Rhodium-catalyzed 1,3-Acyloxy Migration and Subsequent Intramolecular [4+2] Cycloaddition of Vinylallene and Unactivated Alkyne

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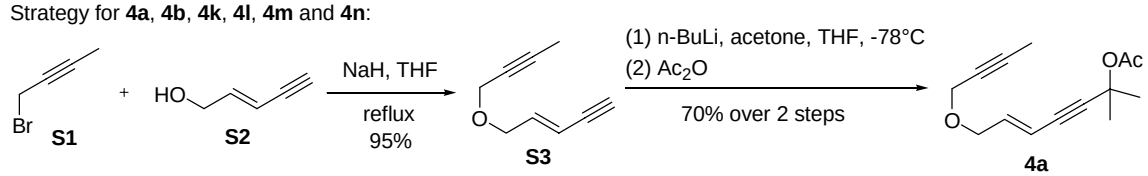
General remarks

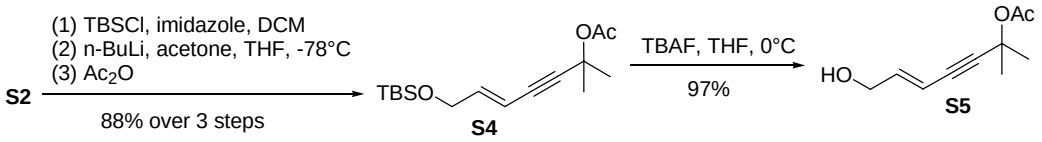
All reactions in non-aqueous media were conducted under a positive pressure of dry argon in glassware that had been oven dried prior to use unless noted otherwise. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Reagents were purchased from Aldrich, Acros, TCI, or VWR unless otherwise noted. Thin layer chromatography was performed using precoated silica gel plates (EMD Chemical Inc. 60, F254). Flash column chromatography was performed with silica gel (Sillicycle, 40-63μm). Infrared spectra (IR) were obtained as neat oils on a Bruker Equinox 55 Spectrophotometer. ^{1}H and ^{13}C Nuclear magnetic resonance spectra (NMR) were obtained on a Varian Unity-Inova 400 MHz or 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$, CD_3OD. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint),or multiplet (m), with coupling constants (*J*) in hertz. High resolution mass spectra (HRMS) were performed by Analytical Instrument Center at the School of Pharmacy or Department of Chemistry on an Electron Spray Injection (ESI) mass spectrometer.

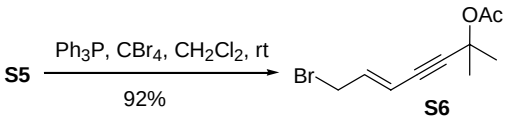
General strategies for the preparation of substrates:

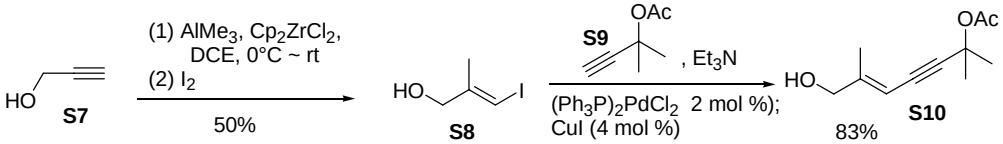
Strategy for **4a**, **4b**, **4k**, **4l**, **4m** and **4n**:

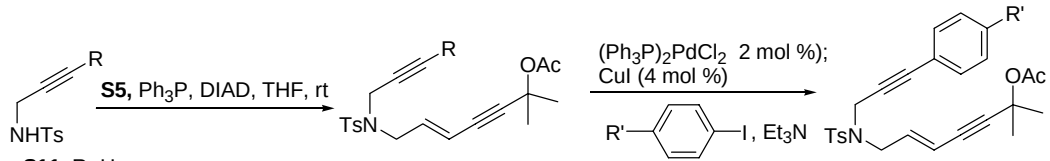


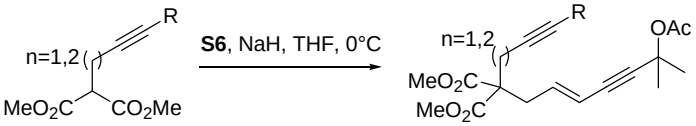
Strategy for **4c** - **4j** and **9b** - **9c**::

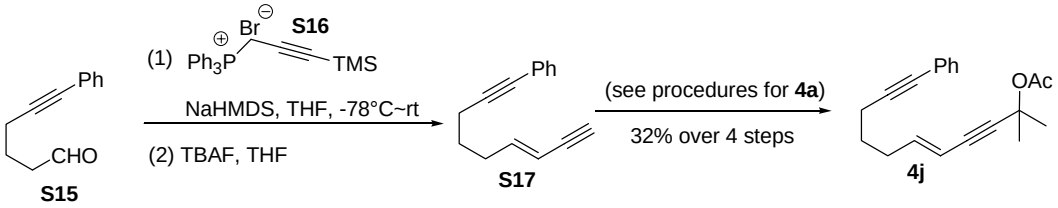






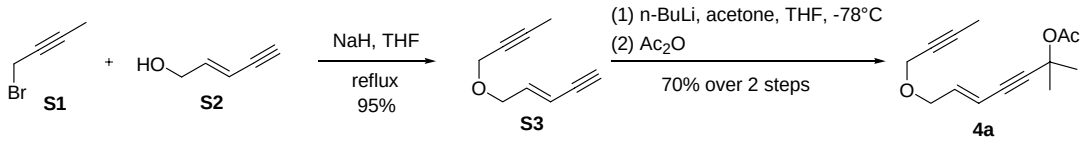






Representative experimental procedures:

Preparation of substrates **4a, 4b**, **4k**, **4l**, **4m**, and **4n**:

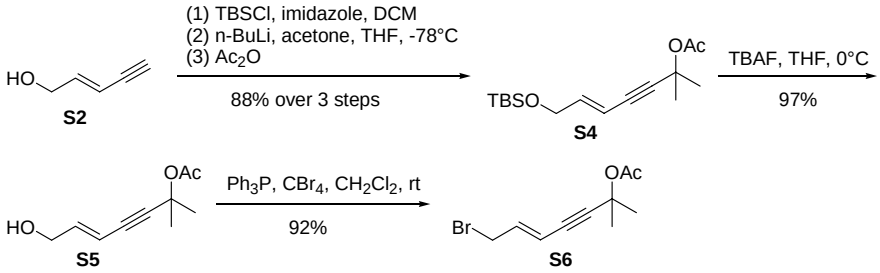


To a stirred suspension of NaH (670 mg, 16.7 mmol, 55-65% in mineral oil) in anhydrous THF (10 mL) was added commercially available alcohol **S2** (2.50 g, 30.4 mmol) in THF (15 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The solution of bromide **S1** (2.00 g, 15.2 mmol) in THF (10 mL) was added to the above reaction. The reaction mixture was heated under reflux for overnight. It was then quenched with water (30 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 20) to give the enyne **S3** (1.90 g, 95%) as a yellow oil.

To a stirred solution of enyne **S3** (465 mg, 3.47 mmol) in anhydrous THF (17 mL) was added n-BuLi in hexane (1.6 M, 2.39 mL, 3.82 mmol) at -78 °C. After stirring for 30 min at -78 °C, acetone (302 mg, 5.20 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 30 min. After the reaction mixture was cooled to 0 °C, acetic anhydride (390 mg, 3.82 mmol) was added. When the reaction was completed as determined by TLC, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (15 mL) and extracted with ethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 10) to yield **4a** (380 mg, 70% over 2 steps) as a colorless oil.

Substrates **4b**, **4k**, **4l**, **4m**, and **4n** was obtained following procedures similar to **4a**.

Preparation of **S5** and **S6**:



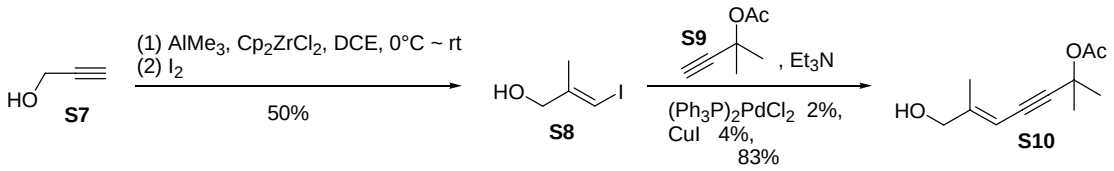
To a stirred suspension of imidazole (5.00g, 73.2 mmol) in anhydrous CH_2Cl_2 (100 mL) was added commercially available alcohol **S2** (3.00 g, 36.6 mmol) in CH_2Cl_2 (10 mL) at 0°C. TBSCl (6.62 g, 43.9 mmol) in CH_2Cl_2 (10 mL) was then added to the above solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the reaction was completed, the reaction mixture was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and concentrated under vacuum to give crude TBS-protected alcohol for the next step without purification.

Product **S4** was obtained from crude TBS-protected alcohol according to procedures described for **4a**. The yield was 88% over 3 steps.

To a stirred solution of **S4** (4.00 g, 13.5 mmol) in anhydrous THF (120 mL) was added TBAF in THF (1.0 M, 14.8 mL, 14.8 mmol) at 0 °C. The reaction mixture was stirred for 10 min at 0°C. It was then quenched with saturated aqueous ammonium chloride (60 mL) and was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 2) to yield **S5** (2.36 g, 97%) as a colorless oil.

To a stirred solution of alcohol **S5** (529 mg, 2.9 mmol) in anhydrous CH_2Cl_2 (20 mL) was added CBr_4 (1.25 g, 3.8 mmol) and PPh_3 (1.14 g, 4.4 mmol) at 0°C. The reaction mixture was stirred for 15 min at 0°C and then concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 10) to yield **S6** (650 mg, 92%) as a colorless oil.

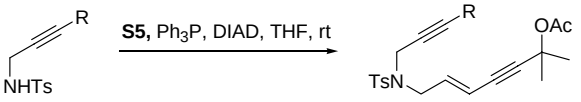
Preparation of **S10**:



To a stirred solution of vinyl iodide **S8**[1,2] (2.60 g, 13.1 mmol) and propargyl ester **S9** (1.58 g,

12.5 mmol) in anhydrous Et_3N (15 mL) was added $(Ph_3P)_2PdCl_2$ (175 mg, 0.25 mmol) and CuI (95 mg, 0.50 mmol) at rt. The reaction mixture was stirred overnight. It was then quenched with saturated aqueous ammonium chloride (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 2) to yield **S10** (2.00 g, 83%) as a colorless oil.

Preparation of substrates **4c**, **4d** and **4g**:



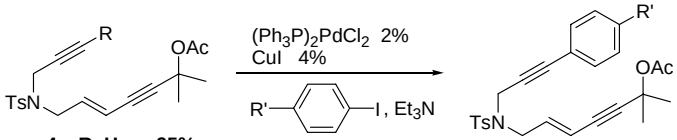
S11 R=H
S12 R=Me

4c. R=H 95%
4d. R=Me 88%

To a stirred solution of alcohol **S5** (958 mg, 5.26 mmol) and Ph_3P (1.38 g, 5.26 mmol) in anhydrous THF (25 mL) was added amide **S11**[3] (1.00 g, 4.78 mmol) in THF (5 mL) at 0 °C and stirred for 10 min. To the above solution was added diisopropyl azodicarboxylate (1.11 mL, 5.74 mmol) dropwise at 0 °C. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was quenched by addition of saturated aqueous sodium bicarbonate (20 mL) and extracted with ethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 5) to yield **4c** (1.70 g, 95%) as a colorless oil.

Following procedures similar to **4c**, substrate **4d** was prepared from **S12**[4] and substrate **4g** was prepared from **S11** and **S10**.

Preparation of substrate **4e** and **4f**:



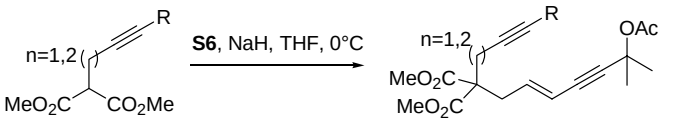
4c. R=H 95%
4d. R=Me 88%

4e. R'=H 93%
4f. R'=Br 87%

To a stirred solution of propargyl ester **4c** (208 mg, 0.56 mmol) and iodobenzene (147 mg, 0.72 mmol) in anhydrous Et_3N (6 mL) was added $(Ph_3P)_2PdCl_2$ (7.8 mg, 0.011 mmol) and CuI

(4.2 mg, 0.022 mmol) at rt. The reaction mixture was stirred overnight. It was then quenched with saturated aqueous ammonium chloride (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 2) to yield **4e** (230 g, 93%) as a yellow oil. Substrate **4f** was prepared from **4d** following similar procedure.

Preparation of **4h** and **4i**:

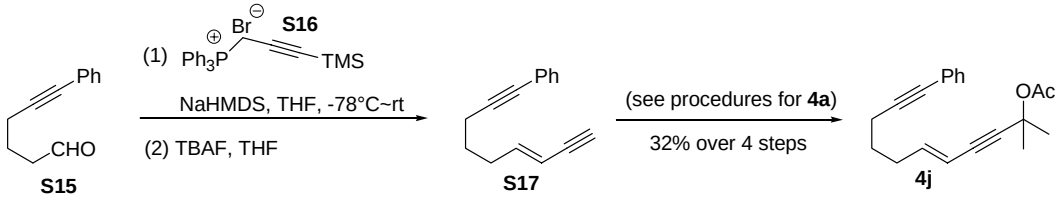


S13 n=1 R=Me
S14 n=2 R=H

4h. n=1, R=Me 79%
4i. n=2, R=H 89%

To a stirred suspension of NaH (37 mg, 0.925 mmol, 55-65% in mineral oil) in anhydrous THF (5 mL) was added **S13**[5] (169 mg, 0.918 mmol) in THF (5 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Then the mixture was cooled to 0°C, the bromide **S6** (152 mg, 0.623 mmol) in THF (10 mL) was added dropwise. The reaction mixture was stired 1 h at room temperature, then was quenched with saturated aqueous ammonium chloride (20 mL), and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (Ethyl acetate/ Hexane = 1 : 5) to give substrate **4h** (170 mg, 79%) as a colorless oil. Substrate **4i** was prepared from **S14**[6] following similar procedure.

Preparation of substrate **4j**:



S15 **S17** **4j**

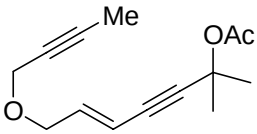
To a stirred suspension of commercially available phosphonium bromide **S16** (1.47 g, 3.24 mmol) in anhydrous THF (30 mL) was added NaHMDS in THF (1.0 M, 3.24 mL, 3.24 mmol) at 0°C.[8] The reaction mixture was allowed to warm to room temperature and stirred for 40 min. The mixture was cooled to -78 °C. A solution of aldehyde **S15**[7] (493 mg, 2.90 mmol) in THF (5 mL)

was added to the above reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was poured into H_2O (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous $NaSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (Hexane/Ethyl acetate = 99 : 1) to yield a TMS-protected enyne (390 mg, 51%) as a yellow oil.

To a stirred solution of TMS-protected enyne (390 mg, 1.47 mmol) in anhydrous THF (8 mL) was added TBAF in THF (1.0 M, 1.47 mL, 1.47 mmol) at 0 ^oC. The reaction mixture was stirred for 10 min at 0^oC and was then quenched with H_2O (10 mL). The mixture was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to yield crude enyne **S17** for next step without purification.

Substrate **4j** was prepared from crude enyne **S17** according to procedures described for **4a**. The yield was 32% over 4 steps.

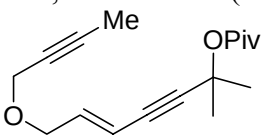
Characterization data for substrates:



4a

(E)-7-(but-2-ynyloxy)-2-methylhept-5-en-3-yn-2-yl acetate (4a)

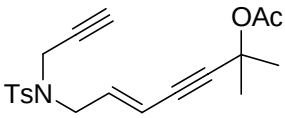
^{1}H NMR (400MHz, $CDCl_3$) δ 1.67 (s, 6H), 1.85 (t, *J*= 2.4 Hz, 3H), 2.02 (s, 3H), 4.07 (dd, *J*= 1.6, 5.6 Hz, 2H), 4.09 (q, *J*= 2.4 Hz, 2H), 5.76 (td, *J*= 1.6, 16.0 Hz, 1H), 6.15 (td, *J*= 5.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 22.2, 29.2, 58.0, 69.2, 72.6, 75.0, 82.0, 83.0, 91.1, 112.0, 139.4, 169.5. IR (film): 2988, 2851, 2360, 1742, 1365, 1241, 1192, 1136, 1112, 1016, 957, 913, 832, 732. HRMS (ESI) *m/z* calcd. For $C_{14}H_{18}O_3$ $(M+Na)^+$ 257.1148, found 257.1157.



4b

(E)-7-(but-2-ynyloxy)-2-methylhept-5-en-3-yn-2-yl pivalate (4b)

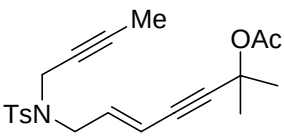
^{1}H NMR (400MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.64 (s, 6H), 1.84 (t, *J*= 2.4 Hz, 3H), 4.05 (dd, *J*= 1.6, 5.6 Hz, 2H), 4.08 (q, *J*= 2.4 Hz, 2H), 5.75 (td, *J*= 1.6, 16.0 Hz, 1H), 6.12 (td, *J*= 5.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 27.3, 29.1, 39.3, 58.1, 69.3, 72.1, 75.0, 81.7, 83.0, 91.4, 112.2, 139.2, 176.8. IR (film): 2980, 2733, 1479, 1362, 1285, 1171, 1124, 1029, 953, 846, 770, 733. HRMS (ESI) *m/z* calcd. For $C_{17}H_{24}O_3$ $(M+Na)^+$ 299.1618, found 299.1616.



4c

(E)-2-methyl-7-(4-methyl-N-(prop-2-ynyl)phenylsulfonamido)hept-5-en-3-yn-2-yl acetate (4c)

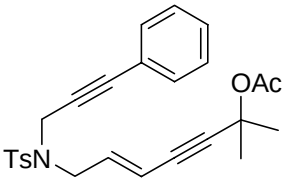
^{1}H NMR (400MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.02 (s, 3H), 2.02 (t, *J*= 2.8 Hz, 1H), 2.43 (s, 3H), 3.85 (dd, *J*= 1.2, 6.4 Hz, 2H), 4.08 (d, *J*= 2.4 Hz, 2H), 5.74 (td, *J*= 1.6, 16.0 Hz, 1H), 5.99 (td, *J*= 6.8, 15.6 Hz, 1H), 7.30 (dd, *J*= 0.8, 8.4 Hz, 2H), 7.72 (td, *J*= 2.0, 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.8, 22.2, 29.1, 36.3 48.1, 72.4, 74.3, 76.4, 81.5, 91.8, 114.4, 128.0, 129.8, 136.0, 136.9, 143.9, 169.6. IR (film): 1740, 1600, 1435, 1350, 1244, 1193, 1162, 1137, 1093, 1052, 1018, 961, 897, 817, 738, 704, 660. HRMS (ESI) *m/z* calcd. For $C_{20}H_{23}NO_4S$ $(M+Na)^+$ 396.1240, found 396.1230.



4d

(E)-7-(N-(but-2-ynyl)-4-methylphenylsulfonamido)-2-methylhept-5-en-3-yn-2-yl acetate (4d)

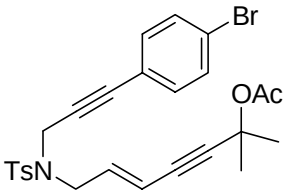
^{1}H NMR (400MHz, $CDCl_3$) δ 1.54 (t, *J*= 2.4 Hz, 3H), 1.66 (s, 6H), 2.02 (s, 3H), 2.42 (s, 3H), 3.81 (dd, *J*= 1.6, 6.4 Hz, 2H), 4.00 (q, *J*= 2.4 Hz, 2H), 5.72 (td, *J*= 1.6, 16.0 Hz, 1H), 5.99 (td, *J*= 6.4, 16.0 Hz, 1H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.72 (td, *J*= 1.6, 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.4, 21.7, 22.2, 29.1, 36.9, 48.1, 71.6, 72.4, 81.6, 82.2, 91.6, 114.0, 128.1, 129.5, 136.2, 137.3, 143.6, 169.6. IR (film): 1740, 1598, 1434, 1348, 1241, 1160, 1136, 1091, 1047, 1016, 958, 905, 815, 731, 656. HRMS (ESI) *m/z* calcd. For $C_{21}H_{25}NO_4S$ $(M+Na)^+$ 410.1397, found 410.1394.



4e

(E)-2-methyl-7-(4-methyl-N-(3-phenylprop-2-ynyl)phenylsulfonamido)hept-5-en-3-yn-2-yl acetate (4e)

^{1}H NMR (400MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.02 (s, 3H), 2.34 (s, 3H), 3.91 (dd, *J*= 1.2, 6.4 Hz, 2H), 4.29 (s, 2H), 5.77 (td, *J*= 1.2, 16.0 Hz, 1H), 6.06 (td, *J*= 6.8, 15.6 Hz, 1H), 7.03-7.09 (m, 2H), 7.20-7.31 (m, 5H), 7.76 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.6, 22.2, 29.1, 37.3, 48.5, 72.4, 81.6, 81.6, 86.2, 91.8, 114.3, 122.3, 128.0, 128.3, 128.7, 129.8, 131.7, 136.0, 137.1, 143.9, 169.6. IR (film): 2360, 2341, 1739, 1598, 1491, 1442, 1349, 1265, 1246, 1162, 1136, 1049, 1017, 959, 900, 815, 735, 703, 659. HRMS (ESI) *m/z* calcd. For $C_{26}H_{27}NO_4S$ $(M+Na)^+$ 472.1553, found 472.1551.

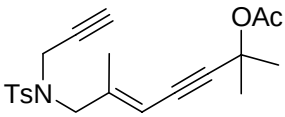


4f

(E)-7-(N-(3-(4-bromophenyl)prop-2-ynyl)-4-methylphenylsulfonamido)-2-methylhept-5-en-3-yn-2-yl acetate (4f)

^{1}H NMR (400MHz, $CDCl_3$) δ 1.66 (s, 6H), 2.02 (s, 3H), 2.35 (s, 3H), 3.90 (dd, *J*= 1.2, 6.4 Hz, 2H), 4.26 (s, 2H), 5.76 (td, *J*= 1.2, 16.0 Hz, 1H), 6.05 (td, *J*= 6.4, 16.0 Hz, 1H), 6.93 (td, *J*= 2.4, 8.8 Hz, 2H), 7.26 (d, *J*= 8.8 Hz, 2H), 7.38 (td, *J*= 2.0, 8.4 Hz, 2H), 7.74 (td, *J*= 2.0, 8.4 Hz, 2H);

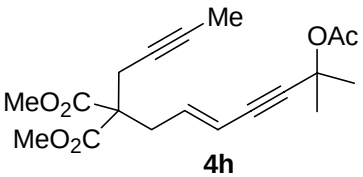
^{13}C NMR (100MHz, $CDCl_3$) δ 21.7, 22.2, 29.1, 37.2, 48.6, 72.4, 81.5, 83.0, 85.1, 91.9, 114.3, 121.2, 123.0, 128.0, 129.8, 131.6, 133.2, 136.1, 137.0, 143.9, 169.6. IR (film): 1738, 1485, 1348, 1243, 1161, 1135, 1011, 958, 898, 824, 733, 702, 660. HRMS (ESI) *m/z* calcd. For $C_{26}H_{26}BrNO_4S$ $(M+Na)^+$ 550.0658, found 550.0667.



4g

(E)-2,6-dimethyl-7-(4-methyl-N-(prop-2-ynyl)phenylsulfonamido)hept-5-en-3-yn-2-yl acetate (4g)

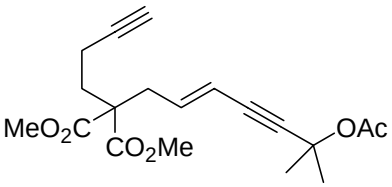
^{1}H NMR (400MHz, $CDCl_3$) δ 1.69 (s, 6H), 1.90 (s, 3H), 1.97 (t, *J*= 2.4 Hz, 1H), 2.02 (s, 3H), 2.43 (s, 3H), 3.77 (s, 2H), 4.02 (d, *J*= 2.4 Hz, 2H), 5.51-5.54 (m, 1H), 7.27-7.32 (m, 2H), 7.70-7.75 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 17.2, 21.8, 22.2, 29.3, 36.0, 52.6, 72.6, 74.4, 76.2, 81.0, 95.0, 109.4, 128.0, 129.7, 136.1, 143.9, 145.2, 169.6. IR (film): 3296, 2987, 1738, 1598, 1432, 1349, 1268, 1243, 1160, 1136, 1112, 1092, 1014, 958, 899, 816, 736, 703, 660. HRMS (ESI) *m/z* calcd. For $C_{21}H_{25}NO_4S$ $(M+Na)^+$ 410.1397, found 410.1402.



4h

(E)-dimethyl 2-(6-acetoxy-6-methylhept-2-en-4-ynyl)-2-(but-2-ynyl)malonate (4h)

^{1}H NMR (400MHz, $CDCl_3$) δ 1.66 (s, 6H), 1.75 (t, *J*= 2.4 Hz, 3H), 2.02 (s, 3H), 2.73 (q, *J*= 2.4 Hz, 2H), 2.83 (d, *J*= 7.6 Hz, 2H), 3.74 (s, 6H), 5.63 (d, *J*=16.0 Hz, 1H), 5.91 (td, *J*= 7.6, 15.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.7, 22.2, 23.4, 29.2, 36.0, 53.1, 57.3, 72.6, 73.2, 79.5, 82.2, 90.1, 114.0, 137.7, 169.6, 170.4. IR (film): 2955, 1736, 1437, 1377, 1265, 1244, 1209, 1136, 1099, 1066, 1017, 958, 736, 703. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}O_6$ $(M+Na)^+$ 371.1465, found 371.1472.

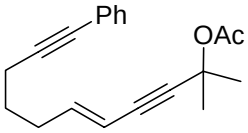


4i

(E)-dimethyl 2-(6-acetoxy-6-methylhept-2-en-4-ynyl)-2-(but-3-ynyl)malonate (4i)

^{1}H NMR (400MHz, $CDCl_3$) δ 1.66 (s, 6H), 1.97 (t, *J*= 2.0 Hz, 1H), 2.02 (s, 3H), 2.11-2.22 (m,

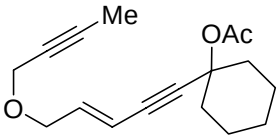
4H), 2.71 (dd, *J*= 1.2, 7.6 Hz, 2H), 3.74 (s, 6H), 5.58 (d, *J*=15.6 Hz, 1H), 5.91 (td, *J*= 7.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.2, 22.2, 29.2, 31.8, 36.9, 52.9, 57.1, 69.2, 72.6, 82.1, 83.1, 90.3, 113.8, 137.6, 169.6, 171.0. IR (film): 2954, 1731, 1435, 1366, 1241, 1197, 1135, 1079, 1016, 959, 834, 737, 702. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}O_6$ $(M+Na)^+$ 371.1465, found 371.1480.



4j

(E)-2-methyl-11-phenylundeca-5-en-3,10-diyn-2-yl acetate (4j)

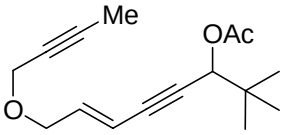
^{1}H NMR (400MHz, $CDCl_3$) δ 1.64-1.73 (m, 2H), 1.67 (s, 6H), 2.01 (s, 3H), 2.27 (dt, *J*= 7.2, 7.2 Hz, 2H), 2.41 (t, *J*= 7.2 Hz, 2H), 5.56 (d, *J*= 15.6 Hz, 1H), 6.15 (td, *J*= 7.2, 16.0 Hz, 1H), 7.24-7.30 (m, 3H), 7.35-7.41 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.0, 22.2, 27.8, 29.3, 32.2, 72.7, 81.4, 82.8, 89.2, 89.7, 110.1, 124.1, 127.8, 128.4, 131.8, 144.2, 169.6. IR (film): 1740, 1489, 1440, 1365, 1240, 1192, 1134, 1014, 956, 829, 756, 736, 692. HRMS (ESI) *m/z* calcd. For $C_{20}H_{22}O_2$ $(M+Na)^+$ 317.1512, found 317.1515.



4k

(E)-1-(5-(but-2-ynyloxy)pent-3-en-1-ynyl)cyclohexyl acetate (4k)

^{1}H NMR (400MHz, $CDCl_3$) δ 1.26-1.40 (m, 1H), 1.46-1.56 (m, 1H), 1.56-1.66 (m, 4H), 1.79-1.89 (m, 2H), 1.85 (t, *J*= 2.4 Hz, 3H), 2.03 (s, 3H), 2.07-2.18 (m, 2H), 4.08 (dd, *J*= 1.6, 5.6 Hz, 2H), 4.10 (q, *J*= 2.4 Hz, 2H), 5.80 (td, *J*= 1.6, 16.0 Hz, 1H), 6.16 (td, *J*= 5.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 22.2, 22.8, 25.4, 37.3, 58.1, 69.2, 75.0, 76.0, 83.0, 84.2, 90.1, 112.2, 139.3, 169.4. IR (film): 2937, 1737, 1446, 1367, 1302, 1266, 1231, 1184, 1134, 1074, 1019, 962, 913, 735, 703. HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}O_3$ $(M+Na)^+$ 297.1461, found 297.1458.

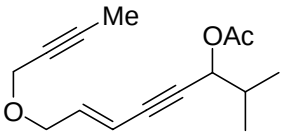


4l

(E)-8-(but-2-ynyloxy)-2,2-dimethyloct-6-en-4-yn-3-yl acetate (4l)

^{1}H NMR (400MHz, $CDCl_3$) δ 0.99 (s, 9H), 1.84 (t, *J*= 2.4 Hz, 3H), 2.09 (s, 3H), 4.07 (dd, *J*= 1.6, 5.6 Hz, 2H), 4.09 (q, *J*= 2.4 Hz, 2H), 5.20 (d, *J*= 1.6 Hz, 1H), 5.75 (dtd, *J*= 1.6, 1.6, 16.0 Hz, 1H),

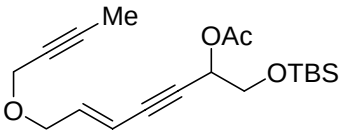
6.17 (td, *J*= 5.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 21.1, 25.8, 35.5, 58.2, 69.2, 72.5, 75.0, 83.1, 83.7, 86.5, 111.7, 139.9, 170.4. IR (film): 2967, 1738, 1369, 1234, 1165, 1139, 1076, 1017, 976, 909, 736, 702. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}O_3$ $(M+Na)^+$ 285.1461, found 285.1464.



4m

(E)-8-(but-2-ynyloxy)-2-methyloct-6-en-4-yn-3-yl acetate (4m)

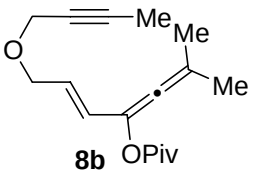
^{1}H NMR (400MHz, $CDCl_3$) δ 0.99 (d, *J*= 6.8 Hz, 3H), 1.02 (d, *J*= 6.8 Hz, 3H), 1.86 (t, *J*= 2.4 Hz, 3H), 1.94-2.05 (m, 1H), 2.09 (s, 3H), 4.08 (dd, *J*= 1.6, 5.6 Hz, 2H), 4.10 (q, *J*= 2.4 Hz, 2H), 5.33 (dd, *J*= 2.0, 5.6 Hz, 1H), 5.77 (dtd, *J*= 2.0, 2.0, 16.0 Hz, 1H), 6.19 (td, *J*= 5.6, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 17.8, 18.4, 21.2, 32.7, 58.2, 69.2, 69.6, 75.0, 83.1, 83.9, 86.2, 111.6, 140.0, 170.3. IR (film): 2967, 1738, 1446, 1371, 1355, 1229, 1168, 1111, 1077, 1018, 981, 954, 904, 737. HRMS (ESI) *m/z* calcd. For $C_{15}H_{20}O_3$ $(M+Na)^+$ 271.1305, found 271.1313.



4n

(E)-7-(but-2-ynyloxy)-1-(tert-butyldimethylsilyloxy)hept-5-en-3-yn-2-yl acetate (4n)

^{1}H NMR (400MHz, $CDCl_3$) δ 0.08 (d, *J*=1.6Hz, 6H), 0.89 (s, 9H), 1.86 (t, *J*= 2.0 Hz, 3H), 2.10 (s, 3H), 3.80 (d, *J*= 1.6 Hz, 1H), 3.82 (s, 1H), 4.06-4.12 (m, 4H), 5.56 (dt, *J*= 2.0, 6.8 Hz, 1H), 5.75 (qd, *J*= 1.6, 16.0 Hz, 1H), 6.19 (td, *J*= 5.2, 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ -5.1, 3.8, 18.5, 21.2, 25.9, 58.2, 65.0, 65.5, 69.1, 74.9, 83.1, 84.1, 85.0, 111.2, 140.5, 170.1. IR (film): 2952, 2929, 2857, 1747, 1472, 1370, 1252, 1227, 1132, 1079, 1040, 954, 836, 778. HRMS (ESI) *m/z* calcd. For $C_{19}H_{30}O_4Si$ $(M+Na)^+$ 373.1806, found 373.1801.



8b

(E)-7-(but-2-ynyloxy)-2-methylhepta-2,3,5-trien-4-yl pivalate (8b)

Allene **8b** was obtained as an unseparable mixture with isomer enyne **4b** (**4b**/**8b**=1:2).

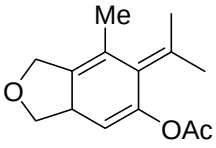
^{1}H NMR (400MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.83 (s, 6H), 1.84-1.87 (m, 3H), 4.04-4.13 (m, 4H),

5.69 (td, *J*= 6.0, 16.0 Hz, 1H), 6.07 (d, *J*= 16.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 3.8, 21.4, 27.5, 39.4, 58.0, 69.7, 75.3, 82.7, 108.3, 118.6, 123.8, 127.2, 175.9, 196.1.

General procedures for the Rh-catalyzed tandem acyloxy migration cycloaddition:

Condition A: To a solution of $[Rh(CO)_2Cl]_2$ (1.9 mg, 5 mol %) in DCE (0.05 M) was added substrate (0.10 mmol). The solution was stirred at 80^{o}C until the reaction was complete as determined by TLC analysis. Then the reaction mixture was added to the solution of K_2CO_3 (28 mg, 0.20 mmol) in methanol (2 mL) at 0 ^{o}C. After the reaction was completed, the mixture was quenched with saturated aqueous ammonium chloride (5 mL) and was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel to afford the corresponding cyclohexenone.

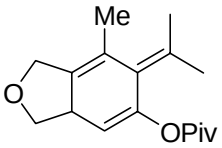
Condition B: To a solution of $[Rh(CO)_2Cl]_2$ (1.9 mg, 5 mol %) and $[(CF_3)_2CHO]_3P$ (10.6 mg, 20 mol %) in DCE (0.05 M) was added propargylic ester (0.10 mmol). The solution was stirred at 80^{o}C until the reaction was complete as determined by TLC analysis. Then the reaction mixture was added to the solution of K_2CO_3 (28 mg, 0.20 mmol) in methanol (2 mL) at 0 ^{o}C. After the reaction was completed, the mixture was quenched with saturated aqueous ammonium chloride (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel to afford the corresponding cyclohexenone.



