Supporting Information

for

$PhI(OAc)_2$-mediated functionalisation of unactivated alkenes for synthesis of pyrazoline and isoxazoline derivatives

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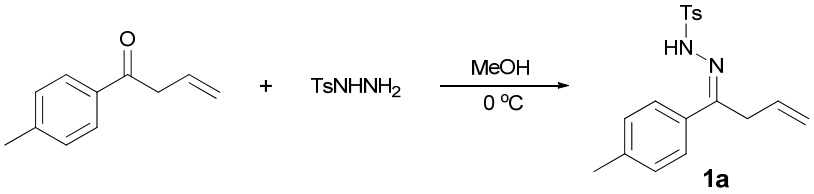
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm, DMSO-d^6: 39.5 ppm). Mass spectra were measured on MS spectrometer (EI) or LC/MS/MS (ESI-MS). HRMS were recorded using MALDI (TOF analyzer), ESI (TOF analyzer).

2. Preparation and Spectral Data of Substrates

2.1 General procedure for preparation of β,γ-unsaturated hydrazones 1.[1, 2]

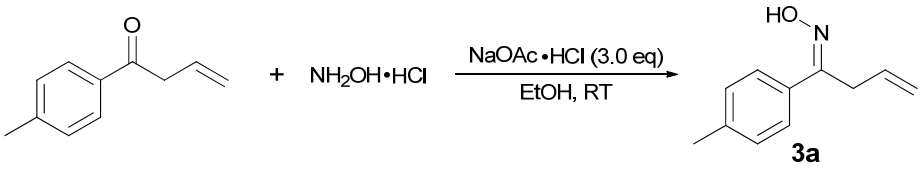


1a

To a stirred solution of 1-(p-tolyl)but-3-en-1-one (20 mmol, 1.0 eq.) in MeOH (10 mL), p-toluenesulfonyl hydrazide (30 mmol, 1.5 eq.) was added at 0 °C. The mixture was stirred at the same temperature until the reaction was completed, monitored by TLC. Then, the solvent was removed and the residue was purified by flash column chromatography to give compound **1a** as a white solid in 49% yield.

The other β,γ-unsaturated hydrazones were prepared according to the above procedure. The β,γ-unsaturated hydrazones **1a-1n** are kown compounds.[3]

2.2 General procedure for preparation of β,γ-unsaturated oximes 3.[4, 5]



To a stirred solution of 1-(p-tolyl)but-3-en-1-one (10 mmol, 1.0 eq.) in EtOH (10 mL), Hydroxylammonium chloride (50 mmol, 5.0 eq.) and sodium acetate trihydrate (70 mmol, 7.0 eq) were added at 0 ^{o}C. Then, the mixture was stirred at room temperature until the reaction was completed, monitored by TLC. Then, the solvent was removed and the residue was purified by flash column chromatography to give compound **3a** as a white solid in 67% yield.

The other β,γ-unsaturated oximes were prepared according to the above procedure. The β,γ-unsaturated oximes **3a, 3d, 3e and 3g** are kown compounds

References: [1] X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, Y.-Q. Zou and W.-J. Xiao, *Eur. J. Org. Chem.* 2014, 3082-3086.

[2] X.-Q. Hu, J.-R. Chen, S. Gao, B. Feng, L.-Q. Lu and W.-J. Xiao, *Chem. Commun*. 2013, **49**, 7905-7907.

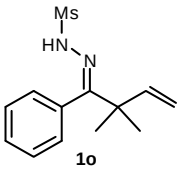
[3] X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin and W.-J. Xiao, *Angew. Chem. Int. Ed*., 2014, **53**, 12163-12167.

[4] B. Han, X.-L. Yang, R. Fang, W. Yu, C. Wang, X.-Y. Duan and S. Liu, *Angew. Chem. Int. Ed*., 2012, **51**, 8816-8820.

[5] C. B. Tripathi and S. Mukherjee, *Angew. Chem. Int. Ed*., 2013, **52**, 8450-8453.

2.3 Spectral data of β,γ-unsaturated hydrazones and oximes

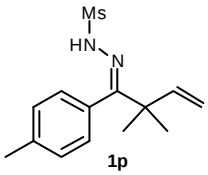
β,γ-Unsaturated hydrazone 1o



1o

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ = 7.50 – 7.44 (3 H, m), 7.07 – 7.05 (2 H, m), 6.88 (1 H, s), 5.94 (1 H, dd, *J* = 17.4 Hz, 10.6 Hz), 5.09 (1 H, d, *J* = 10.6 Hz), 5.02 (1 H, d, *J* = 17.4 Hz), 3.11 (3 H, s), 1.30 (6 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.52, 143.80, 131.43, 129.36, 129.14, 127.72, 113.27, 44.37, 38.42, 25.16. M.P.: 101 – 102 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{18}N_2O_2S$: 267.1162; found: 267.1162.

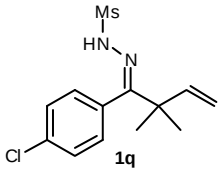
β,γ-Unsaturated hydrazone 1p



1p

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.32 – 7.29 (2 H, m), 6.97 (2 H, d, *J* = 7.9 Hz), 6.95 (1 H, s), 5.97 (1 H, dd, *J* = 17.4 Hz, 10.6 Hz), 5.11 (1 H, d, *J* = 10.6 Hz), 5.05 (1 H, d, *J* = 17.4 Hz), 3.13 (3 H, s), 2.43 (3 H, s), 1.32 (6 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.78, 143.83, 139.33, 129.79, 128.23, 127.56, 113.14, 44.36, 38.37, 25.08, 21.17. M.P.: 83 – 84 °C. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{20}N_2O_2S$: 303.1138; found: 303.1121.

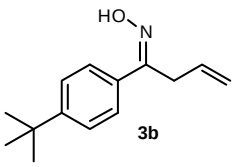
β,γ-Unsaturated hydrazone 1q



1q

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.43 (2 H, d, *J* = 8.3 Hz), 6.99 (2 H, d, *J* = 8.3 Hz), 6.84 (1 H, s), 5.87 (1 H, dd, *J* = 17.4 Hz, 10.6 Hz), 5.08 (1 H, d, *J* = 10.6 Hz), 4.99 (1 H, d, *J* = 17.4 Hz), 3.08 (3 H, s), 1.26 (6 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 161.31, 143.49, 135.54, 129.71, 129.43, 129.30, 113.71, 44.41, 38.38, 25.05. M.P.: 113 – 114 °C. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{17}ClN_2O_2S$: 323.0591; found: 323.0601.

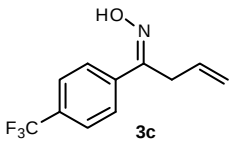
β,γ-Unsaturated oxime 3b



3b

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 9.52 (1 H, s), 7.60 (2 H, d, *J* = 8.4 Hz), 7.42 (2 H, d, *J* = 8.4 Hz), 6.01 – 5.95 (1 H, m), 5.21 (1 H, dd, *J* = 17.2 Hz, 1.5 Hz), 5.13 (1 H, dd, *J* = 10.1 Hz, 1.3 Hz), 3.62 (2 H, d, *J* = 6.1 Hz), 1.35 (9 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.45, 152.43, 132.69, 132.20, 126.03, 125.46, 117.00, 34.64, 31.18, 31.10. M.P.: 88 – 89 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{19}NO$: 218.1539; found: 218.1545.

β,γ- Unsaturated oxime 3c

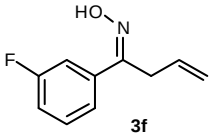


3c

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 9.01 (1 H, s), 7.73 (2 H, d, *J* = 8.2 Hz), 7.62 (2 H, d, *J* = 8.2 Hz), 5.94 – 5.87 (1 H, m), 5.15 (1 H, d, *J* = 17.2 Hz), 5.12 (1 H, d, *J* = 10.2 Hz), 3.59 (2 H, d, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 156.10, 138.89, 131.69, 131.42, 131.37, 131.04, 130.72, 127.99, 126.71, 125.53, 125.29,

122.58, 119.88, 117.59, 31.08. M.P.: 54 – 55 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{10}F_3NO$: 230.0787; found: 230.0791.

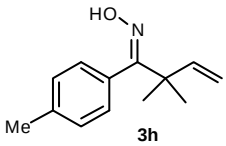
β,γ-Unsaturated oxime 3f



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ = 9.06 (1 H, s), 7.60 – 7.58 (2 H, m), 7.04 (2 H, t, *J* = 8.7 Hz), 5.93 – 5.86 (1 H, m), 5.14 (1 H, dd, *J* = 17.2 Hz, 1.5 Hz), 5.09 (1 H, dd, *J* = 10.1 Hz, 1.4 Hz), 3.55 (2 H, d, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.67, 162.19, 156.04, 131.83, 131.67, 131.63, 128.28, 128.20, 117.28, 115.64, 115.43, 31.14. M.P.: 45 – 46 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{10}H_{10}FNO$: 180.0819; found: 180.0819.

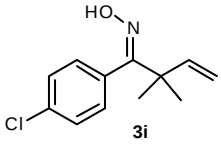
β,γ-Unsaturated oxime 3h



3h

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.50 (1 H, s), 7.21 (2 H, d, *J* = 7.7 Hz), 7.01 (2 H, d, *J* = 7.7 Hz), 5.97 (1 H, dd, J = 17.3 Hz, 10.5 Hz), 5.06 (1 H, d, *J* = 10.6 Hz), 5.02 (1 H, d, *J* = 17.4 Hz), 2.37 (3 H, s), 1.23 (6 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.40, 143.96, 137.70, 130.19, 128.55, 127.73, 112.94, 43.24, 25.26, 21.26. M.P.: 165 – 166 °C. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{17}NO$: 226.1206; found: 226.1202.

β,γ-Unsaturated oxime 3i

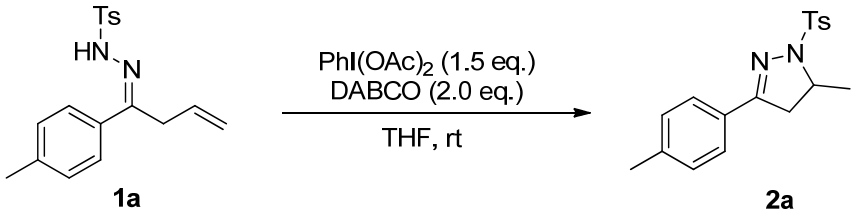


3i

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.54 (1 H, s), 7.43 (2 H, d, *J* = 8.5 Hz), 7.11 (2 H, d, *J* = 8.4 Hz), 5.99 (1 H, dd, *J* = 17.5 Hz, 10.6 Hz), 5.14 (1 H, d, *J* = 10.6 Hz), 5.08 (1 H, d, *J* = 17.4 Hz), 1.28 (6 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.38, 138.46, 129.03, 126.42, 124.24, 123.09, 108.41, 38.12, 20.11. M.P.: 151 – 152 °C. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{14}ClNO$: 246.0656; found: 246.0653.

3. General Procedure and Spectral Data of Products

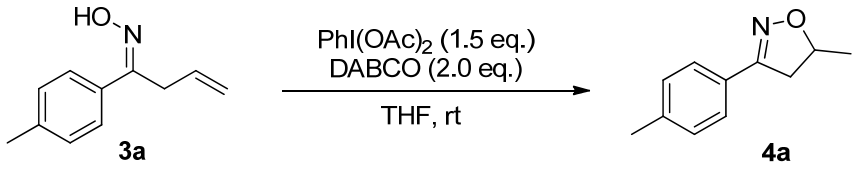
3.1 General procedure hydroamination of β,γ-unsaturated hydrazones



1a 2a

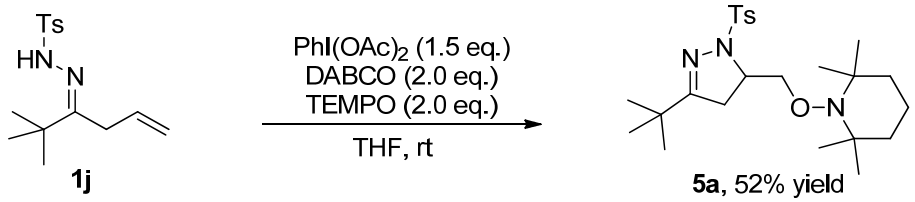
1a (0.3 mmol, 98.5 mg) and DABCO (0.6 mmol, 67.3 mg) were dissolved in freshly distilled THF (4.5 mL) under Ar. Then, $PhI(OAc)_2$ (0.45 mmol, 144.9 mg) was added to the mixture. After that, the solution was stirred at room temperature about 2 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1~5:1) directly to give the desired product **2a** in 61% yield as a white solid.

3.2 General procedure hydroxygenation of β,γ-unsaturated oximes



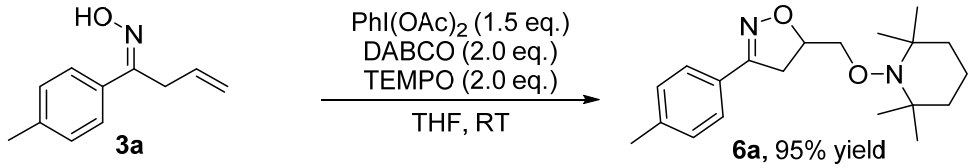
3a (0.3 mmol, 52.5 mg) and DABCO (0.6 mmol, 67.3 mg) were dissolved in freshly distilled THF (4.5 mL) under Ar. Then, $PhI(OAc)_2$ (0.45 mmol, 144.9 mg) was added to the mixture. After that, the solution was stirred at room temperature about 2 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1~10:1) directly to give the desired product **4a** in 67% yield as a white solid.

3.3 General procedure for oxyamination of β,γ-unsaturated hydrazones



1j (0.3 mmol, 88.2 mg), DABCO (0.6 mmol, 67.3 mg), TEMPO (2.0 eq.) were dissolved in freshly distilled THF (4.5 mL) under Ar. Then, $PhI(OAc)_2$ (0.45 mmol, 144.9 mg) was added to the mixture. After that, the solution was stirred at room temperature about 2 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1~10:1) directly to give the TEMPO adduct **5a** in 52% yield as a yellow oil.

3.4 General procedure for dioxygenation of β,γ-unsaturated oximes



3a (0.3 mmol, 52.5 mg), DABCO (0.6 mmol, 67.3 mg), TEMPO (2.0 eq.) were dissolved in freshly distilled THF (4.5 mL) under Ar. Then, $PhI(OAc)_2$ (0.45 mmol, 144.9 mg) was added to the mixture. After that, the solution was stirred at room temperature about 2 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1~10:1) directly to give the TEMPO adduct **6a** in 95% yield as a yellow oil.

3.5 Control experiments for dioxygenation of β,γ-unsaturated oximes

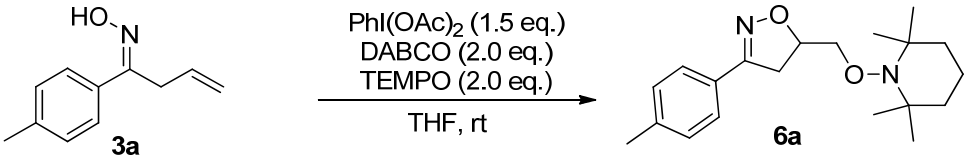


Table S1. Control experiments

Entry	Solvent	Oxidant	Base	Temperature	Yield[a] [%]
1	THF	$PhI(OAc)_2$	DABCO	25 °C	95
2[b]	THF	-	DABCO	25 °C	trace
3[c]	THF	$PhI(OAc)_2$	-	25 °C	27
4[d]	THF	$PhI(OAc)_2$	DABCO	60 °C	10

[a] Isolated yield. [b] Without $PhI(OAc)_2$. [c] Without Base. [d] Conducted the reaction at 60 °C for 24 h

The results of Table S1 revealed that the dioxygenation of β,γ-unsaturated oximes is a radical process mediated by $PhI(OAc)_2$. In this type of reaction, oxime radicals were directly generated from the oxidation of β,γ-unsaturated oximes by $PhI(OAc)_2$ under basic condition at room temperature.

3.6 Try catalytic protocol

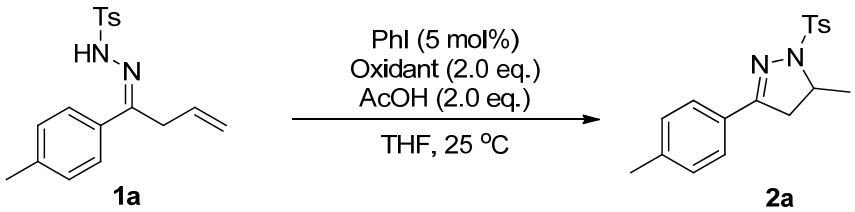


Table S2. Catalytic protocol[a]

Entry	Solvent	Oxidant	Time (h)	Temperature	Yield[a] [%][b]
1	THF	oxone	4	25 °C	0

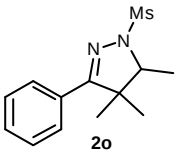
2	THF	IBX	4	25 °C	0
3	THF	*m*CPBA	4	25 °C	15

[a] Unless otherwise noted, reactions were carried out with **1a** (0.1 mmol), PhI (0.005 mmol), AcOH (0.2 mmol), Oxidant (0.2 mmol) in the THF (1.0 mL) at 25 °C. [b] Determined by GC using biphenyl as internal standard.

We preliminarily examined catalytic protocol by using different oxidants such as oxone, IBX and mCPBA. However, we couldn't observe the hydroamination product 2a when using oxone and IBX as oxidants (Table S2, entries 1-2). Fortunately, by using *m*CPBA as the oxidant, the desired product can be obtained in 15% GC yield. Further studies to improve the reaction efficiency are ongoing in our laboratory.

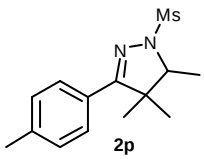
3.7 Spectral data of the new cyclic products

Product 2o



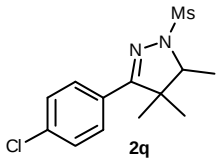
Yield of **2o** : 79% as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ = 7.72 (2 H, d, *J* = 7.2 Hz), 7.41 (3 H, t, *J* = 6.9 Hz), 3.71 – 3.66 (1 H, m), 3.10 (3 H, s), 1.48 (3 H, d, *J* = 6.5 Hz), 1.39 (3 H, s), 1.24 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.66, 130.60, 129.98, 128.44, 127.52, 67.57, 51.38, 35.95, 24.30, 19.10, 13.27. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{18}N_2O_2S$: 267.1162; found: 267.1162.

Product 2p



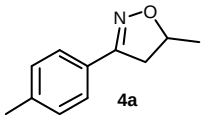
Yield of **2p** : 73% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.63 (2 H, d, *J* = 8.2 Hz), 7.20 (2 H, d, *J* = 8.0 Hz), 3.65 – 3.63 (1 H, m), 3.08 (3 H, s), 2.38 (3 H, s), 1.48 (3 H, d, *J* = 6.5 Hz), 1.38 (3 H, s), 1.23 (3 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) δ = 164.61, 140.22, 129.11, 127.65, 127.40, 67.49, 51.29, 35.70, 24.30, 21.28, 19.12, 13.24. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{14}H_{20}N_2O_2S$: 303.1138; found: 303.1038.

Product 2q



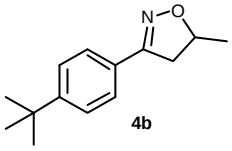
Yield of **2q** : 92% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.65 (2 H, d, *J* = 8.2 Hz), 7.34 (2 H, d, *J* = 8.2 Hz), 3.67 – 3.64 (1 H, m), 3.07 (3 H, s), 1.45 (3 H, d, *J* = 6.4 Hz), 1.35 (3 H, s), 1.19 (3 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) δ = 163.42, 136.01, 128.97, 128.75, 128.67, 67.60, 51.16, 35.97, 24.18, 18.98, 13.15. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{13}H_{17}ClN_2O_2S$: 323.0597; found: 323.0591.

Product 4a



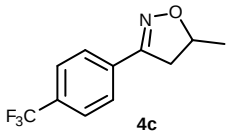
Yield of **4a** : 67% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.58 (2 H, d, *J* = 8.1 Hz), 7.23 (2 H, d, *J* = 8.0 Hz), 4.92 – 4.86 (1 H, m), 3.44 (1 H, dd, *J* = 16.3 Hz, 10.1 Hz), 2.94 (1 H, dd, *J* = 16.3 Hz, 8.0 Hz), 2.40 (3 H, s), 1.45 (3 H, d, *J* = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 156.32, 139.99, 129.27, 127.04, 126.46, 77.32, 41.63, 21.33, 20.91. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{11}H_{13}NO$: 176.1070; found: 176.1078.

