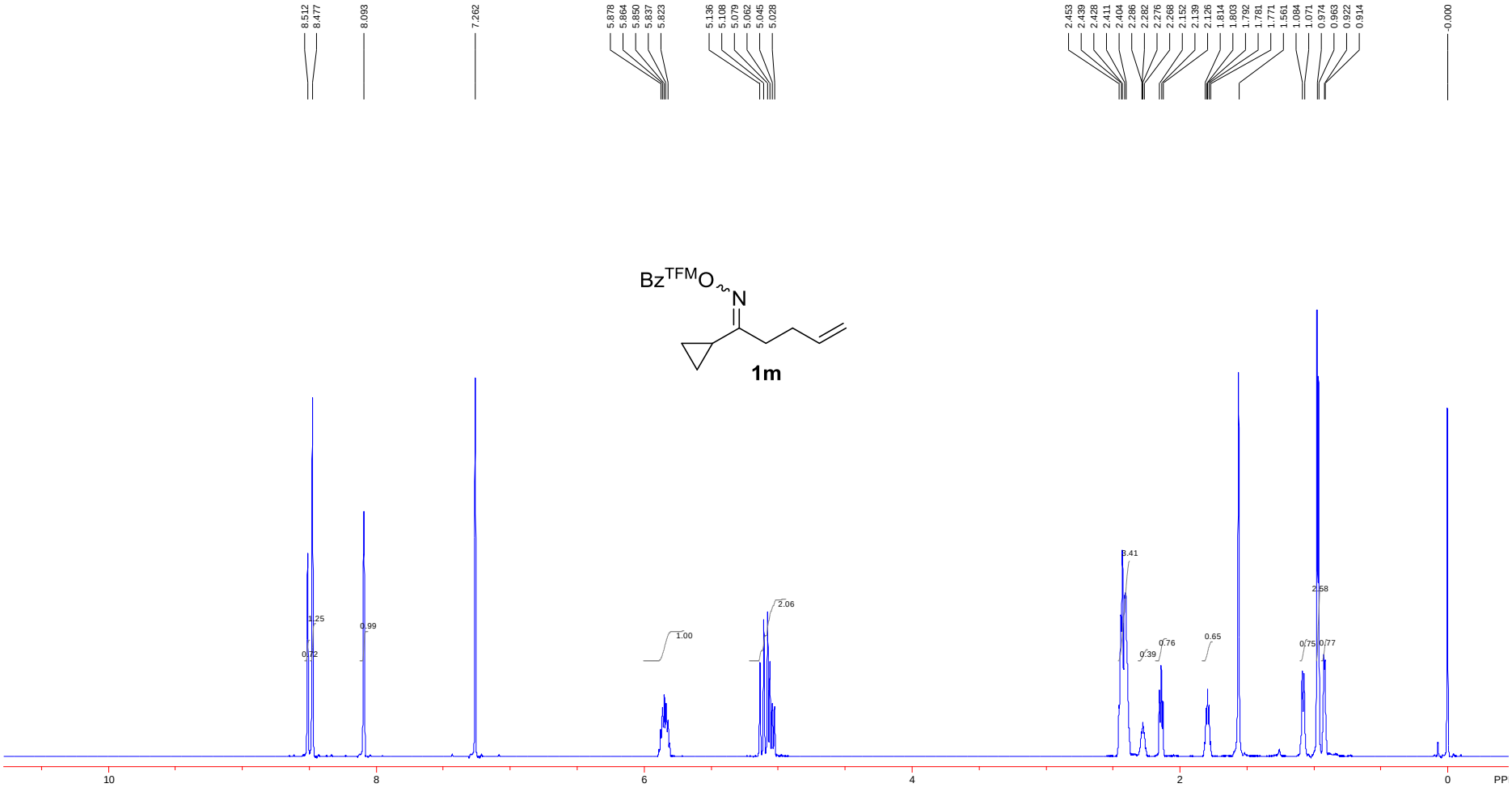

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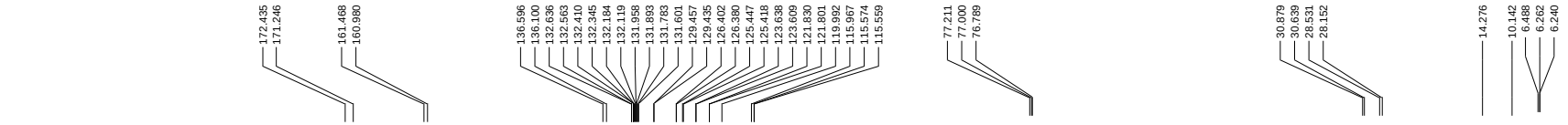

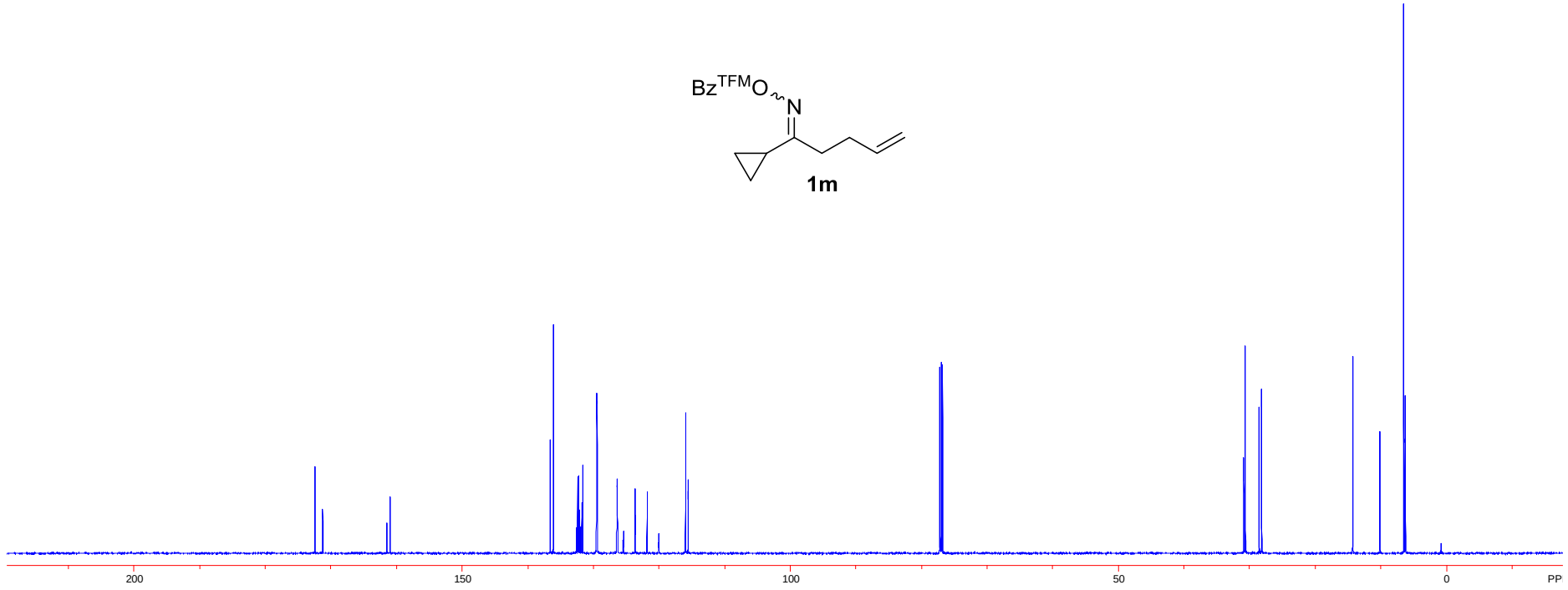

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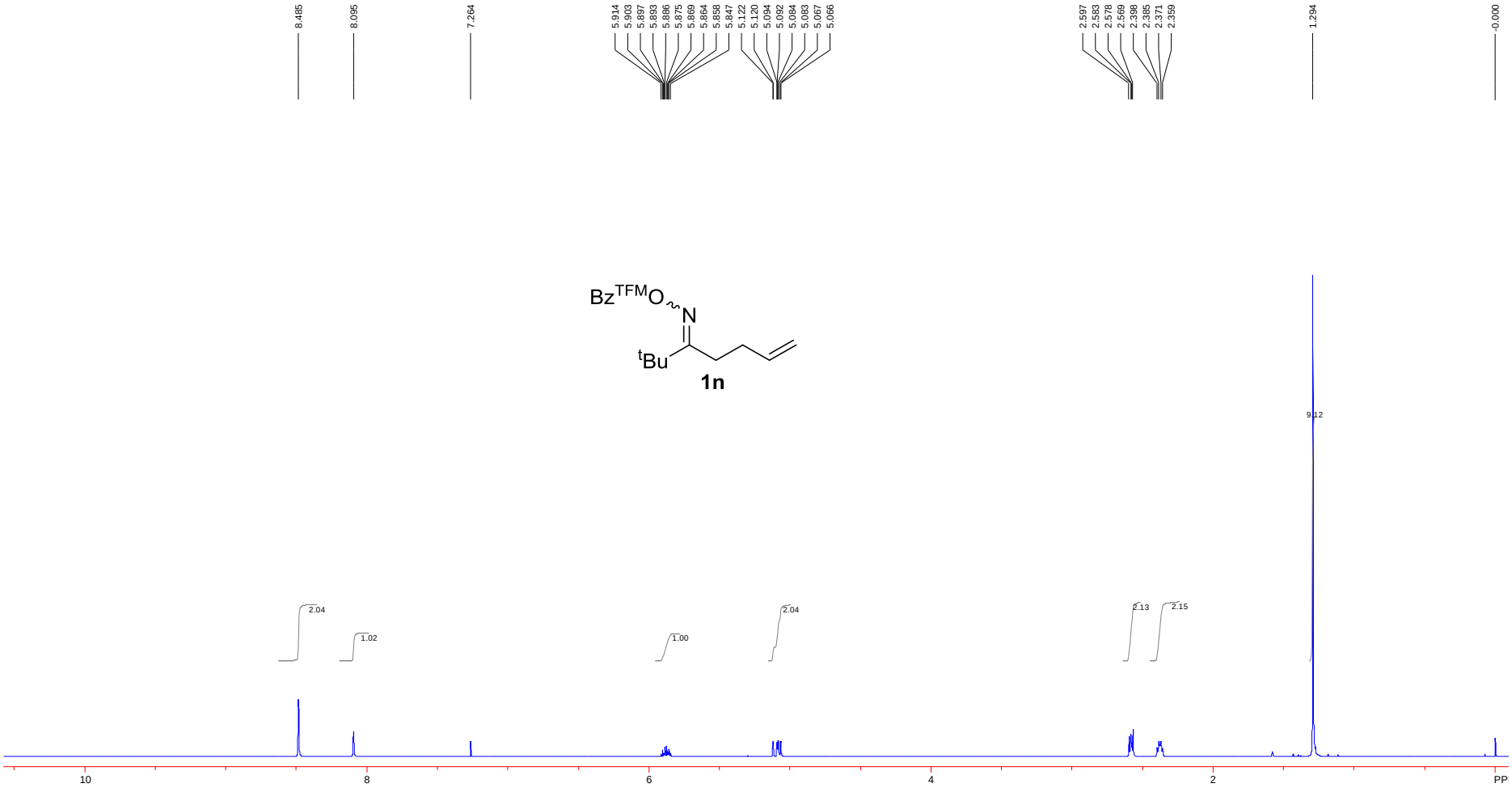

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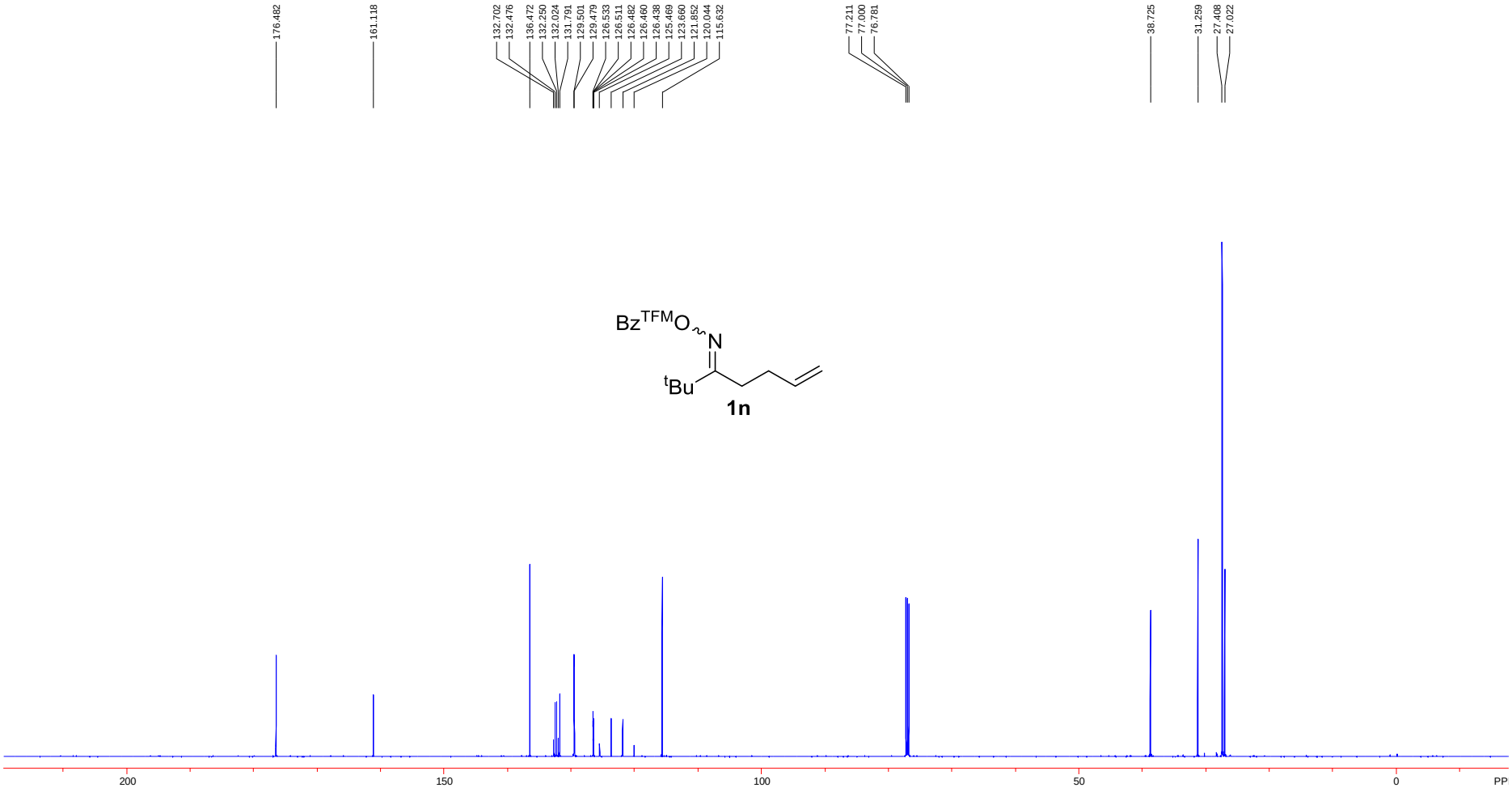

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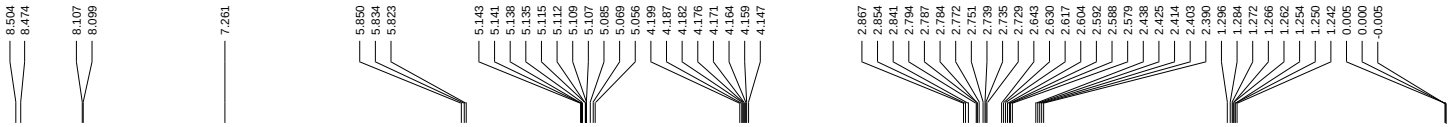

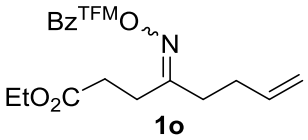

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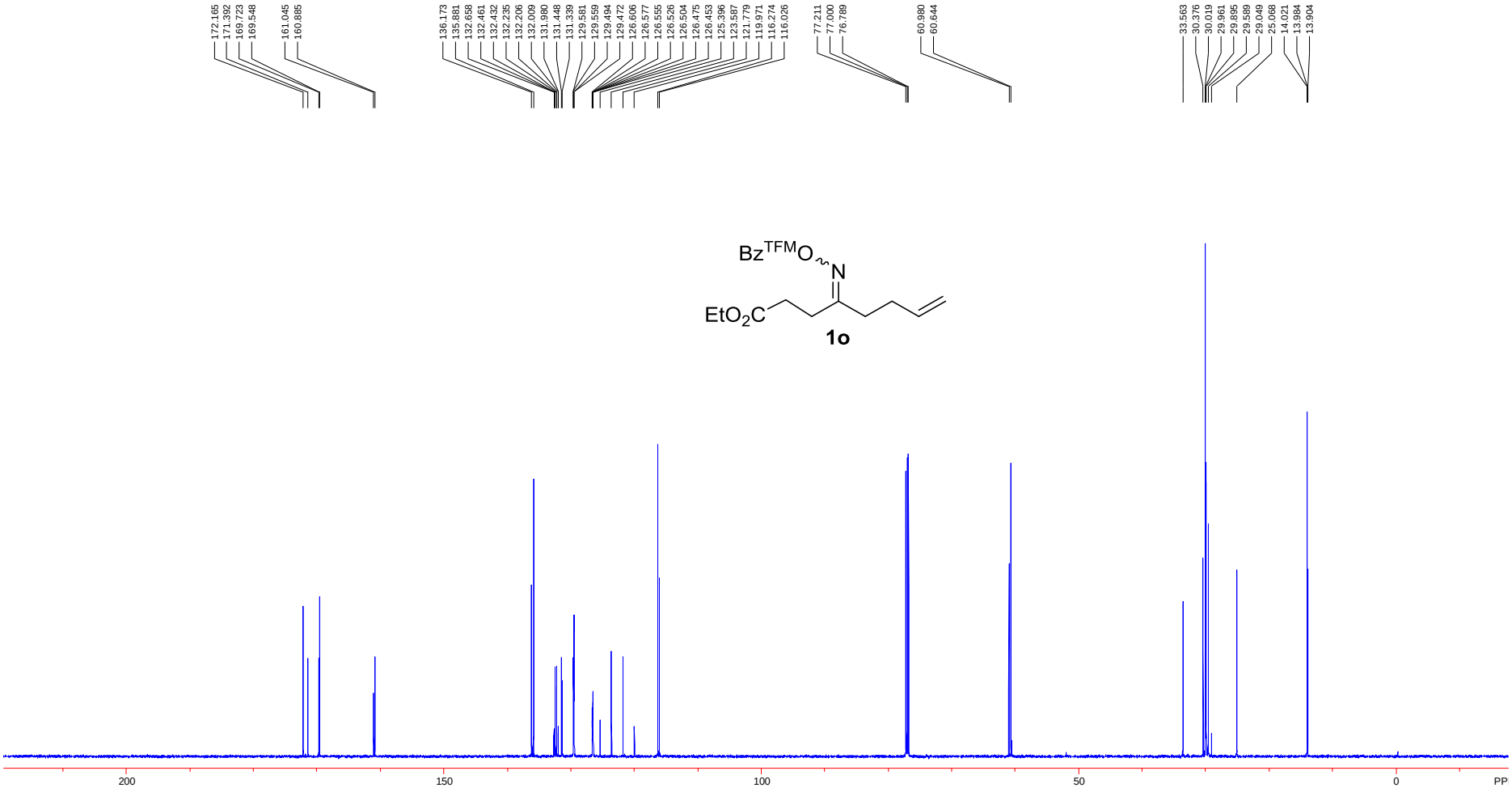

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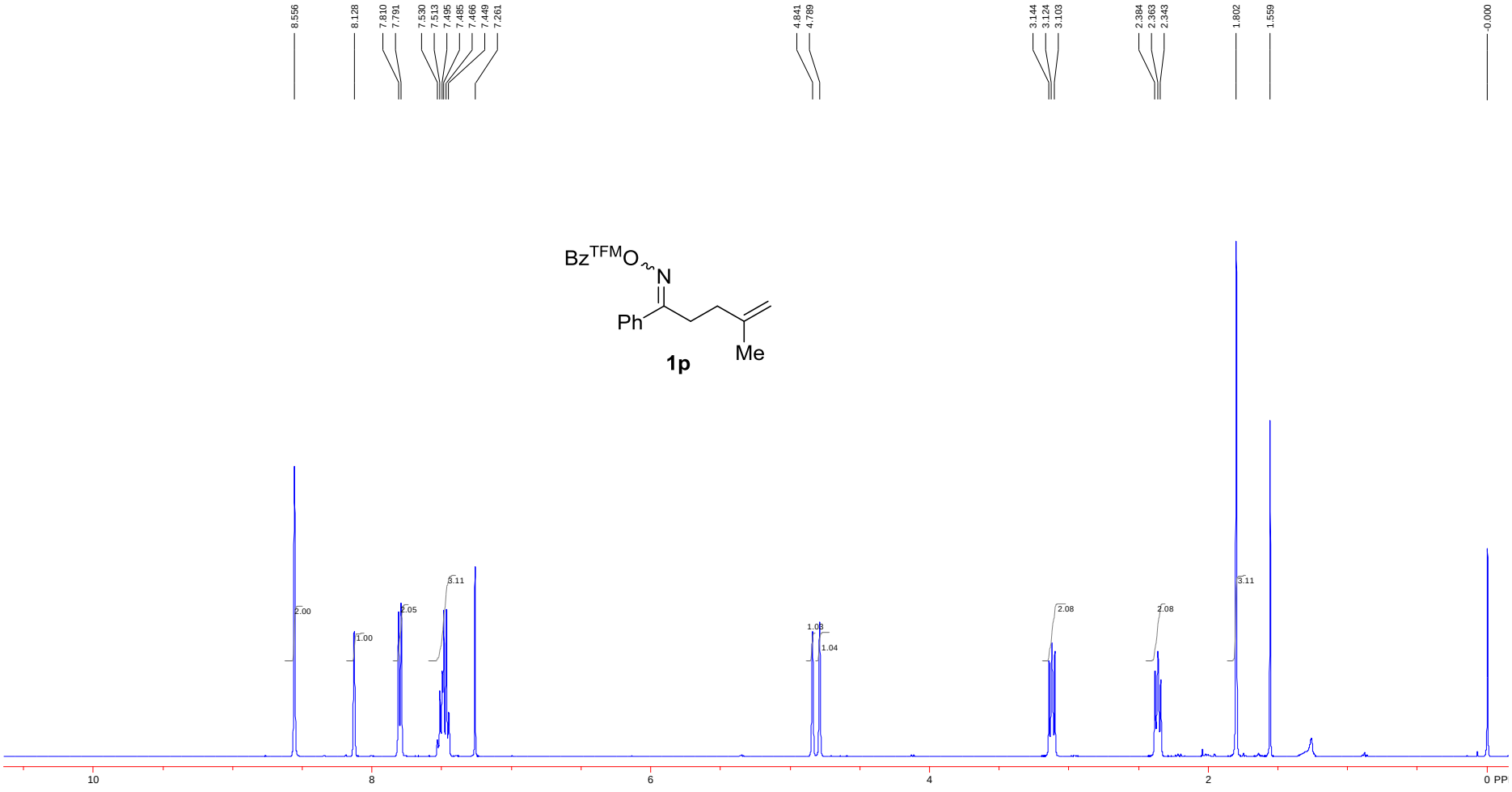

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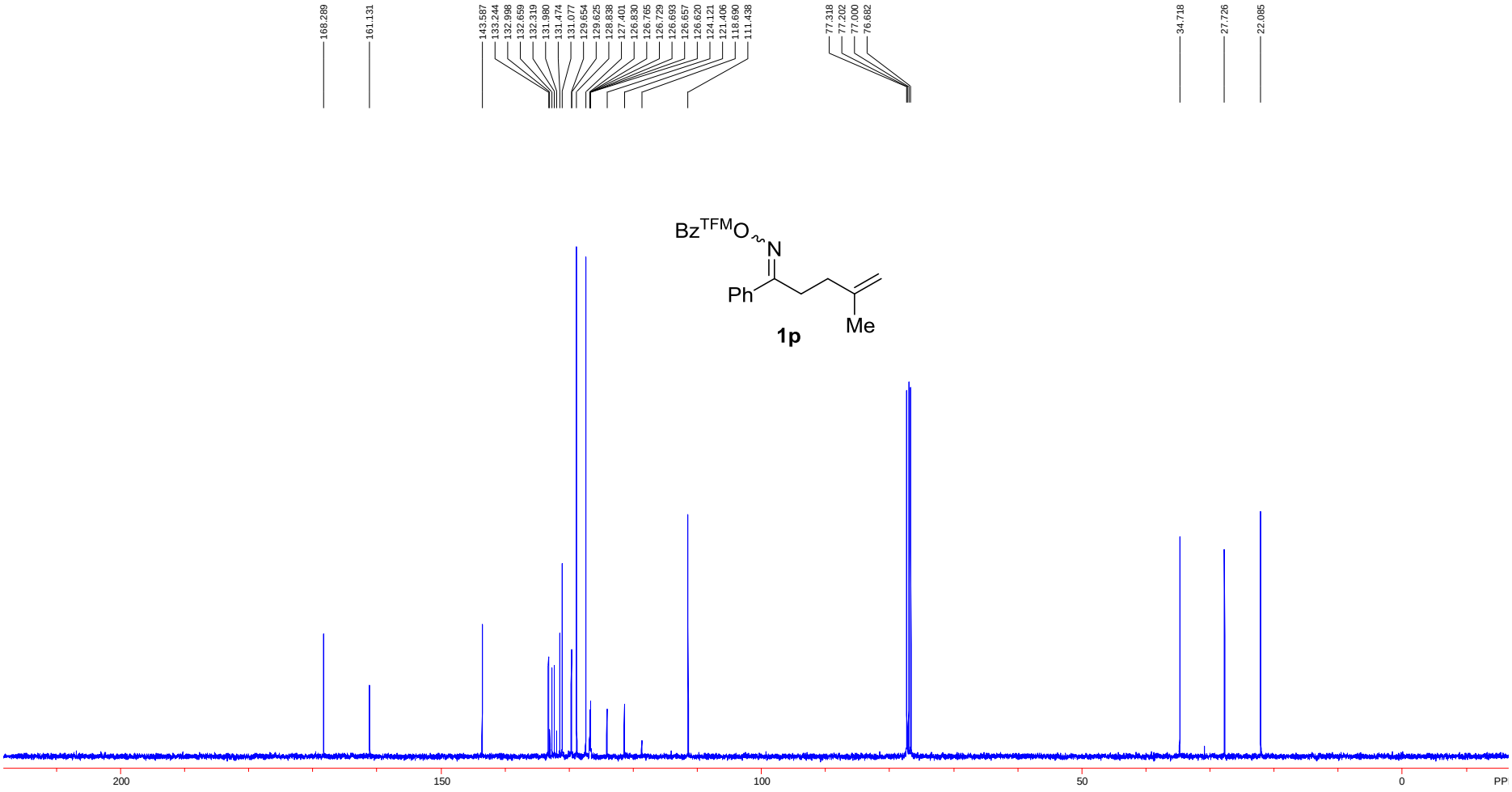

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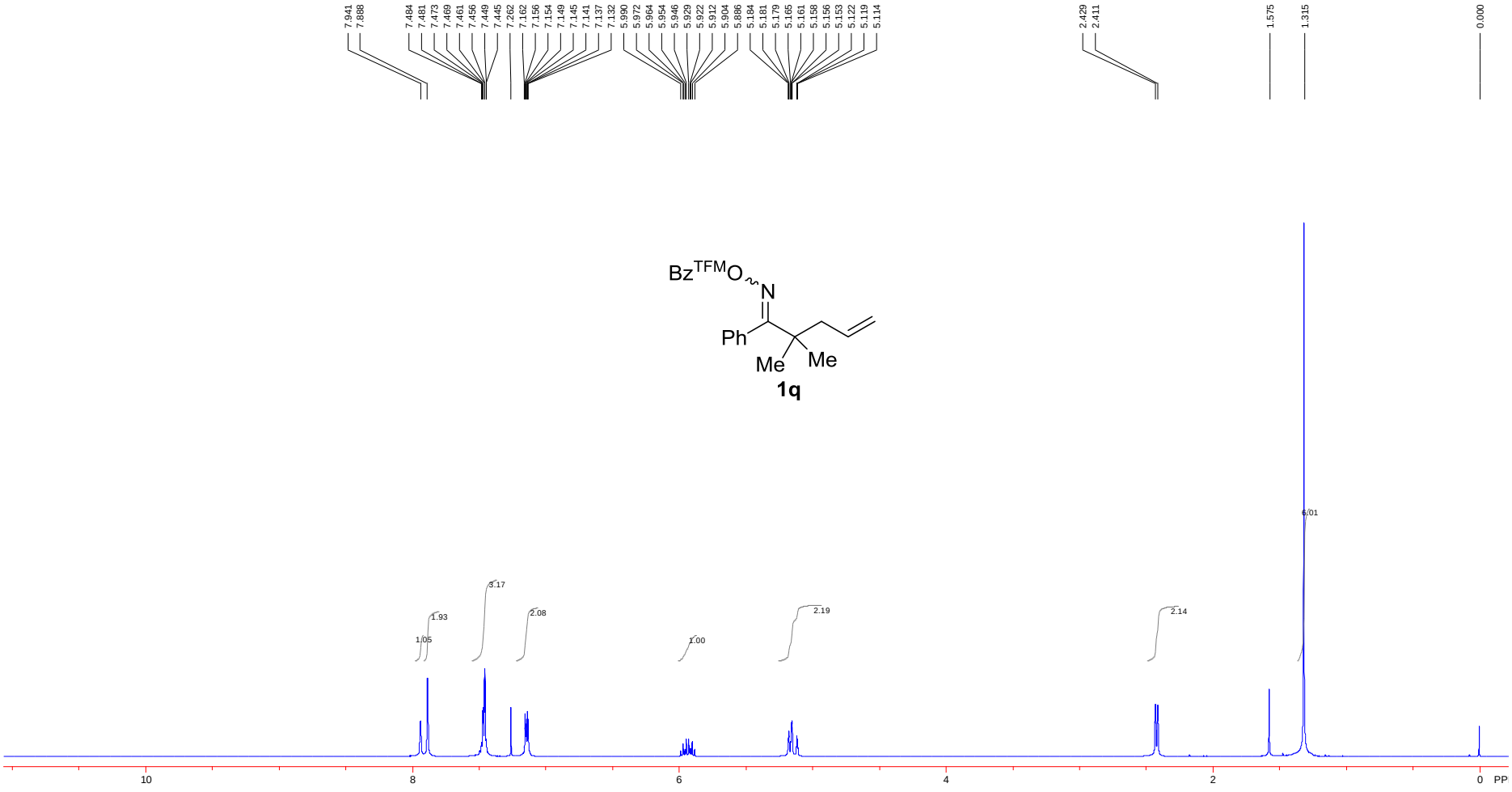

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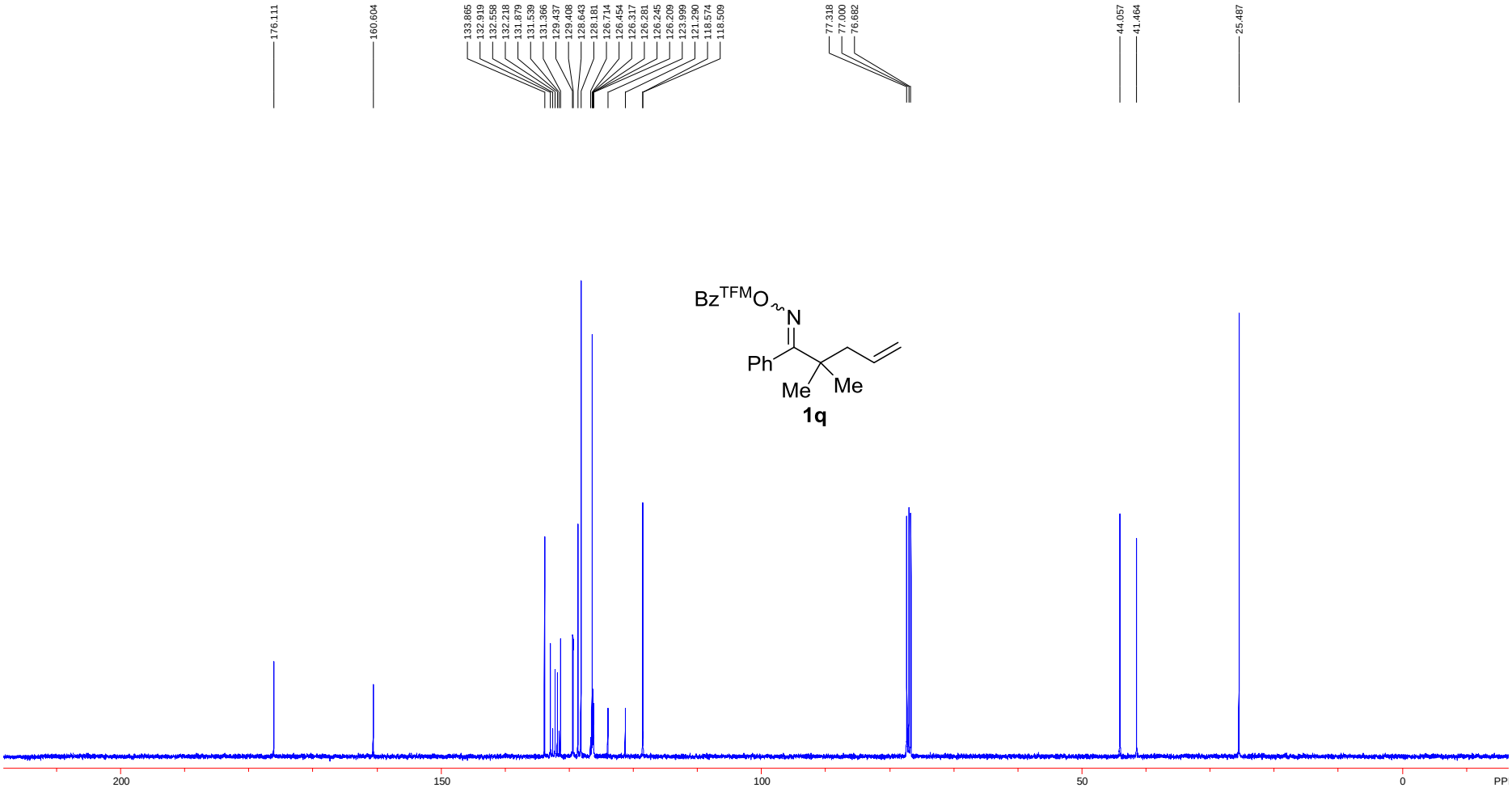

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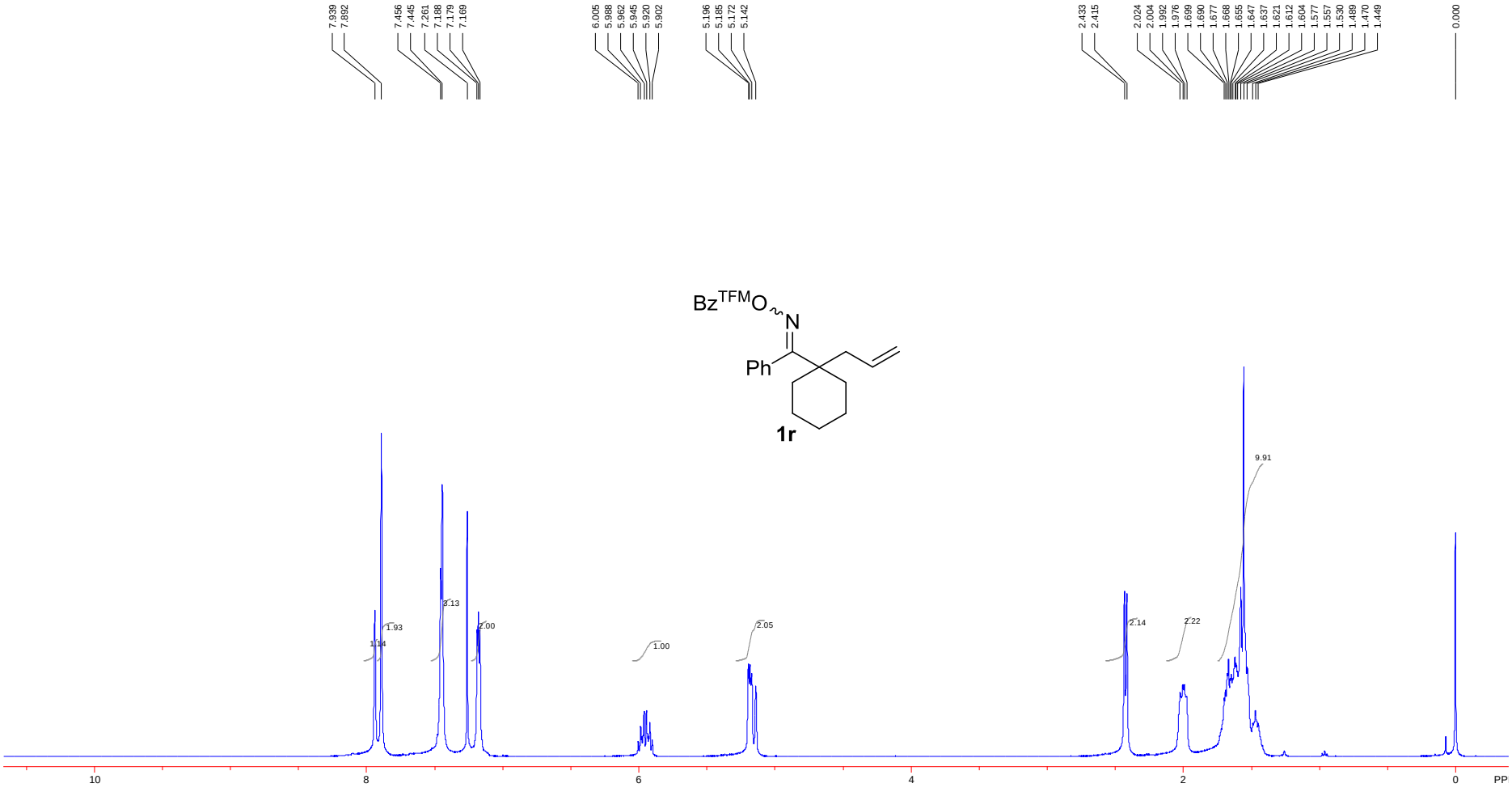

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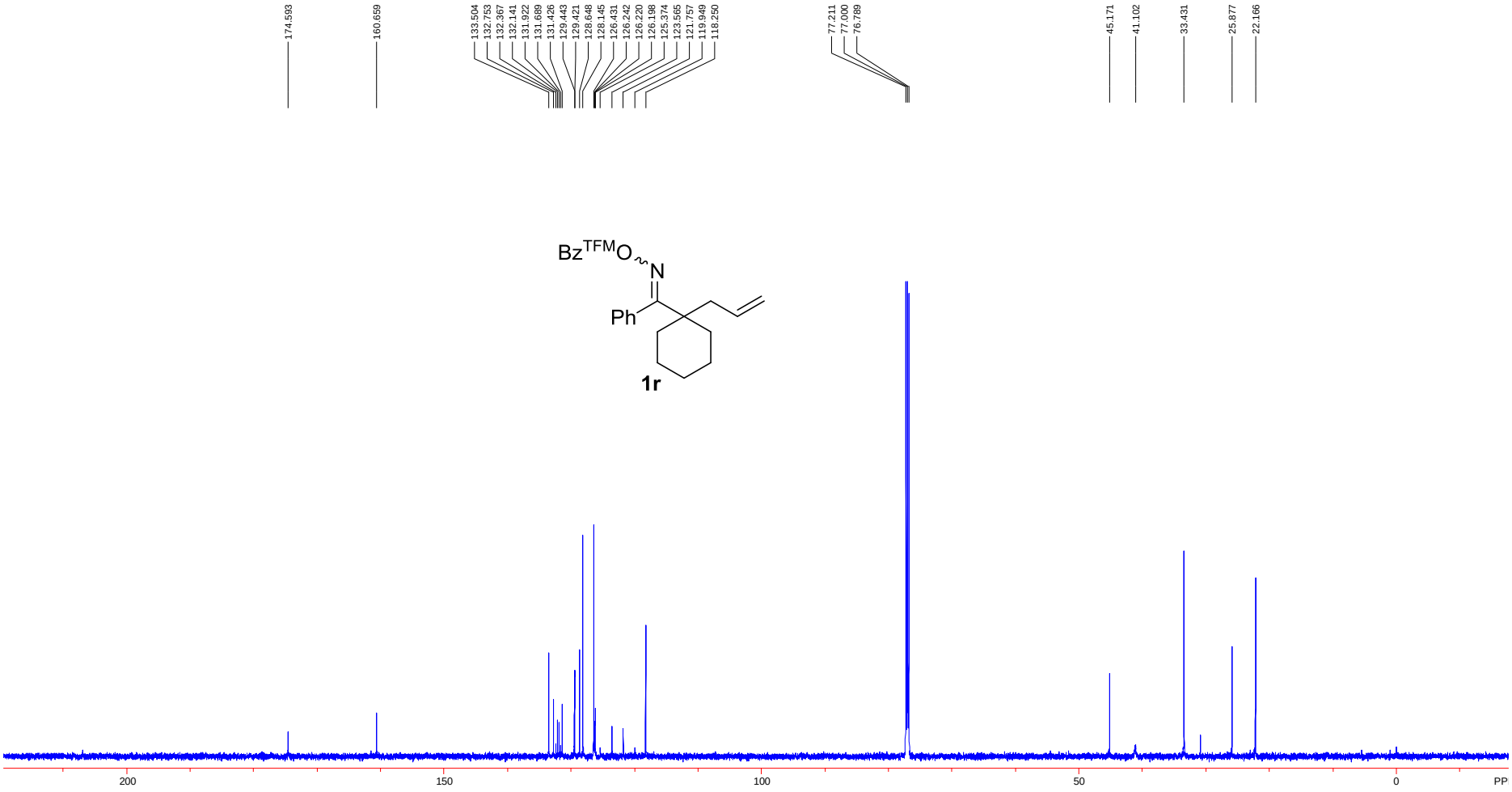

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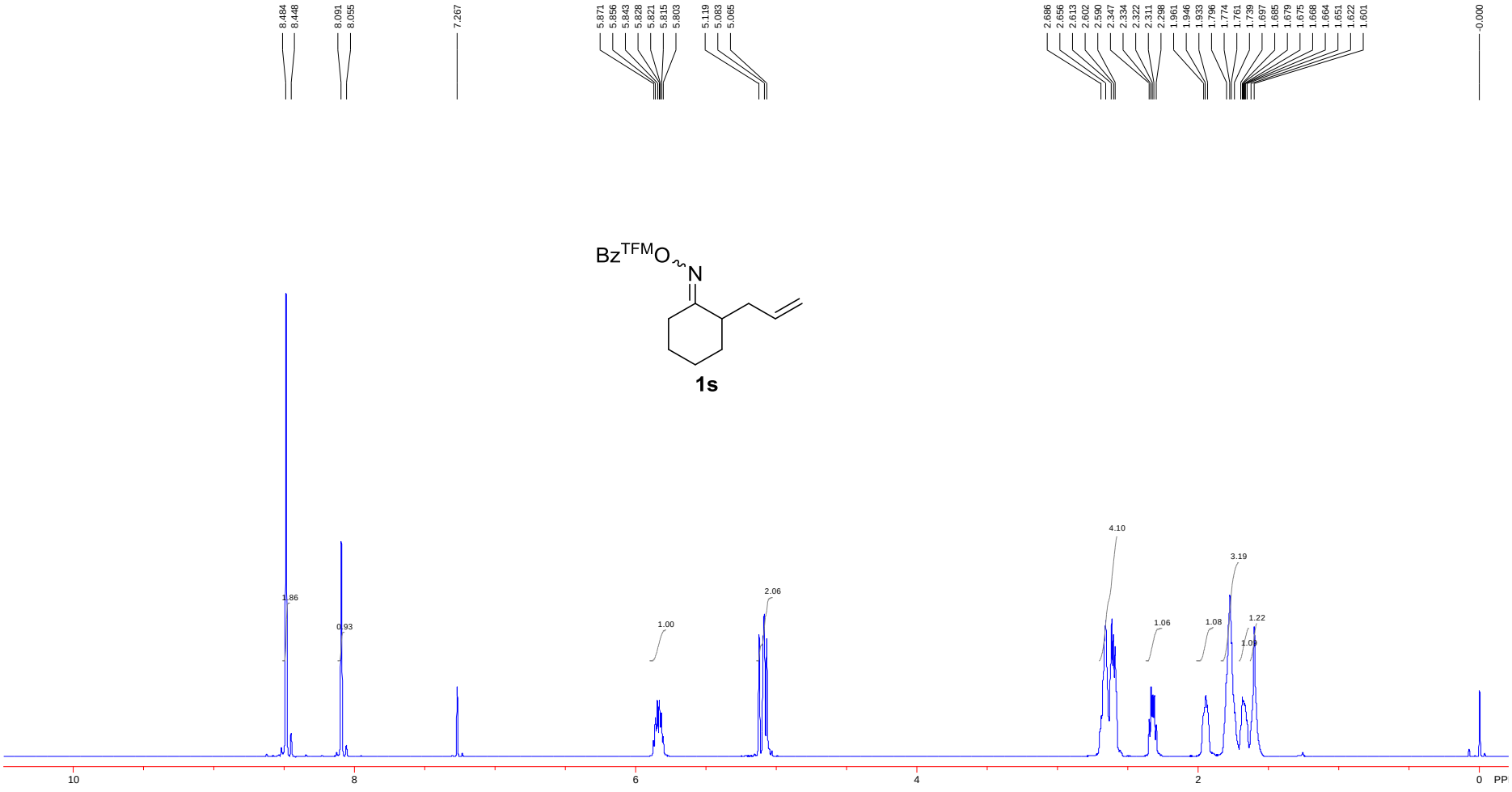

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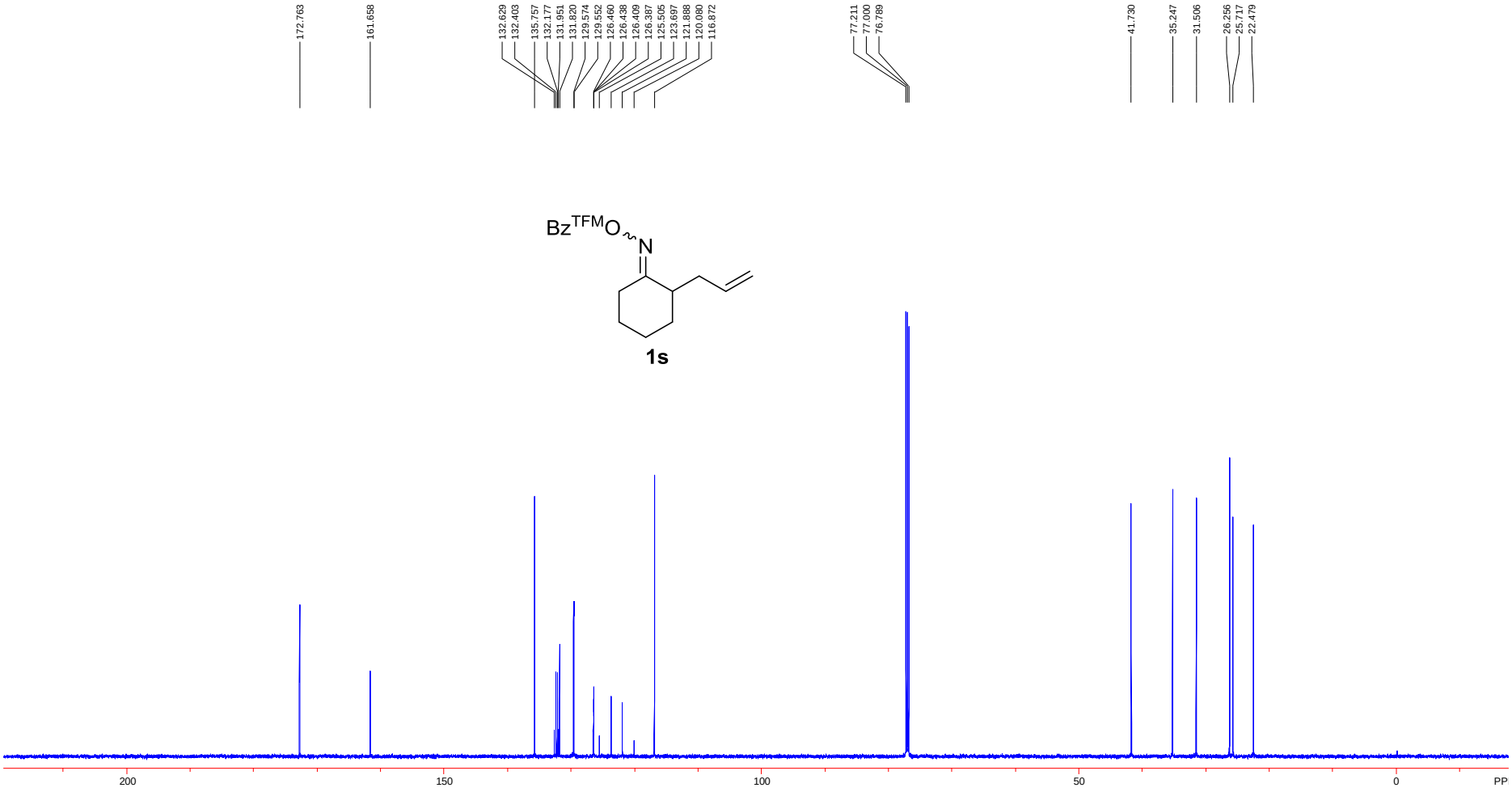
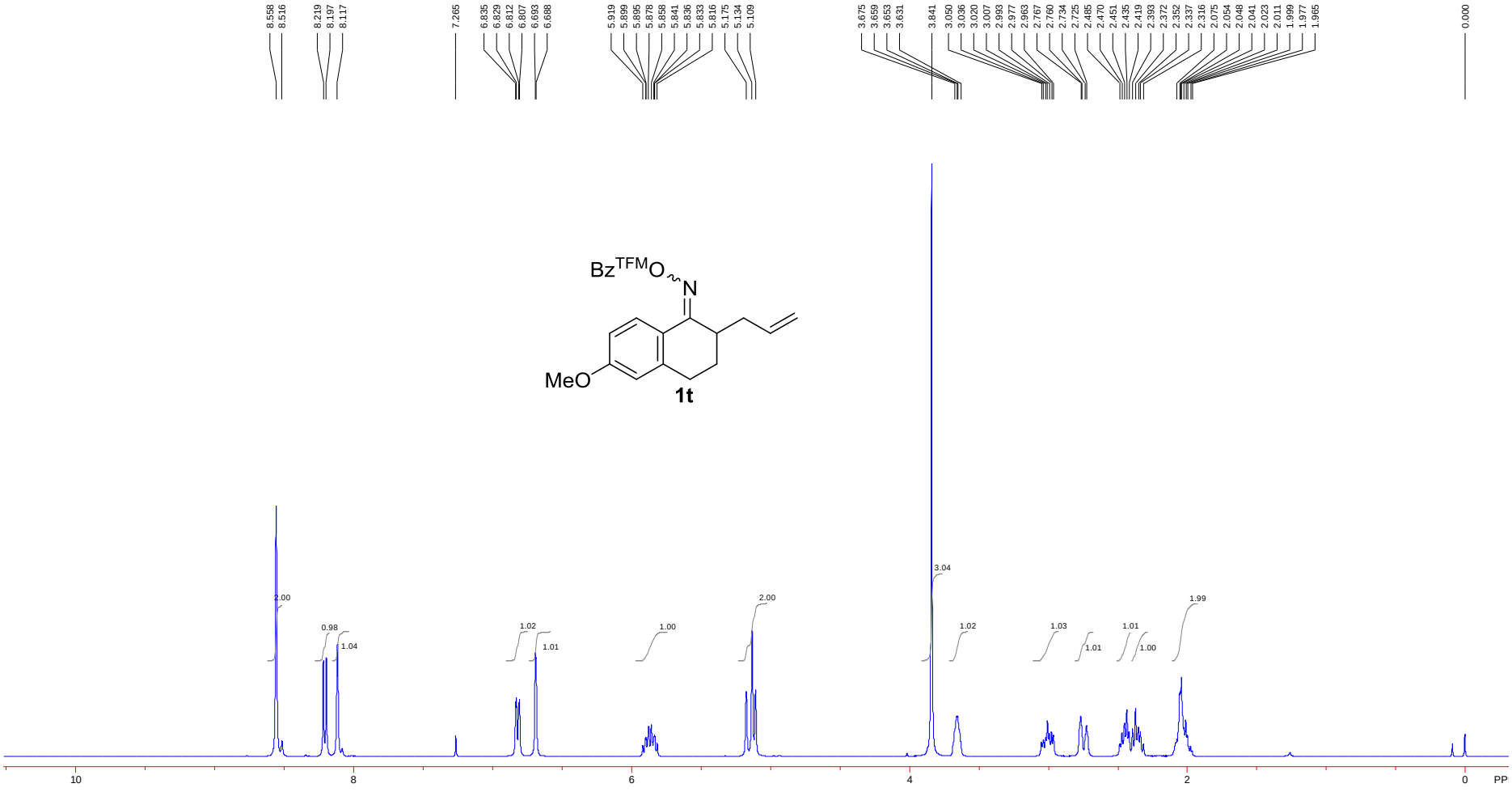
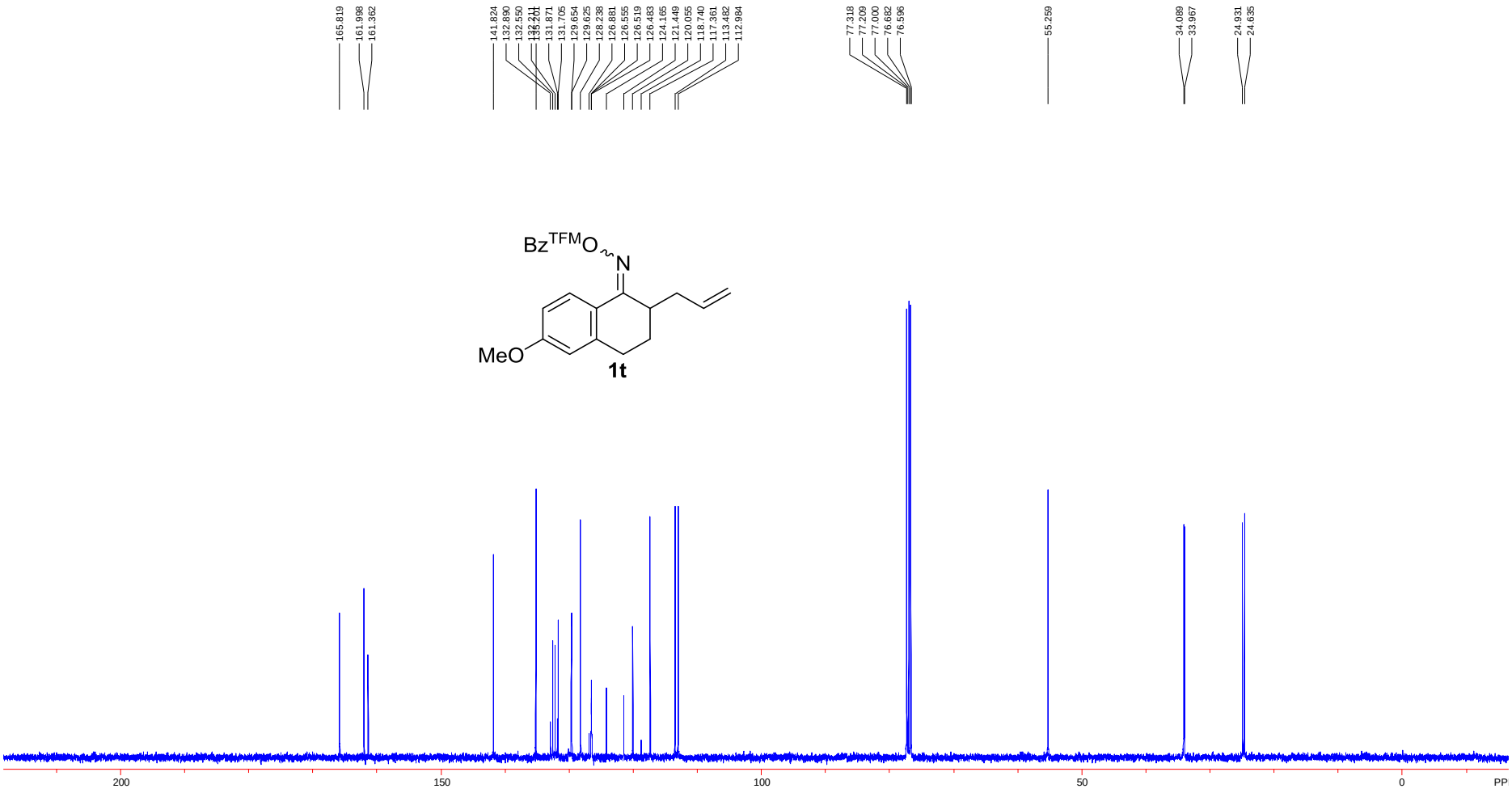


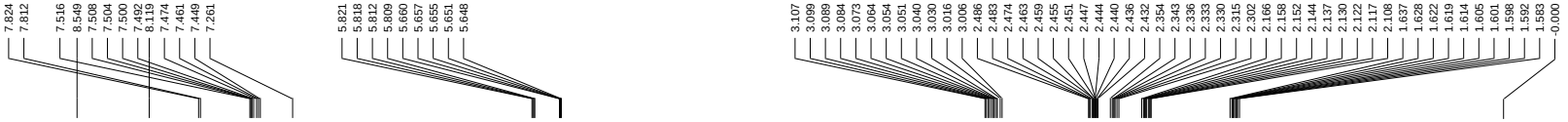
^{1}H NMR(400 MHz, $CDCl_3$)

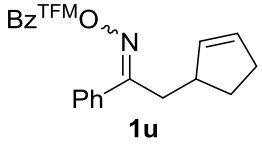


^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(600 MHz, $CDCl_3$)





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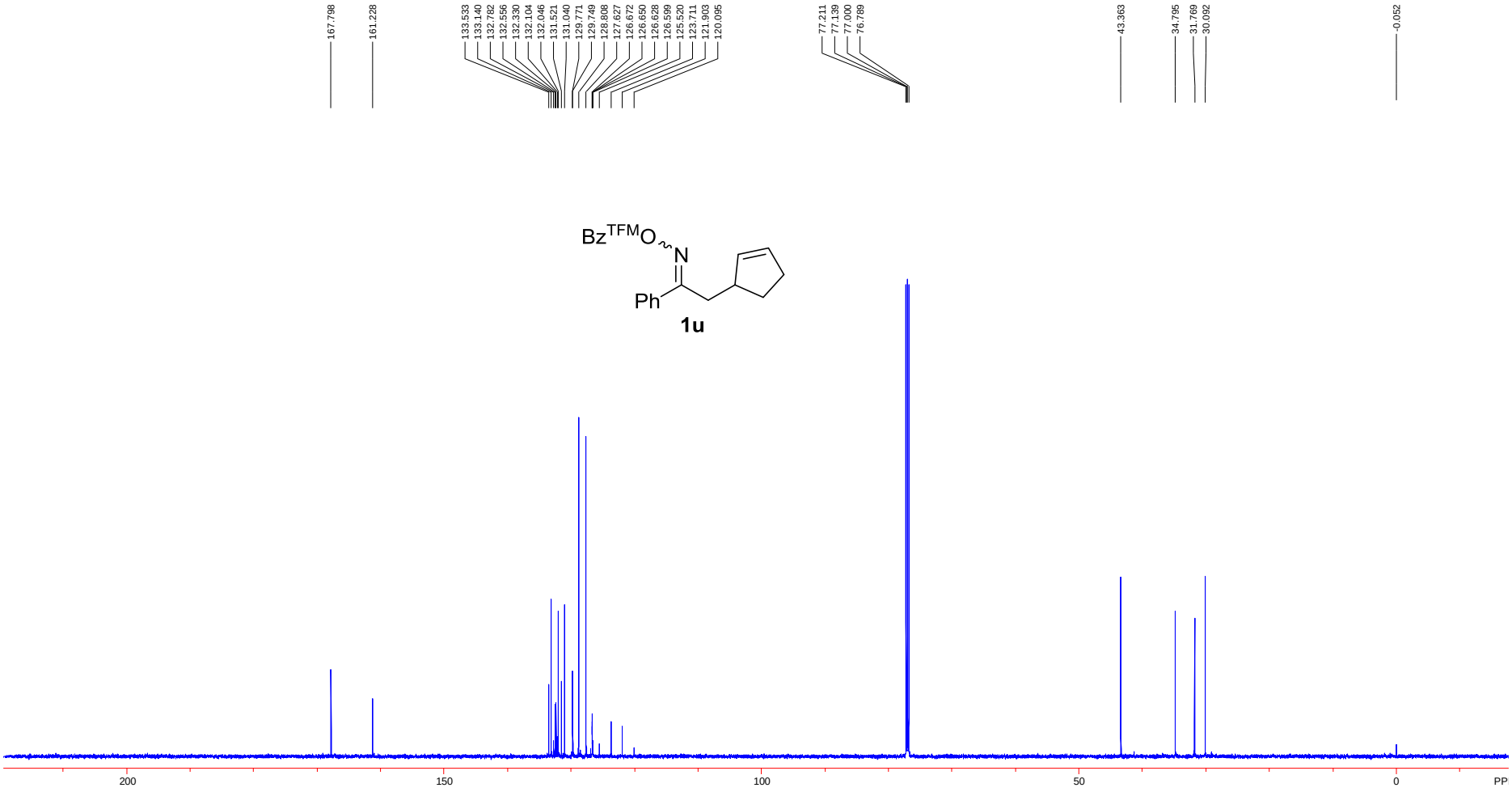
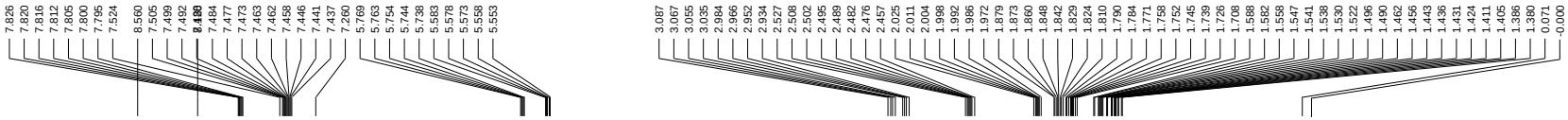
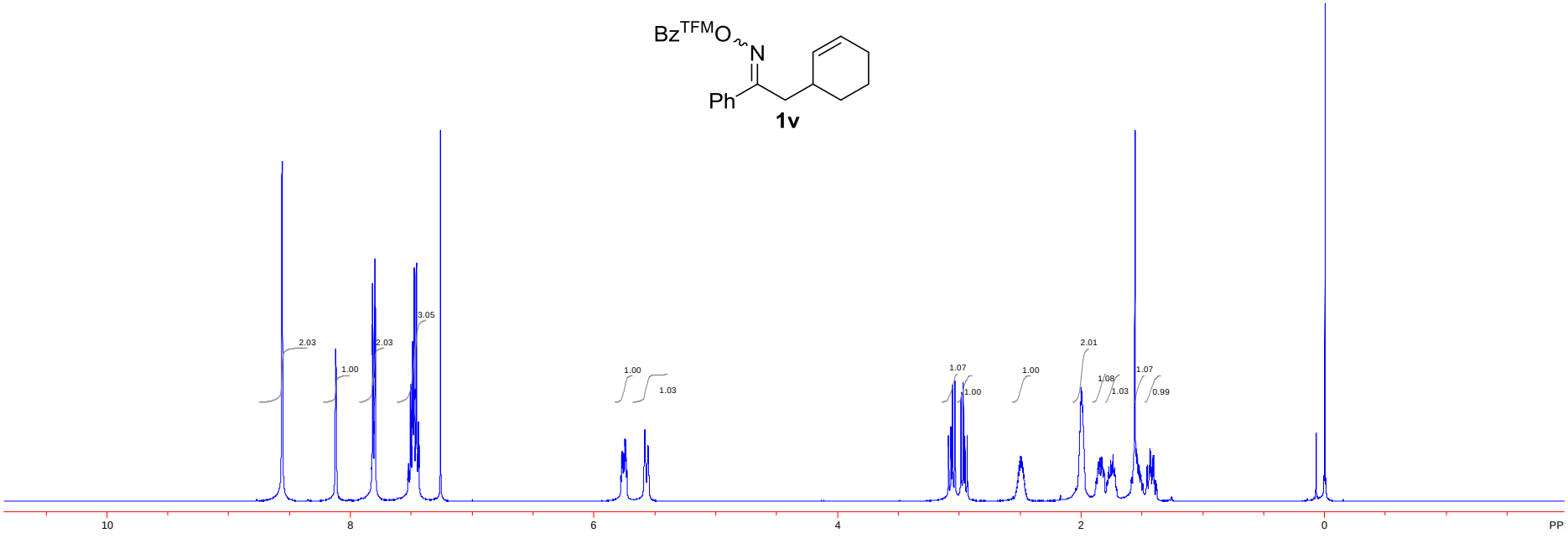
^{13}C NMR(151 MHz, $CDCl_3$)

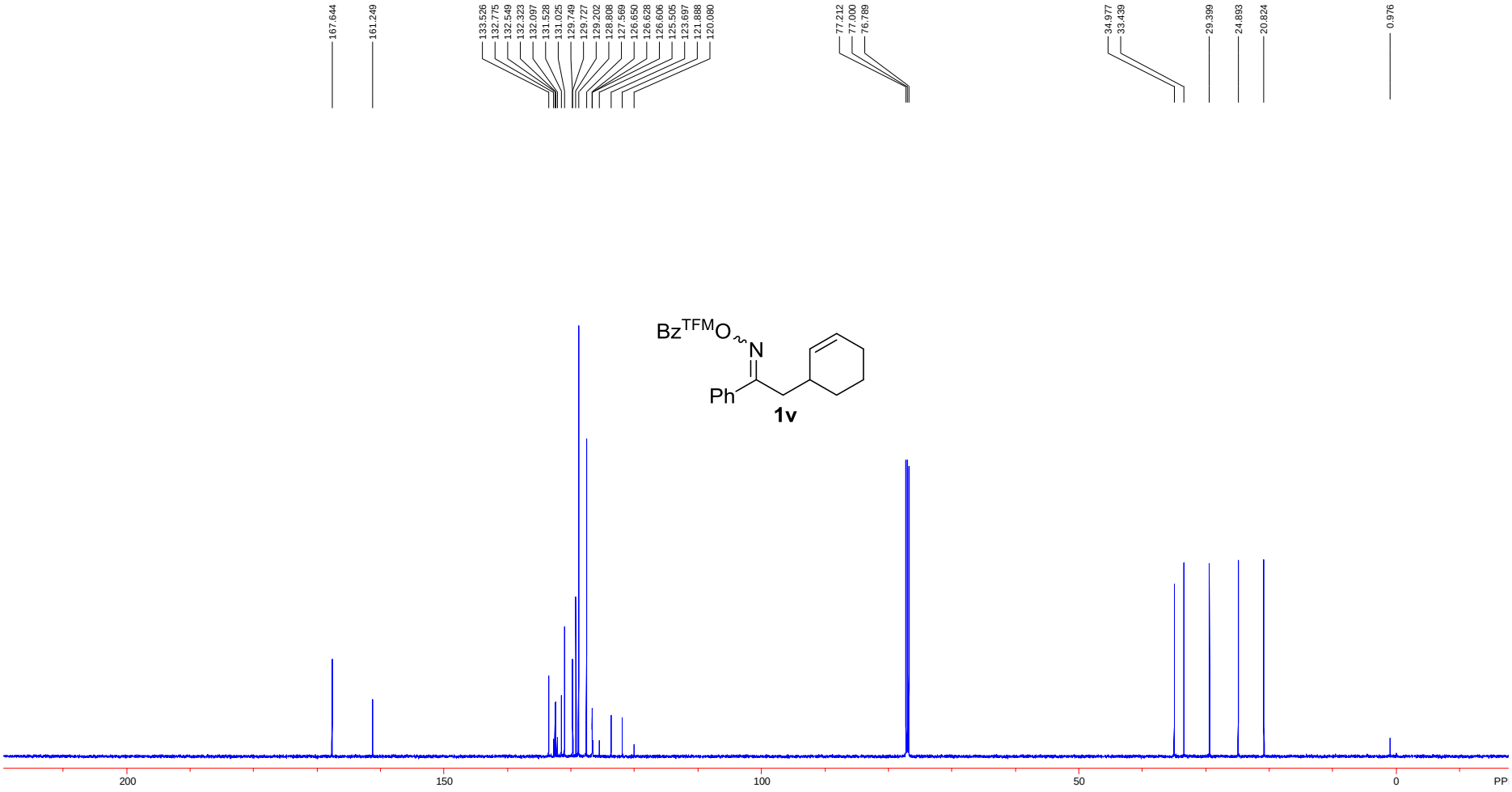


^{1}H NMR(400 MHz, $CDCl_3$)

