Supporting Information

Palladium Precatalysts Containing *meta*-Terarylphosphine Ligands for Expedient Copper-Free Sonogashira Cross-Coupling Reactions

Yong Yang,*[a] Joyce Fen Yan Lim,[b] Xinying Chew,[a] Edward G. Robins,[c] Charles W. Johannes,[a] Yee Hwee Lim[a] and Howard Jong*[a]

[a] Institute of Chemical and Engineering Sciences (ICES), Agency for Science, Technology and Research (A*STAR), 11 Biopolis Way, Helios, #03-08, Singapore 138667

[b] School of Medical and Life Sciences, Nanyang Polytechnic, 180 Ang Mo Kio Avenue 8, Singapore 569830

[c] Singapore Bioimaging Consortium (SBIC), Agency for Science, Technology and Research (A*STAR), 11 Biopolis Way, Helios, #02-02, Singapore 138667

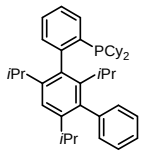
Table of Contents

1. General Considerations

Unless otherwise noted, all reagents were purchased commercially from Strem Chemicals, Sigma-Aldrich, or Alfa Aesar and used as received without further purification. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were obtained from an argon purged solvent purification system comprised of columns of activated alumina and molecular sieves. Anhydrous *N,N'*-dimethylformamide (DMF), acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO) and 1,4-dioxane were purchased from Sigma-Aldrich as sure-sealed solvents and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent. E. Column chromatography was carried out on silica gel (200-300 mesh) by elution with appropriate solvents. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5MS capillary column using helium carrier gas. NMR spectra were from a Bruker DRX-400, or DRX-600, instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm) as an internal reference. Infrared (IR) spectra were recorded on a Perkin−Elmer Spectrum One FT-IR spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using EI (electron ionization), or ESI (electrospray ionization).

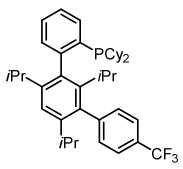
2. Synthesis of Cy*Phine Ligands

Dicyclohexyl(2',4',6'-triisopropyl-[1,1':3',1''-terphenyl]-2-yl)phosphane (Cy*Phine, L1)



Synthesis of **L1** was previously reported and duplicated here for convenience.[1] To an oven-dried flask fitted with a septum was sequentially added activated Mg (0.29 g, 12.2 mmol, 2.2 equiv.), THF (6 mL), and 3-bromo-2,4,6-triisopropyl-1,1'-biphenyl[2] (2 g, 5.6 mmol, 1.0 equiv.). The mixture was then heated to 70 °C in an oil bath and stirred for 2 h prior to the dropwise addition of 2-bromochlorobenzene (1.2 g, 6.2 mmol, 1.1 equiv.) at room temperature, after which the mixture was reheated to 70 °C and stirred for another 2 h. CuCl (27.7 mg, 0.28 mmol, 5 mol%) and PCy_2Cl (1.43 g, 6.2 mmol, 1.1 equiv.) were subsequently added sequentially at room temperature, and the mixture was stirred overnight (16 h). After the reaction was complete, as determined by ^{31}P NMR spectroscopy and GC analysis, ethyl acetate was added, and the mixture was washed several times with 28% aq. NH_4OH (50 mL). The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated to give the crude product; recrystallization (MeOH) afforded pure **L1** as a white solid (2.6 g, 84%). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 5 H), 7.30–7.19 (m, 4 H), 7.15 (s, 1 H), 2.61 (sept, J = 7.3 Hz, 1 H), 2.45 (sept, J = 6.5 Hz, 1 H), 2.34 (sept, J = 6.9 Hz, 1 H), 1.92 (m, 3 H), 1.84–1.50 (m, 10 H), 1.24 (m, 12 H), 1.11 (d, J = 6.8 Hz, 3 H), 1.03 (d, J = 6.8 Hz, 3 H), 0.97 (d, J = 6.7 Hz, 3 H), 0.89 (d, J = 6.9 Hz, 3 H), 0.53 (d, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.00 (d, J_{CP} = 30.5 Hz), 142.42, 139.92, 139.72 (d, J_{CP} = 5.9 Hz), 135.92 (d, J_{CP} = 18.8 Hz), 135.04, 134.96 (d, J_{CP} = 1.9 Hz), 134.17, 132.93 (d, J_{CP} = 3.2 Hz), 130.96 (d, J_{CP} = 5.9 Hz), 129.69 (d, J_{CP} =16.0 Hz), 128.90, 128.72, 126.58 (d, J_{CP} = 26.4 Hz), 35.12 (d, J_{CP} = 15.4 Hz), 33.25 (d, J_{CP} = 13.8 Hz), 31.04 (d, J_{CP} = 12.0 Hz), 30.43 (dd, J_{CP} = 27.1, 14.9 Hz), 29.55 (d, J_{CP} = 10.9 Hz), 28.09 (dd, J_{CP} = 14.6, 9.5 Hz), 27.65 (d, J_{CP} = 10.1 Hz), 26.86 (d, J_{CP} = 17.5 Hz), 21.85 (d, J_{CP} = 6.2 Hz), 21.31, 20.37 ppm. ^{31}P (243 MHz, $CDCl_3$): δ = –11.78 ppm. Anal. Calcd. for $C_{39}H_{53}P$: C 84.73, H 9.66; found C 84.50, H 9.33.

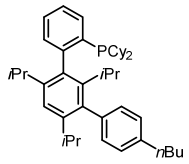
Dicyclohexyl(2',4',6'-triisopropyl-4''-(trifluoromethyl)-[1,1':3',1''-terphenyl]-2-yl)phosphane (Cy*Phine-CF_3, L2)



Synthesized using the same procedure as **L1** with the exception of starting from 3-bromo-2,4,6-triisopropyl-4'-(trifluoromethyl)-1,1'-biphenyl[2] (427

mg, 1.0 mmol) to afford the title compound as a white solid (483 mg, 78%). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.71 (d, *J* = 6.7 Hz, 1 H), 7.63 (s, 1 H), 7.58–7.47 (m, 4 H), 7.46–7.39 (m, 3 H), 3.21 (p, *J* = 7.1 Hz, 1 H), 2.86 (p, *J* = 6.9 Hz, 1 H), 2.67 (p, *J* = 6.8 Hz, 1 H), 2.15 (d, *J* = 12.5 Hz, 3 H), 2.06–1.77 (m, 16 H), 1.65 (d, *J* = 6.9 Hz, 3 H), 1.51–1.38 (m, 3 H), 1.33 (dd, *J* = 8.6, 6.7 Hz, 8 H), 1.24 (d, *J* = 7.2 Hz, 3 H), 0.95 (d, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, C_6D_6) δ = 148.59 (d, J_{CP} = 31.3 Hz), 146.17 , 139.88 (d, J_{CP} = 6.0 Hz), 138.27, 136.24 (d, J_{CP} = 20.9 Hz), 135.44, 134.14, 132.72 (d, J_{CP} = 2.8 Hz), 130.67 (d, J_{CP} = 5.9 Hz), 130.07, 129.82, 129.03, 128.66, 126.51, 125.54 (dd, J_{CP} = 12.6, 3.8 Hz), 34.33 (d, J_{CP} = 16.5 Hz), 34.01 (d, J_{CP} = 16.1 Hz), 31.17–30.69 (m), 30.62, 29.99 (d, J_{CP} = 14.9 Hz), 29.75 (d, J_{CP} = 13.4 Hz), 28.12–26.87 (m), 26.59 (d, J_{CP} = 9.2 Hz), 21.57, 20.62, 20.06 ppm. ^{31}P NMR (243 MHz, $CDCl_3$) δ = –11.63 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = –61.92 ppm. Anal. Calcd. for $C_{40}H_{52}F_3P$: C 77.39, H 8.44; found C 77.69, H 8.13.

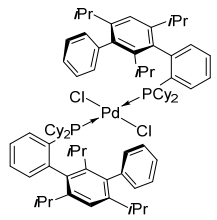
(4''-butyl-2',4',6'-triisopropyl-[1,1':3',1''-terphenyl]-2-yl)dicyclohexylphosphane (Cy*Phine-*n*Bu, L3)



Synthesized using the same procedure as **L1** with the exception of starting from 3-bromo-2,4,6-triisopropyl-4'-(trifluoromethyl)-1,1'-biphenyl[3] (622 mg, 1.5 mmol) to afford the title compound as a white solid (712 mg, 78%). ^{1}H NMR (400 MHz, C_6D_6) δ = 7.64 (d, *J* = 7.0 Hz, 1 H), 7.59 (s, 1H), 7.52–7.47 (m, 2 H), 7.45 (d, *J* = 7.7 Hz, 2 H), 7.28 (d, *J* = 2.4 Hz, 1 H), 7.20 (td, *J* = 6.0, 2.9 Hz, 2 H), 3.20 (p, *J* = 7.1 Hz, 1 H), 2.95 (p, *J* = 6.9 Hz, 1 H), 2.81 (p, *J* = 6.8 Hz, 1 H), 2.68–2.54 (m, 2 H), 2.08 (d, *J* = 12.8 Hz, 2 H), 2.00–1.87 (m, 4 H), 1.81 (m, 2 H), 1.79–1.72 (m, 4 H), 1.62 (dd, *J* = 16.4, 7.3 Hz, 4 H), 1.46–1.19 (m, 25 H), 1.09 (d, *J* = 7.2 Hz, 3 H), 0.96 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, C_6D_6) δ = 149.04, 148.72, 147.55, 145.93, 142.75, 140.91, 139.07, 138.11 (d, J_{CP} = 5.9 Hz), 137.76, 136.99 (d, J_{CP} = 19.1 Hz), 132.54–131.84 (m), 131.49 (d, J_{CP} = 5.8 Hz), 130.85, 127.15, 126.25, 119.13, 35.37, 34.26 (dd, J_{CP} = 17.4, 9.1 Hz), 33.52, 32.61, 31.48 (dd, J_{CP} = 18.4, 9.5 Hz), 30.99, 29.56, 29.19 (dd, J_{CP} = 11.0, 8.4 Hz), 27.57 (dd, J_{CP} = 12.1, 5.7 Hz), 27.29 (dd, J_{CP} = 7.7, 5.0 Hz), 26.50, 25.91, 25.44, 24.40 (d, J_{CP} = 7.3 Hz), 24.13, 23.45, 23.08, 22.34 ppm. ^{31}P NMR (243 MHz, $CDCl_3$) δ = –11.70 ppm. Anal. Calcd. for $C_{43}H_{61}P$: C 84.80, H 10.10; found C 84.76, H 9.69.

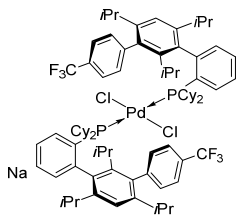
3. Synthesis of Precatalysts

$PdCl_2$(Cy*Phine)$_2$ (P1)



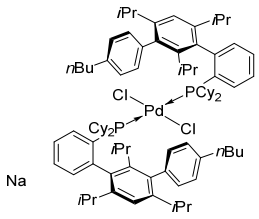
To an oven-dried flask was added $PdCl_2(CH_3CN)_2$ (520 mg, 2 mmol, 1.0 equiv.) and anhydrous acetonitrile (20 mL). With rapid stirring, **L1** (1.1 g, 4 mmol, 2.0 equiv.) was added potion-wise. The flask was capped under argon and placed into an 80 °C preheated oil bath for 30 min with vigorously stirring, during which period an orange precipitate formed. The precipitate was filtered through a sintered glass frit, washed with pentane (3 × 8 mL), and dried under reduced pressure to afford a yellow solid (2.7 g, 85%). *Alternative procedure:* To an oven-dried vial was added $PdCl_2$(COD) (28.6 mg, 0.1 mmol, 1.0 equiv.) and anhydrous THF (5 mL). With rapid stirring, Cy*Phine (110.8 mg, 0.2 mmol, 2.0 equiv.) was added. The vial was capped under nitrogen and stirred vigorously at room temperature overnight. The solvent was removed *in vacuo* and pentane (10 mL) was added. The yellow solid precipitates out immediately and was filtered through a sintered glass frit, washed with pentane (3 × 5 mL), and dried under reduced pressure to afford a yellow powder (111 mg, 85%). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 45.28 ppm. Anal. Calcd. for $C_{78}H_{107}Cl_2P_2Pd$: C 73.02, H 8.33; found C 72.98, H 8.25. HRMS (ESI) calcd for $C_{78}H_{107}Cl_2NaP_2Pd^+$ $(M+Na)^+$, 1303.6079, found: 1303.6082. The ^{1}H and ^{13}C NMR spectra displayed very broad resonances, which were unassignable.

$PdCl_2$(Cy*Phine-CF_3)$_2$ (P2)



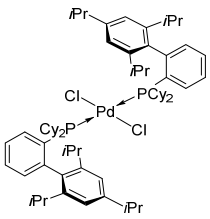
Synthesized according to the same procedure to $PdCl_2$(Cy*Phine)$_2$ and starting from Cy*Phine-CF_3 (400 mg, 0.66 mmol) as a ligand to afford the complex $PdCl_2$(Cy*Phine-CF_3)$_2$ (0.37 g, 80%) as a yellow powder. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 45.28 ppm. Anal. Calcd. for $C_{80}H_{104}Cl_2F_6P_2Pd$: C 67.22, H 7.39; found C 68.00, H 7.19. HRMS (ESI) calcd for $C_{80}H_{104}Cl_2F_6NaP_2Pd^+$ $(M+Na)^+$, 1439.5827, found: 1439.5851. The ^{1}H and ^{13}C NMR spectra displayed very broad resonances, which were unassignable.

$PdCl_2$(Cy*Phine-*n*Bu)$_2$ (P3)



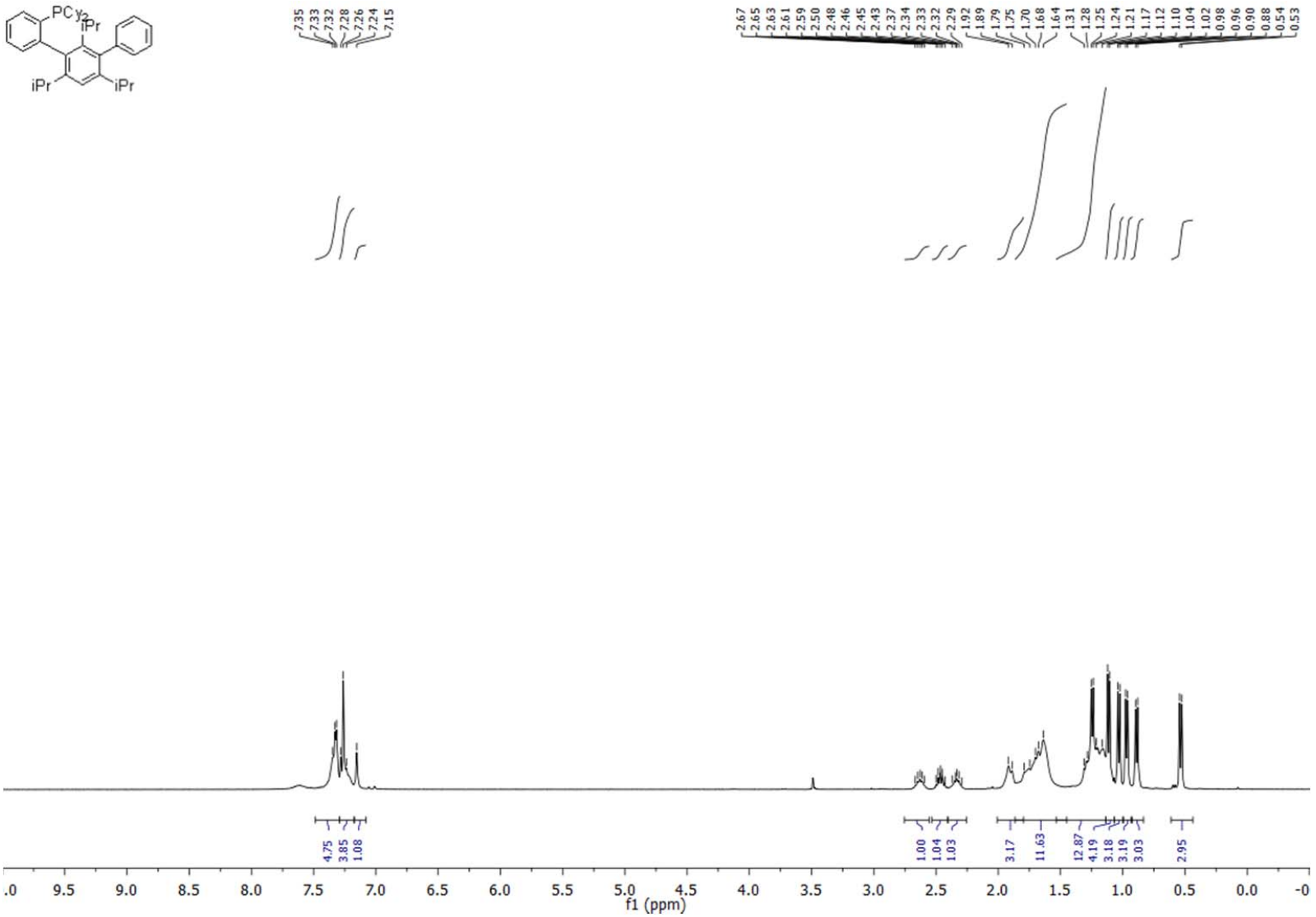
Synthesized according to the same procedure to $PdCl_2$(Cy*Phine)$_2$ and starting from Cy*Phine-*n*Bu (200 mg, 0.32 mmol) as a ligand to afford the complex $PdCl_2$(Cy*Phine-*n*Bu)$_2$ (0.18 g, 80%) as a yellow powder. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 45.31 ppm. Anal. Calcd. for $C_{86}H_{122}Cl_2P_2Pd$: C 74.04, H 8.81; found C 73.63, H 8.52. HRMS (ESI) calcd for $C_{86}H_{122}Cl_2NaP_2Pd^+$ $(M+Na)^+$, 1415.7331, found: 1415.7316. The ^{1}H and ^{13}C NMR spectra displayed very broad resonances, which were unassignable.

$PdCl_2$(XPhos)$_2$ (P4)

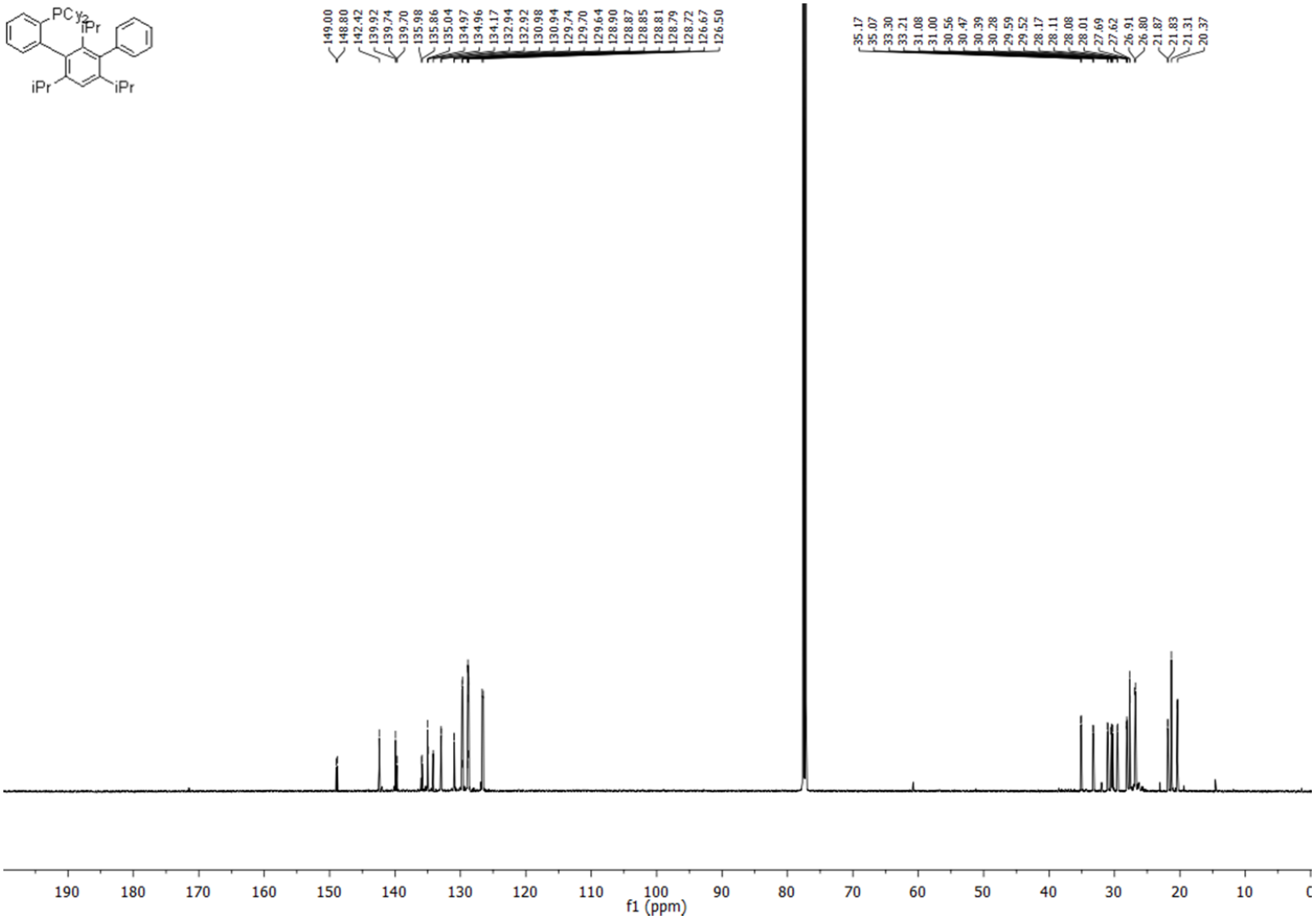


Synthesized according to the same procedure to **P1** and starting from XPhos (0.95 g, 2 mmol) as a ligand to afford the complex $PdCl_2$(XPhos)$_2$ (0.92 g, 81%) as yellow powder. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 45.32 ppm. Anal. Calcd. for $C_{66}H_{98}Cl_2P_2Pd$: C 70.10, H 8.74; found C 69.52, H 8.34. HRMS (ESI) calcd for $C_{66}H_{98}Cl_2NaP_2Pd^+$ $(M+Na)^+$, 1151.5453, found: 1151.5516. The ^{1}H and ^{13}C NMR spectra displayed very broad resonances, which were unassignable.

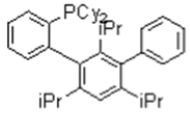
^{1}H NMR spectrum of ligand Cy*Phine (**L1**)



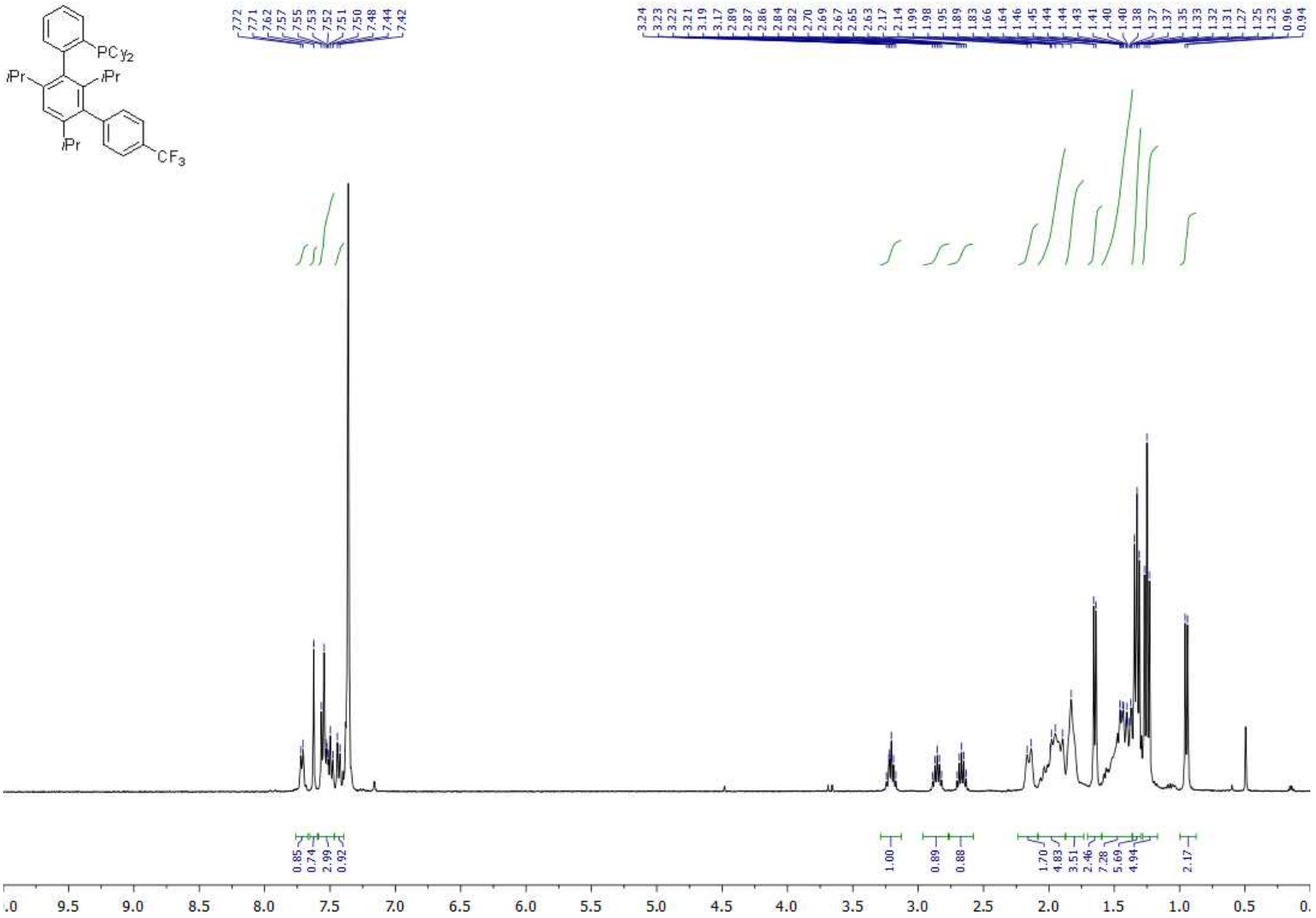
^{13}C NMR spectrum of ligand Cy*Phine (**L1**)



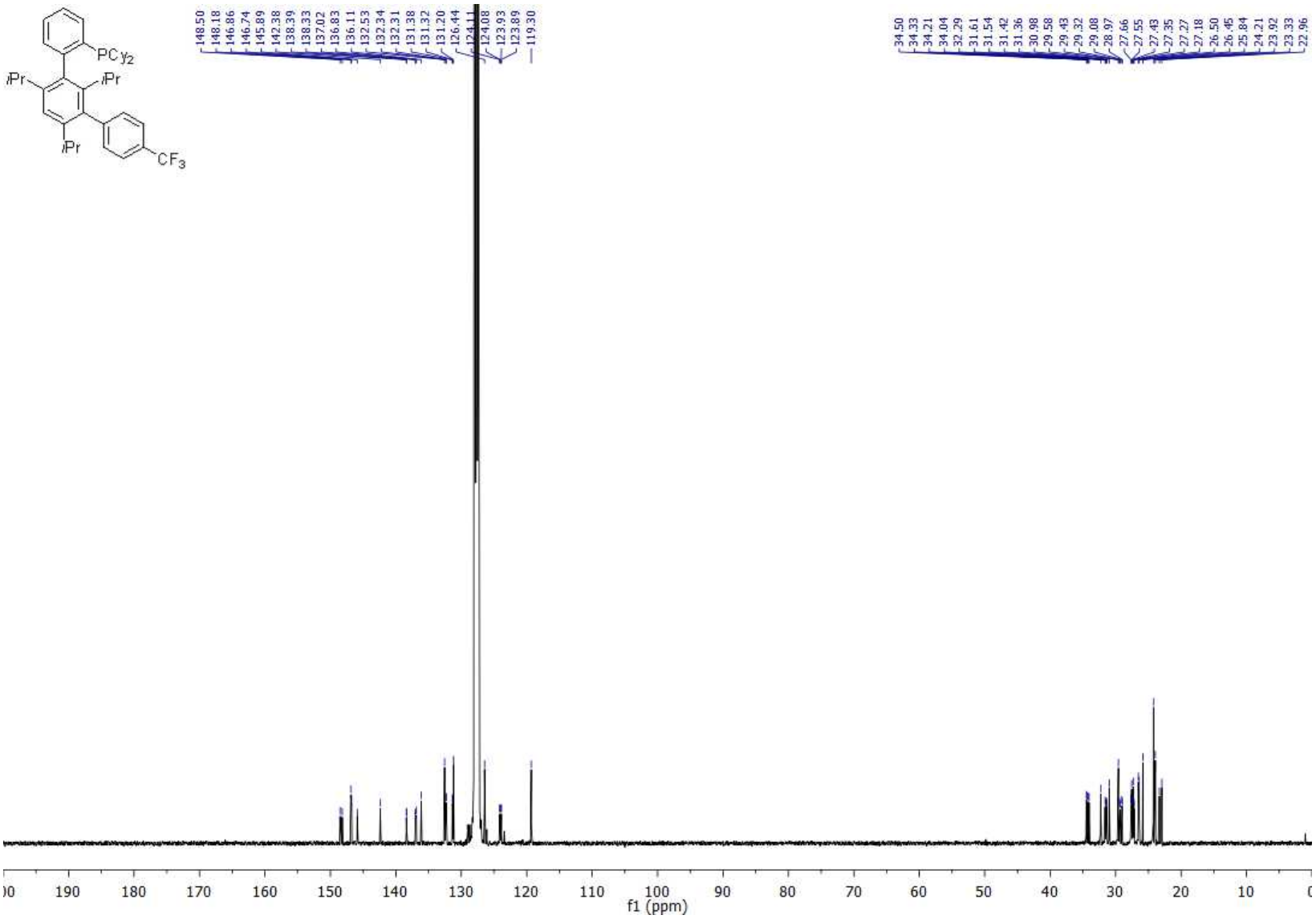
^{31}P NMR spectrum of ligand Cy*Phine (**L1**)



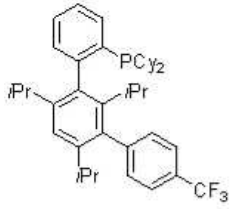
^{1}H NMR spectrum of ligand Cy*Phine-CF_3 (**L2**)



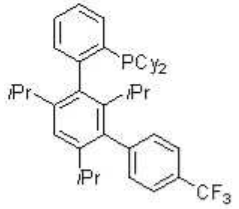
^{13}C NMR spectrum of ligand Cy*Phine-CF_3 (**L2**)



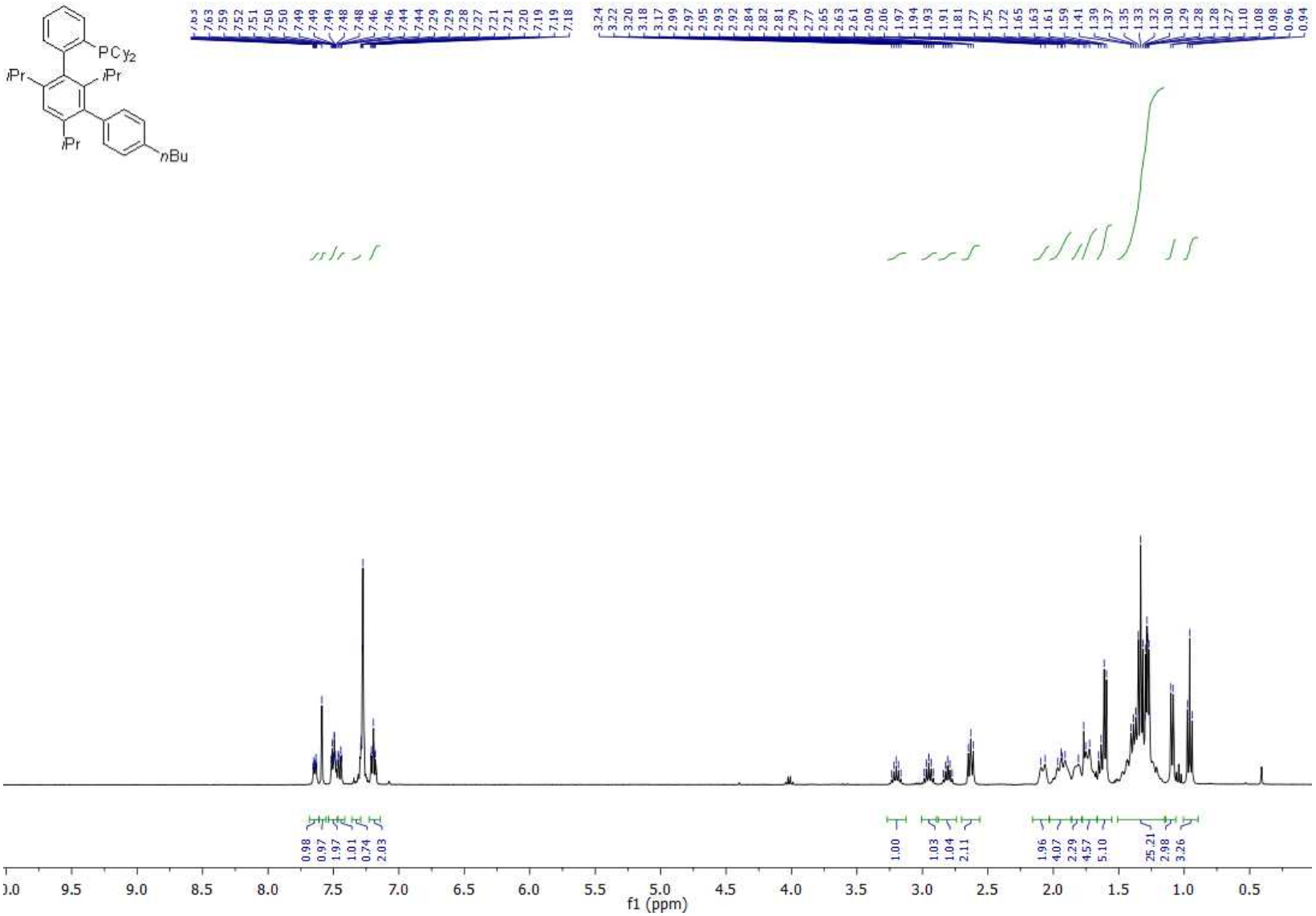
^{19}F NMR spectrum of ligand Cy*Phine-CF_3 (**L2**)



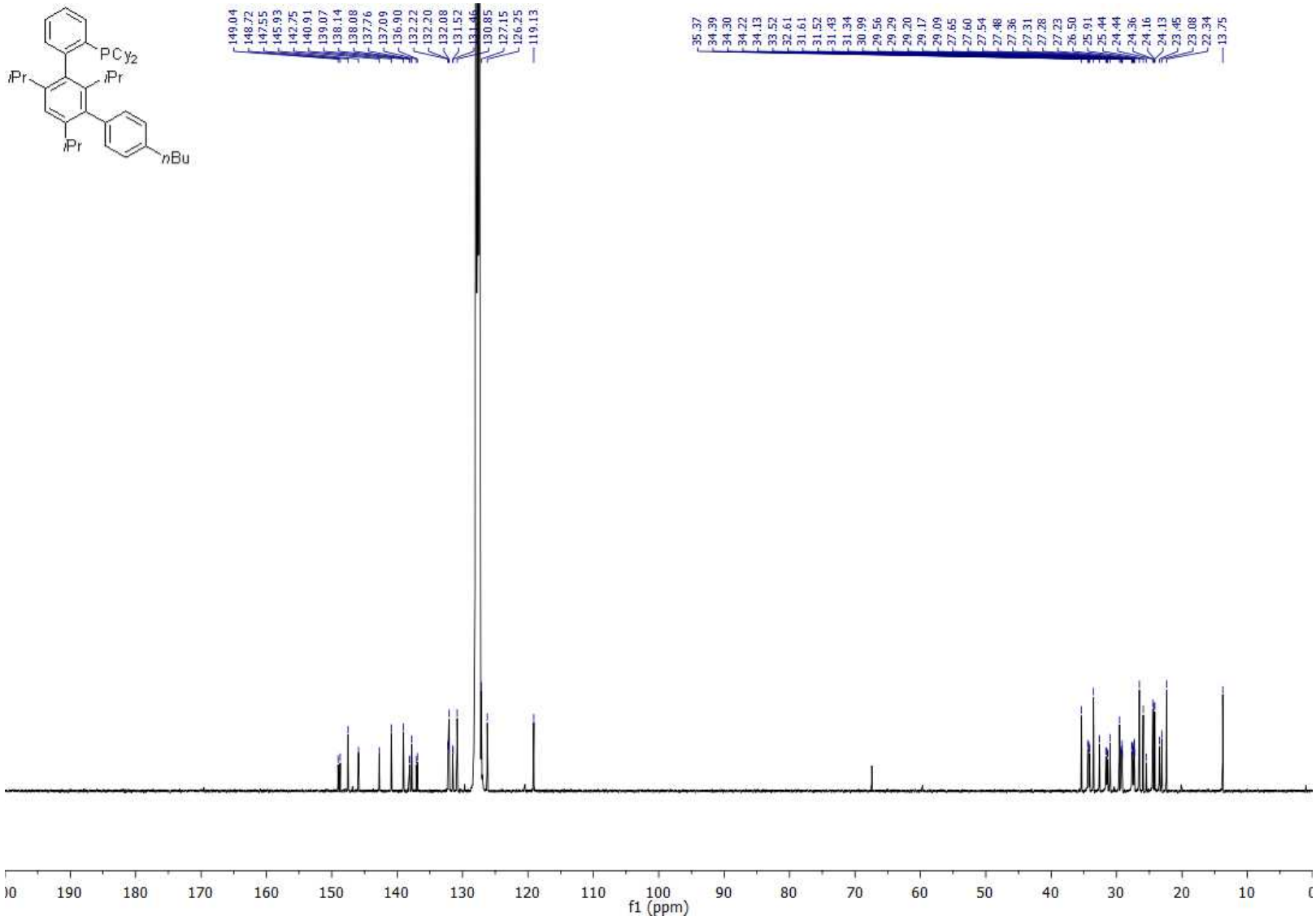
^{31}P NMR spectrum of ligand Cy*Phine-CF_3 (**L2**)



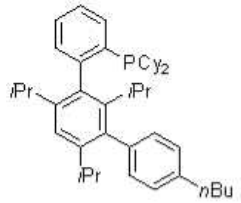
^{1}H NMR spectrum of ligand Cy*Phine-*n*Bu (**L3**)



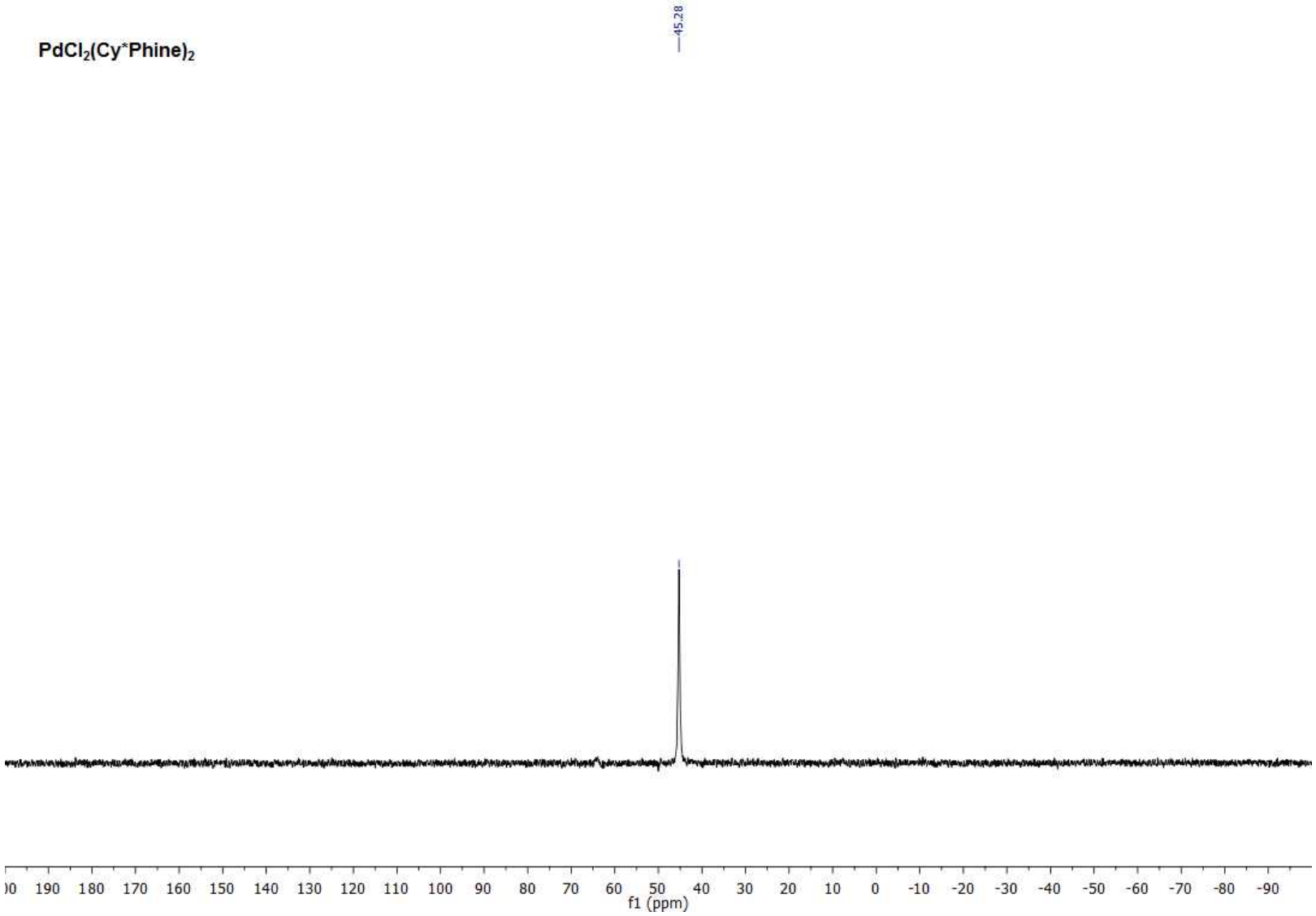
^{13}C NMR spectrum of ligand Cy*Phine-*n*Bu (**L3**)



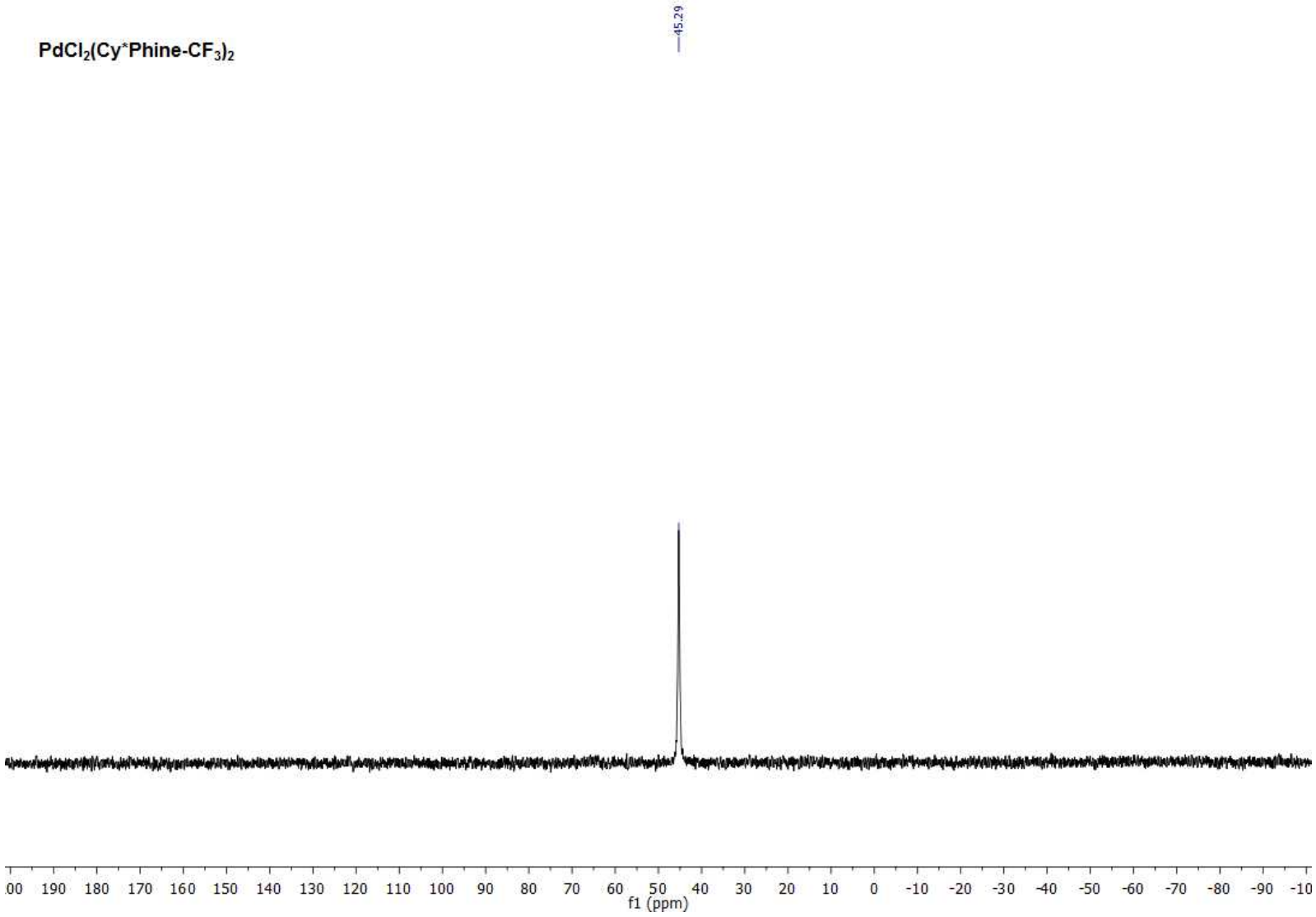
^{31}P NMR spectrum of ligand Cy*Phine-*n*Bu (**L3**)



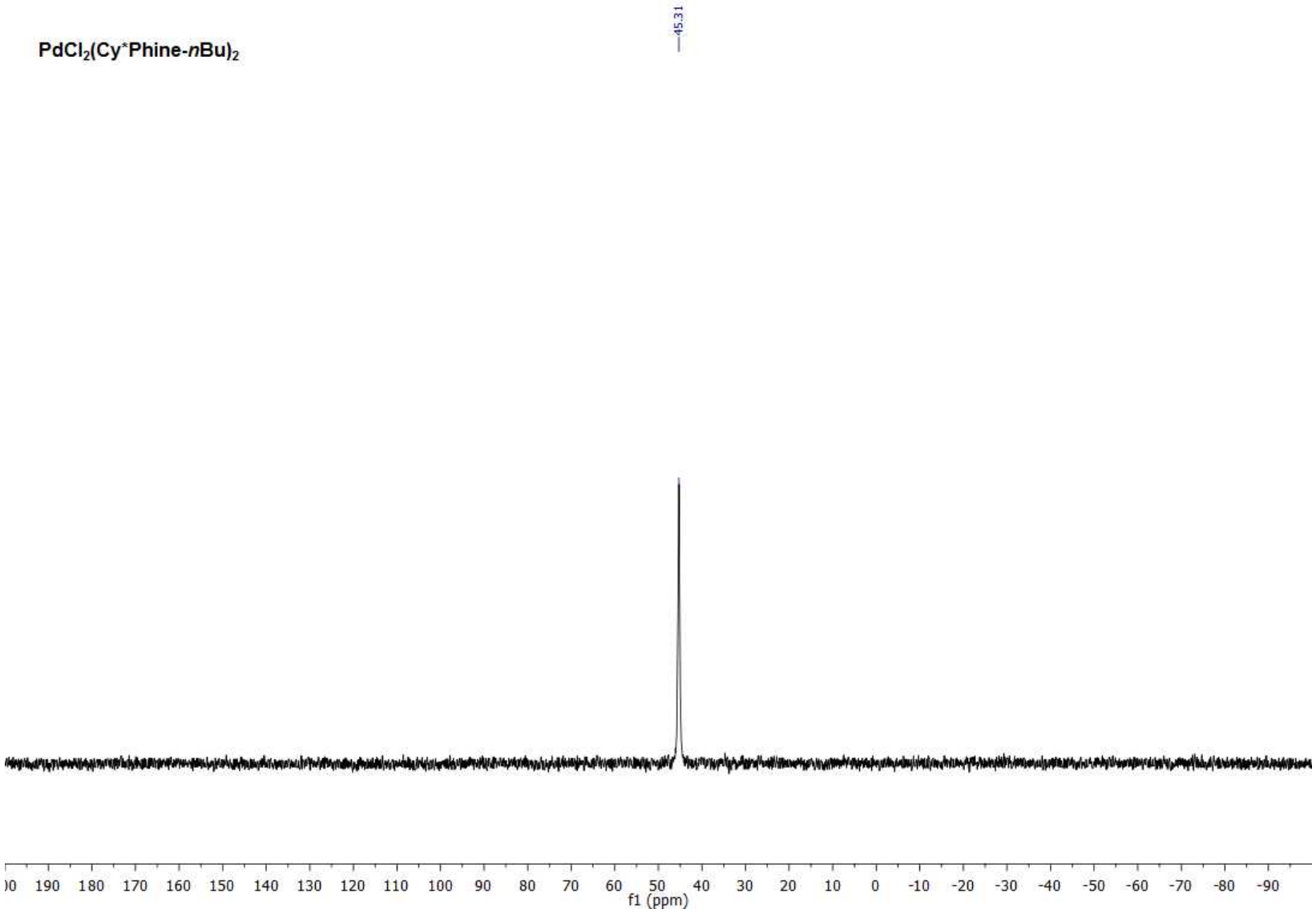
^{31}P NMR spectrum of preformed complex $PdCl_2(Cy^*Phine)_2$ (**P1**)



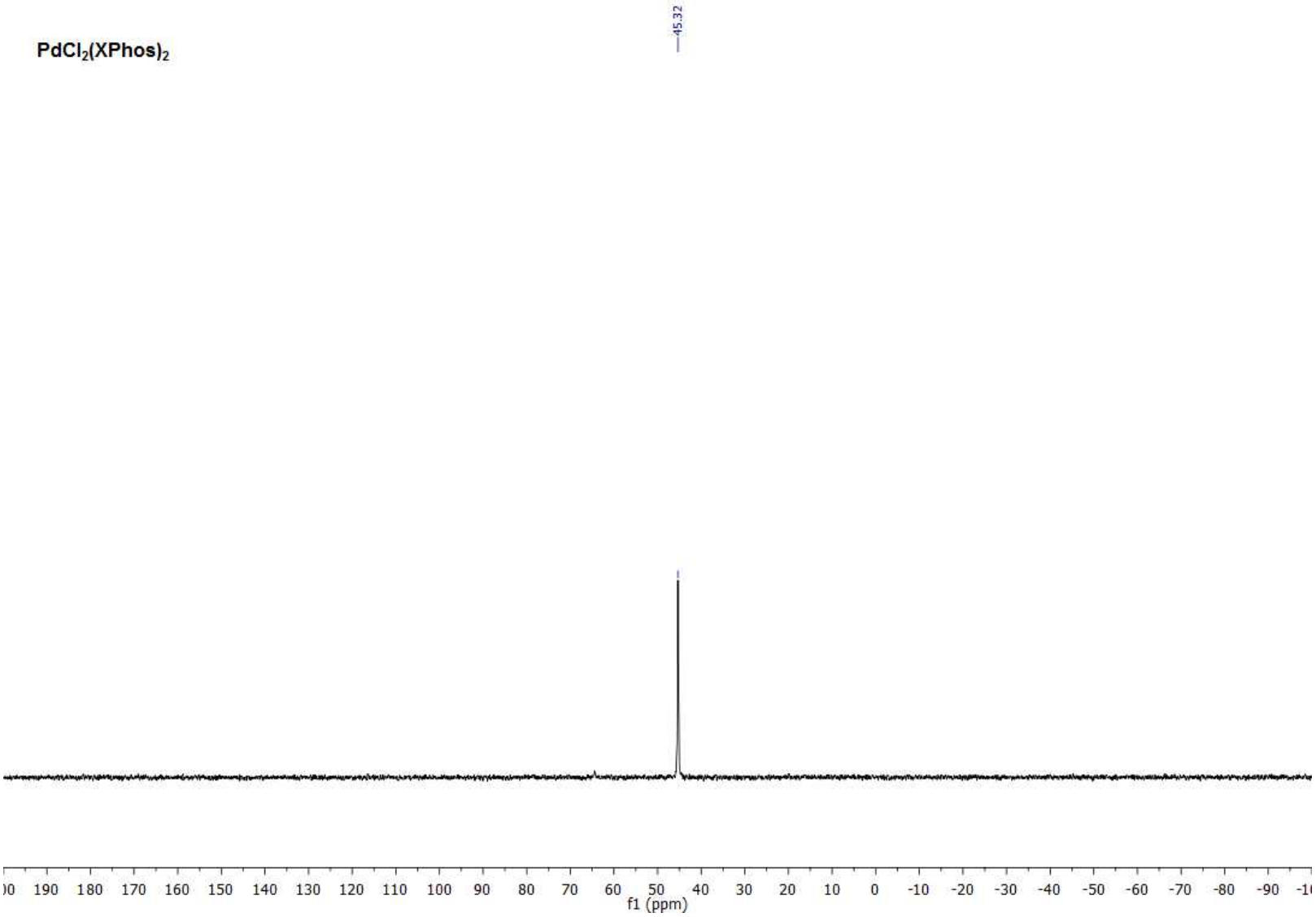
^{31}P NMR spectrum of preformed complex $PdCl_2(Cy^*Phine\text{-}CF_3)_2$ (**P2**)



^{31}P NMR spectrum of preformed complex $PdCl_2$(Cy*Phine-*n*Bu)$_2$ (**P3**)



^{31}P NMR spectrum of preformed complex $PdCl_2(XPhos)_2$ (**P4)**



4. General Procedures for Copper-Free Sonogashira Reactions

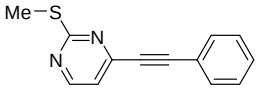
Method I:

To a sealable reaction tube equipped with a magnetic stir bar was charged with Pd catalyst (1 mol%), K_3PO_4 (212.4 mg, 1 mmol), the aryl chloride (0.5 mmol), the terminal alkyne (0.6 mmol) and MeCN (1 mL). The tube was then crimp-sealed with a cap fitted with a Teflon-lined septum and heated to 90 °C for 6 h with vigorous stirring. The mixture was cooled to room temperature, diluted with EtOAc and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* affording the crude product which was purified by flash chromatography on silica gel.