Product 4b



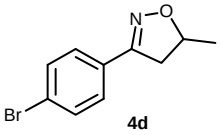
Yield of **4b** : 66% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.62 (2 H, d, *J* = 8.3 Hz), 7.44 (2 H, d, *J* = 8.3 Hz), 4.90 – 4.86 (1 H, m), 3.44 (1 H, dd, *J* = 16.2 Hz, 10.1 Hz), 2.94 (1 H, dd, *J* = 16.2 Hz, 7.9 Hz), 1.43 (3 H, d, *J* = 6.2 Hz), 1.34 (9 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 156.23, 153.17, 126.98, 126.33, 125.53, 77.32, 41.62, 34.75, 31.10, 20.93. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{14}H_{19}ClNO$: 218.1539; found: 218.1549.

Product 4c



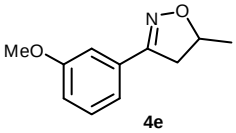
Yield of **4c** : 69% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.78 (2 H, d, *J* = 8.2 Hz), 7.66 (2 H, d, *J* = 8.2 Hz), 4.97 – 4.91 (1 H, m), 3.45 (1 H, dd, *J* = 16.3 Hz, 10.2 Hz), 2.95 (1 H, dd, *J* = 16.3 Hz, 8.1 Hz), 1.46 (3 H, d, *J* = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 155.34, 133.36, 131.98, 131.65, 131.32, 130.99, 126.75, 125.58, 125.17, 122.47, 78.15, 41.14, 20.87. M.P.: 57 – 58 °C. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{11}H_{10}F_3NO$: 230.0787; found: 230.0777.

Product 4d



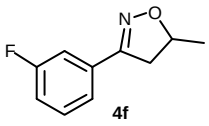
Yield of **4d** : 73% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ = 7.53 (4 H, s), 4.93 – 4.87 (1 H, m), 3.41 (1 H, dd, *J* = 16.3 Hz, 10.2 Hz), 2.90 (1 H, dd, *J* = 16.3 Hz, 8.1 Hz), 1.44 (3 H, d, *J* = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 155.54, 131.78, 128.75, 127.94, 124.02, 77.82, 41.23, 20.91. M.P.: 70 – 71 °C. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{10}H_{10}BrNO$: 240.0019; found: 240.0013.

Product 4e



Yield of **4e** : 63% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.31 (1 H, t, *J* = 8.0 Hz), 7.28 (1 H, s), 7.17 (1 H, d, *J* = 7.6 Hz), 6.95 (1 H, dd, *J* = 8.3 Hz, 2.5 Hz), 4.91 – 4.85 (1 H, m), 3.84 (3 H, s), 3.42 (1 H, dd, *J* = 16.3 Hz, 10.2 Hz), 2.92 (1 H, dd, *J* = 16.3 Hz, 8.0 Hz), 1.43 (3 H, d, *J* = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 159.52, 156.29, 131.01, 129.50, 119.11, 116.08, 111.03, 77.45, 55.19, 41.46, 20.84. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{11}H_{13}NO_2$: 192.1019; found: 192.1027.

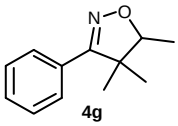
Product 4f



4f

Yield of **4f** : 57% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.66 (2 H, dd, *J* = 8.8 Hz, 5.4 Hz), 7.10 (2 H, t, *J* = 8.7 Hz), 4.91 – 4.87 (1 H, m), 3.42 (1 H, dd, *J* 16.3 Hz, 10.1 Hz), 2.92 (1 H, dd, *J* = 16.3 Hz, 8.0 Hz), 1.45 (3 H, d, *J* = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 164.70, 162.22, 155.34, 128.37, 128.29, 126.04, 115.71, 115.50, 77.49, 41.45, 20.79. M.P.: 41 – 42 °C. HRMS (EI): m/z [M + H] $^{+}$ calcd for $C_{10}H_{10}FNO$: 180.0819; found: 180.0820.

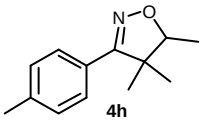
Product 4g



4g

Yield of **4g** : 92% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.63 (2 H, dd, *J* = 7.3 Hz, 2.2 Hz), 7.40 – 7.35 (3 H, m), 4.24 – 4.21 (1 H, m), 1.31 (6 H, s), 1.19 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 165.08, 129.63, 129.48, 128.46, 127.15, 86.68, 50.69, 23.68, 19.20, 12.44. M.P.: 51 – 52 °C. HRMS (EI): m/z [M + Na] $^{+}$ calcd for $C_{12}H_{15}NO$: 212.1046; found: 212.1048.

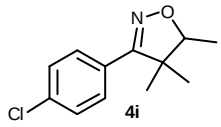
Product 4h



4h

Yield of **4h** : 94% as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.61 (2 H, d, *J* = 6.8 Hz), 7.26 (2 H, d, *J* = 7.3 Hz), 4.29 – 4.28 (1 H, m), 2.43 (3 H, s), 1.38 (6 H, s), 1.26 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 164.99, 139.57, 129.16, 127.02, 126.69, 86.53, 50.64, 23.69, 21.24, 19.19, 12.42. HRMS (EI): m/z [M + Na] $^{+}$ calcd for $C_{13}H_{17}NO$: 226.1202; found: 226.1205.

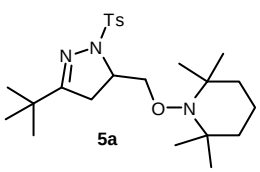
Product 4i



4i

Yield of **4i** : 81% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.62 (2 H, d, *J* = 8.6 Hz), 7.39 (2 H, d, *J* = 8.5 Hz), 4.28 – 4.25 (1 H, m), 1.34 (6 H, s), 1.21 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ = 164.09, 135.54, 128.75, 128.38, 128.12, 86.90, 50.50, 23.64, 19.17, 12.39. M.P.: 63 – 64 °C. HRMS (EI): m/z [M + Na] $^{+}$ calcd for $C_{12}H_{14}ClNO$: 246.0656; found: 246.0658.

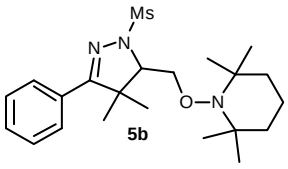
Product 5a



5a

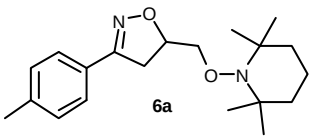
Yield of **5a** : 52% as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.72 (2 H, d, *J* = 8.0 Hz), 7.29 (d, *J* = 7.9 Hz, 2H), 4.14 (1 H, dd, *J* = 9.1 Hz, 3.4 Hz), 4.00 – 3.98 (1 H, m), 3.78 – 3.77 (1 H, m), 2.76 – 2.71 (1 H, m), 2.59 – 2.54 (1 H, m), 2.42 (3H, s), 1.52 – 1.44 (6 H, m), 1.18 – 1.14 (7 H, s), 1.08 – 1.06 (14 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.11, 143.80, 131.67, 129.00, 128.54, 78.02, 59.46, 39.48, 36.01, 34.07, 32.90, 27.79, 21.43, 19.95, 16.91. HRMS (EI): m/z [M+H]$^{+}$ calcd for $C_{24}H_{39}N_3O_3S$: 449.2712; found: 449.2701.

Product 5b



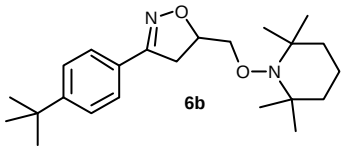
Yield of **5b** : 46% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ = 7.70 – 7.57 (2 H, m), 7.36 – 7.30 (3 H, m), 4.43 (1 H, dd, *J* = 10.0 Hz, 4.4 Hz), 4.13 (1 H, t, *J* = 9.9 Hz), 3.86 (1 H, dd, *J* = 9.7 Hz, 4.4 Hz), 3.02 (3 H, s), 1.51 (4 H, s), 1.40 – 1.37 (8 H, m), 1.15 (6 H, s), 1.02 (6 H, d, *J* = 10.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.63, 130.42, 129.90, 128.38, 127.77, 75.15, 68.54, 59.70, 52.21, 39.66, 39.52, 36.19, 33.34, 32.51, 26.27, 20.22, 19.99, 16.98. M.P.: 148 – 150 °C. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{22}H_{35}N_3O_3S$: 422.2472; found: 422.2475

Product 5c



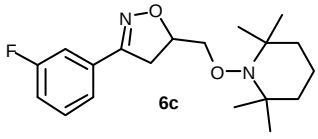
Yield of **6a** : 95% as a white soild. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.47 (2 H, d, *J* = 7.9 Hz), 7.09 (2 H, d, *J* = 7.9 Hz), 4.76 – 4.72 (1 H, m), 3.88 – 3.86 (2 H, m), 3.25 (1 H, dd, *J* = 16.3 Hz, 10.9 Hz), 3.12 (1 H, dd, *J* = 16.4 Hz, 7.4 Hz), 2.27 (3 H, s), 1.43 – 1.42 (1 H, m), 1.37 – 1.33 (4 H, m), 1.21 -1.17 (1 H, m), 1.11 (6 H, s), 0.97 (6 H, d, *J* = 4.3 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.82, 139.80, 129.12, 126.65, 126.34, 78.74, 77.44, 59.85, 59.79, 39.38, 36.93, 32.87, 32.77, 21.23, 19.87, 16.80. M.P.: 54 – 55 °C. HRMS (EI): m/z $[M+Na]^+$ calcd for $C_{20}H_{30}N_2O_2$: 353.2199; found: 353.2221.

Product 5d



Yield of **6b** : 94% as a white soild. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.57 (2 H, d, *J* = 8.3 Hz), 7.37 (2 H, d, *J* = 8.4 Hz), 4.82 – 4.78 (1 H, m), 3.94 – 3.89 (2 H, m), 3.31 (1 H, dd, *J* = 16.4 Hz, 10.9 Hz), 3.19 (1 H, dd, *J* = 16.4 Hz, 7.5 Hz), 1.49 – 1.46 (1 H, m), 1.38 (4 H, s), 1.27 (10 H, s), 1.14 (6 H, s), 1.03 (6 H, s). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.72, 152.95, 126.64, 126.23, 125.37, 78.73, 77.32, 59.85, 59.80, 39.40, 36.95, 34.59, 32.85, 32.82, 30.97, 19.90, 16.81. M.P.: 114 – 115 °C. HRMS (EI): m/z $[M+Na]^+$ calcd for $C_{26}H_{36}N_2O_2$: 395.2669; found: 395.2689.

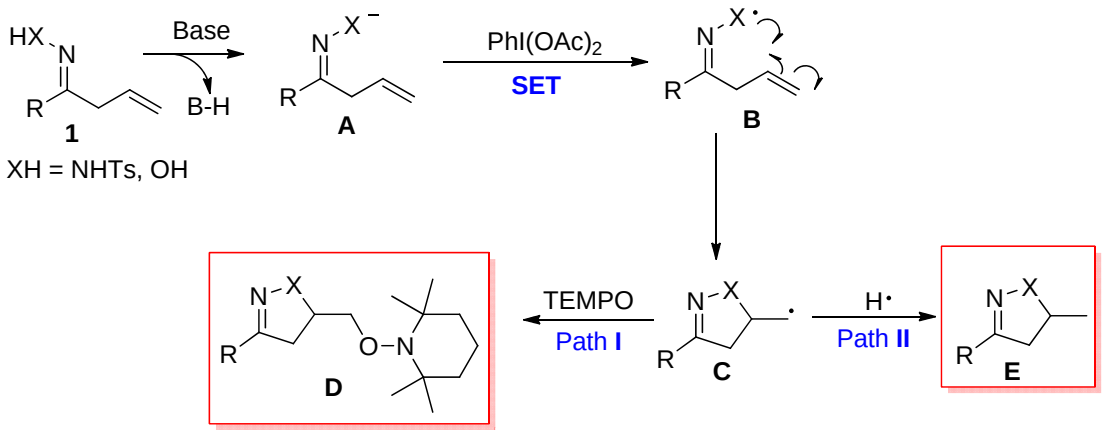
Product 5e



Yield of **6c** : 96% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) δ = 7.60 – 7.58 (2 H, m), 7.00 (2 H, t, *J* = 8.6 Hz), 4.81 – 4.76 (1 H, m), 3.89 (2 H, d, *J* = 4.7 Hz), 3.28 (1 H, dd, *J* = 16.3 Hz, 10.9 Hz), 3.15 (1 H, dd, *J* = 16.3 Hz, 7.4 Hz), 1.45 – 1.41 (1 H, m), 1.38 – 1.34 (4 H, m), 1.22 (1 H, d, *J* = 12.3 Hz), 1.10 (6 H, d, *J* = 6.1 Hz), 0.98 (6 H, d, *J* = 6.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.34, 162.68, 155.08, 128.46,

128.41, 125.89, 125.87, 115.75, 115.61, 79.21, 77.47, 60.02, 59.94, 39.49, 36.95, 32.98, 32.85, 19.98, 16.90. M.P.: 80 – 81 °C. HRMS (EI): m/z $[M+Na]^+$ calcd for $C_{19}H_{27}FN_2O_2$: 357.1949; found: 357.1966

4. Plausible reaction mechanism.[6]

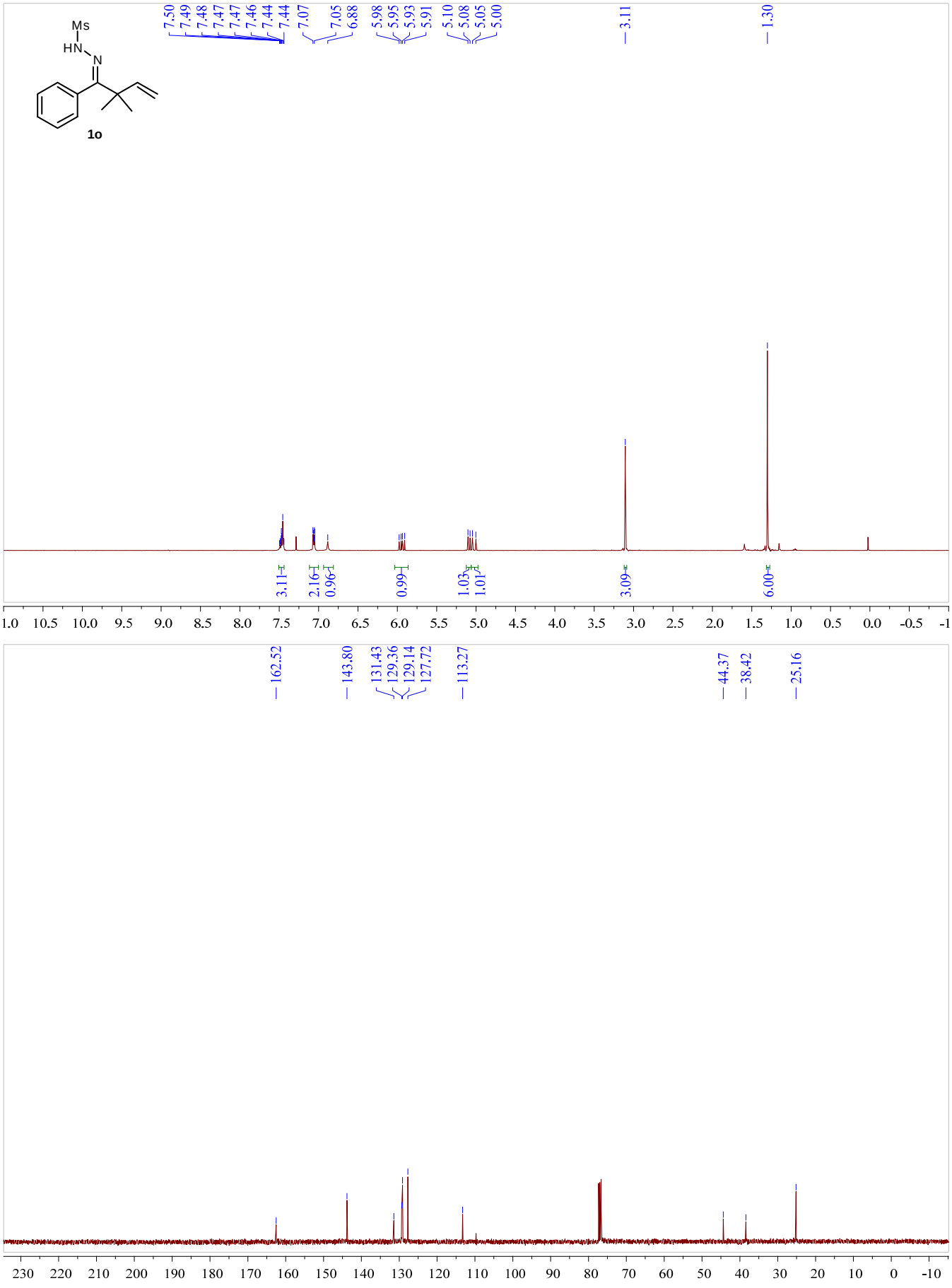


A possible reaction mechanism was proposed, as follows: Firstly, deprotonation of the hydrazone or oxime in the presence of DABCO to afford the anionic intermediate **A**. Then, a single-electron oxidation of **A** by $PhI(OAc)_2$ gives the *N*-centered radical or oxime **B**. Subsequently, a 5-exo-trig cyclization of **B** affords the *C*-centered radical **C**. There are two pathways for the following transformations of intermediate **C**. On the one hand, it can abstract a H atom from the reaction mixture (e.g., THF) to give the hydroamination or hydroxygenation products **E**. On the other hand, the intermediate **C** can be captured by TEMPO to afford the corresponding oxyamination or dioxygenation products **D**.

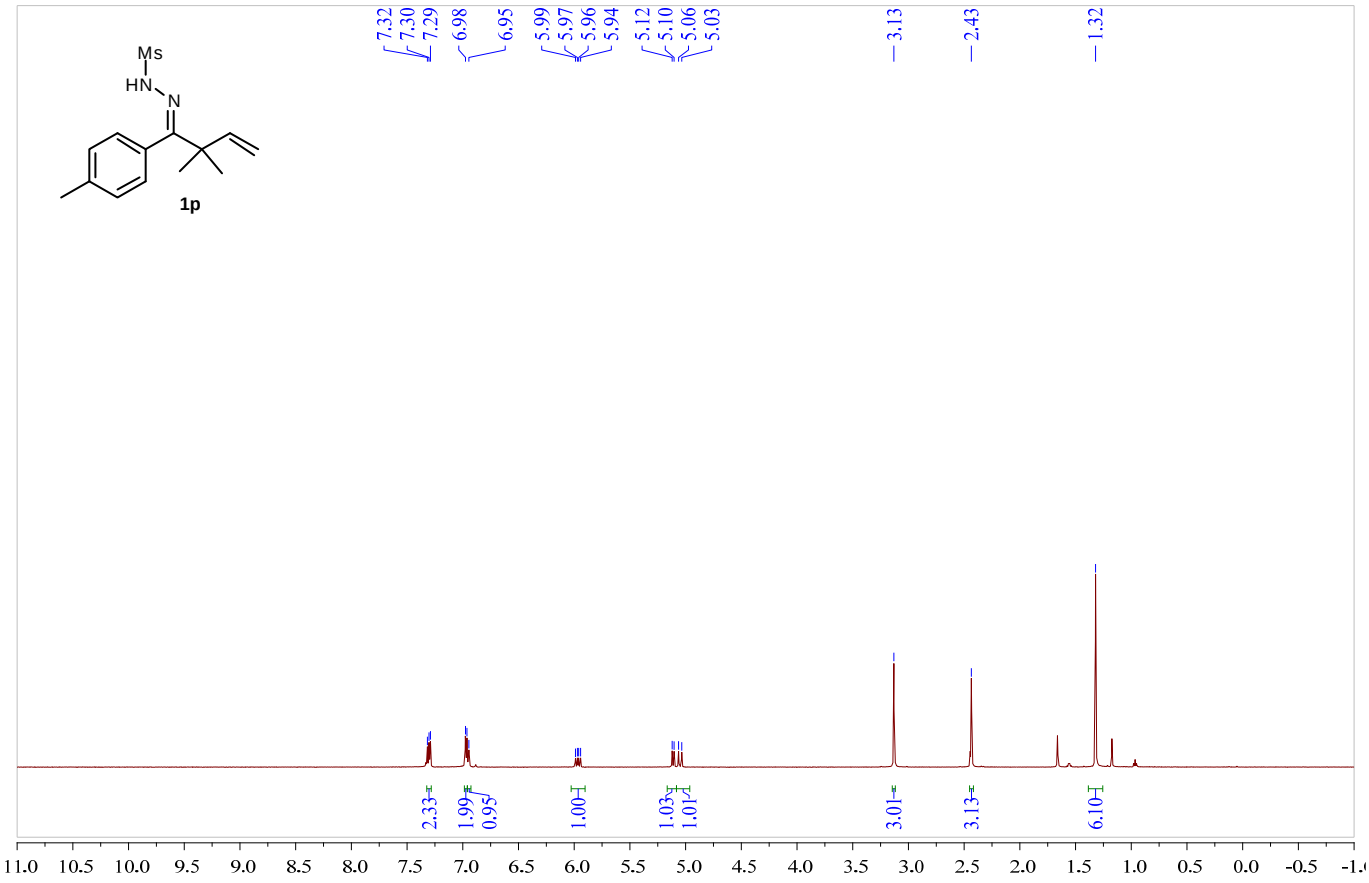
Reference: [6] K. C. Nicolaou, P. S. Baran, R. Kranich, Y.-L. Zhong, K. Sugita and N. Zou, *Angew. Chem. Int. Ed.*, 2001, **40**, 202-206.

