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Supporting Information

for

Rh(I)-Catalyzed Enantioselective Cyclization of Enyne through Site-Selective C(sp^3)-H Bond Activation Triggered by Formation of Rhodacycle

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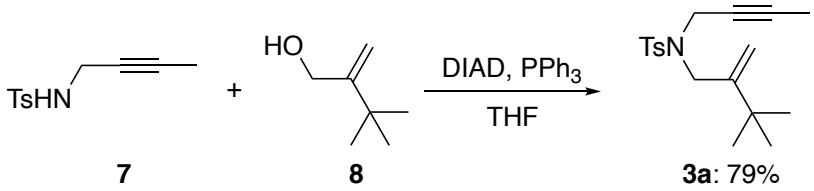
General Considerations

All manipulations were performed under an argon atmosphere unless stated otherwise. Solvents were purified under argon using The Ultimate Solvent System (Glass Counter Inc.) (THF, Et_2O. DMF), and were distilled under an argon atmosphere from CaH_2 (DCE). All other solvents and reagents were purified when necessary by standard procedures. Column chromatography was performed on silica gel 60 N (spherical, neutral; Kanto Kagaku, 45-50 μm), or silica gel 60 N (spherical, neutral; Kanto Kagaku, 63-210 μm) with the indicated solvent as eluent. TLC and PTLC were performed on Silica gel 60 $PF_{254\alpha}$ (Merck). IR spectra were obtained on a JASCO FT/IR 460Plus spectrometer. ^{1}H NMR spectra were recorded on JEOL ECX400P (400 MHz), JEOL ECS400 (400 MHz), and JEOL ECA500 (500 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on JEOL ECX400P (100 MHz), JEOL ECS400 (100 MHz), and JEOL ECA500 (125 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent as the internal standard ($CDCl_3$: δ = 77.00 ppm). Mass spectra were obtained on JEOL JMS-T100LP and JMS-T100GCV and JEOL JMS-FAB mate mass spectrometer, and Thermo Scientific Exactive mass spectrometer. Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). Chiral HPLC analyses were carried out using a JASCO PU-980 and using indicated chiral column.

Experimental Procedure and Spectral Data

Synthesis of Substrate

Enyne 3a (Scheme S1)



Scheme S1. Synthesis of Enyne **3a**.

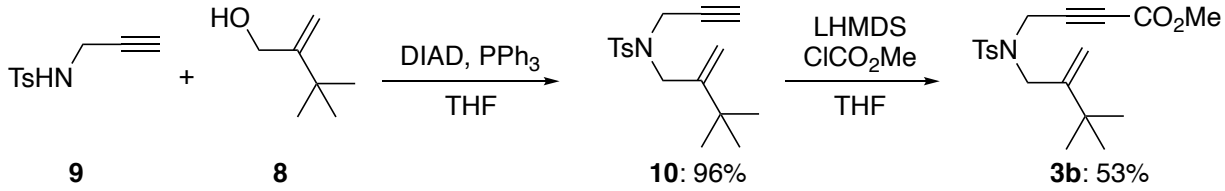
To a solution of **7**[1] (537 mg, 2.41 mmol), **8**[2] (228 mg, 2.00 mmol), and PPh_3 (630 mg, 2.37 mmol) in THF (5.0 mL) was added DIAD (0.47 mL, 2.40 mmol) at 0 °C, and the reaction mixture was

[1] Kavanagh, Y.; O'Brien, M.; Evans, P. *Tetrahedron* **2009**, *65*, 8259.

[2] Li, C.; Qingjie, D.; Jin-Jun, L.; Song, Y.; Zhuming, Z. U.S. Pat. Appl. Publ. US 20080009486 A1 Jan 10, 2008.

stirred at room temperature for 1 h. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 9/1) to give **3a** (502 mg, 79% yield) as a colorless oil. Spectral data of **3a**: IR (neat) 2964, 2871, 1775, 1598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, *J* = 6.4 Hz, 2H), 7.29 (d, *J* = 6.4 Hz, 2H), 5.07 (s, 2H), 4.01 (s, 2H), 3.83 (s, 2H), 2.43 (s, 3H), 1.50 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 143.4, 136.4, 129.4, 128.1, 111.1, 82.0, 74.6, 71.8, 47.9, 36.2, 35.6, 29.4, 21.8, 21.7, 3.4 (^{13}C NMR spectra indicate rotamers are present); LRMS (EI) *m/z* 304 [(M-Me)$^+$], 262, 155; HRMS (EI) calcd for $C_{17}H_{22}NO_2S$ [(M-Me)$^+$] 304.1371, found 304.1361.

Enyne 3b (Scheme S2)



Scheme S2. Synthesis of Enyne **3b**.

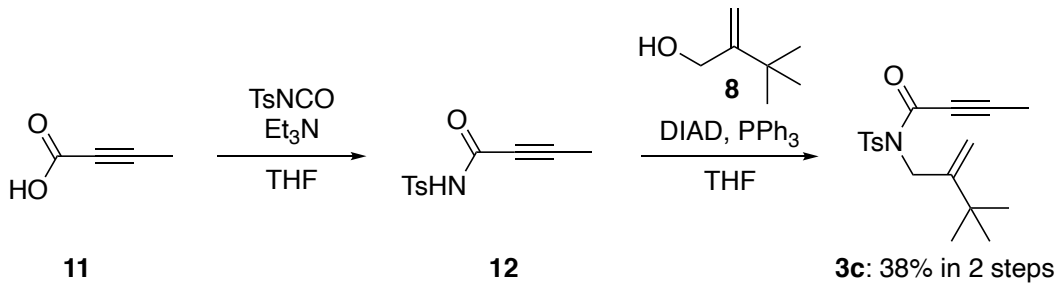
To a solution of **9**[3] (1.26 g, 6.00 mmol) in THF (12.5 mL) were added **8**[2] (0.68 mL, 5.00 mmol), PPh_3 (1.58 g, 6.02 mmol), and DIAD (1.2 mL, 6.00 mmol) at 0 °C. The mixture was stirred at room temperature for 1.5 h, and the mixture was concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 9:1) to give **10** (1.47 g, 96% yield). Spectral data of **10**: IR (neat) 3275, 2962, 2871, 1349, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.09 (d, *J* = 3.6 Hz, 2H), 4.09 (d, *J* = 2.4 Hz, 2H), 3.87 (s, 2H), 2.43 (s, 3H), 1.95 (t, *J* = 2.4 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 143.4, 136.0, 129.4, 127.8, 111.0, 76.6, 73.9, 47.6, 35.4, 30.9, 29.1, 21.5 ; LRMS (EI) *m/z* 305 [M$^+$], 248, 155, 91.

To a solution of **10** (306 mg, 1.00 mmol) in THF (5 mL) was added LHMDS (1.3 M in THF, 0.92 mL, 1.20 mmol) at -78 °C, and the reaction mixture was stirred at the same temperature for 1 h. To the solution was added methyl chloroformate (120 μL, 1.50 mmol), and the mixture was stirred and warmed to room temperature for 16 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to give **3b** (194 mg, 53% yield) as a colorless oil. Spectral data of **3b**: IR (nujol) 3019, 2966, 2254, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H),

[3] Brummond , K. M.; Chen, H.; Peter Sill, P.; You, L. *J. Am. Chem. Soc.* **2002**, *124* , 15186.

7.32 (d, J = 8.4 Hz, 2H), 5.12 (s, 1H), 5.06 (s, 1H), 4.20 (s, 2H), 3,85 (s, 2H), 3.69 (s, 3H), 2.43 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 149.4, 143.6, 134.9, 129.3, 127.4, 127.3, 111.5, 80.1, 76.9, 52.3, 48.0, 35.3, 35.2, 29.0, 21.4 (^{13}C NMR spectra indicate rotamers are present); LRMS (EI) *m/z* 348 [(M-Me)$^+$], 331, 208; HRMS (EI) calcd for $C_{18}H_{22}NO_4S$ [(M-Me)$^+$] 348.1270, found 348.1259.

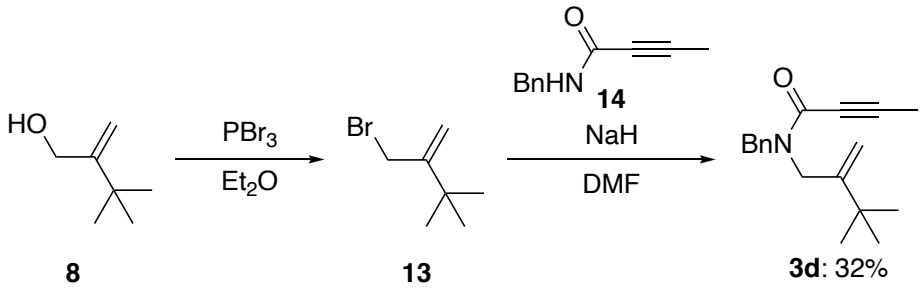
Enyne 3c (Scheme S3)



Scheme S3. Synthesis of Enyne **3c**.

To a solution of tetrolic acid **11** (169 mg, 2.00 mmol) in THF (6.7 mL) were added *N*-tosyl isocyanate (340 μL, 2.20 mmol) and Et_3N (840 μL, 6.00 mmol) dropwise at 0 °C and the reaction mixture was stirred at room temperature for 16 h, then the mixture was concentrated. The residue was roughly purified by column chromatography on silica gel (AcOEt / MeOH = 9:1) to give a crude product **12**. To a solution of the crude amide **12** in THF (4.0 mL) were added **8**[2] (300 μL, 2.20 mmol), PPh_3 (577 mg, 1.93 mmol), and DIAD (430 μL, 2.20 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h, and the mixture was concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 8:1) to give **3c** (253 mg, 38% yield in 2 steps from tetrolic acid **11**). Spectral data of **3c**: IR (neat) 2966, 2239, 1672, 1360 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.01 (s, 1H), 4.78 (s, 1H), 4.69 (s, 2H), 2.43 (s, 3H), 1.93 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 151.9, 145.3, 136.0, 129.5, 129.3, 107.4, 73.6, 49.2, 35.4, 29.5, 29.4, 29.2, 22.3, 22.2, 21.9, 4.3 (^{13}C NMR spectra indicate rotamers are present); LRMS (EI) *m/z* 318 [(M-Me)$^+$], 252, 178; HRMS (EI) calcd for $C_{17}H_{20}NO_3S$ [(M-Me)$^+$] 318.1164, found 318.1263.

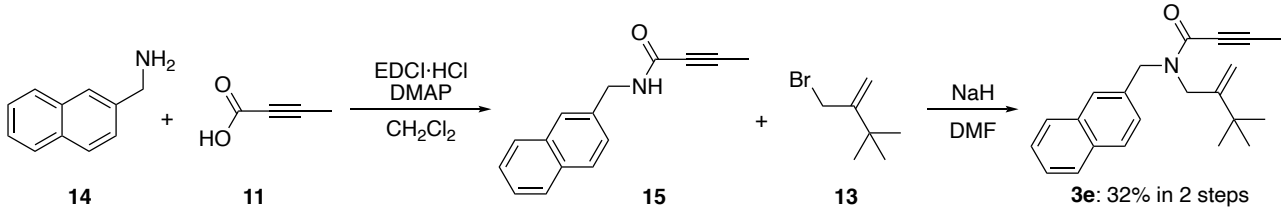
Enyne 3d (Scheme S4)



Scheme S4. Synthesis of Enyne **3d**.

To a solution of **8**[2] (400 μL, 3.00 mmol) in Et_2O (2.5 mL) was added PBr_3 (280 μL, 3.00 mmol) at 0 °C, and the mixture was stirred at same temperature for 14 h. To the mixture was added water at 0 °C, and the aqueous layer was extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and the crude bromide **13** was obtained after removal of the solvent. To a suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 2.10 mmol) in DMF (1.0 mL) was added **14**[4] (278 mg, 1.60 mmol) in DMF (1.0 mL) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the crude bromide **13** in DMF (1.2 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 12 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with Et_2O. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1) to give **3d** (139 mg, 32% yield) as a colorless oil. Spectral data of **3d**: IR (neat) 2963, 1651, 1604, 1454, 1173 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5H), 5.03 & 4.99 (s, 1H), 4.76 & 4.72 (s, 1H), 4.66 & 4.57 (s, 1H), 4.08 & 3.94 (s, 1H), 2.00 & 1.96 (s, 3H), 1.07 & 1.04 (s, 9H) (^1H NMR spectra indicate rotamers are present); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.0, 151.5, 151.0, 138.3, 128.8, 128.0, 127.3, 126.2, 110.1, 106.6, 105.9, 91.8, 67.9, 60.3, 50.8, 48.4, 46.4, 34.8, 29.2, 21.0, 19.1, 14.1 (^{13}C NMR spectra indicate rotamers are present); LRMS (EI) *m/z* 254 [$(M\text{-}Me)^+$], 212, 91; HRMS (EI) calcd for $C_{17}H_{20}NO$ [$(M\text{-}Me)^+$] 254.1545, found 254.1537.

Enyne 3e (Scheme S5)

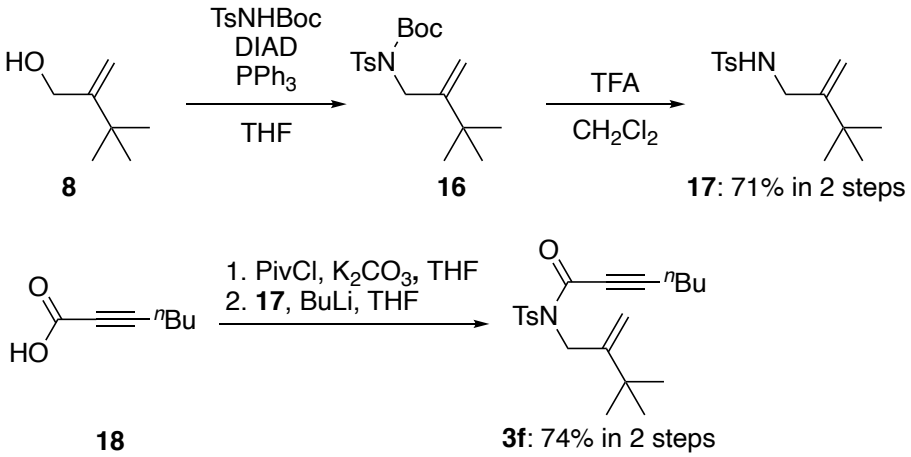


Scheme S5. Synthesis of Enyne **3e**.

[4] Wang, J.; Xie, X.; Ma, F.; Peng, Z.; Zhang, L.; Zhang, Z. *Tetrahedron* **2010**, *66*, 4212.

To a solution of tetrolic acid **11** (235 mg, 2.80 mmol) and (2-naphthyl)methylamine **14**[5] (357 mg, 2.30 mmol) was added EDCI·HCl (537 mg, 2.80 mmol) and DMAP (70.9 mg, 0.580 mmol) at 0 °C, and the mixture was stirred at room temperature for 10 h, then the mixture was concentrated. The residue was roughly purified by column chromatography on silica gel (AcOEt) to give a crude amide **15**. To a suspension of NaH (60% dispersion in mineral oil, 68.0 mg, 1.70 mmol) in DMF (1.0 mL) was added the crude amide **15** in DMF (1.0 mL) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the bromide **13** (ca. 1.7 mmol) freshly prepared from alcohol **8**[2] (400 μL, 3.0 mmol) and PBr_3 (280 μL, 3.0 mmol) in DMF (1.2 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 12 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with Et_2O. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1) to give **3e** (235 mg, 32% yield in 2 steps from **14**) as a colorless oil. Spectral data of **3e**: IR (neat) 2964, 2247, 1629, 1454, 1420, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5H), 5.03 & 4.99 (s, 1H), 4.76 & 4.72 (s, 1H), 4.66 & 4.57 (s, 1H), 4.08 & 3.94 (s, 1H), 2.00 & 1.96 (s, 3H), 1.07 & 1.04 (s, 9H) (^1H NMR spectra indicate rotamers are present); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 134.3, 134.0, 133.3, 133.0, 132.8, 128.7, 127.0, 126.3, 126.2, 126.1, 125.9, 106.9, 89.4, 88.4, 73.5, 73.2, 48.6, 47.2, 44.0, 35.2, 35.0, 29.0, 4.2, 4.0 (^{13}C NMR spectra indicate rotamers are present); LRMS (EI) *m/z* 304 [(M-Me)$^+$], 262, 222; HRMS (EI) calcd for $C_{21}H_{22}NO$ [(M-Me)$^+$] 304.1701, found 304.1694.

Enyne 3f (Scheme S6)



Scheme S6. Synthesis of Enyne **3f**.

To a solution of **8**[2] (680 μL, 4.98 mmol) and TsNHBoc (1.36 g, 5.03 mmol) in THF (17 mL) were

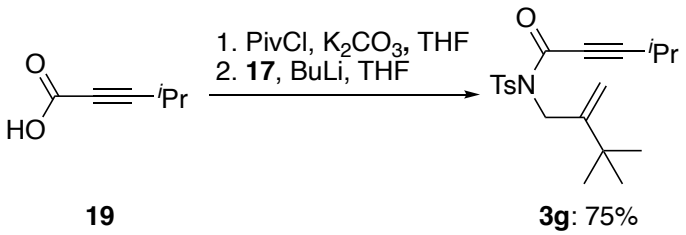
[5] Ahlford, K.; Livendahl, M.; Adolfsson, H. *Tetrahedron Lett.* **2009**, 50, 6321.

added PPh_3 (1.31 g, 5.00 mmol), and DIAD (980 μL, 4.99 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h, and the mixture was concentrated. The residue was roughly purified by column chromatography on silica gel (*n*-hexane/AcOEt = 9:1) to give crude **16**. Then to a solution of the crude amide **16** in CH_2Cl_2 was added trifluoroacetic acid (1.1 mL, 14.4 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. To the mixture was added saturated $NaHCO_3$ aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1) to give **17** (954 mg, 71% in 2 steps) as a colorless oil. Spectral data of **17**: IR (neat) 2926, 2853, 1463, 1377 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 1H), 4.90 (s, 1H), 3.56 (s, 2H), 2.43 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 143.5, 136.6, 129.7, 127.1, 109.4, 44.2, 35.3, 29.0, 21.5; LRMS (EI) *m/z* 267 [$(M)^+$], 252, 210,155.

To a solution of K_2CO_3 (497 mg, 3.59 mmol) in THF (3.6 mL) were added **18**[6] (460 μL, 3.57 mmol) and PivCl (440 μL, 3.58 mmol) at 0 °C, and the mixture (A) was stirred at room temperature for 3 h. To a solution of **17** (802 mg, 3.00 mmol) in THF (25 mL) was added ^{n}BuLi (1.6 M in THF, 2.1 mL, 3.30 mmol) at -78 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the reaction mixture (A) at -78 °C, and the resulting mixture was stirred at room temperature for 15 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 9/1) to give **3f** (834 mg, 74% yield) as a colorless oil. Spectral data of **3f**: IR (neat) 2960, 2872, 2226, 1671, 1361, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.01 (s, 1H), 4.76 (s, 1H), 4.69 (s, 2H), 2.42 (s, 3H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.48 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.36 (qt, *J* = 7.0, 7.0 Hz, 2H), 1.17 (s, 9H), 0.87 (t, *J* = 7.0 Hz, 3H) ;^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 151.5, 144.9, 135.8, 129.1, 129.1, 107.2, 74.0, 48.9, 35.1, 29.3, 29.1, 27.8, 26.9, 22.9, 21.9, 21.6, 18.6, 13.4 (^{13}C NMR spectra indicate rotamers are present); LRMS (ESI) *m/z* 398.18 [$(M+Na)^+$]; HRMS (ESI) calcd for $C_{21}H_{29}O_3NNaS$ [$(M+Na)^+$] 398.1760, found 398.1757.

Enyne 3g (Scheme S7)

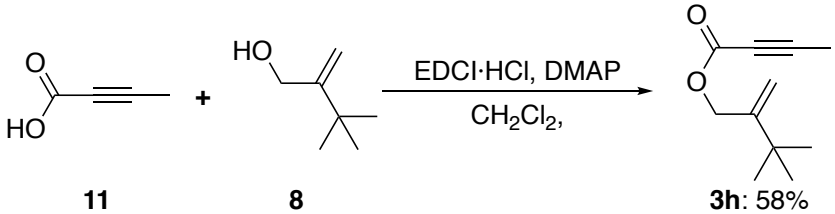
[6] Rooke, D. A; Ferreira, E. M. *Angew. Chem. Int. Ed.* **2012***, 51,* 3225.



Scheme S7. Synthesis of Enyne **3g**.

To a solution of K_2CO_3 (128 mg, 0.92 mmol) in THF (920 μL) were added **19**[7] (103.2 mg, 0.92 mmol) and PivCl (110 μL, 0.92 mmol) at 0 °C, and the mixture (A) was stirred at room temperature for 2 h. To a solution of **17** (205 mg, 0.77 mmol) in THF (5.0 mL) was added ^{n}BuLi (1.6 M in THF, 570 μL, 0.85 mmol) at -78 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the reaction mixture (A) at -78 °C, and the resulting mixture was stirred at room temperature for 13 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 9/1) to give **3g** (209 mg, 75% yield) as a colorless oil. Spectral data of **3g**: IR (neat) 3019, 2970, 2224, 1665, 1362, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.01 (s, 1H), 4.76 (s, 1H), 4.70 (s, 2H), 2.63 (sept, J = 6.8 Hz, 1H), 2.43 (s, 3H), 1.18 (s, 9H), 1.15 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.3, 129.7, 129.5, 129.4, 128.8, 107.5, 49.3, 35.4, 29.5, 29.4, 22.0, 21.8, 21.0 (^{13}C NMR spectra indicate rotamers are present); LRMS (ESI) *m/z* 384.16 [$(M+Na)^+$]; HRMS (ESI) calcd for $C_{20}H_{27}O_3NNaS$ [$(M+Na)^+$] 384.1604, found 384.1599.

Enyne 3h (Scheme S8)



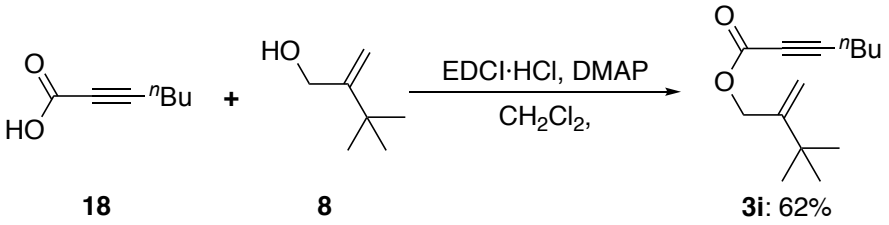
Scheme S8. Synthesis of Enyne **3h**.

To a solution of tetrolic acid **11** (101 mg, 1.20 mmol) in CH_2Cl_2 (2.0 mL) were added alcohol **8**[2] (130 μL, 0.95 mmol), EDCI·HCl (232 mg, 1.21 mmol), and DMAP (14.5 mg, 0.120 mmol) at 0 °C,

[7] Ngi, S. I.; Petrignet, J.; Duwald, R.; Hilali, E. M. E.; Abarbri, M.; Duchêne, A.; Thibonnet J. *Adv. Synth. Catal.* **2013**, *355*, 2936.

and the mixture was stirred at room temperature for 1 h, then the mixture was concentrated. The residue was roughly purified by column chromatography on silica gel (*n*-hexane/AcOEt = 9:1) to give **3h** (100 mg, 58% yield) as a colorless oil. Spectral data of **3h**: IR (neat) 3048, 3097, 2967, 1776, 1714, 1256, 1074 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (s, 1H), 5.07 (s, 1H), 4.71 (s, 2H), 1.99 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 150.5, 110.5, 85.3, 74.0, 72.1, 65.2, 34.7, 28.9, 21.3, 3.5; LRMS (EI) *m/z* 165 [(M-Me)$^+$], 123, 67; HRMS (EI) calcd for $C_{10}H_{13}O_2$ [(M-Me)$^+$] 165.0916, found 165.0911.

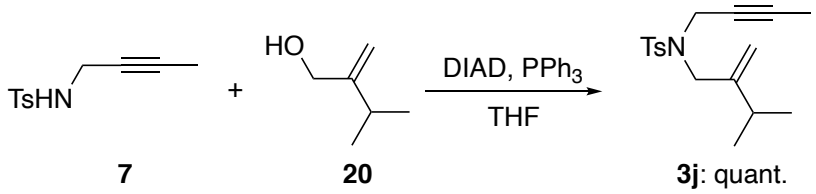
Enyne 3i (Scheme S9)



Scheme S8. Synthesis of Enyne **3i**.

To a solution of **18**[6] (260 μL, 2.00 mmol) in CH_2Cl_2 (4.0 mL) were added alcohol **8**[2] (330 μL, 2.40 mmol), EDCI·HCl (461 mg, 2.40 mmol) and DMAP (26.1 mg, 0.214 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h, then the mixture was concentrated. The residue was roughly purified by column chromatography on silica gel (*n*-hexane/AcOEt = 9:1) to give **3i** (276 mg, 62% yield) as a colorless oil. Spectral data of **3i**: IR (neat) 2962, 2873, 2237, 1713, 1245 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (s, 2H), 4.66 (s, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.57 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.43 (tt, *J* = 7.2 Hz, 2H), 1.10 (s, 9H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 150.6, 110.5, 89.6, 72.9, 65.3, 61.6, 34.8, 29.4, 29.1, 21.8, 18.2, 13.9, 13.3; LRMS (ESI) *m/z* 245.15 [(M+Na)$^+$]; HRMS (ESI) calcd for $C_{14}H_{22}O_2Na$ [(M+Na)$^+$] 245.1512, found 245.1511.

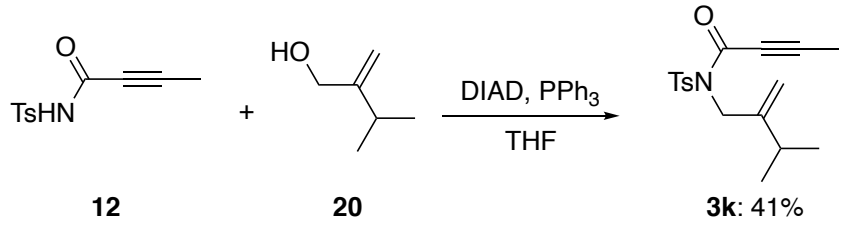
Enyne 3j (Scheme S10)



Scheme S9. Synthesis of Enyne **3i**.

To a solution of **7**[1] (268 mg, 1.20 mmol) in THF (2.5 mL) were added **20**[8] (80 μL, 1.00 mmol), PPh_3 (314 mg, 1.20 mmol), and DIAD (240 μL, 1.20 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h, and the mixture was concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 9:1) to give **3j** (306 mg, quant.). Spectral data of **3j**: IR (neat) 2962, 2923, 1732, 1598, 1348, 1163 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.98 (s, 2H), 3.96 (s, 2H), 3.76 (s, 2H), 2.43 (s, 3H), 2.36 (quin, *J* = 7.2 Hz, 1H), 1.49 (s, 3H), 1.07 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 143.0, 136.0, 129.0, 127.8, 111.9, 81.5, 74.2, 71.2, 50.3, 35.8, 30.3, 21.4, 3.0; LRMS (EI) *m/z* 290 [(M-Me)$^+$], 262, 236, 184, 155; HRMS (EI) calcd for $C_{16}H_{20}NO_2S$ [(M-Me)$^+$] 290.1215, found 290.1204.

Enyne 3k (Scheme S11)

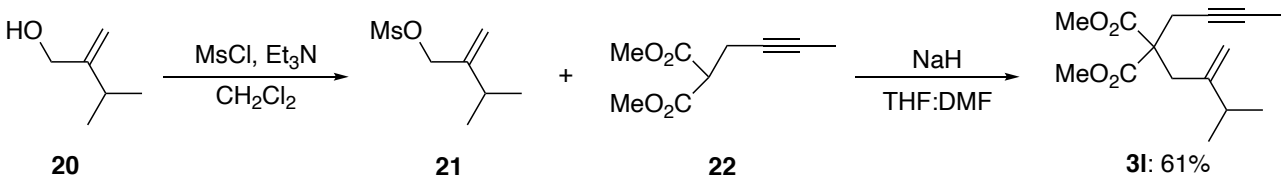


Scheme S11. Synthesis of Enyne **3k**.

To a solution of **12** (521.9 mg, 2.21 mmol) in THF (6.6 mL) were added **20**[8] (240 μL, 2.00 mmol), PPh_3 (577 mg, 2.18 mmol), and DIAD (430 μL, 2.20 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h, and the mixture was concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 4:1) to give **3k** (262 mg, 41% yield). Spectral data of **3k**: IR (neat) 2964, 2236, 1671, 1359, 1171 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 1H), 4.84 (s, 1H), 4.61 (s, 2H), 2.43 (s, 3H), 2.29 (sep, *J* = 6.8 Hz, 1H), 1.95 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 149.5, 144.6, 135.2, 128.8, 128.5, 127.9, 107.8, 91.4, 72.9, 50.0, 31.5, 21.2, 21.1, 3.7 (^{13}C NMR spectra indicate rotamers are present);; LRMS (EI) *m/z* 304 [(M-Me)$^+$], 276, 276, 164; HRMS (EI) calcd for $C_{16}H_{18}NO_3S$ [(M-Me)$^+$] 304.1007, found 304.1009.

Enyne 3l (Scheme S12)

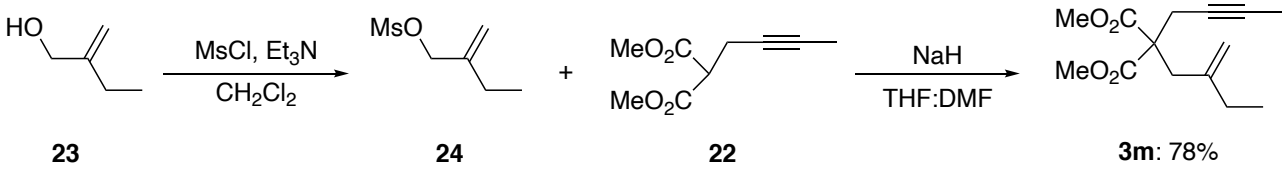
[8] Zhao, Y.; Jiang, X.; Yeung, Y. -Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 8597.



Scheme S12. Synthesis of Enyne **3l**.

To a solution of **20**[8] (135.1 g, 1.35 mmol) in CH_2Cl_2 (4.5mL) was added MsCl (130 μL, 1.62 mmol) and Et_3N (230 μL, 1.62 mmol) at 0 °C, and the mixture was stirred at same temperature for 30 min. To the mixture was added water at 0 °C, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and the crude mesylate **21** was obtained after removal of the solvent. To a suspension of NaH (60% dispersion in mineral oil, 64.8 mg, 1.62 mmol) in THF (2.3 mL) was added **22**[9] (208.5 mg, 1.35 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the crude mesylate **21** in DMF (2.3 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 40 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 19/1) to give **3l** (220 mg, 61% yield) as a colorless oil. Spectral data of **3l**: IR (neat) 2959, 1739, 1437, 1206 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 1H), 4.78 (s, 1H), 3.72 (s, 6H), 2.85 (s, 2H), 2.76 (s, 2H), 2.01 (quin, J = 6.4 Hz, 1H), 1.76 (s, 3H), 1.01 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 150.5, 111.1, 79.1, 73.5, 57.0, 52.5, 36.6, 33.4, 22.7, 21.8, 3.4 ; LRMS (EI) *m/z* 251.1 [$(M\text{-}Me)^+$]; HRMS (EI) calcd for $C_{14}H_{19}O_4$ [$(M\text{-}Me)^+$] 251.1283, found 251.1287.

Enyne 3m (Scheme S13)



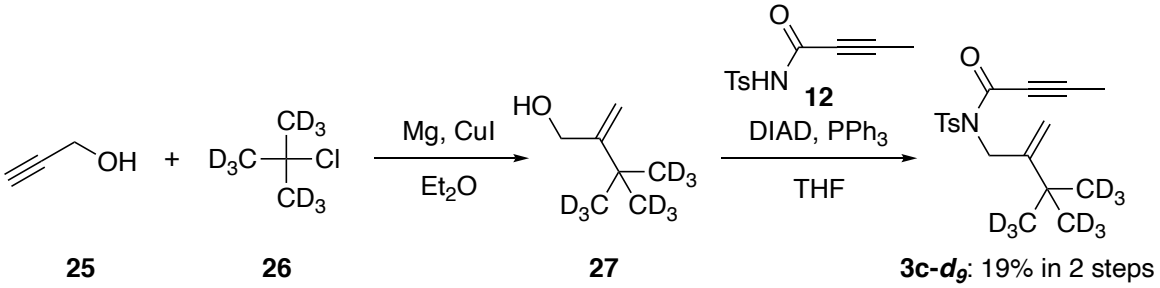
Scheme S13. Synthesis of Enyne **3m**.

To a solution of **23**[8] (160 μL, 1.60 mmol) in CH_2Cl_2 (5.3 mL) was added MsCl (150 μL, 1.90 mmol) and Et_3N (270 μL, 1.90 mmol) at 0 °C, and the mixture was stirred at same temperature for 30 min. To the mixture was added water at 0 °C, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and the crude mesylate **24** was obtained after removal of the solvent. To a suspension of NaH (60% dispersion in mineral oil, 84.6

[9] Saito, N.; Tanaka, Y., Sato, Y. *Organometallics* **2009**, *28*, 669.

mg, 1.91 mmol) in THF (2.3 mL) was added **22**[9] (238 mg, 1.29 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture were added the crude mesylate **24** in DMF (2.3 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 11 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 19/1) to give **3m** (253 mg, 78% yield) as a colorless oil. Spectral data of **3m**: IR (neat) 2955, 1739, 1438, 1293, 1205 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.83 (s,1H), 3.72 (s, 6H), 2.83 (s, 2H), 2.76 (s, 2H), 1.91 (q, *J* = 7.2 Hz, 2H), 1.56 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.8, 145.7, 113.4, 79.0, 73.6, 56.9, 52.5, 37.6, 29.3, 22.9, 12.3, 3.3 ; LRMS (EI) *m/z* 237 [(M-Me)$^+$], 221, 193, 133; HRMS (EI) calcd for $C_{13}H_{17}O_4$ [(M-Me)$^+$] 237.1126, found 237.1121.

