Electronic Supporting Information

A mild preparation of alkynes from alkenyl triflates

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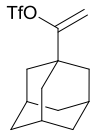
I Experimental Procedures and Spectroscopic Data of Compounds

General procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled immediately before use from sodium-benzophenone ketyl. *N*,*N*-dimethylformamide (DMF) was distilled from calcium hydride and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Titan chemical. Reactions were monitored by thin layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and aqueous ammonium cerium nitrate/ammonium molybdate or basic aqueous potassium permanganate as developing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker AV-400 instrument and calibrated by using residual undeuterated chloroform (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm) as internal references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet, br = broad. IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker APEXIII 7.0 Tesla ESI-FT, a Waters Micromass GCT Premier EI, or an IonSpec 4.7 Tesla FT mass spectrometer.

The general procedure for preparing alkenyl triflates from ketones. To a stirred solution of the ketone (1.00 mmol) and $PhNTf_2$ (1.00 mmol) in THF (5.0 mL) was added KHMDS (1.10 mL, 1.0 M in THF, 1.10 mmol) at −78 ℃. The resultant mixture was stirred at that temperature for 30 min before it was quenched with saturated aq. NH_4Cl (5.0 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography with EtOAc/petroleum ether (1:100 → 1:20) as eluent to give the alkenyl triflate.

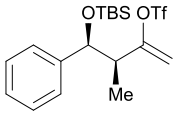
The general procedure for preparing alkynes from alkenyl triflates. To a stirred solution of the alkenyl triflate (0.300 mmol) in DMF (1.0 mL) was added anhydrous LiCl (1.20 mmol) at 22 ℃. The

resultant mixture was stirred at that temperature for 20 min before it was directly subjected to flash column chromatography for purification using EtOAc/petroleum ether/ (1:100 → 1:20) as eluent to give the alkyne product.



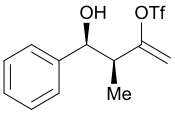
1

Compound 1: 93% yield (a colorless oil); R_f = 0.28 (silica, petroleum ether); IR (film): ν_{max} = 2910, 2855, 1655, 1416, 1210, 924, 795, 599, 507 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.04 (d, *J* = 4.1 Hz, 1 H), 4.87 (d, *J* = 4.1 Hz, 1 H), 2.09–2.02 (m, 3 H), 1.79–1.75 (m, 6 H), 1.74–1.62 (m, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.84, 118.57 (q, *J* = 319.3 Hz), 99.83, 39.33, 38.12, 36.35, 27.96; HRMS (*m/z*): $[M]^+$ calcd for $C_{13}H_{17}F_3O_3S^+$ 310.0851, found 310.0852.



4a

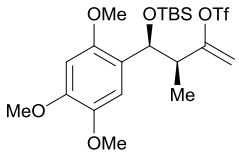
Compound 4a (racemic): 96% yield (a colorless oil); R_f = 0.64 (silica, CH_2Cl_2:petroleum ether 1:5); IR (film): ν_{max} = 2931, 2859, 1420, 1251, 1213, 1138, 936, 828, 777, 609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.18 (m, 5 H), 5.13 (d, *J* = 3.7 Hz, 1 H), 4.92–4.87 (m, 2 H), 2.65–2.56 (m, 1 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 0.88 (s, 9 H), −0.01 (s, 3 H), −0.22 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.50, 142.66, 128.15, 127.50, 126.31, 118.66 (q, *J* = 320.0 Hz), 105.42, 73.90, 47.63, 25.97, 18.39, 11.24, −4.55, −5.30 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{28}F_3O_4SSi^+$ 425.1424, found 425.1421.



3a

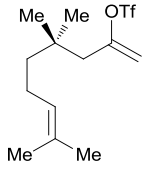
Compound 3a (racemic): To a stirred solution of compound **4a** (95.0 mg, 0.224 mmol) in THF (2.2 mL) was added HF•py (2.2 mL) at 22 °C. The resultant mixture was stirred at that temperature for 2 h before it was poured into saturated aq. Na_2CO_3 (20 mL). The mixture so obtained was extracted with EtOAc (5 × 10 mL). The combined organic phases were sequentially washed with saturated aq. $CuSO_4$ (2 × 10 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The volatile was removed under vacuum, and the residue was subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:5) as eluent to give compound **3a** (59.4 mg, 86%) as a pale yellow oil. R_f =

0.73 (silica, EtOAc:petroleum ether 1:2); IR (film): ν_{max} = 3435, 2986, 1664, 1417, 1213, 1139, 934, 702, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.19 (m, 5 H), 5.14 (d, *J* = 4.0 Hz, 1 H), 4.94 (d, *J* = 4.0 Hz, 1 H), 4.92 (d, *J* = 4.0 Hz, 1 H), 2.67 (qd, *J* = 7.0, 4.0 Hz, 1 H), 1.98–1.83 (m, 1 H), 1.01 (d, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.17, 141.71, 128.52, 127.88, 125.95, 118.59 (q, *J* = 319.7 Hz), 105.42, 73.27, 46.13, 11.30 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{12}H_{13}F_3O_4S^+$ 310.0487, found 310.0484.



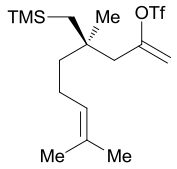
5a

Compound 5a (racemic): 85% yield (a pale yellow oil); R_f = 0.28 (silica, EtOAc:petroleum ether 1:5); IR (film): ν_{max} = 2954, 2857, 1509, 1206, 1128, 1038, 935, 777, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 1 H), 6.47 (s, 1 H), 5.32 (d, *J* = 2.5 Hz, 1 H), 5.16 (d, *J* = 3.6 Hz, 1 H), 4.96 (d, *J* = 3.6 Hz, 1 H), 3.89 (s, 3 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 2.81–2.65 (m, 1 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 0.91 (s, 9 H), 0.02 (s, 3 H), −0.17 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.62, 149.49, 148.56, 142.45, 122.20, 118.69 (q, *J* = 320.0 Hz), 111.69, 104.72, 96.50, 67.37, 56.47, 56.10, 55.60, 44.72, 25.90, 18.32, 10.44, −4.77, −5.44 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{34}F_3O_7SSi^+$ 515.1741, found 515.1744.



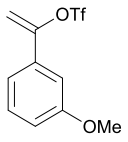
6a

Compound 6a: 92% yield (a colorless oil); R_f = 0.40 (silica, petroleum ether); IR (film): ν_{max} = 2966, 1663, 1420, 1210, 1144, 916, 710, 606 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.17 (d, *J* = 3.3 Hz, 1 H), 5.11–5.04 (m, 1 H), 4.91 (d, *J* = 3.3 Hz, 1 H), 2.25 (s, 2 H), 2.00–1.88 (m, 2 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.34–1.23 (m, 2 H), 0.97 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.31, 131.52, 124.55, 118.65 (q, *J* = 320.0 Hz), 107.21, 46.34, 42.22, 33.68, 26.80, 25.77, 22.84, 17.65 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{13}H_{21}F_3O_3S^+$ 314.1164, found 314.1162.



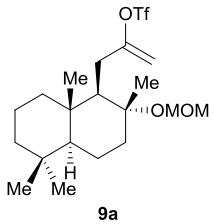
7a

Compound 7a (racemic): 91% yield (a colorless oil); R_f = 0.24 (silica, petroleum ether); IR (film): ν_{max} = 2963, 1663, 1421, 1210, 1142, 901, 838, 712, 611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.19 (d, *J* = 3.3 Hz, 1 H), 5.12–4.99 (m, 1 H), 4.90 (d, *J* = 3.3 Hz, 1 H), 2.31 (s, 2 H), 1.99–1.90 (m, 2 H), 1.69 (d, *J* = 1.5 Hz, 3 H), 1.61 (s, 3 H), 1.40–1.30 (m, 2 H), 1.03 (s, 3 H), 0.75 (d, *J* = 1.5 Hz, 2 H), 0.06 (s, 9 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.41, 131.52, 124.42, 118.65 (q, *J* = 320.1 Hz), 107.35, 47.15, 42.01, 36.87, 29.47, 27.66, 25.84, 22.96, 17.82, 1.06 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{16}H_{29}F_3O_3SSi^+$ 386.1559, found 386.1561.



8a

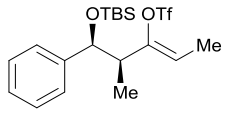
Compound 8a: 89% yield (a pale yellow oil); R_f = 0.70 (silica, EtOAc:petroleum ether 1:10); IR (film): ν_{max} = 3009, 2945, 1601, 1420,, 1213, 1141, 944, 894, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 1 H), 7.16–7.12 (m, 1 H), 7.07–7.04 (m, 1 H), 6.99–6.95 (m, 1 H), 5.60 (d, *J* = 4.0 Hz, 1 H), 5.38 (d, *J* = 4.0 Hz, 1 H), 3.84 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.00, 153.41, 133.48, 130.14, 118.68 (q, *J* = 320.19 Hz), 117.93, 116.13, 111.02, 104.61, 55.50. ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{10}H_9F_3O_4S^+$ 282.0174, found 282.0176.



9a

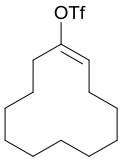
Compound 9a: 89% yield (a pale yellow oil); R_f = 0.33 (silica, EtOAc:petroleum ether 1:10); $[\alpha]_D^{26}$ = −7.4 (*c* = 1.0 in $CHCl_3$); IR (film): ν_{max} = 2930, 1665, 1419, 1208, 1148, 943, 891, 772, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.04 (d, *J* = 3.5 Hz, 1 H), 4.99 (d, *J* = 3.5 Hz, 1 H), 4.70 (d, *J* = 7.6 Hz, 1

H), 4.63 (d, *J* = 7.6 Hz, 1 H), 3.32 (s, 3 H), 2.59 (dd, *J* = 16.3, 5.0 Hz, 1 H), 2.29 (dd, *J* = 16.3, 5.0 Hz, 1 H), 2.04–1.96 (m, 1 H), 1.73–1.51 (m, 5 H), 1.49–1.33 (m, 2 H), 1.30–1.20 (m, 1 H), 1.19 (s, 3 H), 1.17–1.09 (m, 1 H), 1.02–0.92 (m, 2 H), 0.87 (s, 3 H), 0.85 (s, 3 H), 0.79 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.42, 118.71 (q, *J* = 320.2 Hz), 103.88, 89.89, 79.01, 56.51, 56.05, 55.24, 41.80, 40.37, 39.96, 39.31, 33.48, 33.31, 30.65, 21.61, 20.52, 19.98, 18.43, 15.71 ppm; HRMS (*m/z*): $[M + NH_4]^+$ calcd for $C_{20}H_{37}F_3NO_5S^+$ 460.2339, found 460.2338.



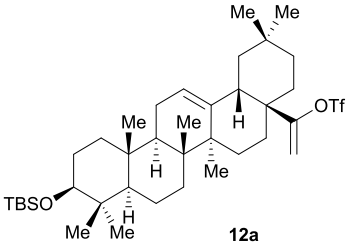
10a

Compound 10a (racemic): 81% yield. The spectroscopic data and physical properties of **10a** were identical with those reported in the literature.[1]



11a

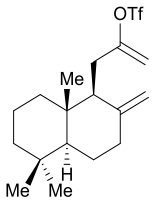
Compound 11a: 86% yield. The spectroscopic data and physical properties of **11a** were identical with those reported in the literature.[2]



12a

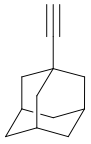
Compound 12a: 94% yield (a white foam); R_f = 0.65 (silica, CH_2Cl_2:petroleum ether 1:5); $[\alpha]_D^{22}$ = +38.3 (*c* = 1.0 in $CHCl_3$); IR (film): ν_{max} = 2950, 2856, 1414, 1212, 1102, 924, 882, 773, 601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27–5.23 (m, 1 H), 5.18 (d, *J* = 4.4 Hz, 1 H), 5.04 (d, *J* = 4.4 Hz, 1 H), 3.18 (dd, *J* = 11.1, 4.5 Hz, 1 H), 2.43 (dd, *J* = 13.5, 4.5 Hz, 1 H), 2.11–1.94 (m, 1 H), 1.92–1.83 (m, 2 H), 1.78 (t, *J* = 13.5 Hz, 1 H), 1.65–1.58 (m, 3 H), 1.56–1.50 (m, 3 H), 1.49–1.29 (m, 6 H), 1.22–1.17 (m, 1 H), 1.15 (s, 3 H), 1.07–0.92 (m, 2 H), 0.92–0.90 (m, 12 H), 0.89 (s, 9 H), 0.87–0.83 (m, 2 H), 0.80

(s, 3 H), 0.75 (s, 3 H), 0.73–0.67 (m, 1 H), 0.03 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.03, 143.77, 123.12, 118.48 (q, *J* = 320.5 Hz) 103.82, 79.60, 55.41, 47.83, 46.89, 43.20, 42.88, 42.10, 39.63, 39.50, 38.68, 37.03, 34.16, 33.03, 32.60, 32.28, 30.79, 28.69, 27.78, 26.68, 26.08, 25.94, 23.74, 23.64, 22.44, 18.62, 18.29, 17.04, 16.25, 15.57, −3.58, −4.73 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{38}H_{64}F_3O_4SSi^+$ 701.4241, found 701.4239.

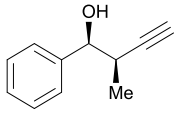


13

Compound 13: 96% yield (a colorless oil); R_f = 0.45 (silica, CH_2Cl_2:petroleum ether 1:10); $[\alpha]_D^{26}$ = +9.1 (*c* = 1.0 in $CHCl_3$); IR (film): ν_{max} = 2938, 1673, 1418, 1210, 1147, 940, 889, 613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.10 (dd, *J* = 3.7, 1.3 Hz, 1 H), 4.90–4.83 (m, 2 H), 4.55 (d, *J* = 0.8 Hz, 1 H), 2.66–2.56 (m, 1 H), 2.47–2.36 (m, 2 H), 2.04–1.95 (m, 2 H), 1.79–1.66 (m, 2 H), 1.61–1.47 (m, 2 H), 1.46–1.27 (m, 2 H), 1.23–1.05 (m, 3 H), 0.89 (s, 3 H), 0.82 (s, 3 H), 0.71 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.23, 146.66, 118.68 (q, *J* = 320.0 Hz), 107.99, 105.07, 55.58, 53.07, 42.05, 39.71, 39.05, 37.96, 33.71, 33.65, 29.39, 24.27, 21.79, 19.40, 14.51 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{18}H_{27}O_3F_3S^+$ 380.1633, found 380.1634.

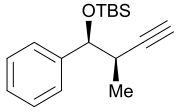

2

Compound 2: 98% yield (a white foam); R_f = 0.42 (silica, petroleum ether); IR (film): ν_{max} = 3303, 2902, 2850, 2103, 1450, 1225, 1098 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 1 H), 1.99–1.92 (m, 3 H), 1.88 (d, *J* = 3.2 Hz, 6 H), 1.69 (t, *J* = 3.2 Hz, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 93.07, 66.75, 42.84, 36.41, 29.45, 28.00; HRMS (*m/z*): $[M]^+$ calcd for $C_{12}H_{16}^+$ 160.1252, found 160.1251. The spectroscopic data of **2** were identical with those reported in the literature.[3]



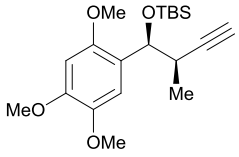
3

Compound 3 (racemic): 84% yield (a colorless oil); R_f = 0.34 (silica, EtOAc:petroleum ether 1:5); IR (film): ν_{max} = 3301, 2963, 2150, 1682, 1603, 1489, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 5 H), 4.75 (d, *J* = 5.5 Hz, 1 H), 2.94–2.81 (m, 1 H), 2.22 (br s, 1 H), 2.13 (d, *J* = 2.5 Hz, 1 H), 1.14 (d, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.32, 128.29, 127.95, 126.63, 85.94, 76.28, 71.04, 34.14, 15.65 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{11}H_{12}O^+$ 160.0888, found 160.0883. The spectroscopic data of **3** were identical with those reported in the literature.[4]



4

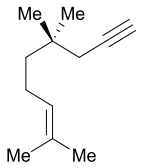
Compound 4 (racemic): 95% yield (a colorless oil); R_f = 0.19 (silica, petroleum ether); IR (film): ν_{max} = 3312, 2929, 1593, 1258, 1088, 869 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.22 (m, 5 H), 4.59 (d, *J* = 6.5 Hz, 1 H), 2.79–2.52 (m, 1 H), 1.99 (d, *J* = 2.5 Hz, 1 H), 1.20 (d, *J* = 6.9 Hz, 3 H), 0.88 (s, 9 H), 0.06 (s, 3 H), −0.19 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.22, 127.84, 127.48, 126.96, 86.90, 77.88, 70.17, 35.65, 25.96, 18.38, 16.60, −4.49, −4.88 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{17}H_{27}OSi^+$ 275.1826, found 275.1825.



5

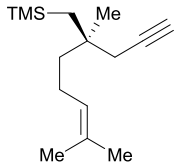
Compound 5 (racemic): 93% yield (a colorless oil); R_f = 0.34 (silica, EtOAc:petroleum ether 1:5); IR (film): ν_{max} = 3310, 2954, 2101, 1612, 1510, 1205, 1128, 1038, 868 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 1 H), 6.46 (s, 1 H), 5.12 (d, *J* = 4.7 Hz, 1 H), 3.89 (s, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 2.82–2.66 (m, 1 H), 1.99 (d, *J* = 2.5 Hz, 1 H), 1.09 (d, *J* = 7.0 Hz, 3 H), 0.90 (s, 9 H), 0.09 (s, 3 H), −0.13 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.01, 148.47, 142.70, 123.00, 111.68, 96.71,

87.94, 70.38, 68.98, 56.41, 56.30, 56.13, 33.55, 26.01, 18.42, 15.33, −4.65, −4.85 ppm; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{33}O_4Si^+$ 365.2143, found 365.2145.



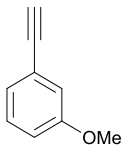
6

Compound 6: 96% yield (a colorless oil); R_f = 0.50 (silica, petroleum ether); IR (film): ν_{max} = 2956, 2923, 2111, 1461, 1259, 1026, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.21–4.99 (m, 1 H), 2.08 (d, *J* = 2.7 Hz, 2 H), 1.97 (t, *J* = 2.7 Hz, 1 H), 2.01–1.89 (m, 2 H), 1.68 (d, *J* = 0.89 Hz, 3 H), 1.61 (s, 3 H), 1.35–1.29 (m, 2 H), 0.97 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.34, 124.94, 82.78, 69.85, 41.47, 33.38, 31.73, 26.73, 25.84, 23.04, 17.70 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{12}H_{20}^+$ 164.1565, found 164.1561



7

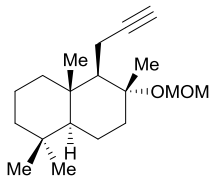
Compound 7 (racemic): 89% yield (a colorless oil); R_f = 0.39 (silica, petroleum ether); IR (film): ν_{max} = 3312, 2957, 2116, 1593, 1249, 857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.13–5.06 (m, 1 H), 2.13 (d, *J* = 2.7 Hz, 2 H), 1.98 (t, *J* = 2.7 Hz, 1 H), 1.96–1.87 (m, 2 H), 1.68 (d, *J* = 0.91 Hz, 3 H), 1.61 (s, 3 H), 1.42–1.33 (m, 2 H), 1.02 (s, 3 H), 0.85–0.73 (m, 2 H), 0.05 (s, 9 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.34, 124.84, 82.99, 70.12, 42.07, 36.45, 32.63, 29.09, 27.60, 25.88, 23.07, 17.80, 1.03 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{15}H_{28}Si^+$ 236.1960, found 236.1961.



8

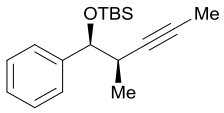
Compound 8: 95% yield (a pale yellow oil); R_f = 0.60 (silica, EtOAc:petroleum ether 1:20); IR (film): ν_{max} = 3292, 2960, 2100, 1602, 1576, 1481, 1319, 1285,-877 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ =

7.25–7.20 (m, 1 H), 7.12–7.07 (m, 1 H), 7.02 (dd, *J* = 2.5, 1.4 Hz, 1 H), 6.94–6.88 (m, 1 H), 3.80 (s, 3 H), 3.06 (s, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.32, 129.45, 124.65, 123.13, 117.03, 115.39, 83.64, 77.16, 55.20 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_9H_8O^+$ 132.0575, found 132.0571. The spectroscopic data of **8** were identical with those reported in the literature.[5]



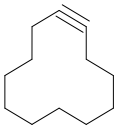
9

Compound 9: 92% yield (a pale yellow oil); R_f = 0.33 (silica, EtOAc:petroleum ether 1:10); $[\alpha]_D^{22}$ = −20.9 (*c* = 1.0 in $CHCl_3$); IR (film): ν_{max} = 3309, 2926, 2117, 1465, 1368, 1131, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (d, *J* = 7.6 Hz, 1 H), 4.66 (d, *J* = 7.6 Hz, 1 H), 3.37 (s, 3 H), 2.50–2.38 (m, 1 H), 2.12–2.02 (m, 1 H), 1.94–1.83 (m, 2 H), 1.78 (dd, *J* = 13.1, 1.1 Hz, 1 H), 1.74–1.61 (m, 3 H), 1.61–1.51 (m, 1 H), 1.46 (dd, *J* = 10.5, 6.9 Hz, 1 H), 1.40–1.32 (m, 1 H), 1.31–1.14 (m, 3 H), 1.12 (s, 3 H), 0.96 (dd, *J* = 12.3, 2.0 Hz, 1 H), 0.86 (s, 3 H), 0.83 (s, 3 H), 0.78 (s, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 89.94, 87.09, 79.09, 67.45, 58.77, 55.79, 55.19, 41.83, 40.23, 39.58, 39.25, 33.43, 33.15, 21.55, 21.13, 20.06, 18.39, 15.49, 13.73 ppm; HRMS (*m/z*): $[M + NH_4]^+$ calcd for $C_{19}H_{36}NO_2^+$ 310.2741, found 310.2740.



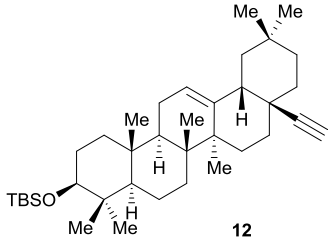
10

Compound 10 (racemic): 94% yield (a pale yellow oil); R_f = 0.20 (silica, petroleum ether); IR (film): ν_{max} = 2956, 1945, 1706, 1472, 1256, 1071 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.08 (m, 5 H), 4.54 (d, *J* = 6.2 Hz, 1 H), 2.61–2.48 (m, 1 H), 1.67 (d, *J* = 2.4 Hz, 3 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 0.85 (s, 9 H), 0.01 (s, 3 H), −0.21 (s, 3 H).ppm; ^{13}C NMR (101 MHz, acetone-d_6): δ = 144.45, 128.42, 127.94, 127.56, 82.24, 78.89, 77.87, 36.31, 26.20, 18.81, 16.91, 3.31, −4.45, −4.81 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{29}OSi^+$ 289.1982, found 289.1982.



