

## Supporting Information

# **Copper-Catalyzed Reaction of Benzoxazinanes with Sulfilimines: Access to 2-Ethynyl-benzoimidazoles via an Abnormal Skeletal Rearrangement**

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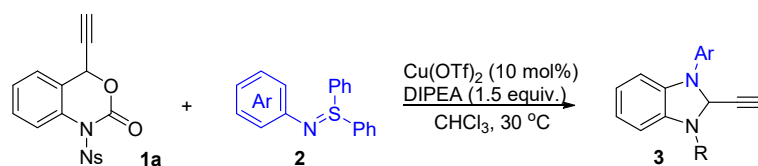
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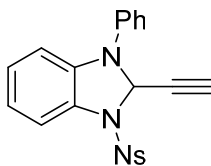
## General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F<sub>254</sub> indicator. For column chromatography, 200-300 mesh silica gel was used. <sup>1</sup>H NMR were recorded on Bruker 300 MHz, 400 MHz spectrometer in CDCl<sub>3</sub>. <sup>13</sup>C NMR were recorded on Bruker 75 MHz or 100 MHz spectrometer in CDCl<sub>3</sub>. <sup>19</sup>F NMR were recorded on Bruker 282 MHz or 377 MHz spectrometer in CDCl<sub>3</sub>. Data for <sup>1</sup>H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm), and were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets and m = multiplet. Data for <sup>13</sup>C NMR spectra were reported relative to CDCl<sub>3</sub> as an internal standard (77.16 ppm), and were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 QTOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus without correction. The Ethynyl benzoxazinanes **1**<sup>[1]</sup>, aza-sulfur ylides **2**<sup>[2]</sup> were prepared according to reported methods.

## General procedure for Scheme 2



To a dry tube was added Cu(OTf)<sub>2</sub> (3.6 mg, 0.01 mmol, 10 mol%), **1a** (0.15 mmol, 1.5 equiv), **2** (0.1 mmol, 1.0 equiv), DIPEA (26 μl, 0.15 mmol, 1.5 equiv ) and anhydrous CHCl<sub>3</sub> (1.5 mL) under argon atmosphere. Then, the mixture was stirred at 30 °C in a heating block for 12 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give products **3**.



**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-phenyl-2,3-dihydro-1H-benzo[d]imidazole (3a):**

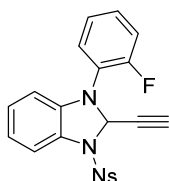
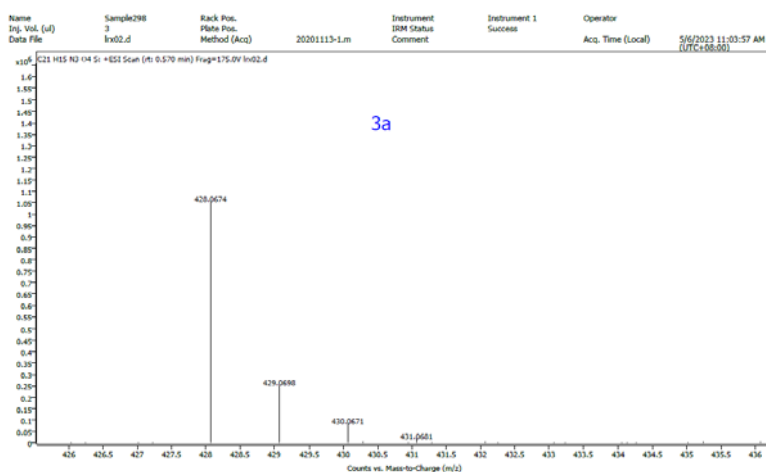
Prepared via **general procedure 2** from N,1,1-triphenyl- $\lambda^4$ -sulfanimine (27.7 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of  $\text{Cu}(\text{OTf})_2$  3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (38.5 mg, 95%), mp: 126-127 °C.

$R_f$  (Petroleum ether/ EtOAc = 4:1) = 0.7

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06-7.92 (m, 2H), 7.72 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.58 (d,  $J = 8.8$  Hz, 2H), 7.22 (dt,  $J = 6.6, 1.9$  Hz, 3H), 7.11-7.01 (m, 2H), 6.95 (dd,  $J = 8.0, 1.1$  Hz, 1H), 6.79 (dd,  $J = 7.6, 1.5$  Hz, 2H), 6.20 (d,  $J = 2.0$  Hz, 1H), 2.63 (d,  $J = 2.0$  Hz, 1H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 141.4, 140.6, 137.5, 130.6, 129.4, 128.4, 127.7, 123.9, 123.6, 121.8, 120.2, 117.1, 113.1, 78.4, 74.3, 73.1.

**HRMS (ESI) m/z:**  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{15}\text{FN}_3\text{O}_4\text{SNa}$  428.0675, found 428.0674.



**2-ethynyl-1-(2-fluorocyclohexa-1,3-dien-1-yl)-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzod[*d*]imidazole (3b):**

Prepared via **general procedure 2** from N-(2-fluorophenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (29.5 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[*d*][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (34.4 mg, 81%), mp: 168-169 °C.

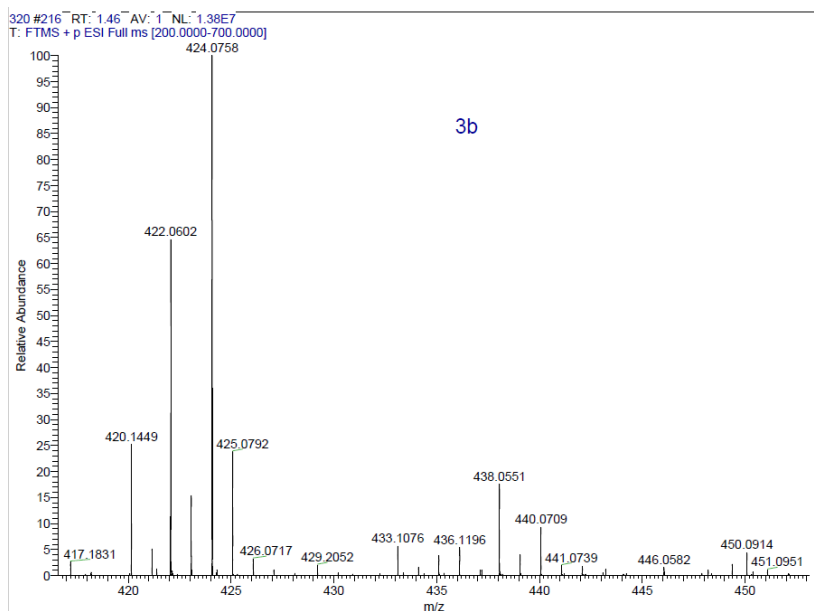
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

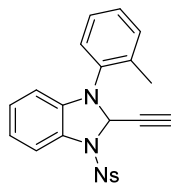
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.11-7.98 (m, 2H), 7.76-7.64 (m, 2H), 7.59 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.19-7.14 (m, 1H), 7.08 (s, 1H), 7.05 (d, *J* = 1.6 Hz, 3H), 6.89 (td, *J* = 7.7, 1.2 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 2.37 (d, *J* = 1.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.6, 150.6, 141.4, 139.2, 129.6, 128.8, 127.4, 127.3, 124.6, 124.5, 124.4, 123.9, 121.1, 119.4, 116.9, 116.7, 110.7, 74.9, 72.2, 72.1.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = -121.1.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>FN<sub>3</sub>O<sub>4</sub>S 424.0762, found 424.0758.





**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(o-tolyl)-2,3-dihydro-1H-benzo[d]imidazole (3c):**

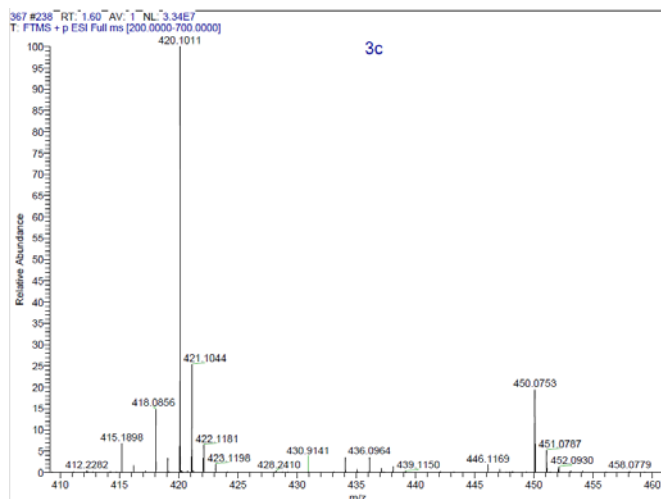
Prepared via **general procedure 2** from 1,1-diphenyl-N-(o-tolyl)- $\lambda^4$ -sulfanimine (29.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of  $\text{Cu}(\text{OTf})_2$  3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 10:1) and obtained as a red solid (36.0 mg, 86%), mp: 168-169 °C.

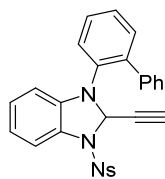
$R_f$  (Petroleum ether/ EtOAc = 5:1) = 0.4

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.31-8.23 (m, 2H), 7.94-7.86 (m, 2H), 7.67 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.27-7.18 (m, 2H), 7.12 (s, 1H), 7.06 (td,  $J = 7.7, 1.2$  Hz, 1H), 6.96 (dd,  $J = 7.7, 1.2$  Hz, 1H), 6.37 (dd,  $J = 7.8, 1.2$  Hz, 1H), 6.15 (d,  $J = 1.9$  Hz, 1H), 2.54 (d,  $J = 1.9$  Hz, 1H), 1.94 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 142.3, 141.4, 135.8, 131.5, 129.3, 128.7, 127.6, 127.0, 126.9, 124.2, 123.6, 120.3, 117.6, 77.9, 75.7, 72.2, 17.9.

**HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}_4\text{S}$  420.1013, found 420.1011.





**1-([1,1'-biphenyl]-2-yl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3d):**

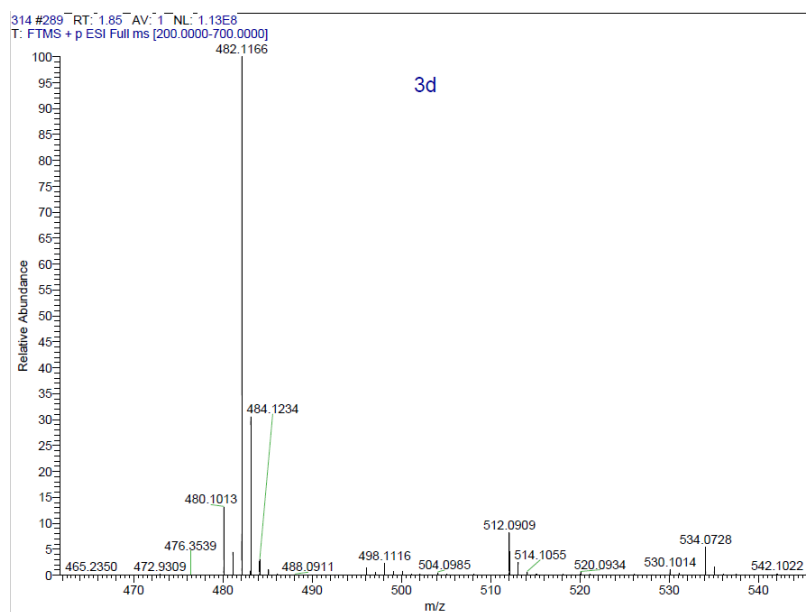
Prepared via **general procedure 2** from N-([1,1'-biphenyl]-2-yl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (35.3 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 10:1) and obtained as a yellow solid (46.2 mg, 96%), mp: 155-156 °C.

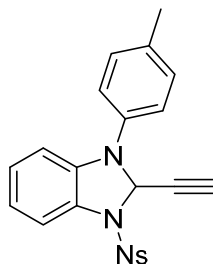
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.4

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.20 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.9 Hz, 2H), 7.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.47-7.34 (m, 5H), 7.31-7.26 (m, 4H), 7.03 (td, *J* = 7.7, 1.2 Hz, 1H), 6.88 (td, *J* = 7.7, 1.2 Hz, 1H), 6.69 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.69 (d, *J* = 1.9 Hz, 1H), 2.42 (d, *J* = 3.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 142.5, 140.5, 140.1, 139.3, 131.5, 129.2, 128.6, 128.6, 128.4, 128.4, 127.5, 127.4, 126.4, 126.0, 124.4, 120.2, 115.4, 109.9, 77.5, 76.0, 71.9.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub>S 482.1169, found 482.1166.





**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(p-tolyl)-2,3-dihydro-1H-benzo[d]imidazole (3e):**

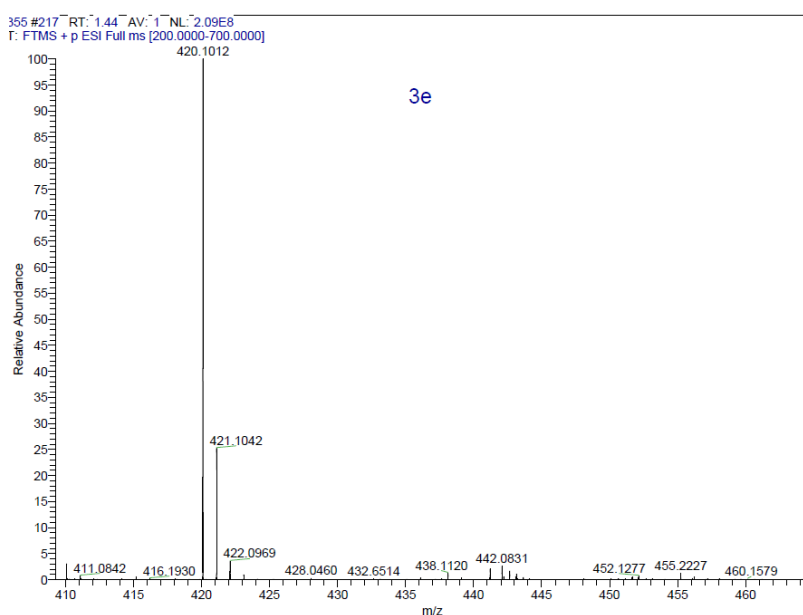
Prepared via **general procedure 2** from 1,1-diphenyl-N-(p-tolyl)- $\lambda^4$ -sulfanimine (29.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of  $\text{Cu}(\text{OTf})_2$  3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (30.2 mg, 72%), mp: 96-97  $^\circ\text{C}$ .

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

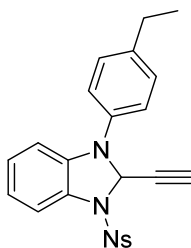
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.99-7.81 (m, 2H), 7.58 (dd,  $J$  = 7.9, 1.2 Hz, 1H), 7.56-7.45 (m, 2H), 7.07 (td,  $J$  = 7.8, 1.3 Hz, 1H), 6.99-6.84 (m, 3H), 6.76 (dd,  $J$  = 7.9, 1.1 Hz, 1H), 6.65-6.50 (m, 2H), 6.05 (d,  $J$  = 2.0 Hz, 1H), 2.50 (d,  $J$  = 2.0 Hz, 1H), 2.20 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 140.7, 138.9, 138.1, 133.7, 130.4, 129.9, 128.4, 127.6, 123.9, 121.4, 120.0, 117.9, 112.8, 78.5, 74.3, 73.3, 20.7.

**HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_4\text{S}$  420.1013, found 420.1012.







**1-(4-ethylphenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3f):**

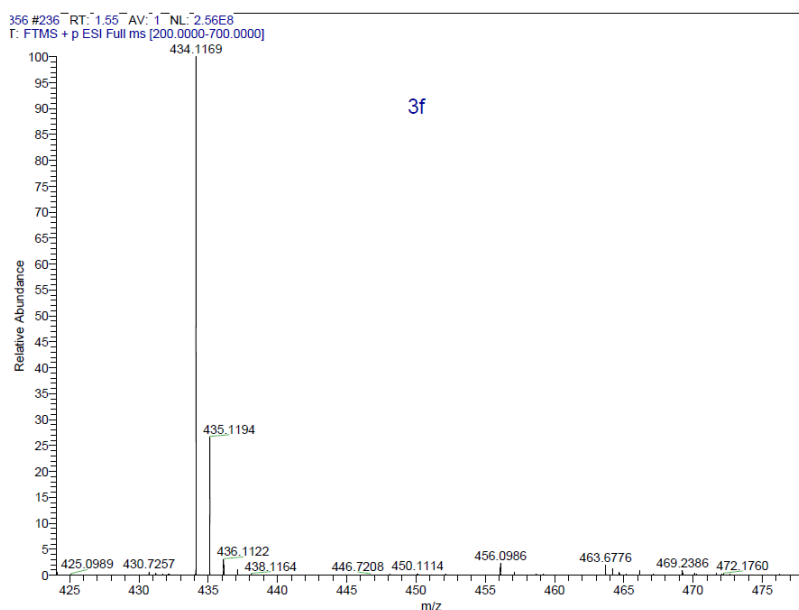
Prepared via **general procedure 2** from N-(4-ethylphenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (30.5 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (32.5 mg, 75%), mp: 84-85 °C.

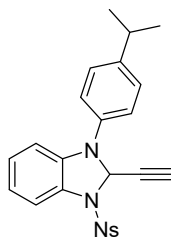
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.6

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.89 (d, *J* = 8.8 Hz, 2H), 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.53-7.44 (m, 2H), 7.08 (td, *J* = 7.8, 1.3 Hz, 1H), 6.93 (td, *J* = 8.1, 1.6 Hz, 3H), 6.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.64-6.55 (m, 2H), 6.05 (d, *J* = 2.0 Hz, 1H), 2.58-2.39 (m, 3H), 1.13 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 140.7, 140.1, 139.0, 138.1, 130.4, 128.7, 128.4, 127.6, 123.8, 121.4, 120.0, 117.7, 112.8, 78.5, 74.3, 73.2, 28.1, 15.5.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub>S 434.1169, found 434.1169.





**2-ethynyl-1-(4-isopropylphenyl)-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3g):**

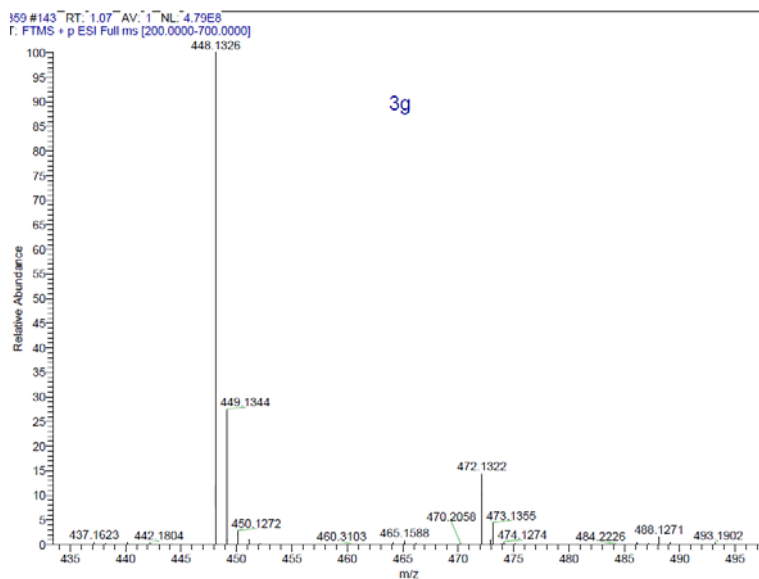
Prepared via **general procedure 2** from N-(4-isopropylphenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (31.9 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a yellow solid (23.2 mg, 52%), mp: 138-139 °C.

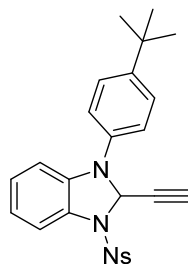
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.7

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.95-7.81 (m, 2H), 7.58 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52-7.45 (m, 2H), 7.06 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.00-6.90 (m, 3H), 6.78 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.65-6.53 (m, 2H), 6.05 (d, *J* = 2.0 Hz, 1H), 2.75 (p, *J* = 6.9 Hz, 1H), 2.49 (d, *J* = 2.0 Hz, 1H), 1.13 (dd, *J* = 6.9, 2.0 Hz, 6H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 144.6, 140.7, 139.1, 138.0, 130.4, 128.4, 127.7, 127.3, 123.8, 121.4, 120.1, 117.5, 112.8, 78.6, 74.2, 73.2, 33.4, 23.9, 23.9.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>O<sub>4</sub>S 448.1326, found 448.1326.





**1-(4-(tert-butyl)phenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3h):**

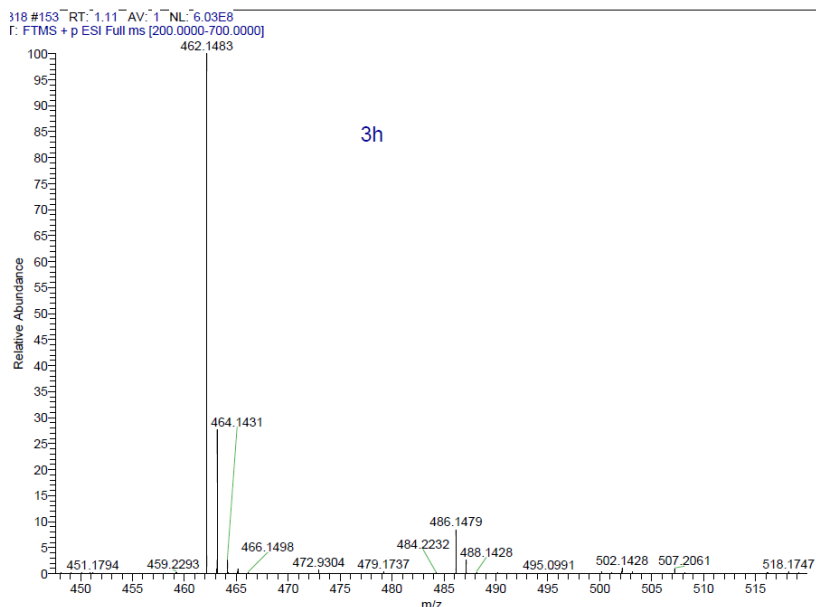
Prepared via **general procedure 2** from N-(4-(tert-butyl)phenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (33.3 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 10:1) and obtained as a yellow solid (25.8 mg, 56%), mp: 116-117 °C.

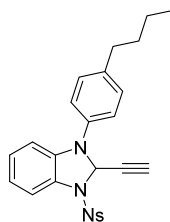
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.6

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.85 (d, *J* = 8.9 Hz, 2H), 7.59 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 3H), 6.93 (d, *J* = 1.2 Hz, 1H), 6.80 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.59 (d, *J* = 8.7 Hz, 2H), 6.05 (d, *J* = 2.0 Hz, 1H), 2.50 (d, *J* = 2.0 Hz, 1H), 1.20 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 146.8, 140.6, 138.8, 138.0, 130.5, 128.4, 127.7, 126.2, 123.8, 121.5, 120.2, 116.9, 113.0, 78.6, 74.2, 73.1, 34.3, 31.2.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>S 482.1482, found 482.1483.





**1-(4-butylphenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3i):**

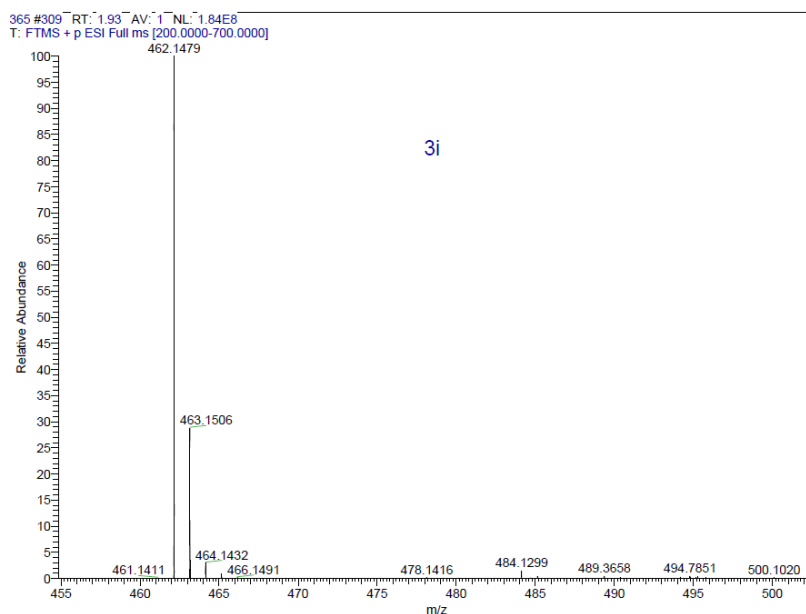
Prepared via **general procedure 2** from N-(4-butylphenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (33.3 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a yellow solid (34.6 mg, 75%), mp: 118-119 °C.

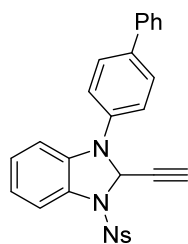
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.7

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.99-7.81 (m, 2H), 7.64-7.54 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54-7.43 (m, 2H), 7.13-7.05 (td, *J* = 7.8, 1.3 Hz, 1H), 6.98-6.83 (m, 3H), 6.82-6.71 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.66-6.49 (m, 2H), 6.12-5.82 (d, *J* = 2.0 Hz, 1H), 2.52-2.49 (d, *J* = 2.0 Hz, 1H), 2.49-2.41 (m, 2H), 1.52-1.43 (t, *J* = 7.9 Hz, 2H), 1.31-1.22 (m, 2H), 0.92-0.82 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 140.7, 139.0, 138.8, 138.1, 130.4, 129.2, 128.4, 127.6, 123.8, 121.4, 120.0, 117.6, 112.8, 78.6, 74.2, 73.2, 34.8, 33.6, 22.3, 13.9.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>S 462.1482, found 462.1479.





**1-([1,1'-biphenyl]-4-yl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3j):**

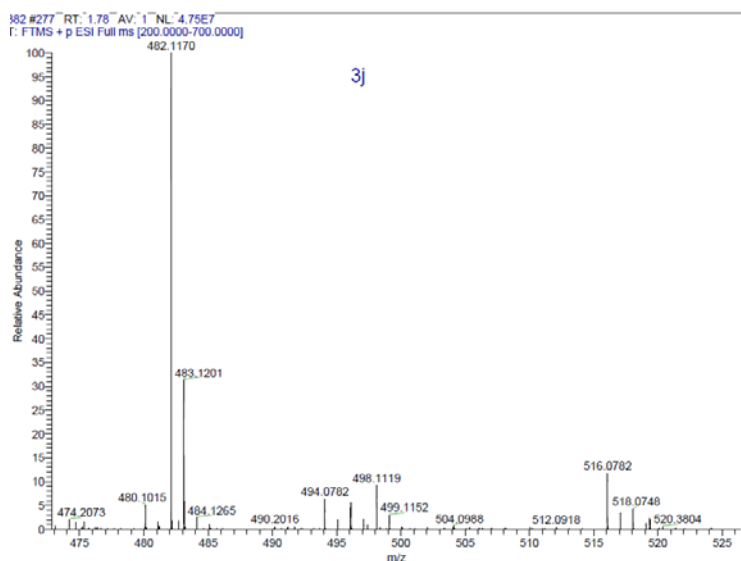
Prepared via **general procedure 2** from N-([1,1'-biphenyl]-4-yl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (35.3 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (38.0 mg, 79%), mp: 140-141 °C.

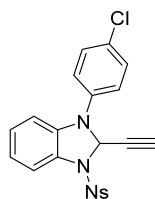
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.6

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  8.00 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.63-7.53 (m, 4H), 7.51-7.41 (m, 4H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 2.0 Hz, 1H), 2.64 (d, *J* = 1.9 Hz, 1H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 140.7, 140.3, 139.9, 137.4, 136.5, 130.5, 128.9, 128.4, 128.0, 127.7, 127.3, 126.6, 123.9, 121.8, 120.2, 117.3, 112.9, 78.3, 74.5, 72.9.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub>S 482.1169, found 482.1170.





