Electronic Supplementary Information (ESI)

A Molecular Beams and Computational Study on the Barrierless Gas Phase Formation of (Iso)Quinoline in Low Temperature Extraterrestrial Environments

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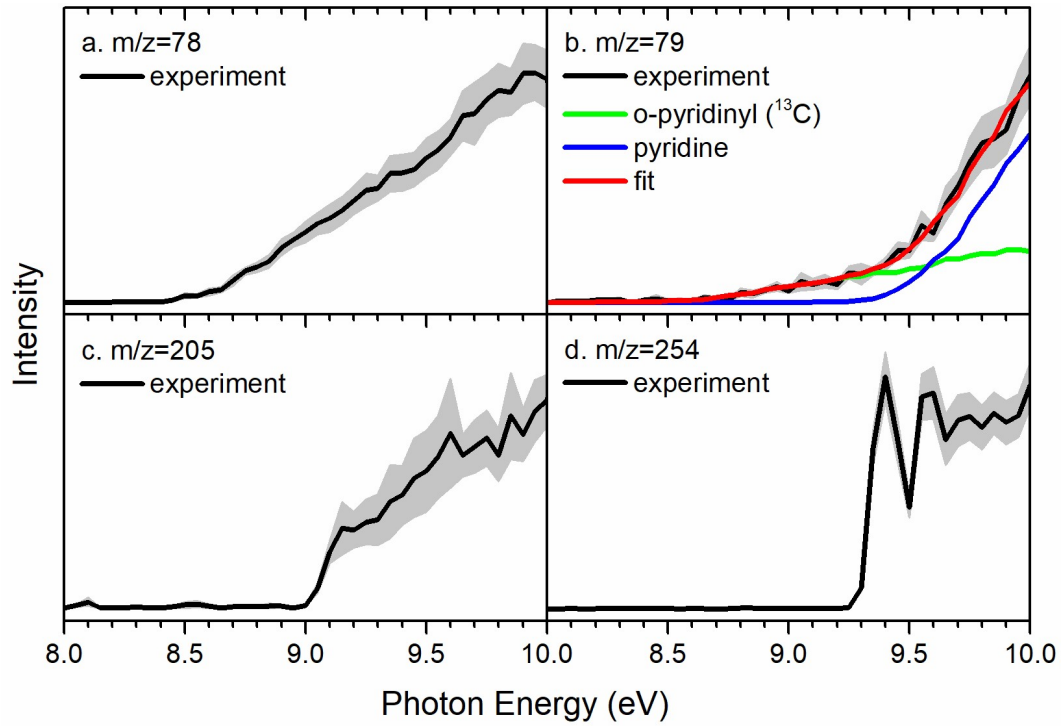


Figure S1. Photoionization efficiency (PIE) curves for reaction of *o*-pyridinyl ($C_5H_4N^{\bullet}$) with vinylacetylene (C_4H_4). Black: experimentally derived PIE curves; colored lines (green and blue): reference PIE curves; red lines: overall fit. The overall error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

m/z = 78 is related to the *o*-pyridinyl radical generated from the pyrolysis of *o*-iodopyridine (*m/z* = 205). The product at *m/z* = 79 is pyridine yielded from the H-addition to *o*-pyridinyl. The recombination of two iodine atoms leads to the signal at *m/z* = 254.

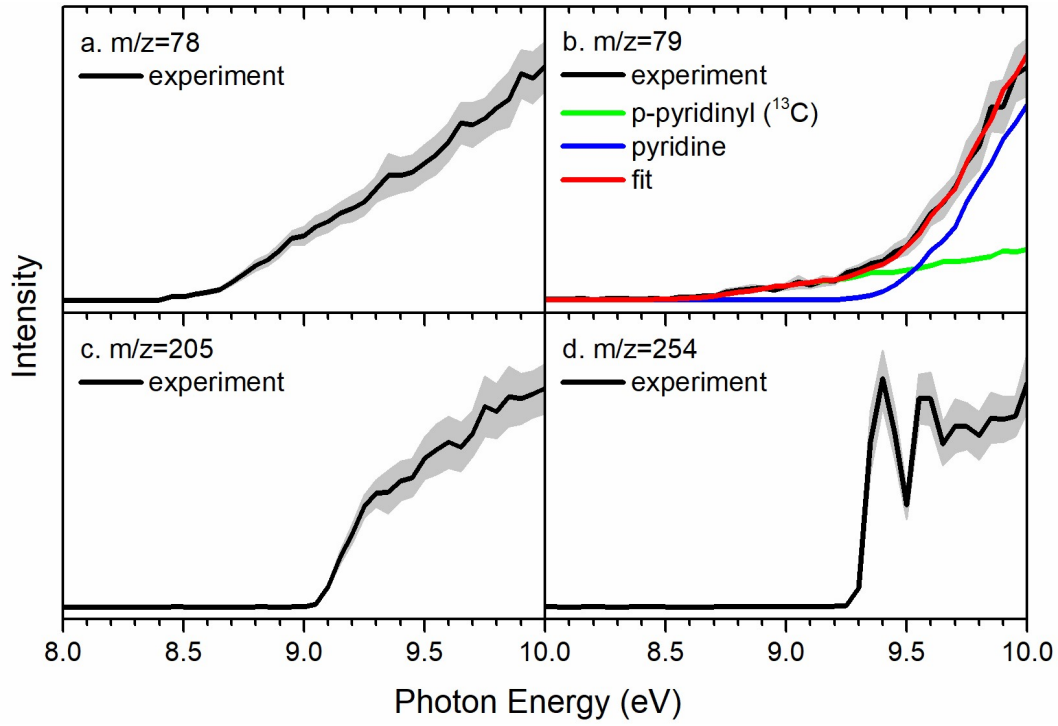


Figure S2. Photoionization efficiency (PIE) curves for reaction m-pyridinyl ($C_5H_4N^{\bullet}$) plus vinylacetylene (C_4H_4). Black: experimentally derived PIE curves; colored lines (green and blue): reference PIE curves; red lines: overall fit. The overall error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

Signal of *m/z* = 78 is related to the *m*-pyridinyl radical generated from the pyrolysis of *m*-iodopyridine (*m/z* = 205). The product at *m/z* = 79 is pyridine formed from the H-addition to *m*-pyridinyl. The recombination of two iodine atoms leads to the signal at *m/z* = 254.

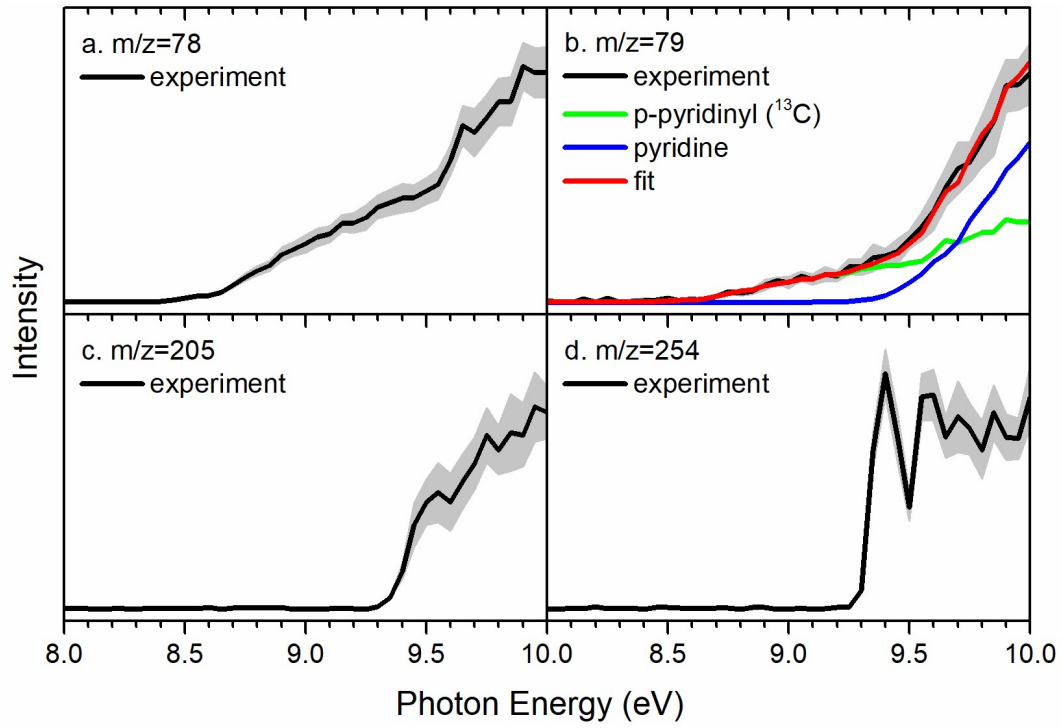


Figure S3. Photoionization efficiency (PIE) curves for reaction *p*-pyridinyl ($C_5H_4N^{\bullet}$) + vinylacetylene (C_4H_4). Black: experimentally derived PIE curves; colored lines (green and blue): reference PIE curves; red lines: overall fit. The overall error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

Signal of *m/z* = 78 is related to the *p*-pyridinyl radical generated from the pyrolysis of *p*-iodopyridine (*m/z* = 205). Signal at *m/z* = 79 is pyridine formed from the H-addition to *p*-pyridinyl. The recombination of two iodine atoms leads to the signal at *m/z* = 254.

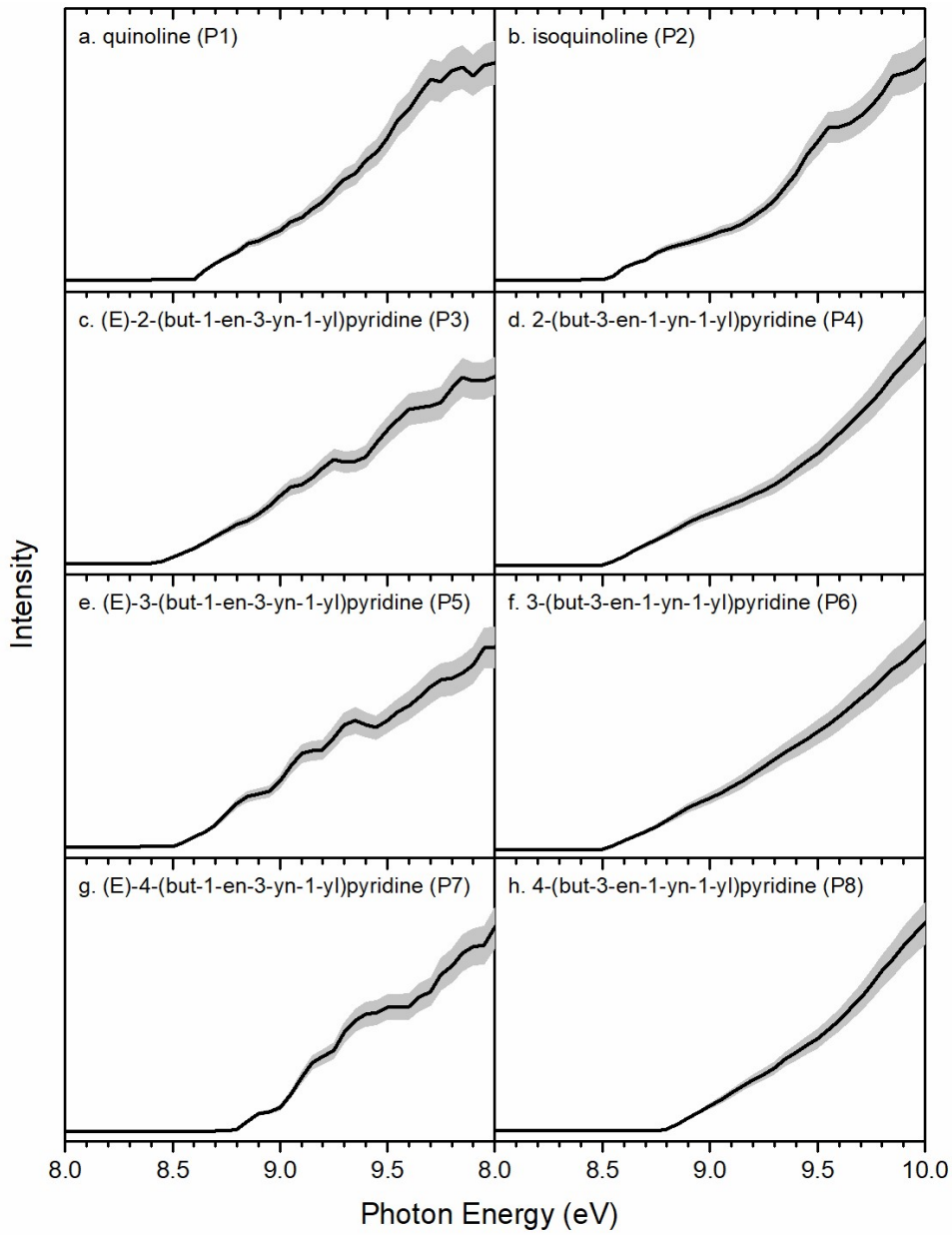


Figure S4. Reference PIE curves collected in this work for distinct C_9H_7N isomers.

