Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Catalytic Aminomethylative Etherification of N-Allenamides with N,O-Acetals Enabled by Lewis/Brønsted Acid Catalysis

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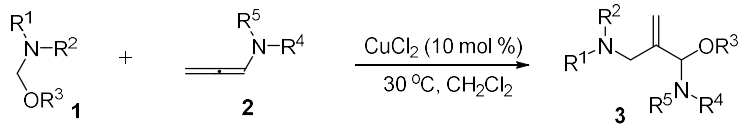
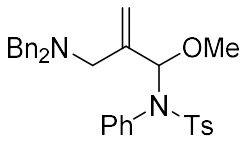
General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz spectrometer in $CDCl_3$. ^{13}C NMR were recorded on Bruker 75 MHz or 100 MHz spectrometer in $CDCl_3$. ^{19}F NMR were recorded on Bruker 282 MHz or 377 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm), and were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets and m = multiplet. Data for ^{13}C NMR spectra were reported relative to $CDCl_3$ as an internal standard (77.16 ppm), and were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 QTOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus without correction. Enantiomeric ratio (er) values were determined by chiral HPLC analysis on Daicel ChiralpakID and IE columns. The allenamide substrates[1], alkoxyallenes[2] and N,O-acetals[3] were prepared according to reported methods.

General procedure for Scheme 2



To a dry tube was added $CuCl_2$ (2.7 mg, 0.02 mmol, 0.1 equiv), **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), and anhydrous DCM (4 mL) under argon atmosphere. Then, the mixture was stirred at 30 °C in a heating block for 12 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give products **3**.



N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzenesulfonamide (3a):

Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as a white solid (82.2 mg, 78%), mp: 106-107 °C.

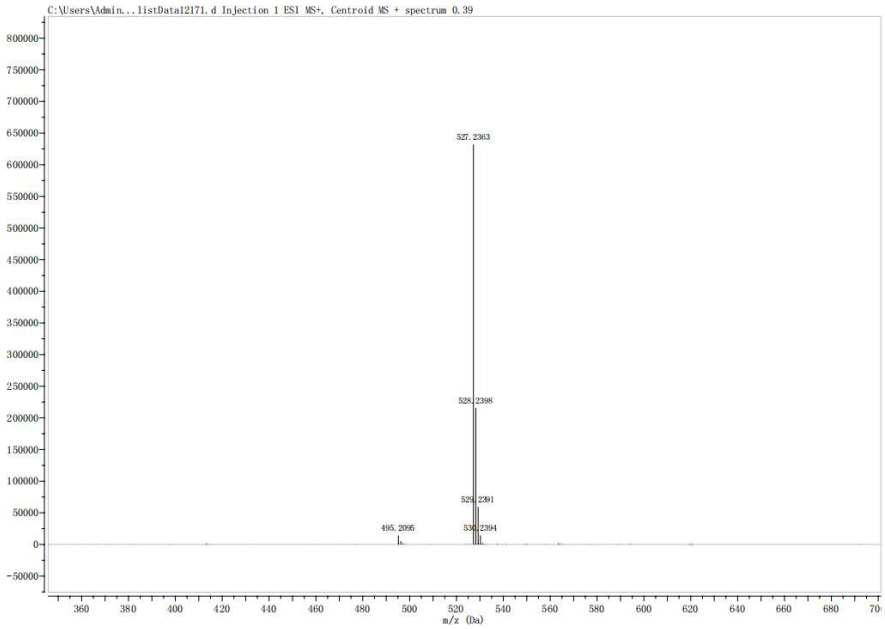
Gram-Scale reaction: N,N-dibenzyl-1-methoxymethanamine (0.83 g, 3.45 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (1.47 g, 5.18 mmol, 1.5 equiv), $CuCl_2$ (46 mg, 0.35 mmol, 10 mol %) in DCM (70 mL), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as a white solid (1.36 g, 75%).

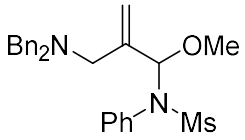
R_f (Petroleum ether/ EtOAc = 10:1) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 4H), 7.40-7.35 (m, 6H), 7.29-7.25 (m, 2H), 7.17-7.13 (m, 3H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.10 (s, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 3.74 (d, *J* = 13.7 Hz, 2H), 3.39 (s, 3H), 3.25 (d, *J* = 13.7 Hz, 2H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.66 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 140.6, 139.3, 137.0, 135.6, 131.3, 128.8, 128.7, 128.5, 128.2, 127.99, 127.96, 126.9, 117.2, 89.4, 58.4, 56.7, 56.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{35}N_2O_3S$ 527.2363, found 527.2363.





N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-phenylmethanesulfonamide (3b):

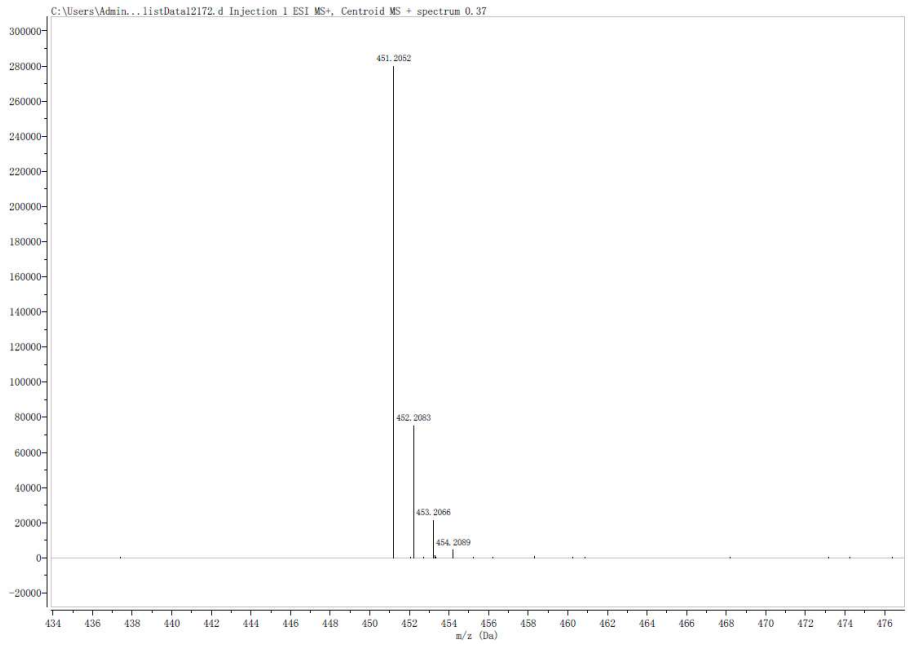
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and N-phenyl-N-(propa-1,2-dien-1-yl)methanesulfonamide (62.7 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 10:1) and obtained as a white solid (68 mg, 75%), mp: 79-80 °C.

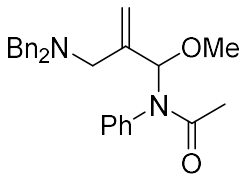
R_f (Petroleum ether/ EtOAc = 10:1) = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.27-7.23 (m, 2H), 7.19-7.12 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.03 (s, 1H), 5.18 (s, 1H), 5.16 (s, 1H), 3.80 (d, *J* = 13.7 Hz, 2H), 3.44 (s, 3H), 3.12 (d, *J* = 13.7 Hz, 2H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.89 (s, 3H), 2.56 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.2, 136.1, 130.6, 128.8, 128.6, 128.5, 128.2, 127.0, 118.0, 89.5, 58.5, 57.1, 56.5, 39.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$ 451.2050, found 451.2052.





N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-phenylacetamide (3c):

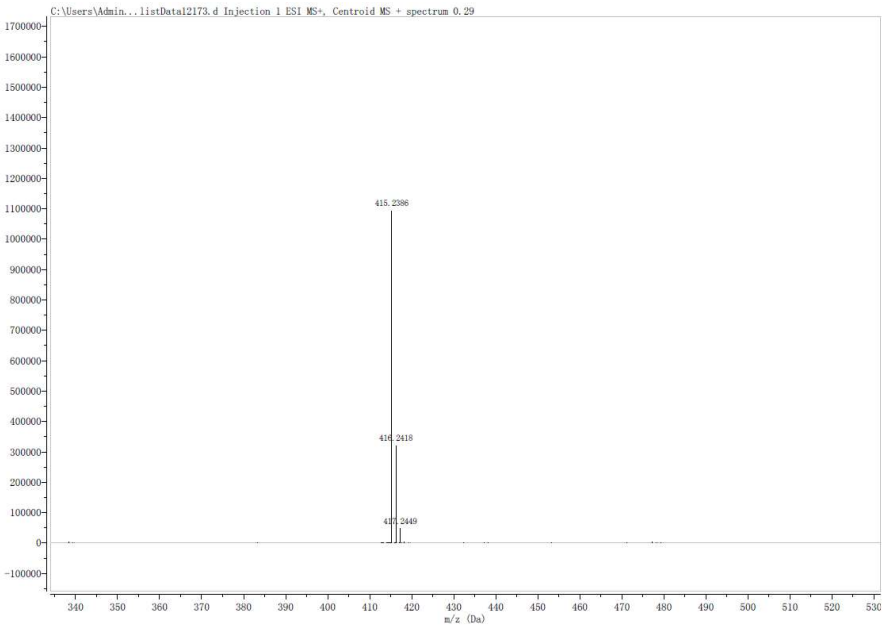
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and N-phenyl-N-(propa-1,2-dien-1-yl)acetamide (51.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 8:1) and obtained as a white solid (52.2 mg, 63%), mp: 89-90 °C.

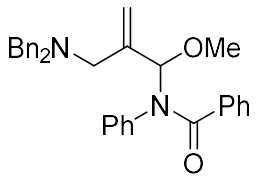
R_f (Petroleum ether/ EtOAc = 10:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 5H), 7.35 (t, *J* = 7.5 Hz, 5H), 7.25-7.23 (m, 2H), 7.19-7.14 (m, 3H), 6.59 (s, 1H), 5.11 (s, 1H), 5.09 (s, 1H), 3.80 (d, *J* = 13.5 Hz, 2H), 3.50 (s, 3H), 3.13 (d, *J* = 13.5 Hz, 2H), 3.03 (d, *J* = 14.2 Hz, 1H), 2.60 (d, *J* = 14.2 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 142.1, 139.7, 139.1, 129.01, 128.96, 128.5, 128.3, 127.6, 126.9, 117.0, 83.1, 58.6, 56.7, 56.6, 23.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{31}N_2O_2$ 415.2380, found 415.2386.





N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-phenylbenzamide (3d):

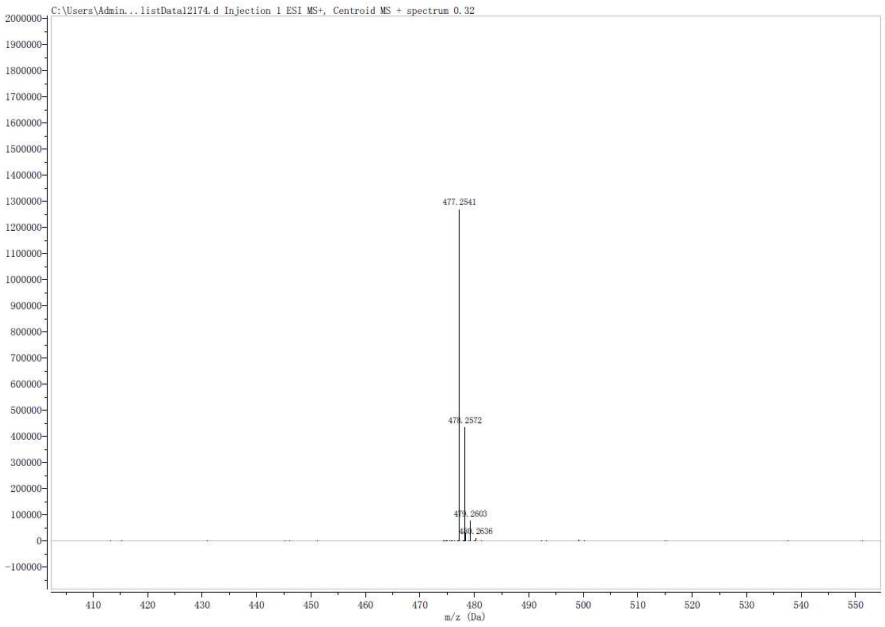
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and N-phenyl-N-(propa-1,2-dien-1-yl)benzamide (70.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 10:1) and obtained as colorless oil (50.5 mg, 53%).

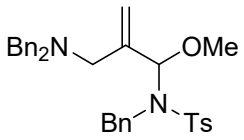
R_f (Petroleum ether/ EtOAc = 10:1) = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.24-7.19 (m, 5H), 7.15-7.11 (m, 2H), 7.02-6.95 (m, 3H), 6.85-6.45 (m, 3H), 5.31 (s, 2H), 3.72 (d, *J* = 13.6 Hz, 2H), 3.57 (s, 3H), 3.20 (d, *J* = 13.6 Hz, 2H), 3.05 (d, *J* = 14.5 Hz, 1H), 2.69 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 142.0, 139.6, 139.4, 136.0, 129.7, 128.9, 128.8, 128.3, 128.1, 127.6, 126.9, 126.6, 117.0, 84.7, 58.6, 56.5, 56.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{33}N_2O_2$ 477.2537, found 477.2541.





N-benzyl-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide (3e):

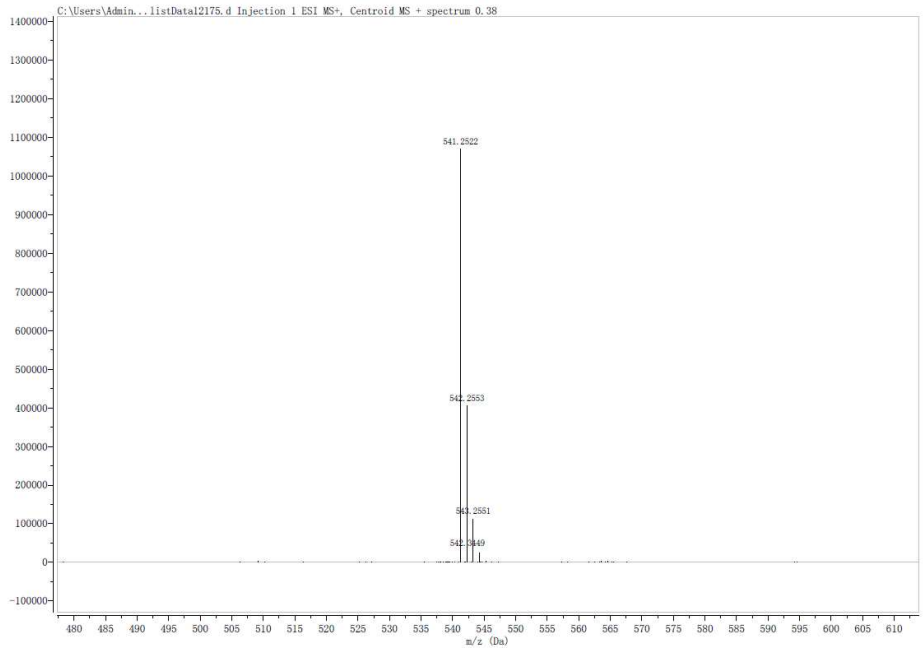
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and N-benzyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (89.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as yellow oil (60.6 mg, 56%).

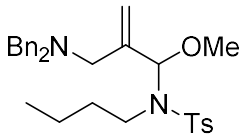
R_f (Petroleum ether/ EtOAc = 10:1) = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.38-7.33 (m, 8H), 7.27-7.24 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11-7.05 (m, 5H), 5.71 (s, 1H), 5.33 (s, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 4.11(d, *J* = 16.0 Hz, 1H), 3.56 (d, *J* = 13.8 Hz, 2H), 3.25 (d, *J* = 13.8 Hz, 2H), 3.16 (s, 3H), 2.80 (d, *J* = 14.6 Hz, 1H), 2.51 (d, *J* = 14.6 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 141.7, 139.2, 137.5, 137.3, 129.3, 128.7, 128.6, 128.4, 127.89, 127.85, 126.9, 126.8, 116.9, 88.3, 58.0, 56.19, 56.16, 46.5, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{37}N_2O_3S$ 541.2519, found 541.2522.





N-butyl-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide (3f):

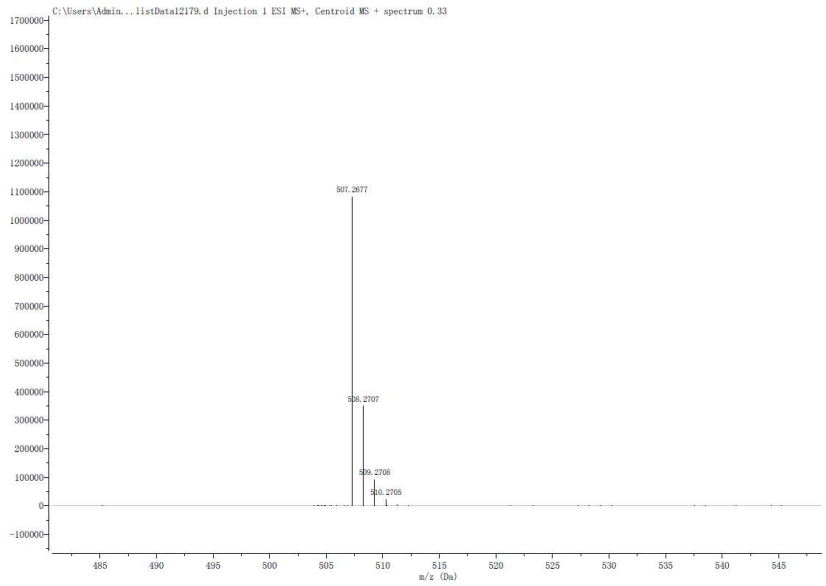
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and N-butyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (79.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as colorless oil (85.1 mg, 84%).

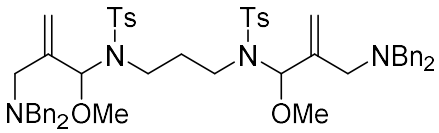
R_f (Petroleum ether/ EtOAc = 10:1) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.23-7.21 (m, 4H), 5.54 (s, 1H), 5.49 (s, 1H), 5.29 (s, 1H), 3.56-3.46 (m, 4H), 3.24 (s, 3H), 3.02-2.94 (m, 1H), 2.90-2.86 (m, 2H), 2.82-2.72 (m, 1H), 2.39 (s, 3H), 1.43-1.26 (m, 2H), 1.09-1.02 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.0, 139.2, 137.8, 129.4, 128.7, 128.3, 127.6, 127.0, 115.4, 88.4, 58.1, 56.2, 56.1, 43.2, 32.1, 21.6, 20.3, 13.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{39}N_2O_3S$ 507.2676, found 507.2677.





N,N'-(propane-1,3-diyl)bis(N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide) (3g):

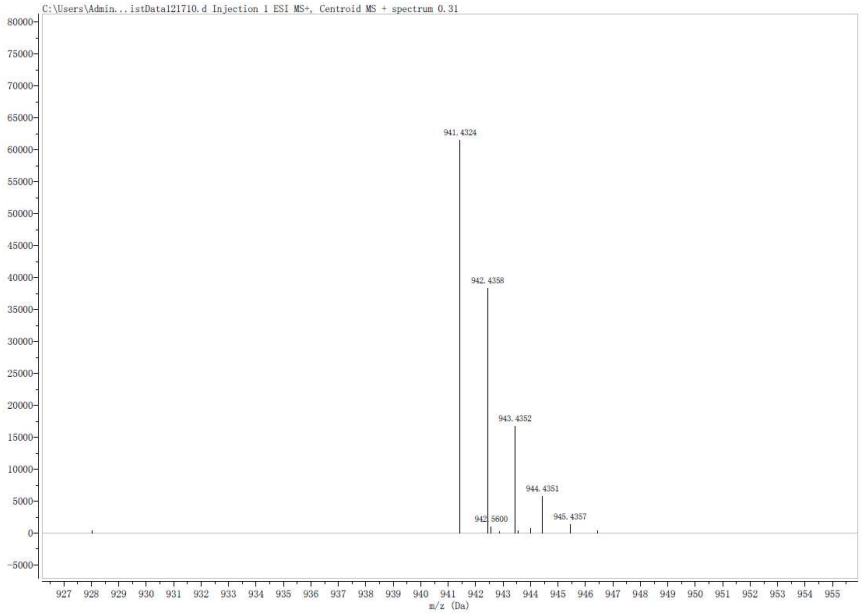
P Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (72.3 mg, 0.3 mmol, 1.5 equiv) and N,N'-(propane-1,3-diyl)bis(4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide) (91.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 7:1) and obtained as colorless oil (114.8 mg, 61%).

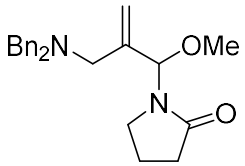
R_f (Petroleum ether/ EtOAc = 5:1) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 4H), 7.34-7.28 (m, 14H), 7.25-7.13 (m, 10H), 5.50 (s, 2H), 5.38 (s, 2H), 5.18 (s, 2H), 3.52-3.43 (m, 8H), 3.15 (s, 3H), 3.14 (s, 3H), 2.91-2.82 (m, 4H), 2.75-2.70 (m, 2H), 2.67-2.58 (m, 2H), 2.39 (s, 6H), 1.58-1.54 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 141.7, 139.0, 137.61, 137.57, 129.4, 128.7, 128.3, 127.6, 126.9, 116.12, 116.05, 88.1, 57.8, 56.06, 56.05, 41.1, 30.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{55}H_{65}N_4O_6S_2$ 941.4340, found 941.4324.





1-(2-((dibenzylamino)methyl)-1-methoxyallyl)pyrrolidin-2-one (3h):

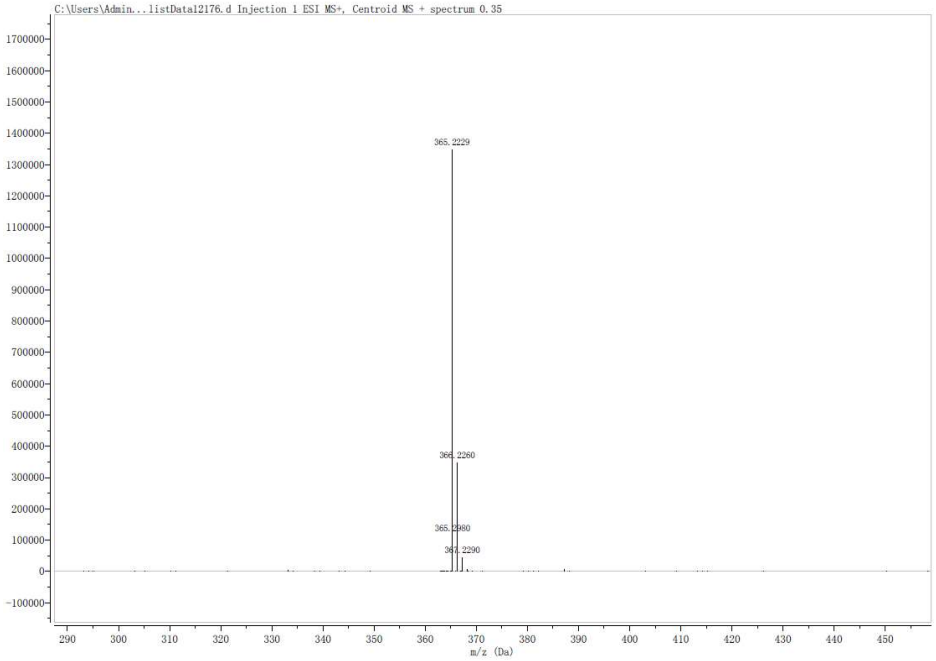
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 1-(propa-1,2-dien-1-yl)pyrrolidin-2-one (36.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 4:1) and obtained as colorless oil (49.6 mg, 68%).

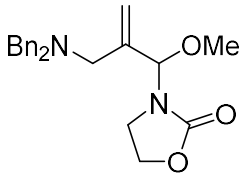
R_f (Petroleum ether/ EtOAc = 5:1) = 0.25.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (m, 4H), 7.34-7.28 (m, 4H), 7.24-7.19 (m, 2H), 5.72 (s, 1H), 5.46 (s, 1H), 5.43 (s, 1H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.29 (d, *J* = 13.6 Hz, 2H), 3.28 (s, 3H), 3.17-3.09 (m, 1H), 2.97 (d, *J* = 14.3 Hz, 1H), 2.89-2.83 (m, 1H), 2.76 (d, *J* = 14.3 Hz, 1H), 2.44-2.32 (m, 1H), 2.28-2.18 (m, 1H), 1.89-1.80 (m, 1H), 1.56-1.46 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.3, 139.4, 128.8, 128.3, 126.9, 115.5, 80.9, 58.5, 56.4, 55.9, 41.5, 31.7, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{29}N_2O_2$ 365.2224, found 365.2229.





3-(2-((dibenzylamino)methyl)-1-methoxyallyl)oxazolidin-2-one (3i):

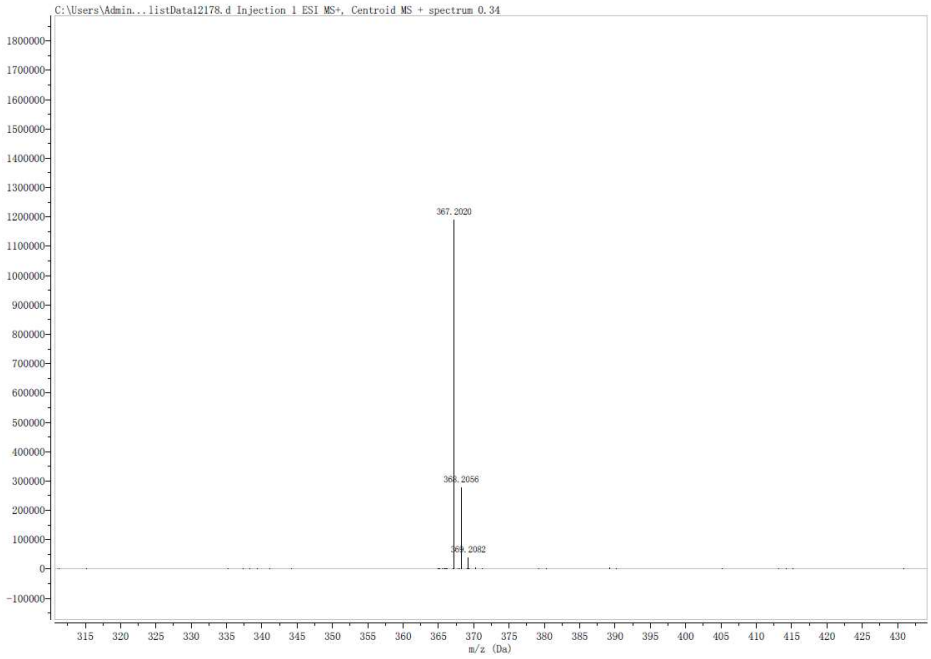
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 3-(propa-1,2-dien-1-yl)oxazolidin-2-one (37.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 5:1) and obtained as a white solid (47.6 mg, 65%), mp: 81-82 °C.

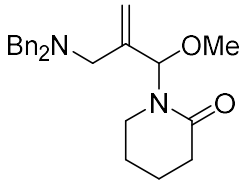
R_f (Petroleum ether/ EtOAc = 5:1) = 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 4H), 7.26-7.21 (m, 2H), 5.57 (s, 1H), 5.45 (s, 1H), 5.42 (s, 1H), 4.23-4.17 (m, 1H), 3.79-3.72 (m, 3H), 3.38-3.32 (m, 4H), 3.24 (d, *J* = 13.6 Hz, 2H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.96-2.90 (m, 1H), 2.79 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.1, 139.2, 128.8, 128.4, 127.0, 116.3, 83.1, 62.1, 58.5, 56.6, 56.3, 39.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{27}N_2O_3$ 367.2016, found 367.2020.





1-(2-((dibenzylamino)methyl)-1-methoxyallyl)piperidin-2-one (3j):

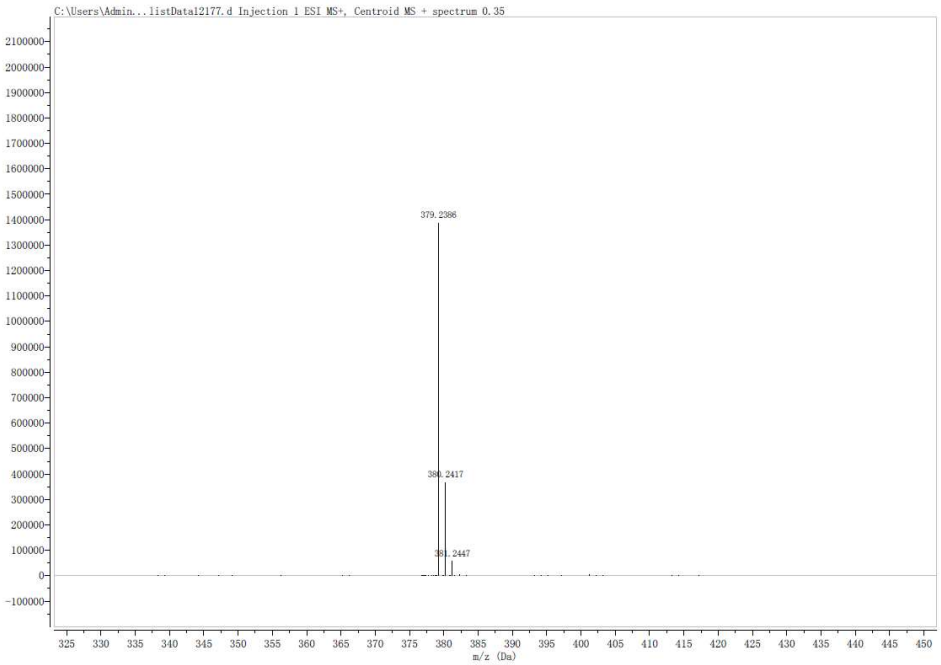
Prepared via **general procedure 2** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 1-(propa-1,2-dien-1-yl)piperidin-2-one (41.1 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 4:1) and obtained as yellow oil (53.8 mg, 77%).

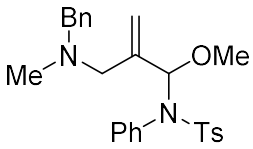
R_f (Petroleum ether/ EtOAc = 5:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.23-7.18 (m, 2H), 6.28 (s, 1H), 5.53 (s, 1H), 5.40 (s, 1H), 3.65 (d, *J* = 13.6 Hz, 2H), 3.36 (d, *J* = 13.6 Hz, 2H), 3.27 (s, 3H), 2.03-2.95 (m, 2H), 2.79-2.70 (m, 2H), 2.45-2.27 (m, 2H), 1.70-1.55 (m, 2H), 1.53-1.38 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 142.4, 139.5, 128.8, 128.3, 126.8, 115.3, 82.0, 58.5, 56.0, 55.8, 40.2, 32.5, 22.8, 20.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{31}N_2O_2$ 379.2380, found 379.2386.





N-(2-((benzyl(methyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzenesulfonamide (3k):

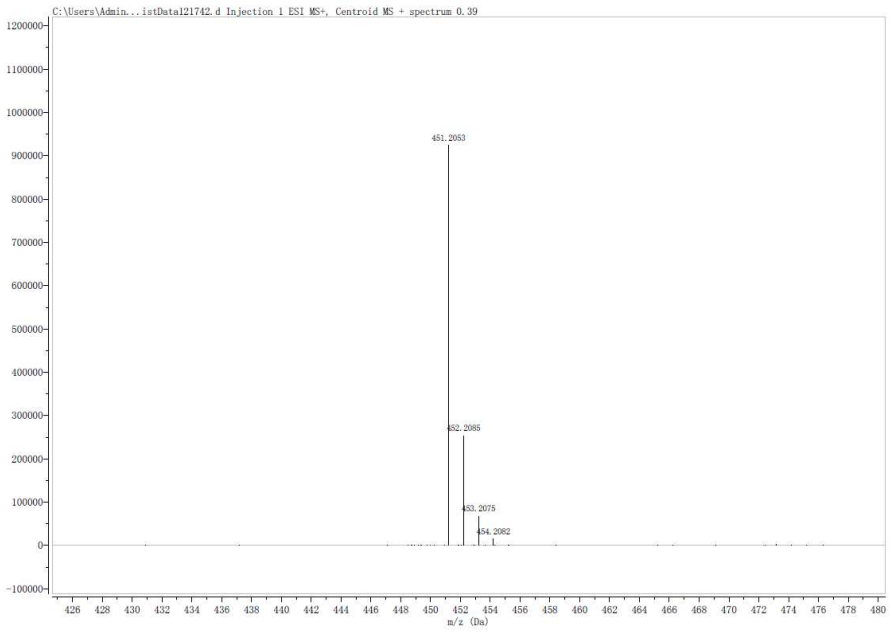
Prepared via **general procedure 2** from N-benzyl-1-methoxy-N-methylmethanamine (33.0 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as yellow oil (72.1 mg, 80%).

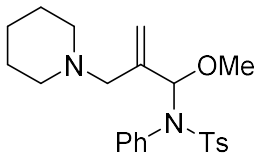
R_f (Petroleum ether/ EtOAc = 10:1) = 0.55.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 2H), 7.26-7.12 (m, 6H), 6.96-6.93 (m, 2H), 6.09 (s, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 3.60 (d, *J* = 13.3 Hz, 1H), 3.46 (s, 3H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.8, 139.3, 137.1, 135.6, 131.4, 129.0, 128.9, 128.4, 128.18, 128.16, 128.1, 127.0, 117.2, 89.0, 62.2, 60.0, 56.6, 42.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_3S$ 451.2050, found 451.2053.





N-(1-methoxy-2-(piperidin-1-ylmethyl)allyl)-4-methyl-N-phenylbenzenesulfonamide (3l):

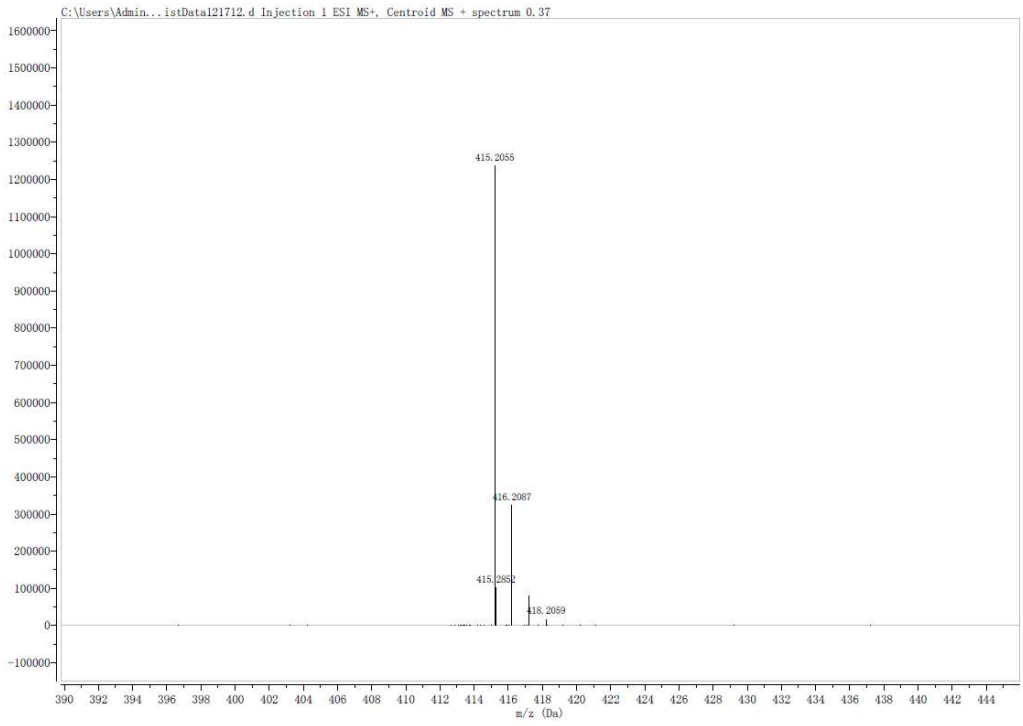
Prepared via **general procedure 2** from 1-(methoxymethyl)piperidine (25.8 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 4:1) and obtained as a white solid (53.1 mg, 64%), mp: 62-63 °C.

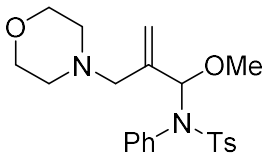
R_f (Petroleum ether/ EtOAc = 5:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.24-7.16 (m, 5H), 7.04-7.01 (m, 2H), 5.97 (s, 1H), 4.92 (s, 1H), 4.91 (s, 1H), 3.47 (s, 3H), 2.91 (d, *J* = 13.8 Hz, 1H), 2.56 (d, *J* = 13.8 Hz, 1H), 2.40 (s, 3H), 2.38-2.31 (m, 2H), 2.28-2.18 (m, 2H), 1.62-1.55 (m, 4H), 1.43-1.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 140.4, 137.4, 135.6, 131.4, 129.0, 128.21, 128.20, 128.1, 116.7, 89.1, 61.2, 56.4, 54.7, 26.1, 24.5, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{31}N_2O_3S$ 415.2050, found 415.2055.





N-(1-methoxy-2-(morpholinomethyl)allyl)-4-methyl-N-phenylbenzenesulfonamide (3m):

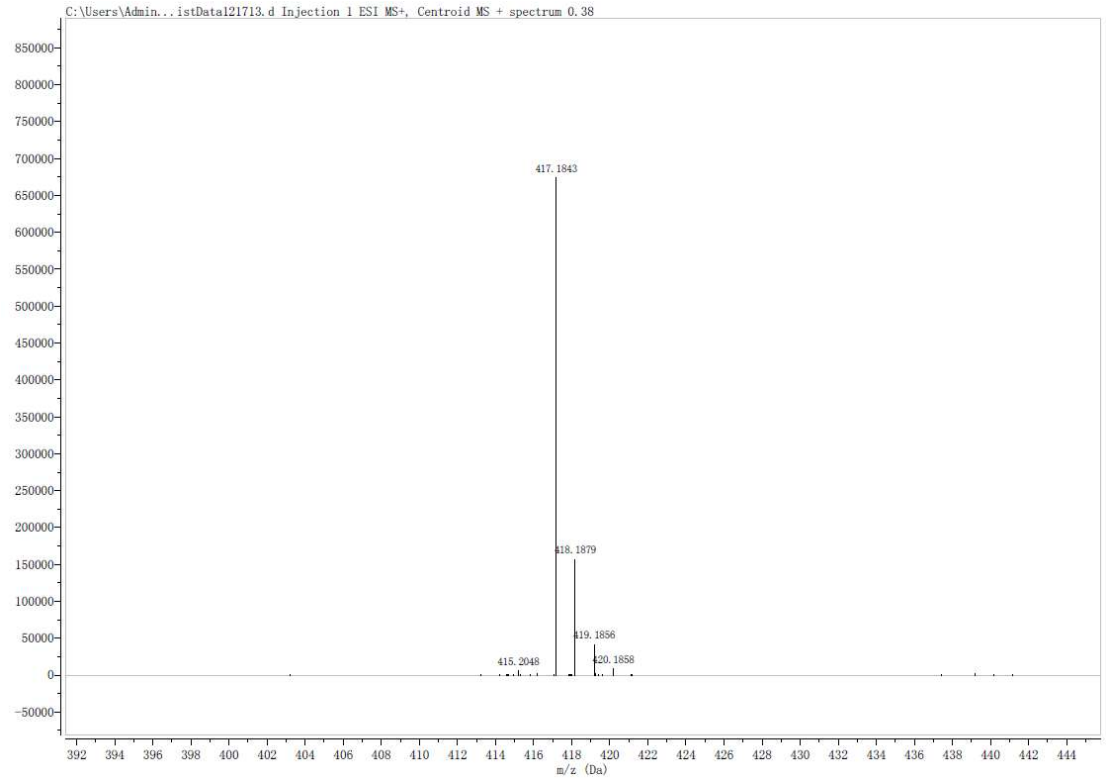
Prepared via **general procedure 2** from 4-(methoxymethyl)morpholine (26.2 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 5:1) and obtained as a white solid (71.6 mg, 86%), mp: 76-77 °C.

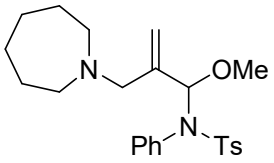
R_f (Petroleum ether/ EtOAc = 5:1) = 0.3.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.25-7.16 (m, 5H), 7.07-7.03 (m, 2H), 6.00 (s, 1H), 4.94 (s, 2H), 3.78-3.66 (m, 4H), 3.44 (s, 3H), 3.01 (d, J = 13.7 Hz, 1H), 2.61 (d, J = 13.7 Hz, 1H), 2.48-2.41 (m, 2H), 2.39 (s, 3H), 2.38-2.30 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.5, 137.1, 135.5, 131.4, 129.1, 128.3, 128.0, 117.4, 88.9, 67.1, 60.8, 56.5, 53.7, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{29}N_2O_4S$ 417.1843, found 417.1843.





N-(2-(azepan-1-ylmethyl)-1-methoxyallyl)-4-methyl-N-phenylbenzenesulfonamide (3n):

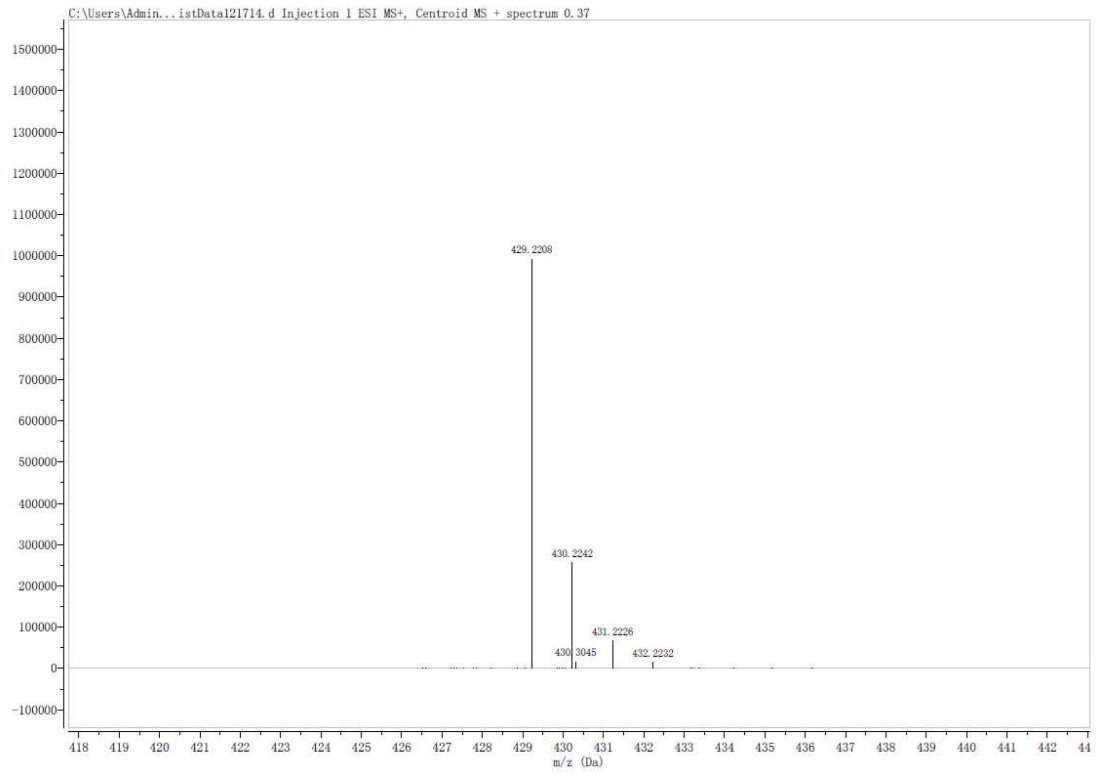
Prepared via **general procedure 2** from 1-(methoxymethyl)azepane (28.6 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 5:1) and obtained as colorless oil (57.4 mg, 67%).

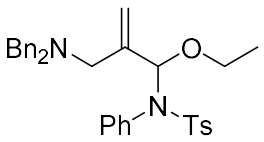
R_f (Petroleum ether/ EtOAc = 5:1) = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H, 7.24-7.16 (m, 5H), 7.05-7.03 (m, 2H), 6.06 (s, 1H), 4.91 (s, 1H), 4.86 (s, 1H), 3.45 (s, 3H), 3.02 (d, *J* = 13.9 Hz, 1H), 2.82 (d, *J* = 13.9 Hz, 1H), 2.62-2.51 (m, 4H), 2.40 (s, 3H), 1.70-1.62 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.6, 137.3, 135.7, 131.4, 129.0, 128.18, 128.15, 128.1, 116.4, 88.9, 60.7, 56.5, 55.5, 28.6, 27.1, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{33}N_2O_3S$ 429.2206, found 429.2208.





N-(2-((dibenzylamino)methyl)-1-ethoxyallyl)-4-methyl-N-phenylbenzenesulfonamide (3o):

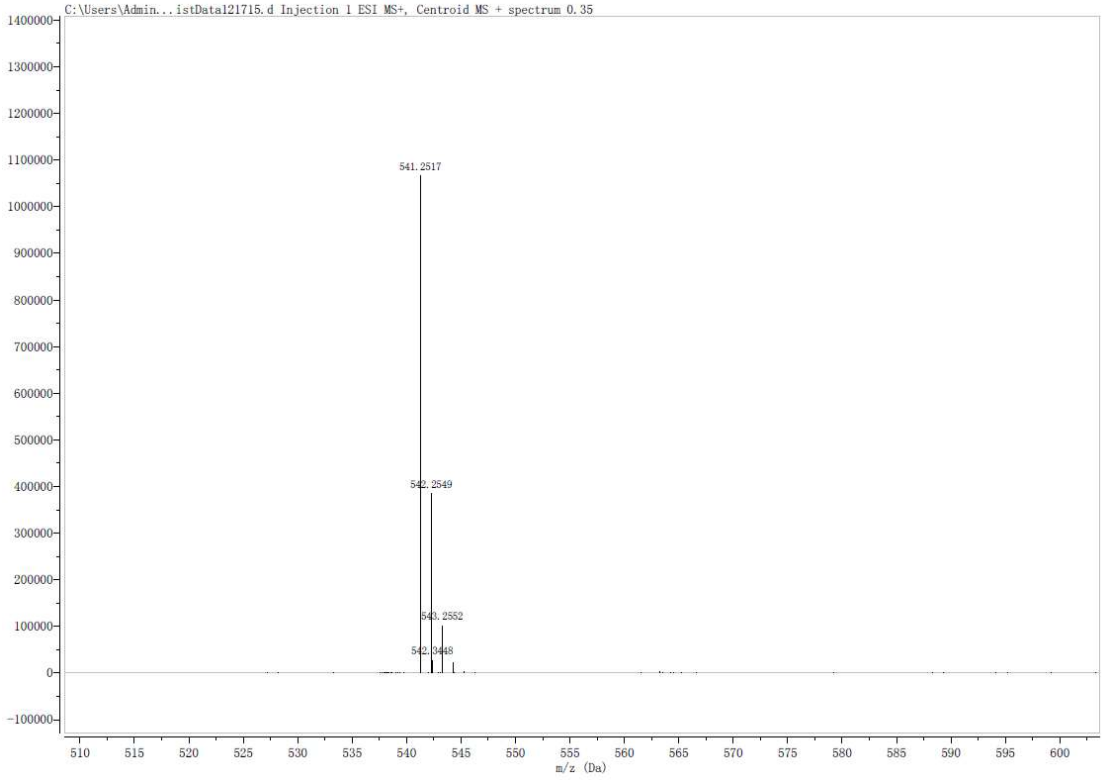
Prepared via **general procedure 2** from N,N-dibenzyl-1-ethoxymethanamine (51.1 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (66.0 mg, 61%), mp: 49-50 °C.

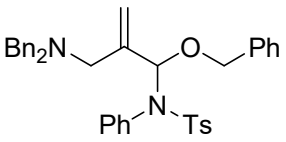
R_f (Petroleum ether/ EtOAc = 10:1) = 0.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 7.41-7.35 (m, 6H), 7.26-7.24 (m, 2H), 7.17-7.11 (m, 3H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.18 (s, 1H), 5.13 (s, 1H), 5.01 (s, 1H), 3.74 (d, *J* = 13.7 Hz, 2H), 3.69-3.63 (m, 1H), 3.53-3.46 (m, 1H), 3.23 (d, *J* = 13.7 Hz, 2H), 3.10 (d, *J* = 14.3 Hz, 1H), 2.66 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.1, 139.3, 137.0, 135.8, 131.4, 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 126.9, 117.2, 87.6, 64.5, 58.4, 56.4, 21.6, 15.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{37}N_2O_3S$ 541.2519, found 541.2517.





N-(1-(benzyloxy)-2-((dibenzylamino)methyl)allyl)-4-methyl-N-phenylbenzenesulfonamide (3p):

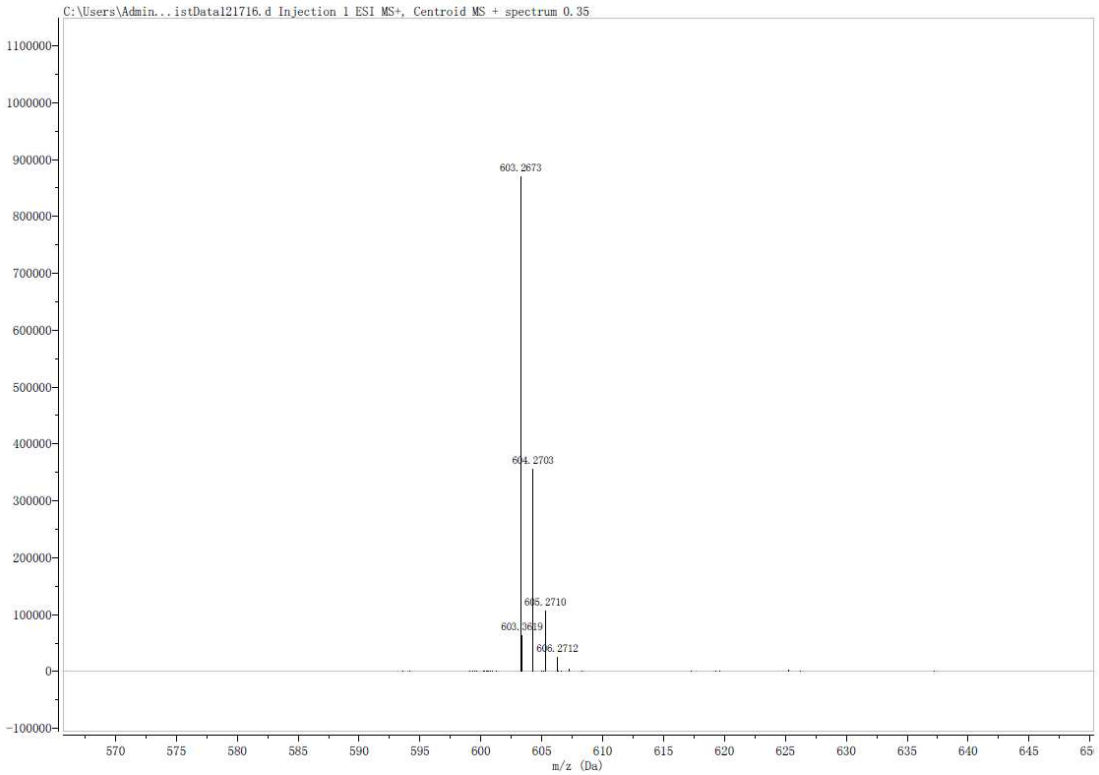
Prepared via **general procedure 2** from N,N-dibenzyl-1-(benzyloxy)methanamine (63.5 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as colorless oil (86.8 mg, 72%).

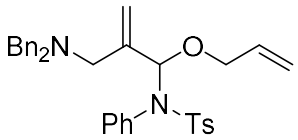
R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 4H), 7.41-7.32 (m, 6H), 7.32-7.26 (m, 5H), 7.21-7.13 (m, 3H), 7.08-7.04 (m, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.82-6.79 (m, 2H), 6.34 (s, 1H), 5.17 (s, 1H), 5.08 (s, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 3.74 (d, *J* = 13.8 Hz, 2H), 3.28 (d, *J* = 13.8 Hz, 2H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.4 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 140.8, 139.3, 137.6, 136.9, 135.6, 131.4, 128.9, 128.8, 128.5, 128.23, 128.17, 128.1, 128.0, 127.5, 127.4, 127.0, 117.6, 87.7, 70.8, 58.5, 56.5, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{39}N_2O_3S$ 603.2676, found 603.2673.





N-(1-(allyloxy)-2-((dibenzylamino)methyl)allyl)-4-methyl-N-phenylbenzenesulfonamide (3q):

Prepared via **general procedure 2** from 1-(allyloxy)-N,N-dibenzylmethanamine (53.4 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (67.4 mg, 61%), mp: 63-64 °C.

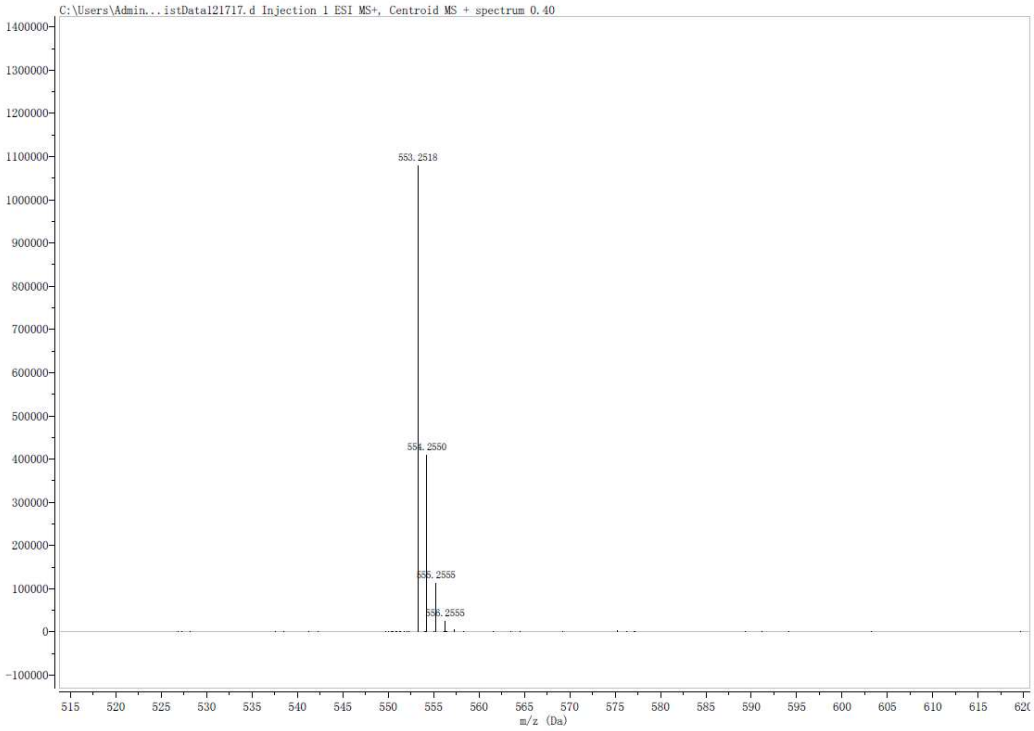
R_f (Petroleum ether/ EtOAc = 10:1) = 0.7.

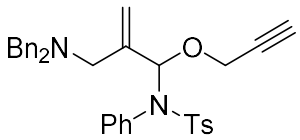
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 7.40-7.35 (m, 6H), 7.27-7.23 (m, 2H), 7.17-7.13 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.06-7.02 (m, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 6.25 (s, 1H), 5.91-5.82 (m, 1H), 5.19-5.10 (m, 3H), 5.03 (s, 1H), 4.19-4.15 (m, 1H), 4.03-3.98 (m, 1H), 3.74 (d, *J* =

13.8 Hz, 2H), 3.23 (d, *J* = 13.8 Hz, 2H), 3.10 (d, *J* = 14.3 Hz, 1H), 2.66 (d, *J* = 14.3 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.8, 139.3, 136.8, 135.7, 133.8, 131.4, 128.83, 128.75, 128.5, 128.3, 128.1, 128.0, 127.0, 117.5, 116.7, 87.4, 69.8, 58.5, 56.5, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{37}N_2O_3S$ 553.2519, found 553.2518.





N-(2-((dibenzylamino)methyl)-1-(prop-2-yn-1-yloxy)allyl)-4-methyl-N-phenylbenzene-sulfonamide (3r):

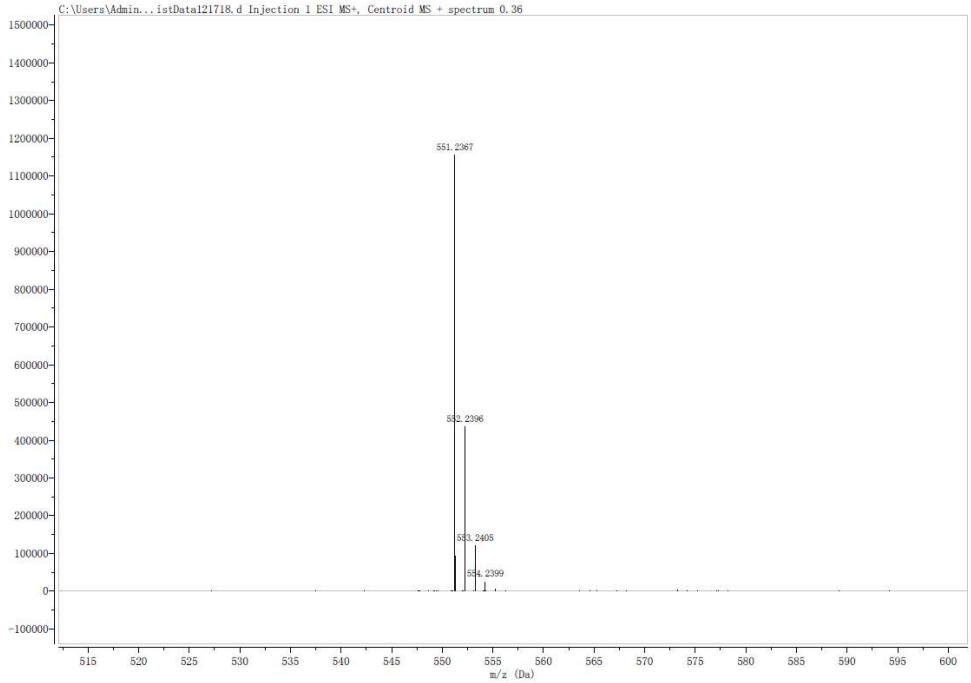
Prepared via **general procedure 2** from N,N-dibenzyl-1-(prop-2-yn-1-yloxy)methanamine (53.0 mg, 0.2 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (85.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of JohnPhosAu(MeCN)SbF_6 (7.7 mg, 0.01 mmol, 5 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as colorless oil (82.6 mg, 75%).

R_f (Petroleum ether/ EtOAc = 10:1) = 0.6.

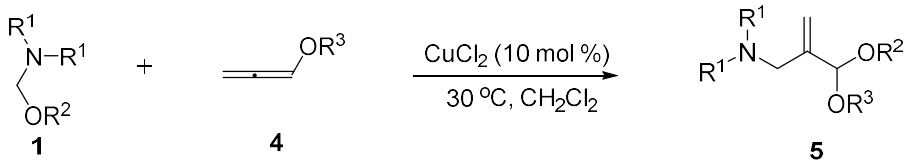
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 6H), 7.40-7.35 (m, 4H), 7.28-7.22 (m, 2H), 7.17-7.12 (m, 3H), 7.06-7.02 (m, 2H), 6.75-6.71 (m, 2H), 6.39 (s, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.20 (d, *J* = 2.4 Hz, 2H), 3.76 (d, *J* = 13.8 Hz, 2H), 3.24 (d, *J* = 13.8 Hz, 2H), 3.12 (d, *J* = 14.3 Hz, 1H), 2.66 (d, *J* = 14.3 Hz, 1H), 2.44 (t, *J* = 2.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 140.3, 139.2, 136.7, 135.5, 131.4, 128.9, 128.8, 128.5, 128.4, 128.12, 128.08, 127.0, 117.9, 87.0, 79.0, 75.2, 58.4, 56.5, 56.2, 21.6.

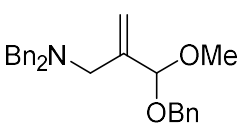
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{35}N_2O_3S$ 551.2363, found 551.2367.



General procedure for Scheme 3



To a dry tube was added $CuCl_2$ (2.7 mg, 0.02 mmol, 0.1 equiv), **1** (0.2 mmol, 1.0 equiv), **4** (0.3 mmol, 1.5 equiv), and anhydrous DCM (4 mL) under argon atmosphere. Then, the mixture was stirred at 30 °C in a heating block for 12 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give products **5**.



N,N-dibenzyl-2-((benzyloxy)(methoxy)methyl)prop-2-en-1-amine (5a):

Prepared via **general procedure 3** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (43.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (65.9 mg, 85%).