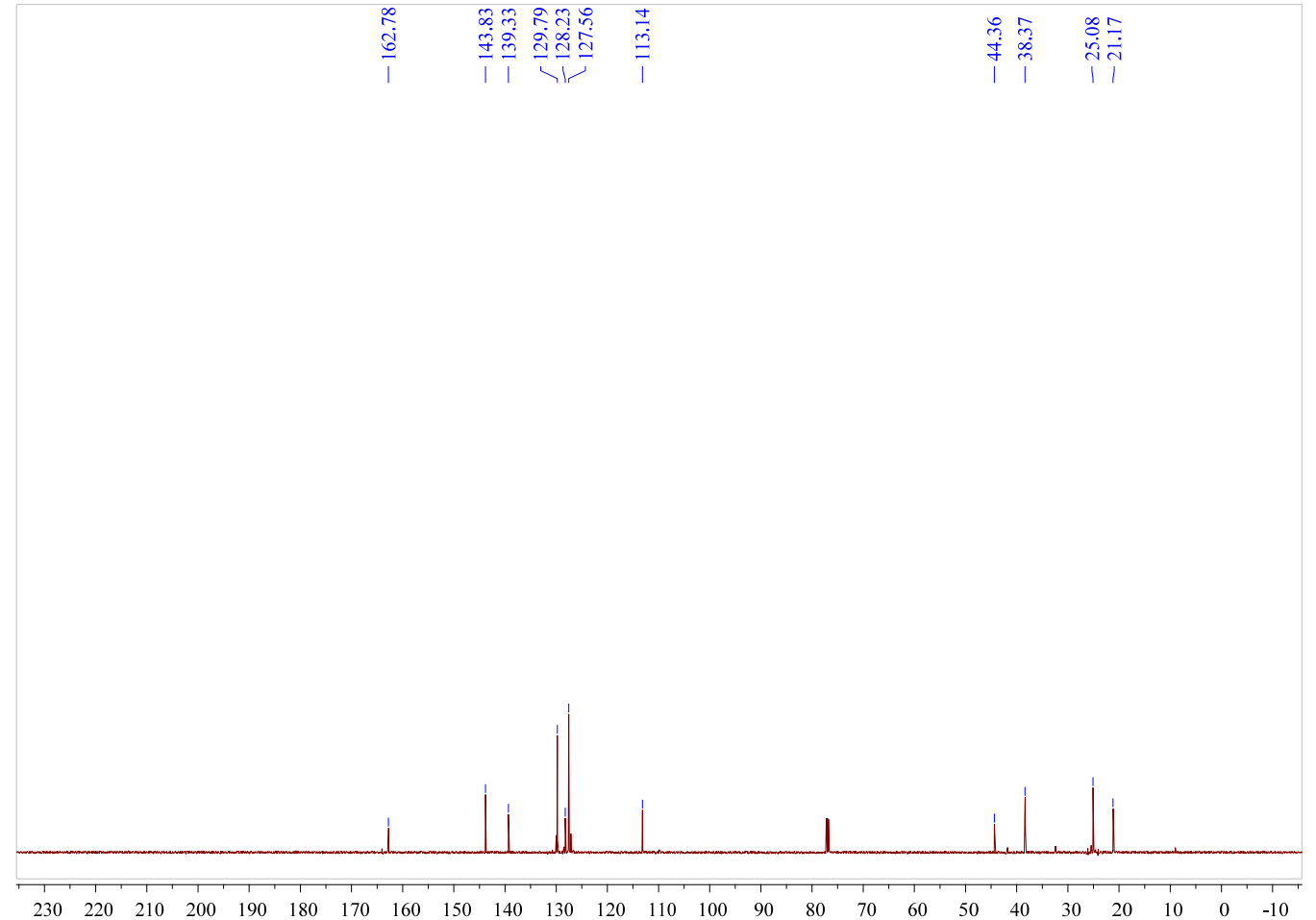
5. NMR and HRMS Spectra of Hydrazones, Oximes and the Cyclic Products

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of hydrazone 1o

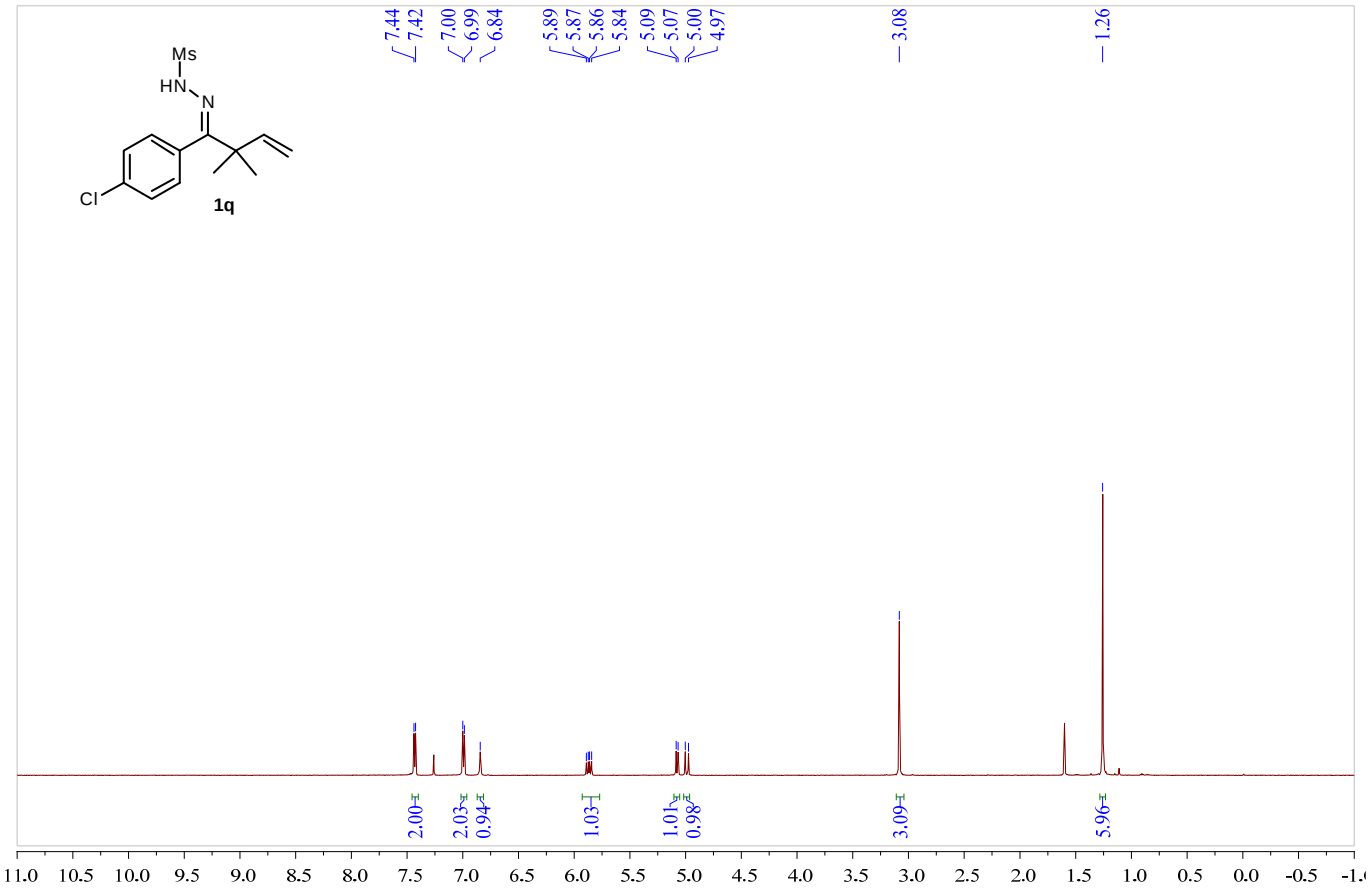


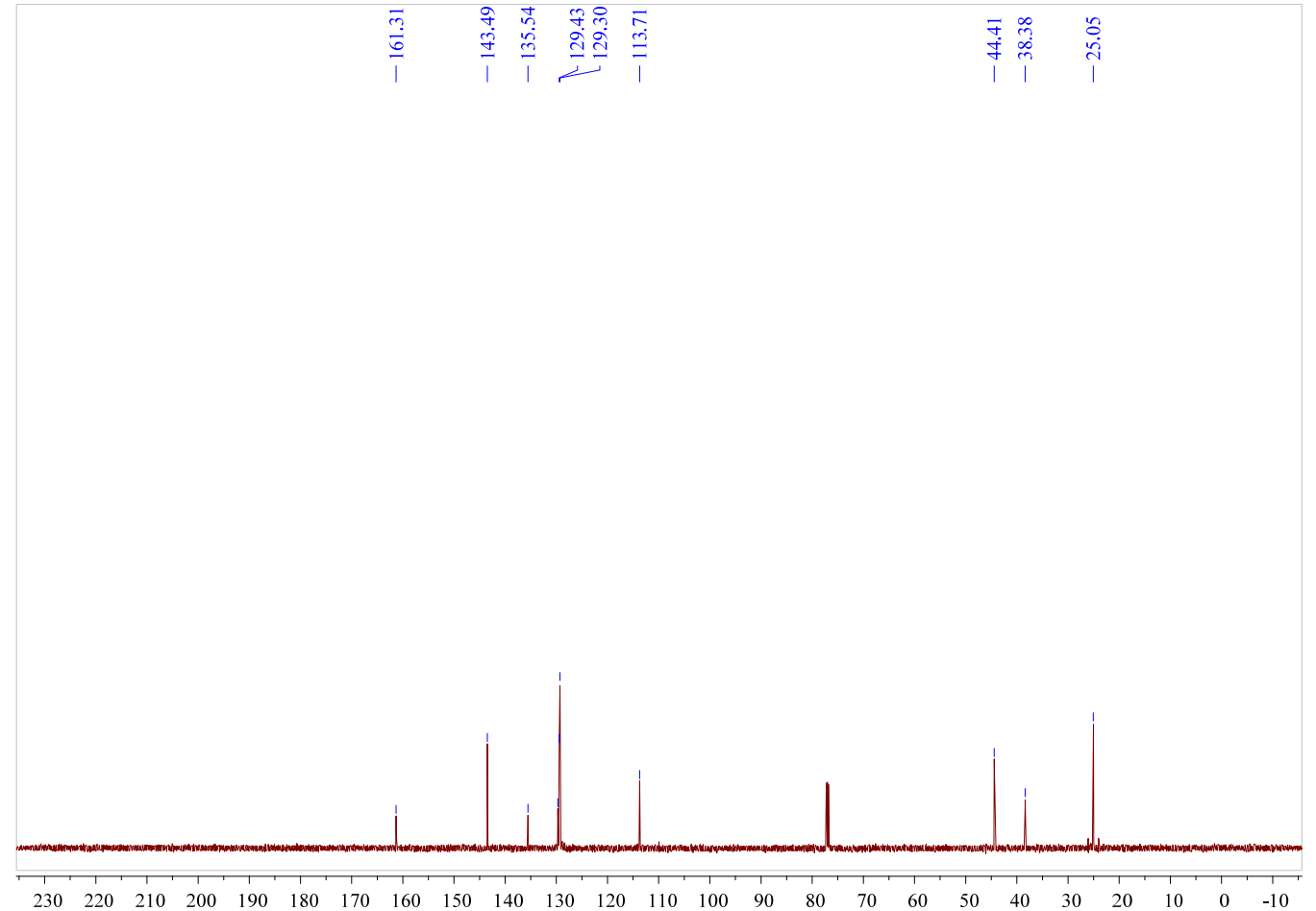
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of hydrazone 1p