Enyne 3c-*d*$_9$ (Scheme S14)



Scheme S14. Synthesis of Enyne **3c-*d*$_9$**.

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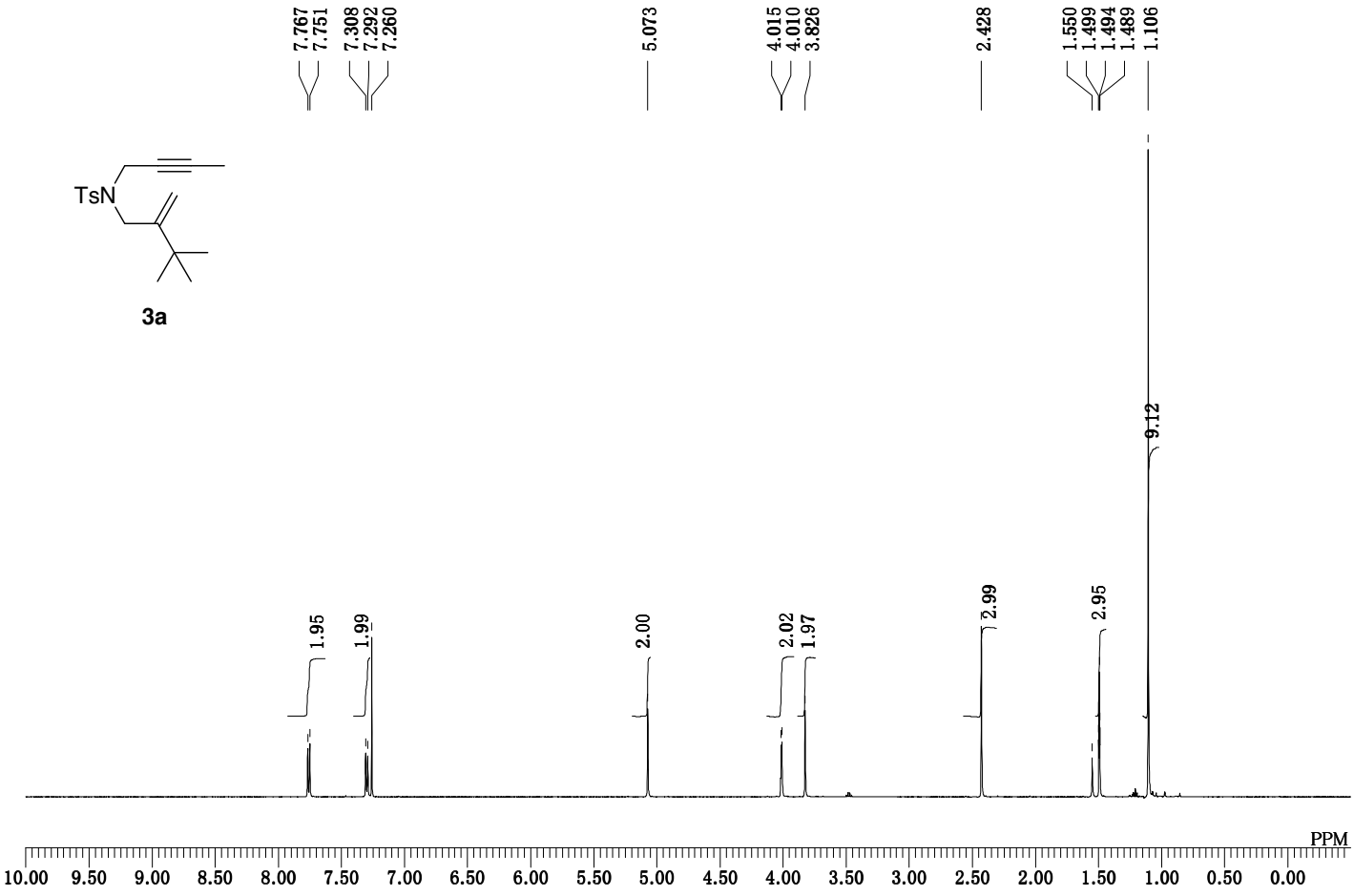
To a solution of **26** (3.3 mL, 30.0 mmol) in THF (30 mL) were added Mg (729 mg, 30.0 mmol) at room temperature, and the reaction mixture was stirred at 45 °C for 5 h. Then to a solution of **25** (250 μl, 4.30 mmol) and CuI (831 mg, 4.36 mol) in Et_2O (66.0 mL) was added freshly prepared ^{t}BuMgCl-*d*$_9$ at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was roughly purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to give crude alcohol **27**. To a solution of crude alcohol **27** in THF (3.4 mL) were added **12** (253 mg, 1.07 mmol), and PPh_3 (280.1 mg, 1.07 mmol), and DIAD (210 μL, 2.4 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 9/1) to give **3c-*d*$_9$** (279 mg, 19% yield in 2 steps) as a colorless oil. Spectral data of **3c-*d*$_9$**: IR (neat) 2967, 2239, 1672, 1360, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H),