**1-(4-chlorophenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3k):**

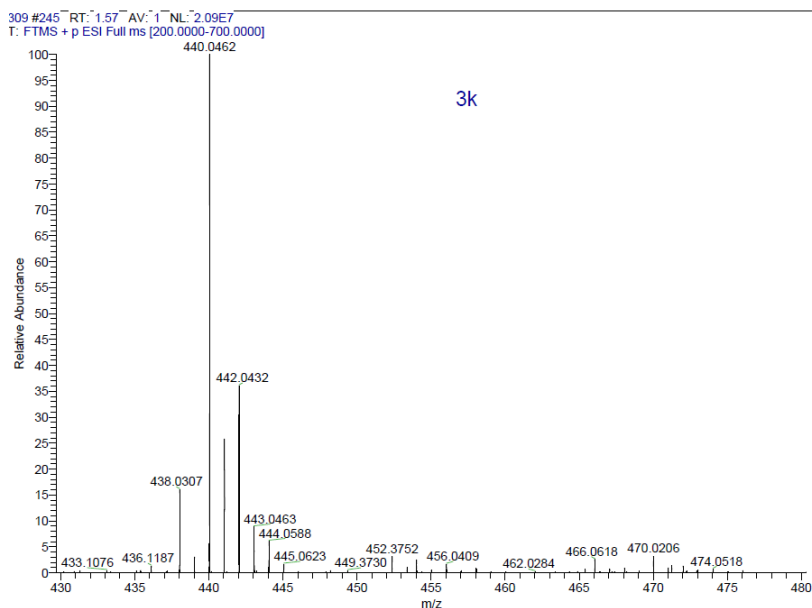
Prepared via **general procedure 2** from N-(4-chlorophenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (31.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a red solid (42.1 mg, 96%), mp: 150-151 °C.

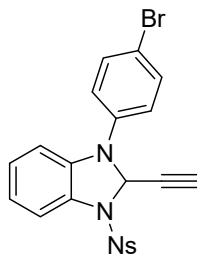
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.7

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.07 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 1.3 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.27-7.16 (m, 3H), 7.07 (td, *J* = 7.8, 1.2 Hz, 1H), 6.88 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.85-6.76 (m, 2H), 6.19 (d, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 2.0 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 140.9, 139.6, 137.3, 130.4, 129.5, 129.0, 128.5, 127.6, 123.9, 121.9, 119.9, 119.0, 112.4, 78.0, 74.8, 72.8.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>ClN<sub>3</sub>O<sub>4</sub>S 440.0466, found 440.0462.





**1-(4-bromophenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole**

**(3l):**

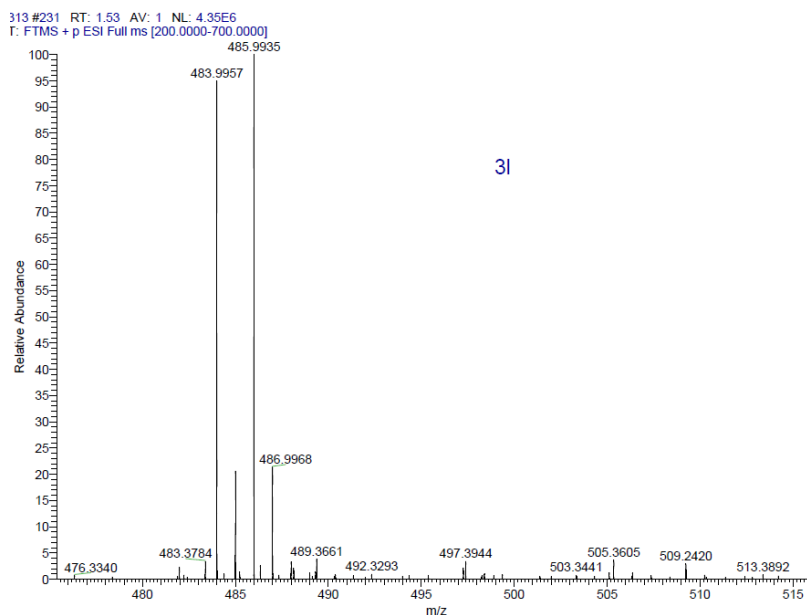
Prepared via **general procedure 2** from N-(4-bromophenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (35.5 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a red solid (47.4 mg, 98%), mp: 152-153 °C.

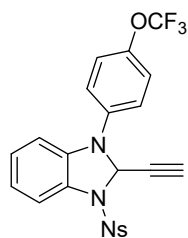
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.11-8.00 (m, 2H), 7.69 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.67-7.54 (m, 2H), 7.38-7.29 (m, 2H), 7.26-7.16 (m, 1H), 7.12-7.03 (m, 1H), 6.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.79-6.69 (m, 2H), 6.20 (d, *J* = 2.0 Hz, 1H), 2.64 (d, *J* = 2.0 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 140.8, 140.1, 137.2, 132.4, 130.5, 128.5, 127.6, 123.9, 122.1, 119.9, 119.2, 116.3, 112.6, 78.0, 74.9, 72.7.

**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>BrN<sub>3</sub>O<sub>4</sub>S 483.9961, found 483.9957.





**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1H-benzo[d]imidazole (3m):**

Prepared via **general procedure 2** from 1,1-diphenyl-N-(4-(trifluoromethoxy)phenyl)- $\lambda^4$ -sulfanimine (36.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a yellow solid (43.0 mg, 88%), mp: 77-78 °C.

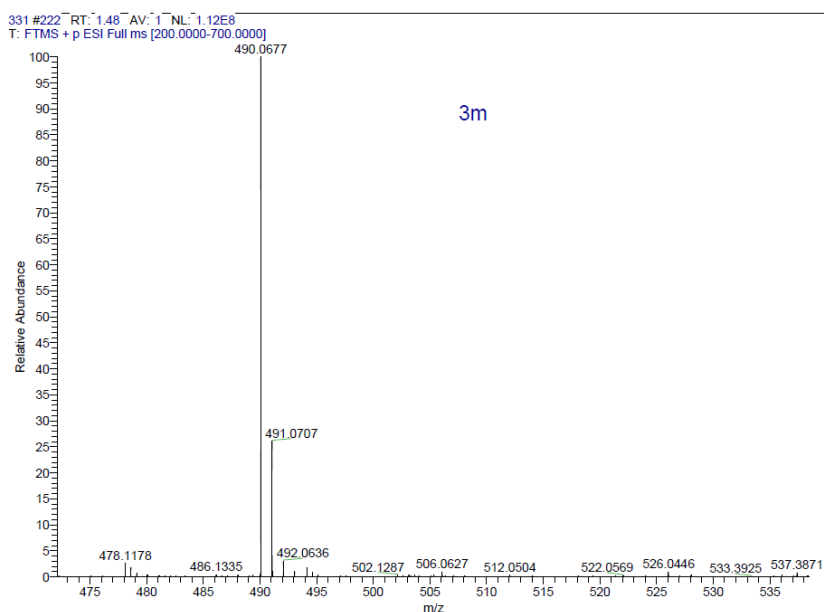
$R_f$  (Petroleum ether/ EtOAc = 5:1) = 0.7

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.03-7.88 (m, 2H), 7.63-7.47 (m, 3H), 7.08 (dd,  $J$  = 7.8, 1.3 Hz, 1H), 7.06-6.90 (m, 3H), 6.85- 6.71 (m, 3H), 6.10 (d,  $J$  = 2.0 Hz, 1H), 2.53 (d,  $J$  = 2.0 Hz, 1H).

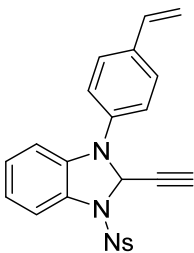
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 144.8, 140.9, 139.6, 137.3, 130.4, 128.5, 127.6, 123.9, 122.4, 122.1, 120.4 (q,  $J$  = 255.7 Hz), 119.9, 118.8, 112.4, 78.0, 74.9, 72.8.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = -58.2.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>15</sub>F<sub>3</sub>N<sub>3</sub>O<sub>5</sub>S 490.0679, found 490.0677.







**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(4-vinylphenyl)-2,3-dihydro-1H-benzo[d]imidazole (3n):**

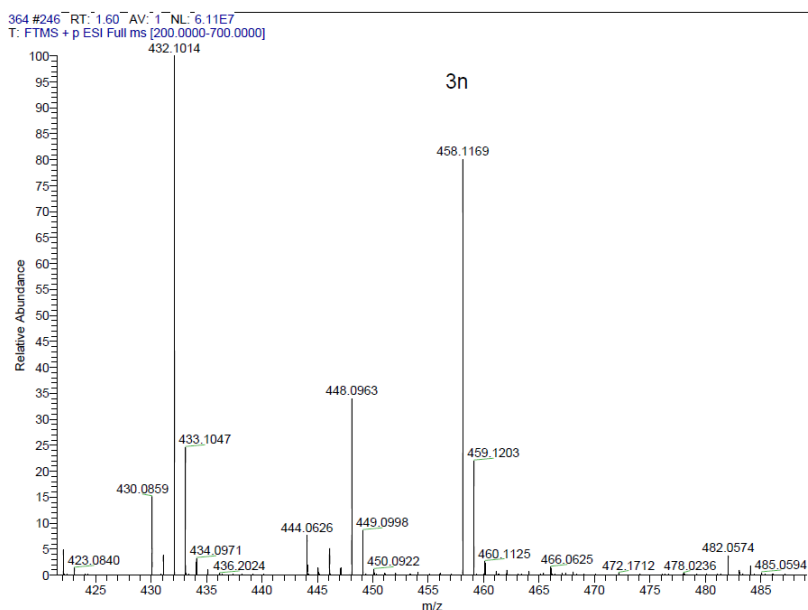
Prepared via **general procedure 2** from 1,1-diphenyl-N-(4-vinylphenyl)- $\lambda^4$ -sulfanimine (30.3 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of  $\text{Cu}(\text{OTf})_2$  3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (21.6 mg, 50%), mp: 92-93  $^{\circ}\text{C}$ .

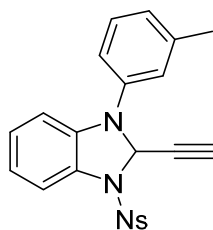
$R_f$  (Petroleum ether/ EtOAc = 5:1) = 0.5

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.95-7.79 (m, 2H), 7.60 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.52-7.42 (m, 2H), 7.18-7.06 (m, 3H), 6.96 (td,  $J = 7.8, 1.2$  Hz, 1H), 6.83 (d,  $J = 8.0$  Hz, 1H), 6.63 (d,  $J = 8.5$  Hz, 2H), 6.54 (dd,  $J = 17.6, 10.9$  Hz, 1H), 6.09 (d,  $J = 2.0$  Hz, 1H), 5.57 (d,  $J = 17.6$  Hz, 1H), 5.13 (d,  $J = 10.9$  Hz, 1H), 2.52 (d,  $J = 2.0$  Hz, 1H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 140.7, 140.5, 137.4, 135.5, 133.1, 130.6, 128.4, 127.7, 127.2, 123.9, 121.9, 120.2, 117.0, 113.4, 113.2, 78.3, 74.5, 72.9.

**HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_3\text{O}_4\text{S}$  432.1013, found 432.1014.





**2-ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(m-tolyl)-2,3-dihydro-1H-benzo[d]imidazole (3o):**

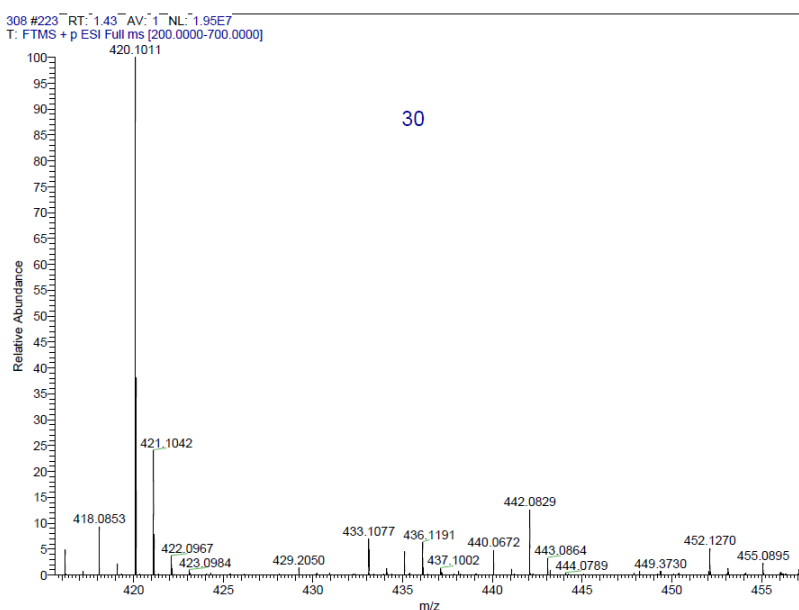
Prepared via **general procedure 2** from 1,1-diphenyl-N-(m-tolyl)- $\lambda^4$ -sulfanimine (29.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (38.4 mg, 92%), mp: 124-125 °C.

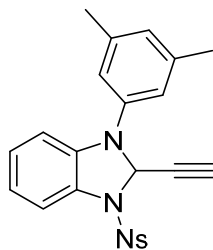
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.94-7.84 (m, 2H), 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50-7.43 (m, 2H), 7.10 (td, *J* = 7.8, 1.3 Hz, 1H), 7.01-6.90 (m, 2H), 6.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.78-6.70 (m, 1H), 6.55-6.41 (m, 2H), 6.08 (d, *J* = 2.0 Hz, 1H), 2.52 (d, *J* = 2.0 Hz, 1H), 2.15 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 141.4, 140.7, 139.5, 137.7, 130.5, 129.2, 128.4, 127.7, 124.5, 123.8, 121.7, 120.2, 117.5, 114.2, 113.2, 78.6, 74.2, 73.1, 21.3.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>S 420.1013, found 420.101.





**1-(3,5-dimethylphenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3p):**

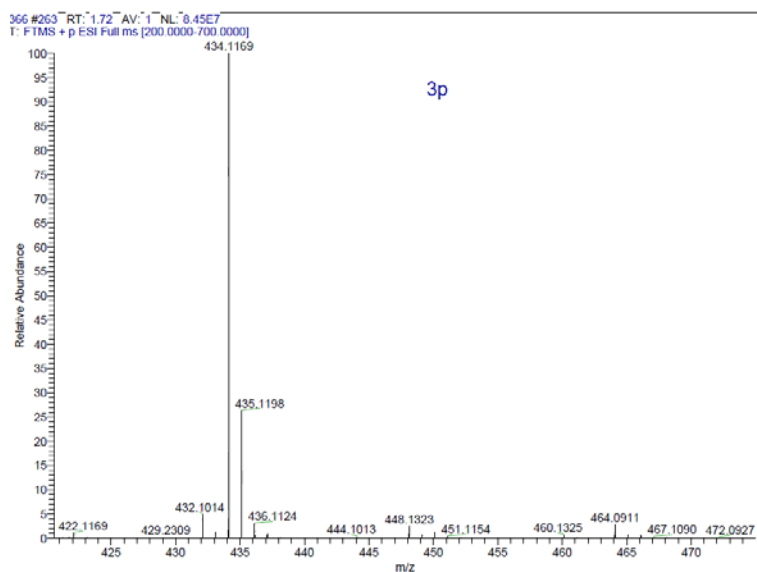
Prepared via **general procedure 2** from N-(3,5-dimethylphenyl)-1,1-diphenyl- $\lambda^4$ -sulfanimine (30.5 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (39.0 mg, 90%), mp: 194-195 °C.

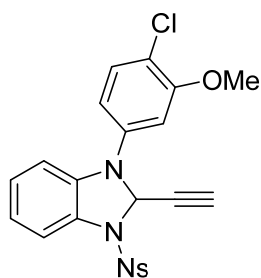
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.09-7.96 (m, 2H), 7.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.63-7.52 (m, 2H), 7.21 (td, *J* = 7.8, 1.3 Hz, 1H), 7.05 (td, *J* = 7.7, 1.2 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.69 (s, 1H), 6.36 (d, *J* = 1.5 Hz, 2H), 6.19 (d, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 2.0 Hz, 1H), 2.22 (s, 6H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 141.4, 140.8, 139.3, 137.8, 130.5, 128.5, 127.7, 125.4, 123.7, 121.5, 120.2, 114.8, 113.2, 78.7, 77.3, 74.1, 73.1, 21.2.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub>S 434.1169, found 434.1169.





***1-(4-chloro-3-methoxyphenyl)-2-ethynyl-3-((4-nitrophenyl)sulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3q):***

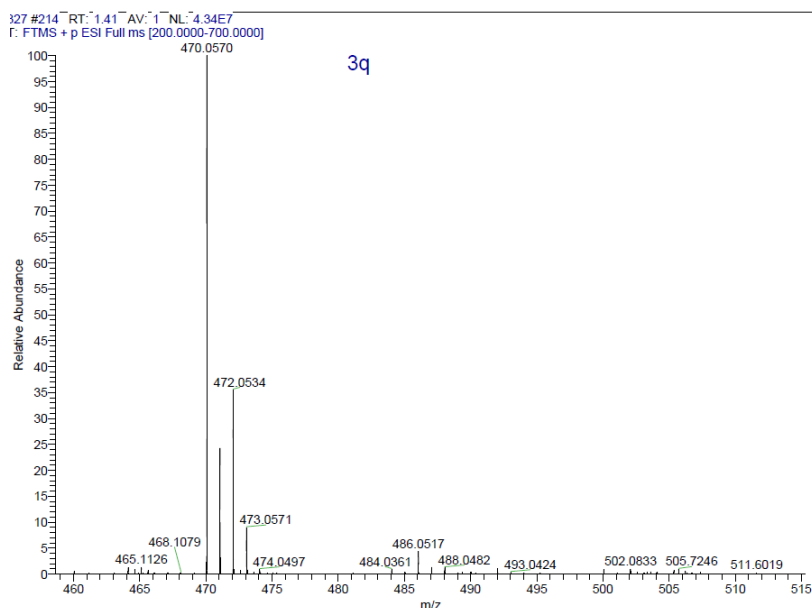
Prepared via **general procedure 2** from N-(4-chloro-3-methoxyphenyl)-1,1-diphenyl- $\lambda^4$ -Sulf-animine (34.1 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-thionitroso-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (53.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a yellow solid (38.5 mg, 82%), mp: 180-181 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5

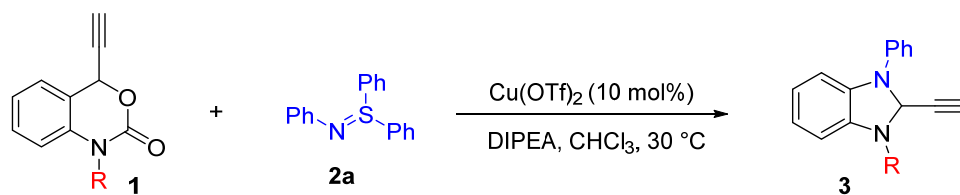
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.16-8.07 (m, 2H), 7.68 (td, *J* = 7.3, 1.6 Hz, 3H), 7.25-7.14 (m, 2H), 7.08 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.36 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.24 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H), 2.65 (d, *J* = 1.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.7, 150.5, 141.1, 140.8, 130.6, 130.5, 128.5, 127.6, 123.9, 122.0, 119.8, 112.4, 110.5, 102.2, 78.1, 77.3, 74.9, 72.9, 56.1.

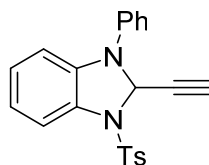
**HRMS (ESI)** *m/z*: [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>17</sub>ClN<sub>3</sub>O<sub>5</sub>S 470.0572, found 470.0570.



### General procedure for Scheme 3



To a dry tube was added Cu(OTf)<sub>2</sub> (3.6 mg, 0.01 mmol, 10 mol%), **1** (0.15 mmol, 1.5 equiv), **2a** (0.1 mmol, 1.0 equiv), DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) and anhydrous CHCl<sub>3</sub> (1.5 mL) under argon atmosphere. Then, the mixture was stirred at 30 °C in a heating block for 12 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give products **3**.



#### **2-ethynyl-1-phenyl-3-tosyl-2,3-dihydro-1H-benzo[d]imidazole (3r):**

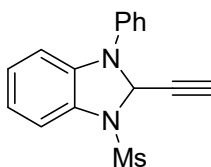
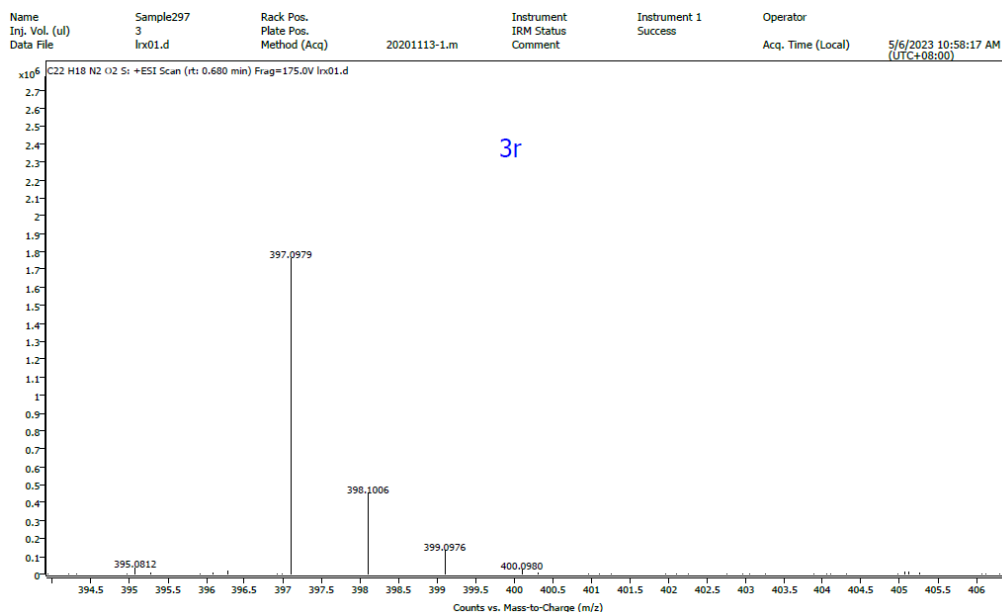
Prepared via **general procedure 3** from N,1,1-triphenyl- $\lambda^4$ -sulfanimine (27.7 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-tosyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (49.1 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a white solid (29.5 mg, 79%), mp: 160-161 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 4:1) = 0.8

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  7.68 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 7.08-6.92 (m, 4H), 6.92-6.86 (m, 1H), 6.86-6.76 (m, 2H), 6.19 (d, *J* = 2.0 Hz, 1H), 2.58 (d, *J* = 2.0 Hz, 1H), 2.27 (s, 3H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 141.5, 137.8, 132.3, 131.3, 129.4, 129.1, 127.2, 126.8, 123.1, 121.1, 120.0, 117.7, 112.1, 79.3, 73.7, 72.9, 21.5.

**HRMS (ESI)** *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>SNa 397.0981, found 397.0979.



***2-ethynyl-1-(methylsulfonyl)-3-phenyl-2,3-dihydro-1H-benzo[d]imidazole (3s):***

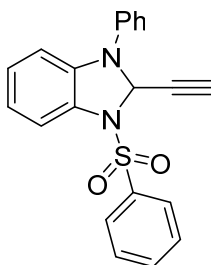
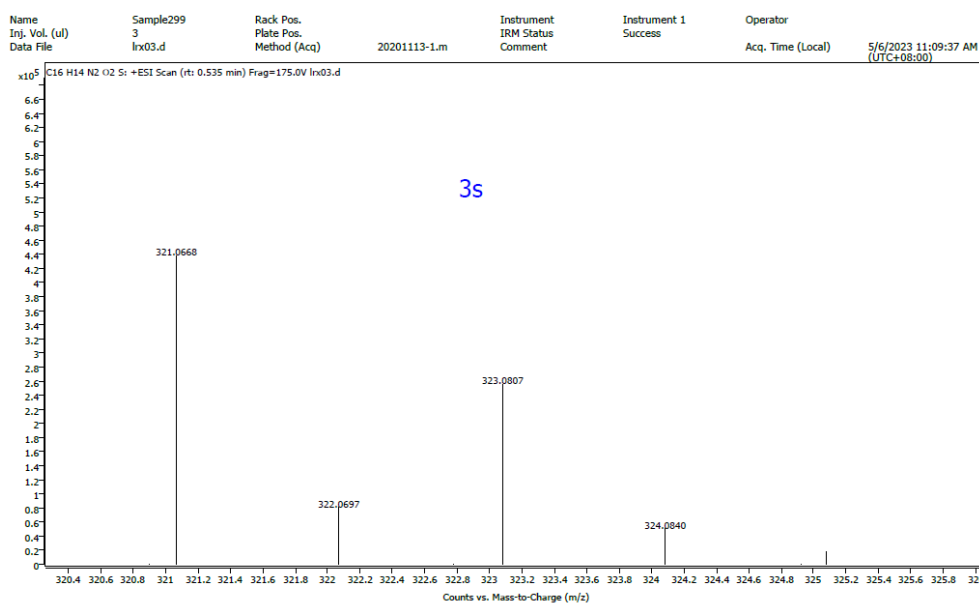
Prepared via **general procedure 3** from N,1,1-triphenyl- $\lambda^4$ -sulfanimine (27.7 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-(methylsulfonyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (37.7 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 10:1) and obtained as a white solid (28.3 mg, 95%), mp: 121-122 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.3

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.37-7.24 (m, 5H), 7.10-7.04 (m, 1H), 7.04-6.96 (m, 2H), 6.88-6.79 (m, 1H), 6.30 (d, *J* = 1.9 Hz, 1H), 2.85 (s, 3H), 2.54 (d, *J* = 1.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8, 137.1, 131.0, 129.7, 125.7, 124.1, 121.1, 119.3, 116.4, 111.3, 78.7, 74.9, 72.3, 37.1.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>SNa 321.0668, found 321.0668.



**2-ethynyl-1-phenyl-3-(phenylsulfonyl)-2,3-dihydro-1H-benzo[d]imidazole (3t):**

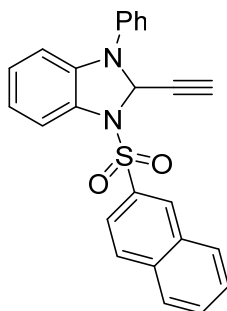
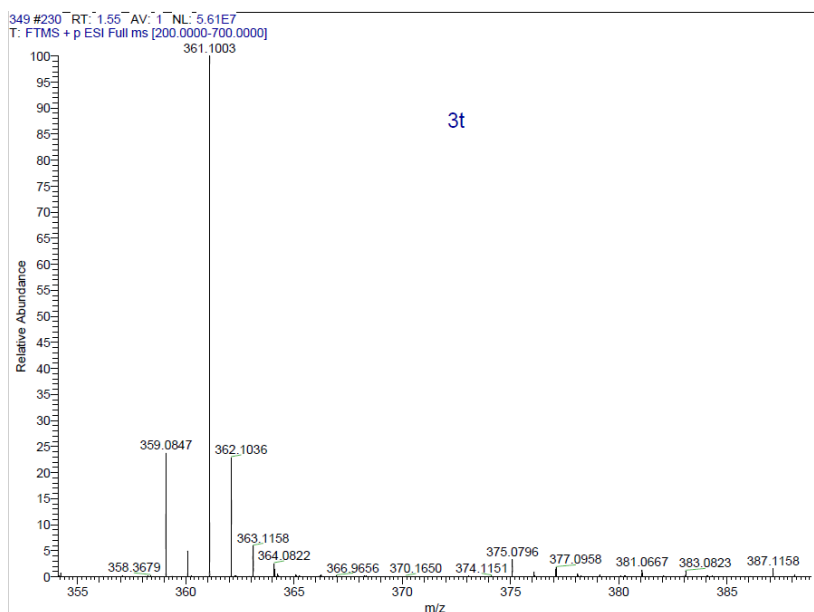
Prepared via **general procedure 3** from N,1,1-triphenyl- $\lambda^4$ -sulfanimine (27.7 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-(phenylsulfonyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (47.0 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of  $\text{Cu}(\text{OTf})_2$  3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 50:1 to 10:1) and obtained as a white solid (29.2 mg, 81%), mp: 131-132  $^{\circ}\text{C}$ .

$R_f$  (Petroleum ether/ EtOAc = 5:1) = 0.8

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.50-7.41 (m, 3H), 7.23 (dtd,  $J = 8.4, 7.5, 2.0$  Hz, 4H), 7.13 (td,  $J = 7.7, 1.3$  Hz, 1H), 7.08-6.95 (m, 2H), 6.90-6.81 (m, 3H), 6.25 (d,  $J = 2.0$  Hz, 1H), 2.60 (d,  $J = 2.0$  Hz, 1H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 137.9, 135.5, 133.6, 131.1, 129.3, 128.8, 127.2, 126.9, 123.4, 121.0, 119.9, 118.1, 111.7, 79.2, 73.9, 72.7.

**HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  361.1005, found 361.1003.



**2-ethynyl-1-(naphthalen-2-ylsulfonyl)-3-phenyl-2,3-dihydro-1H-benzo[d]imidazole (3u):**

Prepared via **general procedure 3** from N,1,1-triphenyl- $\lambda^4$ -sulfanimine (27.7 mg, 0.1 mmol, 1.0 equiv), 4-ethynyl-1-(naphthalen-2-ylsulfonyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (54.5 mg, 0.15 mmol, 1.5 equiv) and DIPEA (26  $\mu$ l, 0.15 mmol, 1.5 equiv) according to the general procedure in the presence of Cu(OTf)<sub>2</sub> 3.6 mg, 0.01 mmol, 10 mol%), purified by silica gel column chromatography (petroleum ether/ EtOAc = 40:1 to 10:1) and obtained as a white solid (36.5 mg, 89%), mp: 138-139 °C.

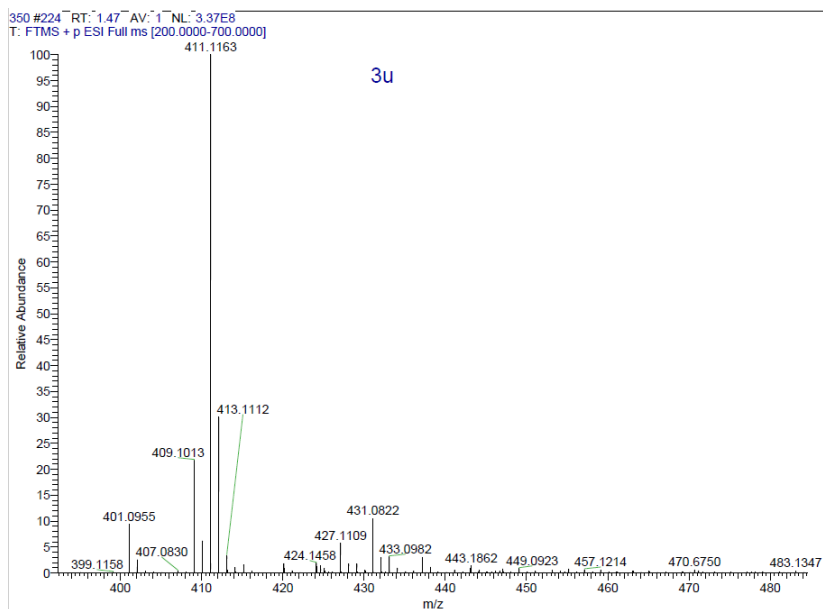
**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.7

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.86 (d, *J* = 1.9 Hz, 1H), 7.65 (dt, *J* = 8.0, 1.6 Hz, 2H), 7.52-7.46 (m, 3H), 7.41-7.36 (m, 1H), 7.22 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.92 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.80 (dd, *J* = 8.5, 7.1 Hz, 2H), 6.73-6.63 (m, 2H), 6.49-6.42 (m, 2H), 6.17 (d, *J* = 2.0 Hz, 1H), 2.49 (d, *J* = 2.0 Hz, 1H).



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 137.8, 135.1, 132.1, 131.8, 131.4, 129.1, 129.0, 129.0, 128.9, 128.9, 127.6, 127.4, 127.0, 123.1, 122.1, 121.3, 120.2, 117.3, 112.4, 79.3, 73.8, 73.1.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$  411.1162, found 411.1163.

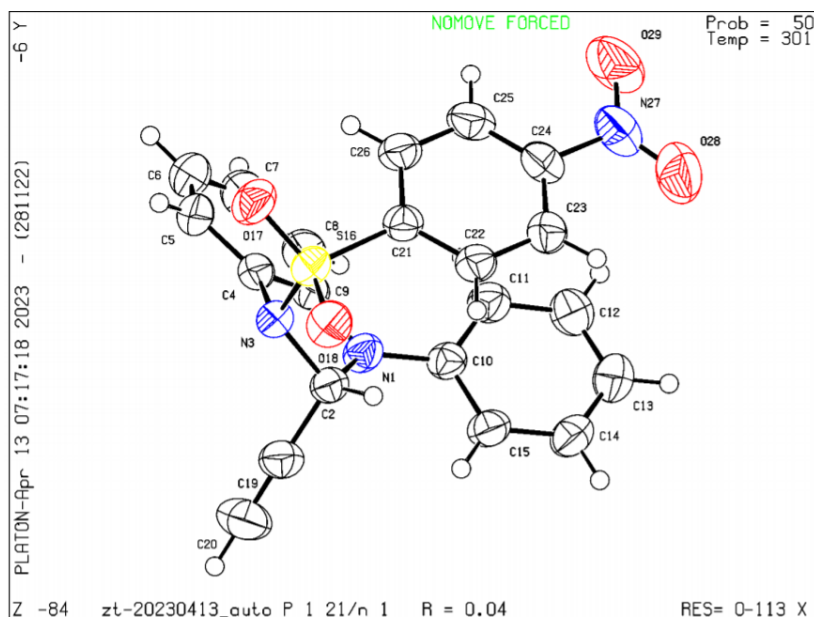


## X-ray crystallographic data of **3a** and **3r**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (2255981, **3a**) and (2252236, **3r**). The data can be obtained free of charge via the internet at <https://www.ccdc.cam.ac.uk/structures/>. The measurements were taken in a Bruker APEX-II CCD diffractometer. The data were integrated by Bruker APEX2 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL(2018/3).

**Method of crystallization:** A solution of **3a** in  $\text{CHCl}_3$  and petroleum ether was evaporated the solvent slowly at room temperature.

### Crystal data structure for **3a**

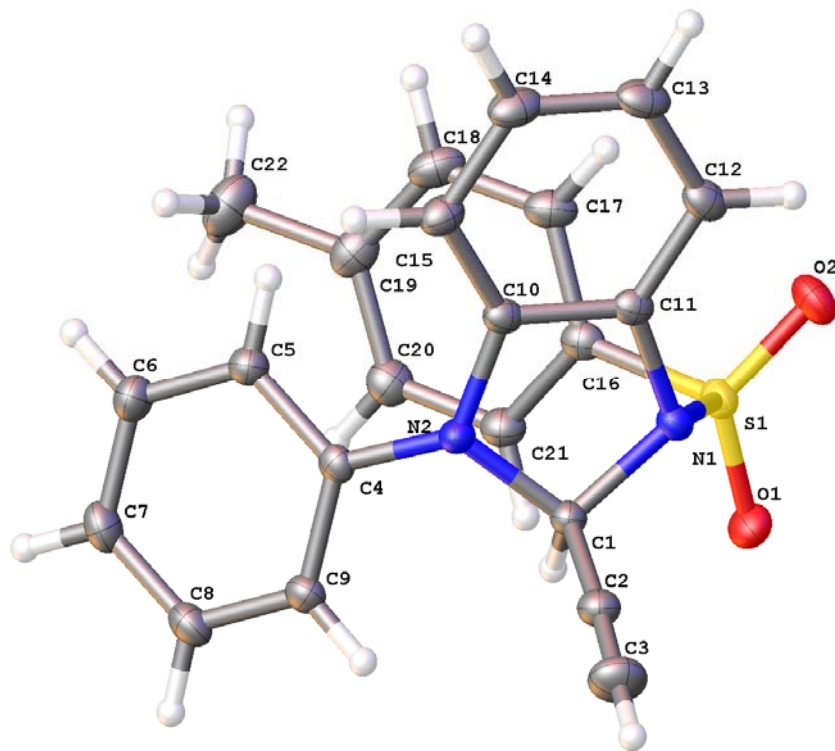


X-ray structure of **3a**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	C <sub>21</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	
Formula weight	405.42	
Temperature	301 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2 <sub>1</sub> /n	
Unit cell dimensions	a = 9.1583(2) Å	$\alpha = 90^\circ$
	b = 21.8770(4) Å	$\beta = 114.233(2)^\circ$
	c = 10.2542(2) Å	$\gamma = 90^\circ$
Volume	1873.46(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.437 g/cm <sup>3</sup>	
Absorption coefficient	1.837 mm <sup>-1</sup>	
Crystal size	0.20x 0.20 x 0.20 mm <sup>3</sup>	
$\theta$ range for data collection	5.144 to 77.261°	
Reflections collected	12222	
Independent reflections	3785 (R <sub>int</sub> = 0.0225)	
Max. and min. transmission	0.972 and 0.978	
restraints / parameters	0 / 263	
Goodness-of-fit on F <sup>2</sup>	1.054	
Final R indices [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0380, wR <sub>2</sub> = 0.1045	
R indices (all data)	R <sub>1</sub> = 0.0400, wR <sub>2</sub> = 0.1060	
Largest diff. peak and hole	0.227 and -0.417 e.Å <sup>-3</sup>	

**Method of crystallization:** A solution of **3r** in CHCl<sub>3</sub> and petroleum ether was evaporated the solvent slowly at room temperature.

**Crystal data structure for 3r**



X-ray structure of **3r**. Thermal ellipsoids are shown at the 50% level.

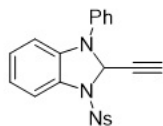
Empirical formula	C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	
Formula weight	374.44	
Temperature	213 K	
Wavelength	01.34139 Å	
Crystal system	Monoclinic	
Space group	'P 21/c'	
Unit cell dimensions	a = 9.1365(2) Å	$\alpha = 90^\circ$
	b = 21.8460(4) Å	$\beta = 116.0440(10)^\circ$
	c = 10.2421(2) Å	$\gamma = 90^\circ$
Volume	1836.70(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.354 g/cm <sup>3</sup>	
Absorption coefficient	1.125 mm <sup>-1</sup>	
F(000)	784.0	
Crystal size	0.07x 0.07 x 0.05 mm <sup>3</sup>	
$\theta$ range for data collection	9.374 to 109.898°	
Index ranges	-10 ≤ h ≤ 11, -26 ≤ k ≤ 26, -12 ≤ l ≤ 12	

Reflections collected	19091
Independent reflections	3476 ( $R_{\text{int}} = 0.0417$ )
Completeness to $\theta = 67.679^\circ$	99.9 %
Max. and min. transmission	0.972 and 0.978
Data / restraints / parameters	3476 / 0 / 245
Goodness-of-fit on $F^2$	1.050
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0351$ , $wR_2 = 0.0922$
R indices (all data)	$R_1 = 0.0389$ , $wR_2 = 0.0948$
Largest diff. peak and hole	0.22 and $-0.38 \text{ e.}\text{\AA}^{-3}$

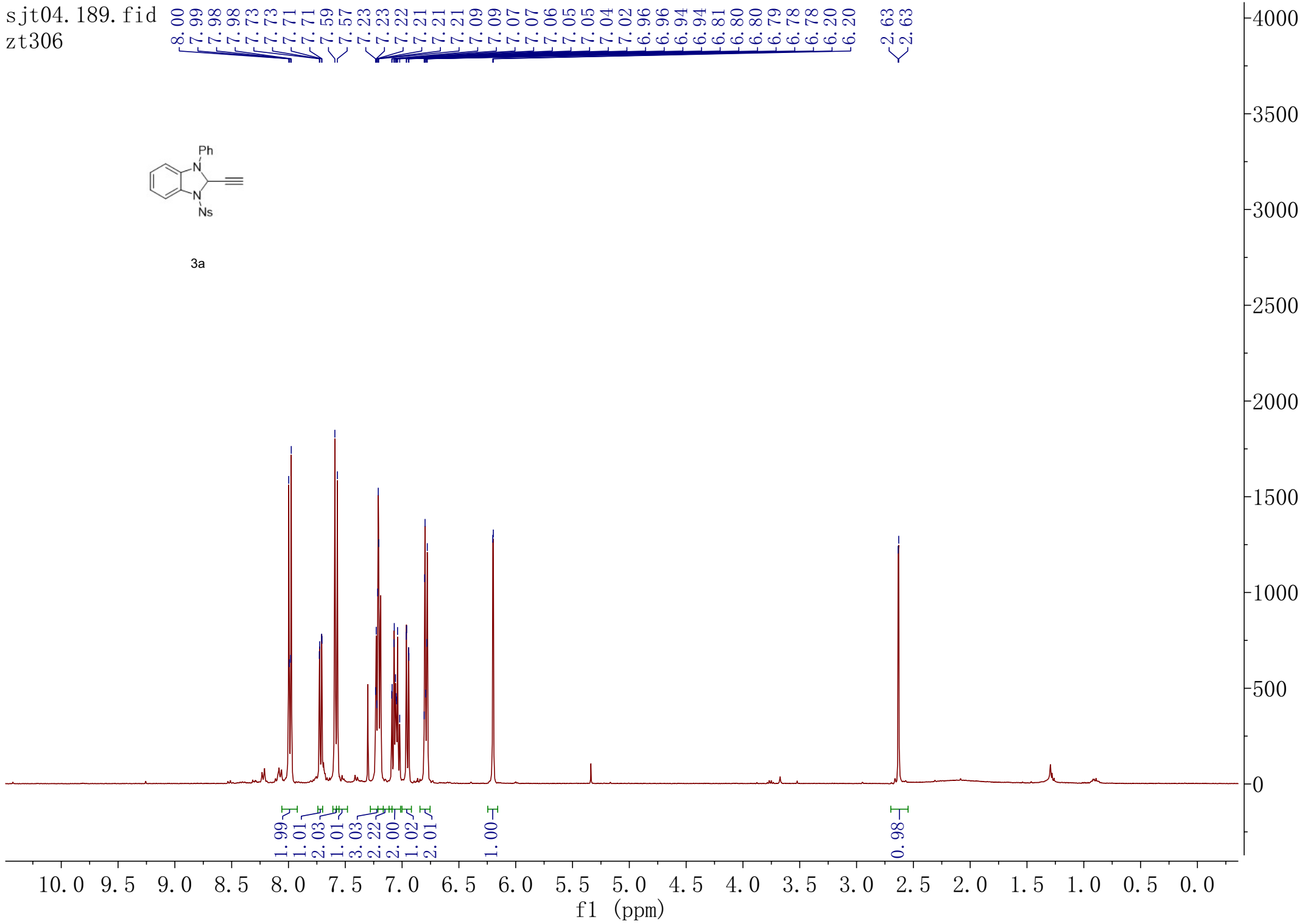
## References

- [1] a) D. Zhong, F. Jiang, S.-Y. Shen, L. Wang, W. Wang, Y.-G. Wu, Y.-M. Xiao, H.-C. Guo, *Angew. Chem. Int. Ed.* 2020, **362**, 5026-5030; b) T.-R. Li, B.-Y. Cheng, Y.-N. Wang, M.-M. Zhang, L.-Q. Lu, W.-J. Xiao, *Angew. Chem. Int. Ed.* 2016, **55**, 12422-12426; c) Q. Wang, T.-R. Li, L.-Q. Lu, M.-M. Li, K. Zhang, W.-J. Xiao, *J. Am. Chem. Soc.* 2016, **138**, 8360-8363.
- [2] a) T.-T. Meng, T.-X. Wang, T.-Z. Jia, *J. Am. Chem. Soc.* 2022, **144**, 12476-12487; b) X. Tian, L. Song, M. Rudolph, Frank. Rominger, T. Oeser, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 2019, **58**, 3589-3593; c) S. Yoshida, T. Yano, Y. Misawa, Y. Sugimura, K. Igawa, S. Shimizu, K. Tomooka, T. Hosoya, *J. Am. Chem. Soc.* 2015, **137**, 14071-14074.

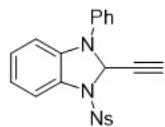
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zt306



3a



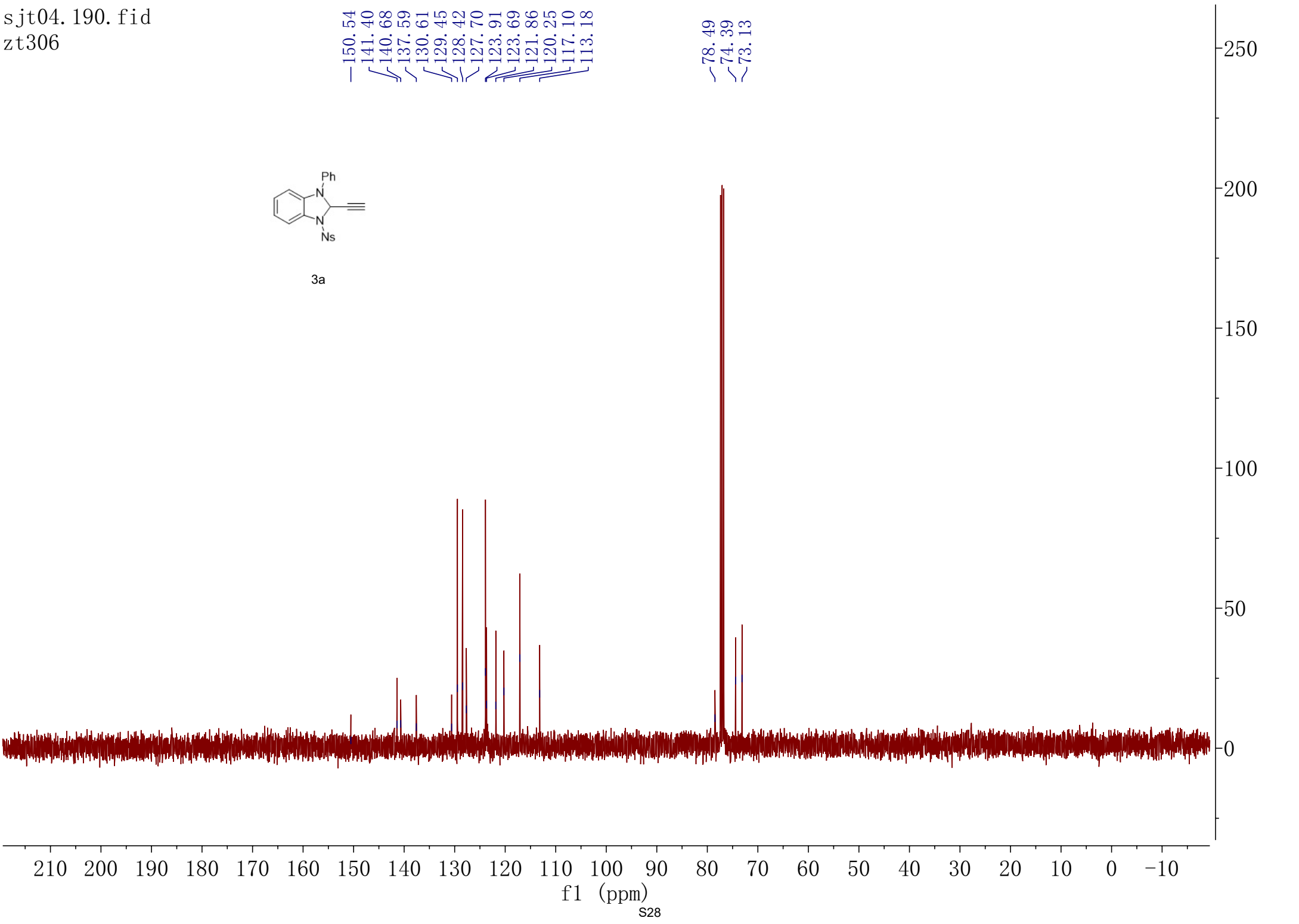
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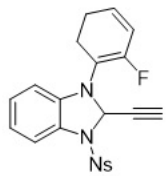
3a

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140.68  
137.59  
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123.91  
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121.86  
120.25  
117.10  
113.18

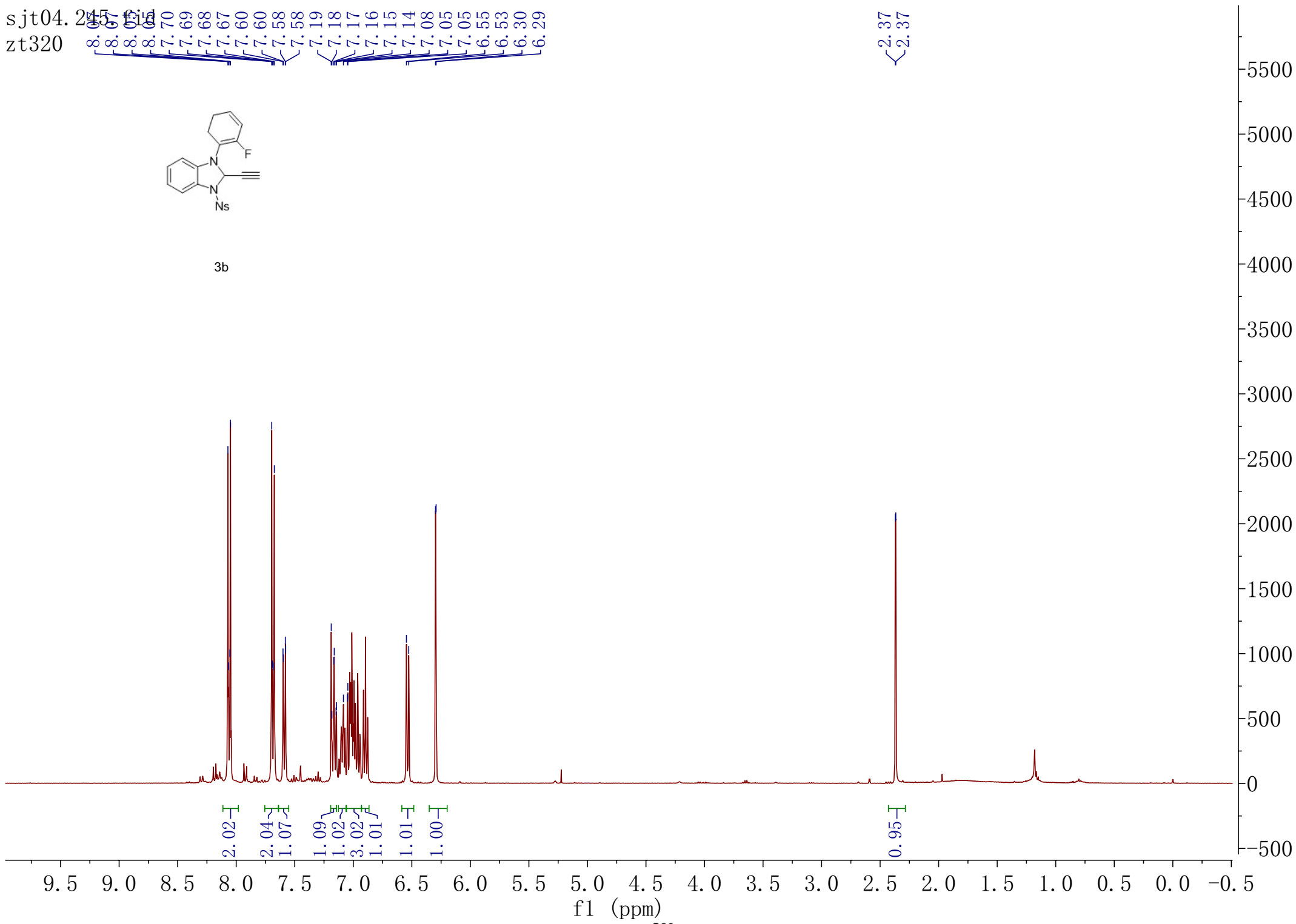
78.49  
74.39  
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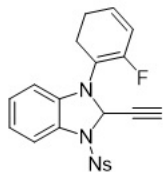


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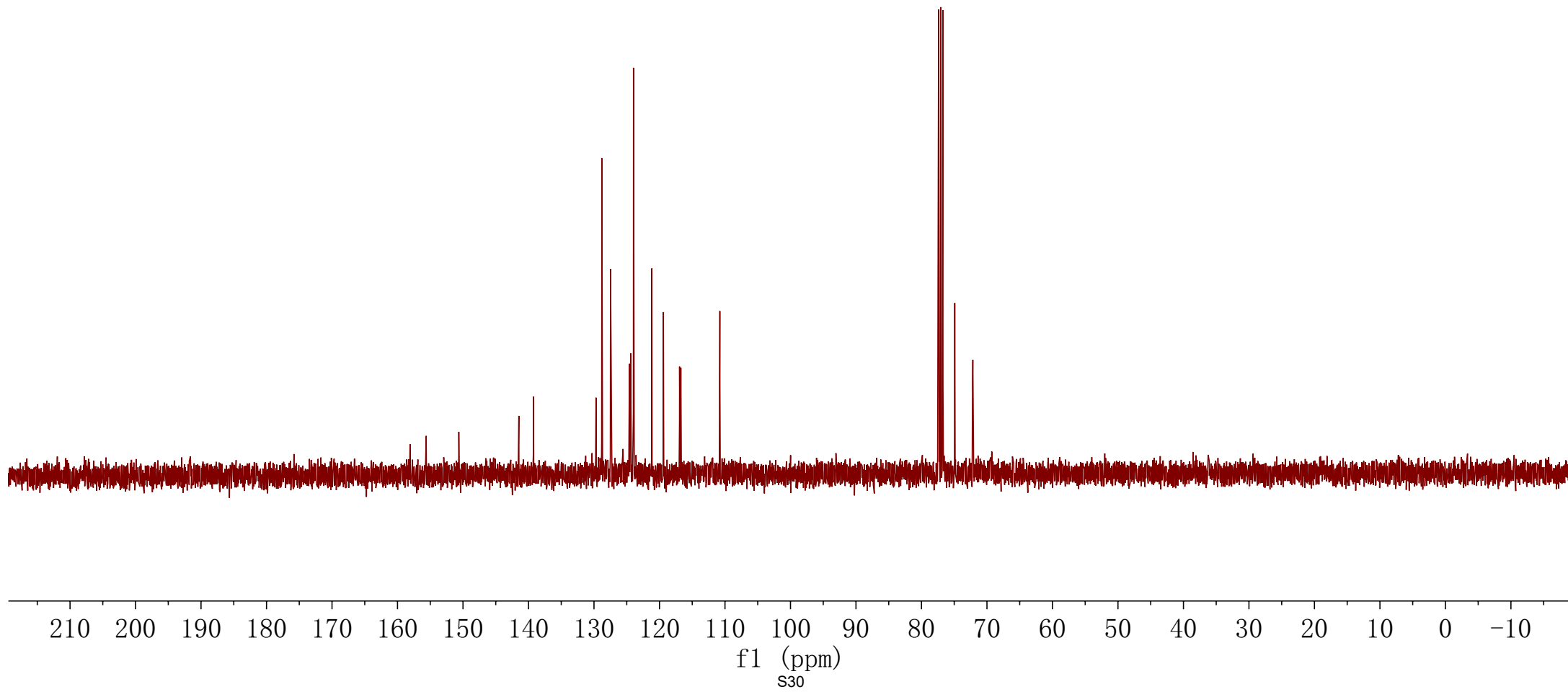
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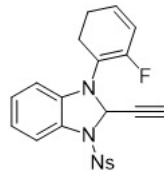
3b

