

Supporting Information

[3+1+1] Cyclization of Vinyl Oxiranes with Azides and CO by Tandem Palladium Catalysis: Efficient Synthesis of Oxazolidinones

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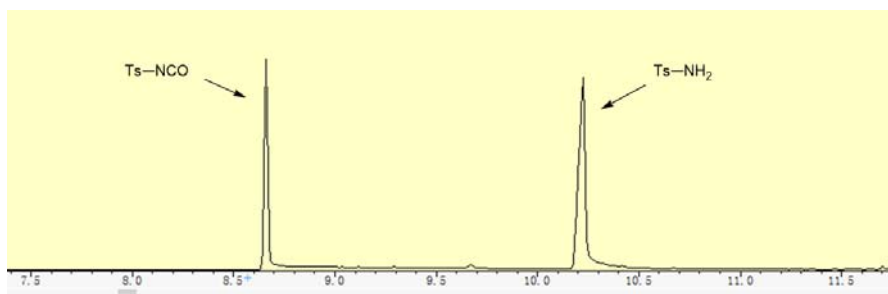
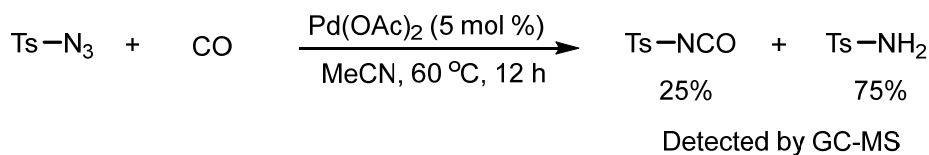
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I. General Information

All intermolecular amidation reactions were carried out under atmospheric pressure of carbon monoxide (CO) in oven-dried Schlenk tube. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference DMSO- d_6 and CDCl_3 as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of DMSO- d_6 (δ 2.50) and residual proton (δ 7.26) in CDCl_3 . Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); m (multiplet); br (broad). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of DMSO- d_6 (δ 40.00) and CDCl_3 (77.16). Materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, or other commercial suppliers and used as received unless otherwise noted. Sulfonyl azides were purchased if commercially available or prepared from sulfonyl chlorides and sodium azide according to the well-established methods.

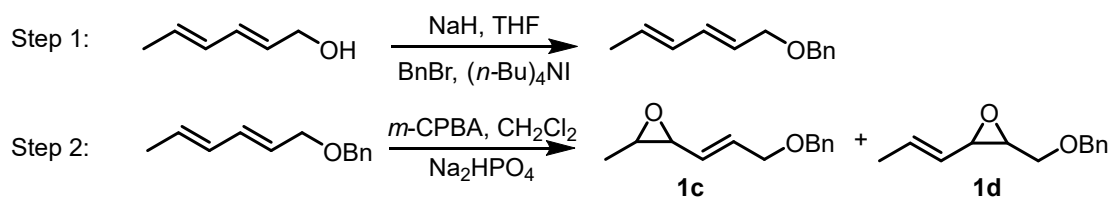
II. Mechanistic Studies



Scheme S1. Control experiments.

III. General Procedure for the Synthesis of Starting Materials

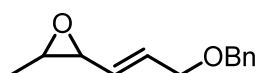
General Procedure for the Synthesis of Vinyl Oxiranes **1c** and **1d**.¹



Step 1: A 100 mL flask equipped with a stir bar containing THF (20 mL), tetrabutylammonium iodide (0.46g, 1.25 mmol) and sodium hydride (60% dispersion in mineral oil, 0.6 g, 15 mmol), and then a solution of (2*E*, 4*E*)-2,4-hexadien-1-ol (0.98 g, 10 mmol) in THF was slowly added. After 20 min, benzyl bromide (1.88 g, 11 mmol) were added. After 4 hours, the reaction was quenched with water and diluted with diethyl ether. The layers were separated, and the aqueous layer was extracted (2x) with diethyl ether. The combined organic portions were then washed with brine, dried over MgSO₄, and the solvent was removed *in vacuo*. The crude product was purified by chromatography to give the product (*E,E*)-1-benzyloxy-2,4-hexadiene as a colorless oil (1.6 g, 85%).

Step 2: To a 100 mL RBF equipped with a stir bar was added methylene chloride (20

mL), (*E,E*)-1-benzyloxy-2,4-hexadiene (0.94 g, 5 mmol), Na₂HPO₄ (1.2 g, equal mass with *m*-CPBA), and *m*-CPBA (85%, 1.2 g, 5.5 mmol). After 1 hour, the reaction was cooled to 0 °C and filtered through celite. It was then diluted with additional diethyl ether and washed with 1 M NaOH (1x), a saturated NaHCO₃ solution (2x), water, and dried over MgSO₄. The solvent was removed *in vacuo* to give a clear oil (1.0 g, 98%) that was a 1.5:1 (**1c**:**1d**) mixture of regioisomers. The regioisomeric vinyl oxiranes could be separated by column chromatography (10-20% Et₂O : 90-80% pentane).

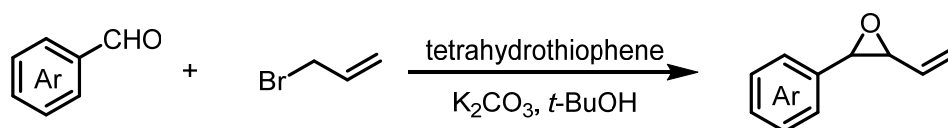


(*E*)-2-(3-(Benzyloxy)prop-1-en-1-yl)-3-methyloxirane 1c (>20:1 dr): ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 3.9 Hz, 5H), 6.02 (dt, *J* = 15.6, 5.6 Hz, 1H), 5.49 (ddt, *J* = 15.6, 7.9, 1.6 Hz, 1H), 4.51 (s, 2H), 4.03 (dd, *J* = 5.7, 1.6 Hz, 2H), 3.08 (dd, *J* = 7.9, 2.1 Hz, 1H), 2.91 (qd, *J* = 5.2, 2.2 Hz, 1H), 1.33 (d, *J* = 5.2 Hz, 3H). The other analytical data are in accordance with the literature.¹



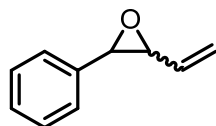
(*E*)-2-((Benzyloxy)methyl)-3-(prop-1-en-1-yl)oxirane 1d (>20:1 dr): ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.24 (m, 5H), 5.95 (dq, *J* = 15.4, 6.6 Hz, 1H), 5.21 (ddd, *J* = 15.4, 8.2, 1.7 Hz, 1H), 4.64 – 4.50 (m, 2H), 3.75 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.51 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.25 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.10 (ddd, *J* = 5.5, 3.2, 2.2 Hz, 1H), 1.74 (dd, *J* = 6.6, 1.7 Hz, 3H). The other analytical data are in accordance with the literature.¹

General Procedure for the Synthesis of Vinyl Oxiranes 1f–i.²

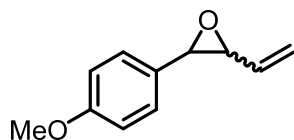


To a Schlenk tube were added tetrahydrothiophene (57 mg, 0.6 mmol), allylbromide (1.68 mL, 19.4 mmol), corresponding aromatic aldehyde (6.5 mmol), dry K₂CO₃ (powdered, 1.07 g, 7.8 mmol) and *t*-BuOH (2 mL, was distilled over sodium) under

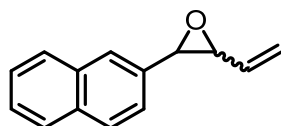
N₂ atmosphere. The resulting mixture was refluxed for 12 hours, and then filtered rapidly through a short silica gel column (ethyl acetate as the eluent). The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 200/1, v/v) on silica gel to afford the desired product.



2-Phenyl-3-vinyloxirane 1f (3:1 dr): For major: ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.12 (m, 5H), 5.63 (ddd, *J* = 17.6, 10.1, 7.8 Hz, 1H), 5.48 – 5.37 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 3.67 (s, 1H), 3.26 (d, *J* = 7.4 Hz, 1H). For minor: ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.12 (m, 5H), 5.50 – 5.39 (m, 1H), 5.36 – 5.27 (m, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 4.14 (d, *J* = 4.2 Hz, 1H), 3.56 (dd, *J* = 8.2, 4.3 Hz, 1H). The other analytical data are in accordance with the literature.²

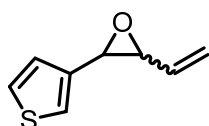


2-(4-Methoxyphenyl)-3-vinyloxirane 1g (1:1 dr): For major: ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.72 (ddd, *J* = 17.5, 10.3, 7.3 Hz, 1H), 5.57 – 5.46 (m, 1H), 5.35 – 5.19 (m, 1H), 3.79 (s, 3H), 3.71 (s, 1H), 3.35 (dd, *J* = 7.4, 1.9 Hz, 1H). For minor: ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.57 – 5.46 (m, 1H), 5.46 – 5.35 (m, 1H), 5.34 – 5.18 (m, 1H), 4.18 (d, *J* = 4.1 Hz, 1H), 3.79 (s, 3H), 3.61 (dd, *J* = 8.0, 4.1 Hz, 1H). The other analytical data are in accordance with the literature.²



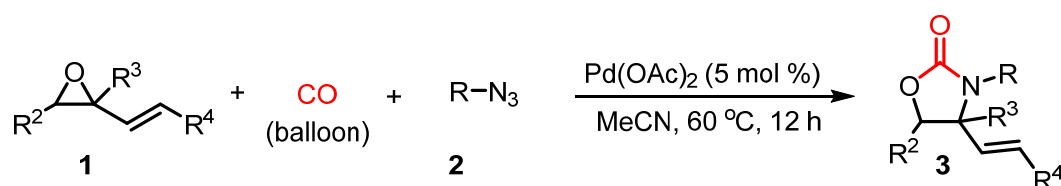
2-(Naphthalen-2-yl)-3-vinyloxirane 1h (1.8:1 dr): For major: ¹H NMR (400 MHz, CDCl₃) δ 7.85 (m, 4H), 7.51 (m, 2H), 7.38 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.92 – 5.69 (m, 1H), 5.67 – 5.54 (m, 1H), 5.40 (dd, *J* = 10.5, 2.9 Hz, 1H), 3.97 (s, 1H), 3.50 (dd, *J* =

7.7, 2.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.2, 133.4, 133.1, 132.2, 128.5, 128.0, 127.9, 126.5, 126.2, 125.1, 122.9, 119.7, 63.1, 60.6. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.85 (m, 4H), 7.51 (m, 3H), 5.67 – 5.52 (m, 1H), 5.52 – 5.43 (m, 1H), 5.28 (dd, $J = 10.3, 2.6$ Hz, 1H), 4.44 (t, $J = 3.1$ Hz, 1H), 3.80 – 3.66 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.6, 133.3, 133.1, 132.8, 128.0, 127.9, 126.4, 126.1, 125.5, 124.4, 122.1, 60.1, 59.1.



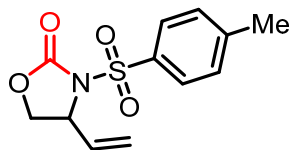
2-(Thiophen-3-yl)-3-vinyloxirane 1i (2.2:1 dr): **For major:** ^1H NMR (400 MHz, CDCl_3) δ 7.28 (dd, $J = 10.6, 3.5$ Hz, 2H), 6.98 (d, $J = 4.9$ Hz, 1H), 5.70 (dt, $J = 17.5, 8.8$ Hz, 1H), 5.52 (d, $J = 16.7$ Hz, 1H), 5.32 (t, $J = 9.7$ Hz, 1H), 3.83 (s, 1H), 3.46 (d, $J = 7.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.0, 135.1, 126.5, 125.1, 122.5, 119.7, 62.3, 57.2. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.28 (dd, $J = 10.6, 3.5$ Hz, 1H), 7.22 (s, 1H), 7.05 (d, $J = 5.1$ Hz, 1H), 5.52 (d, $J = 16.7$ Hz, 2H), 5.32 (t, $J = 9.7$ Hz, 1H), 4.23 (d, $J = 4.1$ Hz, 1H), 3.62 (dd, $J = 7.5, 4.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.8, 132.4, 126.0, 122.3, 121.9, 119.7, 59.7, 56.3.

IV. General Procedure for the Synthesis of Oxazolidinones and Characterization Data of Oxazolidinones



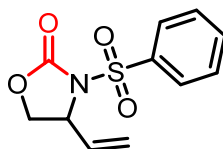
To an oven-dried Schlenk tube (10 mL) was added the organic azide **2** (0.5 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 5 mol%). The tube was purged and backfilled with CO (3 cycles) from a balloon. Anhydrous CH_3CN (3.0 mL) was injected into the tube, and then 2-vinyloxiranes **1** (0.75 mmol) was injected into the tube. After stirring at 60 °C for 12 h under CO atmosphere (balloon). The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum

ether/EtOAc 4:1~2:1) to give the desired product.



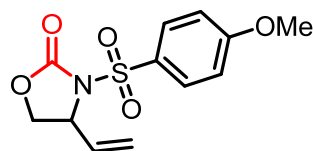
3-Tosyl-4-vinyloxazolidin-2-one 3a

Yield = 92% (123.0 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.81 (ddd, J = 16.8, 10.0, 8.4 Hz, 1H), 5.46 (d, J = 16.8 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 4.90 (td, J = 8.0, 3.6 Hz, 1H), 4.48 (t, J = 8.4 Hz, 1H), 4.03 (dd, J = 8.8, 4.0 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.9, 145.7, 135.1, 133.7, 129.8, 128.7, 120.9, 68.2, 59.7, 21.8. The other analytical data are in accordance with the literature.³



3-(Phenylsulfonyl)-4-vinyloxazolidin-2-one 3b

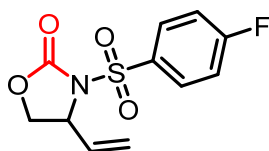
Yield = 87% (110.6 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.04 – 8.02 (m, 2H), 7.69 – 7.61 (m, 1H), 7.56 – 7.52 (m, 2H), 5.80 (ddd, J = 16.8, 10.0, 8.4 Hz, 1H), 5.46 (d, J = 17.2 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 4.92 (td, J = 8.4, 4.0 Hz, 1H), 4.49 (t, J = 8.8 Hz, 1H), 4.04 (dd, J = 8.8, 3.6 Hz, 1H). The other analytical data are in accordance with the literature.³



3-((4-Methoxyphenyl)sulfonyl)-4-vinyloxazolidin-2-one 3c

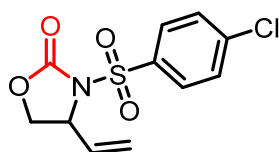
Yield = 89% (126.1 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 5.81 (ddd, J = 16.8, 10.0, 8.4 Hz, 1H), 5.46 (d, J = 16.8 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 4.89 (td, J = 8.0, 3.6 Hz, 1H), 4.47 (t, J = 8.8 Hz, 1H), 4.03 (dd, J = 8.8, 4.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ

164.4, 152.0, 133.8, 131.1, 129.4, 120.7, 114.3, 68.1, 59.7, 55.8. HRMS (ESI) calculated for C₁₂H₁₄NO₅S (M+H)⁺ 284.0587, found 284.0583.



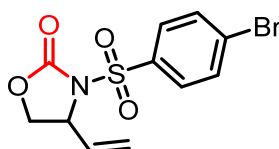
3-((4-Fluorophenyl)sulfonyl)-4-vinyloxazolidin-2-one 3d

Yield = 77% (104.5 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.04 (m, 2H), 7.24 – 7.18 (m, 2H), 5.80 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.48 (d, *J* = 16.8 Hz, 1H), 5.39 (d, *J* = 10.0 Hz, 1H), 4.92 (td, *J* = 8.4, 3.6 Hz, 1H), 4.52 (t, *J* = 8.8 Hz, 1H), 4.06 (dd, *J* = 8.8, 3.6 Hz, 1H). The other analytical data are in accordance with the literature.³



3-((4-Chlorophenyl)sulfonyl)-4-vinyloxazolidin-2-one 3e

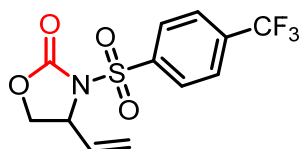
Yield = 64% (92.1 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 5.80 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.48 (d, *J* = 16.8 Hz, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 4.92 (td, *J* = 8.4, 3.6 Hz, 1H), 4.52 (t, *J* = 8.4 Hz, 1H), 4.06 (dd, *J* = 8.8, 3.6 Hz, 1H). The other analytical data are in accordance with the literature.³



3-((4-Bromophenyl)sulfonyl)-4-vinyloxazolidin-2-one 3f

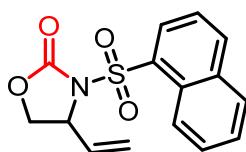
Yield = 62% (103.0 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 5.79 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.48 (d, *J* = 16.8 Hz, 1H), 5.39 (d, *J* = 10.0 Hz, 1H), 4.92 (td, *J* = 8.4, 3.6 Hz, 1H), 4.52 (t, *J* = 8.4 Hz, 1H), 4.06 (dd, *J* = 8.8, 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 137.0,

133.4, 132.5, 130.3, 129.9, 121.3, 68.3, 59.7. HRMS (ESI) calculated for $C_{11}H_{11}BrNO_4S$ ($M+H$)⁺ 331.9587, found 331.9585.



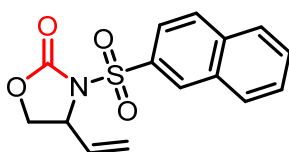
3-((4-(Trifluoromethyl)phenyl)sulfonyl)-4-vinyloxazolidin-2-one 3g

Yield = 51% (81.9 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 5.80 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.51 (d, *J* = 16.8 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 4.96 (td, *J* = 8.4, 3.6 Hz, 1H), 4.55 (t, *J* = 8.8 Hz, 1H), 4.09 (dd, *J* = 8.8, 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 141.5, 136.0 (q, *J* = 33.1 Hz), 133.2, 129.4, 126.3 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 271.5 Hz), 121.6, 68.4, 59.8. HRMS (ESI) calculated for $C_{12}H_{10}F_3NO_4SNa$ ($M+Na$)⁺ 344.0175, found 344.0167.



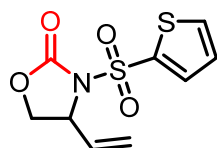
3-(Naphthalen-1-ylsulfonyl)-4-vinyloxazolidin-2-one 3h

Yield = 74% (112.2 mg). White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.64 – 7.57 (m, 2H), 5.89 (ddd, *J* = 16.8, 10.0, 8.0 Hz, 1H), 5.52 (d, *J* = 16.8 Hz, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 5.02 (td, *J* = 8.0, 4.4 Hz, 1H), 4.39 (t, *J* = 8.4 Hz, 1H), 4.02 (dd, *J* = 8.8, 4.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 136.2, 134.2, 133.9, 133.3, 132.6, 129.4, 129.0, 128.5, 127.2, 124.2, 124.0, 120.6, 67.8, 59.9. HRMS (ESI) calcd for $C_{15}H_{14}NO_4S$ ($M+H$)⁺ 304.0638, found 304.0638.



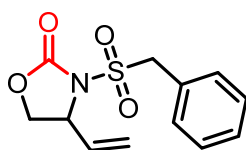
3-(Naphthalen-2-ylsulfonyl)-4-vinyloxazolidin-2-one 3i

Yield = 72% (114.3 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.61 (s, 1H), 7.99 – 7.94 (m, 3H), 7.89 (d, J = 8.0 Hz, 1H), 7.67 – 7.58 (m, 2H), 5.81 (ddd, J = 16.8, 10.0, 8.4 Hz, 1H), 5.49 (d, J = 16.8 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 4.96 (td, J = 8.4, 4.0 Hz, 1H), 4.48 (t, J = 8.8 Hz, 1H), 4.02 (dd, J = 8.8, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 135.6, 134.8, 133.7, 131.9, 130.9, 129.7, 129.4, 128.0, 127.8, 122.8, 120.9, 120.8, 68.2, 59.7. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 304.0638, found 304.0646.



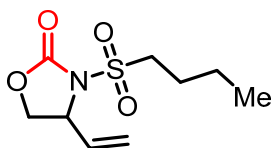
3-(Thiophen-2-ylsulfonyl)-4-vinyloxazolidin-2-one 3j

Yield = 67% (86.9 mg). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, J = 4.0, 1.6 Hz, 1H), 7.72 (dd, J = 4.8, 1.6 Hz, 1H), 7.13 (dd, J = 4.8, 4.0 Hz, 1H), 5.87 (ddd, J = 16.8, 10.0, 8.4 Hz, 1H), 5.48 (d, J = 16.8 Hz, 1H), 5.40 (d, J = 10.0 Hz, 1H), 4.90 (td, J = 8.4, 4.0 Hz, 1H), 4.50 (t, J = 8.4 Hz, 1H), 4.07 (dd, J = 8.8, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 137.7, 135.8, 134.8, 133.2, 127.7, 121.2, 68.1, 60.0. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{NO}_4\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 281.9865, found 281.9866.



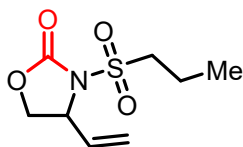
3-(Benzylsulfonyl)-4-vinyloxazolidin-2-one 3k

Yield = 77% (102.6 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.37 (m, 5H), 5.30 (ddd, J = 16.8, 10.0, 8.0 Hz, 1H), 5.17 (d, J = 16.8 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 4.74 – 4.63 (m, 2H), 4.33 – 4.26 (m, 2H), 4.00 – 3.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 133.1, 131.1, 129.6, 129.1, 127.4, 120.2, 68.5, 59.3, 58.8. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 268.0638, found 268.0635.



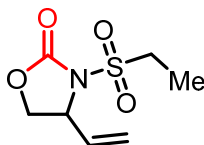
3-(Butylsulfonyl)-4-vinyloxazolidin-2-one 3l

Yield = 71% (82.9 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 5.93 (ddd, $J = 16.8, 10.0, 8.4$ Hz, 1H), 5.46 (d, $J = 16.8$ Hz, 1H), 5.39 (d, $J = 10.0$ Hz, 1H), 4.85 (td, $J = 8.4, 4.0$ Hz, 1H), 4.56 (t, $J = 8.8$ Hz, 1H), 4.13 (dd, $J = 8.8, 3.6$ Hz, 1H), 3.51 – 3.28 m, 2H), 1.85 – 1.75 (m, 2H), 1.50 – 1.40 (m, 2H), 0.93 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 133.6, 121.1, 68.5, 58.8, 53.7, 24.7, 21.4, 13.5. HRMS(ESI) calcd for $\text{C}_9\text{H}_{16}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 234.0795, found 234.0803.



3-(Propylsulfonyl)-4-vinyloxazolidin-2-one 3m

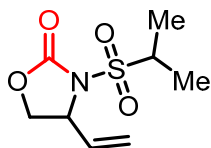
Yield = 77% (84.9 mg). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 5.93 (ddd, $J = 16.8, 10.0, 8.4$ Hz, 1H), 5.46 (d, $J = 16.8$ Hz, 1H), 5.40 (d, $J = 10.0$ Hz, 1H), 4.85 (td, $J = 8.4, 3.6$ Hz, 1H), 4.56 (t, $J = 8.8$ Hz, 1H), 4.14 (dd, $J = 8.8, 3.6$ Hz, 1H), 3.49 – 3.27 (m, 2H), 1.92 – 1.81 (m, 2H), 1.05 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 133.5, 121.2, 68.5, 58.8, 55.6, 16.6, 12.8. HRMS (ESI) calcd for $\text{C}_8\text{H}_{14}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 220.0638, found 220.0636.



3-(Ethylsulfonyl)-4-vinyloxazolidin-2-one 3n

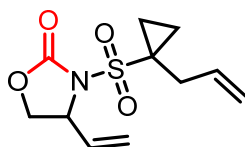
Yield = 68% (69.8 mg). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 5.94 (ddd, $J = 16.8, 10.0, 8.4$ Hz, 1H), 5.48 (d, $J = 16.8$ Hz, 1H), 5.42 (d, $J = 10.0$ Hz, 1H), 4.87 (td, $J = 8.4, 3.6$ Hz, 1H), 4.58 (t, $J = 8.8$ Hz, 1H), 4.16 (dd, $J = 8.8, 3.6$ Hz, 1H), 3.57 – 3.36 (m, 2H), 1.41 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 133.5,

121.4, 68.5, 58.9, 48.5, 7.6. HRMS (ESI) calcd for C₇H₁₁NO₄SNa (M+Na)⁺ 228.0301, found 228.0291.



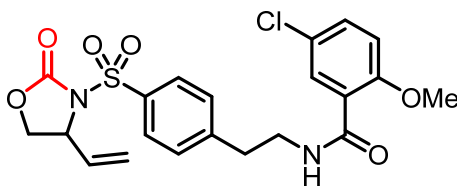
3-(Isopropylsulfonyl)-4-vinyloxazolidin-2-one 3o

Yield = 65% (71.3 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.94 (ddd, *J* = 16.8, 10.0, 8.4 Hz, 1H), 5.47 (d, *J* = 16.8 Hz, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 4.86 (td, *J* = 8.4, 4.0 Hz, 1H), 4.58 (t, *J* = 8.8 Hz, 1H), 4.16 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.87 (hept, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 133.9, 121.2, 68.5, 59.0, 54.6, 16.2, 15.9. HRMS (ESI) calcd for C₈H₁₄NO₄S (M+H)⁺ 220.0638, found 220.0629.



3-((1-Allylcyclopropyl)sulfonyl)-4-vinyloxazolidin-2-one 3p

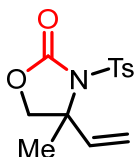
Yield = 62% (79.8 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.96 (ddd, *J* = 16.8, 10.0, 8.0 Hz, 1H), 5.79 – 5.67 (m, 1H), 5.45 (d, *J* = 16.8 Hz, 1H), 5.38 (d, *J* = 10.0 Hz, 1H), 5.18 – 5.10 (m, 2H), 4.81 (td, *J* = 8.0, 4.0 Hz, 1H), 4.53 (t, *J* = 8.4 Hz, 1H), 4.11 (dd, *J* = 8.8, 4.0 Hz, 1H), 2.80 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.52 (ddt, *J* = 15.2, 6.4, 1.6 Hz, 1H), 1.74 – 1.63 (m, 2H), 1.06 – 0.94 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 134.5, 132.6, 120.4, 119.2, 68.3, 59.4, 40.7, 34.8, 12.0, 11.9. HRMS(ESI) calcd for C₁₁H₁₆NO₄S (M+H)⁺ 258.0795, found 258.0795.



5-Chloro-2-methoxy-N-(4-((2-oxo-4-vinyloxazolidin-3-yl)sulfonyl)phenethyl)benzamide

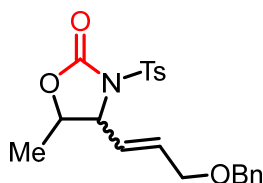
amide 3q

Yield = 77% (179.0 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 2.8$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.81 (t, $J = 5.6$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.36 (dd, $J = 8.8, 2.8$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 1H), 5.81 (ddd, $J = 16.8, 10.0, 8.4$ Hz, 1H), 5.47 (d, $J = 16.8$ Hz, 1H), 5.38 (d, $J = 10.0$ Hz, 1H), 4.91 (td, $J = 8.4, 4.0$ Hz, 1H), 4.49 (t, $J = 8.4$ Hz, 1H), 4.04 (dd, $J = 8.8, 4.0$ Hz, 1H), 3.79 (s, 3H), 3.77 – 3.70 (m, 2H), 3.01 (t, $J = 6.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 156.1, 151.8, 146.9, 136.2, 133.6, 132.5, 132.0, 129.7, 129.0, 126.8, 122.8, 121.0, 113.0, 68.2, 59.7, 56.4, 40.6, 35.8. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{22}\text{ClN}_2\text{O}_6\text{S}$ ($\text{M}+\text{H}$) $^+$ 465.0882, found 465.0872.



4-Methyl-3-tosyl-4-vinyloxazolidin-2-one 3r

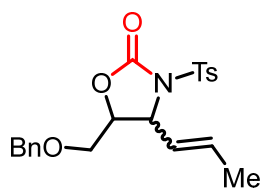
Yield = 88% (123.7 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.08 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.43 – 5.35 (m, 2H), 4.10 (d, $J = 8.8$ Hz, 1H), 3.99 (d, $J = 8.8$ Hz, 1H), 2.42 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 145.4, 138.2, 135.7, 129.5, 129.0, 117.2, 74.5, 66.1, 23.4, 21.7. The other analytical data are in accordance with the literature.⁴



(*E*)-4-(3-(Benzyloxy)prop-1-en-1-yl)-5-methyl-3-tosyloxazolidin-2-one 3s (3:1 dr)

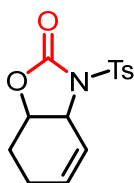
Yield = 54% (108.4 mg). White solid. **For major:** ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 2H), 7.39 – 7.30 (m, 5H), 7.26 (d, $J = 8.0$ Hz, 2H), 5.99 (dt, $J = 15.6, 4.8$ Hz, 1H), 5.71 (dd, $J = 15.6, 8.8$ Hz, 1H), 4.55 (s, 2H), 4.43 (dd, $J = 8.8, 4.4$ Hz, 1H), 4.30 – 4.24 (m, 1H), 4.06 (d, $J = 5.2$ Hz, 2H), 2.40 (s, 3H), 1.39 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 145.5, 138.0, 135.1, 133.4, 129.7, 128.6,

128.6, 127.9, 127.8, 127.0, 76.9, 72.8, 69.1, 65.5, 21.8, 19.4. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.0$ Hz, 2H), 7.39 – 7.30 (m, 5H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.81 (dd, $J = 15.6, 8.4$ Hz, 1H), 6.16 (d, $J = 15.6$ Hz, 1H), 5.53 (dd, $J = 15.6, 9.6$ Hz, 1H), 5.25 – 5.17 (m, 2H), 4.81 (dt, $J = 40.8, 6.8$ Hz, 2H), 2.37 (s, 3H), 1.25 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 141.5, 135.2, 129.9, 129.6, 128.9, 128.8, 128.6, 127.7, 125.5, 123.2, 75.9, 75.4, 66.9, 64.1, 63.4, 15.3. The other analytical data are in accordance with the literature.⁵



(E)-5-((Benzyloxy)methyl)-4-(prop-1-en-1-yl)-3-tosyloxazolidin-2-one 3t (1.8:1 dr)

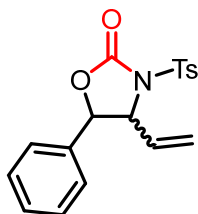
Yield = 57% (114.4 mg). White solid. **For major:** ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.36 – 7.23 (m, 7H), 5.88 (dq, $J = 13.6, 6.4$ Hz, 1H), 5.43 (dd, $J = 15.2, 8.4$ Hz, 1H), 4.77 – 4.70 (m, 1H), 4.52 – 4.43 (m, 2H), 4.22 – 4.20 (m, 1H), 3.59 – 3.47 (m, 2H), 2.39 (s, 3H), 1.73 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.6, 145.3, 137.2, 135.4, 134.5, 132.5, 129.5, 128.6, 128.5, 127.8, 122.5, 78.9, 73.6, 68.7, 61.1, 21.7, 17.7. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.36 – 7.23 (m, 7H), 5.88 (dq, $J = 13.6, 6.4$ Hz, 1H), 5.17 (dd, $J = 14.0, 9.6$ Hz, 1H), 4.92 – 4.87 (m, 1H), 4.77 – 4.70 (m, 1H), 4.52 – 4.43 (m, 2H), 3.59 – 3.47 (m, 2H), 2.42 (s, 3H), 1.69 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.3, 145.4, 137.3, 135.5, 129.5, 128.8, 128.5, 128.0, 128.0, 127.7, 127.3, 79.0, 73.6, 67.5, 62.1, 55.6, 17.7, 13.2. HRMS(ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$)⁺ 402.1370, found 402.1362.



3-Tosyl-3a,6,7,7a-tetrahydrobenzo[d]oxazol-2(3H)-one 3u

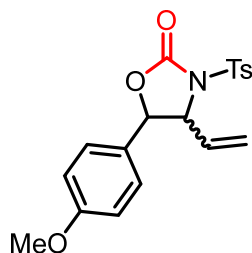
Yield = 62% (90.9 mg). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.4$

Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 6.11 – 6.05 (m, 1H), 5.98 – 5.93 (m, 1H), 4.88 – 4.80 (m, 2H), 2.43 (s, 3H), 2.20 – 2.13 (m, 2H), 2.03 – 1.96 (m, 1H), 1.81 – 1.72 (m, 1H). The other analytical data are in accordance with the literature.⁴



5-Phenyl-3-tosyl-4-vinylloxazolidin-2-one 3v (2.6:1 dr)

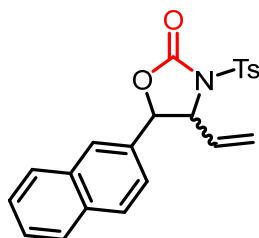
Yield = 71% (121.9 mg). White solid. **For major:** ¹H NMR (400 MHz, CDCl₃) 7.90 (d, $J = 8.0$ Hz, 2H), 7.39 – 7.32 (m, 5H), 7.22 – 7.17 (m, 2H), 5.96 (ddd, $J = 17.6, 10.0, 8.4$ Hz, 1H), 5.46 – 5.41 (m, 1H), 5.23 – 5.09 (m, 2H), 4.69 (dd, $J = 8.4, 4.8$ Hz, 1H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.6, 145.7, 136.5, 134.9, 133.7, 129.8, 129.2, 128.6, 126.0, 125.4, 121.1, 80.7, 67.3, 21.8. **For minor:** ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.39 – 7.32 (m, 5H), 7.22 – 7.17 (m, 2H), 5.75 (d, $J = 7.2$ Hz, 1H), 5.46 – 5.41 (m, 2H), 5.23 – 5.09 (m, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.5, 145.7, 135.1, 132.6, 130.5, 129.7, 129.6, 129.0, 128.7, 122.0, 19.8, 64.6, 21.8. The other analytical data are in accordance with the literature.⁶



5-(4-Methoxyphenyl)-3-tosyl-4-vinylloxazolidin-2-one 3w (2.6:1 dr)

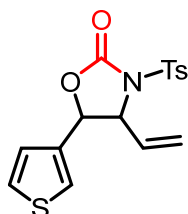
Yield = 75% (140.0 mg). White solid. **For major:** ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 5.93 (ddd, $J = 17.6, 10.0, 8.0$ Hz, 1H), 5.43 – 5.37 (m, 1H), 5.26 – 5.22 (m, 1H), 5.04 (d, $J = 4.8$ Hz, 1H), 4.67 (dd, $J = 8.4, 4.8$ Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 151.6, 145.7, 135.0, 133.8, 129.8, 128.6, 127.2, 121.0, 114.6, 114.1, 80.9, 67.3, 55.5, 21.8. **For minor:** ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 2H), 6.85 (d, J

= 8.8 Hz, 2H), 5.69 (d, $J = 7.2$ Hz, 1H), 5.43 – 5.37 (m, 2H), 5.14 – 5.11 (m, 1H), 4.95 – 4.90 (m, 1H), 3.78 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 151.6, 145.6, 135.2, 130.7, 129.7, 129.0, 128.2, 127.6, 124.5, 121.8, 79.8, 64.8, 55.4, 21.8. HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$) $^+$ 374.1057, found 374.1056.