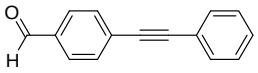
Method II:

To a sealable reaction tube equipped with a magnetic stir bar was charged with Pd catalyst (1 mol%), Et_3N (139 μL, 1 mmol), the aryl chloride (0.5 mmol), the terminal alkyne (0.6 mmol) and THF (1 mL). The tube was then crimp-sealed with a cap fitted with a Teflon-lined septum and heated to 60 °C for 12 h with vigorous stirring. The mixture was cooled to room temperature, diluted with EtOAc and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* affording the crude product which was purified by flash chromatography on silica gel.

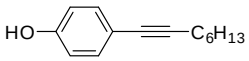
5. Characterization Substrates in Manuscript



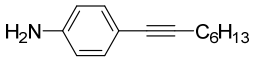
4-(methylthio)-2-(phenylethynyl)pyrimidine (3a). Following general Method I, 80 mg (0.5 mmol) of 2-chloro-4-(methylthio)pyrimidine and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellow solid (107 mg, 95%) using 1:25 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.50 (s, 1 H), 7.64–7.59 (m, 2 H), 7.45–7.36 (m, 3 H), 7.11 (d, *J* = 4.8 Hz, 1 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.19, 156.97, 150.89, 132.39, 129.90, 128.52, 121.17, 118.47, 93.80, 86.79, 14.18 ppm. HRMS (ESI) calcd for $C_{13}H_{11}N_2S^+$ $(M+H)^+$, 227.0565, found: 227.0647.



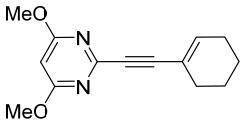
4-(phenylethynyl)benzaldehyde (3b). Following general Method I, 70 mg (0.5 mmol) of 4-chlorobenzaldehyde and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellowish-brown solid (64 mg, 82%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.04 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2 H), 7.61–7.50 (m, 2 H), 7.44–7.35 (m, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 192.18, 192.17, 136.15, 132.86, 132.54, 130.36, 130.34, 129.73, 129.23, 123.24, 94.21, 89.27 ppm. HRMS (ESI) calcd for $C_{15}H_{11}O^+$ $(M+H)^+$, 207.0732, found: 207.0832.



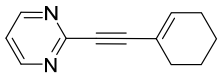
4-(oct-1-yn-1-yl)phenol (3c). Following general Method I, 64.0 mg (0.5 mmol) of 4-chlorophenol and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a yellow oil (92.0 mg, 91%) using 5:1 hexanes:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.7 Hz, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 5.26 (s, 1 H), 2.40 (t, *J* = 7.1 Hz, 2 H), 1.60 (p, *J* = 7.2 Hz, 2 H), 1.49–1.40 (m, 2 H), 1.37–1.29 (m, 2 H), 0.92 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.98, 133.07, 116.39, 115.30, 88.89, 80.14, 31.40, 28.83, 28.65, 22.61, 19.41, 14.12 ppm. HRMS (ESI) calcd for $C_{14}H_{19}O^+$ $(M+H)^+$, 203.1358, found: 203.2079.



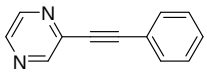
4-(oct-1-yn-1-yl)aniline (3d). Following general Method I, 63.5 mg (0.5 mmol) of 4-chloroaniline and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a yellow oil (82.4 mg, 82%) using 10:1 hexanes:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.5 Hz, 2 H), 6.60 (d, *J* = 8.6 Hz, 2 H), 3.51 (s, 2 H), 2.39 (t, *J* = 7.2 Hz, 2 H), 1.60 (p, *J* = 7.2 Hz, 2 H), 1.53–1.42 (m, 2 H), 1.33 (t, 7.8 Hz, 2 H), 0.92 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.85, 132.72, 114.77, 113.62, 87.93, 80.72, 31.43, 28.95, 28.66, 22.62, 19.46, 14.14 ppm. HRMS (ESI) calcd for $C_{14}H_{20}N^+$ $(M+H)^+$, 202.1517, found: 202.2671.



2-(cyclohex-1-en-1-ylethynyl)-4,6-dimethoxypyrimidine (3e). Following general Method I, 87 mg (0.5 mmol) of 2-chloro-4,6-dimethoxypyrimidine and 64 mg (0.6 mmol) of 1-ethynylcyclohex-1-ene afforded the title compound as a pale yellow solid (92 mg, 75%) using 1:25 ethyl acetate:hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.54–6.28 (m, 1 H), 5.97 (s, 1 H), 3.96 (s, 6 H), 2.35–2.02 (m, 4 H), 1.78–1.36 (m, 4 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.05, 151.52, 139.01, 119.63, 89.55, 88.72, 85.90, 54.25, 28.60, 25.90, 22.14, 21.33 ppm. HRMS (ESI) calcd for $C_{14}H_{17}N_2O_2^+$ $(M+H)^+$, 245.1212, found: 245.1287.

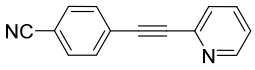


2-(cyclohex-1-en-1-ylethynyl)pyrimidine (3f). Following general Method I, 57 mg (0.5 mmol) of 2-chloropyrimidine and 64 mg (0.6 mmol) of 1-ethynylcyclohex-1-ene afforded the title compound as a brown oil (80 mg, 87%) using 7:3 hexane:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 5.0 Hz, 2 H), 7.18 (s, 1 H), 6.46 (d, *J* = 2.0 Hz, 1 H), 2.33–2.05 (m, 4 H), 1.65 (ddd, *J* = 31.1, 4.9, 1.9 Hz, 4 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.18, 153.61, 139.64, 119.57, 119.18, 90.36, 85.76, 28.55, 25.96, 22.10, 21.27 ppm. HRMS (ESI) calcd for $C_{12}H_{13}N_2^+$ $(M+H)^+$, 185.1000, found: 185.1080.

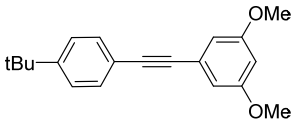


2-(phenylethynyl)pyrazine (3g). Following general Method I, 57 mg (0.5 mmol) of 2-chloropyrazine and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a

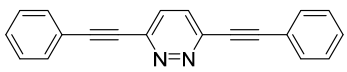
yellow oil (89 mg, 99%) using 1:5 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 1.6 Hz, 1 H), 8.60 (dd, *J* = 2.6, 1.6 Hz, 1 H), 8.51 (d, *J* = 2.6 Hz, 1 H), 7.67–7.61 (m, 2 H), 7.46–7.36 (m, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 147.76, 144.45, 142.79, 140.41, 132.17, 129.60, 128.53, 121.49, 93.34, 85.80 ppm. HRMS (ESI) calcd for $C_{12}H_9N_2^+$ $(M+H)^+$, 181.0687, found: 181.0769.



4-(pyridin-2-ylethynyl)benzonitrile (3h). Following general Method I, 68.5 mg (0.5 mmol) of 4-chlorobenzonitrile and 62 mg (0.6 mmol) of 2-ethynylpyridine afforded the title compound as a pale yellow solid (82 mg, 80%) using 4:1 hexanes:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.70–8.61 (m, 1 H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.71–7.63 (m, 4 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.32 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.25, 142.43, 136.57, 132.58, 132.18, 127.59, 127.15, 123.63, 118.43, 112.33, 92.31, 87.28 ppm. HRMS (ESI) calcd for $C_{14}H_9N_2^+$ $(M+H)^+$, 205.0687, found: 205.0754.

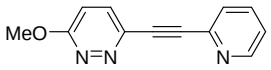


1-((4-(tert-butyl)phenyl)ethynyl)-3,5-dimethoxybenzene (3i). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 97.2 mg (0.6 mmol) of 1-ethynyl-3,5-dimethoxybenzene afforded the title compound as a yellow solid (135 mg, 92%) using 97:3 hexane:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 1.1 Hz, 2 H), 7.41 (d, *J* = 1.1 Hz, 2 H), 6.72 (dd, *J* = 2.4, 1.5 Hz, 2 H), 6.49 (q, *J* = 1.1 Hz, 1 H), 3.83 (s, 6 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.52, 151.64, 131.38, 125.36, 124.80, 120.05, 105.50 (d, *J* = 1152.4 Hz), 89.14, 88.74, 55.43, 34.81, 31.19 ppm. HRMS (ESI) calcd for $C_{20}H_{23}O_2^+$ $(M+H)^+$, 295.1620, found: 295.1782.

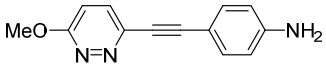


3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine (3j). Following general Method II, 74.5 mg (0.5 mmol) of 3,6-dichloropyridazine and 122.8 mg (1.2 mmol) of phenylacetylene afforded the title compound as a yellow solid (118 mg, 84%) using 5:1 hexane:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 1.5 Hz, 2 H), 7.63 (d, *J* = 1.8 Hz, 2 H), 7.60 (s, 2 H), 7.43–7.37 (m, 6 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.82, 132.20, 129.75,

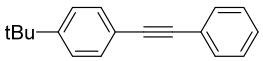
128.86, 128.55, 121.41, 95.49, 85.97 ppm. HRMS (ESI) calcd for $C_{20}H_{13}N_2^+$ $(M+H)^+$, 281.1000, found: 281.1843.



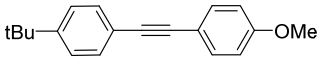
3-methoxy-6-(pyridin-2-ylethynyl)pyridazine (3k). Following general Method II, 72 mg (0.5 mmol) of 3-chloro-6-methoxypyridazine and 62 mg (0.6 mmol) of 2-ethynlpyridine afforded the title compound as a yellow solid (64 mg, 60%) using 3:2 ethyl acetate:hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.65 (s, 1 H), 7.77–7.68 (m, 1 H), 7.66–7.54 (m, 2 H), 7.31 (ddd, *J* = 6.6, 3.3, 1.7 Hz, 1 H), 7.03–6.90 (m, 1 H), 4.18 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.66, 150.19, 143.02, 142.32, 136.37, 132.67, 127.80, 123.61, 116.61, 90.67, 85.03, 55.18, 55.16 ppm. HRMS (ESI) calcd for $C_{12}H_{10}N_3O^+$ $(M+H)^+$, 212.0746, found: 212.0828.



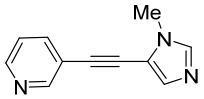
4-{(6-methoxypyridazin-3-yl)ethynyl}aniline (3l). Following general Method II, 72 mg (0.5 mmol) of 3-chloro-6-methoxypyridazine and 70.2 mg (0.6 mmol) of 4-ethynylaniline afforded the title compound as a yellow solid (101 mg, 90%) using 65:35 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 9.1 Hz, 1 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 6.94 (d, *J* = 9.1 Hz, 1 H), 6.66 (d, *J* = 8.6 Hz, 2 H), 4.17 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.15, 147.56, 144.23, 133.51, 132.20, 116.57, 114.65, 110.96, 93.43, 83.99, 54.99 ppm. HRMS (ESI) calcd for $C_{13}H_{12}N_3O^+$ $(M+H)^+$, 226.0902, found: 226.0974.



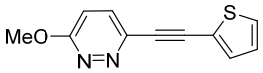
1-(*tert*-butyl)-4-(phenylethynyl)benzene (3m). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a white solid (105 mg, 90%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 7.41–7.31 (m, 5 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.83, 131.88, 131.63, 128.61, 128.36, 125.65, 123.81, 120.53, 89.83, 89.02, 35.11, 31.50 ppm. HRMS (ESI) calcd for $C_{18}H_{19}^+$ $(M+H)^+$, 235.1409, found: 235.1502.



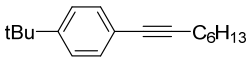
1-(*tert*-butyl)-4-{(4-methoxyphenyl)ethynyl}benzene (3n). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 73 mg (0.6 mmol) of 1-ethynyl-4-methoxybenzene afforded the title compound as a yellow solid (128 mg, 97%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (dd, *J* = 10.4, 8.7 Hz, 4 H), 7.38 (d, *J* = 8.6 Hz, 2 H), 6.89 (d, *J* = 8.9 Hz, 2 H), 3.85 (s, 3 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.47, 151.17, 133.00, 131.16, 125.31, 120.55, 115.65, 113.96, 88.65, 88.17, 55.31, 34.77, 31.20 ppm. HRMS (ESI) calcd for $C_{19}H_{21}O^+$ $(M+H)^+$, 265.1514, found: 265.1445.



3-{(1-methyl-1*H*-imidazol-5-yl)ethynyl}pyridine (3o). Following general Method I, 56.5 mg (0.5 mmol) of 3-chloropyridine and 64 mg (0.6 mmol) of 5-ethynyl-1-methyl-1*H*-imidazole afforded the title compound as a white solid (78 mg, 85%) using 1:19 Methanol: Dichloromethane as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 7.3 Hz, 1 H), 8.53 (s, 1H), 7.77 (d, *J* = 2.1 Hz, 1 H), 7.49 (s, 1 H), 7.39–7.18 (m, 1 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.73, 151.81, 148.85, 138.71, 138.09, 135.09, 123.10, 119.75, 92.95, 80.45, 32.12 ppm. HRMS (ESI) calcd for $C_{11}H_{10}N_3^+$ $(M+H)^+$, 184.0796, found: 184.0866.

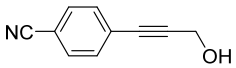


3-methoxy-6-(thiophen-2-ylethynyl)pyridazine (3p). Following general Method I, 72 mg (0.5 mmol) of 3-chloro-6-methoxypyridazine and 65 mg (0.6 mmol) of 2-ethynlthiophene afforded the title compound as a yellow solid (119 mg, 97%) using 3:7 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.47 (d, *J* = 9.1 Hz, 1 H), 7.29 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.22 (dd, *J* = 5.0, 1.2 Hz, 1 H), 6.92 (d, *J* = 9.1 Hz, 1 H), 4.12 (s, 3 H) ppm.^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.36, 143.65, 132.29, 130.48, 129.83, 125.76, 120.93, 116.66, 87.43, 85.35, 55.08 ppm. HRMS (ESI) calcd for $C_{11}H_9N_2O^+$ $(M+H)^+$, 217.0357, found: 217.0432.



1-(*tert*-butyl)-4-(oct-1-yn-1-yl)benzene (3q). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzen and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as

a yellow oil (88 mg, 95%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39–7.34 (m, 2 H), 7.34–7.31 (m, 2 H), 2.42 (ddd, *J* = 7.1, 4.2, 1.4 Hz, 2 H), 1.67–1.57 (m, 2 H), 1.52–1.44 (m, 2 H), 1.36 (d, *J* = 1.5 Hz, 4 H), 1.33 (s, 9 H), 1.03–0.87 (m, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.31, 131.98, 125.91, 121.87, 90.43, 81.30, 35.42, 32.17, 31.97, 29.59, 29.38, 23.36, 20.21, 14.85 ppm. HRMS (ESI) calcd for $C_{18}H_{27}^{+}$ $(M+H)^{+}$, 243.2035, found: 243.3124.

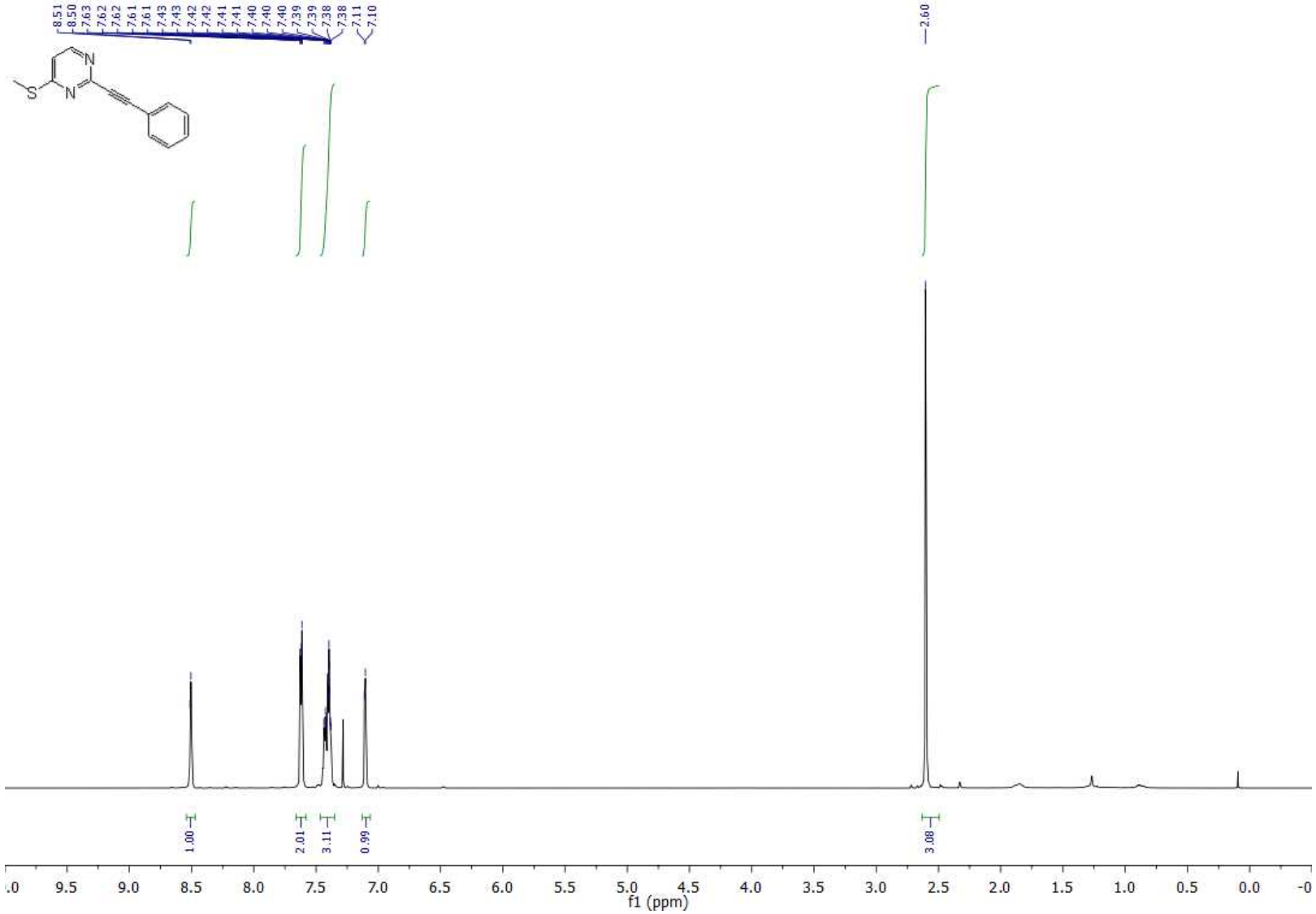


4-(3-hydroxyprop-1-yn-1-yl)benzonitrile (3r). Following general Method I, 68.5 mg (0.5 mmol) of 4-chlorobenzonitrile and 35 mg (0.6 mmol) of propargol alcohol afforded the title compound as a yellow oil (50 mg, 52%) using 4:1 petroleum ether: ethyl acetate as the column eluent. When another molar equivalent of Cy*Phine (with respect to the P1) was added, 83% yield was obtained. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.63–7.58 (m, 2 H), 7.54–7.49 (m, 2 H), 4.52 (s, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 132.33, 132.19, 127.62, 118.50, 112.08, 91.76, 84.22, 51.68 ppm. HRMS (ESI) calcd for $C_{10}H_8NO^{+}$ $(M+H)^{+}$, 158.0528, found: 158.1032.

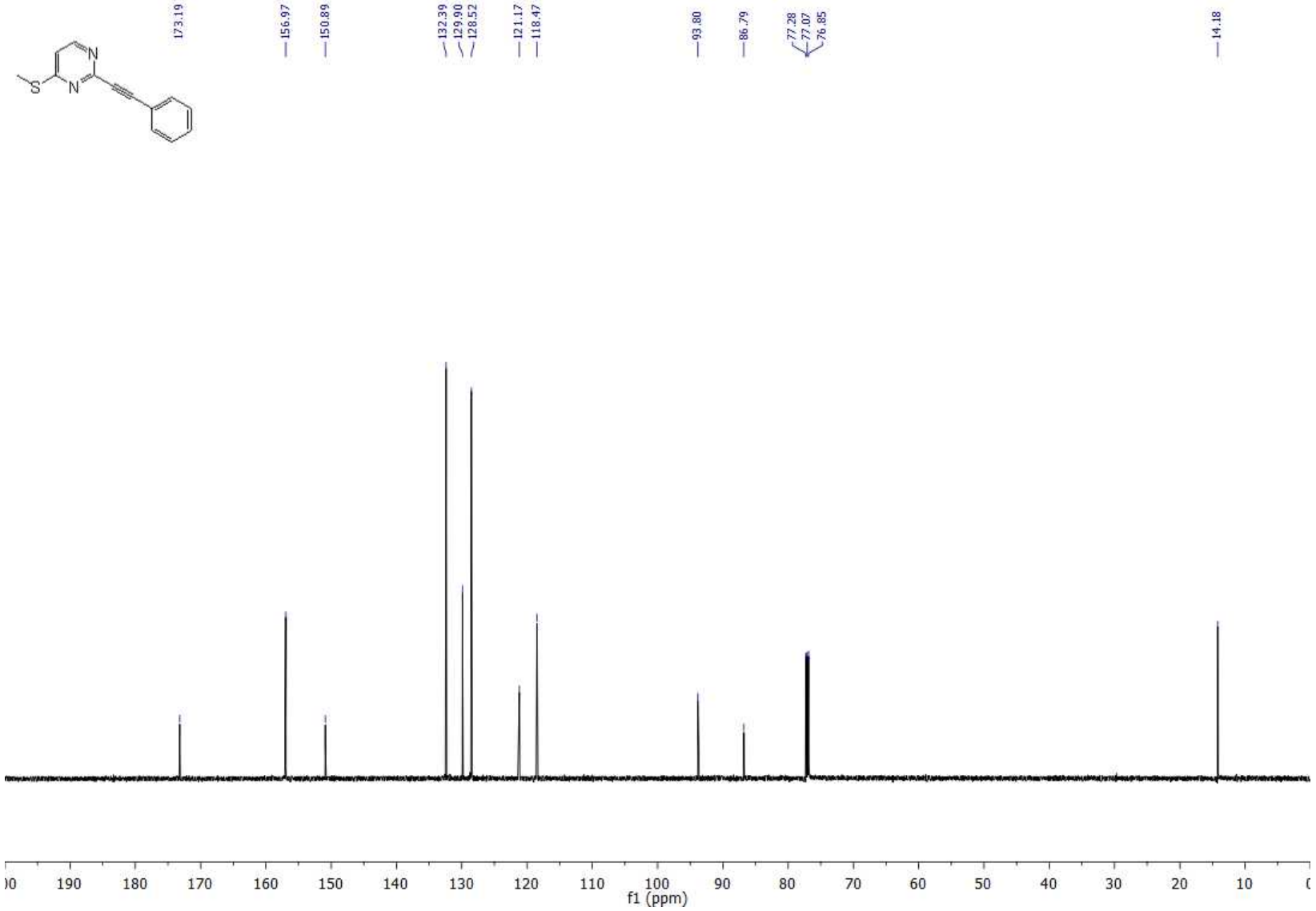
References:

1. Y. Yang, X. -Y. Chew; C. W. Johannes, E. G. Robins, H. Jong, Y. H. Lim, *Eur. J. Org. Chem.* **2014**, 7184.
2. a) S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2004**, **43**, 1871; *Angew. Chem.* **2004**, *116*, 1907; b) L.-C. Liang, P.-S. Chien, M.-H. Huang, *Organometallics* **2005**, *24*, 353; c) A. C. Tagne Kuate, S. Sameni, M. Freytag, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2013**, *52*, 8638; *Angew. Chem.* **2013**, *125*, 8800. d) S. Kajigaeshi, T. Kakinami, M. Moriwaki, T. Tanaka, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 439.
3. H. G. Lee, P. J. Milner, S. L. Buchwald, *J. Am. Chem. Soc.* **2014**, *136*, 3792.

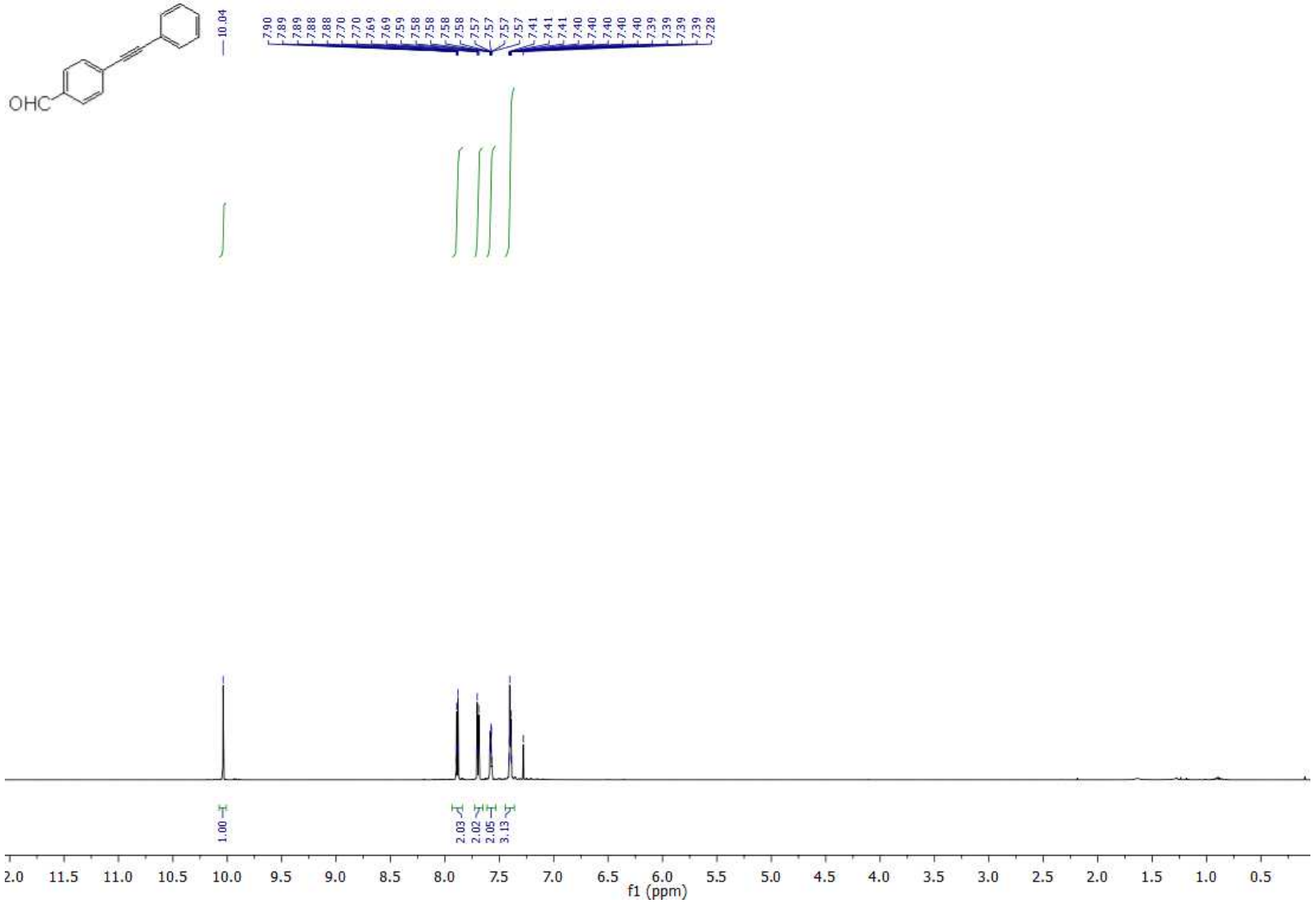
^{1}H NMR spectrum of 4-(methylthio)-2-(phenylethynyl)pyrimidine **(3a)**



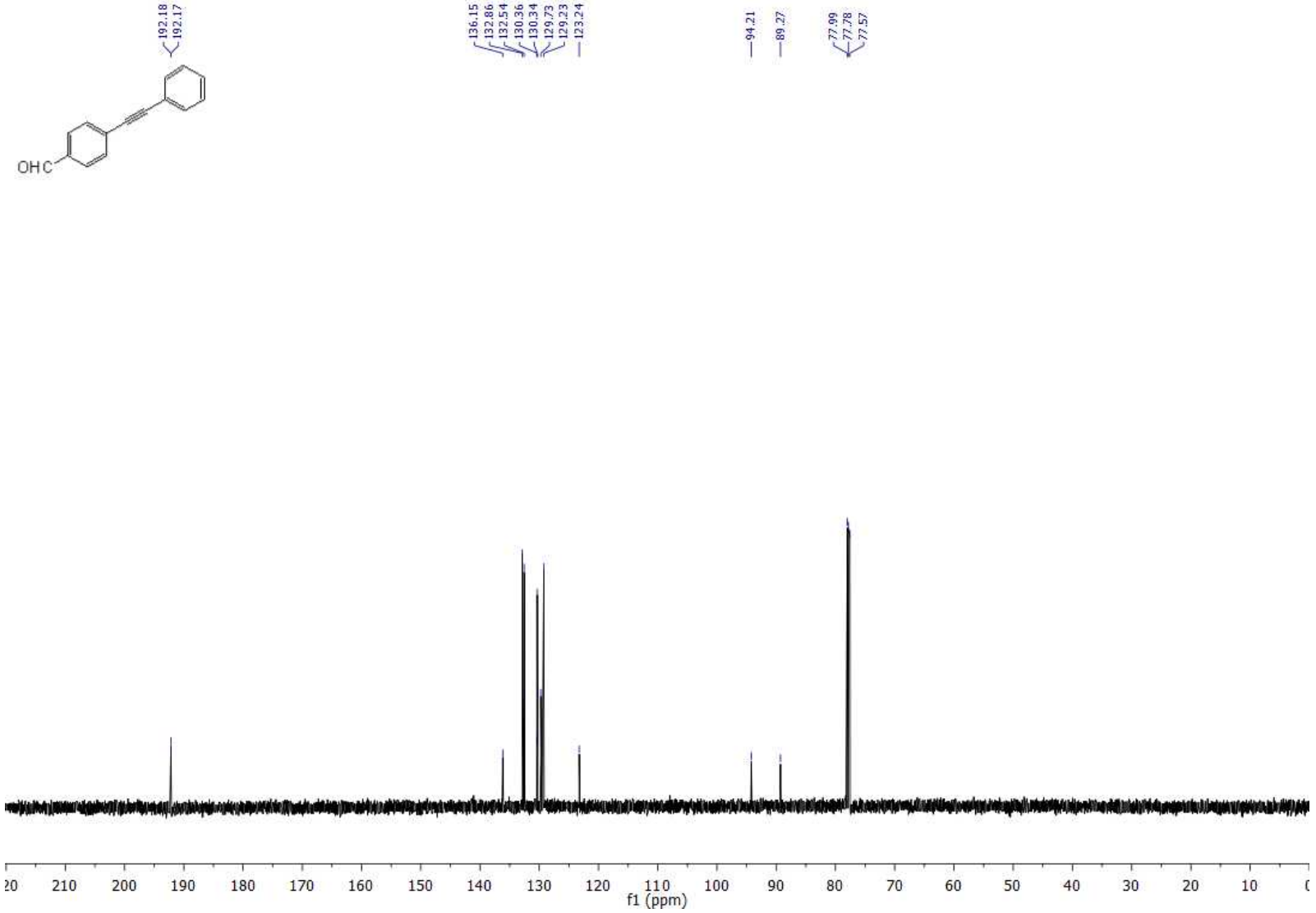
^{13}C NMR spectrum of 4-(methylthio)-2-(phenylethynyl)pyrimidine **(3a)**



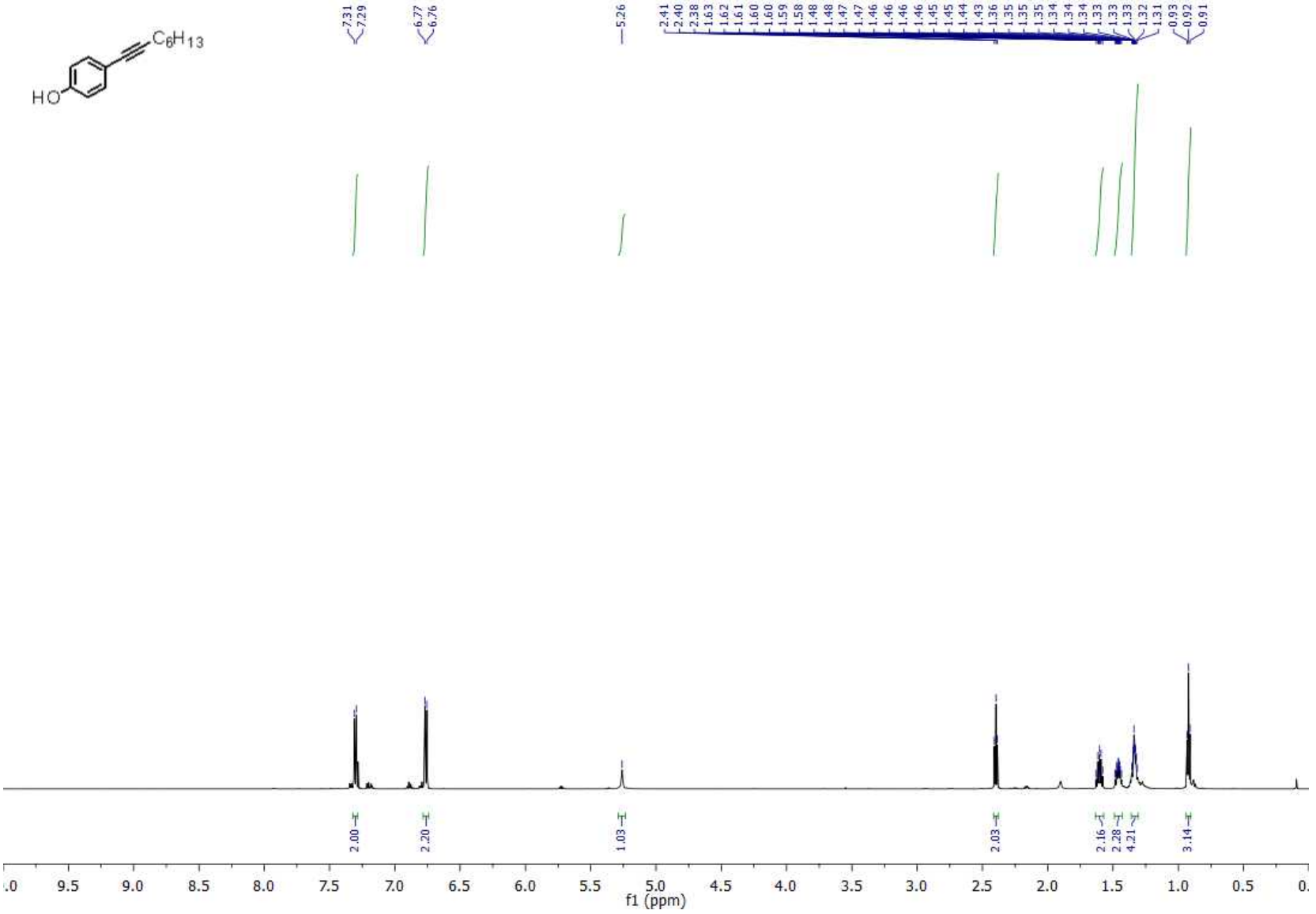
^{1}H NMR spectrum of 4-(phenylethynyl)benzaldehyde **(3b)**



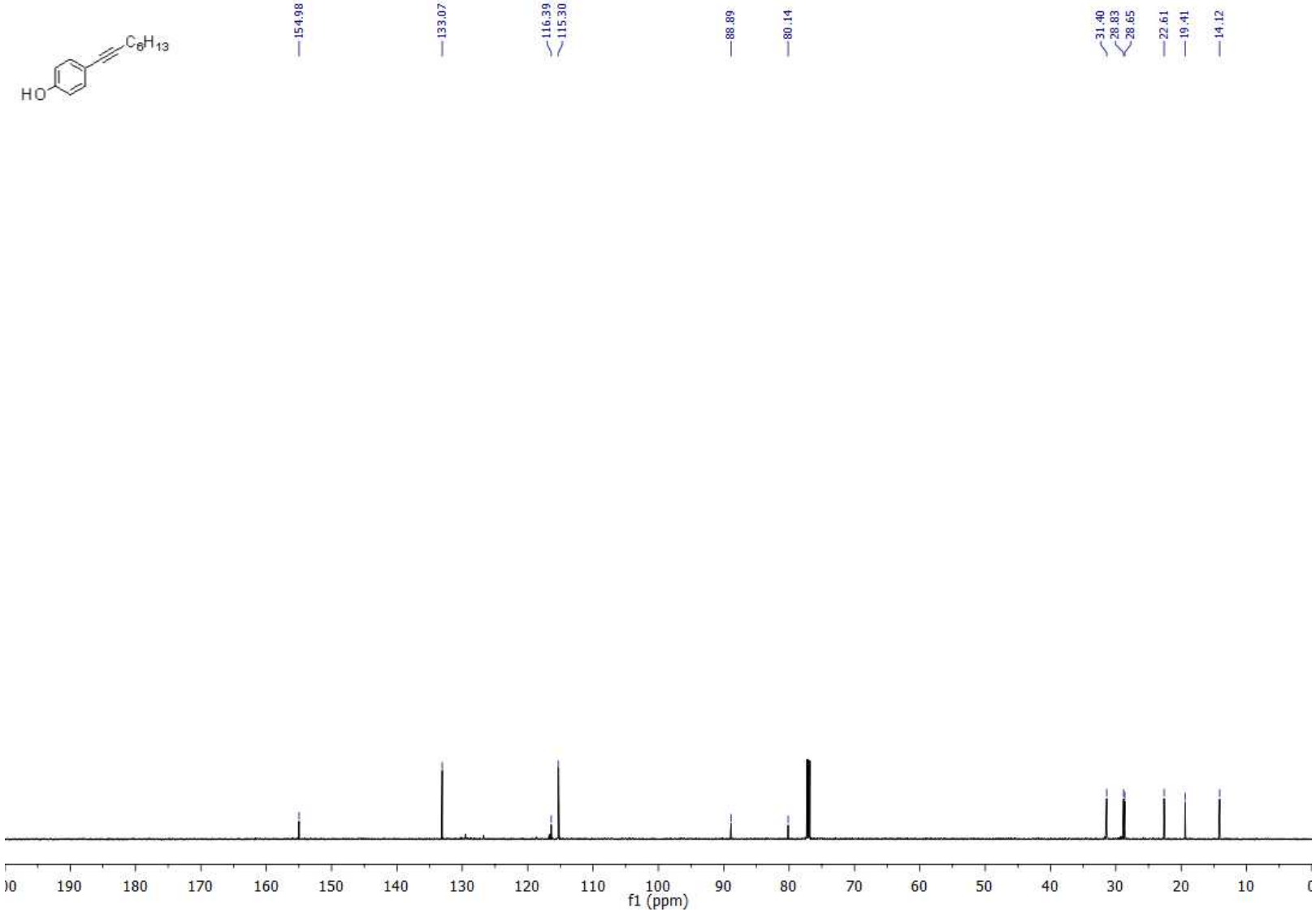
^{13}C NMR spectrum of 4-(phenylethynyl)benzaldehyde **(3b)**



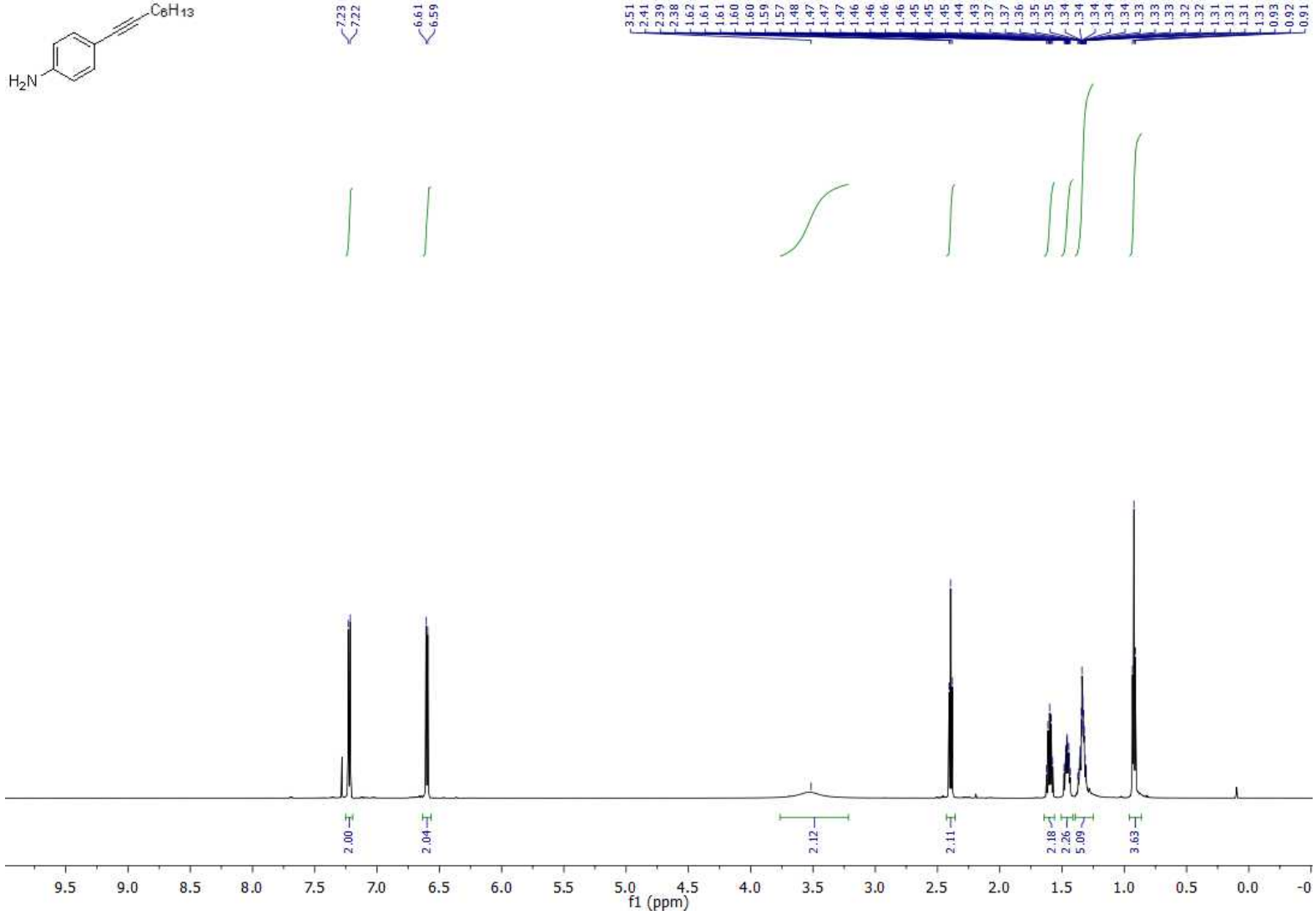
^{1}H NMR spectrum of 4-(oct-1-yn-1-yl)phenol **(3c)**