5a

7-methyl-6-(propan-2-ylidene)-1,3,3a,6-tetrahydroisobenzofuran-5-yl acetate (5a)

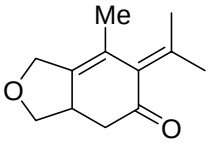
^{1}H NMR (400MHz, $CDCl_3$) δ 1.88 (s, 3H), 1.89 (s, 3H), 1.91-1.94 (m, 3H), 2.16 (s, 3H), 3.20-3.31 (m, 1H), 3.34 (dd, *J*= 7.6, 11.6 Hz, 1H), 4.26 (t, *J*= 7.6 Hz, 1H), 4.37 (d, *J*= 14.0 Hz, 1H), 4.44 (d, *J*= 13.6 Hz, 1H), 5.47 (d, *J*= 1.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.7, 21.1, 23.3, 24.4, 42.0, 69.1, 72.2, 113.4, 125.6, 128.4, 130.9, 139.3, 150.8, 168.7. IR (film): 2851, 1759, 1683, 1438, 1368, 1270, 1203, 1157, 1073, 1038, 1017, 958, 918, 820, 736. HRMS (ESI) *m/z* calcd. For $C_{14}H_{18}O_3$ $(M+Na)^+$ 257.1148, found 257.1158.



5b

7-methyl-6-(propan-2-ylidene)-1,3,3a,6-tetrahydroisobenzofuran-5-yl pivalate (5b)

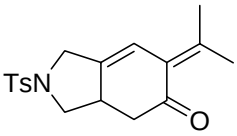
^{1}H NMR (400MHz, $CDCl_3$) δ 1.27 (s, 9H), 1.87 (s, 3H), 1.88 (s, 3H), 1.92-1.96 (m, 3H), 3.20-3.30 (m, 1H), 3.34 (dd, *J*= 7.6, 11.2 Hz, 1H), 4.25 (t, *J*= 8.0 Hz, 1H), 4.36 (d, *J*= 13.6 Hz, 1H), 4.44 (d, *J*= 13.6 Hz, 1H), 5.41 (d, *J*= 1.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.6, 23.7, 24.0, 27.5, 39.2, 42.0, 69.0, 72.1, 113.4, 125.8, 128.8, 130.7, 139.3, 151.5, 176.4. IR (film): 2976, 2855, 1748, 1687, 1640, 1482, 1463, 1398, 1368, 1274, 1157, 1128, 1112, 1074, 1039, 924, 835, 764, 738. HRMS (ESI) *m/z* calcd. For $C_{17}H_{24}O_3$ $(M+Na)^+$ 299.1618, found 299.1631.



7a

7-methyl-6-(propan-2-ylidene)-3,3a,4,6-tetrahydroisobenzofuran-5(1H)-one (7a)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.84-1.87 (m, 3H), 1.90 (s, 3H), 2.07 (dd, *J*= 10.8, 18.0 Hz, 1H), 2.11 (s, 3H), 2.60 (dd, *J*= 6.4, 18.0 Hz, 1H), 2.92-3.06 (m, 1H), 3.38 (t, *J*= 8.4 Hz, 1H), 4.30 (t, *J*= 8.4 Hz, 1H), 4.37 (d, *J*= 14.0 Hz, 1H), 4.47 (d, *J*= 14.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.4, 23.2, 25.0, 38.1, 41.5, 69.5, 74.8, 123.8, 134.6, 141.5, 143.1, 203.5. IR (film): 2936, 2844, 2360, 1683, 1596, 1433, 1365, 1331, 1302, 1225, 1193, 1167, 1107, 1074, 1037, 1000, 979, 922, 876, 802, 700. HRMS (ESI) *m/z* calcd. For $C_{12}H_{16}O_2$ $(M+Na)^+$ 215.1043, found 215.1041.

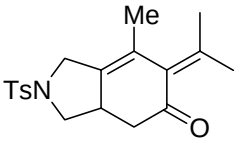


7c

6-(propan-2-ylidene)-2-tosyl-2,3,3a,4-tetrahydro-1H-isoindol-5(6H)-one (7c)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.89 (s, 3H), 2.16 (s, 3H), 2.19 (dd, *J*= 12.4, 13.6 Hz, 1H), 2.44 (s, 3H), 2.62 (dd, *J*= 5.6, 13.6 Hz, 1H), 2.70 (t, *J*= 9.6 Hz, 1H), 2.88-3.04 (m, 1H), 3.84 (d, *J*= 15.2 Hz, 1H), 3.89 (dd, *J*= 7.6, 9.2 Hz, 1H), 4.19 (d, *J*= 15.2 Hz, 1H), 6.44 (q, *J*= 2.4 Hz, 1H), 7.34 (d, *J*= 8.0 Hz, 2H), 7.72 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.8, 23.1, 23.7, 39.1, 44.3, 51.2, 54.7, 119.6, 127.0, 127.9, 130.1, 133.3, 137.1, 144.1, 146.9, 199.1. IR (film): 3055, 2935, 1681, 1585, 1451, 1342, 1289, 1265, 1214, 1161, 1093, 1056, 1036, 985,

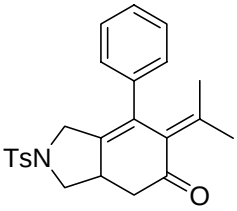
923, 868, 824, 810, 736, 705, 667. HRMS (ESI) *m/z* calcd. For $C_{18}H_{21}NO_3S$ $(M+Na)^+$ 354.1134, found 354.1125.



7d

7-methyl-6-(propan-2-ylidene)-2-tosyl-2,3,3a,4-tetrahydro-1H-isoindol-5(6H)-one (7d)

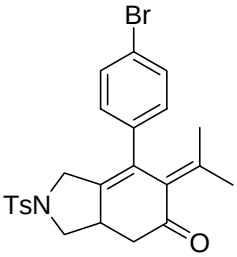
Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.79-1.83 (m, 3H), 1.85 (s, 3H), 1.93 (dd, *J*= 10.8, 18.0 Hz, 1H), 2.07 (s, 3H), 2.45 (s, 3H), 2.55 (dd, *J*= 6.4, 17.6 Hz, 1H), 2.62 (t, *J*= 8.8 Hz, 1H), 2.92-3.08 (m, 1H), 3.68 (d, *J*= 14.8 Hz, 1H), 3.81 (dd, *J*= 8.4, 9.2 Hz, 1H), 4.04 (d, *J*= 14.4 Hz, 1H), 7.36 (dd, *J*= 0.8, 8.0 Hz, 2H), 7.73 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.4, 21.8, 23.2, 25.0, 36.8, 42.0, 50.4, 54.2, 126.5, 128.2, 130.0, 132.3, 134.2, 137.2, 143.8, 144.2, 202.3. IR (film): 2923, 1683, 1598, 1345, 1266, 1163, 1094, 1033, 816, 736, 704, 666. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}NO_3S$ $(M+Na)^+$ 368.1291, found 368.1292.



7e

7-phenyl-6-(propan-2-ylidene)-2-tosyl-2,3,3a,4-tetrahydro-1H-isoindol-5(6H)-one (7e)

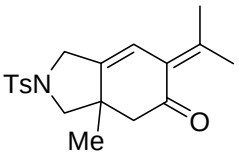
Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.33 (s, 3H), 2.10 (s, 3H), 2.12 (dd, *J*= 11.6, 17.6 Hz, 1H), 2.43 (s, 3H), 2.61 (dd, *J*= 5.6, 17.6 Hz, 1H), 2.99 (dd, *J*= 5.6, 10.0 Hz, 1H), 3.08-3.20 (m, 1H), 3.57 (dd, *J*= 8.4, 10.0 Hz, 1H), 3.89 (dd, *J*= 2.0, 14.4 Hz, 1H), 4.18 (dd, *J*= 1.2, 14.8 Hz, 1H), 7.07-7.14 (m, 2H), 7.22-7.28 (m, 1H), 7.29-7.37 (m, 4H), 7.65-7.71 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.8, 23.5, 25.5, 37.5, 42.7, 51.4, 52.6, 127.5, 127.7, 128.2, 128.9, 130.0, 132.3, 132.8, 133.0, 138.0, 140.1, 144.2, 147.8, 202.1. IR (film): 1682, 1597, 1440, 1344, 1160, 1092, 1034, 815, 764, 734, 701, 665. HRMS (ESI) *m/z* calcd. For $C_{24}H_{25}NO_3S$ $(M+Na)^+$ 430.1447, found 430.1459.



7f

7-(4-bromophenyl)-6-(propan-2-ylidene)-2-tosyl-2,3,3a,4-tetrahydro-1H-isoindol-5(6H)-one (7f)

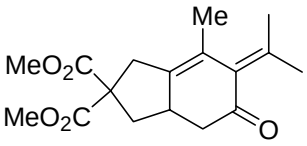
Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.35 (s, 3H), 2.10 (s, 3H), 2.13 (dd, *J*= 11.6, 17.6 Hz, 1H), 2.44 (s, 3H), 2.62 (dd, *J*= 5.6, 17.6 Hz, 1H), 2.98 (dd, *J*= 5.2, 10.0 Hz, 1H), 3.07-3.20 (m, 1H), 3.57 (dd, *J*= 8.4, 9.6 Hz, 1H), 3.83 (dd, *J*= 2.0, 14.8 Hz, 1H), 4.14 (d, *J*= 15.2 Hz, 1H), 6.99 (td, *J*= 2.4, 8.4 Hz, 2H), 7.34 (d, *J*= 8.0 Hz, 2H), 7.46 (td, *J*= 2.4, 8.4 Hz, 2H), 7.68 (d, *J*= 8.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.8, 23.4, 25.7, 37.6, 42.5, 51.3, 52.6, 121.4, 128.2, 129.4, 130.1, 132.0, 132.1, 132.2, 132.4, 138.8, 139.0, 144.3, 148.1, 201.7. IR (film): 2923, 1683, 1597, 1488, 1344, 1266, 1161, 1092, 1035, 1009, 814, 735, 707, 665. HRMS (ESI) *m/z* calcd. For $C_{24}H_{24}BrNO_3S$ $(M+Na)^+$ 508.0552, found 508.0558.



7g

3a-methyl-6-(propan-2-ylidene)-2-tosyl-2,3,3a,4-tetrahydro-1H-isoindol-5(6H)-one (7g)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.89 (s, 3H), 2.18 (s, 3H), 2.36 (d, *J*= 13.6 Hz, 1H), 2.44 (s, 3H), 2.47 (d, *J*= 13.6 Hz, 1H), 2.85 (d, *J*= 8.8 Hz, 1H), 3.50 (d, *J*= 9.2 Hz, 1H), 3.83 (d, *J*= 14.8 Hz, 1H), 4.24 (d, *J*= 15.2 Hz, 1H), 6.34 (s, 1H), 7.34 (d, *J*= 8.4 Hz, 2H), 7.73 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.8, 23.2, 23.8, 24.3, 44.0, 50.5, 51.5, 61.2, 118.3, 126.6, 127.9, 130.0, 133.4, 140.8, 144.0, 147.3, 199.0. IR (film): 2924, 1687, 1597, 1345, 1290, 1267, 1163, 1093, 1047, 815, 736, 705, 666. HRMS (ESI) *m/z* calcd. For $C_{19}H_{23}NO_3S$ $(M+Na)^+$ 368.1291, found 368.1296.

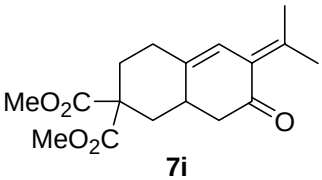


7h

Dimethyl-7-methyl-5-oxo-6-(propan-2-ylidene)-3a,4,5,6-tetrahydro-1H-indene-2,2(3H)-dicarboxylate (7h)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.81 (dd, *J*= 10.0, 12.8 Hz, 1H), 1.86 (s, 6H), 2.00 (dd, *J*= 11.2, 17.6 Hz, 1H), 2.07 (s, 3H), 2.63 (dd, *J*= 5.6, 17.6 Hz, 1H), 2.72 (ddd, *J*= 0.8, 8.0, 12.8 Hz, 1H), 2.78-2.92 (m, 1H), 2.96 (d, *J*= 18.4 Hz, 1H), 3.06 (d, *J*= 18.4 Hz, 1H), 3.75 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.5, 23.1, 25.1, 36.8, 37.9, 40.9, 44.3, 53.1, 53.1, 60.2, 125.9, 134.9, 141.2, 142.0, 172.1, 172.2, 204.1. IR (film): 2954, 1732, 1681, 1598, 1434,

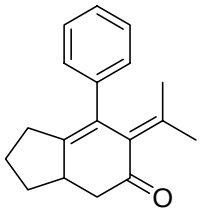
1254, 1200, 1172, 1105, 1066, 1001, 957, 868, 800, 734, 702. HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}O_5$ $(M+Na)^+$ 329.1359, found 329.1363.



7i

Dimethyl-7-oxo-6-(propan-2-ylidene)-3,4,6,7,8,8a-hexahydronaphthalene-2,2(1H)-dicarboxylate (7i)

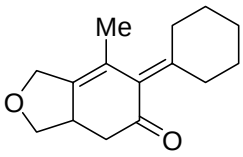
Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.56 (t, *J*= 12.8 Hz, 1H), 1.80 (dt, *J*= 4.4, 13.2 Hz, 1H), 1.88 (s, 3H), 2.09 (s, 3H), 2.20-2.33 (m, 1H), 2.31 (dd, *J*= 9.6, 14.0 Hz, 1H), 2.35-2.43 (m, 1H), 2.43-2.56 (m, 2H), 2.65 (dd, *J*= 6.0, 13.6 Hz, 1H), 2.69-2.80 (m, 1H), 3.72 (s, 3H), 3.77 (s, 3H), 6.25 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 22.0, 23.1, 30.7, 32.0, 35.5, 39.2, 47.5, 52.9, 53.1, 54.9, 120.9, 129.3, 137.3, 141.5, 171.2, 172.3, 201.1. IR (film): 2954, 1730, 1688, 1434, 1295, 1248, 1157, 1087, 1024, 864, 735. HRMS (ESI) *m/z* calcd. For $C_{17}H_{22}O_5$ $(M+Na)^+$ 329.1359, found 329.1357.



7j

7-phenyl-6-(propan-2-ylidene)-2,3,3a,4-tetrahydro-1H-inden-5(6H)-one (7j)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.42-1.53 (m, 1H), 1.57-1.70 (m, 1H), 1.76-1.88 (m, 1H), 1.98-2.09 (m, 1H), 2.05-2.15 (m, 4H), 2.38-2.49 (m, 1H), 2.59 (dd, *J*= 5.2, 17.6 Hz, 1H), 2.62-2.73 (m, 1H), 2.84-2.97 (m, 1H), 7.14-7.25 (m, 3H), 7.25-7.32 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 23.1, 25.2, 25.8, 31.4, 32.5, 38.3, 44.2, 126.3, 128.3, 128.4, 130.6, 134.8, 141.7, 143.9, 148.4, 205.6. IR (film): 2952, 1682, 1598, 1492, 1443, 1266, 1236, 1207, 1171, 1037, 762, 736, 701. HRMS (ESI) *m/z* calcd. For $C_{18}H_{20}O$ $(M+Na)^+$ 275.1406, found 275.1416.

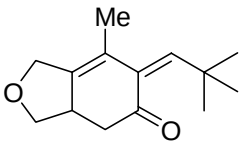


7k

6-cyclohexylidene-7-methyl-3,3a,4,6-tetrahydroisobenzofuran-5(1H)-one (7k)

Condition A ^{1}H NMR (400MHz, $CDCl_3$) δ 1.50-1.80 (m, 6H), 1.82-1.88 (m, 3H), 2.05 (dd, *J*=

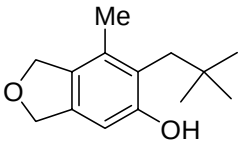
10.0, 17.6 Hz, 1H), 2.12-2.22 (m, 1H), 2.24-2.35 (m, 1H), 2.54-2.72 (m, 3H), 2.96-3.09 (m, 1H), 3.40 (t, *J*= 8.8 Hz, 1H), 4.29 (t, *J*= 8.4 Hz, 1H), 4.35 (d, *J*= 14.4 Hz, 1H), 4.44 (d, *J*= 14.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.5, 26.5, 28.8, 28.9, 31.0, 33.6, 38.2, 41.4, 69.4, 74.8, 123.4, 132.6, 141.7, 149.3, 204.3. IR (film): 2926, 2835, 1680, 1598, 1446, 1177, 1088, 1070, 1039, 987, 920, 731. HRMS (ESI) *m/z* calcd. For $C_{15}H_{20}O_2$ $(M+Na)^+$ 255.1356, found 255.1352.



7l

(Z)-6-(2,2-dimethylpropylidene)-7-methyl-3,3a,4,6-tetrahydroisobenzofuran-5(1H)-one (7l)

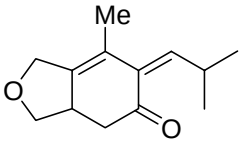
Condition B ^{1}H NMR (400MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.73 (d, *J*= 1.2 Hz, 3H), 2.40 (t, *J*= 12.4, 1H), 2.67 (dd, *J*= 5.2, 12.4 Hz, 1H), 2.94-3.10 (m, 1H), 3.35 (dd, *J*= 8.4, 10.4 Hz, 1H), 4.24 (t, *J*= 8.0 Hz, 1H), 4.44 (d, *J*= 14.0 Hz, 1H), 4.52 (d, *J*= 14.4 Hz, 1H), 5.80 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 15.7, 30.6, 33.6, 41.5, 43.8, 69.7, 74.5, 126.2, 134.1, 138.5, 146.3, 202.4. IR (film): 2957, 2867, 1701, 1463, 1387, 1363, 1334, 1266, 1165, 1041, 919, 737, 704. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}O_2$ $(M+Na)^+$ 243.1356, found 243.1361.



7l'

7-methyl-6-neopentyl-1,3-dihydroisobenzofuran-5-ol (7l')

^{1}H NMR (400MHz, $CDCl_3$) δ 0.98 (s, 9H), 2.16 (s, 3H), 2.62 (s, 2H), 4.83 (s, 1H), 5.03 (s, 2H), 5.08 (s, 2H), 6.54 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 17.6, 30.4, 34.5, 38.5, 73.8, 74.2, 105.6, 124.1, 131.0, 132.3, 137.0, 154.7. IR (film): 3242, 2952, 2864, 1604, 1449, 1363, 1327, 1306, 1260, 1159, 1061, 1024, 986, 907, 891, 829, 731. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}O_2$ $(M+Na)^+$ 243.1356, found 243.1367.

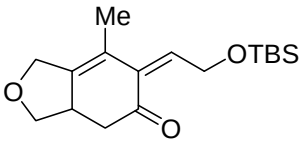


7m

(Z)-7-methyl-6-(2-methylpropylidene)-3,3a,4,6-tetrahydroisobenzofuran-5(1H)-one (7m)

Condition B ^{1}H NMR (400MHz, $CDCl_3$) δ 1.00 (d, *J*= 6.4 Hz, 3H), 1.07 (d, *J*= 6.8 Hz, 3H), 1.76 (s, 3H), 2.31 (dd, *J*= 12.0, 13.2 Hz, 1H), 2.68 (dd, *J*= 5.6, 13.2 Hz, 1H), 2.93-3.07 (m, 1H),

3.35 (dd, *J*= 8.0, 10.4 Hz, 1H), 3.42-3.56 (m, 1H), 4.27 (t, *J*= 8.0 Hz, 1H), 4.47 (d, *J*= 14.0 Hz, 1H), 4.55 (d, *J*= 14.4 Hz, 1H), 5.72 (d, *J*= 9.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 15.4, 23.1, 23.3, 27.8, 40.1, 43.5, 69.8, 74.7, 124.8, 131.3, 138.4, 145.9, 200.6. IR (film): 2963, 2866, 1694, 1596, 1466, 1388, 1361, 1332, 1218, 1138, 1040, 953, 920, 735. HRMS (ESI) *m/z* calcd. For $C_{13}H_{18}O_2$ $(M+Na)^+$ 229.1199, found 229.1203.



7n

(Z)-6-(2-(tert-butyldimethylsilyloxy)ethylidene)-7-methyl-3,3a,4,6-tetrahydroisobenzofuran -5(1H)-one (7n)

Condition B ^{1}H NMR (400MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.92 (s, 9H), 1.80 (d, *J*= 1.2 Hz, 3H), 2.27 (dd, *J*= 12.4, 14.4 Hz, 1H), 2.71 (dd, *J*= 5.2, 14.4 Hz, 1H), 2.94-3.10 (m, 1H), 3.37 (dd, *J*= 8.4, 10.4 Hz, 1H), 4.30 (t, *J*= 8.0 Hz, 1H), 4.49 (d, *J*= 14.4 Hz, 1H), 4.85 (d, *J*= 14.0 Hz, 1H), 4.70-4.84 (m, 2H), 6.08 (t, *J*= 4.8 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ -4.98, -4.97, 15.3, 18.5, 26.2, 39.7, 42.4, 63.7, 69.7, 74.7, 124.1, 131.4, 139.5, 141.8, 200.1. IR (film): 2929, 2856, 1693, 1387, 1360, 1331, 1263, 1089, 1040, 1012, 921, 837, 778, 736, 704. HRMS (ESI) *m/z* calcd. For $C_{17}H_{28}O_3Si$ $(M+Na)^+$ 331.1700, found 331.1700.

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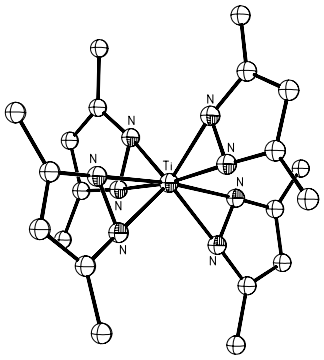

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STRUCTURAL REPORT ON 7f

AUGUST 1, 2011

Crystallographic Experimental Section

Data Collection

A colorless crystal with approximate dimensions 0.51 x 0.48 x 0.42 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.95 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with the exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 7099 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. A total of 18915 data were harvested by collecting 5 sets of frames with 0.5° scans in ω and φ with exposure times of 1 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The *E*-statistics suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [2-4].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 274 parameters against 5277 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0274 and 0.0646, respectively. The final difference Fourier map was featureless.

The molecular diagram is drawn with 50% probability ellipsoids.

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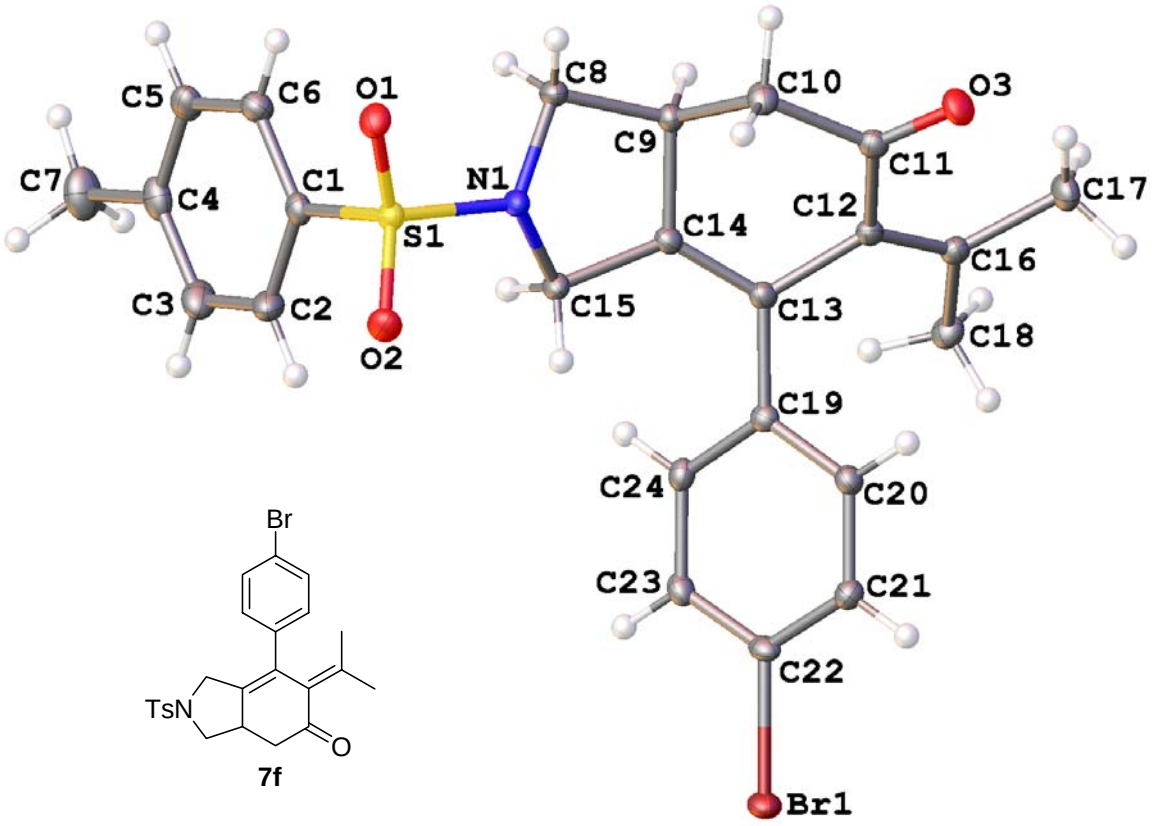


Figure 1. A molecular drawing of **7f**. All H atoms are omitted.

Table 1. Crystal data and structure refinement for **7f**.

Identification code	**7f**	
Empirical formula	C_{24} H_{24} Br N O_3 S	
Formula weight	486.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.652(2) Å	α= 81.281(11)°.
	b = 8.0993(19) Å	β= 84.362(11)°.
	c = 18.213(5) Å	γ = 72.965(17)°.
Volume	1065.0(5) $Å^3$	
Z	2	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	2.054 mm^{-1}	
F(000)	500	
Crystal size	0.51 x 0.48 x 0.42 mm^3	
Theta range for data collection	2.27 to 28.32°.	
Index ranges	-9<=h<=10, -10<=k<=10, -24<=l<=24	
Reflections collected	18915	
Independent reflections	5277 [R(int) = 0.0335]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Numerical with SADABS	
Max. and min. transmission	0.4791 and 0.4205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5277 / 0 / 274	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0625	
R indices (all data)	R1 = 0.0336, wR2 = 0.0646	
Largest diff. peak and hole	0.501 and -0.363 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-1372(1)	-718(1)	7173(1)	19(1)
S(1)	5517(1)	6424(1)	6383(1)	14(1)
O(1)	5868(2)	8037(2)	6449(1)	18(1)
O(2)	4074(2)	6401(2)	5943(1)	20(1)
O(3)	1896(2)	5773(2)	10061(1)	21(1)
N(1)	5005(2)	5643(2)	7235(1)	14(1)
C(1)	7550(2)	4970(2)	6070(1)	15(1)
C(2)	7455(3)	3603(2)	5710(1)	21(1)
C(3)	9052(3)	2428(2)	5488(1)	24(1)
C(4)	10761(3)	2583(2)	5613(1)	21(1)
C(5)	10819(2)	3986(2)	5959(1)	20(1)
C(6)	9240(2)	5168(2)	6192(1)	18(1)
C(7)	12487(3)	1275(3)	5374(1)	31(1)
C(8)	6093(2)	5752(2)	7841(1)	16(1)
C(9)	5249(2)	4824(2)	8520(1)	14(1)
C(10)	3755(2)	6043(2)	8961(1)	17(1)
C(11)	2718(2)	5061(2)	9534(1)	14(1)
C(12)	2790(2)	3255(2)	9410(1)	13(1)
C(13)	3187(2)	2927(2)	8615(1)	13(1)
C(14)	4363(2)	3681(2)	8197(1)	13(1)
C(15)	4671(2)	3912(2)	7362(1)	15(1)
C(16)	2557(2)	2022(2)	9975(1)	15(1)
C(17)	2077(3)	2314(2)	10775(1)	20(1)
C(18)	2797(2)	167(2)	9860(1)	18(1)
C(19)	2125(2)	1987(2)	8283(1)	13(1)
C(20)	277(2)	2204(2)	8499(1)	14(1)
C(21)	-751(2)	1391(2)	8173(1)	15(1)
C(22)	70(2)	342(2)	7628(1)	15(1)
C(23)	1905(2)	72(2)	7411(1)	16(1)
C(24)	2921(2)	891(2)	7742(1)	15(1)

Table 3. Bond lengths [Å] and angles [°] for **7f**.

Br(1)-C(22)	1.8949(17)	C(10)-H(10A)	0.9900
S(1)-O(2)	1.4331(13)	C(10)-H(10B)	0.9900
S(1)-O(1)	1.4332(13)	C(11)-C(12)	1.498(2)
S(1)-N(1)	1.6389(14)	C(12)-C(16)	1.359(2)
S(1)-C(1)	1.7568(18)	C(12)-C(13)	1.497(2)
O(3)-C(11)	1.219(2)	C(13)-C(14)	1.345(2)
N(1)-C(8)	1.475(2)	C(13)-C(19)	1.485(2)
N(1)-C(15)	1.478(2)	C(14)-C(15)	1.507(2)
C(1)-C(6)	1.391(2)	C(15)-H(15A)	0.9900
C(1)-C(2)	1.393(2)	C(15)-H(15B)	0.9900
C(2)-C(3)	1.378(3)	C(16)-C(17)	1.504(2)
C(2)-H(2)	0.9500	C(16)-C(18)	1.504(2)
C(3)-C(4)	1.393(3)	C(17)-H(17A)	0.9800
C(3)-H(3)	0.9500	C(17)-H(17B)	0.9800
C(4)-C(5)	1.393(3)	C(17)-H(17C)	0.9800
C(4)-C(7)	1.504(3)	C(18)-H(18A)	0.9800
C(5)-C(6)	1.379(3)	C(18)-H(18B)	0.9800
C(5)-H(5)	0.9500	C(18)-H(18C)	0.9800
C(6)-H(6)	0.9500	C(19)-C(20)	1.397(2)
C(7)-H(7A)	0.9800	C(19)-C(24)	1.400(2)
C(7)-H(7B)	0.9800	C(20)-C(21)	1.385(2)
C(7)-H(7C)	0.9800	C(20)-H(20)	0.9500
C(8)-C(9)	1.535(2)	C(21)-C(22)	1.387(2)
C(8)-H(8A)	0.9900	C(21)-H(21)	0.9500
C(8)-H(8B)	0.9900	C(22)-C(23)	1.383(2)
C(9)-C(14)	1.508(2)	C(23)-C(24)	1.387(2)
C(9)-C(10)	1.524(2)	C(23)-H(23)	0.9500
C(9)-H(9)	1.0000	C(24)-H(24)	0.9500
C(10)-C(11)	1.519(2)		
O(2)-S(1)-O(1)	120.23(8)	C(5)-C(6)-H(6)	120.3
O(2)-S(1)-N(1)	106.25(7)	C(1)-C(6)-H(6)	120.3
O(1)-S(1)-N(1)	105.17(7)	C(4)-C(7)-H(7A)	109.5
O(2)-S(1)-C(1)	108.10(8)	C(4)-C(7)-H(7B)	109.5
O(1)-S(1)-C(1)	108.94(8)	H(7A)-C(7)-H(7B)	109.5
N(1)-S(1)-C(1)	107.48(8)	C(4)-C(7)-H(7C)	109.5
C(8)-N(1)-C(15)	107.90(12)	H(7A)-C(7)-H(7C)	109.5
C(8)-N(1)-S(1)	118.83(11)	H(7B)-C(7)-H(7C)	109.5
C(15)-N(1)-S(1)	118.48(11)	N(1)-C(8)-C(9)	102.34(13)
C(6)-C(1)-C(2)	120.30(16)	N(1)-C(8)-H(8A)	111.3
C(6)-C(1)-S(1)	120.26(13)	C(9)-C(8)-H(8A)	111.3
C(2)-C(1)-S(1)	119.43(14)	N(1)-C(8)-H(8B)	111.3
C(3)-C(2)-C(1)	119.32(17)	C(9)-C(8)-H(8B)	111.3
C(3)-C(2)-H(2)	120.3	H(8A)-C(8)-H(8B)	109.2
C(1)-C(2)-H(2)	120.3	C(14)-C(9)-C(10)	107.34(14)
C(2)-C(3)-C(4)	121.46(17)	C(14)-C(9)-C(8)	104.45(13)
C(2)-C(3)-H(3)	119.3	C(10)-C(9)-C(8)	114.12(14)
C(4)-C(3)-H(3)	119.3	C(14)-C(9)-H(9)	110.2
C(3)-C(4)-C(5)	118.11(17)	C(10)-C(9)-H(9)	110.2
C(3)-C(4)-C(7)	120.58(18)	C(8)-C(9)-H(9)	110.2
C(5)-C(4)-C(7)	121.31(18)	C(11)-C(10)-C(9)	112.22(14)
C(6)-C(5)-C(4)	121.46(17)	C(11)-C(10)-H(10A)	109.2
C(6)-C(5)-H(5)	119.3	C(9)-C(10)-H(10A)	109.2
C(4)-C(5)-H(5)	119.3	C(11)-C(10)-H(10B)	109.2
C(5)-C(6)-C(1)	119.32(16)	C(9)-C(10)-H(10B)	109.2

H(10A)-C(10)-H(10B)	107.9	H(17A)-C(17)-H(17C)	109.5
O(3)-C(11)-C(12)	124.35(15)	H(17B)-C(17)-H(17C)	109.5
O(3)-C(11)-C(10)	118.78(15)	C(16)-C(18)-H(18A)	109.5
C(12)-C(11)-C(10)	116.87(14)	C(16)-C(18)-H(18B)	109.5
C(16)-C(12)-C(13)	123.42(15)	H(18A)-C(18)-H(18B)	109.5
C(16)-C(12)-C(11)	122.49(14)	C(16)-C(18)-H(18C)	109.5
C(13)-C(12)-C(11)	114.07(13)	H(18A)-C(18)-H(18C)	109.5
C(14)-C(13)-C(19)	121.44(14)	H(18B)-C(18)-H(18C)	109.5
C(14)-C(13)-C(12)	117.94(14)	C(20)-C(19)-C(24)	118.25(15)
C(19)-C(13)-C(12)	120.16(14)	C(20)-C(19)-C(13)	120.14(14)
C(13)-C(14)-C(15)	128.48(15)	C(24)-C(19)-C(13)	121.60(15)
C(13)-C(14)-C(9)	120.87(14)	C(21)-C(20)-C(19)	120.85(15)
C(15)-C(14)-C(9)	109.16(13)	C(21)-C(20)-H(20)	119.6
N(1)-C(15)-C(14)	100.67(12)	C(19)-C(20)-H(20)	119.6
N(1)-C(15)-H(15A)	111.6	C(20)-C(21)-C(22)	119.47(16)
C(14)-C(15)-H(15A)	111.6	C(20)-C(21)-H(21)	120.3
N(1)-C(15)-H(15B)	111.6	C(22)-C(21)-H(21)	120.3
C(14)-C(15)-H(15B)	111.6	C(23)-C(22)-C(21)	121.14(15)
H(15A)-C(15)-H(15B)	109.4	C(23)-C(22)-Br(1)	120.03(12)
C(12)-C(16)-C(17)	125.21(15)	C(21)-C(22)-Br(1)	118.83(13)
C(12)-C(16)-C(18)	122.45(15)	C(22)-C(23)-C(24)	118.88(15)
C(17)-C(16)-C(18)	112.33(14)	C(22)-C(23)-H(23)	120.6
C(16)-C(17)-H(17A)	109.5	C(24)-C(23)-H(23)	120.6
C(16)-C(17)-H(17B)	109.5	C(23)-C(24)-C(19)	121.39(16)
H(17A)-C(17)-H(17B)	109.5	C(23)-C(24)-H(24)	119.3
C(16)-C(17)-H(17C)	109.5	C(19)-C(24)-H(24)	119.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	24(1)	20(1)	18(1)	-6(1)	-1(1)	-13(1)
S(1)	15(1)	15(1)	11(1)	0(1)	0(1)	-6(1)
O(1)	22(1)	14(1)	17(1)	-1(1)	2(1)	-7(1)
O(2)	19(1)	26(1)	16(1)	0(1)	-4(1)	-8(1)
O(3)	25(1)	20(1)	18(1)	-8(1)	4(1)	-6(1)
N(1)	17(1)	15(1)	11(1)	-1(1)	0(1)	-8(1)
C(1)	18(1)	16(1)	11(1)	0(1)	1(1)	-5(1)
C(2)	24(1)	23(1)	19(1)	-7(1)	3(1)	-13(1)
C(3)	32(1)	20(1)	24(1)	-8(1)	7(1)	-12(1)
C(4)	26(1)	19(1)	14(1)	2(1)	2(1)	-3(1)
C(5)	18(1)	26(1)	14(1)	0(1)	-3(1)	-5(1)
C(6)	20(1)	19(1)	15(1)	-3(1)	-2(1)	-7(1)
C(7)	30(1)	27(1)	27(1)	-2(1)	5(1)	1(1)
C(8)	17(1)	19(1)	13(1)	-3(1)	0(1)	-9(1)
C(9)	15(1)	15(1)	11(1)	-2(1)	0(1)	-6(1)
C(10)	22(1)	14(1)	17(1)	-3(1)	2(1)	-7(1)
C(11)	15(1)	15(1)	14(1)	-1(1)	-2(1)	-4(1)
C(12)	12(1)	15(1)	13(1)	-3(1)	-1(1)	-5(1)
C(13)	12(1)	14(1)	13(1)	-2(1)	-1(1)	-3(1)
C(14)	14(1)	14(1)	12(1)	-3(1)	-1(1)	-4(1)
C(15)	18(1)	15(1)	12(1)	-2(1)	1(1)	-9(1)
C(16)	14(1)	18(1)	15(1)	-2(1)	-1(1)	-6(1)
C(17)	26(1)	23(1)	13(1)	0(1)	1(1)	-10(1)
C(18)	20(1)	16(1)	18(1)	1(1)	-1(1)	-7(1)
C(19)	15(1)	12(1)	13(1)	0(1)	-1(1)	-5(1)
C(20)	16(1)	15(1)	13(1)	-3(1)	0(1)	-5(1)
C(21)	15(1)	16(1)	15(1)	-2(1)	0(1)	-6(1)
C(22)	21(1)	13(1)	14(1)	-2(1)	-2(1)	-9(1)
C(23)	21(1)	14(1)	13(1)	-3(1)	2(1)	-6(1)
C(24)	16(1)	15(1)	14(1)	-1(1)	2(1)	-5(1)

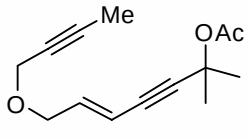
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7f**.

	x	y	z	U(eq)
H(2)	6301	3481	5617	25
H(3)	8986	1491	5245	29
H(5)	11973	4131	6035	24
H(6)	9305	6108	6433	22
H(7A)	12526	121	5641	46
H(7B)	13552	1611	5487	46
H(7C)	12507	1242	4837	46
H(8A)	5957	6978	7903	19
H(8B)	7406	5147	7752	19
H(9)	6227	4095	8854	16
H(10A)	4315	6740	9216	21
H(10B)	2884	6857	8613	21
H(15A)	5744	2999	7193	17
H(15B)	3578	3913	7112	17
H(17A)	896	2090	10932	31
H(17B)	1996	3521	10828	31
H(17C)	3027	1522	11087	31
H(18A)	3473	-59	9383	27
H(18B)	1592	-29	9858	27
H(18C)	3481	-621	10264	27
H(20)	-282	2919	8874	17
H(21)	-2009	1551	8321	18
H(23)	2460	-662	7043	19
H(24)	4185	704	7599	18

Table 6. Torsion angles [°] for **7f**.

