General one-step access to unsymmetric propargylic acetals via alcohol functionalization with allenyl ethers

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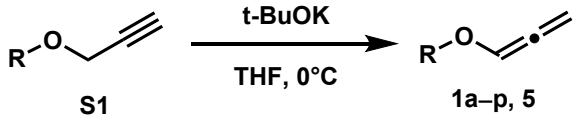
1. General Information

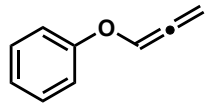
All reactions were performed under nitrogen atmosphere. Reagents were used as purchased from Macklin, Energy-Chemical, BidePharm, or TLC (supplier) unless otherwise noted. Chromatographic separations were performed using silica gel (Analytical Reagent, 200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 400 MHz NMR instrument using $CDCl_3$ or CD_3OD as the solvent, with the solvents provided by the School of Pharmaceutical Sciences, Guizhou University. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer using KBr pellets. TLC analysis was visualized using UV, p-anisaldehyde, and phosphomolybdic acid stains. High-resolution mass spectra were obtained using AB SCIEX X500R QTOF. All spectral data for new compounds are reported herein.

2. Synthesis of 1a−p and 5



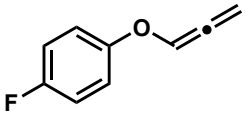
Allenyl ethers **1a–p** and compound **5** were synthesized following literature procedures[1,2].

To a solution of propargyl ethers **S1**(1.0 equiv) in THF (0.1 M) was added *t*-BuOK (1.0 M THF solution, 0.3 equiv) at 0 °C. The reaction mixture was stirred at room temperature (rt) for 1 hour. The mixture was then concentrated under reduced pressure. The residue was suspended in CH_2Cl_2 and filtered through Celite™. The filtrate was concentrated under reduced pressure, and the crude residue was purified by flash column chromatography on silica gel (eluent: 0.5% EtOAc/petroleum ether) to yield allenyl ethers **1a − p** and **5**.



1a

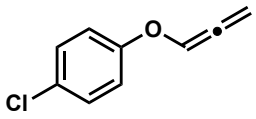
1a: 173 mg (87% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 8.0 Hz, 2H), 7.08 – 6.98 (m, 3H), 6.81 (td, *J* = 5.9, 0.8 Hz, 1H), 5.39 (d, *J* = 5.9Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 157.2, 129.6, 122.8, 117.9, 116.8, 89.6; IR (KBr) cm^{-1} 3032m, 2913m, 2854m, 1592s, 1485s, 1437m, 1336m, 1223s, 1163m, 1009m, 988m, 884s, 750s; HRMS: C_9H_8O for $[M+H]^+$, calculated 133.0648, found 133.0649.



1b

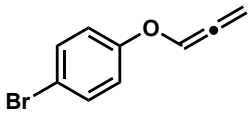
1b: 178 mg (89% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.97 (m, 4H), 6.80 (t, *J* = 5.9 Hz, 1H), 5.42 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 158.7 (d, *J* = 239.4 Hz, 1C), 153.2 (d,

J = 2.3 Hz, 1C), 118.8, 118.6, 118.5, 116.2, 115.9, 90.2. IR (KBr) cm-[1] 2918w, 1965w, 1499s, 1341m, 1200s, 997m, 827s, 769 m, 516 m; HRMS: $C_{10}H_9FO_2$ for $[M+H]^+$, calculated 181.0659, found 181.0663.



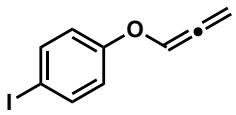
1c

1c: 172 mg (86% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 2H), 7.02 – 6.91 (m, 2H), 6.77 (t, *J* = 5.9 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 155.7, 129.5, 127.8, 118.3, 117.9, 90.0; IR (KBr) cm^{-1} 3030w, 2964m, 1676m, 1593s, 1488s, 1440s, 1340m, 1238s, 1168s, 1091s, 1008s, 889m, 823s, 682m; HRMS: C_9H_7ClO for $[M+H]^+$, calculated 167.0264, found 167.0279.



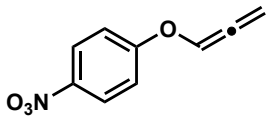
1d

1d: 123 mg (61% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 2H), 7.10 – 7.01 (m, 2H), 6.78 (t, *J* = 5.9 Hz, 1H), 5.45 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7 162.1, 142.8, 125.9, 116.4 116.4 90.4; IR (KBr) cm^{-1} 3032m, 2913m, 2854m, 1578m, 1482s, 1438m, 1331m, 1233s, 1167m, 1066m, 884m, 816s; HRMS: C_9H_7BrO for $[M+H]^+$, calculated 210.9753, found 210.9745.



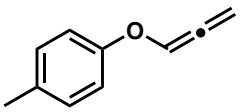
1e

1e: 182 mg (91% yield); white solid; mp 29-30°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 6.87 – 6.80 (m, 2H), 6.78 (t, *J* = 5.9 Hz, 1H), 5.45 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7 157.1, 138.5 119.2, 117.6, 90.1, 85.6; IR (KBr) cm^{-1} 3077w, 3029w, 1961m, 1637w, 1583m, 1571m, 1479s, 1437s, 1330s, 1244s, 1172s, 1015m, 844s, 809s; HRMS: C9H7IO for $[M-H]^+$, calculated 256.9469, found 256.9467.



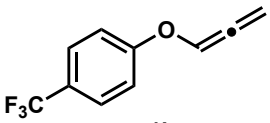
1f

1f: 176 mg (88% yield); yellow solid; mp 92-93°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.05 (m, 2H), 7.11 – 7.00 (m, 2H), 6.78 (t, *J* = 5.9 Hz, 1H), 5.45 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 162.1, 142.8, 125.9, 116.4, 116.4, 90.4; IR (KBr) cm^{-1} 3077w, 2929w, 1612s, 1622s, 1585s, 1490s, 1342s, 1262s, 1107s, 1015s, 947s, 843s, 751s; HRMS: $C_9H_7NO_3$ for $[M+H]^+$, calculated 178.0497, found 178.0500.



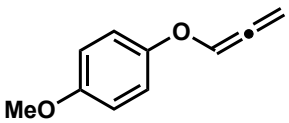
1g

1g: 158 mg (79% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.04 (m, 2H), 6.98 – 6.89 (m, 2H), 6.81 (t, *J* = 5.9 Hz, 1H), 5.41 (d, *J* = 5.9 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 155.1, 132.3, 130.0, 118.5, 116.9, 89.7, 20.7; IR (KBr) cm^{-1} 3029w, 2916m, 2857m, 1610m, 1583m, 1503s, 1434s, 1342s, 1226s, 1175m, 1015m, 994m, 878m, 872s; HRMS: $C_{10}H_{10}O$ for $[M+H]^+$, calculated 147.0804, found 147.0804.



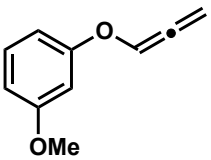
1h

1h: 190 mg (95% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 2H), 7.17 – 7.07 (m, 2H), 6.82 (t, *J* = 5.9 Hz, 1H), 5.47 (d, *J* = 5.9 Hz, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 159.8 (d, *J* = 1.5 Hz, 1C), 127.1 (dd, *J* = 3.7 Hz, 2C), 124.9 (q, *J* = 33.0 Hz, 1C), 124.4 (q, *J* =269.7 Hz, 1C), 117.0, 116.7, 90.1; IR (KBr) cm^{-1} 2924m, 2853m, 1740m, 1615s, 1515s, 1328s, 1244s, 1166s, 1123s, 1066s, 1012s, 837s; HRMS: $C_{10}H_7F_3O$ for $[M+H]^+$, calculated 201.0522, found 201.0529.



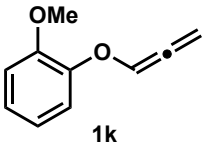
1i

1i: 161 mg (81% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.88 (m, 2H), 6.79 – 6.71 (m, 3H), 5.33 (d, *J* = 5.9 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 155.5, 151.1, 119.4, 118.5, 114.6, 90.0, 55.7; IR (KBr) cm^{-1} 2942w, 2901w, 2836m, 1506s, 1437m, 1339m, 1223s, 1035m, 1012m, 991m, 818s, 759s; HRMS: $C_{10}H_{10}O_2$ for $[M+H]^+$, calculated 163.0754, found 163.0753.



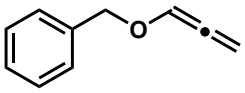
1j

1j: 152 mg (76% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.03 (ddd, *J* = 8.9, 7.4, 1.6 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.88 – 6.82 (m, 1H), 5.40 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 150.3, 146.3, 123.8, 120.7, 119.3, 117.9, 112.4, 90.1, 56.0. IR (KBr) cm^{-1} 2960w, 2836w, 1966w, 1591s, 1488s, 1437s, 1341m, 1128s, 1171s, 1039s, 836s, 765s, 685s; HRMS: $C_{10}H_{10}O_2$ for $[M+H]^+$, calculated 163.0754, found 163.0746.



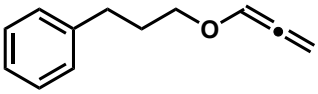
1k

1k: 164 mg (82% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.1 Hz, 1H), 6.82 (t, *J* = 5.9 Hz, 1H), 6.70 – 6.56 (m, 3H), 5.44 (d, *J* = 5.9 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 160.9, 158.5, 130.1, 117.7, 108.9, 108.5, 103.0, 89.6, 55.4. IR (KBr) cm^{-1} 2942w, 2837w, 1963w, 1735m, 1598m, 1498s, 1438m, 1254s, 1178s, 1111m, 994s, 889m, 743s; HRMS: $C_{10}H_{10}O_2$ for $[M+H]^+$, calculated 163.0754, found 163.0757.



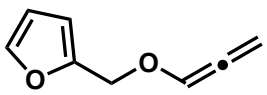
1l

1l: 162 mg (81% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 6.82 (t, *J* = 5.9 Hz, 1H), 5.46 (d, *J* = 5.9 Hz, 2H), 4.60 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 137.4, 128.5, 128.0, 127.9, 121.7, 91.2, 70.7; IR (KBr) cm^{-1} 3086m, 3036m, 2866m, 1953s, 1491m, 1456s, 1435s, 1375m, 1349s, 1188s, 1042s, 884s, 739s, 694s; HRMS: $C_{10}H_{10}O$ for $[M+H]^+$, calculated 147.0804, found 147.0805.



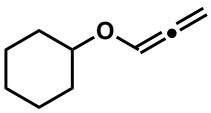
1m

1m: 156 mg (78% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.7, 6.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.74 (t, *J* = 5.9 Hz, 1H), 5.40 (d, *J* = 5.9 Hz, 2H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.01 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 141.8, 128.5, 128.4, 125.9, 1217, 90.5, 67.9, 32.3, 30.9. IR (KBr) cm^{-1} 3027w, 2945w, 1952m, 1445m, 1351m, 1197s, 1043s, 889m, 746m, 698s; HRMS: $C_{12}H_{14}O$ for $[M+APCl]^+$, calculated 175.1117, found 175.1123.



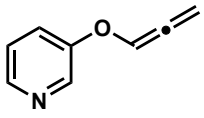
1n

1n: 146 mg (73% yield); yellow oil; ^{1}H NMR (400 MHz, MeOD) δ 7.47 (t, *J* = 1.4 Hz, 1H), 6.77 (t, *J* = 6.0 Hz, 1H), 6.38 (d, *J* = 1.4 Hz, 2H), 5.48 (d, *J* = 6.0 Hz, 2H), 4.53 (s, 2H). ^{13}C NMR (101 MHz, MeOD) δ 202.5, 152.3, 144.2, 121.8, 111.4, 111.0, 91.4, 63.4. IR (KBr) cm^{-1} 2923w, 1955w, 1444w, 1182s, 1032s, 890s, 790m, 740s, 586m; HRMS: $C_8H_8O_2$ for $[M+Na]^+$, calculated 159.0417, found 159.0412.



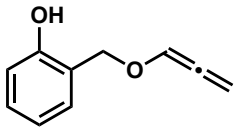
1o

1o: 136 mg (68% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (t, *J* = 6.0 Hz, 1H), 5.36 (d, *J* = 5.9 Hz, 2H), 3.65 (tt, *J* = 8.8, 3.9 Hz, 1H), 1.89 (dd, *J* = 9.8, 4.0 Hz, 2H), 1.73 (dt, *J* = 10.3, 4.1 Hz, 2H), 1.52 (dd, *J* = 9.2, 4.5 Hz, 1H), 1.45 – 1.35 (m, 2H), 1.33 – 1.22 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 120.0, 89.6, 76.7, 31.9, 25.8, 23.9; IR (KBr) cm^{-1} 2933m, 1953w, 1445m, 1344w, 1199s, 1048s, 886m; HRMS: $C_9H_{14}O$ for $[M+APCl]^+$, calculated 139.1117, found 139.1123.



1p

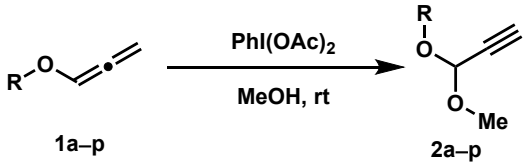
1p: 130 mg (65% yield); colorless oil; ^{1}H NMR (400 MHz, MeOD) δ 8.34 (d, *J* = 2.7 Hz, 1H), 8.23 (dd, *J* = 4.8, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.5, 2.9, 1.3 Hz, 1H), 7.39 (dd, *J* = 8.5, 4.8 Hz, 1H), 7.05 (t, *J* = 6.0 Hz, 1H), 5.48 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, MeOD) δ 203.6, 155.2, 144.3, 140.2, 126.0, 125.8, 118.6, 90.7. IR (KBr) cm^{-1} 3038w, 1713w, 1575m, 1424m, 1225s, 989m, 980m, 800m, 704m, 614w; HRMS: C_8H_7ON for $[M+H]^+$, calculated 134.0600, found 134.0593.



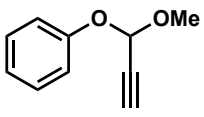
5

5: 181 mg (90% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.06 (td, *J* = 8.9, 8.5, 1.6 Hz, 2H), 6.85 (t, *J* = 5.9 Hz, 1H), 5.44 (d, *J* = 5.9 Hz, 2H), 4.72 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 155.0, 130.7, 129.1, 128.9, 123.2, 118.1, 115.7, 90.1, 61.3. IR (KBr) cm^{-1} 3322w, 1588w, 1487m, 1454m, 1340m, 1223s, 995s, 888m, 753s; HRMS: $C_9H_{10}O_2$ for $[M+APCl]^+$, calculated 163,0754, found 163.0759.

3. Synthesis of 2a－p

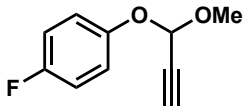


To a solution of allenyl ethers **1** (1.0 equiv) in MeOH (0.3 M) was added iodobenzene diacetate (1.2 equiv) at rt. The reaction was stirred at rt for 5 minutes and monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: 1.0% EtOAc/petroleum ether) to obtain the unsymmetric propargylic acetals (**2a － p**).



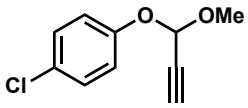
2a

2a: 109 mg (89% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 5.86 (d, *J* = 1.8 Hz, 1H), 3.51 (s, 3H), 2.66 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 129.6, 122.9, 117.3, 91.3, 77.8, 52.1; IR (KBr) cm^{-1} 3290w, 2130w, 1597m, 1493s, 1217s, 1098s, 1011s, 754s, 686s, 507m; HRMS: $C_{10}H_{10}O_2$ for $[M+APCl]^+$, calculated 163.0754, found 163.0757.



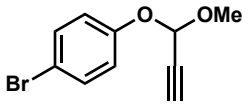
2b

2b: 84 mg (70% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 9.2, 4.5 Hz, 2H), 6.98 (dd, *J* = 9.2, 8.1 Hz, 2H), 5.76 (d, *J* = 1.8 Hz, 1H), 3.52 (s, 3H), 2.67 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (d, *J* = 239.3 Hz, 1C), 152.0 (d, *J* = 2.5 Hz, 1C), 119.1, 119.0, 116.1, 115.9, 92.0, 77.6, 75.3, 52.3; IR (KBr) cm^{-1} 3298w, 2941w, 1501s, 1201s, 1096s, 1006s, 820s, 773m, 667m, 544m, 512m; HRMS: $C_{10}H_9FO_2$ for $[M+H]^+$, calculated 181.0659, found 181.0664.



2c

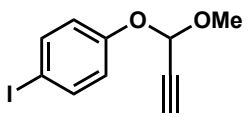
2c: 100 mg (85% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.05 – 7.00 (m, 2H), 5.80 (d, *J* = 1.9 Hz, 1H), 3.50 (s, 3H), 2.68 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 129.5, 127.9, 118.7, 91.4, 77.3, 75.4, 52.2; IR (KBr) cm^{-1} 3294w, 2940w, 2131w, 1488s, 1224s, 1091s, 984s, 824s, 663m, 507m; HRMS: $C_{10}H_9ClO_2$ for $[M+H]^+$, calculated 197.0364, found 197.0373.



2d

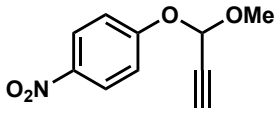
2d: 107 mg (94% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.81 (d, *J* = 1.9 Hz, 1H), 3.50 (s, 3H), 2.69 (d, *J* = 1.9 Hz, 1H). C NMR (101 MHz, $CDCl_3$) δ 154.9, 132.4, 119.1, 115.3, 91.3, 77.3, 75.5, 52.2; IR (KBr) cm^{-1} 3292w, 2939 w, 2131w, 1580w, 1484s, 1223s, 1095s, 980s, 821s, 663m, 504m; HRMS: $C_{10}H_{10}BrO_2$ for $[M+APCl]^+$, calculated 240.9859, found 240.9864.

For gram scale synthesis of **2d**: The reaction was performed with **1d** (4.0 g, 11.8 mmol, 1.0 equiv), MeOH (63.2 mL, 0.3 M) and iodobenzene diacetate (4.6 g, 14.2 mmol, 1.2 equiv) following the above procedure, affording 4.28 g of the product in 94% yield.



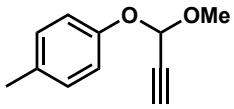
2e

2e: 95 mg (85% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.82 (d, *J* = 1.9 Hz, 1H), 3.50 (s, 3H), 2.69 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 138.4, 119.6, 91.2, 85.6, 77.3, 75.47, 52.3; IR (KBr) cm^{-1} 3290w, 2938w, 2130, 1574w, 1481s, 1222s, 1095s, 978.30s, 819s, 662m, 504m; HRMS: $C_{10}H_9IO_2$ for $[M+H]^+$, calculated 288.9720, found 288.9721.

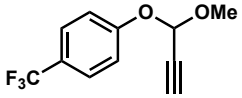


2f

2f: 105 mg (90% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.3 Hz, 2H), 7.18 (d, *J* = 9.3 Hz, 2H), 5.95 (d, *J* = 1.8 Hz, 1H), 3.52 (s, 3H), 2.74 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 142.8, 125.68, 116.9, 91.1, 76.4, 76.1, 52.7; IR (KBr) cm^{-1} 3260w, 2939w, 2129w, 1591s, 1493s, 1333s, 1241s, 1099s, 971s, 847s, 751s, 687m, 500m; HRMS: $C_{10}H_9NO_4$ for $[M+H]^+$, calculated 208.0604, found 208.0607.

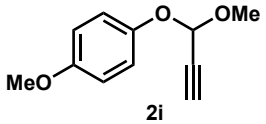


2g: 72 mg (60% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.80 (d, *J* = 1.9 Hz, 1H), 3.50 (s, 3H), 2.63 (d, *J* = 1.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 132.3, 130.0, 117.3, 91.5, 77.9, 74.9, 52.0, 20.7; IR (KBr) cm^{-1} 3284w, 2939 w, 2130w, 1508s, 1337m, 1219s, 1098s, 1007s, 815 m, 663m, 509m; HRMS: $C_{11}H_{13}O_2$ for $[M+APCl]^+$, calculated 177.0910, found 177.0917.



2h

2h: 69 mg (60% yield); colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 5.91 (d, *J* = 1.8 Hz, 1H), 3.52 (s, 3H), 2.70 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 127.0 (dd, *J* = 3.8 Hz, 2C), 124.9 (q, J = 32.6 Hz, 1C), 124.4 (q, *J* = 269.7 Hz, 1C), 117.1, 91.2, 77.1, 75.7, 52.4; IR (KBr) cm^{-1} 3306 w, 2944w, 2133w, 1616m, 1515.83m, 1323.73s, 1235.42m, 1102.02s, 977.27s, 837.04s, 666.53m; HRMS: $C_{11}H_8O_2F_3$ for $[M+APCl]^+$, calculated 229.0482, found 229.0481.

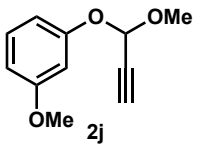


2i

2i: 74 mg (62% yield); yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 5.74 (d, *J* = 1.8 Hz, 1H), 3.77 (s, 4H), 3.53 (s, 3H), 2.66 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 149.8, 118.9, 114.5, 92.1, 77.8, 74.9, 55.6, 52.1; IR (KBr) cm^{-1} 3283 w, 2940 w, 2129w, 1590s, 1491s, 1263m, 1195m, 1146s, 1095s, 1007s, 830m, 766m, 685s; HRMS: $C_{11}H_{12}O_3$ for $[M+H]^+$,

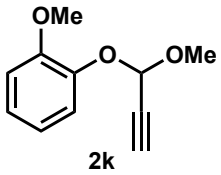
calculated 193.0859, found 193.0866.

For gram scale synthesis of **2i**: The reaction was performed with **1i** (3.2 g, 19.3 mmol, 1.0 equiv), iodobenzene diacetate (7.6 g, 23.7 mmol, 1.2 equiv) and MeOH (65.8 mL, 0.3 M) following the above procedure, affording 2.41 g of the product in 64% yield.



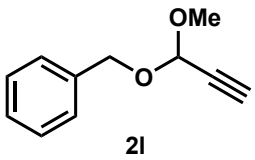
2j

2j: 108 mg (91% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.2 Hz, 1H), 6.73 – 6.63 (m, 2H), 6.59 (d, *J* = 8.9 Hz, 1H), 5.84 (d, *J* = 1.9 Hz, 1H), 3.77 (s, 3H), 3.50 (s, 3H), 2.66 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 157.2, 130.0, 109.2, 108.5, 103.5, 91.2, 77.7, 75.0, 55.4, 52.0; IR (KBr) cm^{-1} 3283w, 2941w, 2129w, 1590s, 1491s, 1263m, 1194m, 1145s, 1095s, 1006s, 767m, 684s; HRMS: $C_{11}H_{12}O_3$ for $[M+H]^+$, calculated 193.0859, found 193.0853.



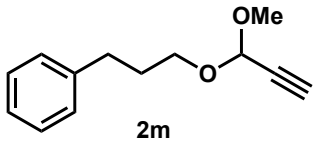
2k

2k: 98 mg (83% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.05 (td, *J* = 7.9, 1.6 Hz, 1H), 6.90 (ddd, *J* = 15.3, 8.0, 1.6 Hz, 2H), 5.86 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 4H), 3.57 (s, 3H), 2.66 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 144.8, 124.1, 120.8, 119.8, 119.7, 112.4, 112.4, 92.4, 77.9, 75.0, 55.9, 52.5; IR (KBr) cm^{-1} 3280w, 2941w, 2128w, 1593m, 1499s, 1251s, 1210m, 1094s, 973s, 745s; HRMS: $C_{11}H_{12}O_3$ for $[M+Na]^+$, calculated 215.0679, found 215.0670.



2l

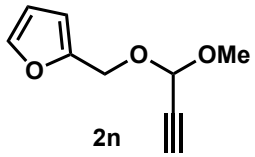
2l: 104 mg (86% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 5.29 (d, *J* = 1.9 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 3.41 (s, 3H), 2.58 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.27, 128.50, 128.11, 127.90, 91.49, 78.46, 74.25, 67.34, 52.60; IR (KBr) cm^{-1} 3284.95w, 2938.18w, 2126.60w, 1454.96w, 1338.79w, 1103.29s, b1039.17s, 736.96m, 696.69s; HRMS: $C_{11}H_{12}O_2$ for $[M+Na]^+$, calculated 199.0730, found 199.0723.



2m

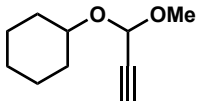
2m: 95 mg (81% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.17 (dt, *J* = 8.1, 1.9 Hz, 3H), 5.17 (d, *J* = 1.9 Hz, 1H), 3.68 (dt, *J* = 9.5, 6.4 Hz, 1H), 3.49 (dt, *J* = 9.3, 6.4 Hz,

1H), 3.36 (s, 3H), 2.69 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.53 (d, *J* = 1.9 Hz, 1H), 1.97 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 128.4, 128.3, 125.8, 92.0, 78.5, 73.90, 64.9, 52.2, 32.3, 31.1; IR (KBr) cm^{-1} 3283w, 2939w, 2126w, 1454w, 1355w, 1043s, 966m, 746m, 699s; HRMS: $C_{13}H_{16}O_2$ for $[M+Na]^+$, calculated 227.1043, found 227.1033.



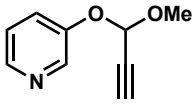
2n

2n: 101 mg (83% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.35 (dq, *J* = 4.9, 3.1 Hz, 2H), 5.29 (d, *J* = 1.8 Hz, 1H), 4.65 (d, *J* = 12.6 Hz, 1H), 4.56 (d, *J* = 12.6 Hz, 1H), 3.42 (s, 3H), 2.59 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 143.2, 110.5, 110.0, 91.2, 78.1, 74.5, 59.2, 52.6; IR (KBr) cm^{-1} 3289w, 2939w, 2127w, 1355 w, 1151m, 1102s, 1032s, 817m, 740s, 664m, 600m; HRMS: $C_9H_{10}O_3$ for $[M+Na]^+$, calculated 189.0522, found 189.0526.



2o

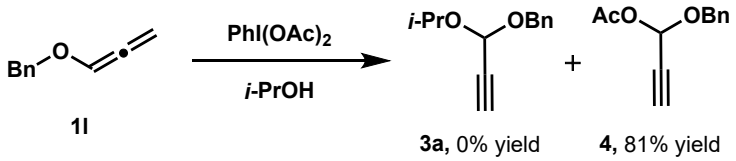
2o: 94 mg (77% yield); colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (d, *J* = 1.8 Hz, 1H), 3.68 (tt, *J* = 9.6, 3.9 Hz, 1H), 3.40 (s, 3H), 2.56 (d, *J* = 1.8 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.83 – 1.68 (m, 2H), 1.54 (ddd, *J* = 7.5, 3.9, 1.5 Hz, 1H), 1.47 – 1.13 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 90.4, 79.2, 75.1, 73.5, 51.6, 33.3, 32.3, 25.6, 24.4, 24.2; IR (KBr) cm^{-1} 3271w, 2933m, 2125w, 1450 w, 1339w, 1102s, 1036s, 987m, 891m, 352m; HRMS: $C_{10}H_{16}O_2$ for $[M+Na]^+$, calculated 191.1042, found 191.1037.



2p

2P: 121 mg (69% yield); colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.9 Hz, 1H), 8.31 (d, *J* = 4.4 Hz, 1H), 7.43 (ddd, *J* = 8.4, 2.9, 1.3 Hz, 1H), 7.23 (dd, *J* = 8.4, 4.7 Hz, 1H), 5.85 (d, *J* = 1.9 Hz, 1H), 3.52 (s, 3H), 2.70 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 144.1, 140.5, 124.5, 123.9, 91.7, 75.9, 52.7. IR (KBr) cm^{-1} 3290w, 2129w, 1759w, 1575m, 1426m, 1223s, 1097s, 972s, 802m, 704s; HRMS: $C_9H_9O_2N$ for $[M+H]^+$, calculated 164.0706, found 164.0704.

4. Synthesis of 4



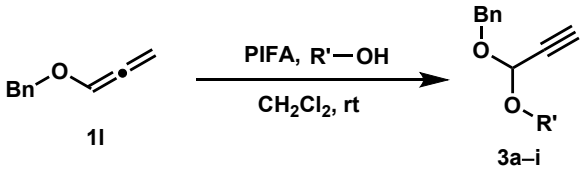
1l **3a,** 0% yield **4,** 81% yield

To a solution of allenyl ether **1l** (100 mg, 0.68 mmol, 1.0 equiv) in *i*-PrOH (2.28 mL, 0.3 M) was added iodobenzene diacetate (264 mg, 0.82 mmol, 1.2 equiv) at rt. The reaction was stirred at rt for 5 minutes and

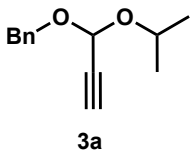
monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: 1.0% EtOAc/petroleum ether) to obtain the acetal **4.**

4: 113 mg (81% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 4.4 Hz, 5H), 6.52 (d, J = 1.9 Hz, 1H), 4.84 (d, J = 11.7 Hz, 1H), 4.71 (d, J = 11.7 Hz, 1H), 2.65 (d, J = 1.9 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 136.8, 128.5, 128.1, 127.9, 85.5, 77.5, 75.0, 69.4, 20.8; IR (KBr) cm^{-1} 3283w, 2128w, 1741s, 1372m, 1218s, 1109s, 999s, 910s, 696s, 540m; HRMS: $C_{12}H_{12}O_3$ for $[M+Na]^+$, calculated 227.0679, found 227.0669.

5. Synthesis of 3a−i

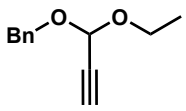


To a solution of allenyl ether **1l** (100 mg, 0.68 mmol, 1.0 equiv) and corresponding alcohols (1.03 mmol, 1.5 equiv) in CH_2Cl_2 (2.28 mL, 0.3 M) was added [bis(trifluoroacetyl)iodo]benzene (353 mg, 0.82 mmol, 1.2 equiv) at rt. The reaction was stirred at rt for 5 minutes and monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: 1.0% EtOAc/petroleum ether) to obtain the unsymmetric propargylic acetals **3a − i**.



3a

3a: 117 mg (84% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 5.44 (d, J = 1.8 Hz, 1H), 4.79 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.09 (hept, J = 6.2 Hz, 1H), 2.59 (d, J = 1.8 Hz, 1H), 1.23 (dd, J = 9.2, 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 128.5, 128.1, 127.8, 89.6, 79.4, 73.8, 69.3, 66.3, 23.3, 22.2; IR (KBr) cm^{-1} 3286w, 2974w, 2126w, 1455w, 1321w, 1094s, 1023s, 736m, 665s; HRMS: $C_{13}H_{16}O_2$ for $[M+Na]^+$, calculated 227.1043, found 227.1044.

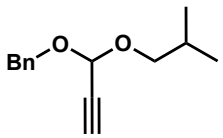


3b

3b: 94 mg (72% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 5.35 (d, J = 1.8 Hz, 1H), 4.75 (d, J = 11.7 Hz, 1H), 4.61 (d, J = 11.7 Hz, 1H), 3.79 (dq, J = 9.5, 7.1 Hz, 1H), 3.62 (dq, J = 9.5, 7.1 Hz, 1H), 2.57 (d, J = 1.8 Hz, 1H), 1.24 (t, J = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 128.6, 128.2, 127.9, 90.8, 79.0, 74.0, 67.1, 61.6, 15.1; IR (KBr) cm^{-1} 3285w, 2978w, 2126, 1455m, 1328m, 1101s,

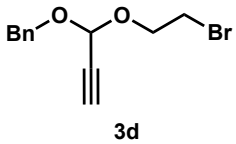
1023s, 736m, 696s; HRMS: $C_{12}H_{14}O_2$ for $[M+Na]^+$, calculated 213.0886, found 213.0880.

For gram scale synthesis of **3b**: The reaction was performed with **1l** (3.0 g, 20.5 mmol, 1.0 equiv), EtOH (1.8 mL, 30.8 mmol, 1.5 equiv), CH_2Cl_2 (60.8 mL, 0.3 M) and [bis(trifluoroacetyl)iodo]benzene (10.6 g, 24.6 mmol, 1.2 equiv) following the above procedure, affording 2.94 g of the product in 75% yield.



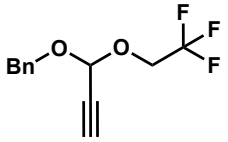
3c

3c: 104 mg (70% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 5.34 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 3.50 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.33 (dd, *J* = 9.2, 6.5 Hz, 1H), 2.56 (d, *J* = 1.8 Hz, 1H), 1.89 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.94 (dd, *J* = 6.7, 1.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 128.6, 128.2, 127.9, 91.1, 79.1, 73.9, 72.6, 67.3, 28.5, 19.6; IR (KBr) cm^{-1} 3289w, 2958w, 2126w, 1455w, 1330w, 1099s, 1038s, 736m, 696m; HRMS: $C_{14}H_{18}O_2$ for $[M+Na]^+$, calculated 241.1199, found 241.1190.



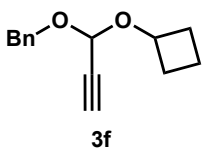
3d

3d: 110 mg (60% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.41 (s, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.05 (dt, *J* = 11.9, 6.2 Hz, 1H), 3.93 (dt, *J* = 11.9, 6.4 Hz, 1H), 3.49 (t, *J* = 6.2 Hz, 2H), 2.62 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 128.7, 128.3, 128.1, 90.8, 78.2, 74.8, 68.2, 65.3, 30.4; IR (KBr) cm^{-1} 3286w, 2872w, 2127w, 1455m, 1277m, 1104s, 1019s, 737m, 696s, 570m; HRMS: $C_{12}H_{13}BrO_2$ for $[M+Na]^+$, calculated 290.9991, found 290.9980.



3e

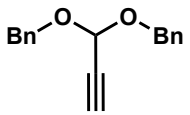
3e: 106 mg (63% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.45 (d, *J* = 1.8 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.14 – 3.93 (m, 2H), 2.66 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 128.8, 128.4, 124.0 (q, *J* = 275.8 Hz, 1C), 90.7, 77.1, 75.6, 68.9, 61.9 (q, *J* = 35.2 Hz, 1C); IR (KBr) cm^{-1} 3293w, 2947w, 2130w, 1456w, 1278s, 1162s, 1048s, 965m, 739m, 697m; HRMS: $C_{12}H_{11}F_3O_2$ for $[M+Na]^+$, calculated 267.0603, found 267.0608.



3f

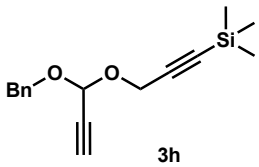
3f: 126 mg (85% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 5.32 (d, *J* = 1.8 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.34 (p, *J* = 7.6 Hz, 1H), 2.57 (d, *J* = 1.8 Hz, 1H), 2.32 – 2.17 (m, 2H), 2.07 (tt, *J* = 20.0, 10.3 Hz, 2H), 1.70 (q, *J* = 9.9 Hz, 1H), 1.50 (dtd, *J* = 18.6, 10.5, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 128.5, 128.1, 127.9, 89.7, 79.3, 73.9, 70.3, 67.0, 31.5, 31.0, 13.1; IR (KBr) cm^{-1} 3286w, 2941w, 2125 w, 1326m, 1108s, 1020s, 736m, 696s, 660m; HRMS: $C_{14}H_{16}O_2$ for $[M+Na]^+$, calculated 239.1043, found 239.1037.

For gram scale synthesis of **3f**: The reaction was performed with **1l** (2.5 g, 17.1 mmol, 1.0 equiv), Cyclobutanol (2.1 mL, 25.7 mmol, 1.5 equiv), CH_2Cl_2 (57.0 mL, 0.3 M) and [bis(trifluoroacetyl)iodo]benzene (8.8 g, 20.5 mmol, 1.2 equiv) following the above procedure，affording 3.10 g of the product in 84% yield.



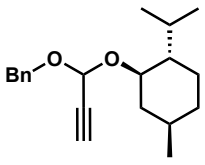
3g

3g: 116 mg (67% yield); colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 10H), 5.45 (d, J = 1.8 Hz, 1H), 4.79 (d, J = 11.6 Hz, 2H), 4.63 (d, J = 11.6 Hz, 2H), 2.61 (d, J = 1.8 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 137.3, 128.6, 128.2, 128.0, 90.5, 78.7, 74.5, 67.5; IR (KBr) cm^{-1} 3284w, 2874w, 2126w, 1454m, 1334w, 1098m, 1020s, 735s, 695s, 664m; HRMS: $C_{17}H_{16}O_2$ for [M+Na]+, calculated 275.1043, found 275.1030.



3h

3h: 145 mg (78% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.08 (m, 5H), 5.34 (d, *J* = 1.8 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 1.8 Hz, 2H), 2.44 (d, *J* = 1.8 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 128.6, 128.2, 128.0, 100.6, 92.1, 90.1, 78.3 74.8, 67.7, 54.0, -0.1; IR (KBr) cm^{-1} 3286w, 2960w, 2128w, 1455w, 1355w, 1251m, 1097s, 1024s, 840s, 760m, 696s, 660m; HRMS: $C_{16}H_{20}O_2Si$ for $[M+Na]^+$, calculated 295.1125, found 295.1116.

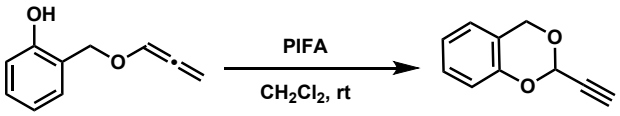


3i

3i: 138 mg (67% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 5.48 (dd, *J* = 48.4, 1.9 Hz, 1H), 4.83 (t, *J* = 10.9 Hz, 1H), 4.66 (dd, *J* = 24.5, 11.5 Hz, 1H), 3.52 (dtd, *J* = 79.8, 10.6, 4.3 Hz, 1H), 2.59 (d, *J* = 1.9 Hz, 1H), 2.35 – 2.08 (m, 2H), 1.70 – 1.60 (m, 2H), 1.38 – 1.25 (m, 2H), 1.11 – 0.87 (m, 9H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 128.4, 127.8, 127.6, 92.1, 80.0, 79.6, 74.0, 66.6, 48.6, 42.7, 34.4, 31.5, 25.1, 23.1, 22.2, 21.2, 16.0; IR (KBr) cm^{-1} 3309w, 2922m,

2125w, 1455m, 1319m, 1095s, 1025s, 734m, 695m, 655m; HRMS: $C_{20}H_{28}O_2$ for $[M+Na]^+$, calculated 323.1982, found 232.1968.

6. Synthesis of 6



5 **6**, 85%yield

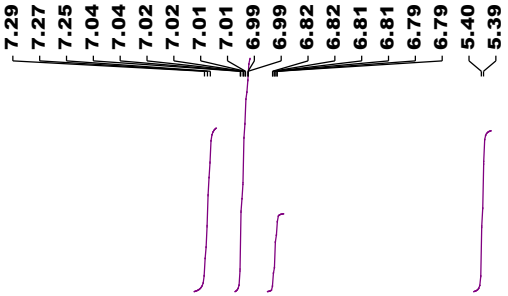
To a solution of 2-hydroxybenzyl allenyl ether **5** (100 mg, 0.62 mmol, 1.0 equiv) in CH_2Cl_2 (2.06 mL, 0.3 M) was added [bis(trifluoroacetyl)iodo]benzene (318 mg, 0.74 mmol, 1.2 equiv) at rt. The reaction was stirred at rt for 5 minutes and monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: 1.0% EtOAc/petroleum ether) to obtain the cyclic acetal **6**.

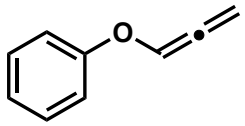
6: 82 mg (83% yield); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dt, *J* = 8.6, 4.4 Hz, 1H), 6.97 (d, *J* = 4.5 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.87 (d, *J* = 1.8 Hz, 1H), 5.12 (d, *J* = 14.6 Hz, 1H), 4.91 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 128.4, 124.9, 122.0, 120.6, 117.3, 87.7, 77.7, 77.5, 74.7, 63.9. IR (KBr) cm^{-1} 3286w, 1589m, 1489m, 1381m,1207s, 1115s, 1079s, 960s, 752s, 684s; HRMS: $C_{10}H_8O_2$ for $[M+APCl]^+$, calculated 159.0452, found 159.0445.

7. References

1. X. Huang, W. Thor, X. Feng, L. Kang, M. Yang, C. Lee, Y. Cheng and S. He, *Org. Chem. Front*, 2020,**7**, 255.
2. W. Lei, Y. Song, A. Long, Y. Que, S. He and Y. Cheng, *Frontiers in Plant Science*, 2022, **12**, 1087899
3. R. Huang, P. Xu, W. Wang, G. Peng and H. Yu, *Tetrahedron Letters*, 2020, **61**, 151753.

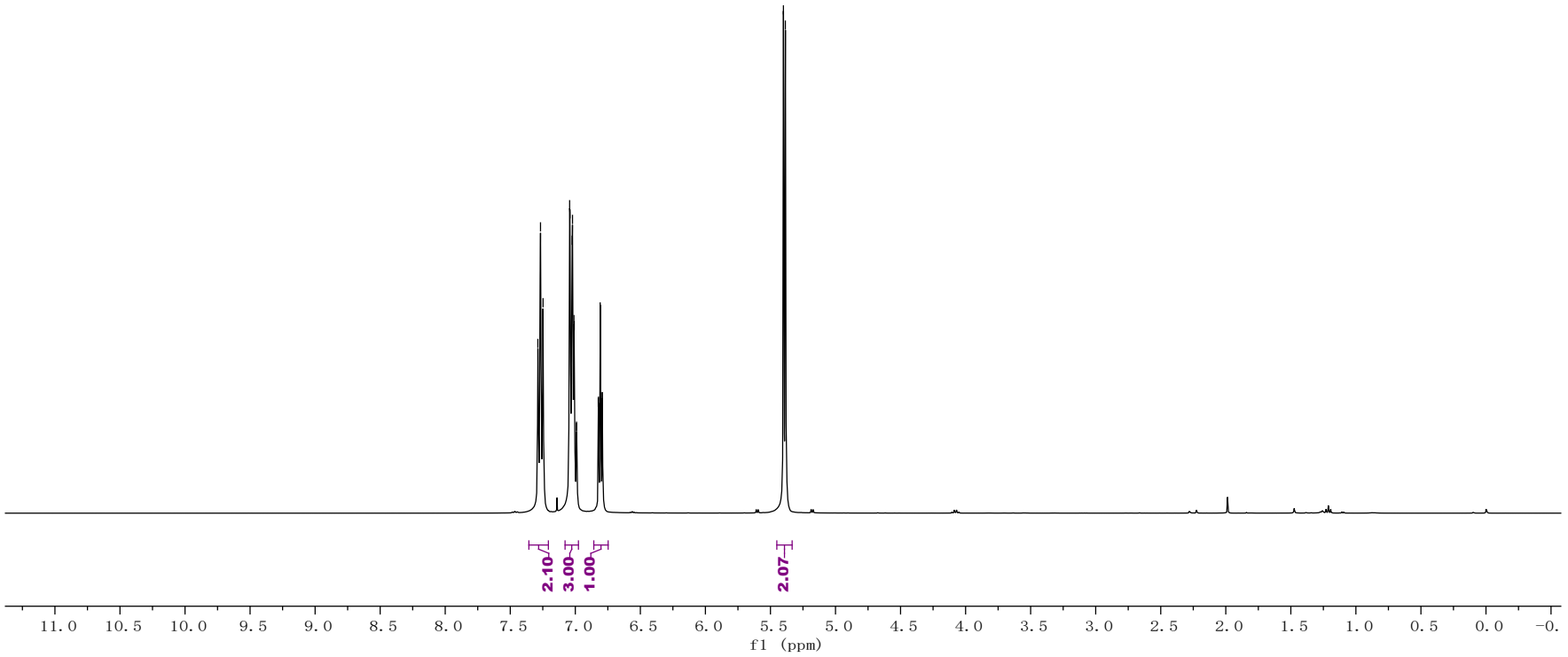
8. ^{1}H NMR and ^{13}C NMR spectra for compounds

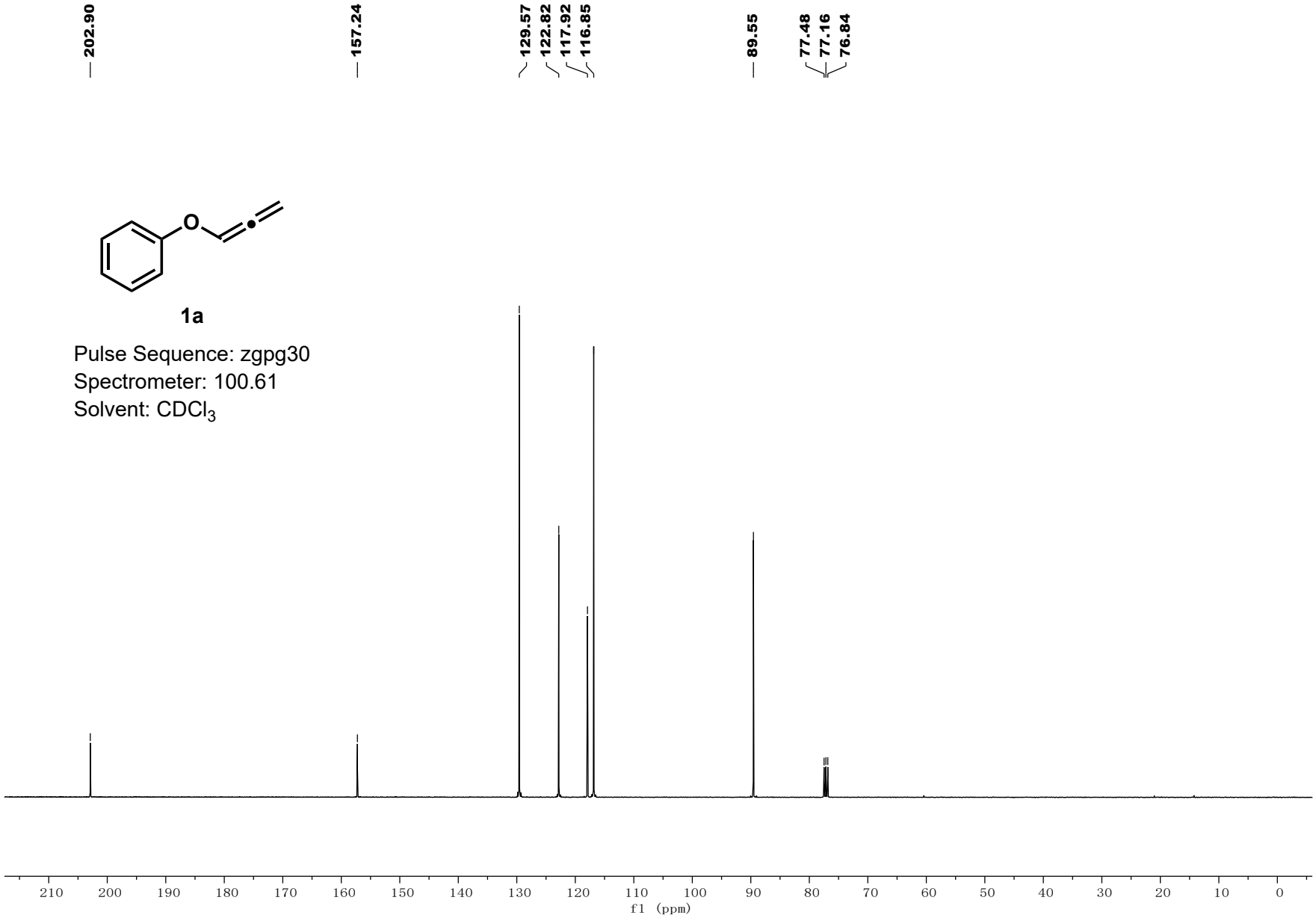




1a

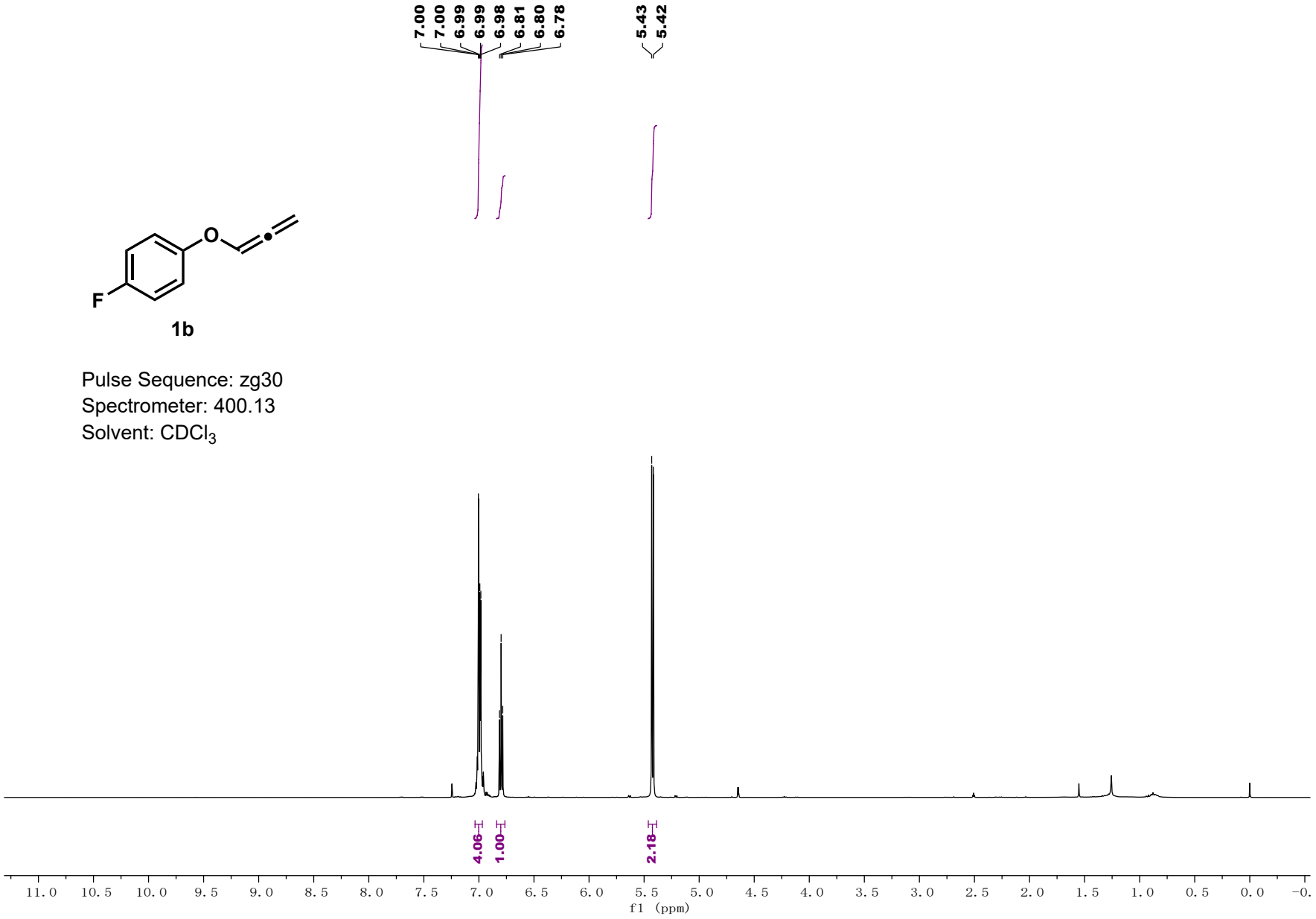
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