5-(Naphthalen-2-yl)-3-tosyl-4-vinyloxazolidin-2-one 3x (2.5:1 dr)

Yield = 74% (145.6 mg). White solid. **For major:** ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.78 (m, 4H), 7.75 – 7.71 (m, 1H), 7.61 (s, 1H), 7.53 – 7.51 (m, 2H), 7.26 – 7.18 (m, 3H), 6.07 – 5.98 (m, 1H), 5.48 – 5.44 (m, 1H), 5.29 – 5.20 (m, 2H), 4.76 (dd, $J = 7.2$, 4.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 145.7, 134.8, 133.8, 133.7, 133.5, 132.9, 129.8, 129.5, 128.5, 128.2, 127.6, 127.1, 127.0, 125.0, 122.2, 121.0, 80.9, 67.3, 21.8. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.95 (m, 1H), 7.87 – 7.78 (m, 4H), 7.53 – 7.51 (m, 2H), 7.33 – 7.30 (m, 1H), 7.26 – 7.18 (m, 3H), 5.90 – 5.88 (m, 1H), 5.49 – 5.44 (m, 2H), 5.29 – 5.20 (m, 1H), 5.05 – 5.26 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 145.7, 135.1, 133.3, 132.9, 130.4, 130.0, 129.7, 129.0, 128.6, 128.1, 127.8, 126.8, 126.8, 125.4, 123.3, 79.8, 64.6. HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 394.1108, found 394.1096.



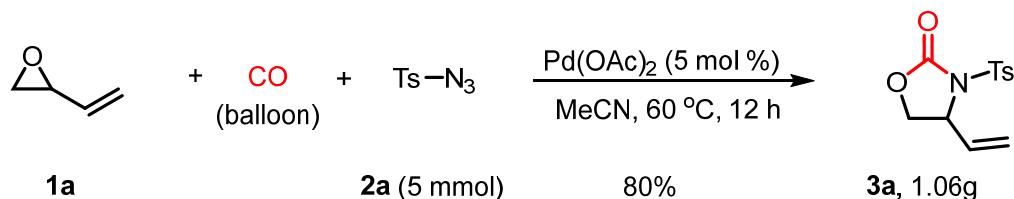
5-(Thiophen-3-yl)-3-tosyl-4-vinyloxazolidin-2-one 3y (2.0:1 dr)

Yield = 54% (94.3 mg). Yellow oil. **For major:** ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$, 2H), 7.38 – 7.32 (m, 3H), 7.22 – 7.09 (m, 1H), 6.99 – 83 (m, 1H), 5.98 – 5.88 (m, 1H), 5.49 – 5.28 (m, 2H), 5.23 – 5.16 (m, 1H), 4.81 – 4.67 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 145.8, 137.3, 134.9, 133.5, 129.8, 128.1, 125.4, 124.4, 123.6, 121.2, 77.5, 66.6, 21.8. **For minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$, 2H), 7.49 – 7.47 (m, 1H), 7.38 – 7.32 (m, 2H), 7.22 – 7.10 (m, 1H), 6.99 –

6.83 (m, 1H), 5.80 – 5.78 (m, 1H), 5.49 – 5.29 (m, 2H), 5.23 – 5.16 (m, 1H), 5.10 – 5.07 (m, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 145.7, 135.1, 133.6, 130.5, 129.7, 129.0, 127.0, 125.4, 123.4, 122.1, 77.3, 64.3, 21.8. HRMS(ESI) calcd for C₁₆H₁₅NO₄S₂Na (M+Na)⁺ 372.0335, found 372.0331.

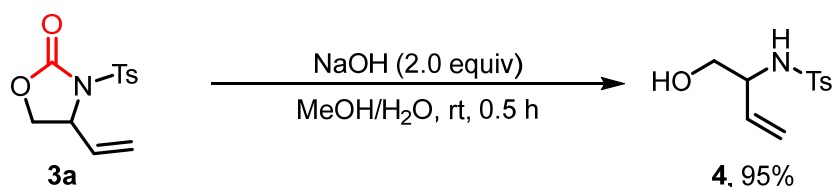
V. Synthetic Applications

Scale-up reaction



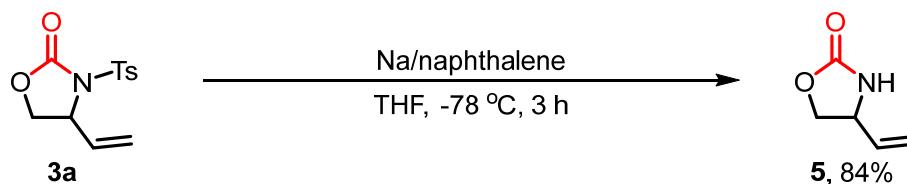
To an oven-dried Schlenk tube (50 mL) was added the organic azide **2a** (5 mmol, 0.99 g), Pd(OAc)₂ (56 mg, 5 mol %). The tube was purged and backfilled with CO (3 cycles) from a balloon. Anhydrous CH₃CN (5.0 mL) was injected into the tube, and then 2-vinyloxiranes **1a** (7.5 mmol, 0.53 g) was injected into the tube. After stirring at 60 °C for 12 h under CO atmosphere (balloon). The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 4:1~2:1) to give the desired product **3a** in 80% yield (1.06 g).

Derivatization of Oxazolidinones **3a**

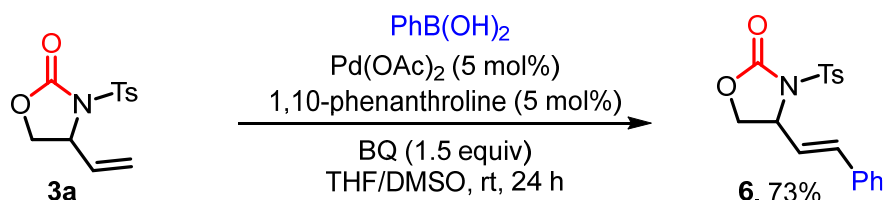


To an oven-dried Schlenk tube (10 mL) was added the **3a** (133.7 mg, 0.5 mmol), NaOH (40.0 mg, 1.0 mmol), and MeOH/H₂O (4/1, 3.0 mL). After stirring at 25 °C for 0.5 h. The mixture was extracted with EtOAc (3x10 mL), and the organic extracts were combined, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 3:1) to give the desired product **4** in 95% yield (120.7 mg) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.76 (d, *J* = 7.6 Hz, 1H), 5.59 (ddd, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.09 – 5.02 (m, 2H), 3.87 (brs, 1H), 3.63 – 3.52 (m, 2H), 3.00 (brs, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 137.5, 134.4, 129.7, 127.3, 117.9, 64.8, 57.9, 21.6. The other analytical data are in

accordance with the literature.⁷



To a stirred solution of naphthalene (0.65 g, 5 mmol) in THF (10 mL) was added sodium (0.175g, 7.5 mmol) at room temperature, and the mixture was stirred for 1h to give a deep green solution of sodium naphthalenide. To a stirred solution of **3a** (133.7 mg, 0.5 mmol) in THF (3 mL) was added the sodium naphthalenide solution (4 mL) at $-78\text{ }^\circ\text{C}$, and the mixture was stirred for 3 h at $-78\text{ }^\circ\text{C}$. Saturated aqueous NaHCO_3 was added to quench the reaction, and the mixture was extracted with EtOAc. And the organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 1:1) to give the desired product **5** in 84% yield (47.5 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 6.43 (brs, 1H), 5.80 (ddd, $J = 16.8, 10.0, 7.2$ Hz, 1H), 5.32 – 5.21 (m, 2H), 4.52 (t, $J = 8.4$ Hz, 1H), 4.40 – 4.34 (m, 1H), 4.04 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 135.8, 118.7, 70.1, 55.3. The other analytical data are in accordance with the literature.⁸



To an oven-dried Schlenk tube (10 mL) was added the **3a** (133.7 mg, 0.5 mmol), PhB(OH)_2 (91.4 mg, 0.75 mmol), Pd(OAc)_2 (5.6 mg, 5 mol%), 1,10-phenanthroline (4.5 mg, 5 mol%), benzoquinone (54.1 mg, 0.75 mmol) and THF/DMSO (1:1, 3.0 mL). After stirring at room temperature for 24 h. The mixture was washed with a solution of 1 M NaOH, and extracted with EtOAc. The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the desired product **6** in 73% yield (125.3 mg) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.0$ Hz, 2H), 7.36 – 7.30 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.76 (d, $J = 15.6$ Hz, 1H), 6.02 – 5.95 (m, 1H), 5.12 – 5.07 (m, 1H), 4.56 (t, $J = 8.4$ Hz, 1H), 4.14 – 4.10 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 145.6,

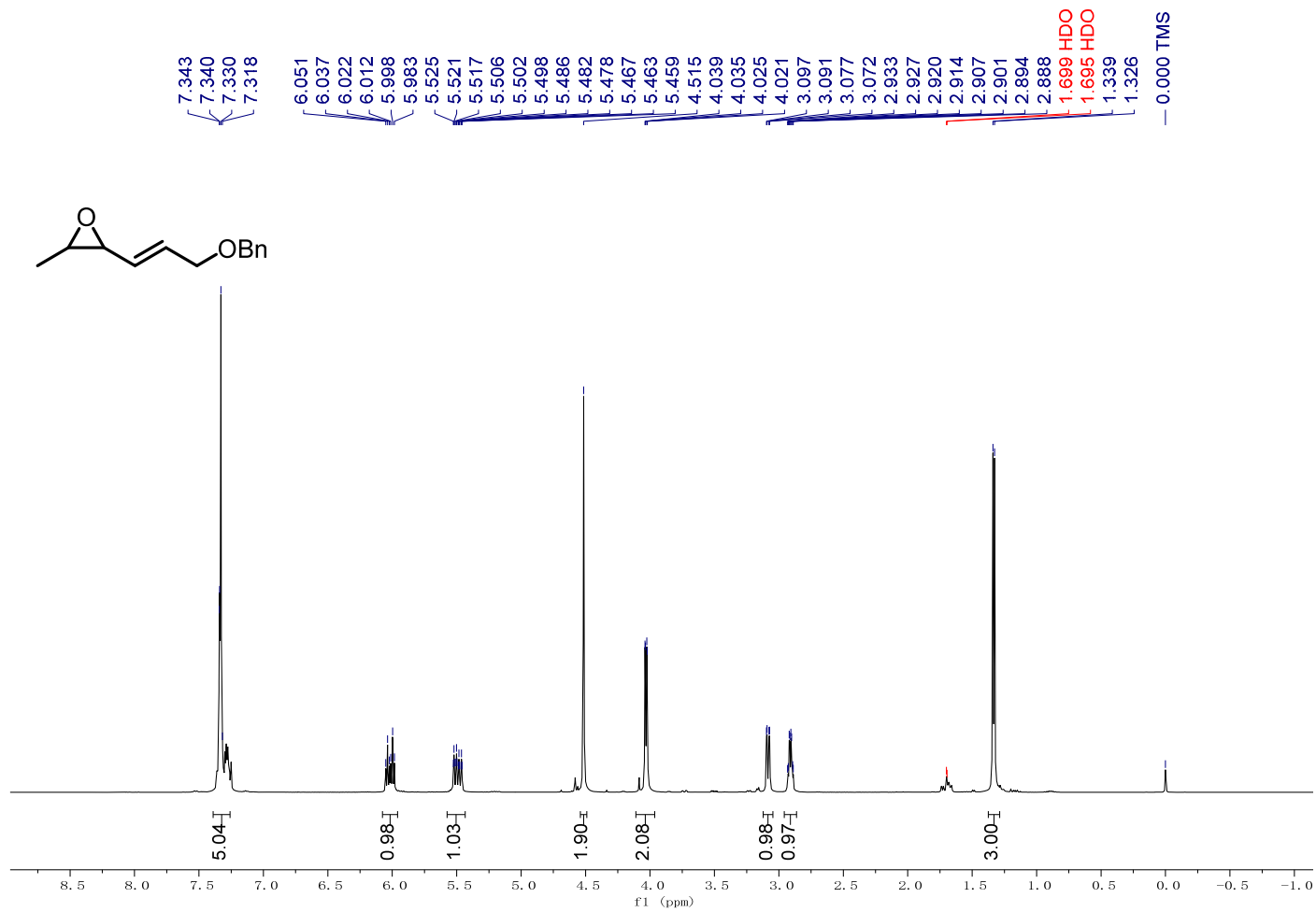
136.2, 135.3, 135.1, 129.7, 129.1, 128.9, 128.9, 127.0, 123.7, 68.4, 59.8, 21.8. The other analytical data are in accordance with the literature.⁷

Reference:

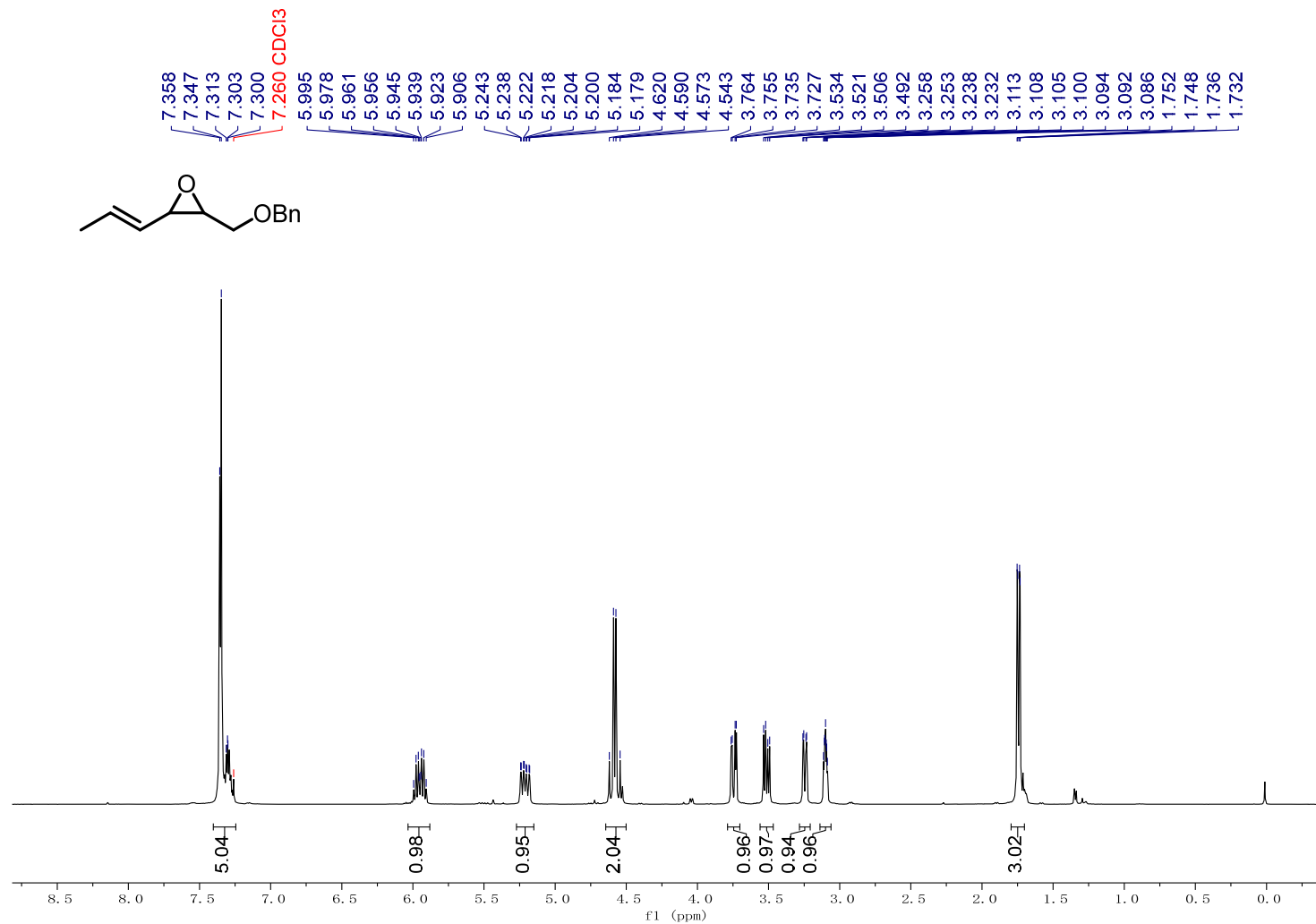
1. Brichacek, M., Batory, L. and Njardarson, J. *Angew. Chem. Int. Ed.* **2010**, 49, 1648-1651.
2. Li, K.; Deng, X.-M. and Tang, Y. *Chem. Commun.* **2003**, 2074-2075.
3. Overman, L. E. and Remarchuk, T. P. *J. Am. Chem. Soc.* **2002**, 124, 12-13.
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5. Olofsson, B. and Somfai, P. *J. Org. Chem.* **2002**, 67, 8574-8583.
6. Xu, D. and Sharpless, K. B. *Tetrahedron Lett.* **1993**, 34, 951-952.
7. Joosten, A.; Persson, A. K. A.; Millet, R.; Johnson, M. T. and Backvall, J. *Chem. Eur. J.* **2012**, 18, 15151-15157.
8. Derrien, N.; Sharley, J. S.; Rubtsov, A. E. and Malkov, A. V. *Org. Lett.* **2017**, 19, 234-237.

VI. Copy of NMR Spectra

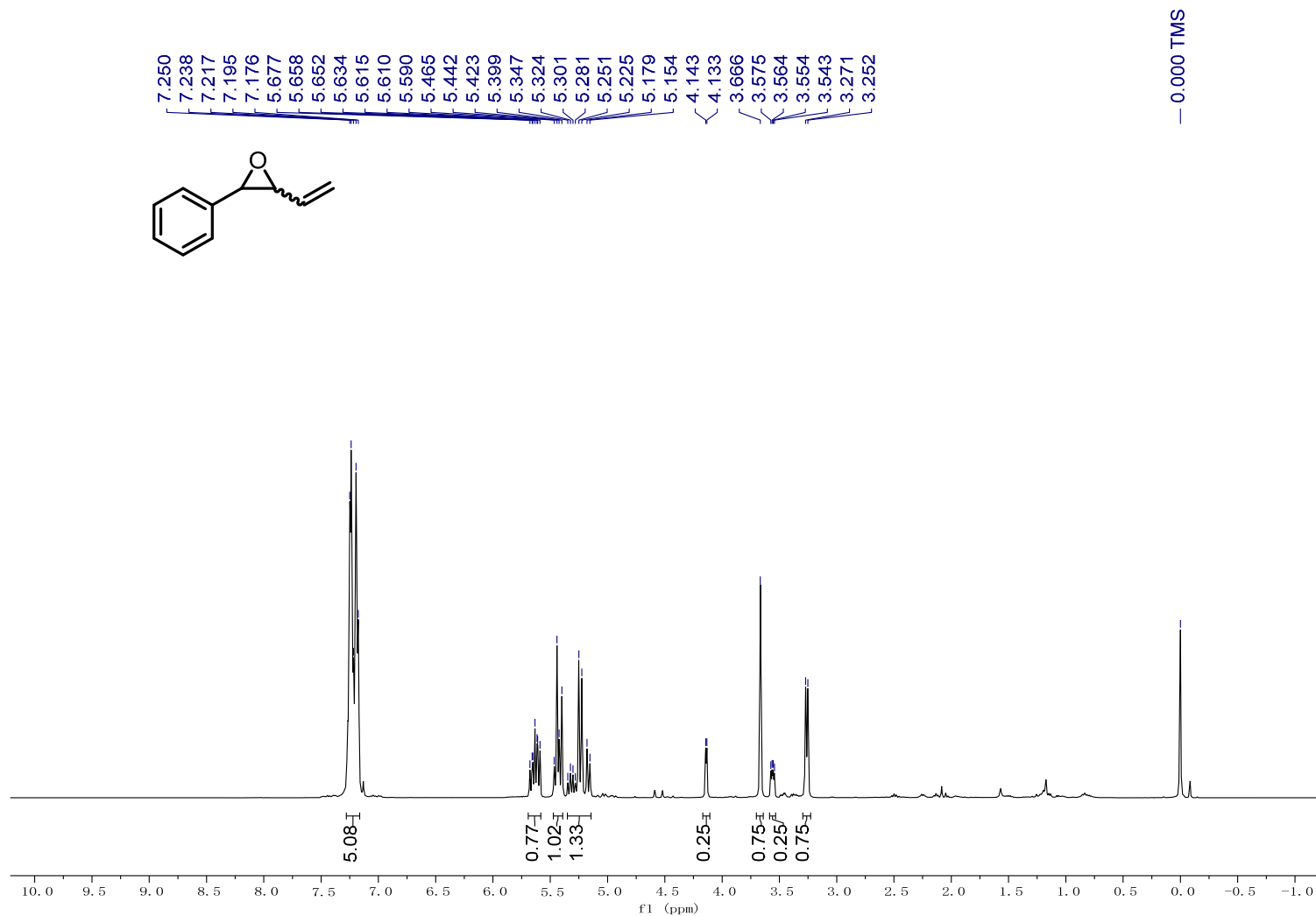
^1H NMR (400 MHz, CDCl_3) Spectrum of (*E*)-2-(3-(benzyloxy)prop-1-en-1-yl)-3-methyloxirane **1c**



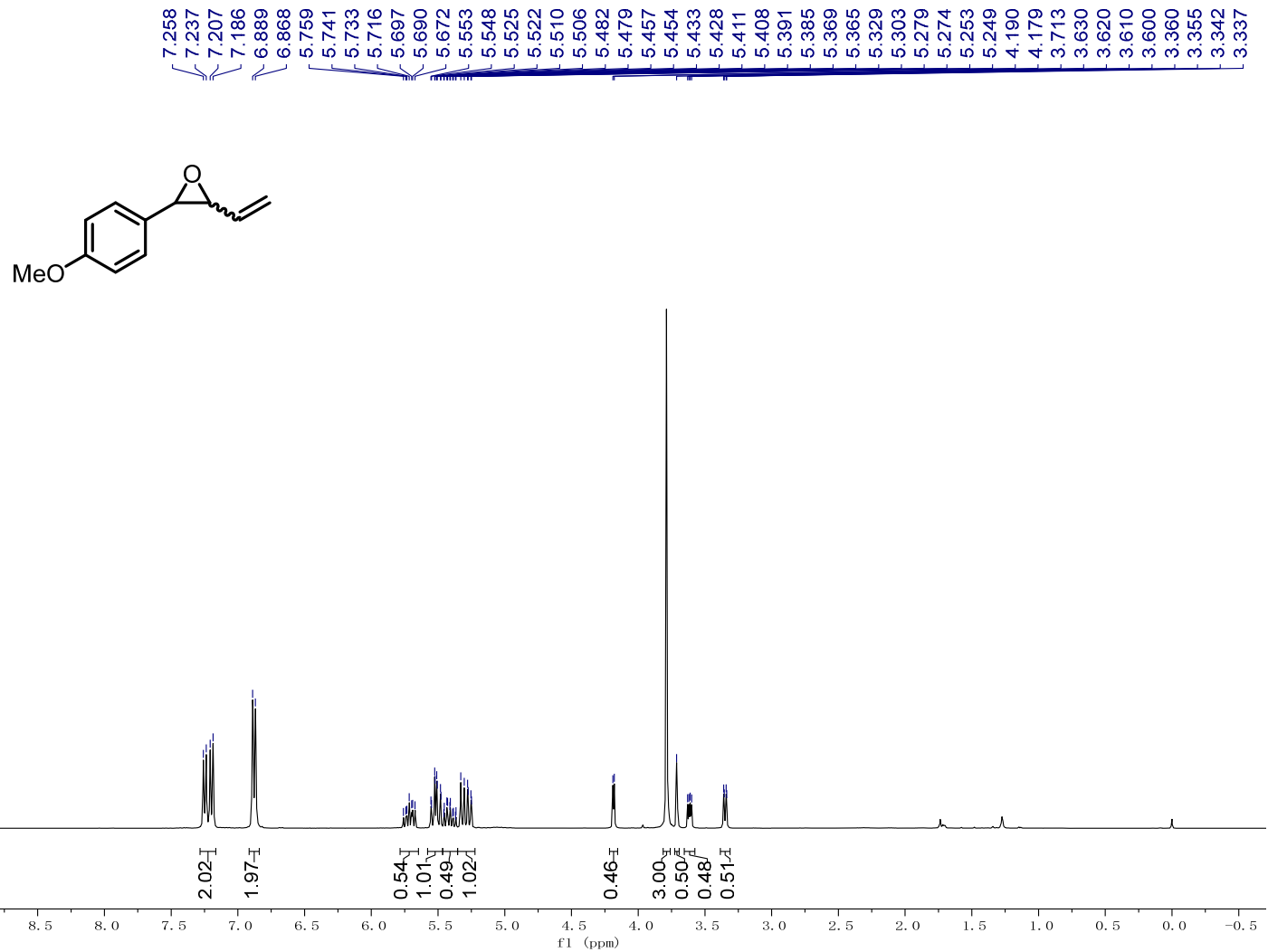
¹H NMR (400 MHz, CDCl₃) Spectrum of (*E*)-2-((benzyloxy)methyl)-3-(prop-1-en-1-yl)oxirane 1d



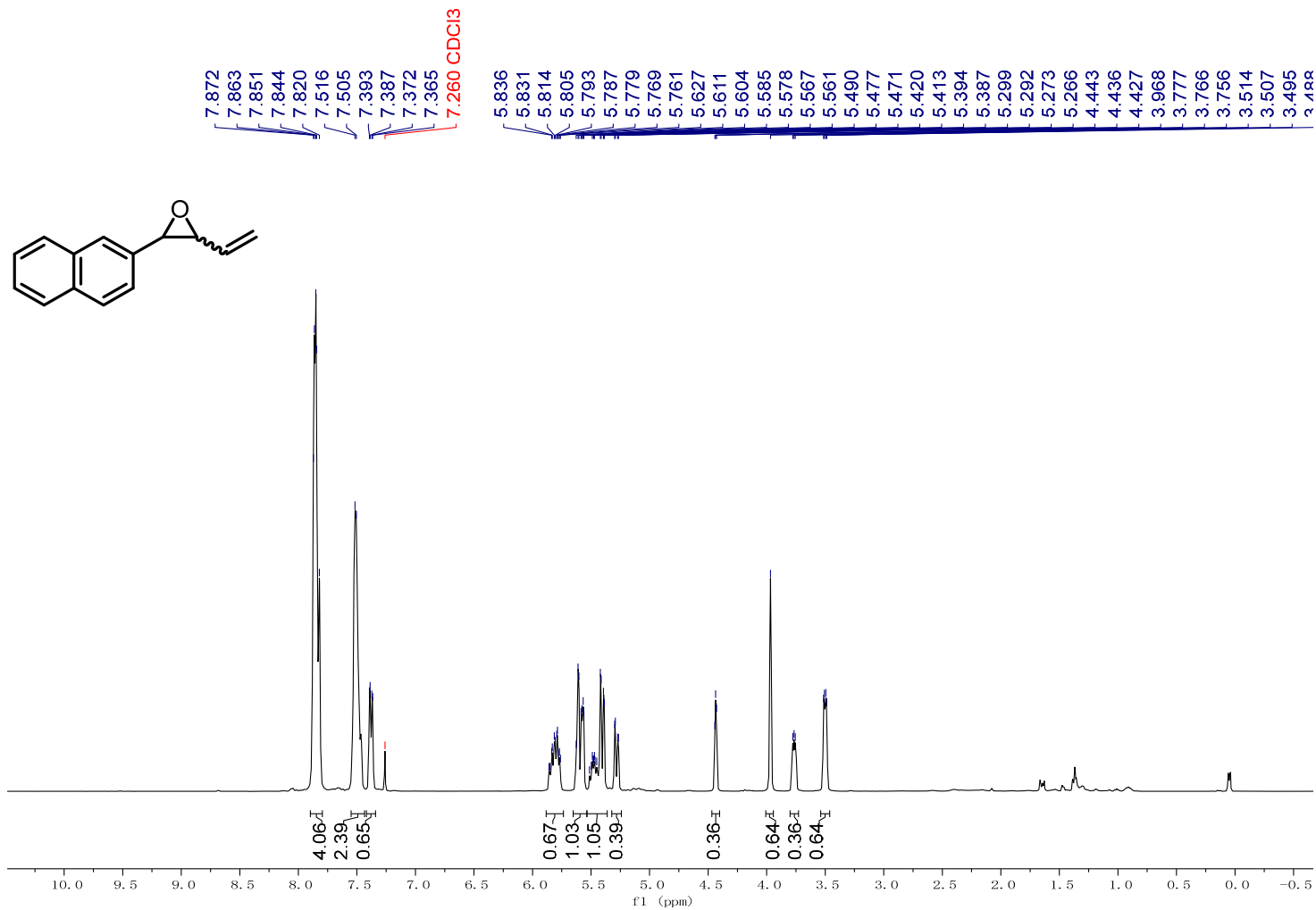
¹H NMR (400 MHz, CDCl₃) Spectrum of 2-phenyl-3-vinylloxirane 1f



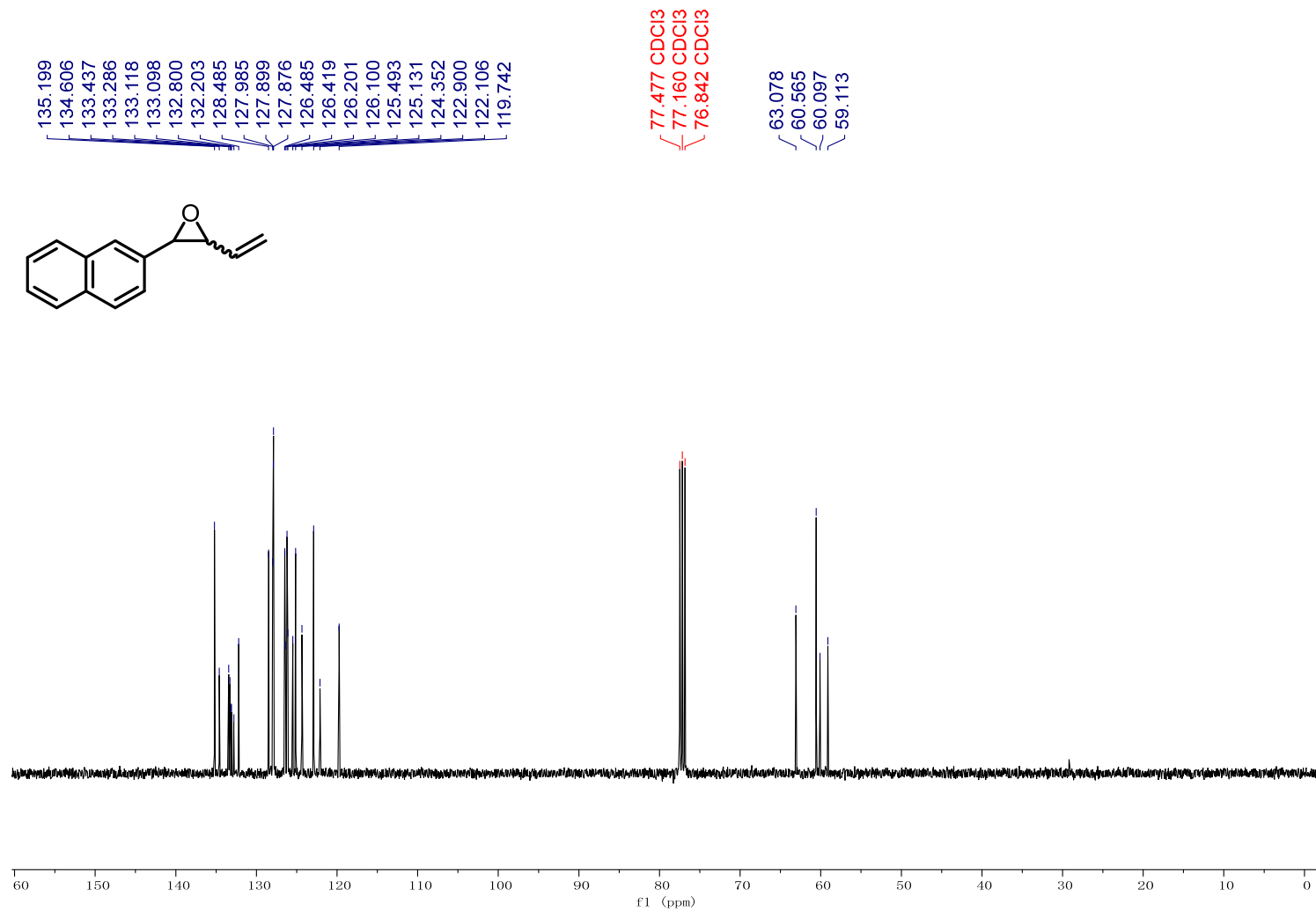
¹H NMR (400 MHz, CDCl₃) Spectrum of 2-(4-methoxyphenyl)-3-vinylloxirane 1g