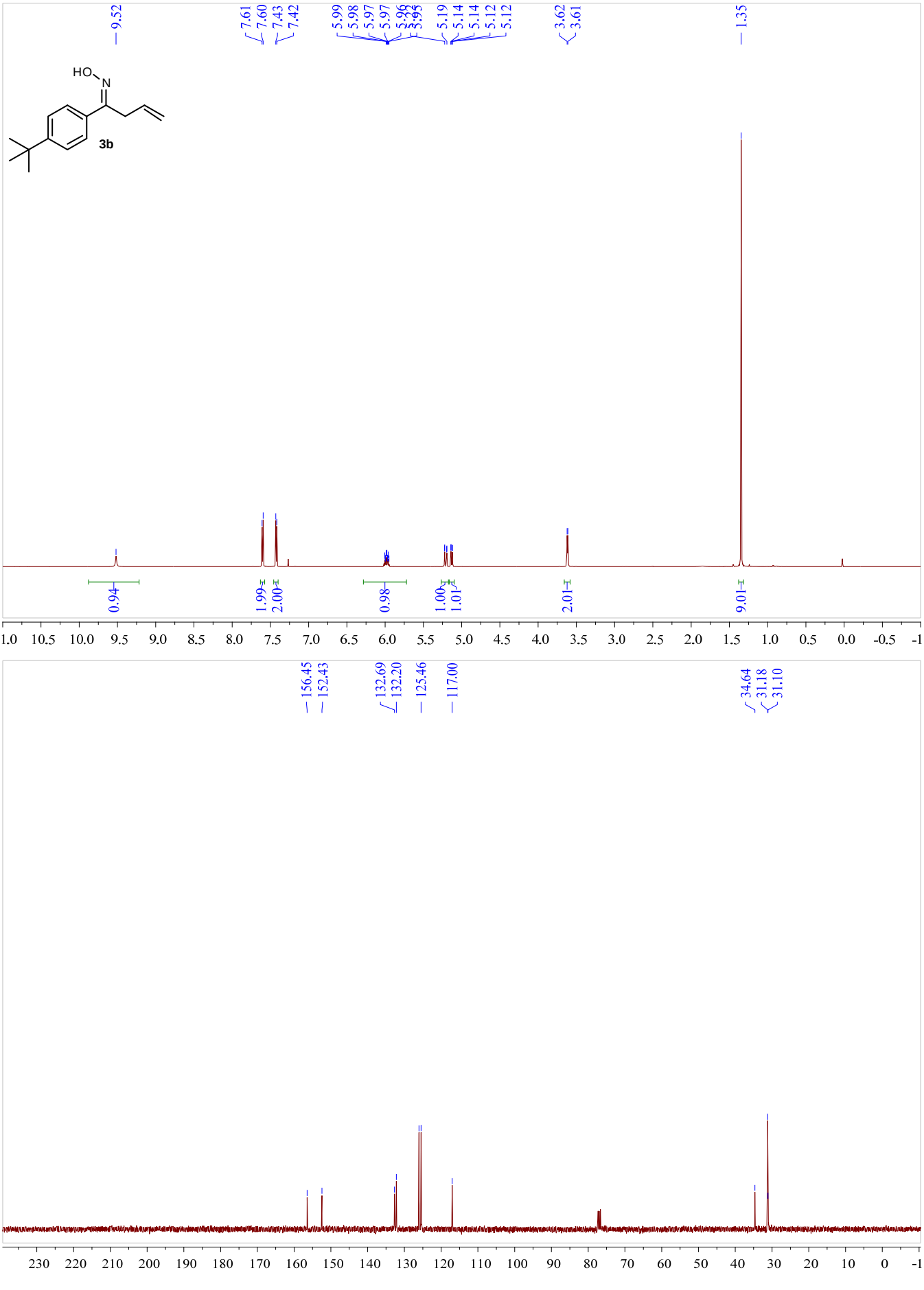


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of hydrazone 1q

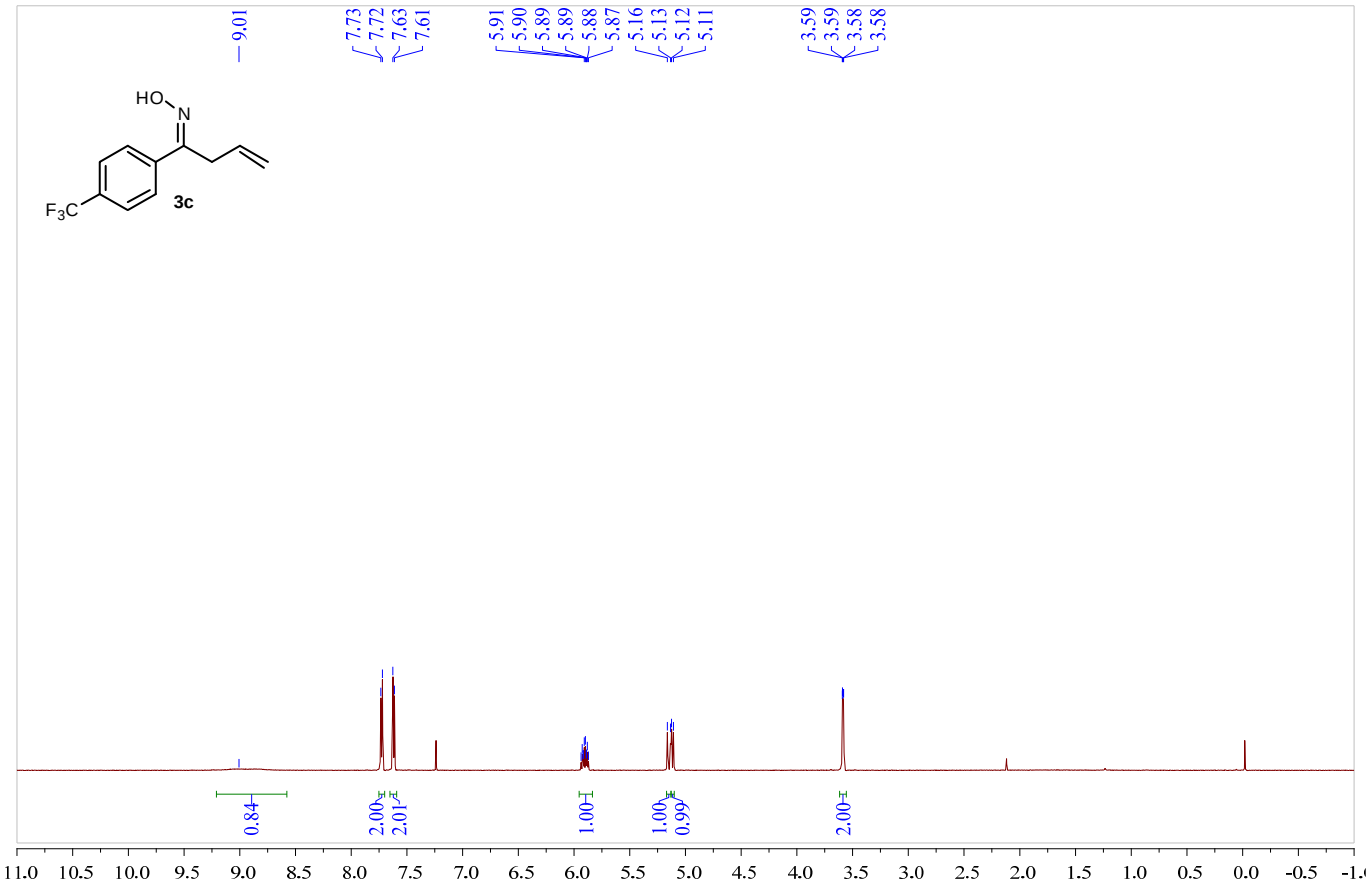


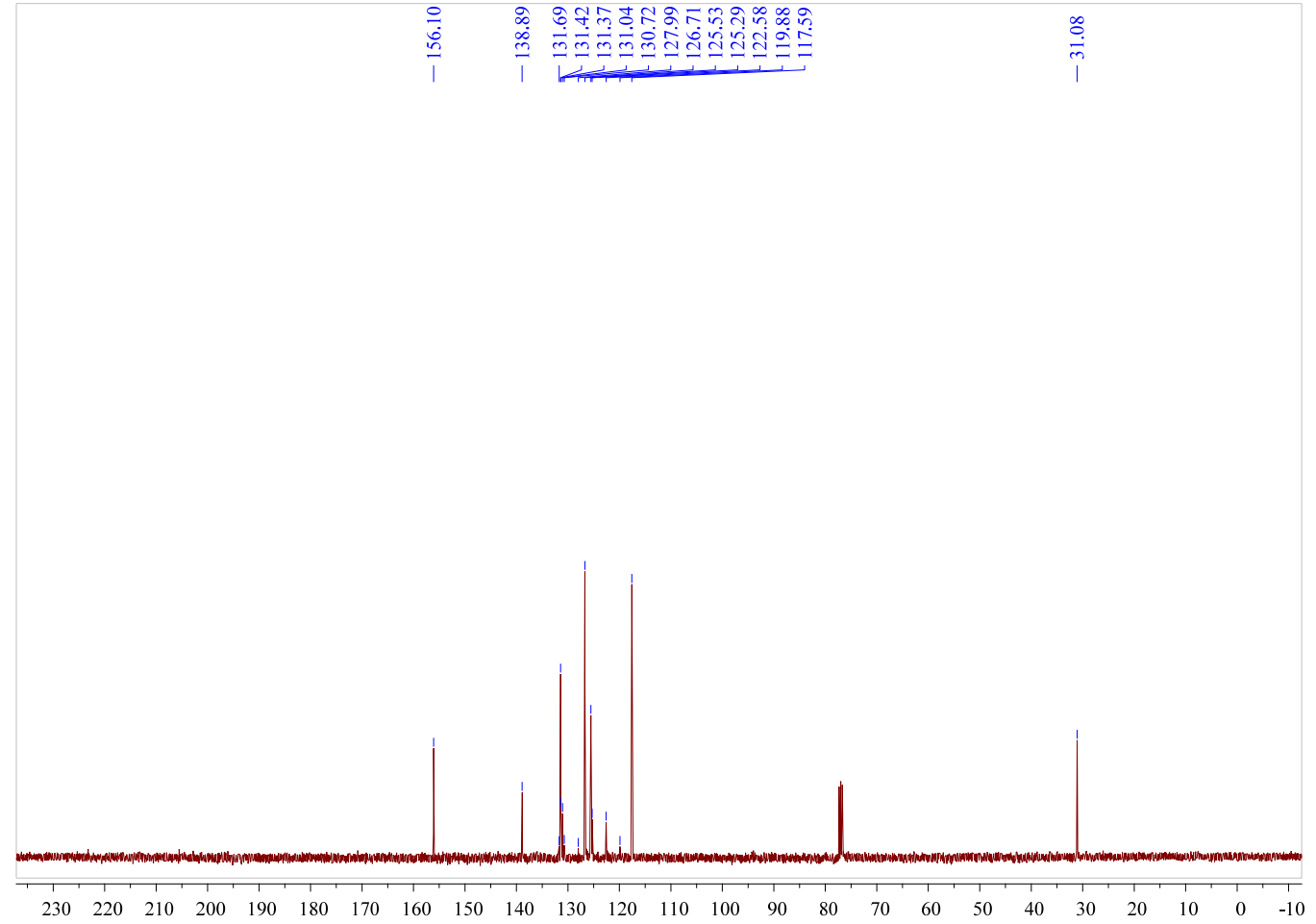


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of oxime 3b

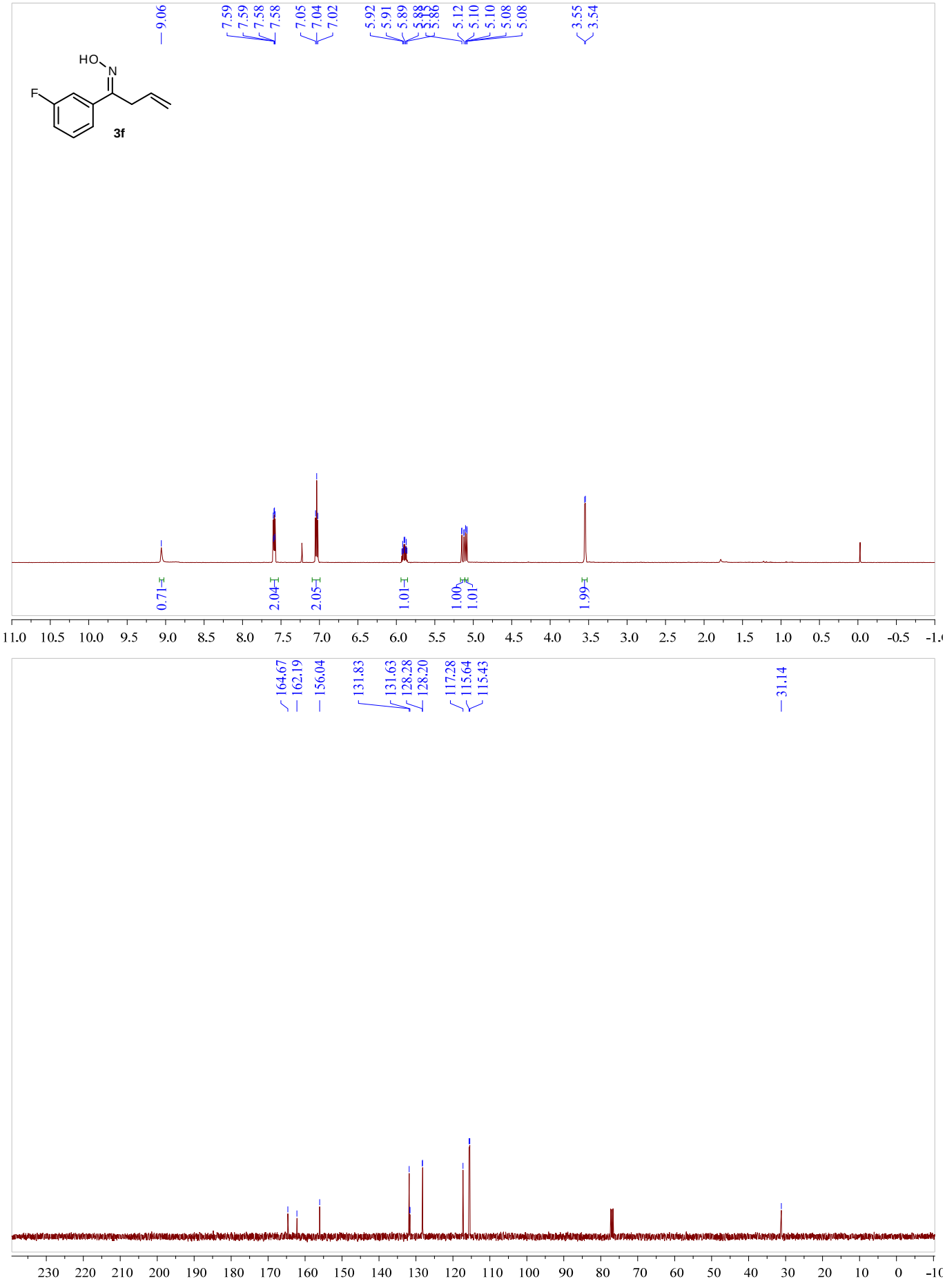


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of oxime 3c

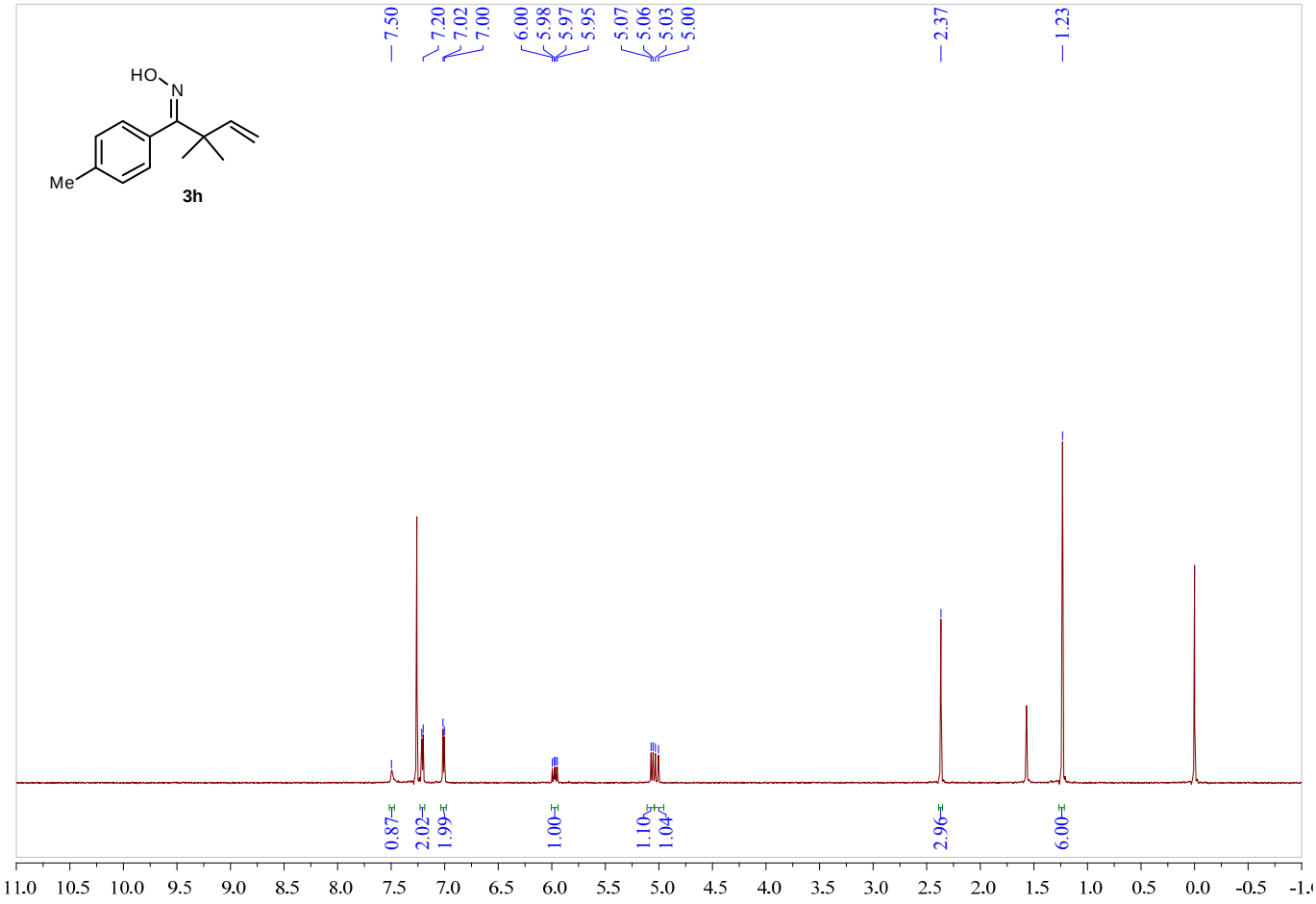


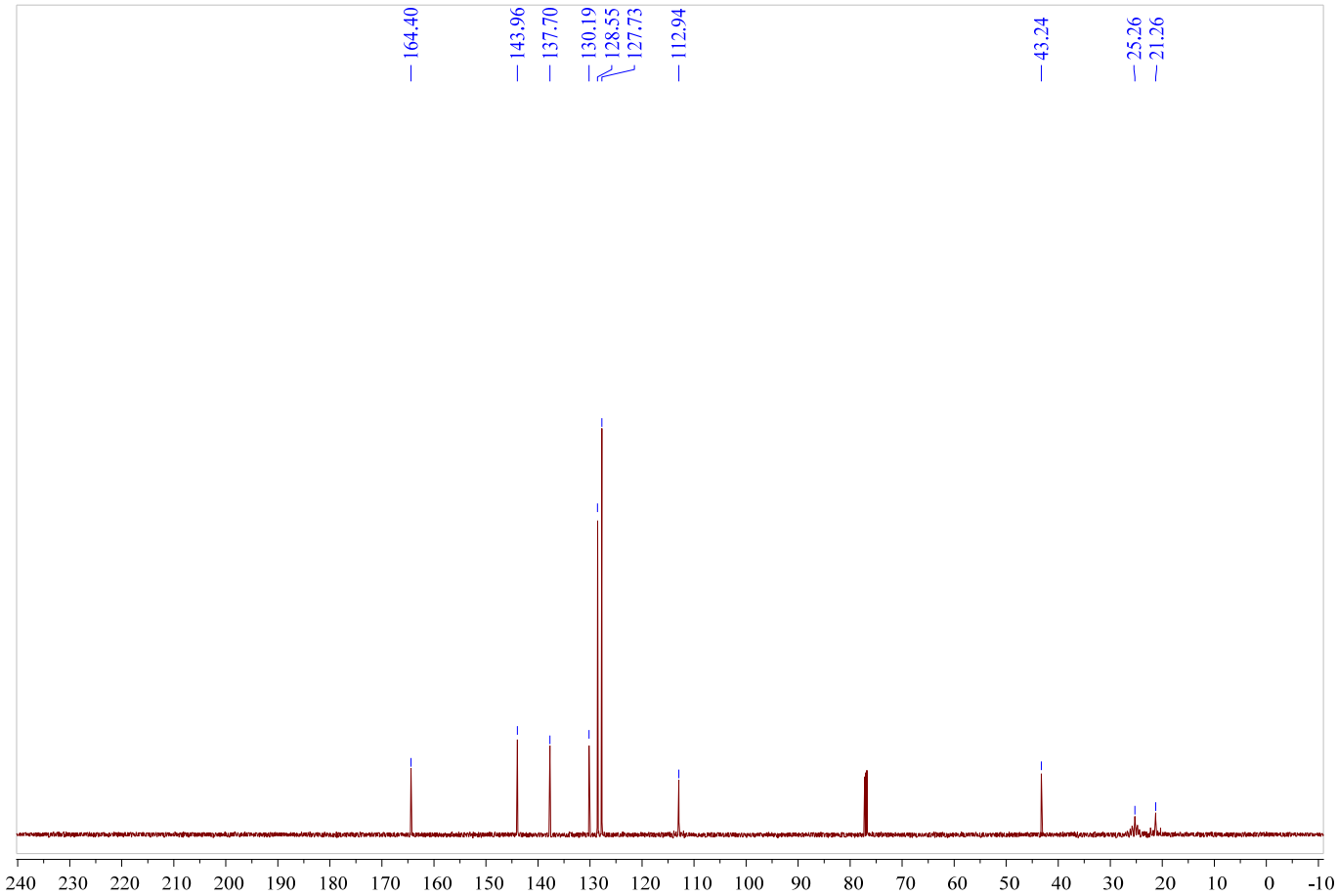


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of oxime 3f

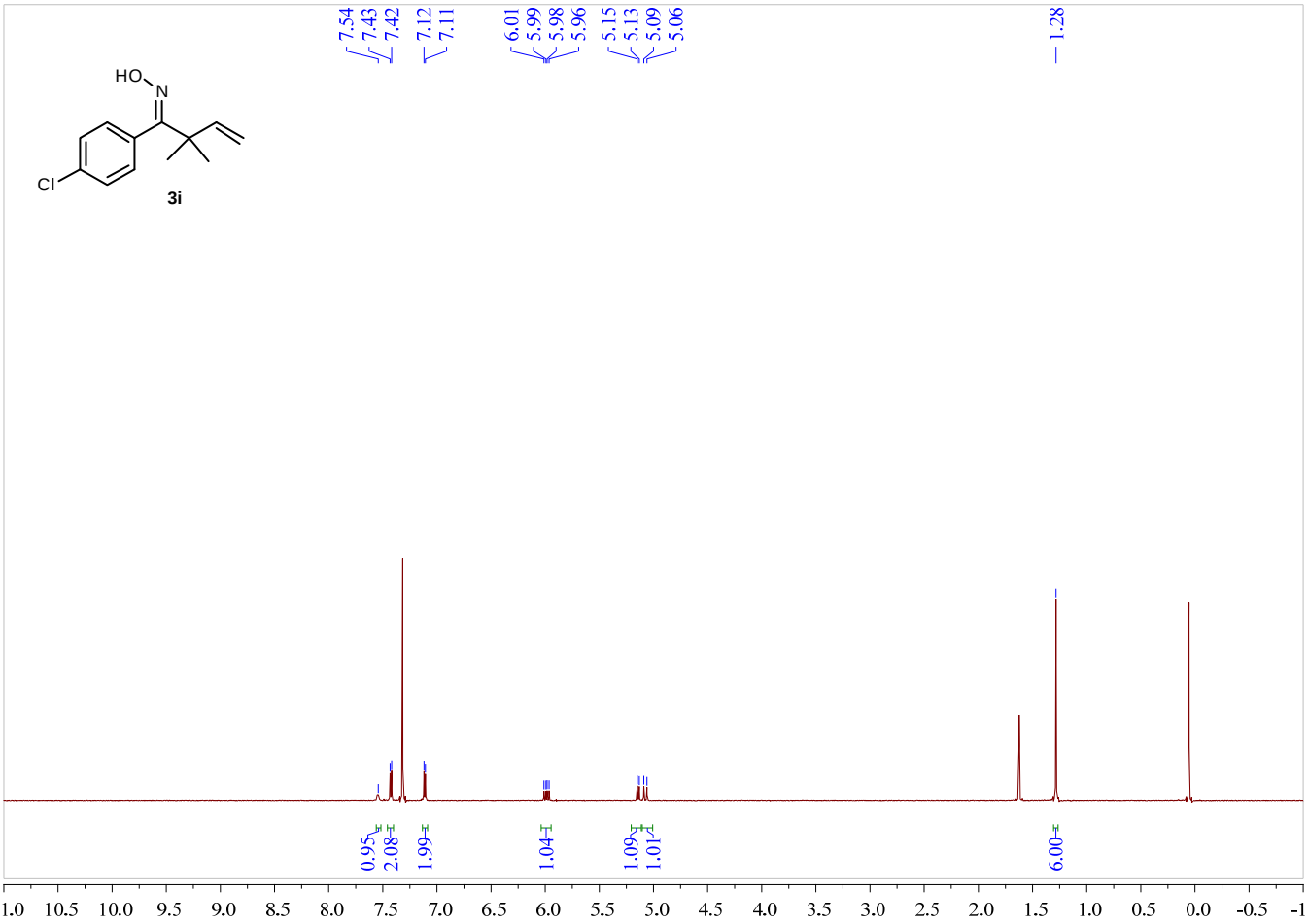


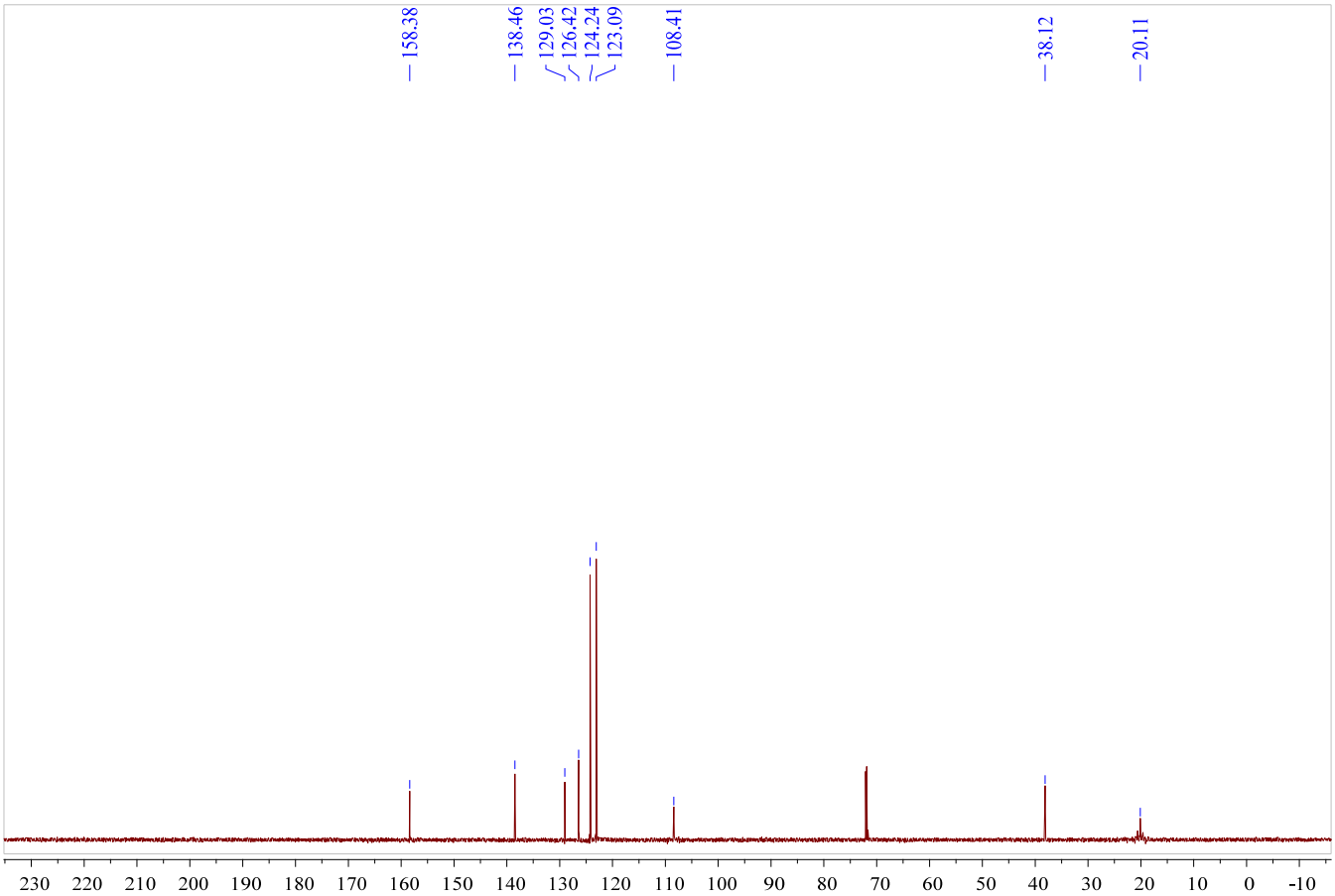
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of oxime 3h