4.99 (s, 1H), 4.77 (s, 1H), 4.68 (s, 2H), 2.42 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 151.9, 145.3, 136.0, 129.4, 129.3, 107.3, 91.5, 77.2, 73.3, 48.9, 34.4, 28.0 (sept, J = 15.3 Hz), 21.6, 4.1; LRMS (EI) *m/z* 324 [$(M\text{-}CD_3)^+$], 276, 258; HRMS (EI) calcd for $C_{17}H_{14}D_6NO_3S$ [$(M\text{-}CD_3)^+$] 325.1451, found 324.1533.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4.010
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1.489
1.106
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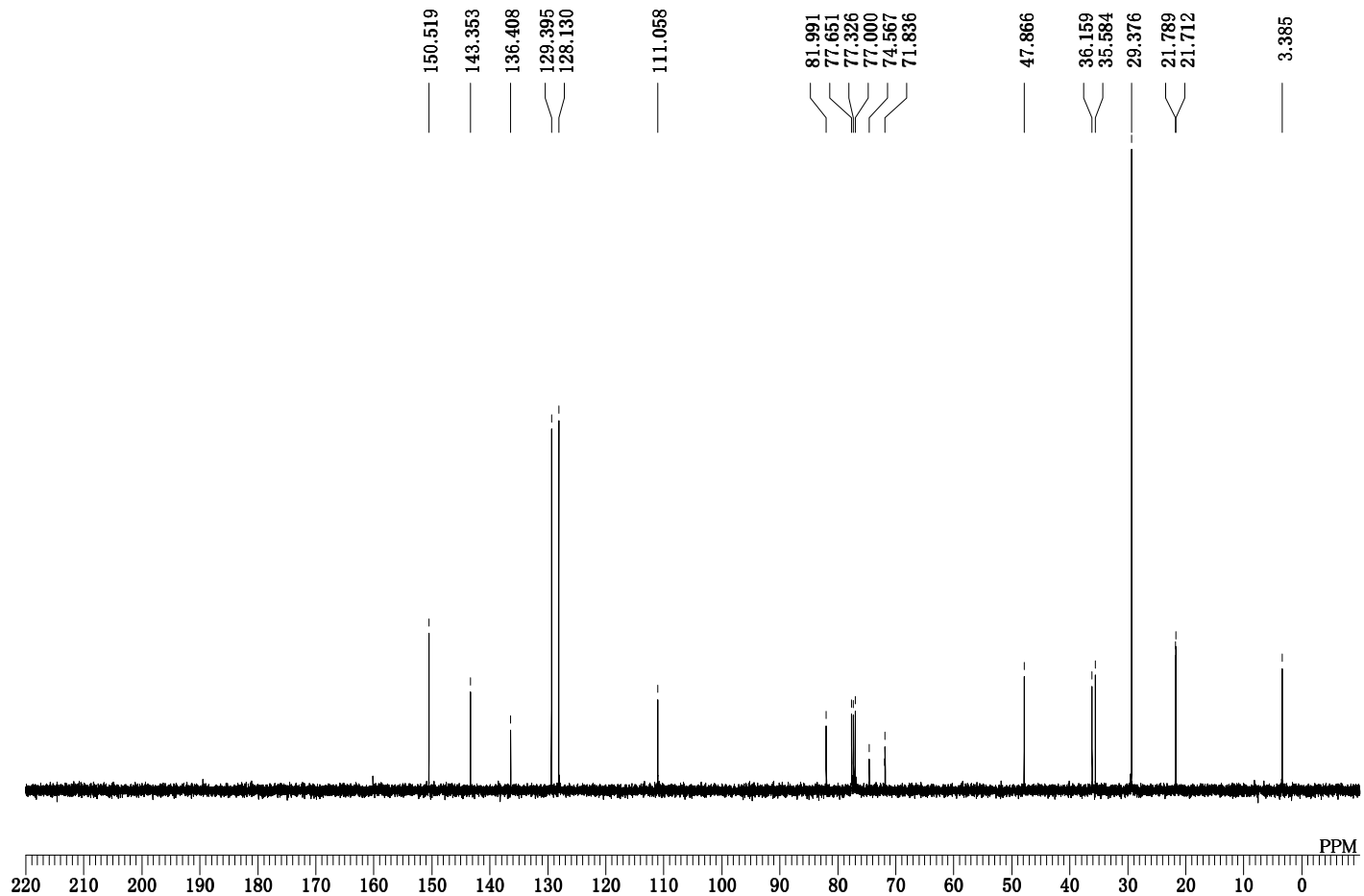
3a
9.12
1.95
1.99
2.00
2.02
1.97
2.99
2.95
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00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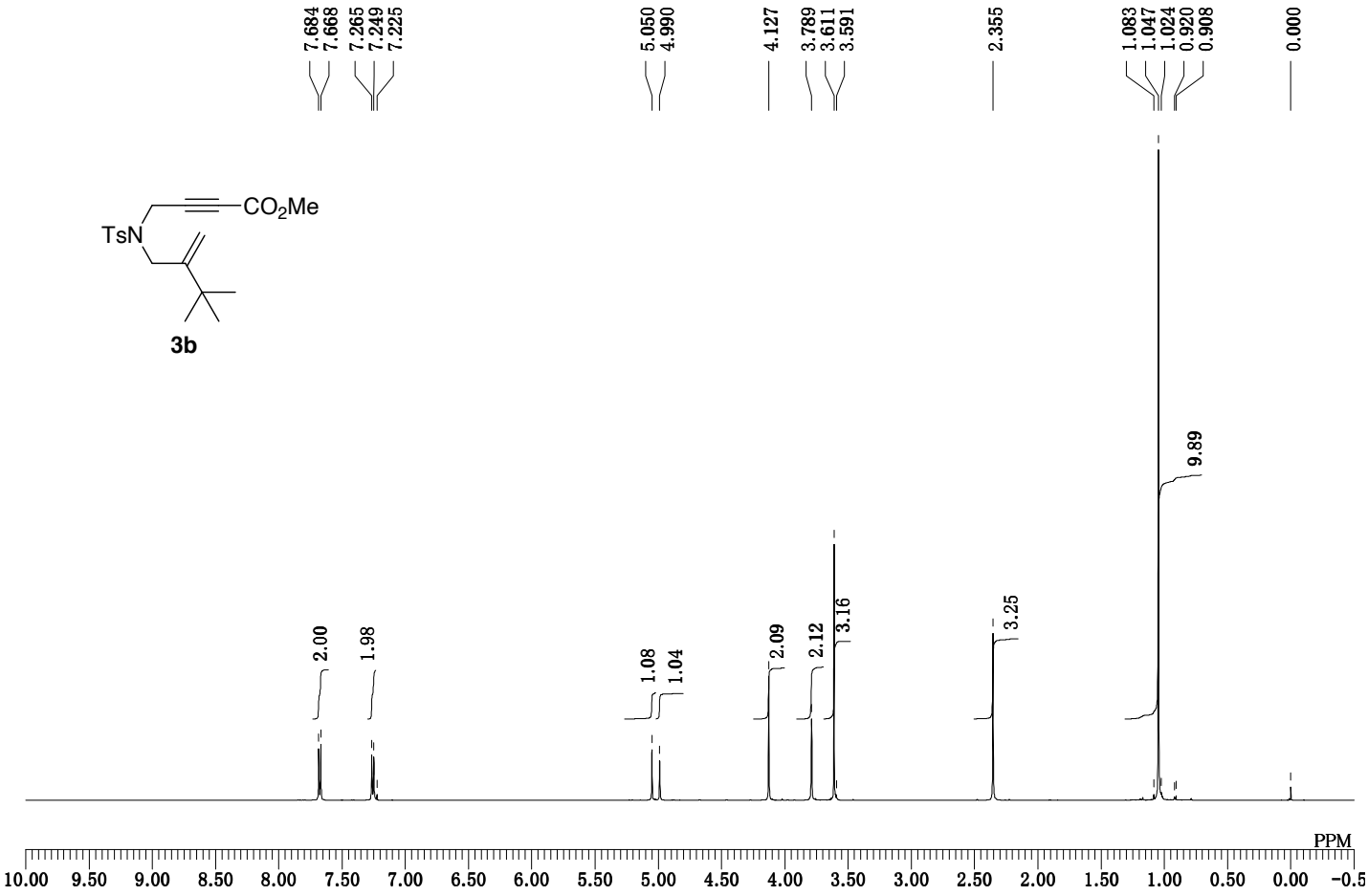
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1.047
1.024
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0.908
0.000
CO2Me
TsN
3b
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2.00
1.98
1.08
1.04
2.09
2.12
3.16
3.25
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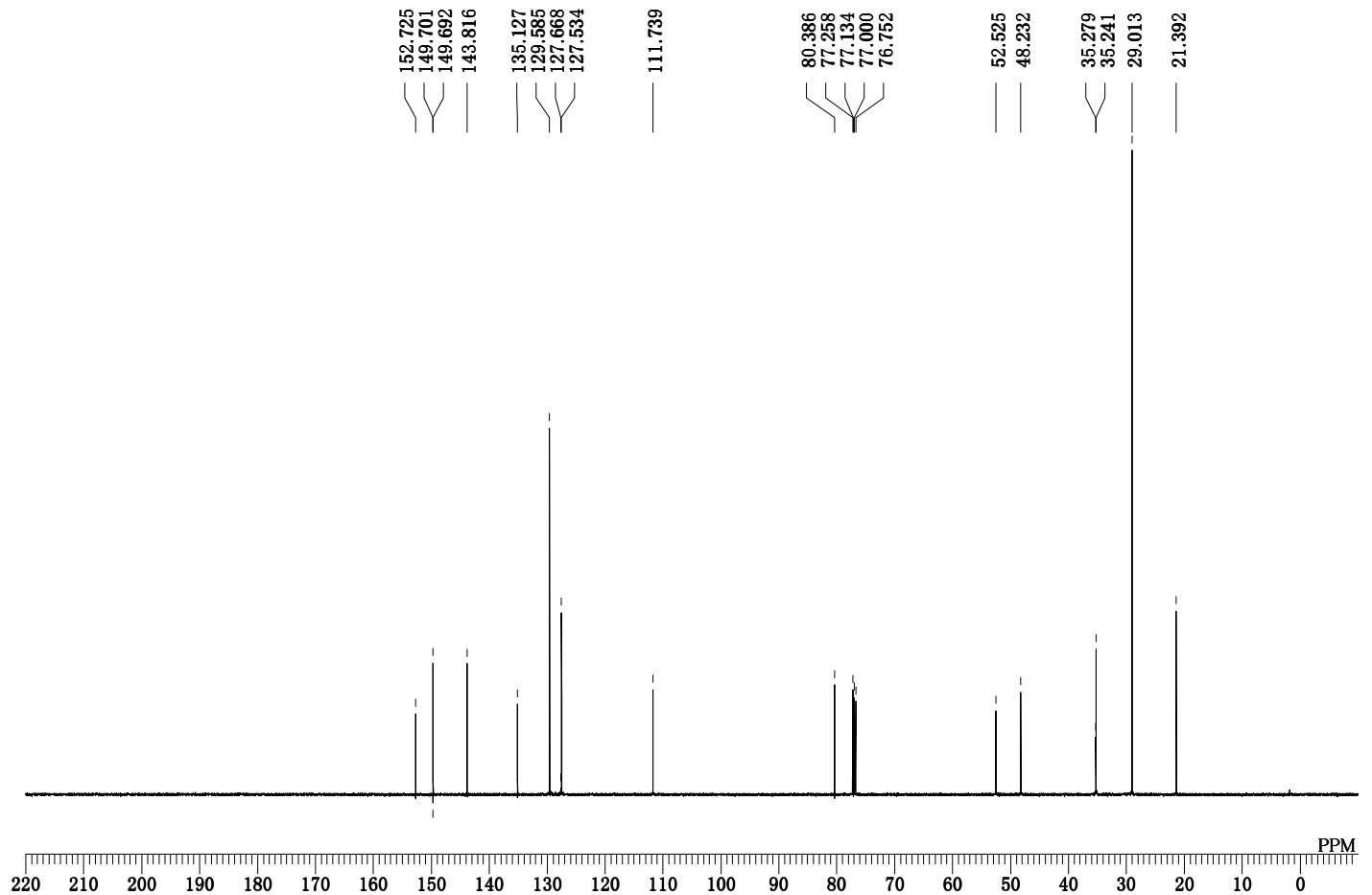
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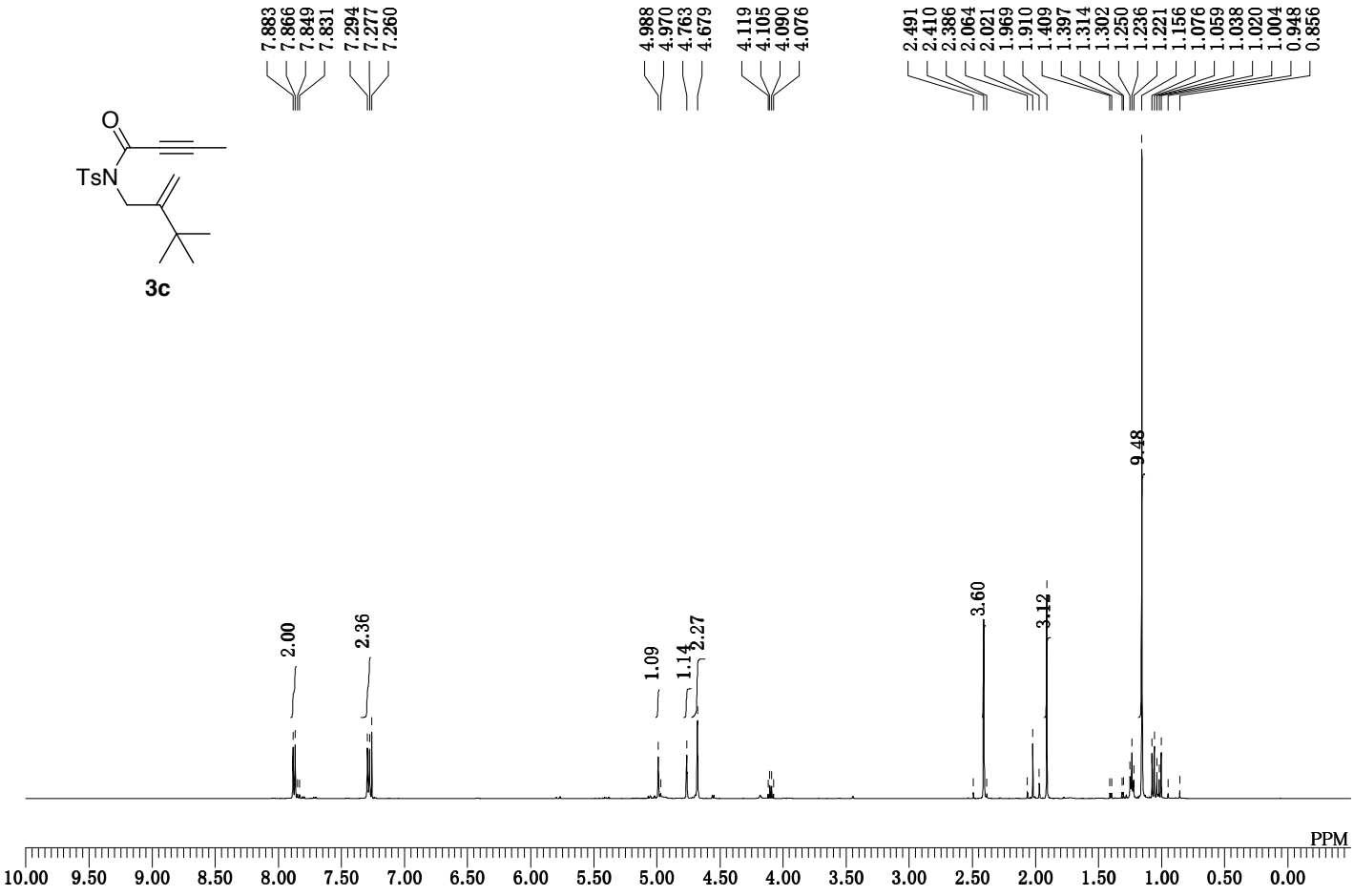
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2.410
2.386
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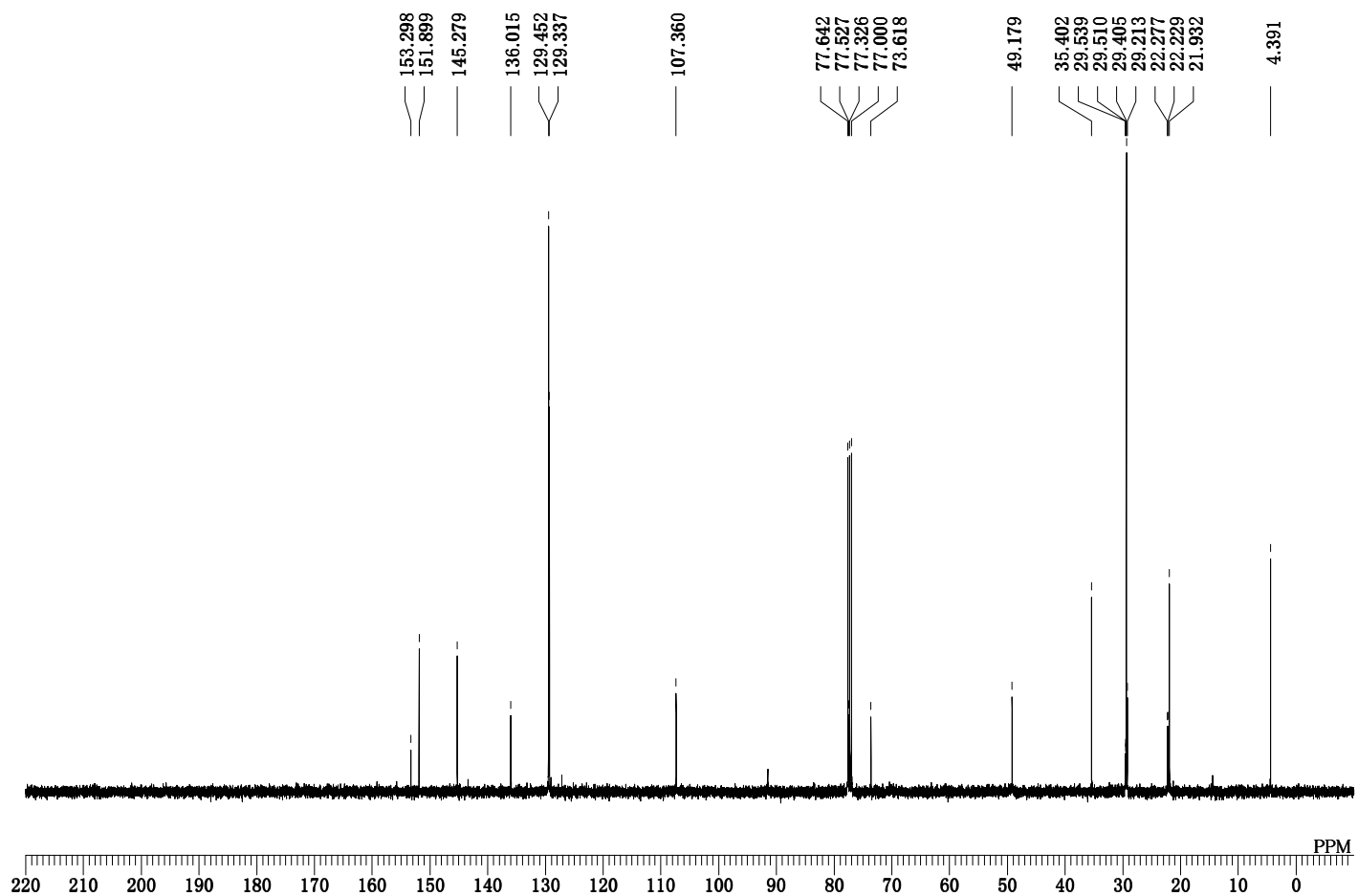
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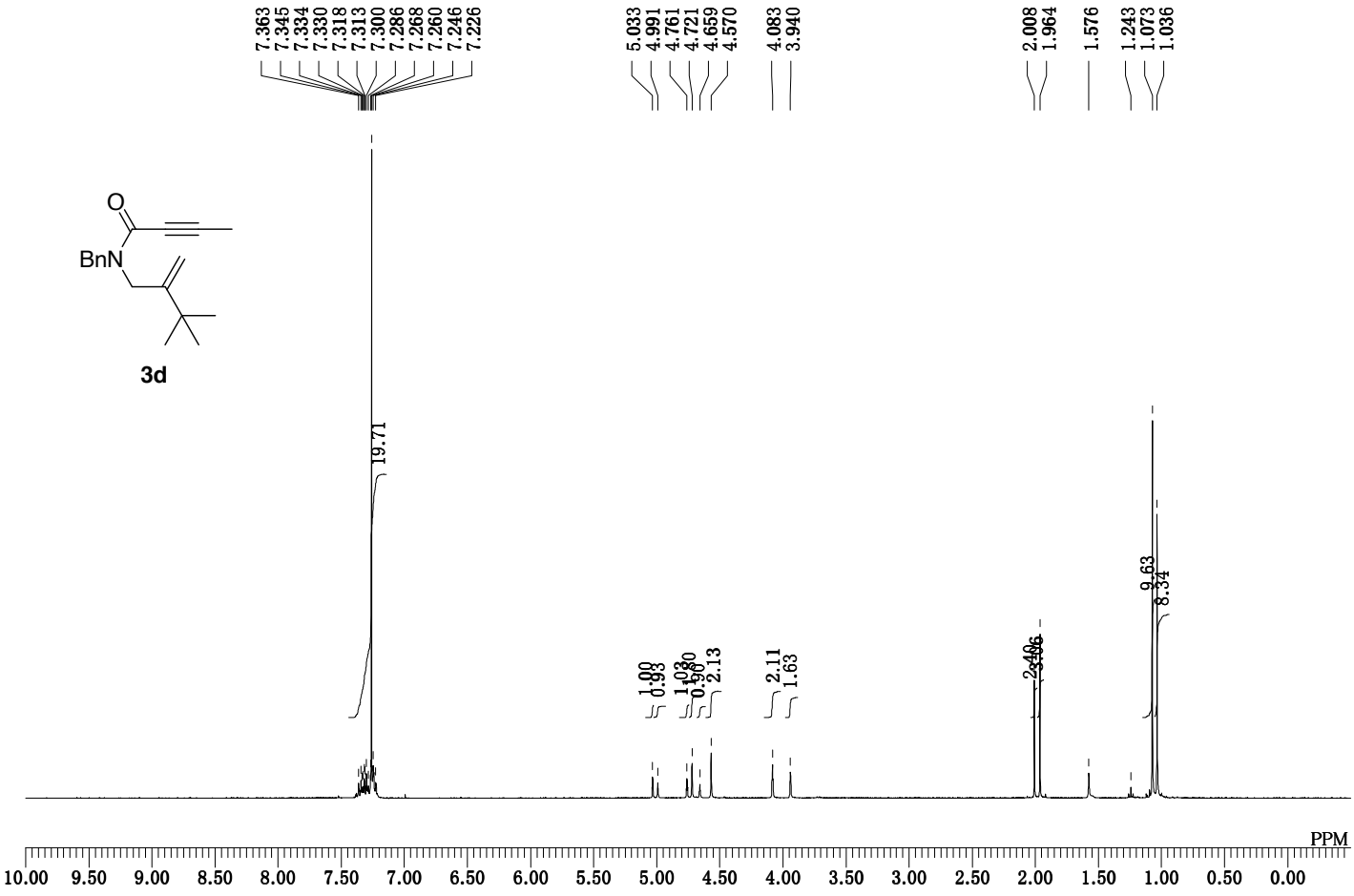
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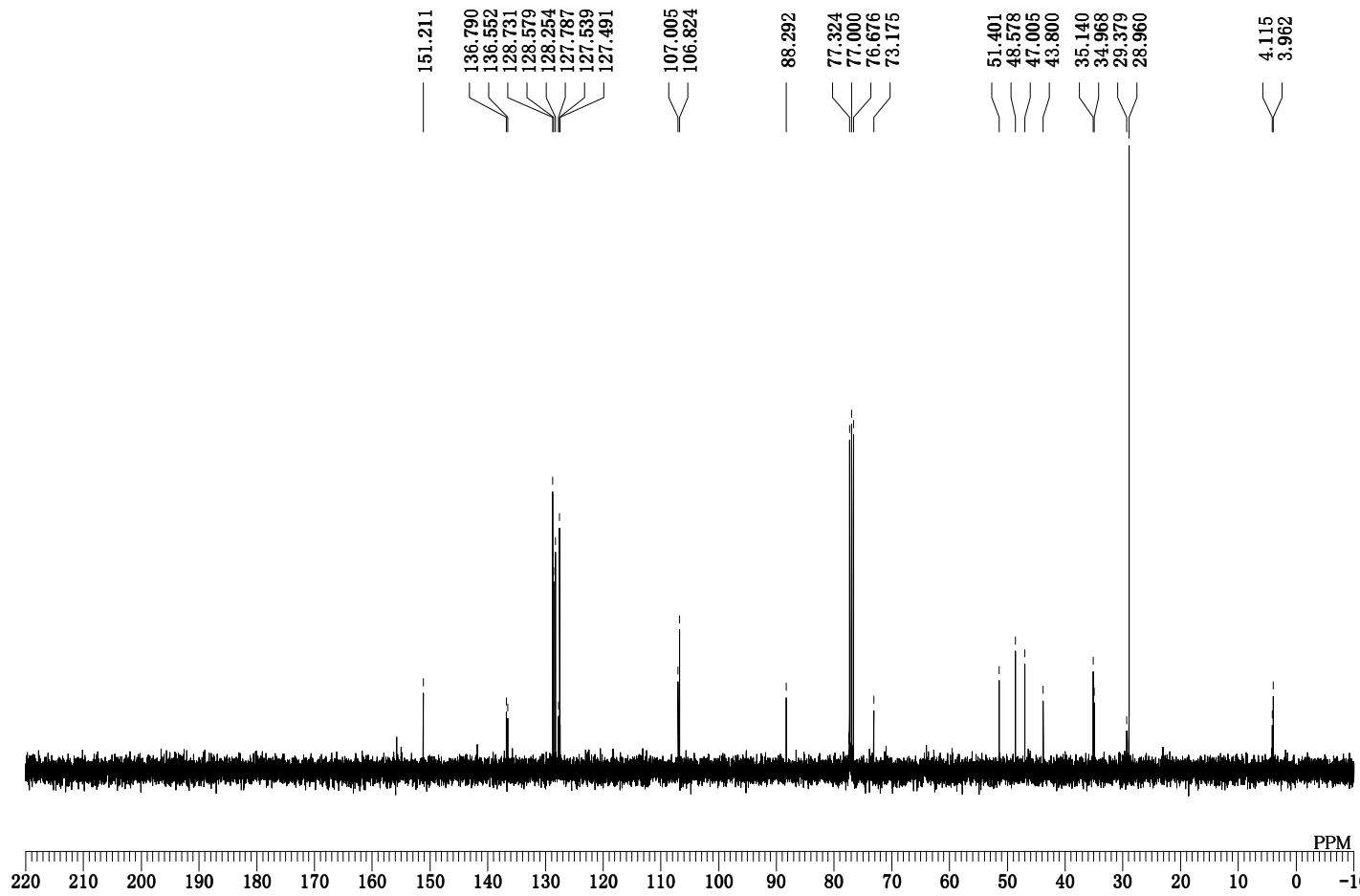
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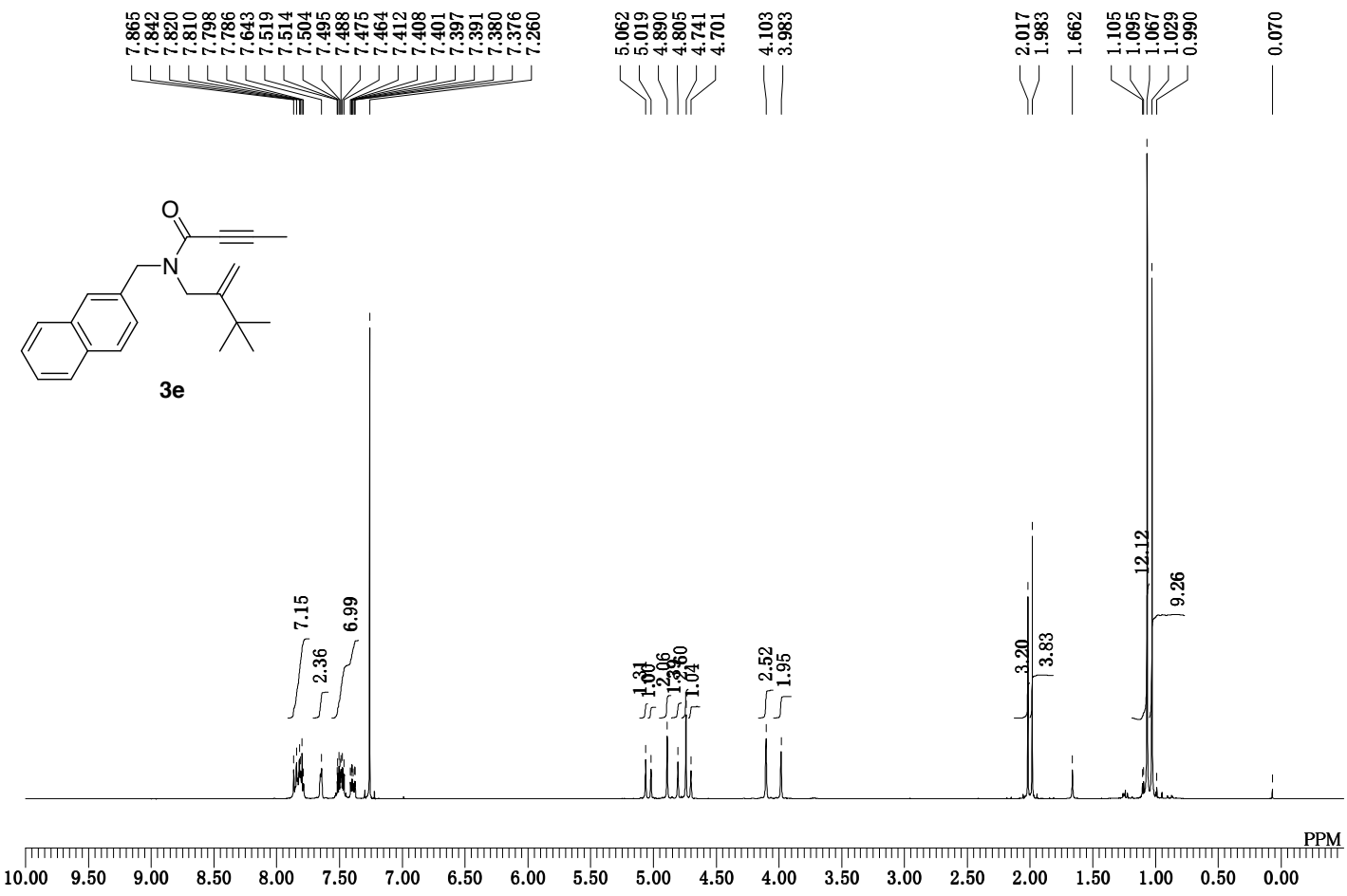