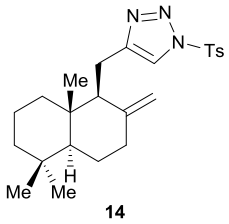
11

Compound 11: 94% yield (a colorless oil); R_f = 0.42 (silica, petroleum ether); IR (film): ν_{max} = 2932, 2858, 1461, 1446, 1322, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25–2.14 (m, 4 H), 1.57–1.52 (m, 8 H), 1.47–1.40 (m, 8 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 81.71, 25.80, 25.70, 25.02, 24.70, 18.62 ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{12}H_{20}^+$ 164.1565, found 164.1569. The spectroscopic data of **11** were identical with those reported in the literature.[2]



12

Compound 12: 98% yield (a white foam); R_f = 0.72 (silica, CH_2Cl_2:petroleum ether 1:5); $[\alpha]_D^{24}$ = +54.5 (*c* = 1.0 in $CHCl_3$); IR (film): ν_{max} = 3309, 2928, 2106, 1657, 1471, 1388, 1255, 1101,882 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.26 (t, *J* = 3.7 Hz, 1 H), 3.18 (dd, *J* = 11.1, 4.6 Hz, 1 H), 2.41 (dd, *J* = 13.8, 3.7 Hz, 1 H), 2.19–2.08 (m, 2 H), 2.07–1.78 (m, 4 H), 1.69–1.43 (m, 8 H), 1.42 (s, 3 H), 1.39–1.31 (m, 2 H), 1.25 (s, 3 H), 1.22–1.14 (m, 2 H), 1.12 (s, 3 H), 1.10–1.05 (m, 2 H), 0.99 (s, 3 H), 0.93 (s, 6 H), 0.91 (s, 3 H), 0.89 (s, 9 H), 0.85–0.82 (m, 1 H), 0.81–0.76 (m, 1 H), 0.75 (s, 3 H), 0.74–0.68 (m, 1 H), 0.03 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.28, 122.73, 93.24, 79.67, 69.33, 55.50, 47.91, 46.22, 45.86, 42.10, 39.72, 39.51, 38.66, 37.12, 35.68, 35.42, 34.05, 33.36, 33.20, 30.91, 28.74, 28.00, 27.81, 27.08, 26.09, 25.89, 23.79, 23.63, 18.75, 18.29, 17.43, 16.30, 15.55, −3.57, −4.73 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{37}H_{63}OSi^+$ 551.4643, found 551.4642.



14

Triazole 14: To a stirred solution of triflate **13** (78.0 mg, 0.205 mmol) in DMF (1.0 mL) was added anhydrous LiCl (35.0 mg, 0.820 mmol) at 22 ℃. The resultant mixture was stirred at that temperature for 60 min before TsN_3 (55.0 μL, 70.7 mg, 0.358 mmol) and CuTc (20.0 mg, 0.105 mmol) were sequentially added. The mixture so obtained was stirred at 22 ℃ for 5 min before it was directly subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:10) as eluent to give triazole **14** (70 mg, 80%) as a white foam. **14**: R_f = 0.24 (silica, EtOAc:petroleum ether 1:10); $[\alpha]_D^{24}$ = +5.6 (*c* = 2.0 in $CHCl_3$); IR (film): ν_{max} = 3154, 2929, 1644, 1595, 1390, 1194, 1177, 1009, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2 H), 7.75 (s, 1 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 4.79 (s, 1 H), 4.45 (s, 1 H), 2.97 (dd, *J* = 15.8, 1.9 Hz, 1 H), 2.77 (dd, *J* = 15.8, 11.1 Hz, 1 H), 2.44 (s, 3 H), 2.41–2.34 (m, 1 H), 2.11 (d, *J* = 11.1 Hz, 1 H), 2.04–1.93 (m, 1 H), 1.82–1.70 (m, 2 H), 1.64–1.52 (m, 1 H), 1.52–1.46 (m, 1 H), 1.43–1.29 (m, 2 H), 1.22–1.07 (m, 3 H), 0.88 (s, 3 H), 0.82 (s, 3 H), 0.76 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.65, 147.62, 147.06, 133.54, 130.43, 128.66, 120.93, 108.07, 56.05, 55.45, 42.15, 39.86, 39.34, 38.01, 33.73, 33.72, 24.33, 21.94, 21.84, 21.02, 19.46, 14.47.ppm; HRMS (*m/z*): $[M]^+$ calcd for $C_{24}H_{33}N_3O_2S^+$ 427.2293, found 427.2290.

II References

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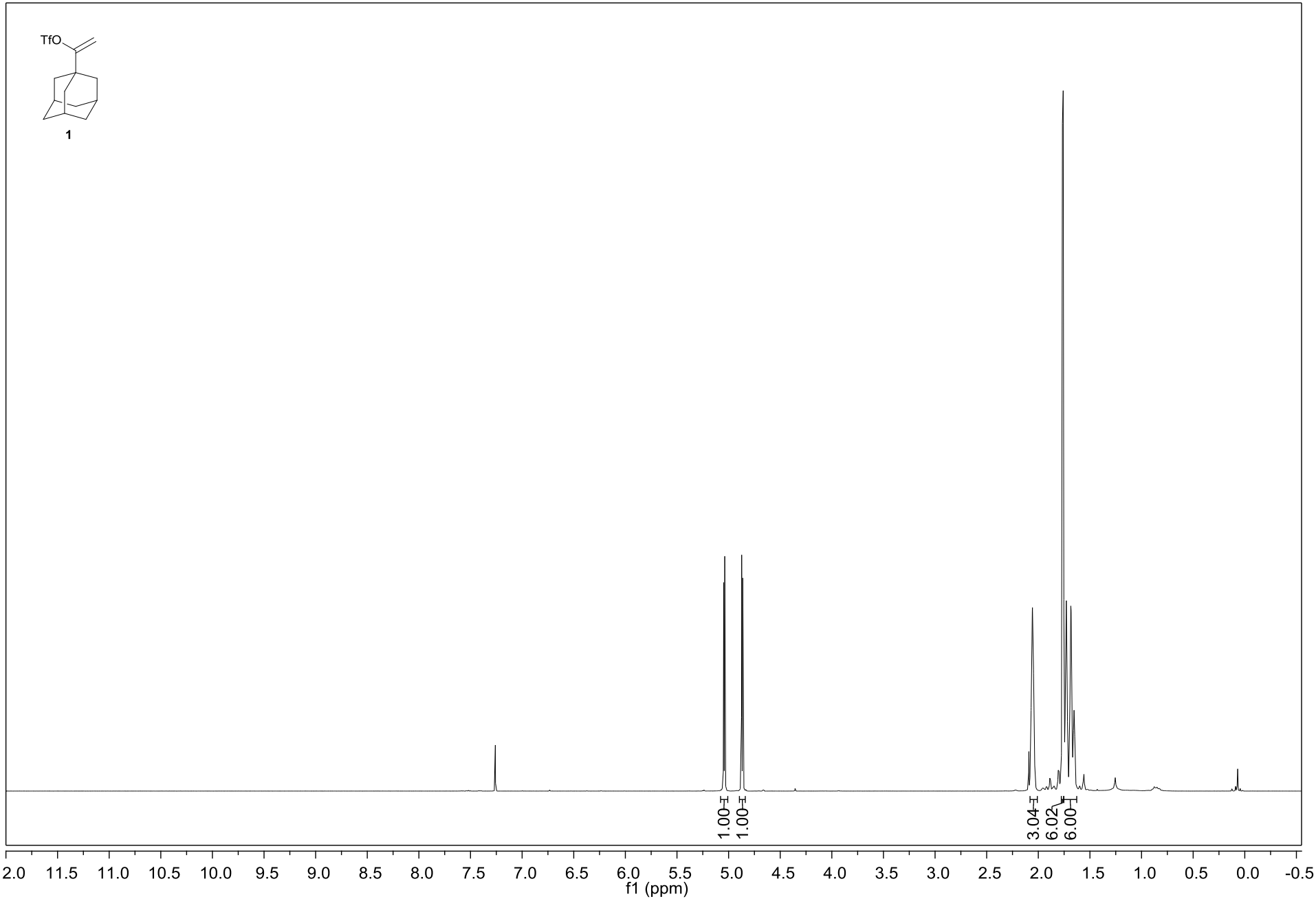
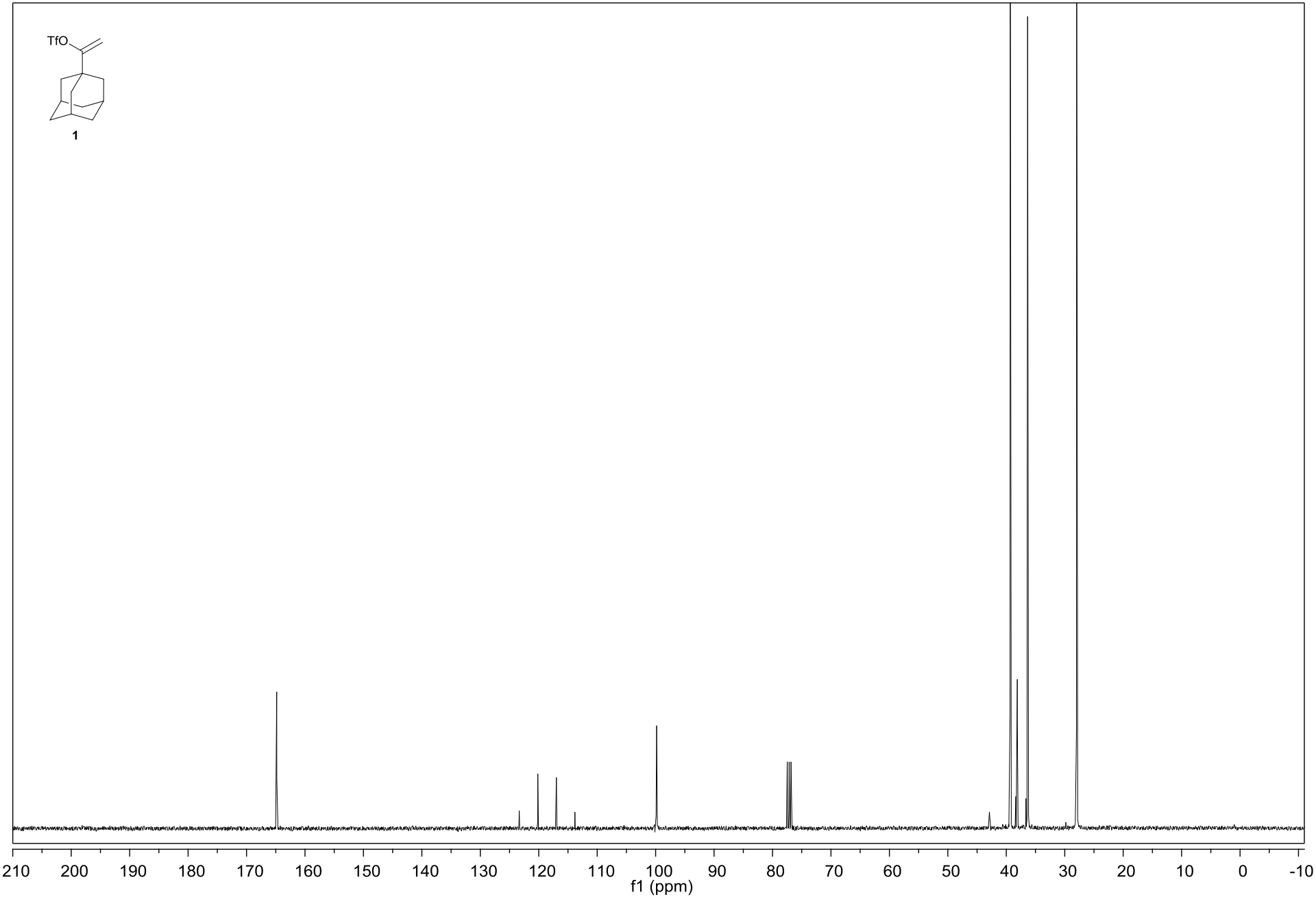
III ^{1}H and ^{13}C NMR Spectra of Compounds

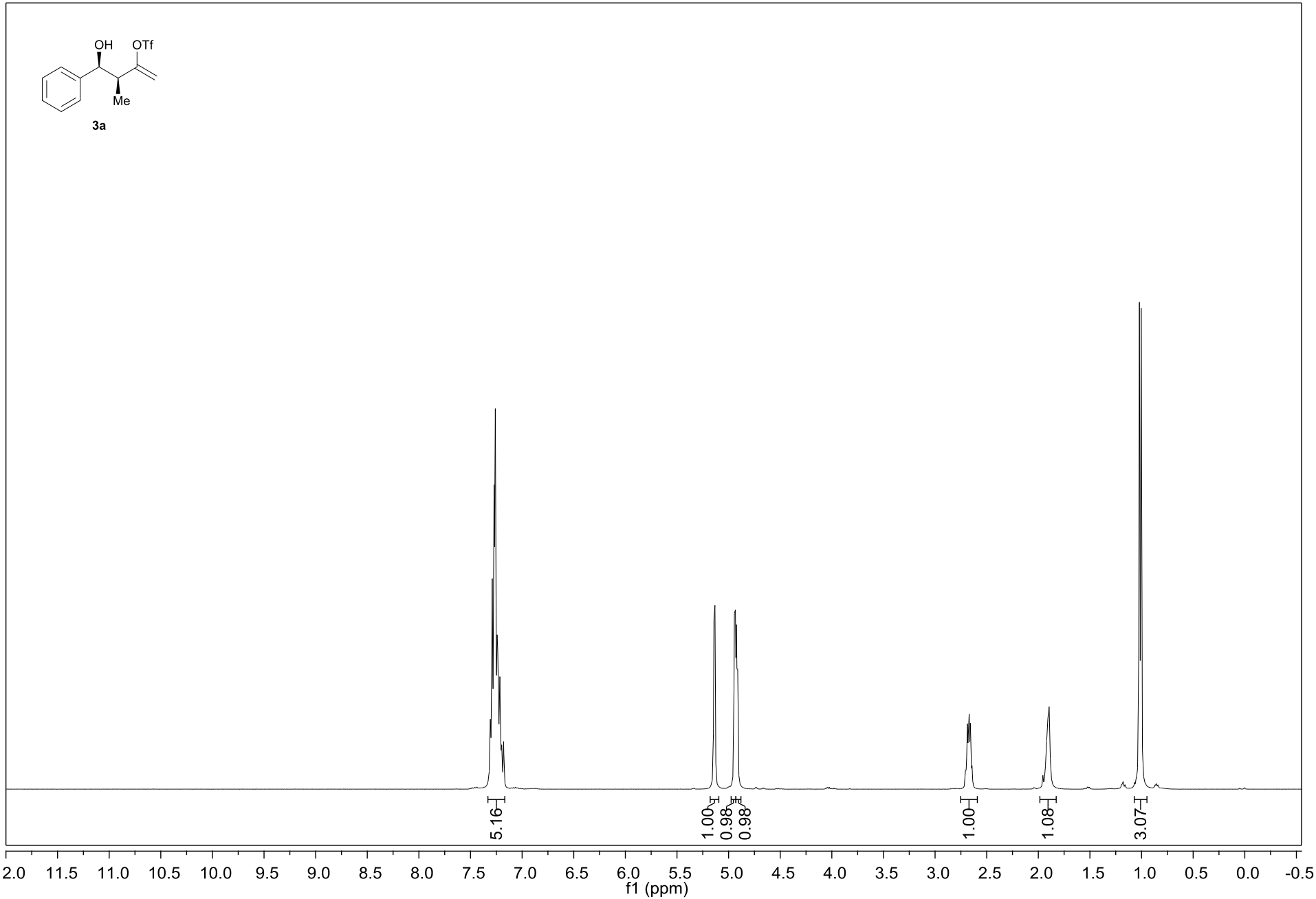
^{1}H NMR Spectrum of 1 (400 MHz, $CDCl_3$)



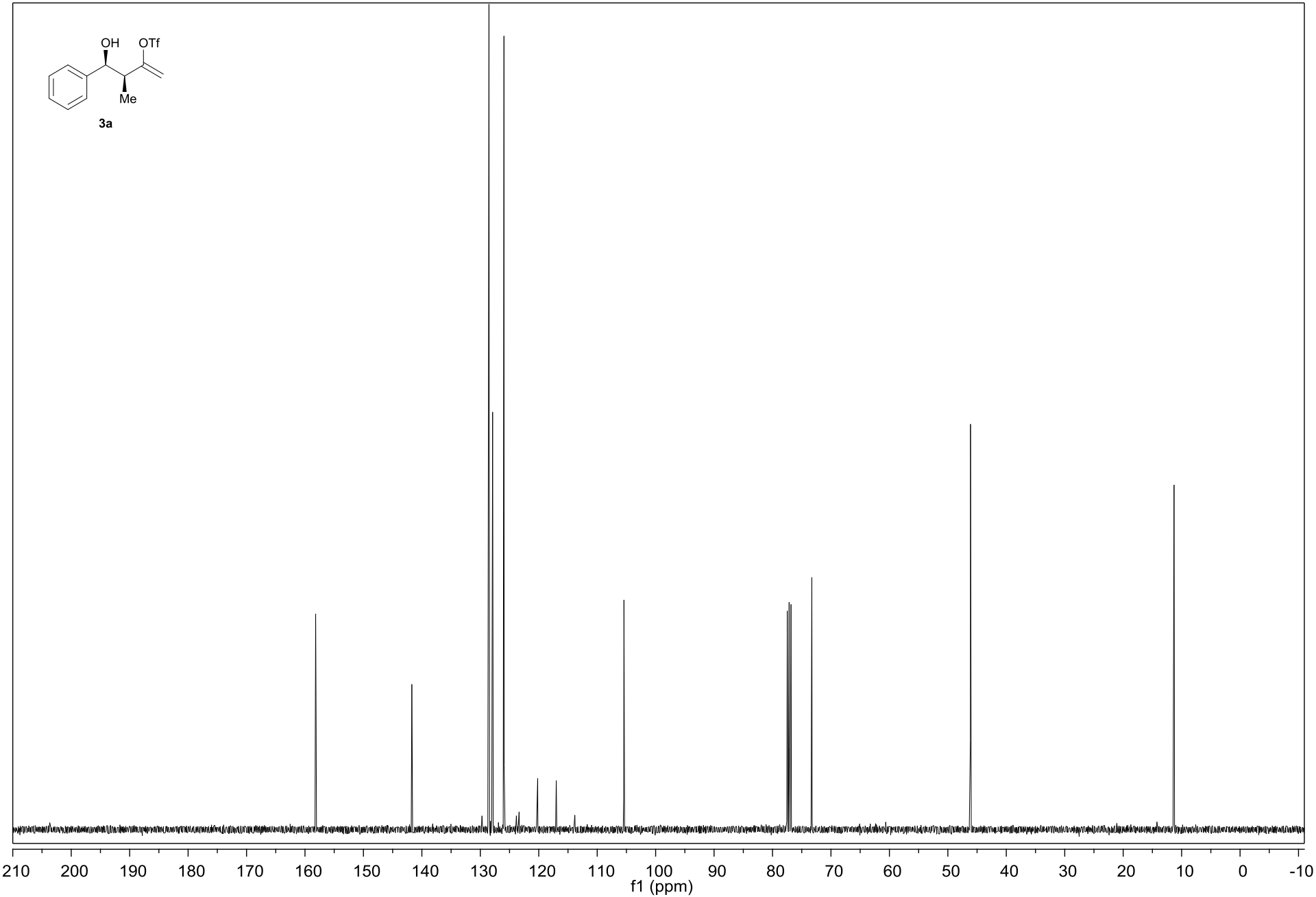
^{13}C NMR Spectrum of 1 (101 MHz, $CDCl_3$)



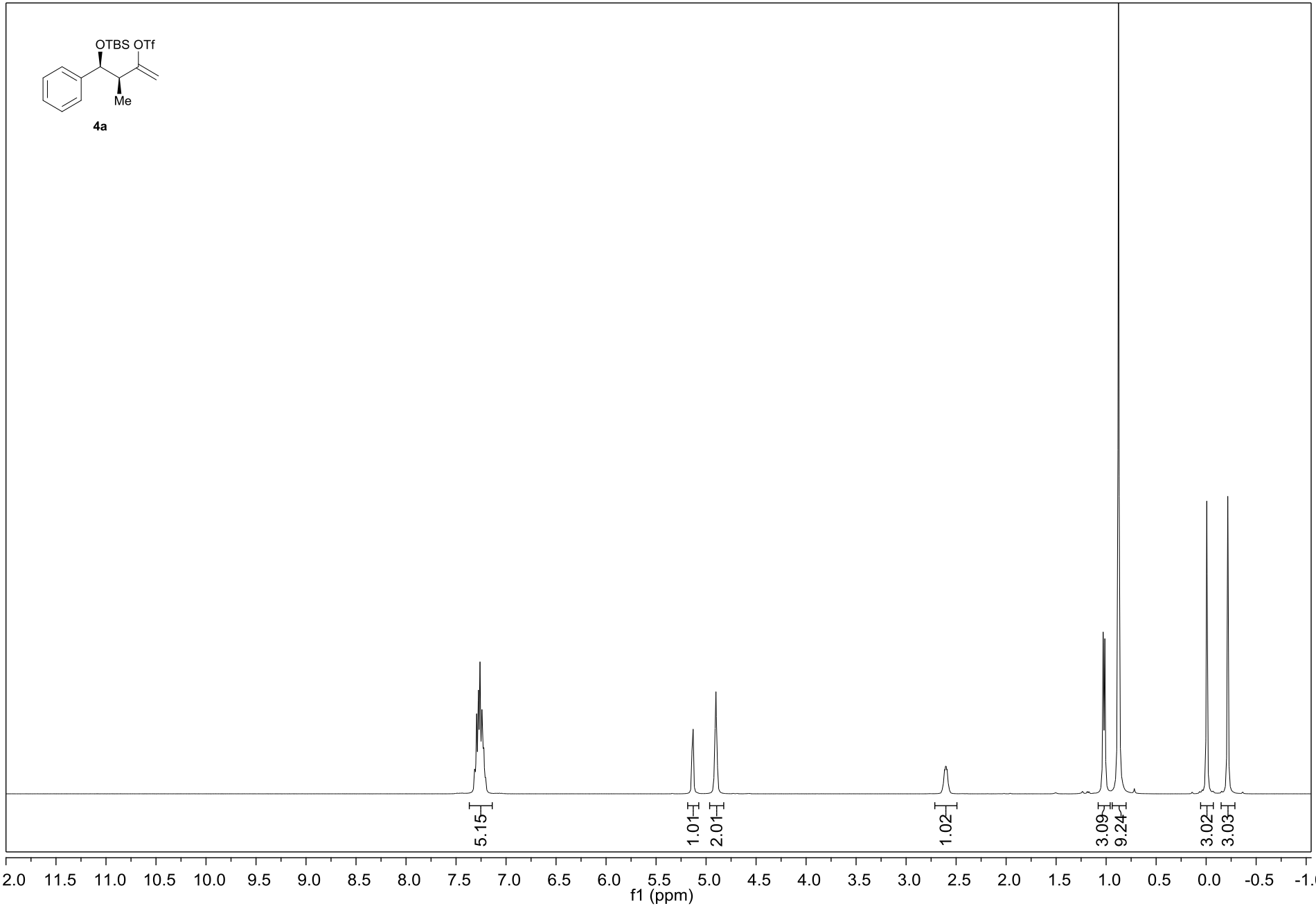
^{1}H NMR Spectrum of 3a (400 MHz, $CDCl_3$)