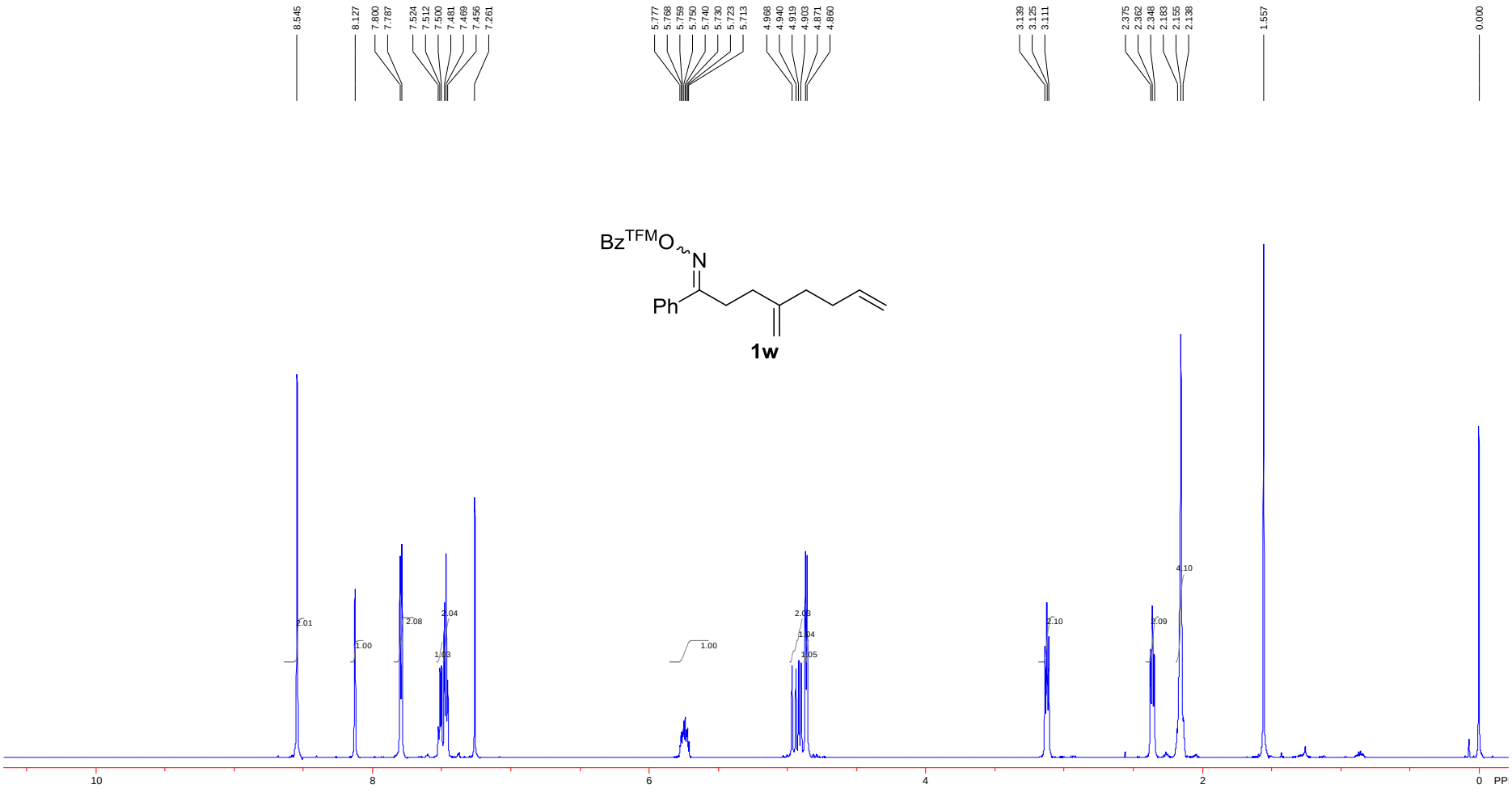




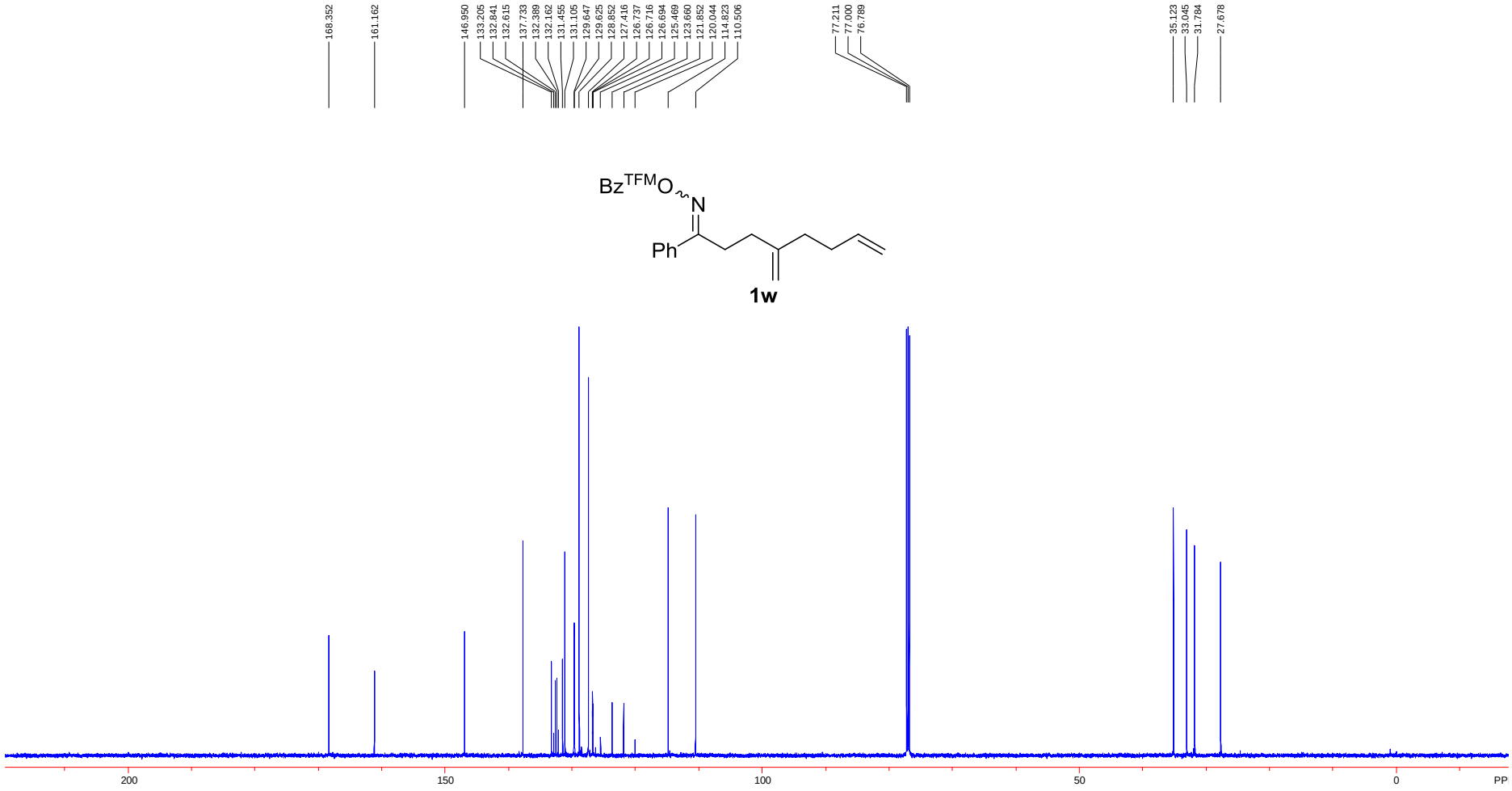
^{13}C NMR(151 MHz, $CDCl_3$)



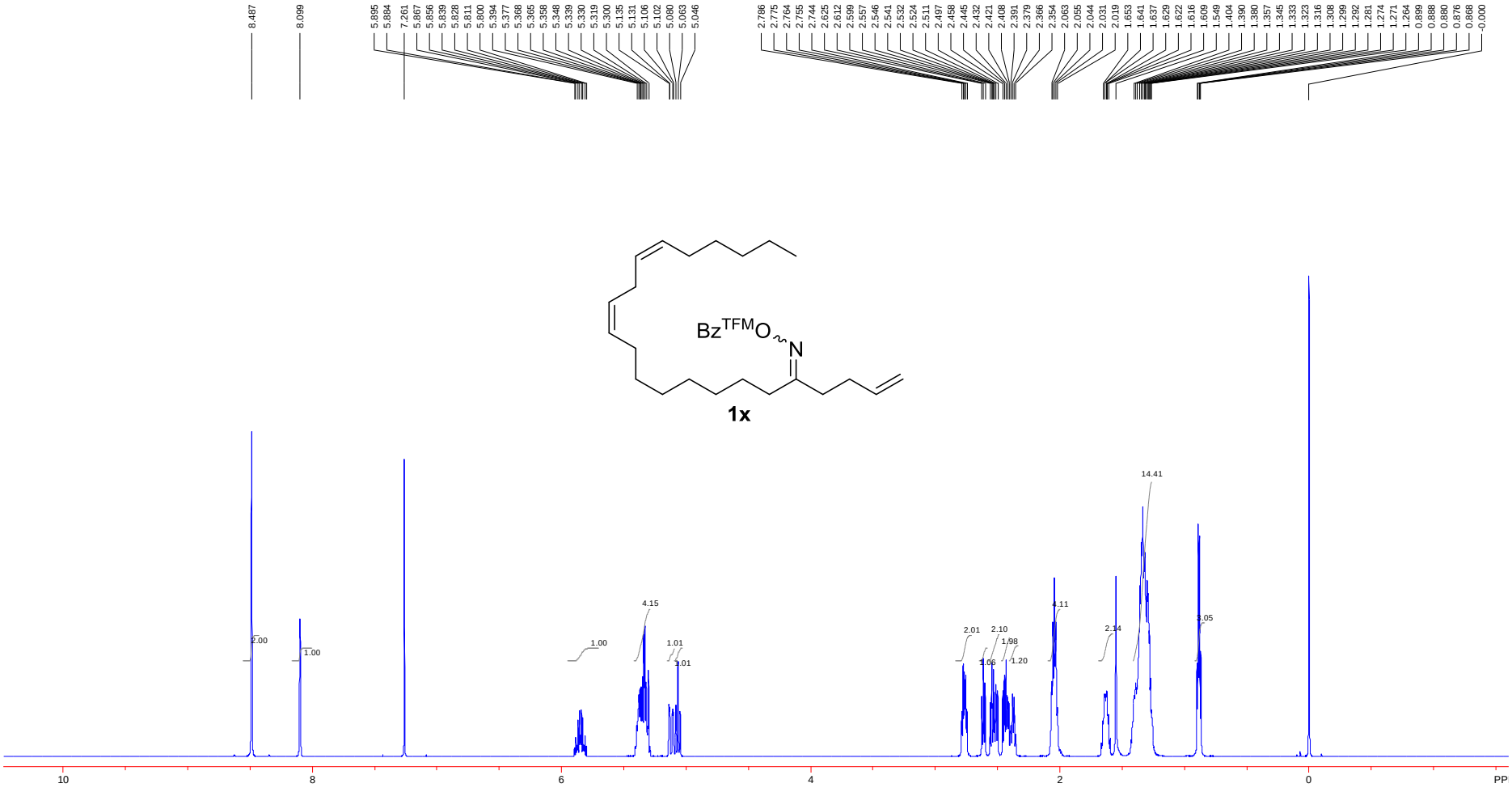
^{1}H NMR(600 MHz, $CDCl_3$)



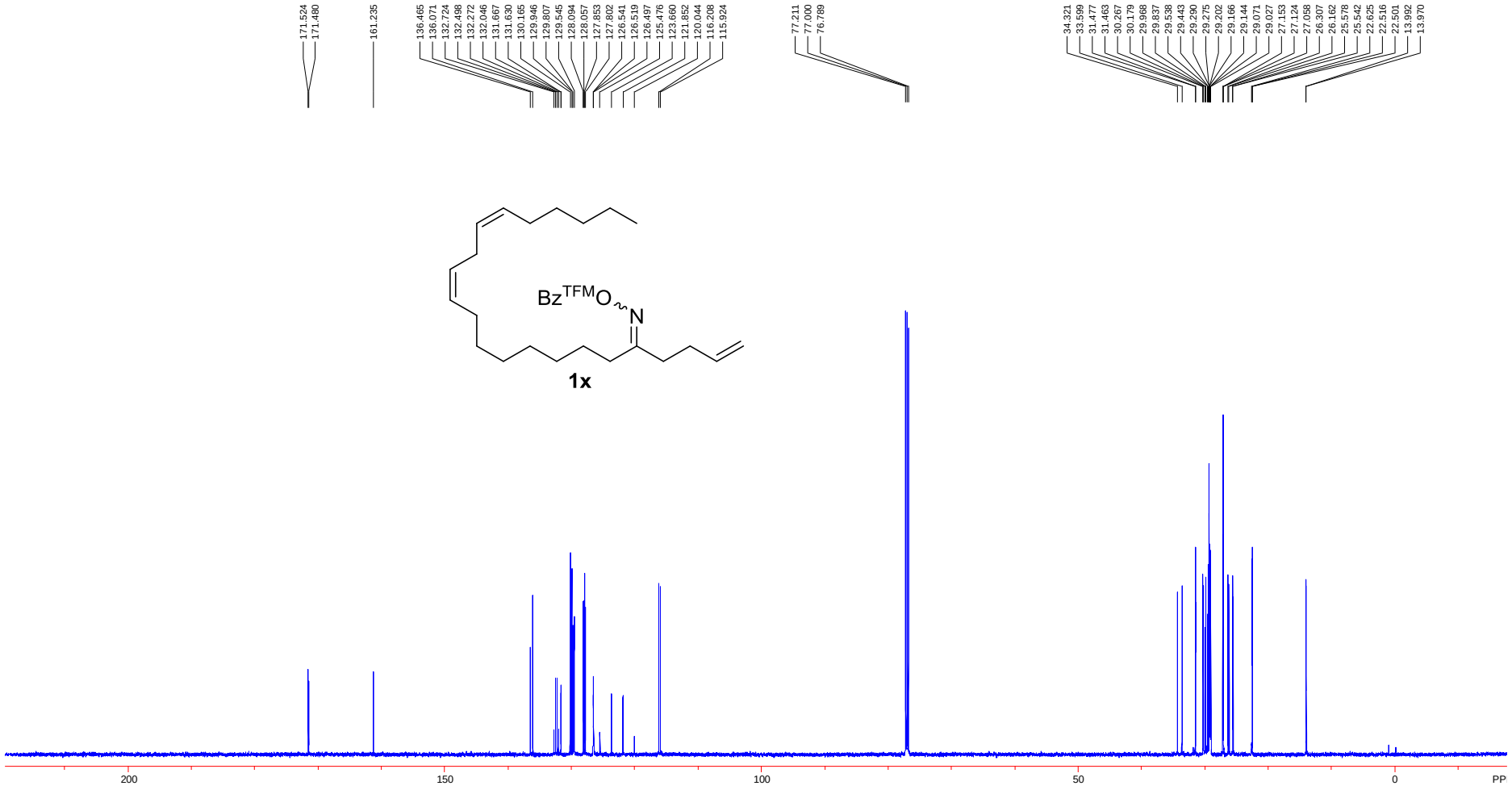
^{13}C NMR(151 MHz, $CDCl_3$)



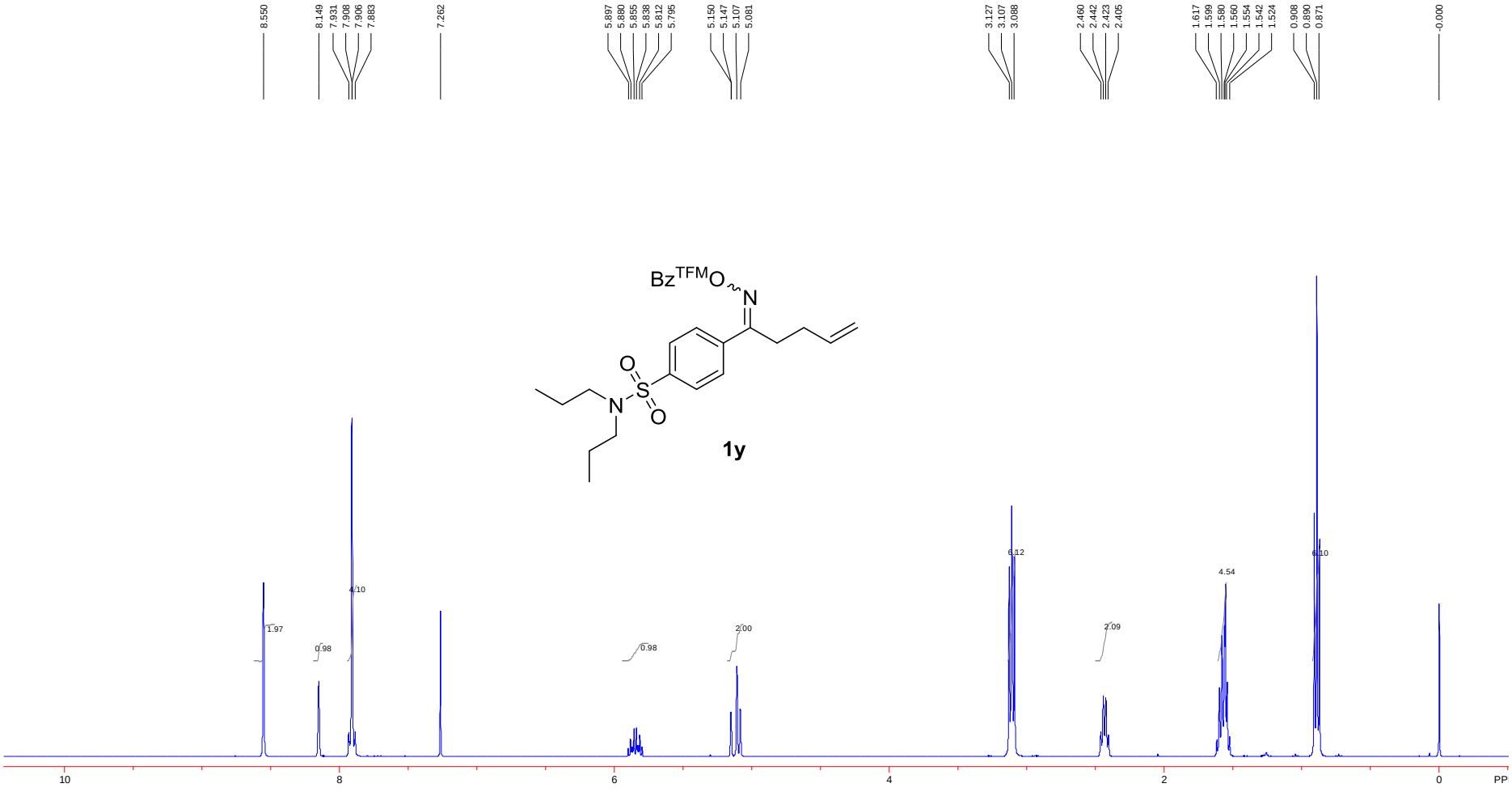
^{1}H NMR(600 MHz, $CDCl_3$)



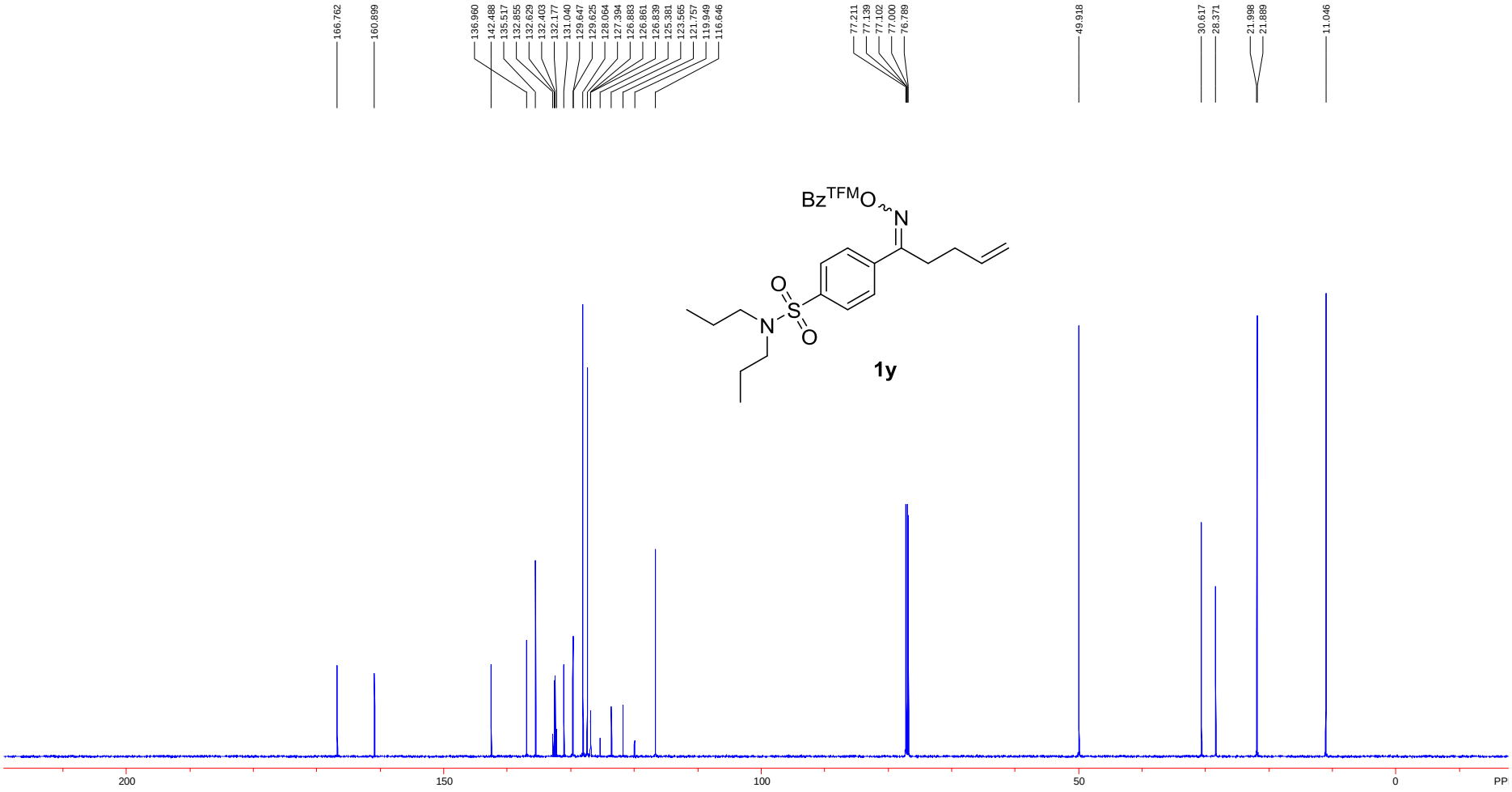
^{13}C NMR(151 MHz, $CDCl_3$)



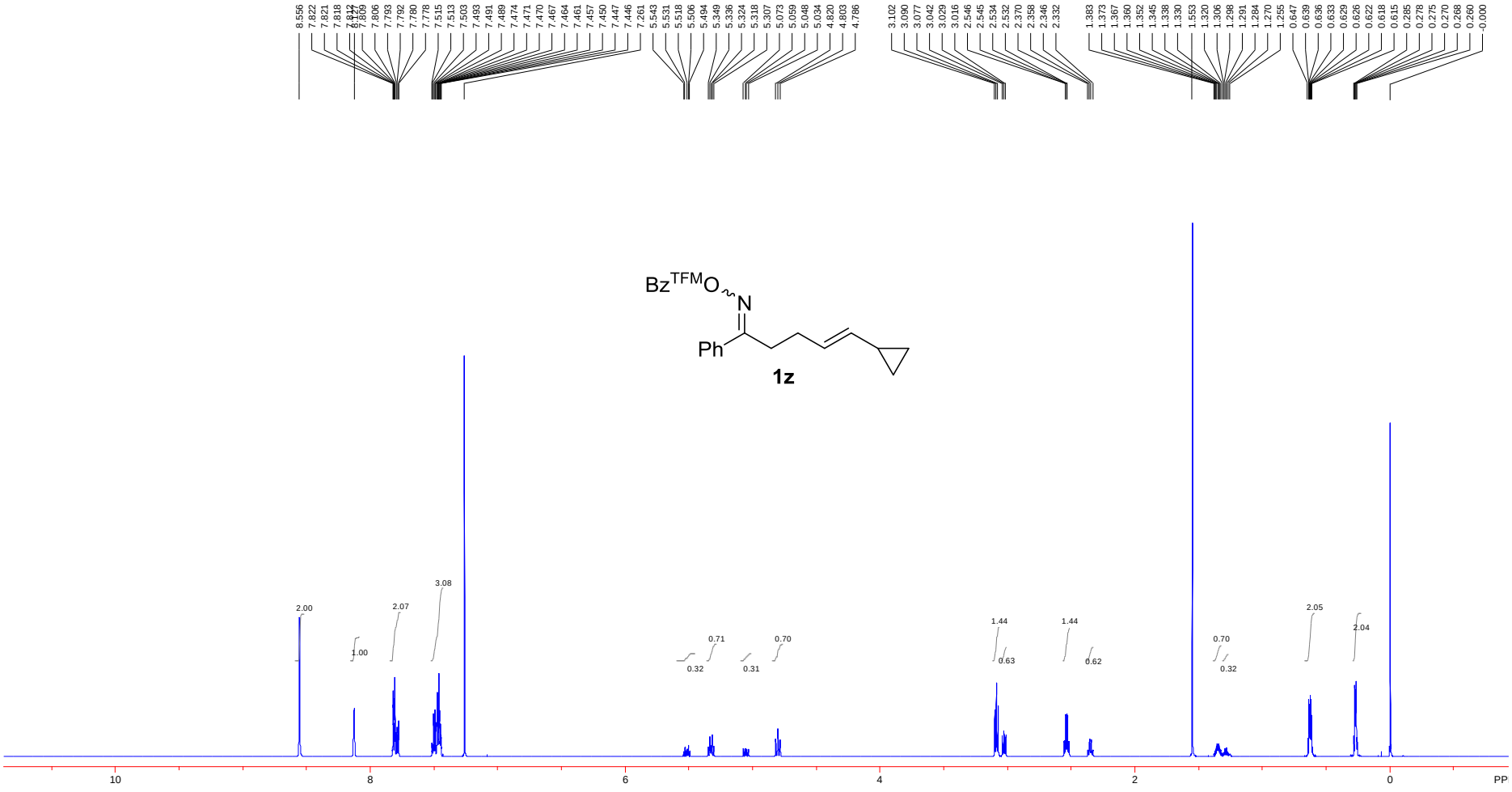
^{1}H NMR(400 MHz, $CDCl_3$)



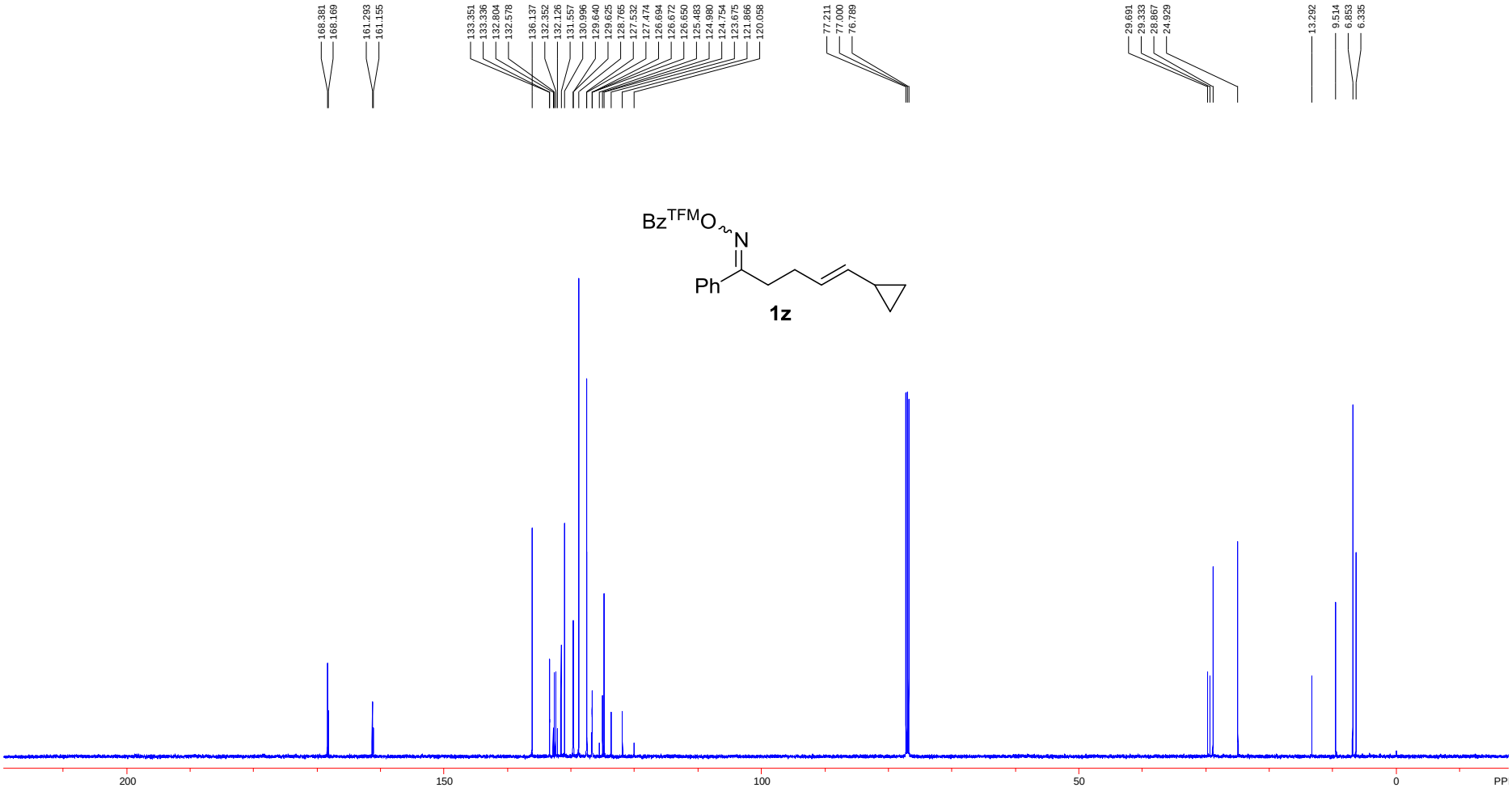
^{13}C NMR(151 MHz, $CDCl_3$)



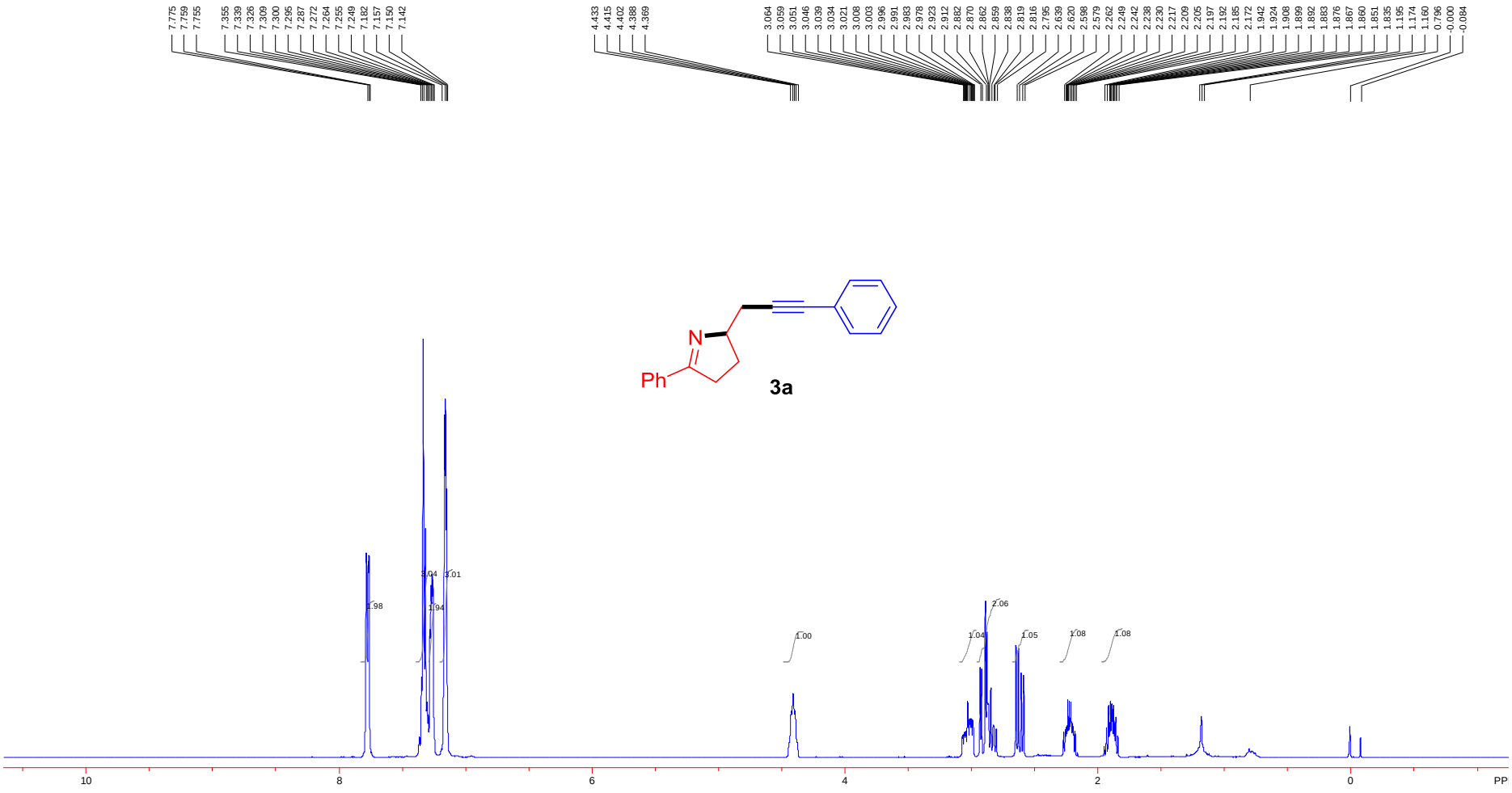
^{1}H NMR(600 MHz, $CDCl_3$)



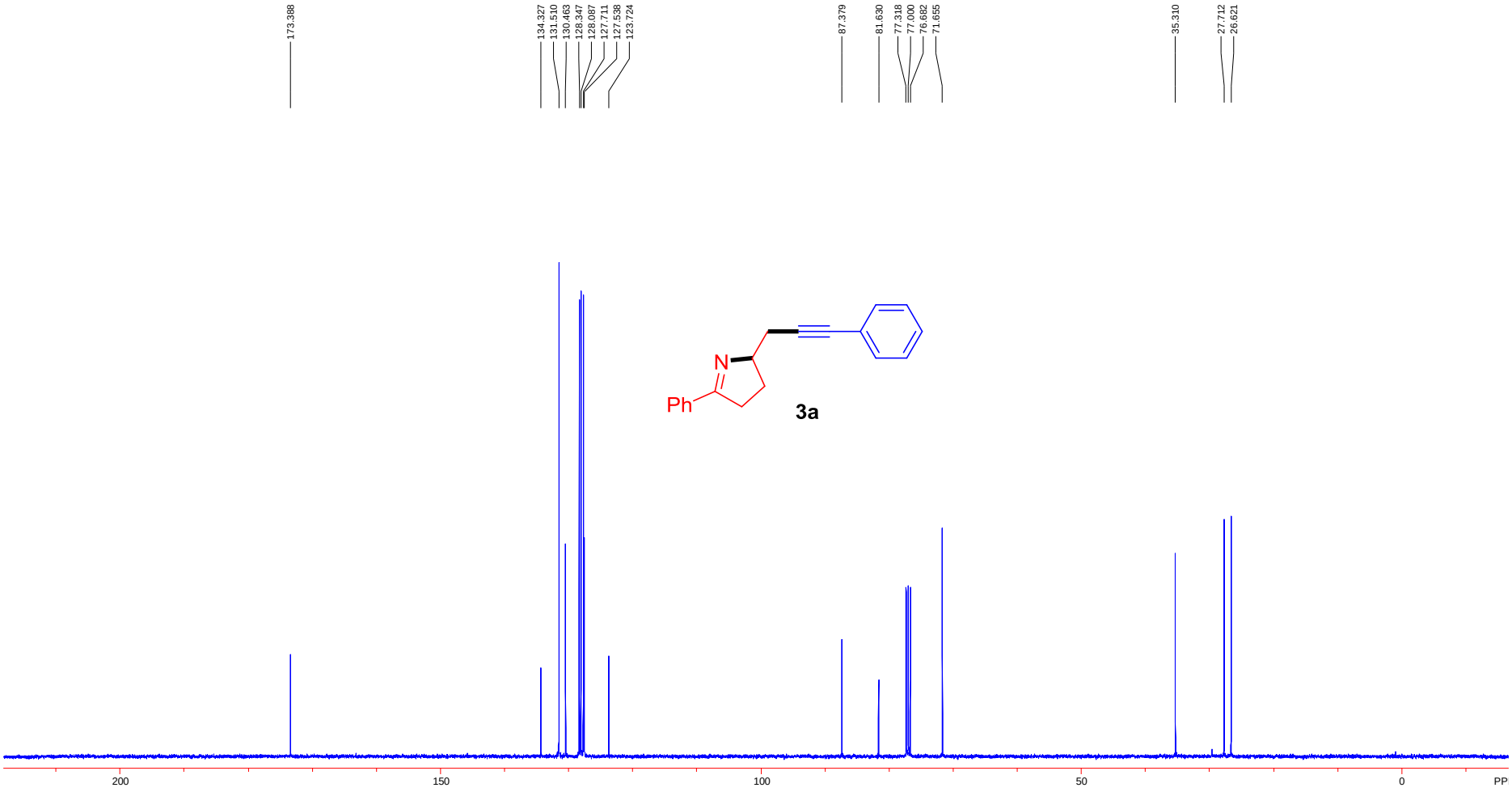
^{13}C NMR(151 MHz, $CDCl_3$)



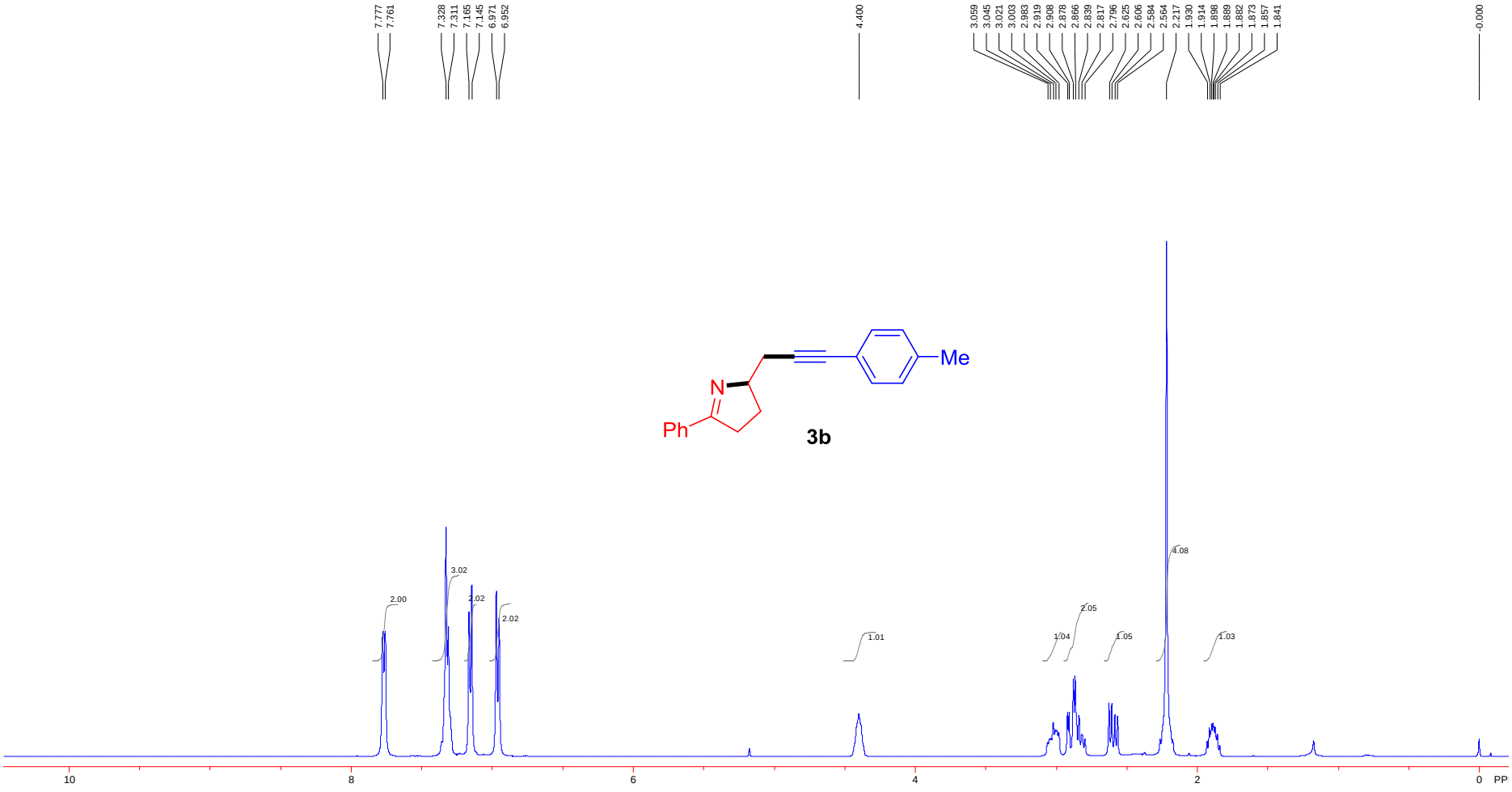
^{1}H NMR(400 MHz, $CDCl_3$)



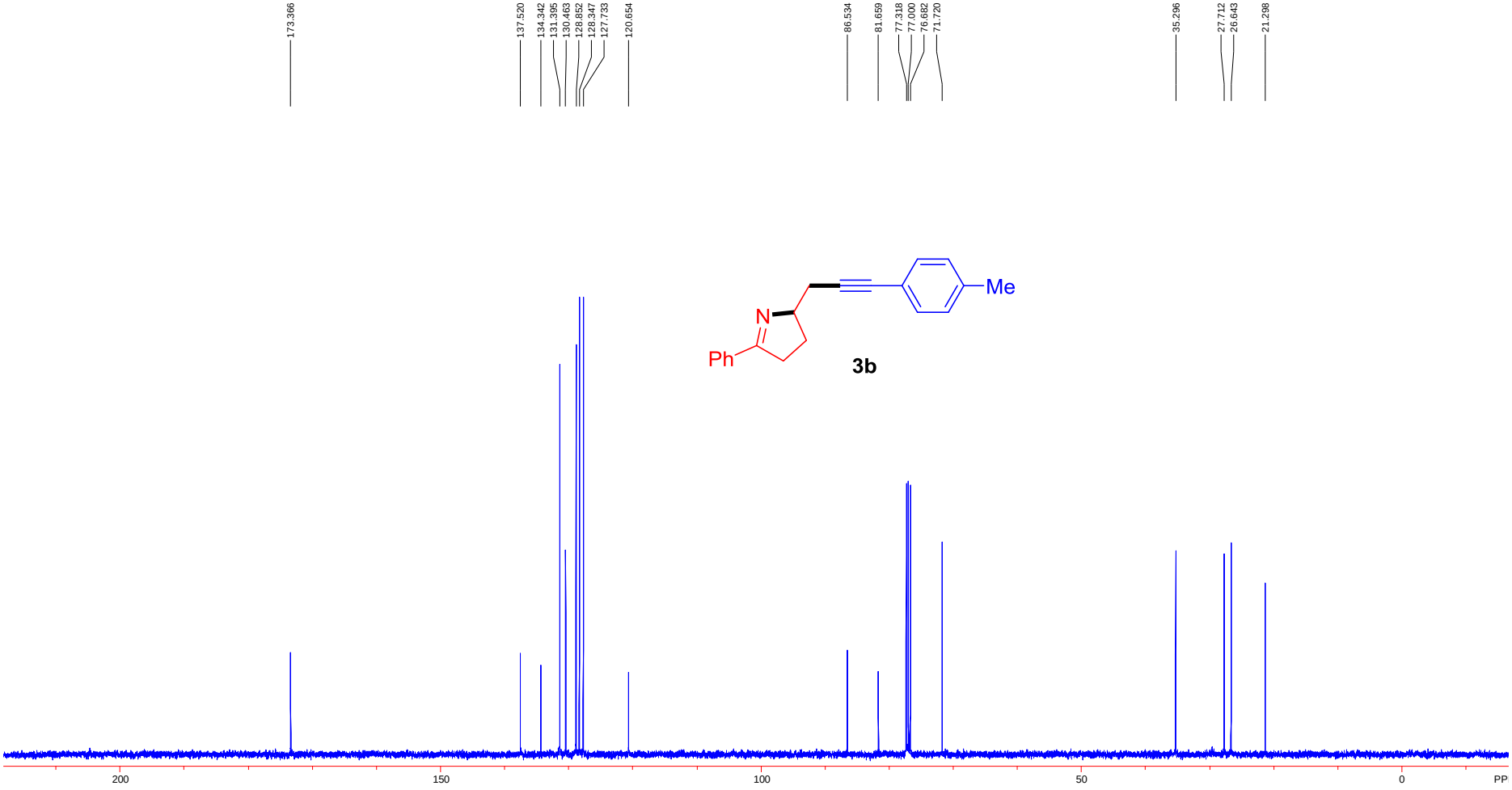
^{13}C NMR(100 MHz, $CDCl_3$)



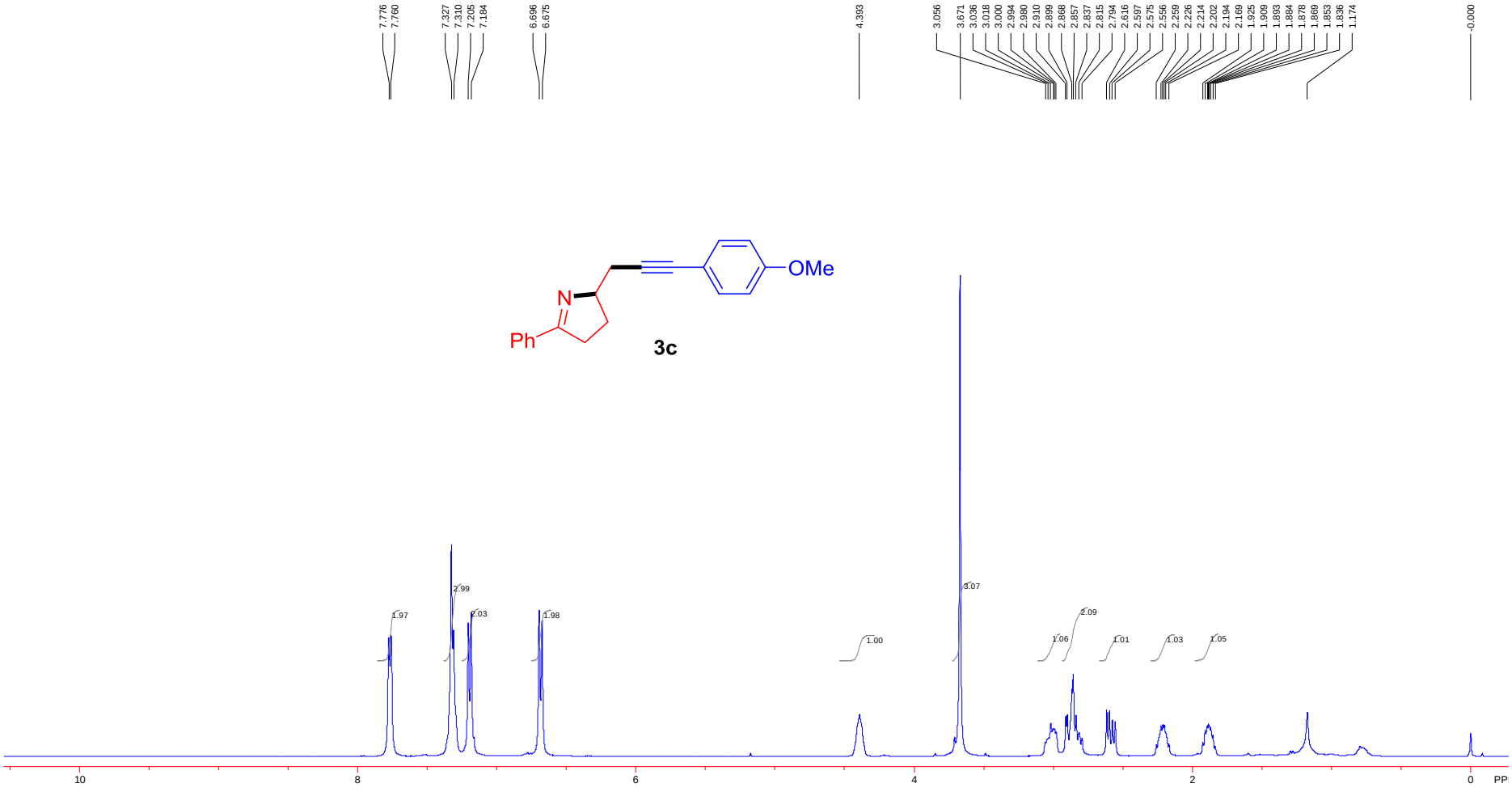
^{1}H NMR(400 MHz, $CDCl_3$)



^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



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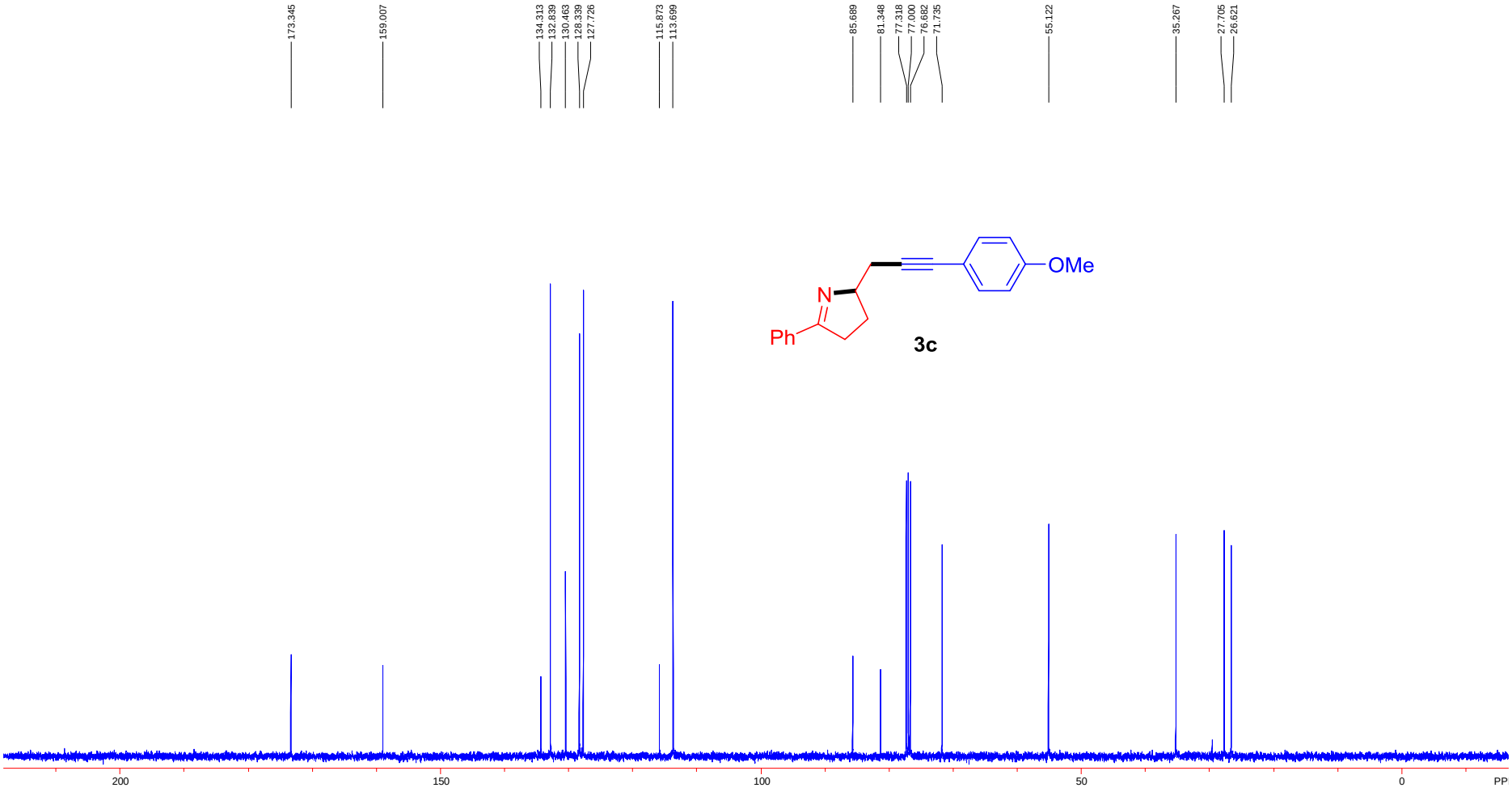

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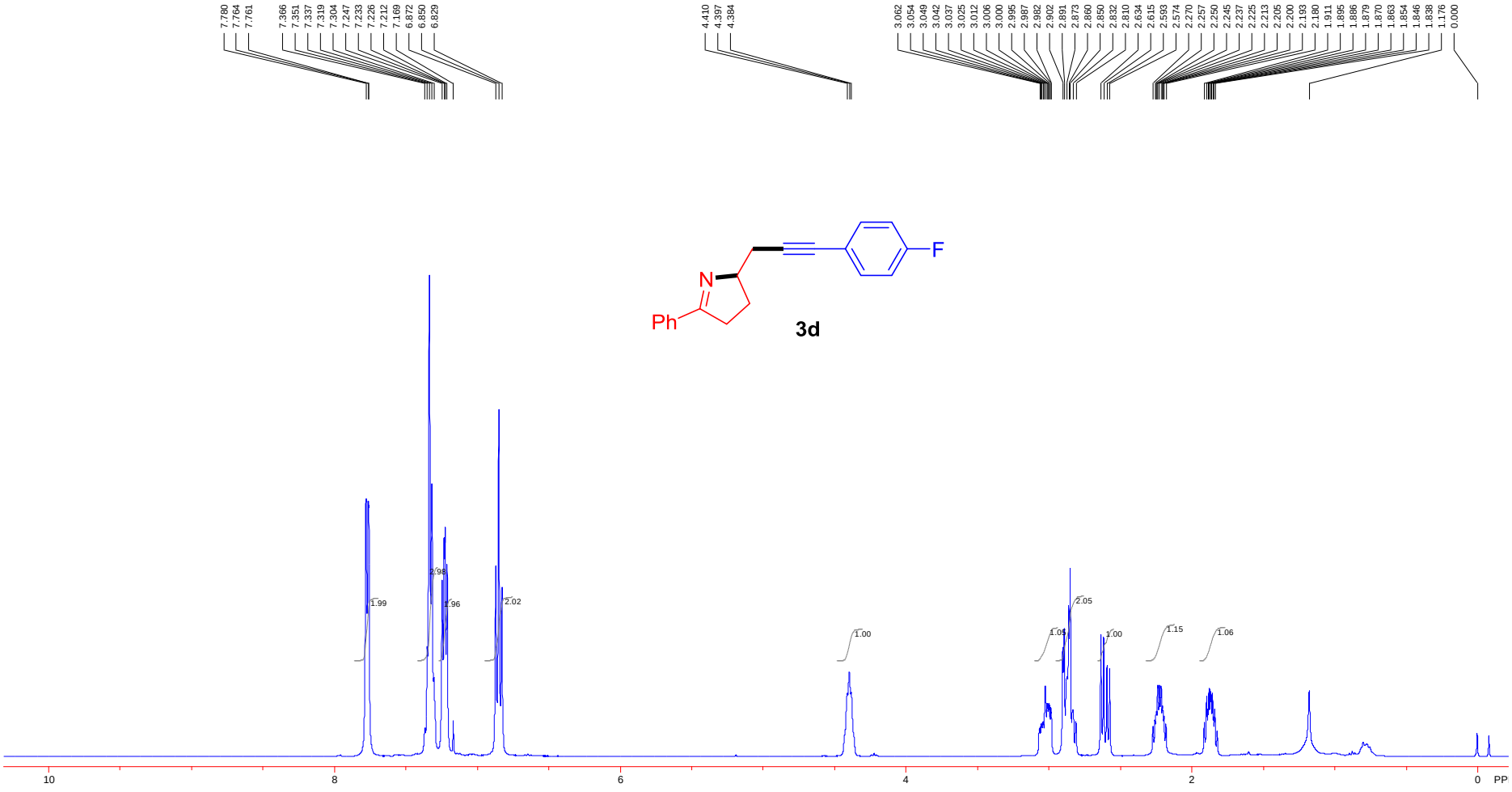
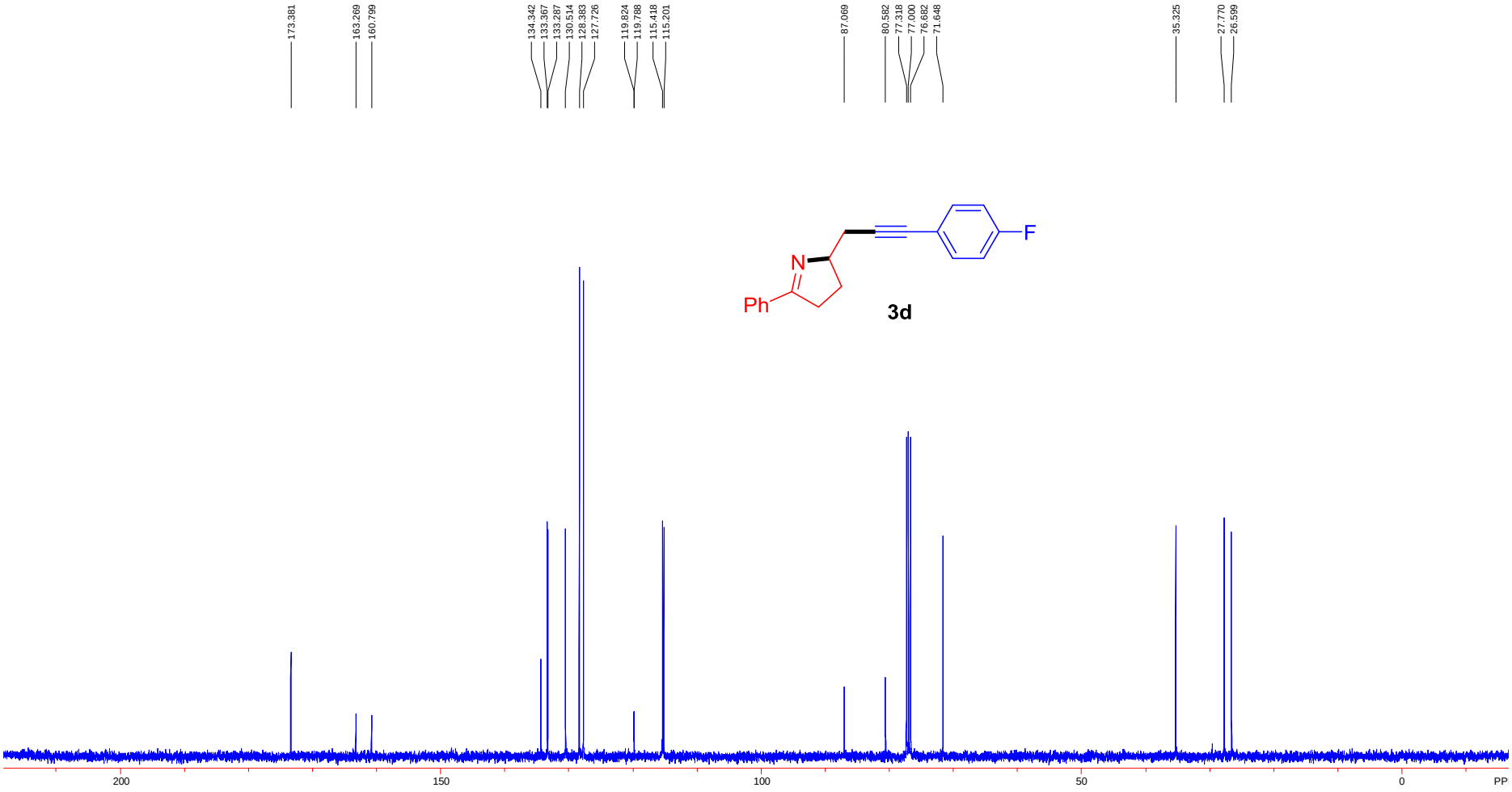


^{13}C NMR(100 MHz, $CDCl_3$)



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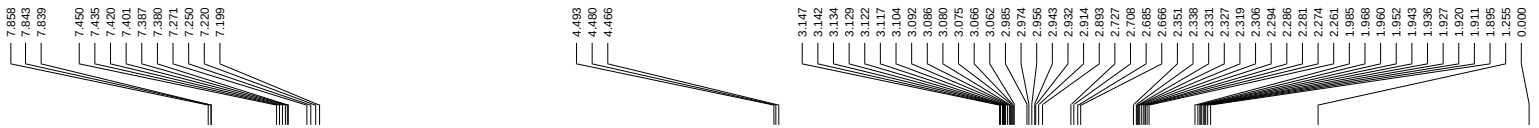
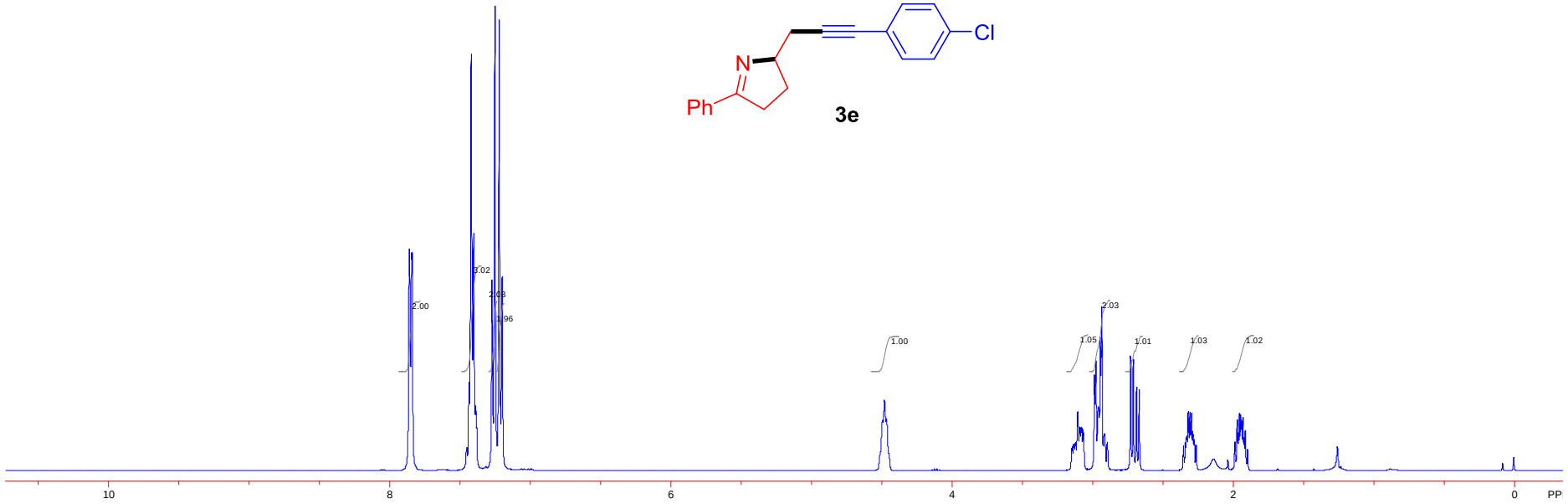
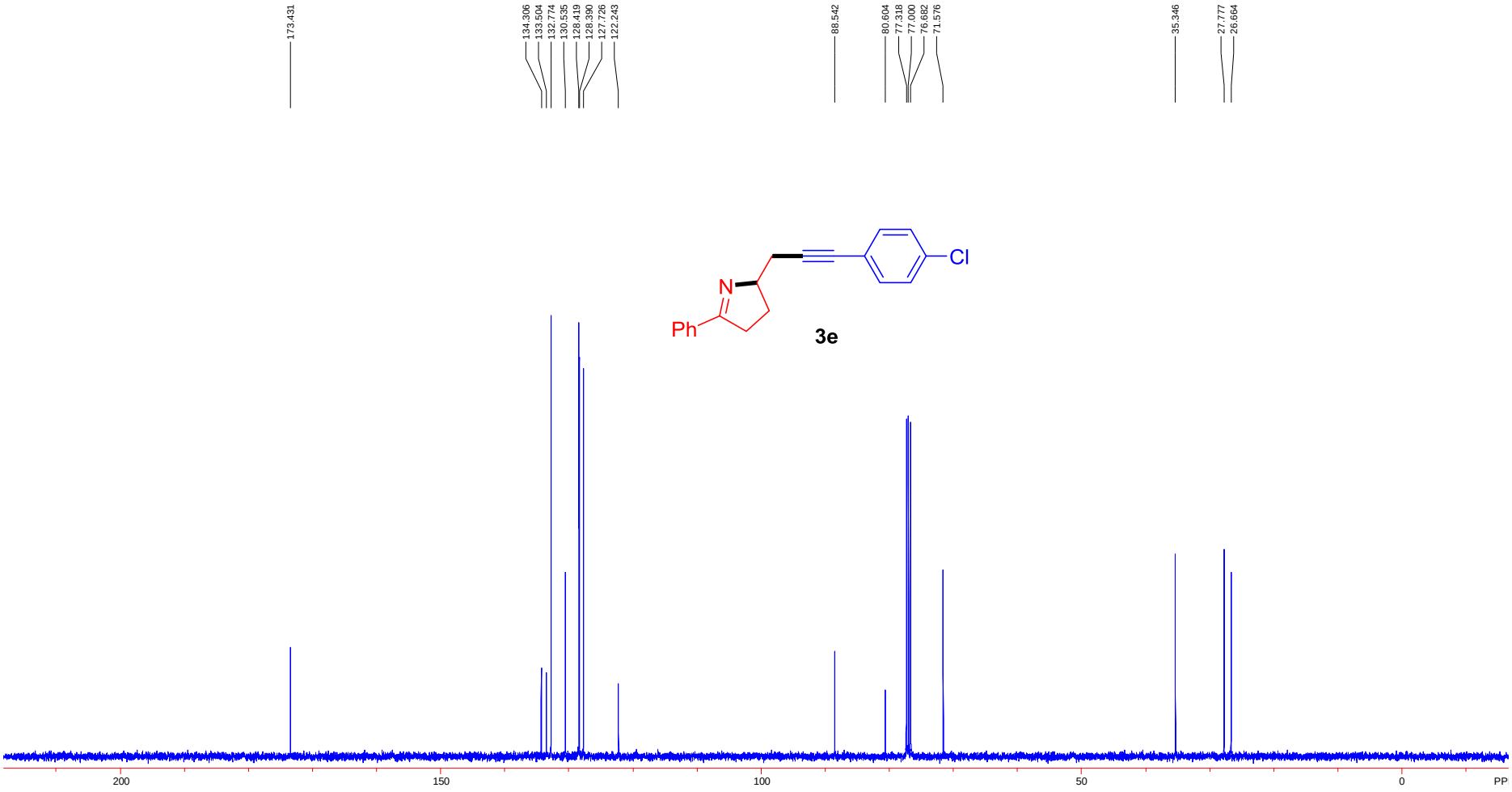




^{13}C NMR(100 MHz, $CDCl_3$)



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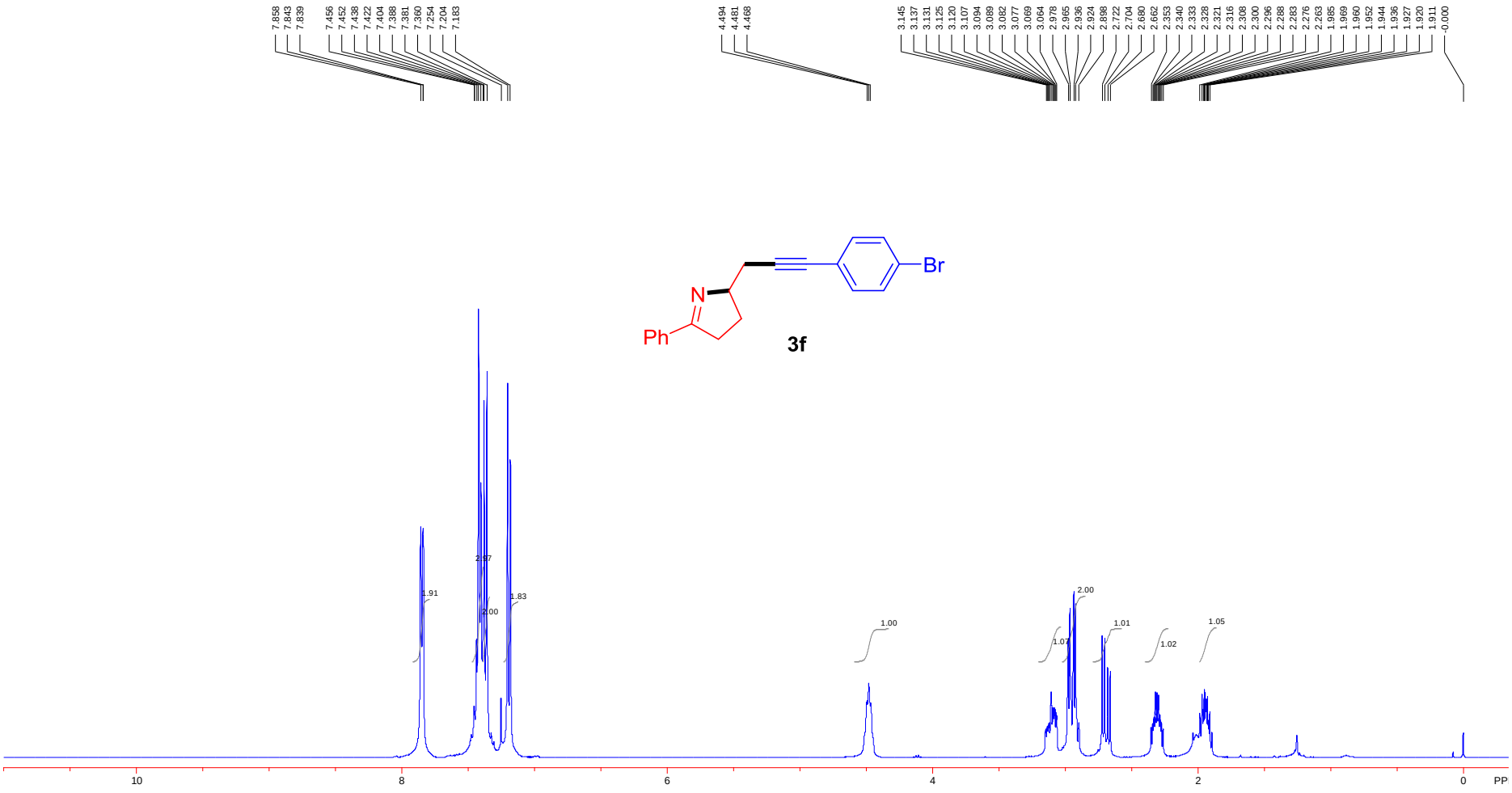
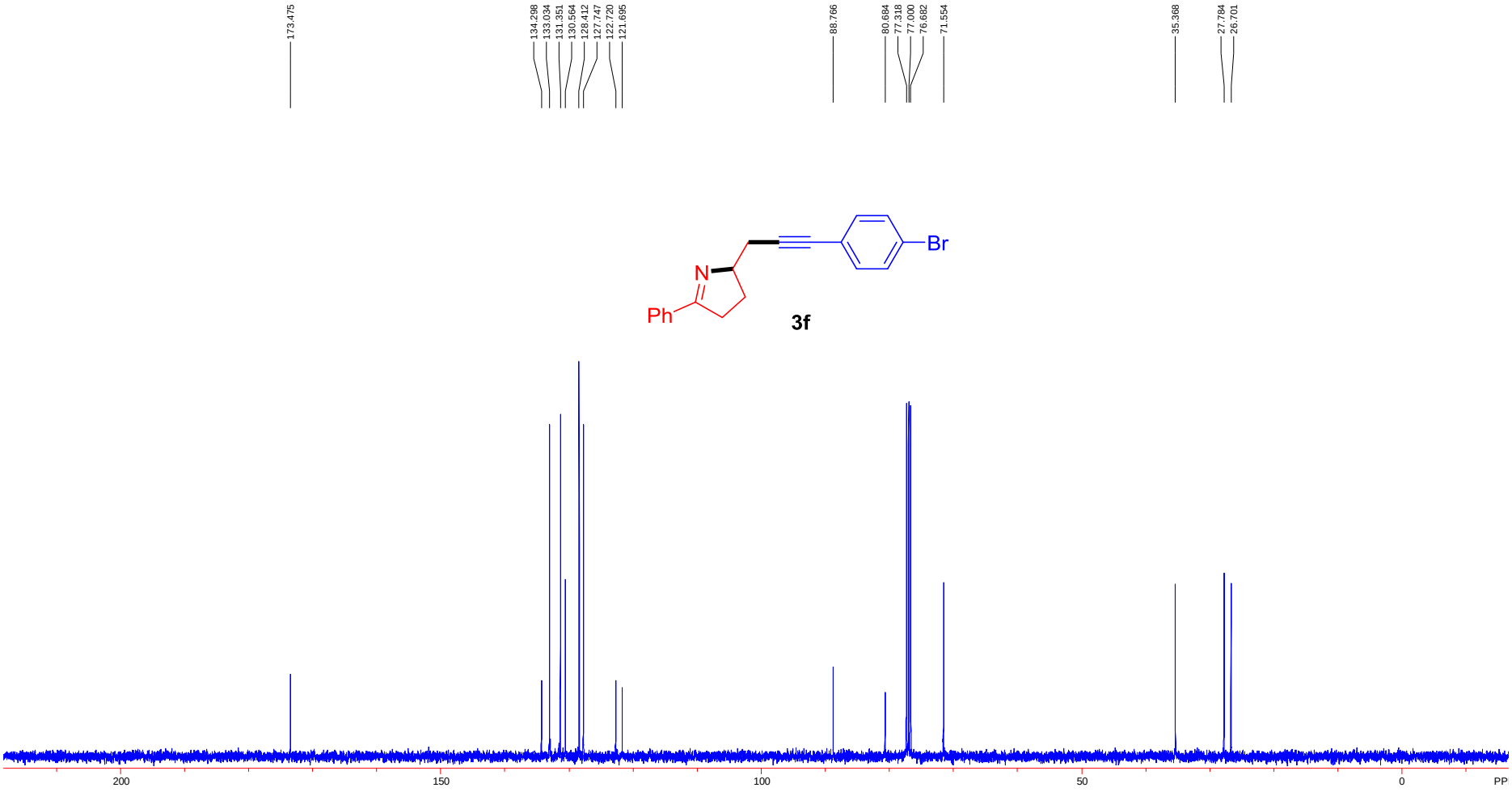