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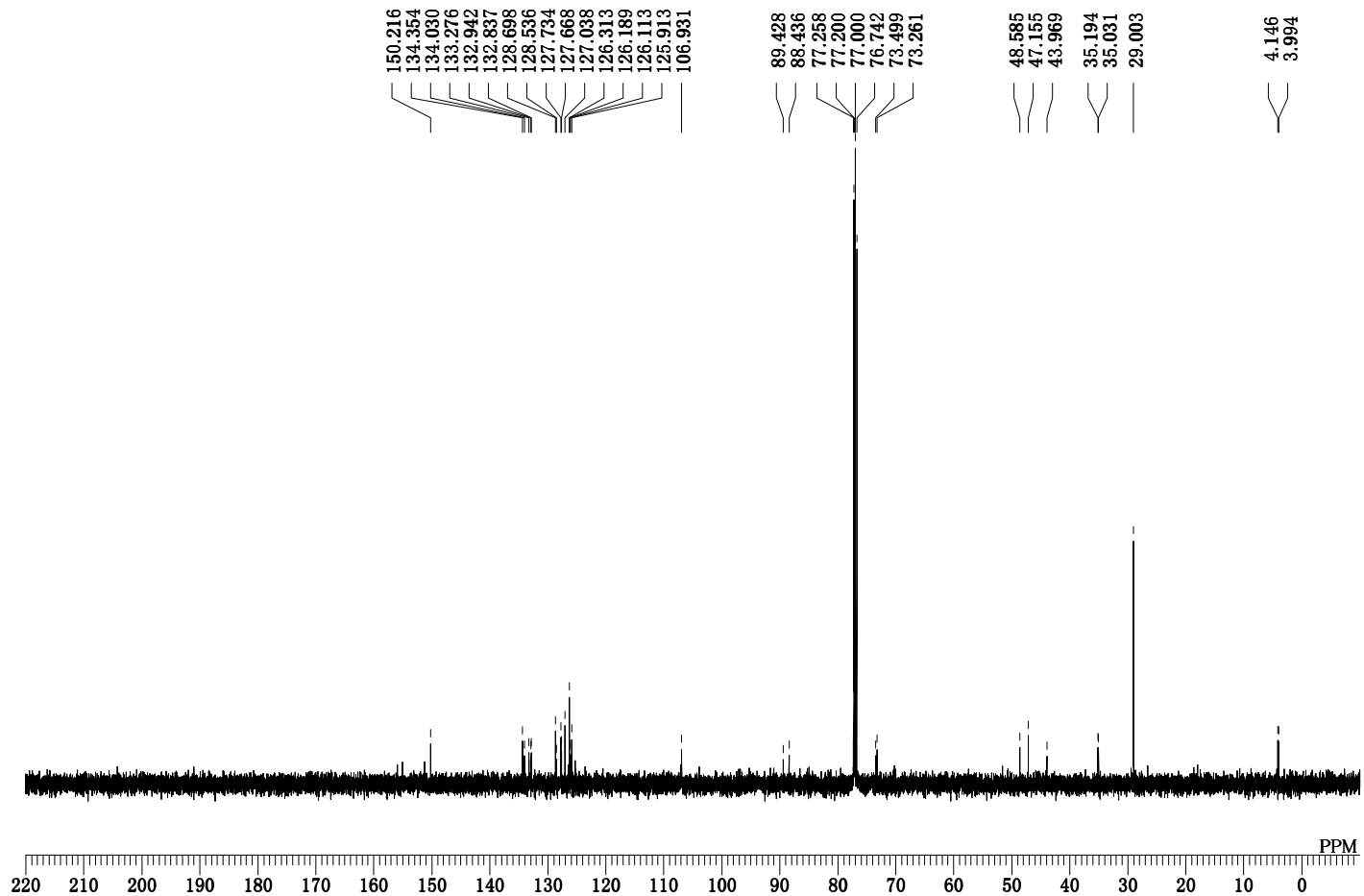
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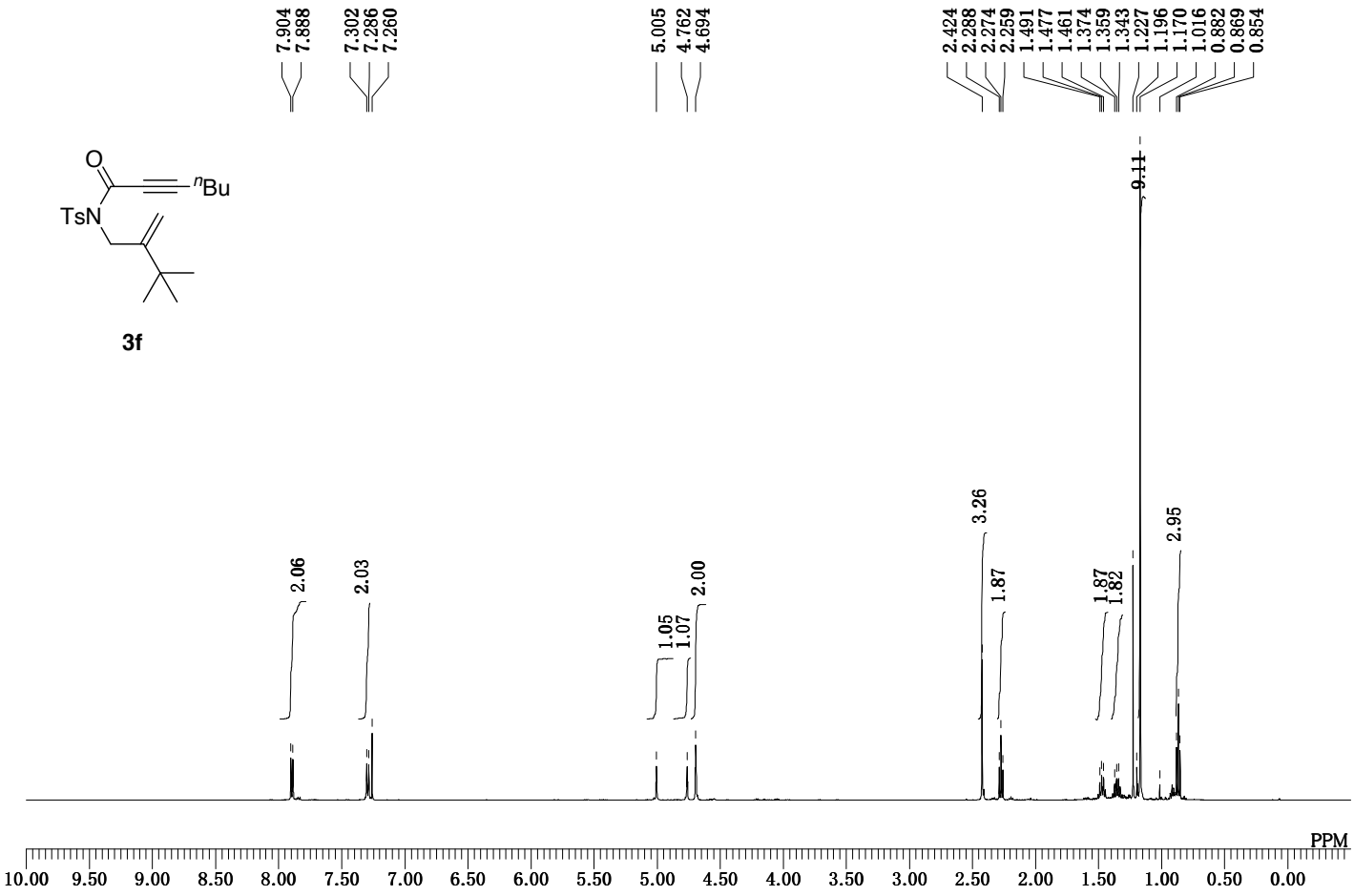
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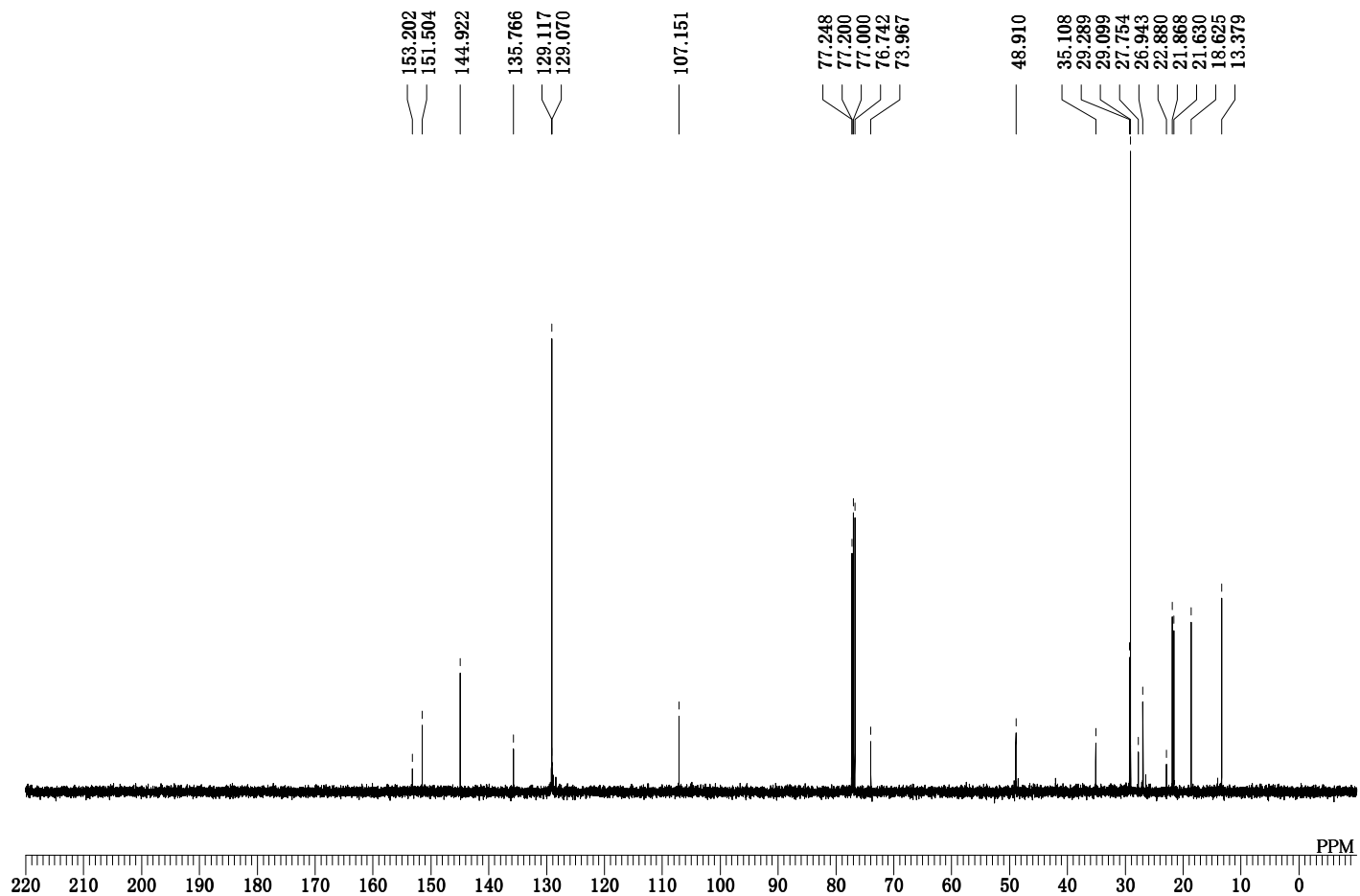
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22.880
21.868
21.630
18.625
13.379
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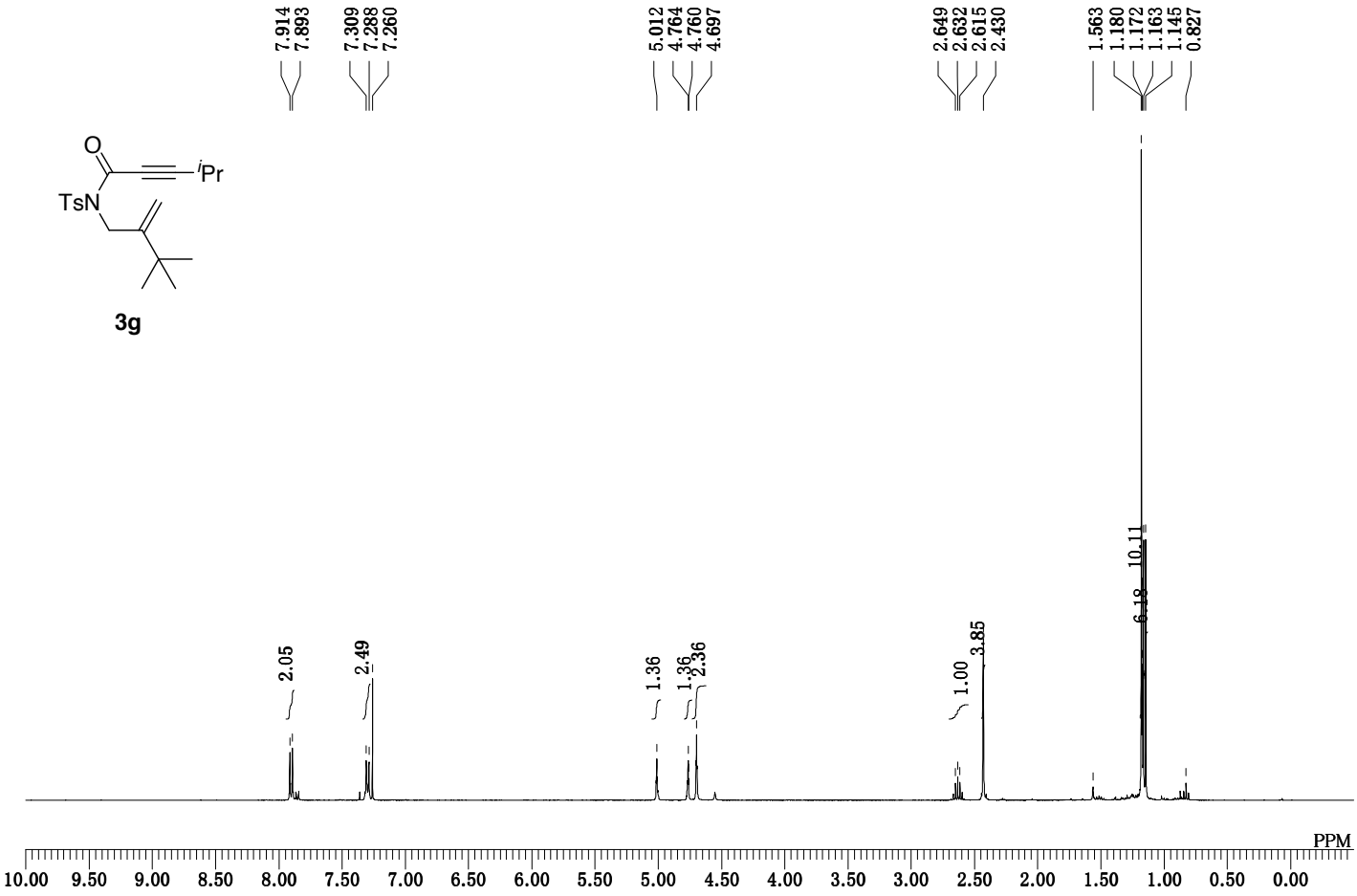
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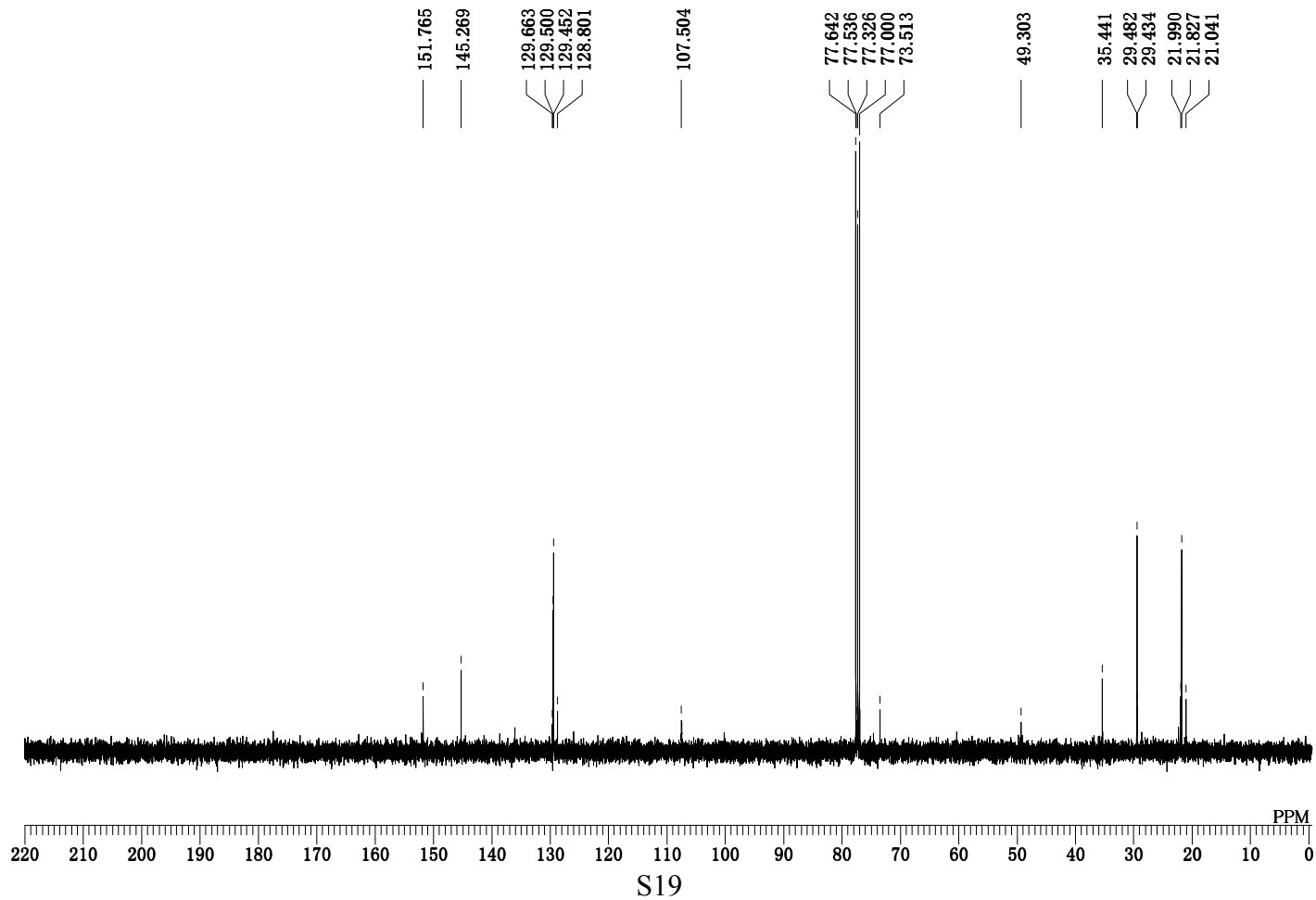
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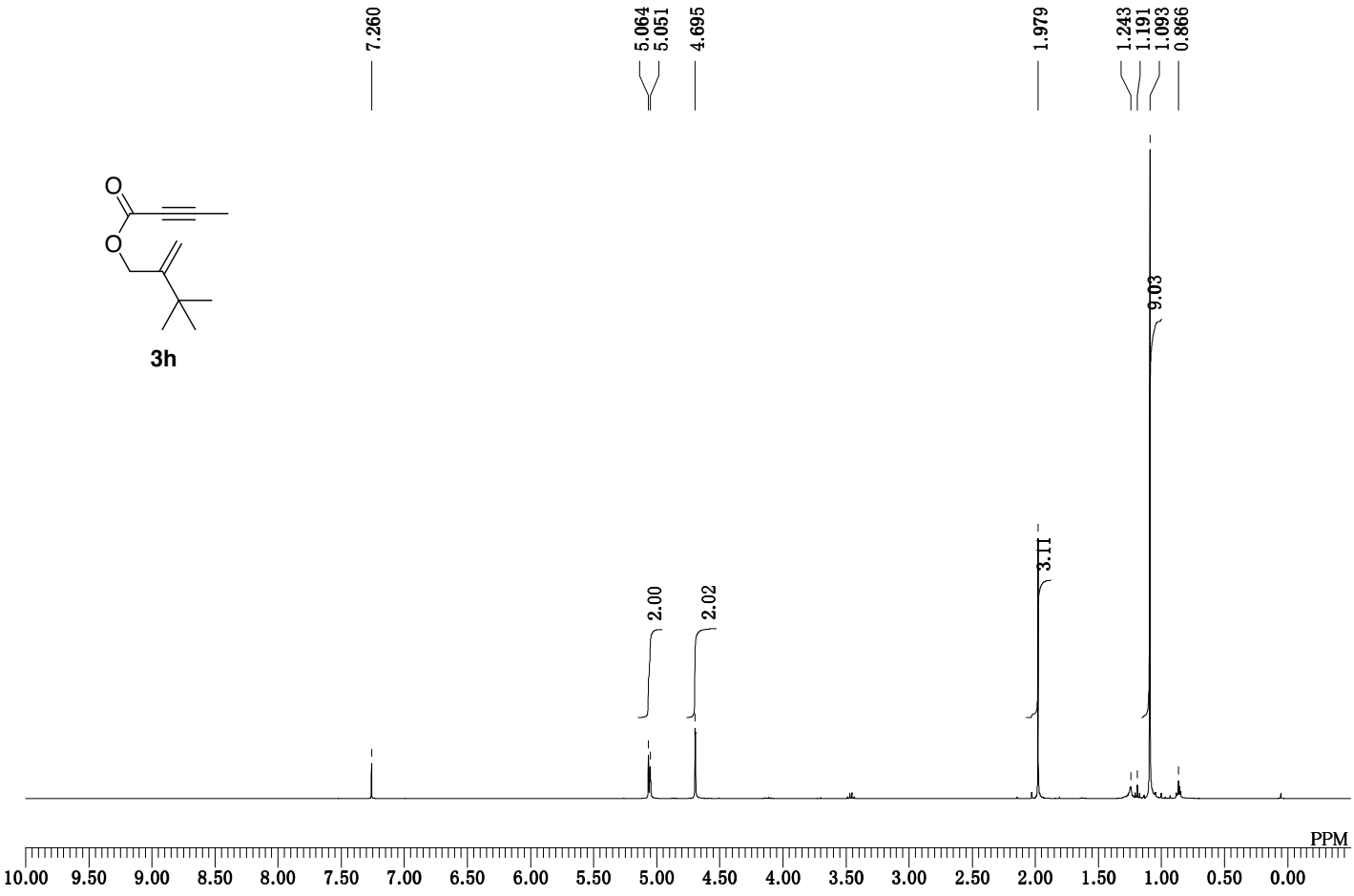
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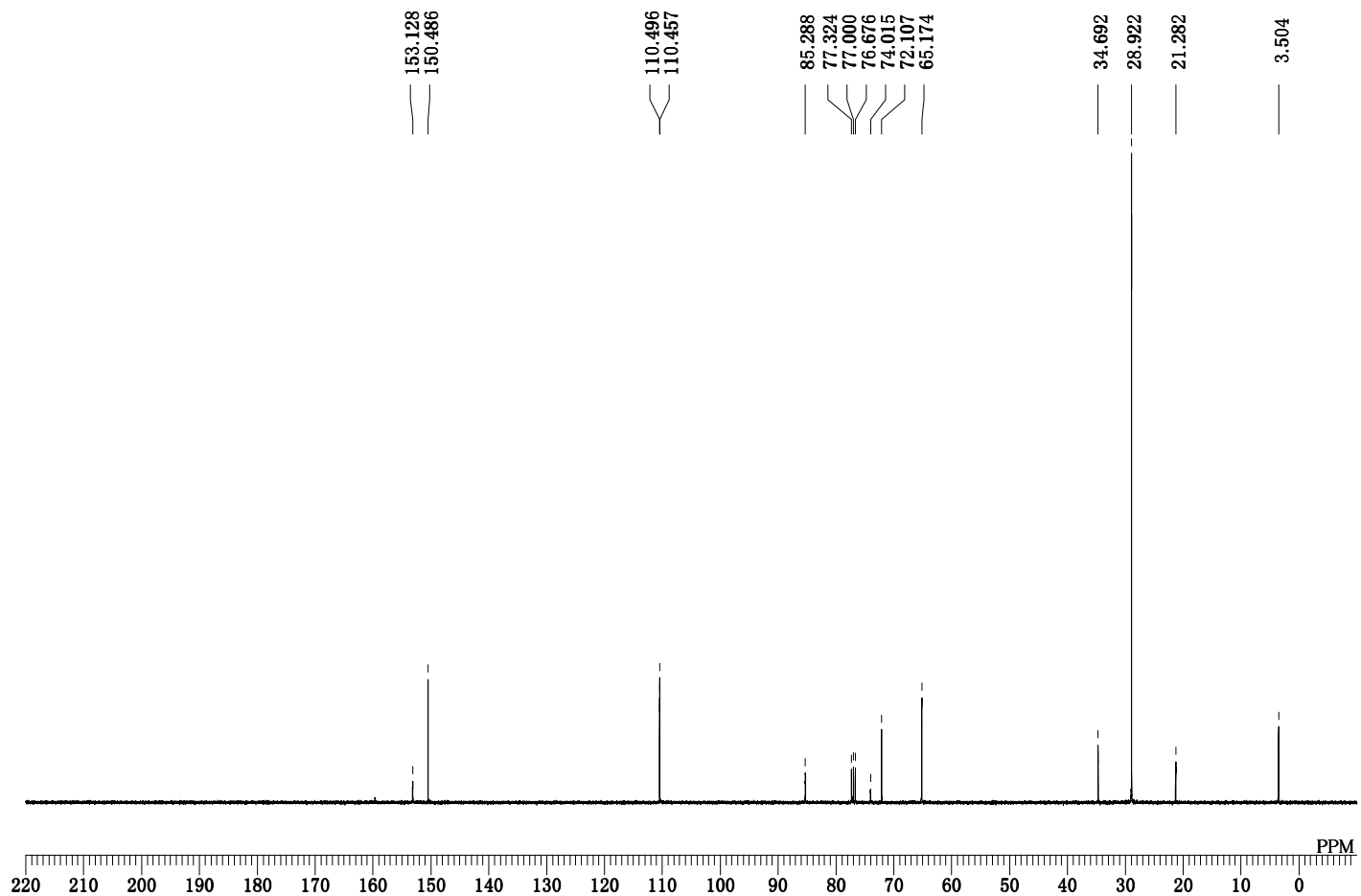
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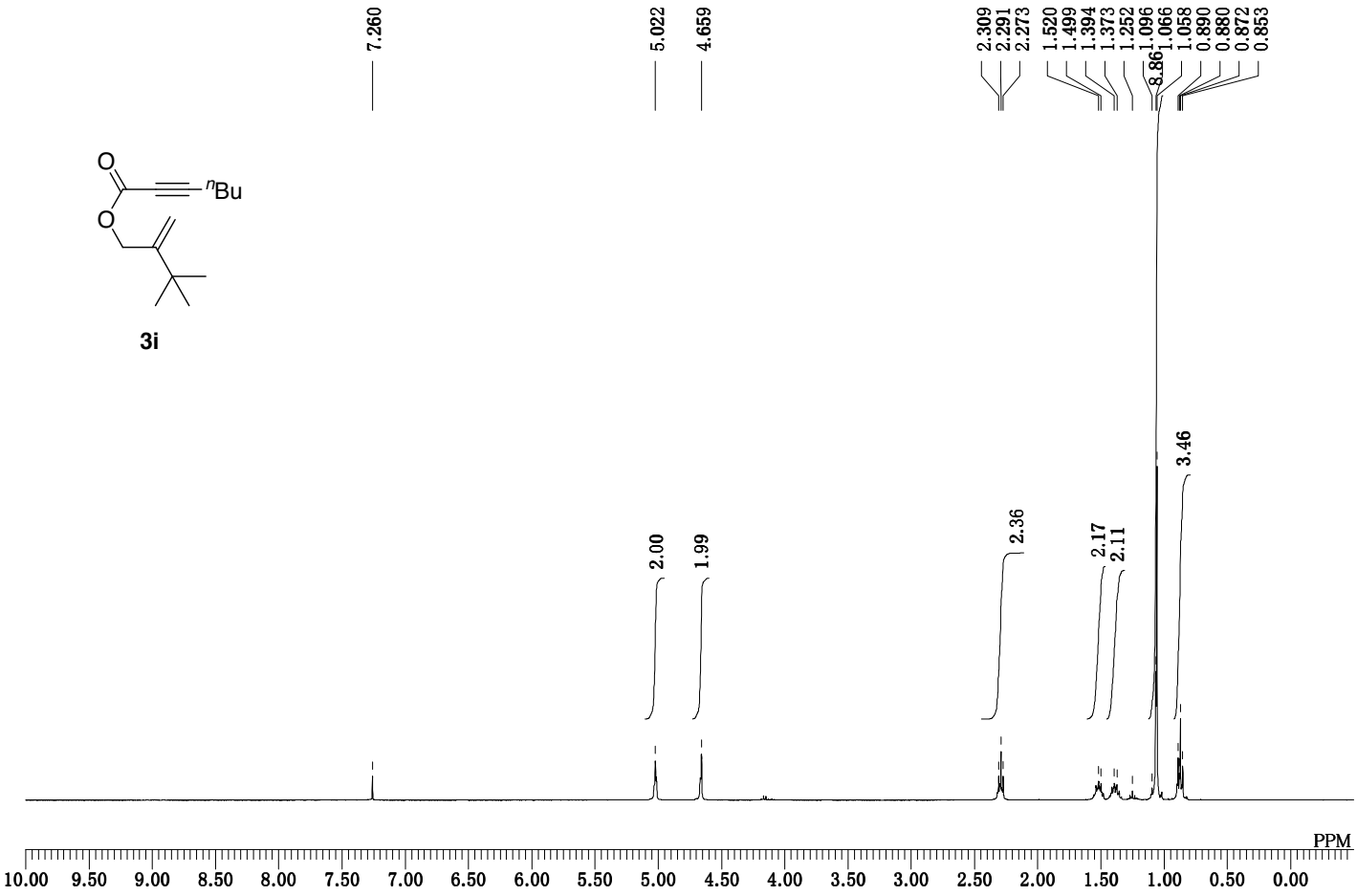
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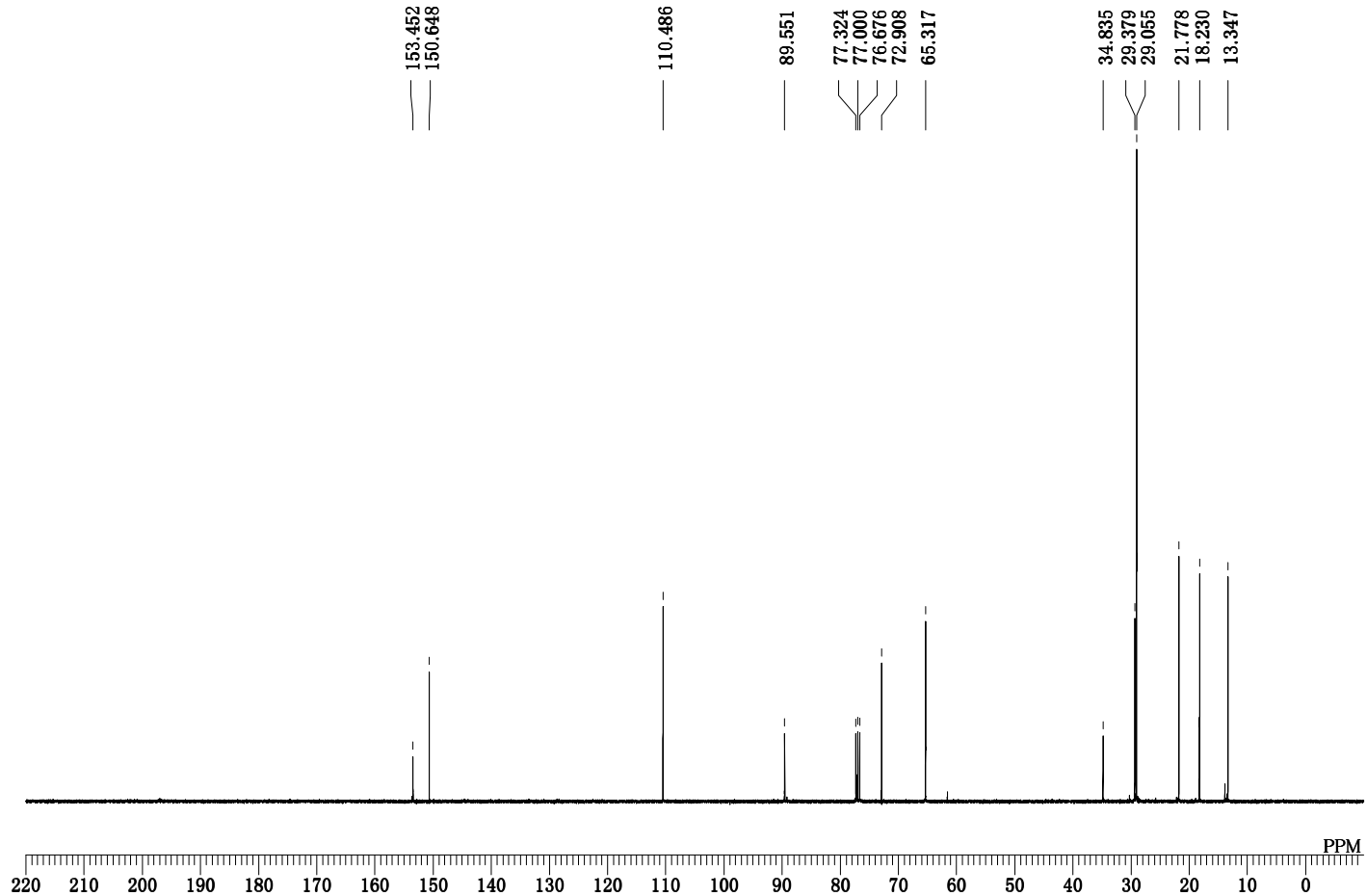
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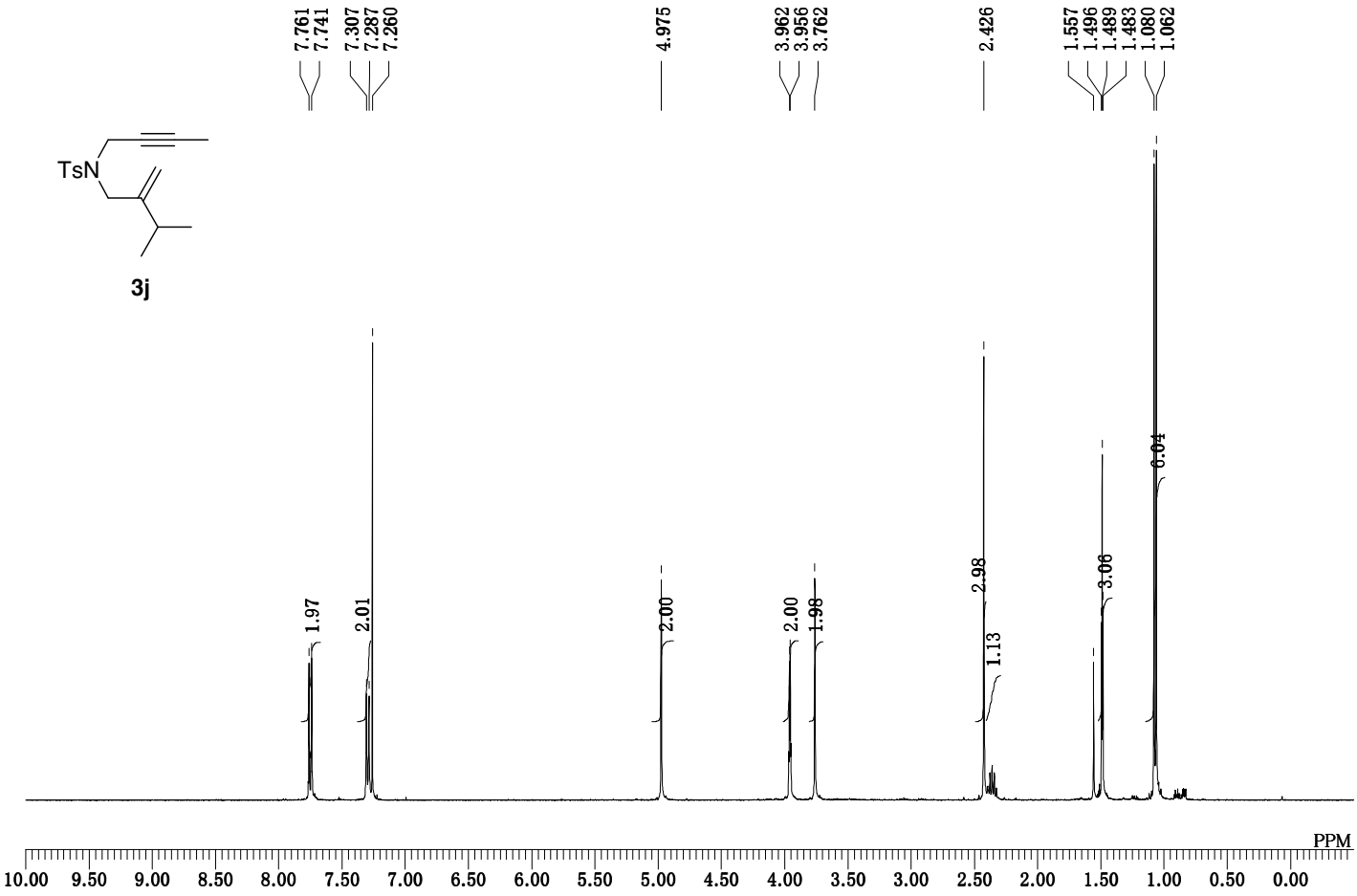
3i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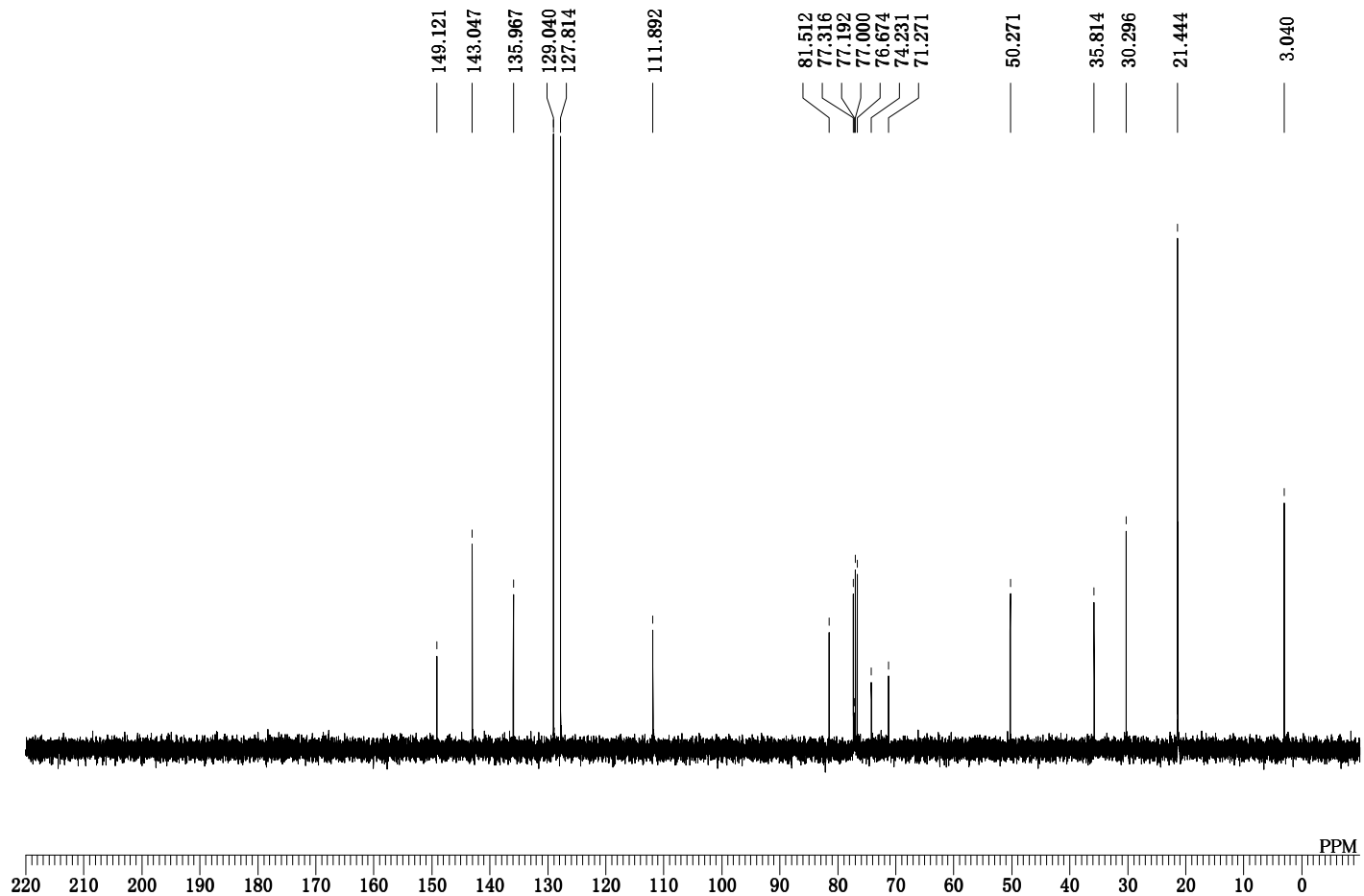
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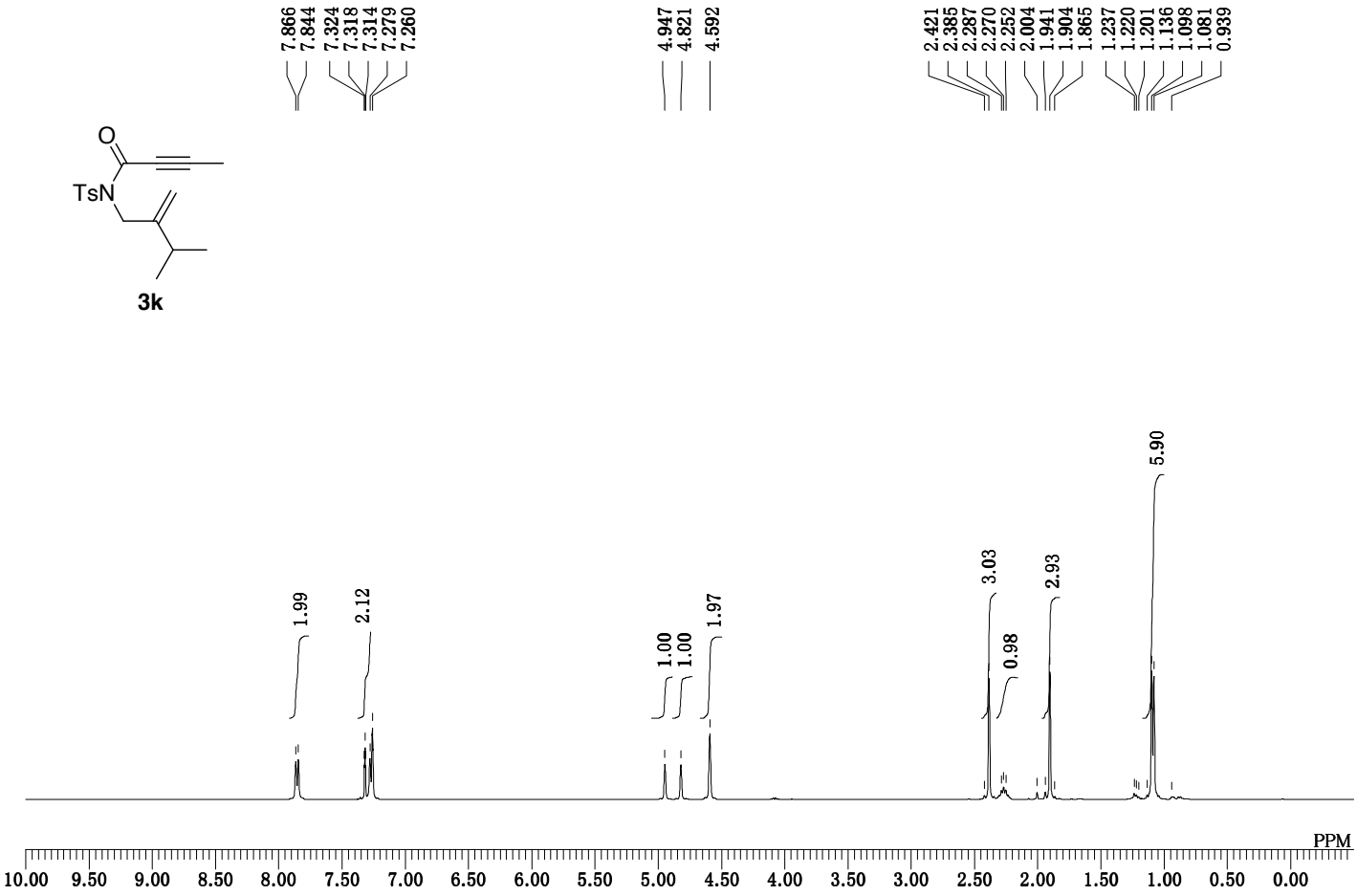
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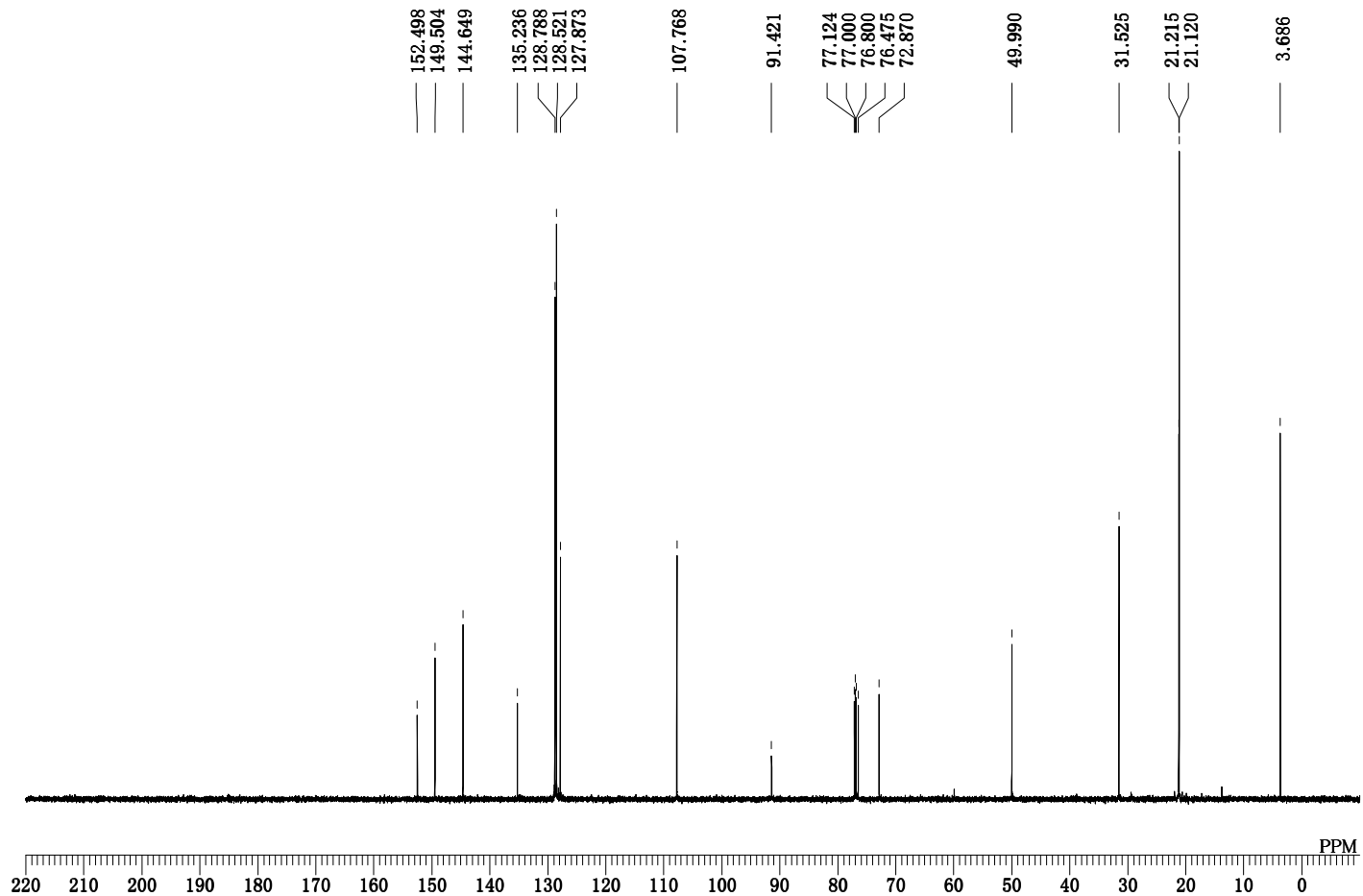
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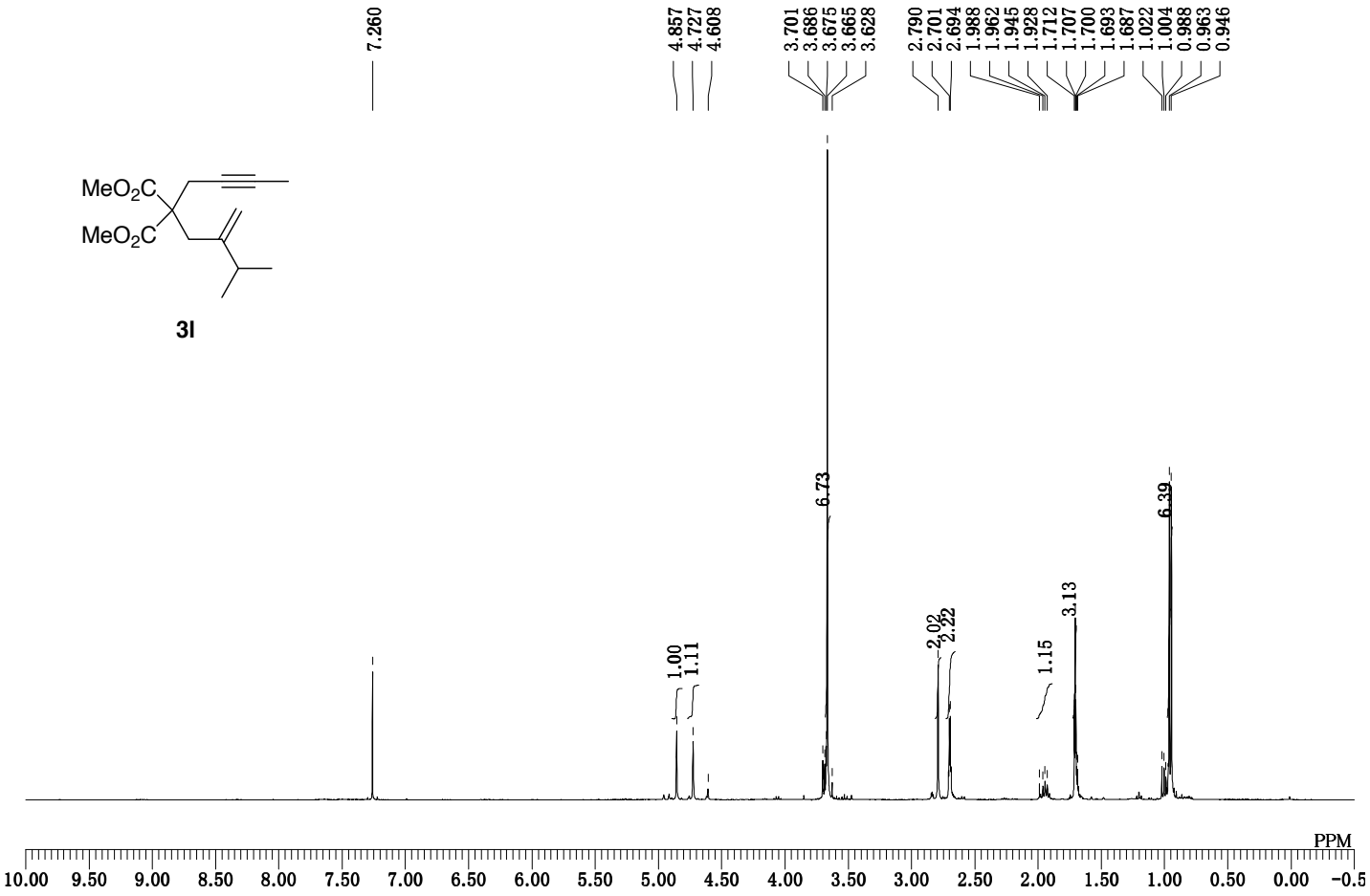
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MeO2C
3l
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6.39
3.13
2.02
2.22
1.15
1.00
1.11