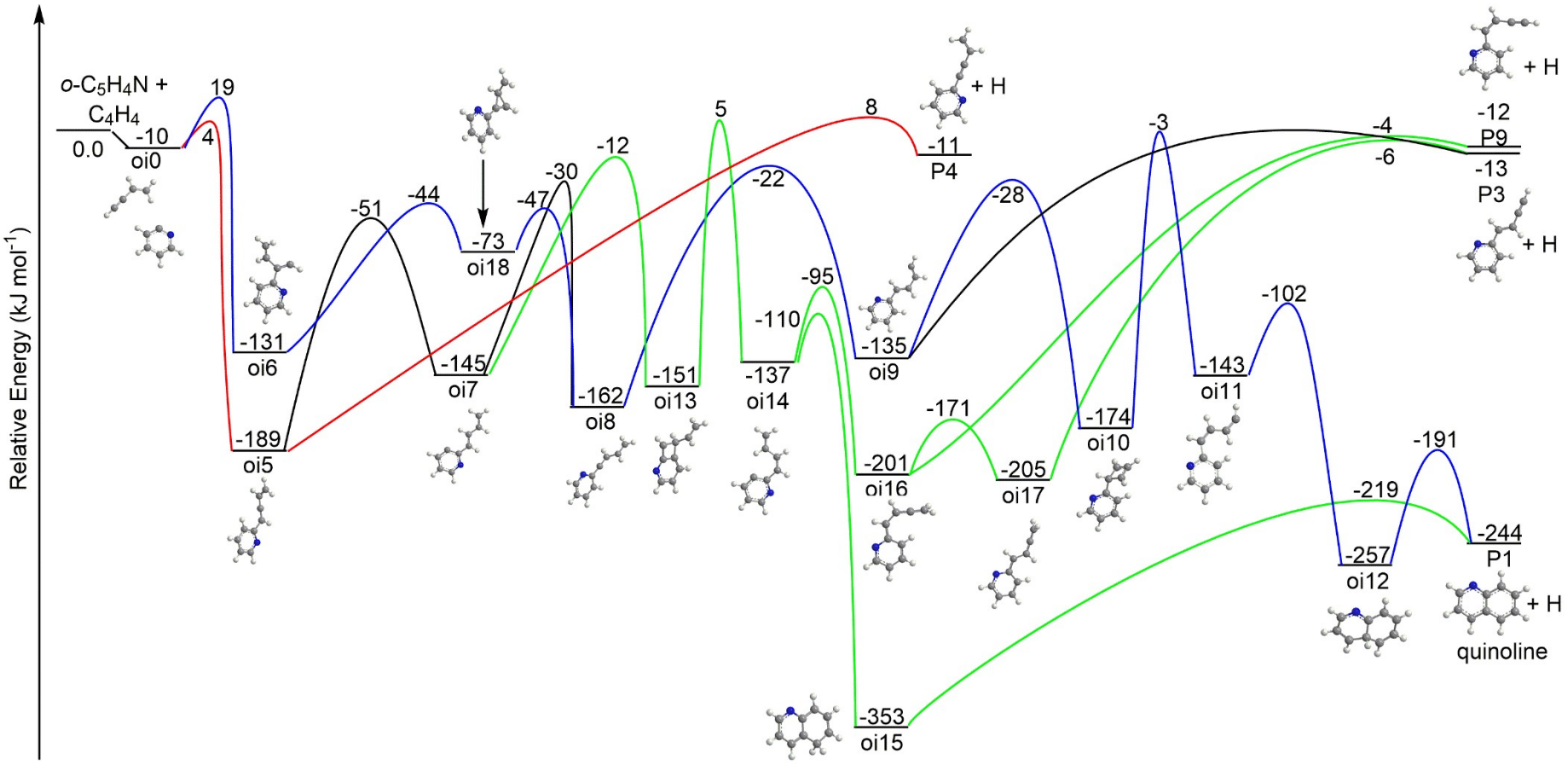


Figure S5a. Computed potential energy surface (PES) for the reaction system of *o*-pyridinyl (C_5H_4N) and vinylacetylene (C_4H_4). The energies calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) + ZPE level of theory are presented in units of kJ mol^{-1}. Only pathways initiated by vinylacetylene addition to the radical site by its C_2H end are shown.

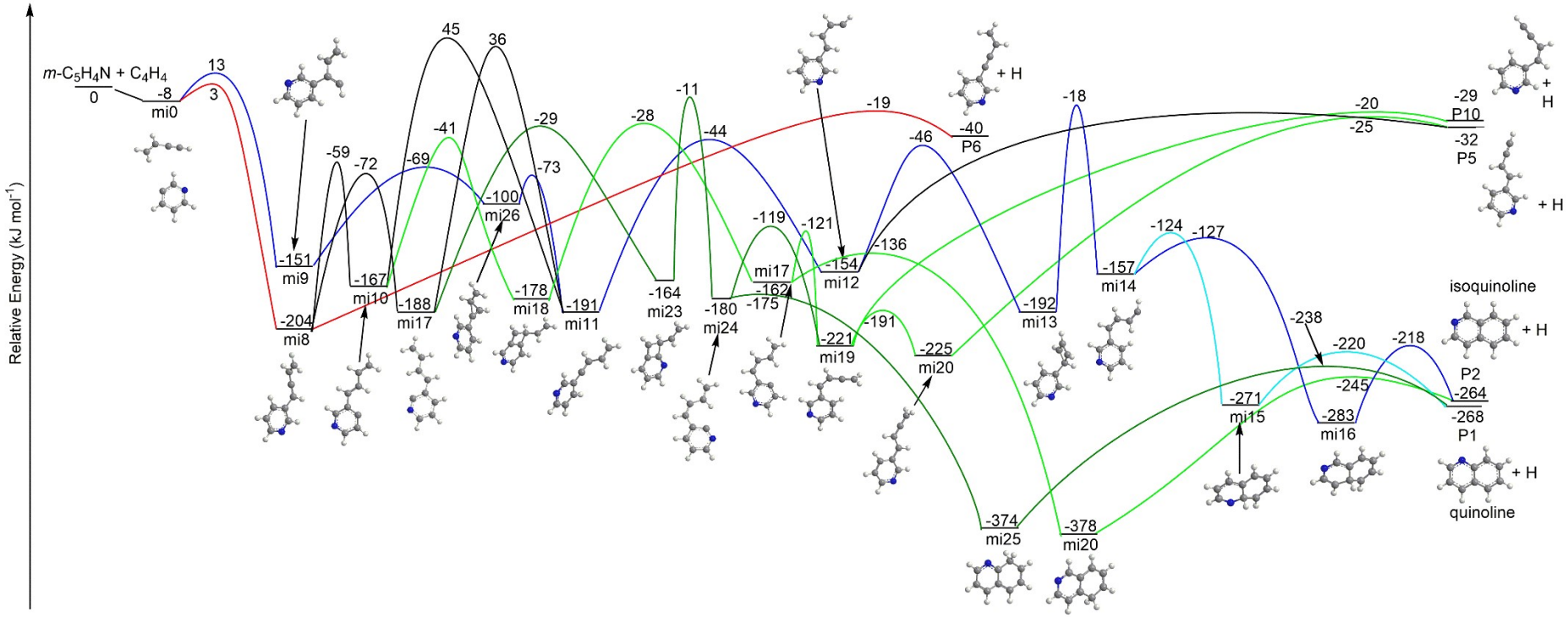


Figure S5b. Computed potential energy surface (PES) for the reaction system of *m*-pyridinyl (C_5H_4N) and vinylacetylene (C_4H_4). The energies calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) + ZPE level of theory are presented in units of kJ mol^{-1}. Only pathways initiated by vinylacetylene addition to the radical site by its C_2H end are shown.

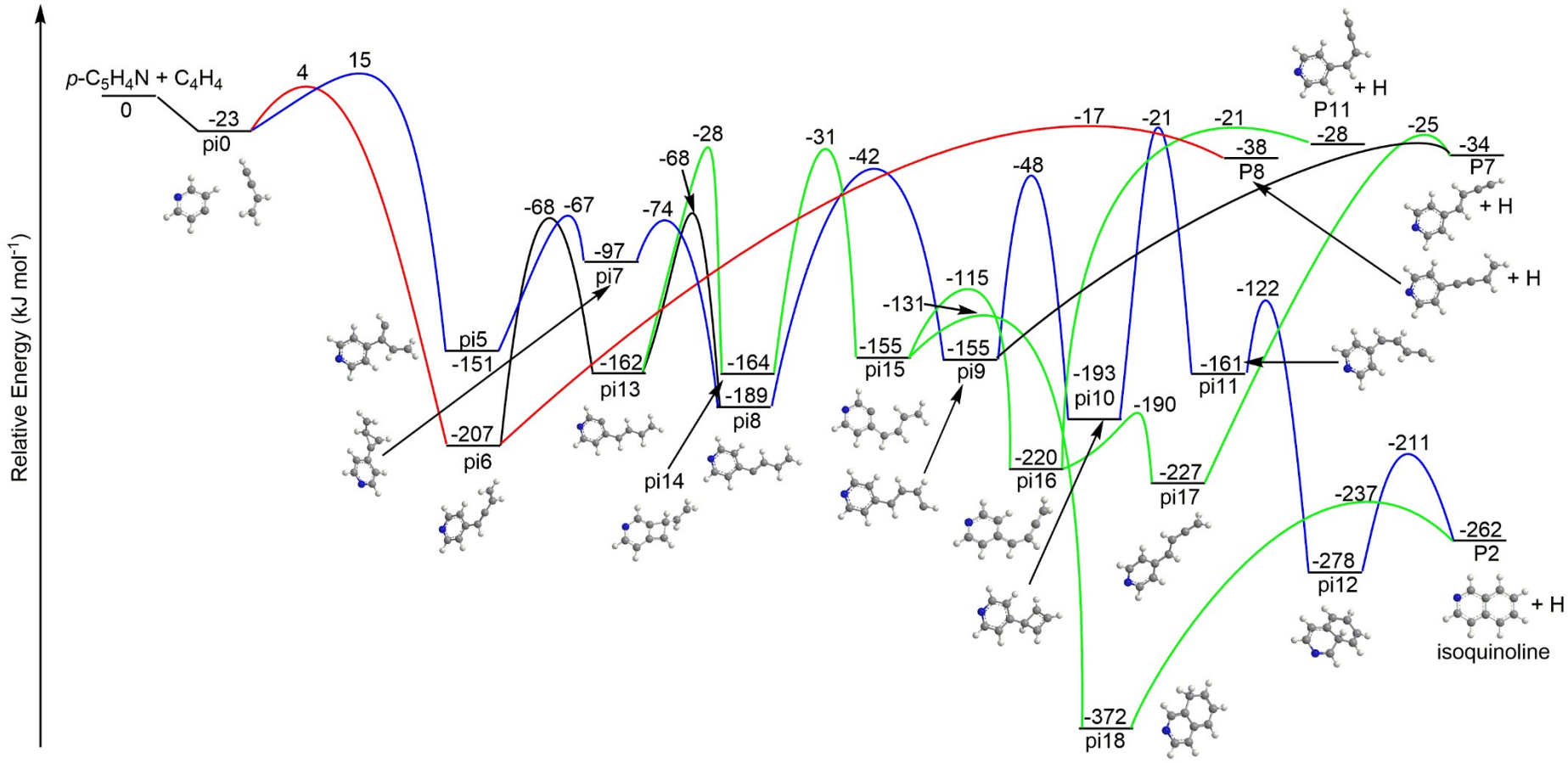
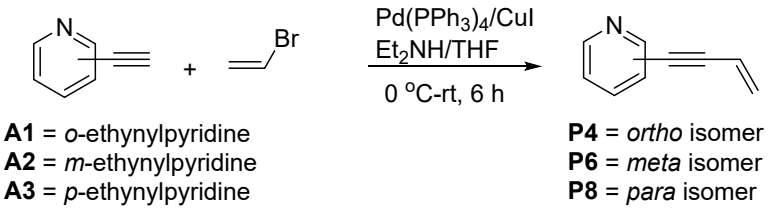


Figure S5c. Computed potential energy surface (PES) for the reaction system of *p*-pyridinyl (C_5H_4N) and vinylacetylene (C_4H_4). The energies calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) + ZPE level of theory are presented in units of kJ mol^{-1}. Only pathways initiated by vinylacetylene addition to the radical site by its C_2H end are shown.

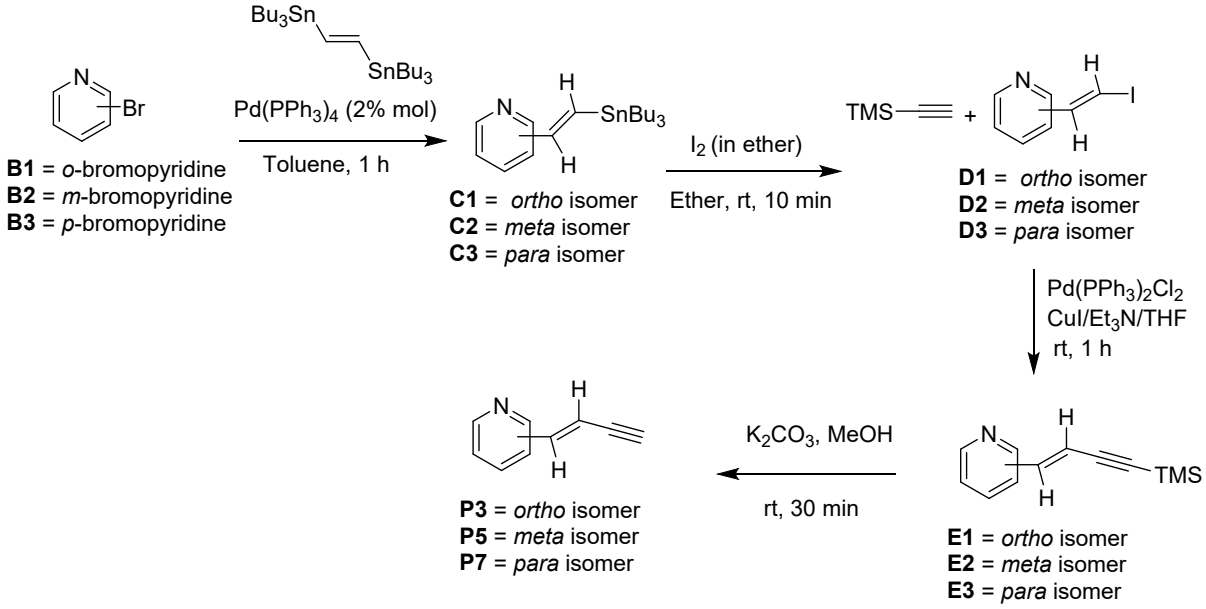
Synthesis of "enyne" and "ynene" isomers of pyridine

The enyne isomers of pyridine **P4**, **P6**, and **P8** were synthesized by CuI/$Pd(PPh_3)_4$-mediated Sonogashira coupling between *o*-ethynylpyridine **A1**, *m*-ethynylpyridine **A2**, *p*-ethynylpyridine **A3** and vinyl bromide in presence of Et_2NH in THF respectively (**Scheme 1**).



