

Highly Selective Intramolecular Addition of C-N and S-N Bonds to Alkynes Catalyzed by Palladium: A Practical Access to Two Distinct Functional Indoles

Supporting Information

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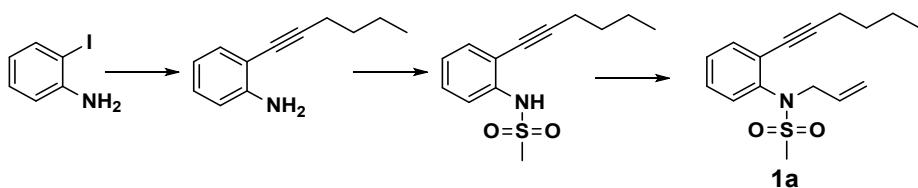
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[‡]These authors contributed equally to this work.

Preparation and Characterization data of the materials.....	2-7
¹ H and ¹³ C NMR Spectra.....	8-45

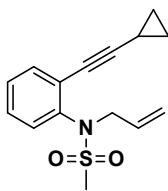
Preparation and Characterization data of the materials

Procedure for the preparation of **1a**

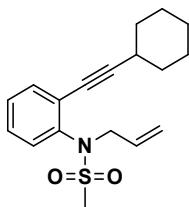


To a solution of 2-iodoaniline (1.0 g, 4.57 mmol) in DMF (5.0 ml) and Et₃N (5.0 ml) was added PdCl₂(PPh₃)₂ (160.2 mg, 0.228 mmol), CuI (87.0 mg, 0.457 mmol), and 1-hexyne (5.48 mmol, 634 µl), and the resulting mixture was stirred at room temperature for 6 hours. Then water was added and the reaction mixture was extracted with ethyl acetate. The organic extracts were washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified to give 2-(Hex-1-yn-1-yl)aniline (720 mg, 91.0%). To a solution of 2-(Hex-1-yn-1-yl)aniline (720 mg, 4.16 mmol) in pyridine (5.0 ml) was added methanesulfonyl chloride (4.57 mmol, 354 µl) dropwise at 0 °C. After addition, the mixture was allowed to stir at room temperature for 5 hours, then 1 mol/L HCl was added and the reaction mixture was extracted with ethyl acetate. The organic extracts were washed with saturated aqueous NaHCO₃ solution, dried over Na₂SO₄ and concentrated. The residue was purified to give *N*-(2-(Hex-1-yn-1-yl)phenyl)methanesulfonamide (960 mg, 91.9%). To a solution of *N*-(2-(Hex-1-yn-1-yl)phenyl)methanesulfonamide (960 mg, 3.82 mmol) in anhydrous DMF (6.0 ml) was added NaH (110.0 mg, 4.58 mmol) by portion at 0 °C, 30 minutes later, allyl bromide (5.73 mmol, 495.1 µL) was added dropwise at 0 °C. The resulting mixture was stirred at room temperature for 8 hours, and water was added and the reaction mixture was extracted with ethyl acetate, the organic extracts were washed with brine, dried over Na₂SO₄ and concentrated. The residue was purified to give *N*-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1a**) (900 mg, 80.9%). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.43 (m, 1H), 7.37-7.33 (m, 1H), 7.32-7.25 (m, 2H), 5.9-5.79 (m, 1H), 5.15-5.05 (m, 2H), 4.35 (d, *J* = 6.3 Hz, 2H), 3.01 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.64-1.58 (m, 2H), 1.53-1.44 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); EI-MS (*m/z*): 291 (M⁺).

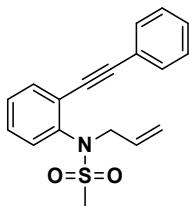
Compounds 1b-1o were prepared following the similar procedure carried out for 1a.



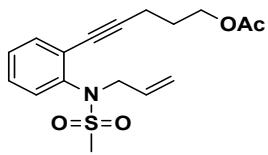
N-Allyl-*N*-(2-(cyclopropylethynyl)phenyl)methanesulfonamide (**1b**): ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.40 (m, 1H), 7.34-7.29 (m, 1H), 7.29-7.22 (m, 2H), 5.92-5.76 (m, 1H), 5.15-5.06 (m, 2H), 4.32 (d, $J = 6.4$ Hz, 2H), 3.01 (s, 3H), 1.53-1.44 (m, 1H), 0.96-0.89 (m, 2H), 0.83-0.78 (m, 2H); EI-MS (m/z): 275 (M^+).



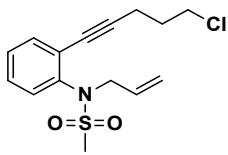
N-Allyl-*N*-(2-(cyclohexylethynyl)phenyl)methanesulfonamide (**1c**): ^1H NMR (400 MHz, CDCl_3) δ 7.45 (dd, $J = 6.8, 2.5$ Hz, 1H), 7.35 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.31-7.25 (m, 2H), 5.93-5.77 (m, 1H), 5.17-5.04 (m, 2H), 4.37 (d, $J = 6.3$ Hz, 2H), 3.01 (s, 3H), 2.67-2.56 (m, 1H), 1.99-1.87 (m, 2H), 1.82-1.70 (m, 2H), 1.60-1.47 (m, 3H), 1.42-1.31 (m, 3H); EI-MS (m/z): 317 (M^+).



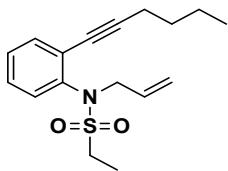
N-Allyl-*N*-(2-(phenylethynyl)phenyl)methanesulfonamide (**1d**): ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.54 (m, 3H), 7.44-7.31 (m, 6H), 5.98-5.86 (m, 1H), 5.22-5.07 (m, 2H), 4.46 (d, $J = 6.5$ Hz, 2H), 3.06 (s, 3H); EI-MS (m/z): 311 (M^+).



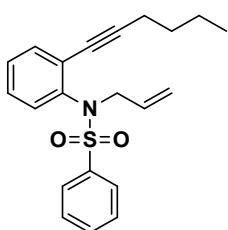
5-(2-(*N*-Allylmethylsulfonamido)phenyl)pent-4-yn-1-yl acetate (**1e**): ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.43 (m, 1H), 7.34-7.26 (m, 3H), 5.91-5.79 (m, 1H), 5.17-5.06 (m, 2H), 4.33 (d, $J = 6.5$ Hz, 2H), 4.22 (t, $J = 6.3$ Hz, 2H), 3.00 (s, 3H), 2.56 (t, $J = 7.2$ Hz, 2H), 2.07 (s, 3H), 2.00-1.92 (m, 2H); EI-MS (m/z): 335 (M^+).



N-Allyl-*N*-(2-(5-chloropent-1-yn-1-yl)phenyl)methanesulfonamide (**1f**): ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.44 (m, 1H), 7.36-7.26 (m, 3H), 5.91-5.79 (m, 1H), 5.16-5.06 (m, 2H), 4.32 (d, $J = 6.4$ Hz, 2H), 3.73 (t, $J = 6.2$ Hz, 2H), 3.01 (s, 3H), 2.67 (t, $J = 6.9$ Hz, 2H), 2.11-2.04 (m, 2H); EI-MS (m/z): 313 ($\text{M}^+, (\text{Cl}^{37})$), 311 ($\text{M}^+, (\text{Cl}^{35})$).

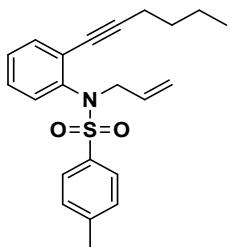


N-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)ethanesulfonamide (**1g**): ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.39 (m, 1H), 7.39-7.31 (m, 1H), 7.30-7.20 (m, 2H), 5.93-5.76 (m, 1H), 5.13-4.97 (m, 2H), 4.35 (d, $J = 6.5$ Hz, 2H), 3.12 (q, $J = 7.4$ Hz, 2H), 2.45 (t, $J = 7.1$ Hz, 2H), 1.64-1.56 (m, 2H), 1.52-1.44 (m, 2H), 1.40 (t, $J = 7.4$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H); EI-MS (m/z): 305 (M^+).

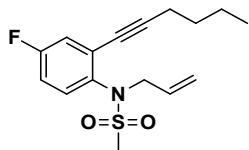


N-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)benzenesulfonamide (**1h**): ^1H NMR (400 MHz,

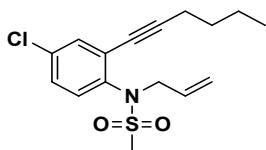
CDCl_3) δ 7.76-7.67 (m, 2H), 7.57-7.50 (m, 1H), 7.47-7.40 (m, 2H), 7.36-7.31 (m, 1H), 7.24-7.16 (m, 3H), 5.89-5.75 (m, 1H), 5.11-4.99 (m, 2H), 4.30 (d, $J = 6.4$ Hz, 2H), 2.11 (t, $J = 6.9$ Hz, 2H), 1.44-1.32 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H); EI-MS (m/z): 353 (M^+).



N-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1i**): ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.37-7.32 (m, 1H), 7.26-7.19 (m, 5H), 5.88-5.77 (m, 1H), 5.09-5.00 (m, 2H), 4.29 (d, $J = 6.4$ Hz, 2H), 2.41 (s, 3H), 2.14 (t, $J = 6.9$ Hz, 2H), 1.46-1.36 (m, 4H), 0.92 (t, $J = 7.1$ Hz, 3H); EI-MS (m/z): 367 (M^+).

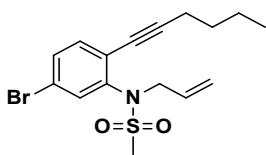


N-Allyl-*N*-(4-fluoro-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1j**): ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.23 (m, 1H), 7.12 (dd, $J = 8.8, 3.0$ Hz, 1H), 7.03-6.91 (m, 1H), 5.91-5.75 (m, 1H), 5.18-5.02 (m, 2H), 4.30 (d, $J = 5.7$ Hz, 2H), 3.00 (s, 3H), 2.45 (t, $J = 7.1$ Hz, 2H), 1.64-1.56 (m, 2H), 1.52-1.42 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); EI-MS (m/z): 309 (M^+).

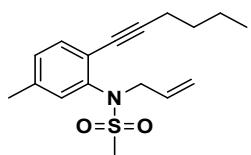


N-Allyl-*N*-(4-chloro-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1k**): ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.41 (m, 1H), 7.27-7.24 (m, 2H), 5.89-5.74 (m, 1H), 5.14-5.08 (m, 2H), 4.32 (d, $J = 6.4$ Hz, 2H), 3.00 (s, 3H), 2.46 (t, $J = 7.1$ Hz, 2H), 1.62-1.58 (m, 2H), 1.51-1.44 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); EI-MS (m/z): 327 (M^+).

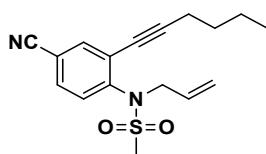
(Cl³⁷)), 325 (M⁺, (Cl³⁵)).



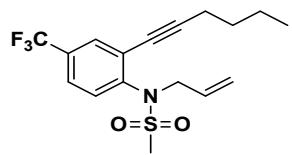
N-Allyl-*N*-(5-bromo-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1l**): ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 2.4 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 5.88-5.76 (m, 1H), 5.14-5.08 (m, 2H), 4.31 (d, *J* = 6.5 Hz, 2H), 2.99 (s, 3H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.64-1.57 (m, 2H), 1.52-1.44 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); EI-MS (*m/z*): 371 (M⁺, (Br⁸¹)), 369 (M⁺, (Br⁷⁹)).



N-Allyl-*N*-(2-(hex-1-yn-1-yl)-5-methylphenyl)methanesulfonamide (**1m**): ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.07 (dd, *J* = 7.9, 1.1 Hz, 1H), 5.90-5.78 (m, 1H), 5.16-5.06 (m, 2H), 4.34 (d, *J* = 6.4 Hz, 2H), 3.00 (s, 3H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.62-1.56 (m, 2H), 1.52-1.43 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); EI-MS (*m/z*): 305 (M⁺).



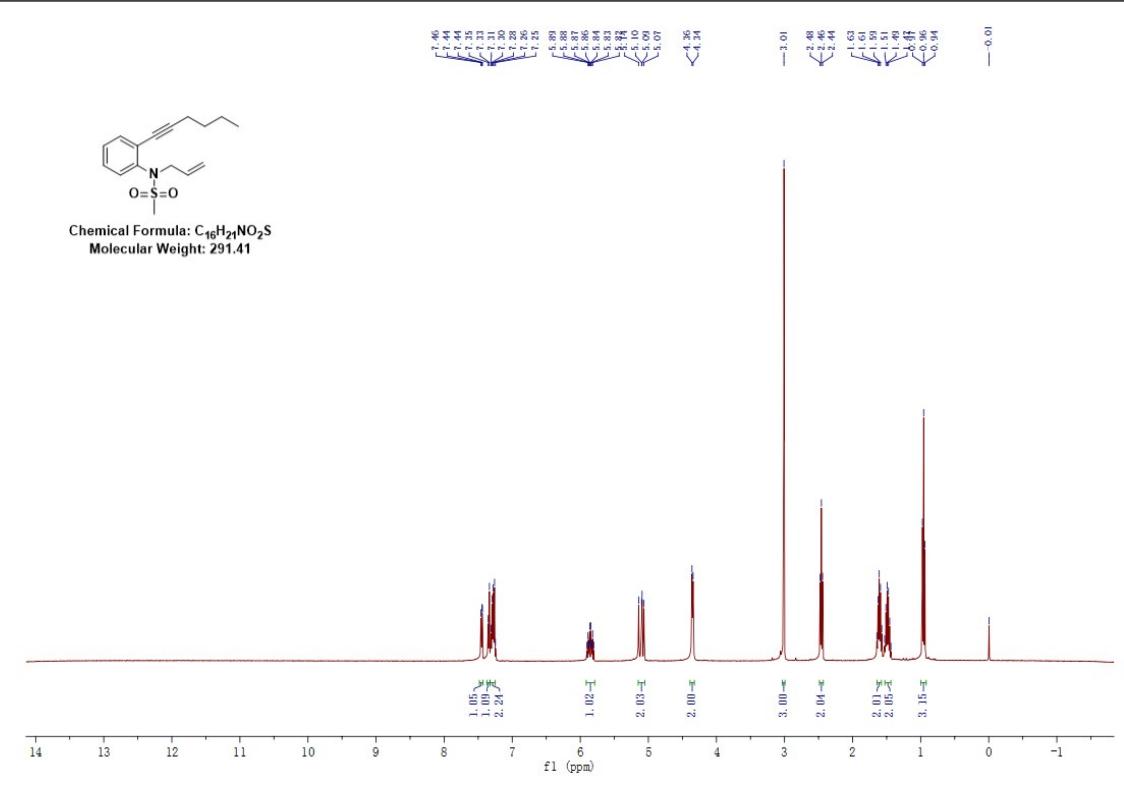
N-Allyl-*N*-(4-cyano-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1n**): ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 5.86-5.70 (m, 1H), 5.20-5.04 (m, 2H), 4.35 (d, *J* = 6.5 Hz, 2H), 3.01 (s, 3H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.65-1.56 (m, 2H), 1.53-1.43 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); EI-MS (*m/z*): 316 (M⁺).



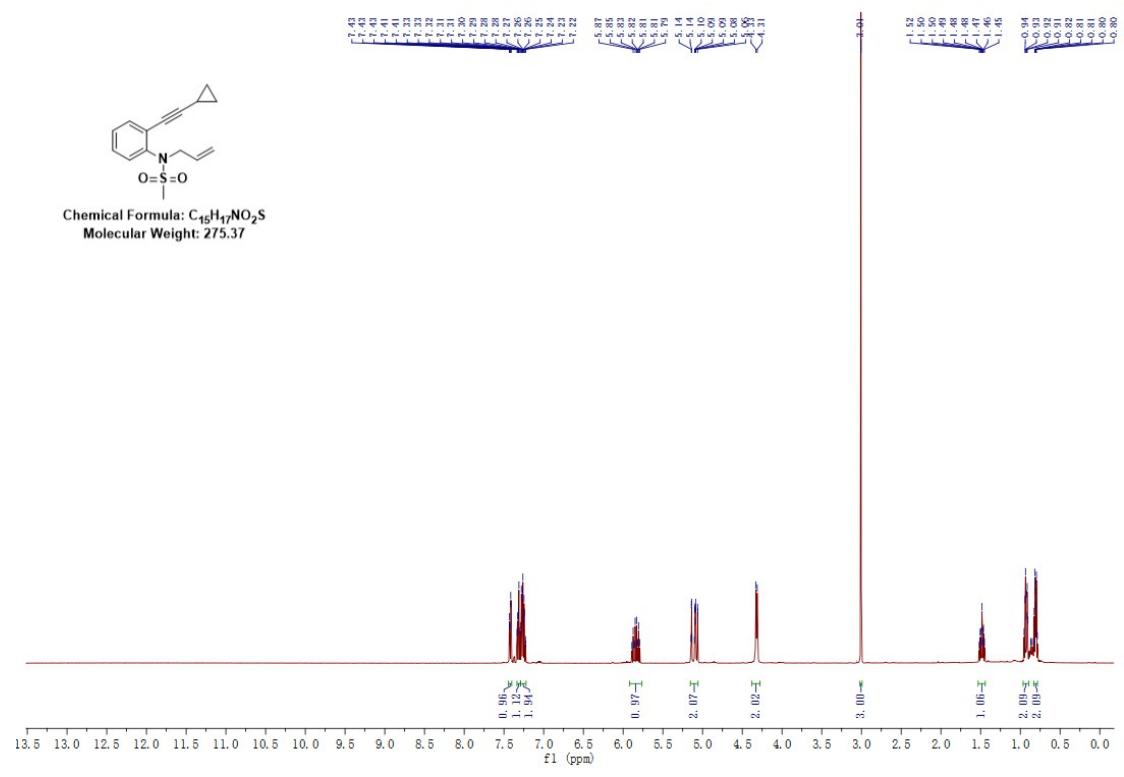
N-Allyl-*N*-(2-(hex-1-yn-1-yl)-4-(trifluoromethyl)phenyl)methanesulfonamide (**1o**): ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 2.0$ Hz, 1H), 7.53 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 5.89-5.77 (m, 1H), 5.15-5.09 (m, 2H), 4.37 (d, $J = 6.5$ Hz, 2H), 3.02 (s, 3H), 2.48 (t, $J = 7.1$ Hz, 2H), 1.64-1.59 (m, 2H), 1.52-1.46 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); EI-MS (m/z): 359 (M^+).