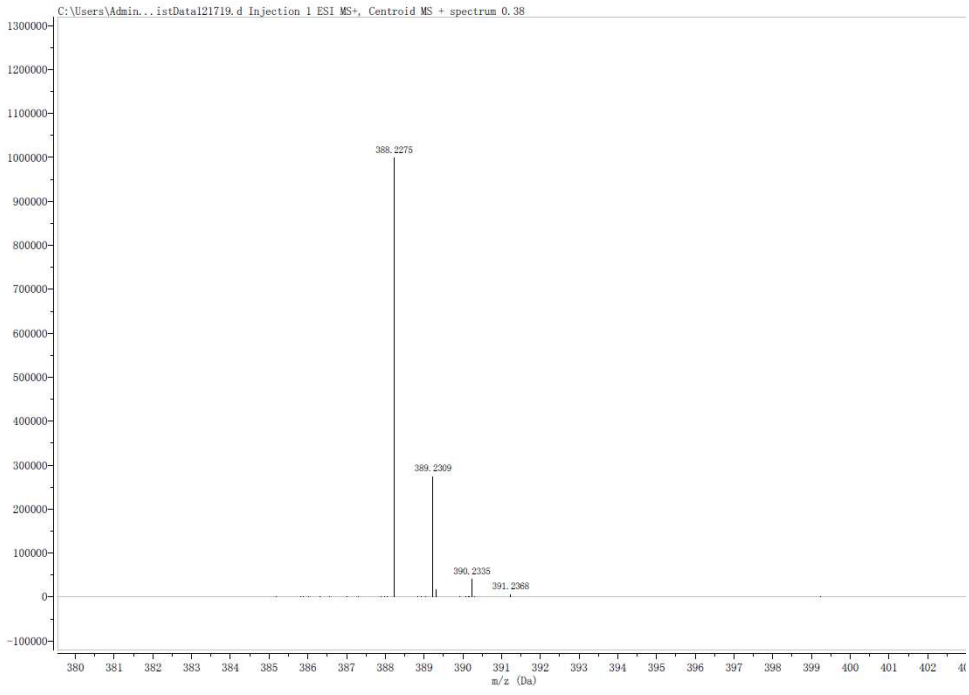
Gram-scale reaction: N,N-dibenzyl-1-methoxymethanamine (1.15 g, 4.80 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (1.05 g, 7.20 mmol, 1.5 equiv), $CuCl_2$ (64 mg, 0.48 mmol, 10 mol %) in DCM (48 mL), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (65.9 mg, 85%).

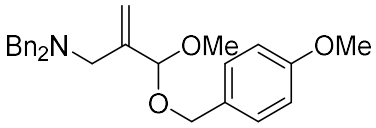
R_f (Petroleum ether/ EtOAc = 10:1) = 0.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.32-7.27 (m, 7H), 7.24-7.19 (m, 4H), 5.49 (s, 1H), 5.46 (s, 1H), 5.00 (s, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 3.55 (s, 4H), 3.27 (s, 3H), 3.07 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 139.6, 138.1, 128.7, 128.4, 128.3, 127.8, 127.5, 126.9, 115.6, 101.8, 67.5, 58.2, 55.5, 53.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{30}NO_2$ 388.2271, found 388.2275.





N,N-dibenzyl-2-(methoxy((4-methoxybenzyl)oxy)methyl)prop-2-en-1-amine (5b):

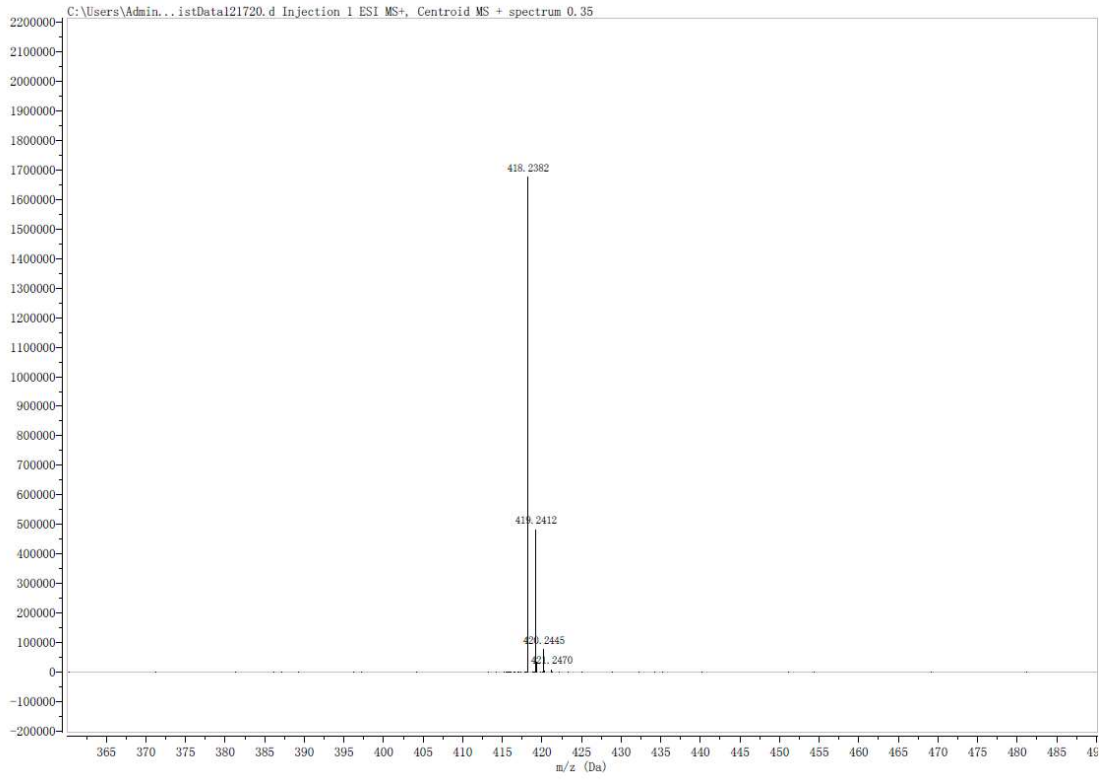
Prepared via **general procedure 3** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 1-methoxy-4-((propa-1,2-dien-1-yloxy)methyl)benzene (52.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as yellow oil (56.8 mg, 68%).

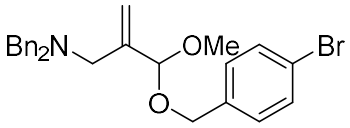
R_f (Petroleum ether/ EtOAc = 10:1) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 4H), 7.23-7.20 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.48 (s, 1H), 5.44 (s, 1H), 4.96 (s, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H), 3.54 (s, 4H), 3.25 (s, 3H), 3.06 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 142.9, 139.6, 130.1, 129.4, 128.6, 128.2, 126.8, 115.4, 113.7, 101.6, 67.3, 58.2, 55.4, 55.3, 53.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{32}NO_3$ 418.2377, found 418.2382.





N,N-dibenzyl-2-(((4-bromobenzyl)oxy)(methoxy)methyl)prop-2-en-1-amine (5c):

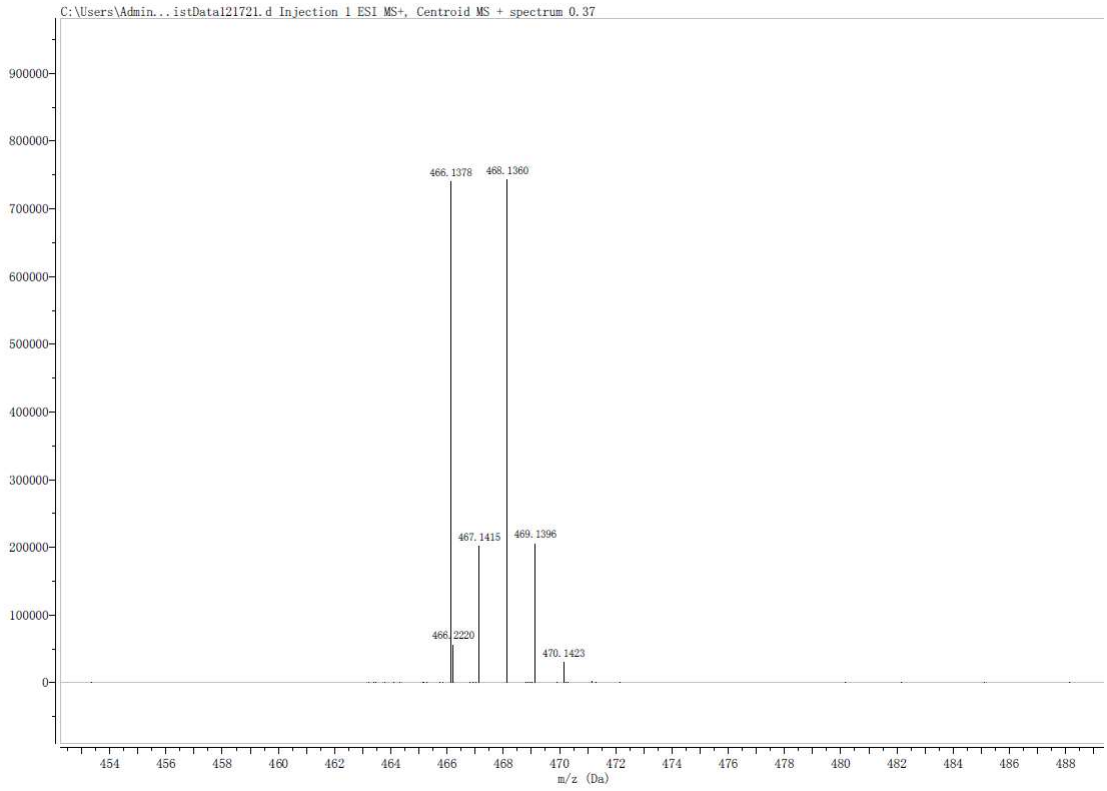
Prepared via **general procedure 3** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and 1-bromo-4-((propa-1,2-dien-1-yloxy)methyl)benzene (67.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as yellow oil (75.6 mg, 81%).

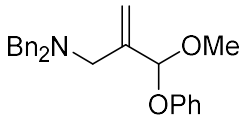
R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 4H), 7.23-7.19 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 5.48 (s, 1H), 5.44 (s, 1H), 4.99 (s, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 3.58-3.49 (m, 4H), 3.25 (s, 3H), 3.09-3.00 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 139.5, 137.2, 131.4, 129.4, 128.7, 128.3, 126.9, 121.4, 115.8, 101.7, 66.5, 58.2, 55.6, 53.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{29}BrNO_2$ 466.1376, found 466.1378.





N,N-dibenzyl-2-(methoxy(phenoxy)methyl)prop-2-en-1-amine (5d):

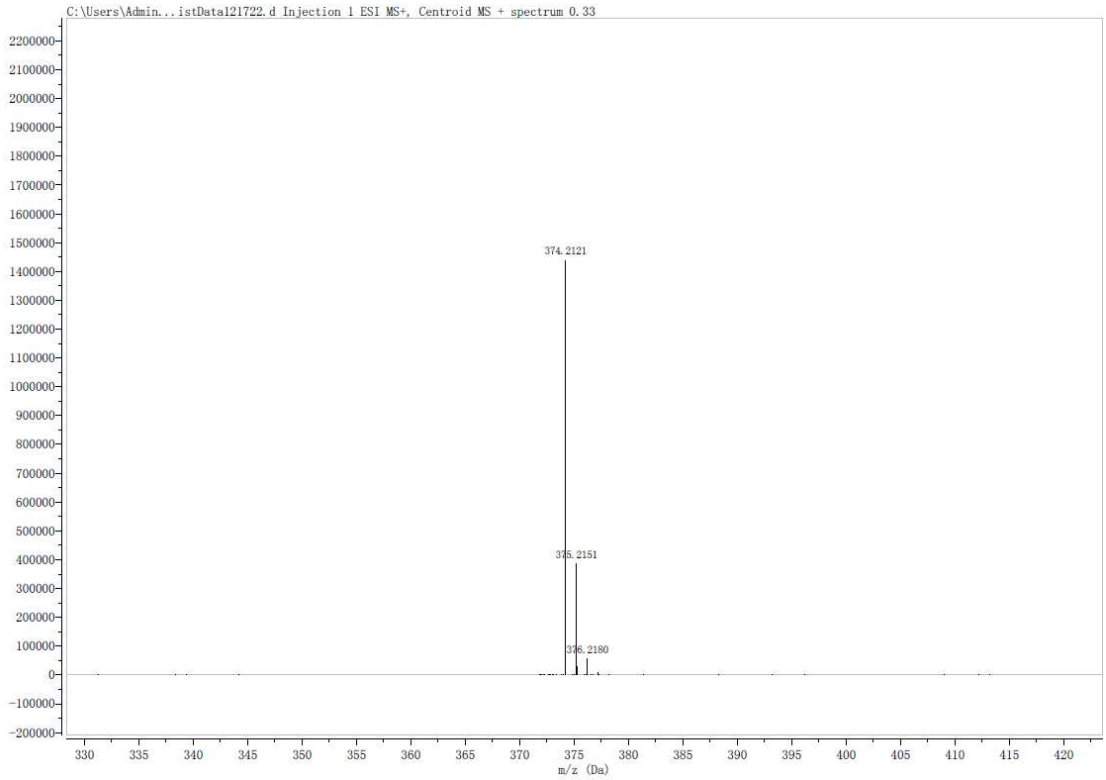
Prepared via **general procedure 3** from N,N-dibenzyl-1-methoxymethanamine (48.2 mg, 0.2 mmol, 1.0 equiv) and (propa-1,2-dien-1-yloxy)benzene (39.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (49.3 mg, 66%).

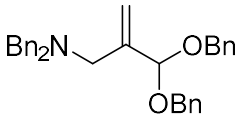
R_f (Petroleum ether/ EtOAc = 10:1) = 0.75.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 4H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.25-7.20 (m, 4H), 6.99-6.92 (m, 3H), 5.55 (s, 1H), 5.52 (s, 1H), 5.47 (s, 1H), 3.68 (d, *J* = 13.8 Hz, 2H), 3.48 (d, *J* = 13.8 Hz, 2H), 3.28 (s, 3H), 3.22 (d, *J* = 14.3 Hz, 1H), 3.06 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 142.5, 139.4, 129.4, 128.7, 128.3, 126.9, 121.9, 117.0, 116.3, 102.0, 58.2, 55.6, 54.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}NO_2$ 374.2115, found 374.2121.





N,N-dibenzyl-2-(bis(benzyloxy)methyl)prop-2-en-1-amine (5e):

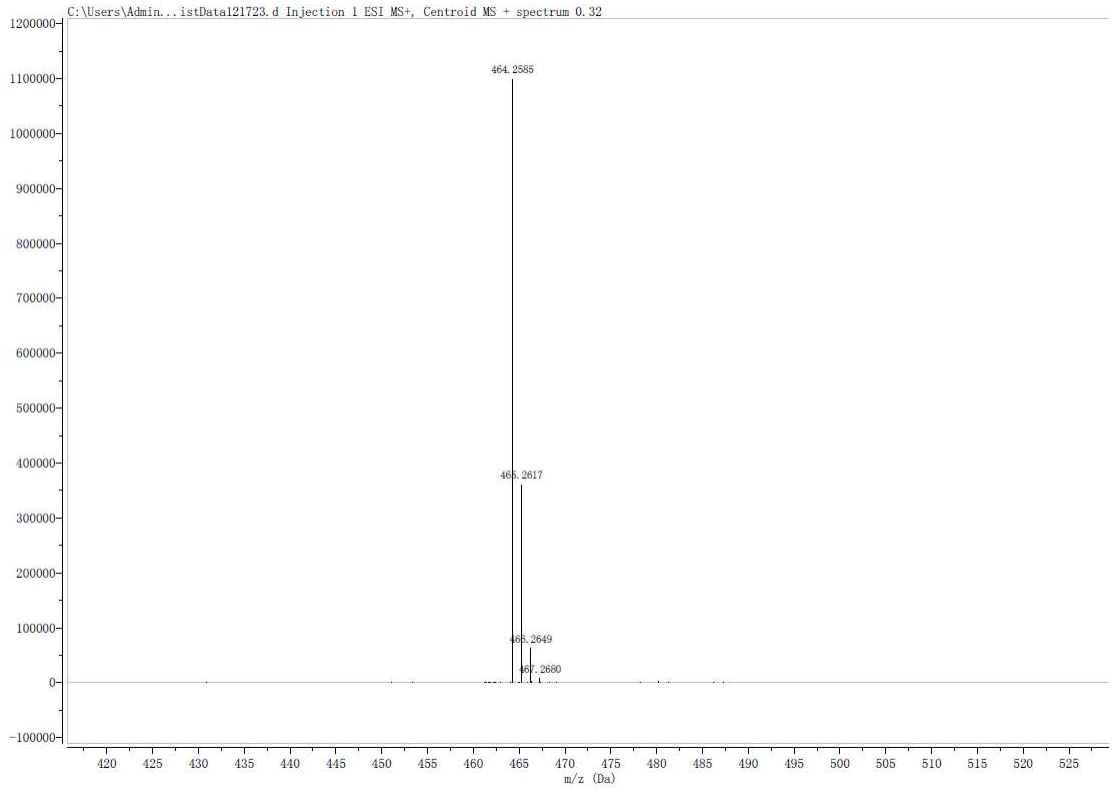
Prepared via **general procedure 3** from N,N-dibenzyl-1-(benzyloxy)methanamine (63.4 mg, 0.2 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (43.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (57.5 mg, 62%).

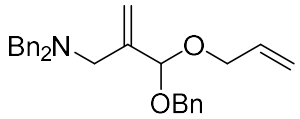
R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 10H), 7.27-7.18 (m, 10H), 5.55 (s, 1H), 5.51 (s, 1H), 5.22 (s, 1H), 4.52 (d, *J* = 11.9 Hz, 2H), 4.45 (d, *J* = 11.8 Hz, 2H), 3.54 (s, 4H), 3.11 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 139.5, 138.1, 128.7, 128.4, 128.3, 127.8, 127.5, 126.9, 115.9, 100.0, 67.4, 58.2, 55.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{34}NO_2$ 464.2584, found 464.2585.





2-((allyloxy)(benzyloxy)methyl)-N,N-dibenzylprop-2-en-1-amine (5f):

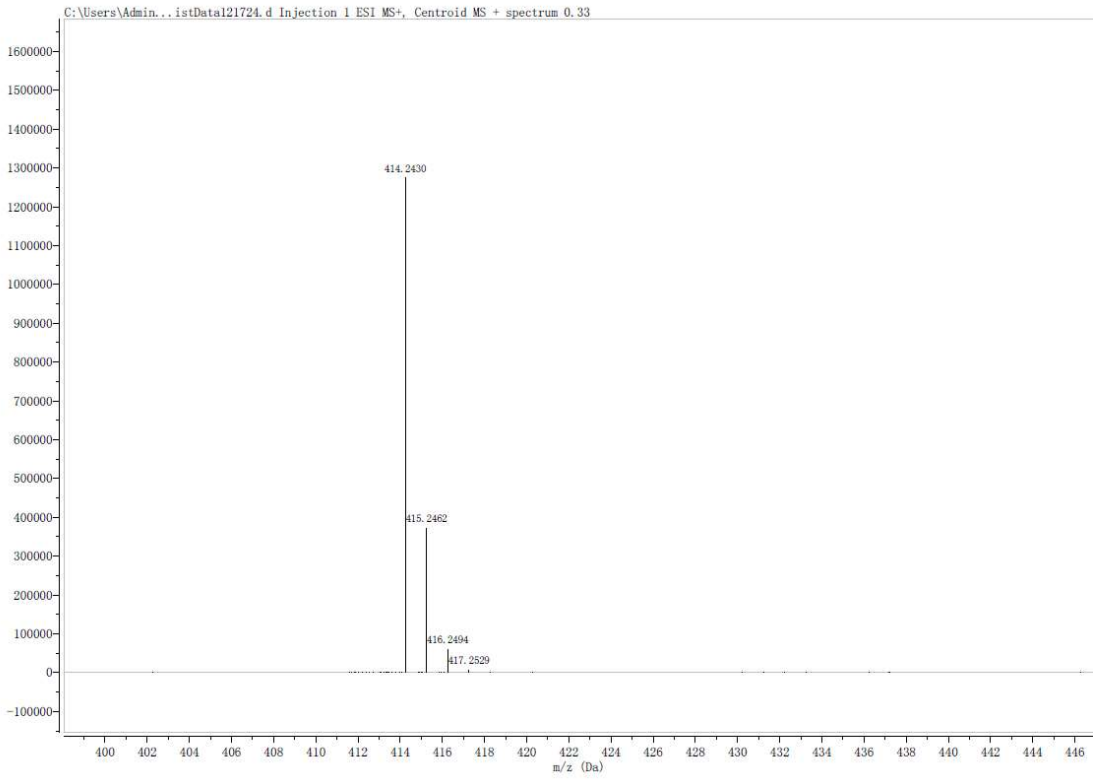
Prepared via **general procedure 3** from 1-(allyloxy)-N,N-dibenzylmethanamine (53.4mg, 0.2 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (43.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (51.3 mg, 62%).

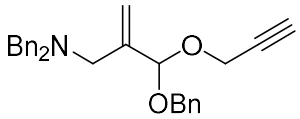
R_f (Petroleum ether/ EtOAc = 10:1) = 0.75.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.31-7.27 (m, 6H), 7.25-7.20 (m, 5H), 5.87-5.78 (m, 1H), 5.49 (s, 2H), 5.21-5.09 (m, 3H), 4.50-4.42 (m, 2H), 4.04-3.91 (m, 2H), 3.55 (s, 4H), 3.09 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 139.5, 138.1, 134.5, 128.7, 128.3, 128.2, 127.8, 127.5, 126.8, 116.8, 115.6, 100.2, 67.3, 66.9, 58.2, 55.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{32}NO_2$ 414.2428, found 414.2430.





N,N-dibenzyl-2-((benzyloxy)(prop-2-yn-1-yloxy)methyl)prop-2-en-1-amine (5g):

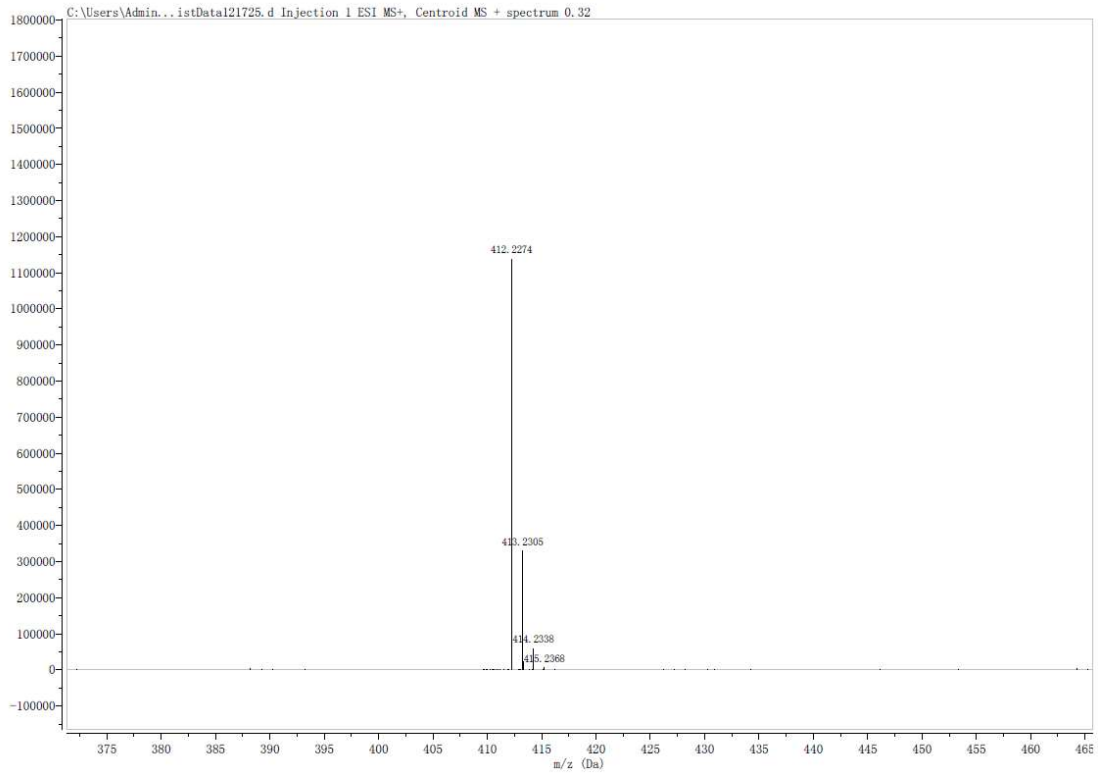
Prepared via **general procedure 3** from N,N-dibenzyl-1-(prop-2-yn-1-yloxy)methanamine (53.0 mg, 0.2 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (43.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of JohnPhosAu(MeCN)SbF_6 (7.7 mg, 0.01 mmol, 5 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 20:1) and obtained as yellow oil (59.3 mg, 72%).

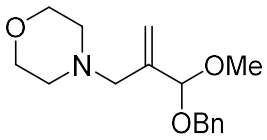
R_f (Petroleum ether/ EtOAc = 10:1) = 0.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.31-7.27 (m, 6H), 7.24-7.18 (m, 5H), 5.50 (s, 2H), 5.29 (s, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.22-4.07 (m, 2H), 3.59-3.49 (m, 4H), 3.14-3.04 (m, 2H), 2.36 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 139.5, 137.8, 128.7, 128.4, 128.3, 127.8, 127.6, 126.9, 116.2, 99.7, 79.8, 74.2, 67.8, 58.1, 55.5, 53.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}NO_2$ 412.2271, found 412.2274.





4-(2-((benzyloxy)(methoxy)methyl)allyl)morpholine (5h):

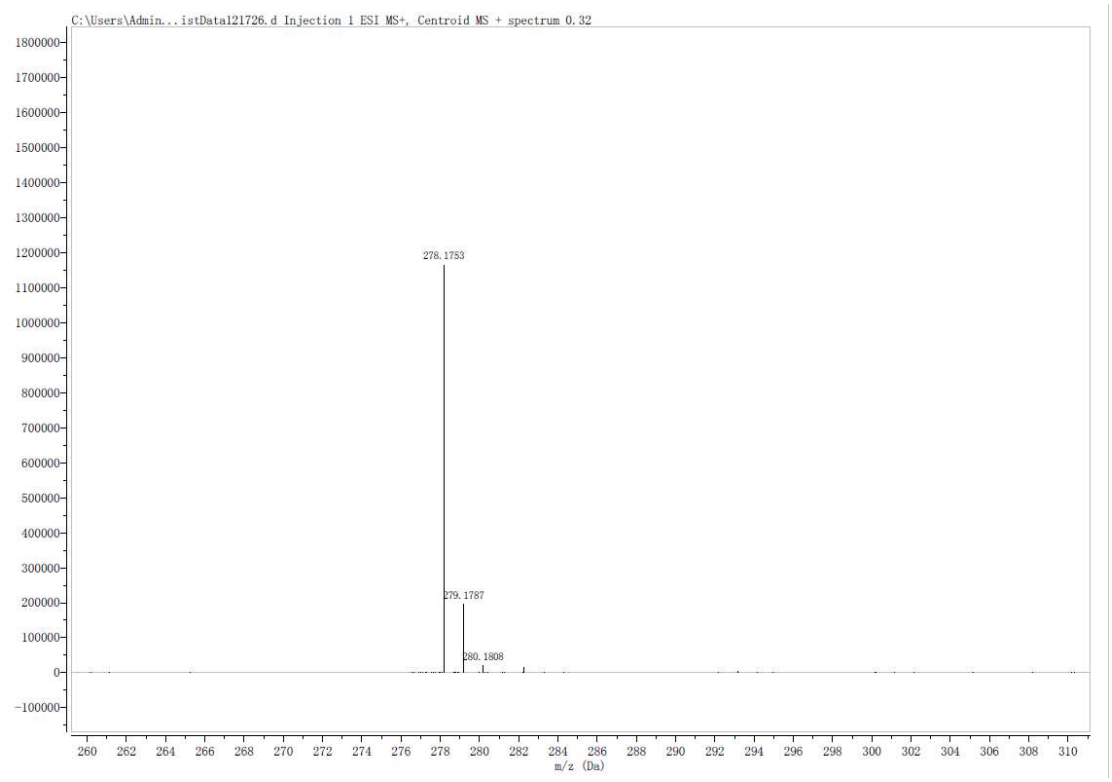
Prepared via **general procedure 3** from 4-(methoxymethyl)morpholine (26.2 mg, 0.2 mmol, 1.0 equiv) and ((propa-1,2-dien-1-yloxy)methyl)benzene (43.8 mg, 0.3 mmol, 1.5 equiv) according to the general procedure in the presence of $CuCl_2$ (4.5 mg, 0.02 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ MTBE = 5:1 to 1:1) and obtained as yellow oil (35.5 mg, 64%).

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

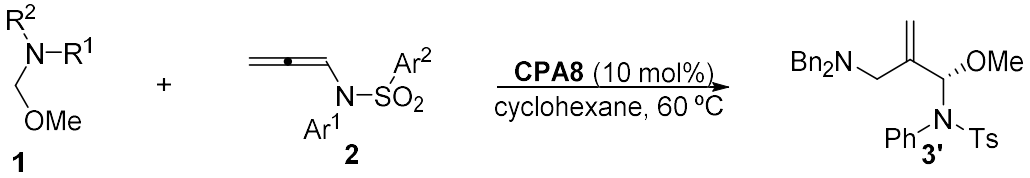
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.24 (m, 5H), 5.45 (s, 1H), 5.28 (s, 1H), 5.00 (s, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.72-3.62 (m, 4H), 3.32 (s, 3H), 2.96 (s, 2H), 2.46-2.34 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 138.3, 128.5, 127.8, 127.7, 116.2, 101.3, 67.6, 67.2, 60.5, 53.8, 53.1.

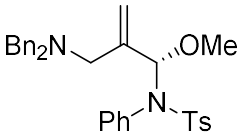
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{24}NO_3$ 278.1751, found 278.1753.



General procedure for Scheme 5



To a dry tube was added chiral phosphoric acid **8** (7.0 mg, 0.01 mmol, 0.1 equiv), then a solution of **1** (0.1 mmol, 1.0 equiv) and **2** (0.25 mmol, 2.5 equiv) in cyclohexane (5 mL) was added gradually under argon atmosphere. The reaction mixture was stirred at 60 °C in a heating block for 24 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum, the crude residue was purified by silica gel column chromatography to give products **3'**.



(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzenesulfonamide (3a'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as a white solid (43.2 mg, 82%), mp: 106-107 °C.

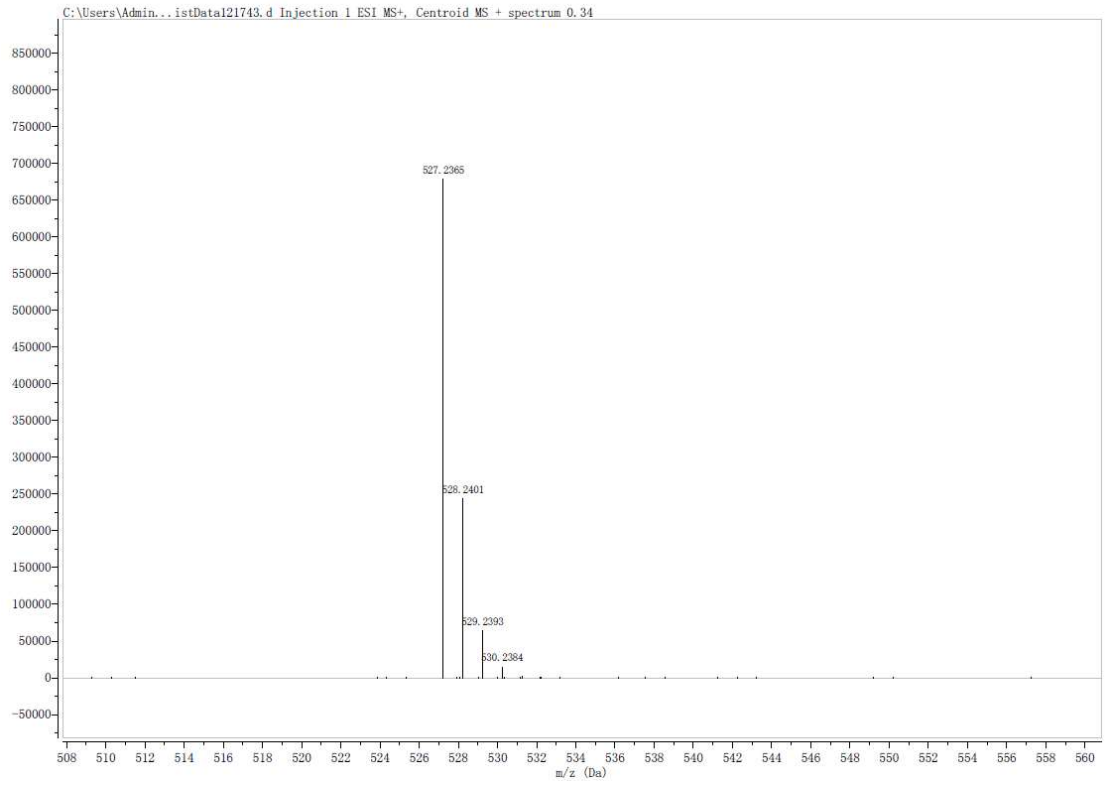
R_f (Petroleum ether/ EtOAc = 10:1) = 0.5.

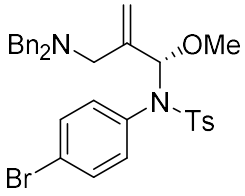
HPLC (IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 18.35 min (major), 19.99 min (mimor), 92:8 er. **$[\alpha]_D^{26}$**: +54.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 4H), 7.42-7.33 (m, 6H), 7.31-7.24 (m, 2H), 7.18-7.10 (m, 3H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.10 (s, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 3.74 (d, *J* = 13.7 Hz, 2H), 3.39 (s, 3H), 3.25 (d, *J* = 13.7 Hz, 2H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.66 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 140.6, 139.3, 137.0, 135.6, 131.3, 128.8, 128.7, 128.5, 128.2, 127.99, 127.96, 126.9, 117.2, 89.4, 58.4, 56.7, 56.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{35}N_2O_3S$ 527.2363, found 527.2365.





(S)-N-(4-bromophenyl)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide (3b'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-(4-bromophenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (91.0 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 15:1) and obtained as a white solid (44.8 mg, 74%), mp: 125-127 °C.

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (0.72 g, 3 mmol, 1.0 equiv) and N-(4-bromophenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2.73 g, 7.5 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (210 mg, 0.3 mmol, 10 mol %) in DCM (75 ml), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 15:1) and obtained as a white solid (1.28 g, 70%).

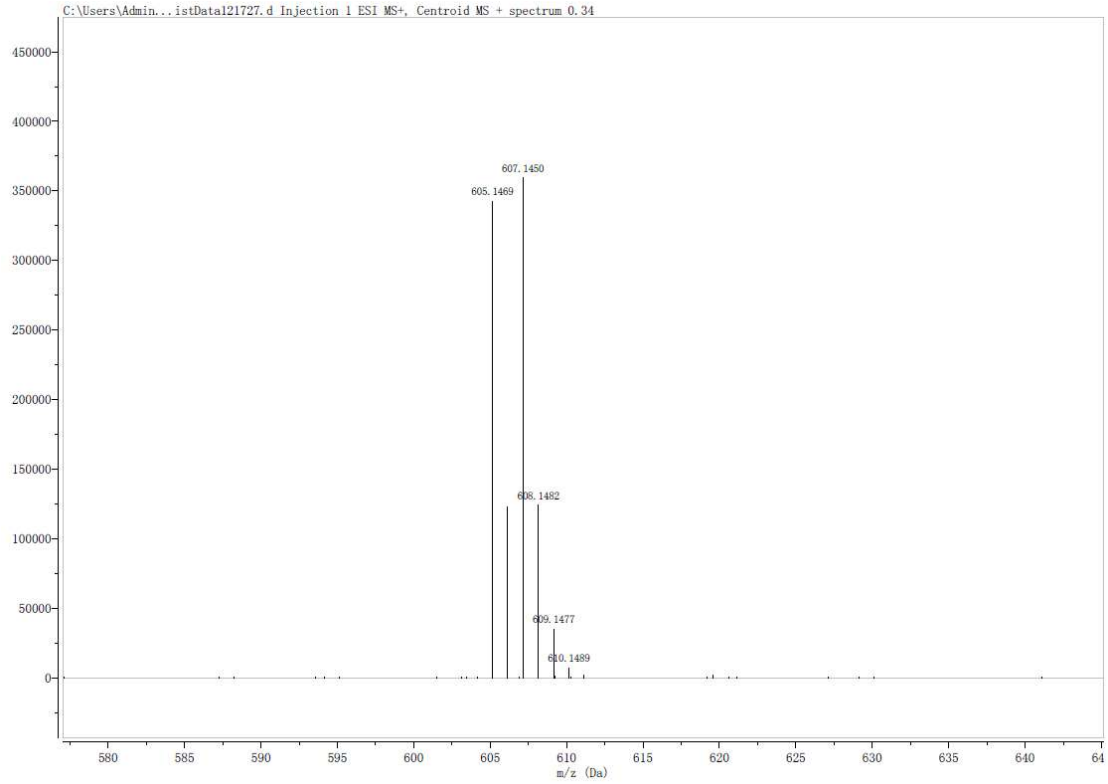
R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

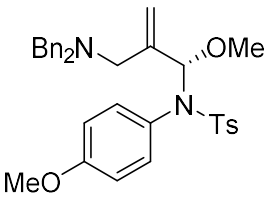
HPLC (IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 13.39 min (major), 14.83 min (mimor), 90:10 er. **$[\alpha]_D^{26}$**: +88.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 4H), 742-7.34 (m, 6H), 7.29-7.23 (m, 2H), 7.16-7.13 (m, 4H), 6.55 (d, *J* = 8.6 Hz, 2H), 6.09 (s, 1H), 5.17 (s, 1H), 5.00 (s, 1H), 3.75 (d, *J* = 13.7 Hz, 2H), 3.37 (s, 3H), 3.23 (d, *J* = 13.7 Hz, 2H), 3.02 (d, *J* = 14.3 Hz, 1H), 2.62 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 140.3, 139.2, 136.6, 134.9, 132.8, 131.3, 129.0, 128.8, 128.6, 128.2, 127.0, 122.2, 117.7, 89.3, 58.5, 56.9, 56.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{34}BrN_2O_3S$ 605.1468, found 605.1469.





(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (3c'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-(4-methoxyphenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (78.8 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as a white solid (40.1 mg, 72%), mp: 105-106 °C.

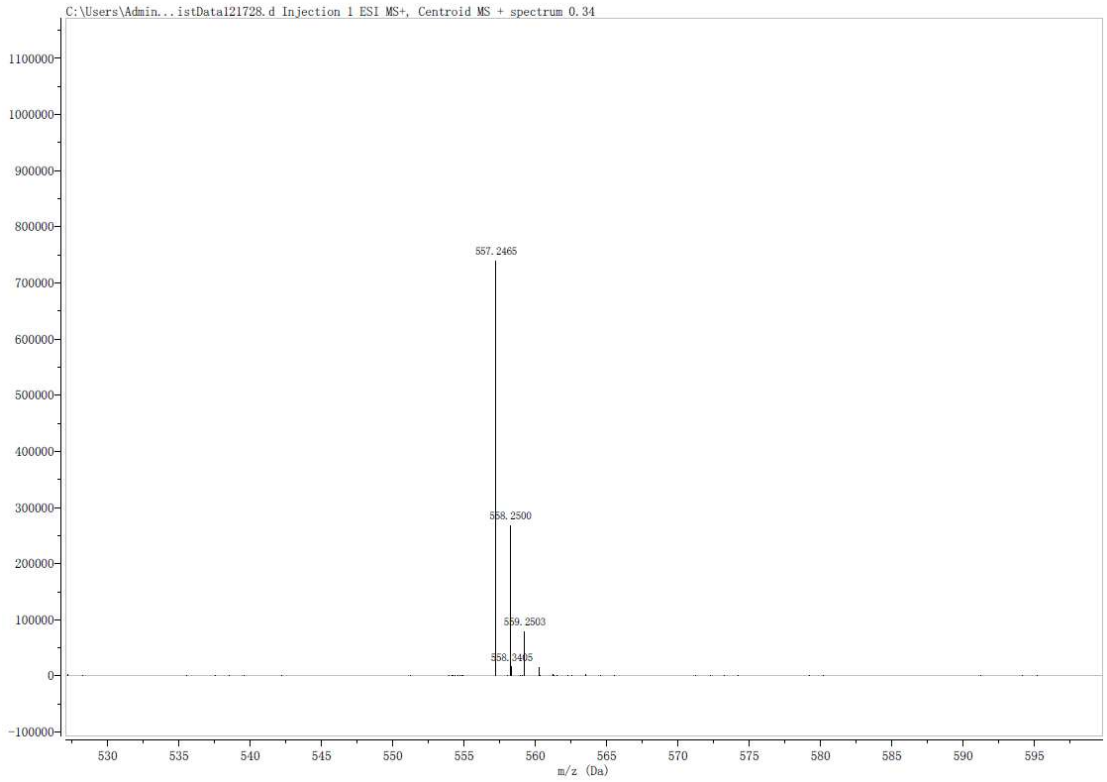
R_f (Petroleum ether/ EtOAc = 10:1) = 0.4.

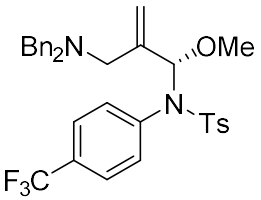
HPLC (IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 18.58 min (major), 19.94 min (mimor), 90:10 er. **$[\alpha]_D^{26}$**: +62.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 4H), 7.42-7.34 (m, 6H), 7.26-7.22 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 9.0 Hz, 1H), 6.07 (s, 1H), 5.16 (s, 1H), 4.98 (s, 1H), 3.74 (d, *J* = 13.8 Hz, 2H), 3.70 (s, 3H), 3.38 (s, 3H), 3.26 (d, *J* = 13.8 Hz, 2H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.68 (d, *J* = 14.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 143.1, 140.7, 139.3, 137.0, 132.5, 128.9, 128.7, 128.5, 128.3, 128.0, 127.0, 117.1, 113.2, 89.3, 58.4, 56.7, 56.4, 55.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{37}N_2O_4S$ 557.2469, found 557.2465.





(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methyl-N-(4-(trifluoromethyl)phenyl)benzenesulfonamide (3d'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-(propa-1,2-dien-1-yl)-N-(4-(trifluoromethyl)phenyl)benzenesulfonamide (88.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (47.6 mg, 80%), mp: 131-132 °C.

R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

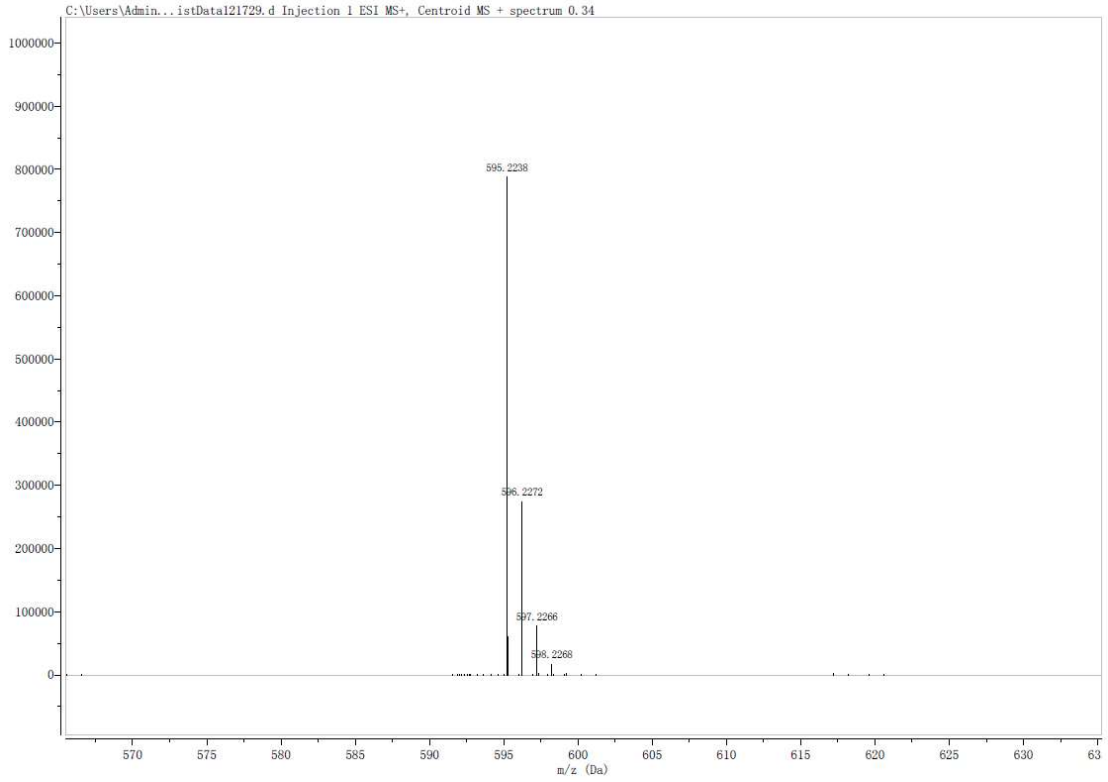
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 5.82 min (major), 7.25 min (mimor), 87:13 er. **$[\alpha]_D^{26}$**: +48.0 (c: 0.10, $CHCl_3$).

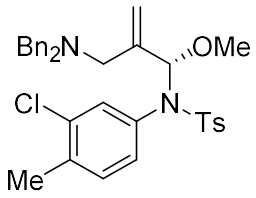
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 4H), 7.40-7.35 (m, 6H), 7.31-7.25 (m, 4H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.13 (s, 1H), 5.17 (s, 1H), 5.03 (s, 1H), 3.76 (d, *J* = 13.7 Hz, 2H), 3.38 (s, 3H), 3.23 (d, *J* = 13.7 Hz, 2H), 3.01 (d, *J* = 14.3 Hz, 1H), 2.61 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 140.2, 139.3 (q, *J* = 1.3 Hz), 139.2, 136.6, 131.3, 129.8 (q, *J* = 32.6 Hz), 129.0, 128.8, 128.6, 128.1, 127.1, 125.1 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.3 Hz), 117.9, 89.4, 58.5, 57.0, 56.3, 21.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{34}F_3N_2O_3S$ 595.2237, found 595.2238.





(S)-N-(3-chloro-4-methylphenyl)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide (3e'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-(3-chloro-4-methylphenyl)-4-methyl-N-(propa-1,2-dien-1-yl)-benzene sulfonamide (83.5 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as colorless oil (42.6 mg, 74%).

R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

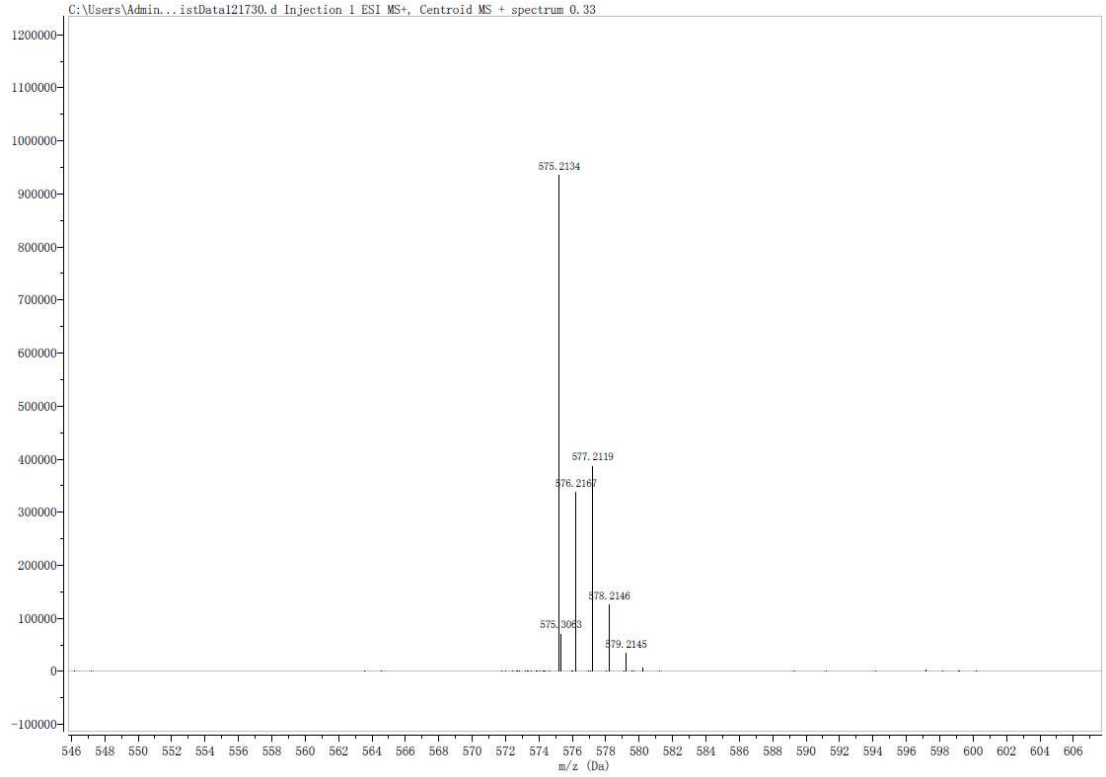
HPLC (ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 254 nm) t_R = 6.95 min (major), 9.38 min (mimor), 91:9 er. **$[\alpha]_D^{26}$**: +156.0 (c: 0.10, $CHCl_3$).

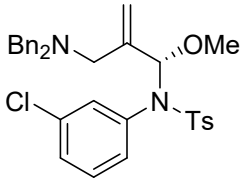
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 4H), 7.42-7.35 (m, 6H), 7.29-7.24 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 2.1 Hz, 1H), 6.50 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.08

(s, 1H), 5.16 (s, 1H), 5.02 (s, 1H), 3.77 (d, J = 13.7 Hz, 2H), 3.36 (s, 3H), 3.20 (d, J = 13.7 Hz, 2H), 3.06 (d, J = 14.2 Hz, 1H), 2.62 (d, J = 14.2 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.4, 139.2, 136.8, 136.0, 134.4, 133.3, 131.5, 130.1, 129.4, 128.9, 128.8, 128.6, 128.2, 127.1, 117.7, 89.3, 58.5, 56.9, 56.4, 21.6, 19.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{36}ClN_2O_3S$ 575.2130, found 575.2134.





(S)-N-(3-chlorophenyl)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-methylbenzenesulfonamide (3f'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-(3-chlorophenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (79.9 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 12:1) and obtained as colorless oil (39.8 mg, 71%).

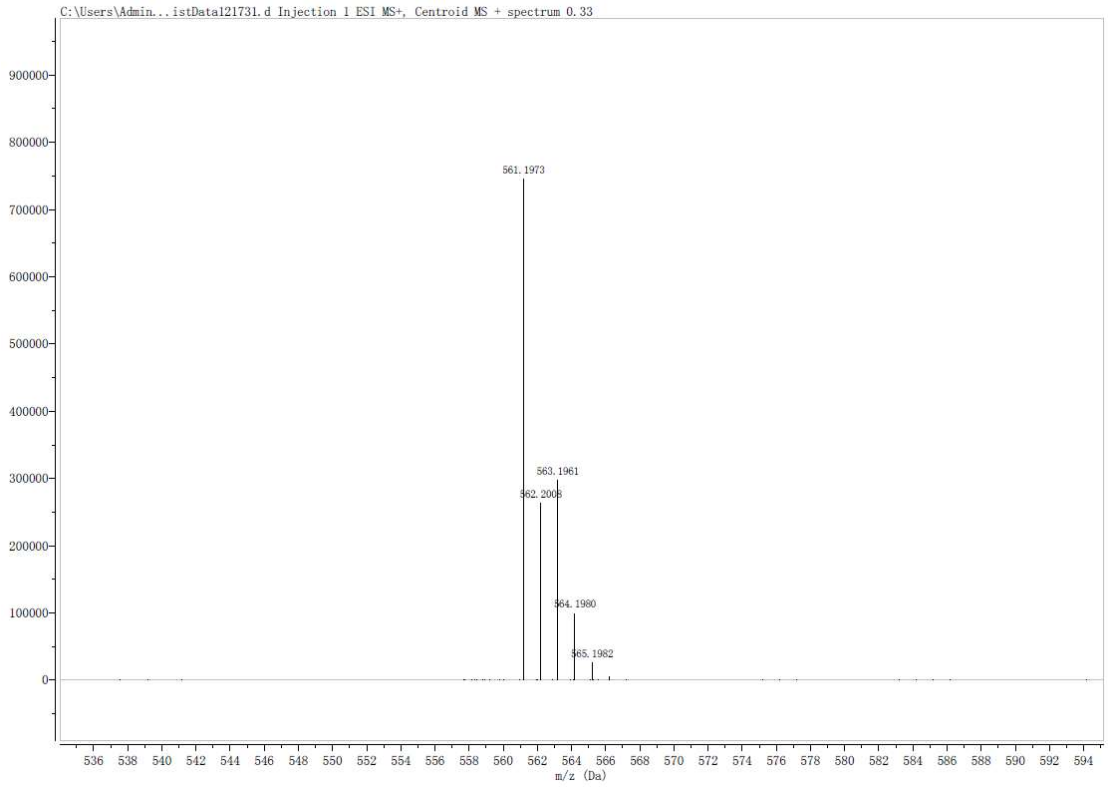
R_f (Petroleum ether/ EtOAc = 10:1) = 0.5.

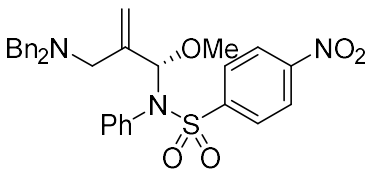
HPLC (ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 254 nm) t_R = 7.58 min (major), 9.80 min (mimor), 92:8 er. **$[\alpha]_D^{26}$**: +42.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 4H), 7.45 (d, *J* = 7.5 Hz, 6H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.22-7.17 (m, 3H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.83-6.81 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 5.22 (s, 1H), 5.08 (s, 1H), 3.84 (d, *J* = 13.7 Hz, 2H), 3.42 (s, 3H), 3.25 (d, *J* = 13.7 Hz, 2H), 3.11 (d, *J* = 14.2 Hz, 1H), 2.67 (d, *J* = 14.2 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.3, 139.2, 137.1, 136.6, 133.3, 131.3, 129.4, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, 127.1, 117.8, 89.3, 58.5, 56.9, 56.4, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{34}ClN_2O_3S$ 561.1973, found 561.1973.





(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-4-nitro-N-phenylbenzenesulfonamide (3g'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and 4-nitro-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (79.0 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg,

0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as a white solid (45.7 mg, 82%), mp: 144-145 °C.

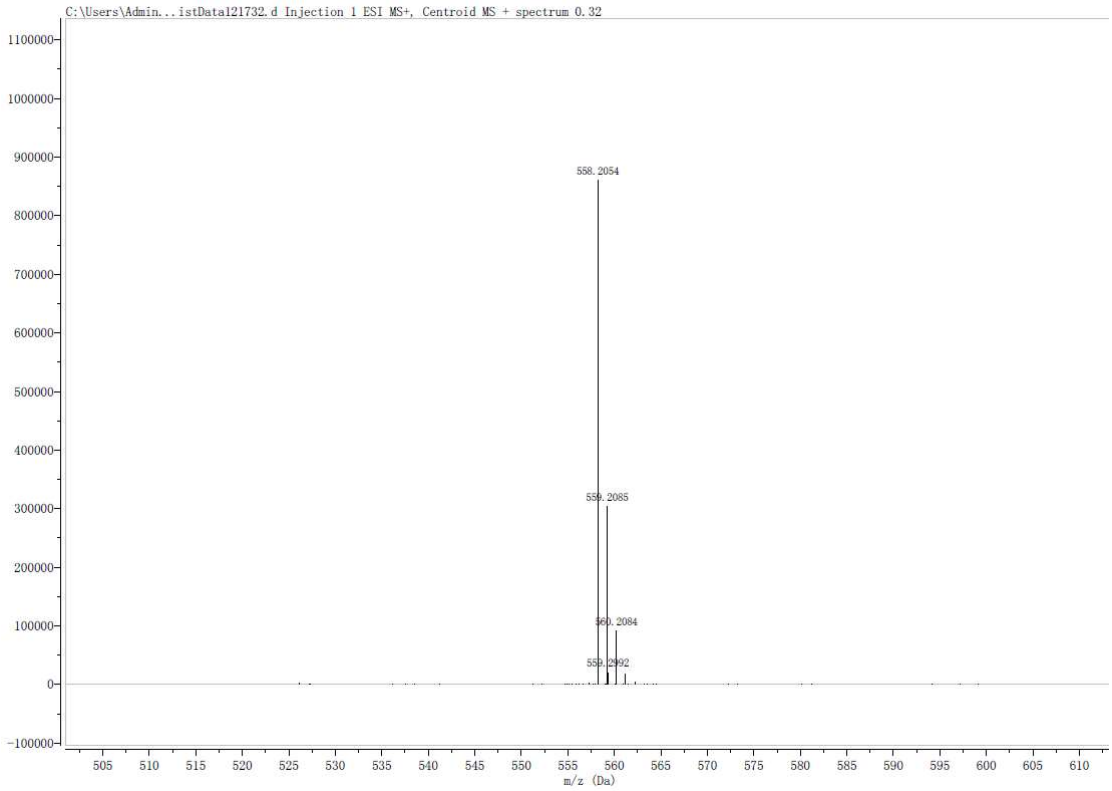
R_f (Petroleum ether/ EtOAc = 10:1) = 0.4.

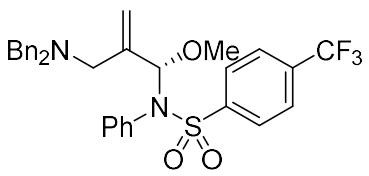
HPLC (IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 254 nm) t_R = 7.39 min (minor), 8.06 min (major), 91:9 er. **$[\alpha]_D^{26}$**: +78.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.49-7.46 (m, 4H), 7.40 (t, *J* = 7.5 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 6.18 (s, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 3.82 (d, *J* = 13.7 Hz, 2H), 3.37 (s, 3H), 3.16 (d, *J* = 13.7 Hz, 2H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.58 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 145.4, 139.7, 139.1, 135.0, 130.9, 129.5, 128.8, 128.6, 128.5, 128.3, 127.1, 123.3, 118.5, 89.5, 58.5, 56.9, 56.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{32}N_3O_5S$ 558.2057, found 558.2054.





(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-phenyl-4-(trifluoromethyl)-benzenesulfonamide (3h'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-phenyl-N-(propa-1,2-dien-1-yl)-4-(trifluoromethyl)benzenesulfonamide (84.8 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (45.3 mg, 78%), mp: 112-113 °C.

R_f (Petroleum ether/ EtOAc = 10:1) = 0.65.

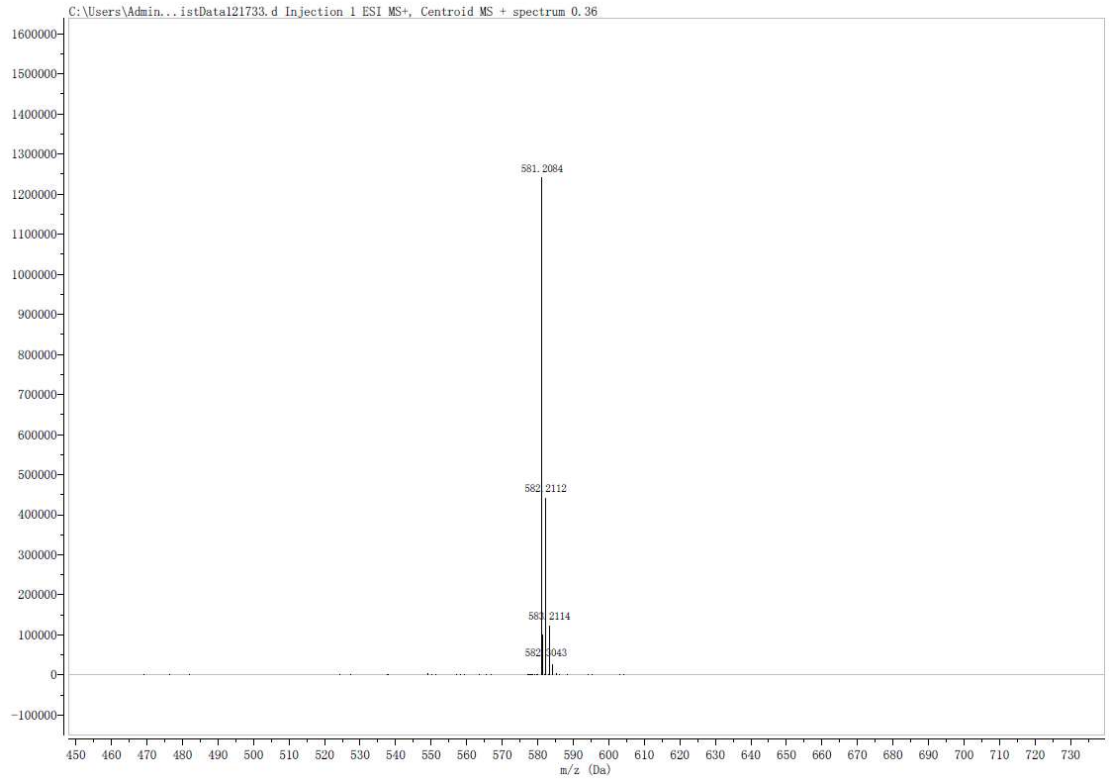
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 5.14 min (major), 5.96 min (minor), 91:9 er. **$[\alpha]_D^{26}$**: +40.0 (c: 0.10, $CHCl_3$).

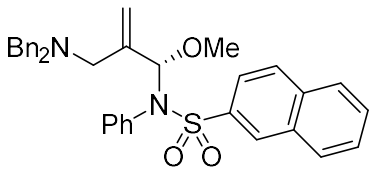
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.49-7.45 (m, 4H), 7.42-7.37 (m, 4H), 7.31-7.26 (m, 2H), 7.19-7.15 (m, 1H), 7.09-7.02 (m, 2H), 6.69-6.65 (m, 2H), 6.17 (s, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 3.80 (d, *J* = 13.7 Hz, 2H), 3.38 (s, 3H), 3.18 (d, *J* = 13.7 Hz, 2H), 3.09 (d, *J* = 14.1 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (q, *J* = 1.2 Hz), 140.0, 139.2, 135.2, 134.0 (q, *J* = 32.9 Hz), 131.1, 128.8 128.6, 128.4, 128.3, 127.1, 125.3 (q, *J* = 3.5 Hz), 123.4 (q, *J* = 272.7 Hz), 118.2, 89.4, 58.5, 56.8, 56.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{32}F_3N_2O_3S$ 581.2080, found 581.2084.