^{13}C NMR(100 MHz, $CDCl_3$)



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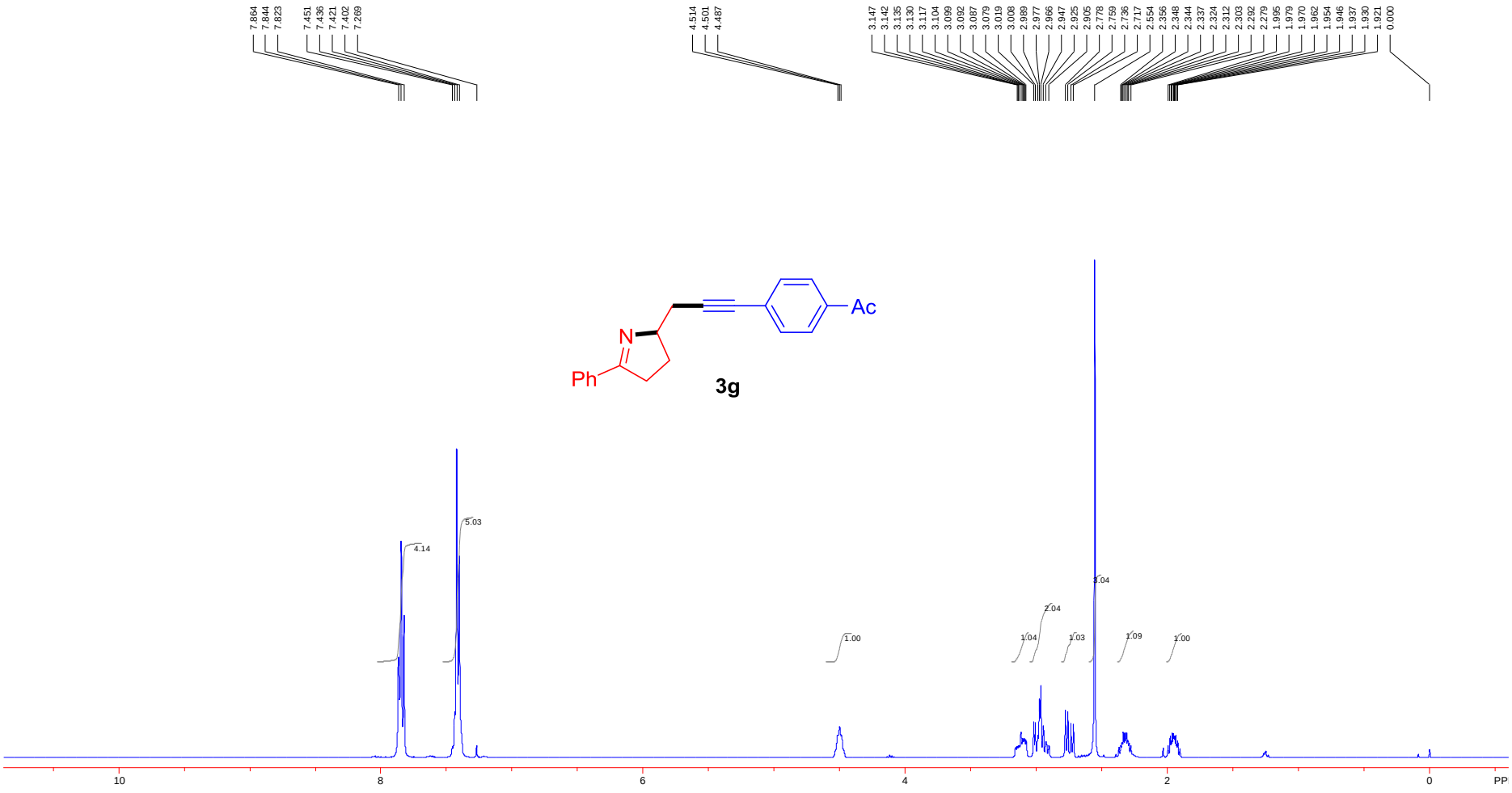
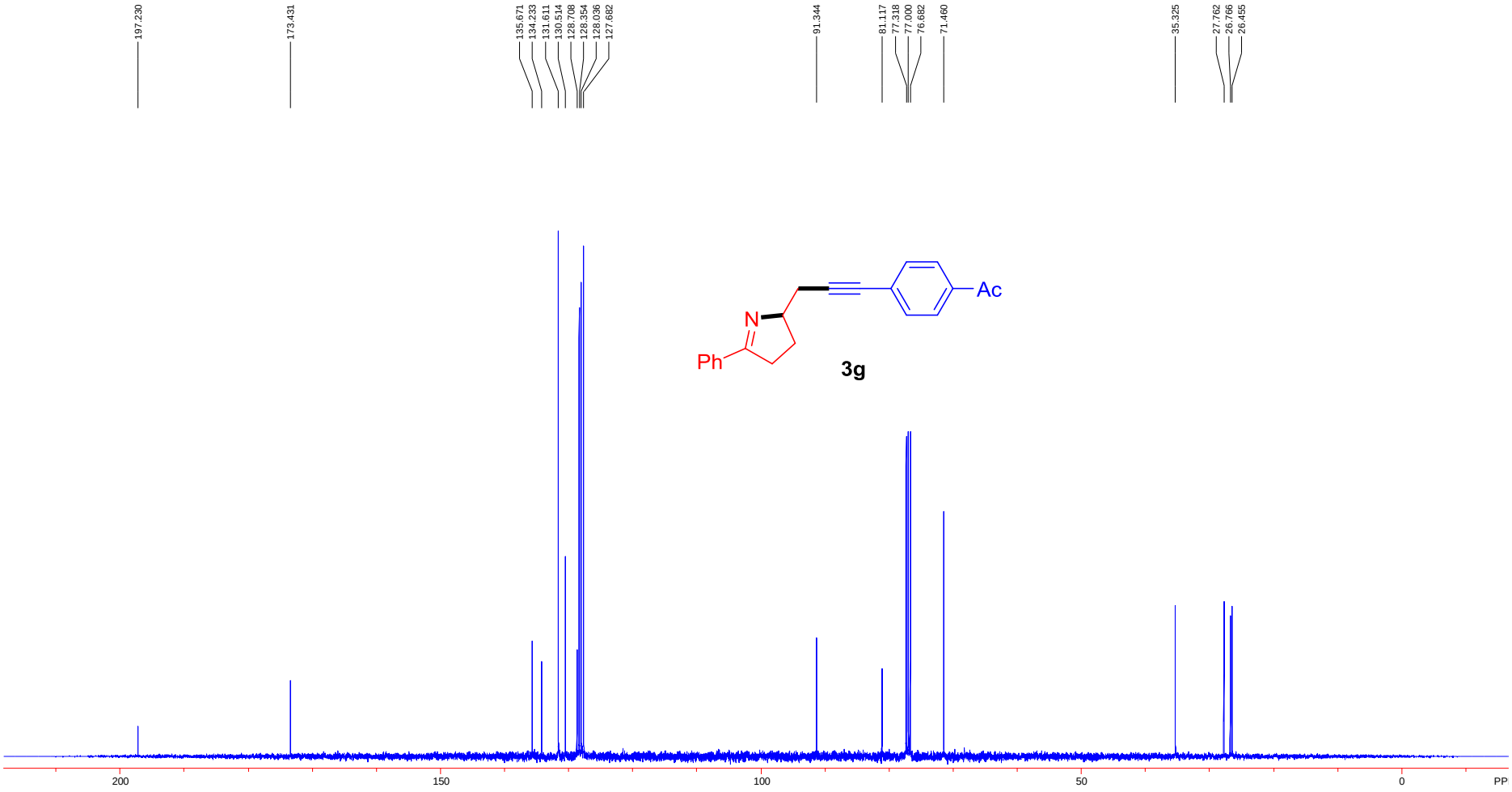
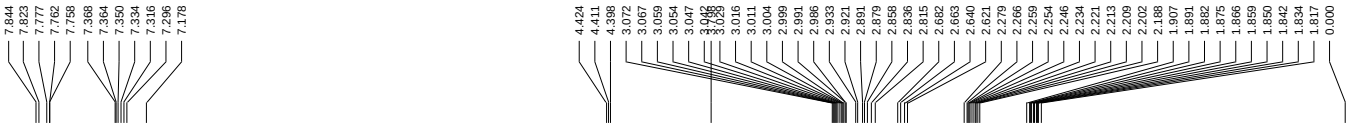
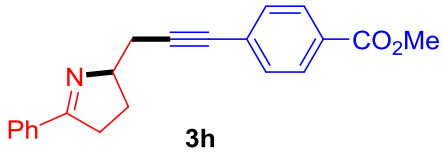


^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)





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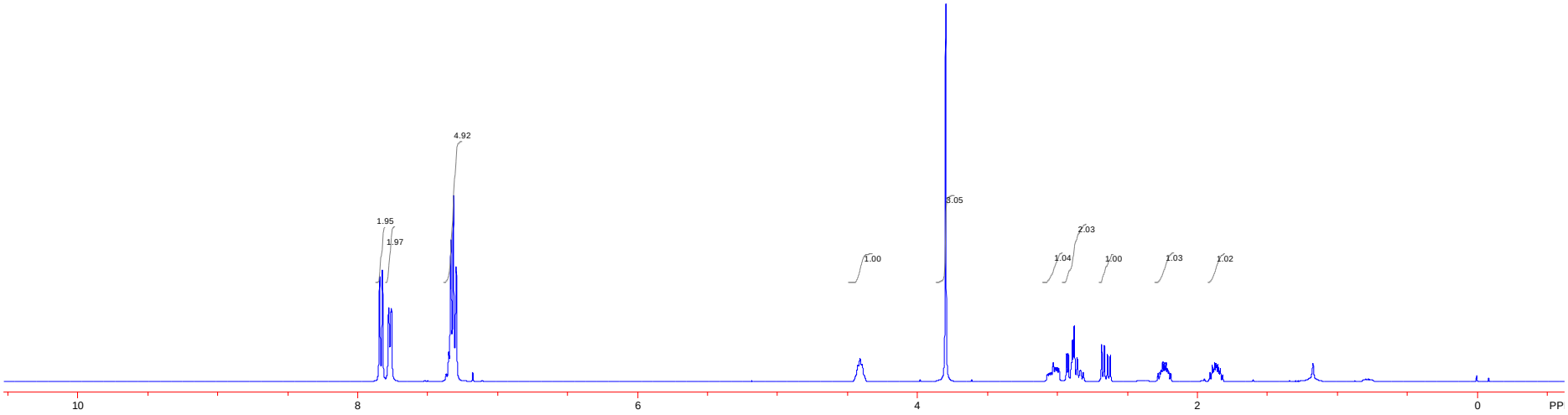
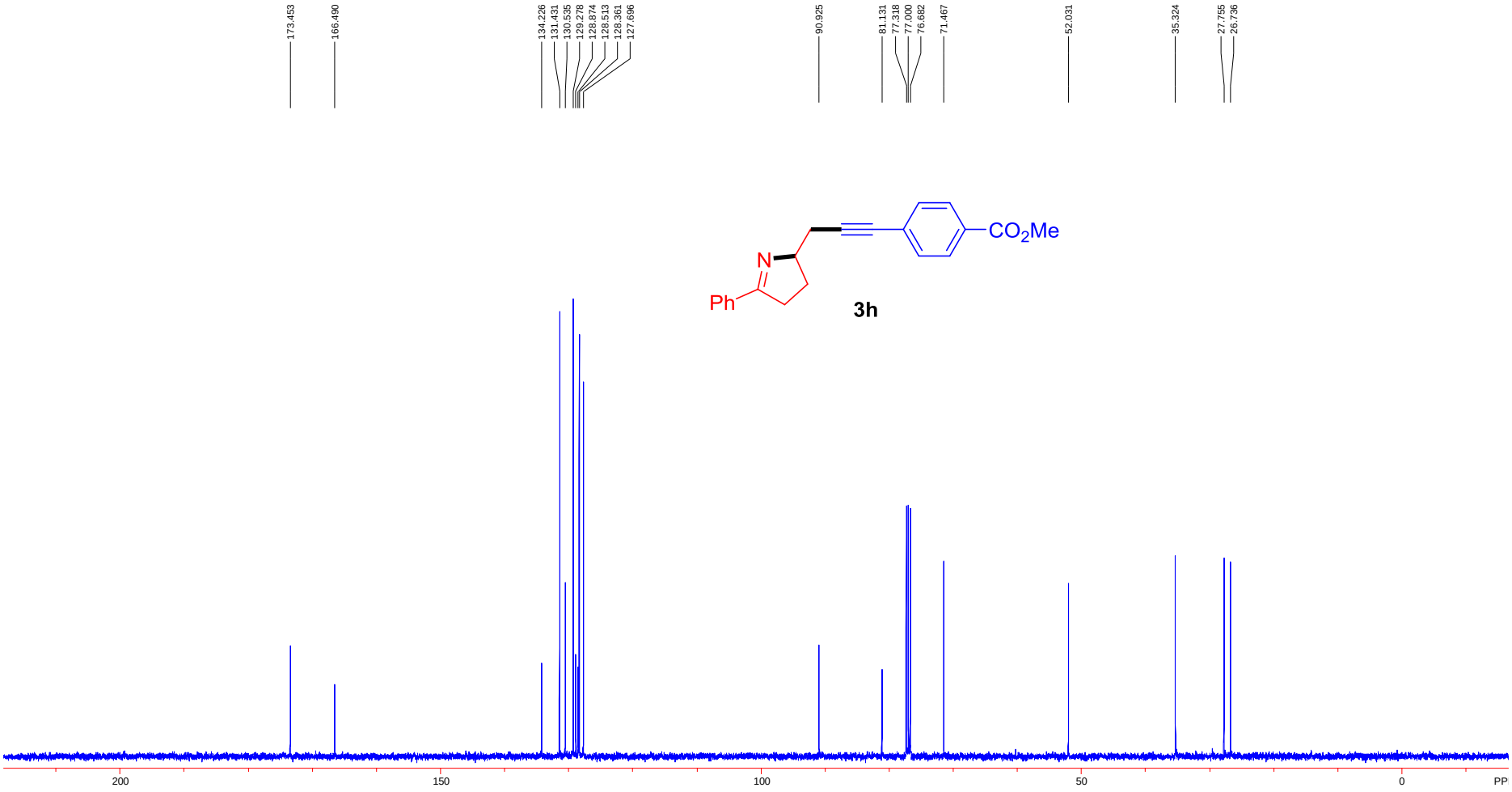
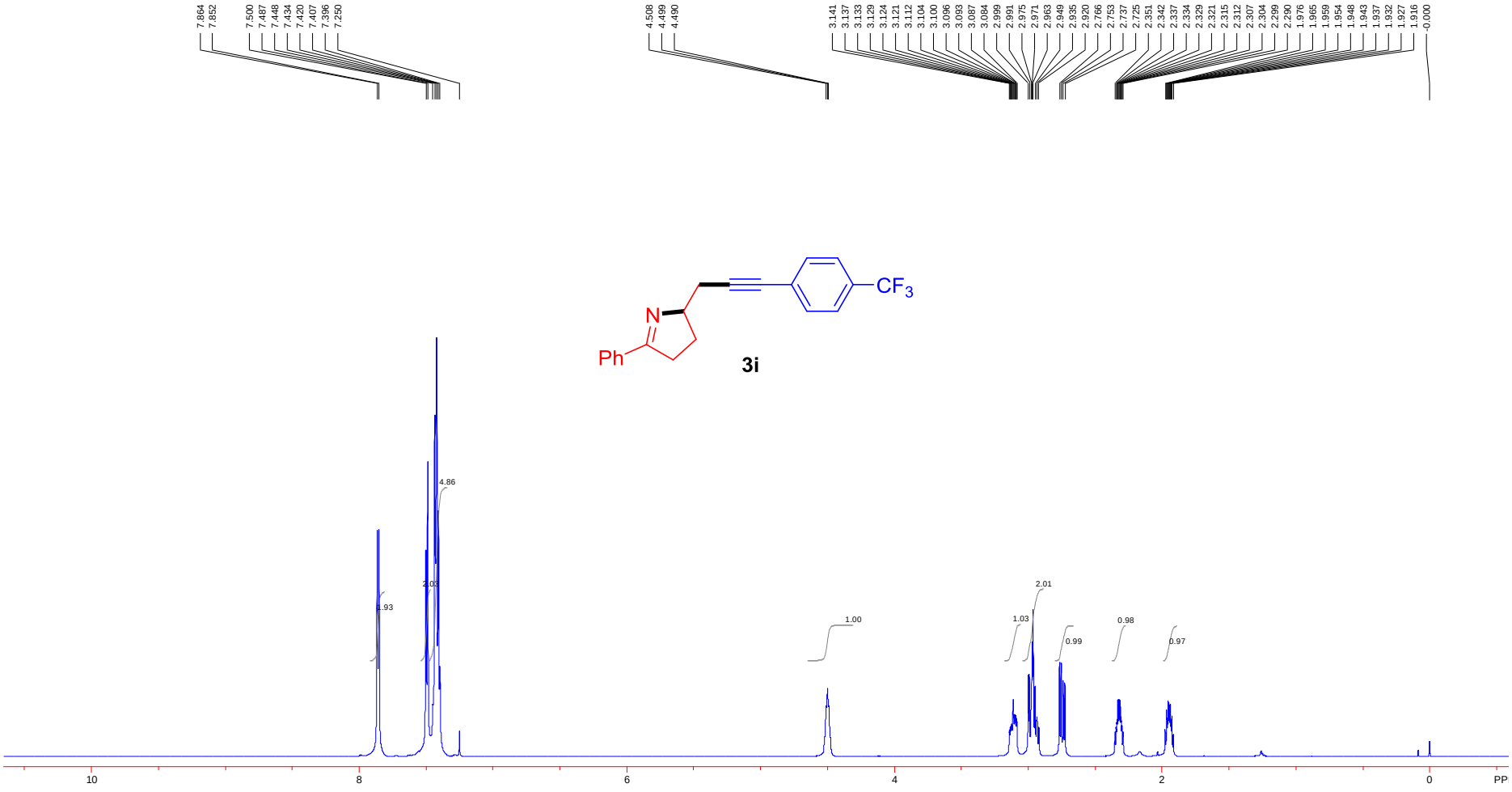


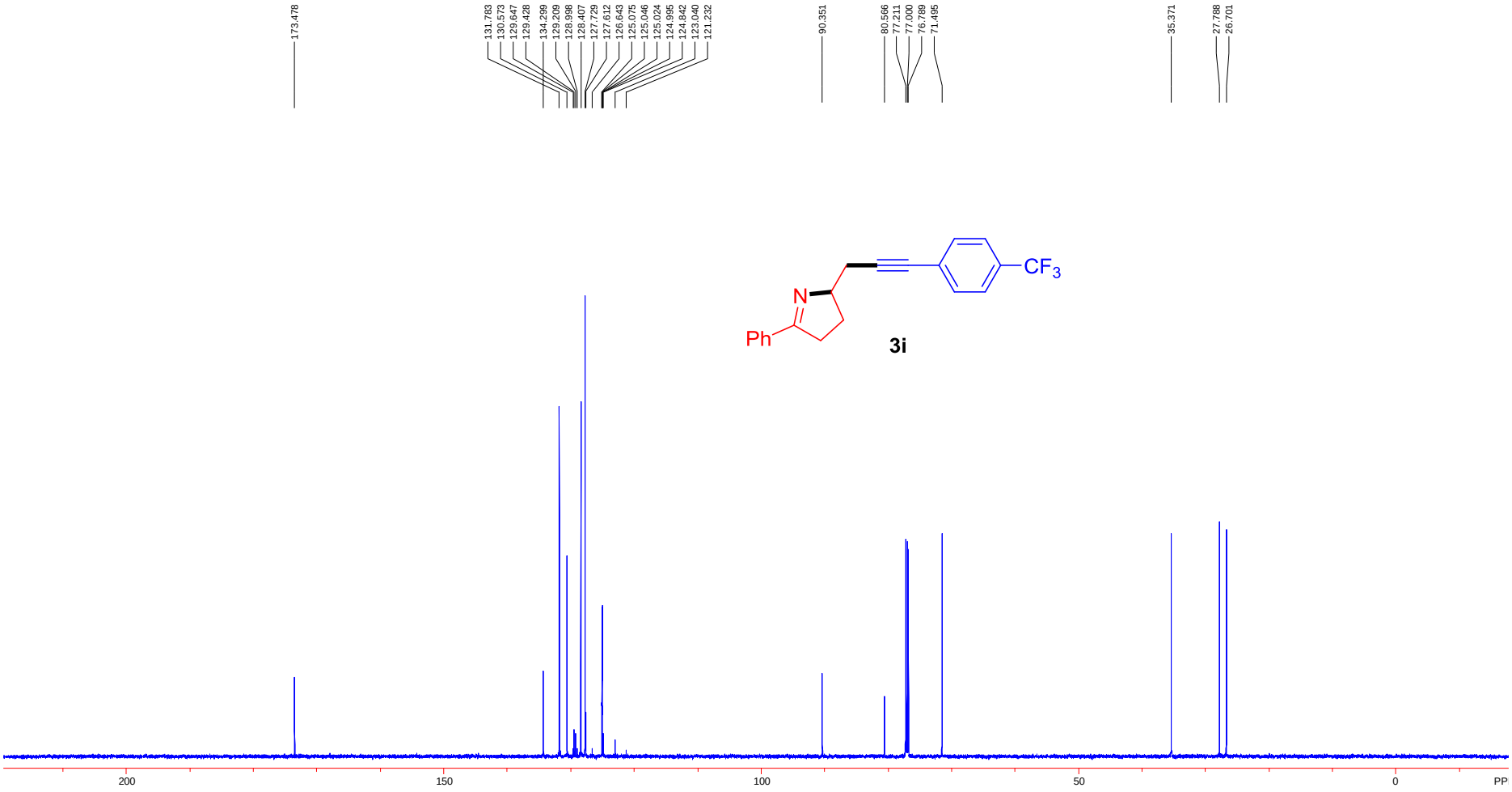
^{13}C NMR(100 MHz, $CDCl_3$)



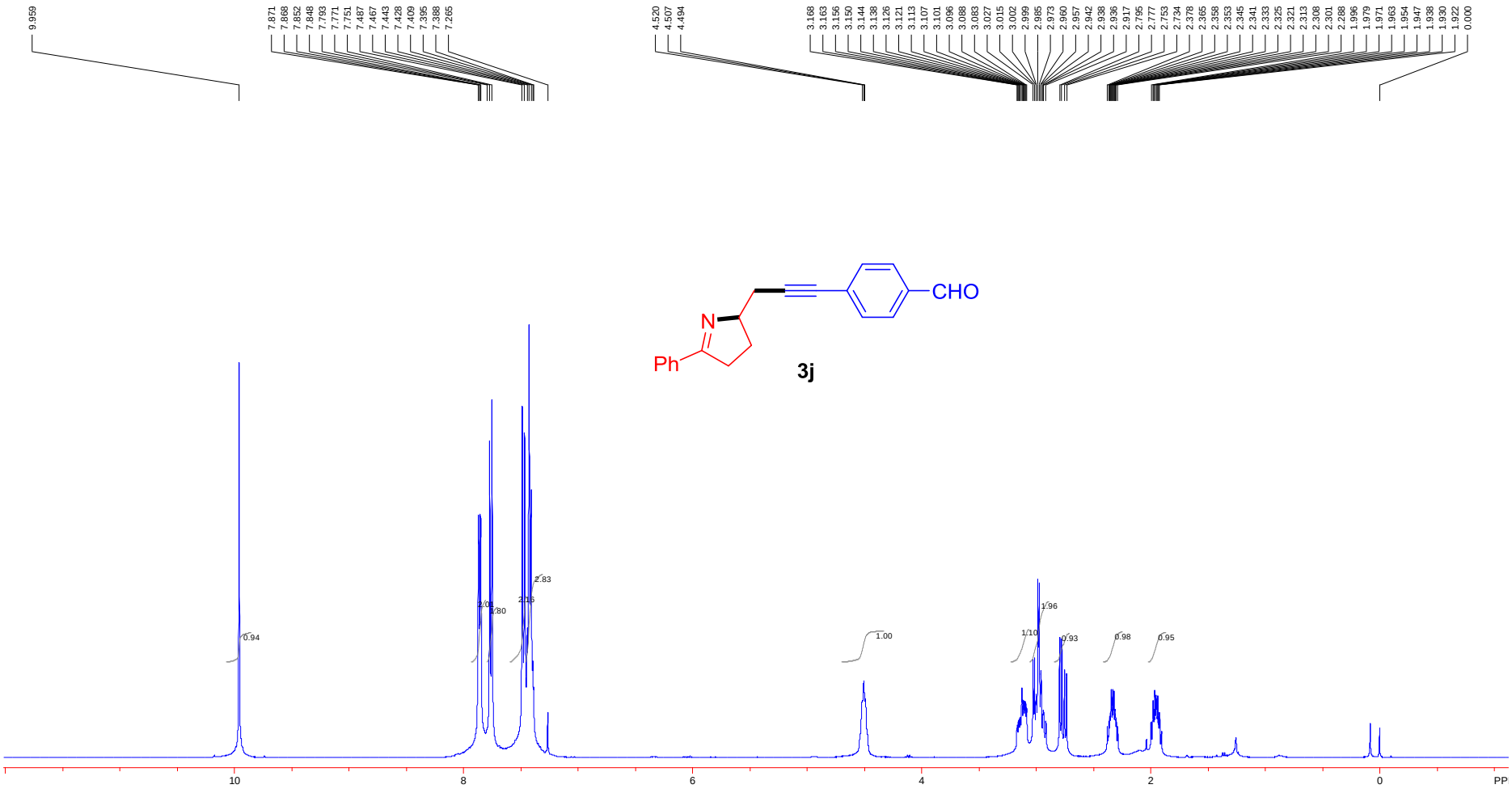
^{1}H NMR(600 MHz, $CDCl_3$)



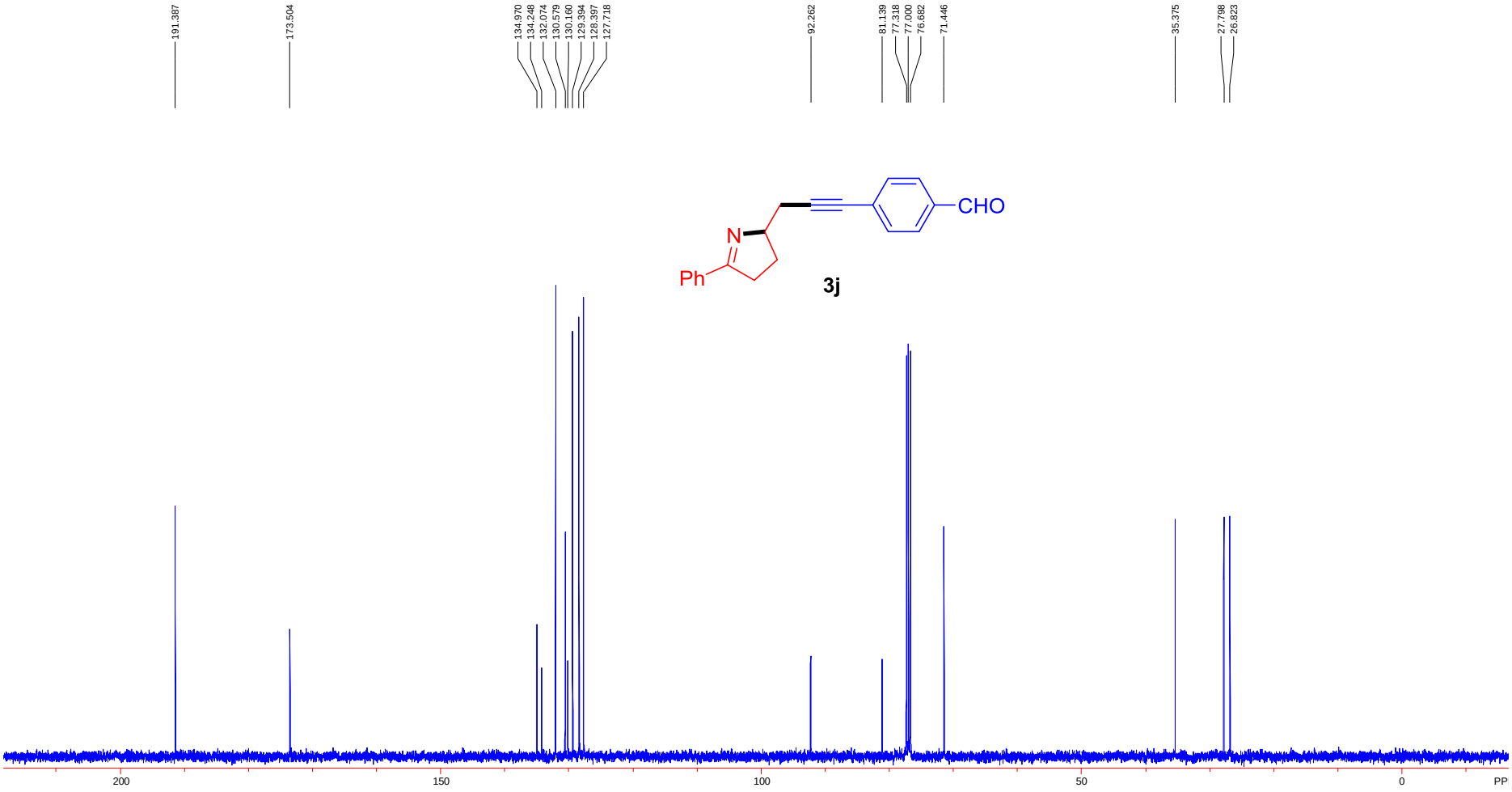
^{13}C NMR(151 MHz, $CDCl_3$)



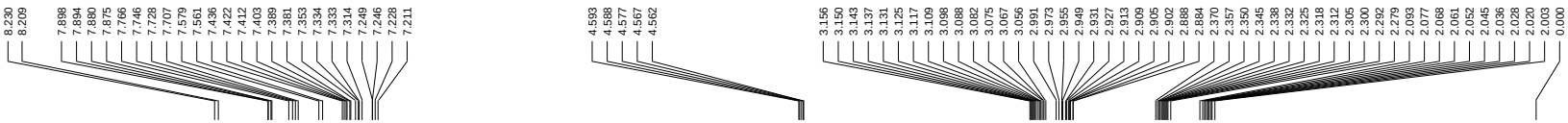
^{1}H NMR(400 MHz, $CDCl_3$)

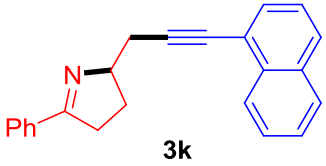


^{13}C NMR(100 MHz, $CDCl_3$)



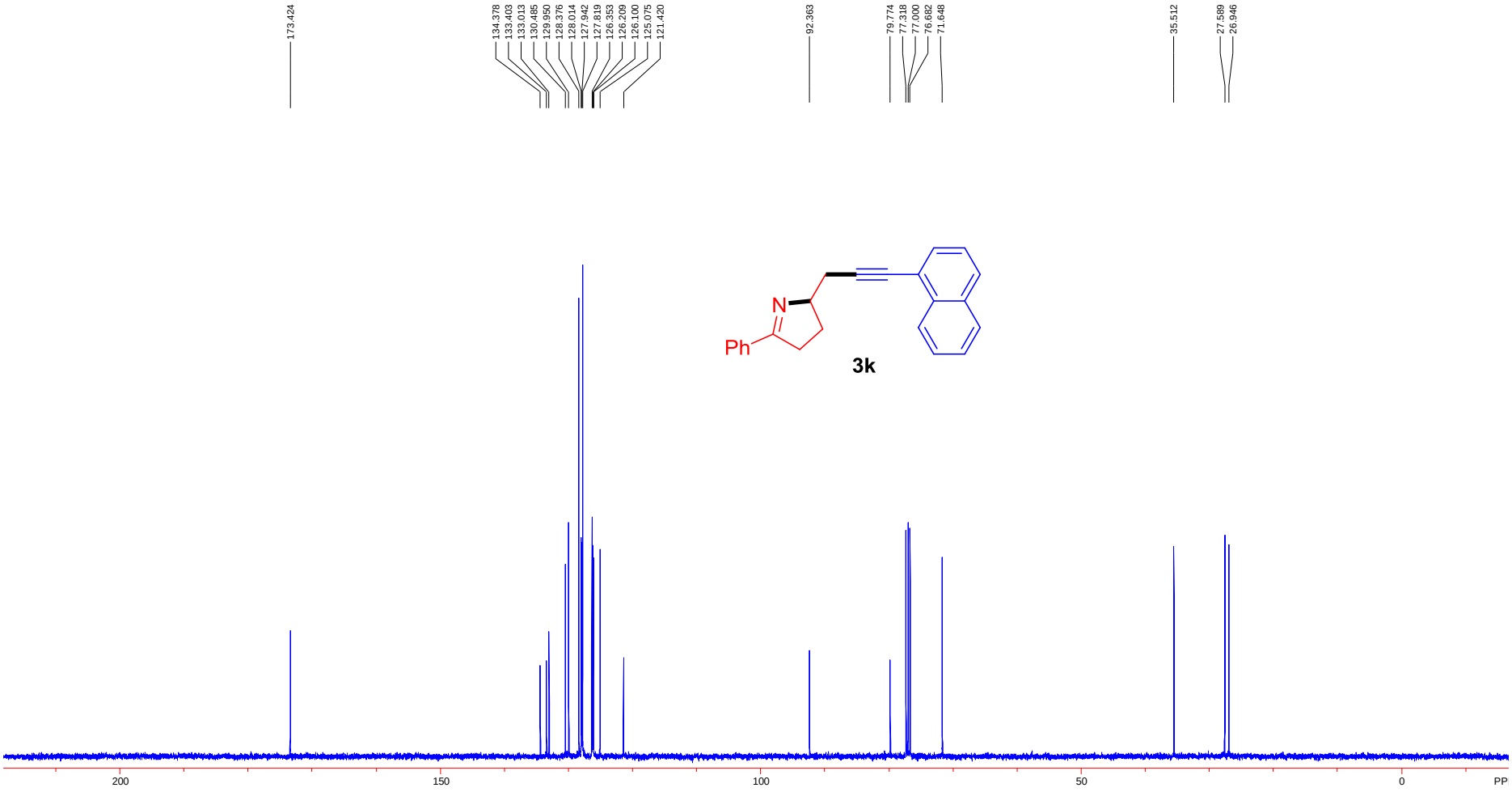
^{1}H NMR(400 MHz, $CDCl_3$)



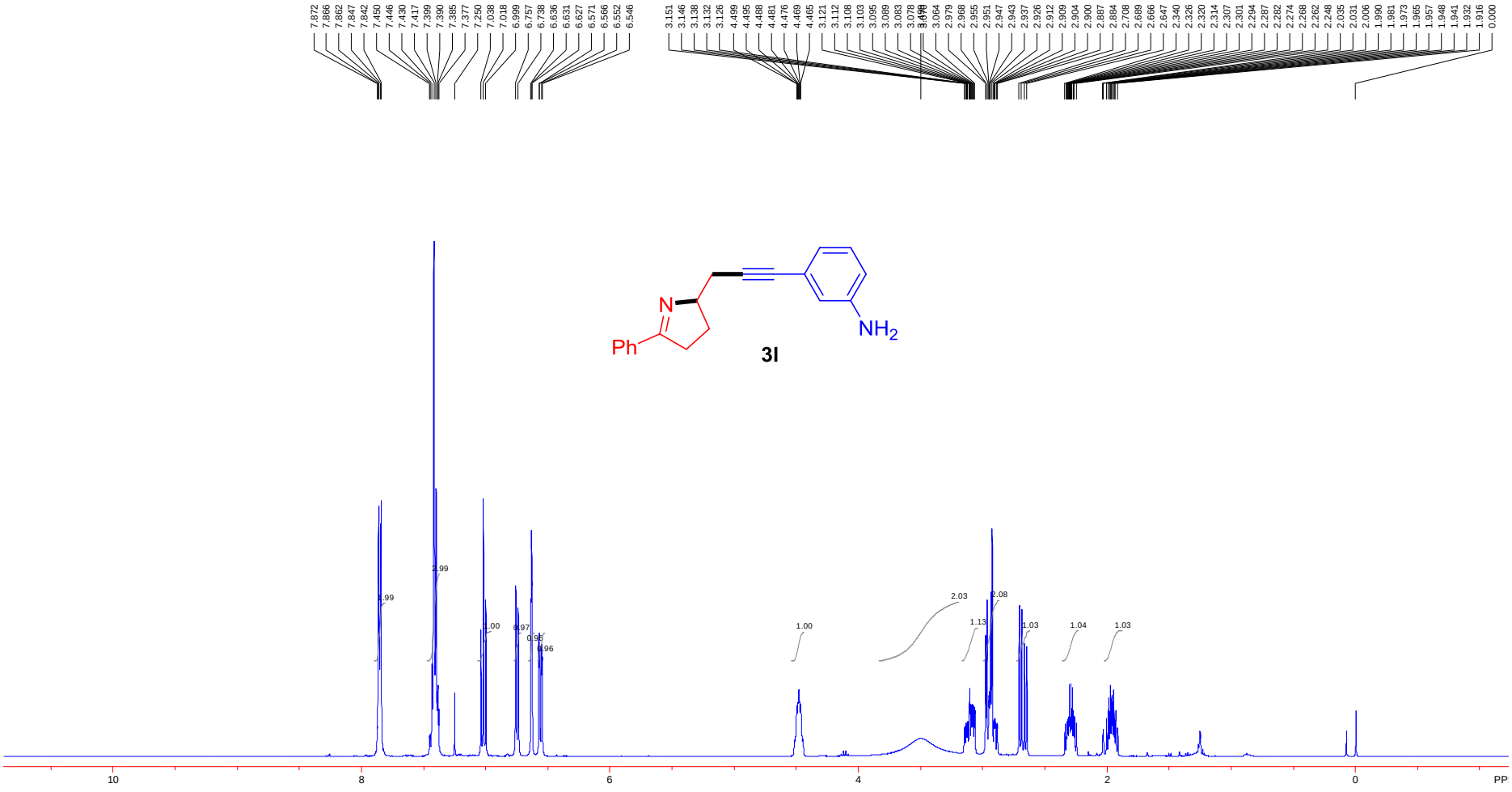


3k

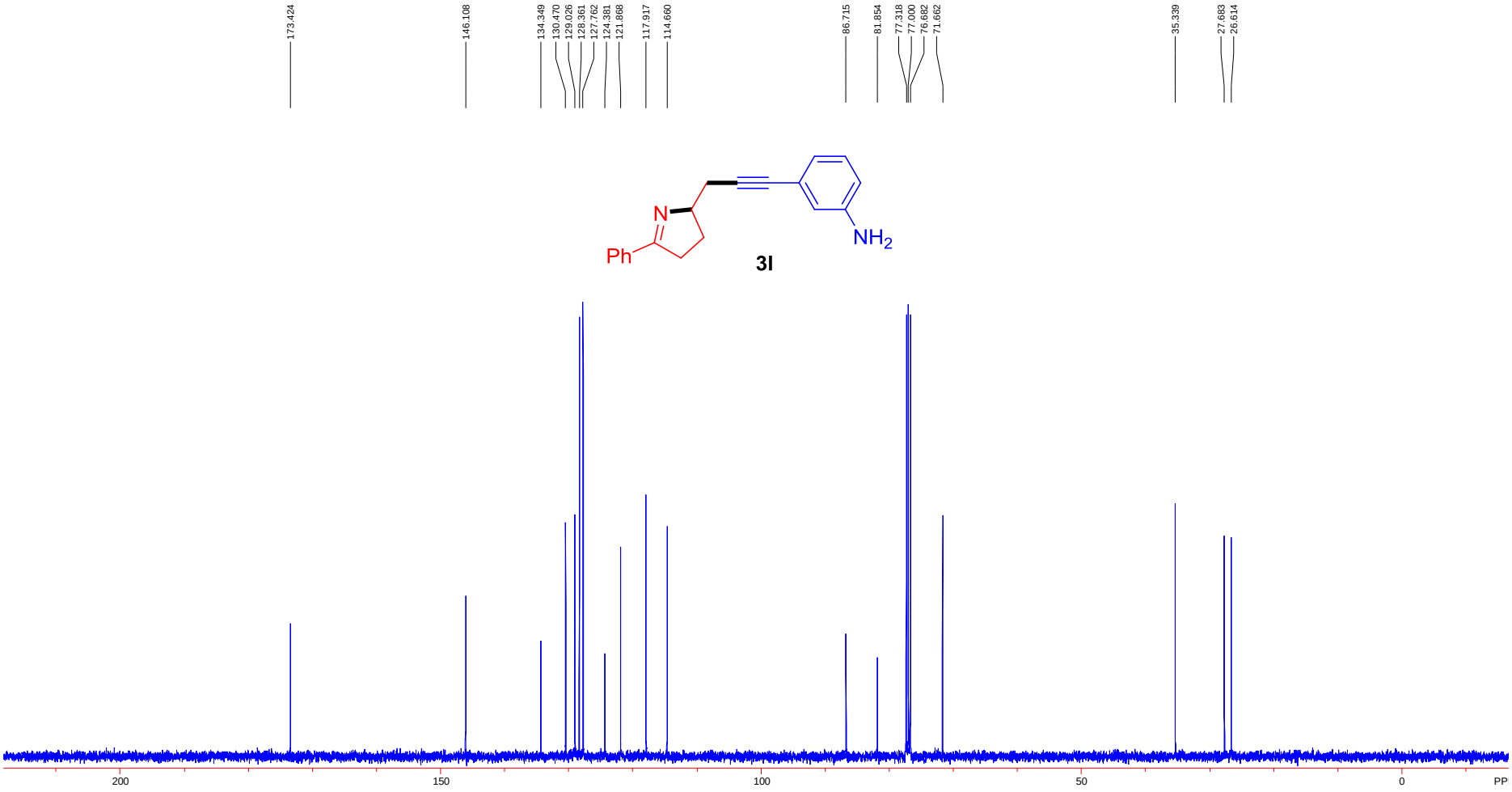
^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)

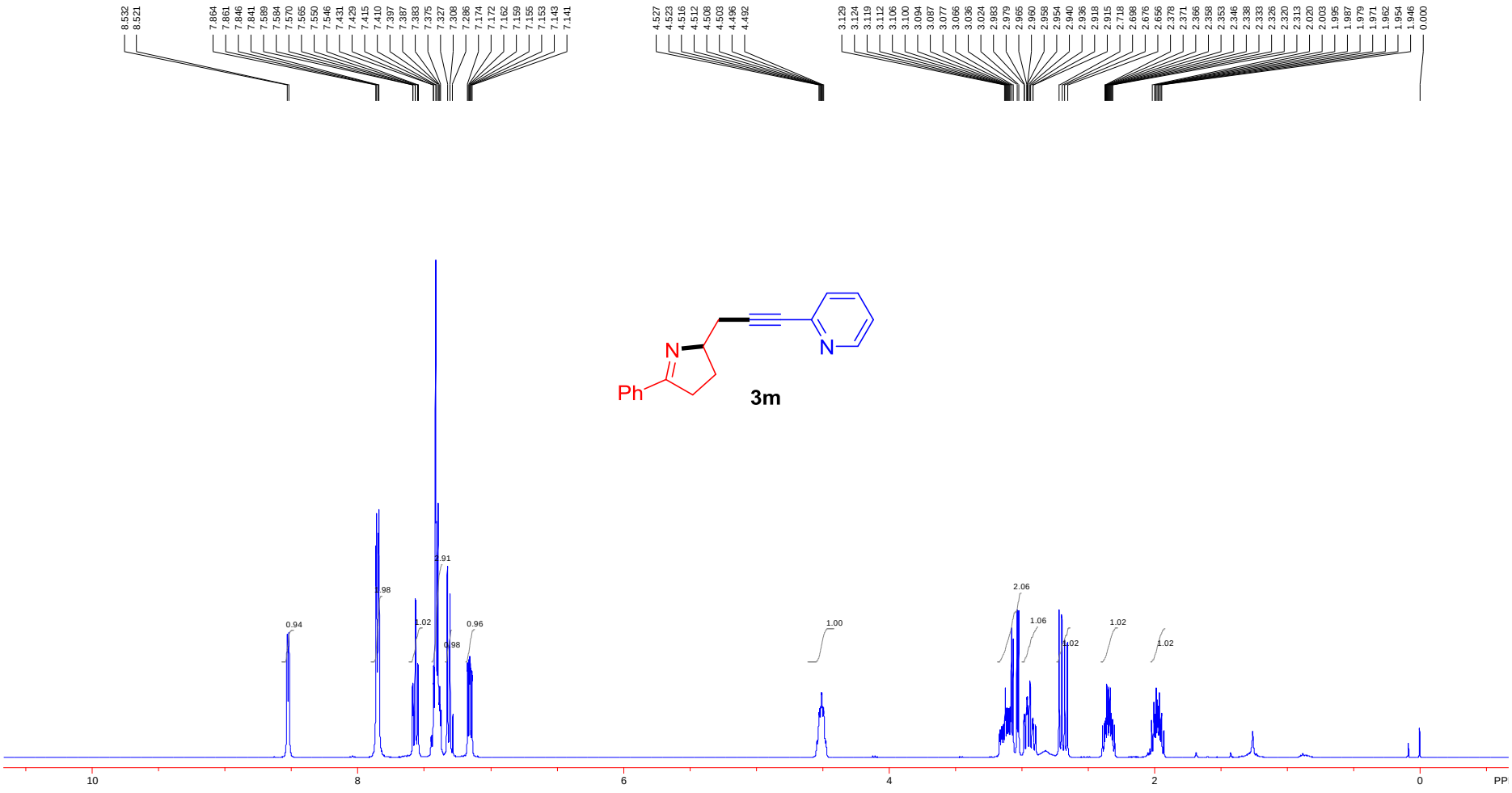


^{13}C NMR(100 MHz, $CDCl_3$)

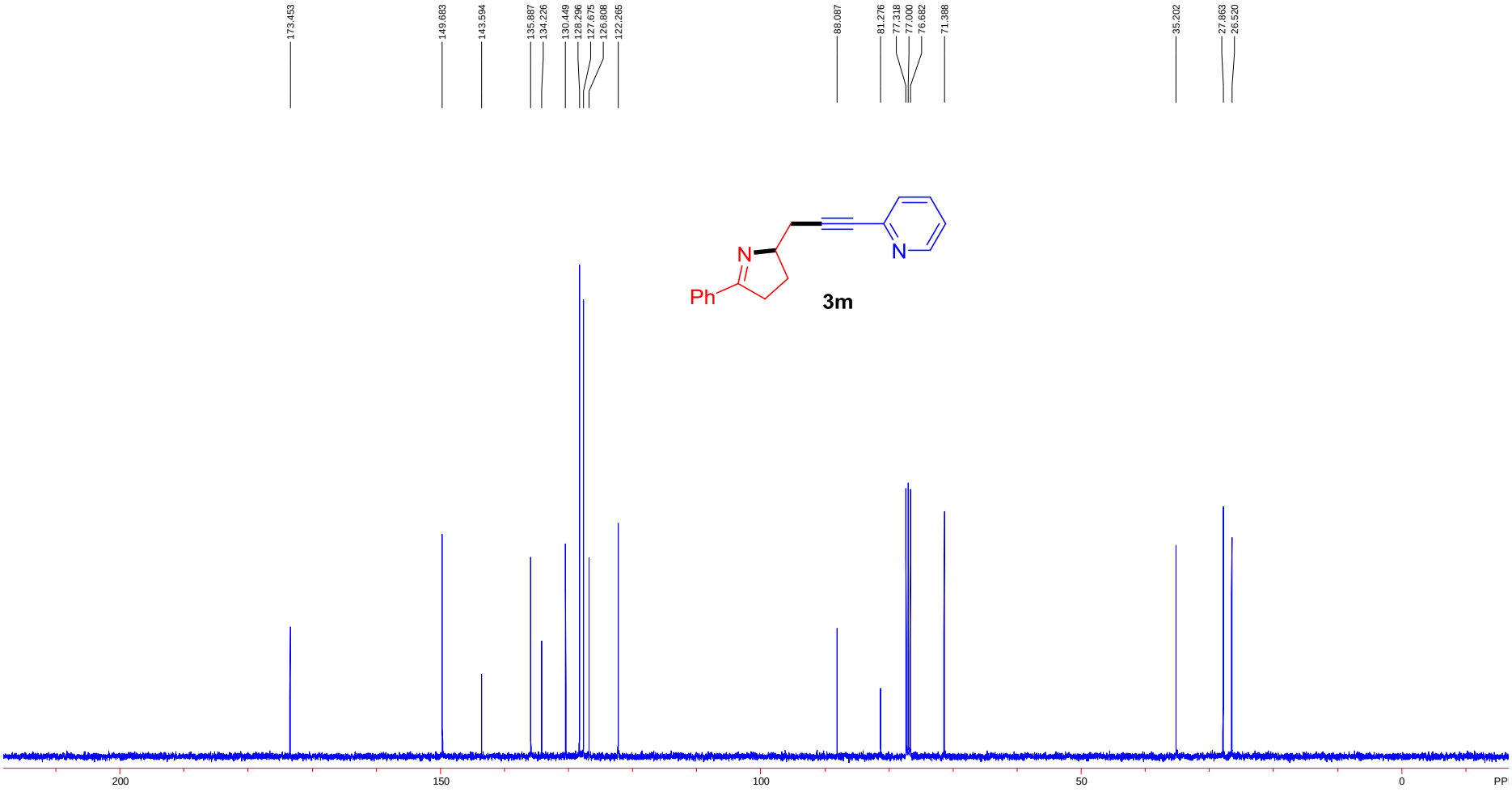


3l

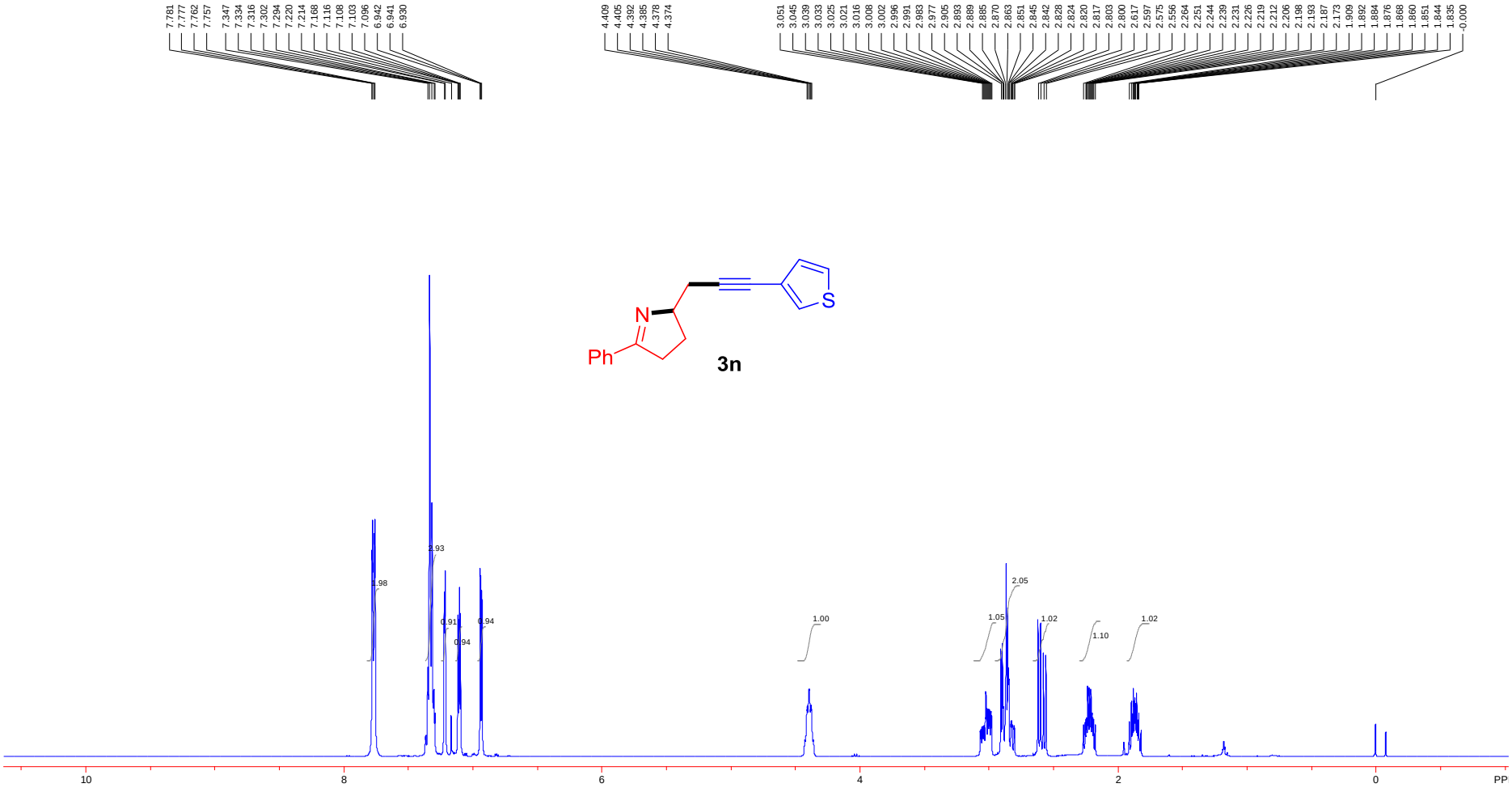
^{1}H NMR(400 MHz, $CDCl_3$)



^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



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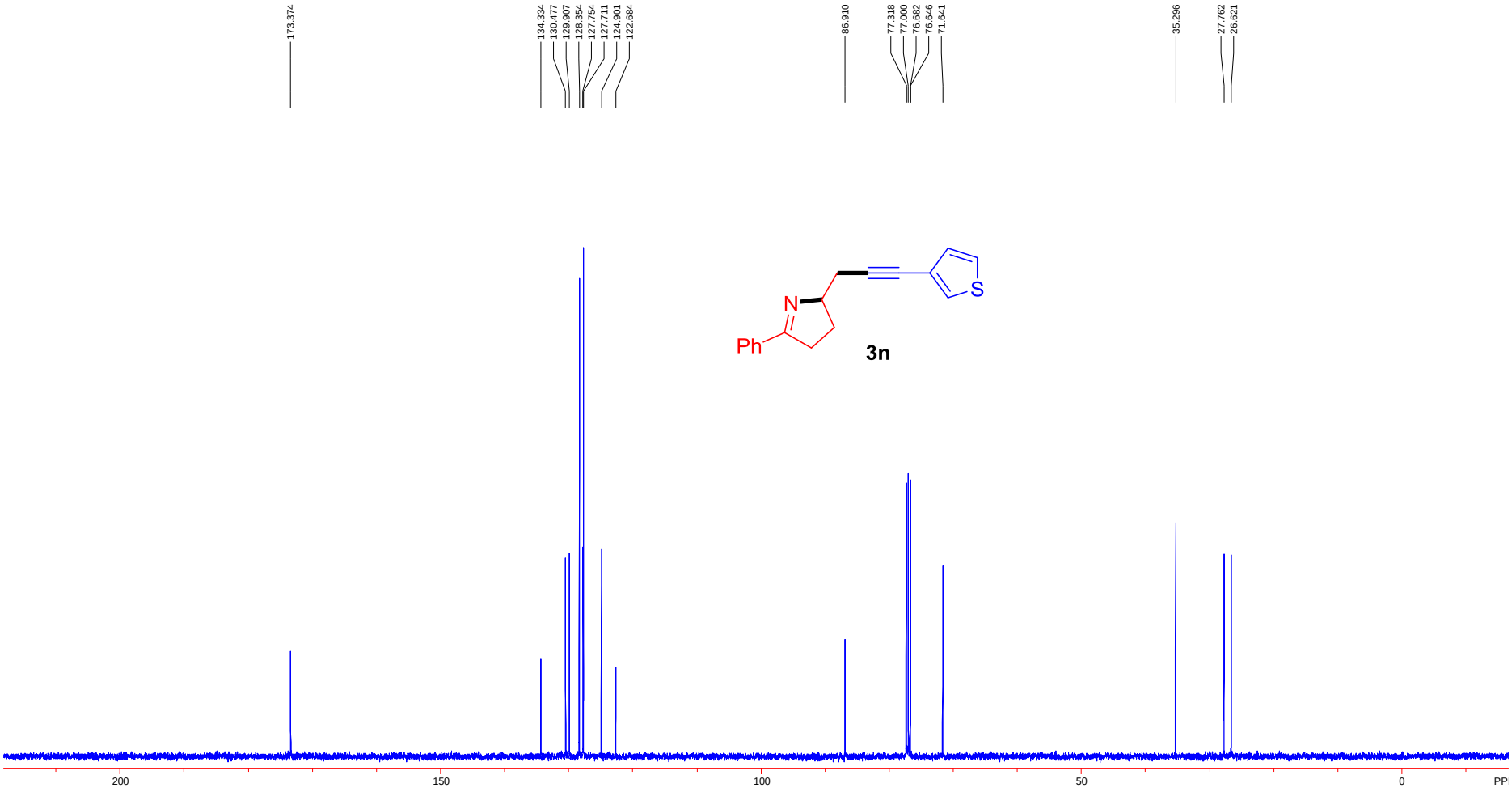
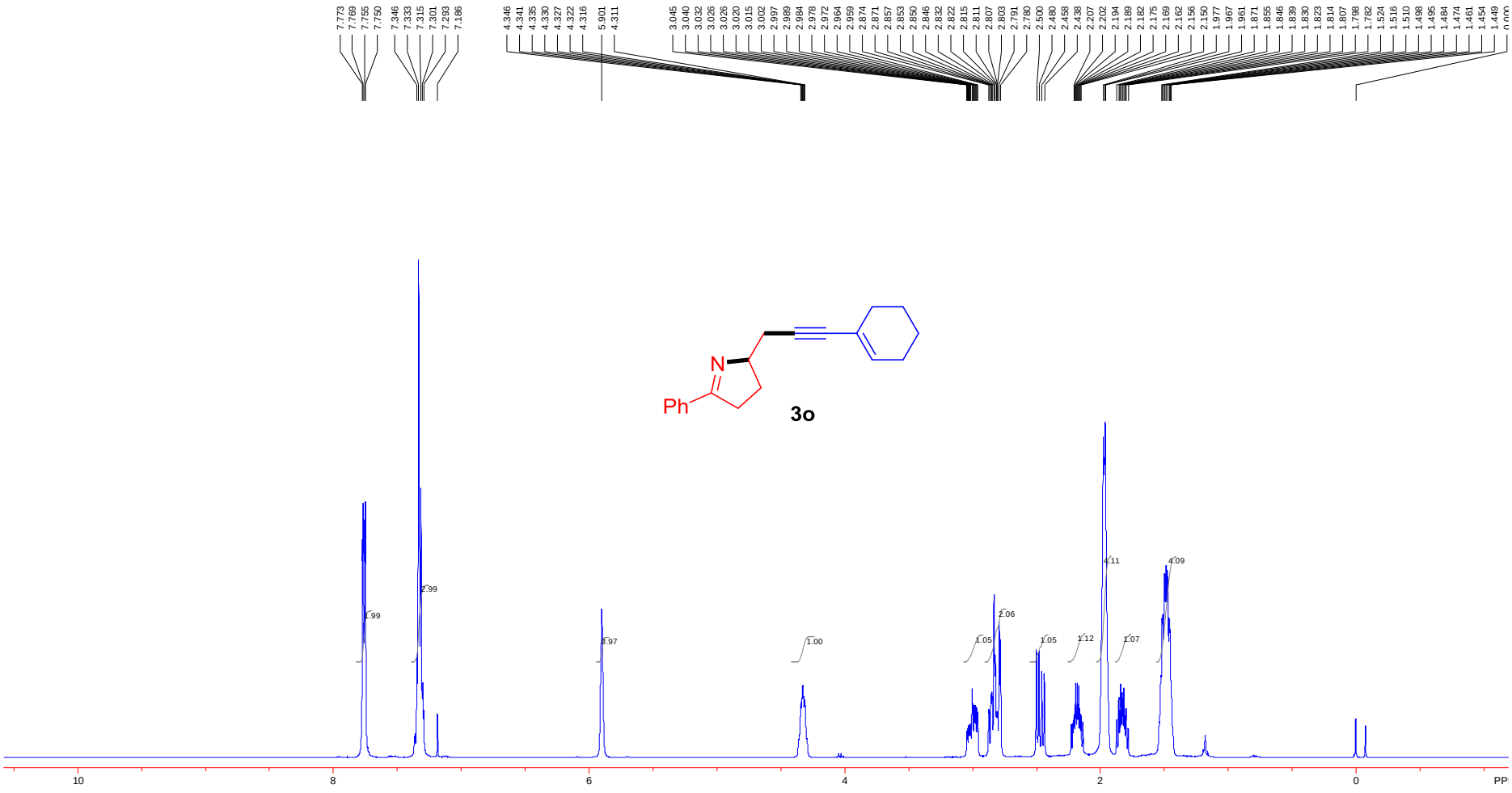
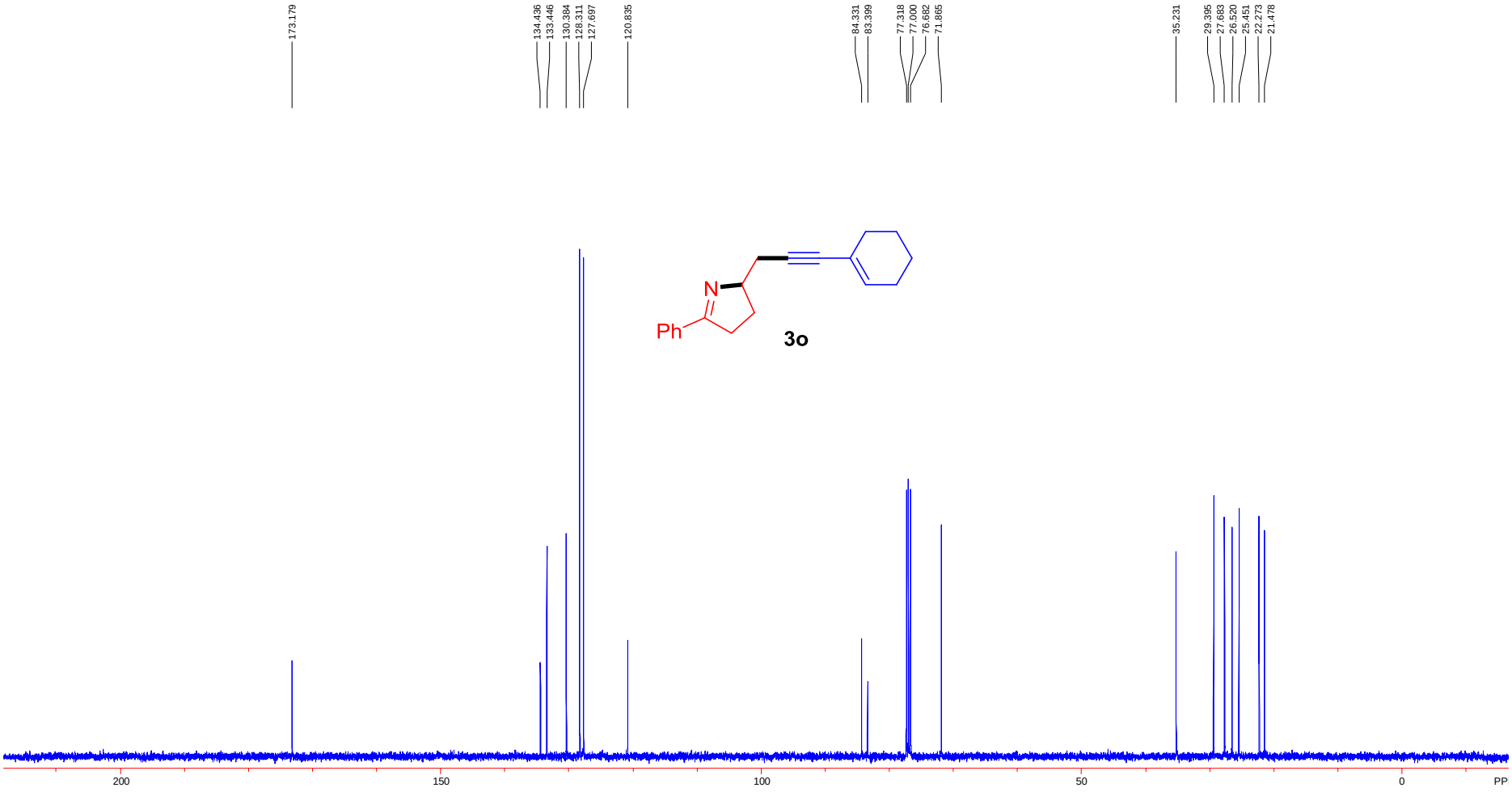


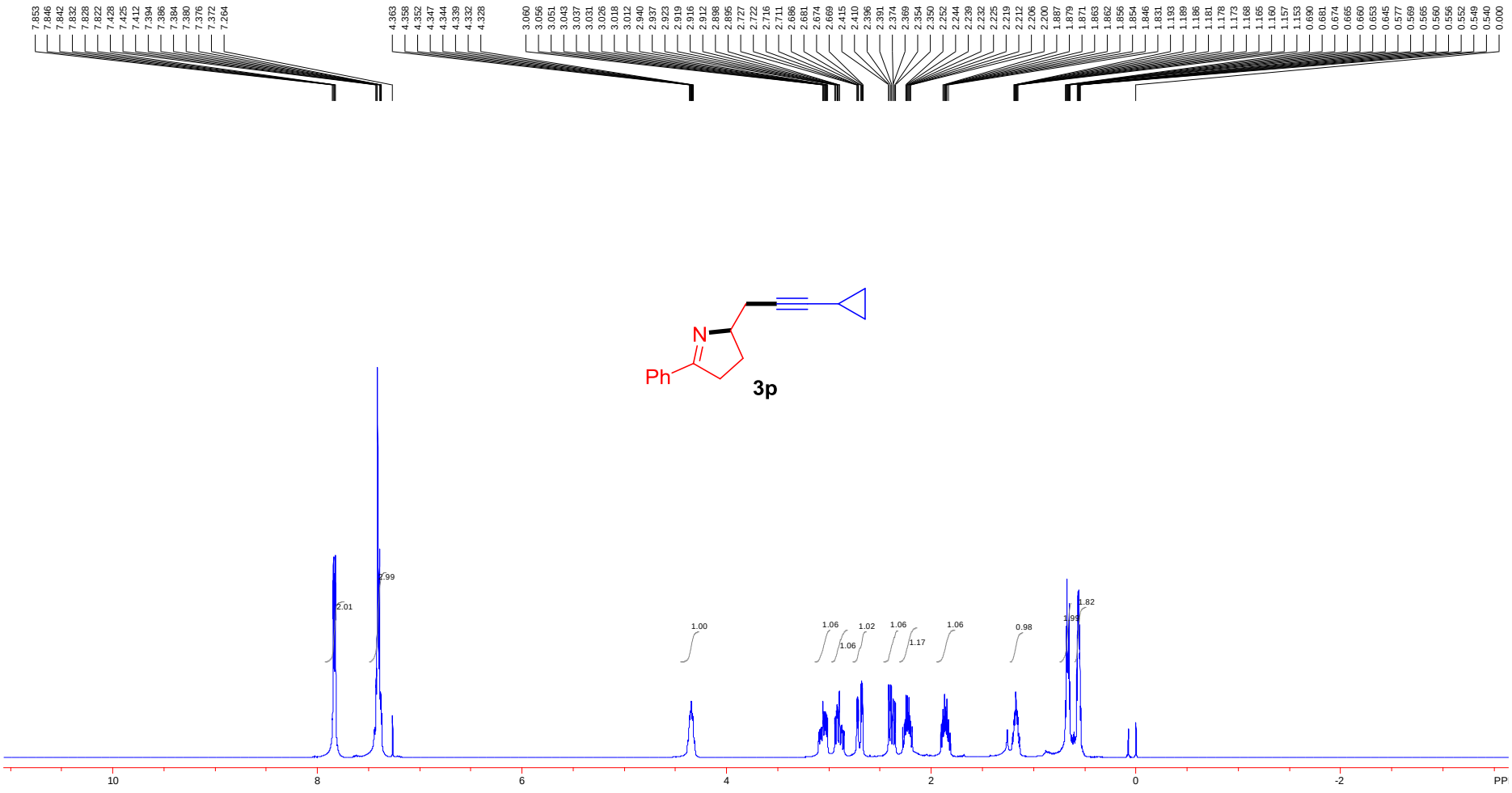
^{1}H NMR(400 MHz, $CDCl_3$)