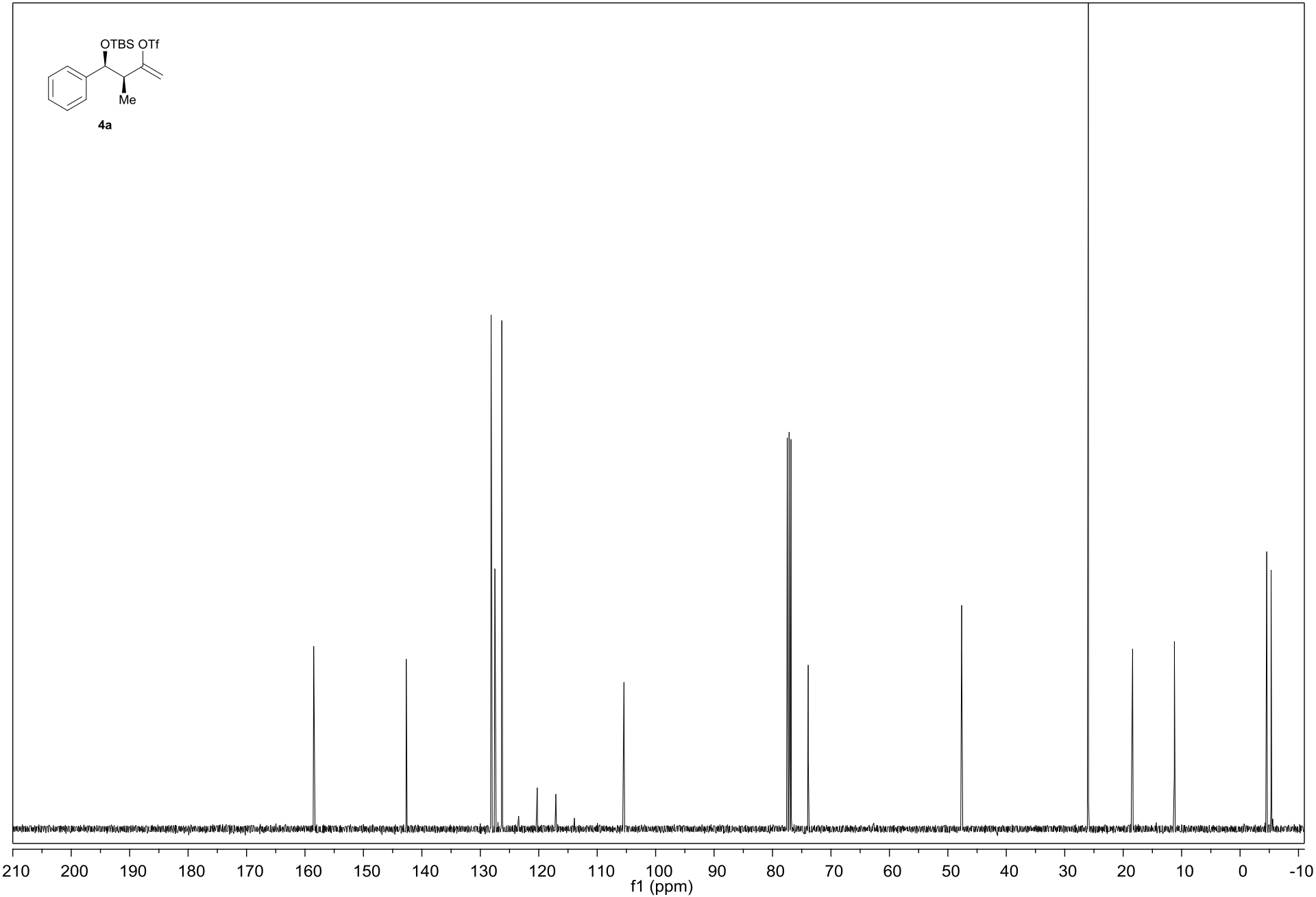
^{13}C NMR Spectrum of 3a (101 MHz, $CDCl_3$)



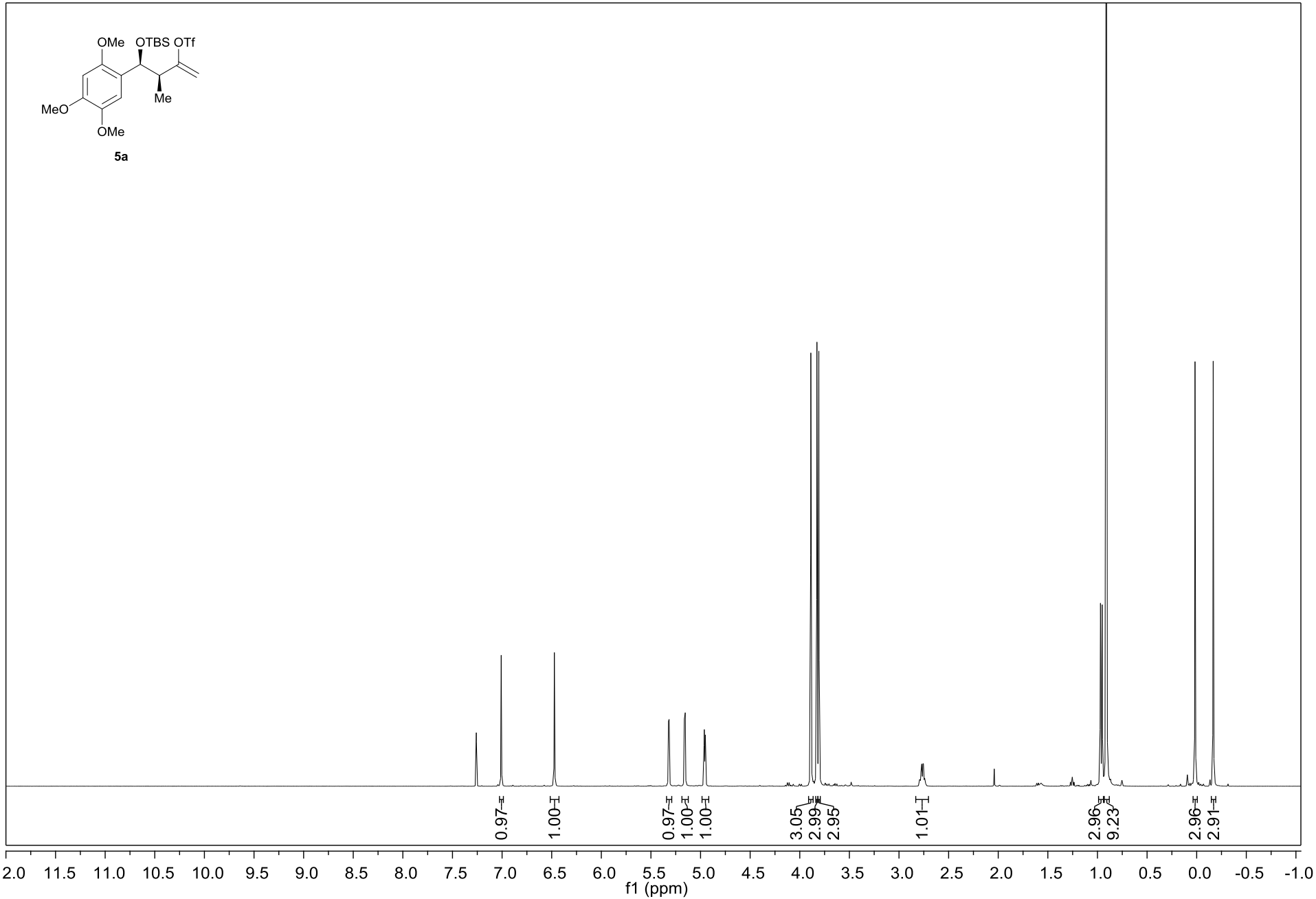
^{1}H NMR Spectrum of 4a (400 MHz, $CDCl_3$)



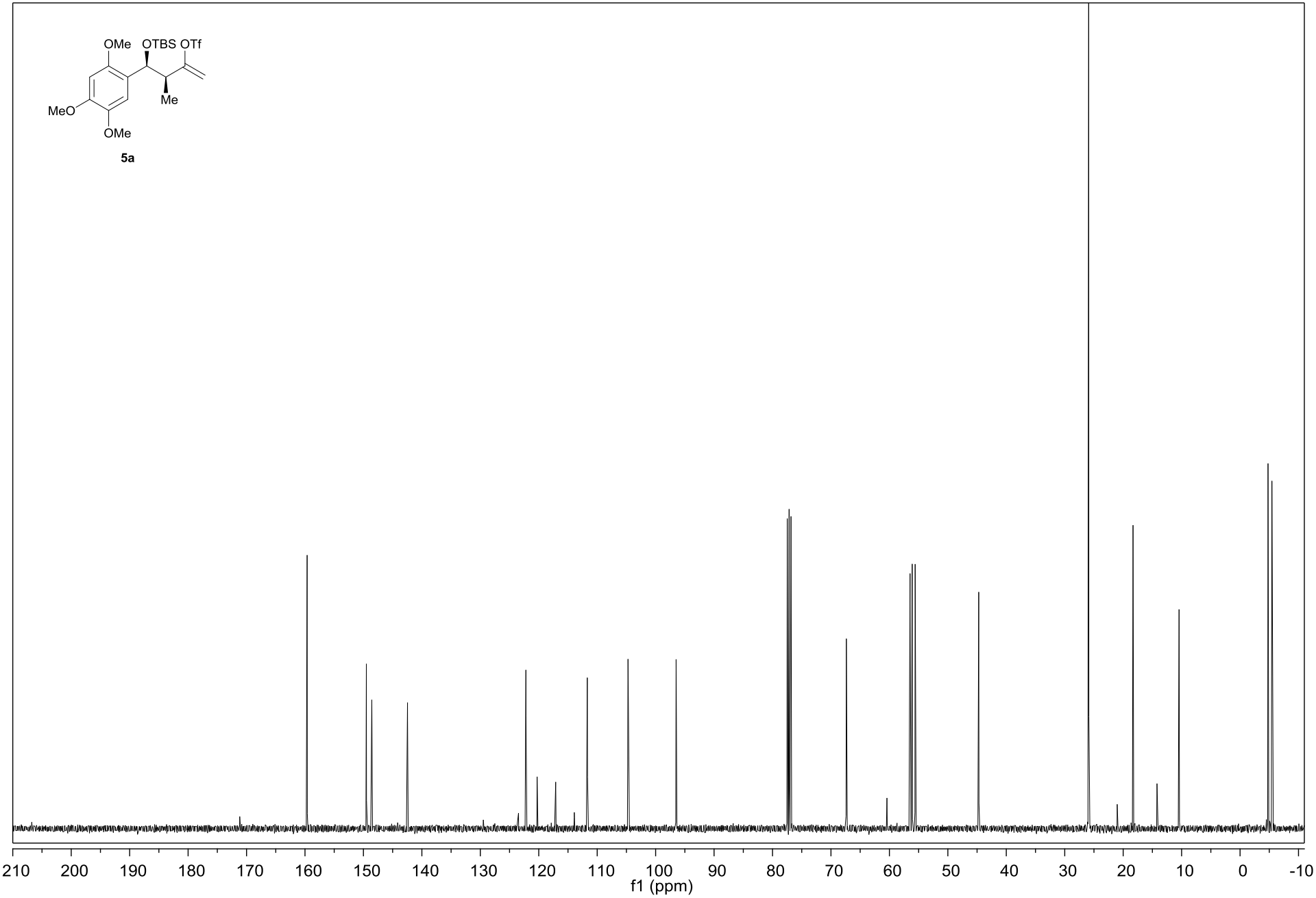
^{13}C NMR Spectrum of 4a (101 MHz, $CDCl_3$)



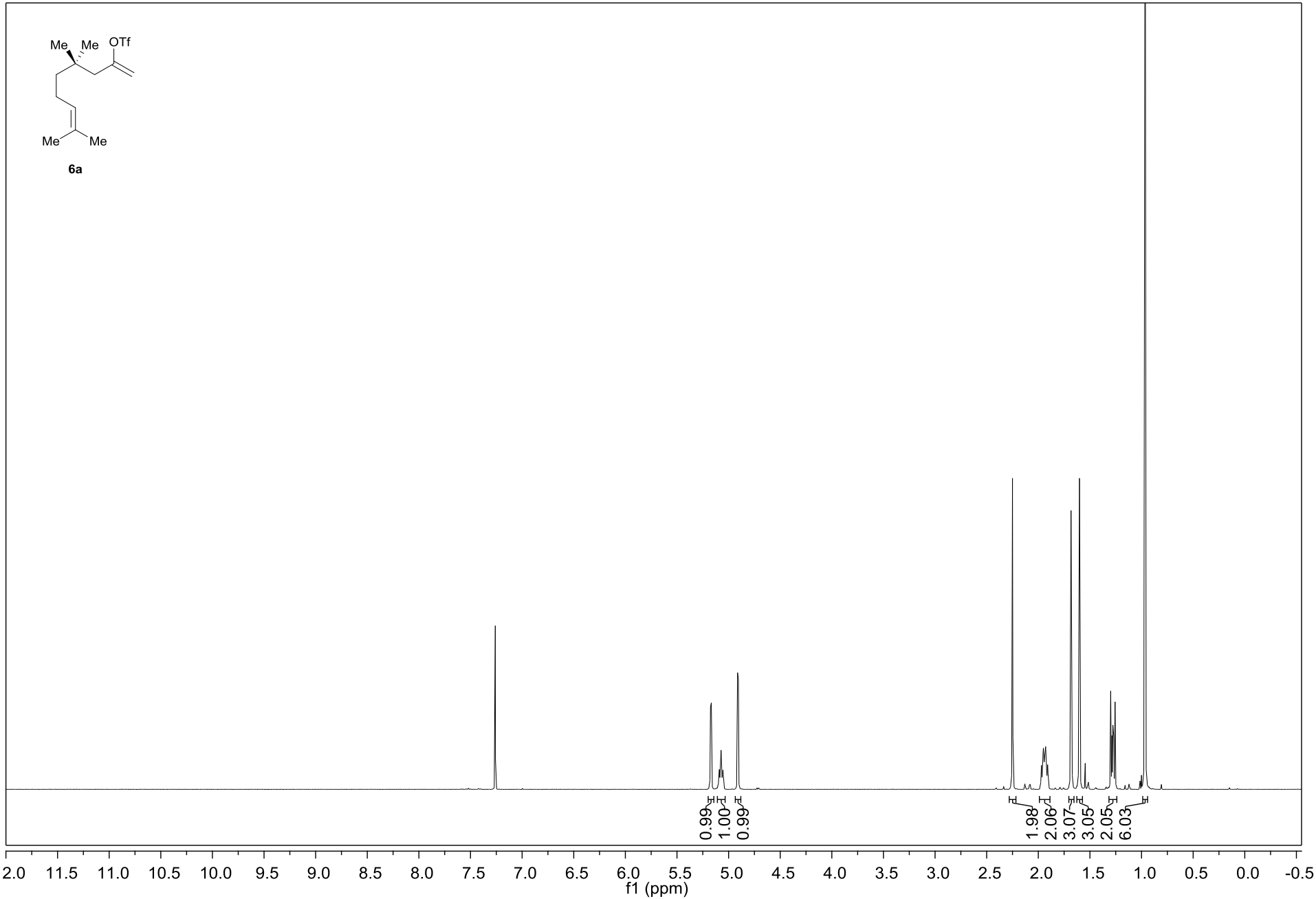
^{1}H NMR Spectrum of 5a (400 MHz, $CDCl_3$)



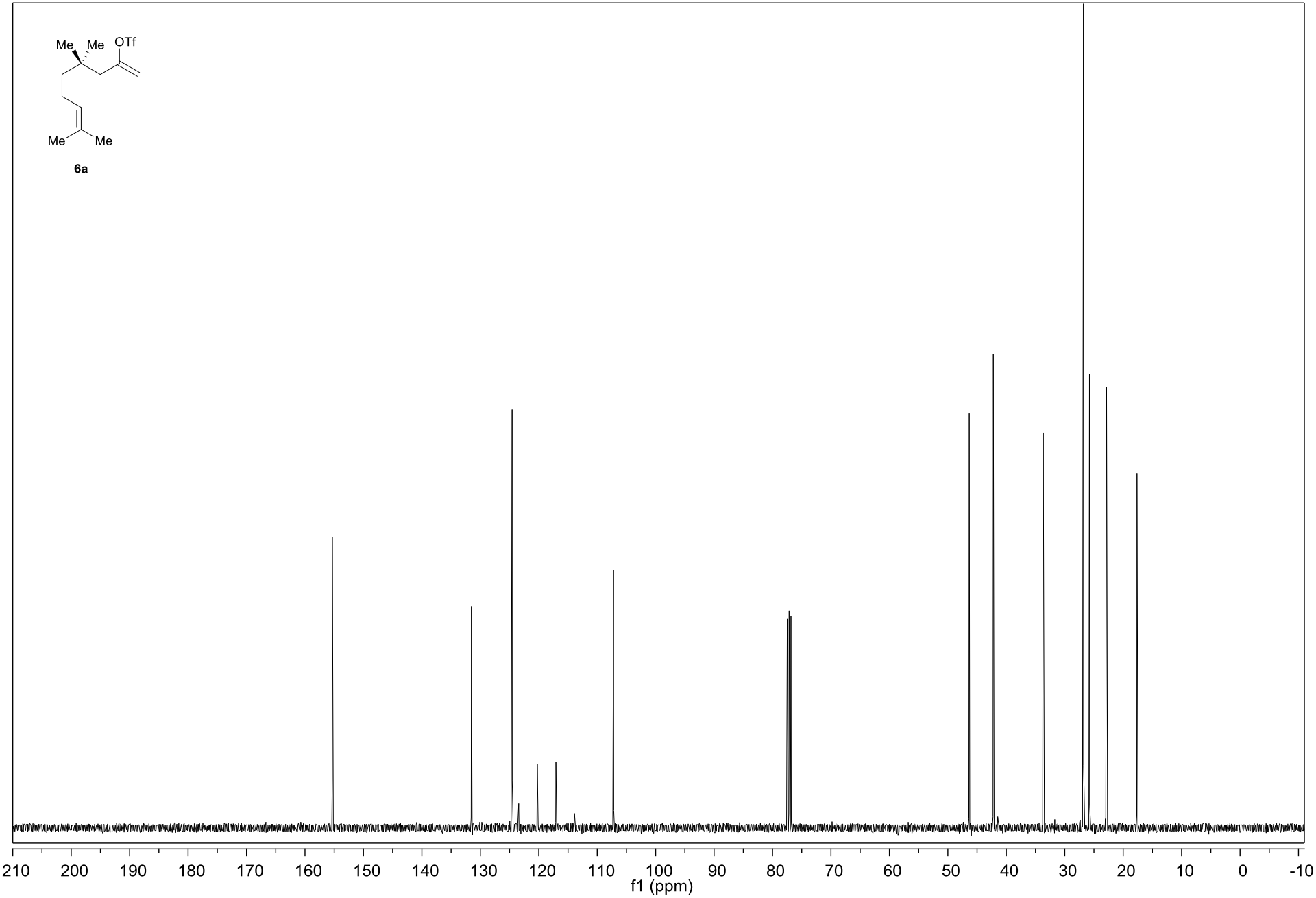
^{13}C NMR Spectrum of 5a (101 MHz, $CDCl_3$)



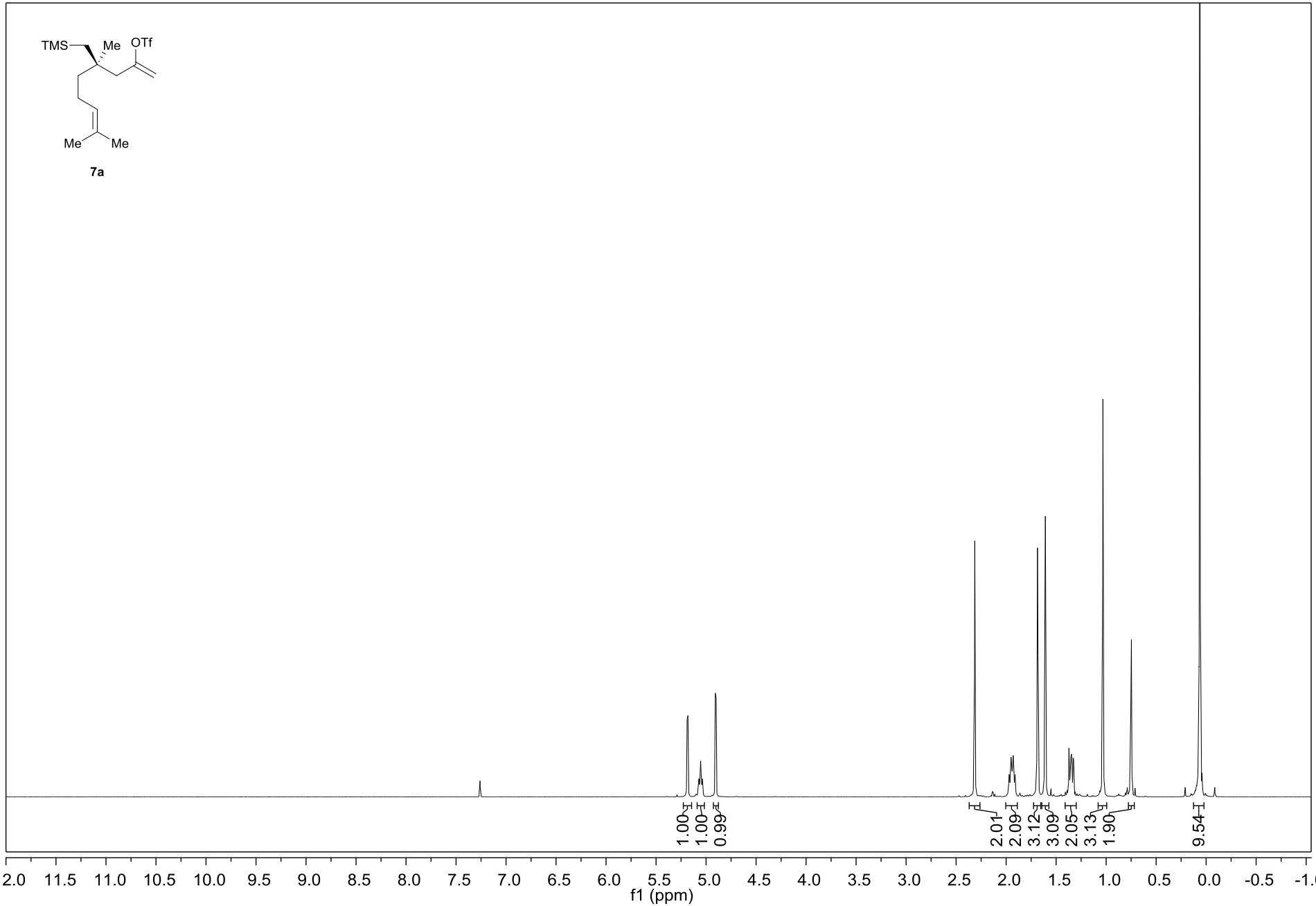
^{1}H NMR Spectrum of 6a (400 MHz, $CDCl_3$)



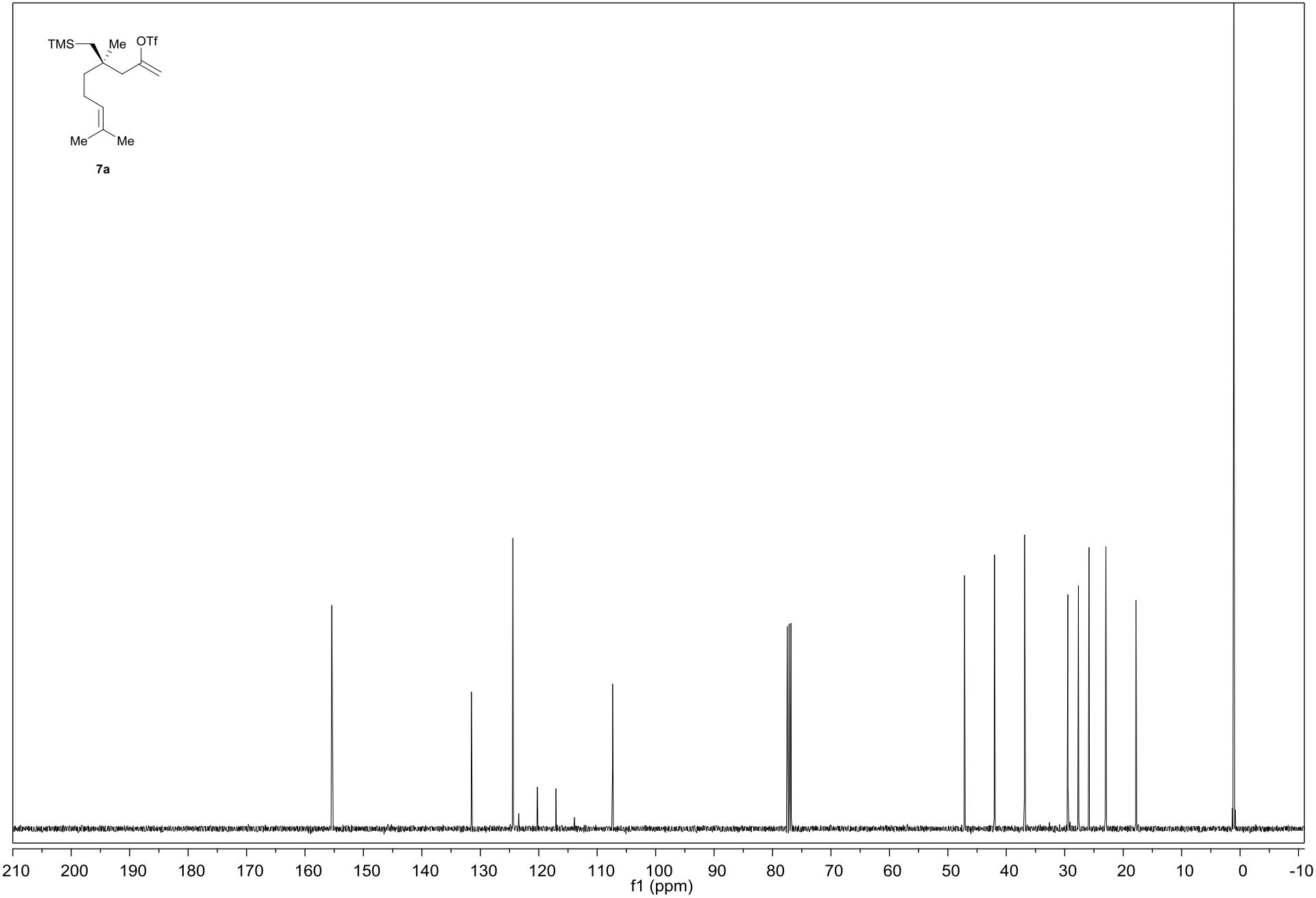
^{13}C NMR Spectrum of 6a (101 MHz, $CDCl_3$)