(S)-N-(2-((dibenzylamino)methyl)-1-methoxyallyl)-N-phenylnaphthalene-2-sulfonamide (3i'):

Prepared via **general procedure 5** N,N-dibenzyl-1-methoxymethanamine (24.1 mg, 0.1 mmol, 1.0 equiv) and N-phenyl-N-(propa-1,2-dien-1-yl)naphthalene-2-sulfonamide (80.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 12:1) and obtained as a white solid (47.8 mg, 85%), mp: 143-144 ºC.

R_f (Petroleum ether/ EtOAc = 10:1) = 0.45.

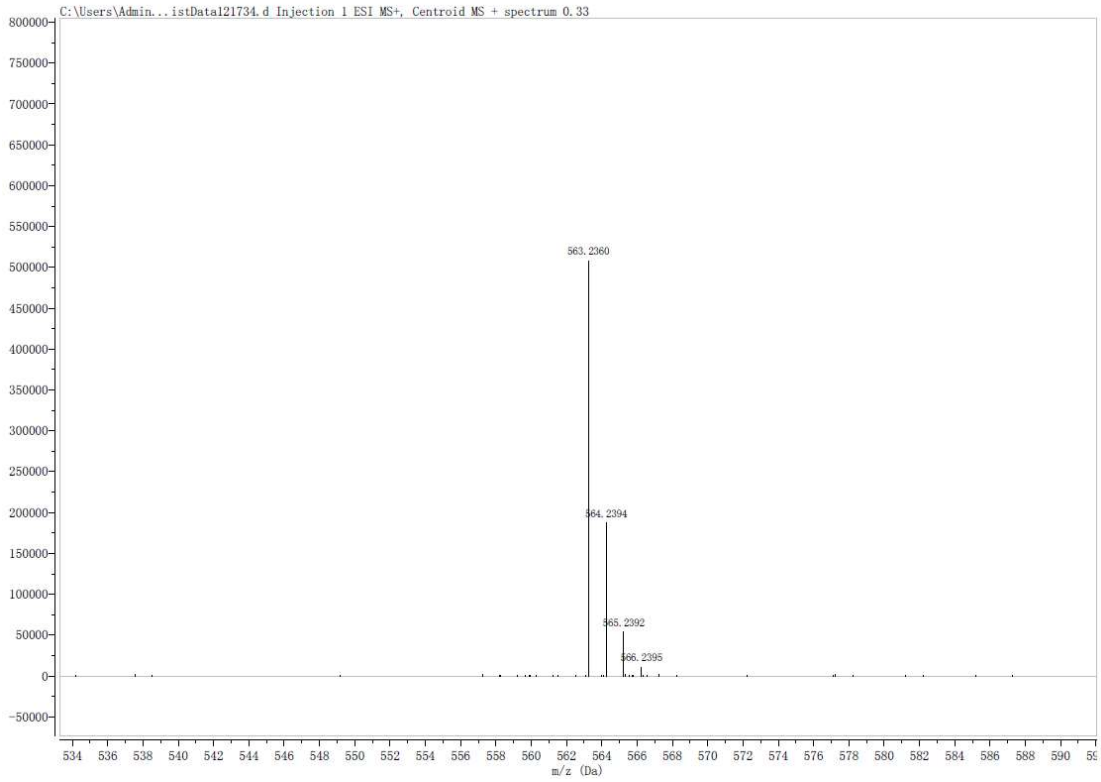
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 11.52 min (major), 13.10 min (minor), 84:16 er. **$[\alpha]_D^{26}$**: +60.0 (c: 0.10, $CHCl_3$).

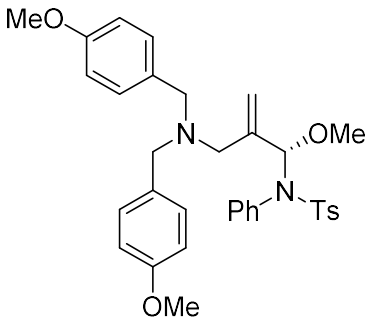
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.83-7.74 (m, 2H), 7.64-7.50 (m, 3H), 7.46-7.44 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.29-7.22 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 2H), 6.18 (s, 1H), 5.15 (s, 1H), 4.97 (s, 1H), 3.74 (d, *J*

= 13.7 Hz, 2H), 3.42 (s, 3H), 3.25 (d, *J* = 13.7 Hz, 2H), 3.11 (d, *J* = 14.3 Hz, 1H), 2.66 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 139.3, 136.9, 135.5, 134.8, 131.9, 131.4, 129.6, 129.3, 128.8, 128.6, 128.5, 128.2, 128.14, 128.10, 127.8, 127.2, 127.0, 123.7, 117.4, 89.4, 58.4, 56.7, 56.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{35}N_2O_3S$ 563.2363, found 563.2360.





(S)-N-(2-((bis(4-methoxybenzyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzene-sulfonamide (3j'):

Prepared via **general procedure 5** 1-methoxy-N,N-bis(4-methoxybenzyl)methanamine (30.1 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral

phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 9:1) and obtained as colorless oil (48.1 mg, 82%).

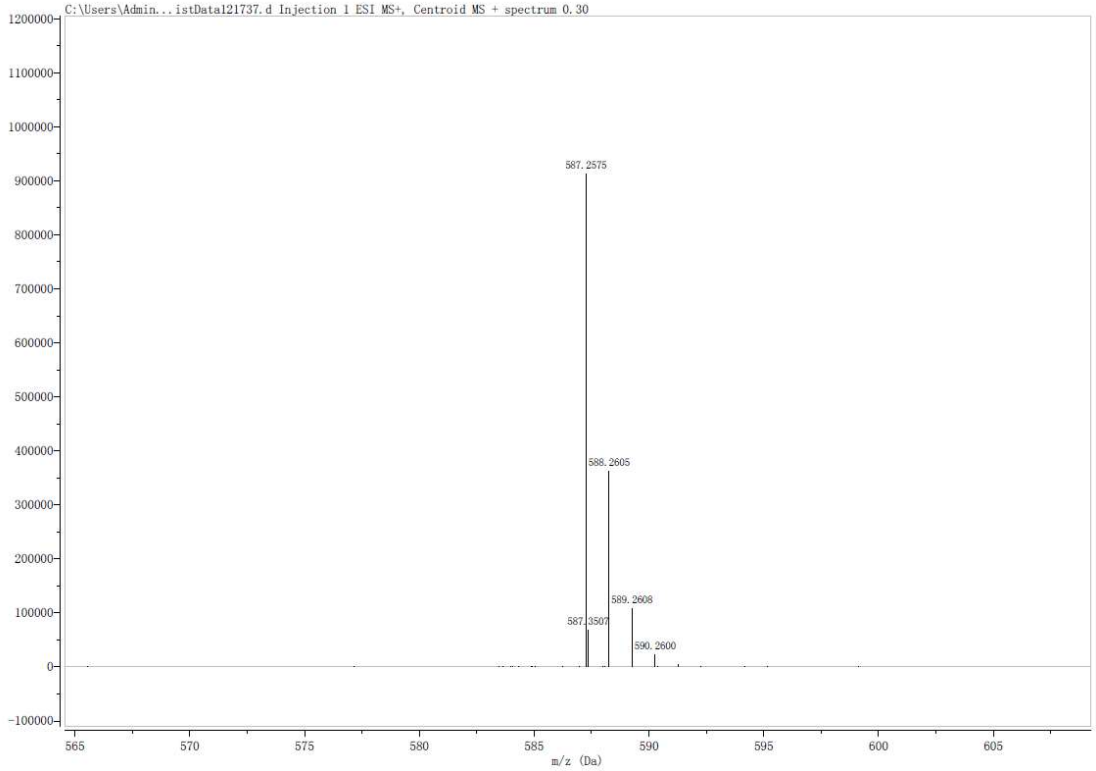
R_f (Petroleum ether/ EtOAc = 10:1) = 0.25.

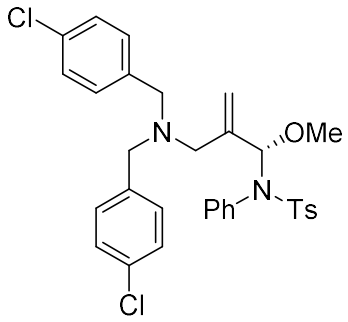
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 8.17 min (minor), 13.62 min (major), 91:9 er. **$[\alpha]_D^{26}$**: +58.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 4H), 7.16-7.12 (m, 3H), 7.08-7.03 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 4H), 6.78-6.73 (m, 2H), 6.08 (s, 1H), 5.12 (s, 1H), 4.97 (s, 1H), 3.82 (s, 6H), 3.65 (d, *J* = 13.5 Hz, 2H), 3.40 (s, 3H), 3.18 (d, *J* = 13.5 Hz, 2H), 3.06 (d, *J* = 14.3 Hz, 1H), 2.63 (d, *J* = 14.3 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 143.1, 140.7, 137.0, 135.6, 131.4, 131.3, 129.8, 128.8, 128.6, 128.2, 128.0, 117.1, 113.9, 89.3, 57.4, 56.7, 56.1, 55.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{39}N_2O_5S$ 587.2574, found 587.2575.





(S)-N-(2-((bis(4-chlorobenzyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzene-sulfonamide (3k'):

Prepared via **general procedure 5** N,N-bis(4-chlorobenzyl)-1-methoxymethanamine (31.0 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 35:1 to 15:1) and obtained as a white solid (46.5 mg, 78%), mp: 86-87 °C.

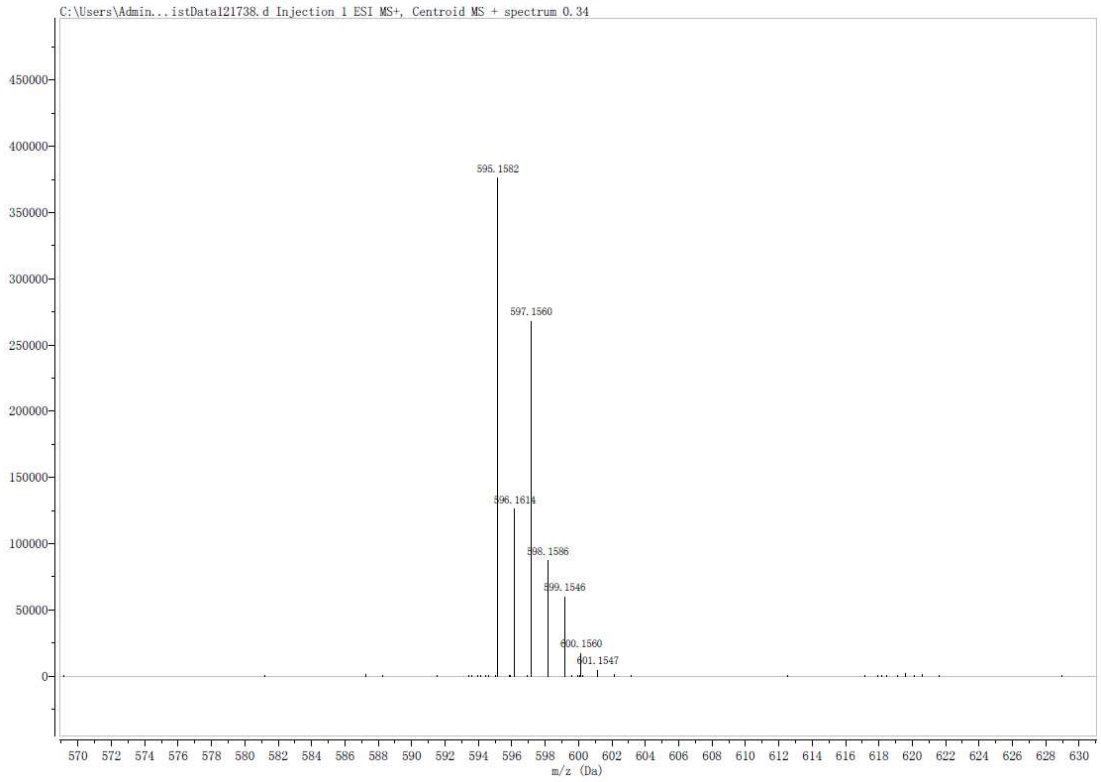
R_f (Petroleum ether/ EtOAc = 10:1) = 0.45.

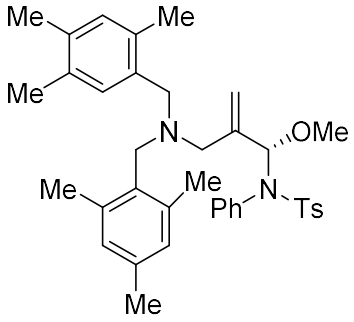
HPLC (IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, I = 215 nm) t_R = 13.14 min (minor), 17.94 min (major), 94:6 er. **$[\alpha]_D^{26}$**: +24.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.37-7.32 (m, 8H), 7.16 (t, *J* = 7.5 Hz, 3H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.06 (s, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 3.65 (d, *J* = 13.9 Hz, 2H), 3.38 (s, 3H), 3.23 (d, *J* = 13.9 Hz, 2H), 3.05 (d, *J* = 14.4 Hz, 1H), 2.66 (d, *J* = 14.4 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 140.3, 137.5, 136.7, 135.5, 132.7, 131.2, 129.9, 128.9, 128.7, 128.2, 128.1, 117.4, 89.3, 57.6, 56.8, 56.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{33}Cl_2N_2O_3S$ 595.1583, found 595.1582.





(S)-N-(2-((bis(2,4,6-trimethylbenzyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzene-sulfonamide (3l'):

Prepared via **general procedure 5** 1-mesityl-N-(methoxymethyl)-N-(2,4,6-trimethylbenzyl)methanamine (32.5 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (42.2 mg, 69%), mp: 150-151 °C.

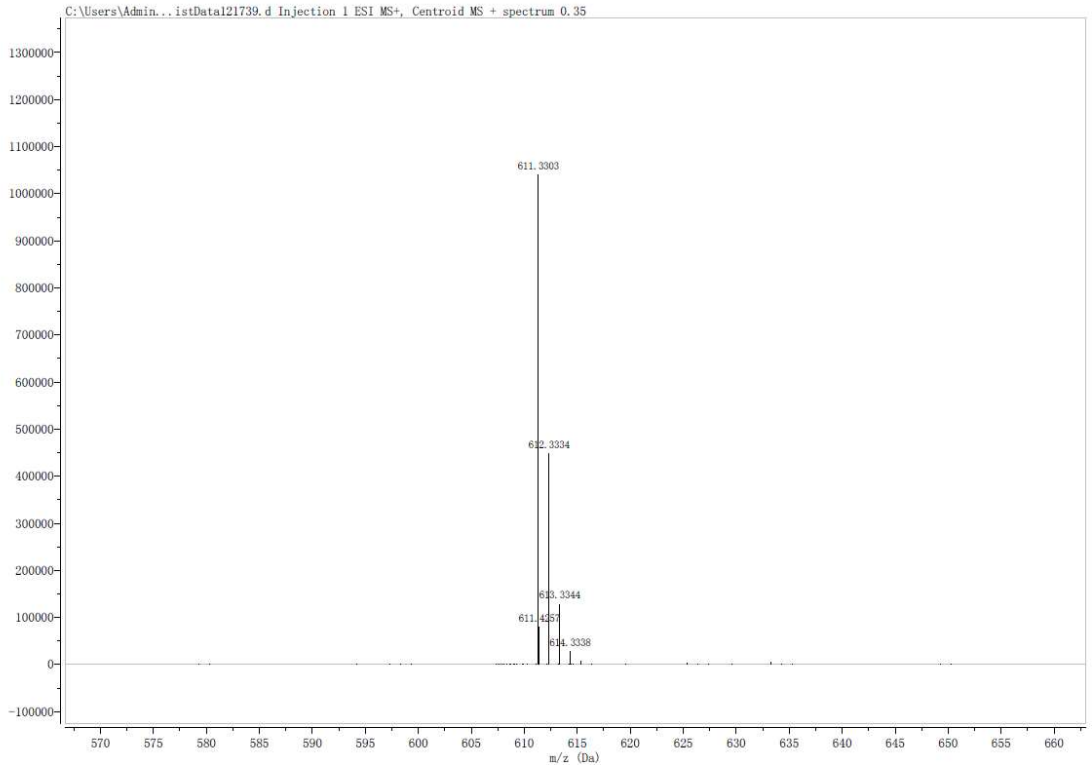
R_f (Petroleum ether/ EtOAc = 10:1) = 0.6.

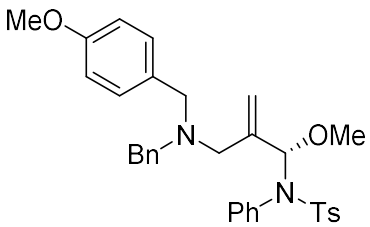
HPLC (IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, I = 254 nm) t_R = 6.93 min (major), 8.63 min (minor), 92:8 er. **$[\alpha]_D^{26}$**: +34.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.11 (m, 3H), 7.10-6.99 (m, 4H), 6.86 (s, 4H), 6.60 (d, *J* = 7.5 Hz, 2H), 5.92 (s, 1H), 4.99 (s, 1H), 4.92 (s, 1H), 3.65 (d, *J* = 12.3 Hz, 2H), 3.44 (s, 3H), 3.25 (d, *J* = 12.3 Hz, 2H), 3.06 (d, *J* = 12.8 Hz, 1H), 2.49 (d, *J* = 12.9 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 12H), 2.27 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 140.9, 138.3, 136.9, 136.4, 135.4, 131.7, 129.1, 128.7, 128.2, 127.9, 127.8, 118.4, 89.5, 56.9, 56.8, 52.7, 21.6, 21.0, 20.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{47}N_2O_3S$ 611.3302, found 611.3303.





(S)-N-(2-((benzyl(4-methoxybenzyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzene-sulfonamide (3m'):

Prepared via **general procedure 5** N-benzyl-1-methoxy-N-(4-methoxybenzyl)methanamine (27.1 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the

presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 12:1) and obtained as a white solid (47.9 mg, 86%), mp: 114-115 ºC.

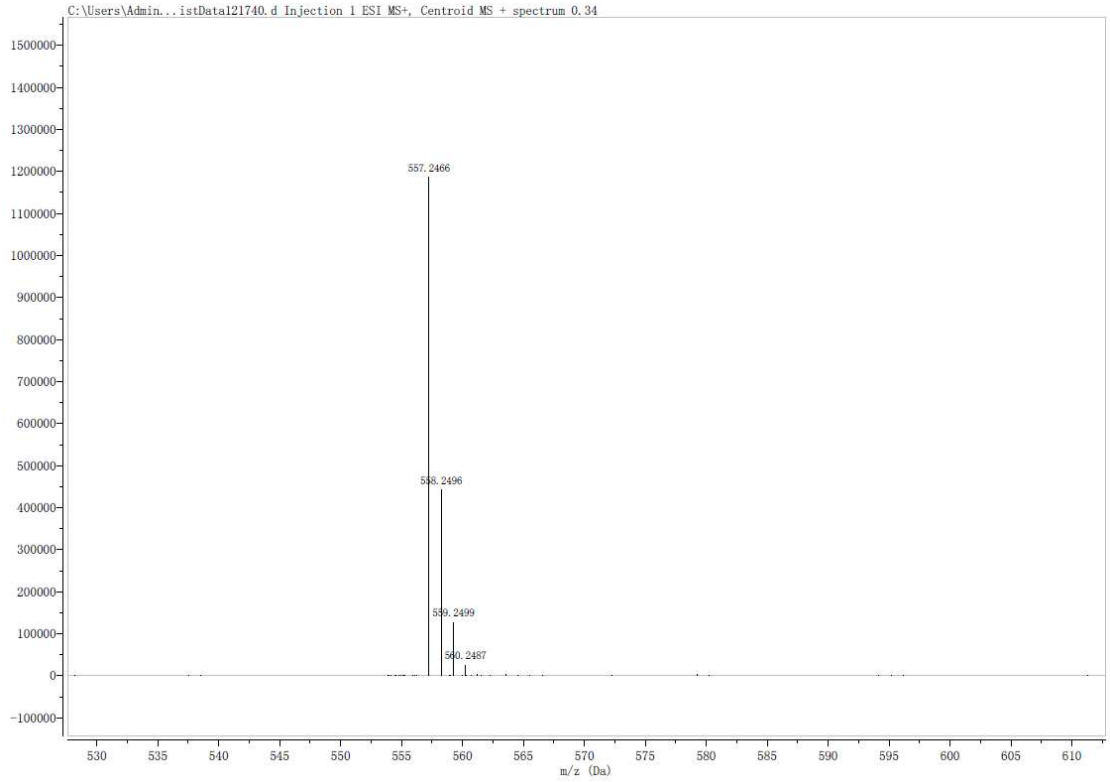
R_f (Petroleum ether/ EtOAc = 10:1) = 0.4.

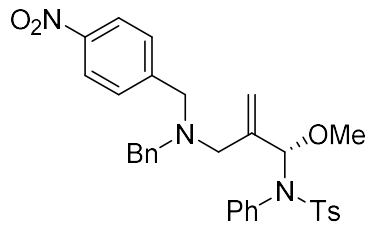
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm) t_R = 22.51 min (minor), 27.68 min (major), 92:8 er. **$[\alpha]_D^{26}$**: +20.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (m, 8H), 7.28-7.23 (m, 1H), 7.17-7.12 (m, 3H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 7.4 Hz, 2H), 6.10 (s, 1H), 5.13 (s, 1H), 4.98 (s, 1H), 3.81 (s, 3H), 3.75-3.65 (m, 2H), 3.39 (s, 3H), 3.25-3.17 (m, 2H), 3.07 (d, *J* = 14.3 Hz, 1H), 2.64 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 143.1, 140.7, 139.4, 137.0, 135.6, 131.4, 131.2, 129.8, 128.8, 128.7, 128.5, 128.2, 128.0, 126.9, 117.2, 113.9, 89.4, 58.2, 57.7, 56.7, 56.2, 55.4, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{37}N_2O_4S$ 557.2469, found 557.2466.





(S)-N-(2-((benzyl(4-nitrobenzyl)amino)methyl)-1-methoxyallyl)-4-methyl-N-phenylbenzene-sulfonamide (3n'):

Prepared via **general procedure 5** N-benzyl-1-methoxy-N-(4-nitrobenzyl)methanamine (28.6 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 25:1 to 10:1) and obtained as yellow oil (41.2 mg, 72%).

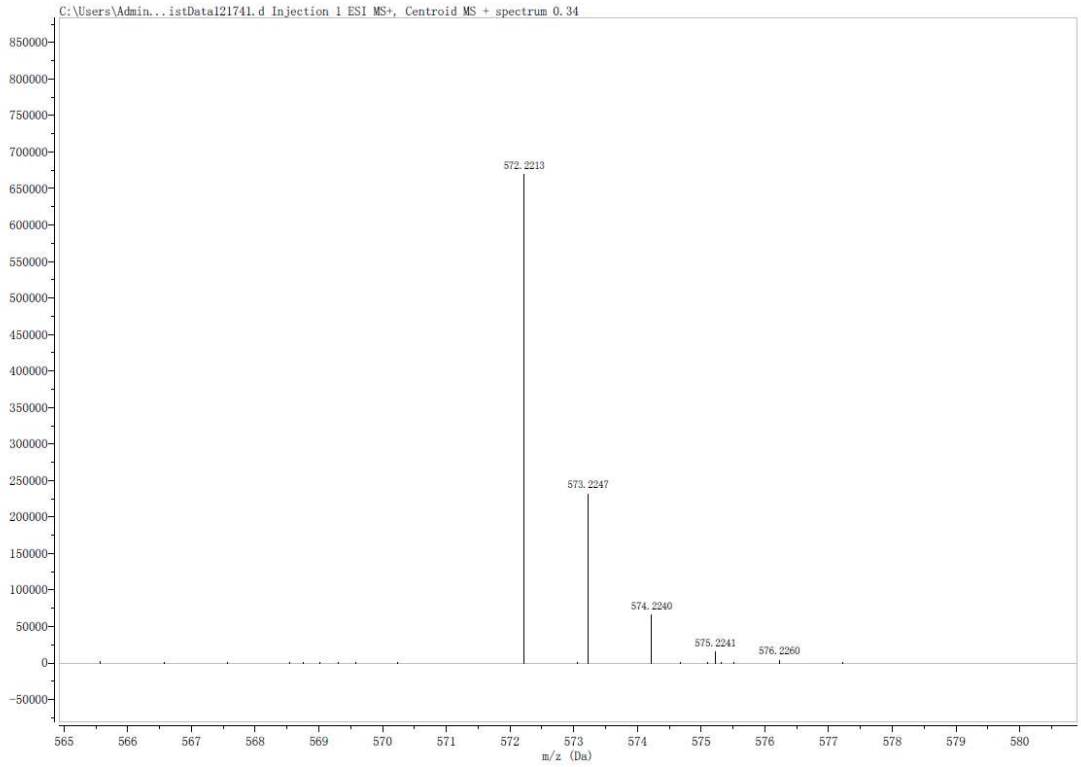
R_f (Petroleum ether/ EtOAc = 10:1) = 0.3.

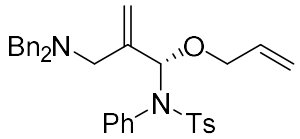
HPLC (ID, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 254 nm) t_R = 26.11 min (minor), 34.53 min (major), 93:7 er. **$[\alpha]_D^{26}$**: +36.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.45-7.37 (m, 6H), 7.31-7.26 (m, 1H), 7.18-7.14 (m, 3H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.12 (s, 1H), 5.17 (s, 1H), 5.04 (s, 1H), 3.83-3.73 (m, 2H), 3.39 (s, 3H), 3.38-3.26 (m, 2H), 3.11 (d, *J* = 14.3 Hz, 1H), 2.70 (d, *J* = 14.3 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 147.1, 143.3, 140.1, 138.5, 136.6, 135.5, 131.1, 129.1, 128.9, 128.69, 128.66, 128.2, 128.1, 127.3, 123.8, 117.7, 89.2, 58.6, 57.8, 56.9, 56.6, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{34}N_3O_5S$ 572.2214, found 572.2213.





(S)-N-(1-(allyloxy)-2-((dibenzylamino)methyl)allyl)-4-methyl-N-phenylbenzenesulfonamide(3o')

Prepared via **general procedure 5** 1-(allyloxy)-N,N-dibenzylmethanamine (26.7 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as a white solid (67.4 mg, 61%), mp: 63-64 ºC.

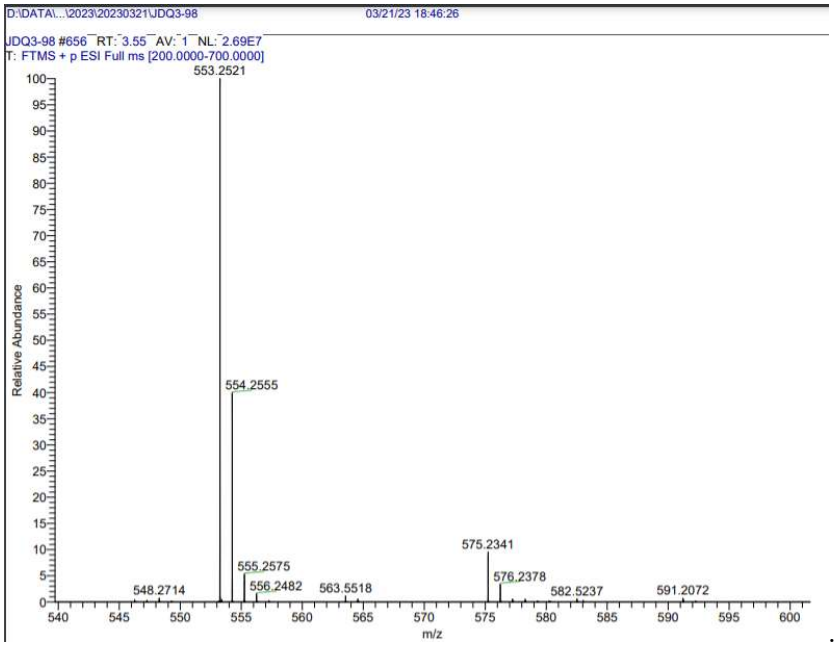
R_f (Petroleum ether/ EtOAc = 10:1) = 0.7.

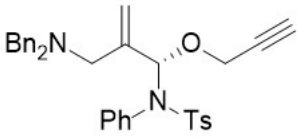
HPLC (ID, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, I = 254 nm) 21.32 min (major) t_R = 22.94 min (minor), 89:11 er. **$[\alpha]_D^{26}$**: +56.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 7.40-7.35 (m, 6H), 7.27-7.23 (m, 2H), 7.17-7.13 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.06-7.02 (m, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 6.25 (s, 1H), 5.91-5.82 (m, 1H), 5.19-5.10 (m, 3H), 5.03 (s, 1H), 4.19-4.15 (m, 1H), 4.03-3.98 (m, 1H), 3.74 (d, *J* = 13.8 Hz, 2H), 3.23 (d, *J* = 13.8 Hz, 2H), 3.10 (d, *J* = 14.3 Hz, 1H), 2.66 (d, *J* = 14.3 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.8, 139.3, 136.8, 135.7, 133.8, 131.4, 128.83, 128.75, 128.5, 128.3, 128.1, 128.0, 127.0, 117.5, 116.7, 87.4, 69.8, 58.5, 56.5, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{37}N_2O_3S$ 553.2519, found 553.2521





(S)-N-(2-((dibenzylamino)methyl)-1-(prop-2-yn-1-yloxy)allyl)-4-methyl-N-phenylbenzenesul -fonamide (3p'):

Prepared via **general procedure 5** N,N-dibenzyl-1-(prop-2-yn-1-yloxy)methanamine (26.5 mg, 0.1 mmol, 1.0 equiv) and 4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (71.3 mg, 0.25 mmol, 2.5 equiv) according to the general procedure in the presence of chiral phosphoric acid **4** (7.0 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 15:1) and obtained as colorless oil (49.0 mg, 89%).

R_f (Petroleum ether/ EtOAc = 10:1) = 0.6.

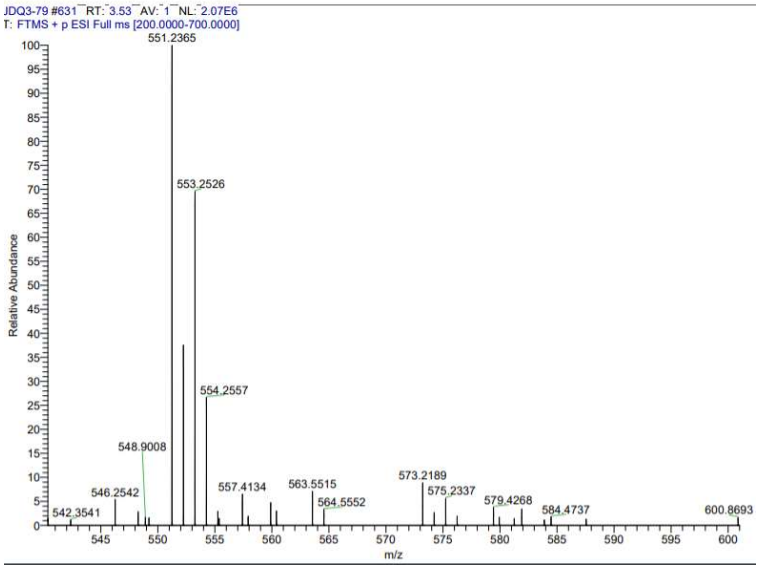
HPLC (ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1 mL/min, I = 254 nm) 9.43 min (minor) t_R = 11.13 min (major), 89:11 er. **$[\alpha]_D^{26}$**: +78.0 (c: 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 6H), 7.40-7.35 (m, 4H), 7.28-7.22 (m, 2H), 7.17-7.12 (m, 3H), 7.06-7.02 (m, 2H), 6.75-6.71 (m, 2H), 6.39 (s, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.20 (d, *J* =

2.4 Hz, 2H), 3.76 (d, J = 13.8 Hz, 2H), 3.24 (d, J = 13.8 Hz, 2H), 3.12 (d, J = 14.3 Hz, 1H), 2.66 (d, J = 14.3 Hz, 1H), 2.44 (t, J = 2.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 140.3, 139.2, 136.7, 135.5, 131.4, 128.9, 128.8, 128.5, 128.4, 128.12, 128.08, 127.0, 117.9, 87.0, 79.0, 75.2, 58.4, 56.5, 56.2, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{35}N_2O_3S$ 551.2363, found 551.2365.

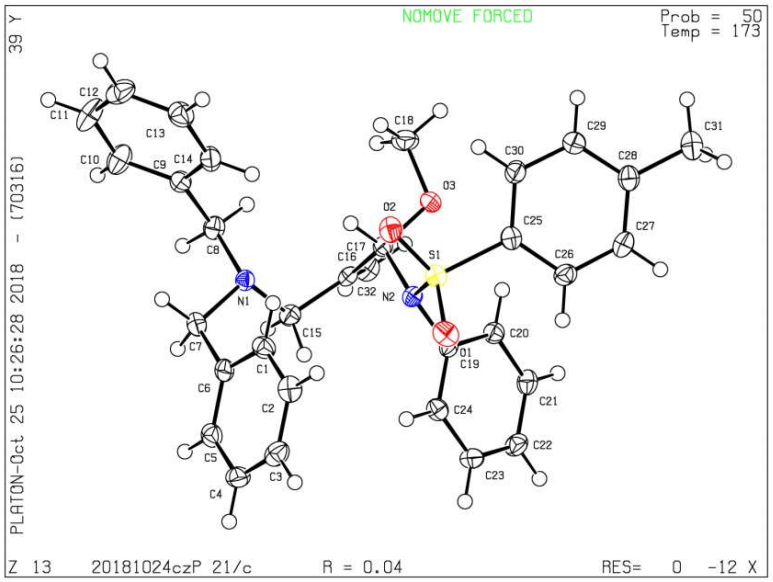


X-ray crystallographic data of 3a and 3b'

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (1958463, **3a**) and (2226527, **3b'**). The data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The measurements were taken in a Bruker APEX-II CCD diffractometer. The data were integrated by Bruker APEX2 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3).

Method of crystallization: A solution of **3a** in $CHCl_3$ and petroleum ether was evaporated the solvent slowly at room temperature.

Crystal data structure for 3a



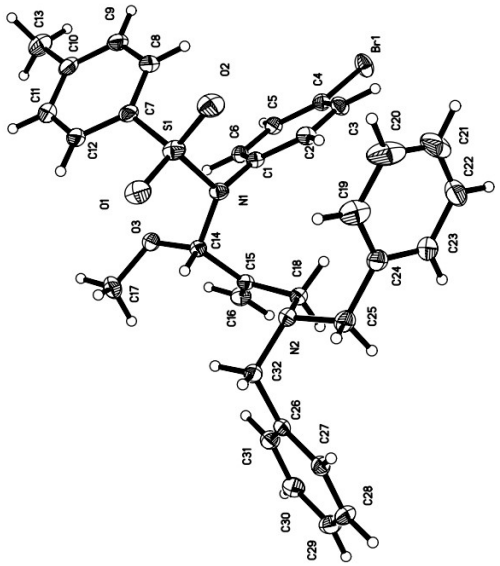
X-ray structure of **3a**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	C32H34N2O3S	
Formula weight	526.67	
Temperature	173 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	'P 21/c'	
Unit cell dimensions	a = 9.8161(5) Å	α = 90 °
	b = 17.3216(10) Å	β = 92.516(2) °
	c = 16.6079(10) Å	γ = 90 °
Volume	2821.1(3) $Å^3$	
Z	4	
Density (calculated)	1.240 g/cm^3	
Absorption coefficient	0.150 mm^{-1}	
F(000)	1120	
Crystal size	0.190x 0.160 x 0.150 mm^3	
θ range for data collection	2.352 to 25.009°	
Index ranges	$-8 \le h \le 11$, $-20 \le k \le 20$, $-19 \le l \le 19$	
Reflections collected	19950	
Independent reflections	4979 (R_{int} = 0.0472)	
Completeness to θ = 67.679 °	99.9 %	
Max. and min. transmission	0.972 and 0.978	
Data / restraints / parameters	4979 / 0 / 345	
Goodness-of-fit on F^2	1.015	
Final R indices [I > 2σ(I)]	R_1 = 0.0374, wR_2 = 0.0877	
R indices (all data)	R_1 = 0.0498, wR_2 = 0.0944	

Largest diff. peak and hole	0.304 and -0.365 e.Å^{-3}

Method of crystallization: A solution of **3b'** in $CHCl_3$ and petroleum ether was evaporated the solvent slowly at room temperature.

Crystal data and structure for 3b'



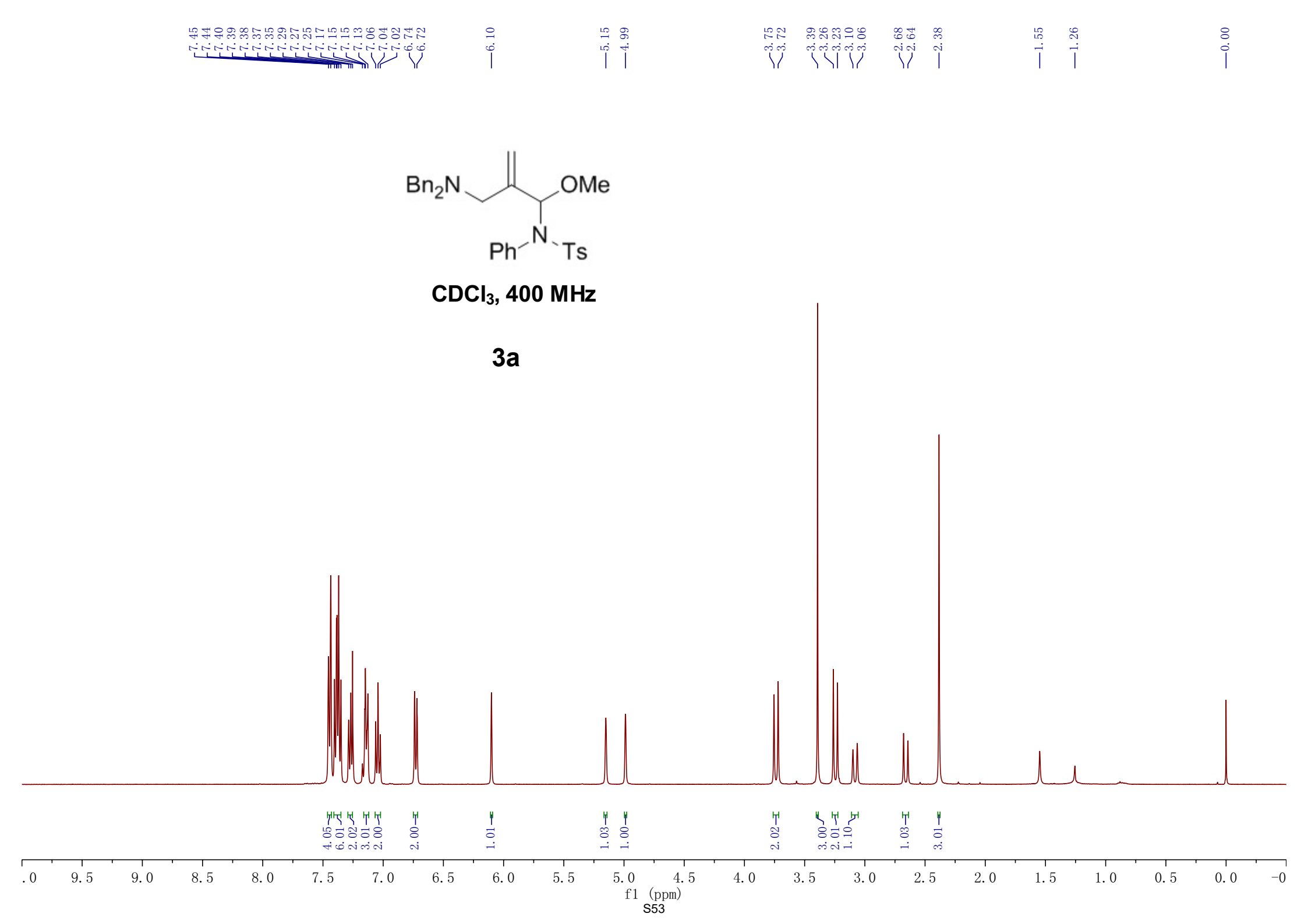
X-ray structure of **3b'**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	C32 H33 Br N2 O3 S	
Formula weight	605.57	
Temperature	193 K	
Wavelength	1. 34139 Å	
Crystal system	orthorhombic	
Space group	'P 21 21 21'	
Unit cell dimensions	a = 9.6485(3) Å	α = 90 °
	b = 13.5819(4) Å	β = 90 °
	c = 22.0979(6) Å	γ = 90 °
Volume	2895.82(15) Å^3	
Z	4	
Density (calculated)	1.389 g/cm^3	
Absorption coefficient	1.904 mm^{-1}	
F(000)	1256	
Crystal size	0.110x 0.090 x 0.080 mm^3	
θ range for data collection	3.323 to 53.857°	
Index ranges	-11≤ h ≤ 9, -16 ≤ k ≤ 12, -26≤ l ≤ 24	
Reflections collected	16873	

Independent reflections	5124 (R_{int} = 0.0435)
Completeness to θ = 67.679 º	97.3%
Max. and min. transmission	0.818 and 0.863
Data / restraints / parameters	5124 / 0 / 354
Goodness-of-fit on F^2	1.045
Final R indices [I > 2σ(I)]	R_1 = 0.0262, wR_2 = 0.0684
R indices (all data)	R_1 = 0.0273, wR_2 = 0.0694
Largest diff. peak and hole	0.210and -0.262 e.Å^{-3}
Flack parameter	0.036(8)