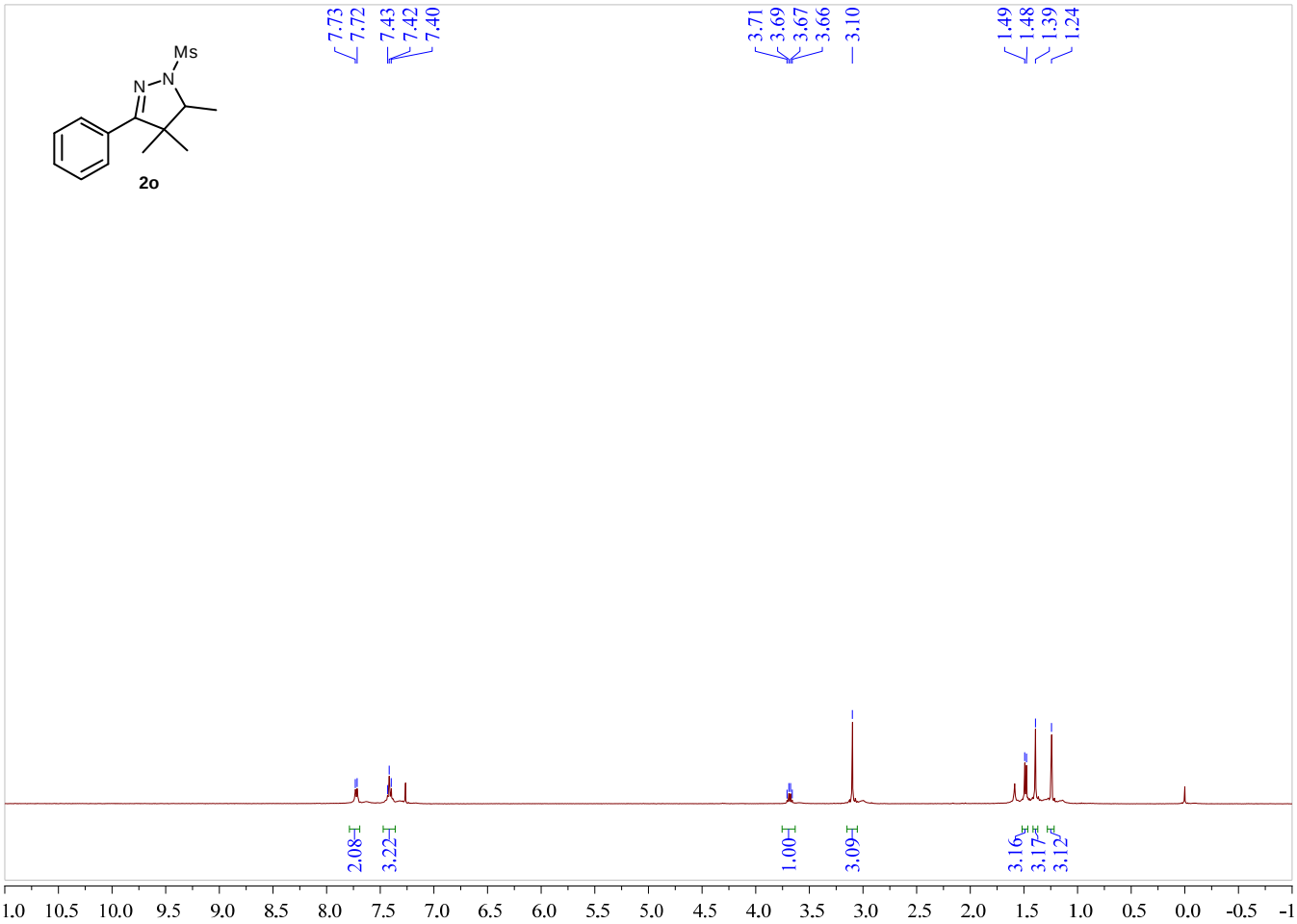


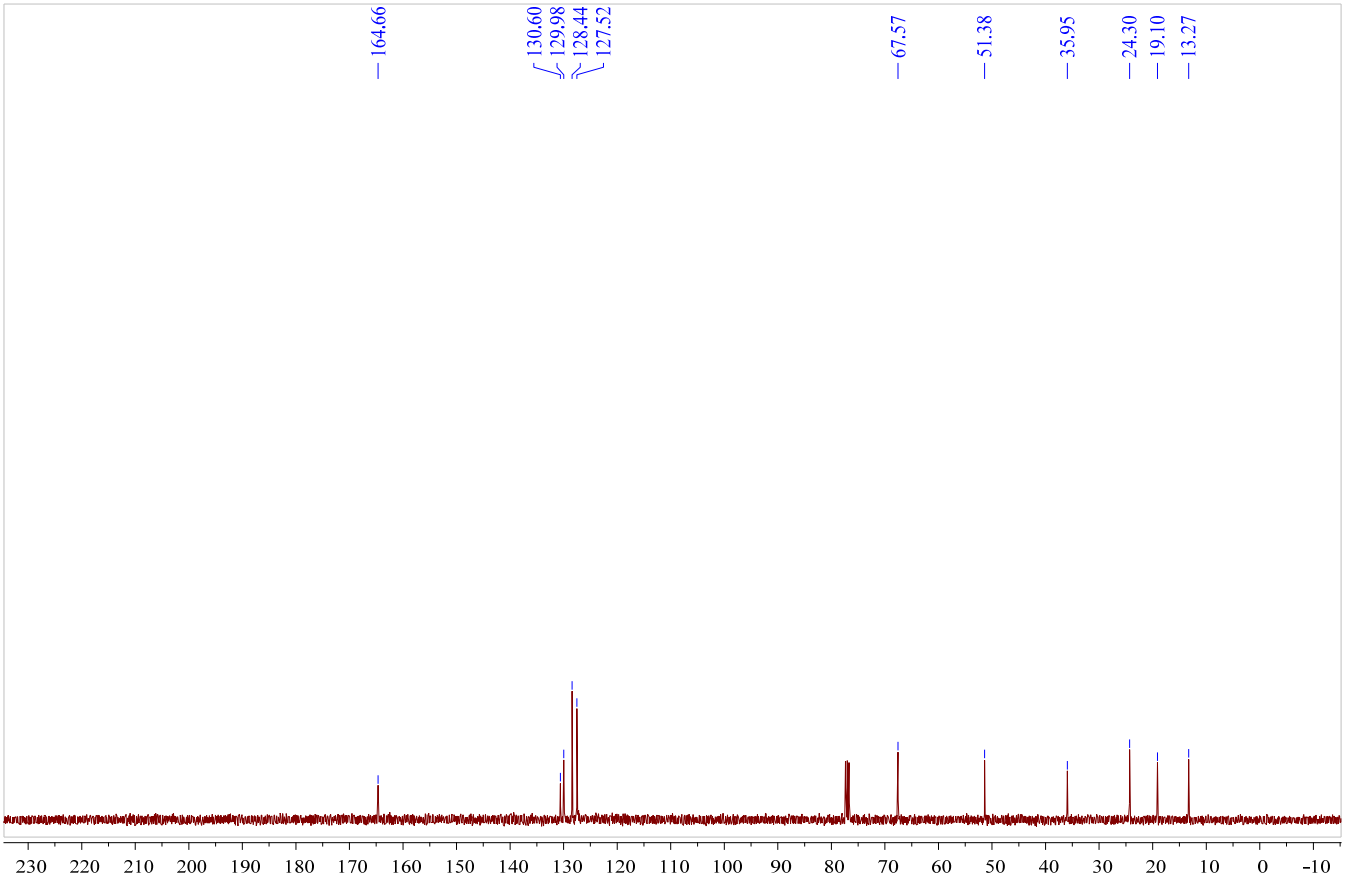
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of oxime 3i



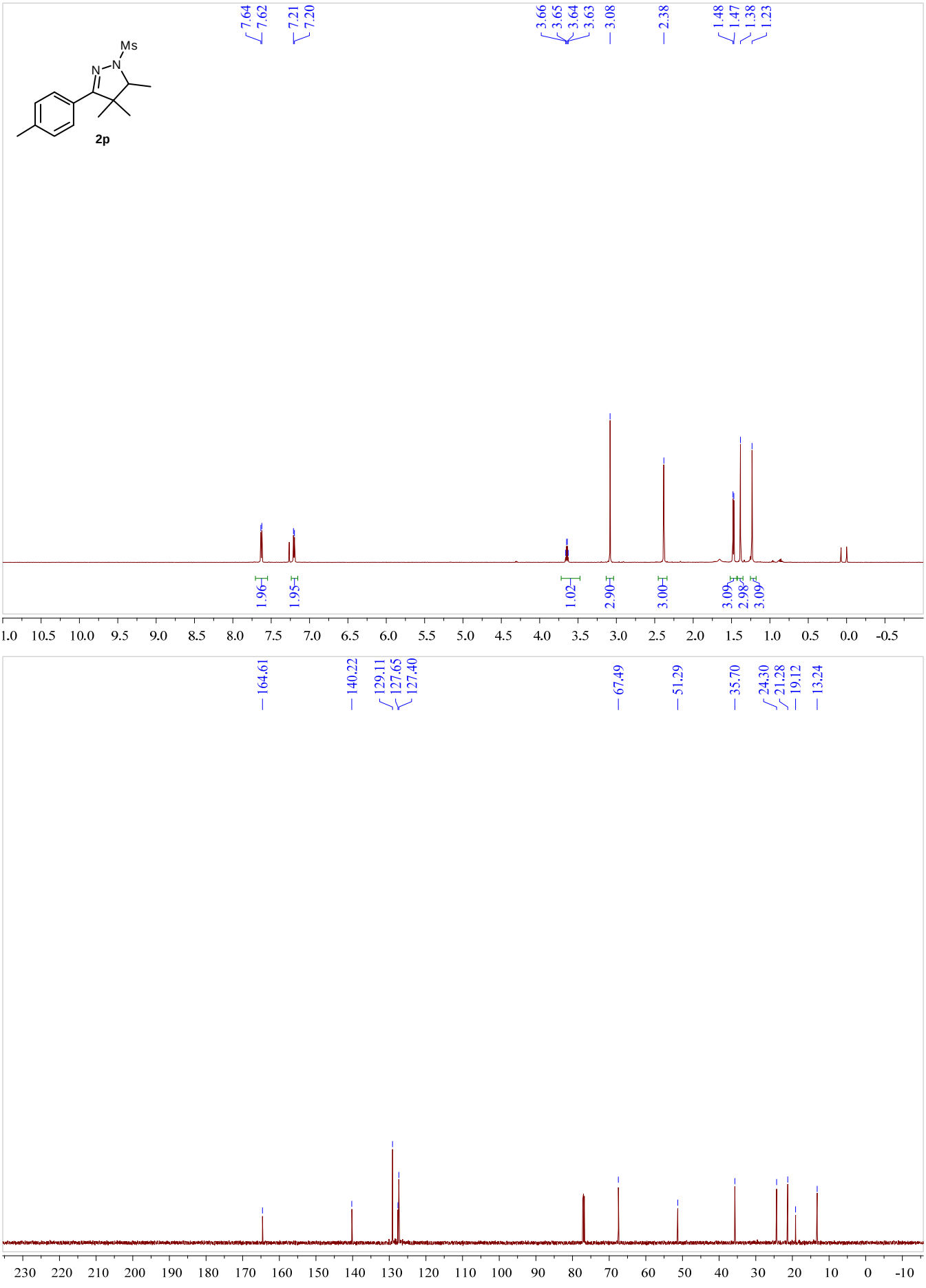


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 2o

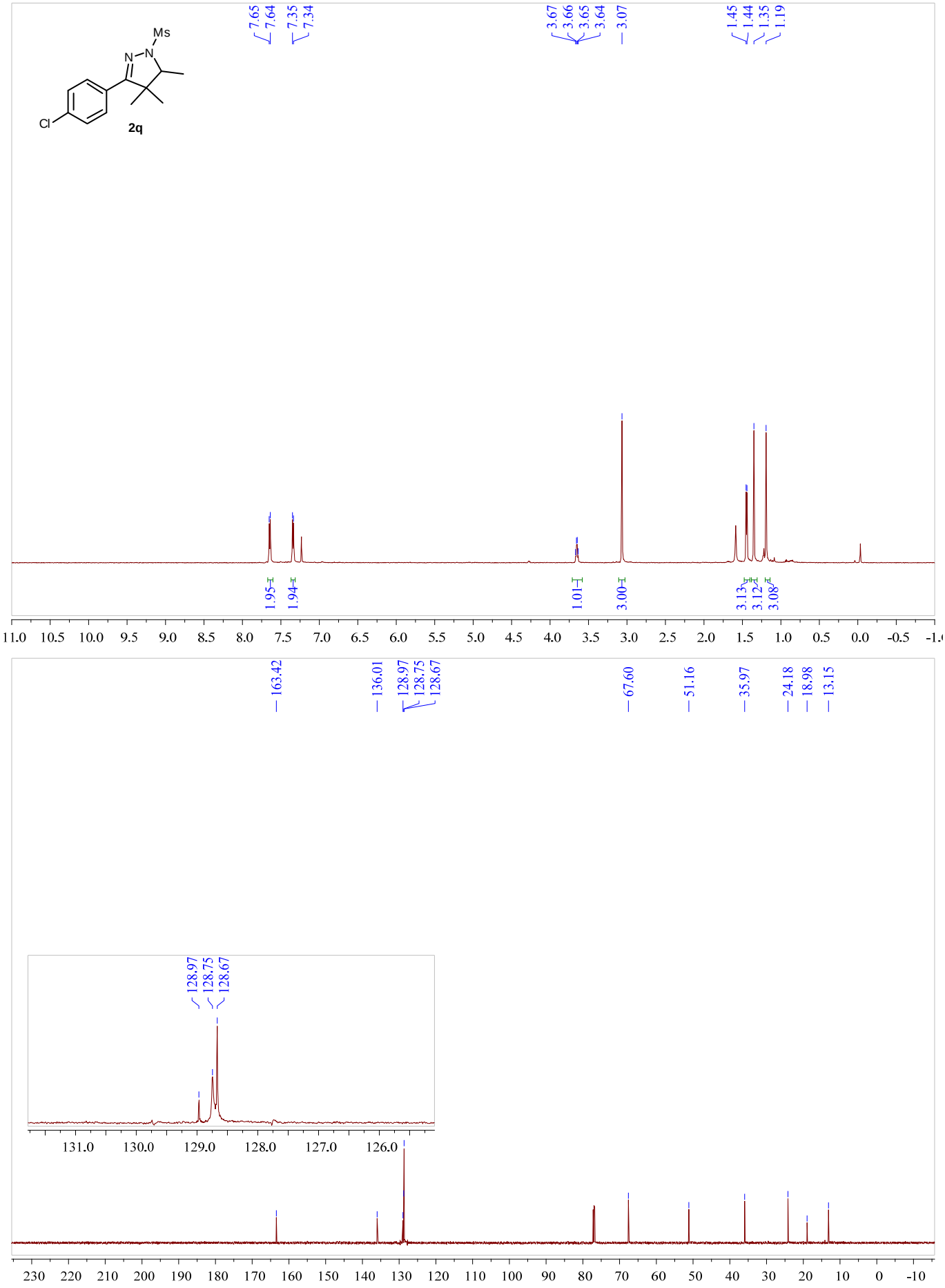




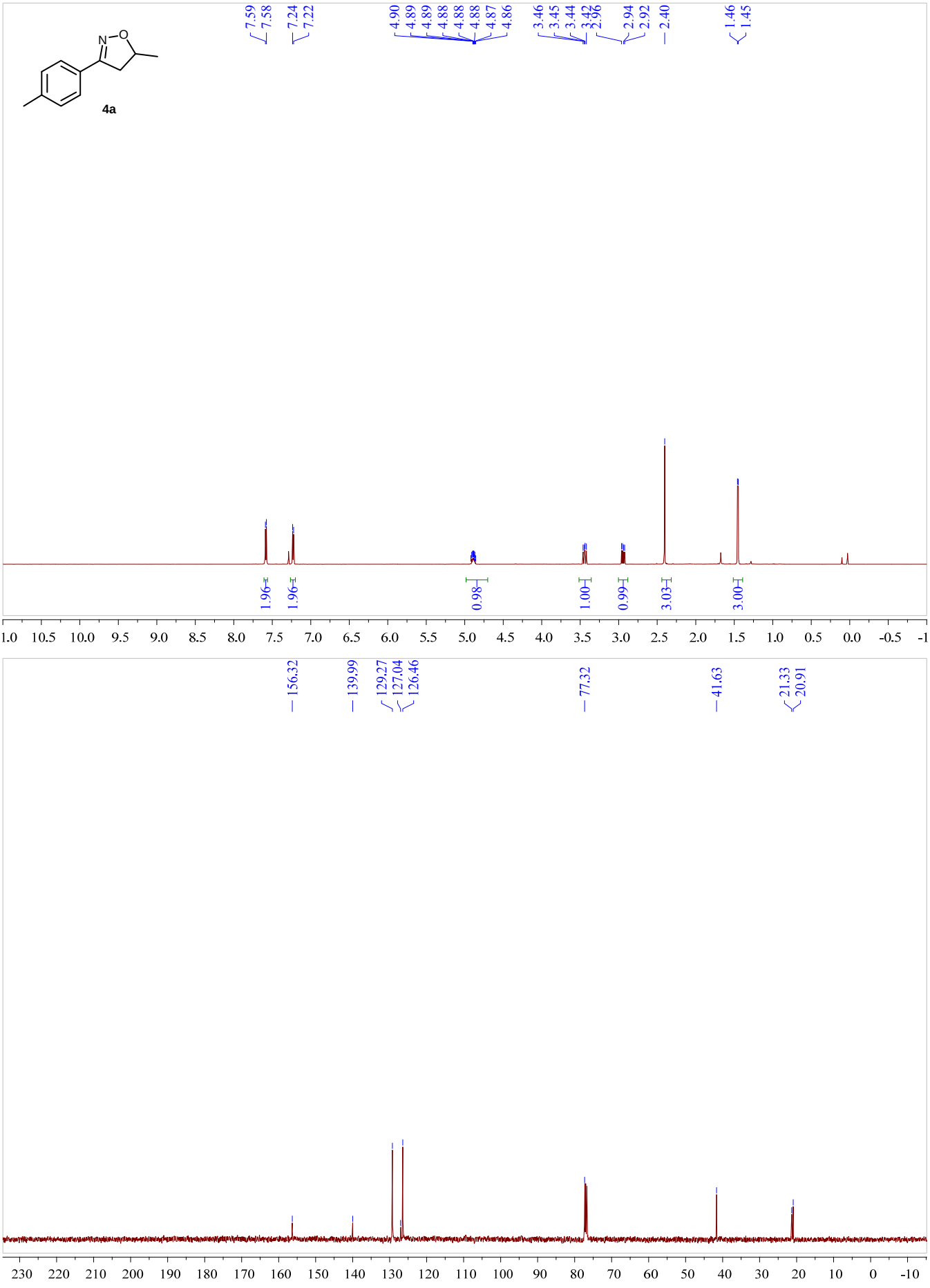
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of cyclic product 2p