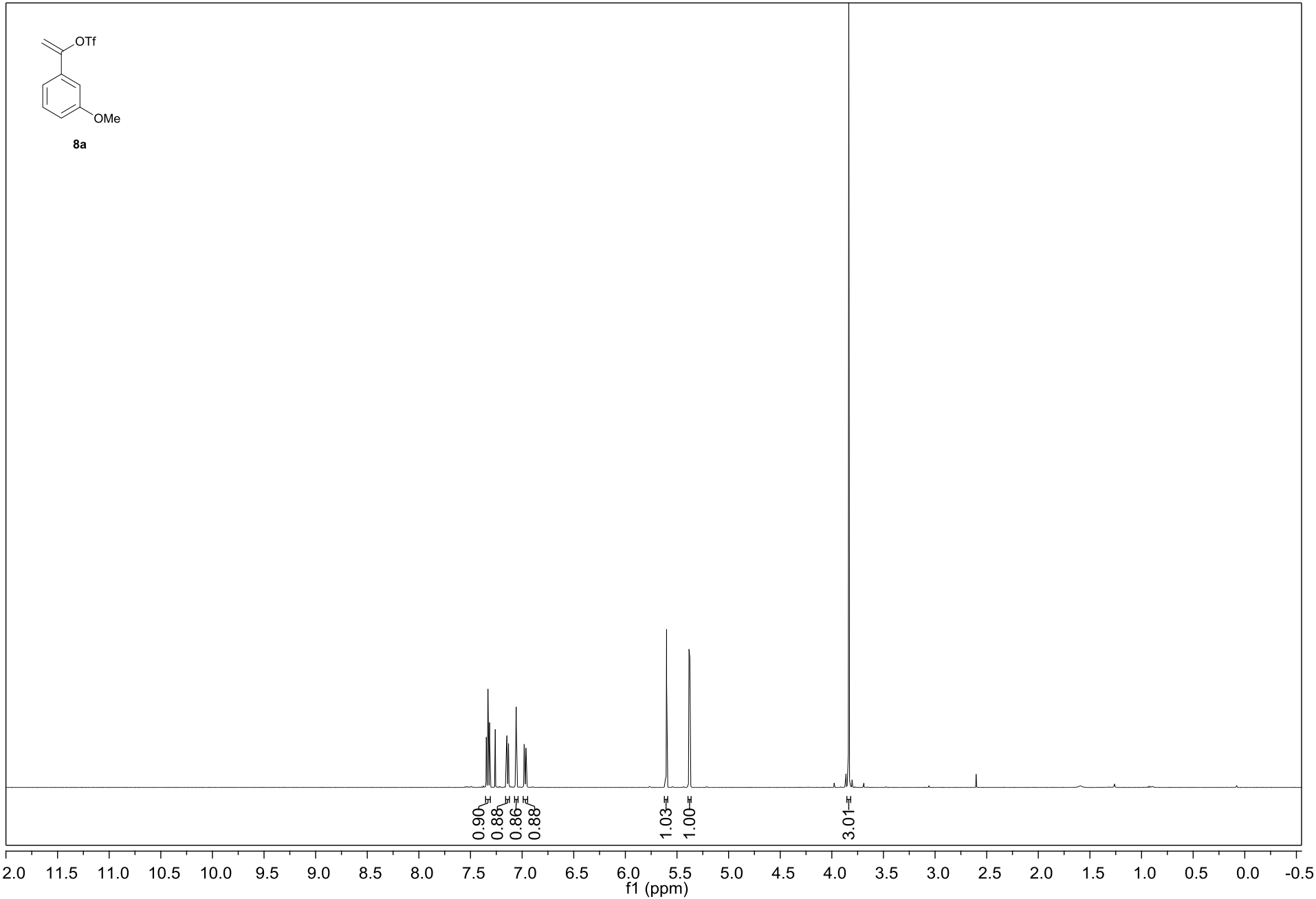
^{1}H NMR Spectrum of 7a (400 MHz, $CDCl_3$)



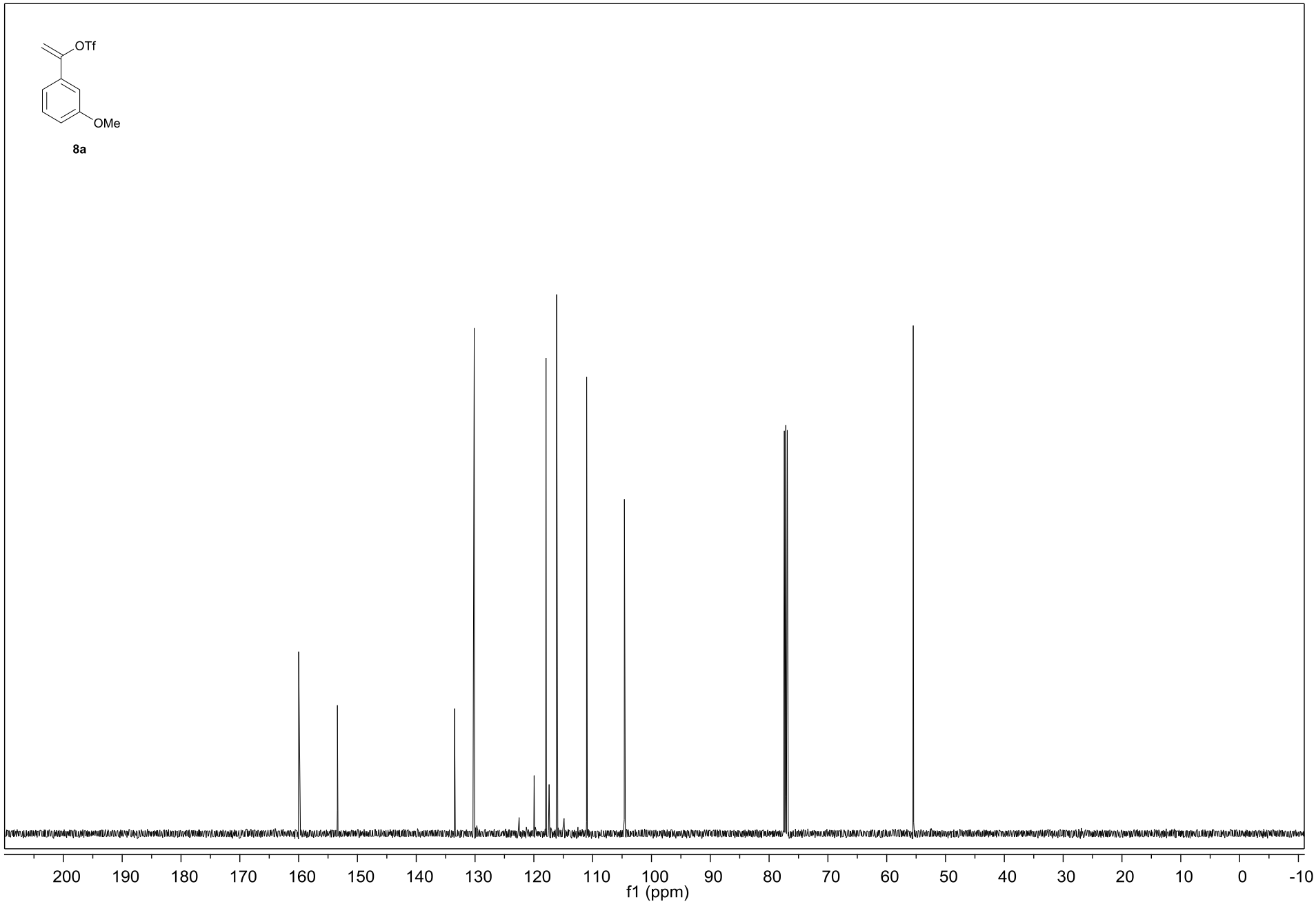
^{13}C NMR Spectrum of 7a (101 MHz, $CDCl_3$)



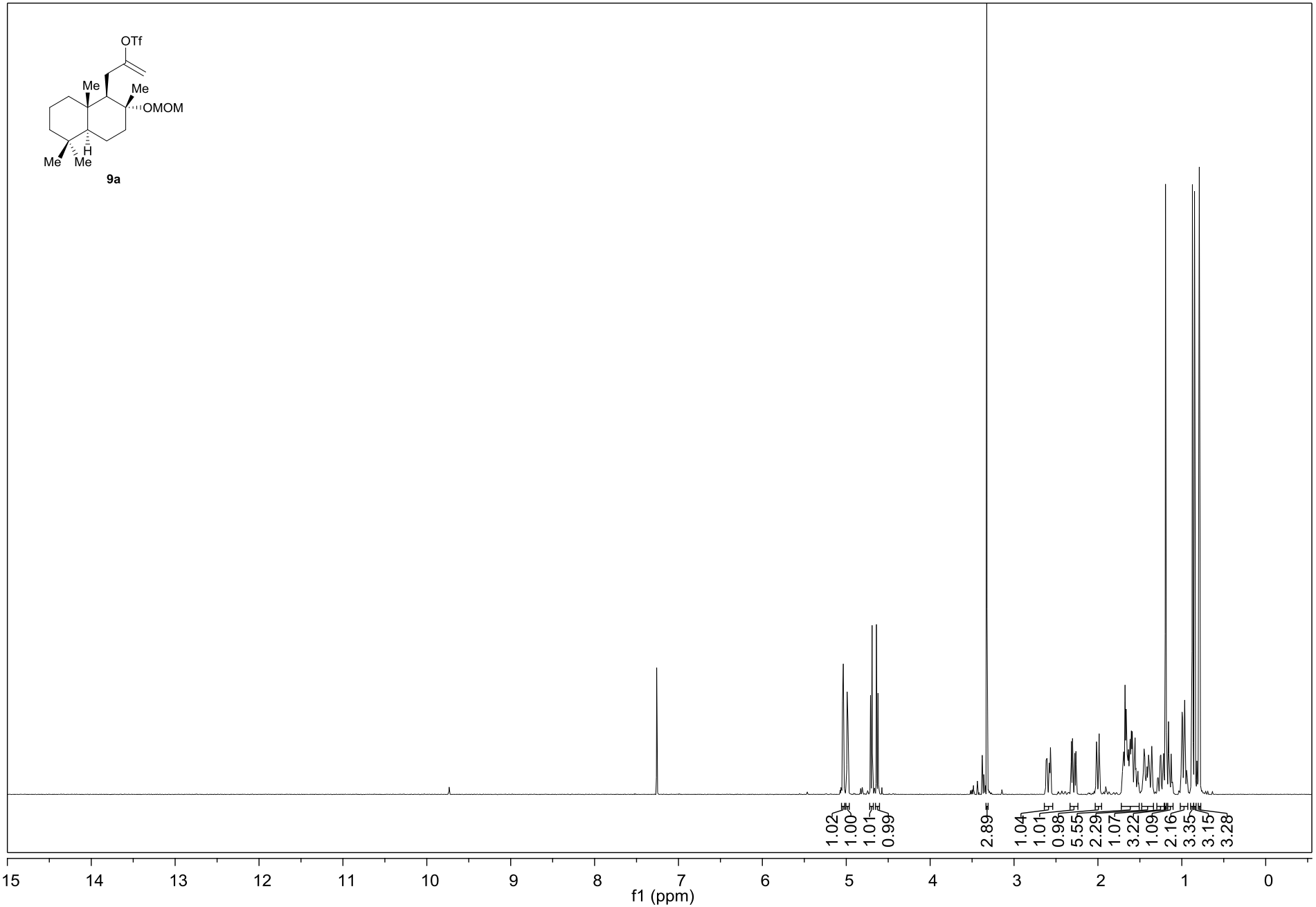
^{1}H NMR Spectrum of 8a (400 MHz, $CDCl_3$)



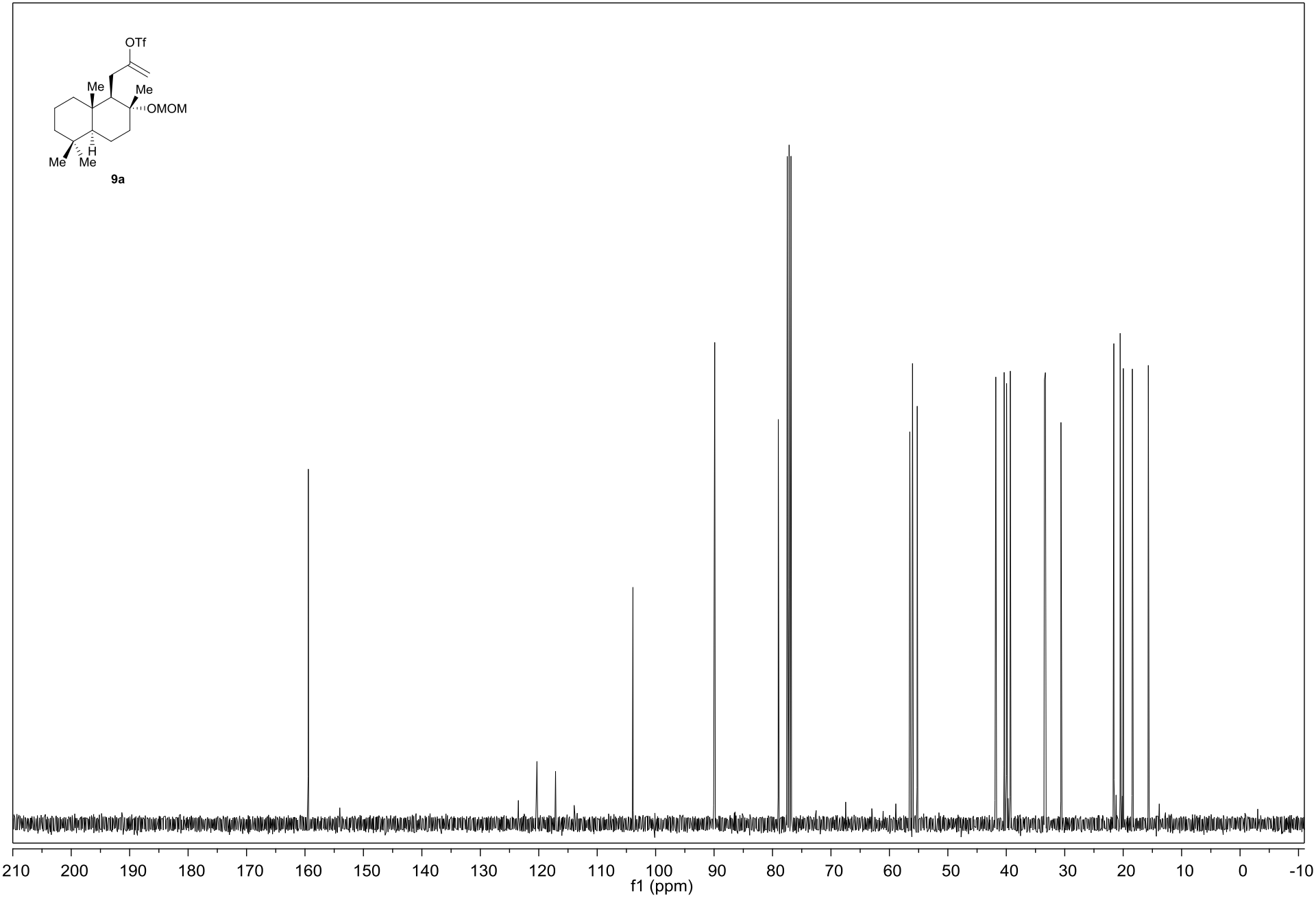
^{13}C NMR Spectrum of 8a (101 MHz, $CDCl_3$)



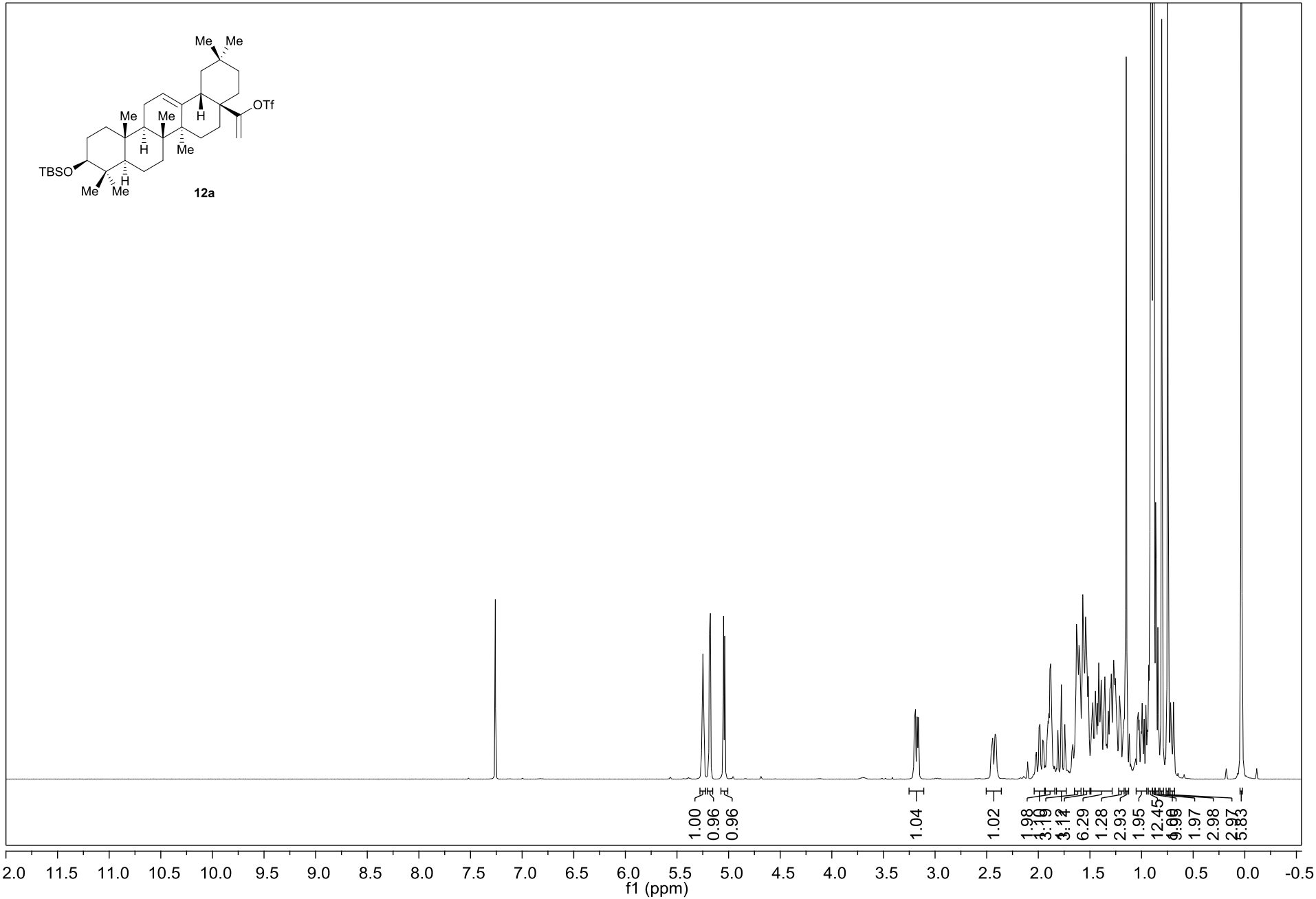
^{1}H NMR Spectrum of 9a (400 MHz, $CDCl_3$)



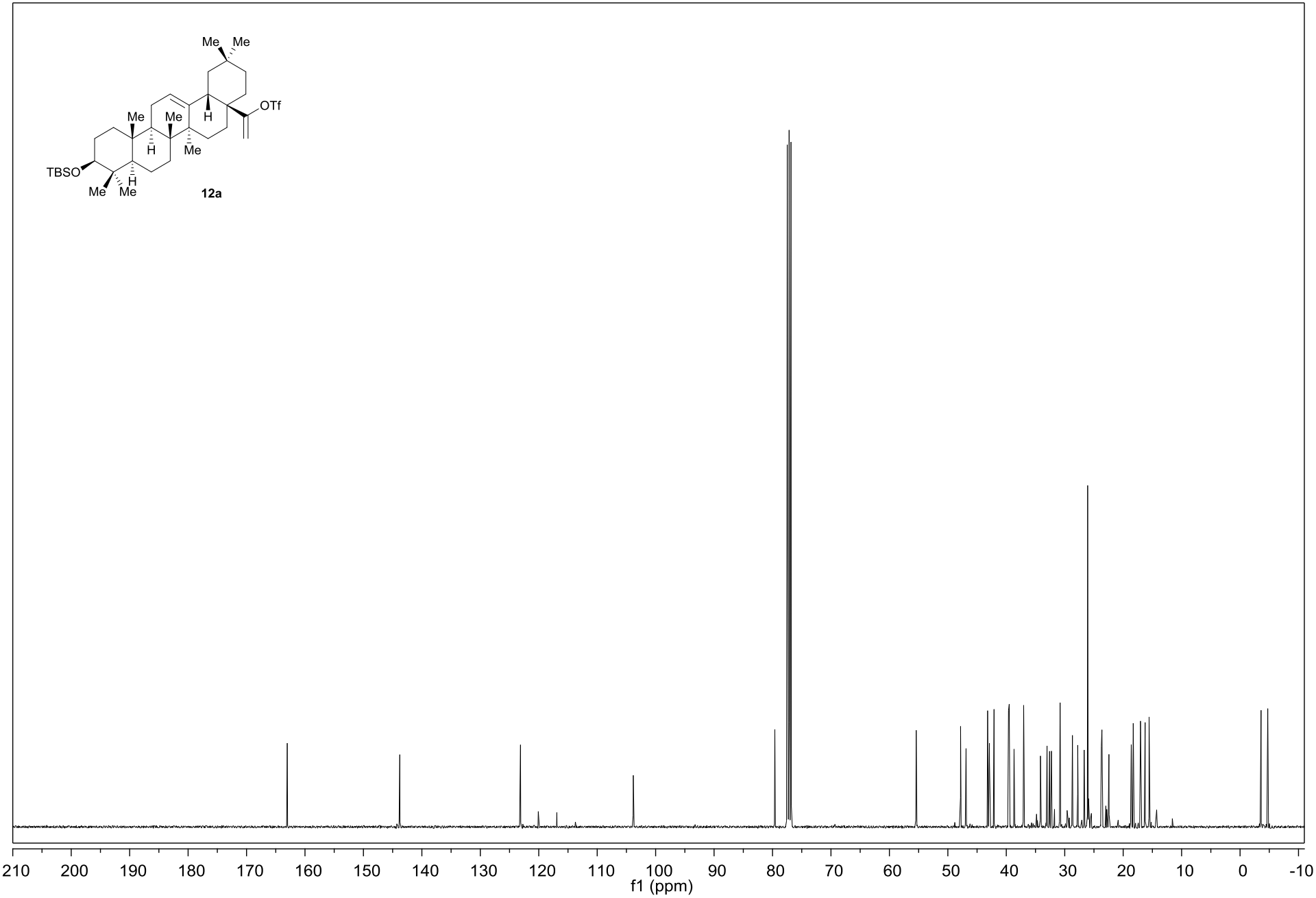
^{13}C NMR Spectrum of 9a (101 MHz, $CDCl_3$)