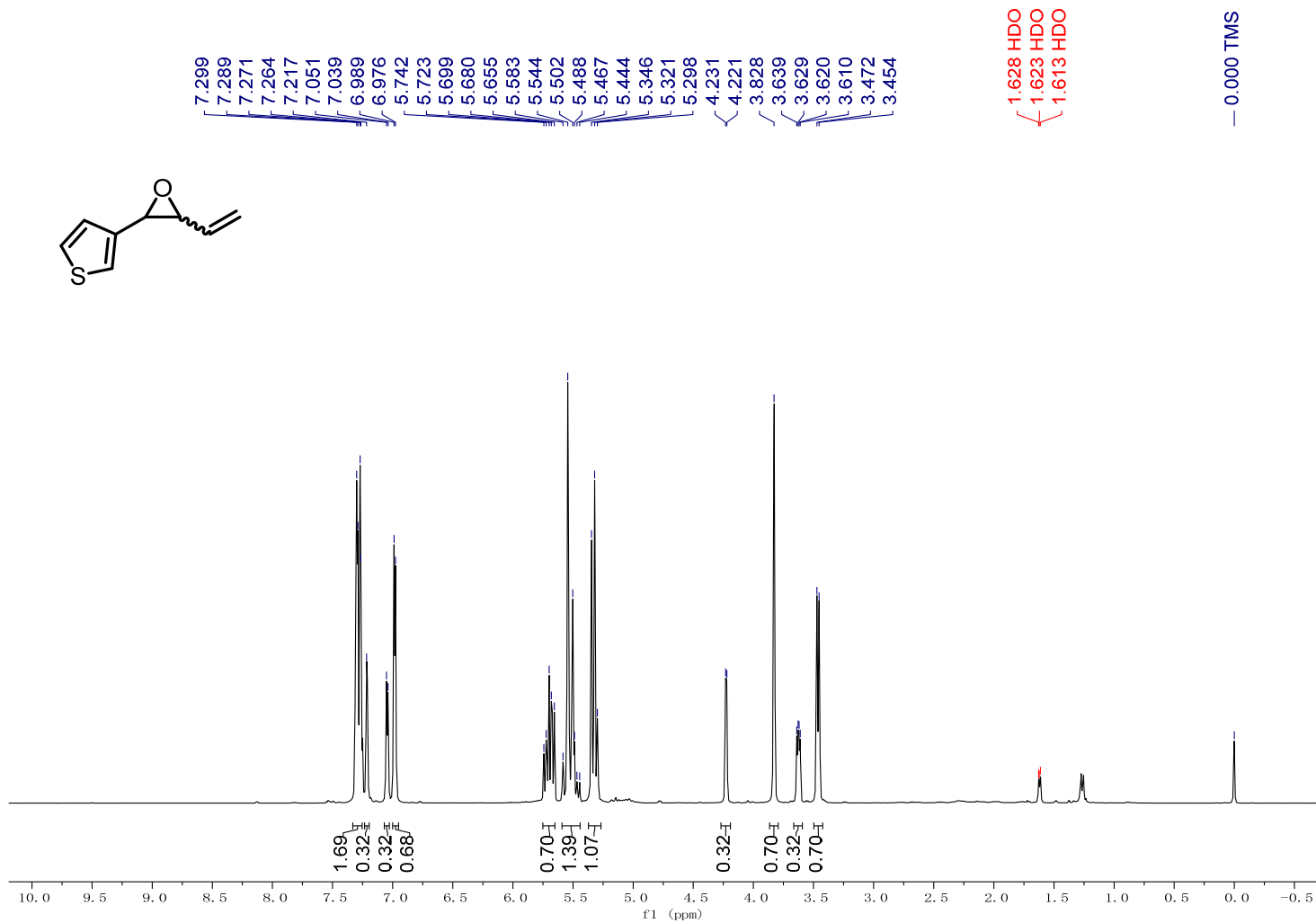
¹H NMR (400 MHz, CDCl₃) Spectrum of 2-(naphthalen-2-yl)-3-vinylloxirane 1h



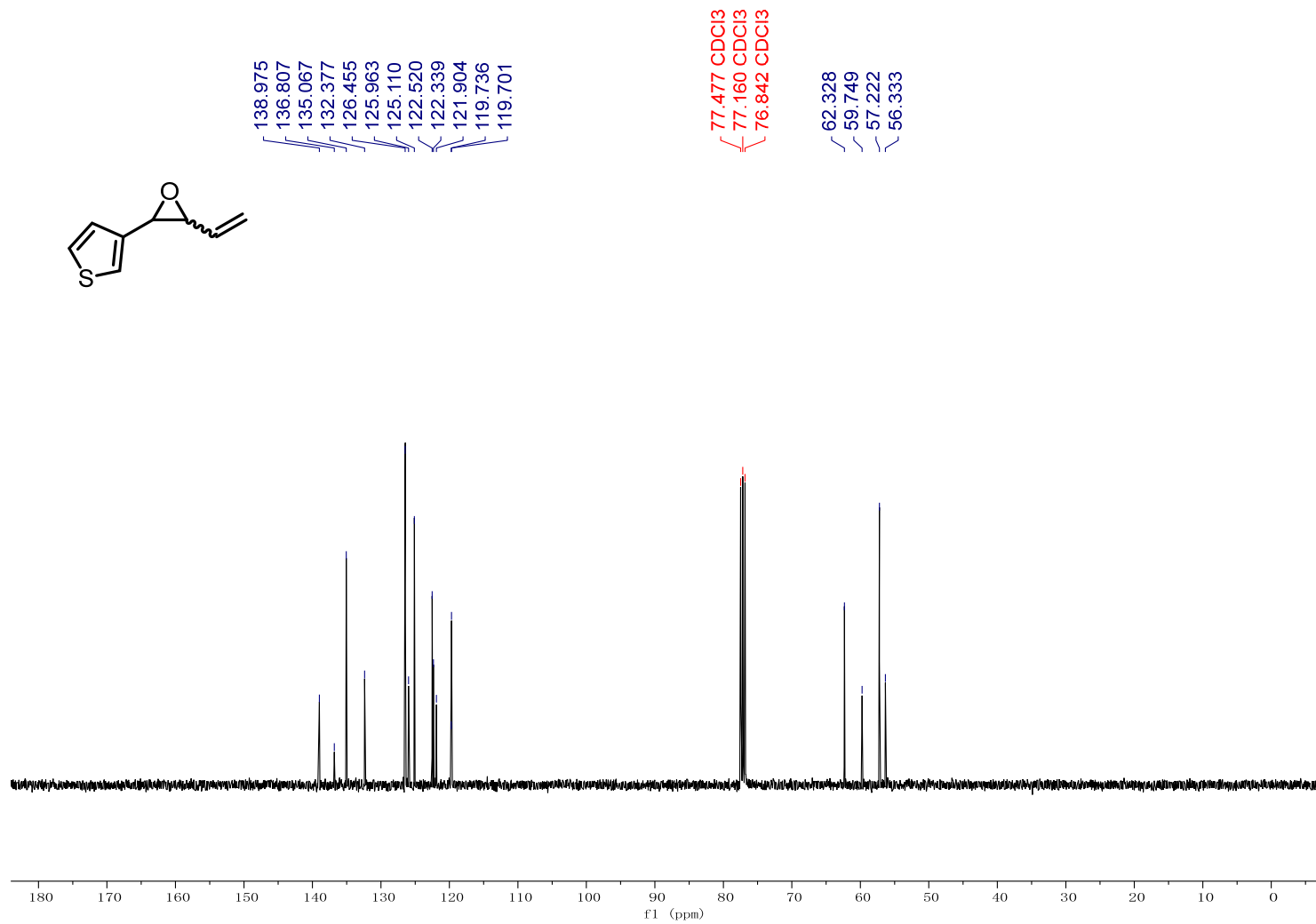
¹³C NMR (100 MHz, CDCl₃) Spectrum of 2-(naphthalen-2-yl)-3-vinyloxirane 1h



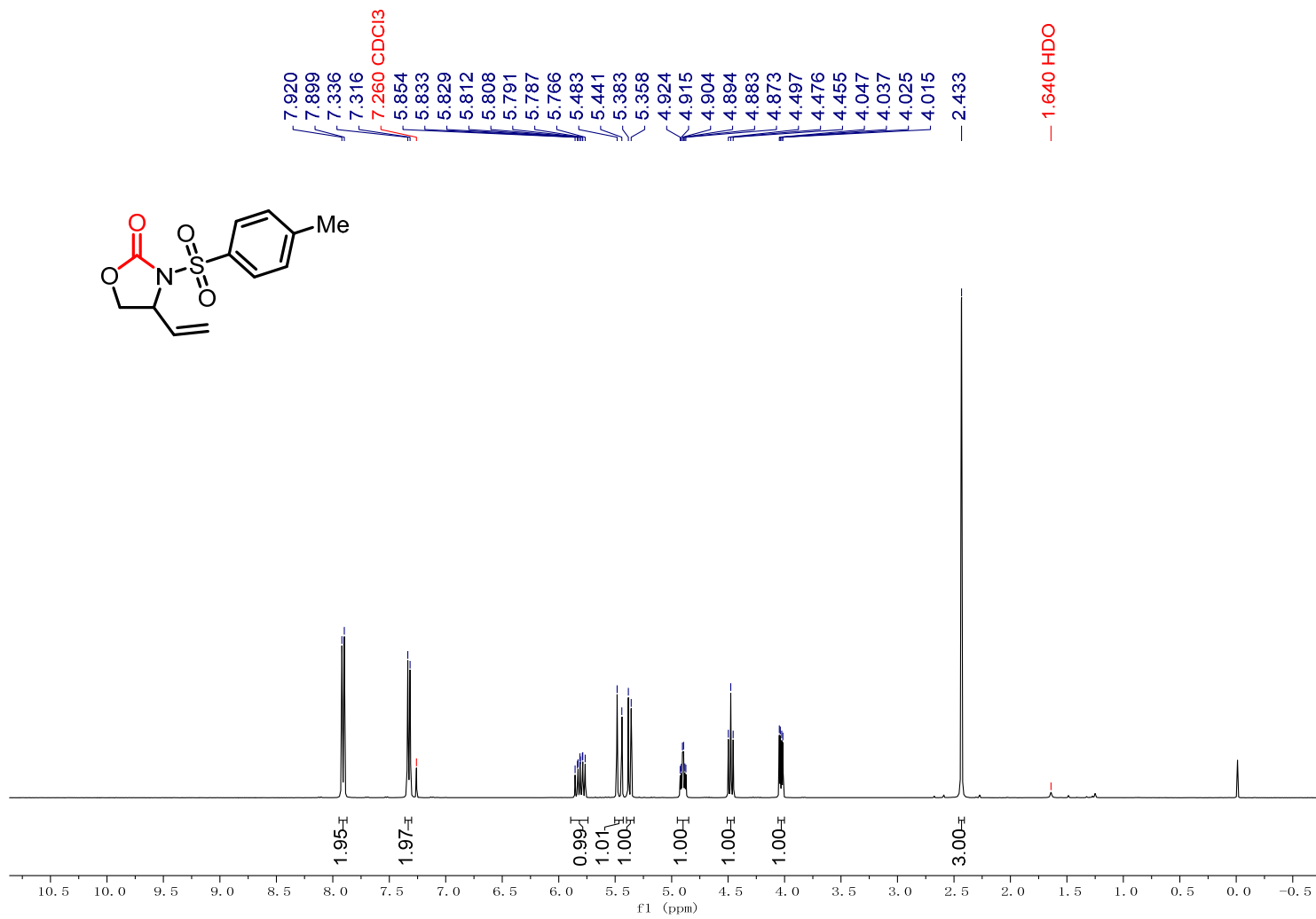
¹H NMR (400 MHz, CDCl₃) Spectrum of 2-(thiophen-3-yl)-3-vinyloxirane 1i



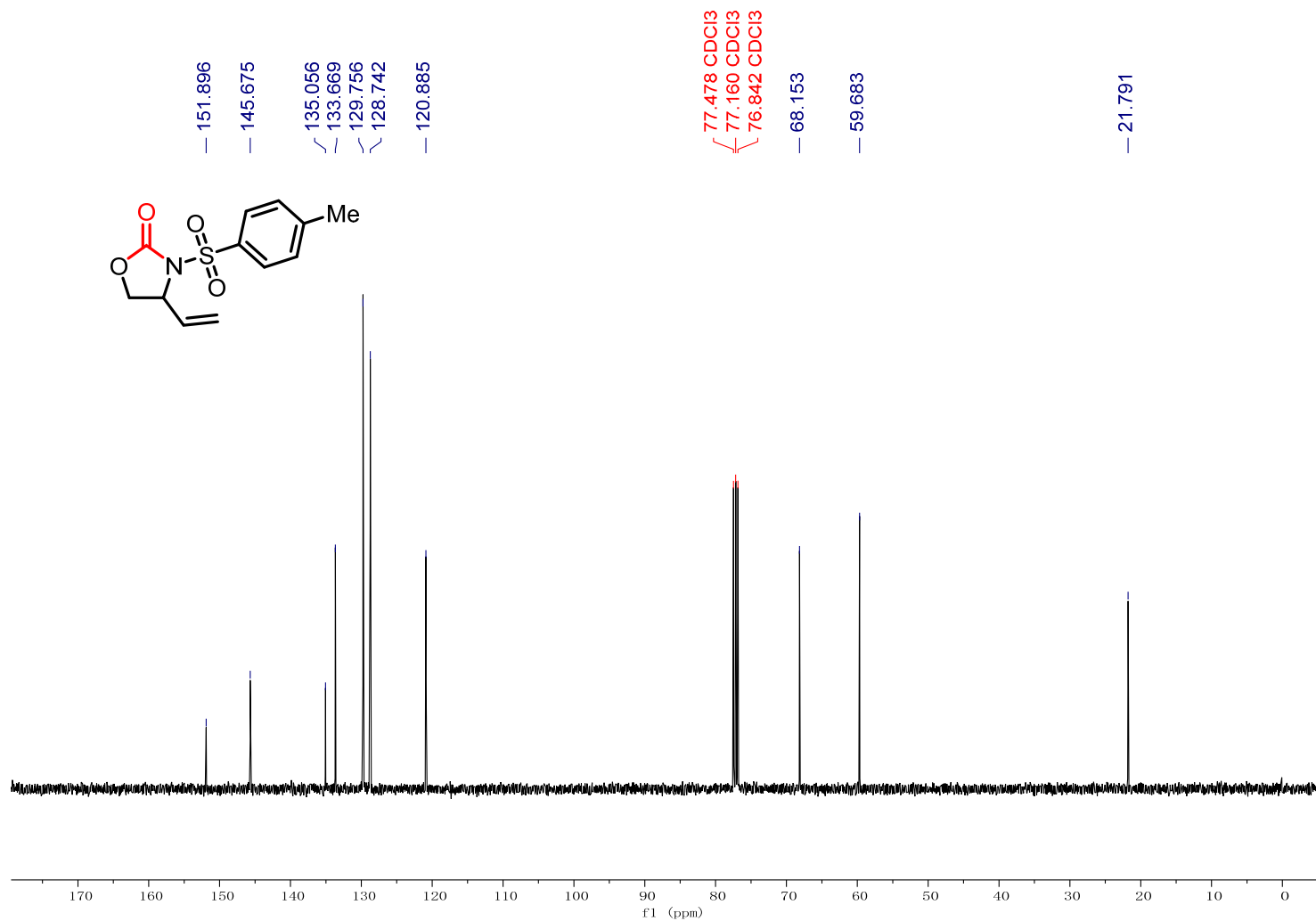
¹³C NMR (100 MHz, CDCl₃) Spectrum of 2-(thiophen-3-yl)-3-vinyloxirane **1i**



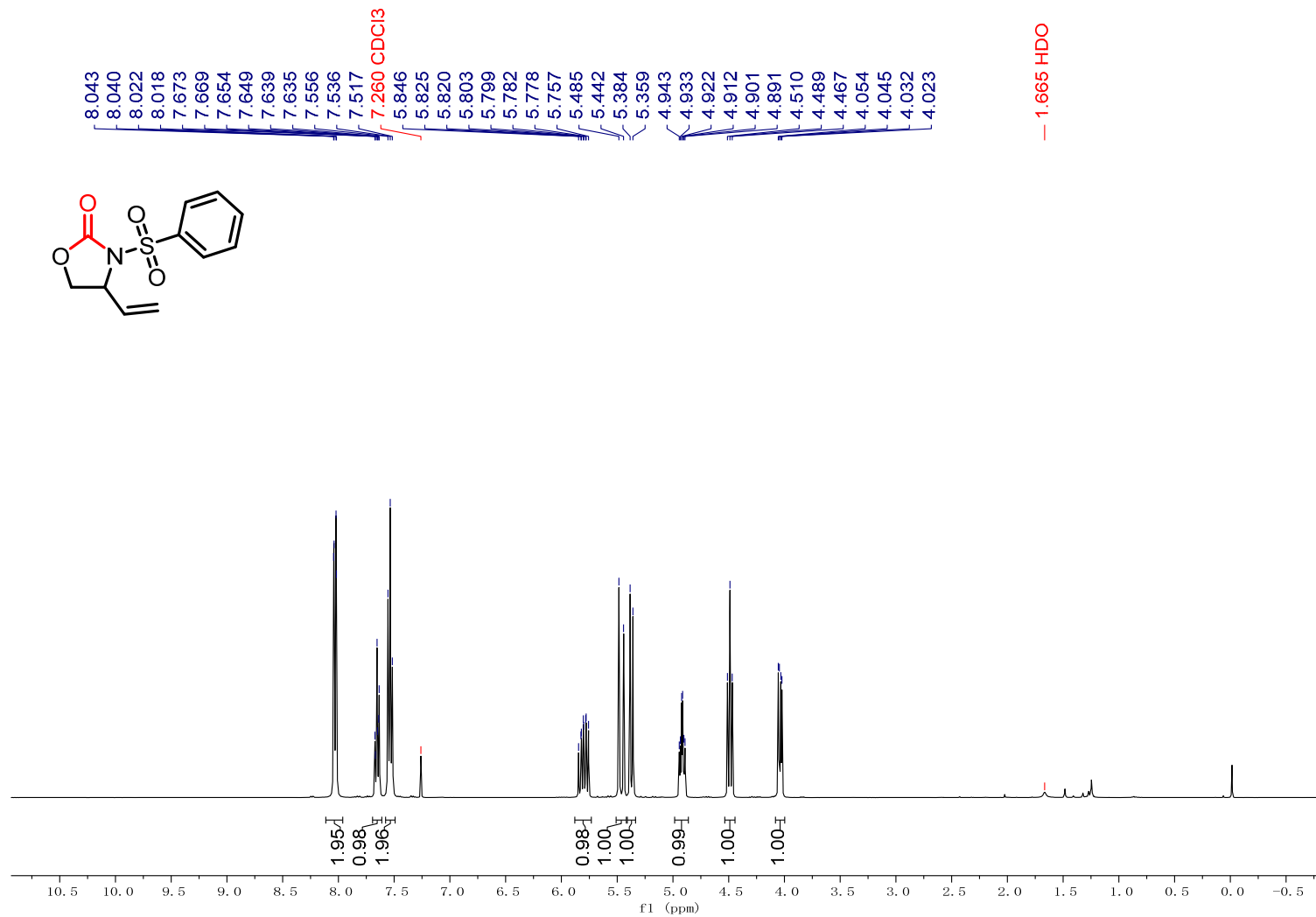
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-tosyl-4-vinyloxazolidin-2-one **3a**



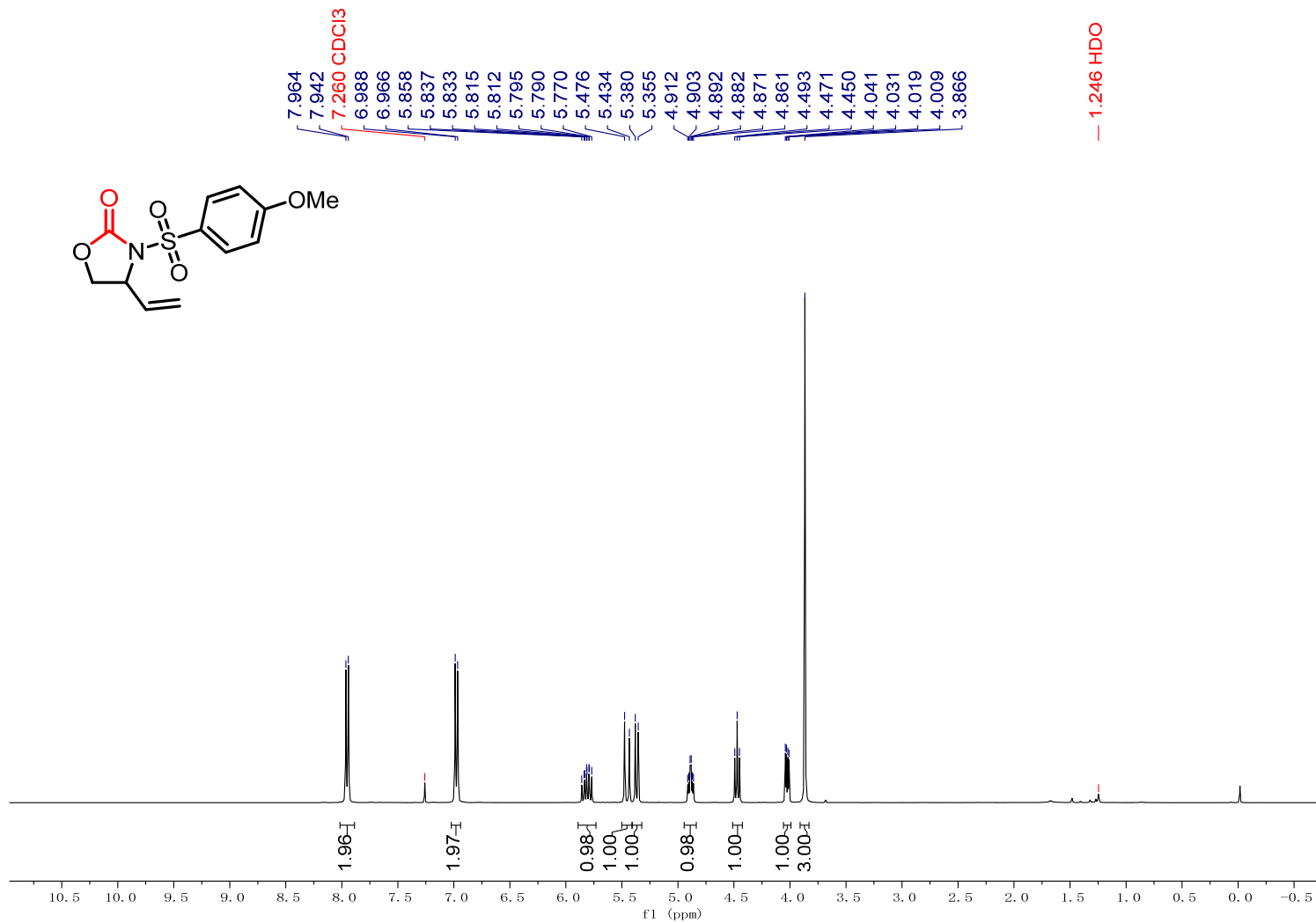
¹³C NMR (100 MHz, CDCl₃) Spectrum of 3-tosyl-4-vinyloxazolidin-2-one 3a



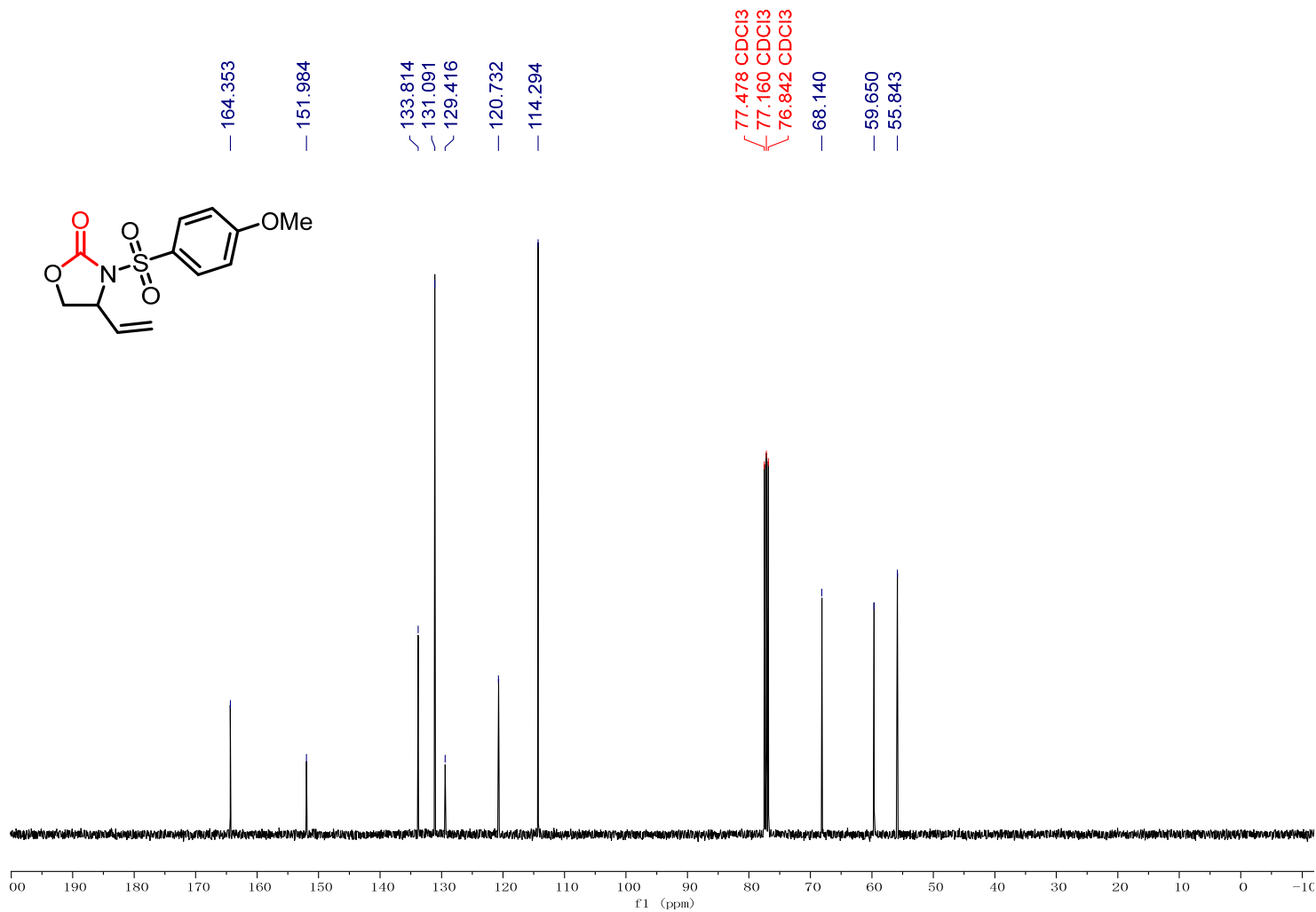
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(phenylsulfonyl)-4-vinyloxazolidin-2-one 3b



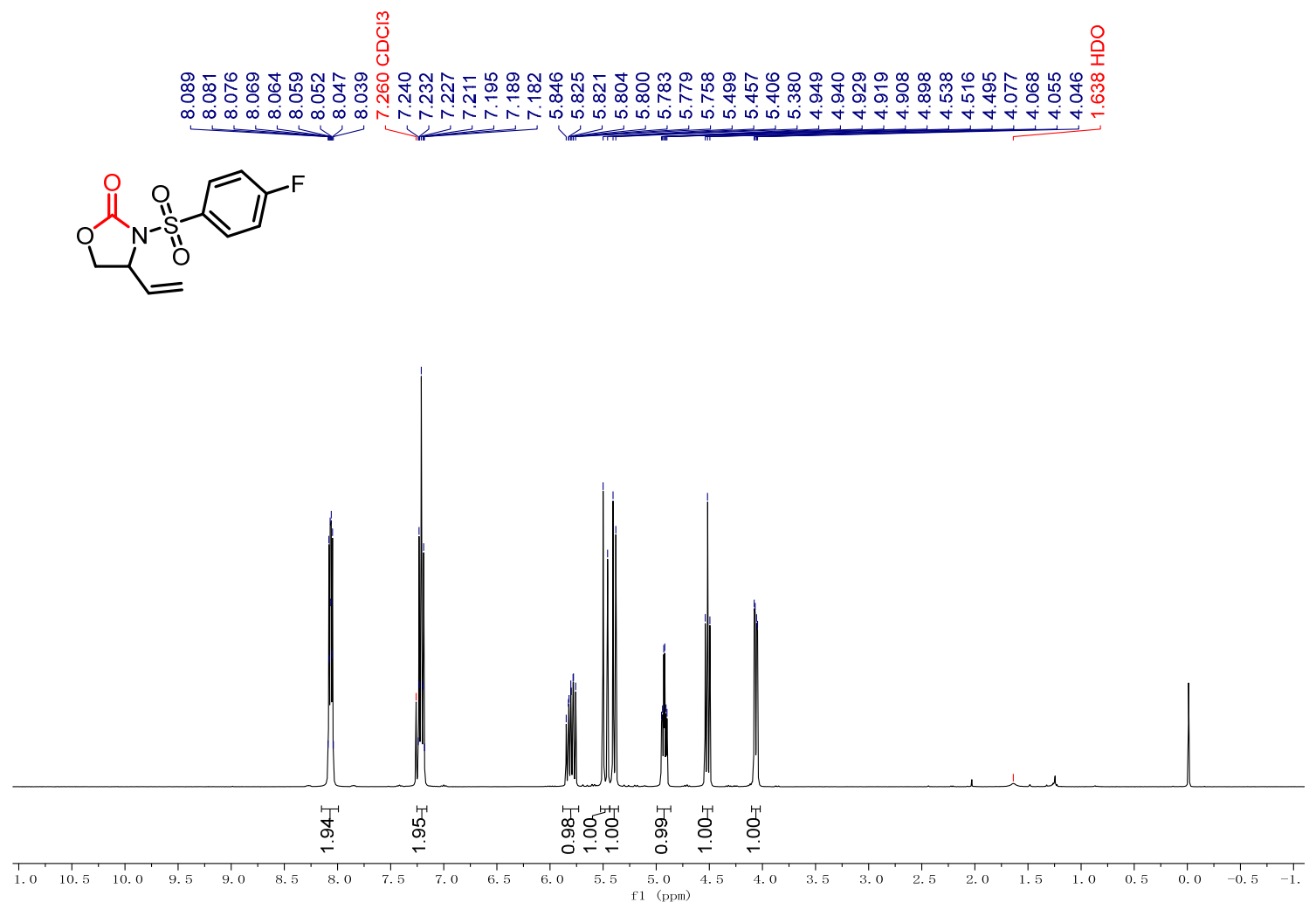
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((4-methoxyphenyl)sulfonyl)-4-vinylazolidin-2-one 3c



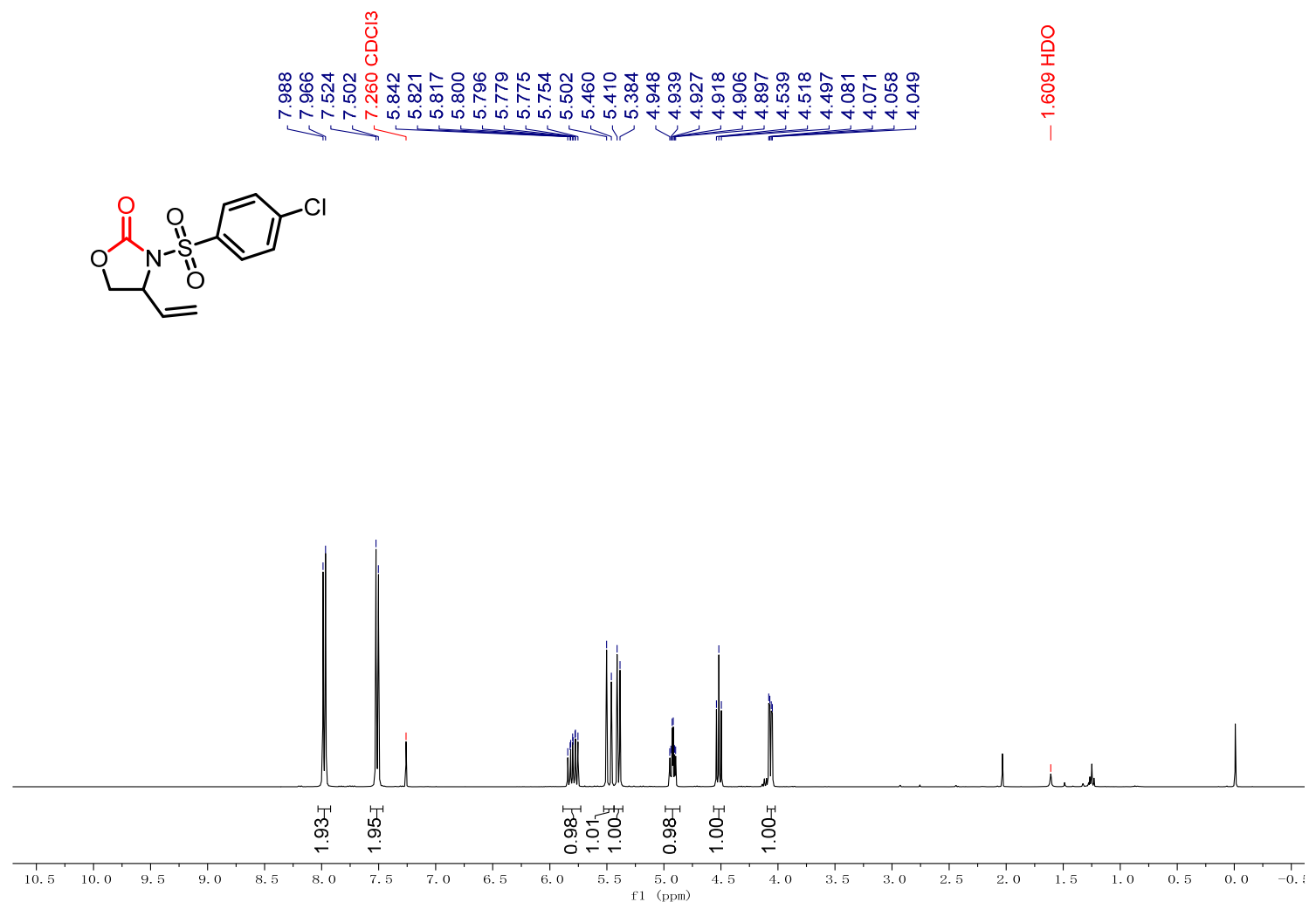
¹³C NMR (100 MHz, CDCl₃) Spectrum of 3-((4-methoxyphenyl)sulfonyl)-4-vinylloxazolidin-2-one 3c