¹H and ¹³C NMR Spectra

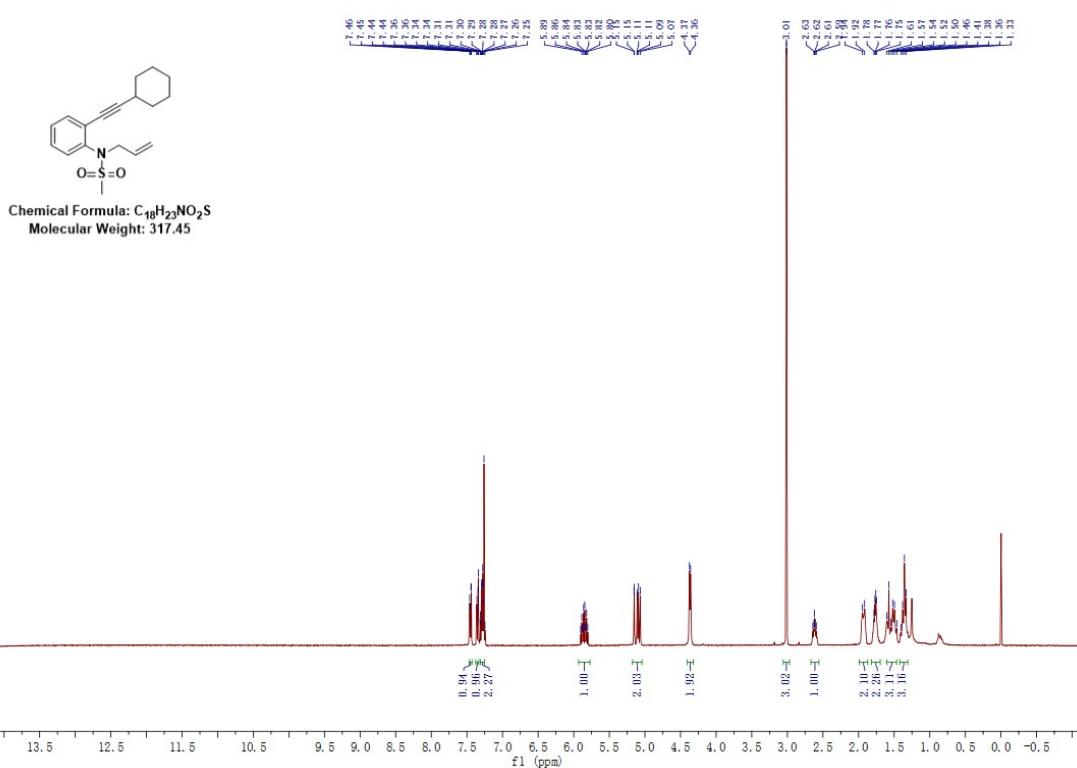
N-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1a**)



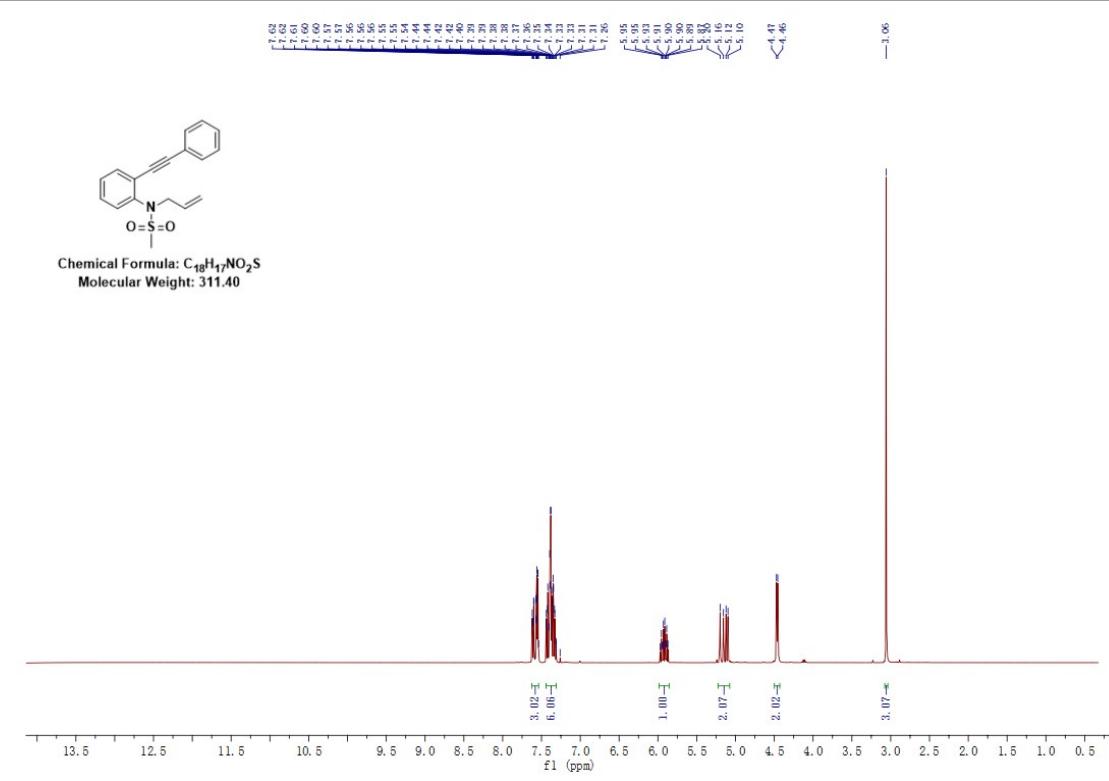
N-Allyl-*N*-(2-(cyclopropylethyynyl)phenyl)methanesulfonamide (**1b**)



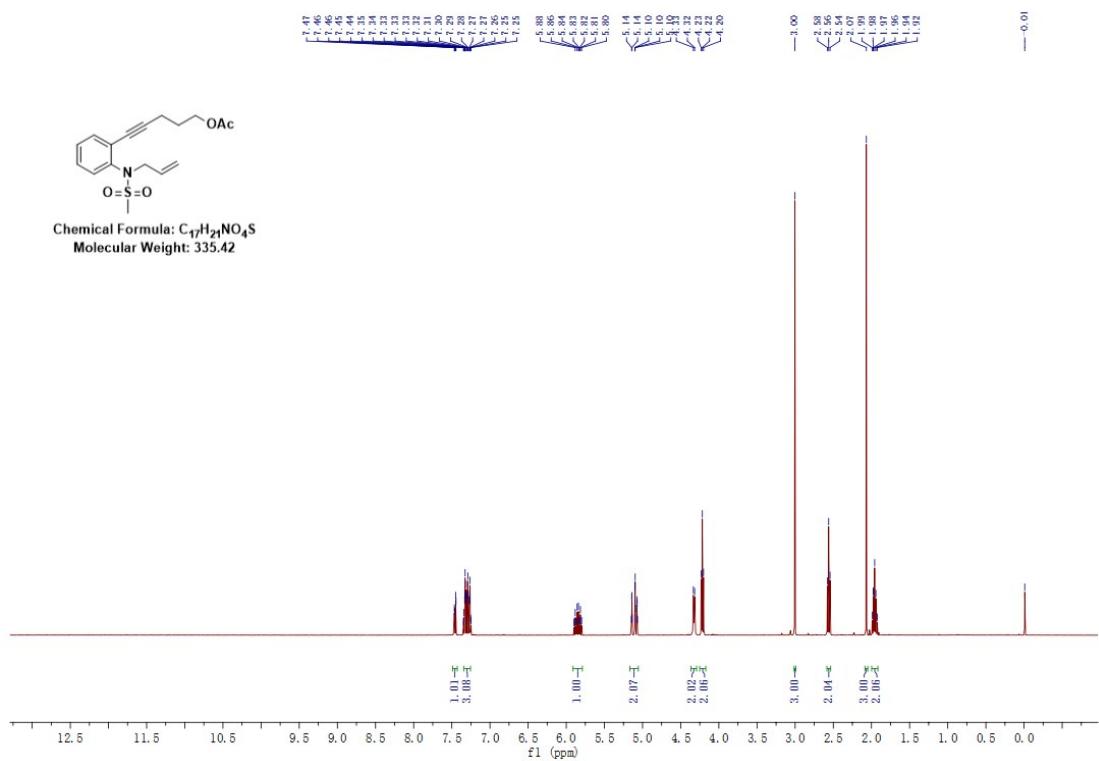
***N*-Allyl-*N*-(2-(cyclohexylethynyl)phenyl)methanesulfonamide (**1c**)**



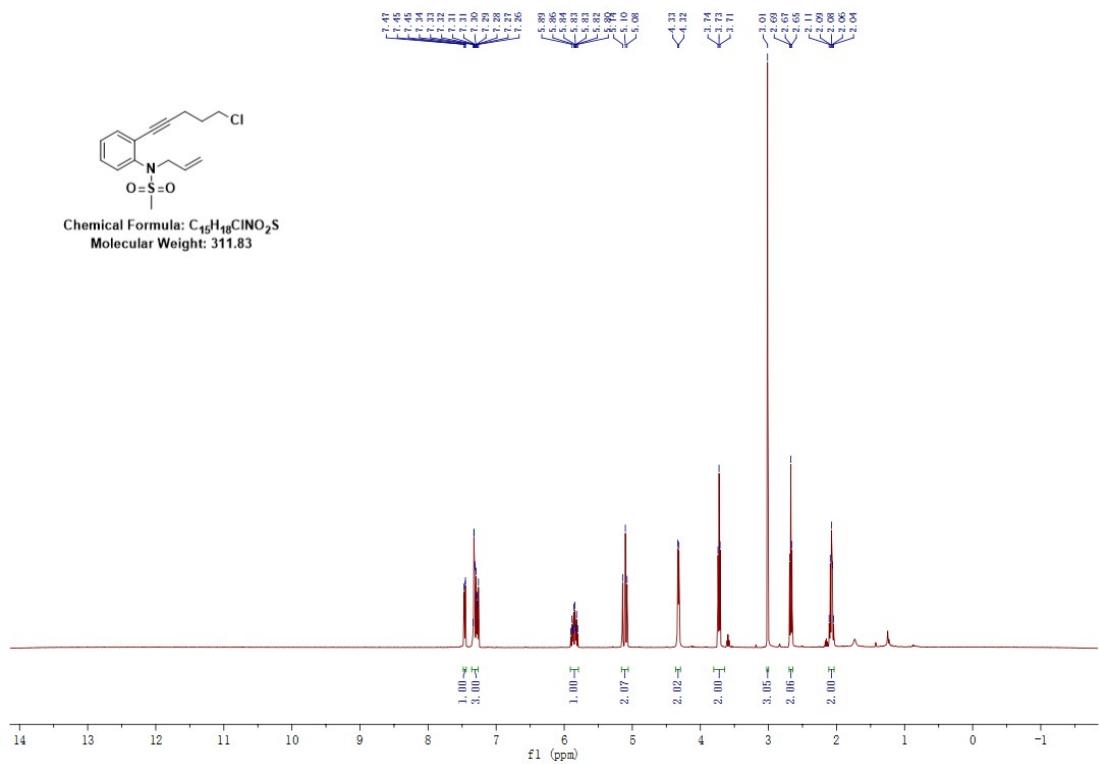
***N*-Allyl-*N*-(2-(phenylethynyl)phenyl)methanesulfonamide (**1d**)**



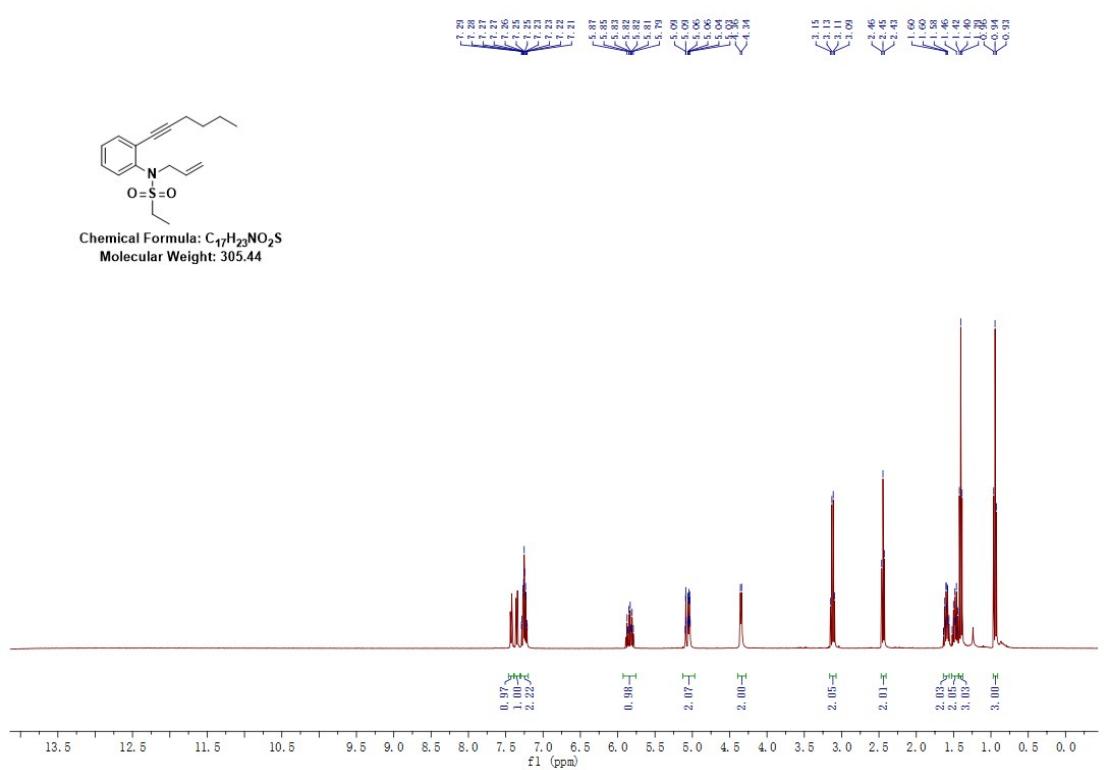
5-(2-(*N*-Allylmethylsulfonamido)phenyl)pent-4-yn-1-yl acetate (1e**)**



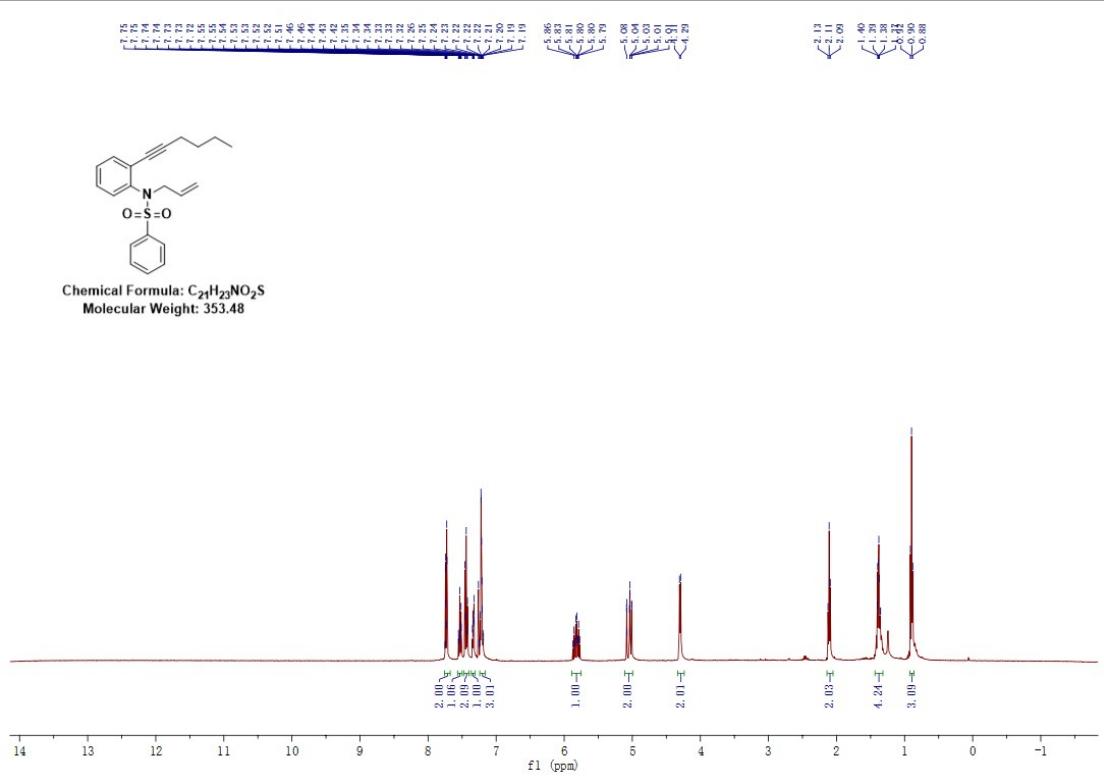
***N*-Allyl-*N*-(2-(5-chloropent-1-yn-1-yl)phenyl)methanesulfonamide (**1f**)**



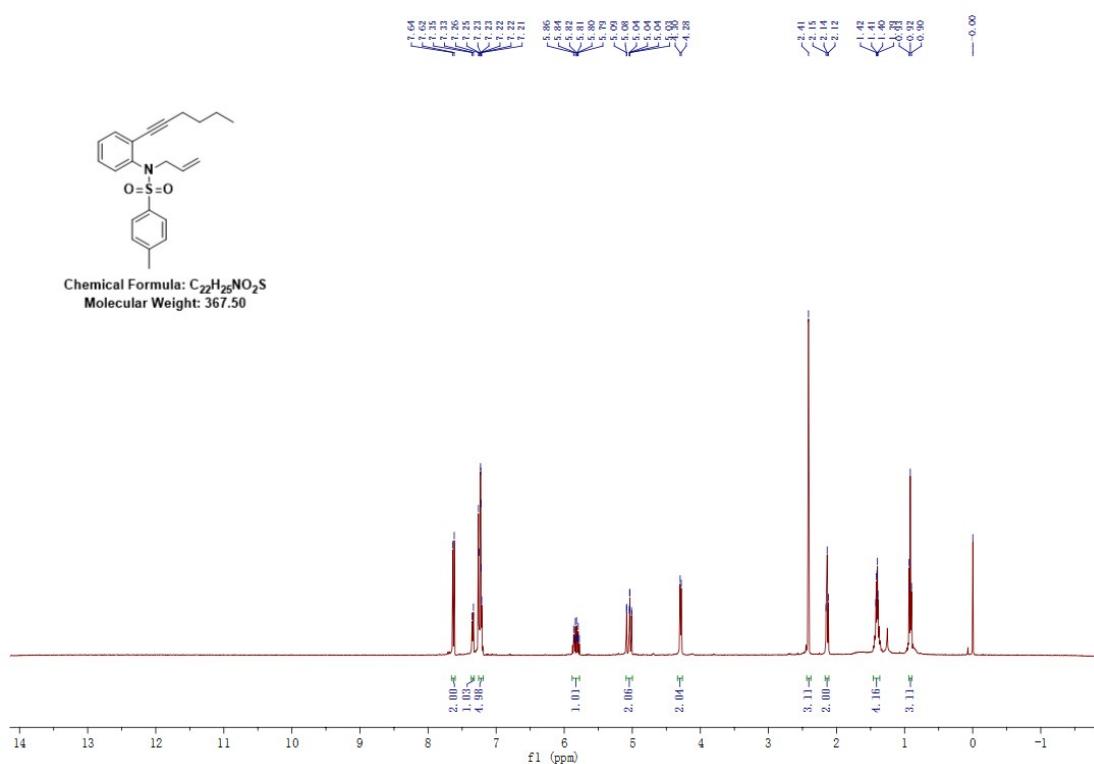
***N*-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)ethanesulfonamide (**1g**)**



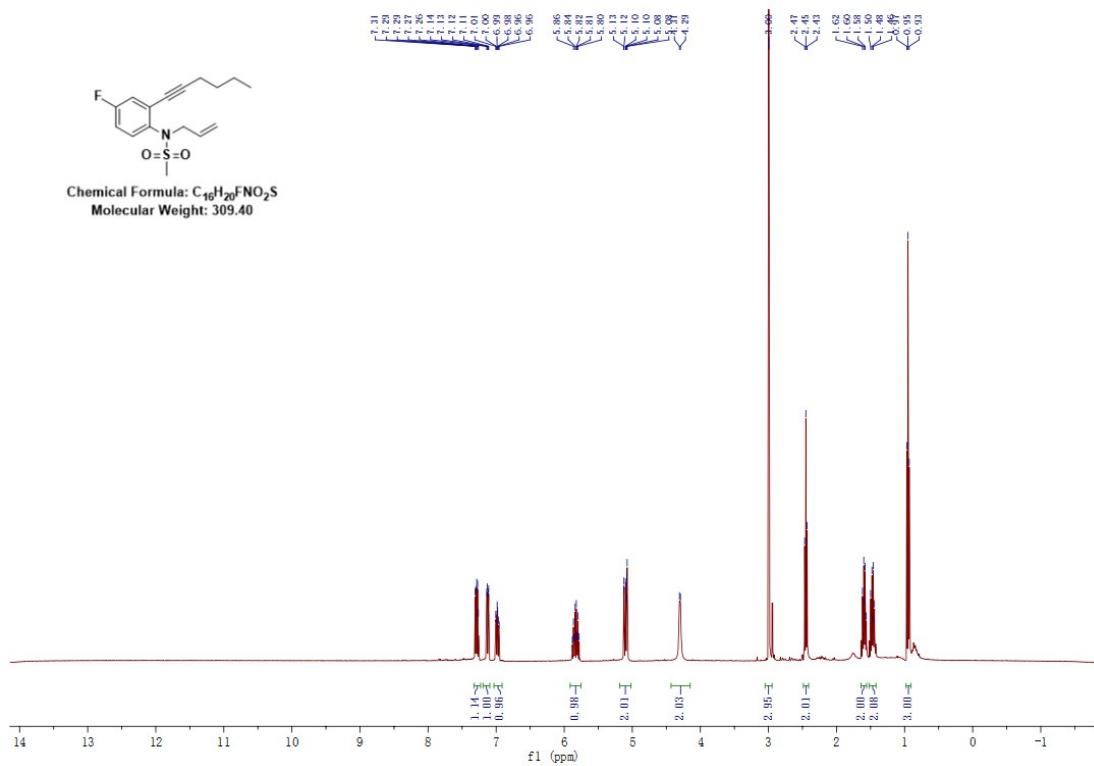
***N*-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)benzenesulfonamide (**1h**)**