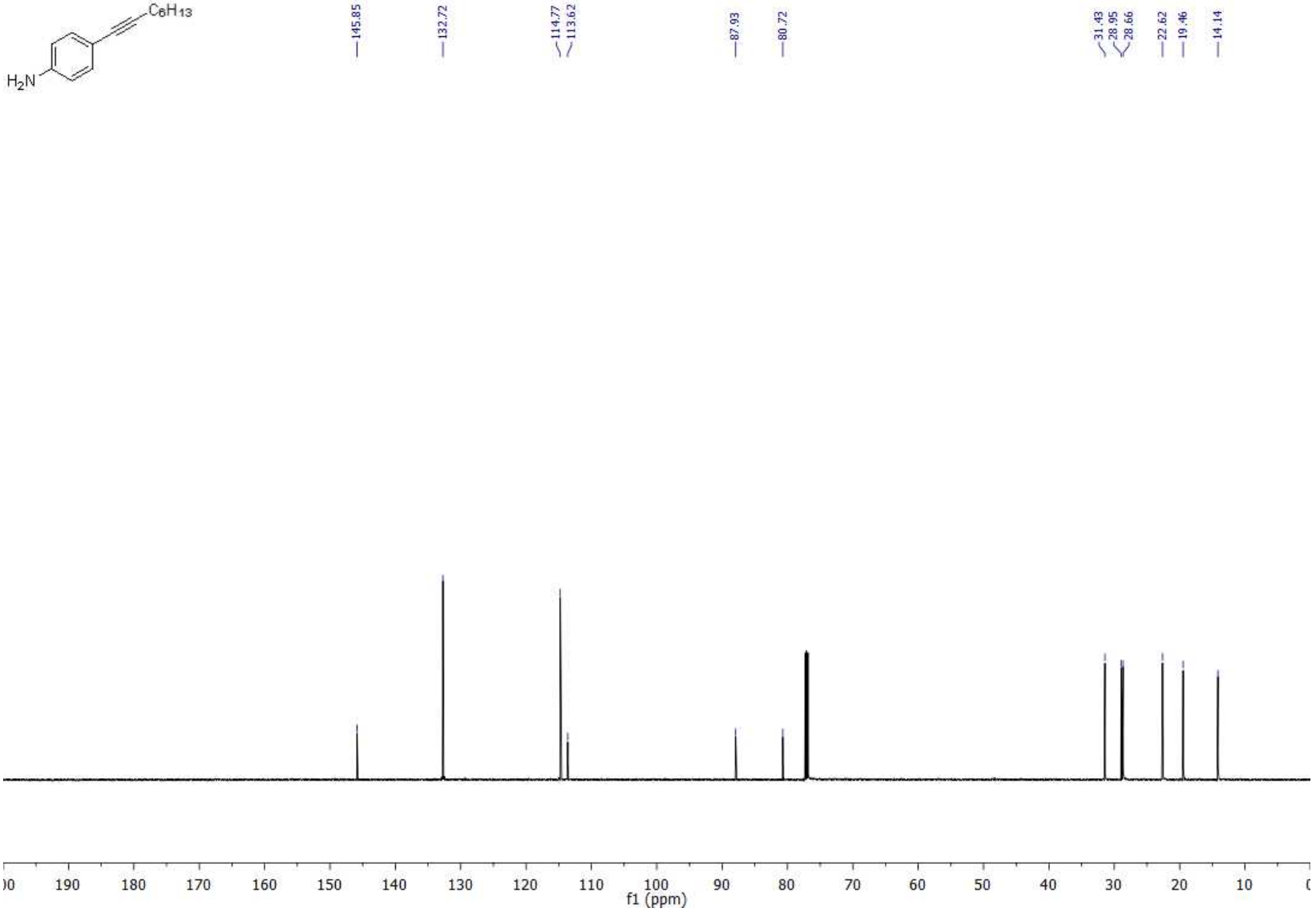
^{13}C NMR spectrum of 4-(oct-1-yn-1-yl)phenol **(3c)**



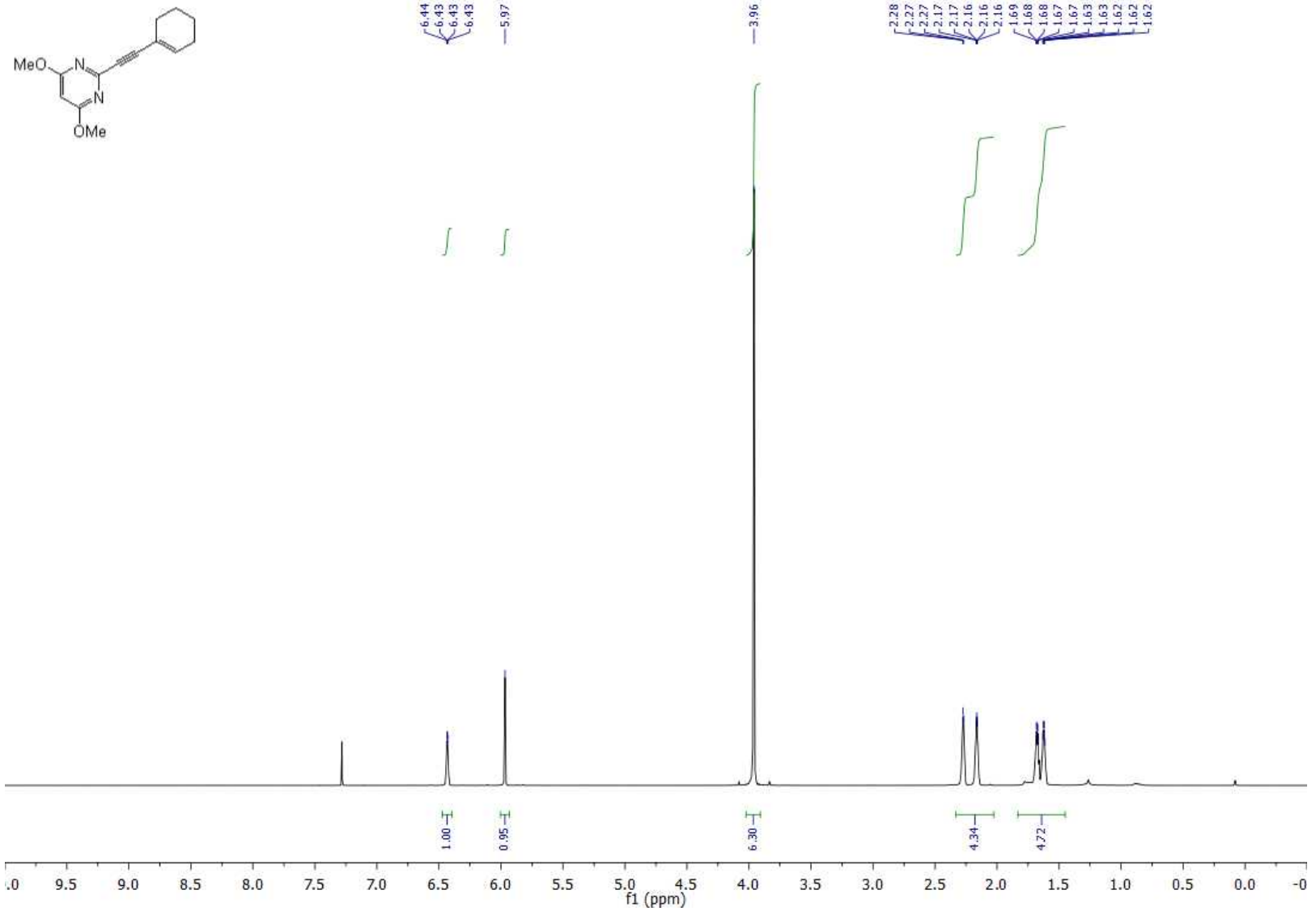
^{1}H NMR spectrum of 4-(oct-1-yn-1-yl)aniline **(3d)**



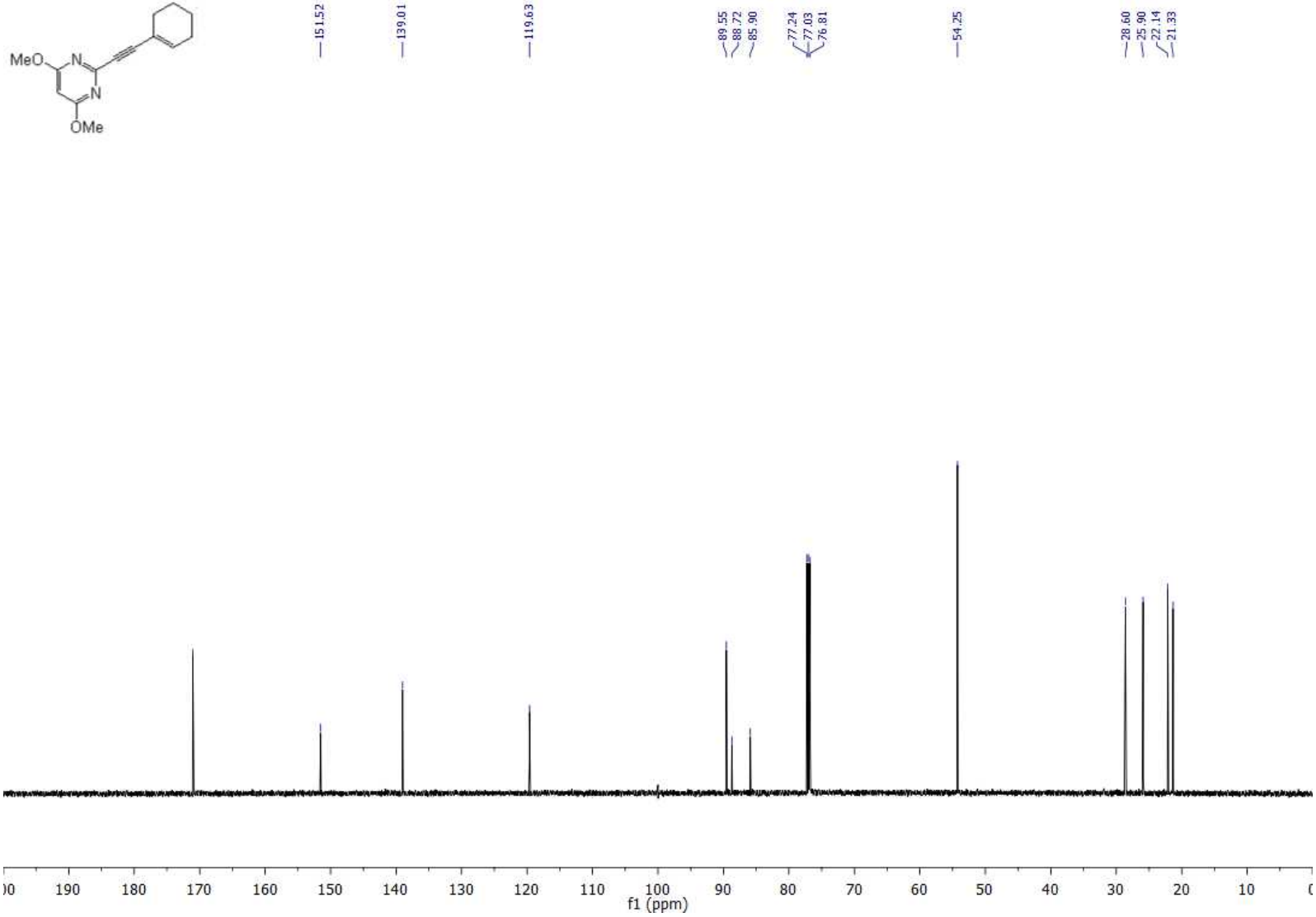
^{13}C NMR spectrum of 4-(oct-1-yn-1-yl)aniline **(3d)**



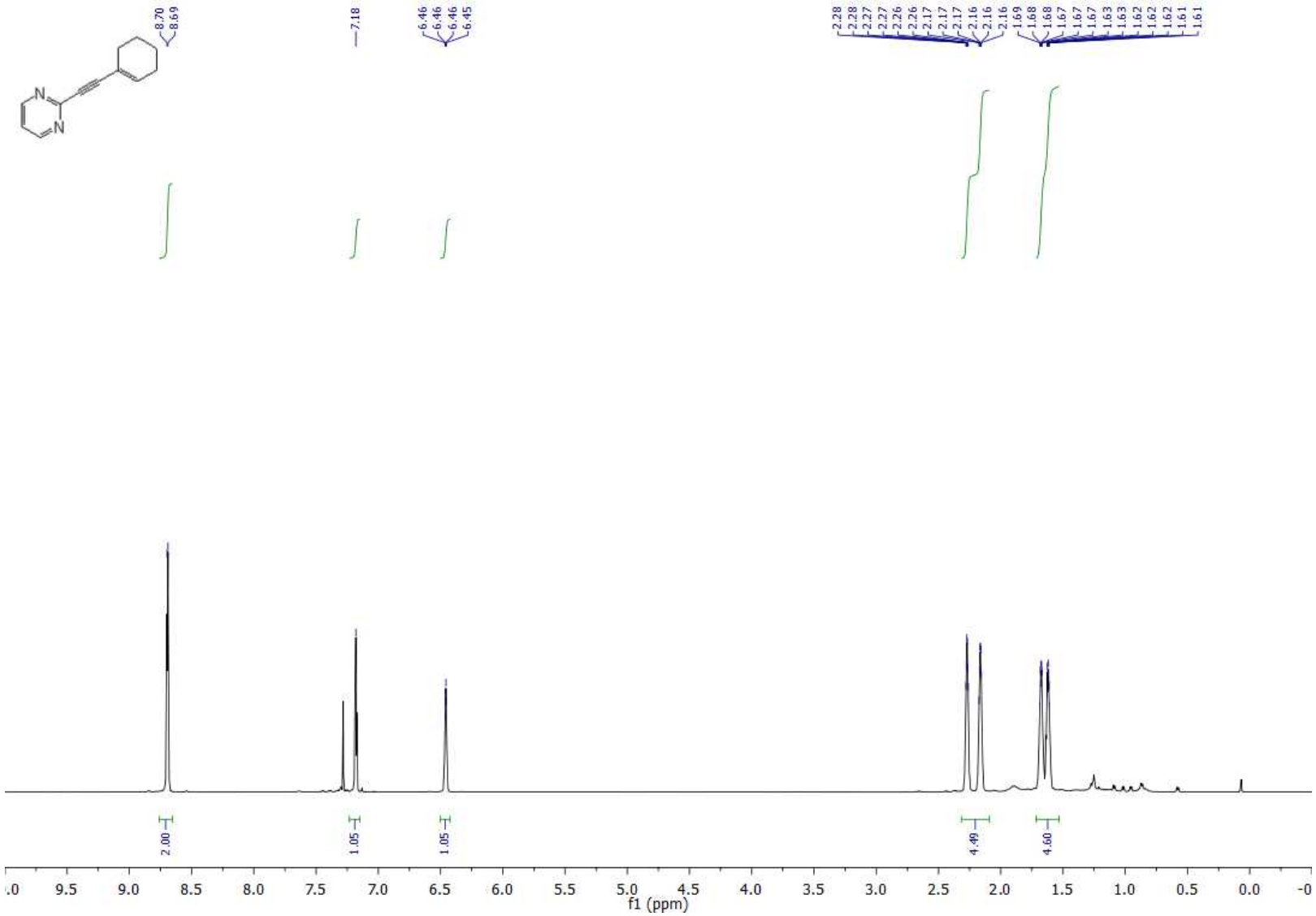
^{1}H NMR spectrum of 2-(cyclohex-1-en-1-ylethynyl)-4,6-dimethoxypyrimidine **(3e)**



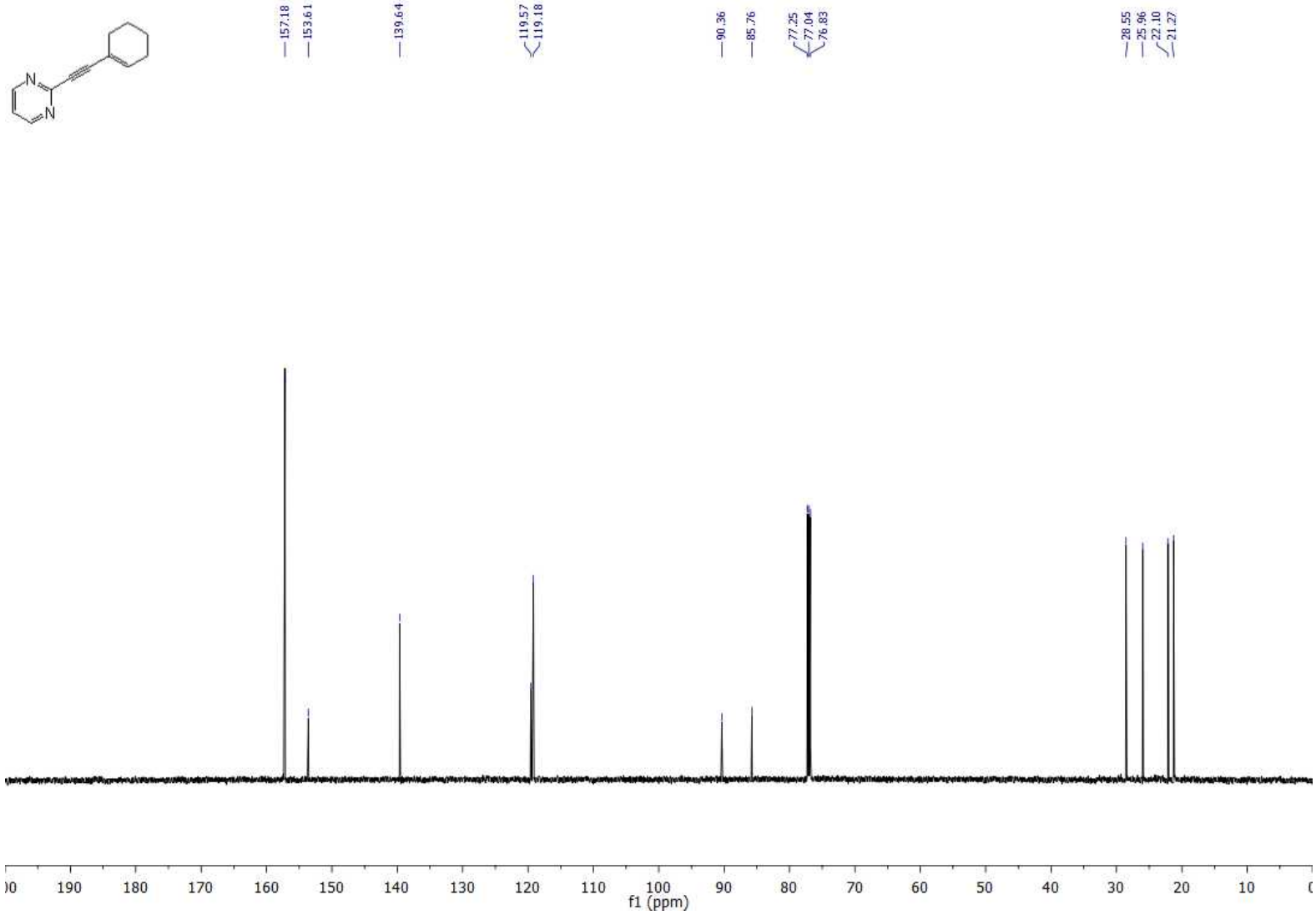
^{13}C NMR spectrum of 2-(cyclohex-1-en-1-ylethynyl)-4,6-dimethoxypyrimidine **(3e)**



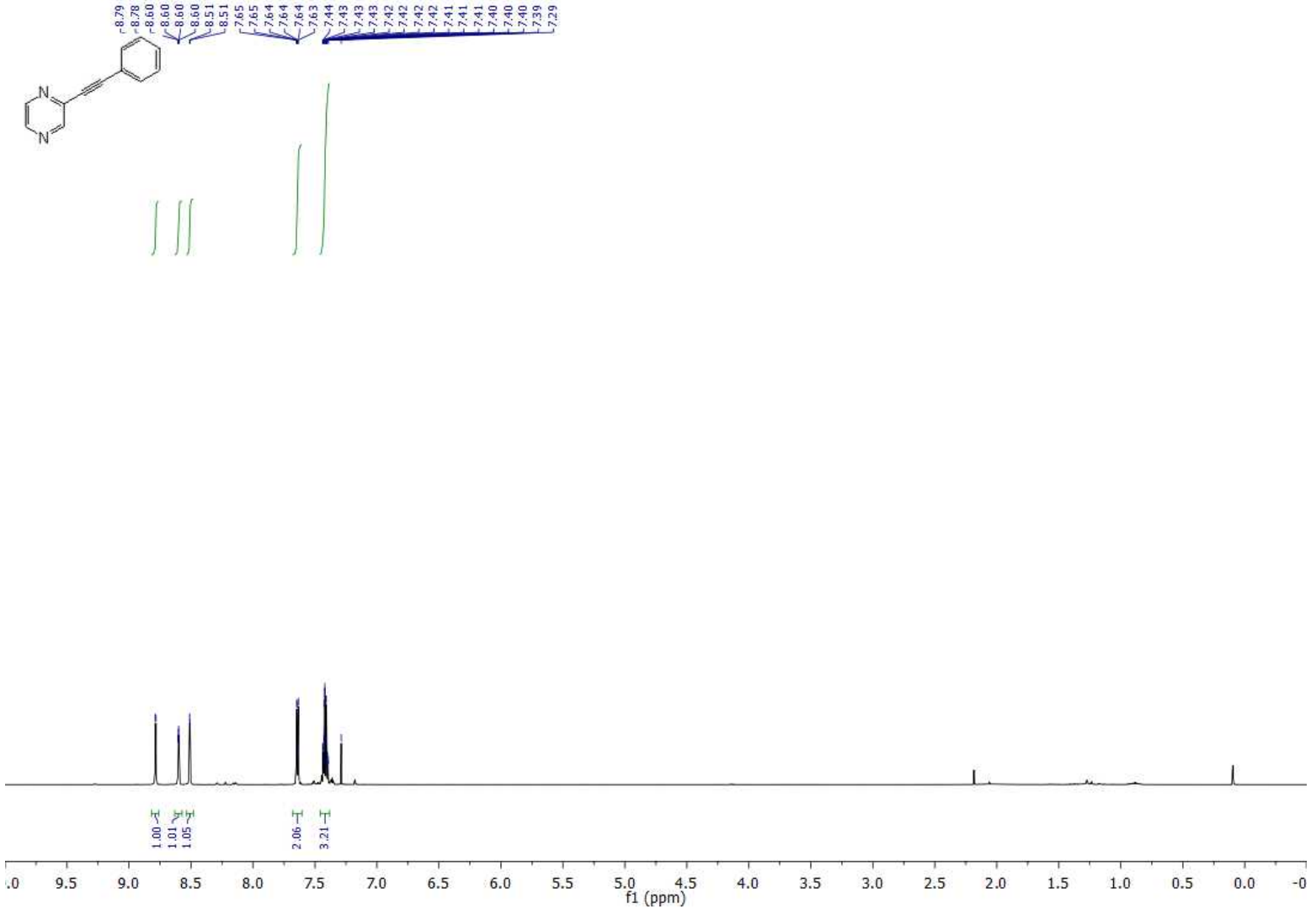
^{1}H NMR spectrum of 2-(cyclohex-1-en-1-ylethynyl)pyrimidine **(3f)**



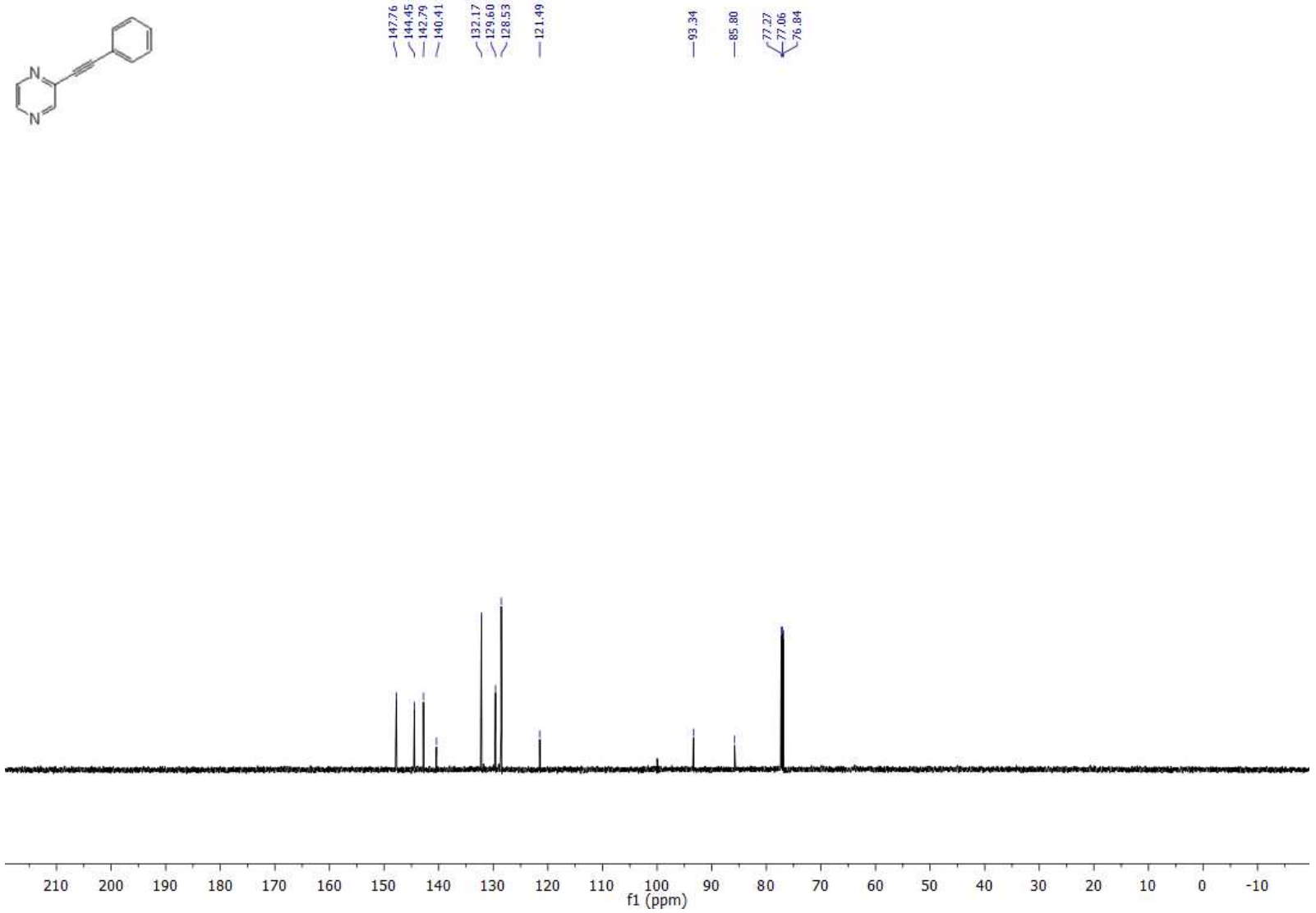
^{13}C NMR spectrum of 2-(cyclohex-1-en-1-ylethynyl)pyrimidine **(3f)**



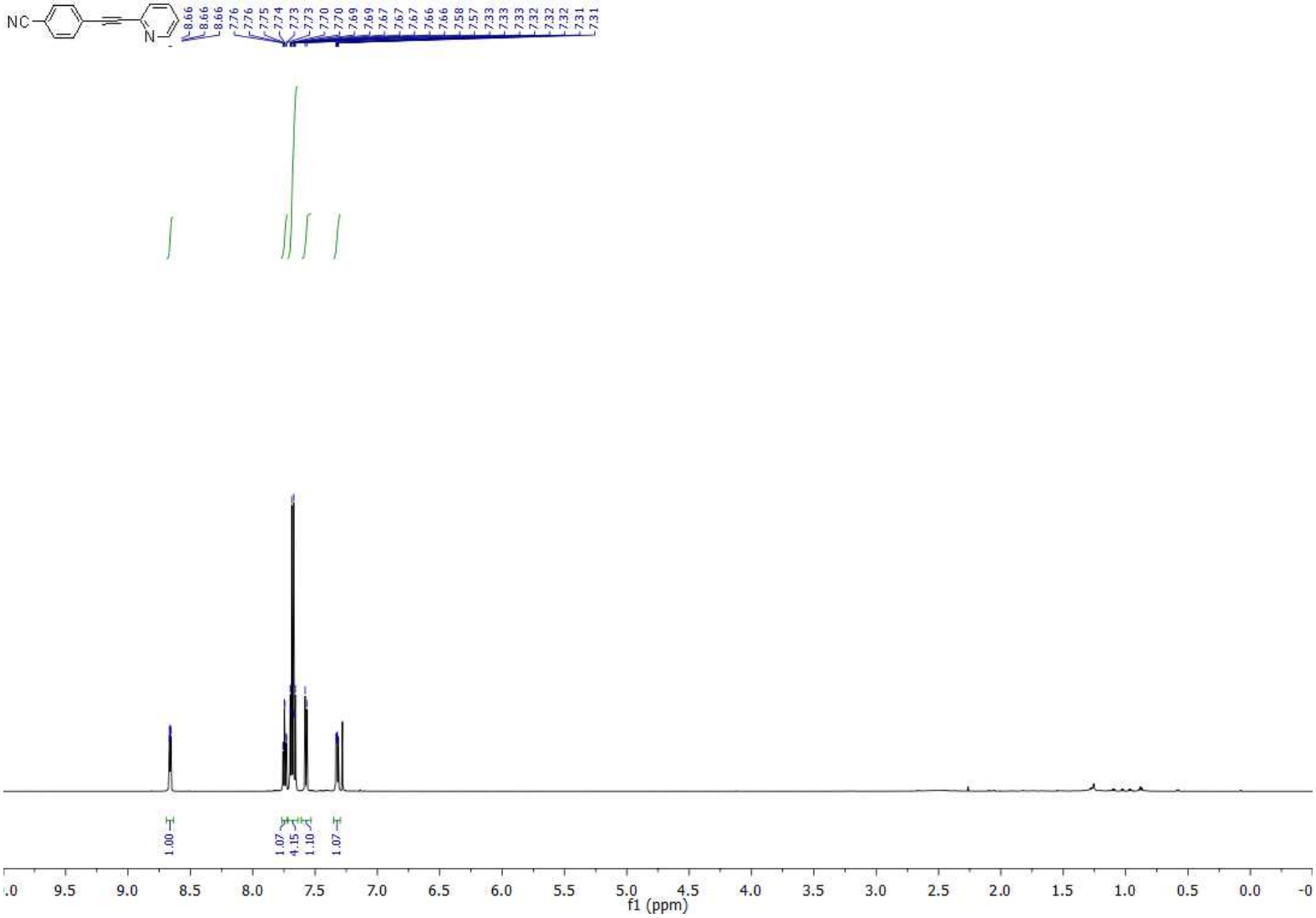
^{1}H NMR spectrum of 2-(phenylethynyl)pyrazine (**3g**)



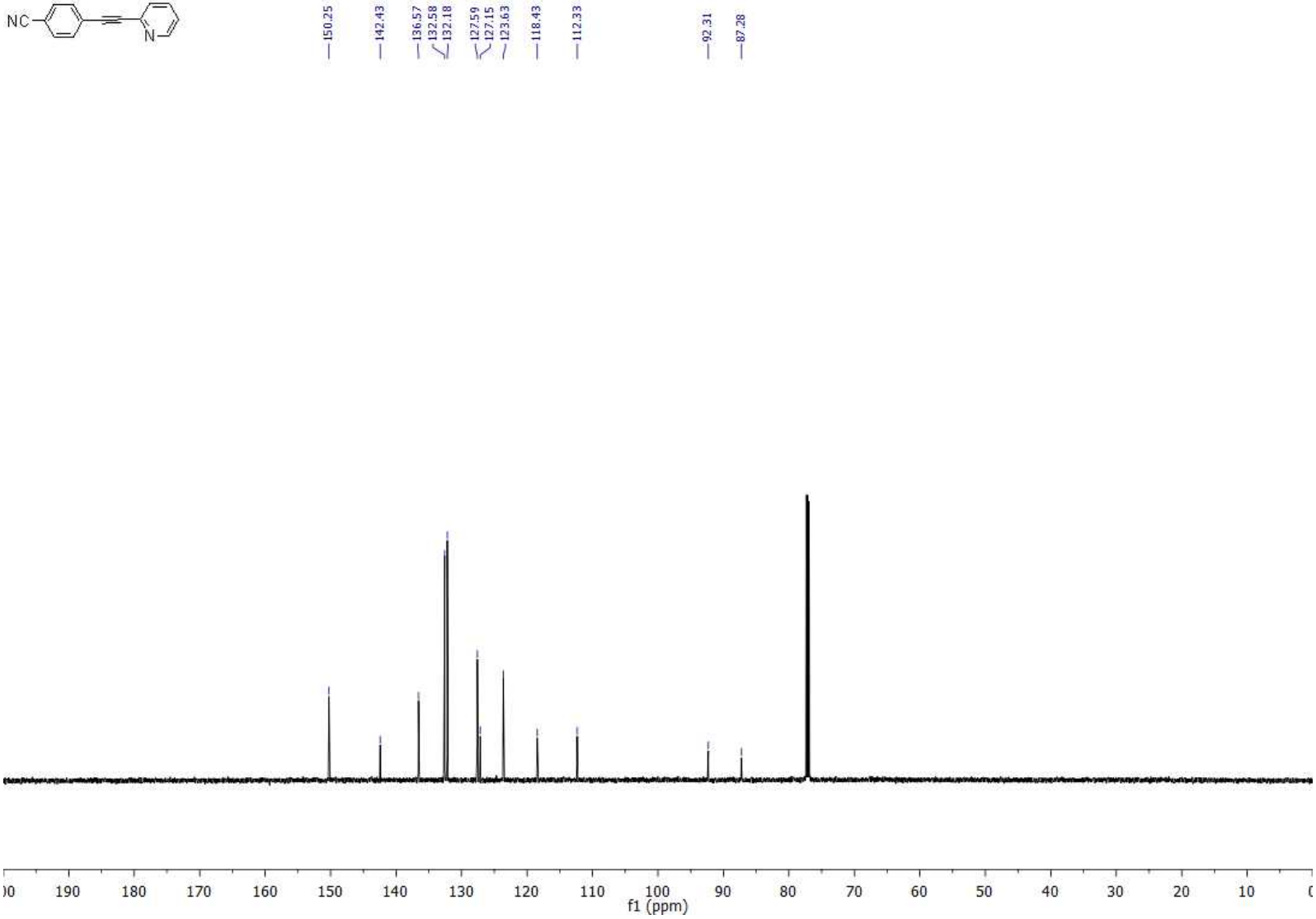
^{13}C NMR spectrum of 2-(phenylethynyl)pyrazine (**3g**)



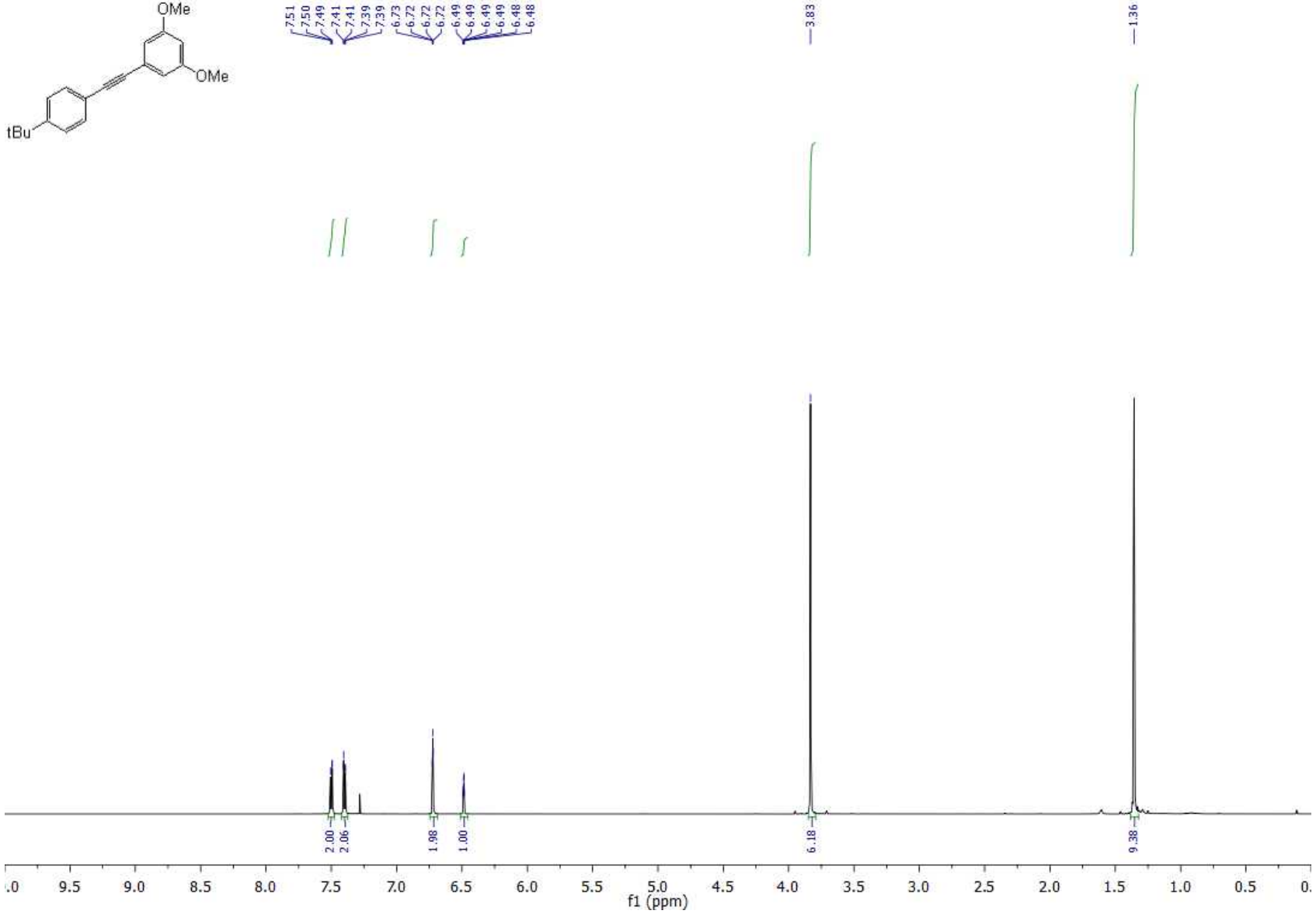
^{1}H NMR spectrum of 4-(pyridin-2-ylethynyl)benzonitrile **(3h)**



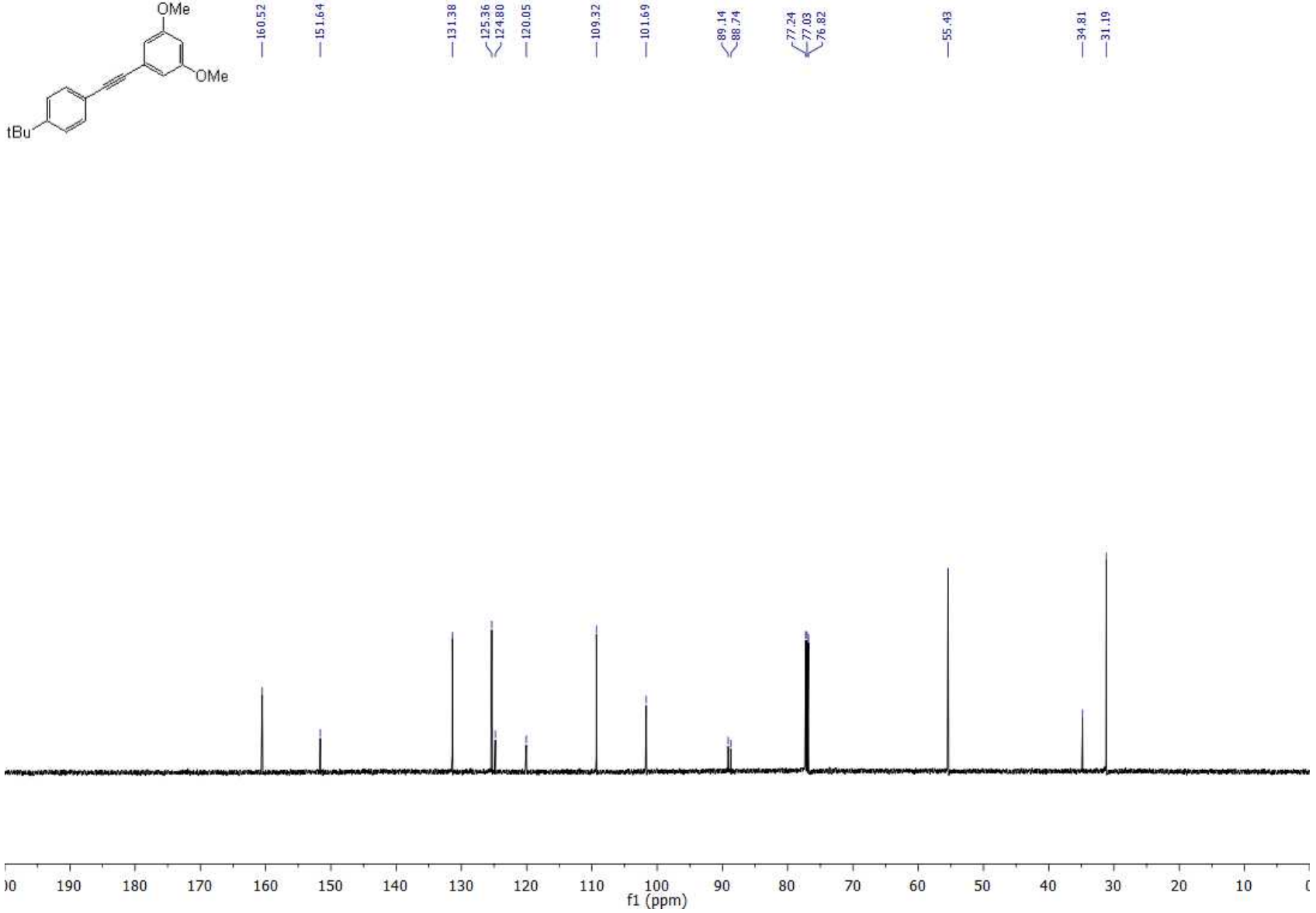
^{13}C NMR spectrum of 4-(pyridin-2-ylethynyl)benzonitrile **(3h)**



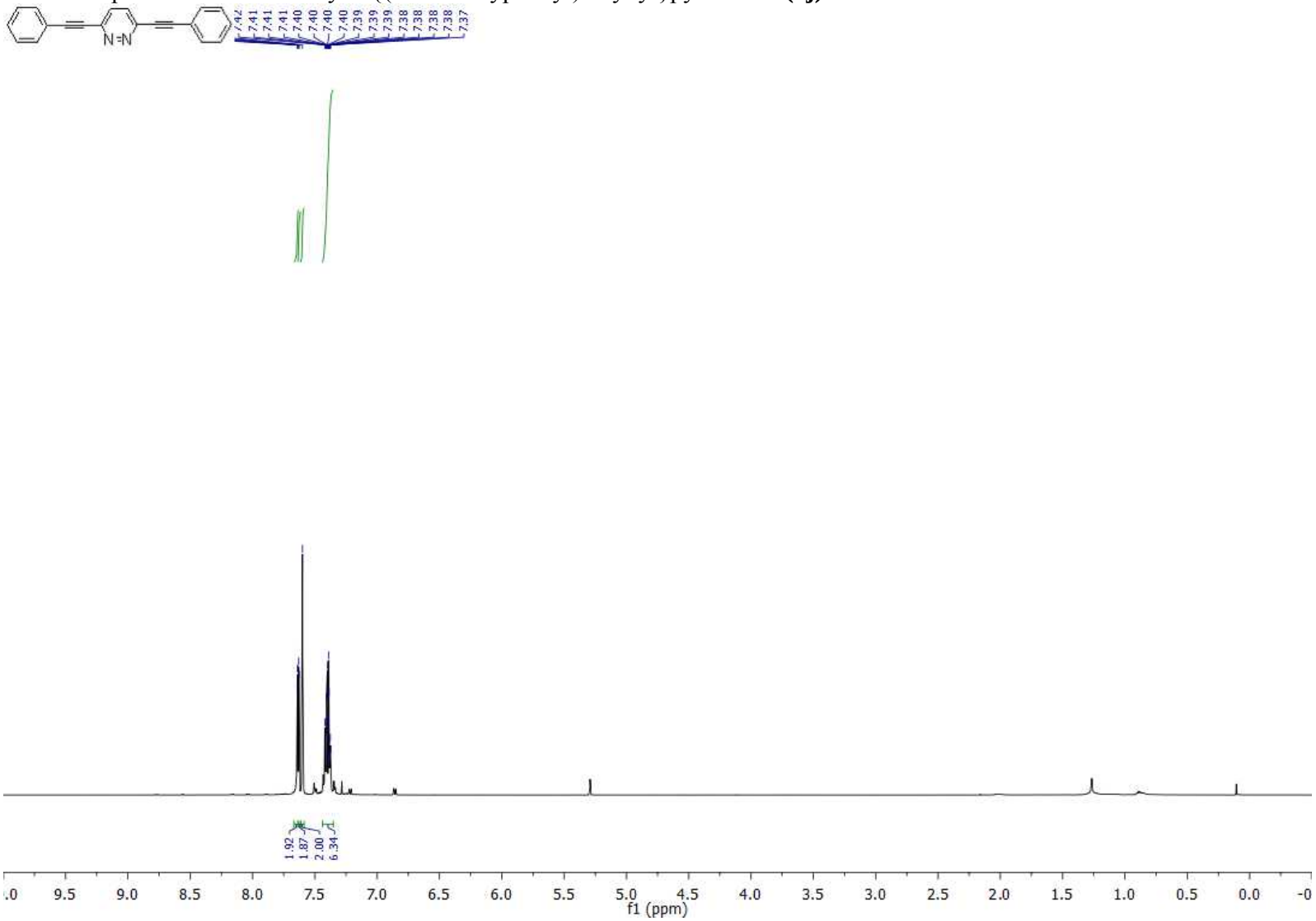
^{1}H NMR spectrum of 2-{(4-(tert-butyl)phenyl)ethynyl}-1,3-dimethoxybenzene **(3i)**



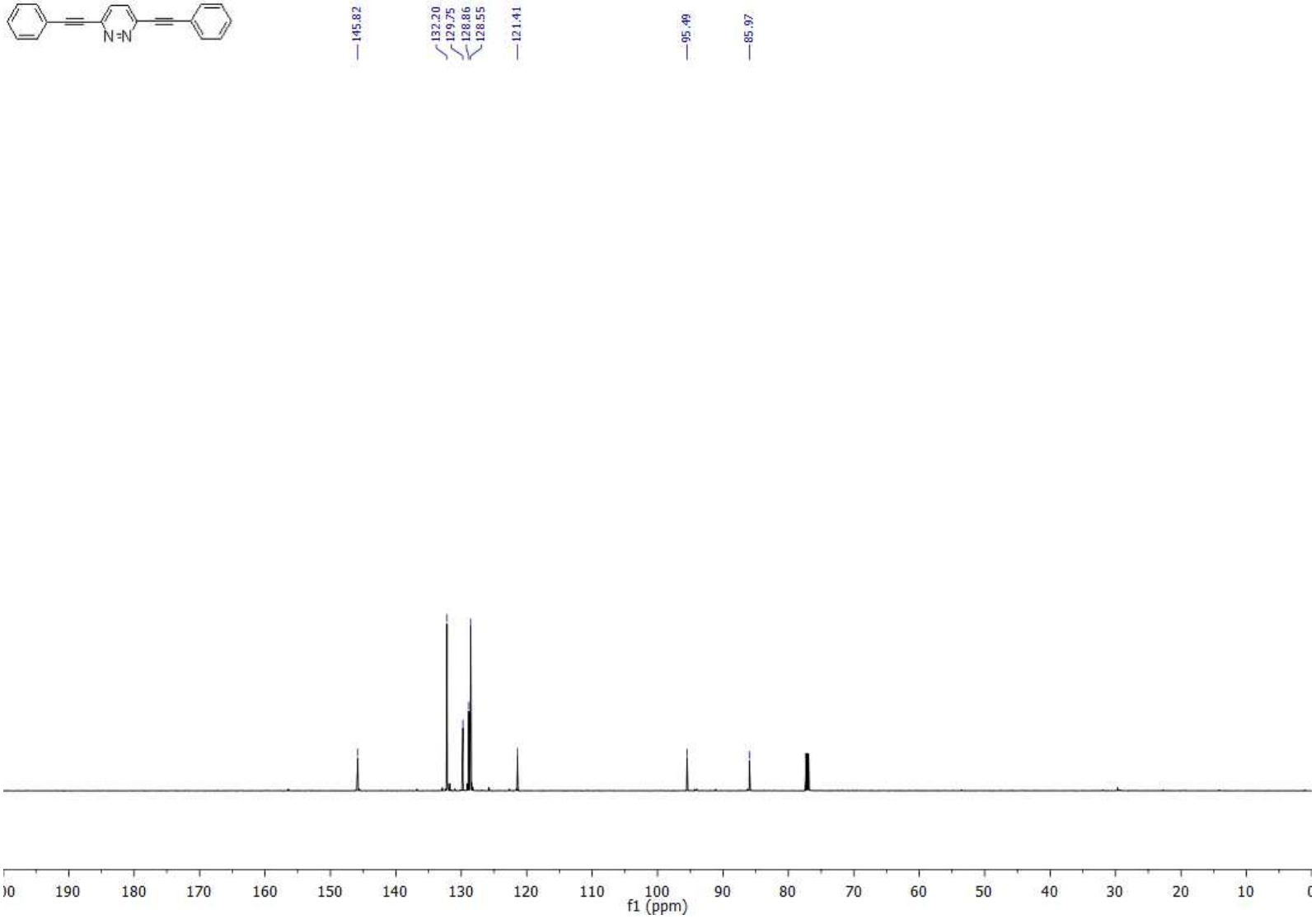
^{13}C NMR spectrum of 2-{(4-(tert-butyl)phenyl)ethynyl}-1,3-dimethoxybenzene **(3i)**