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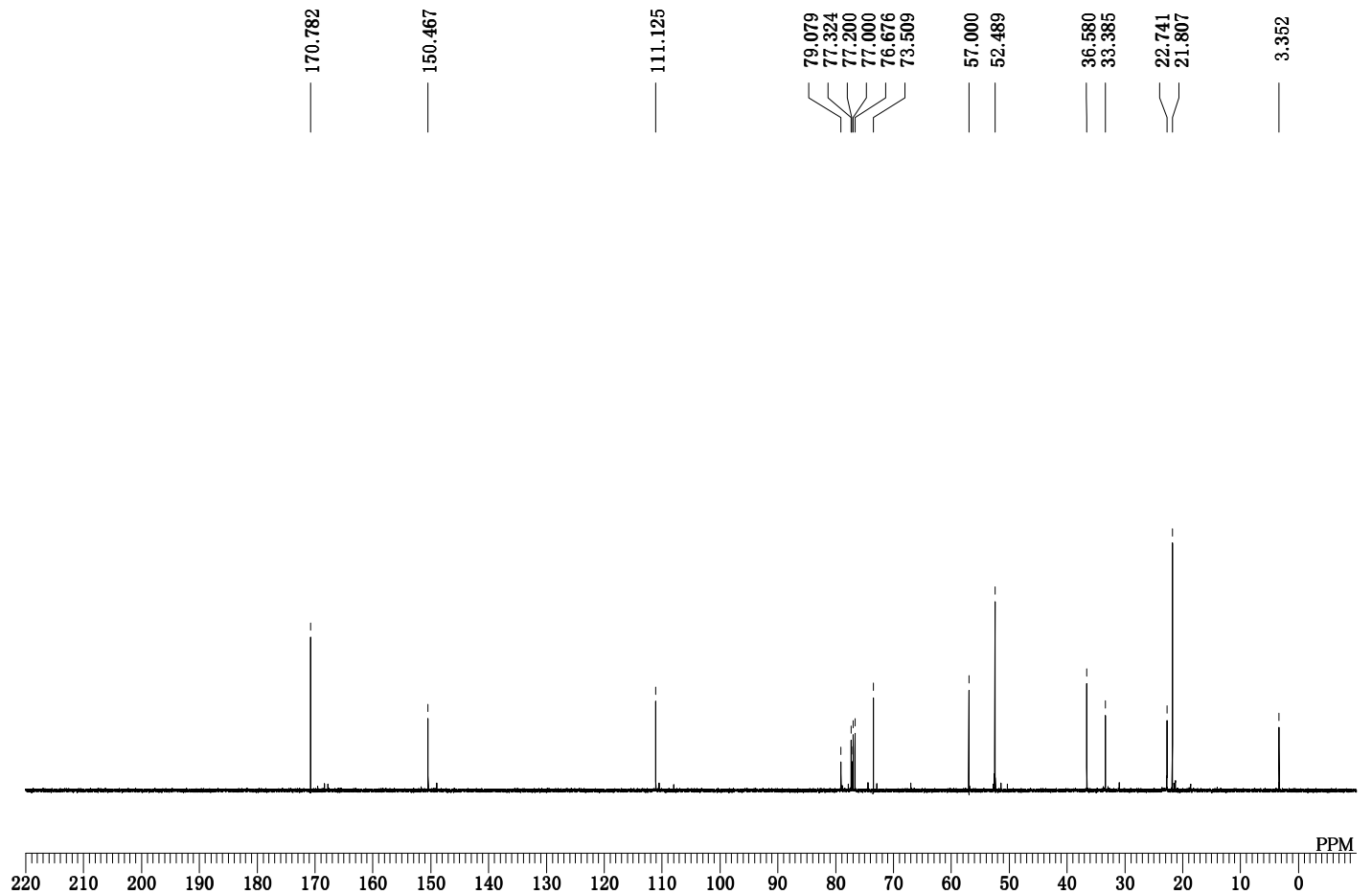
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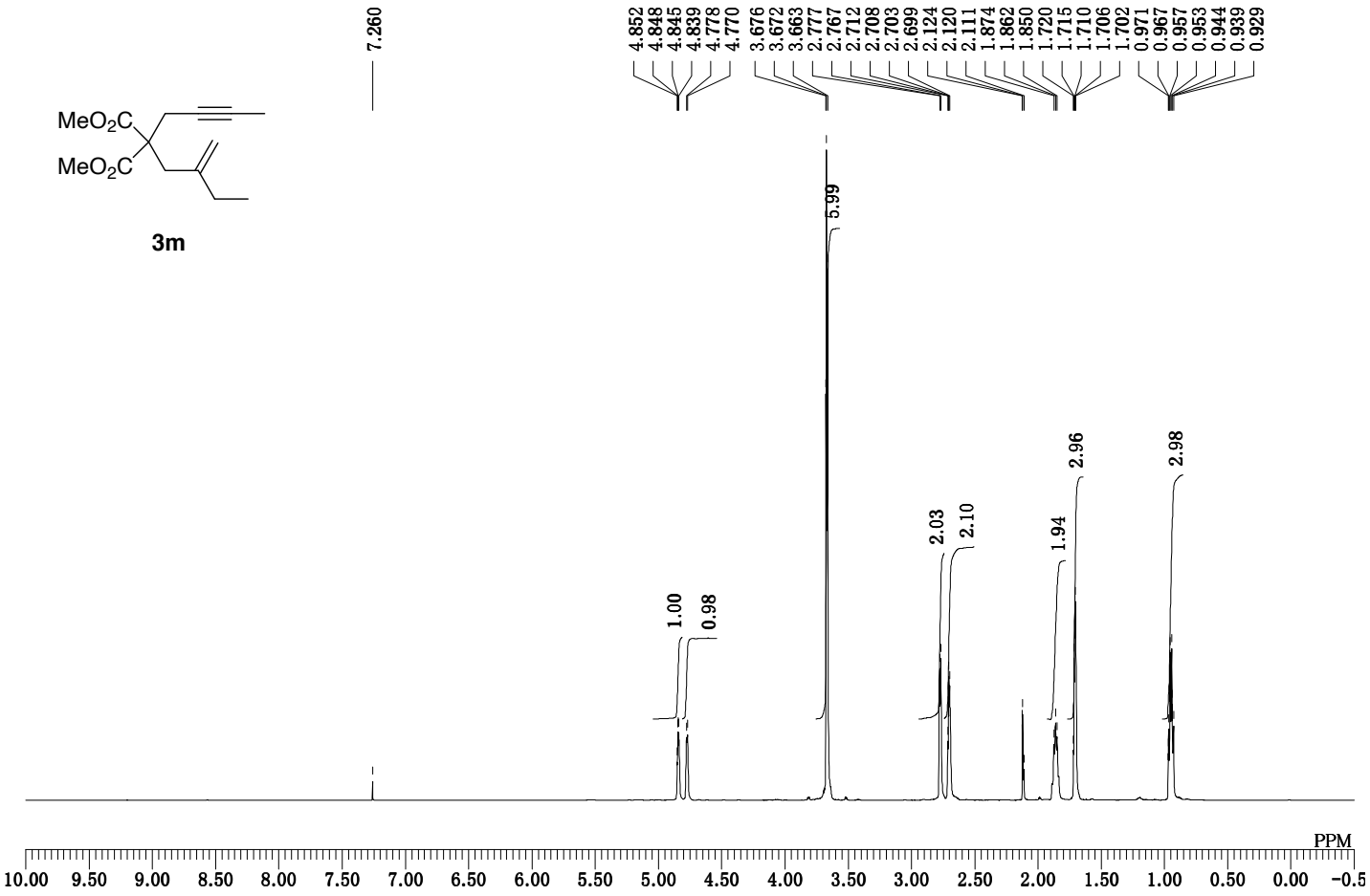
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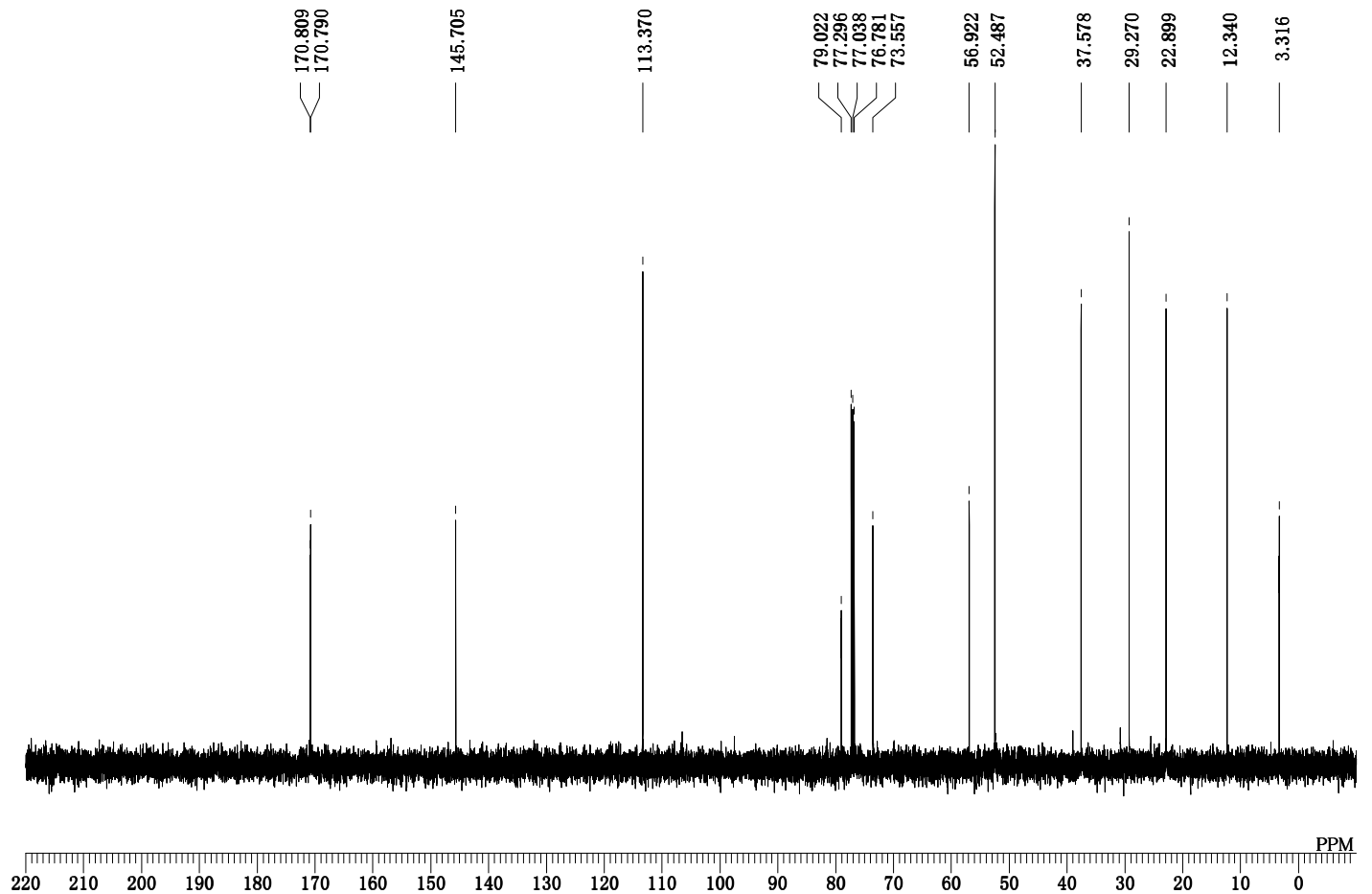
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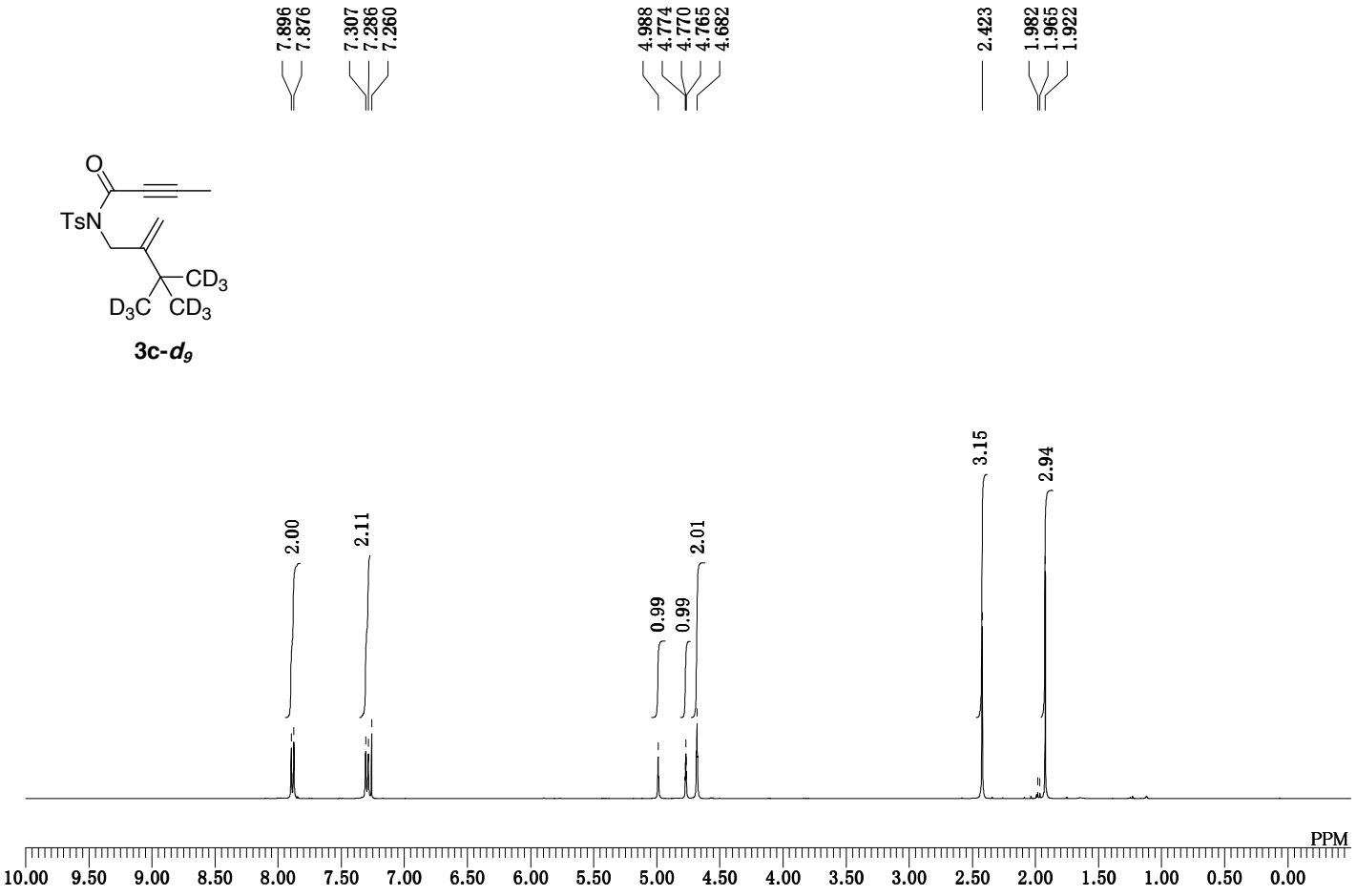
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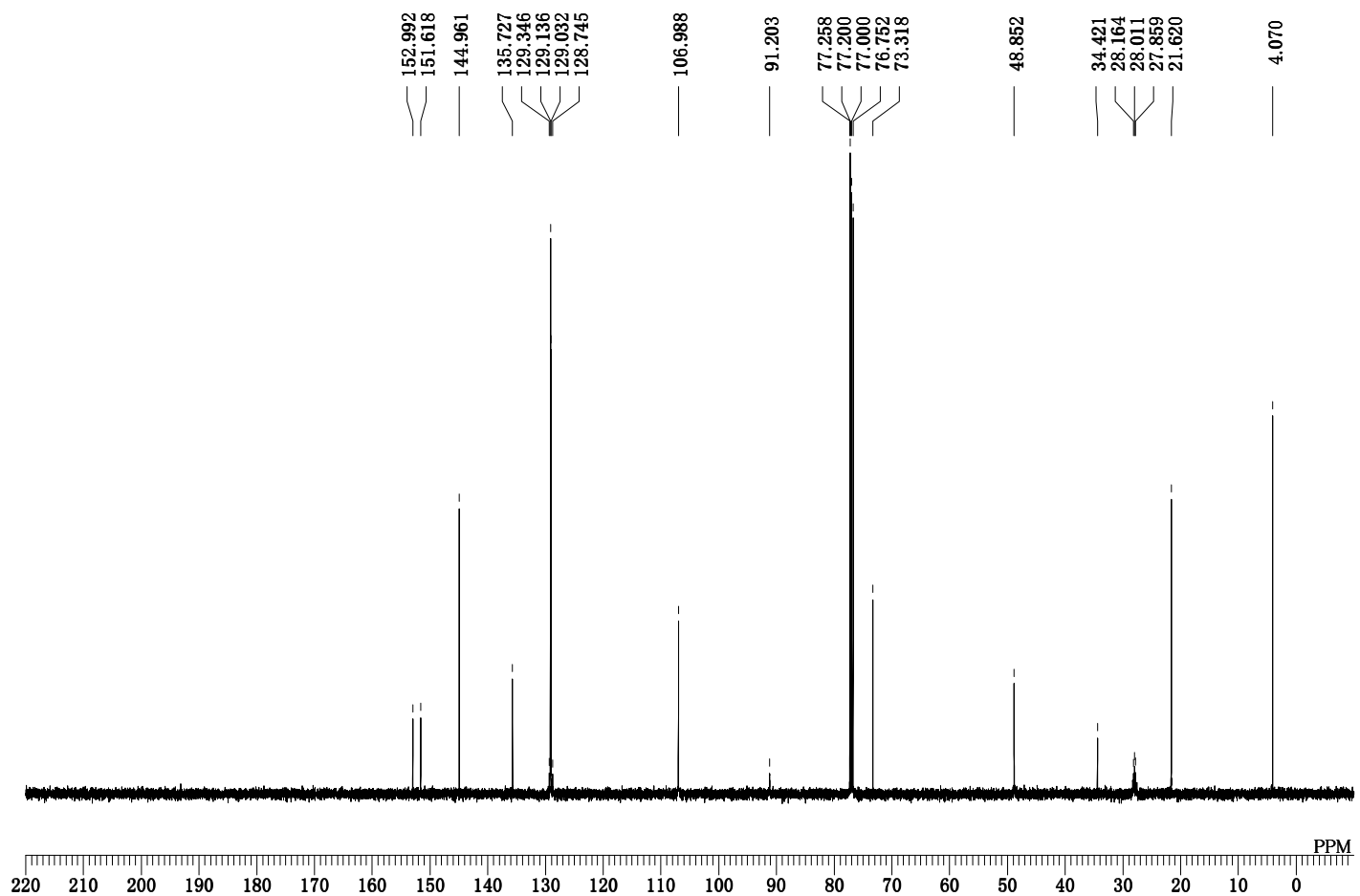
3c-d_9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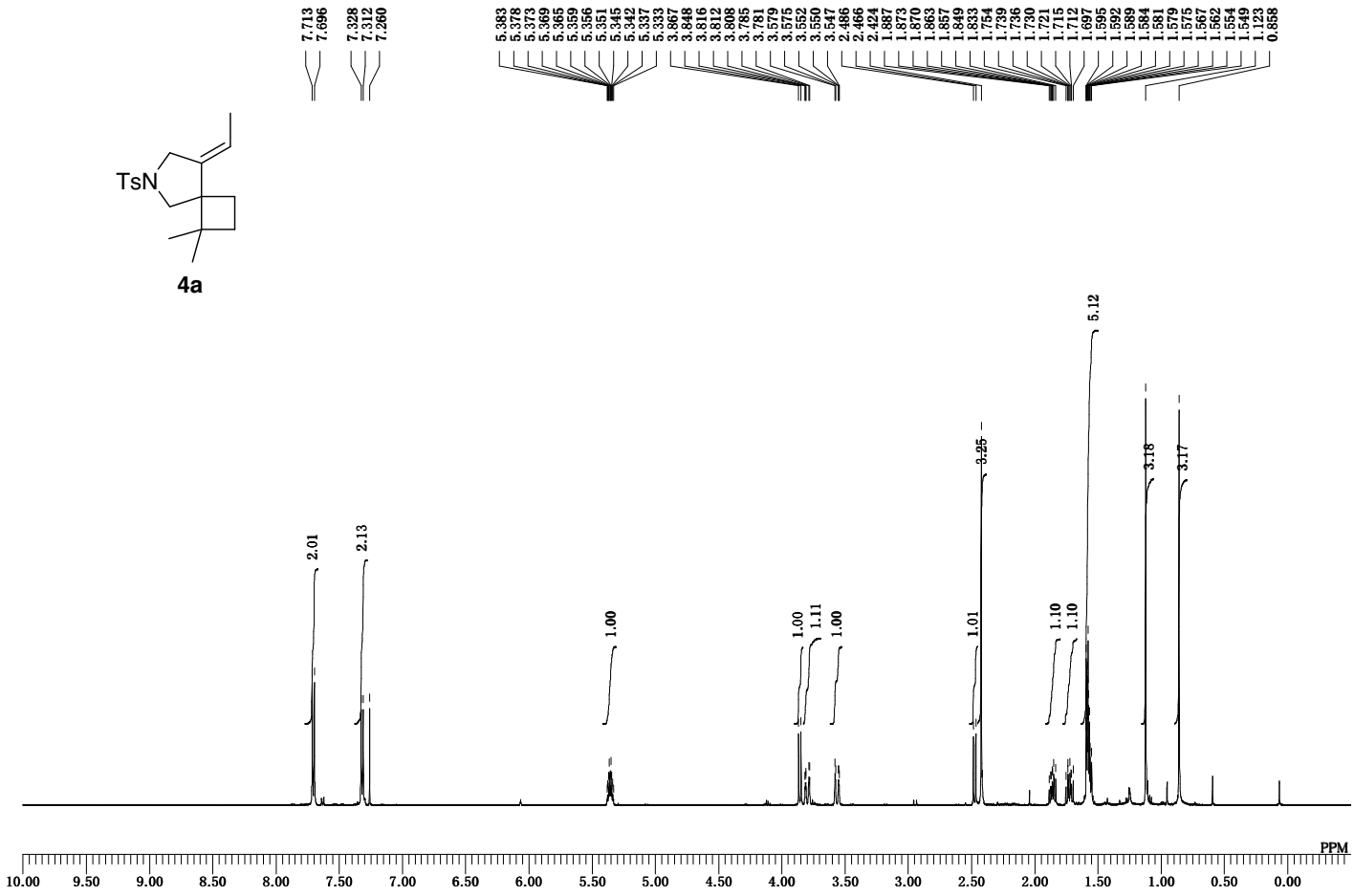
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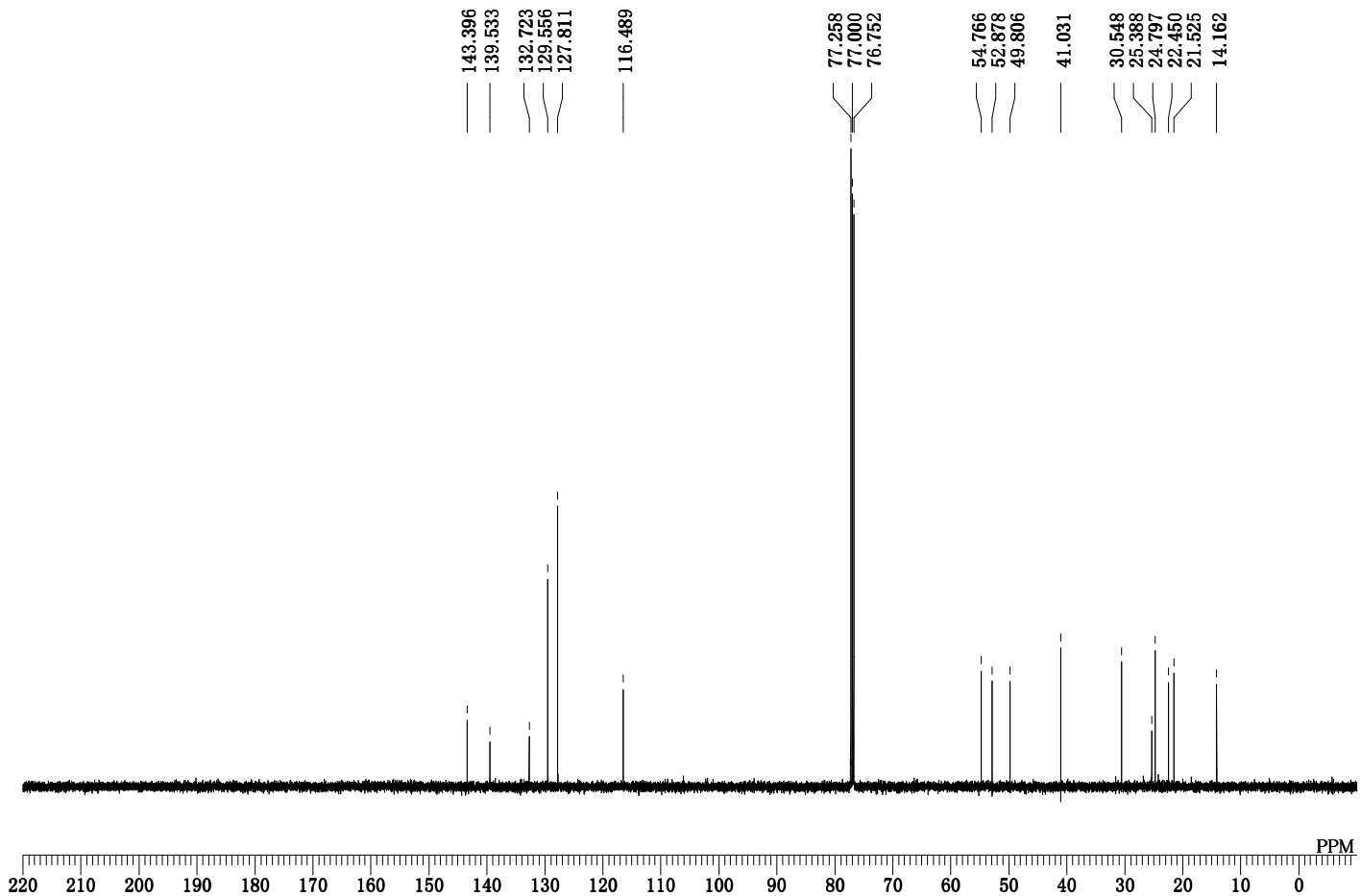
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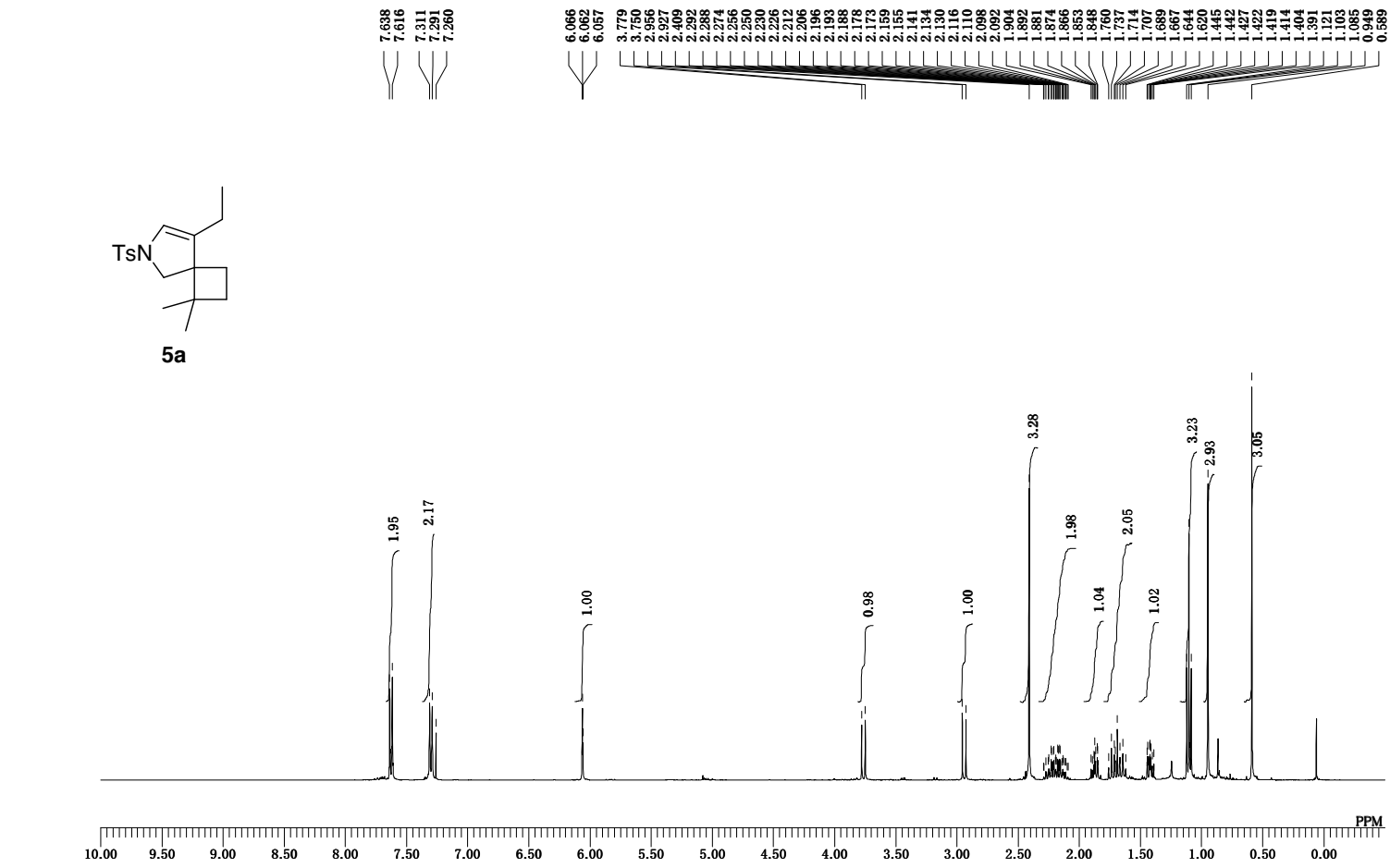
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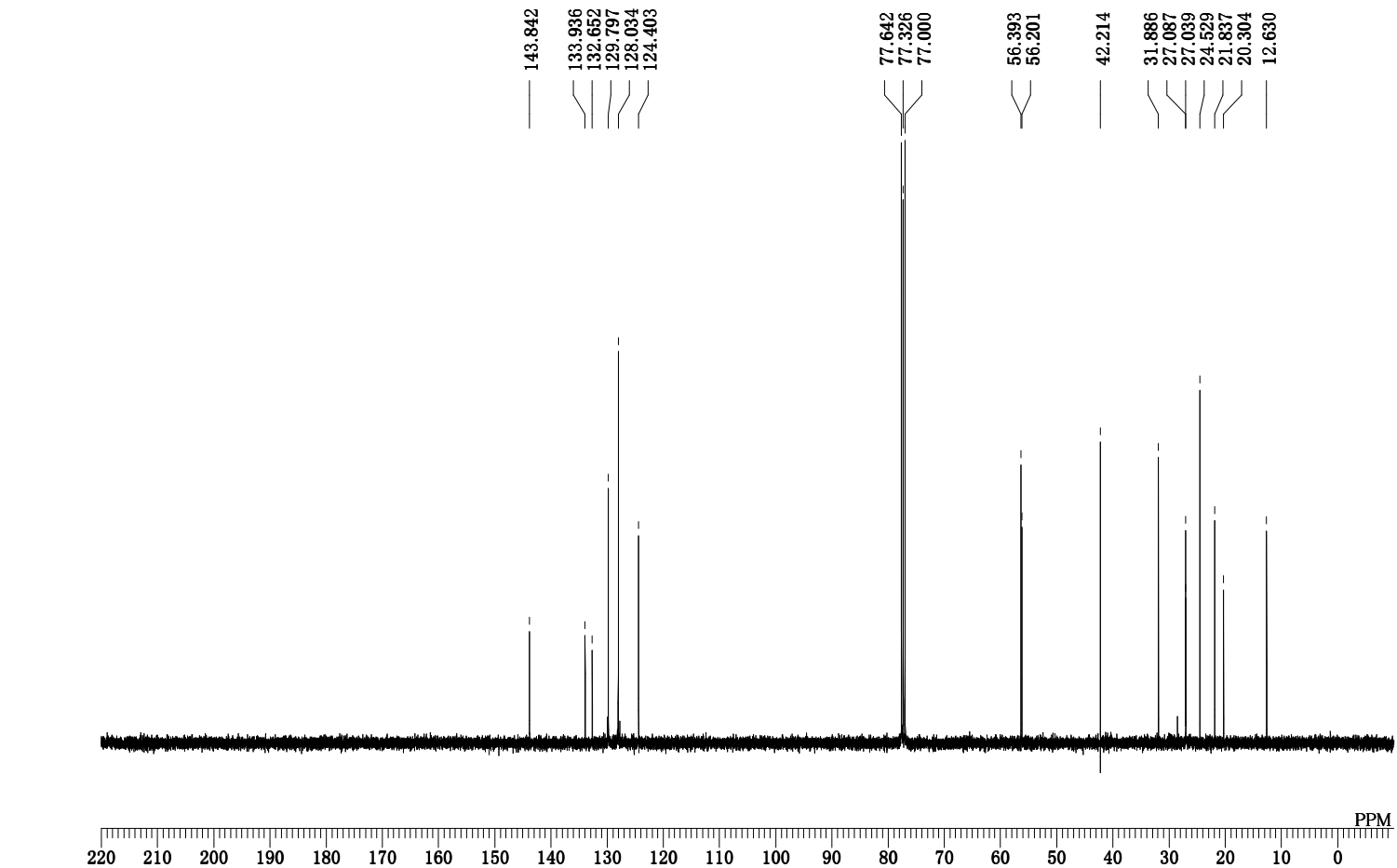
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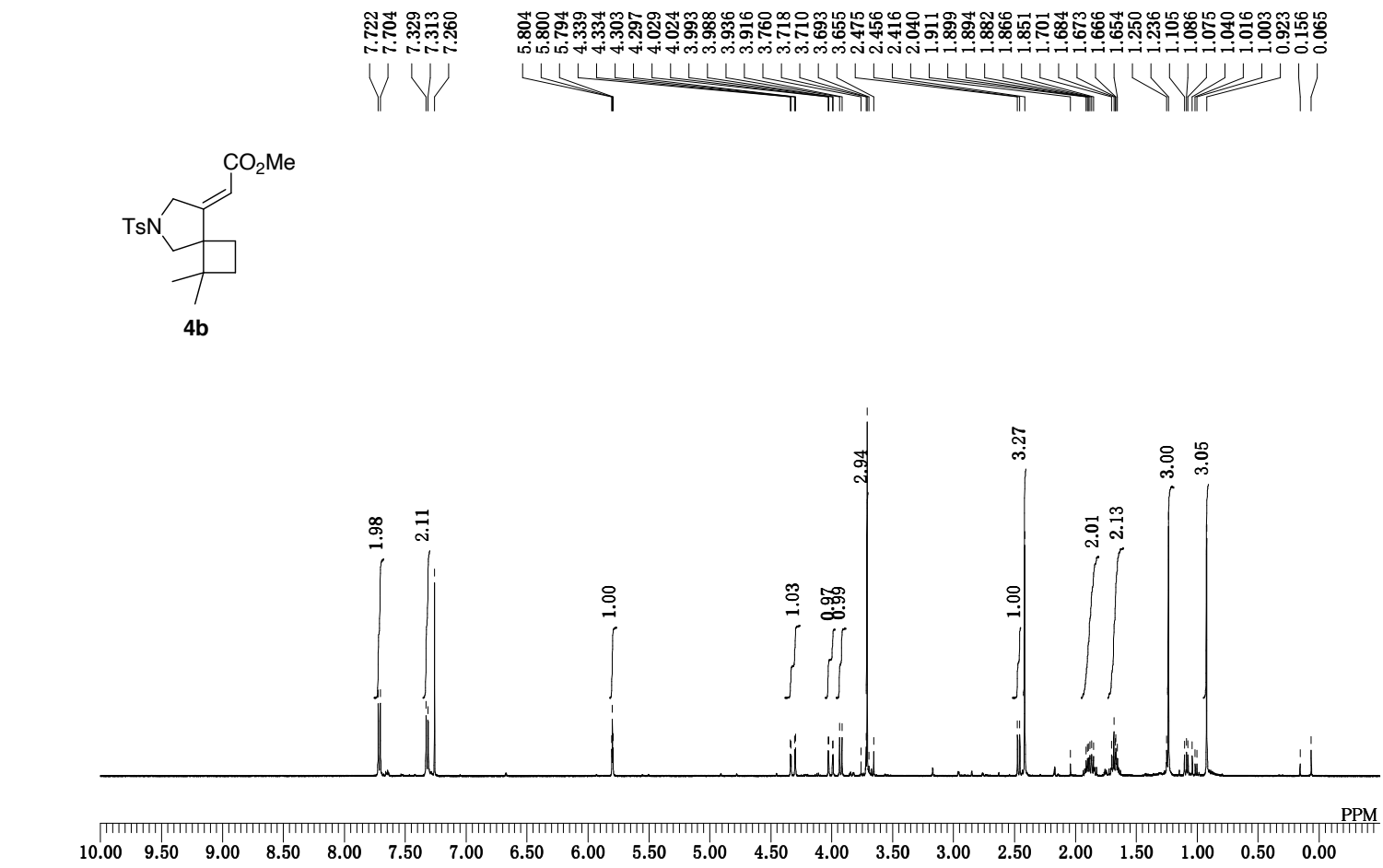
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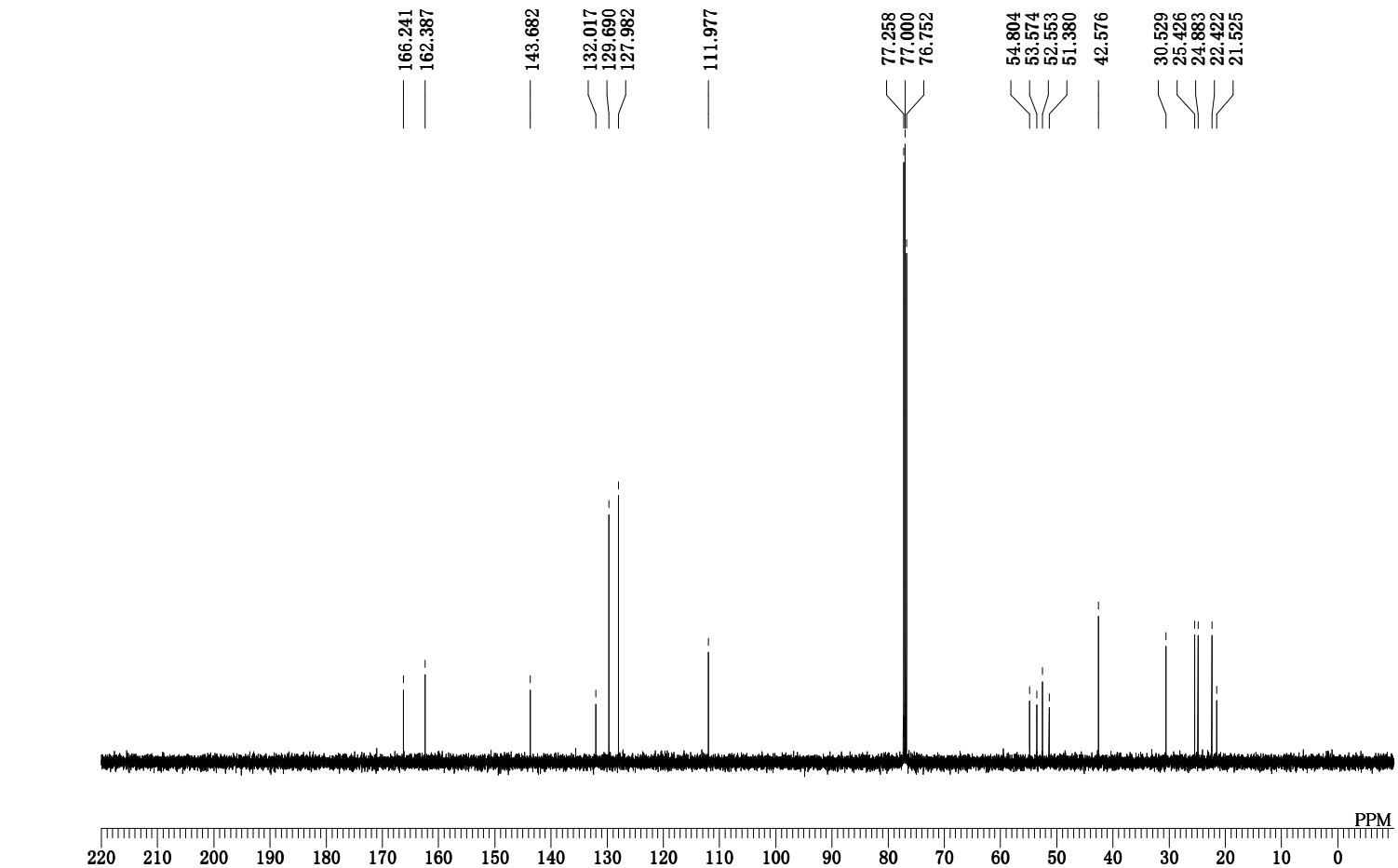
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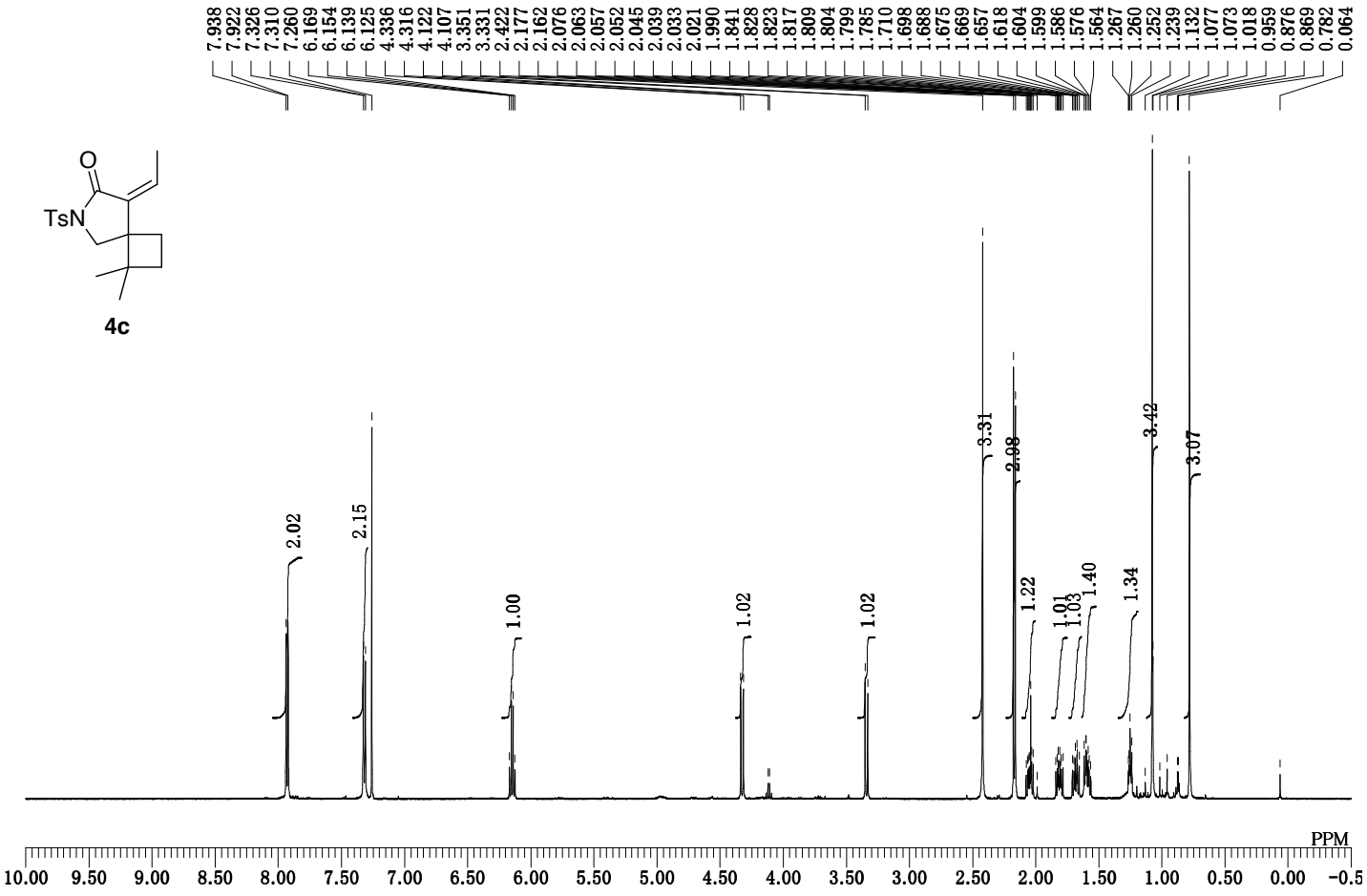
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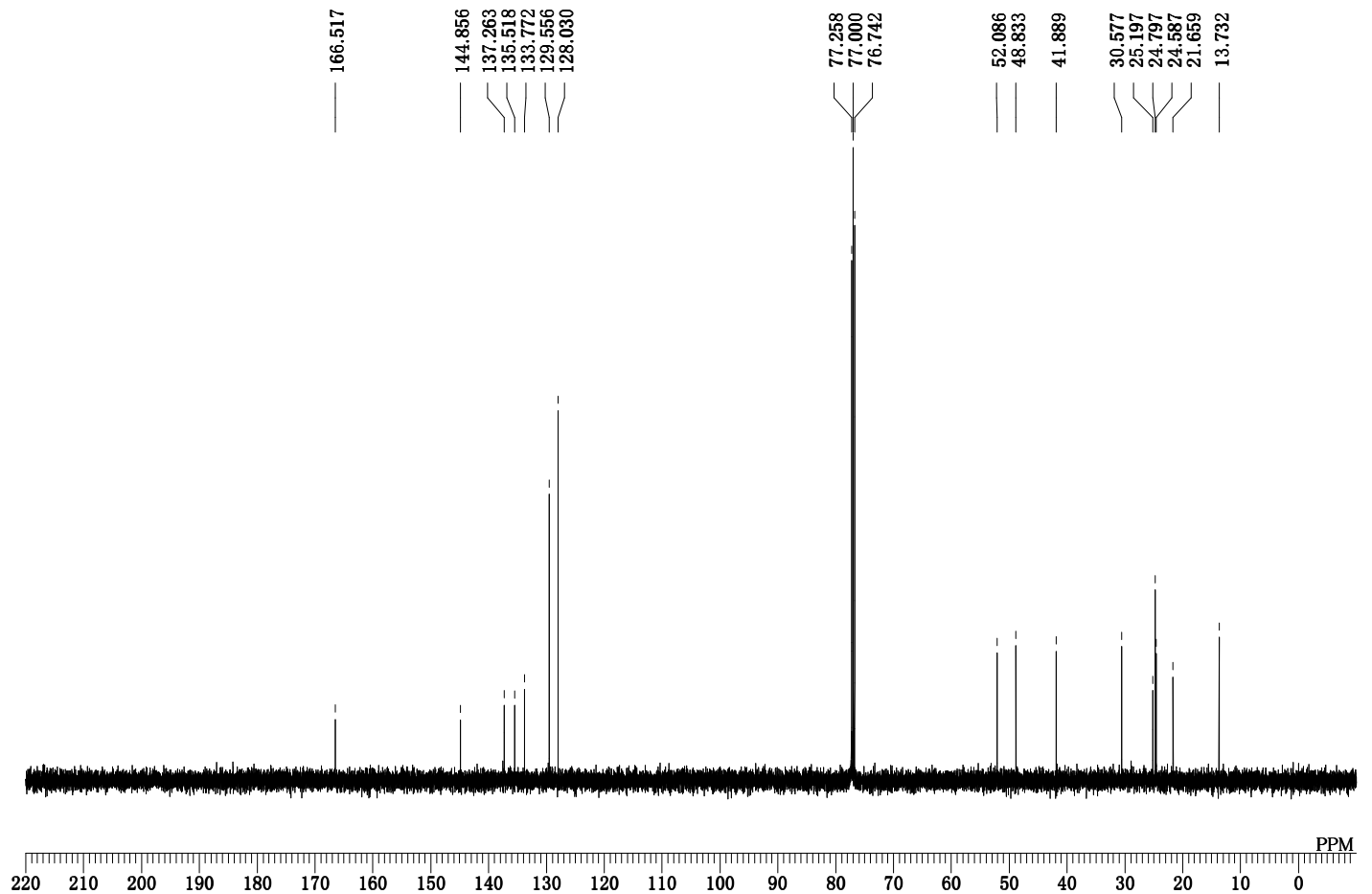
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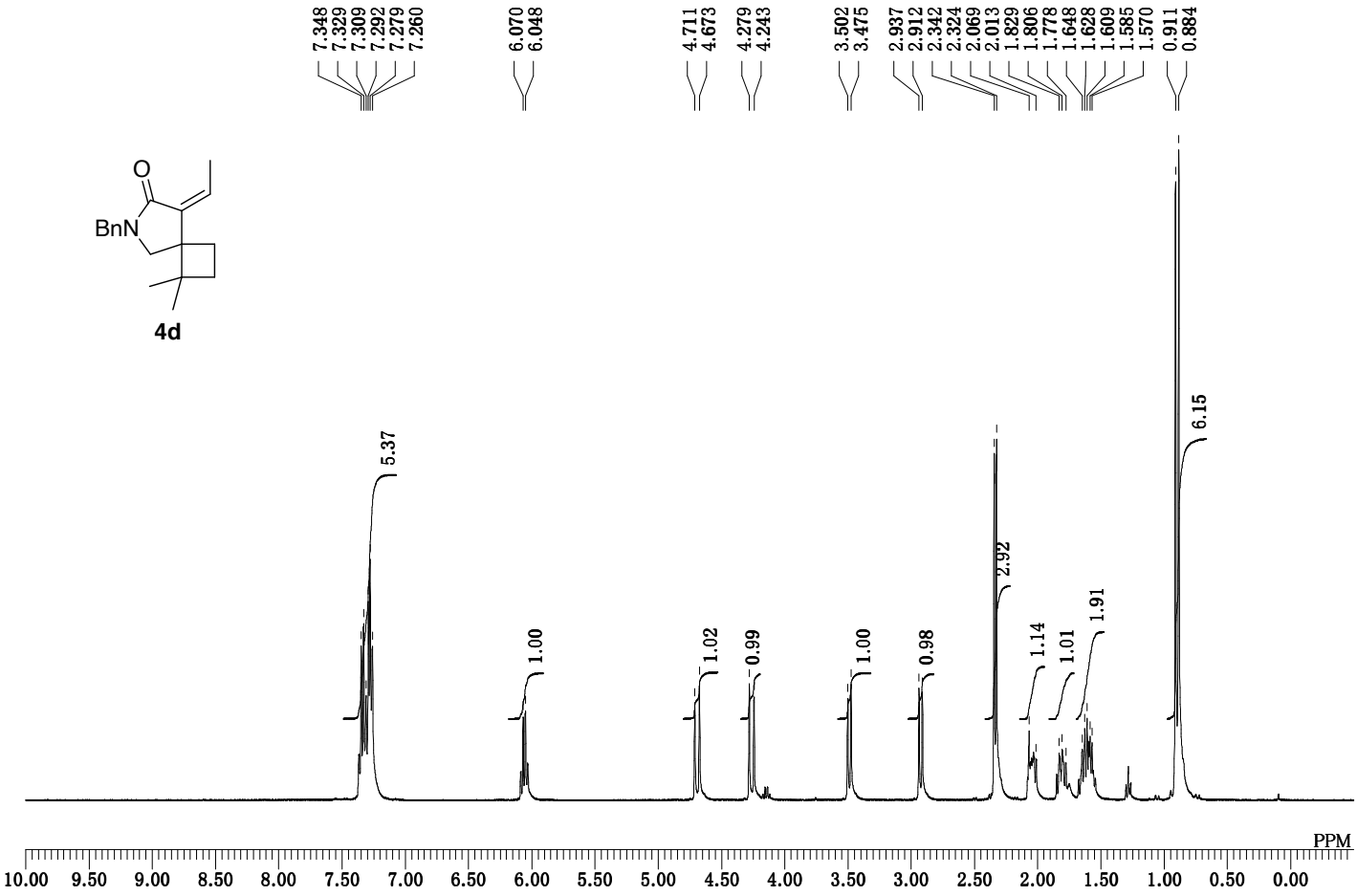
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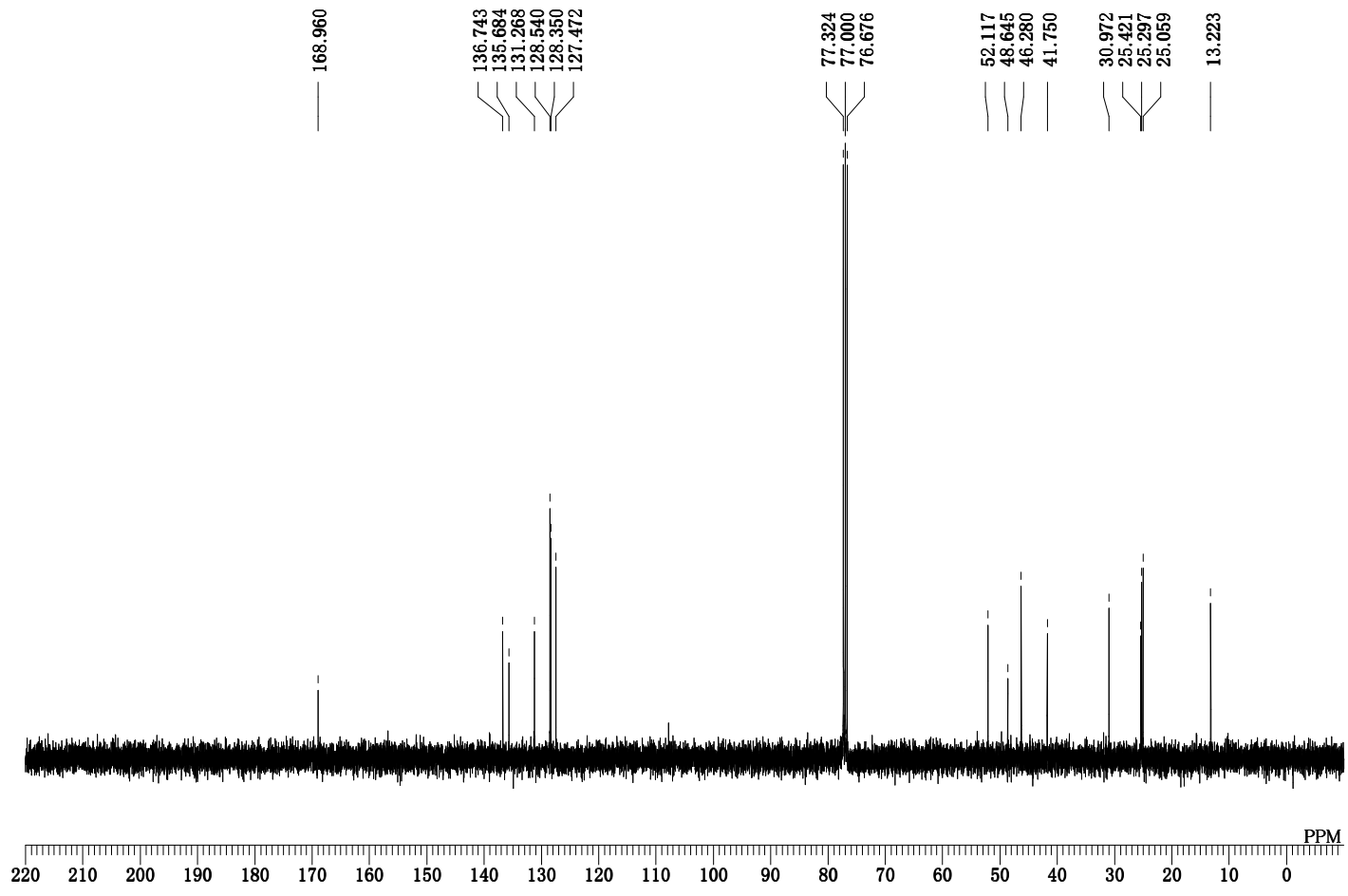
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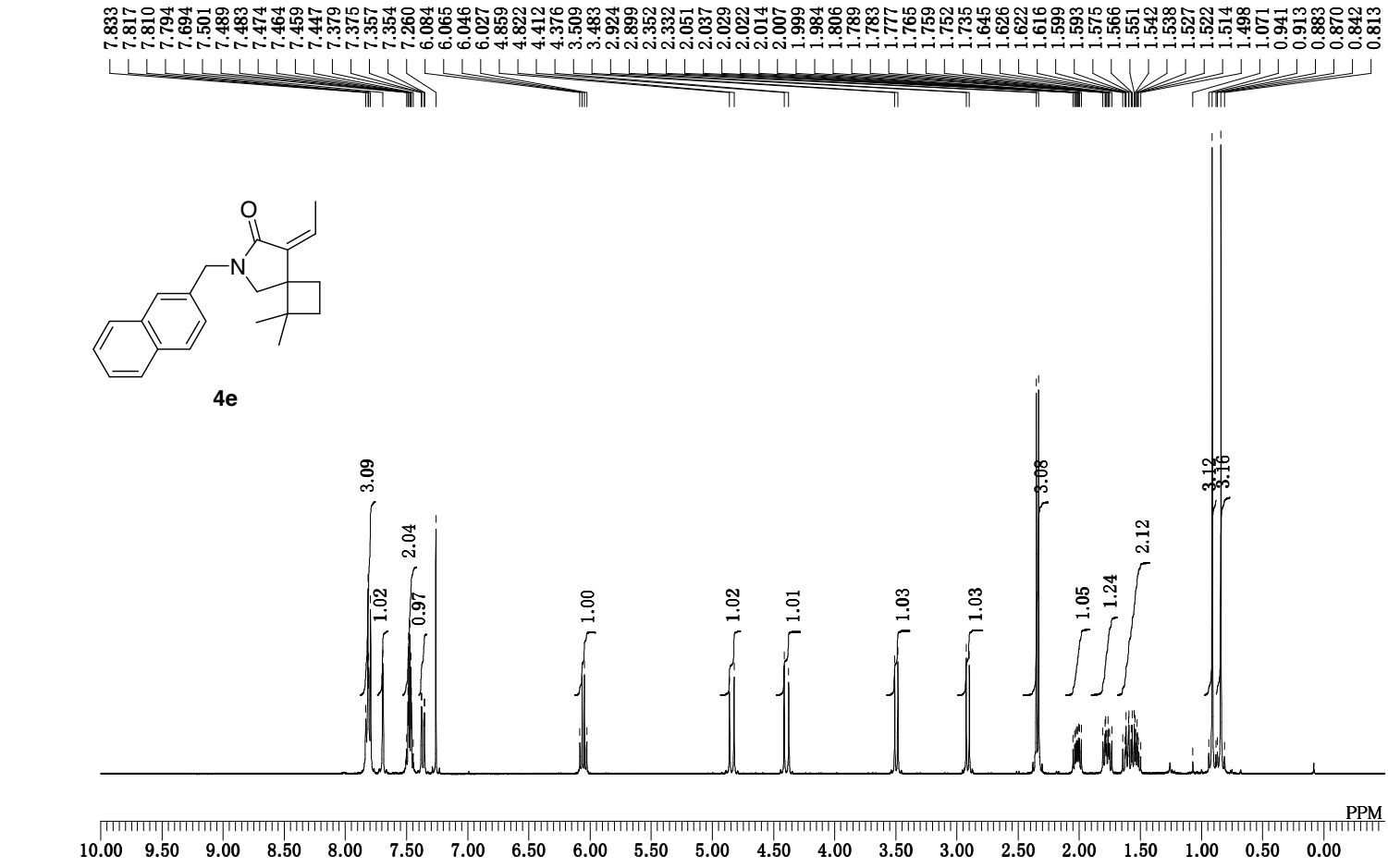
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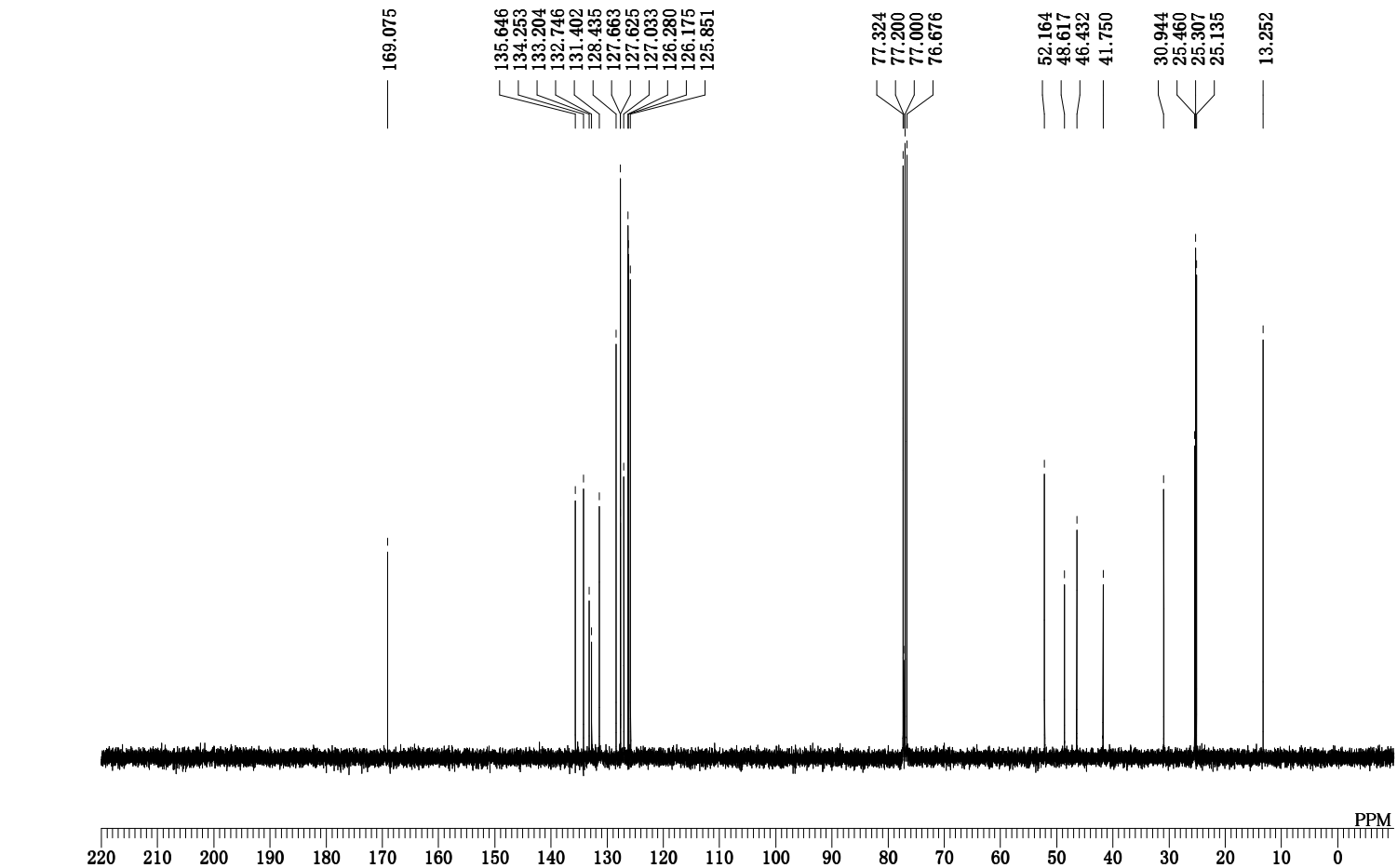