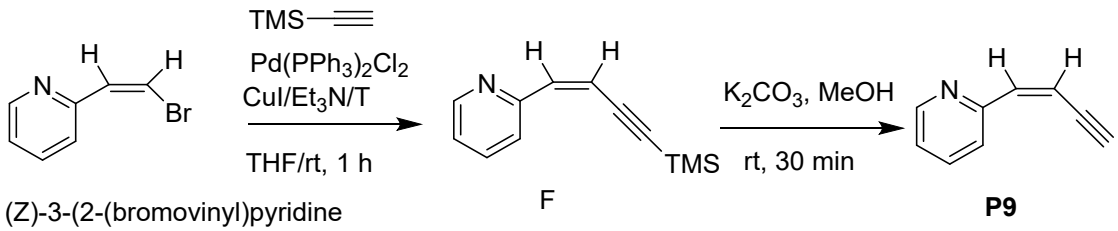
Scheme 1. Synthesis of *ortho*, *meta*, and *para* enyne isomers of pyridine.

The ynene isomers of pyridine **P3**, **P5**, and **P7** were synthesized by Pd-catalyzed Stille cross coupling reaction between *ortho*, *meta*, and *para* isomers of bromopyridine (e.g., **B1**) and *trans*-1,2-Bis(tri-n-butylstannyl)ethylene yielded trans-vinylstannane (e.g., **C1**) which were converted to *trans*-1-alkenyliodide (e.g., **D1**) via iodination followed by Sonogashira cross-coupling with (trimethylsilyl)acetylene and desilylation of resulting protected alkyne(e.g., **E1**) with K_2CO_3 (**Scheme 2**) gave desired products.



Scheme 2. Synthesis of *ortho*, *meta*, and *para* (*E*)-*ynene* isomers of pyridine analogue.

The (*Z*)-3-(but-1-en-3-yn-1-yl)pyridine **P9** was synthesized by CuI/$Pd(PPh_3)_2Cl_2$-mediated Sonogashira cross-coupling of commercially available (*Z*)-3-(2-(bromovinyl)pyridine with (trimethylsilyl)acetylene and desilylation of **F** with K_2CO_3 (**Scheme 3**).



Scheme 3. Synthesis of (*Z*)-3-(but-1-en-3-yn-1-yl)pyridine **P9**.

General Information. ^{1}H NMR spectra at 400 MHz and ^{13}C NMR at 101 MHz were recorded in $CDCl_3$ unless otherwise noted. All chemical shift values are reported in parts per million (ppm) and referenced to the residual solvent peaks of $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm) for ^{1}H NMR and $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) peaks for ^{13}C NMR spectra, with coupling constant (*J*) values reported in Hz. Reaction progress was monitored by TLC on Merck Kieselgel 60-F_{254} sheets with product detection by 254-nm light. Products were purified by column chromatography using Merck Kiselgel 60 (230-400 mesh). Reagent grade chemicals and solvents were used without further purification unless otherwise specified.

2-(But-3-en-1-yn-1-yl)pyridine; P4. Procedure I

$Pd(PPh_3)_4$ (34.67 mg, 0.03 mmol) and Cu(I)I (22.85 mg, 0.12 mmol) were placed in the flame-dried flask under N_2 at 0 ^{o}C (ice-bath). Then Et_2NH (1.50 mL, 1060 mg, 14.5 mmol) and vinyl bromide (1.0 M in THF; 4.0 mL, 4.0 mmol) were added following by slow addition of commercially available 2-ethynylpyridine **A1** (310.0 mg, 3.0 mmol) dissolved in dry THF (2 mL) via a syringe pump (over 3 h). The resulting mixture was allowed to warm up to ambient temperature (30 min) and was stirred for another 2 h. Volatiles were evaporated and the residue was dissolved in EtOAc and filtered. The filtrate was collected and solvent was evaporated. The residue was column chromatographed (10-30% EtOAc in hexane) to give **P4** (300.0 mg, 77%) as a yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.64 (dd, J = 11.2, 2.0 Hz, 1H), 5.85 (dd, J = 17.6, 2.0 Hz, 1H), 6.02 (dd, J = 17.6, 11.2 Hz, 1H), 7.21 (43 (dd, J = 7.2, 5.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.64 (td, J = 7.6, 1.6 Hz, 1H), 8.58

(d, J = 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 88.07, 89.14, 116.65, 122.86, 127.11, 129.05, 136.36, 143.45, 150.02.

3-(But-3-en-1-yn-1-yl)pyridine; P6.

Treatment of commercially available 3-ethynylpyridine **A2** (310.0 mg, 3.0 mmol) with vinyl bromide by Procedure **I** (column chromatography; EtOAc in hexane 10-30%) gave **P6** (270.0 mg, 70%) as a yellow liquid. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 5.72 (dd, J = 11.2, 2.0 Hz, 1H), 5.82 (dd, J = 17.6, 2.0 Hz, 1H), 6.17 (dd, J = 17.6, 11.2 Hz, 1H), 7.43 (dd, J = 8.0, 4.8 Hz, 1H), 7.89 (dt, J = 8.0, 1.6 Hz, 1H), 8.57 (d, J = 4.0 Hz, 1H), 8.67 (s, 1H); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 86.70, 91.24, 116.70, 119.36, 123.89, 129.05, 138.40, 149.08, 151.32.

4-(But-3-en-1-yn-1-yl)pyridine, P8.

Treatment of commercially available 4-ethynylpyridine **A3** (310.0 mg, 3.0 mmol) with vinyl bromide by Procedure **I** (column chromatography; EtOAc in hexane 10-30%) gave **P8** (290.0 mg, 75%) as a yellow liquid. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 5.77 (dd, J = 11.2, 1.6 Hz, 1H), 5.88 (dd, J = 17.6, 1.6 Hz, 1H), 6.18 (dd, J = 17.6, 11.2 Hz, 1H), 7.47 (s, 2H), 8.69 (brs, 2H); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 87.22, 92.41, 116.38, 116.44, 125.69, 129.94, 130.14, 130.18, 149.85.

(*E*)-2-(2-(Tributylstannyl)vinyl)pyridine; C1. Procedure II

A flame dry round bottom flask equipped with a magnetic stirrer was charged with 2-bromopyridine **B1** (191 µL, 316 mg, 2.0 mmol), *trans*-1,2-bis(tri-n-butylstannyl)ethylene (1.3 mL, 1470 mg, 2.4 mmol), dry toluene (10 mL) and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) and the resulting mixture was deoxygenated with N_2. The reaction mixture was stirred at 100 ^{o}C (oil bath) for 1 h. The volatiles were evaporated, and the residue was column chromatographed (0-10% EtOAc in hexane) to give **C1** (633.4 mg, 80%) as a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.6 Hz, 9H), 0.99 (t, J = 8.0 Hz, 6H), 1.35 (m, 6H), 1.54 (m, 6H), 7.02 (d, J = 19.6 Hz, 1H), 7.13 (m, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 19.6, Hz, 1H), 7.66 (td, J = 7.6, 2.0 Hz, 1H), 8.54 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.81, 13.82, 27.46, 29.25, 120.87, 122.24, 136.27, 136.72, 145.94, 149.43, 156.18.

(*E*)-2-(2-(Iodovinyl)pyridine; D1. Procedure III

The vinyl stannane **C1** (600 mg, 1.52 mmol) was dissolved in Et_2O (10 mL) and elemental iodine (386 mg, 1.52 mmol; dissolved in 5 mL Et_2O) was added dropwise while stirring at room temperature. After completion of addition, the reaction mixture was stirred for another 10 min. The excess I_2 was destroyed by aqueous $Na_2S_2O_3$

solution. The reaction mixture was extracted with Et_2O (30 mL x 3) and organic layer was separated. The combined organic layer was dried (Na_2SO_4) and evaporated. The residue was column chromatographed (0-10% EtOAc in hexane) to give **D1** (288 mg, 82%) as a light-yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (m, 2H), 7.50 (s, 2H), 7.65 (td, J = 7.6, 2.0 Hz, 1H), 8.55 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 83.81, 121.69, 122.98, 136.84, 144.60, 149.90, 155.37.

(*E*)-2-(4-(Trimethylsilyl)but-1-en-3-yn-1-yl)pyridine; E1. Procedure IV

$Pd(PPh_3)_2Cl_2$ (32.8 mg, 0.047 mmol) and Cu(I)I (17.8 mg, 0.094 mmol) were added to dry THF (5 mL) in a flame-dried flask equipped with a stir bar under N_2 at room temperature. Then iodovinylpyridine, **D1** (270 mg, 1.17 mmol) was added followed by TMS-acetylene (250 µL, 172.4 mg, 1.76 mmol) and Et_3N (326 µL, 237 mg, 2.34 mmol). The resulting mixture was stirred for 1h [progress of the reaction was monitored by TLC (*n*-hexane)]. Volatiles were evaporated and the residue was column chromatographed (0-10% EtOAc in hexane) to give **E1** as light brown liquid (226 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 6.75 (d, J = 16.0 Hz, 1H), 7.01 (d, J = 16.0 Hz, 1H), 7.16 (ddd, J = 7.6, 4.8, 0.8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.63 (td, J = 7.6, 1.6 Hz, 1H), 8.56 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 0.03, 99.52, 104.16, 113.02, 122.43, 123.23, 136.87, 140.99, 149.72, 154.14.

(*E*)-2-(But-1-en-3-yn-1-yl)pyridine; P3. Procedure V

Anhydrous K_2CO_3 (166 mg, 1.2 mmol) was added to a stirred solution of **E1** (201 mg, 1.0 mmol) in dry MeOH (5 mL) at room temperature. After for 30 min, volatiles were evaporated and the residue was column chromatographed (0-10% EtOAc in hexane) to give **P3** (116 mg, 90%) as light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15 (d, J = 2.4 Hz, 1H), 6.72 (dd, J = 16.0, 2.4 Hz, 1H), 7.05 (d, J = 16.0 Hz, 1H), 7.18 (dd, J = 7.2, 4.8, Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.64 (td, J = 7.6, 1.6 Hz, 1H), 8.56 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 83.25, 84.73, 113.76, 124.47, 125.37, 138.76, 144.00, 151.93, 155.90.

(*E*)-3-(2-(Tributylstannyl)vinyl)pyridine; C2.

Treatment 3-bromopyridine **B2** (500 mg, 3.16 mmol) with *trans*-1,2-bis(tri-n-butylstannyl)ethylene by Procedure **II** (column chromatography; EtOAc in hexane 0-10%) gave **C2** (1230 mg, 90%) as a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.2 Hz, 9H), 0.98 (t, J = 8.0 Hz, 6H), 1.35 (m, 6H), 1.54 (m, 6H), 6.85 (d, J = 19.6 Hz, 1H), 6.99 (d, J = 19.6, Hz, 1H), 7.24 (m, 1H), 7.73 (d, J = 8.0 Hz, 1H), 8.45 (br, 1H), 8.61 (br, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.82, 13.82, 27.41, 29.23, 123.61, 132.46, 133.63, 134.36, 142.55, 148.33, 148.53.

(*E*)-3-(2-(Iodovinyl)pyridine; D2.

Treatment of vinyl stannane **C2** (1200 mg, 3.04 mmol) with I_2 by procedure **III** (column chromatography; EtOAc in hexane 0-10%) gave **D2** (650 mg, 92%) as a light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98 (d, J = 14.8 Hz, 1H), 7.27 (m, 1H), 7.43 (d, J = 15.2 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 8.55 (br, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 79.34, 123.81, 132.66, 133.61, 141.64, 147.60, 149.32.

(*E*)-3-(4-(Trimethylsilyl)but-1-en-3-yn-1-yl)pyridine; E2

Treatment of iodovinylpyridine **D2** (550 mg, 2.38 mmol) with TMS-acetylene by procedure **IV (**column chromatography; EtOAc in hexane 0-10%) gave **E2** (430 mg, 90%) as light brown liquid. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.20 (s, 9H), 6.58 (d, J = 16.8 Hz, 1H), 7.04 (d, J = 16.4 Hz, 1H), 7.39 (m, 1H), 7.98(d, J = 7.6 Hz, 1H), 8.53 (brs, 1H), 8.74 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 0.21, 97.64, 104.54, 110.15, 123.80, 131.54, 132.72, 139.02, 148.17, 149.60.

(*E*)-3-(But-1-en-3-yn-1-yl)pyridine; P5.

Treatment Silyl protected compound **E2** (403 mg, 2.0 mmol) with K_2CO_3 by Procedure **V** (column chromatography; EtOAc in hexane 0-10%) gave **P5** (243 mg, 94%) as a light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.11 (d, J = 2.4 Hz, 1H), 6.20 (dd, J = 16.4, 2.4 Hz, 1H), 7.01 (d, J = 16.4 Hz, 1H), 7.27 (dd, J = 8.0, 4.8, Hz, 1H), 7.71 (dt, J = 8.0, 1.6 Hz, 1H), 7.52 (d, J = 3.2 Hz, 1H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 80.61, 82.27, 109.67, 123.77, 131.76, 132.77, 139.45, 148.24, 149.81.

(*E*)-4-(2-(Tributylstannyl)vinyl)pyridine; C3.