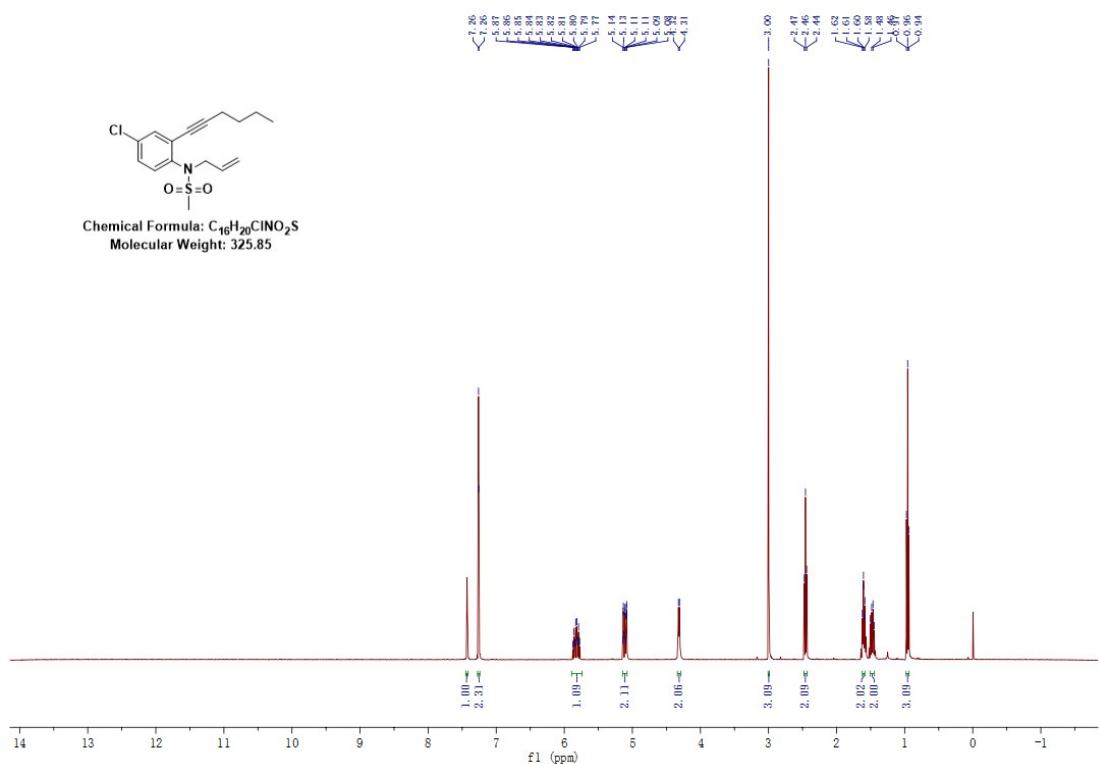
N-Allyl-*N*-(2-(hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1i**)



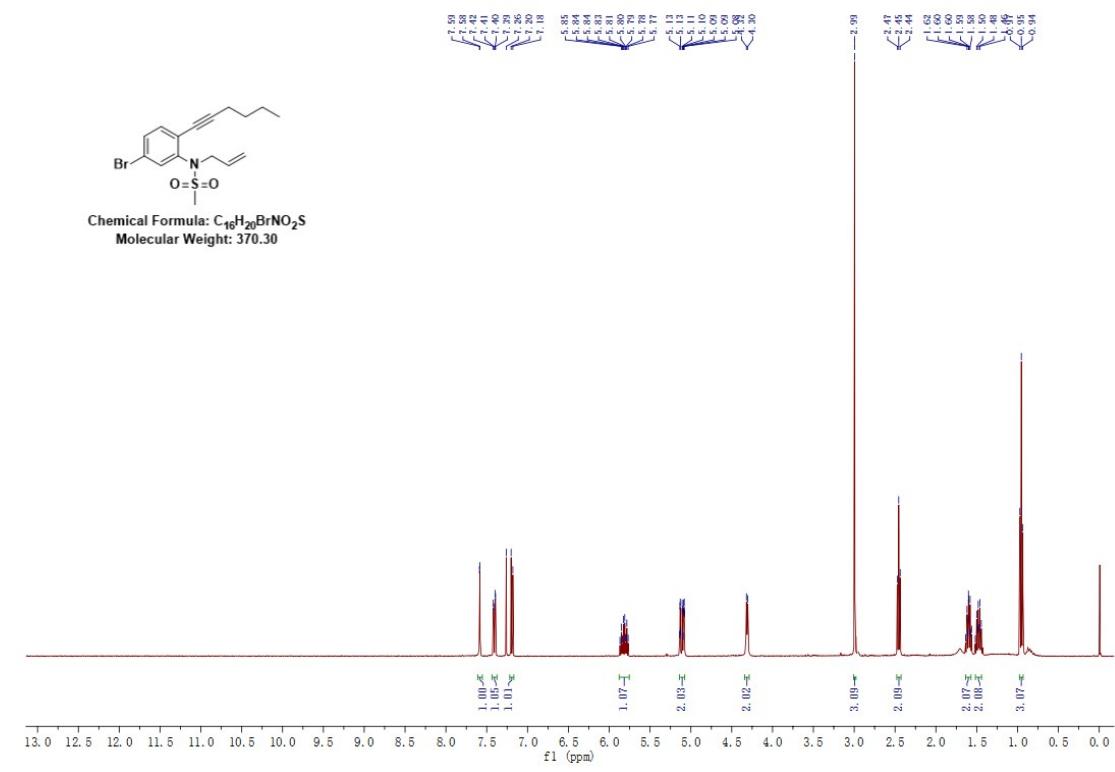
N-Allyl-*N*-(4-fluoro-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1j**)



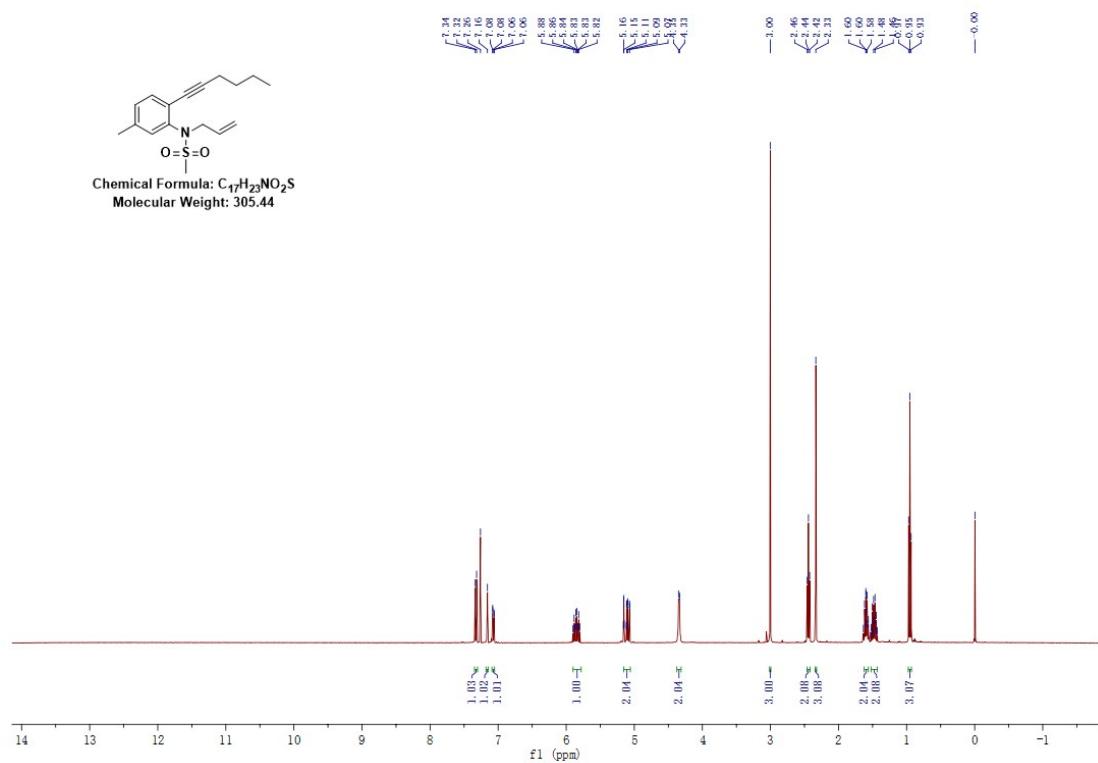
N-Allyl-*N*-(4-chloro-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1k**)



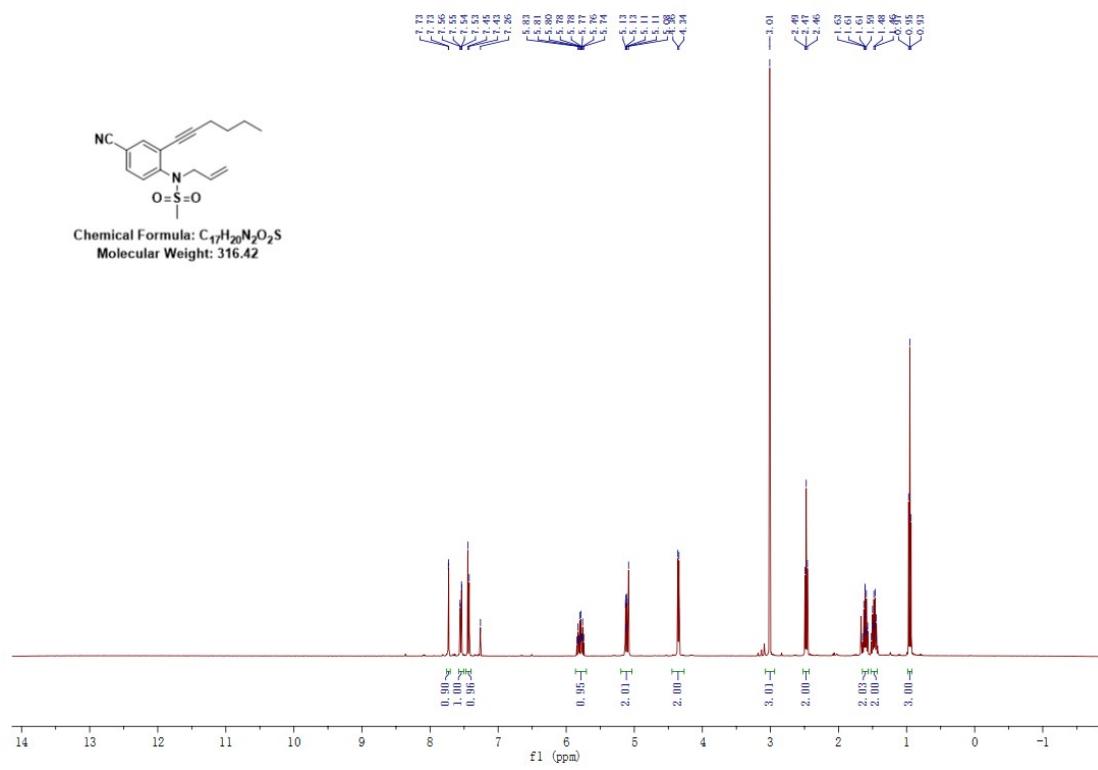
N-Allyl-*N*-(5-bromo-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1l**)



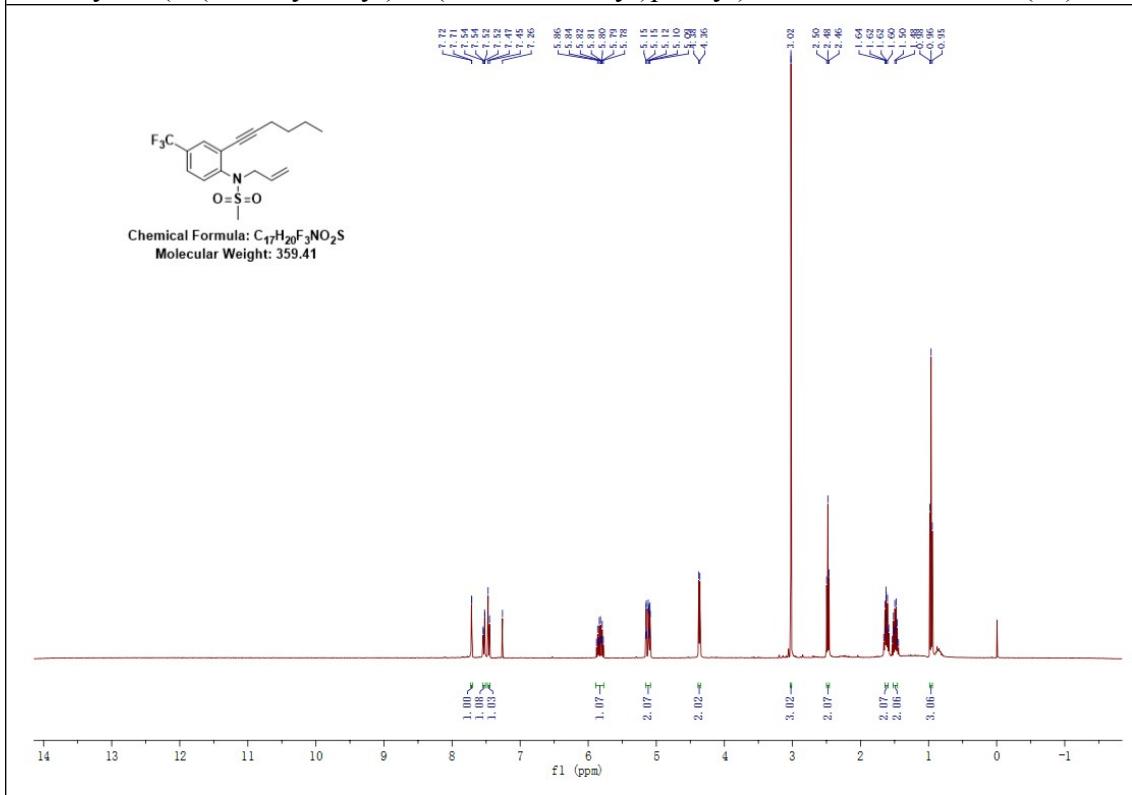
N-Allyl-*N*-(2-(hex-1-yn-1-yl)-5-methylphenyl)methanesulfonamide (**1m**)



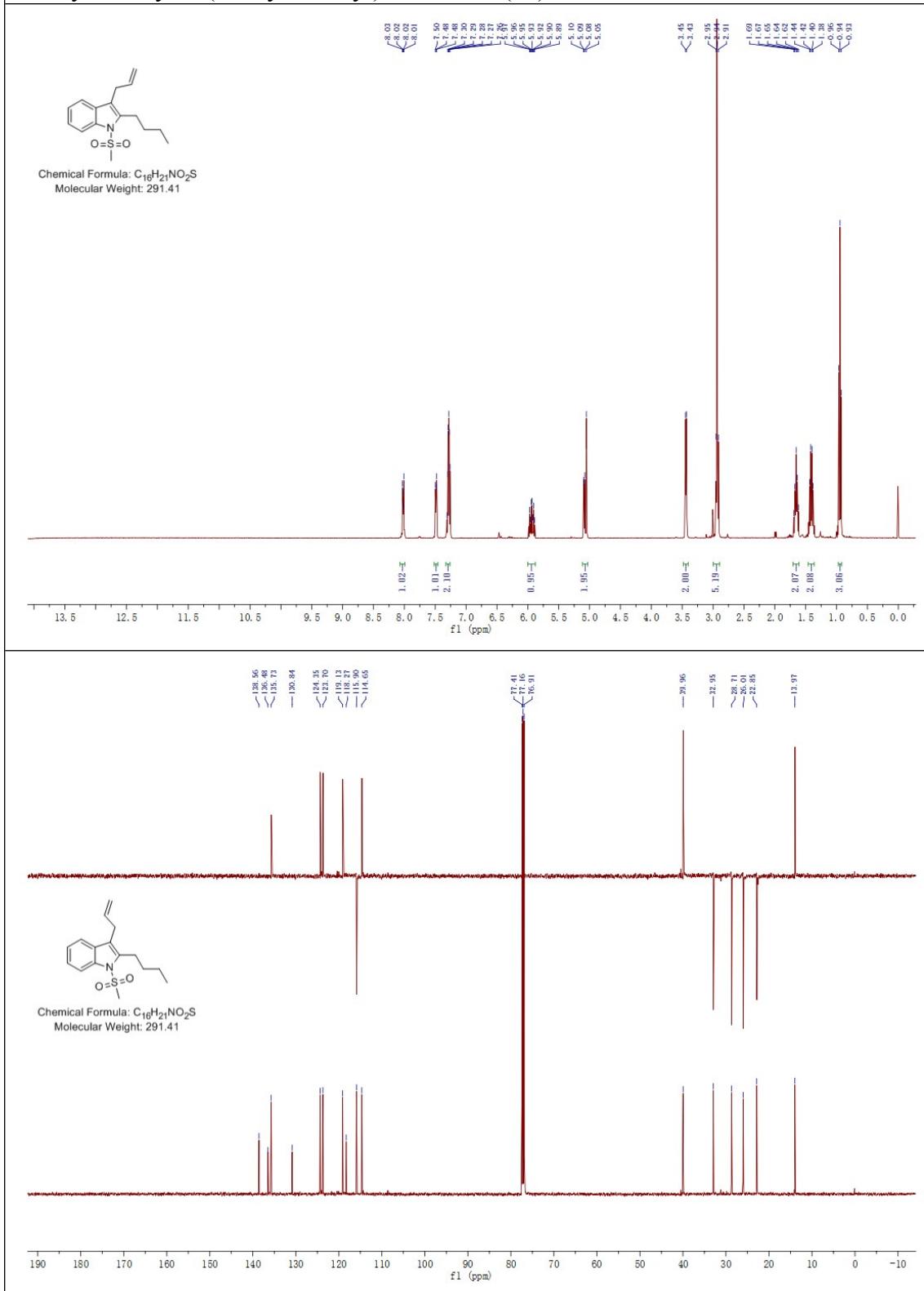
N-Allyl-*N*-(4-cyano-2-(hex-1-yn-1-yl)phenyl)methanesulfonamide (**1n**)



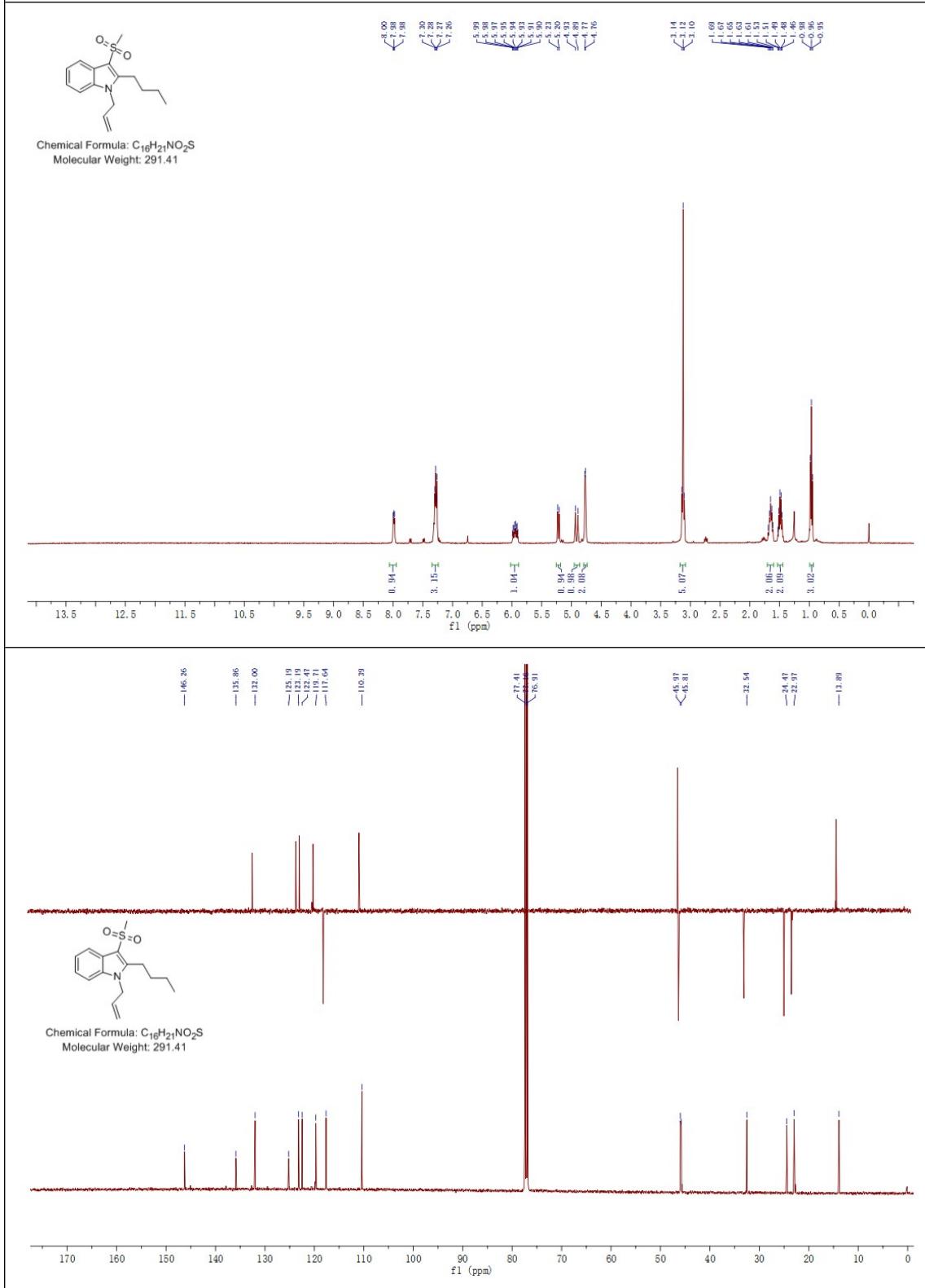
N-Allyl-*N*-(2-(hex-1-yn-1-yl)-4-(trifluoromethyl)phenyl)methanesulfonamide (**1o**)