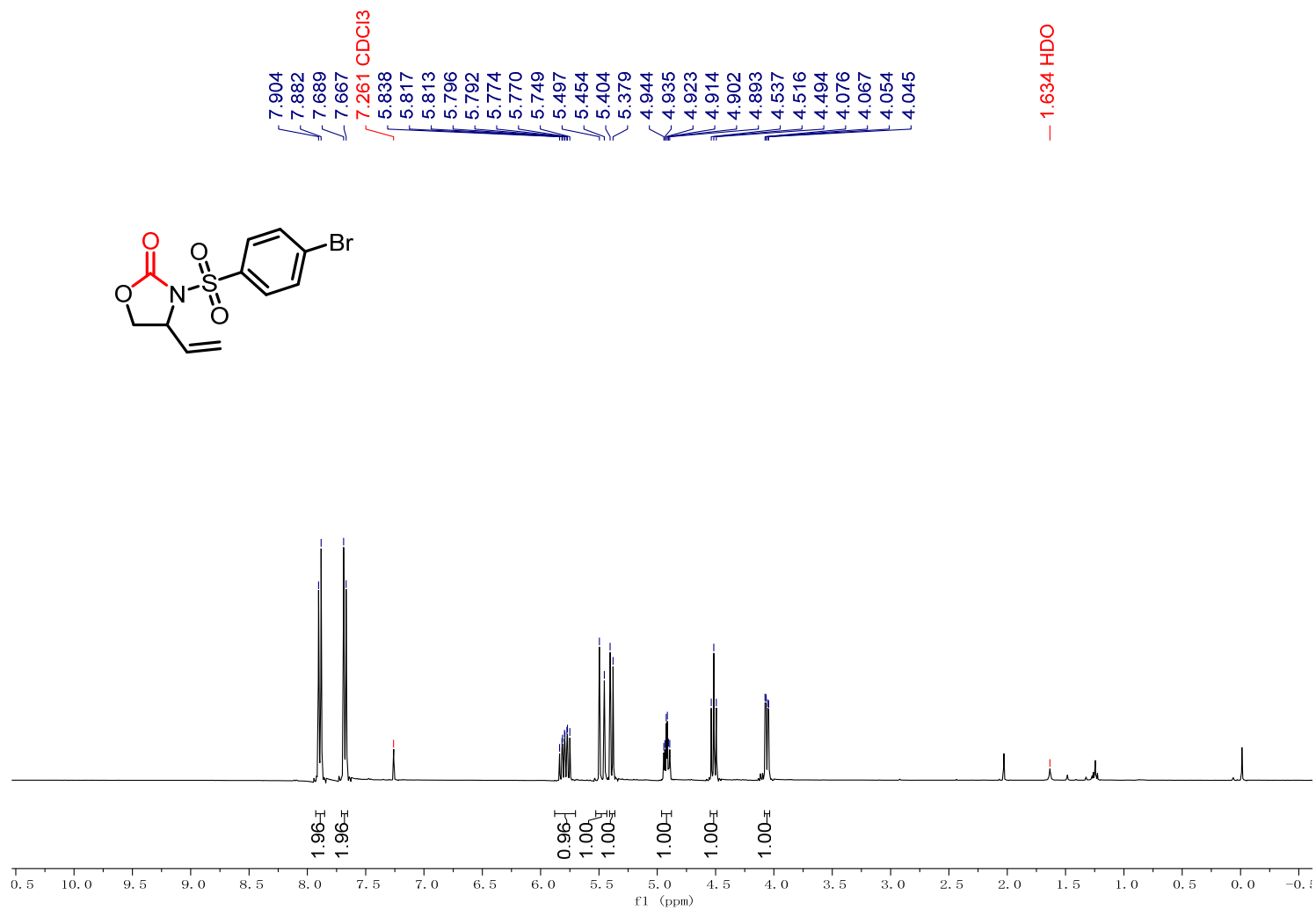
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((4-fluorophenyl)sulfonyl)-4-vinylloxazolidin-2-one 3d



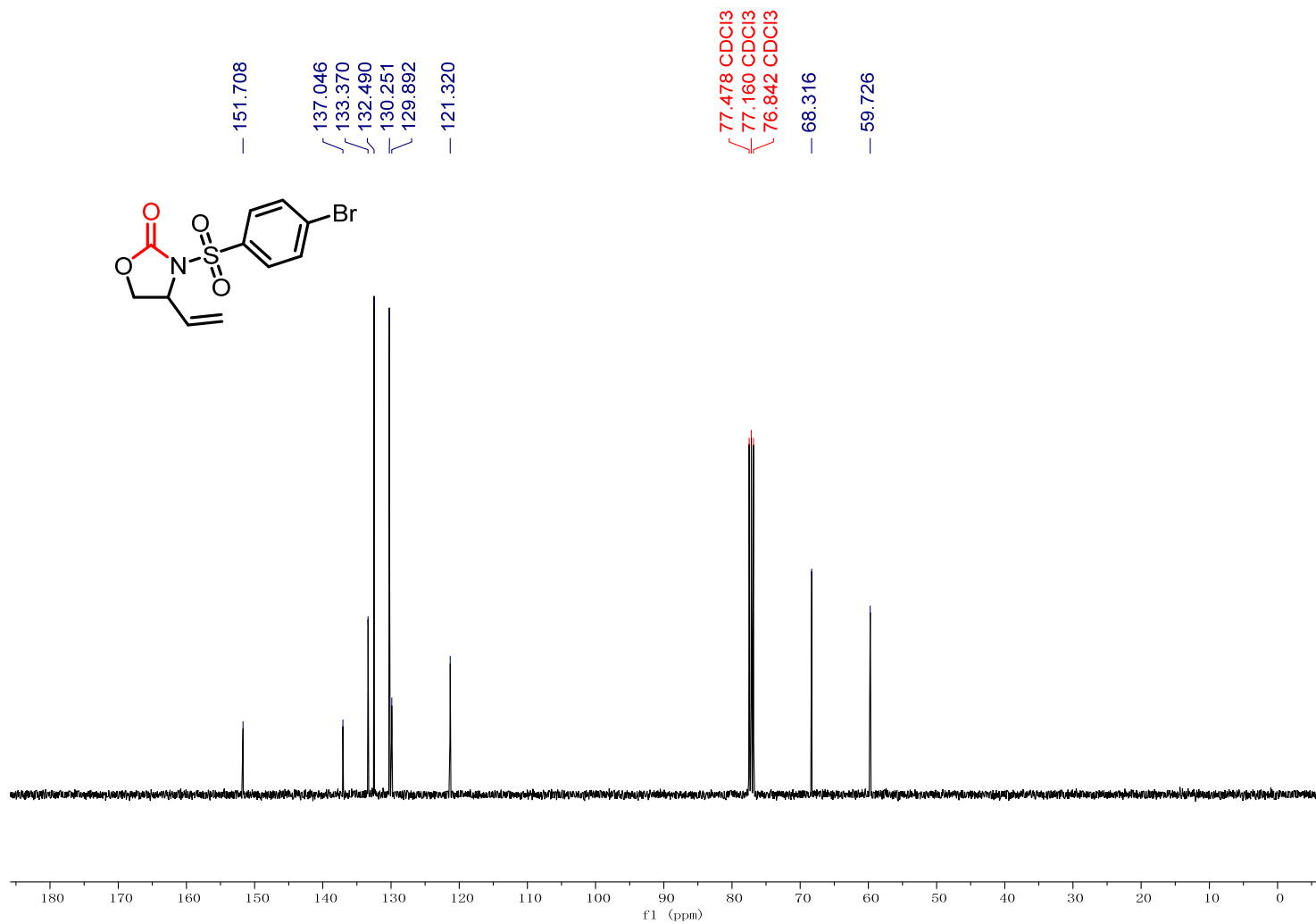
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((4-chlorophenyl)sulfonyl)-4-vinyloxazolidin-2-one 3e



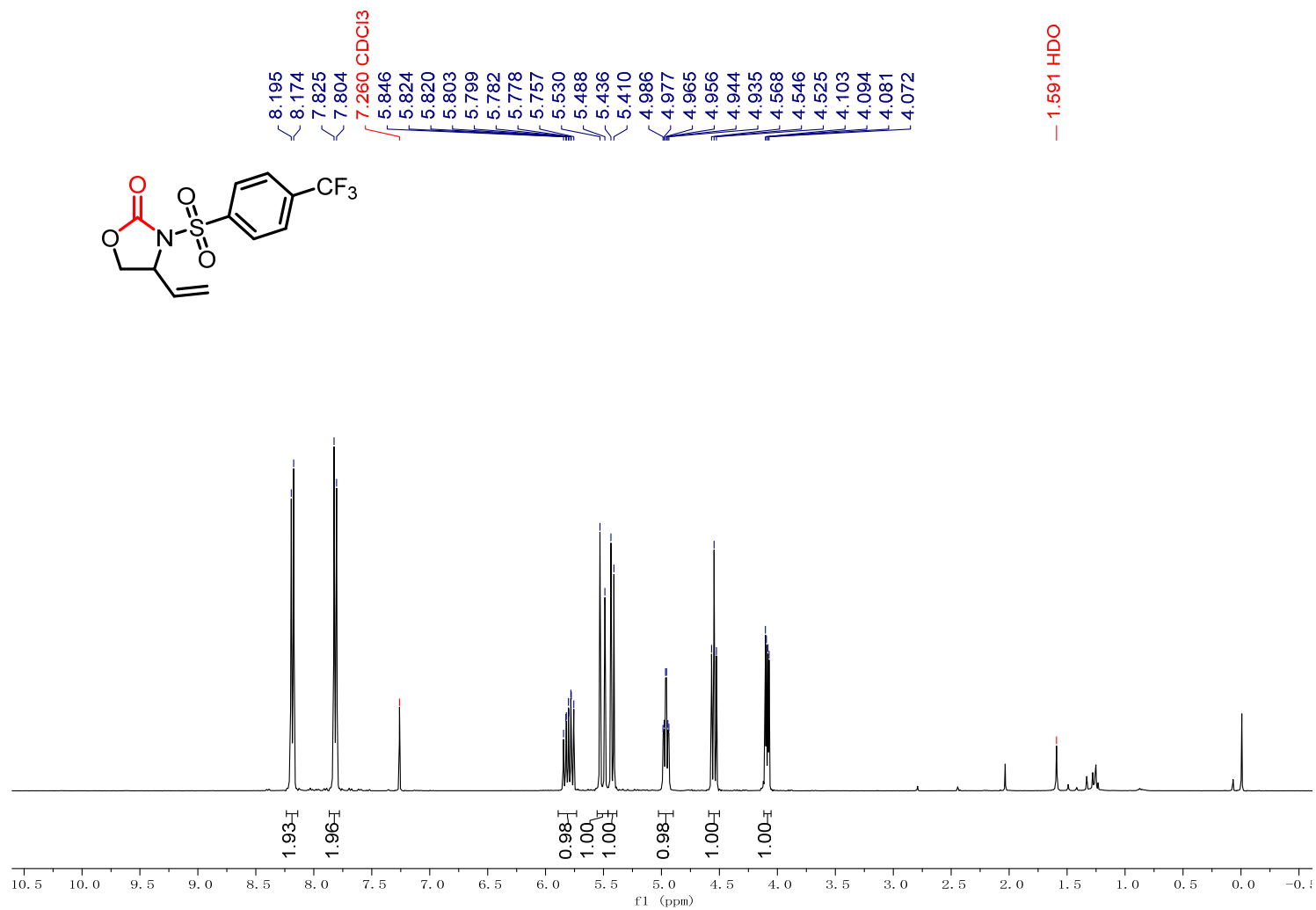
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((4-bromophenyl)sulfonyl)-4-vinyloxazolidin-2-one 3f



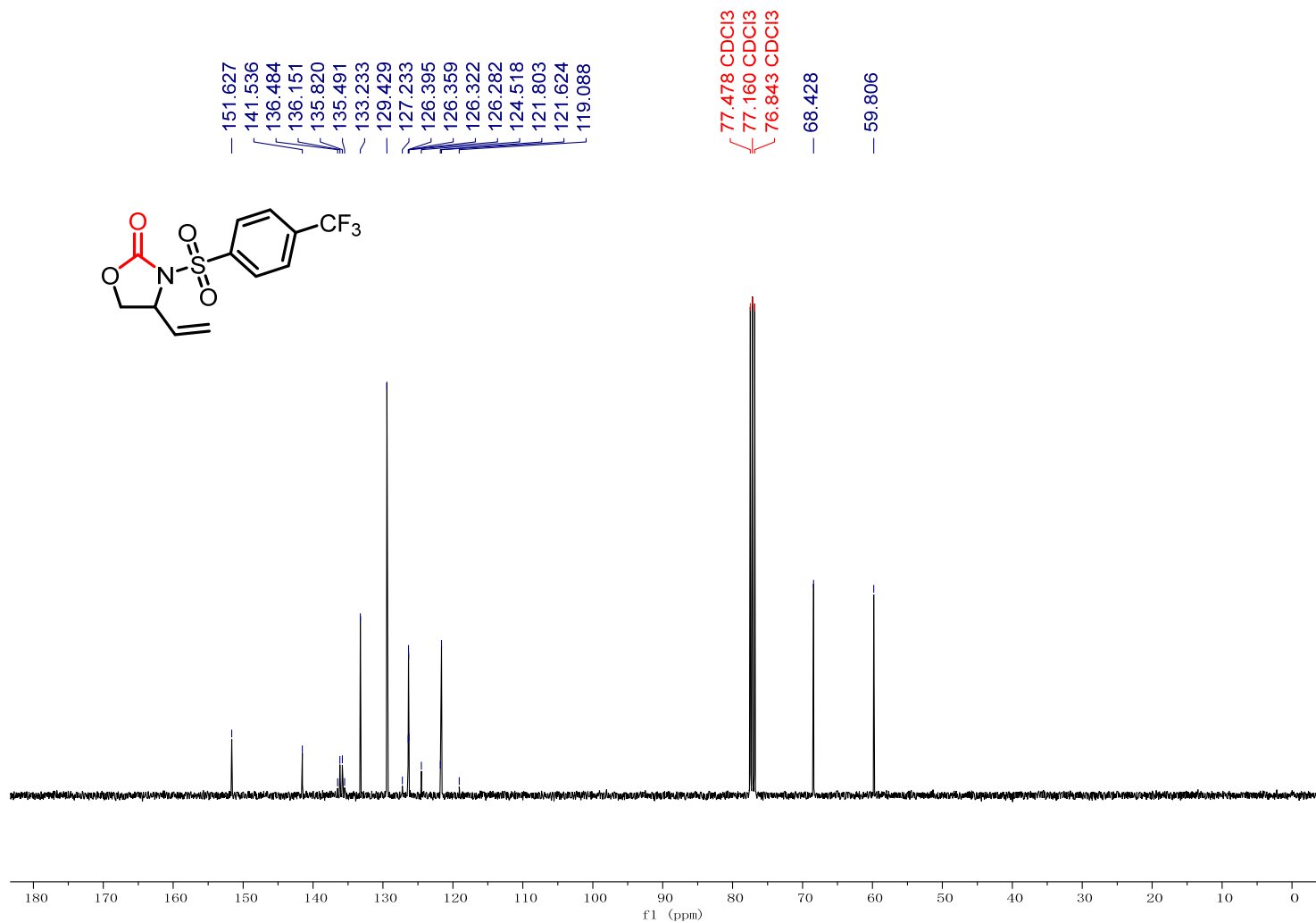
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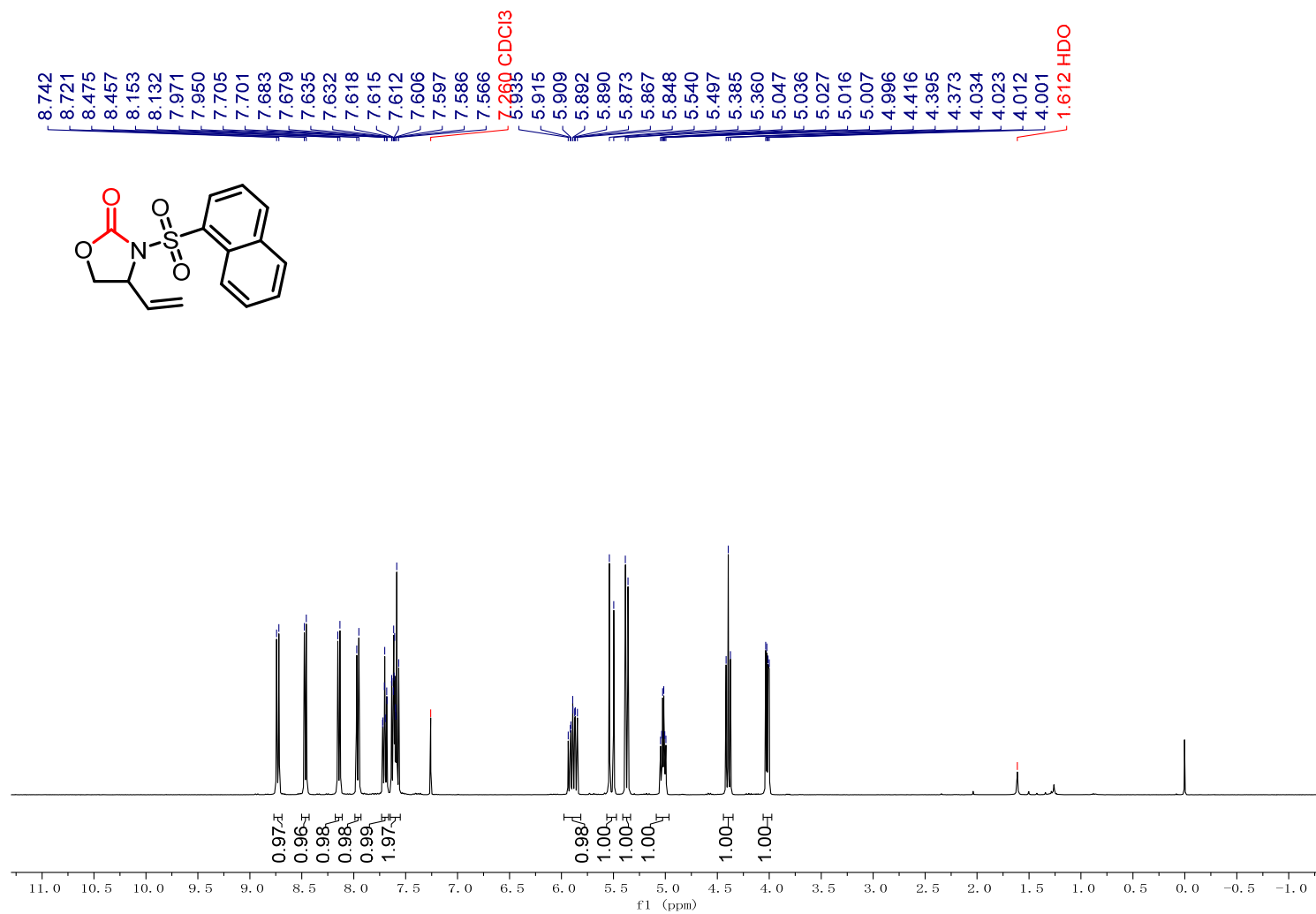
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((4-(trifluoromethyl)phenyl)sulfonyl)-4-vinylloxazolidin-2-one 3g



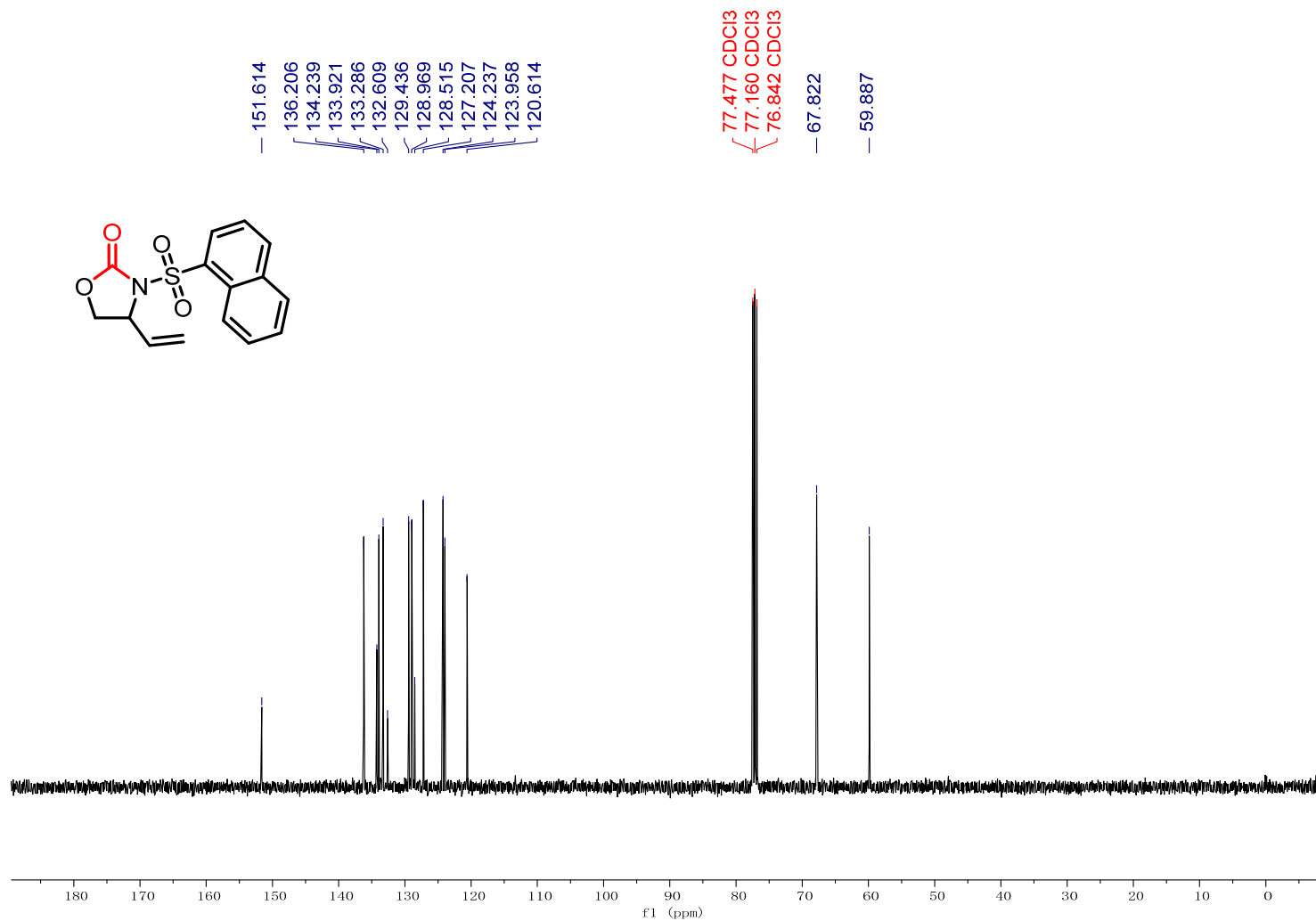
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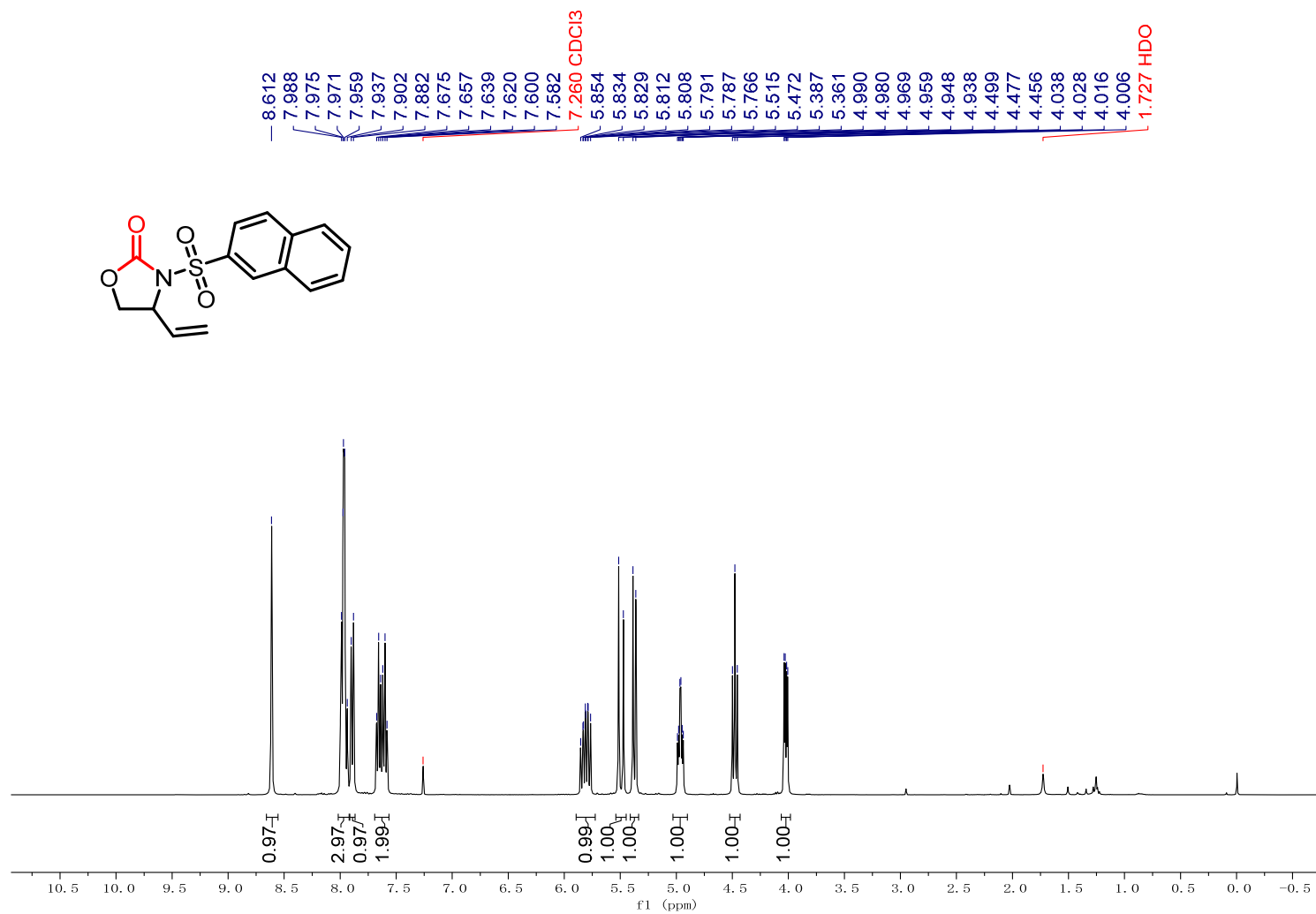
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(naphthalen-1-ylsulfonyl)-4-vinyloxazolidin-2-one 3h



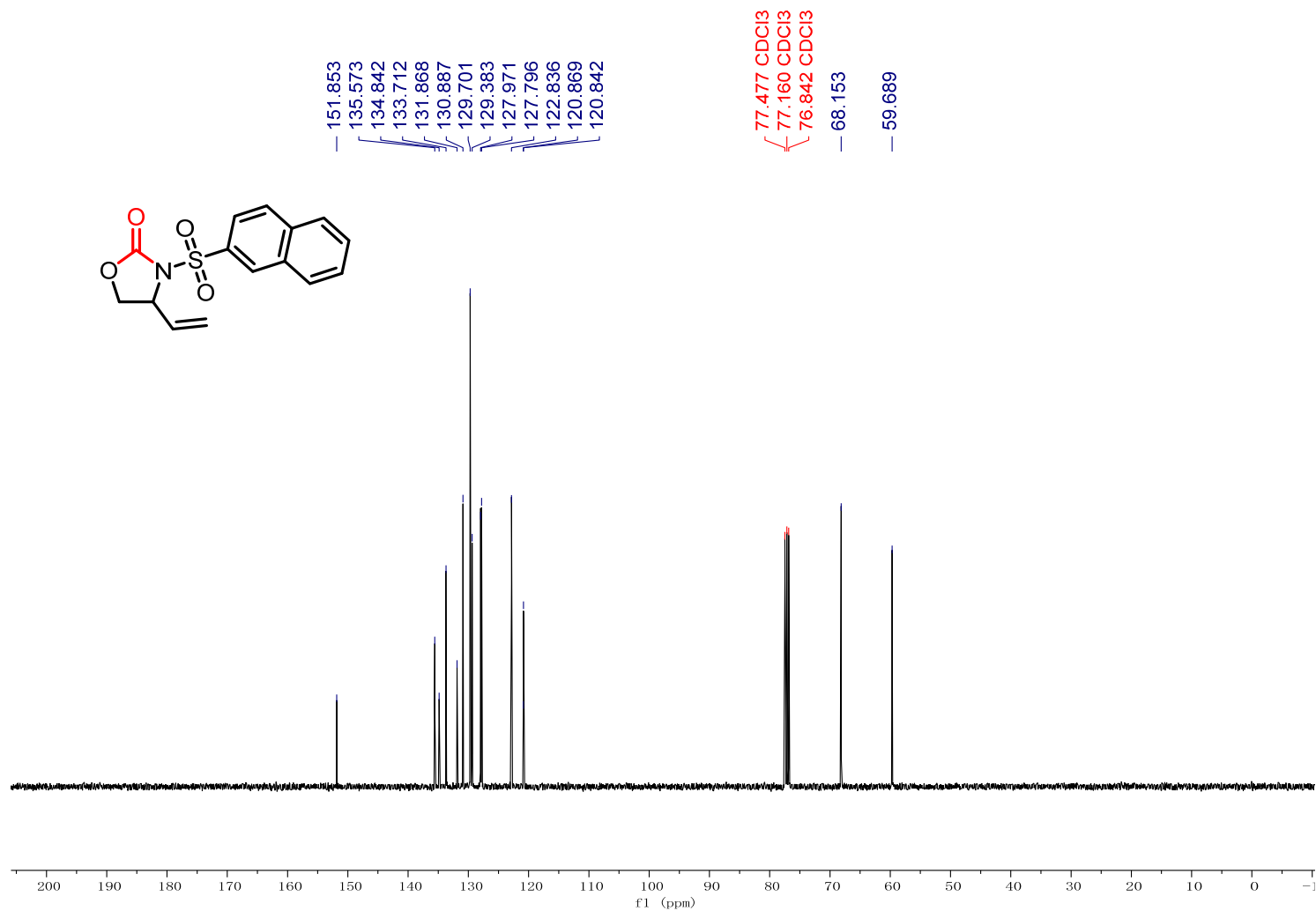
¹³C NMR (100 MHz, CDCl₃) Spectrum of 3-(naphthalen-1-ylsulfonyl)-4-vinylloxazolidin-2-one 3h



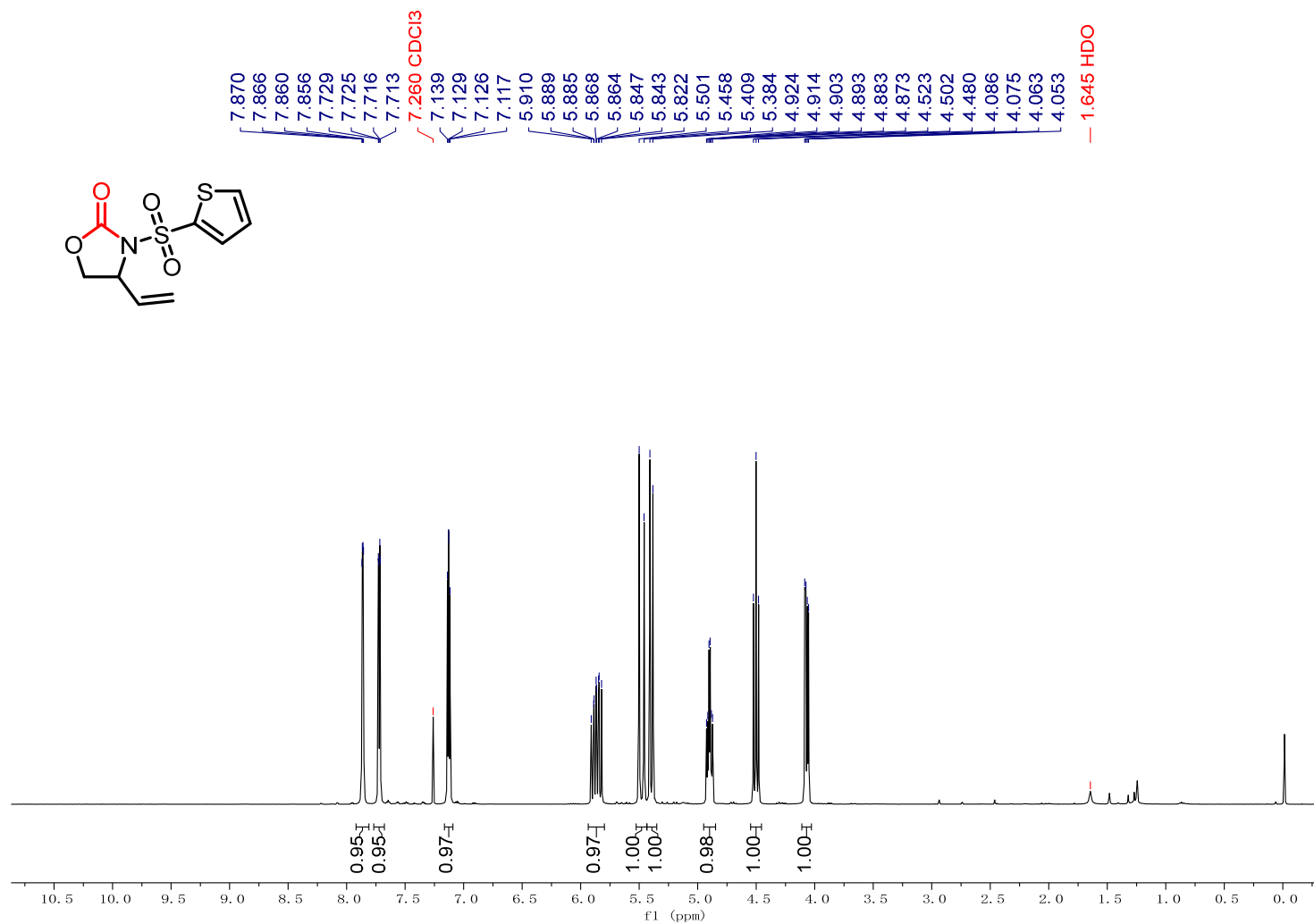
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(naphthalen-2-ylsulfonyl)-4-vinyloxazolidin-2-one 3i