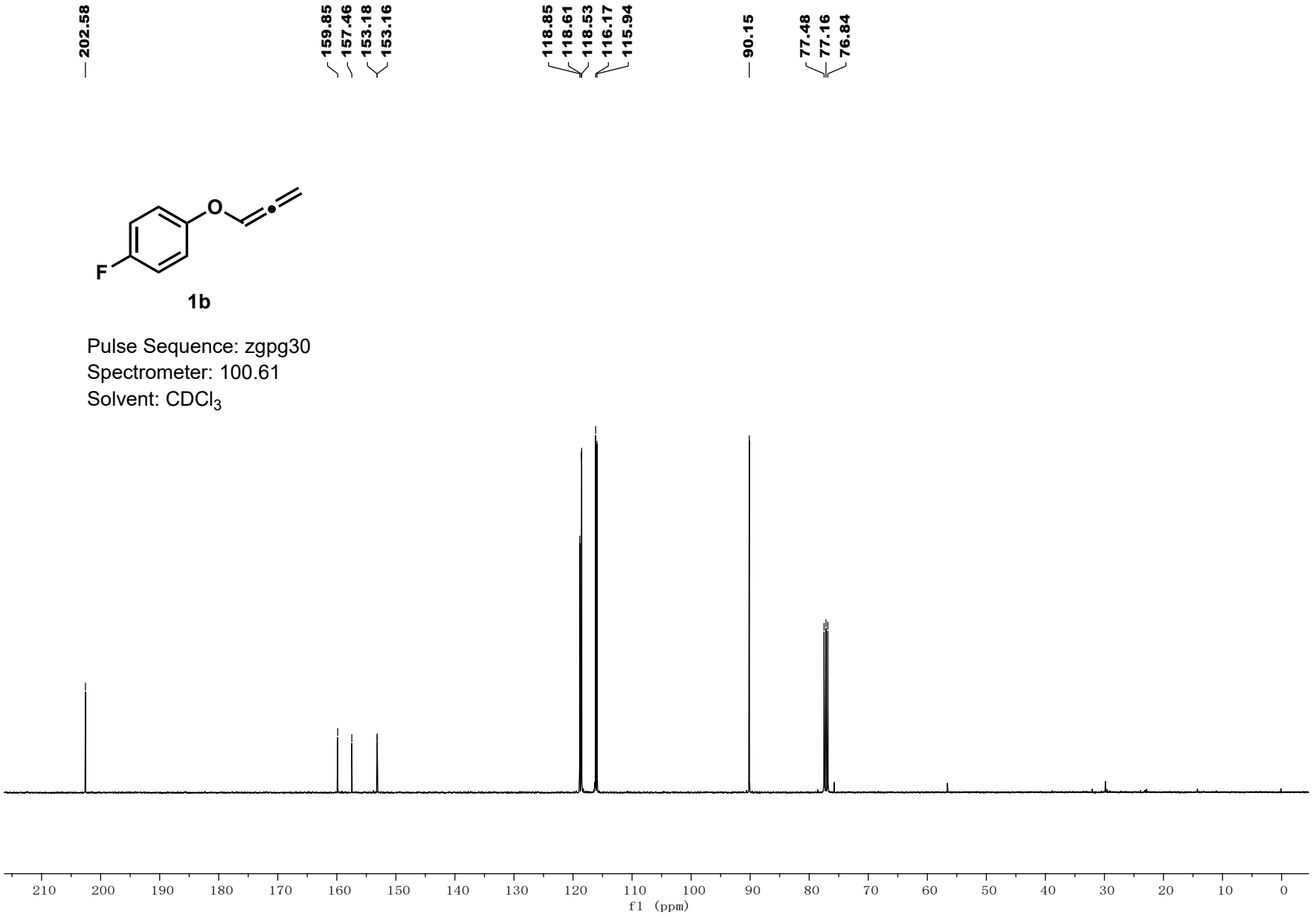


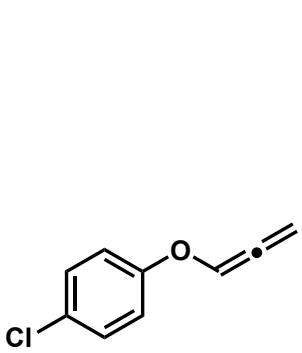

202.90
157.24
129.57
122.82
117.92
116.85
89.55
77.48
77.16
76.84
O
1a
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1b

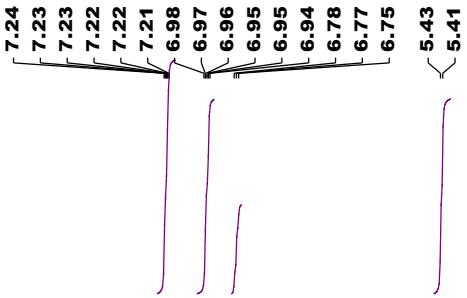
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$



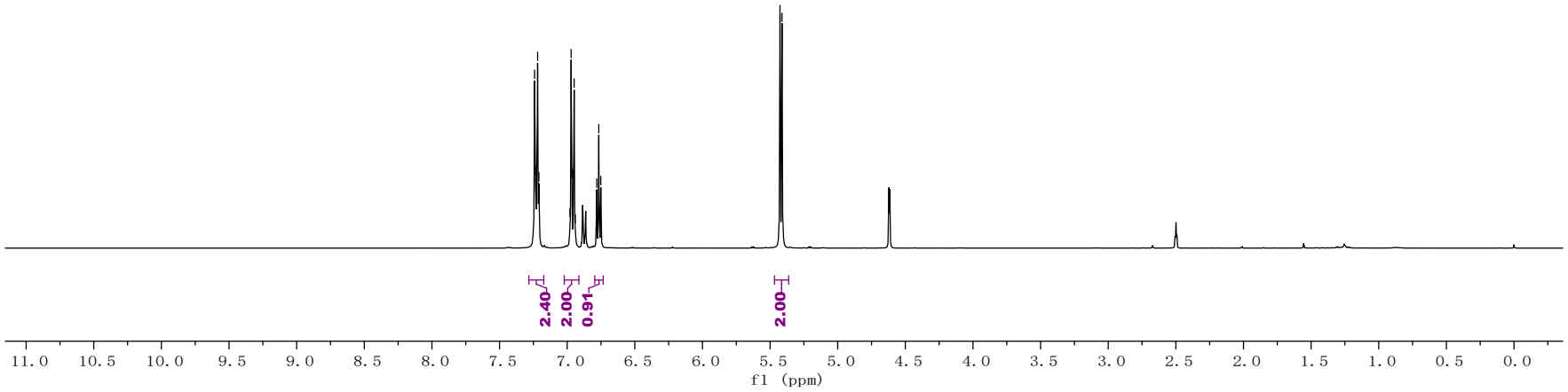

202.58
159.85
157.46
153.18
153.16
118.85
118.61
118.53
116.17
115.94
90.15
77.48
77.16
76.84
O
F
1b
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

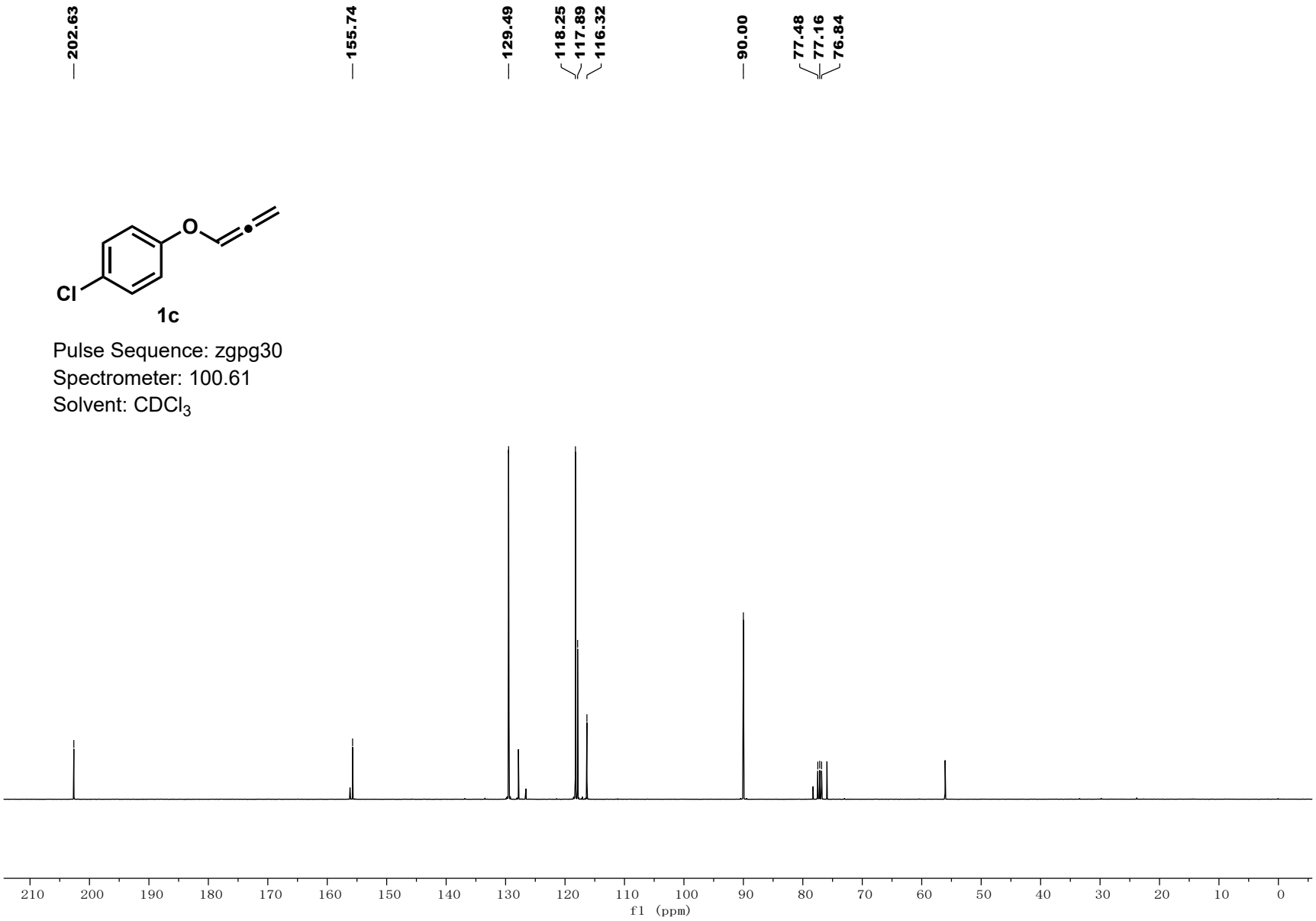


1c



Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

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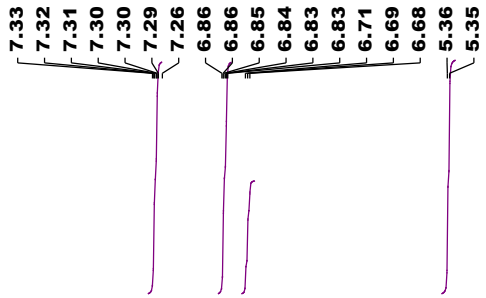
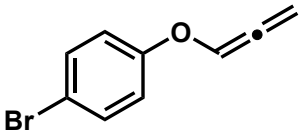
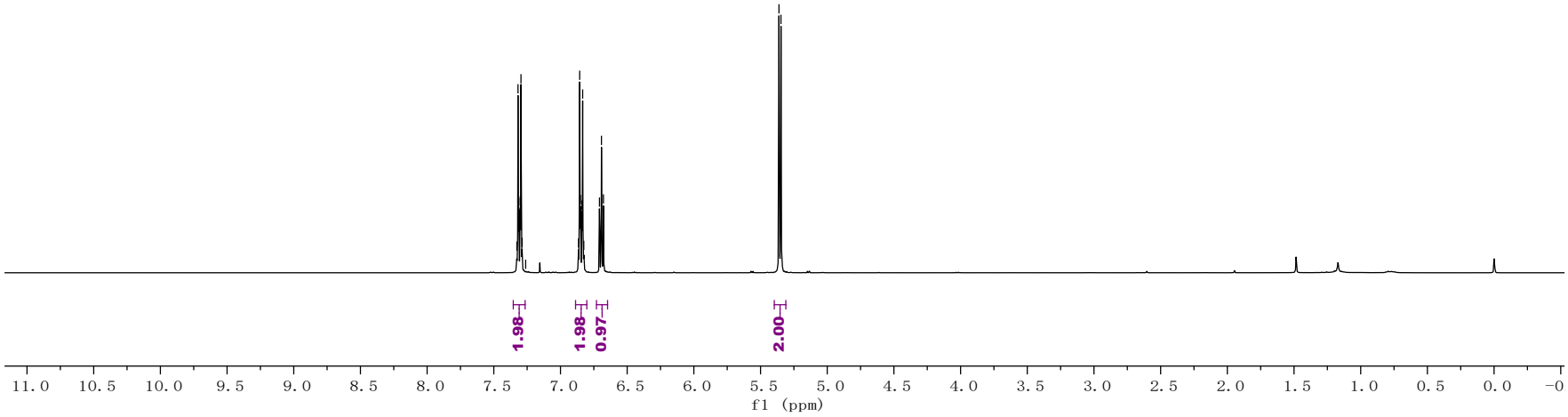
155.74
129.49
118.25
117.89
116.32
90.00
77.48
77.16
76.84
O
Cl
1c
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

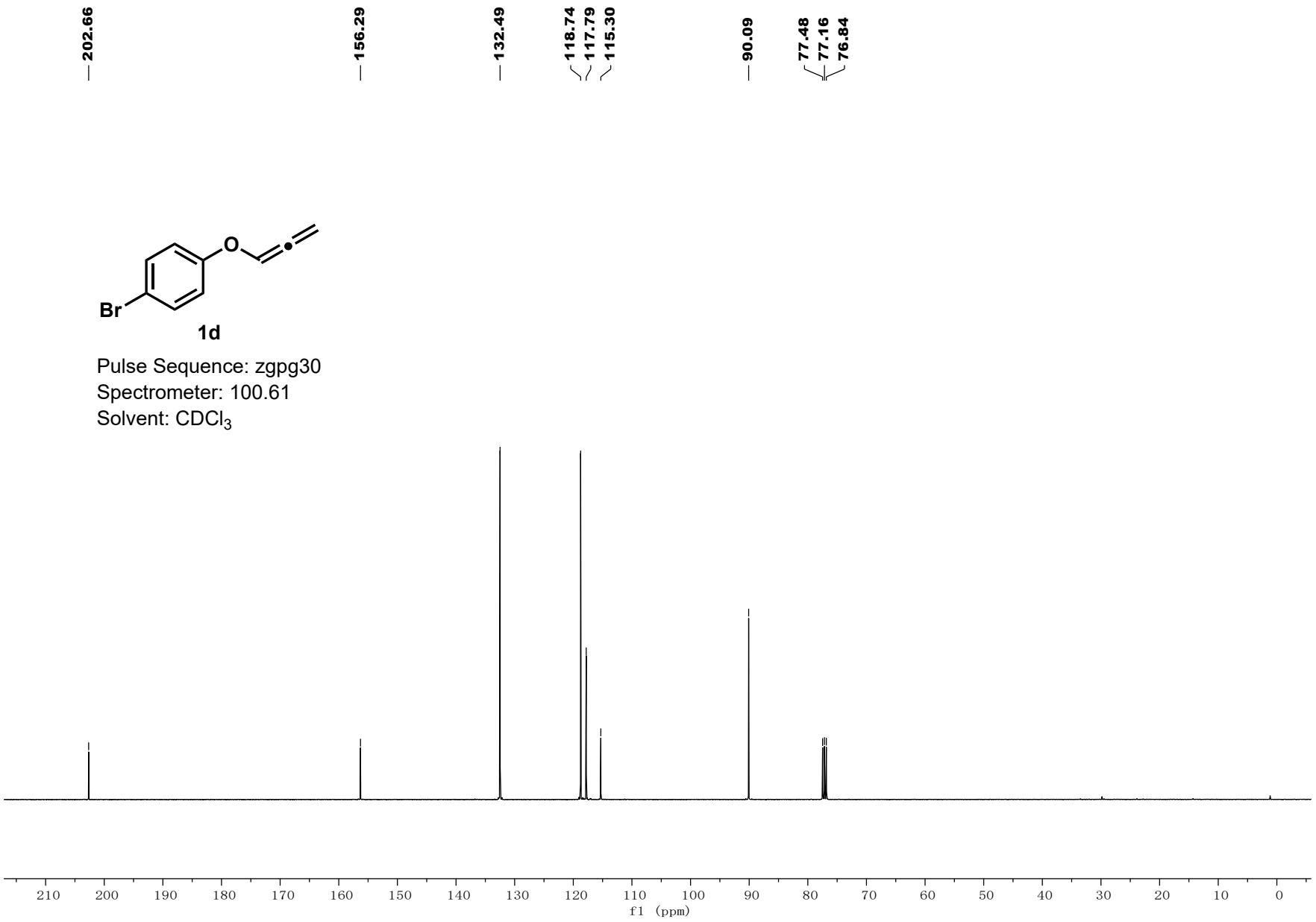


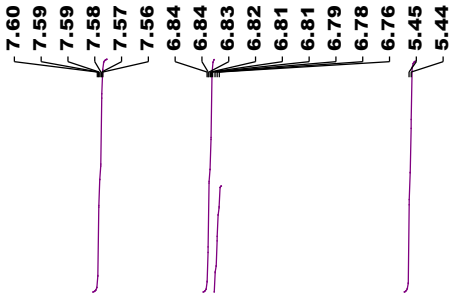


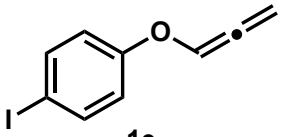
1d

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$



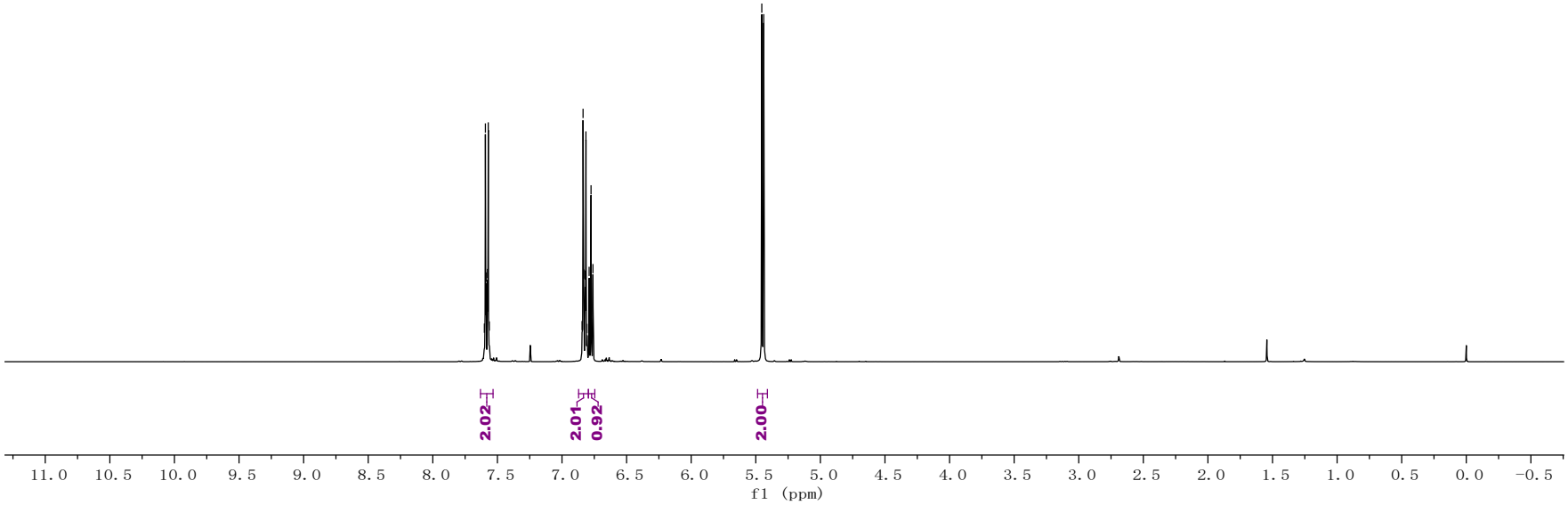

202.66
156.29
132.49
118.74
117.79
115.30
90.09
77.48
77.16
76.84
O
Br
1d
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

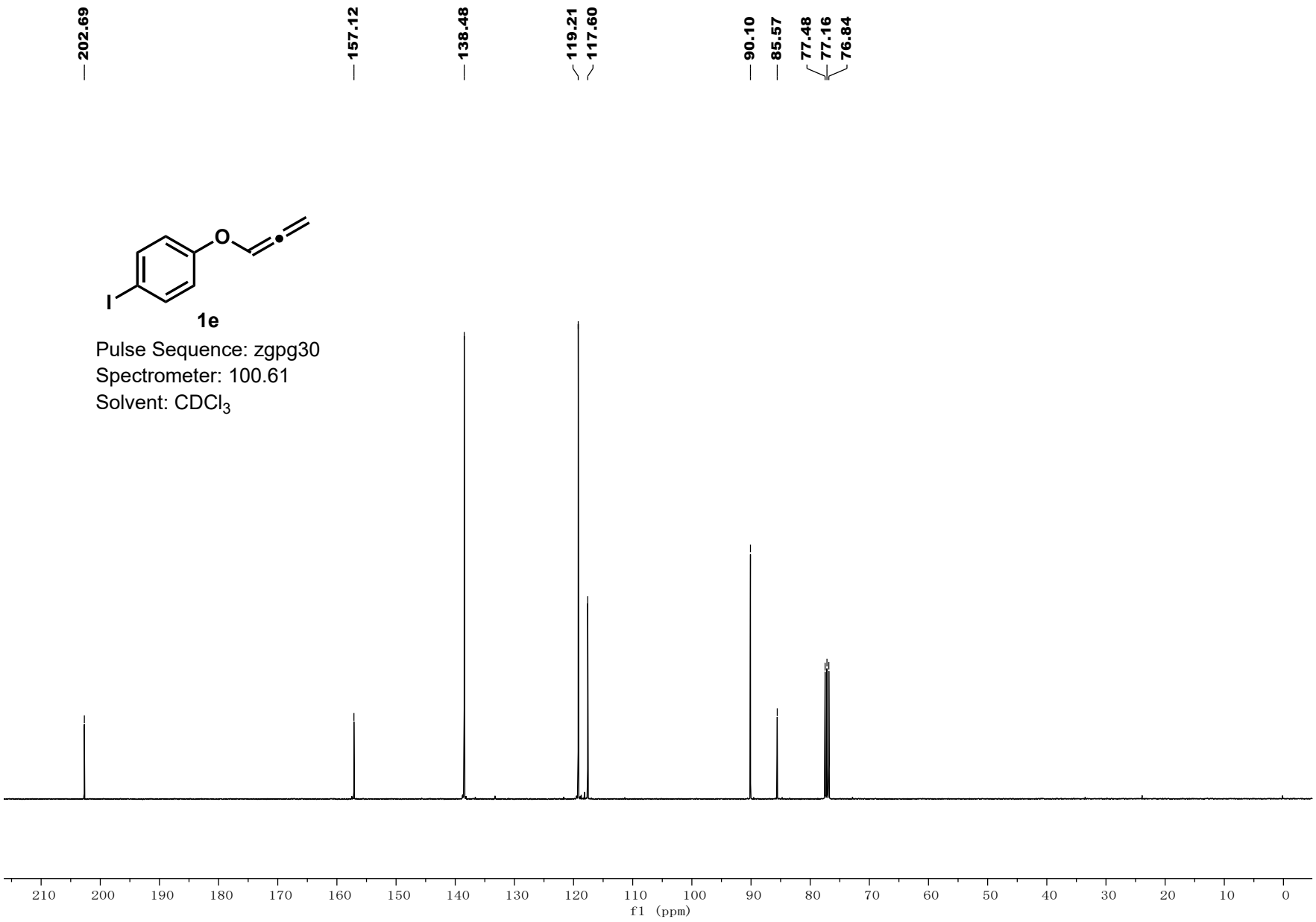




1e

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$




202.69
157.12
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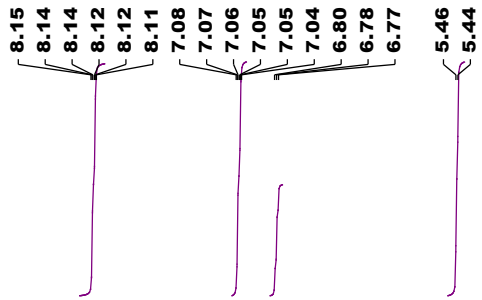
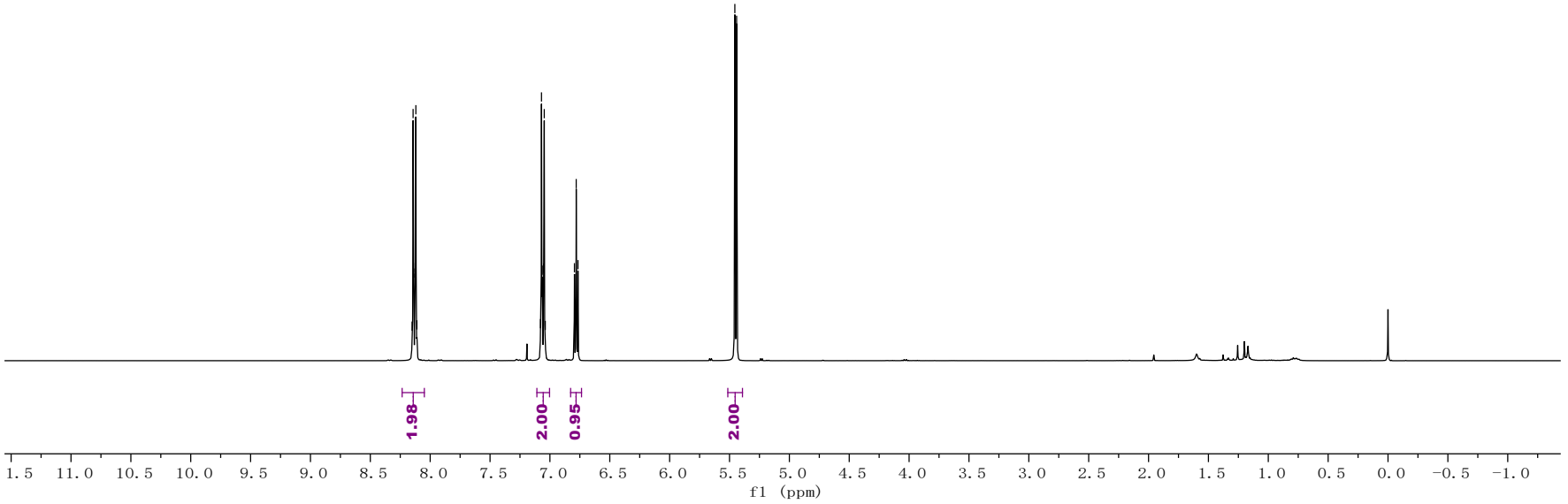
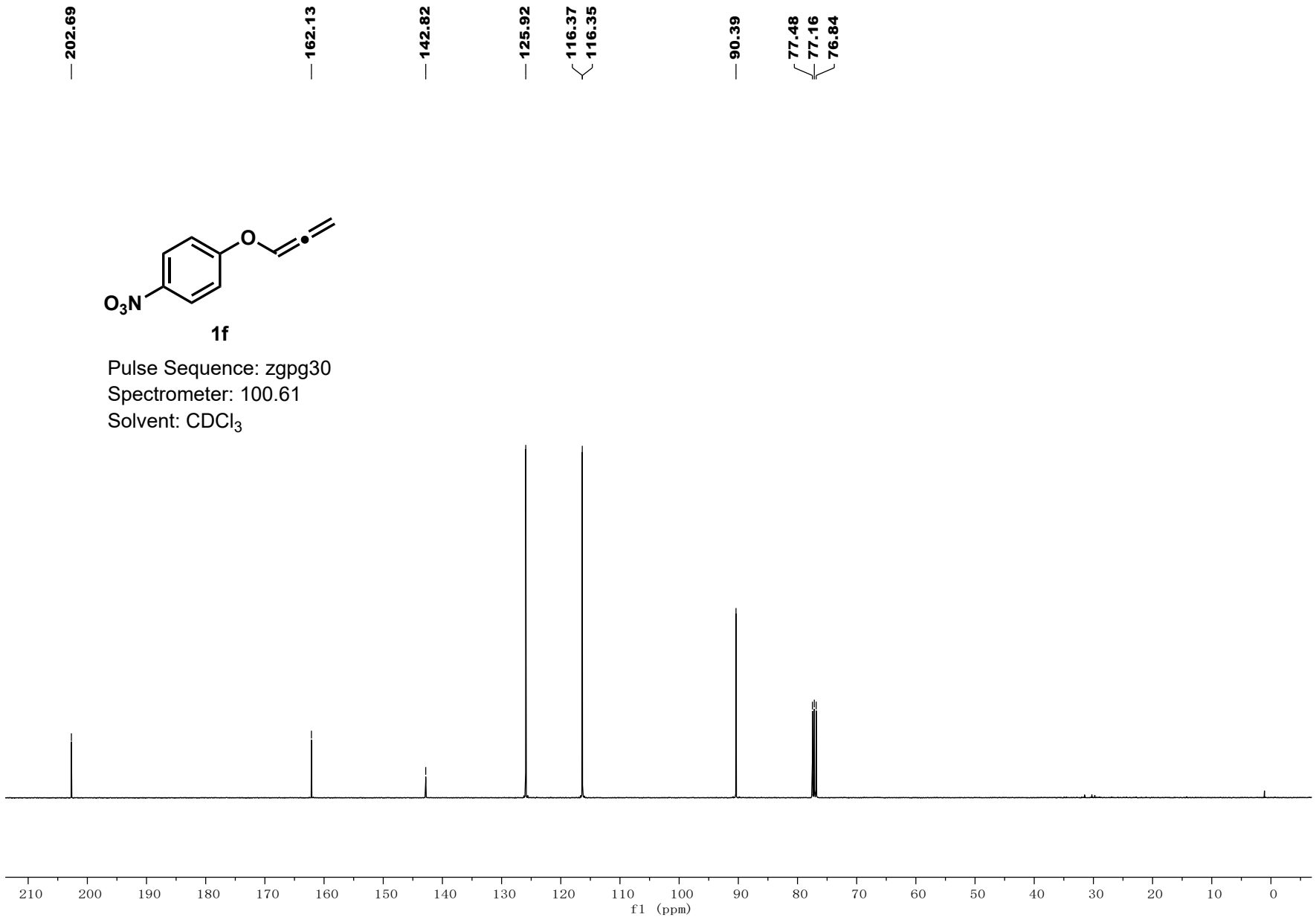
119.21
117.60
90.10
85.57
77.48
77.16
76.84
O
I
1e
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

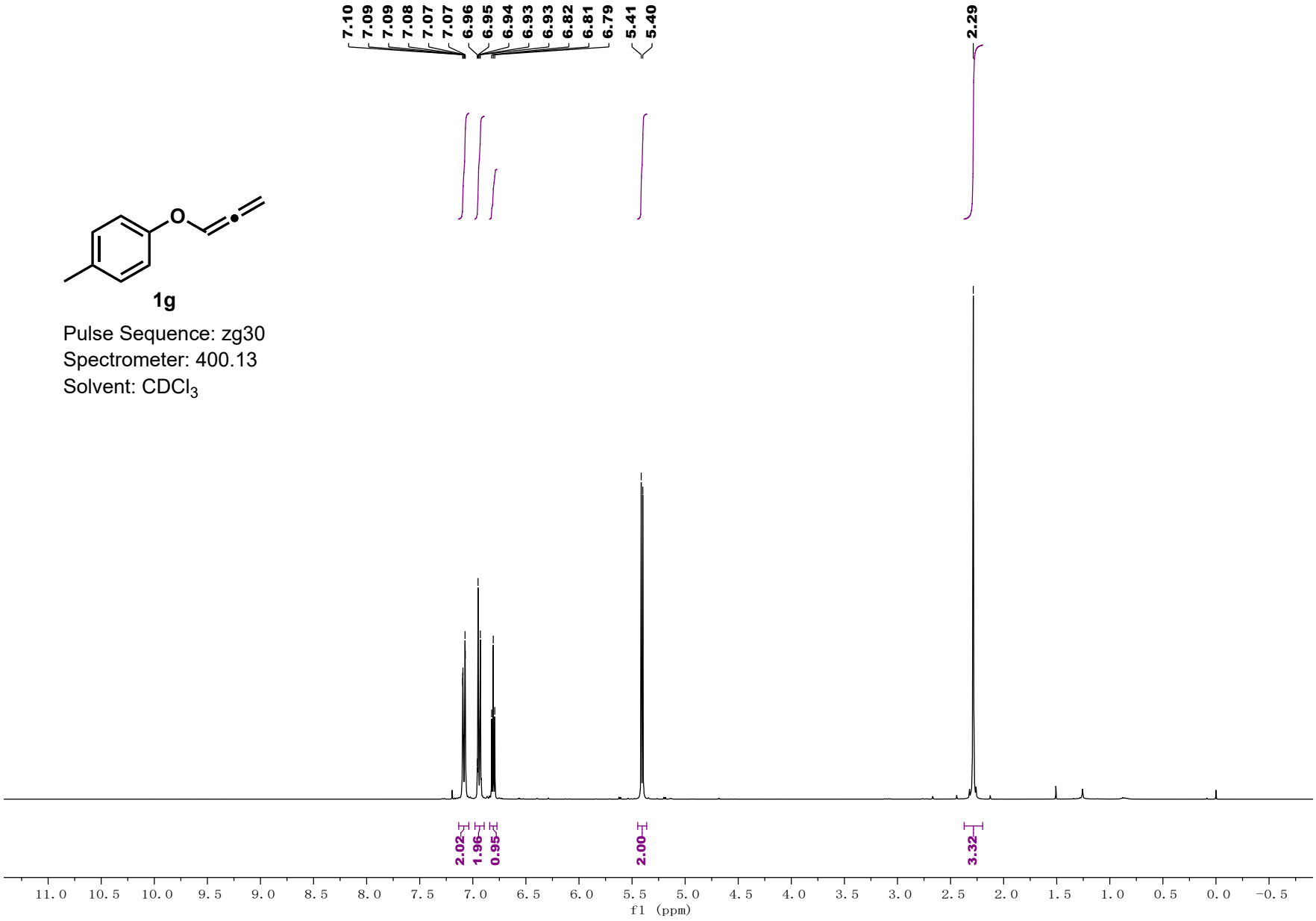


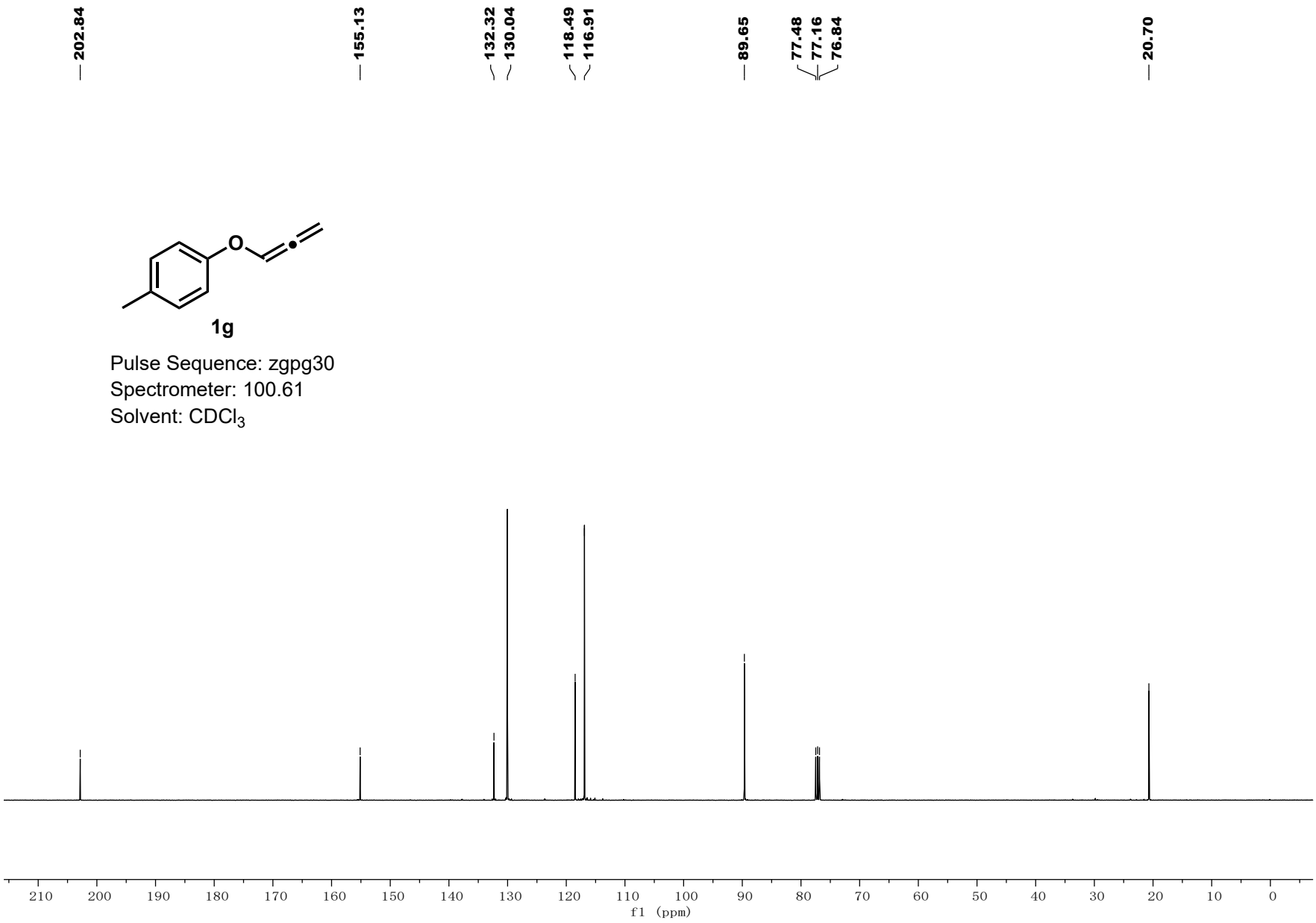
1f

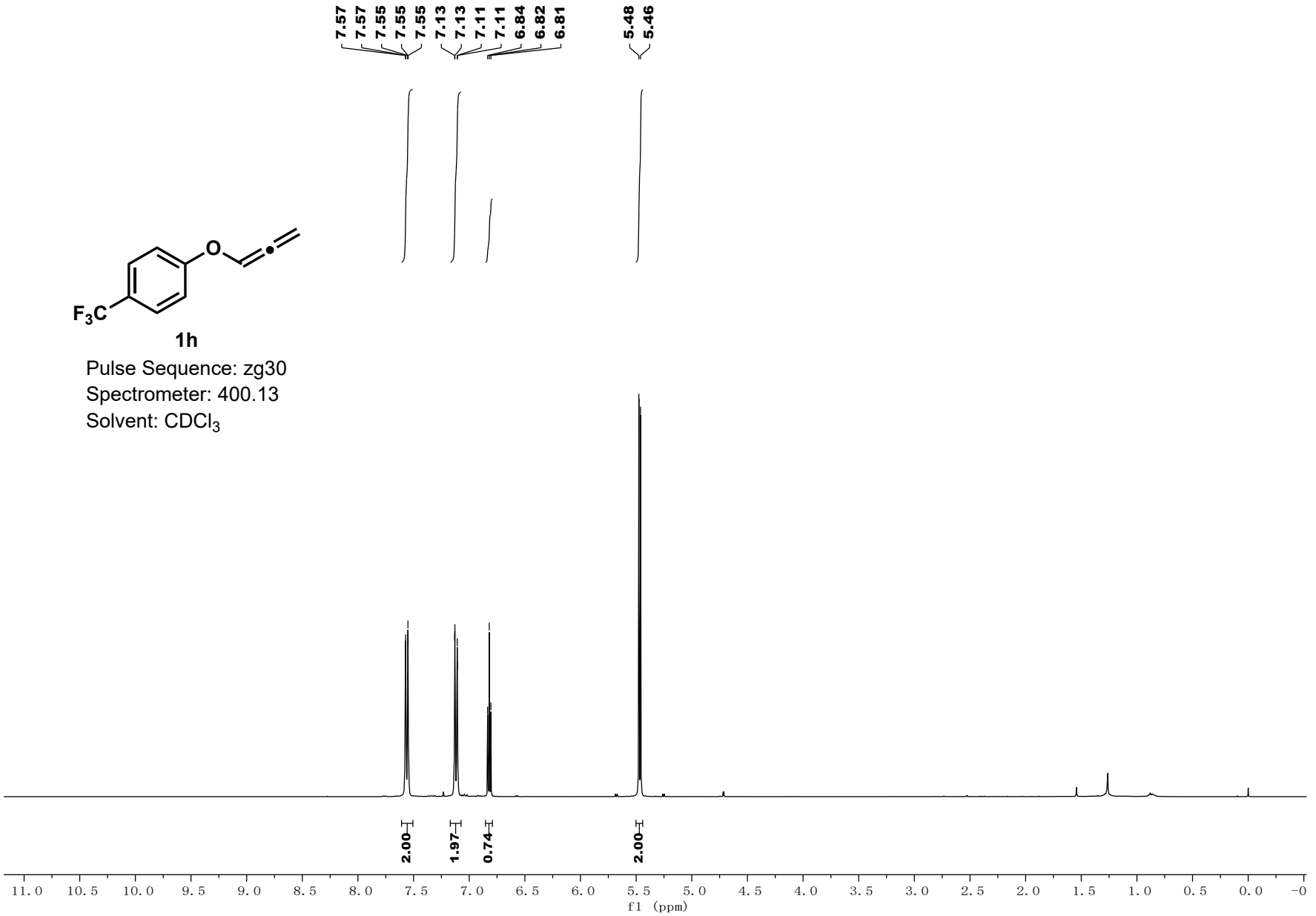
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

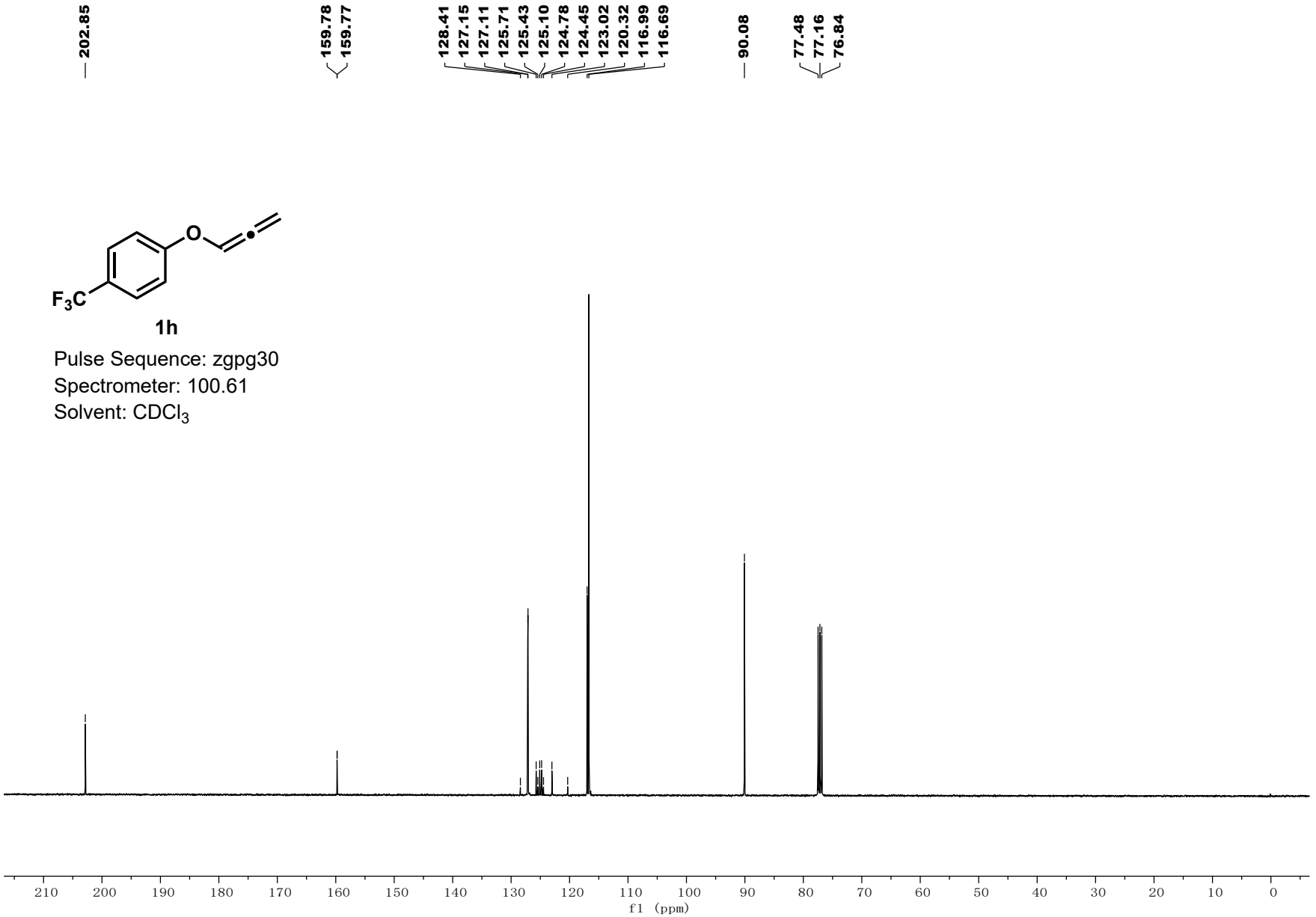



202.69
162.13
142.82
125.92
116.37
116.35
90.39
77.48
77.16
76.84
O
O3N
1f
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.10
7.09
7.09
7.08
7.07
7.07
6.96
6.95
6.94
6.93
6.93
6.82
6.81
6.79
5.41
5.40
2.29
O
1g
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.02
1.96
0.95
2.00
3.32
11.0 10.5 10.0 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 −0.5
f1 (ppm)