References

1. (a) Suárez-Pantiga, S.; Hernández-Díaz, C.; Piedrafita, M.; Rubio, E.; González, J. M. *Adv. Synth. Catal.* **2012**, *354*, 1651. (b) Yang, X.; Toste, F. D. *Chem. Sci.* **2016**, *7*, 2653. (c) Wei, L.-L.; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* **2001**, *57*, 459. (d) De, N.; Song, C. E.; Ryu, D. H.; Yoo, E. J. *Chem. Commun.* **2018**, ***54***, 6911. (e) Li, H.-H.; Li, X.-X.; Zhao, Z.-G.; Yuan, X.; Sun, C.-Y. *Org. Biomol. Chem.***2017**, ***15***, 4005. (f) Peng, S.; Cao, S.; Sun, J. *Org. Lett.* **2017**, *19*, 524. (g) Banerjee, S.; Senthilkumar, B.; Patil N. T. *Org. Lett.* **2019**, *21*, 180. (h) Kawata, Y.; Arai, S.; Nakajima M.; Nishida, A. *Tetrahedron Lett.* **2021**, *69*, 152974. (i) Wang, C.; Xu, G.; Shao, Y.; Tang, S.; Sun, J. *Org. Lett.* **2020**, *22*, 5990. (j) Suarez-Pantiga, S.; Hernandez-Diaz, C.; Rubio, E.; Gonzalez, J. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 11552.
2. (a) Kona, C. N.; Ramana, C. V. *Chem. Commun.* **2014**, *50*, 2152. (b) Wang, Y.; Jiang, M.; Liu, J.-T. *Adv. Synth. Catal.* **2014**, *356*, 2907. (c) Bernar, I.; Fiser, B.; Blanco-Ania, D.; Gomez-Bengoa, E.; Rutjes, F. P. J. T. *Org. Lett.* **2017**, *19*, 4211.
3. (a) Yu, J.; Chen, L.; Sun, J. *Org. Lett.* **2019**, *21*, 1664. (b) Wang, K.; Yu, J.; Shao, Y.; Tang, S.; Sun, J. *Angew. Chem. Int. Ed.* **2020**, *59*, 2351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7.06
7.04
7.02
6.74
6.72
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3.75
3.72
3.39
3.26
3.23
3.10
3.06
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2.64
2.38
1.55
1.26
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Bn2N
OMe
Ph
N
Ts
CDCl3, 400 MHz
3a
4.05
6.01
2.02
3.01
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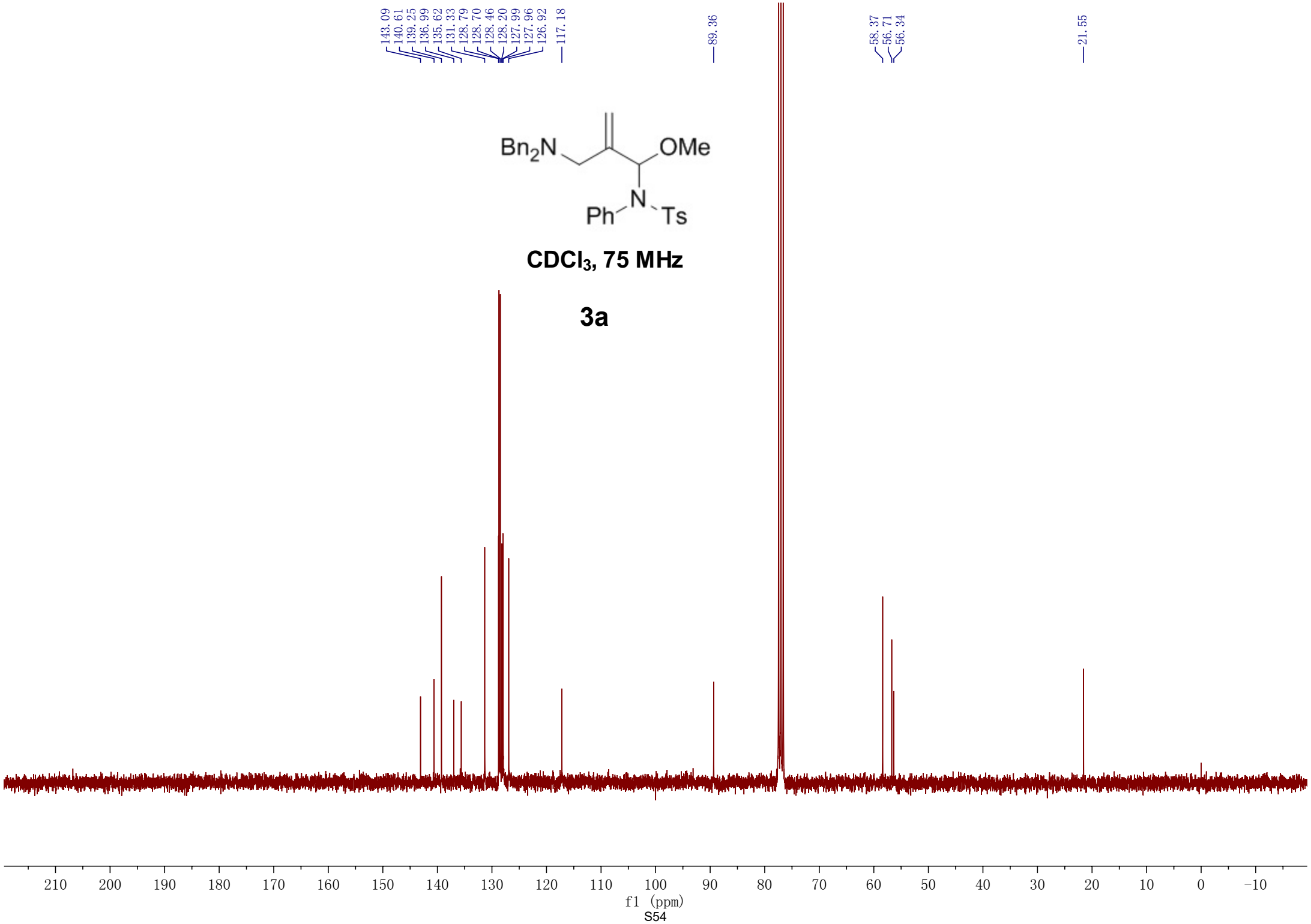
3.01
f1 (ppm)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117.18
89.36
58.37
56.71
56.34
21.55
Bn2N
OMe
N
Ph
Ts
CDCl3, 75 MHz
3a
210
200
190
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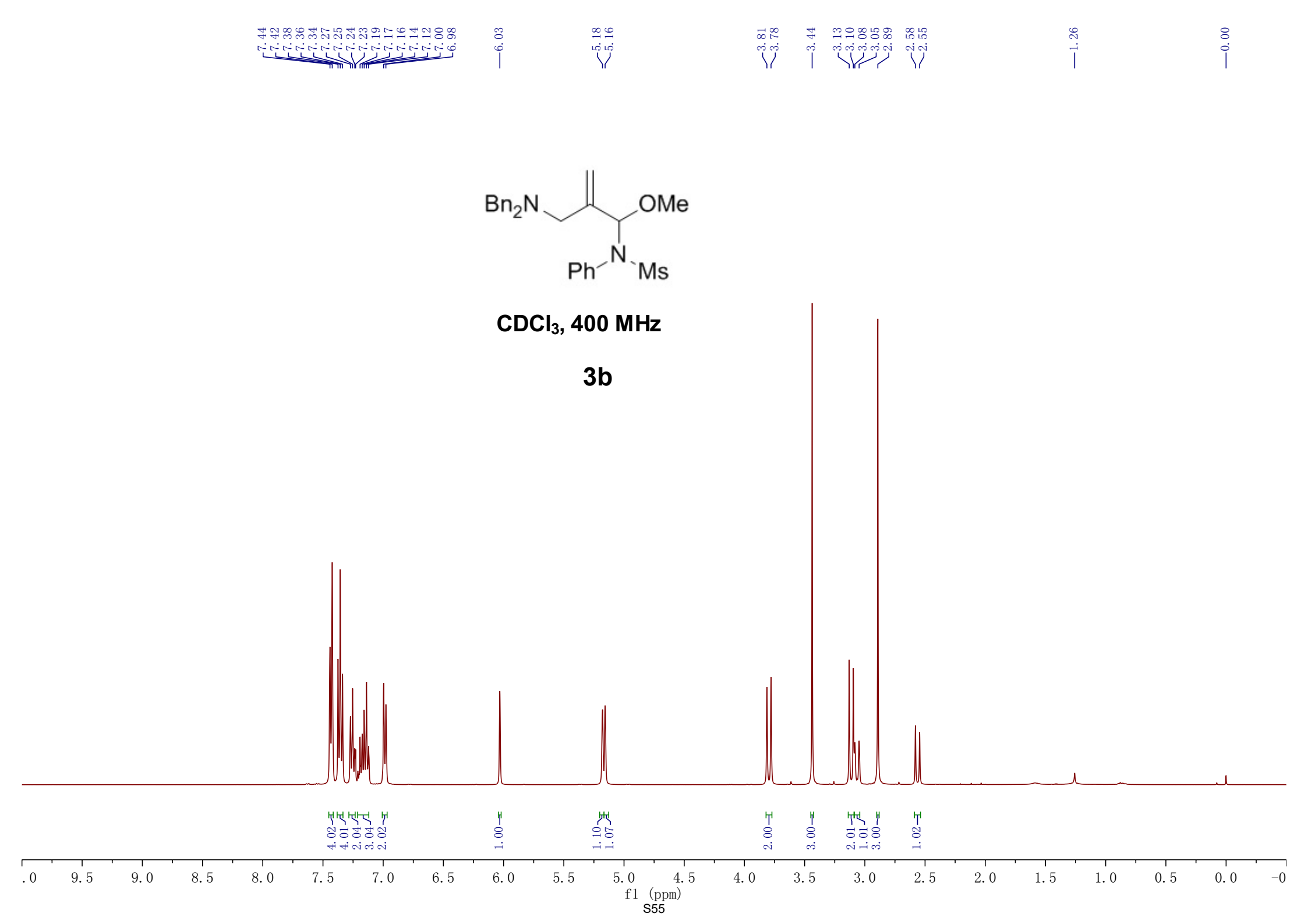
f1 (ppm)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7.00
6.98
6.03
5.18
5.16
3.81
3.78
3.44
3.13
3.10
3.08
3.05
2.89
2.58
2.55
1.26
0.00
Bn2N
OMe
N
Ph
Ms
CDCl3, 400 MHz
3b
4.02
4.01
2.04
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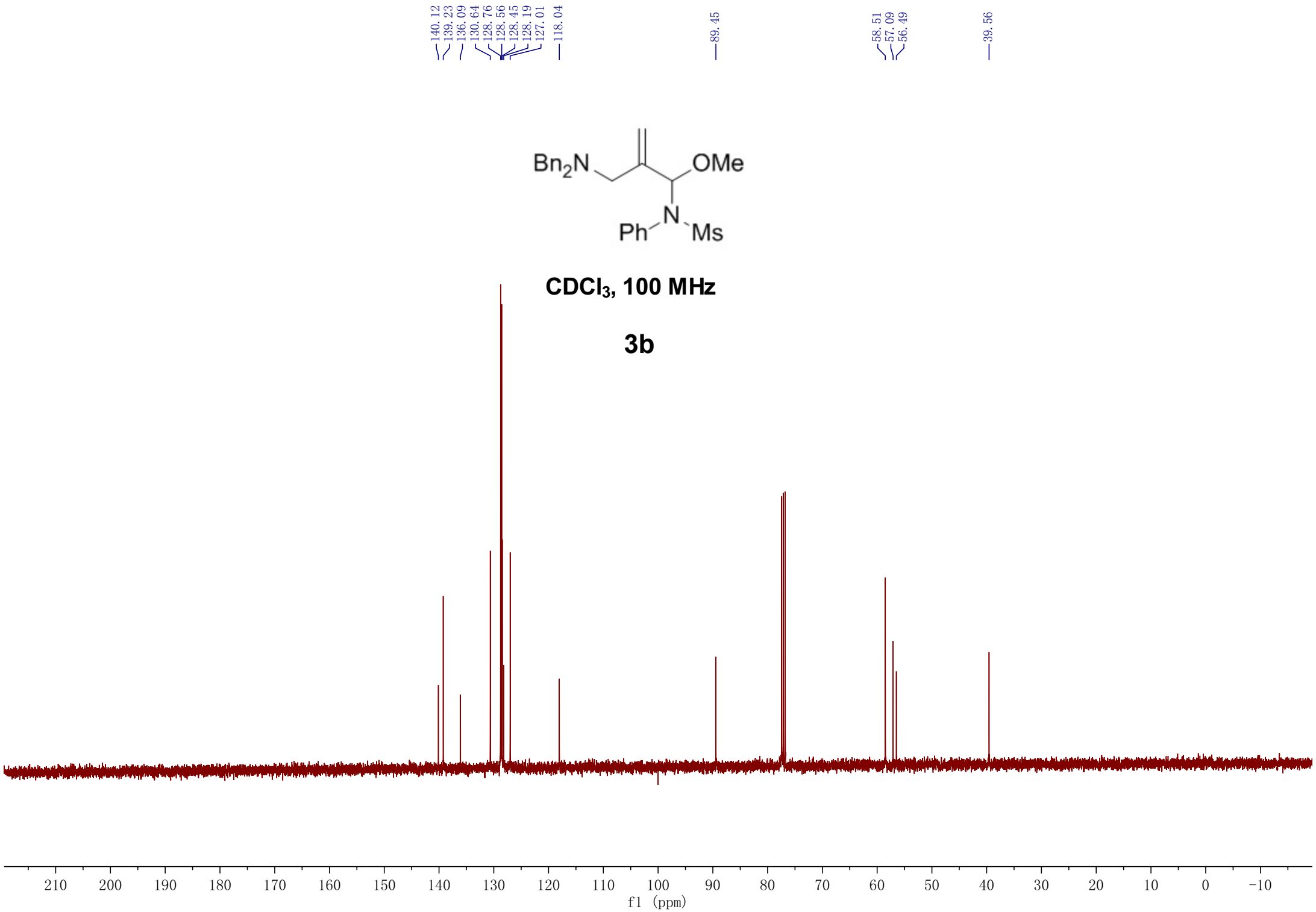
f1 (ppm)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56.49
39.56
Bn2N
OMe
N
Ph
Ms
CDCl3, 100 MHz
3b
210
200
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180
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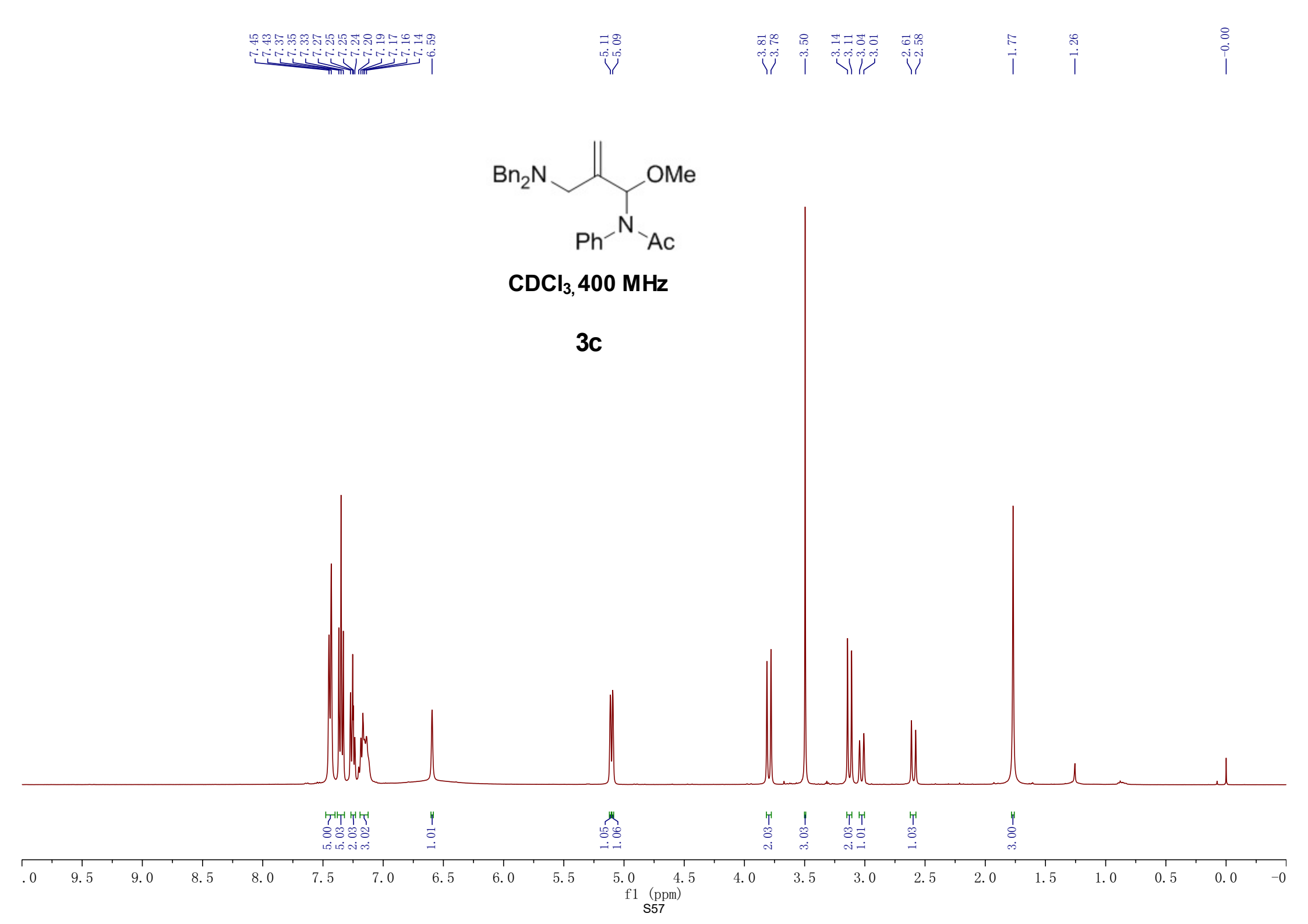
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3.11
3.04
3.01
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2.58
1.77
1.26
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OMe
N
Ph
Ac
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5.03
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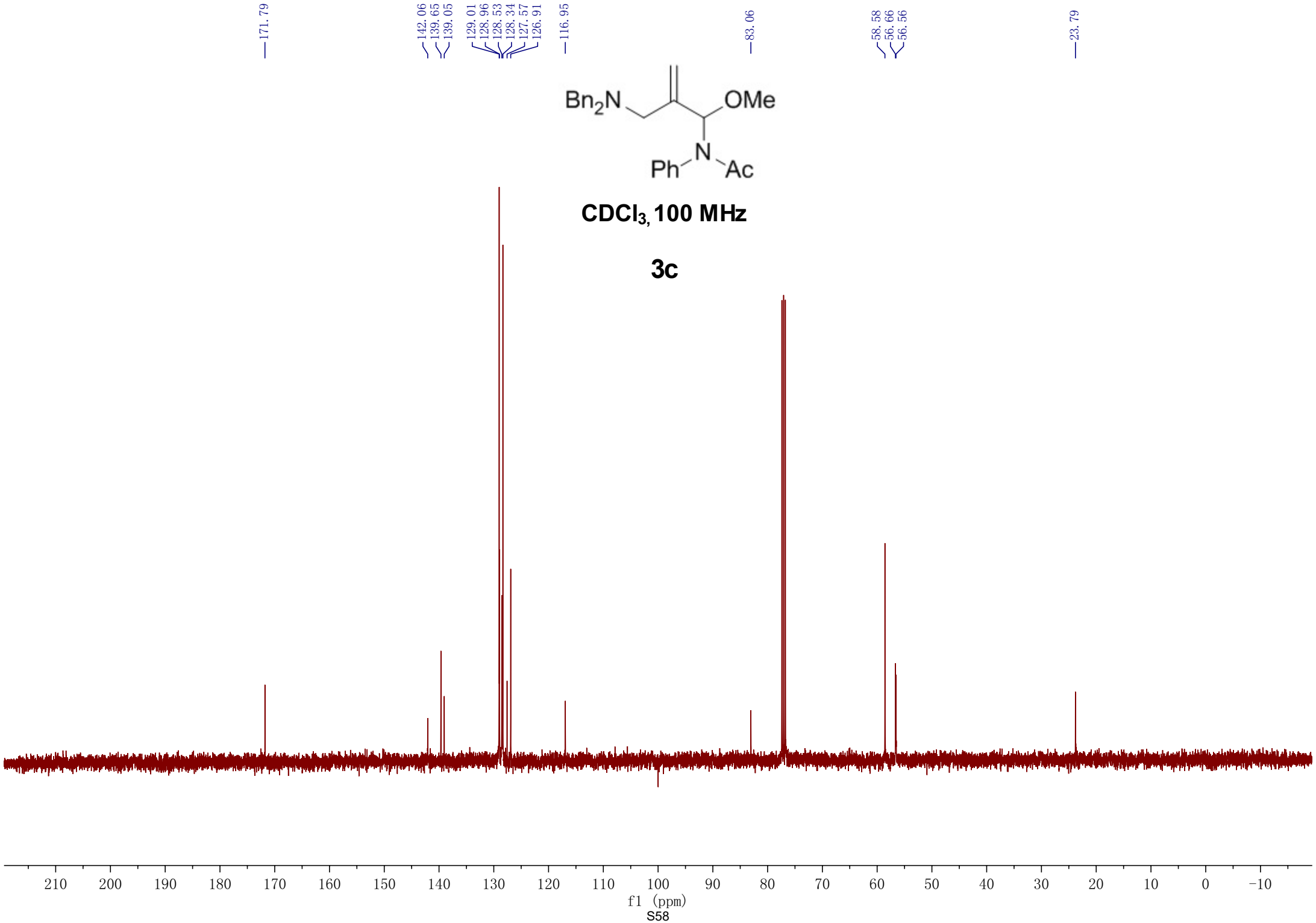
f1 (ppm)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56.66
56.56
23.79
Bn2N
OMe
N
Ph
Ac
CDCl3, 100 MHz
3c
210
200
190
180
170
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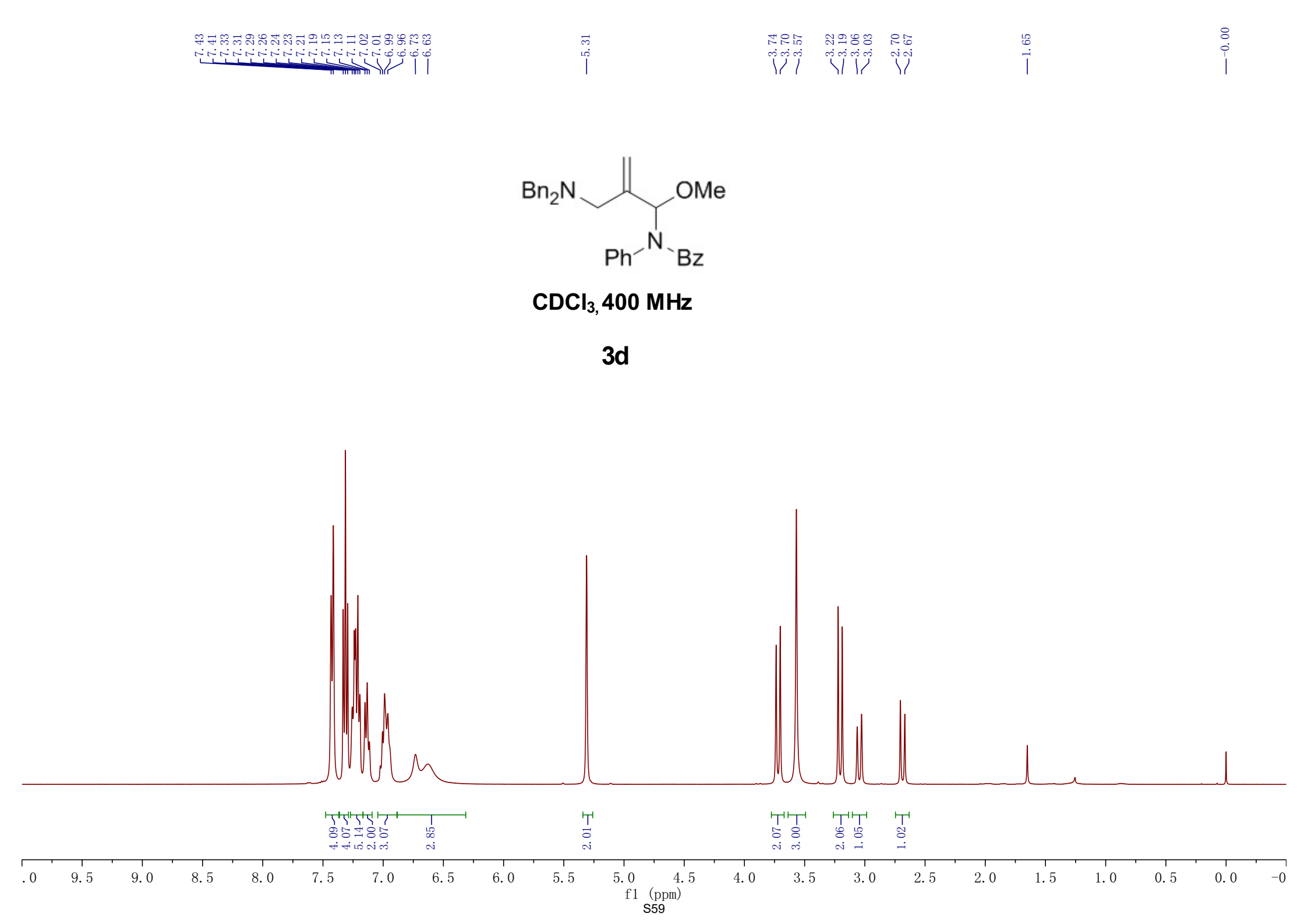
f1 (ppm)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7.19
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7.13
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6.63
5.31
3.74
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3.57
3.22
3.19
3.06
3.03
2.70
2.67
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Bn2N
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N
Ph
Bz
CDCl3, 400 MHz
3d
4.09
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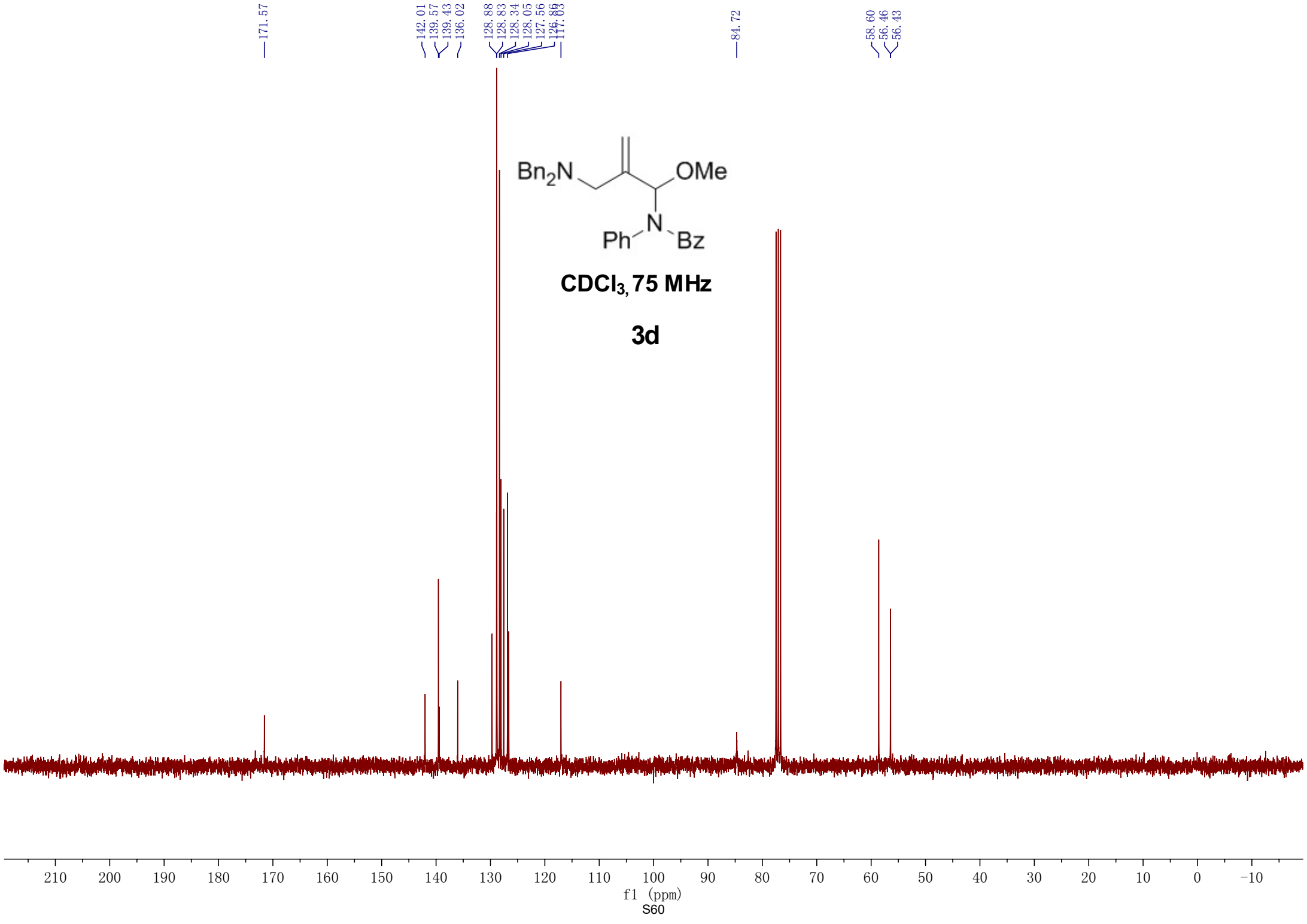
f1 (ppm)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Bn2N
OMe
N
Ph
Bz
CDCl3, 75 MHz
3d
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200
190
180
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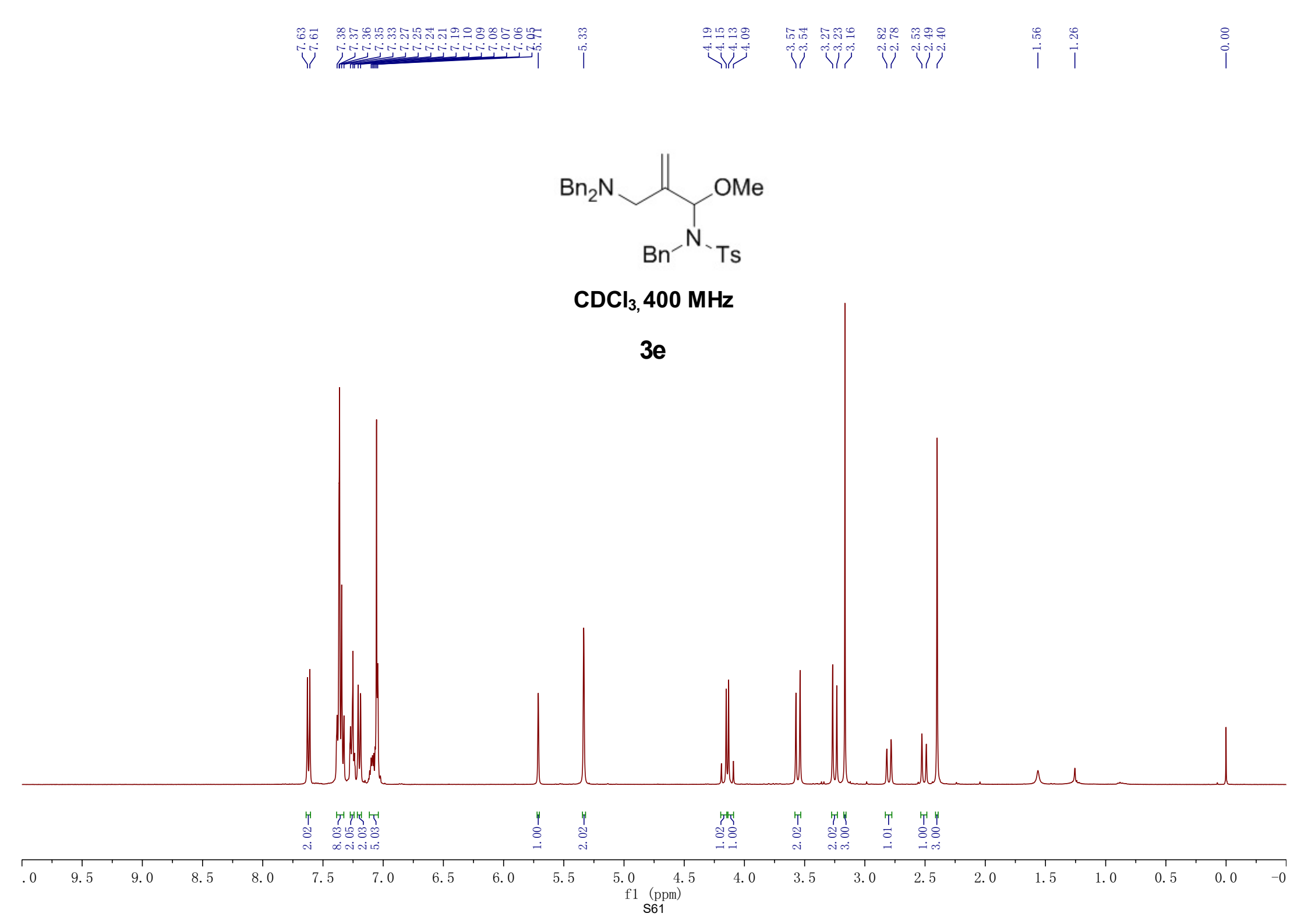
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7.05
7.01
5.33
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4.15
4.13
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2.78
2.53
2.49
2.40
1.56
1.26
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Bn2N
OMe
N
Bn
Ts
CDCl3, 400 MHz
3e
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8.03
2.05
2.03
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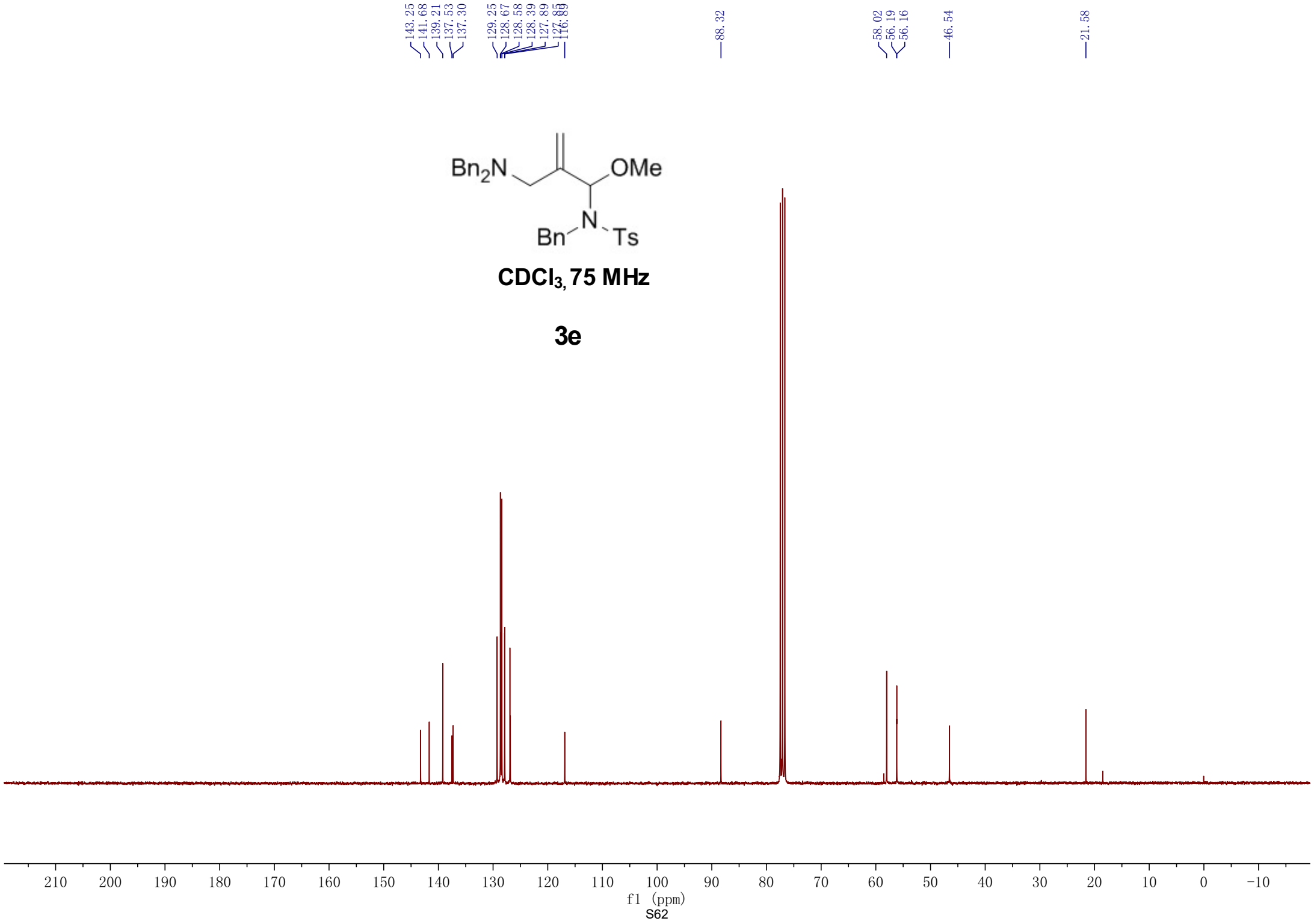
3.00
f1 (ppm)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21.58
Bn2N
OMe
N
Bn
Ts
CDCl3, 75 MHz
3e
210
200
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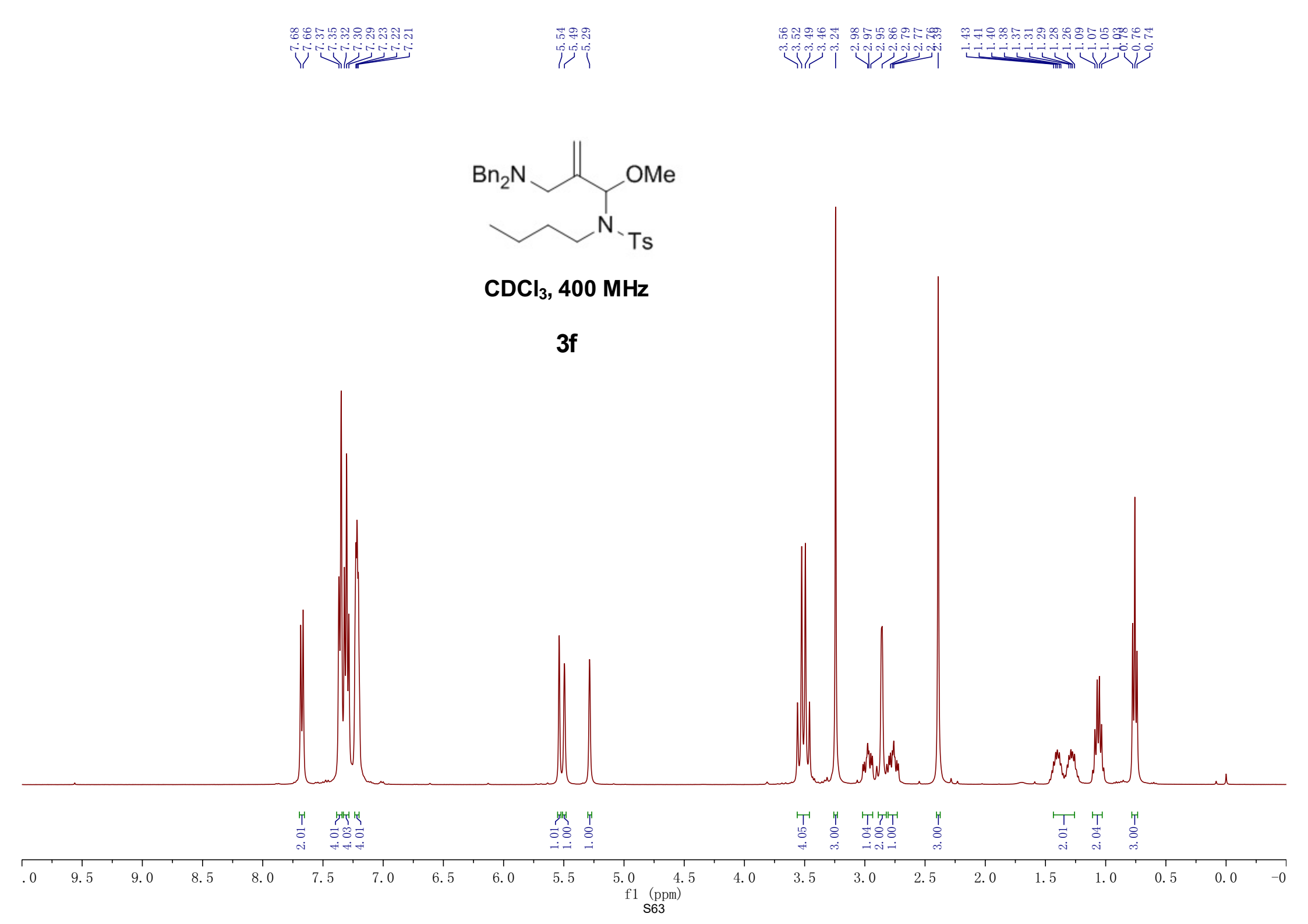
f1 (ppm)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2.39
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1.41
1.40
1.38
1.37
1.31
1.29
1.28
1.26
1.09
1.07
1.05
1.03
0.78
0.76
0.74
Bn2N
OMe
N
Ts
CDCl3, 400 MHz
3f
2.01
4.01
4.03
4.01
1.01
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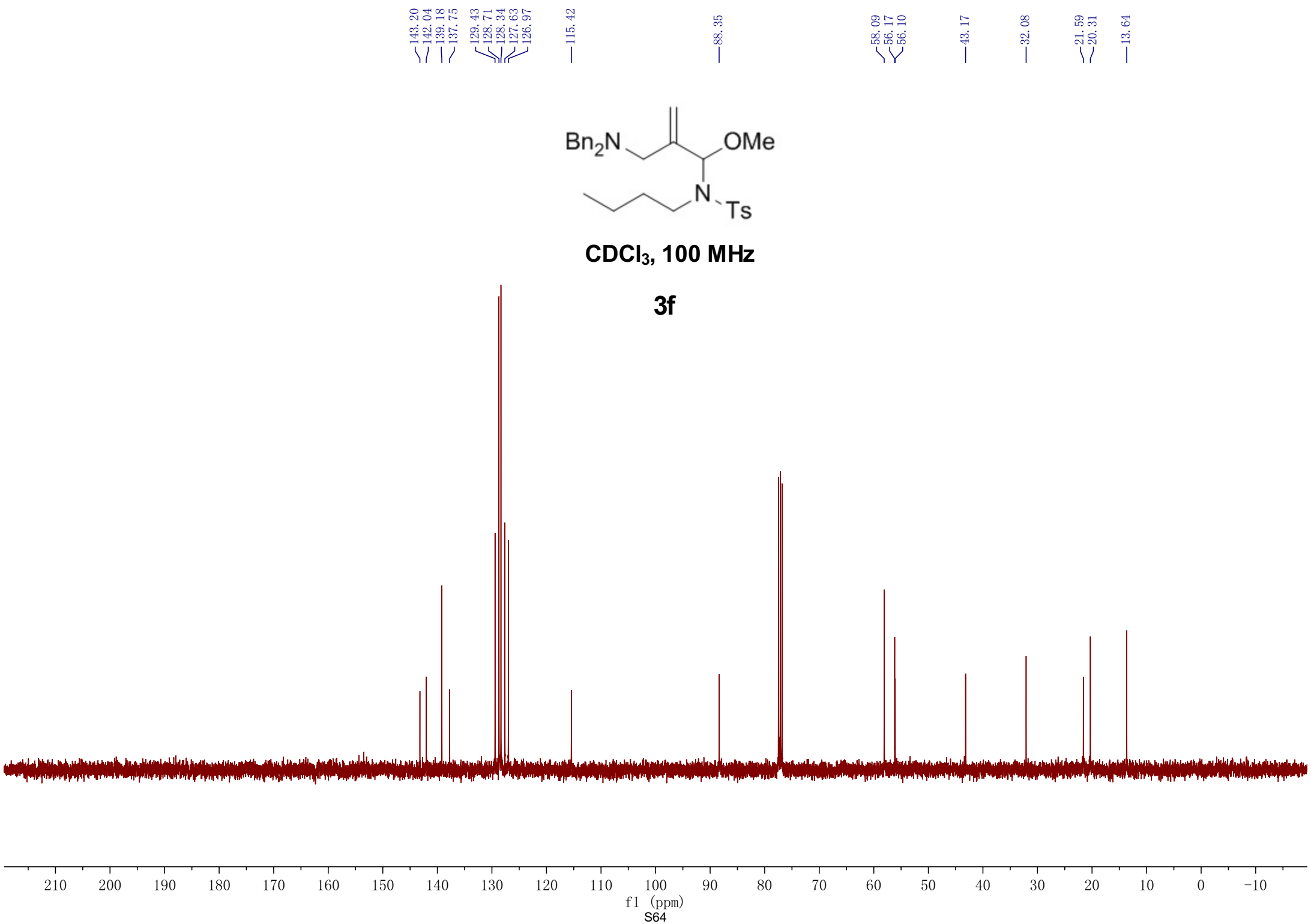
f1 (ppm)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56.10
43.17
32.08
21.59
20.31
13.64
Bn2N
OMe
N
Ts
CDCl3, 100 MHz
3f
210
200
190
180
170
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30
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10
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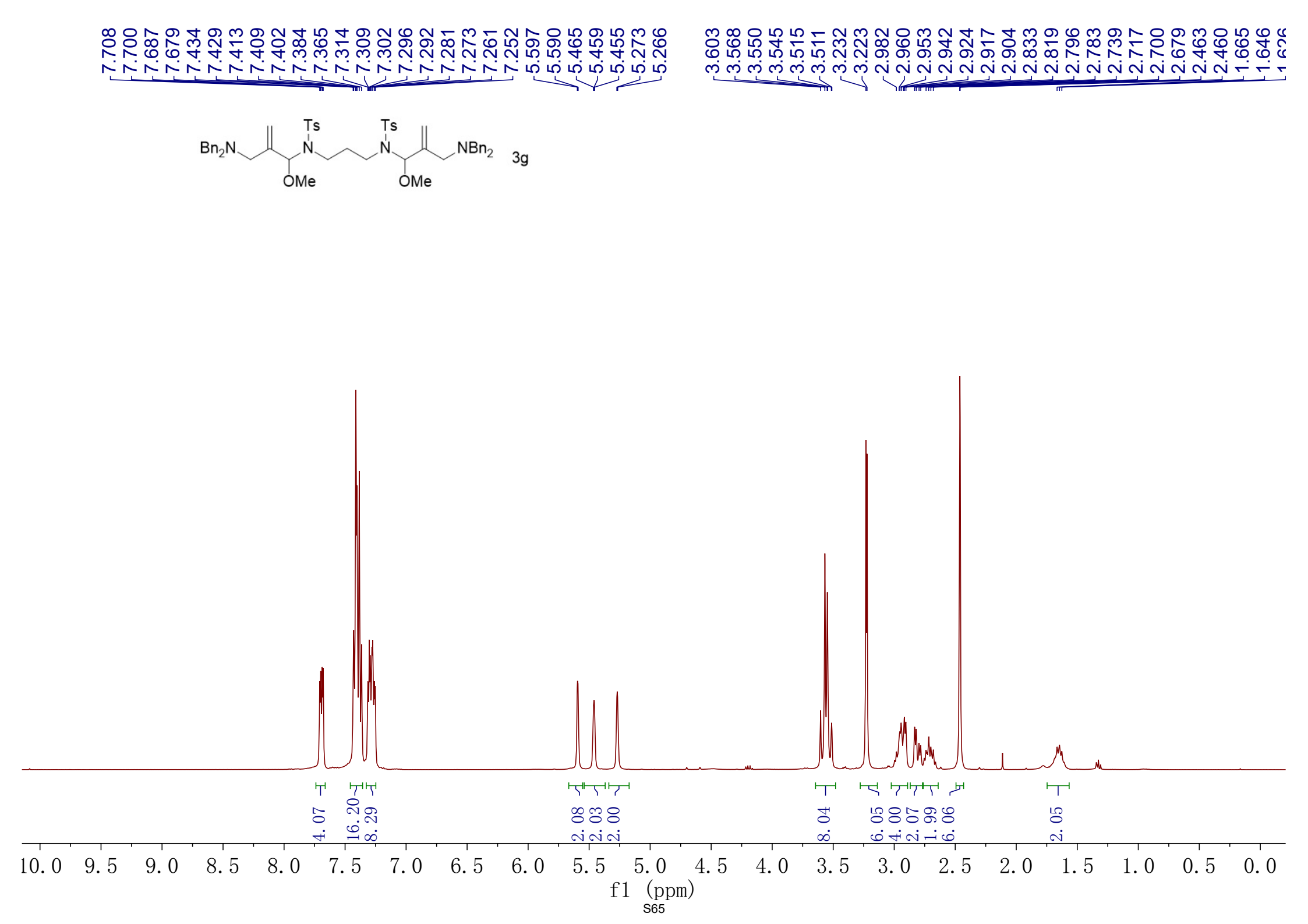
-10
f1 (ppm)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Ts
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NBn2
N
N
OMe
OMe
3g
4.07
16.20
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2.08
2.03
2.00
8.04
6.05
4.00
2.07
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2.05
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7.0
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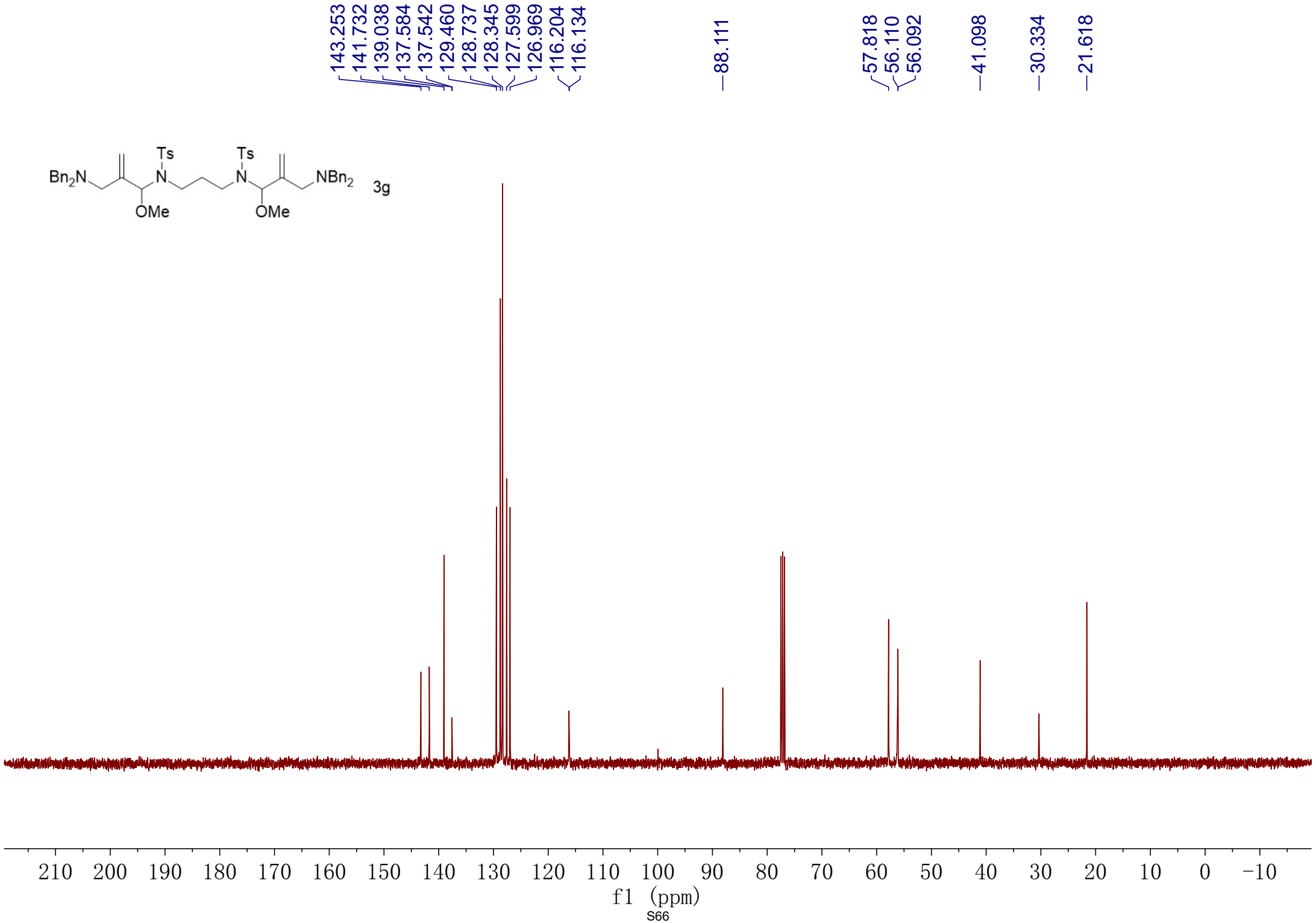
f1 (ppm)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56.110
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41.098
30.334
21.618
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OMe
OMe
3g
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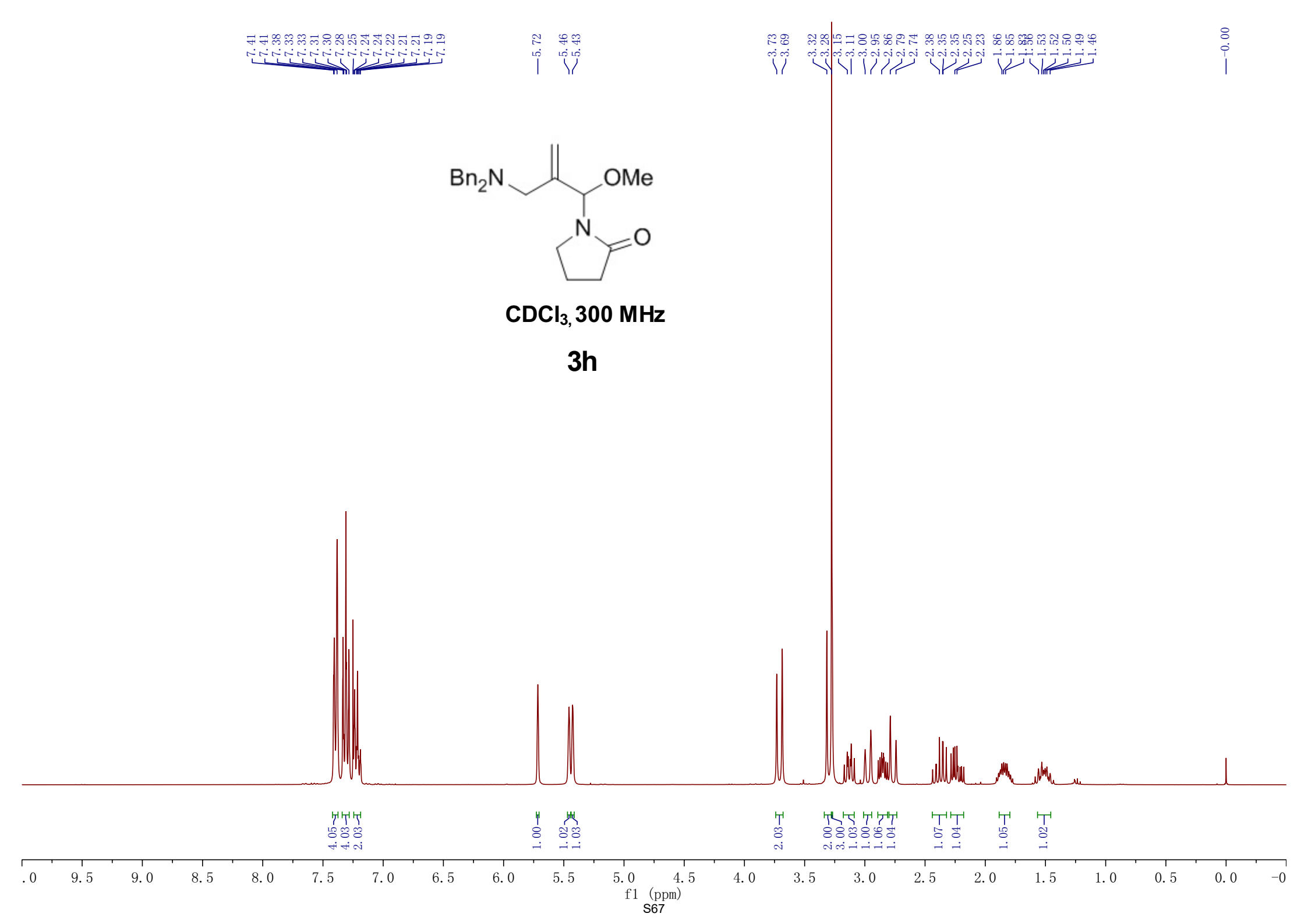
f1 (ppm)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7.21
7.19
7.19
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5.46
5.43
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3.15
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2.35
2.25
2.23
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1.52
1.50
1.49
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Bn2N
OMe
N
O
CDCl3, 300 MHz
3h
4.05
4.03
2.03
1.00
1.02
1.03
2.03
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1.07
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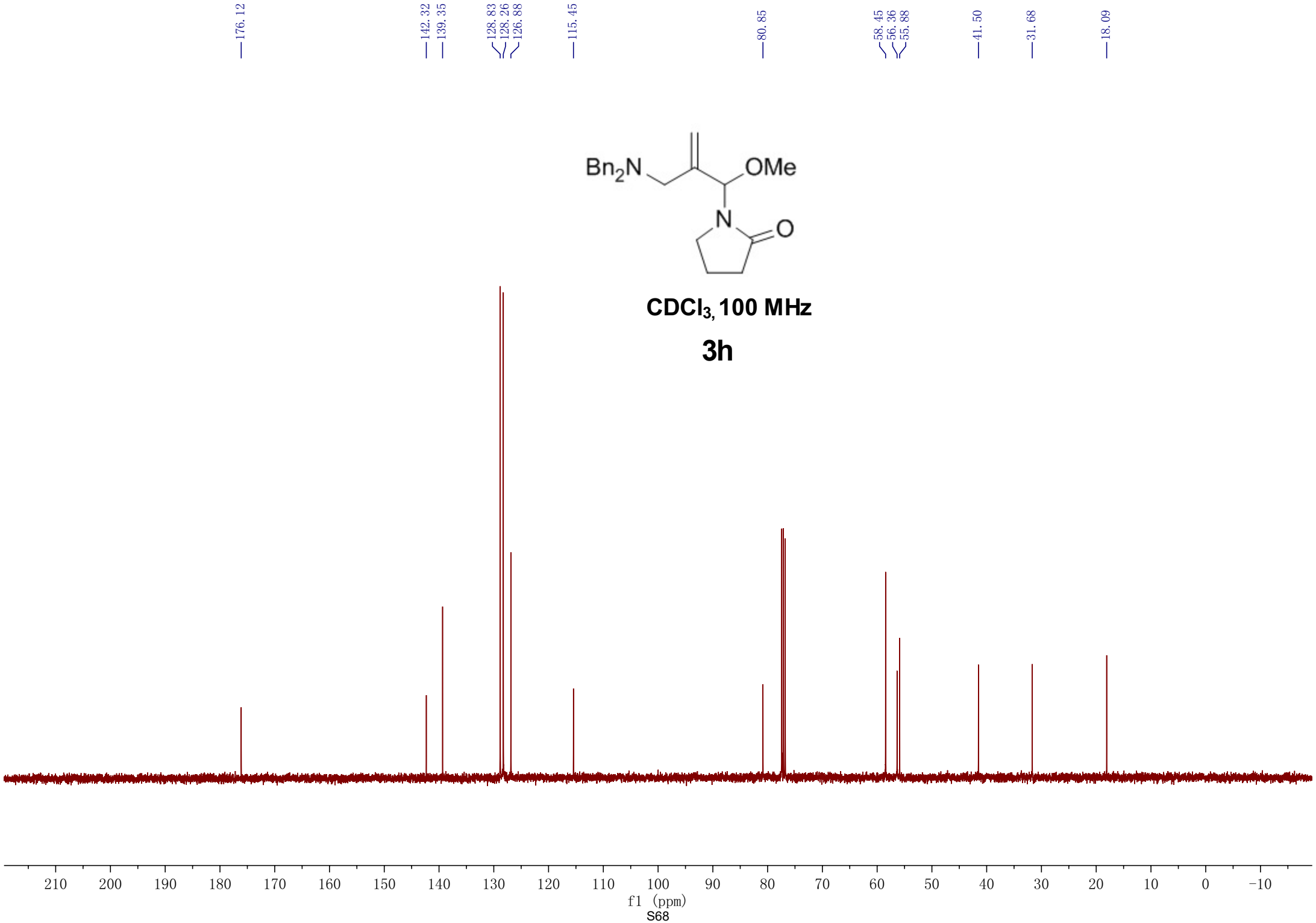
1.05
1.02
f1 (ppm)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31.68
18.09
Bn2N
OMe
N
O
CDCl3, 100 MHz
3h
210
200
190
180
170
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30
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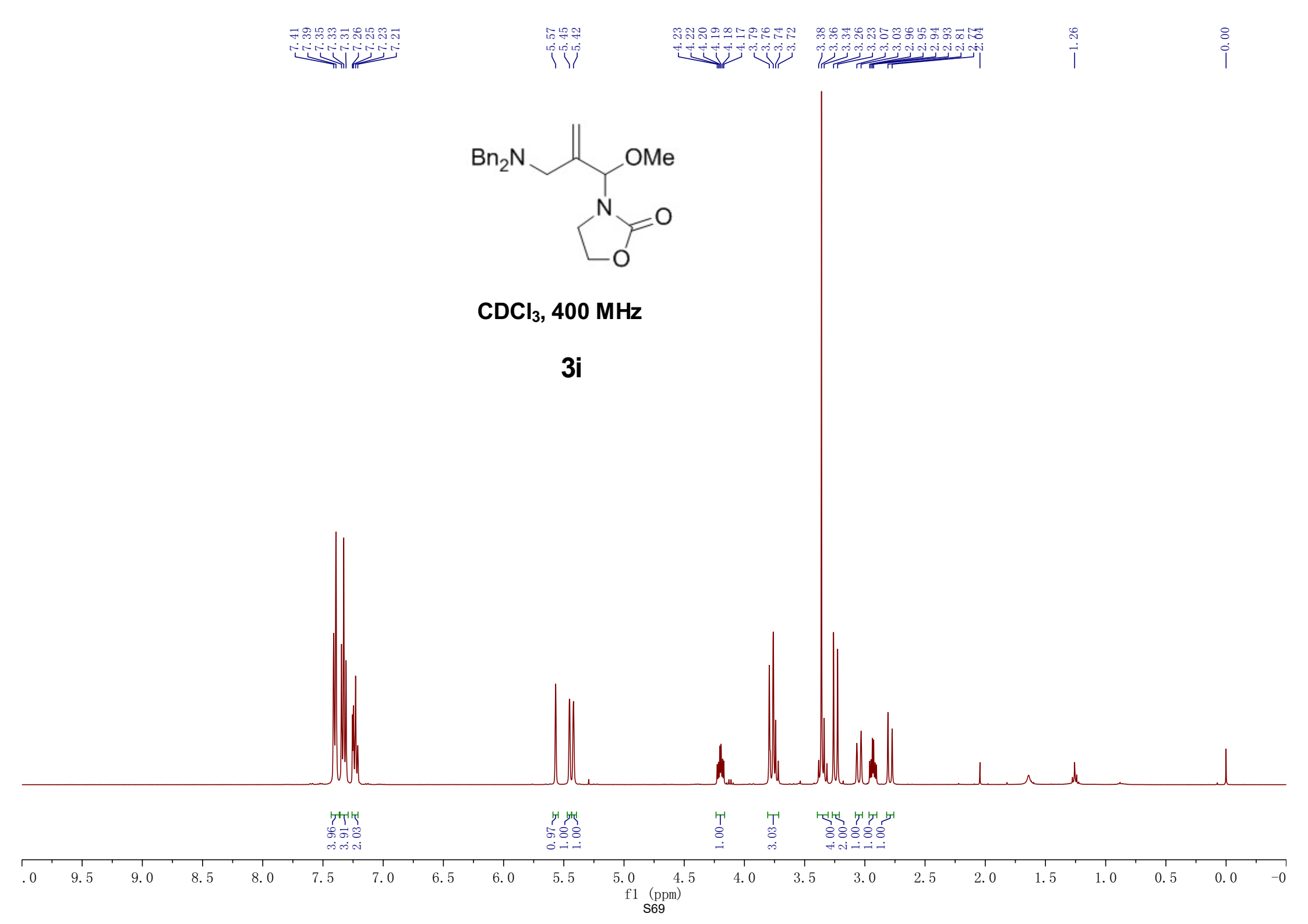
-10
f1 (ppm)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4.22
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OMe
N
O
O
CDCl3, 400 MHz
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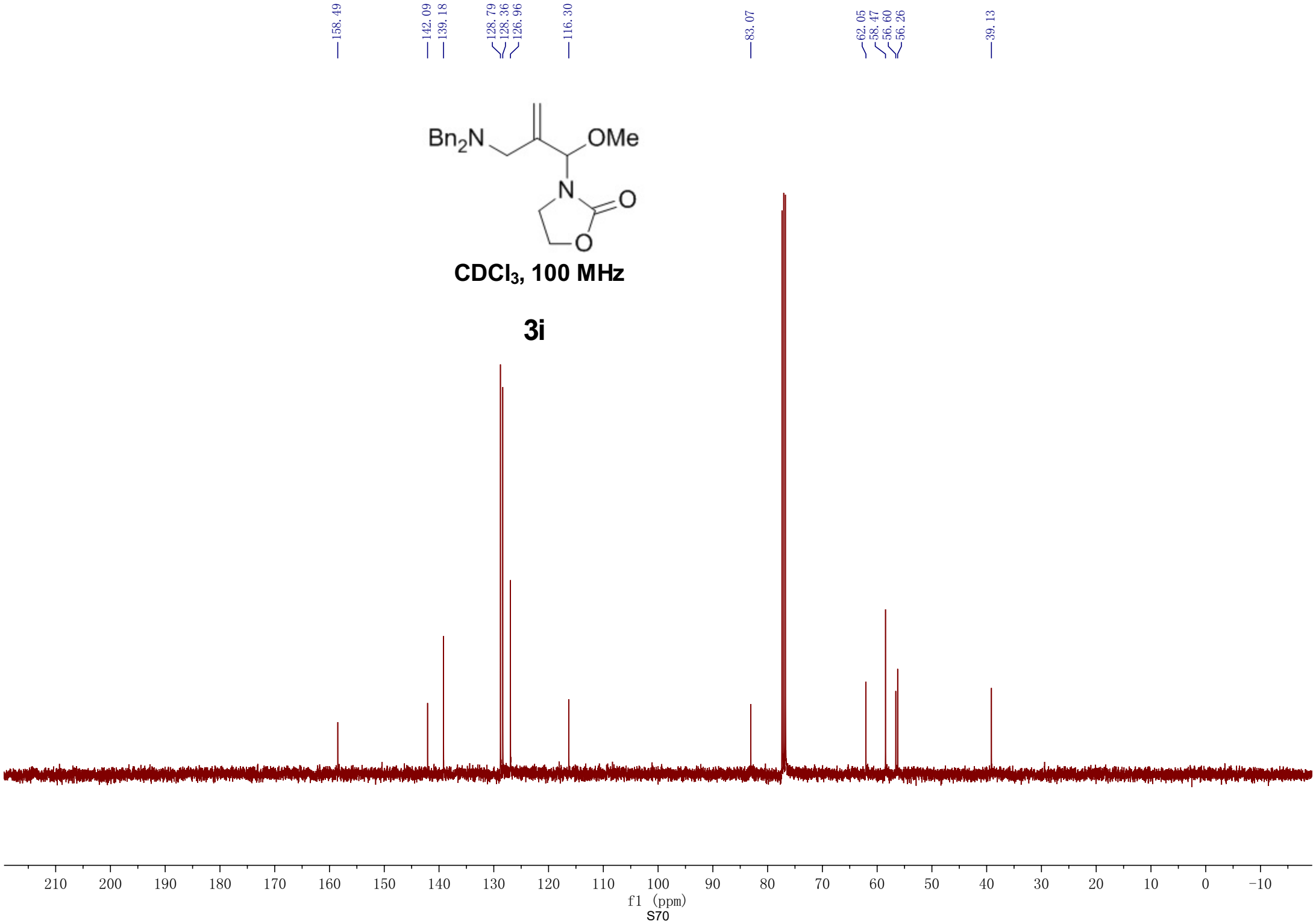
f1 (ppm)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56.26
39.13
Bn2N
OMe
N
O
O
CDCl3, 100 MHz
3i
210
200
190
180
170
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30
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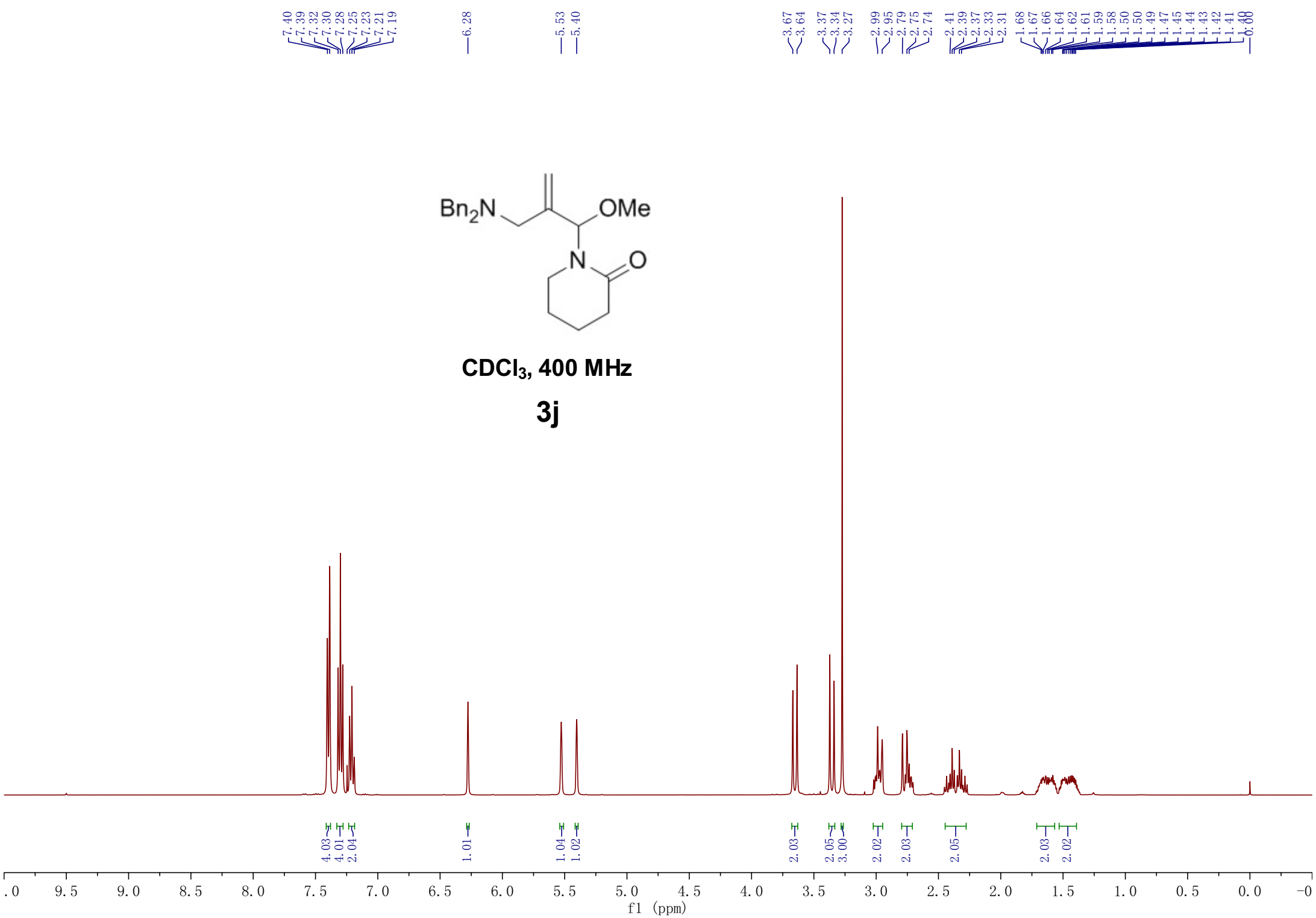
-10
f1 (ppm)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5.40
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2.95
2.79
2.75
2.74
2.41
2.39
2.37
2.33
2.31
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1.43
1.42
1.41
Bn2N
OMe
N
O
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4.01
2.04
1.01
1.04
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2.05
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2.02
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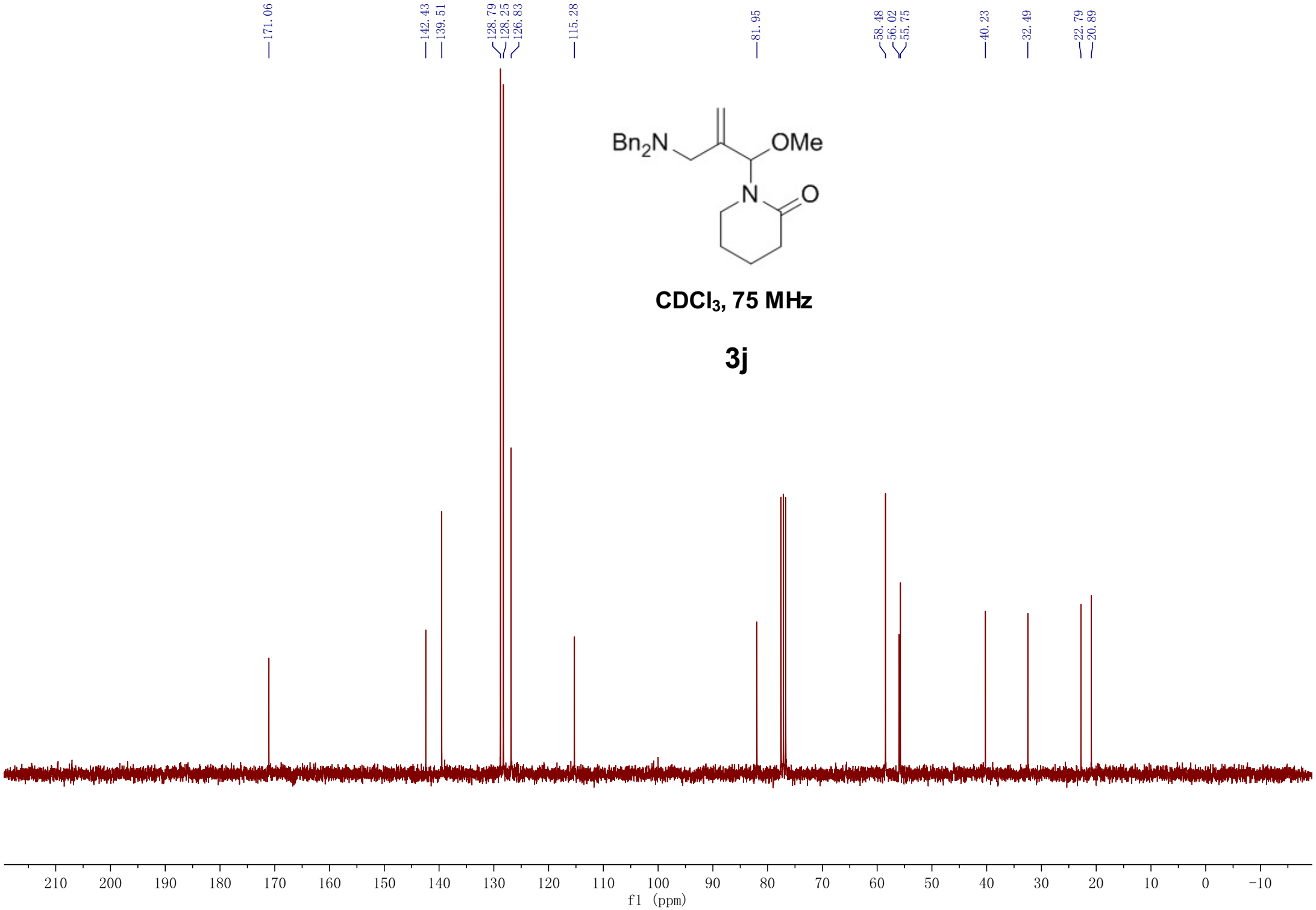
2.05
2.03
2.02
f1 (ppm)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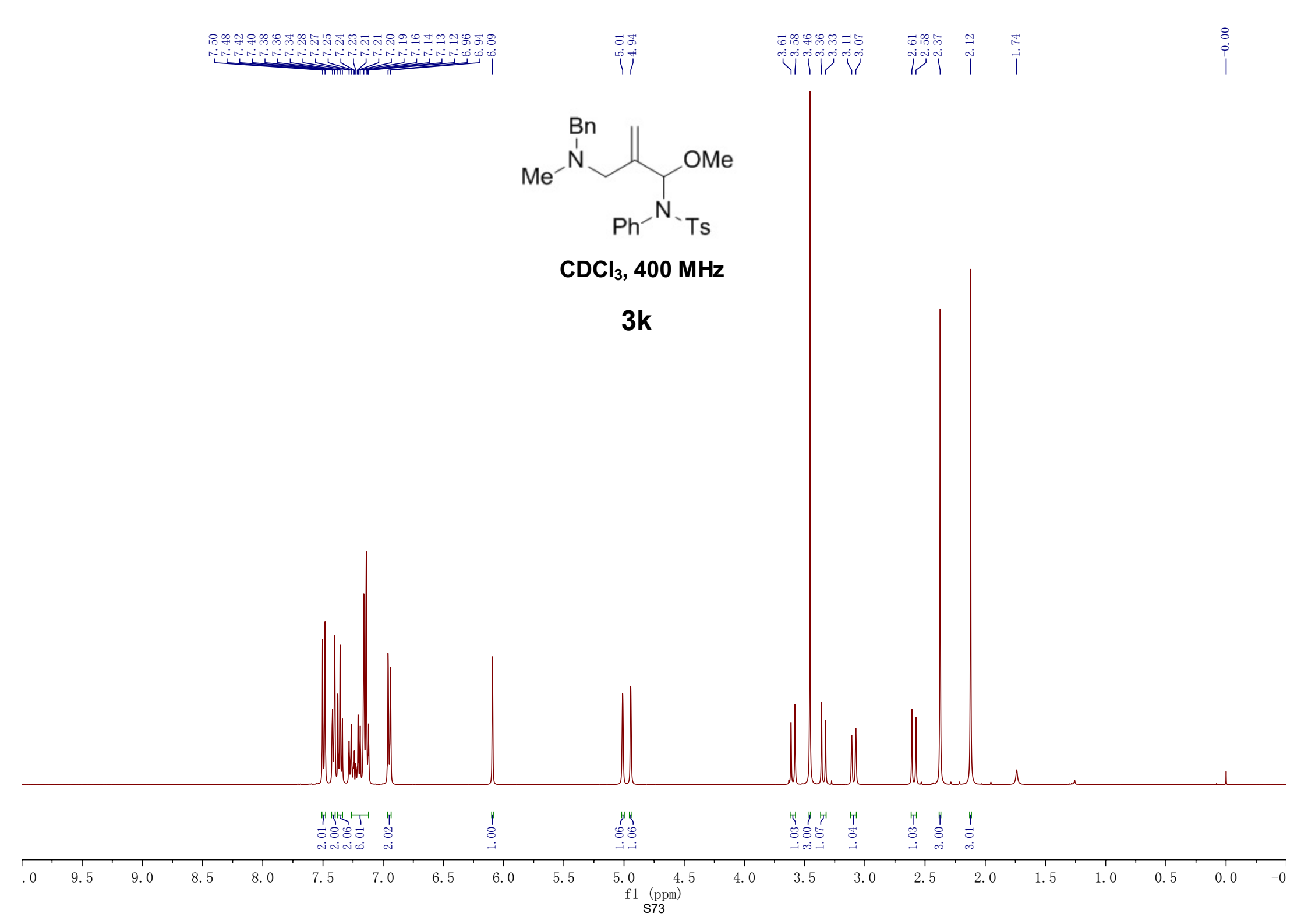
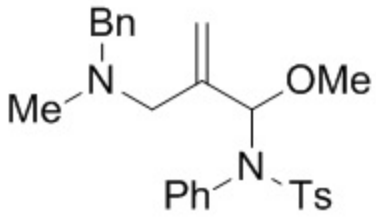
81.95
58.48
56.02
55.75
40.23
32.49
22.79
20.89
Bn2N
OMe
N
O
CDCl3, 75 MHz
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