— 155.621  
— 150.642  
~ 141.474  
~ 139.245  
└ 129.693  
└ 128.799  
└ 127.473  
└ 127.378  
└ 124.625  
└ 124.587  
└ 124.399  
└ 123.967  
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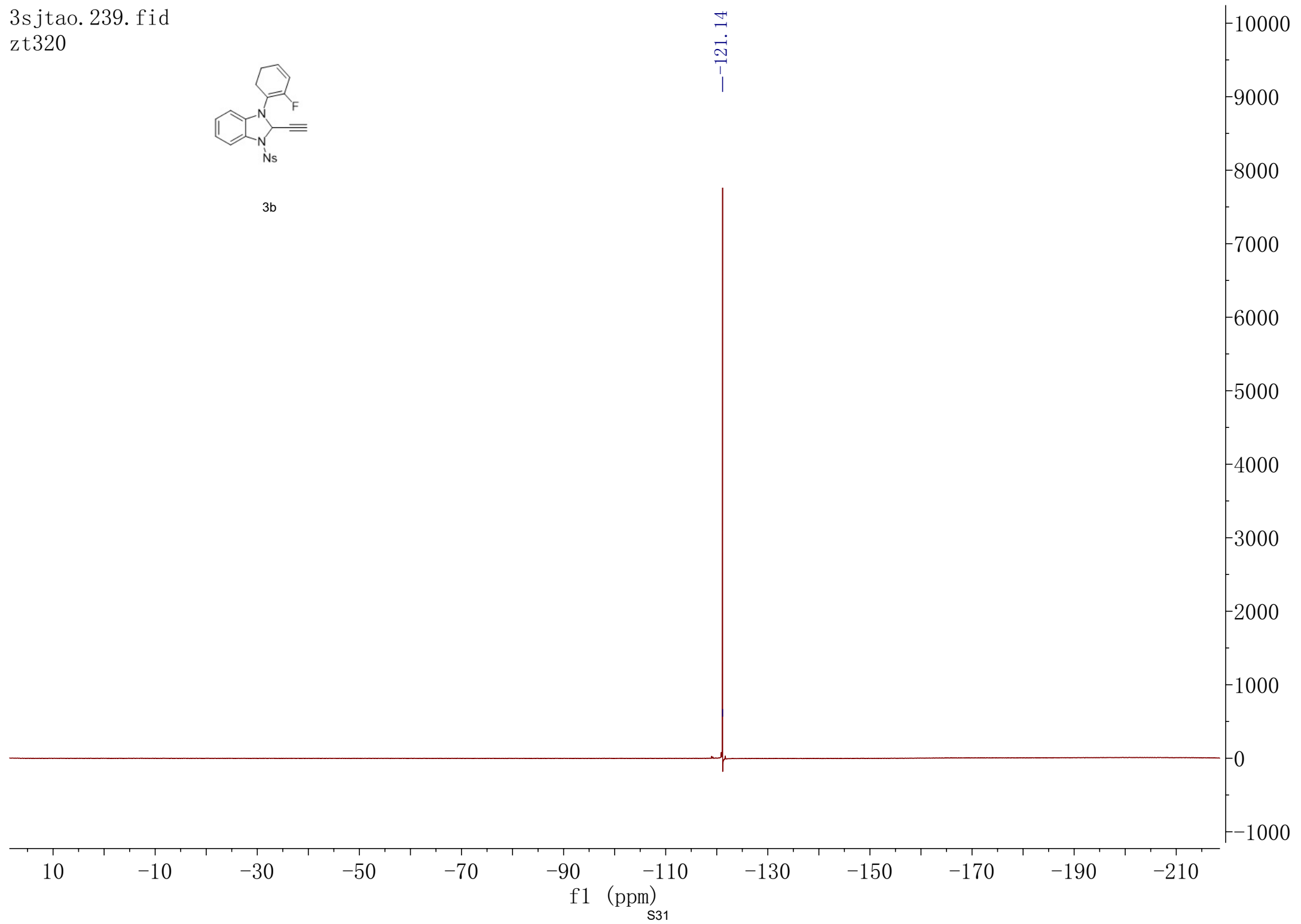




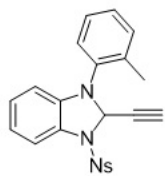
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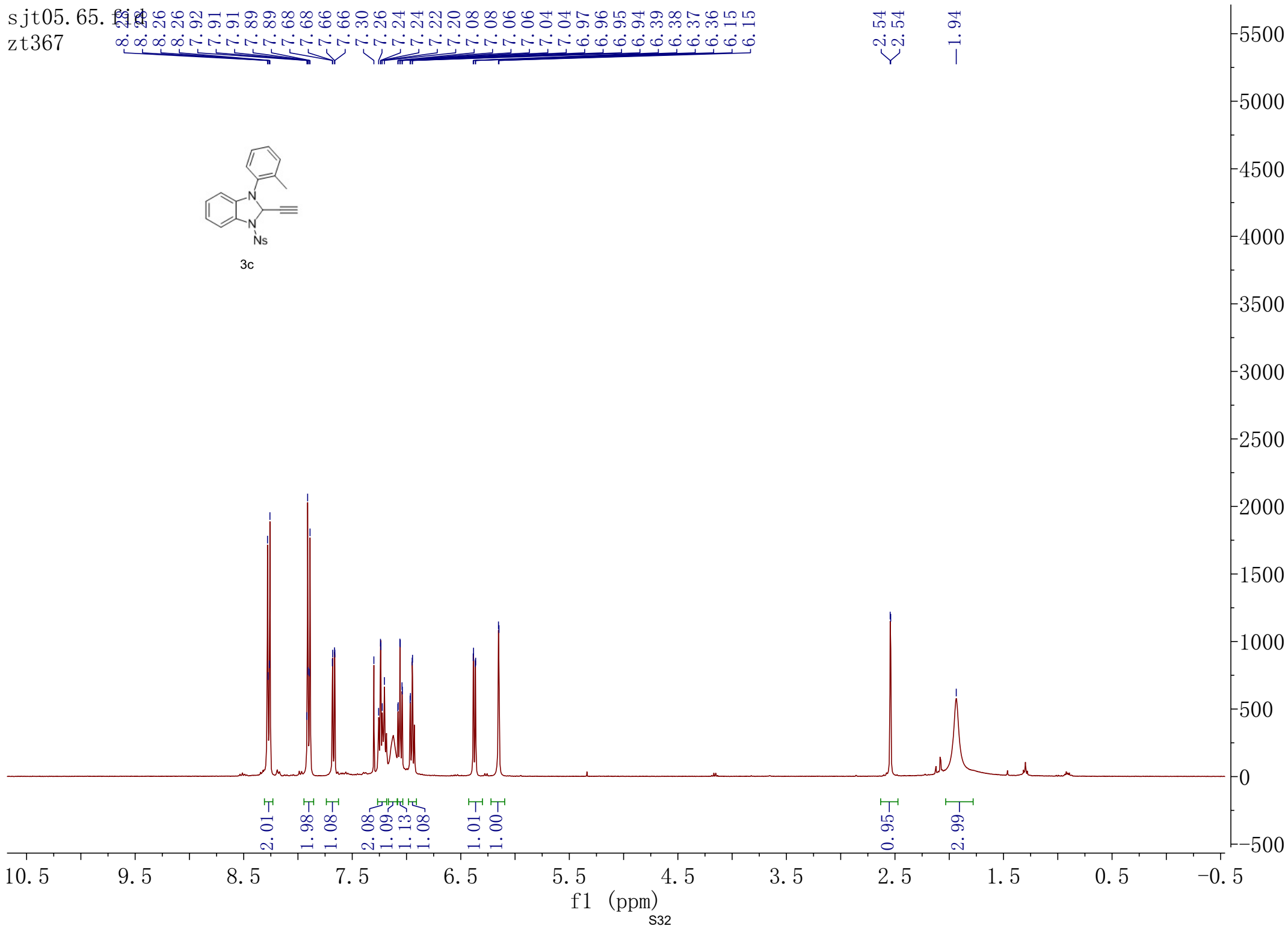
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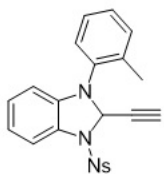
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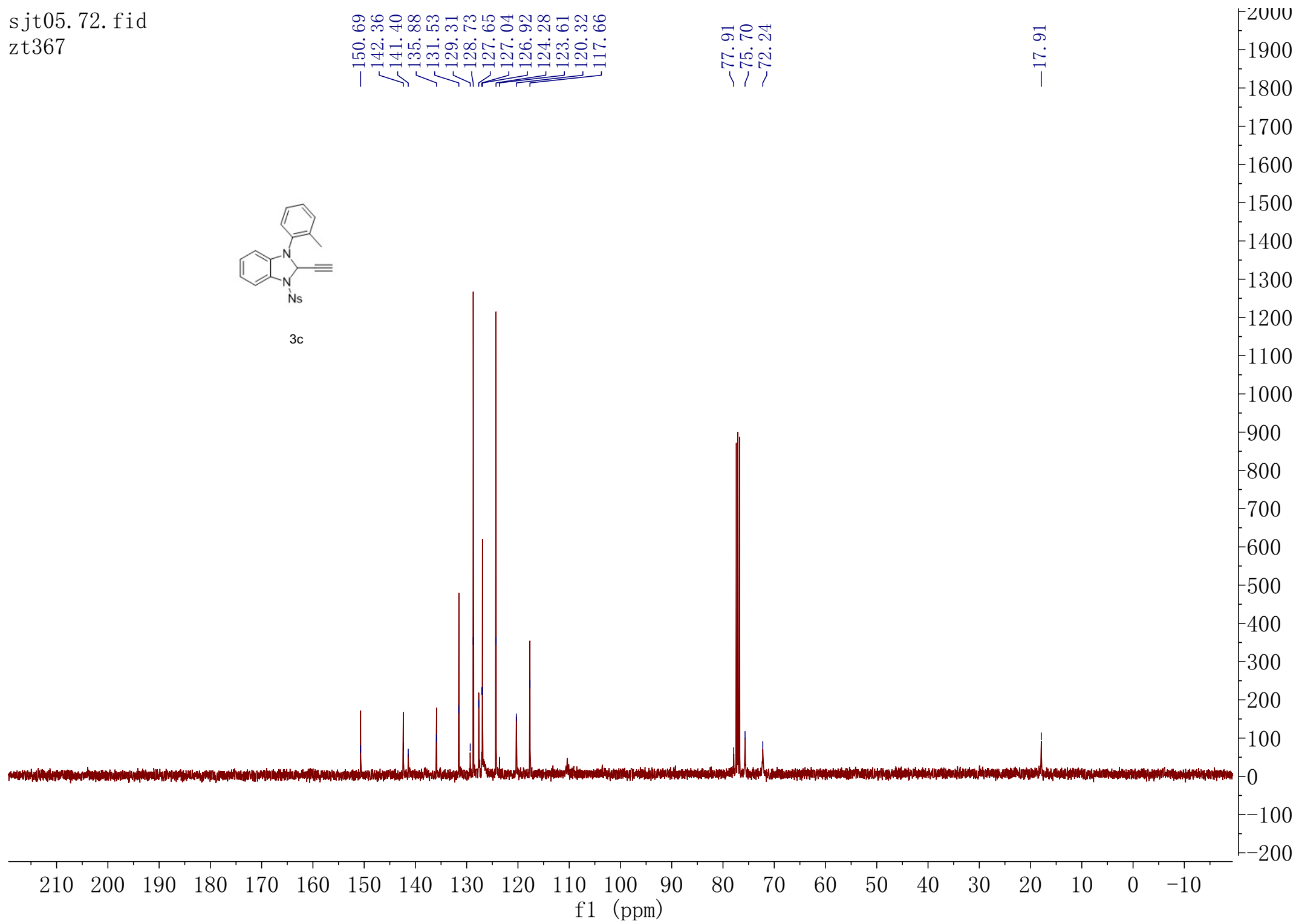
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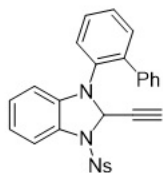
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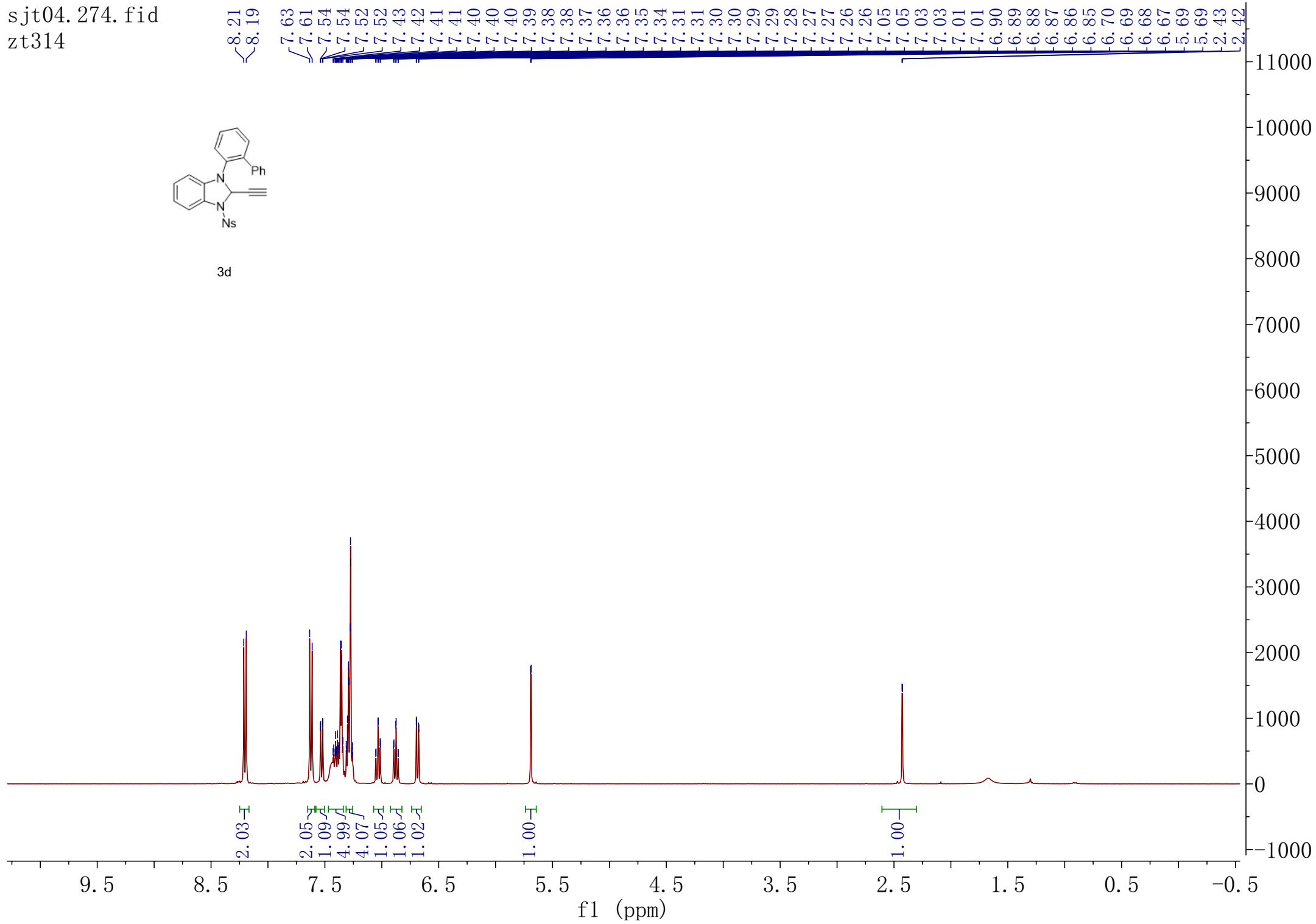
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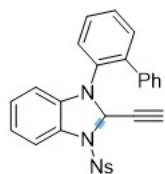
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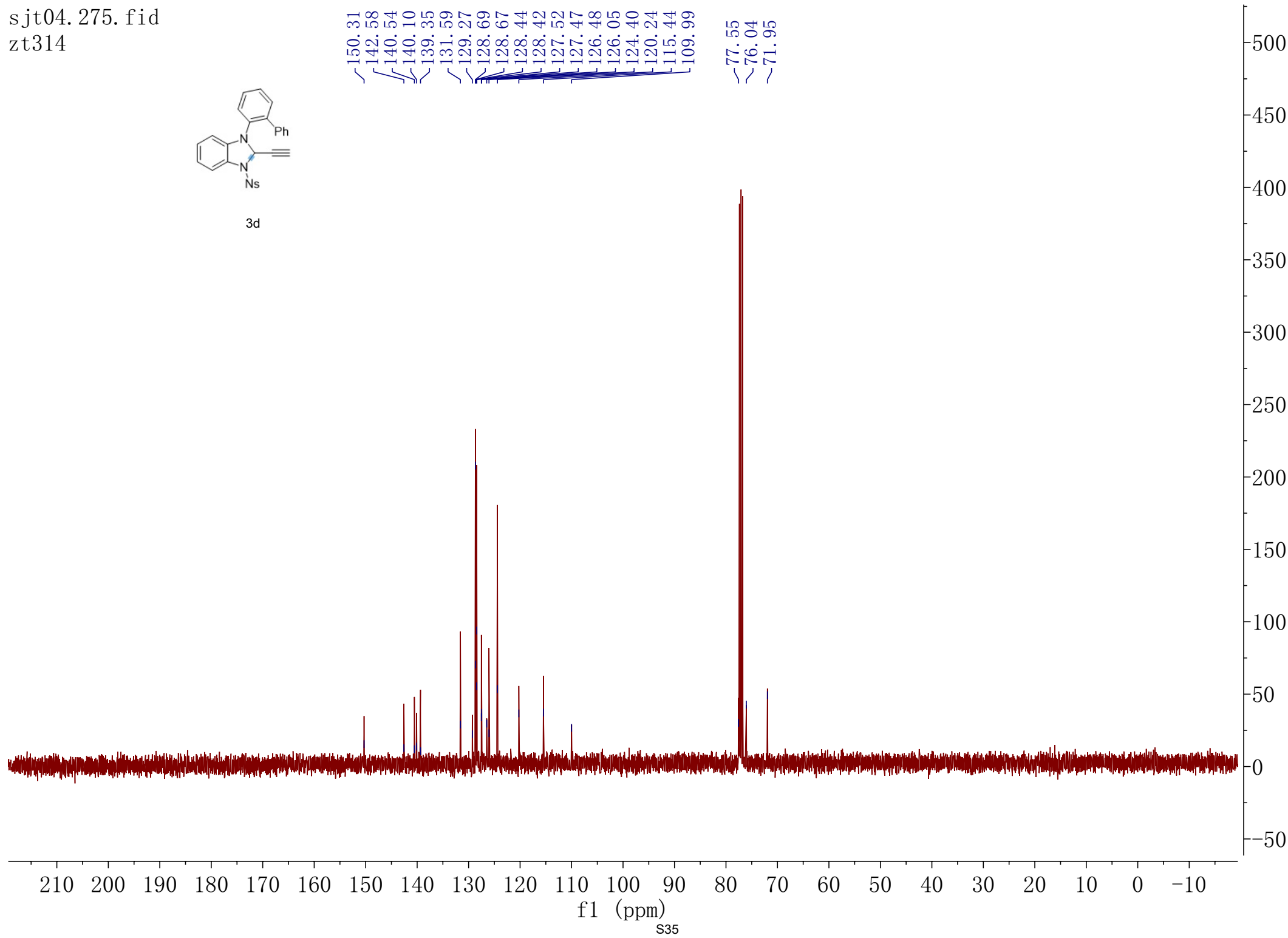
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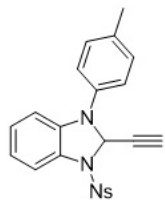
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3d



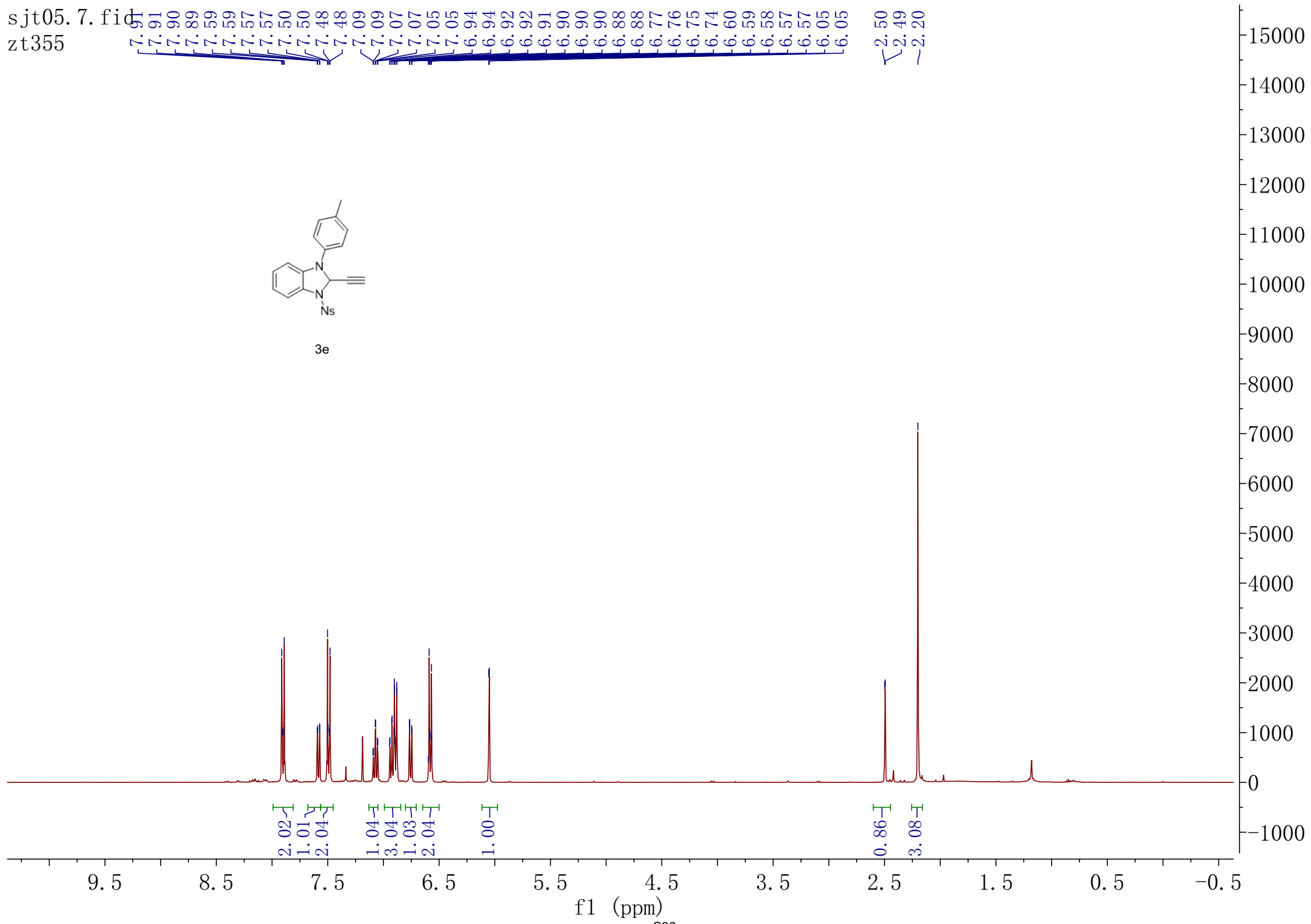
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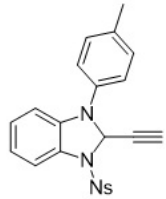
3e

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7.09  
7.09  
7.07  
7.07  
7.05  
7.05  
6.94  
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6.92  
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6.05

2.50  
2.49  
2.20



sjt05.8.fid  
zt355

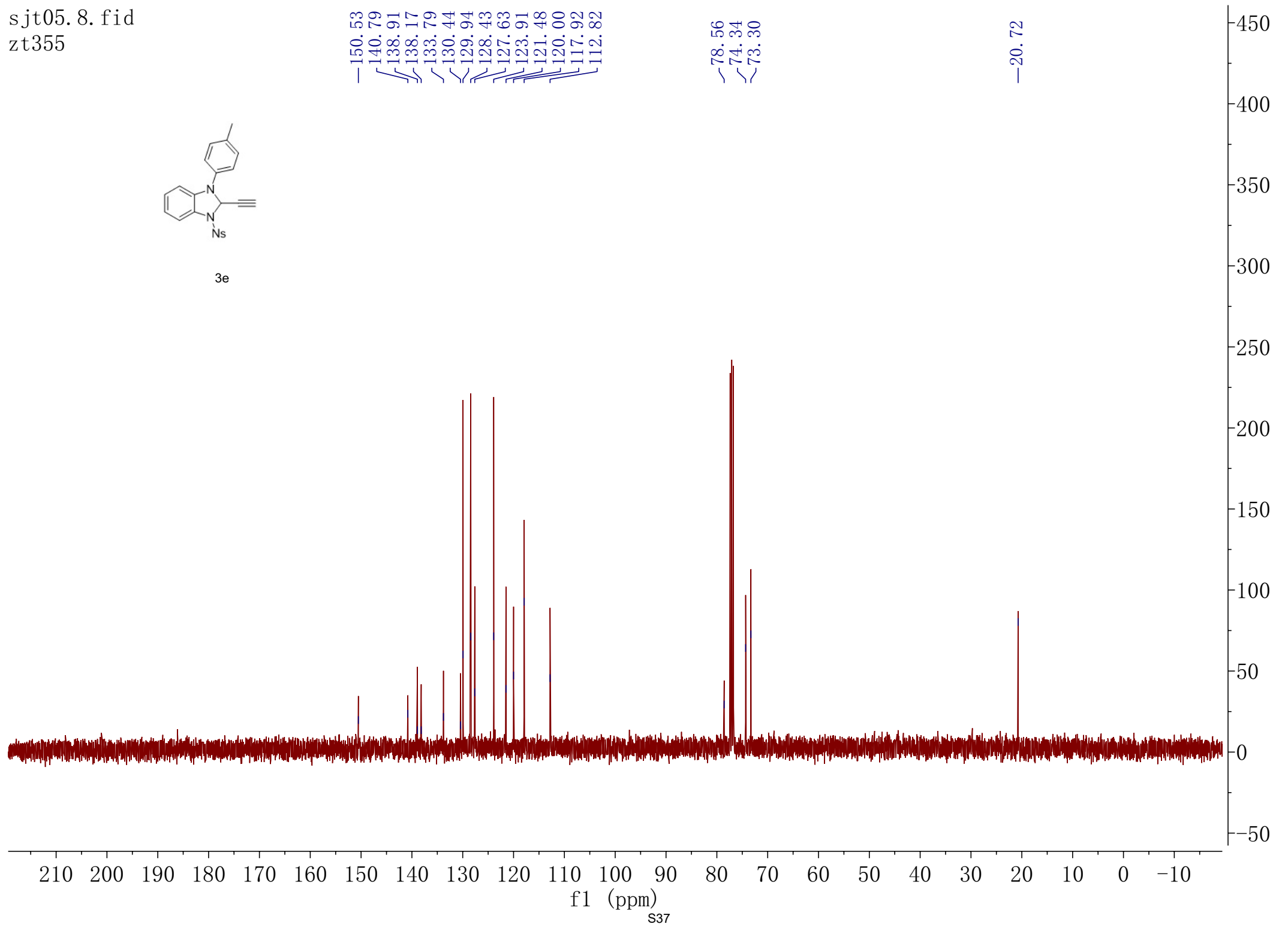


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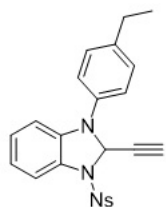
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112.82

78.56  
74.34  
73.30

20.72

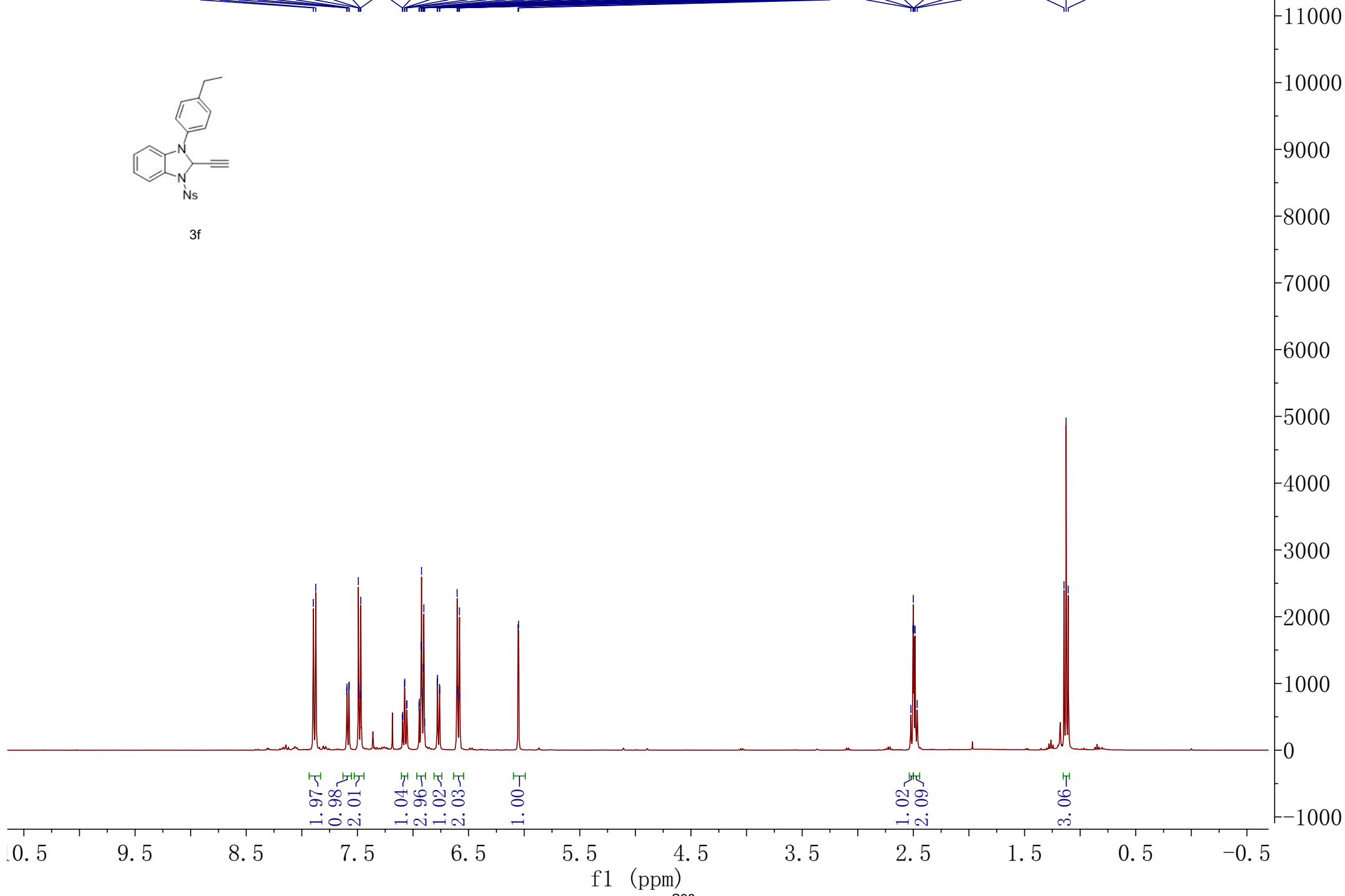


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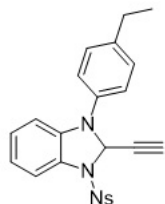
3f