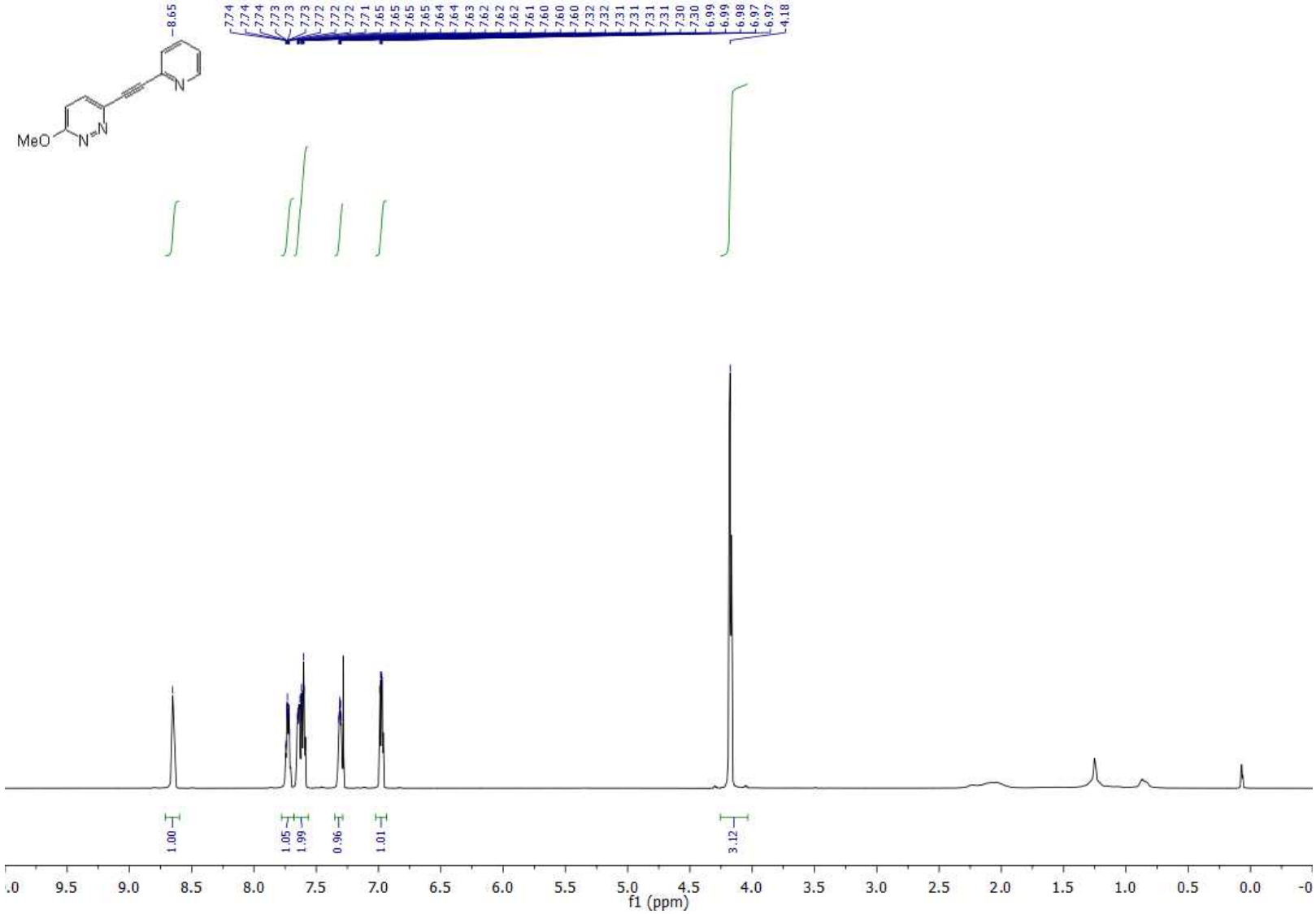
^{1}H NMR spectrum of 3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine **(3j)**



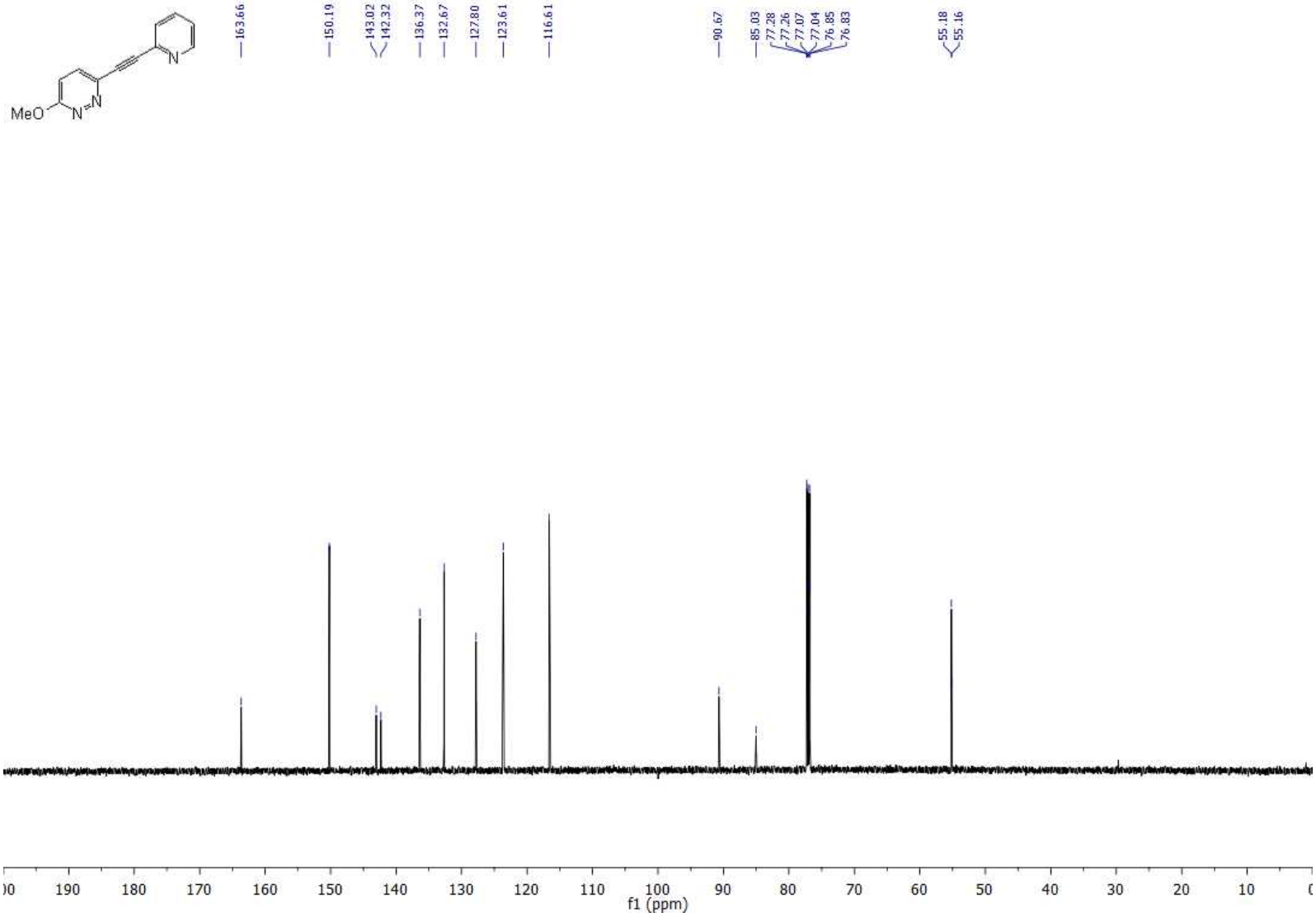
^{13}C NMR spectrum of 3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine **(3j)**



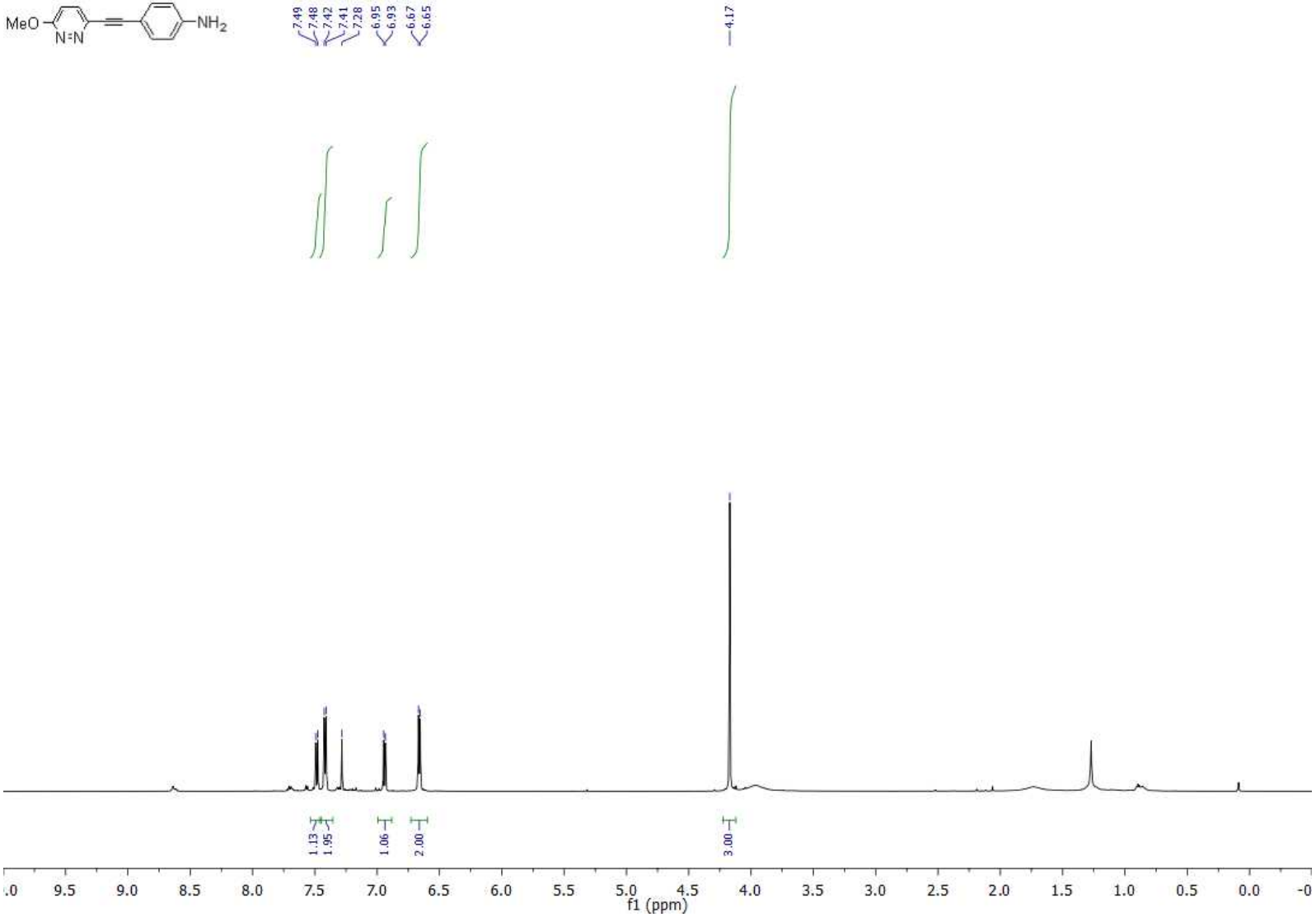
^{1}H NMR spectrum of 3-methoxy-6-(pyridin-2-ylethynyl)pyridazine **(3k)**



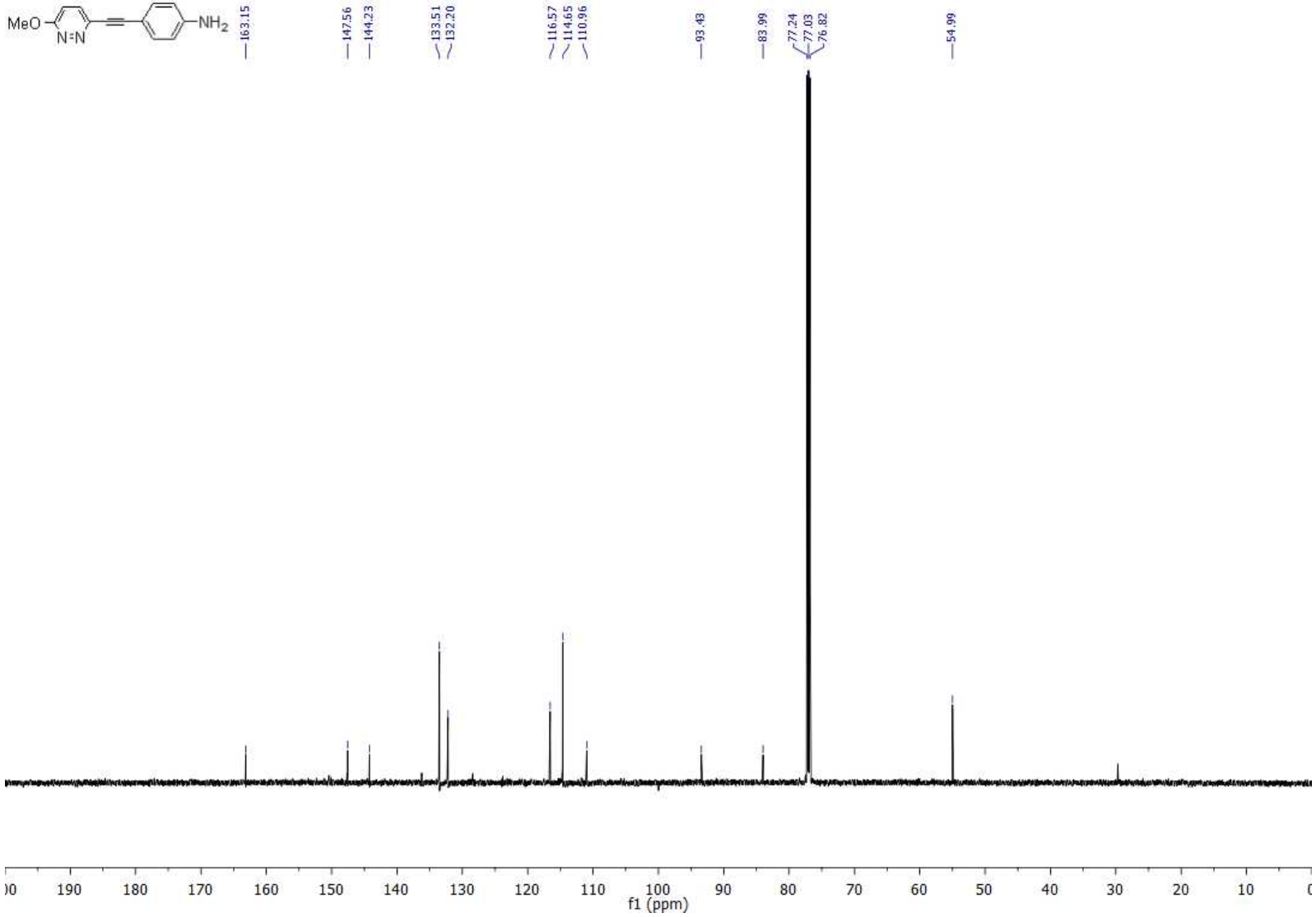
^{13}C NMR spectrum of 3-methoxy-6-(pyridin-2-ylethynyl)pyridazine **(3k)**



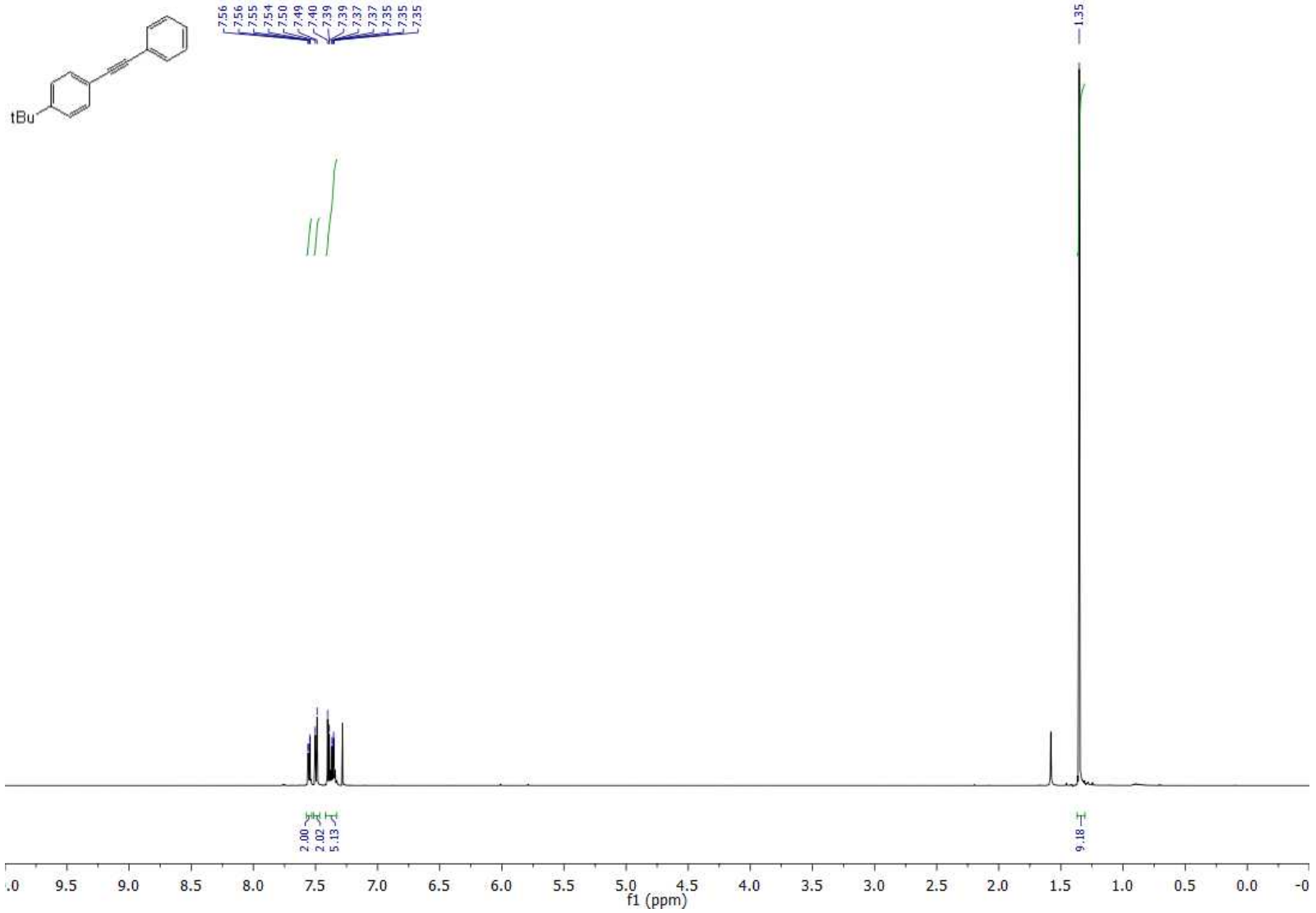
^{1}H NMR spectrum of 4-{(6-methoxypyridazin-3-yl)ethynyl}aniline **(3l)**



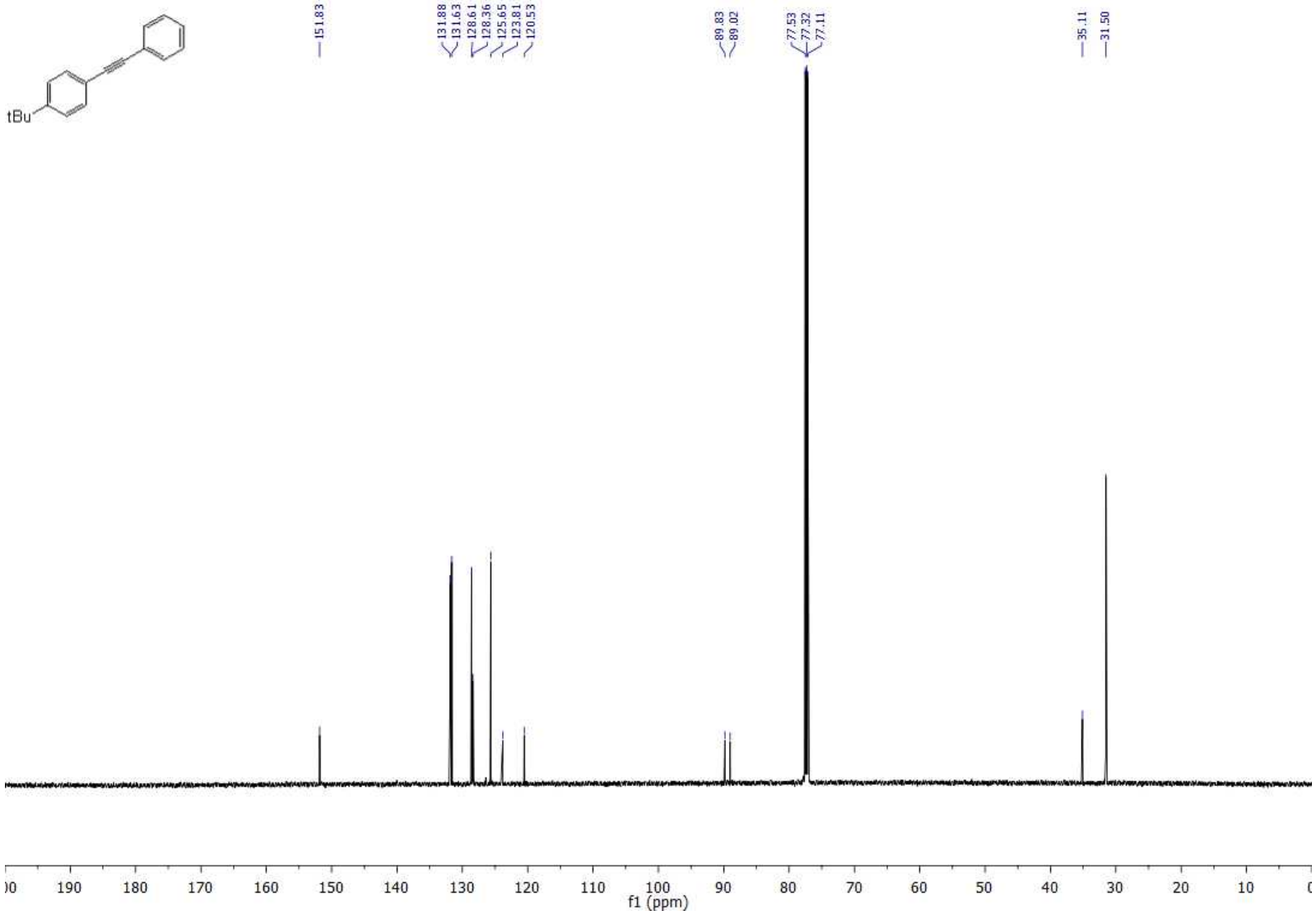
^{13}C NMR spectrum of 4-{(6-methoxypyridazin-3-yl)ethynyl}aniline **(3l)**



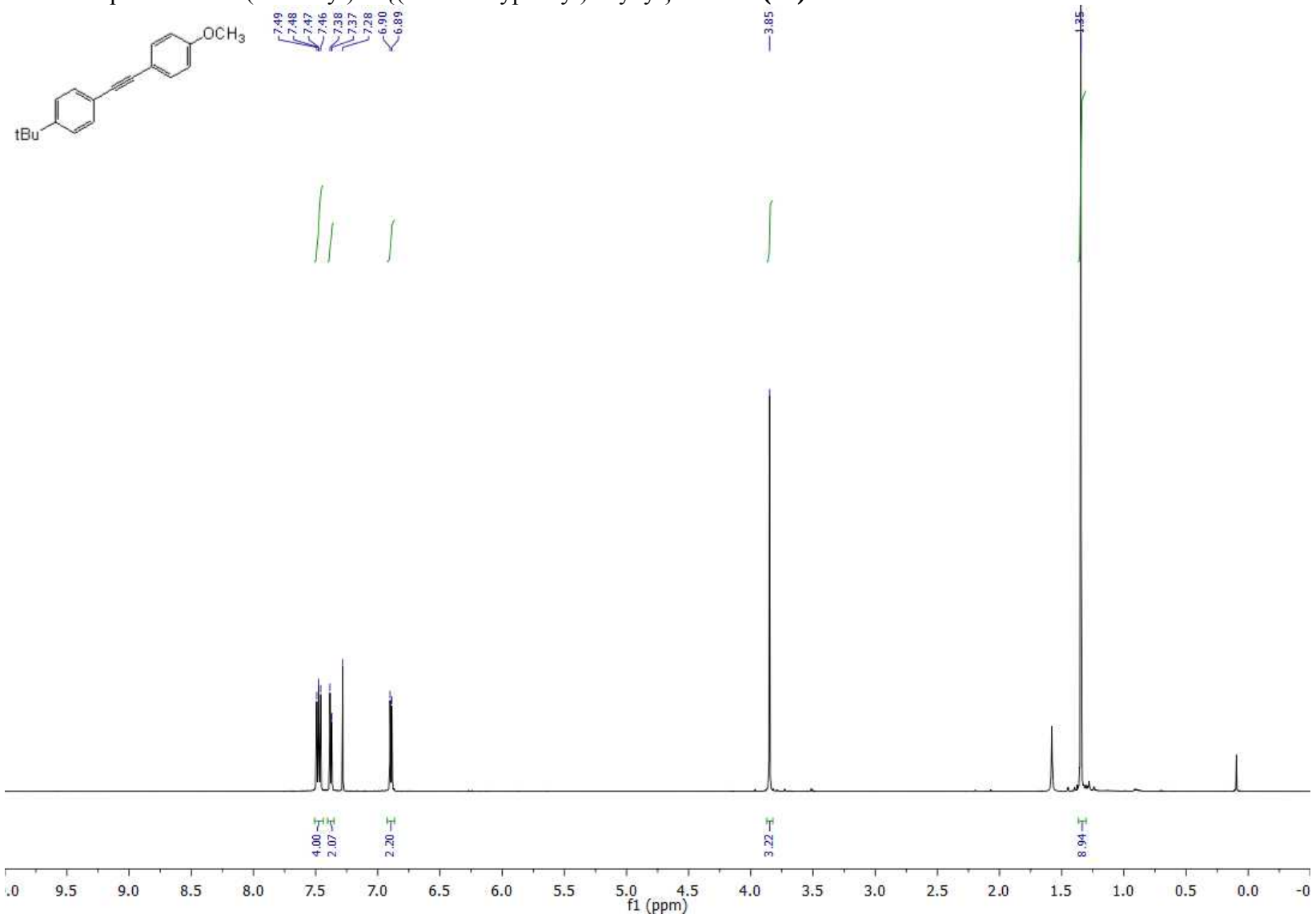
^{1}H NMR spectrum of 1-(*tert*-butyl)-4-(phenylethynyl)benzene **(3m)**



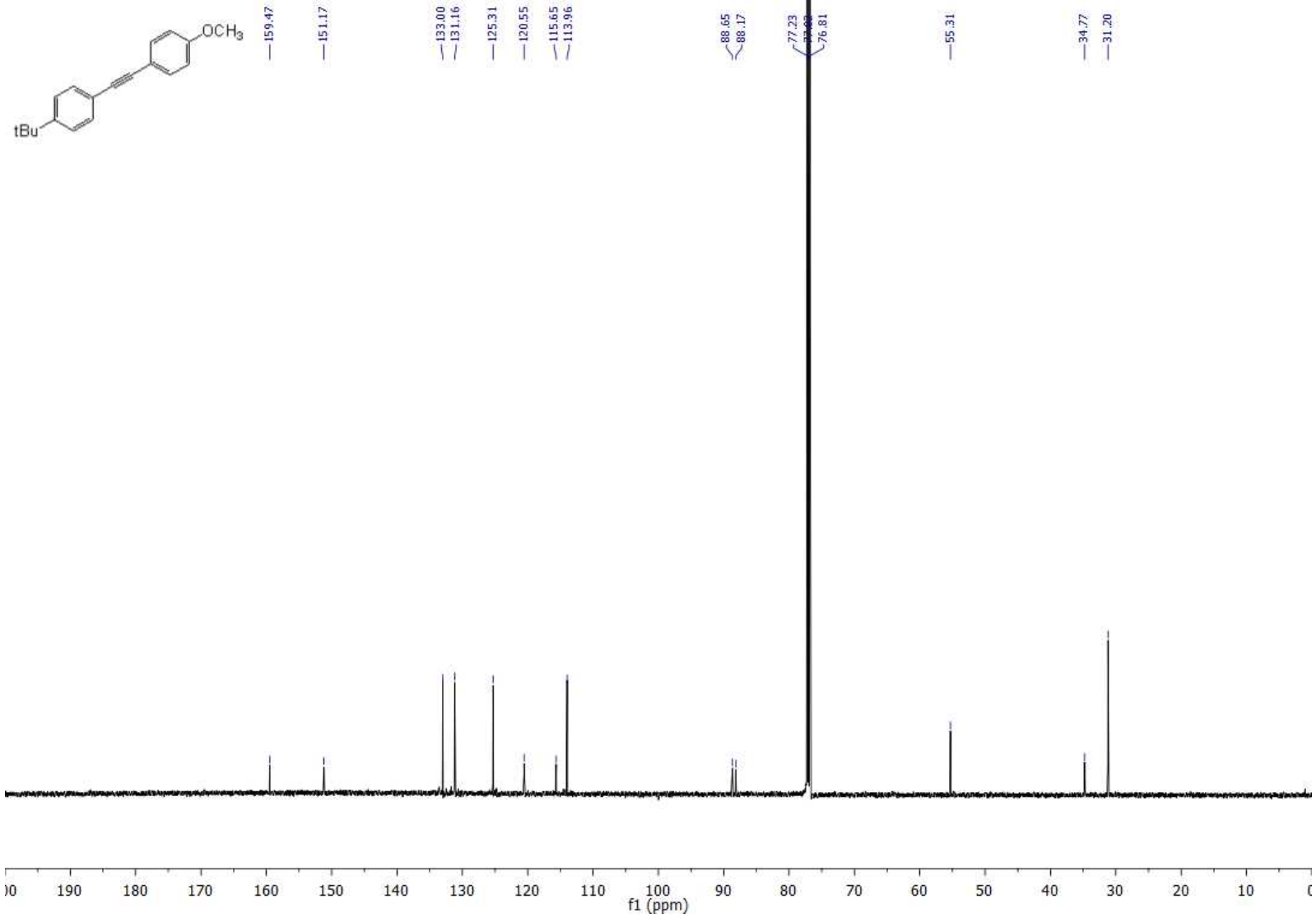
^{13}C NMR spectrum of 1-(*tert*-butyl)-4-(phenylethynyl)benzene **(3m)**



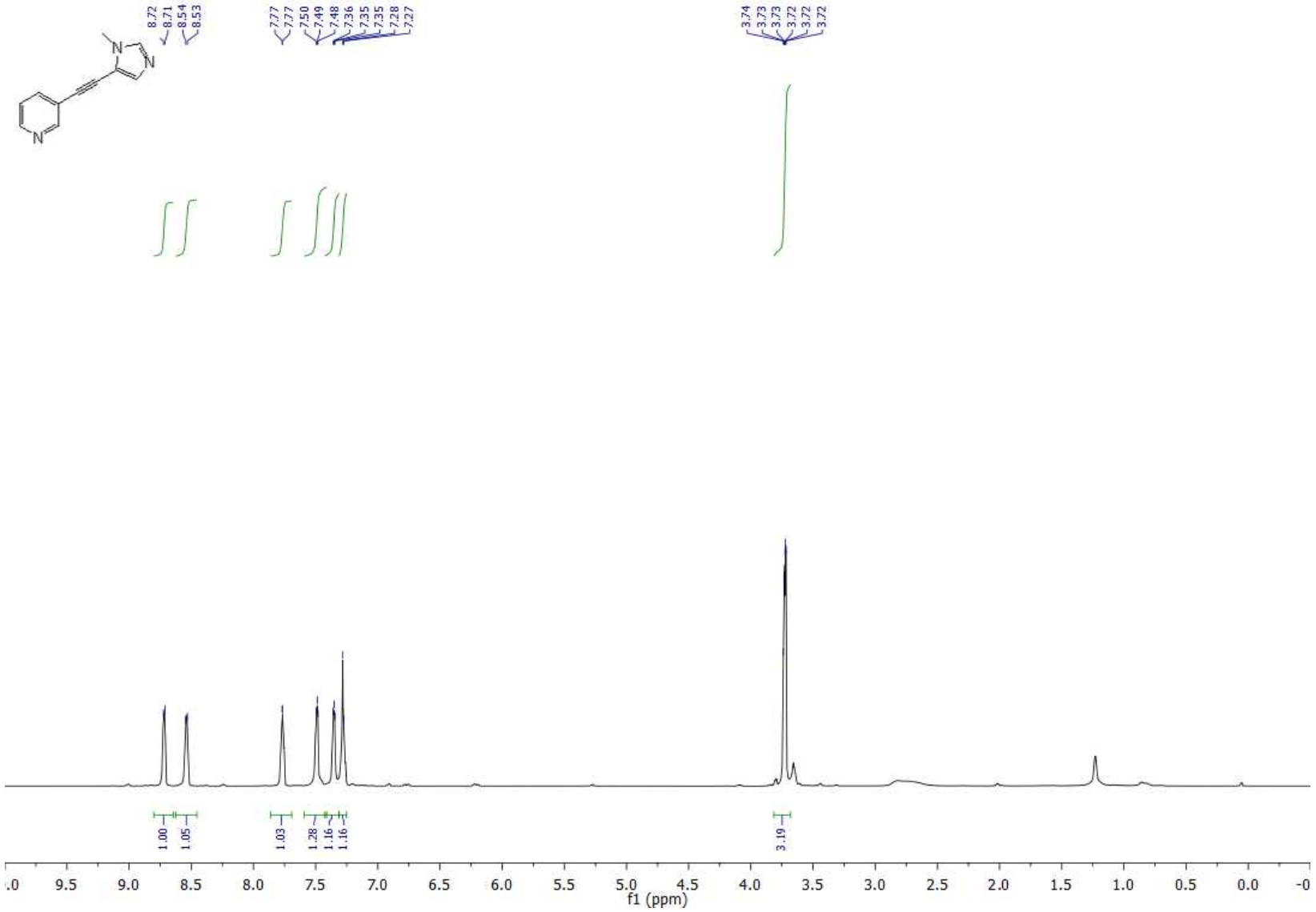
^{1}H NMR spectrum of 1-(tert-butyl)-4-{(4-methoxyphenyl)ethynyl}benzene **(3n)**



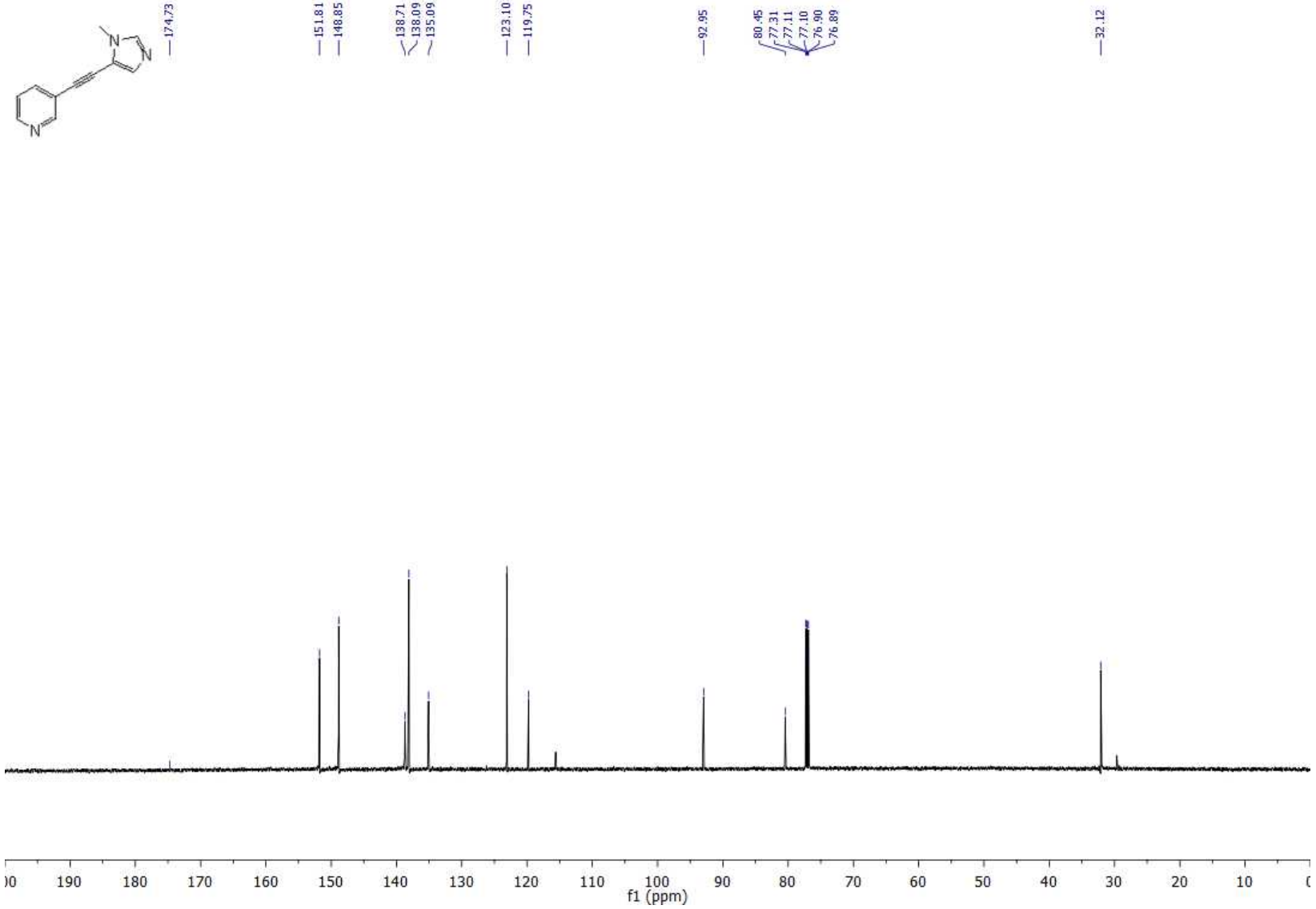
^{13}C NMR spectrum of 1-(tert-butyl)-4-{(4-methoxyphenyl)ethynyl}benzene **(3n)**



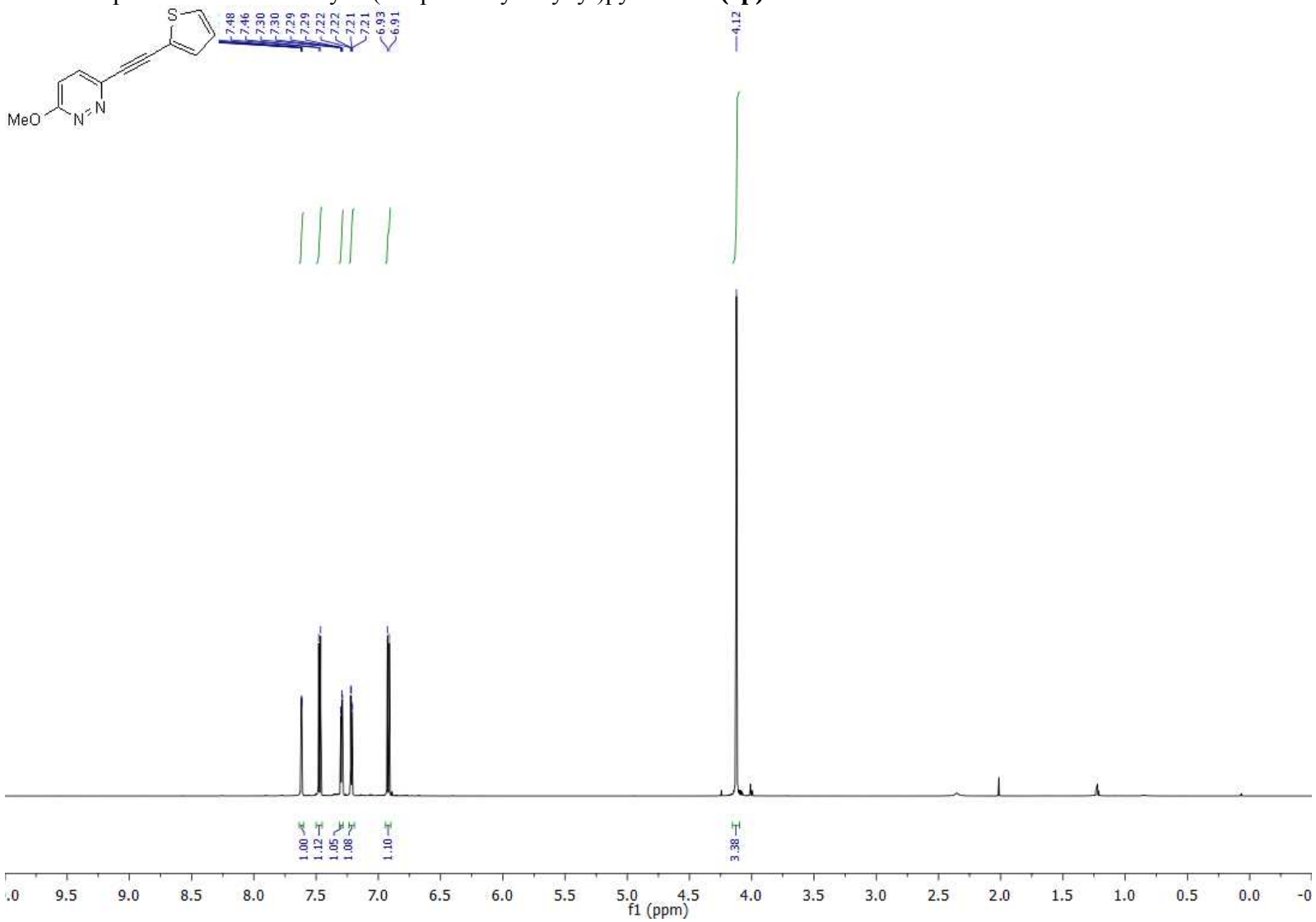
^{1}H NMR spectrum of 3-{(1-methyl-1H-imidazol-5-yl)ethynyl}pyridine **(3o)**



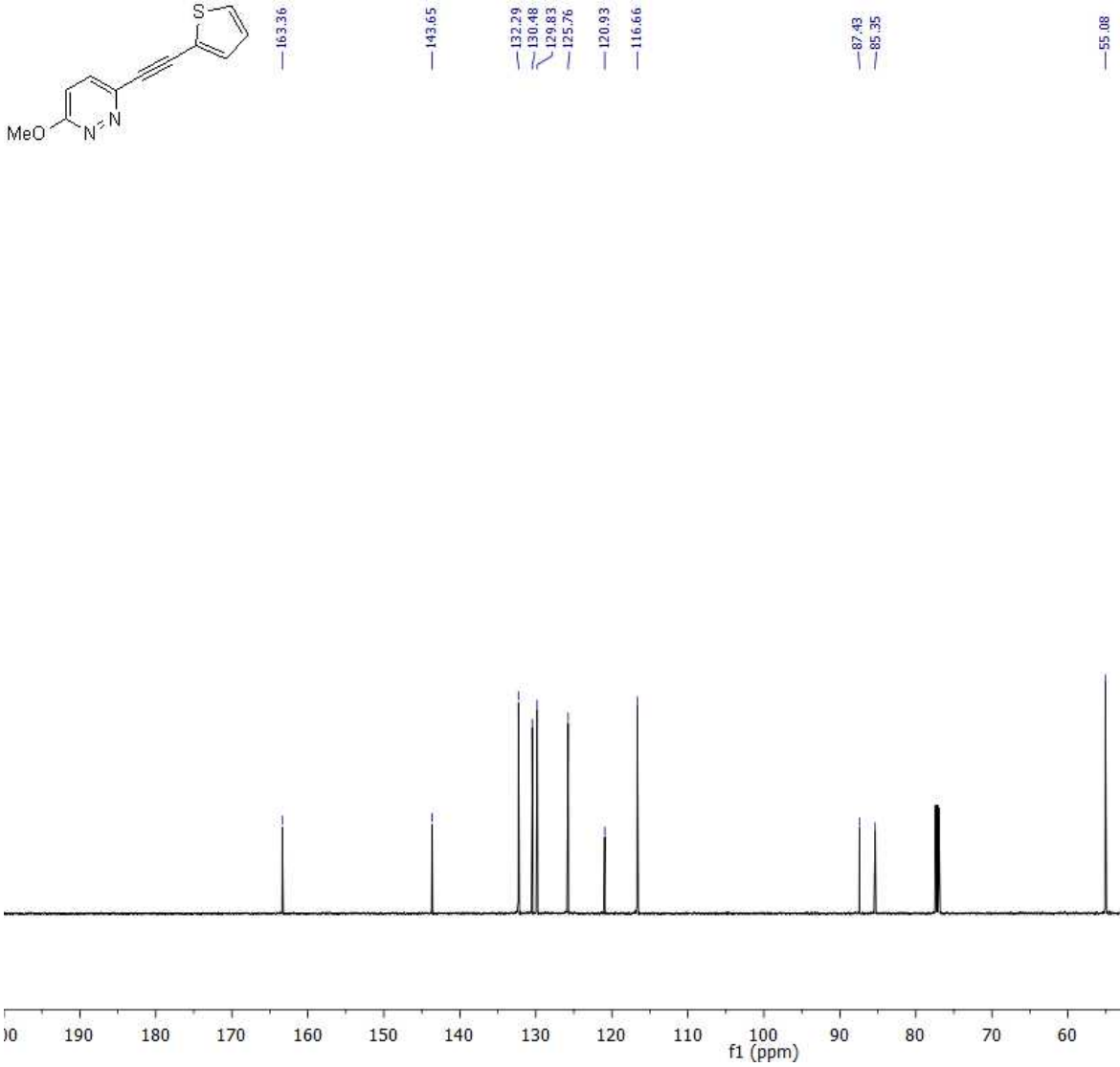
^{13}C NMR spectrum of 3-{(1-methyl-1H-imidazol-5-yl)ethynyl}pyridine **(3o)**



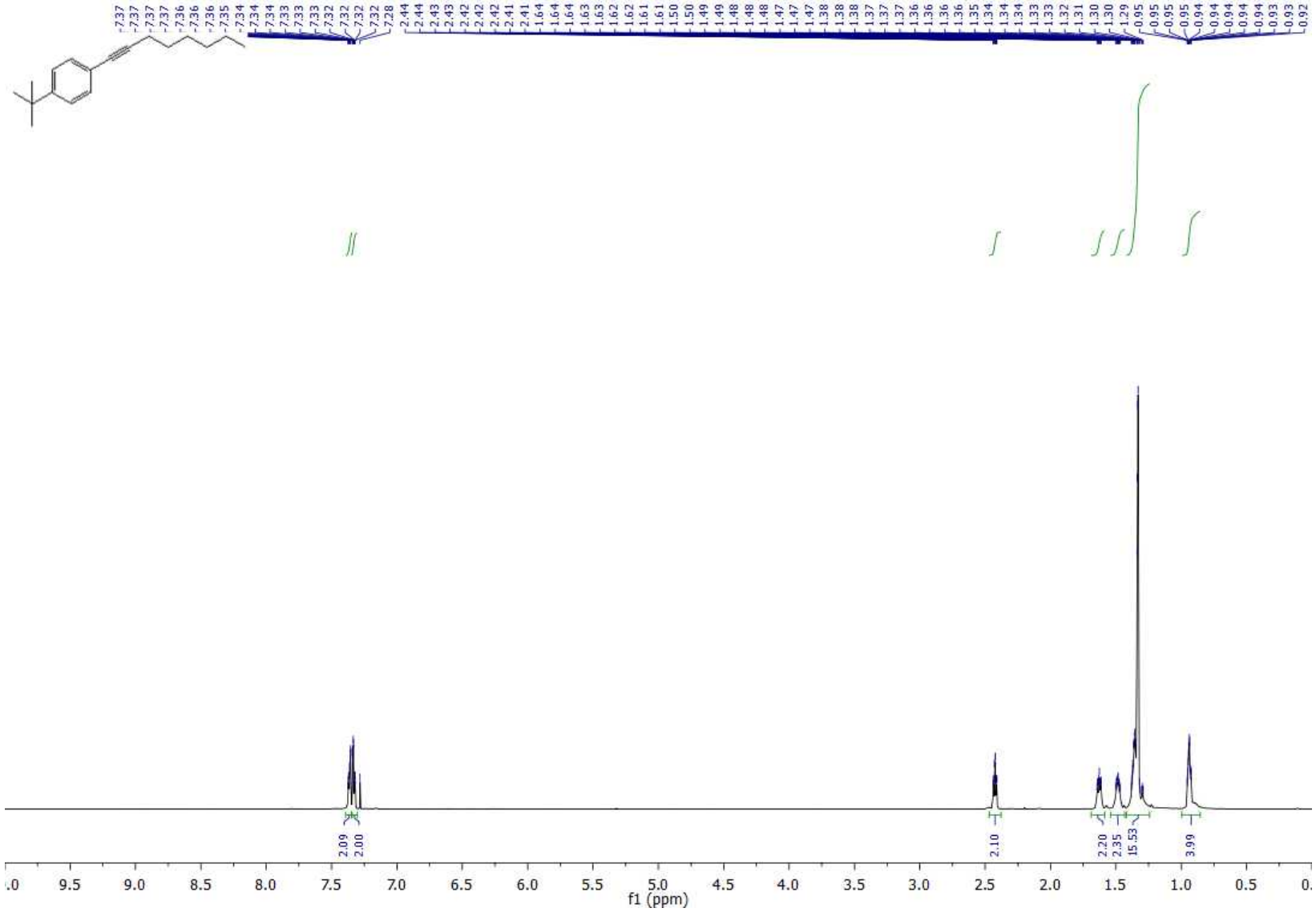
^{1}H NMR spectrum of 3-methoxy-6-(thiophen-2-ylethynyl)pyridazine **(3p)**