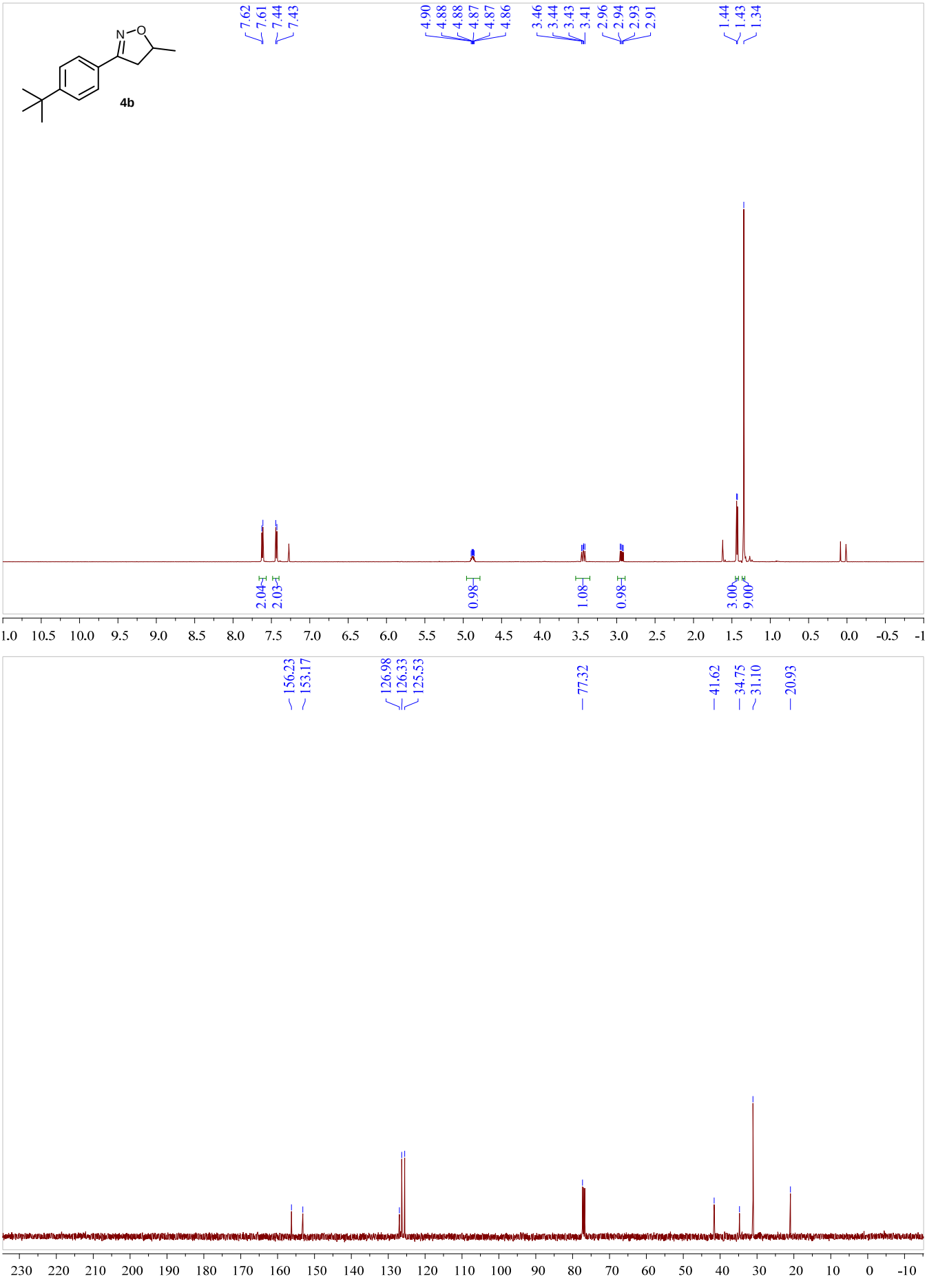
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of cyclic product 2q



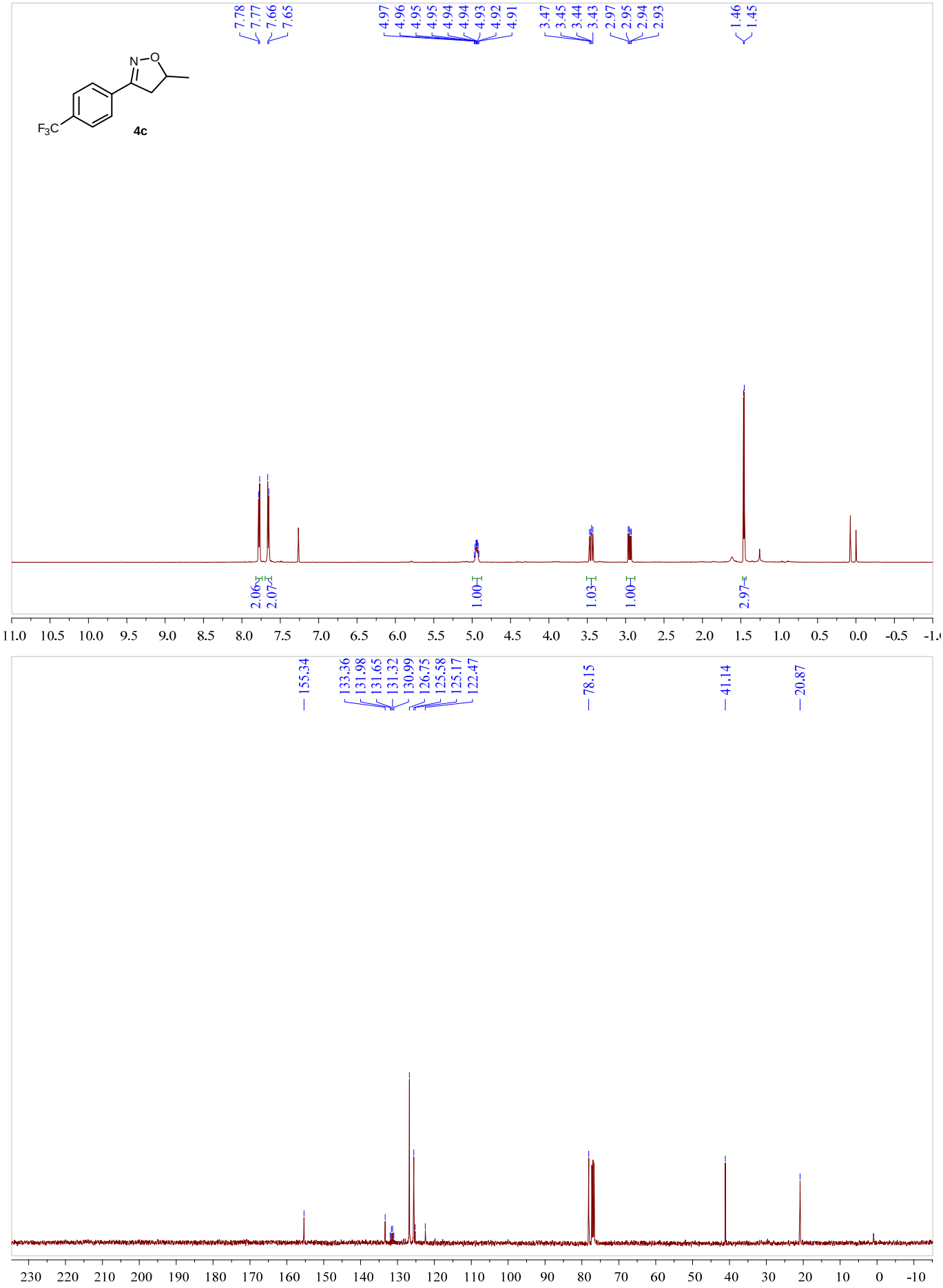
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4a



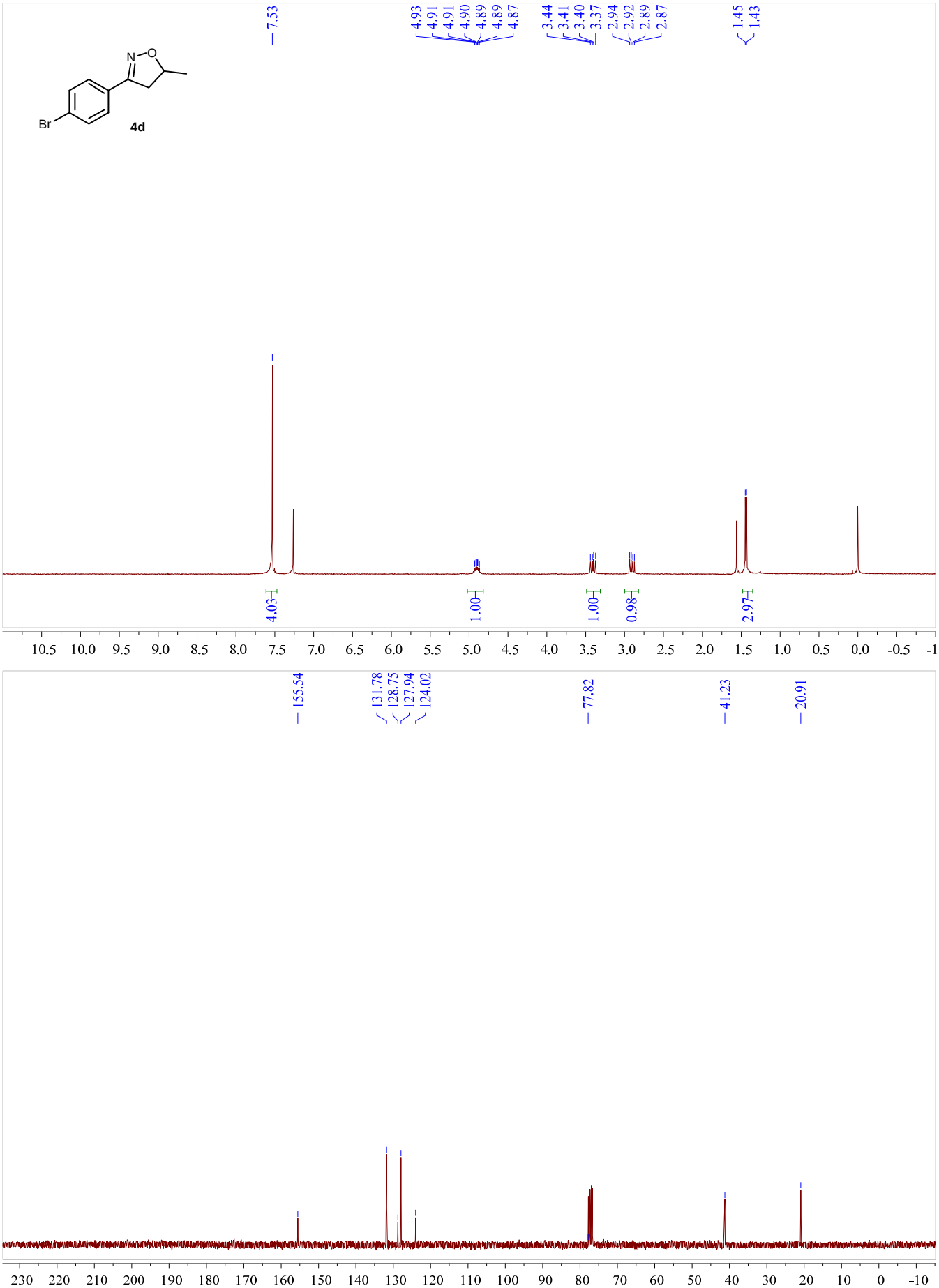
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4b



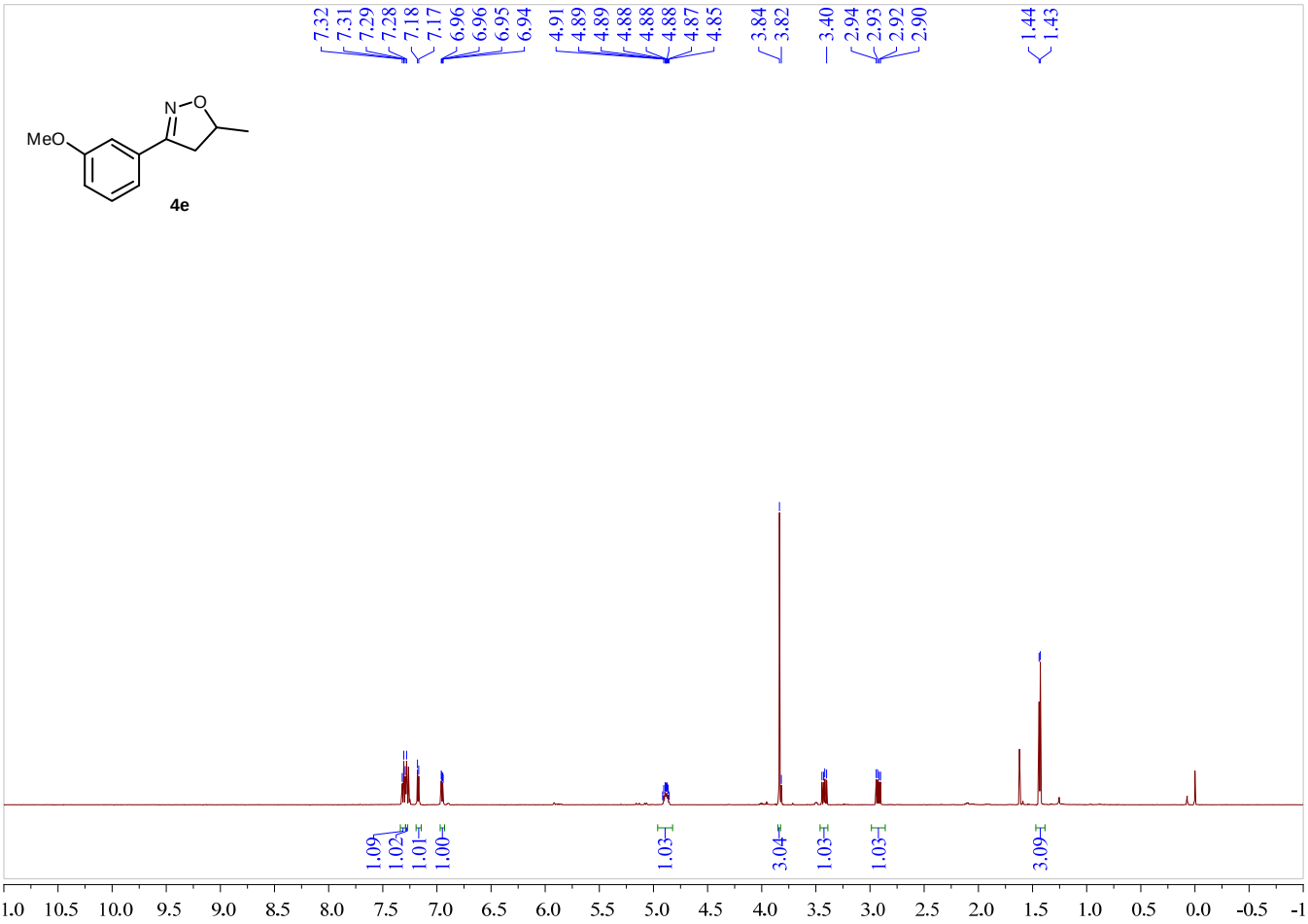
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4c