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7.49  
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7.10  
7.09  
7.08  
7.07  
7.06  
7.05  
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6.94  
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1.11

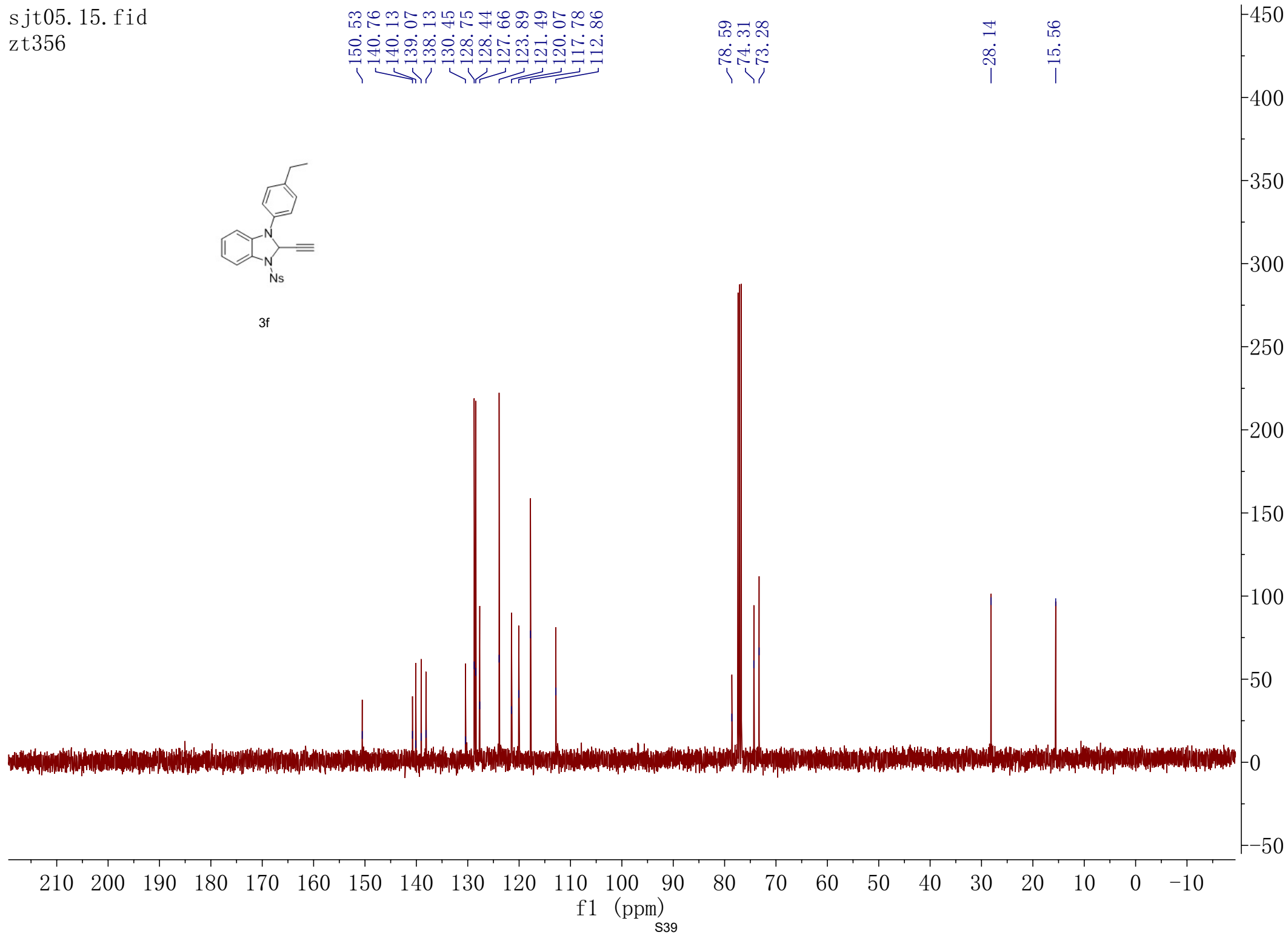




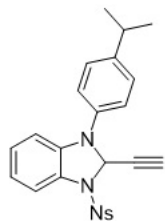
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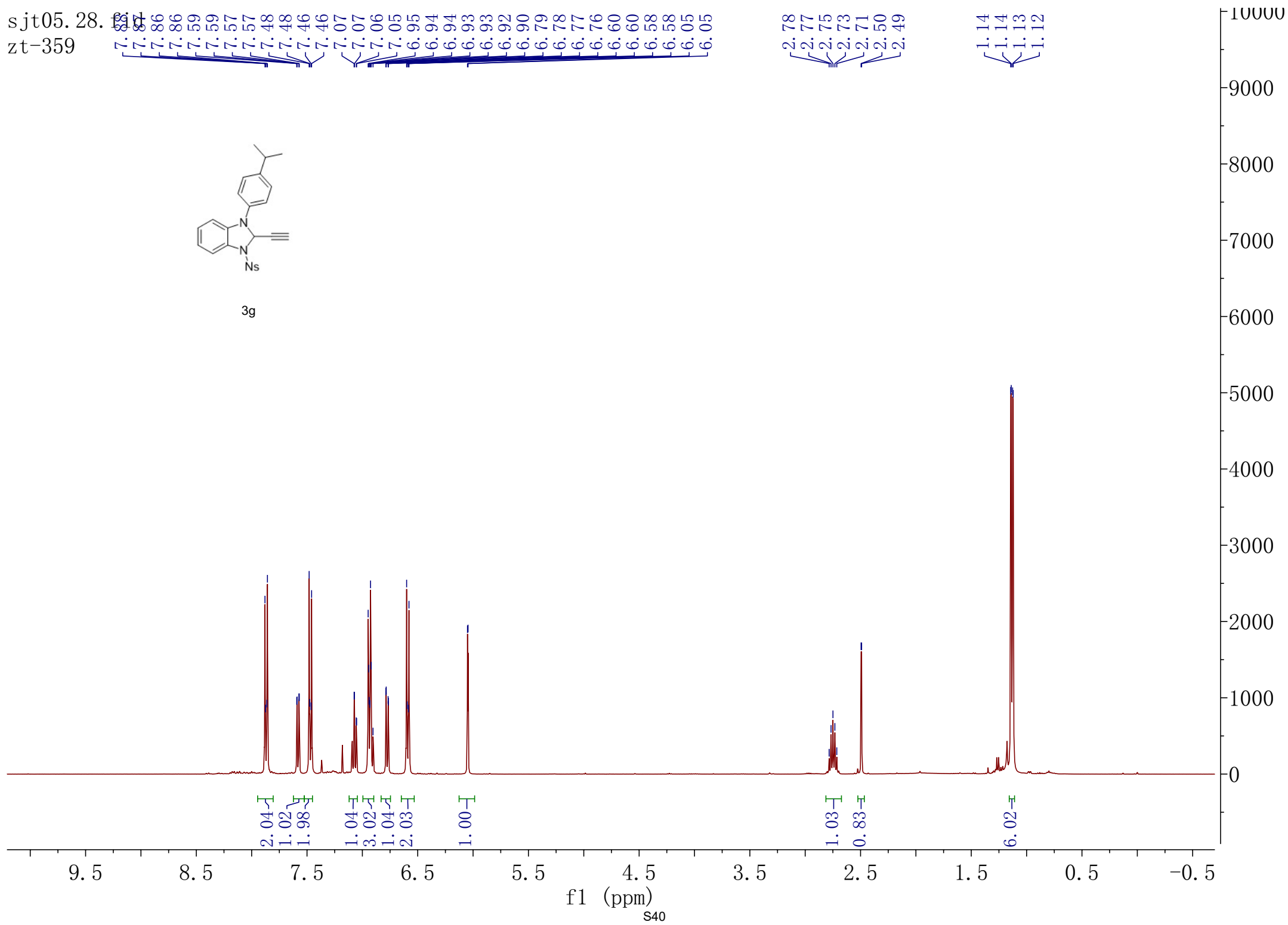
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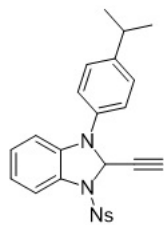
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zt-359



3g



sjt05.29.fid  
zt359

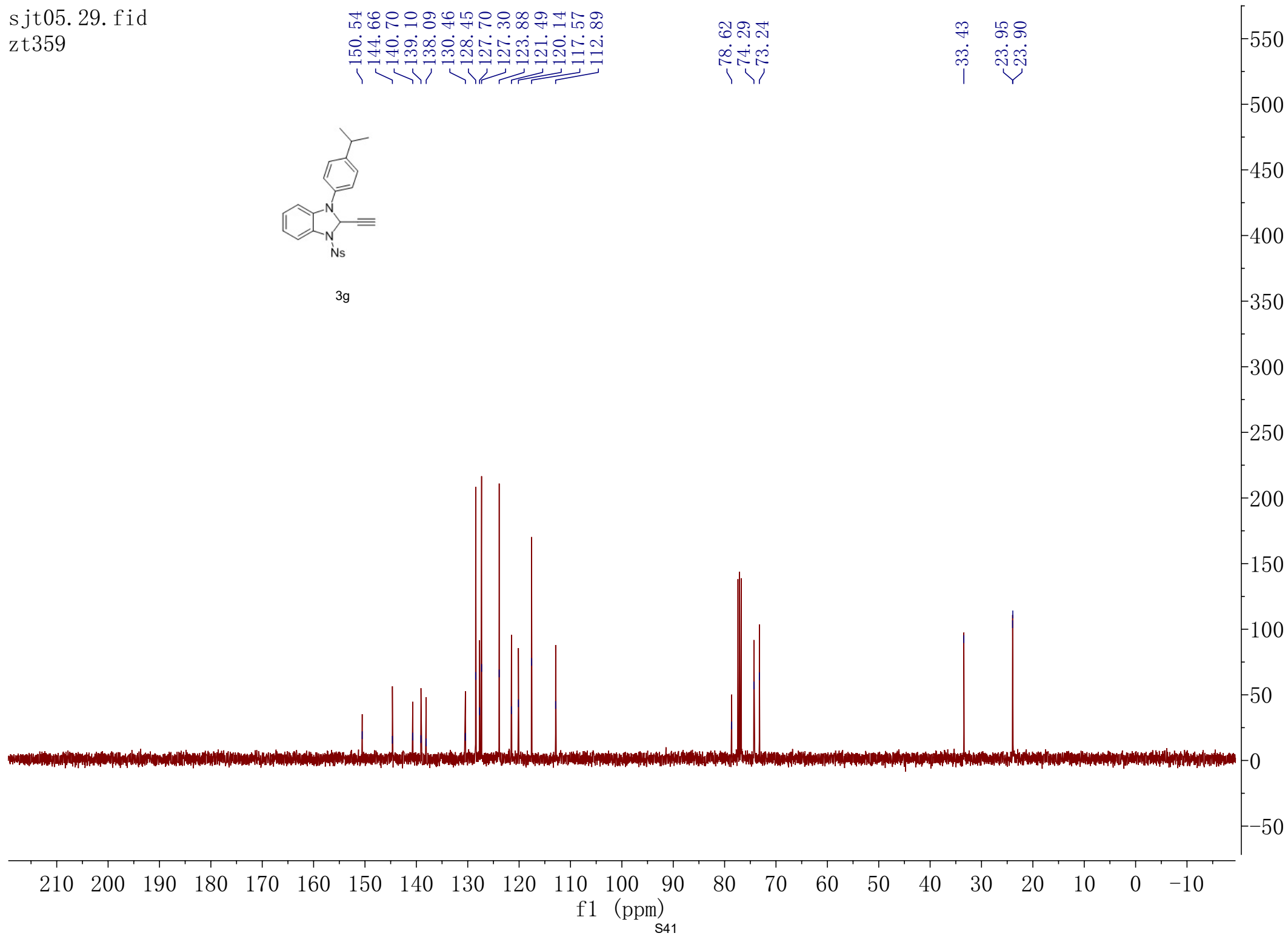


3g

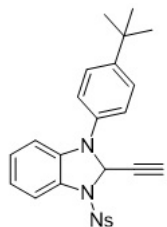
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144.66  
140.70  
139.10  
138.09  
130.46  
128.45  
127.70  
127.30  
123.88  
121.49  
120.14  
117.57  
112.89

78.62  
74.29  
73.24

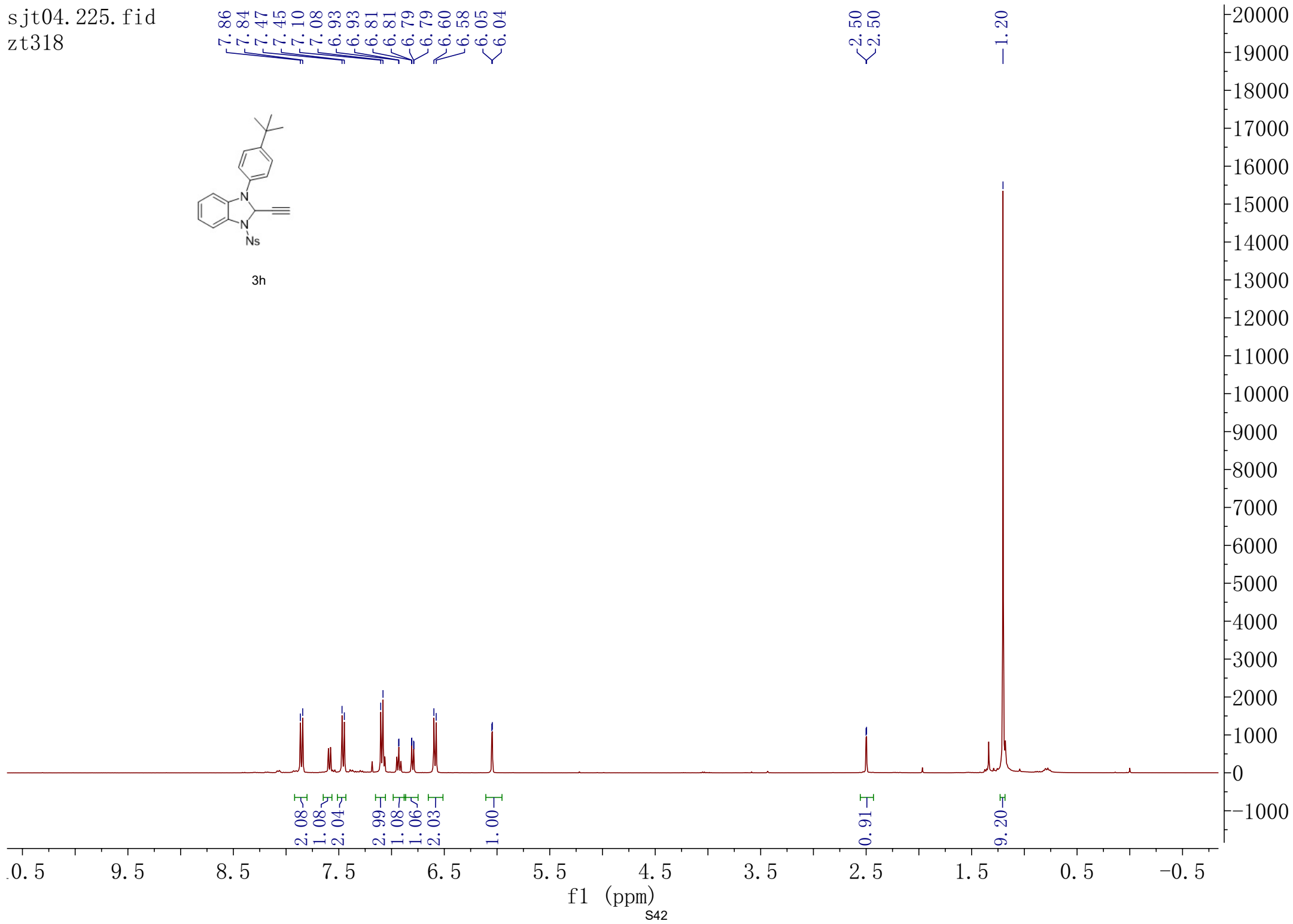
33.43  
23.95  
23.90



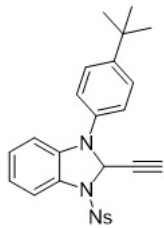
sjt04.225.fid  
zt318



3h



sjt04.226.fid  
zt318

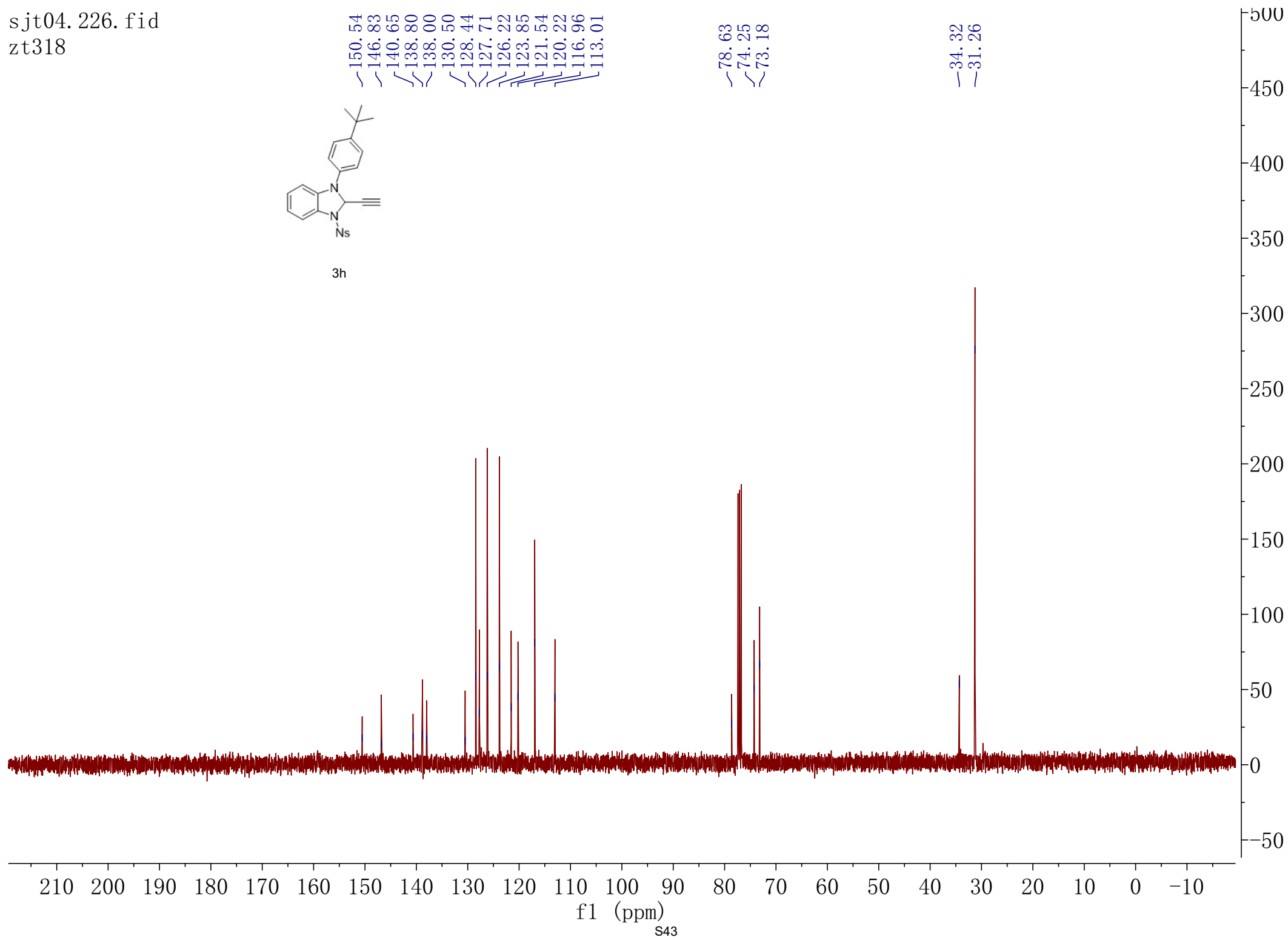


3h

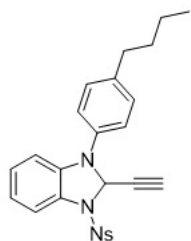
150.54  
146.83  
140.65  
138.80  
138.00  
130.50  
128.44  
127.71  
126.22  
123.85  
121.54  
120.22  
116.96  
113.01

78.63  
74.25  
73.18

34.32  
31.26

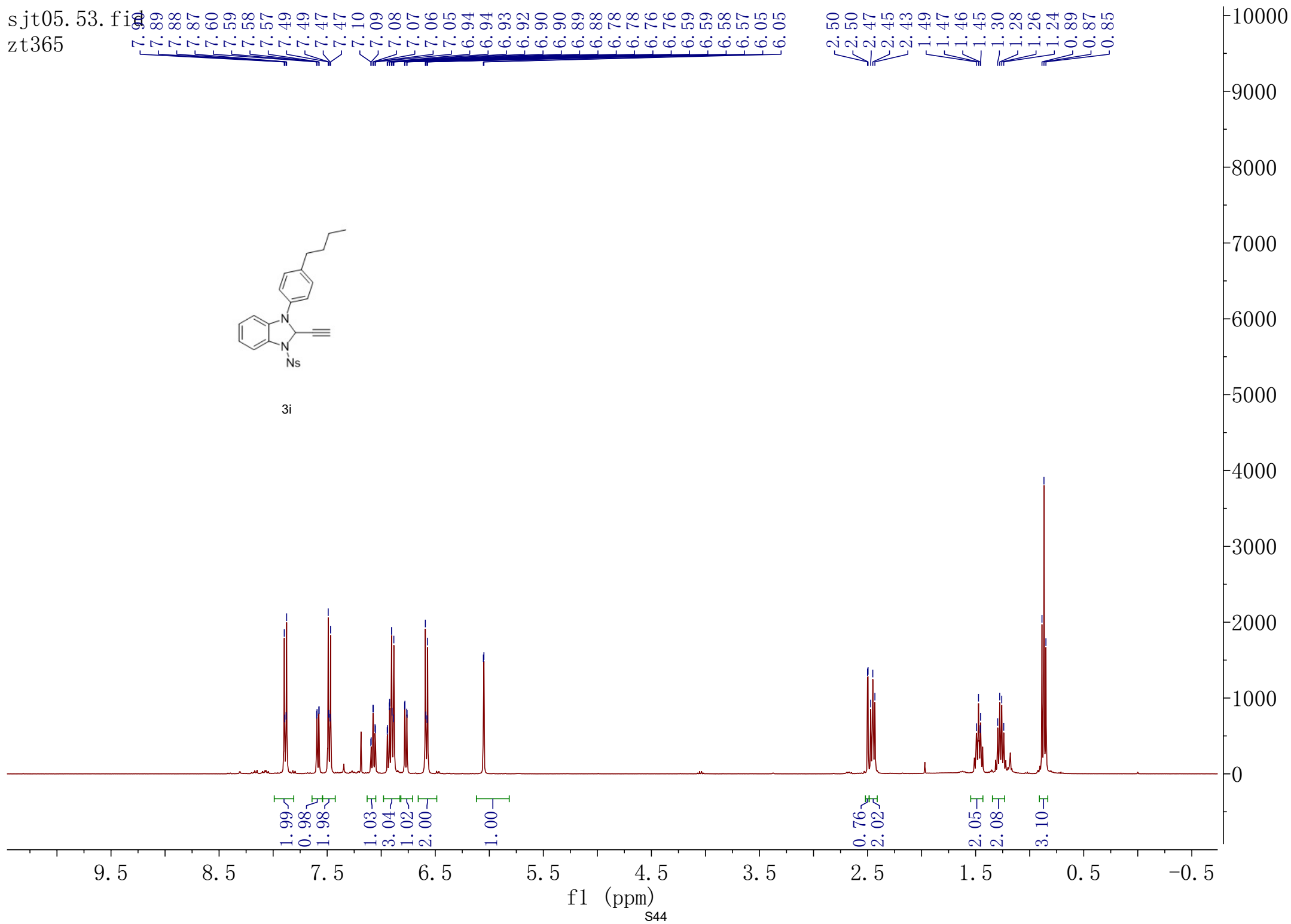


sjt05.53.f1a  
zt365

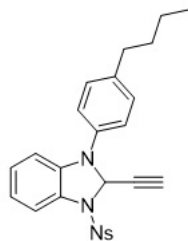


3i

7.89  
7.88  
7.87  
7.60  
7.59  
7.58  
7.57  
7.49  
7.49  
7.47  
7.47  
7.10  
7.09  
7.08  
7.07  
7.06  
7.05  
6.94  
6.94  
6.93  
6.92  
6.90  
6.90  
6.89  
6.88  
6.78  
6.78  
6.76  
6.76  
6.59  
6.59  
6.58  
6.57  
6.05  
6.05  
2.50  
2.50  
2.47  
2.45  
2.43  
1.49  
1.47  
1.46  
1.45  
1.30  
1.28  
1.26  
1.24  
0.89  
0.87  
0.85



sjt05.54.fid  
zt365



3i

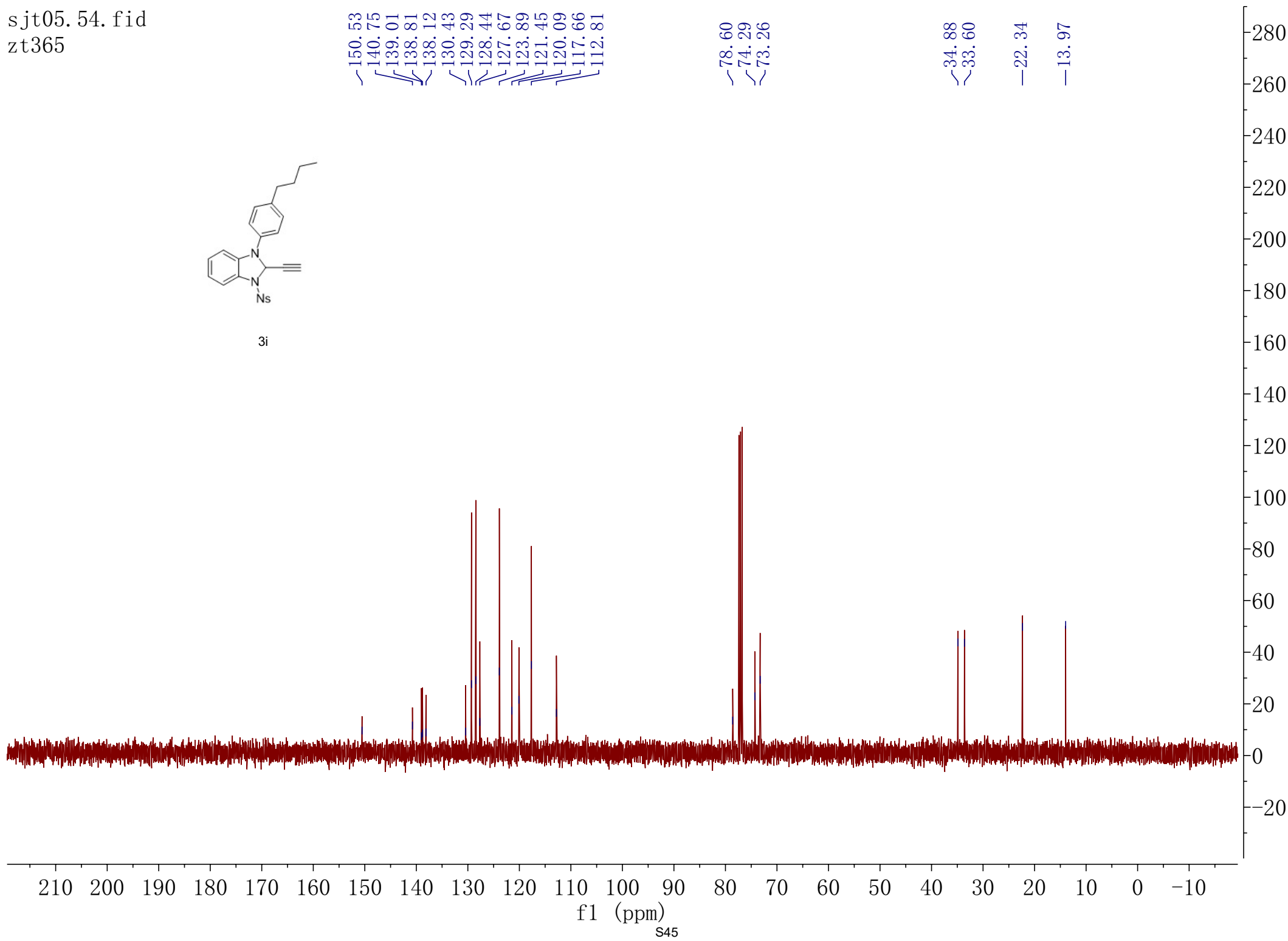
150.53  
140.75  
139.01  
138.81  
138.12  
130.43  
129.29  
128.44  
127.67  
123.89  
121.45  
120.09  
117.66  
112.81