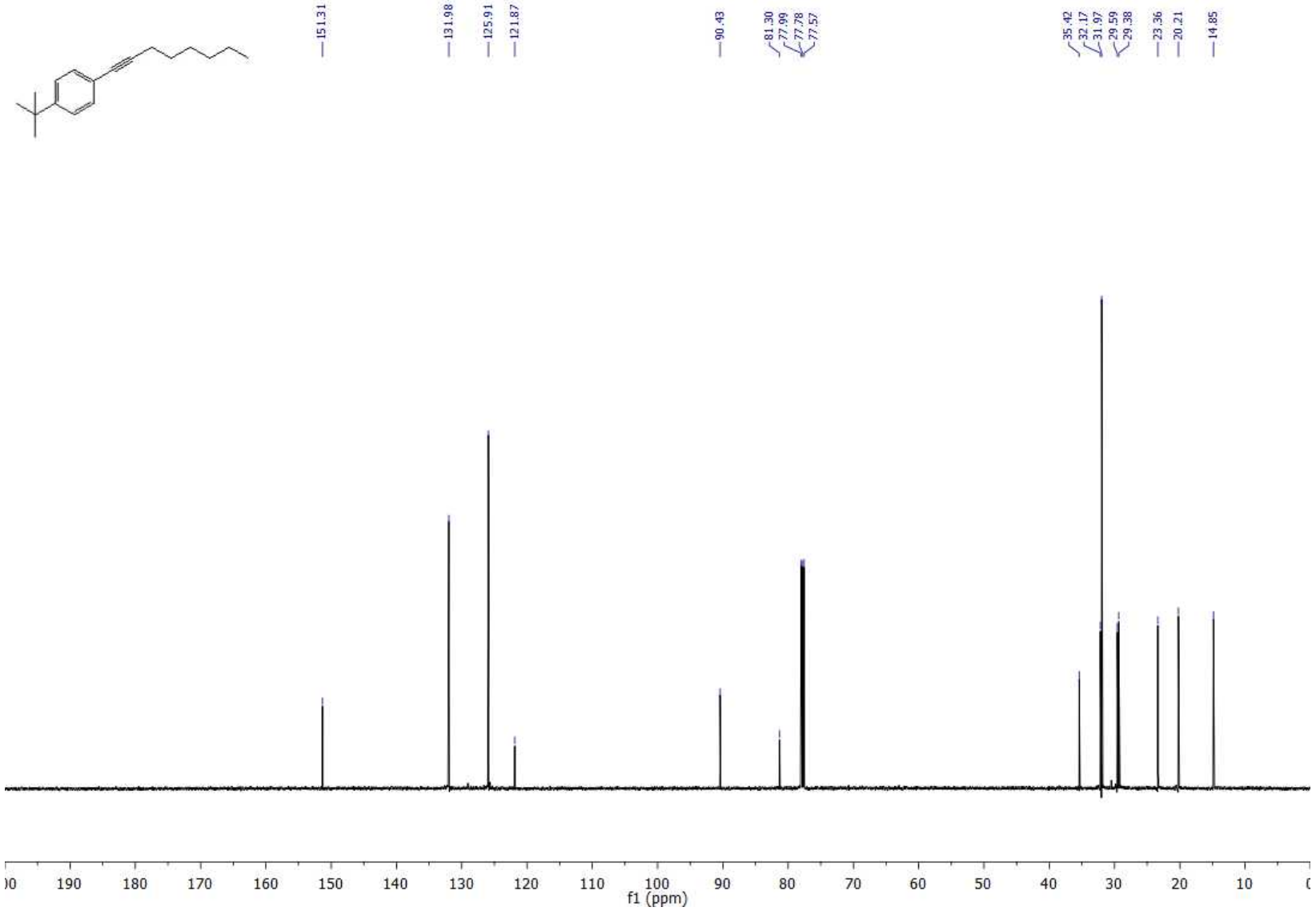
^{13}C NMR spectrum of 3-methoxy-6-(thiophen-2-ylethynyl)pyridazine **(3p)**



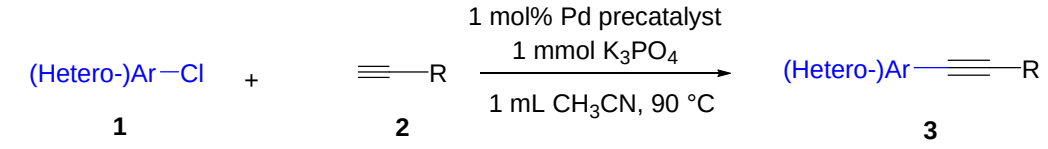
^{1}H NMR spectrum of 1-(tert-butyl)-4-(oct-1-yn-1-yl)benzene (**3q**)



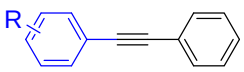
^{13}C NMR spectrum of 1-(tert-butyl)-4-(oct-1-yn-1-yl)benzene (**3q**)



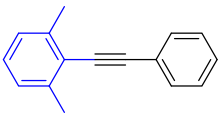
6. Extended Substrate Scope[a]



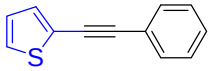
1 **2** **3**



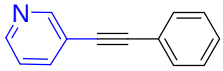
3a' (R = 4-MeO), 80%
3b' (R = 3-MeO), 80%
3c' (R = 2-MeO), 89%
3d' (R = 4-Me), 91%
3e' (R = 3-Me), 94%
3f' (R = 2-Me), 94%
3g' (R = 4-CN), 90%
3h' (R = 4-COMe), 95%



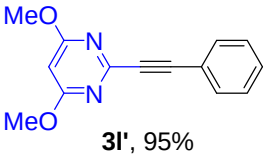
3i', 81%



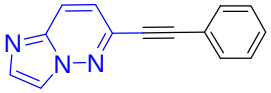
3j', 89%



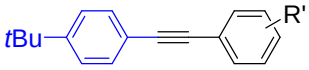
3k', 88%



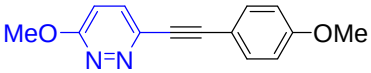
3l', 95%



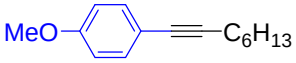
3m', 83%



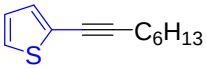
3n' (R' = 2-Me), 84%
3o'(R' = 4-Me), 90%
3p' (R' = 4-CF_3), 90%



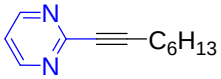
3q', 95%



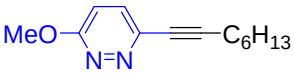
3r', 99%



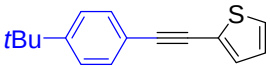
3s', 90%



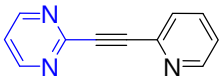
3t', 88%



3u', 91%

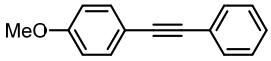


3v', 95%

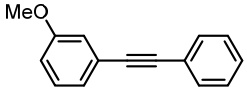


3w', 36%[b]

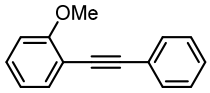
[a] Reaction conditions: 1 mol% $PdCl_2(Cy^*Phine)_2$, 0.5 mmol aryl chloride **1**, 0.6 mmol alkyne **2**, 1 mmol K_3PO_4, 1 mL CH_3CN, 90 °C, 6 h. [b] 1 mmol NEt_3, 1 mL THF, 60 °C, 12 h. Isolated yield of an average of two runs.



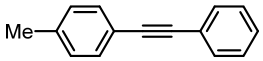
1-methoxy-4-(phenylethynyl)benzene (3a′). Following general Method I, 71.5 mg (0.5 mmol) of 4-chloroanisole and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a brown solid (83.2 mg, 80%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.52 (dd, *J* = 8.1, 1.5 Hz, 2 H), 7.48 (d, *J* = 8.9 Hz, 2 H), 7.40–7.27 (m, 3 H), 6.89 (d, *J* = 8.9 Hz, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.17, 133.61, 132.00, 129.84, 128.86, 128.48, 124.15, 115.94, 89.93, 88.63, 55.85 ppm. HRMS (ESI) calcd for $C_{15}H_{13}O^+$ $(M+H)^+$, 209.0888, found: 209.0979.



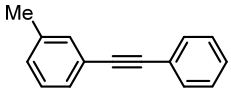
1-methoxy-3-(phenylethynyl)benzene (3b′). Following general Method I, 71.5 mg (0.5 mmol) of 3-chloroanisole and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellow solid (83.2 mg, 80%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.62–7.55 (m, 2 H), 7.40–7.37 (m, 3 H), 7.30 (dd, *J* = 8.4, 7.5 Hz, 1 H), 7.19 (d, *J* = 7.5 Hz, 1 H), 7.12 (dd, *J* = 2.7, 1.4 Hz, 1 H), 6.94 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.34, 131.67, 129.47, 128.41, 128.37, 124.25, 124.21, 123.17, 116.30, 114.99, 89.34, 89.24, 55.32 ppm. HRMS (ESI) calcd for $C_{15}H_{13}O^+$ $(M+H)^+$, 209.0888, found: 209.0982.



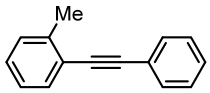
1-methoxy-2-(phenylethynyl)benzene (3c′). Following general Method I, 71.5 mg (0.5 mmol) of 2-chloroanisole and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellow solid (93 mg, 89%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.60 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.54 (dd, *J* = 7.5, 1.7 Hz, 1 H), 7.40–7.34 (m, 4 H), 7.01–6.90 (m, 2 H), 3.95 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.89, 133.61, 131.69, 129.81, 128.78, 128.39, 128.27, 128.15, 126.33, 123.53, 120.50, 112.38, 110.65, 93.45, 85.71, 55.86 ppm. HRMS (ESI) calcd for $C_{15}H_{13}O^+$ $(M+H)^+$, 209.0888, found: 209.0954.



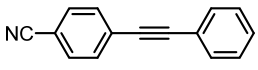
1-methyl-4-(phenylethynyl)benzene (3d′). Following general Method I, 63 mg (0.5 mmol) of 1-chloro-4-methylbenzene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a white solid (87.4 mg, 91%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.58–7.53 (m, 2 H), 7.47 (dd, *J* = 8.1, 1.6 Hz, 2 H), 7.39–7.32 (m, 3 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.39, 131.56, 131.51, 129.13, 128.32, 128.08, 123.49, 120.20, 89.57, 88.73, 21.53 ppm. HRMS (ESI) calcd for $C_{15}H_{13}^{+}$ $(M+H)^{+}$, 193.0939, found: 193.1028.



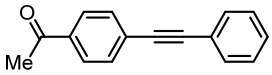
1-methyl-3-(phenylethynyl)benzene (3e′). Following general Method I, 63 mg (0.5 mmol) of 1-chloro-3-methylbenzene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a colourless oil (90 mg, 94%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.63–7.57 (m, 2H), 7.45–7.35 (m, 5 H), 7.30 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 138.05, 132.24, 131.64, 129.22, 128.74, 128.47, 128.38, 128.29, 128.22, 123.43, 123.12, 89.65, 89.11, 21.28 ppm. HRMS (ESI) calcd for $C_{15}H_{13}^{+}$ $(M+H)^{+}$, 193.0939, found: 139.1034.



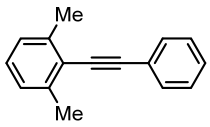
1-methyl-2-(phenylethynyl)benzene (3f′). Following general Method I, 63 mg (0.5 mmol) of 1-chloro-2-methylbenzene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a colourless oil (90 mg, 94%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.64–7.59 (m, 2 H), 7.57 (s, 1 H), 7.40 (dd, *J* = 9.2, 7.1 Hz, 3 H), 7.31–7.27 (m, 2 H), 7.24 (dd, *J* = 7.9, 4.2 Hz, 1 H), 2.59 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 140.22, 131.89, 131.56, 129.52, 128.40, 128.36, 128.22, 125.64, 123.61, 123.07, 93.41, 88.41, 20.81 ppm. HRMS (ESI) calcd for $C_{15}H_{13}^{+}$ $(M+H)^{+}$, 193.0939, found: 193.1012.



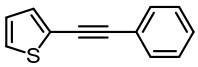
4-(phenylethynyl)benzonitrile (3g′). Following general Method I, 68.5 mg (0.5 mmol) of 4-chlorobenzonitrile and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellow solid (91 mg, 90%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.6 Hz, 2 H), 7.63 (d, *J* = 8.6 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.40 (dd, *J* = 5.2, 2.0 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 132.08, 132.06, 131.80, 129.14, 128.51, 128.26, 122.23, 118.55, 111.48, 93.79, 87.72 ppm. HRMS (ESI) calcd for $C_{15}H_{10}N^+$ $(M+H)^+$, 204.0735, found: 204.0801.



1-(4-(phenylethynyl)phenyl)ethan-1-one (3h′). Following general Method I, 77 mg (0.5 mmol) of 1-(4-chlorophenyl)ethan-1-one and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a yellow solid (104 mg, 95%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98–7.93 (m, 2 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.57 (dd, *J* = 6.7, 3.0 Hz, 2 H), 7.40–7.34 (m, 3 H), 2.62 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 197.30, 136.18, 131.75, 131.70, 128.82, 128.46, 128.28, 128.19, 122.65, 92.73, 88.63, 26.63 ppm. HRMS (ESI) calcd for $C_{16}H_{13}O^+$ $(M+H)^+$, 221.0888, found: 221.0907.

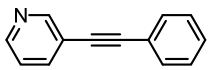


1,3-dimethyl-2-(phenylethynyl)benzene (3i′). Following general Method I, 70 mg (0.5 mmol) of 2-chloro-1,3-dimethylbenzene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a colourless oil (83 mg, 81%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 6.4, 1.9 Hz, 2 H), 7.43–7.31 (m, 3 H), 7.19–7.14 (m, 1 H), 7.11 (dd, *J* = 7.8, 2.3 Hz, 2 H), 2.57 (s, 6 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 140.28, 131.41, 128.38, 128.11, 127.78, 126.71, 123.85, 122.98, 97.85, 87.14, 21.15 ppm. HRMS (ESI) calcd for $C_{16}H_{15}^+$ $(M+H)^+$, 207.1096, found: 207.1166.

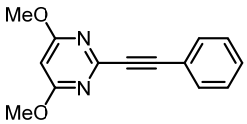


2-(phenylethynyl)thiophene (3j′). Following general Method I, 58.5 mg (0.5 mmol) of 2-chlorothiophene and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a

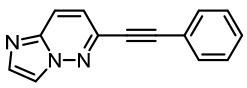
brown oil (82 mg, 89%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.58–7.50 (m, 2 H), 7.37 (dd, *J* = 4.7, 3.0 Hz, 3 H), 7.34–7.29 (m, 2 H), 7.04 (ddd, *J* = 5.0, 3.2, 1.9 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 131.89, 131.42, 128.42, 128.38, 127.25, 127.10, 123.33, 122.93, 93.03, 82.61 ppm. HRMS (ESI) calcd for $C_{12}H_9S^+$ $(M+H)^+$, 185.0347, found: 185.0421.



3-(phenylethynyl)pyridine (3k′). Following general Method I, 56.5 mg (0.5 mmol) of 3-chloropyridine and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a brown oil (79 mg, 88%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.79 (s, 1 H), 8.57 (d, *J* = 4.0 Hz, 1 H), 7.83 (d, *J* = 7.9 Hz, 1 H), 7.61–7.52 (m, 2 H), 7.42–7.37 (m, 3 H), 7.30 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.21, 148.50, 138.47, 128.82, 128.46, 123.06, 122.51, 92.68, 85.92 ppm. HRMS (ESI) calcd for $C_{13}H_{10}N^+$ $(M+H)^+$, 180.0735, found: 180.0817.

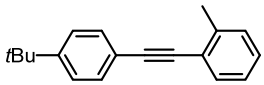


4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3l′). Following general Method I, 87 mg (0.5 mmol) of 2-chloro-4,6-dimethoxypyrimidine and 61.2 mg (0.6 mmol) of phenylacetylene afforded the title compound as a pale yellow solid (107 mg, 95%) using 1:25 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72–7.65 (m, 2 H), 7.44–7.35 (m, 3 H), 6.04 (s, 1 H), 4.01 (s, 6 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.14, 151.21, 132.59, 129.51, 128.35, 121.49, 90.04, 88.11, 86.51, 54.42 ppm. HRMS (ESI) calcd for $C_{14}H_{13}N_2O_2^+$ $(M+H)^+$, 241.0899, found: 241.0981.

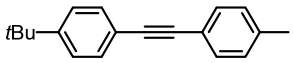


4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3m′). Following general Method I, 87 mg (0.5 mmol) of 2-chloro-4,6-dimethoxypyrimidine and 61.2 mg (0.6 mmol) of phenylacetylene

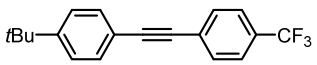
afforded the title compound as a yellow solid (91 mg, 83%) using 2:1 ethyl acetate: hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 9.8 Hz, 2 H), 7.83(s, 1 H), 7.63 (d, *J* = 8.1 Hz, 2 H), 7.42 (m, 3 H), 7.25 (d, *J* =9.3 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, CDCl3) δ = 138.74, 137.75, 134.57, 132.12, 129.70, 128.53, 125.21, 121.21, 120.61, 117.04, 92.43, 84.79 ppm. HRMS (ESI) calcd for $C_{14}H_{10}N_3^+$ $(M+H)^+$, 220.0796, found: 220.0834.



1-{(4-(*tert*-butyl)phenyl)ethynyl}-2-methylbenzene (3n′). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 70 mg (0.6 mmol) of 1-ethynyl-2-methylbenzene afforded the title compound as a white solid (105 mg, 84%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54–7.49 (m, 3 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 7.27–7.24 (m, 2 H), 7.20 (td, *J* = 4.9, 2.6 Hz, 1 H), 2.55 (s, 3 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.46, 140.13, 131.77, 131.24, 129.43, 128.12, 125.55, 125.36, 123.25, 120.54, 93.51, 87.68, 34.80, 31.21, 20.78 ppm. HRMS (ESI) calcd for $C_{19}H_{21}^+$ $(M+H)^+$, 249.1565, found: 249.1654.

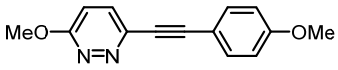


1-{(4-(*tert*-butyl)phenyl)ethynyl}-2-methylbenzene (3o′). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 77 mg (0.6 mmol) of 1-ethynyl-4-methylbenzene afforded the title compound as a brown solid (112 mg, 90%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.7 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 2.39 (s, 3 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.31, 138.15, 131.45, 131.25, 129.06, 125.31, 120.43, 120.42, 88.86, 88.83, 34.77, 31.19, 21.50 ppm. HRMS (ESI) calcd for $C_{19}H_{21}^+$ $(M+H)^+$, 249.1565, found: 249.1642.

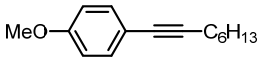


1-(*tert*-butyl)-4-{(4-(trifluoromethyl)phenylethynyl)benzene (3p′). Following general Method I, 84.5 mg (0.5 mmol) of 1-*tert*-butyl-4-chlorobenzene and 102 mg (0.6 mmol) of 1-ethynyl-2-(trifluoromethyl)benzene afforded the title compound as a white solid (136 mg, 90%) using 10:1

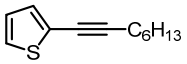
hexanes:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.63 (q, *J* = 8.7 Hz, 4 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.22, 131.75, 131.49, 128.06, 127.37, 126.76, 125.47, 125.25, 125.22, 92.00, 87.39, 34.87, 31.26 ppm. HRMS (ESI) calcd for $C_{19}H_{18}F_3^+$ $(M+H)^+$, 303.1282, found: 303.1367.



3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine (3q′). Following general Method I 72 mg (0.5 mmol) of 3-chloro-6-methoxypyridazine and 79.2 mg (0.6 mmol) of 1-ethynyl-4-methoxybenzene afforded the title compound as a yellow solid (114 mg, 95%) using 2:1 hexane:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 8.9 Hz, 2 H), 7.50 (dd, *J* = 9.1, 2.1 Hz, 1 H), 7.00–6.94 (m, 1 H), 6.93–6.86 (m, 2 H), 4.17 (s, 3 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.28, 160.33, 143.93, 133.59, 132.29, 116.68, 114.11, 113.86, 92.48, 84.59, 55.36, 55.08 ppm. HRMS (ESI) calcd for $C_{14}H_{13}N_2O_2^+$ $(M+H)^+$, 241.0899, found: 241.0974.

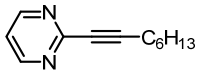


1-methoxy-4-(oct-1-yn-1-yl)benzene (3r′). Following general Method I, 71.3 mg (0.5 mmol) of 1-chloro-4-methoxybenzene and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a brown oil (108.7 mg, 99%) using 99:1 hexanes:diethyl ether as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.9 Hz, 2 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 3.81 (s, 3 H), 2.41 (t, *J* = 7.2 Hz, 2 H), 1.62 (p, *J* = 7.3 Hz, 2 H), 1.54–1.43 (m, 2 H), 1.40–1.21 (m, 6 H), 0.94 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.94, 132.85, 116.25, 113.77, 88.80, 80.25, 55.20, 31.44, 28.89, 28.68, 22.64, 19.44, 14.13 ppm. HRMS (ESI) calcd for $C_{15}H_{21}O^+$ $(M+H)^+$, 217.1514, found: 217.1631.

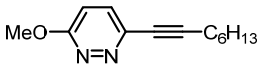


2-(oct-1-yn-1-yl)thiophene (3s′). Following general Method I, 58.5 mg (0.5 mmol) of 2-chlorothiophene and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a yellow oil (86.4 mg, 90%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.19 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.15 (dd, *J* = 3.6, 1.2 Hz, 1 H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 1.68–1.56 (m, 2 H), 1.51–1.44 (m, 2 H), 1.39–1.26 (m, 2 H), 0.94 (t, *J* = 7.0 Hz, 3

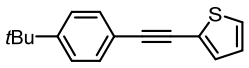
H)ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 130.88, 126.77, 125.84, 124.24, 94.60, 73.65, 31.39, 28.60–28.52 (m), 22.61, 19.72, 14.13 ppm. HRMS (ESI) calcd for $C_{12}H_{17}S^+$ $(M+H)^+$, 193.0973, found: 193.1123.



2-(oct-1-yn-1-yl)pyrimidine (3t′). Following general Method I, 57 mg (0.5 mmol) of 2-chloropyrimidine and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a yellow oil (83.0 mg, 88%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.62 (d, *J* = 5.0 Hz, 2 H), 7.15 (s, 1 H), 2.39 (t, *J* = 7.2 Hz, 2 H), 1.58 (p, *J* = 7.3 Hz, 2 H), 1.39 (dtd, *J* = 9.9, 7.4, 5.5 Hz, 2 H), 1.27–1.15 (m, 2 H), 0.81 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.74 (m), 153.20, 119.41, 90.75, 79.86, 31.26, 28.62, 27.96, 22.45, 19.19, 14.02 ppm. HRMS (ESI) calcd for $C_{12}H_{17}N_2^+$ $(M+H)^+$, 189.1313, found: 189.1390.

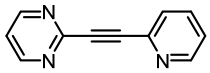


3-methoxy-6-(oct-1-yn-1-yl)pyridazine (3u′). Following general Method I, 72.2 mg (0.5 mmol) of 3-chloro-6-methoxypyridazine and 66 mg (0.6 mmol) of 1-octyne afforded the title compound as a yellow solid (99 mg, 91%) using 9:1 hexanes:ethyl acetate as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 9.1 Hz, 1 H), 6.86 (d, *J* = 9.1 Hz, 1 H), 4.08 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 2 H), 1.59 (p, *J* = 7.3 Hz, 2 H), 1.46–1.37 (m, 2 H), 1.32–1.21 (m, 4 H), 0.85 (t, *J* = 7.0 Hz, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.18, 143.98, 132.28, 116.54, 94.09, 54.89, 31.29, 28.57, 28.16, 22.50, 19.37, 14.04 ppm. HRMS (ESI) calcd for $C_{13}H_{19}N_2O^+$ $(M+H)^+$, 219.1419, found: 219.1502.



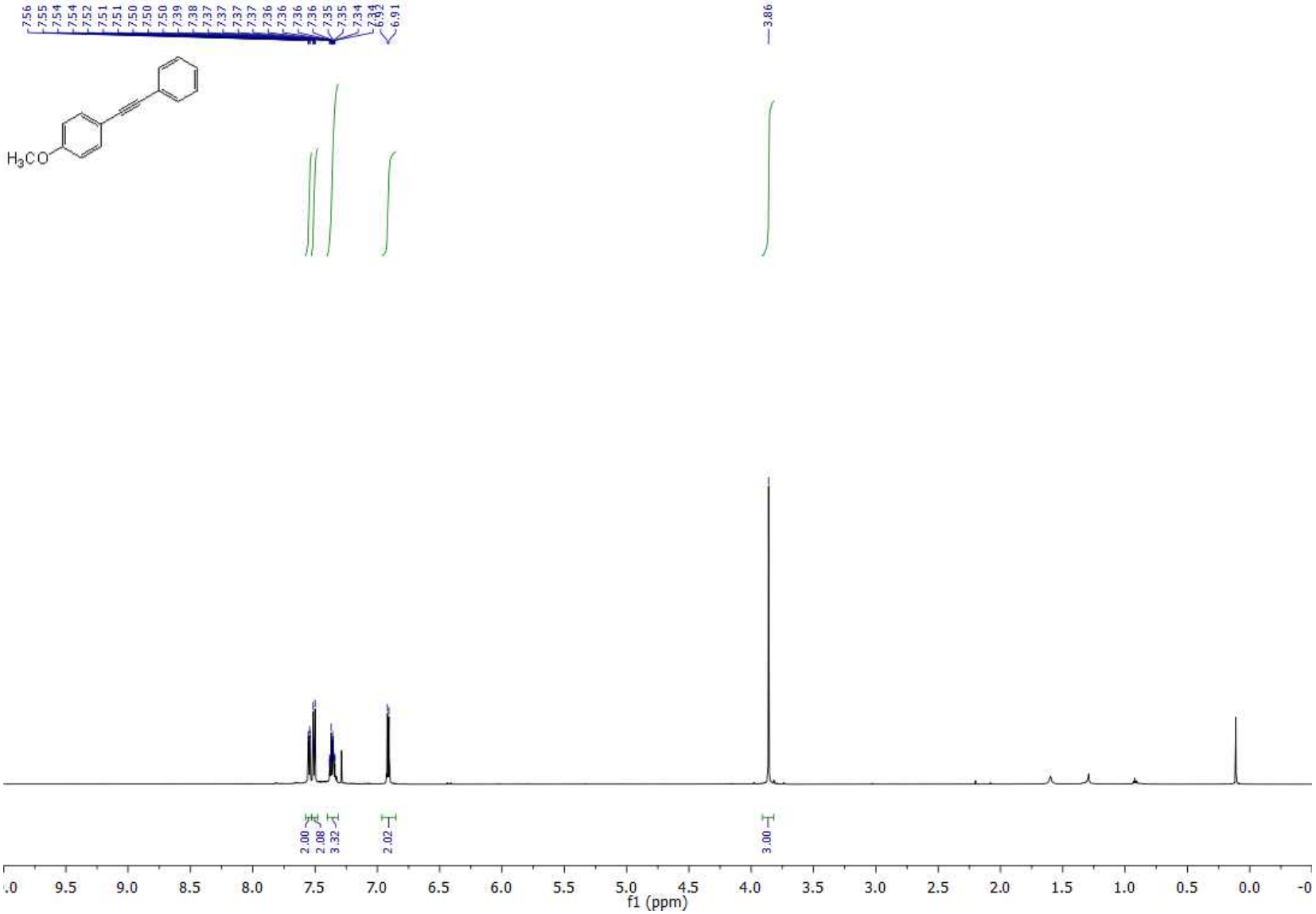
2-{(4-(tert-butyl)phenyl)ethynyl}thiophene (3v′). Following general Method I, 84.5 mg (0.5 mmol) of 1-tert-butyl-4-chlorobenzen and 65 mg (0.6 mmol) of 2-ethynylthiophene afforded the title compound as a brown oil (114 mg, 95%) using hexanes as the column eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.52 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.47 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.22 (dd, *J* = 5.0, 1.1 Hz, 1 H), 1.35 (s, 9 H) ppm. ^{13}C NMR

(151 MHz, $CDCl_3$) δ = 151.49, 131.25, 129.93, 128.32, 125.36, 125.27, 122.53, 120.16, 89.00, 83.81, 34.80, 31.19 ppm. HRMS (ESI) calcd for $C_{16}H_{17}S^+$ $(M+H)^+$, 241.0973, found: 241.1123.

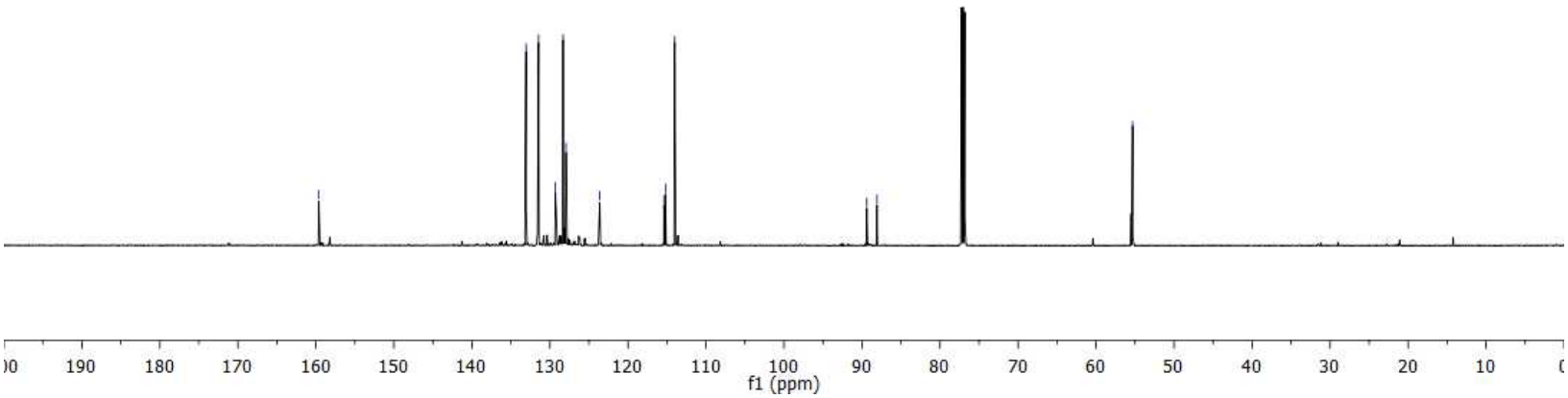


2-(pyridin-2-ylethynyl)pyrimidine (3w′). Following general Method I, 57 mg (0.5 mmol) of 2-chloropyrimidine and 62 mg (0.6 mmol) of 2-ethynlpyridine afforded the title compound as a brown solid (33 mg, 36%) using 100:1 dichloromethane: methanol as the column eluent. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 4.9 Hz, 2H), 8.71–8.67 (m, 1 H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.70–7.65 (m, 1 H), 7.34 (ddd, *J* = 7.5, 4.9, 1.3 Hz, 1 H), 7.30 (t, *J* = 5.0 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.30, 152.90, 150.29, 142.01, 135.17, 128.12, 123.81, 120.13, 86.79, 86.00 ppm. HRMS (ESI) calcd for $C_{11}H_8N_3^+$ $(M+H)^+$, 182.0640, found: 182.0705.

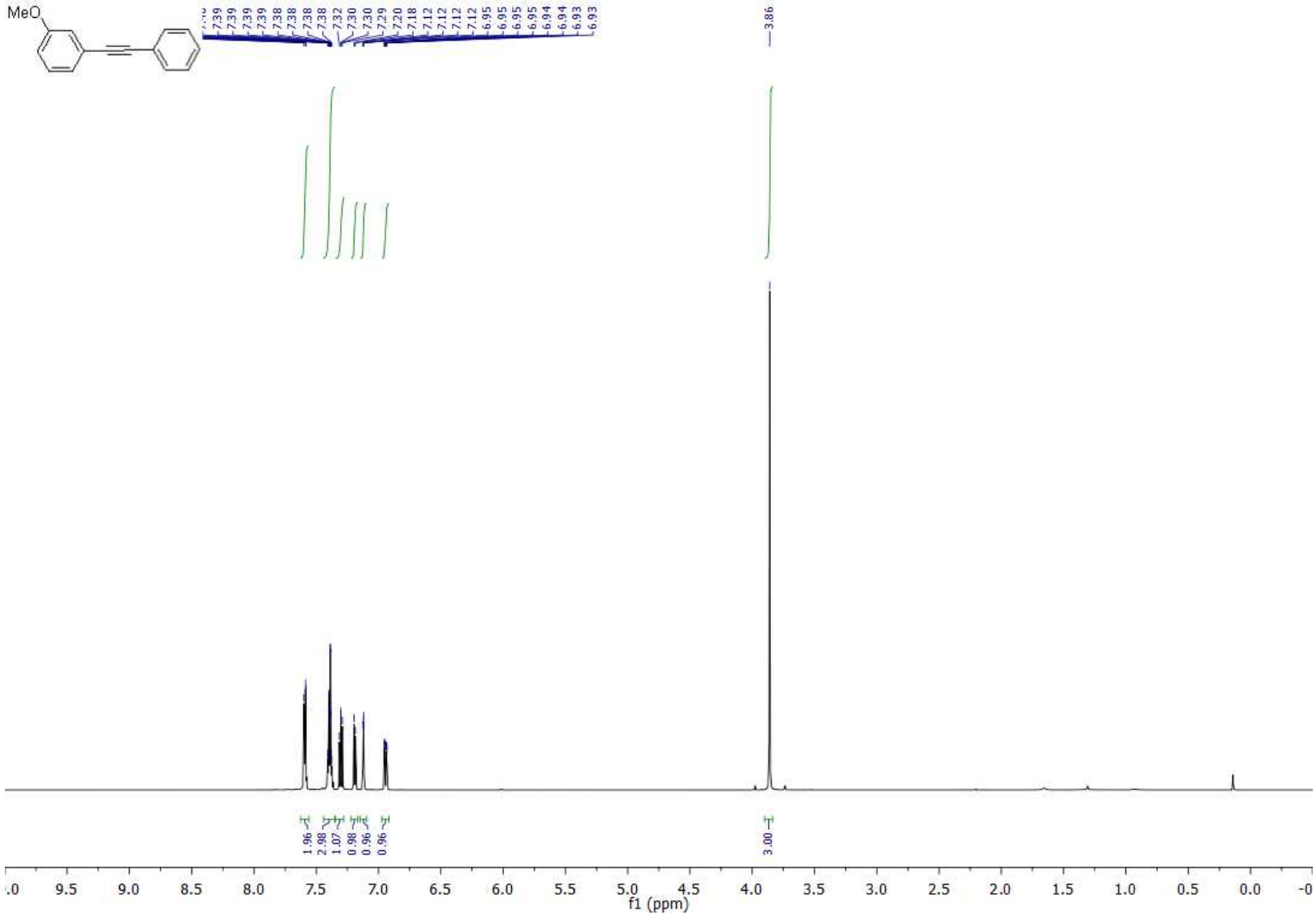
^{1}H NMR spectrum of **1-methoxy-4-(phenylethynyl)benzene (3a′)**.



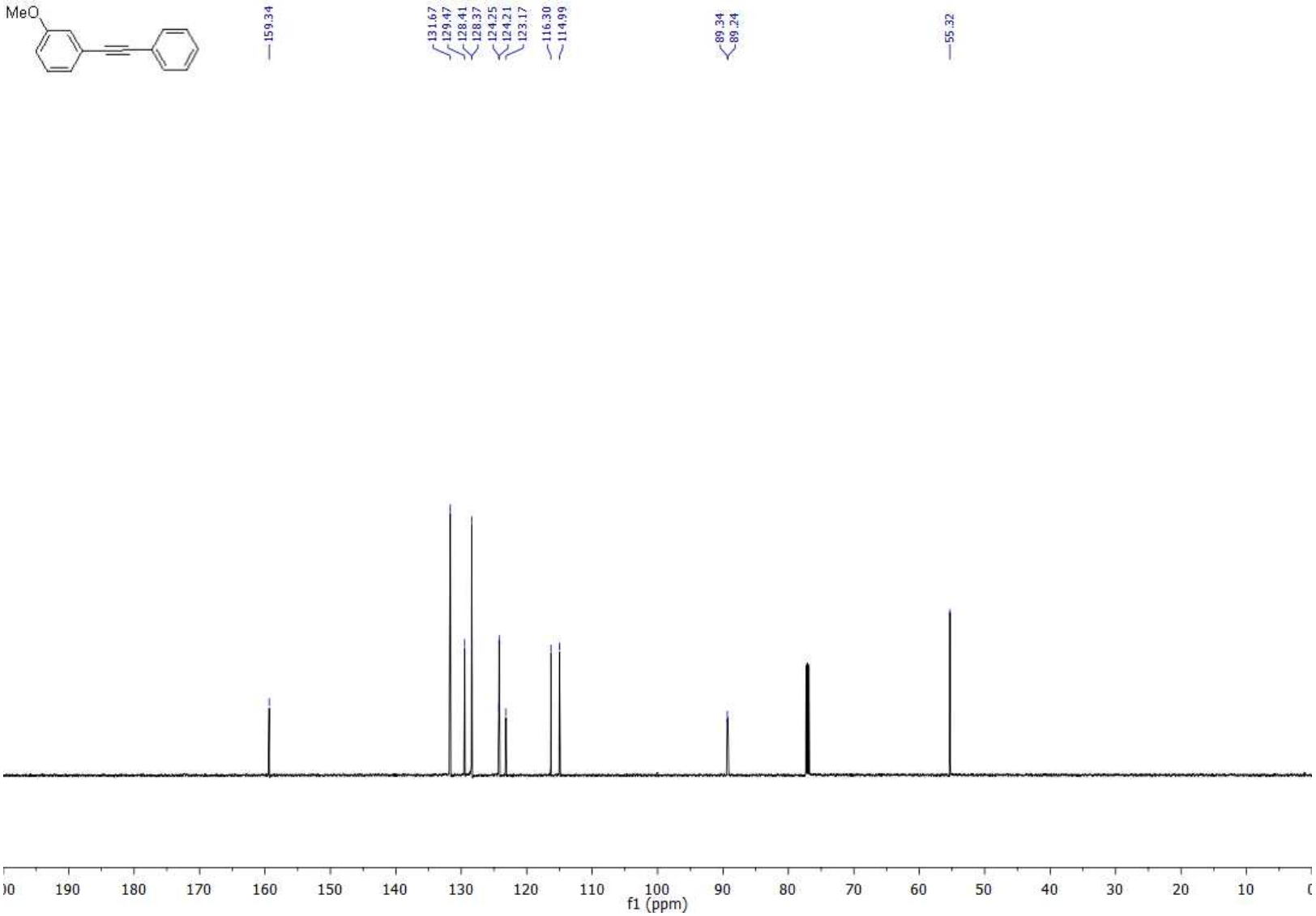
^{13}C NMR spectrum of **1-methoxy-4-(phenylethynyl)benzene (3a′)**.



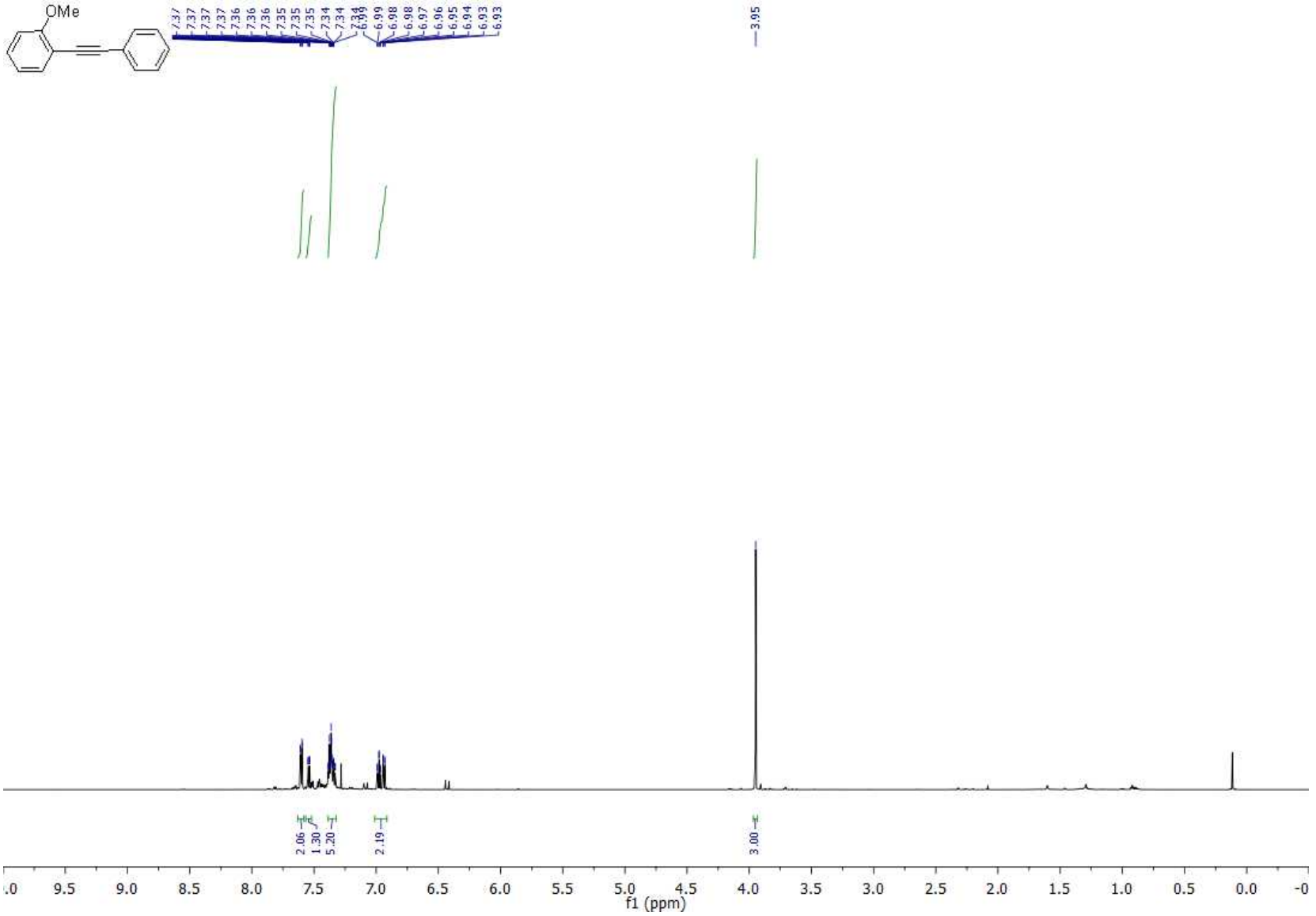
^{1}H NMR spectrum of **1-methoxy-3-(phenylethynyl)benzene (3b′)**



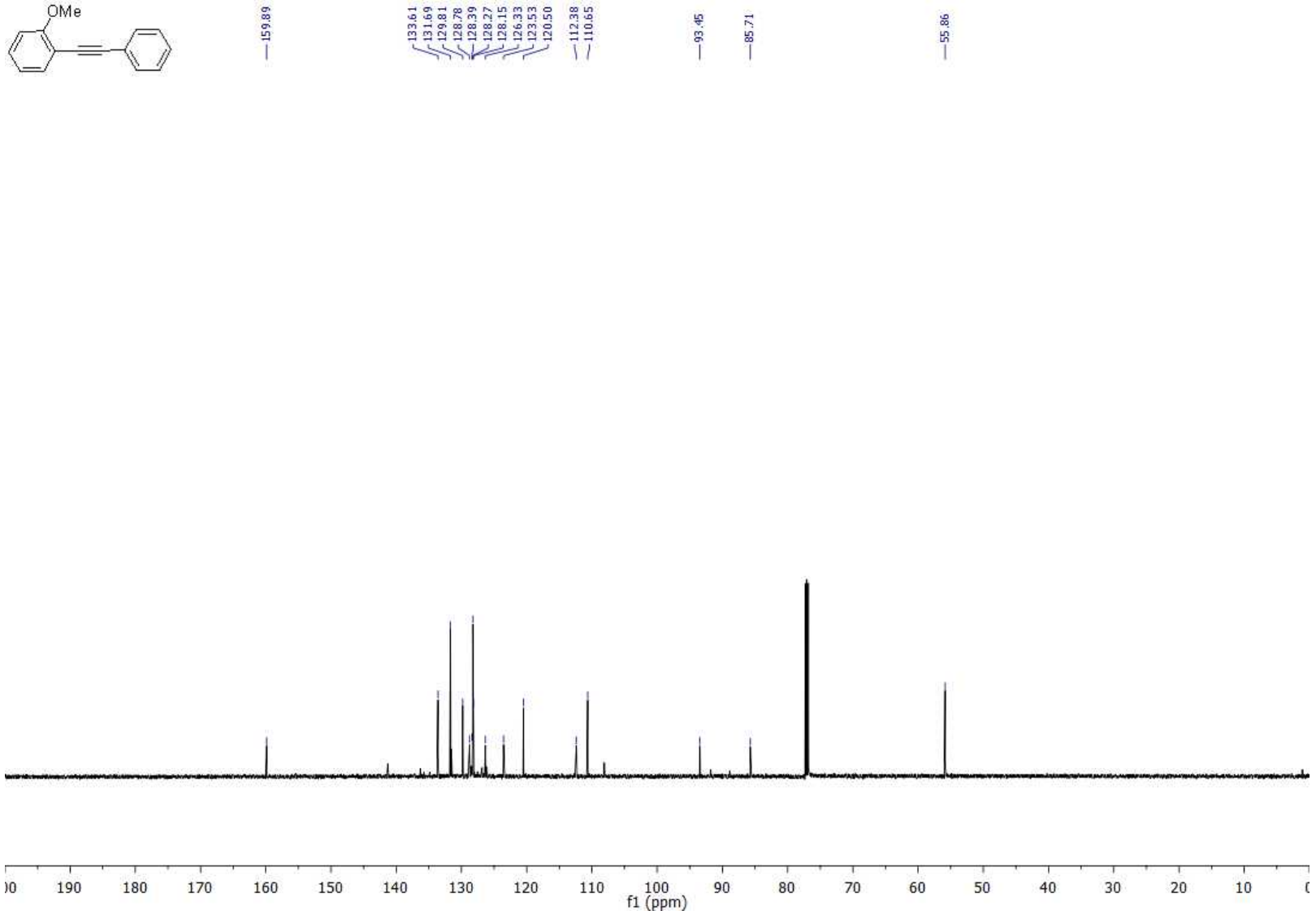
^{13}C NMR spectrum of **1-methoxy-3-(phenylethynyl)benzene (3b′)**



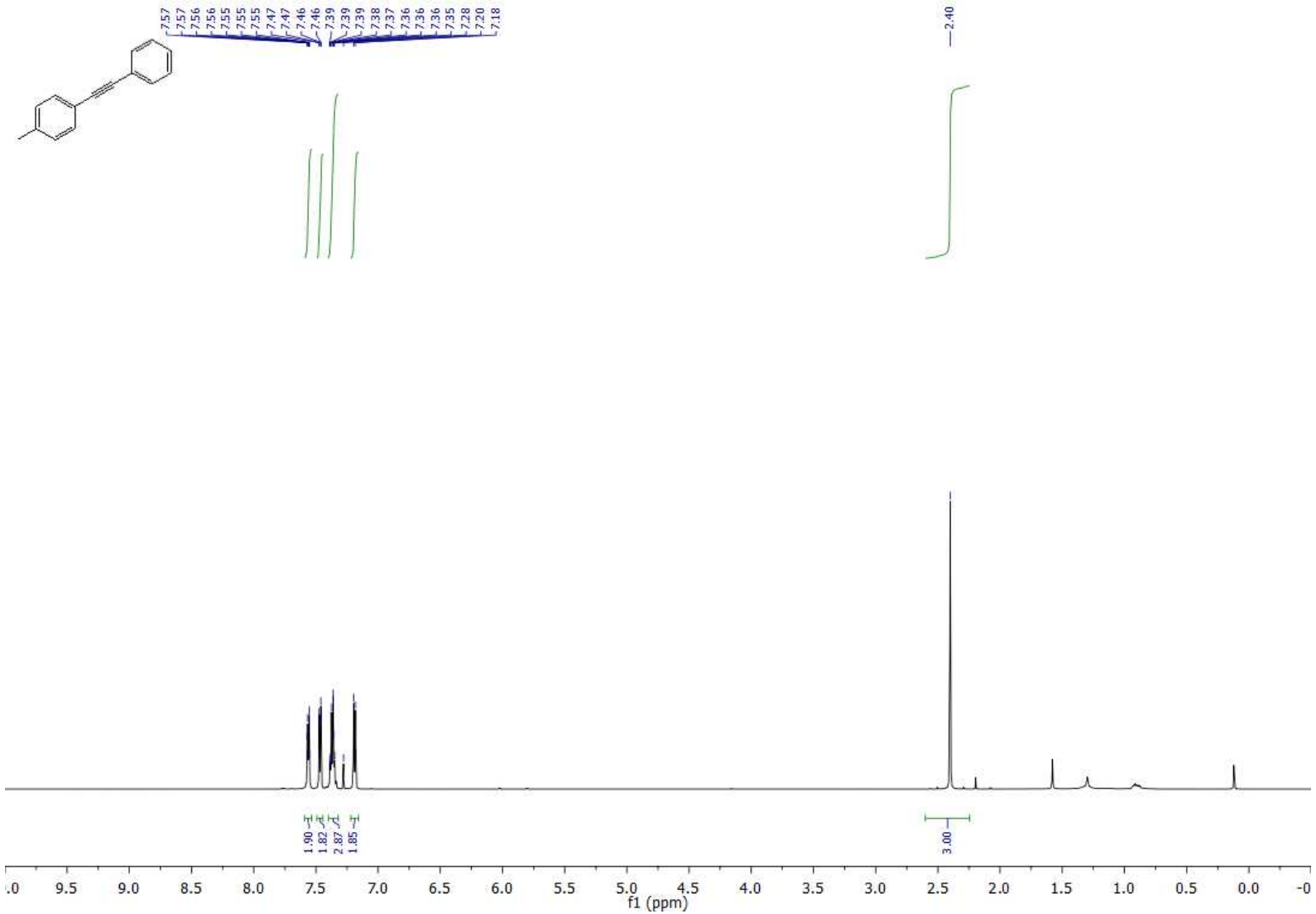
^{1}H NMR spectrum of **1-methoxy-2-(phenylethynyl)benzene (3c′)**