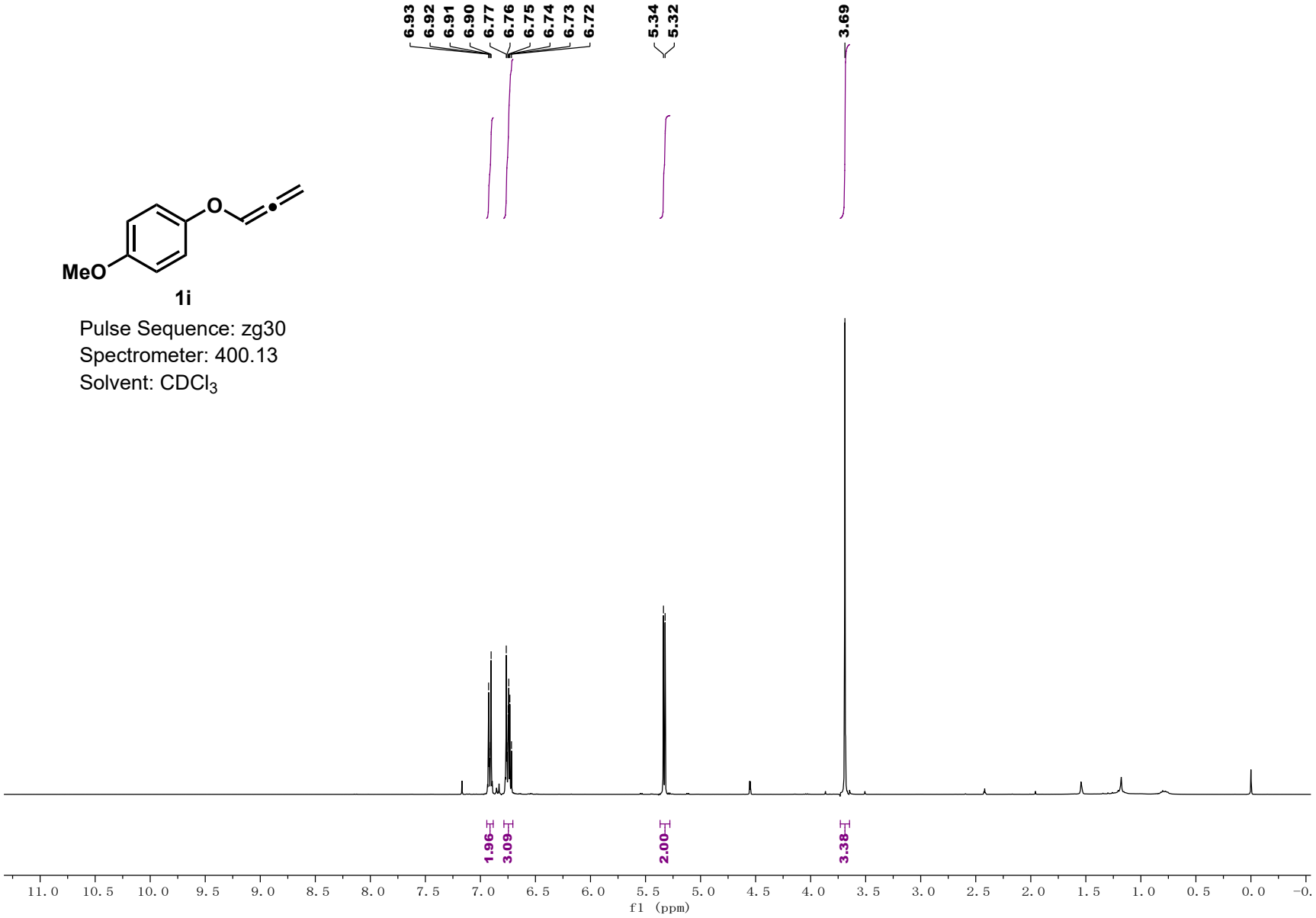

202.84
155.13
132.32
130.04
118.49
116.91
89.65
77.48
77.16
76.84
20.70
O
1g
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

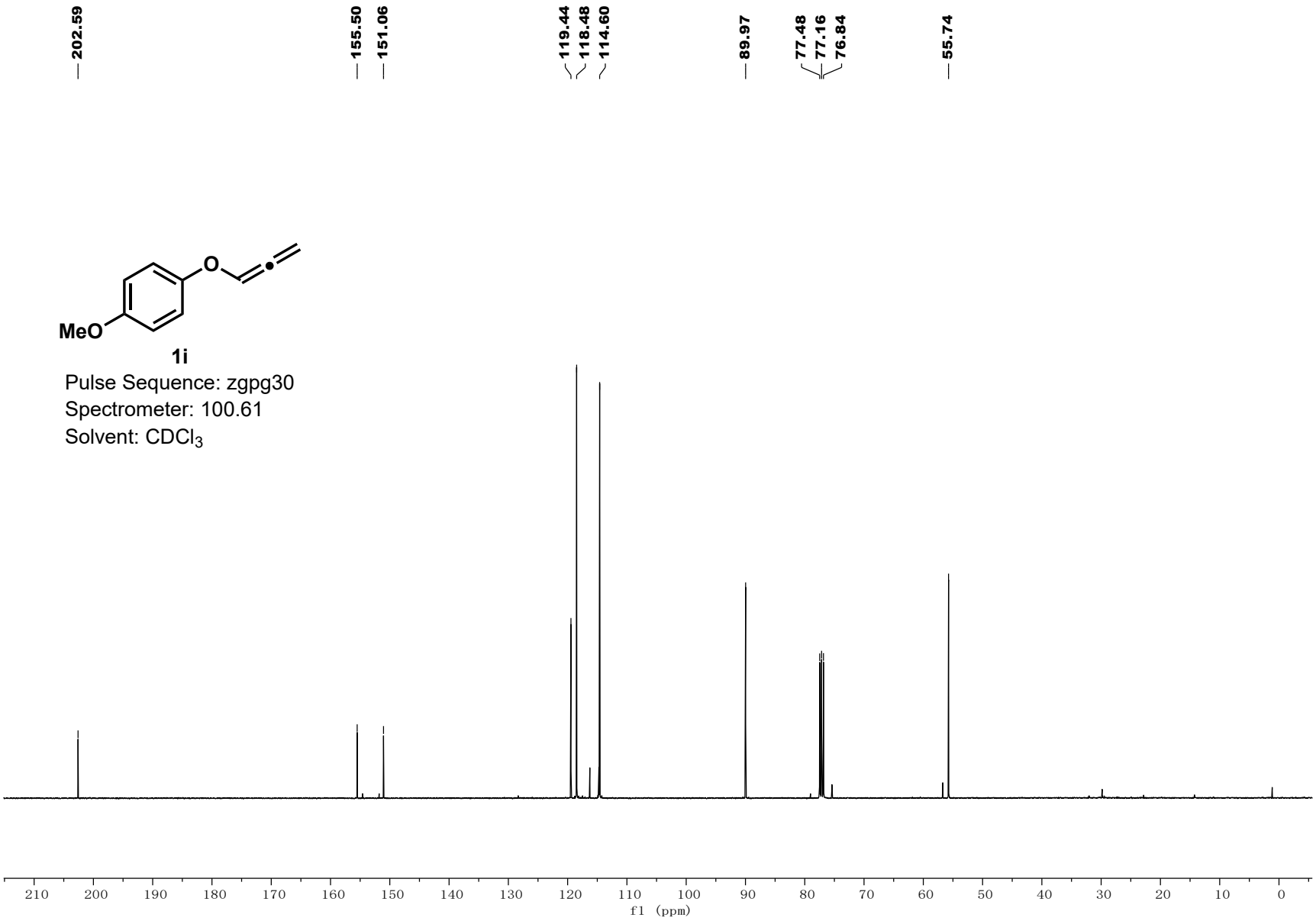

7.57
7.57
7.55
7.55
7.55
7.13
7.13
7.11
7.11
6.84
6.82
6.81
5.48
5.46
O
F3C
1h
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.00
1.97
0.74
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

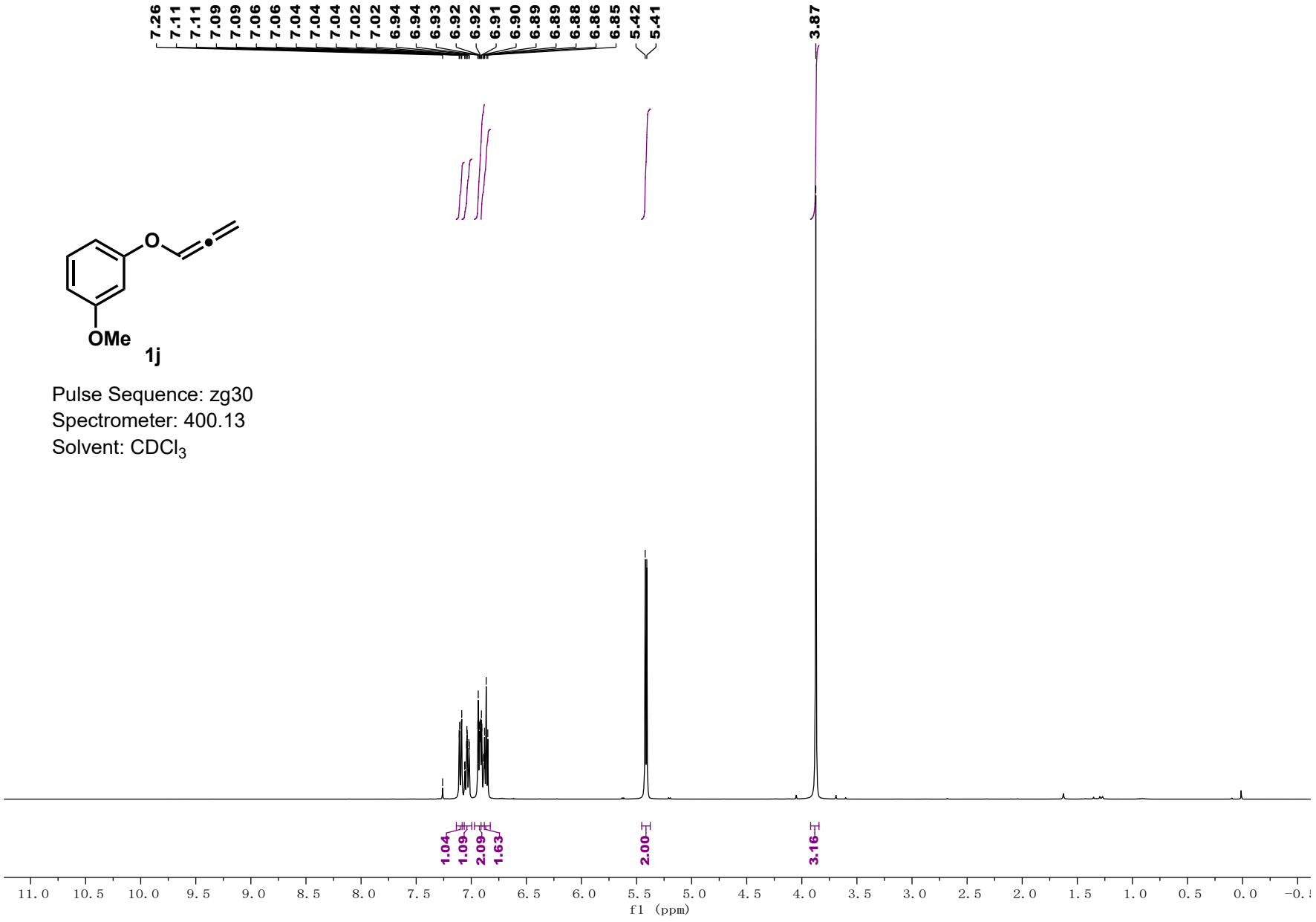

202.85
159.78
159.77
128.41
127.15
127.11
125.71
125.43
125.10
124.78
124.45
123.02
120.32
116.99
116.69
90.08
77.48
77.16
76.84
O
F3C
1h
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

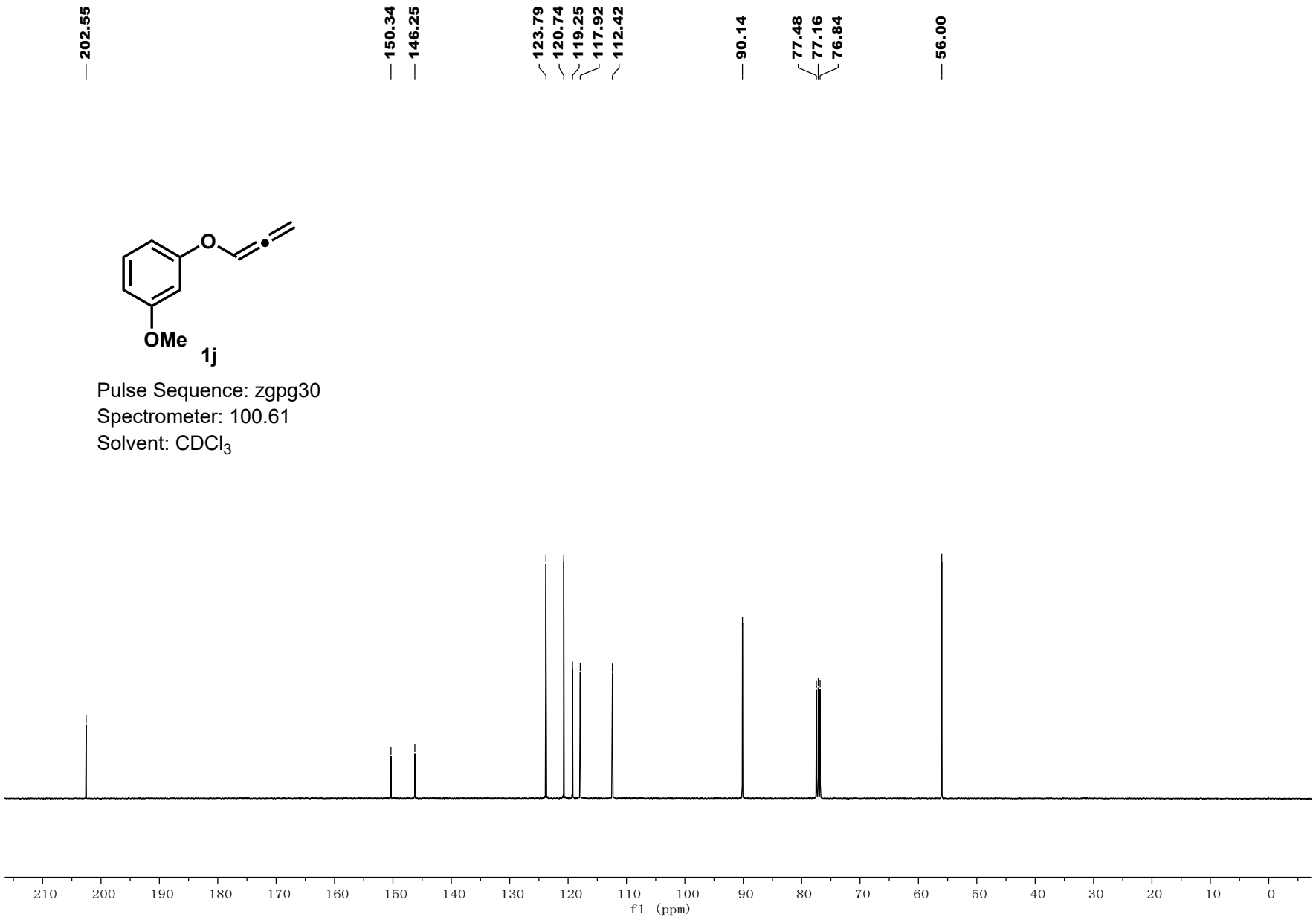
1i

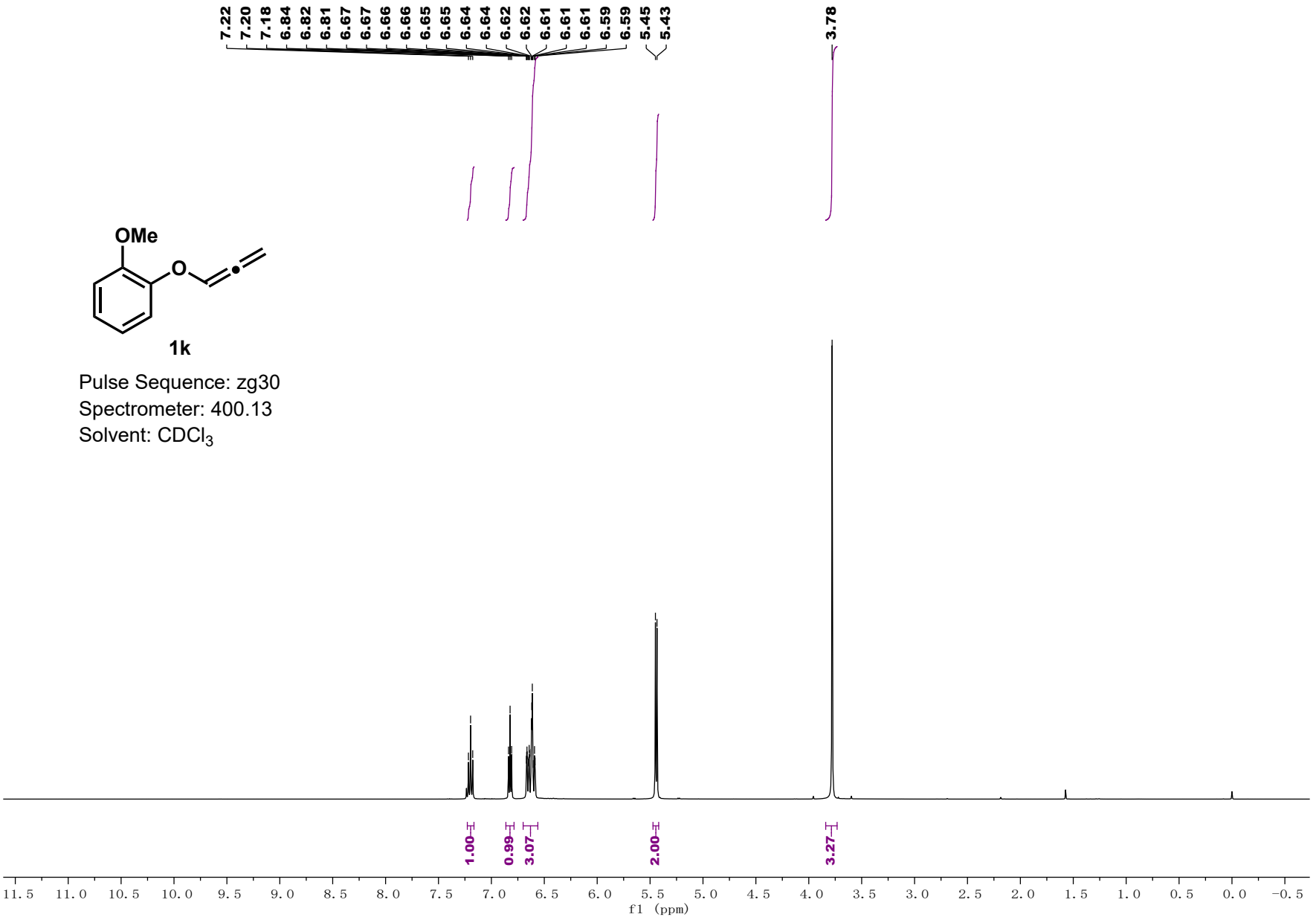
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

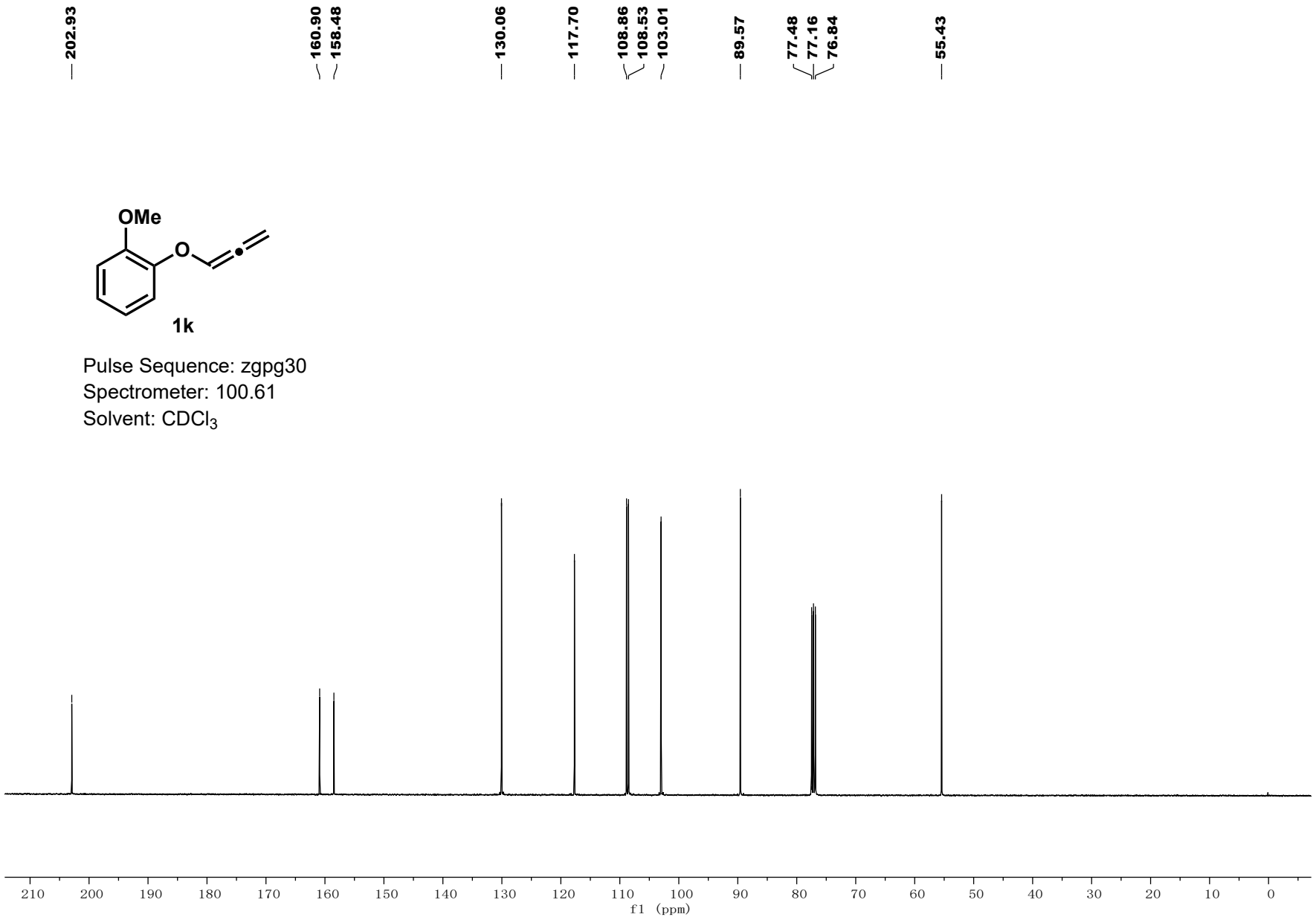


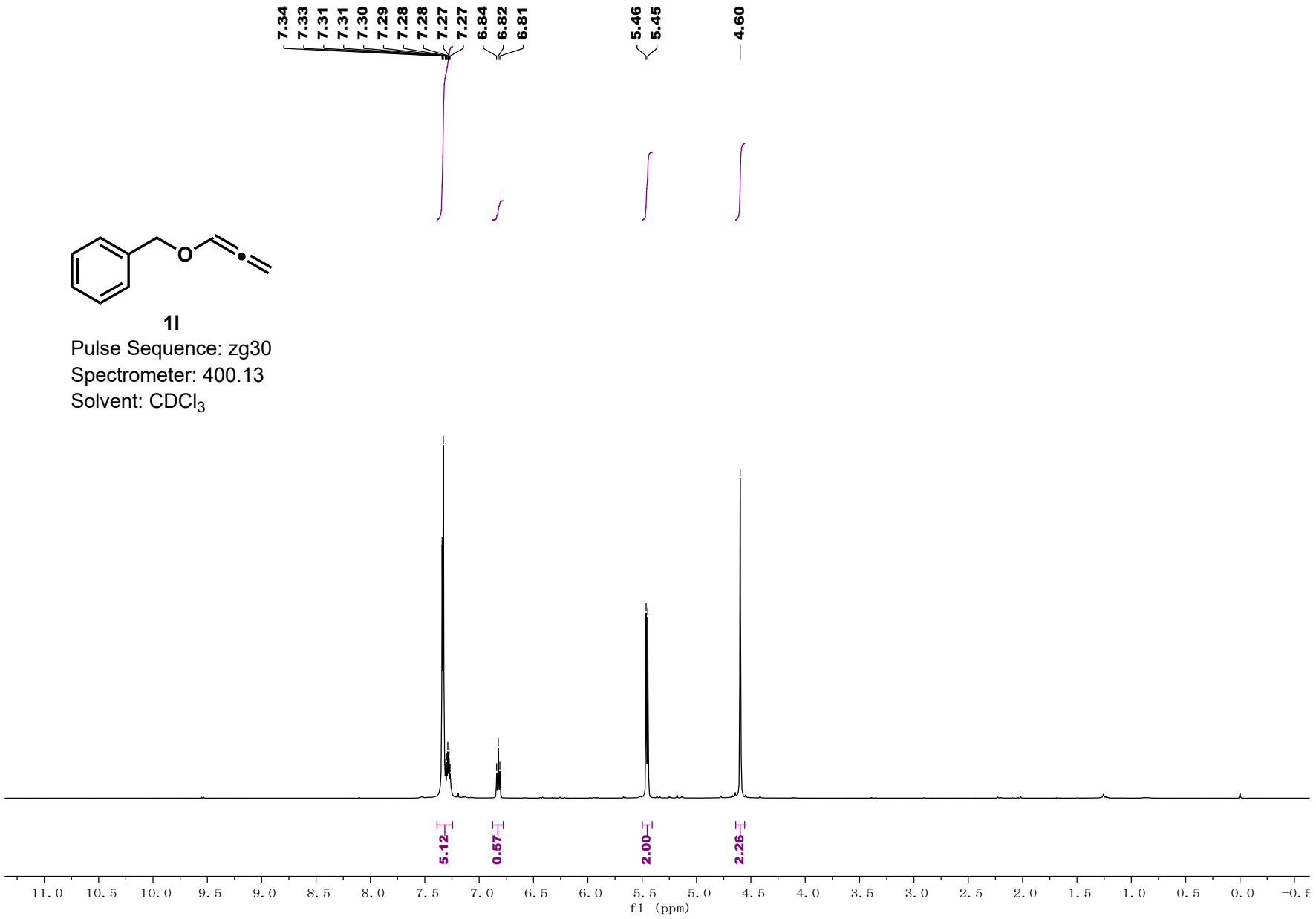

202.59
155.50
151.06
119.44
118.48
114.60
89.97
77.48
77.16
76.84
55.74
O
MeO
1i
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

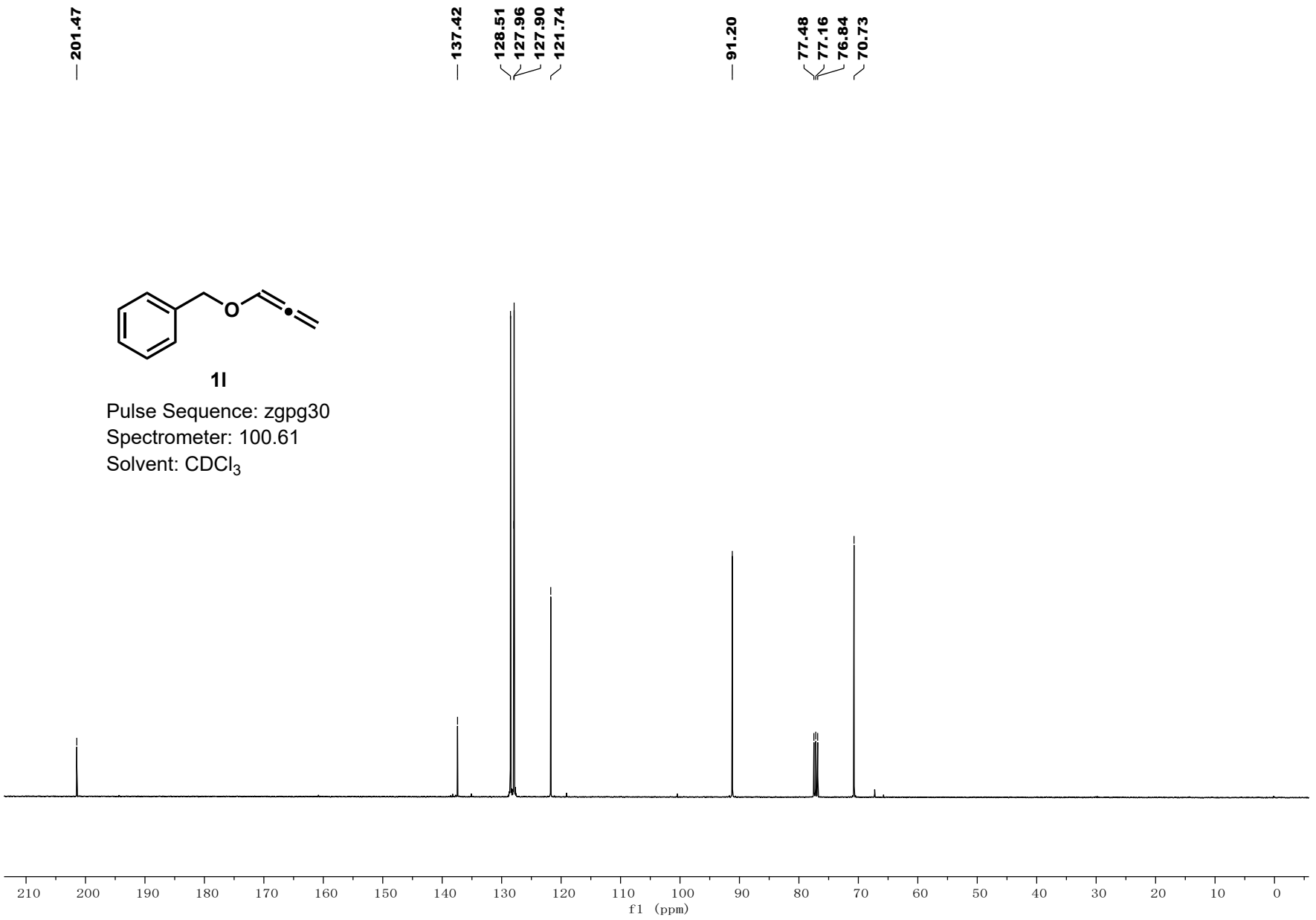

7.26
7.11
7.11
7.09
7.09
7.06
7.06
7.04
7.04
7.04
7.02
7.02
6.94
6.94
6.93
6.92
6.92
6.91
6.90
6.89
6.89
6.88
6.86
6.85
5.42
5.41
3.87
O
OMe
1j
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
1.04
1.09
2.09
1.63
2.00
3.16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

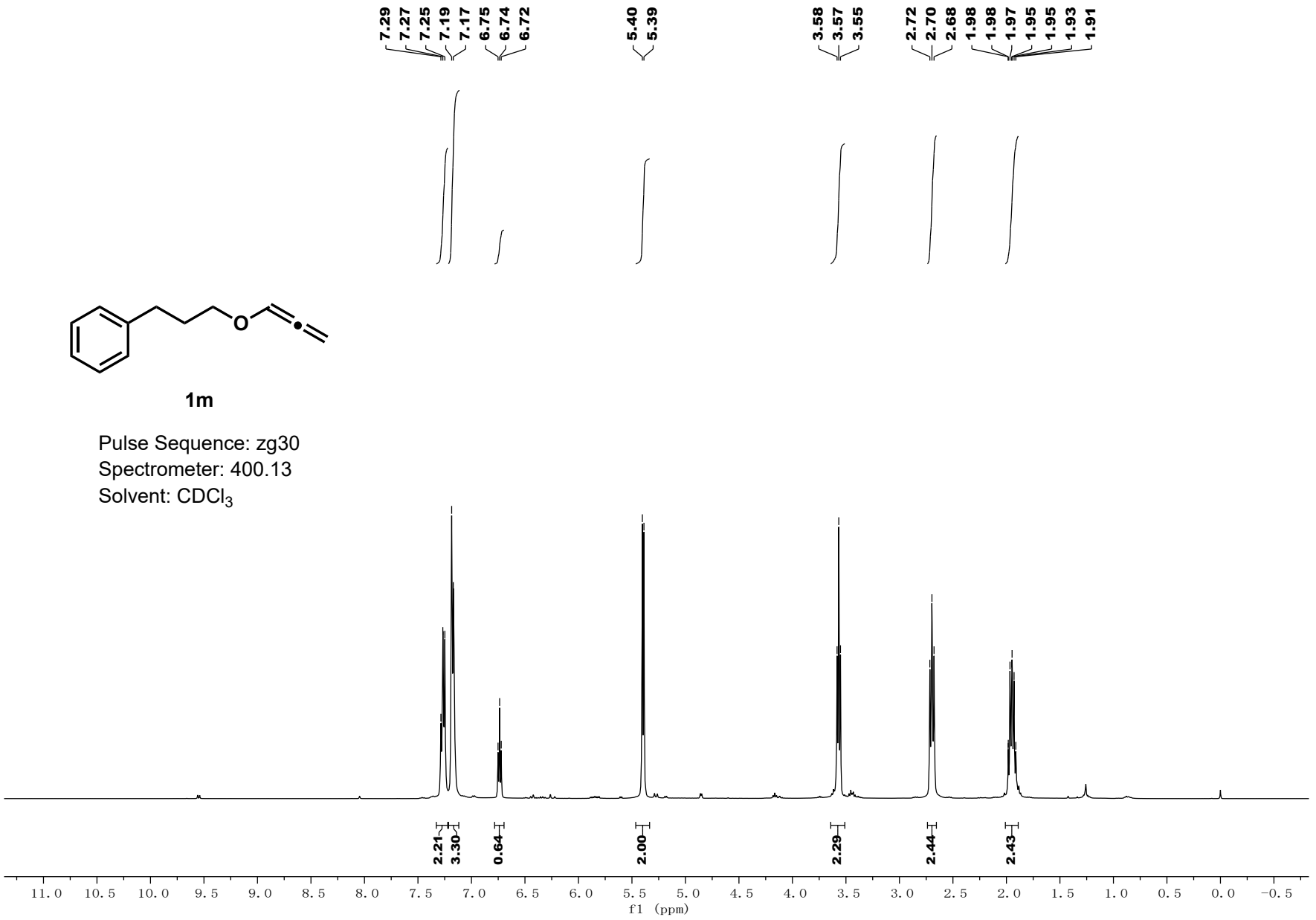

202.55
150.34
146.25
123.79
120.74
119.25
117.92
112.42
90.14
77.48
77.16
76.84
56.00
O
OMe
1j
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

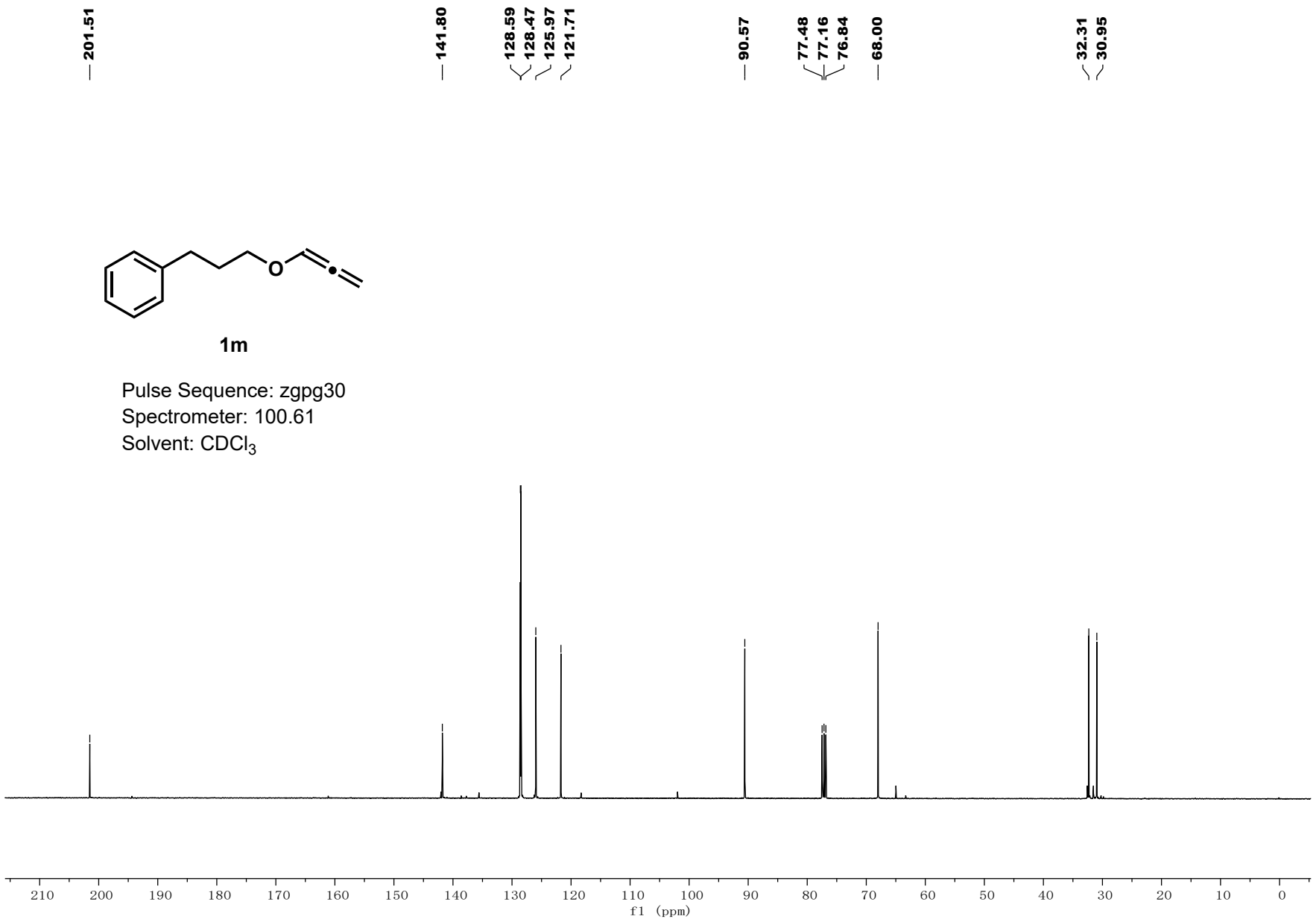

7.22
7.20
7.18
6.84
6.82
6.81
6.67
6.67
6.66
6.66
6.65
6.65
6.64
6.64
6.62
6.62
6.61
6.61
6.61
6.59
6.59
5.45
5.43
3.78
OMe
O
1k
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
1.00
0.99
3.07
2.00
3.27
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


202.93
160.90
158.48
130.06
117.70
108.86
108.53
103.01
89.57
77.48
77.16
76.84
55.43
OMe
O
1k
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.27
6.84
6.82
6.81
5.46
5.45
4.60
O
1l
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.12
0.57
2.00
2.26
11.0
10.5
10.0
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)

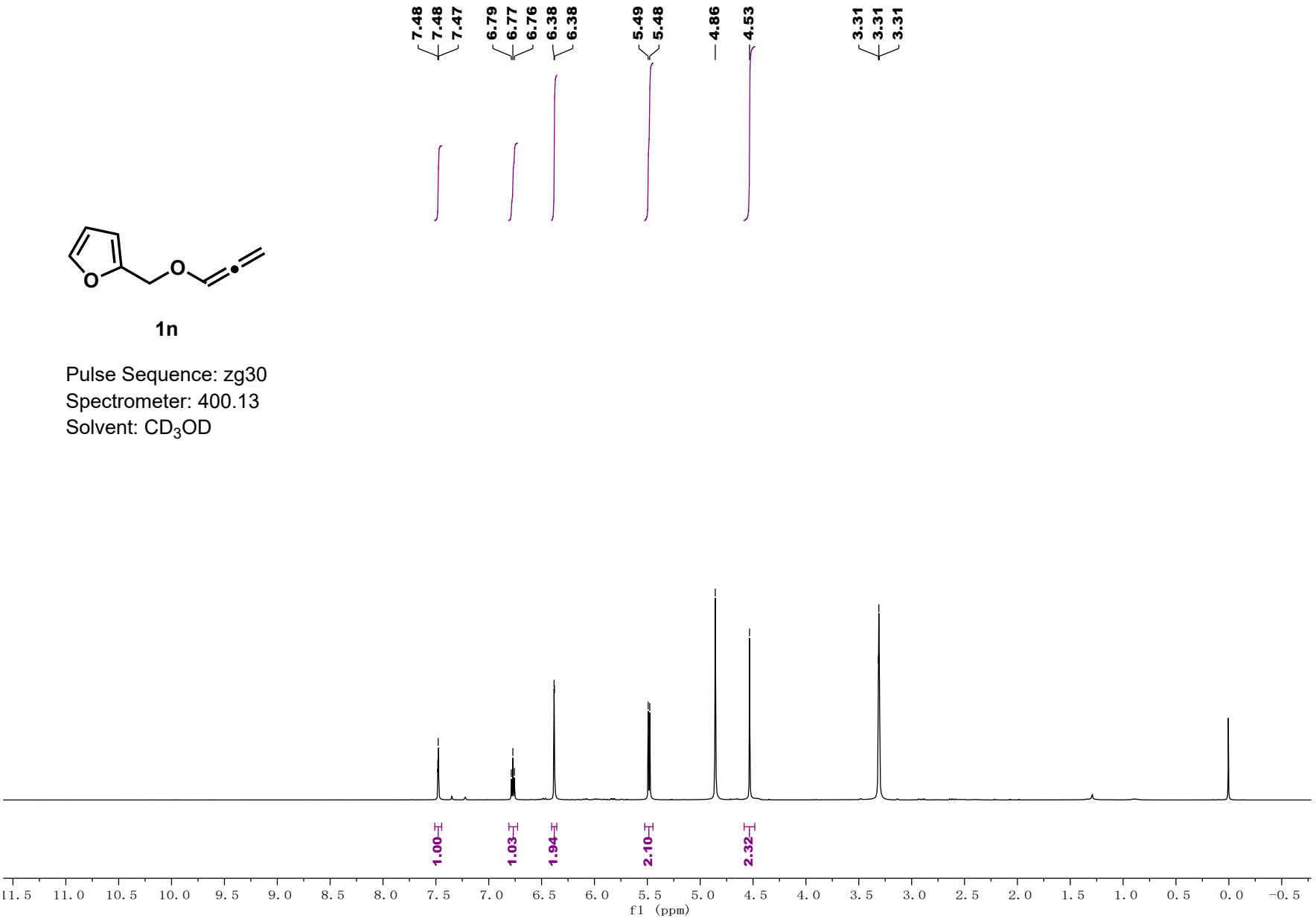

201.47
137.42
128.51
127.96
127.90
121.74
91.20
77.48
77.16
76.84
70.73
O
1l
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

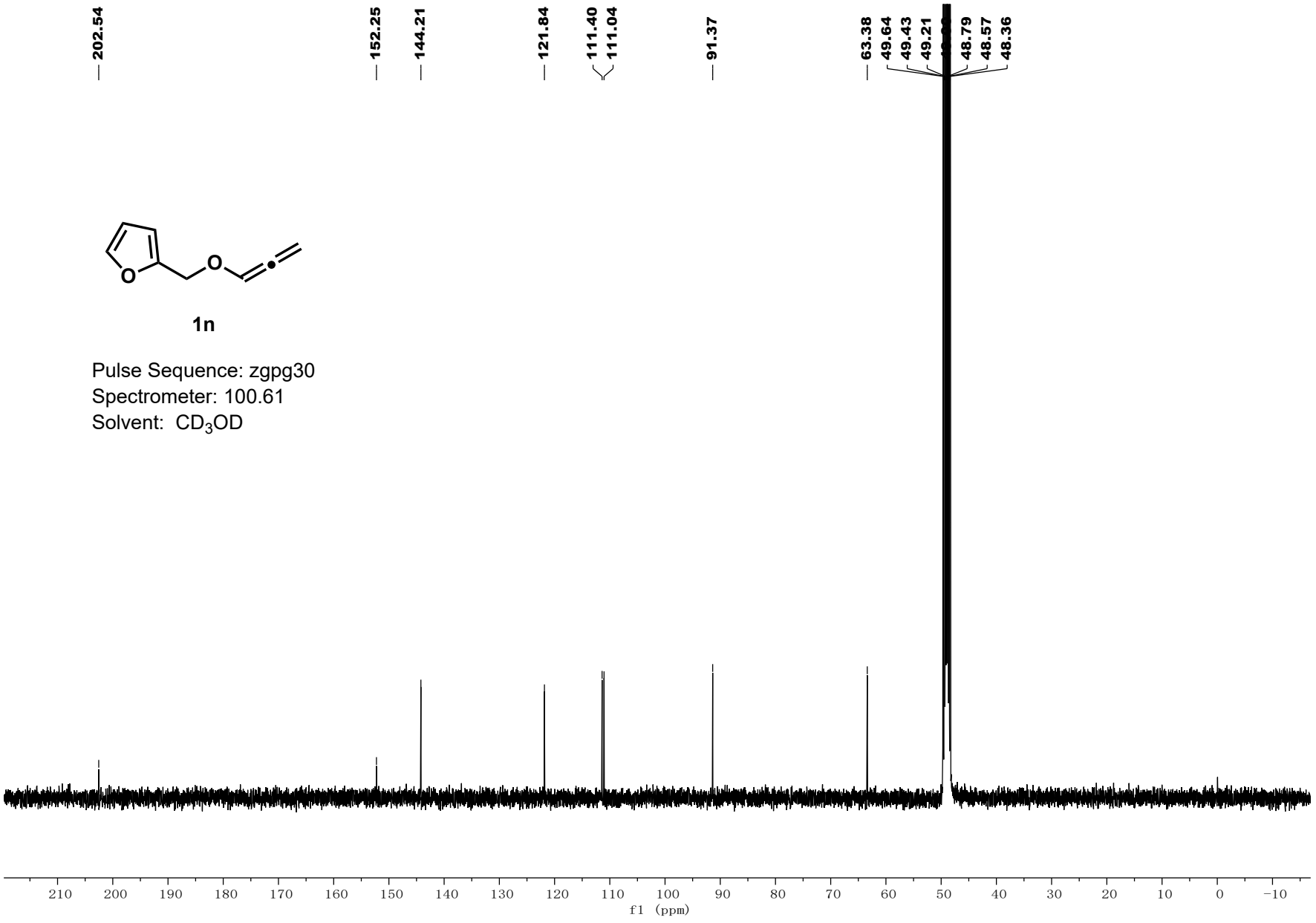

7.29
7.27
7.25
7.19
7.17
6.75
6.74
6.72
5.40
5.39
3.58
3.57
3.55
2.72
2.70
2.68
1.98
1.98
1.97
1.95
1.95
1.93
1.91
O
1m
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.21
3.30
0.64
2.00
2.29
2.44
2.43
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


201.51
141.80
128.59
128.47
125.97
121.71
90.57
77.48
77.16
76.84
68.00
32.31
30.95
O
1m
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1n