O(2)-S(1)-N(1)-C(8)	-170.73(12)	C(14)-C(13)-C(19)-C(20)	-137.52(17)
O(1)-S(1)-N(1)-C(8)	-42.23(14)	C(12)-C(13)-C(19)-C(20)	34.5(2)
C(1)-S(1)-N(1)-C(8)	73.73(14)	C(14)-C(13)-C(19)-C(24)	41.5(2)
O(2)-S(1)-N(1)-C(15)	55.02(14)	C(12)-C(13)-C(19)-C(24)	-146.48(16)
O(1)-S(1)-N(1)-C(15)	-176.49(12)	C(24)-C(19)-C(20)-C(21)	-1.6(2)
C(1)-S(1)-N(1)-C(15)	-60.52(14)	C(13)-C(19)-C(20)-C(21)	177.43(15)
O(2)-S(1)-C(1)-C(6)	156.51(13)	C(19)-C(20)-C(21)-C(22)	0.3(2)
O(1)-S(1)-C(1)-C(6)	24.27(15)	C(20)-C(21)-C(22)-C(23)	1.0(2)
N(1)-S(1)-C(1)-C(6)	-89.18(14)	C(20)-C(21)-C(22)-Br(1)	-178.66(12)
O(2)-S(1)-C(1)-C(2)	-24.44(16)	C(21)-C(22)-C(23)-C(24)	-0.9(2)
O(1)-S(1)-C(1)-C(2)	-156.68(13)	Br(1)-C(22)-C(23)-C(24)	178.74(12)
N(1)-S(1)-C(1)-C(2)	89.87(15)	C(22)-C(23)-C(24)-C(19)	-0.5(2)
C(6)-C(1)-C(2)-C(3)	1.4(3)	C(20)-C(19)-C(24)-C(23)	1.7(2)
S(1)-C(1)-C(2)-C(3)	-177.69(14)	C(13)-C(19)-C(24)-C(23)	-177.33(15)
C(1)-C(2)-C(3)-C(4)	-0.4(3)		
C(2)-C(3)-C(4)-C(5)	-1.2(3)		
C(2)-C(3)-C(4)-C(7)	179.39(17)		
C(3)-C(4)-C(5)-C(6)	1.8(3)		
C(7)-C(4)-C(5)-C(6)	-178.73(16)		
C(4)-C(5)-C(6)-C(1)	-0.9(3)		
C(2)-C(1)-C(6)-C(5)	-0.7(2)		
S(1)-C(1)-C(6)-C(5)	178.33(13)		
C(15)-N(1)-C(8)-C(9)	-38.91(16)		
S(1)-N(1)-C(8)-C(9)	-177.49(11)		
N(1)-C(8)-C(9)-C(14)	22.49(16)		
N(1)-C(8)-C(9)-C(10)	-94.41(16)		
C(14)-C(9)-C(10)-C(11)	53.99(18)		
C(8)-C(9)-C(10)-C(11)	169.22(13)		
C(9)-C(10)-C(11)-O(3)	158.33(15)		
C(9)-C(10)-C(11)-C(12)	-21.4(2)		
O(3)-C(11)-C(12)-C(16)	-25.1(3)		
C(10)-C(11)-C(12)-C(16)	154.64(16)		
O(3)-C(11)-C(12)-C(13)	156.36(16)		
C(10)-C(11)-C(12)-C(13)	-23.9(2)		
C(16)-C(12)-C(13)-C(14)	-142.13(17)		
C(11)-C(12)-C(13)-C(14)	36.4(2)		
C(16)-C(12)-C(13)-C(19)	45.6(2)		
C(11)-C(12)-C(13)-C(19)	-135.88(15)		
C(19)-C(13)-C(14)-C(15)	7.6(3)		
C(12)-C(13)-C(14)-C(15)	-164.64(15)		
C(19)-C(13)-C(14)-C(9)	172.09(15)		
C(12)-C(13)-C(14)-C(9)	-0.1(2)		
C(10)-C(9)-C(14)-C(13)	-45.5(2)		
C(8)-C(9)-C(14)-C(13)	-167.01(15)		
C(10)-C(9)-C(14)-C(15)	121.72(14)		
C(8)-C(9)-C(14)-C(15)	0.23(17)		
C(8)-N(1)-C(15)-C(14)	38.37(16)		
S(1)-N(1)-C(15)-C(14)	177.12(11)		
C(13)-C(14)-C(15)-N(1)	143.31(17)		
C(9)-C(14)-C(15)-N(1)	-22.66(17)		
C(13)-C(12)-C(16)-C(17)	-177.21(16)		
C(11)-C(12)-C(16)-C(17)	4.4(3)		
C(13)-C(12)-C(16)-C(18)	4.1(3)		
C(11)-C(12)-C(16)-C(18)	-174.36(15)		

Symmetry transformations used to generate equivalent atoms:



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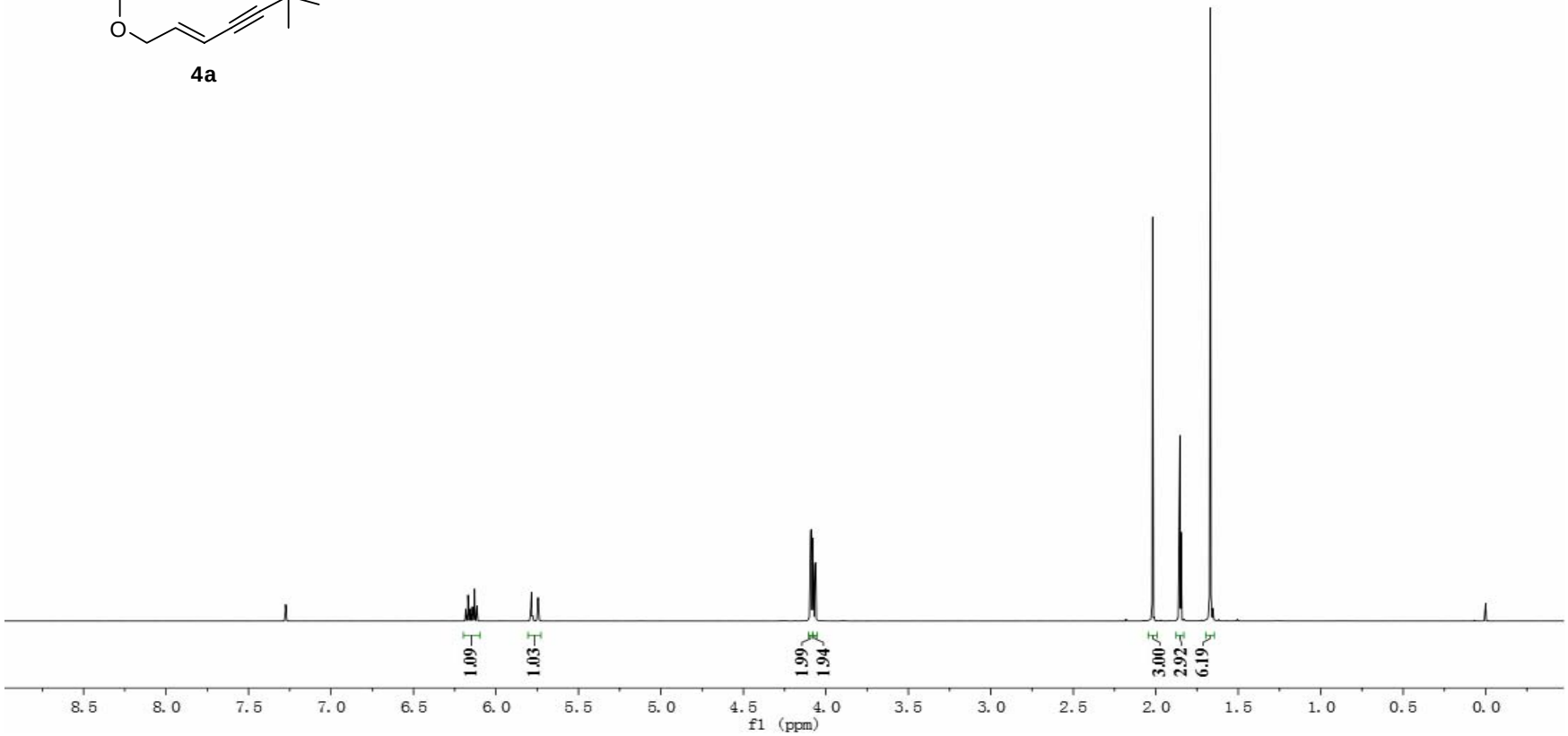

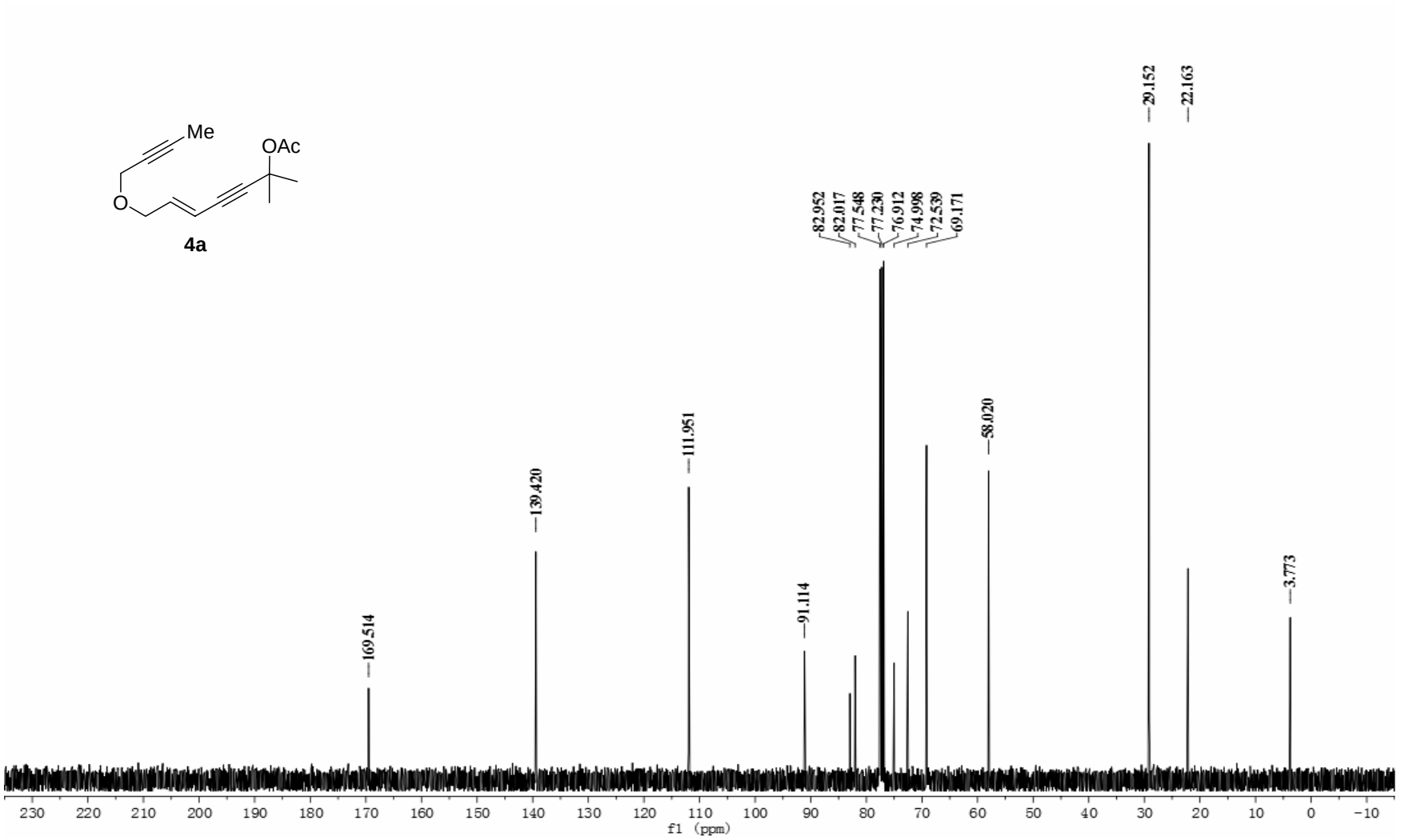
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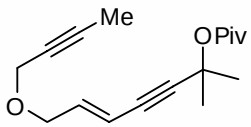

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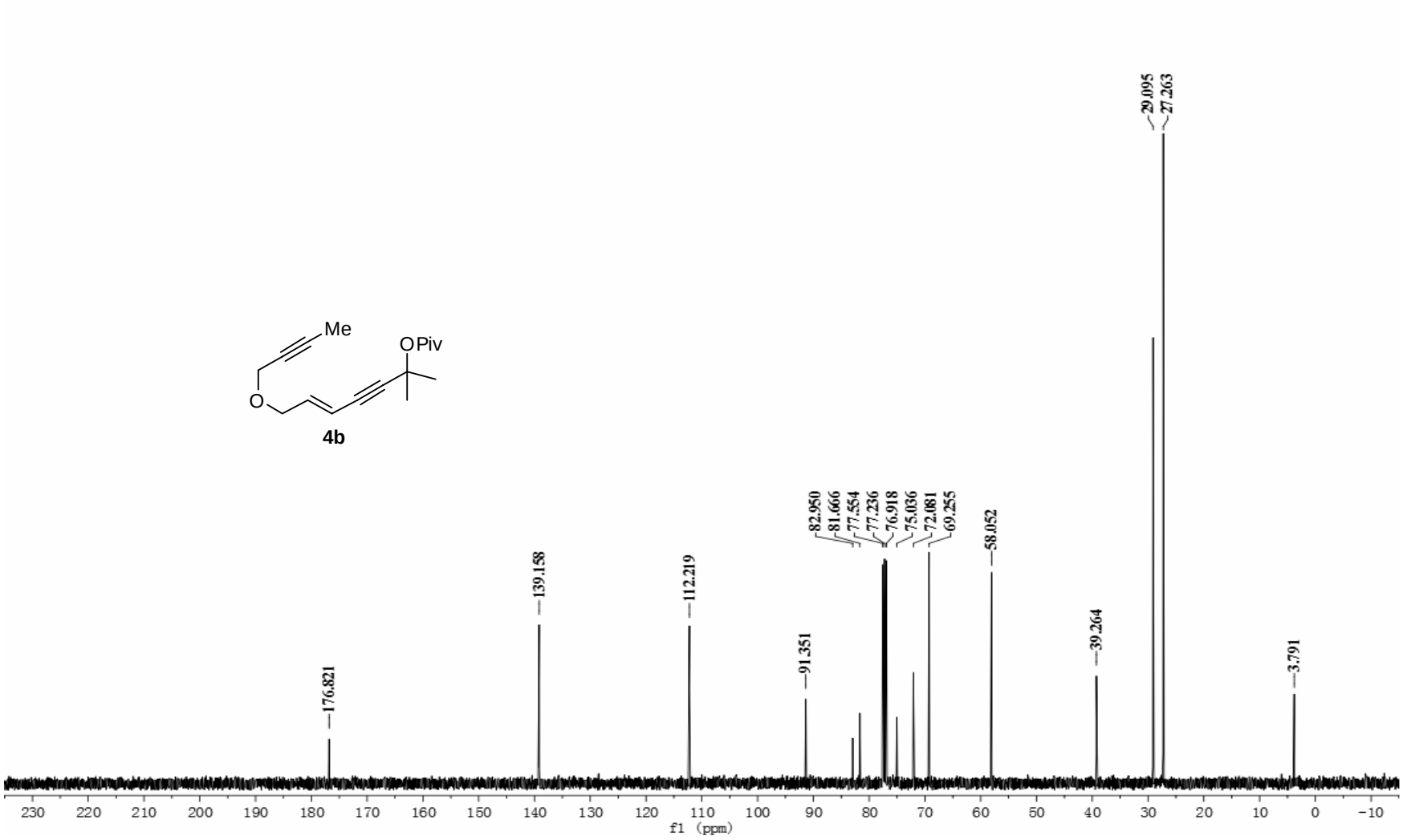
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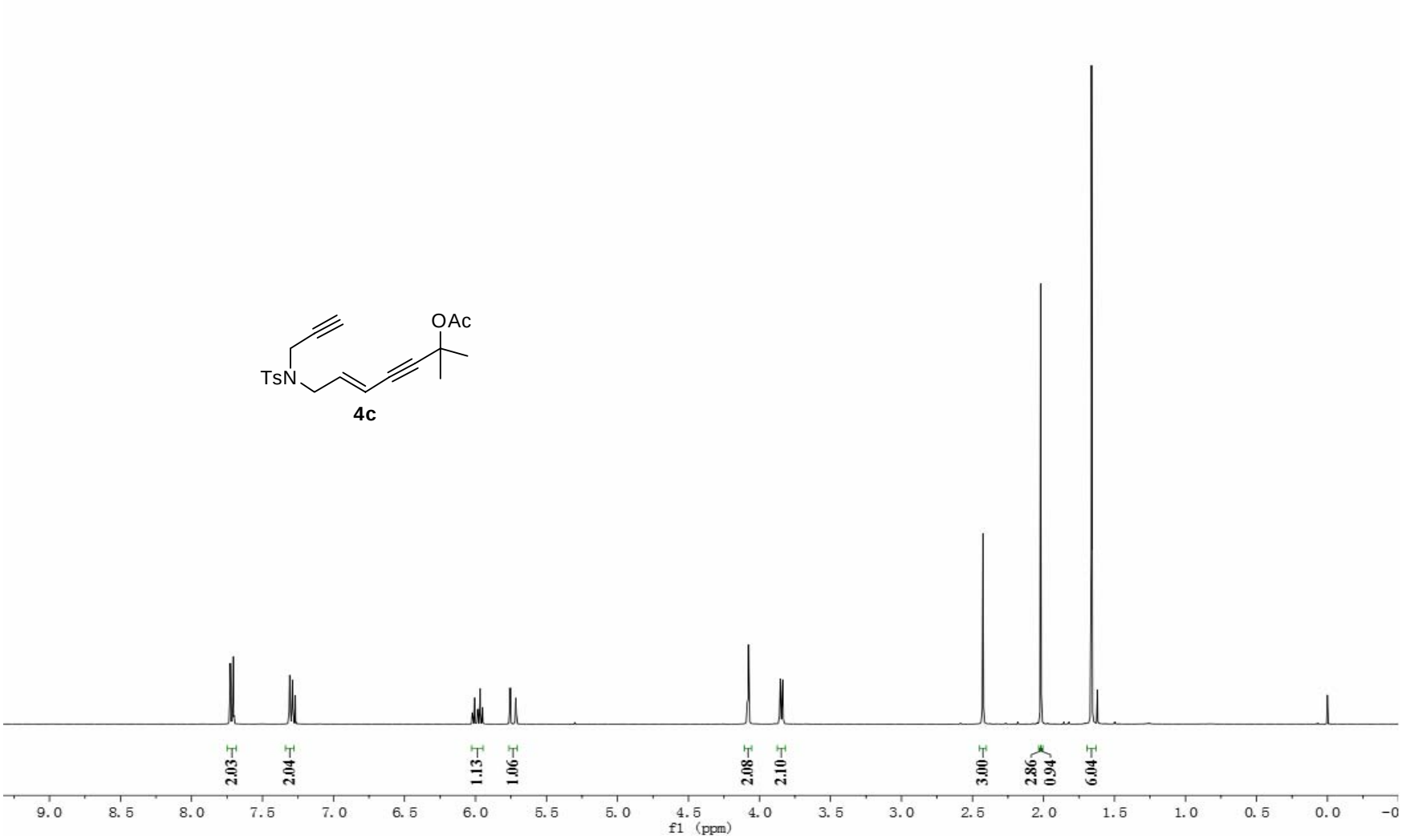
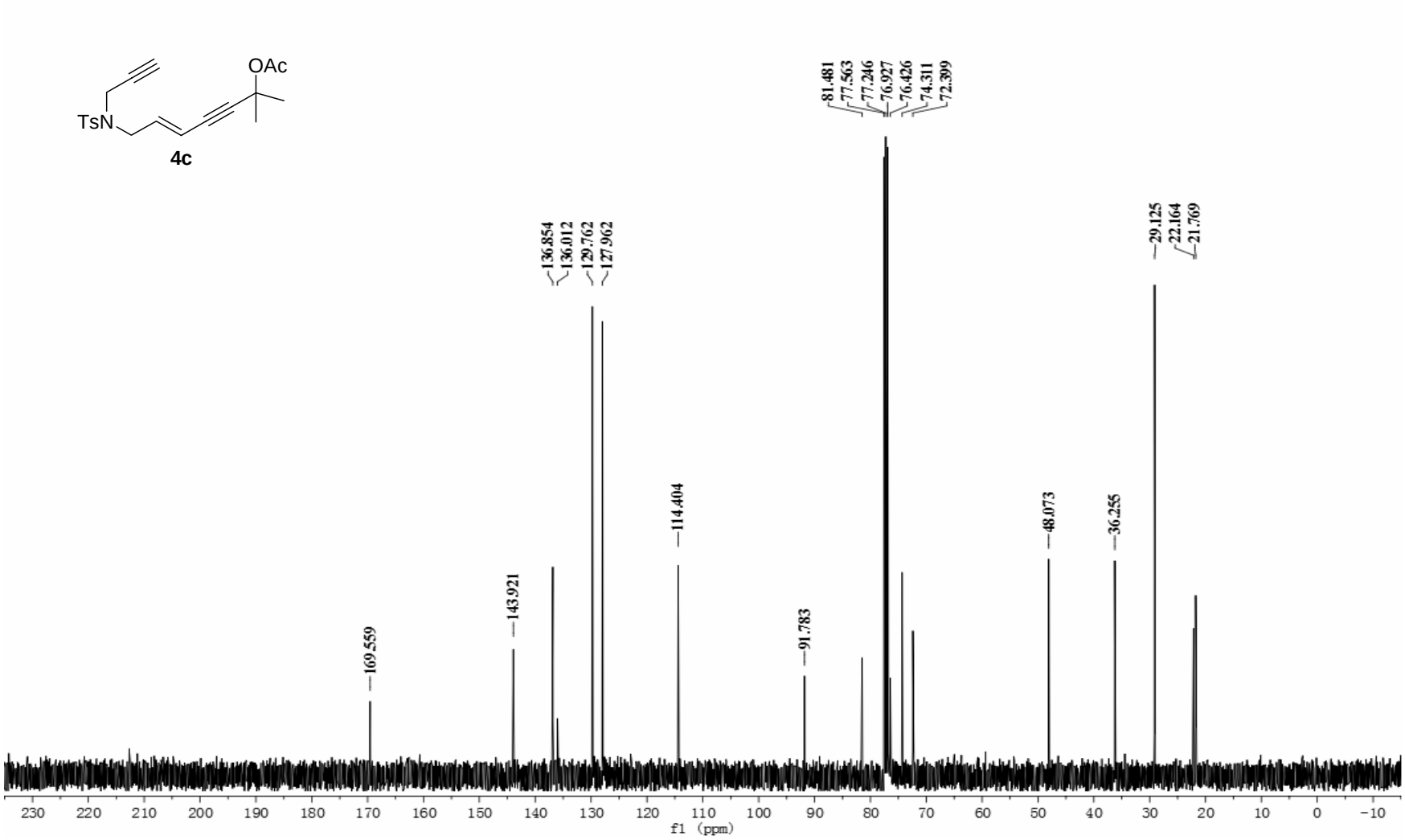
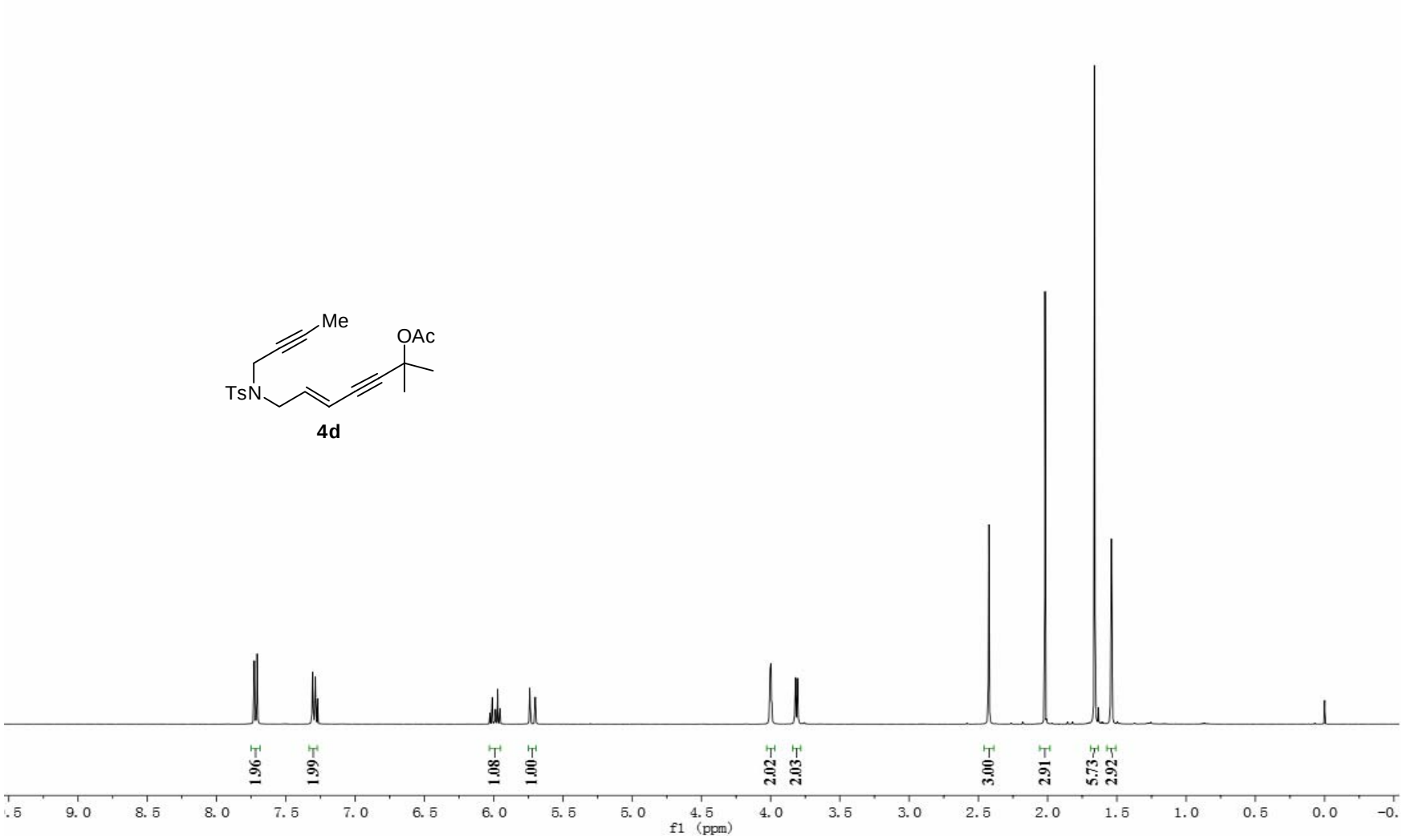
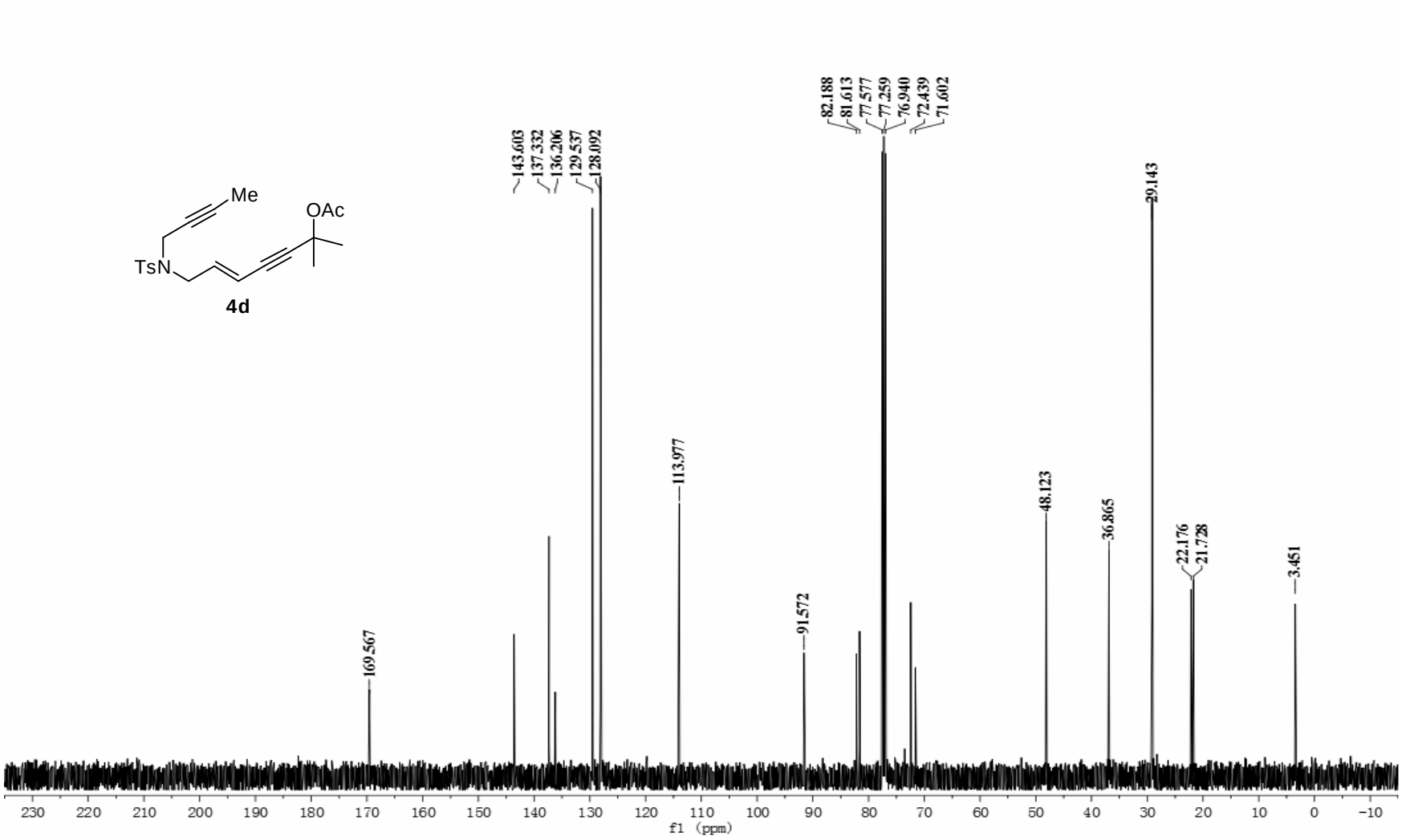
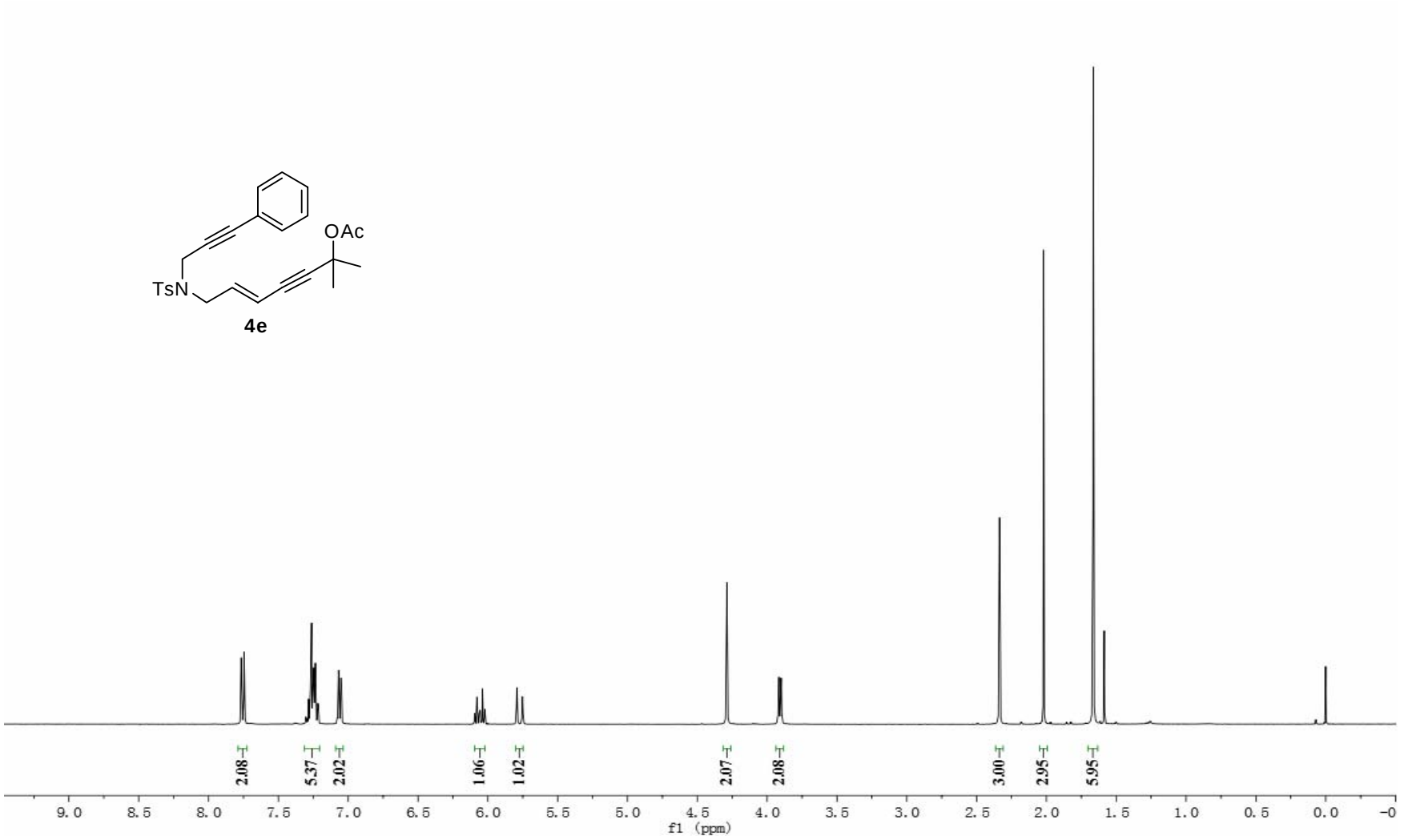
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