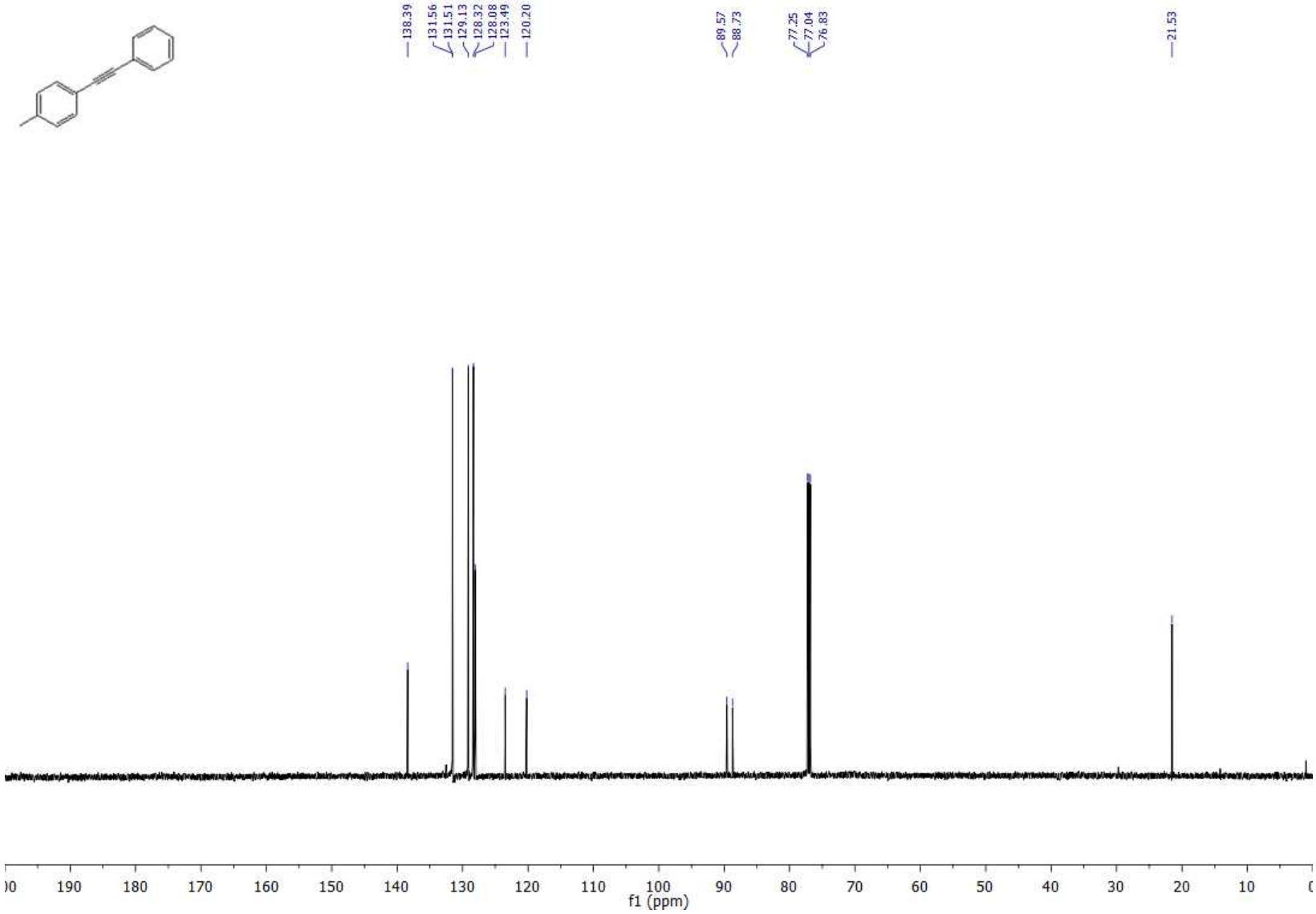
^{13}C NMR spectrum of **1-methoxy-2-(phenylethynyl)benzene (3c′)**



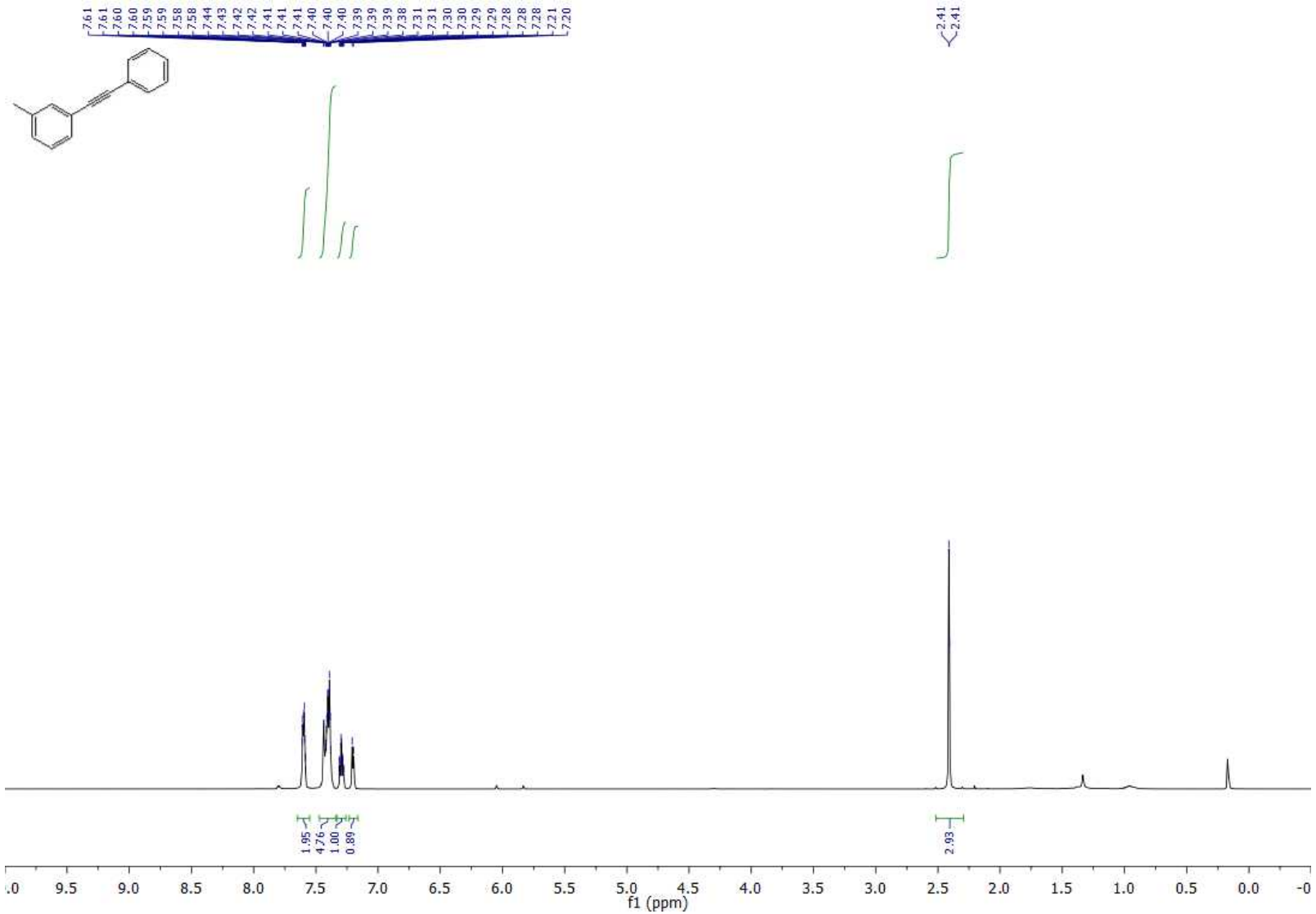
^{1}H NMR spectrum of **1-methyl-4-(phenylethynyl)benzene (3d′)**



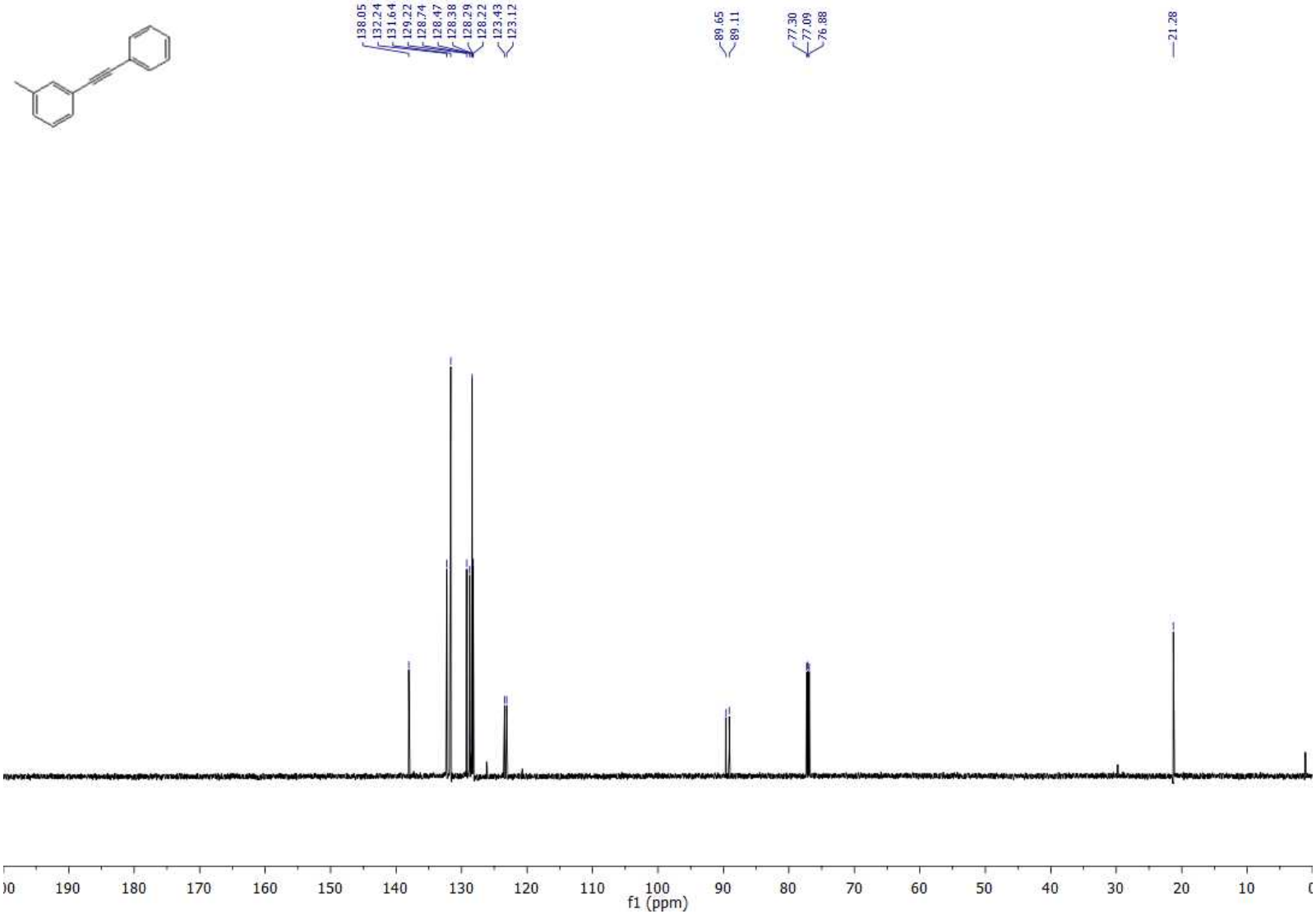
^{13}C NMR spectrum of **1-methyl-4-(phenylethynyl)benzene (3d′)**



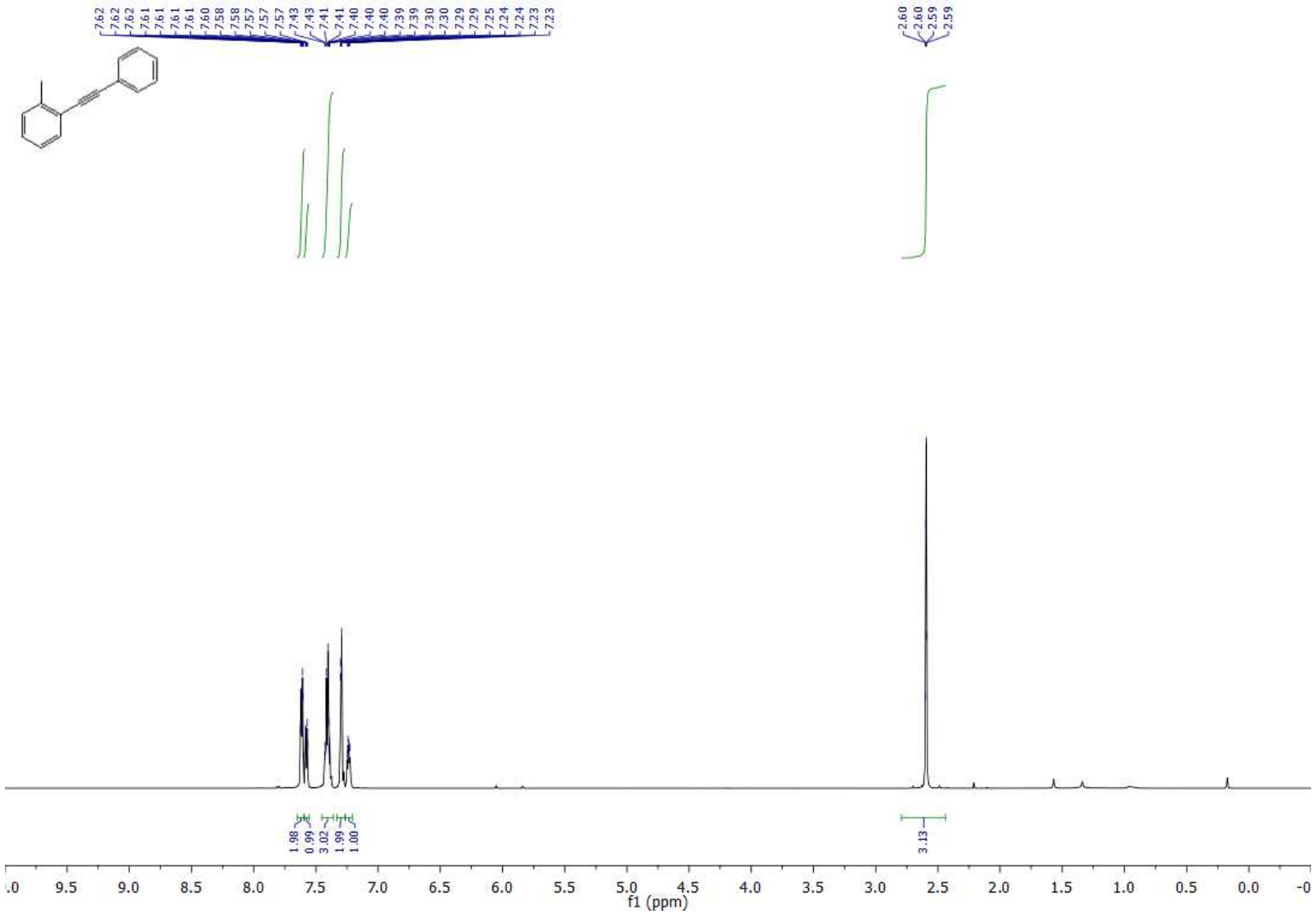
^{1}H NMR spectrum of **1-methyl-3-(phenylethynyl)benzene (3e′)**



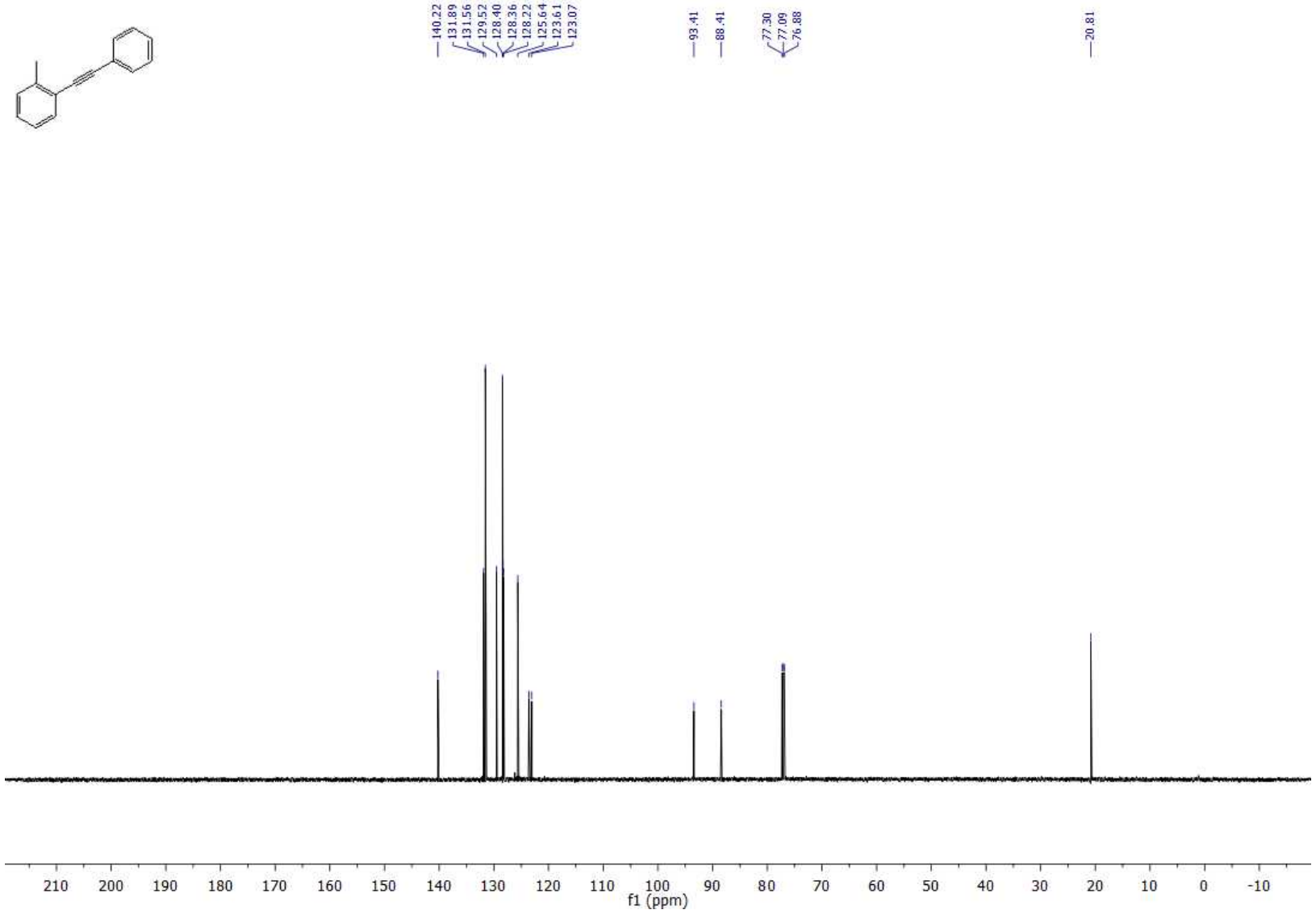
^{13}C NMR spectrum of **1-methyl-3-(phenylethynyl)benzene (3e′)**



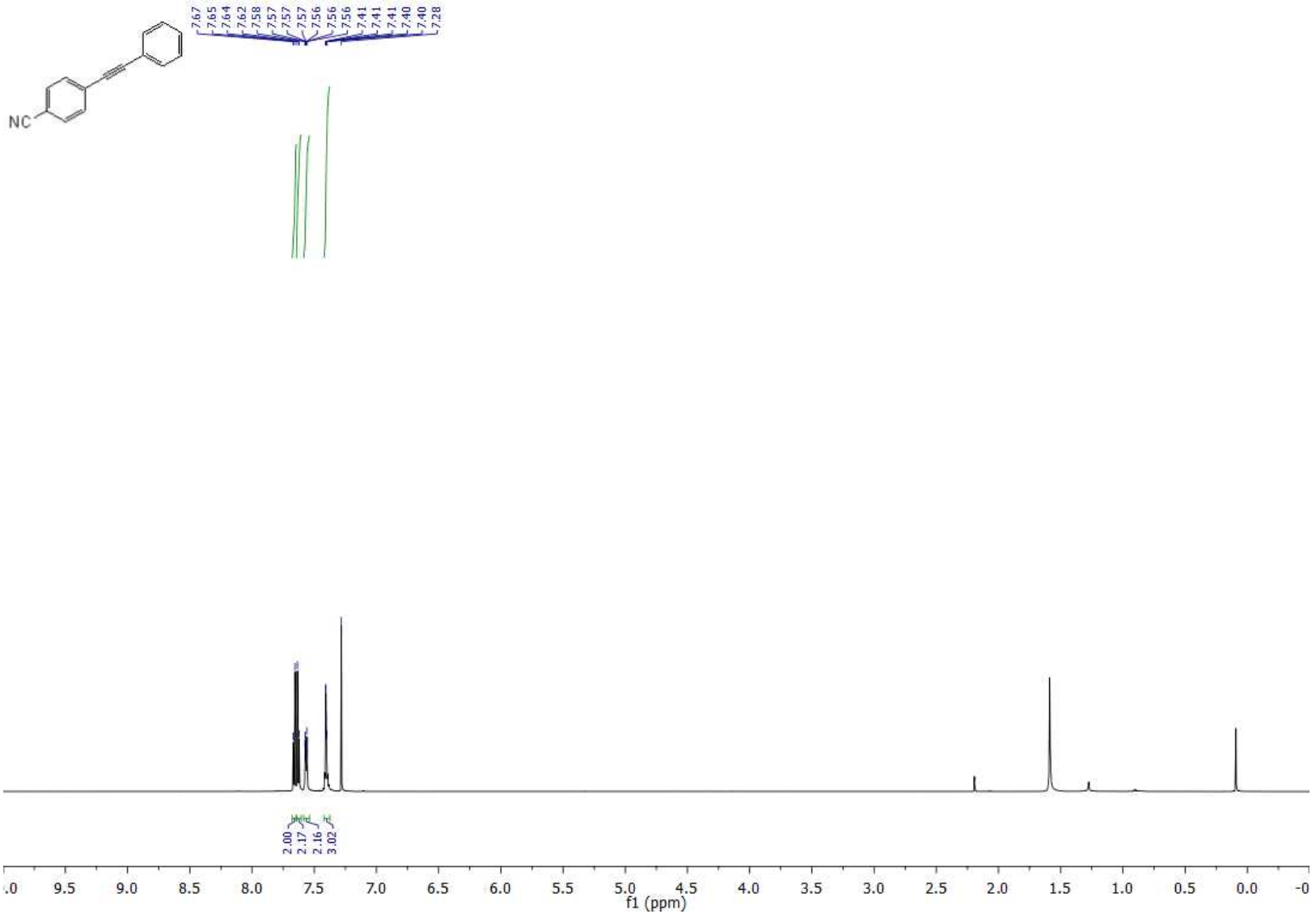
^{1}H NMR spectrum of **1-methyl-2-(phenylethynyl)benzene (3f')**



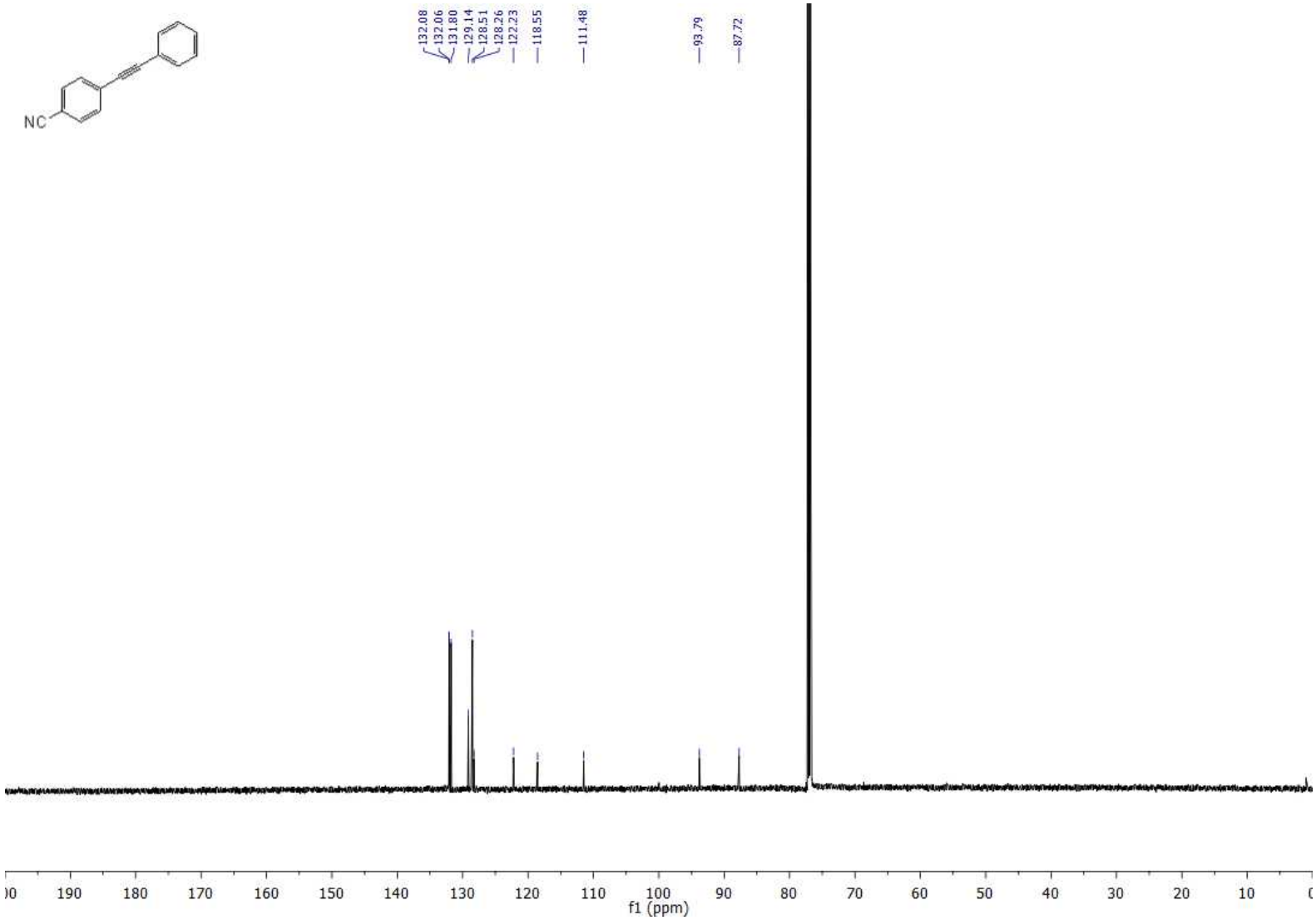
^{13}C NMR spectrum of **1-methyl-2-(phenylethynyl)benzene (3f′)**



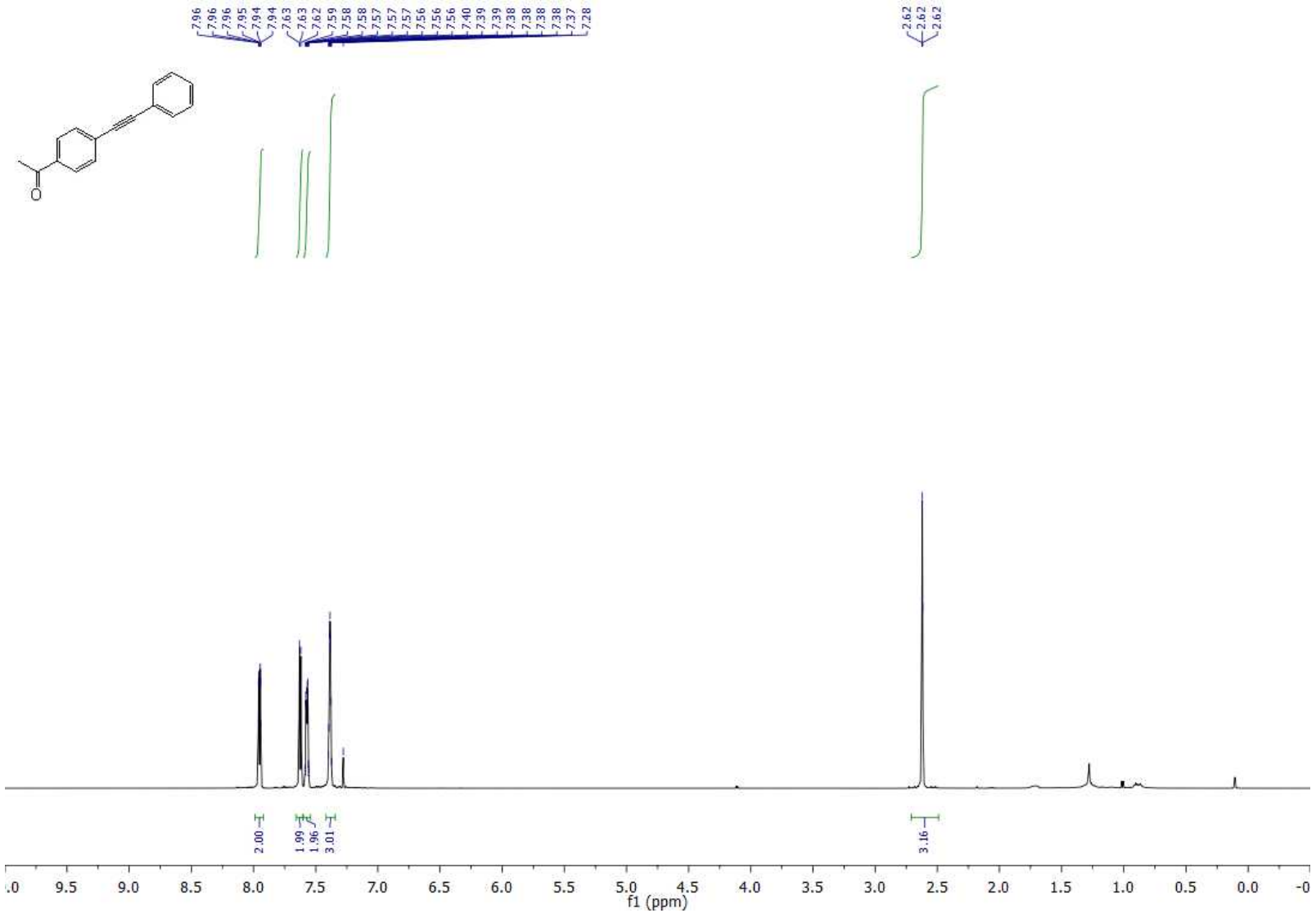
^{1}H NMR spectrum of **4-(phenylethynyl)benzonitrile (3g′)**.



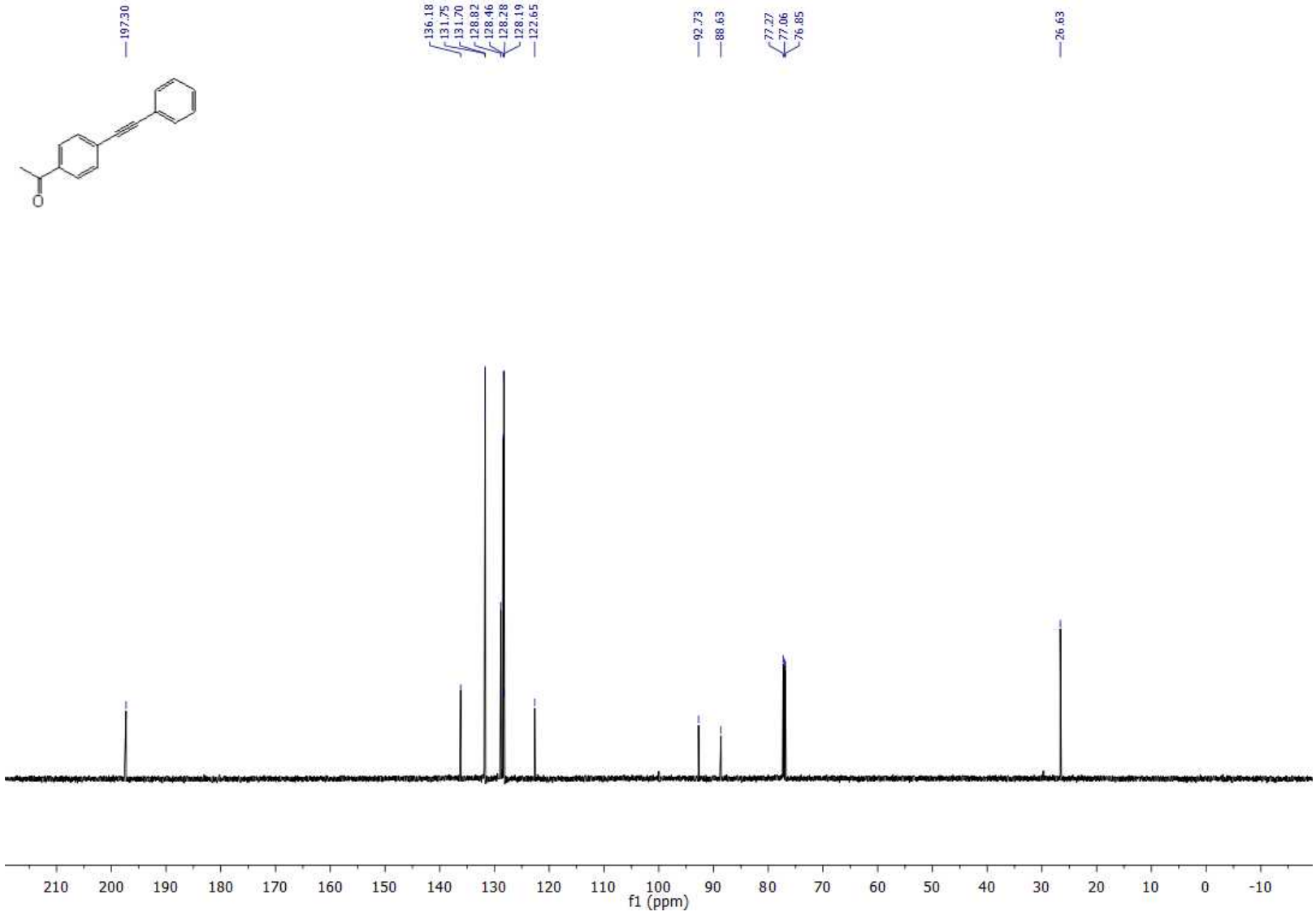
^{13}C NMR spectrum of **4-(phenylethynyl)benzonitrile (3g′)**.



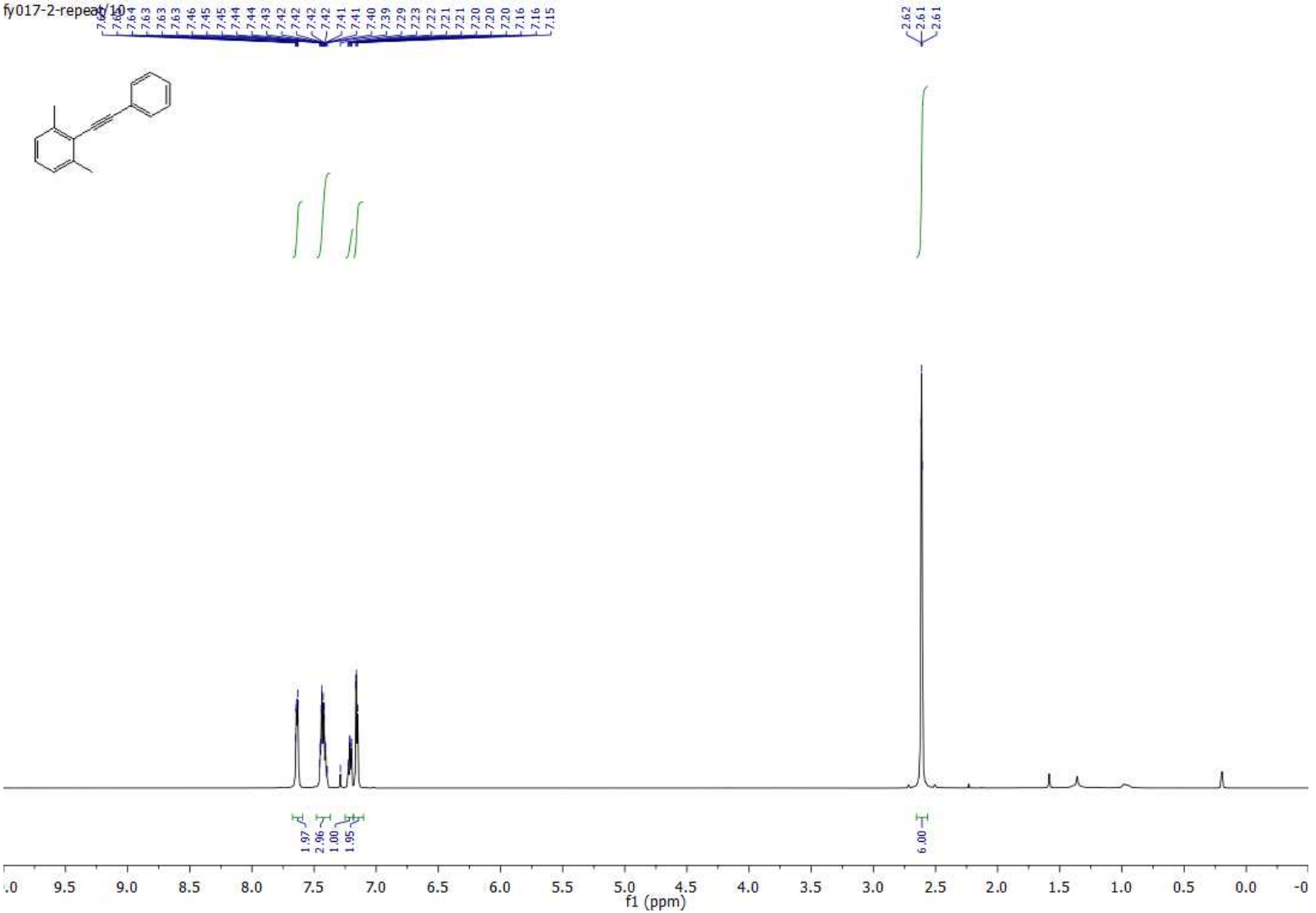
^{1}H NMR spectrum of **1-(4-(phenylethynyl)phenyl)ethan-1-one (3h′)**



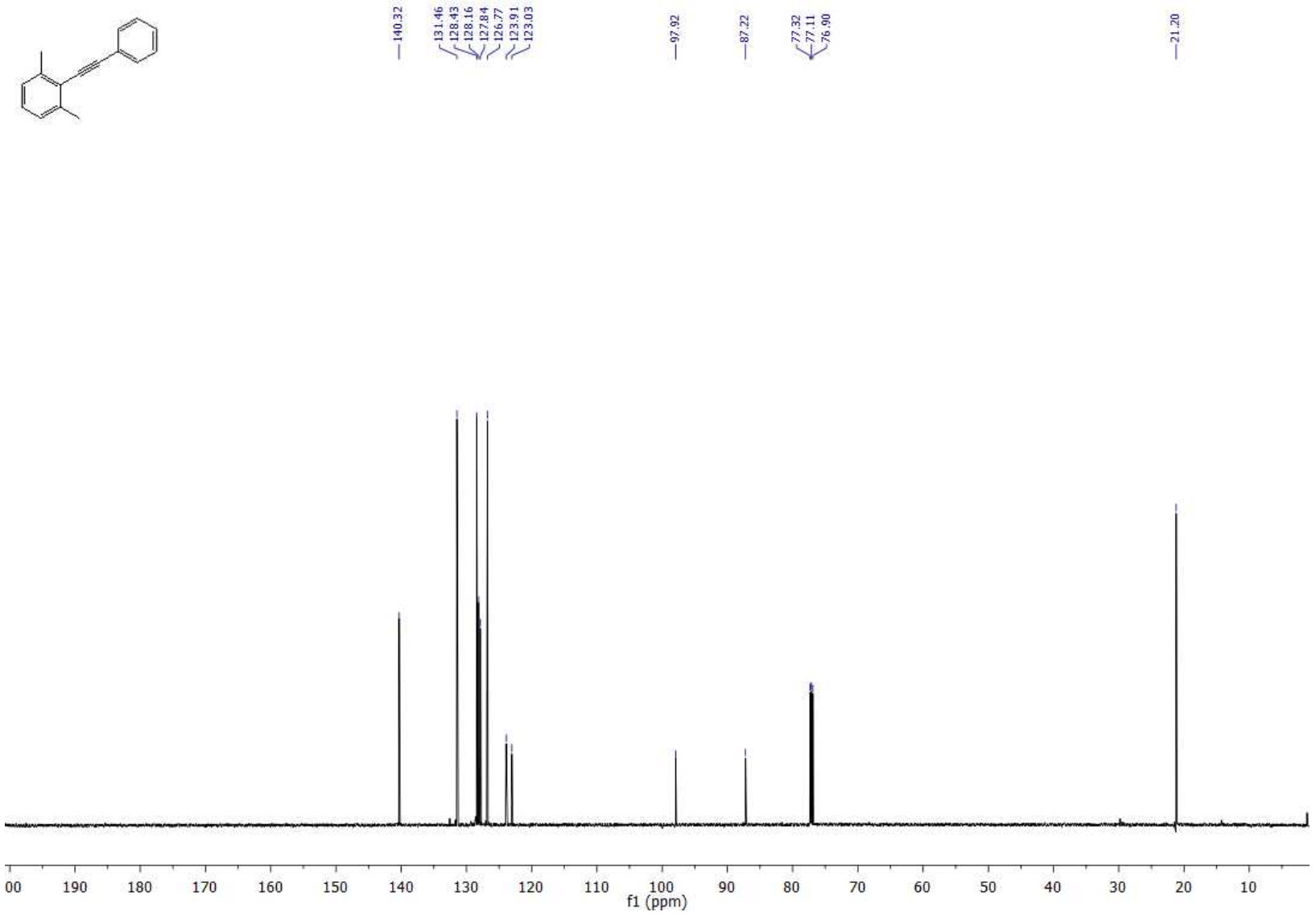
^{13}C NMR spectrum of **1-(4-(phenylethynyl)phenyl)ethan-1-one (3h′)**



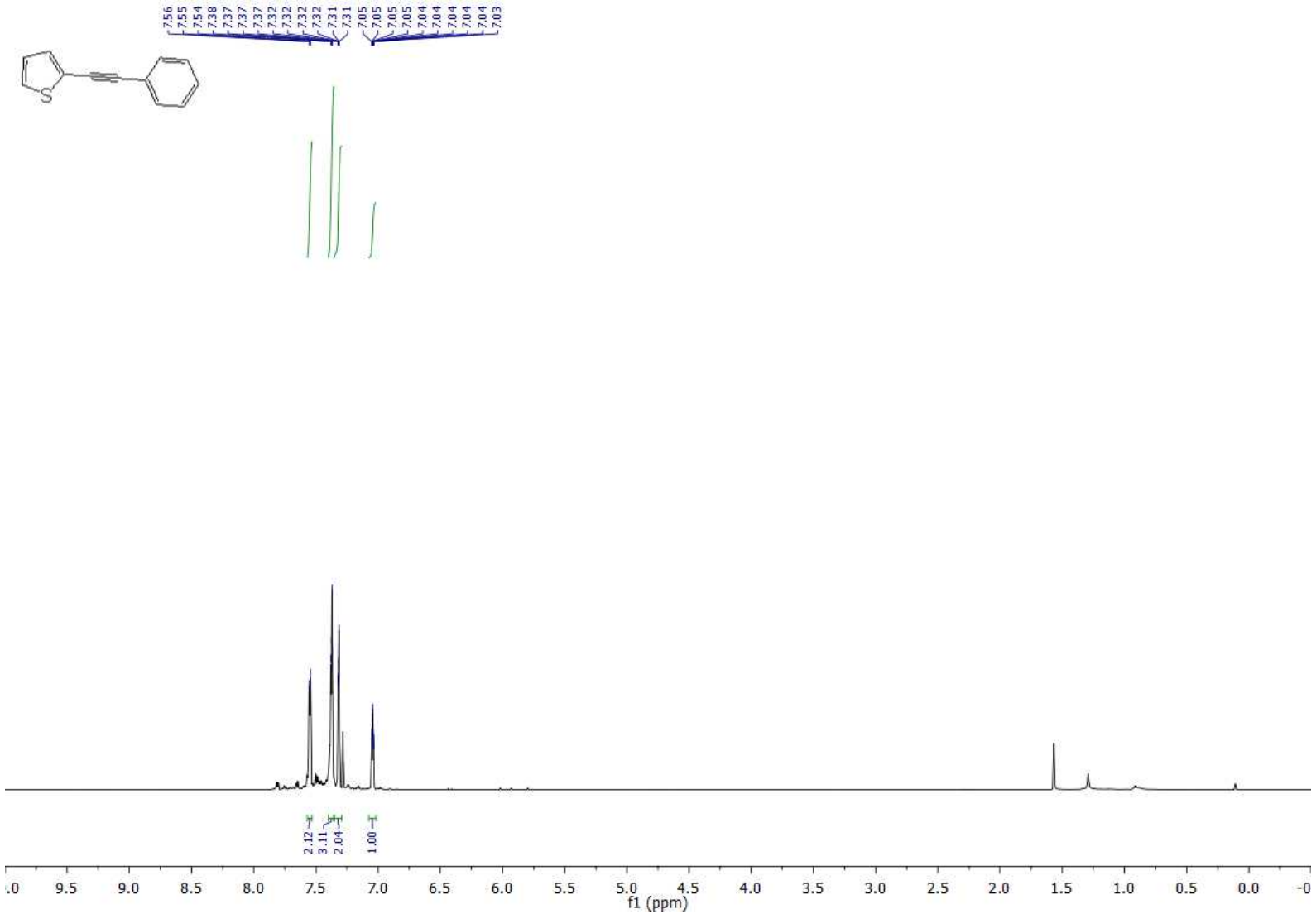
^{1}H NMR spectrum of **1,3-dimethyl-2-(phenylethynyl)benzene (3i′)**.