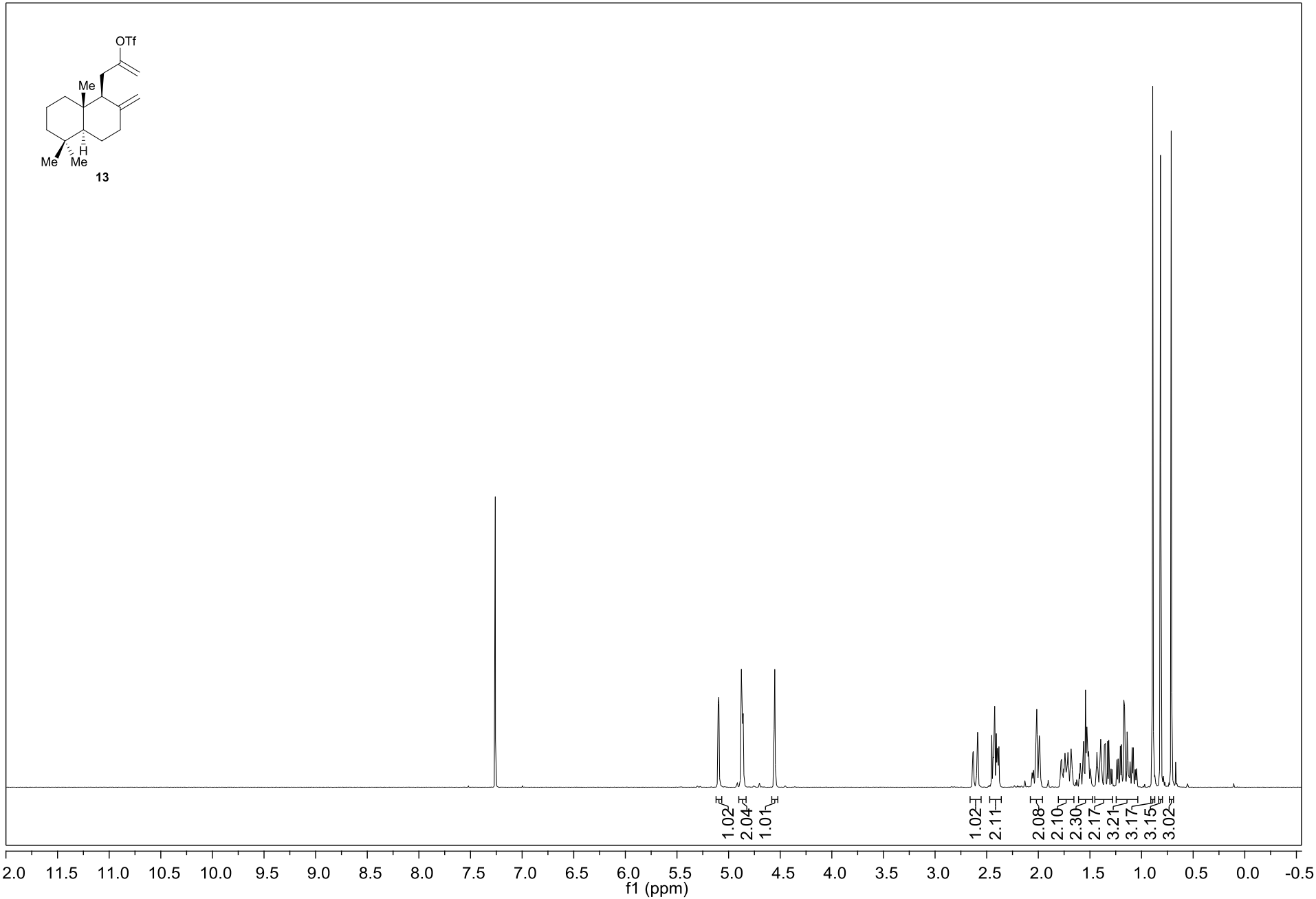
^{1}H NMR Spectrum of 12a (400 MHz, $CDCl_3$)



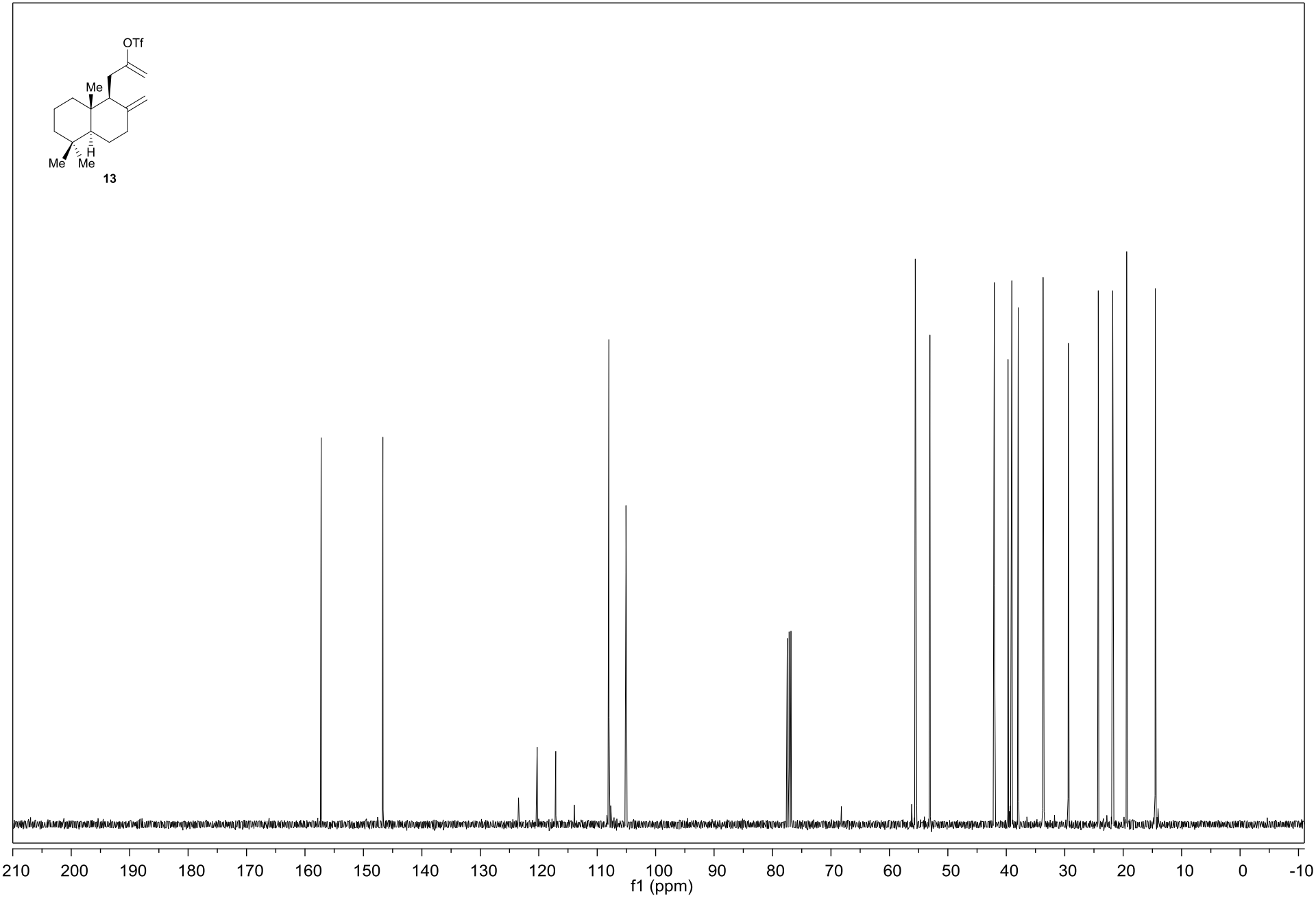
^{13}C NMR Spectrum of 12a (101 MHz, $CDCl_3$)



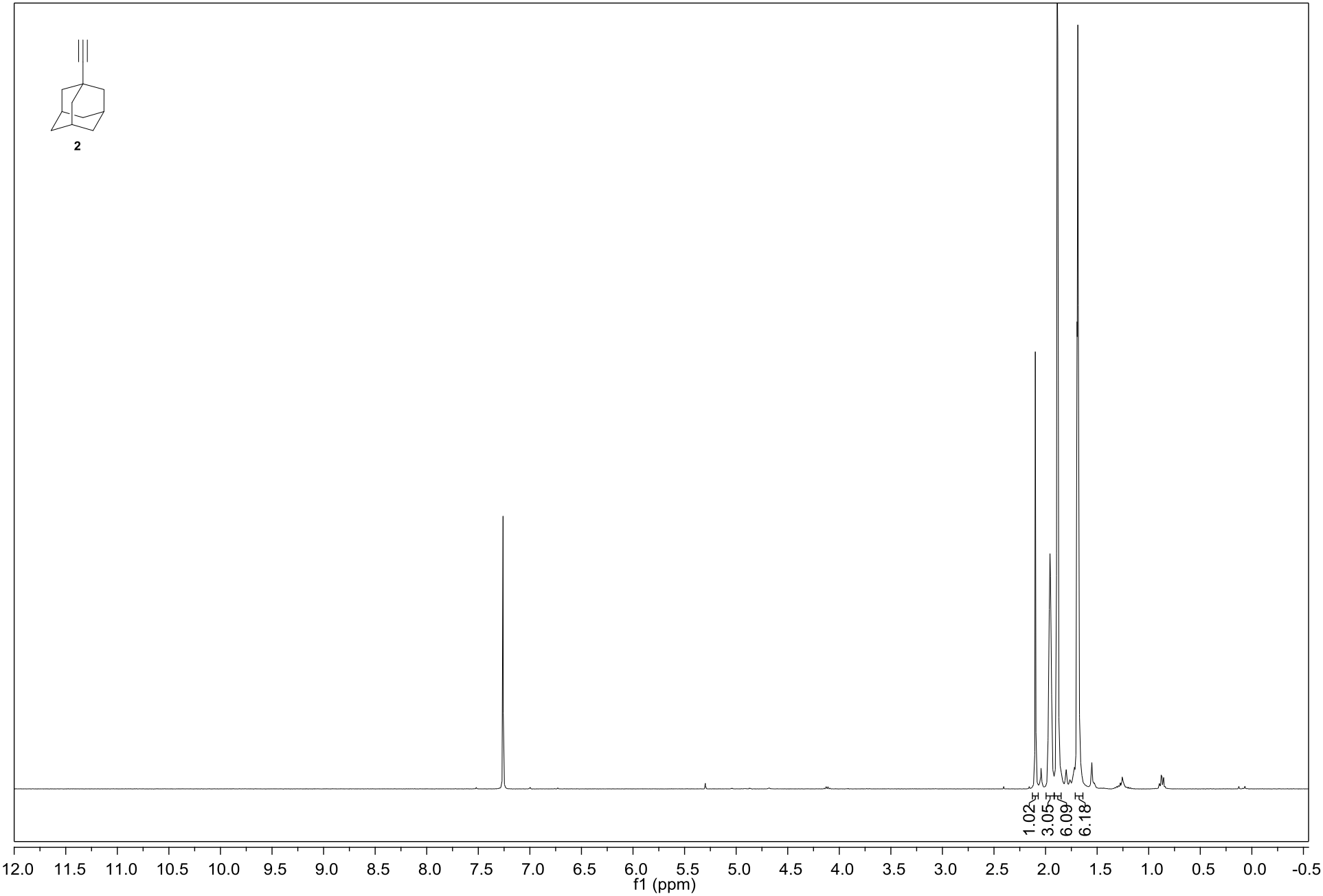
^{1}H NMR Spectrum of 13 (400 MHz, $CDCl_3$)



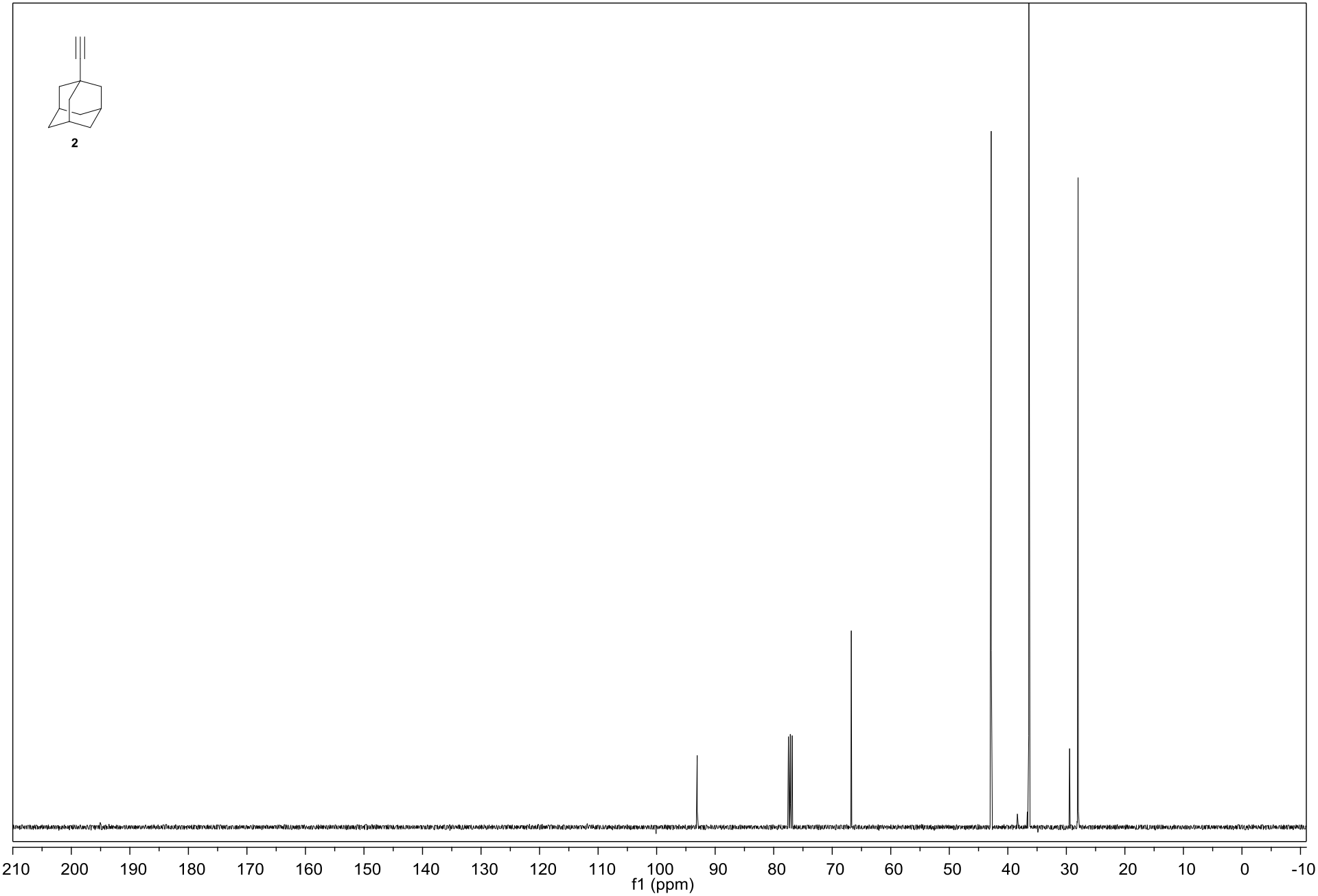
^{13}C NMR Spectrum of 13 (101 MHz, $CDCl_3$)



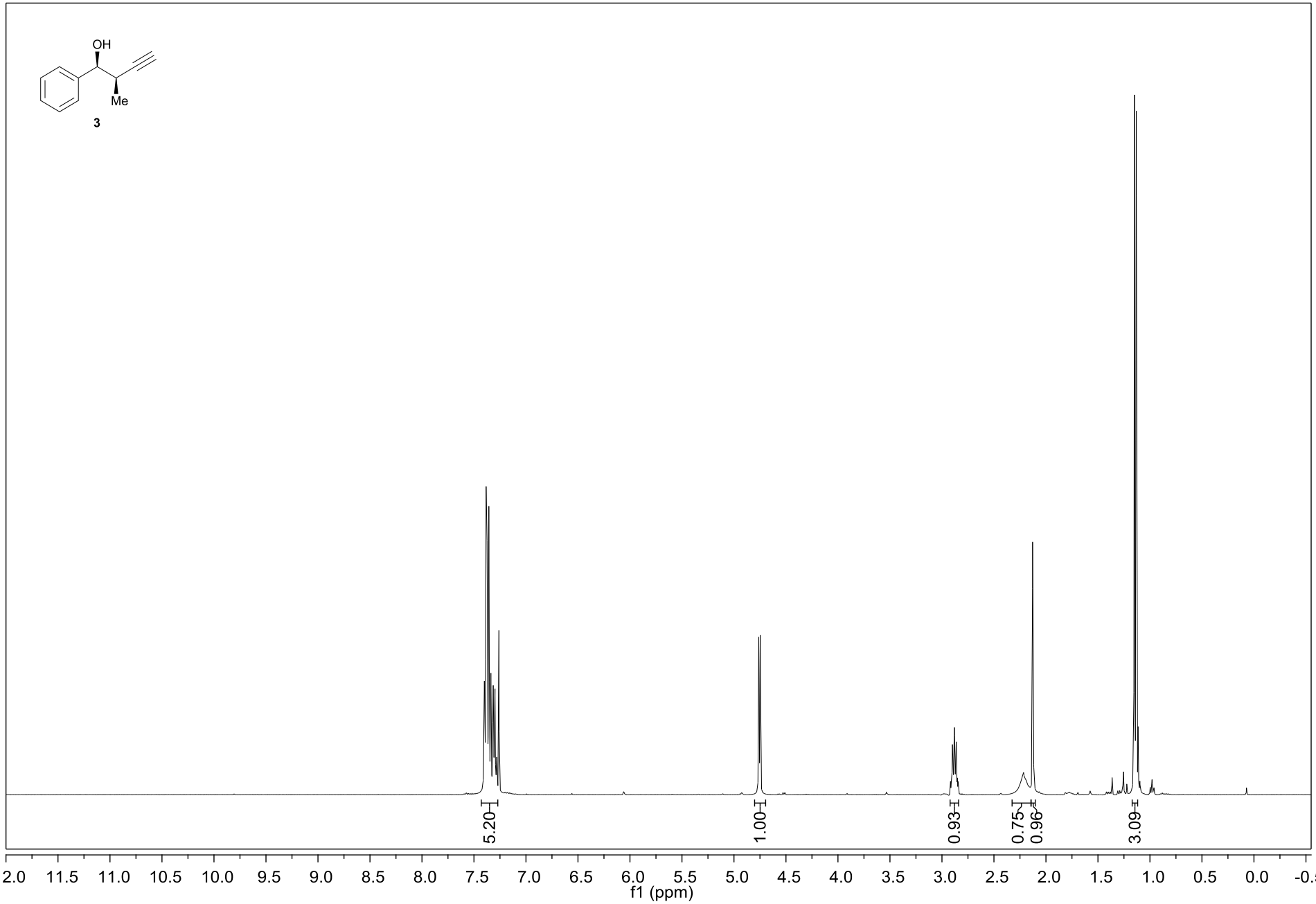
^{1}H NMR Spectrum of 2 (400 MHz, $CDCl_3$)



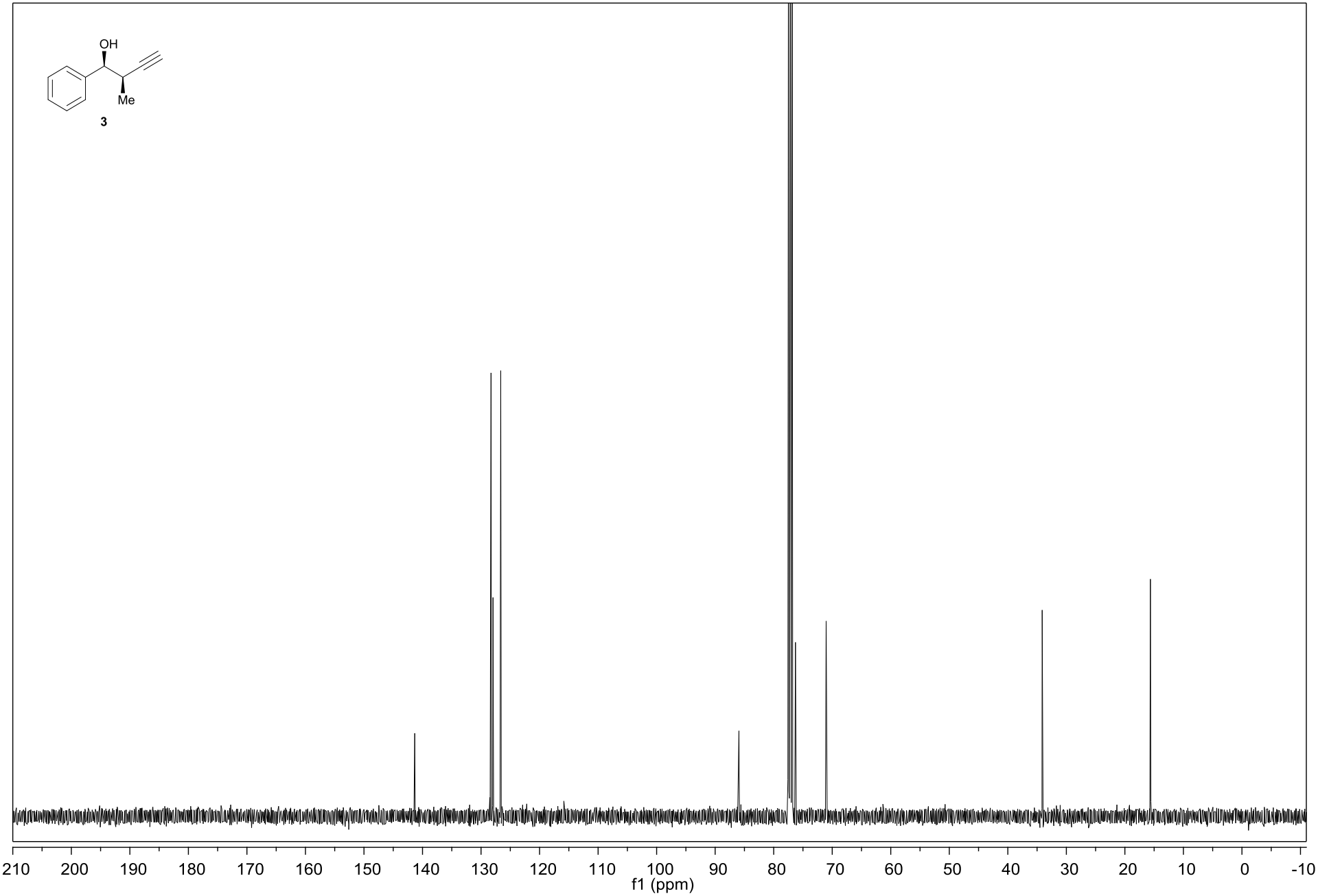
^{13}C NMR Spectrum of 2 (101 MHz, $CDCl_3$)