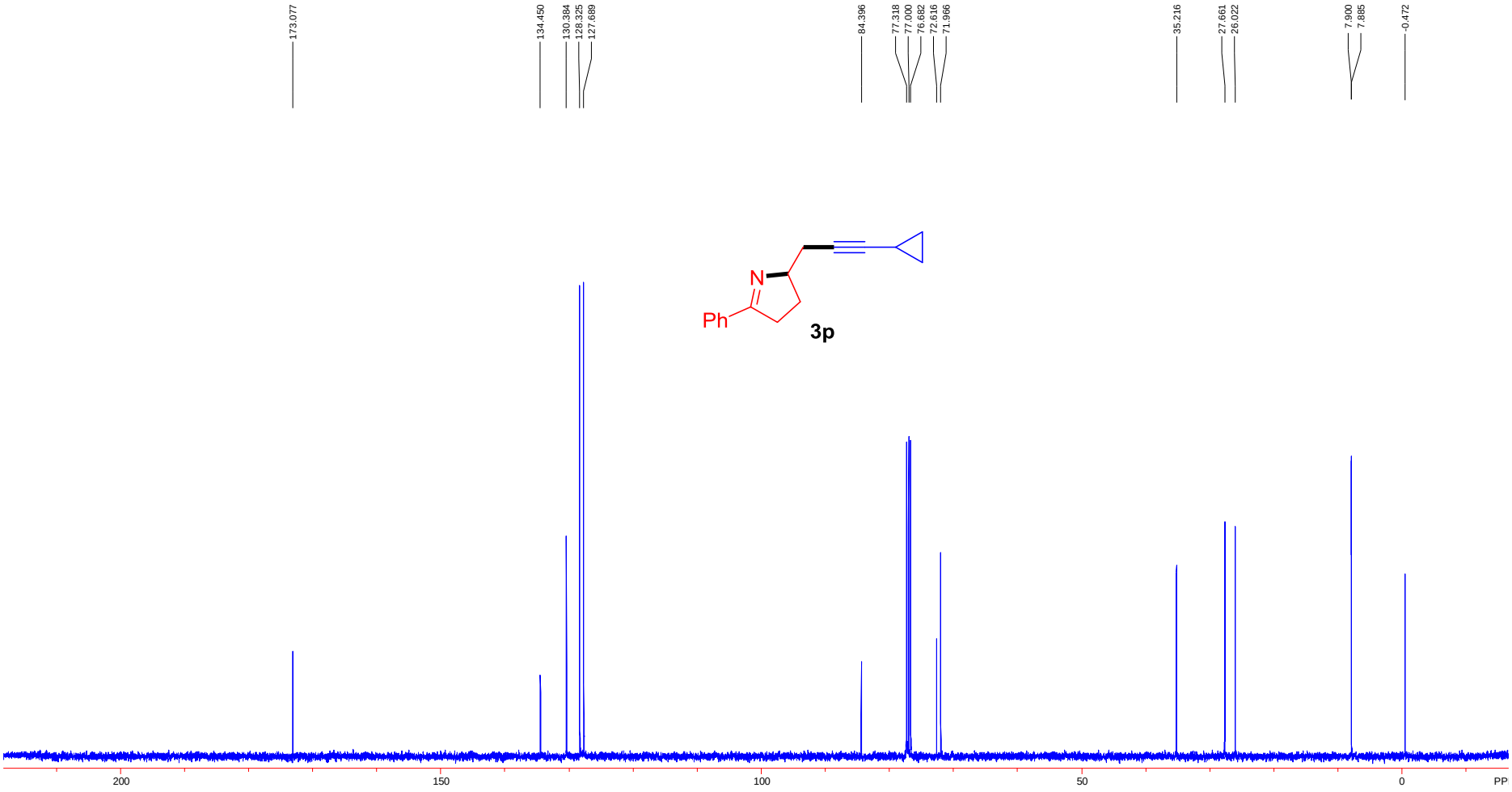
^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



^{13}C NMR(100 MHz, $CDCl_3$)



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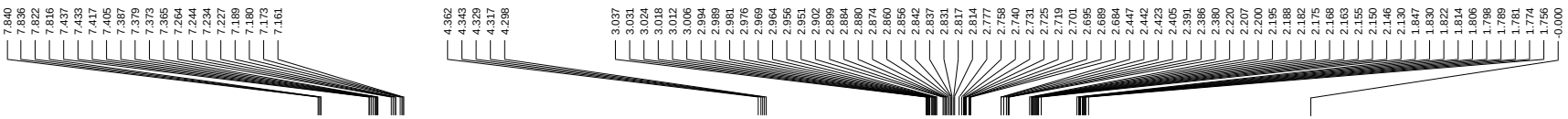
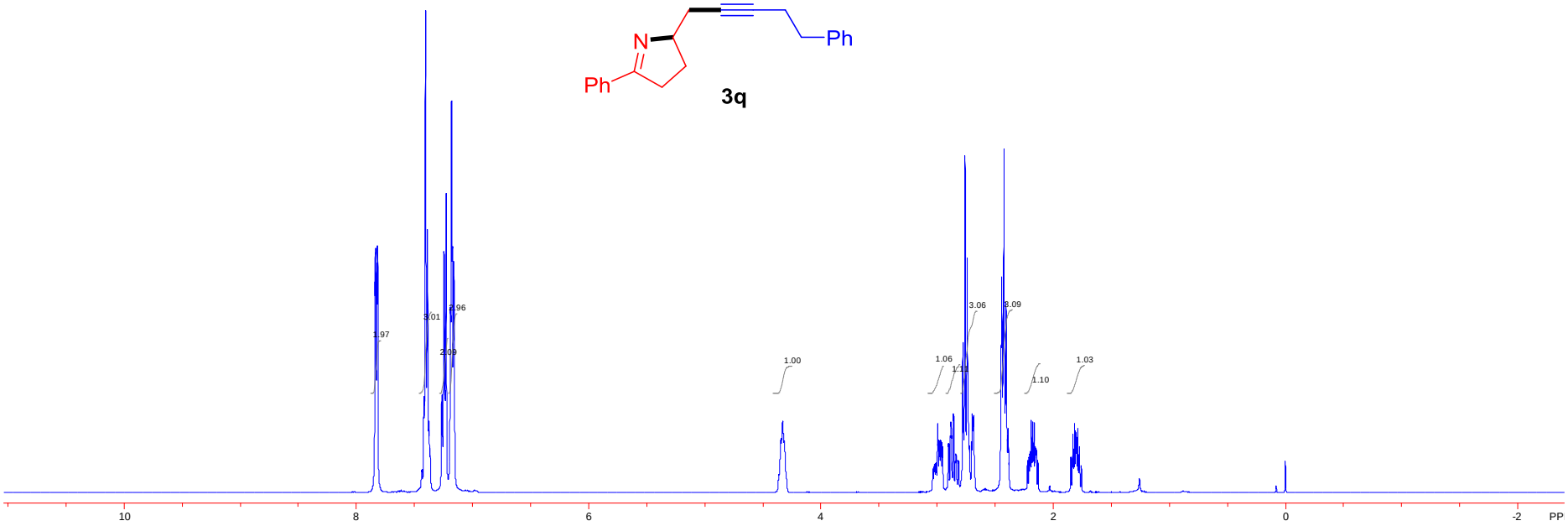
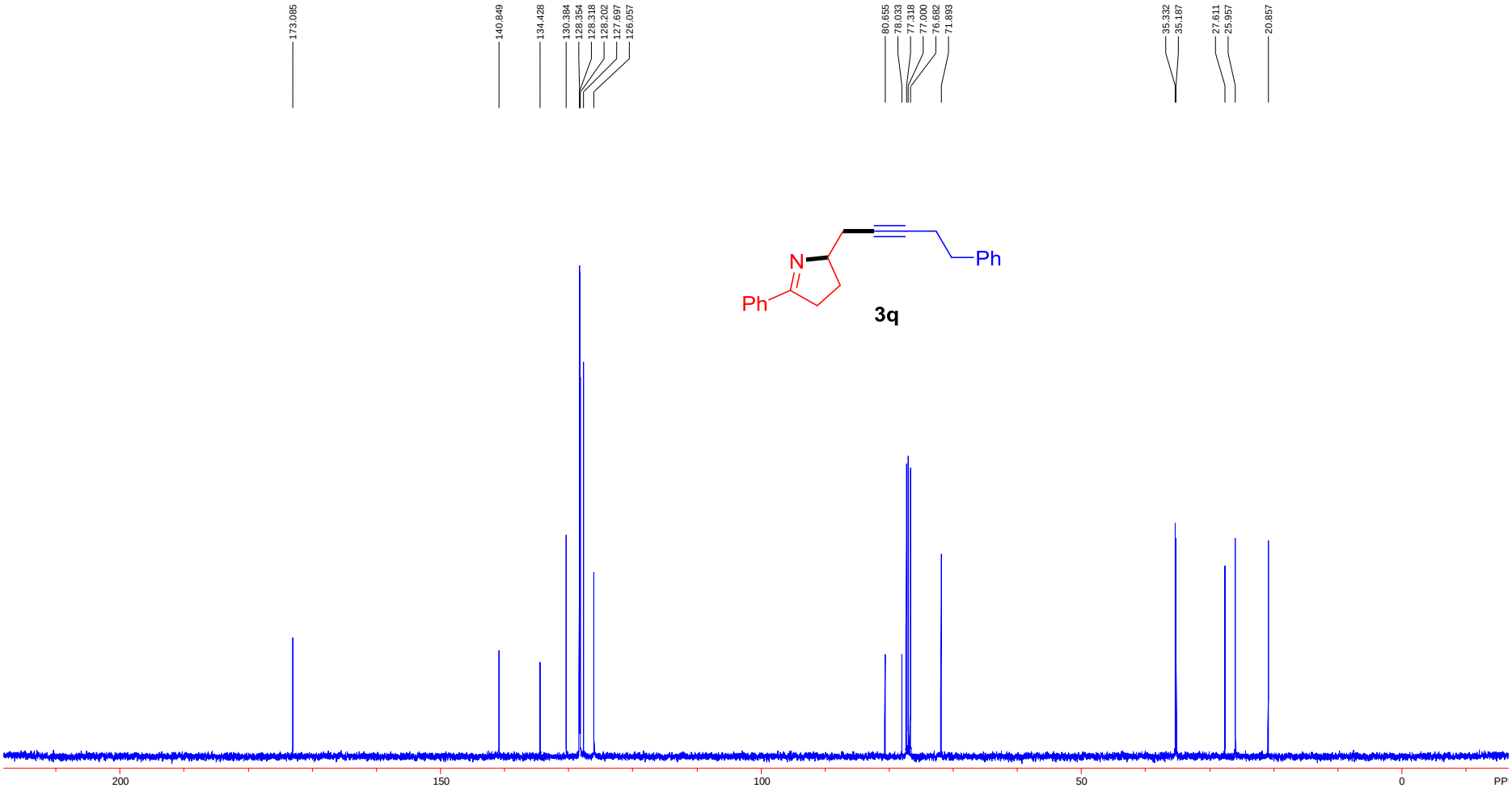
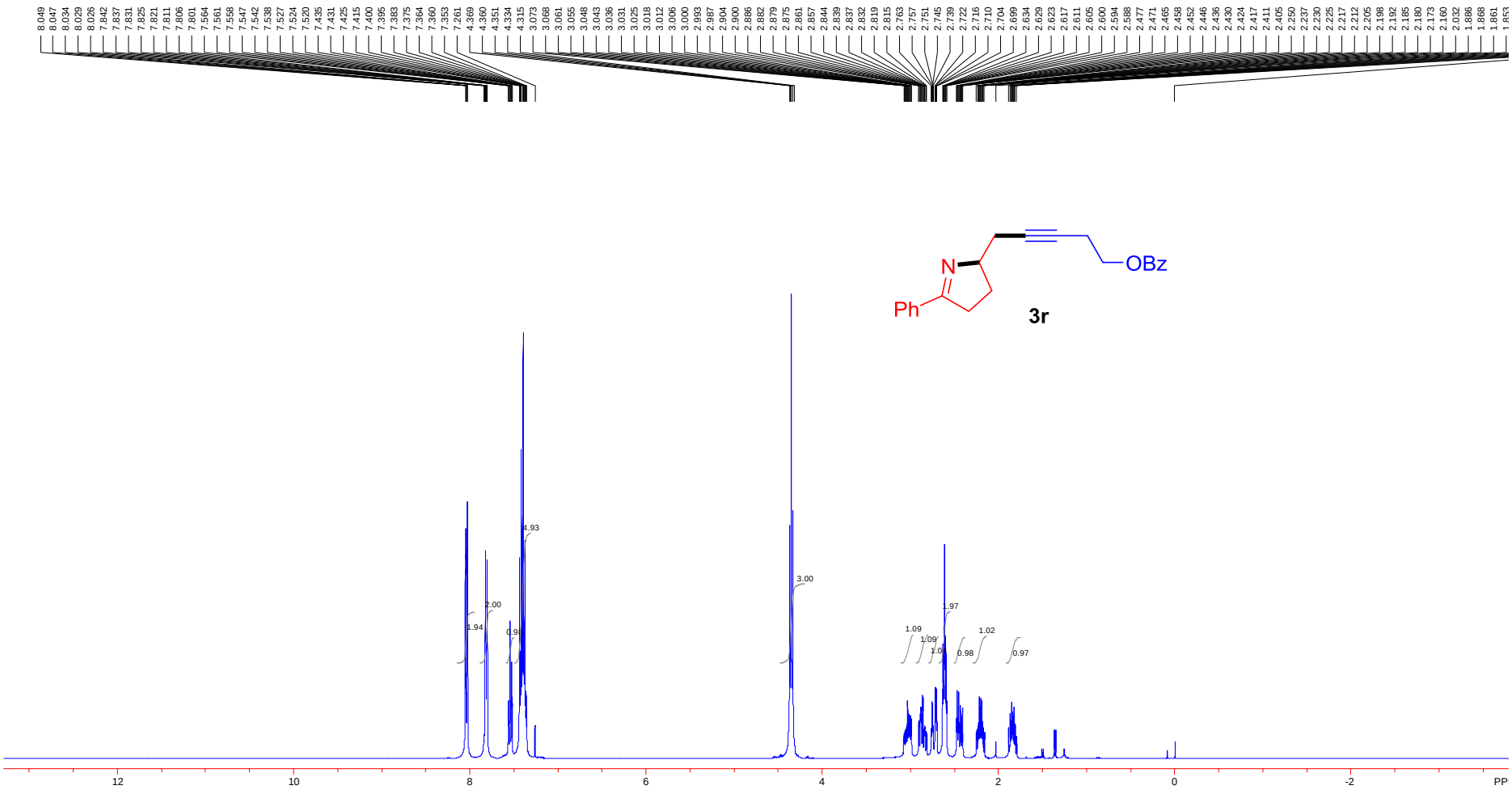




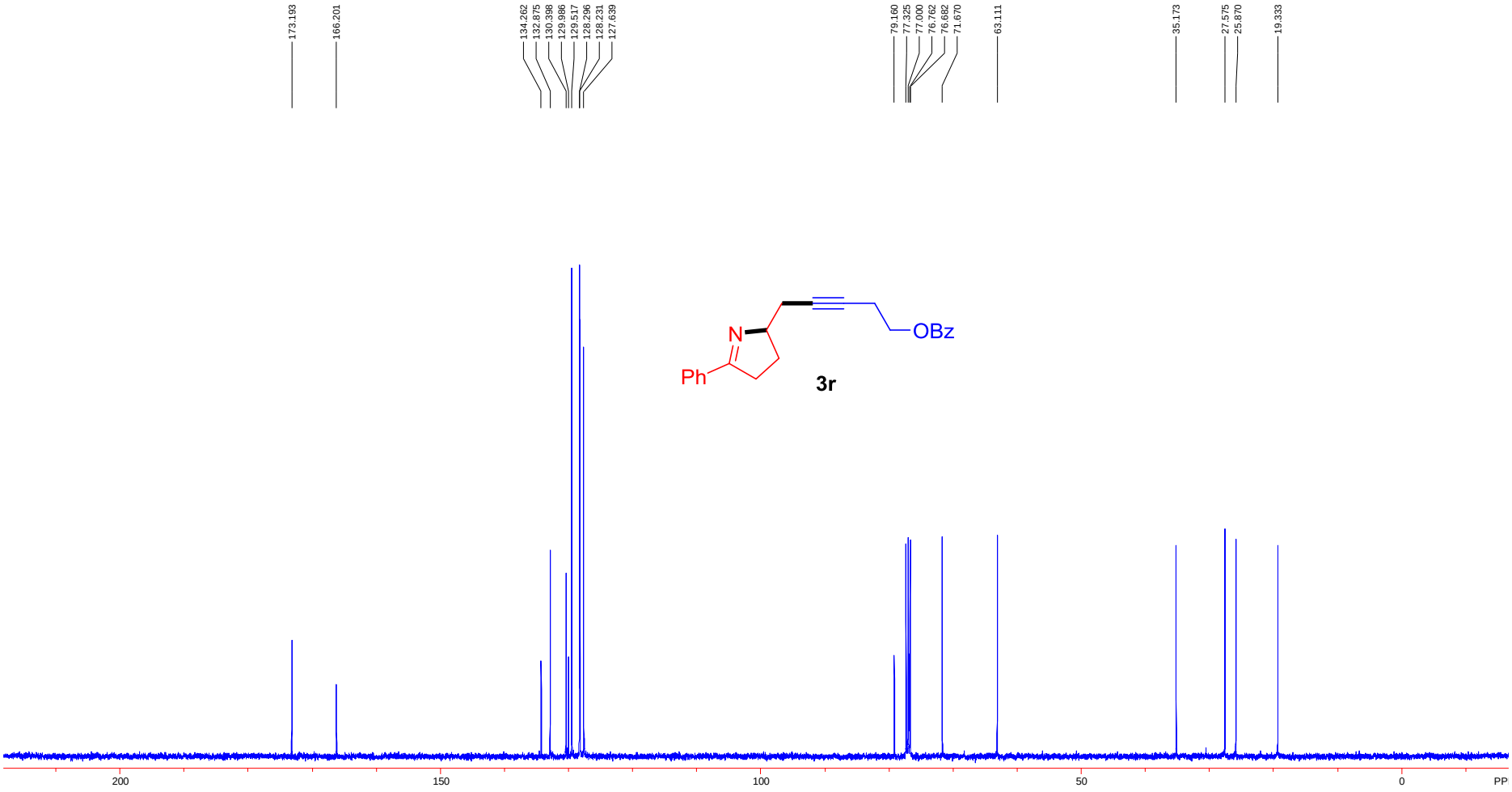
^{13}C NMR(100 MHz, $CDCl_3$)



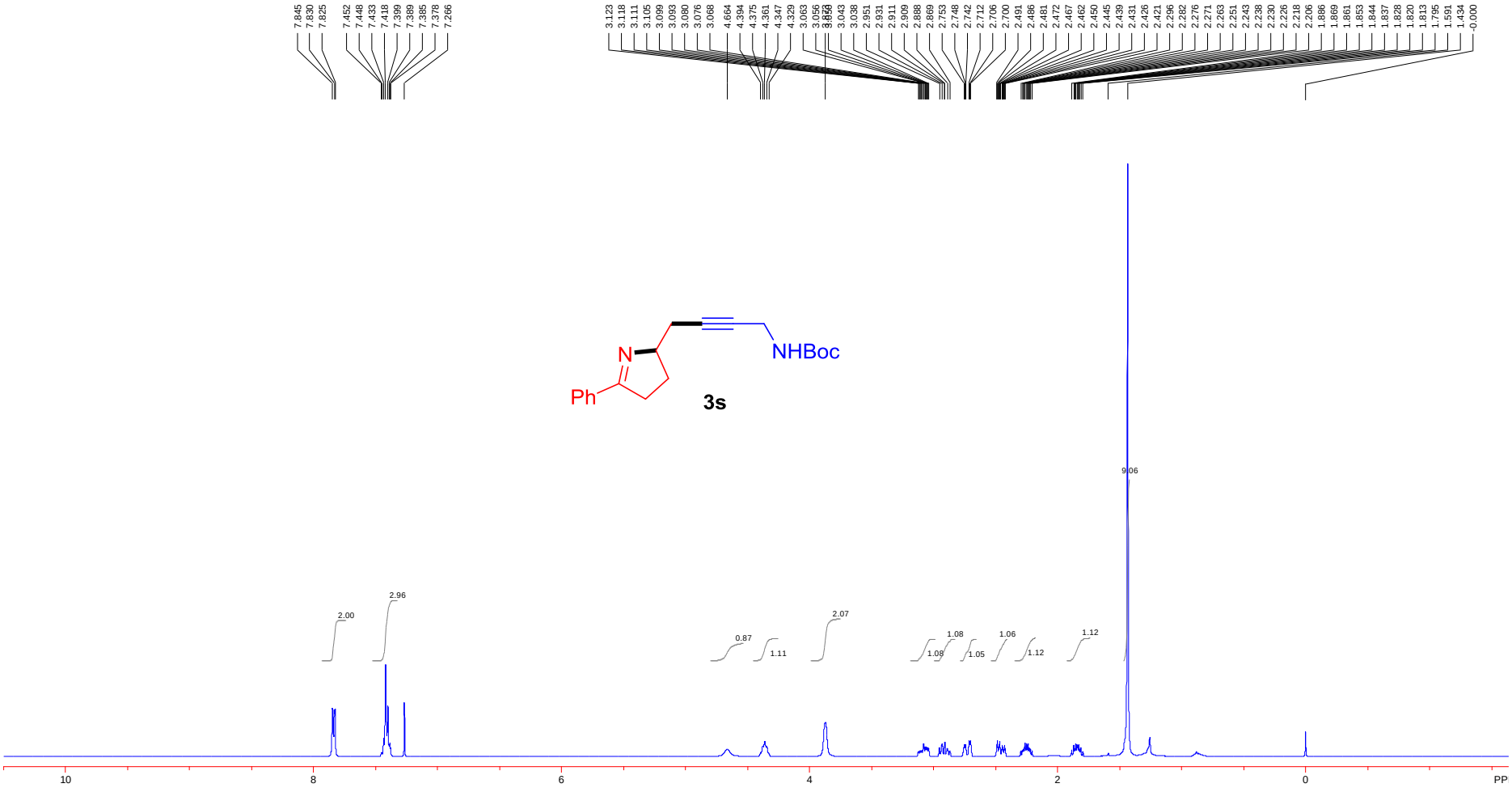
^{1}H NMR(400 MHz, $CDCl_3$)



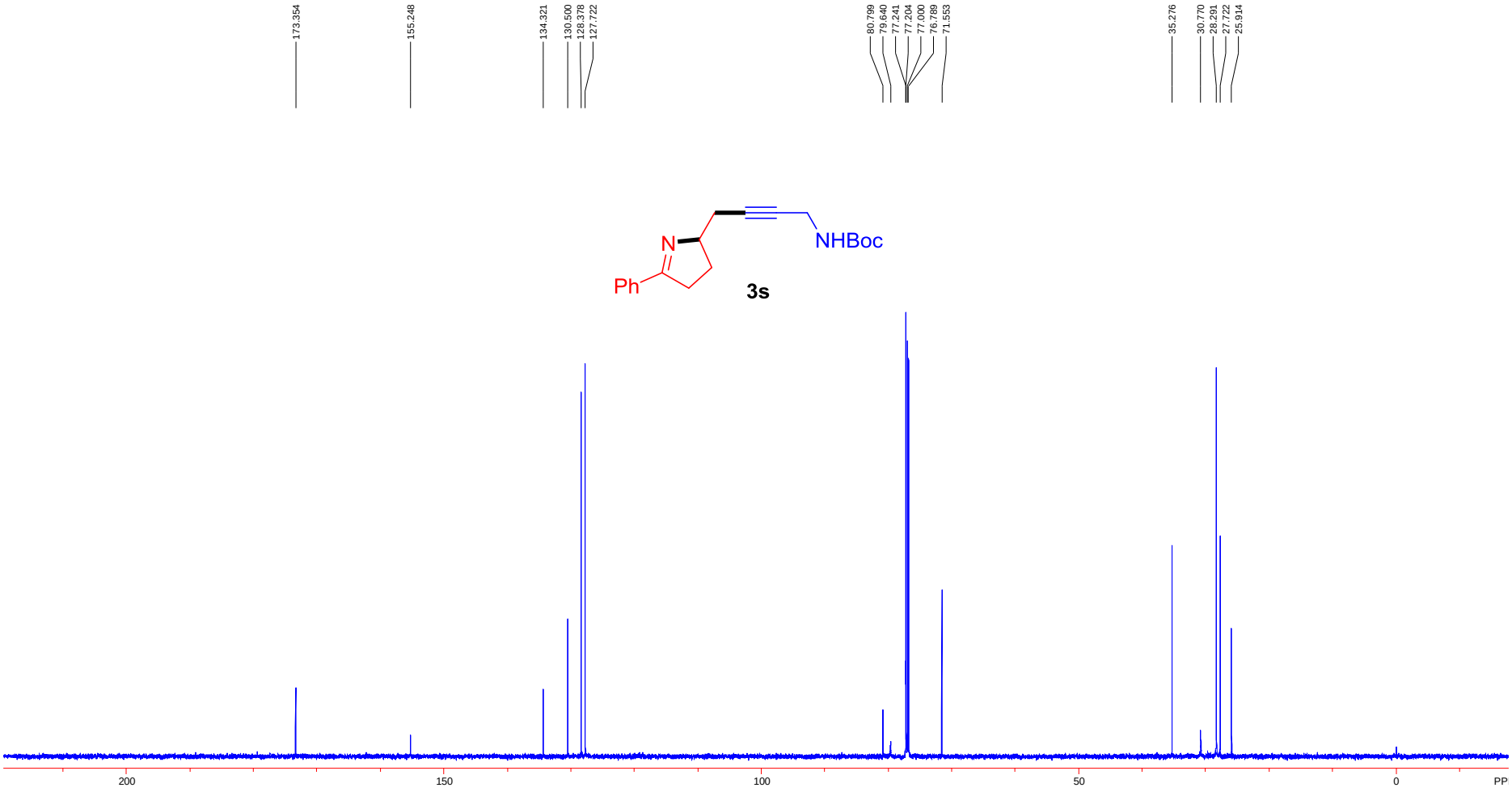
^{13}C NMR(100 MHz, $CDCl_3$)



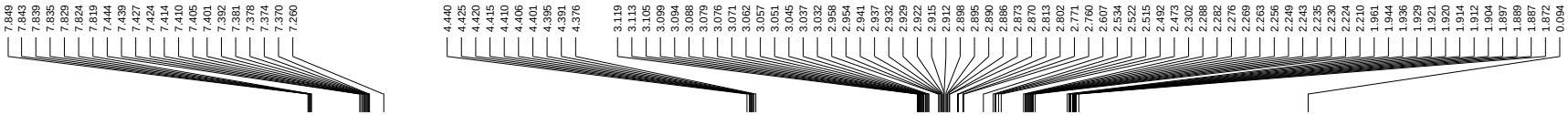
^{1}H NMR(400 MHz, $CDCl_3$)

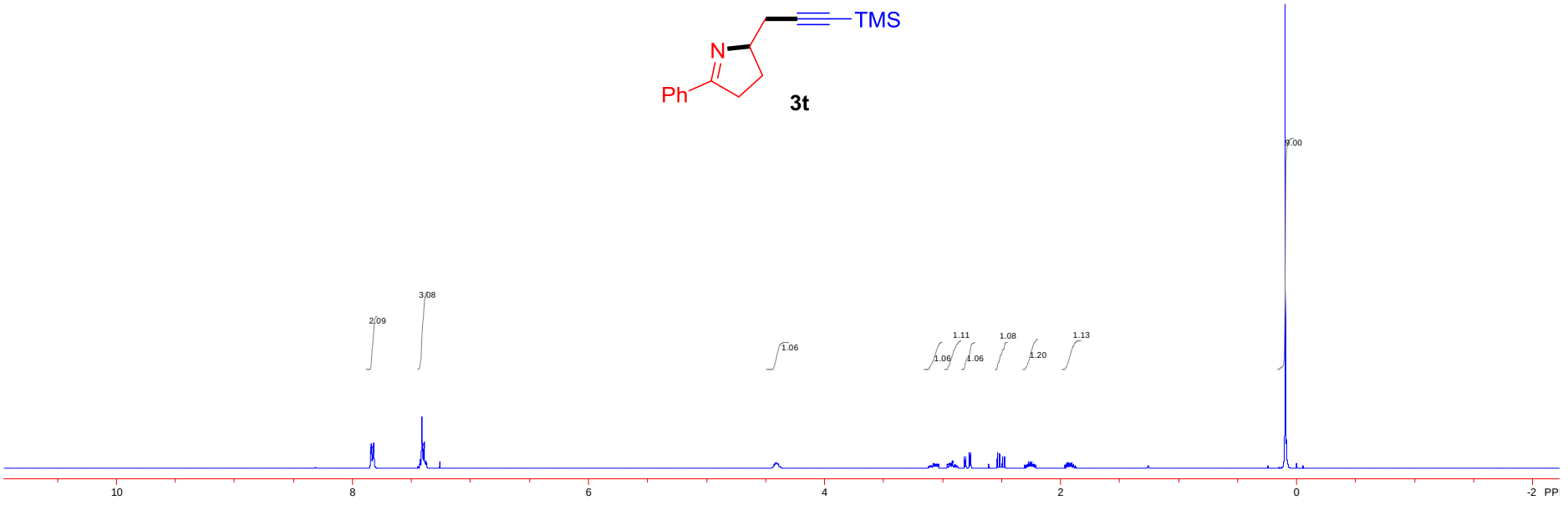


^{13}C NMR(151 MHz, $CDCl_3$)

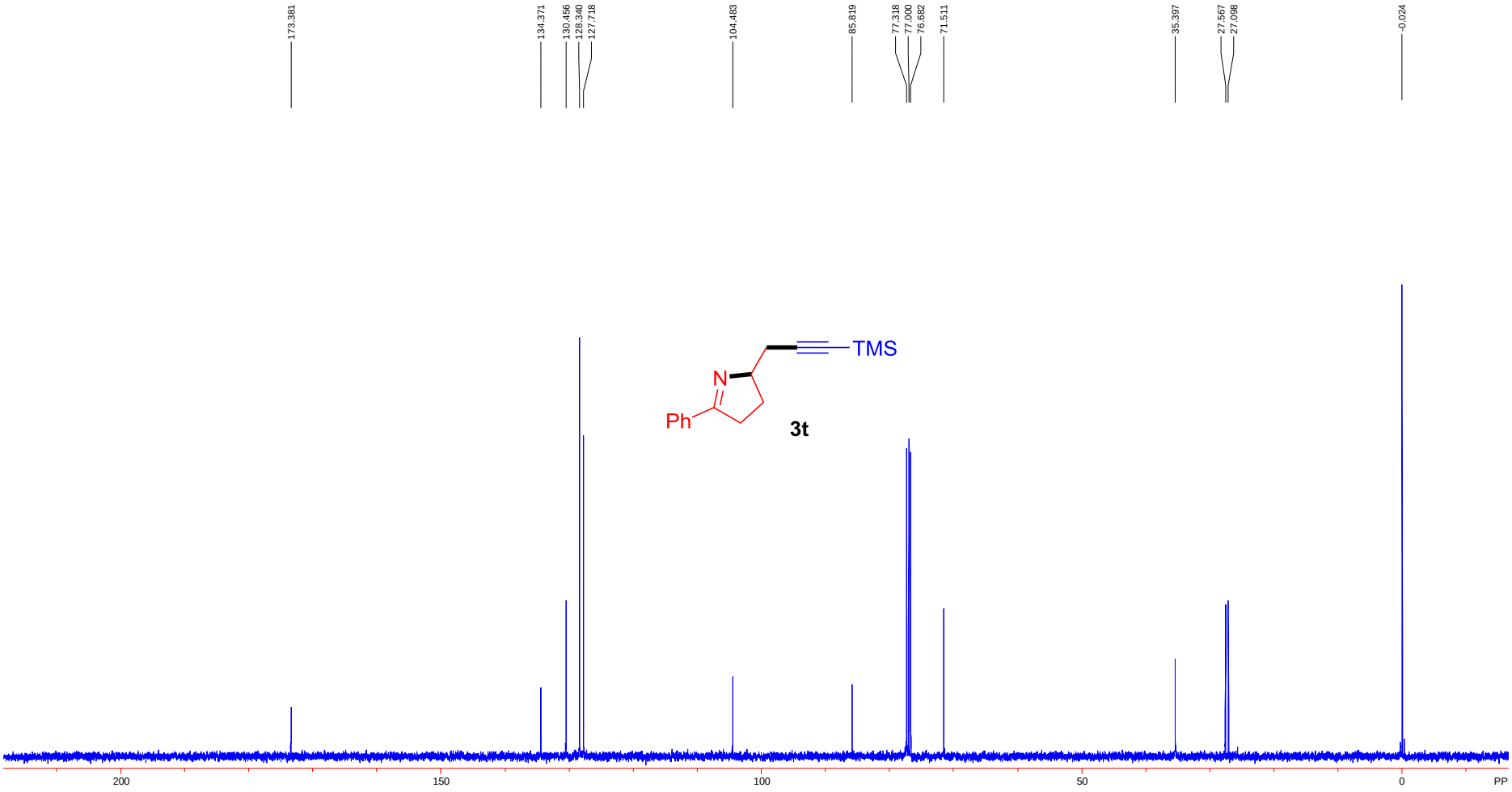


^{1}H NMR(400 MHz, $CDCl_3$)

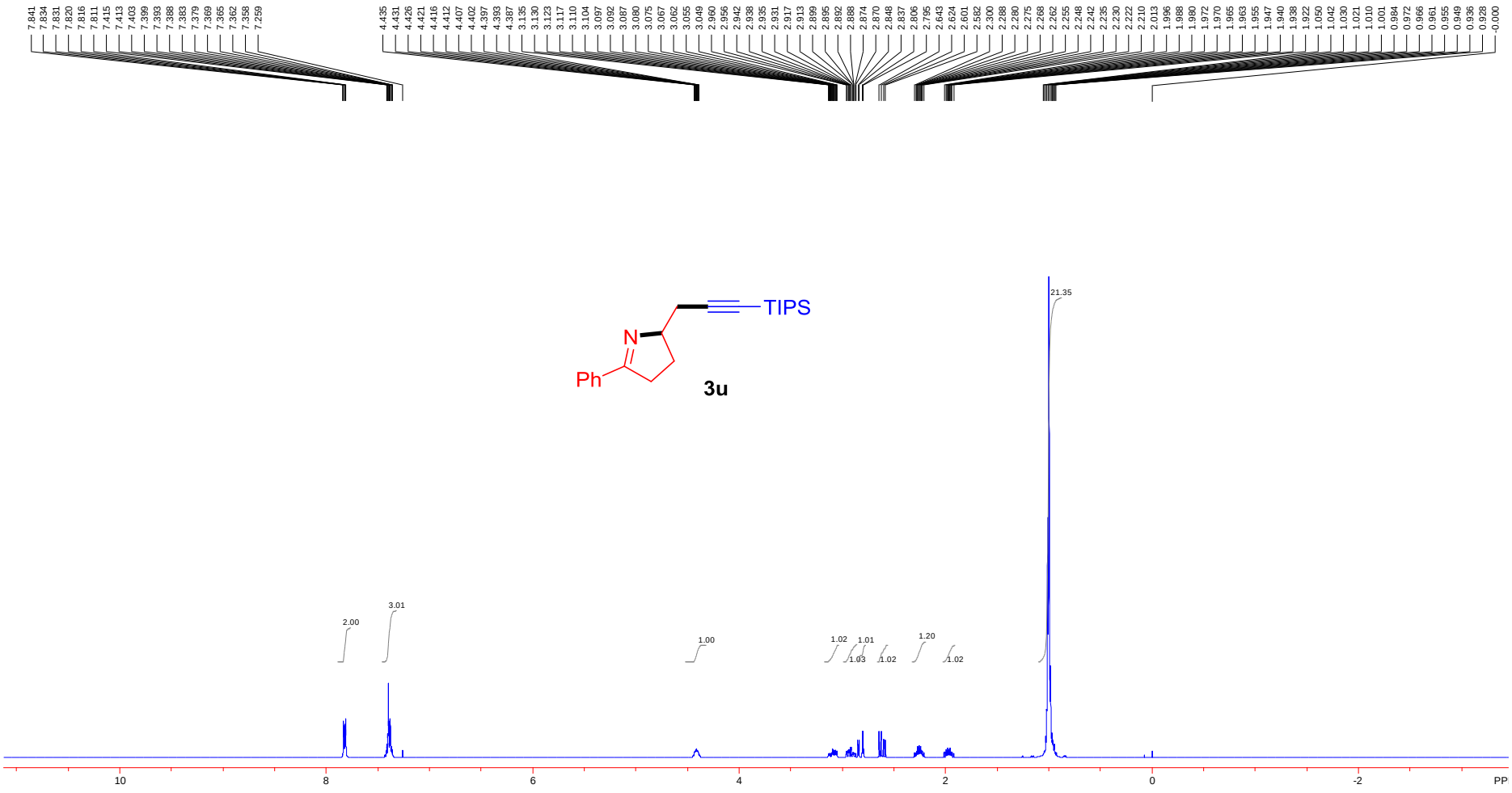




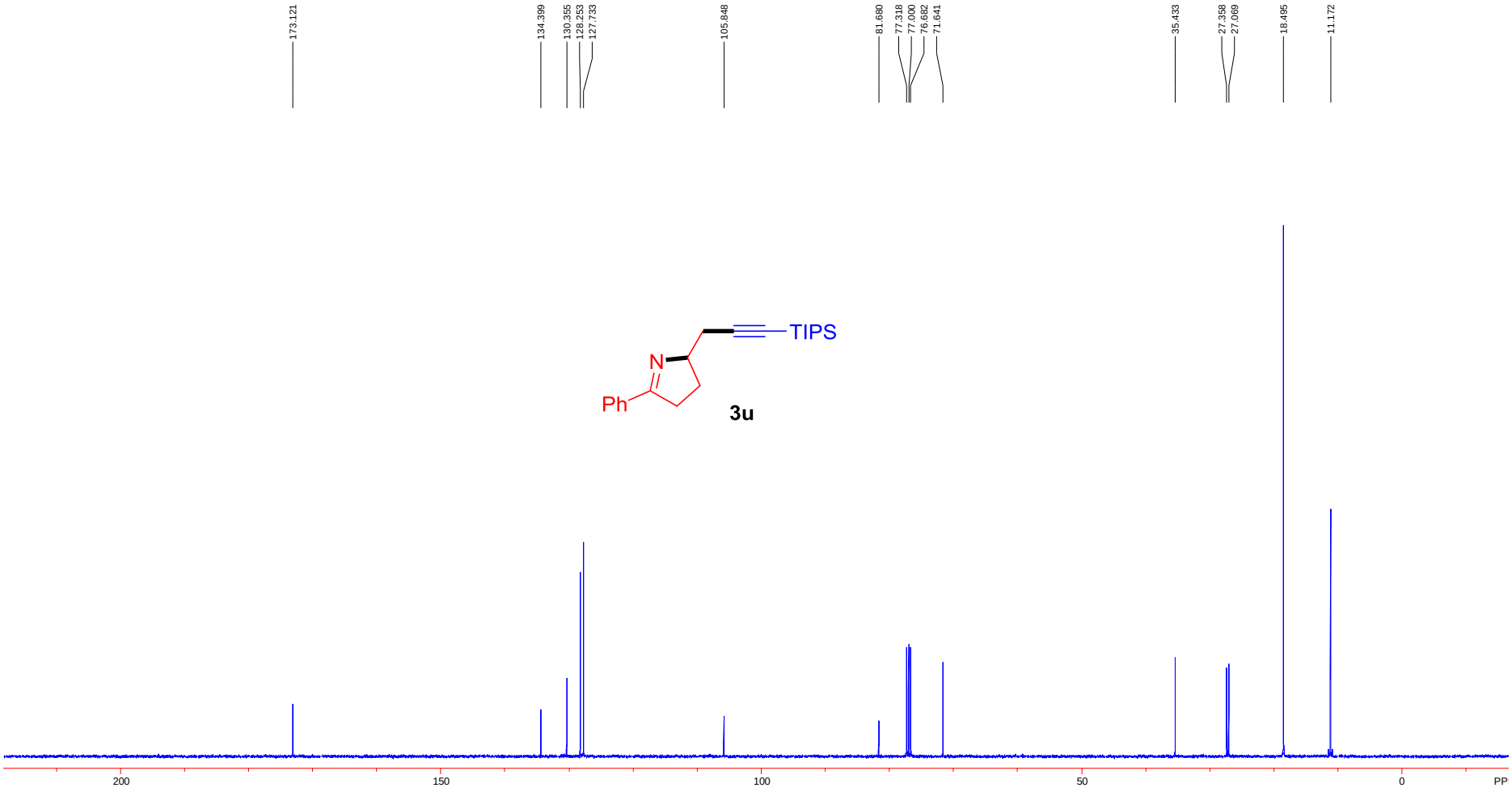
^{13}C NMR(100 MHz, $CDCl_3$)



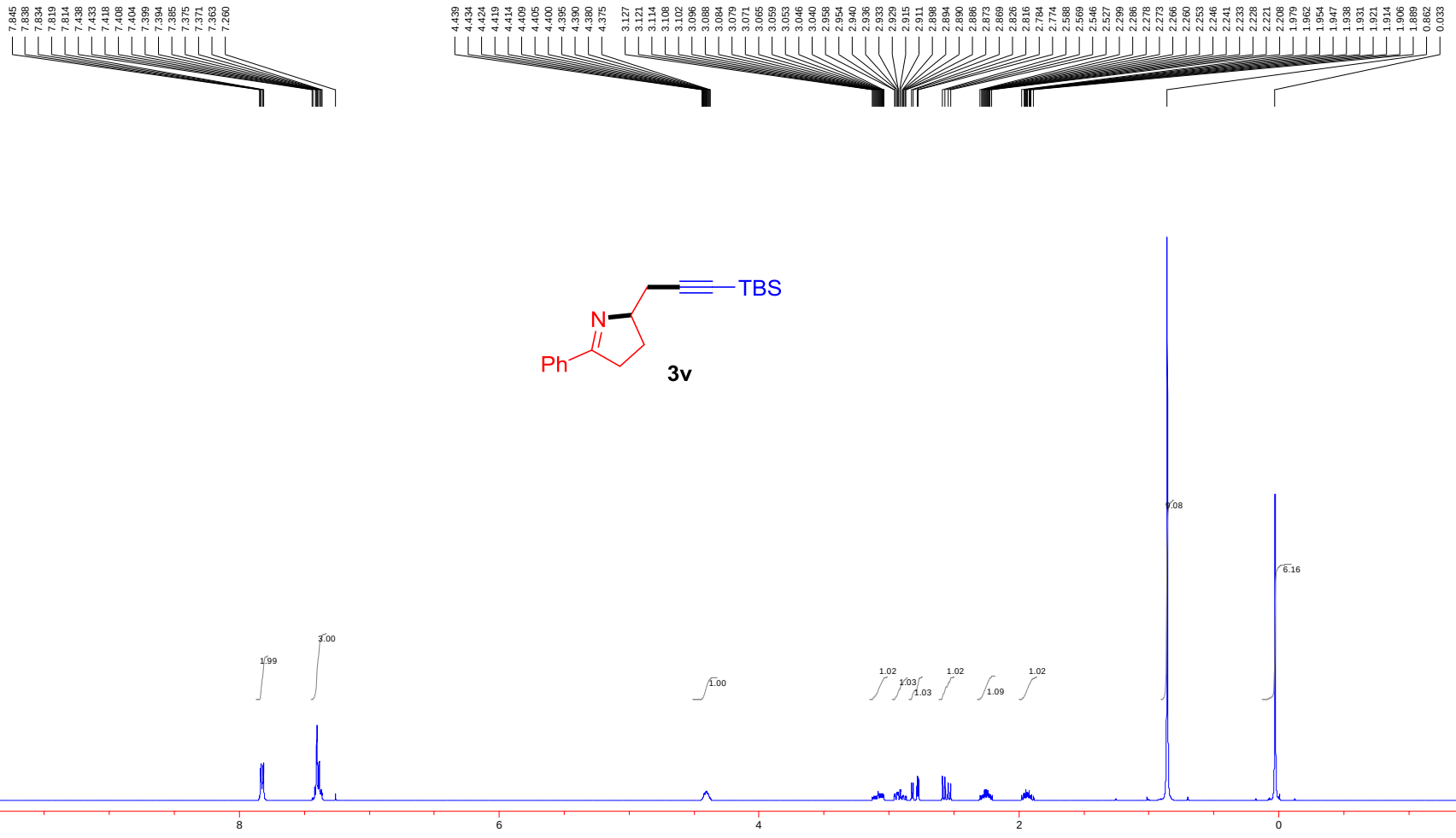
^{1}H NMR(400 MHz, $CDCl_3$)



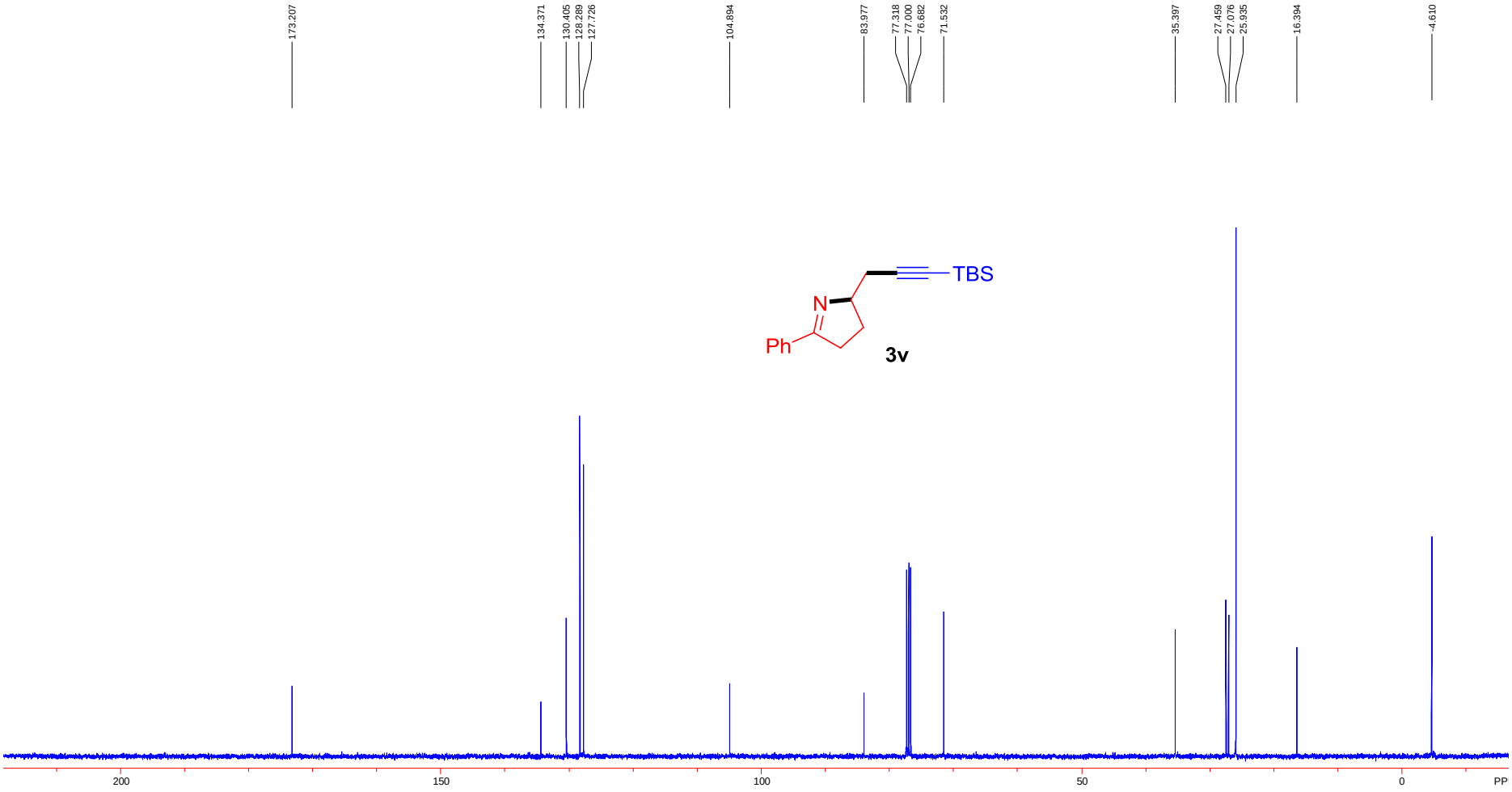
^{13}C NMR(100 MHz, $CDCl_3$)



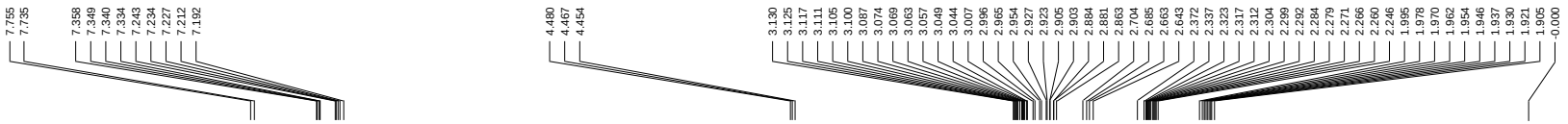
^{1}H NMR(400 MHz, $CDCl_3$)

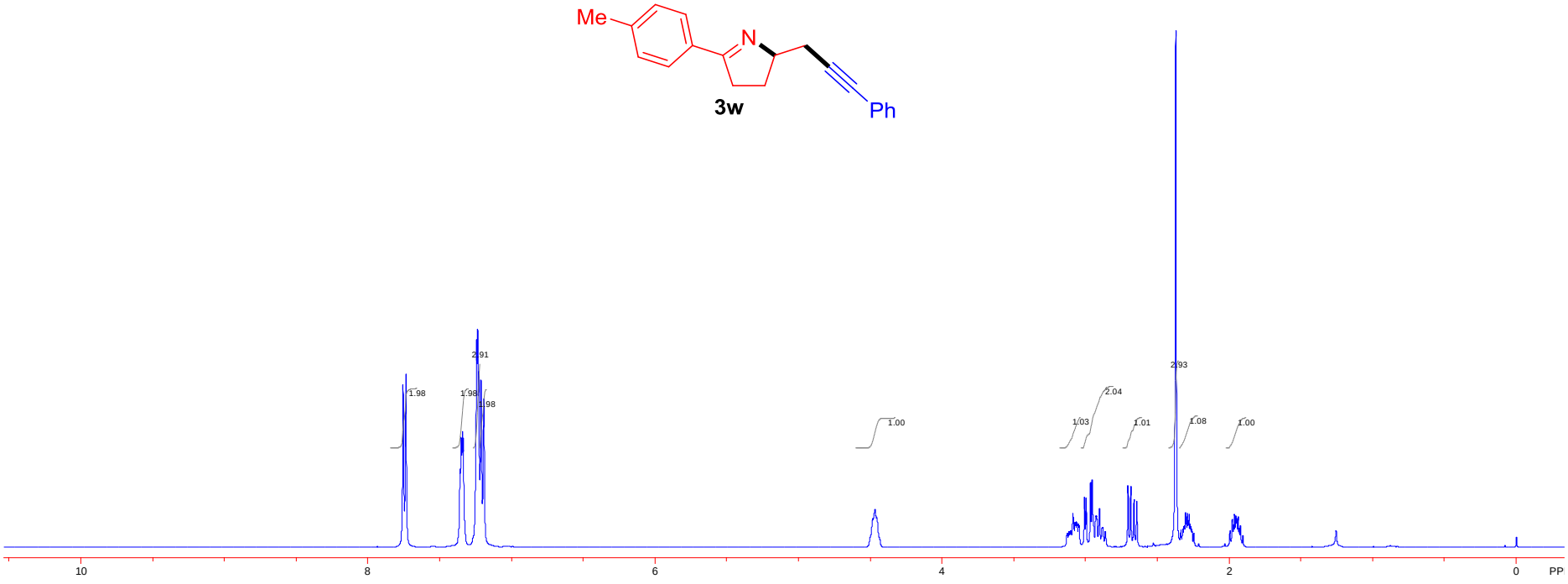


^{13}C NMR(100 MHz, $CDCl_3$)

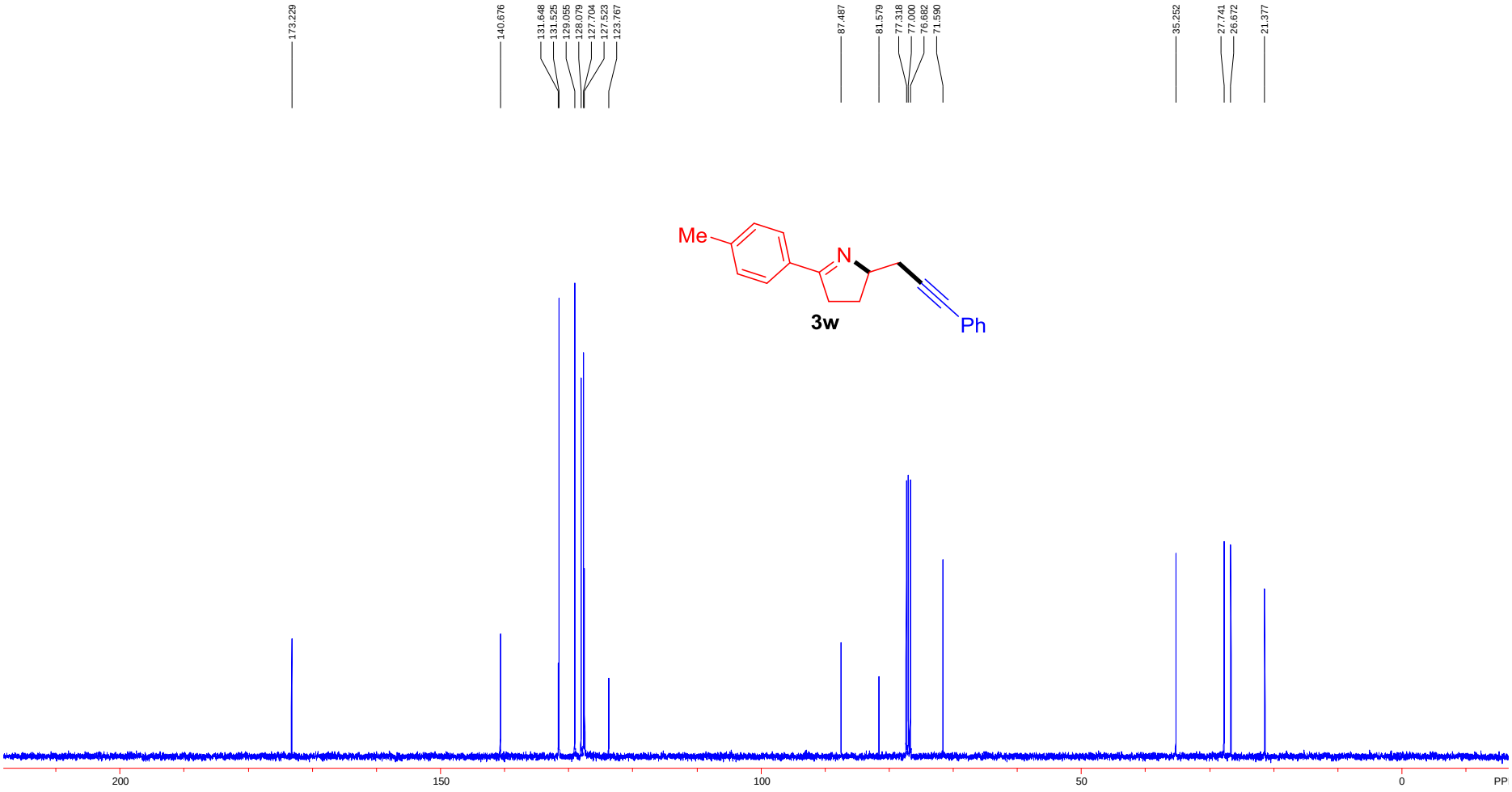


^{1}H NMR(400 MHz, $CDCl_3$)

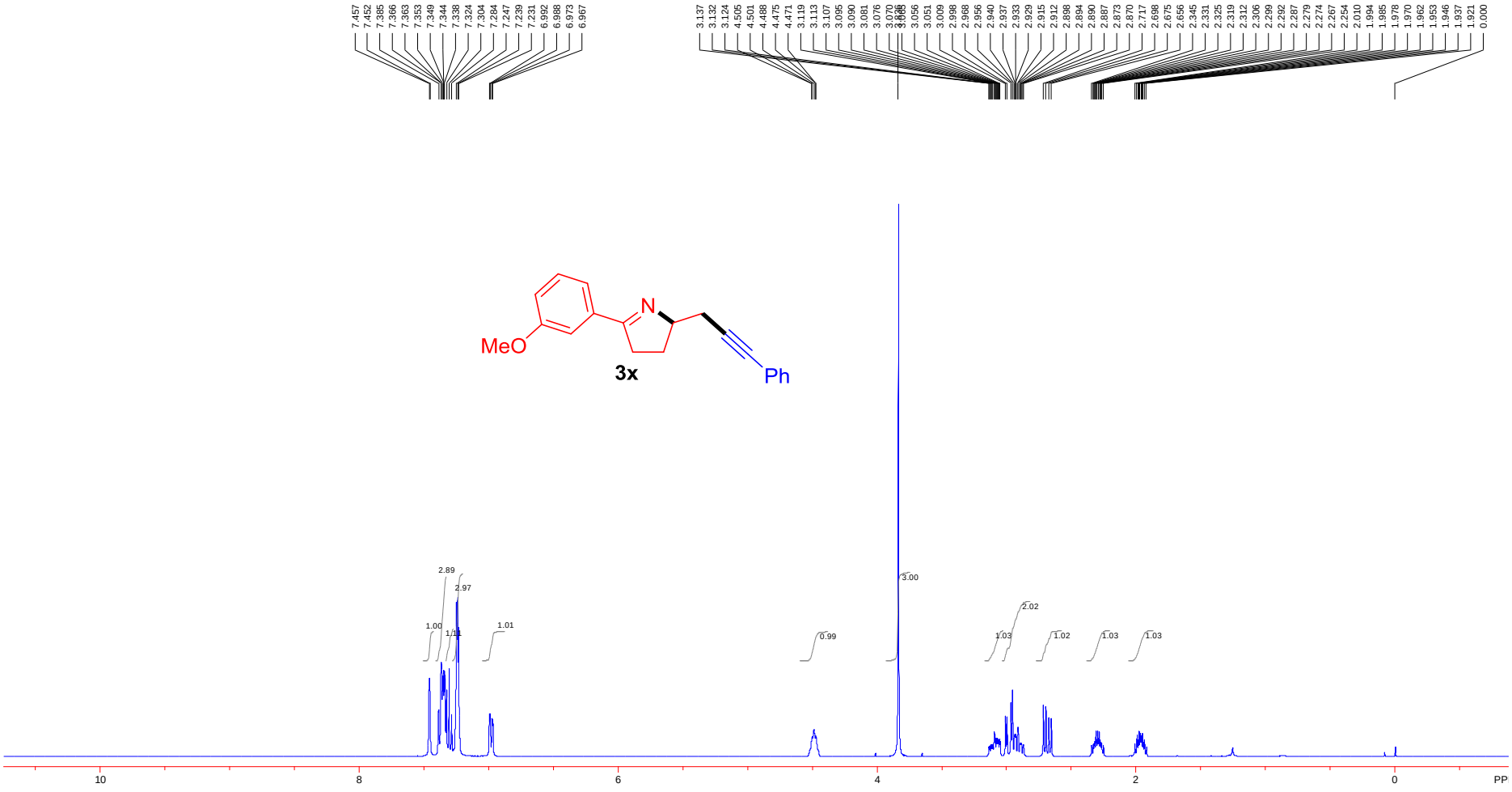




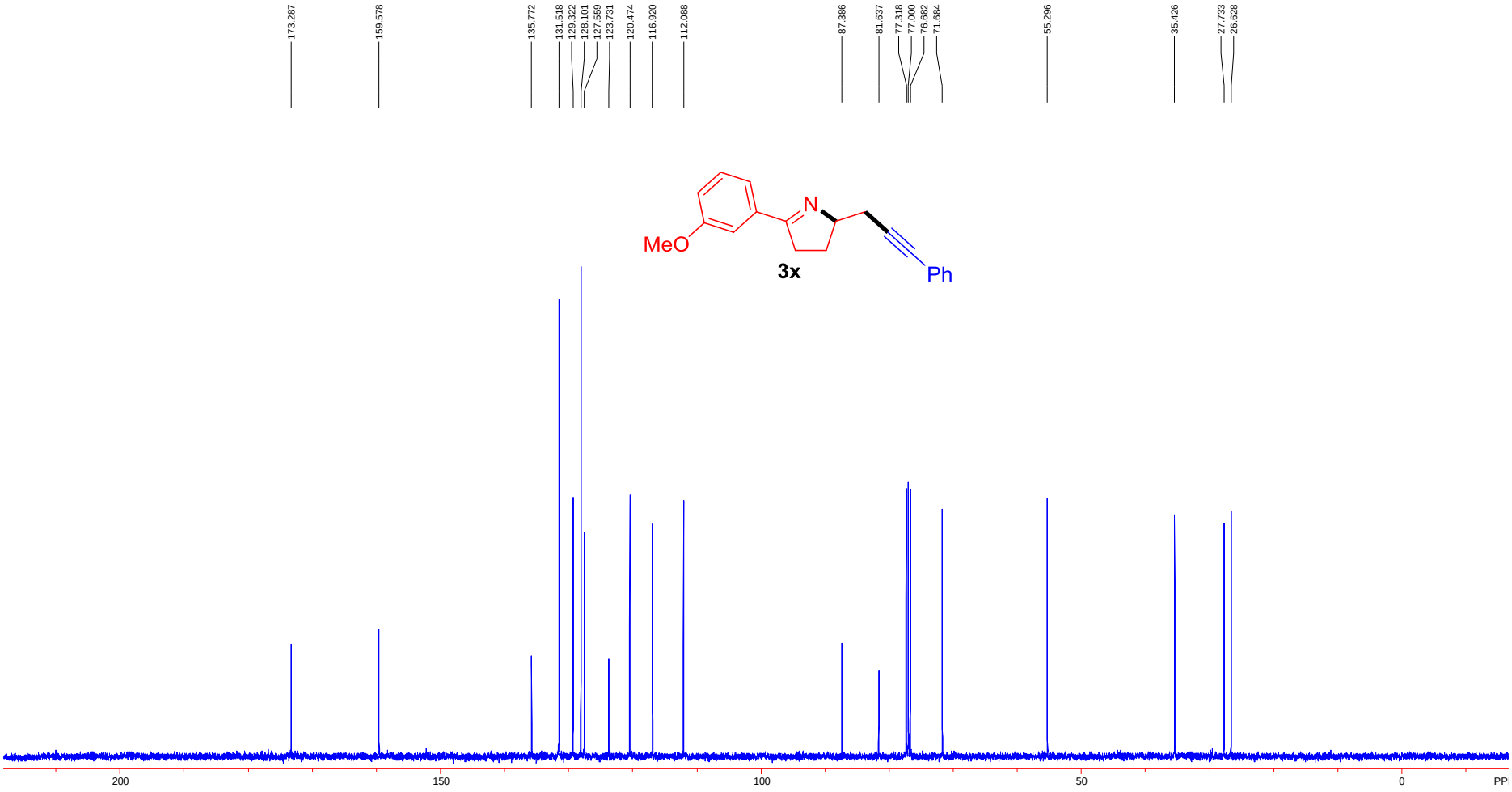
^{13}C NMR(100 MHz, $CDCl_3$)



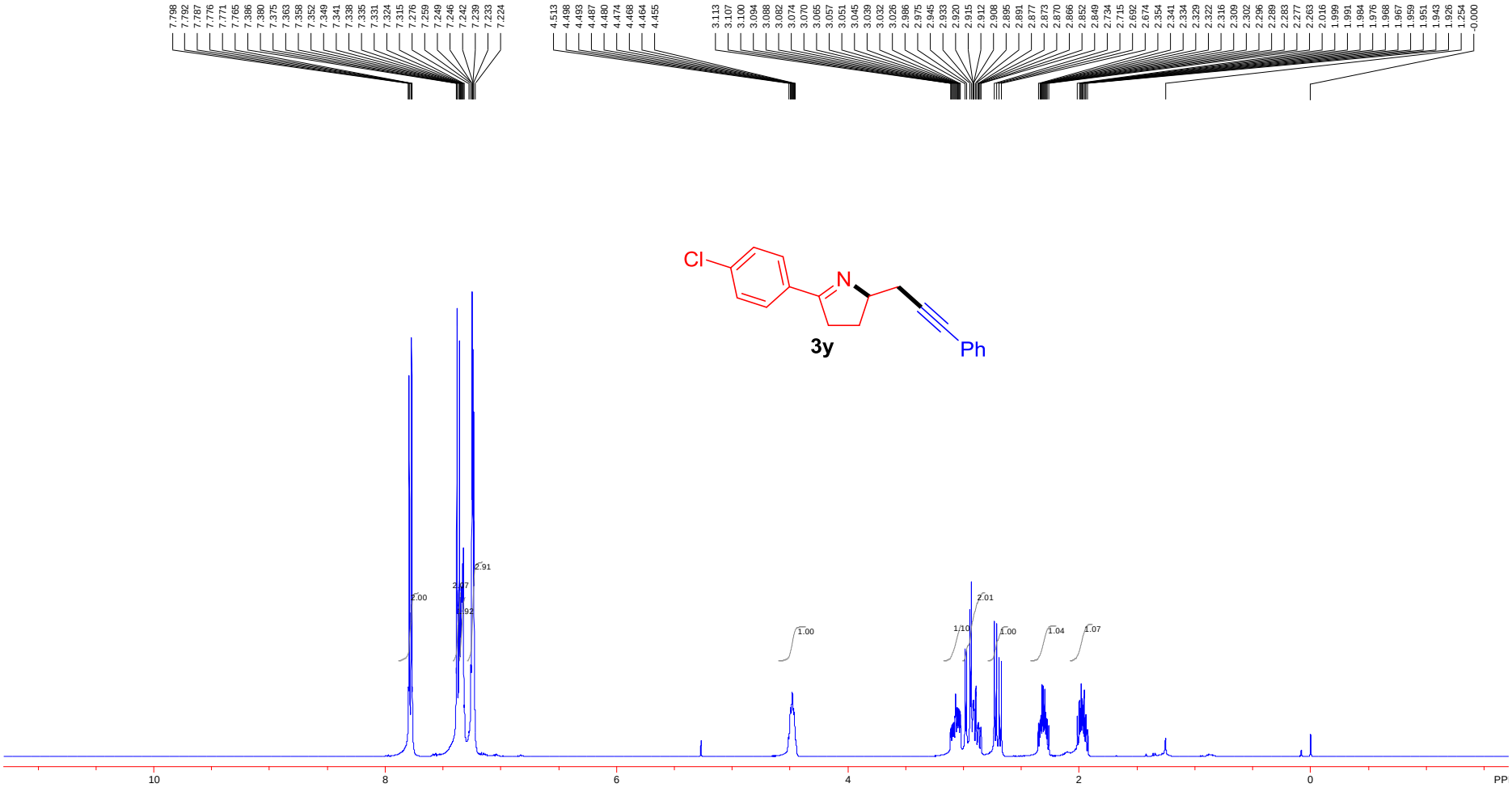
^{1}H NMR(400 MHz, $CDCl_3$)



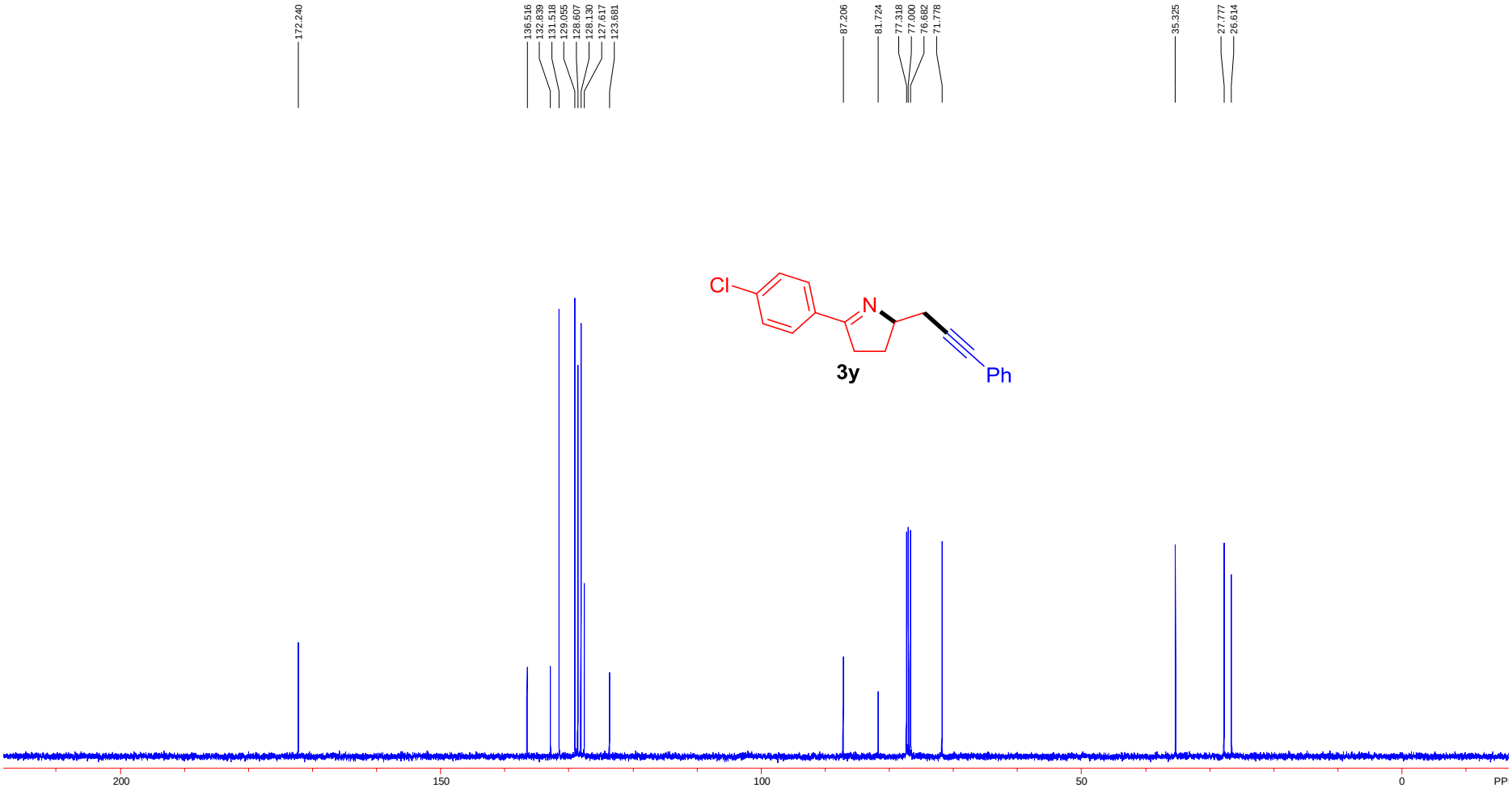
^{13}C NMR(100 MHz, $CDCl_3$)