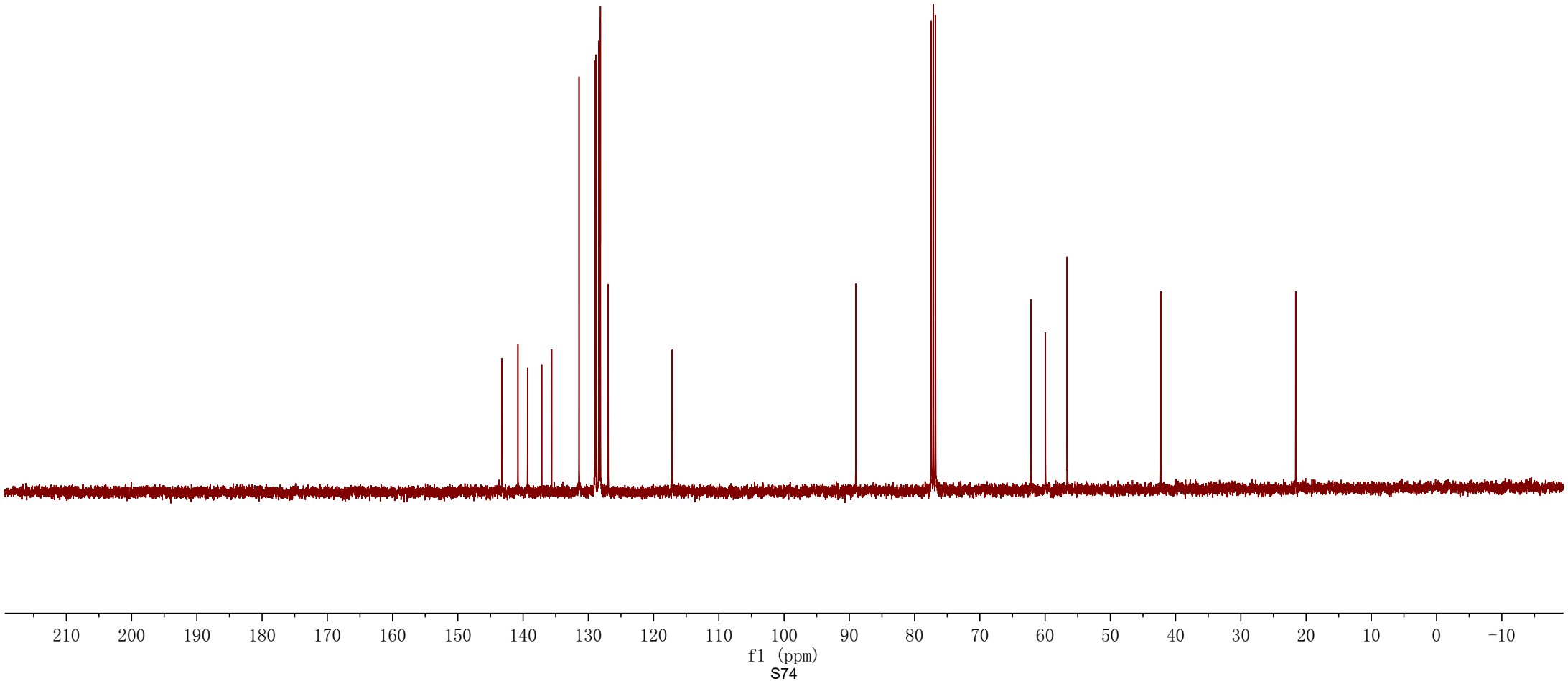

7.50
7.48
7.42
7.40
7.38
7.36
7.34
7.28
7.27
7.25
7.24
7.23
7.21
7.21
7.20
7.19
7.16
7.14
7.13
7.12
6.96
6.94
6.09
5.01
4.94
3.61
3.58
3.46
3.36
3.33
3.11
3.07
2.61
2.58
2.37
2.12
1.74
0.00
Bn
N
Me
OMe
N
Ph
Ts
CDCl3, 400 MHz
3k
2.01
2.00
2.06
6.01
2.02
1.00
1.06
1.06
1.03
3.00
1.07
1.04
1.03
3.00
3.01
f1 (ppm)

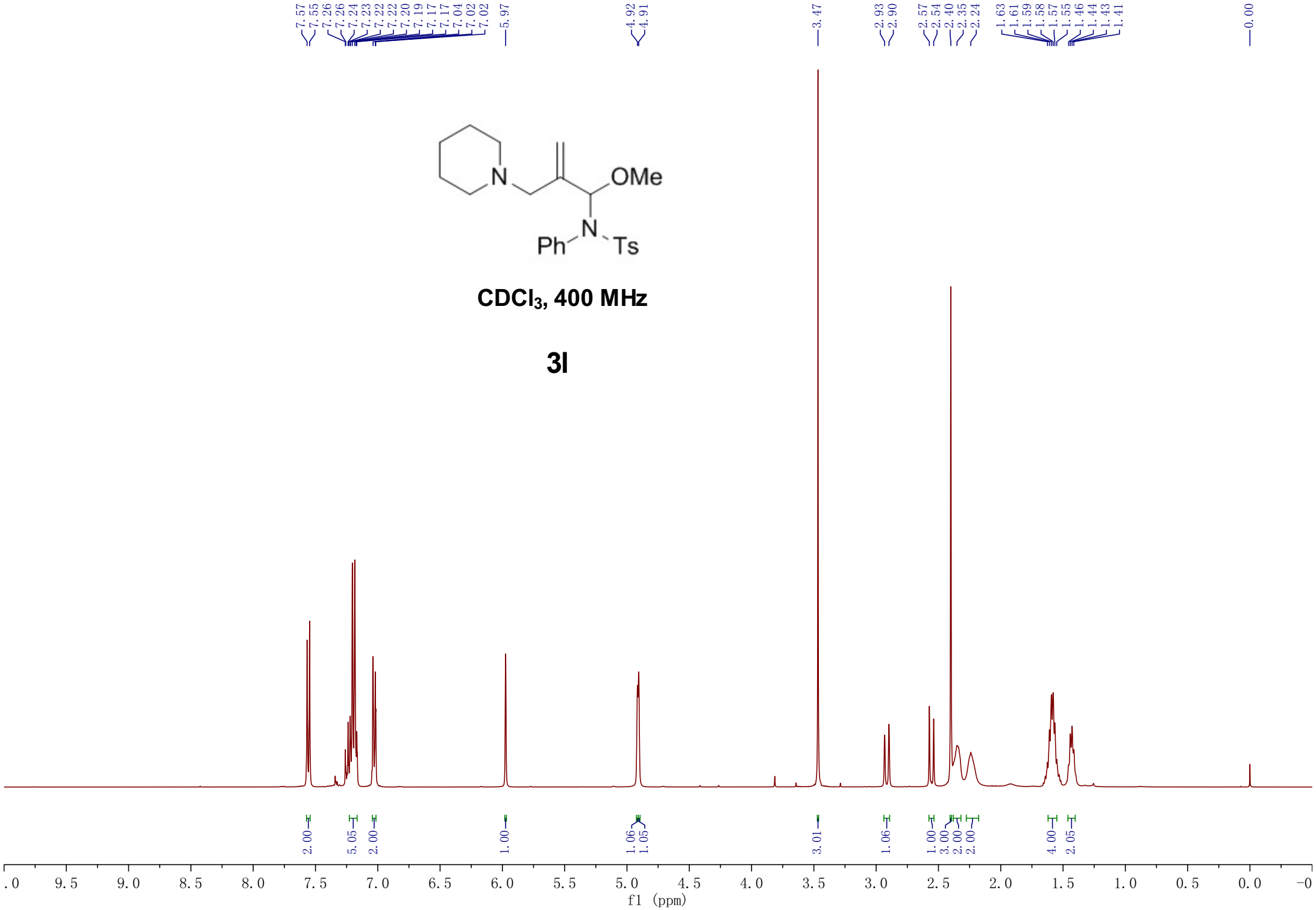
143.24
140.79
139.31
137.14
135.62
131.43
128.98
128.85
128.40
128.18
128.16
128.14
126.96
117.15
89.01
62.17
59.95
56.63
42.26
21.60

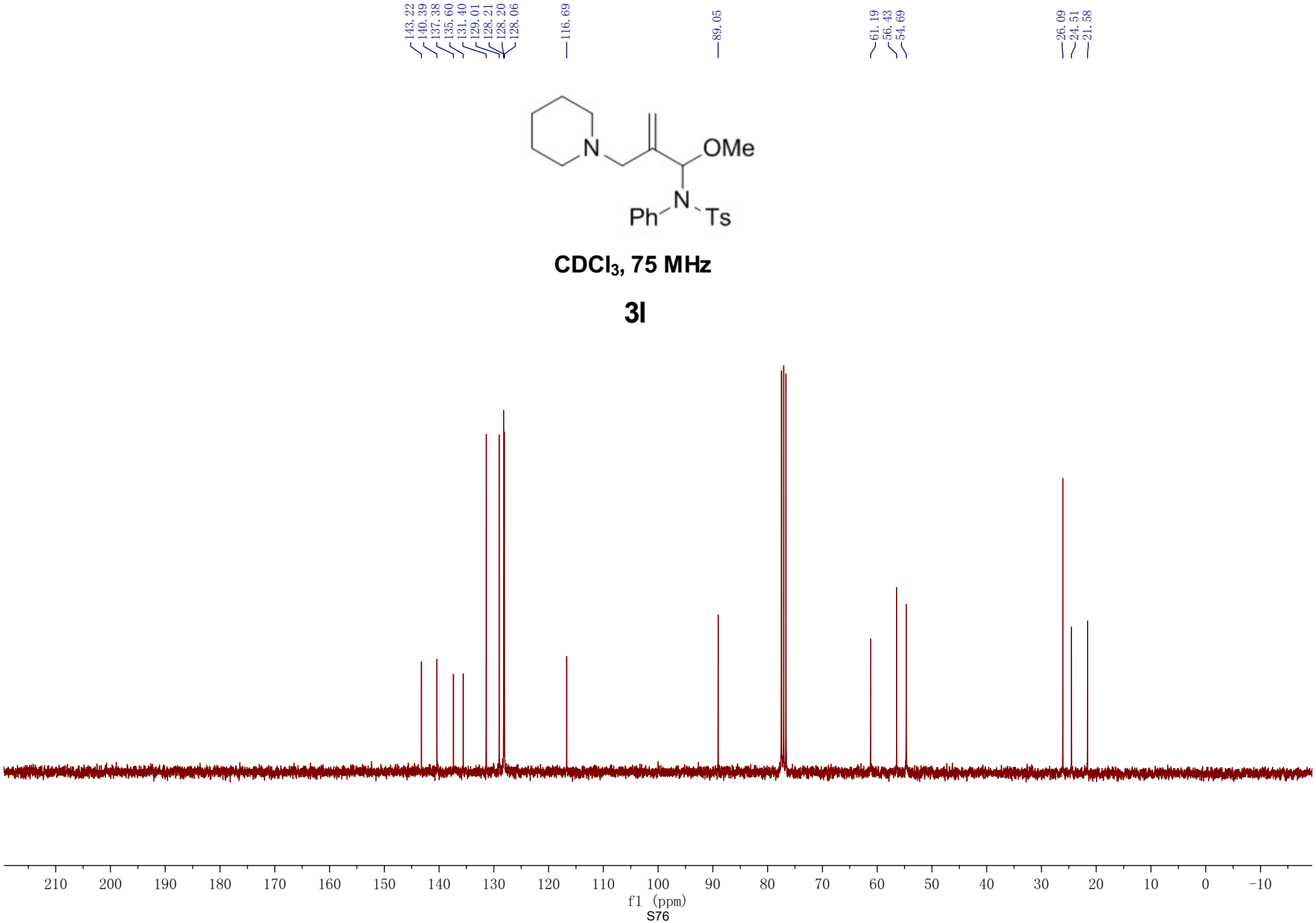


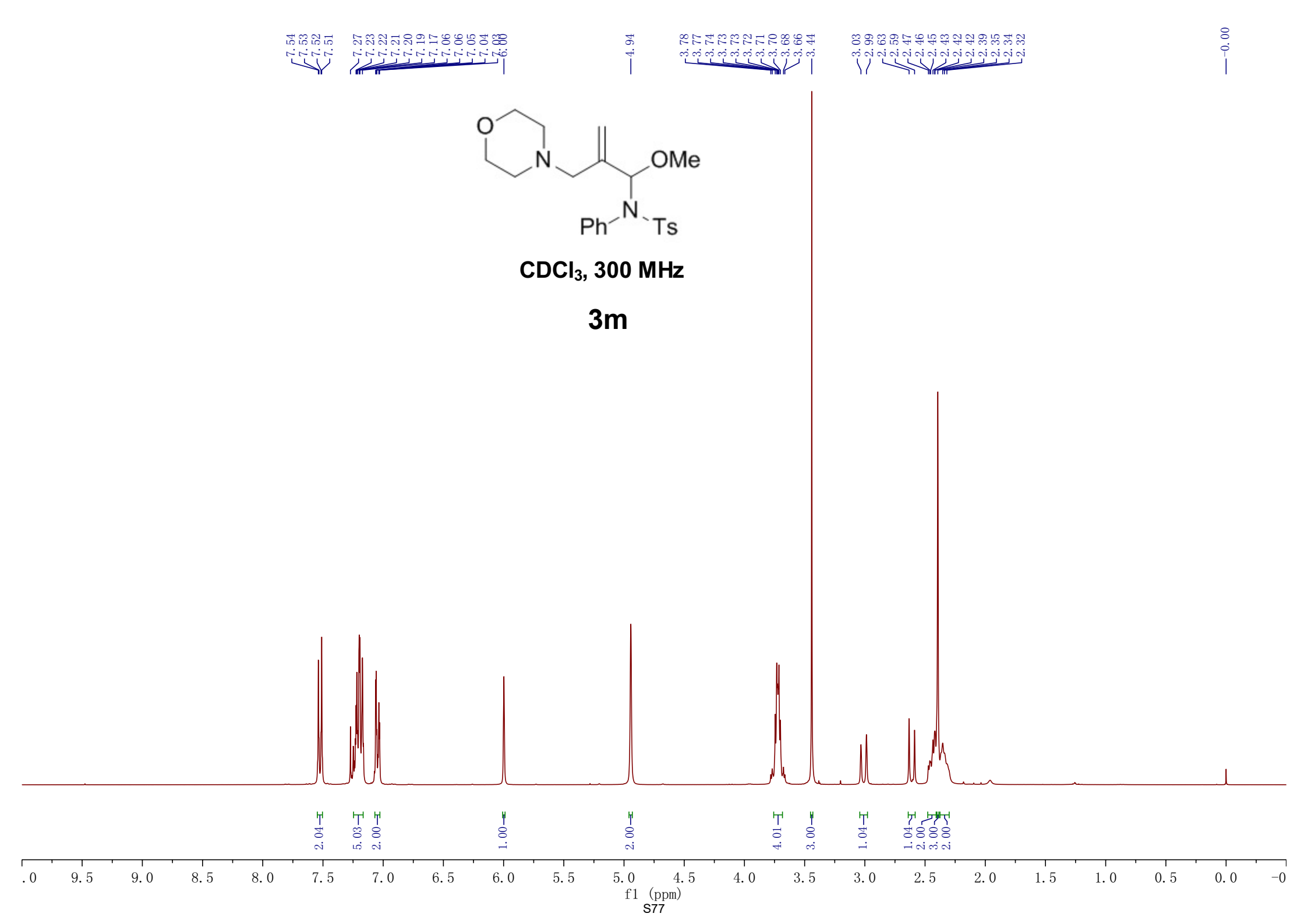
$CDCl_3$, 100 MHz

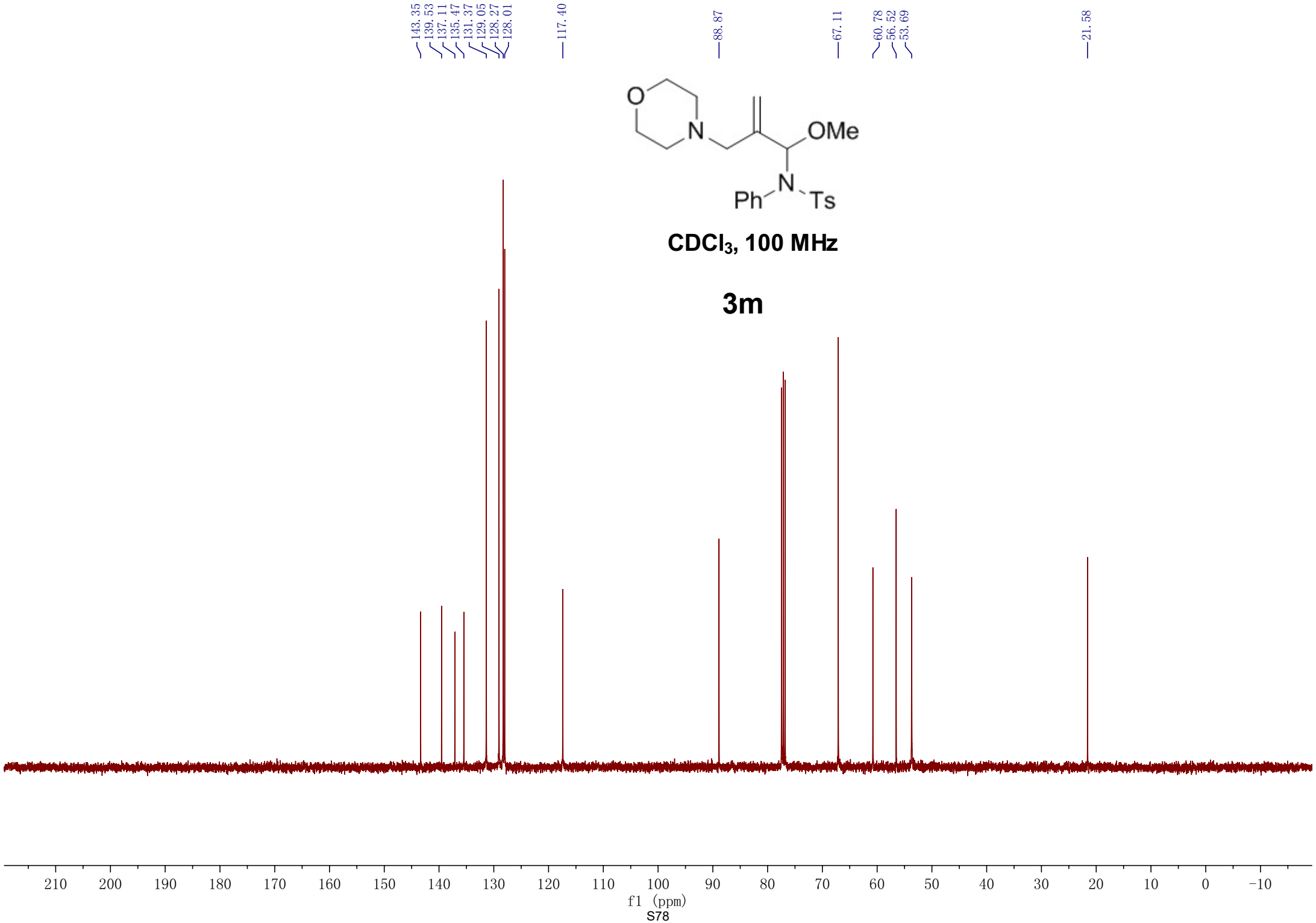
3k

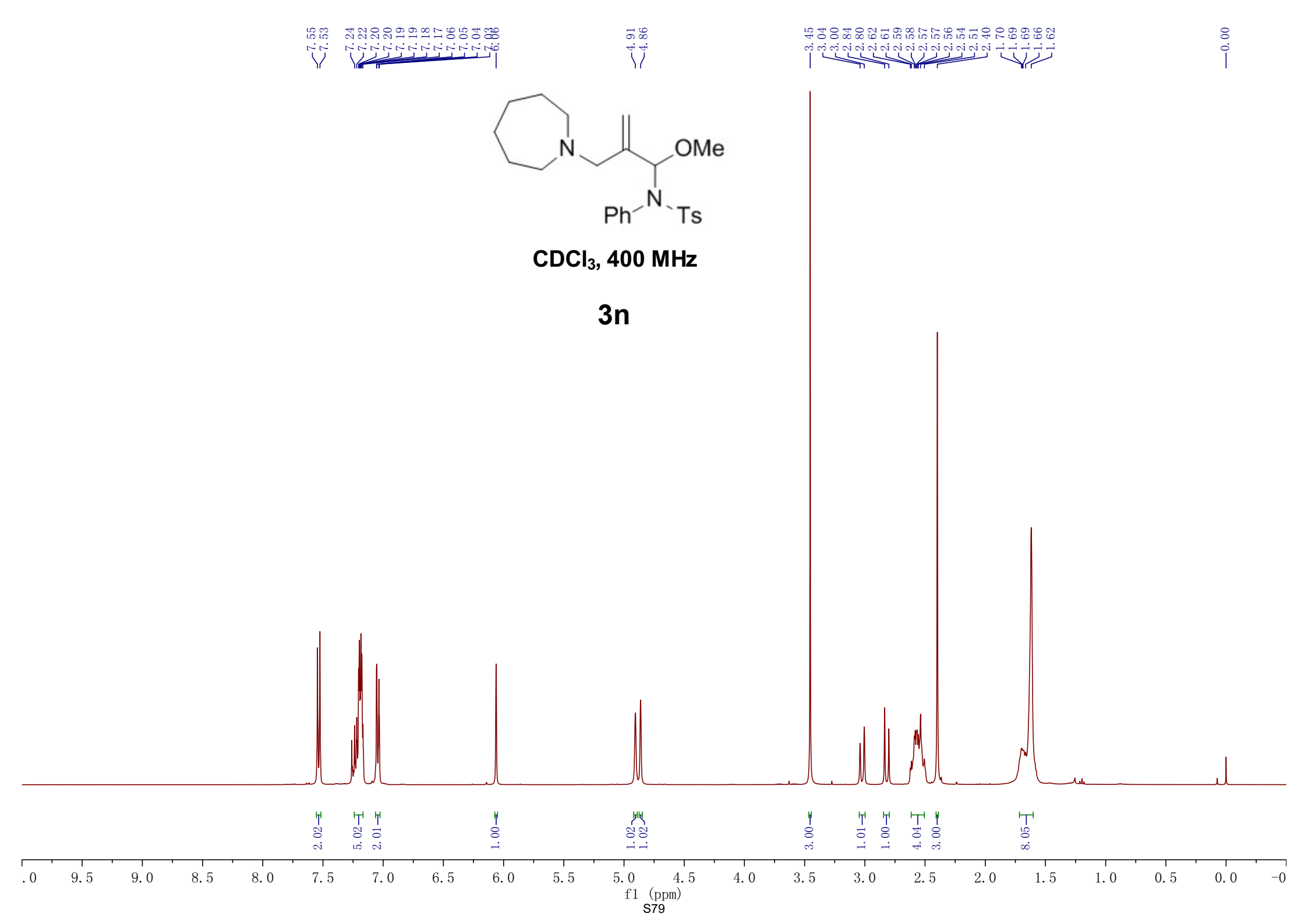


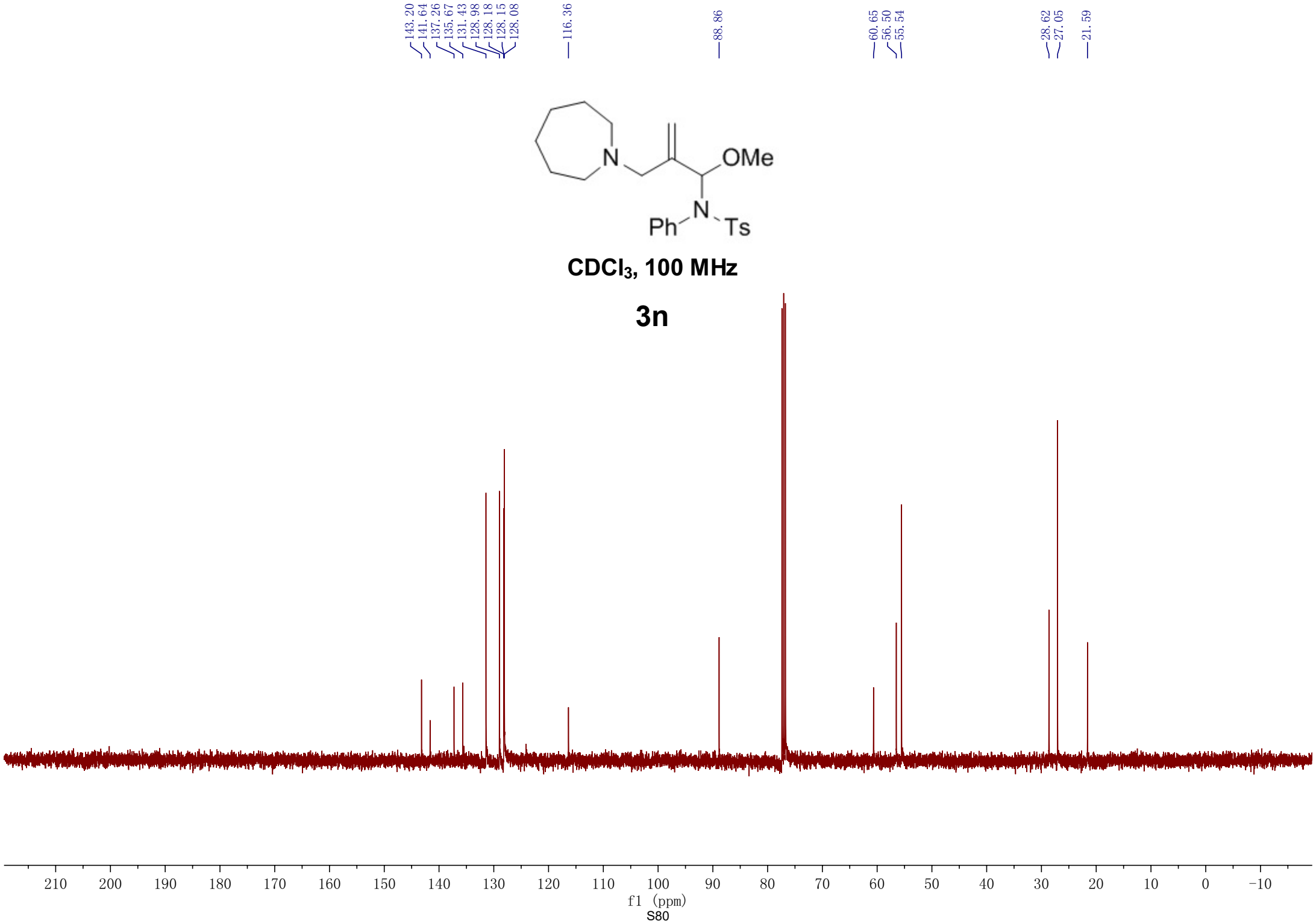

7.57
7.55
7.26
7.26
7.24
7.23
7.22
7.22
7.20
7.19
7.17
7.17
7.04
7.02
7.02
5.97
4.92
4.91
3.47
2.93
2.90
2.57
2.54
2.40
2.35
2.24
1.63
1.61
1.59
1.58
1.57
1.55
1.46
1.44
1.43
1.41
0.00
N
OMe
N
Ph
Ts
CDCl3, 400 MHz
3l
2.00
5.05
2.00
1.00
1.06
1.05
3.01
1.06
1.00
3.00
2.00
2.00
4.00
2.05
f1 (ppm)

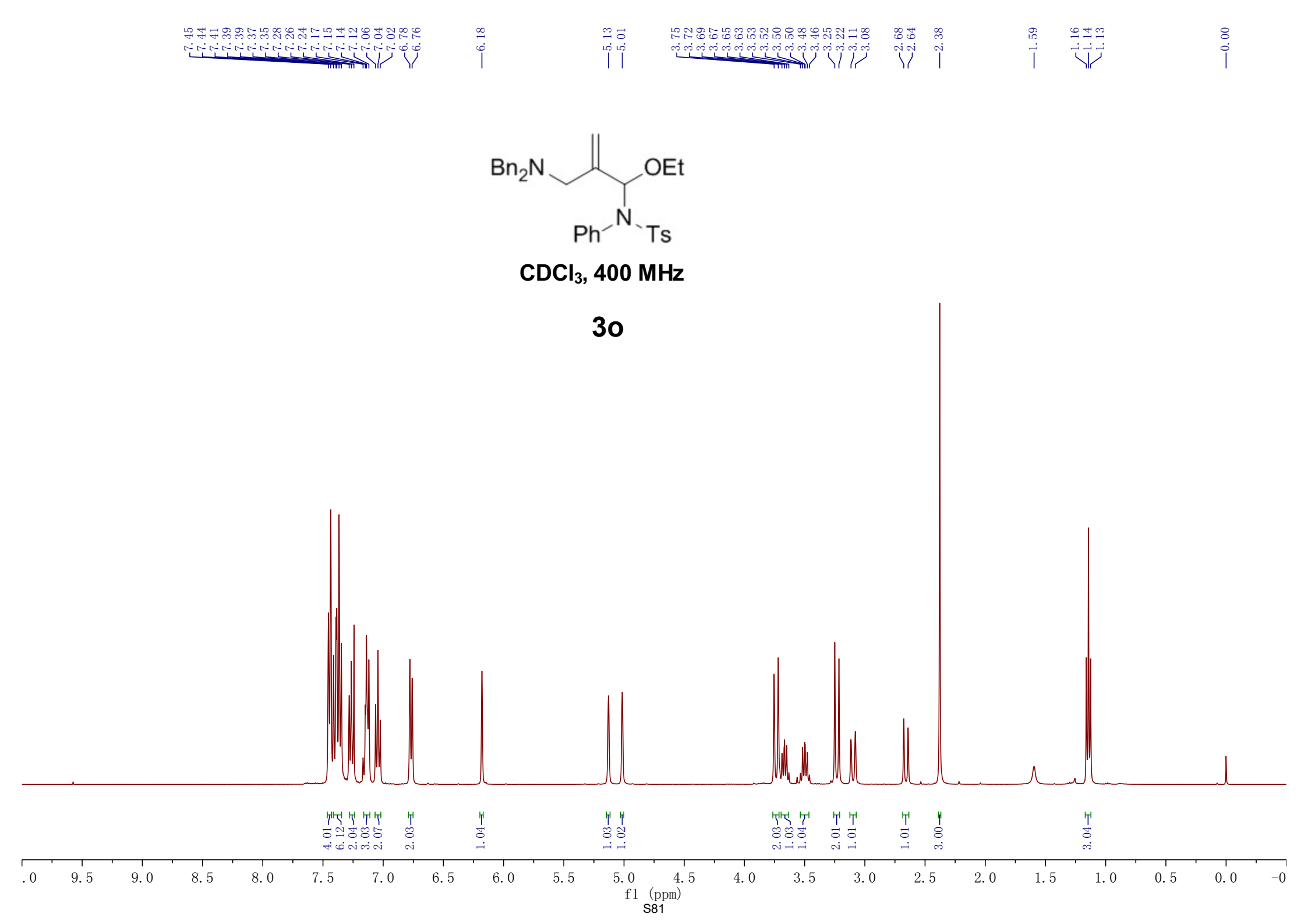

143.22
140.39
137.38
135.60
131.40
129.01
128.21
128.20
128.06
116.69
89.05
61.19
56.43
54.69
26.09
24.51
21.58
N
OMe
N
Ph
Ts
CDCl3, 75 MHz
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

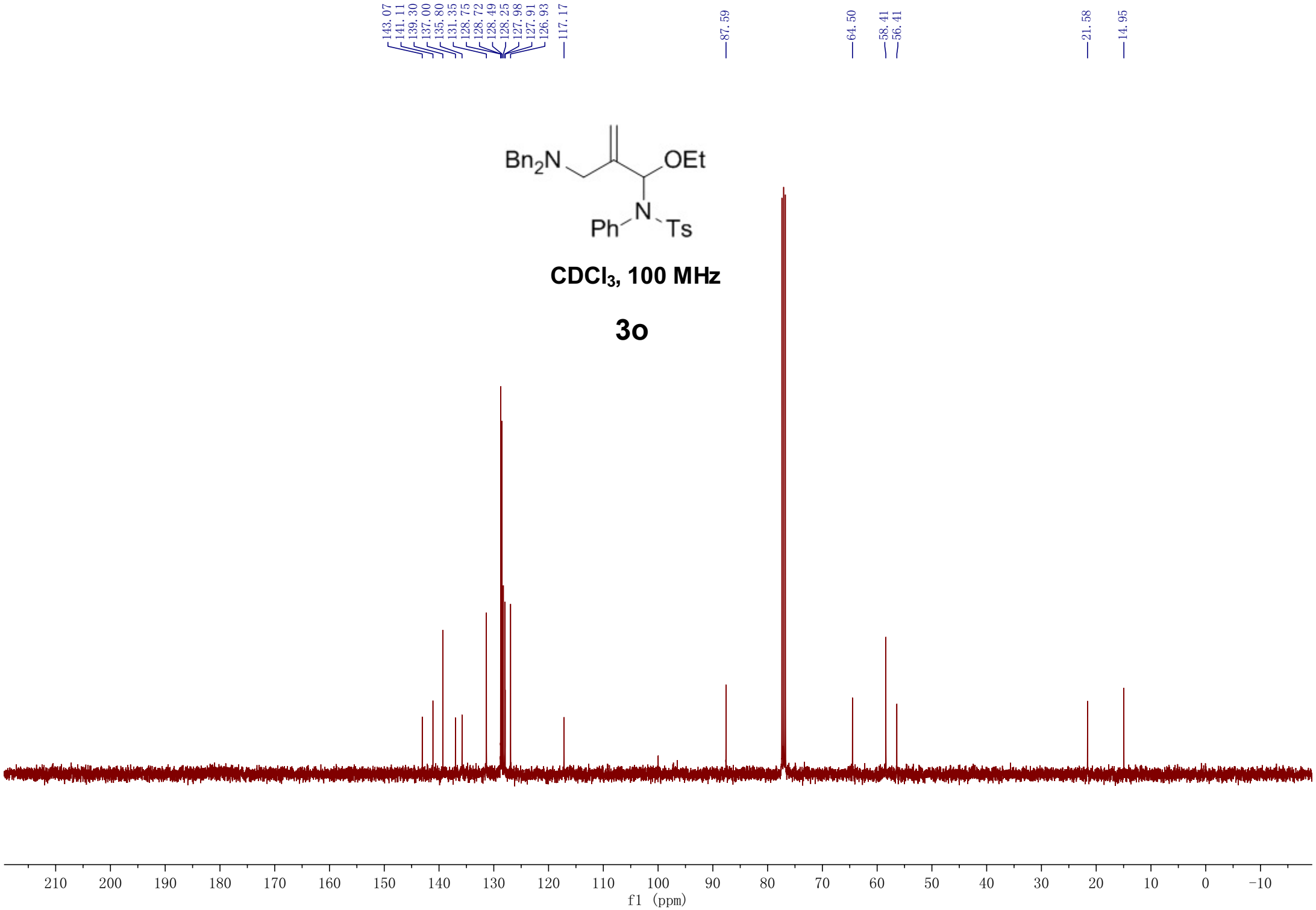

7.54
7.53
7.52
7.51
7.27
7.23
7.22
7.21
7.20
7.19
7.17
7.06
7.06
7.05
7.04
7.03
7.00
4.94
3.78
3.77
3.74
3.73
3.73
3.72
3.71
3.70
3.68
3.66
3.44
3.03
2.99
2.63
2.59
2.47
2.46
2.45
2.43
2.42
2.42
2.39
2.35
2.34
2.32
0.00
O
N
OMe
N
Ph
Ts
CDCl3, 300 MHz
3m
2.04
5.03
2.00
1.00
2.00
4.01
3.00
1.04
1.04
2.00
3.00
2.00
f1 (ppm)

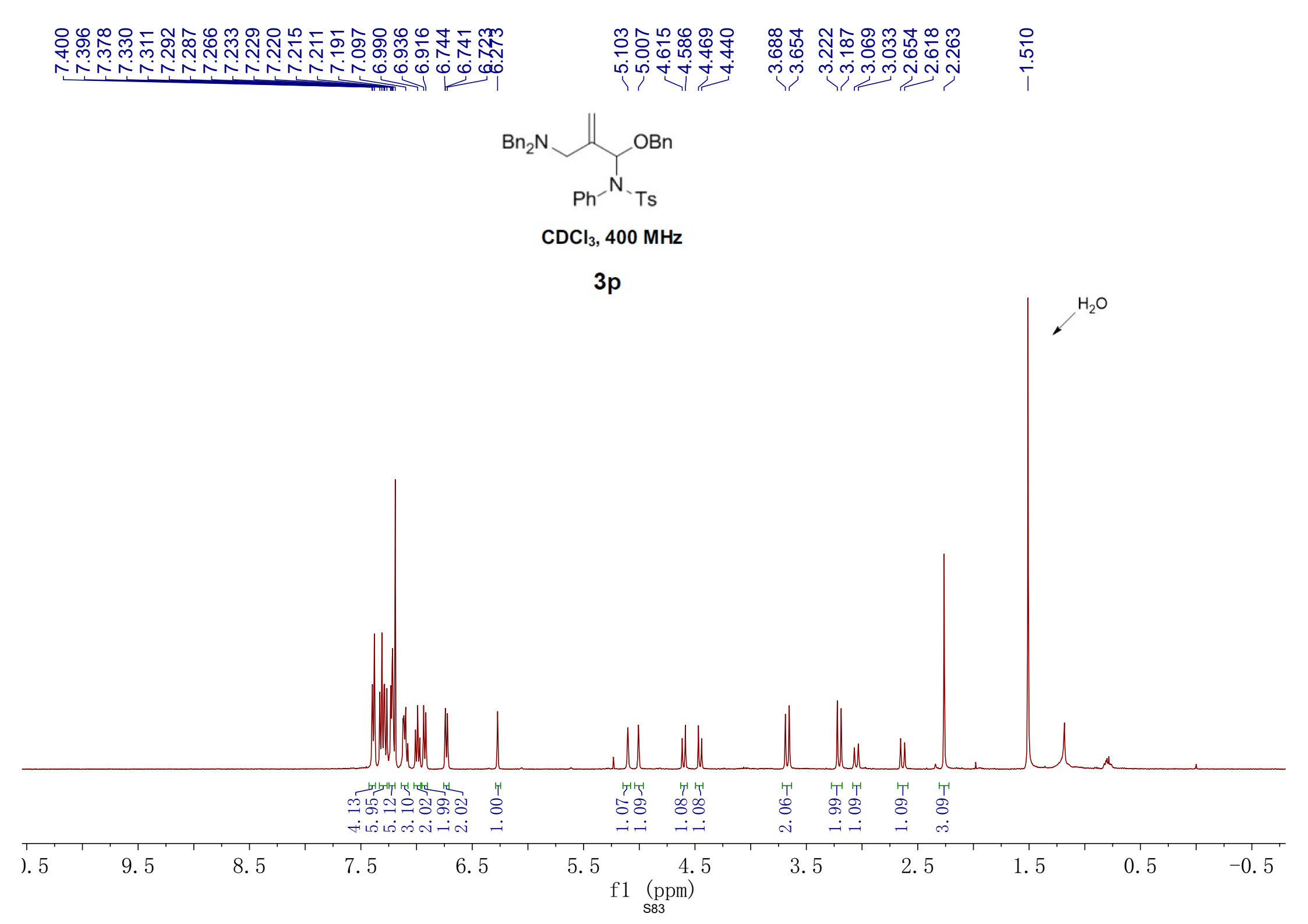

143.35
139.53
137.11
135.47
131.37
129.05
128.27
128.01
117.40
88.87
67.11
60.78
56.52
53.69
21.58
O
N
OMe
N
Ph
Ts
CDCl3, 100 MHz
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.55
7.53
7.24
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.06
7.05
7.04
7.03
6.08
4.91
4.86
3.45
3.04
3.00
2.84
2.80
2.62
2.61
2.59
2.58
2.57
2.57
2.56
2.54
2.51
2.40
1.70
1.69
1.69
1.66
1.62
0.00
N
OMe
N
Ph
Ts
CDCl3, 400 MHz
3n
2.02
5.02
2.01
1.00
1.02
1.02
3.00
1.01
1.00
4.04
3.00
8.05
f1 (ppm)


143.20
141.64
137.26
135.67
131.43
128.98
128.18
128.15
128.08
116.36
88.86
60.65
56.50
55.54
28.62
27.05
21.59
N
OMe
N
Ph
Ts
CDCl3, 100 MHz
3n
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)


7.45
7.44
7.41
7.39
7.39
7.37
7.35
7.28
7.26
7.24
7.17
7.15
7.14
7.12
7.06
7.04
7.02
6.78
6.76
6.18
5.13
5.01
3.75
3.72
3.69
3.67
3.65
3.63
3.53
3.52
3.50
3.50
3.48
3.46
3.25
3.22
3.11
3.08
2.68
2.64
2.38
1.59
1.16
1.14
1.13
0.00
Bn2N
OEt
N
Ph
Ts
CDCl3, 400 MHz
3o
4.01
6.12
2.04
3.03
2.07
2.03
1.04
1.03
1.02
2.03
1.03
1.04
2.01
1.01
1.01
3.00
3.04
f1 (ppm)


143.07
141.11
139.30
137.00
135.80
131.35
128.75
128.72
128.49
128.25
127.98
127.91
126.93
117.17
87.59
64.50
58.41
56.41
21.58
14.95
Bn2N
OEt
N
Ph
Ts
CDCl3, 100 MHz
3o
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)


7.400
7.396
7.378
7.330
7.311
7.292
7.287
7.266
7.233
7.229
7.220
7.215
7.211
7.191
7.097
6.990
6.936
6.916
6.744
6.741
6.723
6.273
5.103
5.007
4.615
4.586
4.469
4.440
3.688
3.654
3.222
3.187
3.069
3.033
2.654
2.618
2.263
1.510
Bn2N
OBn
N
Ph
Ts
CDCl3, 400 MHz
3p
H2O
4.13
5.95
5.12
3.10
2.02
1.99
2.02
1.00
1.07
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1.08
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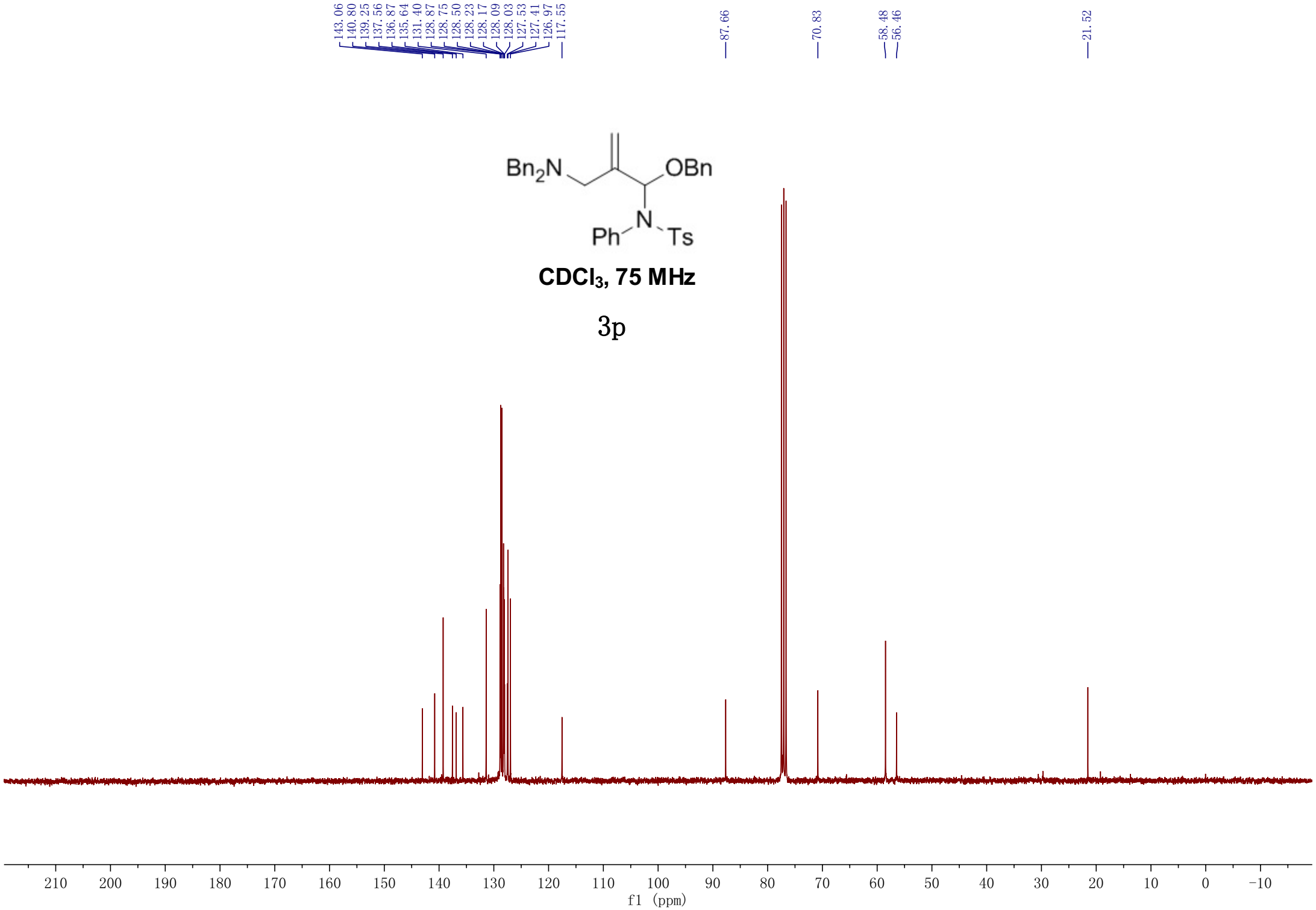
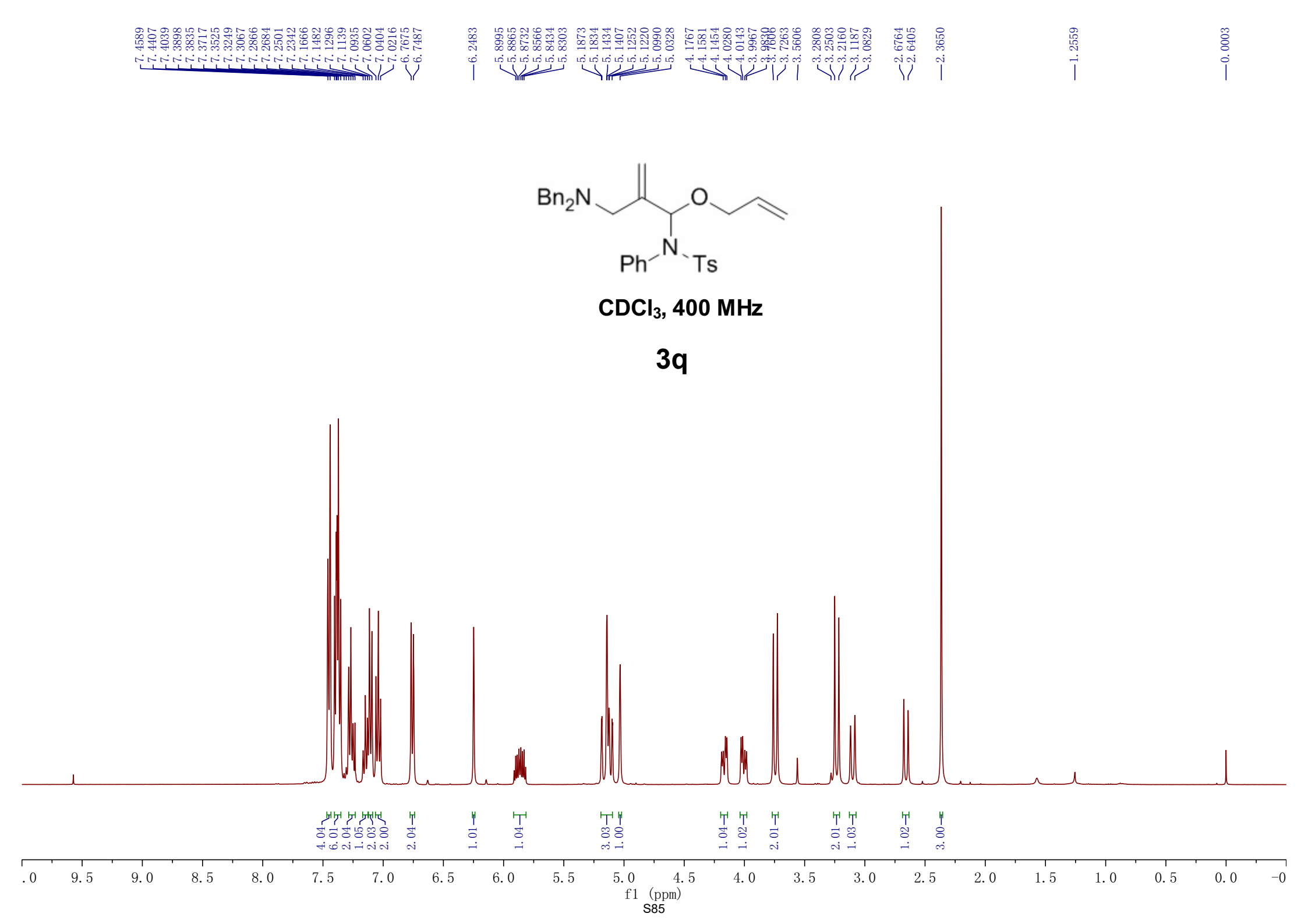
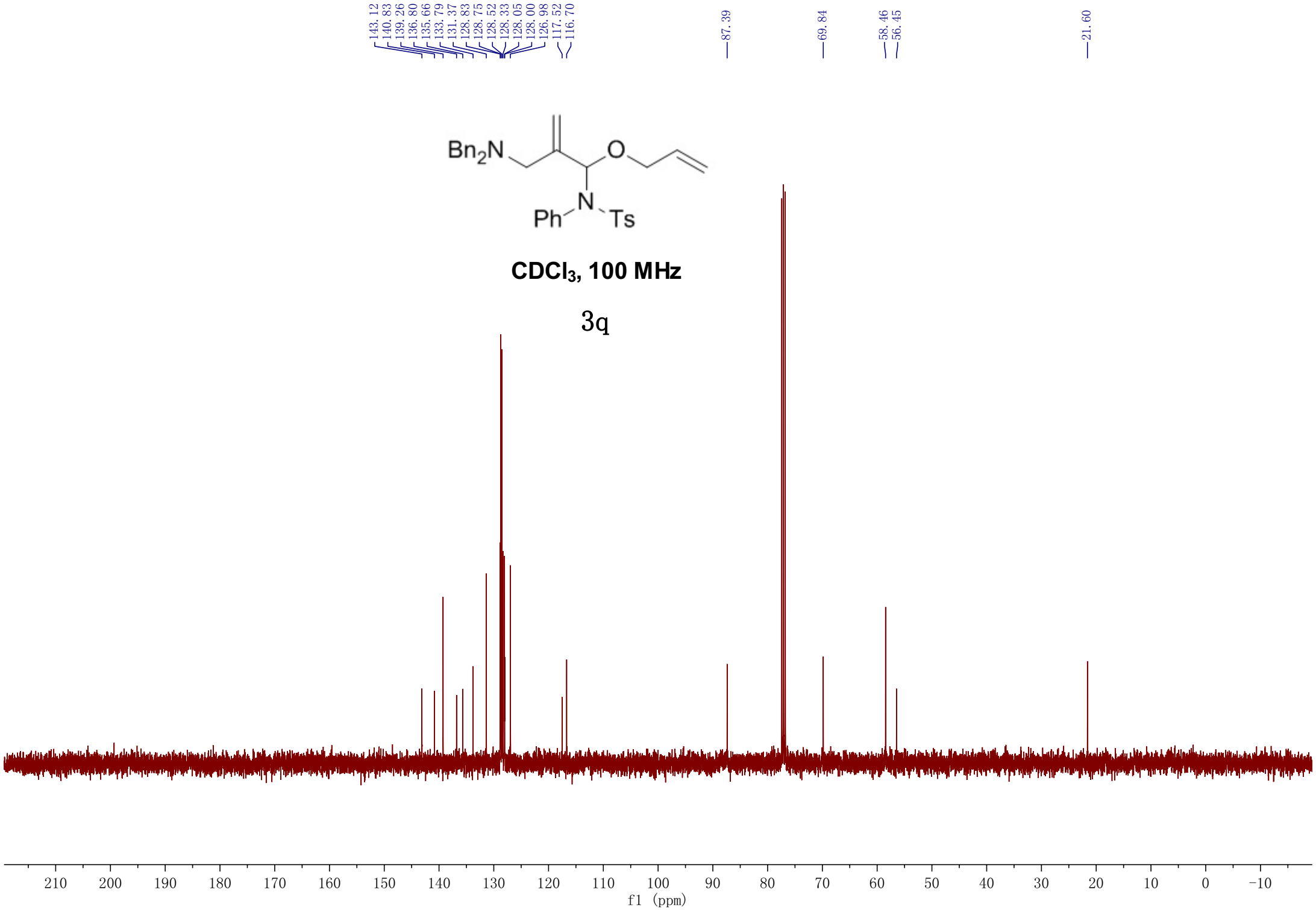
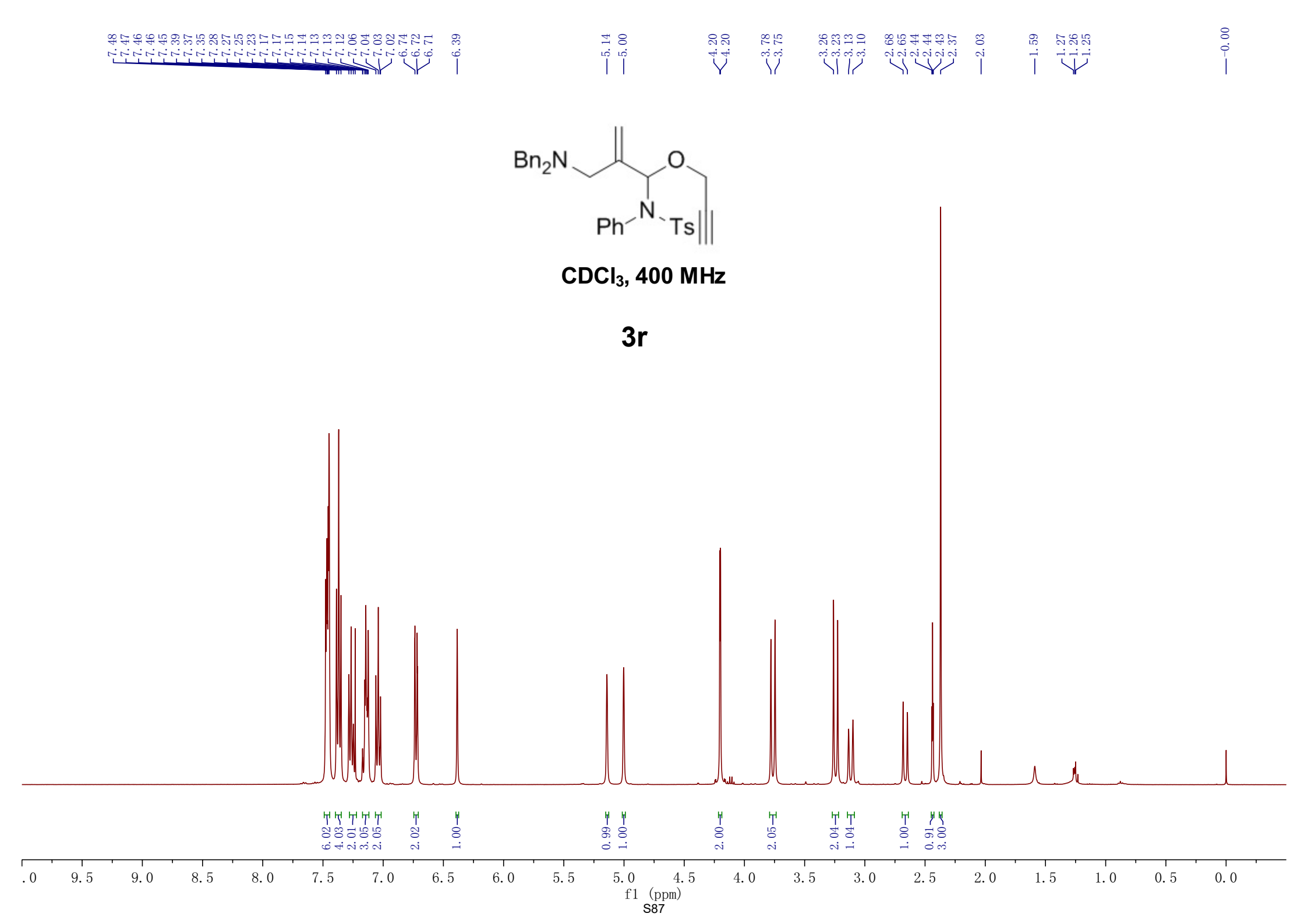
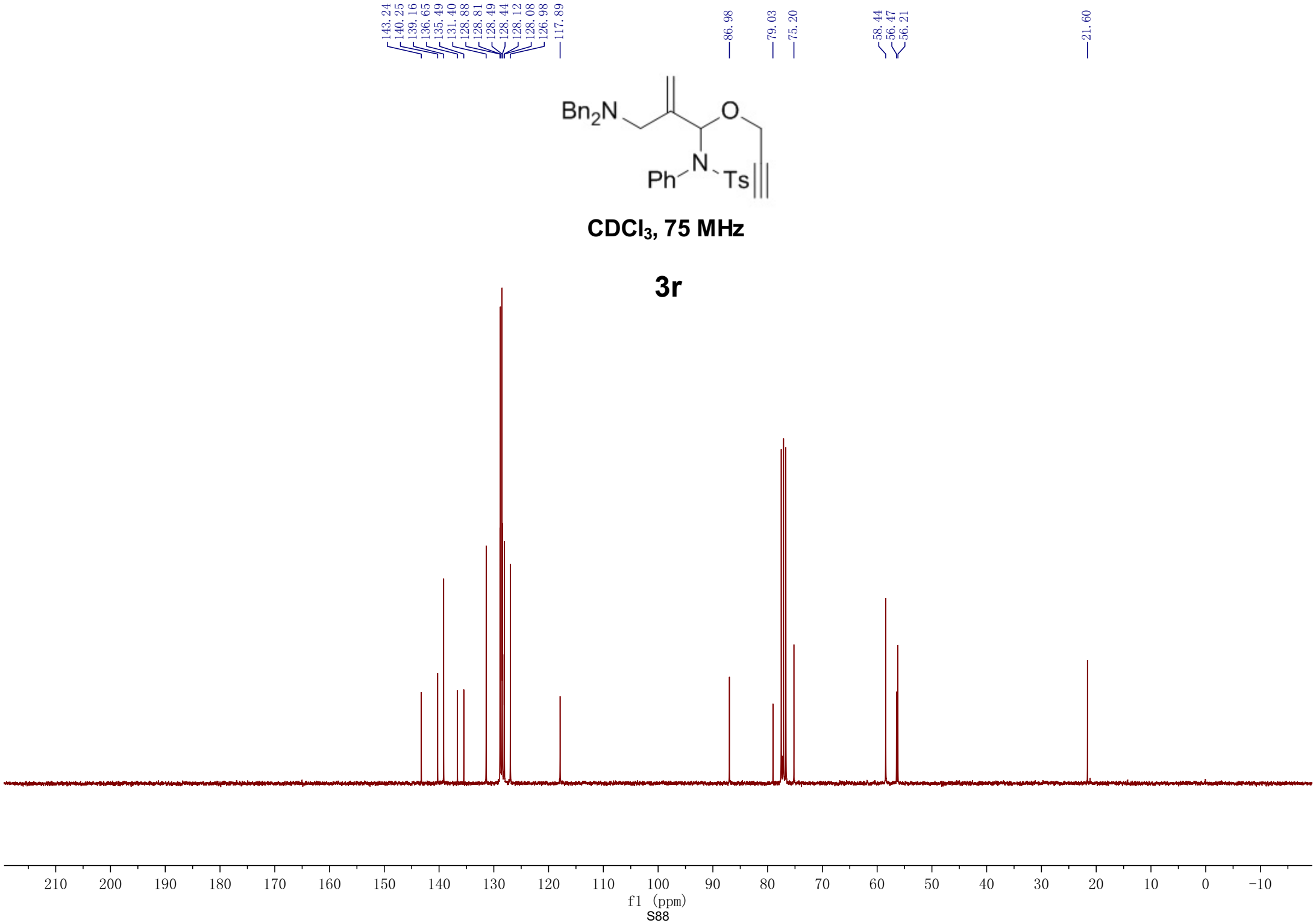
2.06
1.99
1.09
1.09
3.09
f1 (ppm)

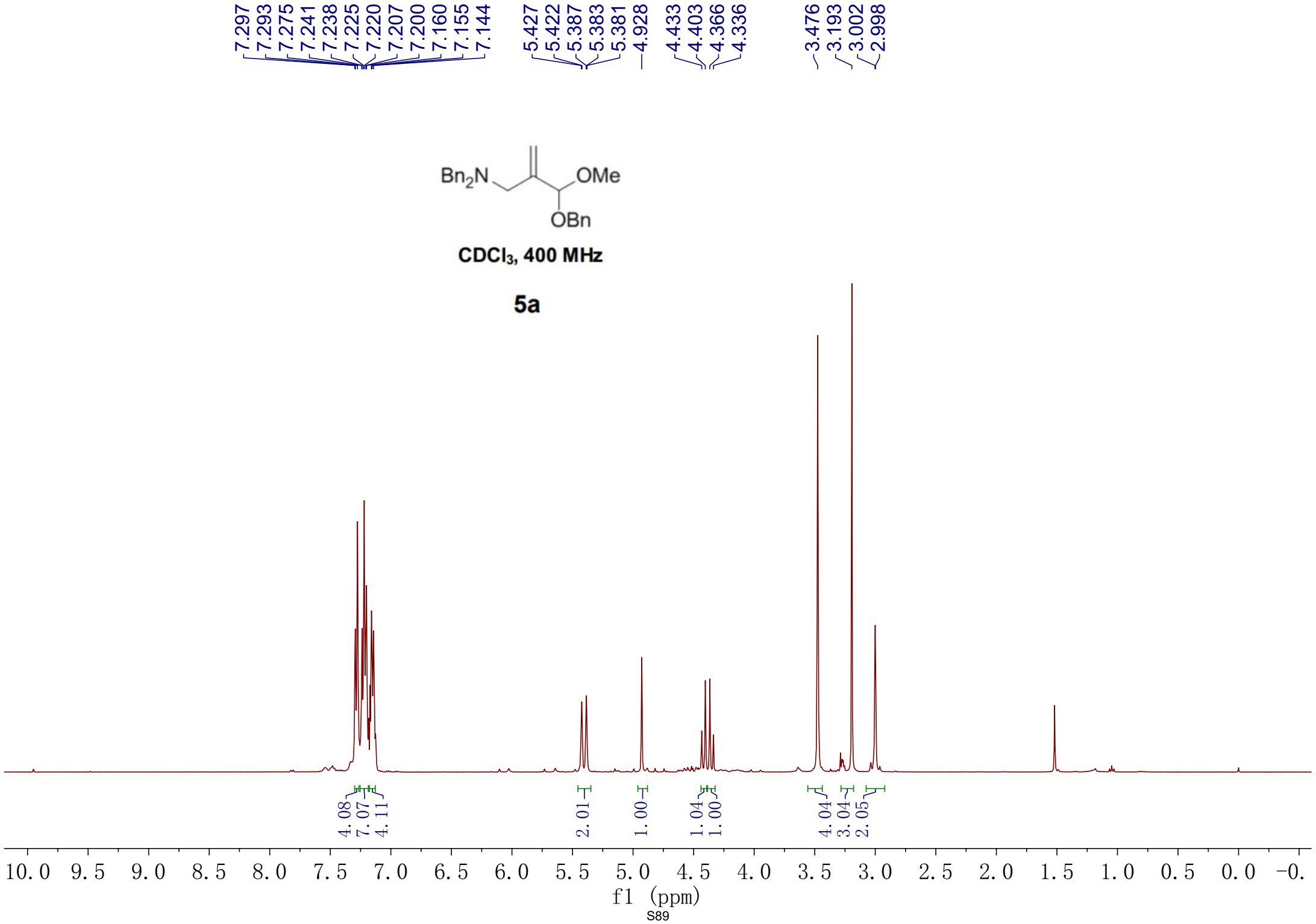

143.06
140.80
139.25
137.56
136.87
135.64
131.40
128.87
128.75
128.50
128.23
128.17
128.09
128.03
127.53
127.41
126.97
117.55
87.66
70.83
58.48
56.46
21.52
Bn2N
OBn
N
Ph
Ts
CDCl3, 75 MHz
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