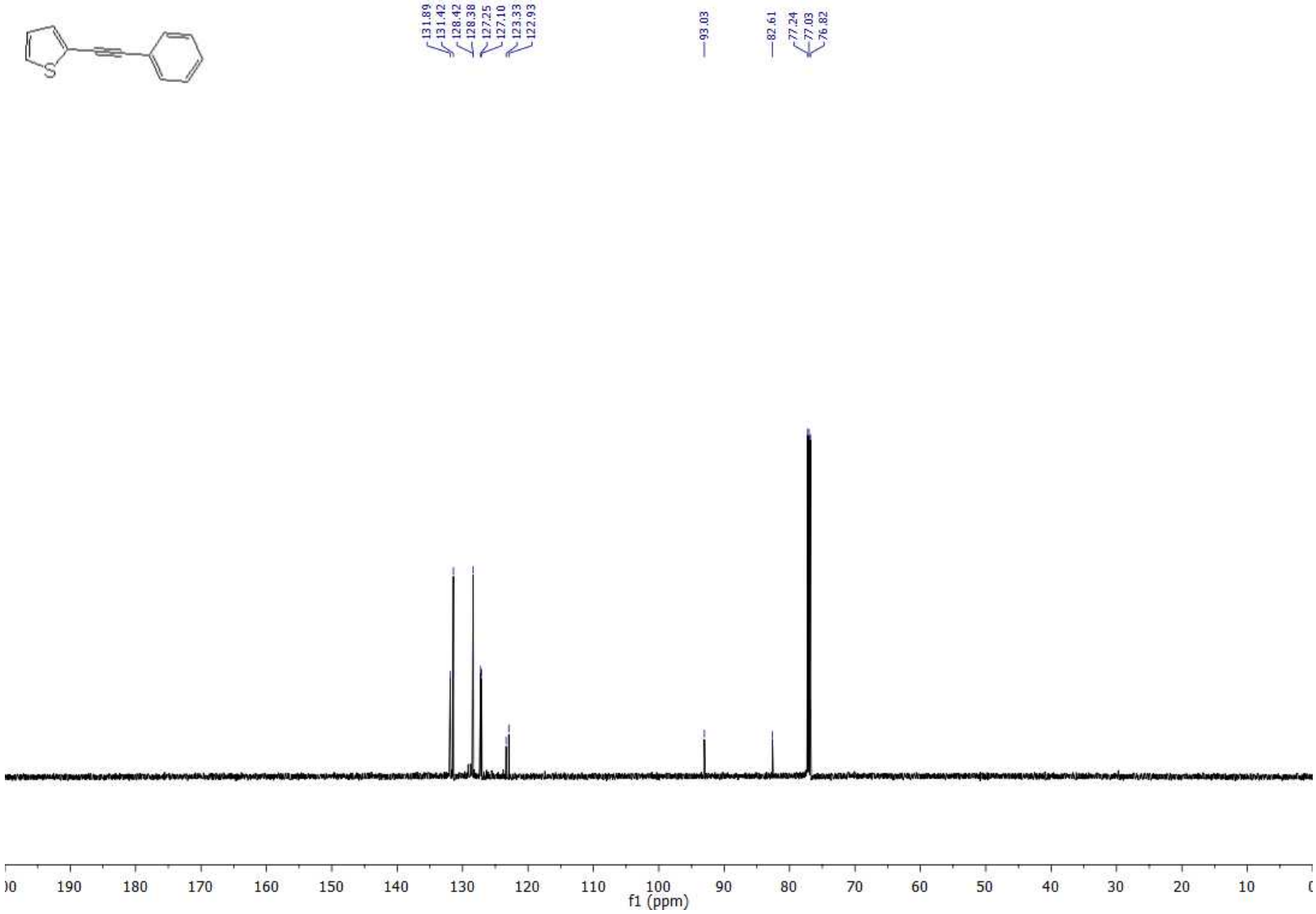
^{13}C NMR spectrum of **1,3-dimethyl-2-(phenylethynyl)benzene (3i′)**.



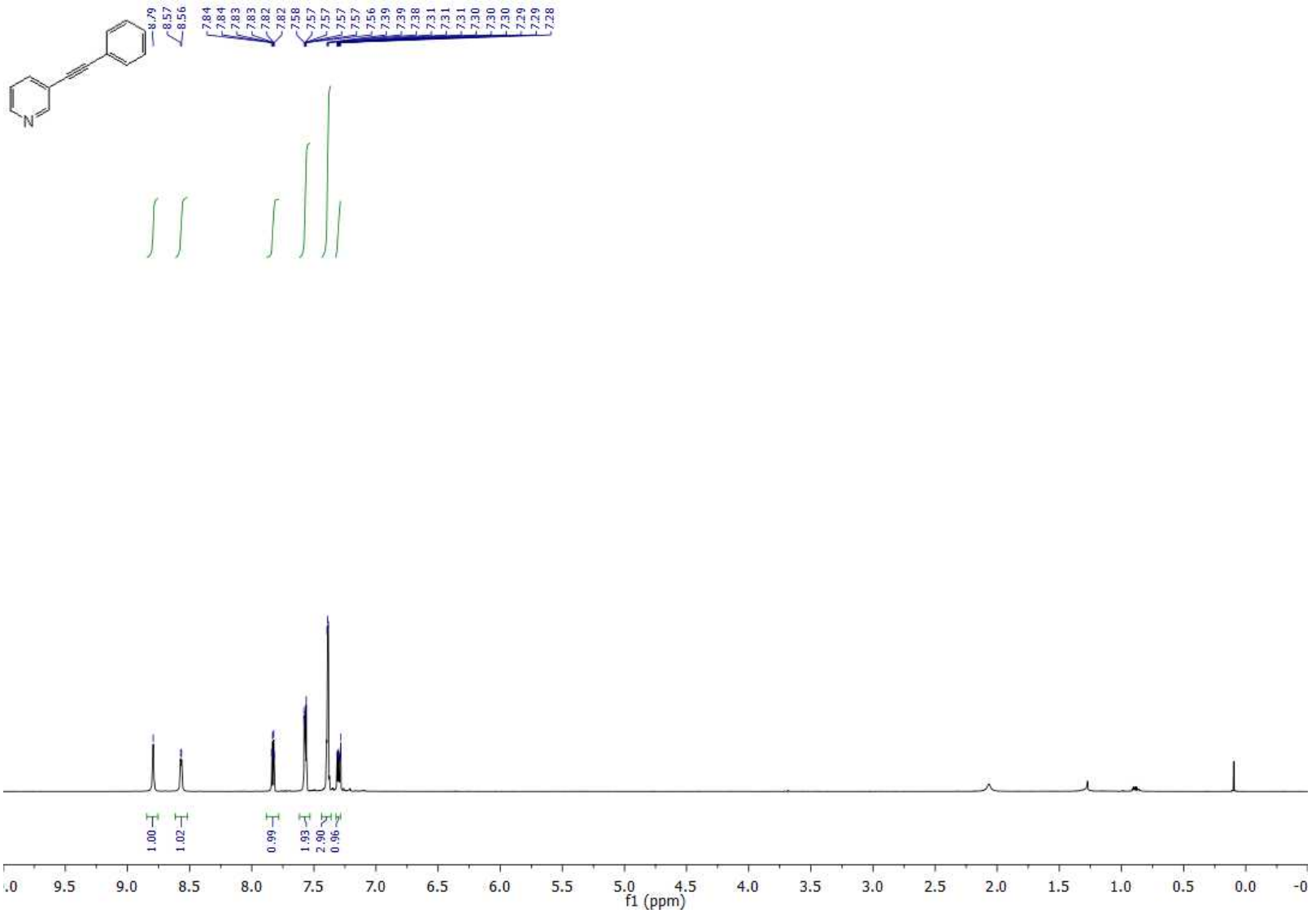
^{1}H NMR spectrum of **2-(phenylethynyl)thiophene (3j′)**



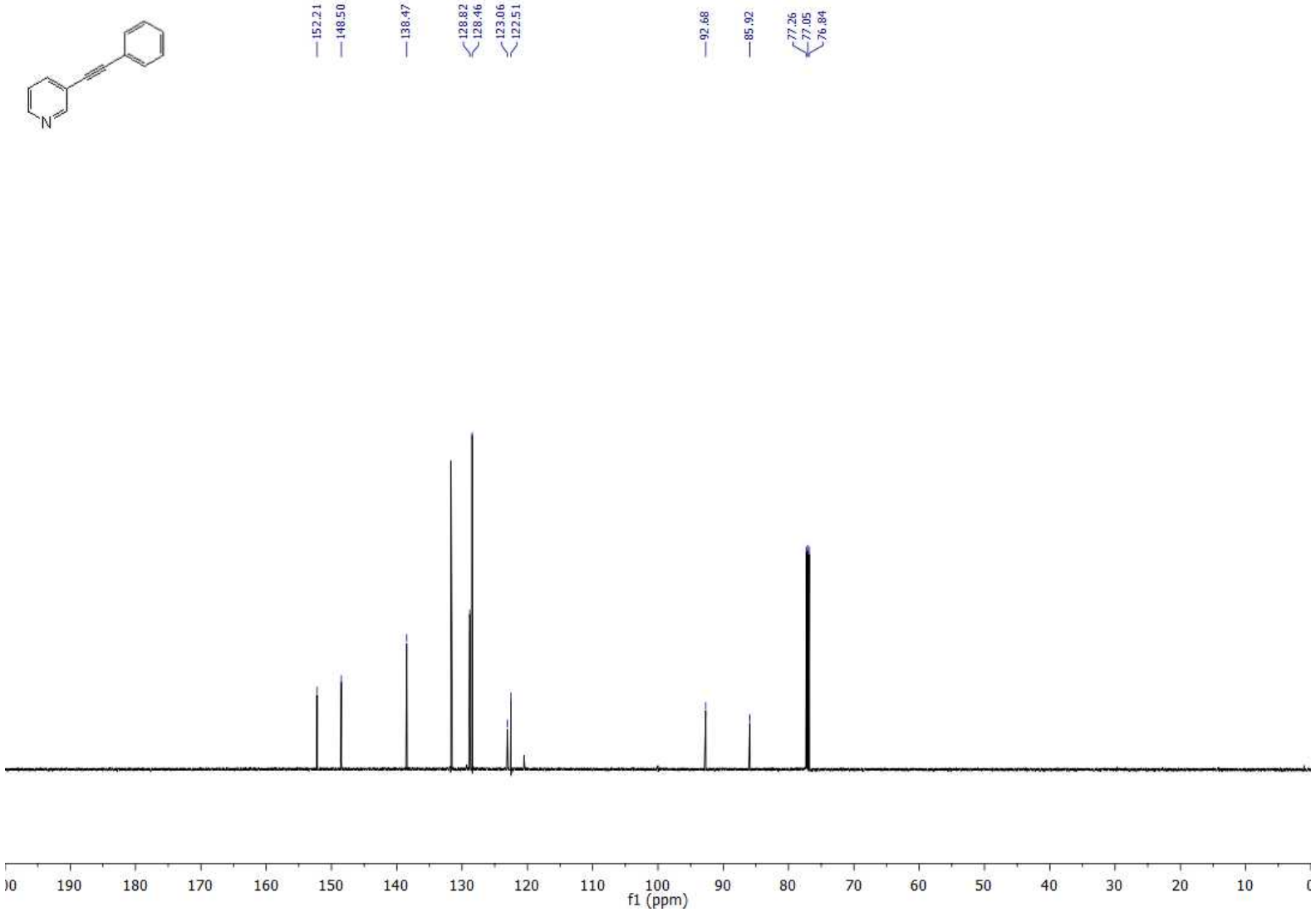
^{13}C NMR spectrum of **2-(phenylethynyl)thiophene (3j′)**



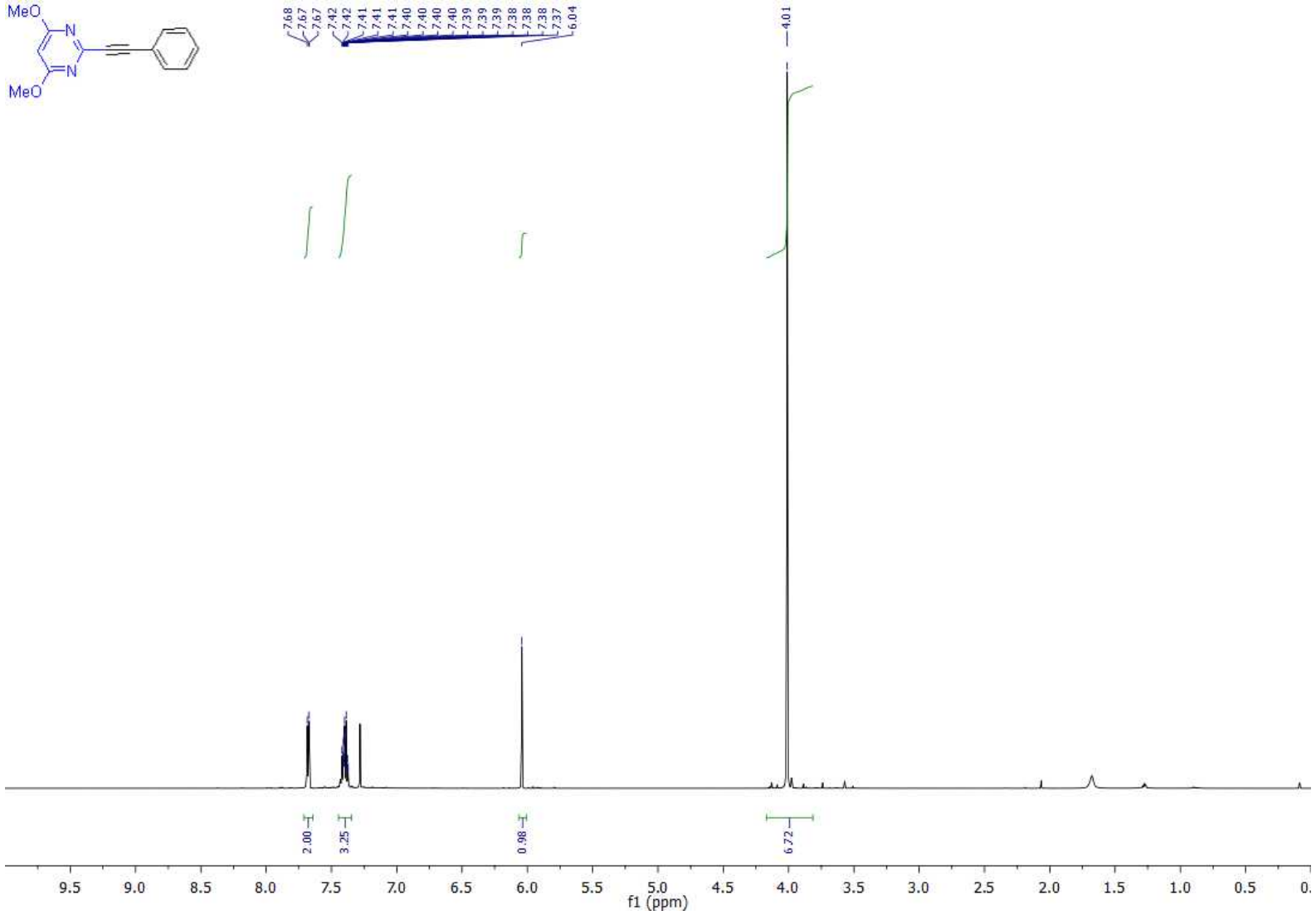
^{1}H NMR spectrum of **3-(phenylethynyl)pyridine (3k′)**.



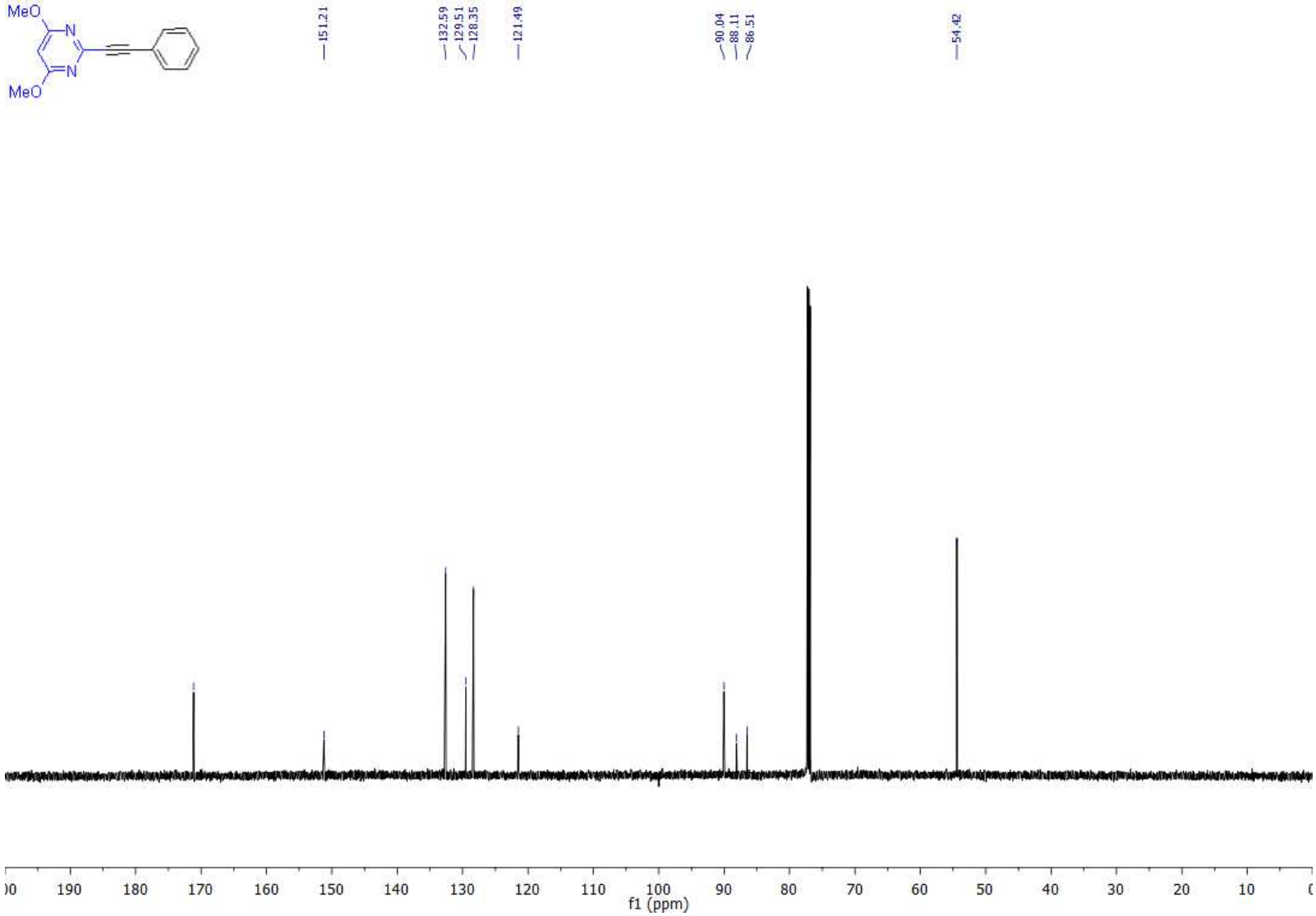
^{13}C NMR spectrum of **3-(phenylethynyl)pyridine (3k′)**.



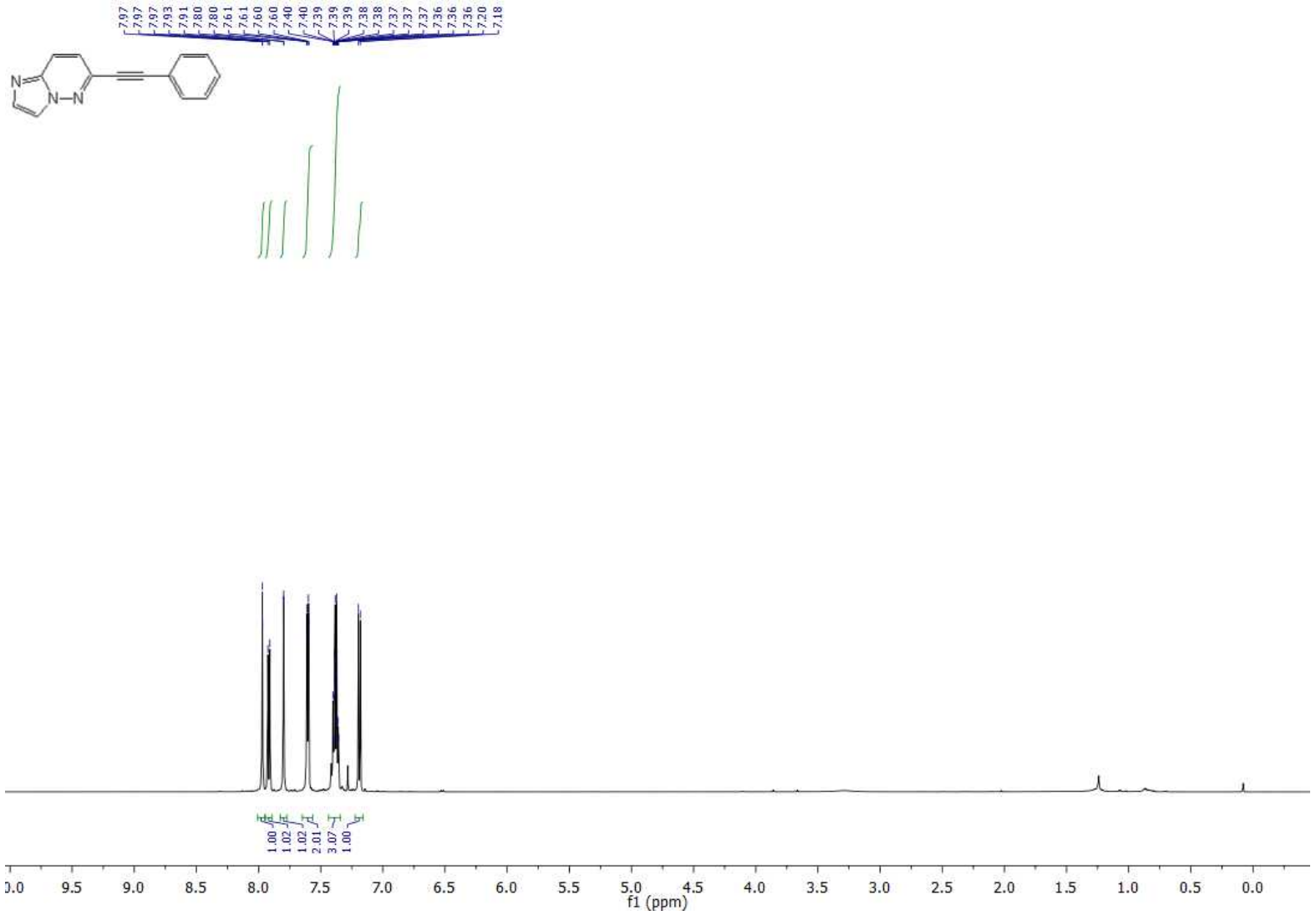
^{1}H NMR spectrum of **4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3l′)**.



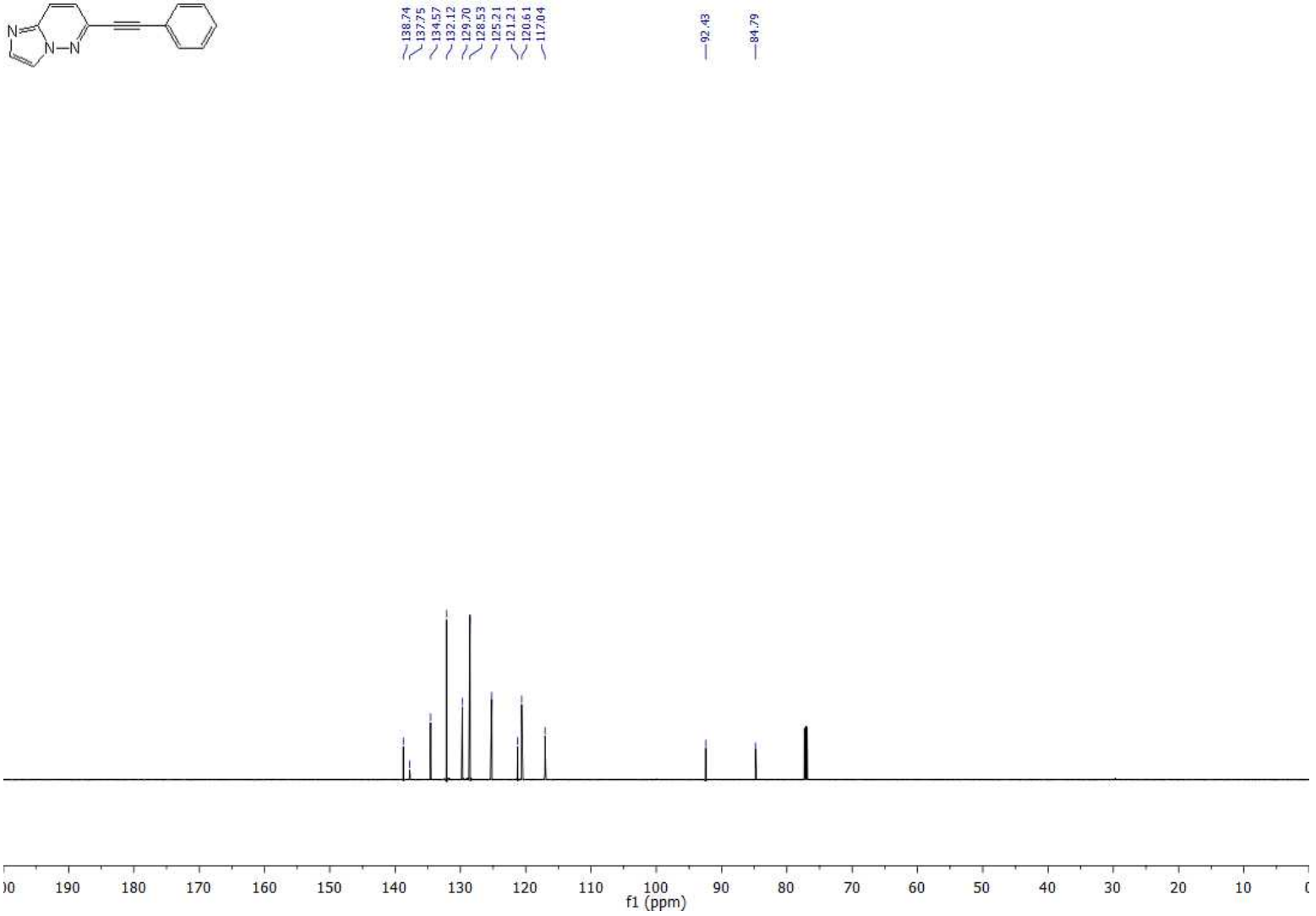
^{13}C NMR spectrum of **4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3l′)**.



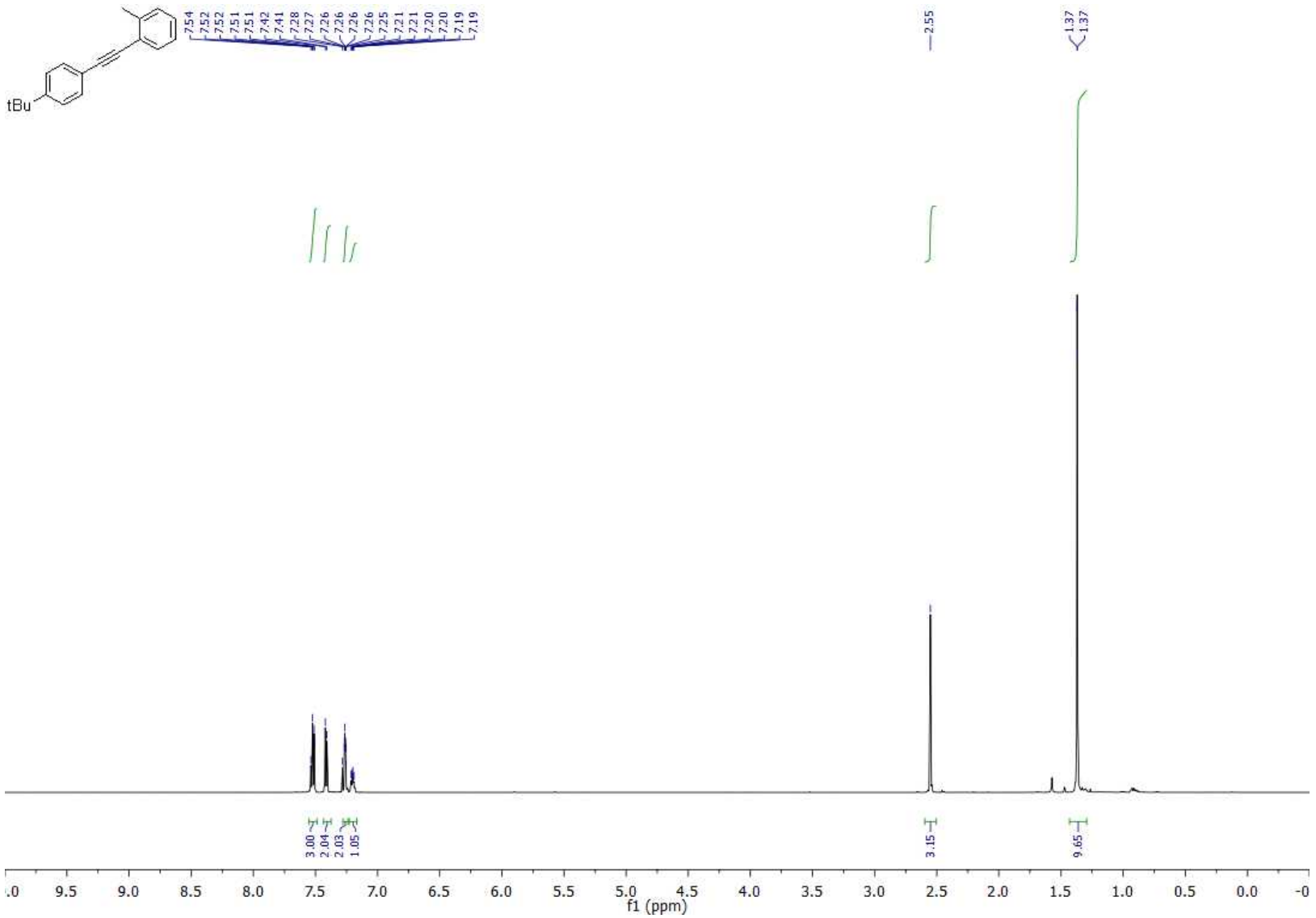
^{1}H NMR spectrum of **4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3m′)**.



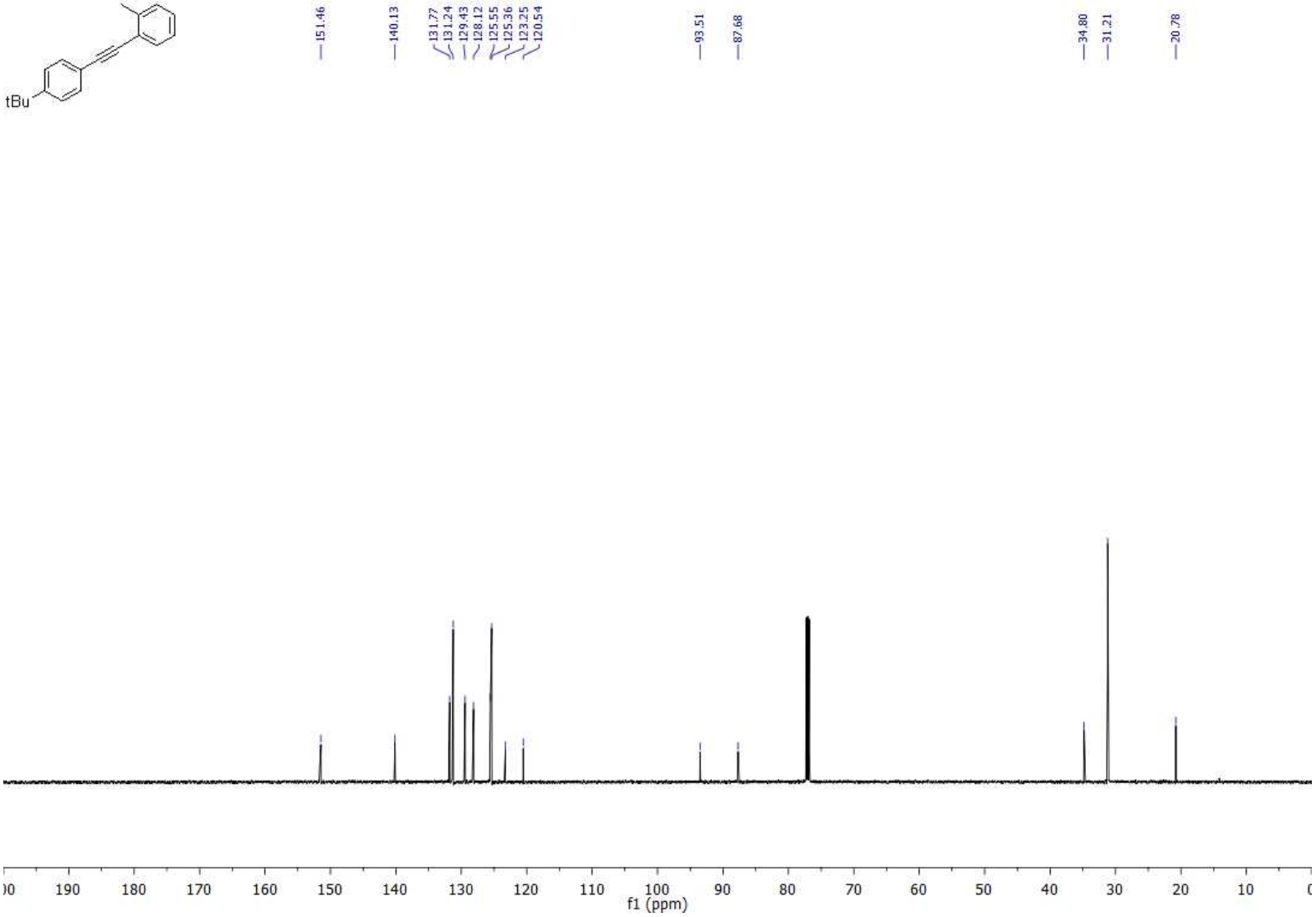
^{13}C NMR spectrum of **4,6-dimethoxy-2-(phenylethynyl)pyrimidine (3m′)**.



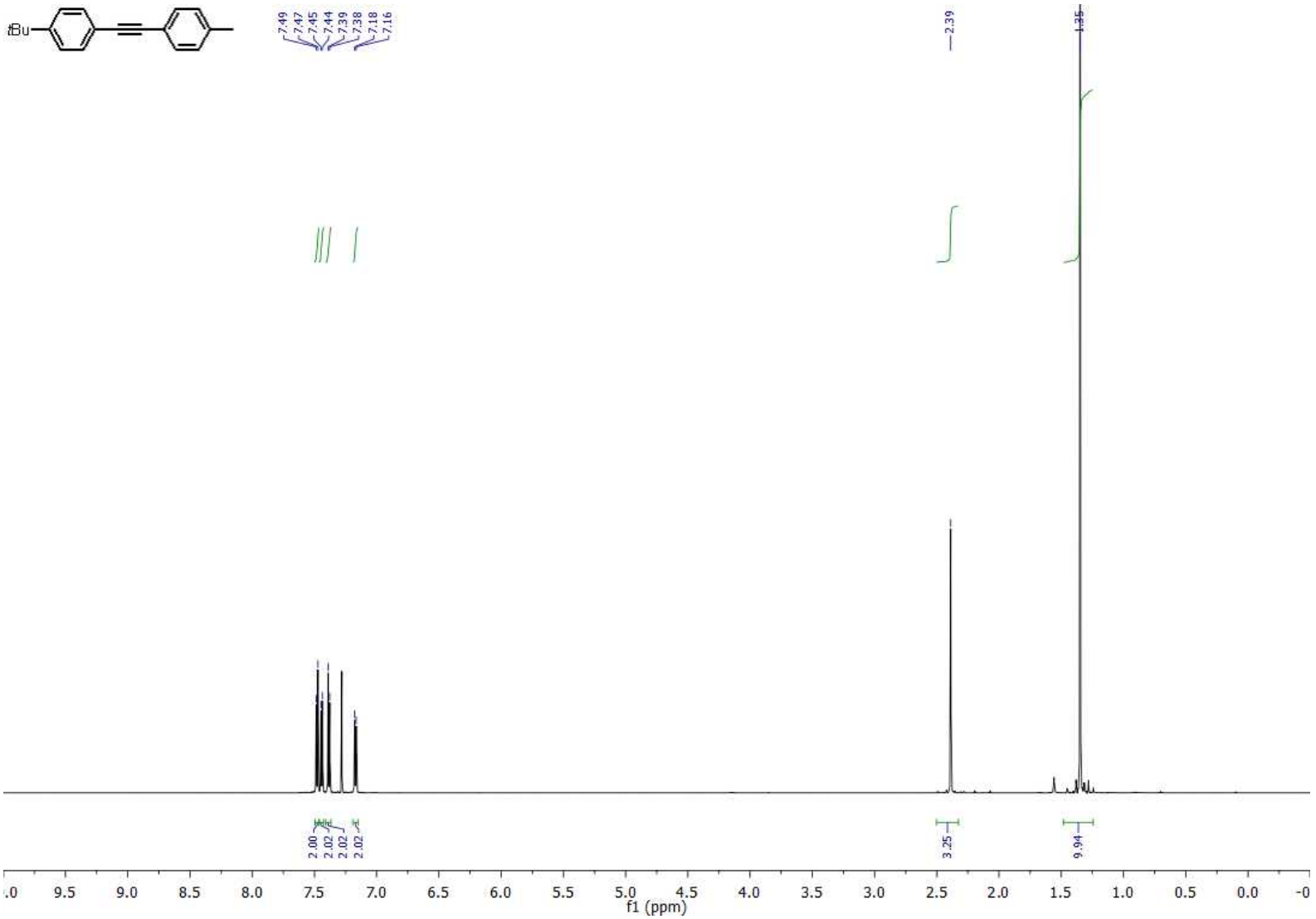
^{1}H NMR spectrum of **1-{(4-(*tert*-butyl)phenyl)ethynyl}-2-methylbenzene (3n′)**



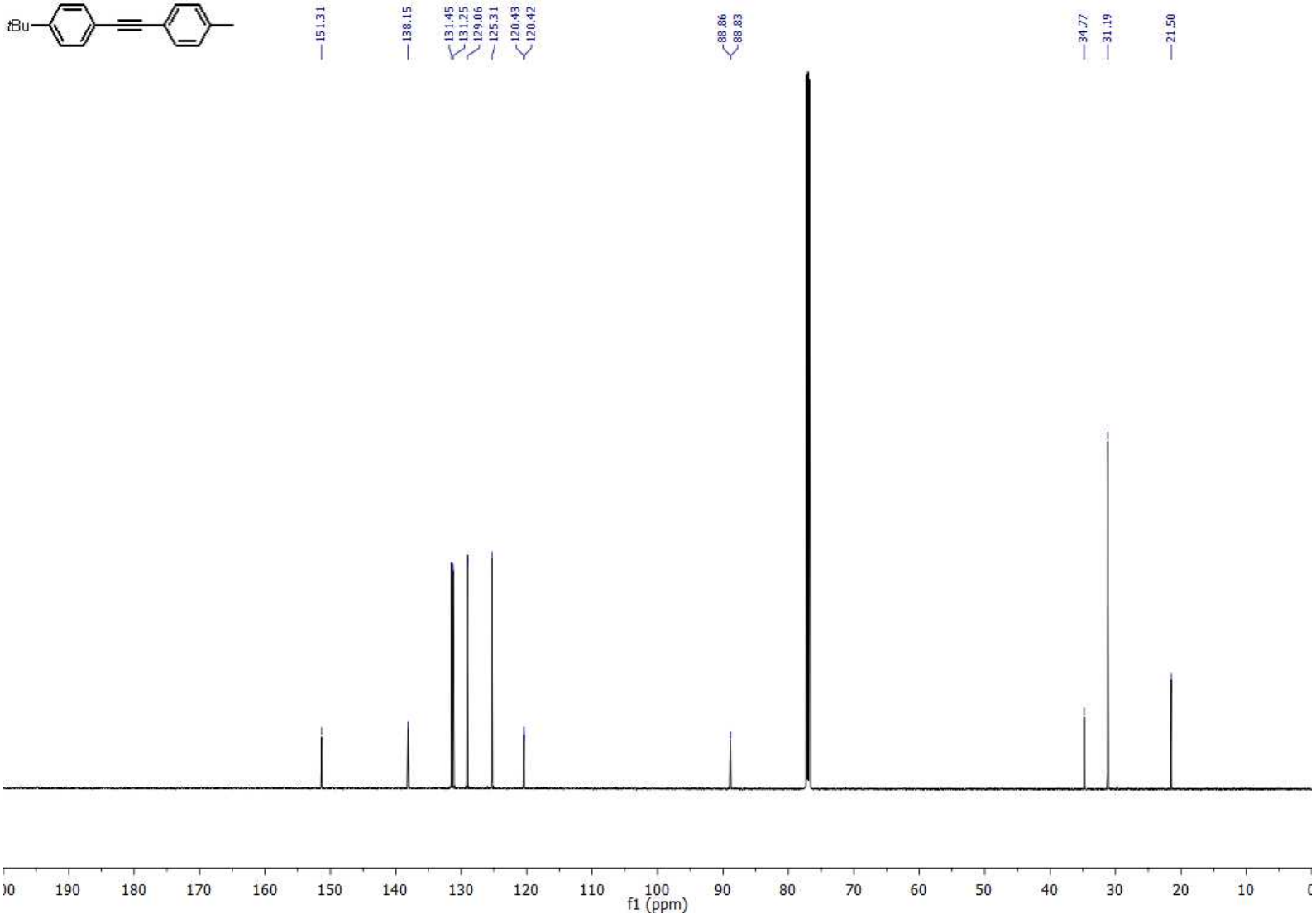
^{13}C NMR spectrum of **1-{(4-(*tert*-butyl)phenyl)ethynyl}-2-methylbenzene (3n′)**



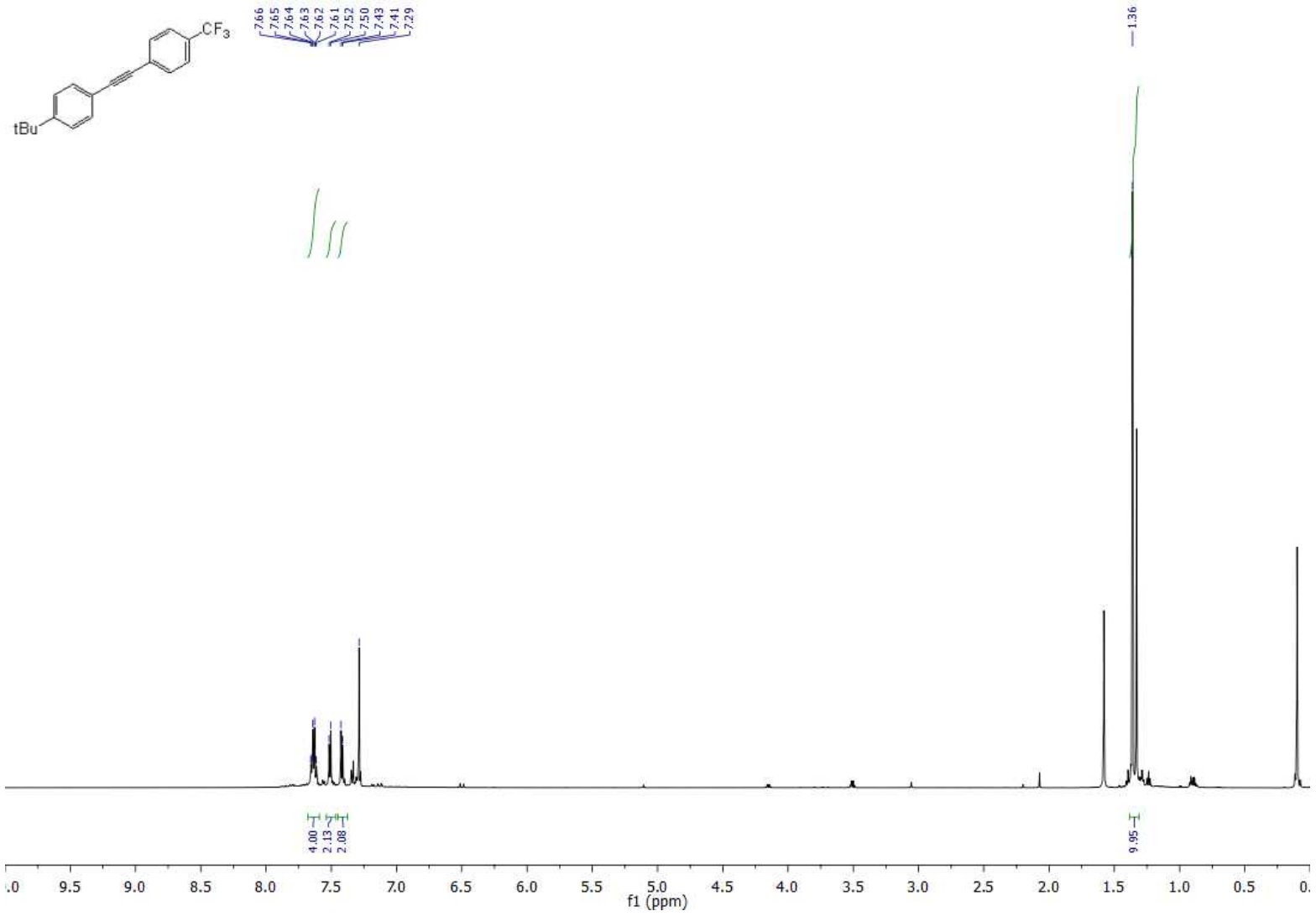
^{1}H NMR spectrum of **1-{(4-(tert-butyl)phenyl)ethynyl}-2-methylbenzene (3o′)**.



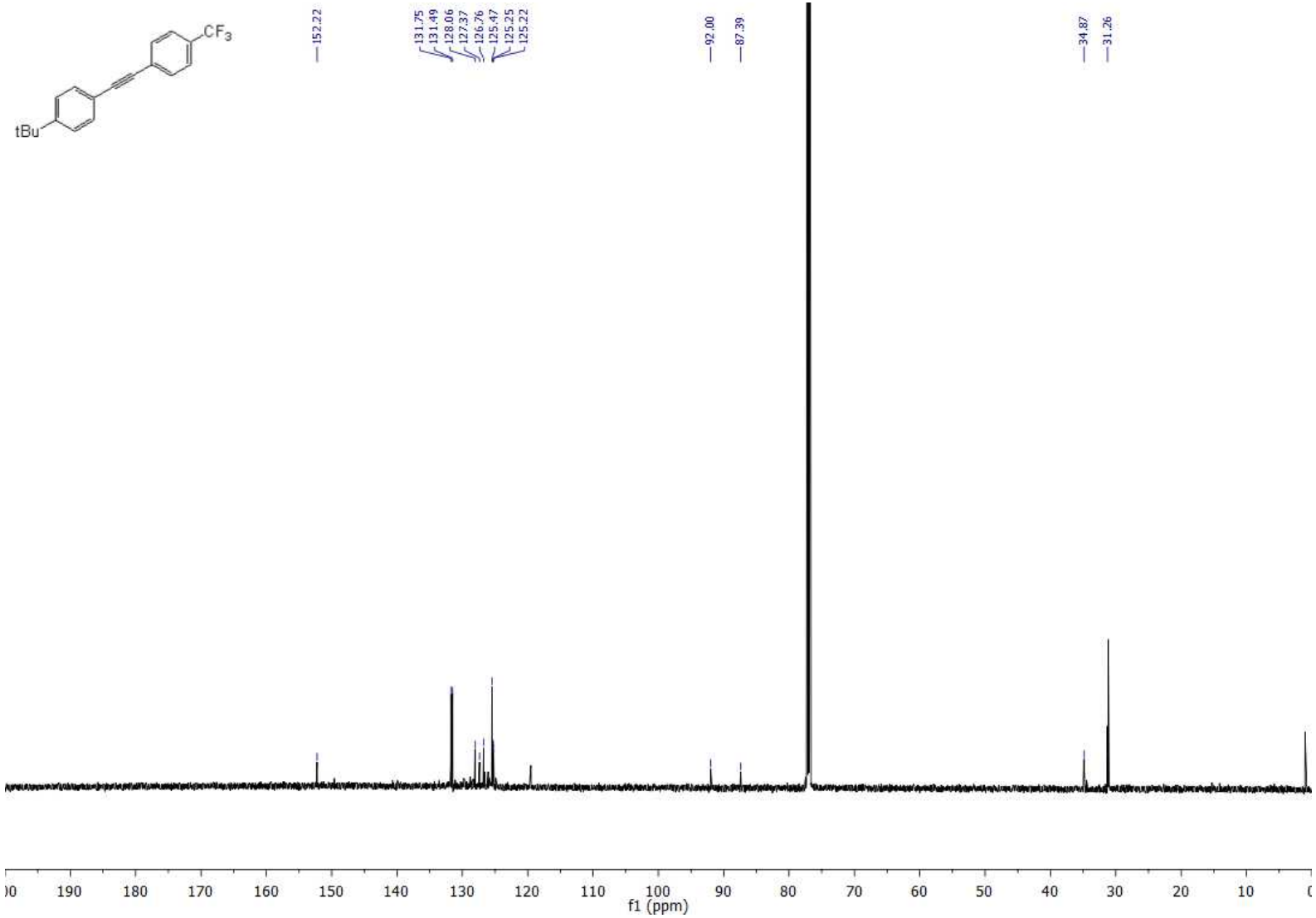
^{13}C NMR spectrum of **1-{(4-(tert-butyl)phenyl)ethynyl}-2-methylbenzene (3o′)**.