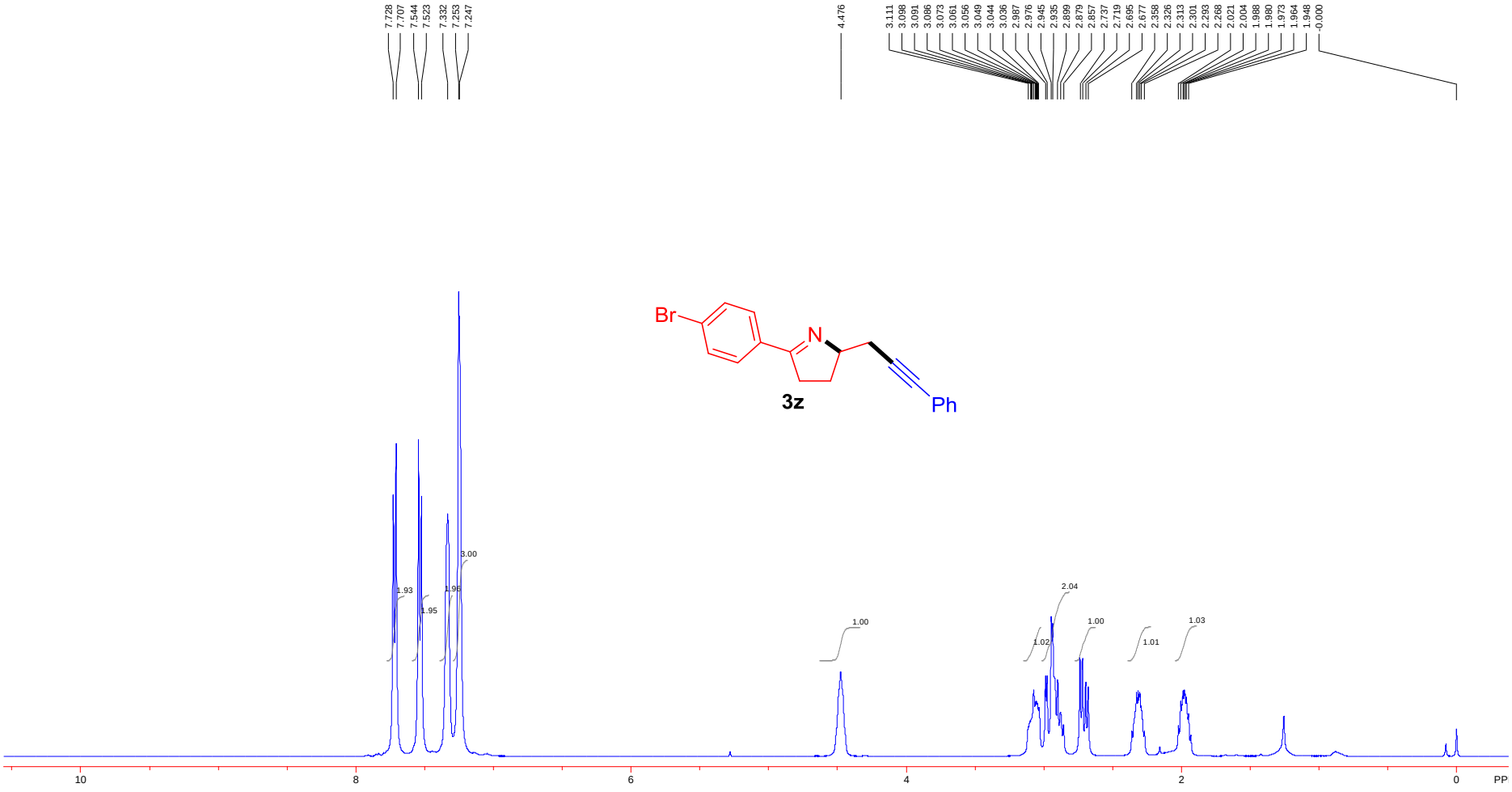
^{1}H NMR(400 MHz, $CDCl_3$)



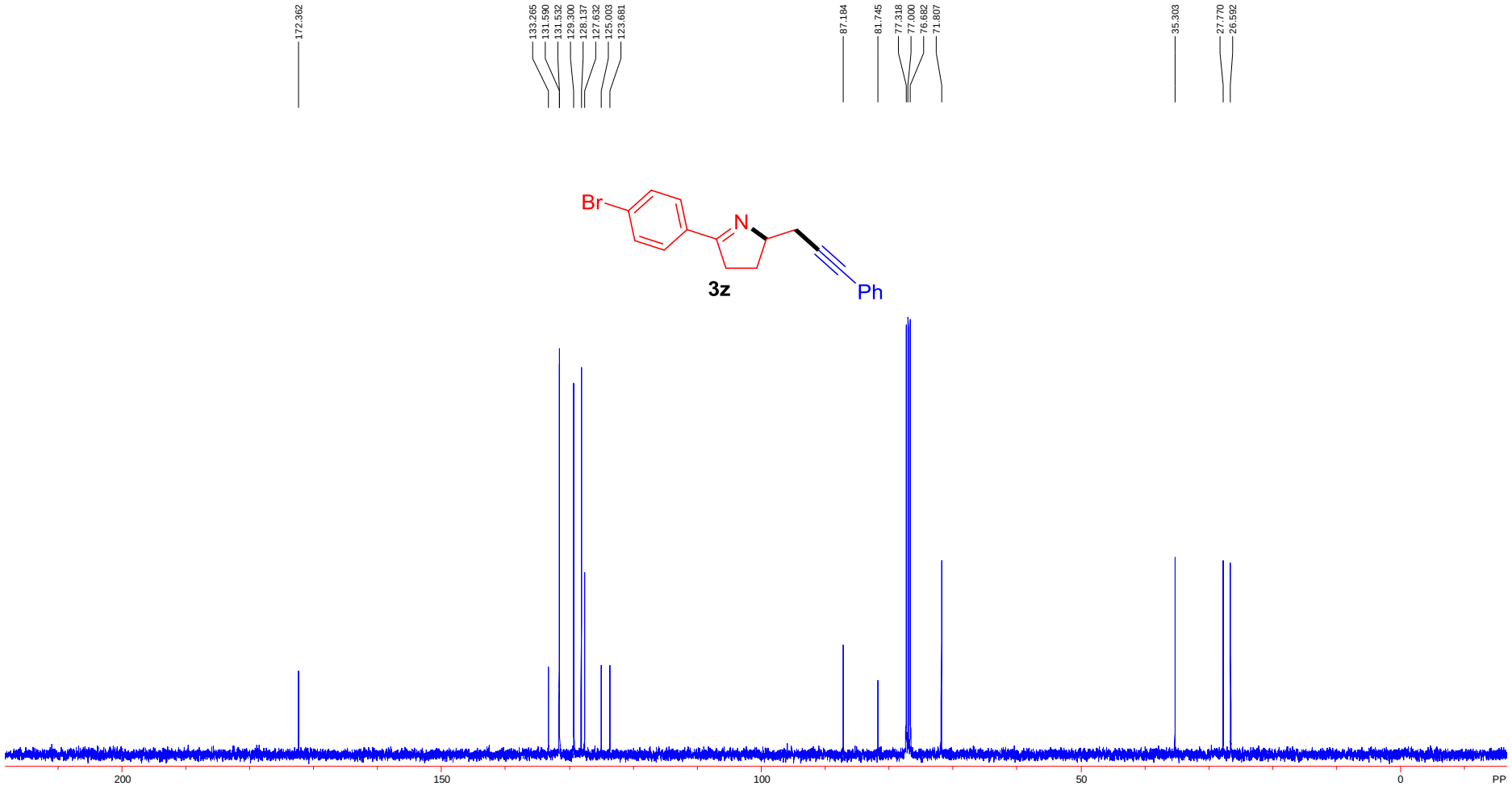
^{13}C NMR(100 MHz, $CDCl_3$)



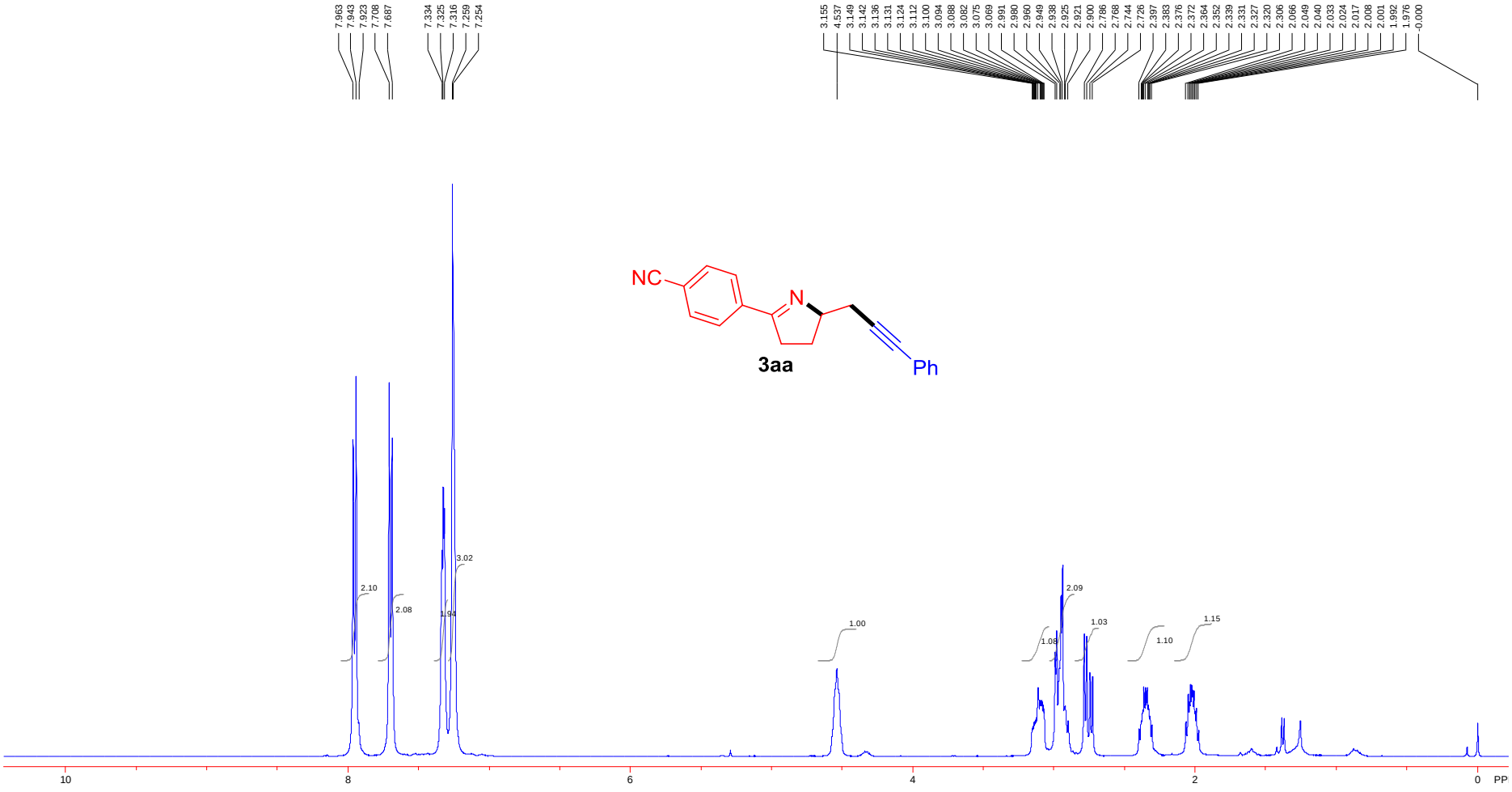
^{1}H NMR(400 MHz, $CDCl_3$)



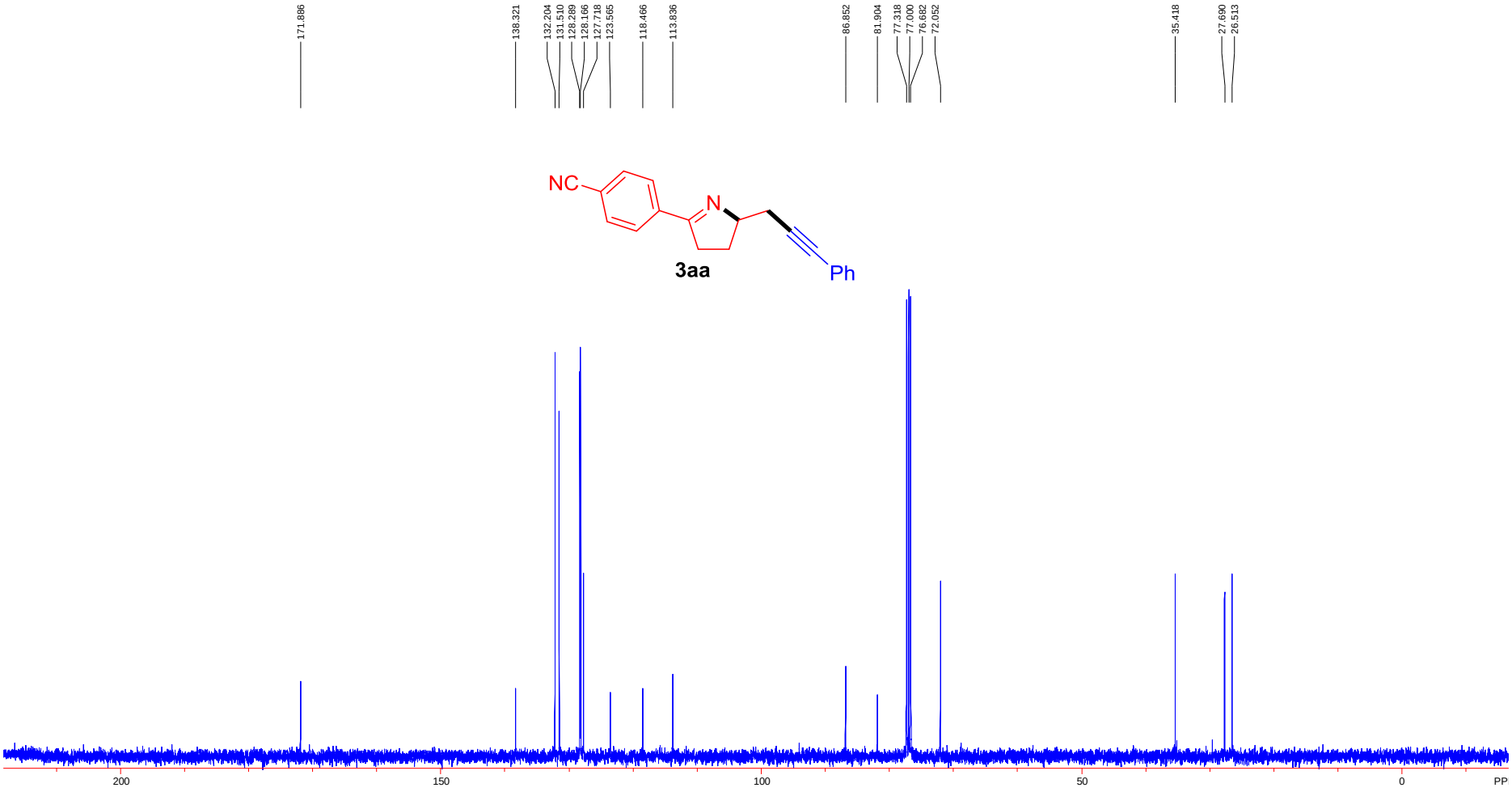
^{13}C NMR(100 MHz, $CDCl_3$)



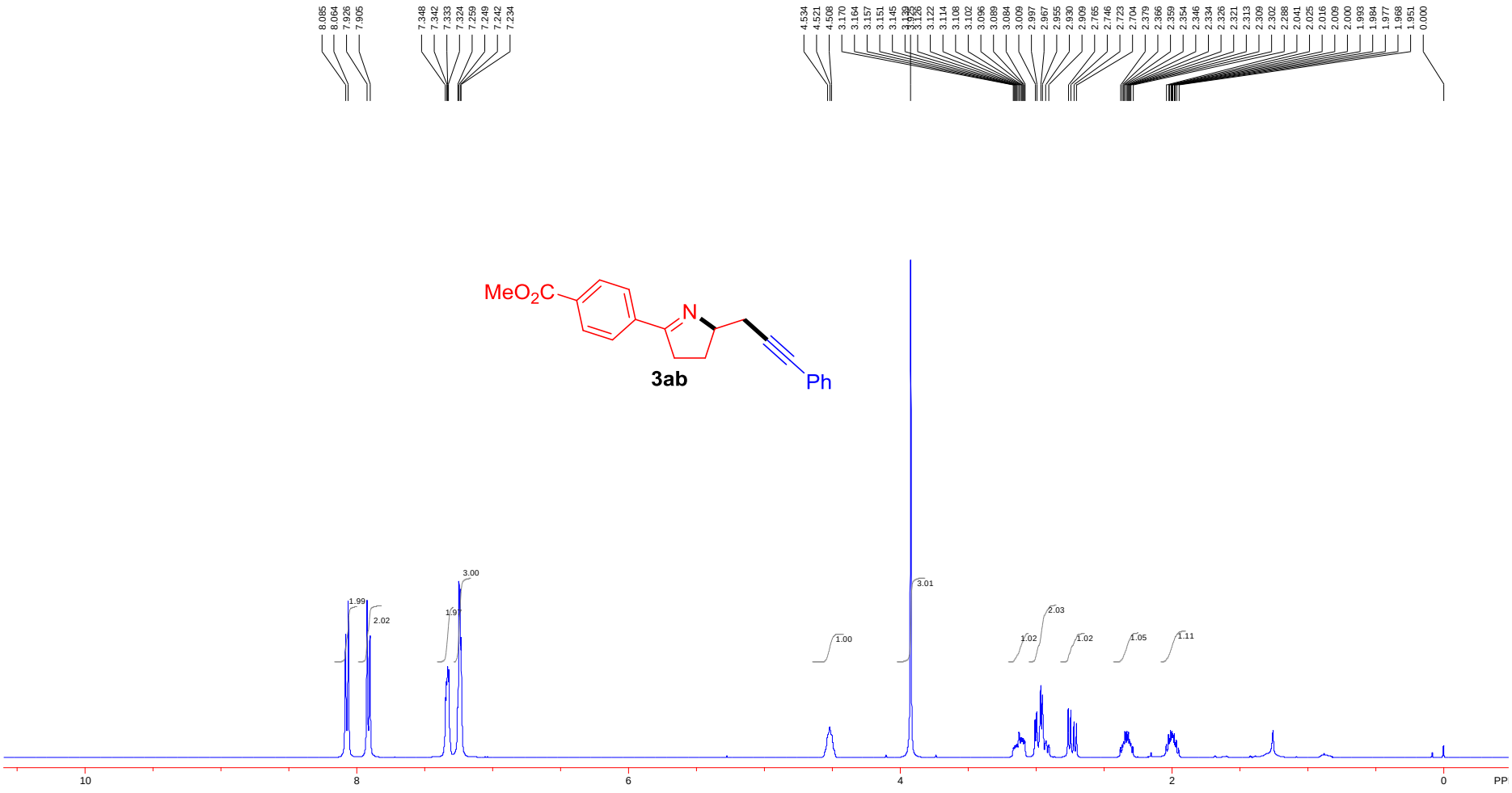
^{1}H NMR(400 MHz, $CDCl_3$)



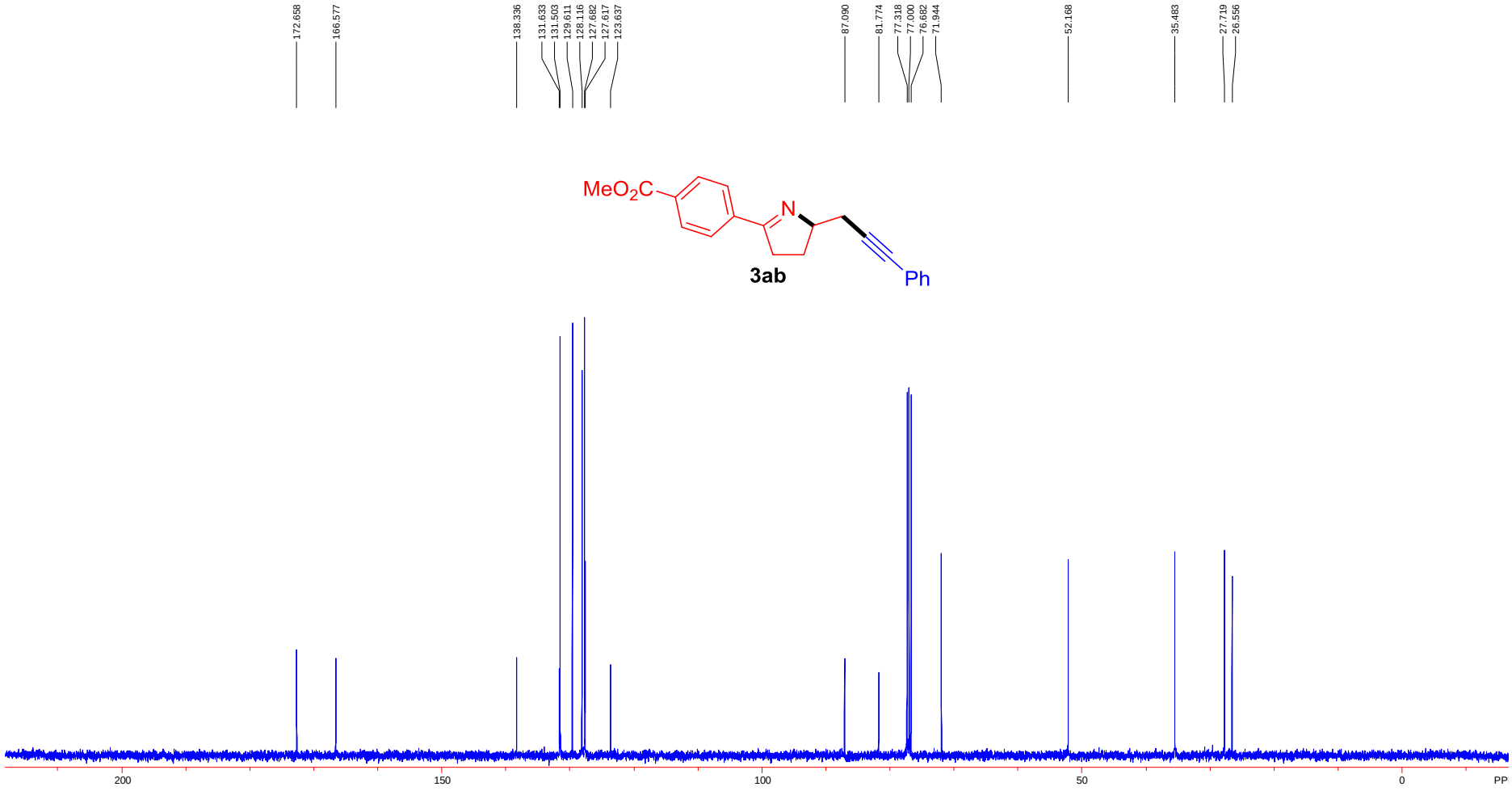
^{13}C NMR(100 MHz, $CDCl_3$)



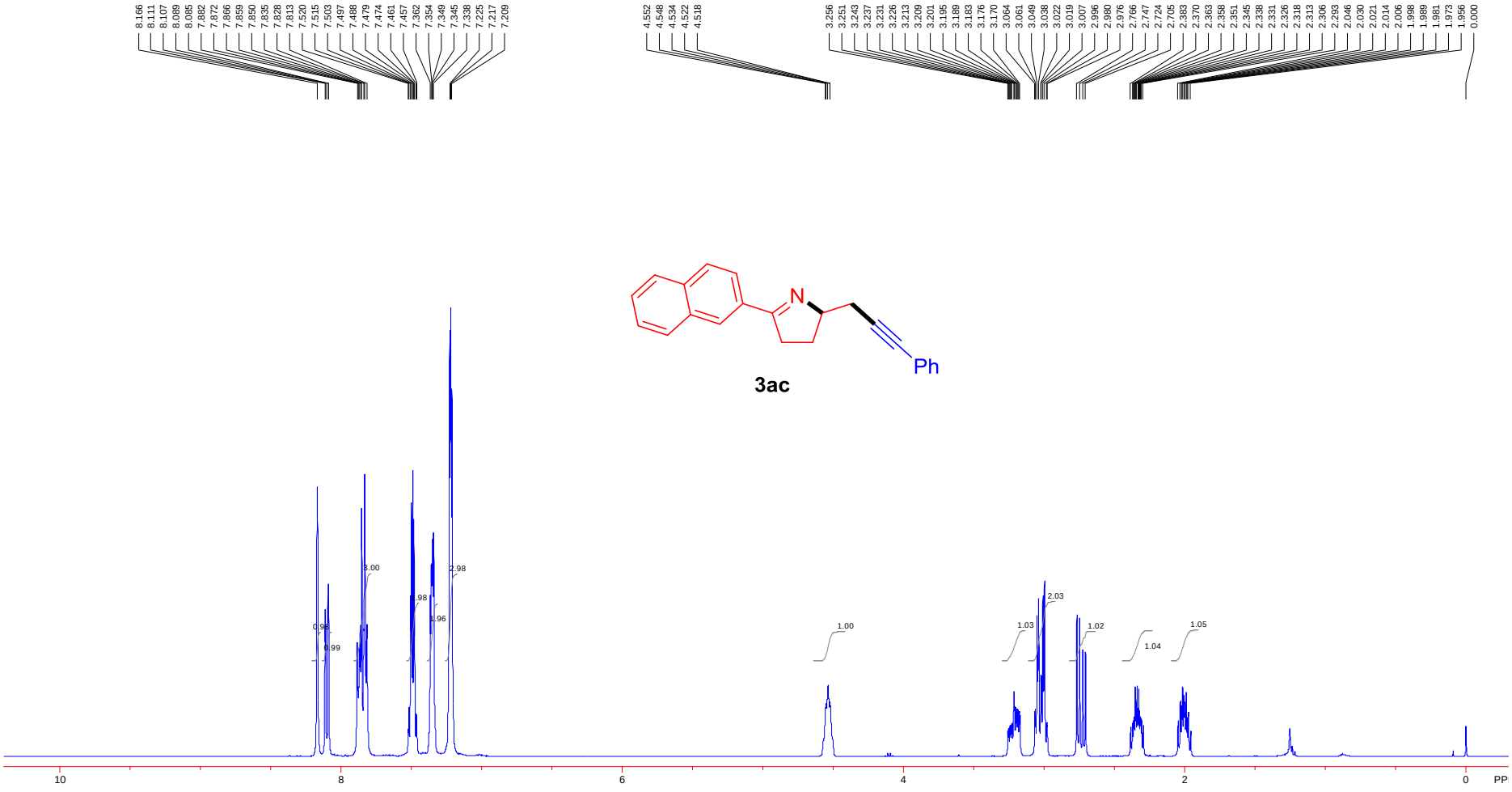
^{1}H NMR(400 MHz, $CDCl_3$)



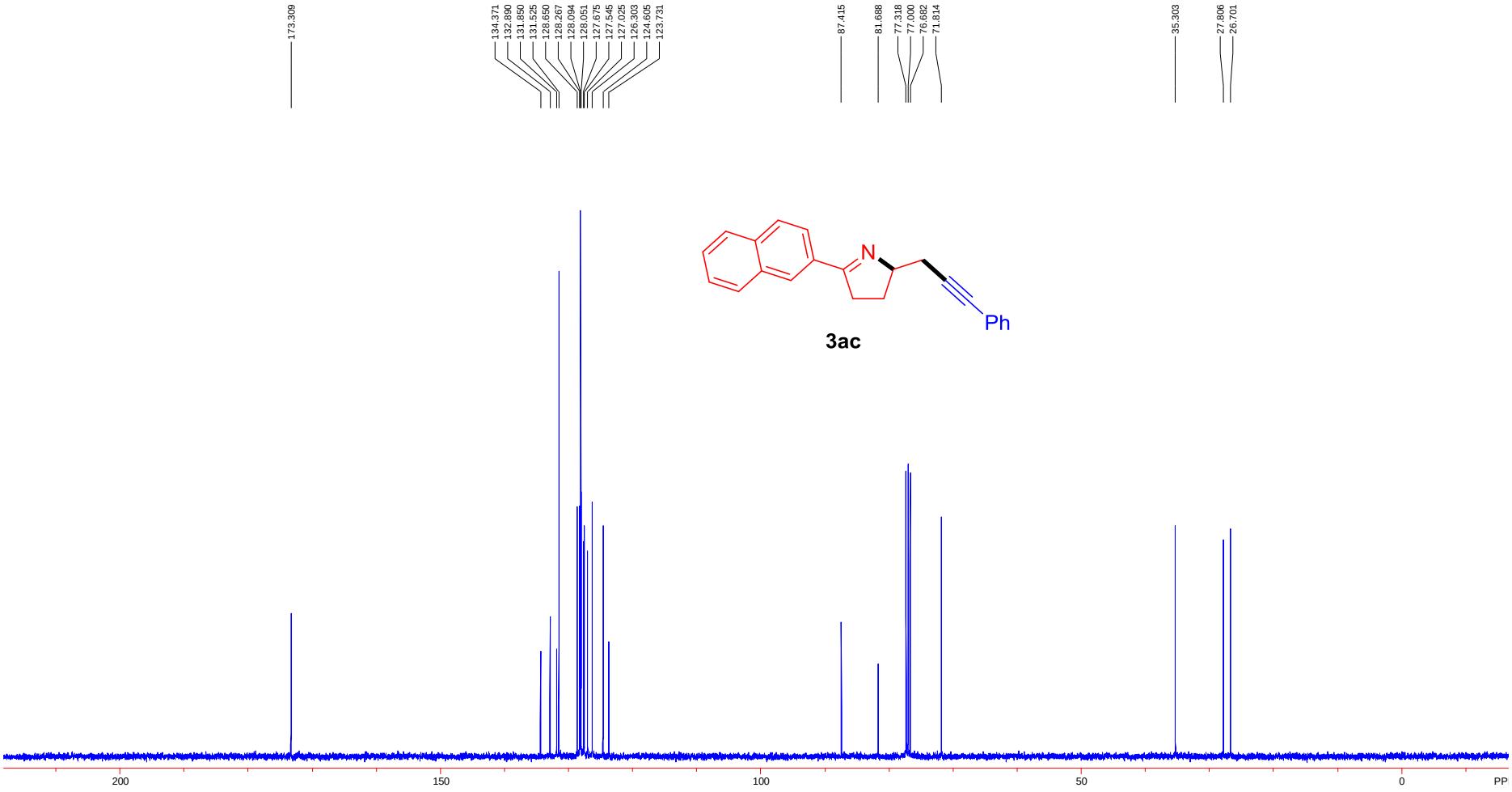
^{13}C NMR(100 MHz, $CDCl_3$)



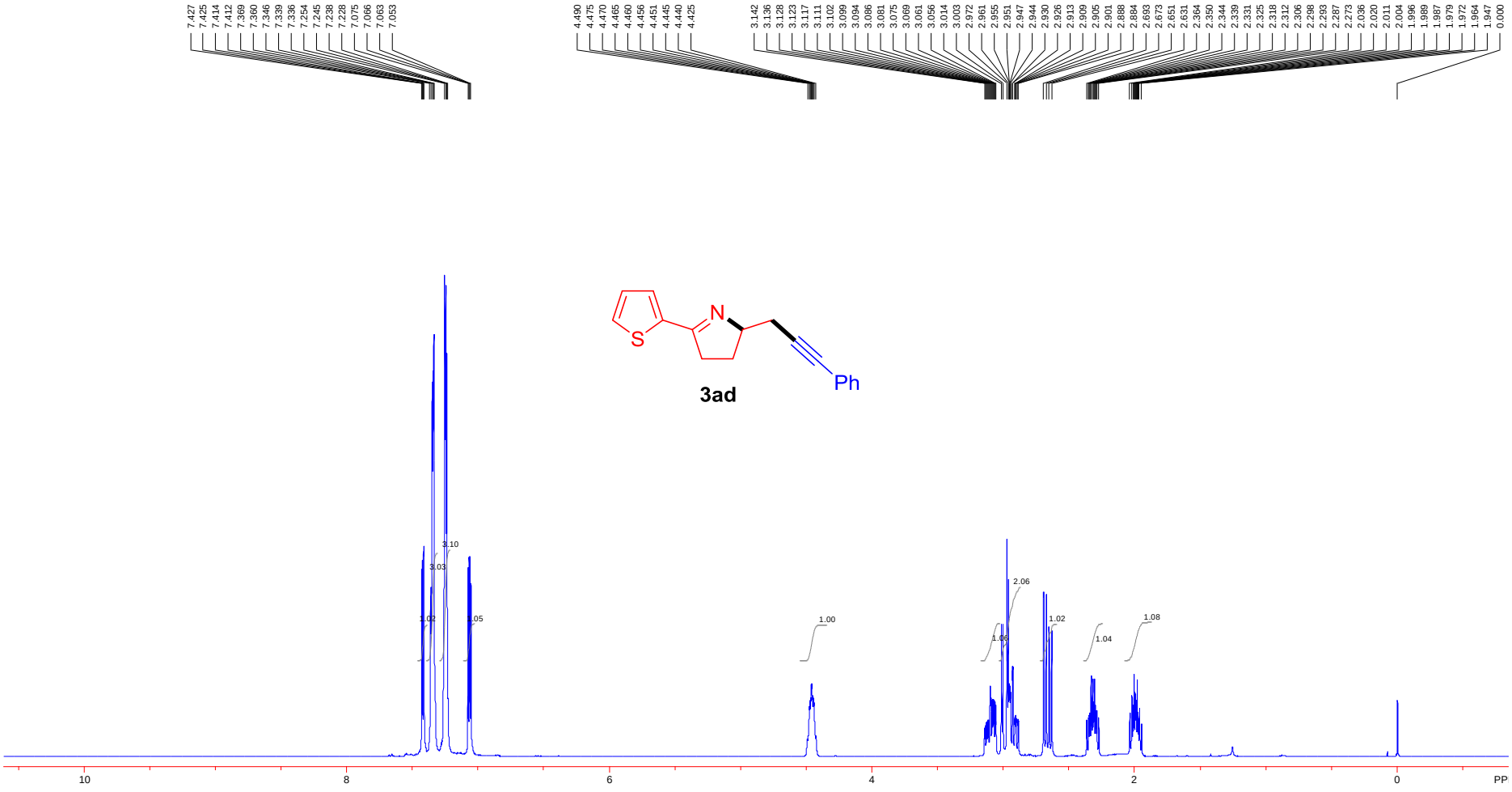
^{1}H NMR(400 MHz, $CDCl_3$)



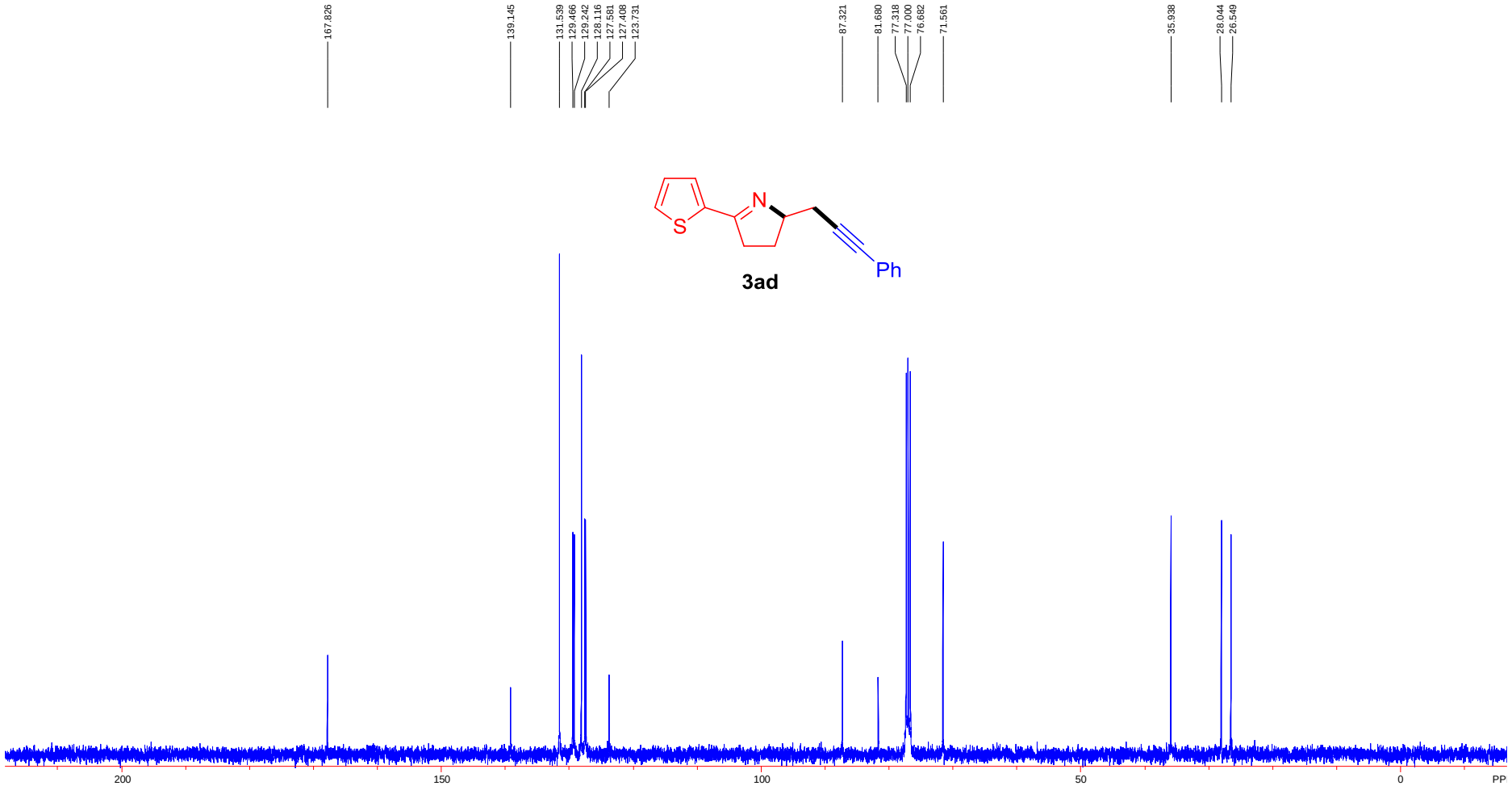
^{13}C NMR(100 MHz, $CDCl_3$)



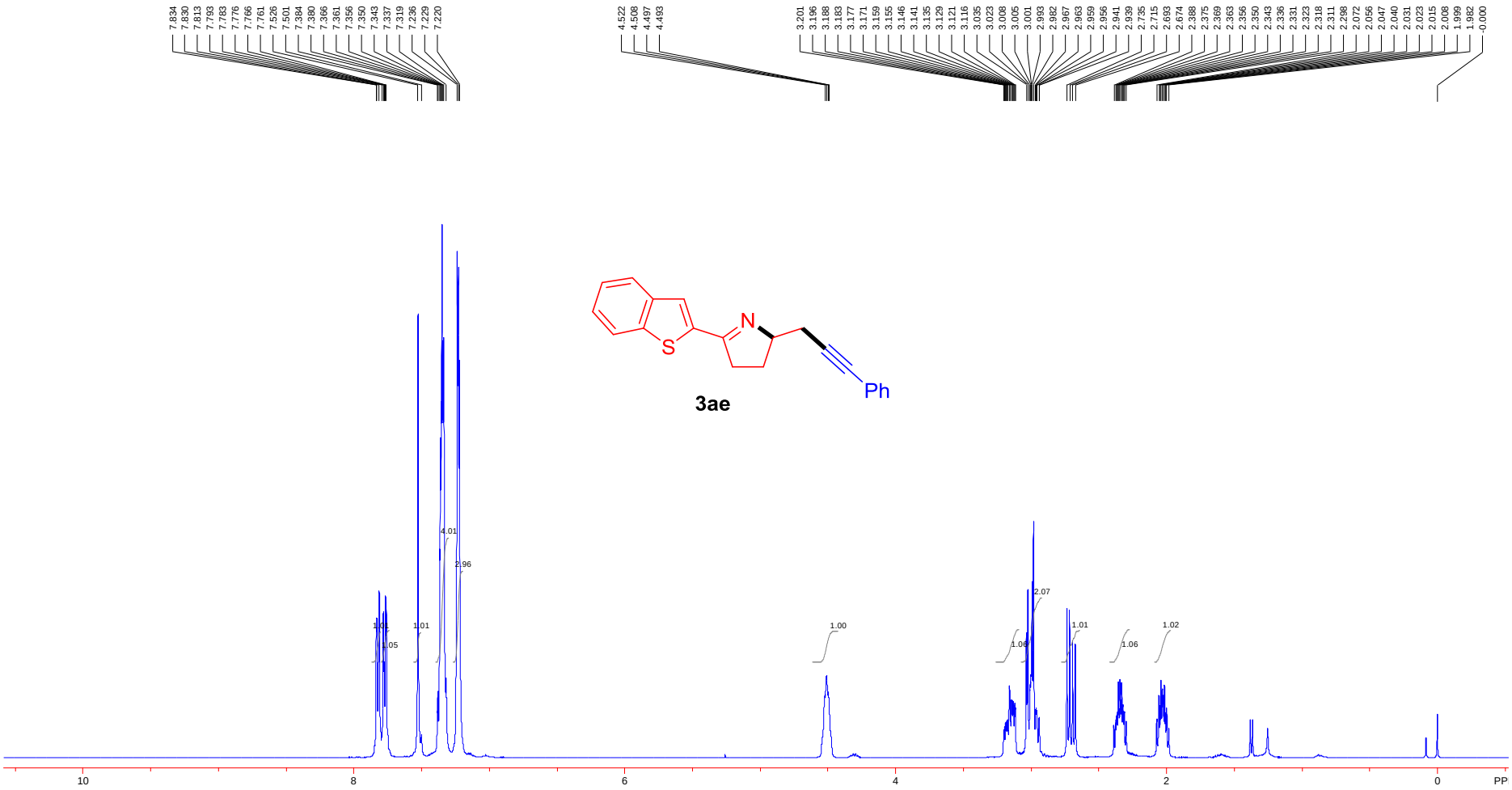
^{1}H NMR(400 MHz, $CDCl_3$)



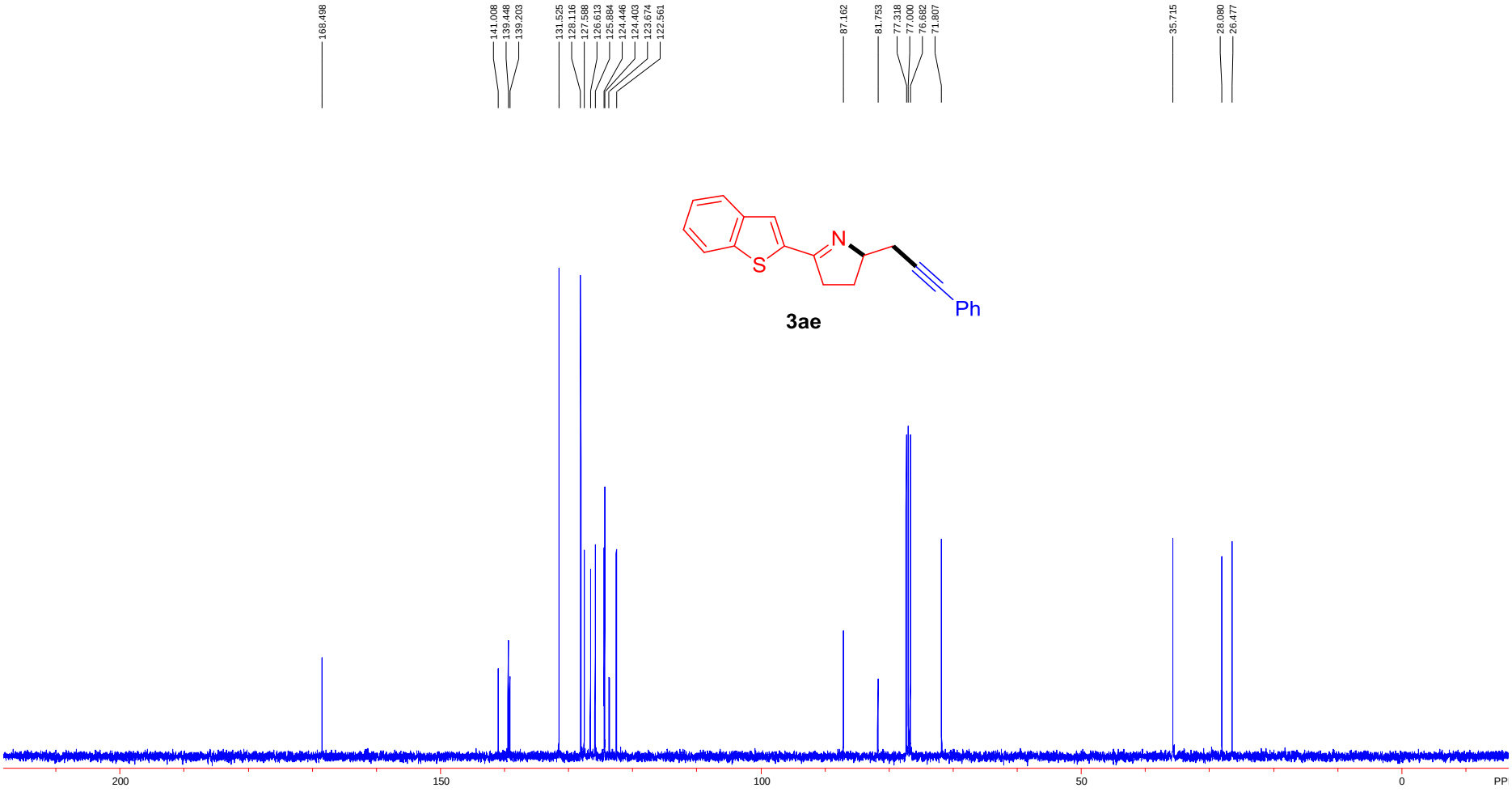
^{13}C NMR(100 MHz, $CDCl_3$)



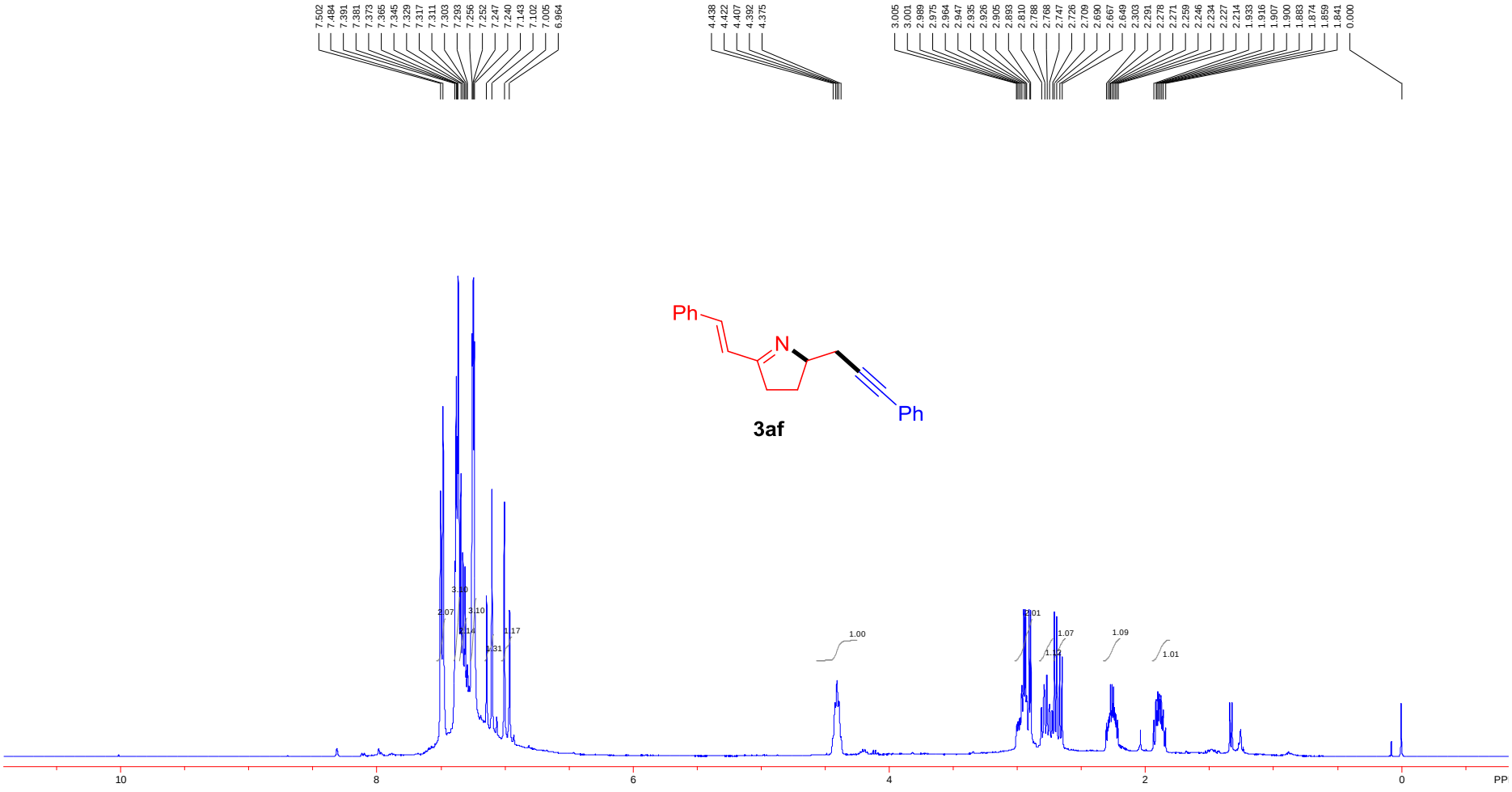
^{1}H NMR(400 MHz, $CDCl_3$)



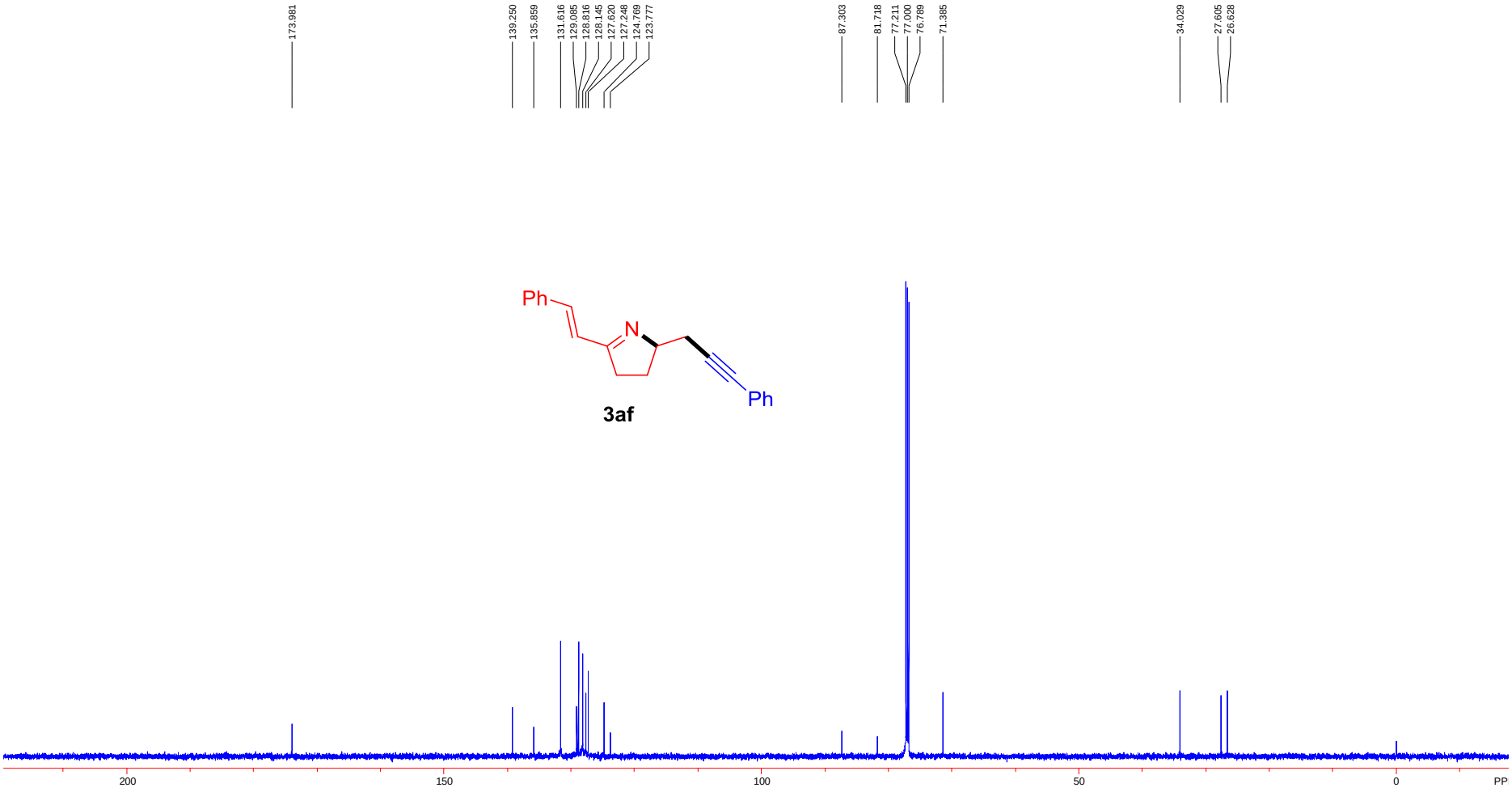
^{13}C NMR(100 MHz, $CDCl_3$)



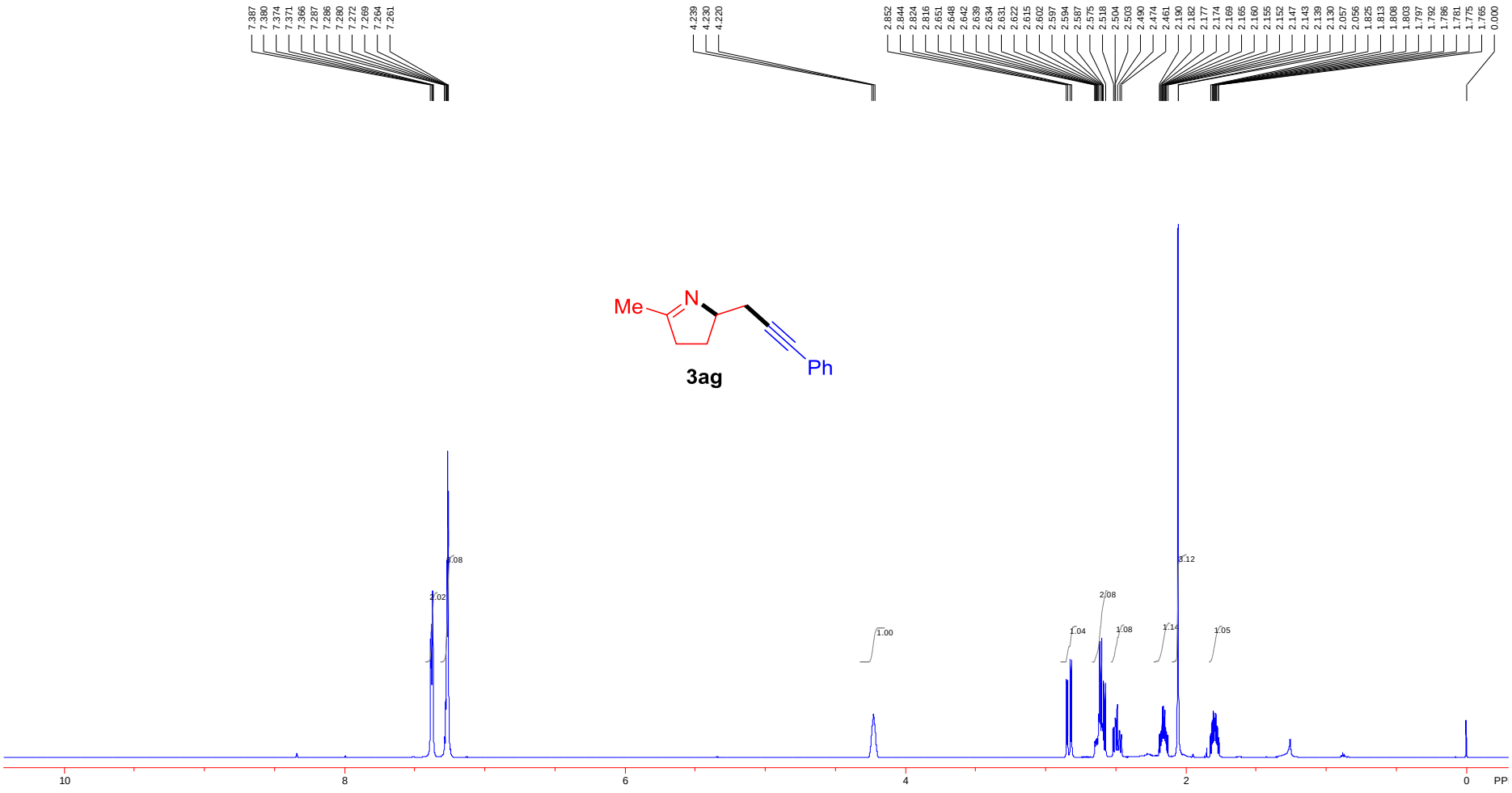
^{1}H NMR(400 MHz, $CDCl_3$)



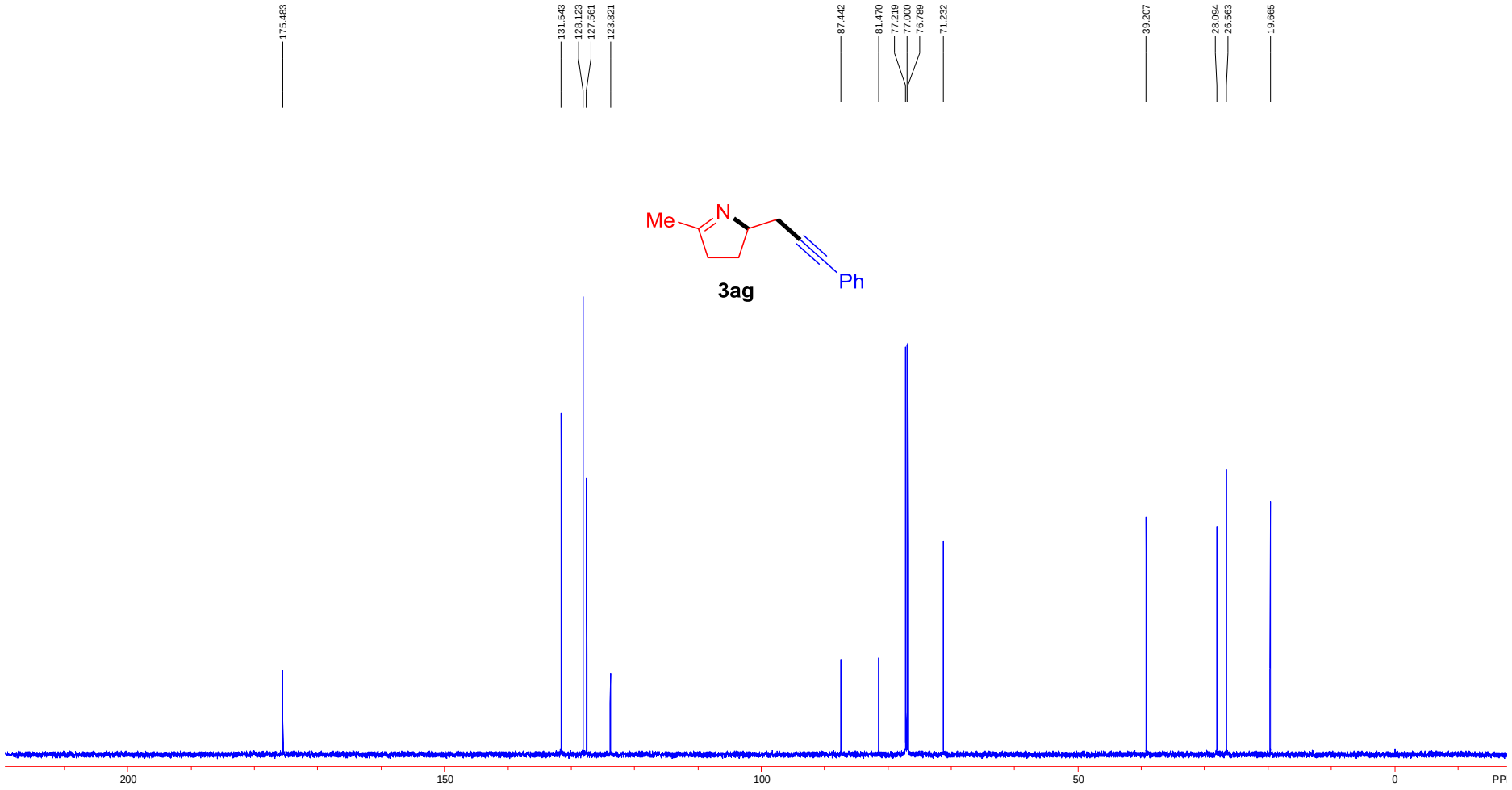
^{13}C NMR(151 MHz, $CDCl_3$)



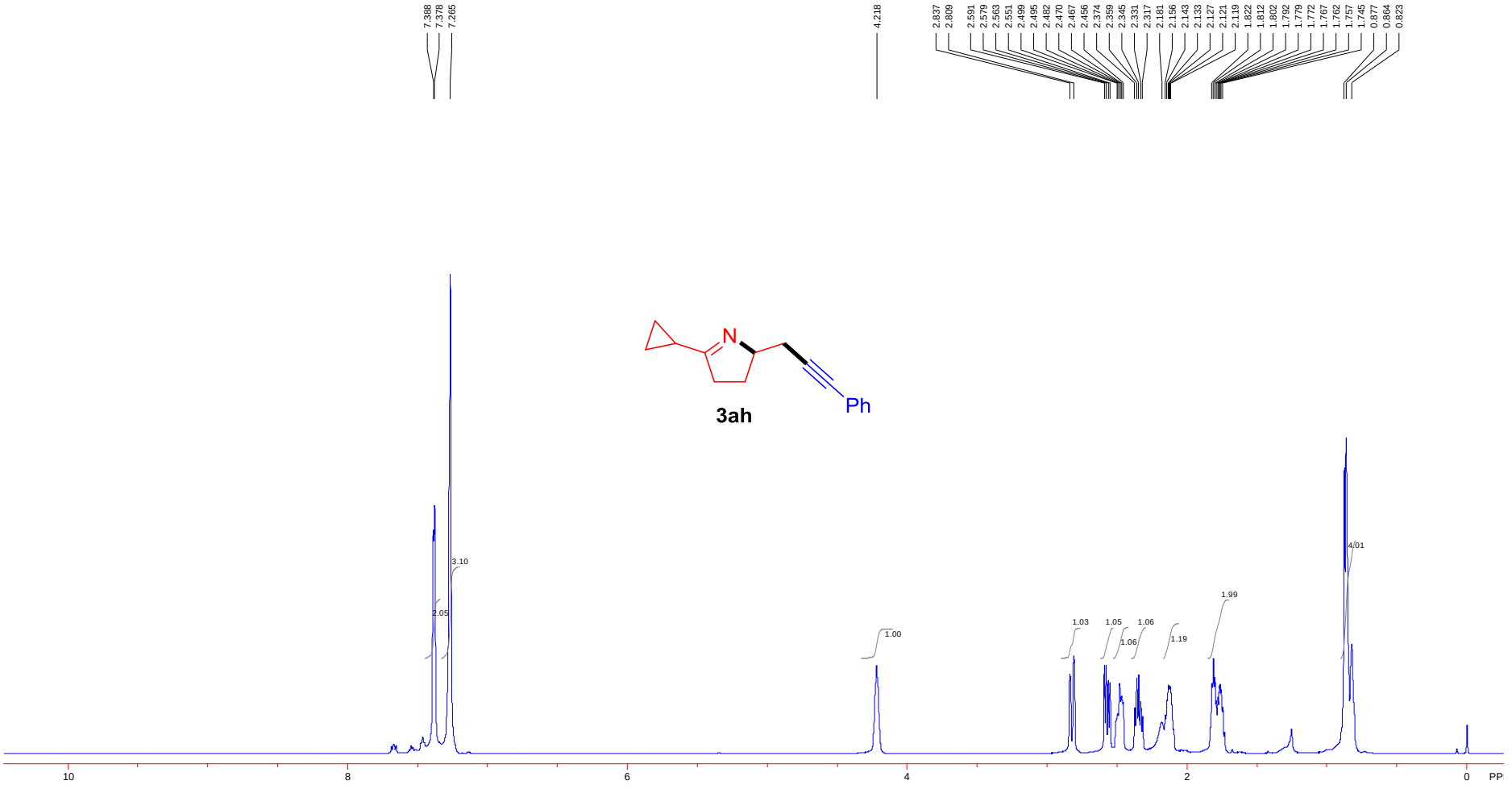
^{1}H NMR(600 MHz, $CDCl_3$)



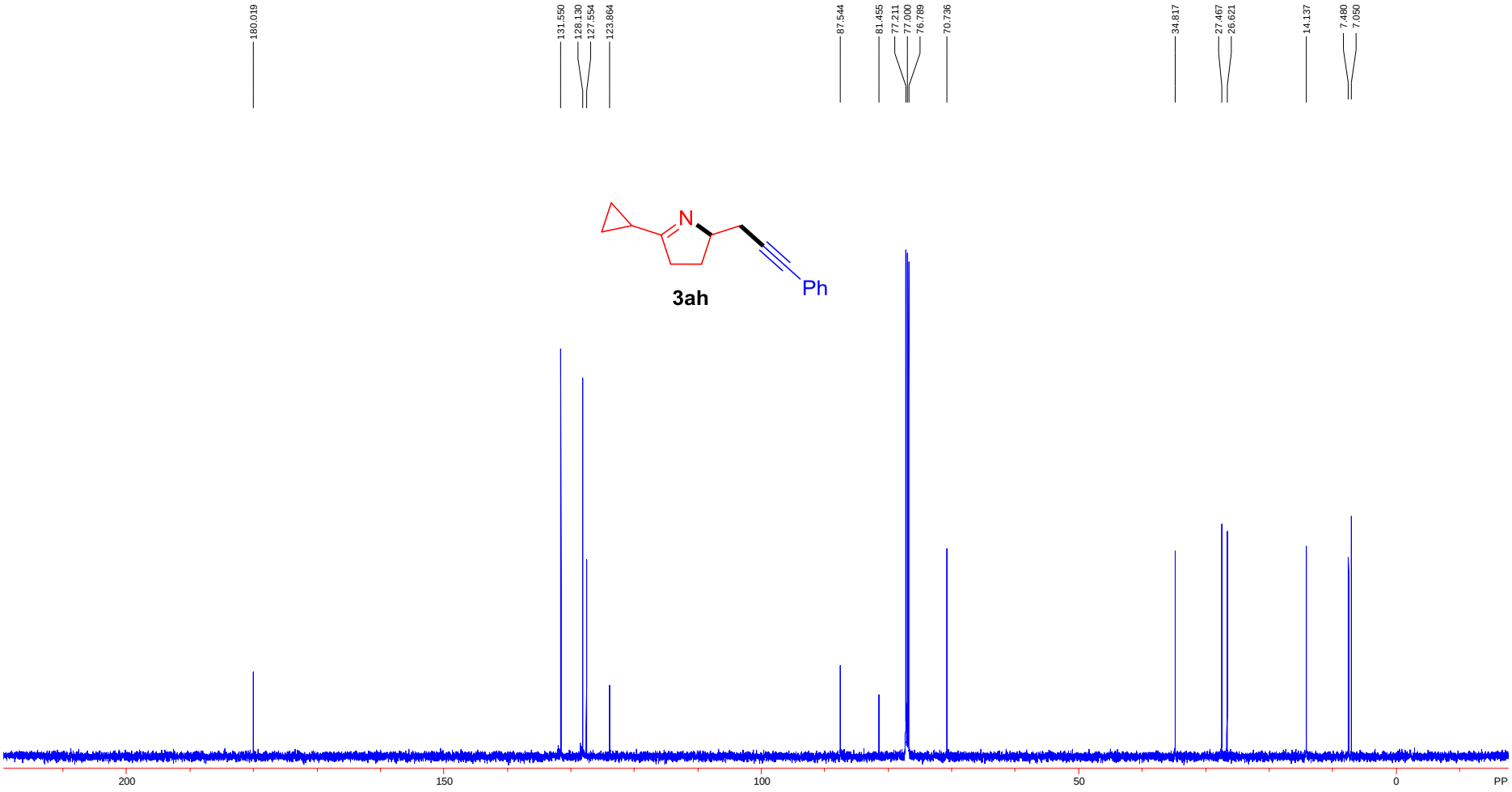
^{13}C NMR(151 MHz, $CDCl_3$)



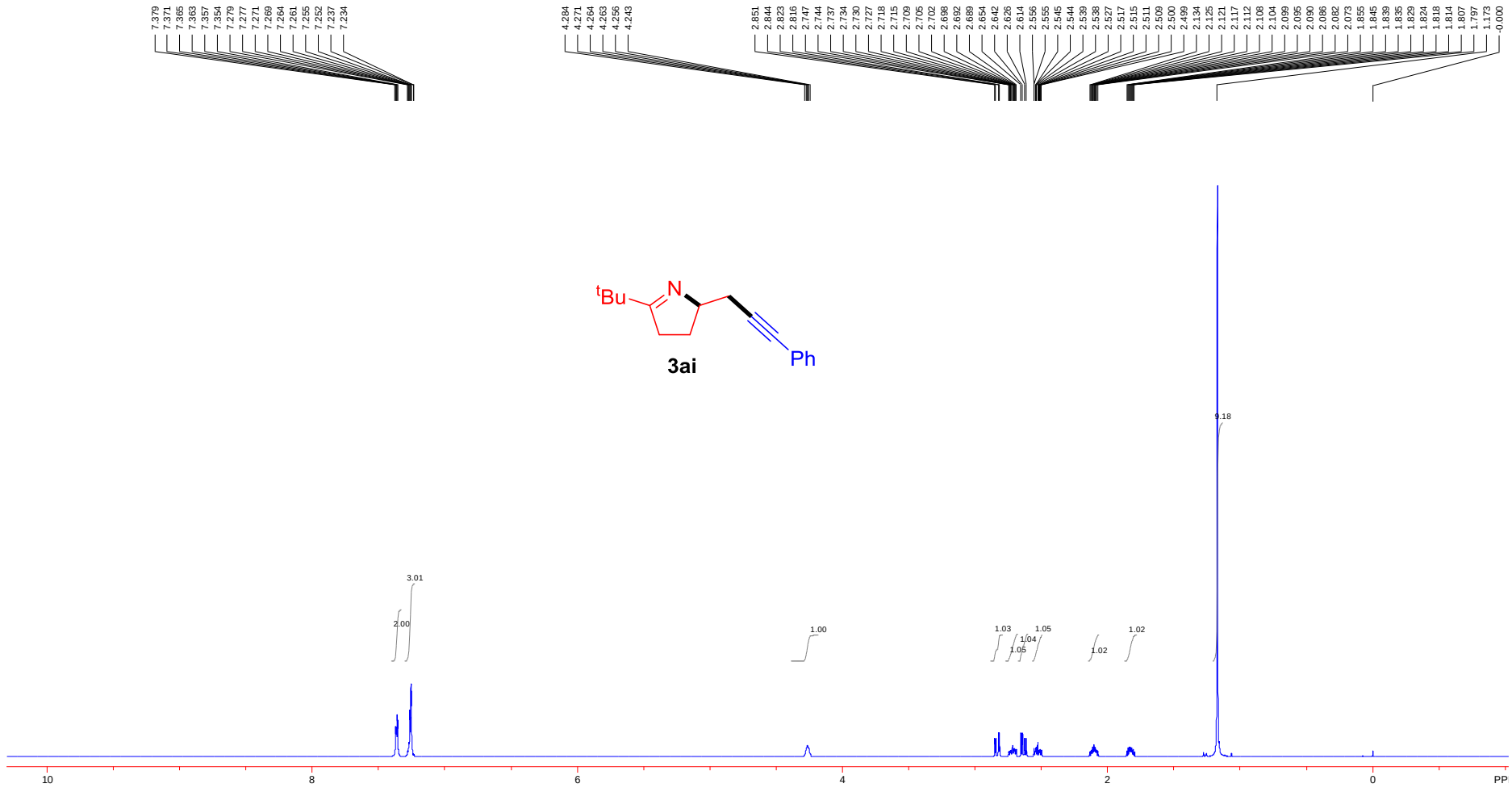
^{1}H NMR(600 MHz, $CDCl_3$)