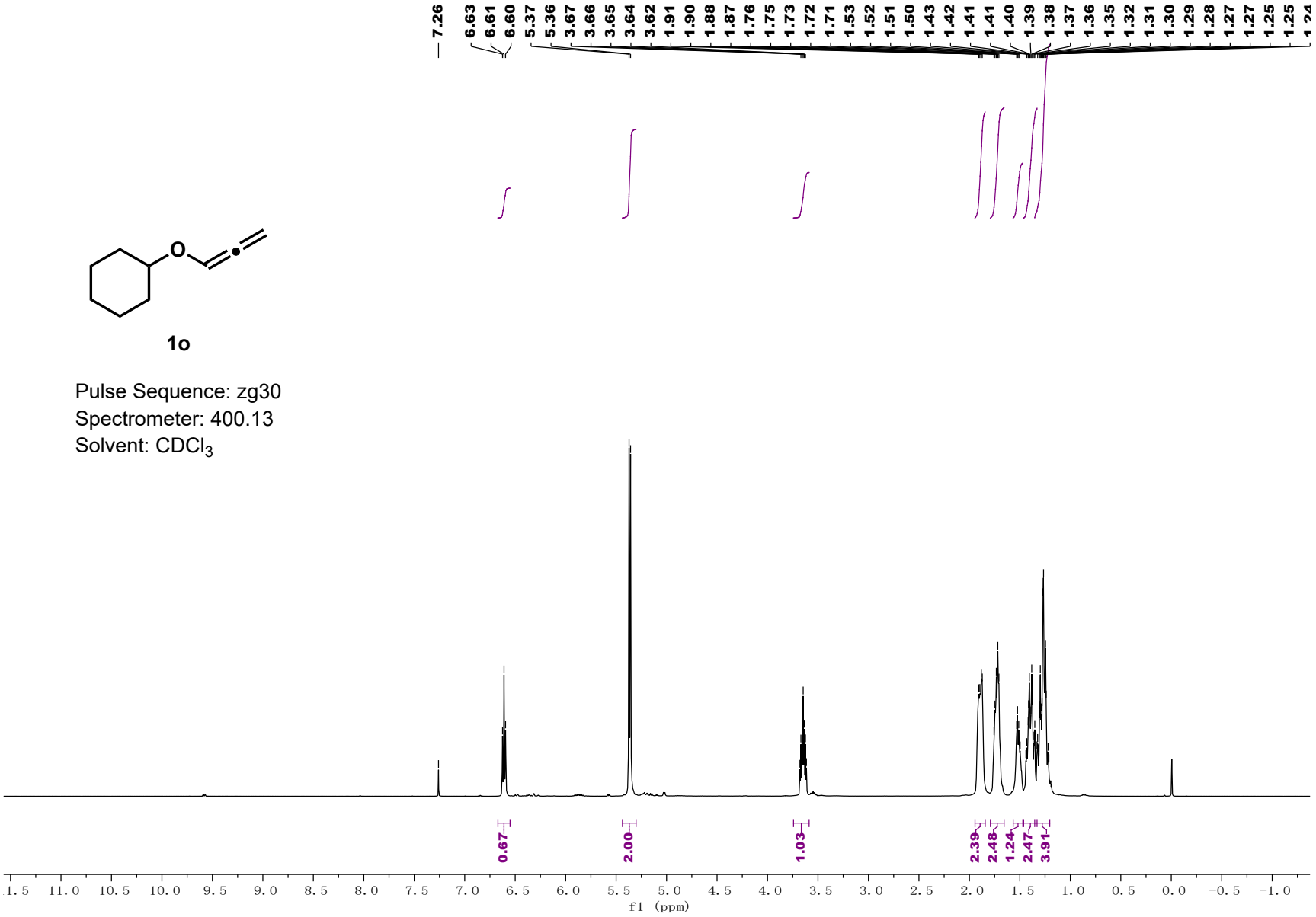
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CD_3OD

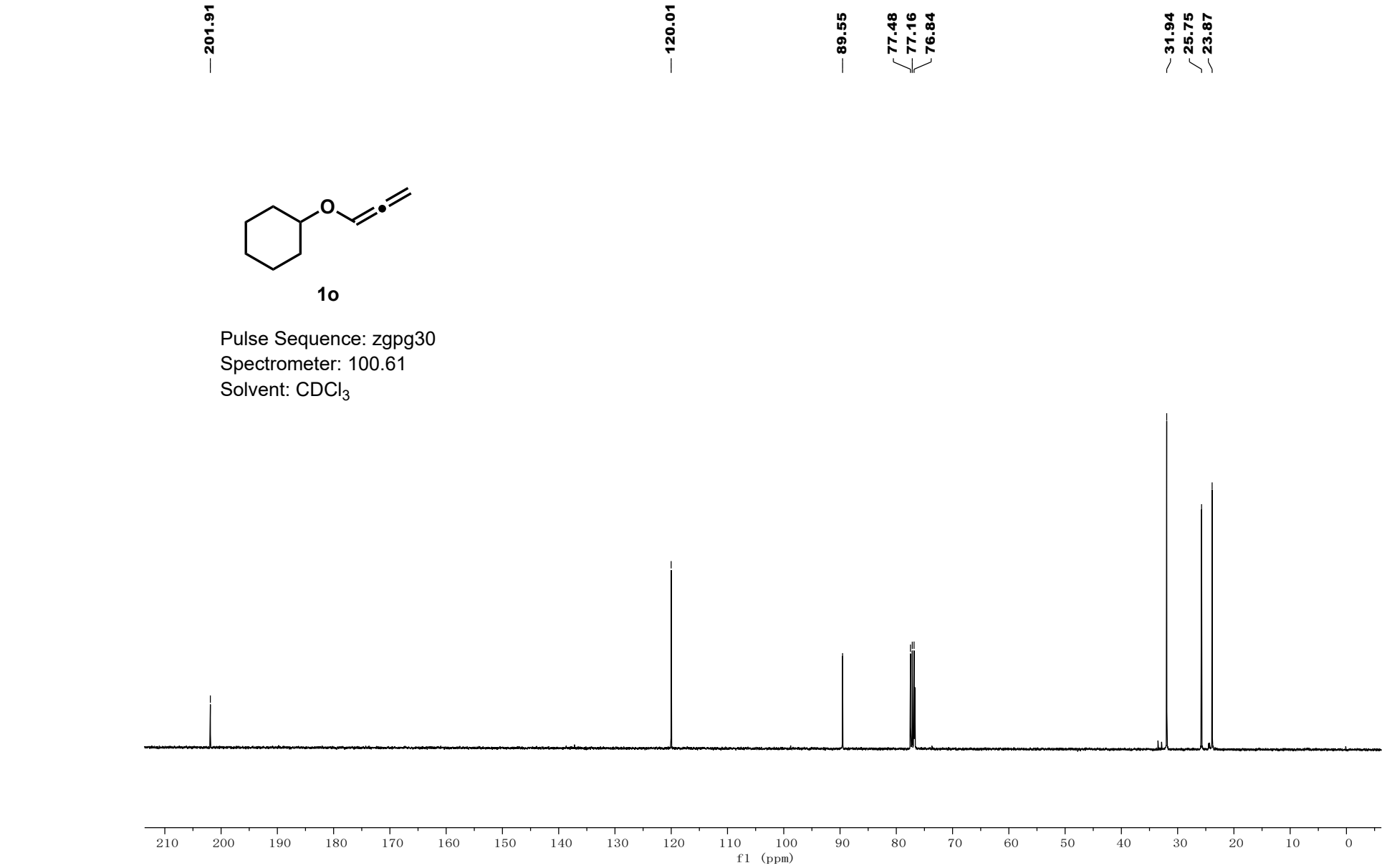


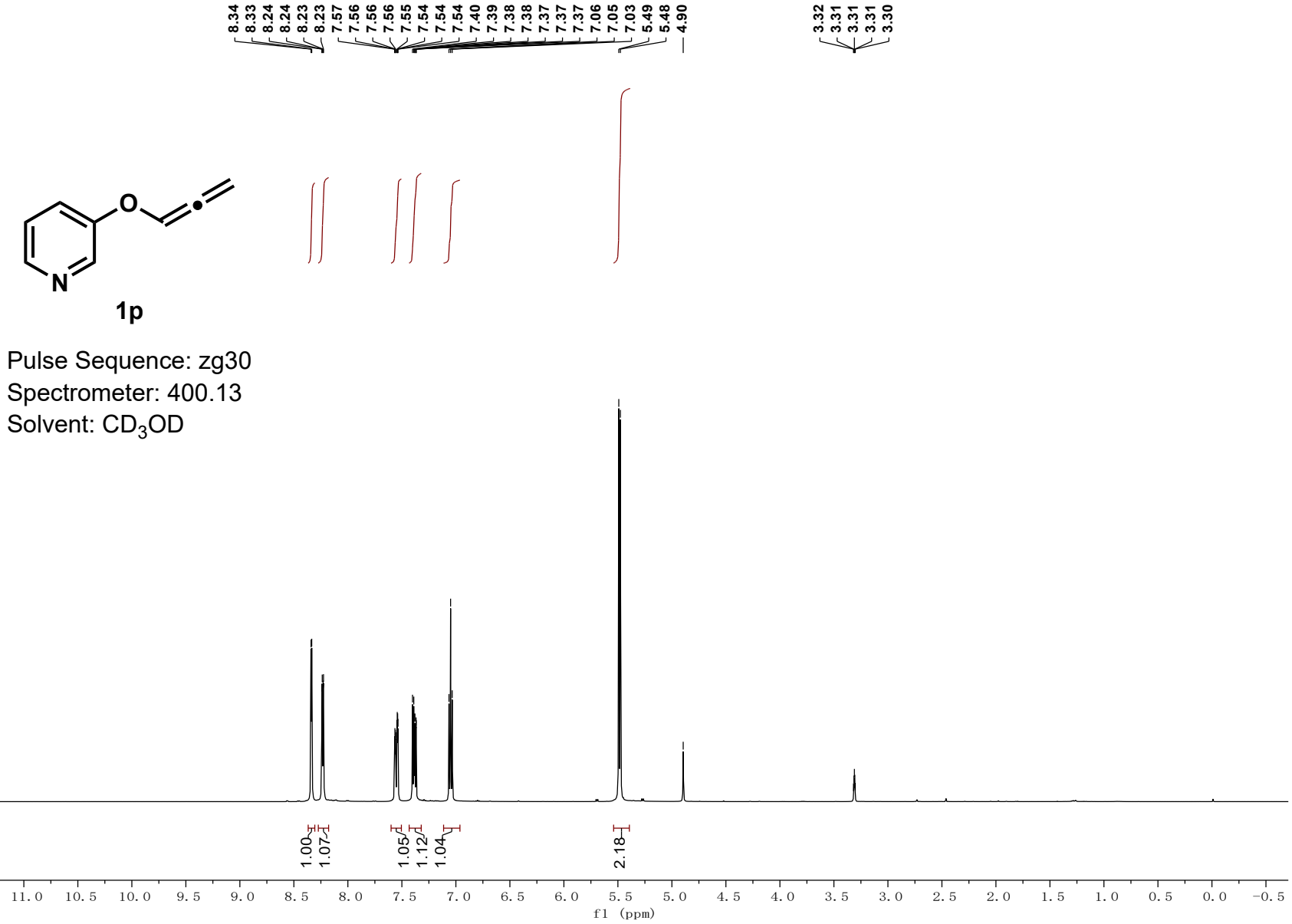

202.54
152.25
144.21
121.84
111.40
111.04
91.37
63.38
49.64
49.43
49.21
48.79
48.57
48.36
O
O
1n
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CD3OD
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

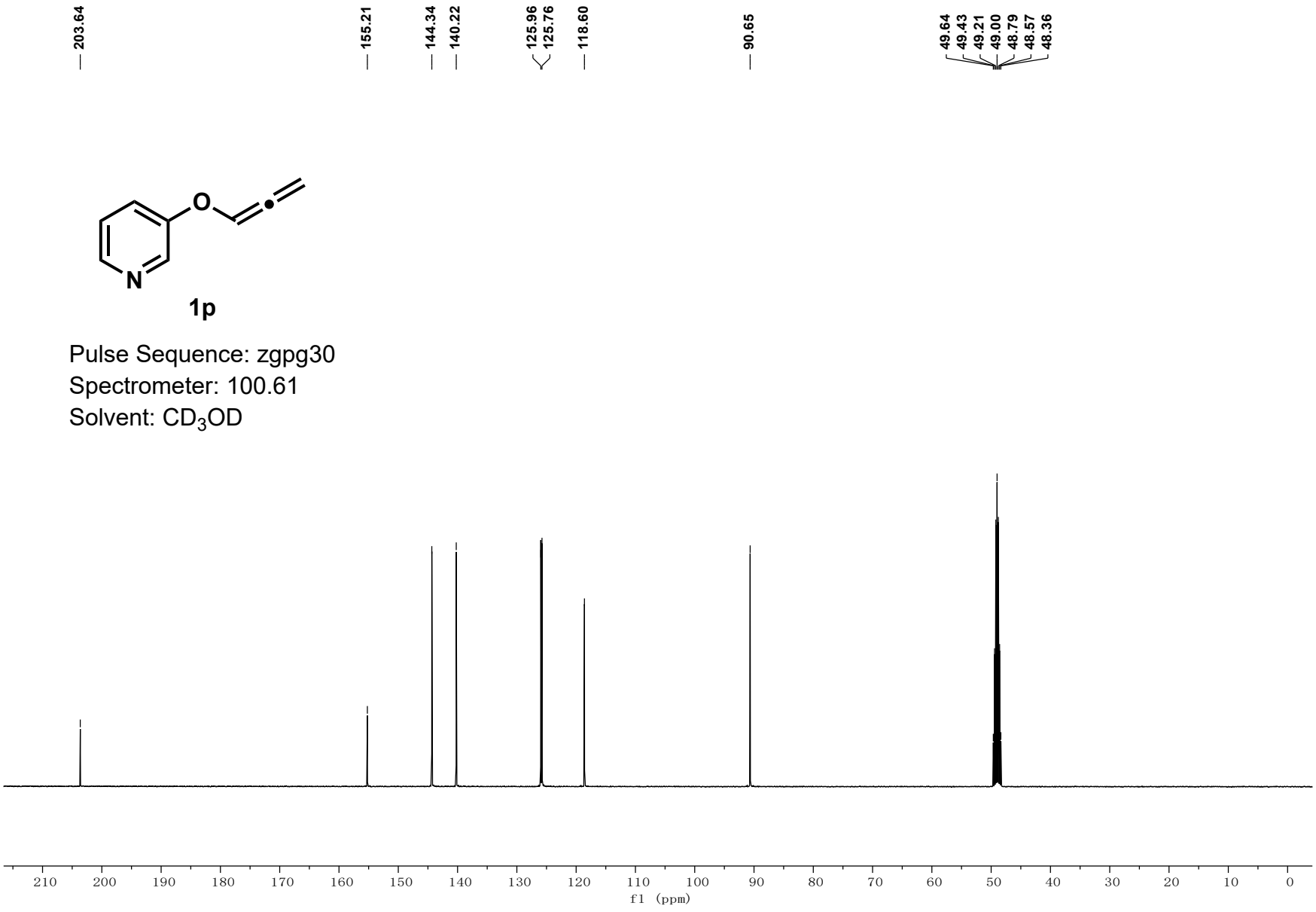
1o

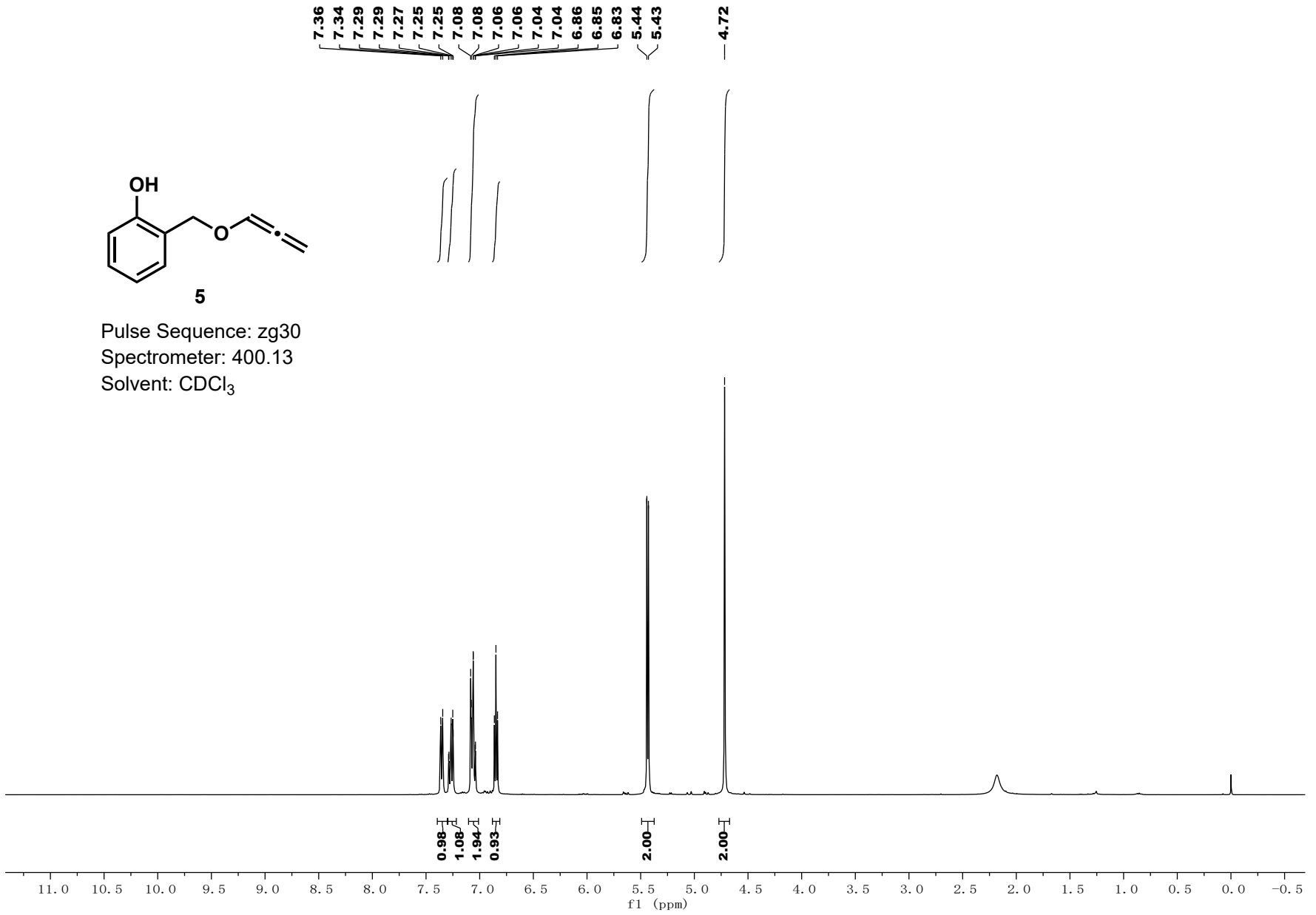
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

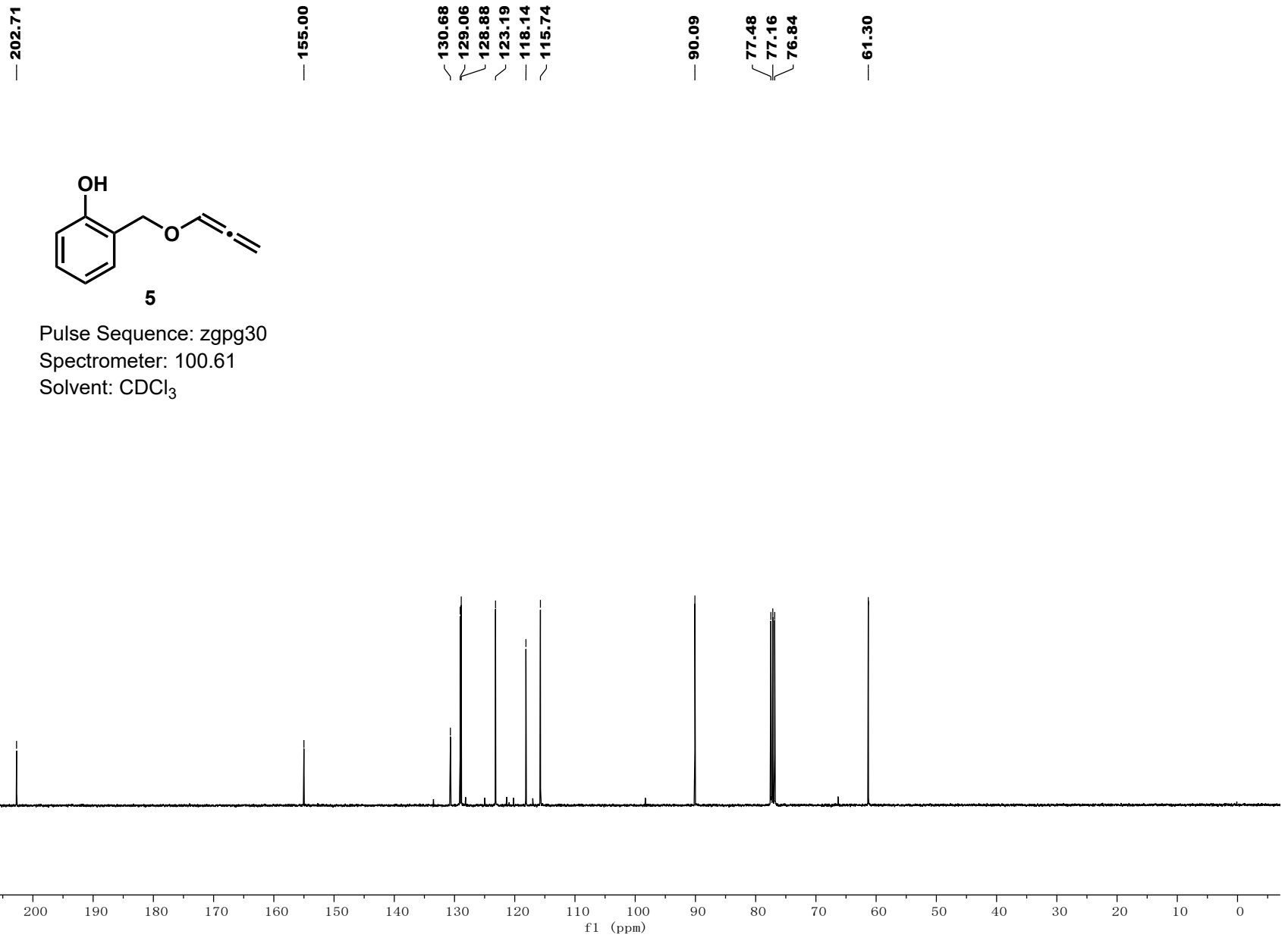


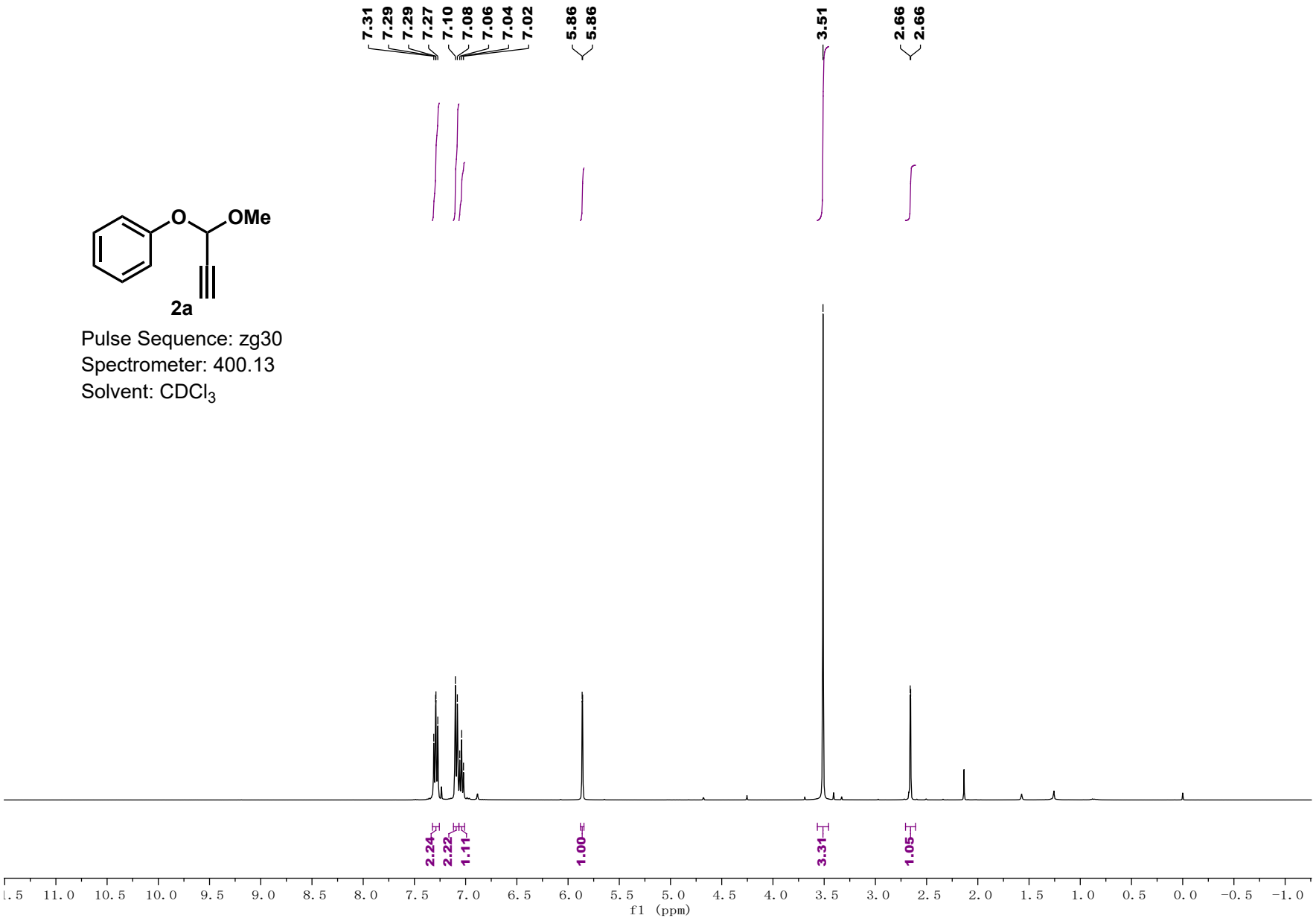

201.91
120.01
89.55
77.48
77.16
76.84
31.94
25.75
23.87
O
1o
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

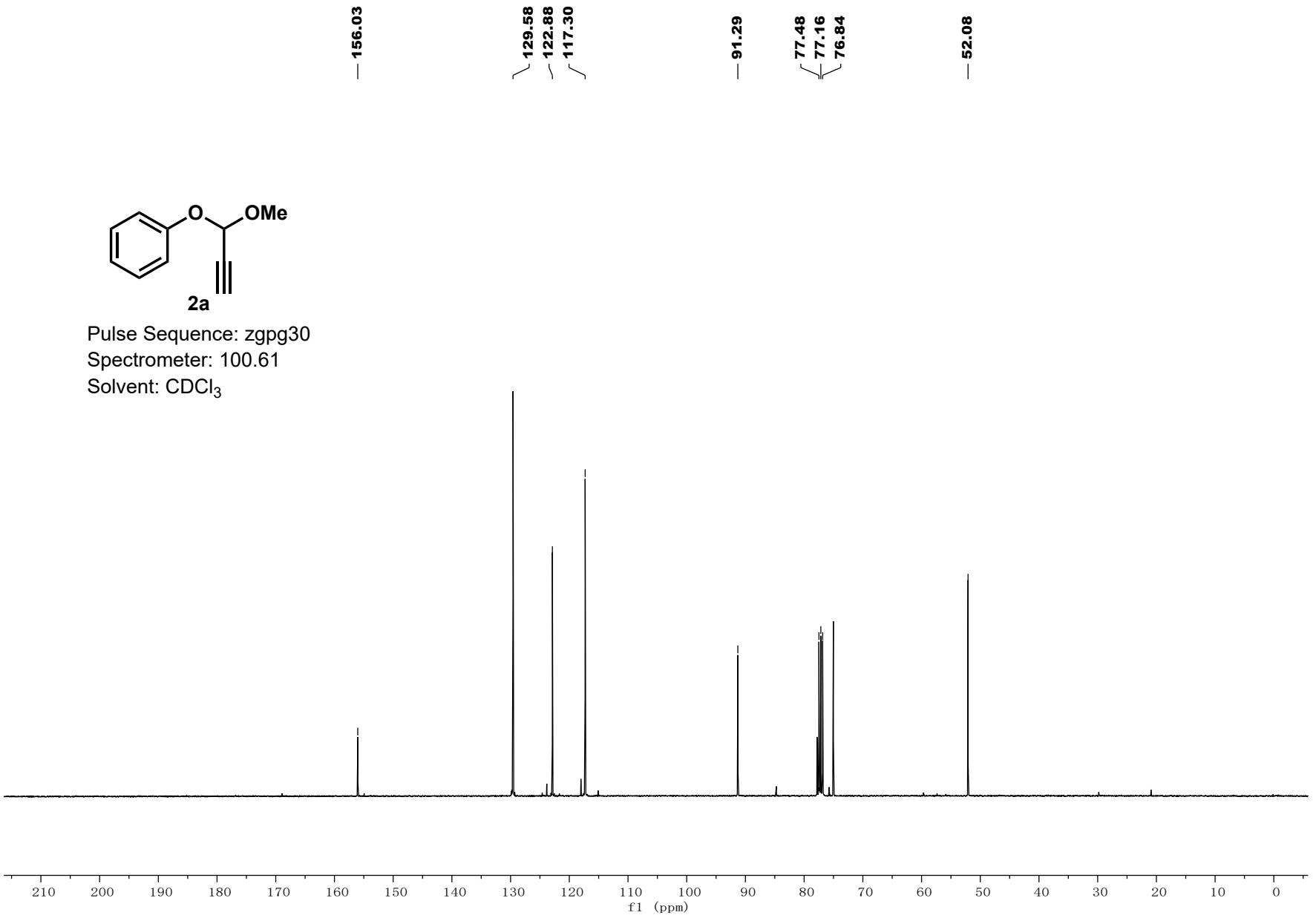

8.34
8.33
8.24
8.24
8.23
8.23
7.57
7.56
7.56
7.56
7.55
7.54
7.54
7.54
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.06
7.05
7.03
5.49
5.48
4.90
3.32
3.31
3.31
3.31
3.30
O
N
1p
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CD3OD
1.00
1.07
1.05
1.12
1.04
2.18
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
−0.5
f1 (ppm)

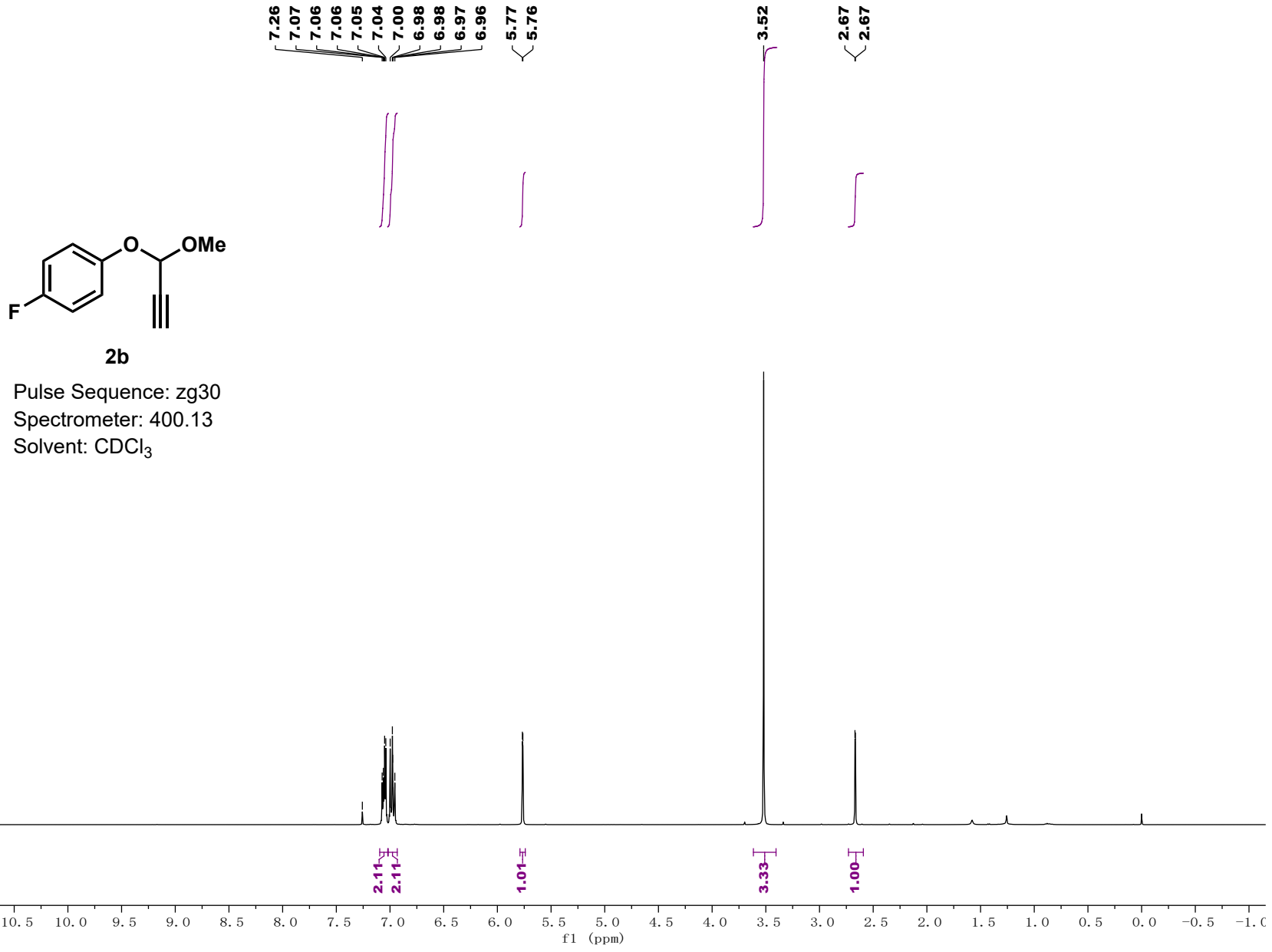

203.64
155.21
144.34
140.22
125.96
125.76
118.60
90.65
49.64
49.43
49.21
49.00
48.79
48.57
48.36
O
N
1p
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CD3OD
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

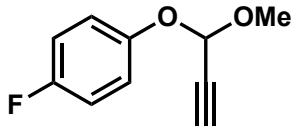

7.36
7.34
7.29
7.29
7.27
7.25
7.25
7.08
7.08
7.06
7.06
7.04
7.04
6.86
6.85
6.83
5.44
5.43
4.72
OH
O
5
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
0.98
1.08
1.94
0.93
2.00
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


202.71
155.00
130.68
129.06
128.88
123.19
118.14
115.74
90.09
77.48
77.16
76.84
61.30
OH
O
5
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.31
7.29
7.29
7.27
7.10
7.08
7.06
7.04
7.02
5.86
5.86
3.51
2.66
2.66
O
OMe
2a
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.24
2.22
1.11
1.00
3.31
1.05
f1 (ppm)

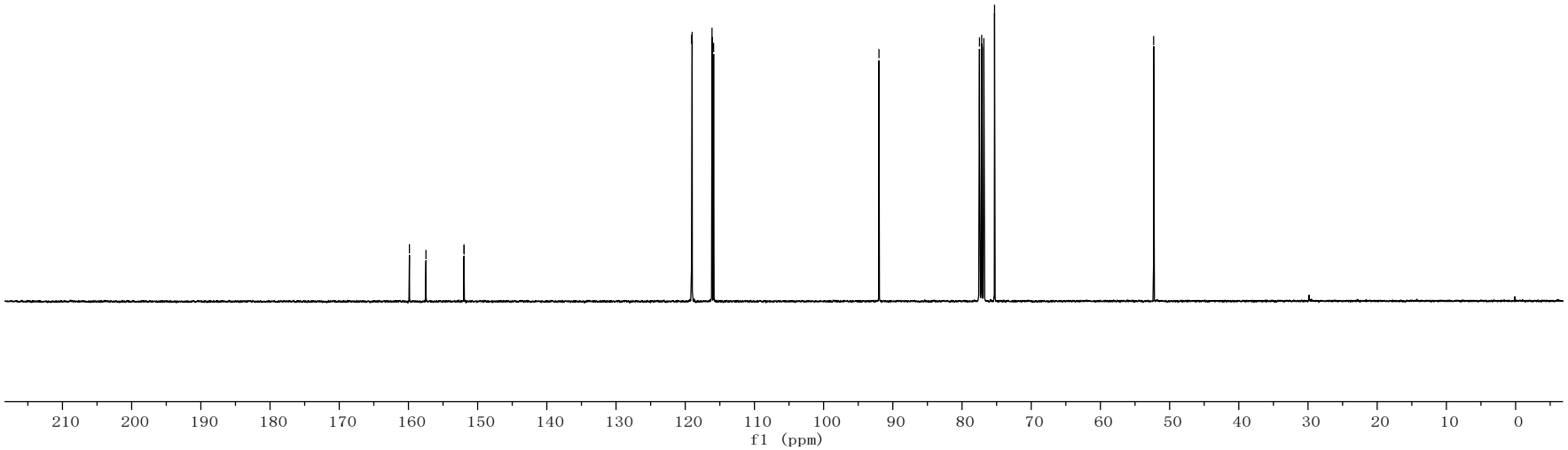

156.03
129.58
122.88
117.30
91.29
77.48
77.16
76.84
52.08
O
OMe
2a
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
7.07
7.06
7.06
7.05
7.04
7.00
6.98
6.98
6.97
6.96
5.77
5.76
3.52
2.67
2.67
O
OMe
F
2b
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.11
2.11
1.01
3.33
1.00
11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)



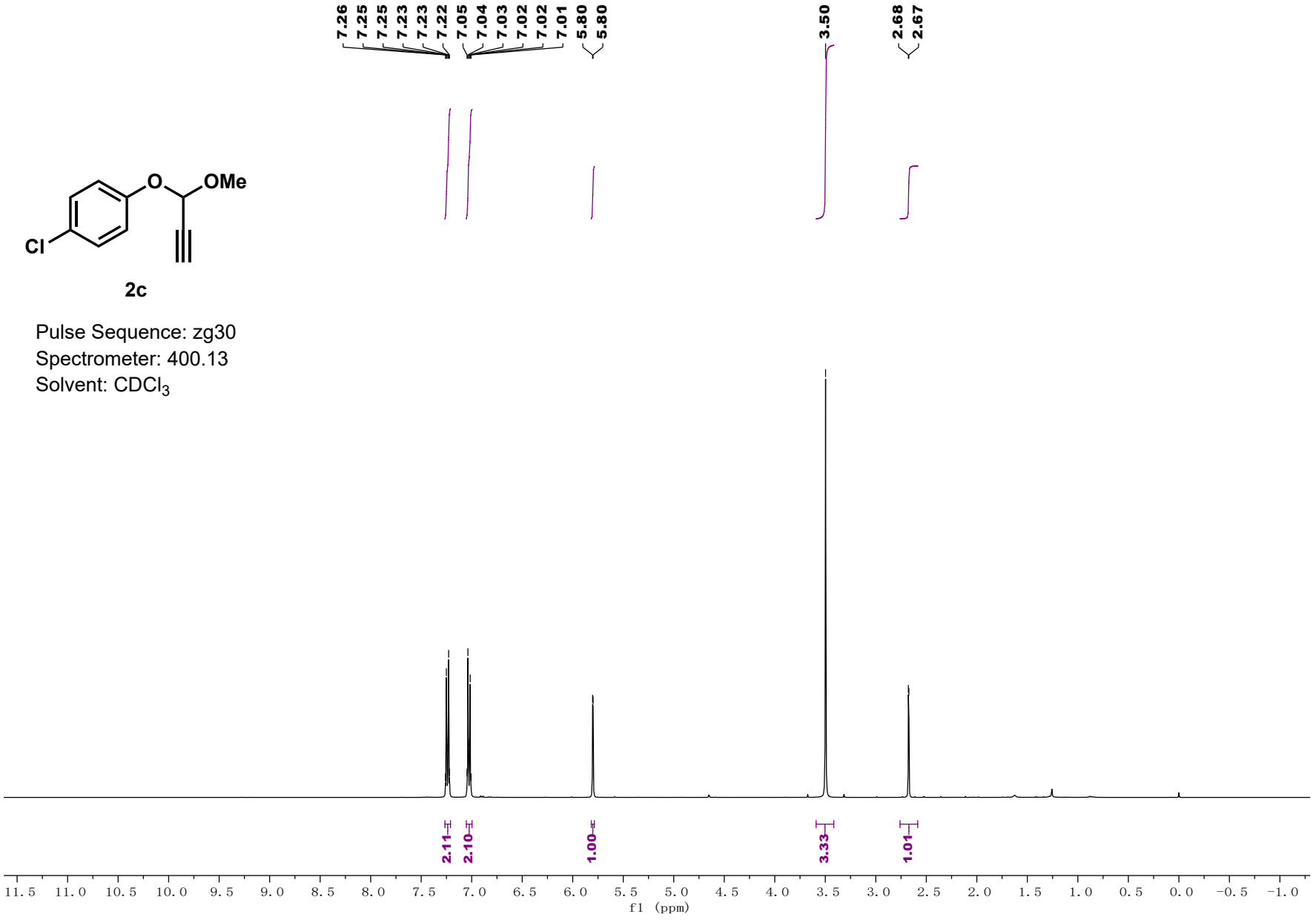
2b

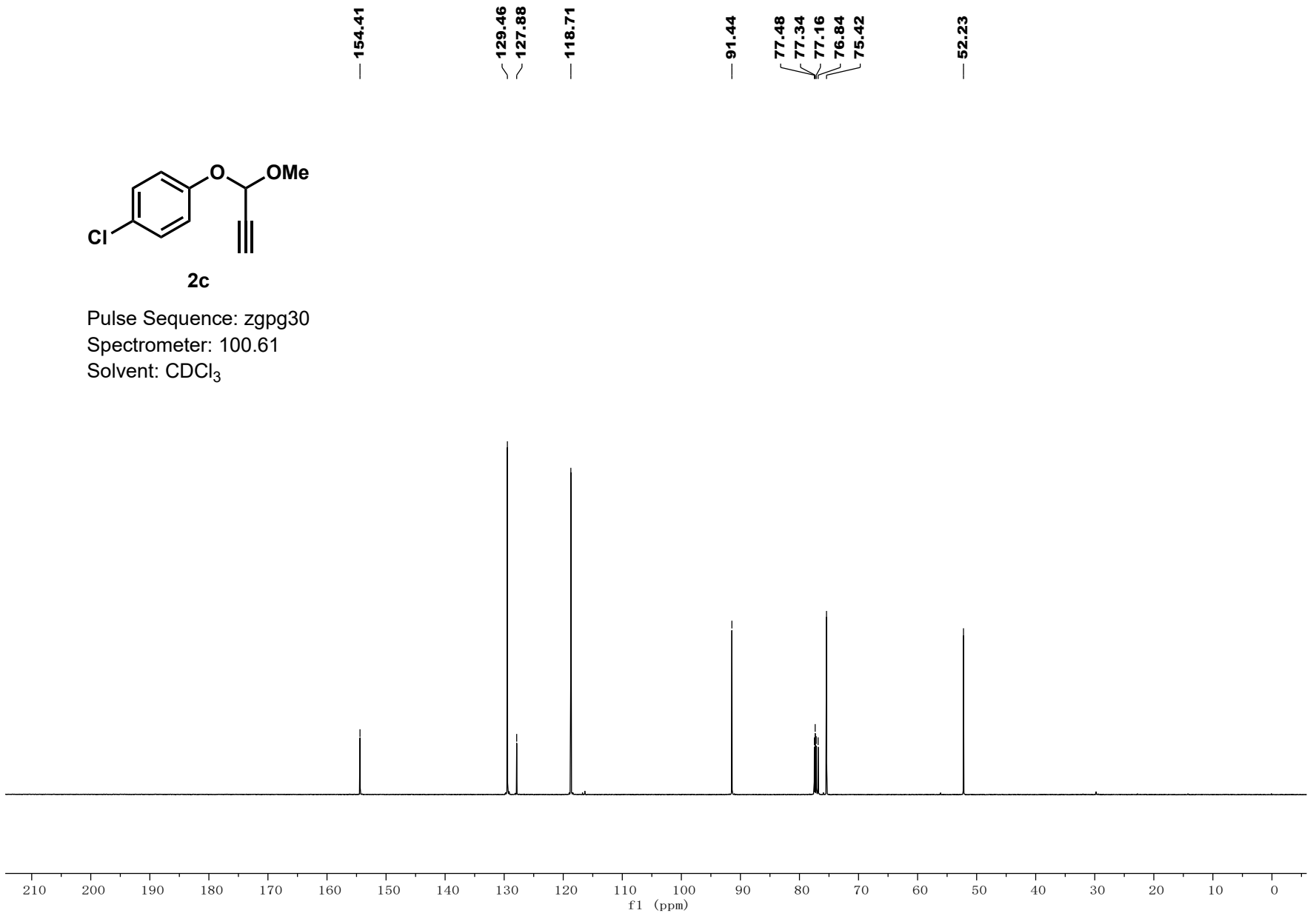
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: $CDCl_3$



2c

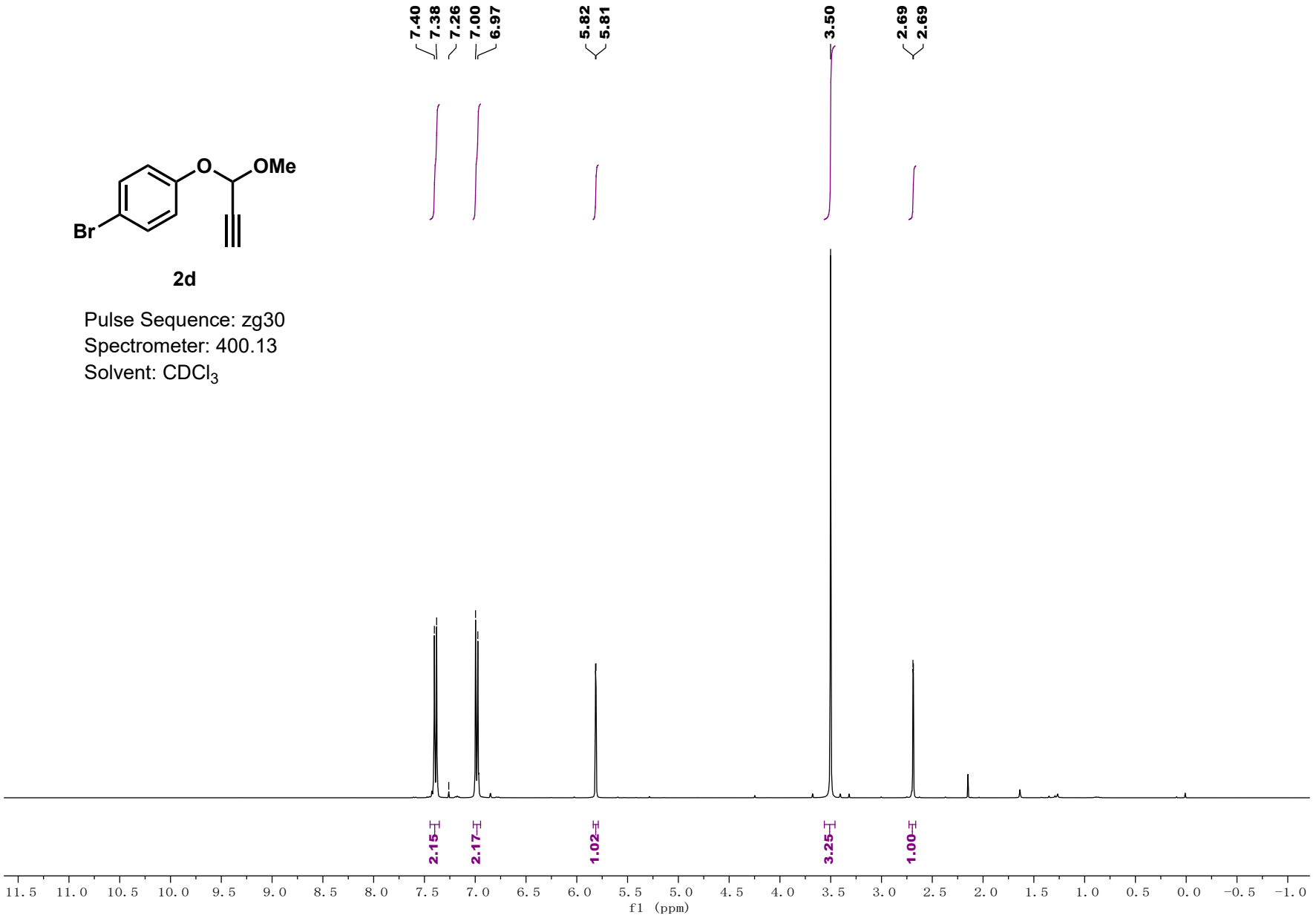
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