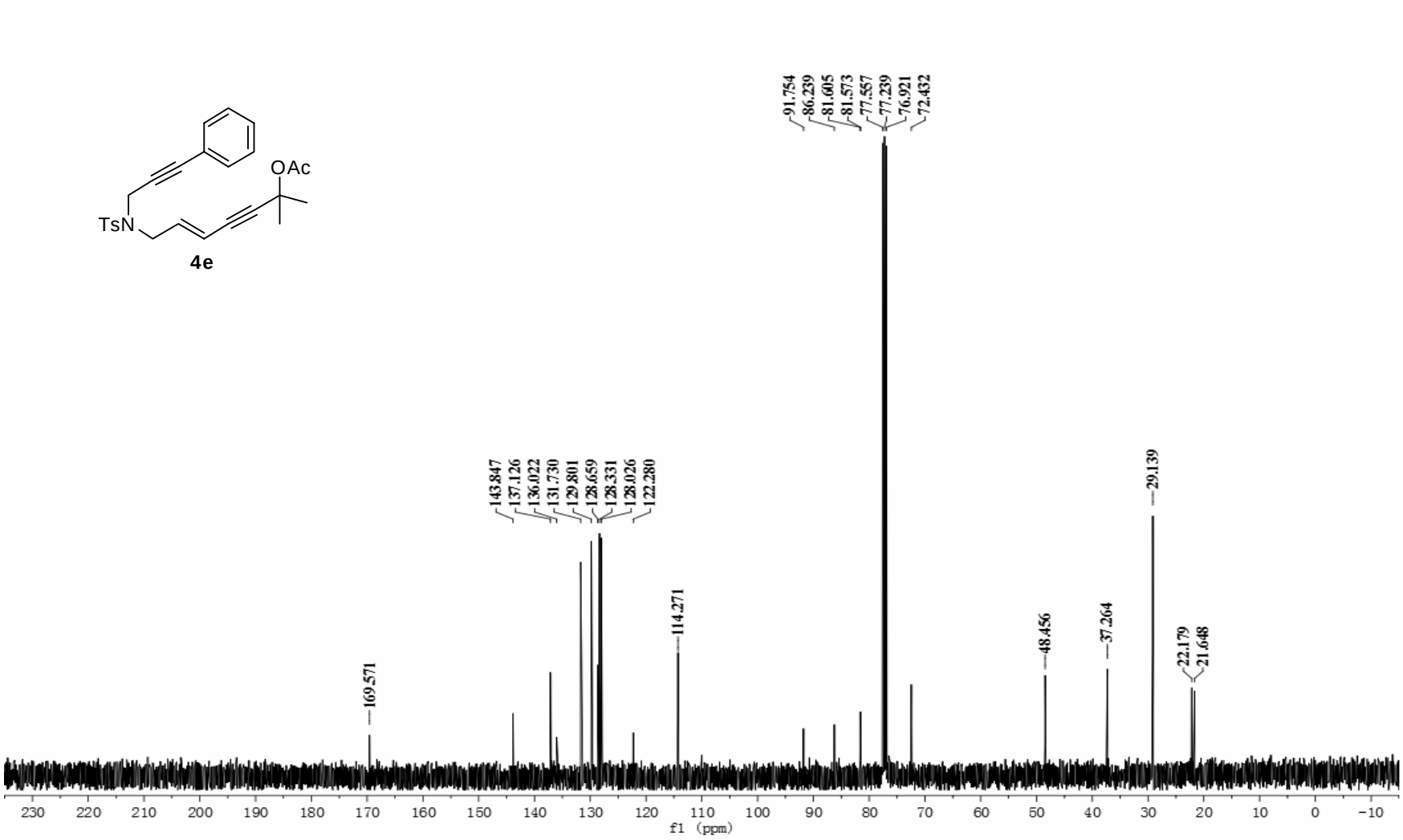


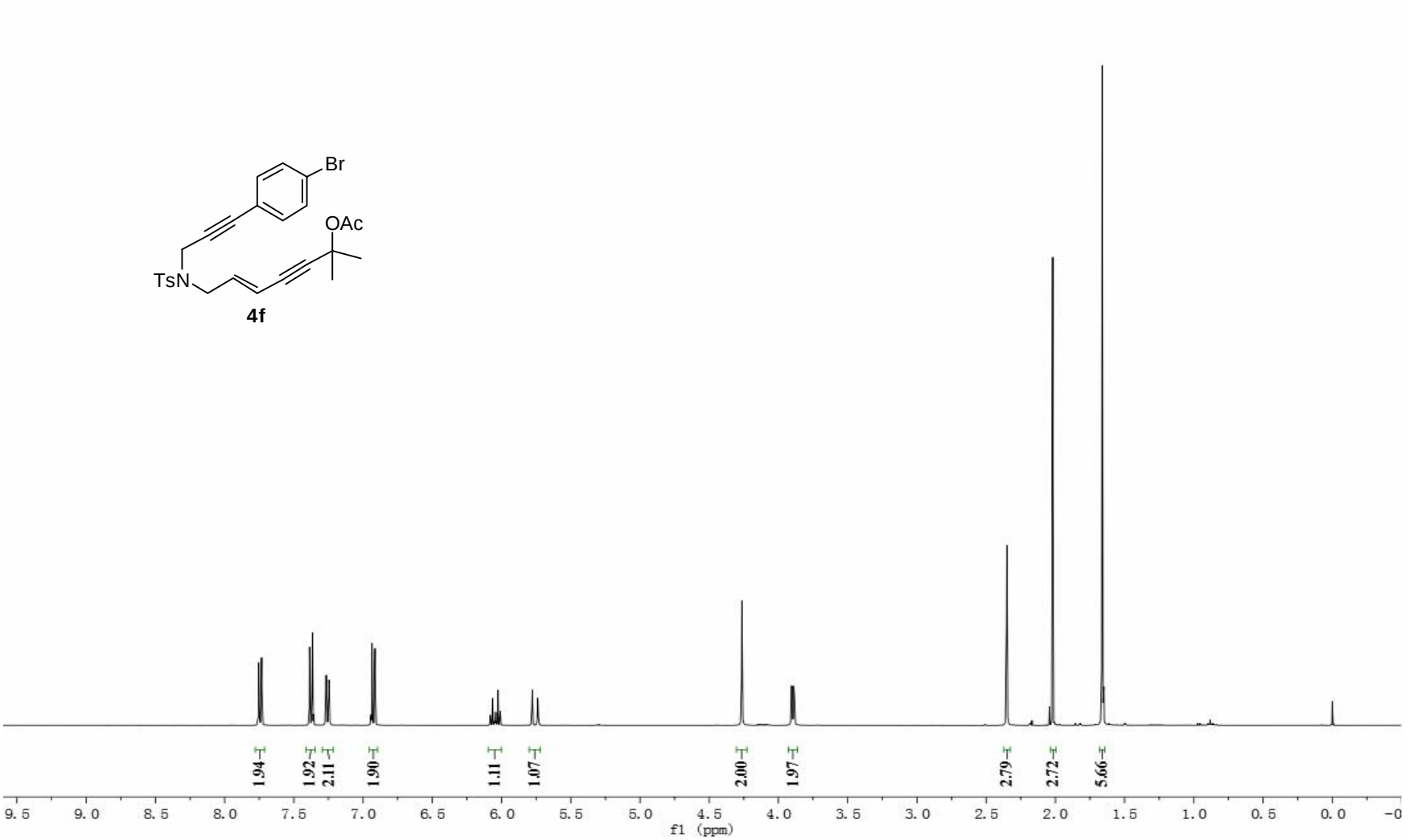

OAc
TsN
4c
81.481
77.563
77.246
76.927
76.426
74.311
72.399
136.854
136.012
129.762
127.962
29.125
22.164
21.769
114.404
143.921
169.559
91.783
48.073
36.255
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

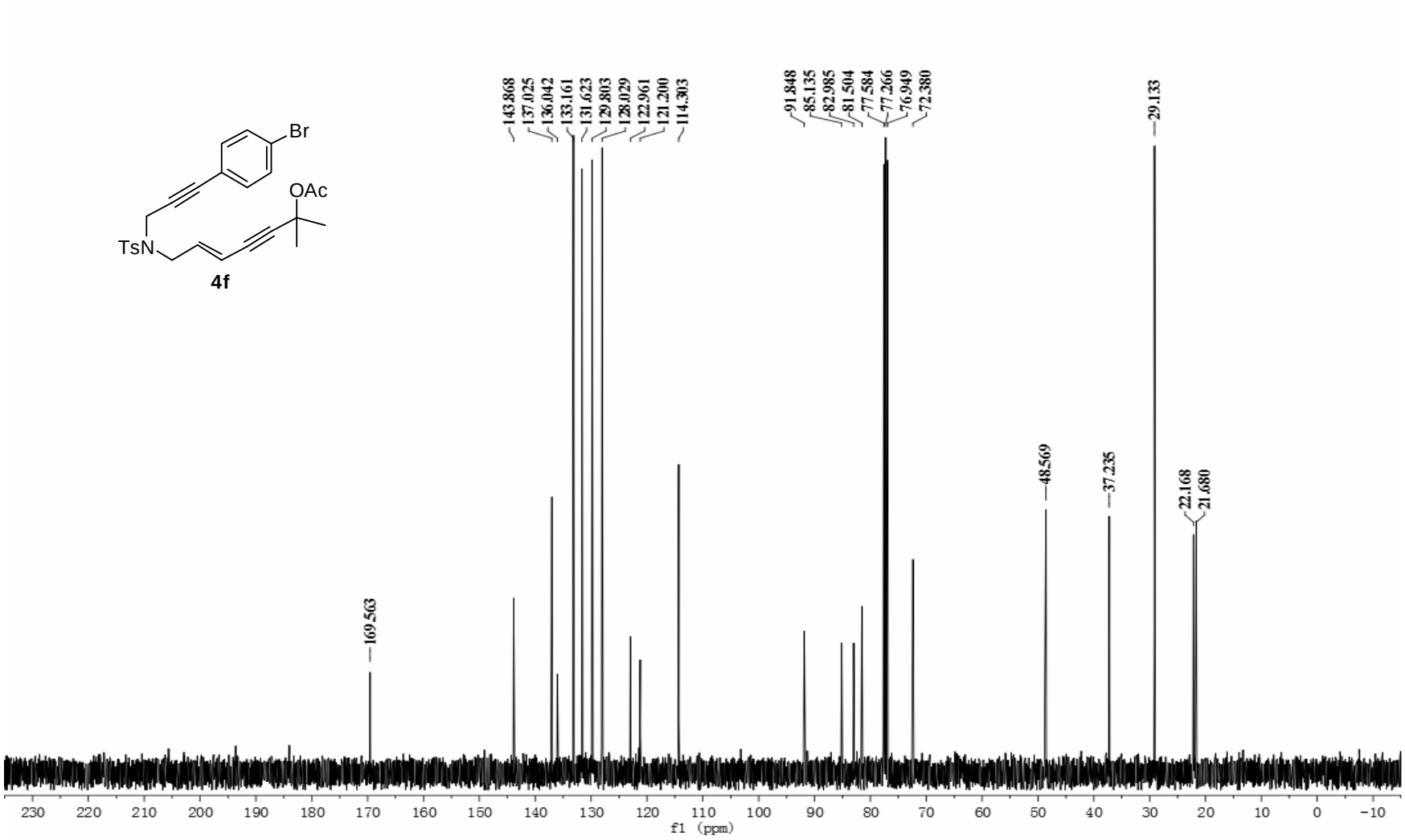


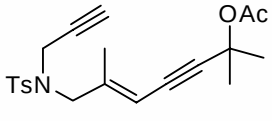




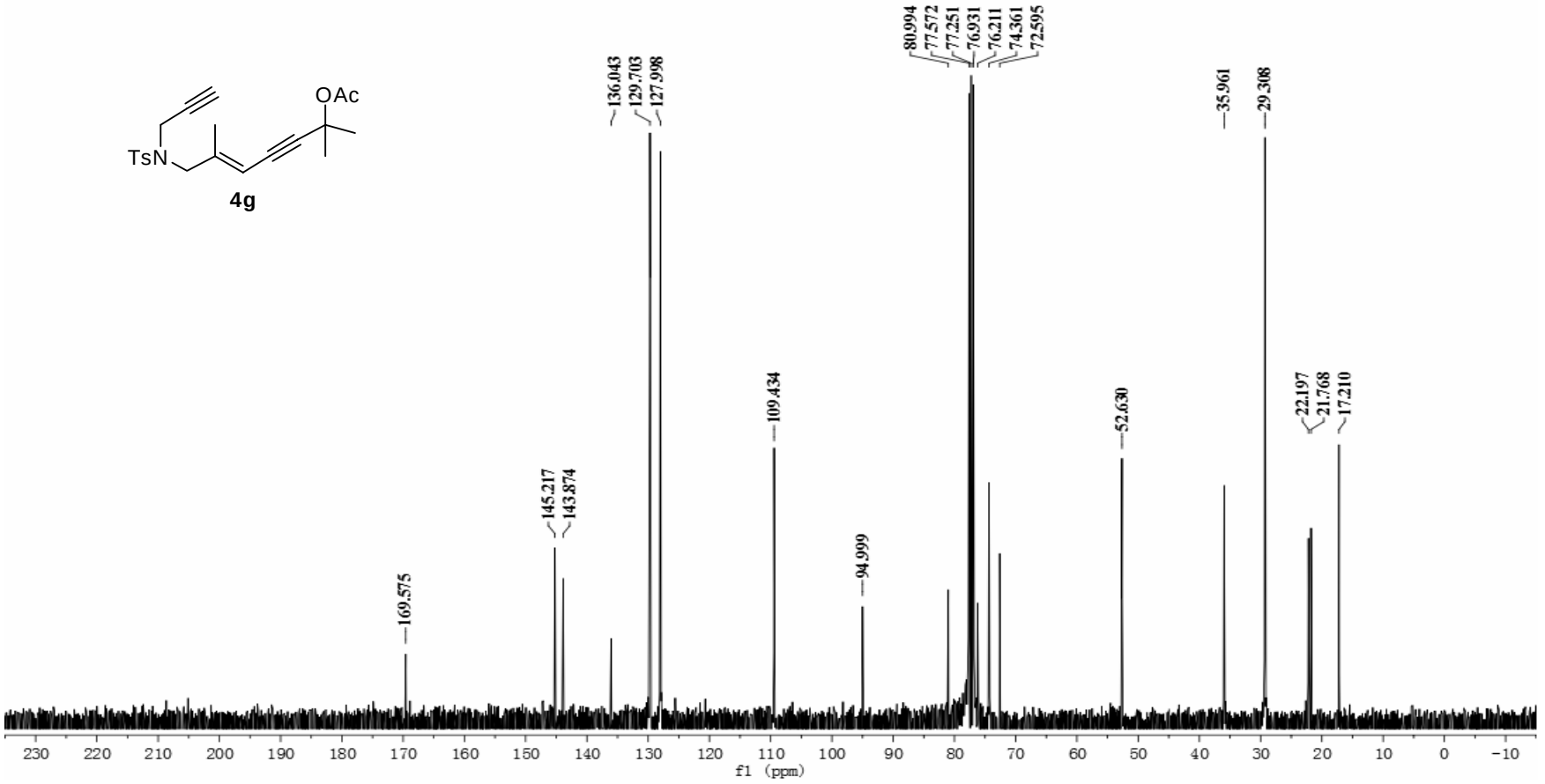

OAc
TsN
4e
91.754
86.239
81.605
81.573
77.557
77.239
76.921
72.432
143.847
137.126
136.022
131.730
129.801
128.659
128.331
128.026
122.280
114.271
169.571
48.456
37.264
29.139
22.179
21.648
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

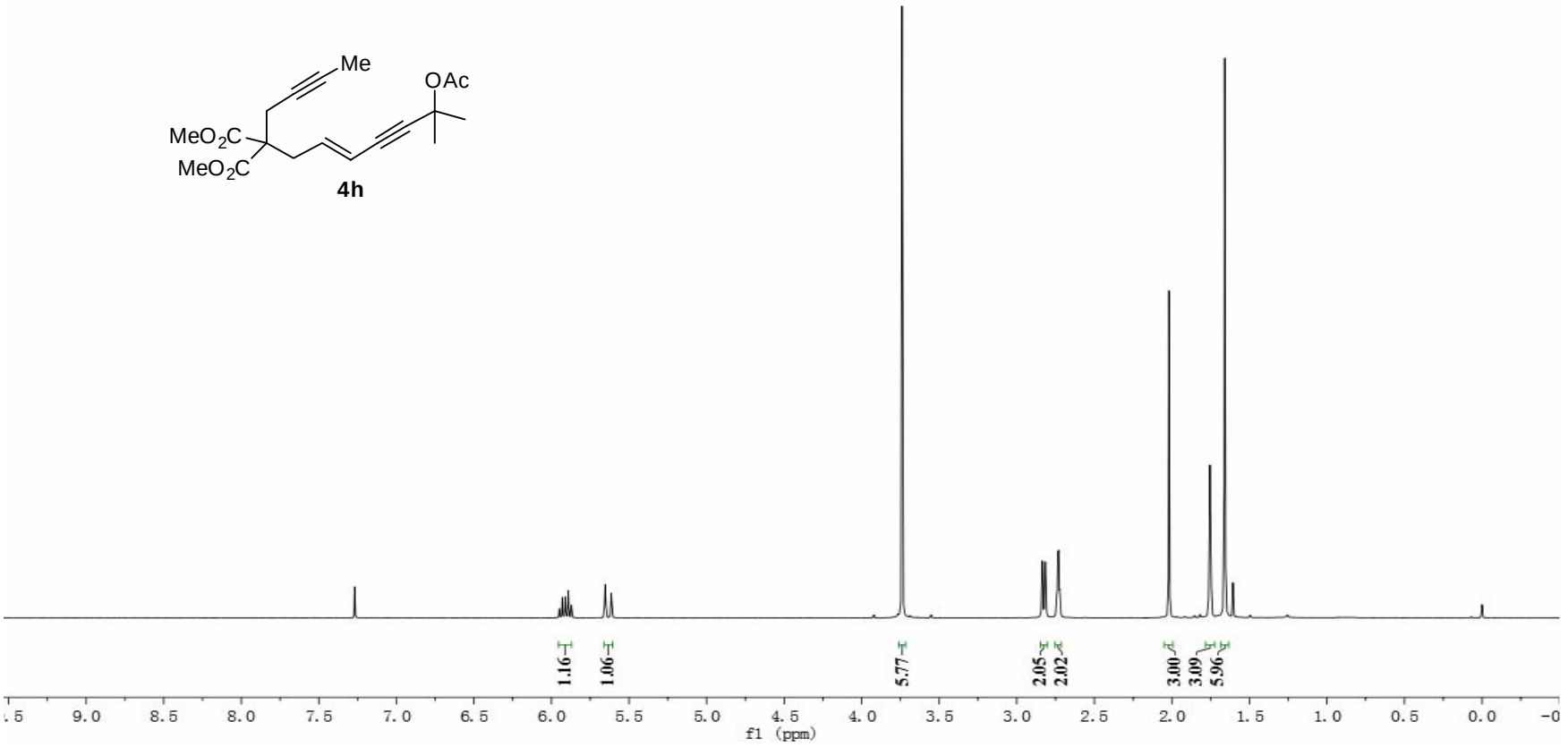


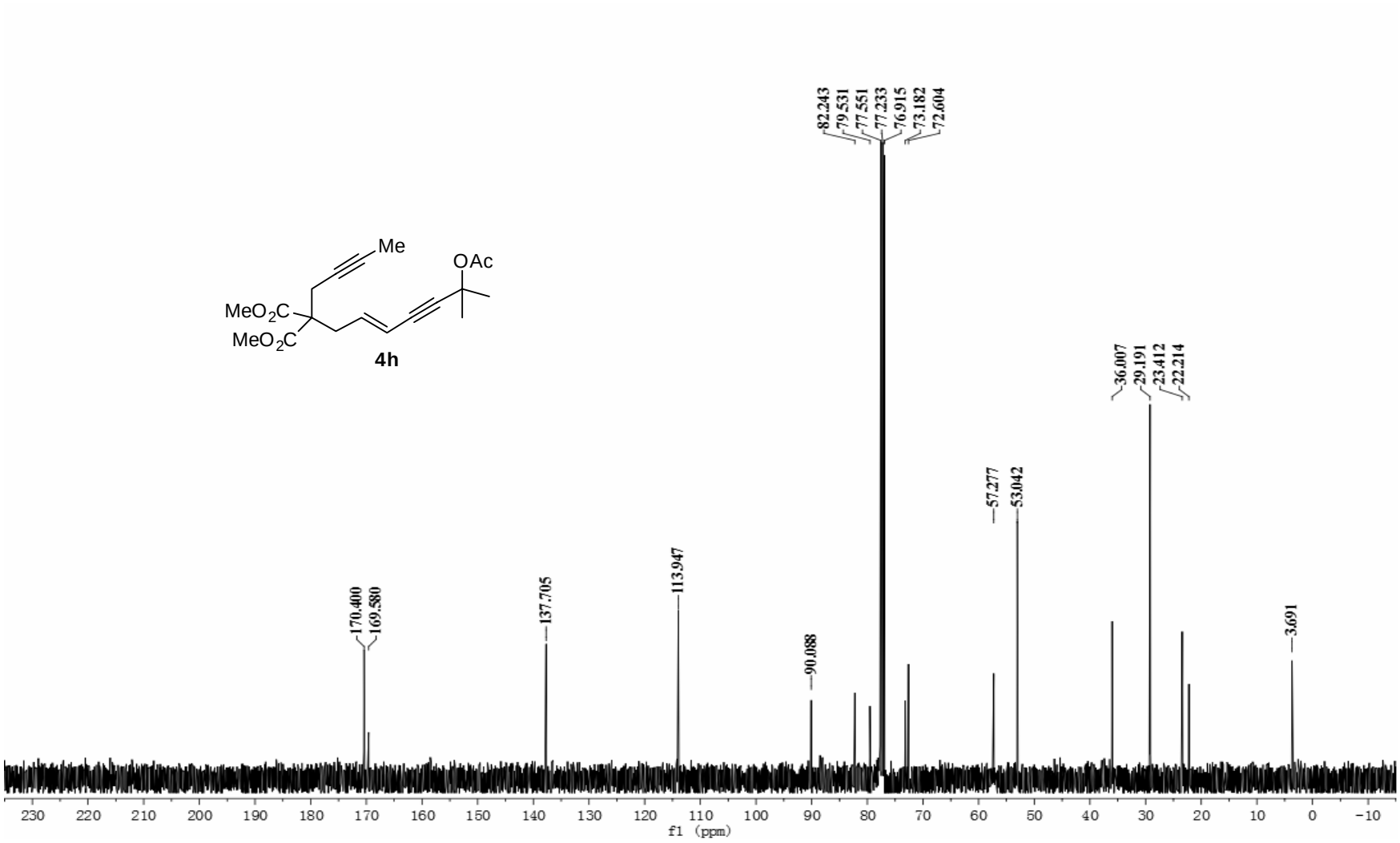

Br
OAc
TsN
4f
143.868
137.025
136.042
133.161
131.623
129.803
128.029
122.961
121.200
114.303
91.848
85.135
82.985
81.504
77.584
77.266
76.949
72.380
29.133
48.569
37.235
22.168
21.680
169.563
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

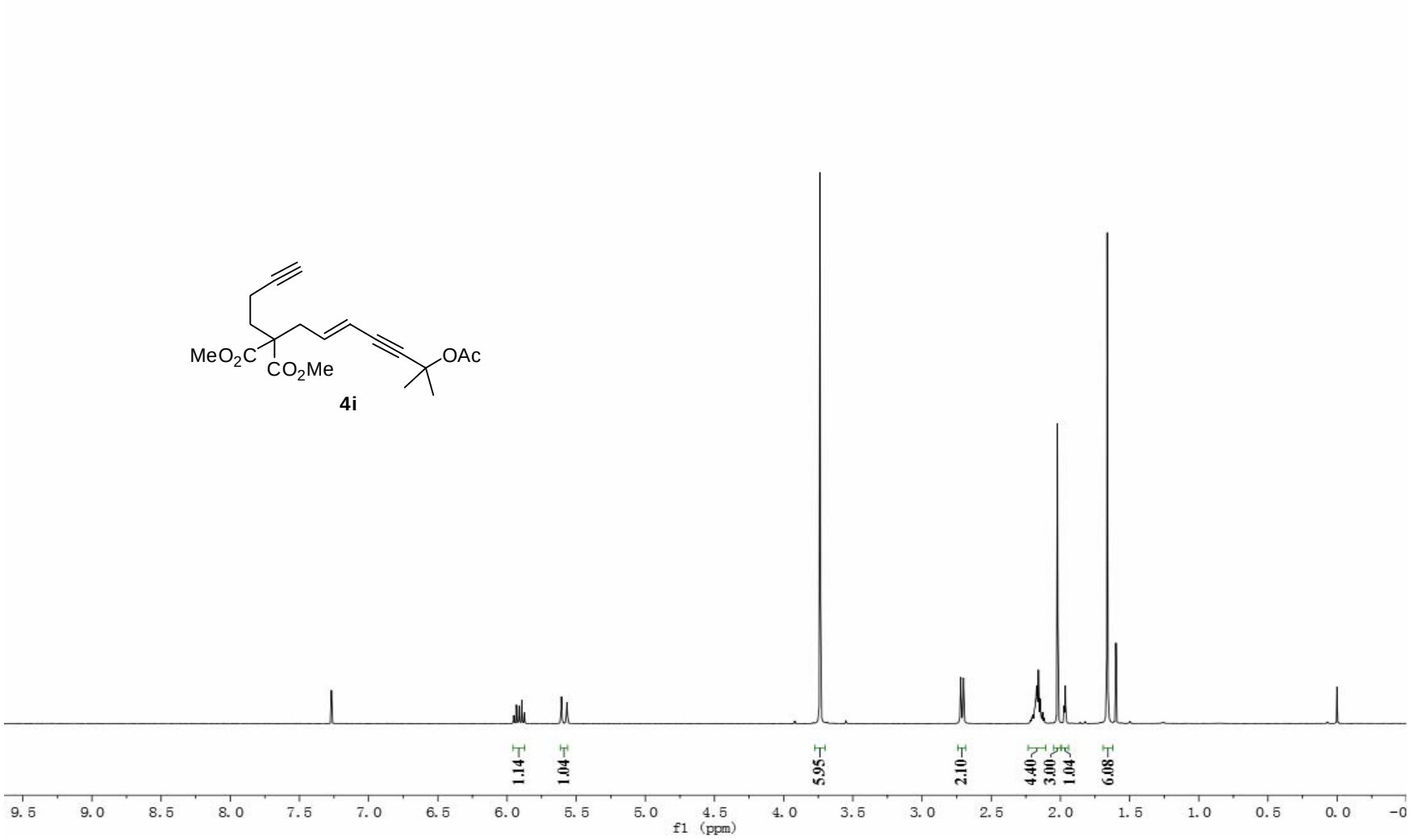


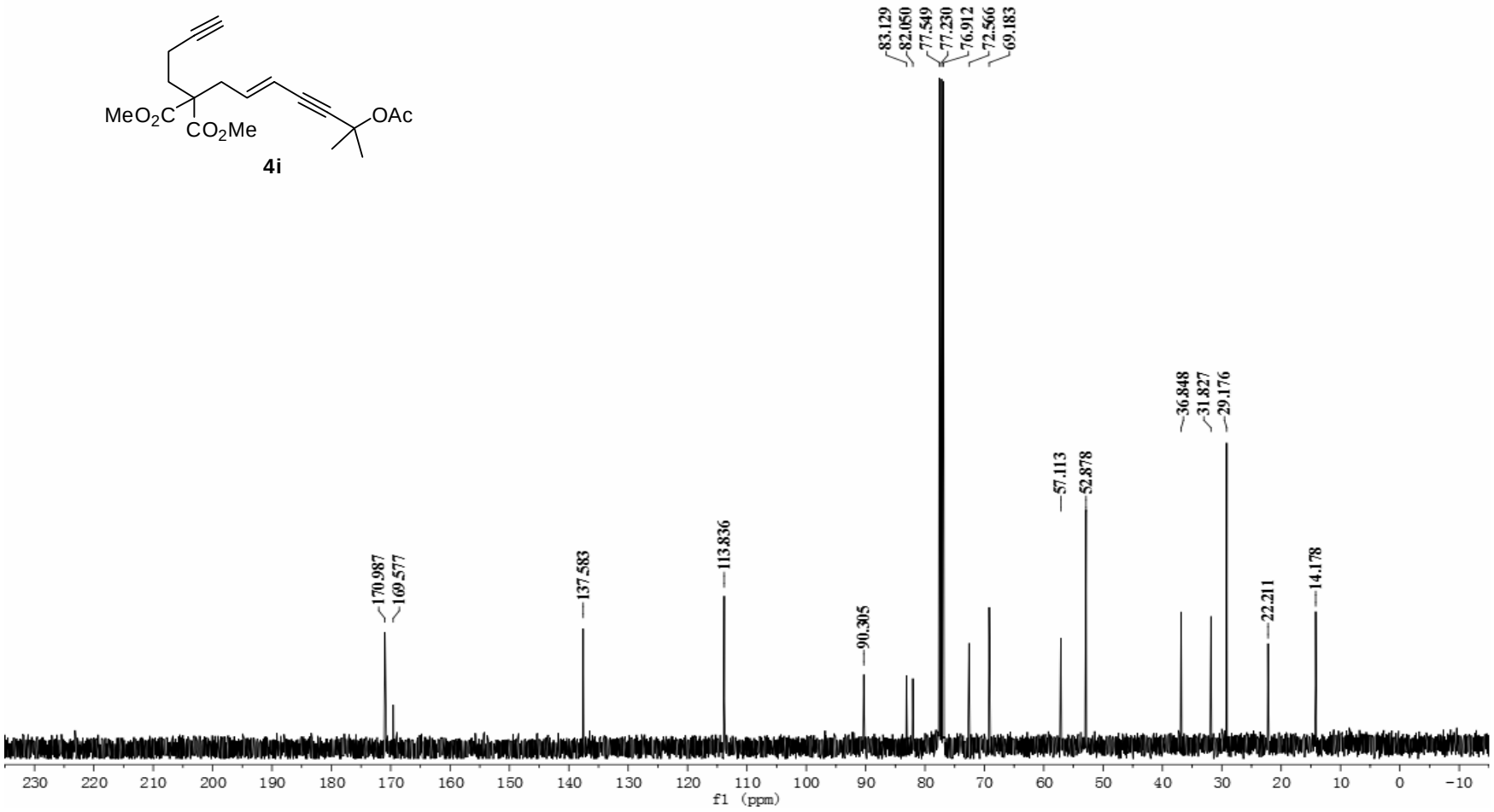
4g

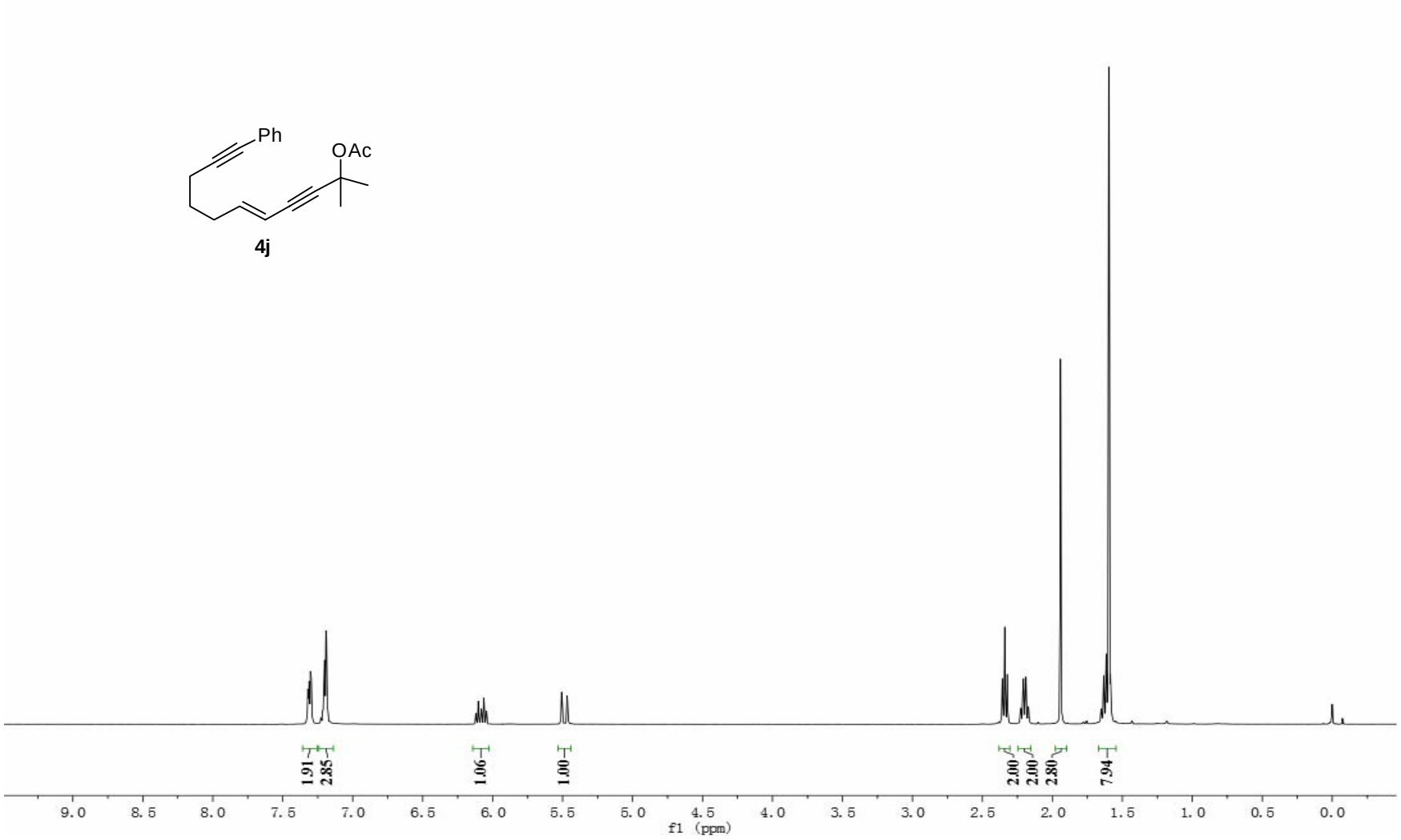

OAc
TsN
4g
169.575
145.217
143.874
136.043
129.703
127.998
109.434
94.999
80.994
77.572
77.251
76.931
76.211
74.361
72.595
52.630
35.961
29.308
22.197
21.768
17.210
f1 (ppm)