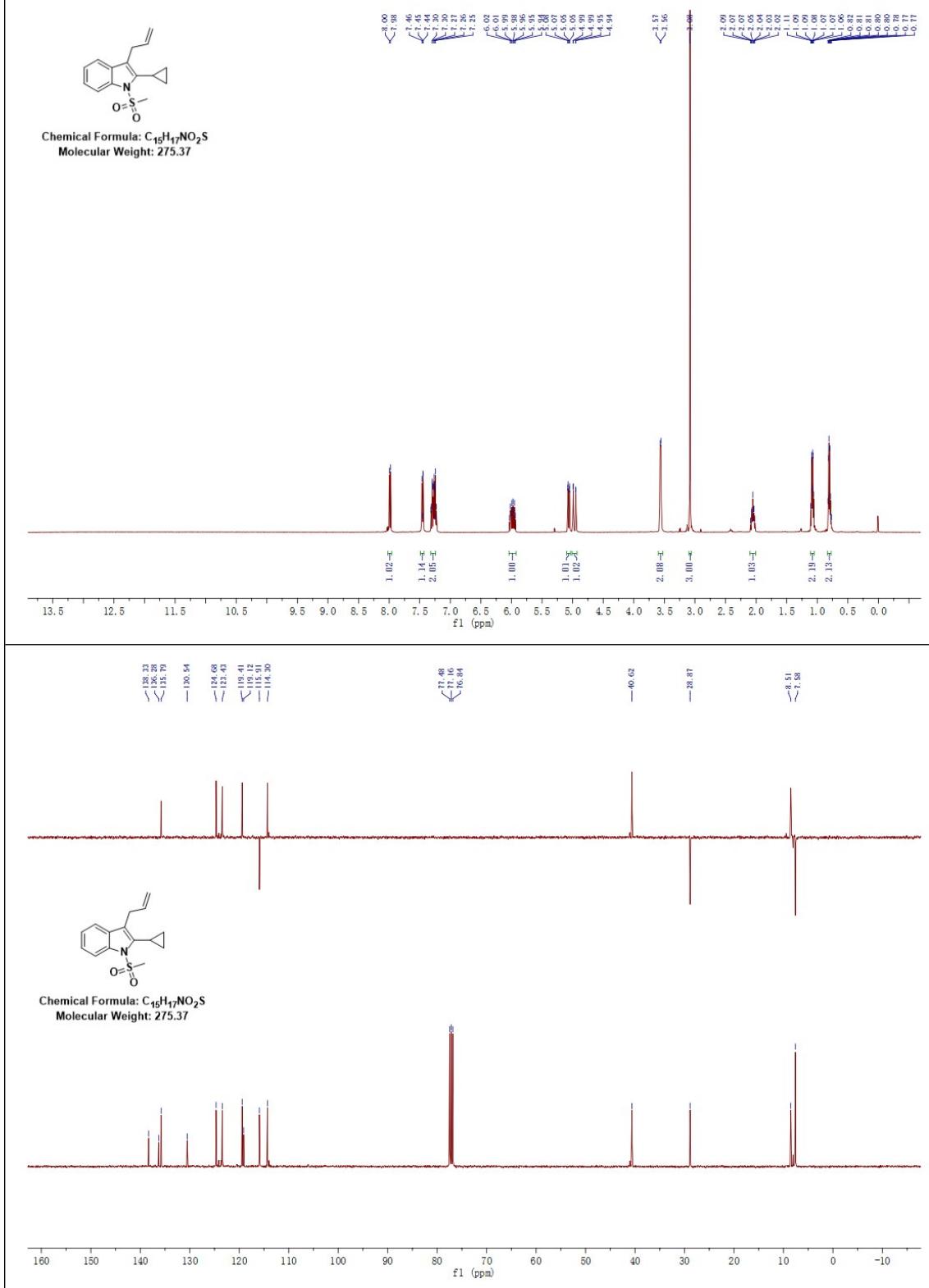
3-Allyl-2-butyl-1-(methylsulfonyl)-1*H*-indole (2a**)**



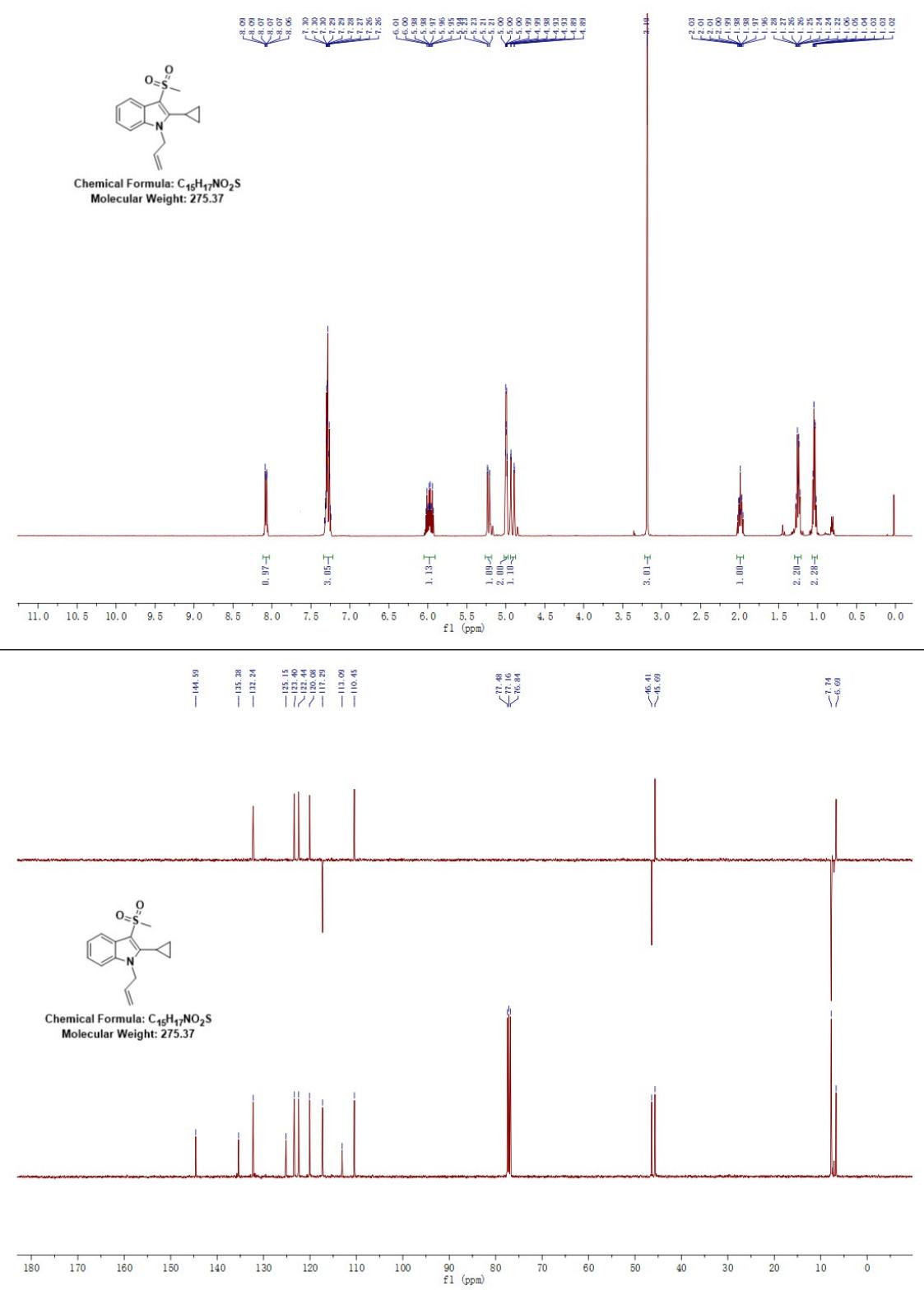
1-Allyl-2-butyl-3-(methylsulfonyl)-*1H*-indole (3a**)**



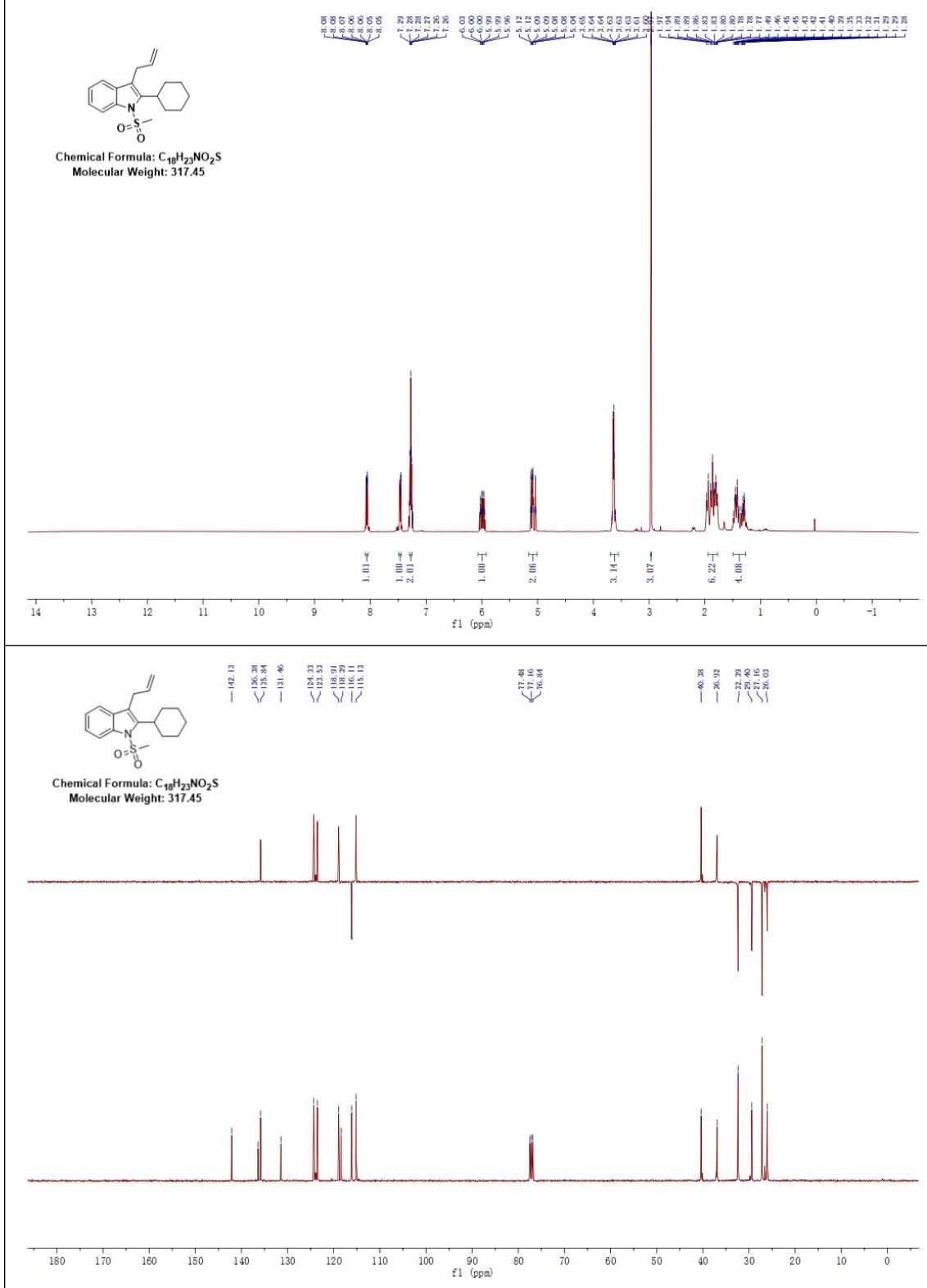
3-Allyl-2-cyclopropyl-1-(methylsulfonyl)-*1H*-indole (2b**)**



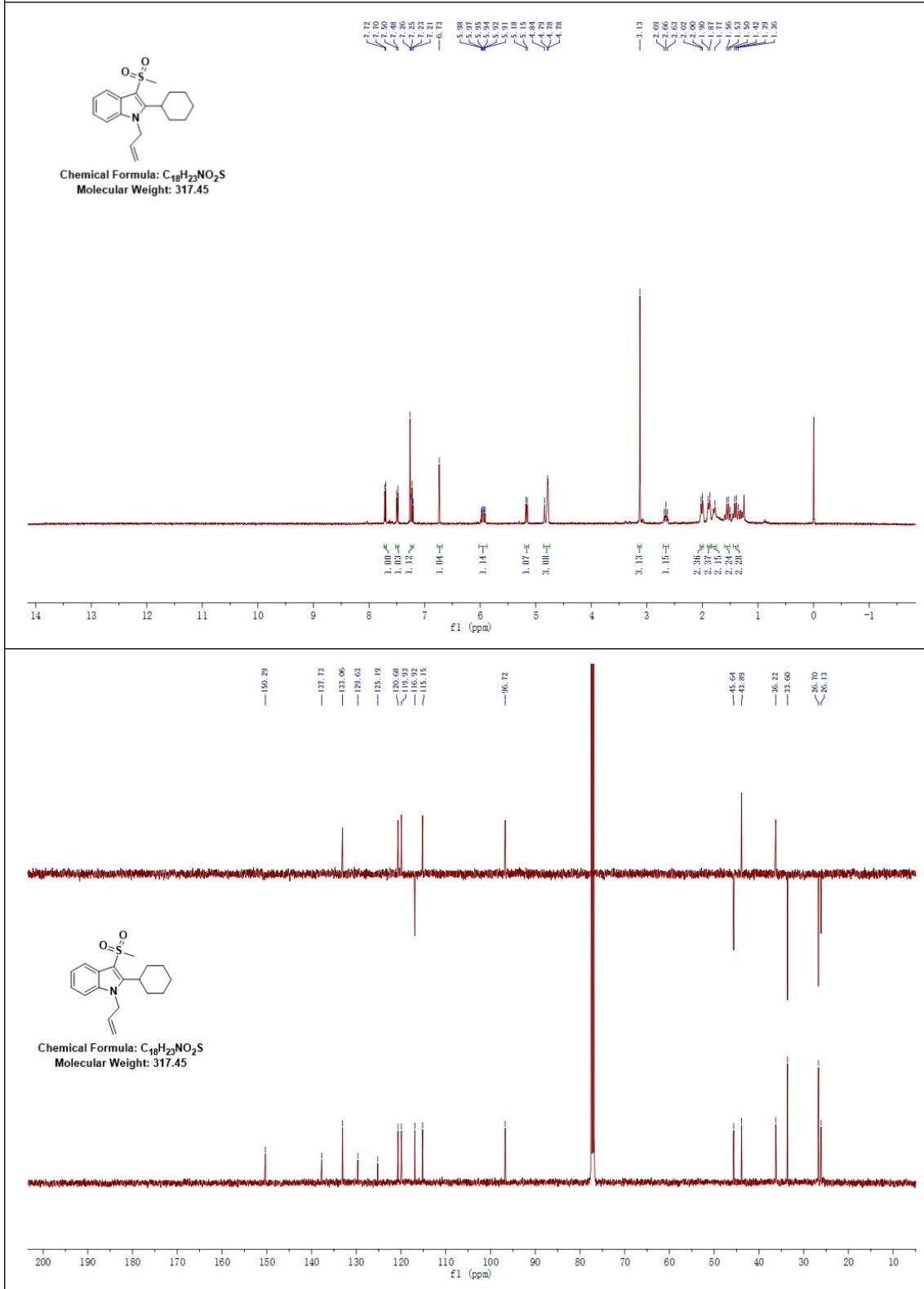
1-Allyl-2-cyclopropyl-3-(methylsulfonyl)-*1H*-indole (3b**)**



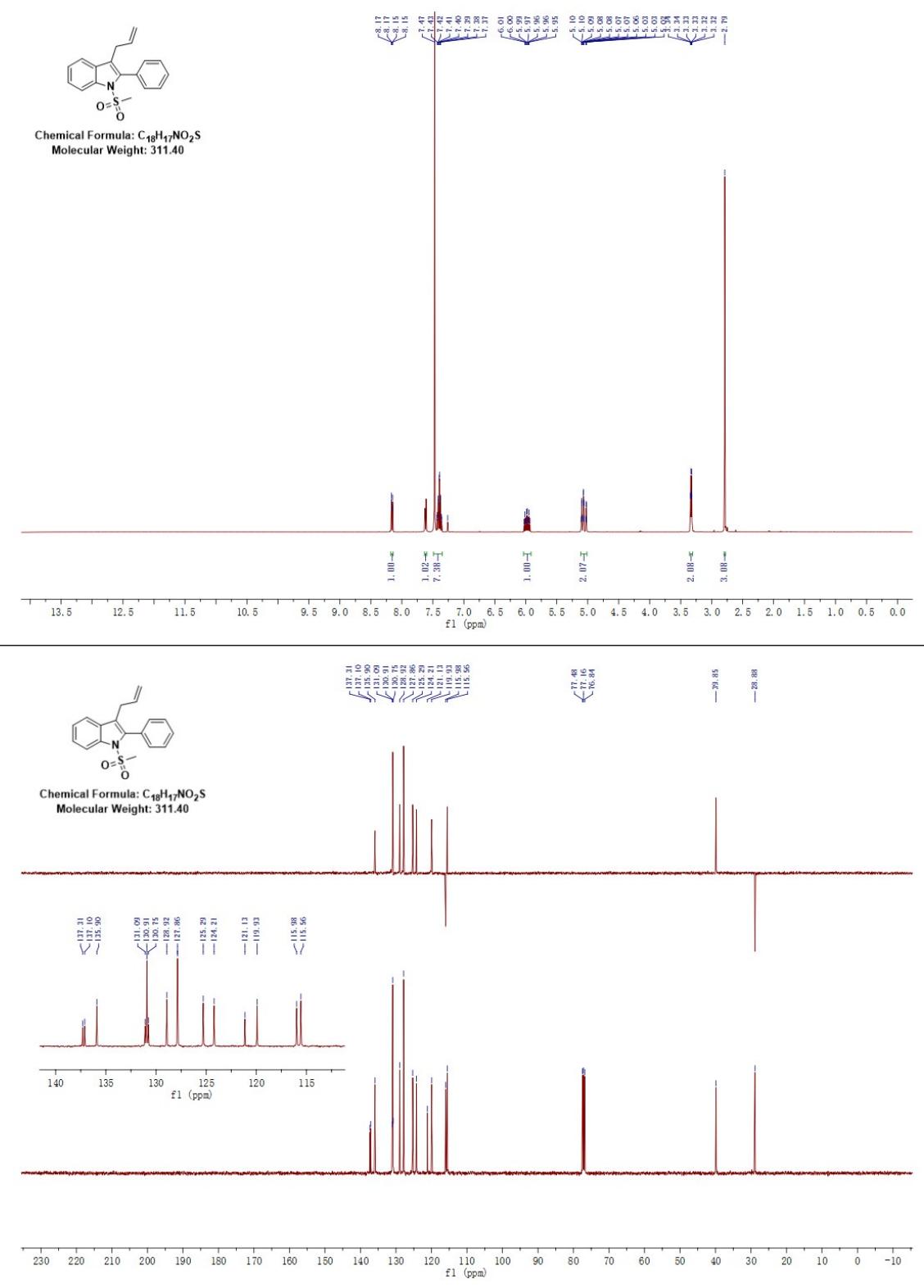
3-Allyl-2-cyclohexyl-1-(methylsulfonyl)-1*H*-indole (2c**)**