78.60  
74.29  
73.26

34.88  
33.60

22.34

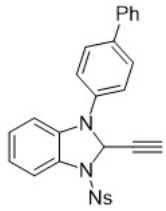
13.97





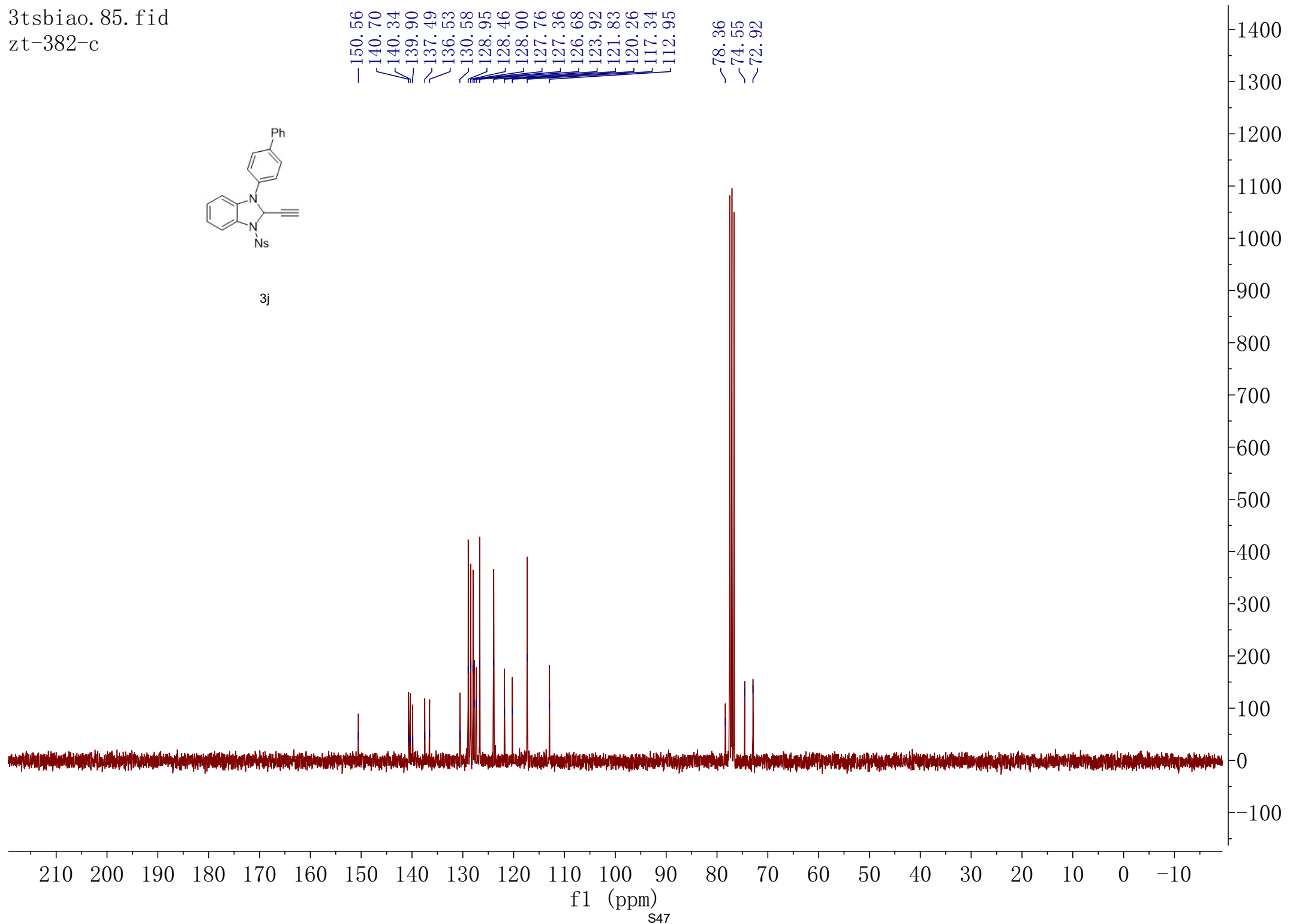


3tsbiao.85.fid  
zt-382-c

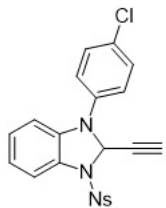


3j

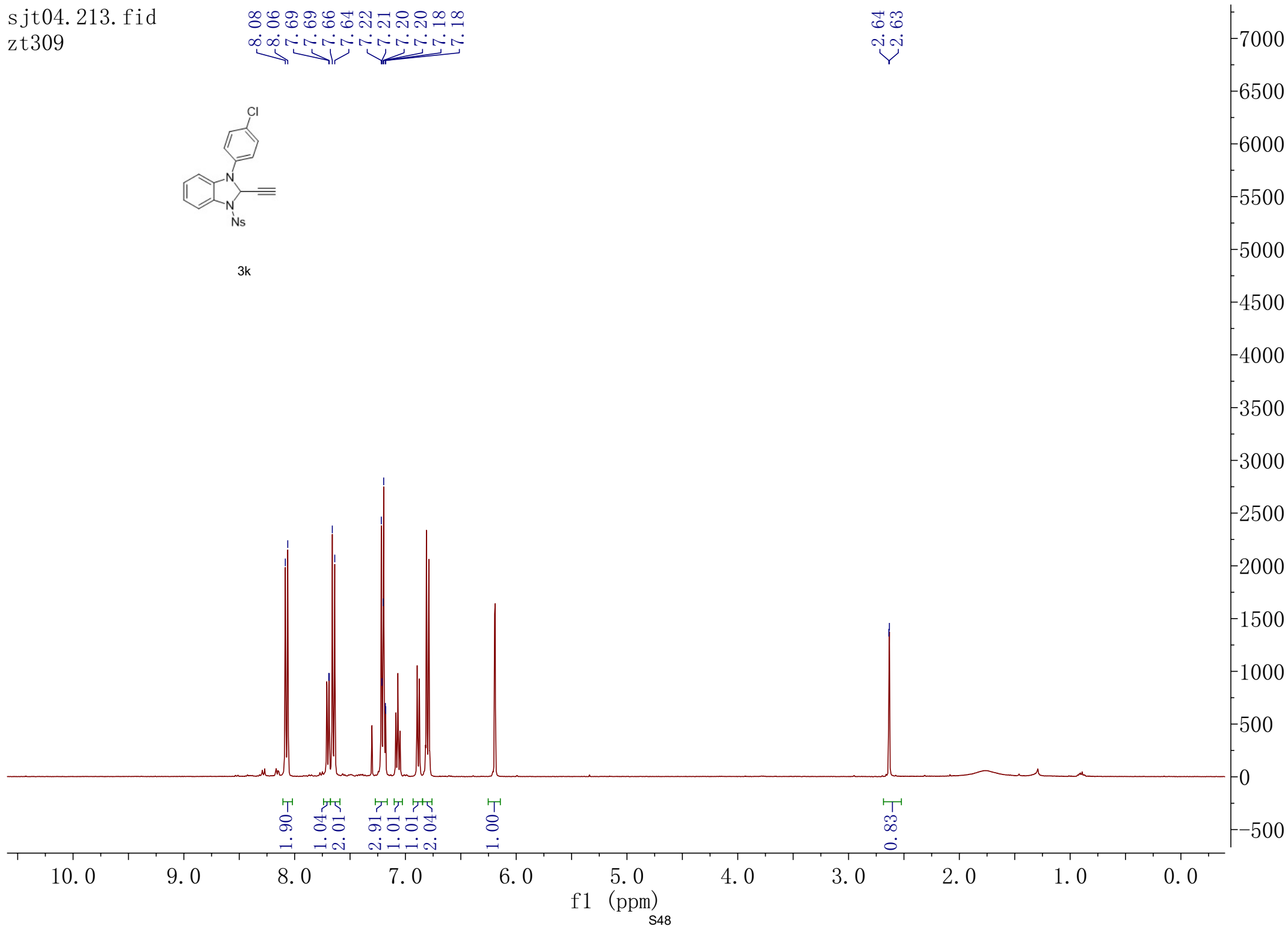
150.56  
140.70  
140.34  
139.90  
137.49  
136.53  
130.58  
128.95  
128.46  
128.00  
127.76  
127.36  
126.68  
123.92  
121.83  
120.26  
117.34  
112.95  
78.36  
74.55  
72.92



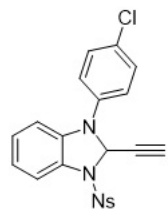
sjt04.213.fid  
zt309



3k



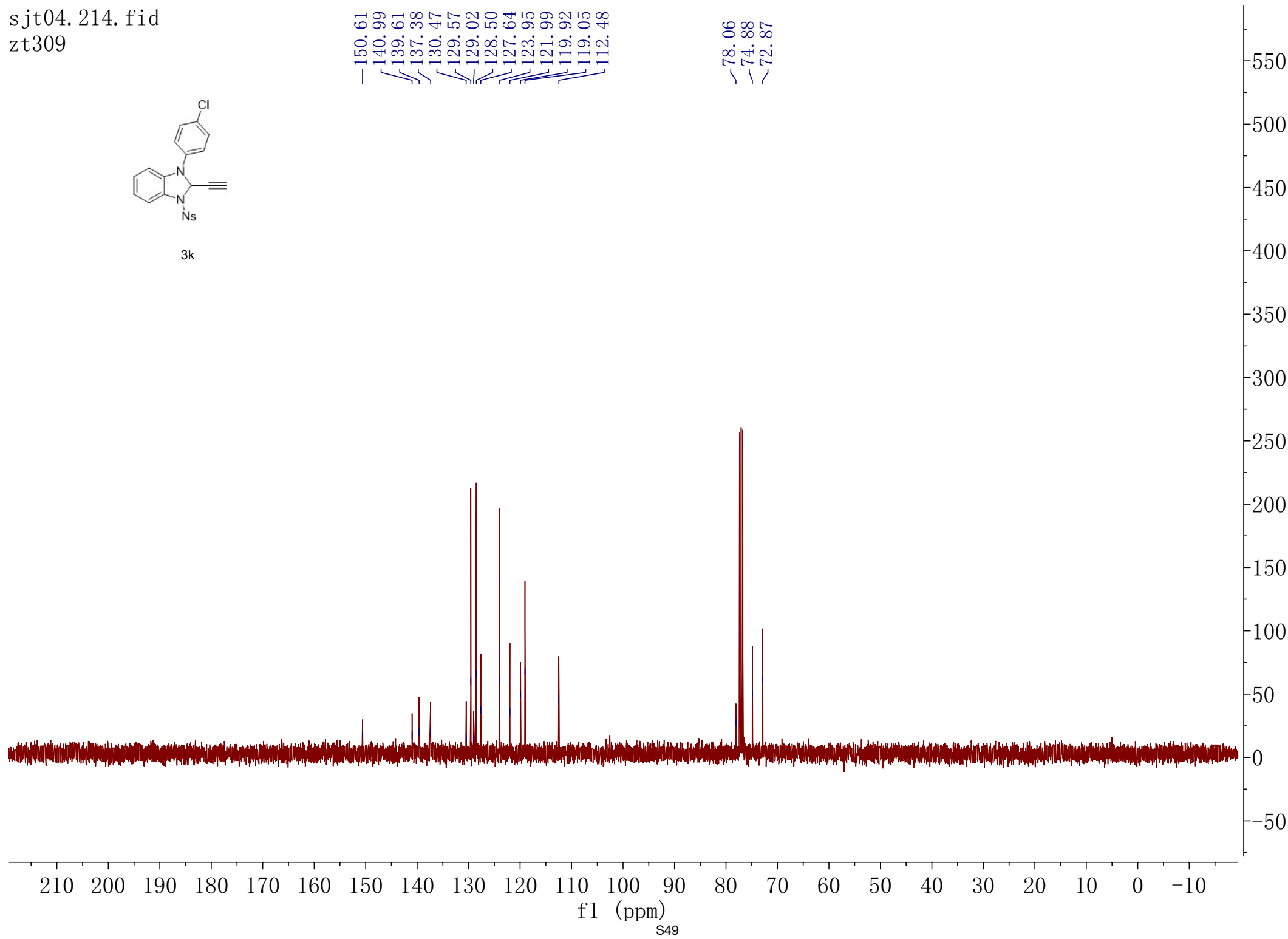
sjt04.214.fid  
zt309



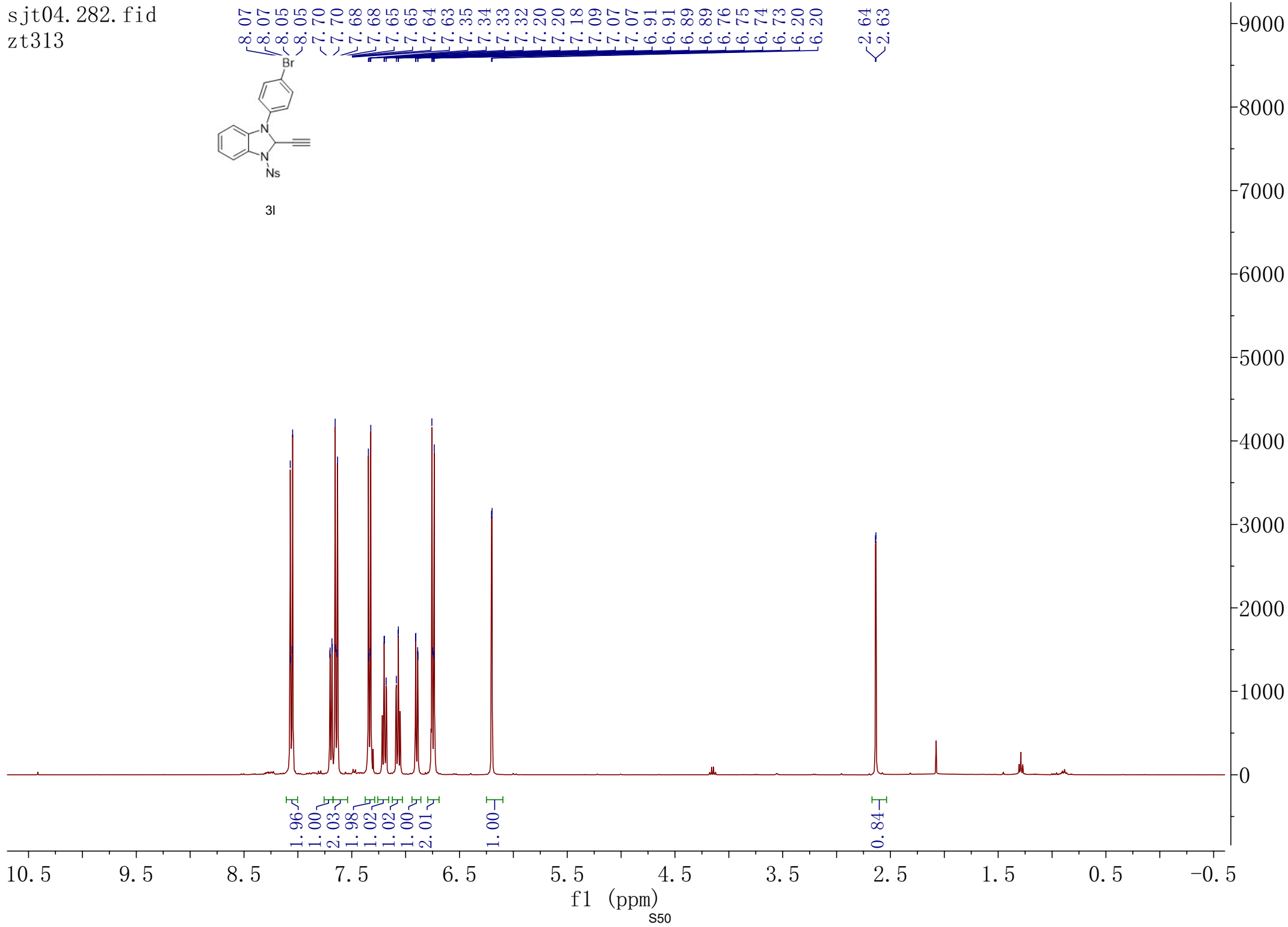
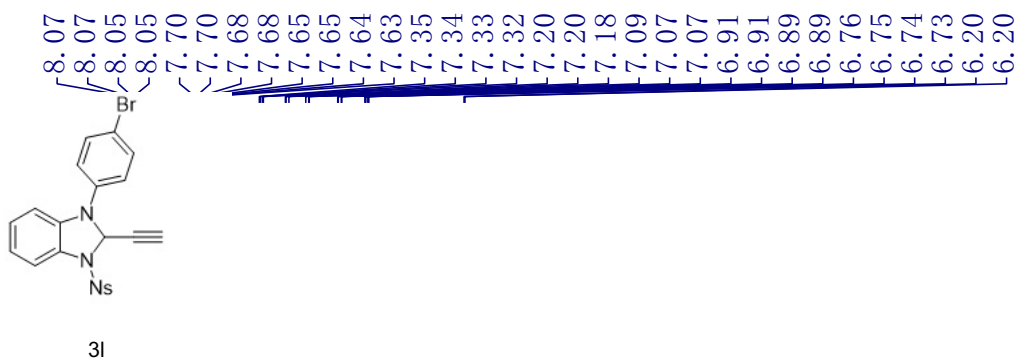
3k

150.61  
140.99  
139.61  
137.38  
130.47  
129.57  
129.02  
128.50  
127.64  
123.95  
121.99  
119.92  
119.05  
112.48

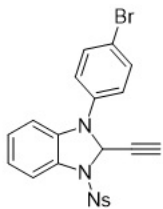
78.06  
74.88  
72.87



sjt04.282.fid  
zt313



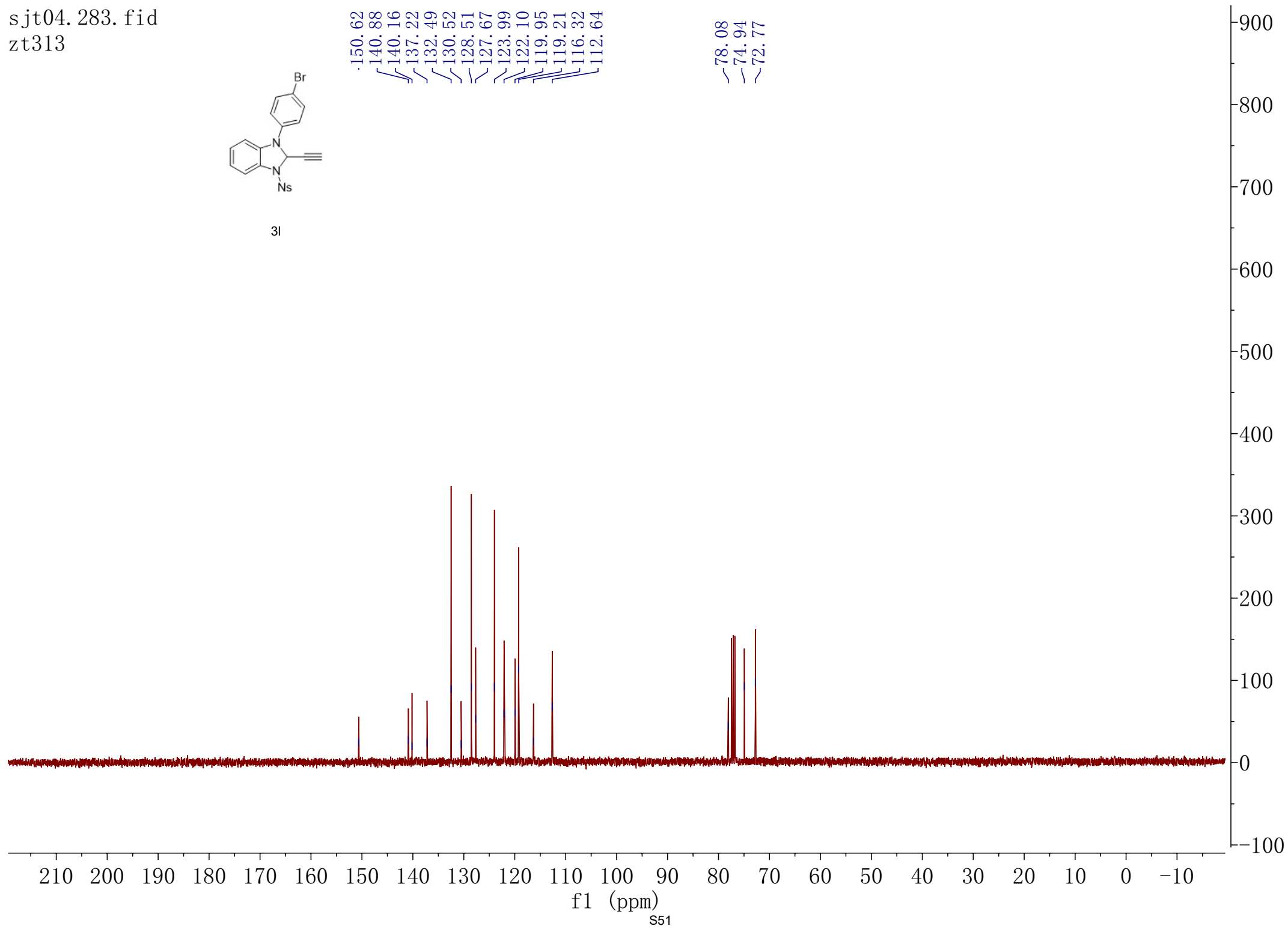
sjt04.283.fid  
zt313



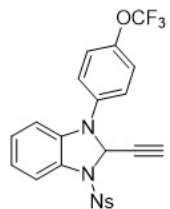
3l

150.62  
140.88  
140.16  
137.22  
132.49  
130.52  
128.51  
127.67  
123.99  
122.10  
119.95  
119.21  
116.32  
112.64

78.08  
74.94  
72.77



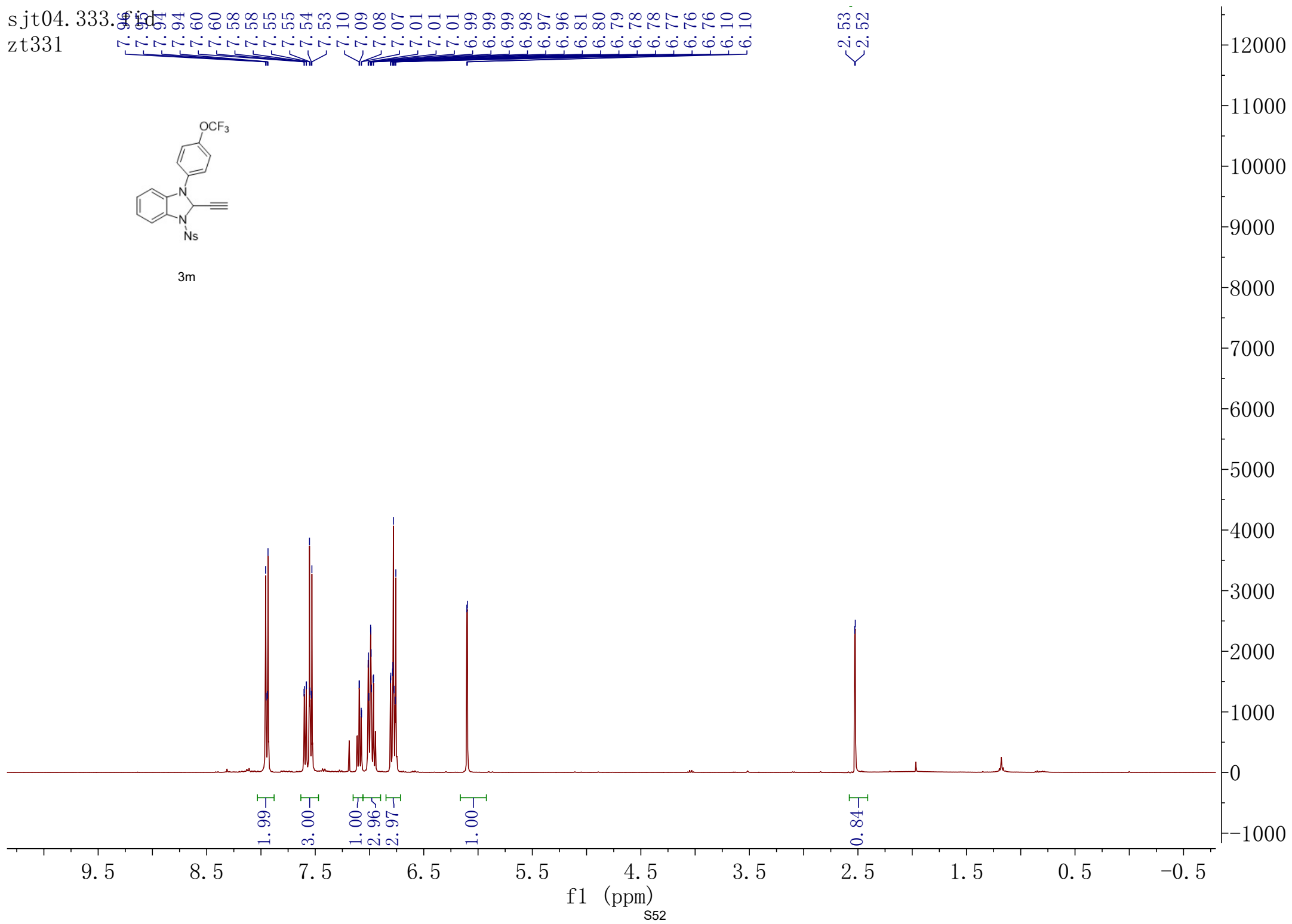
sjt04.333.4  
zt331

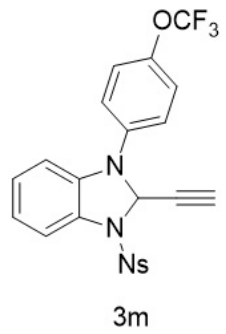


3m

7.95  
7.94  
7.94  
7.60  
7.60  
7.58  
7.58  
7.55  
7.55  
7.54  
7.53  
7.10  
7.09  
7.08  
7.07  
7.01  
7.01  
7.01  
6.99  
6.99  
6.99  
6.98  
6.97  
6.96  
6.81  
6.80  
6.79  
6.78  
6.78  
6.77  
6.76  
6.76  
6.10  
6.10

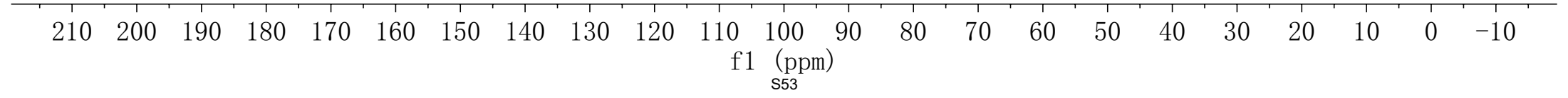
2.53  
2.52

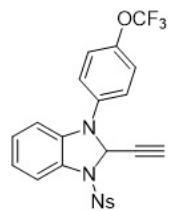




150.635  
144.849  
140.956  
139.657  
137.332  
130.458  
128.529  
127.667  
124.251  
123.915  
122.393  
122.068  
121.699  
119.943  
119.142  
118.811  
116.586  
112.402