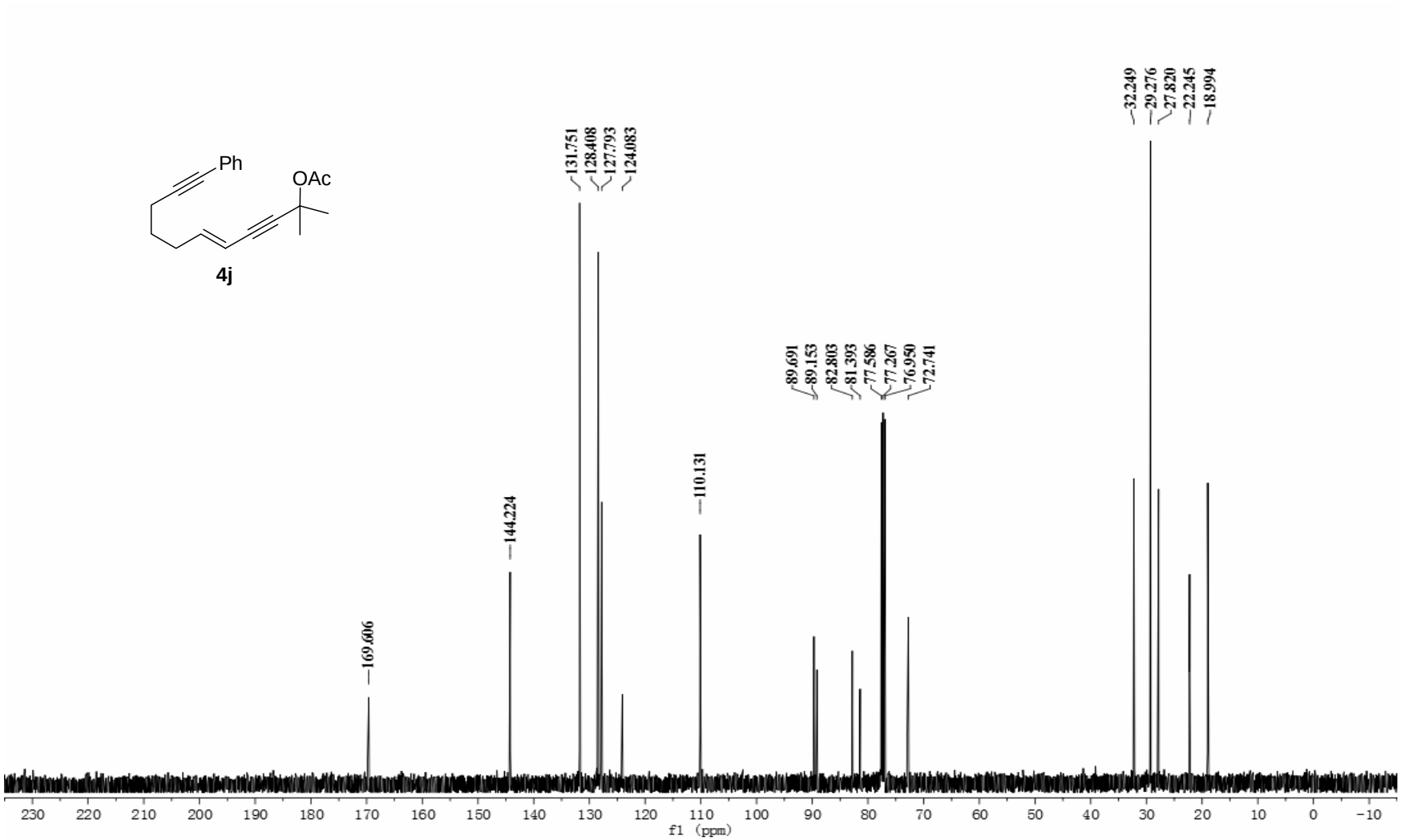

Me
OAc
MeO2C
MeO2C
4h
1.16
1.06
5.77
2.05
2.02
3.00
3.09
5.96
f1 (ppm)

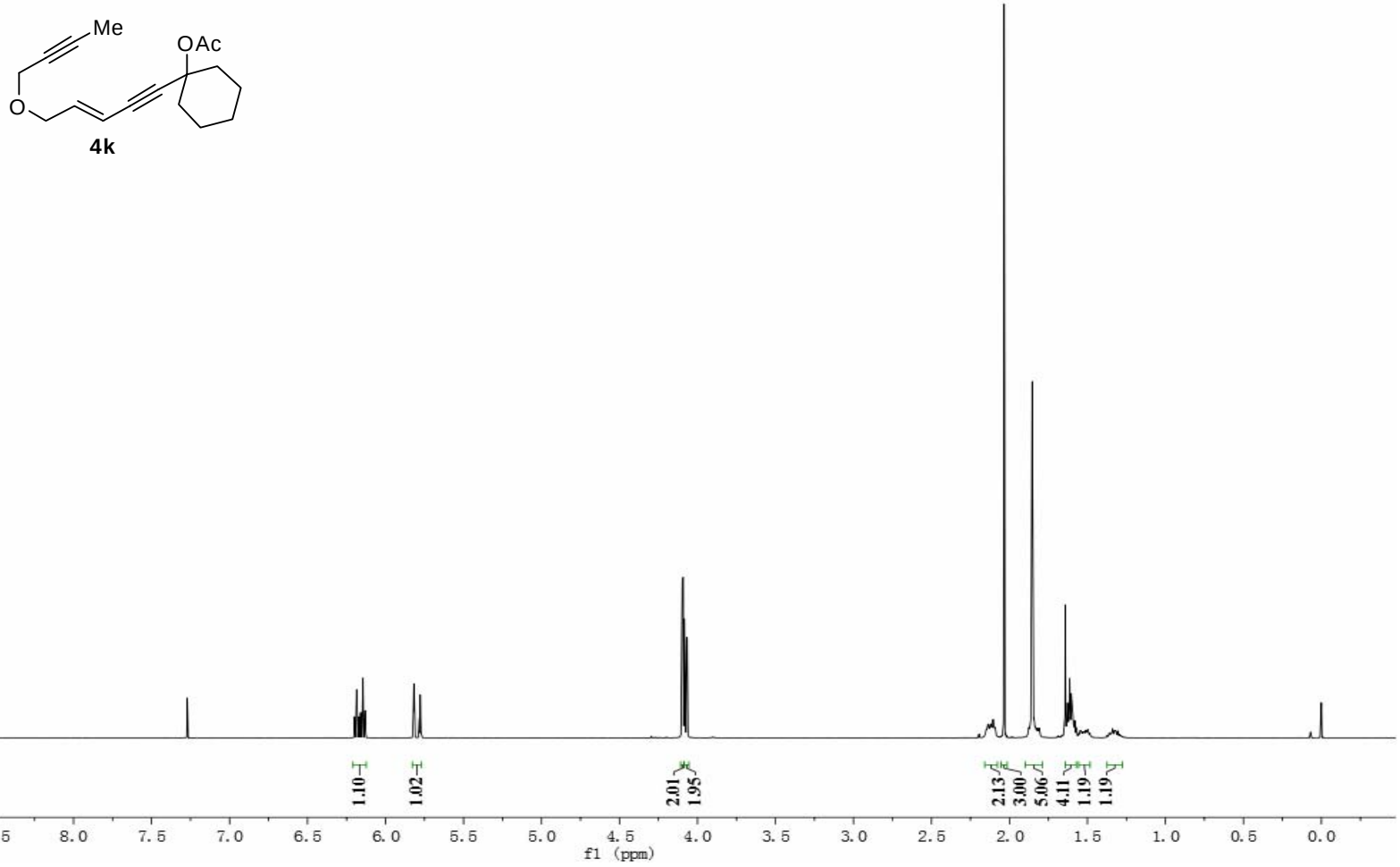

Me
OAc
MeO2C
MeO2C
4h
82.243
79.531
77.551
77.233
76.915
73.182
72.604
36.007
29.191
23.412
22.214
57.277
53.042
170.400
169.580
137.705
113.947
90.088
3.691
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

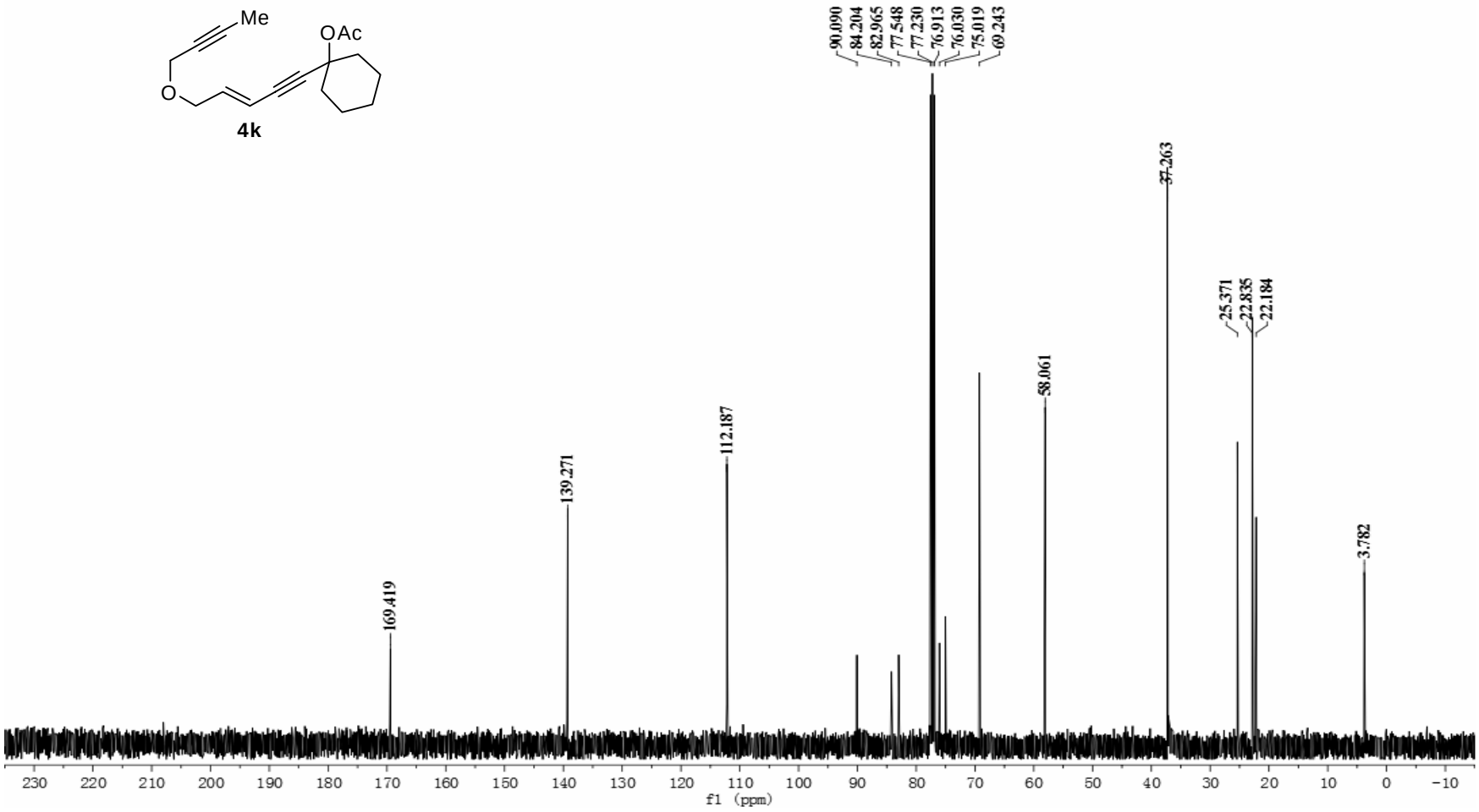


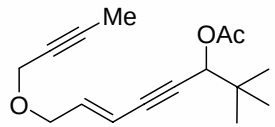

MeO2C
CO2Me
OAc
4i
83.129
82.050
77.549
77.230
76.912
72.566
69.183
170.987
169.577
137.583
113.836
90.305
57.113
52.878
36.848
31.827
29.176
22.211
14.178
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



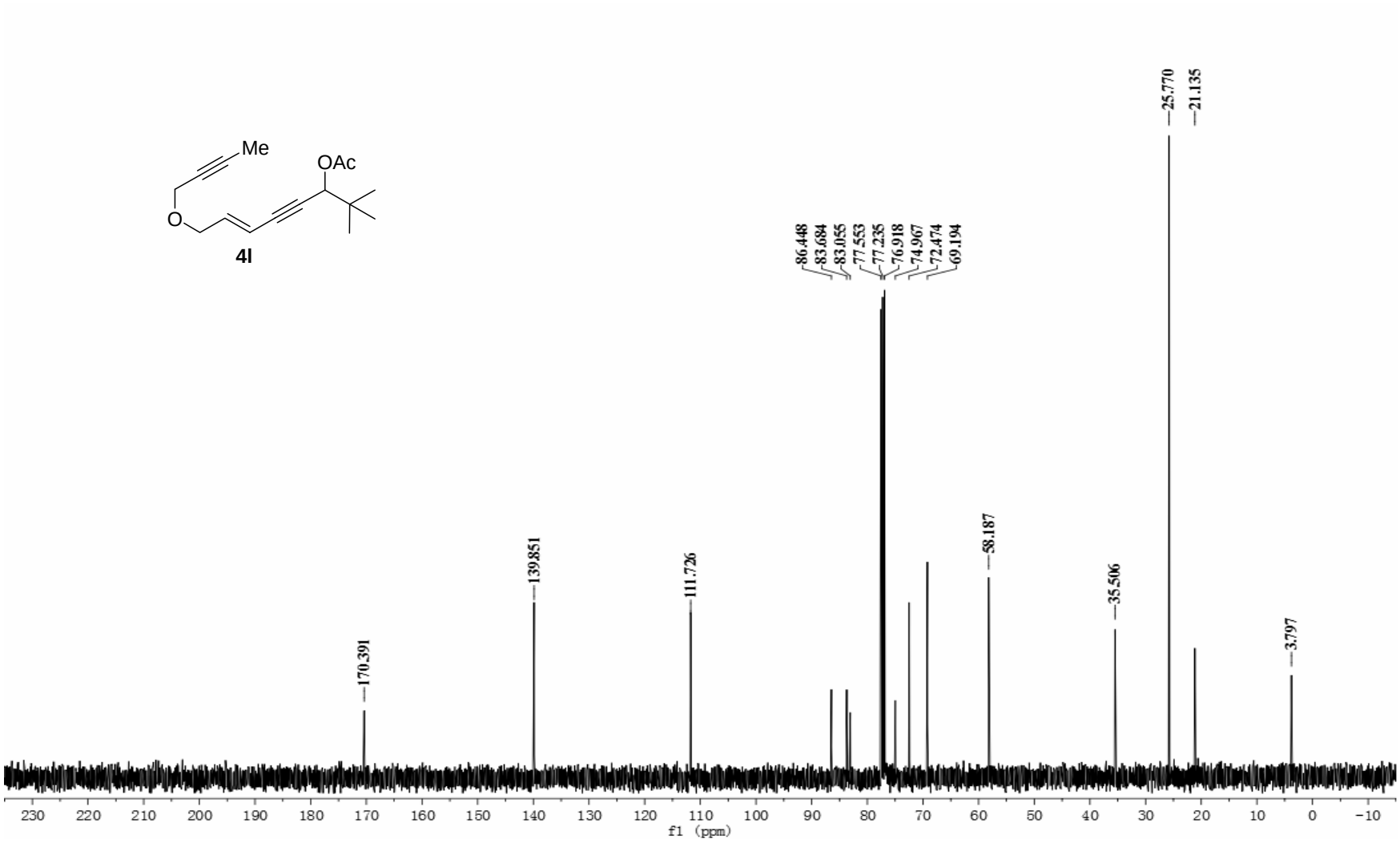

Ph
OAc
4j
131.751
128.408
127.793
124.083
89.691
89.153
82.803
81.393
77.586
77.267
76.950
72.741
32.249
29.276
27.820
22.245
18.994
169.606
144.224
110.131
f1 (ppm)

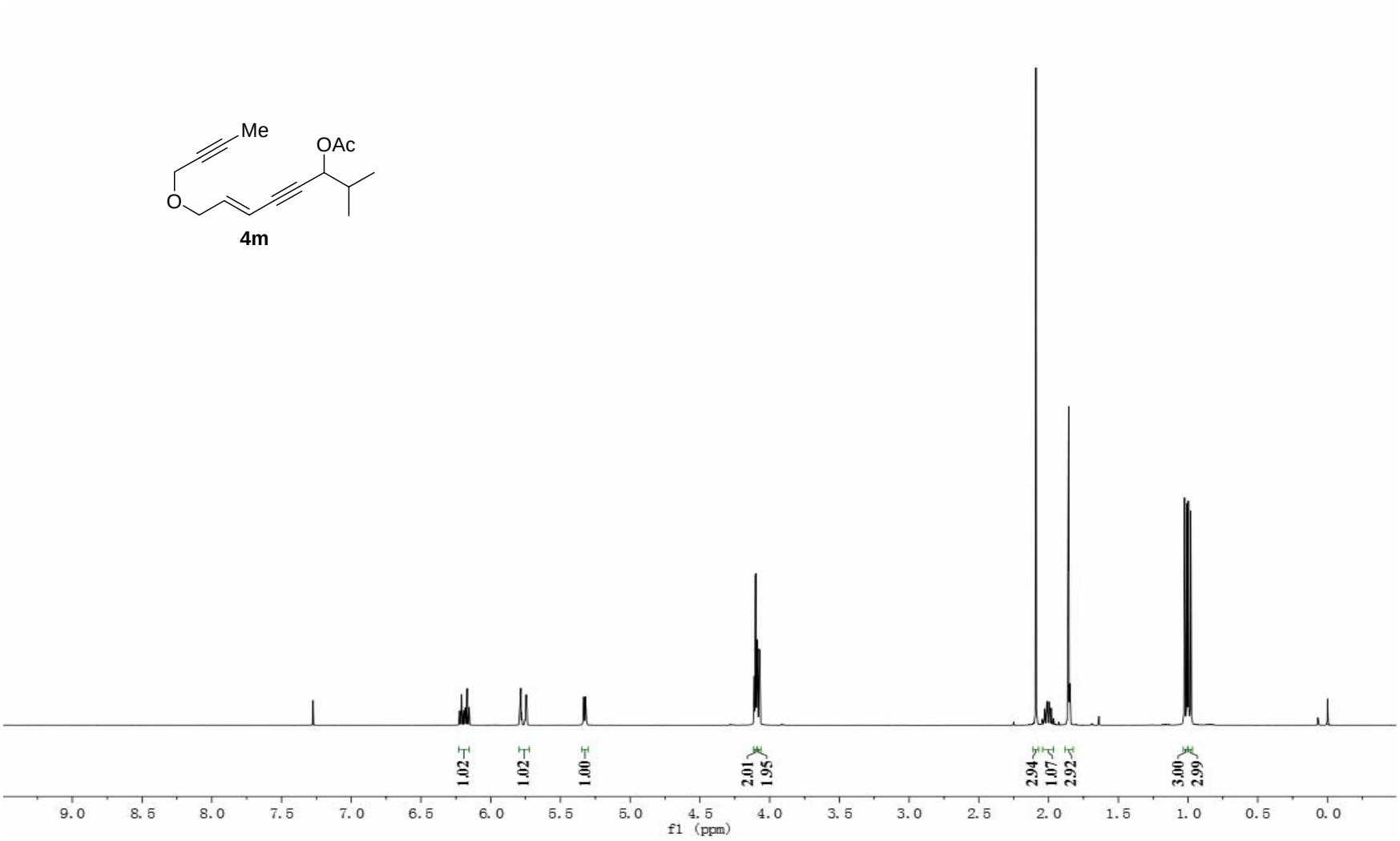


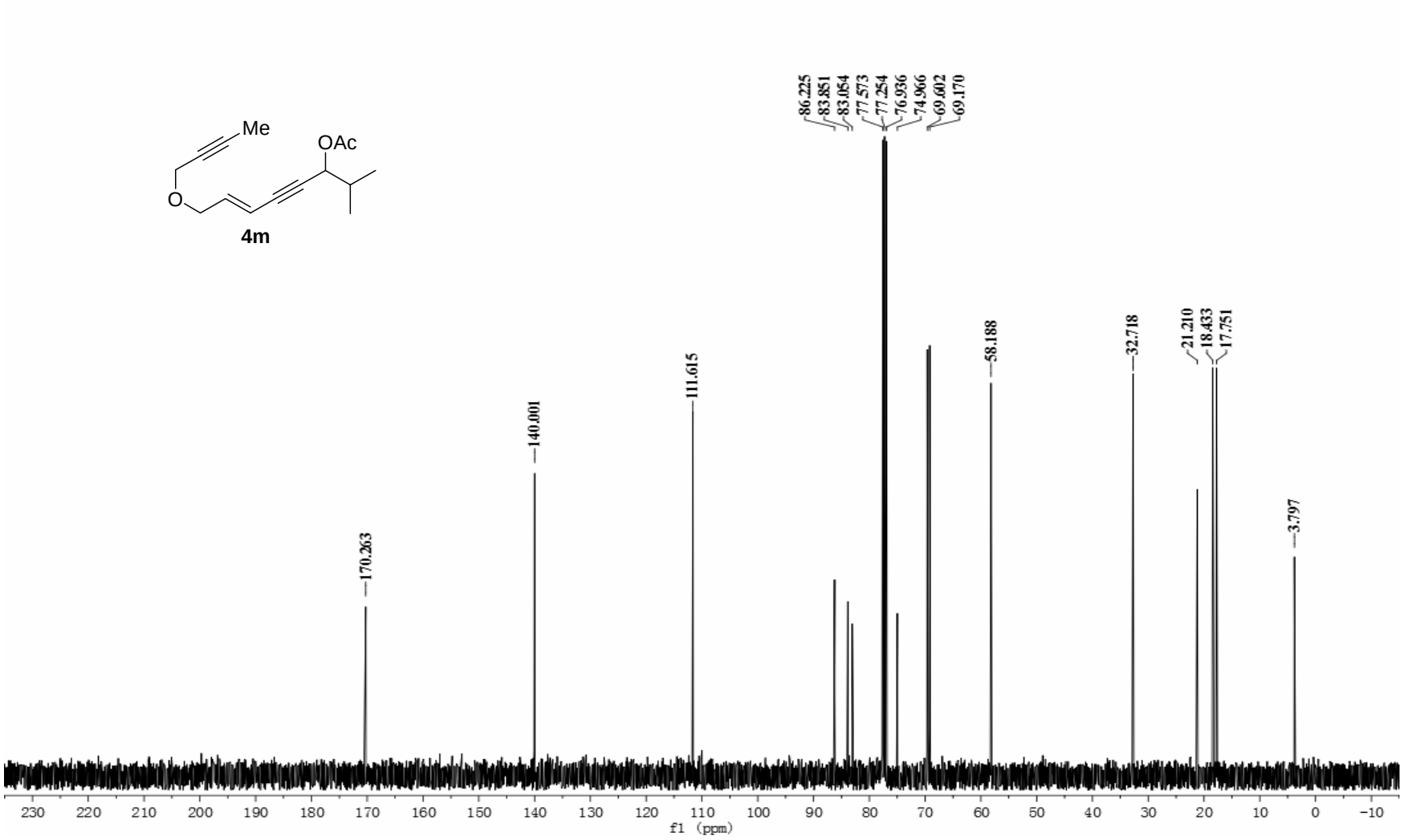

Me
OAc
O
4k
90.090
84.204
82.965
77.548
77.230
76.913
76.030
75.019
69.243
37.263
25.371
22.835
22.184
58.061
112.187
139.271
169.419
3.782
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

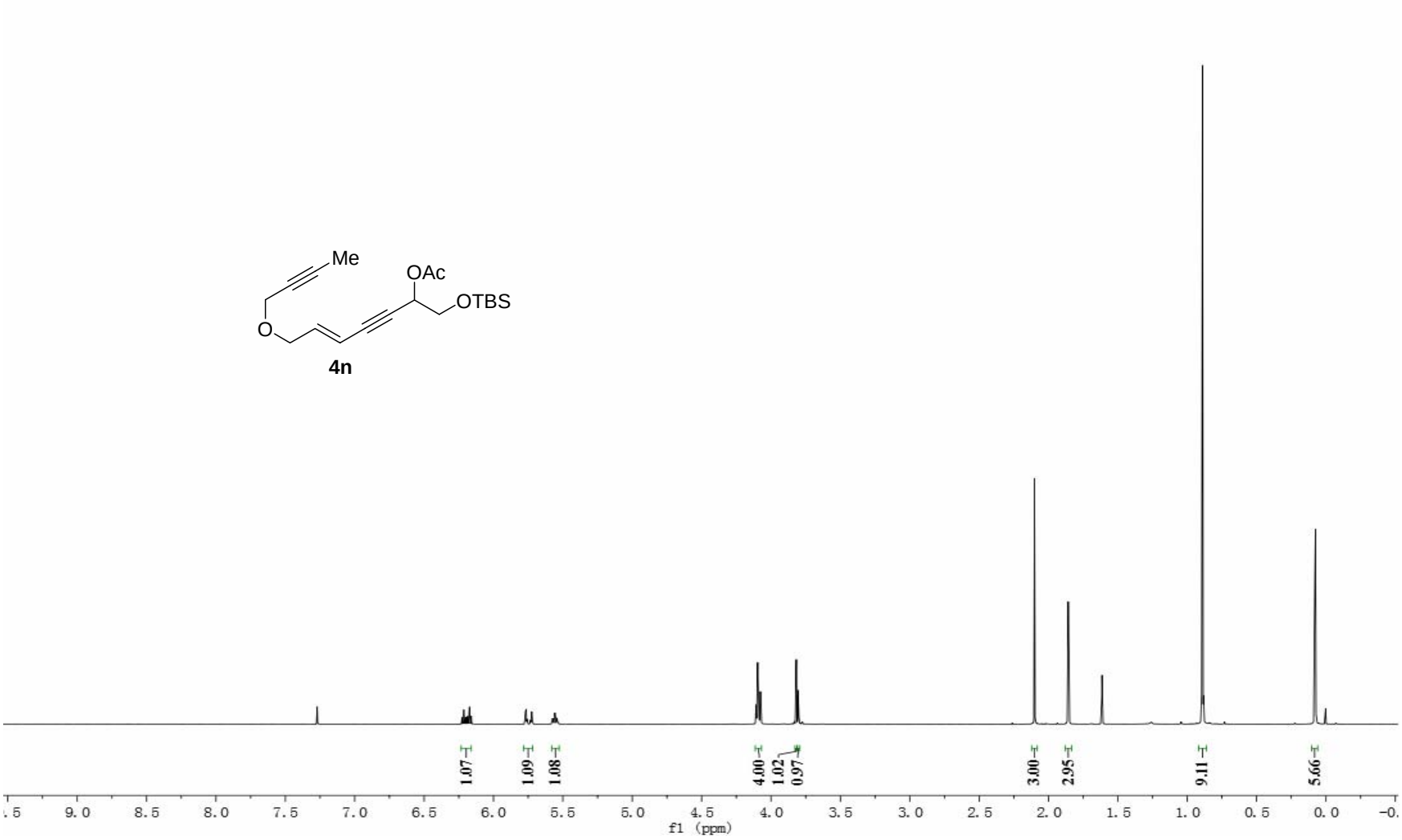


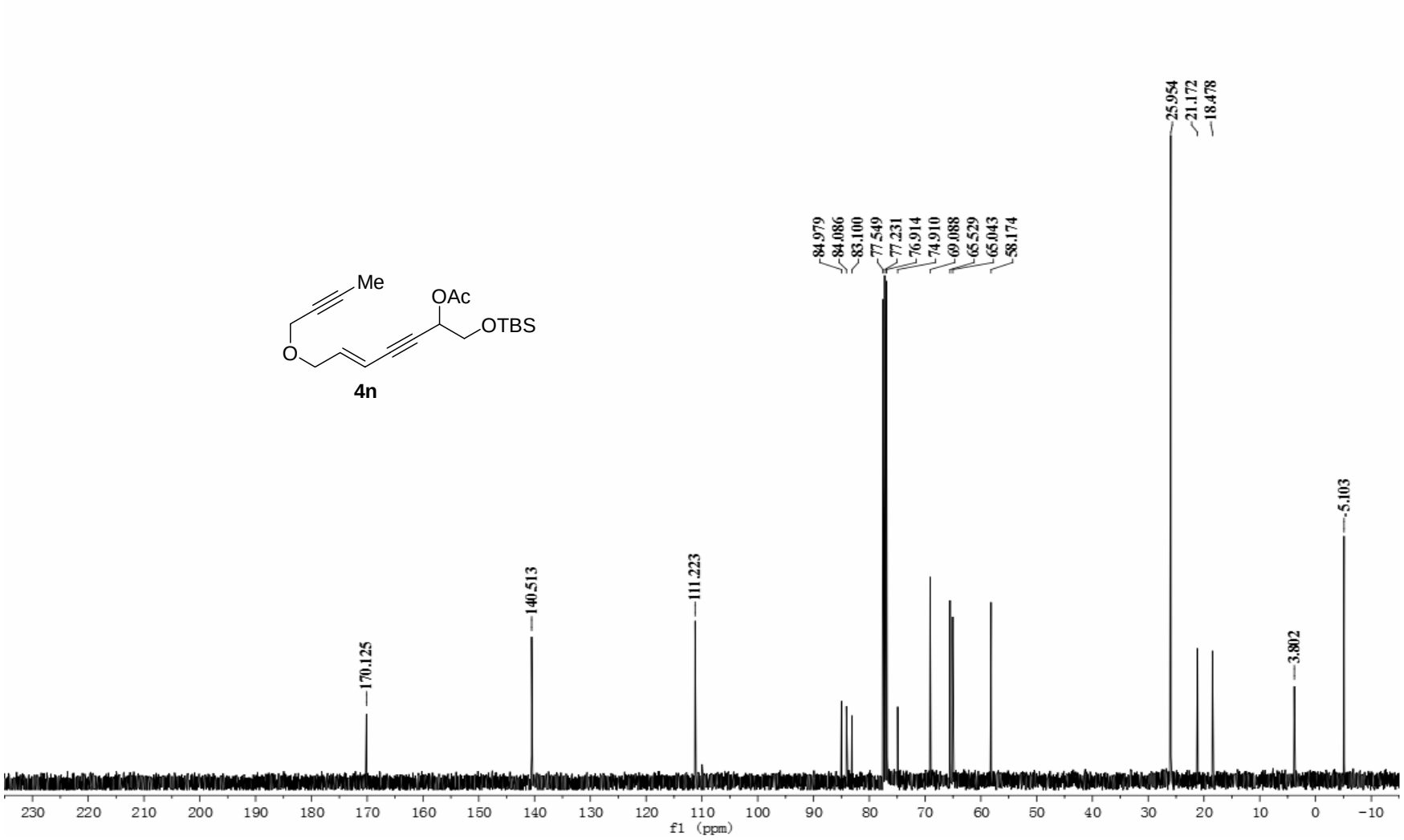
4l

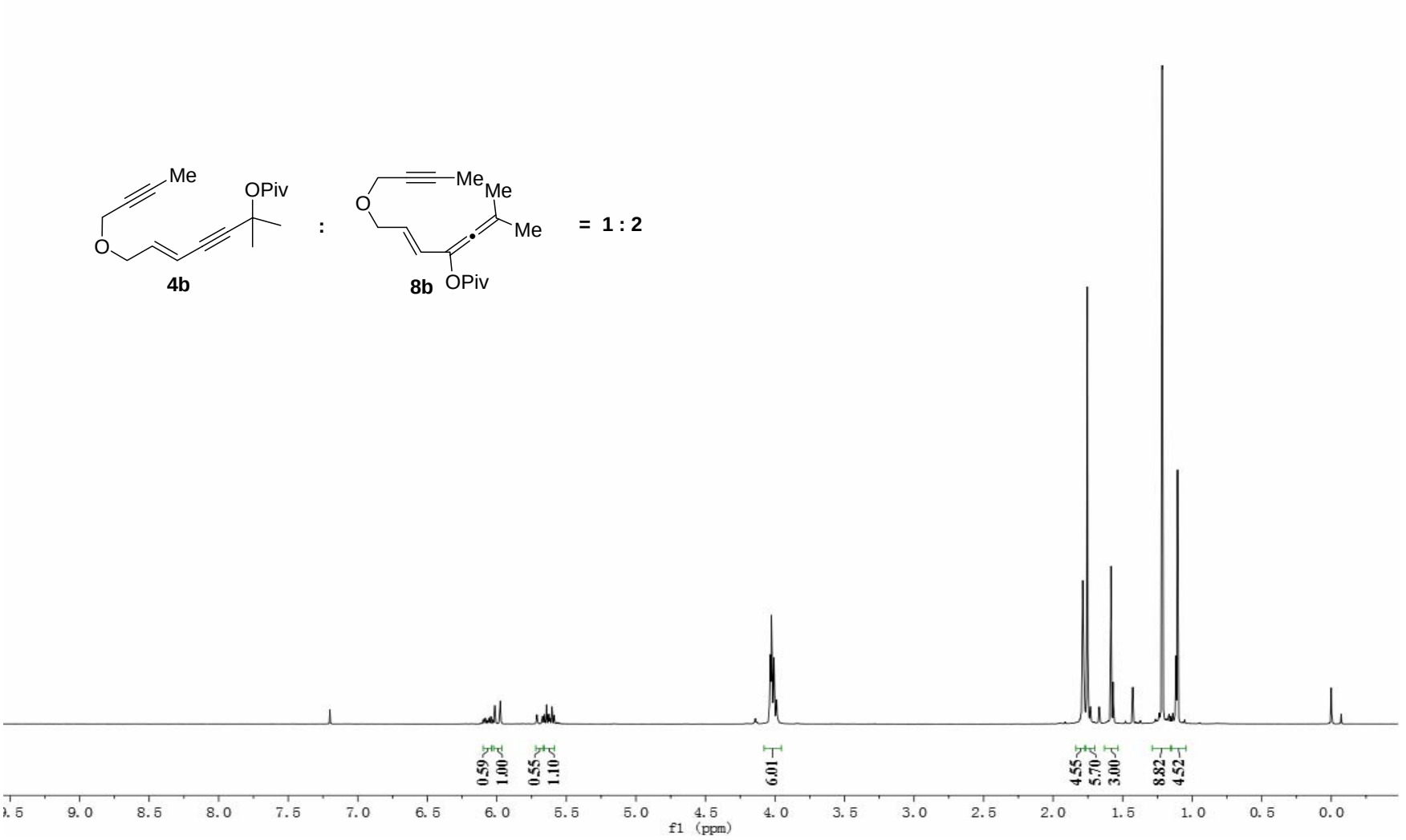

Me
OAc
O
4l
170.391
139.851
111.726
86.448
83.684
83.055
77.553
77.235
76.918
74.967
72.474
69.194
58.187
35.506
25.770
21.135
3.797
f1 (ppm)