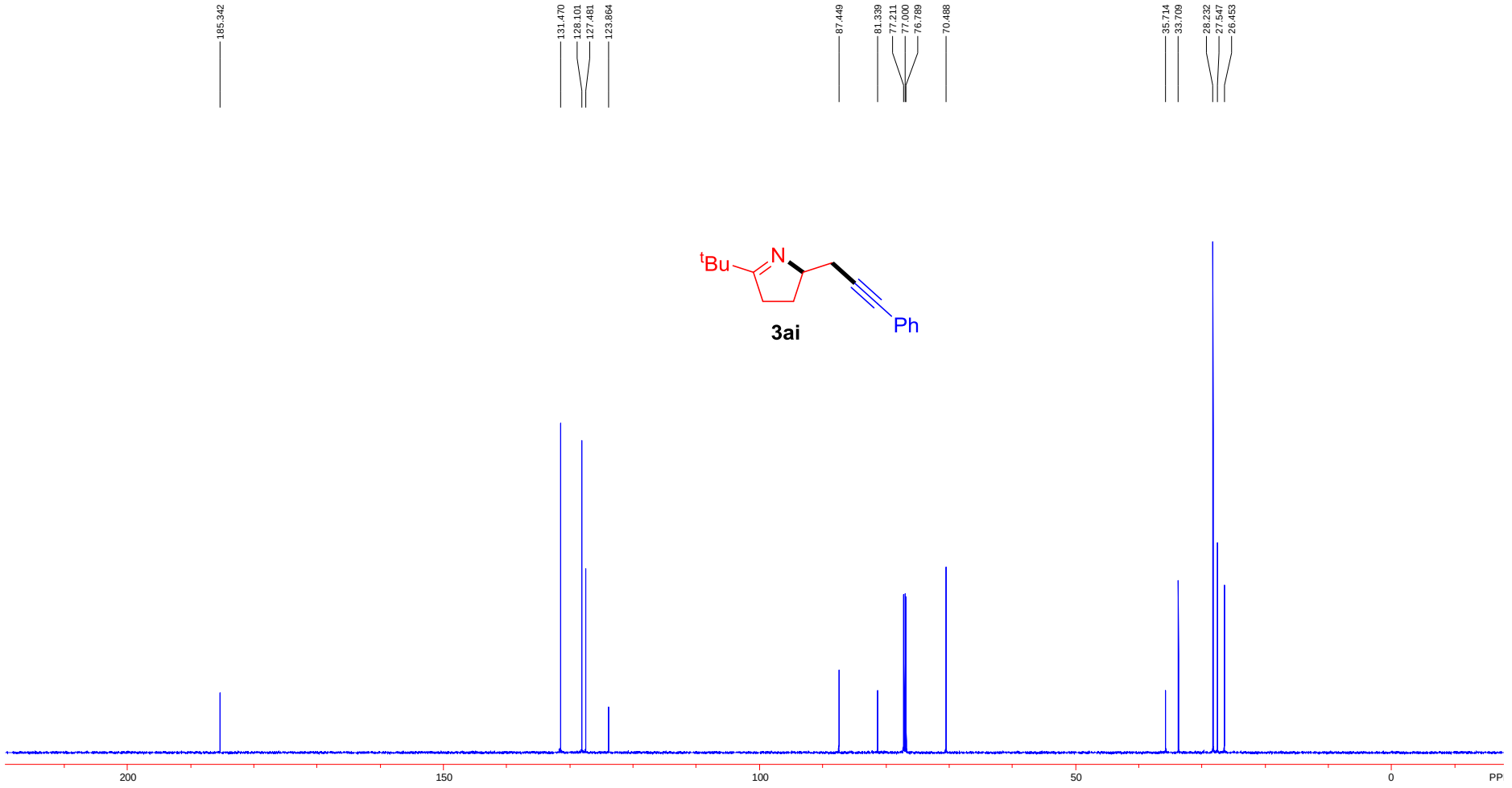
^{13}C NMR(151 MHz, $CDCl_3$)



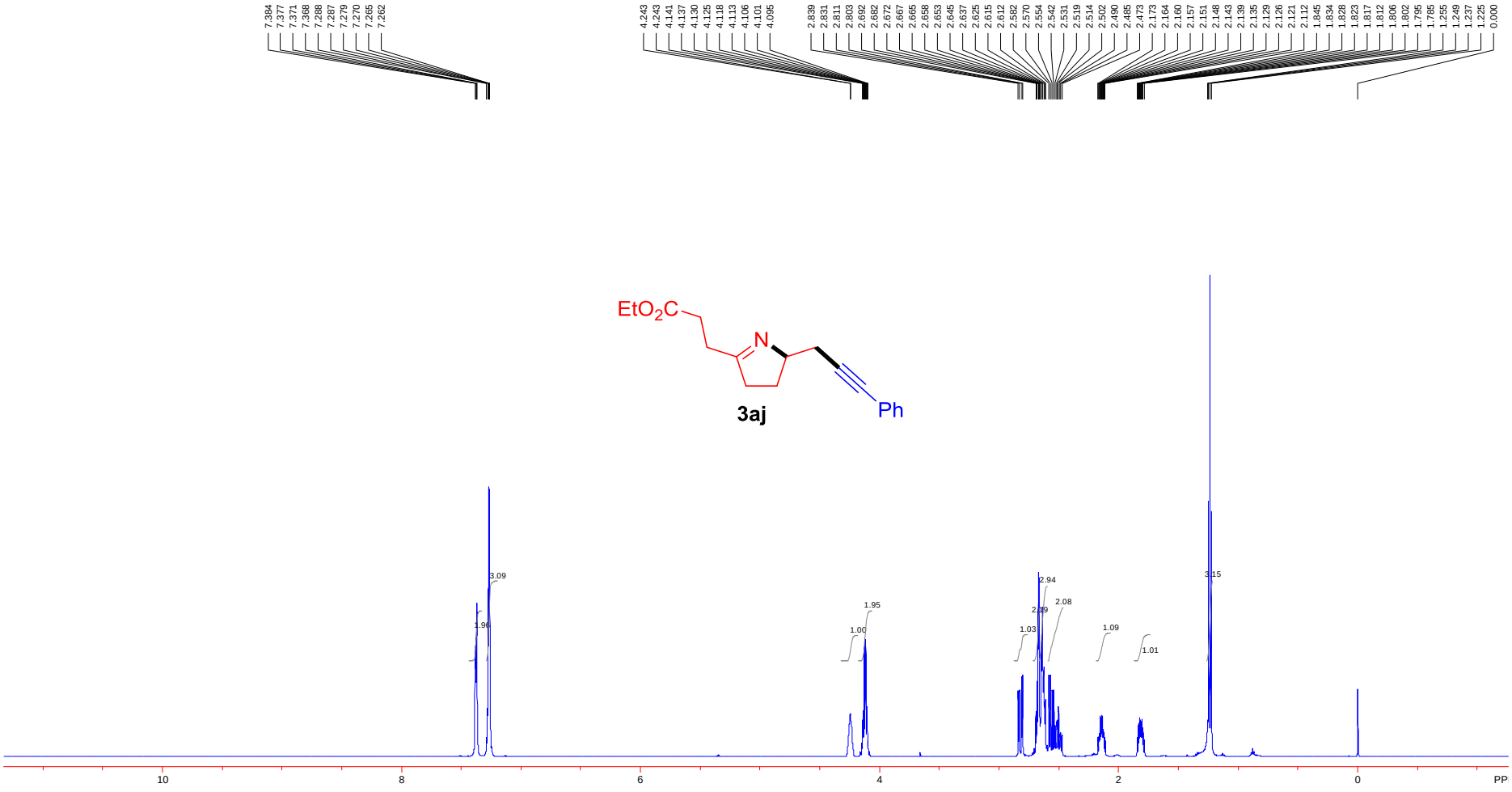
^{1}H NMR(600 MHz, $CDCl_3$)



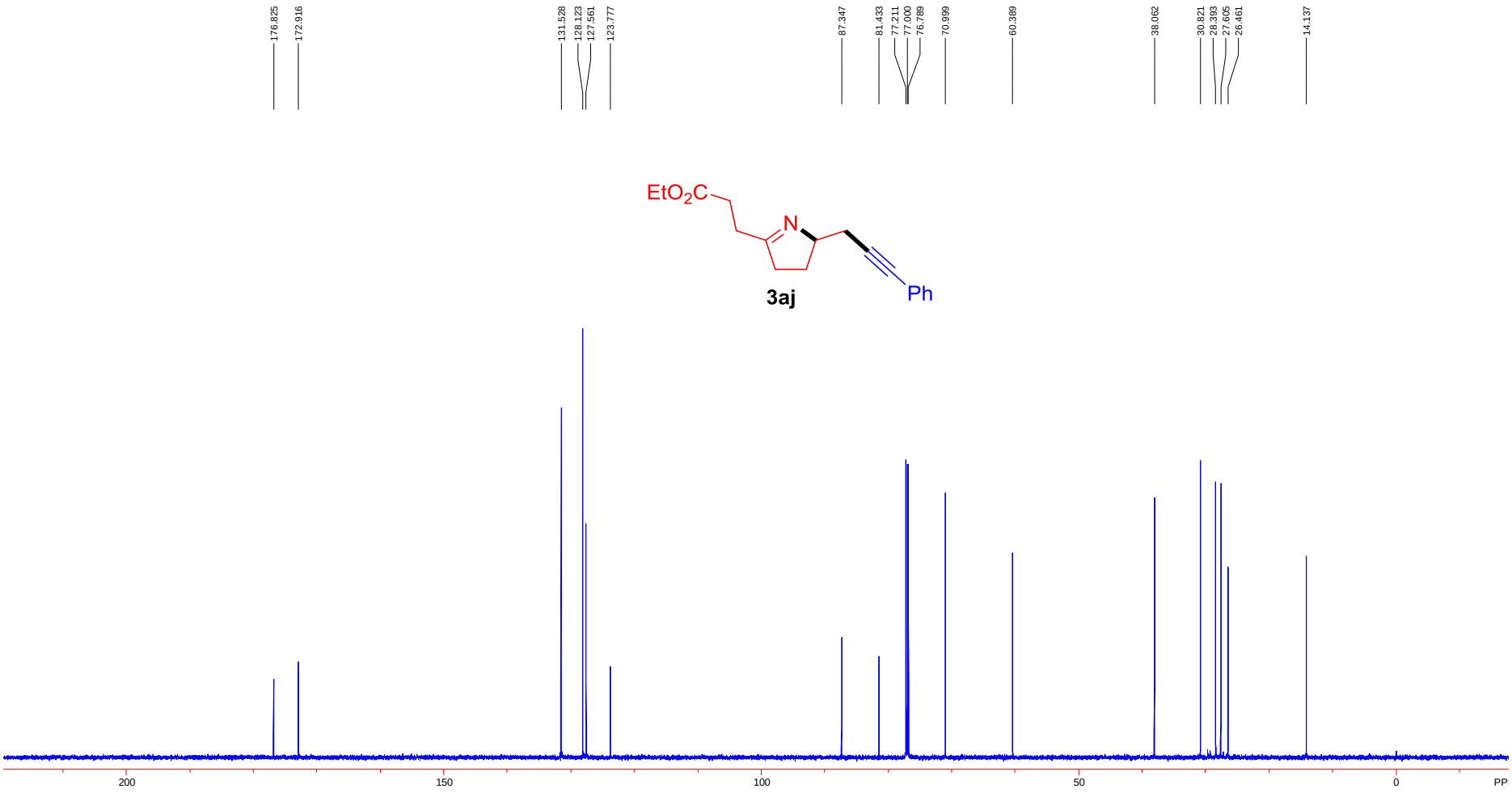
^{13}C NMR(151 MHz, $CDCl_3$)



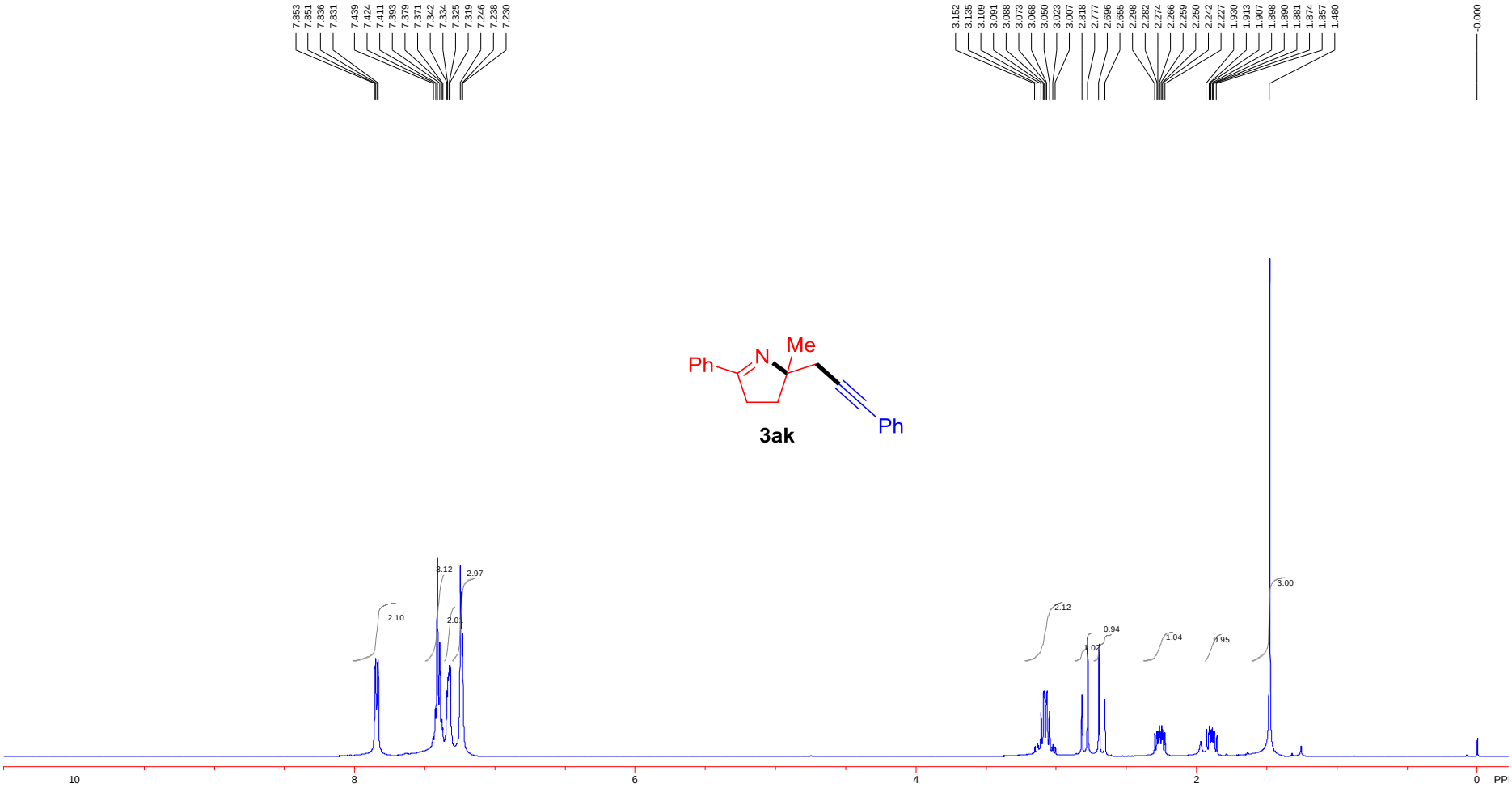
^{1}H NMR(600 MHz, $CDCl_3$)



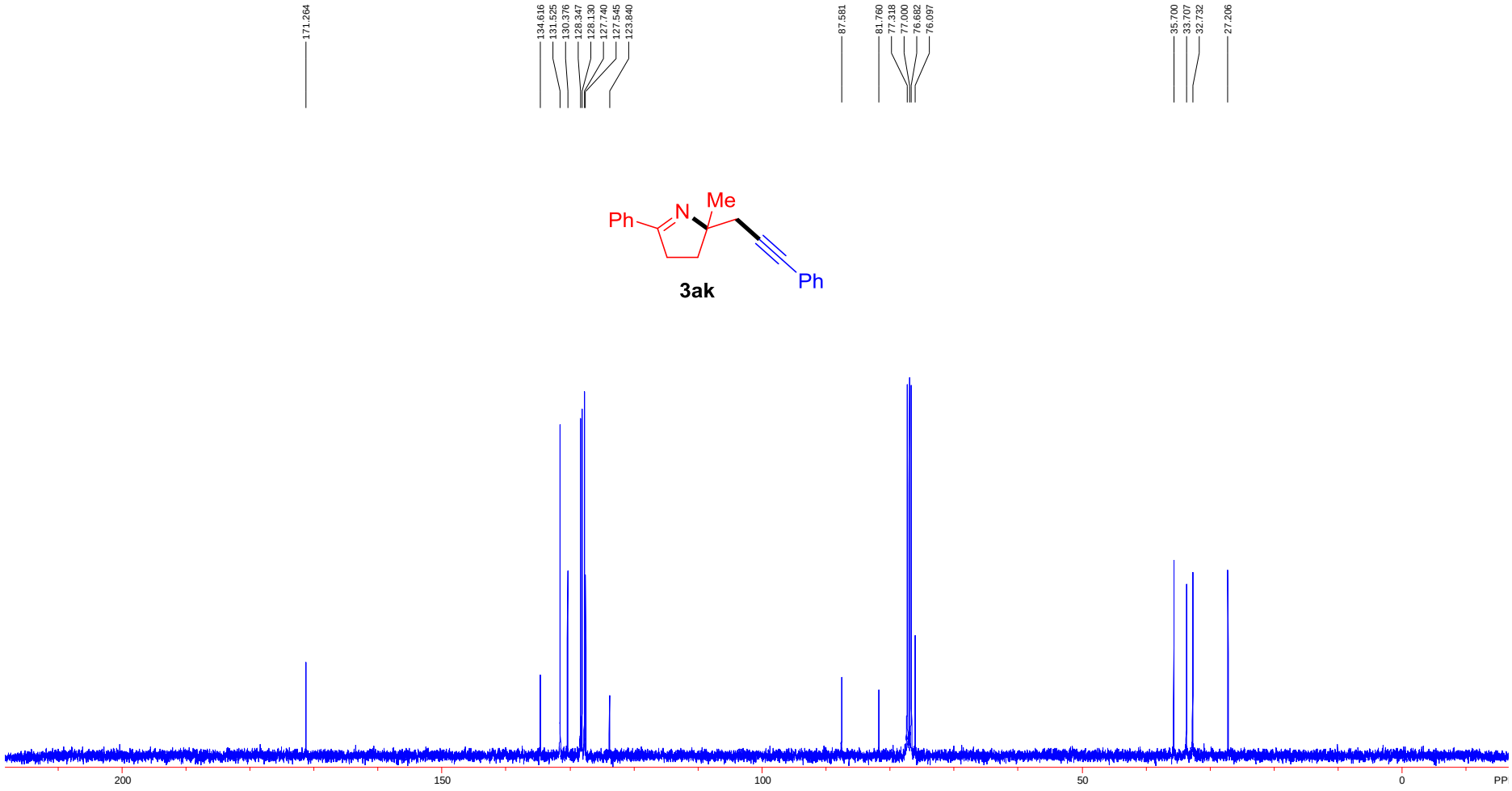
^{13}C NMR(151 MHz, $CDCl_3$)



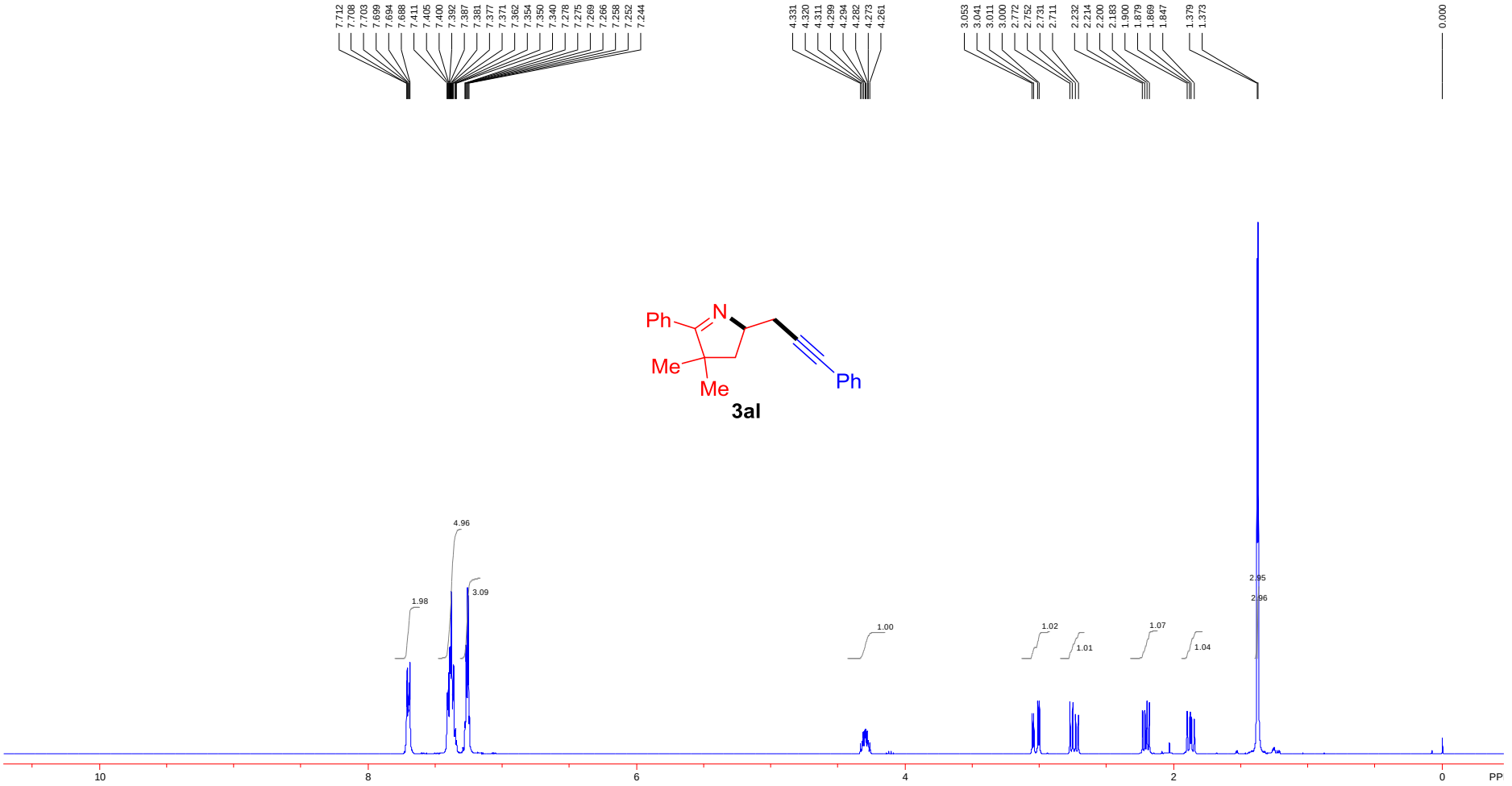
^{1}H NMR(400 MHz, $CDCl_3$)



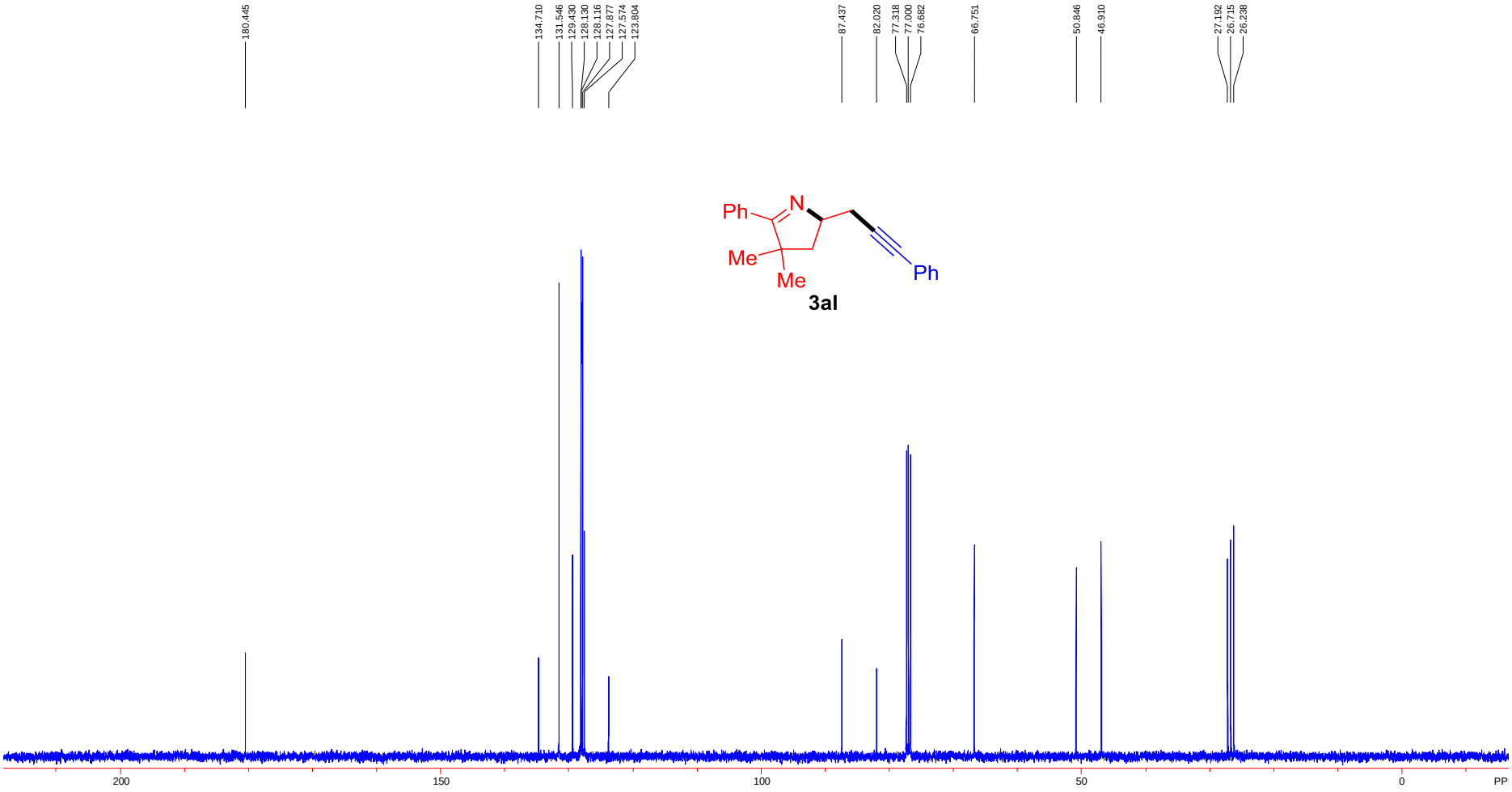
^{13}C NMR(100 MHz, $CDCl_3$)



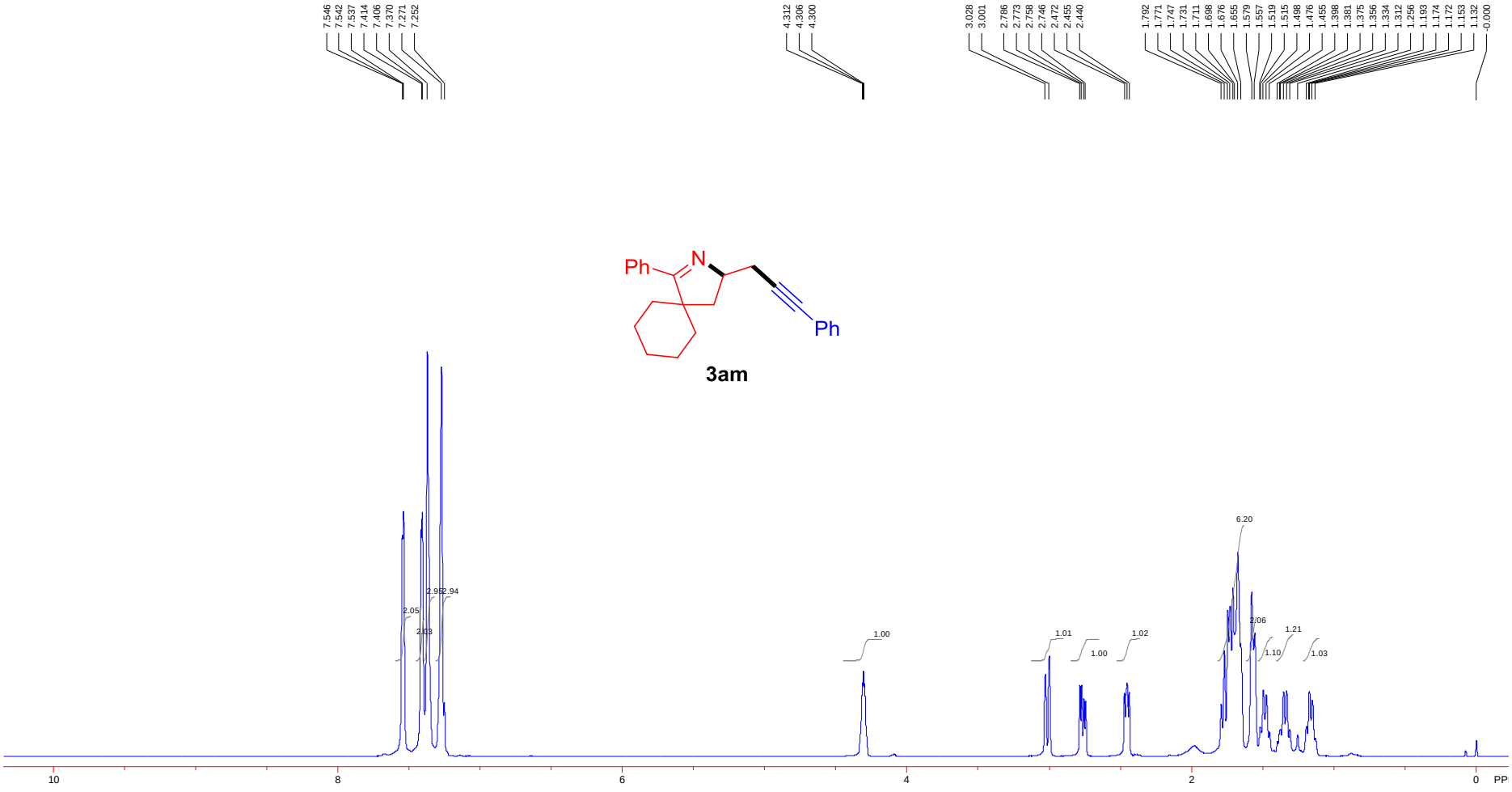
^{1}H NMR(400 MHz, $CDCl_3$)



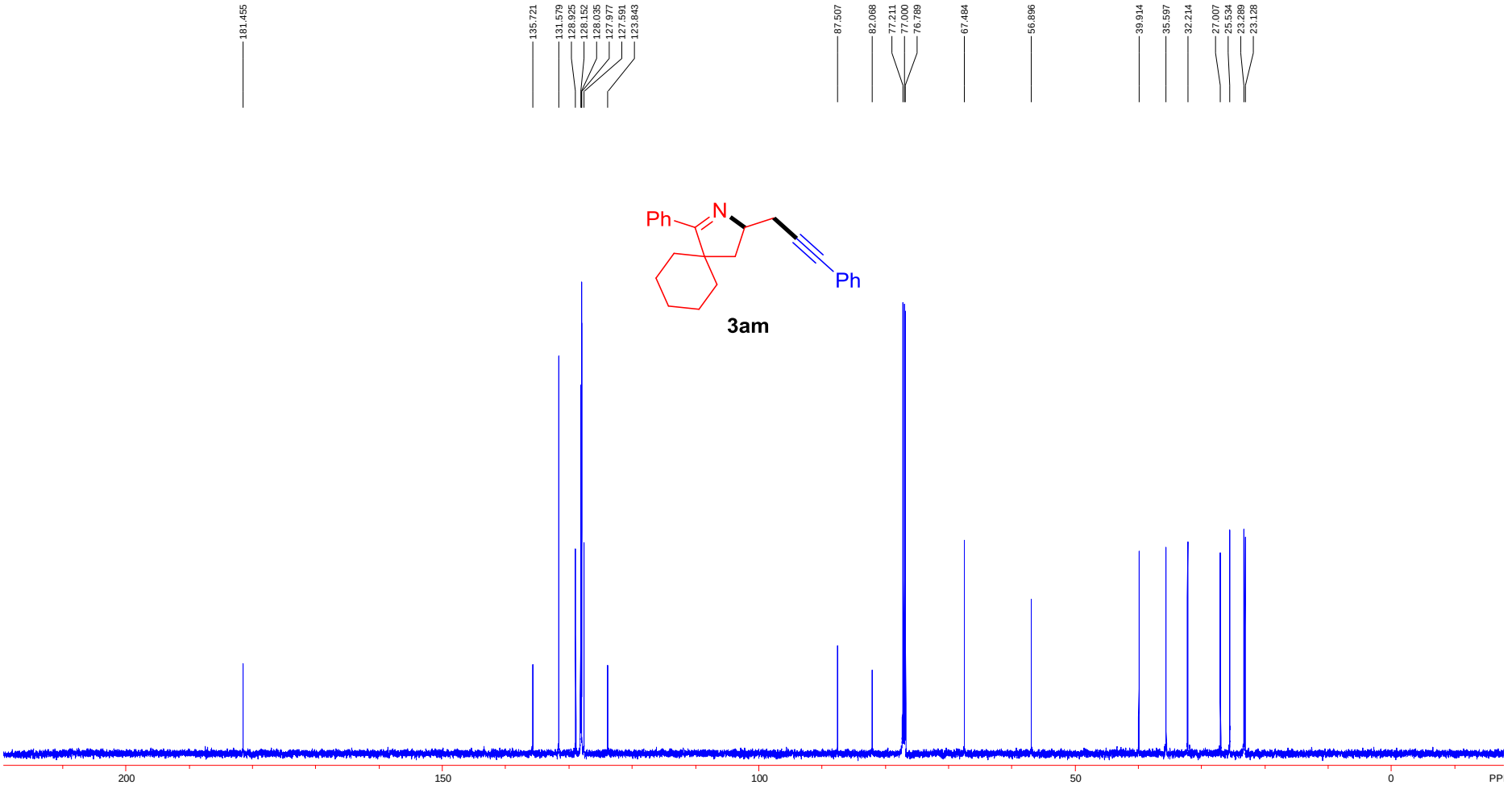
^{13}C NMR(100 MHz, $CDCl_3$)



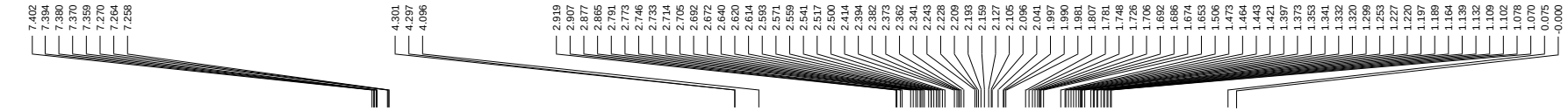
^{1}H NMR(600 MHz, $CDCl_3$)

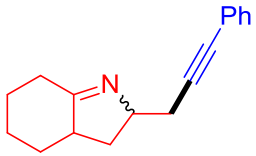


^{13}C NMR(151 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)





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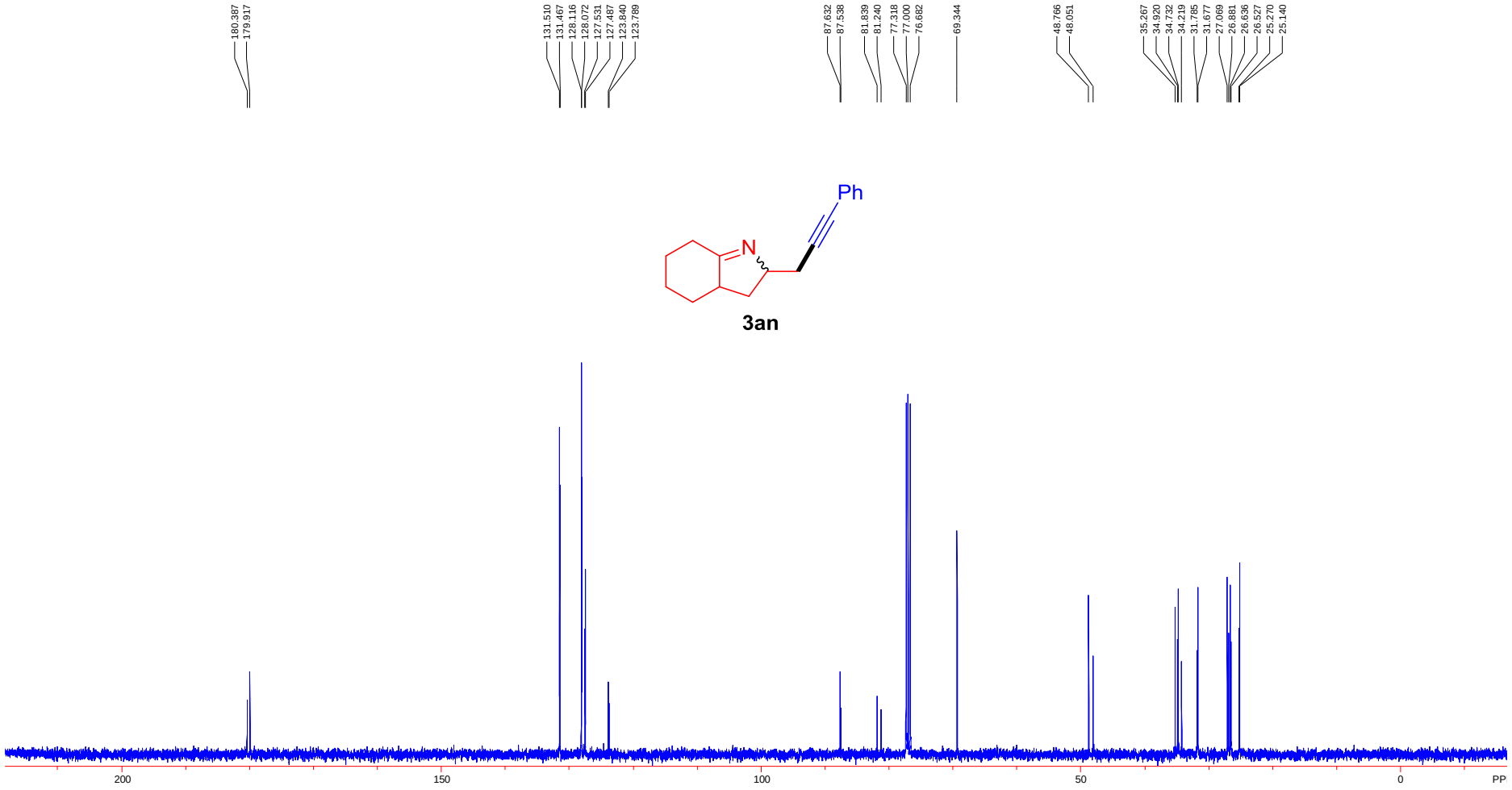
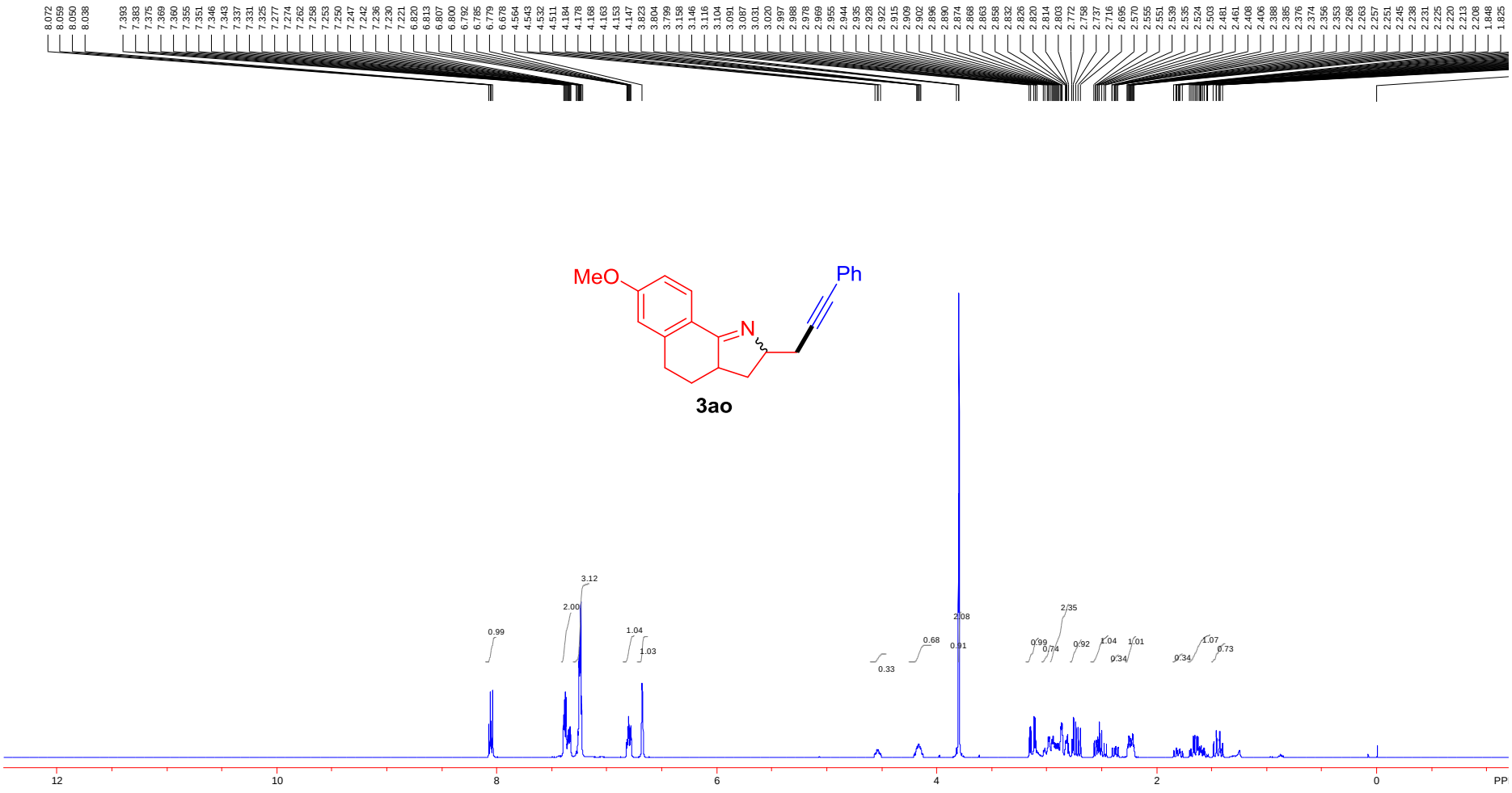
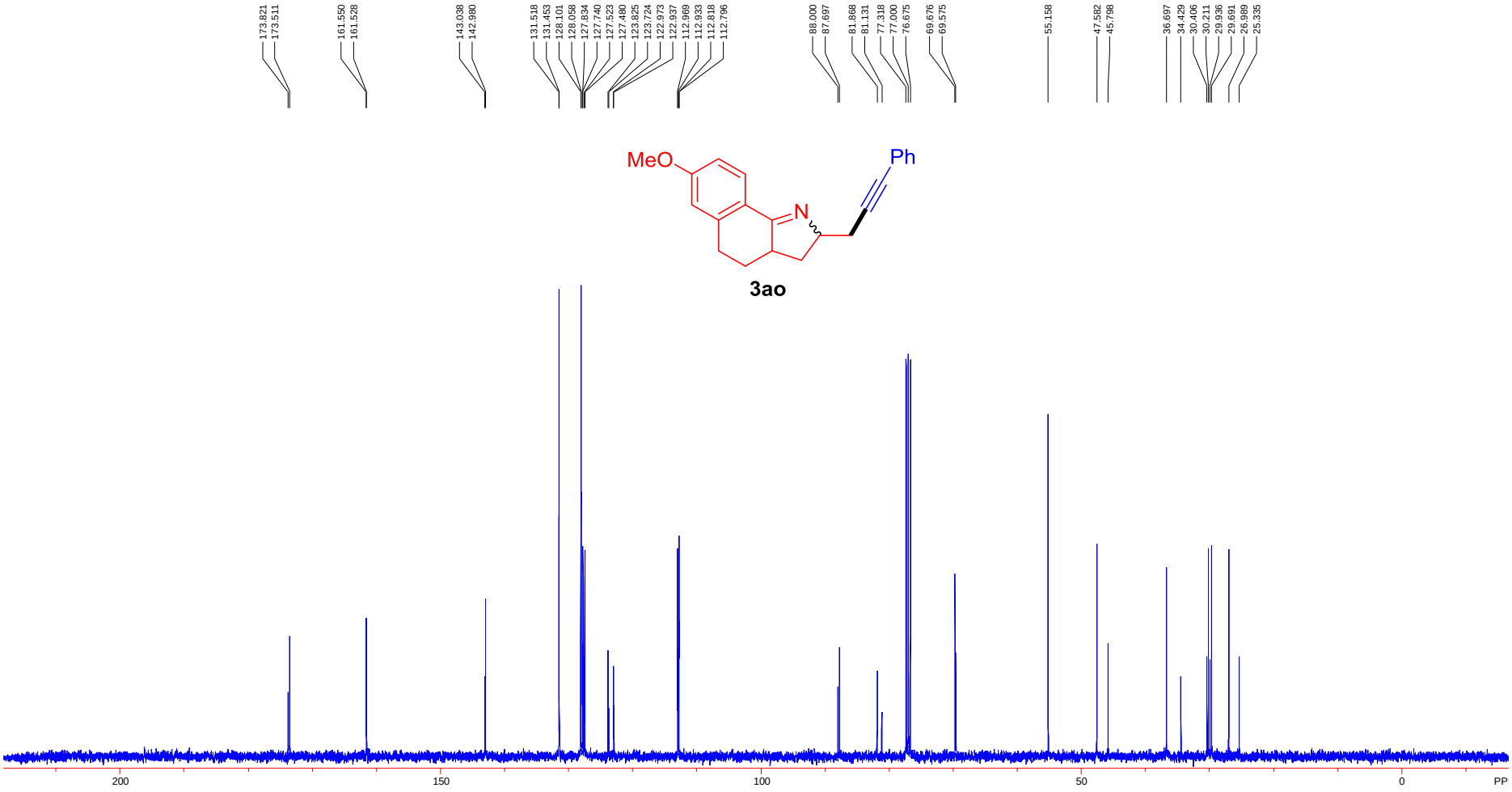
^{13}C NMR(100 MHz, $CDCl_3$)



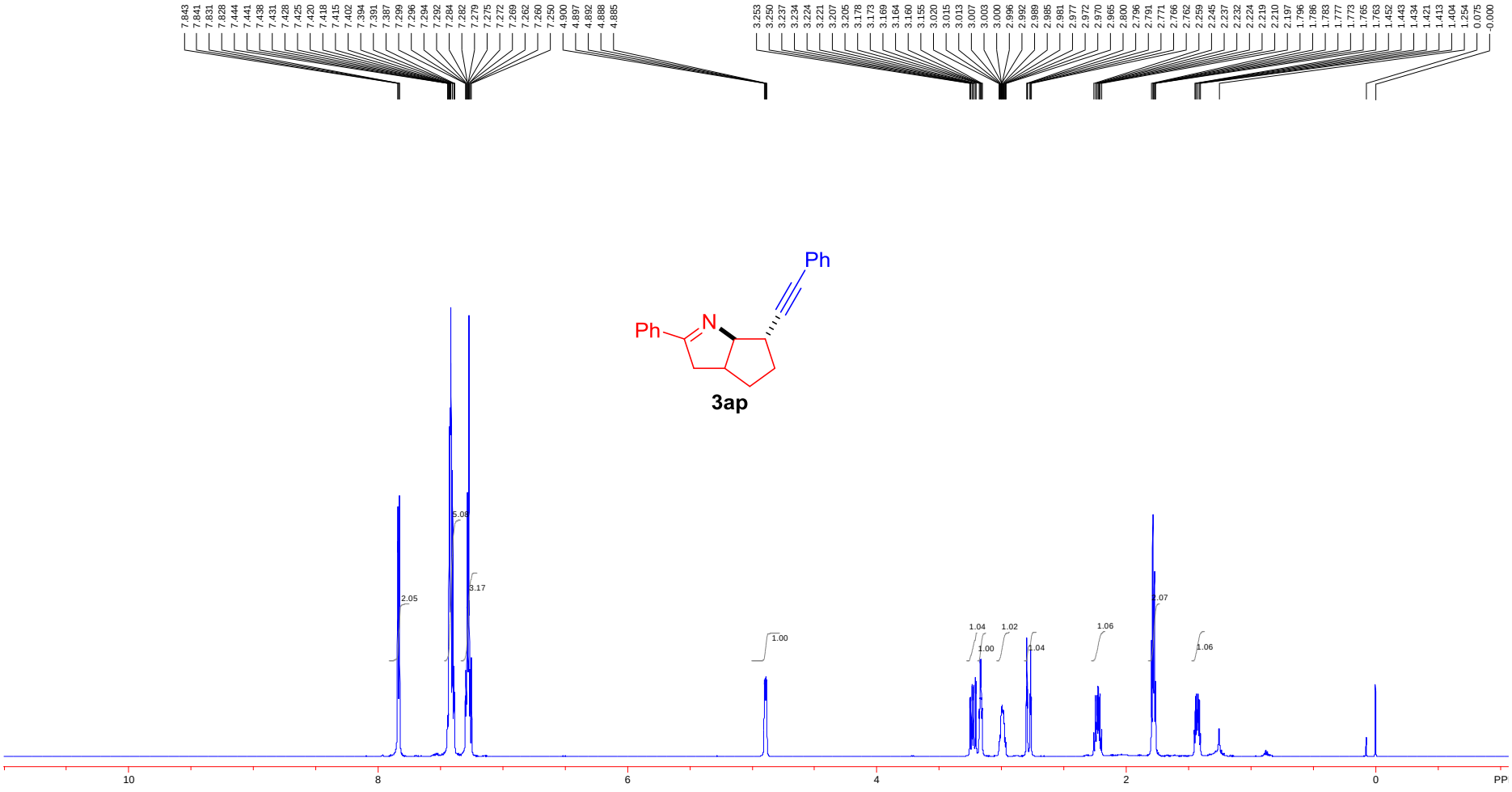
^{1}H NMR(400 MHz, $CDCl_3$)



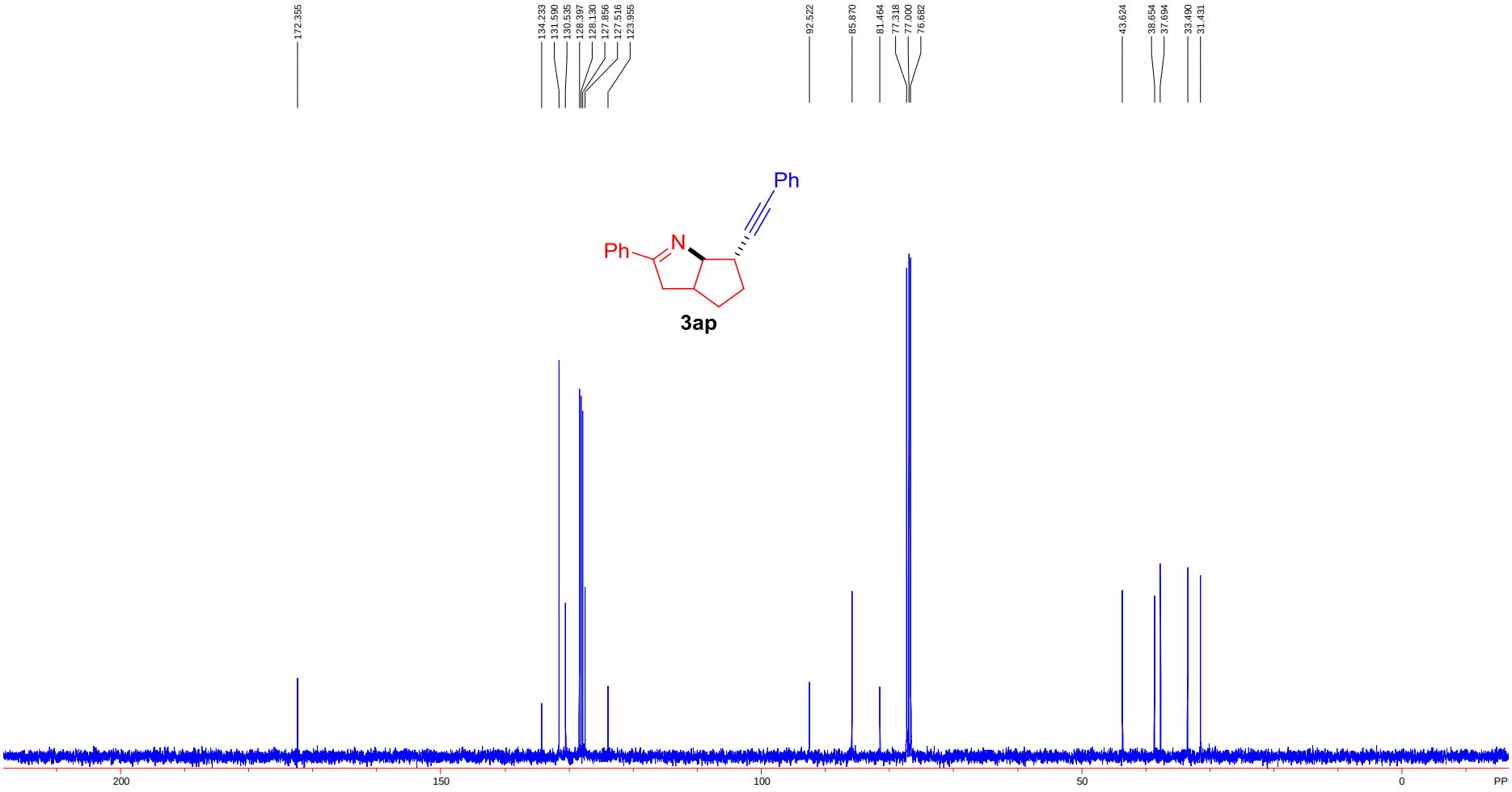
^{13}C NMR(100 MHz, $CDCl_3$)



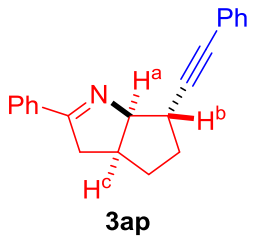
^{1}H NMR(600 MHz, $CDCl_3$)



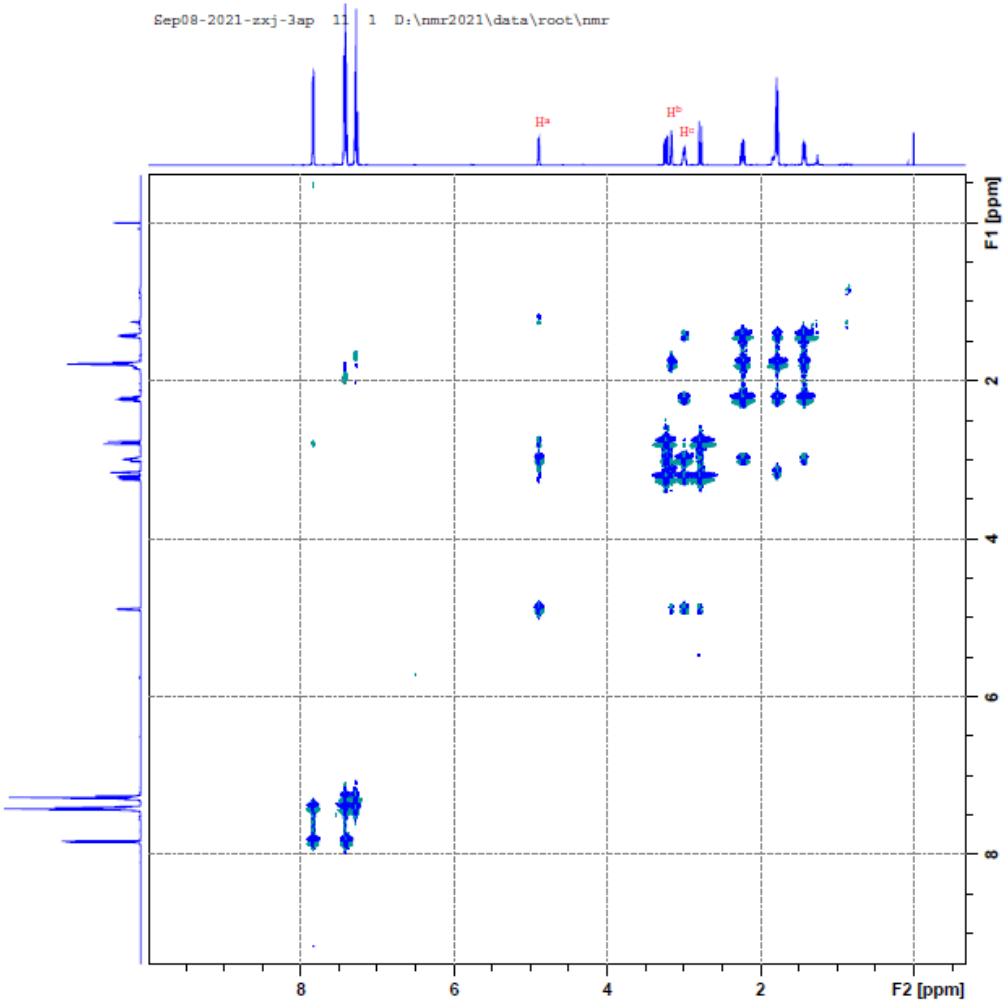
^{13}C NMR(100 MHz, $CDCl_3$)



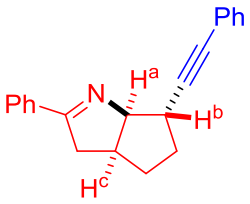
^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)



3ap



NOESY-2D ^{1}H NMR (600 MHz, $CDCl_3$)



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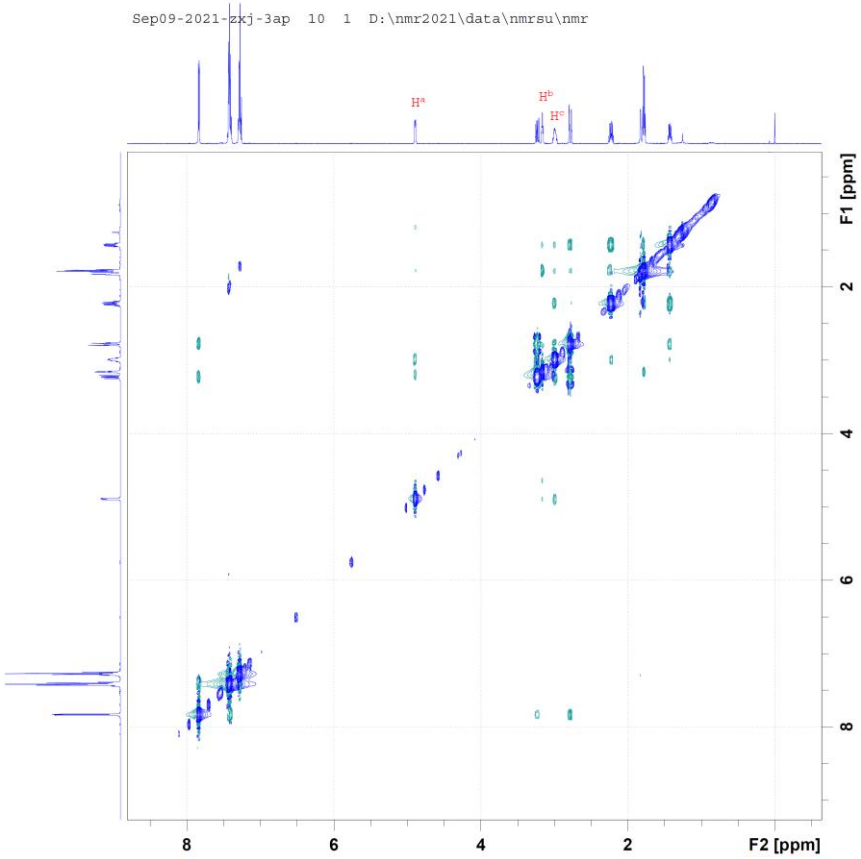
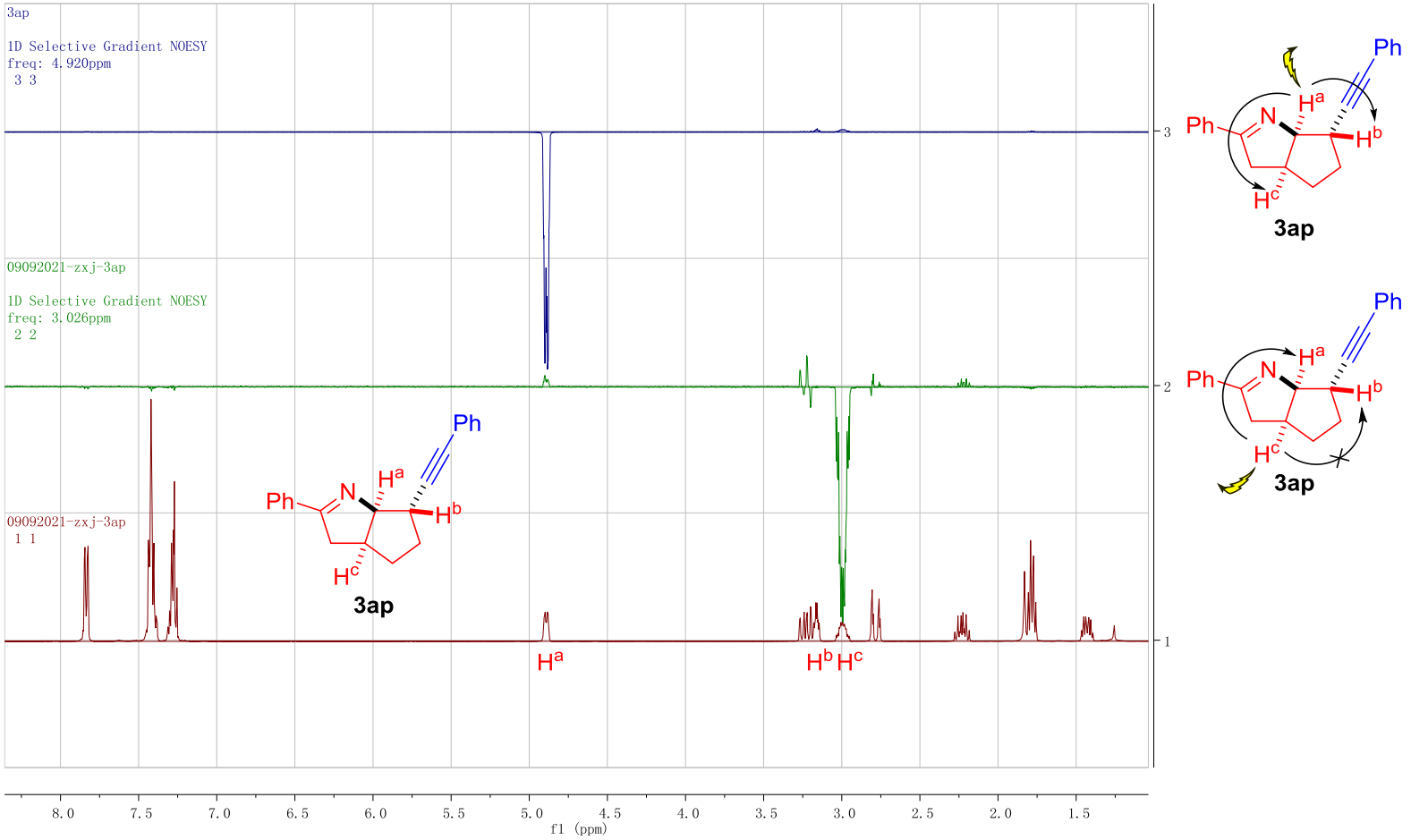
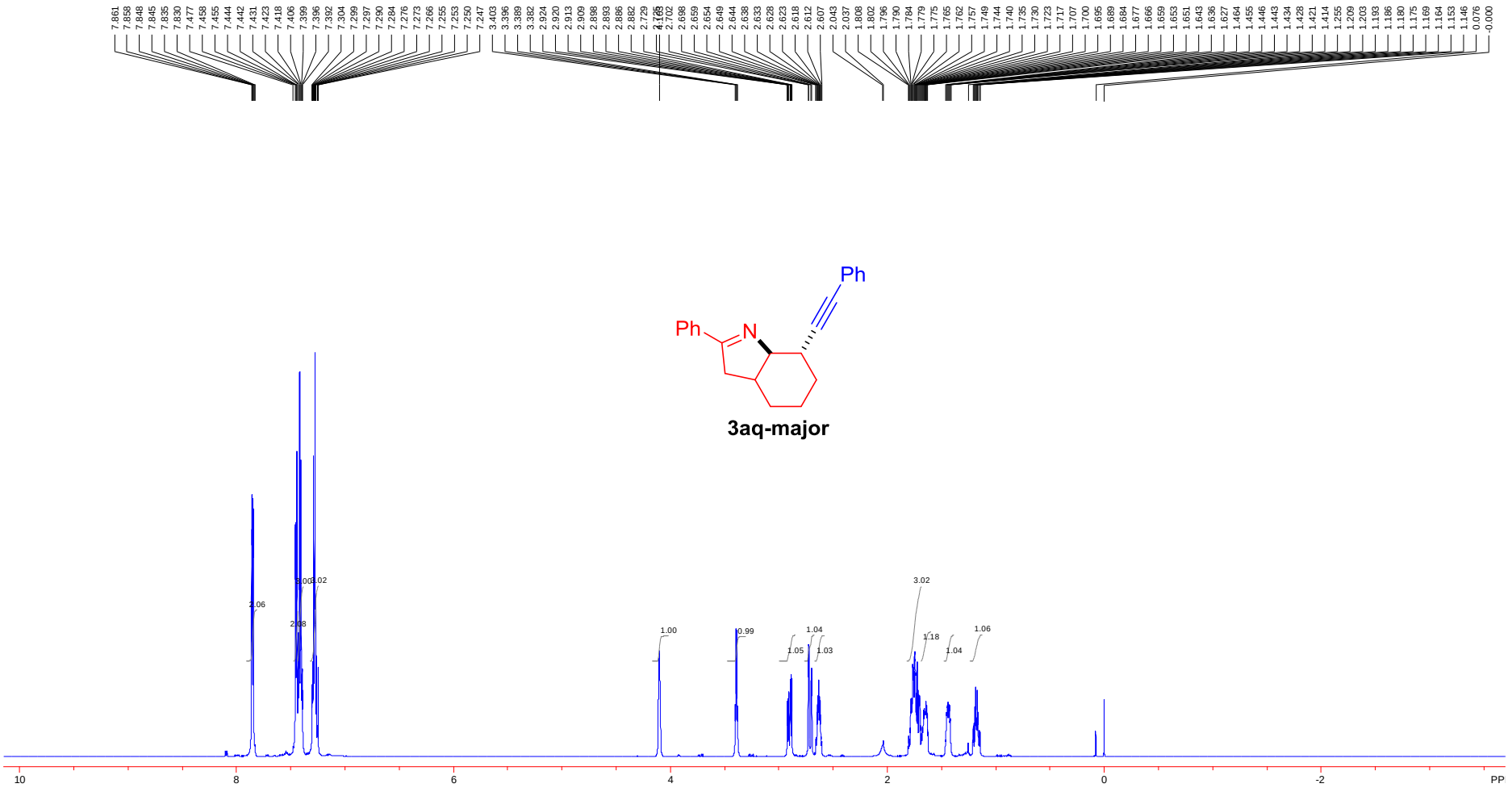