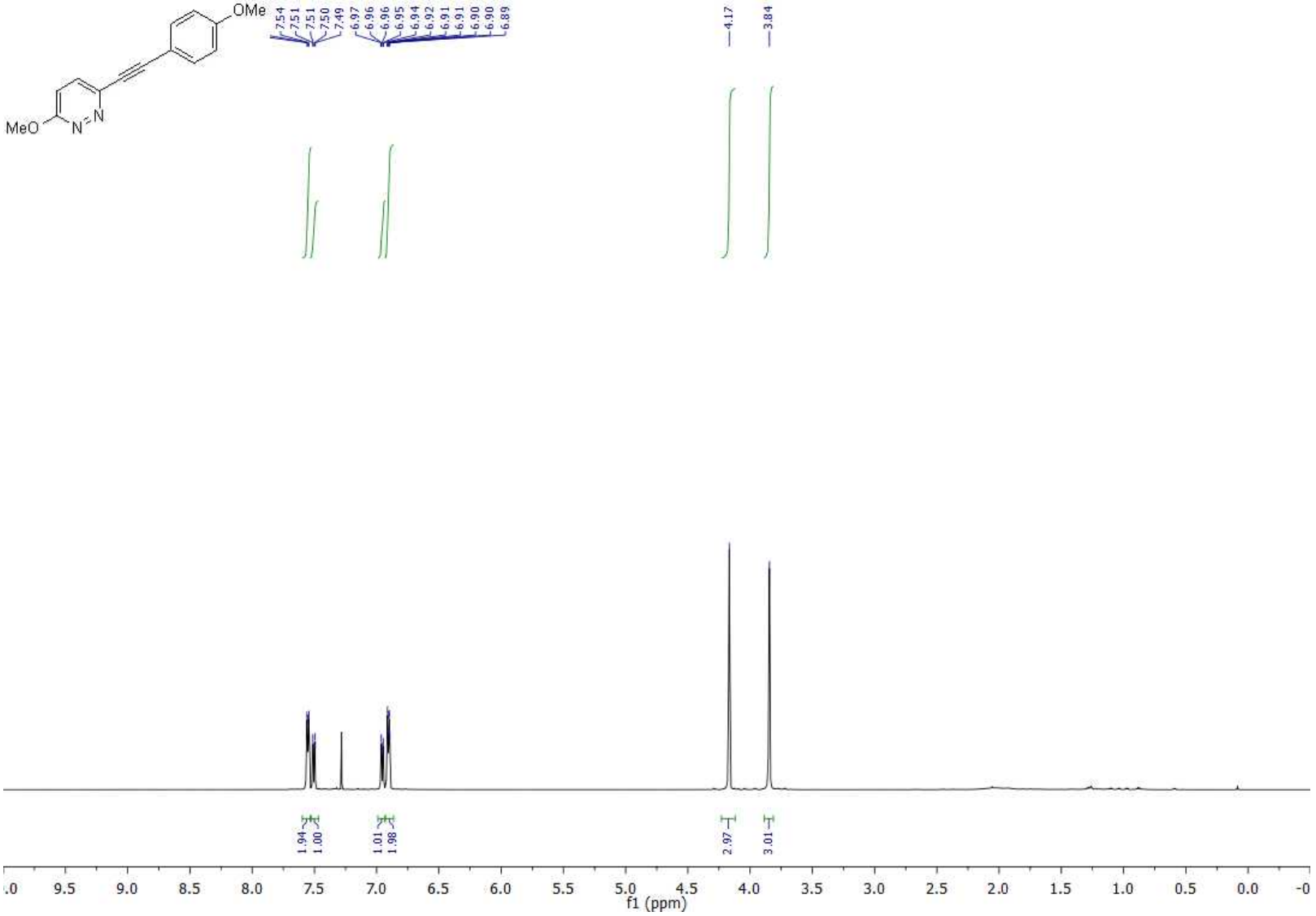
^{1}H NMR spectrum of **1-(tert-butyl)-4-{(4-(trifluoromethyl)phenylethynyl)benzene (3p′)**



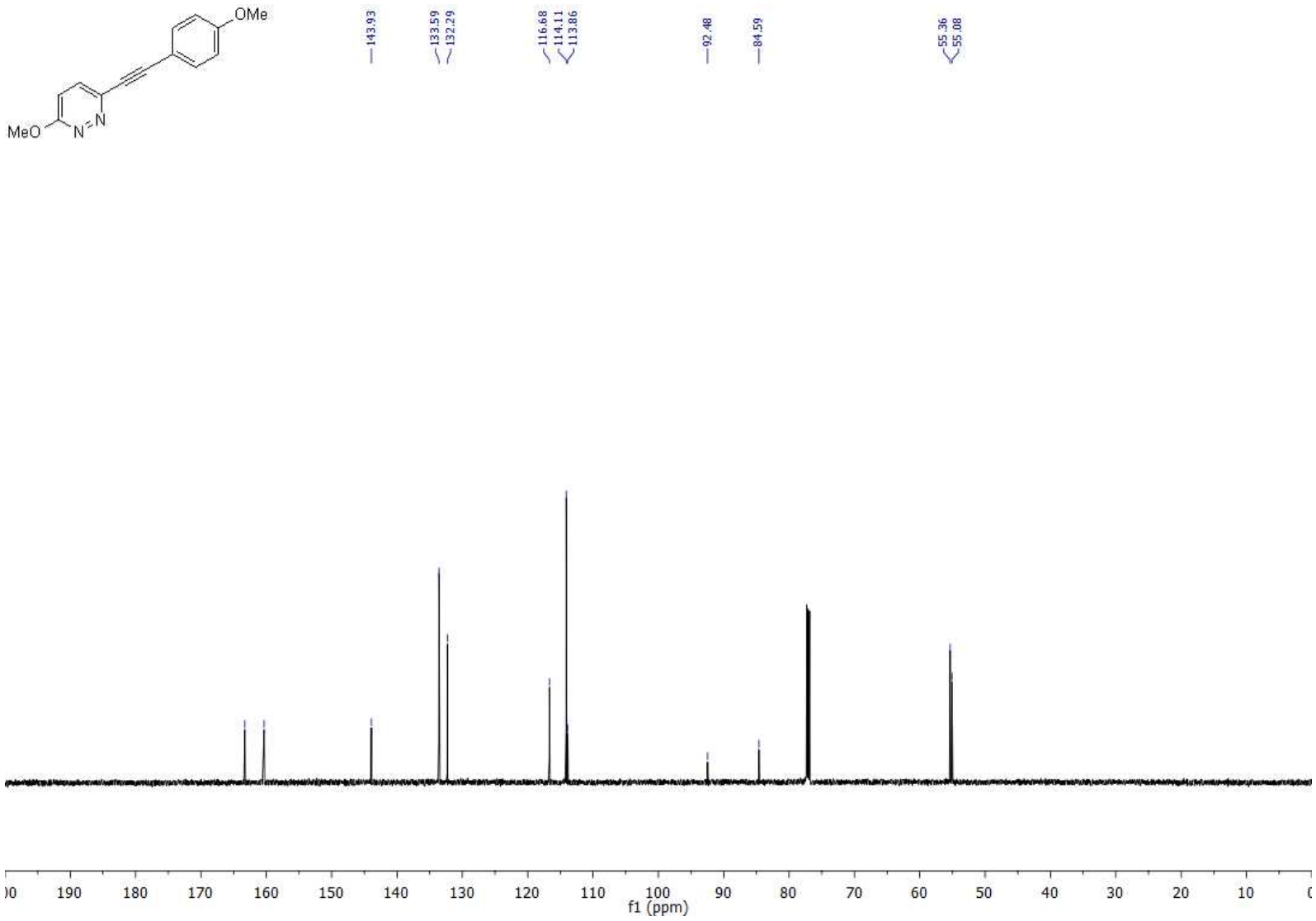
^{13}C NMR spectrum of **1-(tert-butyl)-4-{(4-(trifluoromethyl)phenylethynyl)benzene (3p′)**



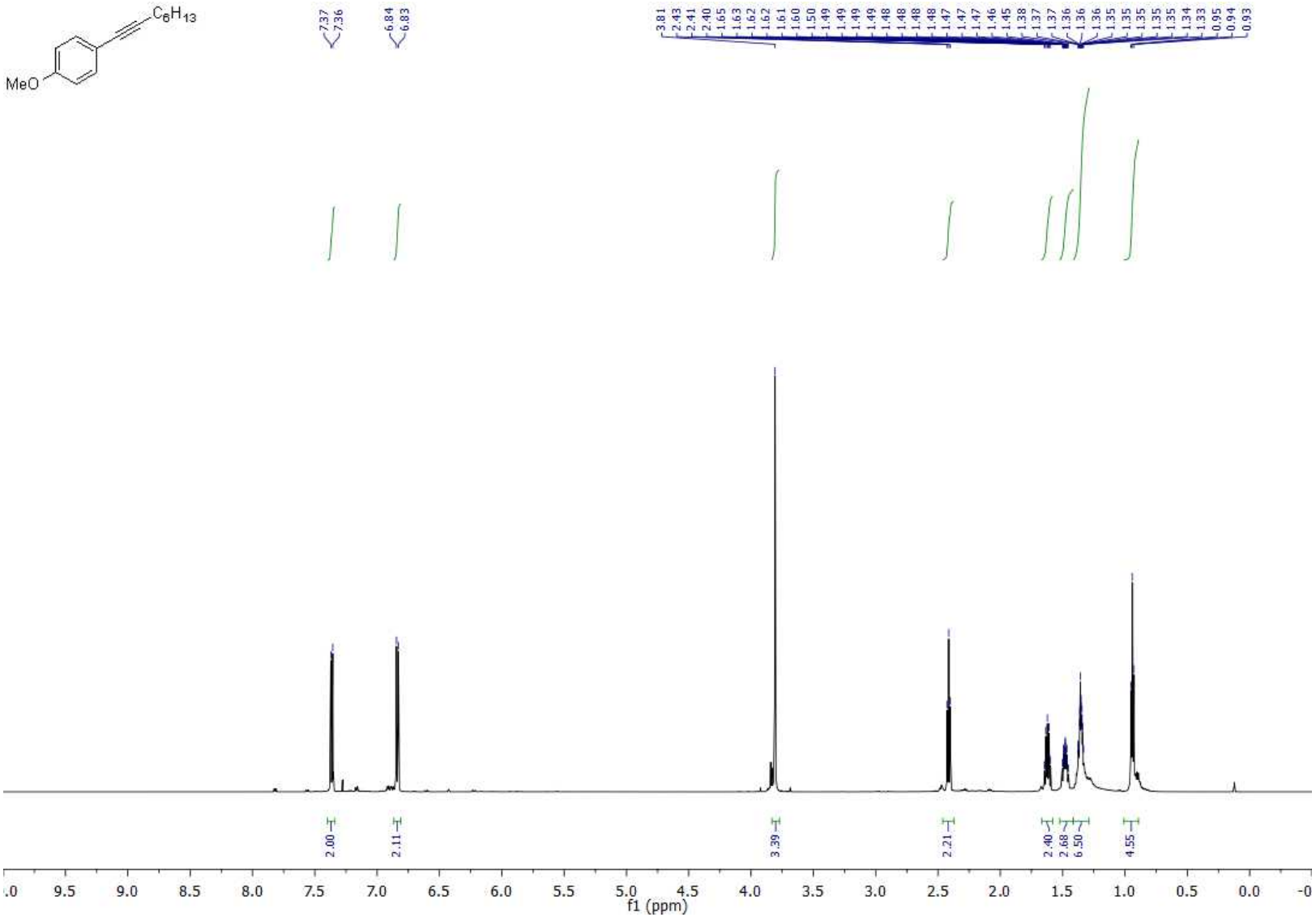
^{1}H NMR spectrum of **3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine (3q′)**.



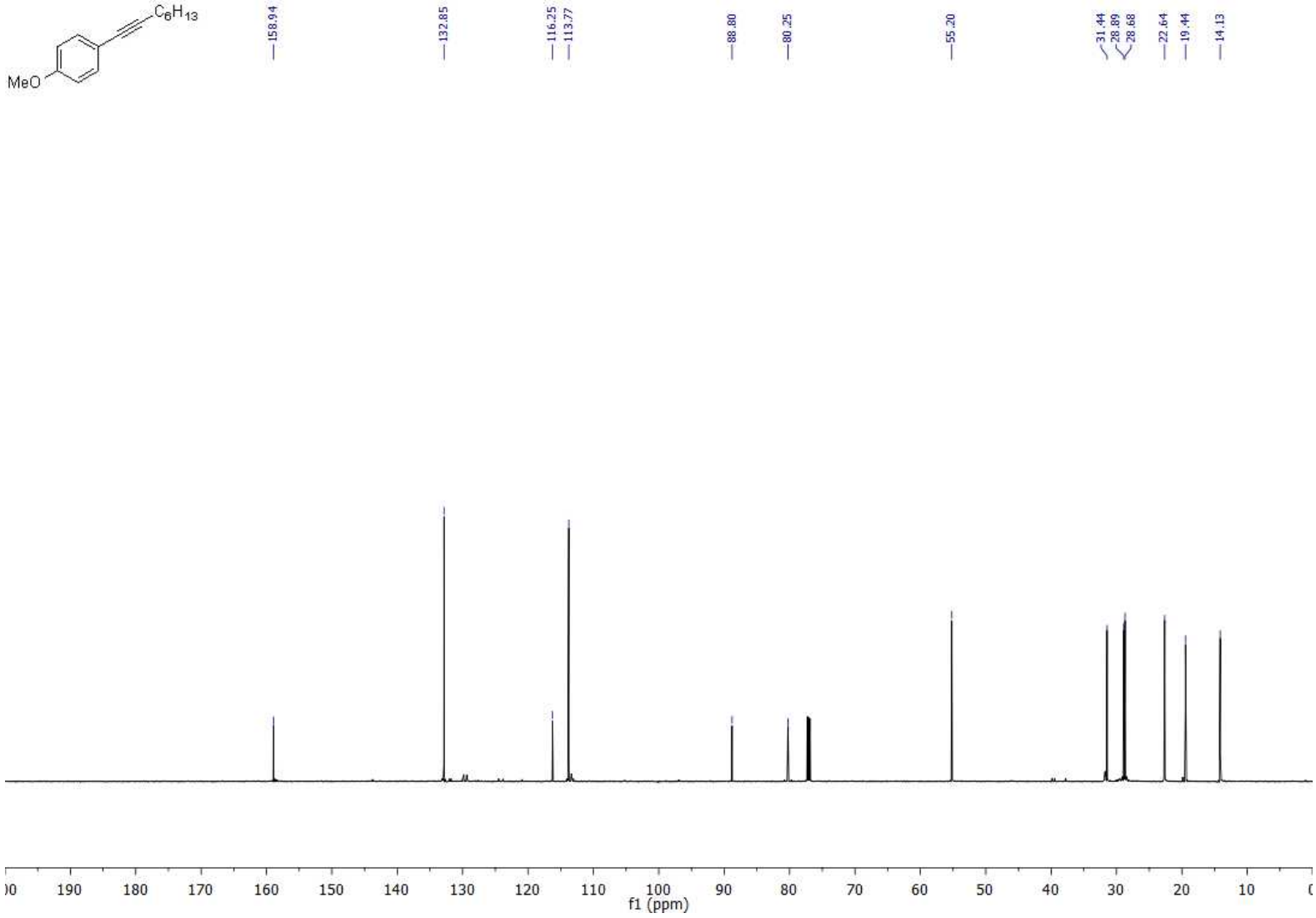
^{13}C NMR spectrum of **3-methoxy-6-{(4-methoxyphenyl)ethynyl}pyridazine (3q′)**.



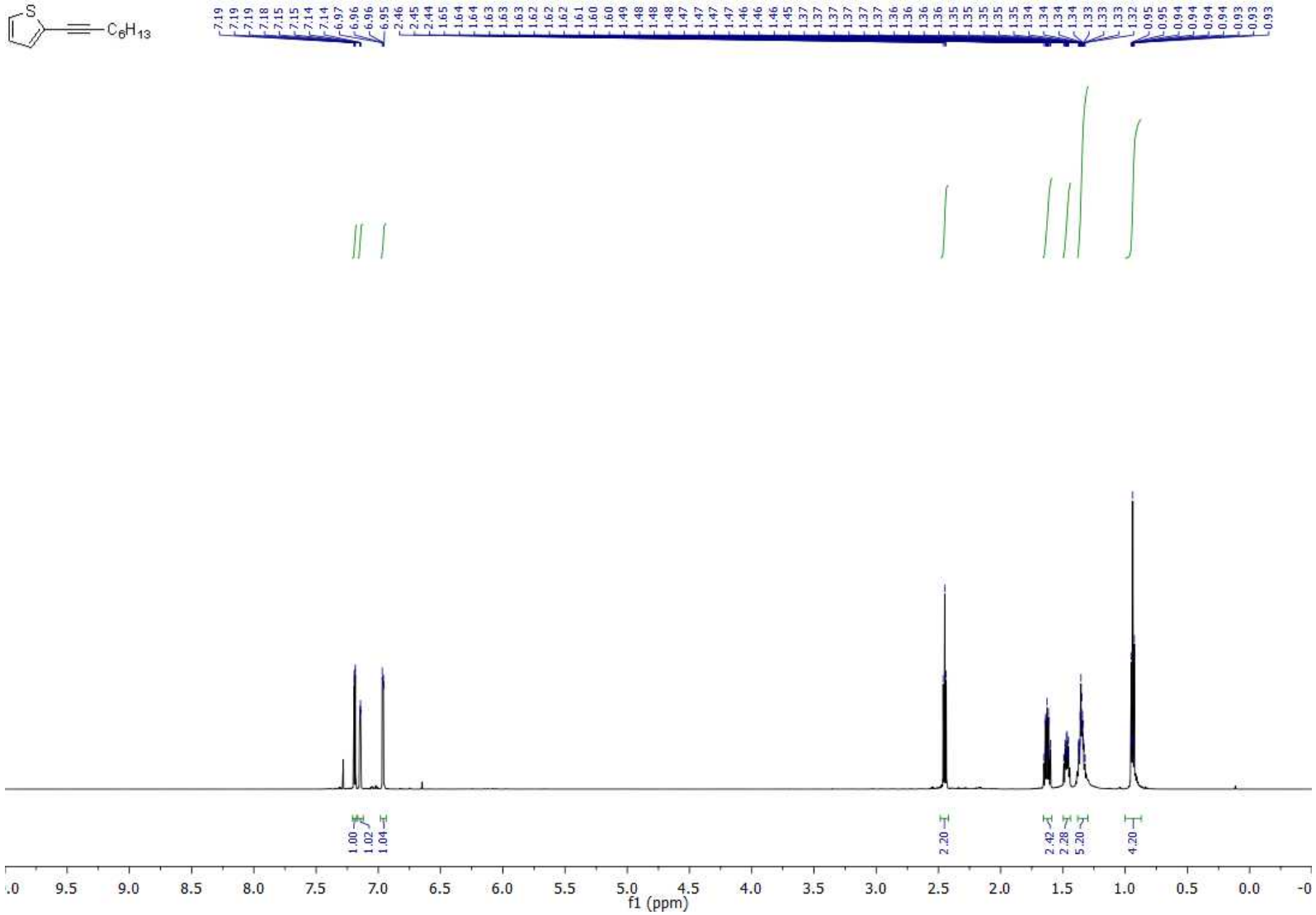
^{1}H NMR spectrum of **1-methoxy-4-(oct-1-yn-1-yl)benzene (3r′)**.



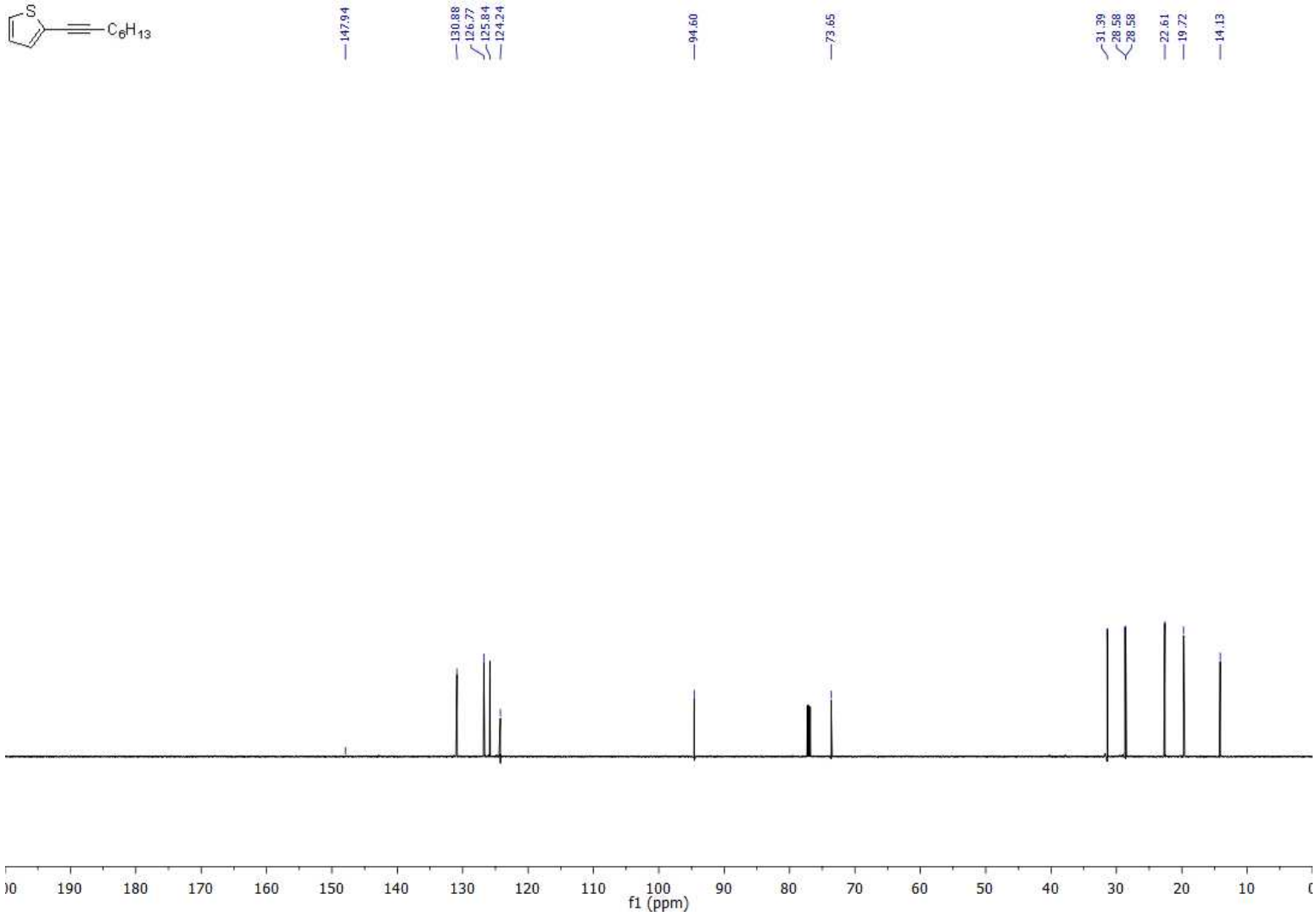
^{13}C NMR spectrum of **1-methoxy-4-(oct-1-yn-1-yl)benzene (3r′)**.



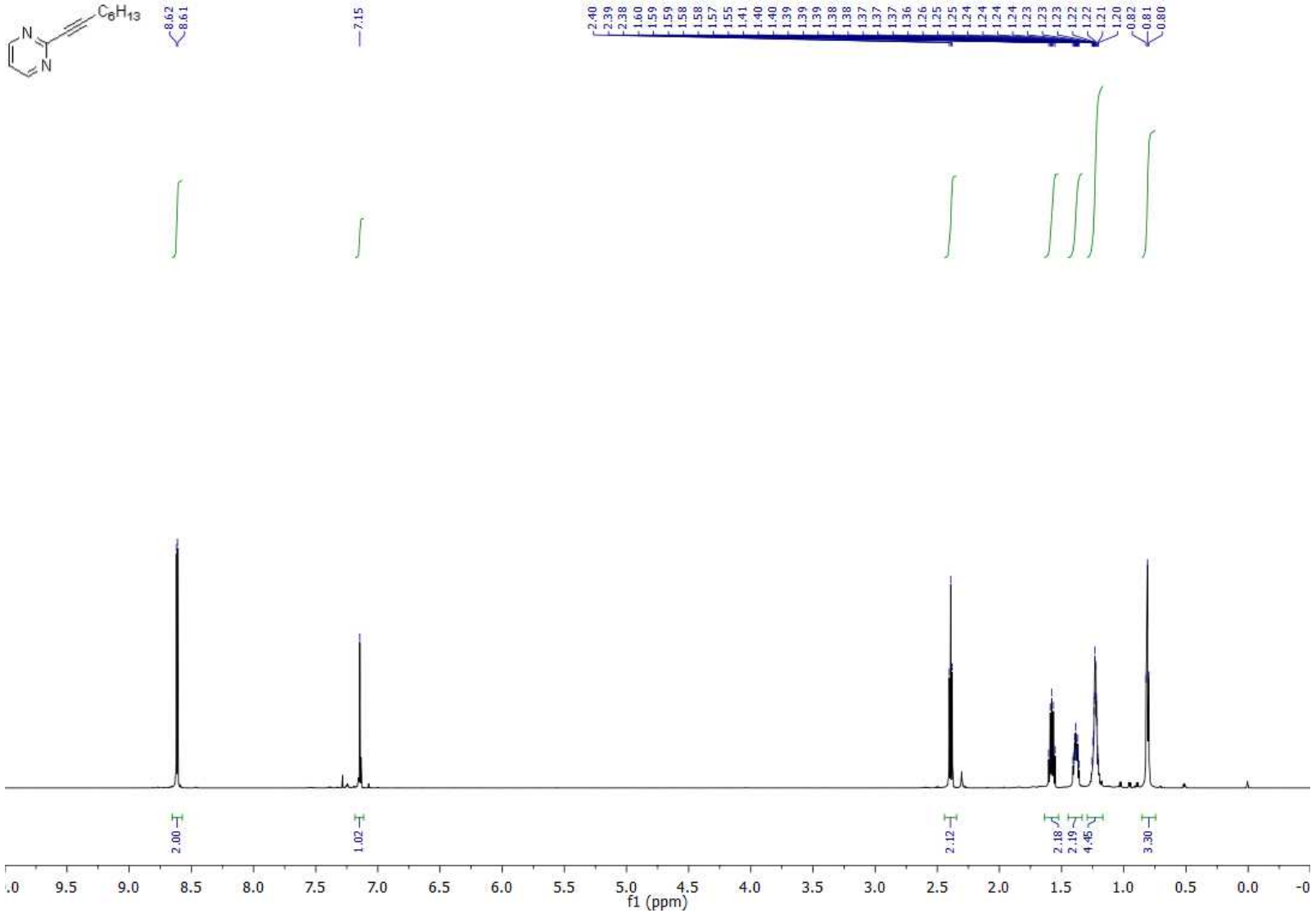
^{1}H NMR spectrum of **2-(oct-1-yn-1-yl)thiophene (3s′)**.



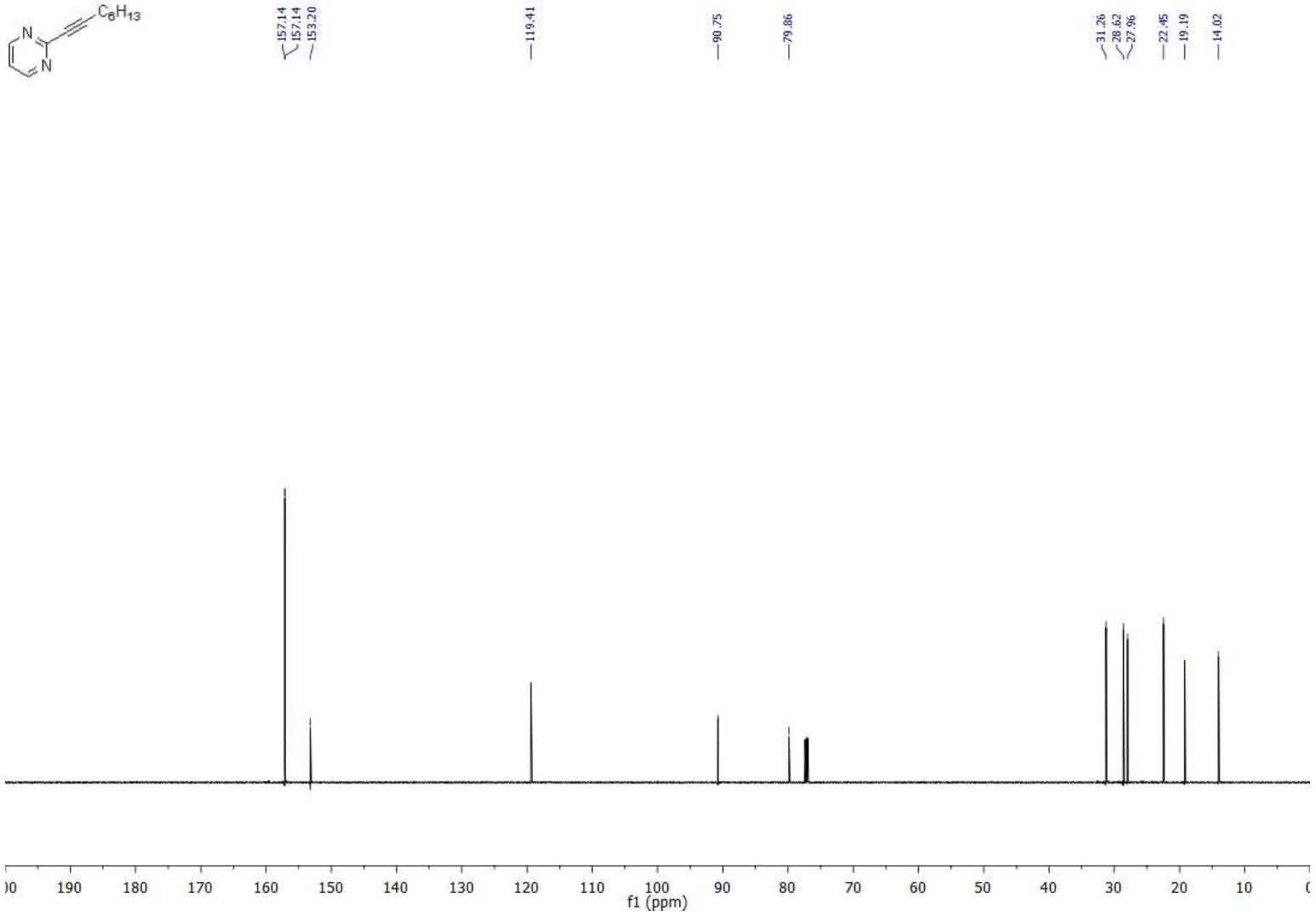
^{13}C NMR spectrum of **2-(oct-1-yn-1-yl)thiophene (3s′)**.



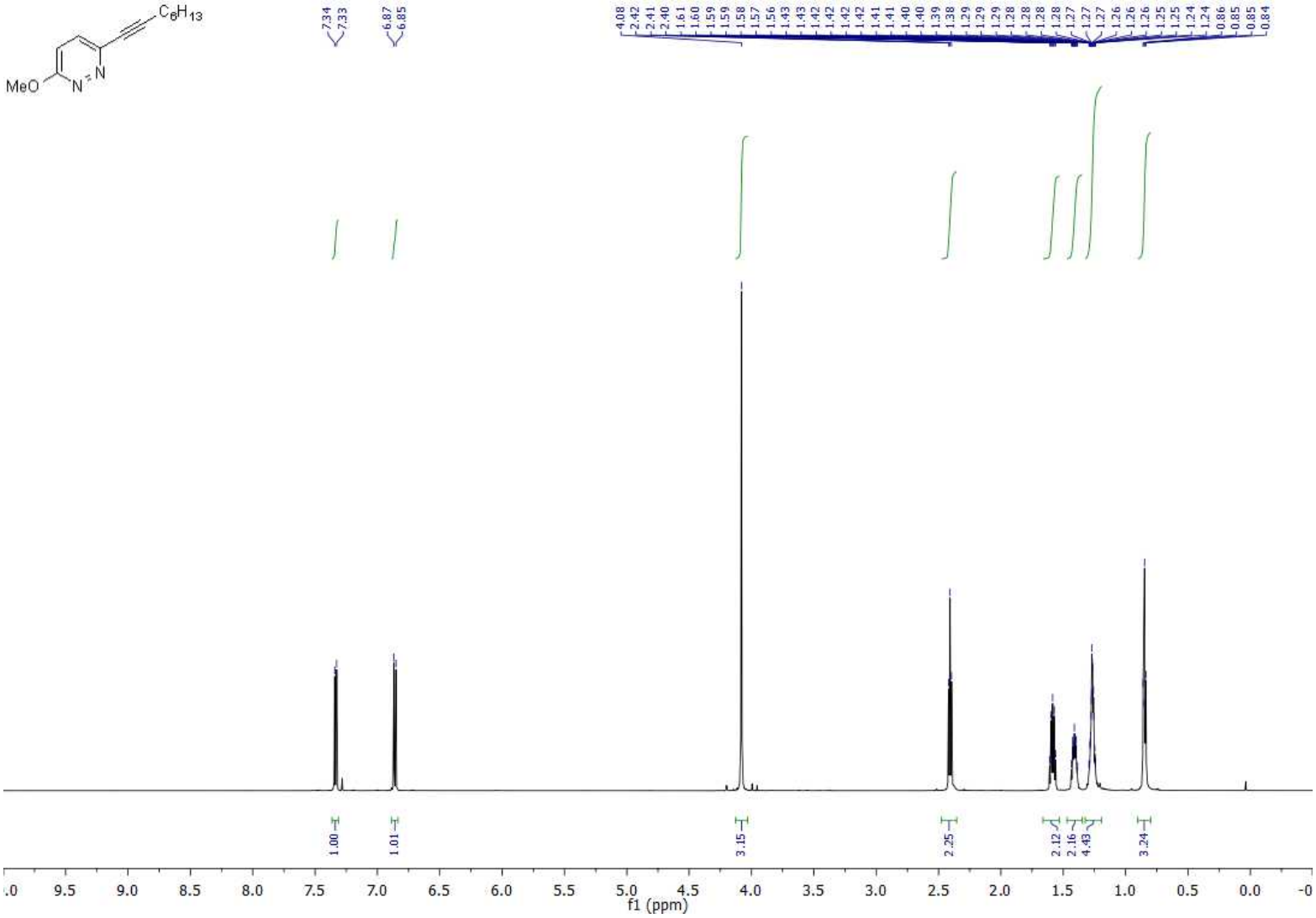
^{1}H NMR spectrum of **2-(oct-1-yn-1-yl)pyrimidine (3t′)**



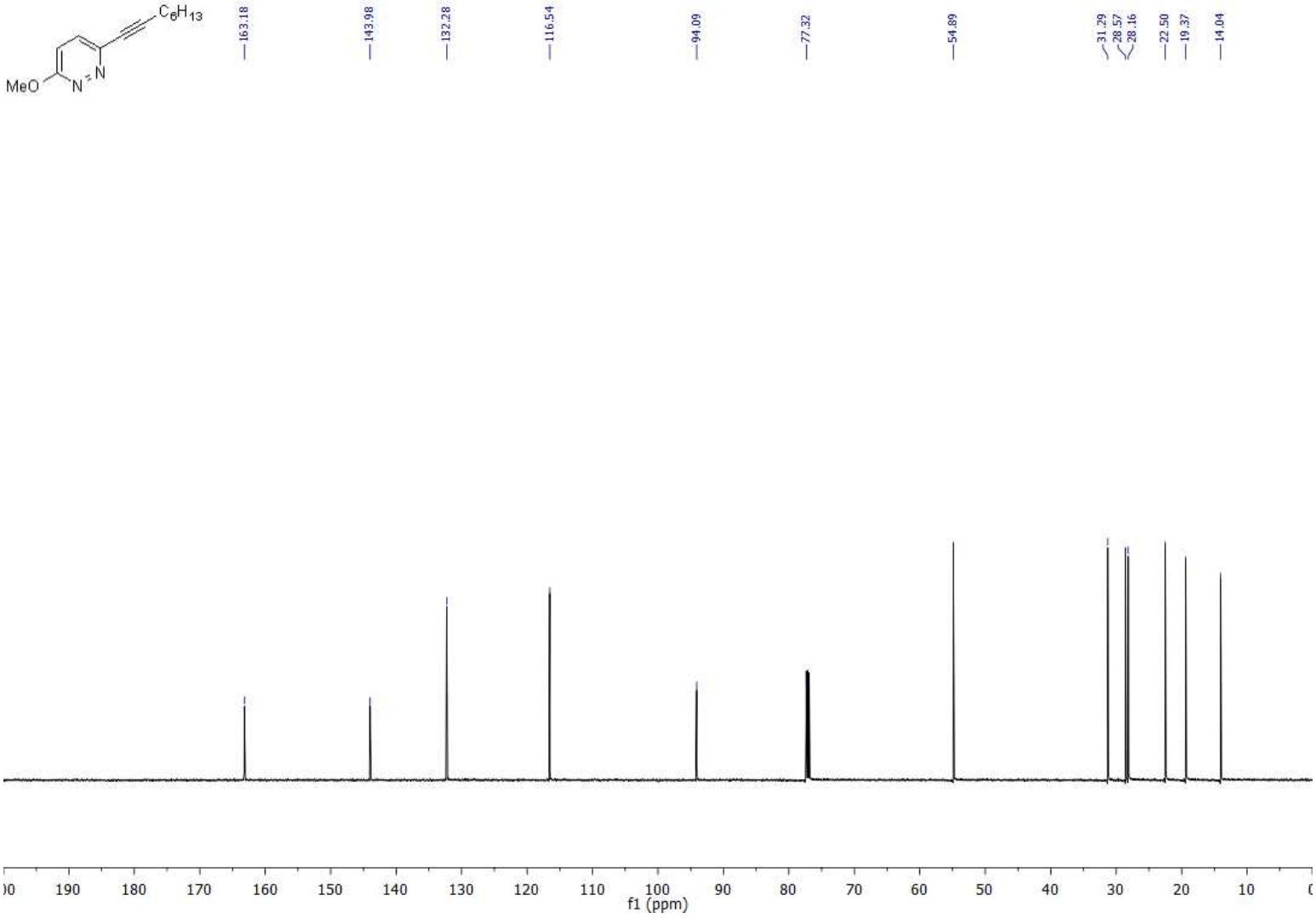
^{13}C NMR spectrum of **2-(oct-1-yn-1-yl)pyrimidine (3t′)**



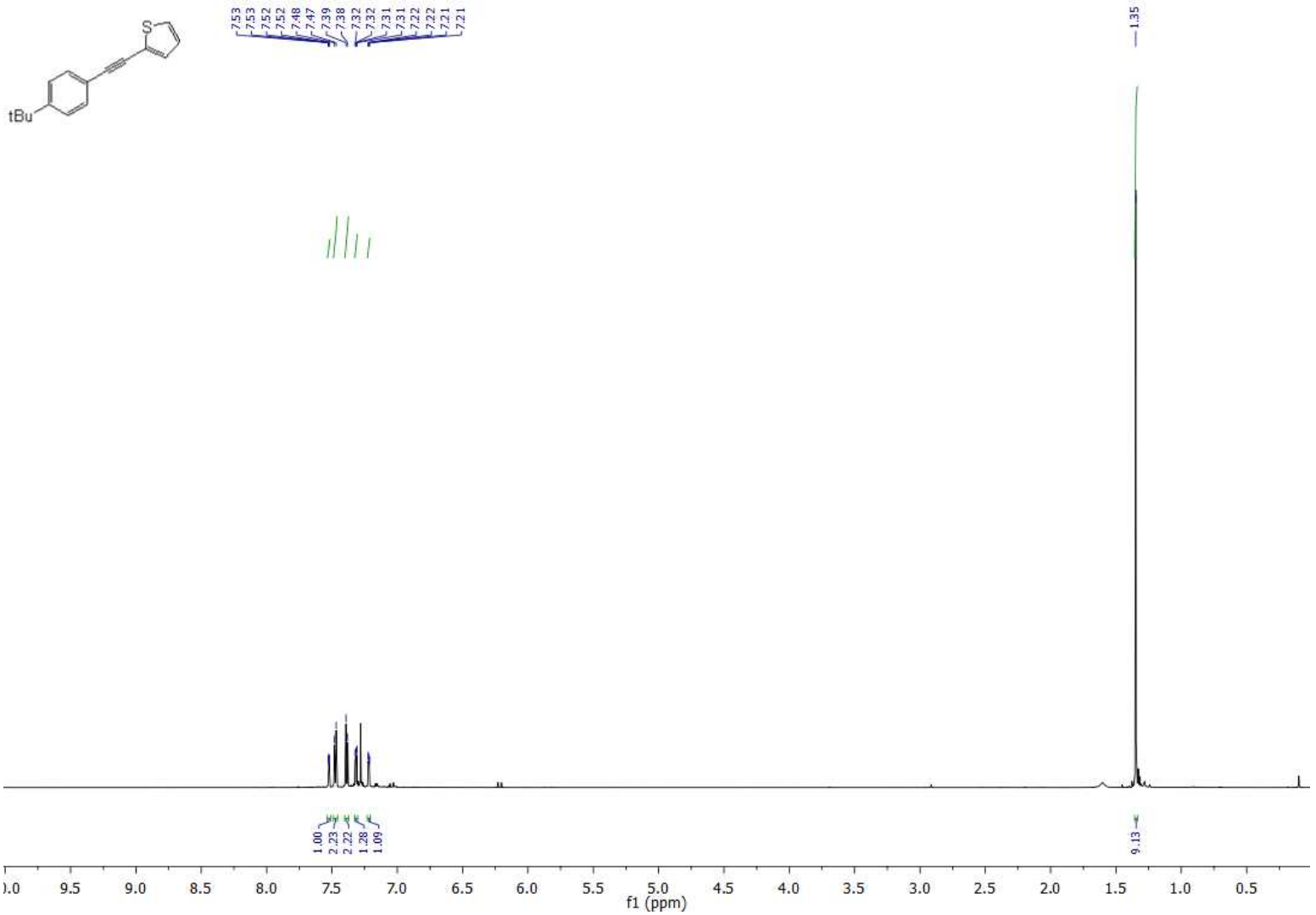
^{1}H NMR spectrum of **3-methoxy-6-(oct-1-yn-1-yl)pyridazine (3u′)**



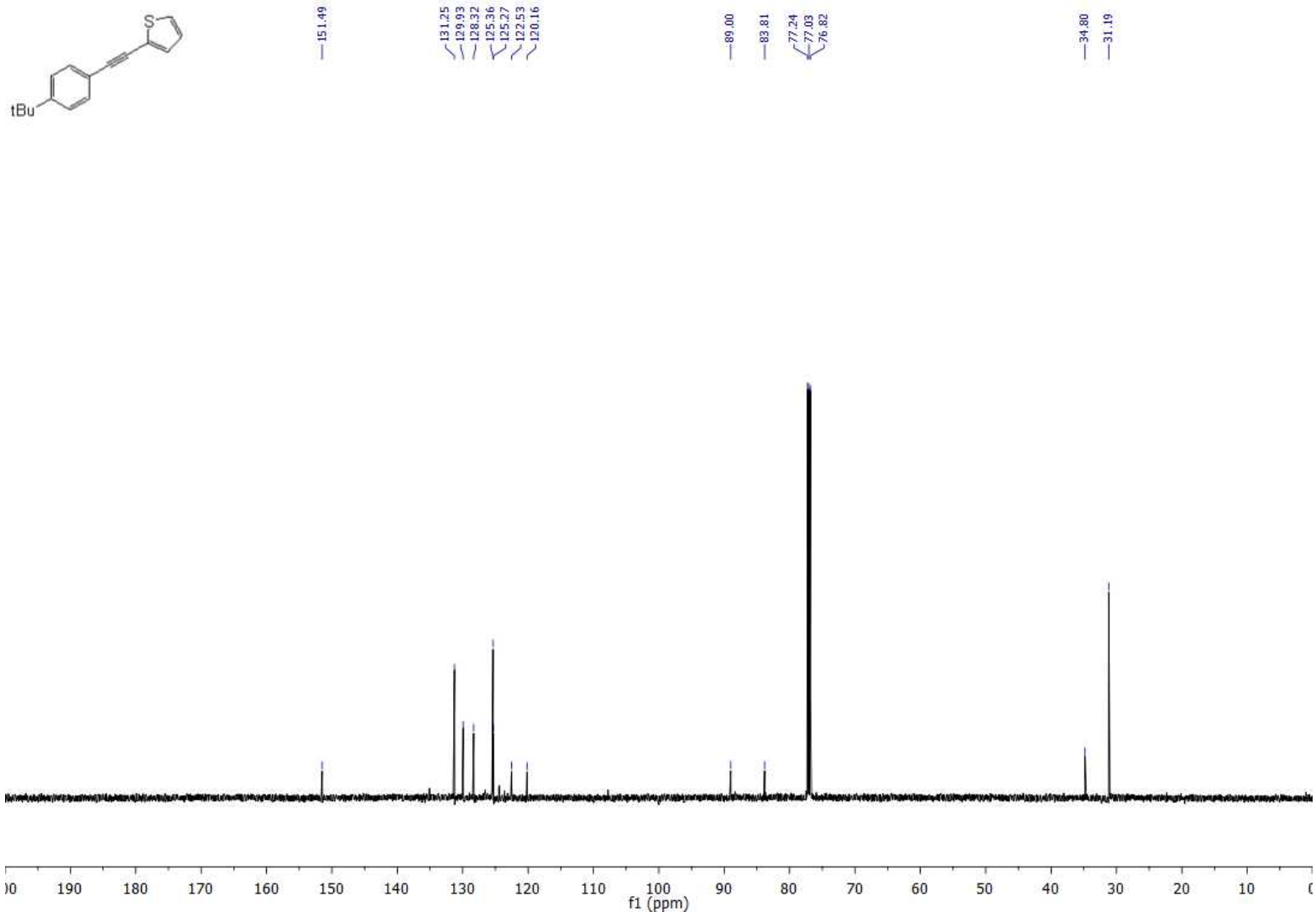
^{13}C NMR spectrum of **3-methoxy-6-(oct-1-yn-1-yl)pyridazine (3u′)**



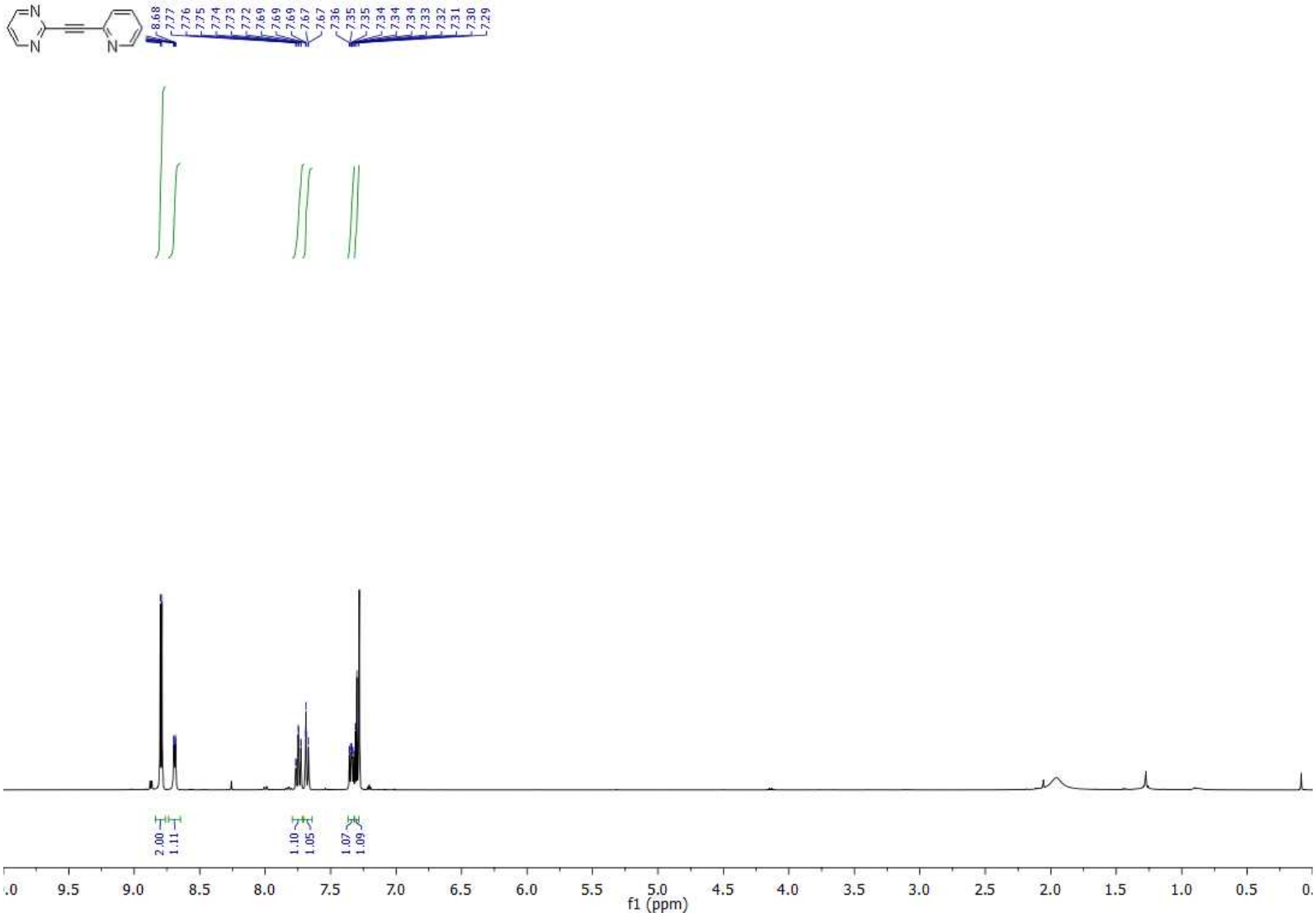
^{1}H NMR spectrum of **2-{(4-(tert-butyl)phenyl)ethynyl}thiophene (3v′)**



^{13}C NMR spectrum of **2-{(4-(tert-butyl)phenyl)ethynyl}thiophene (3v′)**



^{1}H NMR spectrum of **2-(pyridin-2-ylethynyl)pyrimidine (3y′)**



^{13}C NMR spectrum of **2-(pyridin-2-ylethynyl)pyrimidine (3y′)**