78.017  
74.924  
72.870





3m

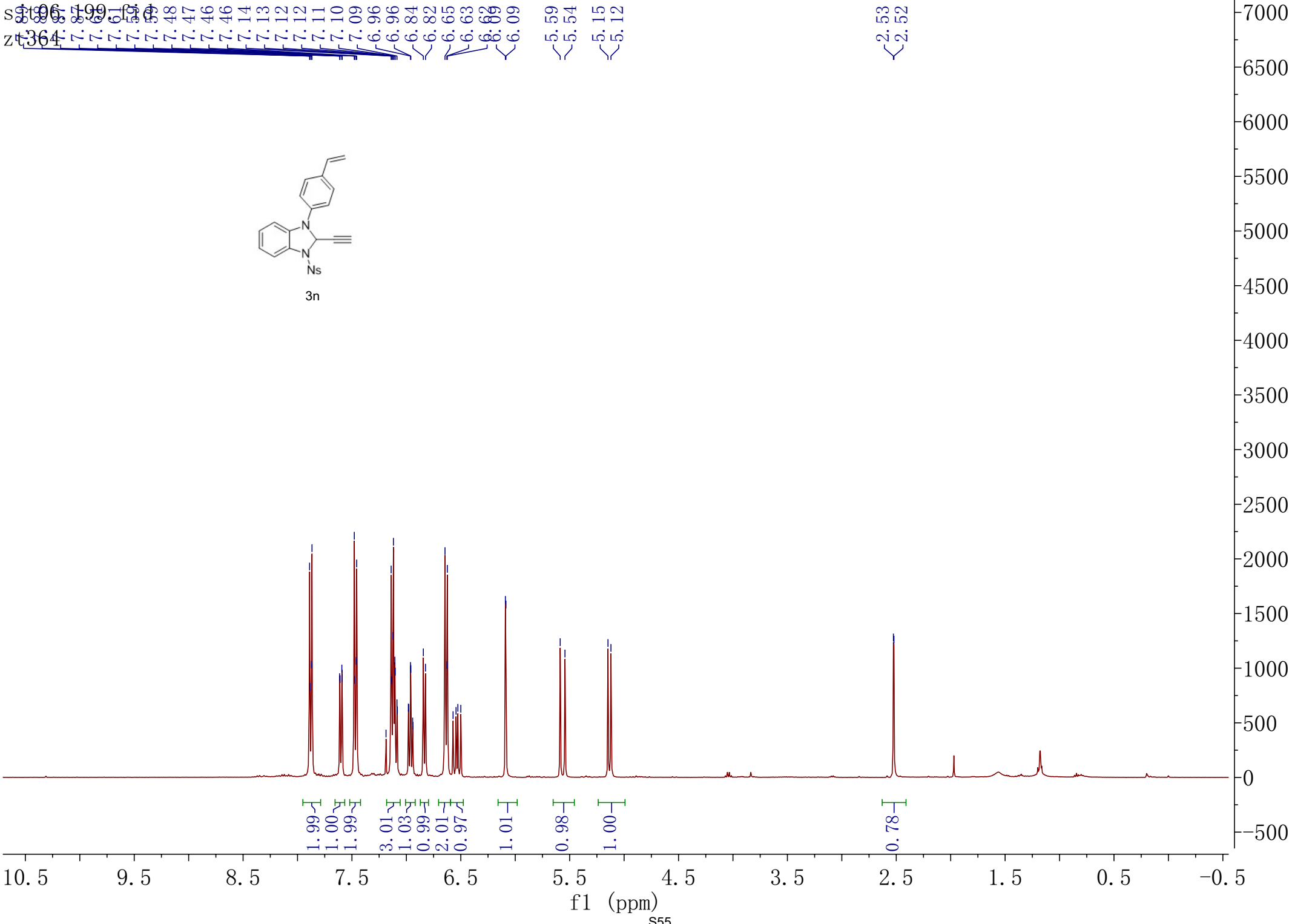
---58.246



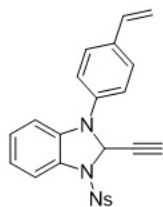
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

f1 (ppm)  
S54





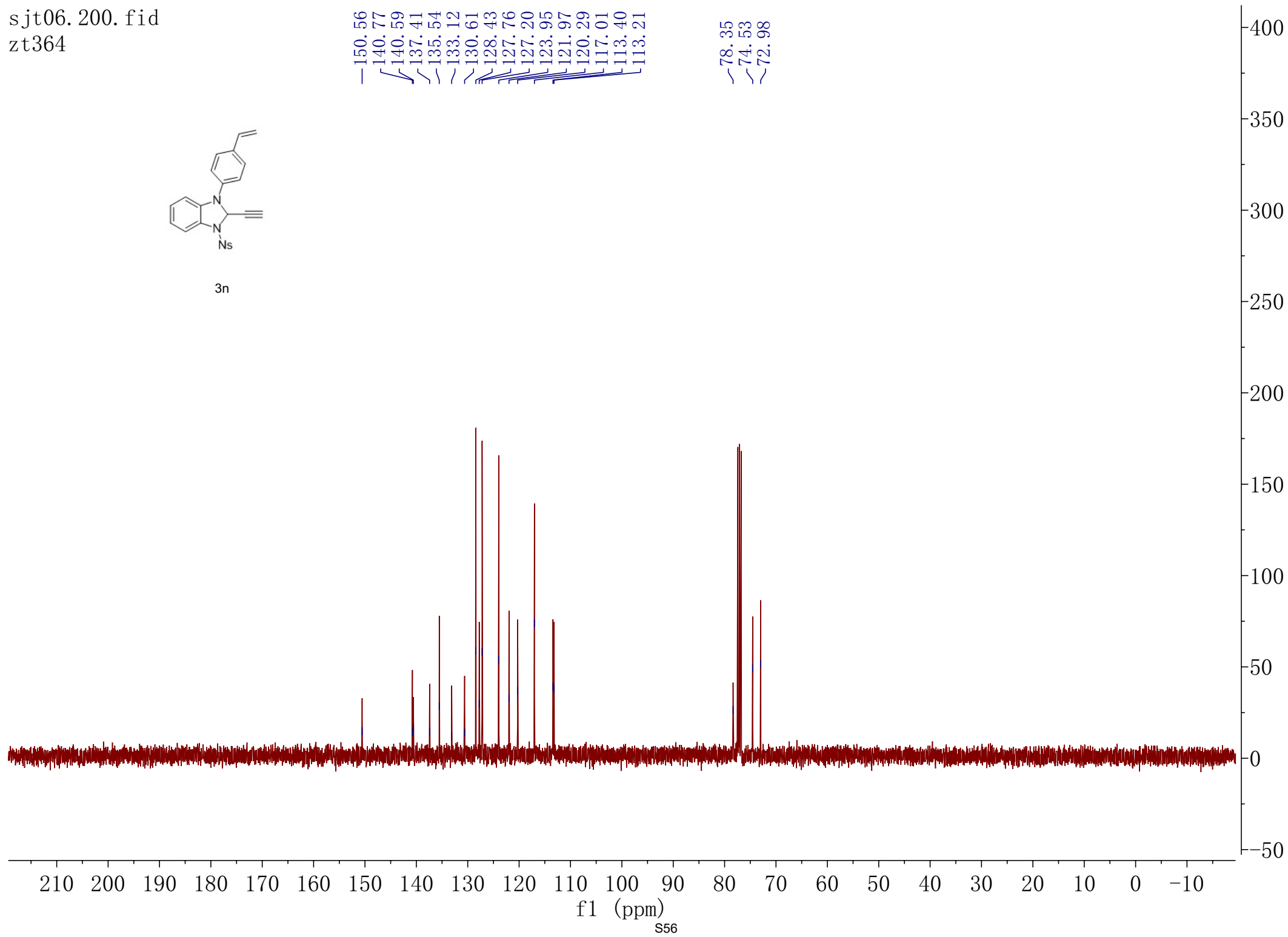
sjt06.200.fid  
zt364



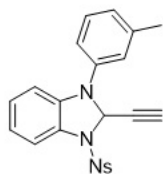
3n

150.56  
140.77  
140.59  
137.41  
135.54  
133.12  
130.61  
128.43  
127.76  
127.20  
123.95  
121.97  
120.29  
117.01  
113.40  
113.21

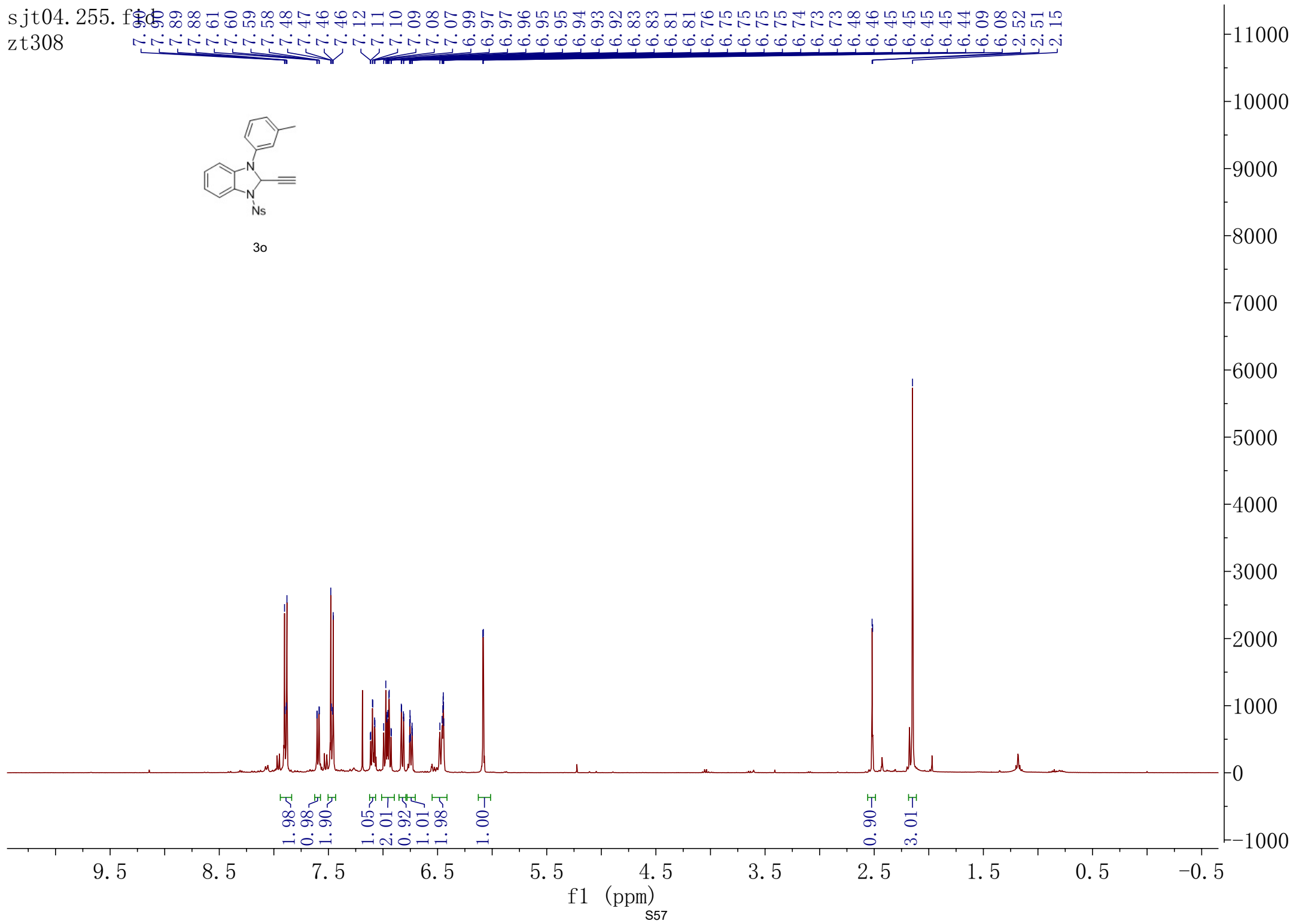
78.35  
74.53  
72.98



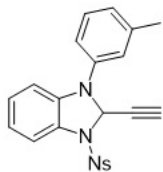
sjt04.255.f1  
zt308



3o



sjt04.202.fid  
zt308

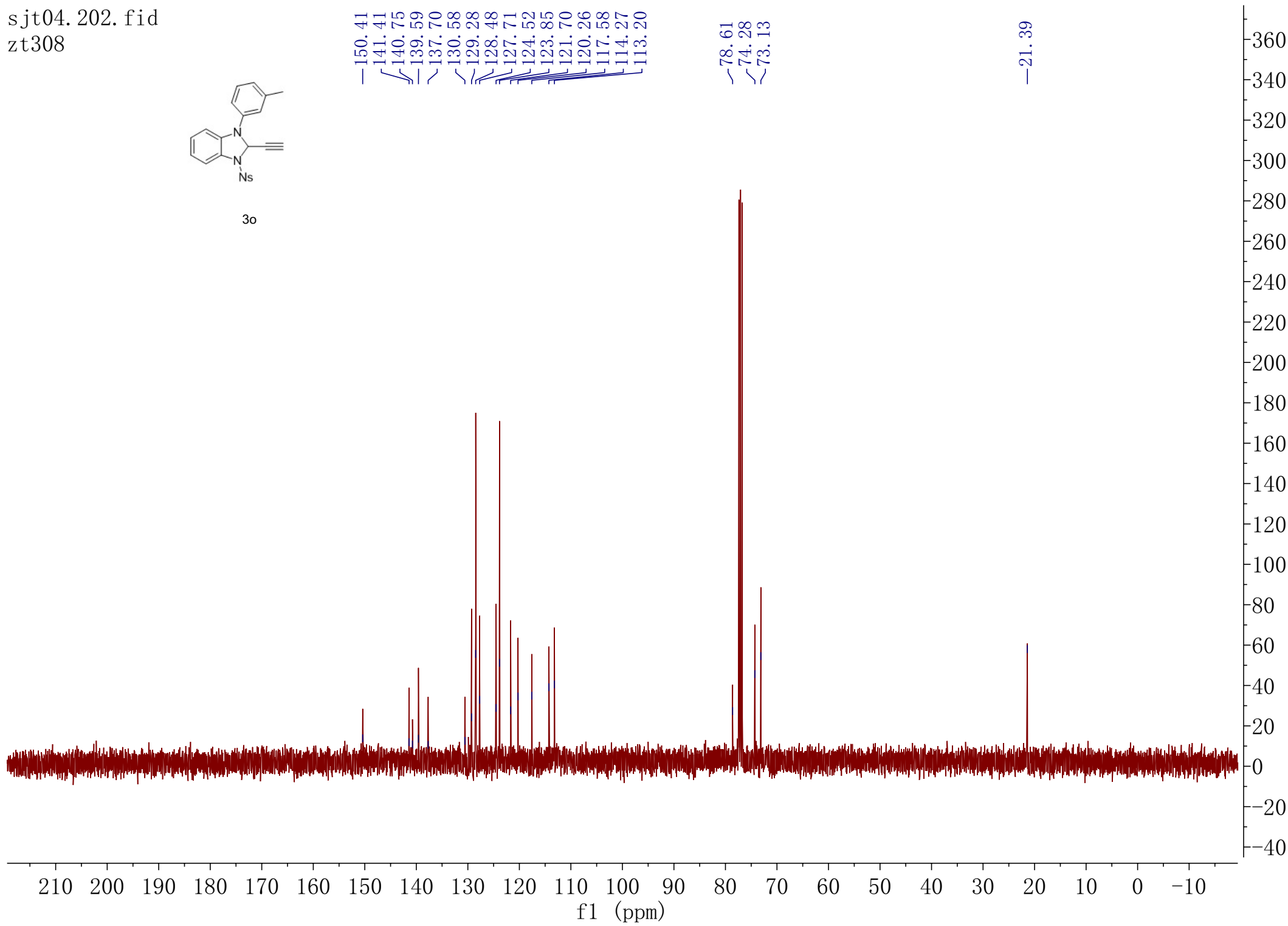


3o

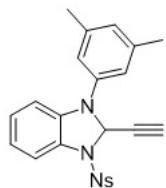
150.41  
141.41  
140.75  
139.59  
137.70  
130.58  
129.28  
128.48  
127.71  
124.52  
123.85  
121.70  
120.26  
117.58  
114.27  
113.20

78.61  
74.28  
73.13

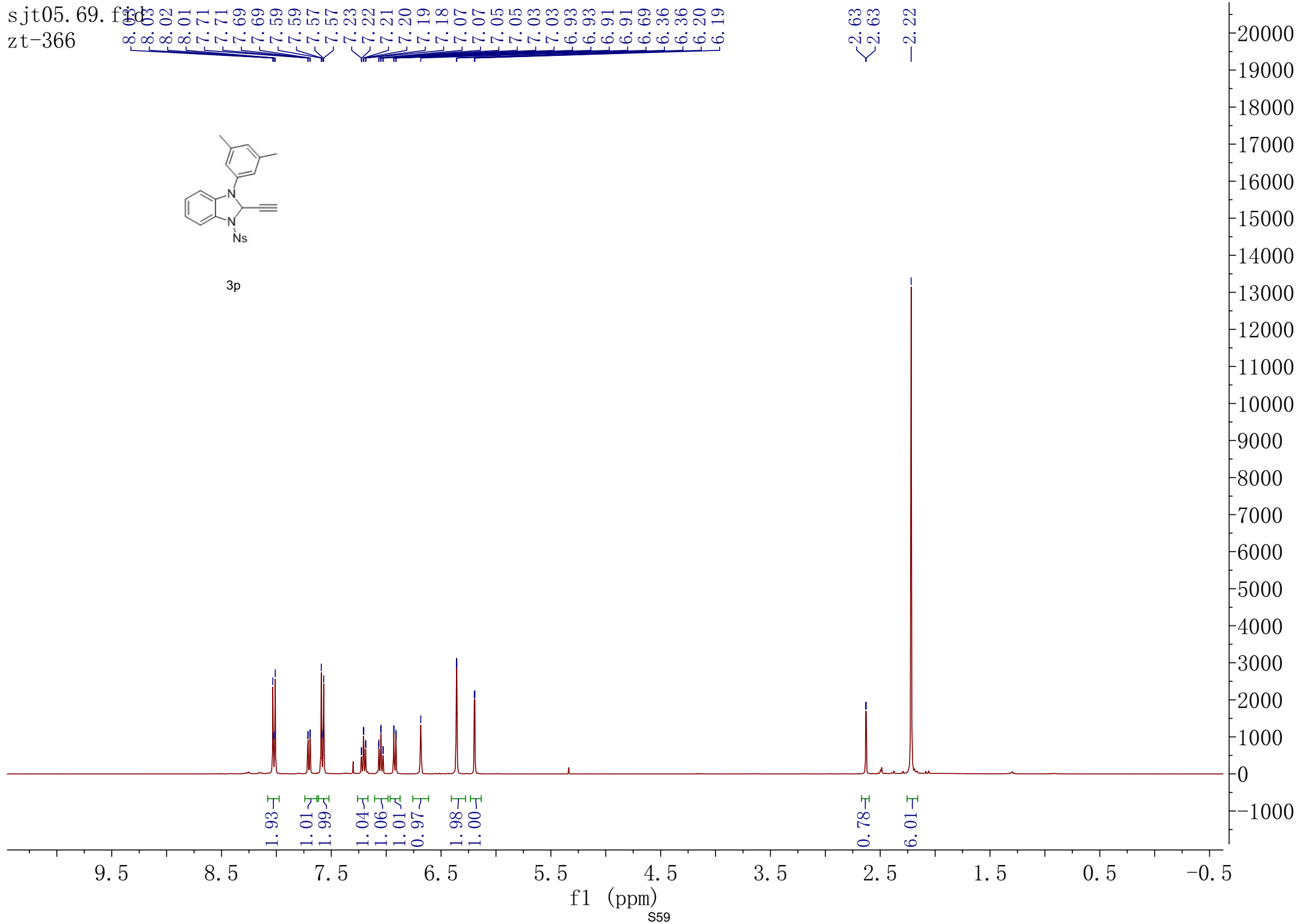
21.39



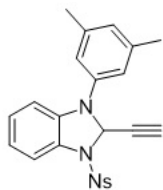
sjt05.69.f1d  
zt-366



3p



sjt05.71.fid  
zt366

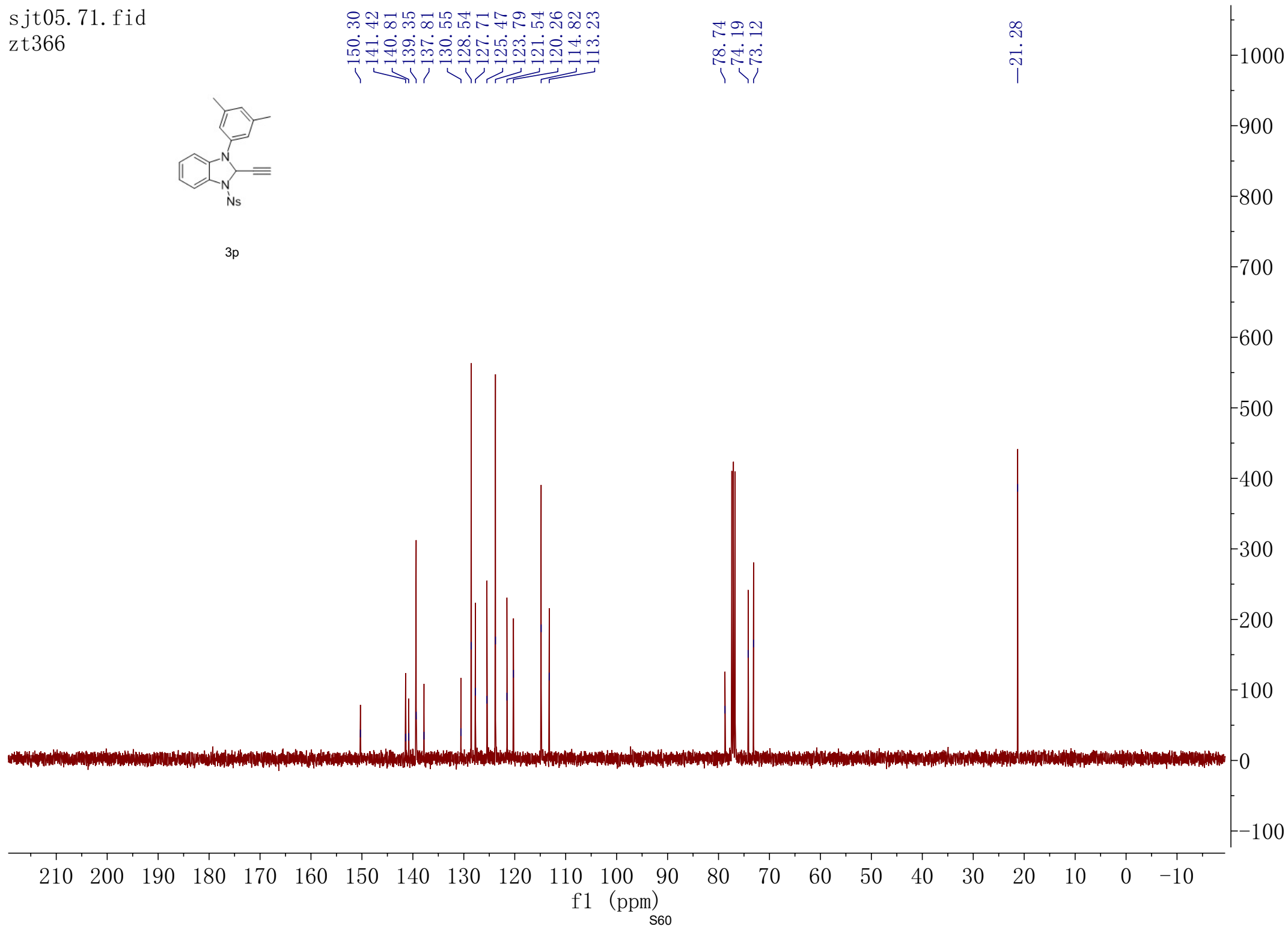


3p

150.30  
141.42  
140.81  
139.35  
137.81  
130.55  
128.54  
127.71  
125.47  
123.79  
121.54  
120.26  
114.82  
113.23

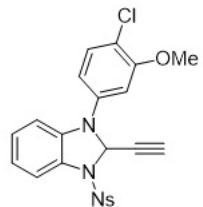
78.74  
74.19  
73.12

21.28

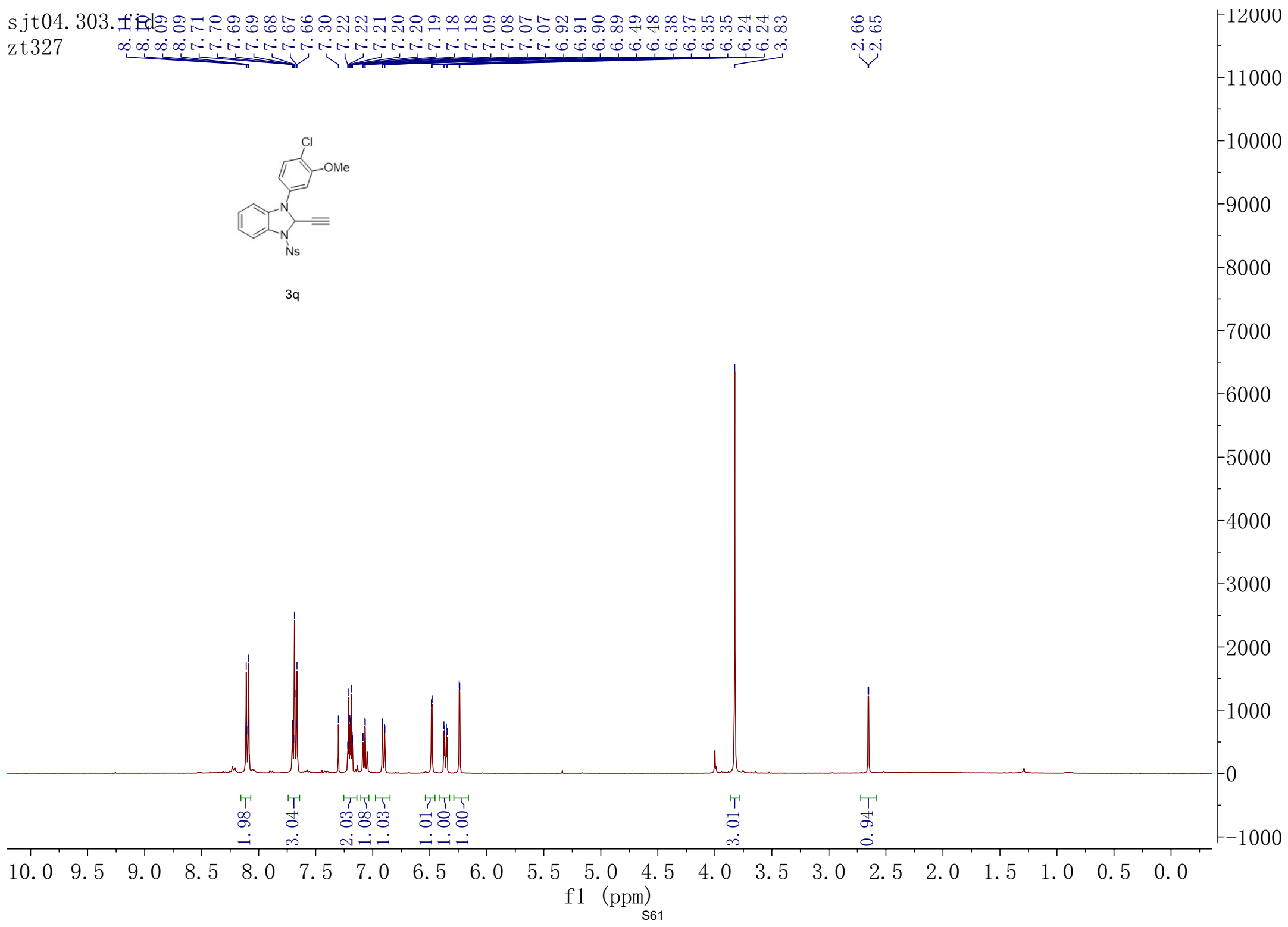


sjt04.303.f1  
zt327

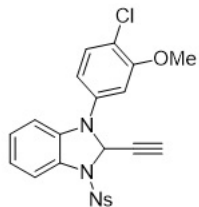
8.09 8.09 8.09 8.09 7.71 7.70 7.69 7.68 7.67 7.66 7.30 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.09 7.08 7.07 7.07 6.92 6.91 6.90 6.89 6.49 6.48 6.38 6.37 6.35 6.35 6.24 6.24 3.83