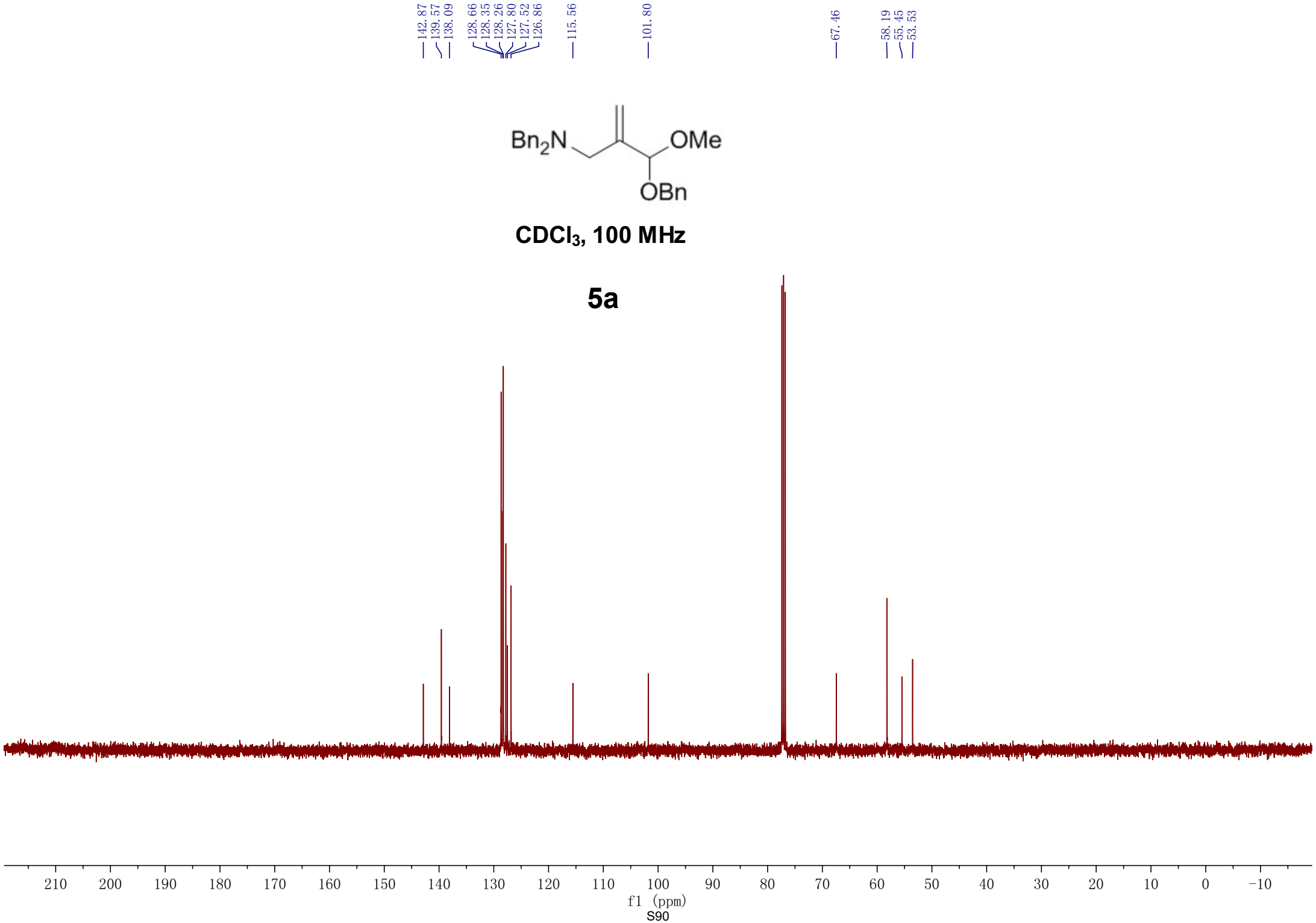

7.4589
7.4407
7.4039
7.3898
7.3835
7.3717
7.3525
7.3249
7.3067
7.2866
7.2684
7.2501
7.2342
7.1666
7.1482
7.1296
7.1139
7.0935
7.0602
7.0404
7.0216
6.7675
6.7487
6.2483
5.8995
5.8865
5.8732
5.8566
5.8434
5.8303
5.1873
5.1834
5.1434
5.1407
5.1252
5.1220
5.0990
5.0328
4.1767
4.1581
4.1454
4.0280
4.0143
3.9967
3.7263
3.5606
3.2808
3.2503
3.2160
3.1187
3.0829
2.6764
2.6405
2.3650
1.2559
0.0003
Bn2N
O
N
Ph
Ts
CDCl3, 400 MHz
3q
4.04
6.01
2.04
1.05
2.03
2.00
2.04
1.01
1.04
3.03
1.00
1.04
1.02
2.01
2.01
1.03
1.02
3.00
f1 (ppm)

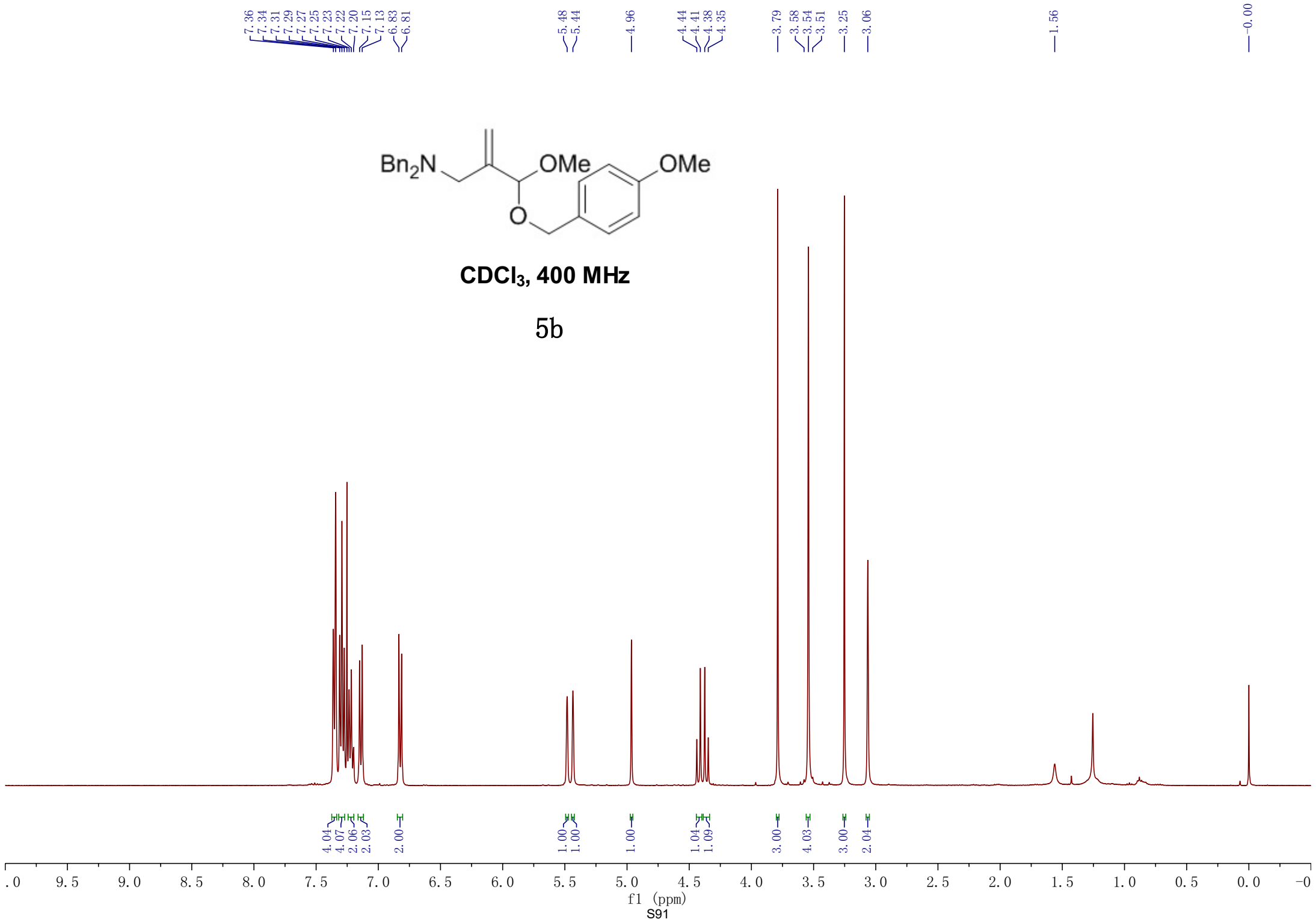

143.12
140.83
139.26
136.80
135.66
133.79
131.37
128.83
128.75
128.52
128.33
128.05
128.00
126.98
117.52
116.70
87.39
69.84
58.46
56.45
21.60
Bn2N
O
N
Ph
Ts
CDCl3, 100 MHz
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

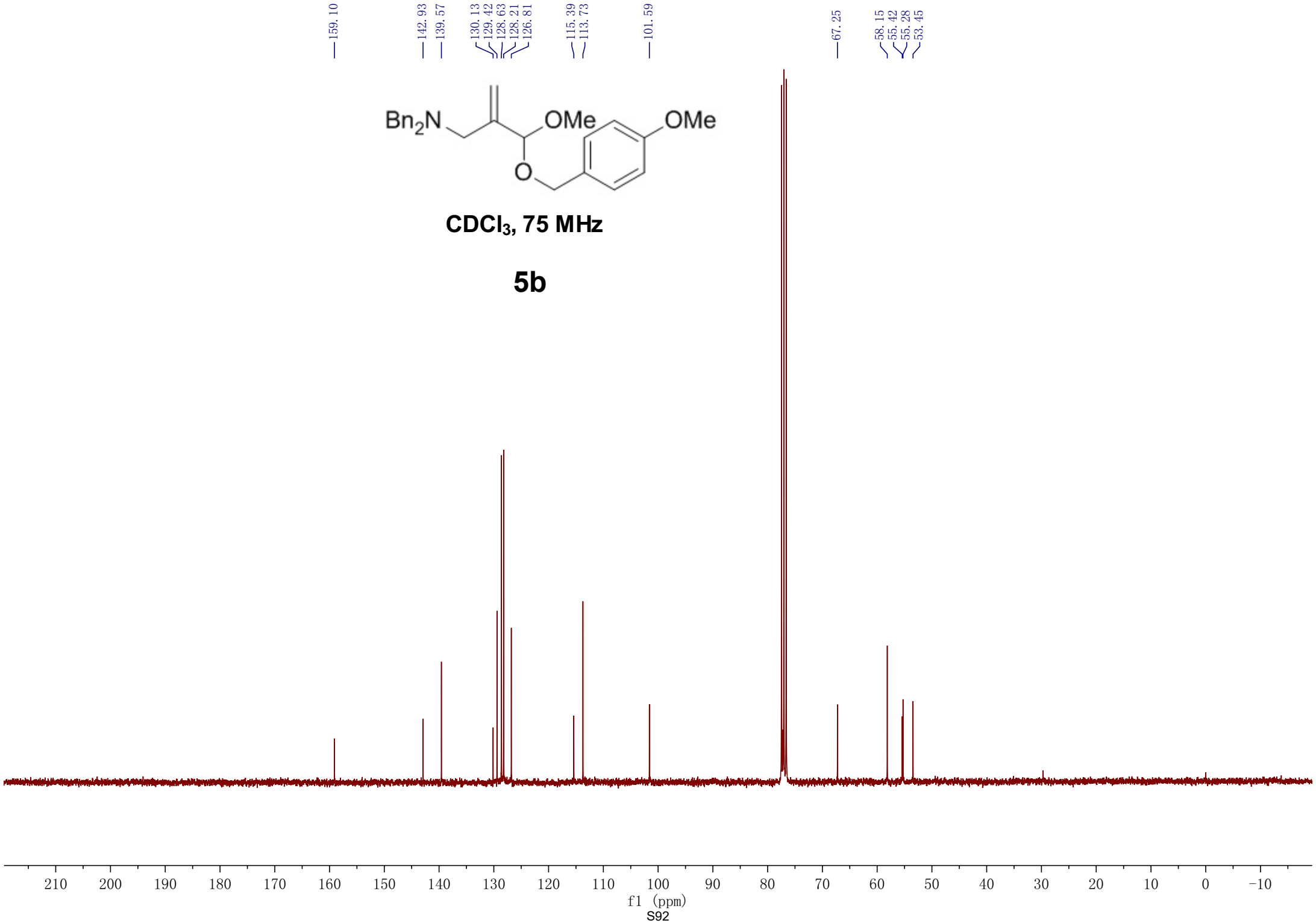

7.48
7.47
7.46
7.46
7.45
7.39
7.37
7.35
7.28
7.27
7.25
7.23
7.17
7.17
7.15
7.14
7.13
7.13
7.12
7.06
7.04
7.03
7.02
6.74
6.72
6.71
6.39
5.14
5.00
4.20
4.20
3.78
3.75
3.26
3.23
3.13
3.10
2.68
2.65
2.44
2.44
2.43
2.37
2.03
1.59
1.27
1.26
1.25
0.00
Bn2N
O
N
Ph
Ts
CDCl3, 400 MHz
3r
6.02
4.03
2.01
3.05
2.05
2.02
1.00
0.99
1.00
2.00
2.05
2.04
1.04
1.00
0.91
3.00
f1 (ppm)

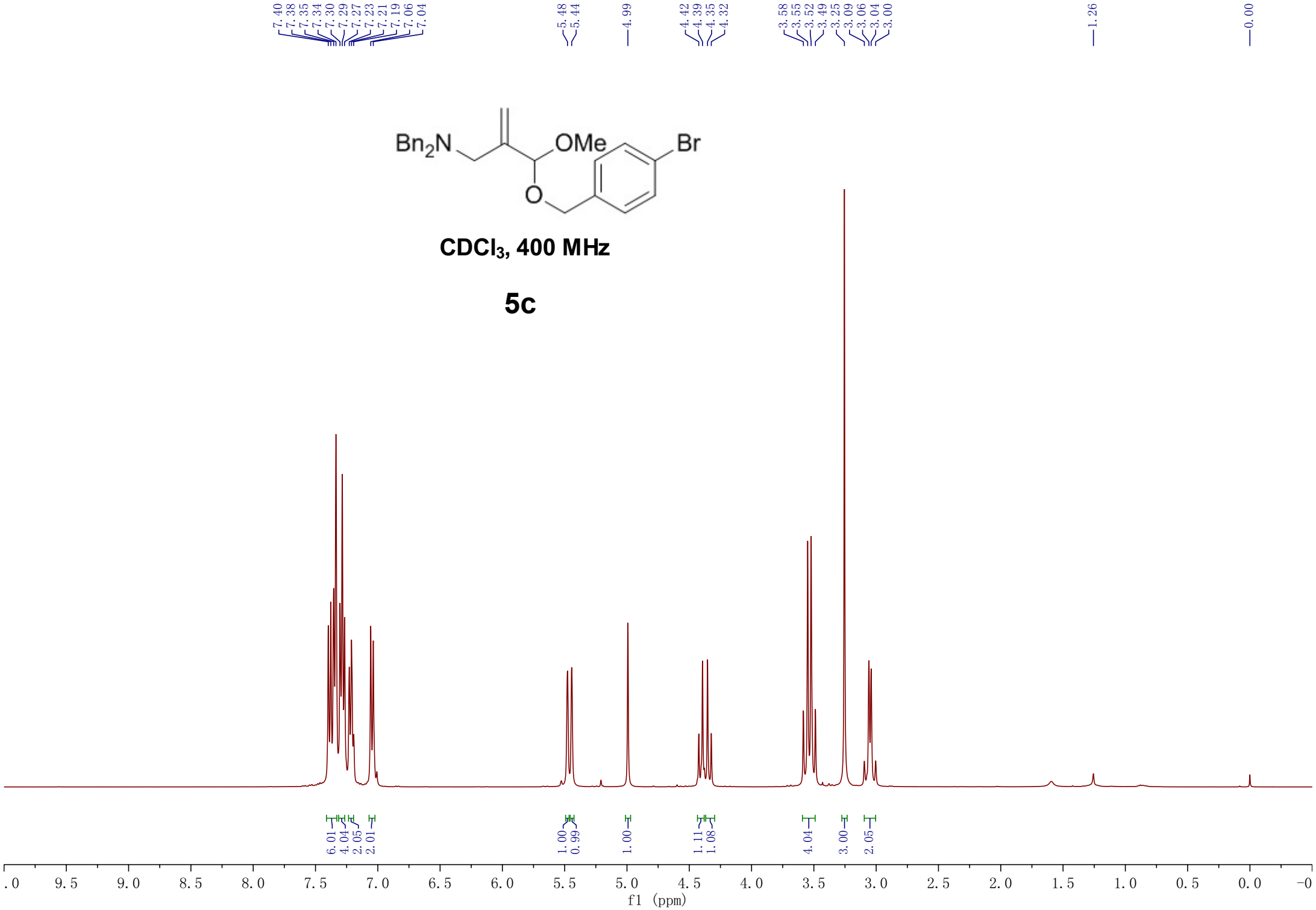

143.24
140.25
139.16
136.65
135.49
131.40
128.88
128.81
128.49
128.44
128.12
128.08
126.98
117.89
86.98
79.03
75.20
58.44
56.47
56.21
21.60
Bn2N
O
N
Ph
Ts
CDCl3, 75 MHz
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

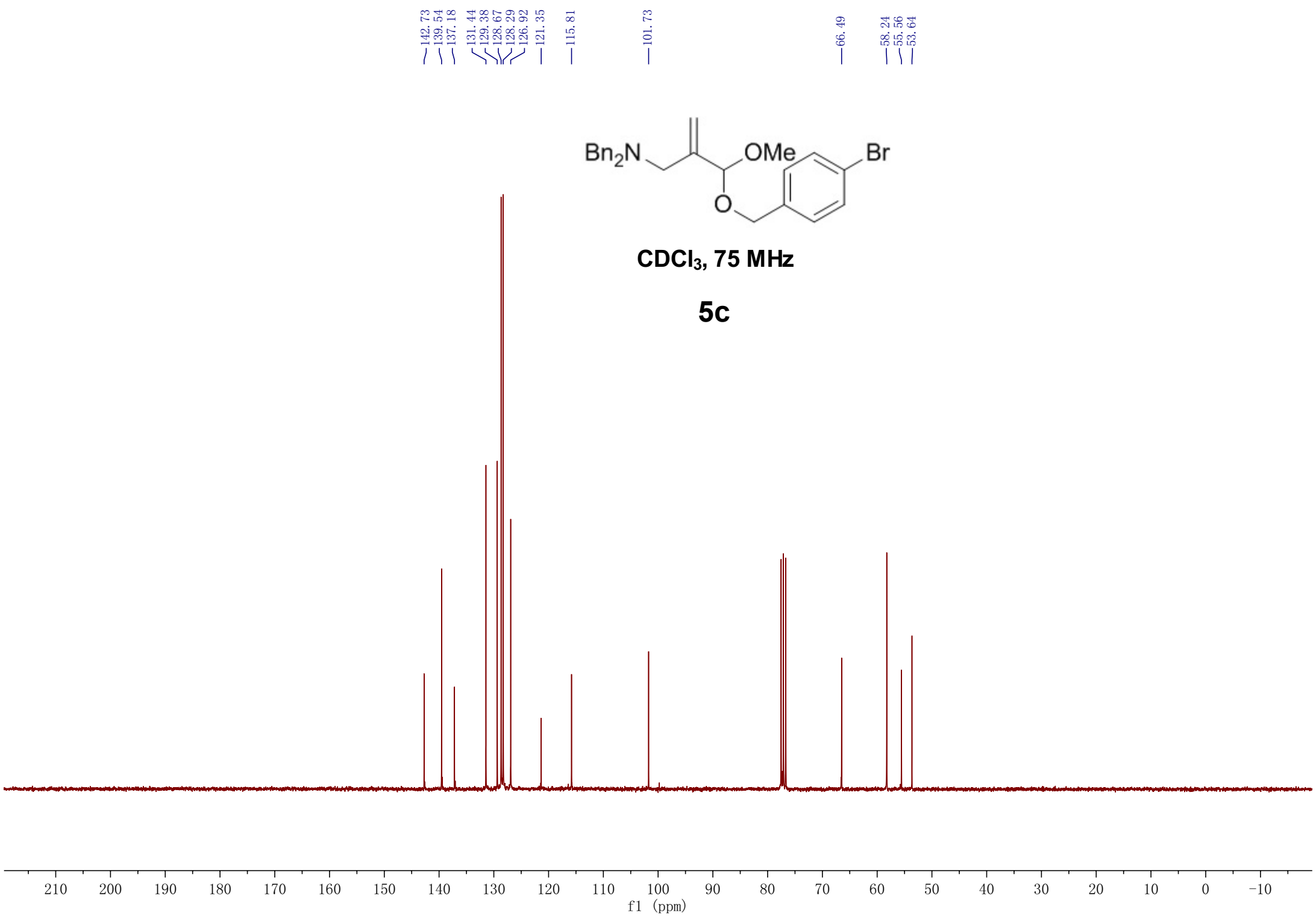

7.297
7.293
7.275
7.241
7.238
7.225
7.220
7.207
7.200
7.160
7.155
7.144
5.427
5.422
5.387
5.383
5.381
4.928
4.433
4.403
4.366
4.336
3.476
3.193
3.002
2.998
Bn2N
OMe
OBn
CDCl3, 400 MHz
5a
4.08
7.07
4.11
2.01
1.00
1.04
1.00
4.04
3.04
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


142.87
139.57
138.09
128.66
128.35
128.26
127.80
127.52
126.86
115.56
101.80
67.46
58.19
55.45
53.53
Bn2N
OMe
OBn
CDCl3, 100 MHz
5a
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)


7.36
7.34
7.31
7.29
7.27
7.25
7.23
7.22
7.20
7.15
7.13
6.83
6.81
5.48
5.44
4.96
4.44
4.41
4.38
4.35
3.79
3.58
3.54
3.51
3.25
3.06
1.56
0.00
Bn2N
OMe
OMe
O
CDCl3, 400 MHz
5b
4.04
4.07
2.06
2.03
2.00
1.00
1.00
1.00
1.04
1.09
3.00
4.03
3.00
2.04
f1 (ppm)


159.10
142.93
139.57
130.13
129.42
128.63
128.21
126.81
115.39
113.73
101.59
67.25
58.15
55.42
55.28
53.45
Bn2N
OMe
OMe
O
CDCl3, 75 MHz
5b
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)


7.40
7.38
7.35
7.34
7.30
7.29
7.27
7.23
7.21
7.19
7.06
7.04
5.48
5.44
4.99
4.42
4.39
4.35
4.32
3.58
3.55
3.52
3.49
3.25
3.09
3.06
3.04
3.00
1.26
0.00
Bn2N
OMe
Br
O
CDCl3, 400 MHz
5c
6.01
4.04
2.05
2.01
1.00
0.99
1.00
1.11
1.08
4.04
3.00
2.05
f1 (ppm)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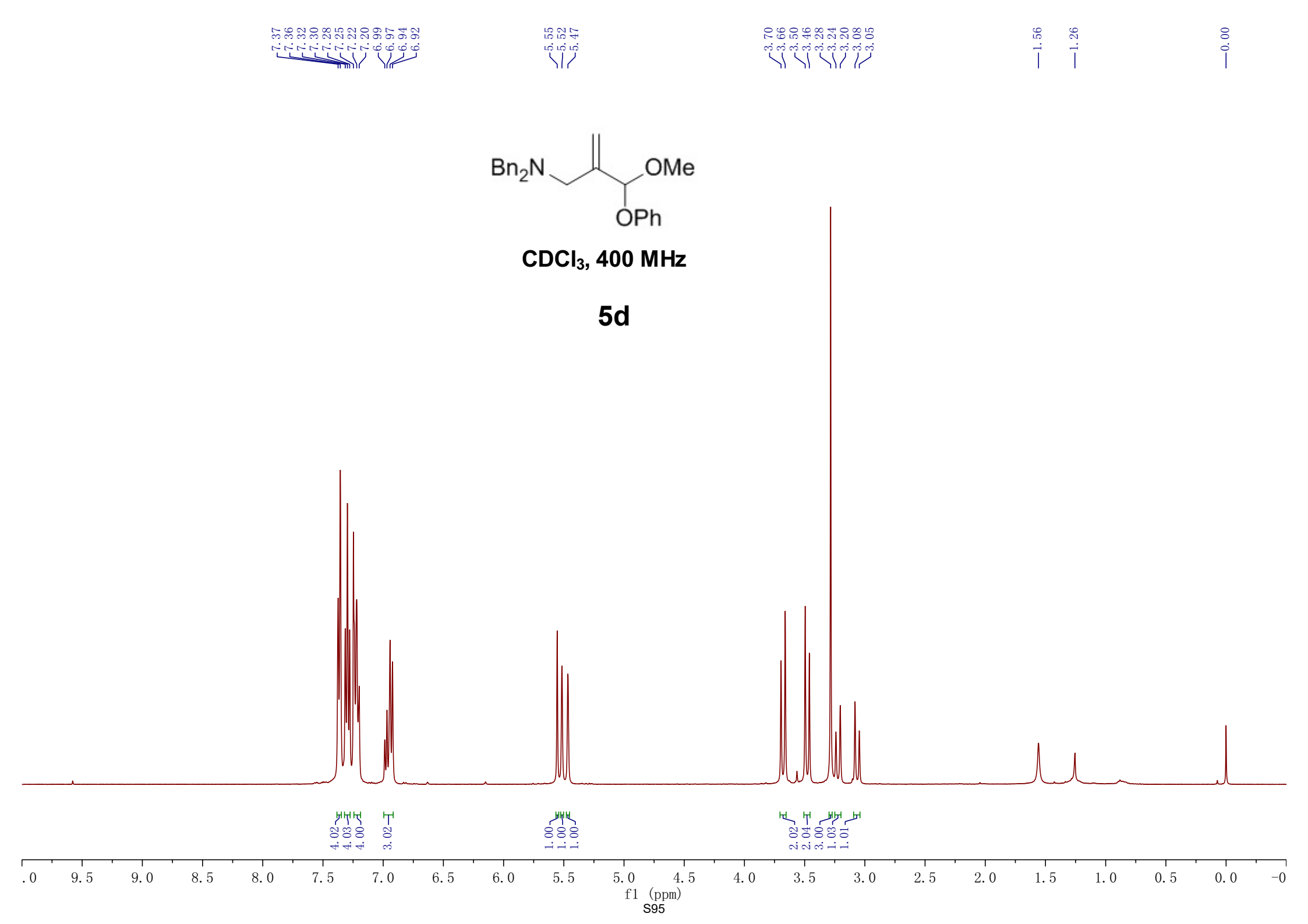
139.54
137.18
131.44
129.38
128.67
128.29
126.92
121.35
115.81
101.73
66.49
58.24
55.56
53.64
Bn2N
OMe
Br
O
CDCl3, 75 MHz
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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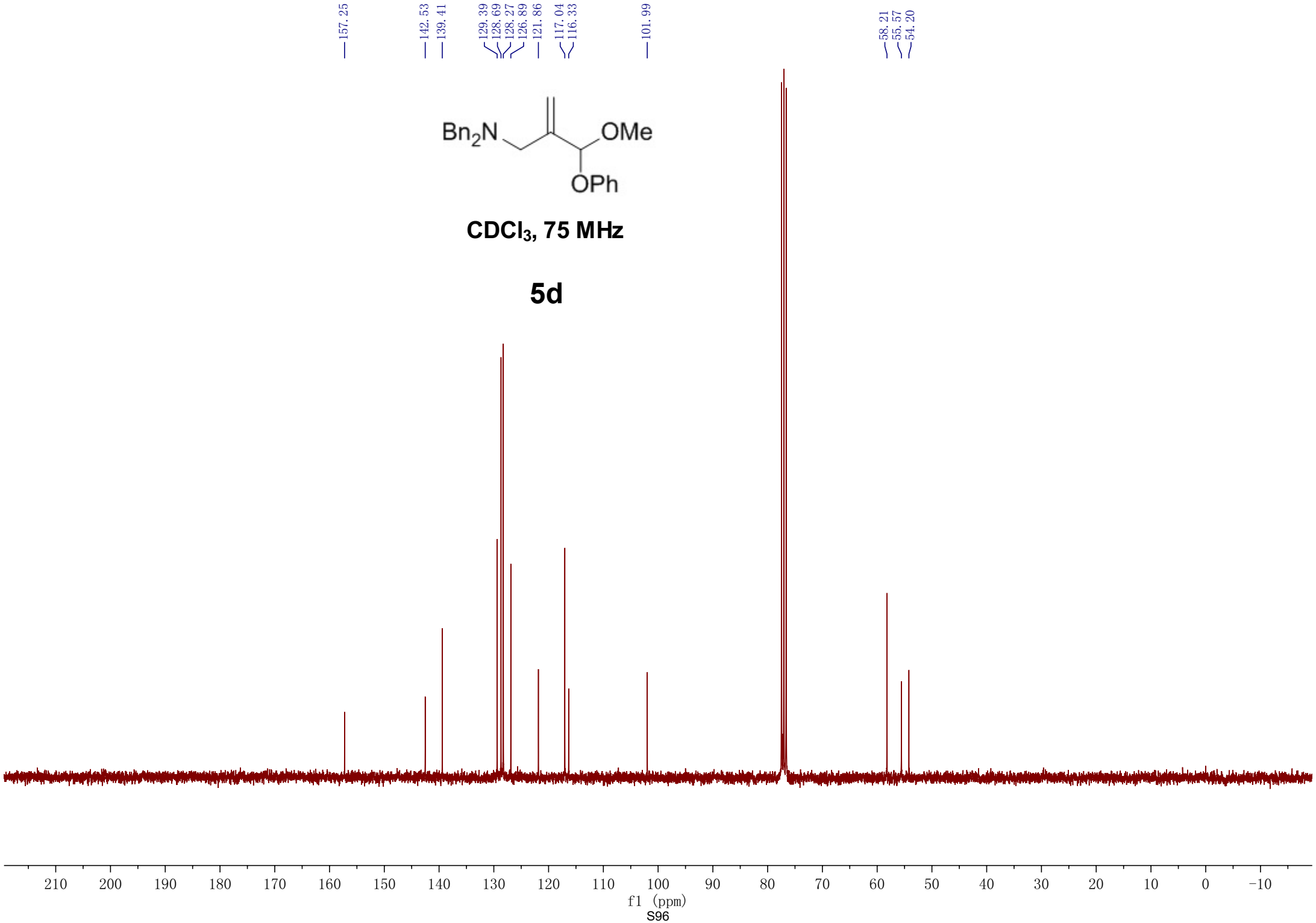
7.36
7.32
7.30
7.28
7.25
7.22
7.20
6.99
6.97
6.94
6.92
5.55
5.52
5.47
3.70
3.66
3.50
3.46
3.28
3.24
3.20
3.08
3.05
1.56
1.26
0.00
Bn2N
OMe
OPh
CDCl3, 400 MHz
5d
4.02
4.03
4.00
3.02
1.00
1.00
1.00
2.02
2.04
3.00
1.03
1.01
f1 (ppm)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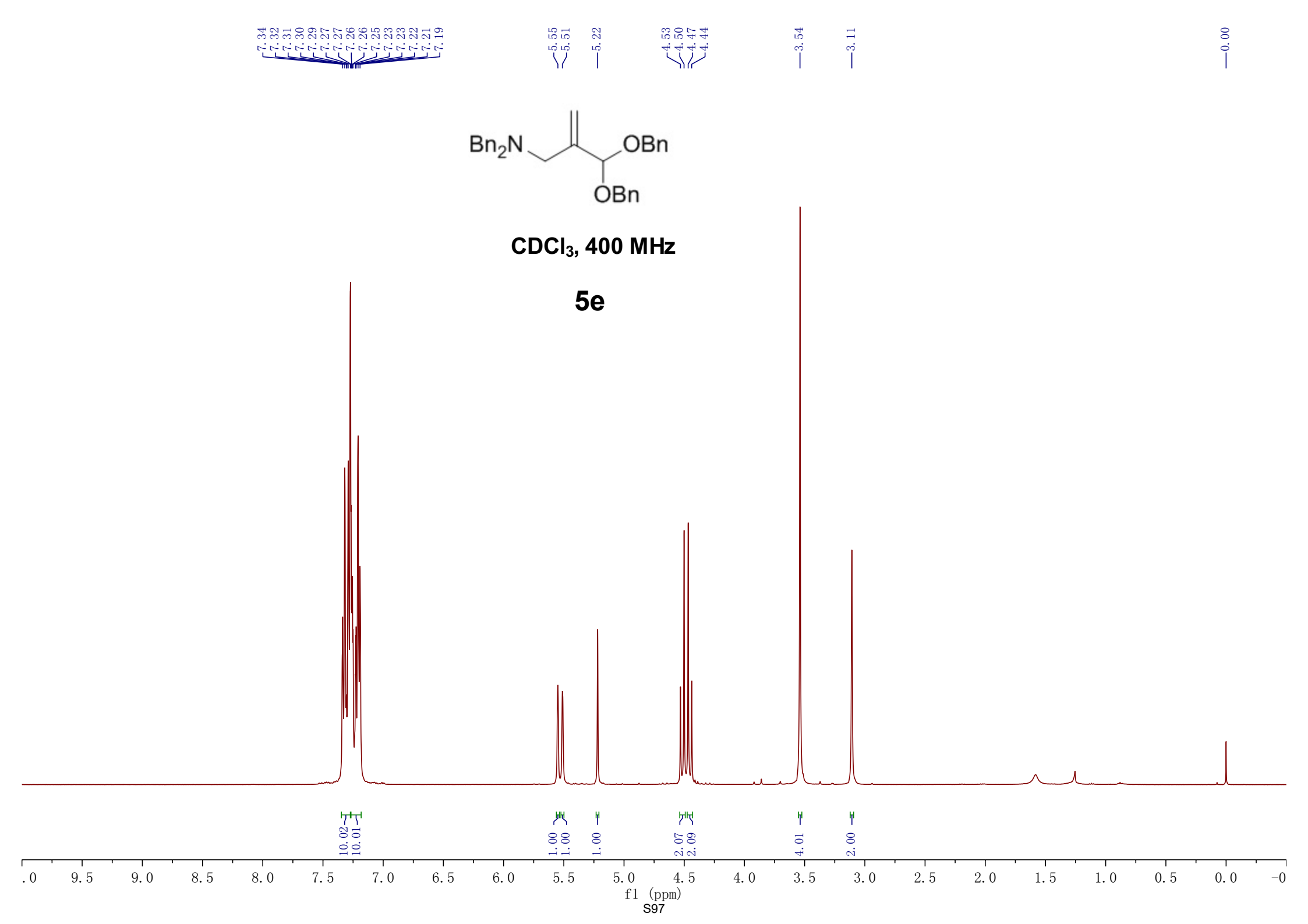
142.53
139.41
129.39
128.69
128.27
126.89
121.86
117.04
116.33
101.99
58.21
55.57
54.20
Bn2N
OMe
OPh
CDCl3, 75 MHz
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.32
7.31
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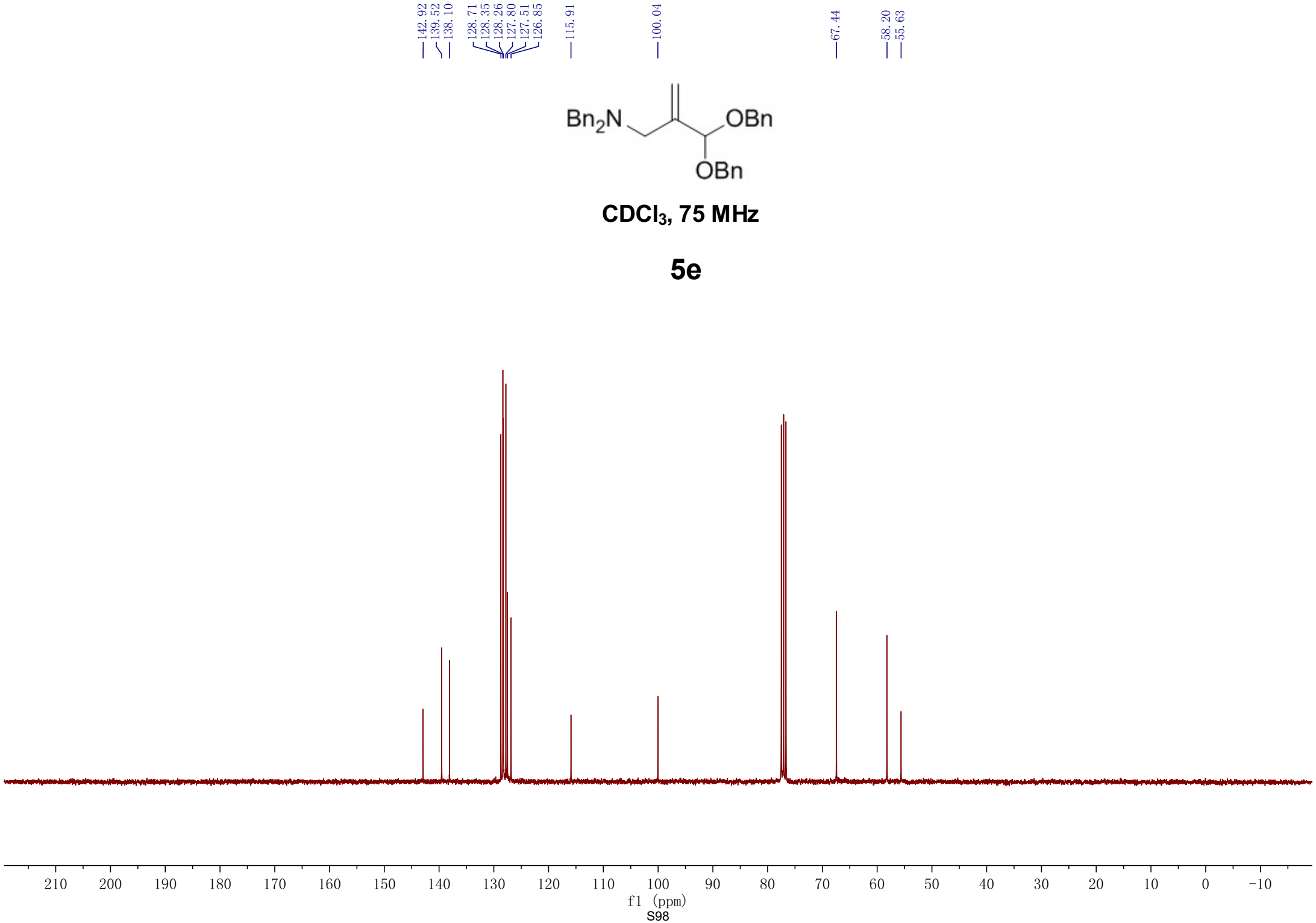
7.27
7.26
7.26
7.25
7.23
7.23
7.22
7.21
7.19
5.55
5.51
5.22
4.53
4.50
4.47
4.44
3.54
3.11
0.00
Bn2N
OBn
OBn
CDCl3, 400 MHz
5e
10.02
10.01
1.00
1.00
1.00
2.07
2.09
4.01
2.00
f1 (ppm)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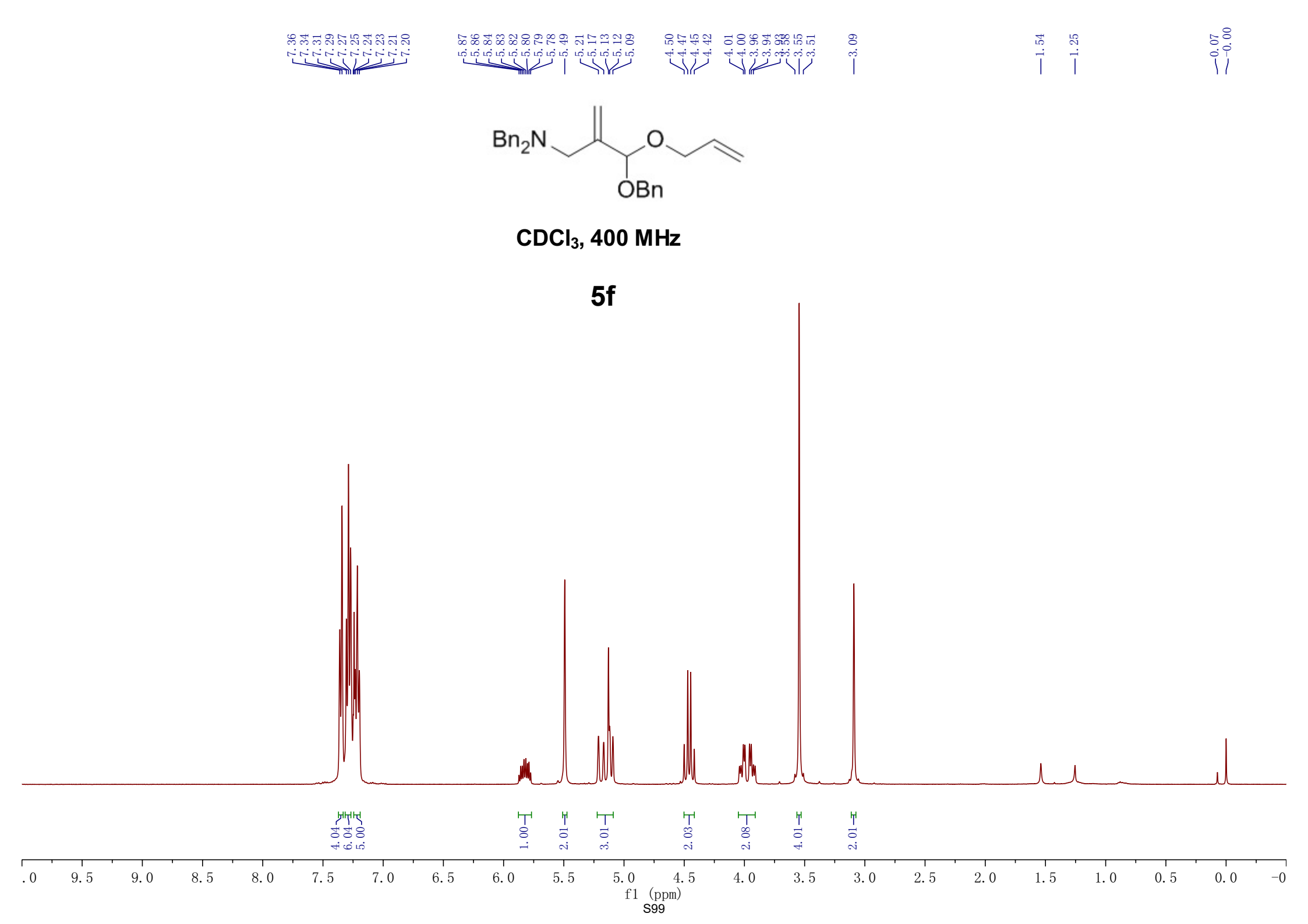
139.52
138.10
128.71
128.35
128.26
127.80
127.51
126.85
115.91
100.04
67.44
58.20
55.63
Bn2N
OBn
OBn
CDCl3, 75 MHz
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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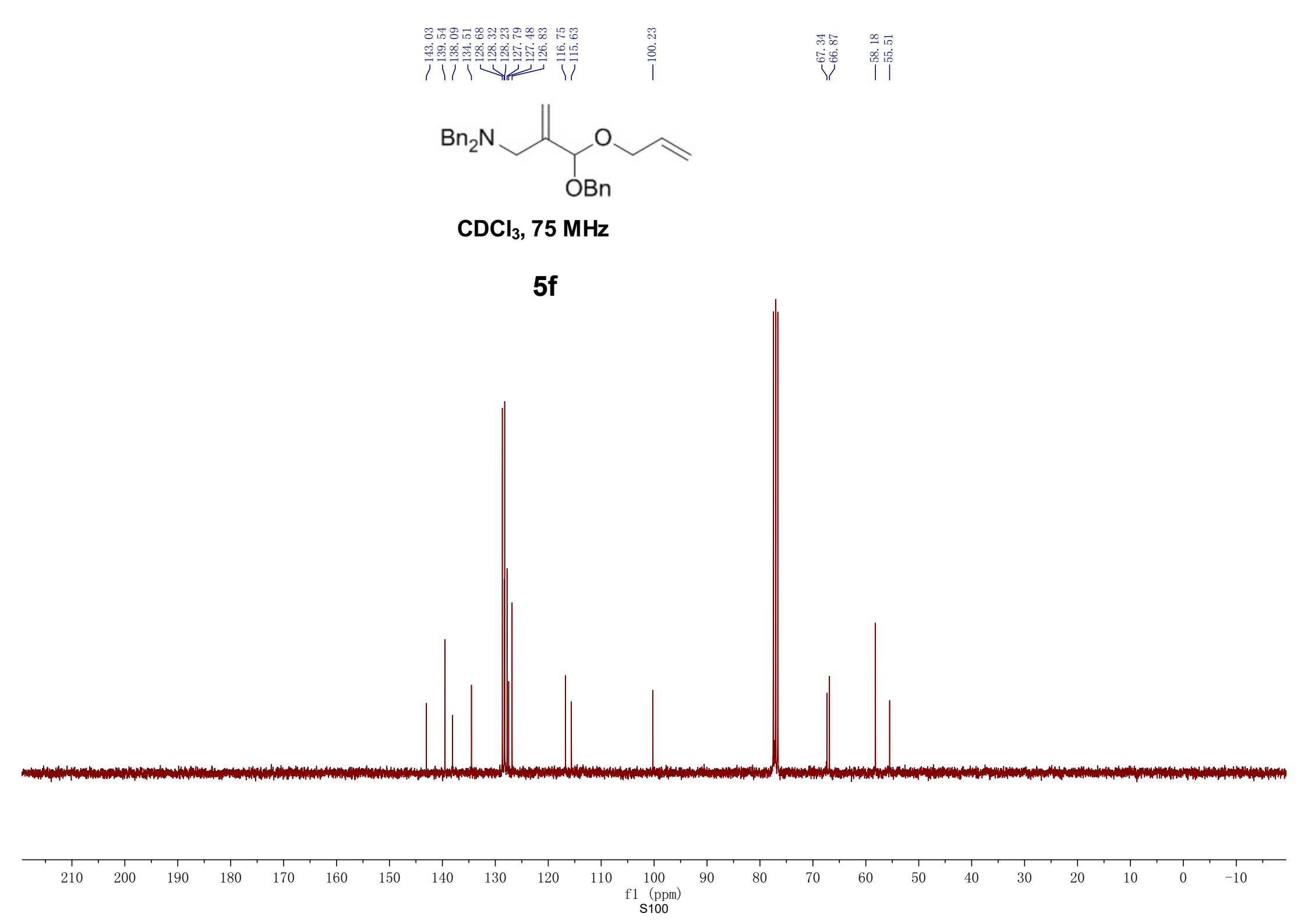
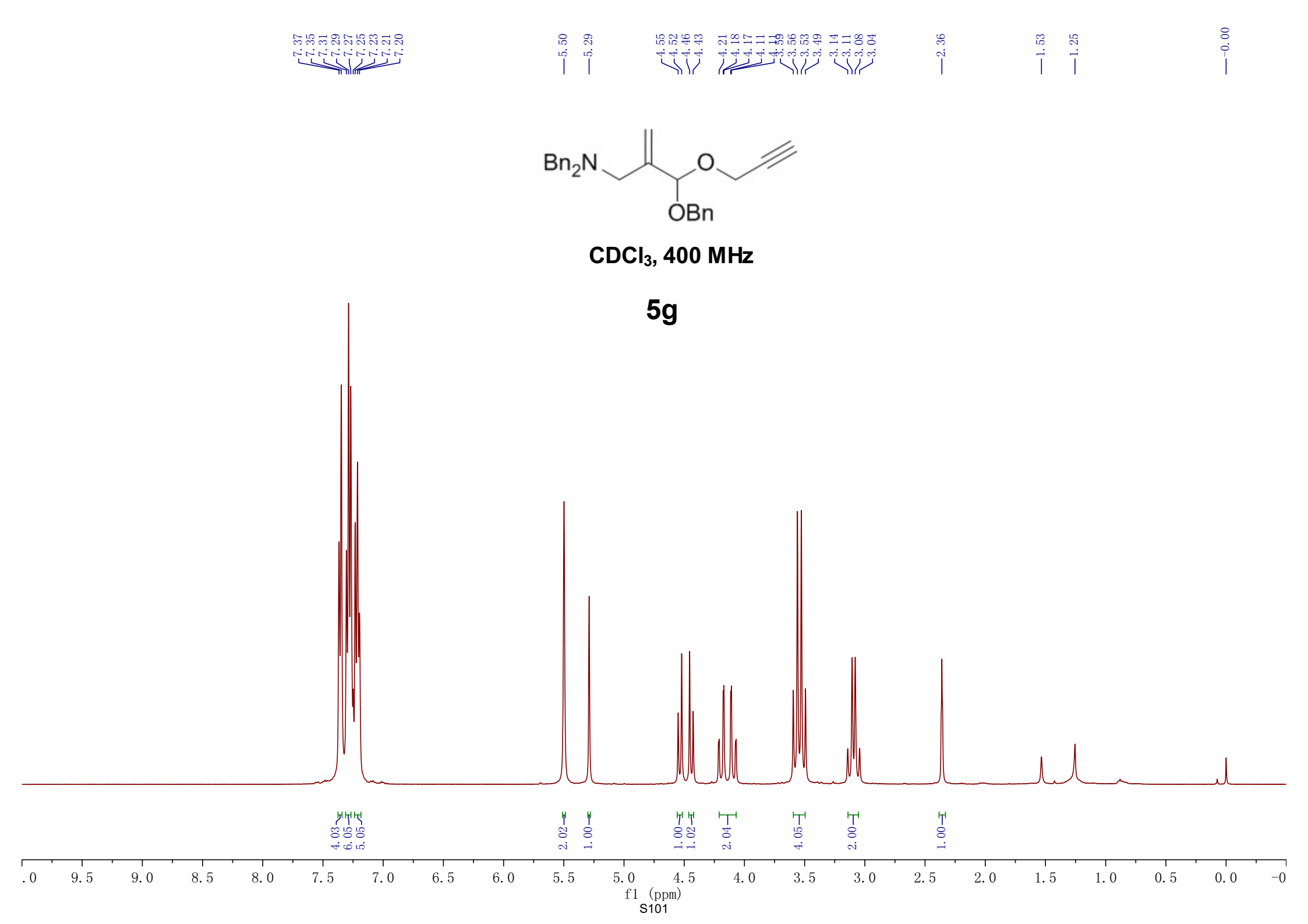
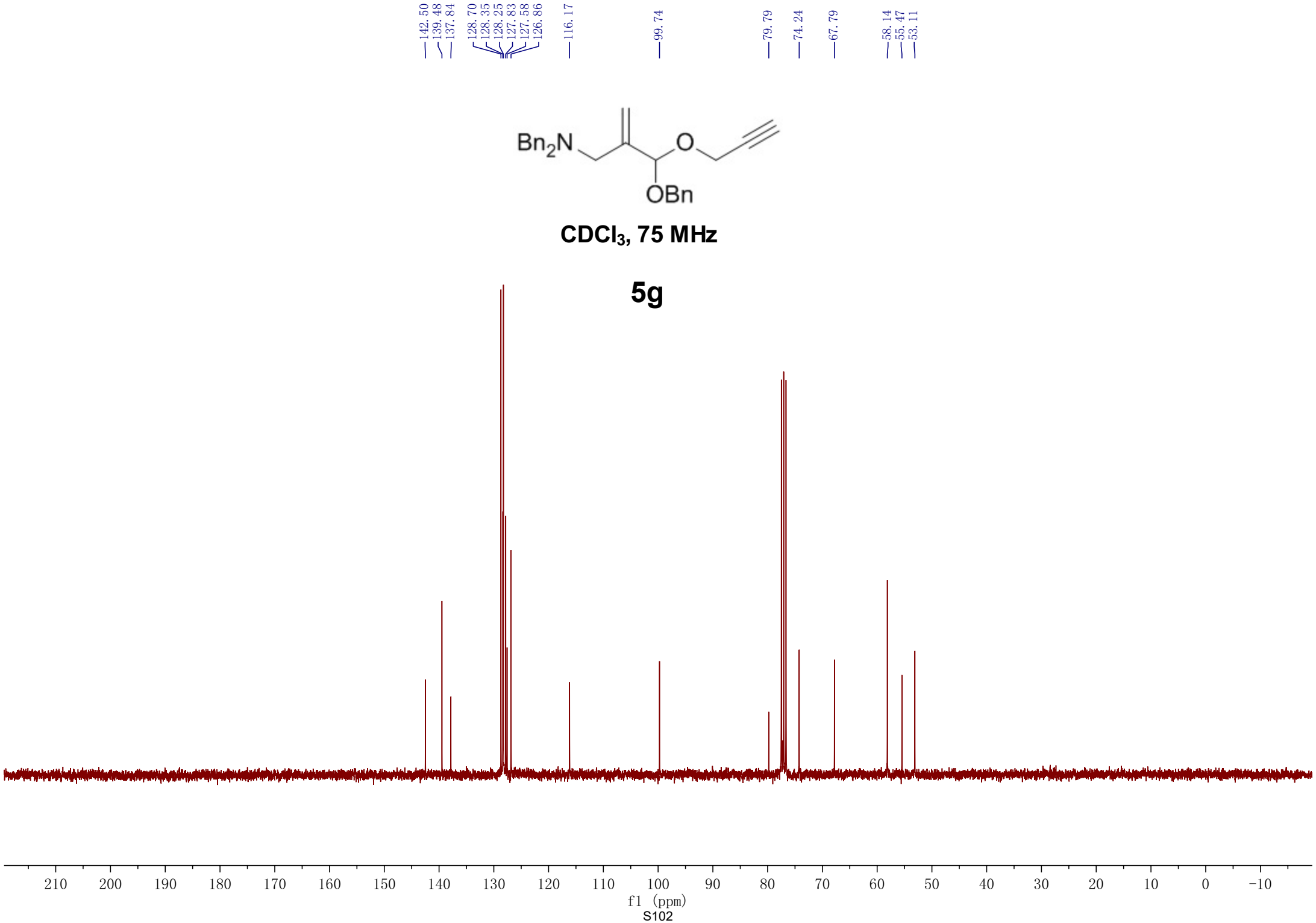
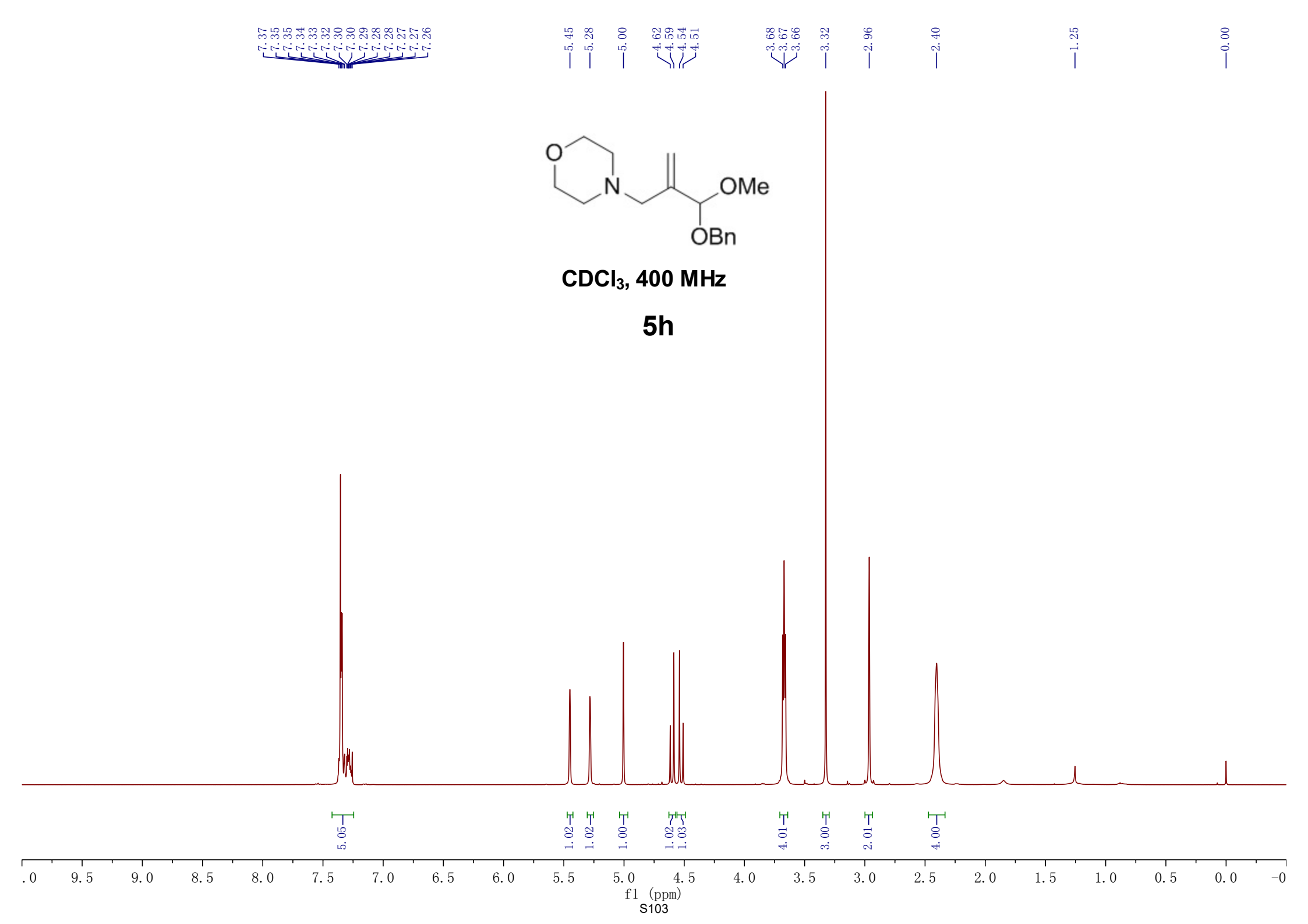
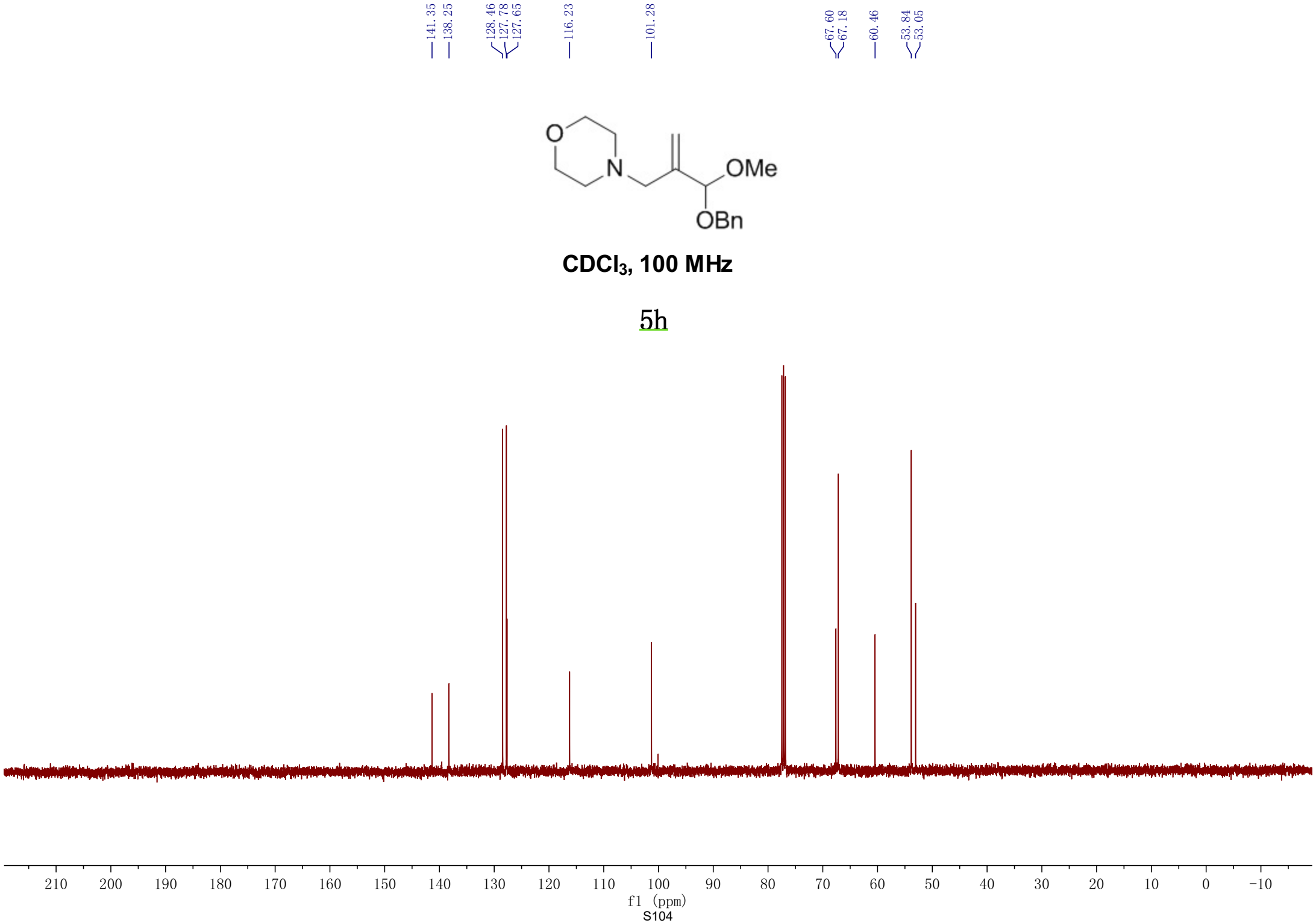
7.34
7.31
7.29
7.27
7.25
7.24
7.23
7.21
7.20
5.87
5.86
5.84
5.83
5.82
5.80
5.79
5.78
5.49
5.21
5.17
5.13
5.12
5.09
4.50
4.47
4.45
4.42
4.01
4.00
3.96
3.94
3.58
3.55
3.51
3.09
1.54
1.25
0.07
-0.00
Bn2N
O
OBn
CDCl3, 400 MHz
5f
4.04
6.04
5.00
1.00
2.01
3.01
2.03
2.08
4.01
2.01
f1 (ppm)