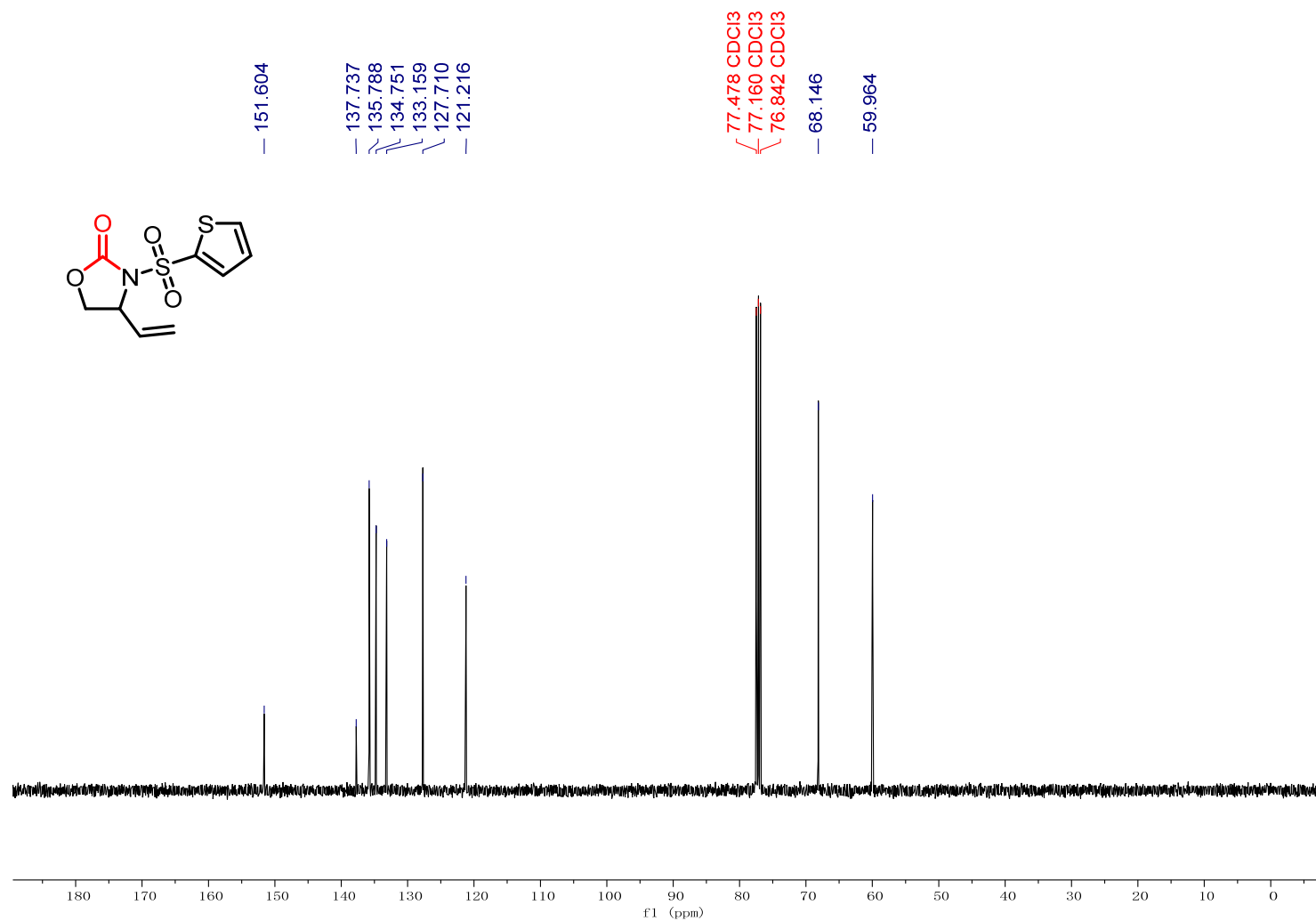
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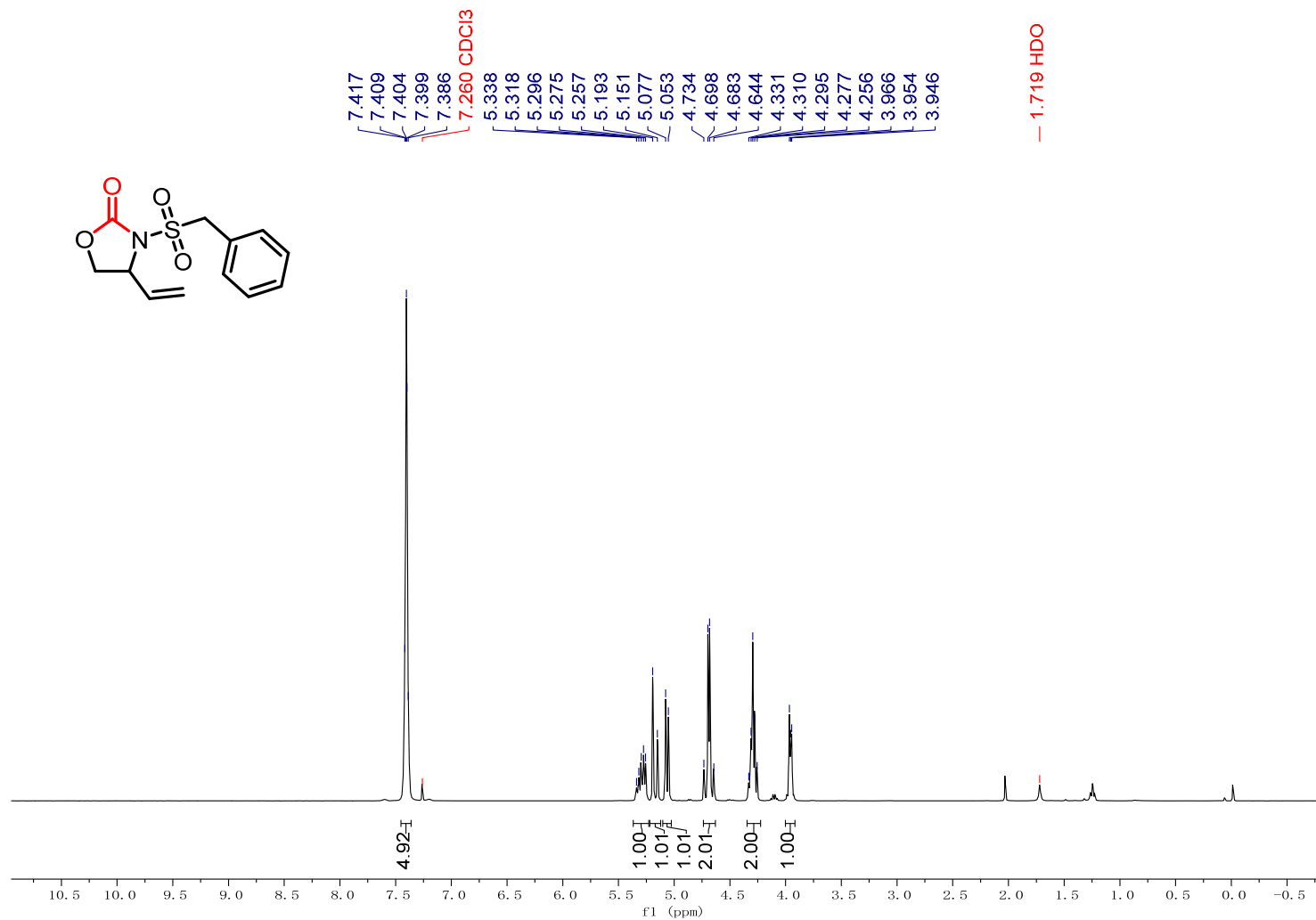
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(thiophen-2-ylsulfonyl)-4-vinyloxazolidin-2-one 3j



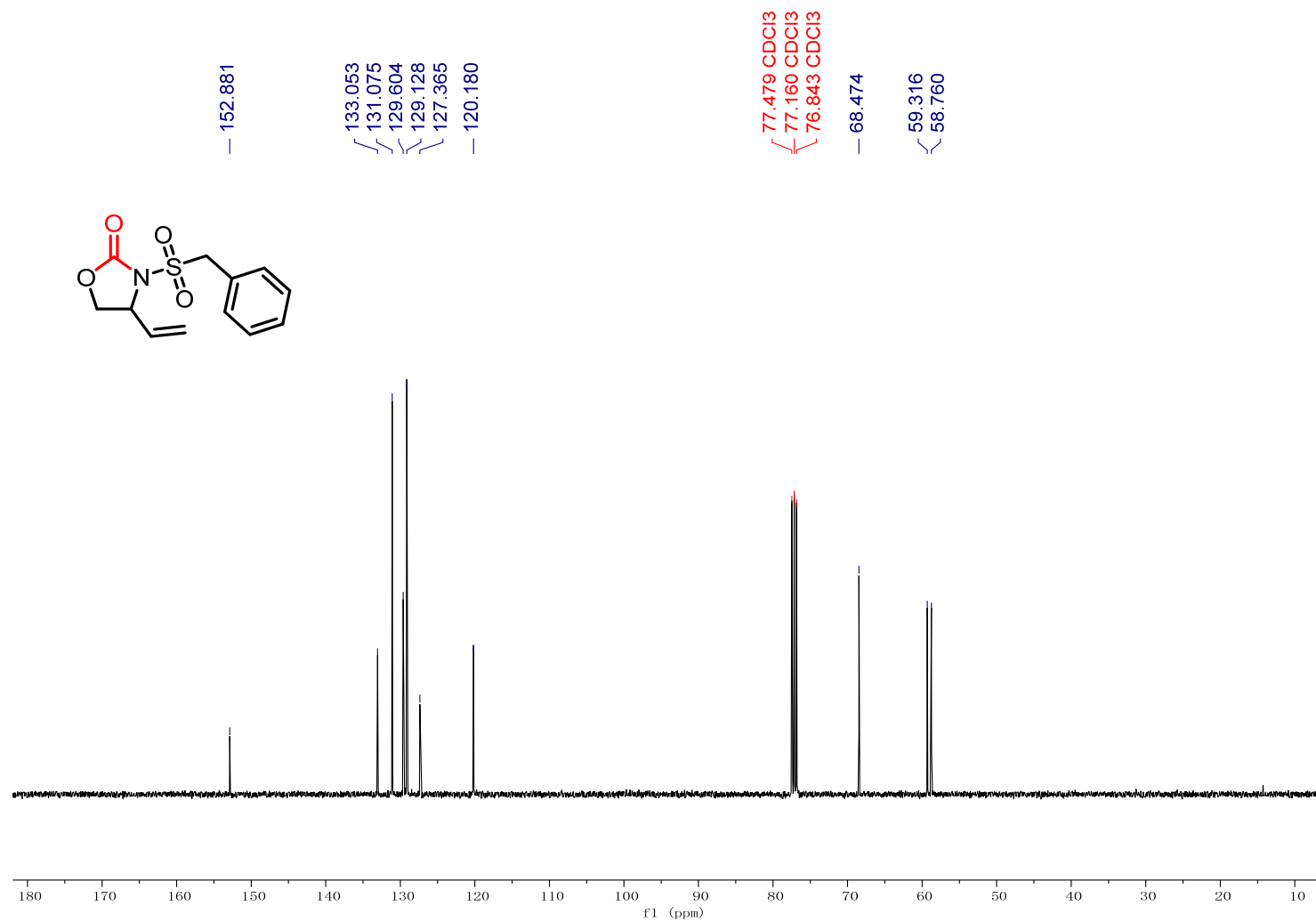
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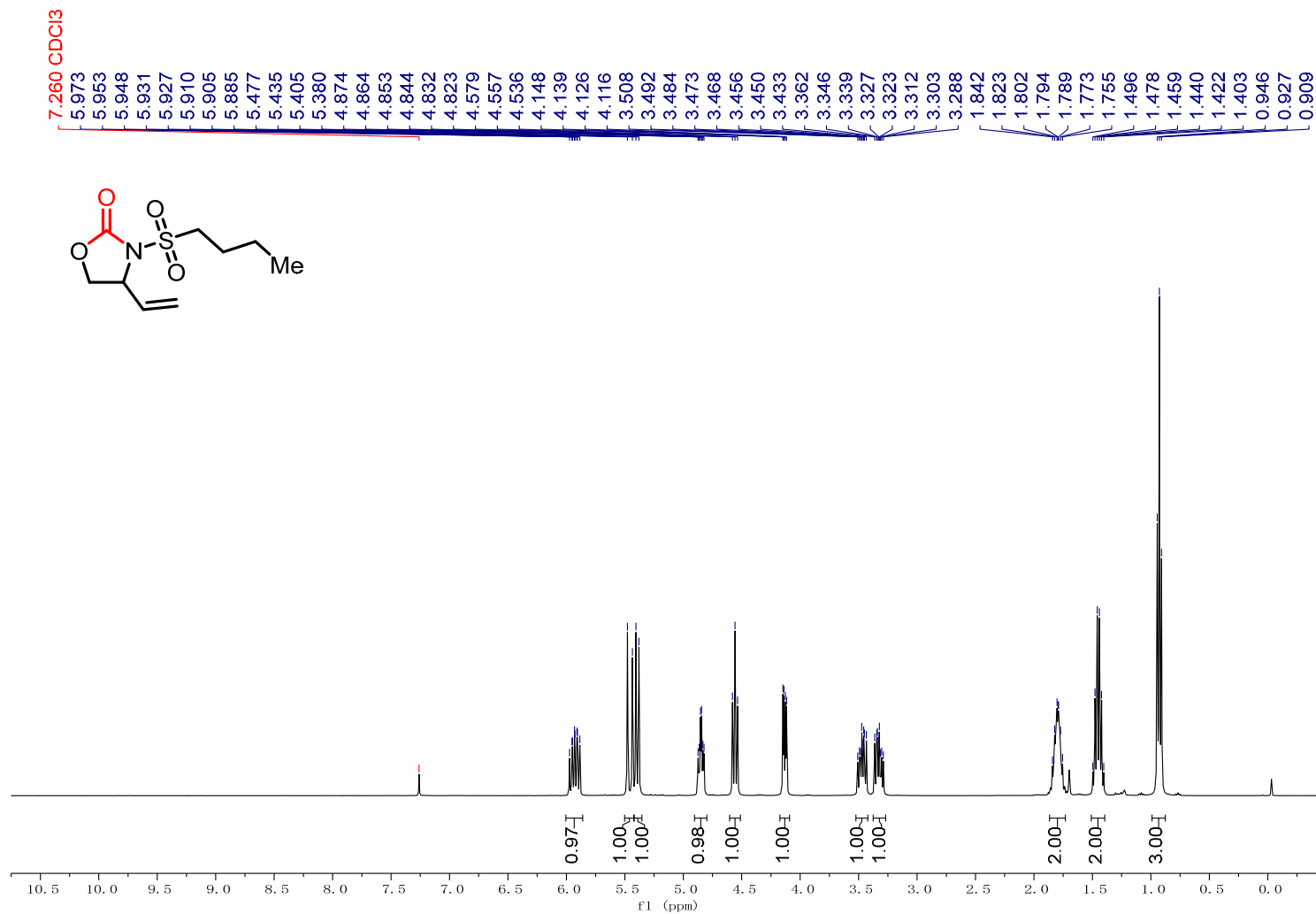
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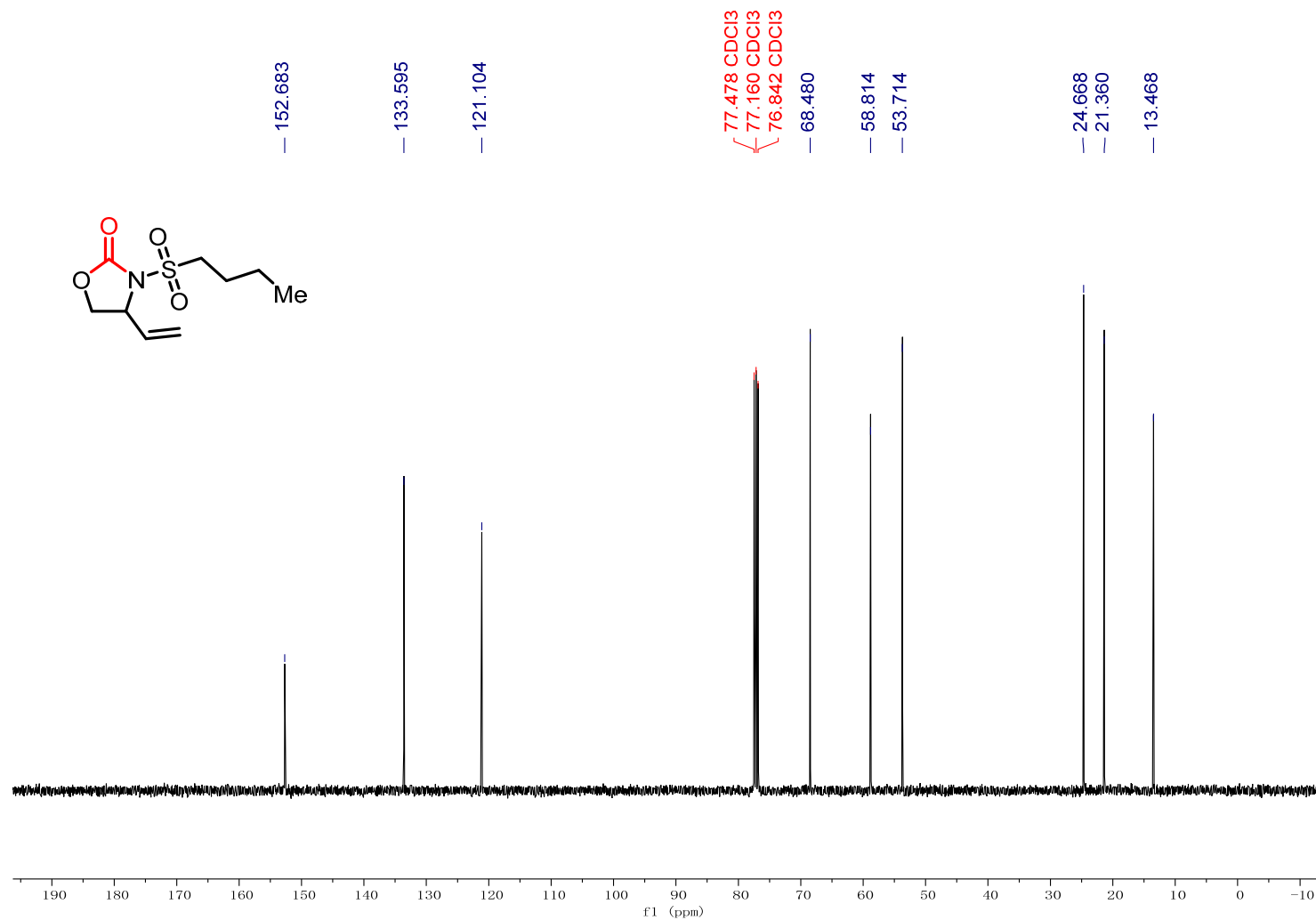
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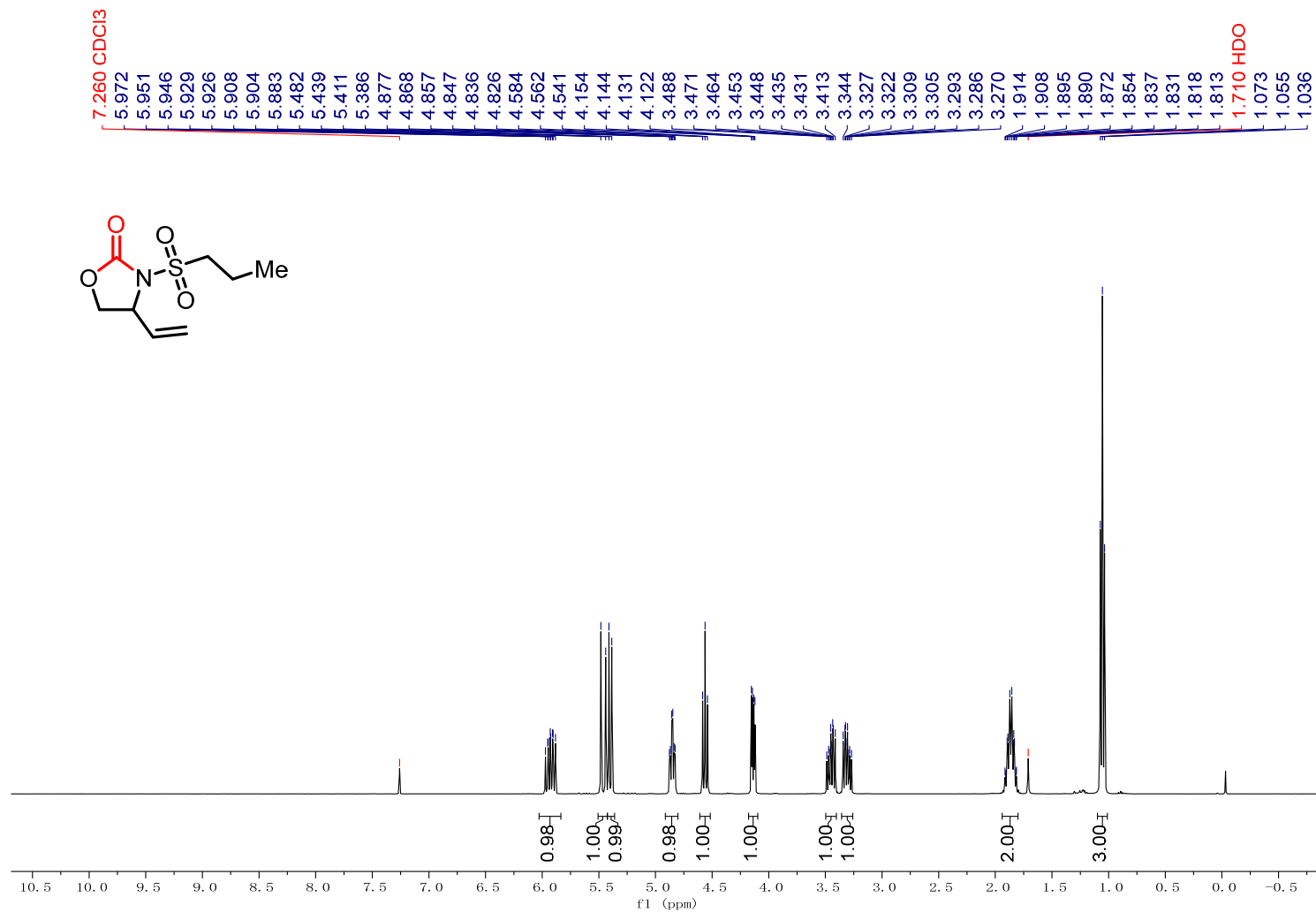
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(butylsulfonyl)-4-vinylloxazolidin-2-one 3l



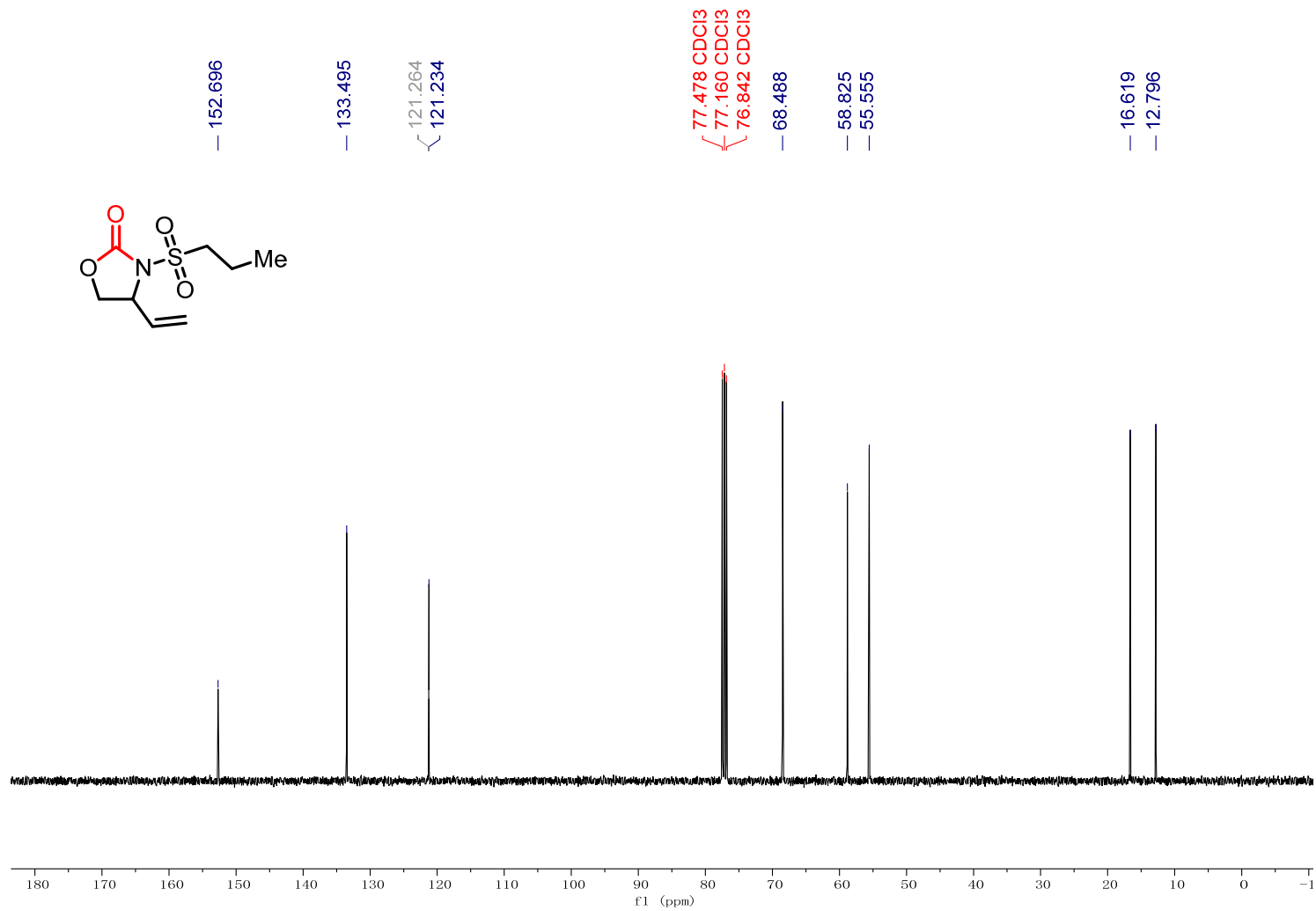
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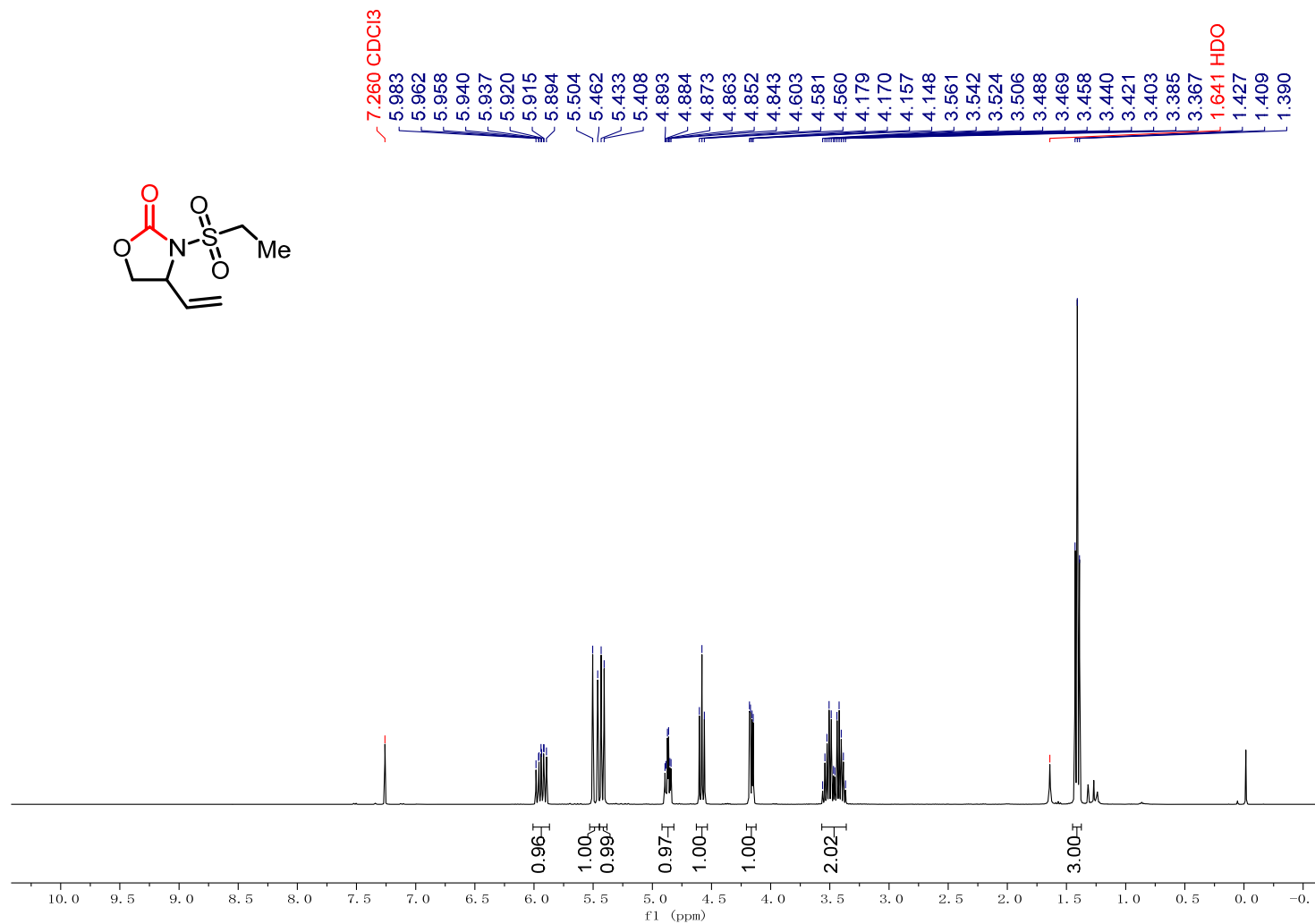
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(propylsulfonyl)-4-vinylloxazolidin-2-one 3m