Treatment 4-bromopyridine **B3** (500 mg, 3.16 mmol) with *trans*-1,2-bis(tri-n-butylstannyl)ethylene by Procedure **II** (column chromatography; EtOAc in hexane 0-10%) gave **C3** (1025 mg, 75%) as a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.2 Hz, 9H), 0.99 (t, J = 8.0 Hz, 6H), 1.3 (sex, J = 7.2 Hz, 6H), 1.54 (m, 6H), 6.81 (d, J = 19.6 Hz, 1H), 7.18 (d, J = 19.6 Hz, 1H), 7.25 (dd, J = 4.4, 1.2 Hz, 2H), 8.54 (dd, J = 4.4, 1.6 Hz, 2H); ^{13}C NMR δ 9.80, 13.82, 27.40, 29.20, 120.57, 137.20, 143.70, 145.50, 150.26.

(*E*)-4-(2-(Iodovinyl)pyridine; D3.

Treatment of **C3** (1000 mg, 2.54 mmol) with I_2 by procedure **III** (column chromatography; EtOAc in hexane 0-10%) gave **D3** (440 mg, 75%) as a light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16 (dd, J = 4.4, 1.6 Hz, 2H), 7.21 (d, J = 14.8 Hz, 1H), 7.40 (d, J = 14.8 Hz, 1H), 8.57 (dd, J = 4.4, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$,

100.6 MHz) δ 83.04, 120.37, 143.02, 145.51, 150.53. This compound is very unstable, decomposes in open air and even in freezer when stored for more than 2 weeks.

(*E*)-4-(4-(Trimethylsilyl)but-1-en-3-yn-1-yl)pyridine; E3

Treatment of iodovinylpyridine **D3** (462 mg, 2.0 mmol) with TMS-acetylene by procedure **IV** (column chromatography; EtOAc in hexane 0-10%) gave **E3** (322 mg, 80%) as a gummy solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 6.36 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 7.22 (d, J = 6.0 Hz, 2H), 8.55 (d, J = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 0.09, 100.26, 103.23, 113.17, 120.73, 139.55, 143.37, 150.36.

(*E*)-4-(But-1-en-3-yn-1-yl)pyridine; P7.

Treatment **E3** (220 mg, 1.09 mmol) with K_2CO_3 by Procedure **V** (column chromatography; EtOAc in hexane 10-20%) gave **P7** (243 mg, 94%) as a light yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.18 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 16.4 Hz, 1H), 6.95 (d, J = 16.4 Hz, 1H), 7.23 (dd, J = 4.4, 1.6 Hz, 2H), 8.58 (dd, J = 4.4, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 81.91, 112.15, 120.59, 140.55, 143.05, 150.54.

(*Z*)-3-(4-(Trimethylsilyl)but-1-en-3-yn-1-yl)pyridine; F.

Treatment of commercially available (*Z*)-3-(2-(bromovinyl)pyridine (300 mg, 1.63 mmol) with TMS-acetylene by procedure IV (column chromatography; EtOAc in hexane 0-10%) gave **F** (322 mg, 98%) as light brown liquid. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.23 (s, 9H), 5.98 (d, J = 12.4 Hz, 1H), 6.86 (d, J = 12.0 Hz, 1H), 7.43(dd, J = 8.0, 4.8 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.52 (br, 1H), 8.95 (br, 1H); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 0.46, 103.07, 103.43, 109.40, 123.28, 131.67, 134.60, 136.67, 149.38, 149.73.

(*Z*)-3-(But-1-en-3-yn-1-yl)pyridine; P9.

Treatment **F** (300 mg, 1.49 mmol) with K_2CO_3 by Procedure **V** (column chromatography; EtOAc in hexane 0-10%) gave **P9** (164 mg, 85%) as a light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (dd, J = 2.4, 0.8 Hz, 1H), 5.82 (dd, J = 12.0, 2.4 Hz, 1H), 6.70 (d, J = 12.0 Hz, 1H), 7.30 (dd, J = 8.0, 4.8, Hz, 1H), 8.38 (dt, J = 8.0, 1.6 Hz, 1H), 7.52 (d, J = 4.0 Hz, 1H), 8.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 81.36, 85.47, 109.19, 123.39, 132.07, 135.16, 136.95, 149.42, 150.31.

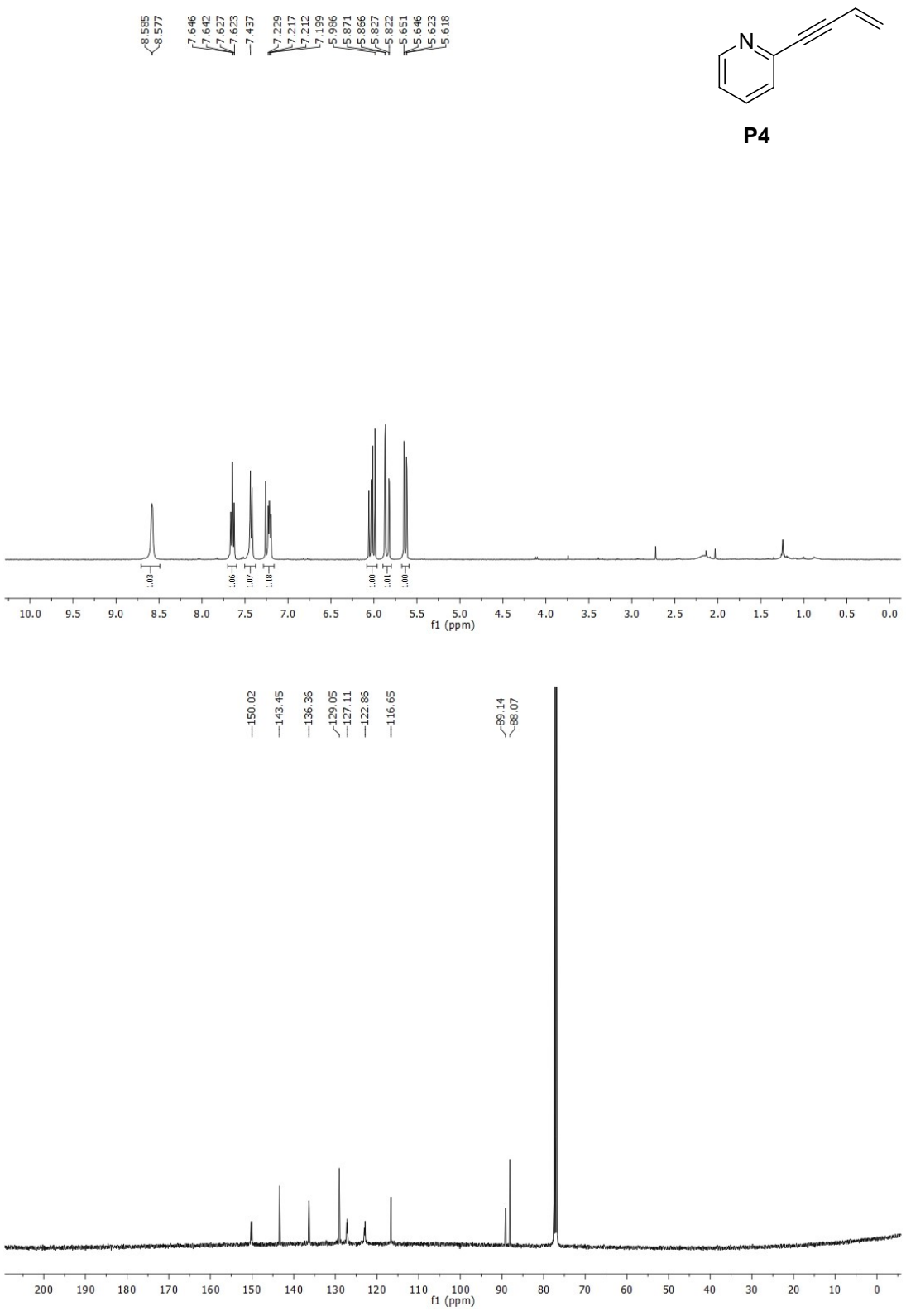


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of compound **P4** in $CDCl_3$.

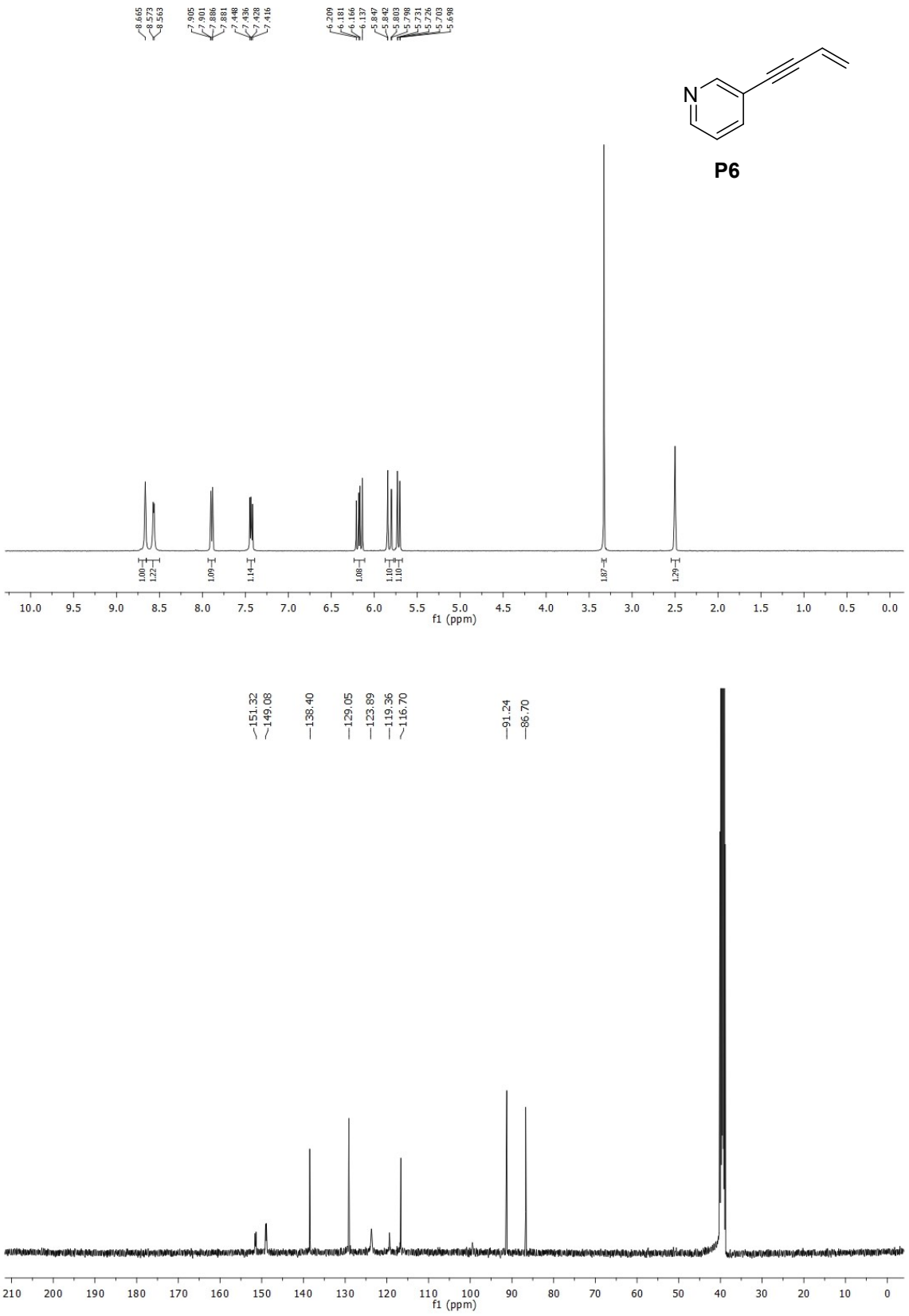


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of compound **P6** in DMSO.

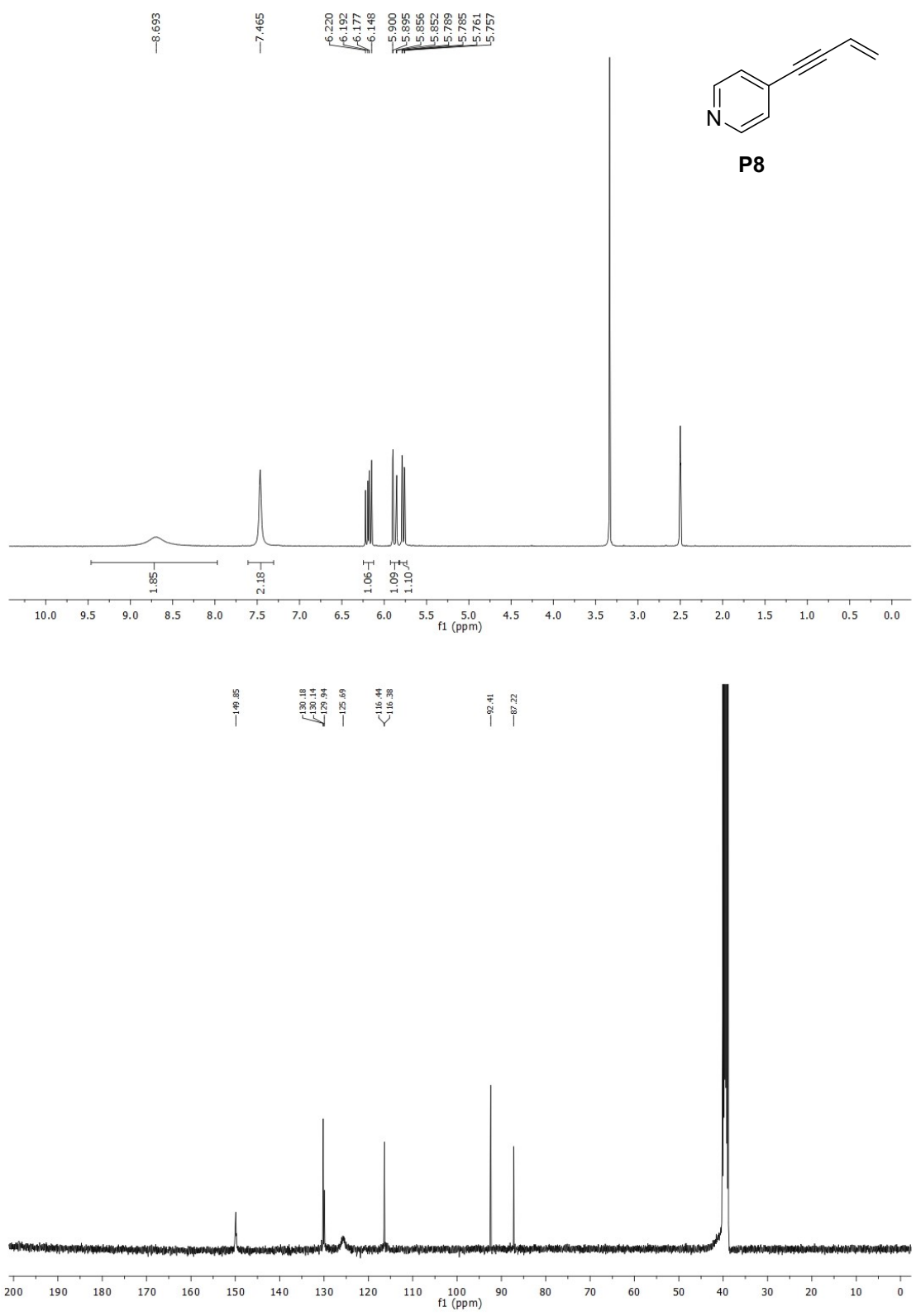


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **P8** in DMSO.