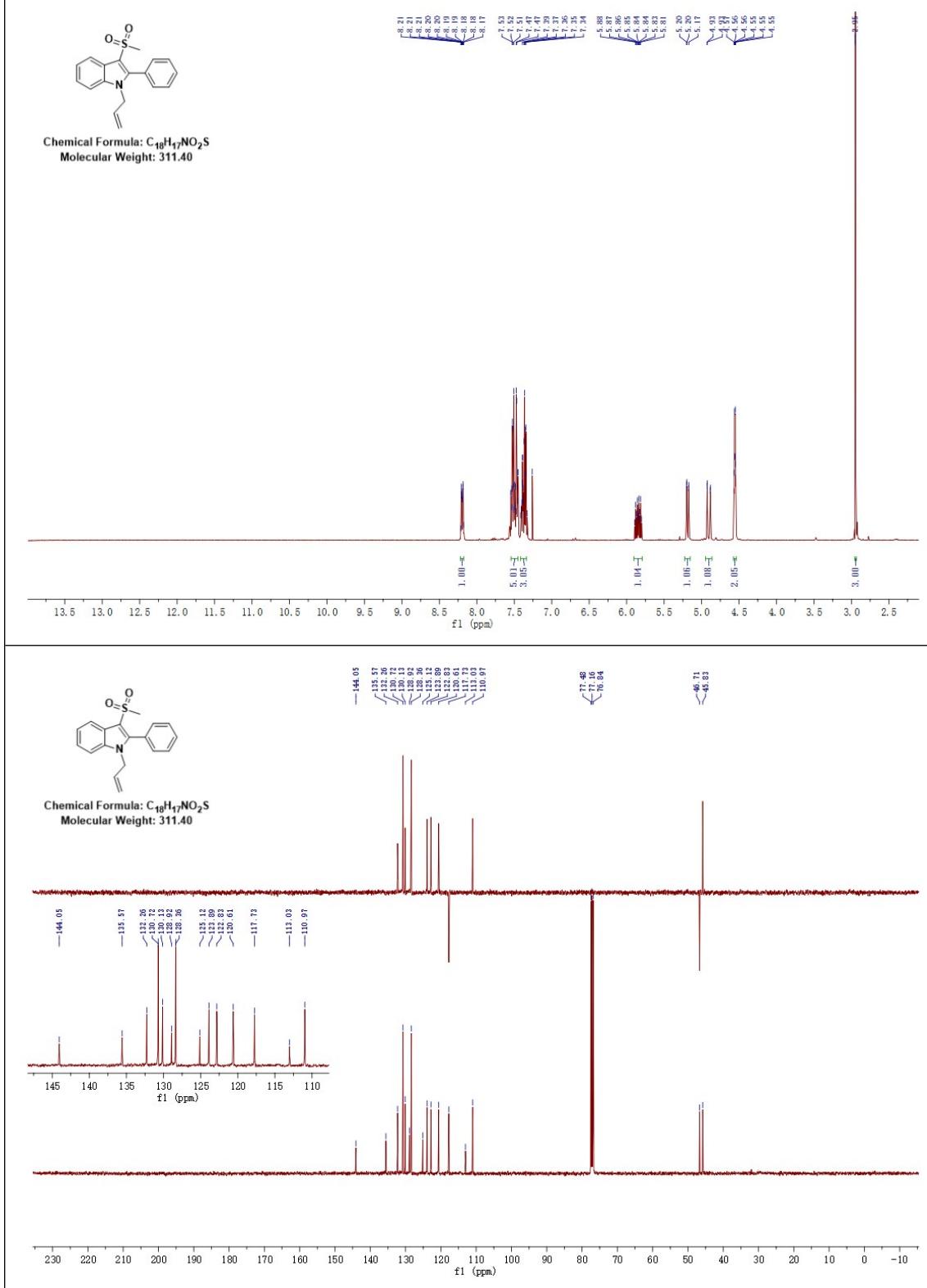
1-Allyl-2-cyclohexyl-3-(methylsulfonyl)-1*H*-indole (3c**)**



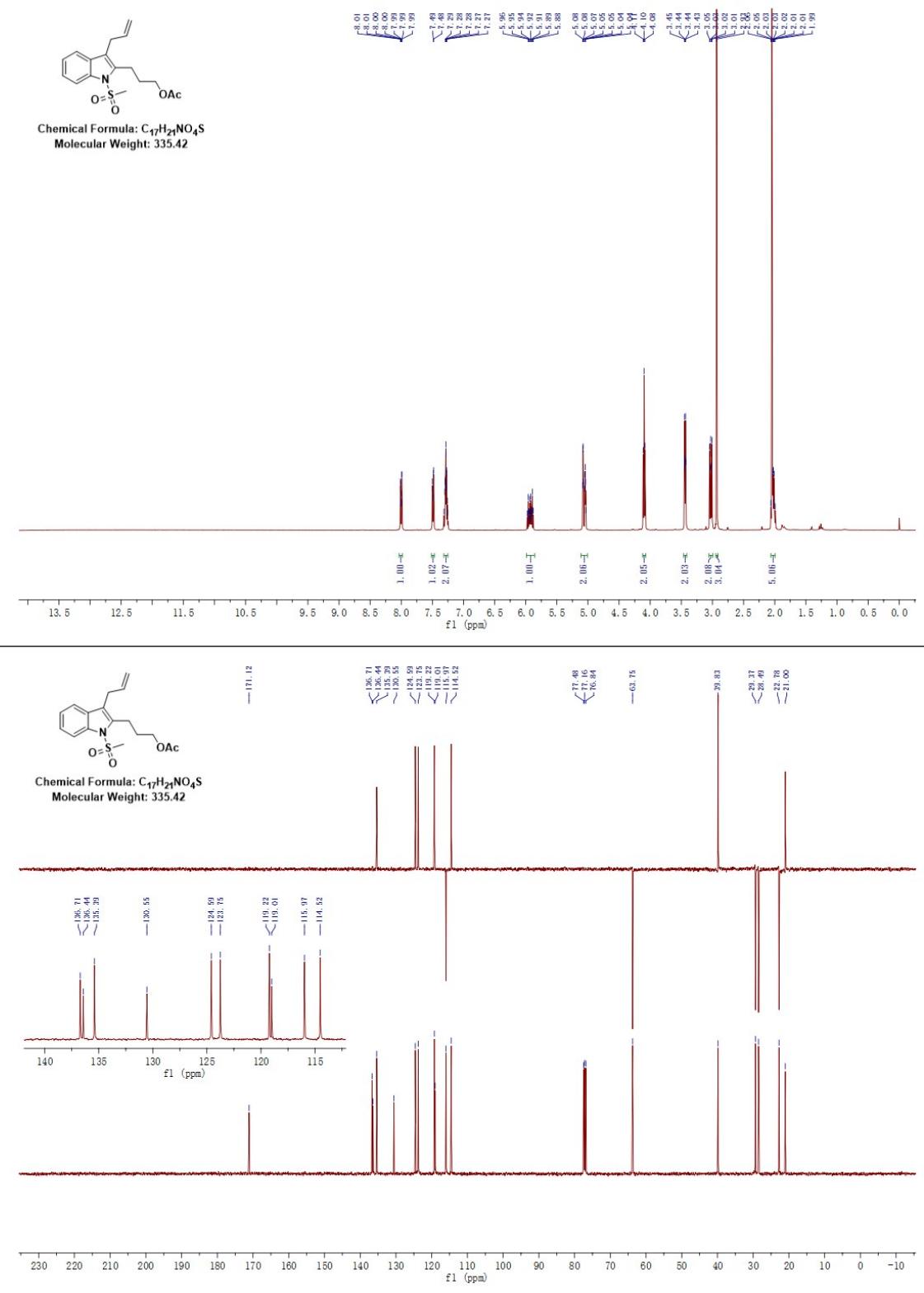
3-Allyl-1-(methylsulfonyl)-2-phenyl-1*H*-indole (2d**)**



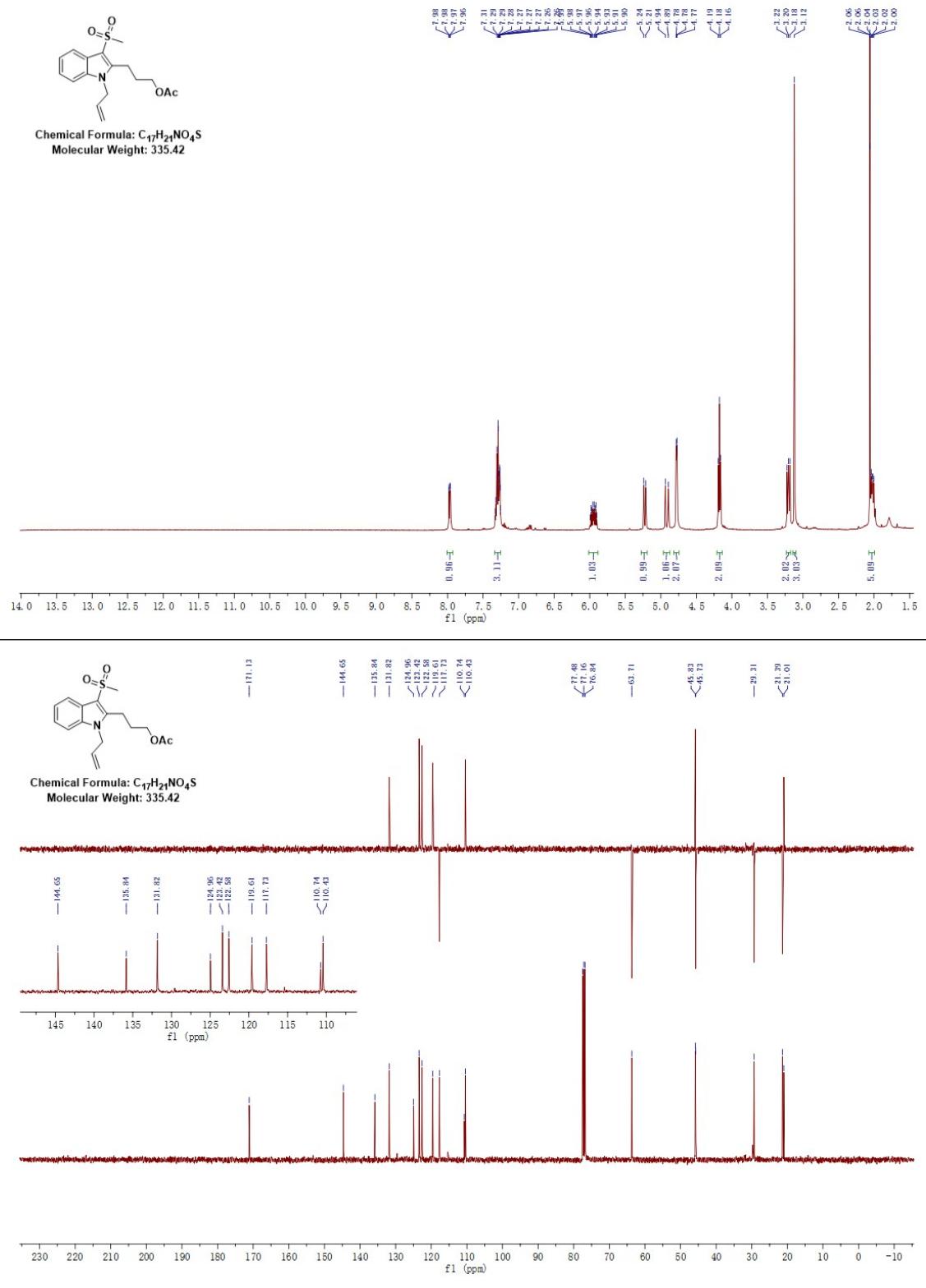
1-Allyl-3-(methylsulfonyl)-2-phenyl-1*H*-indole (3d**)**



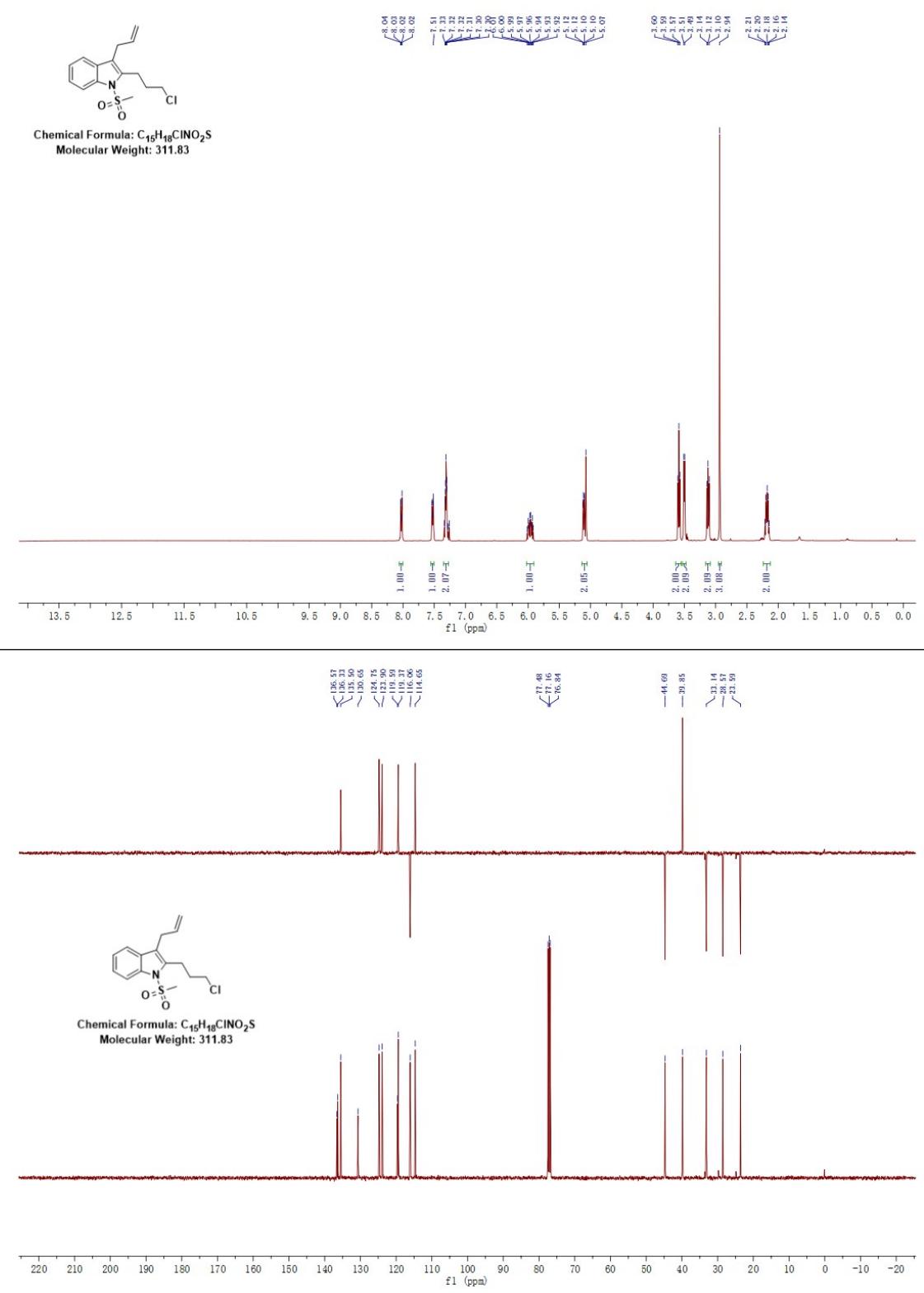
3-(3-Allyl-1-(methylsulfonyl)-1*H*-indol-2-yl)propyl acetate (2e**)**



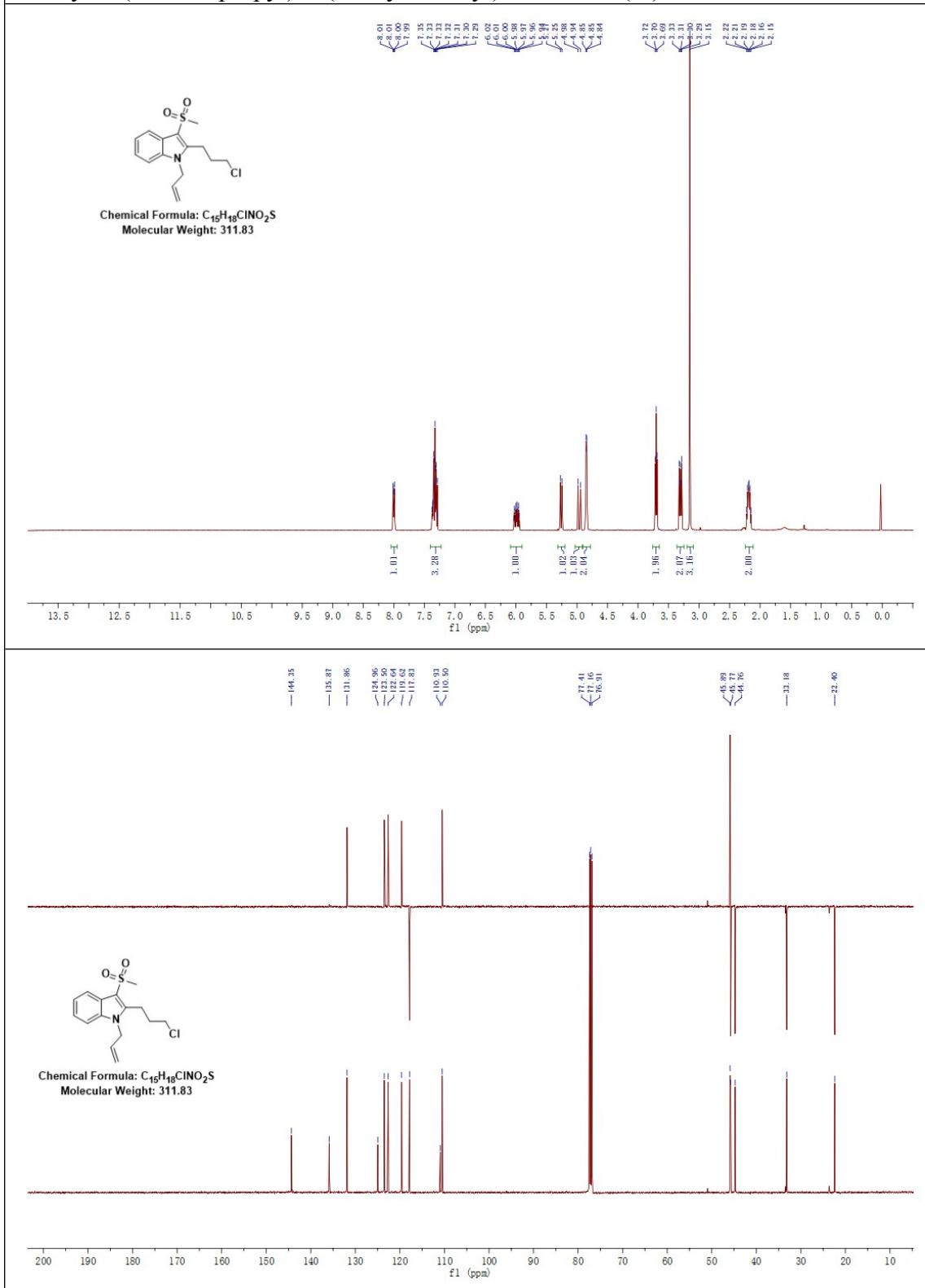
3-(1-Allyl-3-(methylsulfonyl)-*1H*-indol-2-yl)propyl acetate (3e**)**



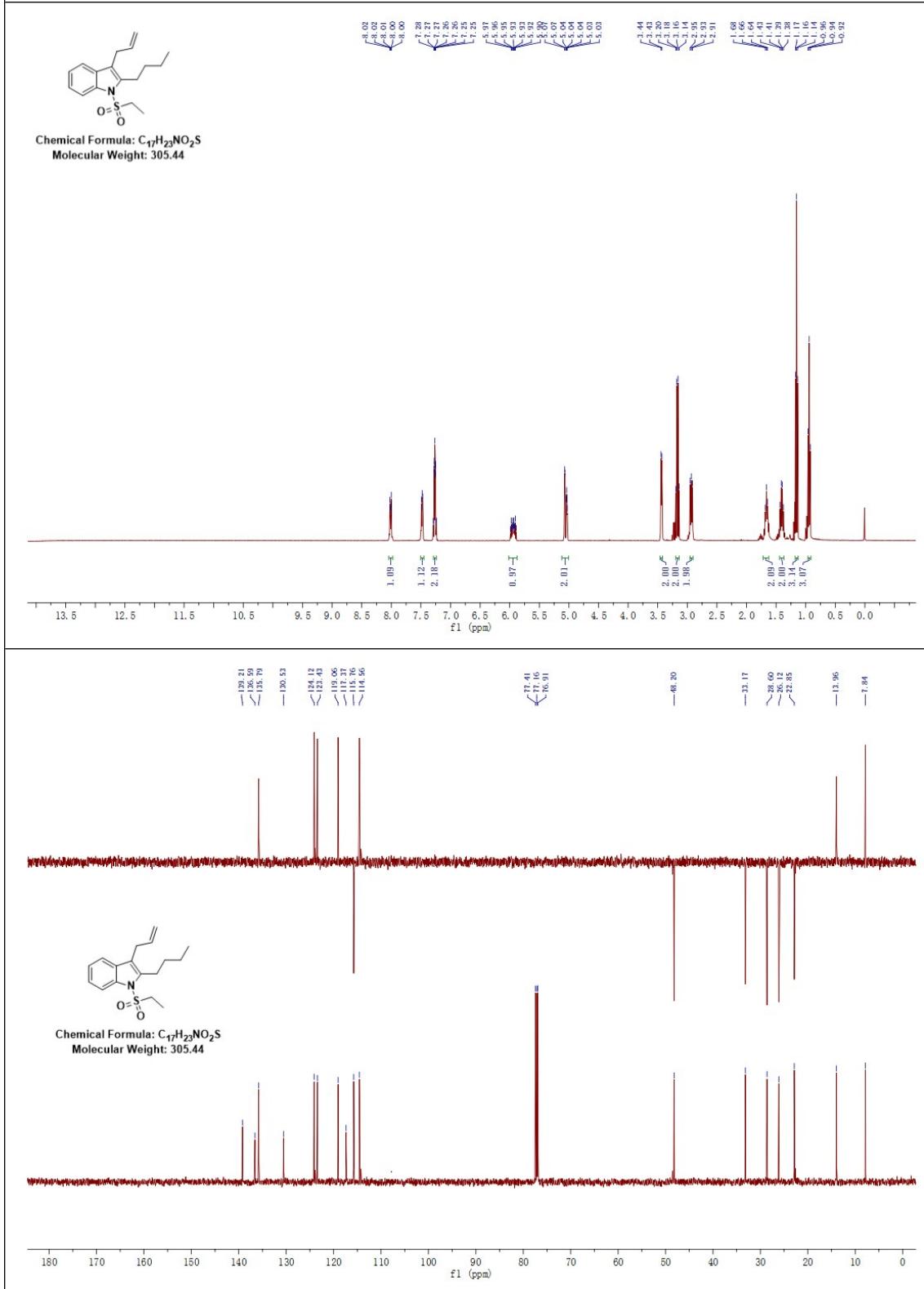
3-Allyl-2-(3-chloropropyl)-1-(methylsulfonyl)-1*H*-indole (2f**)**