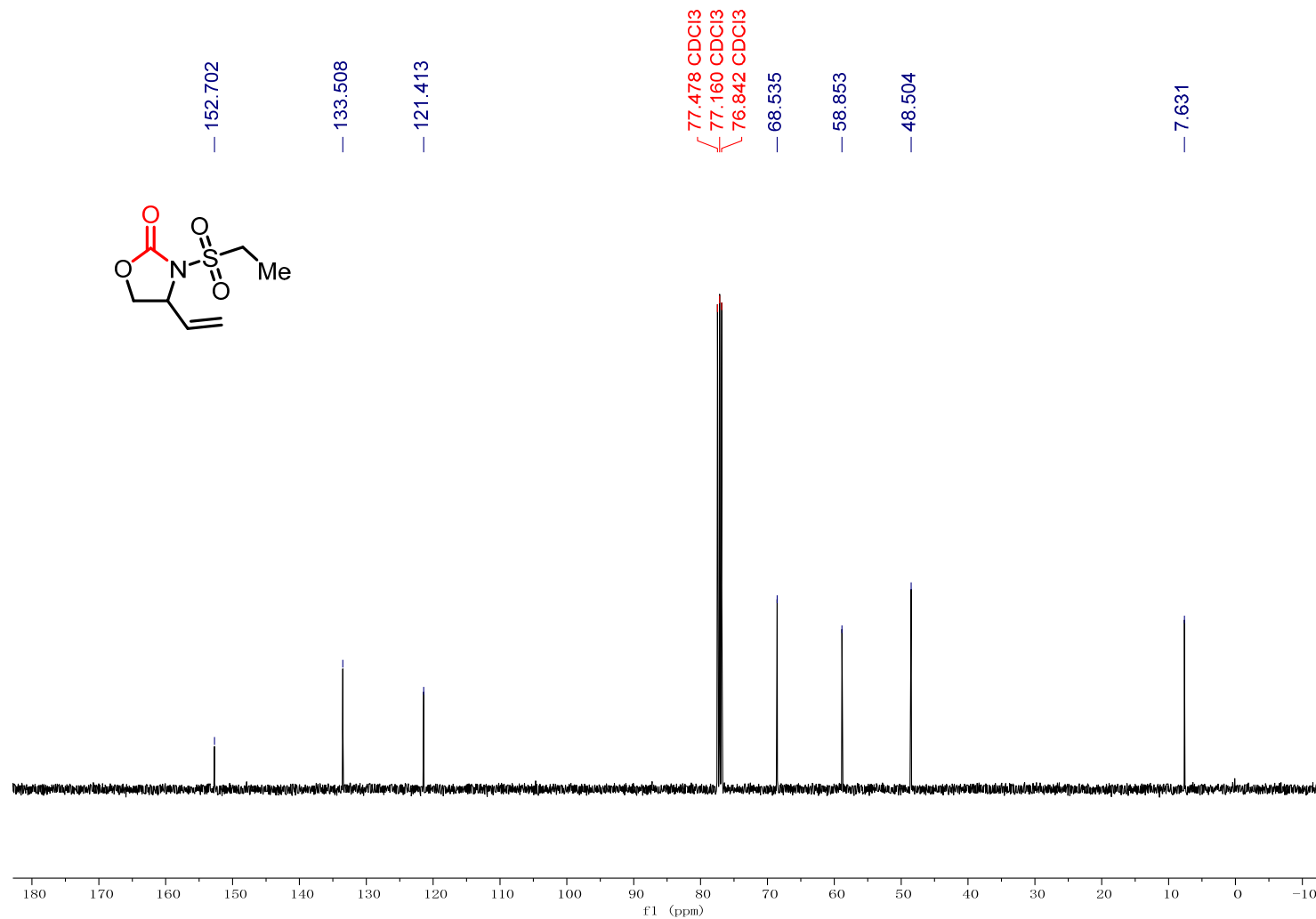
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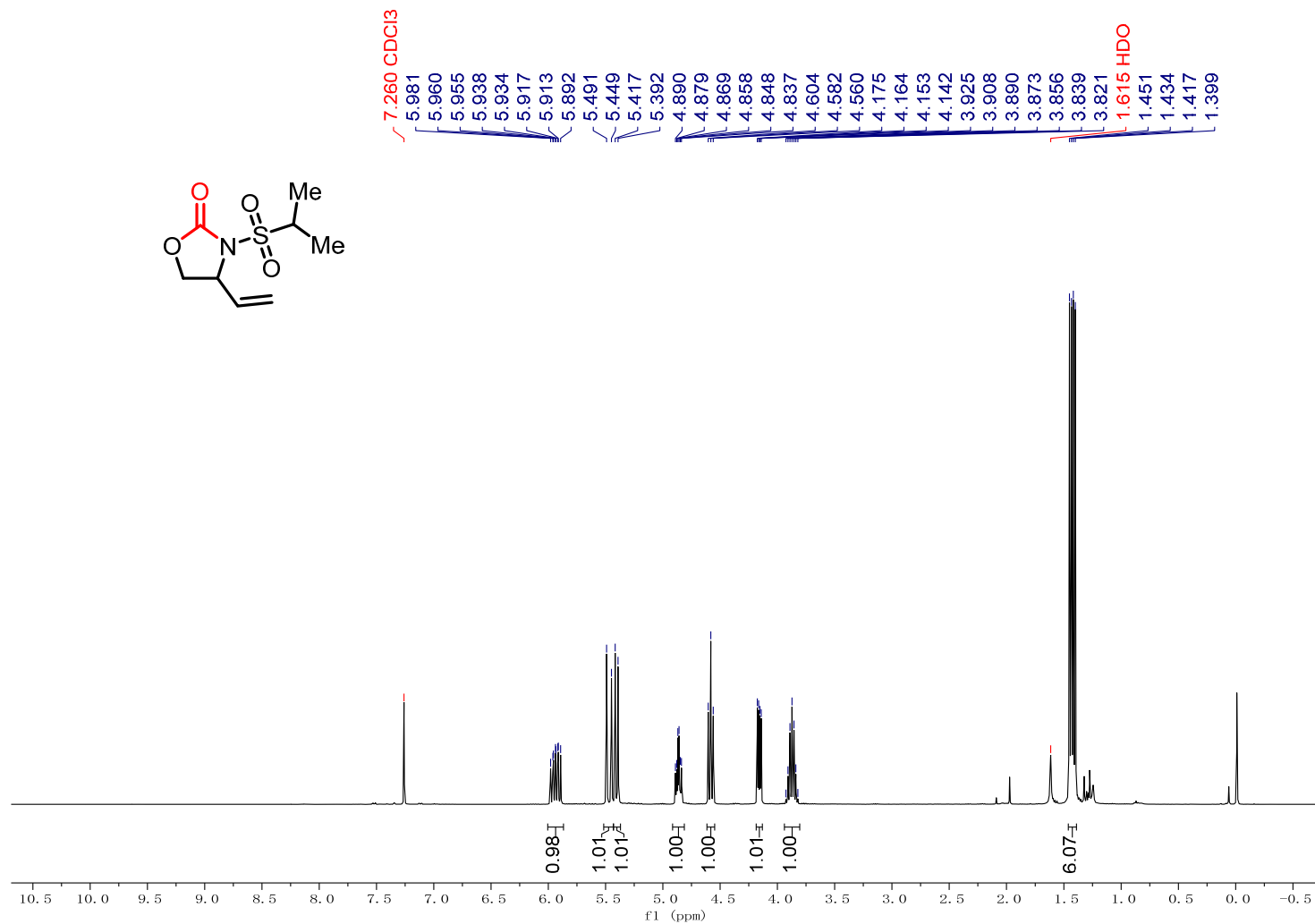
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(ethylsulfonyl)-4-vinylloxazolidin-2-one 3n



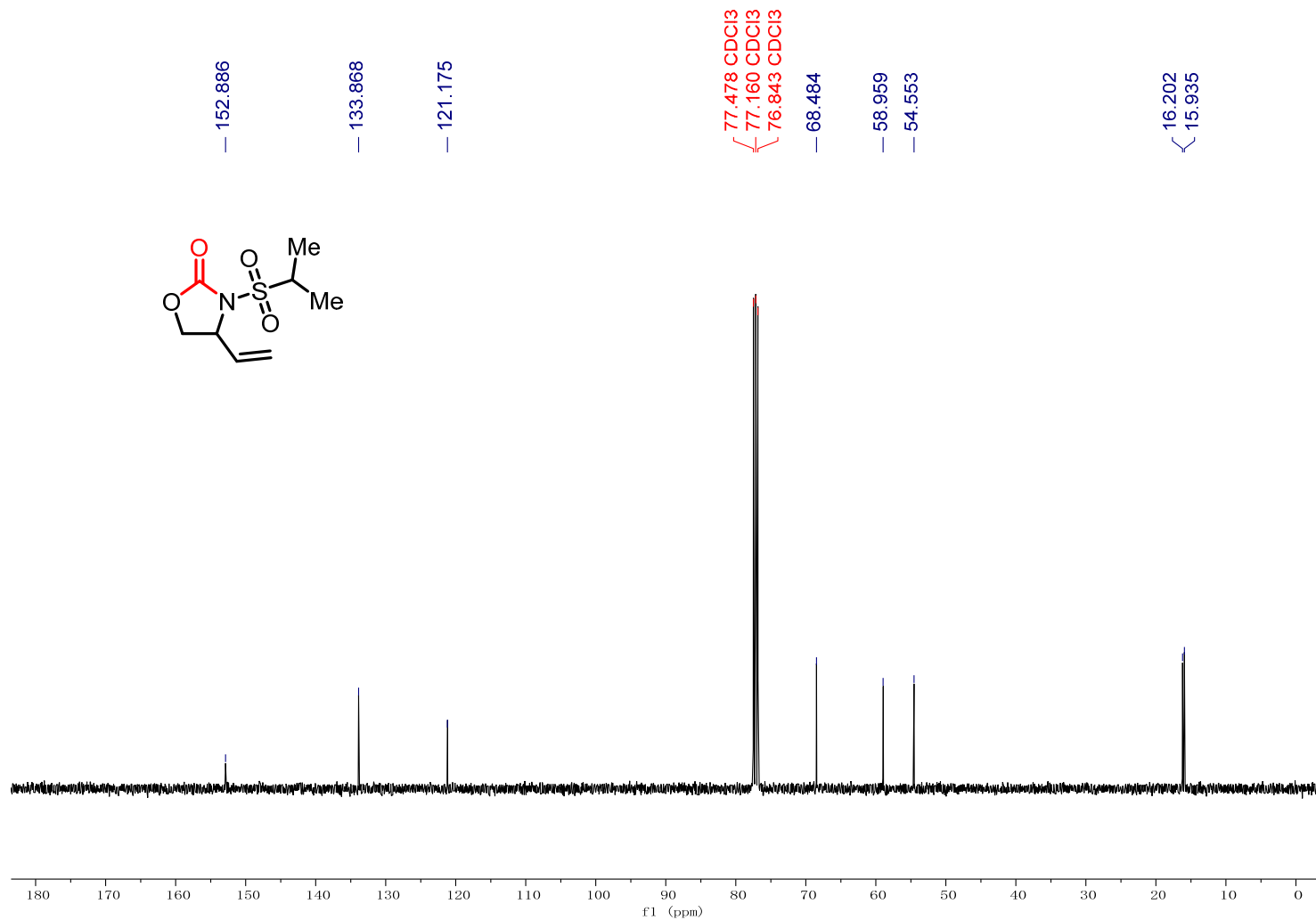
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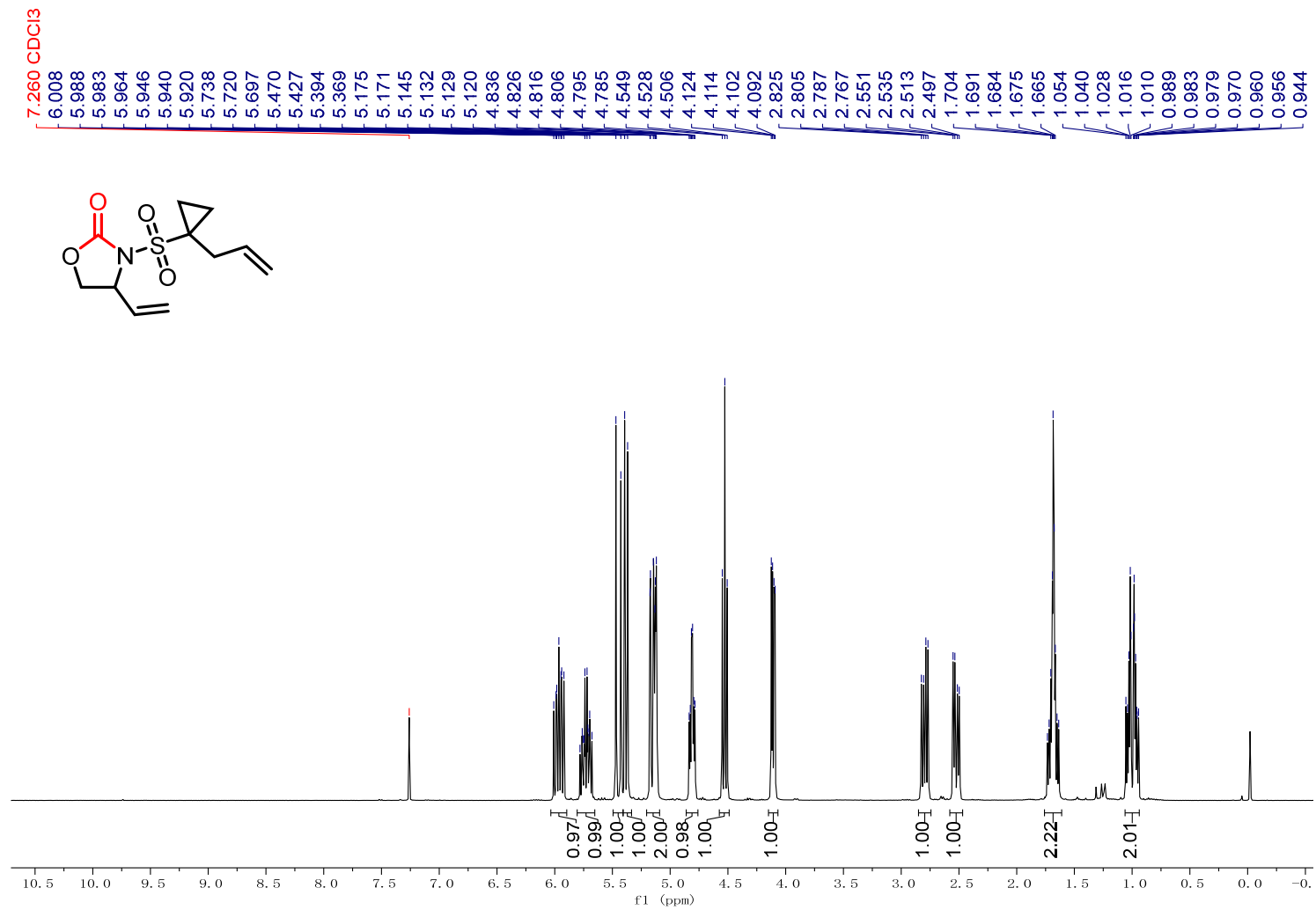
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-(isopropylsulfonyl)-4-vinylazolidin-2-one 3o



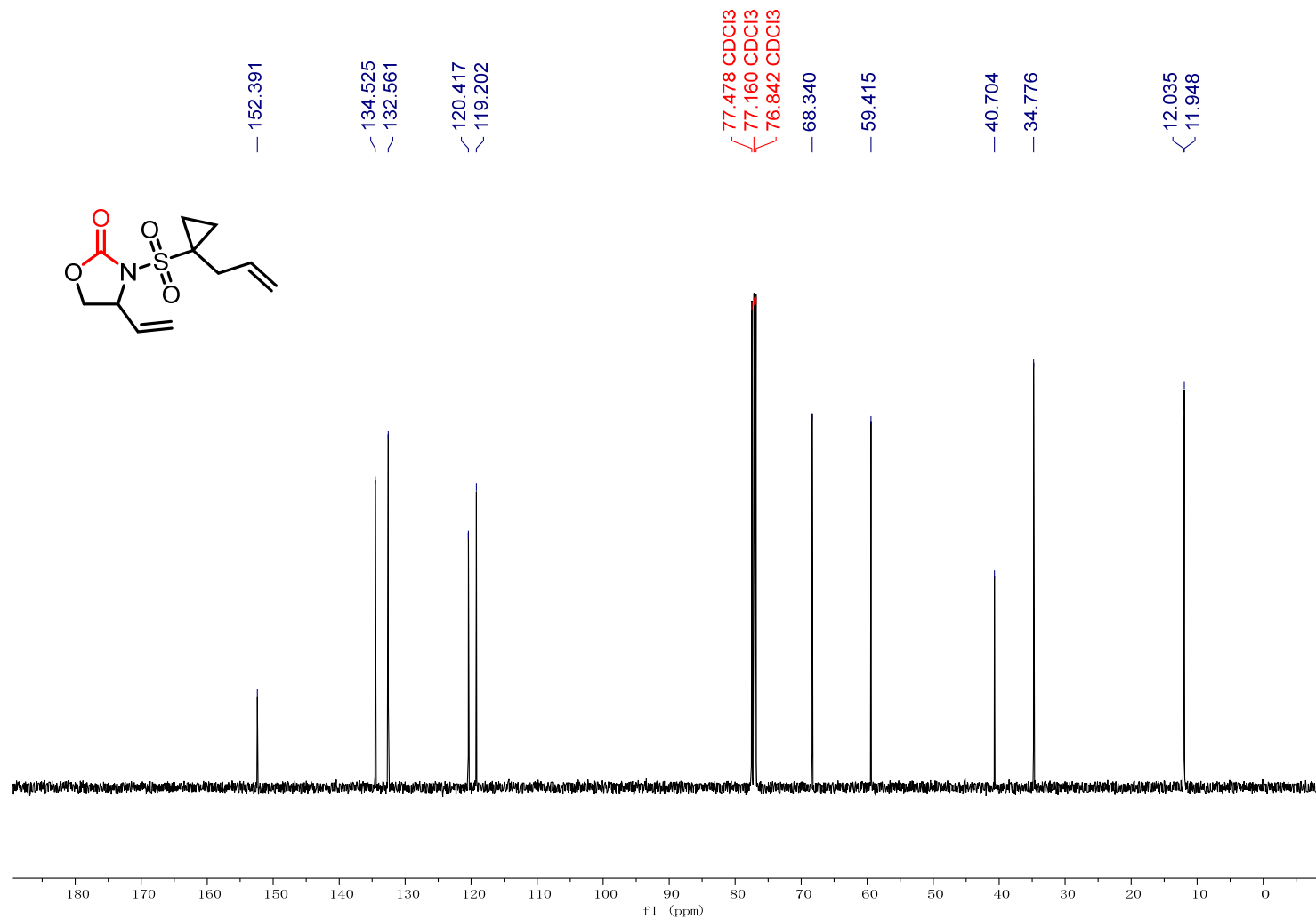
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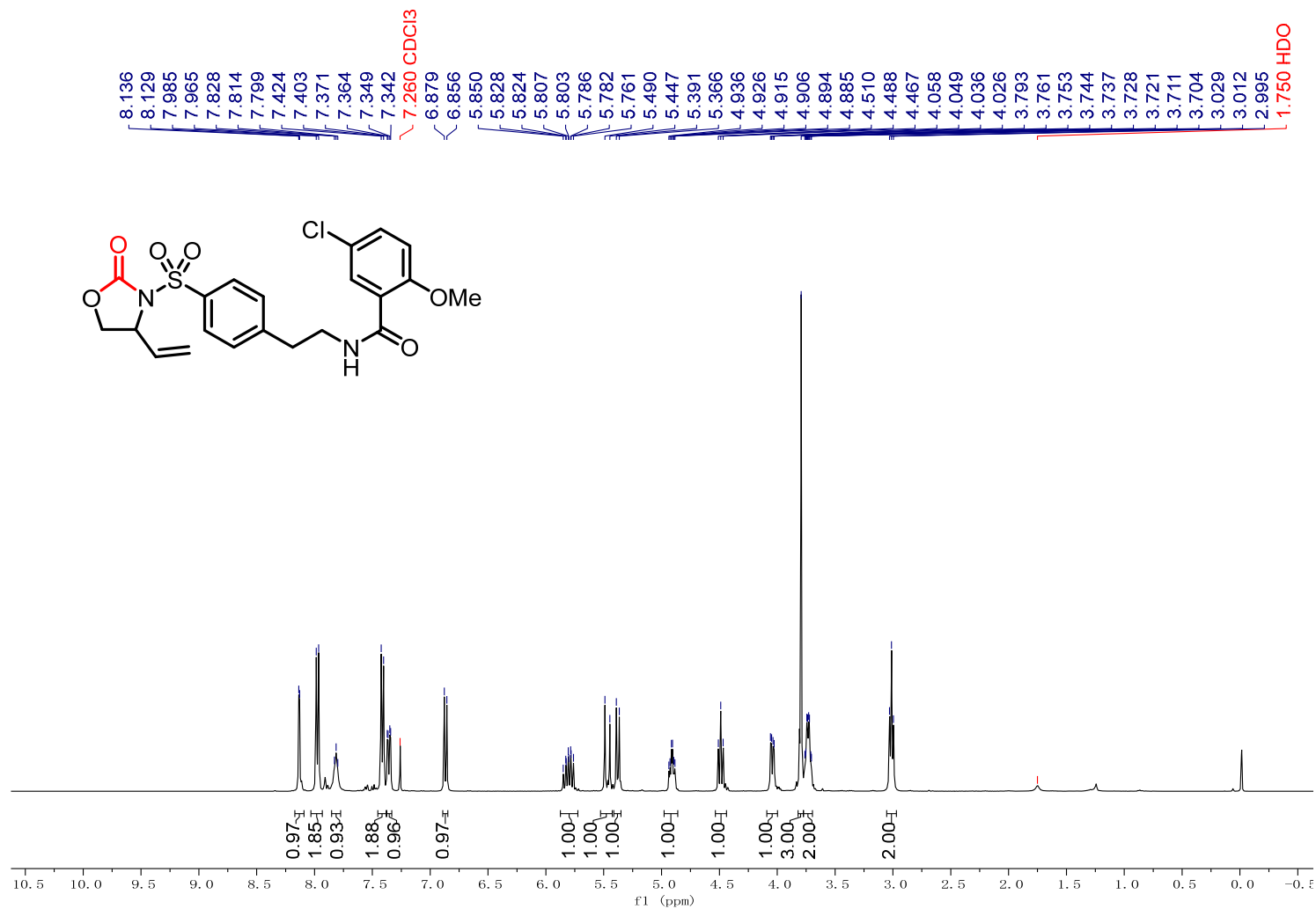
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-((1-allylcyclopropyl)sulfonyl)-4-vinylloxazolidin-2-one 3p



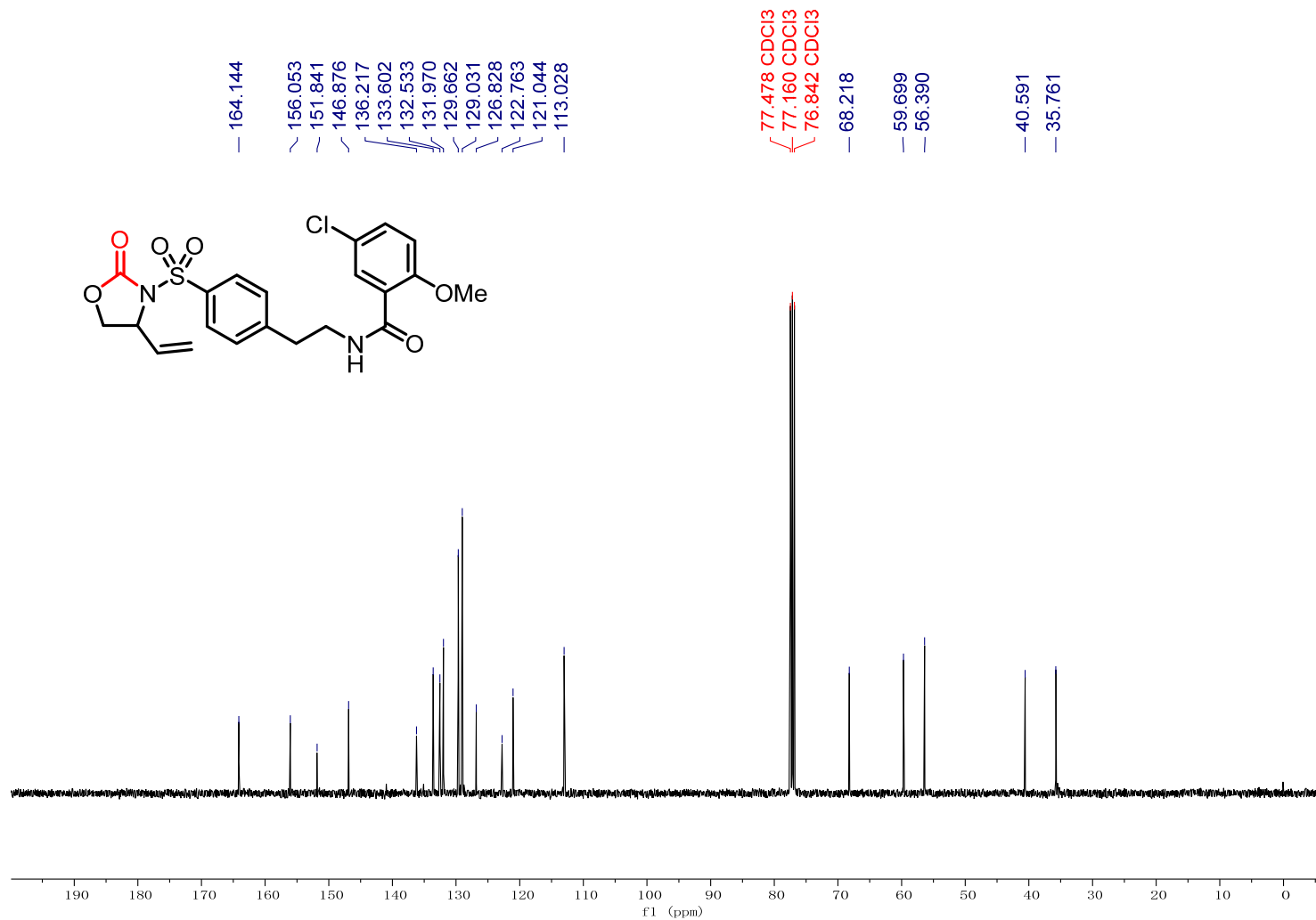
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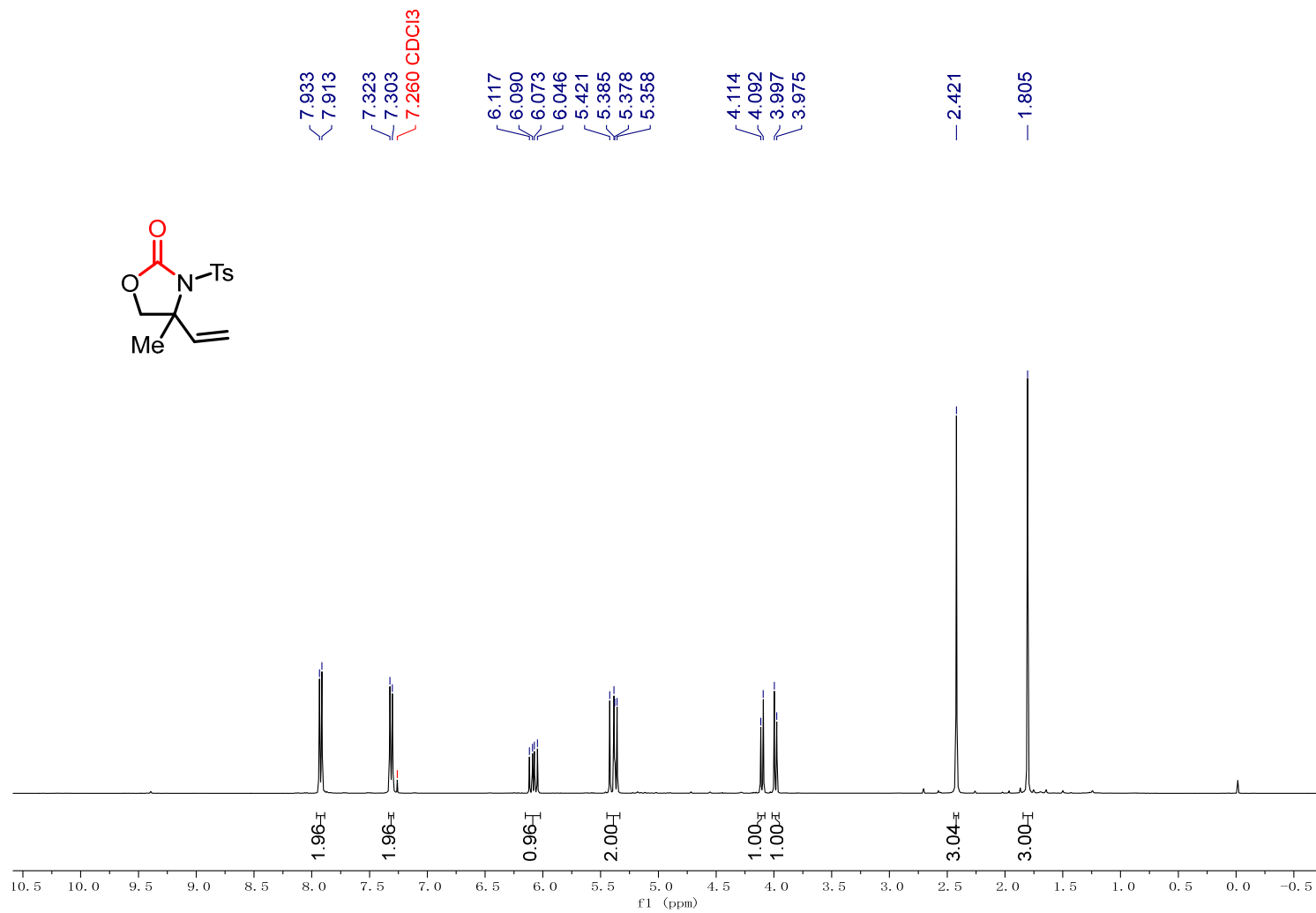
¹H NMR (400 MHz, CDCl₃) Spectrum of 5-chloro-2-methoxy-N-(4-((2-oxo-4-vinylloxazolidin-3-yl)sulfonyl)phenethyl)benzamide 3q



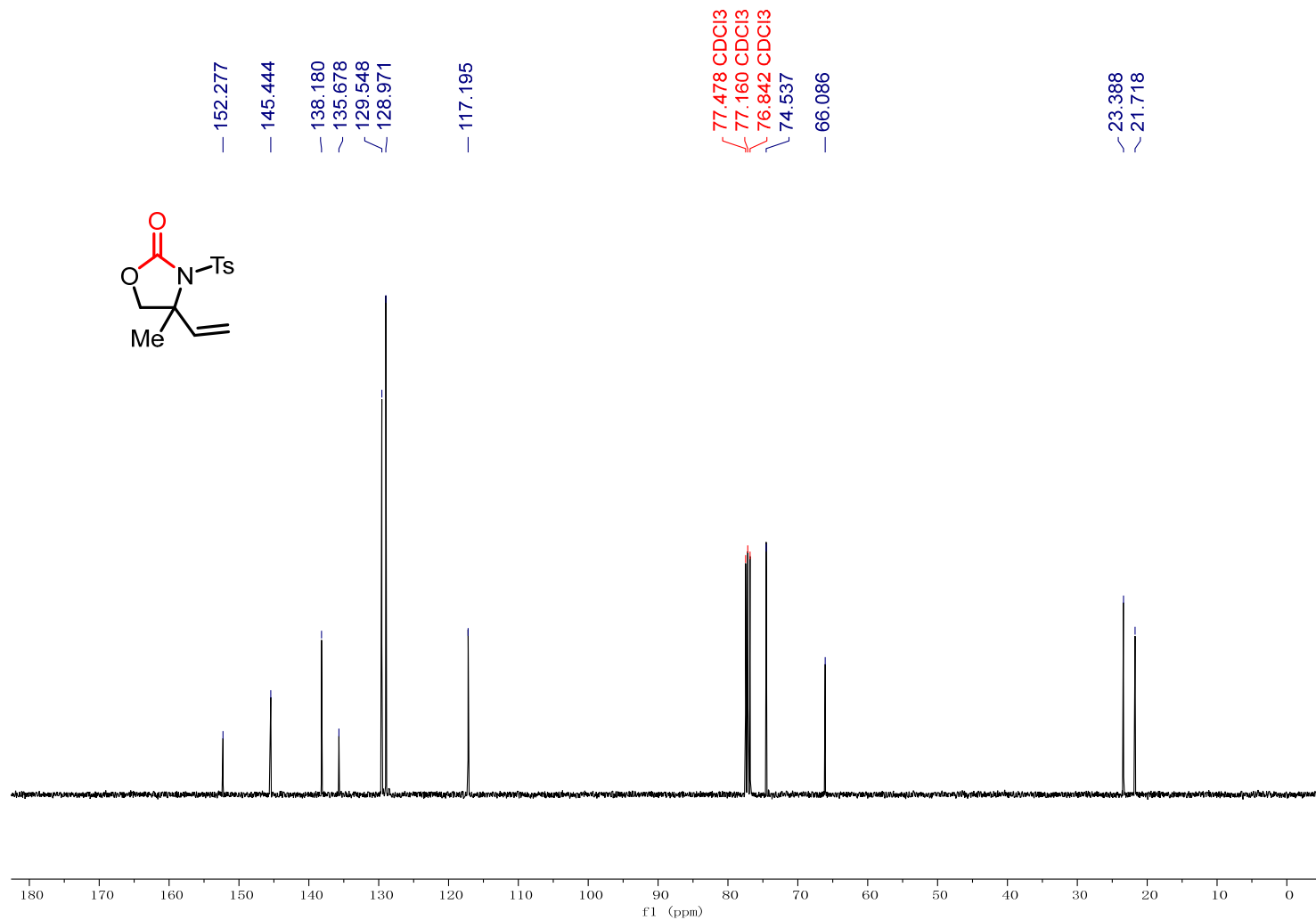
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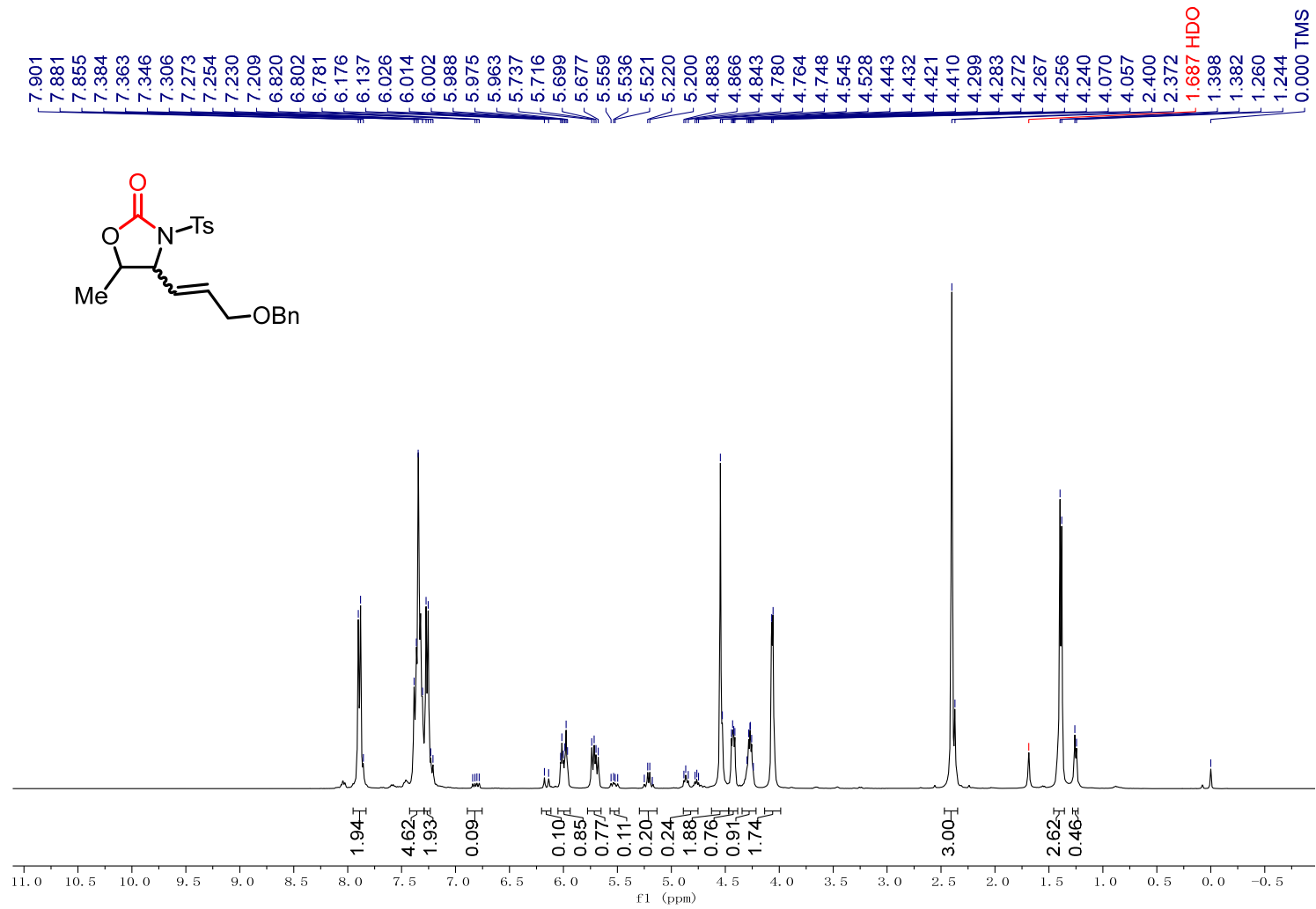
¹H NMR (400 MHz, CDCl₃) Spectrum of 4-methyl-3-tosyl-4-vinylazolidin-2-one 3r