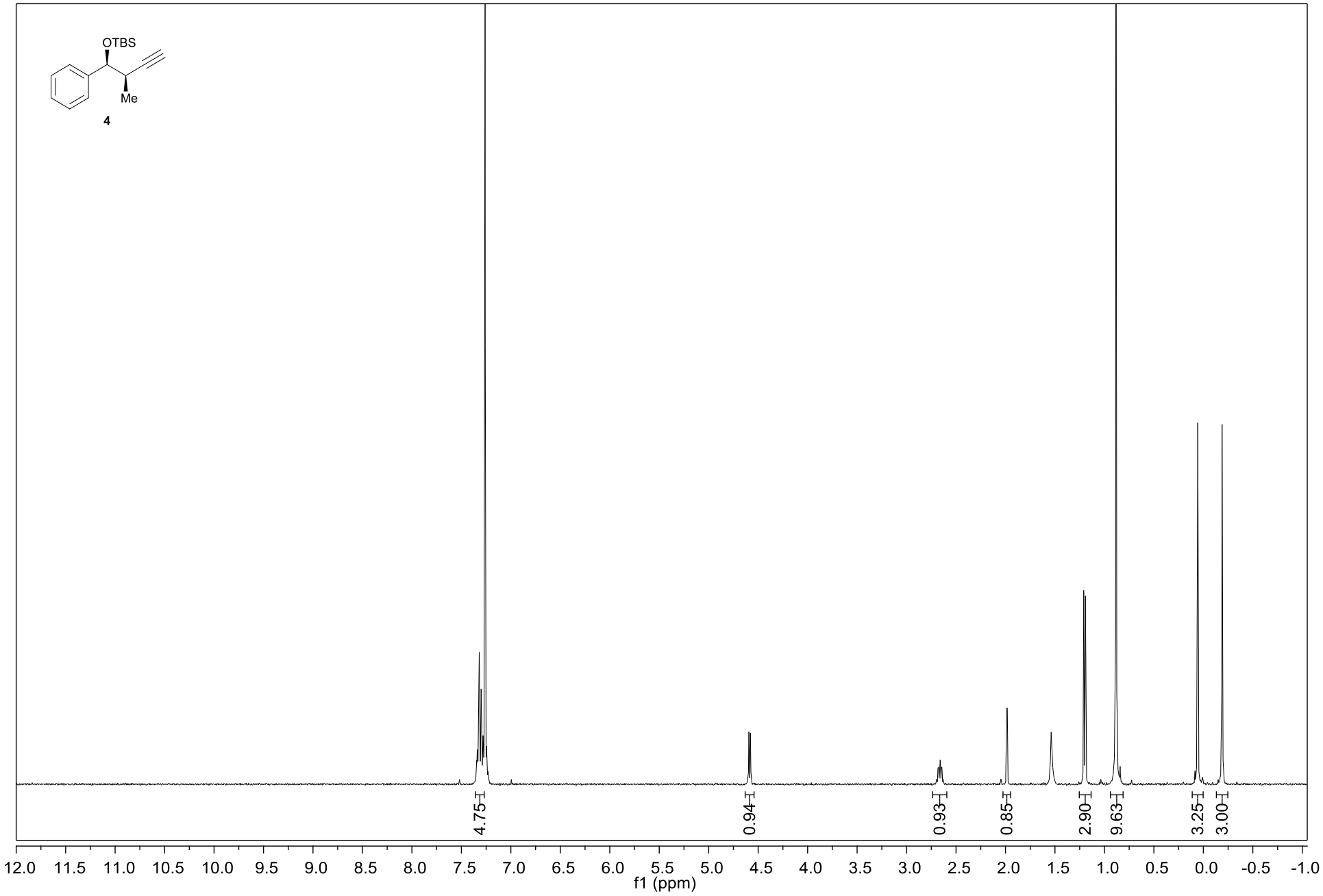
^{1}H NMR Spectrum of 3 (400 MHz, $CDCl_3$)



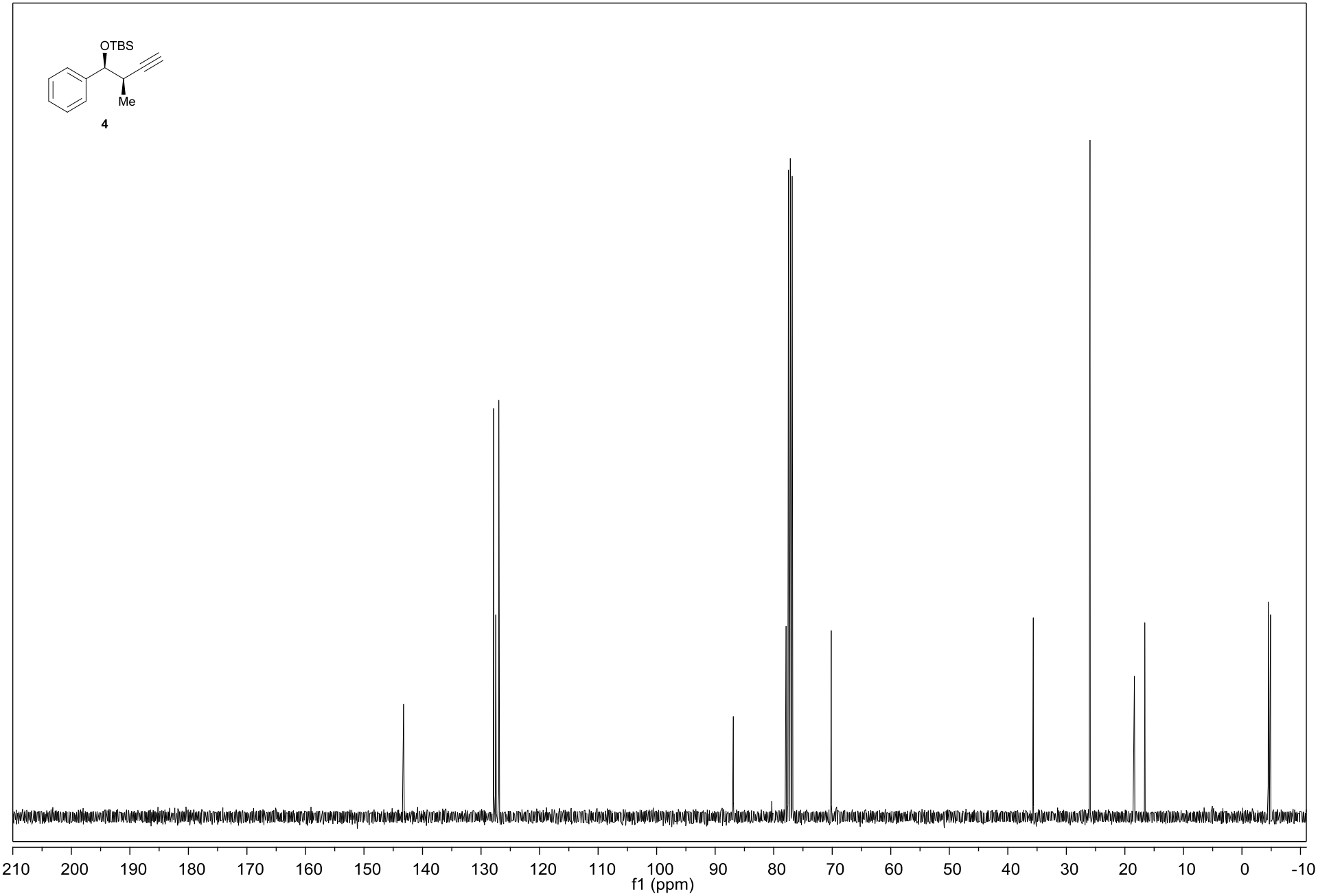
^{13}C NMR Spectrum of 3 (101 MHz, $CDCl_3$)



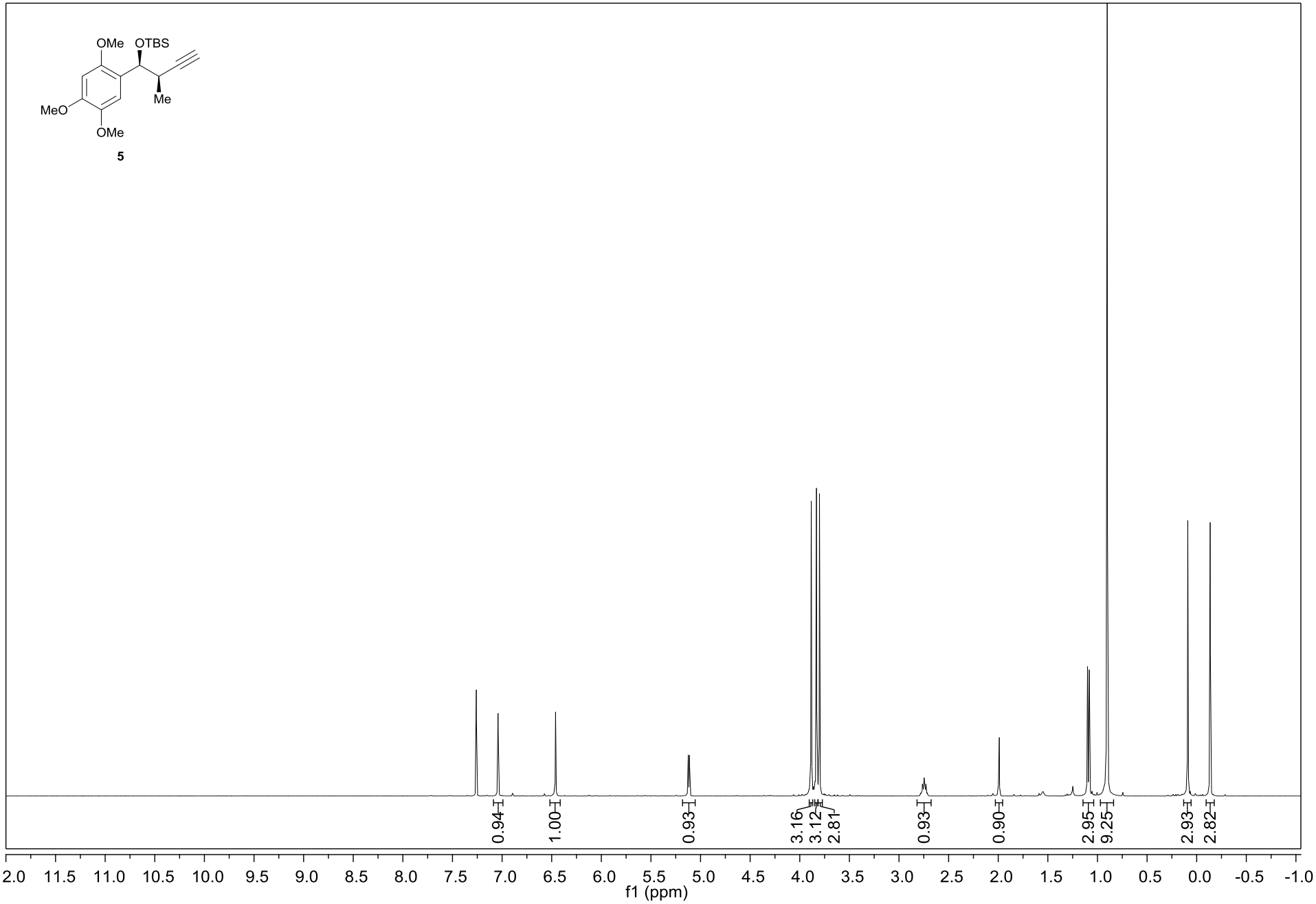
^{1}H NMR Spectrum of 4 (400 MHz, $CDCl_3$)



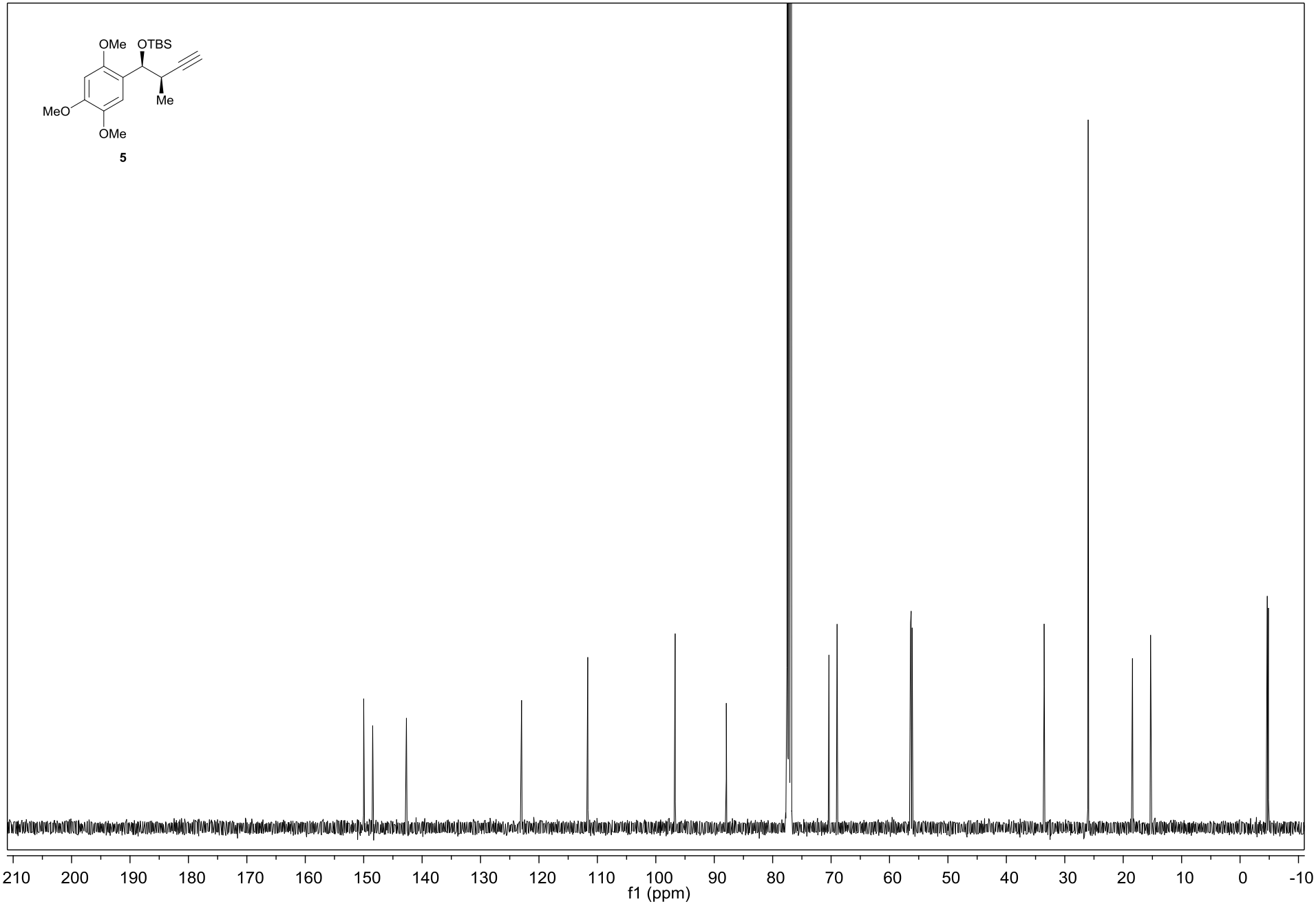
^{13}C NMR Spectrum of 4 (101 MHz, $CDCl_3$)



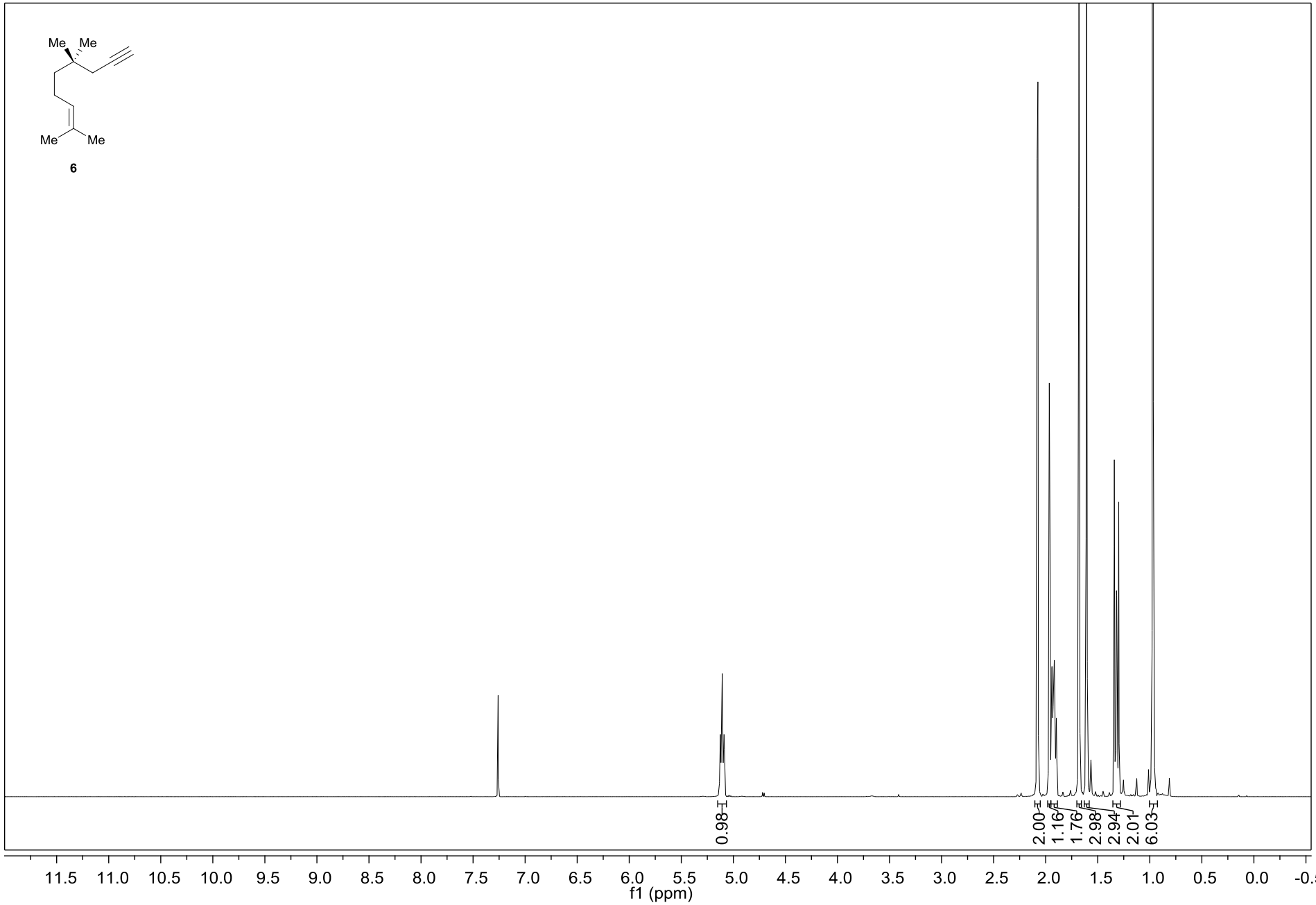
^{1}H NMR Spectrum of 5 (400 MHz, $CDCl_3$)



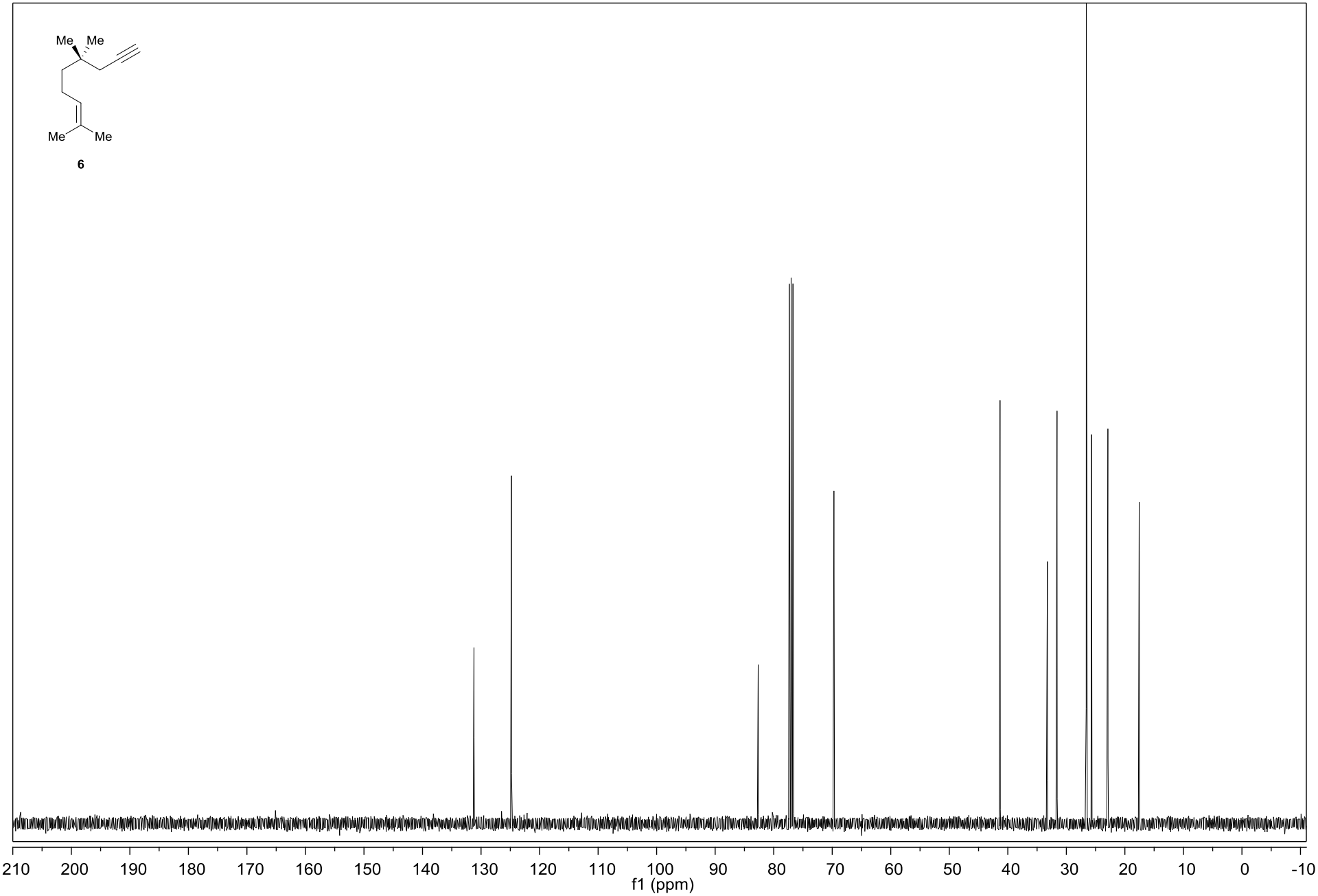
^{13}C NMR Spectrum of 5 (101 MHz, $CDCl_3$)