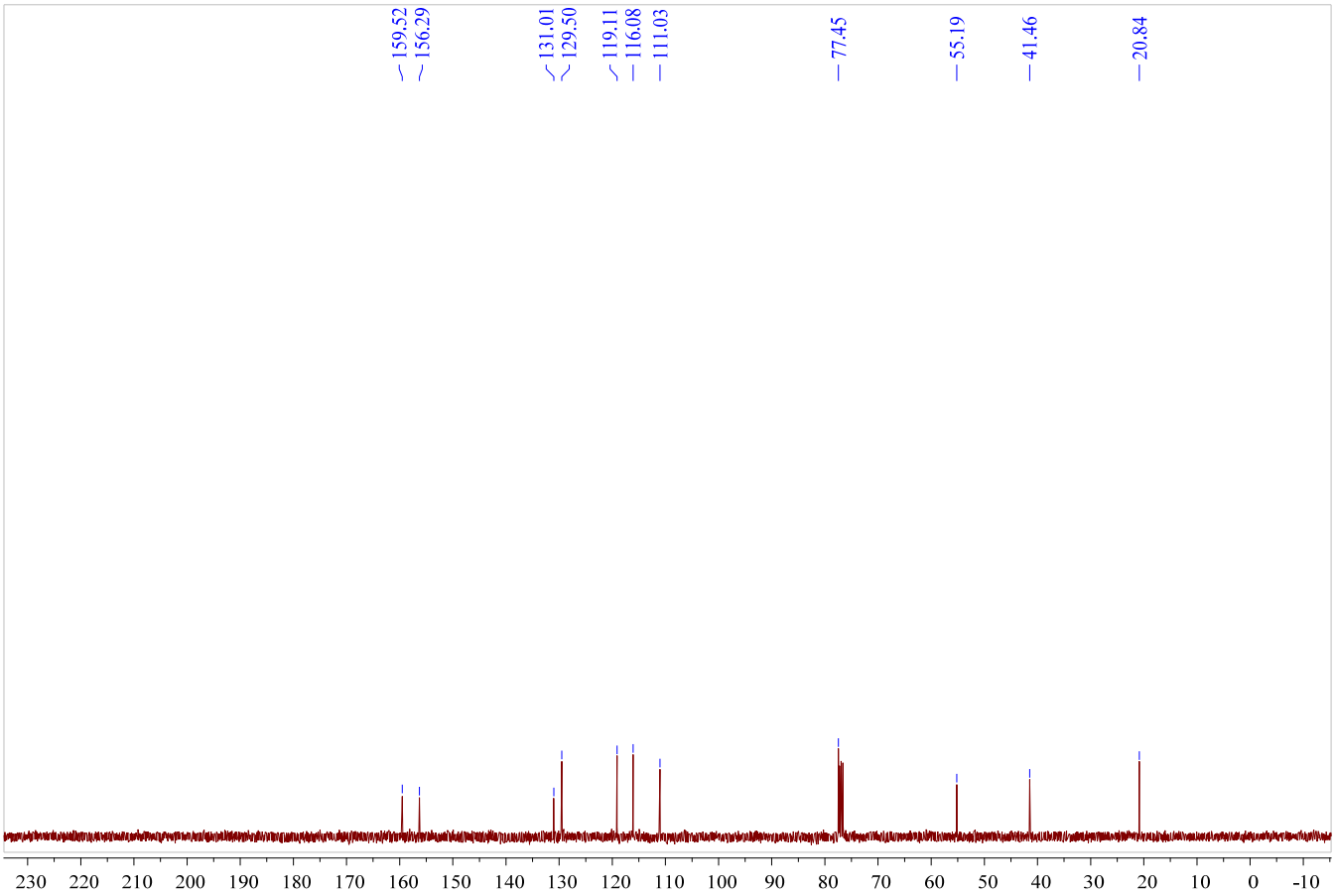


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4d

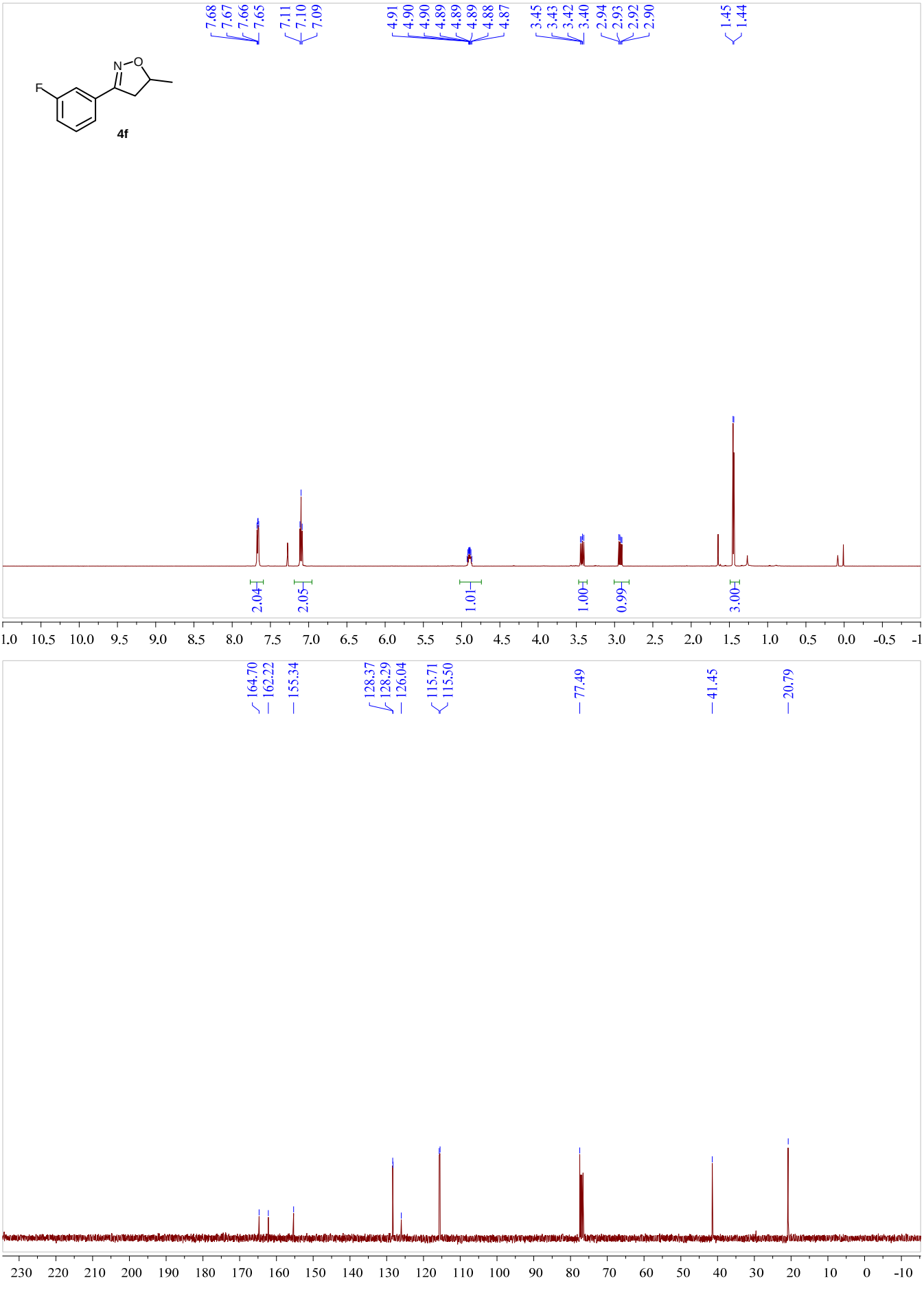


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4e

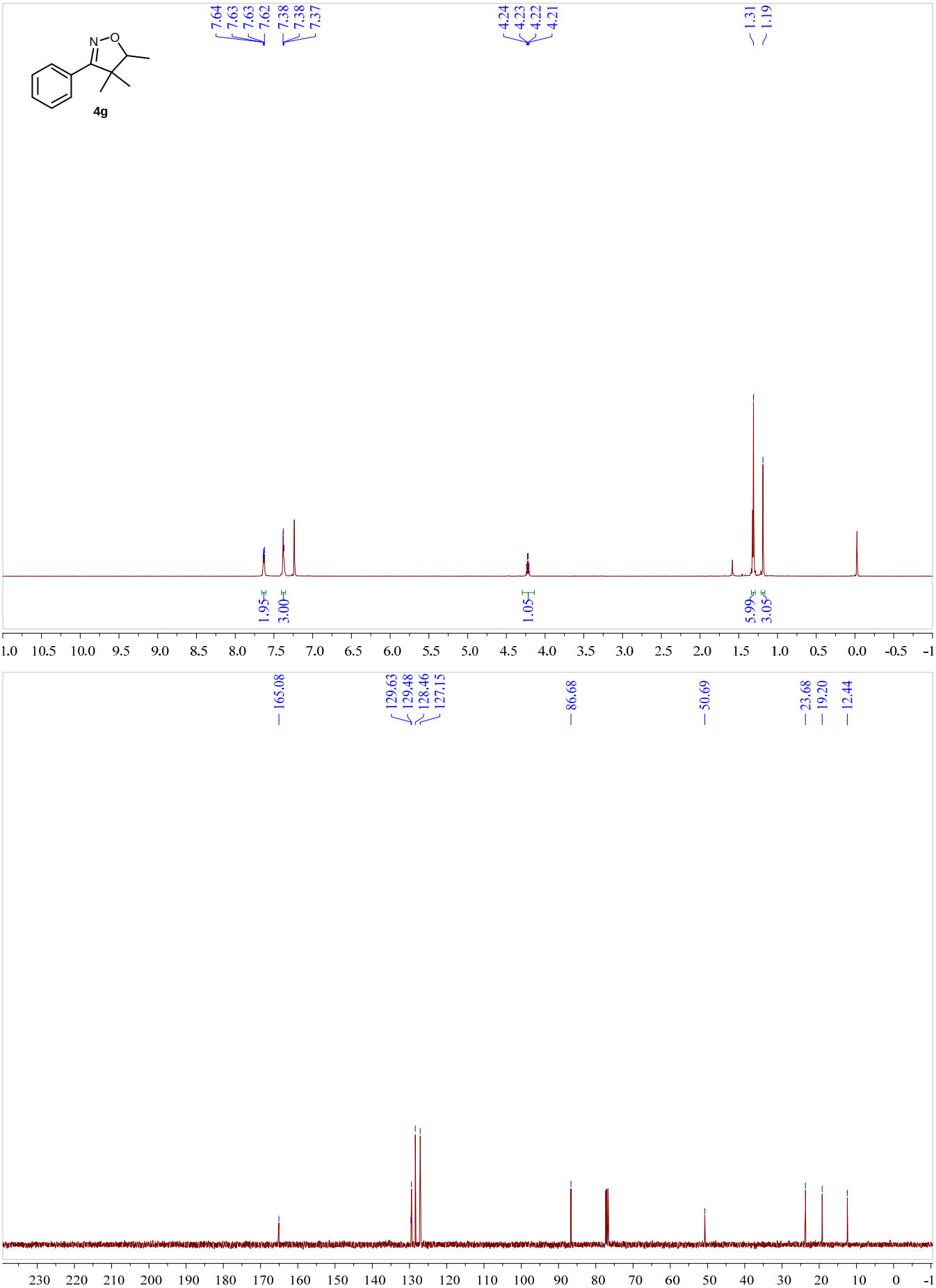




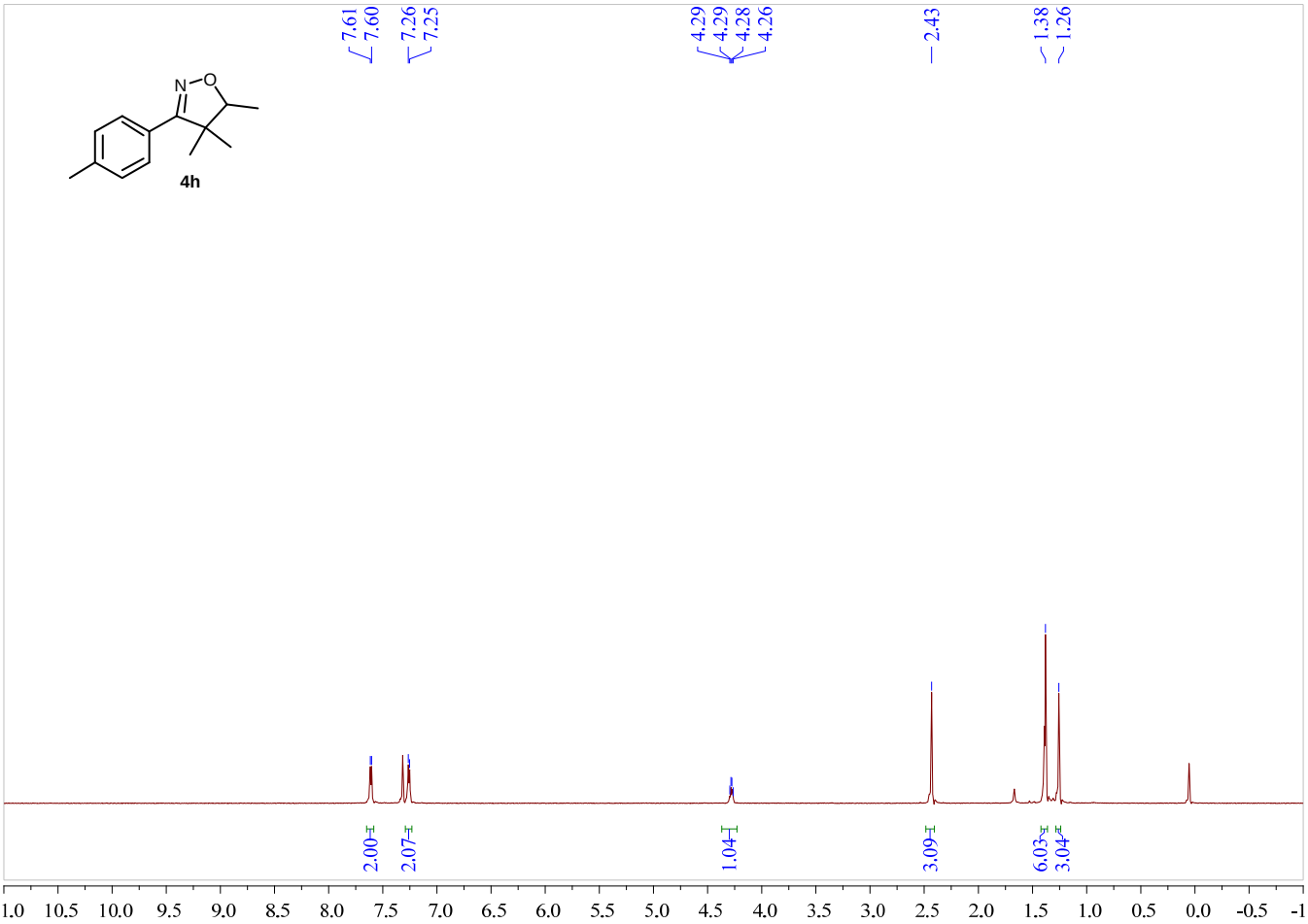
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4f