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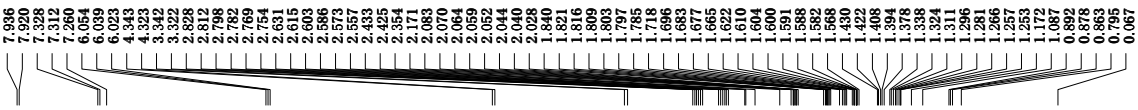
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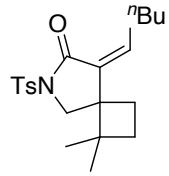
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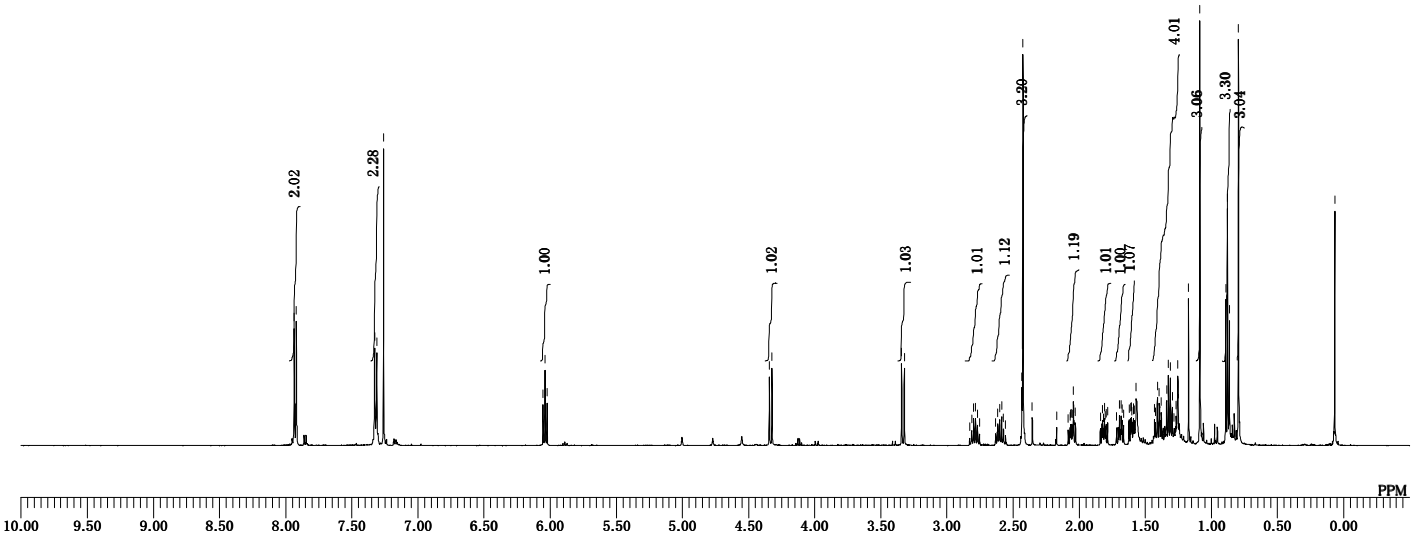
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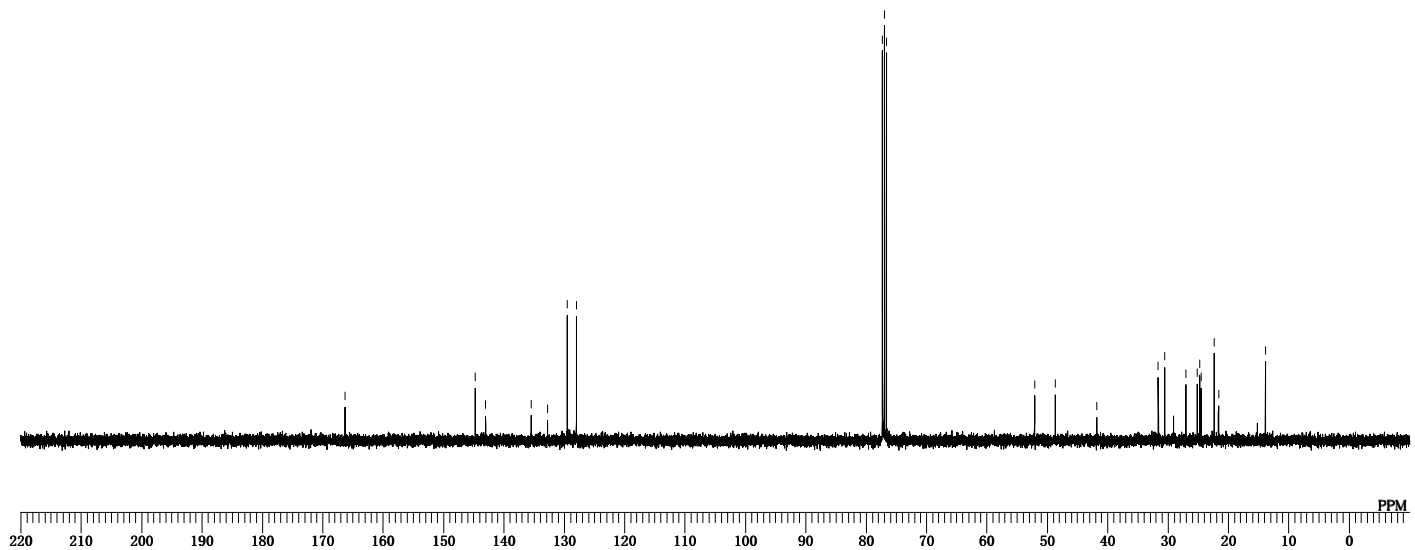
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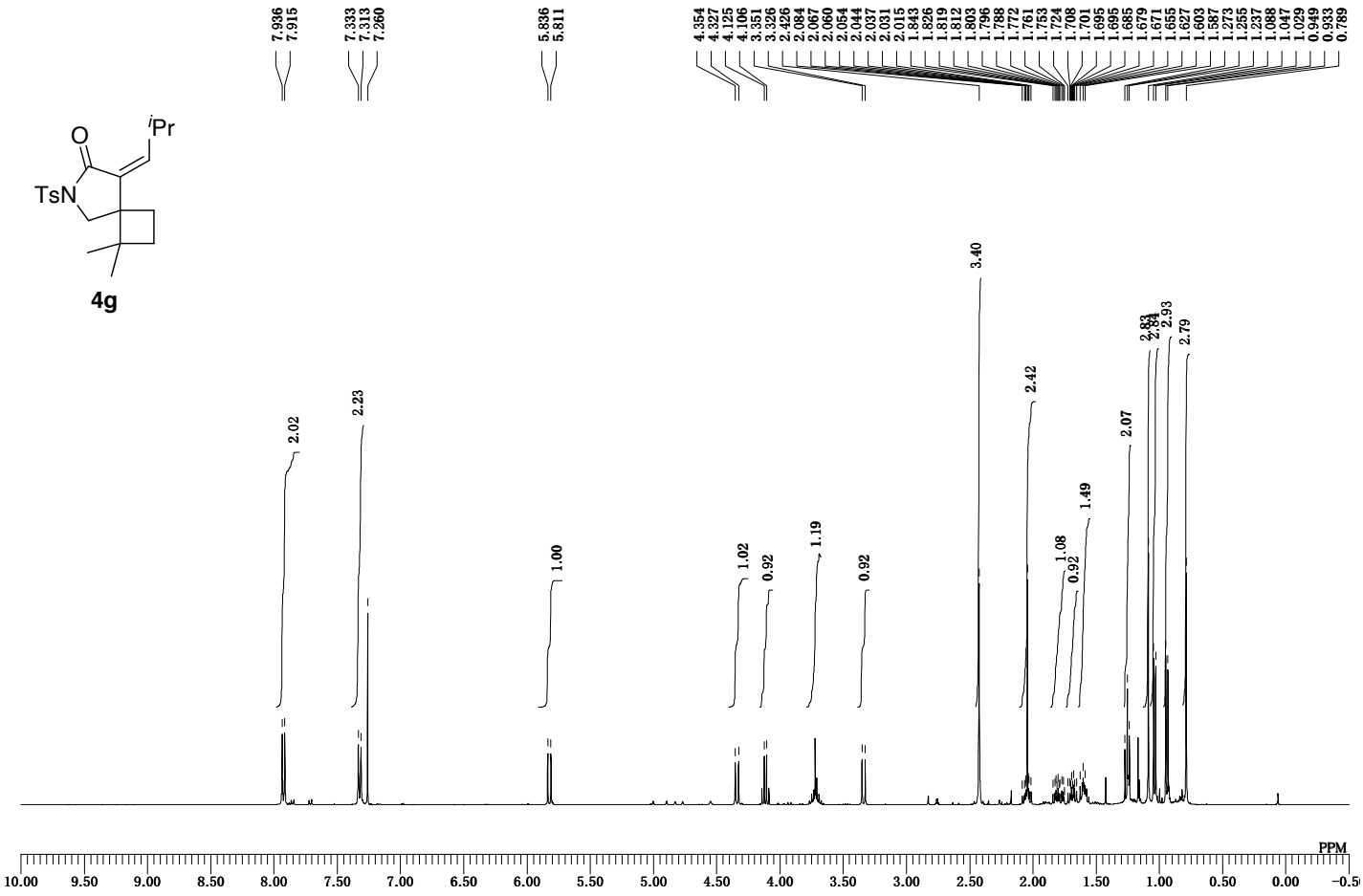
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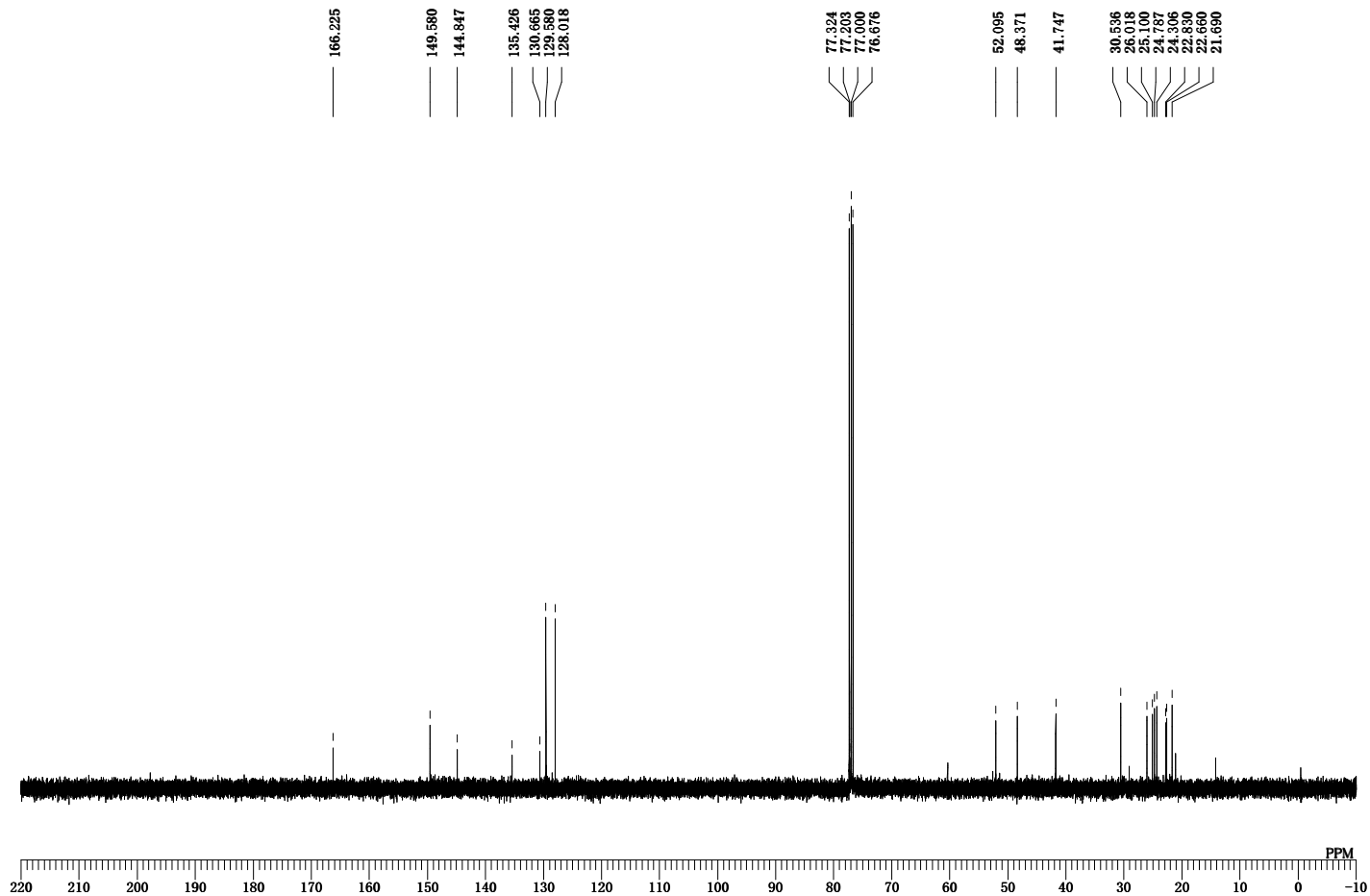
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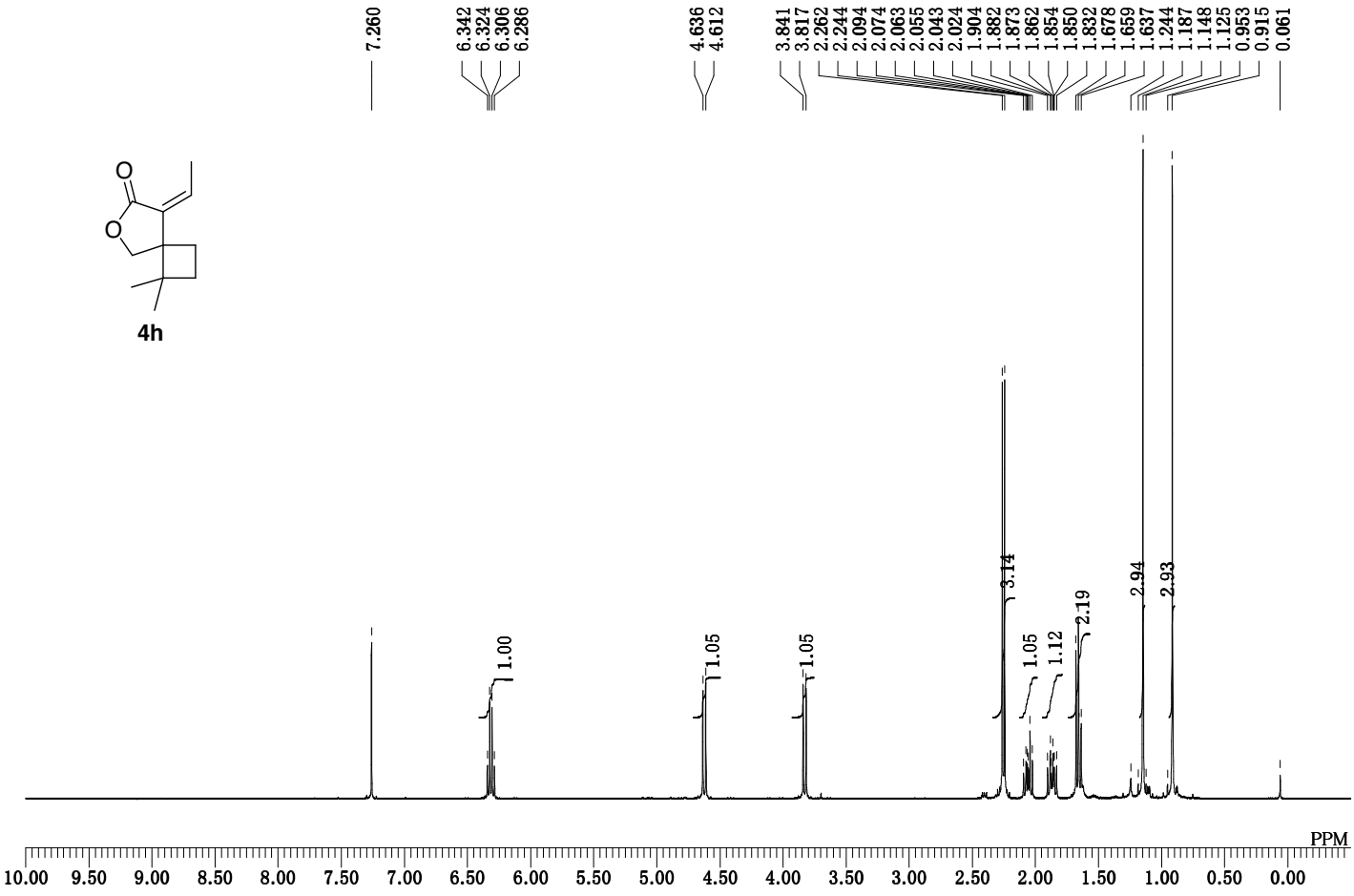
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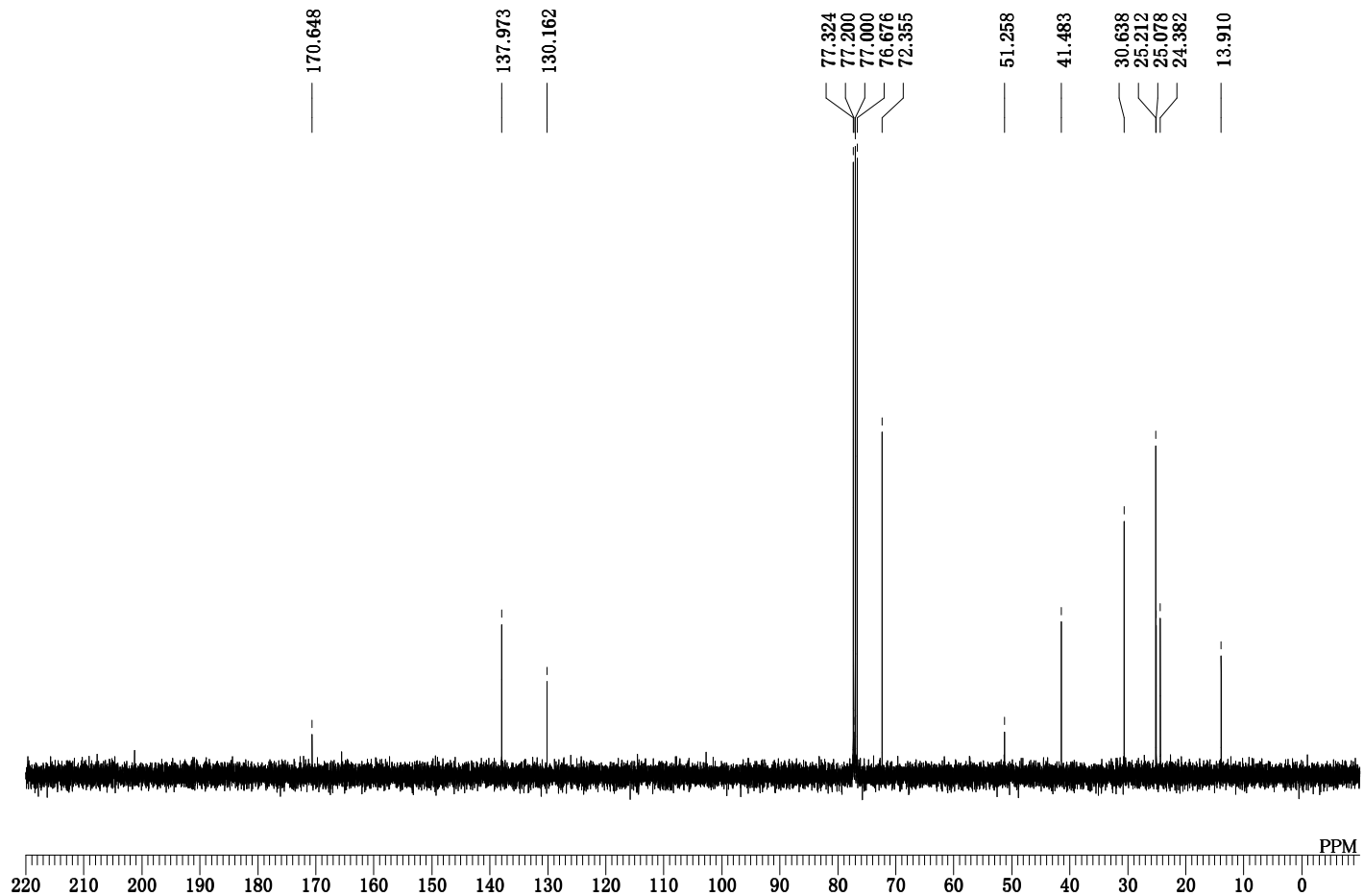
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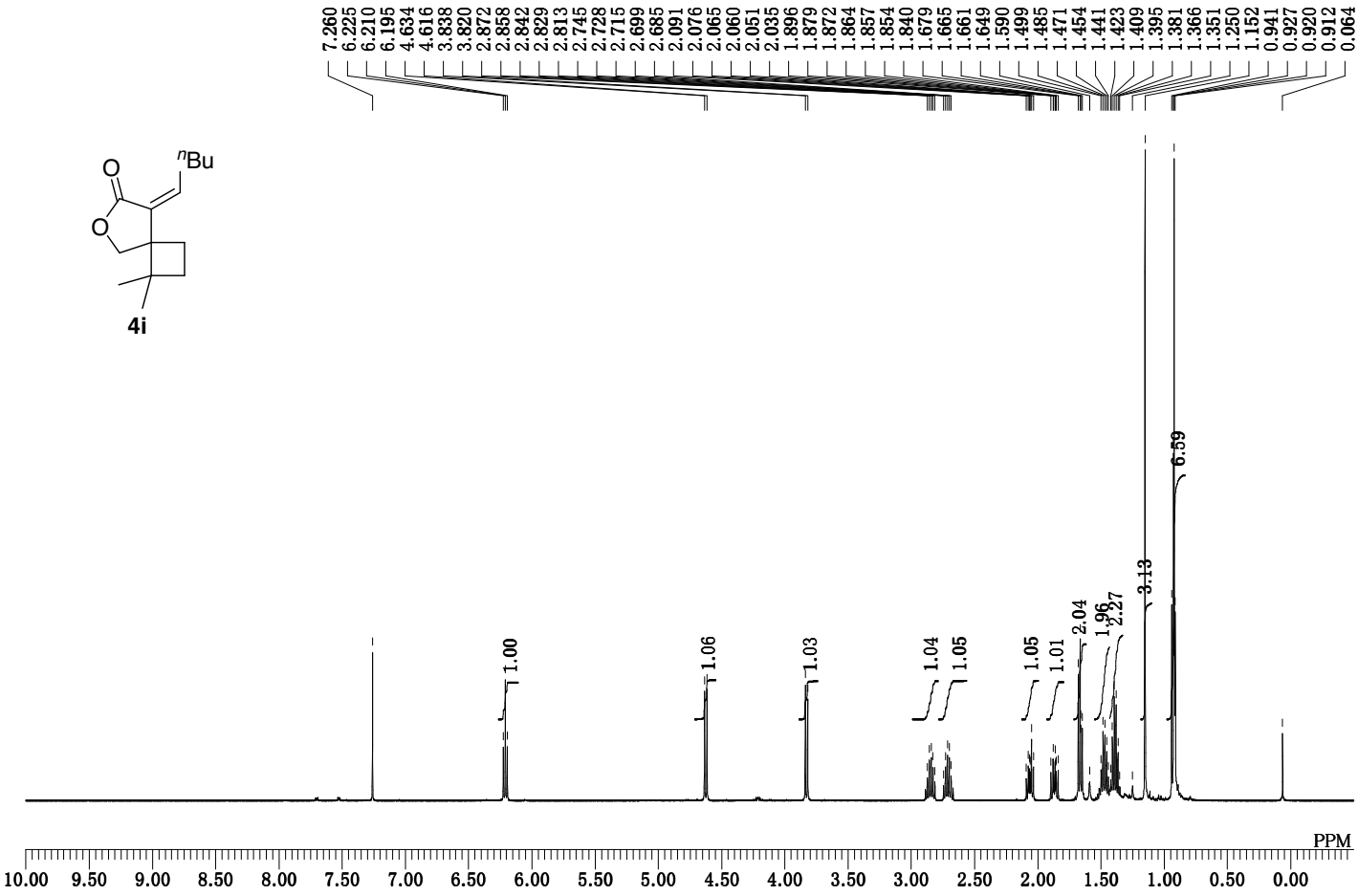
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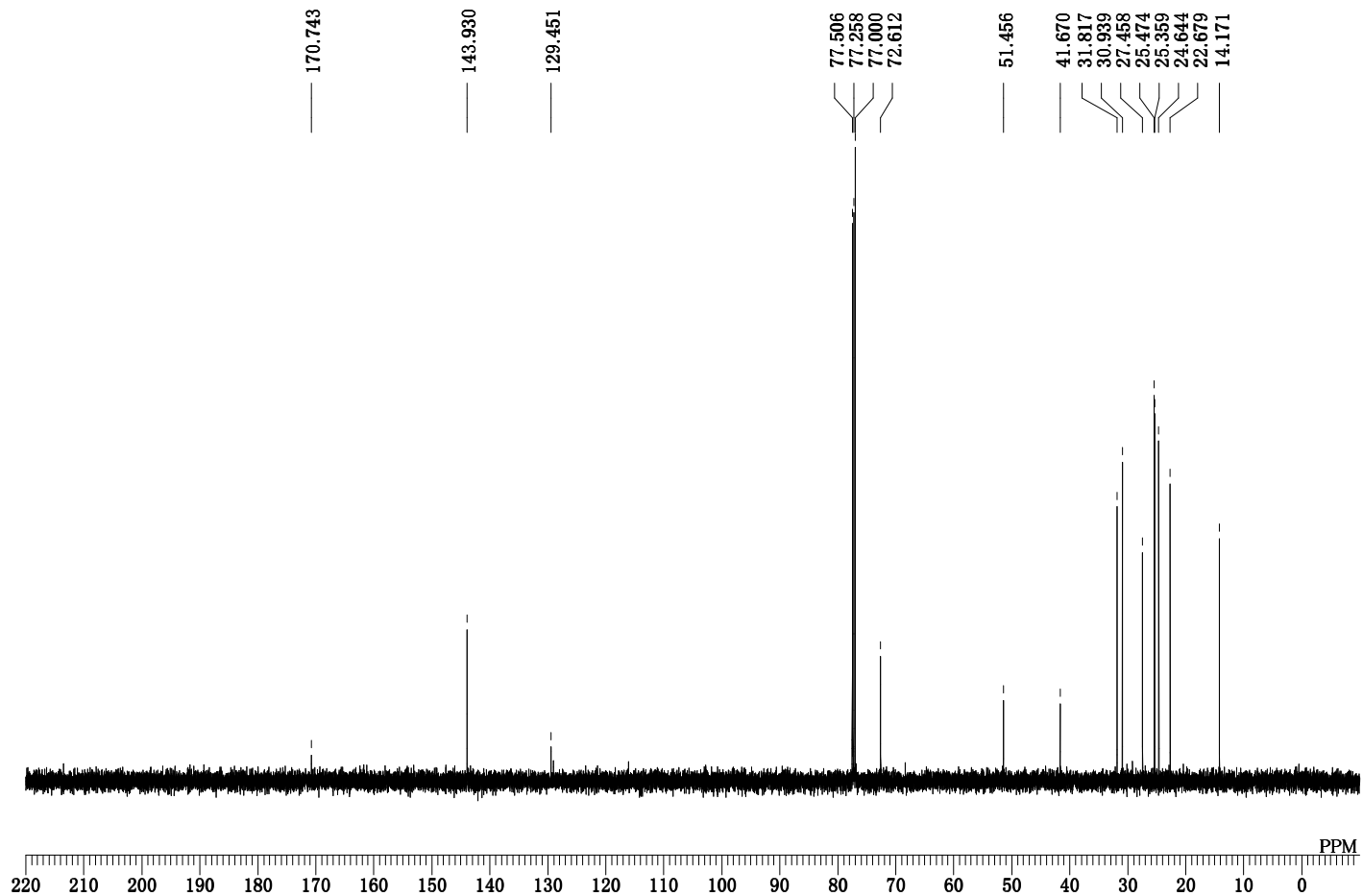
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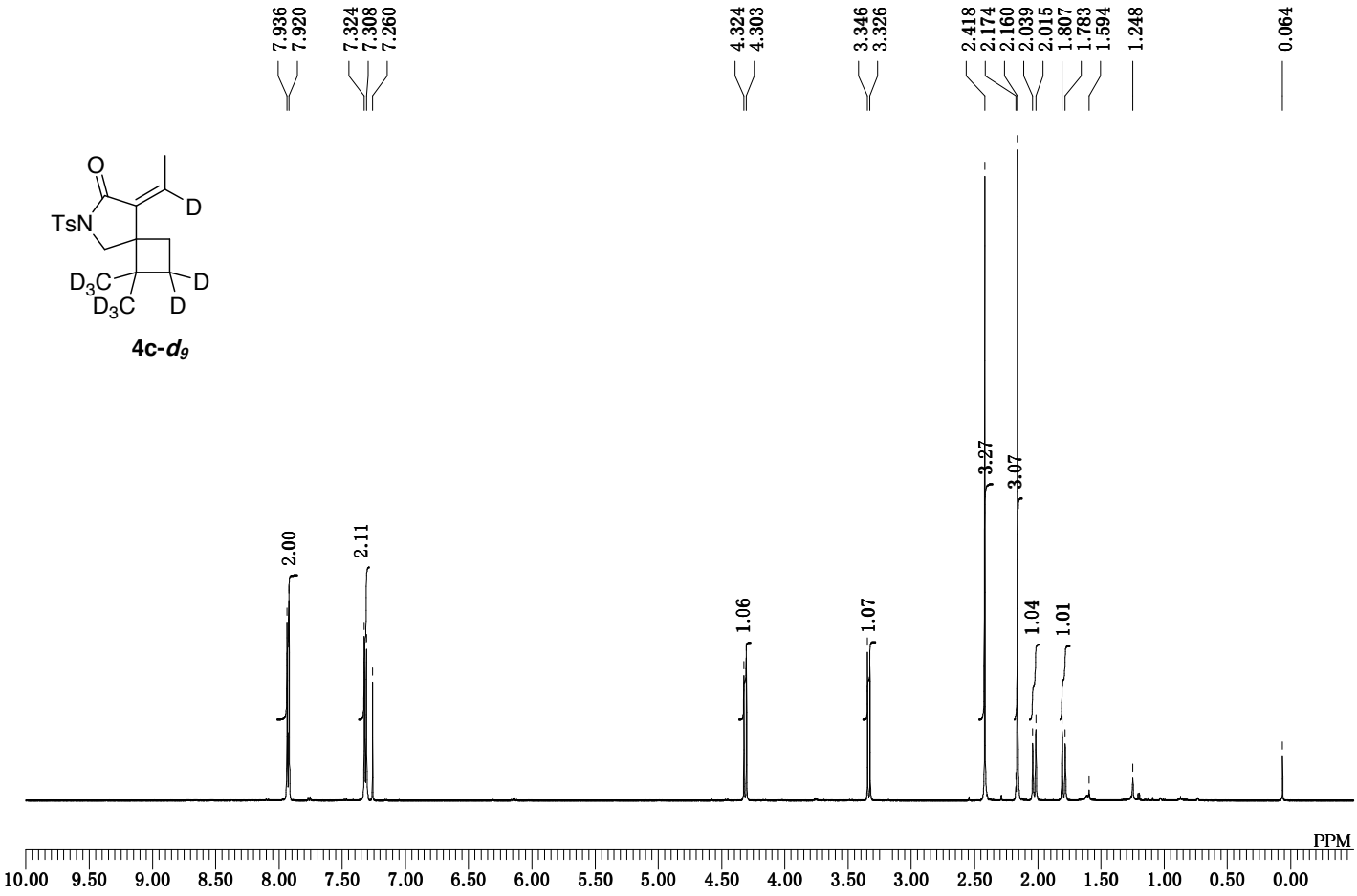
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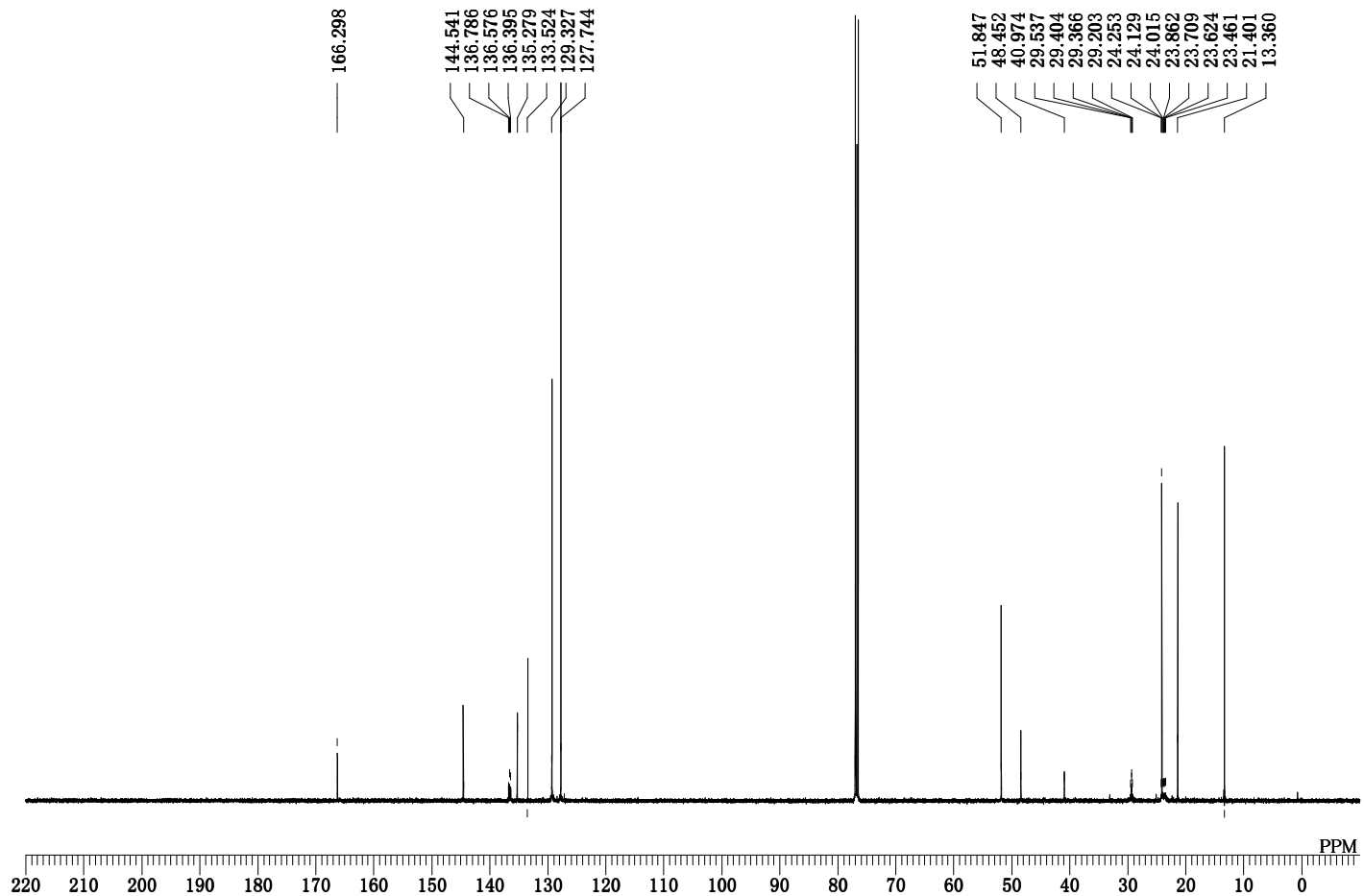
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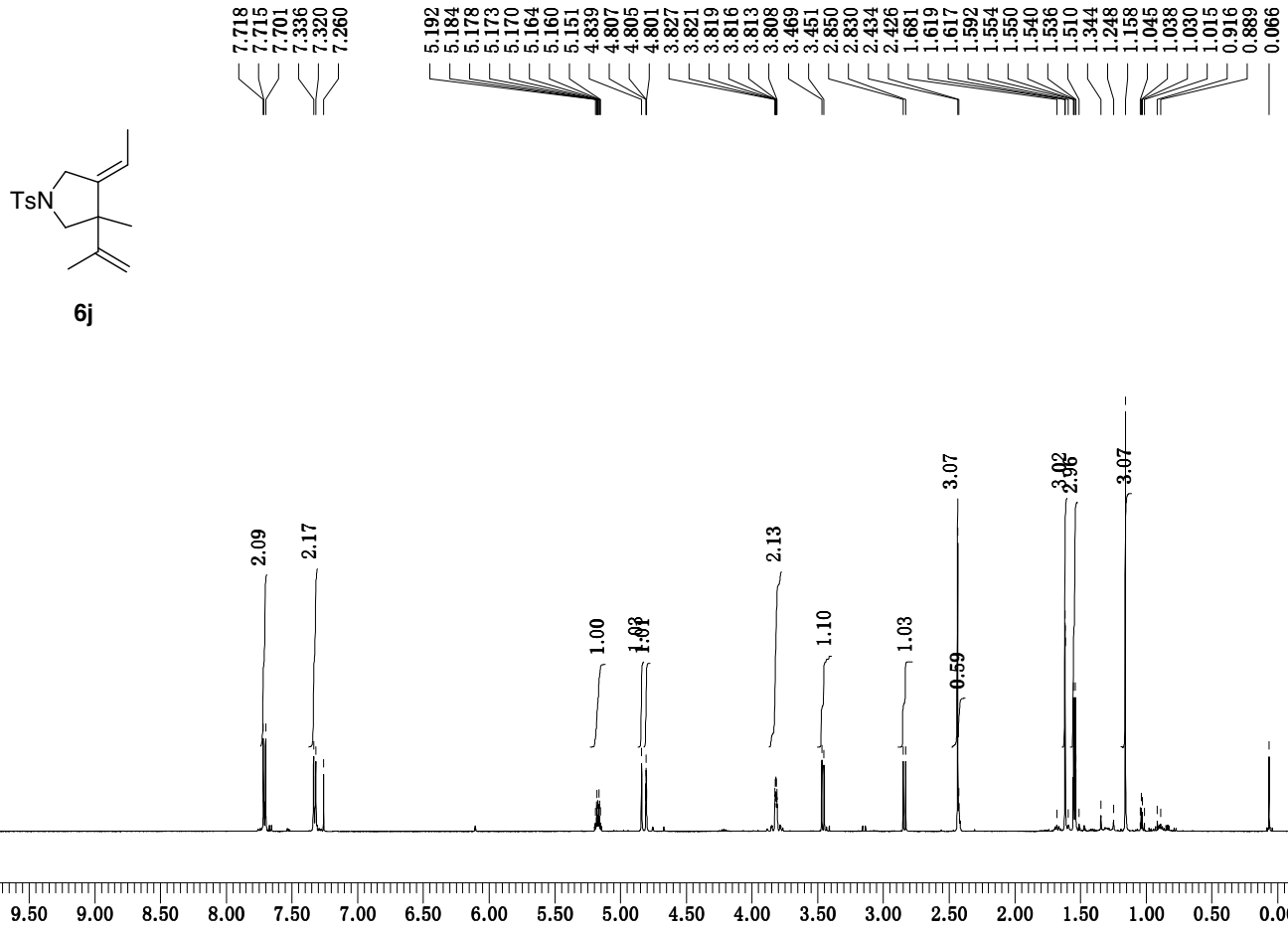
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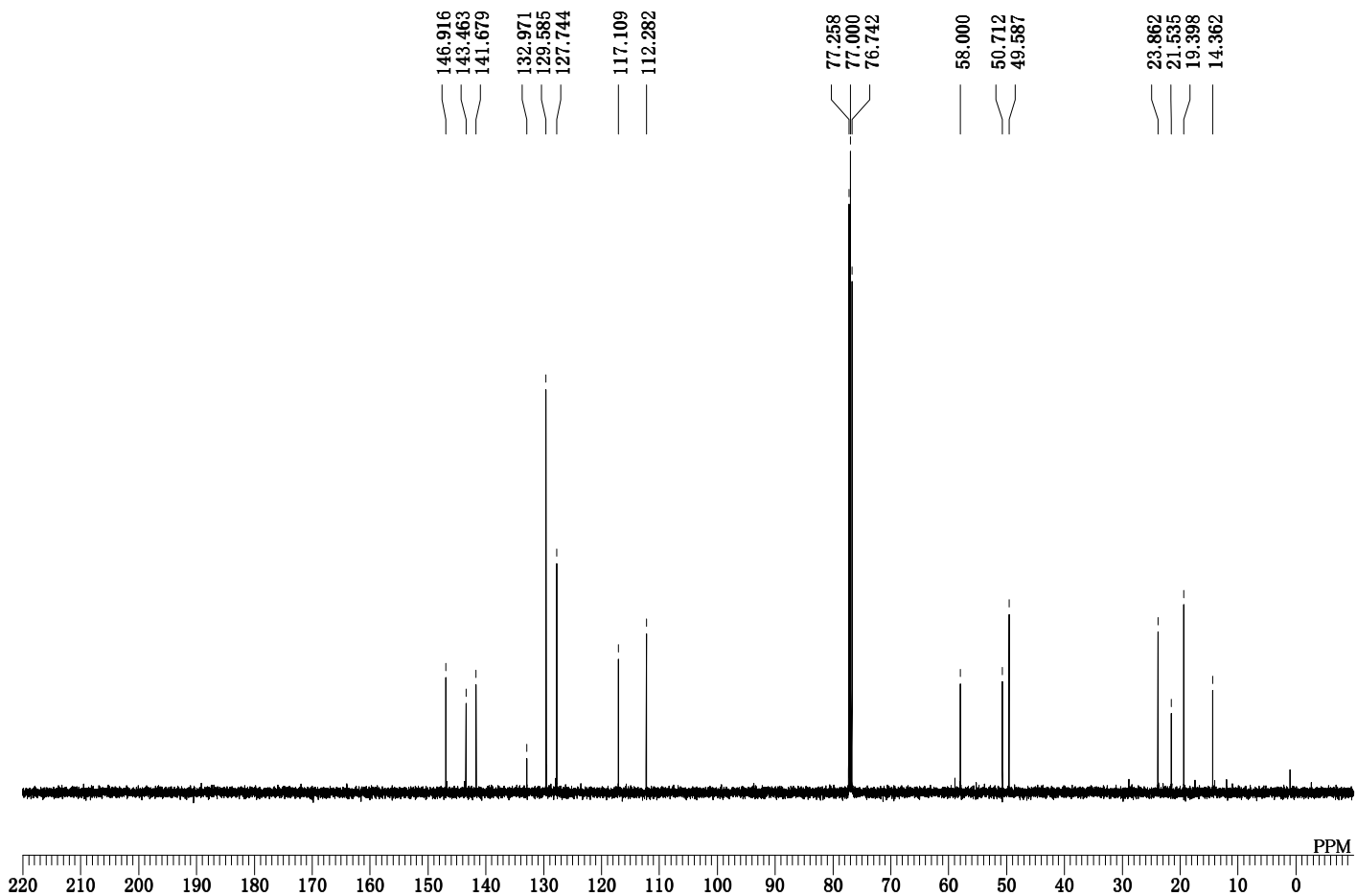
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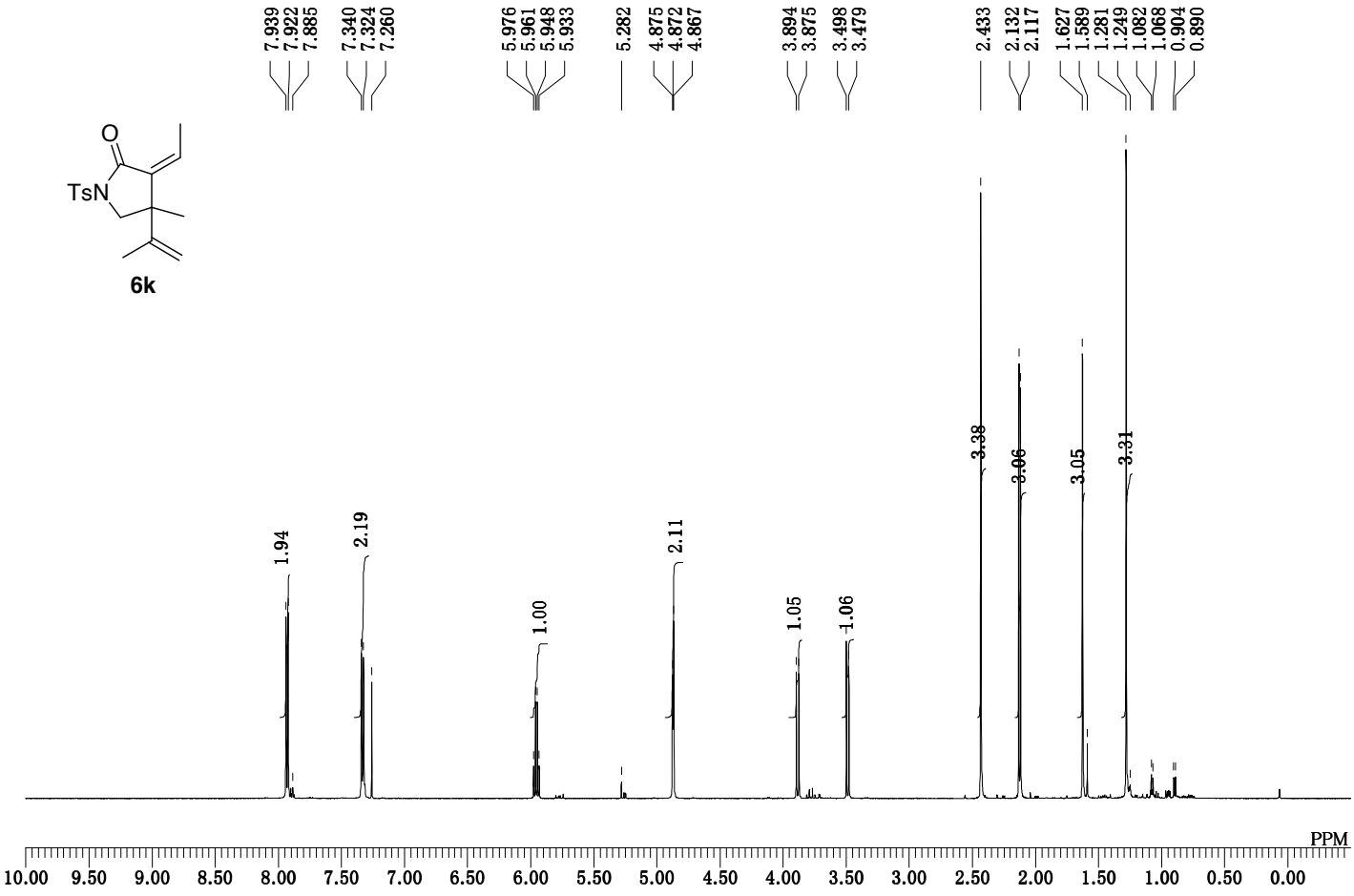
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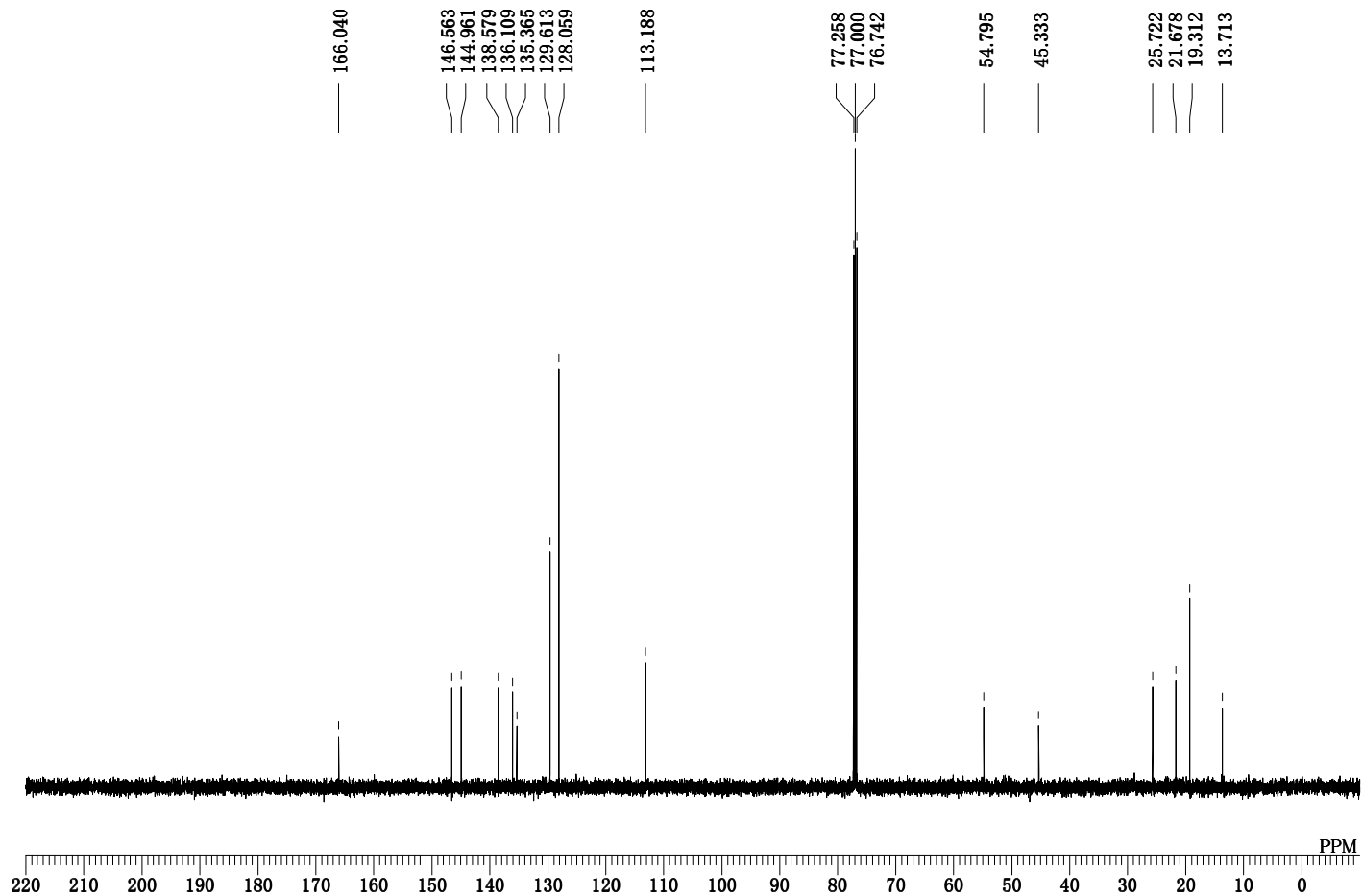
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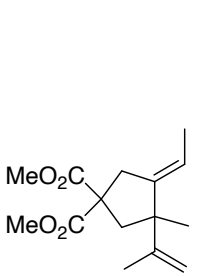
MeO2C
MeO2C