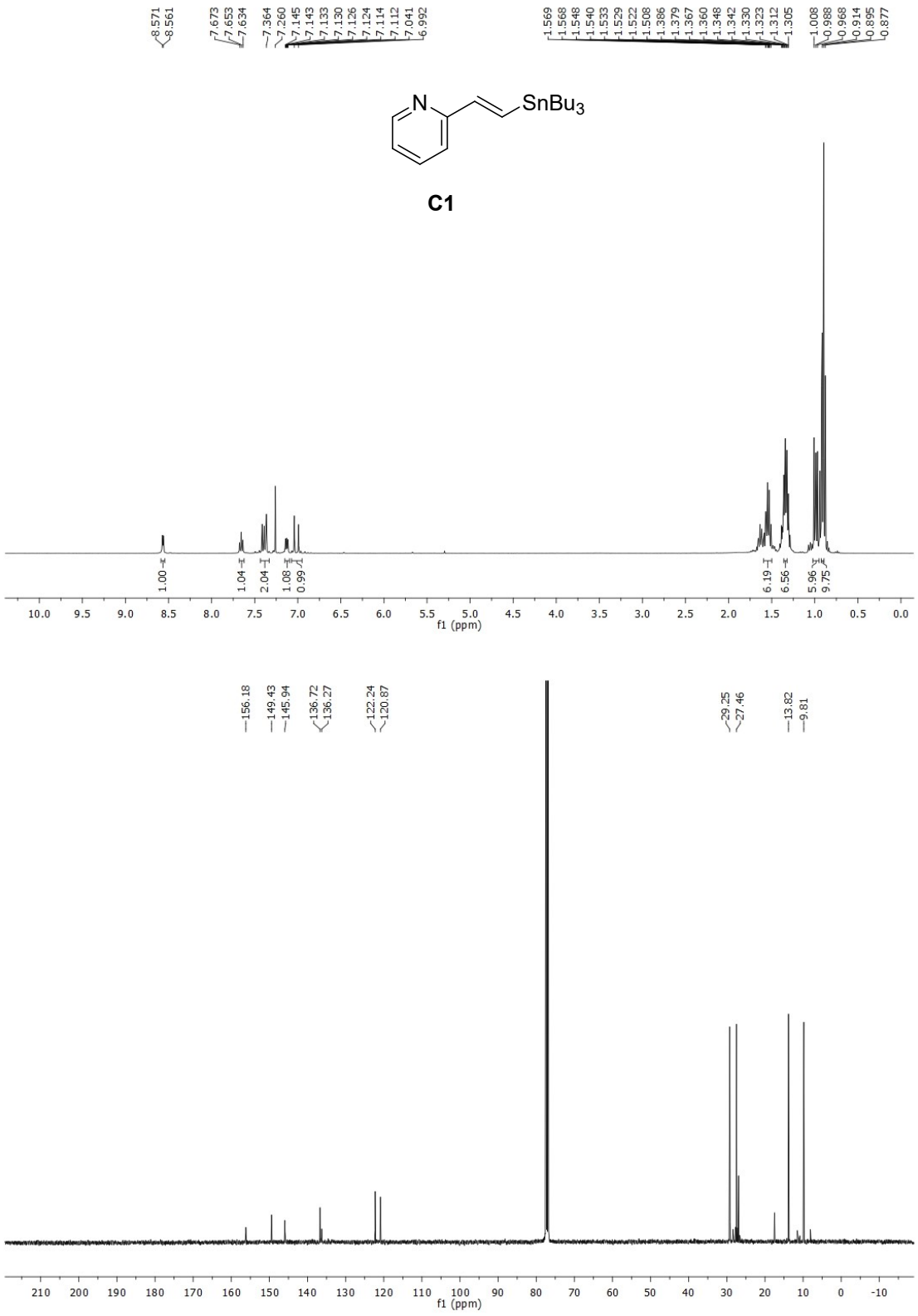


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of compound **C1** in $CDCl_3$.

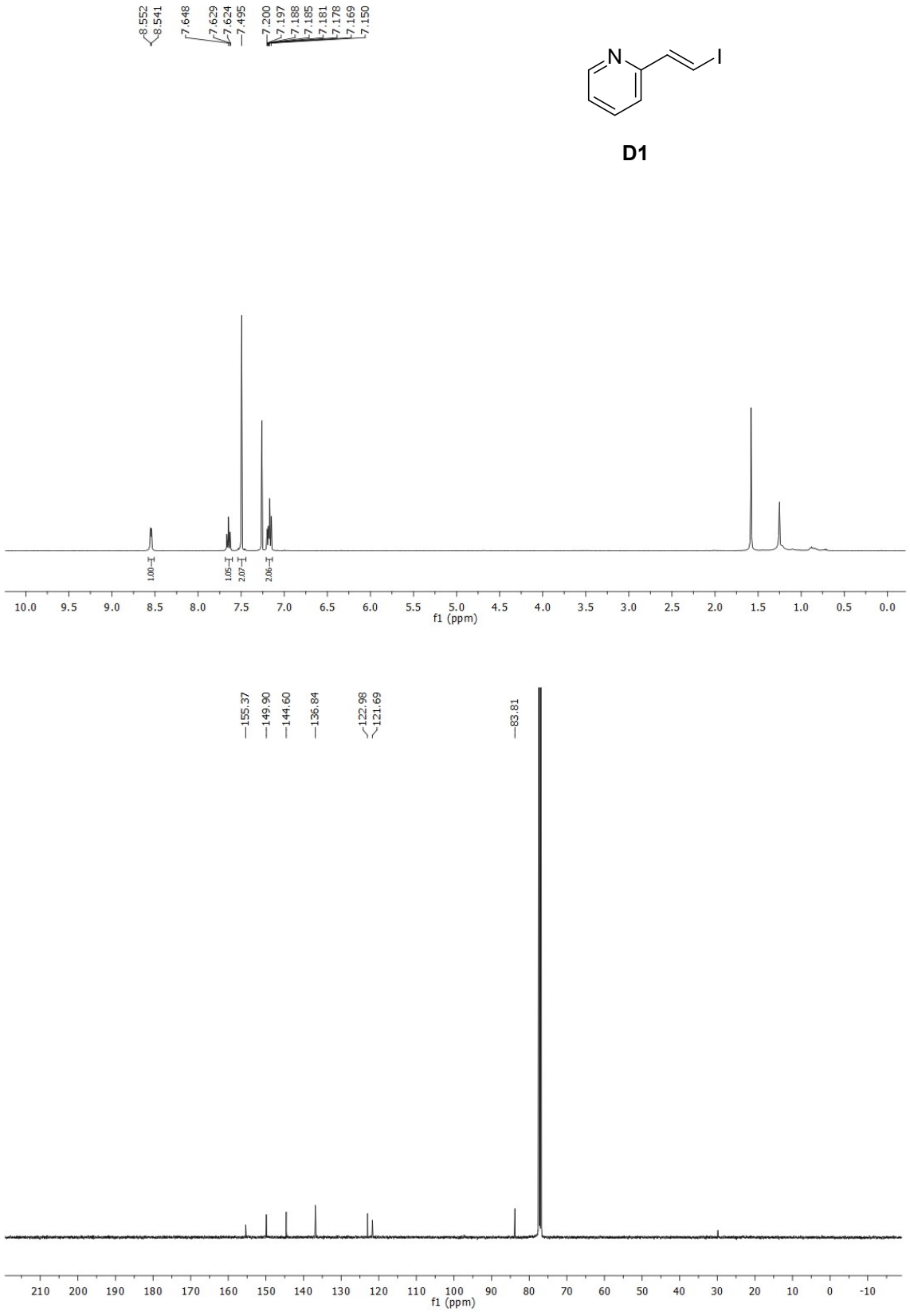


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of compound **D1** in $CDCl_3$.

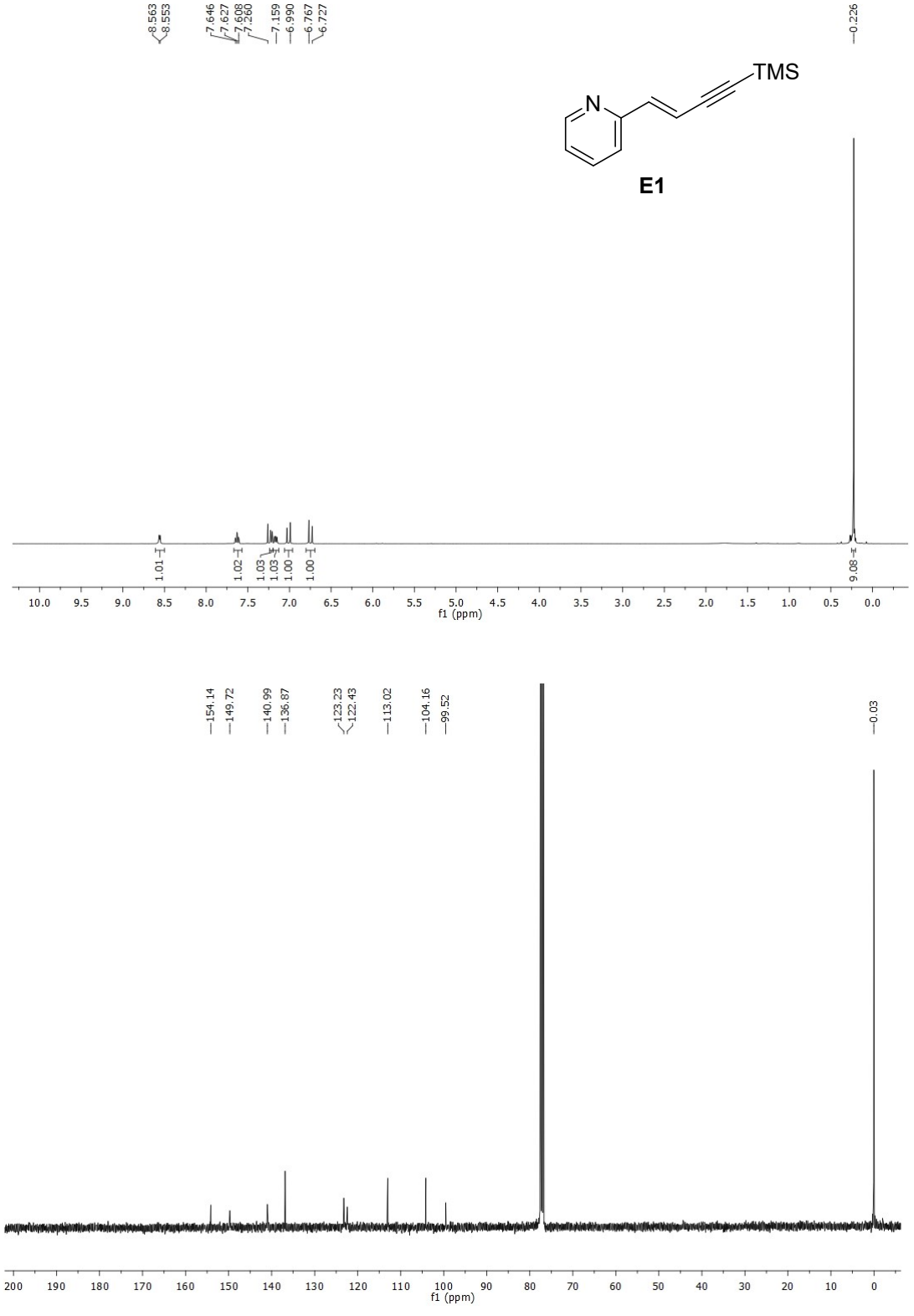


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of compound **E1** in $CDCl_3$.