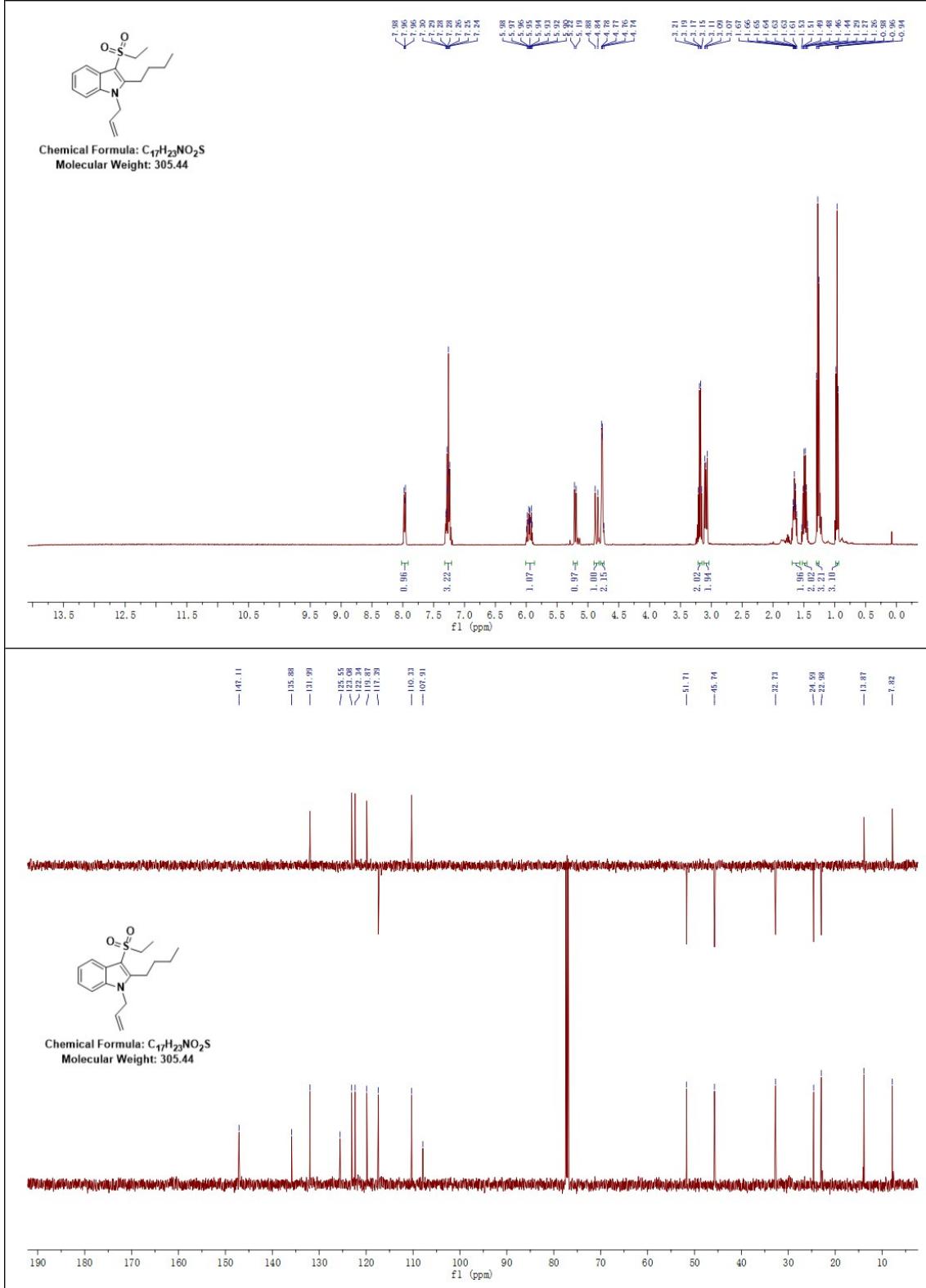
1-Allyl-2-(3-chloropropyl)-1*H*-indole (3f**)**



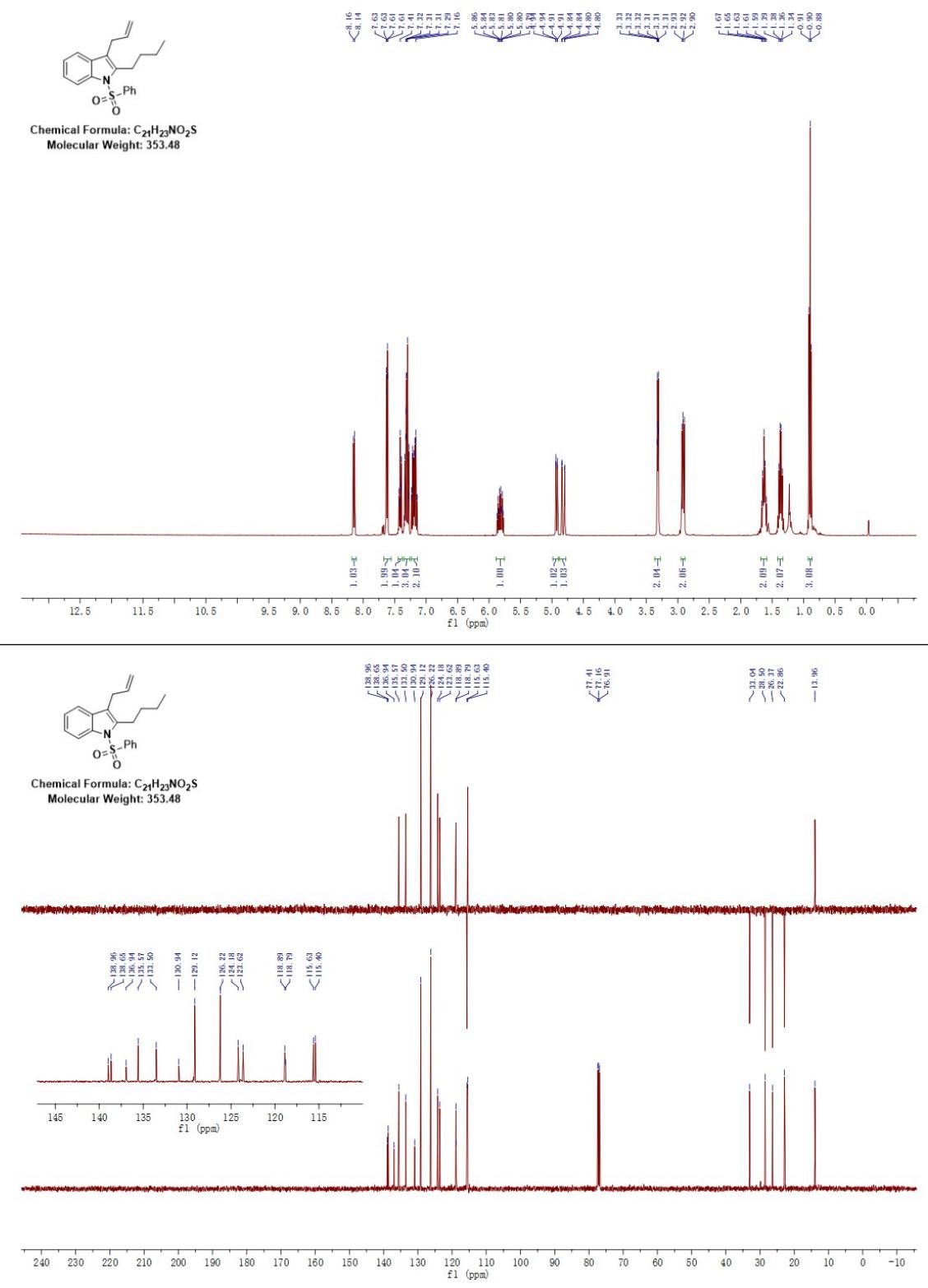
3-Allyl-2-butyl-1-(ethylsulfonyl)-*1H*-indole (2g**)**



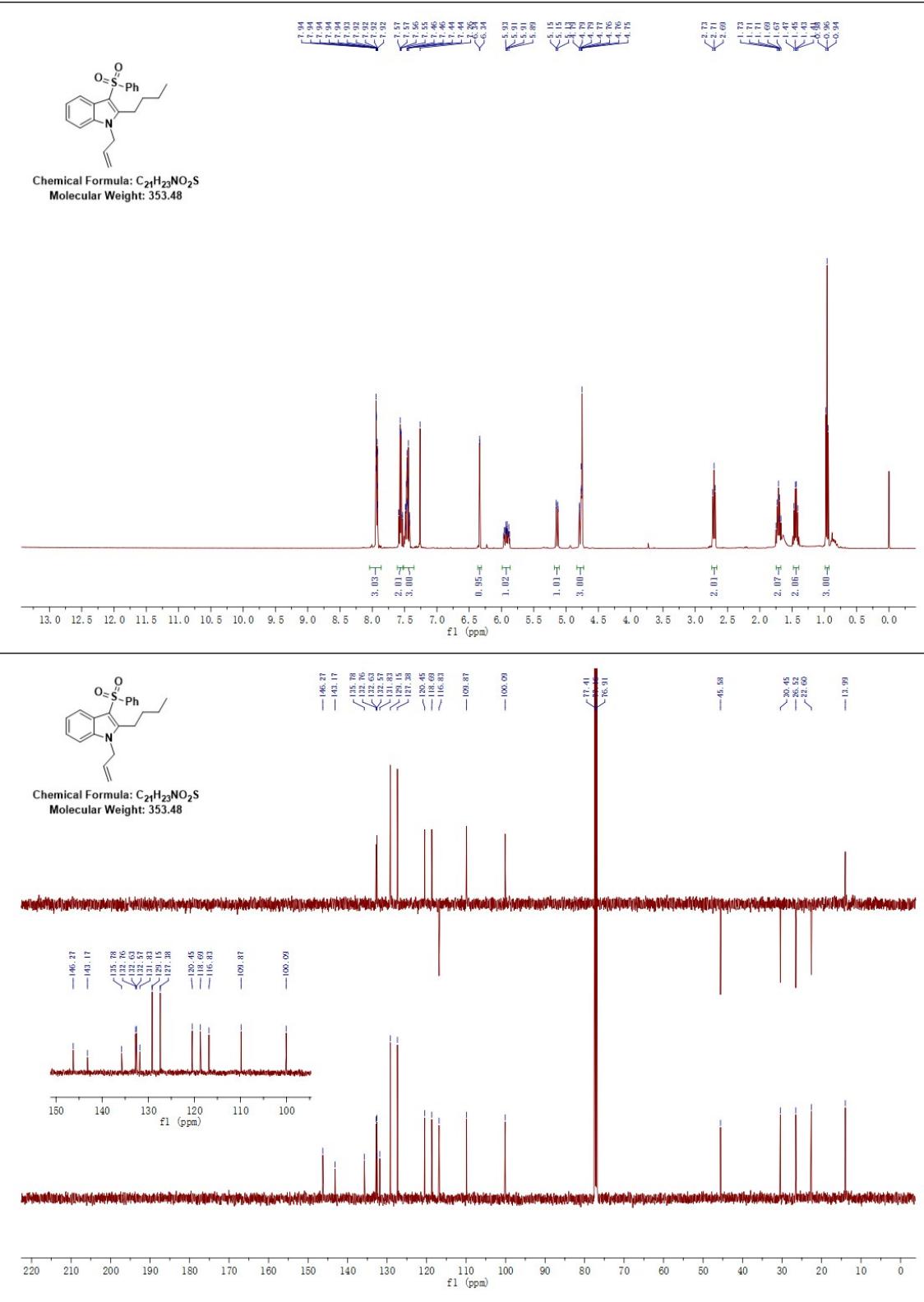
1-Allyl-2-butyl-3-(ethylsulfonyl)-*1H*-indole (3g**)**



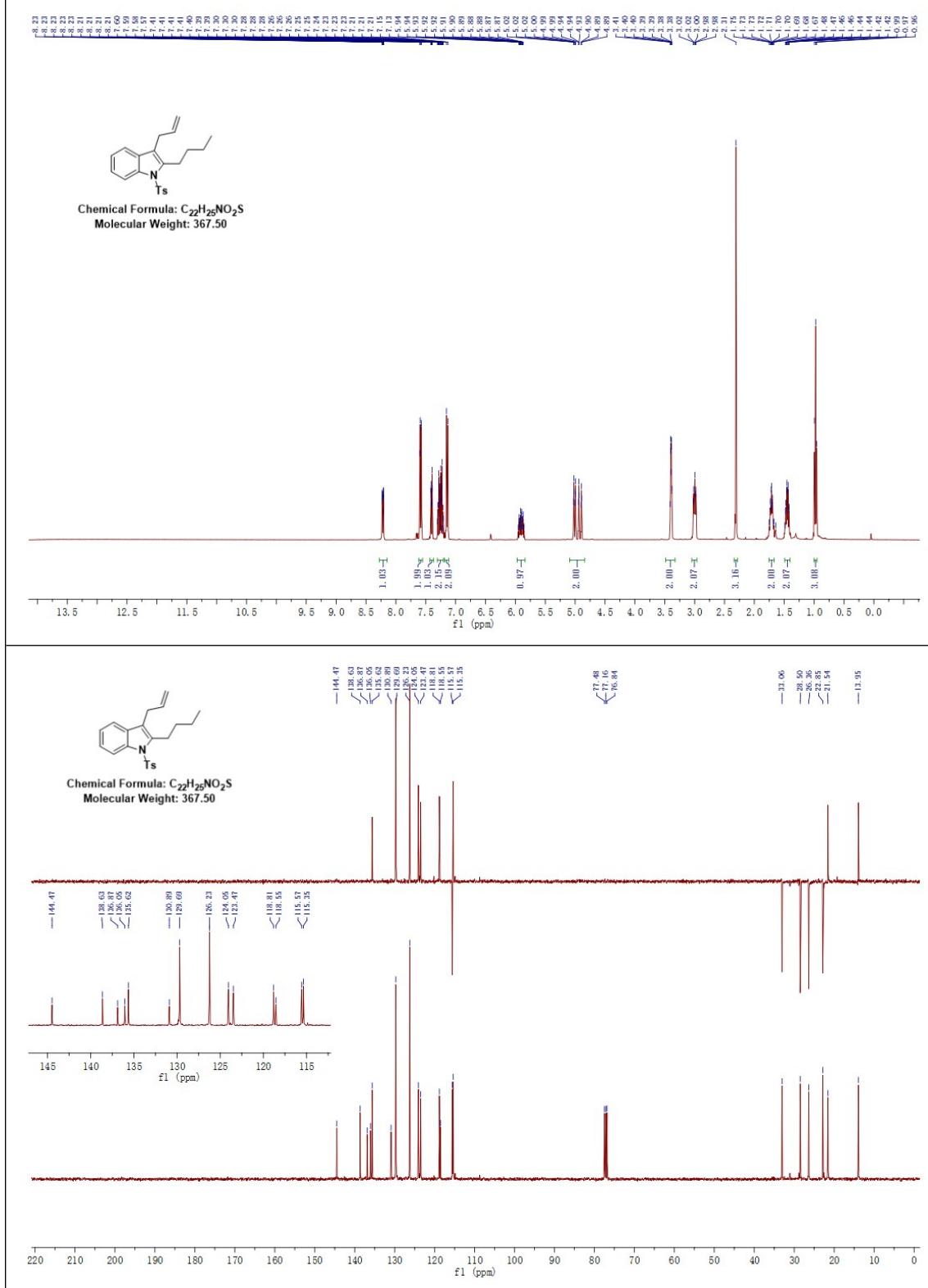
3-Allyl-2-butyl-1-(phenylsulfonyl)-1*H*-indole (2h**)**



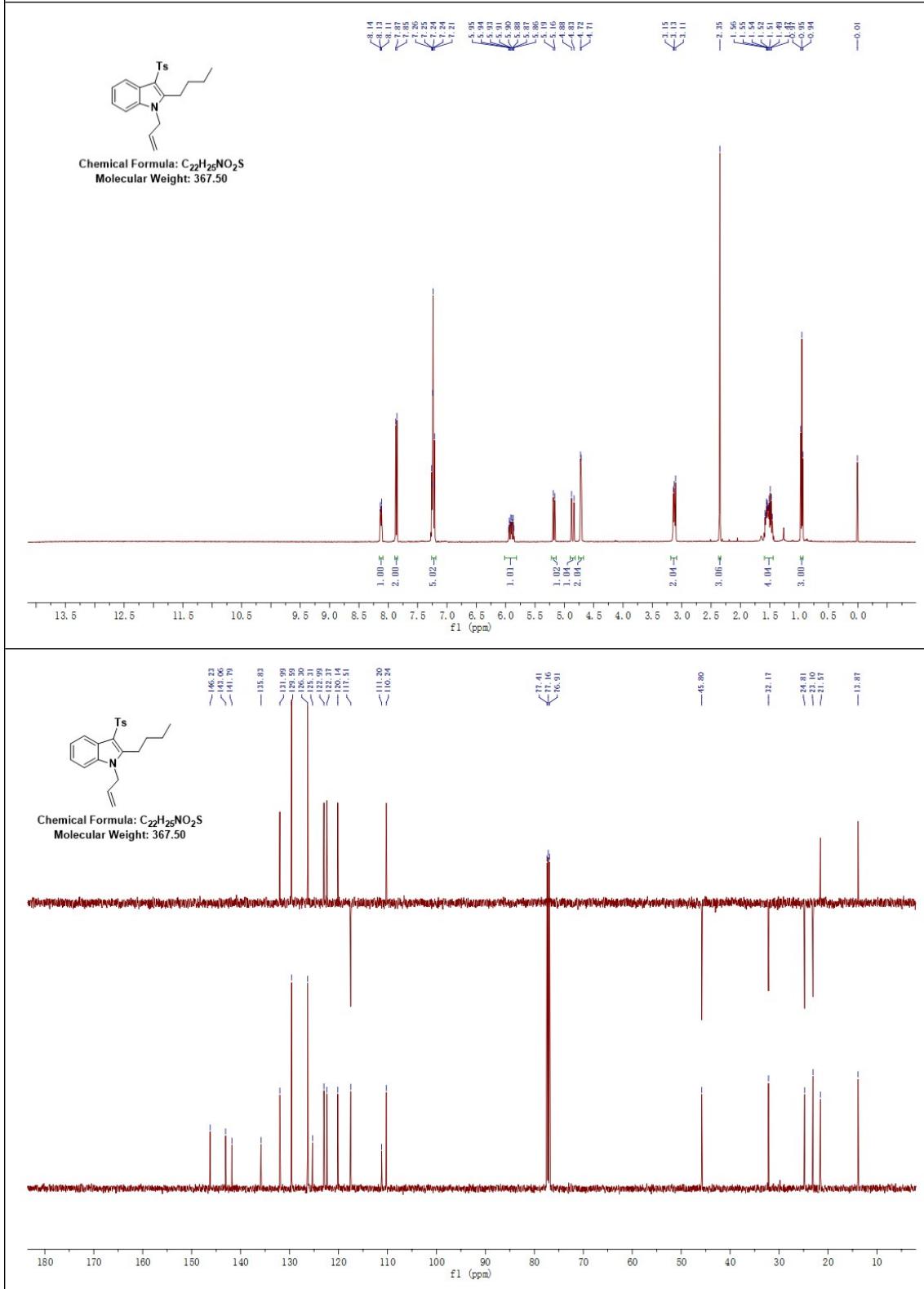
1-Allyl-2-butyl-3-(phenylsulfonyl)-*1H*-indole (3h**)**