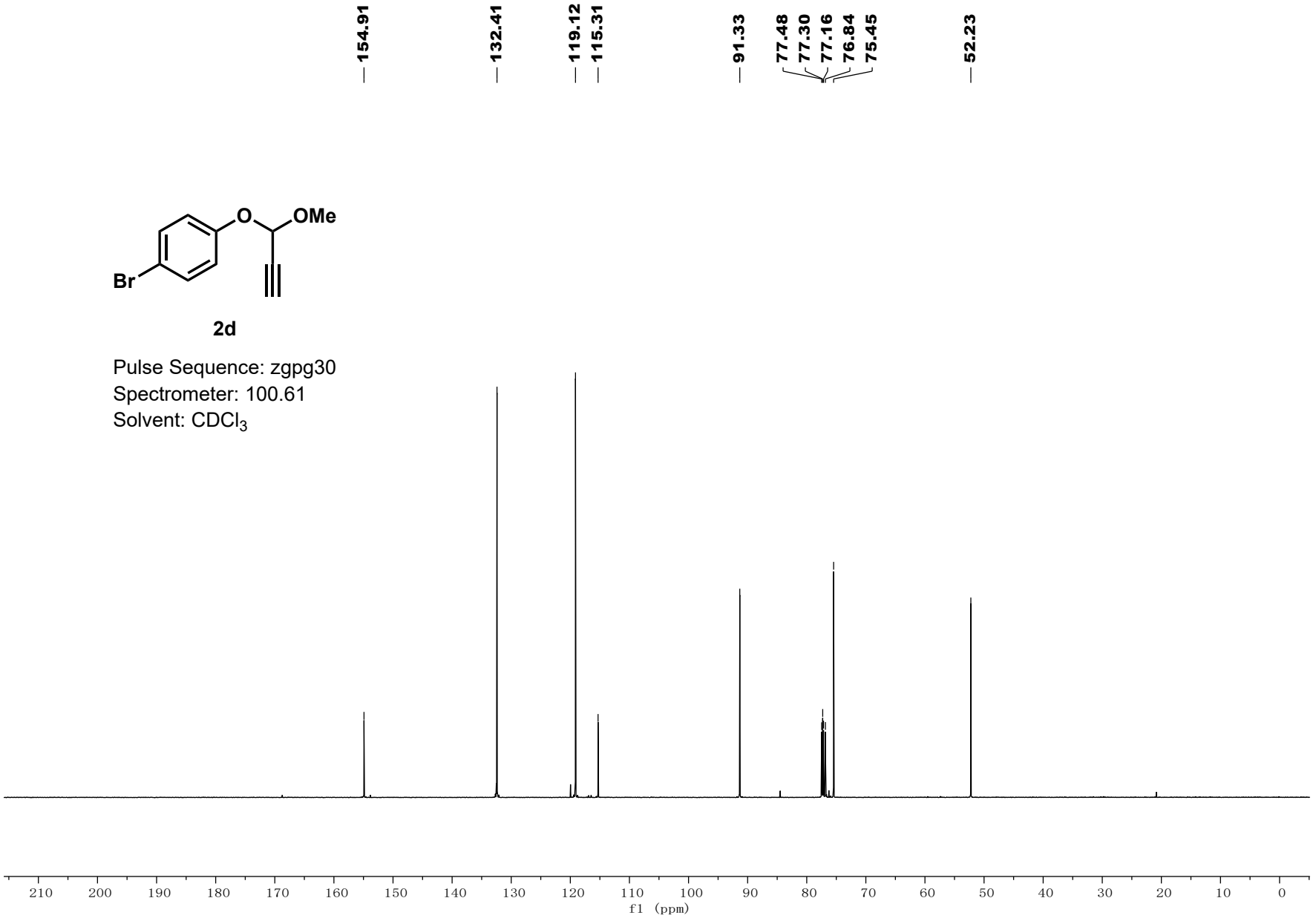



154.41
129.46
127.88
118.71
91.44
77.48
77.34
77.16
76.84
75.42
52.23
O
OMe
Cl
2c
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2d

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

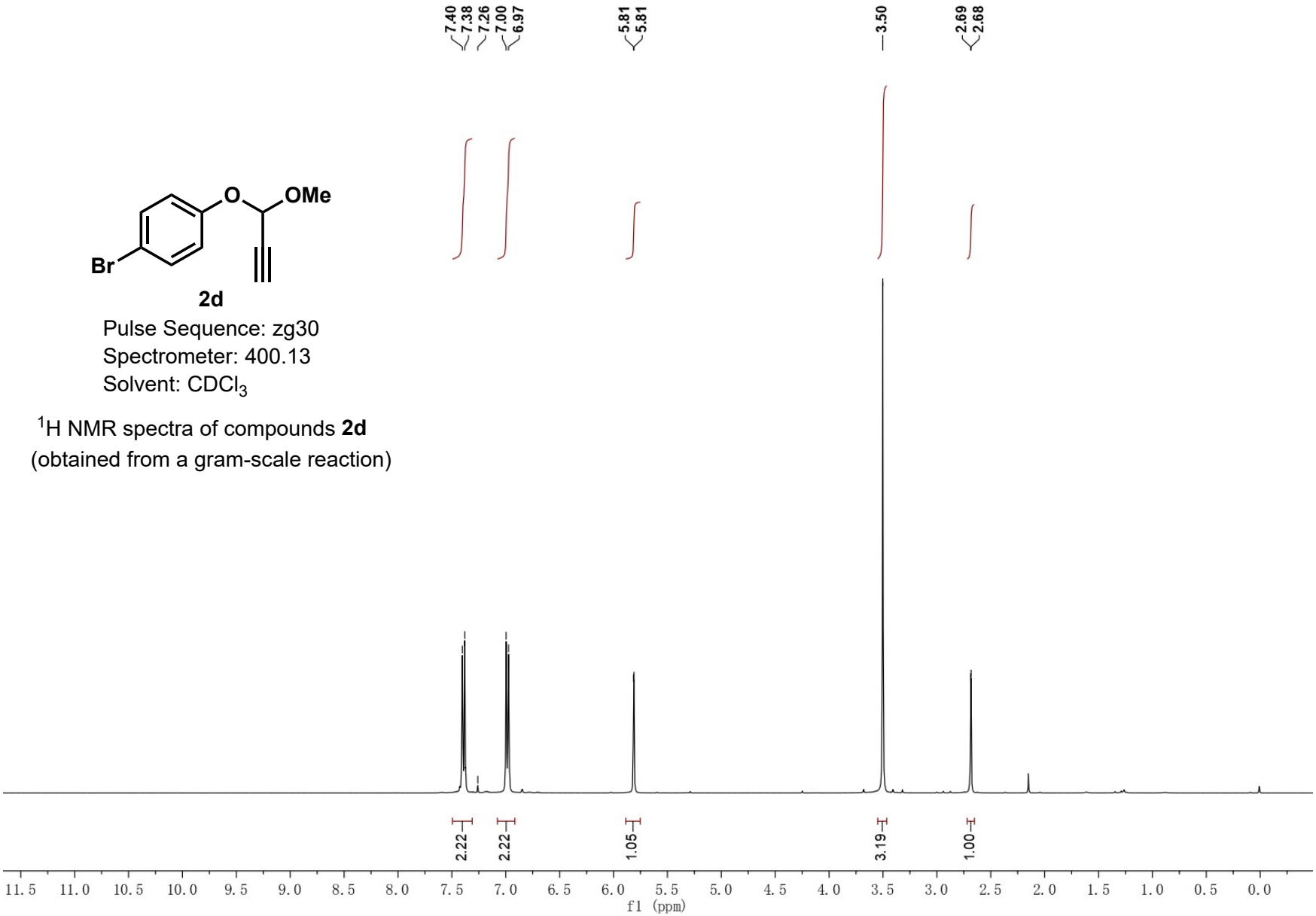



154.91
132.41
119.12
115.31
91.33
77.48
77.30
77.16
76.84
75.45
52.23
O
OMe
Br
2d
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2d

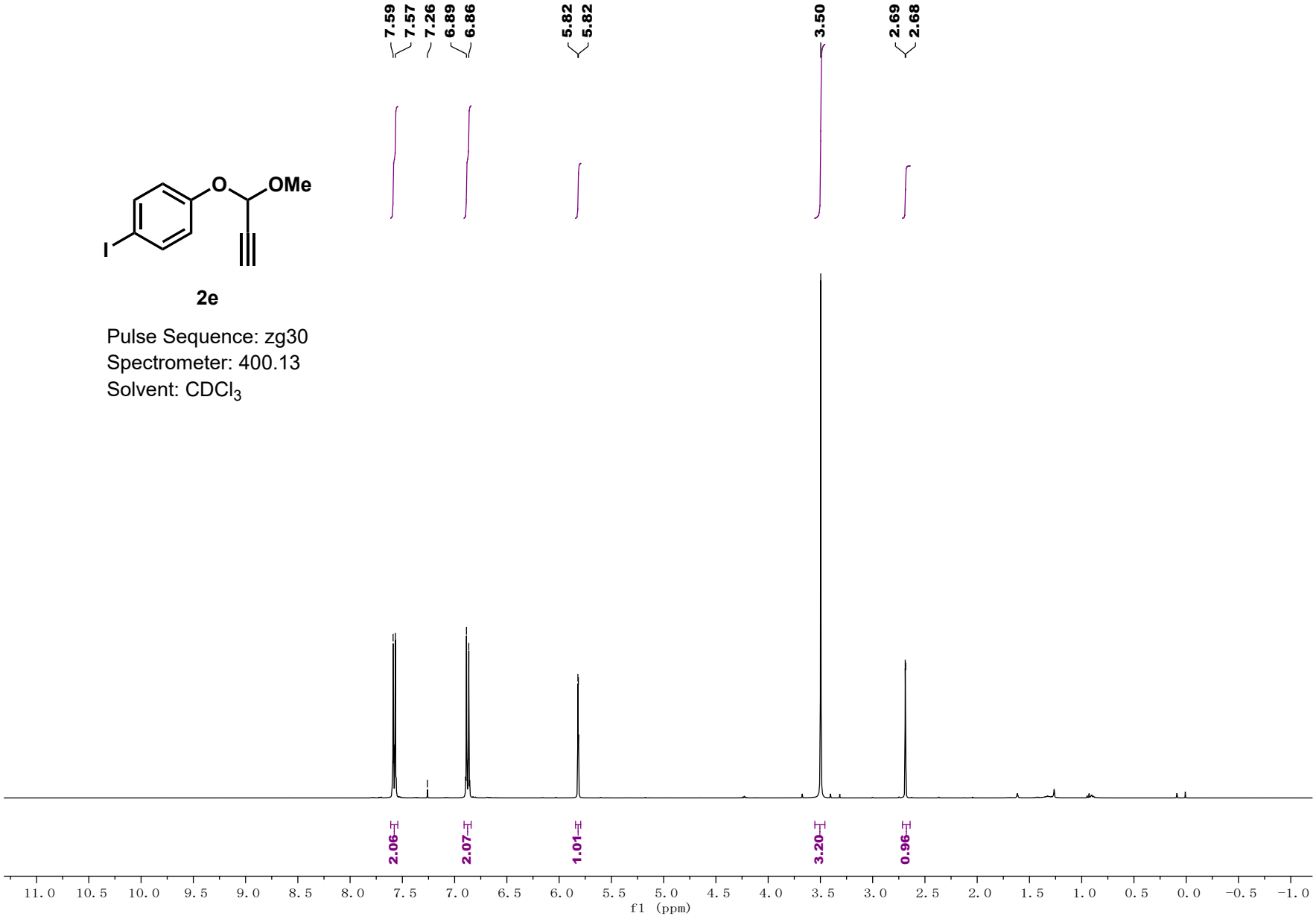
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

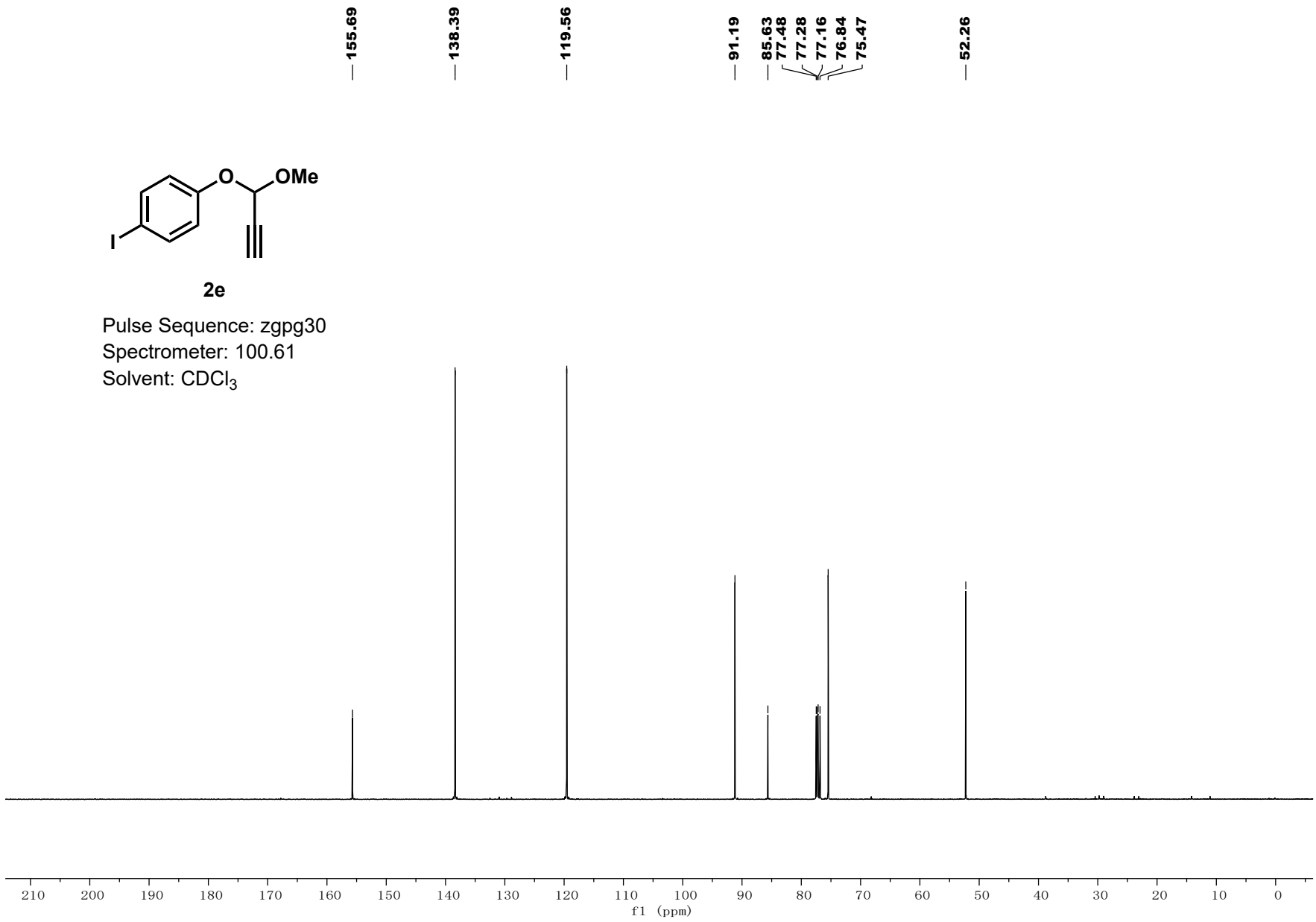
^1H NMR spectra of compounds **2d**
(obtained from a gram-scale reaction)

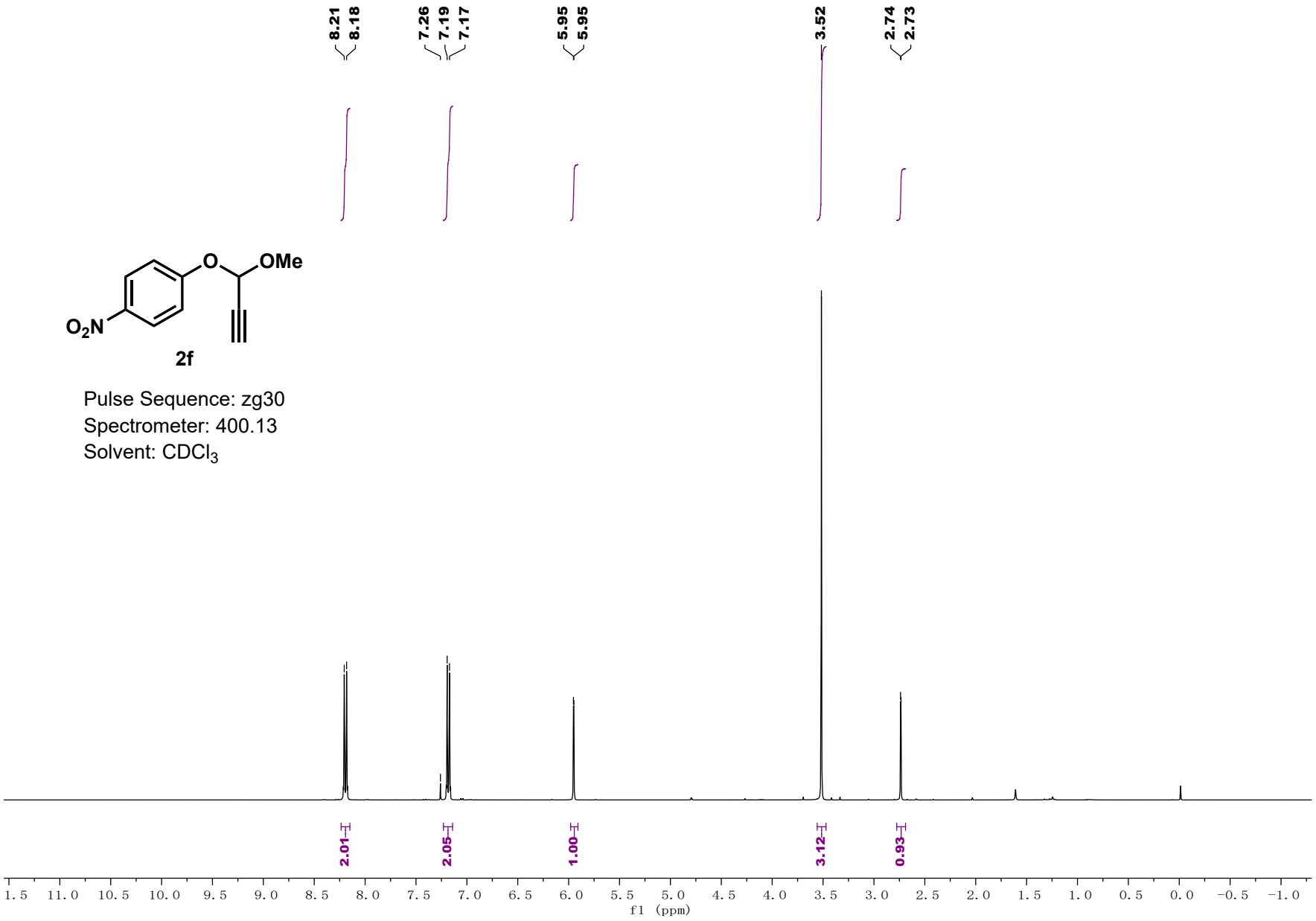


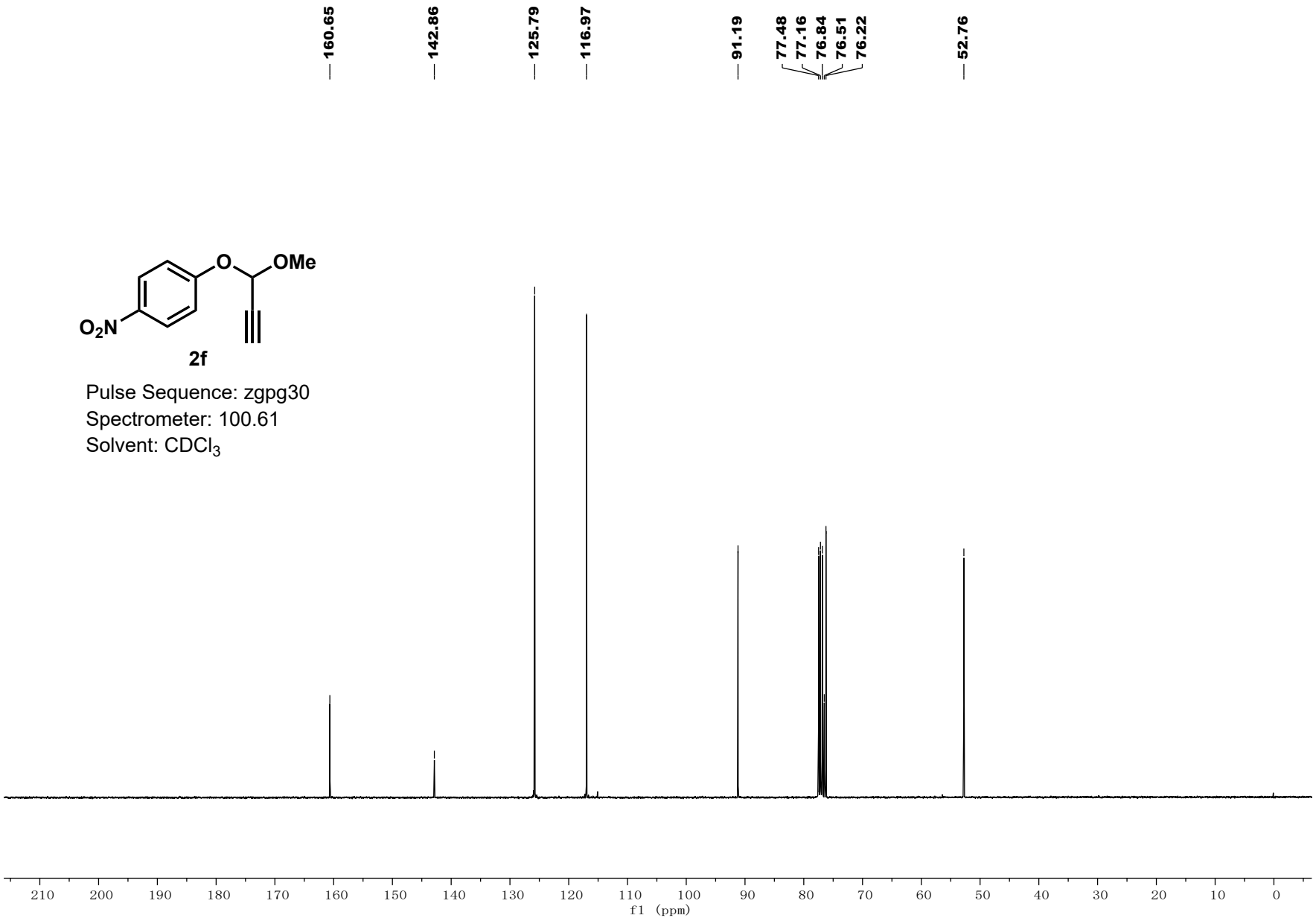
2e

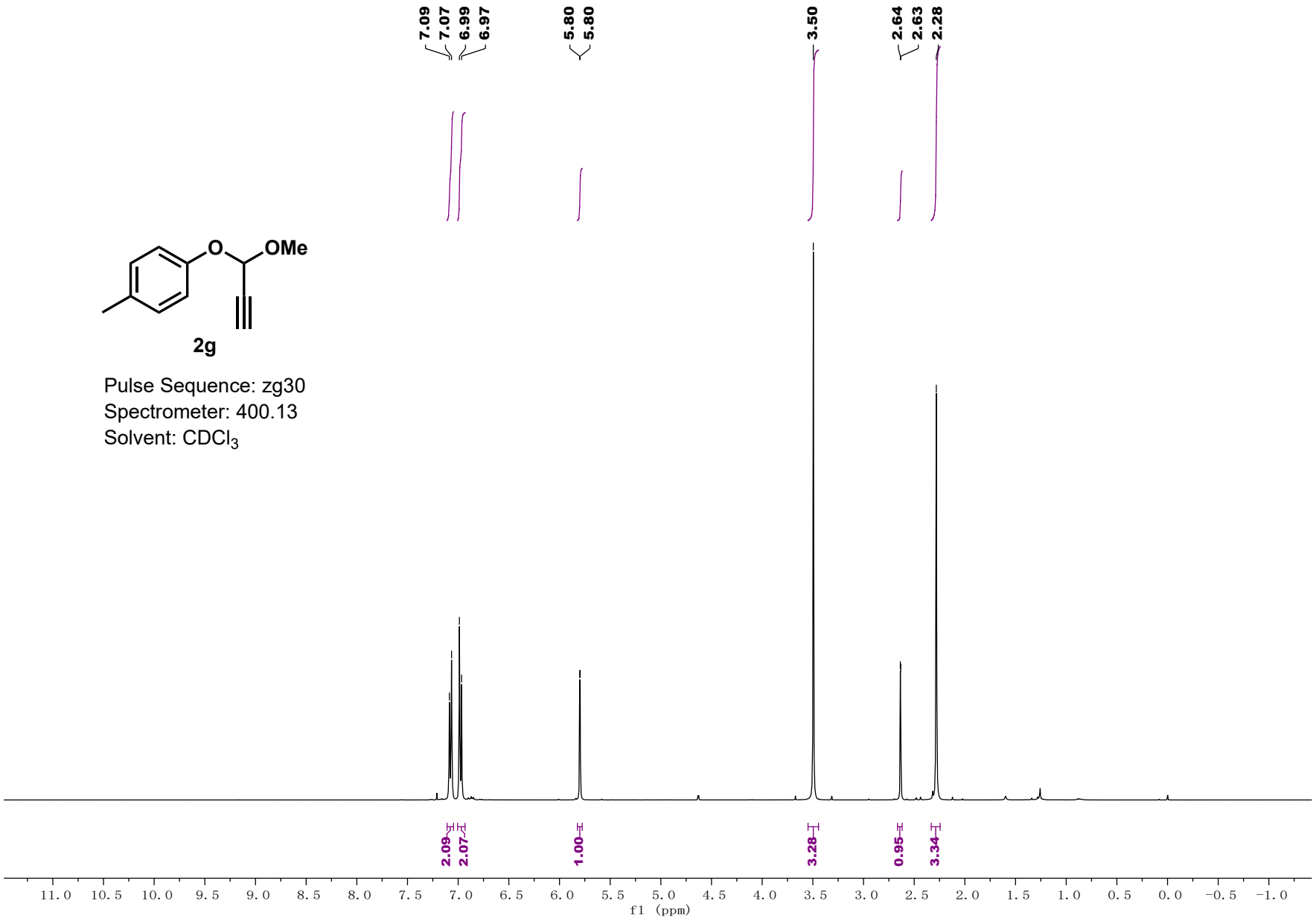
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

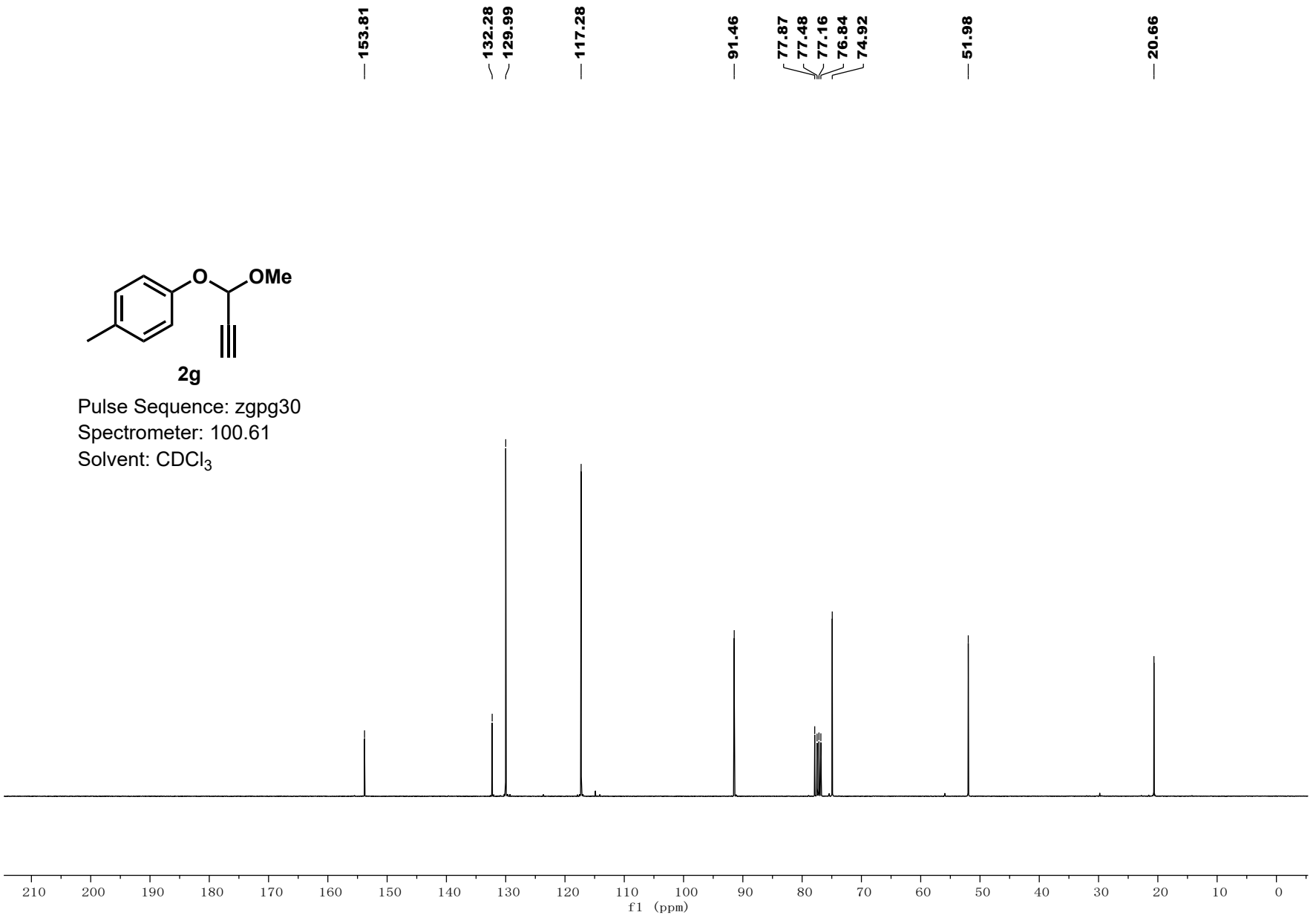


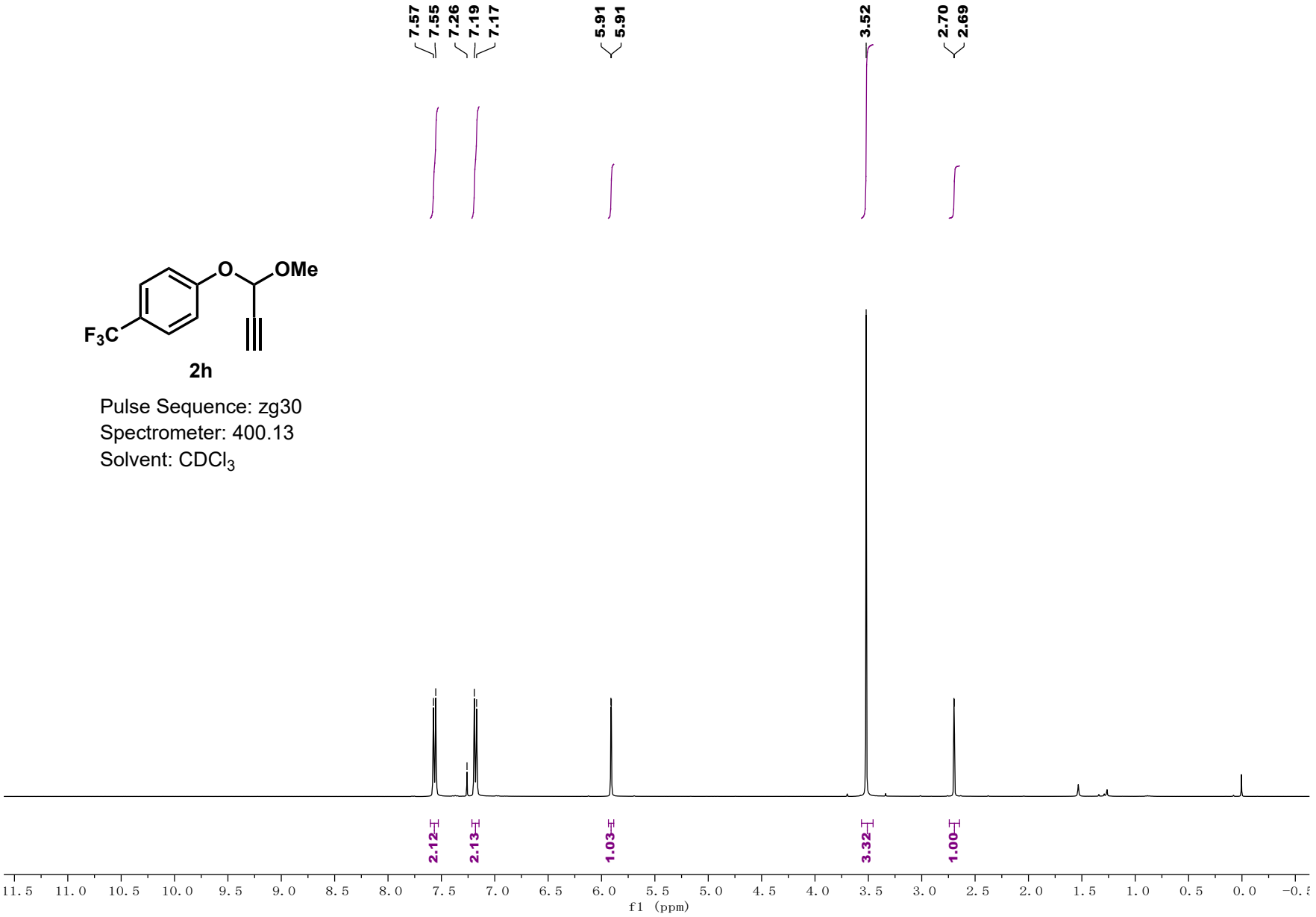

155.69
138.39
119.56
91.19
85.63
77.48
77.28
77.16
76.84
75.47
52.26
O
OMe
I
2e
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

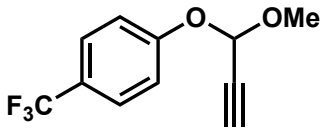

8.21
8.18
7.26
7.19
7.17
5.95
5.95
3.52
2.74
2.73
O
OMe
O2N
2f
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.01
2.05
1.00
3.12
0.93
f1 (ppm)


160.65
142.86
125.79
116.97
91.19
77.48
77.16
76.84
76.51
76.22
52.76
O
OMe
O2N
2f
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.09
7.07
6.99
6.97
5.80
5.80
3.50
2.64
2.63
2.28
O
OMe
2g
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.09
2.07
1.00
3.28
0.95
3.34
11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)

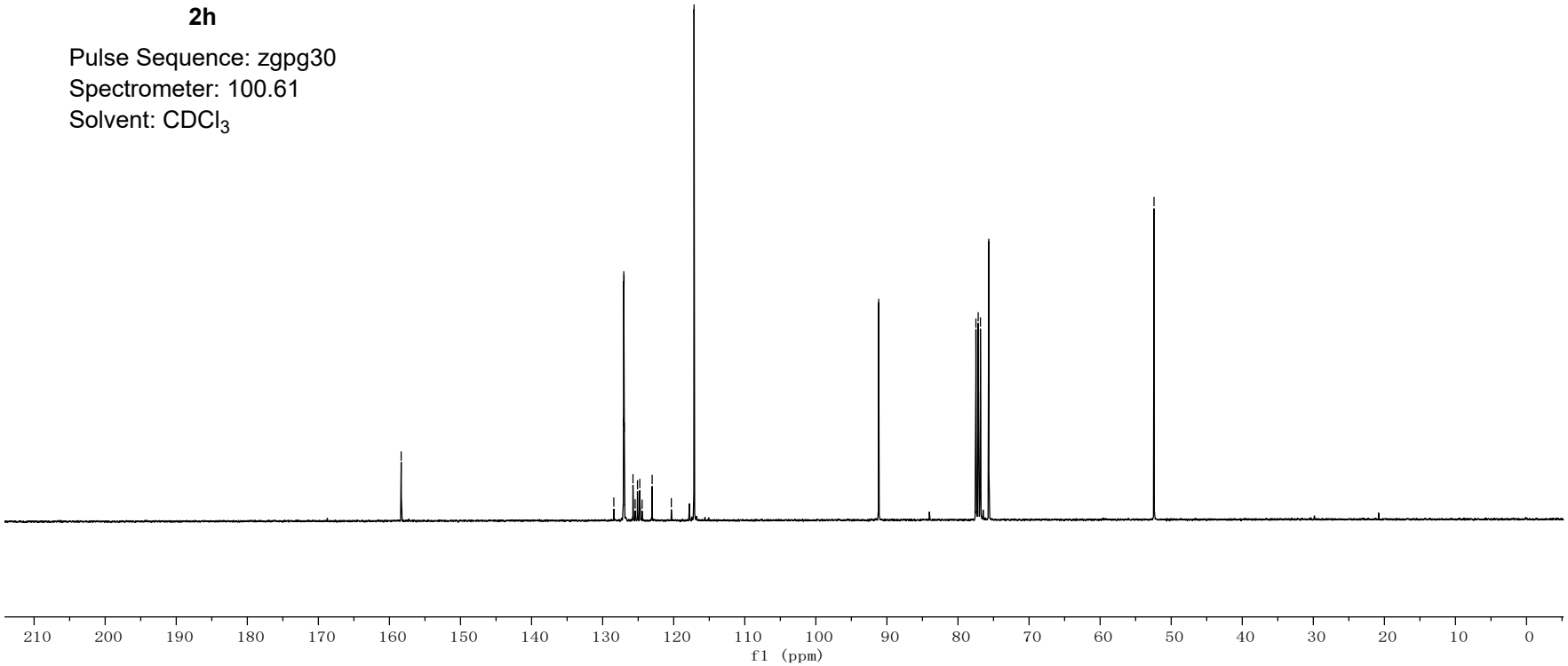

153.81
132.28
129.99
117.28
91.46
77.87
77.48
77.16
76.84
74.92
51.98
20.66
O
OMe
2g
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.57
7.55
7.26
7.19
7.17
5.91
5.91
3.52
2.70
2.69
O
OMe
F3C
2h
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.12
2.13
1.03
3.32
1.00
f1 (ppm)



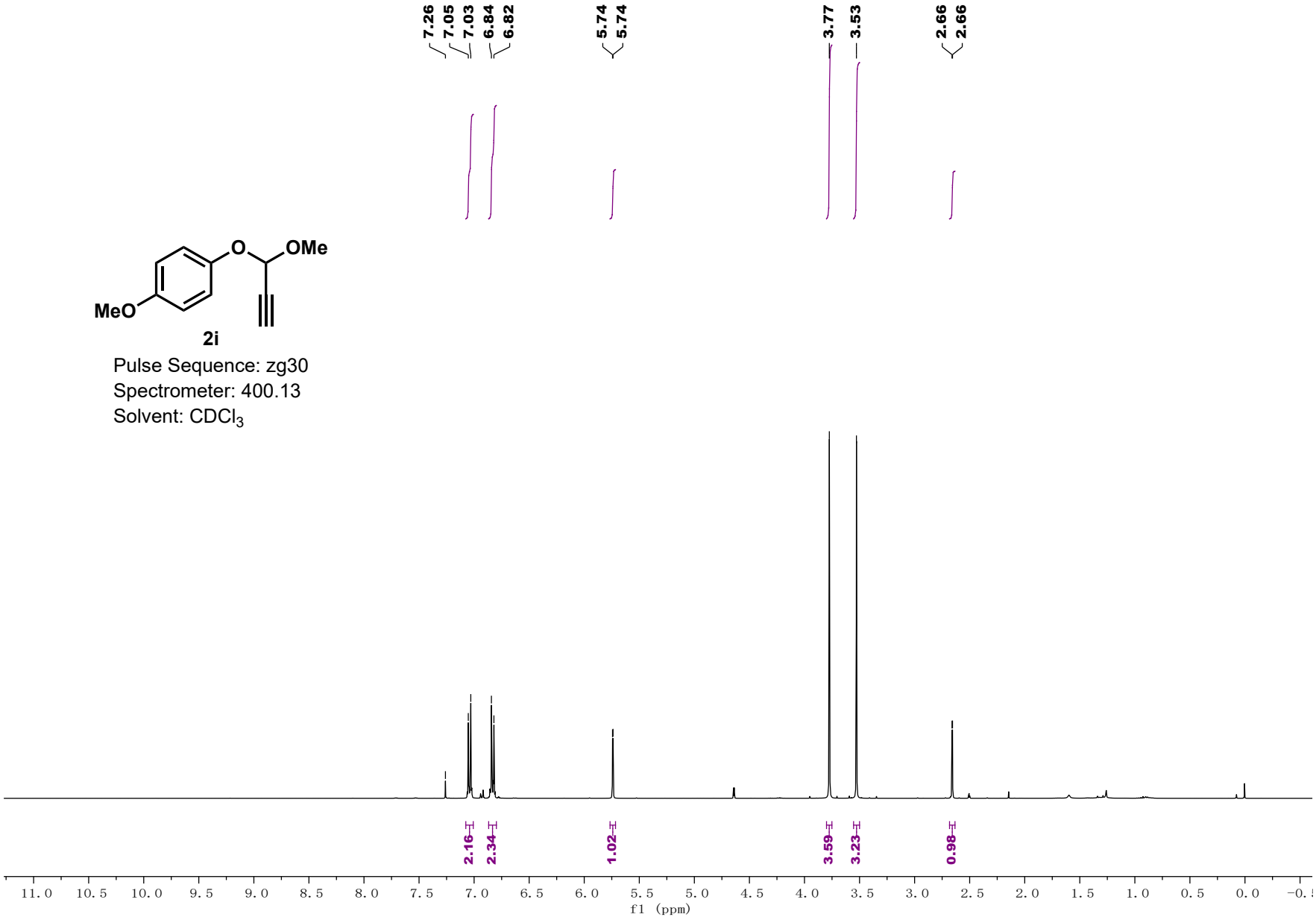
2h

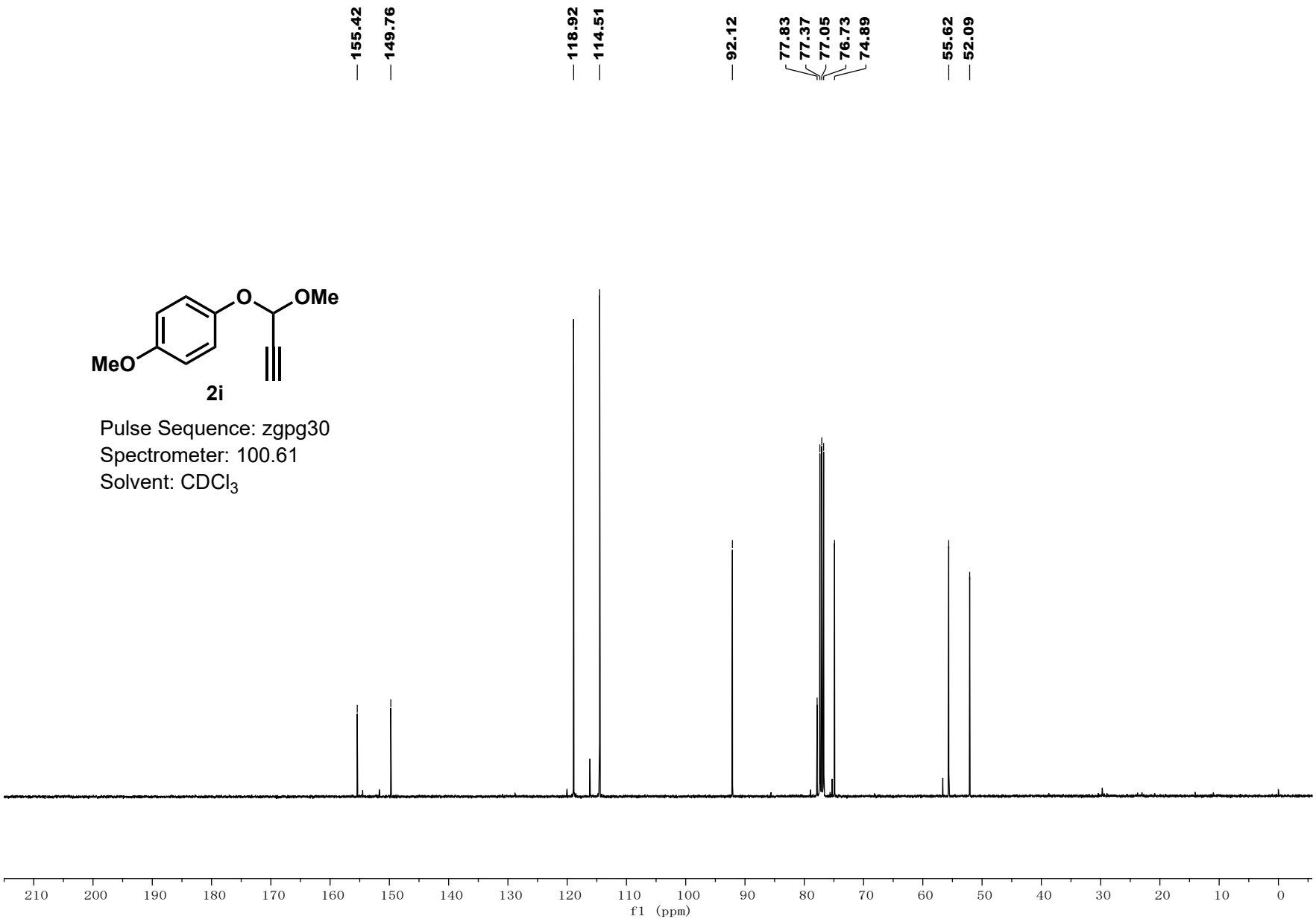
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: $CDCl_3$



2i

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

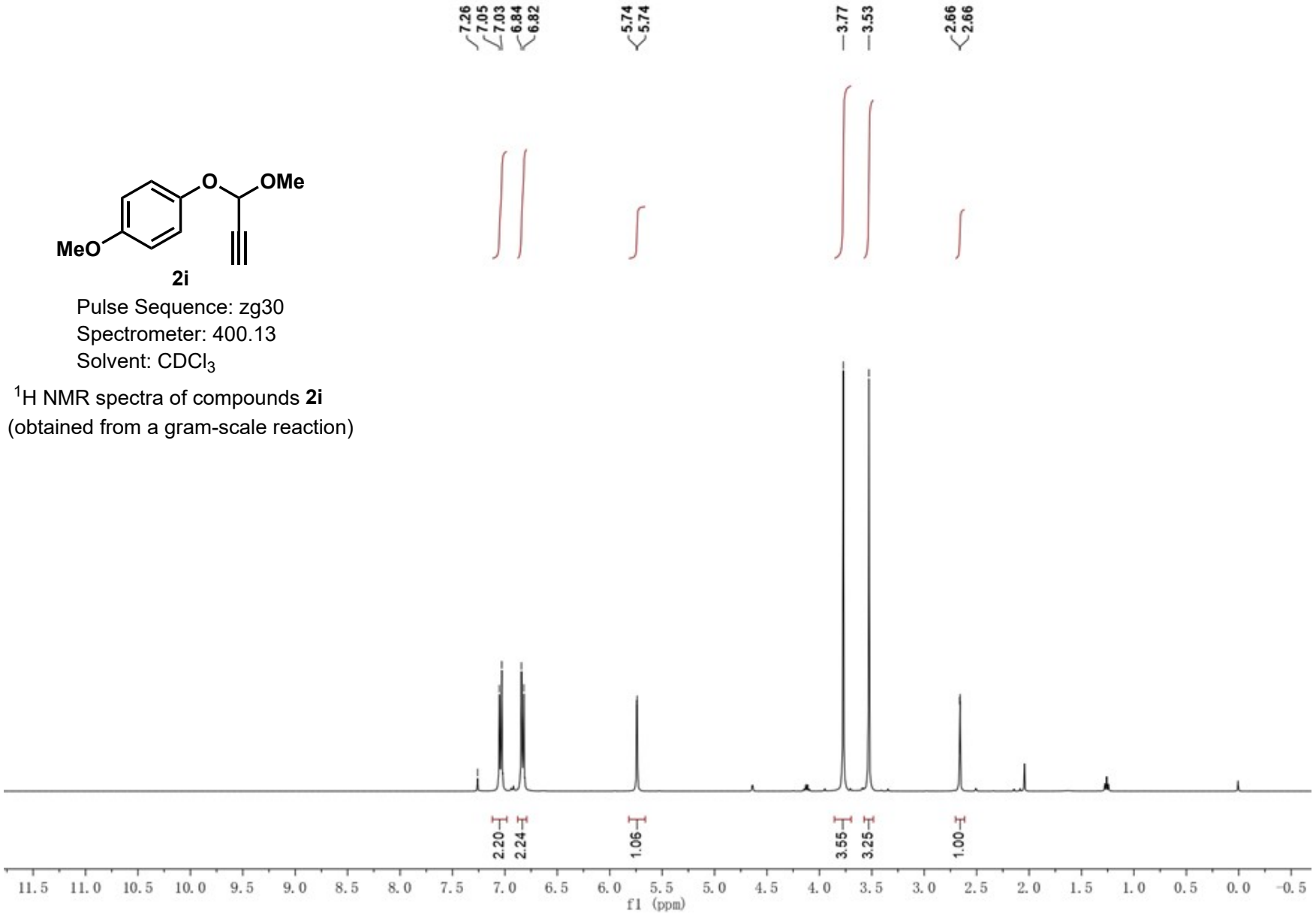


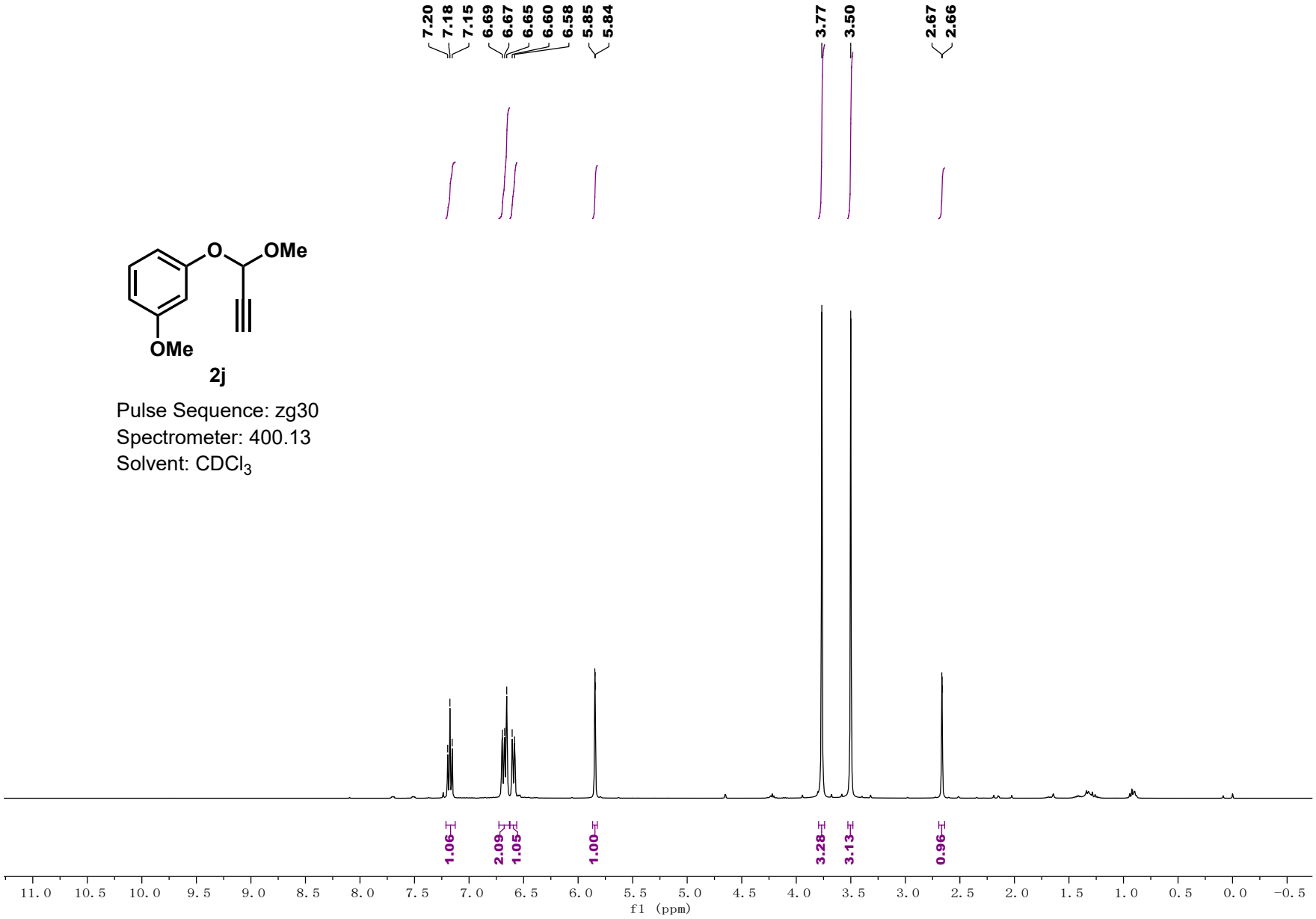

155.42
149.76
118.92
114.51
92.12
77.83
77.37
77.05
76.73
74.89
55.62
52.09
O
OMe
MeO
2i
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2i