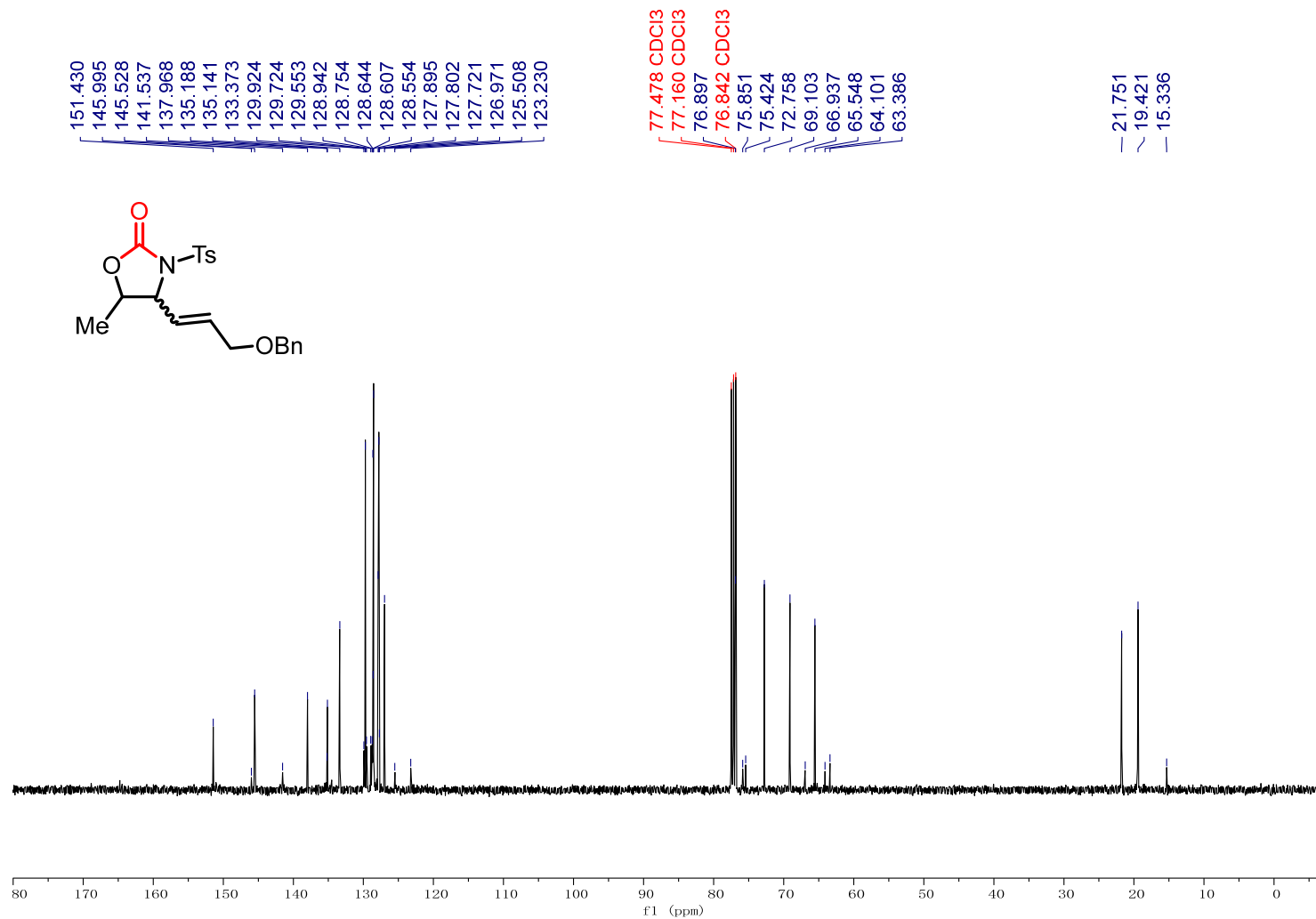
¹³C NMR (100 MHz, CDCl₃) Spectrum of 4-methyl-3-tosyl-4-vinylloxazolidin-2-one 3r



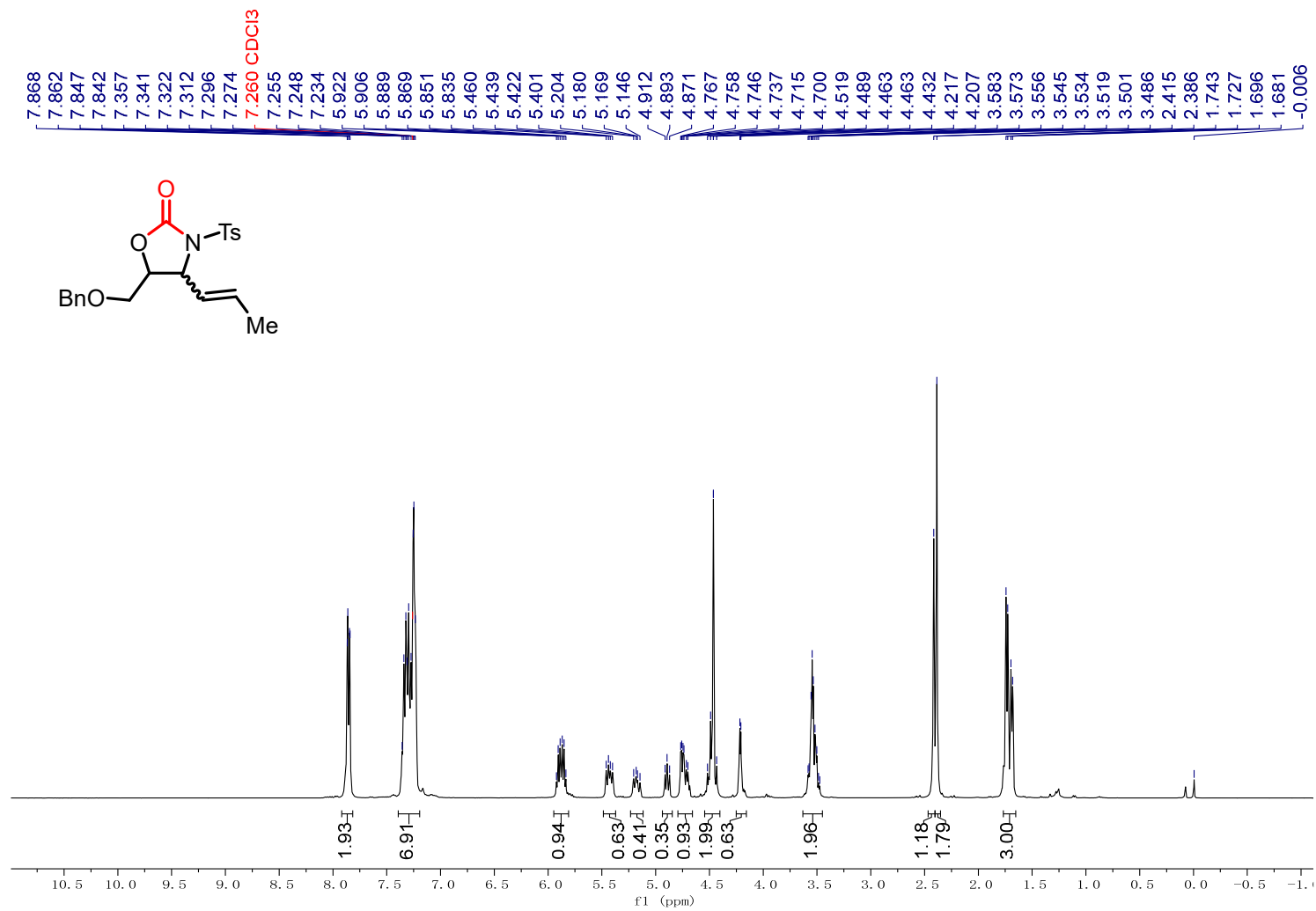
¹H NMR (400 MHz, CDCl₃) Spectrum of (E)-4-(3-(benzyloxy)prop-1-en-1-yl)-5-methyl-3-tosyloxazolidin-2-one 3s



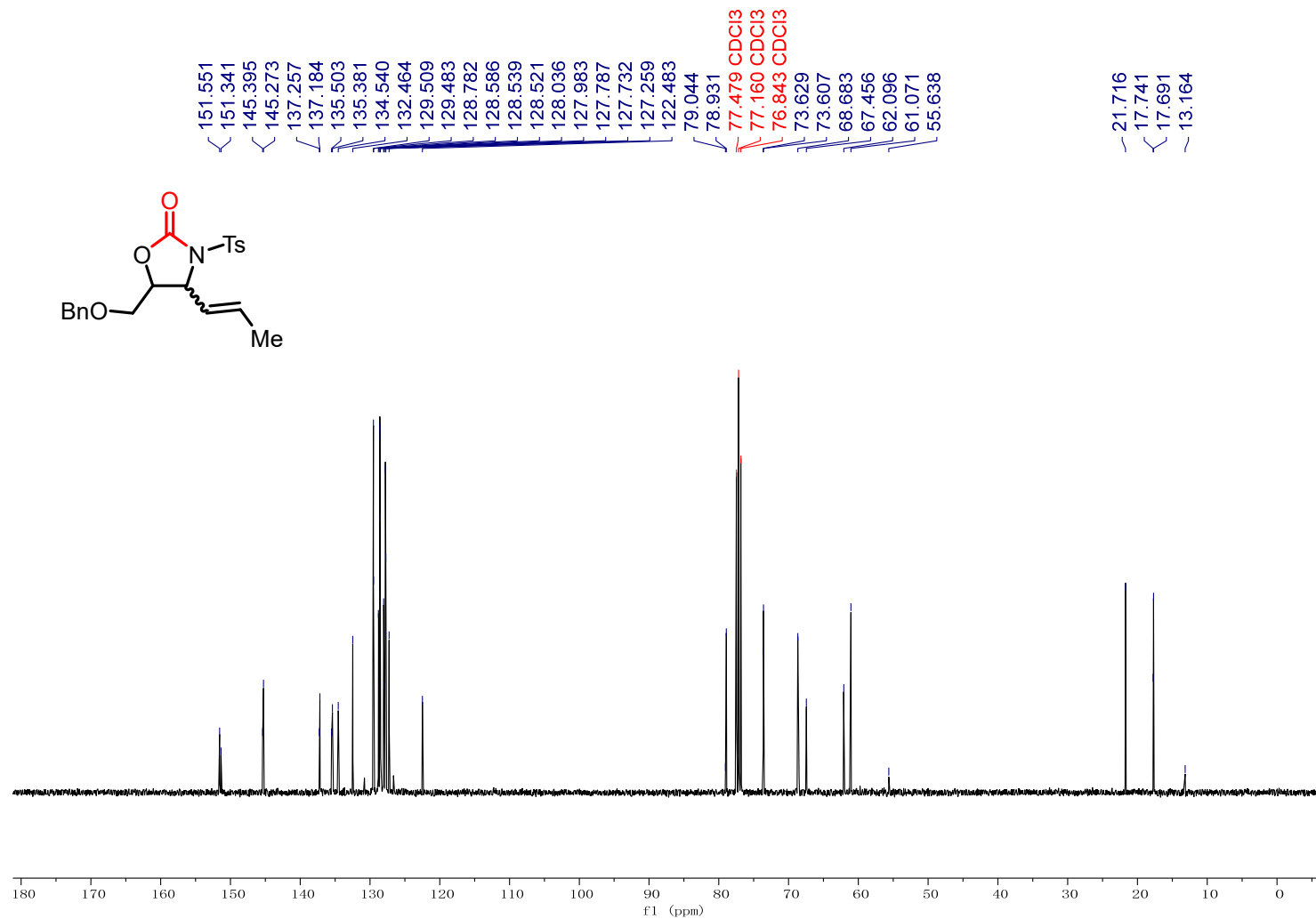
¹³C NMR (100 MHz, CDCl₃) Spectrum of (*E*)-4-(3-(benzyloxy)prop-1-en-1-yl)-5-methyl-3-tosyloxazolidin-2-one 3s



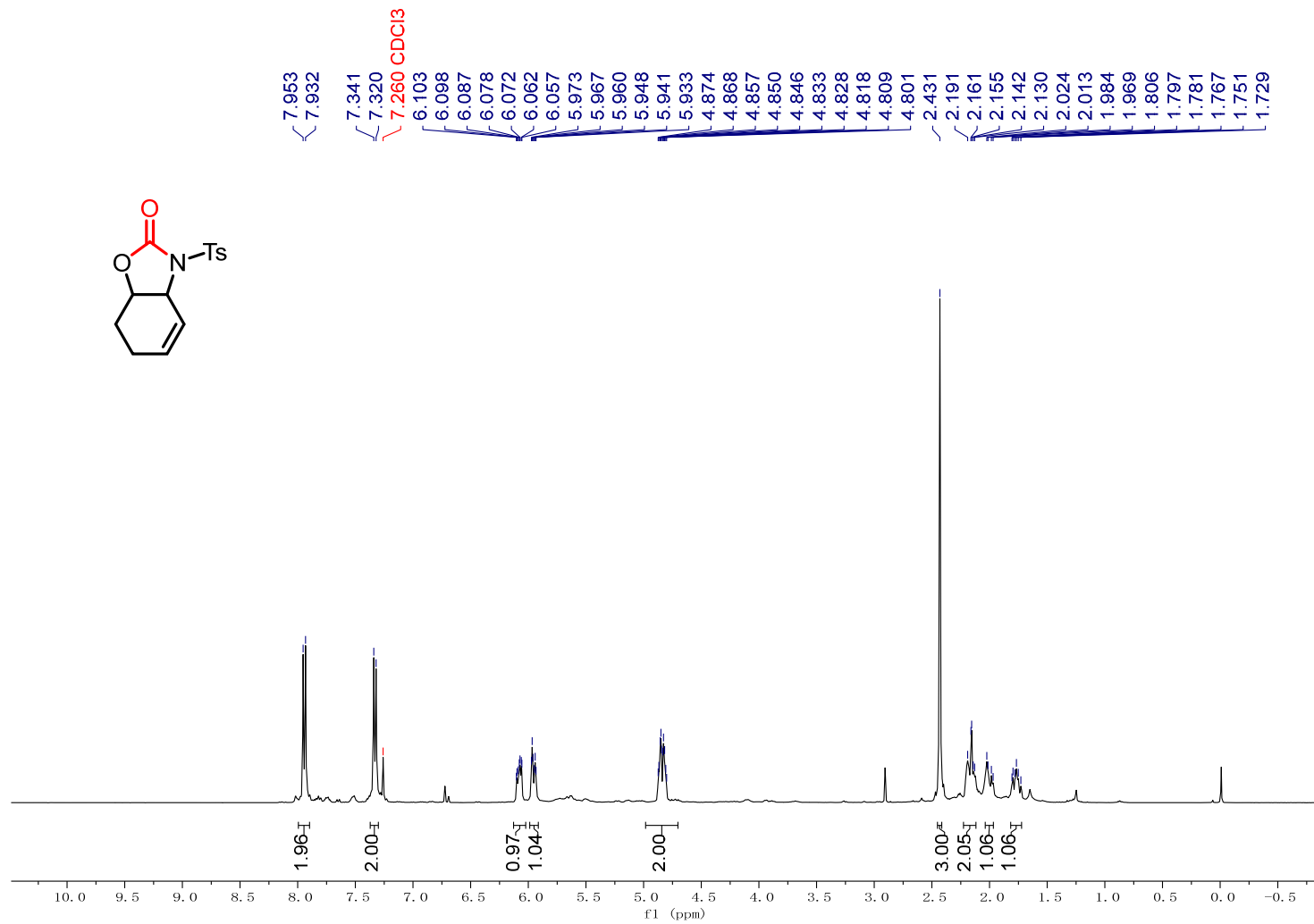
¹H NMR (400 MHz, CDCl₃) Spectrum of (*E*)-5-((benzyloxy)methyl)-4-(prop-1-en-1-yl)-3-tosyloxazolidin-2-one 3t



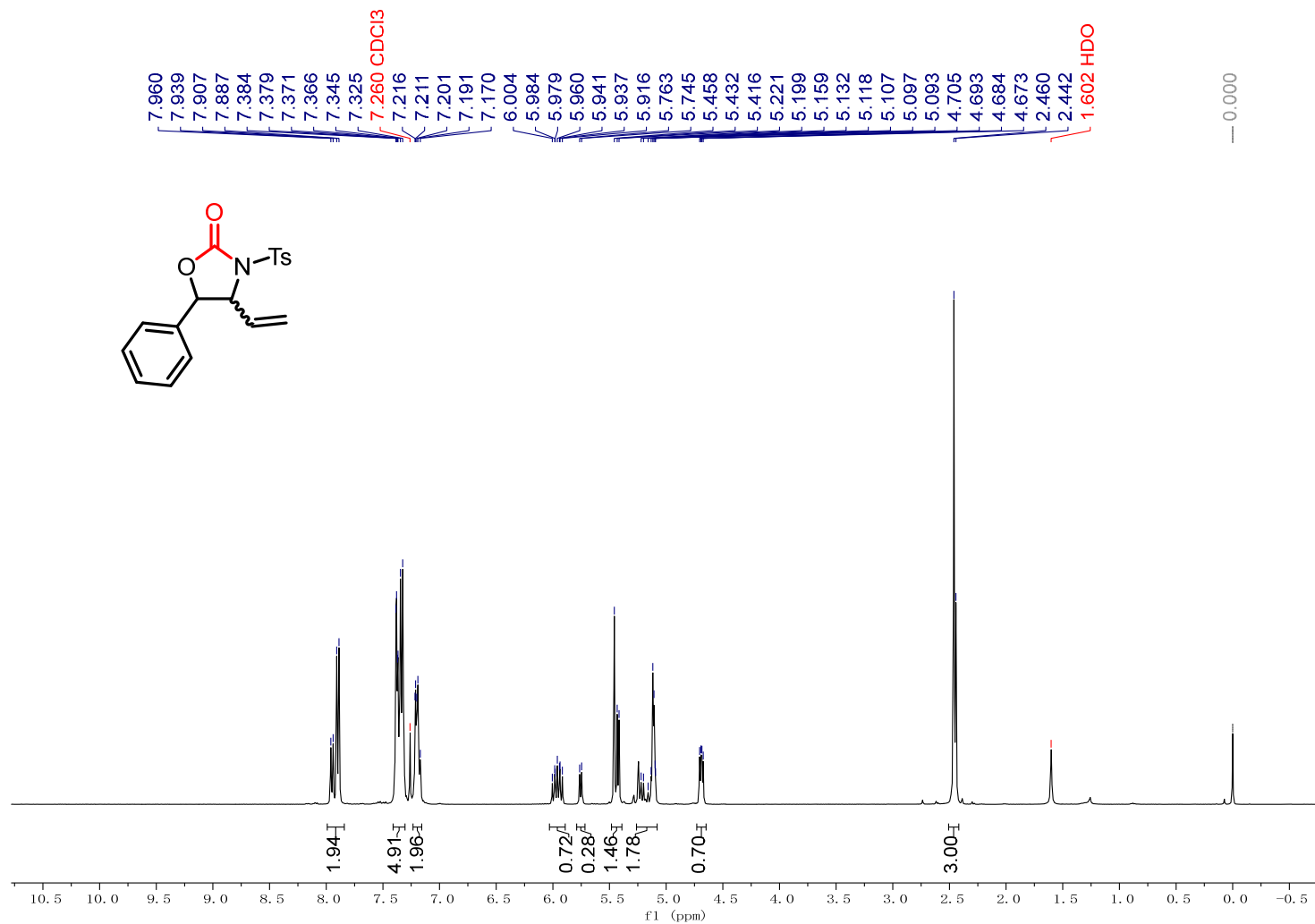
¹³C NMR (100 MHz, CDCl₃) Spectrum of (*E*)-5-((benzyloxy)methyl)-4-(prop-1-en-1-yl)-3-tosyloxazolidin-2-one 3t



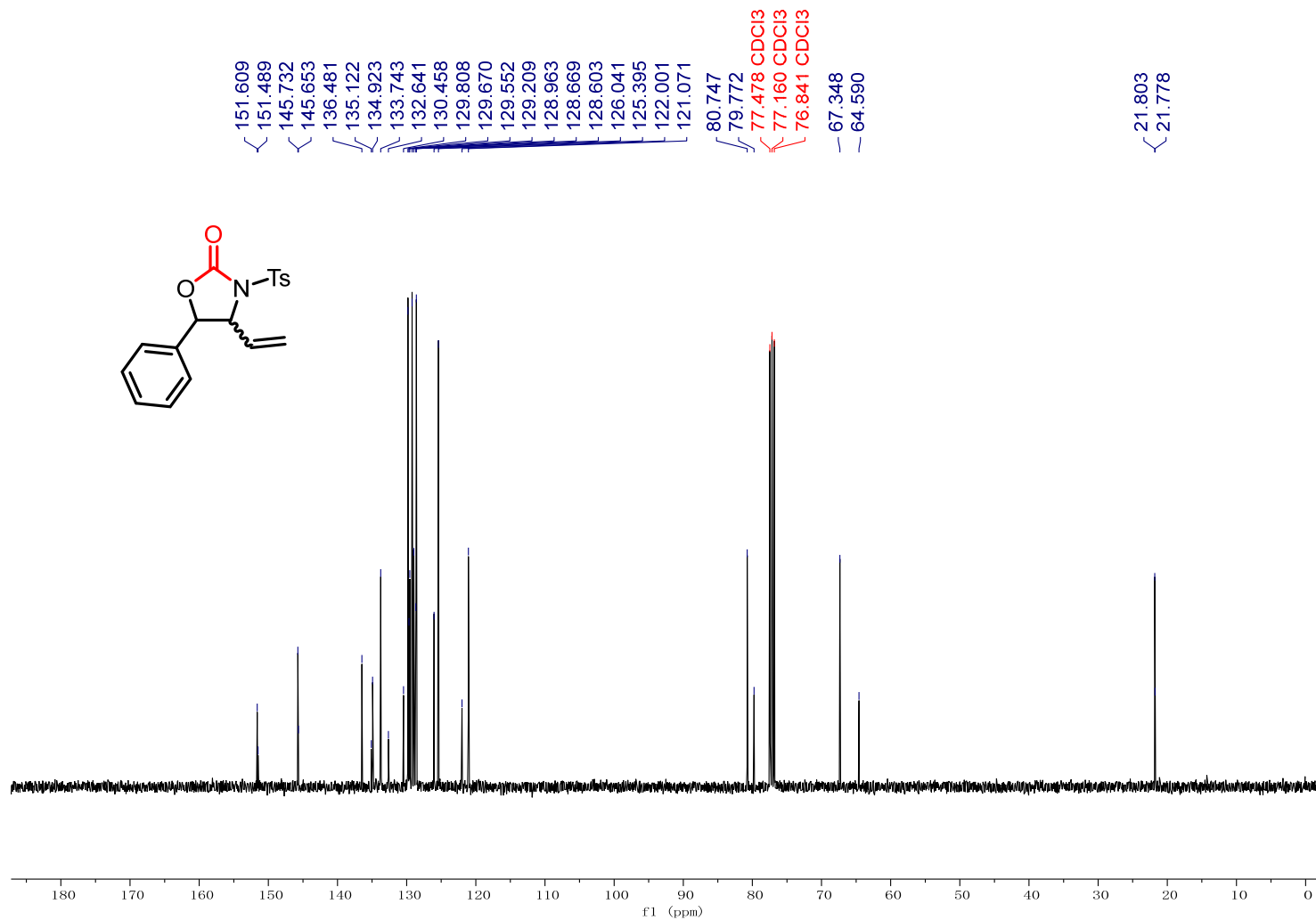
¹H NMR (400 MHz, CDCl₃) Spectrum of 3-tosyl-3a,6,7,7a-tetrahydrobenzo[d]oxazol-2(3H)-one 3u



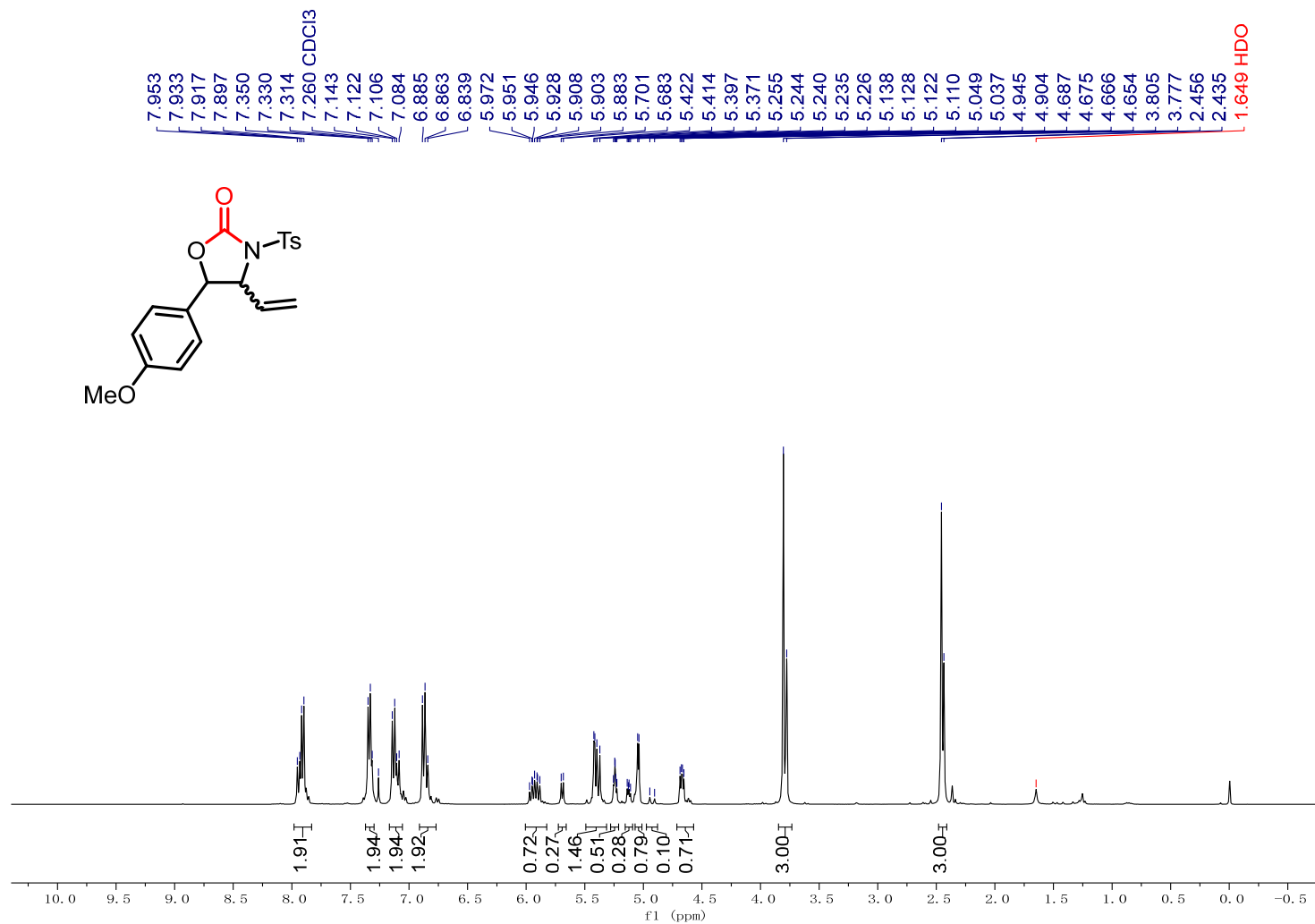
¹H NMR (400 MHz, CDCl₃) Spectrum of 5-phenyl-3-tosyl-4-vinylloxazolidin-2-one 3v



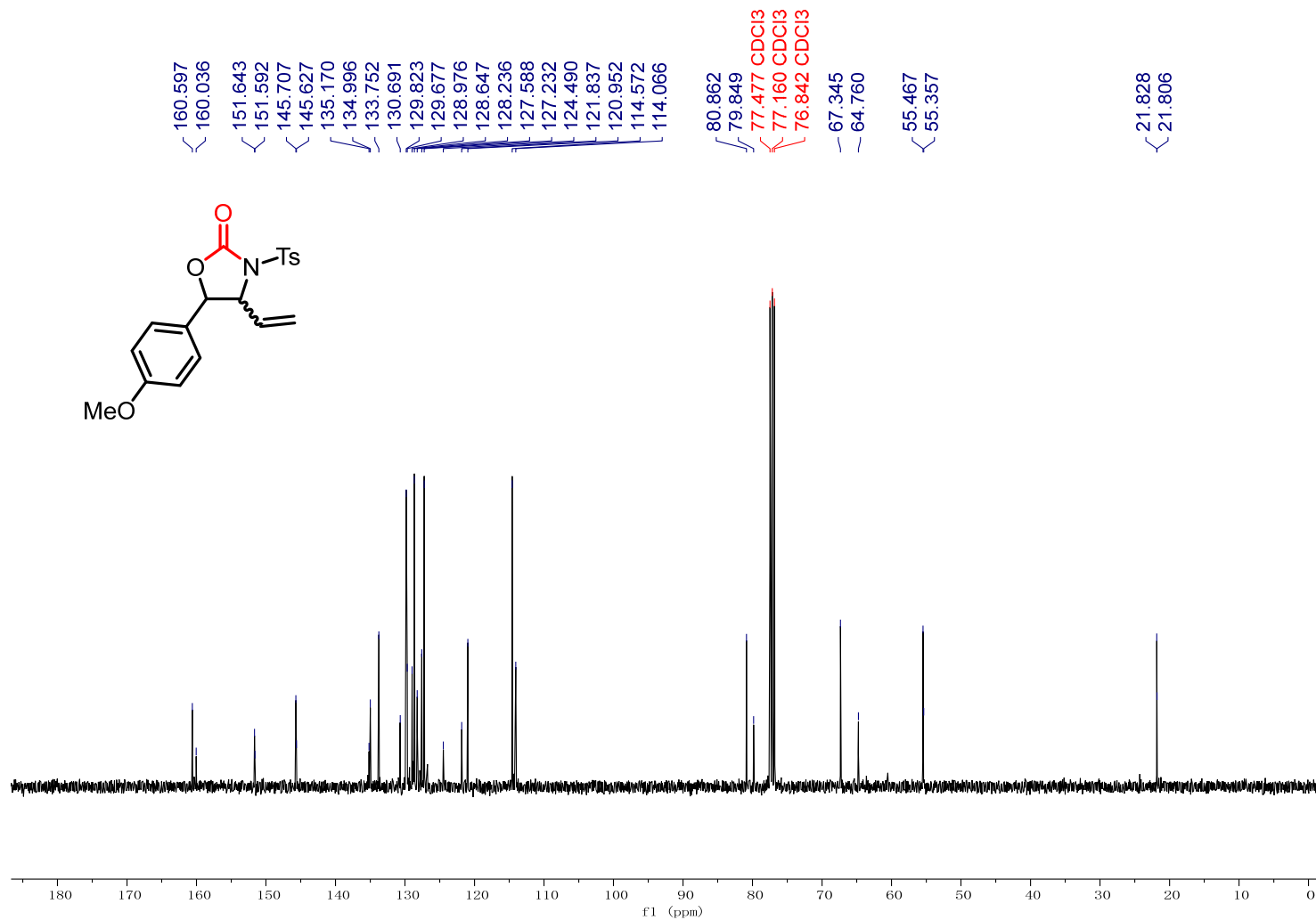
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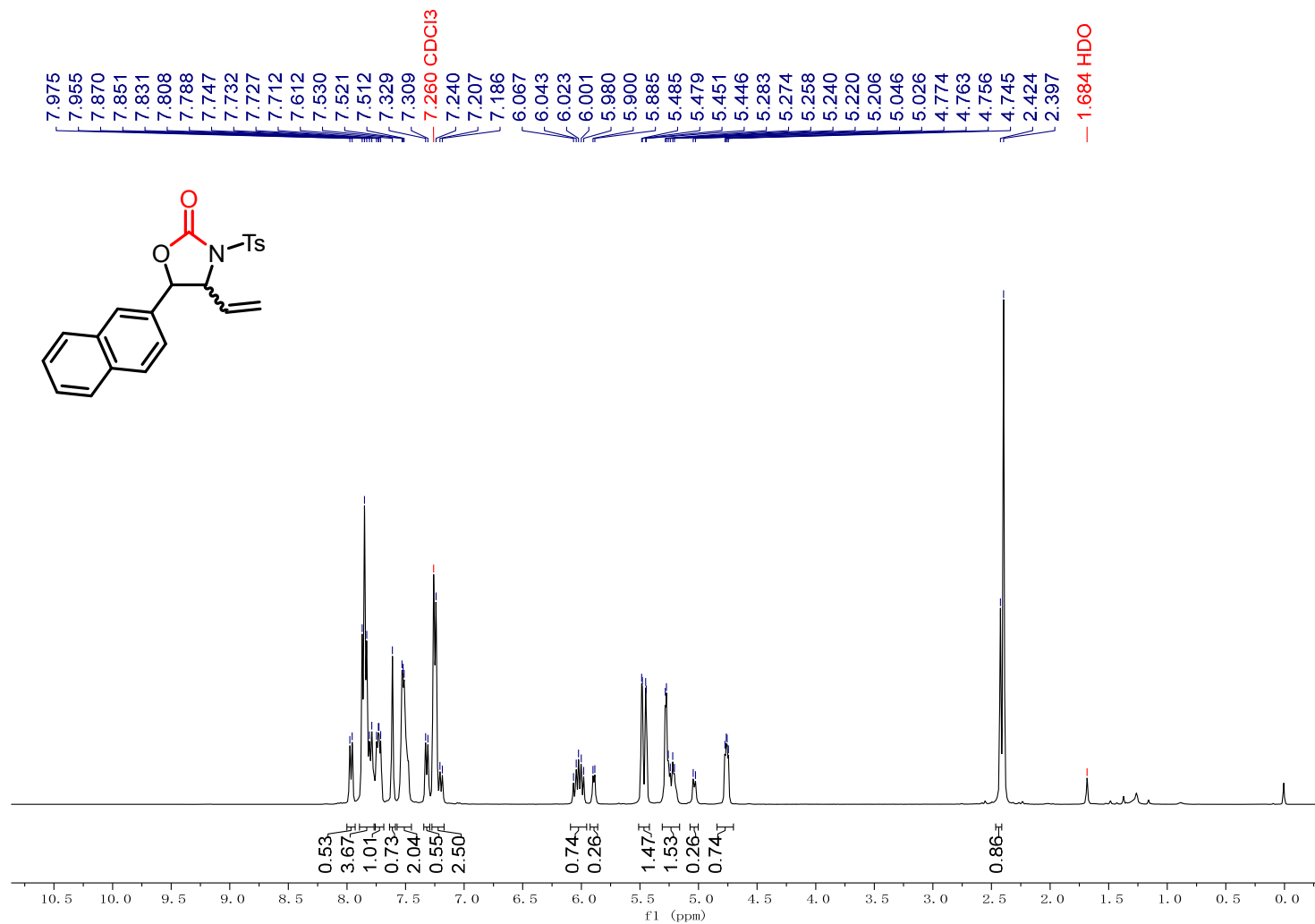
¹H NMR (400 MHz, CDCl₃) Spectrum of 5-(4-methoxyphenyl)-3-tosyl-4-vinylloxazolidin-2-one 3w