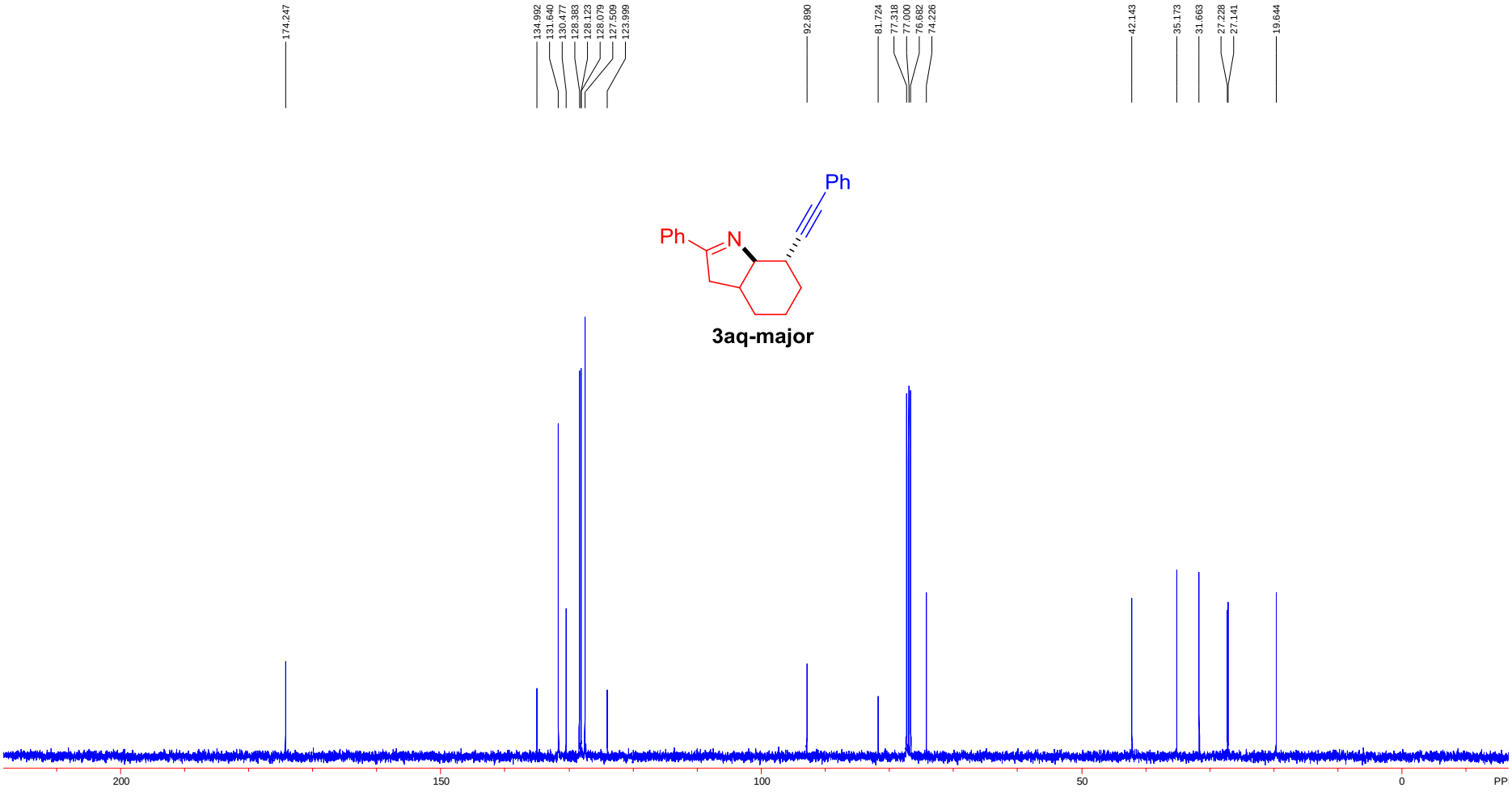
NOESY-1D ^{1}H NMR (400 MHz, $CDCl_3$)



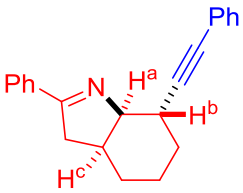
^{1}H NMR(600 MHz, $CDCl_3$)



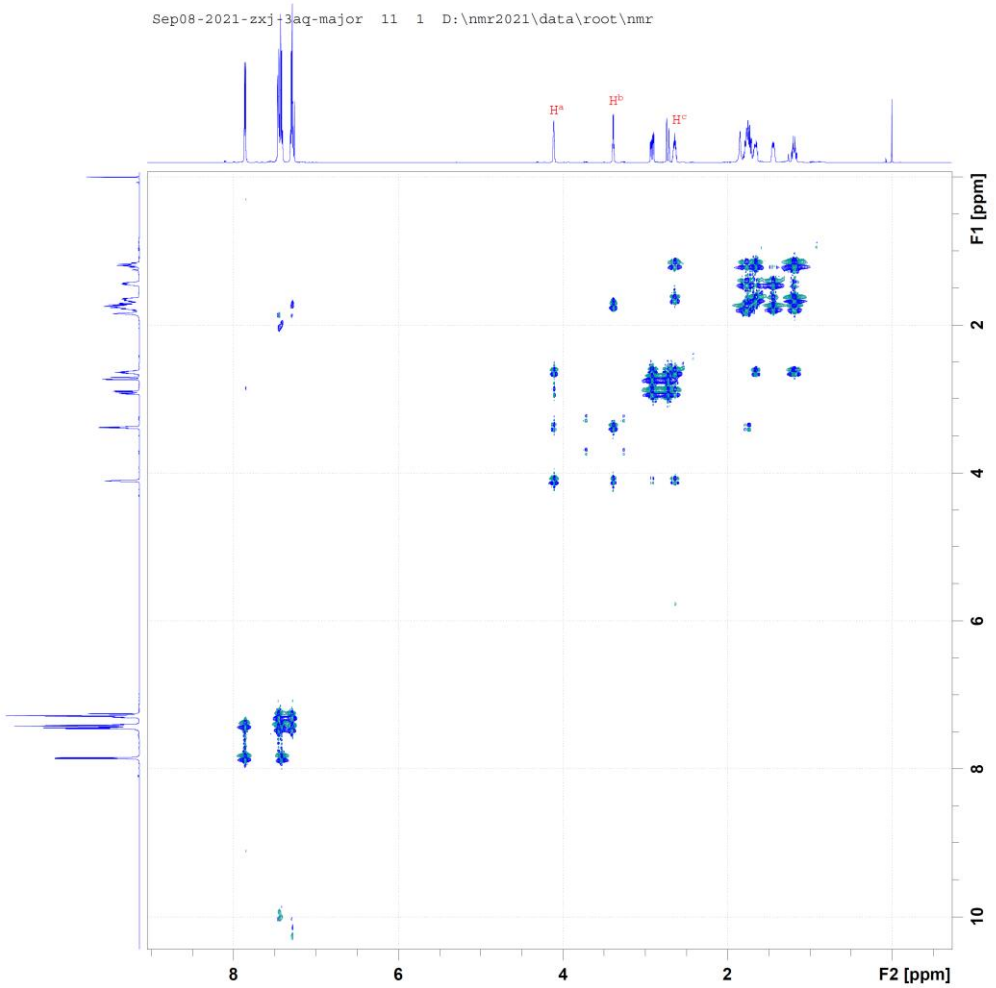
^{13}C NMR(100 MHz, $CDCl_3$)



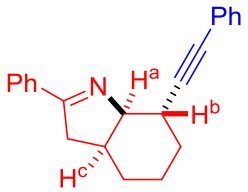
^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)



3aq-major



NOESY-2D ^{1}H NMR (400 MHz, $CDCl_3$)



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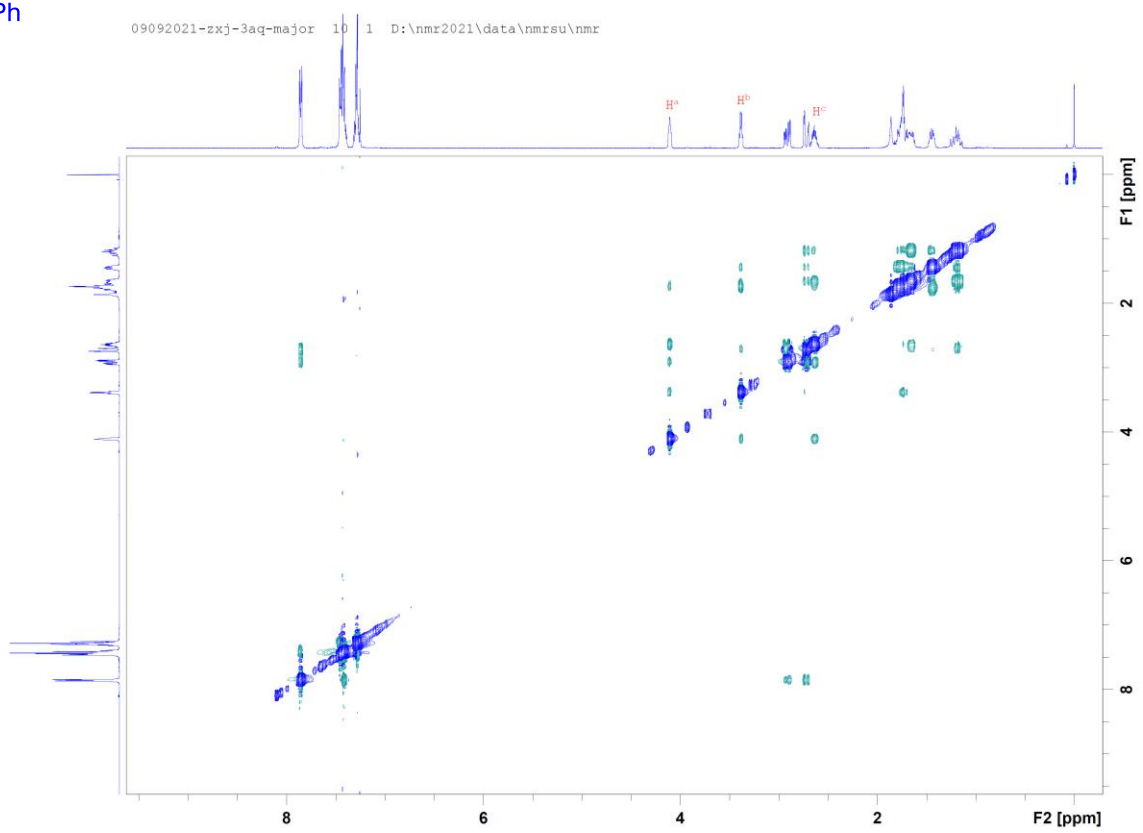
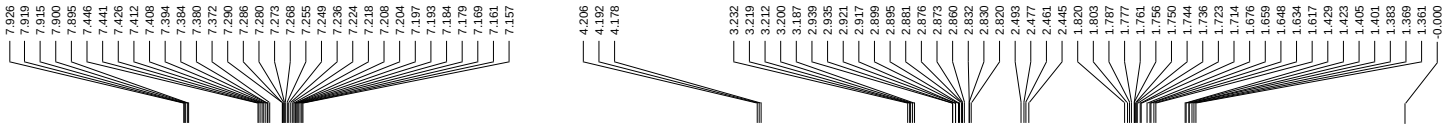
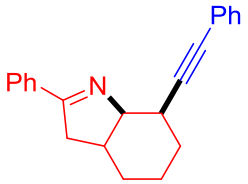
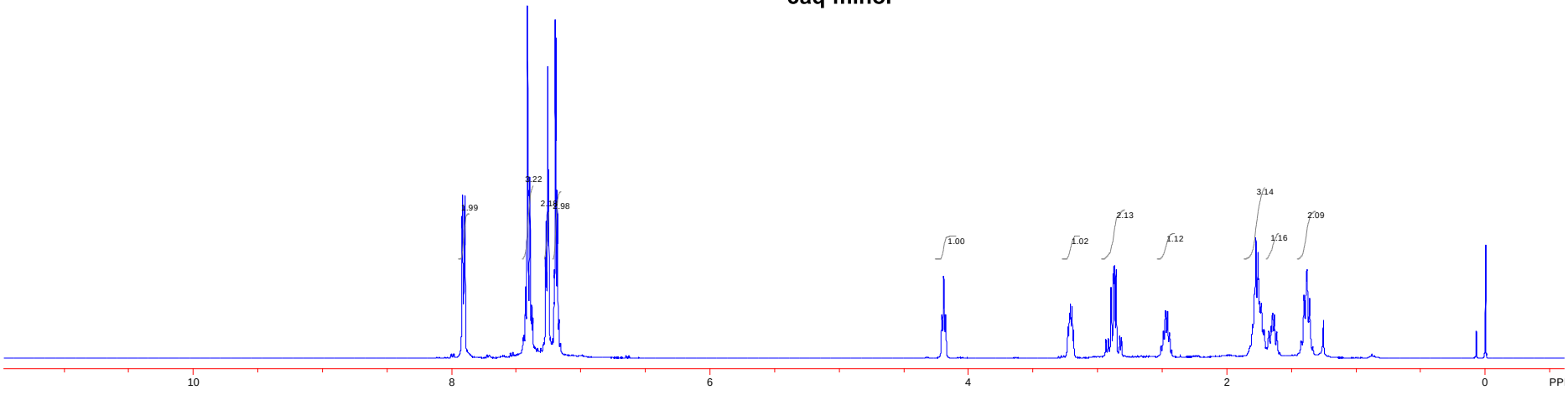


^{1}H NMR(400 MHz, $CDCl_3$)

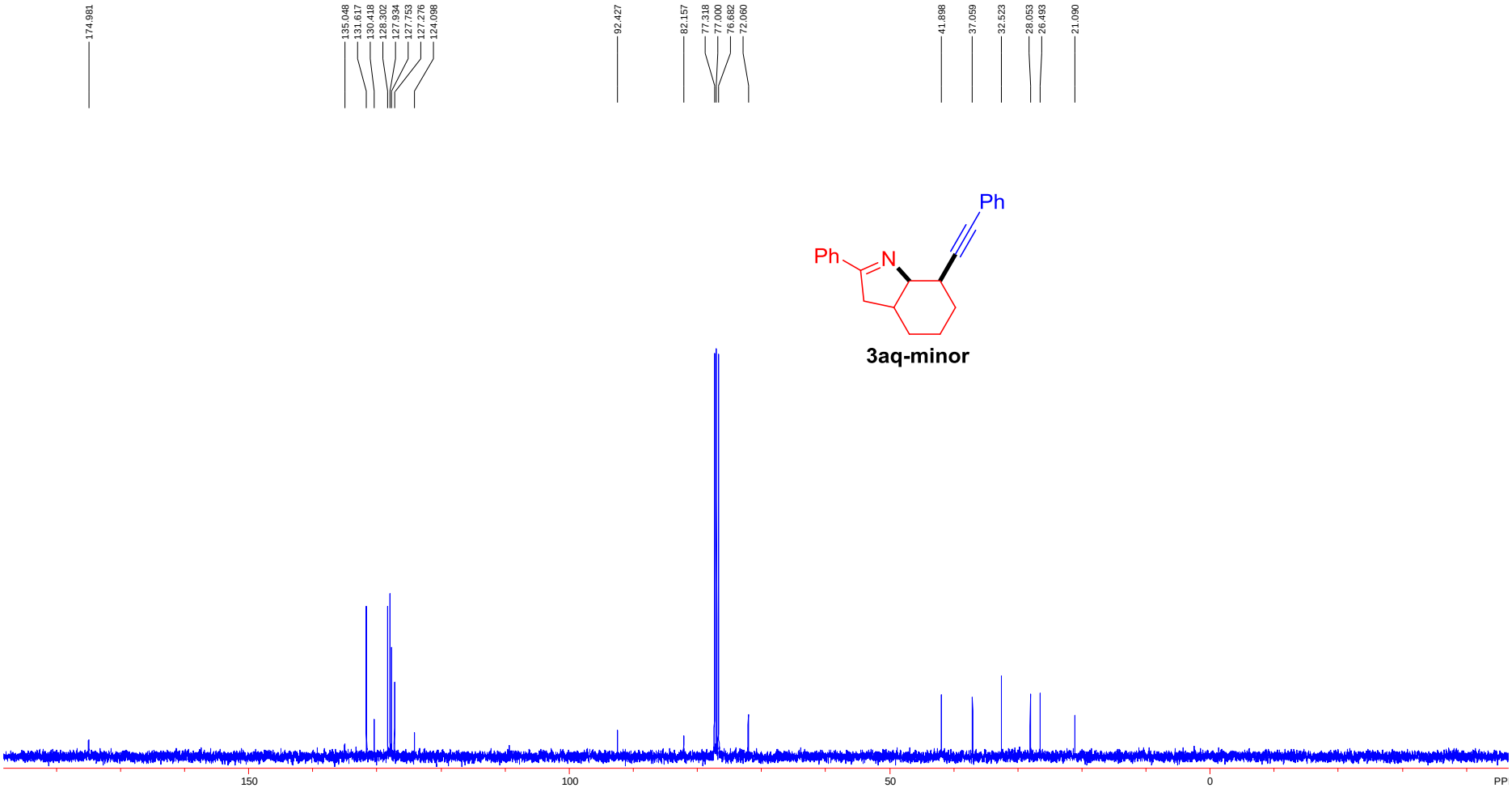




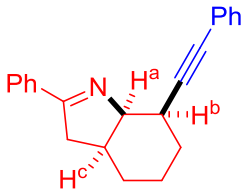
3aq-minor



^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)



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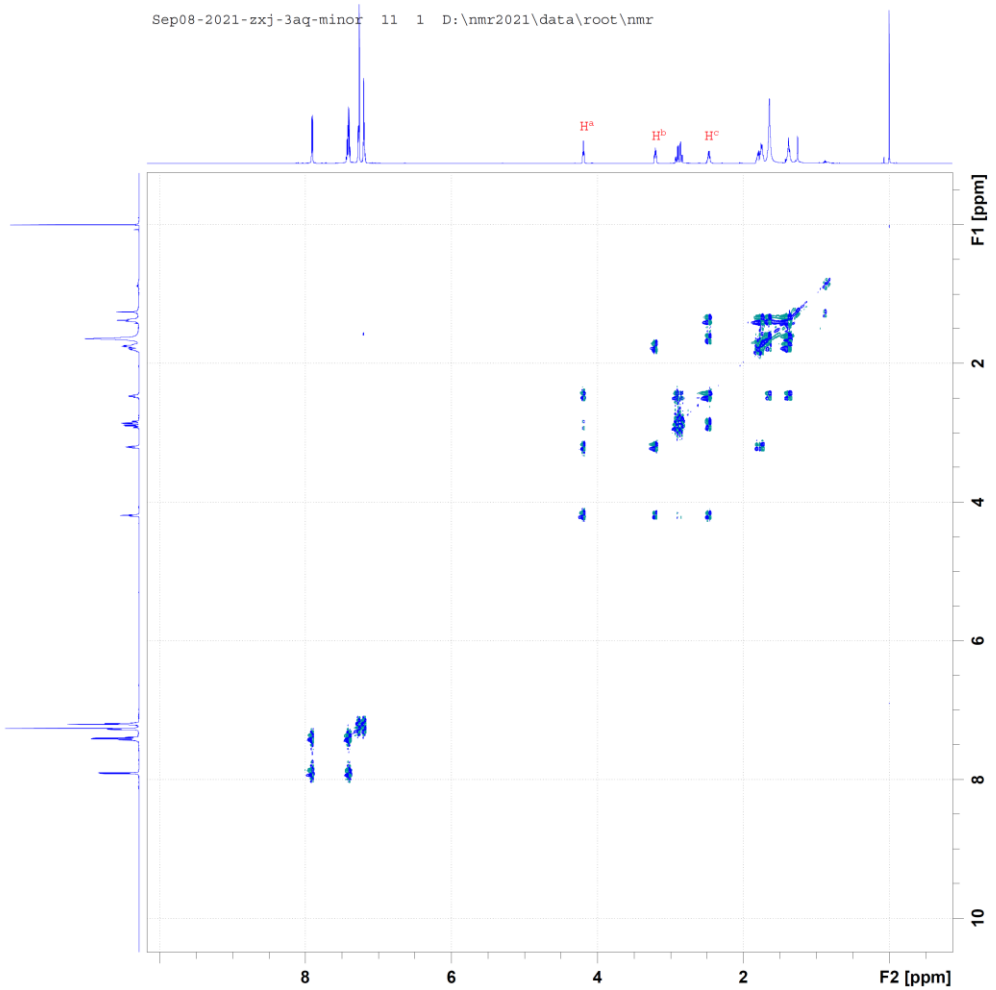
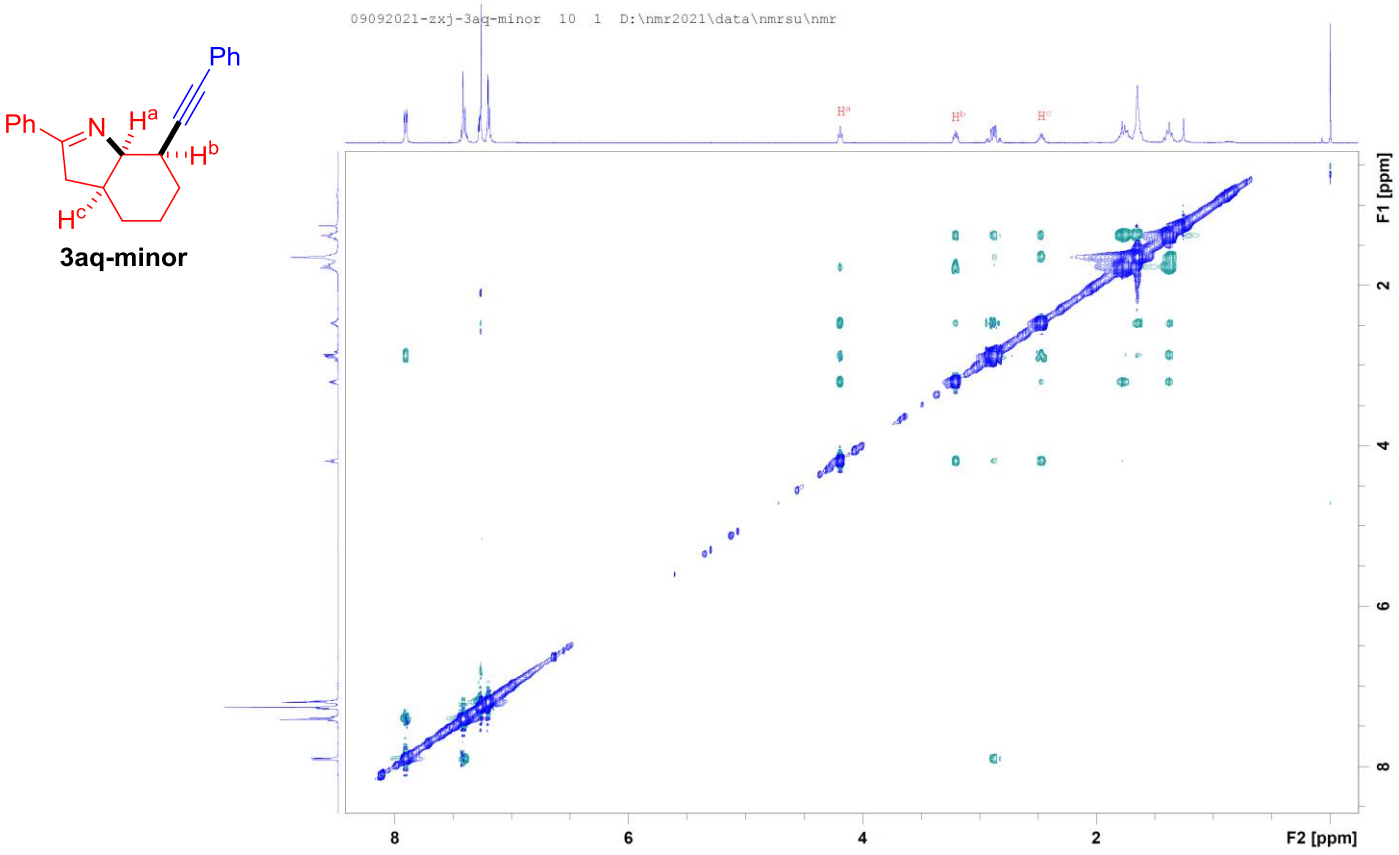
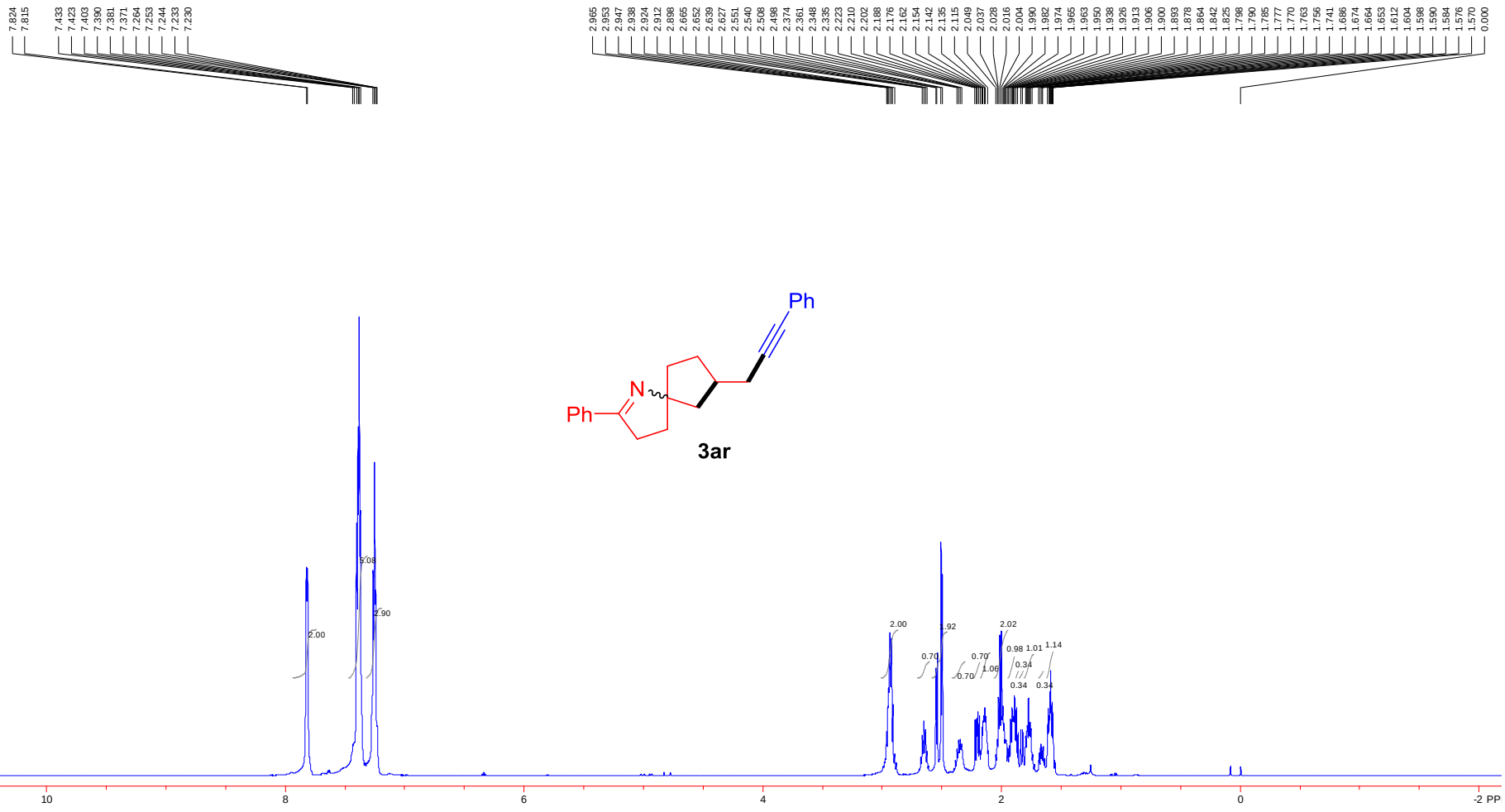


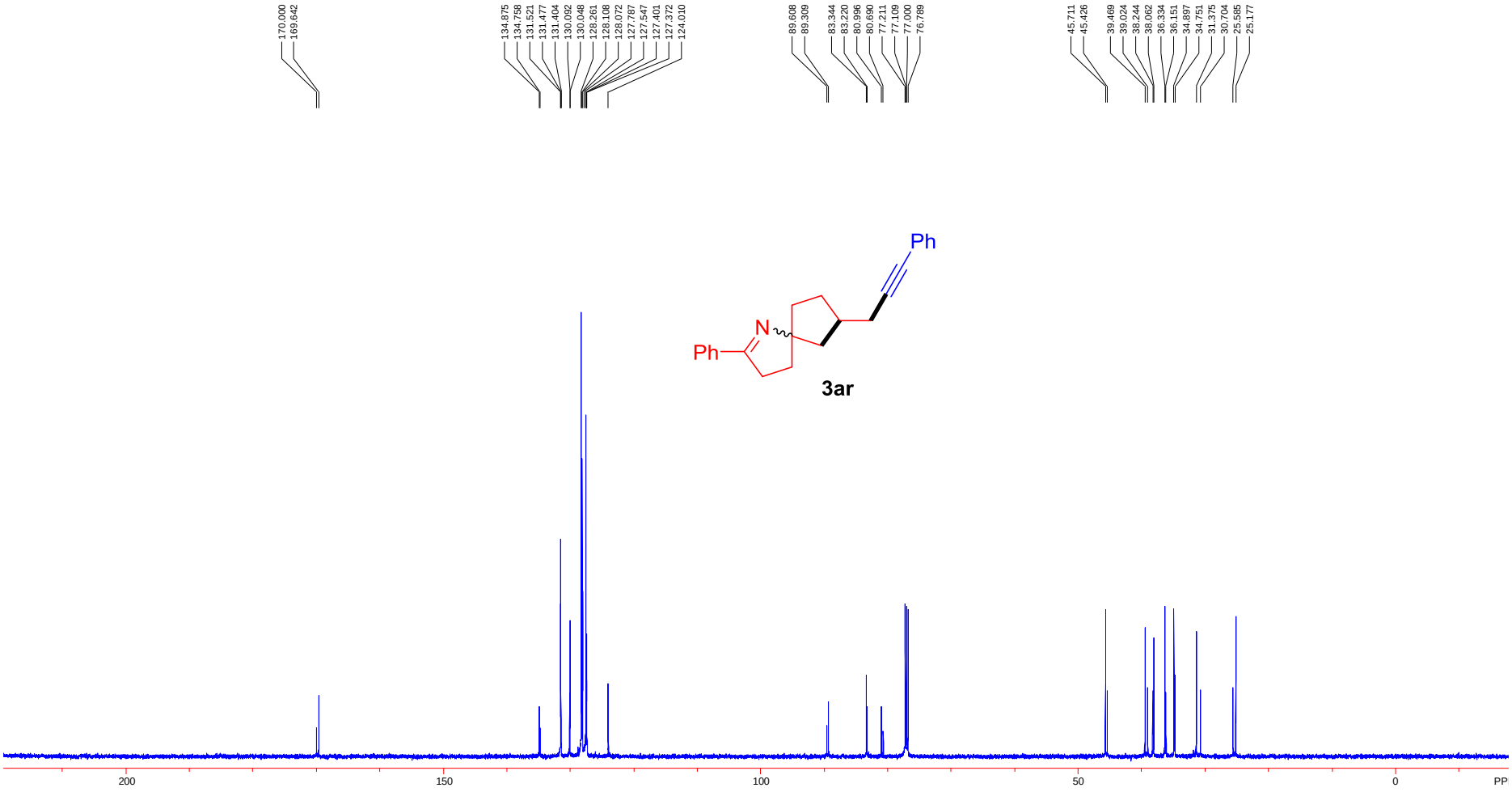
NOESY-2D ^{1}H NMR (400 MHz, $CDCl_3$)



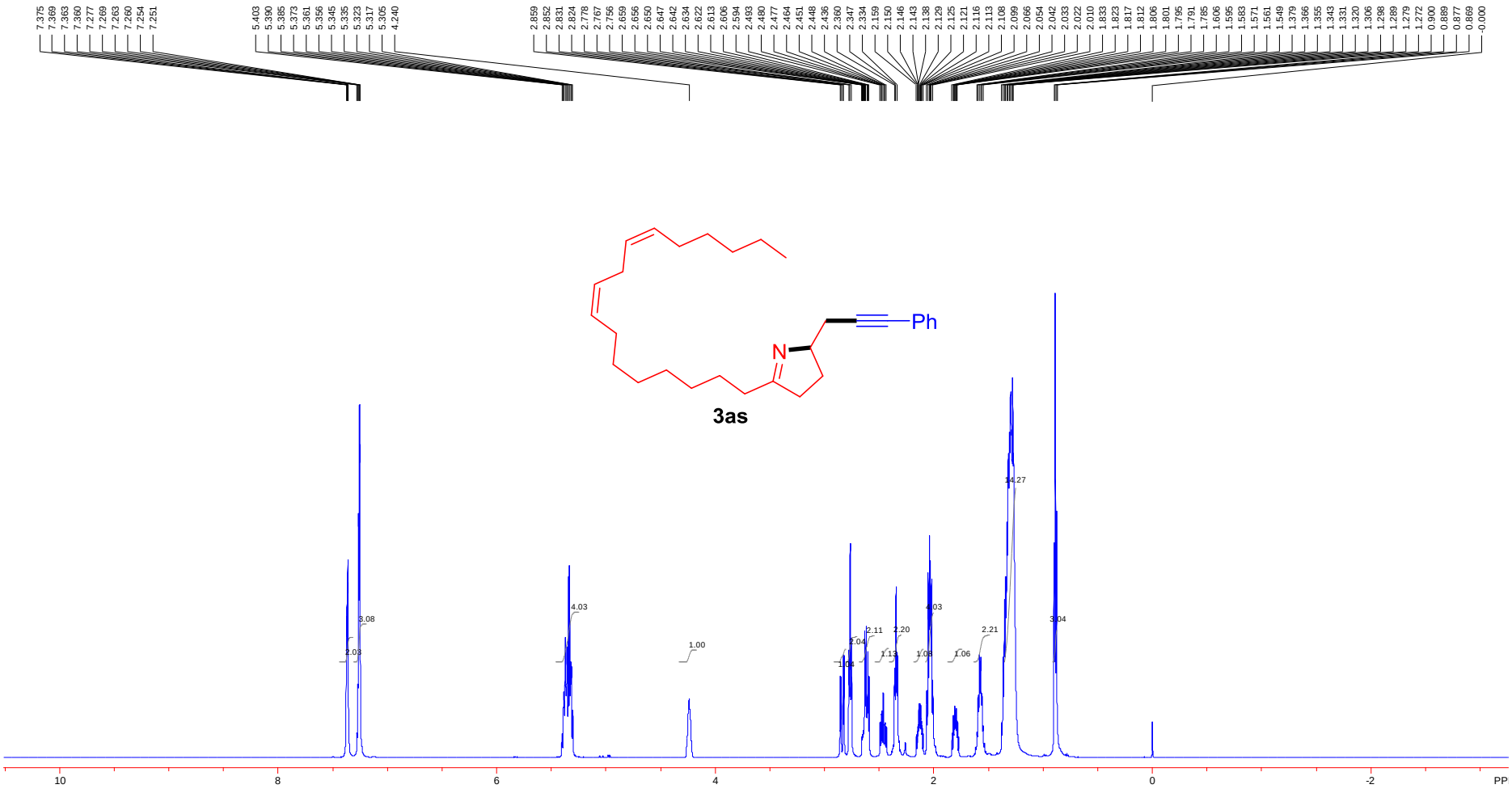
^{1}H NMR(600 MHz, $CDCl_3$)



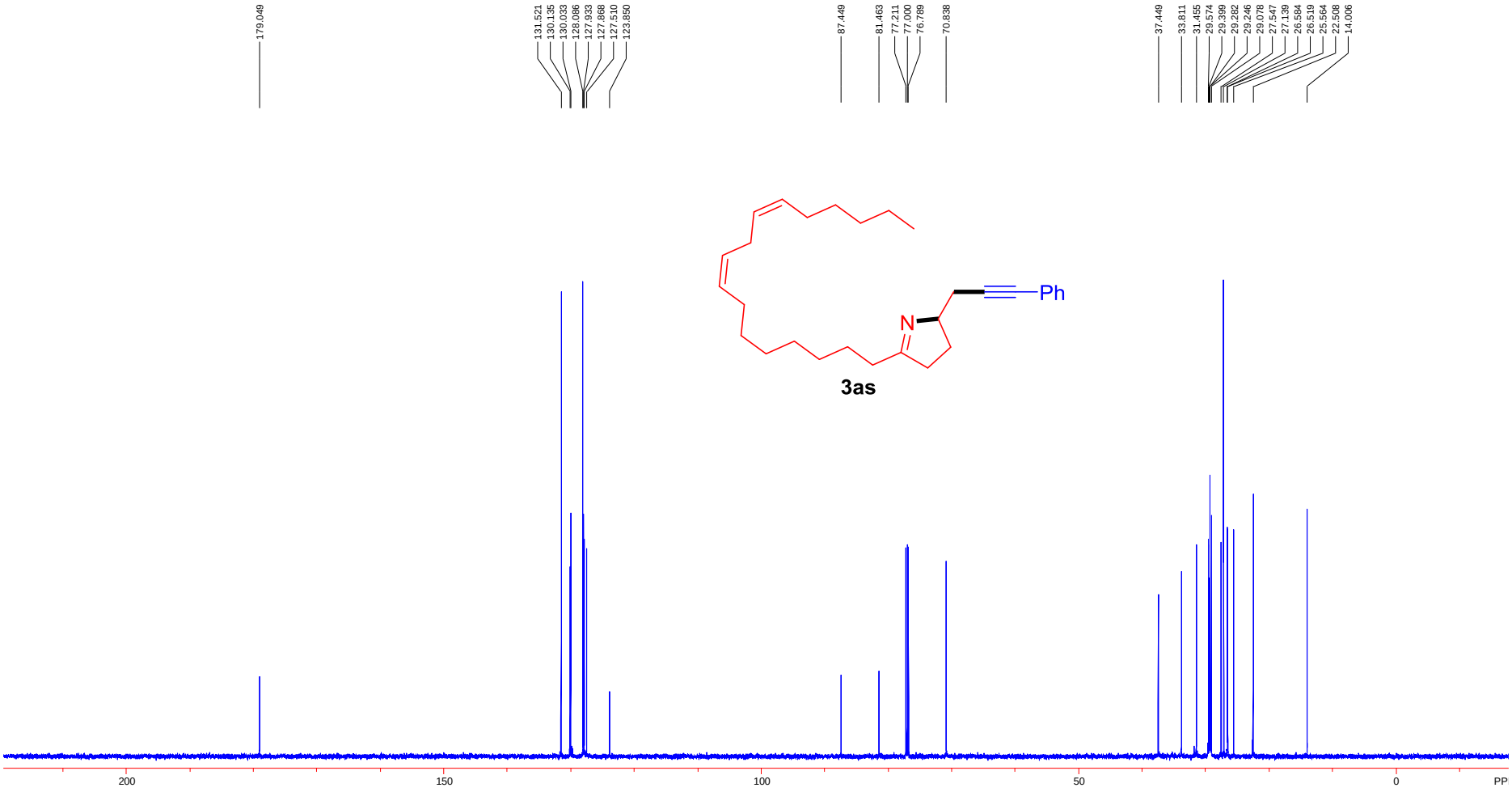
^{13}C NMR(151 MHz, $CDCl_3$)



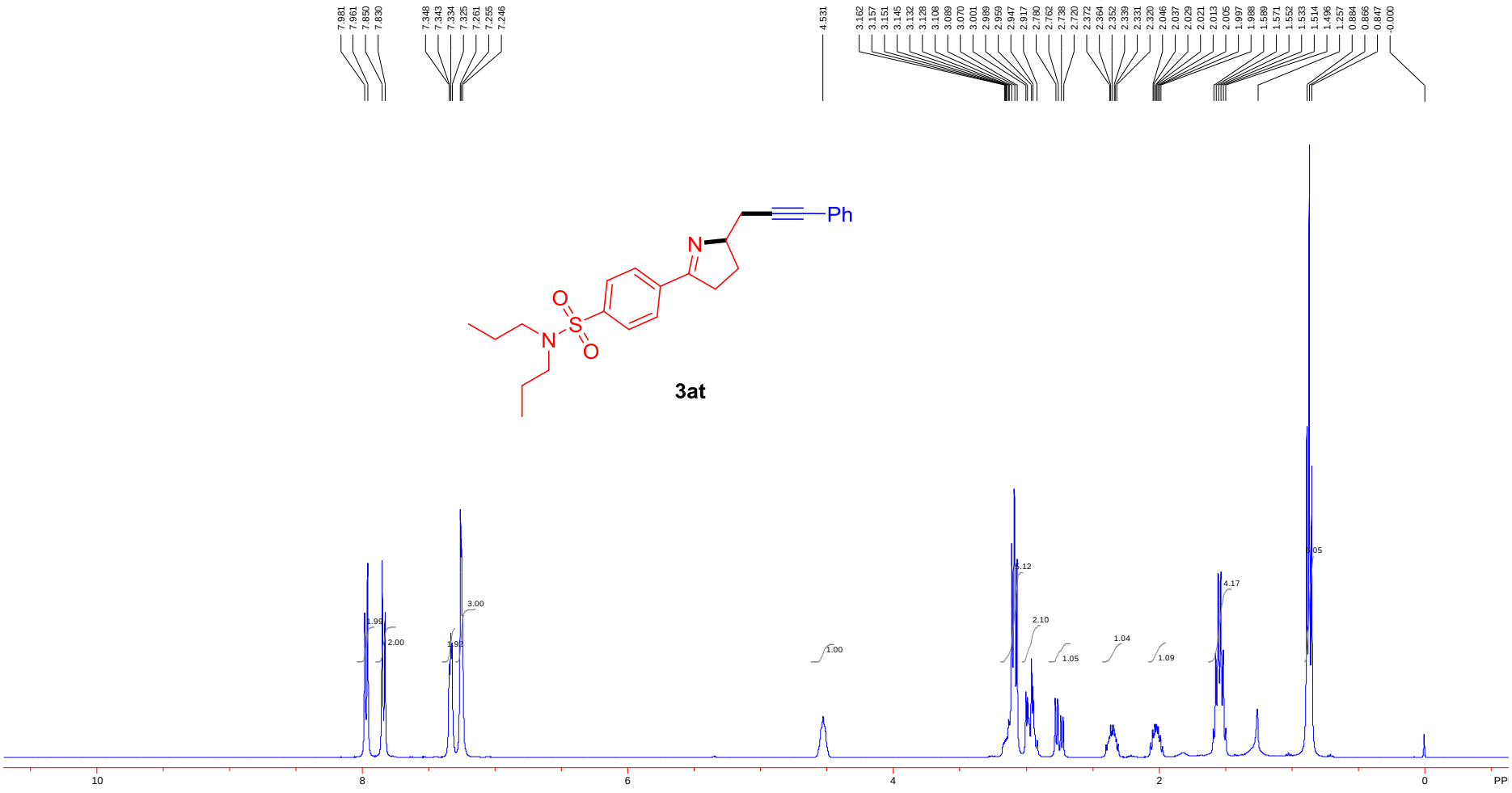
^{1}H NMR(600 MHz, $CDCl_3$)



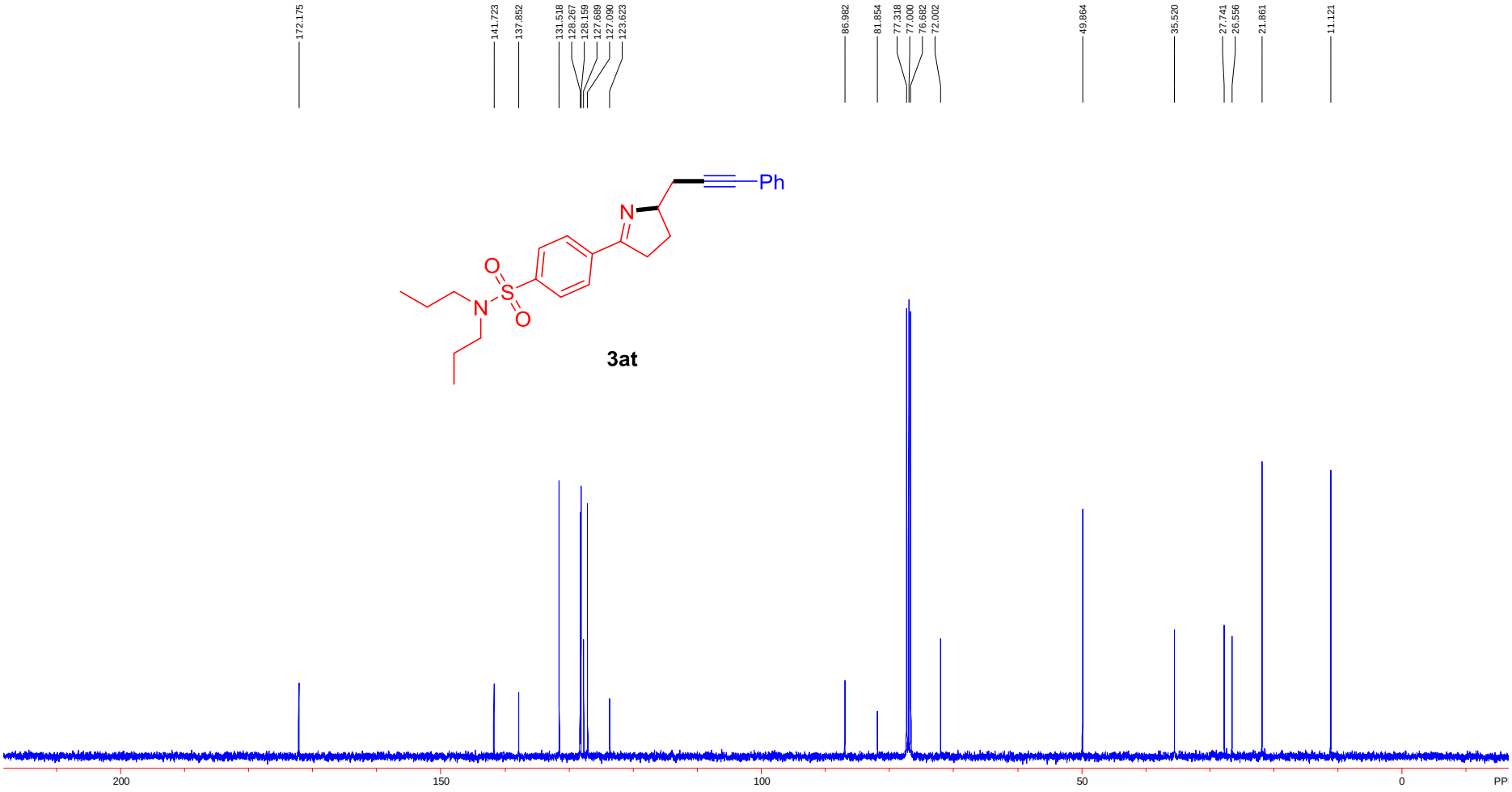
^{13}C NMR(151 MHz, $CDCl_3$)



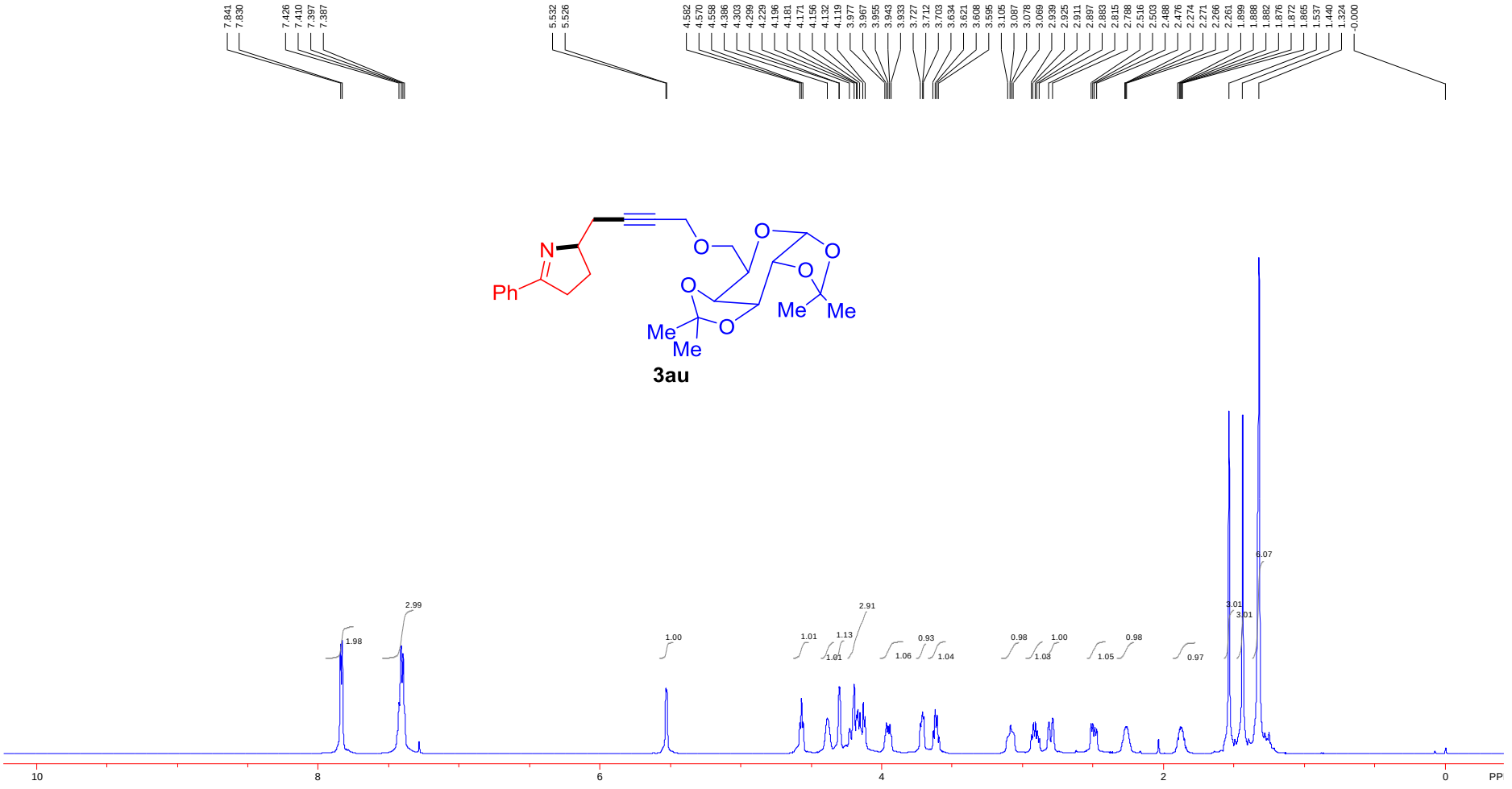
^{1}H NMR(400 MHz, $CDCl_3$)



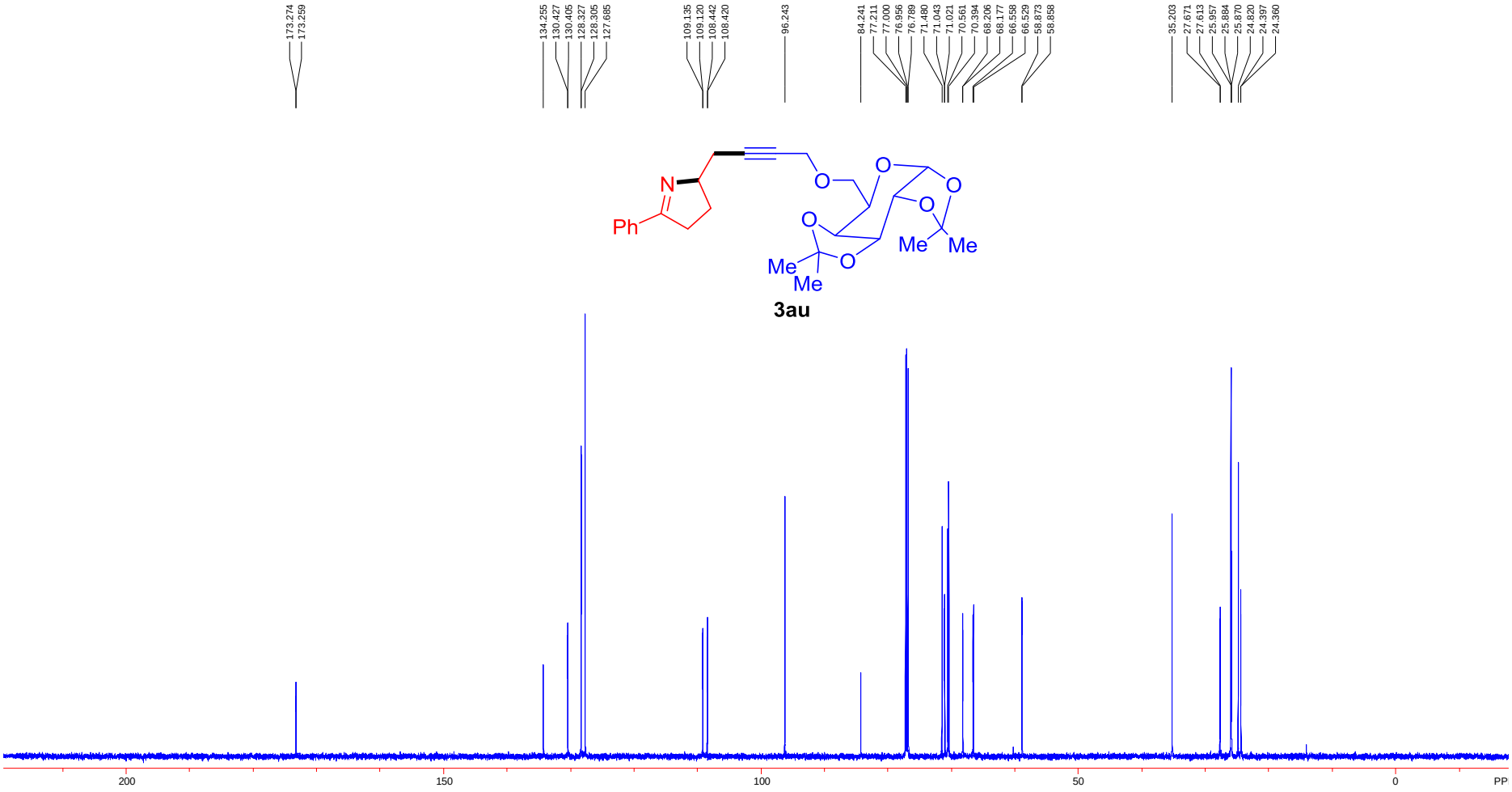
^{13}C NMR(100 MHz, $CDCl_3$)



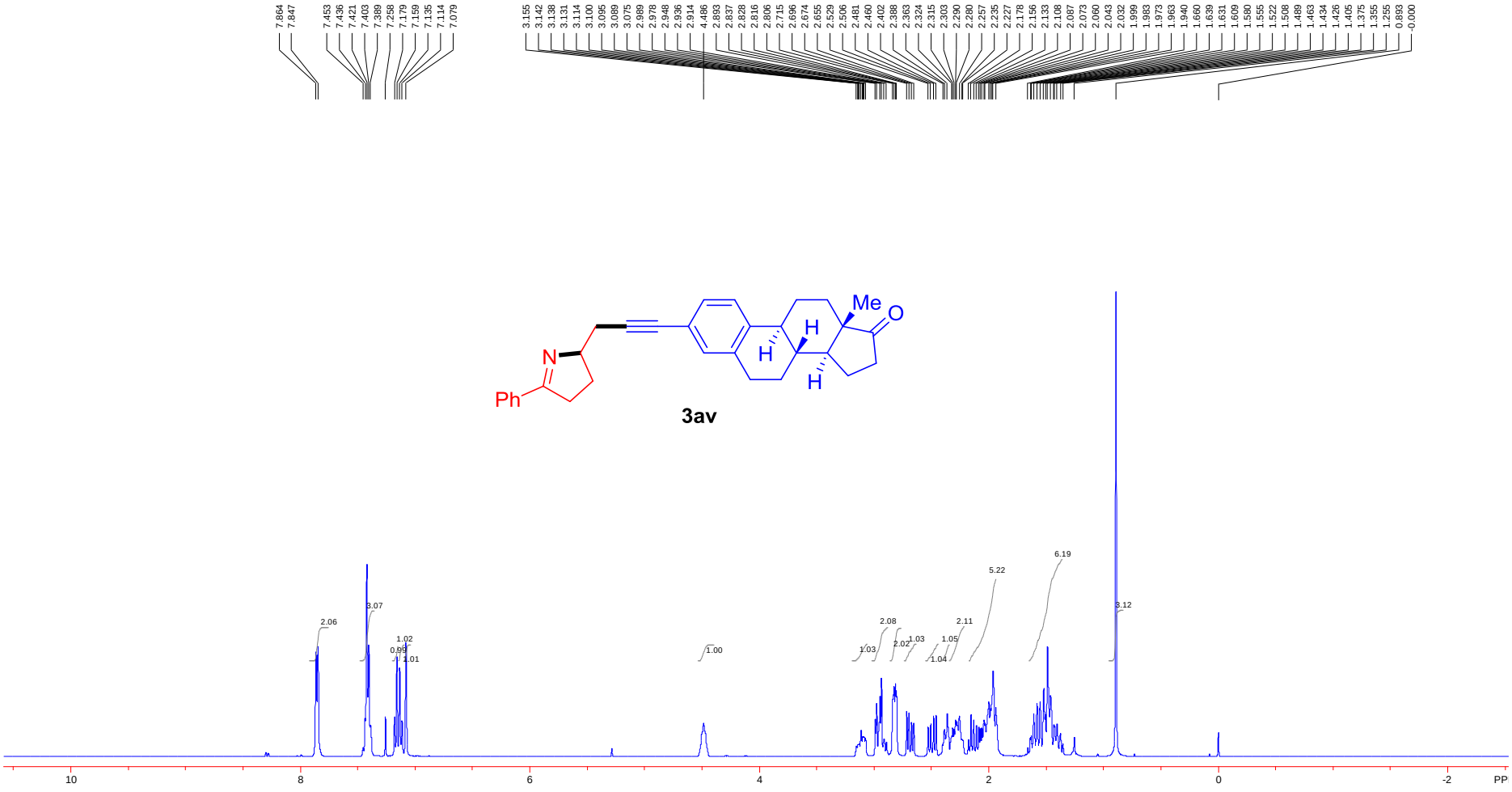
^{1}H NMR(600 MHz, $CDCl_3$)



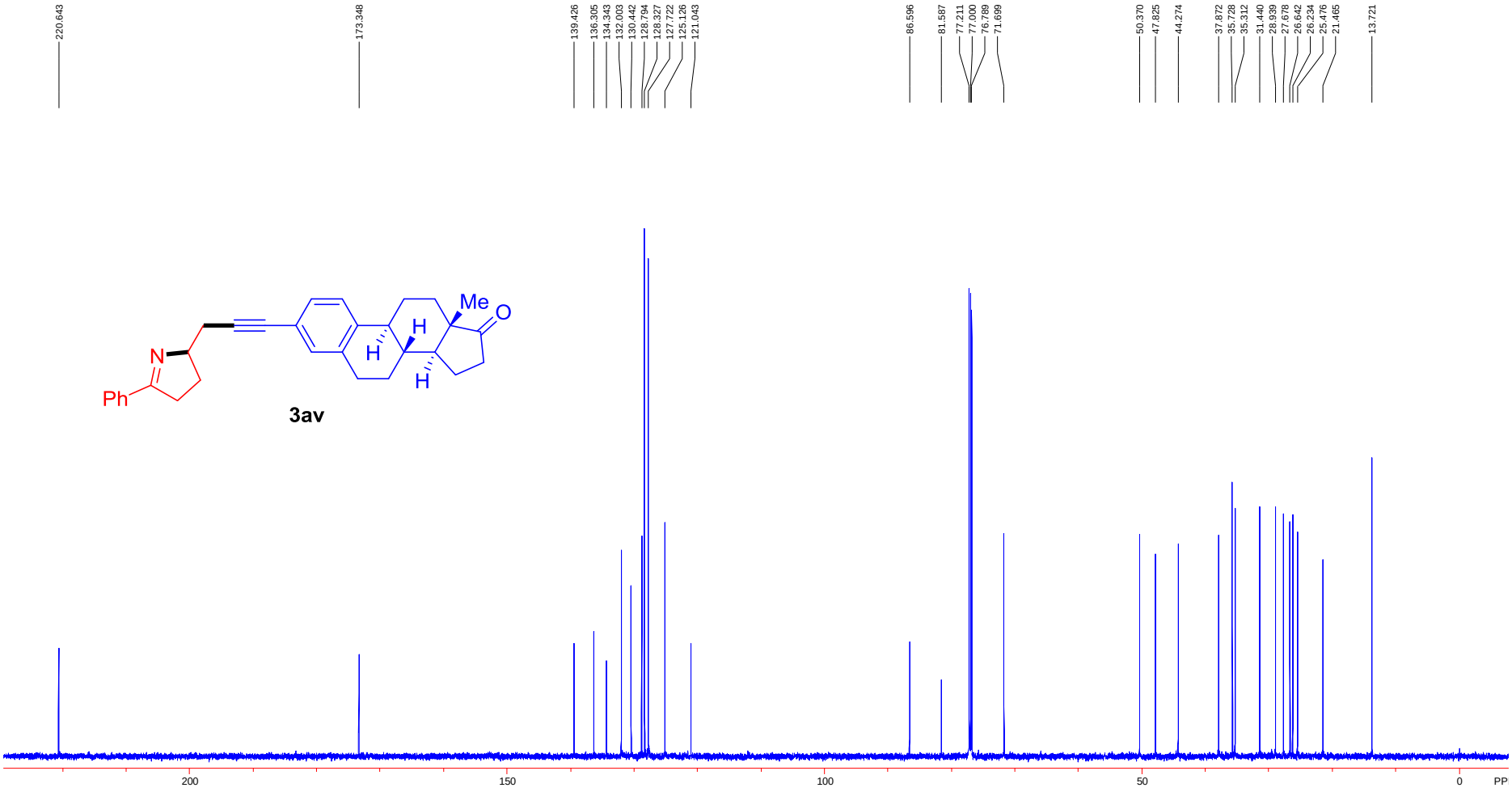
^{13}C NMR(151 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



^{13}C NMR(151 MHz, $CDCl_3$)



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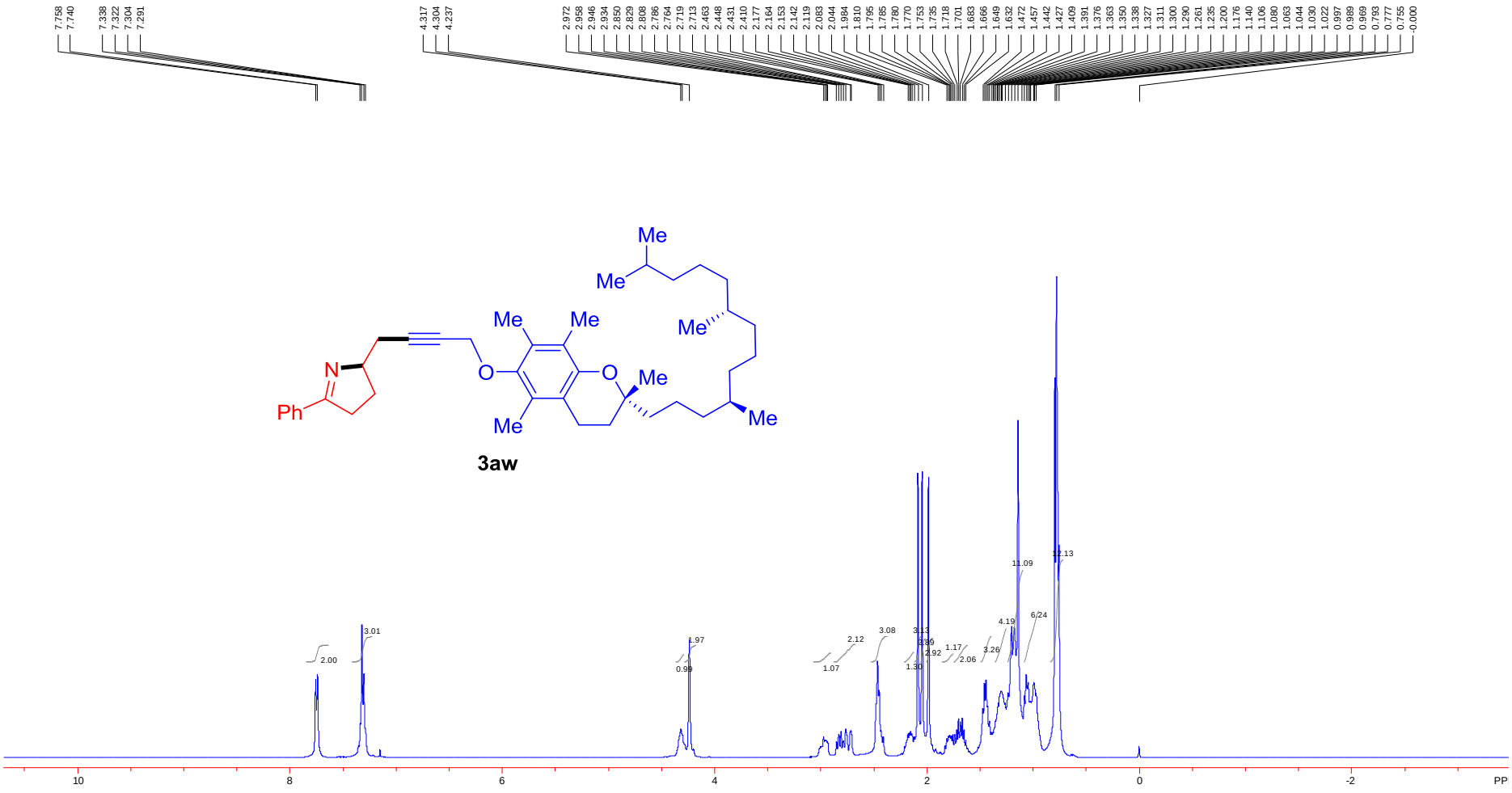
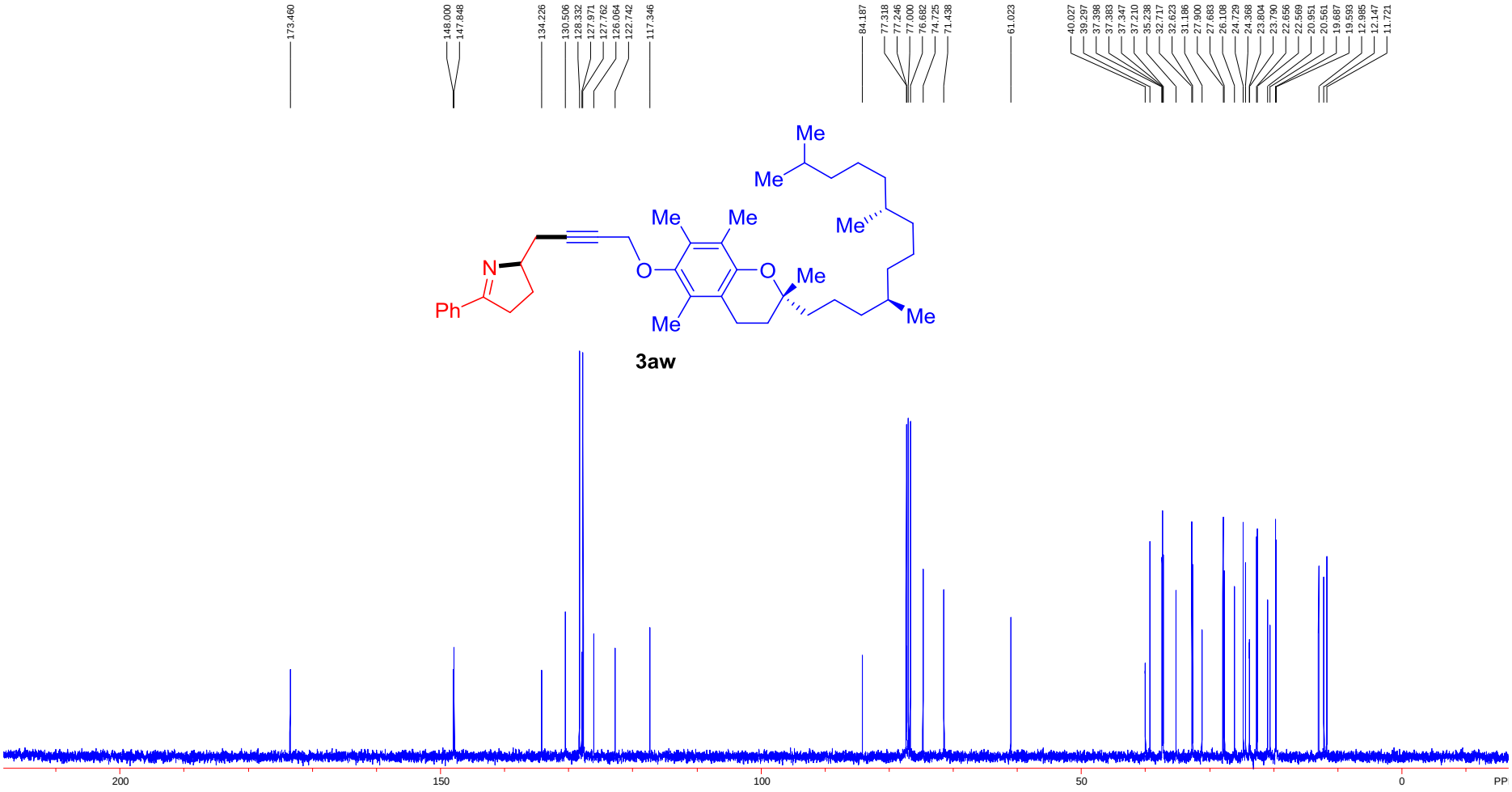
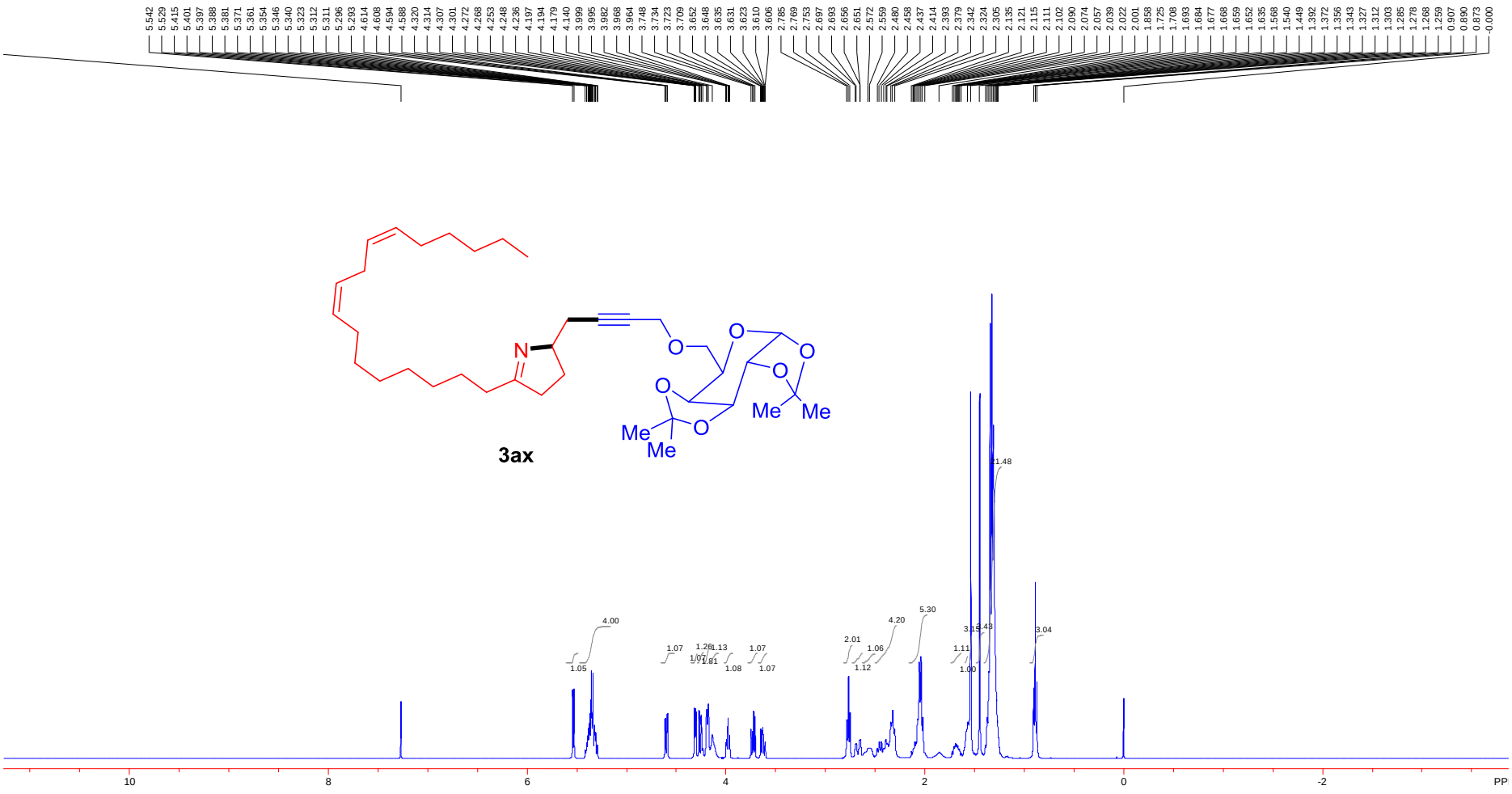