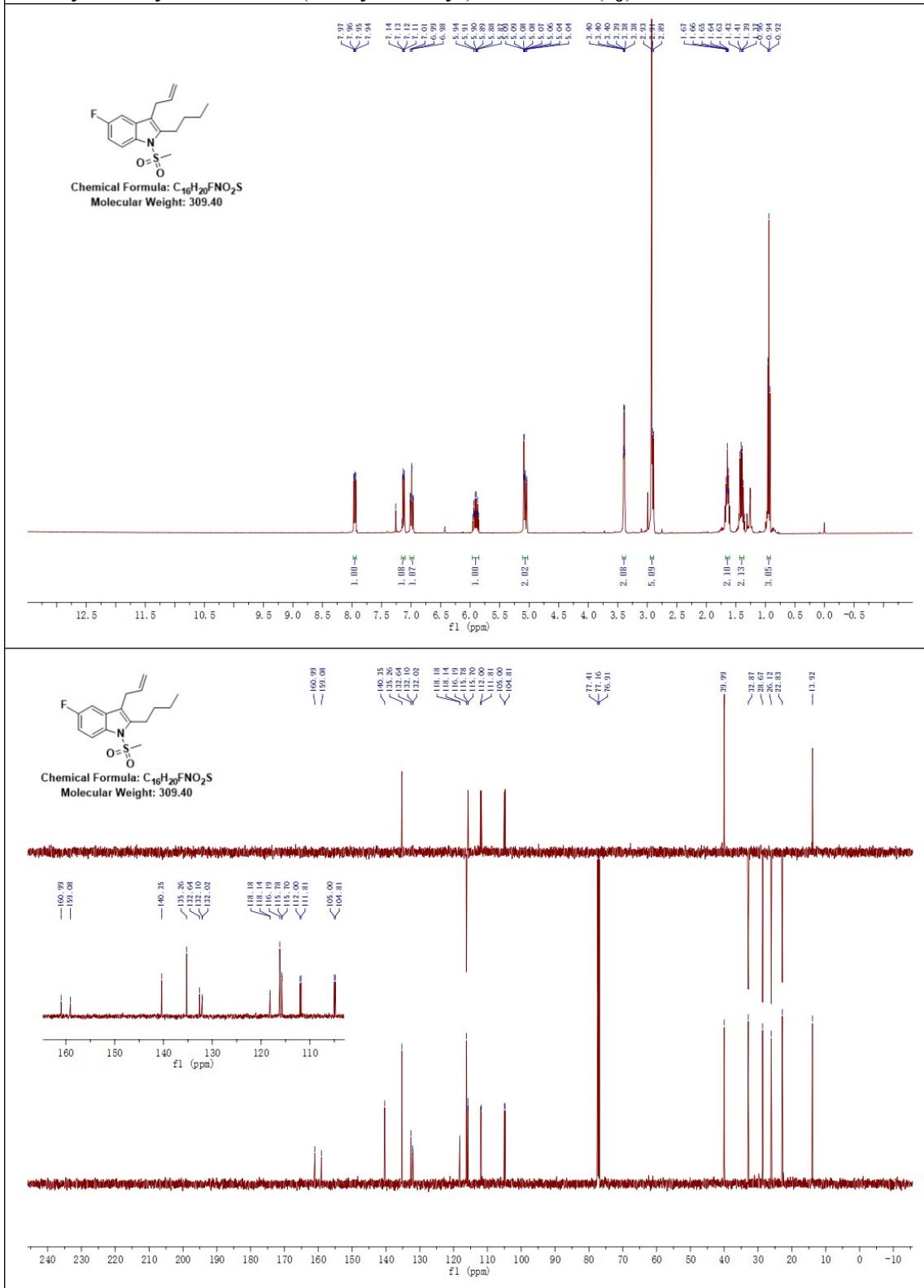
3-Allyl-2-butyl-1-(tosylsulfonyl)-*1H*-indole (2i**)**



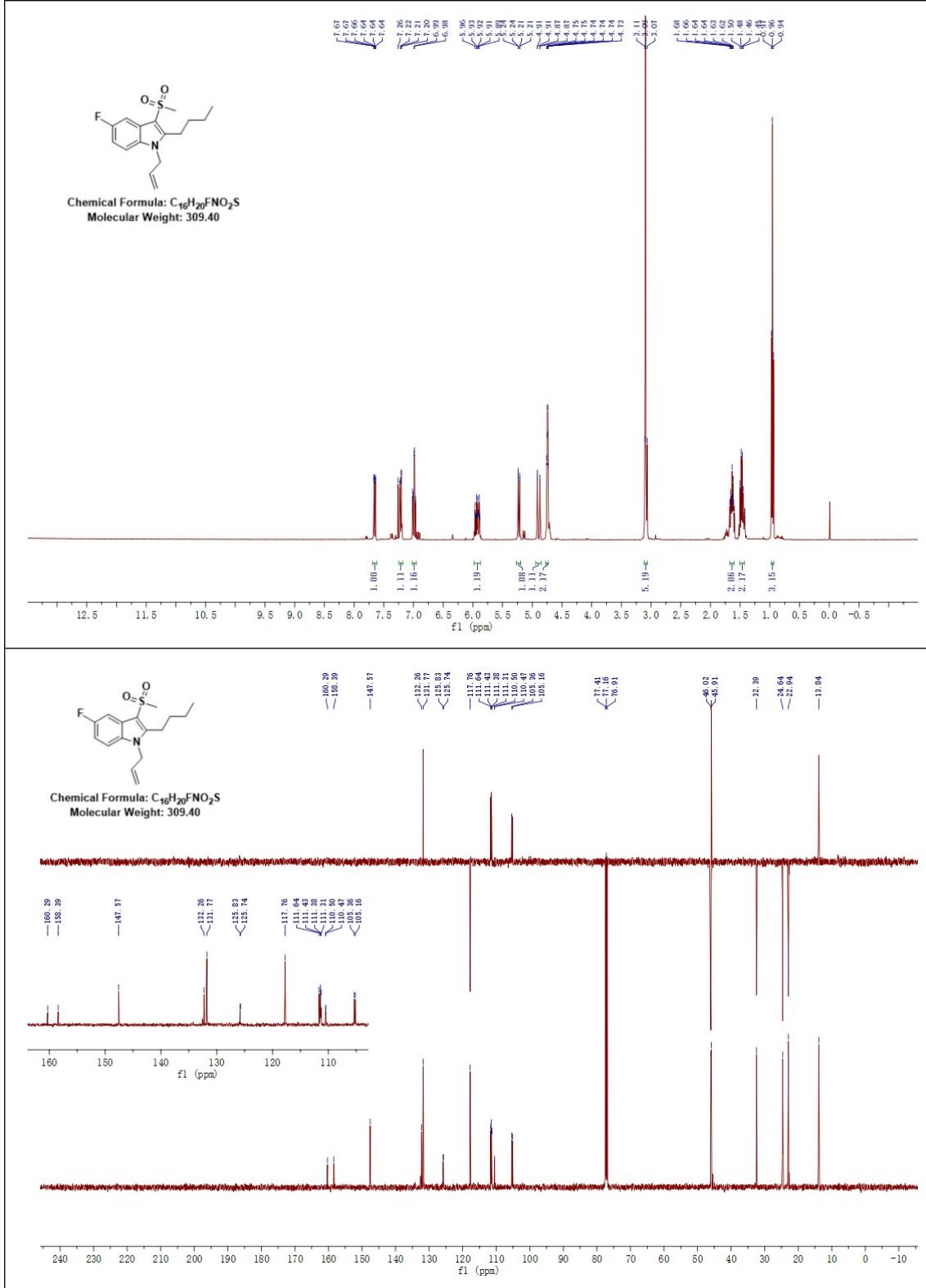
1-Allyl-2-butyl-3-(tosylsulfonyl)-*1H*-indole (3i**)**



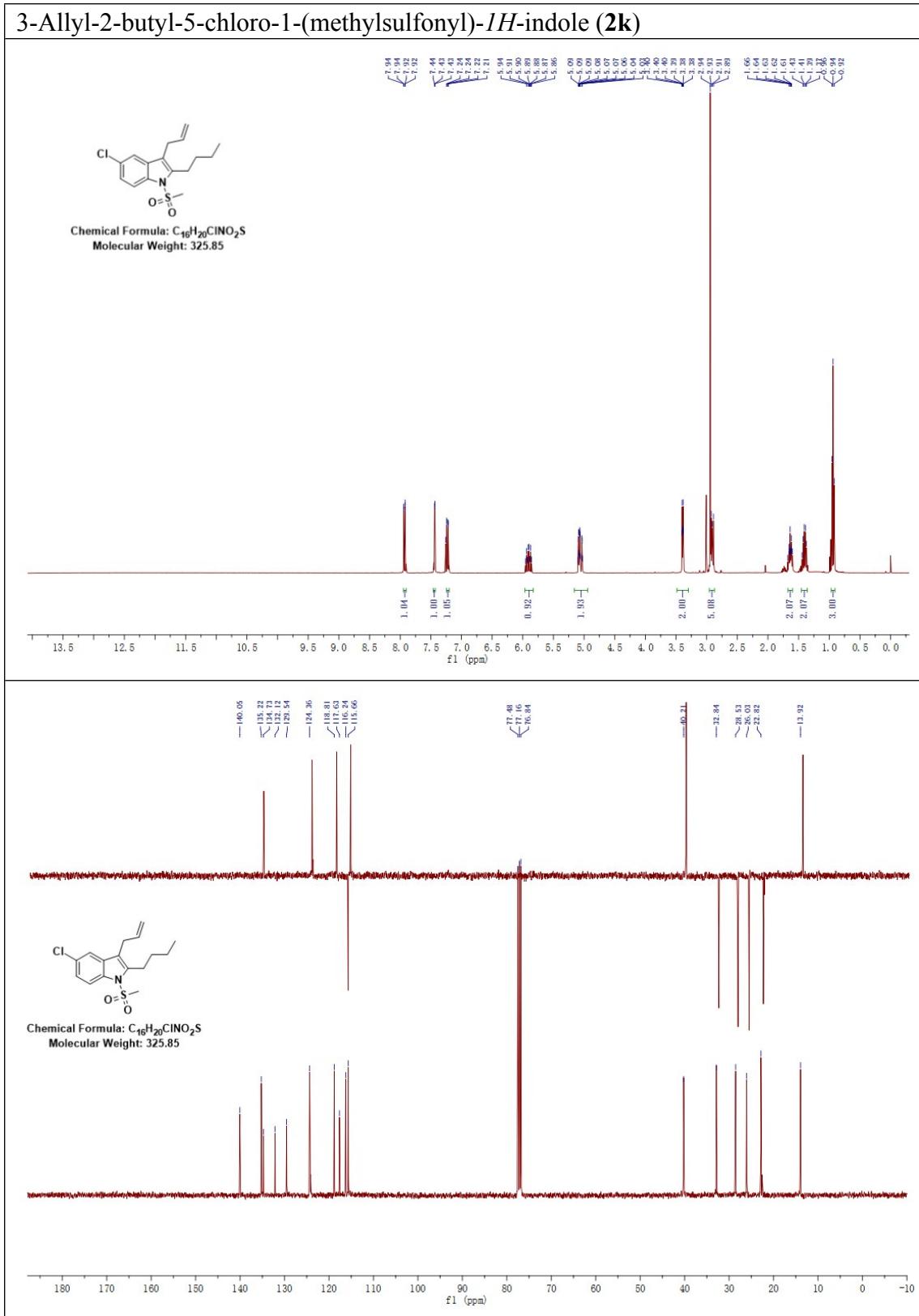
3-Allyl-2-butyl-5-fluoro-1-(methylsulfonyl)-*1H*-indole (2j**)**



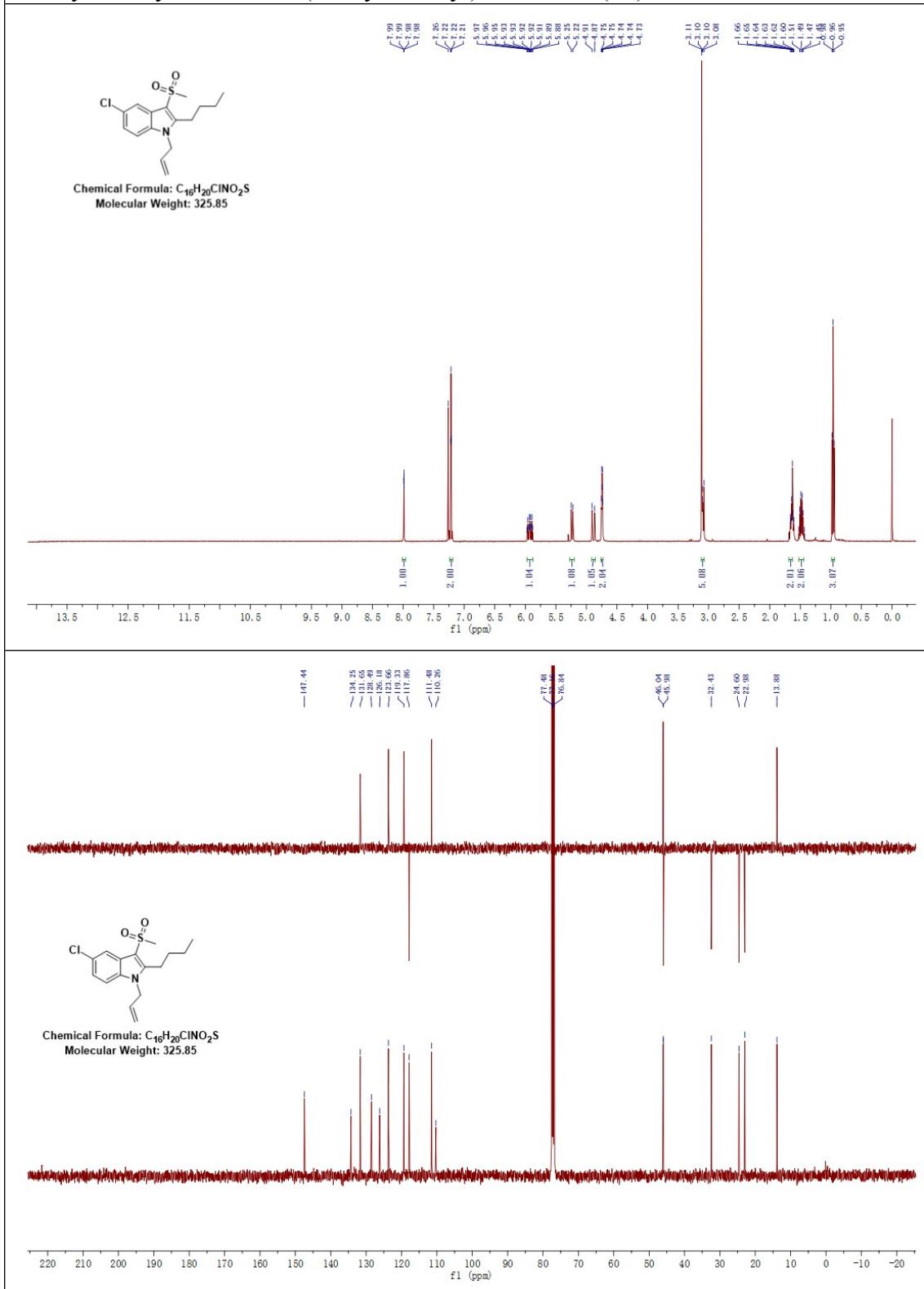
1-Allyl-2-butyl-5-fluoro-3-(methylsulfonyl)-*1H*-indole (3j**)**



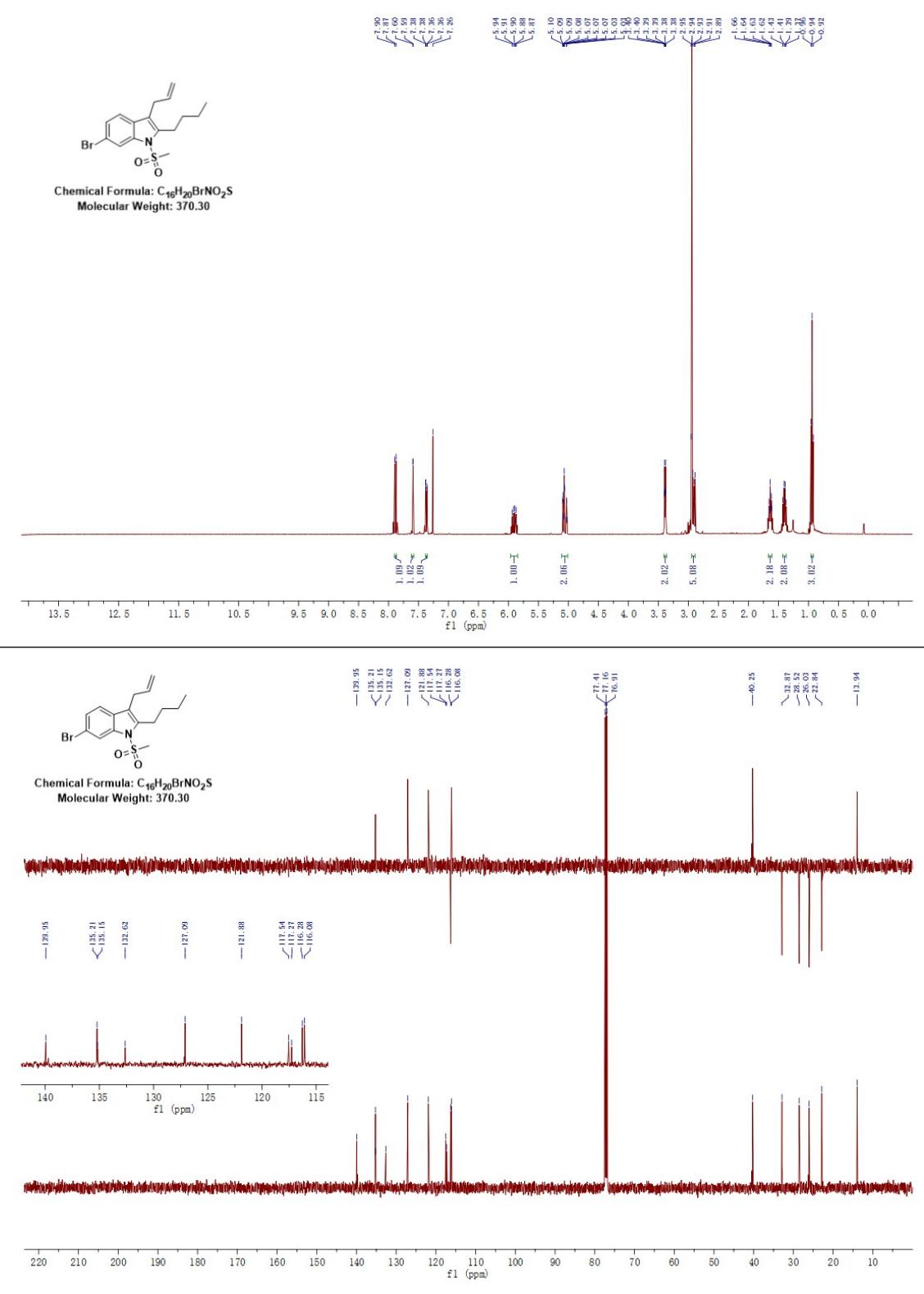
3-Allyl-2-butyl-5-chloro-1-(methylsulfonyl)-*1H*-indole (2k**)**



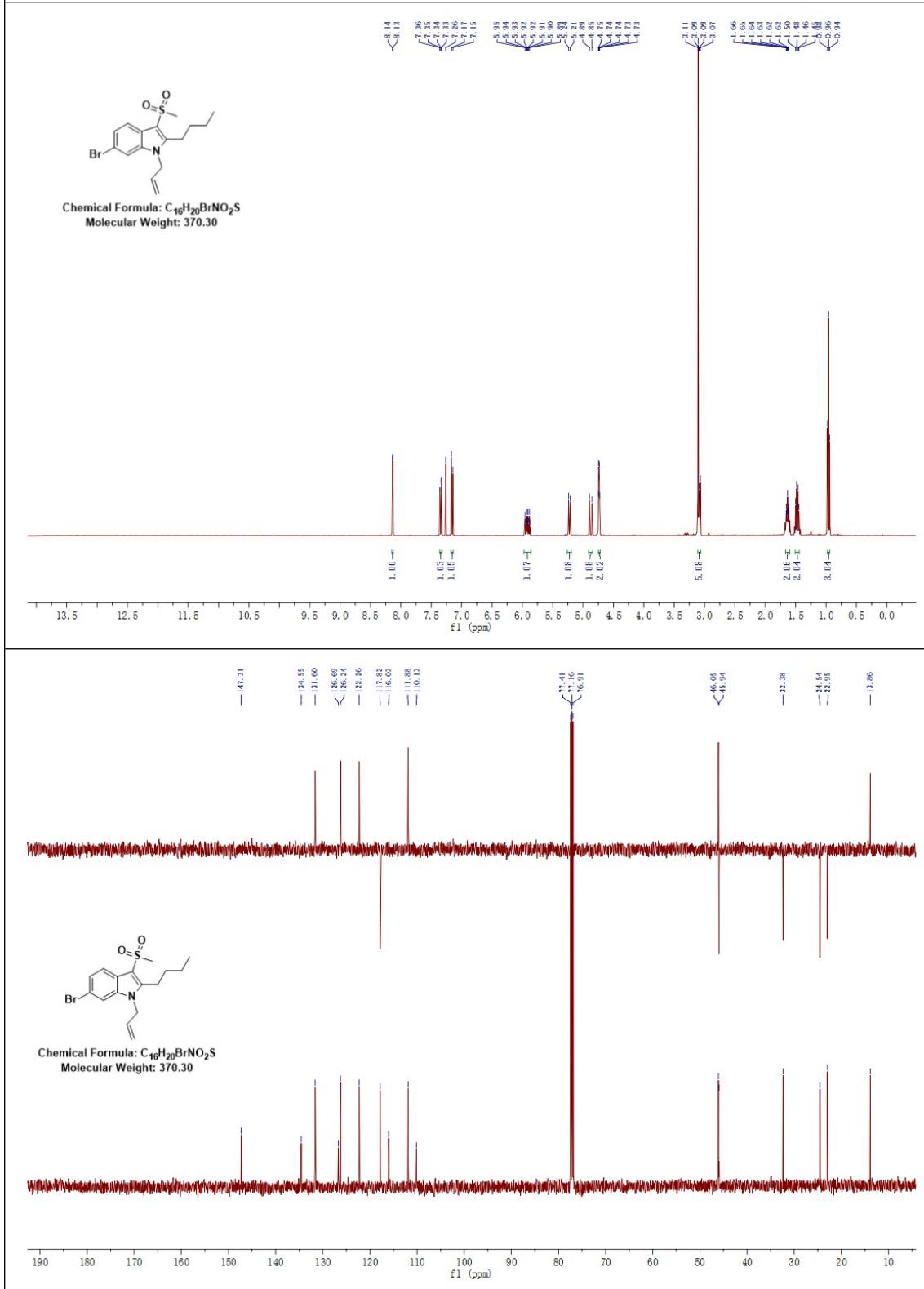
1-Allyl-2-butyl-5-chloro-3-(methylsulfonyl)-*1H*-indole (3k**)**