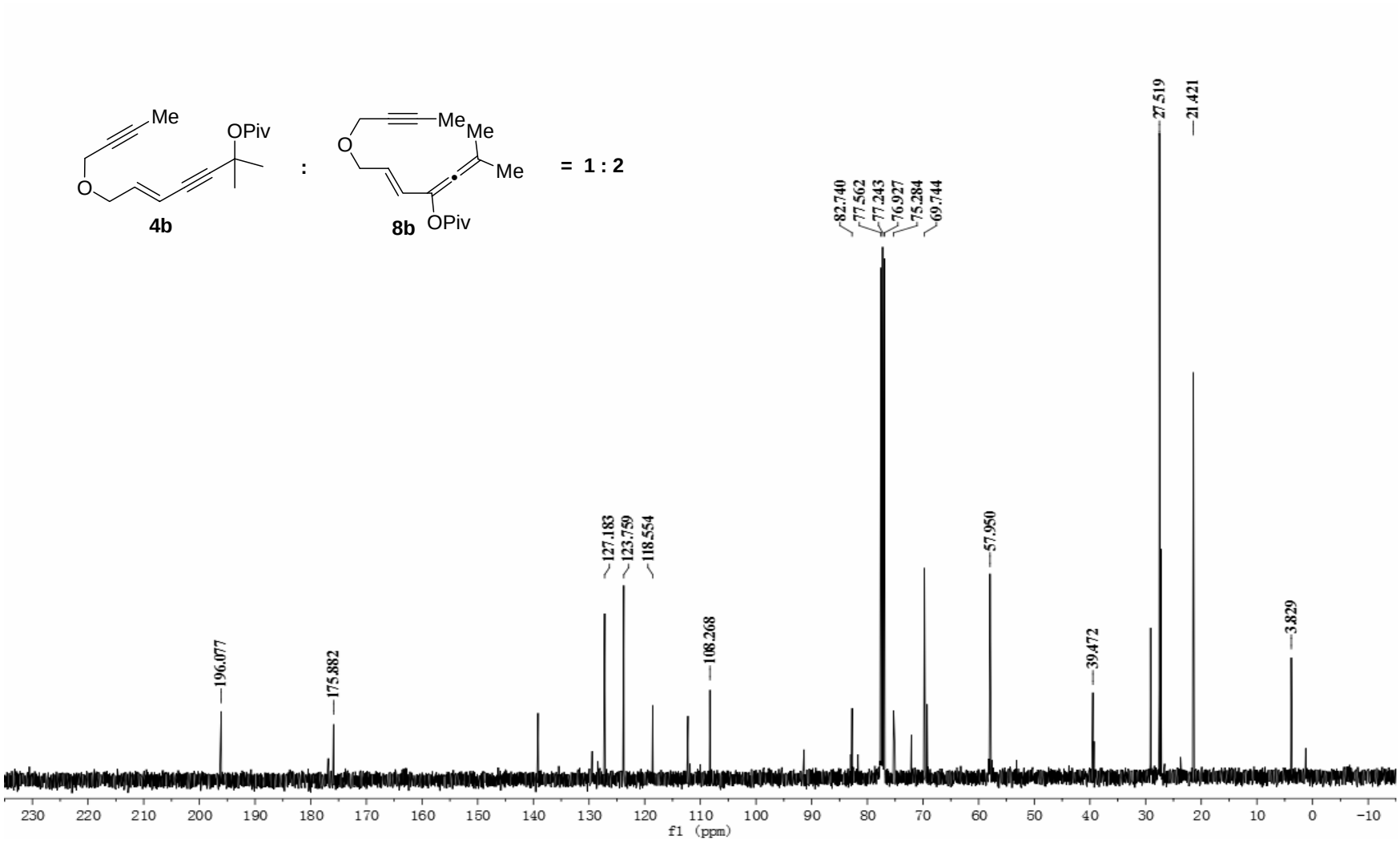

Me
OAc
O
4m
1.02
1.02
1.00
2.01
1.95
2.94
1.07
2.92
3.00
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

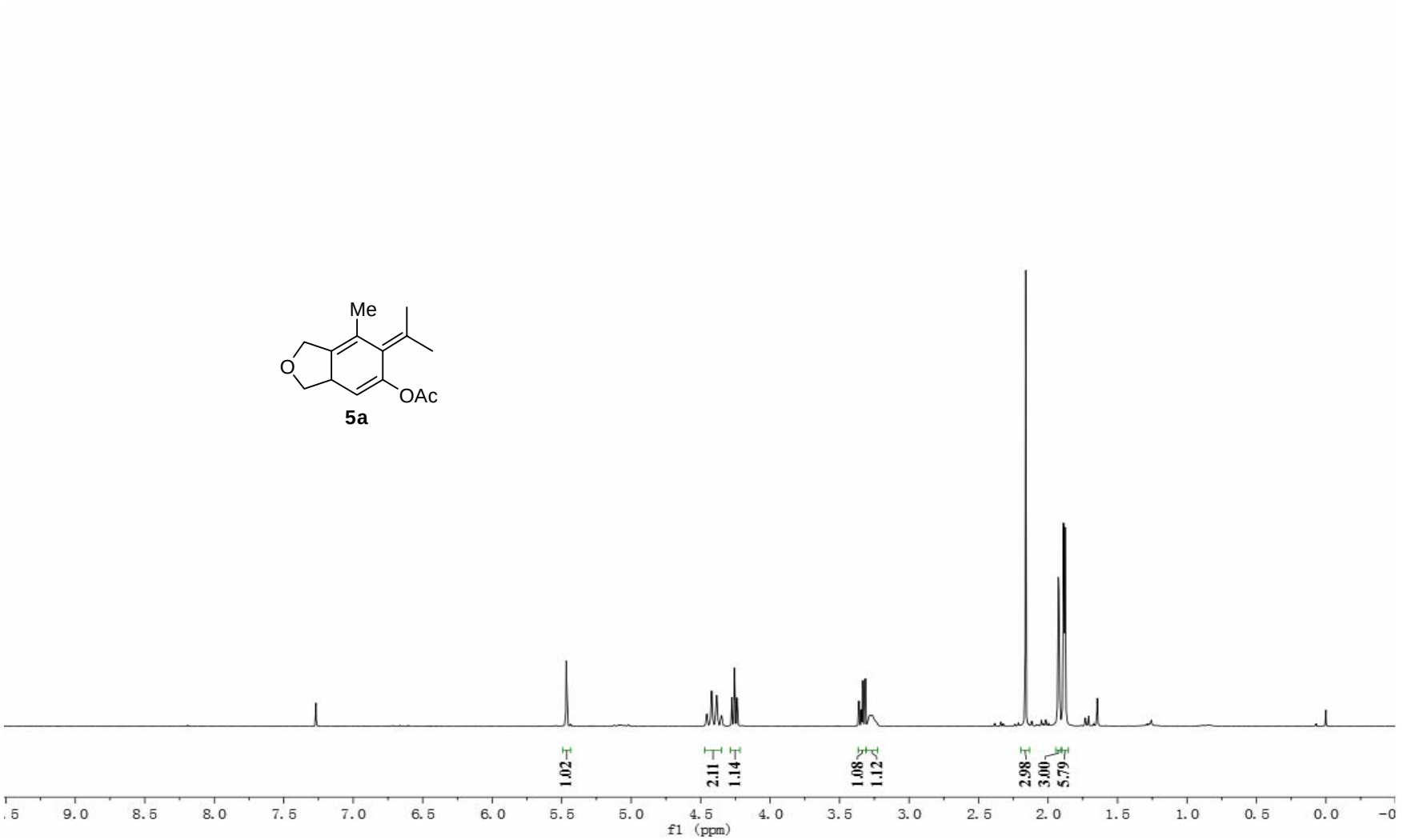


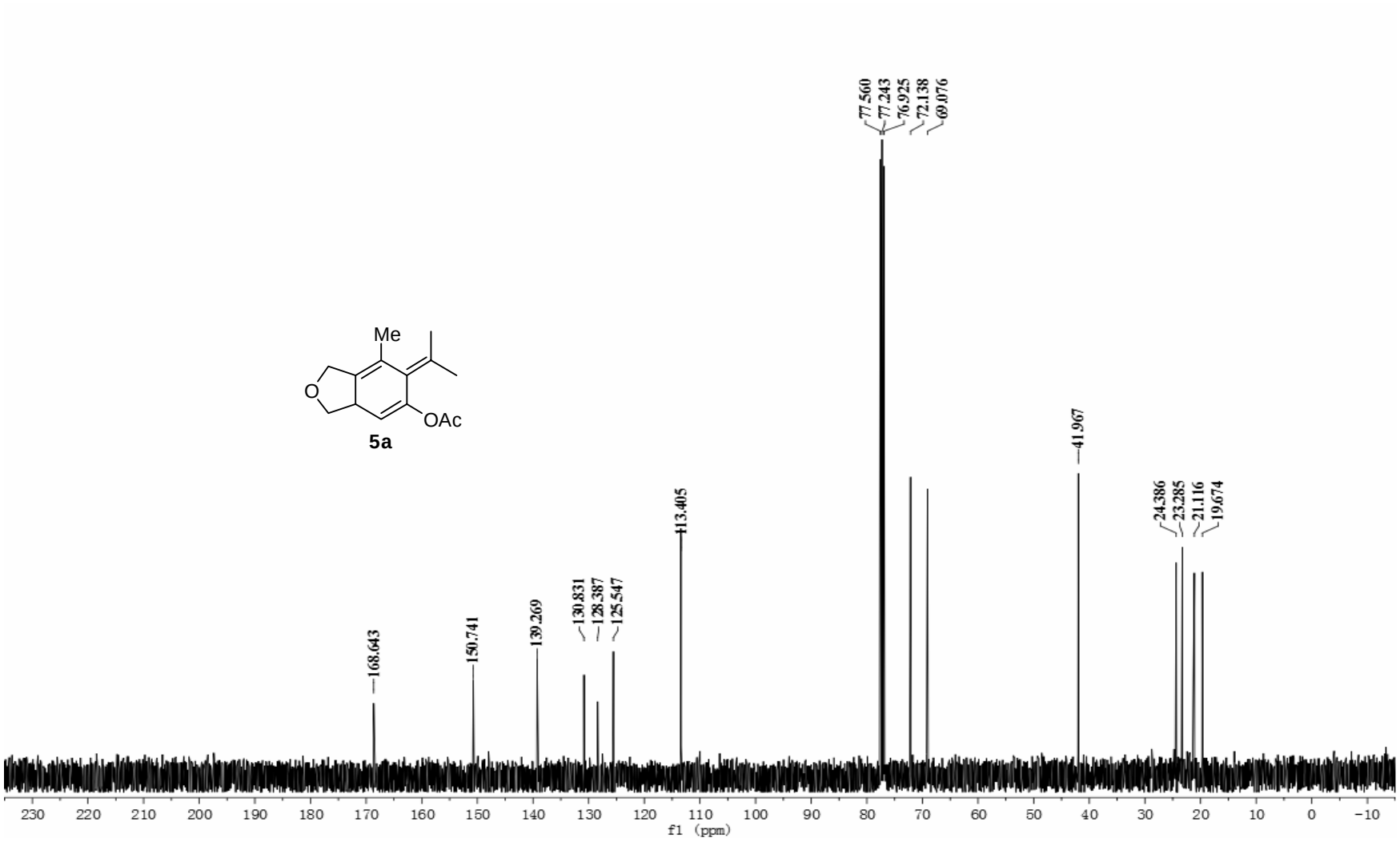


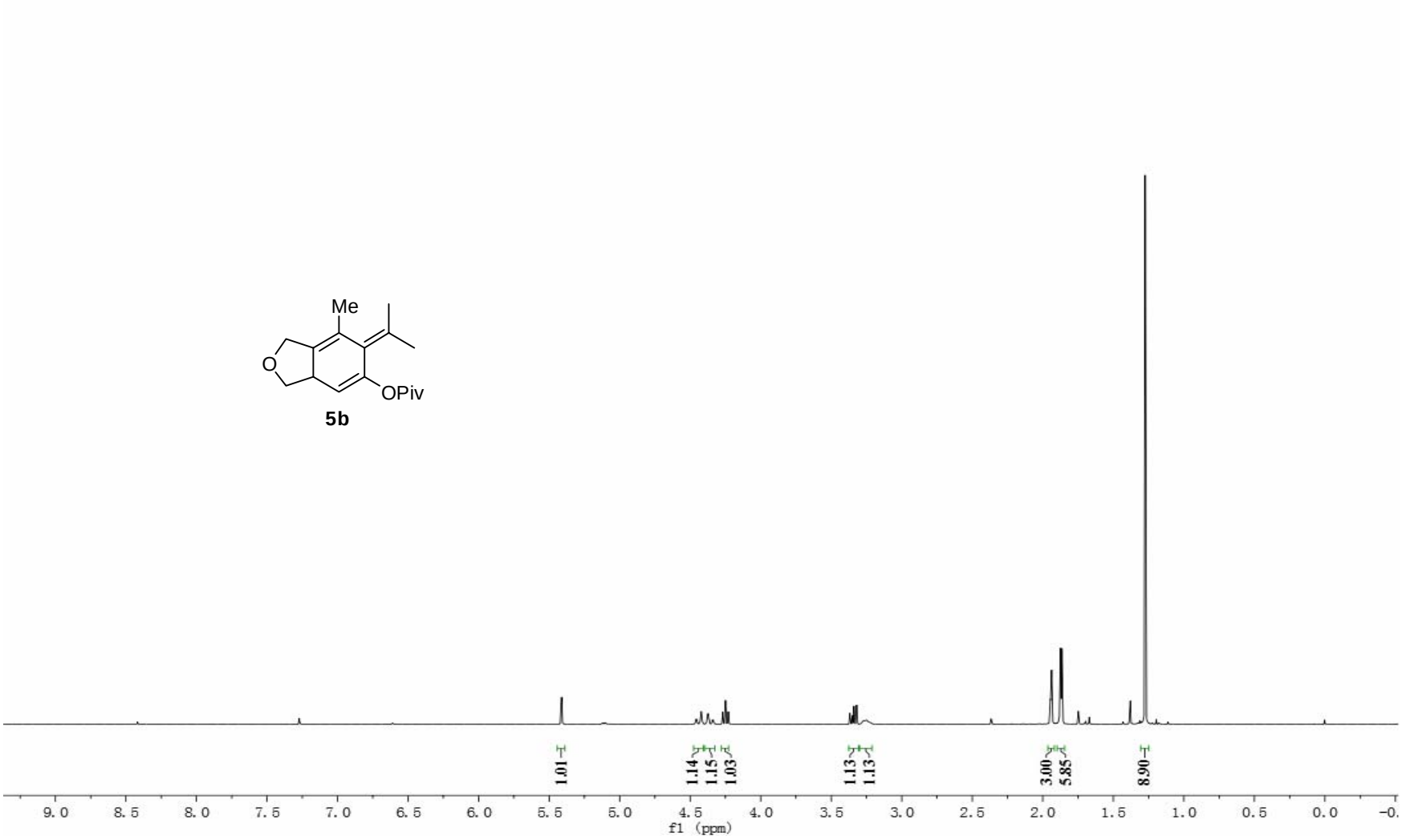

Me
OAc
OTBS
O
4n
84.979
84.086
83.100
77.549
77.231
76.914
74.910
69.088
65.529
65.043
58.174
25.954
21.172
18.478
170.125
140.513
111.223
3.802
-5.103
f1 (ppm)

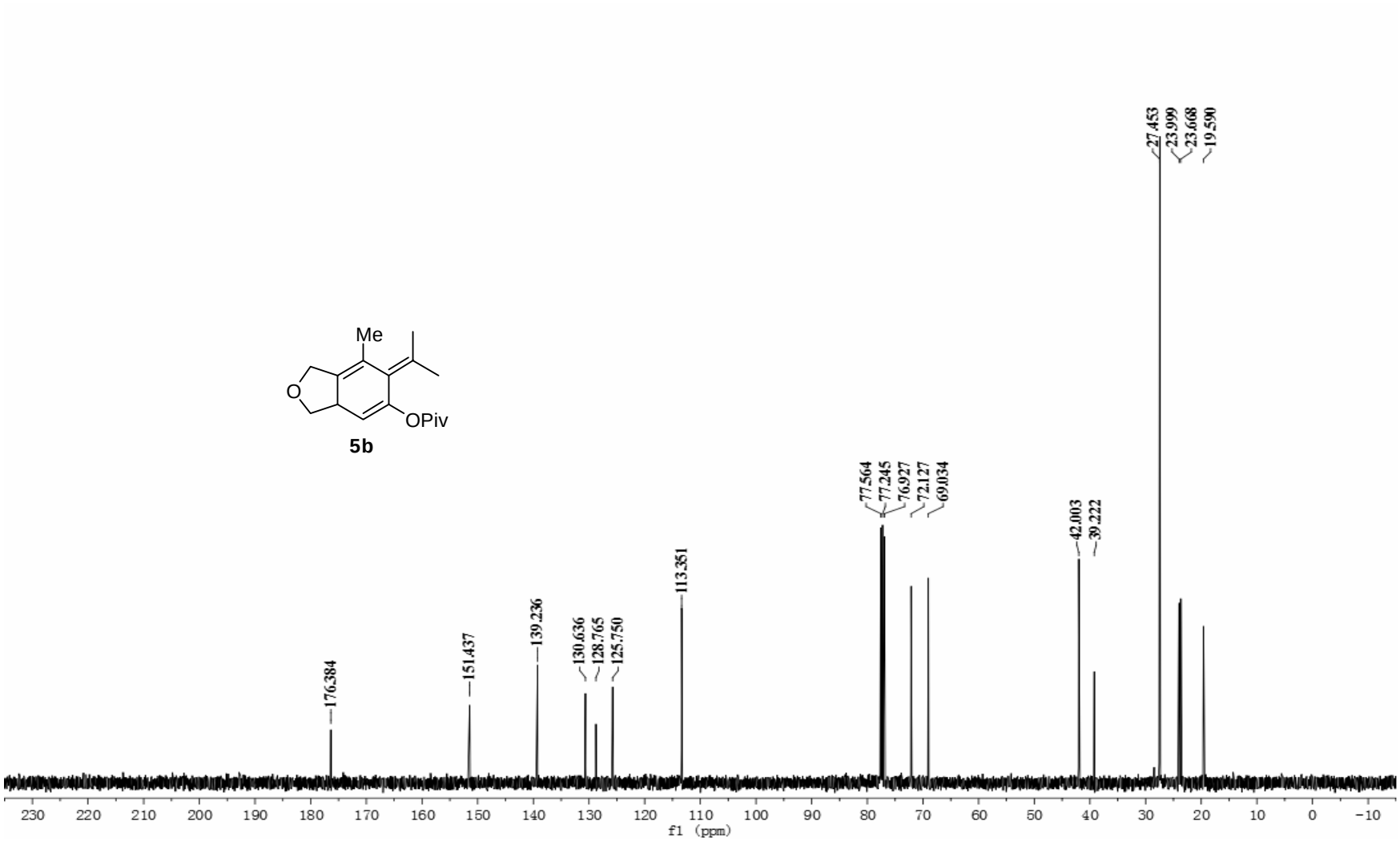


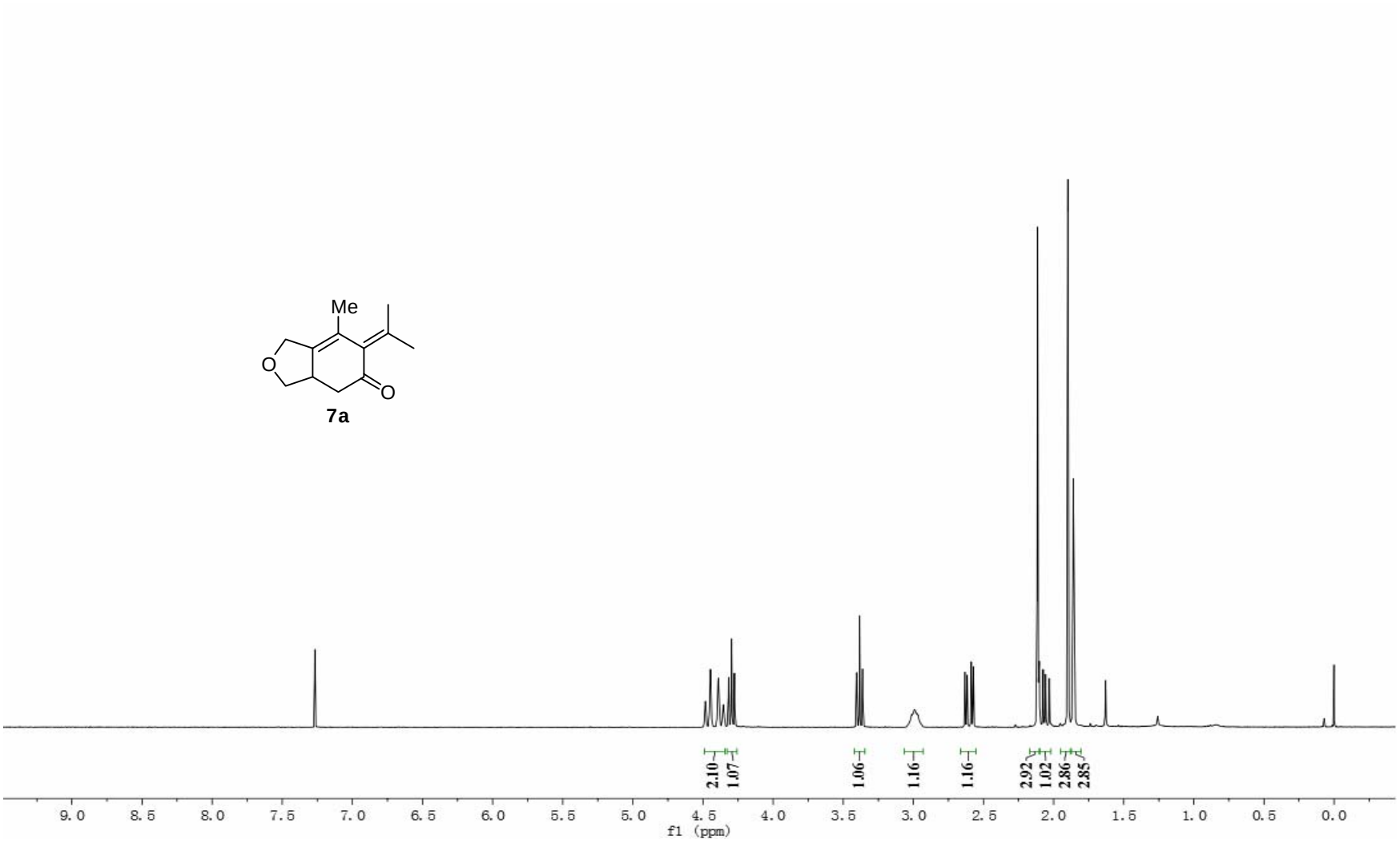


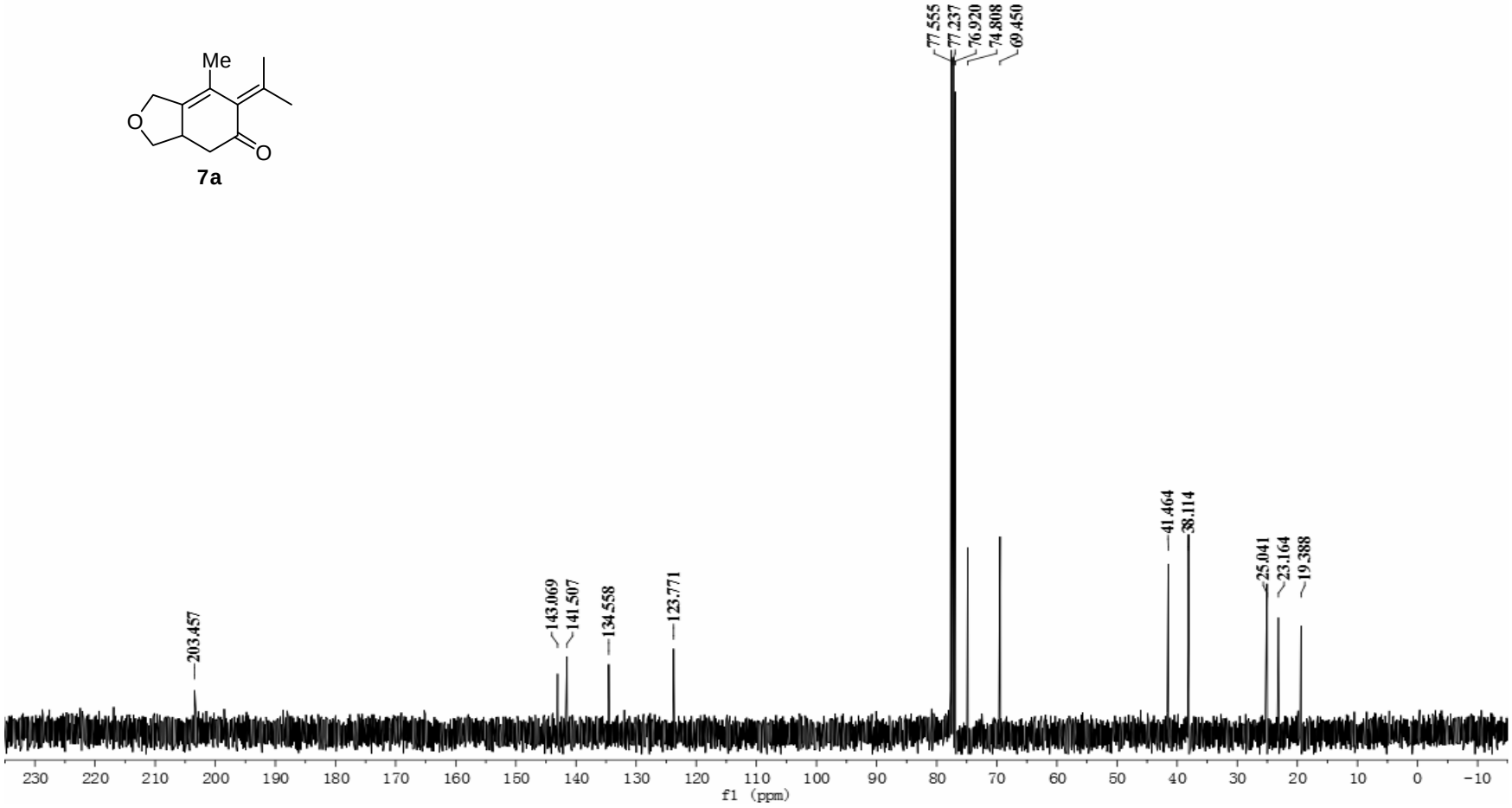


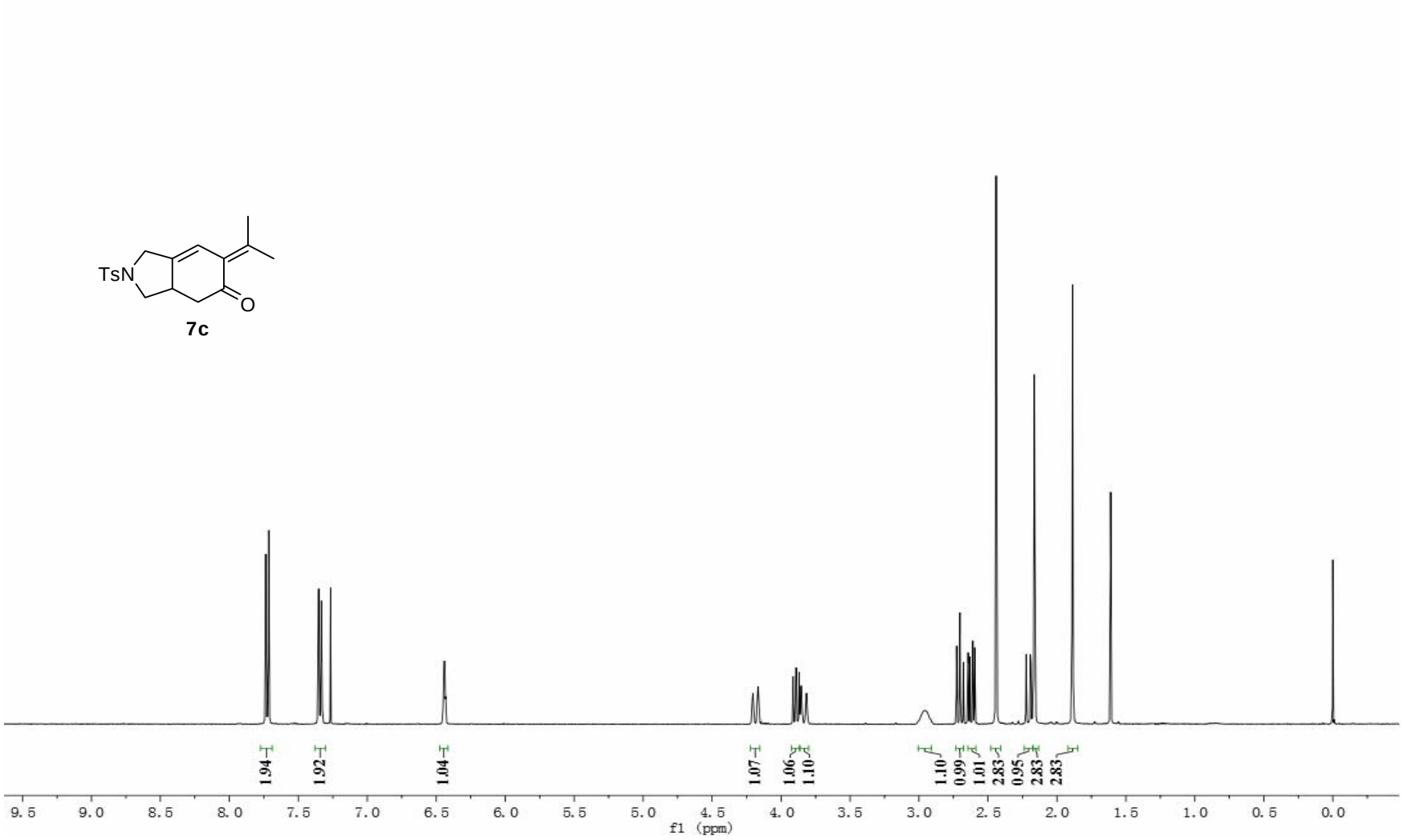

Me
O
OAc
5a
77.560
77.243
76.925
72.138
69.076
41.967
24.386
23.285
21.116
19.674
113.405
168.643
150.741
139.269
130.831
128.387
125.547
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

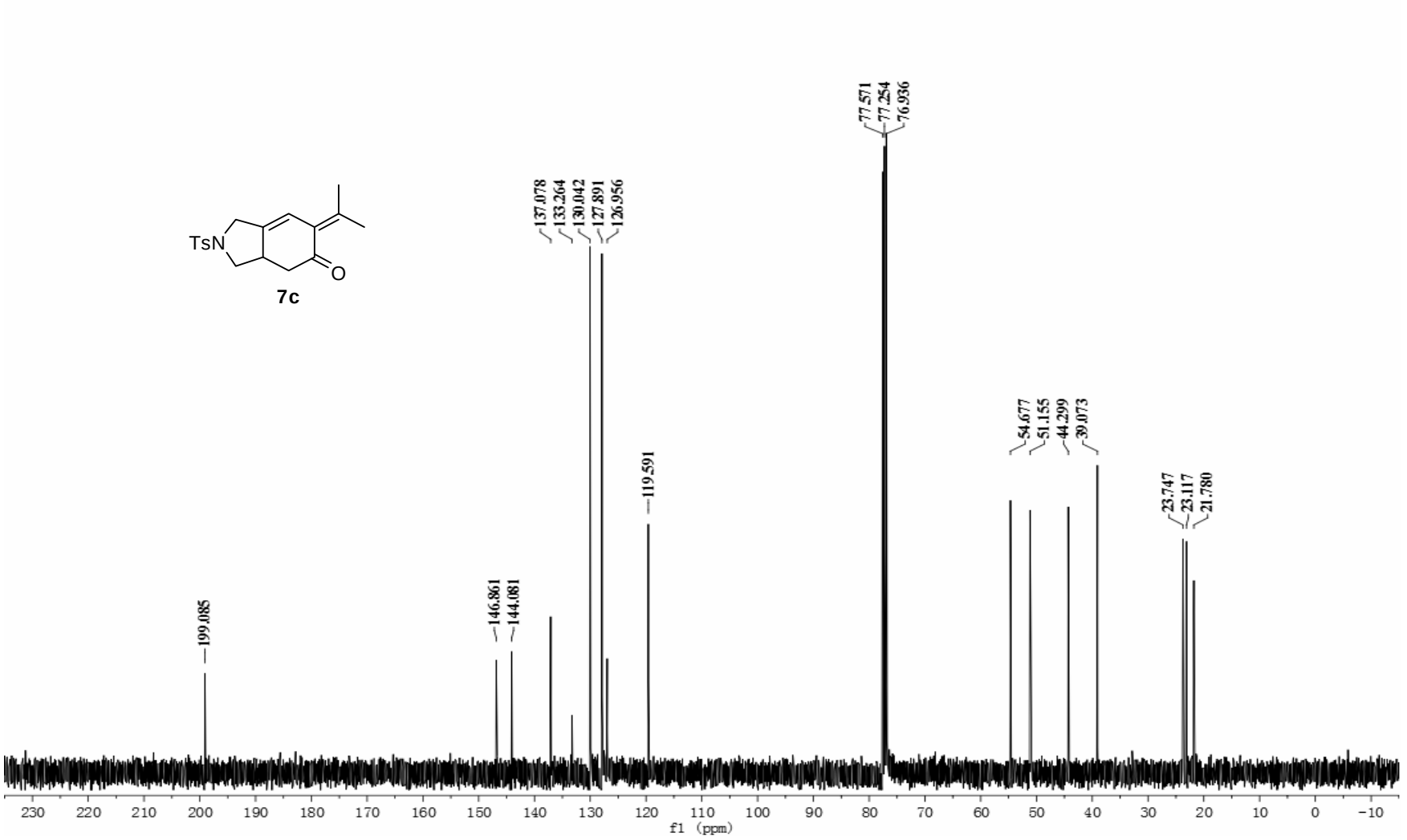


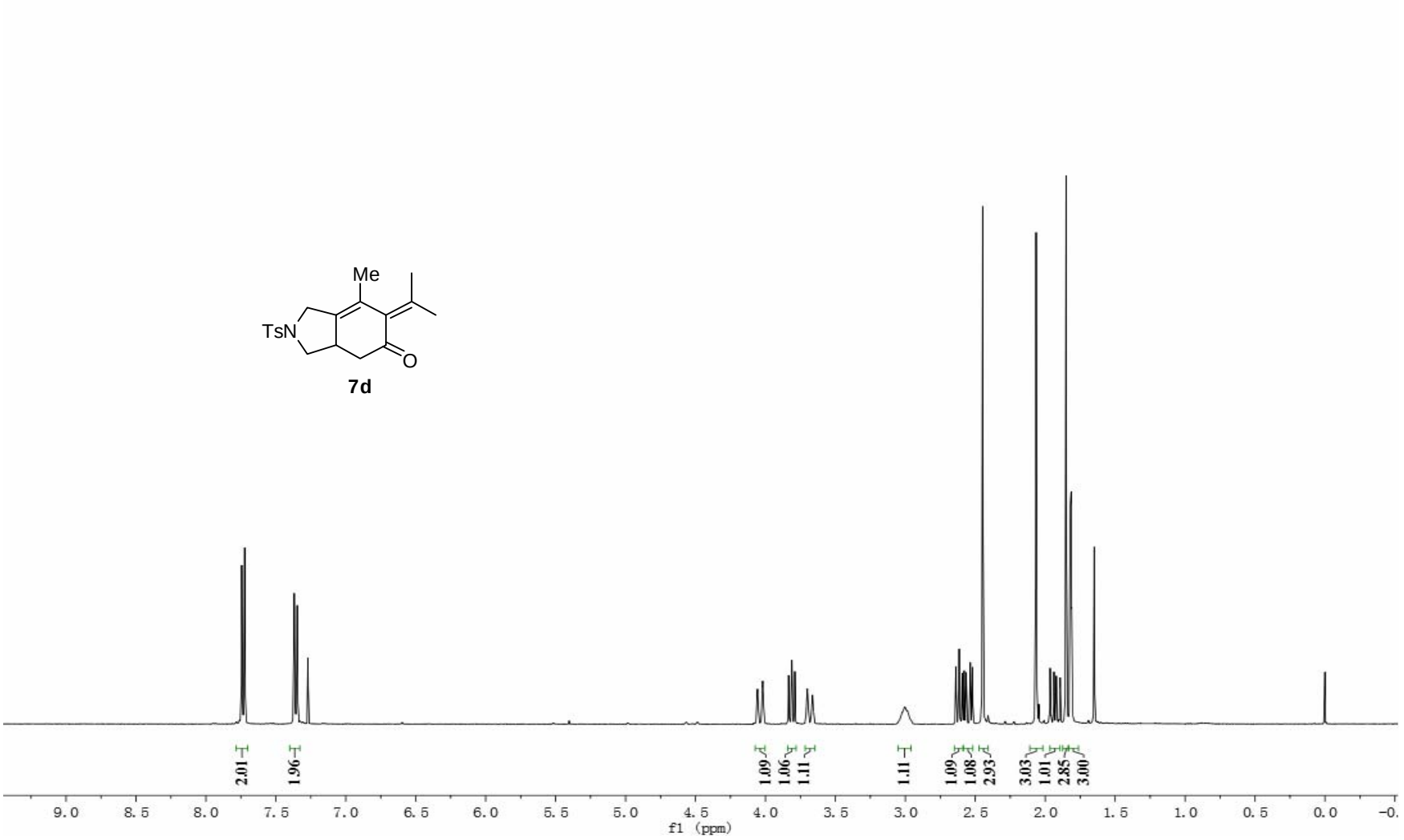

Me
O
OPiv
5b
176.384
151.437
139.236
130.636
128.765
125.750
113.351
77.564
77.245
76.927
72.127
69.034
42.003
39.222
27.453
23.999
23.668
19.590
f1 (ppm)