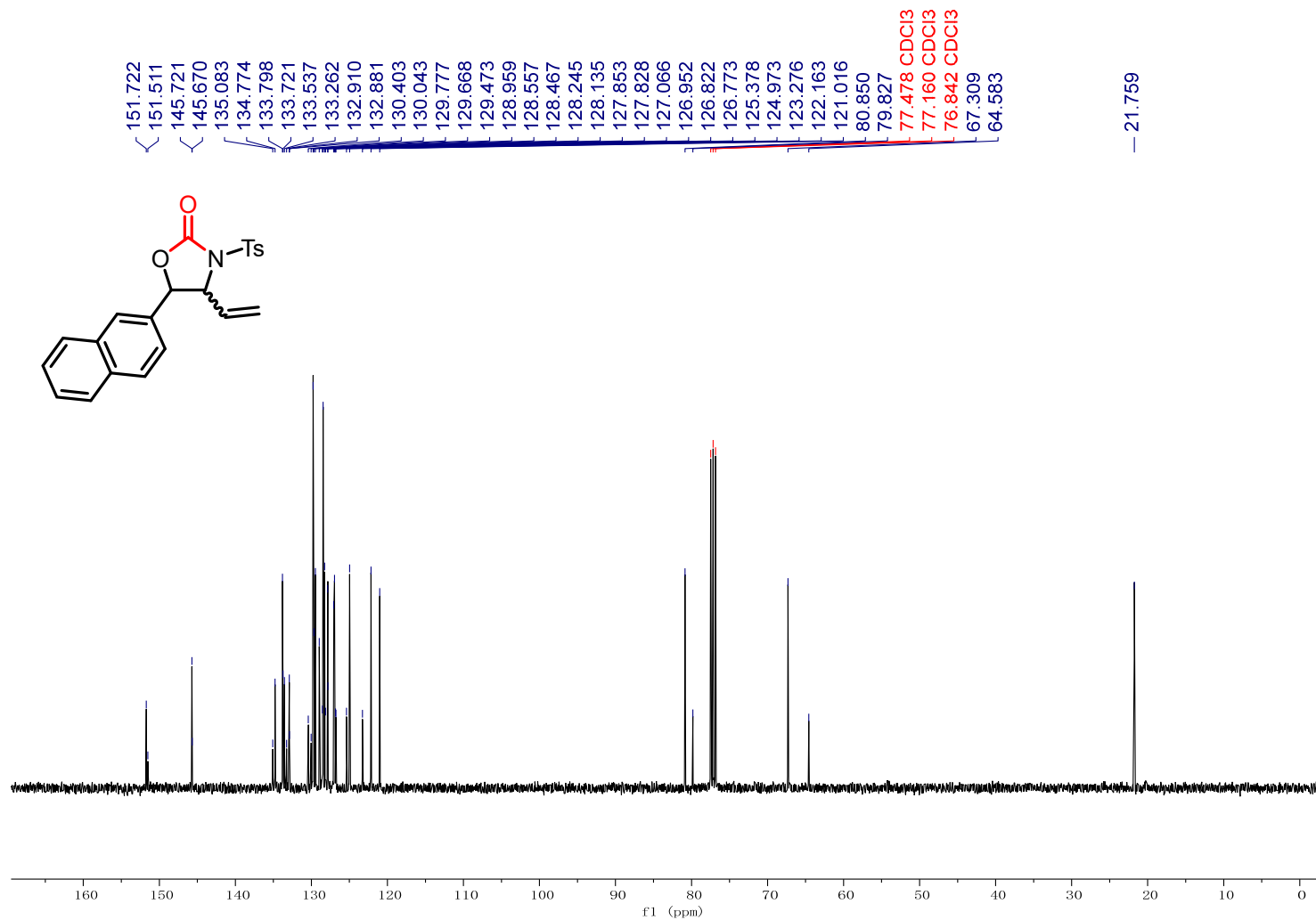
¹³C NMR (100 MHz, CDCl₃) Spectrum of 5-(4-methoxyphenyl)-3-tosyl-4-vinylloxazolidin-2-one 3w



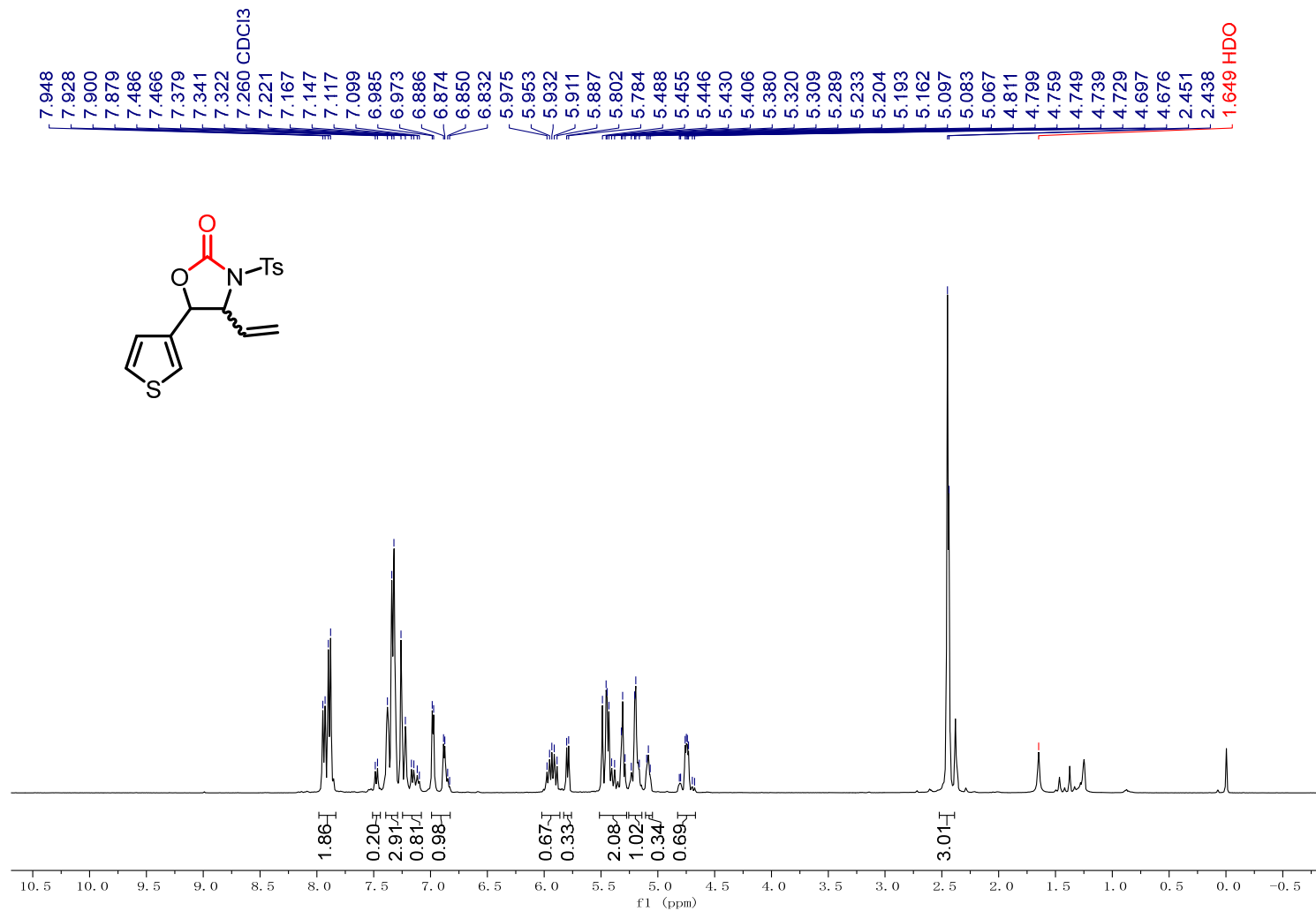
¹H NMR (400 MHz, CDCl₃) Spectrum of 5-(naphthalen-2-yl)-3-tosyl-4-vinyloxazolidin-2-one 3x



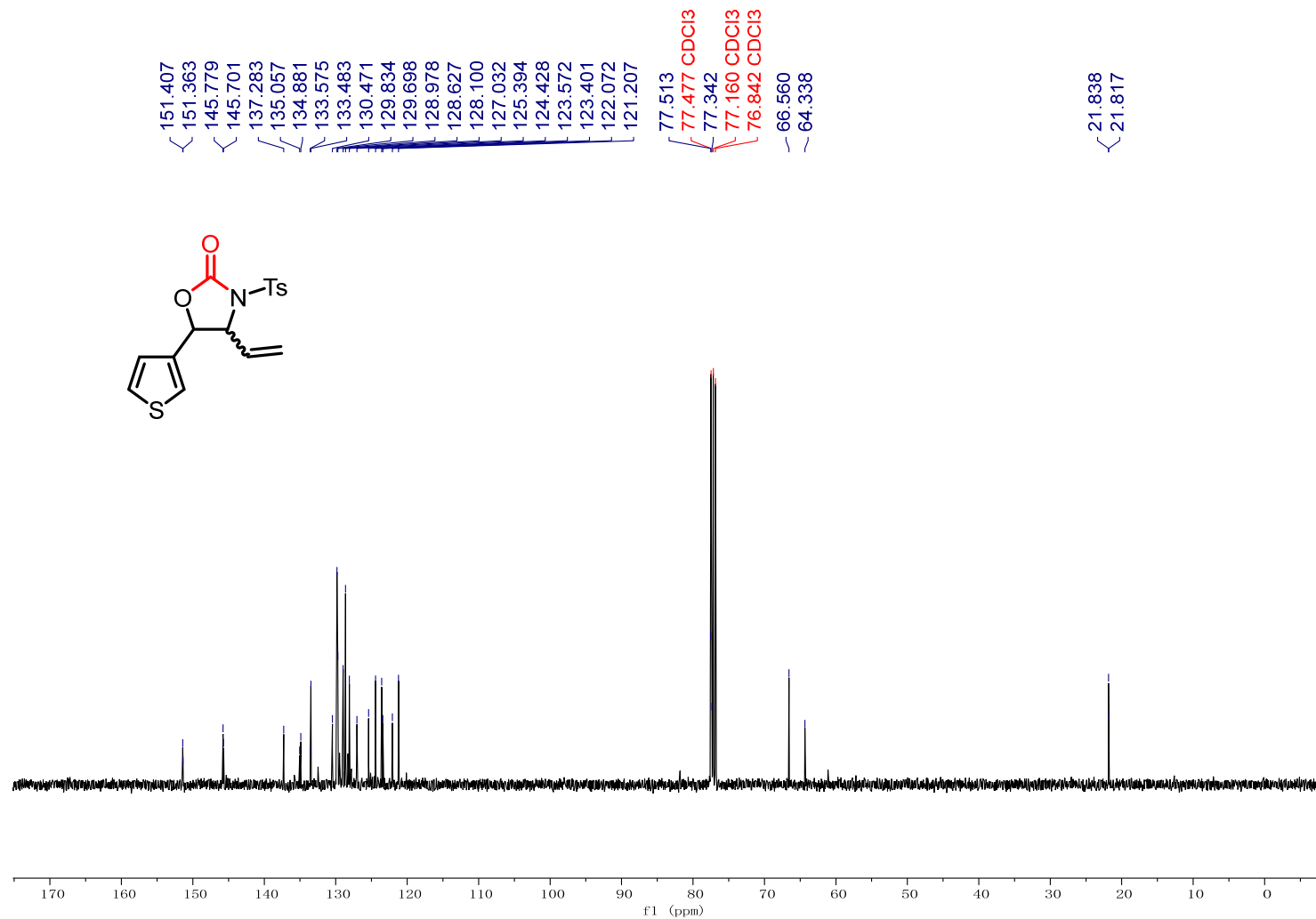
¹³C NMR (100 MHz, CDCl₃) Spectrum of 5-(naphthalen-2-yl)-3-tosyl-4-vinylloxazolidin-2-one 3x



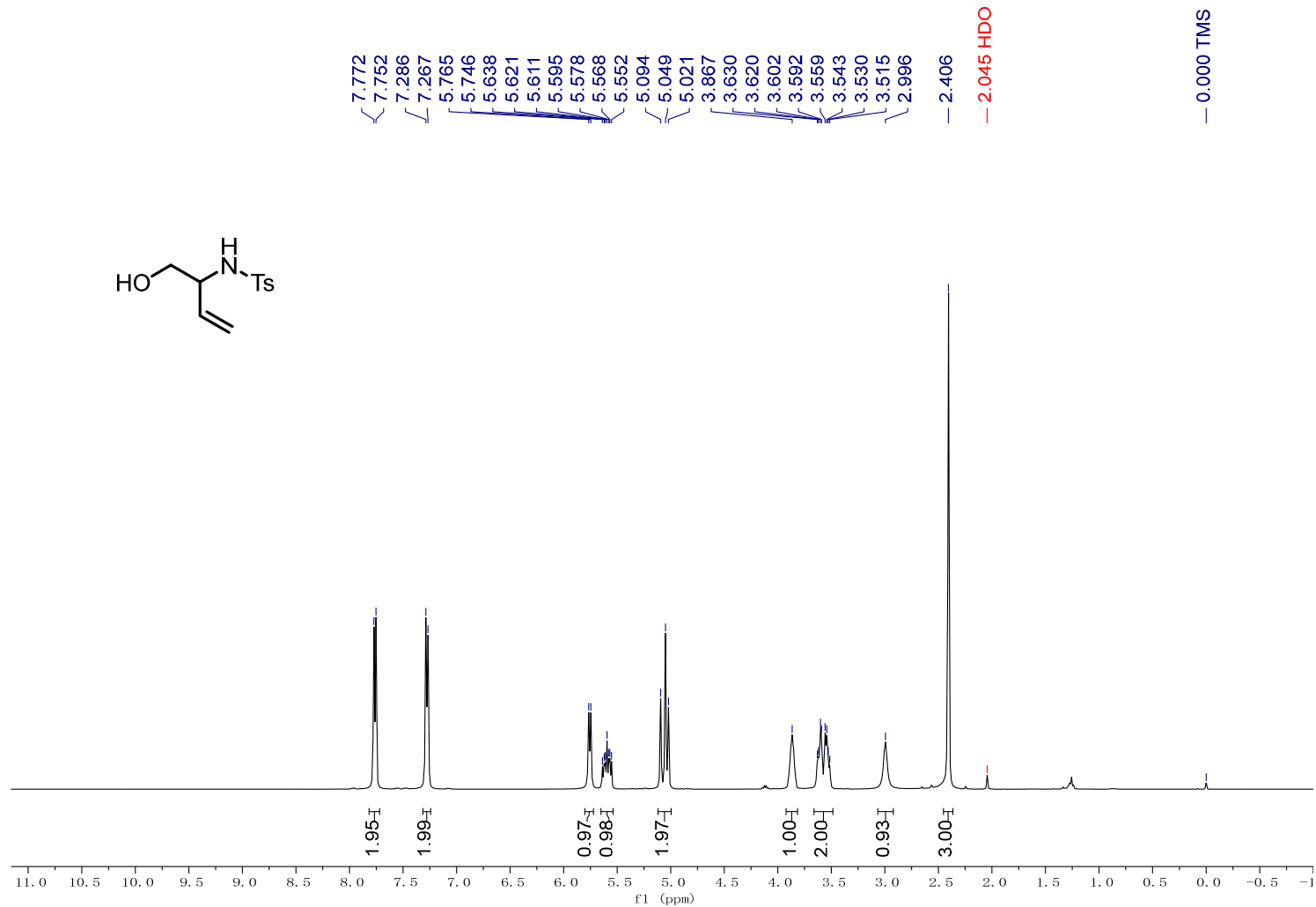
¹H NMR (400 MHz, CDCl₃) Spectrum of 5-(thiophen-3-yl)-3-tosyl-4-vinylloxazolidin-2-one 3y



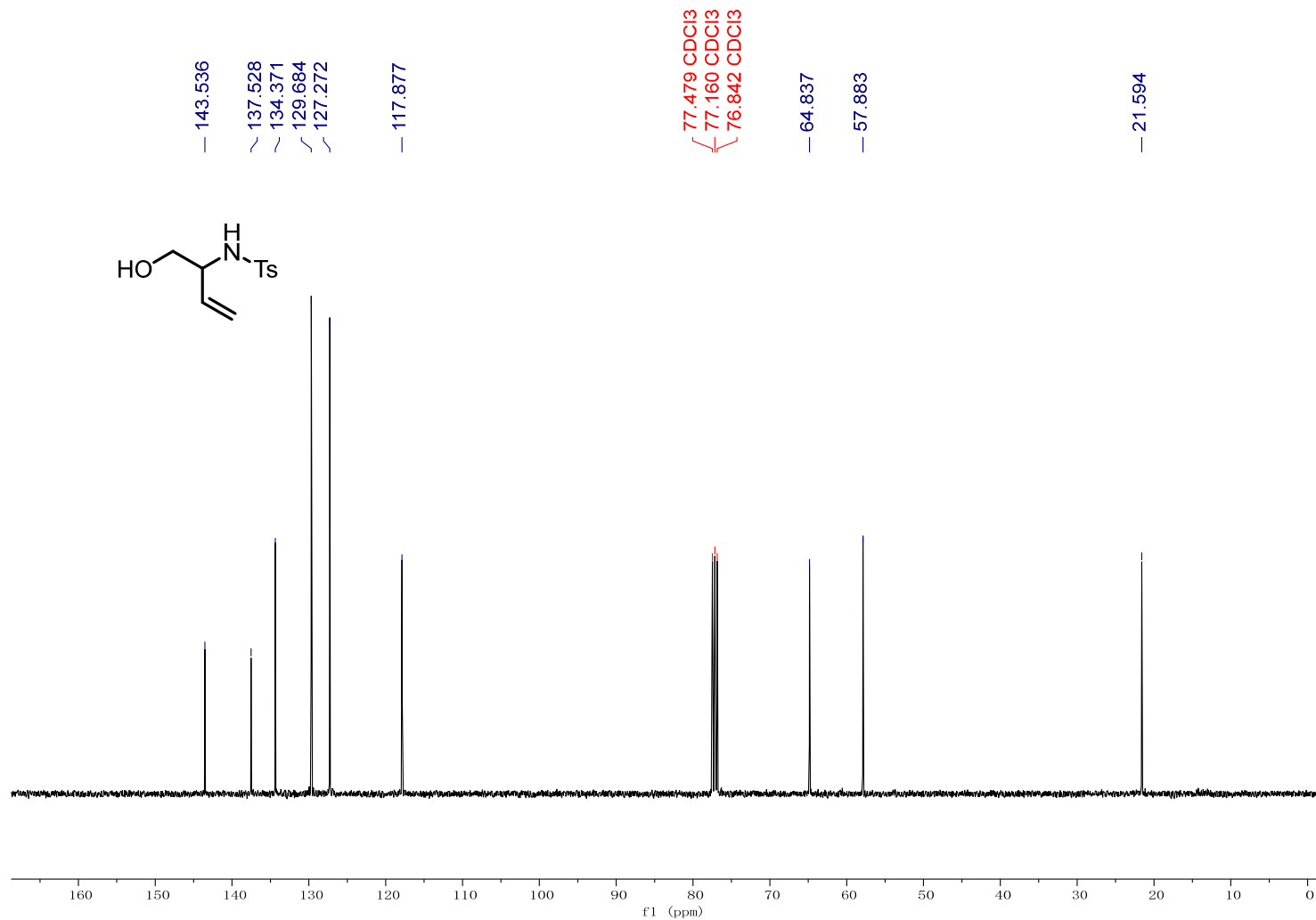
¹³C NMR (100 MHz, CDCl₃) Spectrum of 5-(thiophen-3-yl)-3-tosyl-4-vinyloxazolidin-2-one 3y



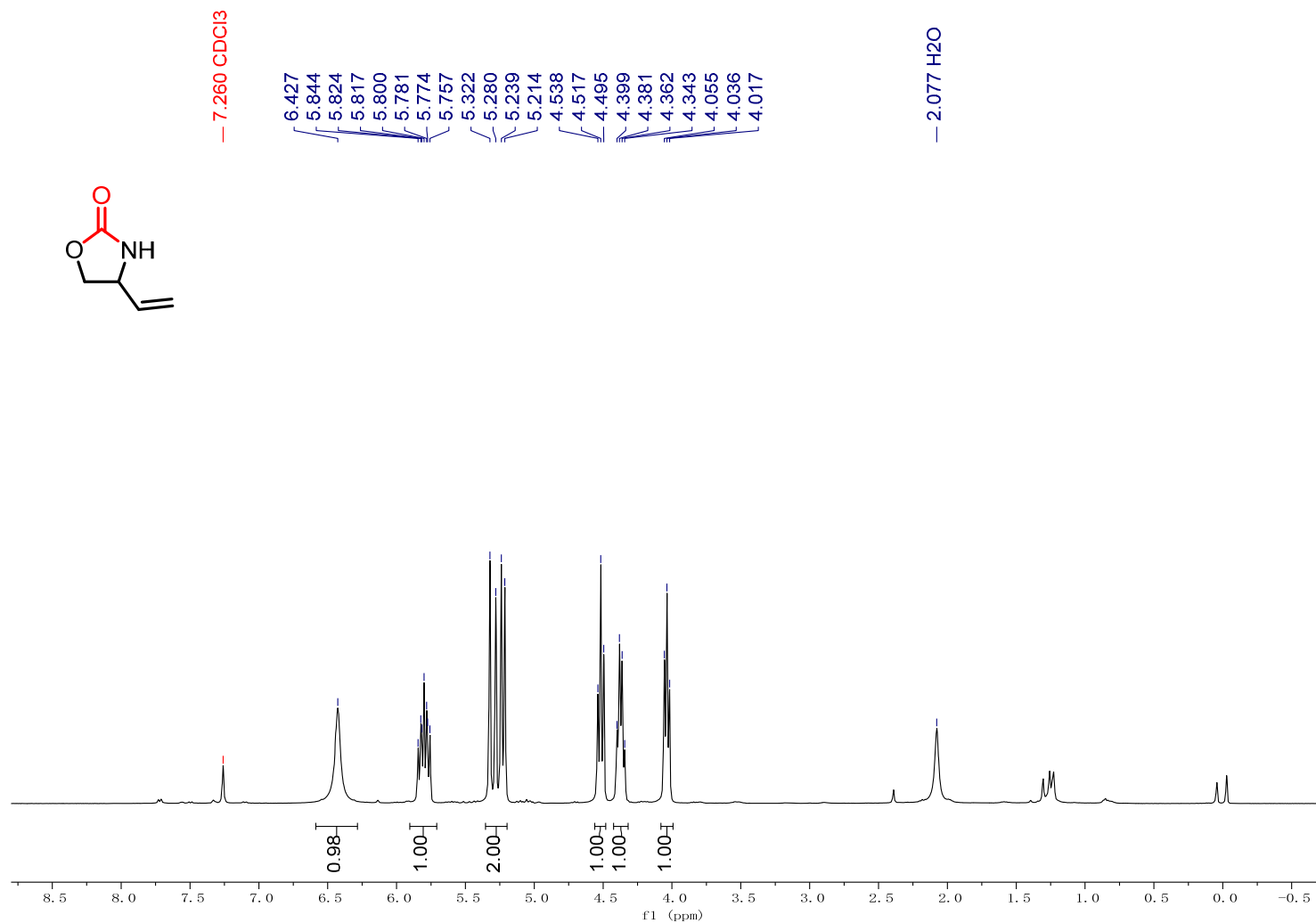
¹H NMR (400 MHz, CDCl₃) Spectrum of *N*-(1-hydroxybut-3-en-2-yl)-4-methylbenzenesulfonamide 4



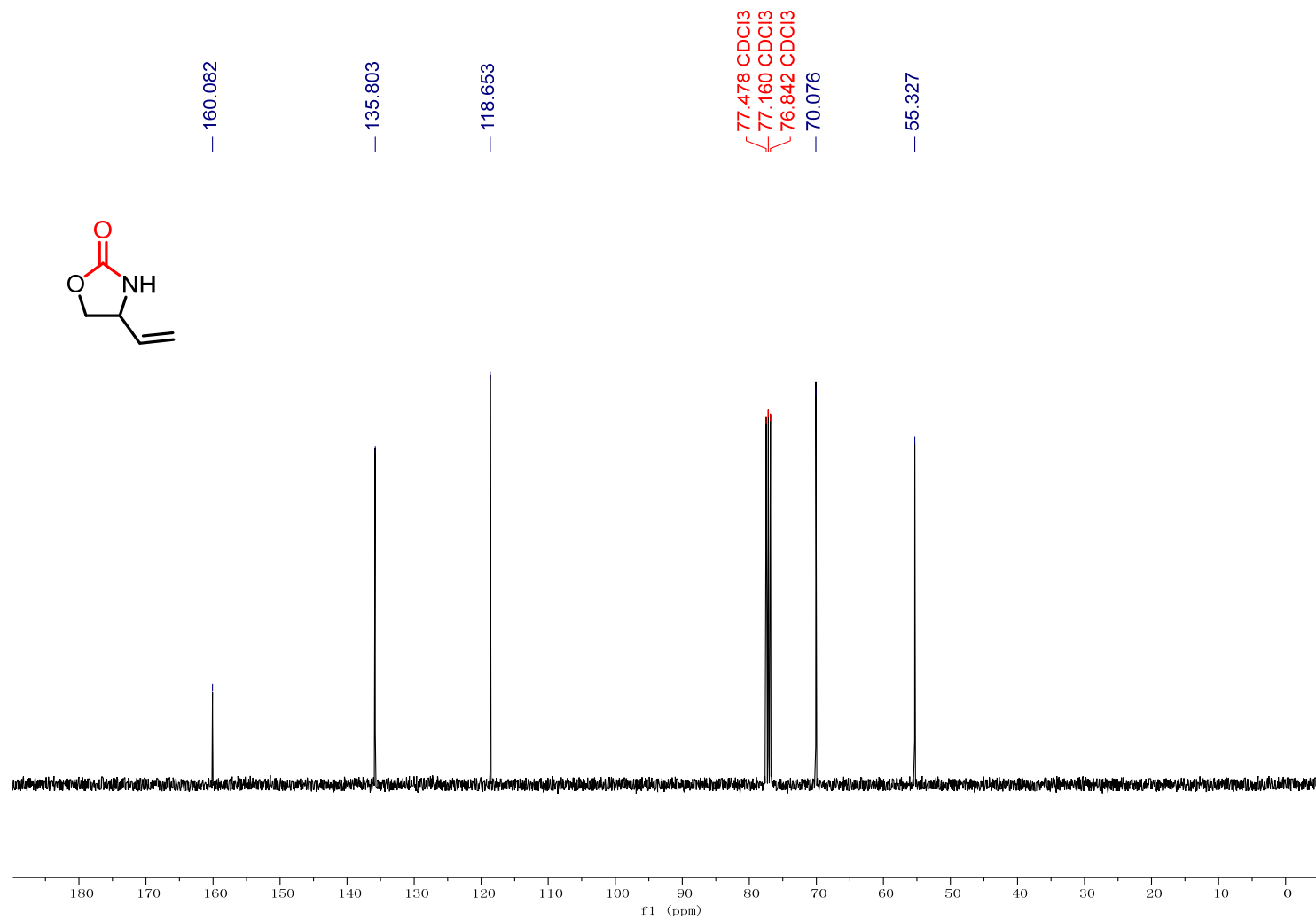
¹³C NMR (100 MHz, CDCl₃) Spectrum of *N*-(1-hydroxybut-3-en-2-yl)-4-methylbenzenesulfonamide 4



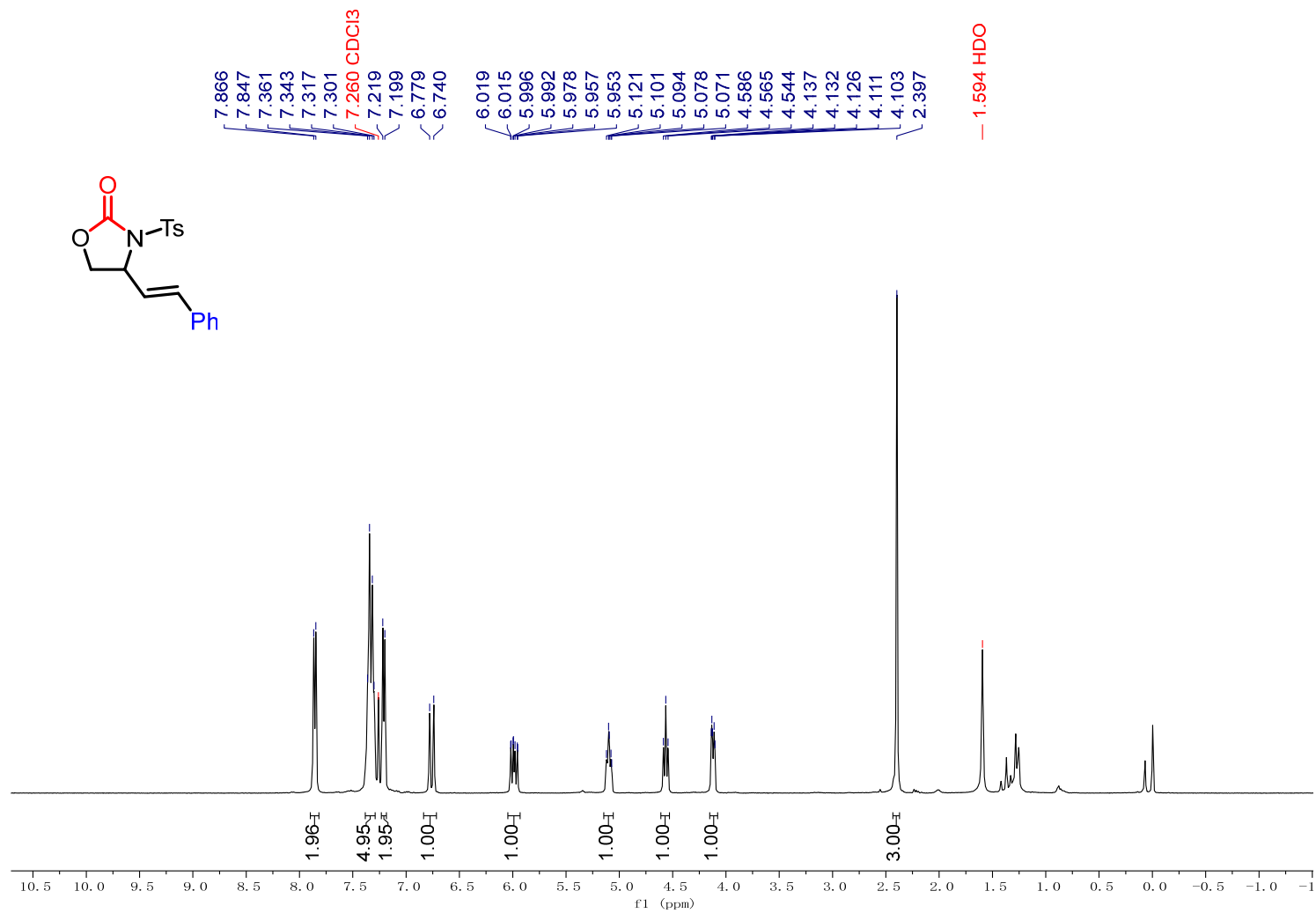
¹H NMR (400 MHz, CDCl₃) Spectrum of 4-vinyloxazolidin-2-one 5



¹³C NMR (100 MHz, CDCl₃) Spectrum of 4-vinyloxazolidin-2-one 5



¹H NMR (400 MHz, CDCl₃) Spectrum of (*E*)-4-styryl-3-tosyloxazolidin-2-one 6



¹³C NMR (100 MHz, CDCl₃) Spectrum of (*E*)-4-styryl-3-tosyloxazolidin-2-one **6**