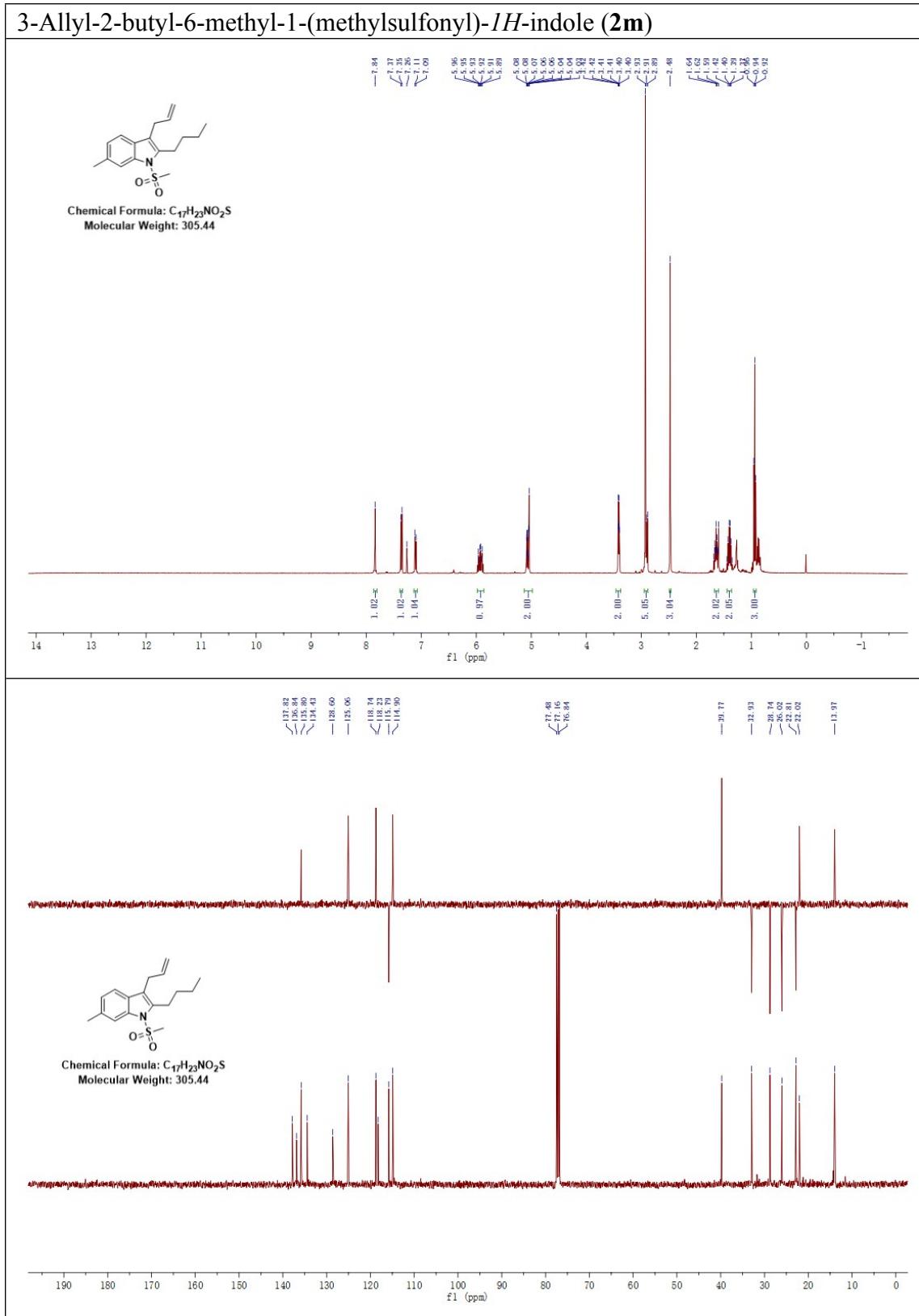
3-Allyl-6-bromo-2-butyl-1-(methylsulfonyl)-*1H*-indole (2l**)**



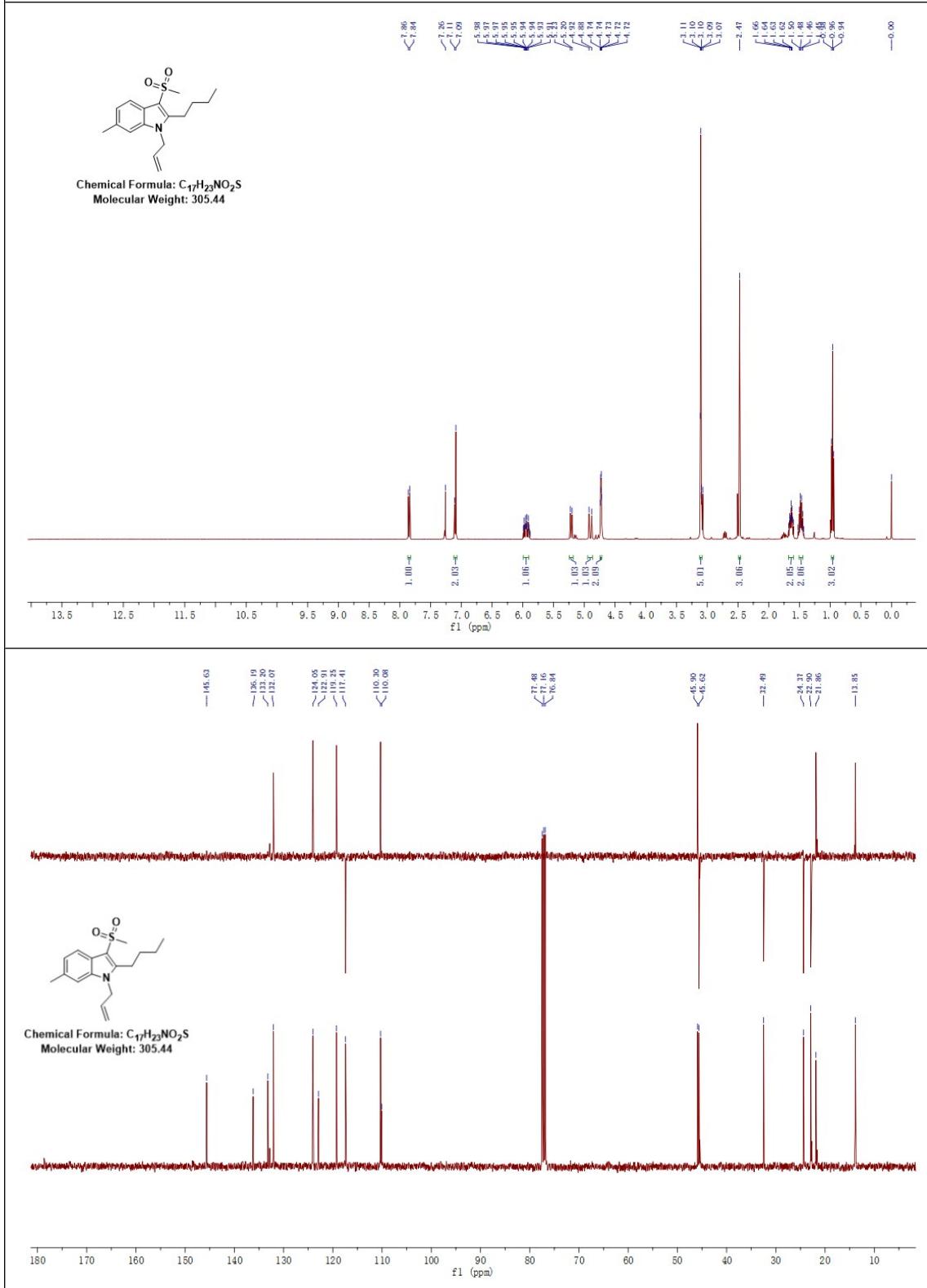
1-Allyl-6-bromo-2-butyl-3-(methylsulfonyl)-*1H*-indole (3I**)**



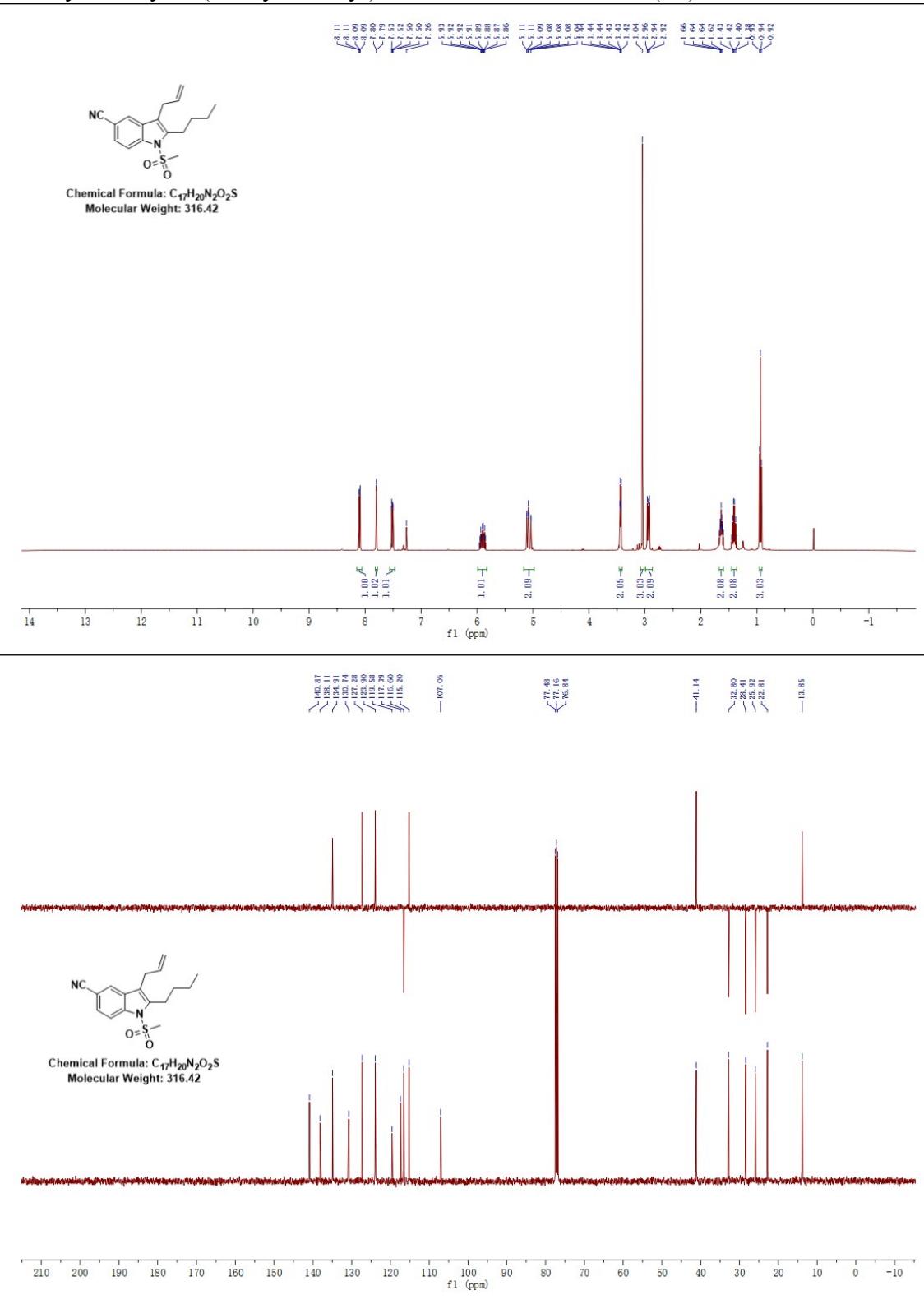
3-Allyl-2-butyl-6-methyl-1-(methylsulfonyl)-1*H*-indole (2m**)**



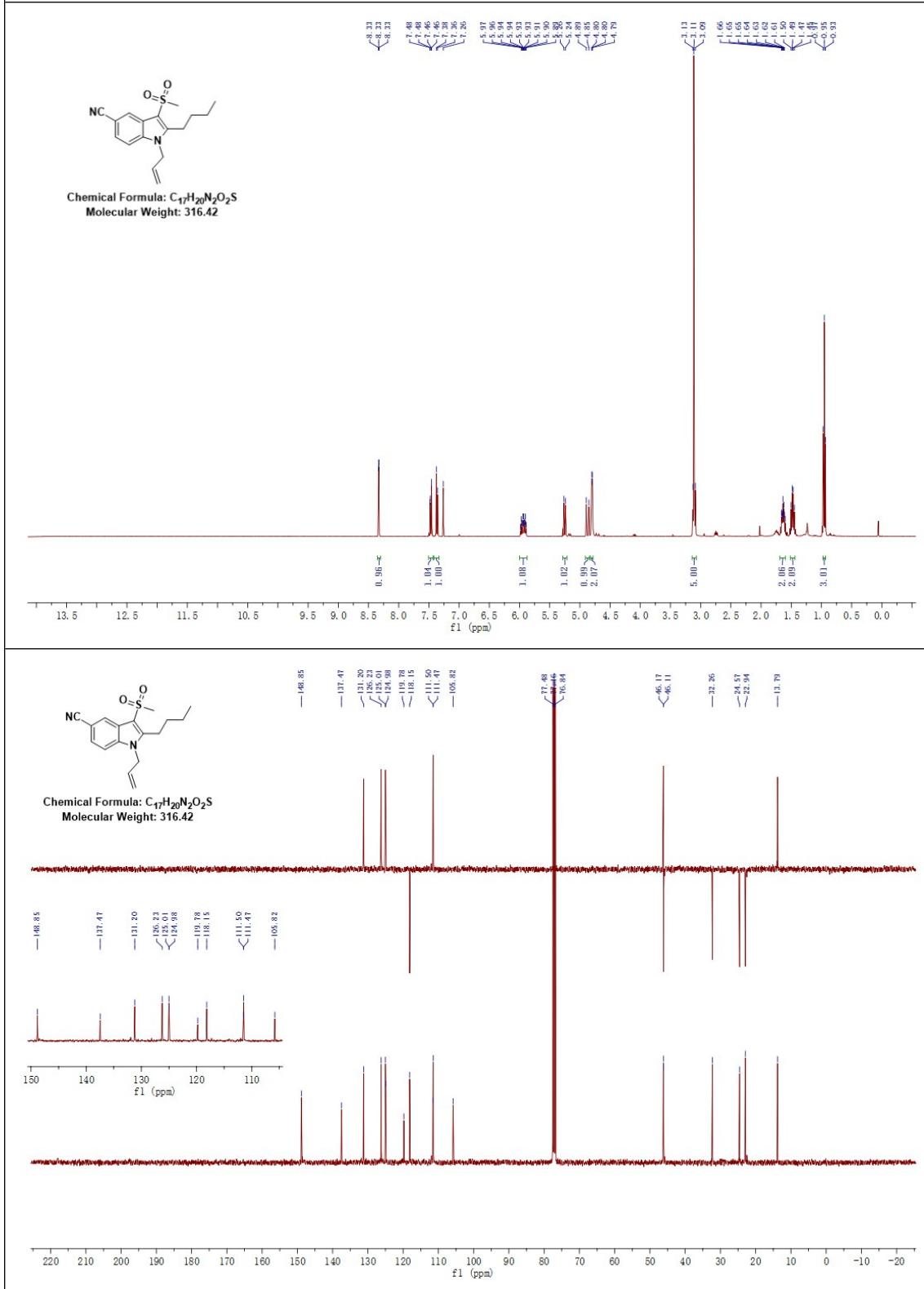
1-Allyl-2-butyl-6-methyl-3-(methylsulfonyl)-1*H*-indole (3m**)**



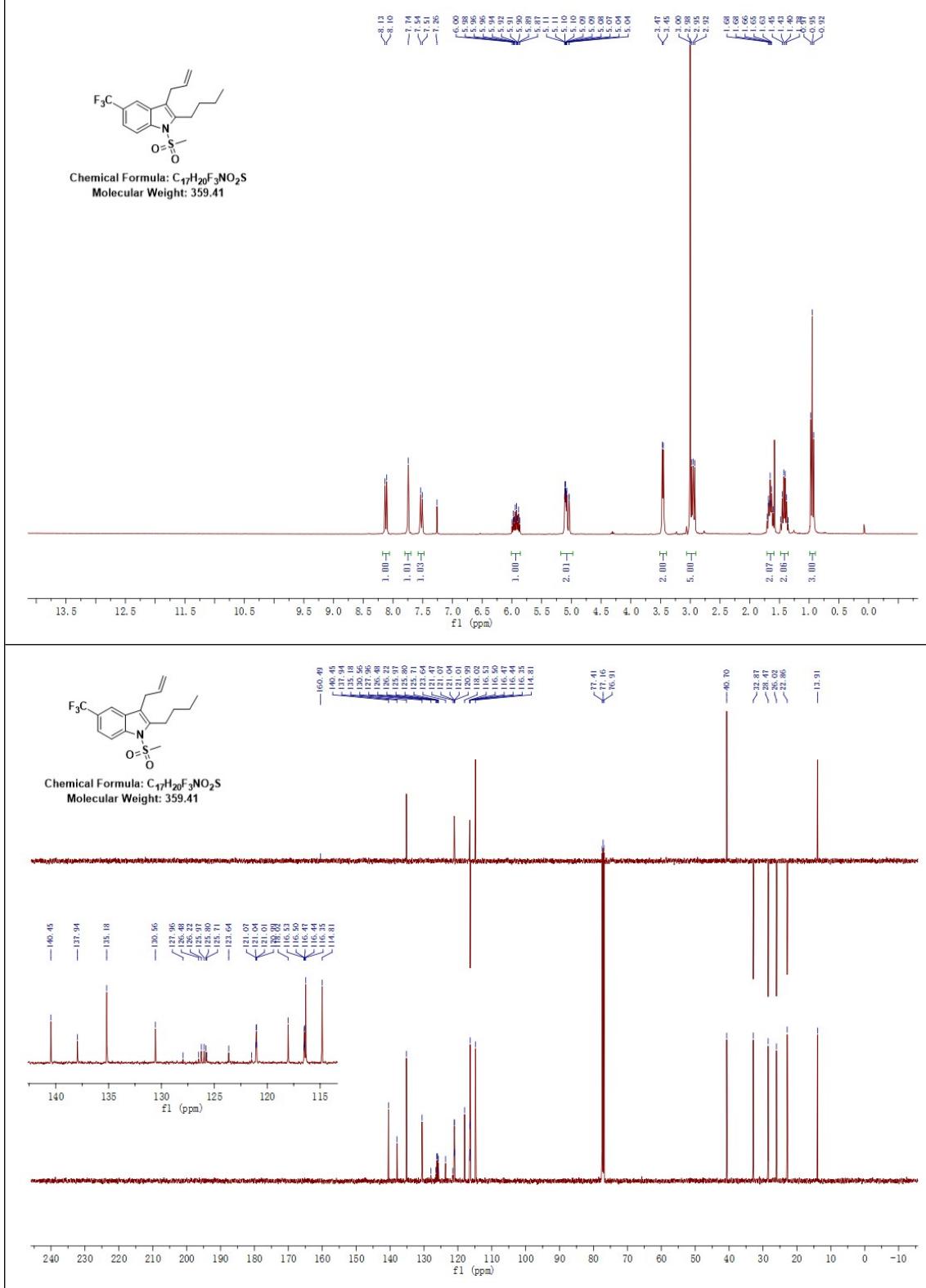
3-Allyl-2-butyl-1-(methylsulfonyl)-*1H*-indole-5-carbonitrile (2n**)**



1-Allyl-2-butyl-3-(methylsulfonyl)-1*H*-indole-5-carbonitrile (3n**)**



3-Allyl-2-butyl-1-(methylsulfonyl)-1*H*-indole (2o**)**



1-Allyl-2-butyl-3-(methylsulfonyl)-1*H*-indole (3o**)**