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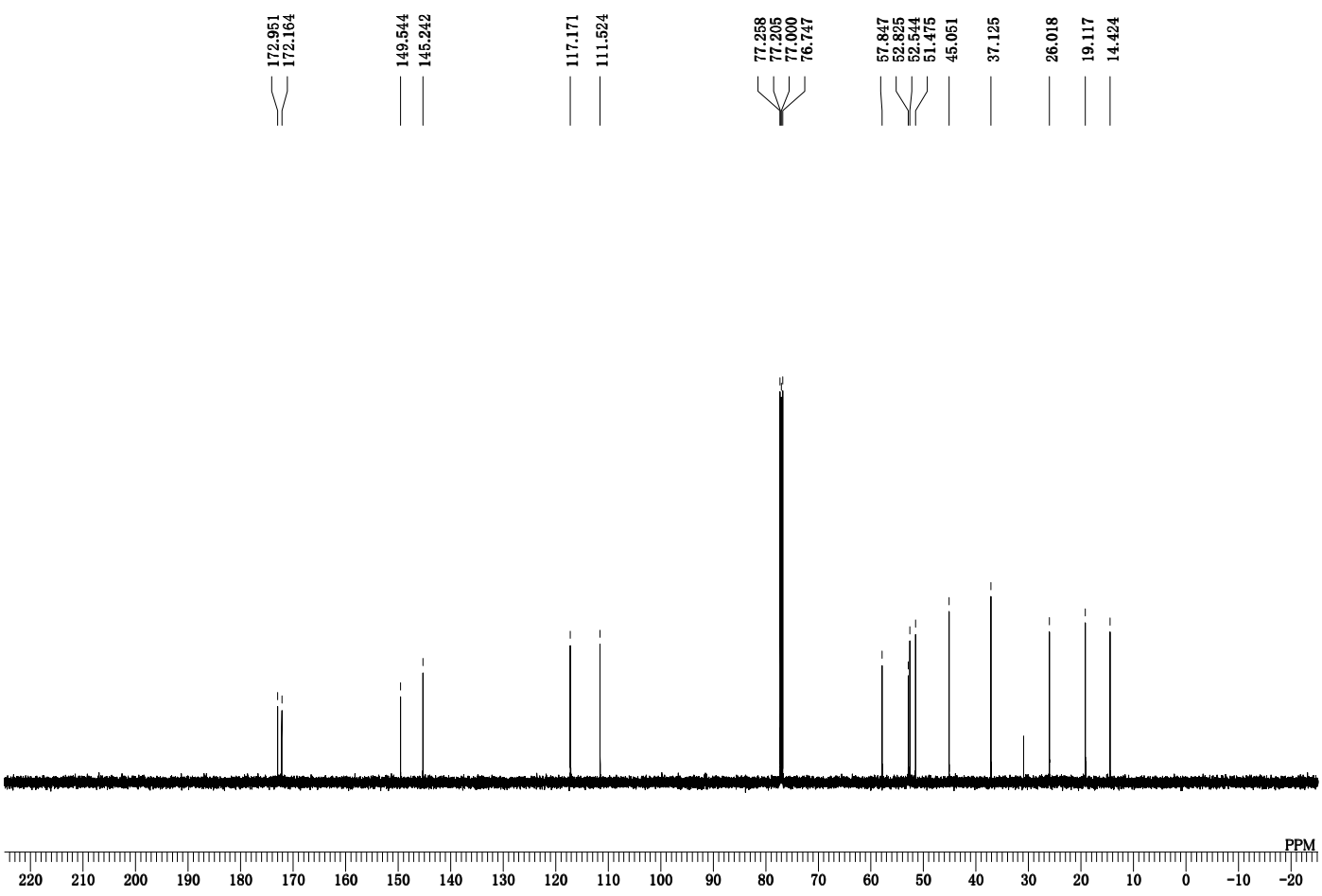
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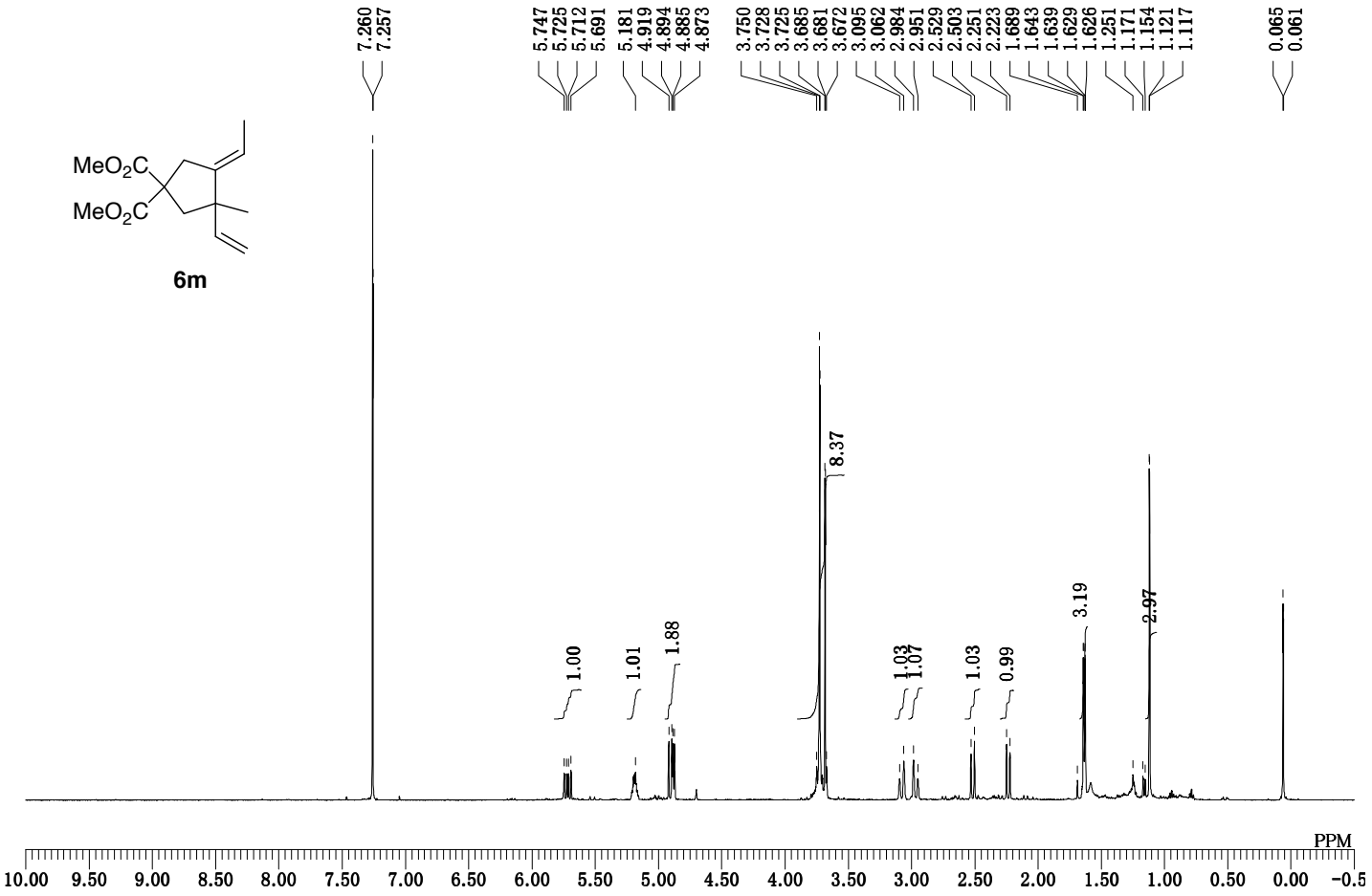
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5.691
5.181
4.919
4.894
4.885
4.873
3.750
3.728
3.725
3.685
3.681
3.672
3.095
3.062
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2.251
2.223
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1.643
1.639
1.629
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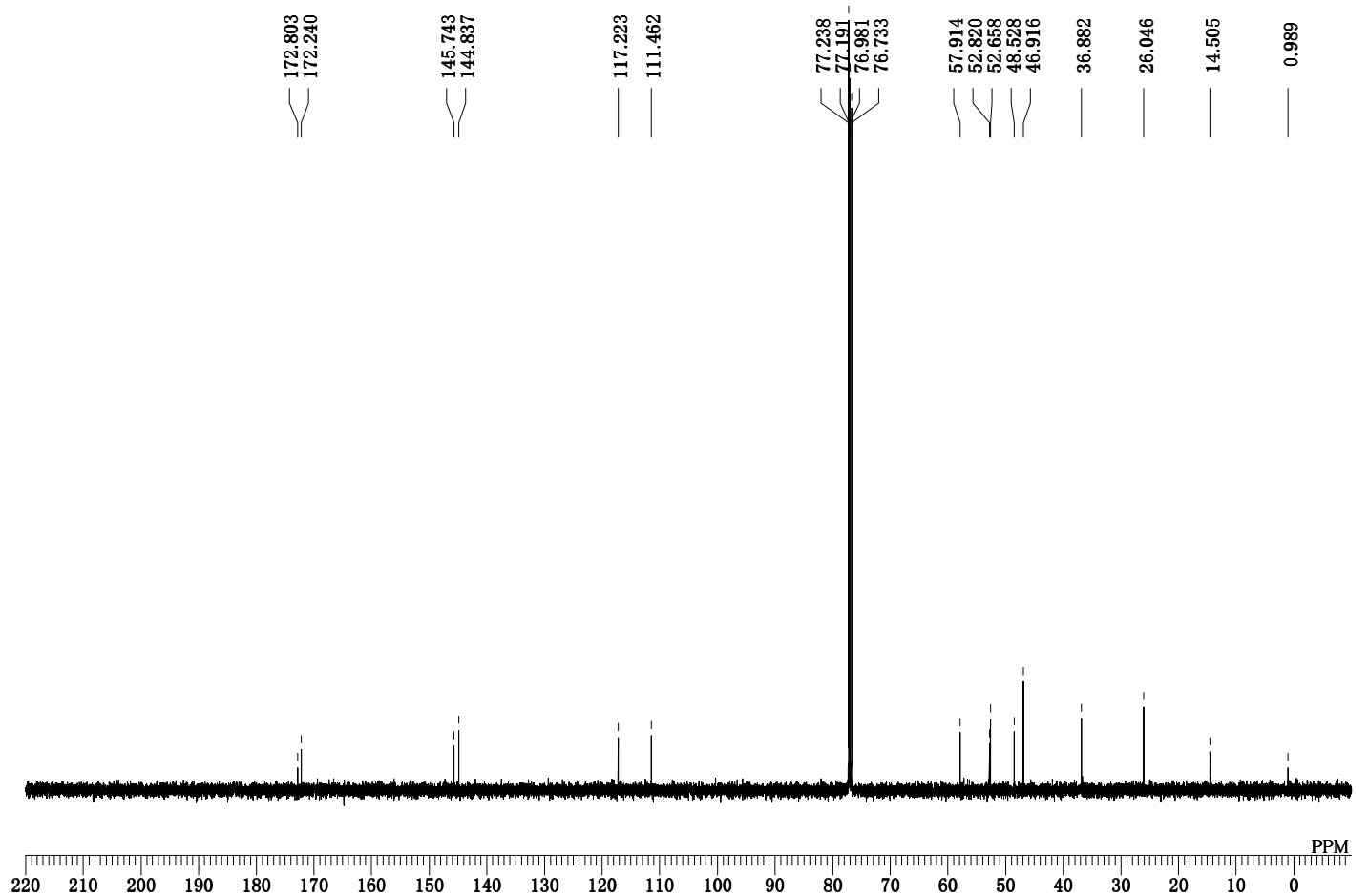
1.251
1.171
1.154
1.121
1.117
0.065
0.061
MeO2C
MeO2C
6m
8.37
1.00
1.01
1.88
1.03
1.07
1.03
0.99
3.19
2.97
PPM
10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00 -0.5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172.240
145.743
144.837
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111.462
77.238
77.191
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57.914
52.820
52.658
48.528
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36.882
26.046
14.505
0.989
PPM
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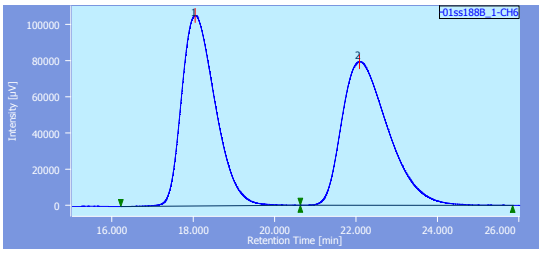
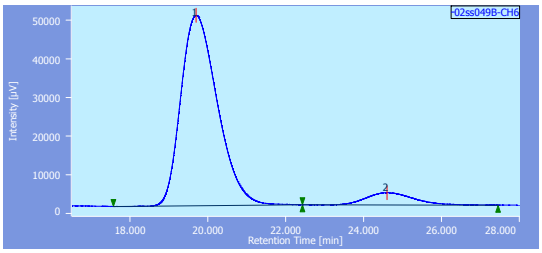
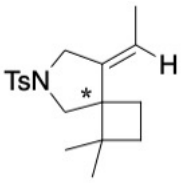