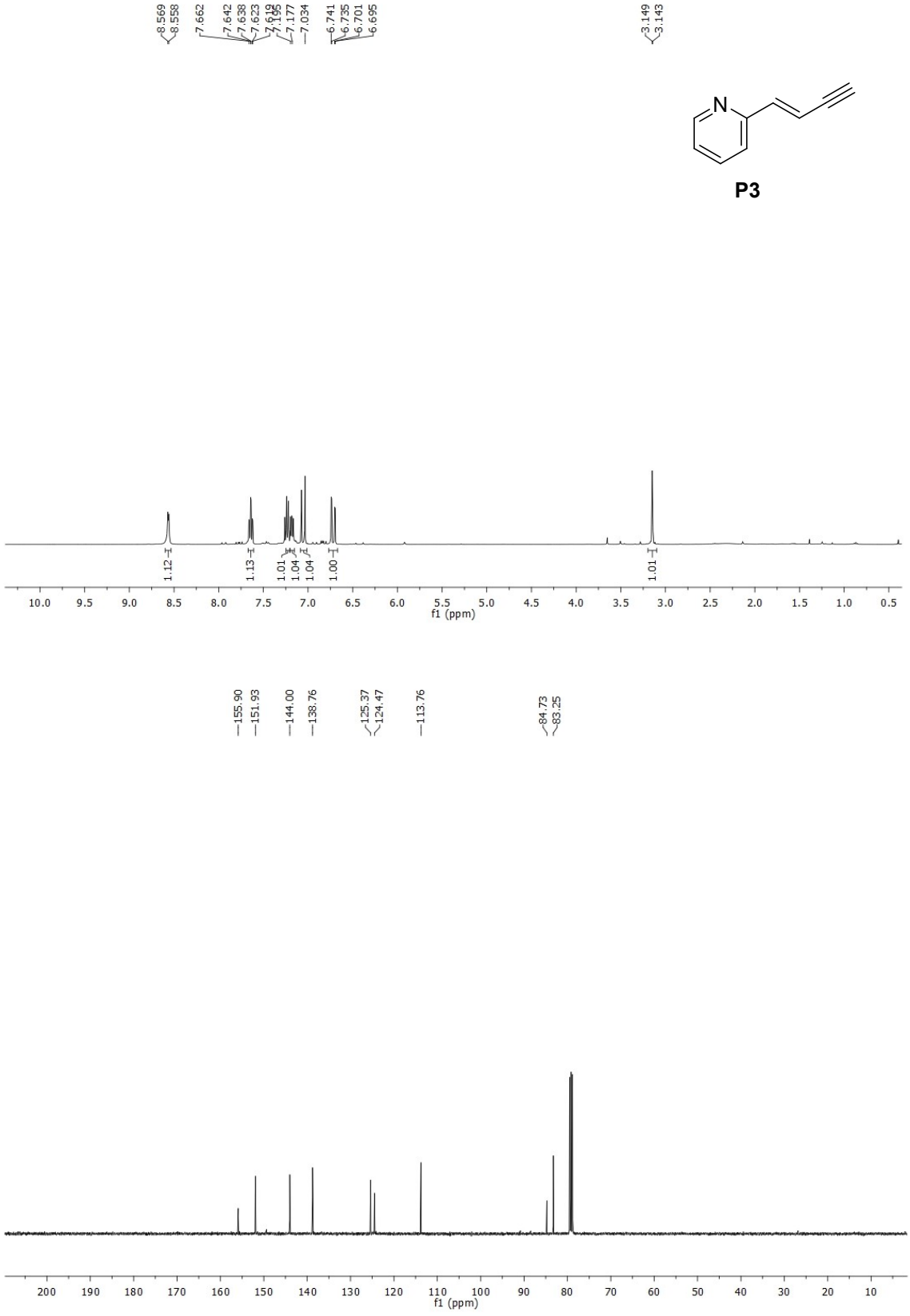


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of compound **P3** in $CDCl_3$.

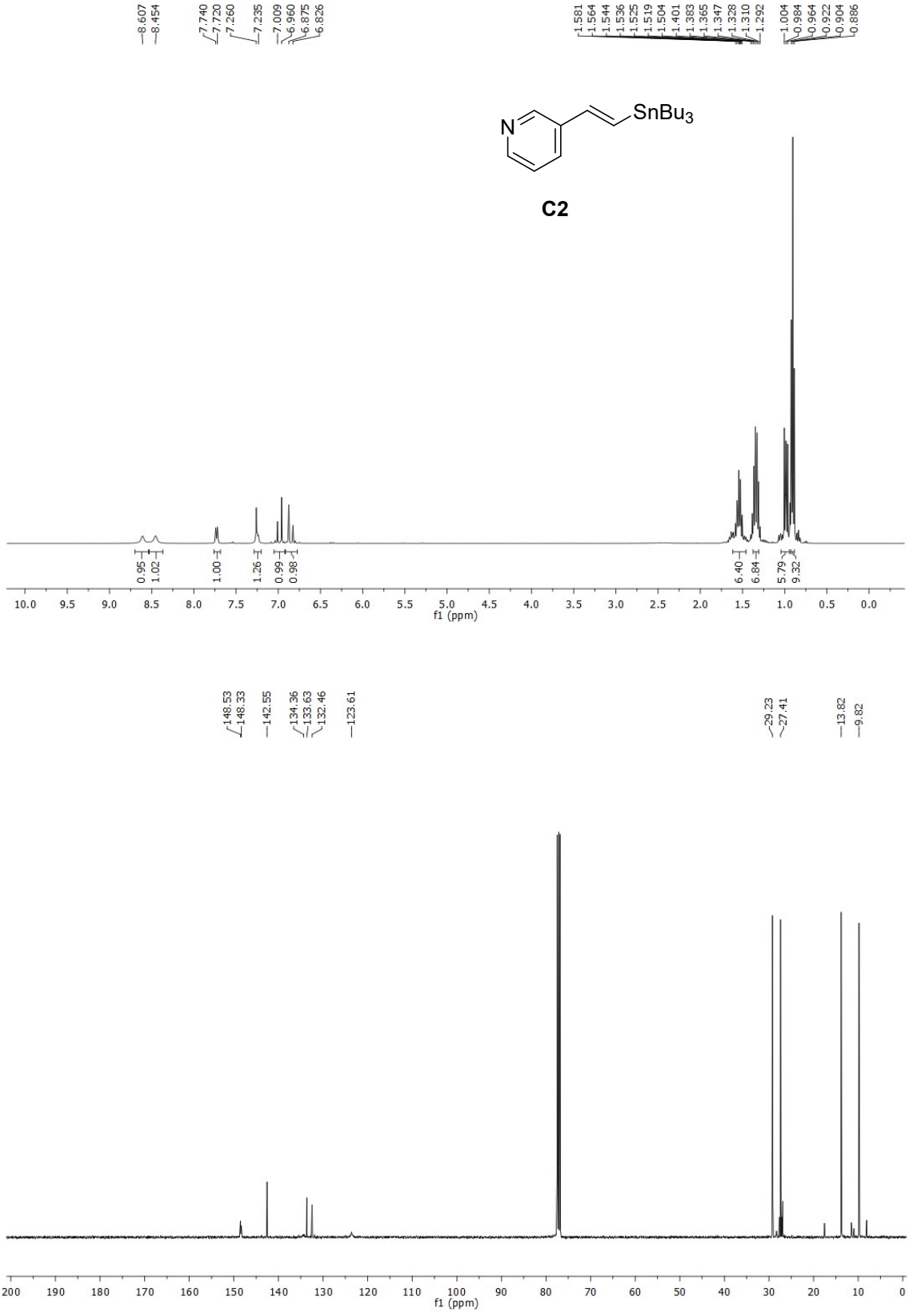


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of compound **C2** in $CDCl_3$.

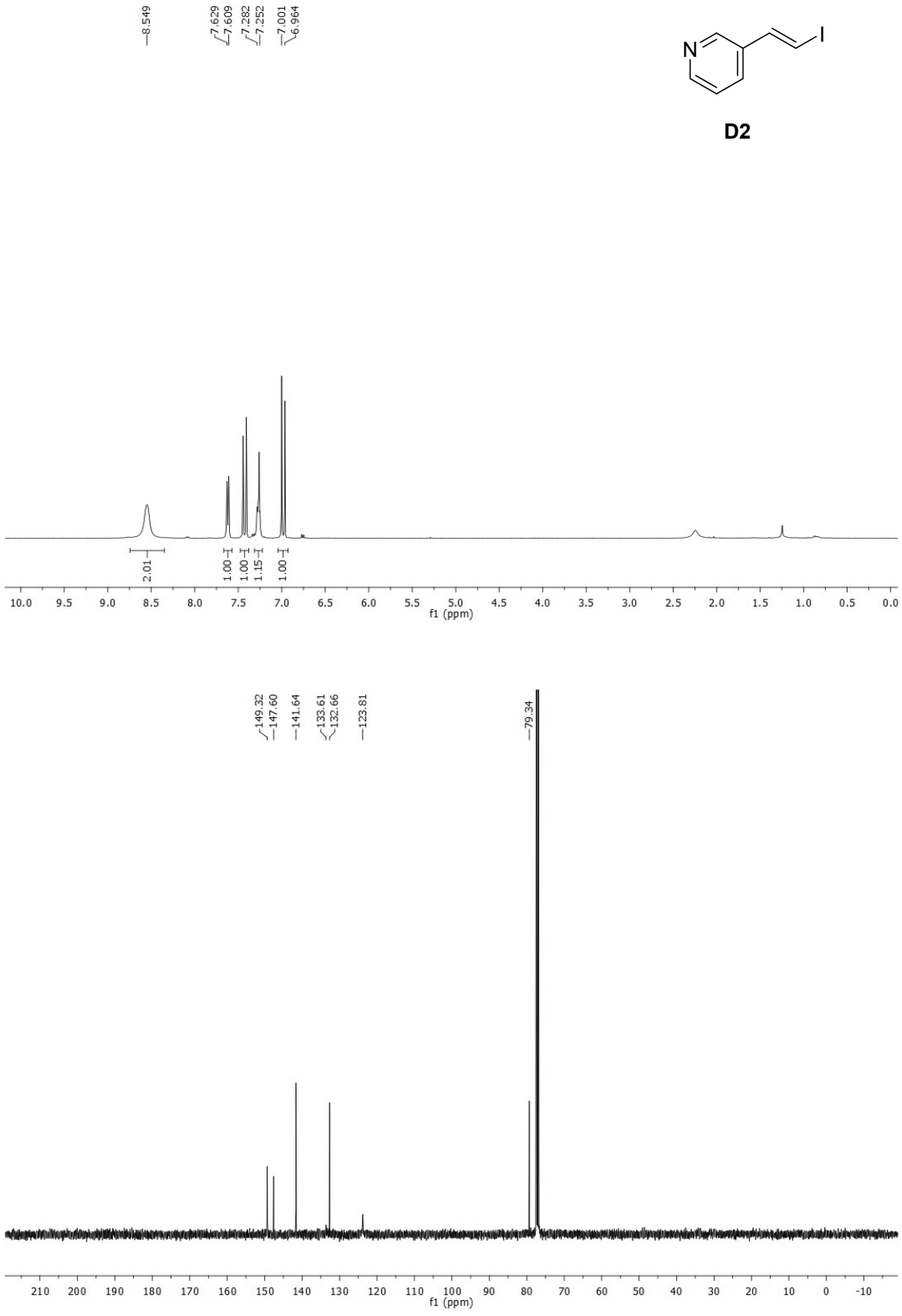


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of compound **D2** in $CDCl_3$.

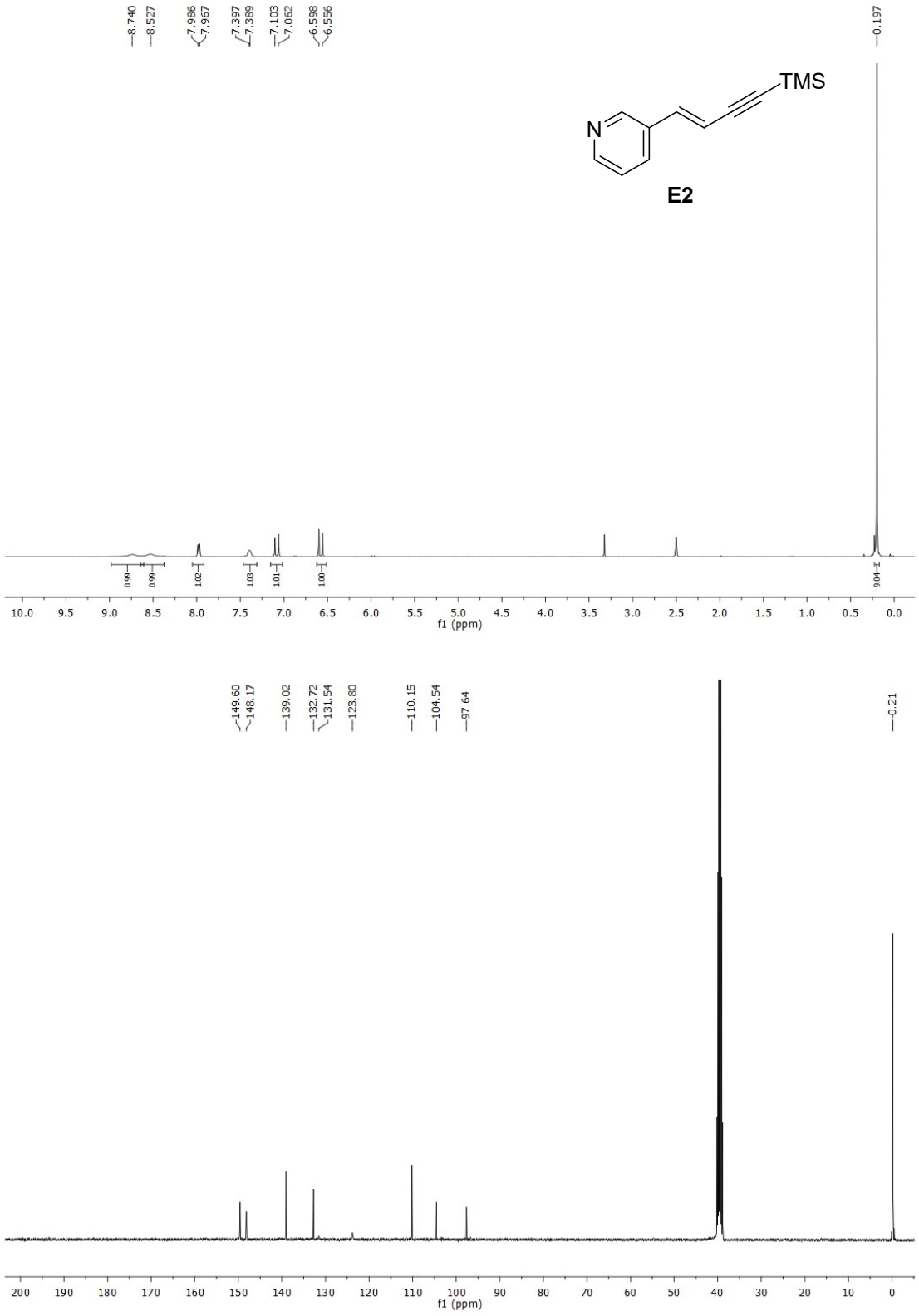


Figure S15. ^{1}H NMR and ^{13}C NMR spectra of compound **E2** in DMSO.