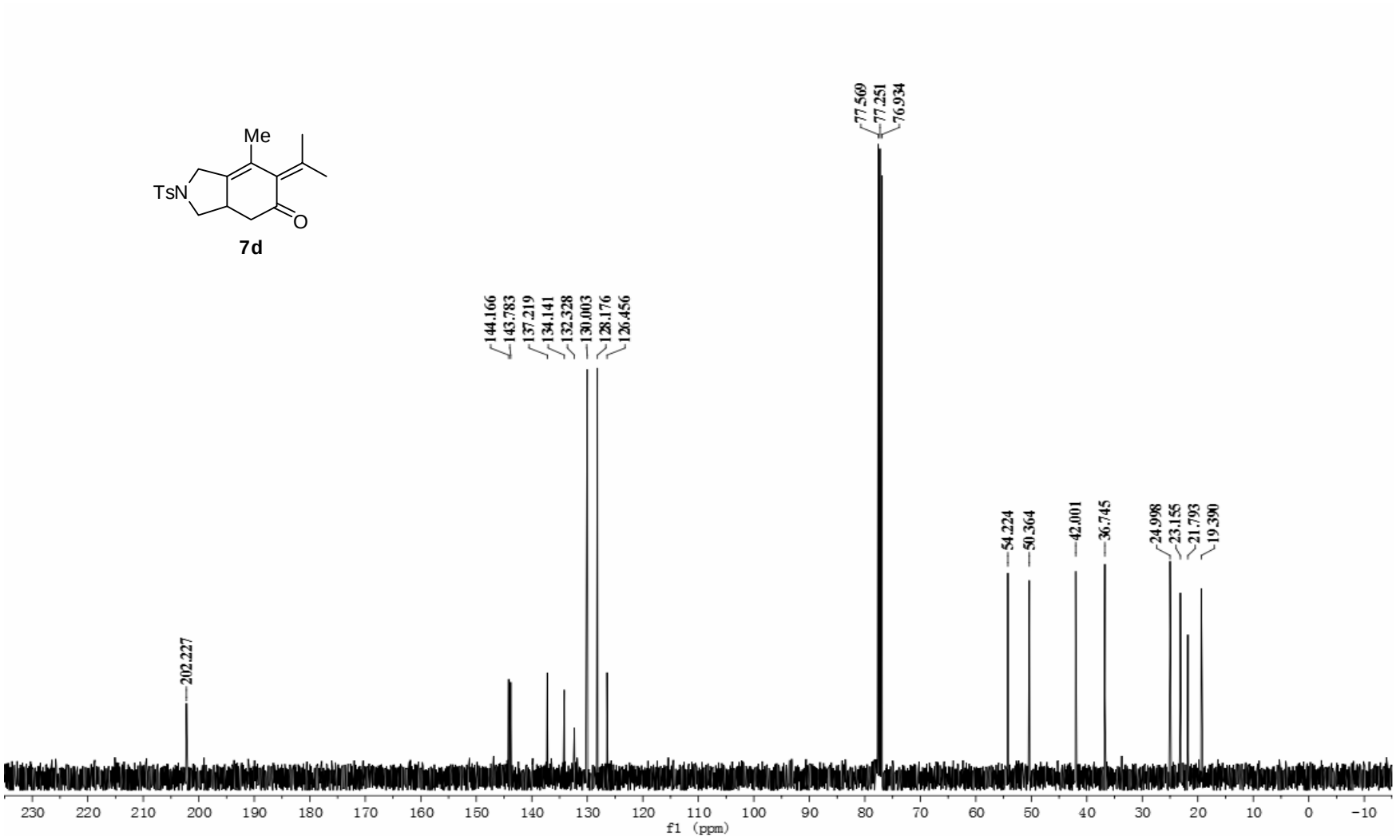

Me
O
O
7a
2.10
1.07
1.06
1.16
1.16
2.92
1.02
2.86
2.85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

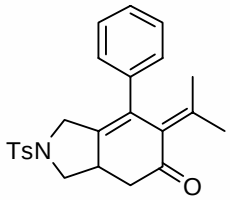

Me
O
O
7a
77.555
77.237
76.920
74.808
69.450
203.457
143.069
141.507
134.558
123.771
41.464
38.114
25.041
23.164
19.388
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


TsN
O
7c
1.94
1.92
1.04
1.07
1.06
1.10
1.10
0.99
1.01
2.83
0.95
2.83
2.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

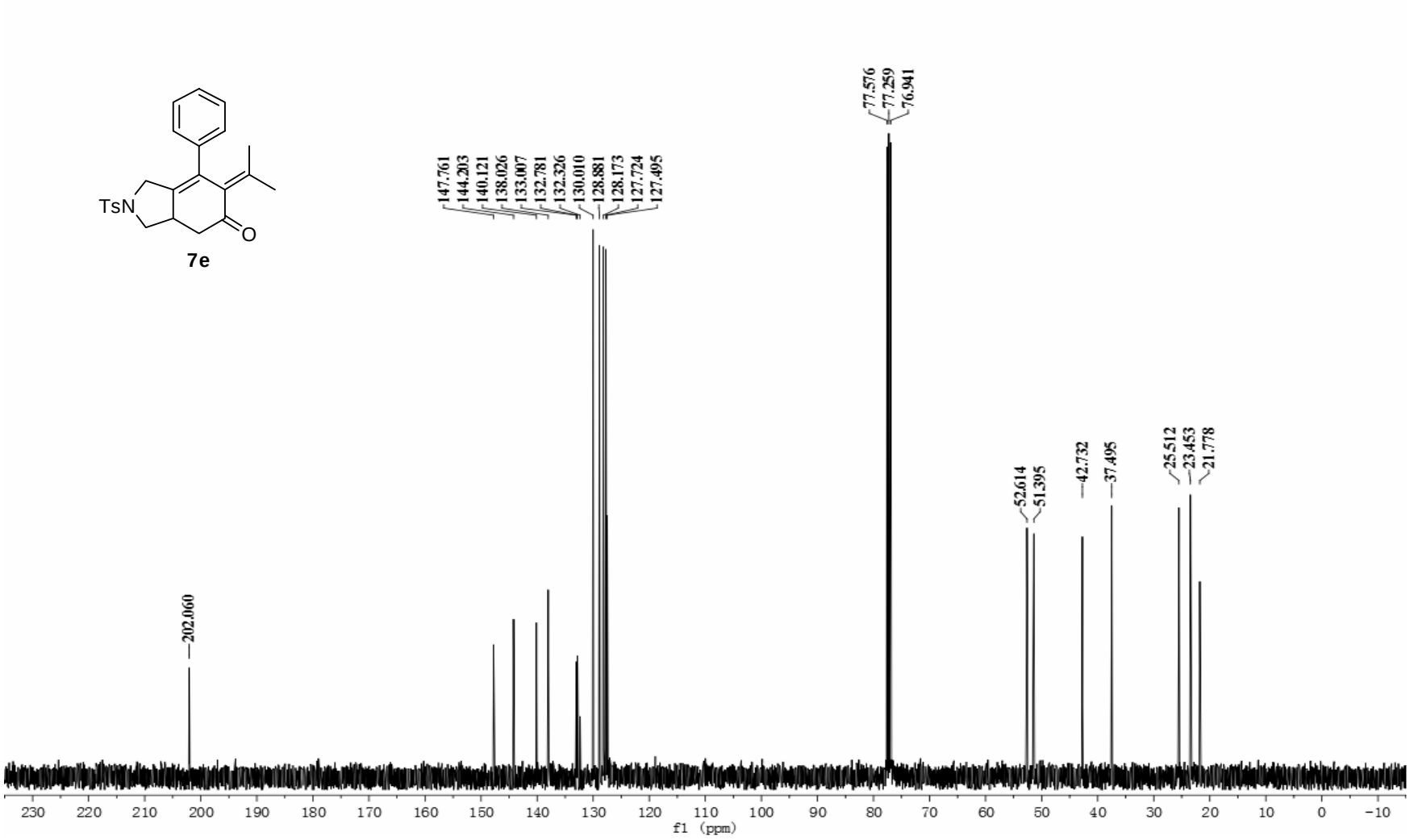


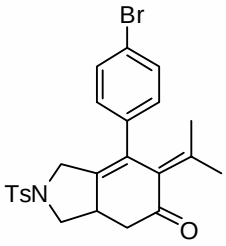




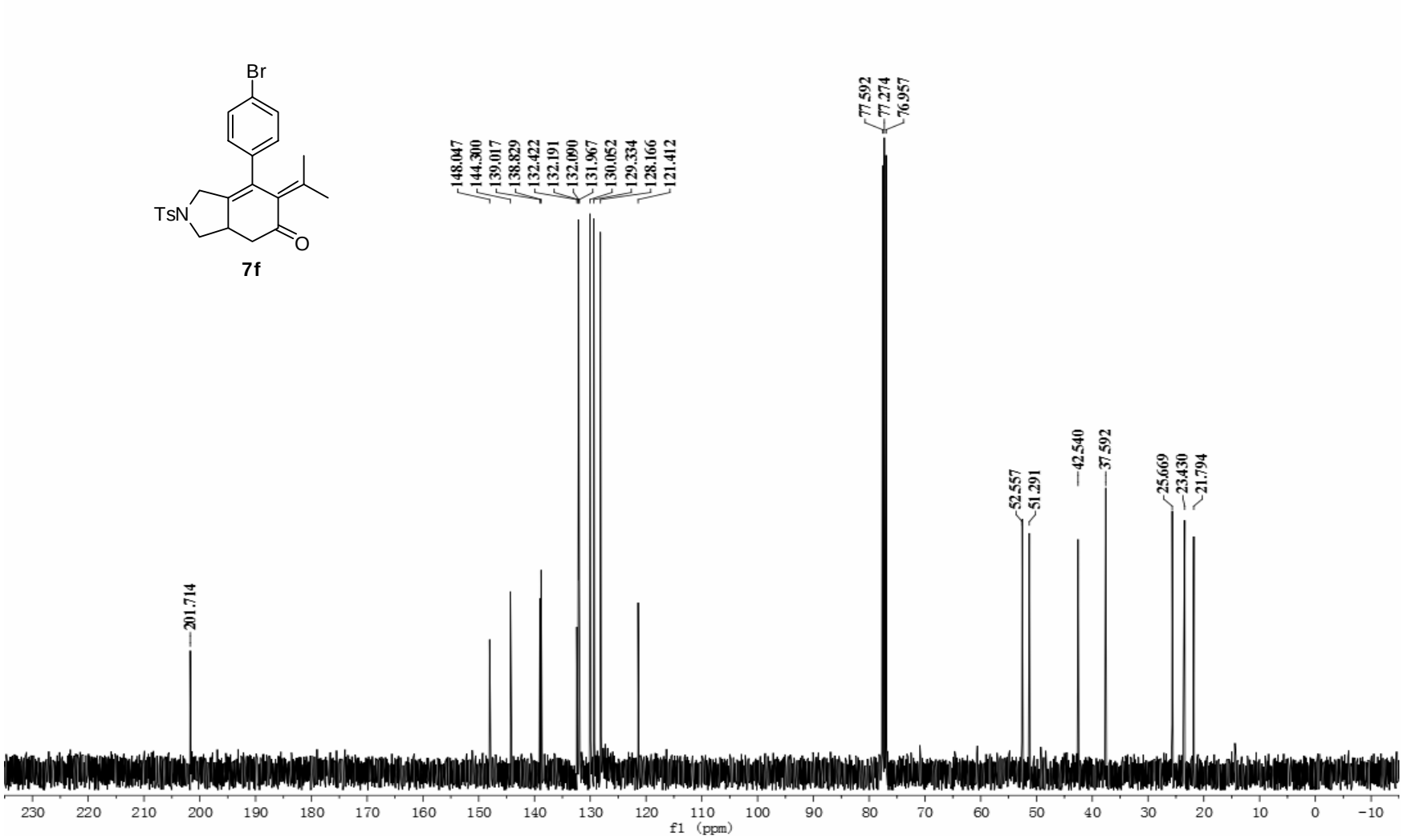


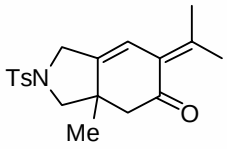
7e


TsN
O
7e
147.761
144.203
140.121
138.026
133.007
132.781
132.326
130.010
128.881
128.173
127.724
127.495
77.576
77.259
76.941
52.614
51.395
42.732
37.495
25.512
23.453
21.778
202.060
f1 (ppm)

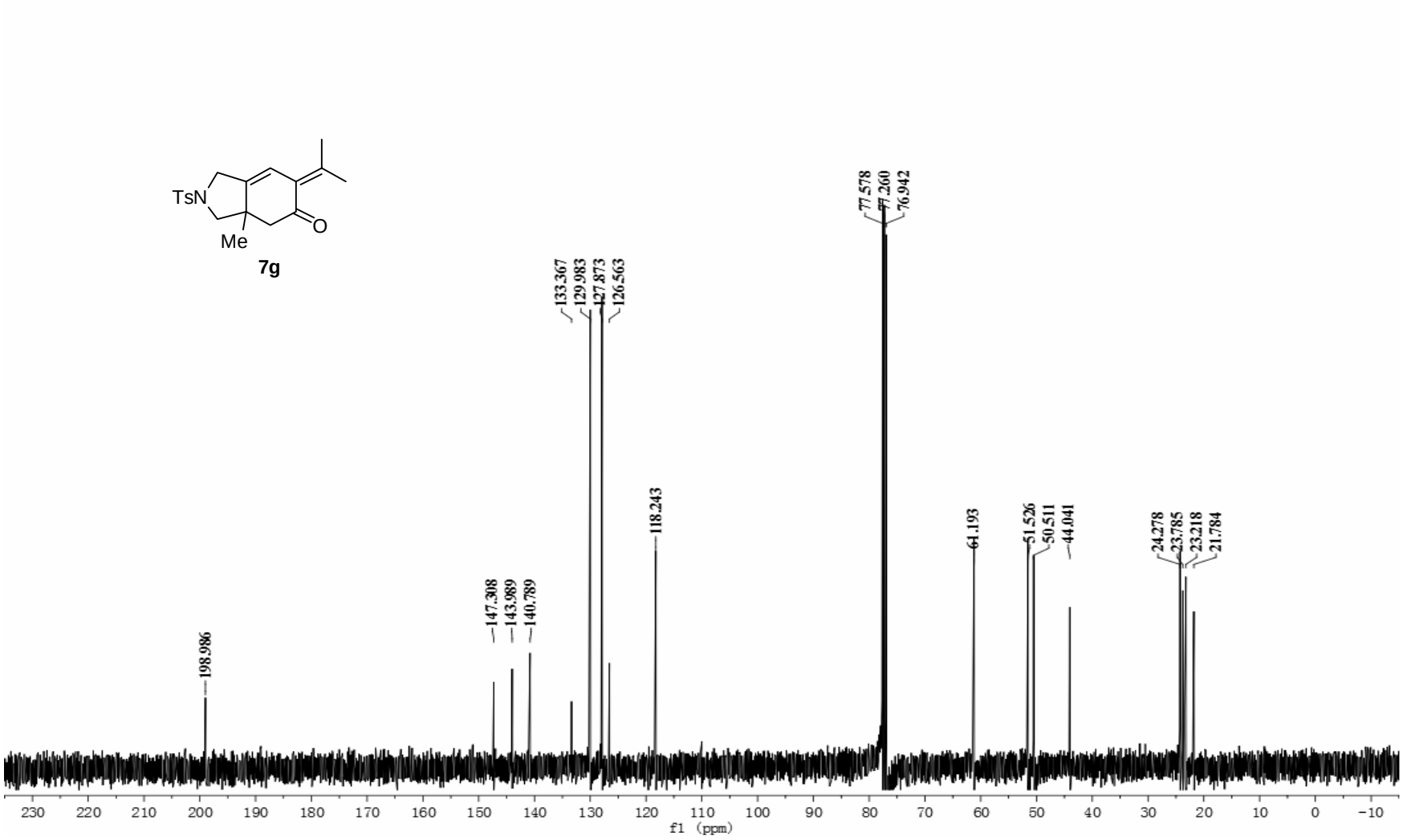


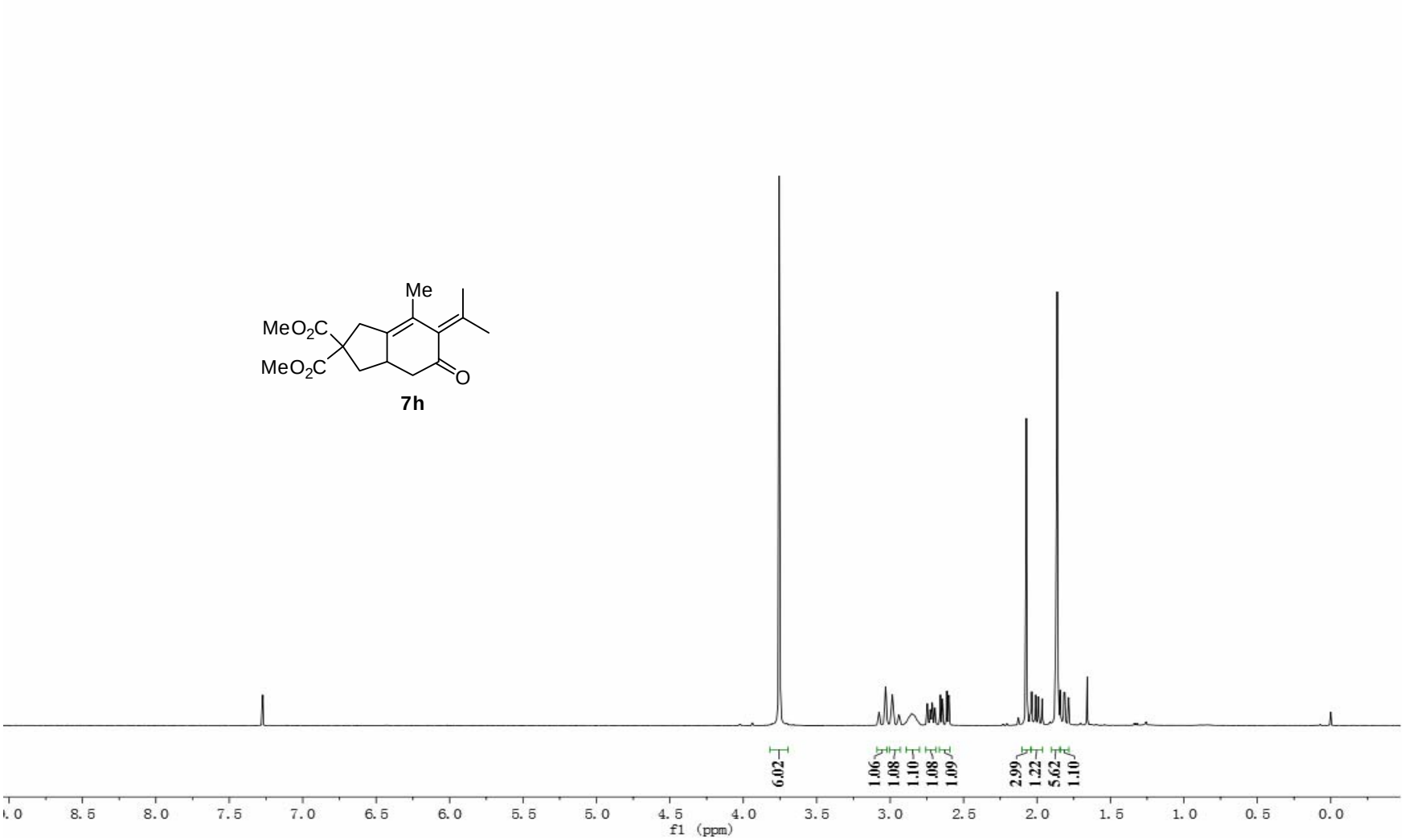
7f

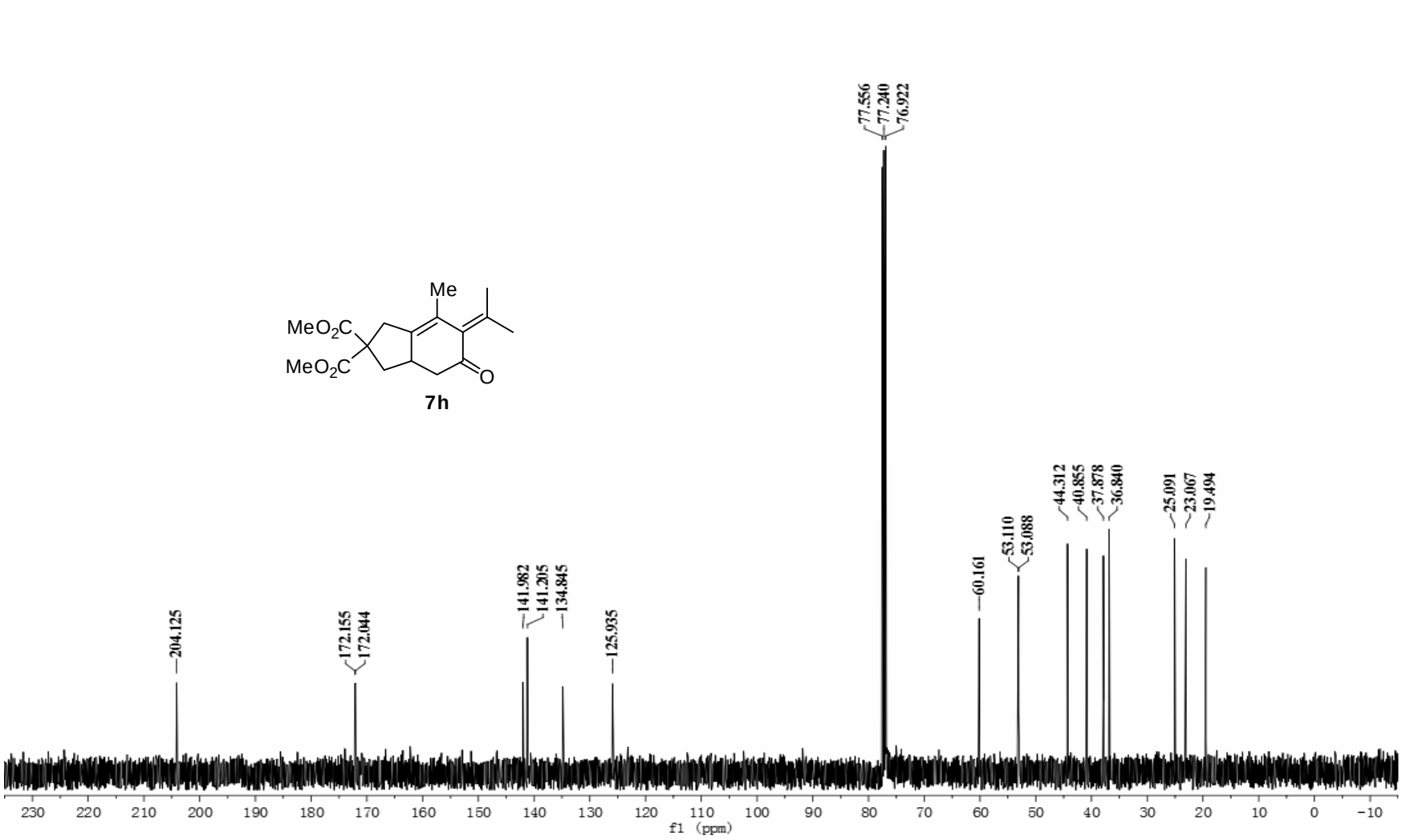

Br
TsN
O
7f
148.047
144.300
139.017
138.829
132.422
132.191
132.090
131.967
130.052
129.334
128.166
121.412
77.592
77.274
76.957
201.714
52.557
51.291
42.540
37.592
25.669
23.430
21.794
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

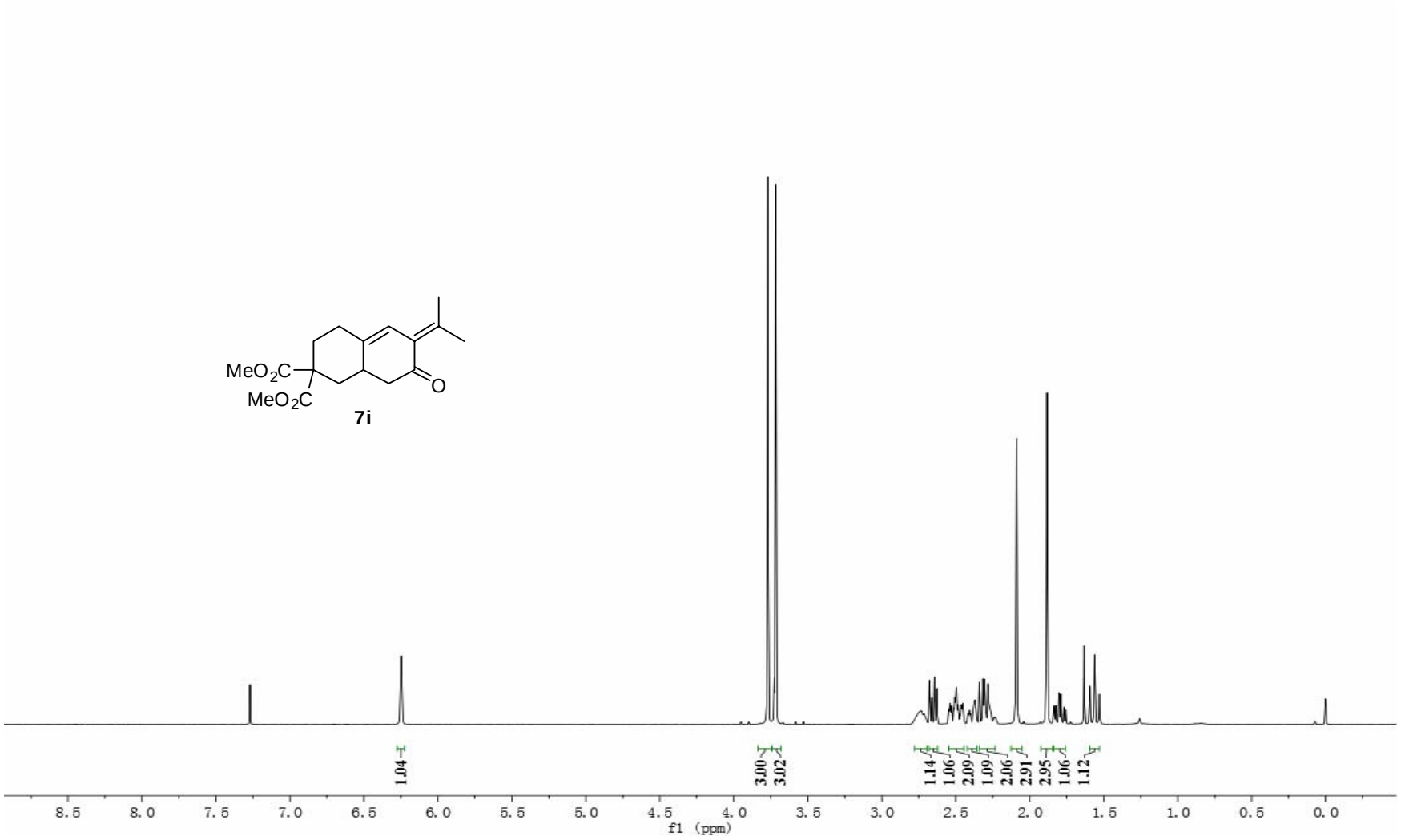


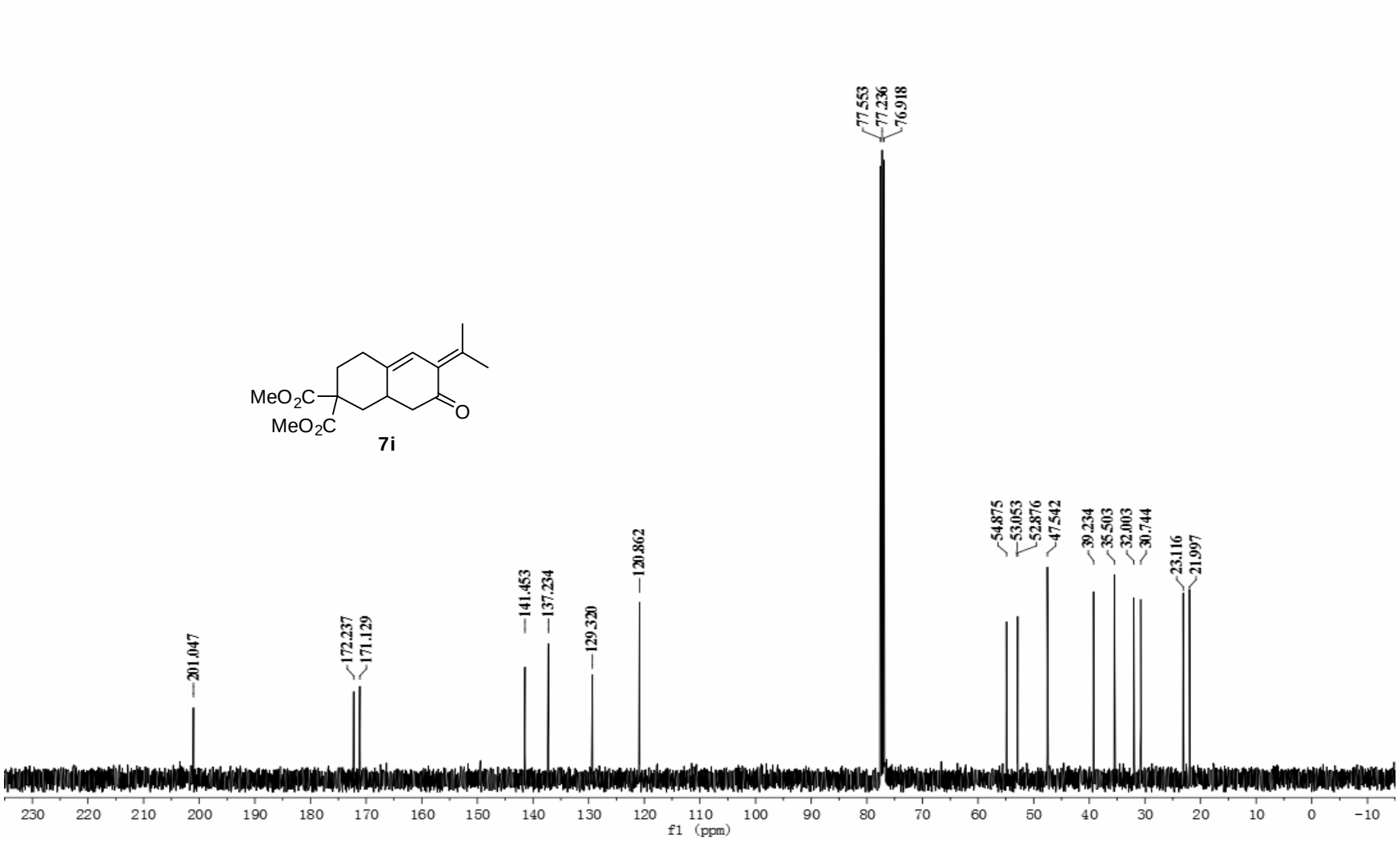
7g

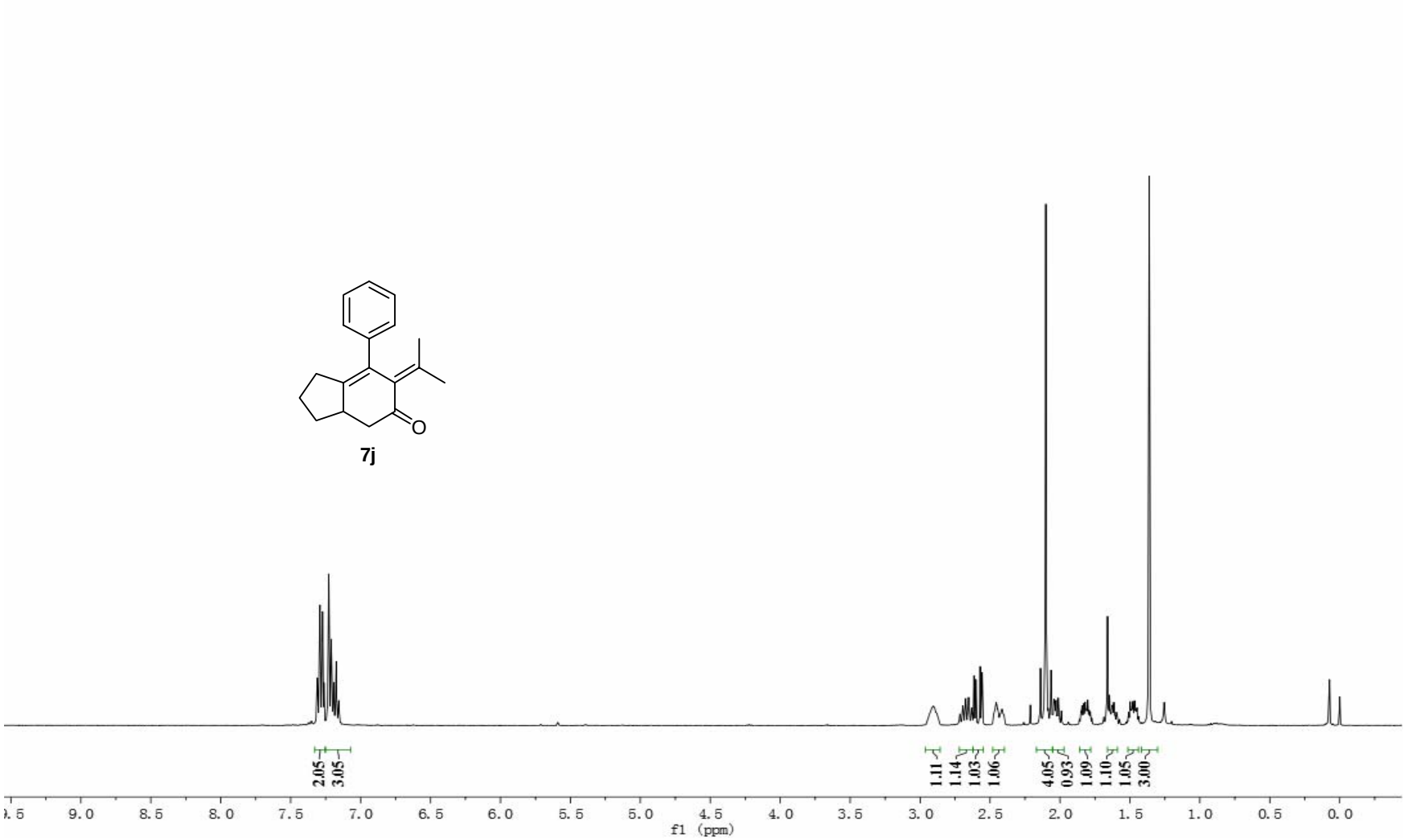

TsN
Me
O
7g
198.986
147.308
143.989
140.789
133.367
129.983
127.873
126.563
118.243
77.578
77.260
76.942
61.193
51.526
50.511
44.041
24.278
23.785
23.218
21.784
f1 (ppm)