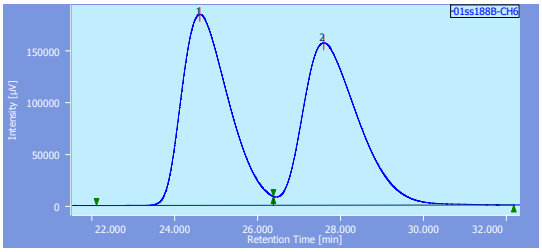
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	18.050	6037938	105280	49.103	57.022
2	Unknown	6	22.083	6258510	79350	50.897	42.978



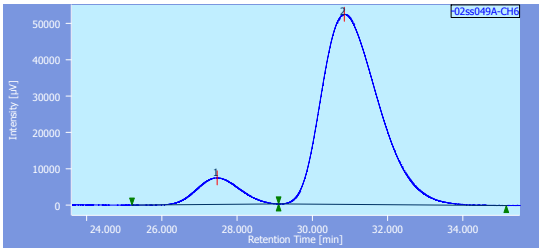
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	19.706	3221147	49243	92.258	93.937
2	Unknown	6	24.597	270308	3178	7.742	6.063



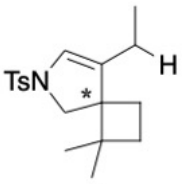
4a
85% ee



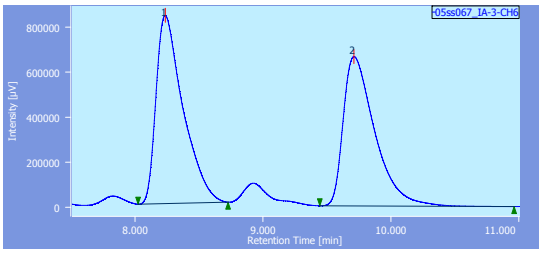
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	24.607	14487055	184048	49.974	54.049
2	Unknown	6	27.592	14502058	156473	50.026	45.951



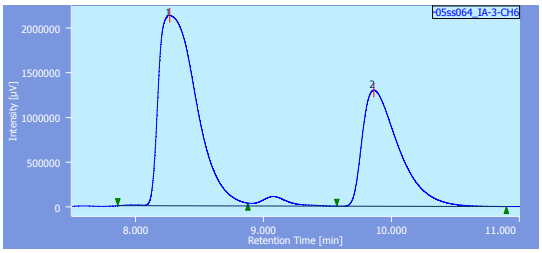
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	27.468	581490	7331	9.613	12.308
2	Unknown	6	30.845	5467300	52230	90.387	87.692



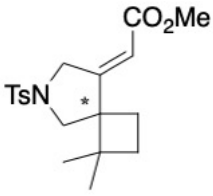
5a
81% ee



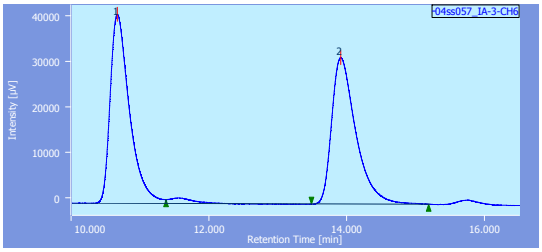
#	Peak	CH	tR [min]	Area [μV·sec]	h [μV]	Area %	h %
1	Unknown	6	8.237	12229563	835242	51.838	55.752
2	Unknown	6	9.710	11362320	662896	48.162	44.248



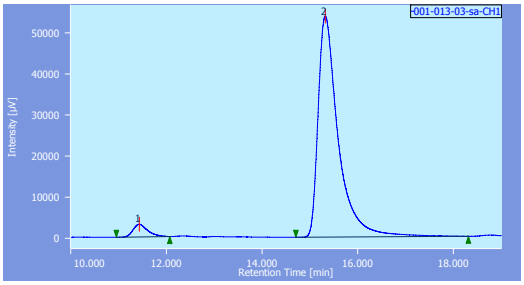
#	Peak	CH	tR [min]	Area [μV·sec]	h [μV]	Area %	h %
1	Unknown	6	8.288	43441873	2128826	62.921	62.099
2	Unknown	6	9.862	25600087	1289271	37.079	37.901



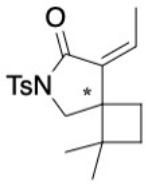
4b
26% ee



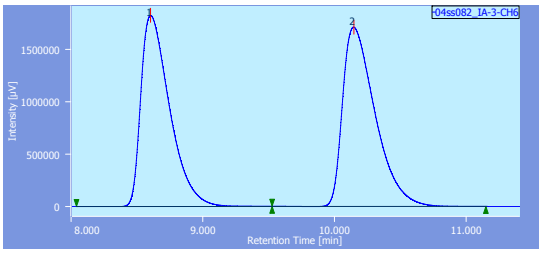
#	Peak	CH	tR [min]	Area [μV·sec]	高さ[μV]	面積%	h %
1	Unknown	6	10.673	803578	41448	50.728	56.332
2	Unknown	6	13.913	780510	32130	49.272	43.668



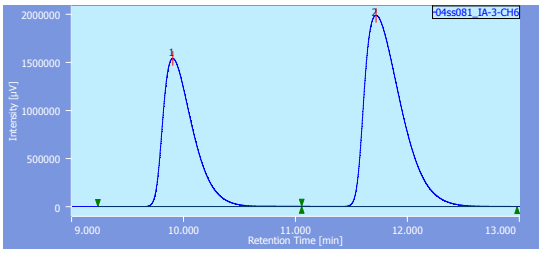
#	Peak	CH	tR [min]	Area [μV·sec]	h [μV]	Area %	h %
1	Unknown	1	11.437	66498	3093	4.058	5.437
2	Unknown	1	15.326	1572040	53794	95.942	94.563



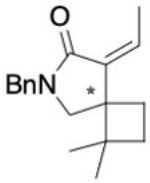
4c
92% ee



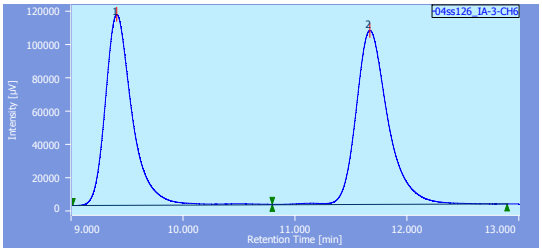
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	8.603	27610946	1823331	48.481	51.586
2	Unknown	6	10.147	29341387	1711247	51.519	48.414



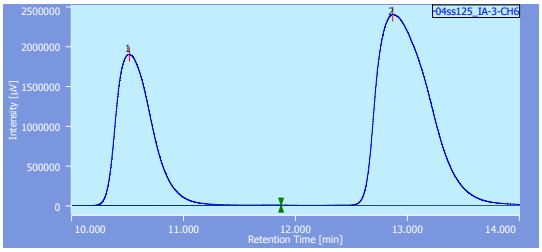
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	9.905	28584615	1539428	38.921	43.671
2	Unknown	6	11.716	44858209	1985616	61.079	56.329



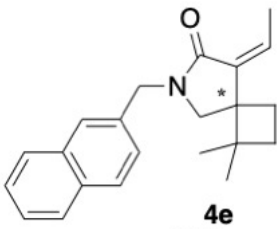
4d
22% ee



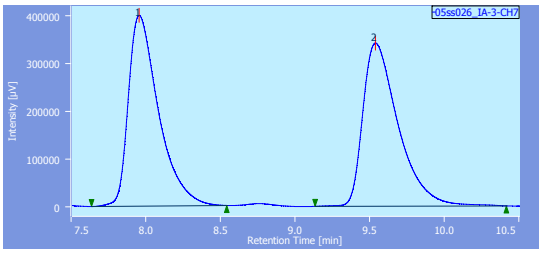
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	9.408	1913172	114722	48.025	52.311
2	Unknown	6	11.668	2070536	104587	51.975	47.689



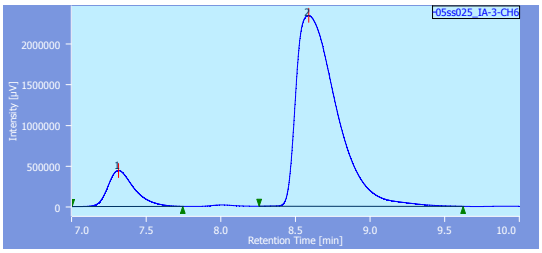
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	10.517	42265113	1898813	35.159	44.181
2	Unknown	6	12.868	77946260	2398974	64.841	55.819



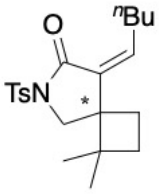
4e
30% ee



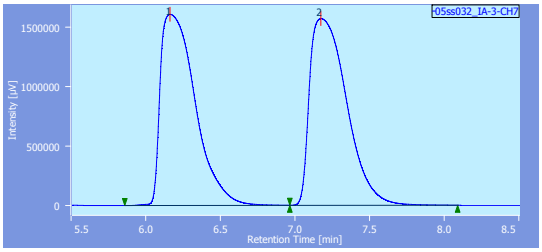
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	7	7.957	5608853	399038	49.901	53.893
2	Unknown	7	9.538	5631017	341385	50.099	46.107



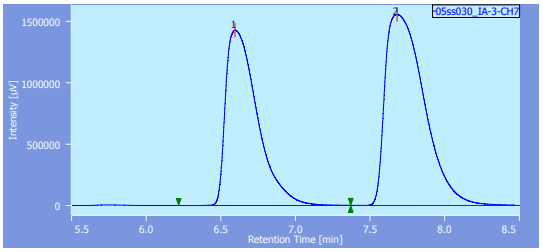
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	7.315	5422124	442423	10.978	15.897
2	Unknown	6	8.588	43969360	2340706	89.022	84.103



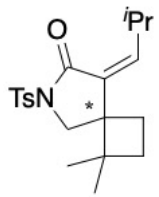
4f
78% ee



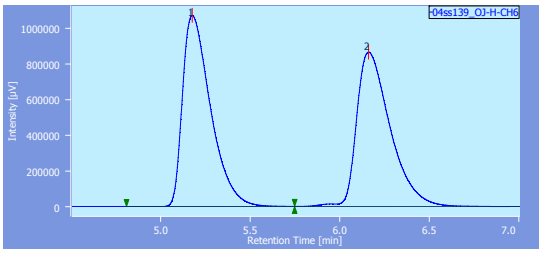
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	7	6.163	26122169	1608251	49.102	50.562
2	Unknown	7	7.173	27078096	1570538	50.898	49.438



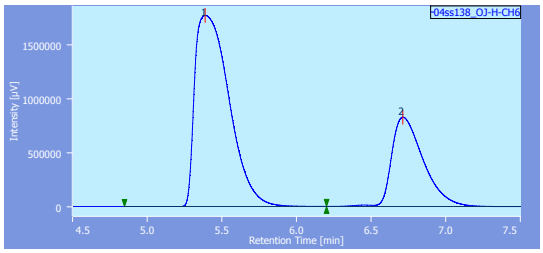
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	7	6.595	21018676	1427549	42.628	47.871
2	Unknown	7	7.680	28289048	1554514	57.372	52.129



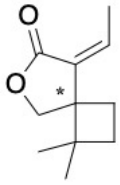
4g
15% ee



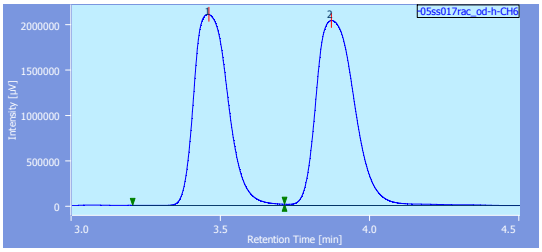
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	5.177	11683355	1070613	50.737	55.298
2	Unknown	6	6.160	11324429	865481	49.263	44.702



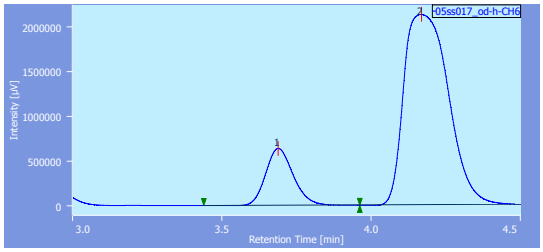
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	5.388	28314347	1770019	69.877	68.128
2	Unknown	6	6.712	12206053	828054	30.123	31.872



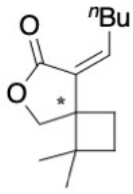
4h
40% ee



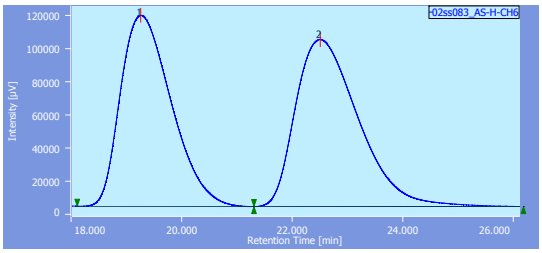
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	3.462	16585565	2103297	47.752	50.796
2	Unknown	6	3.872	18147019	2037389	52.248	49.204



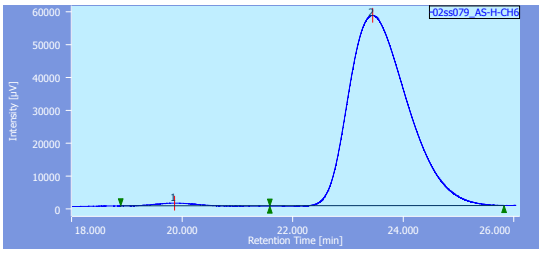
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	3.688	4048251	635082	15.544	23.016
2	Unknown	6	4.168	21998068	2124267	84.456	76.984



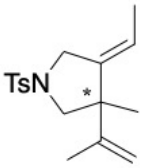
4i
69% ee



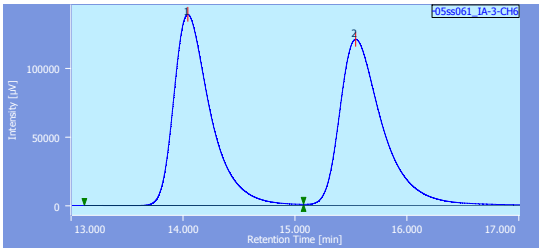
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	19.262	7345551	115145	48.104	53.386
2	Unknown	6	22.505	7924494	100642	51.896	46.645



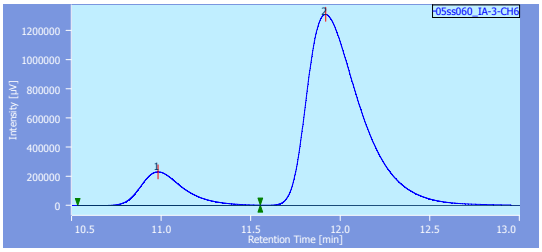
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	19.885	38659	811	0.898	1.382
2	Unknown	6	23.445	4264046	57870	99.102	98.618



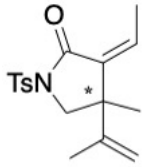
6j
98% ee



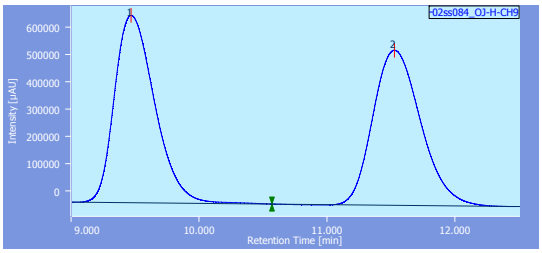
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	14.043	3169846	139049	49.781	53.513
2	Unknown	6	15.542	3197699	120790	50.219	46.487

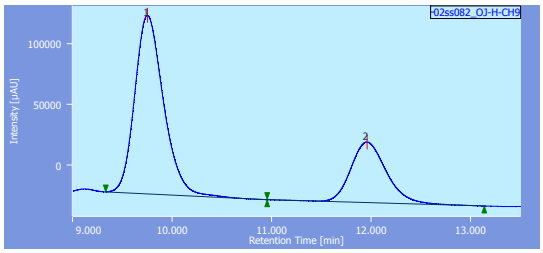


#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	6	10.982	3920109	231078	12.491	14.993
2	Unknown	6	11.918	27483128	1310155	87.509	85.007



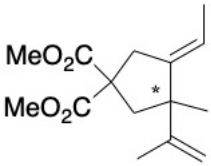
6k
75% ee



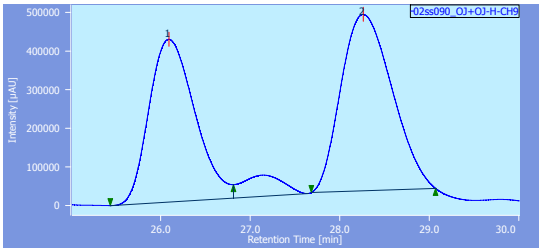


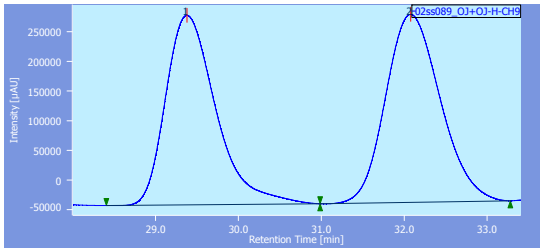
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	9	9.470	15027554	685602	50.502	54.697
2	Unknown	9	11.527	14728908	567856	49.498	45.303

#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	9	9.753	2960892	146985	70.517	74.680
2	Unknown	9	11.958	1237942	49828	29.483	25.320



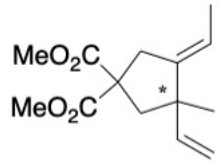
6l
41% ee



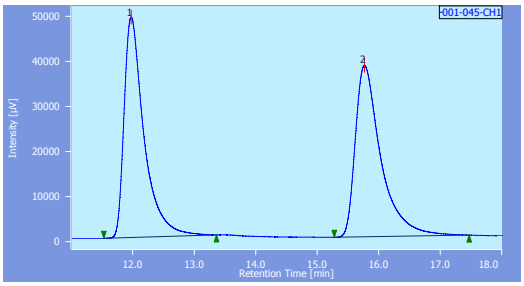


#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	9	26.093	14945539	420990	45.204	47.966
2	Unknown	9	28.282	18116538	456685	54.796	52.034

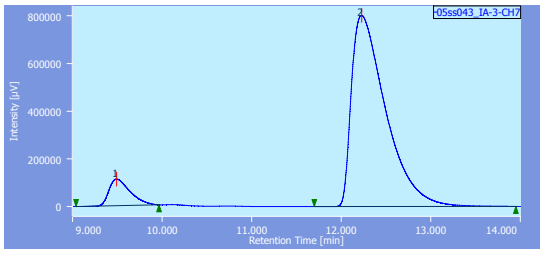
#	Peak	CH	tR [min]	Area [µV·sec]	h [µV]	Area %	h %
1	Unknown	9	29.380	13437158	319428	48.110	50.218
2	Unknown	9	32.077	14492846	316657	51.890	49.782



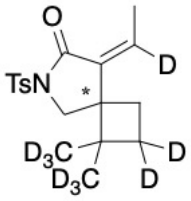
6m
3% ee



#	Peak	CH	tR [min]	Area [µV sec]	h [µV]	Area %	h %
1	Unknown	1	11.977	1096388	48875	49.990	56.225
2	Unknown	1	15.767	1096831	38052	50.010	43.775



#	Peak	CH	tR [min]	Area [µV sec]	h [µV]	Area %	h %
1	Unknown	7	9.480	1837488	112052	7.842	12.27
2	Unknown	7	12.227	21294567	800711	92.057	87.72



4c-d_9
84% ee