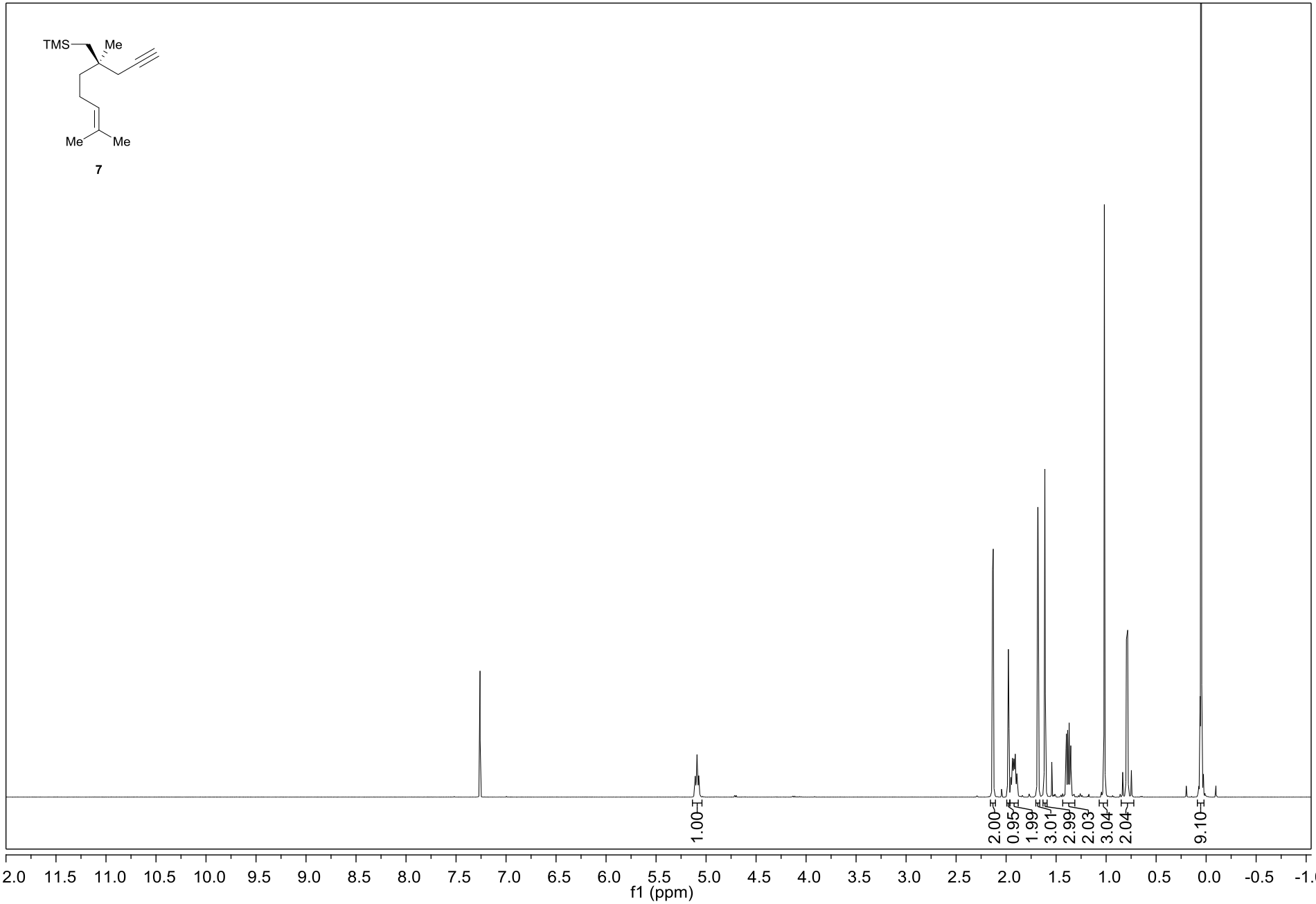
^{1}H NMR Spectrum of 6 (400 MHz, $CDCl_3$)



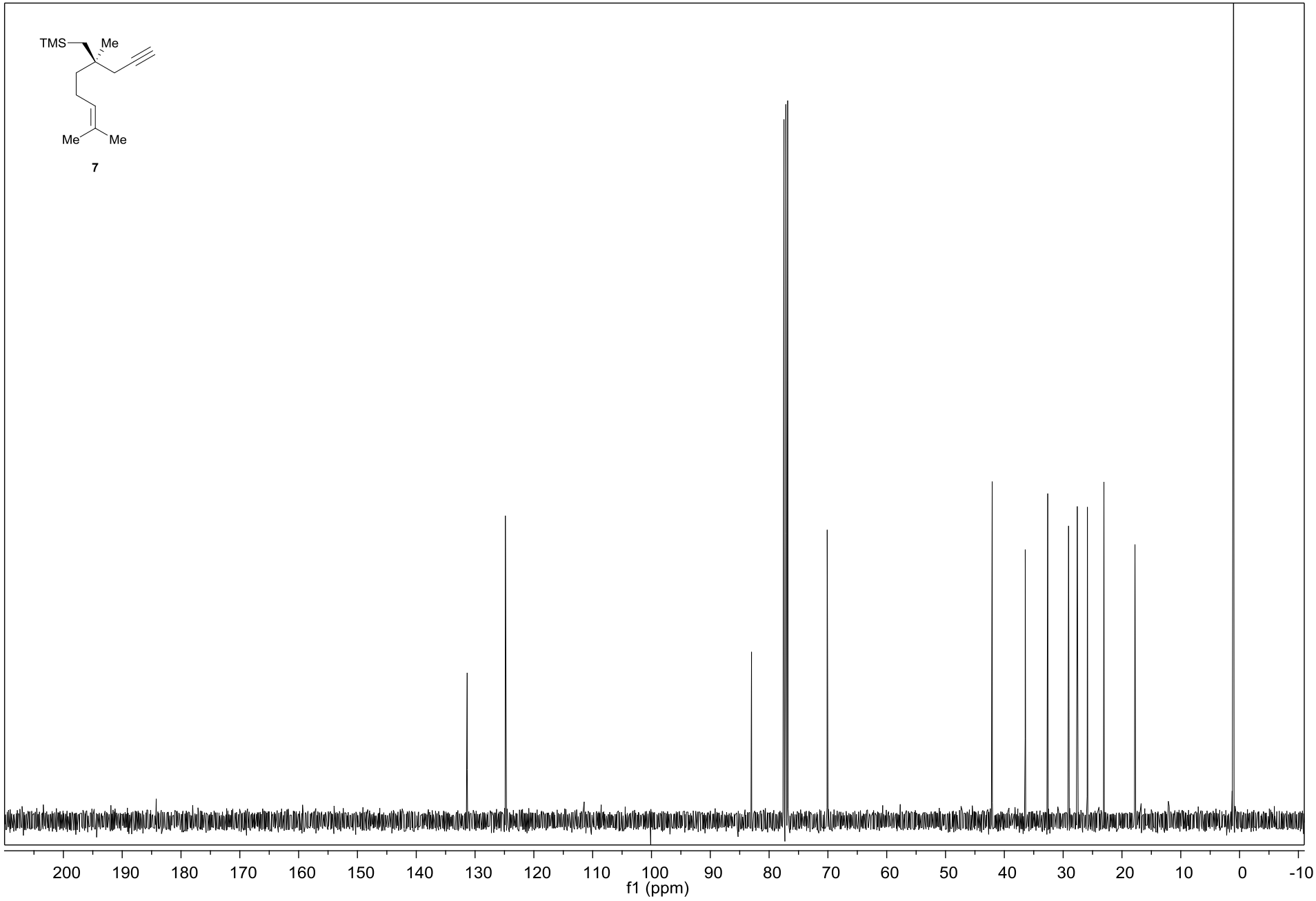
^{13}C NMR Spectrum of 6 (101 MHz, $CDCl_3$)



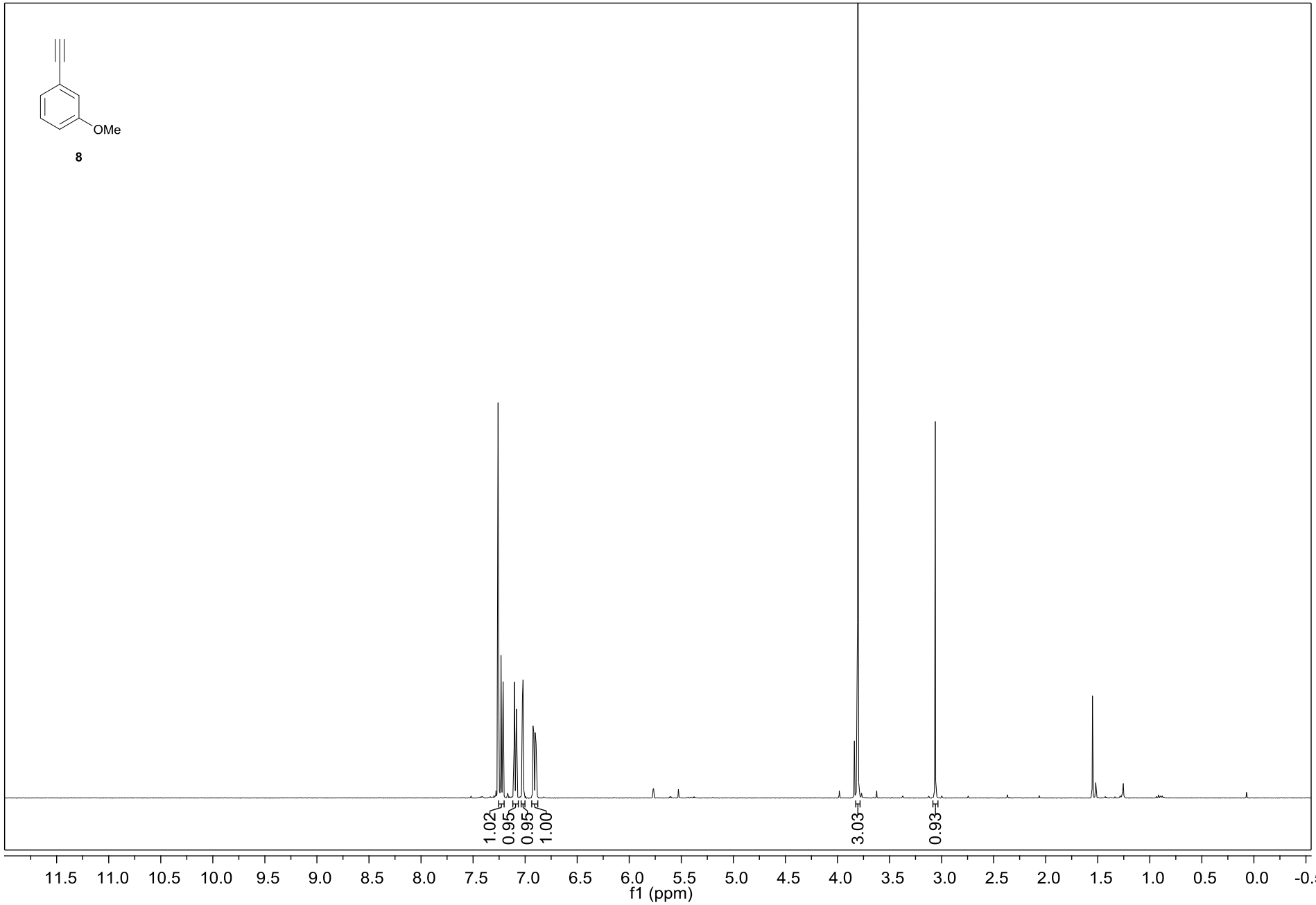
^{1}H NMR Spectrum of 7 (400 MHz, $CDCl_3$)



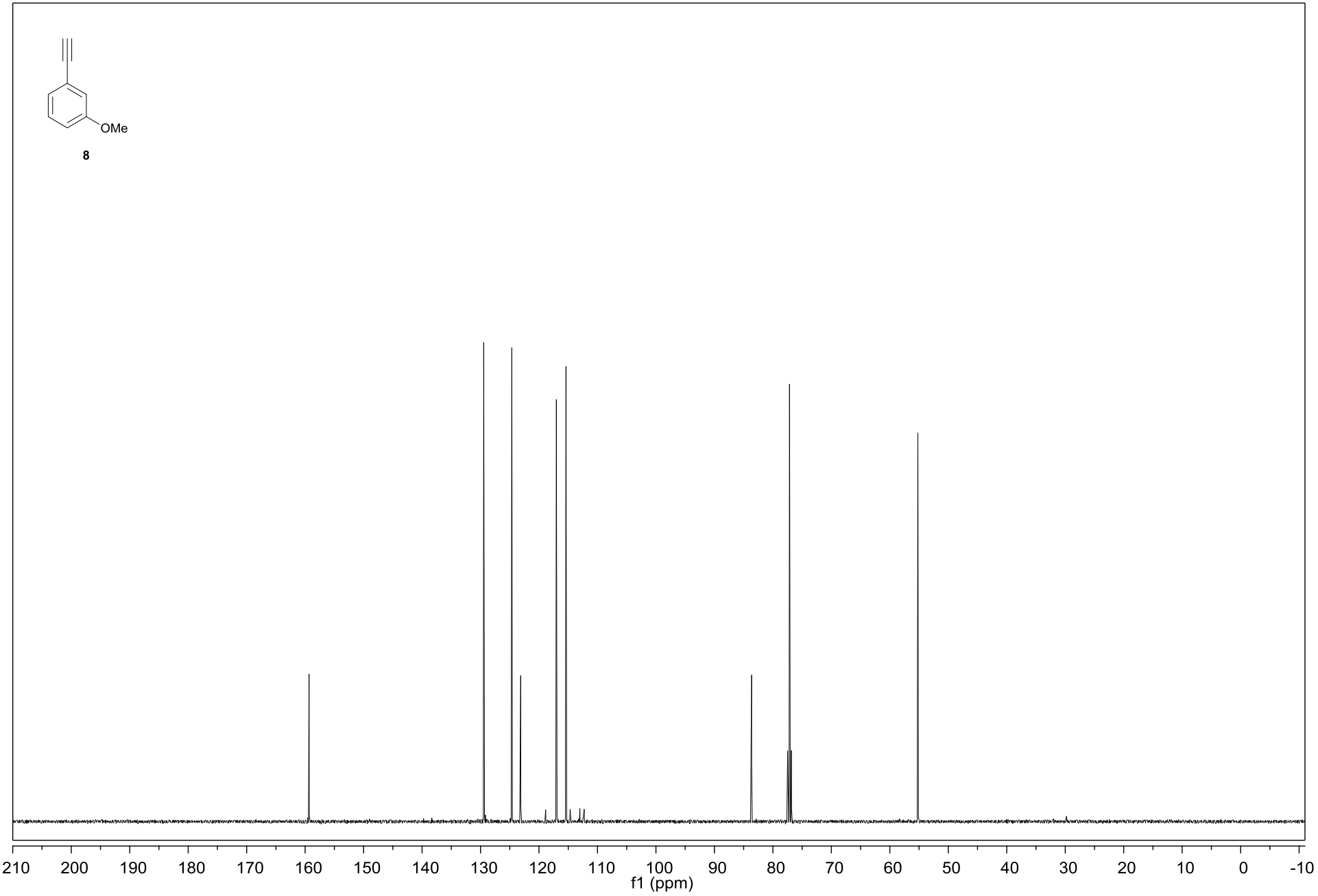
^{13}C NMR Spectrum of 7 (101 MHz, $CDCl_3$)



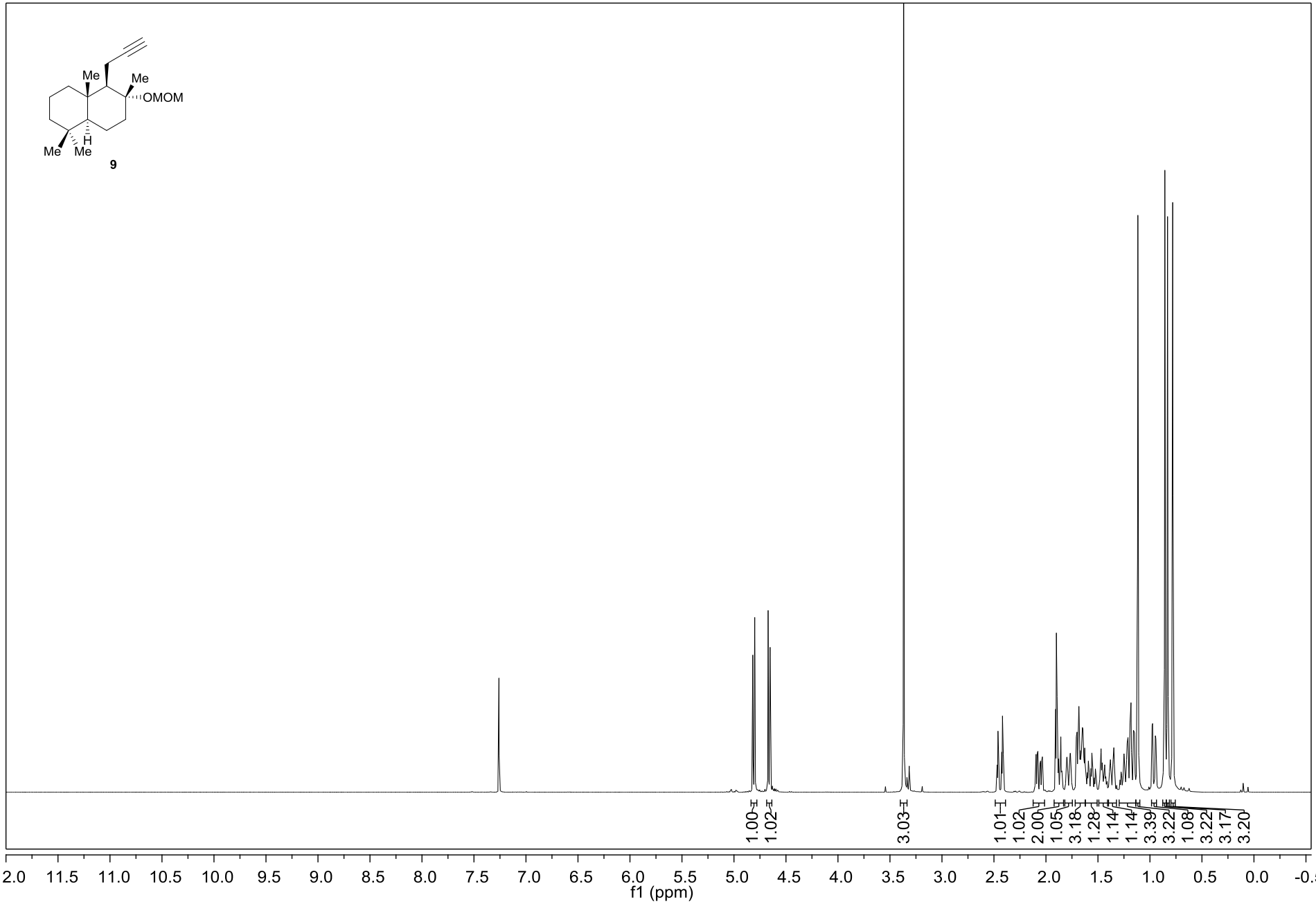
^{1}H NMR Spectrum of 8 (400 MHz, $CDCl_3$)



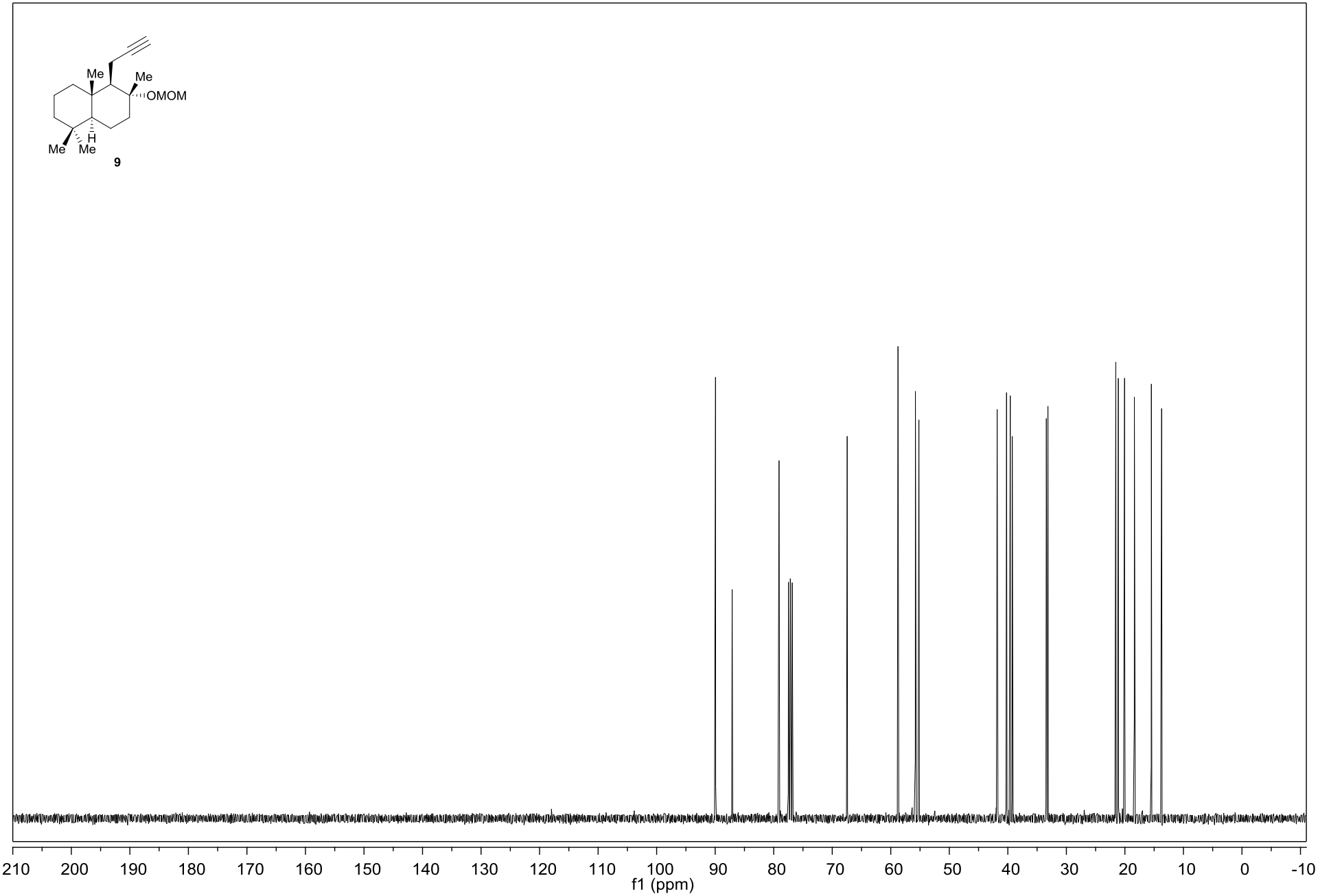
^{13}C NMR Spectrum of 8 (101 MHz, $CDCl_3$)



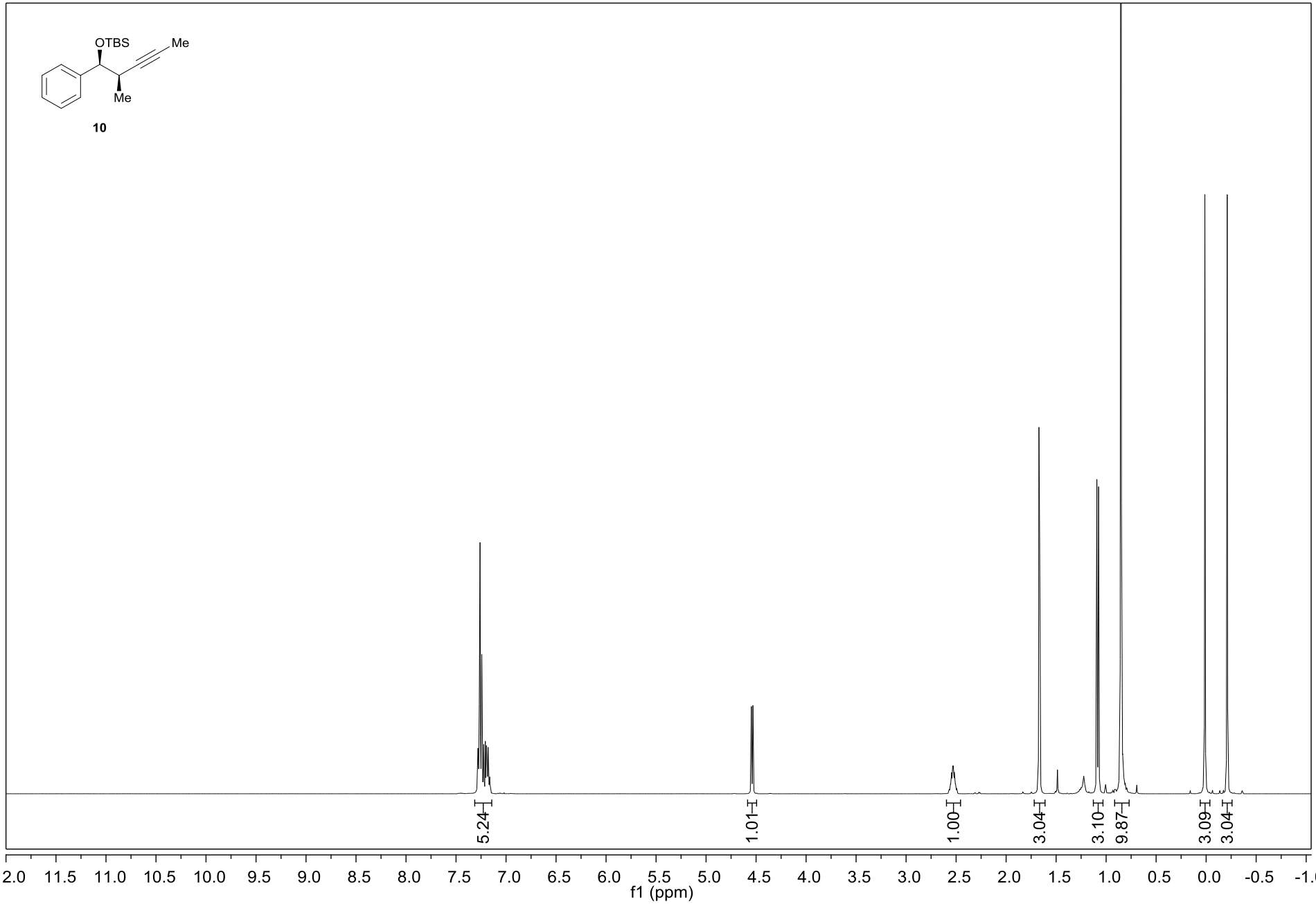
^{1}H NMR Spectrum of 9 (400 MHz, $CDCl_3$)