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

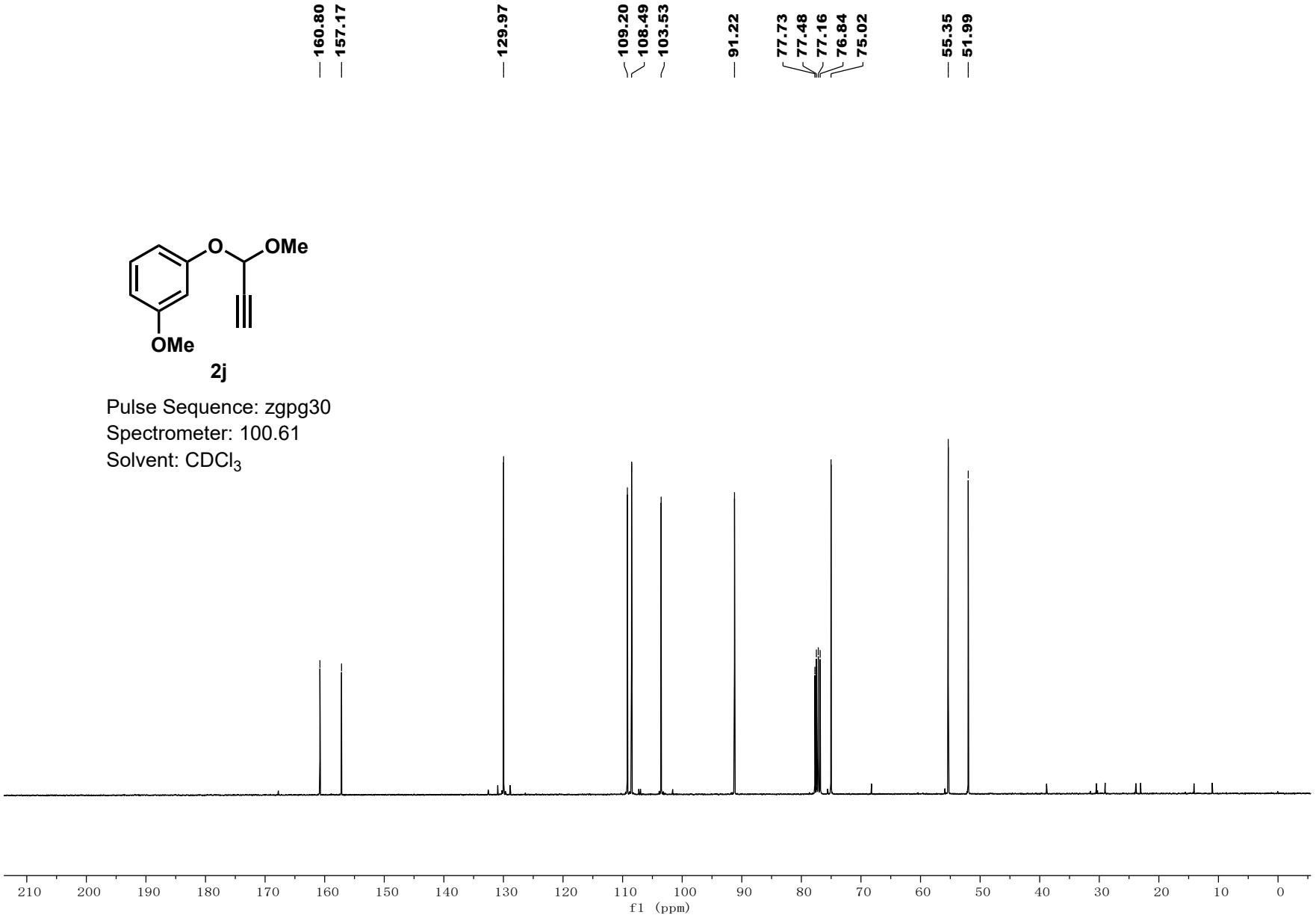
^1H NMR spectra of compounds **2i**
(obtained from a gram-scale reaction)

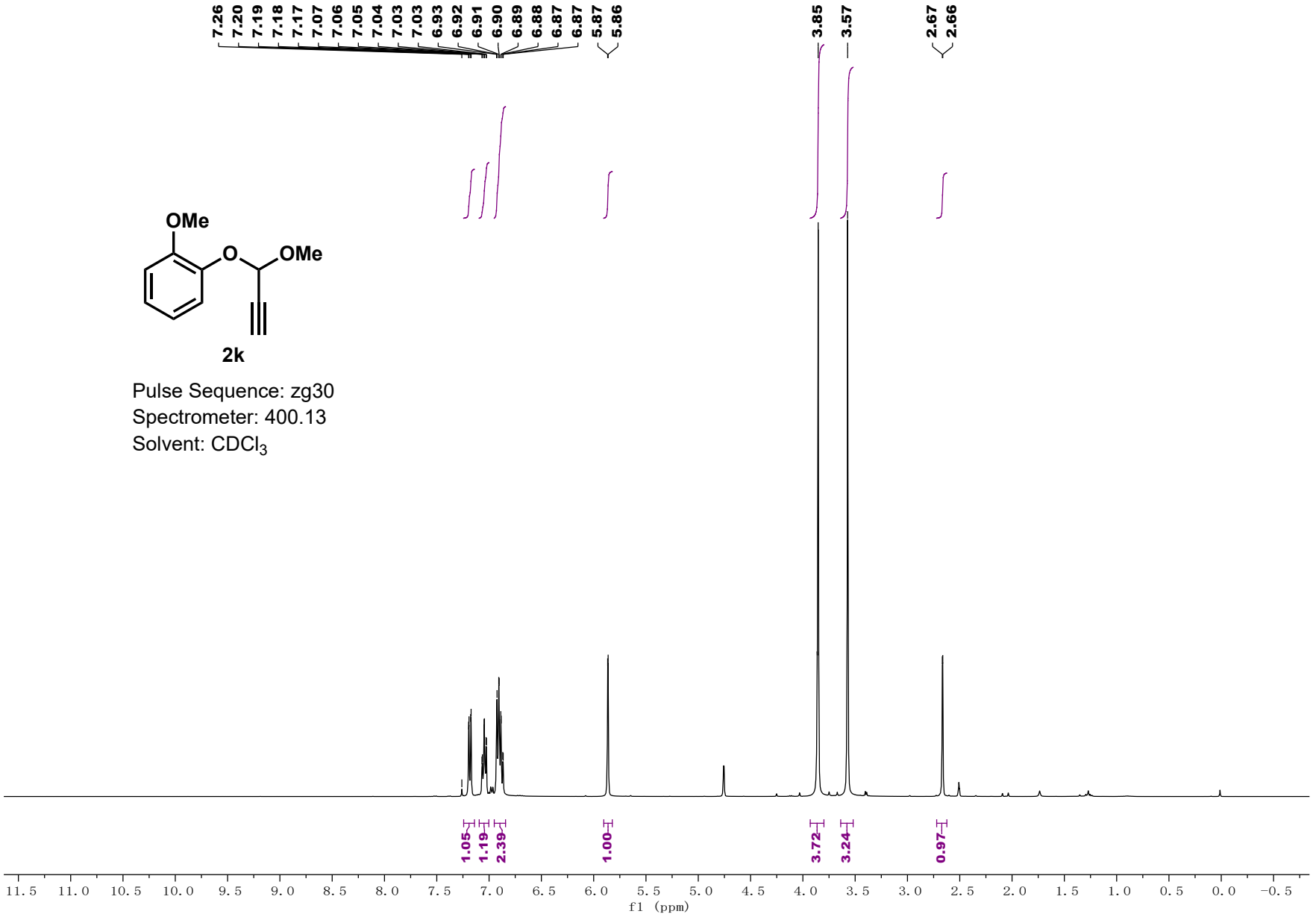




2j

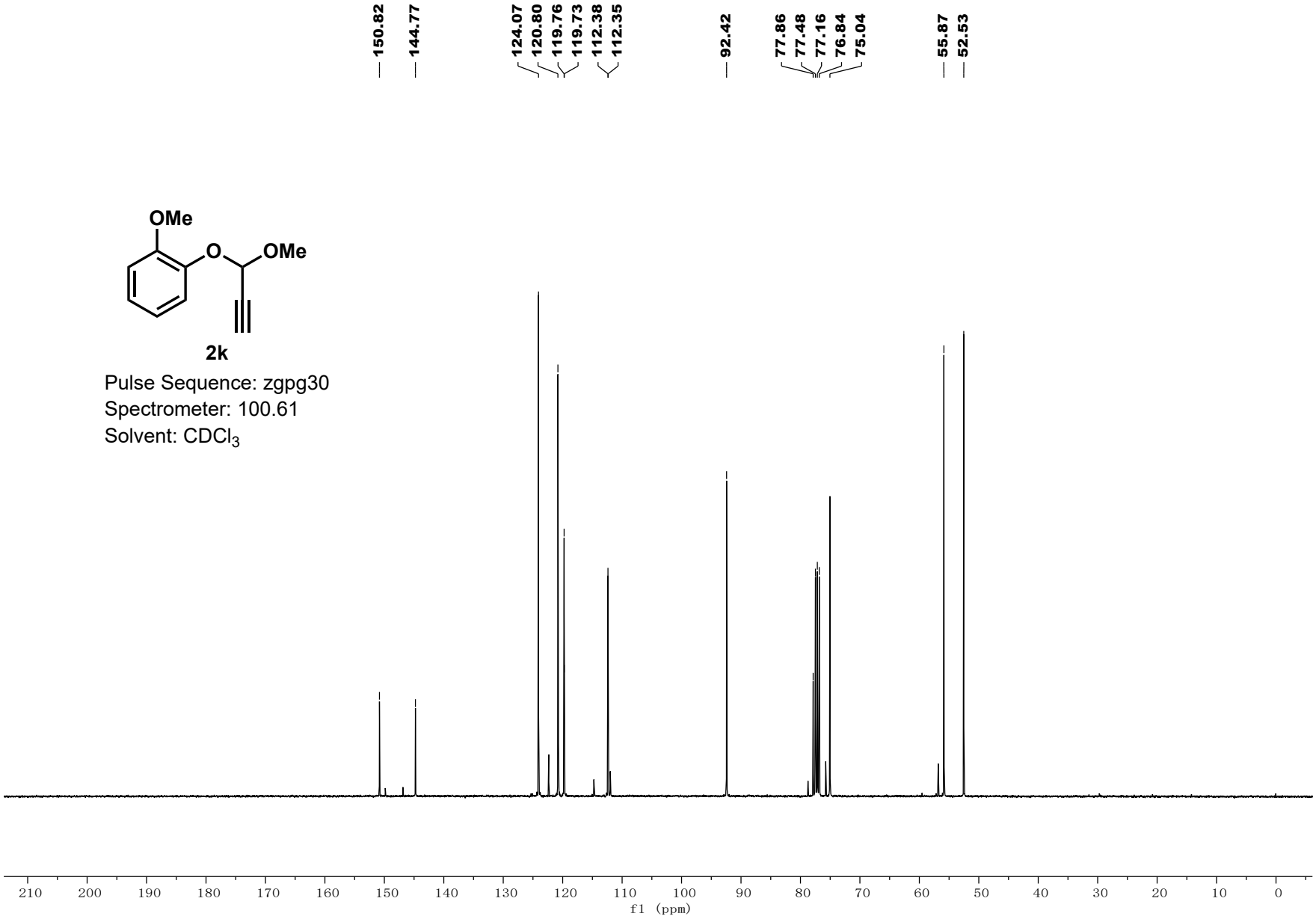
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

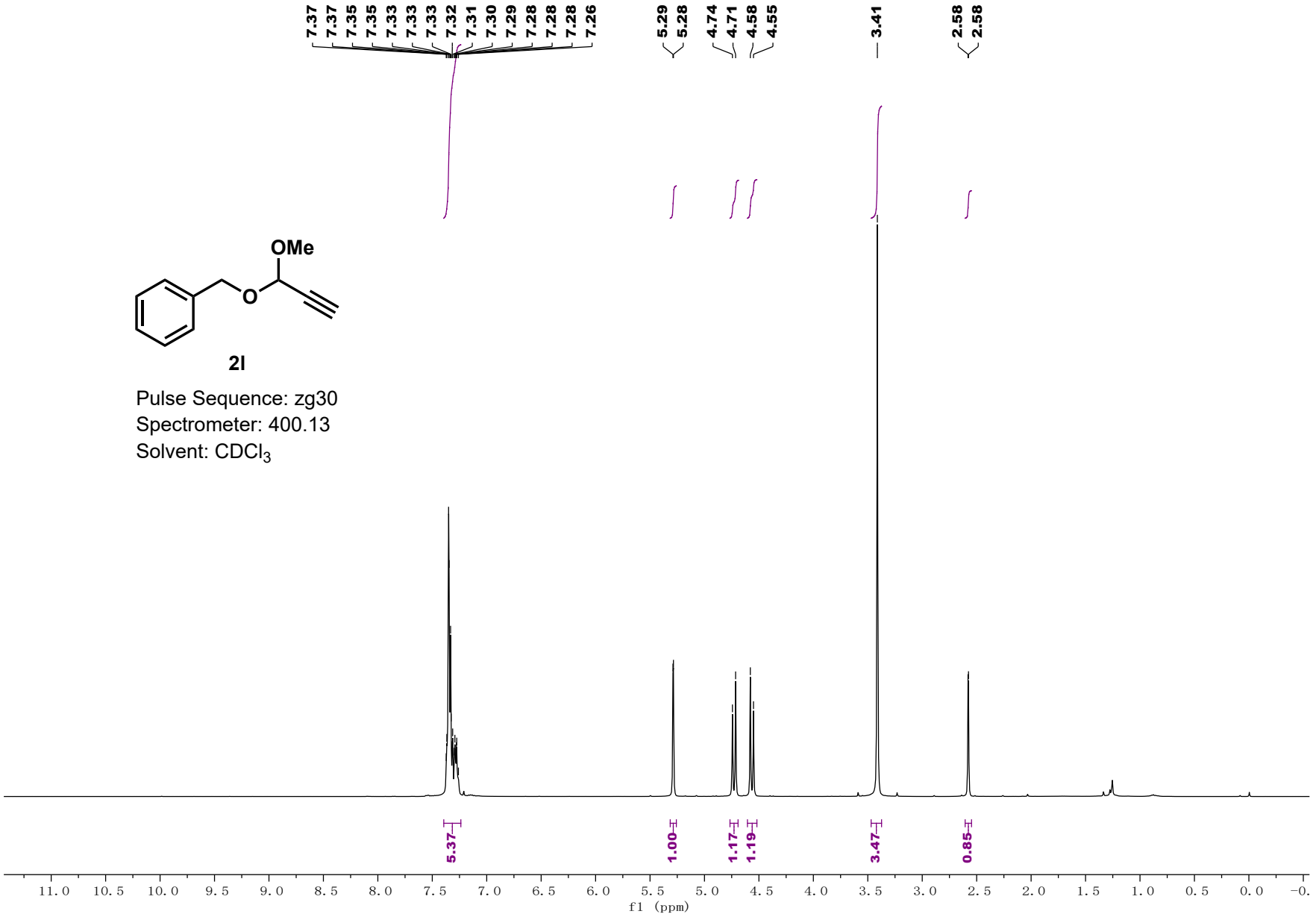

160.80
157.17
129.97
109.20
108.49
103.53
91.22
77.73
77.48
77.16
76.84
75.02
55.35
51.99
O
OMe
OMe
2j
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

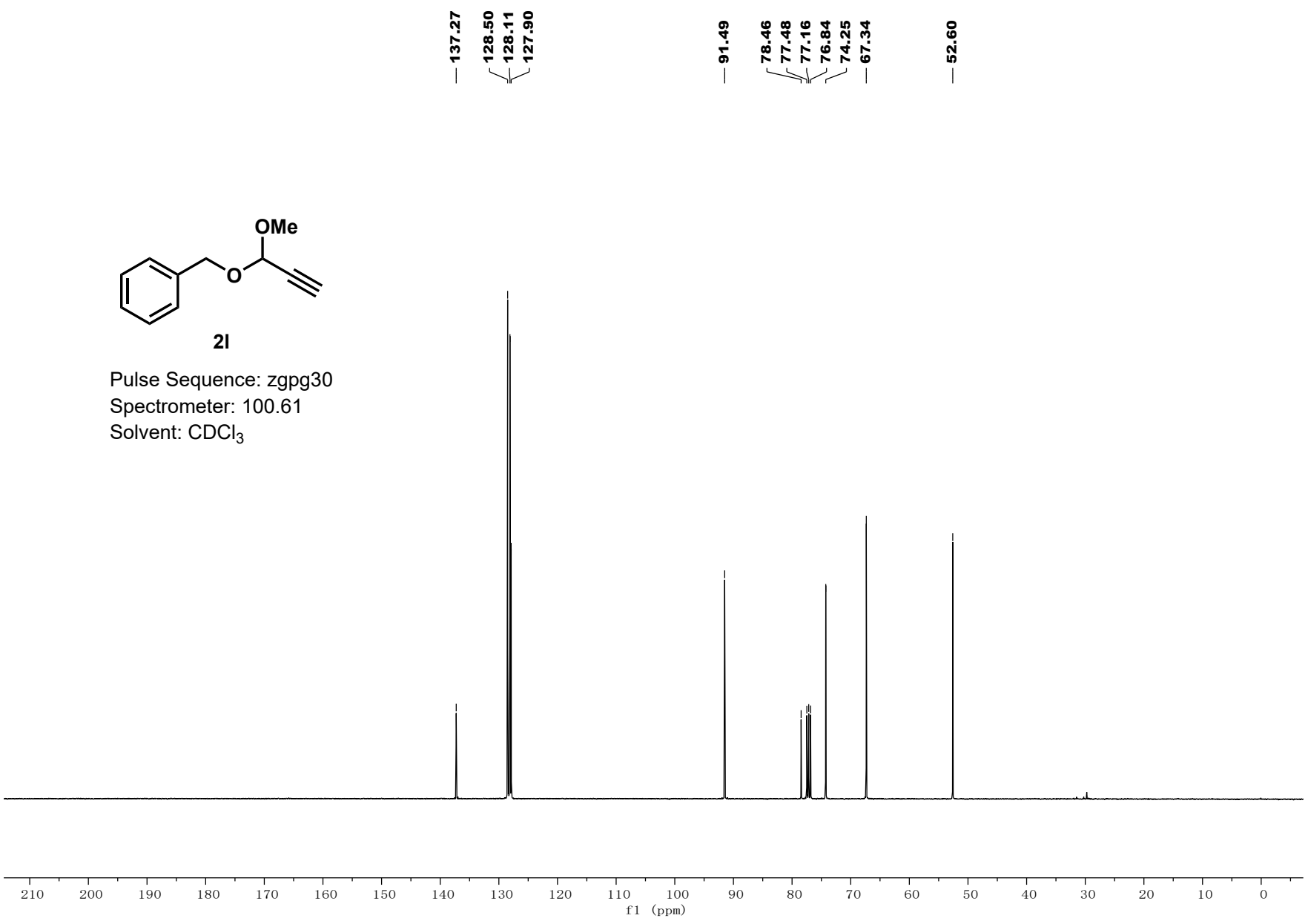


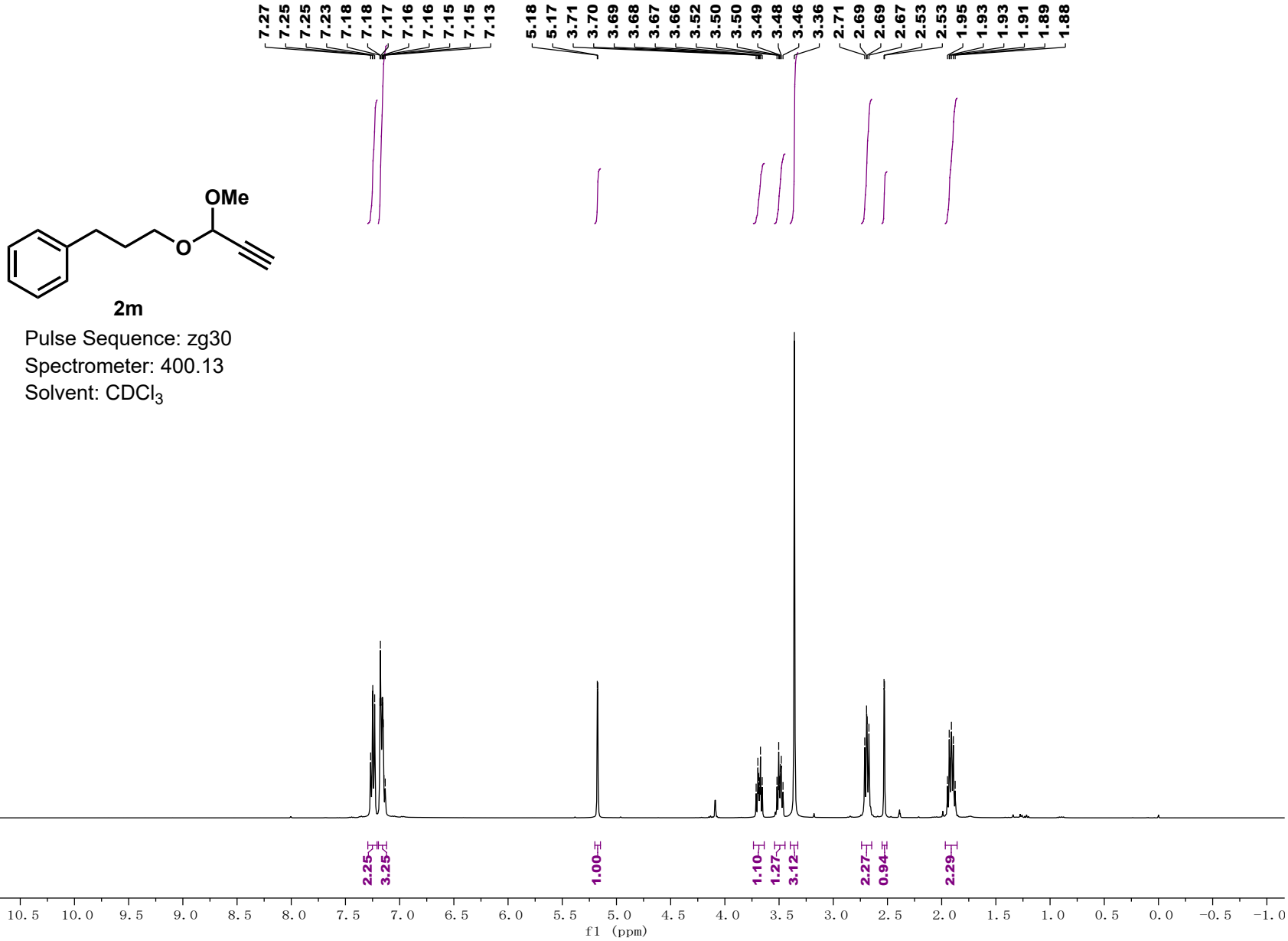
2k

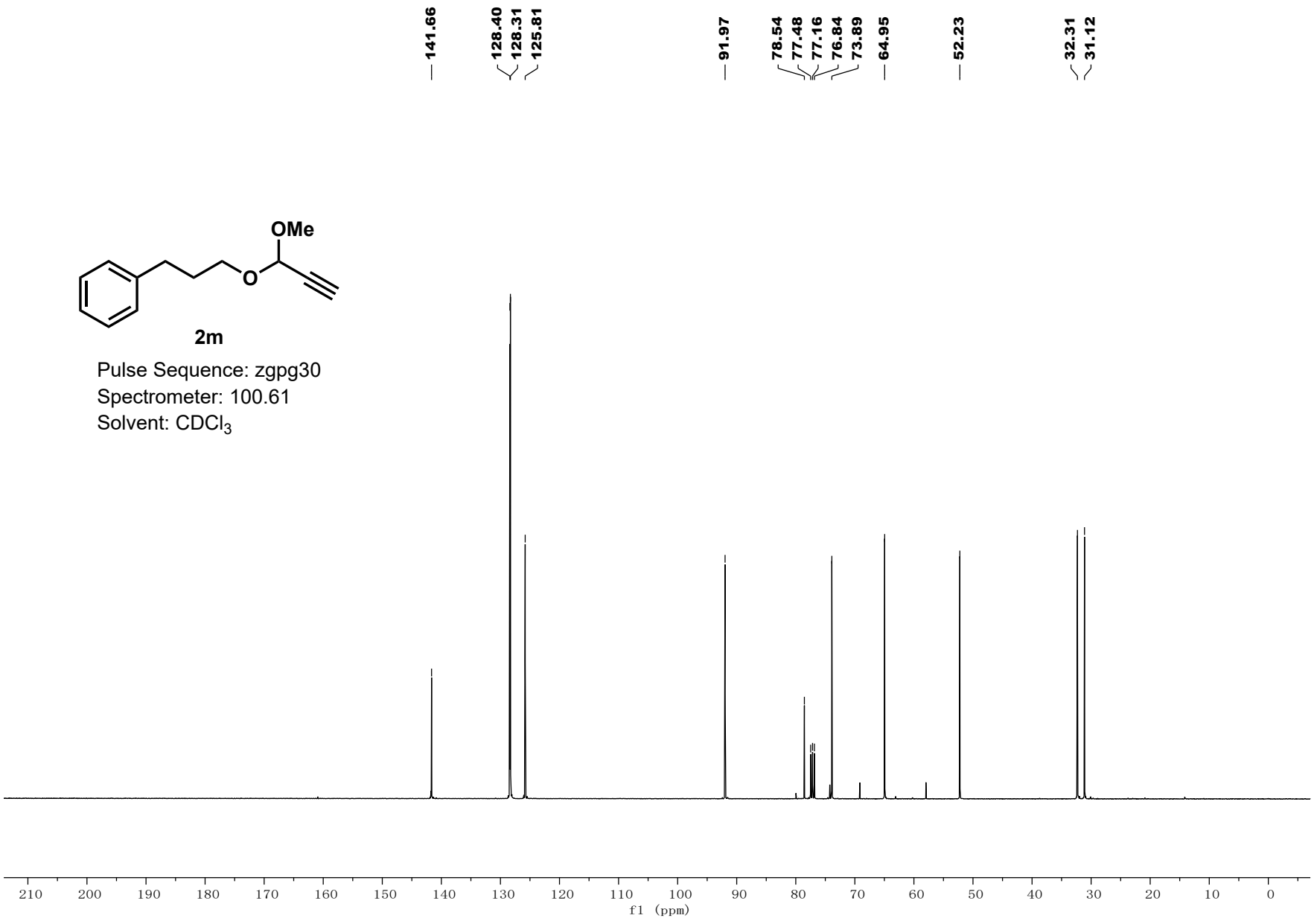
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

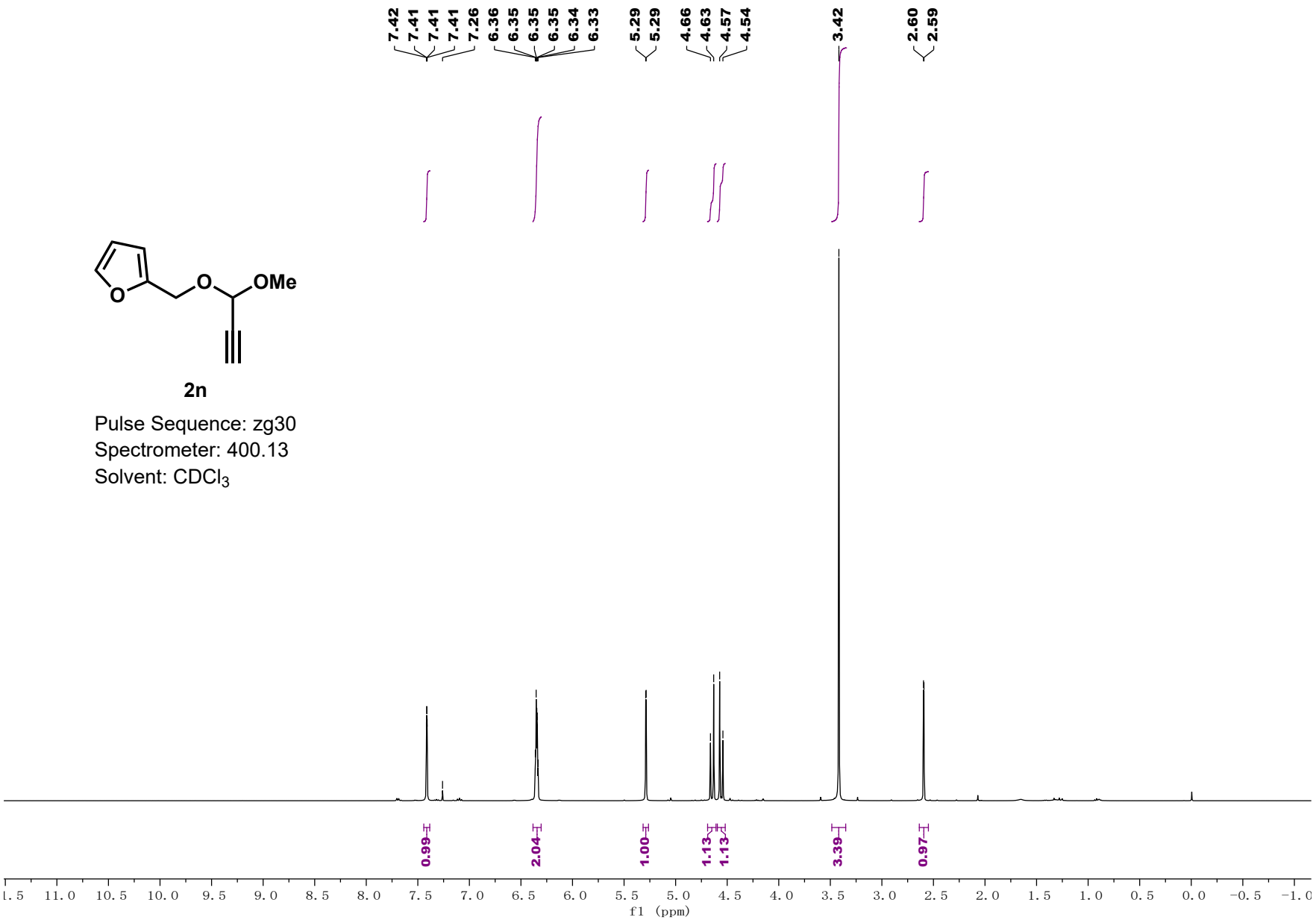

150.82
144.77
124.07
120.80
119.76
119.73
112.38
112.35
92.42
77.86
77.48
77.16
76.84
75.04
55.87
52.53
OMe
O
OMe
2k
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.37
7.37
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.28
7.26
5.29
5.28
4.74
4.71
4.58
4.55
3.41
2.58
2.58
OMe
O
2l
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.37
1.00
1.17
1.19
3.47
0.85
11.0
10.5
10.0
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
−0.
f1 (ppm)


137.27
128.50
128.11
127.90
91.49
78.46
77.48
77.16
76.84
74.25
67.34
52.60
OMe
O
2l
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

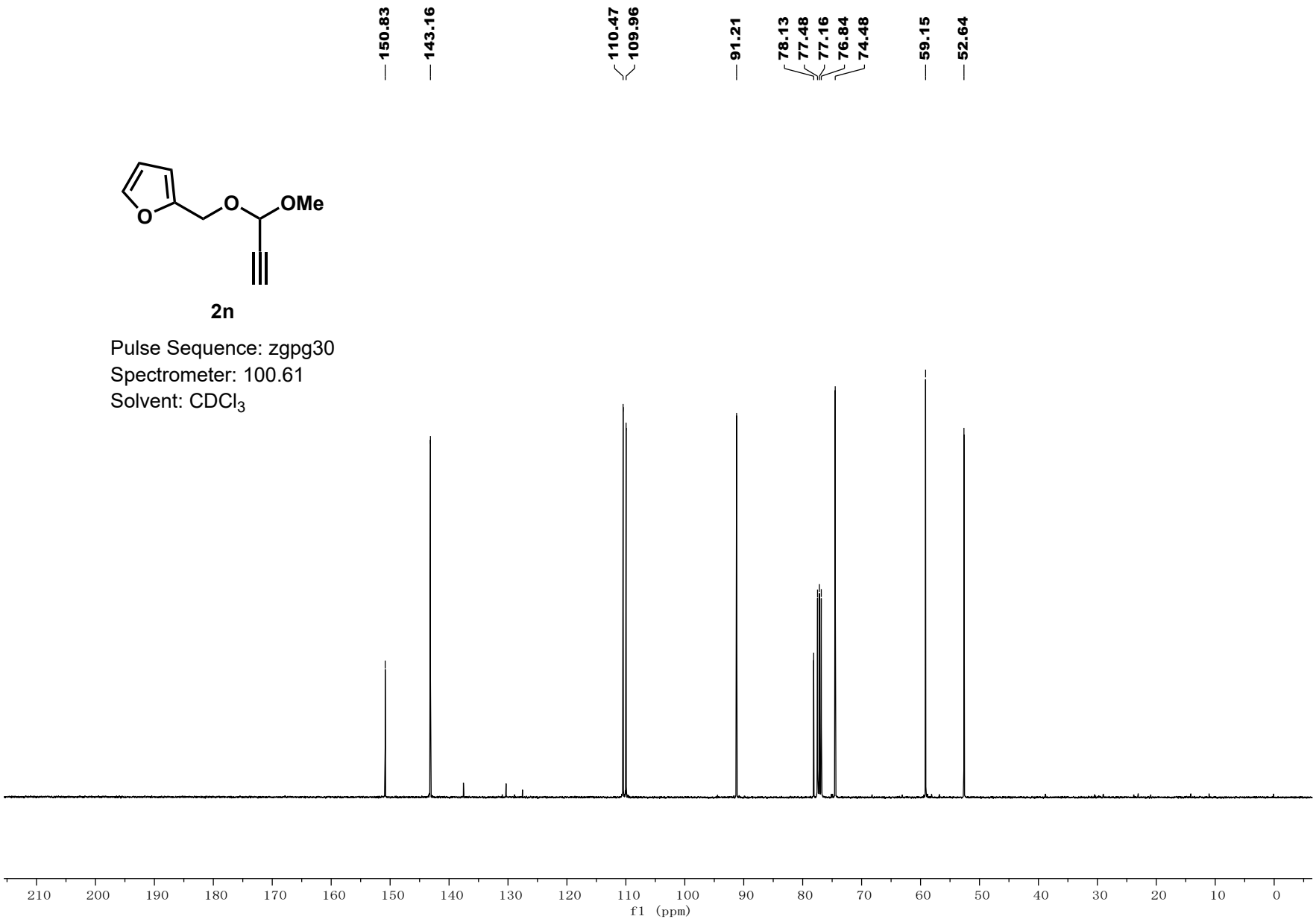

7.27
7.25
7.25
7.23
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.13
5.18
5.17
3.71
3.70
3.69
3.68
3.67
3.66
3.52
3.50
3.50
3.49
3.48
3.46
3.36
2.71
2.69
2.69
2.67
2.53
2.53
1.95
1.93
1.93
1.91
1.89
1.88
OMe
O
2m
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
2.25
3.25
1.00
1.10
1.27
3.12
2.27
0.94
2.29
11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)

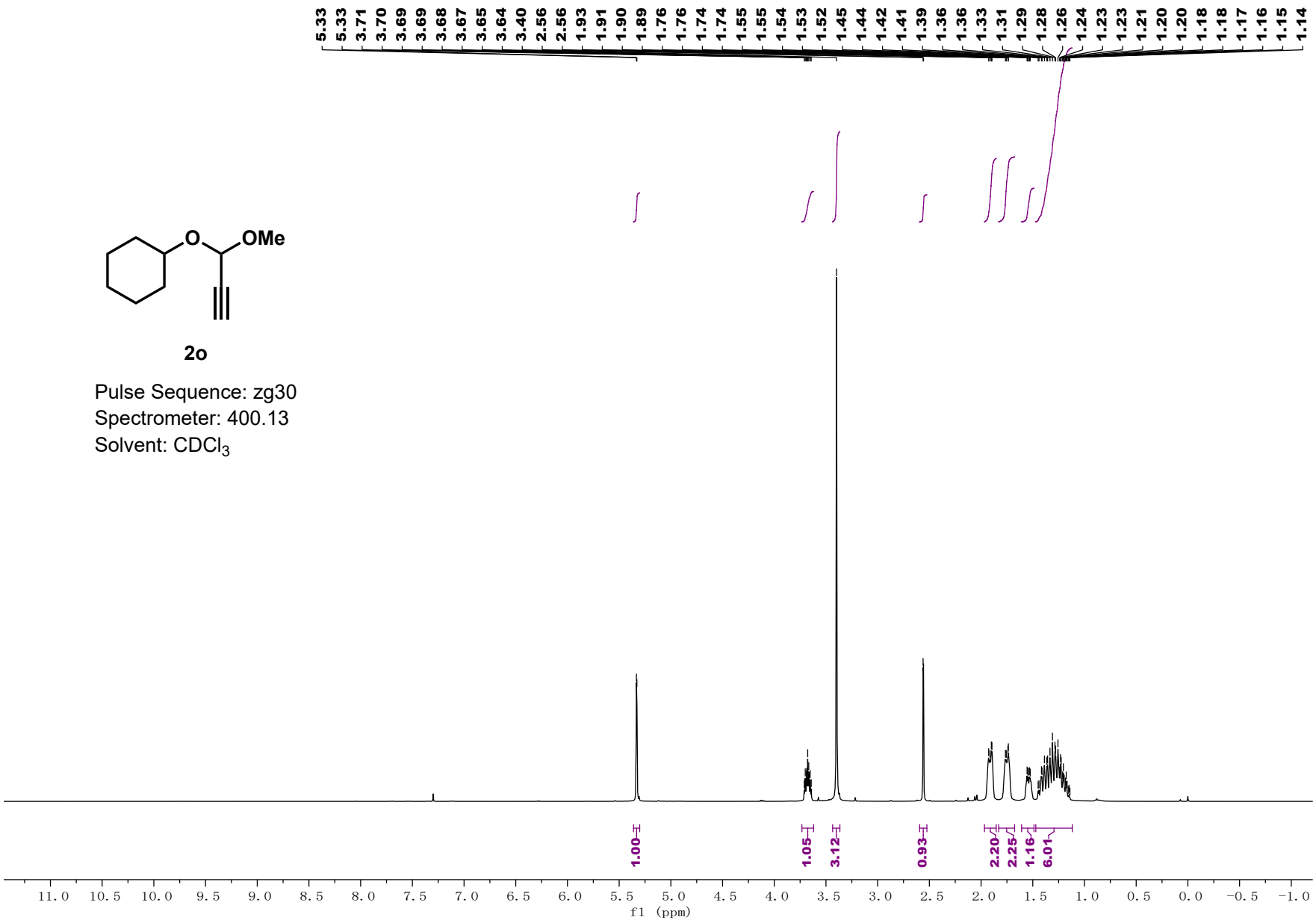

141.66
128.40
128.31
125.81
91.97
78.54
77.48
77.16
76.84
73.89
64.95
52.23
32.31
31.12
OMe
O
2m
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



2n

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$


150.83
143.16
110.47
109.96
91.21
78.13
77.48
77.16
76.84
74.48
59.15
52.64
O
O
OMe
2n
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

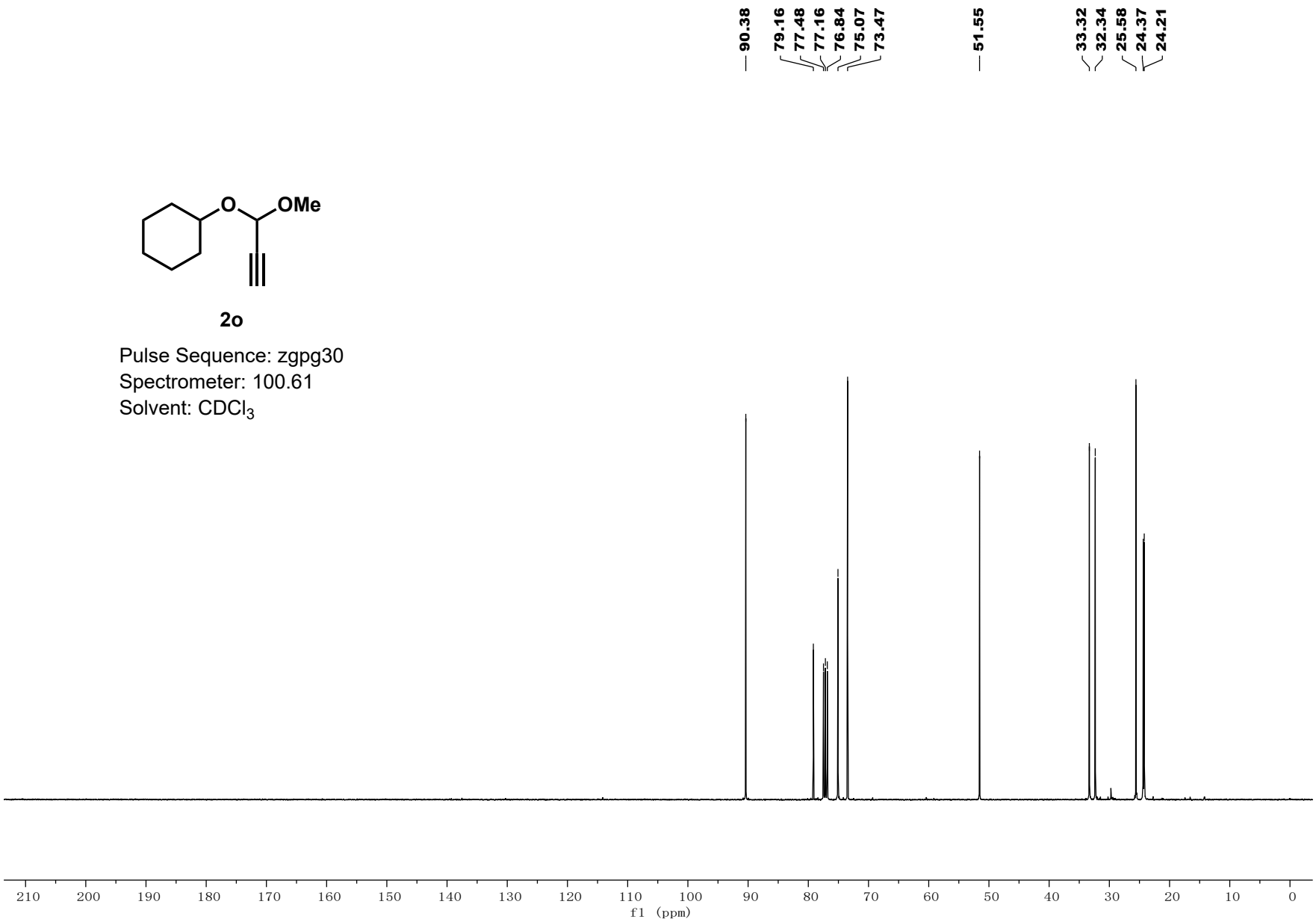


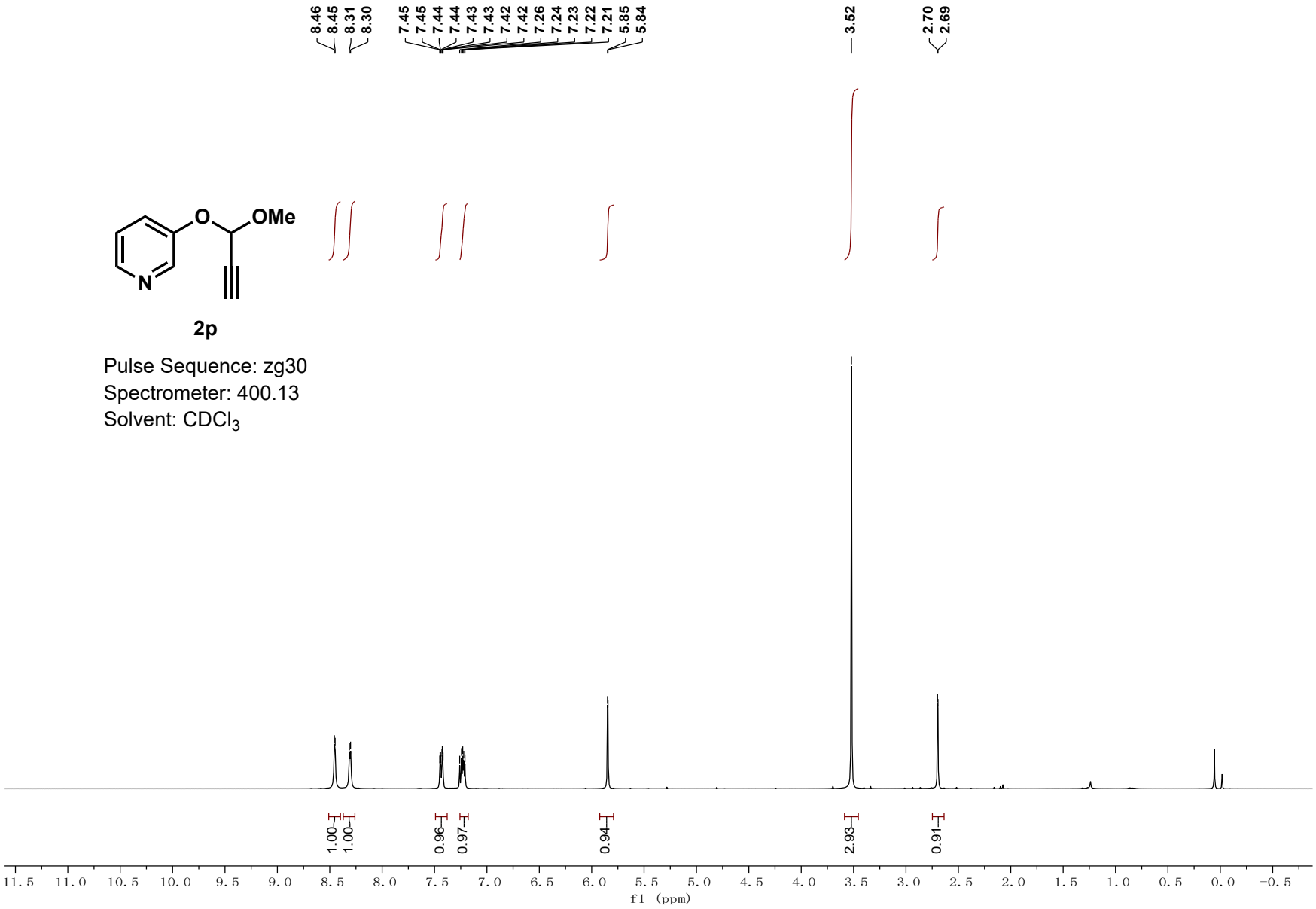
2o

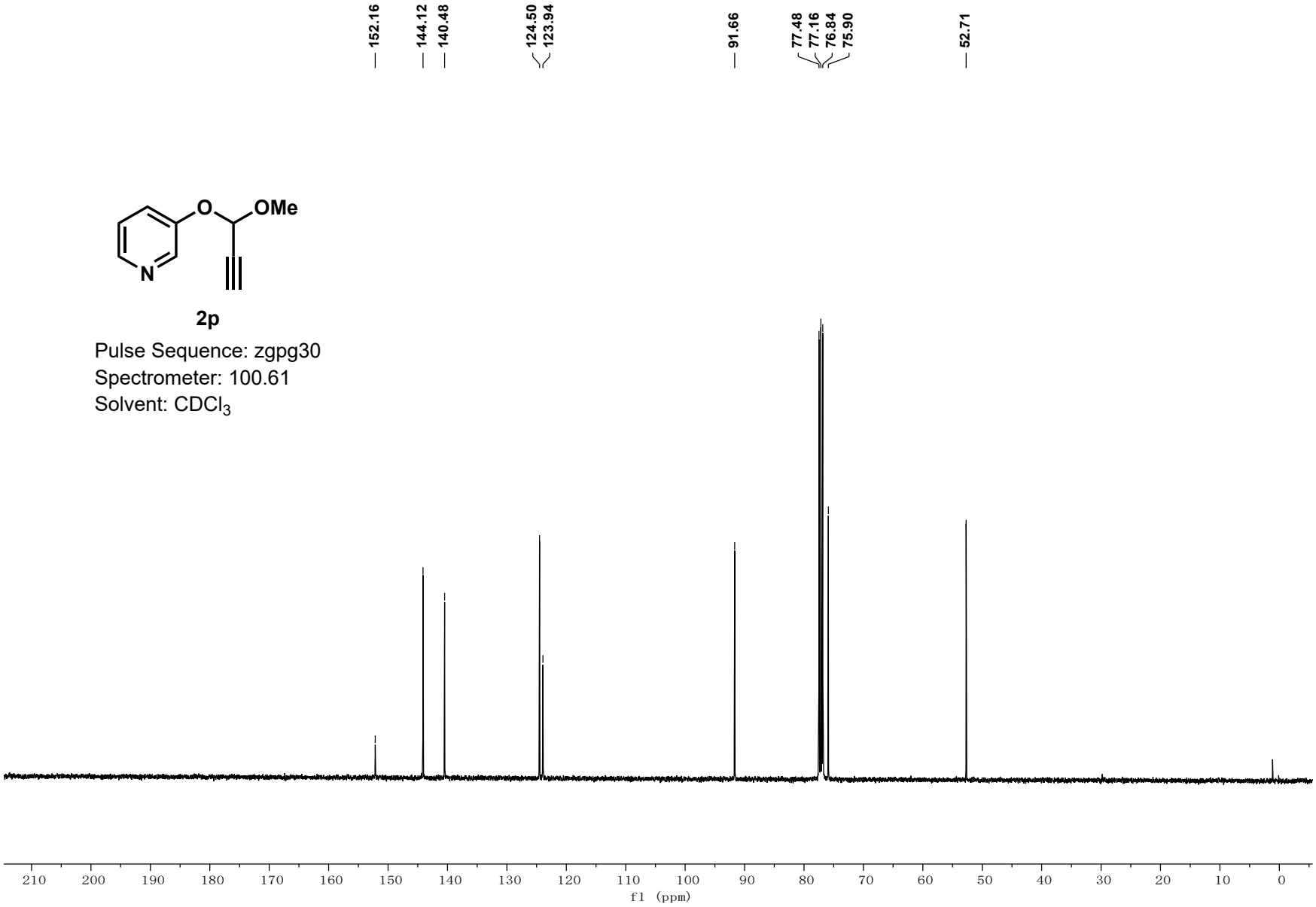
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