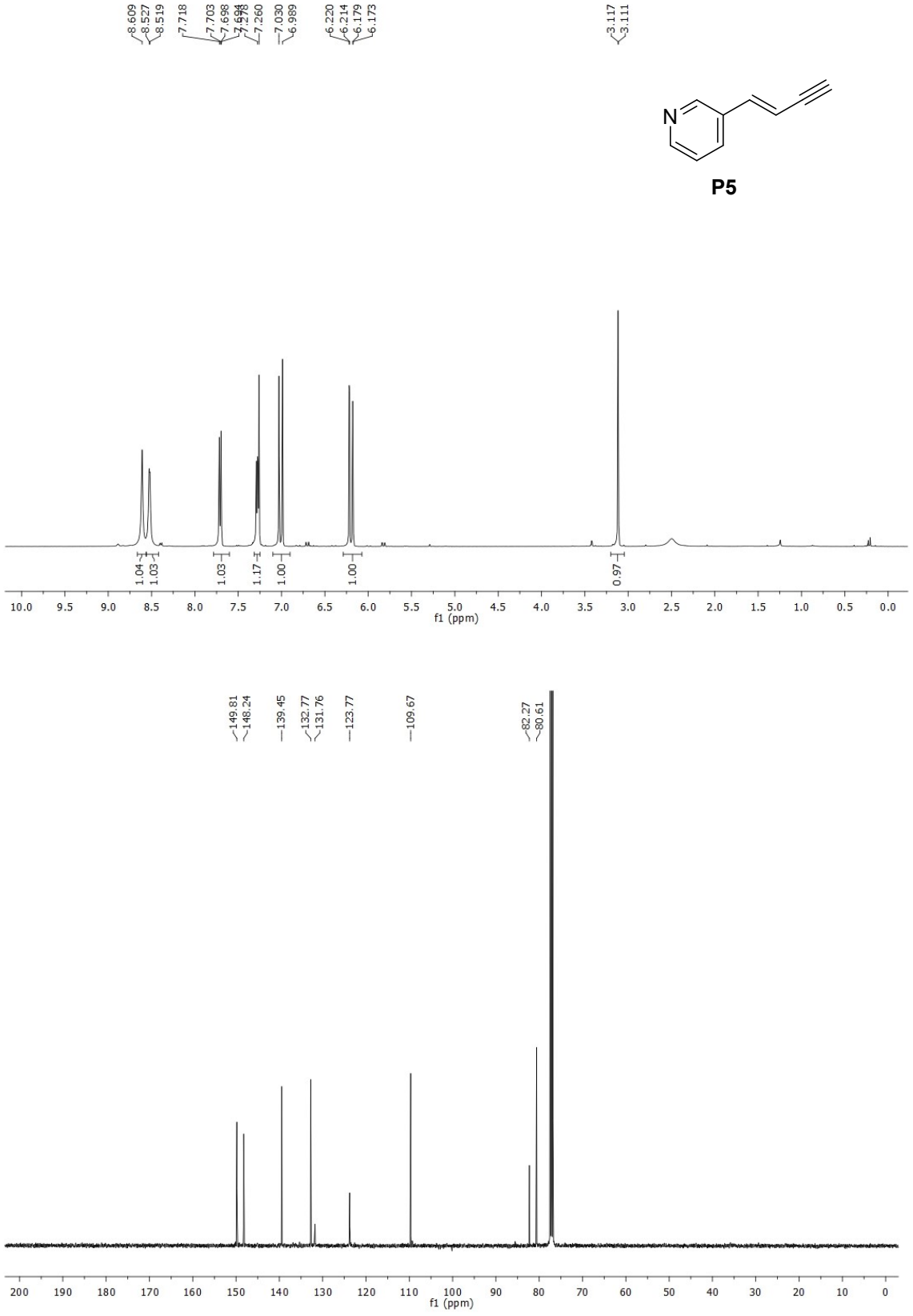


Figure S16. ^{1}H NMR and ^{13}C NMR spectra of compound **P5** in $CDCl_3$.

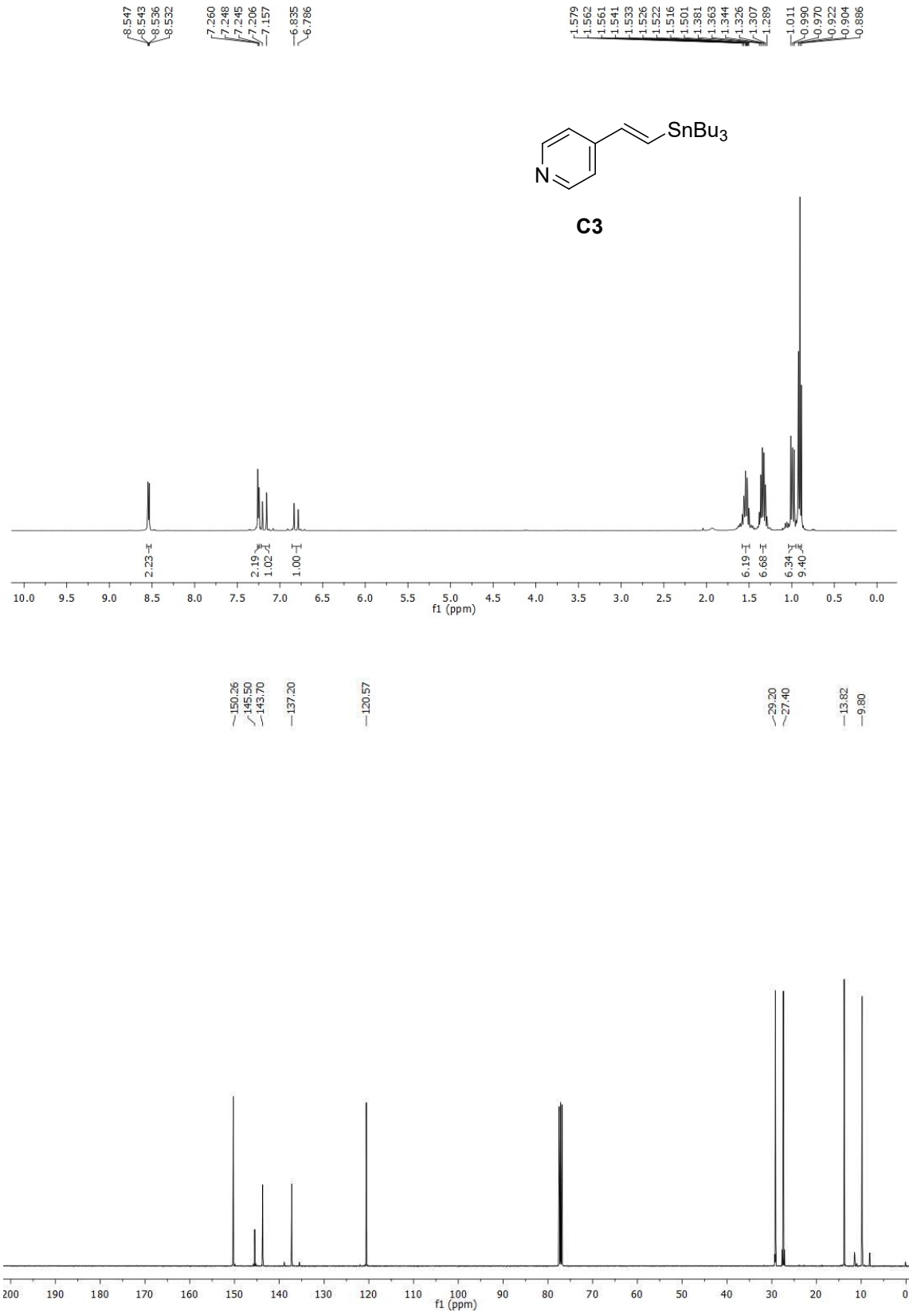


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of compound **C3** in $CDCl_3$.

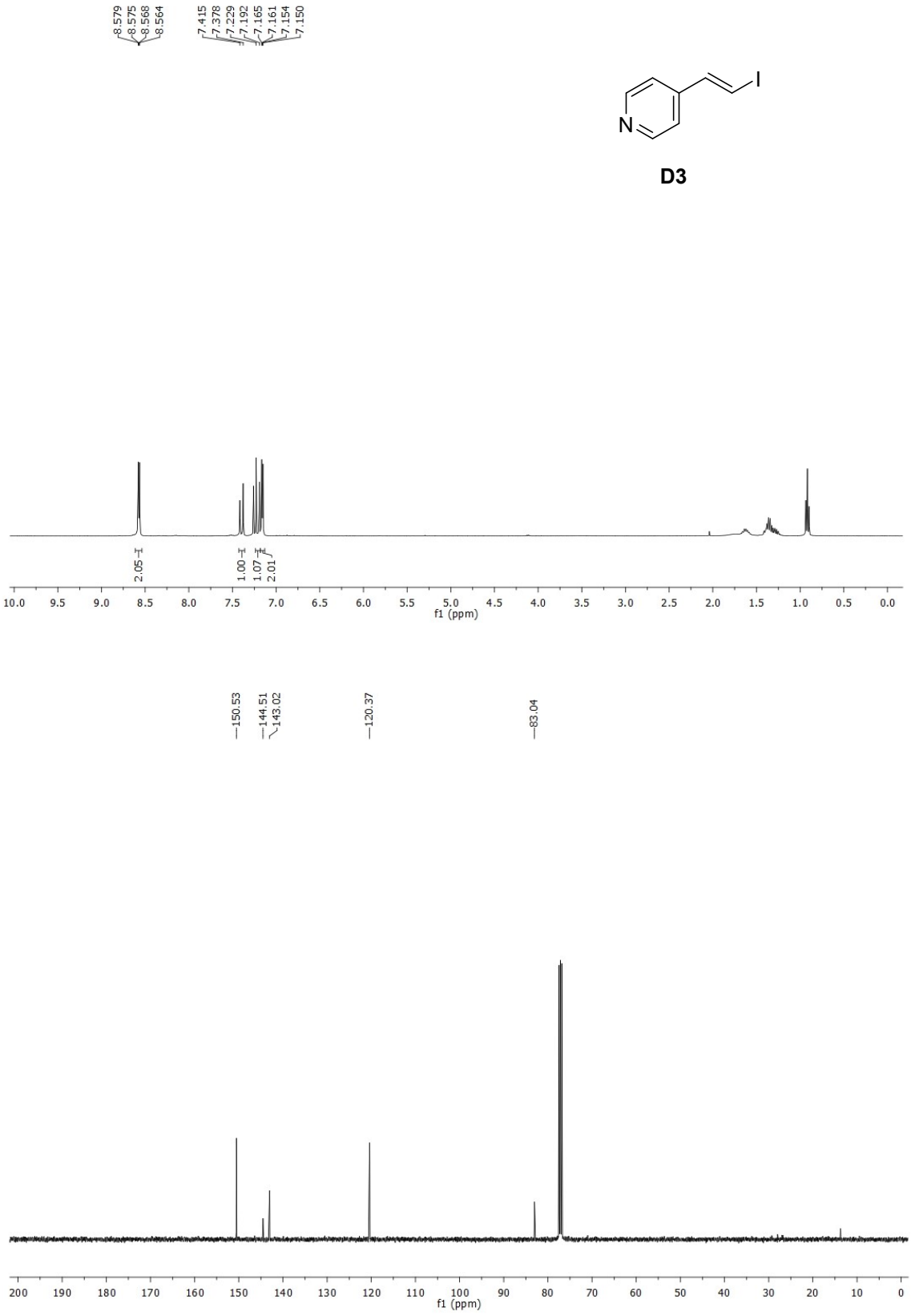


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of compound **D3** in $CDCl_3$.