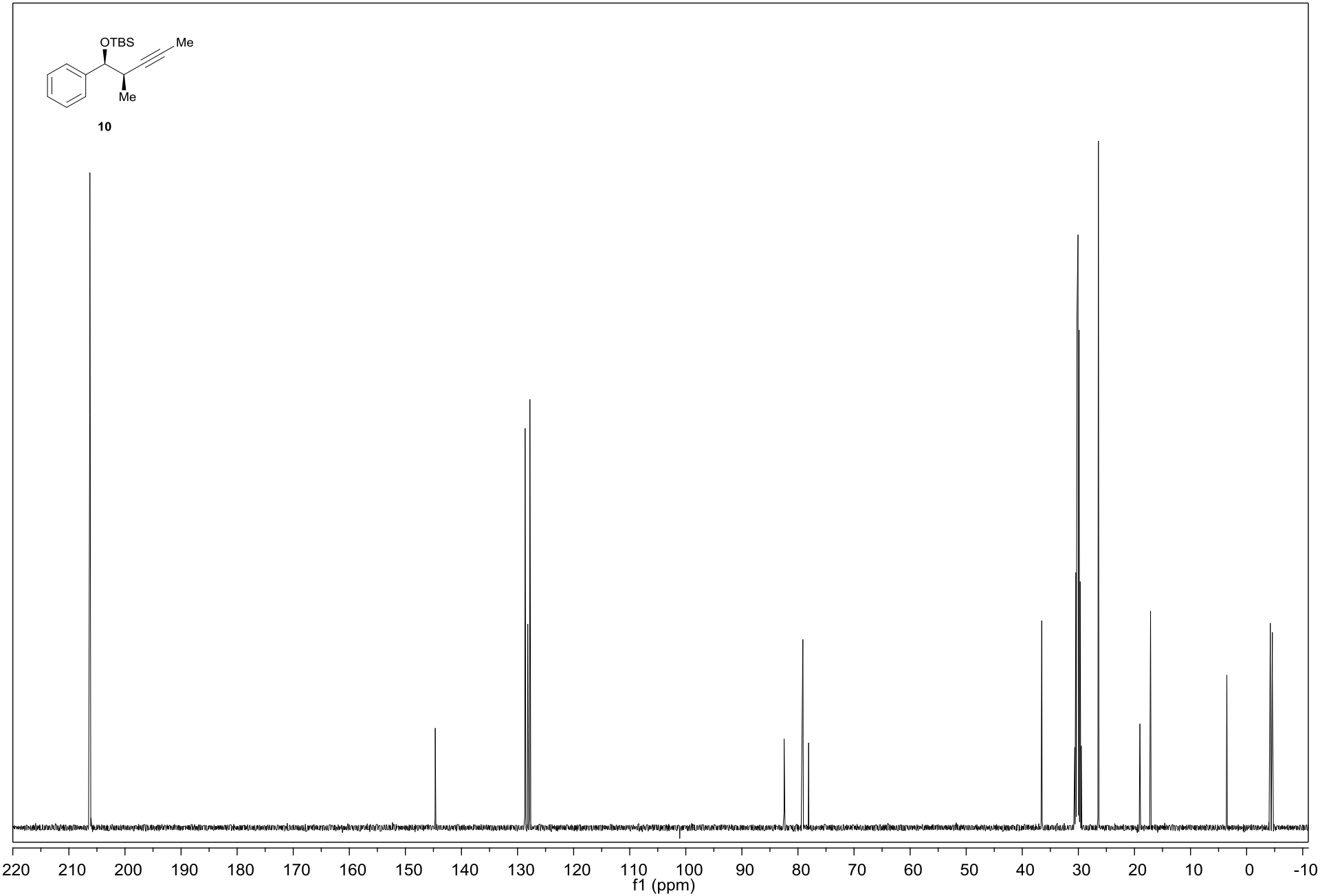
^{13}C NMR Spectrum of 9 (101 MHz, $CDCl_3$)



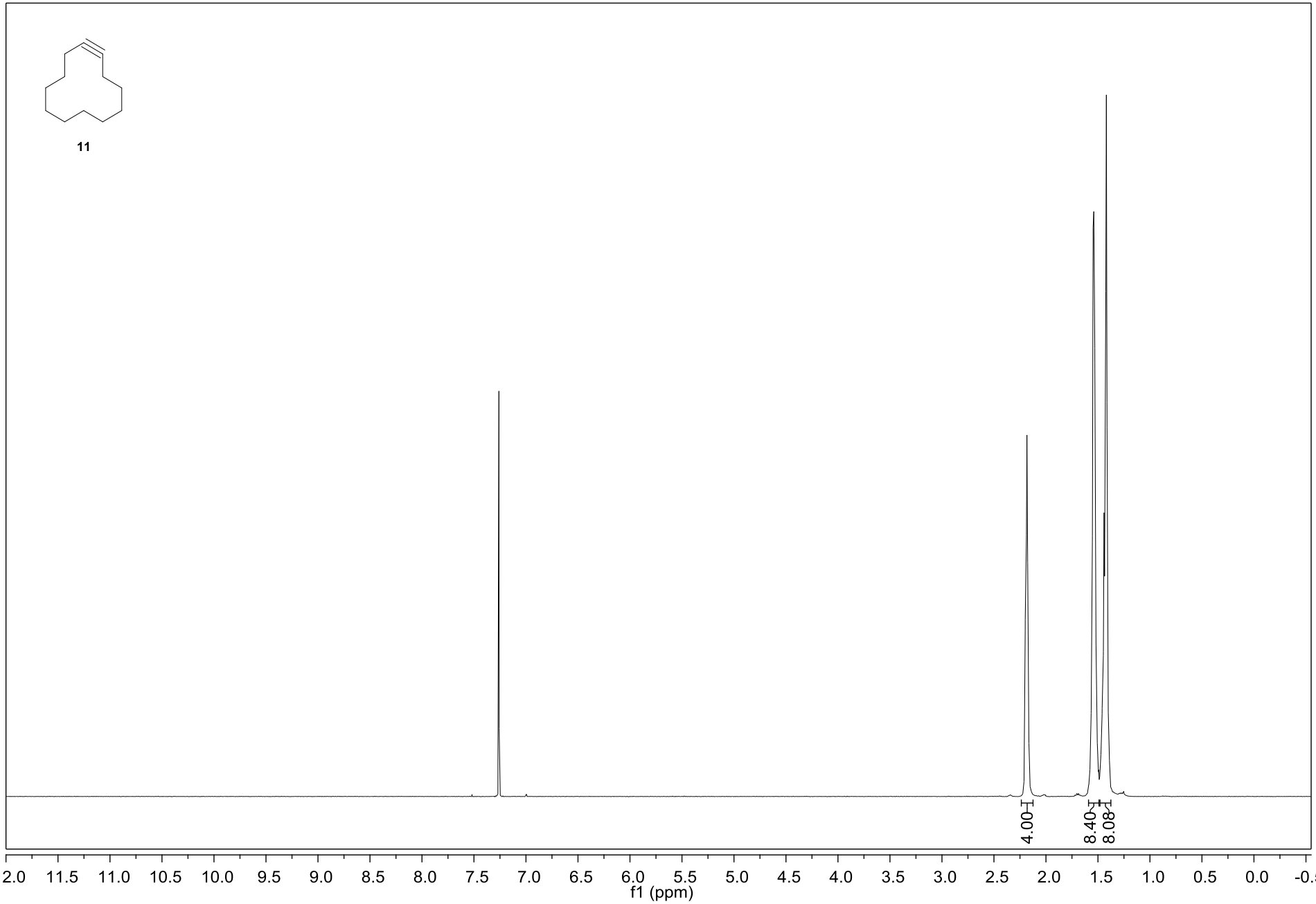
^{1}H NMR Spectrum of 10 (400 MHz, $CDCl_3$)



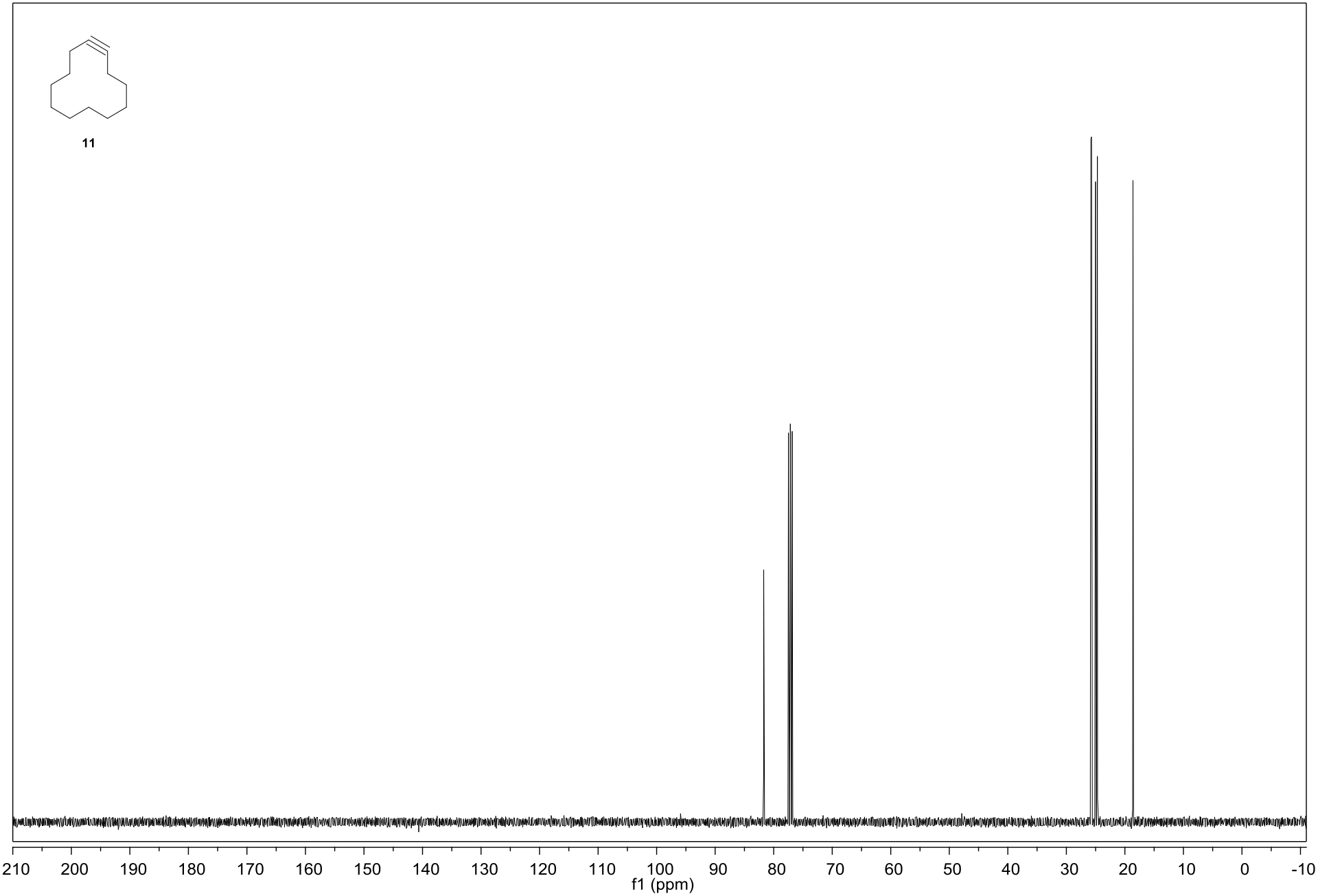
^{13}C NMR Spectrum of 10 (101 MHz, acetone-d_6)



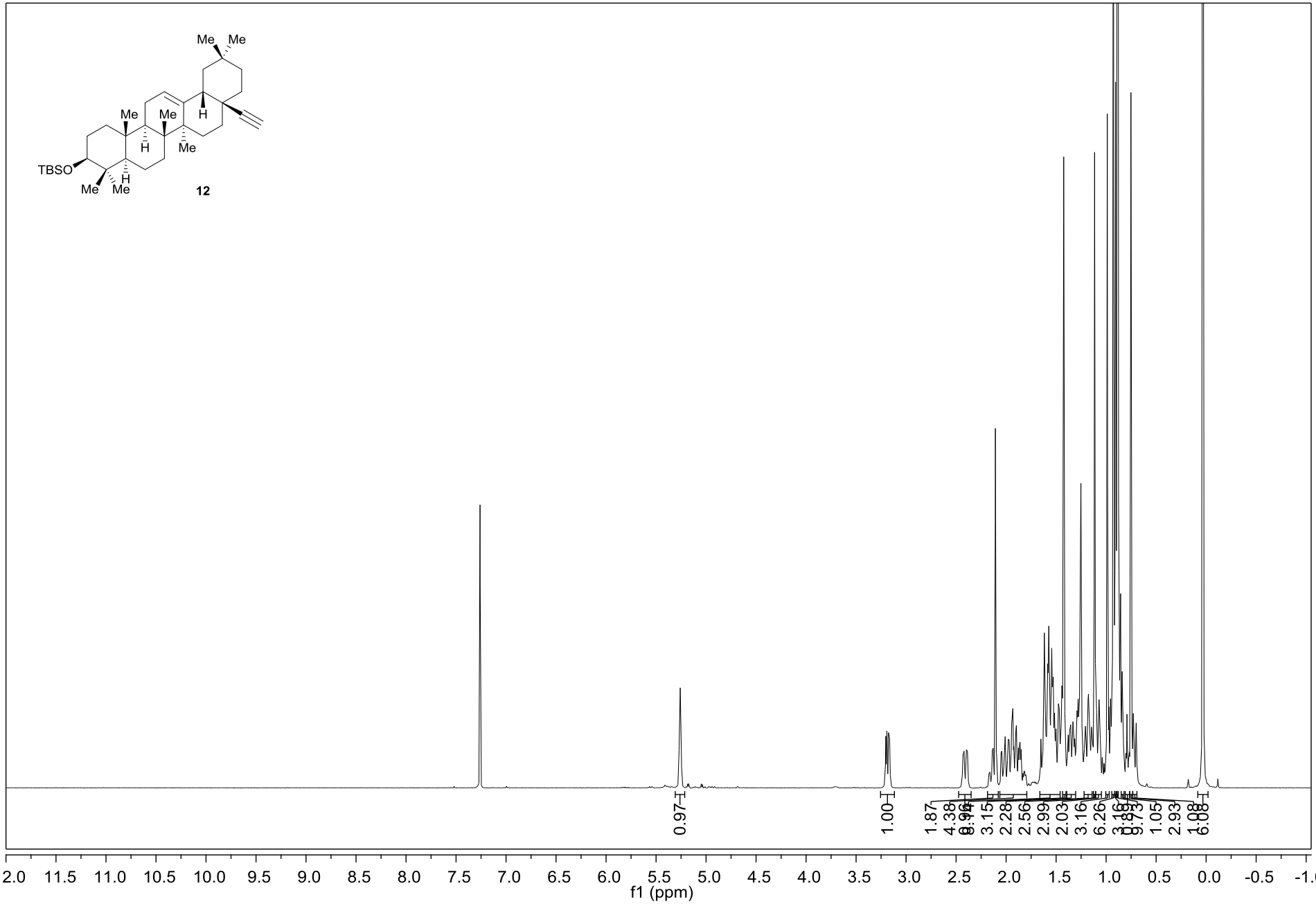
^{1}H NMR Spectrum of 11 (400 MHz, $CDCl_3$)



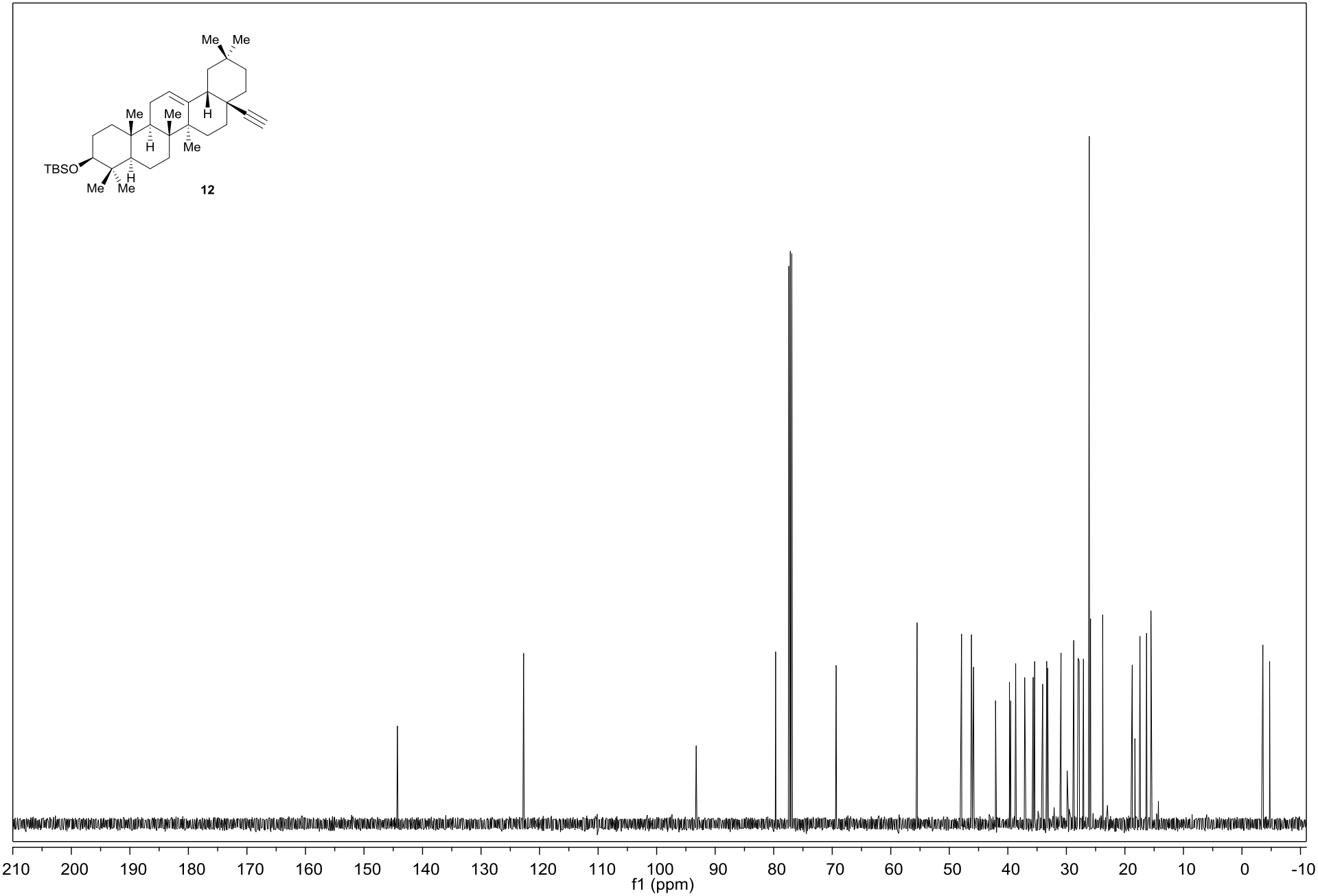
^{13}C NMR Spectrum of 11 (101 MHz, $CDCl_3$)



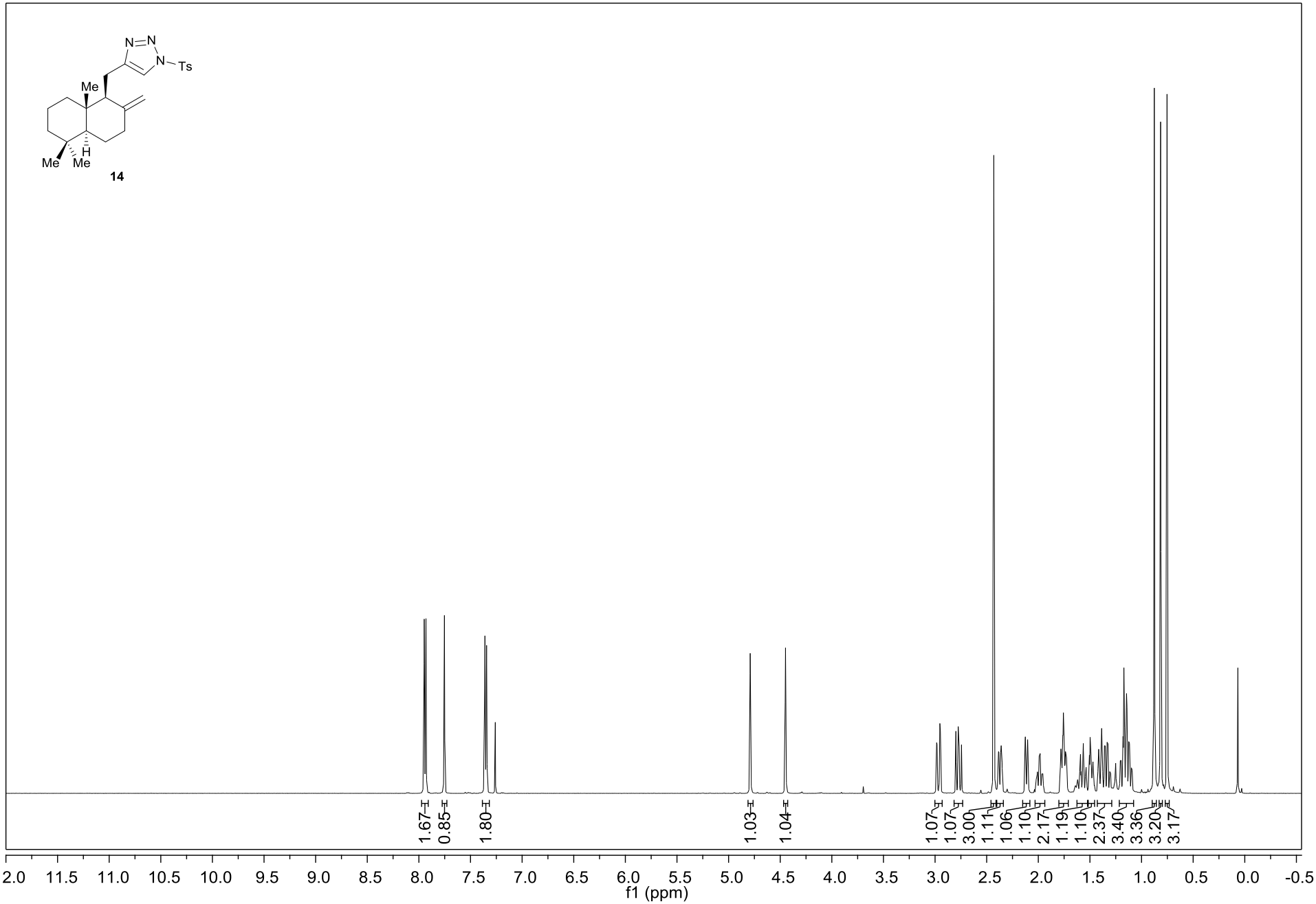
^{1}H NMR Spectrum of 12 (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 12 (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 14 (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 14 (126 MHz, $CDCl_3$)