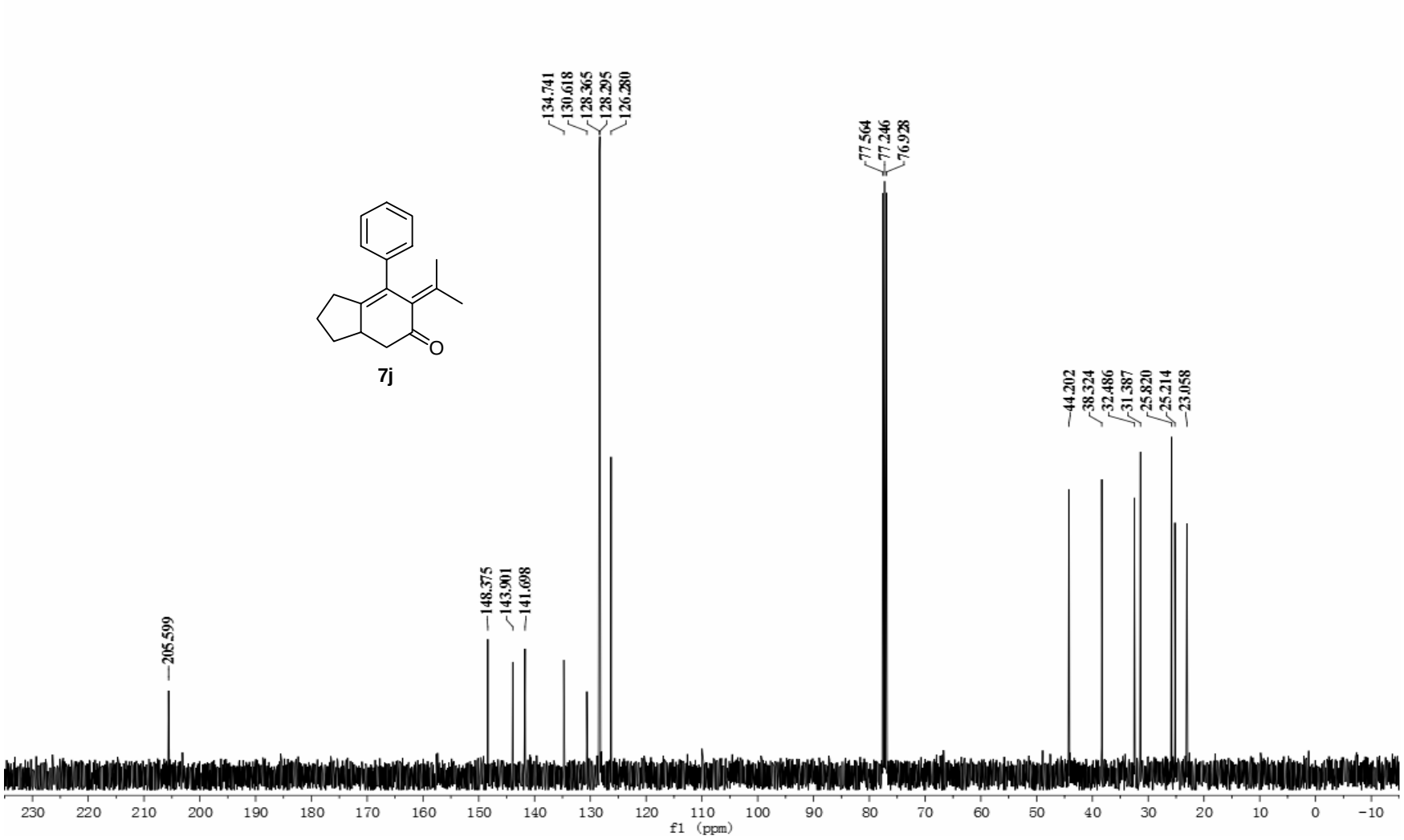


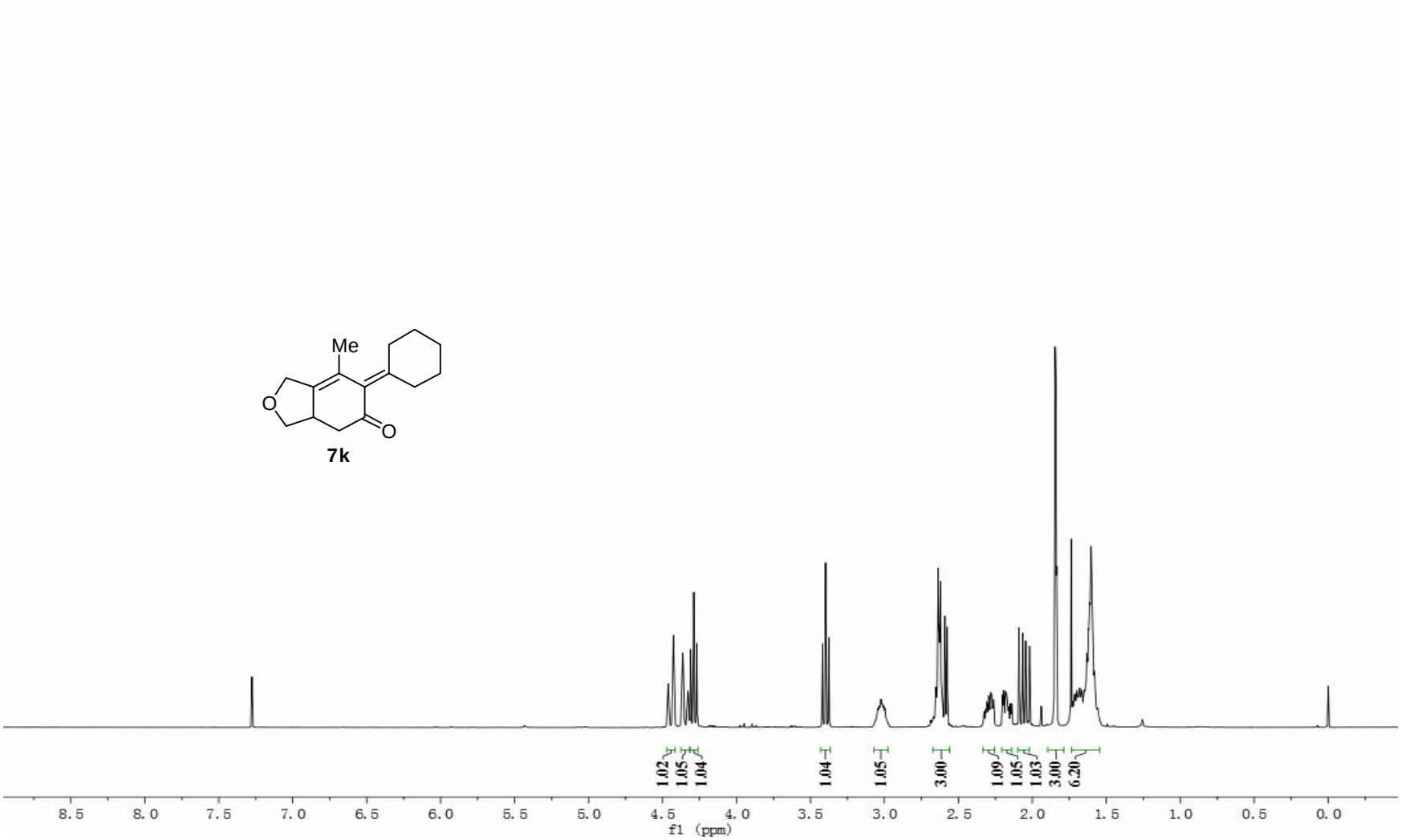


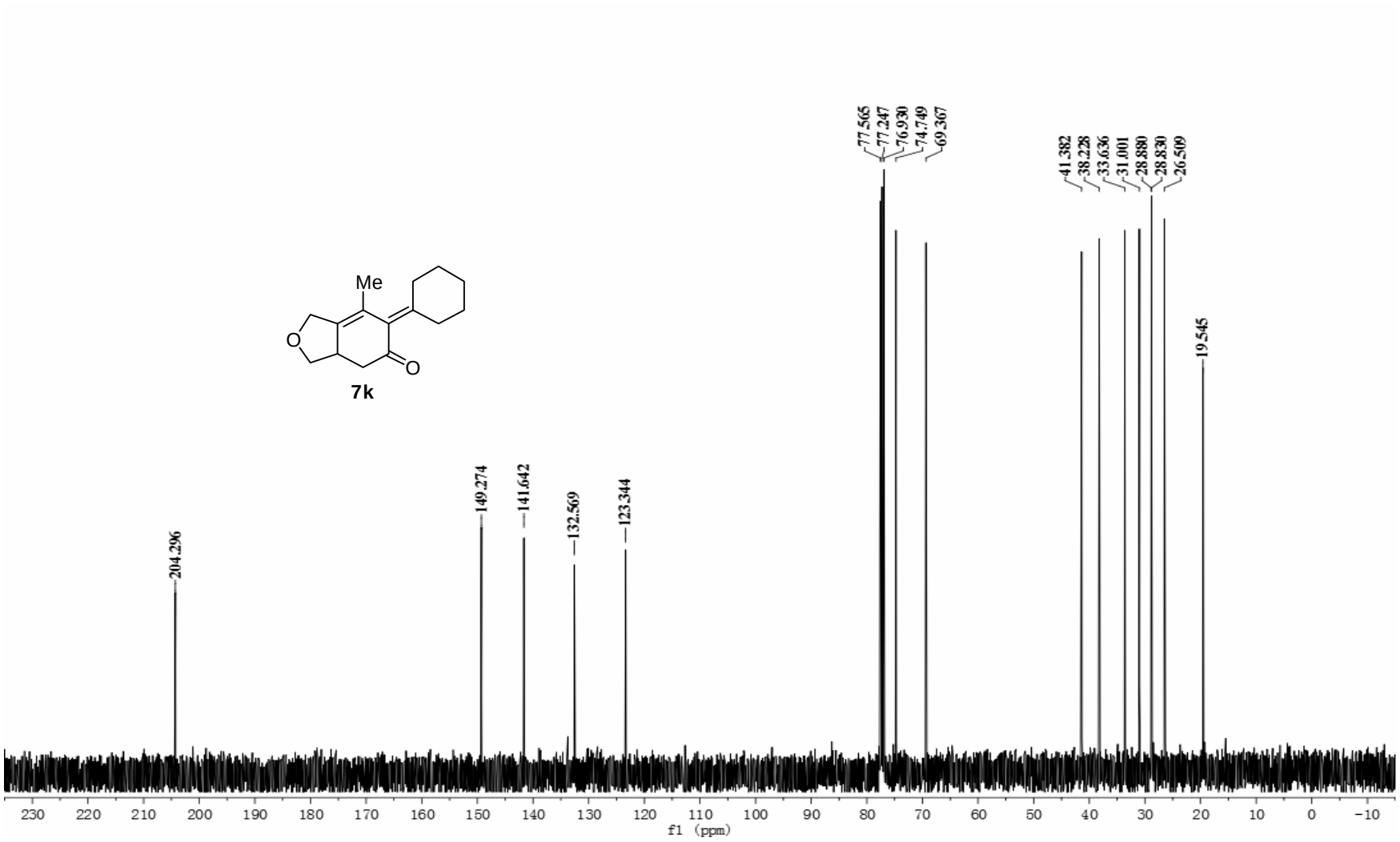


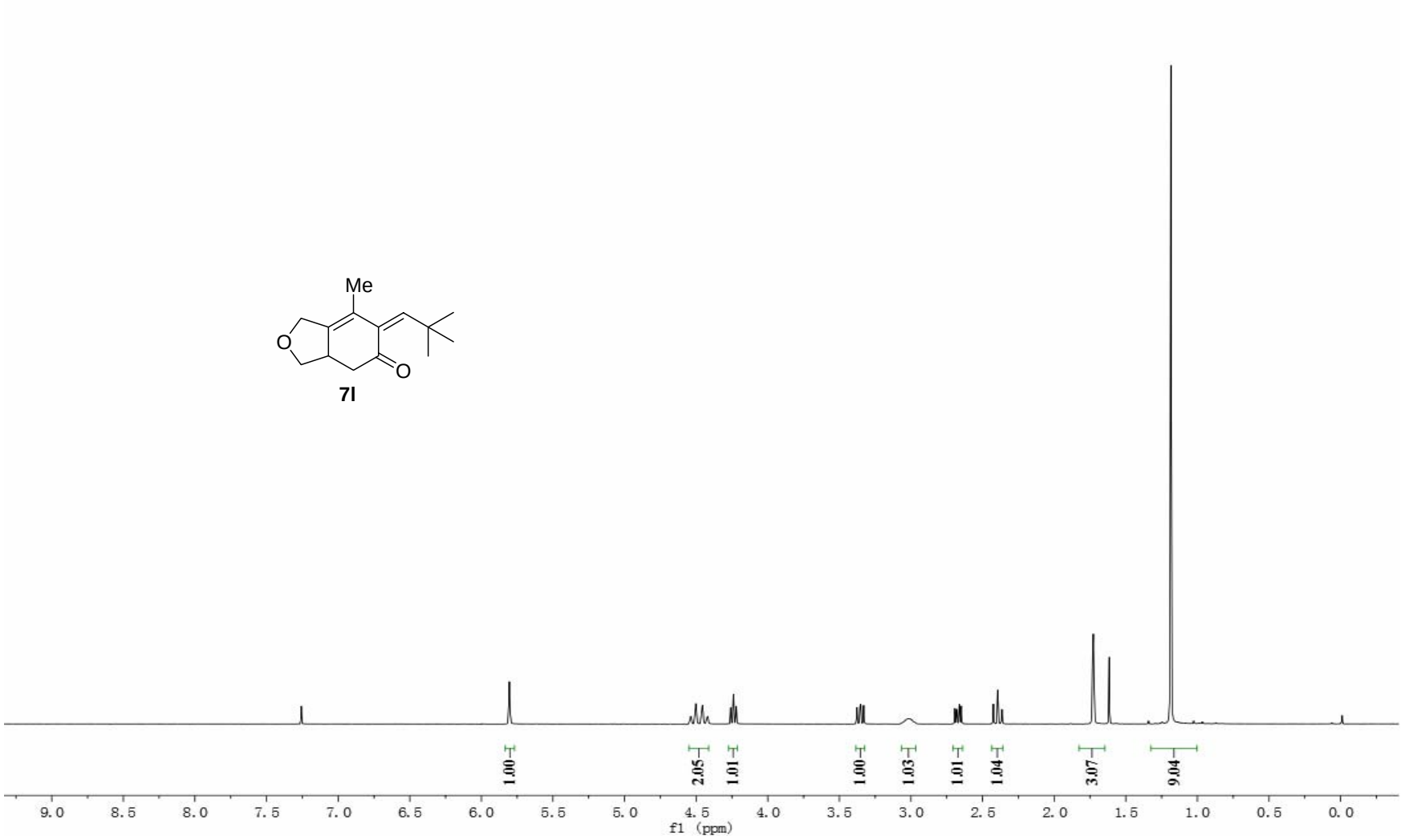


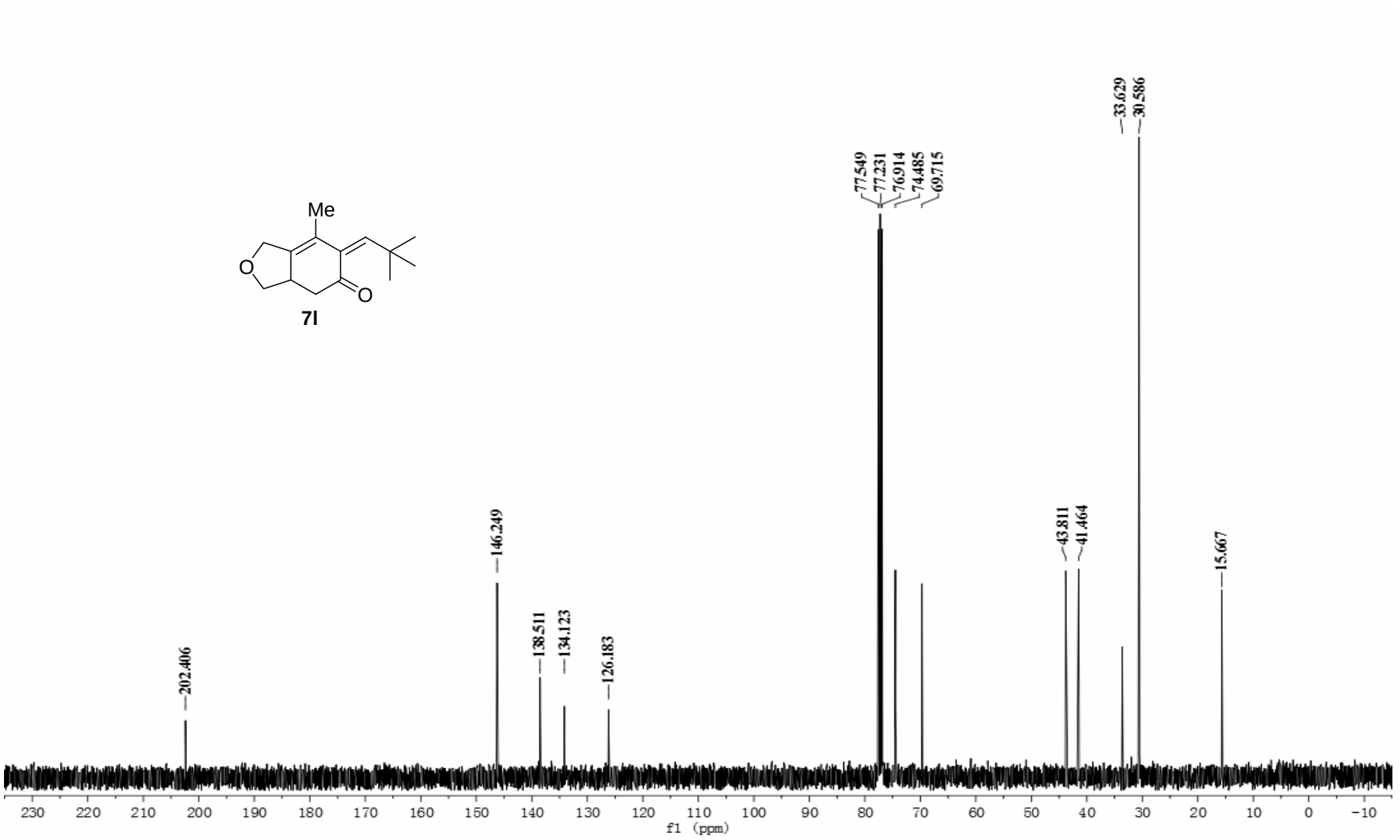


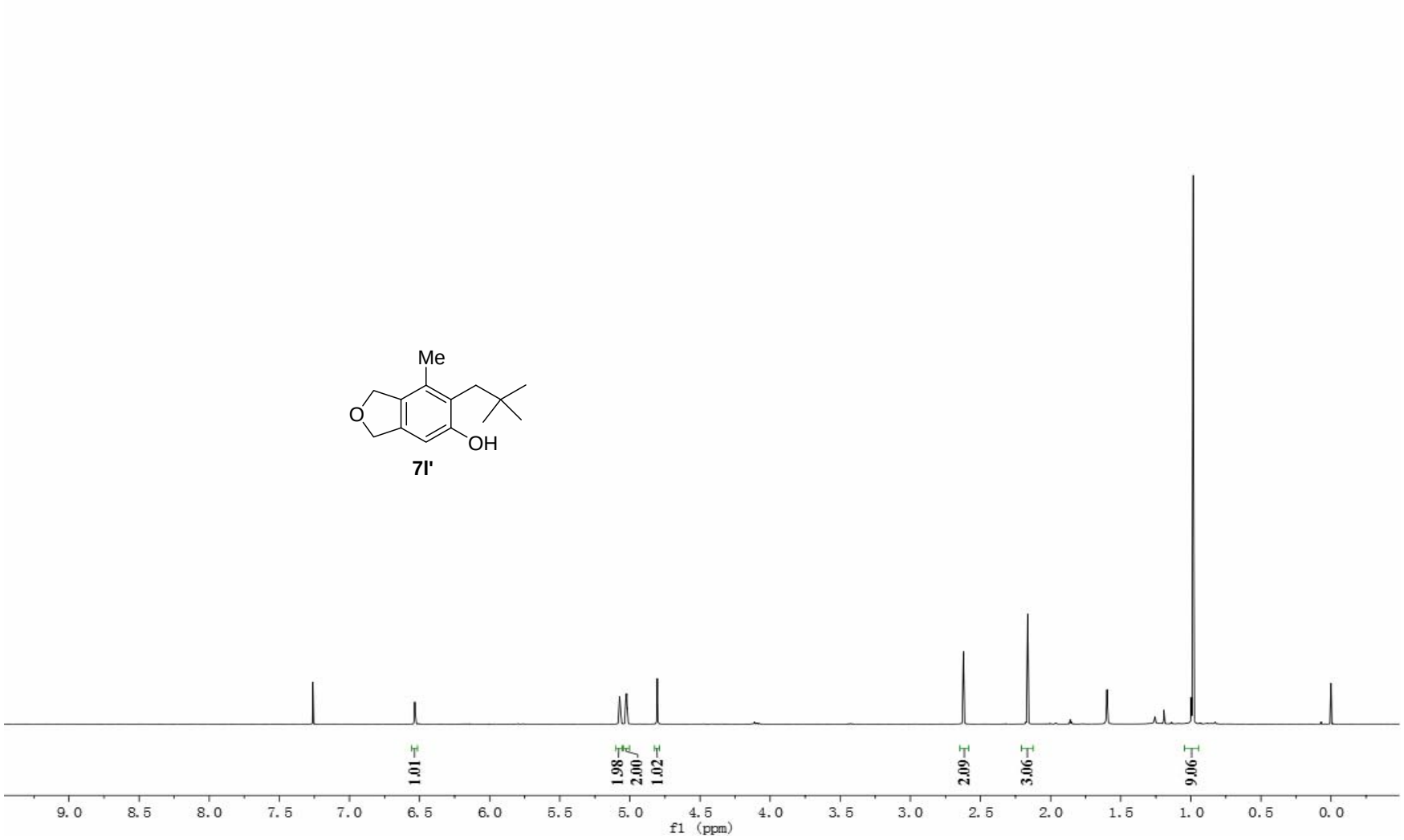


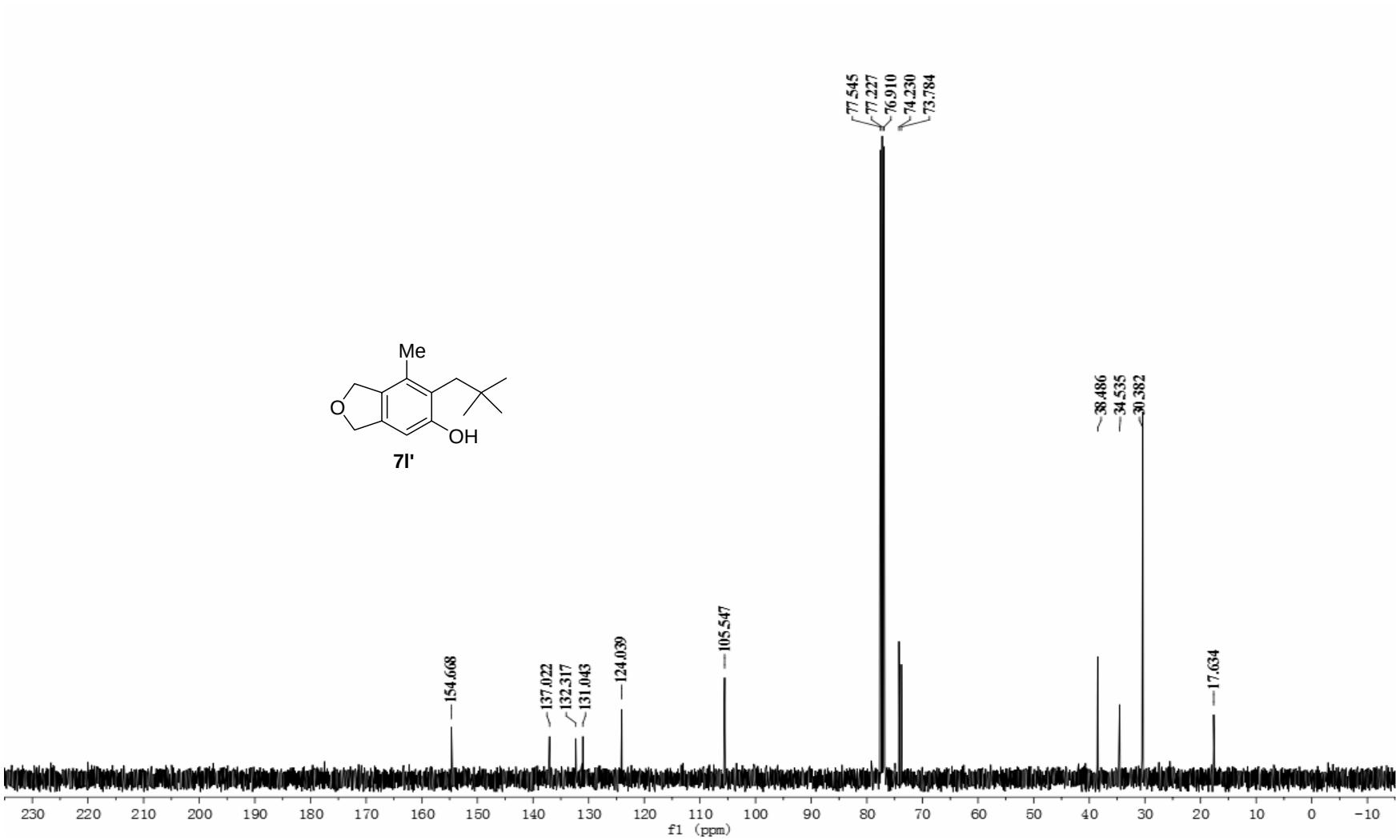


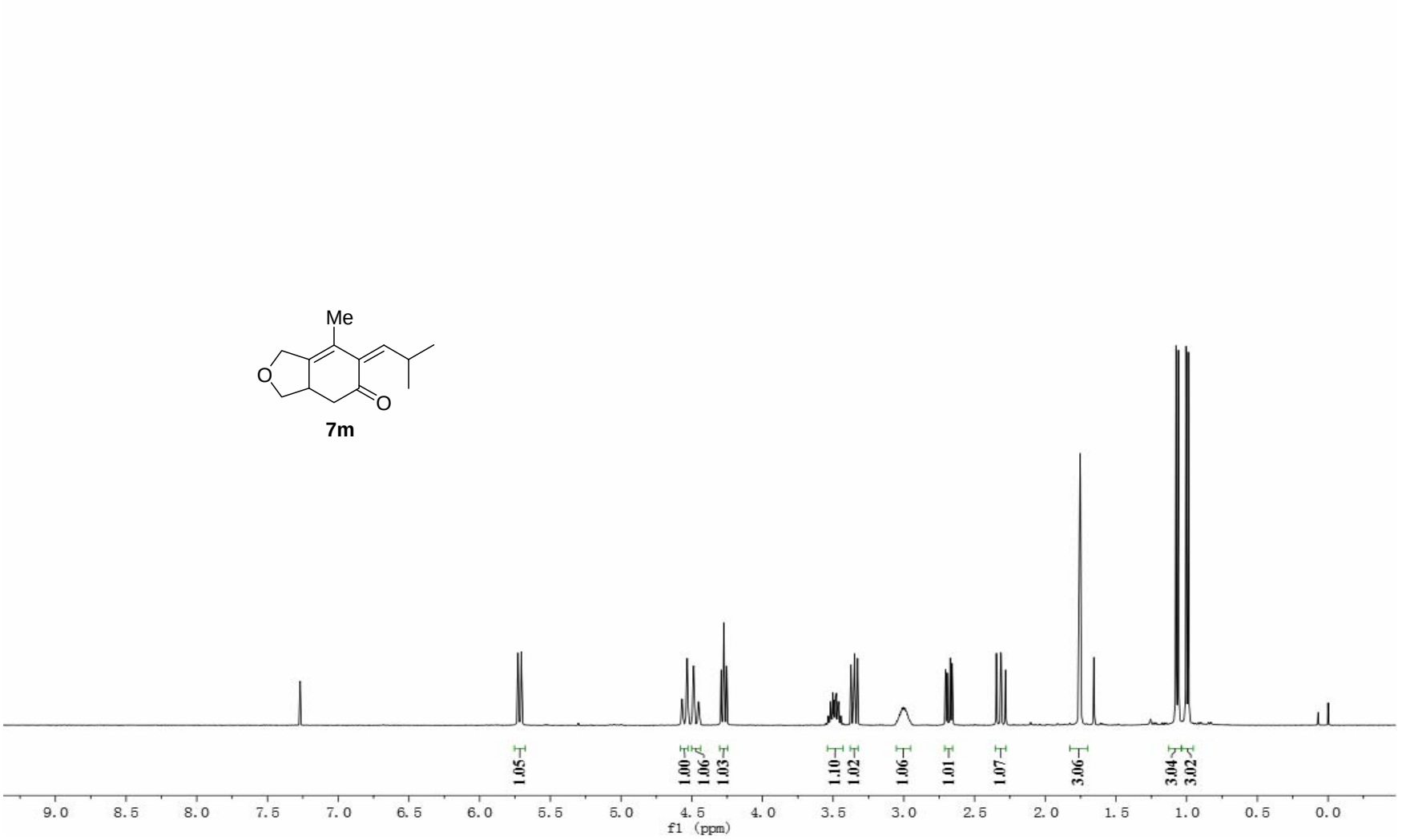

Me
O
O
7k
204.296
149.274
141.642
132.569
123.344
77.565
77.247
76.930
74.749
69.367
41.382
38.228
33.636
31.001
28.880
28.830
26.509
19.545
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

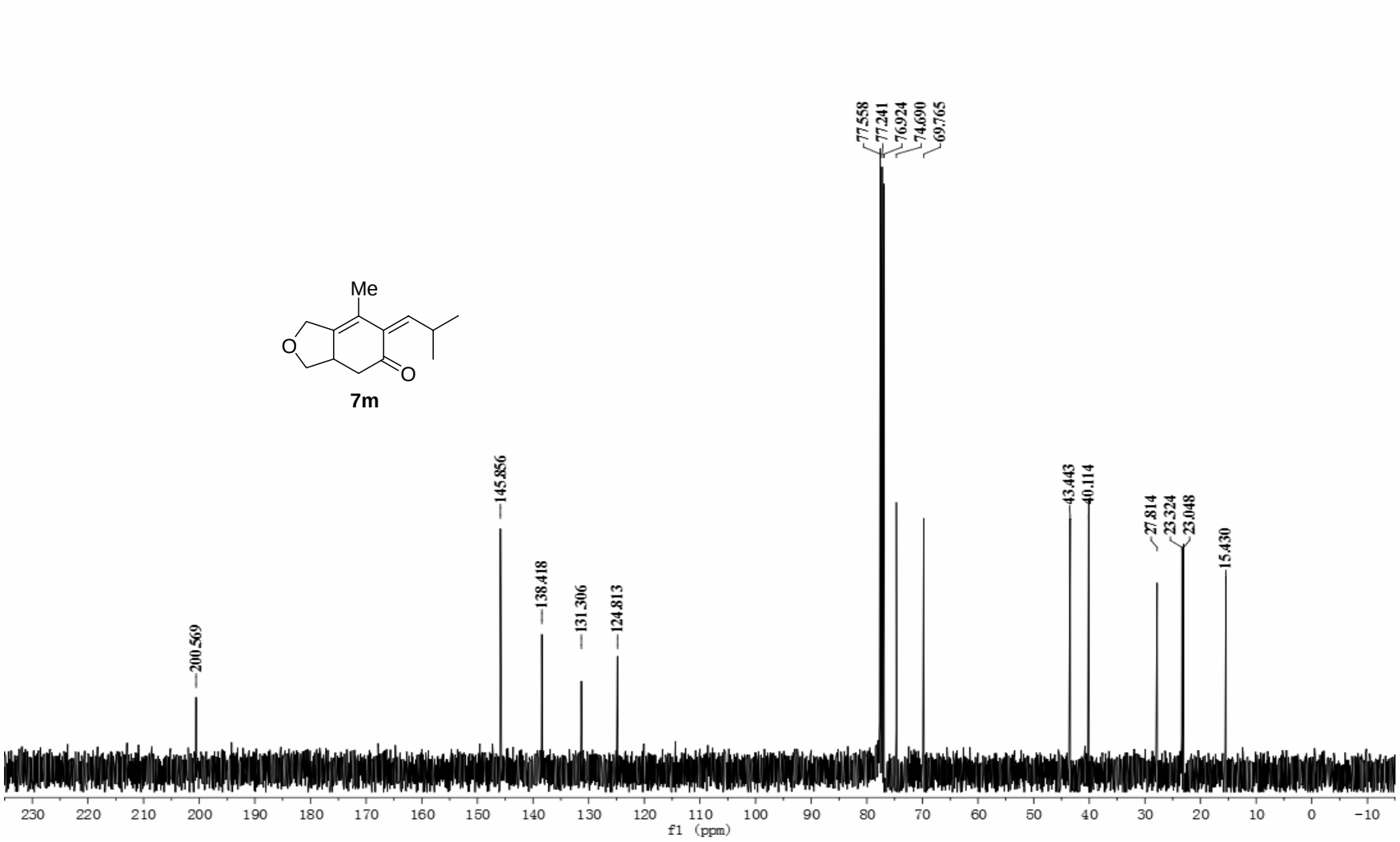


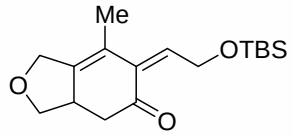





Me
O
OH
7l'
77.545
77.227
76.910
74.230
73.784
38.486
34.535
30.382
17.634
154.668
137.022
132.317
131.043
124.039
105.547
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)







7n