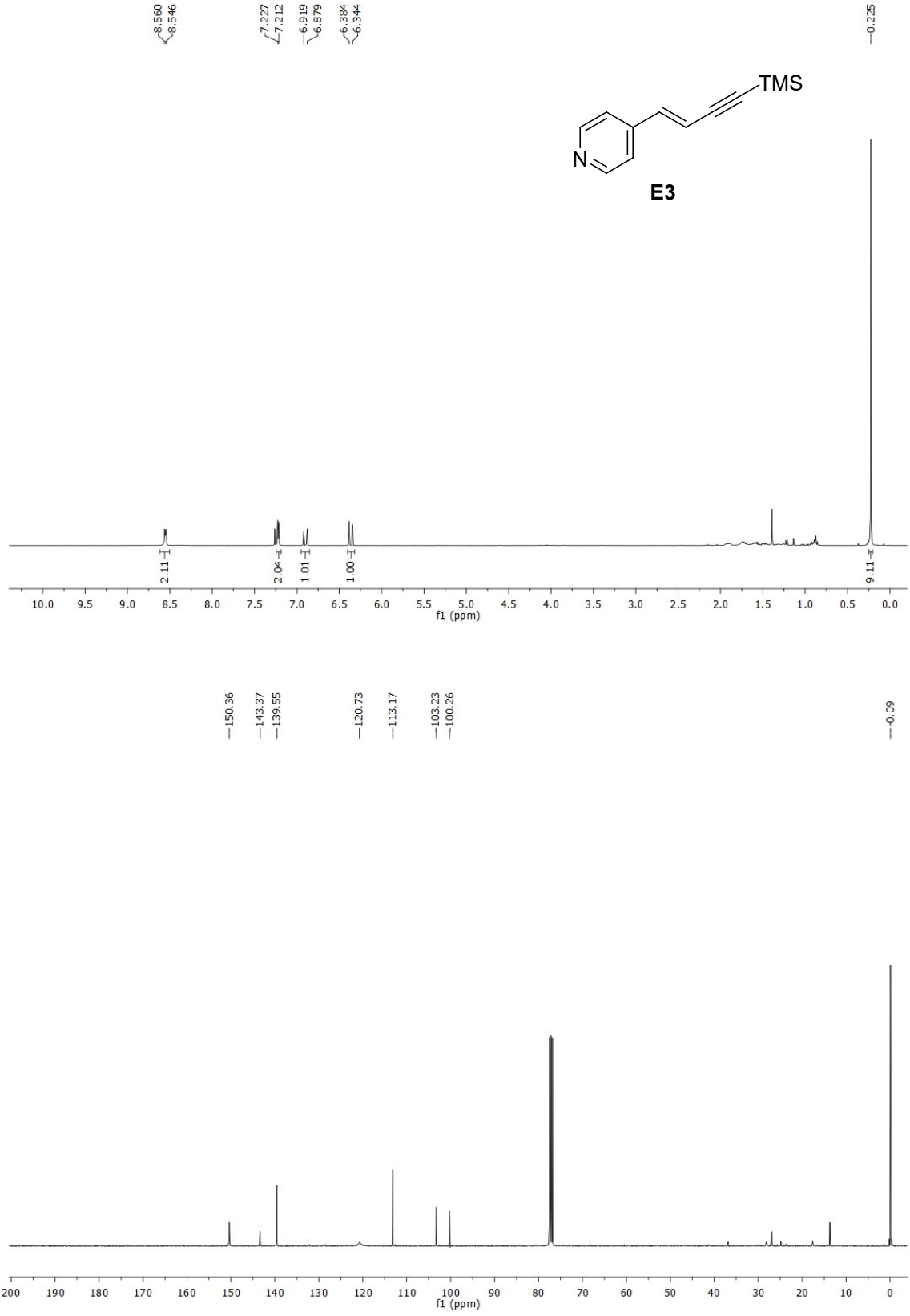


Figure S19. ^{1}H NMR and ^{13}C NMR spectra of compound **E3** in $CDCl_3$.

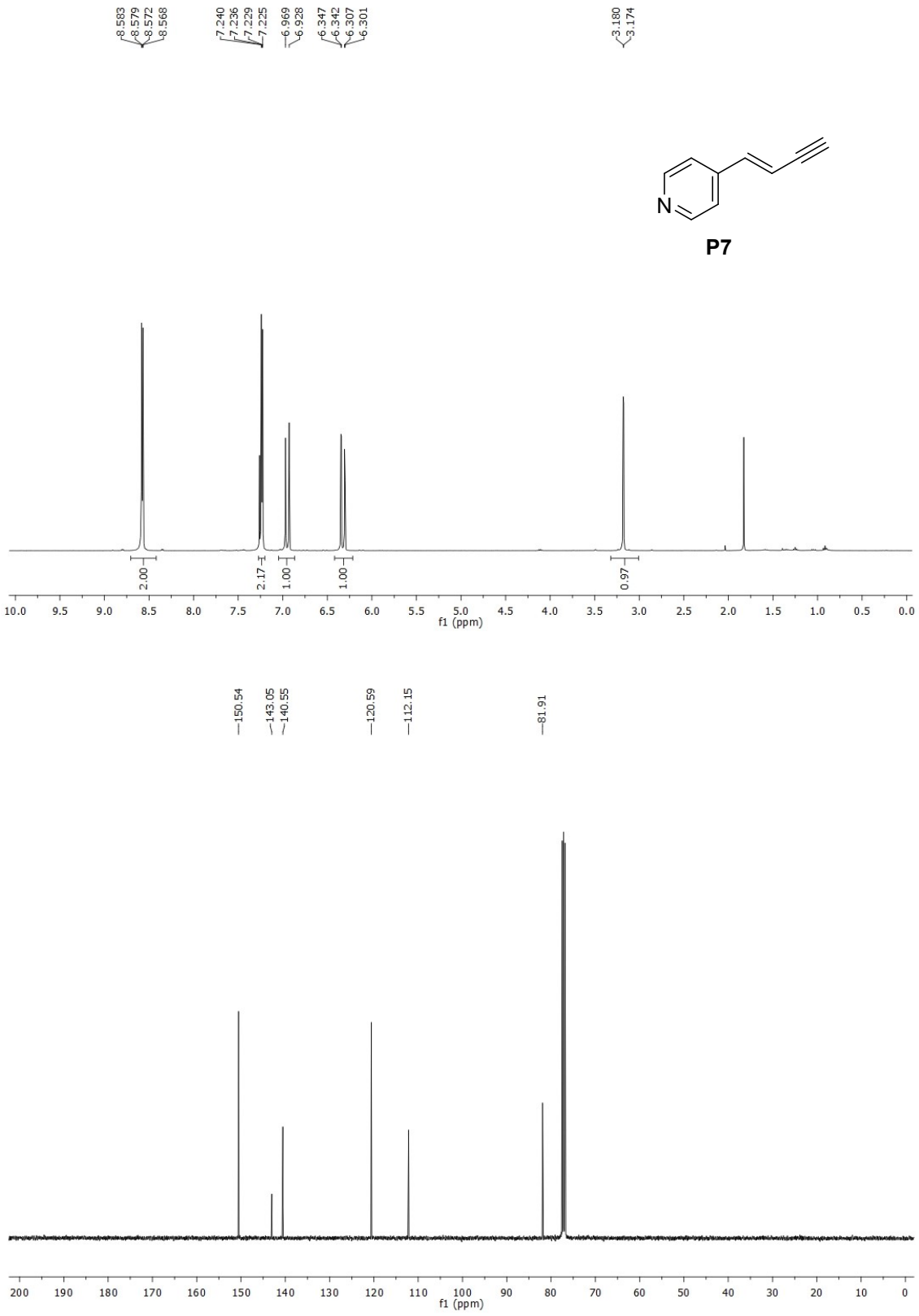


Figure S20. ^{1}H NMR and ^{13}C NMR spectra of compound **P7** in $CDCl_3$.

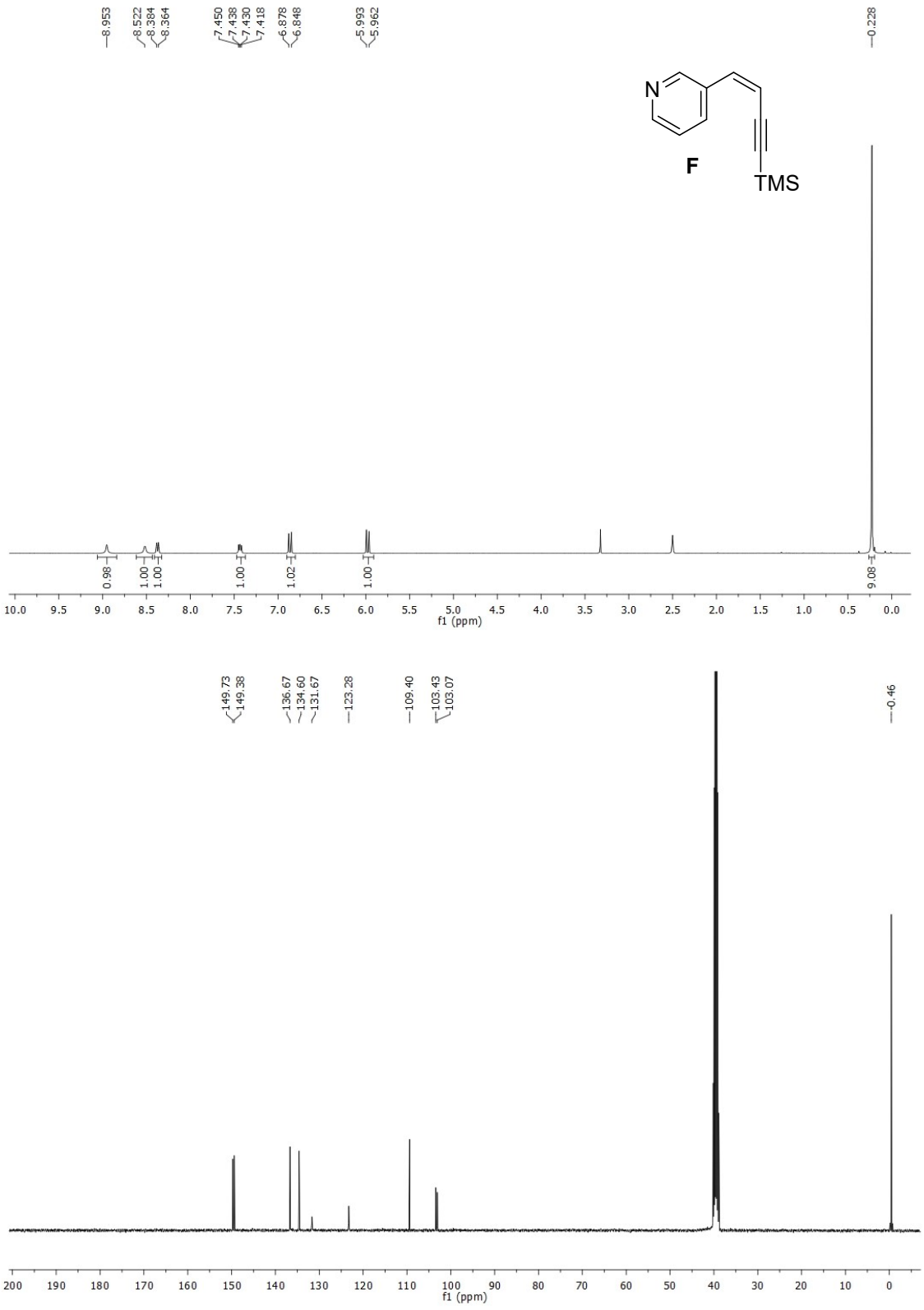


Figure S21. ^{1}H NMR and ^{13}C NMR spectra of compound **F** in DMSO.

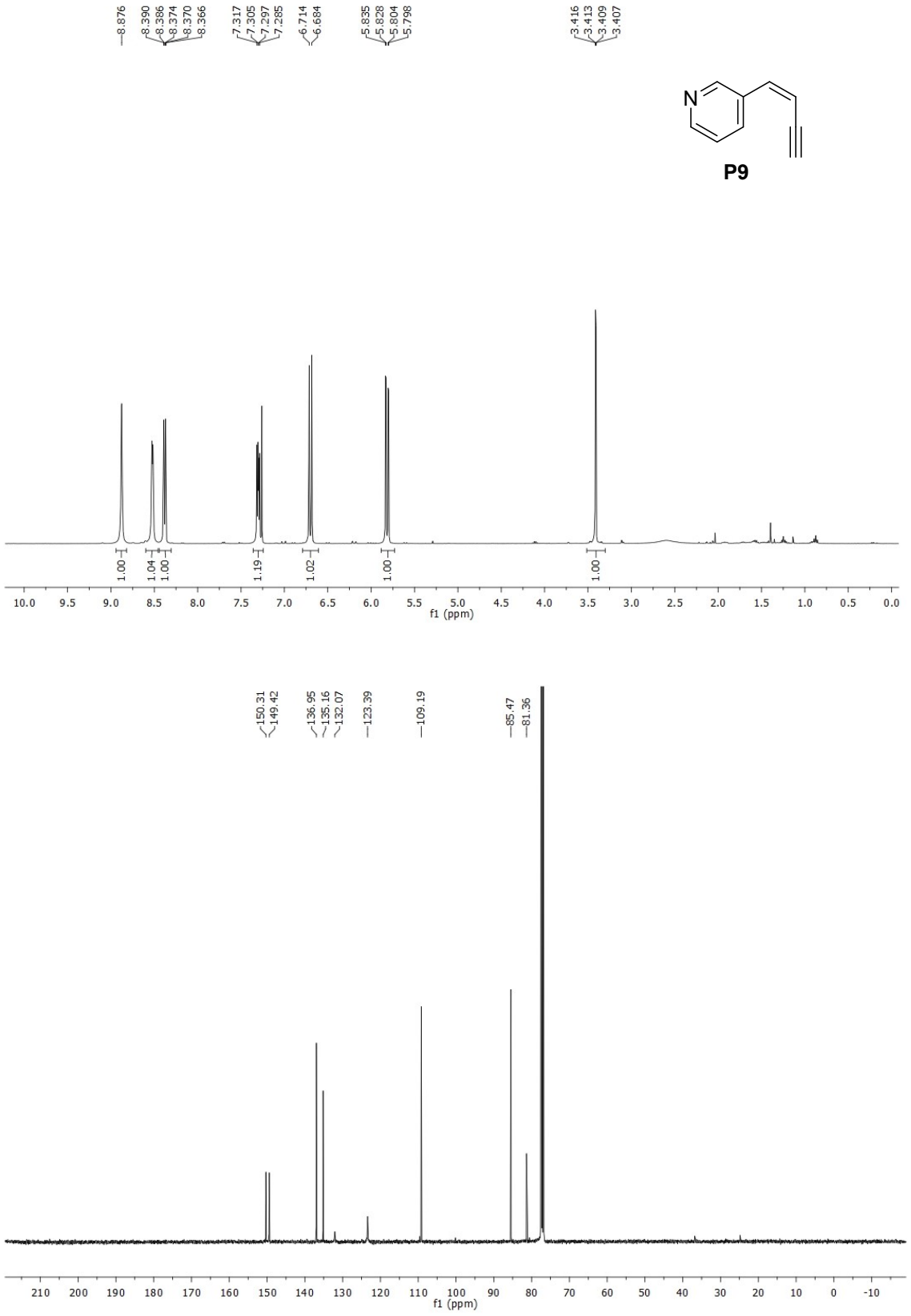


Figure S22. ^{1}H NMR and ^{13}C NMR spectra of compound **P9** in $CDCl_3$.