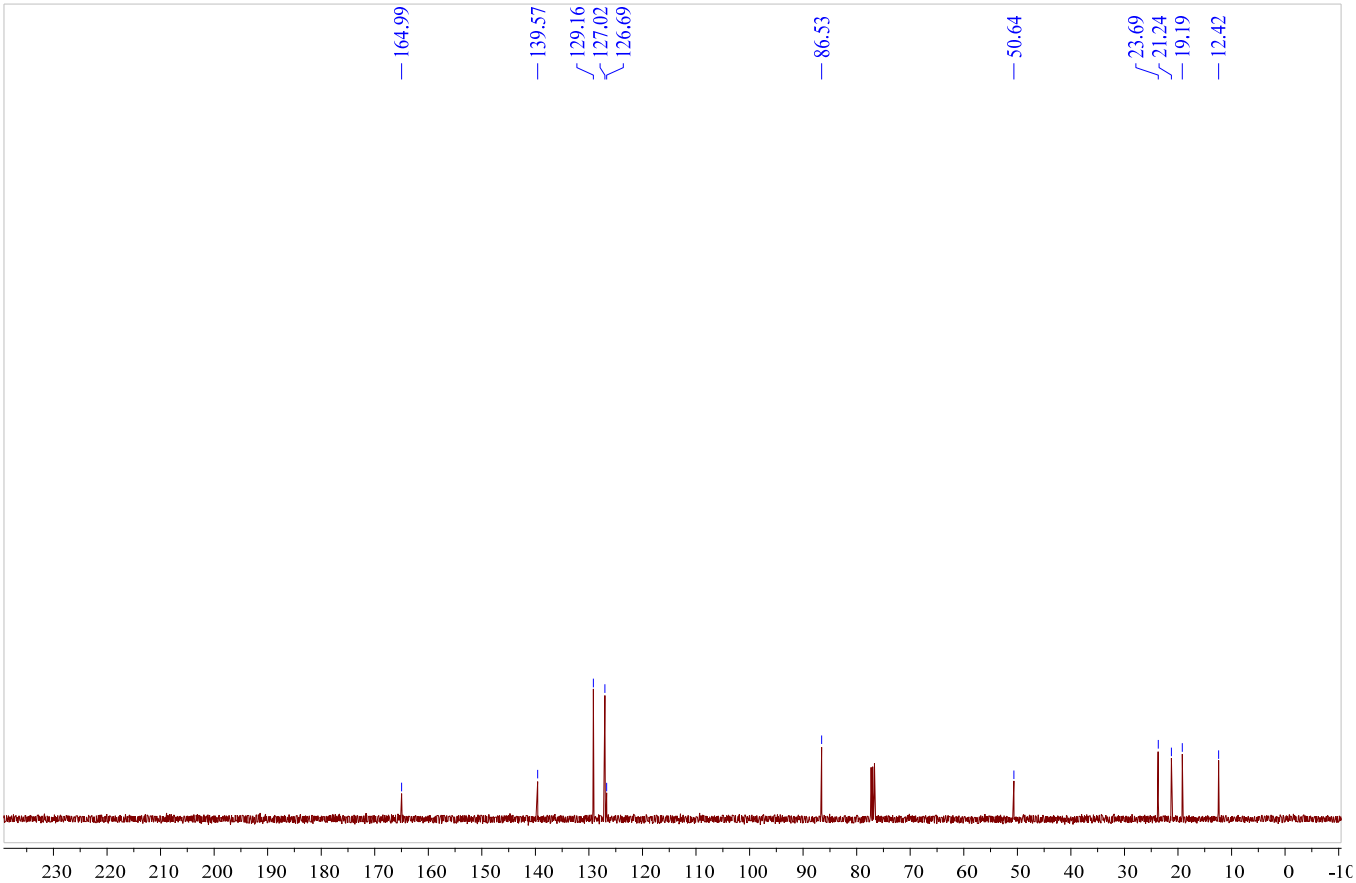


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4g

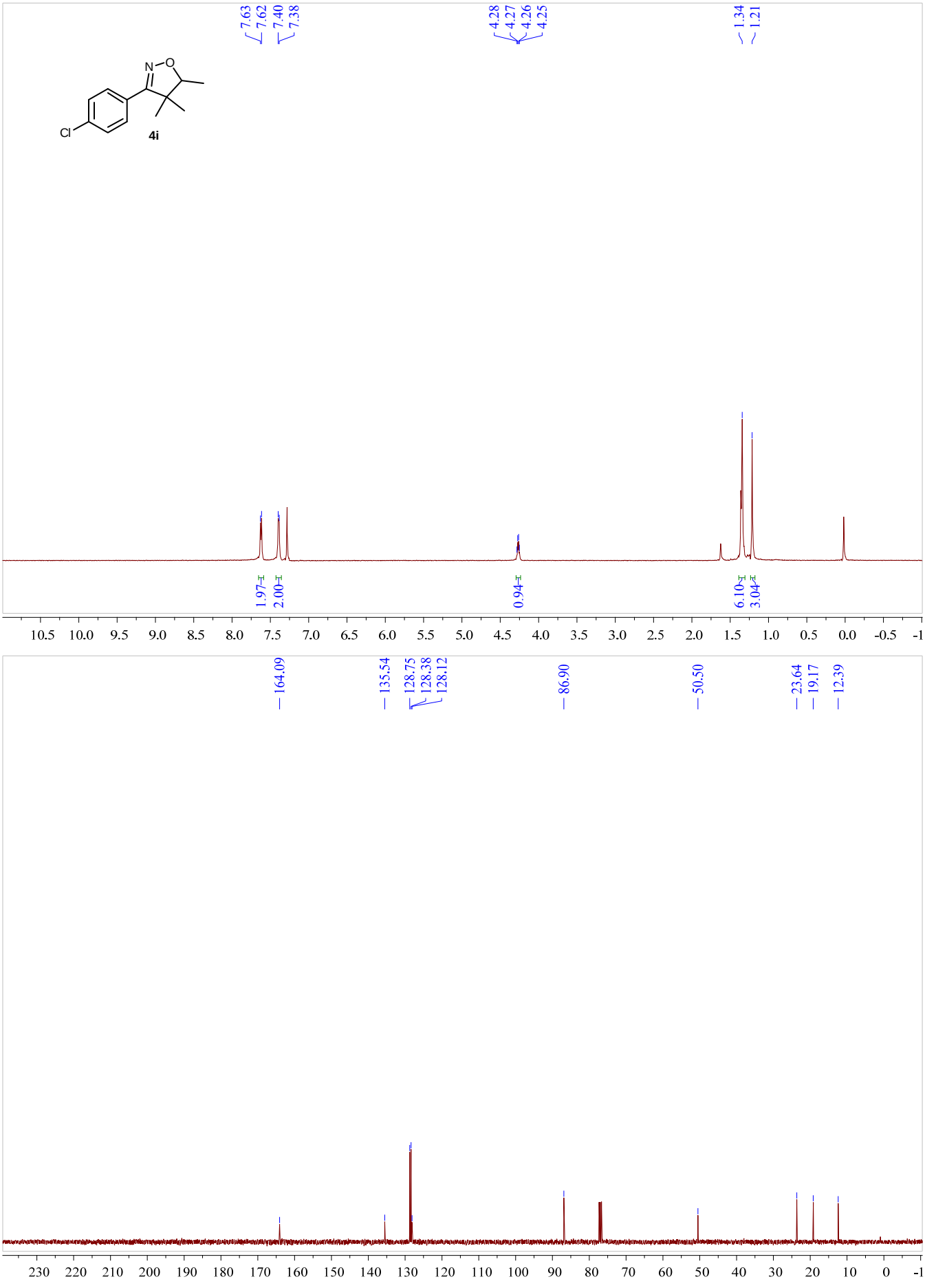


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4h

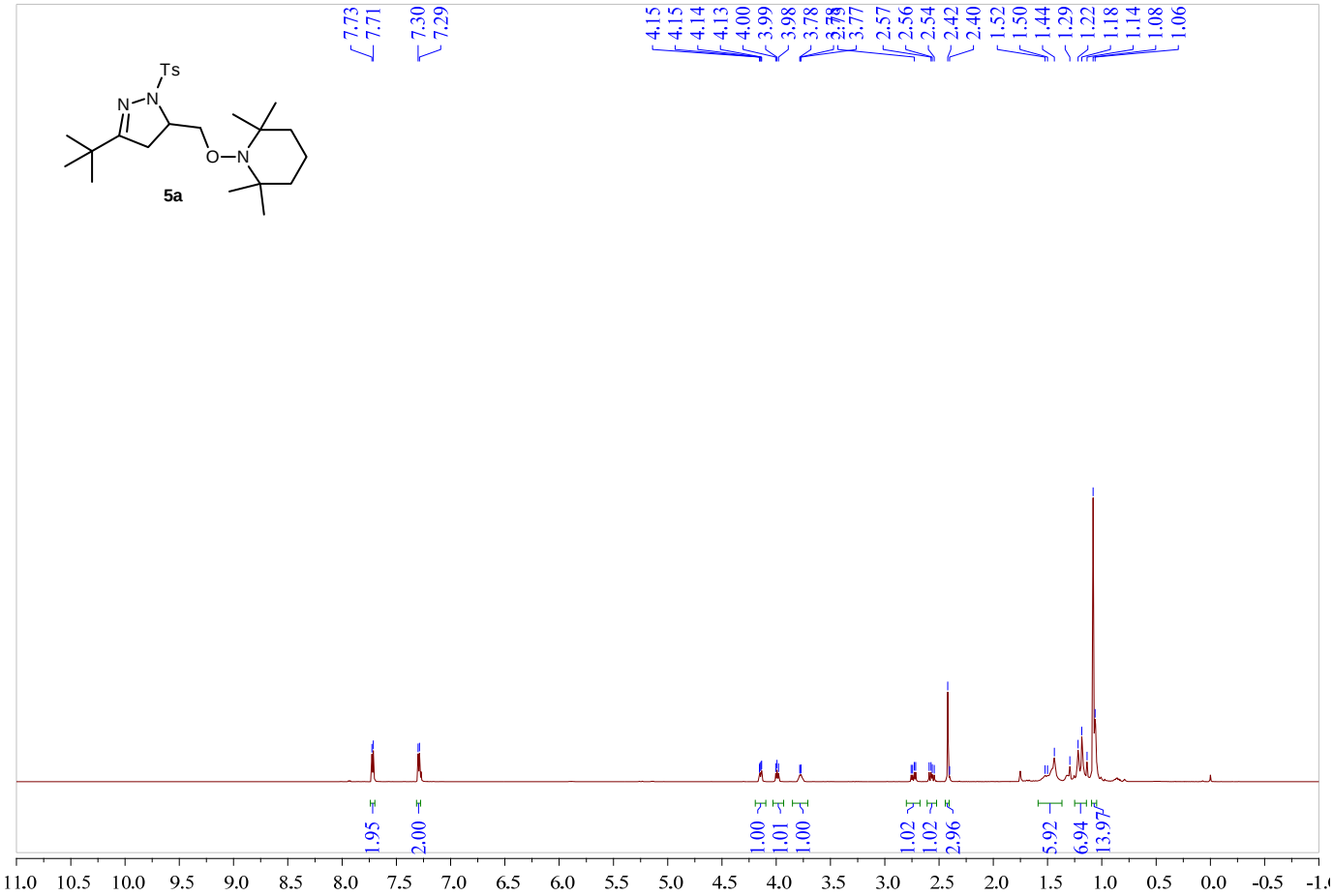


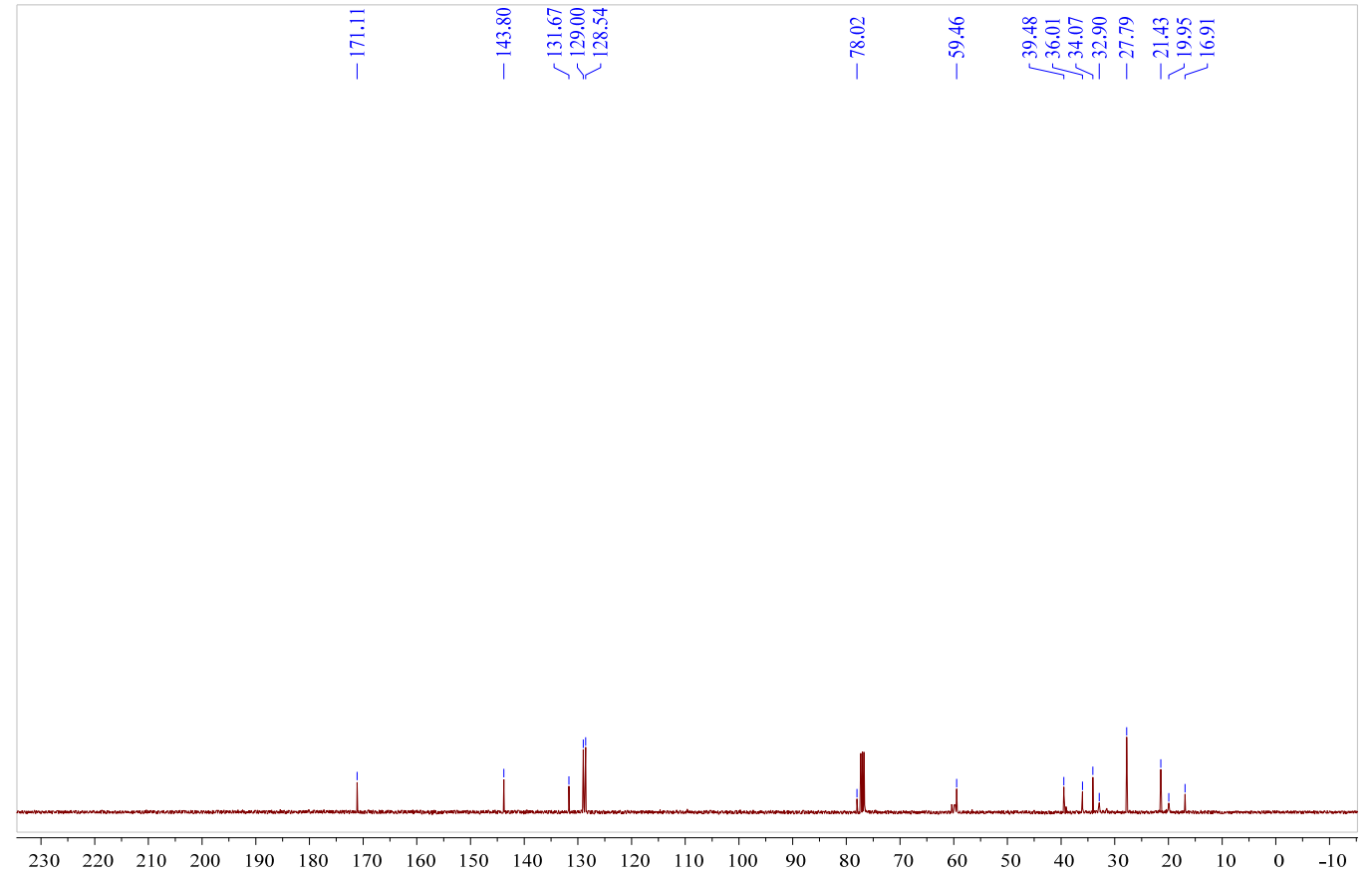


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 4i

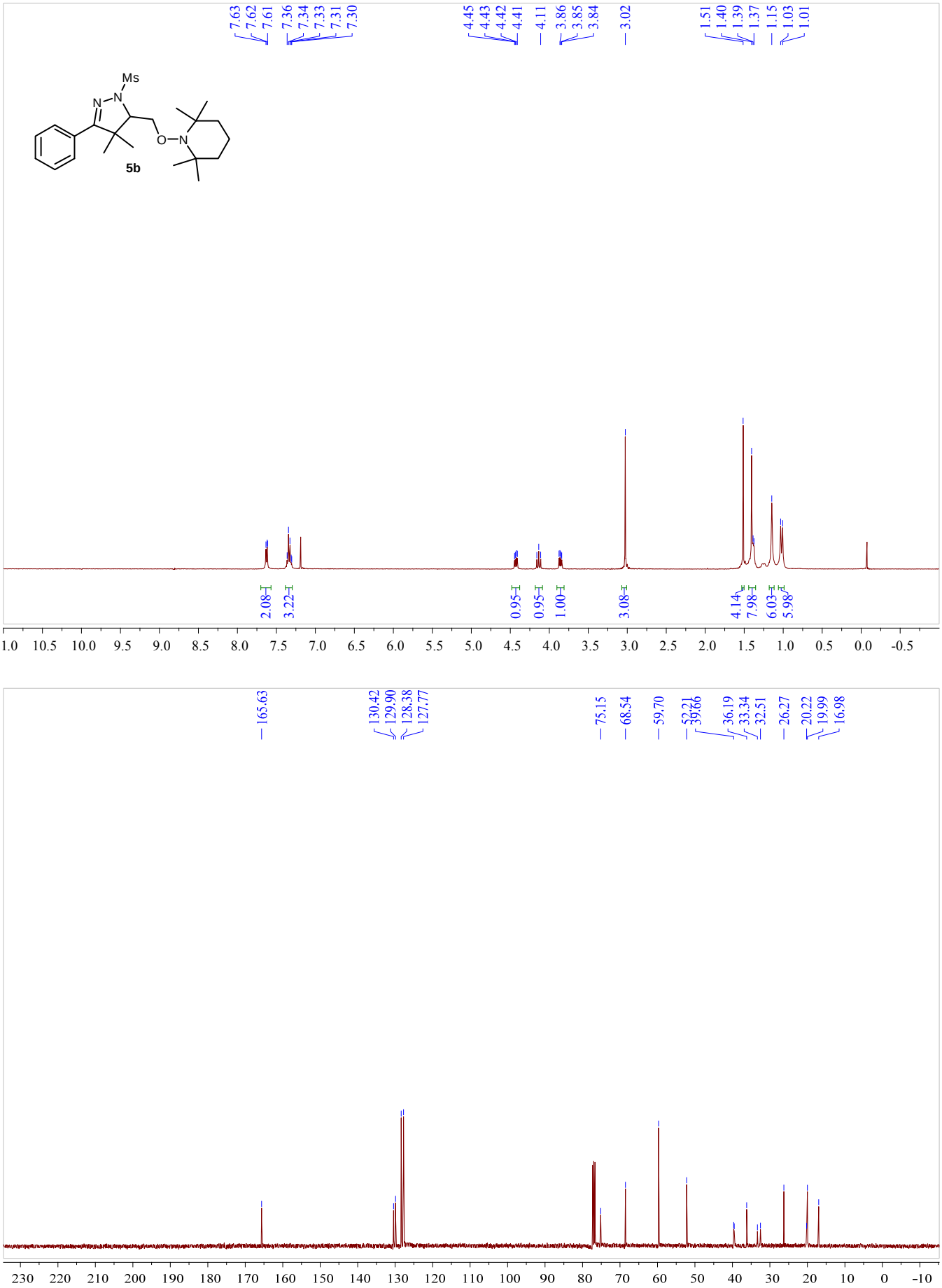


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 5a

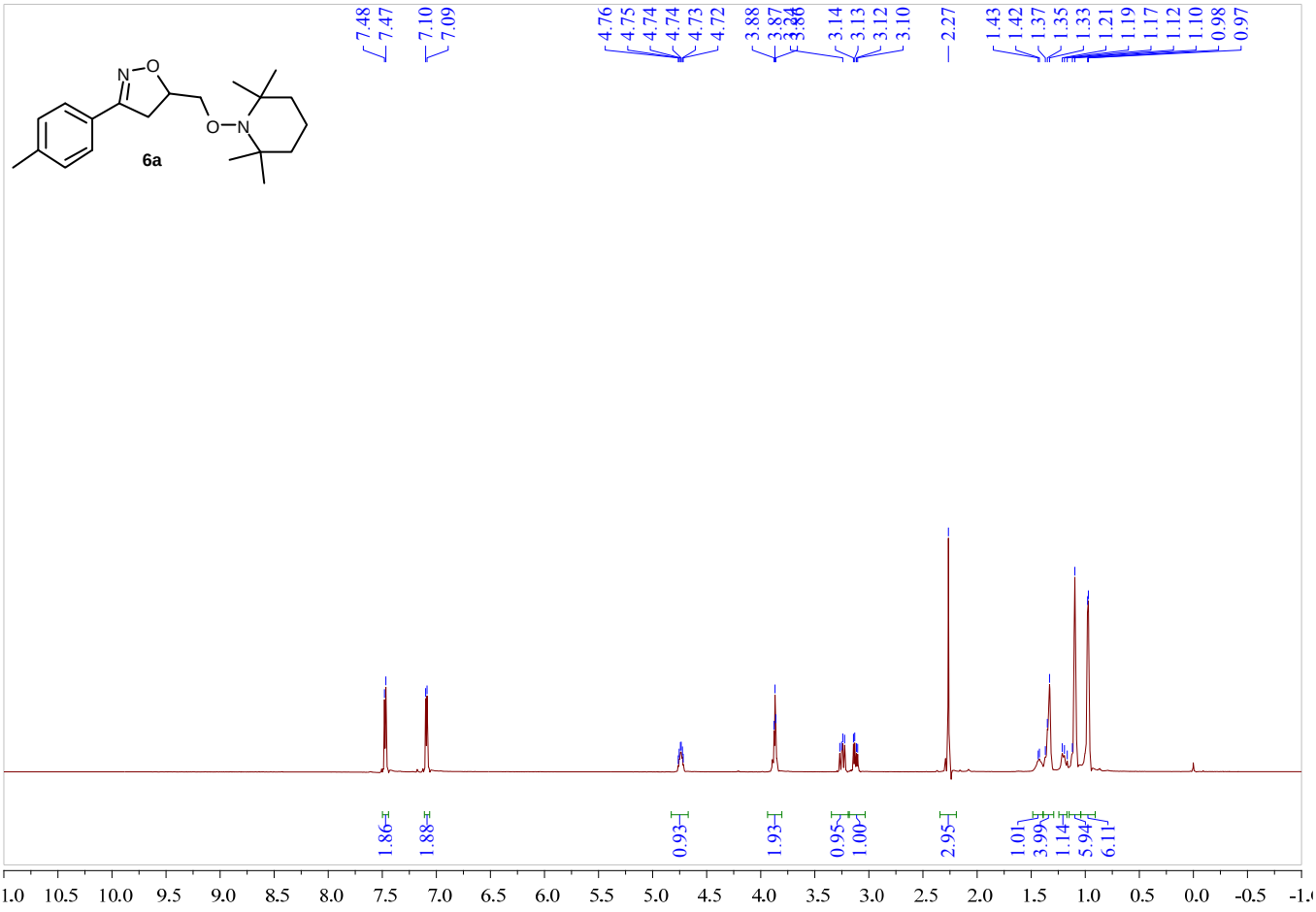


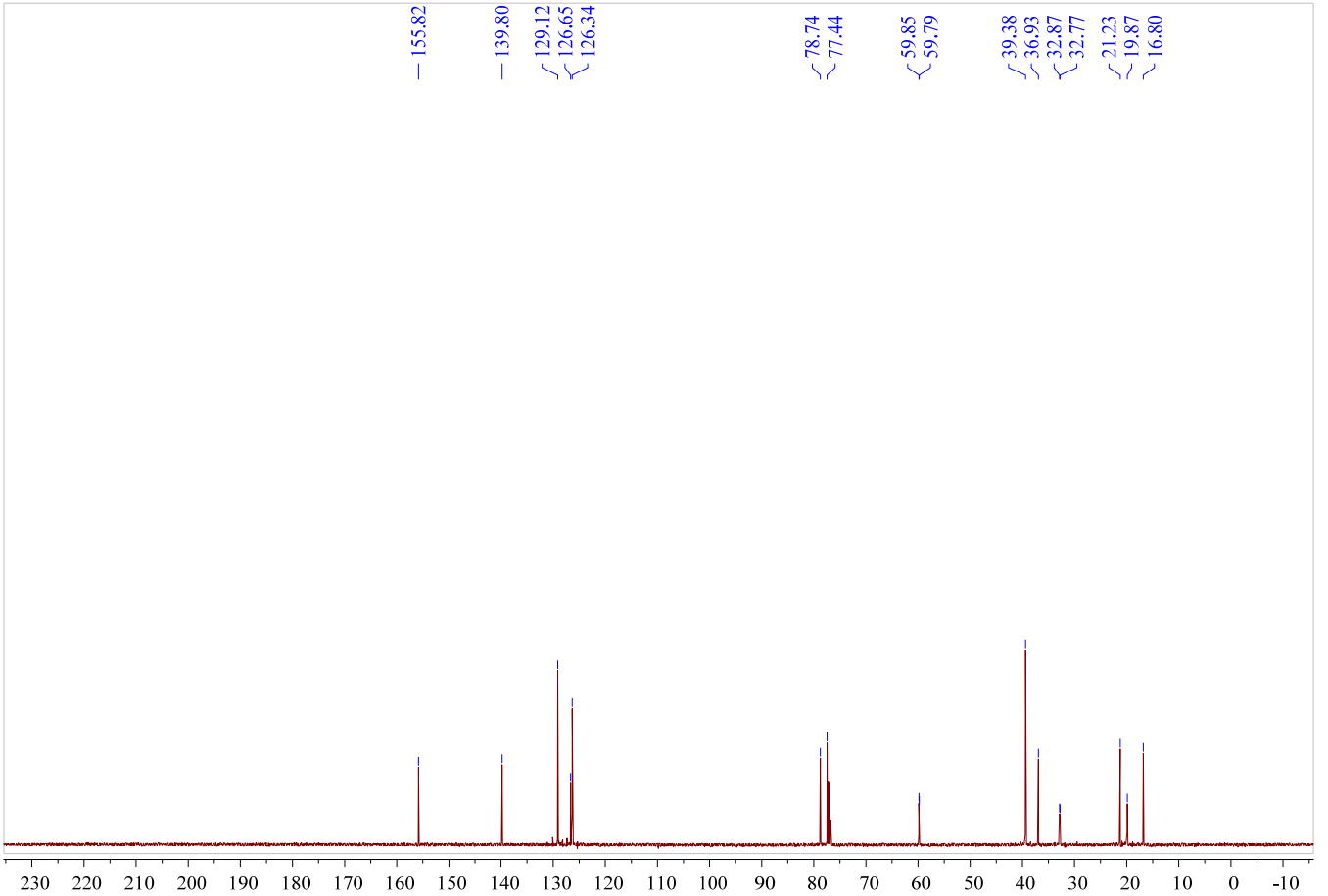


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of cyclic product 5b

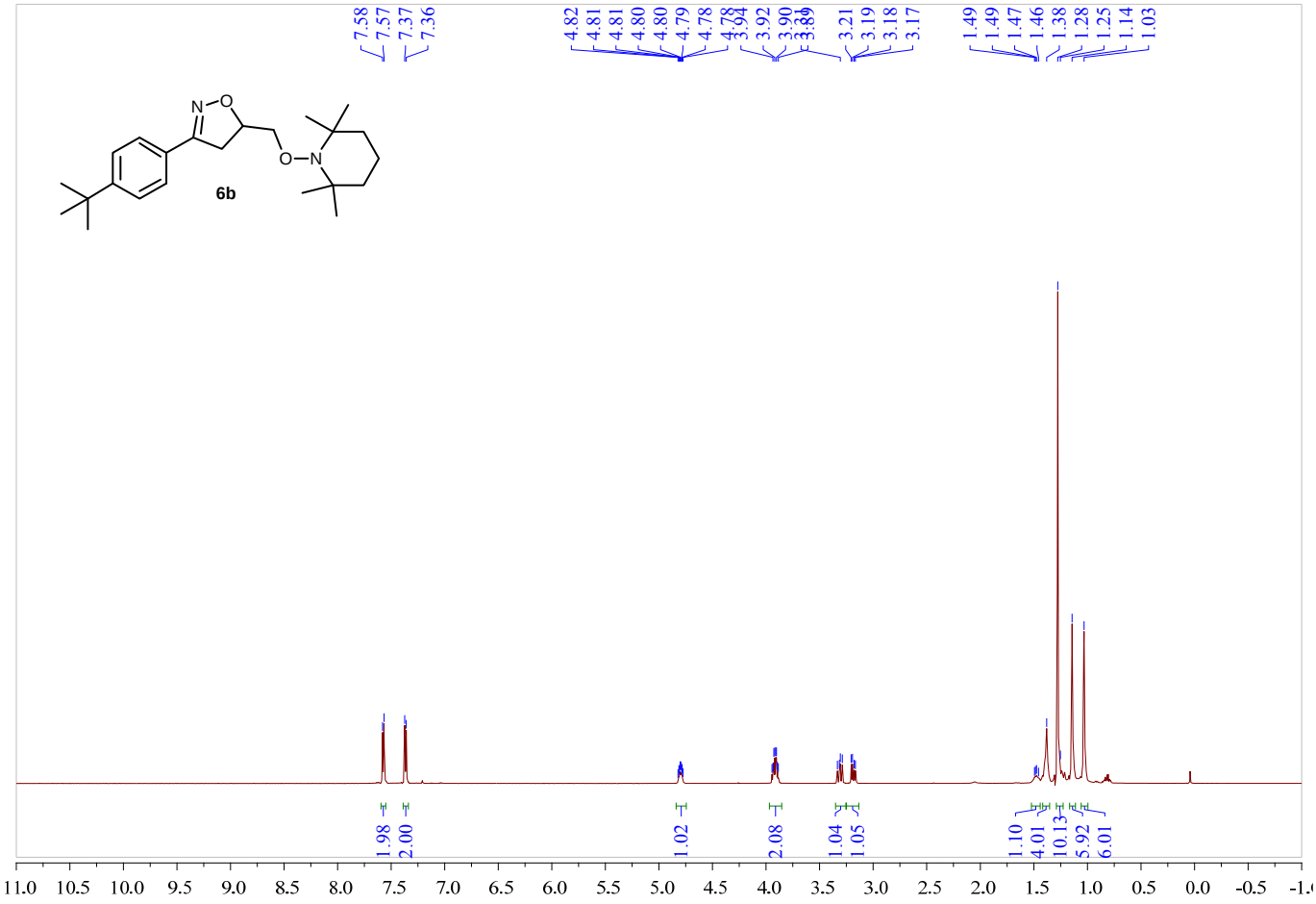


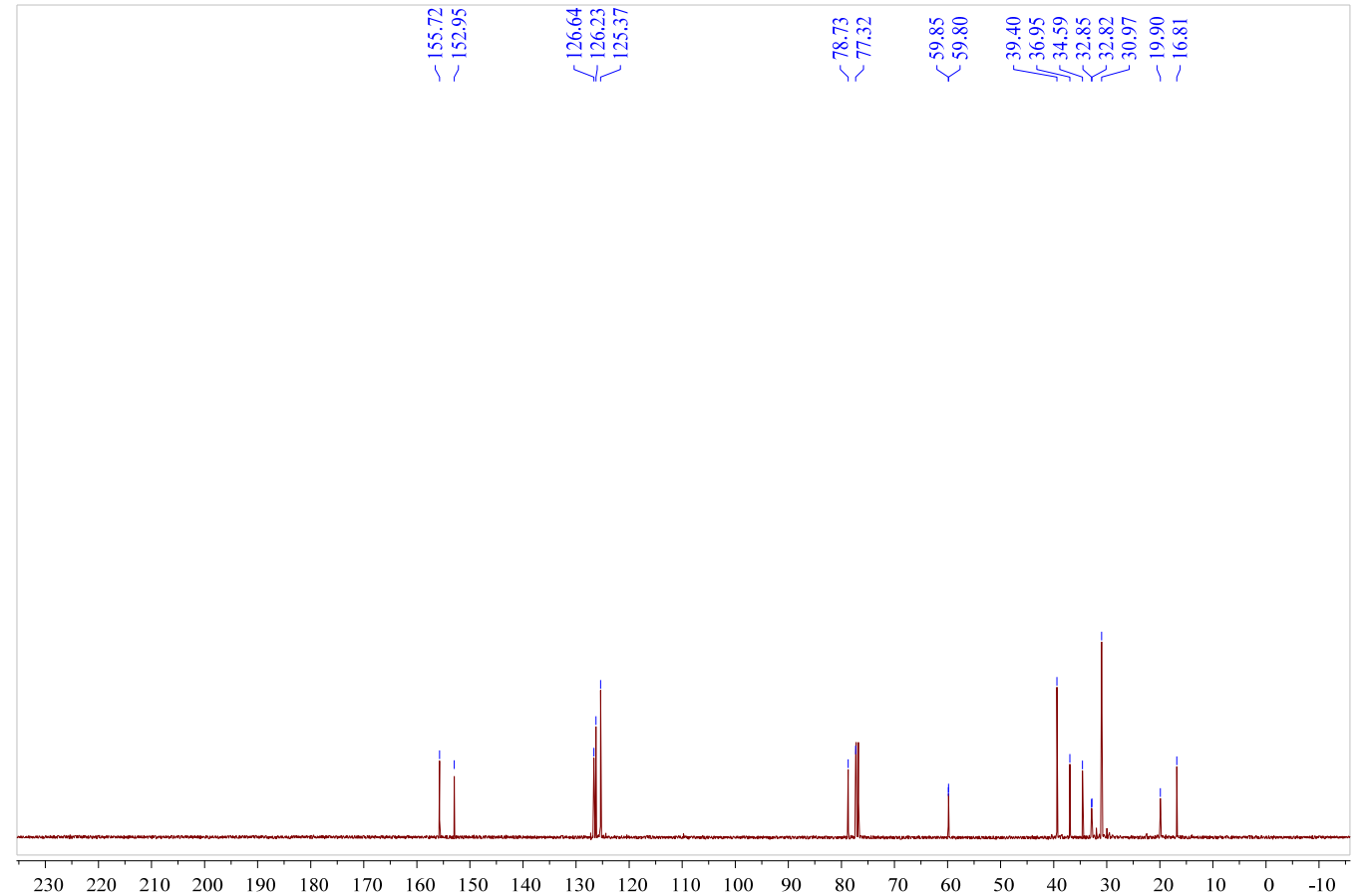
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of cyclic product 6a





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of cyclic product 6b





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of cyclic product 6c