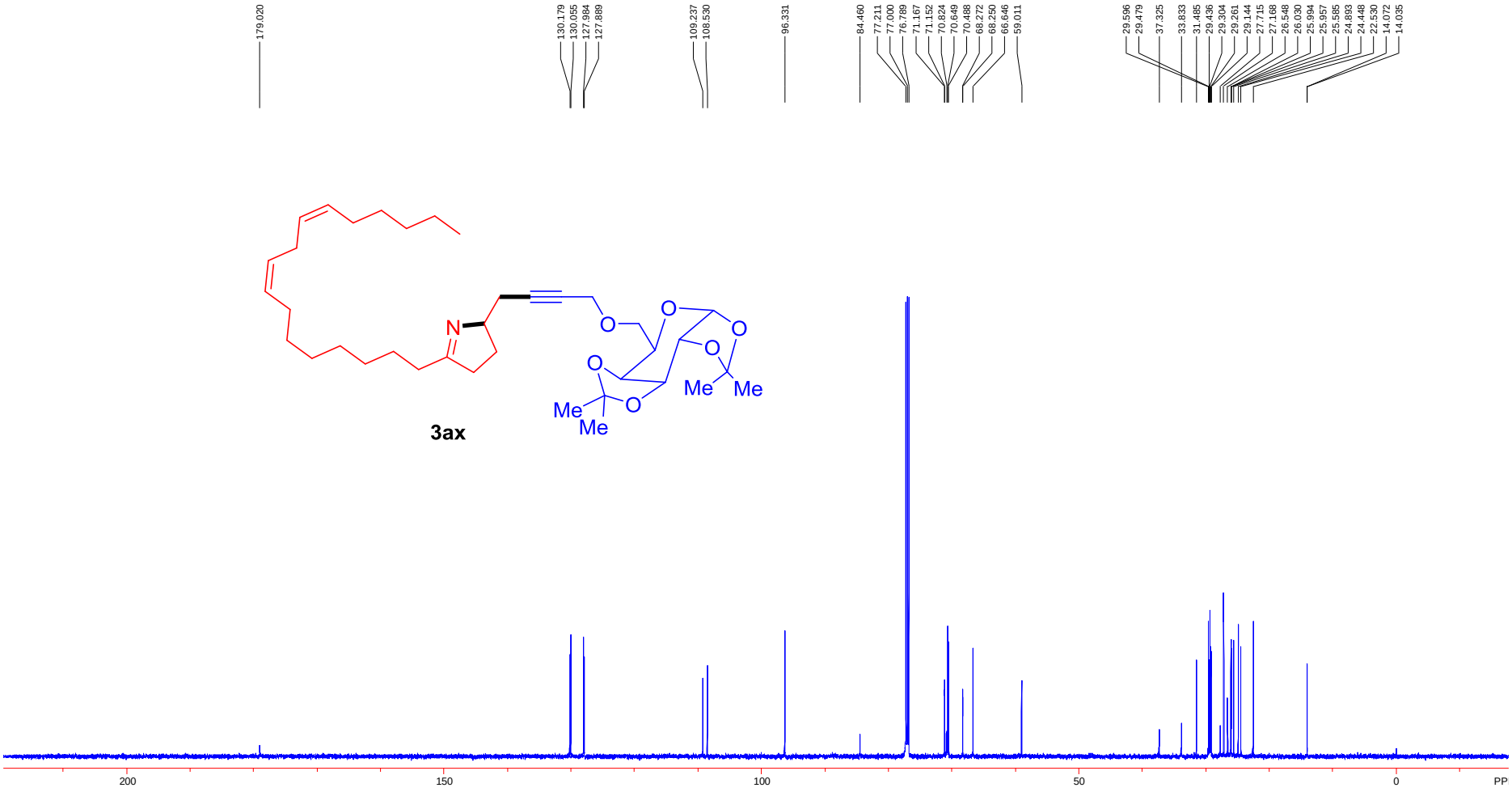
^{13}C NMR(100 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



^{13}C NMR(151 MHz, $CDCl_3$)



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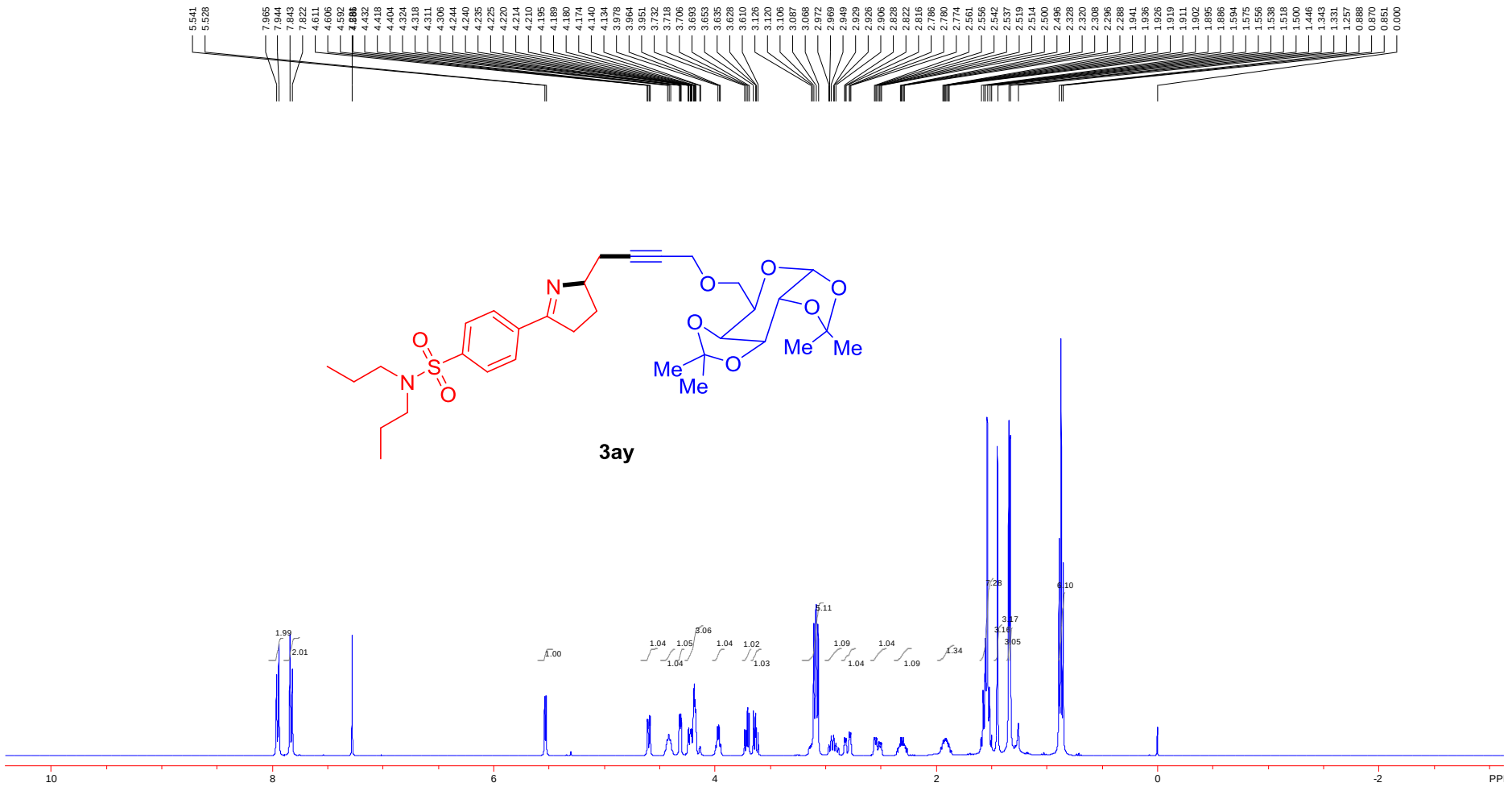
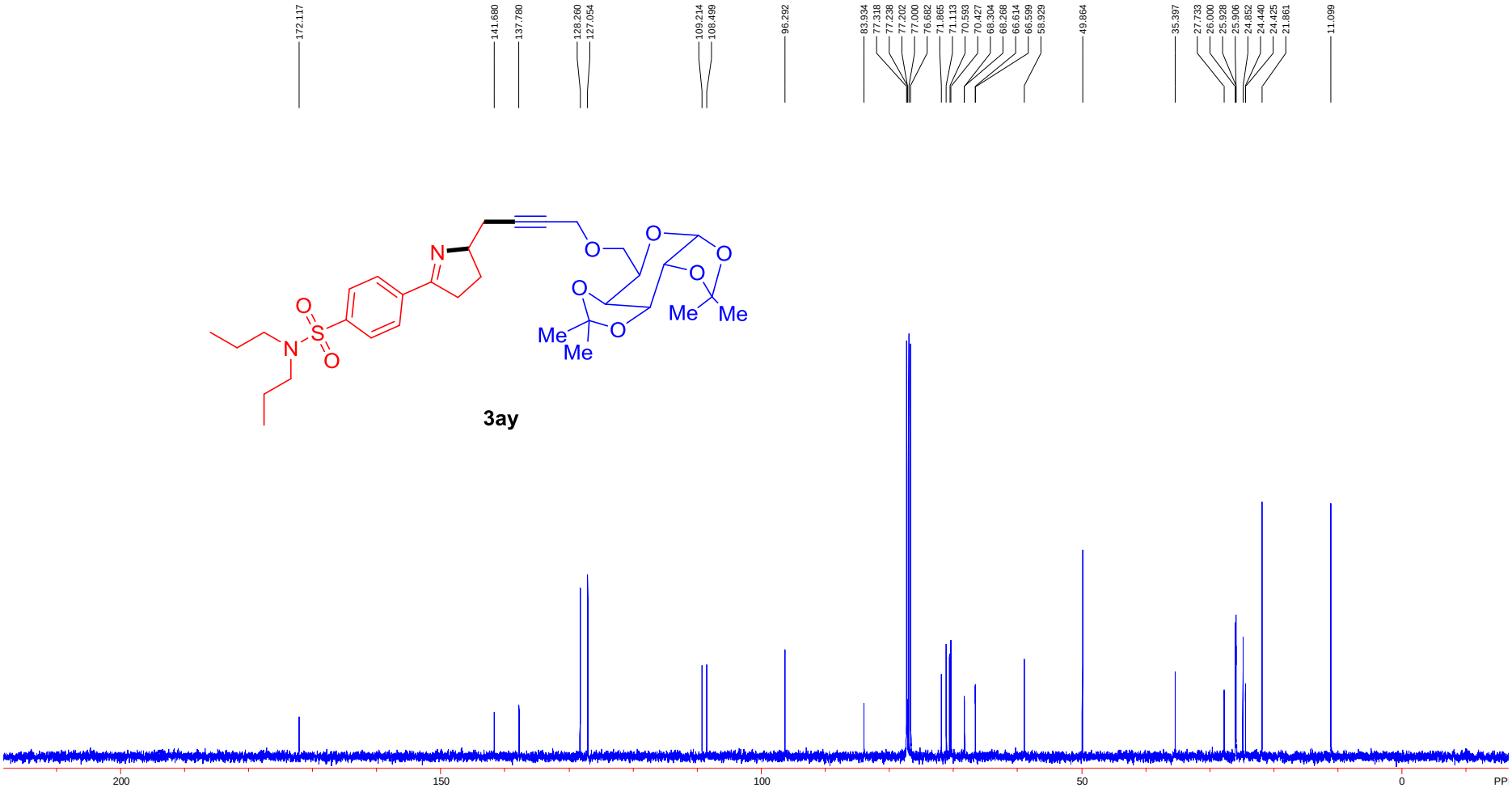
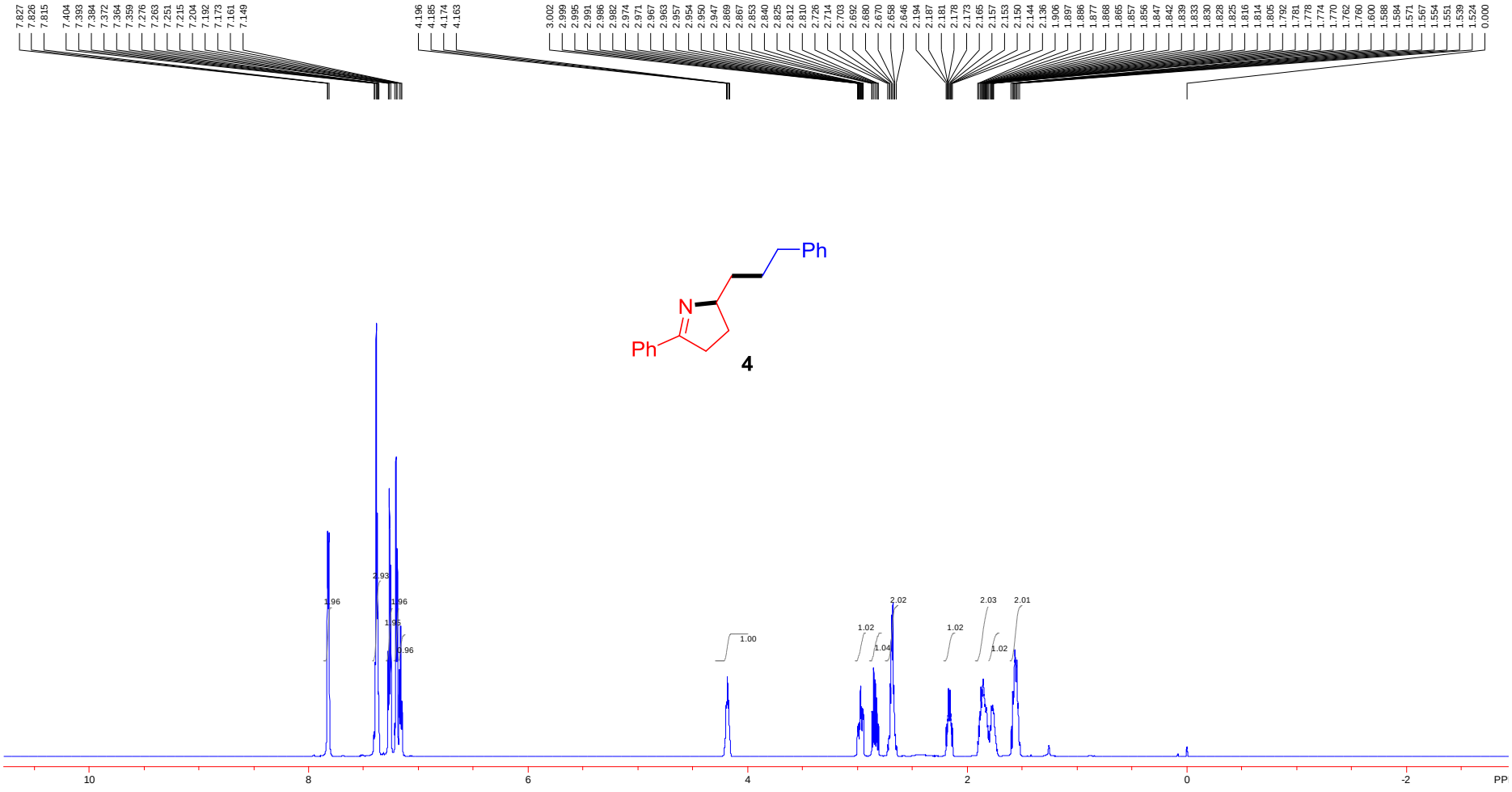


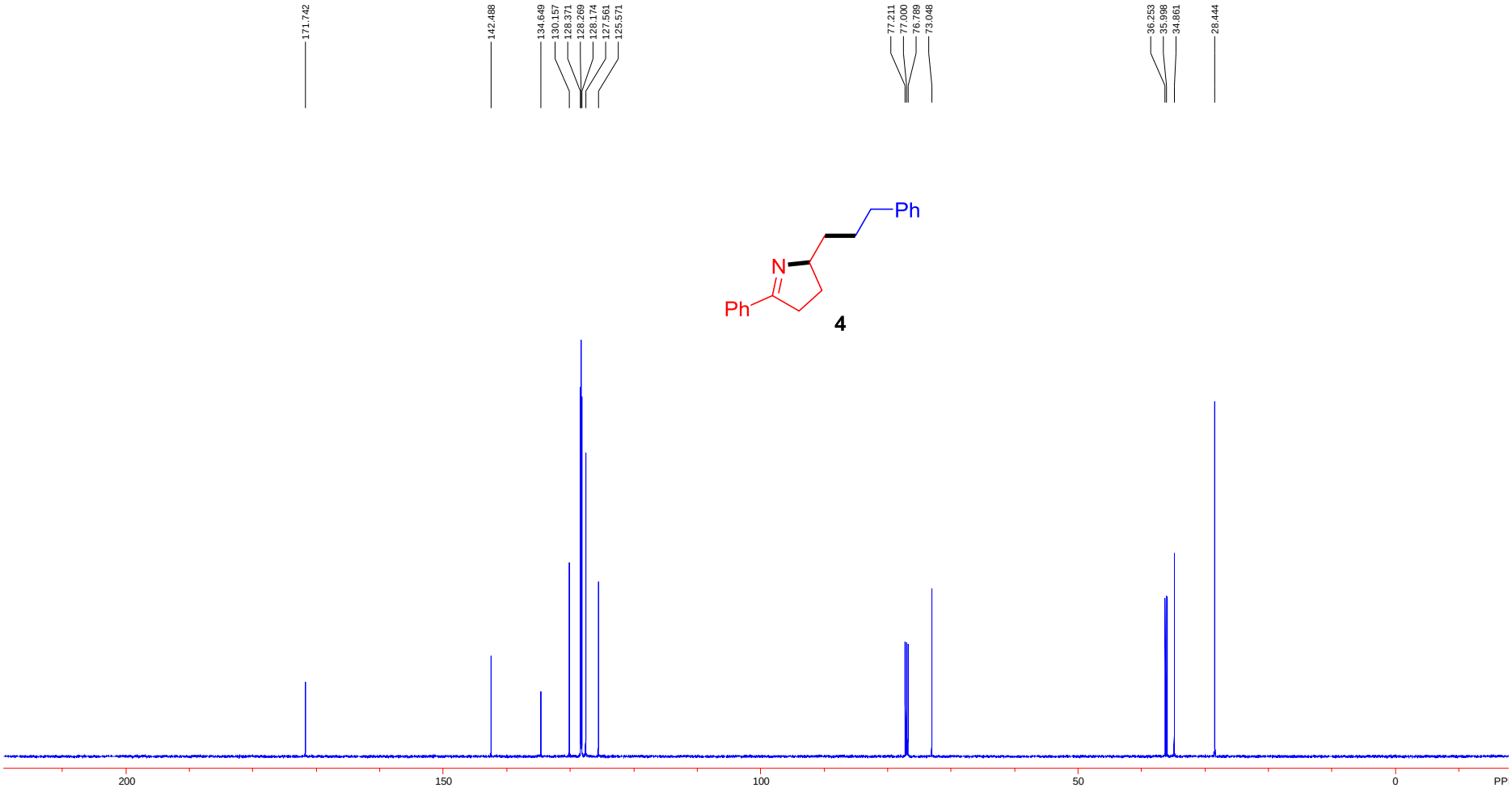
^{13}C NMR(100 MHz, $CDCl_3$)



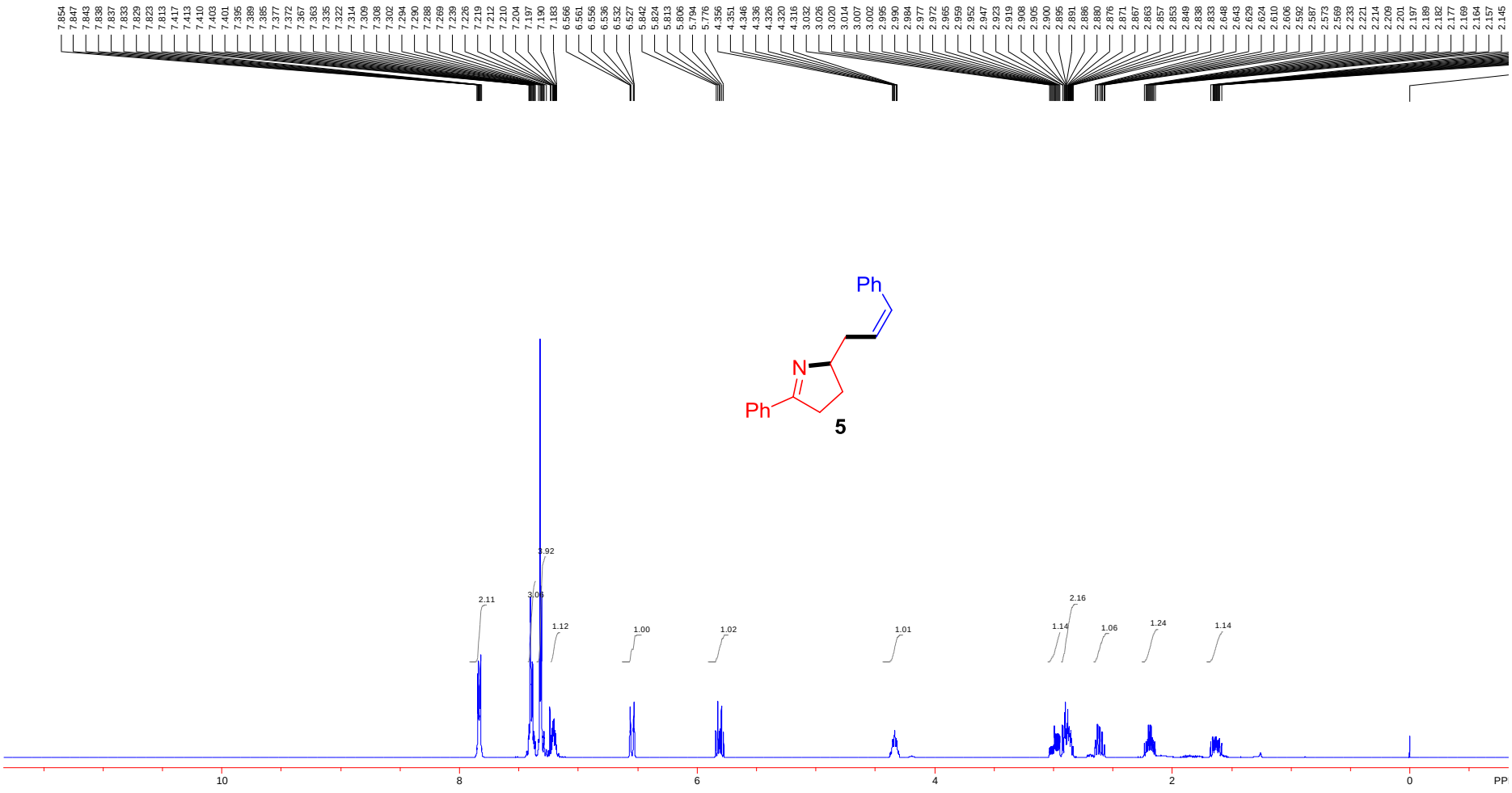
^{1}H NMR(600 MHz, $CDCl_3$)



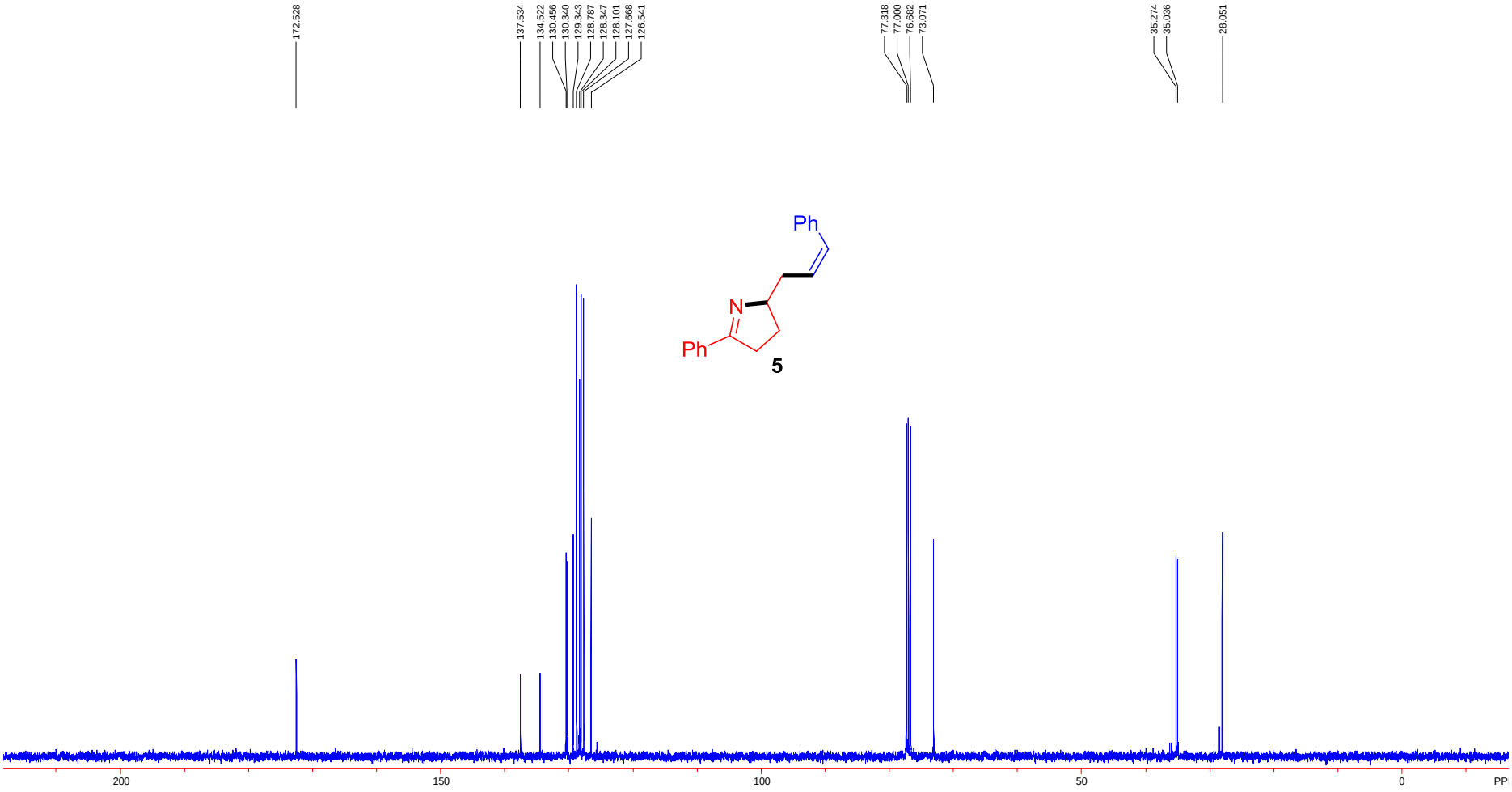
^{13}C NMR(151 MHz, $CDCl_3$)



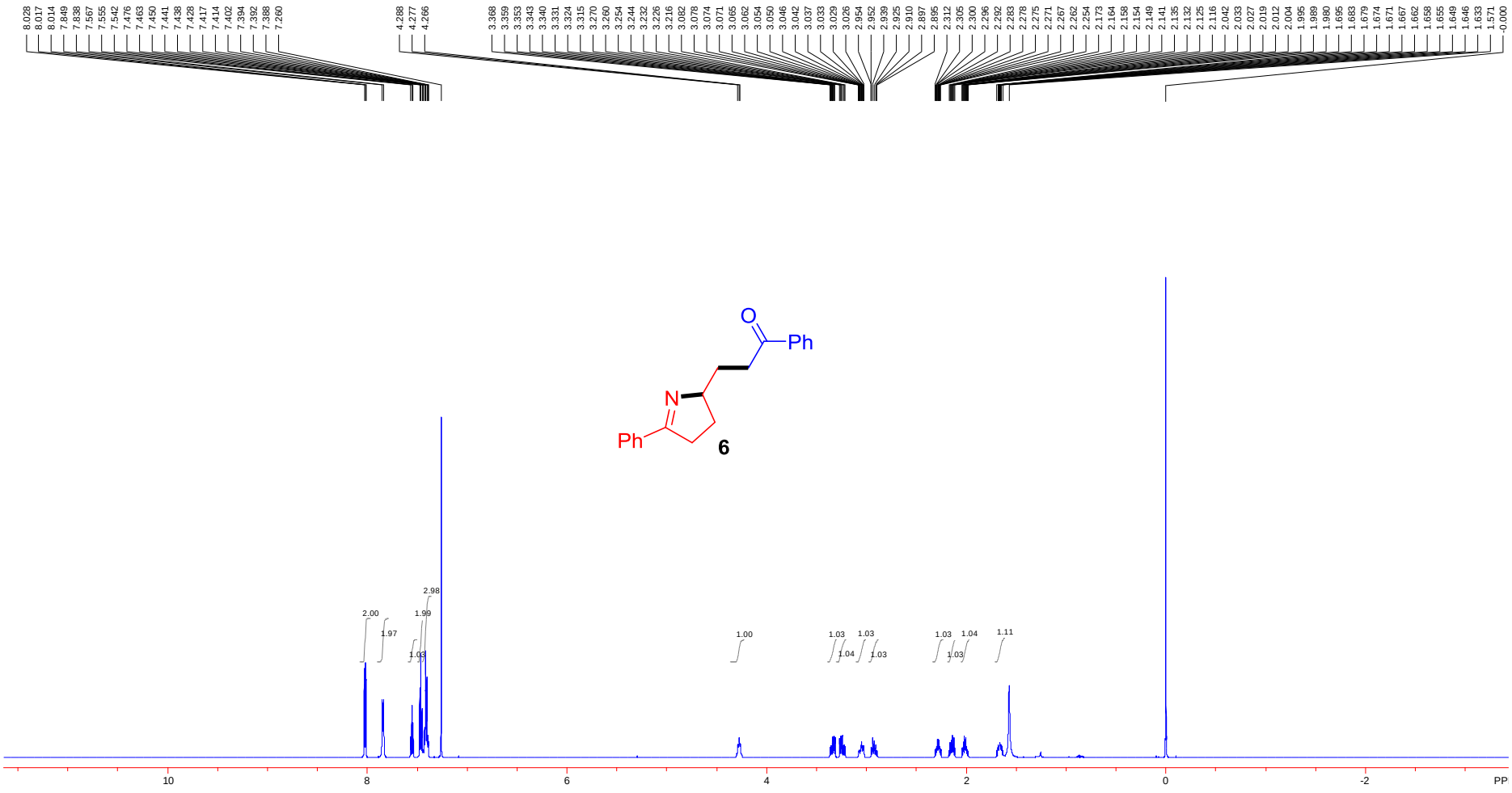
^{1}H NMR(400 MHz, $CDCl_3$)



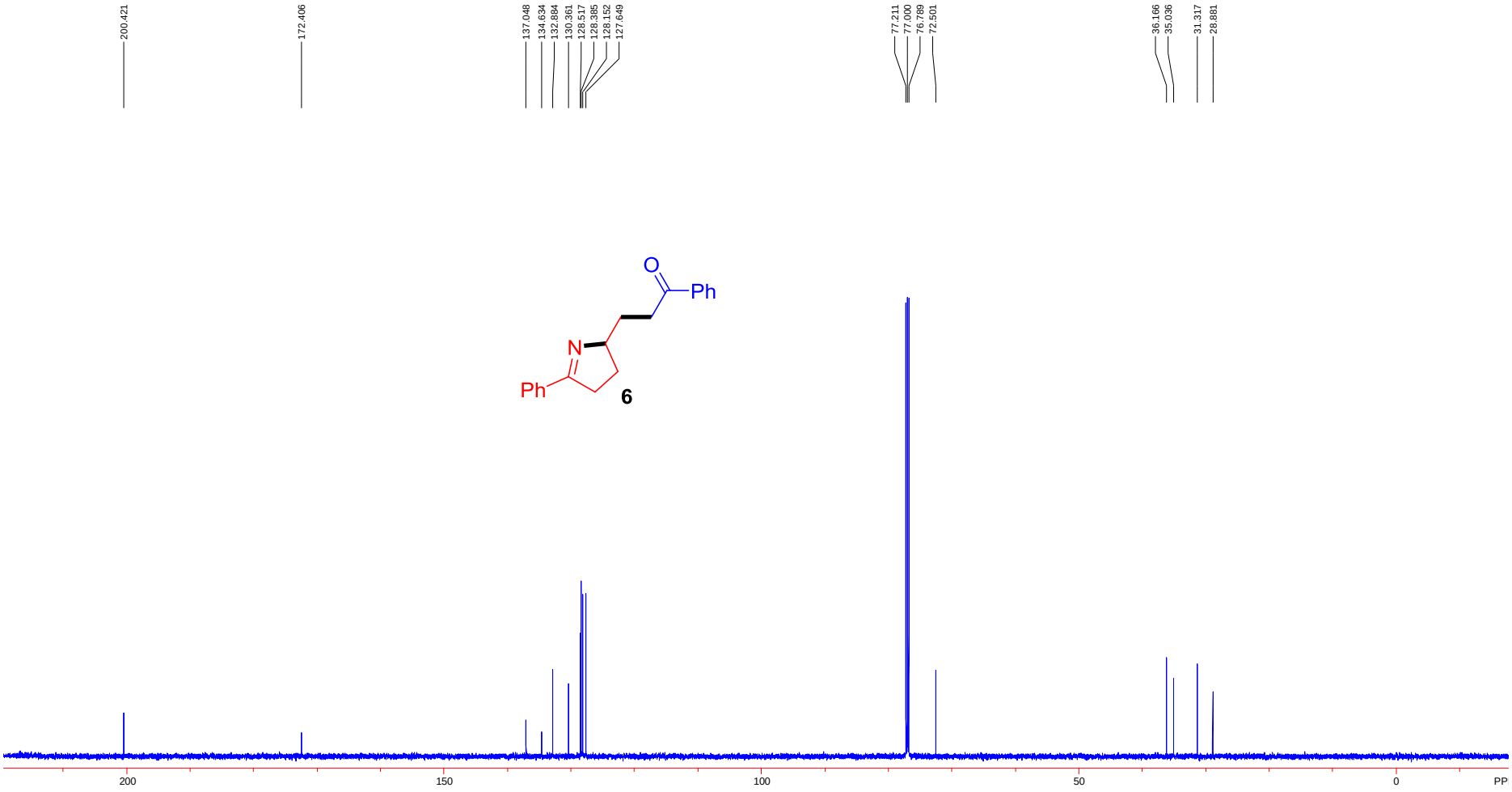
^{13}C NMR(100 MHz, $CDCl_3$)



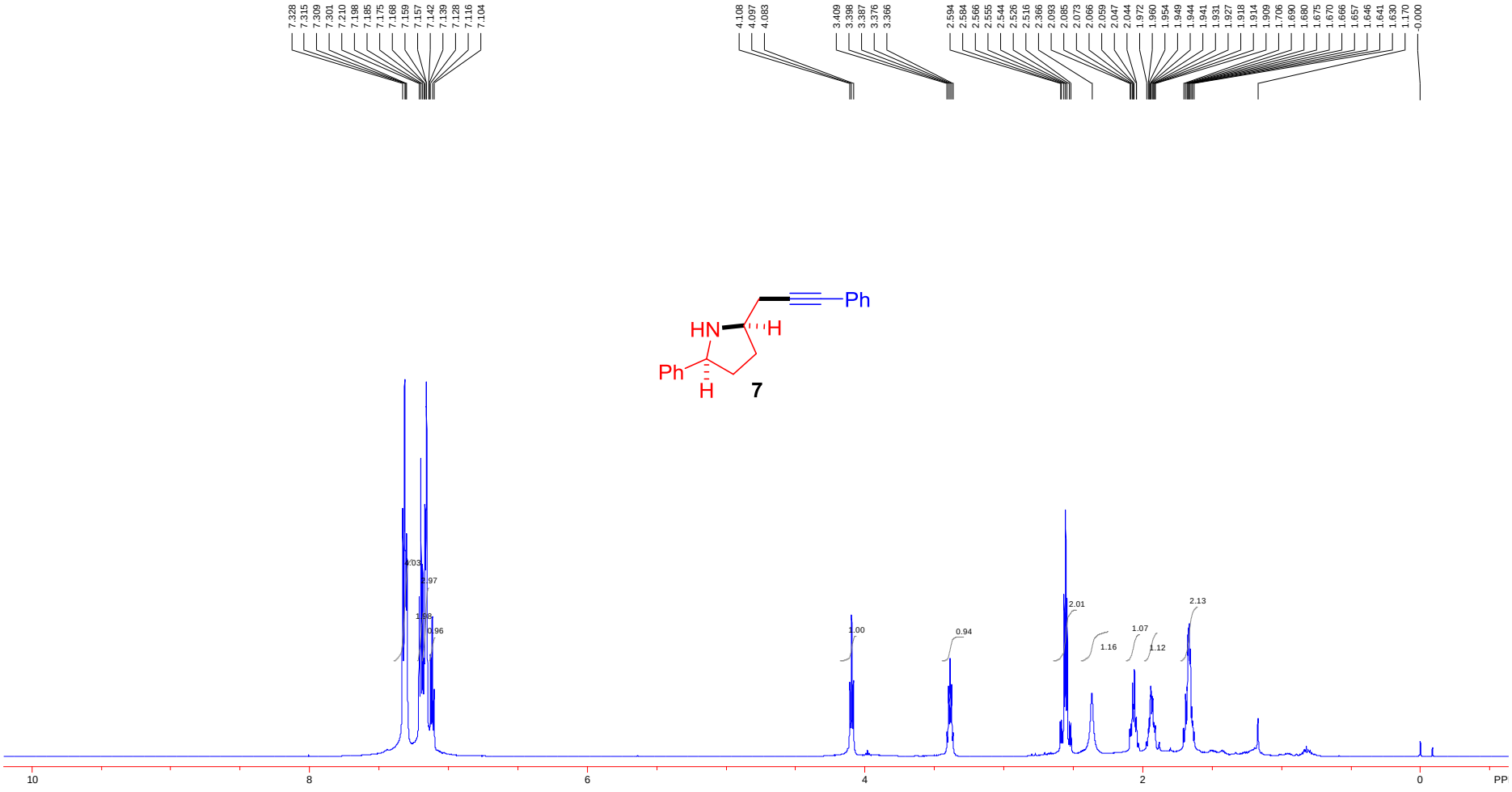
^{1}H NMR(600 MHz, $CDCl_3$)



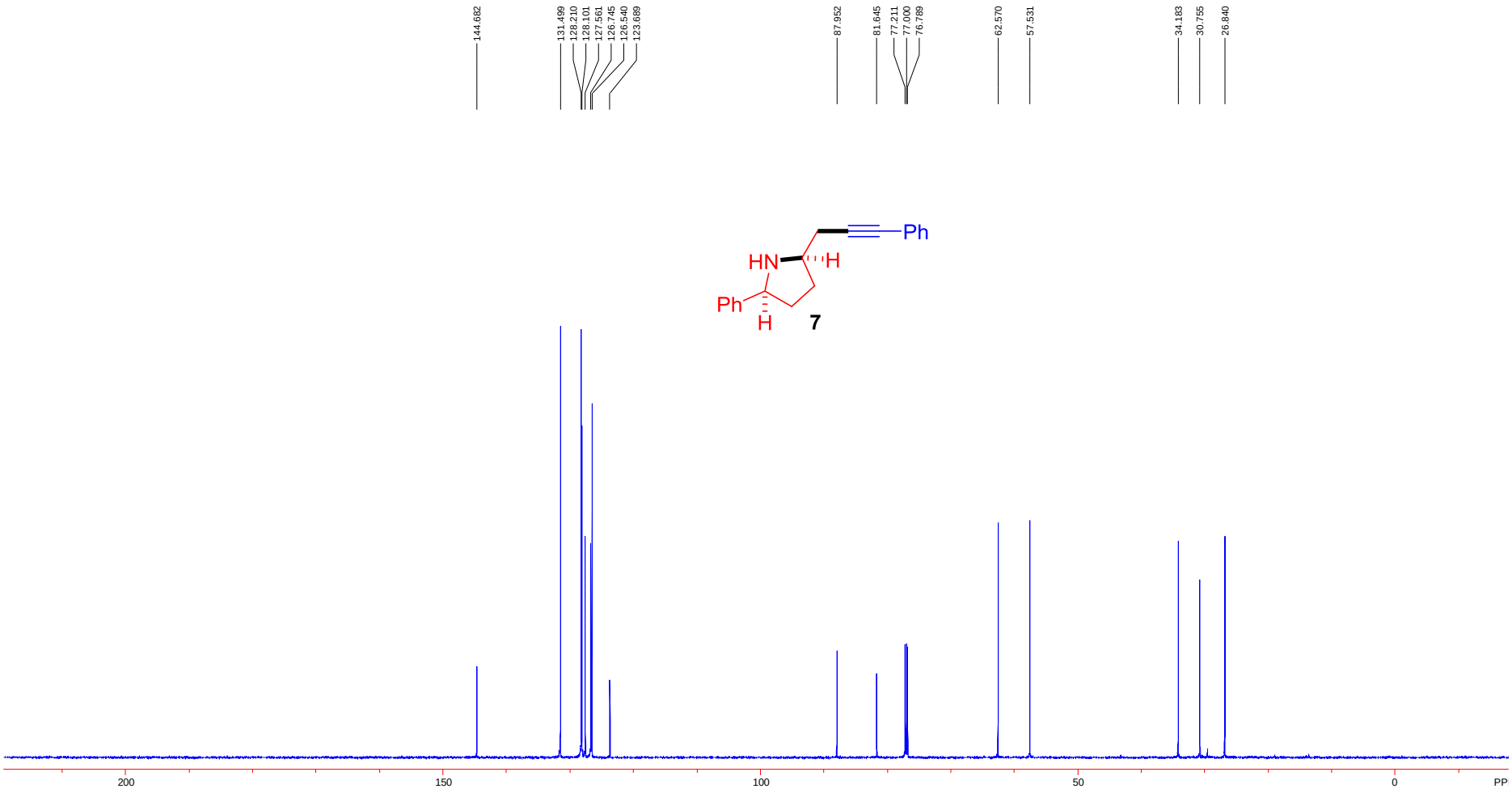
^{13}C NMR(151 MHz, $CDCl_3$)



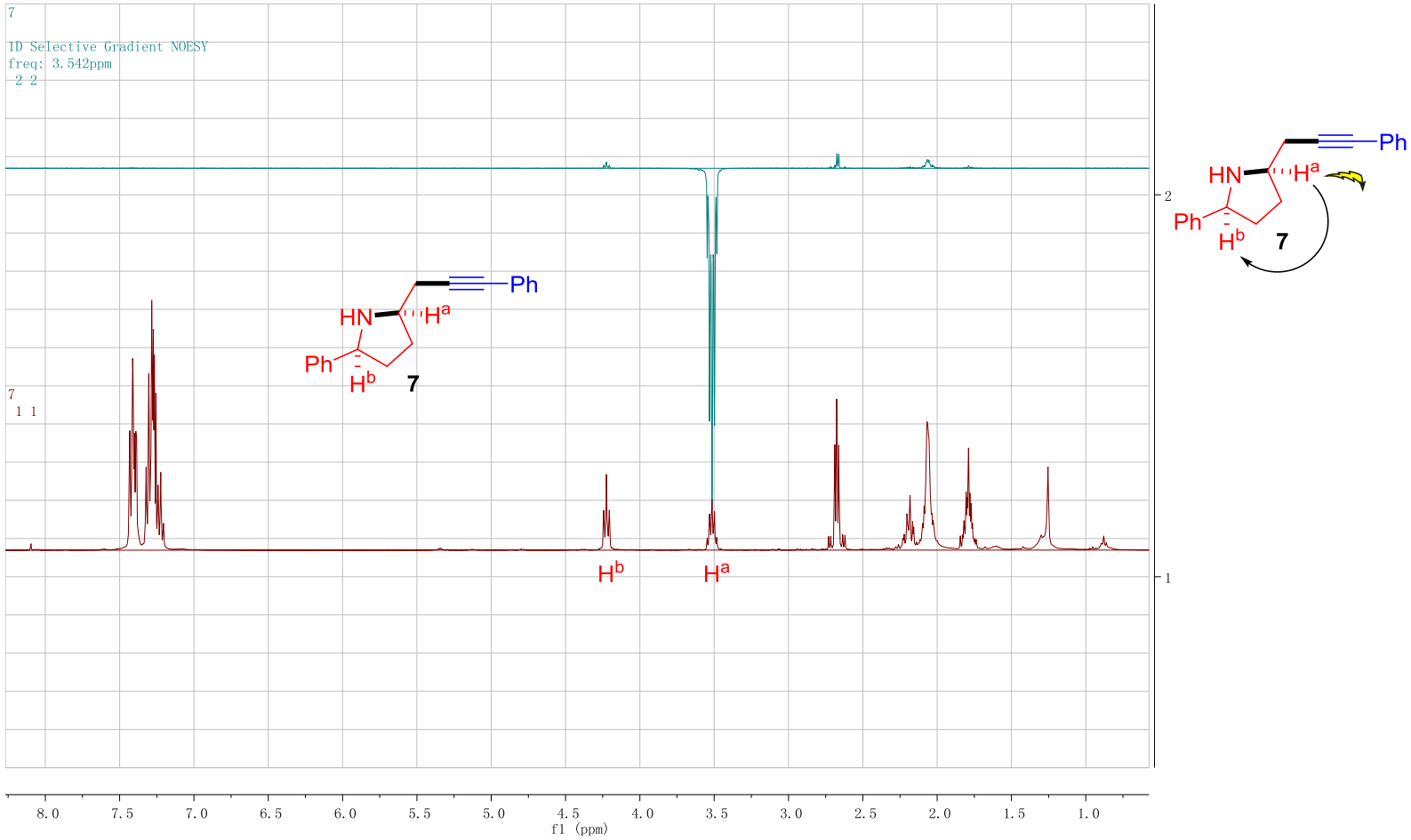
^{1}H NMR(600 MHz, $CDCl_3$)



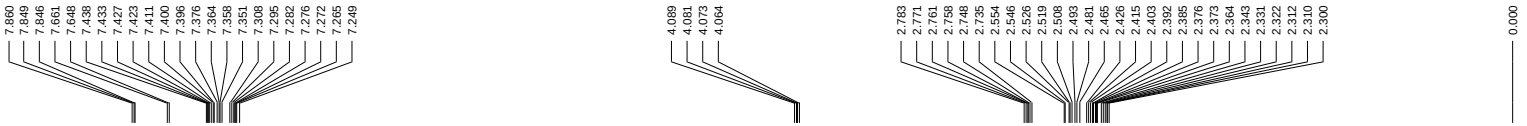
^{13}C NMR(151 MHz, $CDCl_3$)

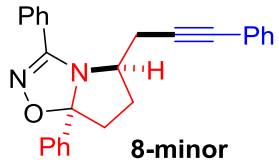


NOESY-1D ^{1}H NMR (400 MHz, $CDCl_3$)

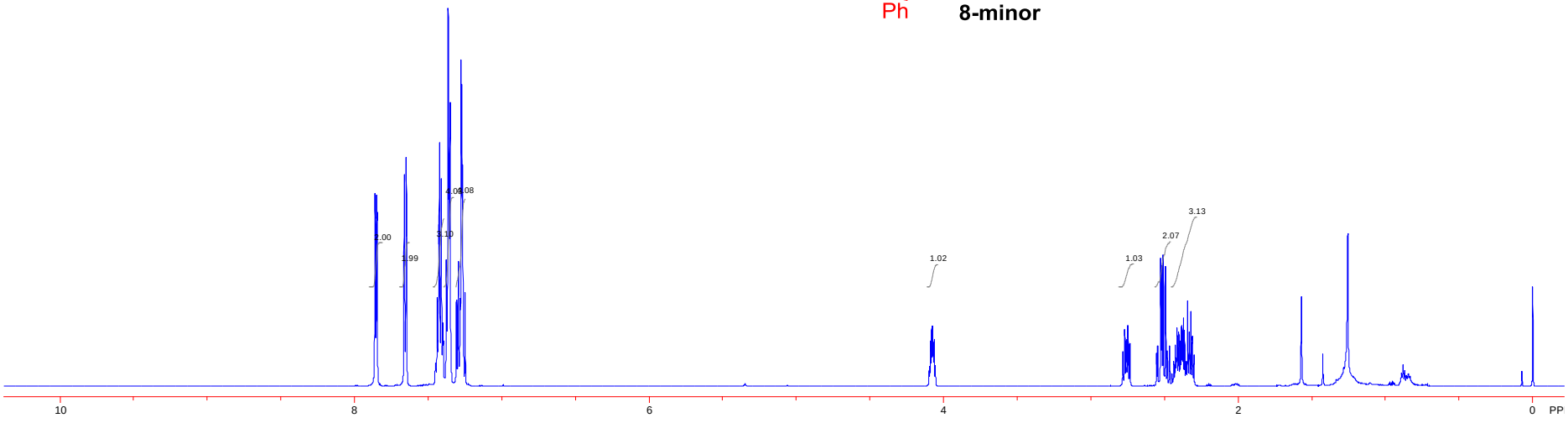


^{1}H NMR(600 MHz, $CDCl_3$)

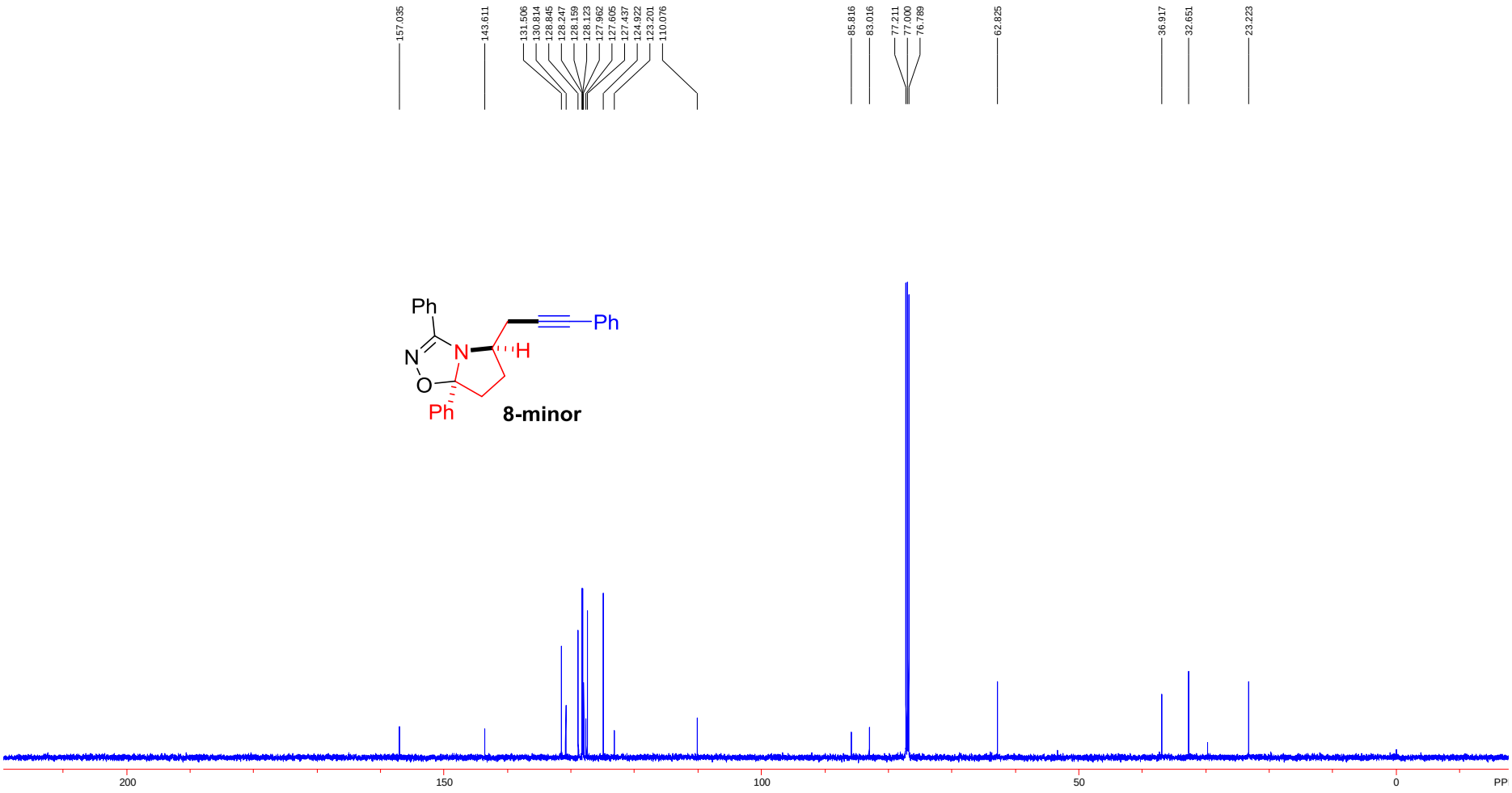




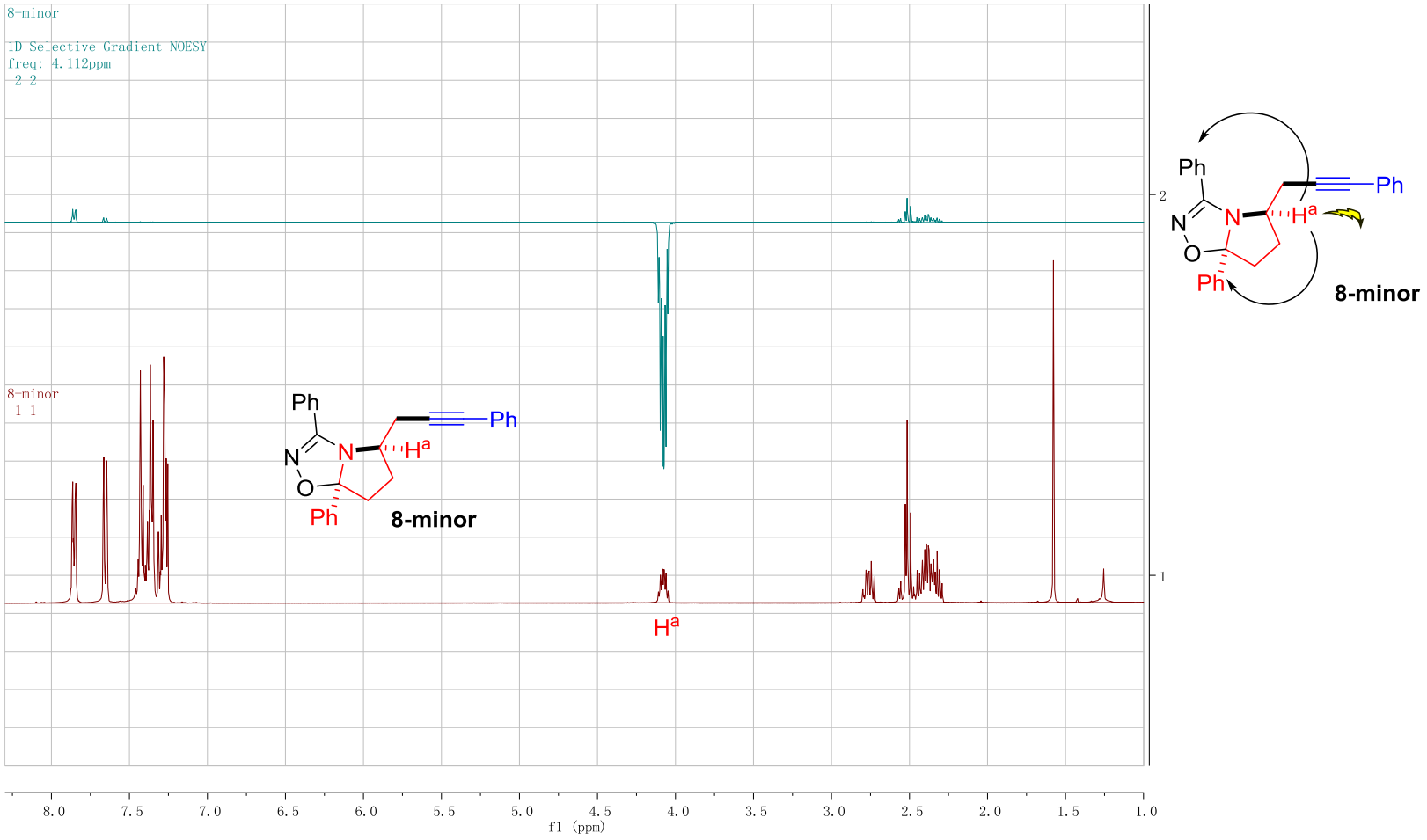
8-minor



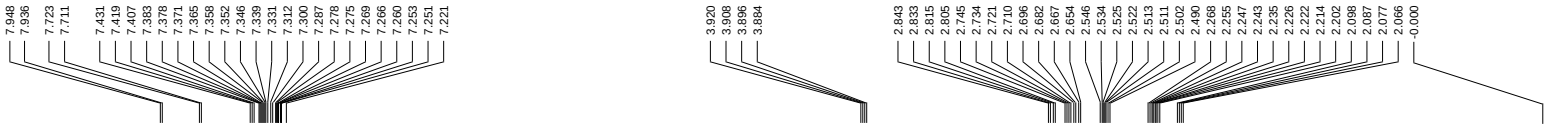
^{13}C NMR(151 MHz, $CDCl_3$)

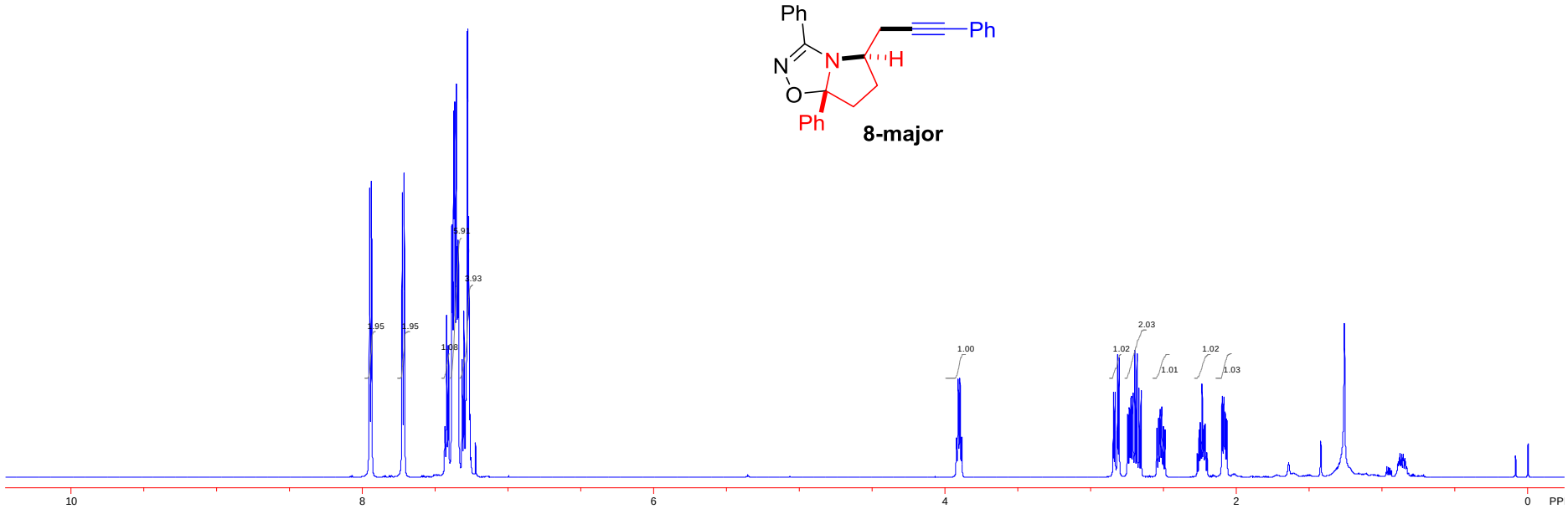


NOESY-1D ^{1}H NMR (400 MHz, $CDCl_3$)

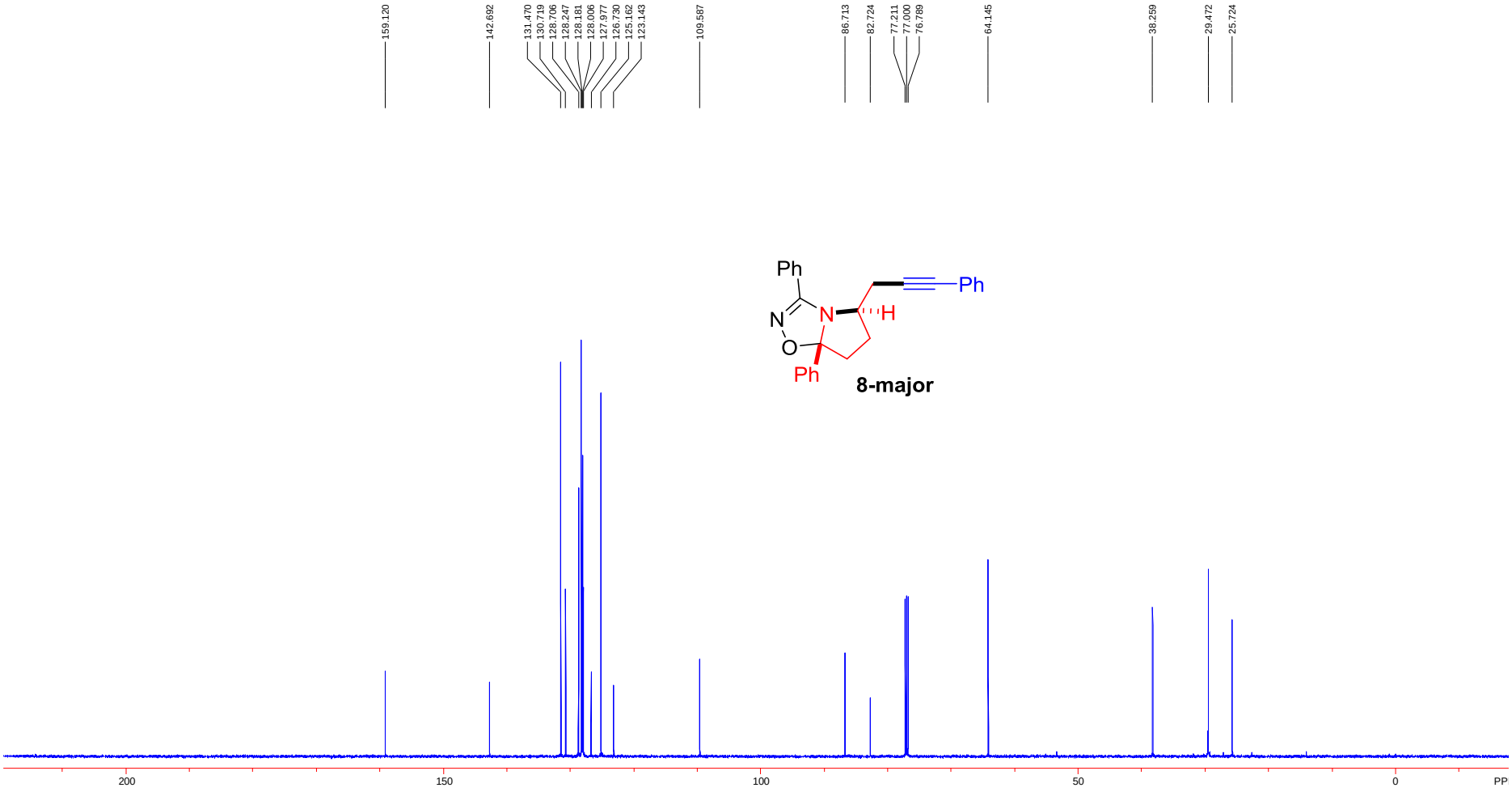


^{1}H NMR(600 MHz, $CDCl_3$)

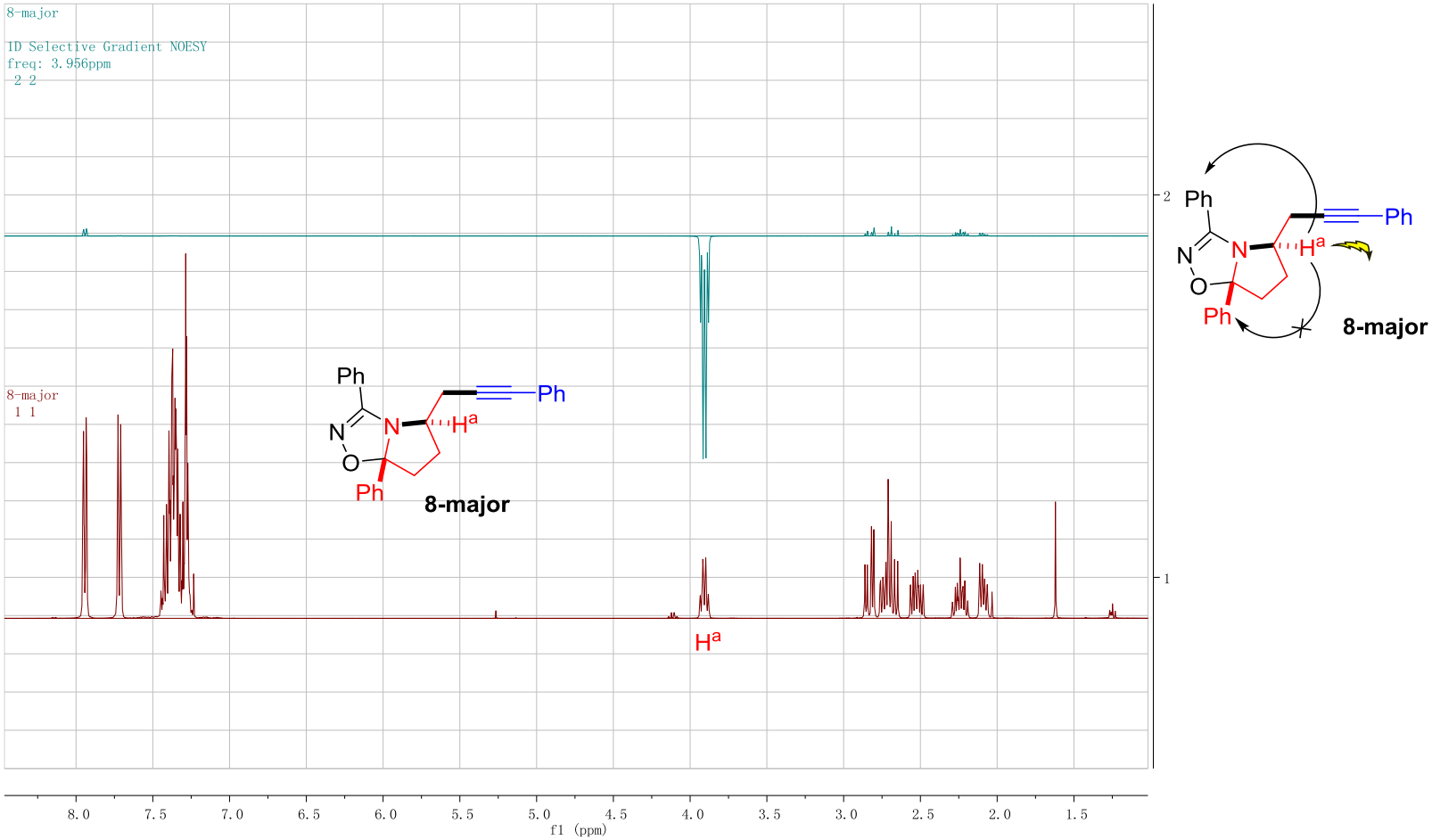




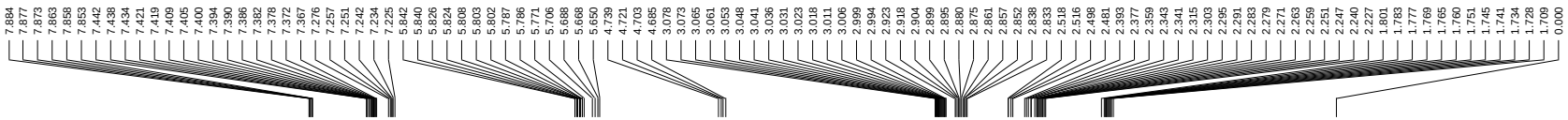
^{13}C NMR(151 MHz, $CDCl_3$)



NOESY-1D ^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR(400 MHz, $CDCl_3$)



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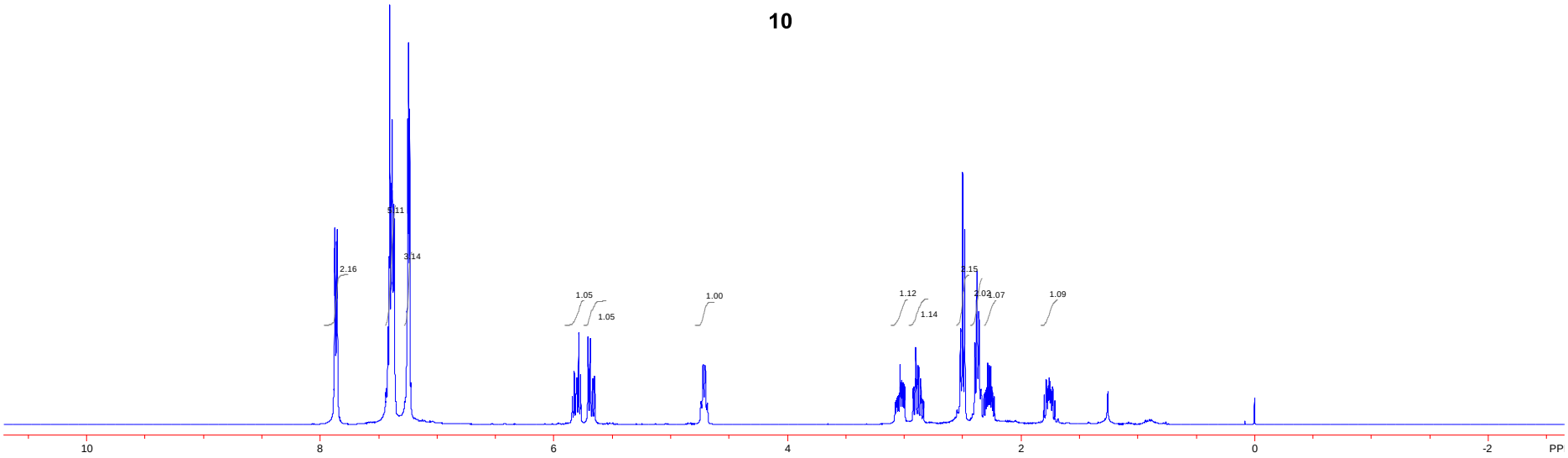

^{13}C NMR(100 MHz, $CDCl_3$)