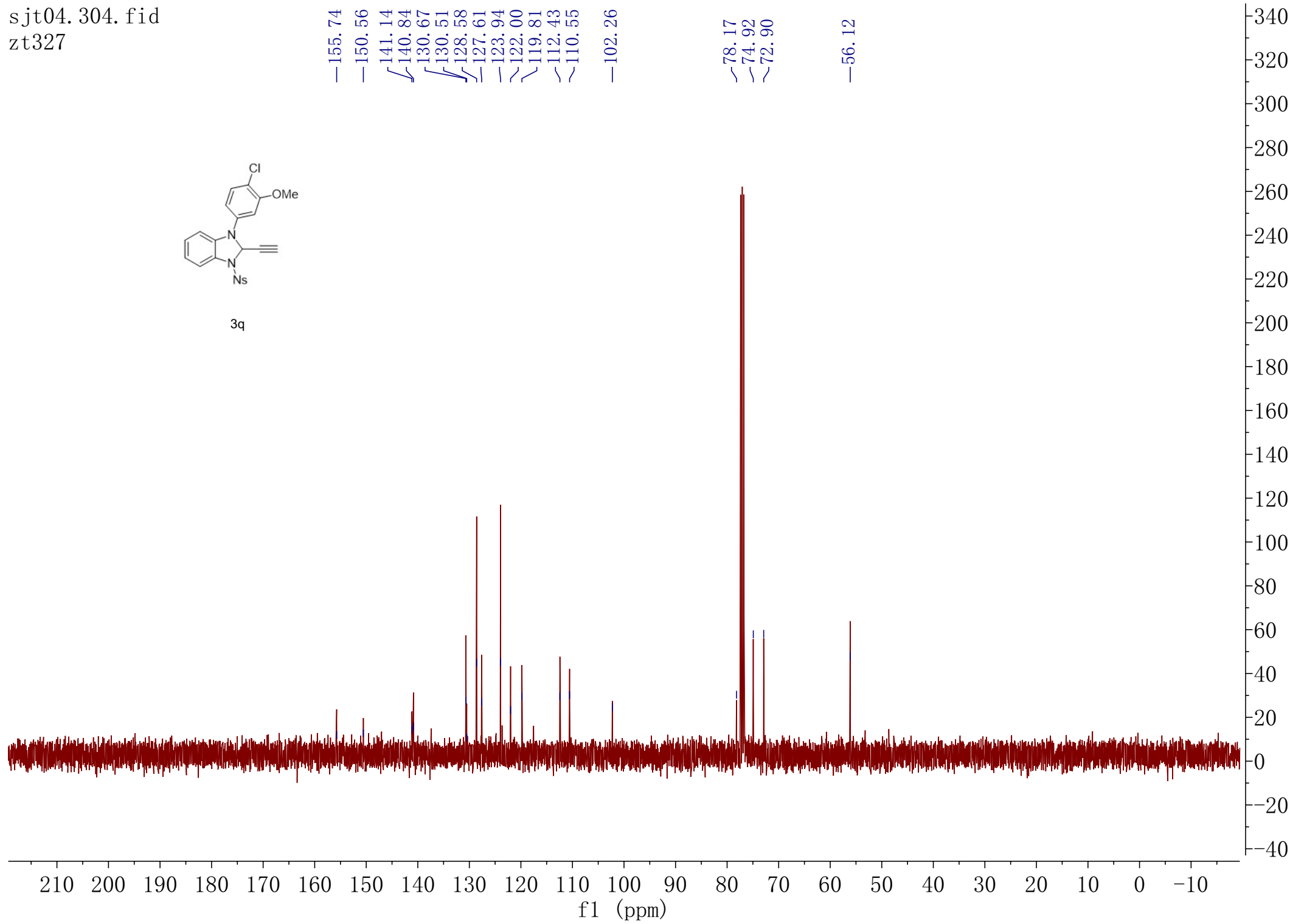
3q



sjt04.304.fid  
zt327



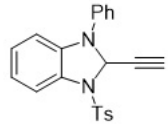
3q







3sjtiao.134.fid  
zt293

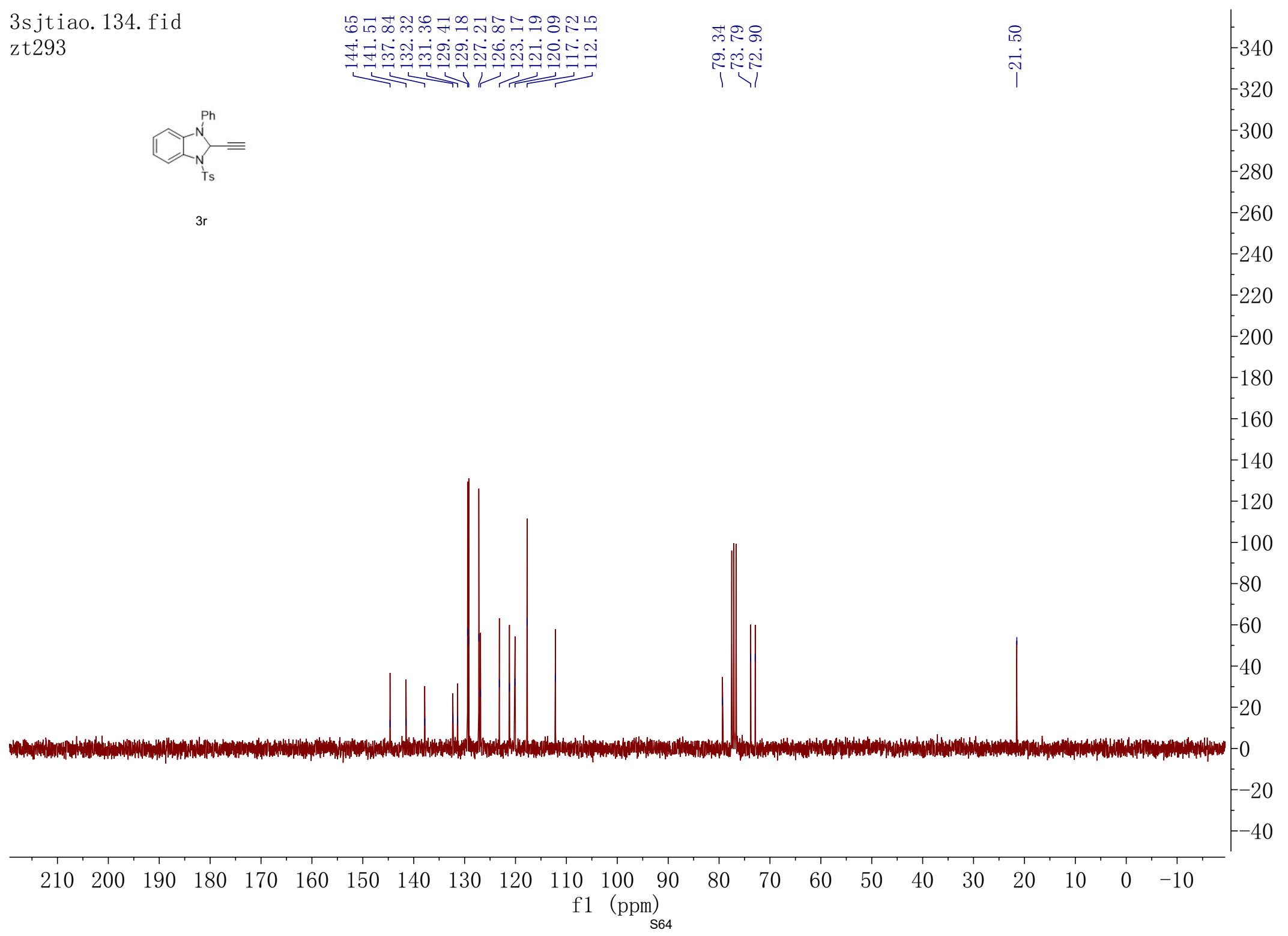


3r

144.65  
141.51  
137.84  
132.32  
131.36  
129.41  
129.18  
127.21  
126.87  
123.17  
121.19  
120.09  
117.72  
112.15

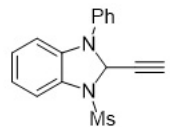
79.34  
73.79  
72.90

21.50

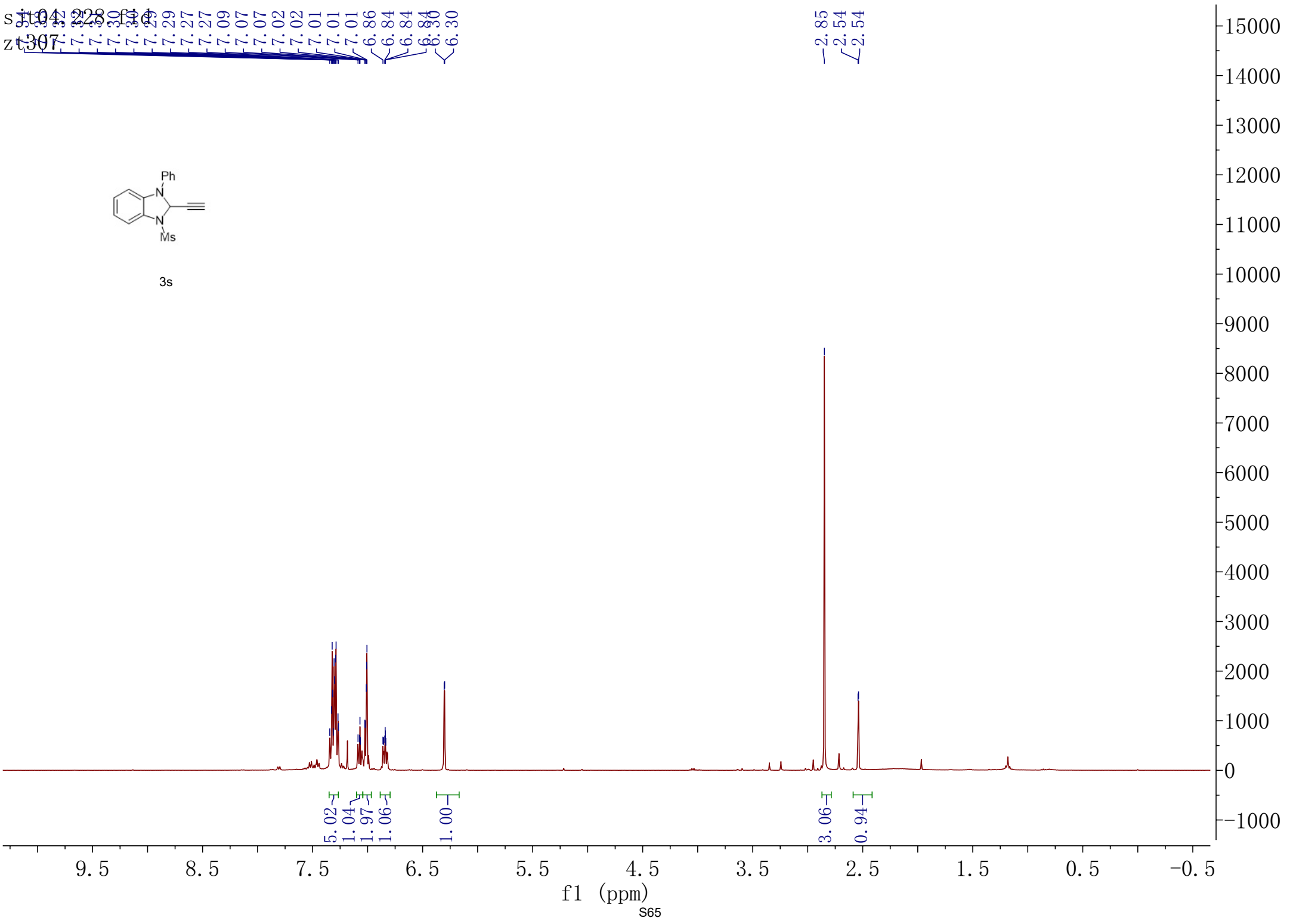


S 1104.228  
Z 307

Chemical Shift (ppm)
7.30
7.29
7.27
7.27
7.09
7.07
7.07
7.02
7.02
7.01
7.01
7.01
7.01
6.86
6.84
6.84
6.84
6.30

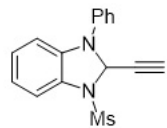


3s



f1 (ppm)  
S65

sjt04.130.fid  
zt307

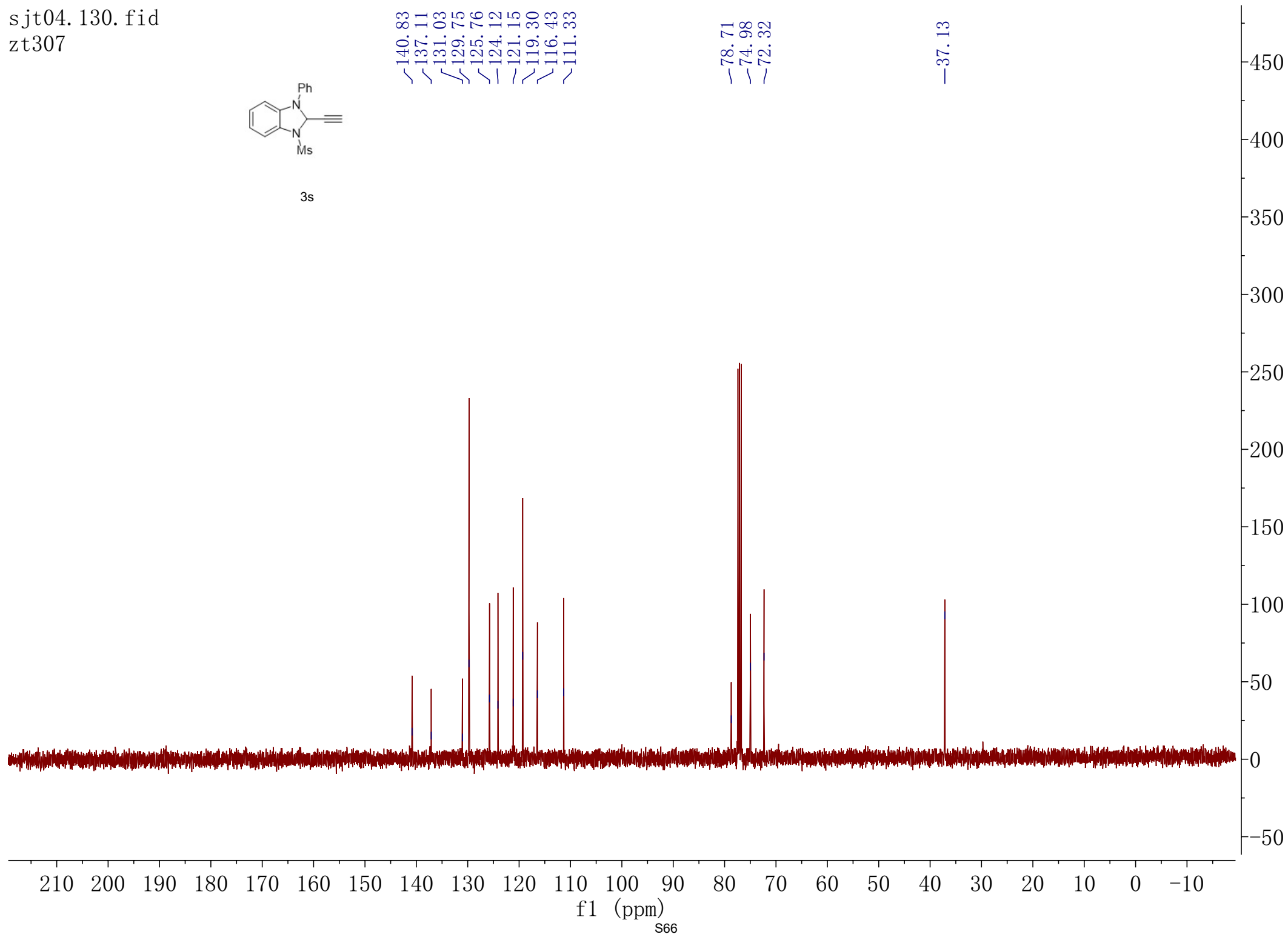


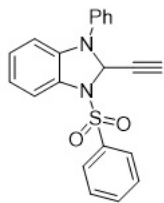
3s

140.83  
137.11  
131.03  
129.75  
125.76  
124.12  
121.15  
119.30  
116.43  
111.33

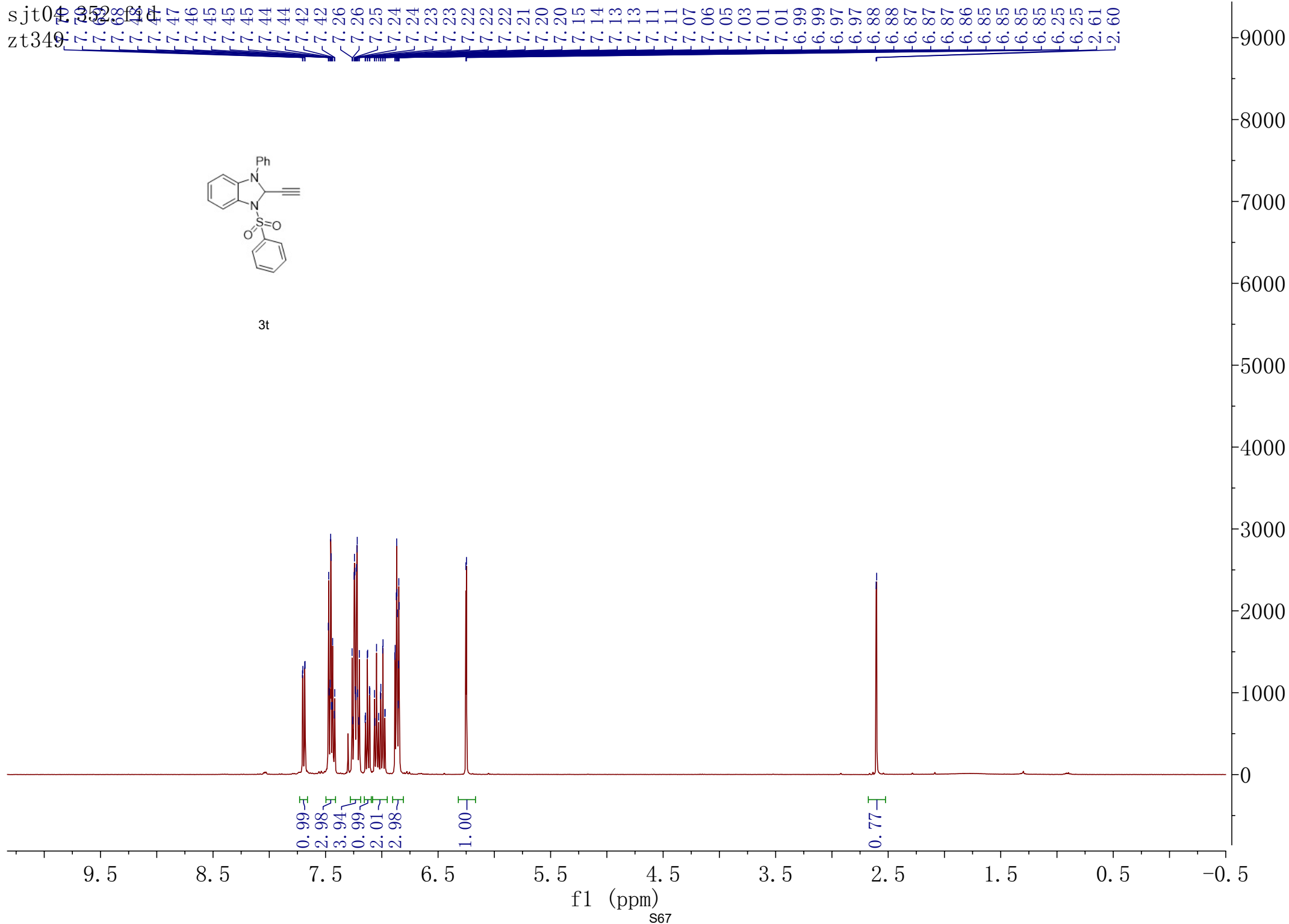
78.71  
74.98  
72.32

37.13

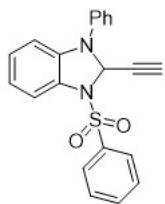




3t



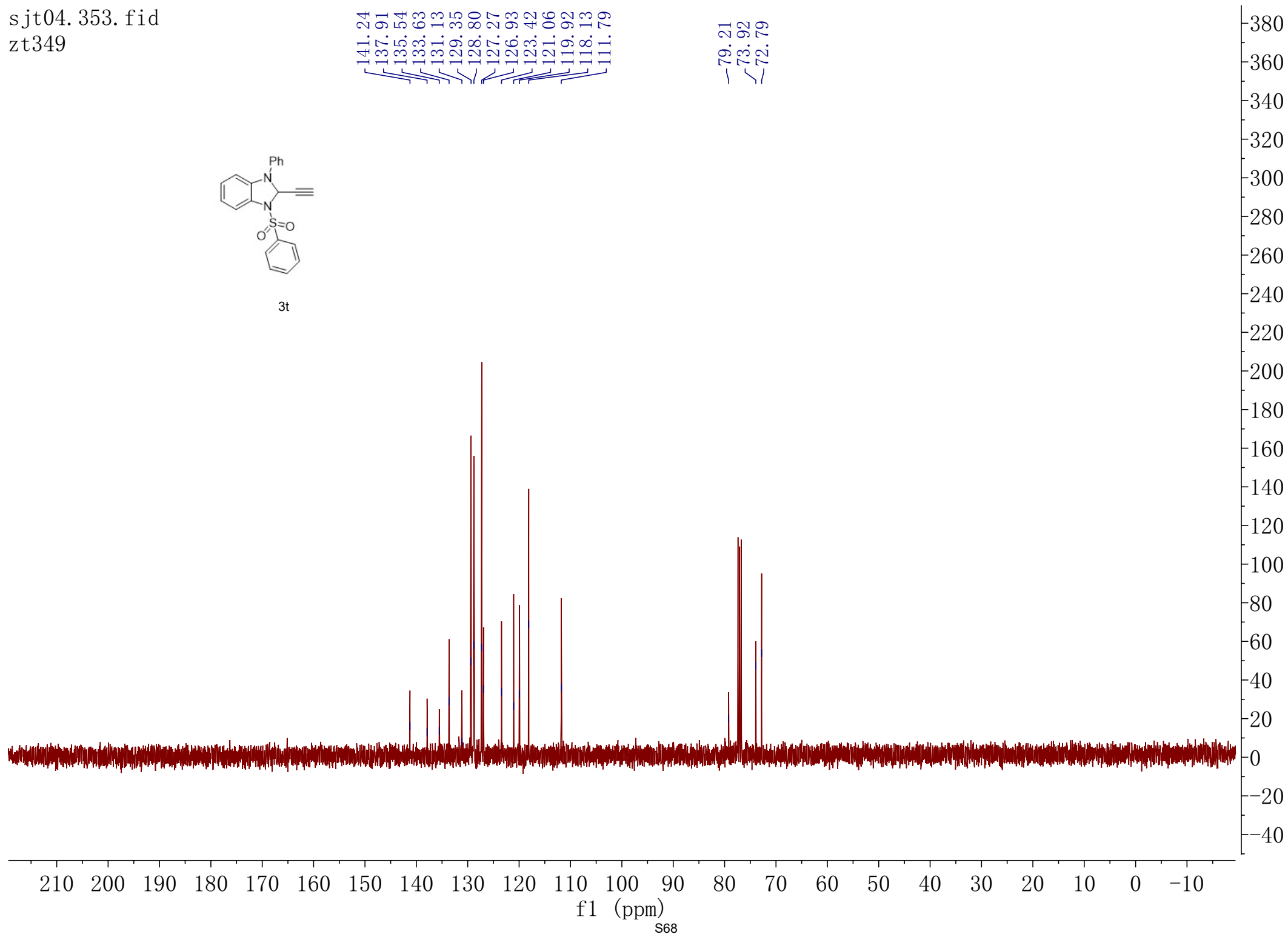
sjt04.353.fid  
zt349

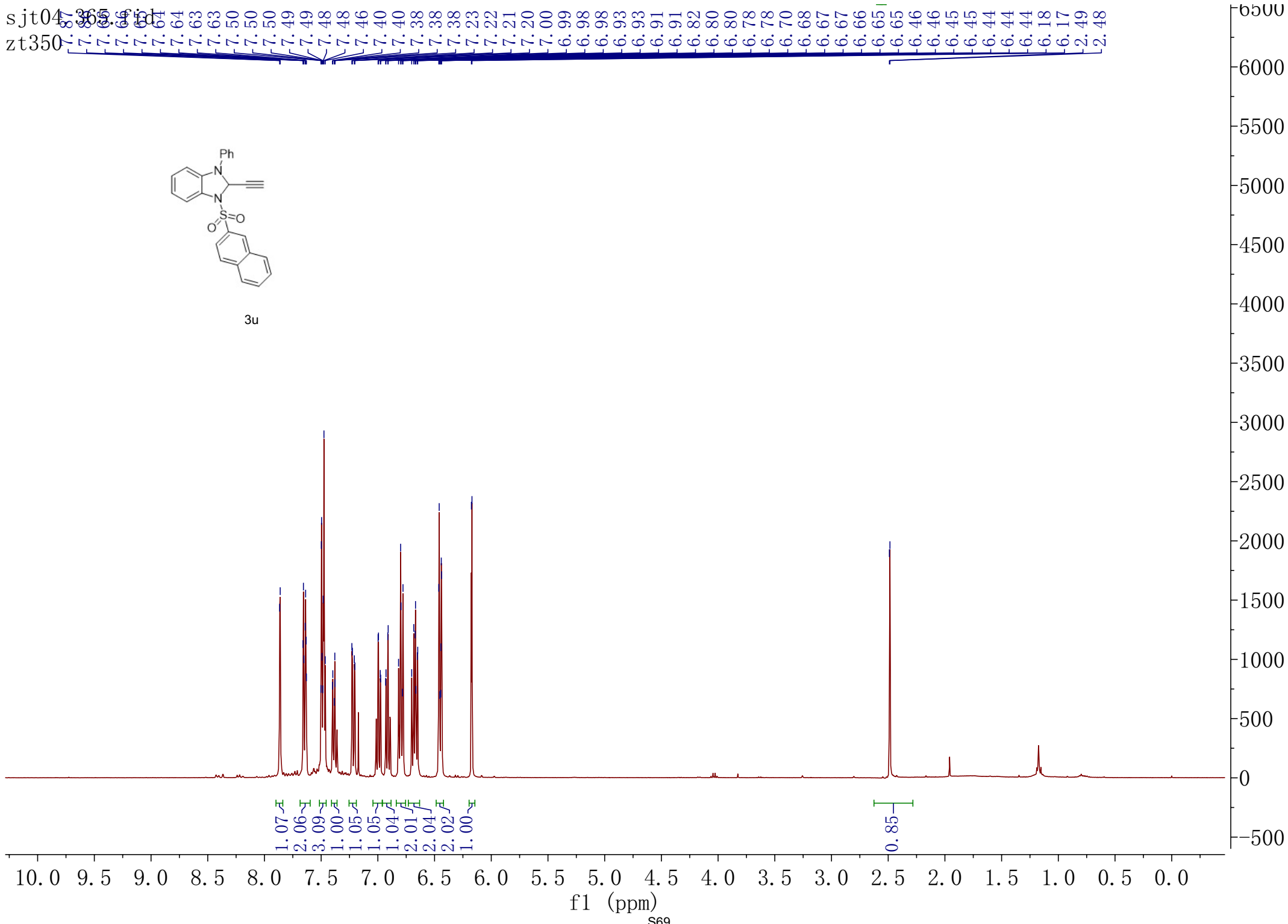


3t

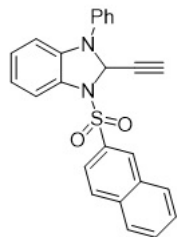
141.24  
137.91  
135.54  
133.63  
131.13  
129.35  
128.80  
127.27  
126.93  
123.42  
121.06  
119.92  
118.13  
111.79

79.21  
73.92  
72.79





sjt04.366.fid  
zt350



3u