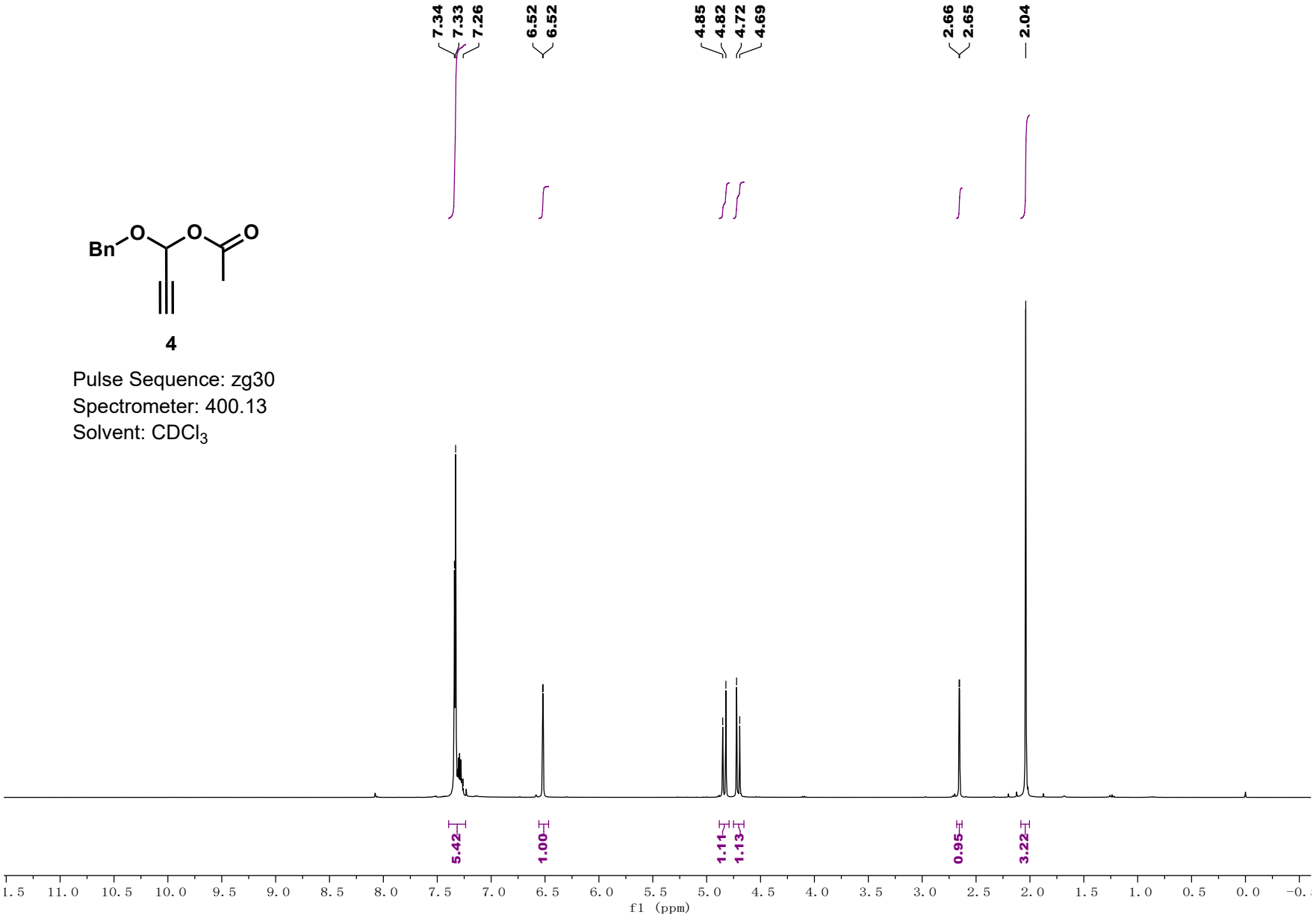
2o

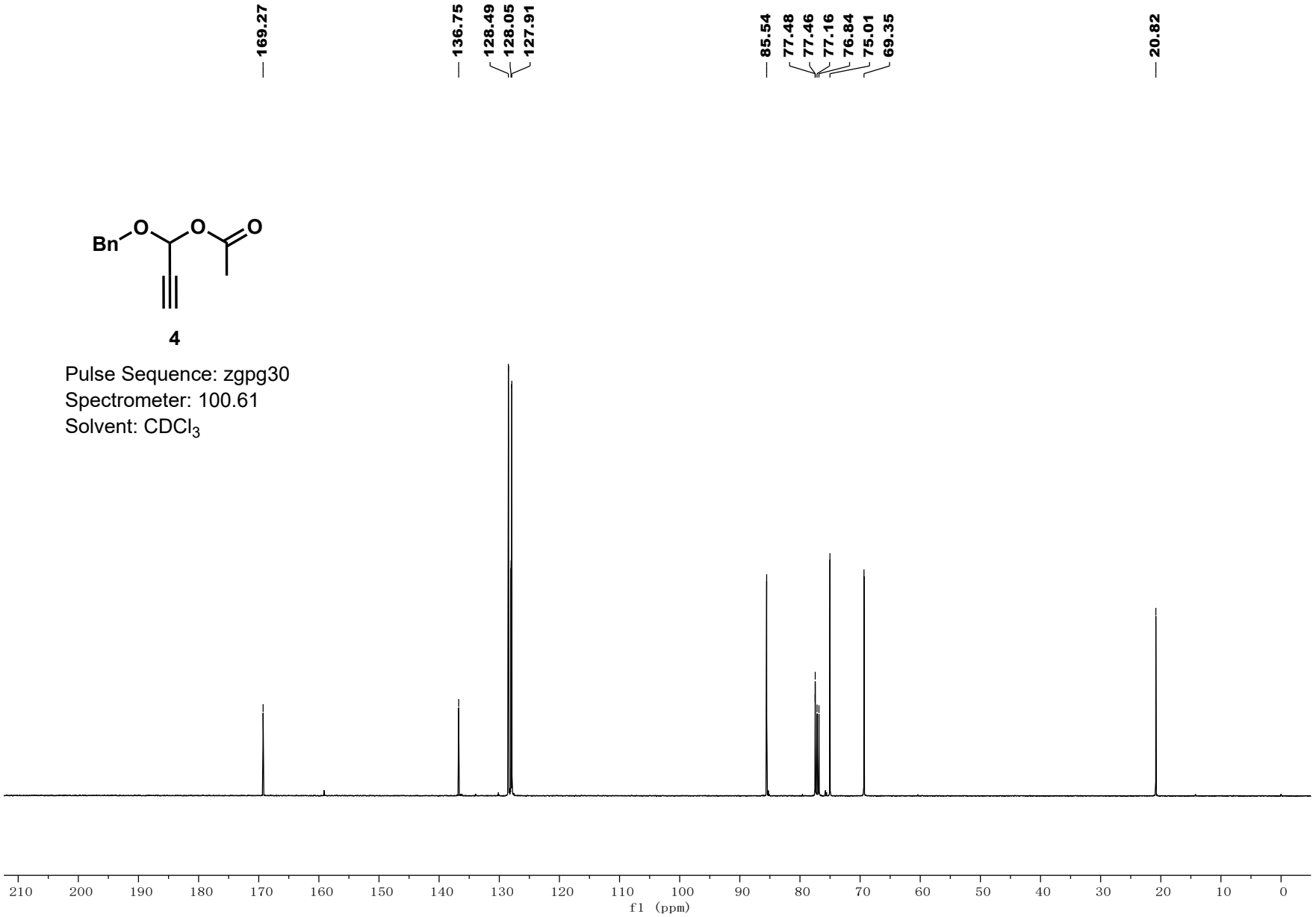
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: $CDCl_3$

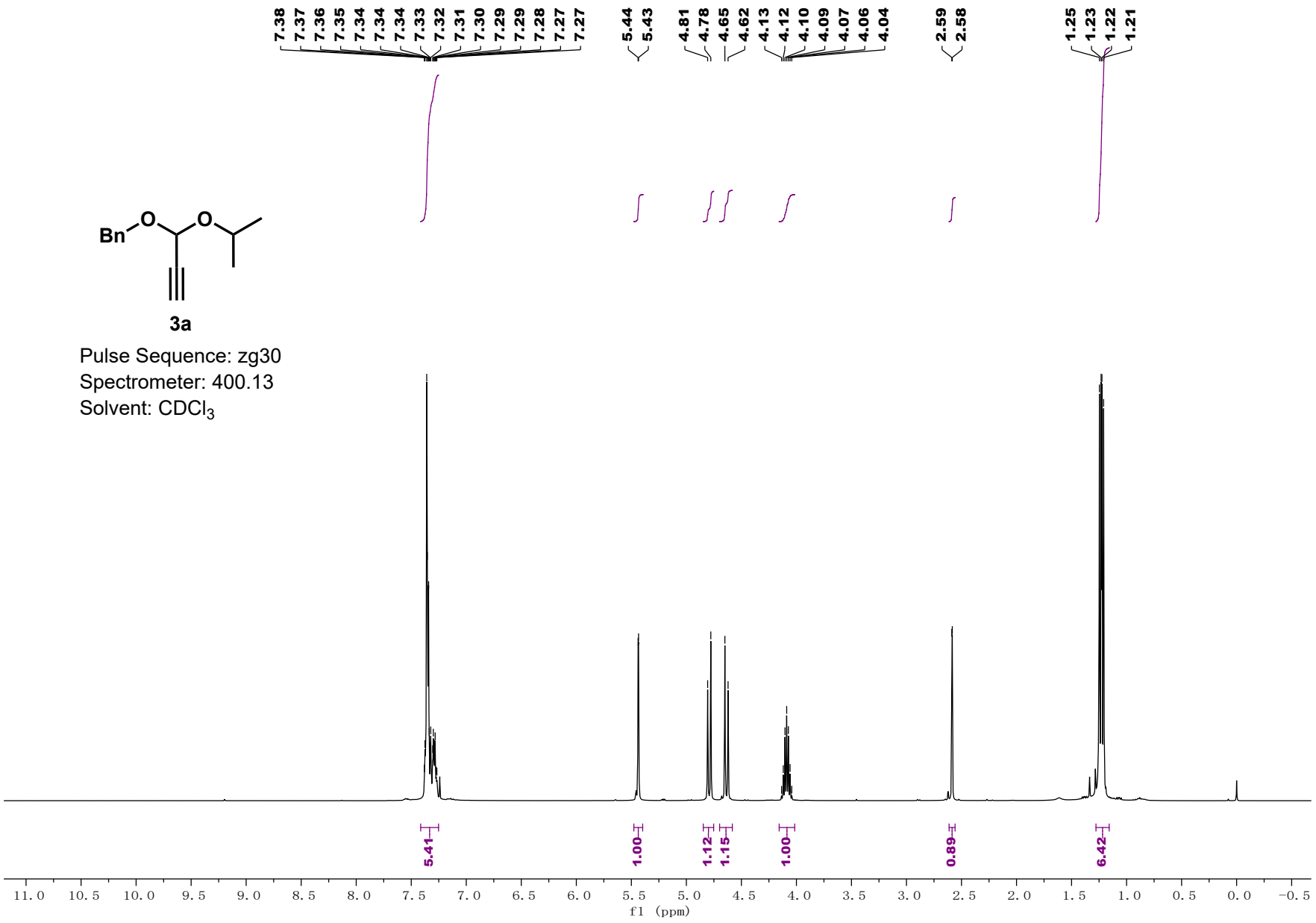


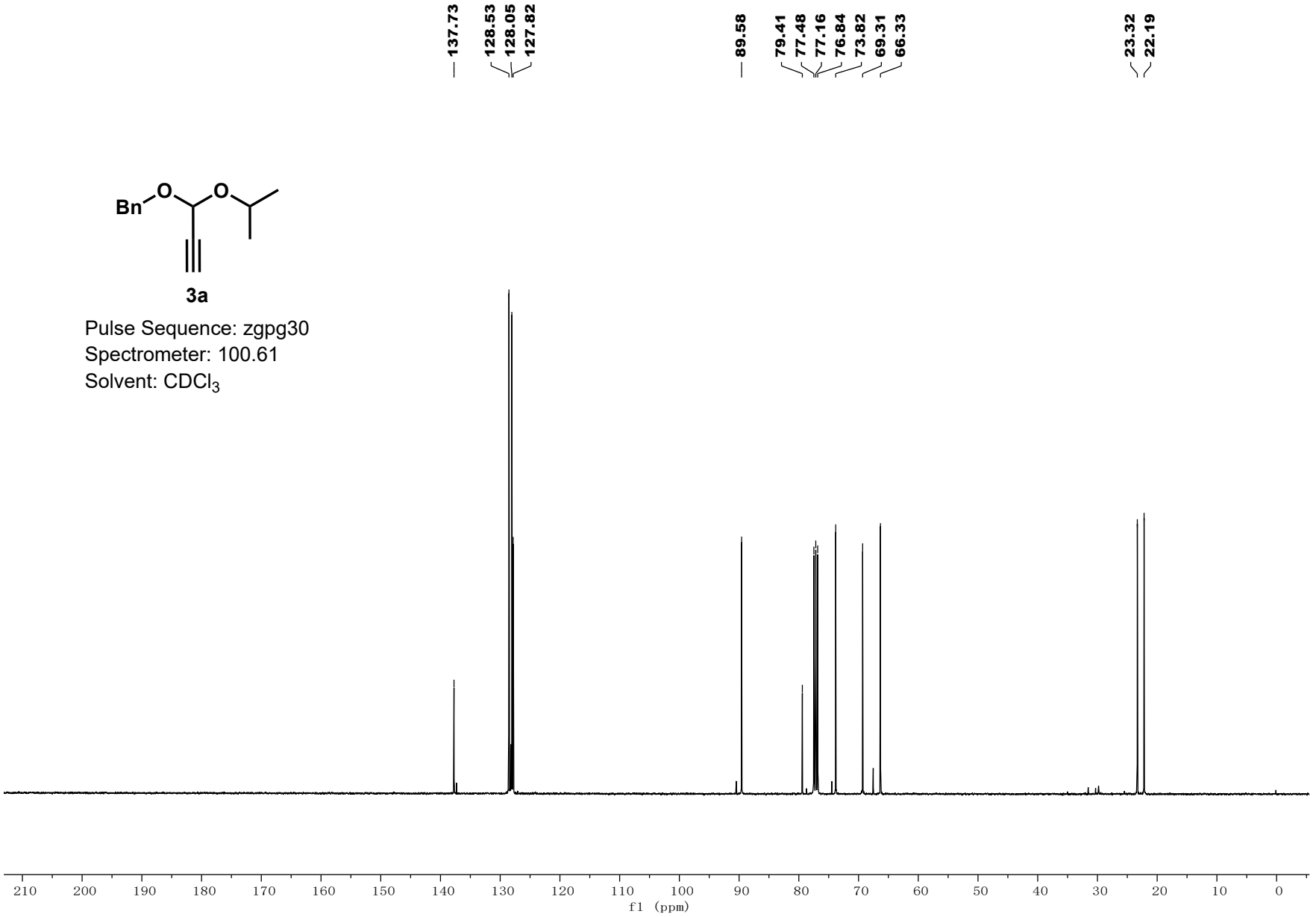

8.46
8.45
8.31
8.30
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26
7.24
7.23
7.22
7.21
5.85
5.84
3.52
2.70
2.69
O
OMe
N
2p
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
1.00
1.00
0.96
0.97
0.94
2.93
0.91
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

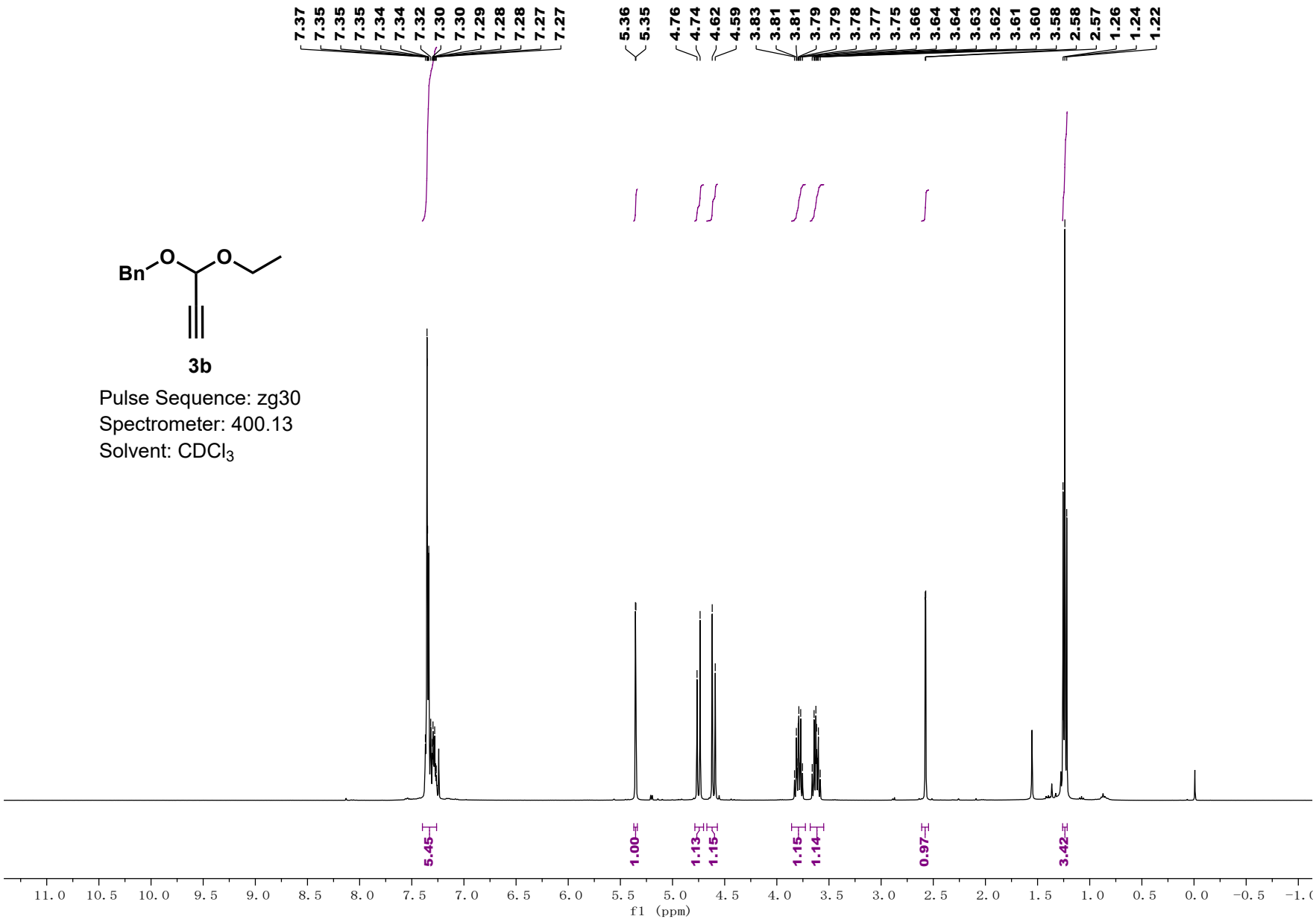

152.16
144.12
140.48
124.50
123.94
91.66
77.48
77.16
76.84
75.90
52.71
O
OMe
N
2p
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

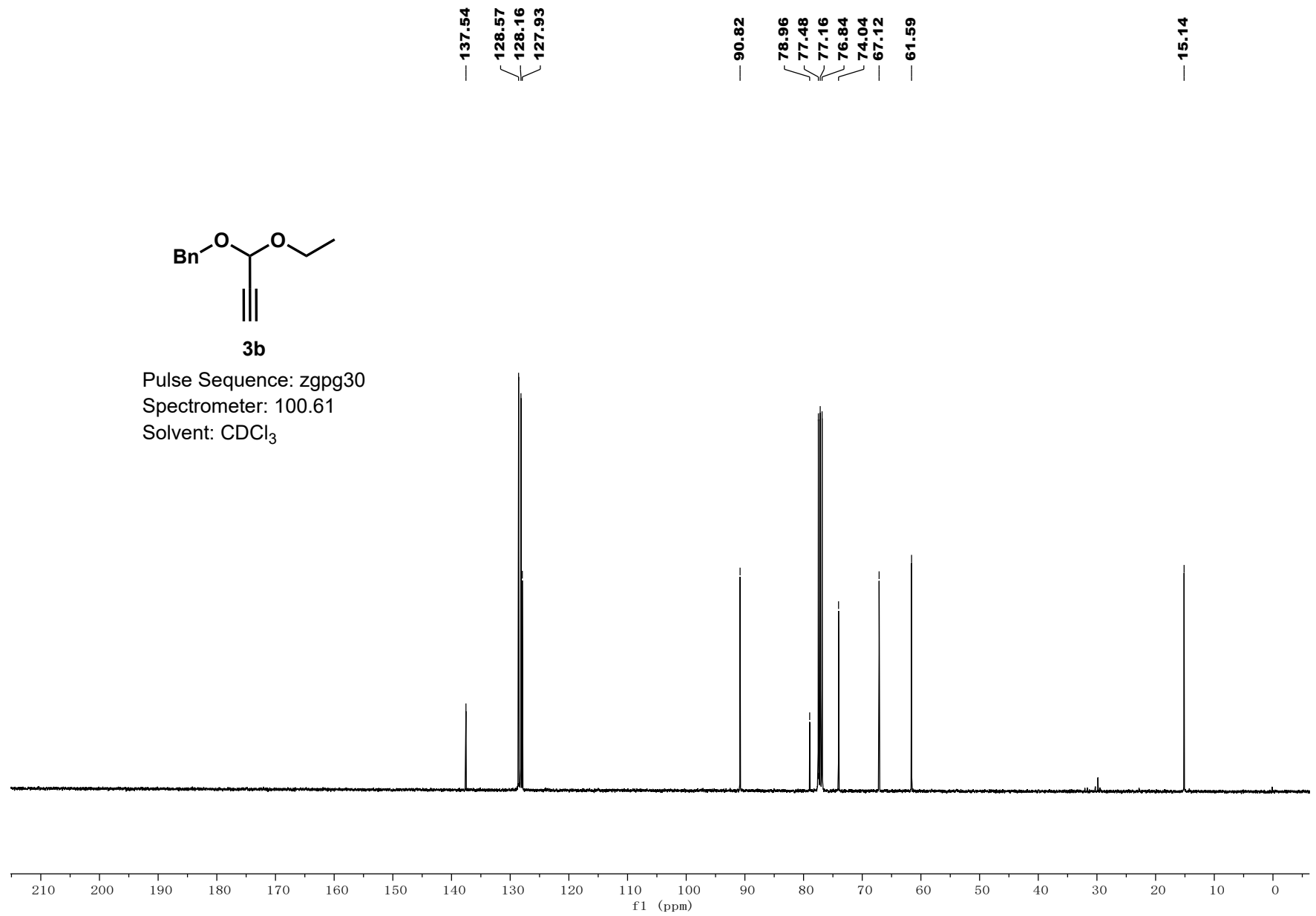

7.34
7.33
7.26
6.52
6.52
4.85
4.82
4.72
4.69
2.66
2.65
2.04
Bn
O
O
O
4
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.42
1.00
1.11
1.13
0.95
3.22
f1 (ppm)


169.27
136.75
128.49
128.05
127.91
85.54
77.48
77.46
77.16
76.84
75.01
69.35
20.82
Bn
O
O
O
4
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.37
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
5.44
5.43
4.81
4.78
4.65
4.62
4.13
4.12
4.10
4.09
4.07
4.06
4.04
2.59
2.58
1.25
1.23
1.22
1.21
Bn
O
O
3a
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.41
1.00
1.12
1.15
1.00
0.89
6.42
11.0
10.5
10.0
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
−0.5
f1 (ppm)


137.73
128.53
128.05
127.82
89.58
79.41
77.48
77.16
76.84
73.82
69.31
66.33
23.32
22.19
Bn
O
O
3a
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

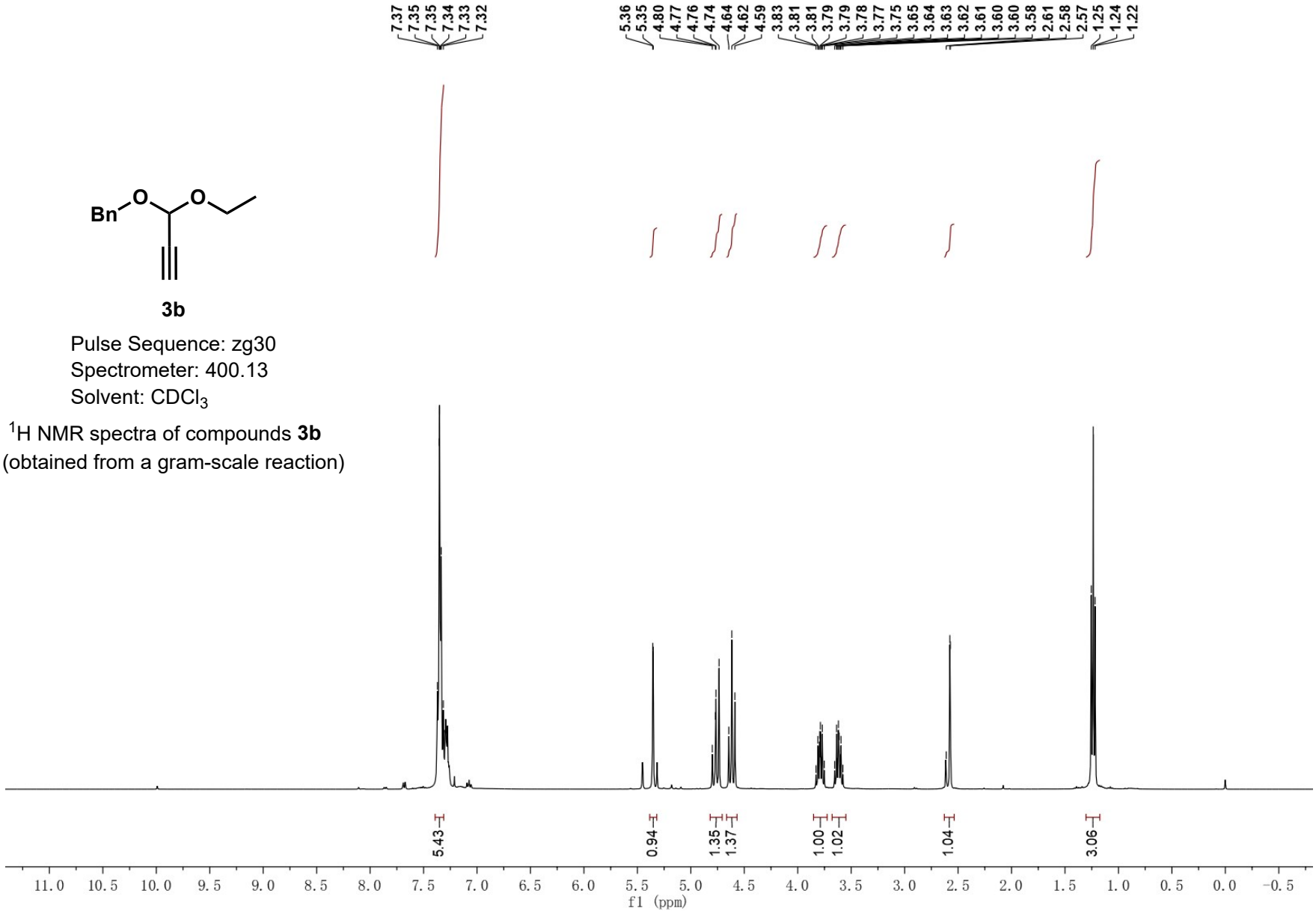

7.37
7.35
7.35
7.35
7.34
7.34
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.27
5.36
5.35
4.76
4.74
4.62
4.59
3.83
3.81
3.81
3.79
3.79
3.78
3.77
3.75
3.66
3.64
3.64
3.63
3.62
3.61
3.60
3.58
2.58
2.57
1.26
1.24
1.22
Bn
O
O
3b
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.45
1.00
1.13
1.15
1.15
1.14
0.97
3.42
11.0
10.5
10.0
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
−0.5
f1 (ppm)

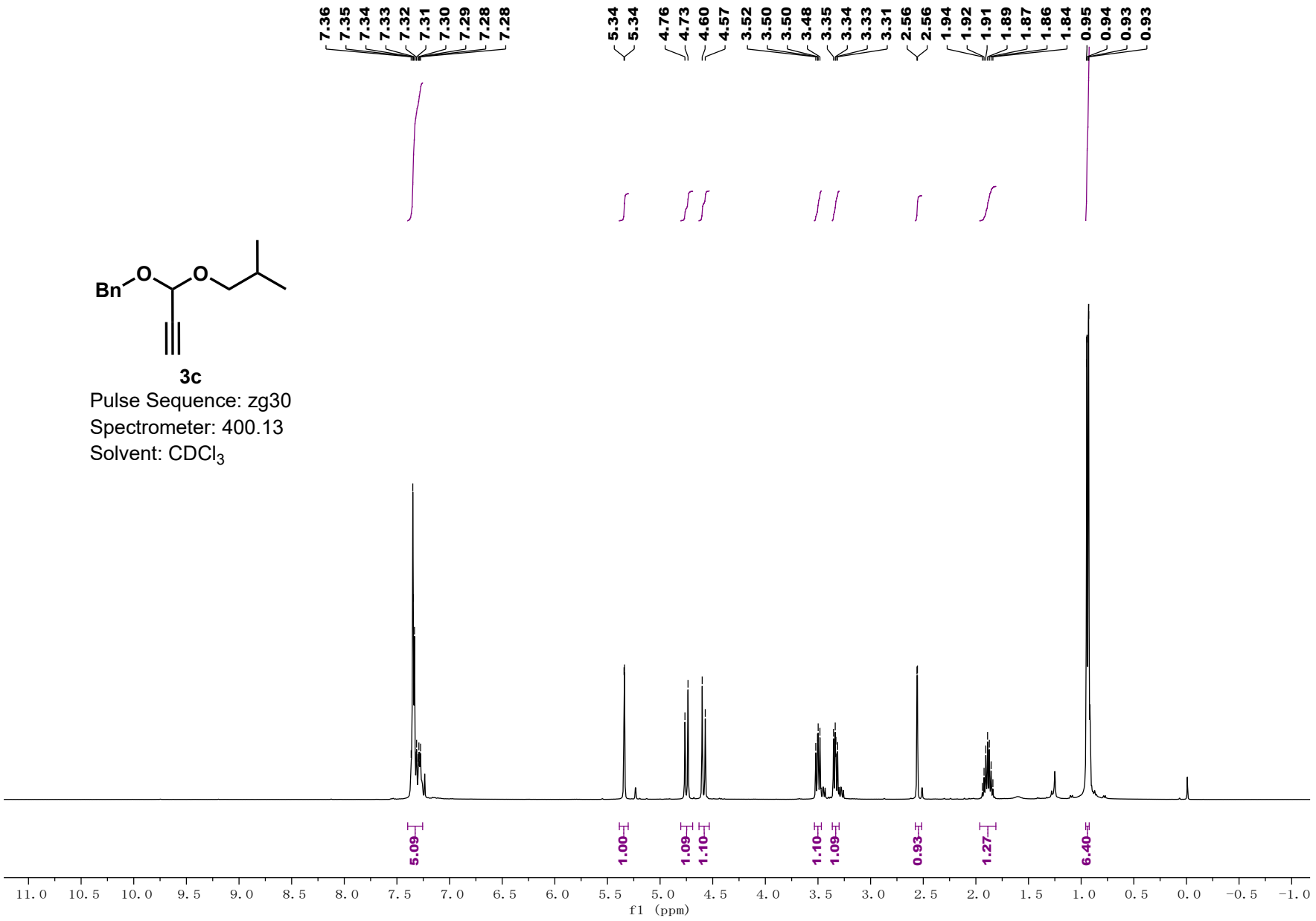

137.54
128.57
128.16
127.93
90.82
78.96
77.48
77.16
76.84
74.04
67.12
61.59
15.14
Bn
O
O
3b
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3b

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

^1H NMR spectra of compounds **3b**
(obtained from a gram-scale reaction)



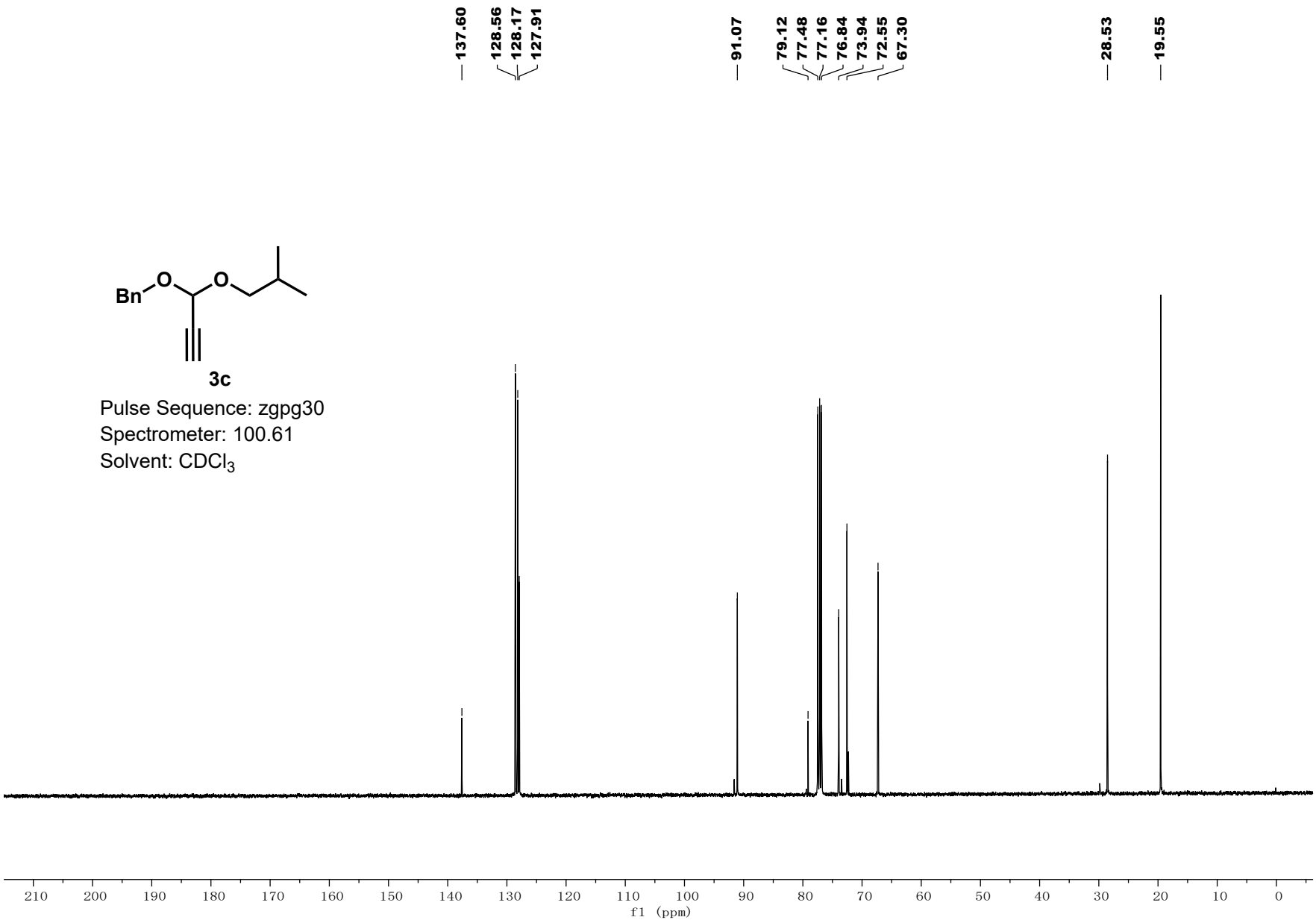


3c

Pulse Sequence: zg30

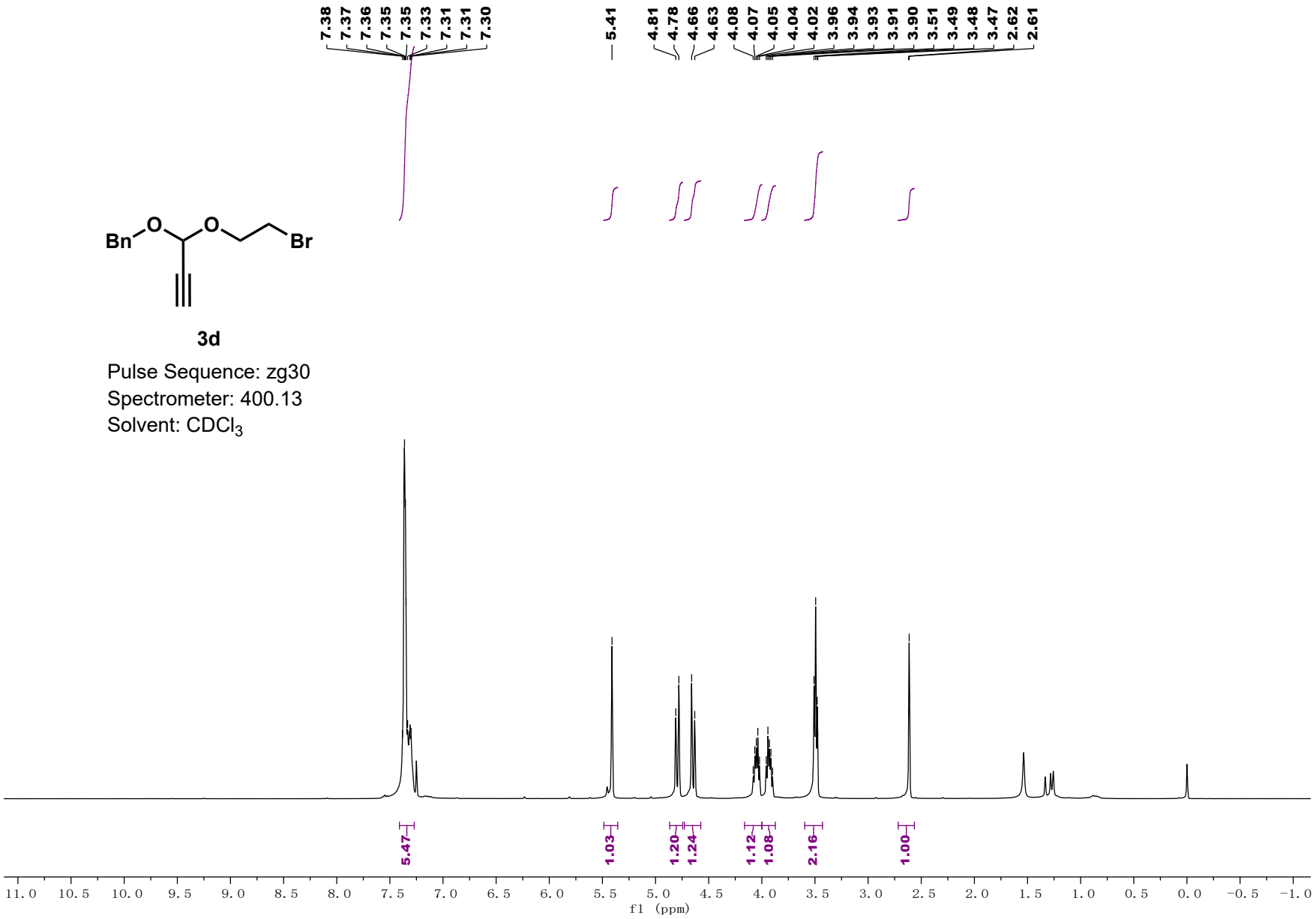
Spectrometer: 400.13

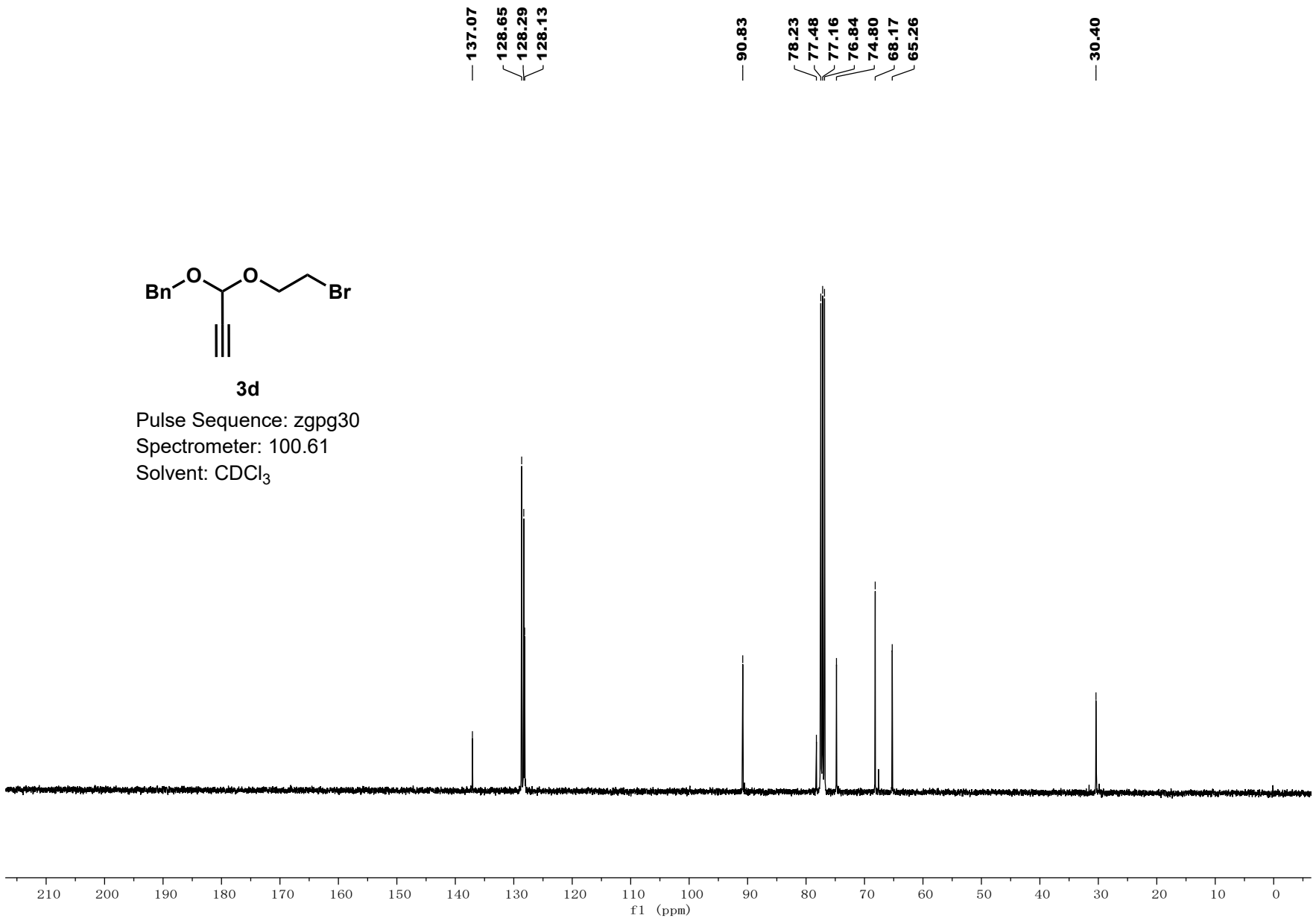
Solvent: $CDCl_3$

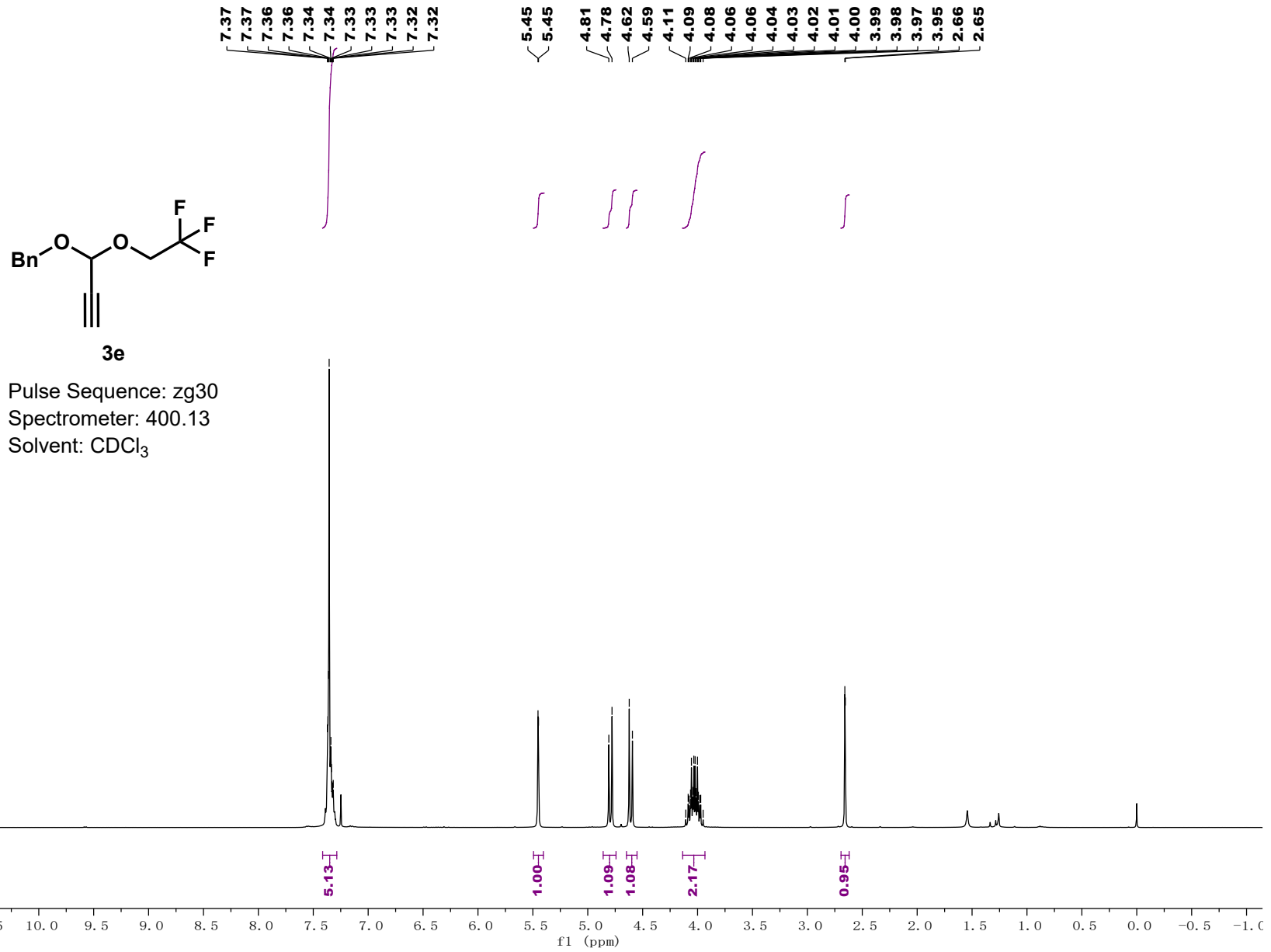

137.60
128.56
128.17
127.91
91.07
79.12
77.48
77.16
76.84
73.94
72.55
67.30
28.53
19.55
Bn
O
O
3c
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