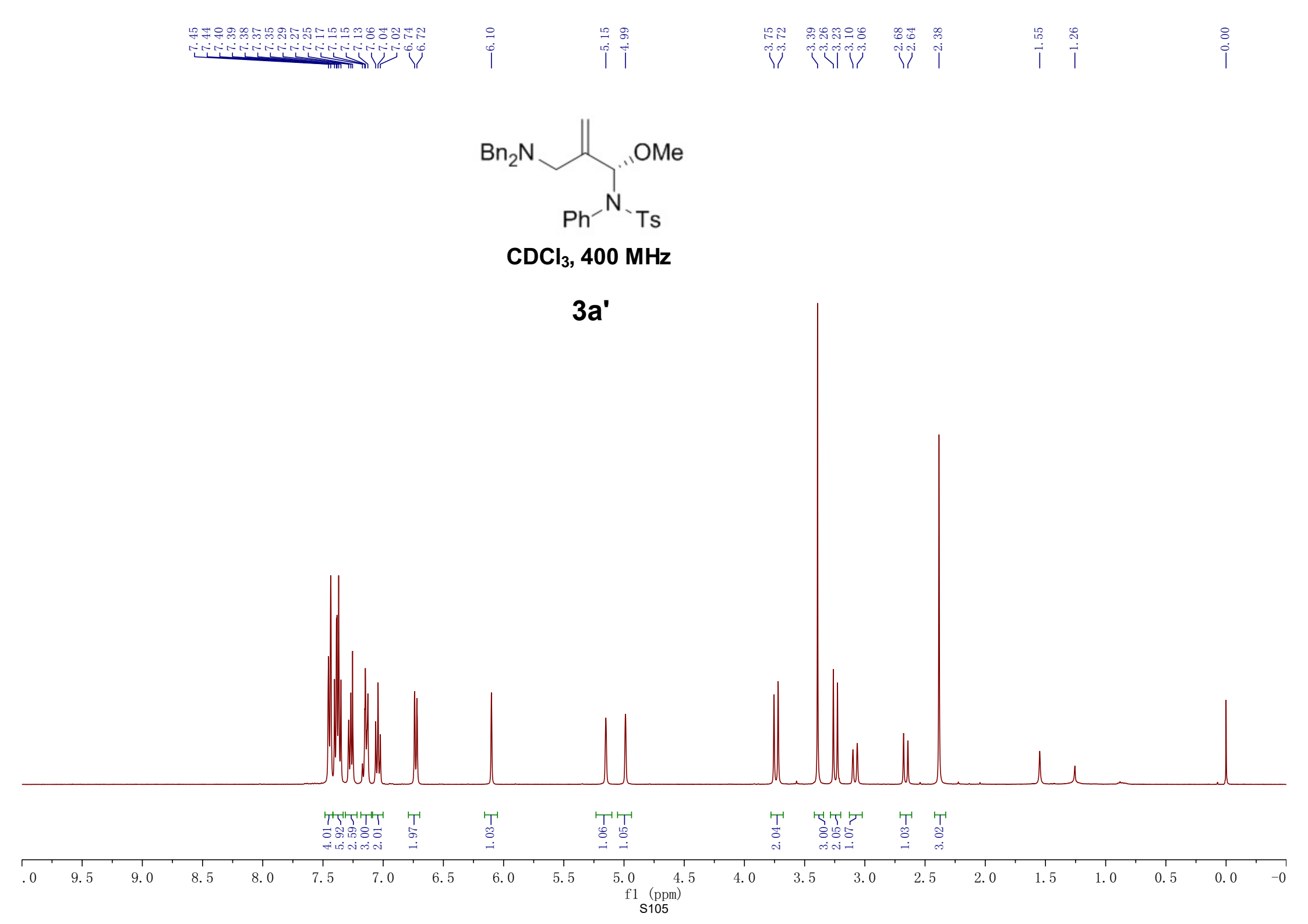

143.03
139.54
138.09
134.51
128.68
128.32
128.23
127.79
127.48
126.83
116.75
115.63
100.23
67.34
66.87
58.18
55.51
Bn2N
O
OBn
CDCl3, 75 MHz
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

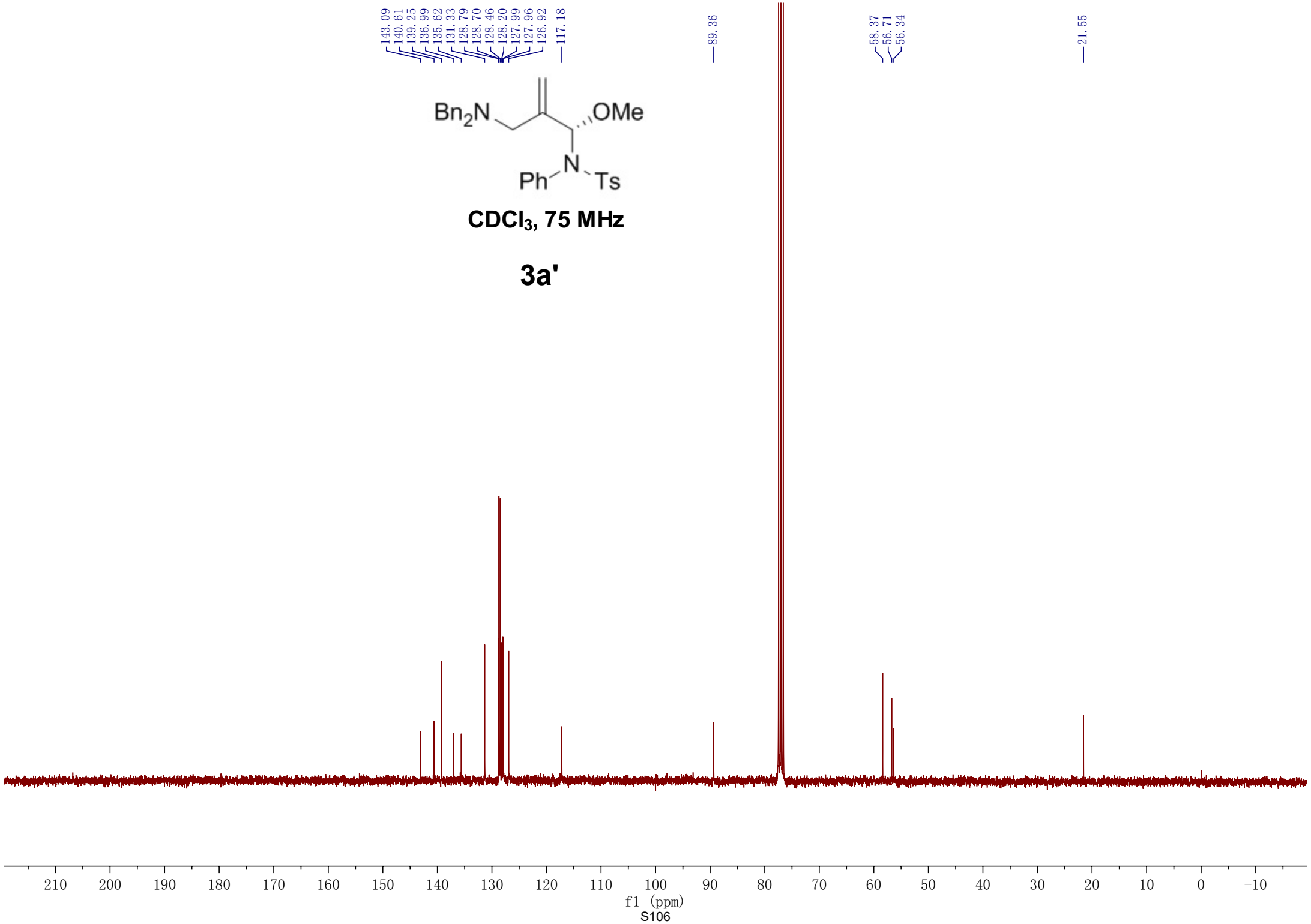

7.37
7.35
7.31
7.29
7.27
7.25
7.23
7.21
7.20
5.50
5.29
4.55
4.52
4.46
4.43
4.21
4.18
4.17
4.11
3.56
3.53
3.49
3.14
3.11
3.08
3.04
2.36
1.53
1.25
0.00
Bn2N
O
OBn
CDCl3, 400 MHz
5g
4.03
6.05
5.05
2.02
1.00
1.00
1.02
2.04
4.05
2.00
1.00
f1 (ppm)

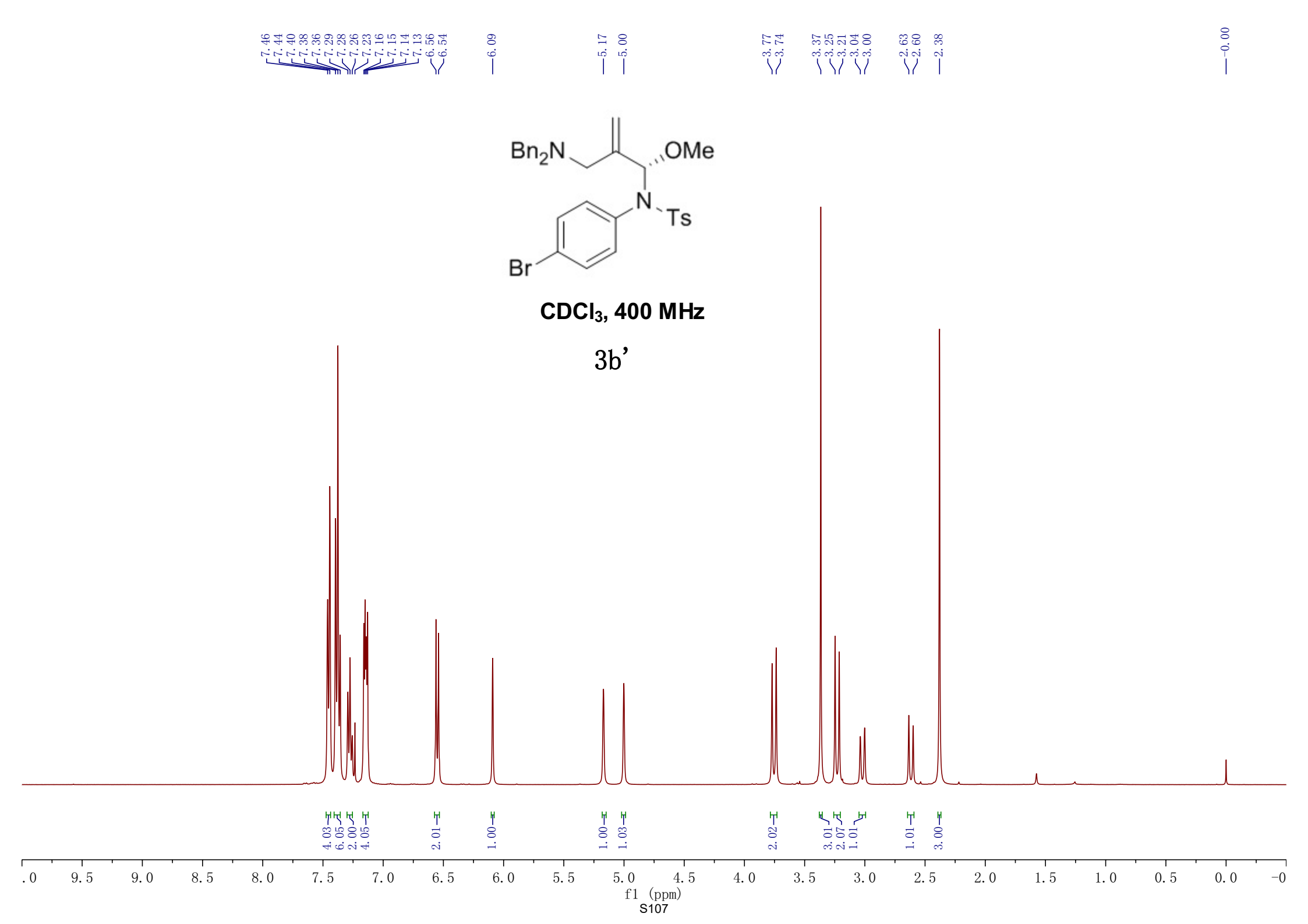

142.50
139.48
137.84
128.70
128.35
128.25
127.83
127.58
126.86
116.17
99.74
79.79
74.24
67.79
58.14
55.47
53.11
Bn2N
O
OBn
CDCl3, 75 MHz
5g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

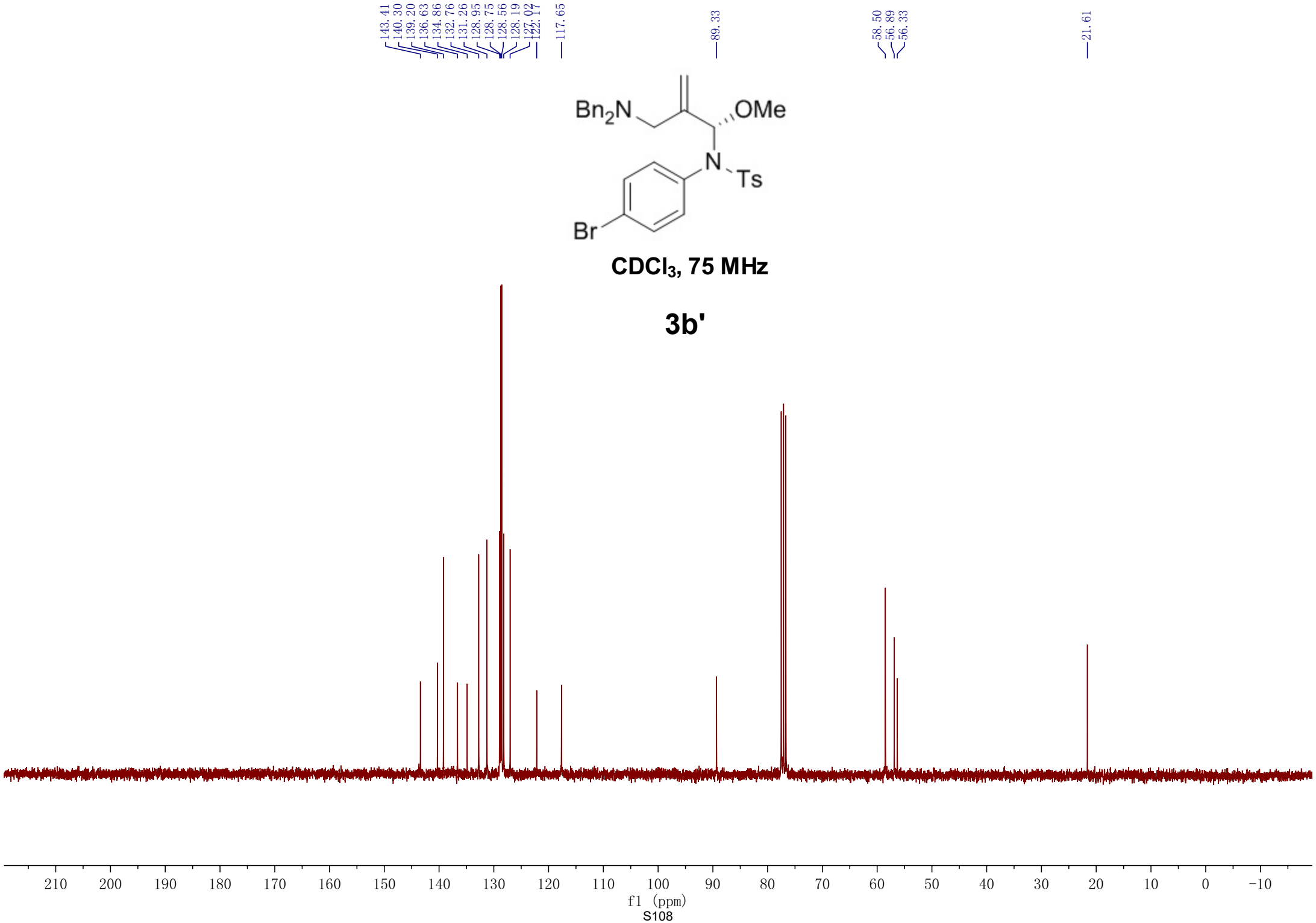

7.37
7.35
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
5.45
5.28
5.00
4.62
4.59
4.54
4.51
3.68
3.67
3.66
3.32
2.96
2.40
1.25
0.00
O
N
OMe
OBn
CDCl3, 400 MHz
5h
5.05
1.02
1.02
1.00
1.02
1.03
4.01
3.00
2.01
4.00
f1 (ppm)

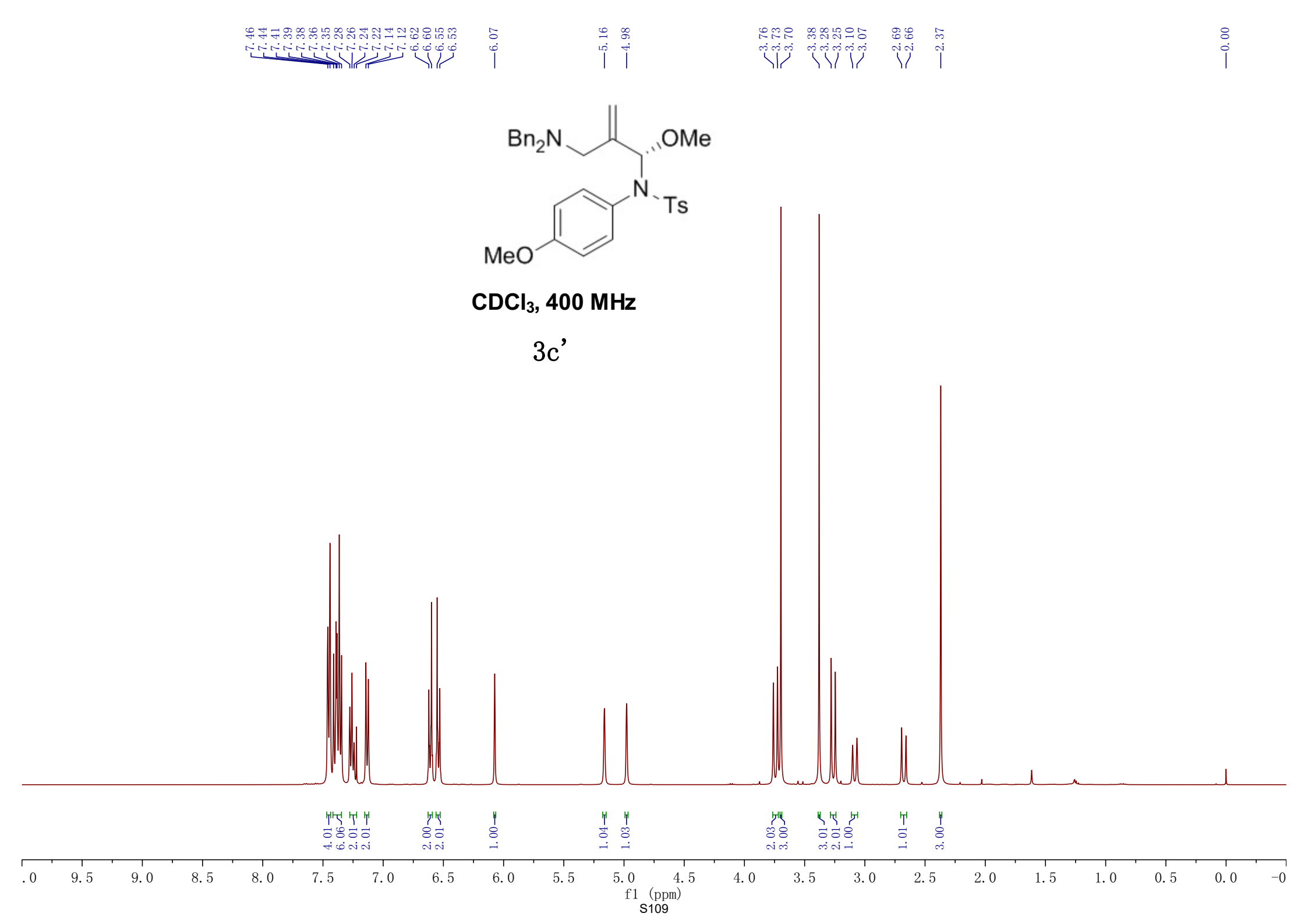

141.35
138.25
128.46
127.78
127.65
116.23
101.28
67.60
67.18
60.46
53.84
53.05
O
N
OMe
OBn
CDCl3, 100 MHz
5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.45
7.44
7.40
7.39
7.38
7.37
7.35
7.29
7.27
7.25
7.17
7.15
7.13
7.06
7.04
7.02
6.74
6.72
6.10
5.15
4.99
3.75
3.72
3.39
3.26
3.23
3.10
3.06
2.68
2.64
2.38
1.55
1.26
0.00
Bn2N
OMe
N
Ph
Ts
CDCl3, 400 MHz
3a'
4.01
5.92
2.59
3.00
2.01
1.97
1.03
1.06
1.05
2.04
3.00
2.05
1.07
1.03
3.02
f1 (ppm)

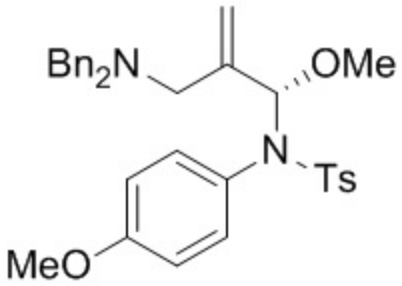

143.09
140.61
139.25
136.99
135.62
131.33
128.79
128.70
128.46
128.20
127.99
127.96
126.92
117.18
89.36
58.37
56.71
56.34
21.55
Bn2N
OMe
N
Ph
Ts
CDCl3, 75 MHz
3a'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.46
7.44
7.40
7.38
7.36
7.29
7.28
7.26
7.23
7.16
7.15
7.14
7.13
6.56
6.54
6.09
5.17
5.00
3.77
3.74
3.37
3.25
3.21
3.04
3.00
2.63
2.60
2.38
0.00
Bn2N
OMe
N
Ts
Br
CDCl3, 400 MHz
3b'
4.03
6.05
2.00
4.05
2.01
1.00
1.00
1.03
2.02
3.01
2.07
1.01
1.01
3.00
f1 (ppm)


143.41
140.30
139.20
136.63
134.86
132.76
131.26
128.95
128.75
128.56
128.19
127.02
122.17
117.65
89.33
58.50
56.89
56.33
21.61
Bn2N
OMe
N
Ts
Br
CDCl3, 75 MHz
3b'
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)

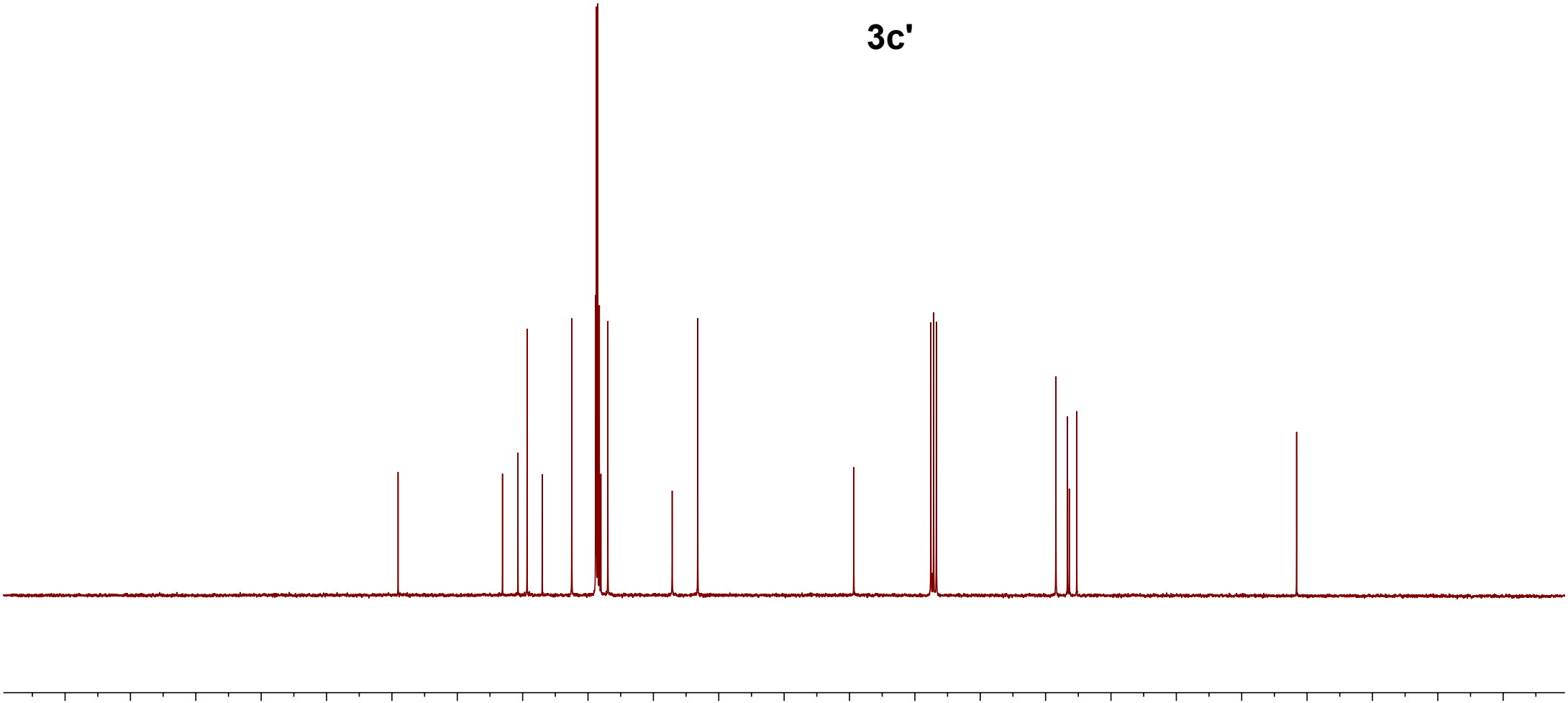

7.46
7.44
7.41
7.39
7.38
7.36
7.35
7.28
7.26
7.24
7.22
7.14
7.12
6.62
6.60
6.55
6.53
6.07
5.16
4.98
3.76
3.73
3.70
3.38
3.28
3.25
3.10
3.07
2.69
2.66
2.37
0.00
Bn2N
OMe
N
Ts
MeO
CDCl3, 400 MHz
3c'
4.01
6.06
2.01
2.01
2.00
2.01
1.00
1.04
1.03
2.03
3.00
3.01
2.01
1.00
1.01
3.00
f1 (ppm)

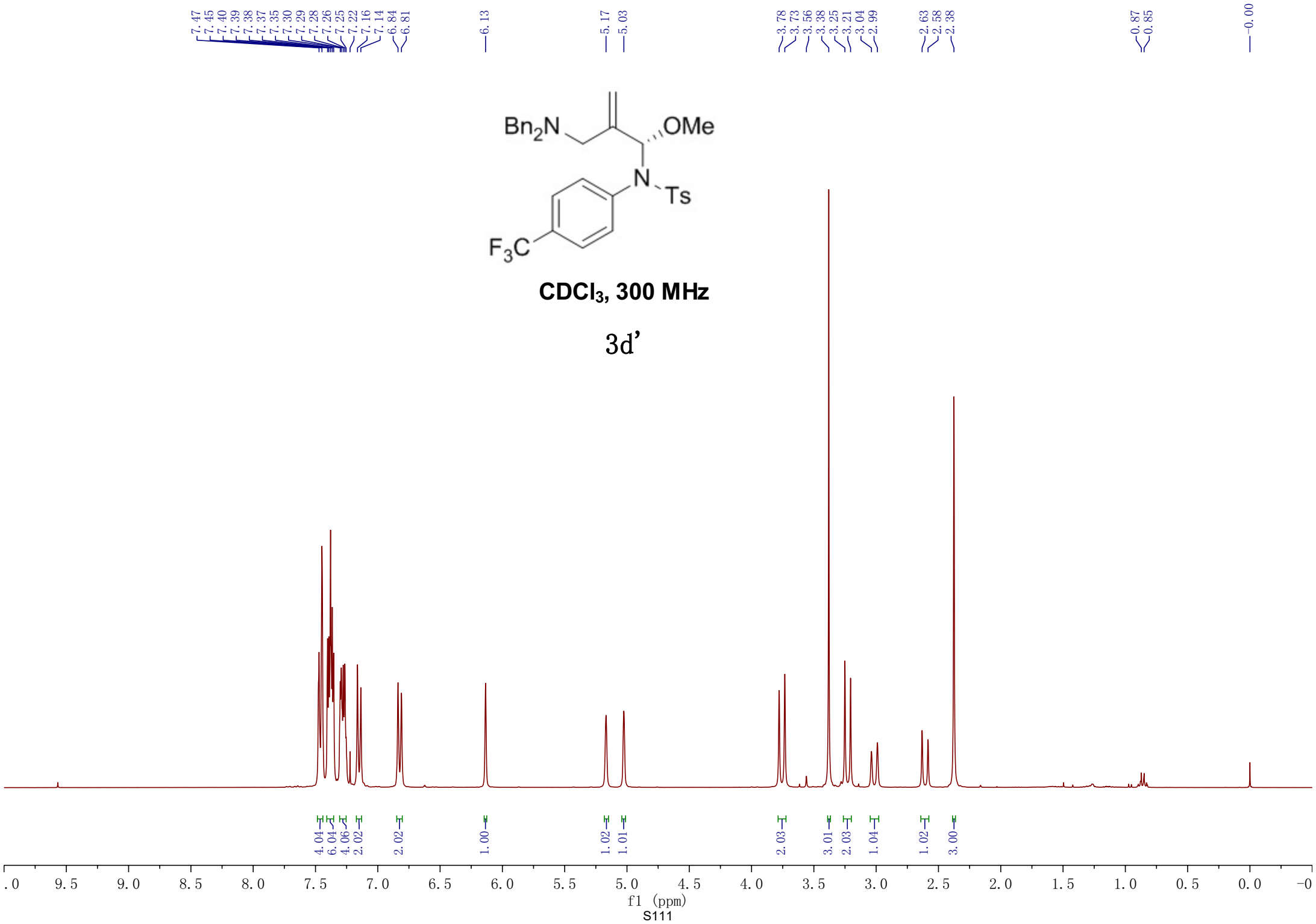
159.06
143.09
140.72
139.33
137.01
132.48
128.85
128.74
128.51
128.26
128.03
126.97
117.12
113.22
89.34
58.42
56.67
56.38
55.24
21.61

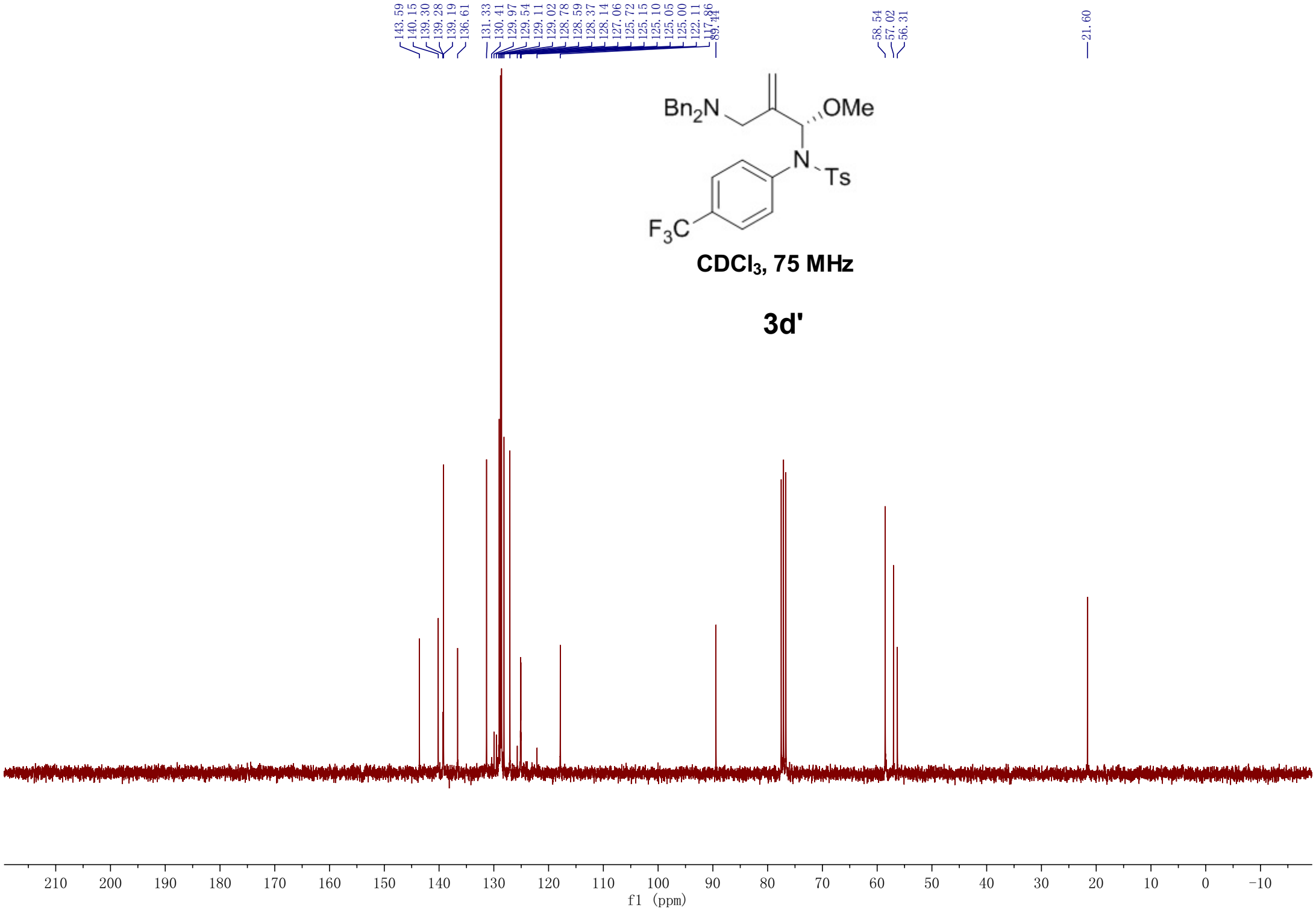


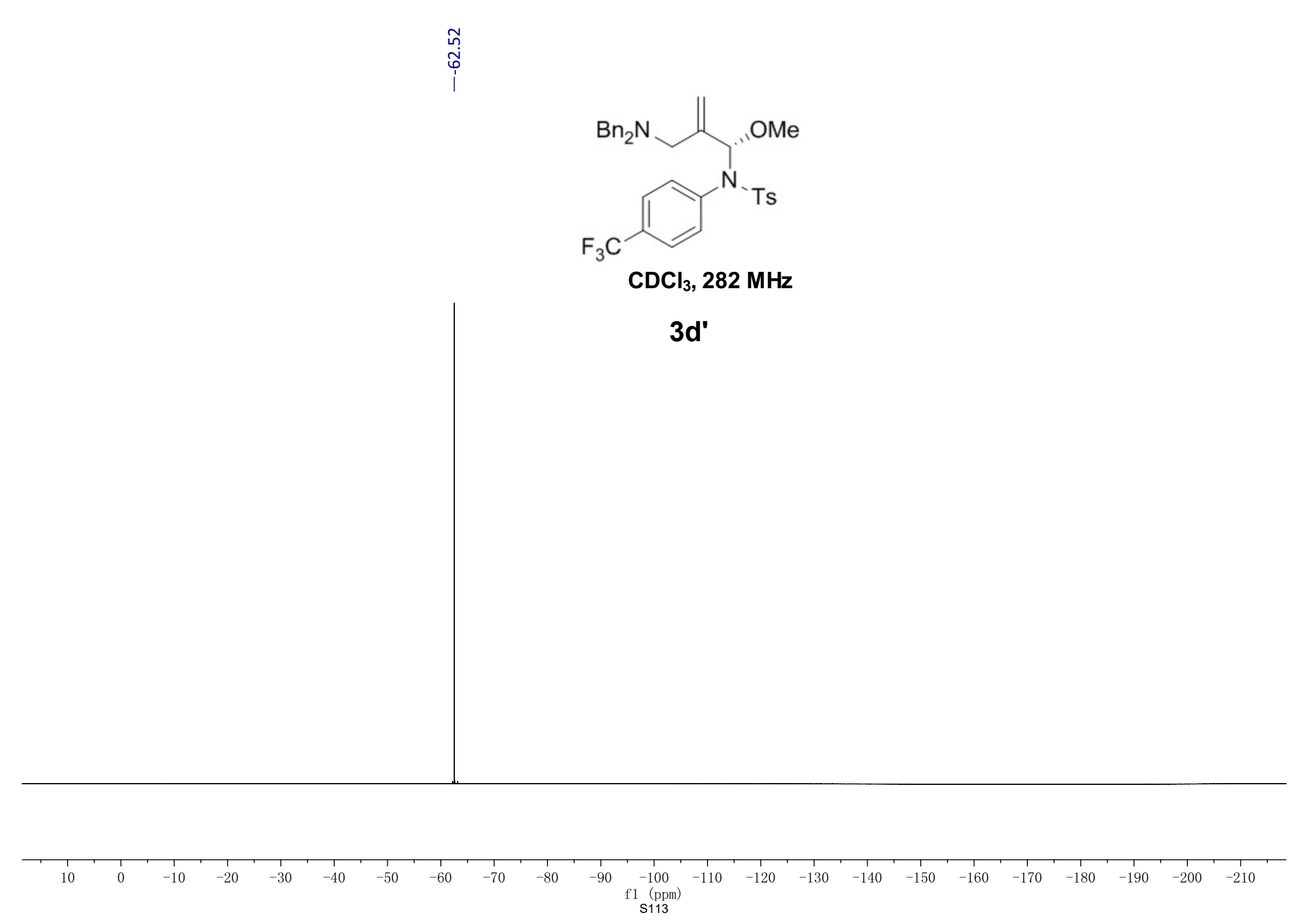
$CDCl_3$, 75 MHz

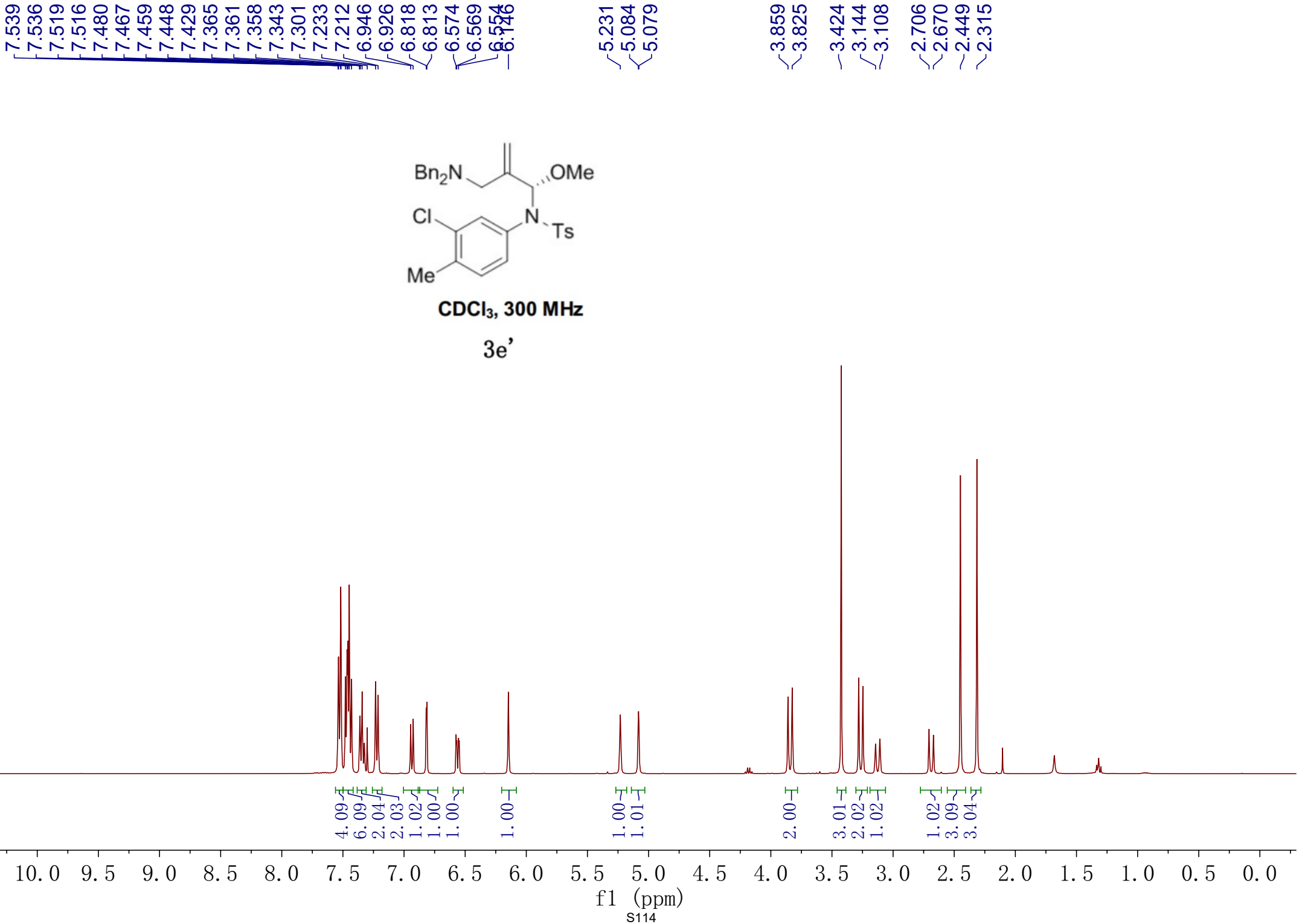
3c'

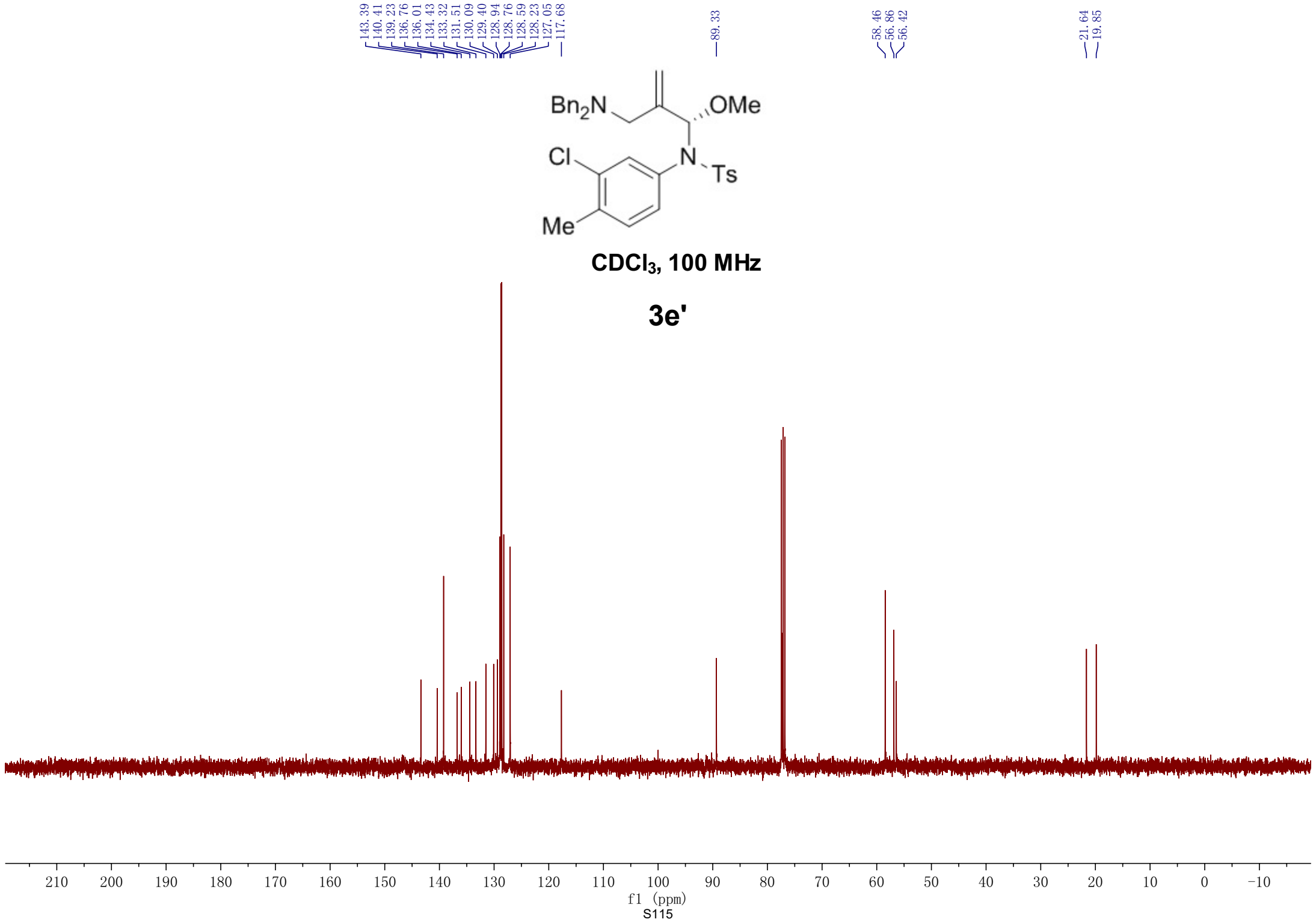


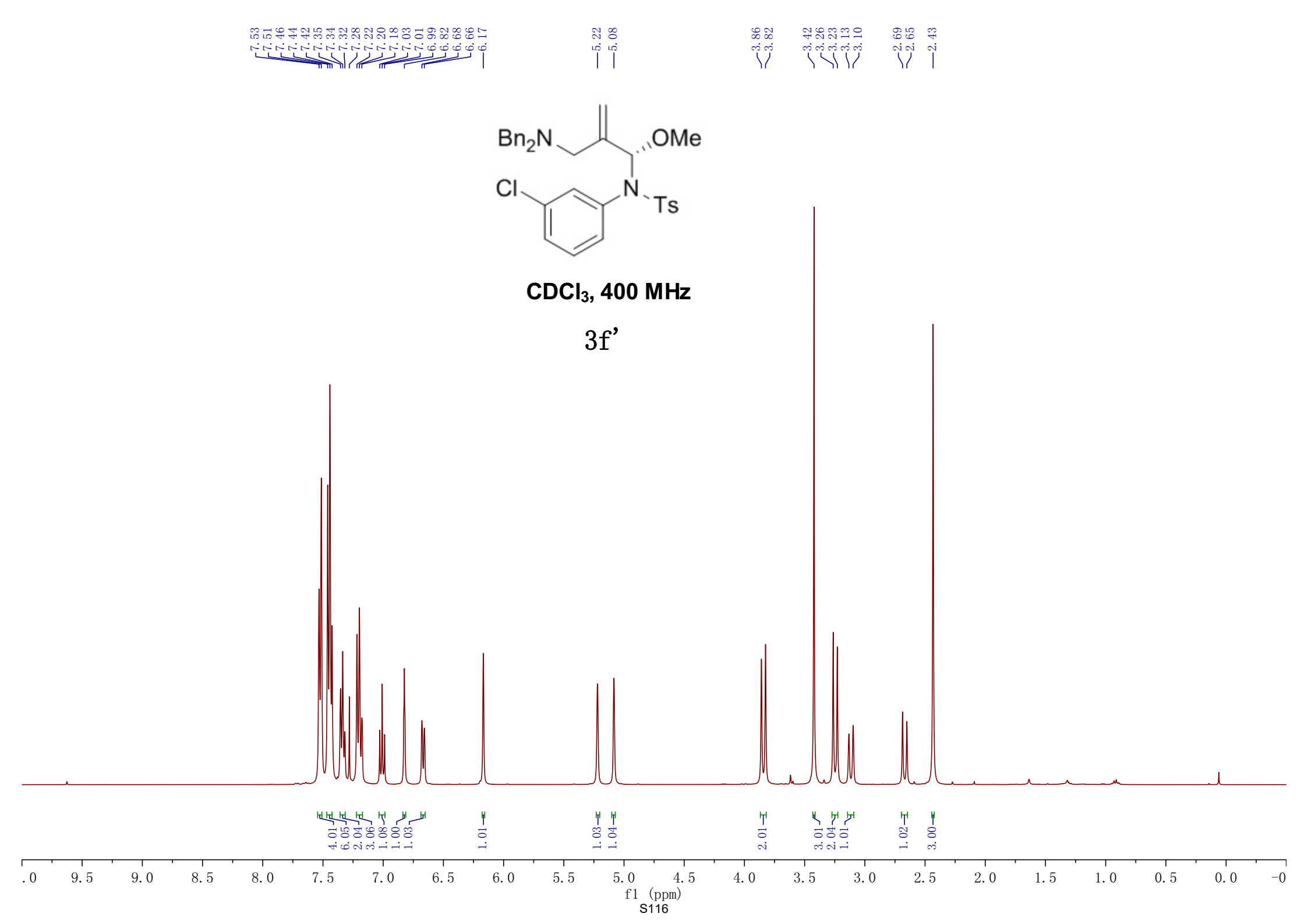

7.47
7.45
7.40
7.39
7.38
7.37
7.35
7.30
7.29
7.28
7.26
7.25
7.22
7.16
7.14
6.84
6.81
6.13
5.17
5.03
3.78
3.73
3.56
3.38
3.25
3.21
3.04
2.99
2.63
2.58
2.38
0.87
0.85
0.00
Bn2N
OMe
N
Ts
F3C
CDCl3, 300 MHz
3d'
4.04
6.04
4.06
2.02
2.02
1.00
1.02
1.01
2.03
3.01
2.03
1.04
1.02
3.00
f1 (ppm)

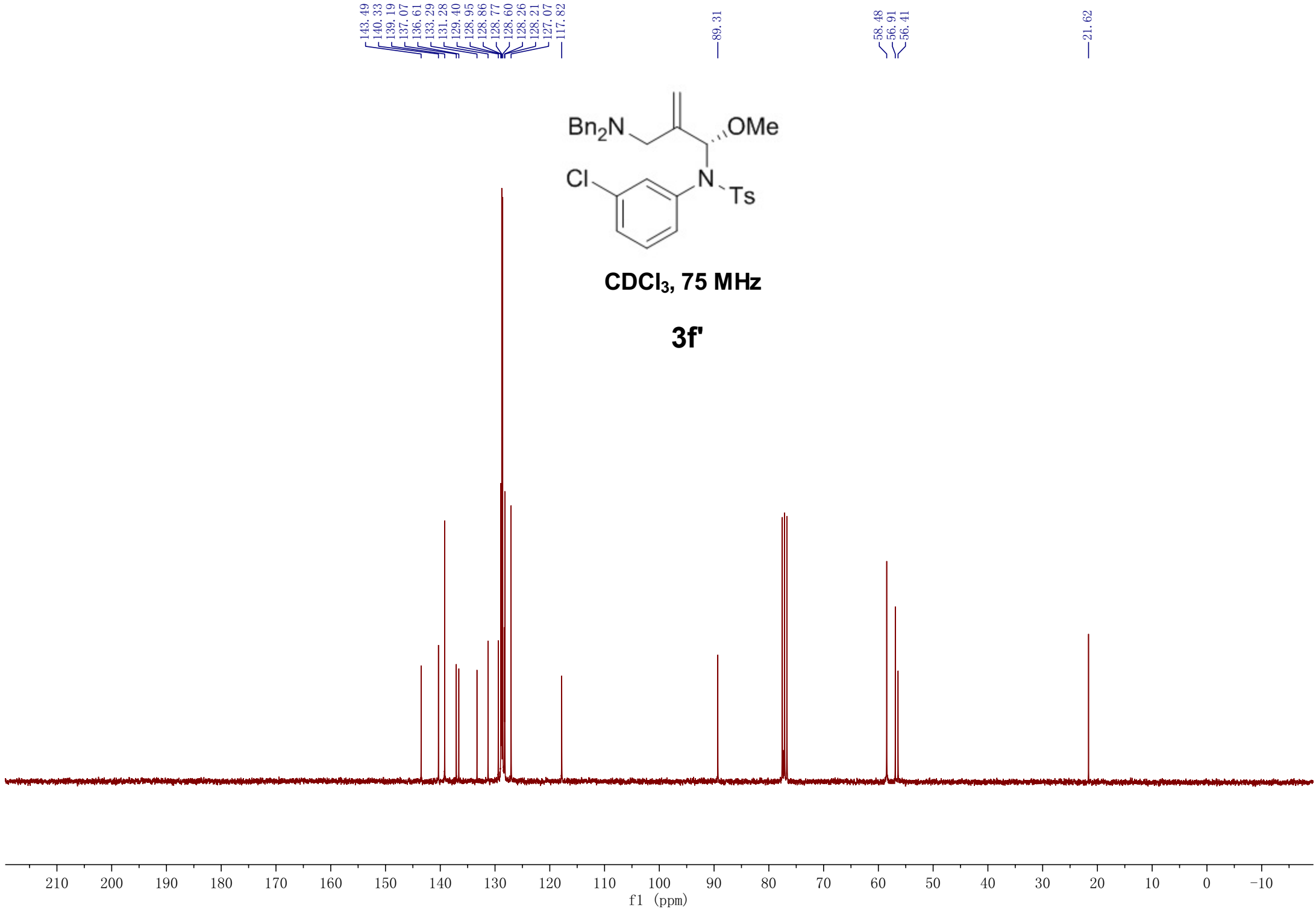

143.59
140.15
139.30
139.28
139.19
136.61
131.33
130.41
129.97
129.54
129.11
129.02
128.78
128.59
128.37
128.14
127.06
125.72
125.15
125.10
125.05
125.00
122.11
117.86
89.44
58.54
57.02
56.31
21.60
Bn2N
OMe
N
Ts
F3C
CDCl3, 75 MHz
3d'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

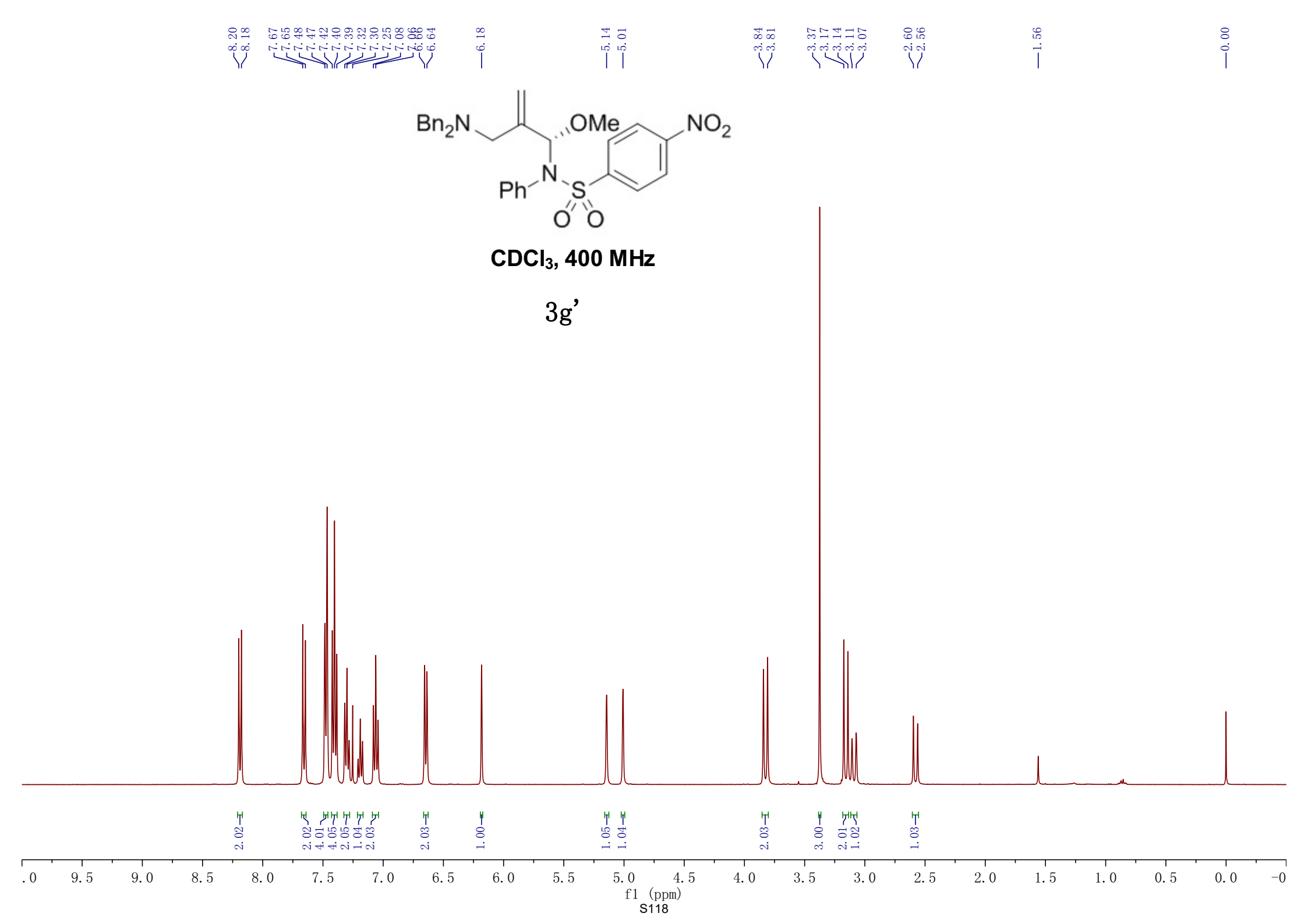

-62.52
Bn2N
OMe
N
Ts
F3C
CDCl3, 282 MHz
3d'
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

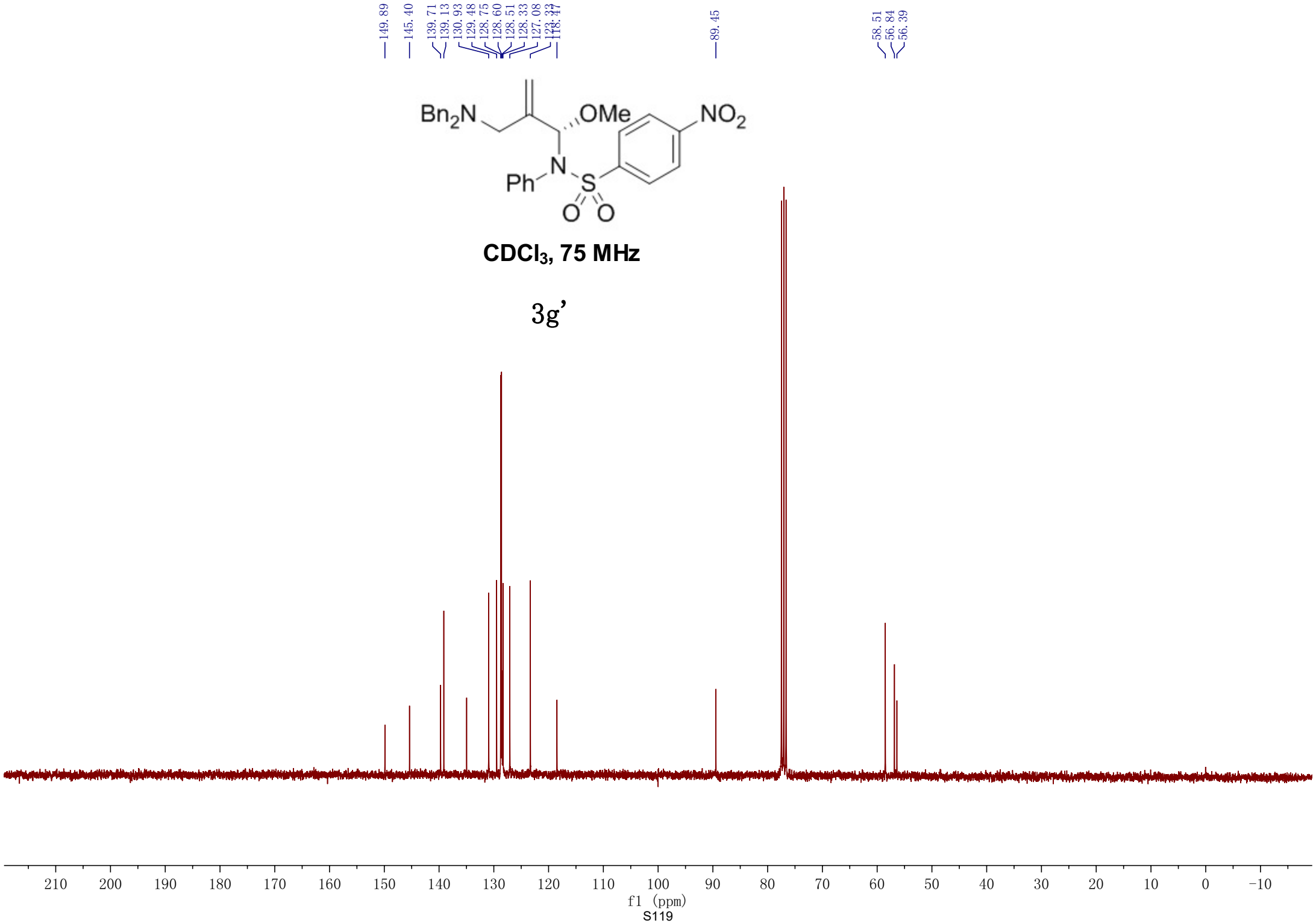

7.539
7.536
7.519
7.516
7.480
7.467
7.459
7.448
7.429
7.365
7.361
7.358
7.343
7.301
7.233
7.212
6.946
6.926
6.818
6.813
6.574
6.569
6.554
6.146
5.231
5.084
5.079
3.859
3.825
3.424
3.144
3.108
2.706
2.670
2.449
2.315
Bn2N
OMe
Cl
N
Ts
Me
CDCl3, 300 MHz
3e'
4.09
6.09
2.04
2.03
1.02
1.00
1.00
1.00
1.00
1.01
2.00
3.01
2.02
1.02
1.02
3.09
3.04
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)