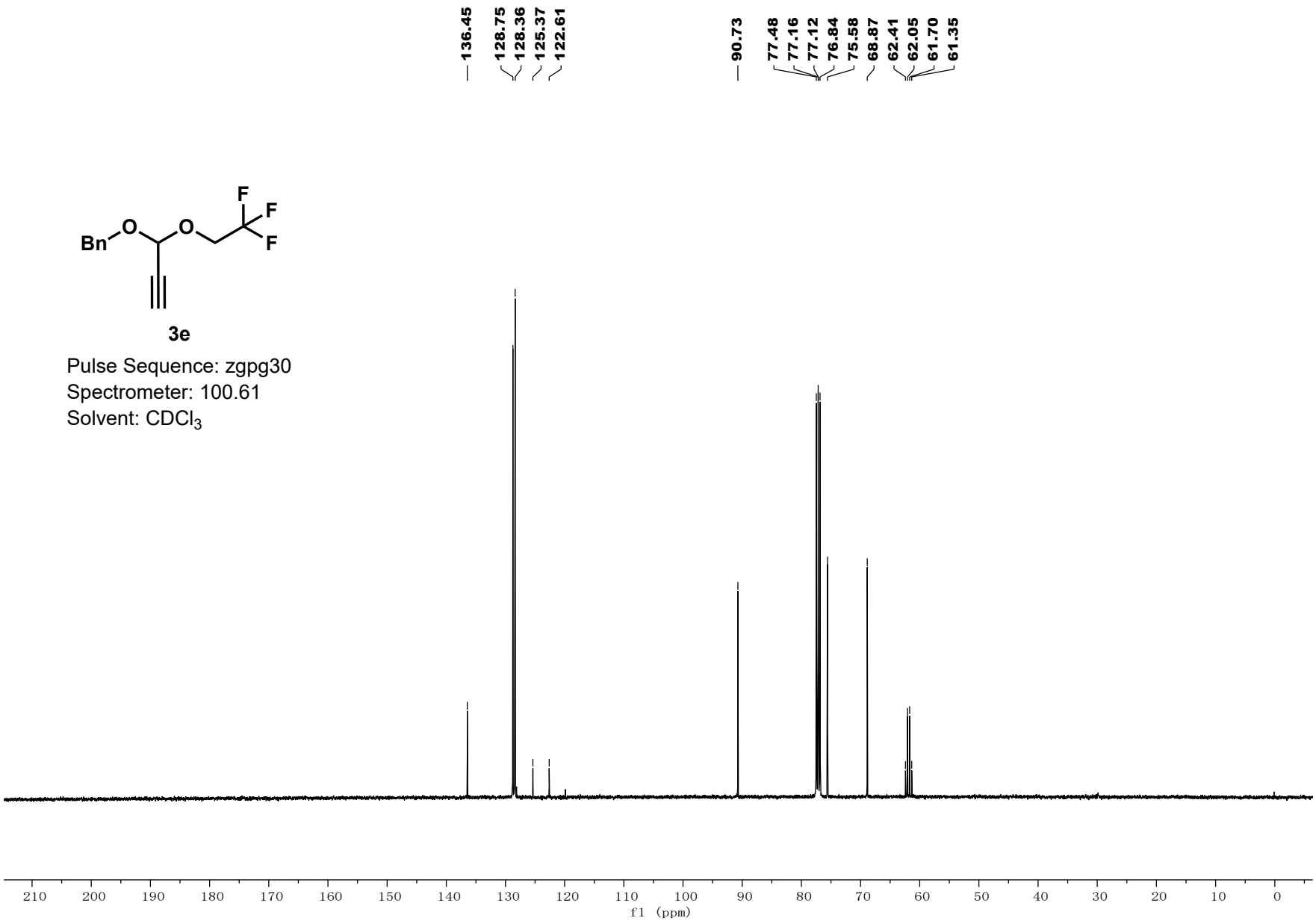
3d

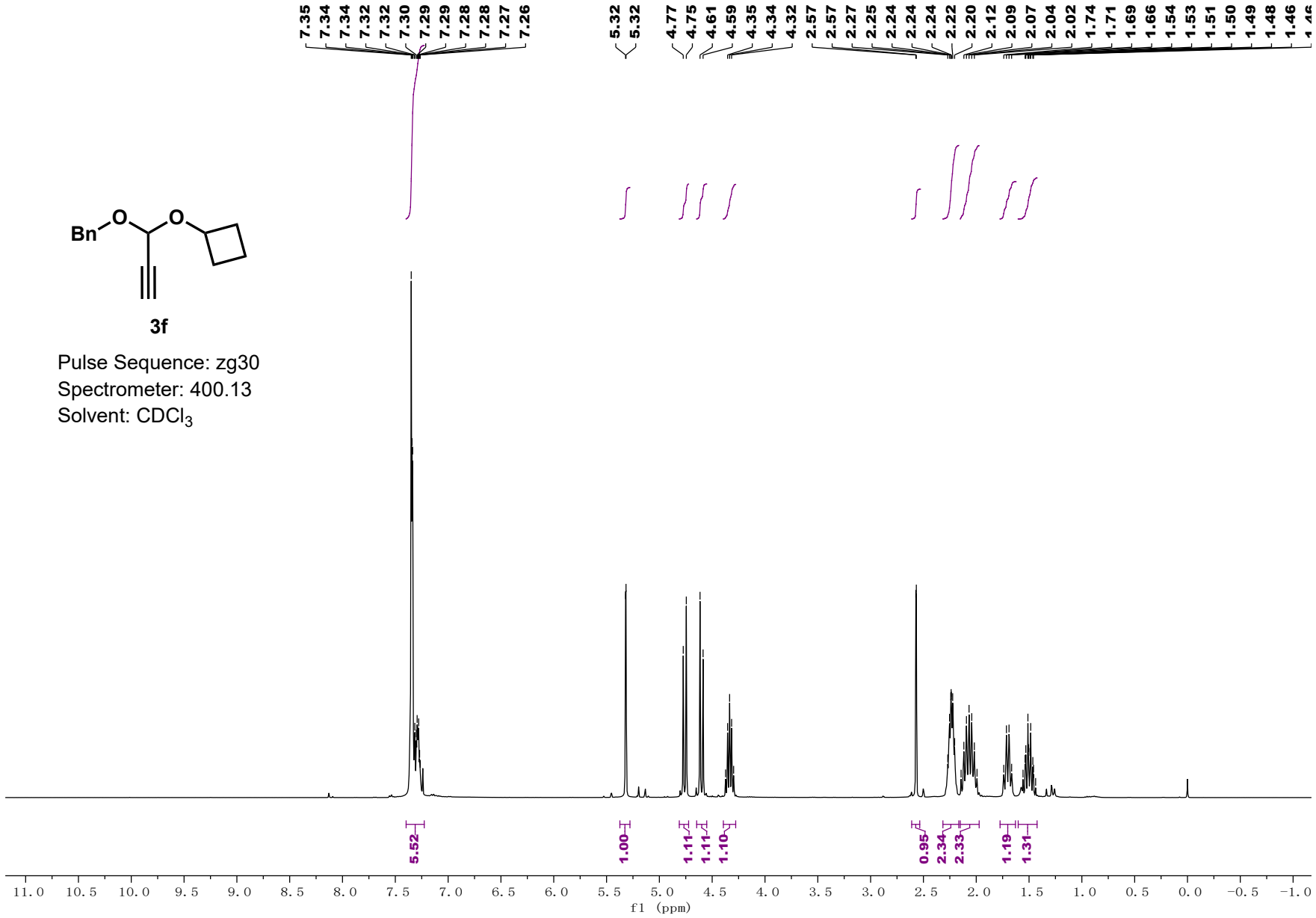
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

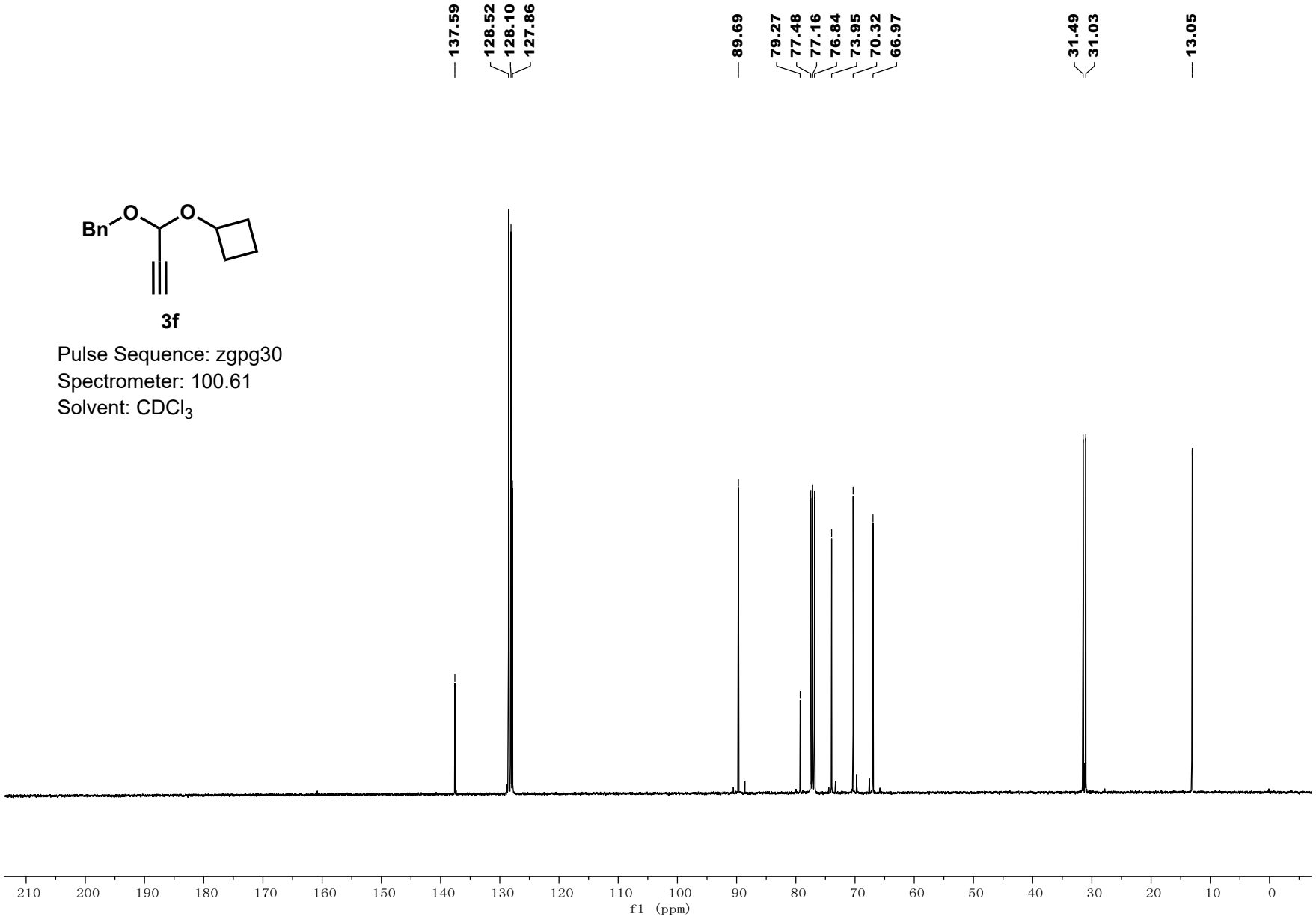


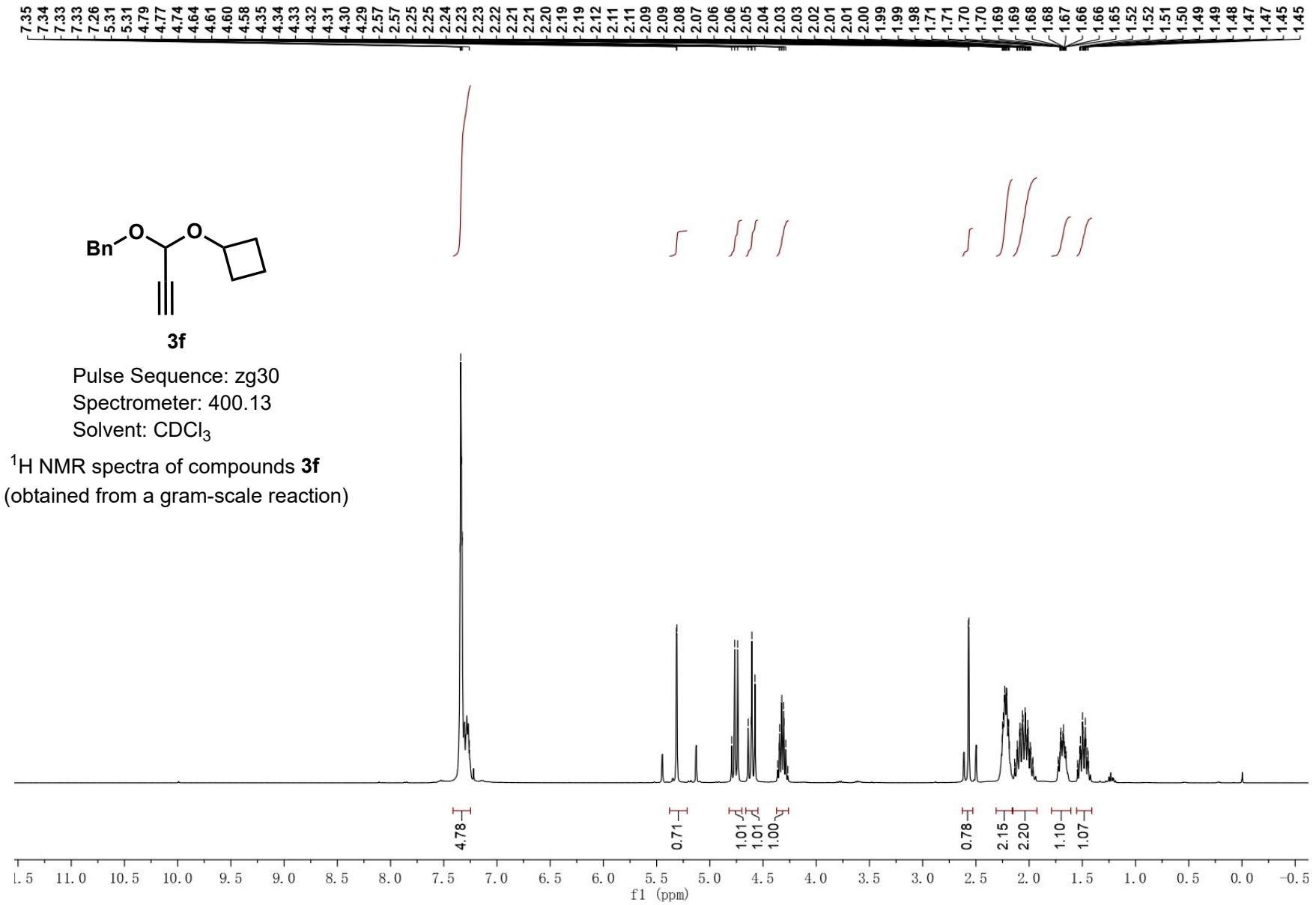

137.07
128.65
128.29
128.13
90.83
78.23
77.48
77.16
76.84
74.80
68.17
65.26
30.40
Bn
O
O
Br
3d
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.37
7.37
7.36
7.36
7.34
7.34
7.33
7.33
7.33
7.32
7.32
5.45
5.45
4.81
4.78
4.62
4.59
4.11
4.09
4.08
4.06
4.06
4.04
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.95
2.66
2.65
Bn
O
O
F
F
F
3e
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.13
1.00
1.09
1.08
2.17
0.95
11.0
10.5
10.0
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
−0.5
f1 (ppm)


136.45
128.75
128.36
125.37
122.61
90.73
77.48
77.16
77.12
76.84
75.58
68.87
62.41
62.05
61.70
61.35
Bn
O
O
F
F
F
3e
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35 7.34 7.34 7.32 7.32 7.30 7.29 7.29 7.28 7.28 7.27 7.26
5.32 5.32
4.77 4.75 4.61 4.59 4.35 4.34 4.32
2.57 2.57 2.27 2.25 2.24 2.24 2.24 2.22 2.20 2.12 2.09 2.07 2.04 2.02 1.74 1.71 1.69 1.66 1.54 1.53 1.51 1.50 1.49 1.48 1.46
Bn
O
O
3f
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.52
1.00
1.11
1.11
1.10
0.95
2.34
2.33
1.19
1.31
11.0 10.5 10.0 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 -0.5 -1.0
f1 (ppm)

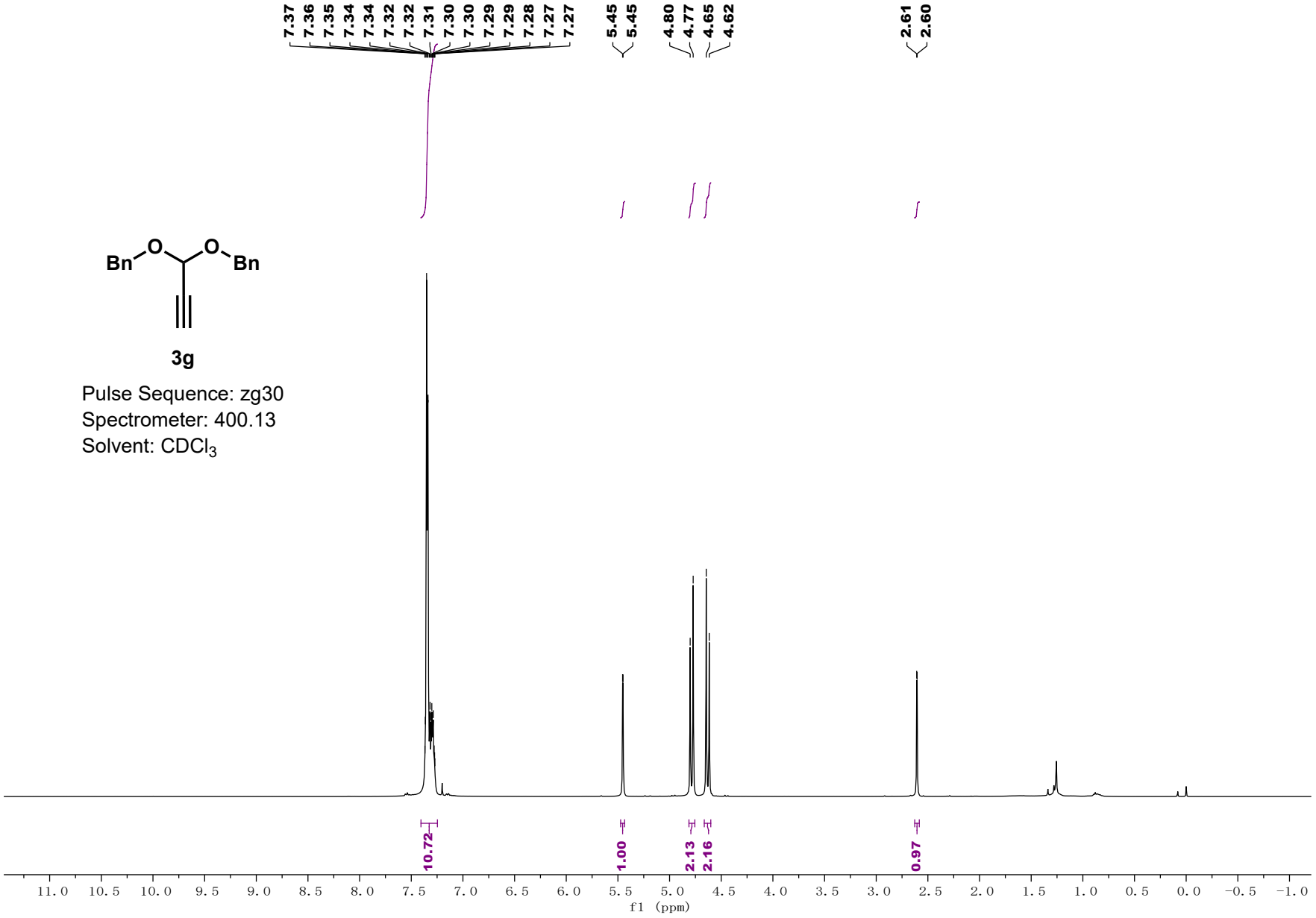

137.59
128.52
128.10
127.86
89.69
79.27
77.48
77.16
76.84
73.95
70.32
66.97
31.49
31.03
13.05
Bn
O
O
3f
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

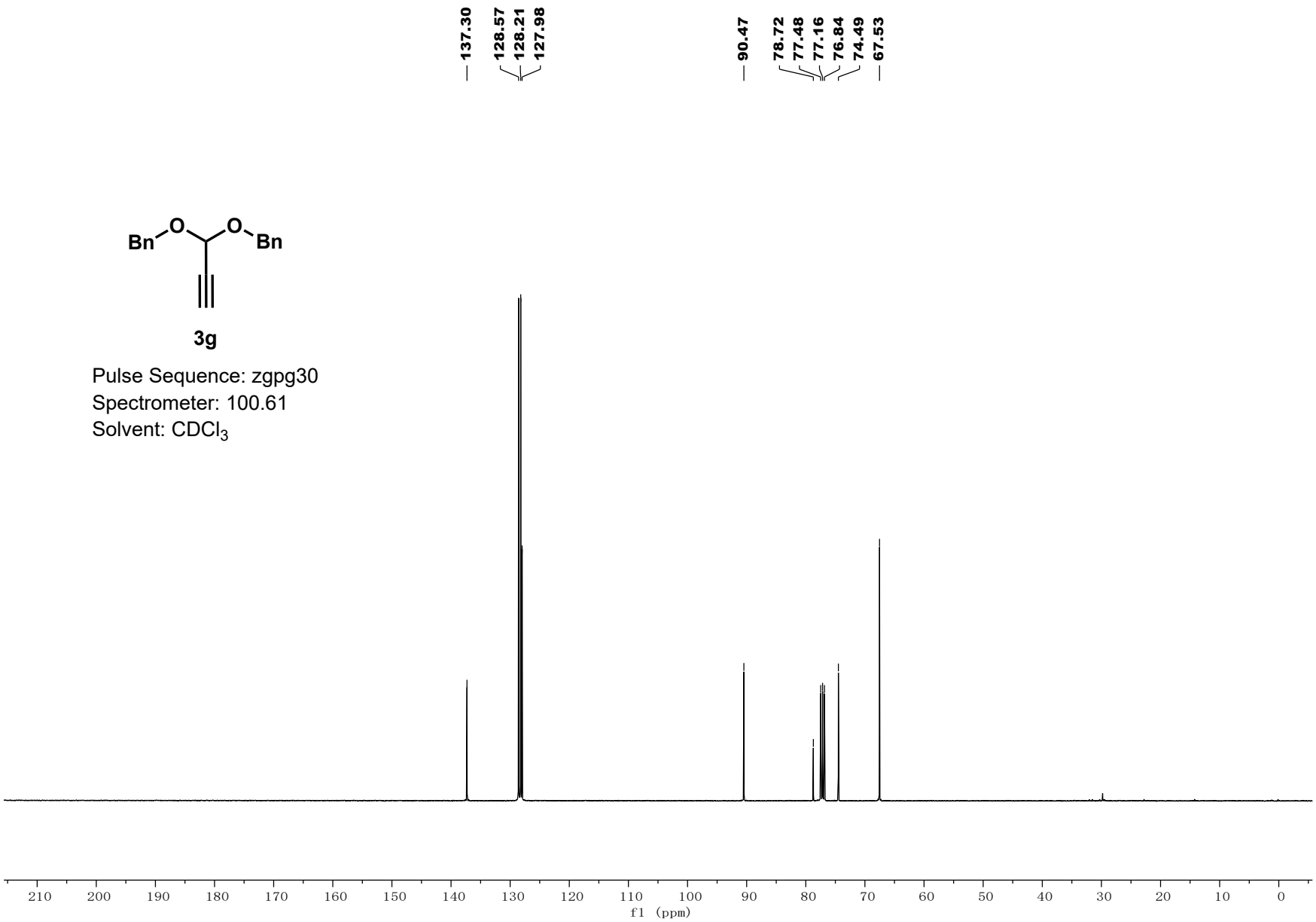


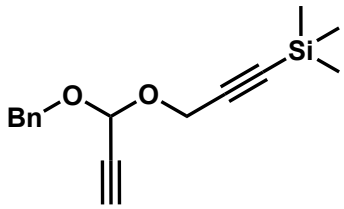
3f

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

^1H NMR spectra of compounds **3f**
(obtained from a gram-scale reaction)

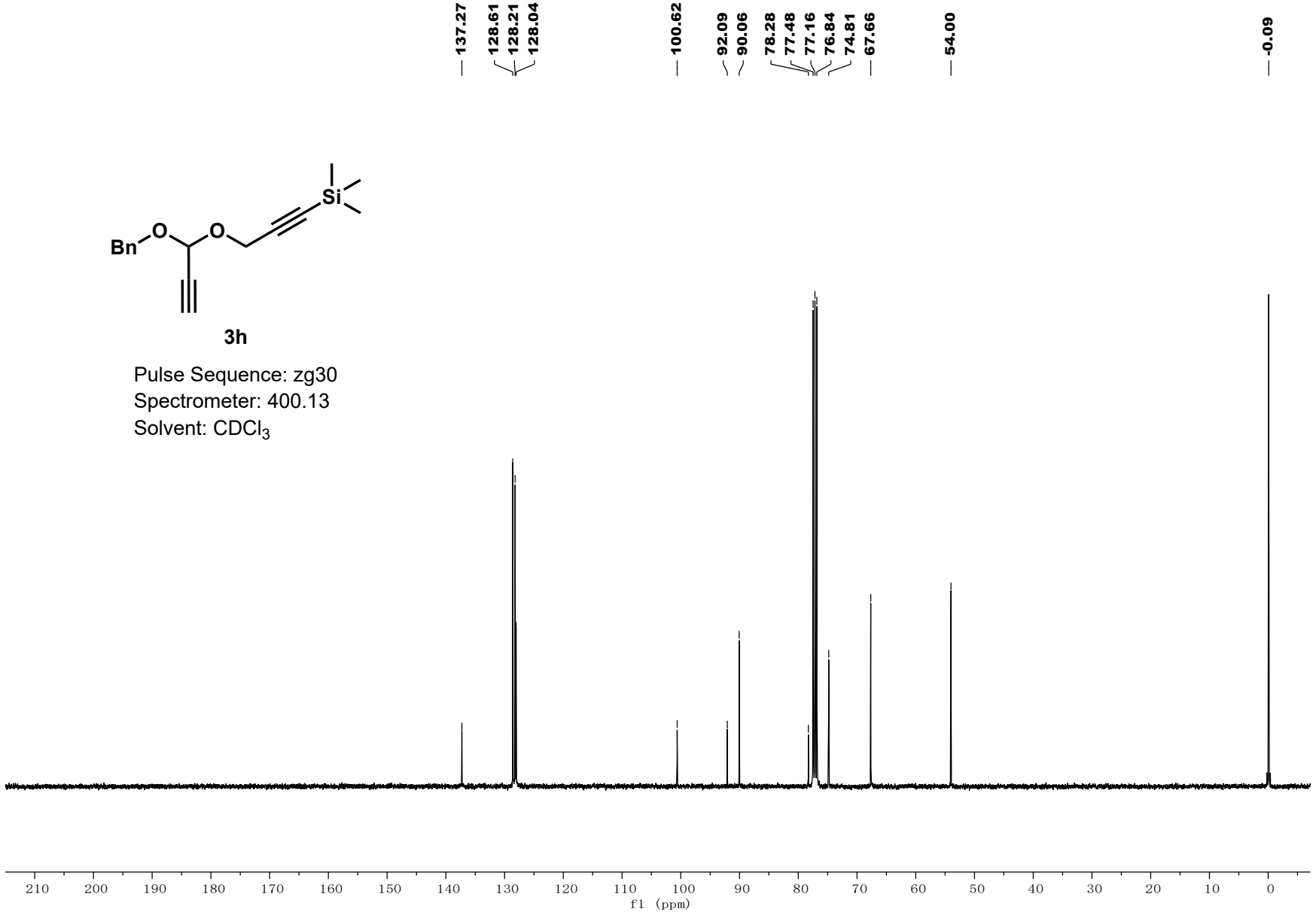

7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
5.45
5.45
4.80
4.77
4.65
4.62
2.61
2.60
Bn
O
O
Bn
3g
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
10.72
1.00
2.13
2.16
0.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

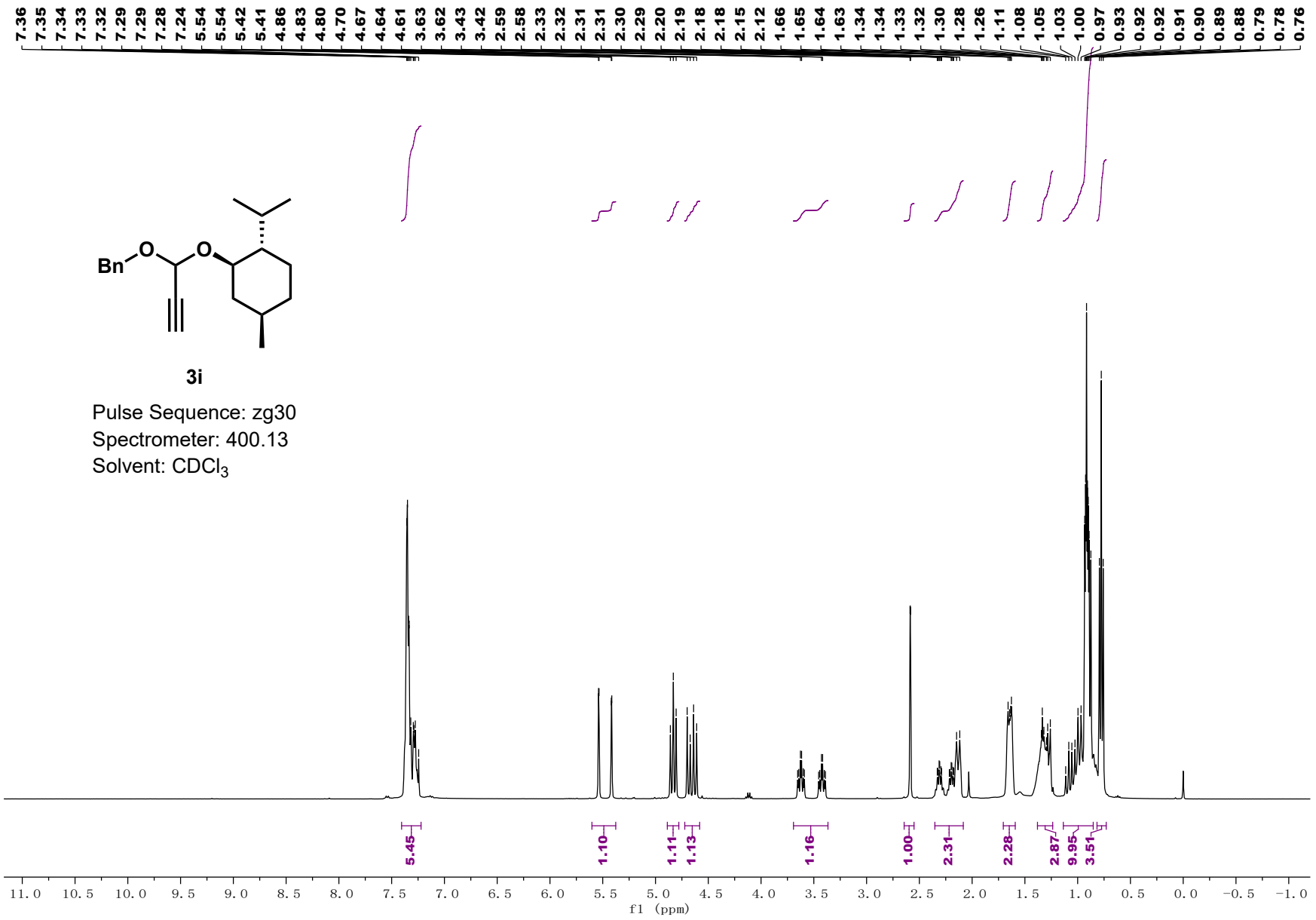

137.30
128.57
128.21
127.98
90.47
78.72
77.48
77.16
76.84
74.49
67.53
Bn
O
O
Bn
3g
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

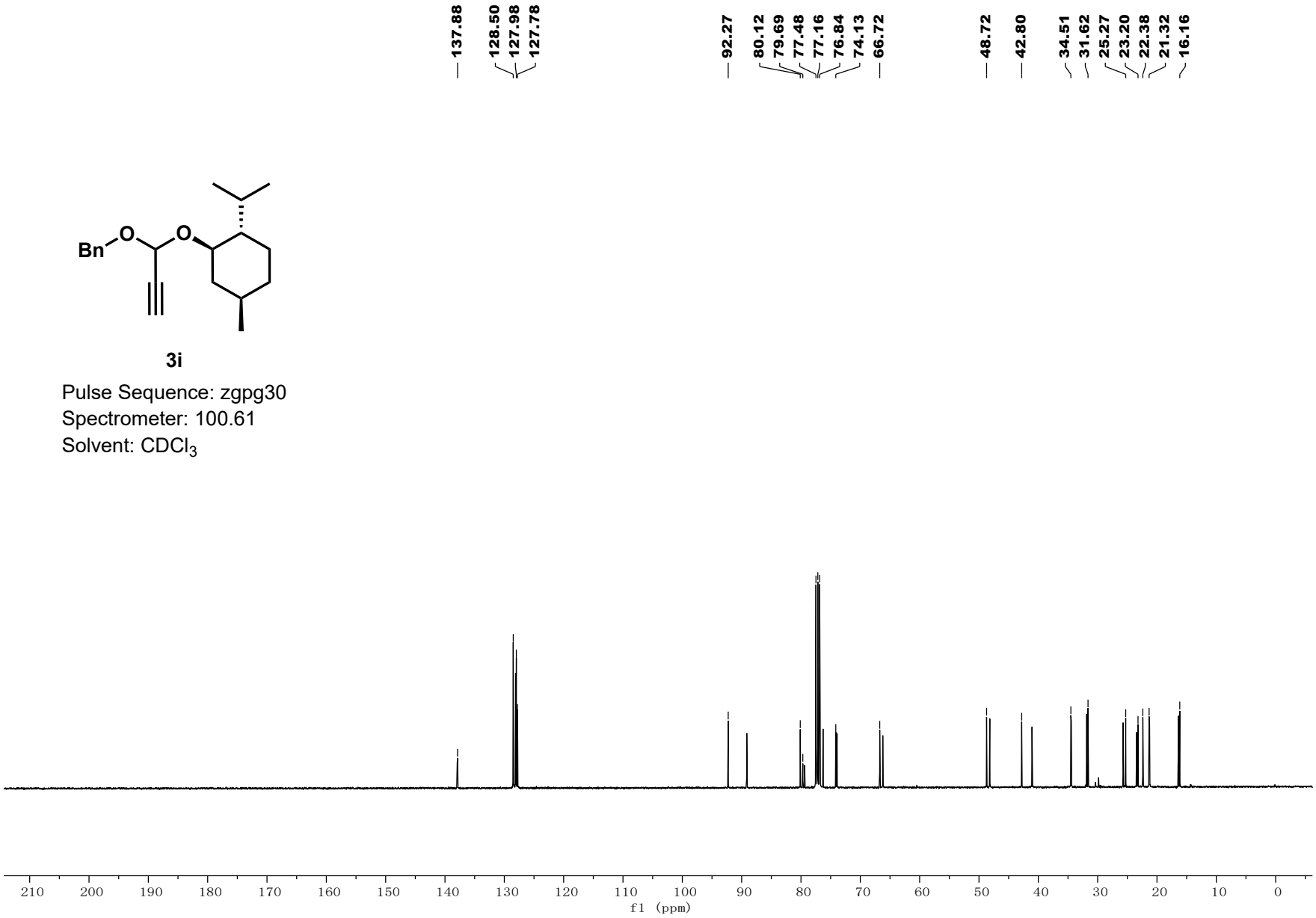


3h

Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: $CDCl_3$

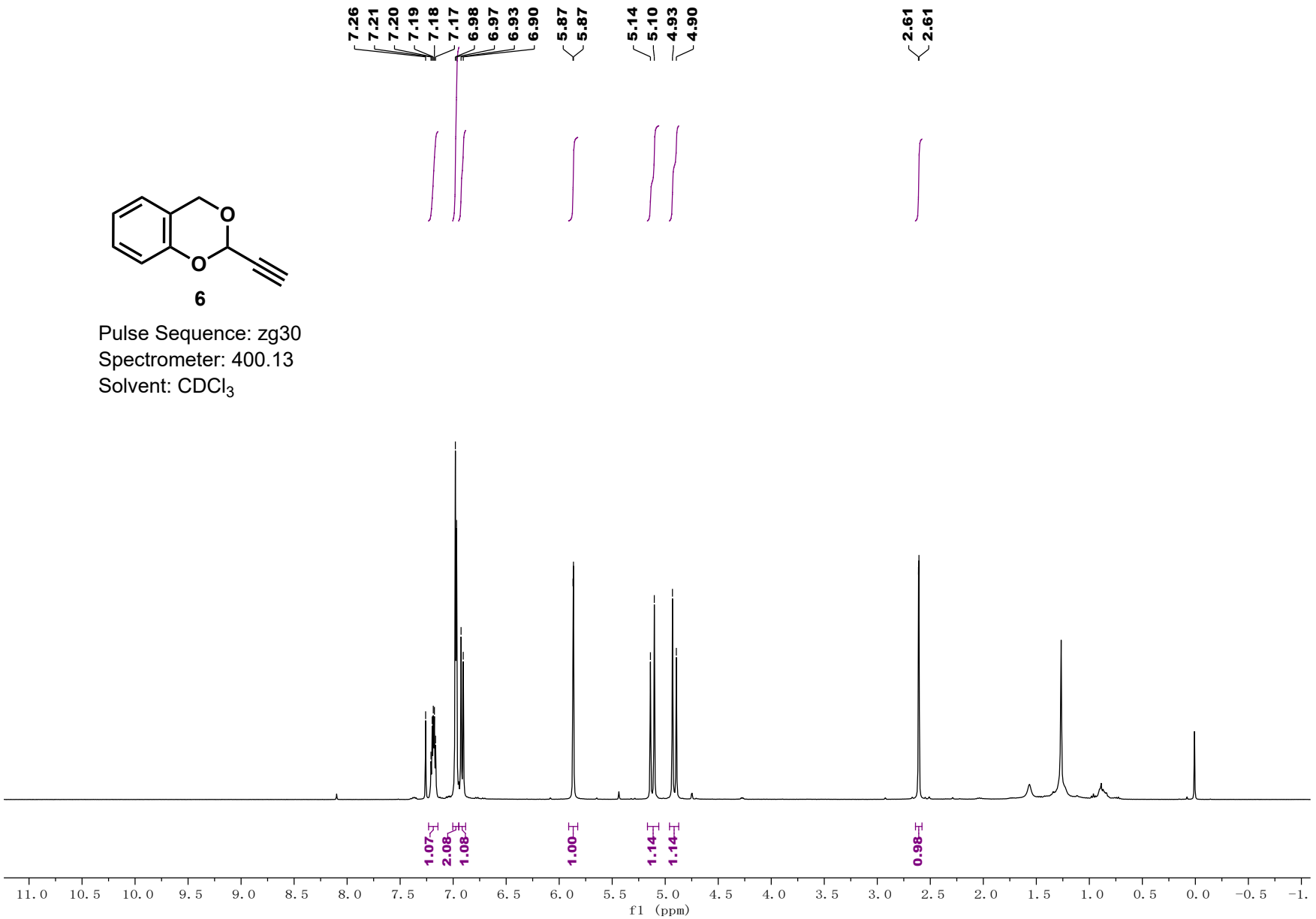

137.27
128.61
128.21
128.04
100.62
92.09
90.06
78.28
77.48
77.16
76.84
74.81
67.66
54.00
-0.09
Bn
O
O
Si
3h
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

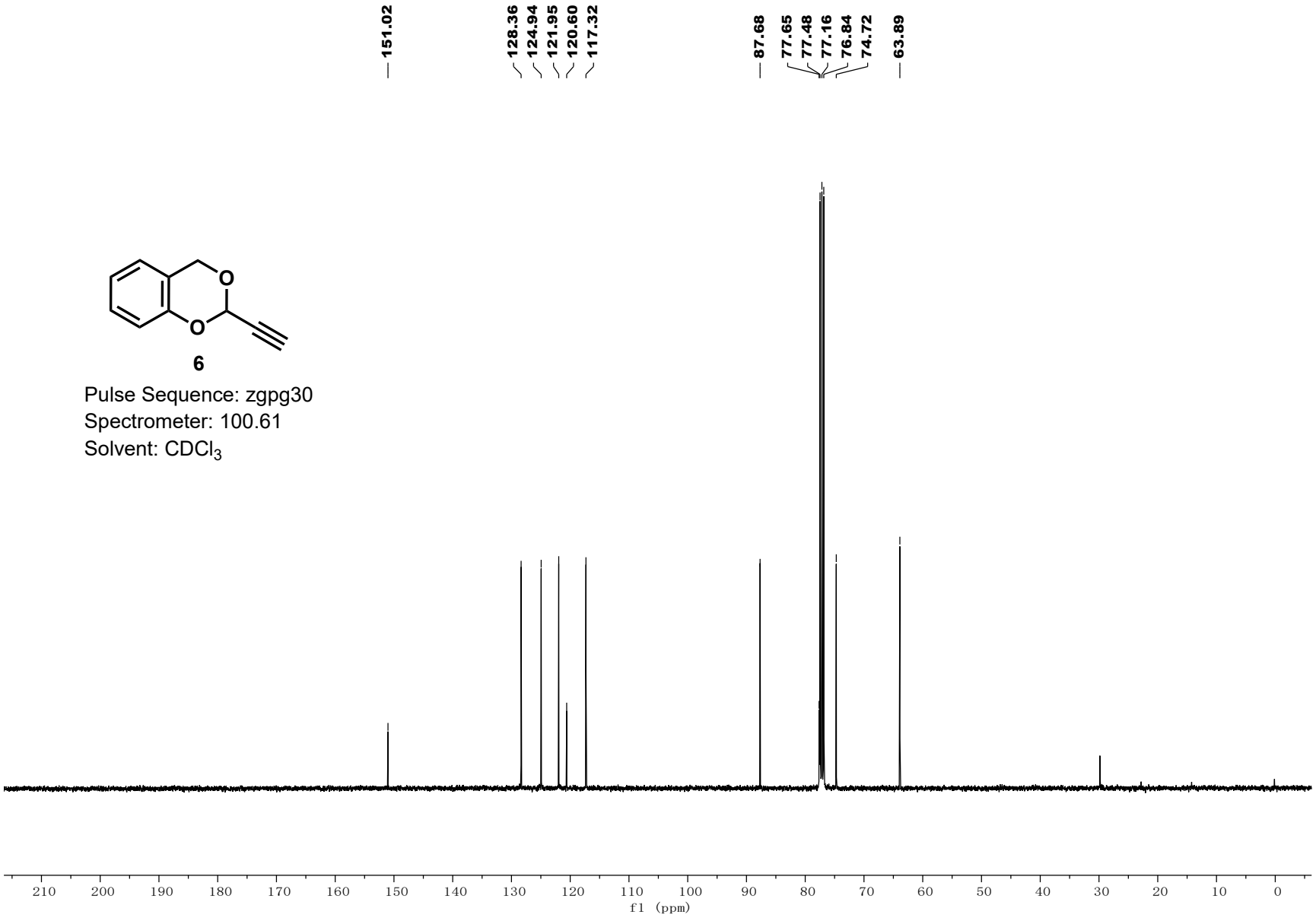

7.36 7.35 7.34 7.33 7.32 7.29 7.29 7.28 7.24 5.54 5.54 5.42 5.41 4.86 4.83 4.80 4.70 4.67 4.64 4.61 3.63 3.62 3.43 3.42 2.59 2.58 2.33 2.32 2.31 2.31 2.30 2.29 2.20 2.19 2.18 2.18 2.15 2.12 1.66 1.65 1.64 1.63 1.34 1.34 1.33 1.32 1.30 1.28 1.26 1.11 1.08 1.05 1.03 1.00 0.97 0.93 0.92 0.92 0.91 0.90 0.89 0.88 0.79 0.78 0.76
Bn
O
O
3i
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
5.45
1.10
1.11
1.13
1.16
1.00
2.31
2.28
2.87
9.95
3.51
11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)



3i

Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: $CDCl_3$


7.26
7.21
7.20
7.19
7.18
7.17
6.98
6.97
6.93
6.90
5.87
5.87
5.14
5.10
4.93
4.90
2.61
2.61
O
O
6
Pulse Sequence: zg30
Spectrometer: 400.13
Solvent: CDCl3
1.07
2.08
1.08
1.00
1.14
1.14
0.98
11.0 10.5 10.0 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 −0.5 −1.
f1 (ppm)


151.02
128.36
124.94
121.95
120.60
117.32
87.68
77.65
77.48
77.16
76.84
74.72
63.89
O
O
6
Pulse Sequence: zgpg30
Spectrometer: 100.61
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)