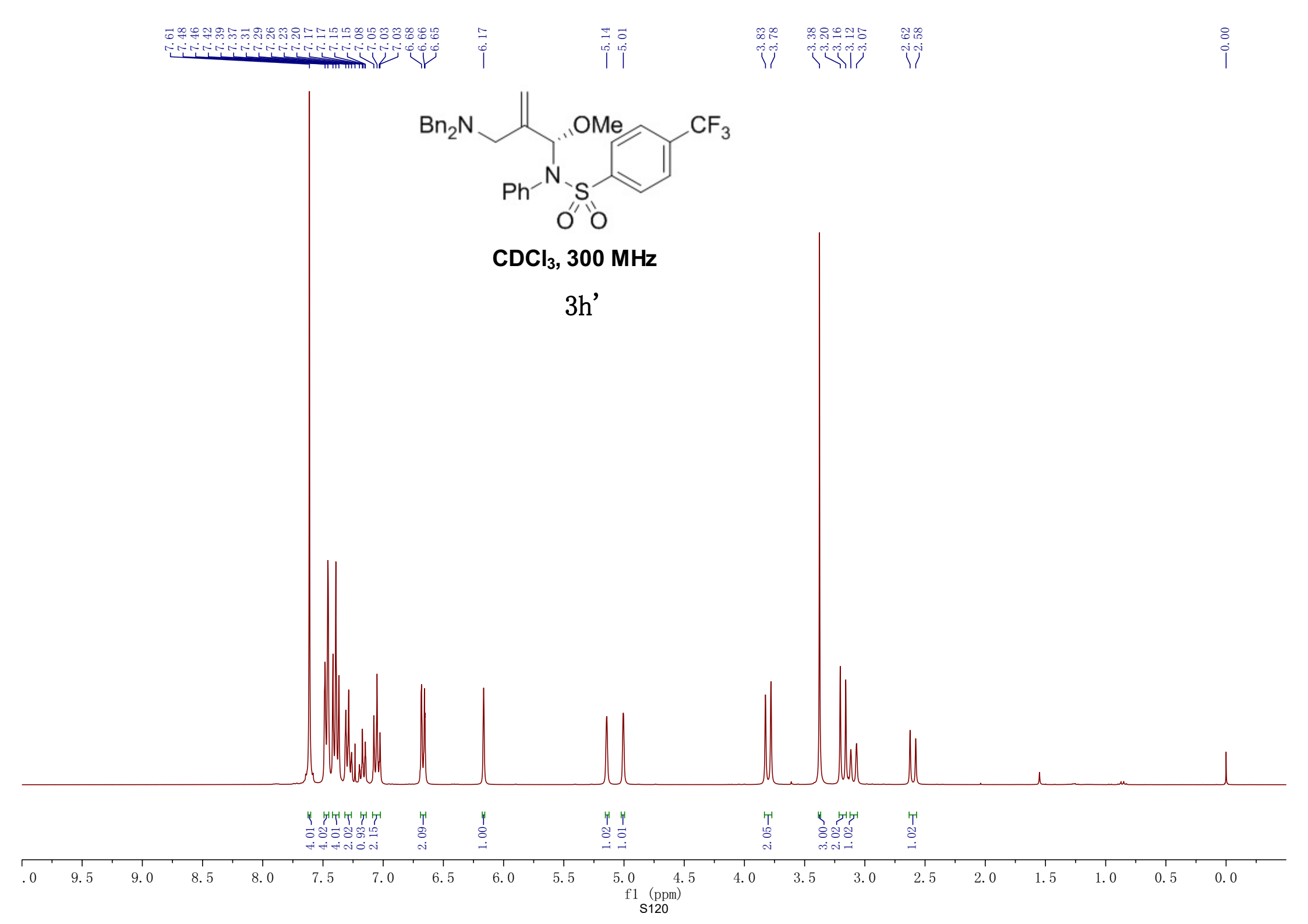

143.39
140.41
139.23
136.76
136.01
134.43
133.32
131.51
130.09
129.40
128.94
128.76
128.59
128.23
127.05
117.68
89.33
58.46
56.86
56.42
21.64
19.85
Bn2N
OMe
Cl
N
Ts
Me
CDCl3, 100 MHz
3e'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

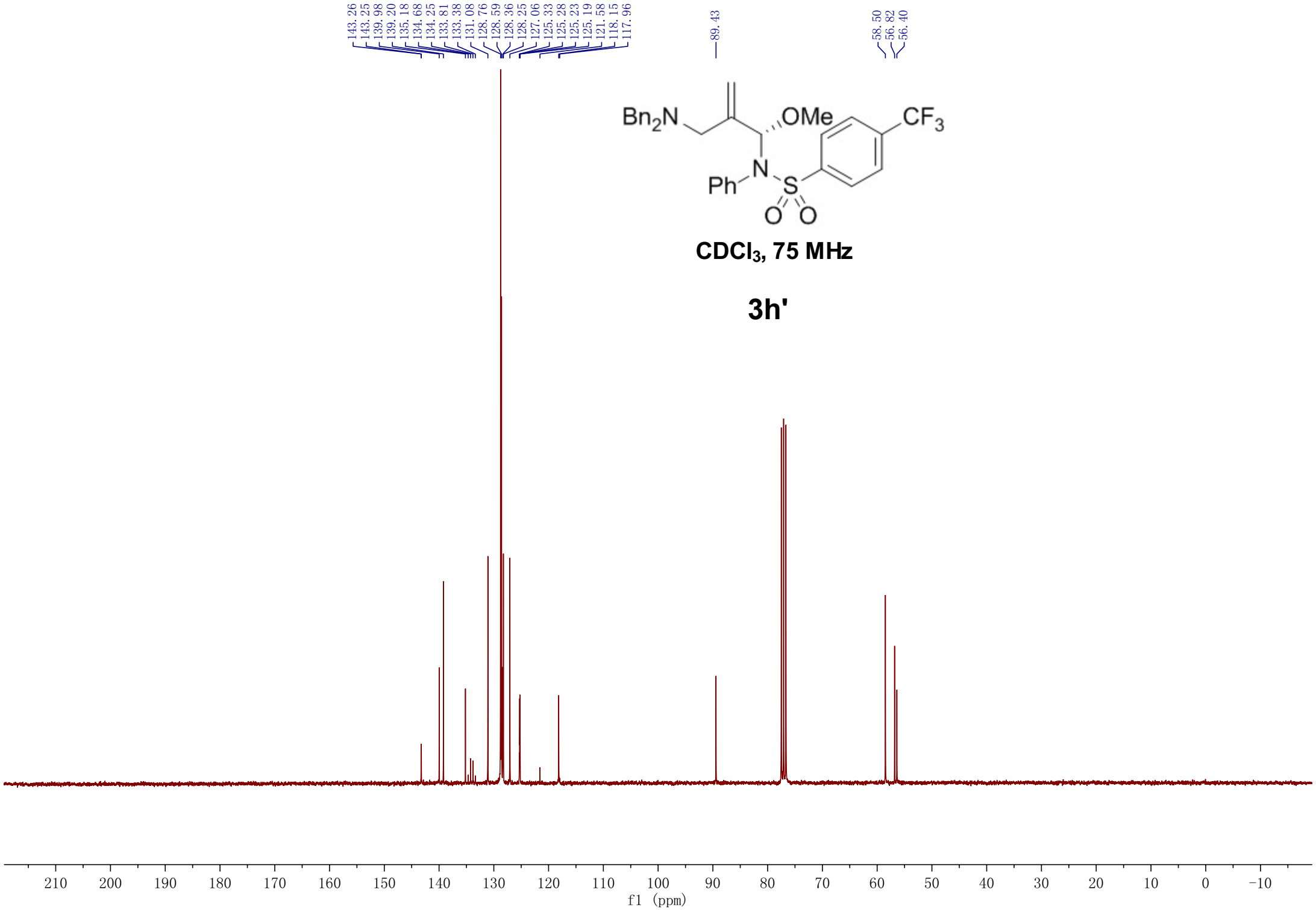

7.53
7.51
7.46
7.44
7.42
7.35
7.34
7.32
7.28
7.22
7.20
7.18
7.03
7.01
6.99
6.82
6.68
6.66
6.17
5.22
5.08
3.86
3.82
3.42
3.26
3.23
3.13
3.10
2.69
2.65
2.43
Bn2N
OMe
Cl
N
Ts
CDCl3, 400 MHz
3f'
4.01
6.05
2.04
3.06
1.08
1.00
1.03
1.01
1.03
1.04
2.01
3.01
2.04
1.01
1.02
3.00
f1 (ppm)

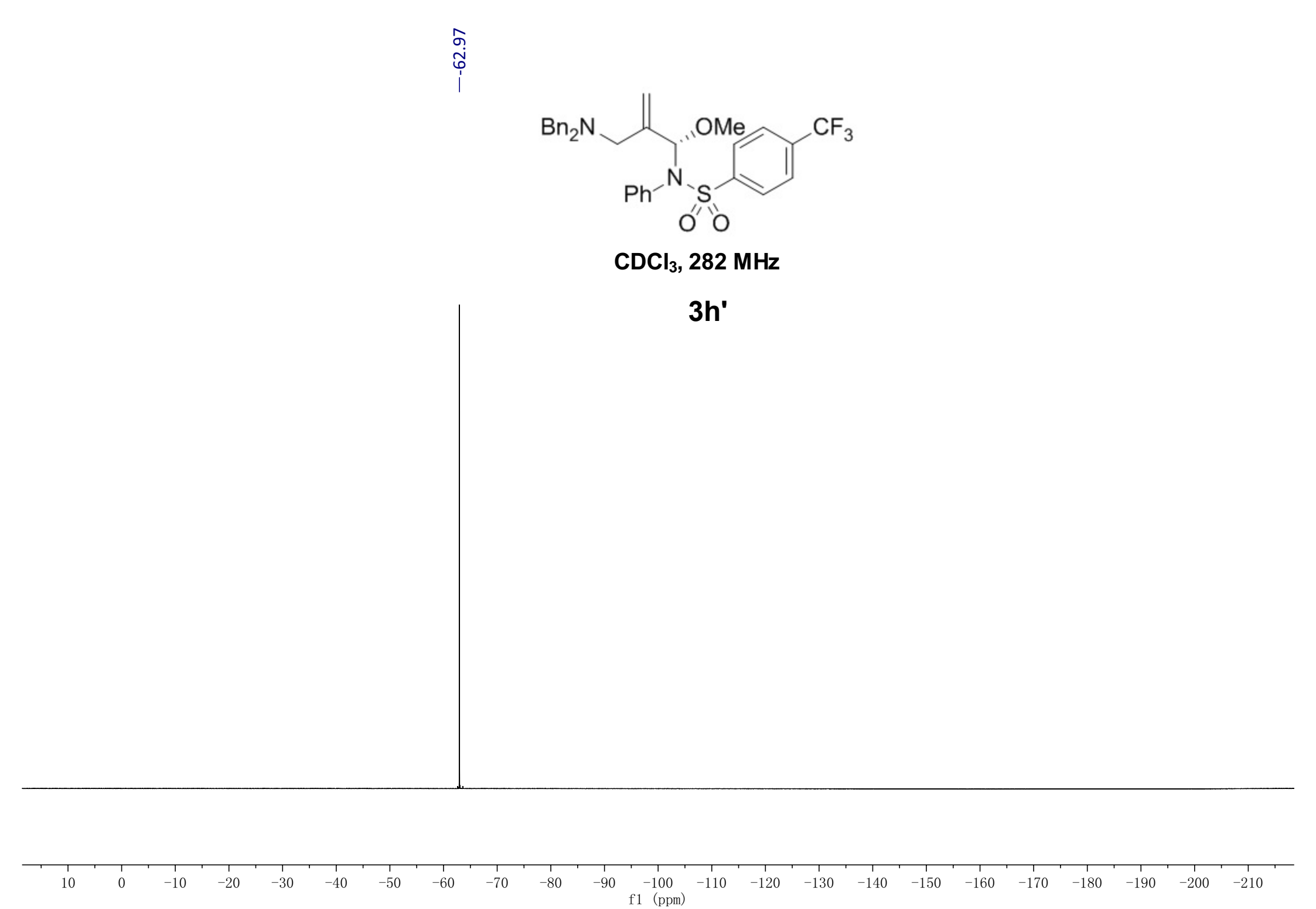

143.49
140.33
139.19
137.07
136.61
133.29
131.28
129.40
128.95
128.86
128.77
128.60
128.26
128.21
127.07
117.82
89.31
58.48
56.91
56.41
21.62
Bn2N
OMe
Cl
N
Ts
CDCl3, 75 MHz
3f'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

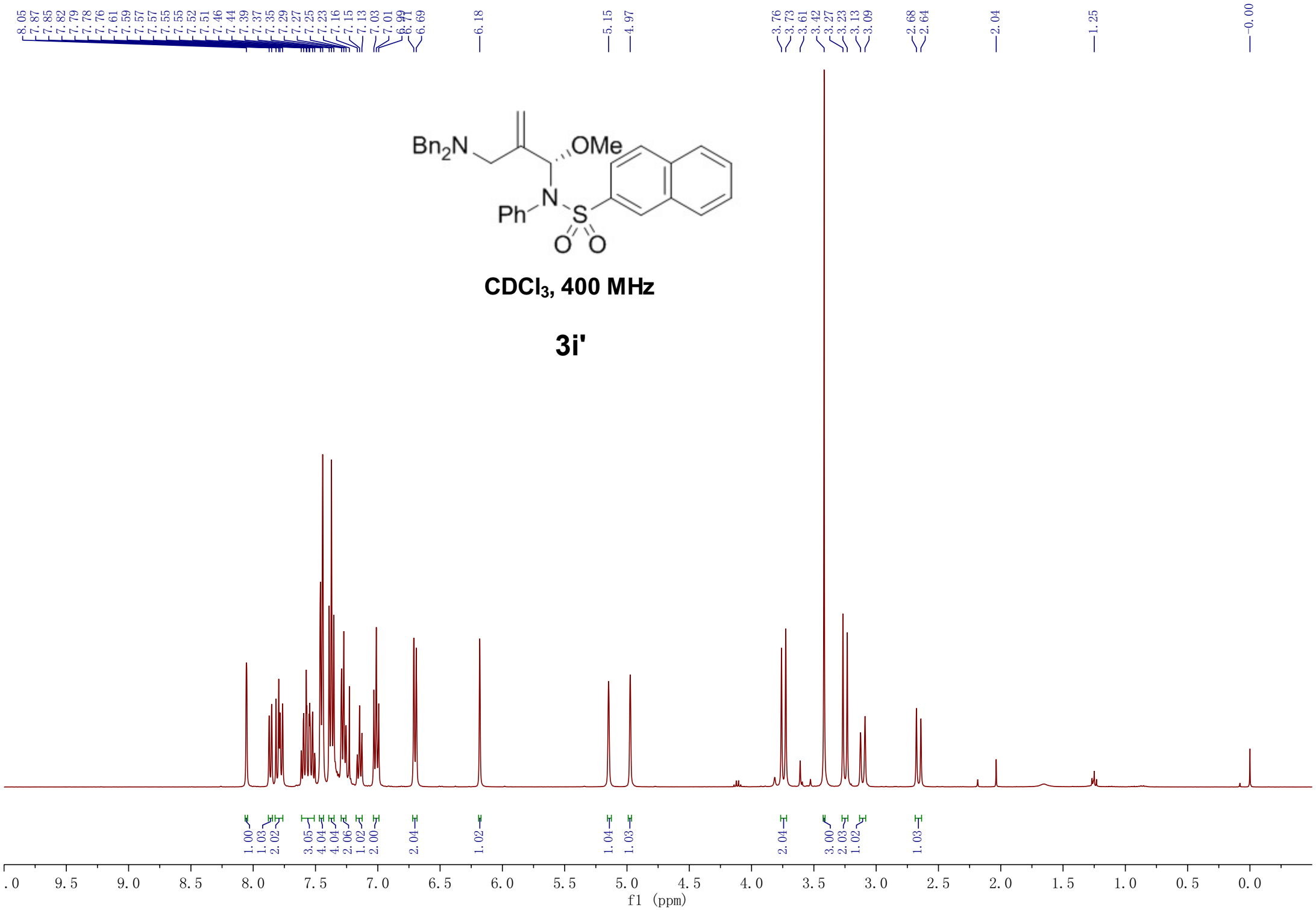

8.20
8.18
7.67
7.65
7.48
7.47
7.42
7.40
7.39
7.32
7.30
7.25
7.08
6.64
6.18
5.14
5.01
3.84
3.81
3.37
3.17
3.14
3.11
3.07
2.60
2.56
1.56
0.00
Bn2N
OMe
NO2
N
Ph
S
O
O
CDCl3, 400 MHz
3g'
2.02
2.02
4.01
4.05
2.05
1.04
2.03
2.03
1.00
1.05
1.04
2.03
3.00
2.01
1.02
1.03
f1 (ppm)

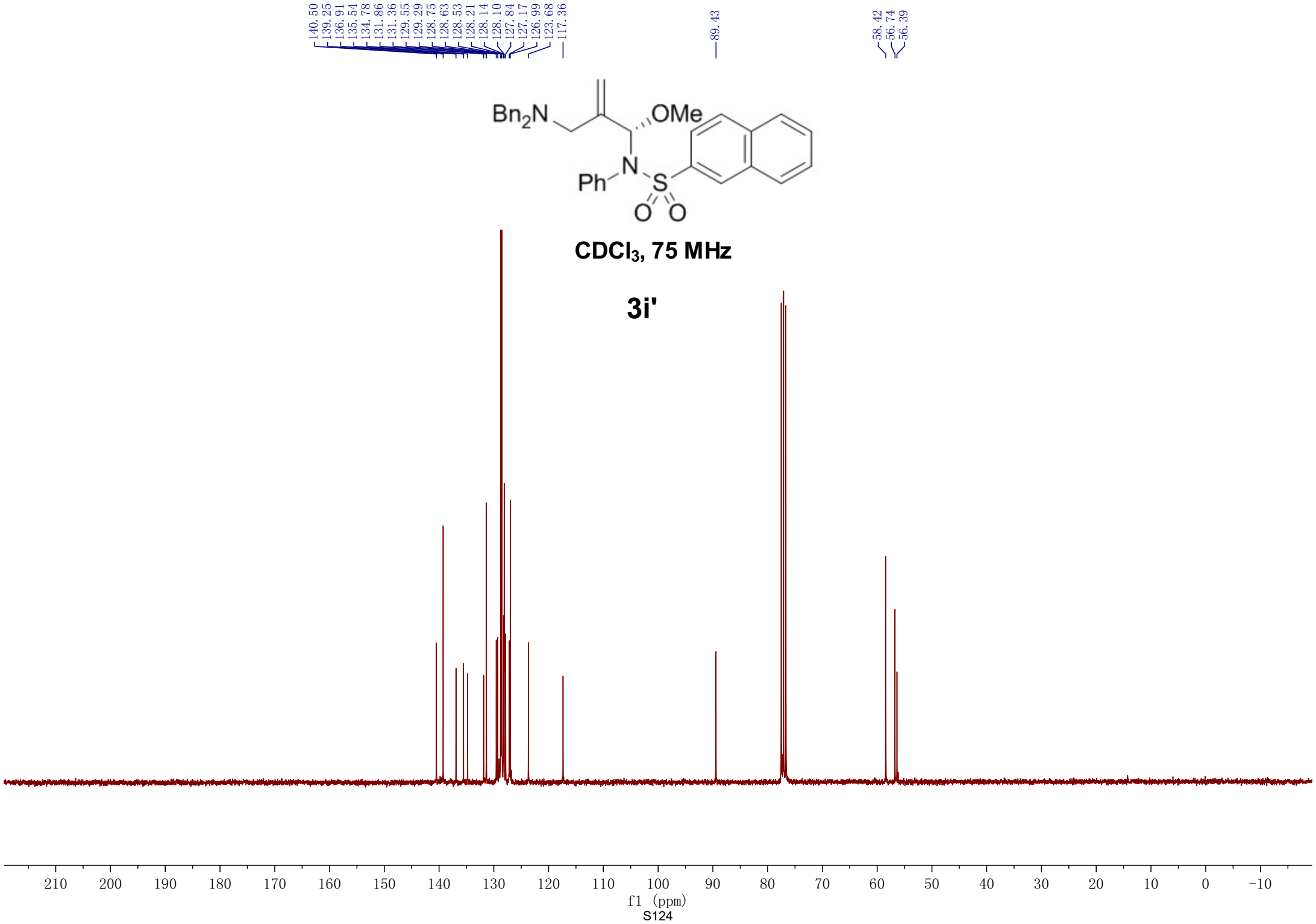

149.89
145.40
139.71
139.13
130.93
129.48
128.75
128.60
128.51
128.33
127.08
89.45
58.51
56.84
56.39
Bn2N
OMe
NO2
N
Ph
S
O
O
CDCl3, 75 MHz
3g'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

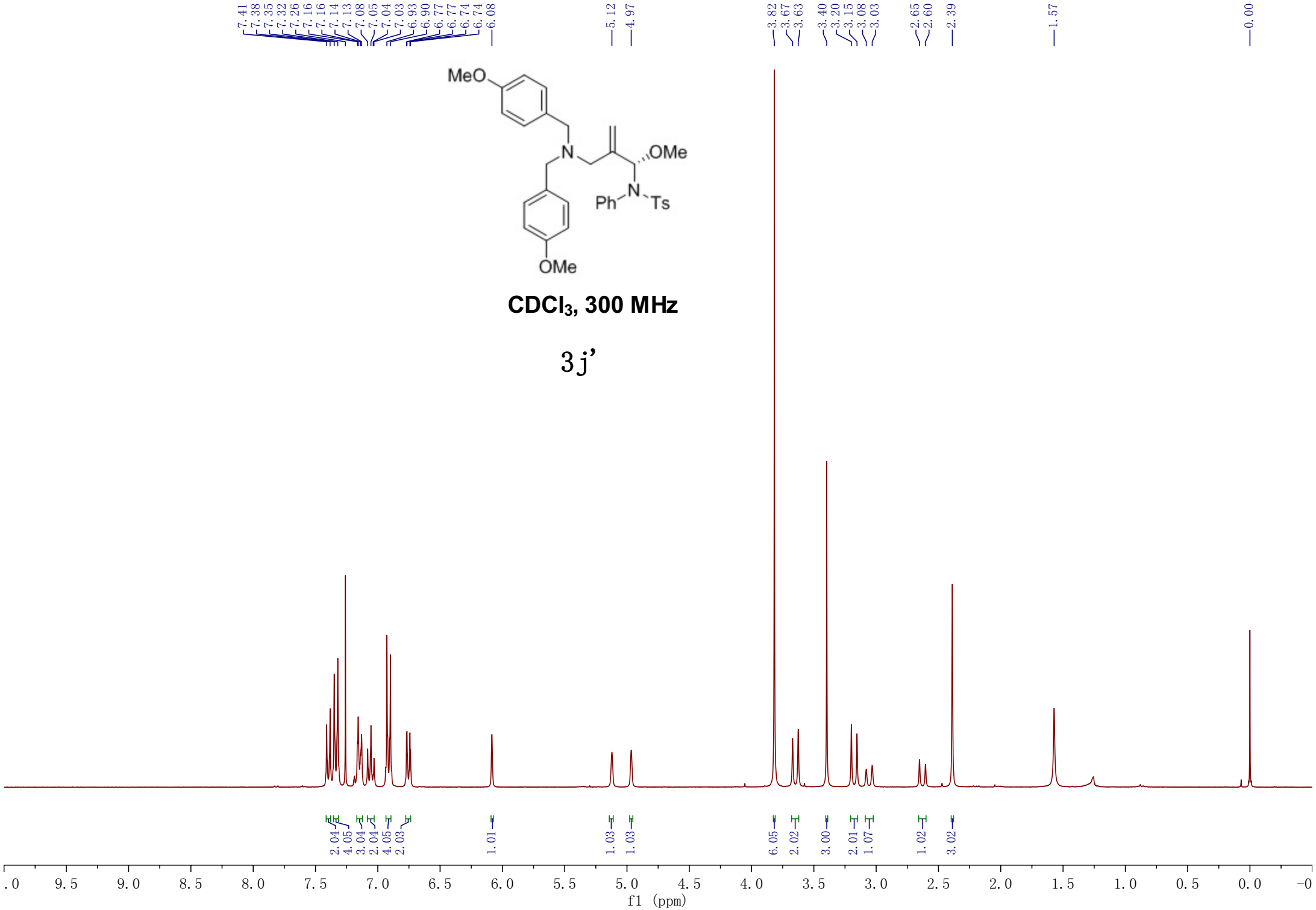

7.61
7.48
7.46
7.42
7.39
7.37
7.31
7.29
7.26
7.23
7.20
7.17
7.17
7.15
7.08
7.05
7.03
7.03
6.68
6.66
6.65
6.17
5.14
5.01
3.83
3.78
3.38
3.20
3.16
3.12
3.07
2.62
2.58
0.00
Bn2N
OMe
CF3
N
Ph
S
O
O
CDCl3, 300 MHz
3h'
4.01
4.02
4.01
2.02
0.93
2.15
2.09
1.00
1.02
1.01
2.05
3.00
2.02
1.02
1.02
f1 (ppm)

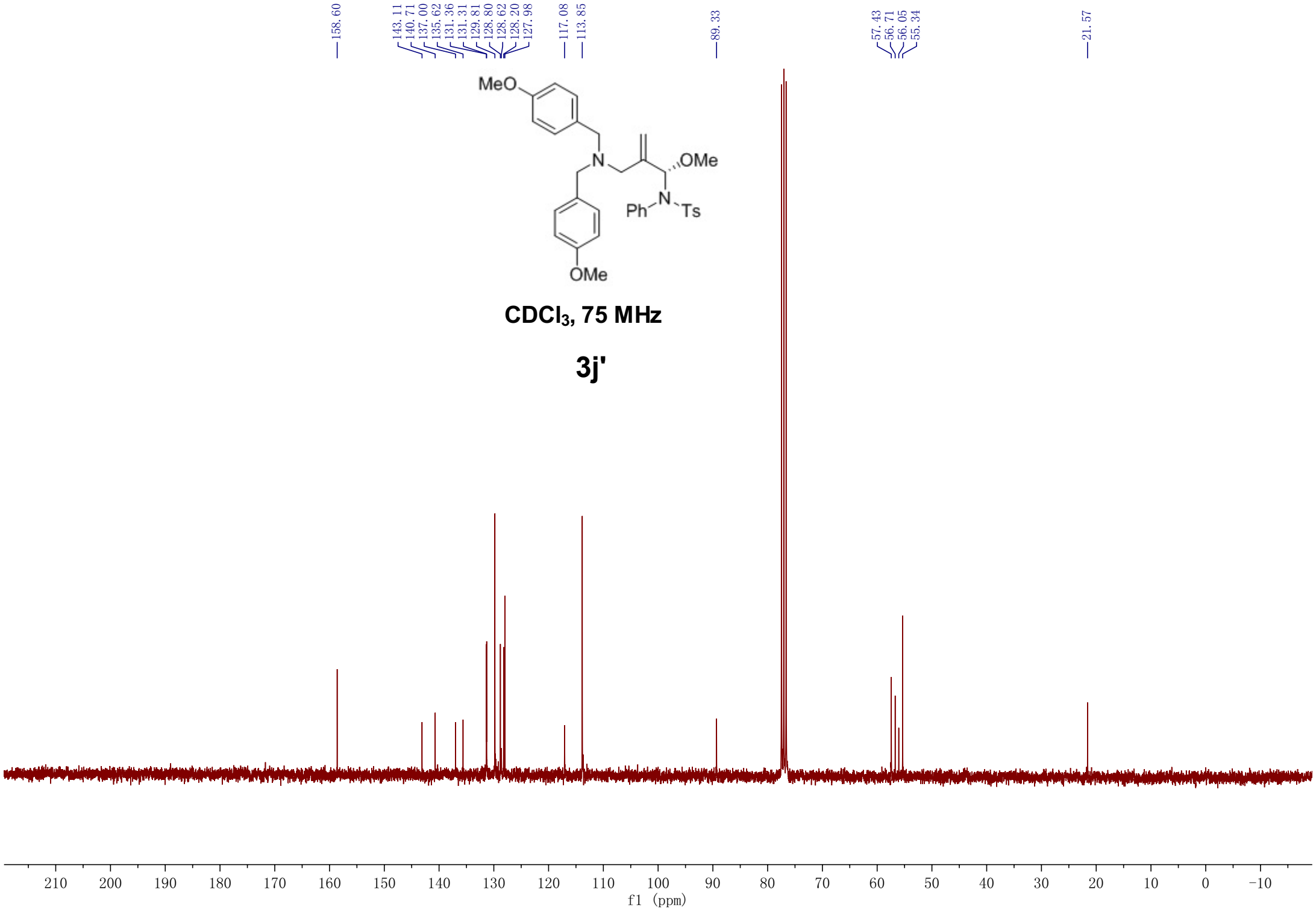

143.26
143.25
139.98
139.20
135.18
134.68
134.25
133.81
133.38
131.08
128.76
128.59
128.36
128.25
127.06
125.33
125.28
125.23
125.19
121.58
118.15
117.96
89.43
58.50
56.82
56.40
Bn2N
OMe
CF3
N
Ph
S
O
O
CDCl3, 75 MHz
3h'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

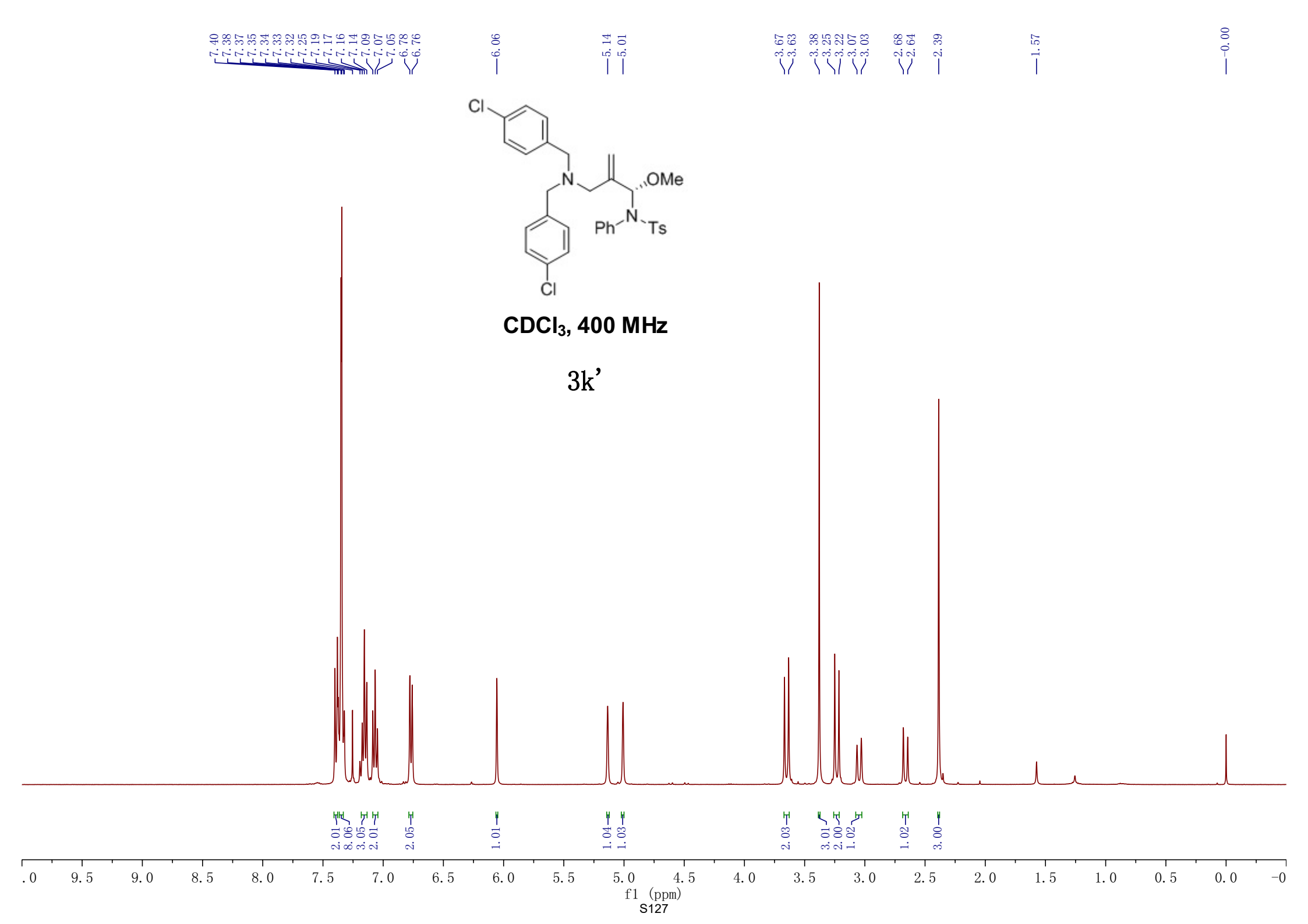

-62.97
Bn2N
OMe
CF3
N
Ph
S
O
O
CDCl3, 282 MHz
3h'
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

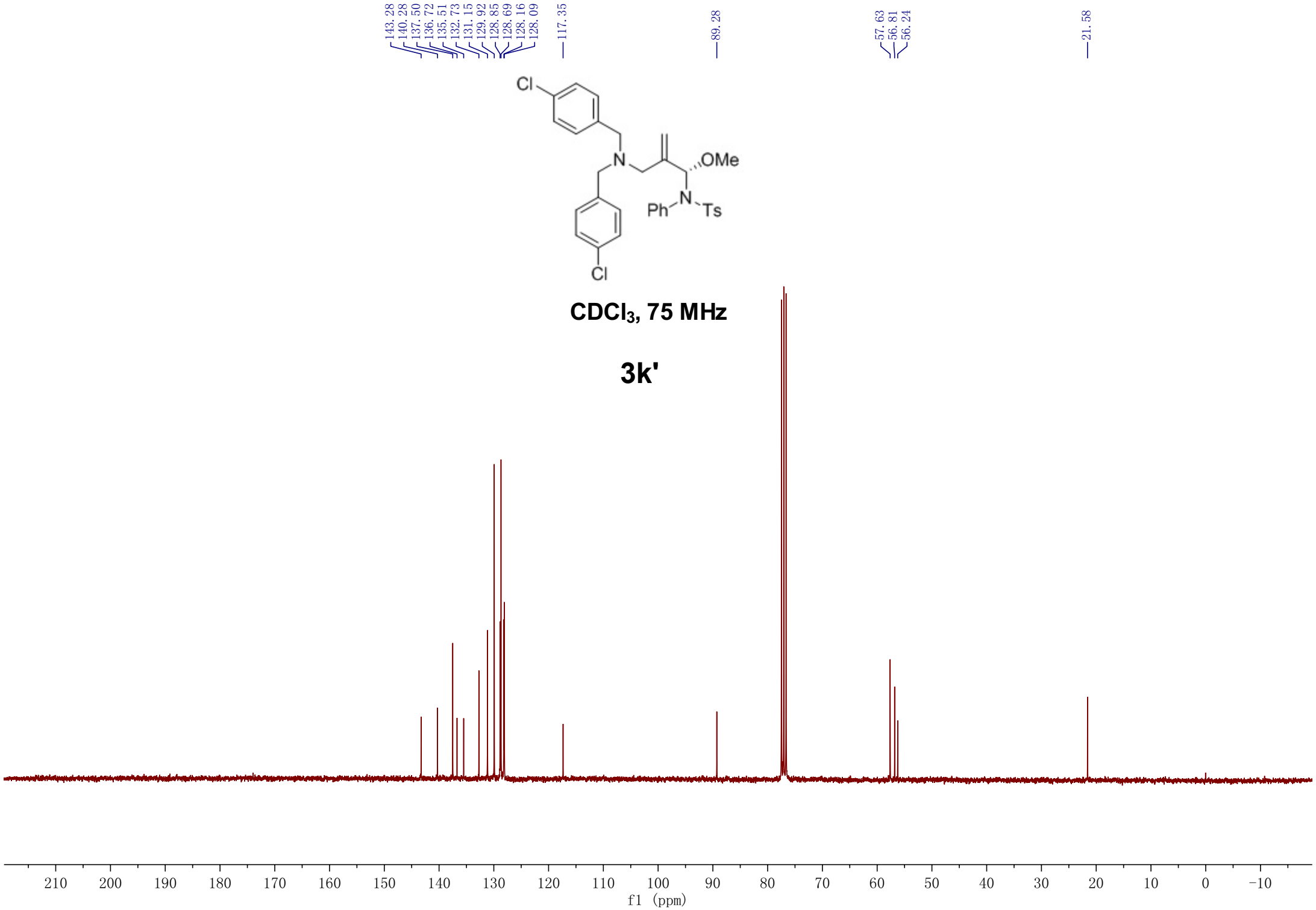

8.05
7.87
7.85
7.82
7.79
7.78
7.76
7.61
7.59
7.57
7.57
7.55
7.55
7.52
7.51
7.46
7.44
7.39
7.37
7.35
7.29
7.27
7.25
7.23
7.16
7.15
7.13
7.03
7.01
6.99
6.97
6.69
6.18
5.15
4.97
3.76
3.73
3.61
3.42
3.27
3.23
3.13
3.09
2.68
2.64
2.04
1.25
0.00
Bn2N
OMe
N
Ph
S
O
O
CDCl3, 400 MHz
3i'
1.00
1.03
2.02
3.05
4.04
4.04
2.06
1.02
2.00
2.04
1.02
1.04
1.03
2.04
3.00
2.03
1.02
1.03
f1 (ppm)

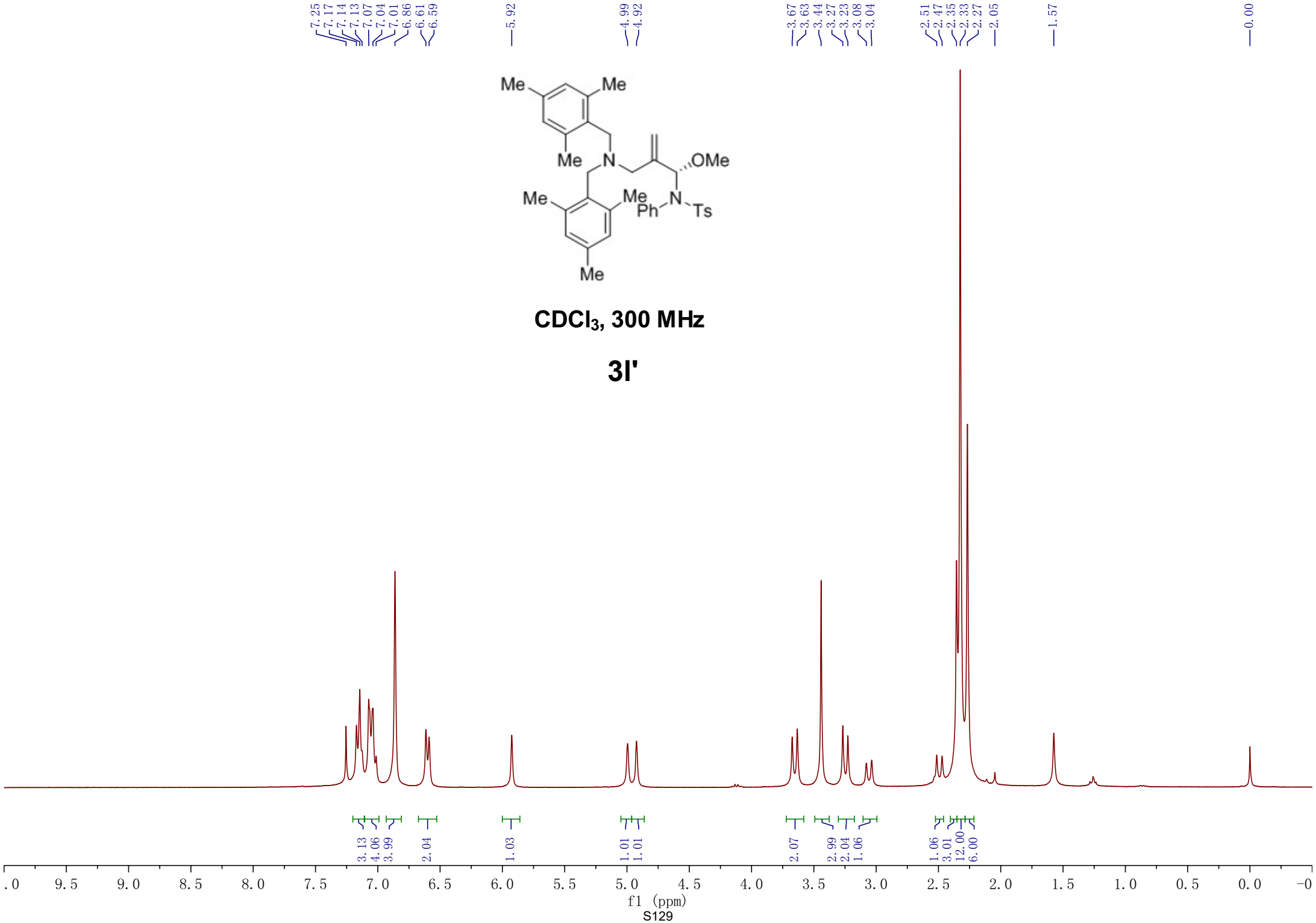

140.50
139.25
136.91
135.54
134.78
131.86
131.36
129.55
129.29
128.75
128.63
128.53
128.21
128.14
128.10
127.84
127.17
126.99
123.68
117.36
89.43
58.42
56.74
56.39
Bn2N
OMe
N
Ph
S
O
O
CDCl3, 75 MHz
3i'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

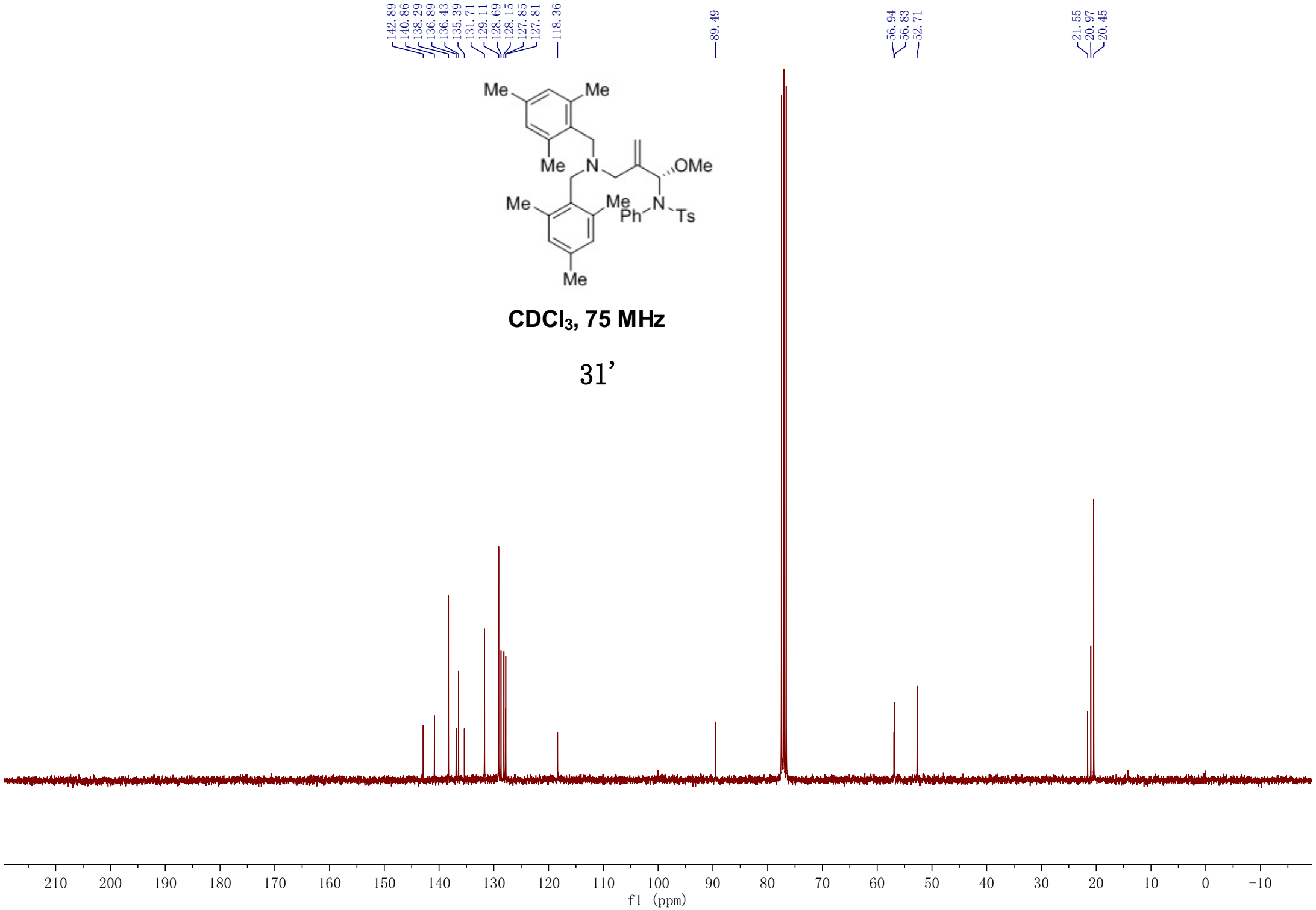

7.41
7.38
7.35
7.32
7.26
7.16
7.14
7.13
7.08
7.05
7.04
7.03
6.93
6.90
6.77
6.77
6.74
6.74
6.08
5.12
4.97
3.82
3.67
3.63
3.40
3.20
3.15
3.08
3.03
2.65
2.60
2.39
1.57
0.00
MeO
N
OMe
N
Ph
Ts
OMe
CDCl3, 300 MHz
3j'
2.04
4.05
3.04
2.04
4.05
2.03
1.01
1.03
1.03
6.05
2.02
3.00
2.01
1.07
1.02
3.02
f1 (ppm)

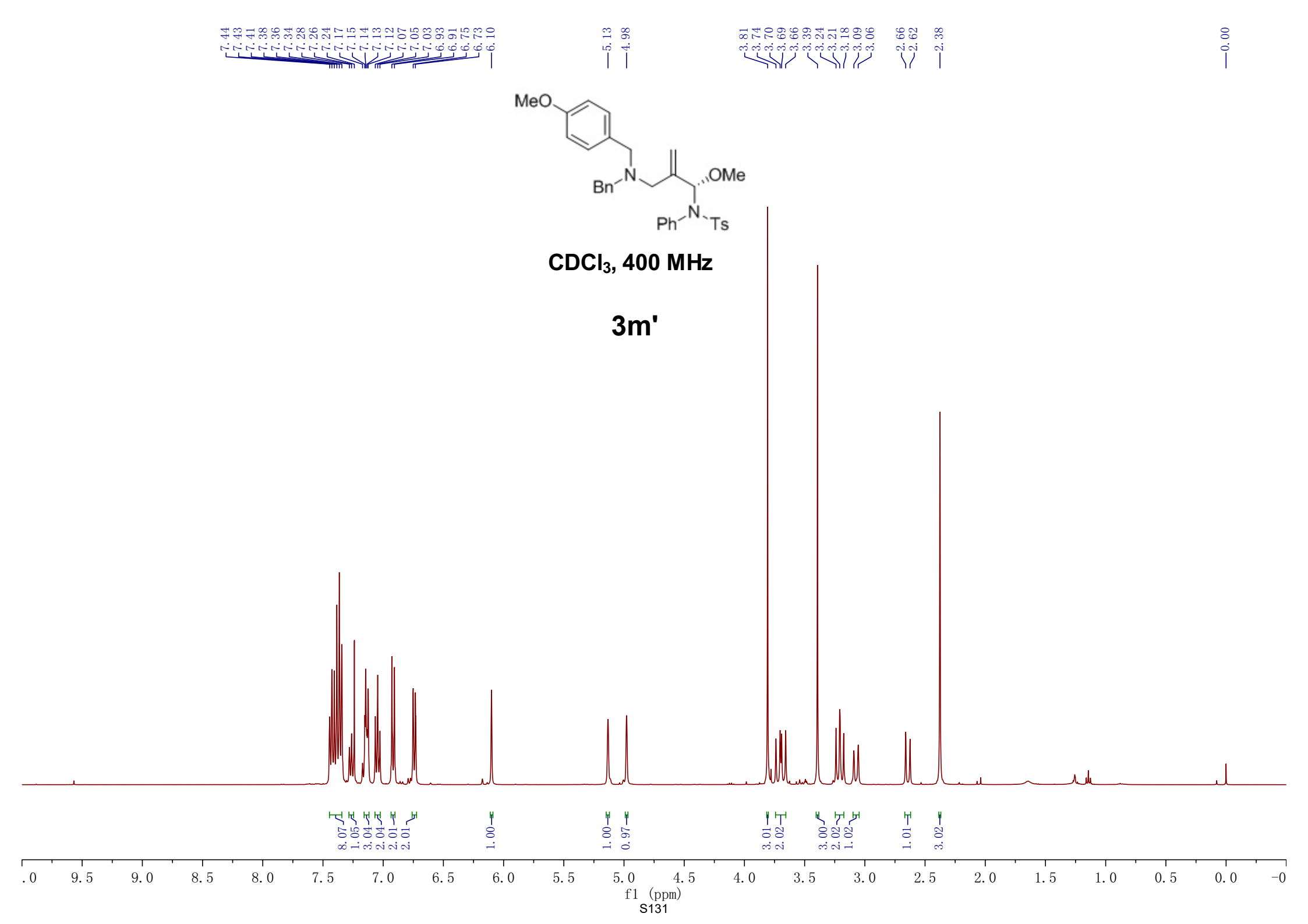

158.60
143.11
140.71
137.00
135.62
131.36
131.31
129.81
128.80
128.62
128.20
127.98
117.08
113.85
89.33
57.43
56.71
56.05
55.34
21.57
MeO
N
OMe
N
Ph
Ts
OMe
CDCl3, 75 MHz
3j'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

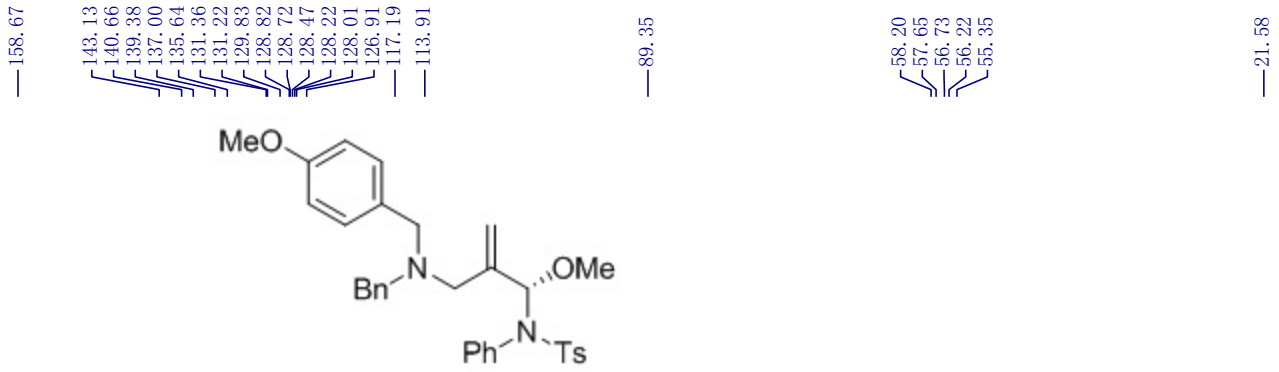

7.40
7.38
7.37
7.35
7.34
7.33
7.32
7.25
7.19
7.17
7.16
7.14
7.09
7.07
7.05
6.78
6.76
6.06
5.14
5.01
3.67
3.63
3.38
3.25
3.22
3.07
3.03
2.68
2.64
2.39
1.57
0.00
Cl
N
OMe
Ph
N
Ts
Cl
CDCl3, 400 MHz
3k'
2.01
8.06
3.05
2.01
2.05
1.01
1.04
1.03
2.03
3.01
2.00
1.02
1.02
3.00
f1 (ppm)


143.28
140.28
137.50
136.72
135.51
132.73
131.15
129.92
128.85
128.69
128.16
128.09
117.35
89.28
57.63
56.81
56.24
21.58
Cl
N
OMe
Ph
N
Ts
Cl
CDCl3, 75 MHz
3k'
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)


7.25
7.17
7.14
7.13
7.07
7.04
7.01
6.86
6.61
6.59
5.92
4.99
4.92
3.67
3.63
3.44
3.27
3.23
3.08
3.04
2.51
2.47
2.35
2.33
2.27
2.05
1.57
0.00
Me
Me
Me
N
OMe
Me
Me
Ph
N
Ts
Me
CDCl3, 300 MHz
3l'
3.13
4.06
3.99
2.04
1.03
1.01
1.01
2.07
2.99
2.04
1.06
1.06
3.01
12.00
6.00
f1 (ppm)

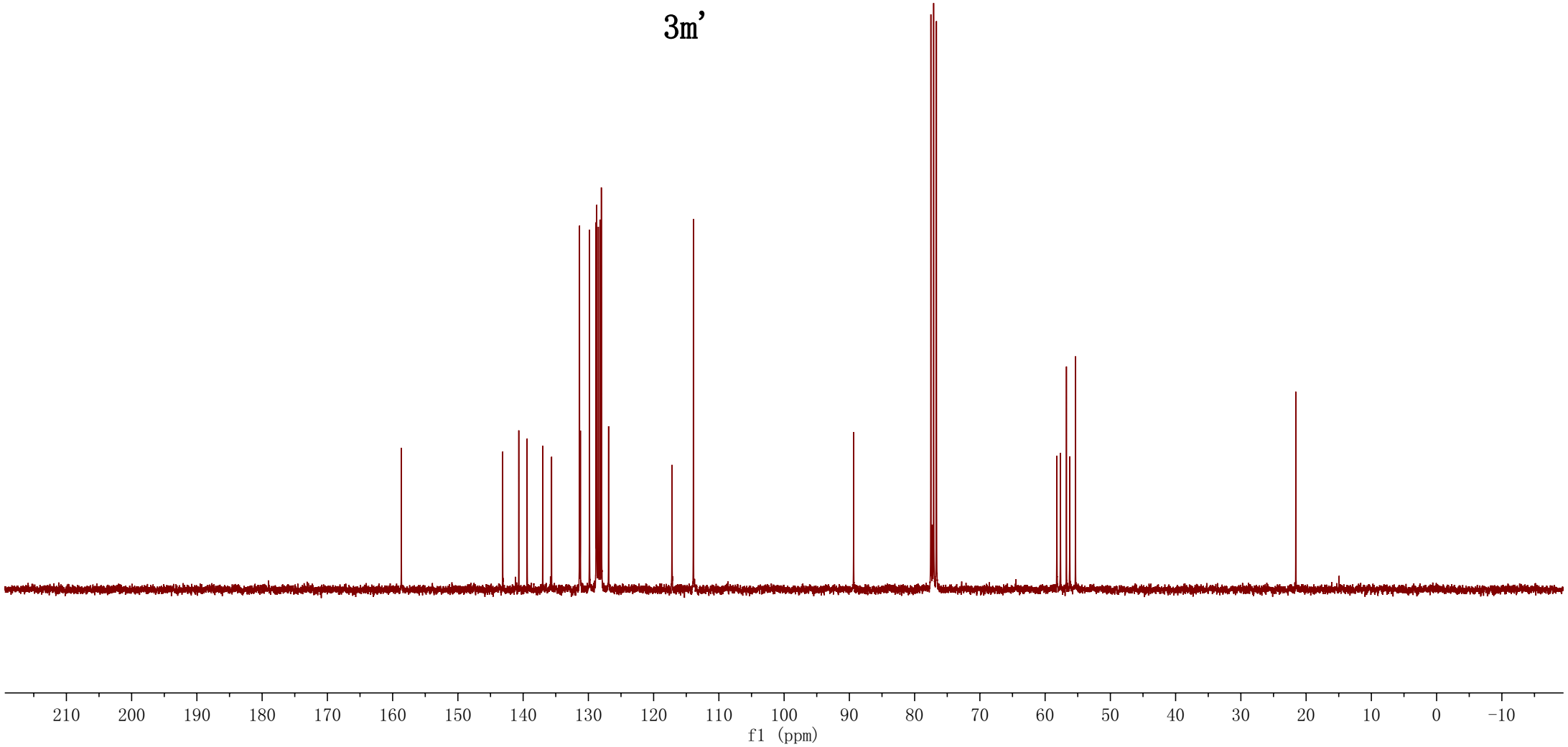

142.89
140.86
138.29
136.89
136.43
135.39
131.71
129.11
128.69
128.15
127.85
127.81
118.36
89.49
56.94
56.83
52.71
21.55
20.97
20.45
Me
Me
Me
N
OMe
Me
Me
Ph
N
Ts
Me
CDCl3, 75 MHz
31’
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

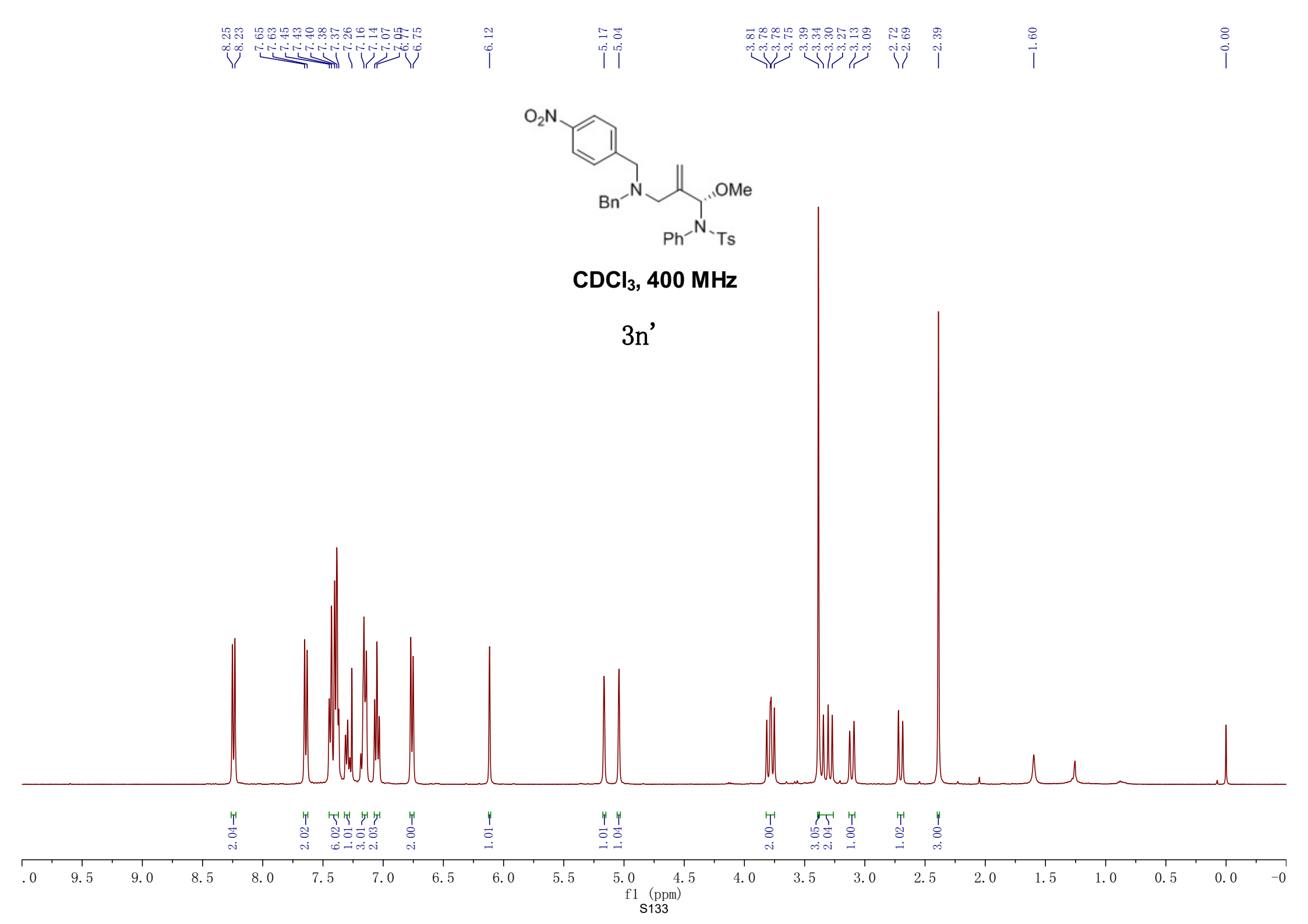

7.44
7.43
7.41
7.38
7.36
7.34
7.28
7.26
7.24
7.17
7.15
7.14
7.13
7.12
7.07
7.05
7.03
6.93
6.91
6.75
6.73
6.10
5.13
4.98
3.81
3.74
3.70
3.69
3.66
3.39
3.24
3.21
3.18
3.09
3.06
2.66
2.62
2.38
0.00
MeO
Bn
N
OMe
Ph
N
Ts
CDCl3, 400 MHz
3m'
8.07
1.05
3.04
2.04
2.01
2.01
1.00
1.00
0.97
3.01
2.02
3.00
2.02
1.02
1.01
3.02
f1 (ppm)

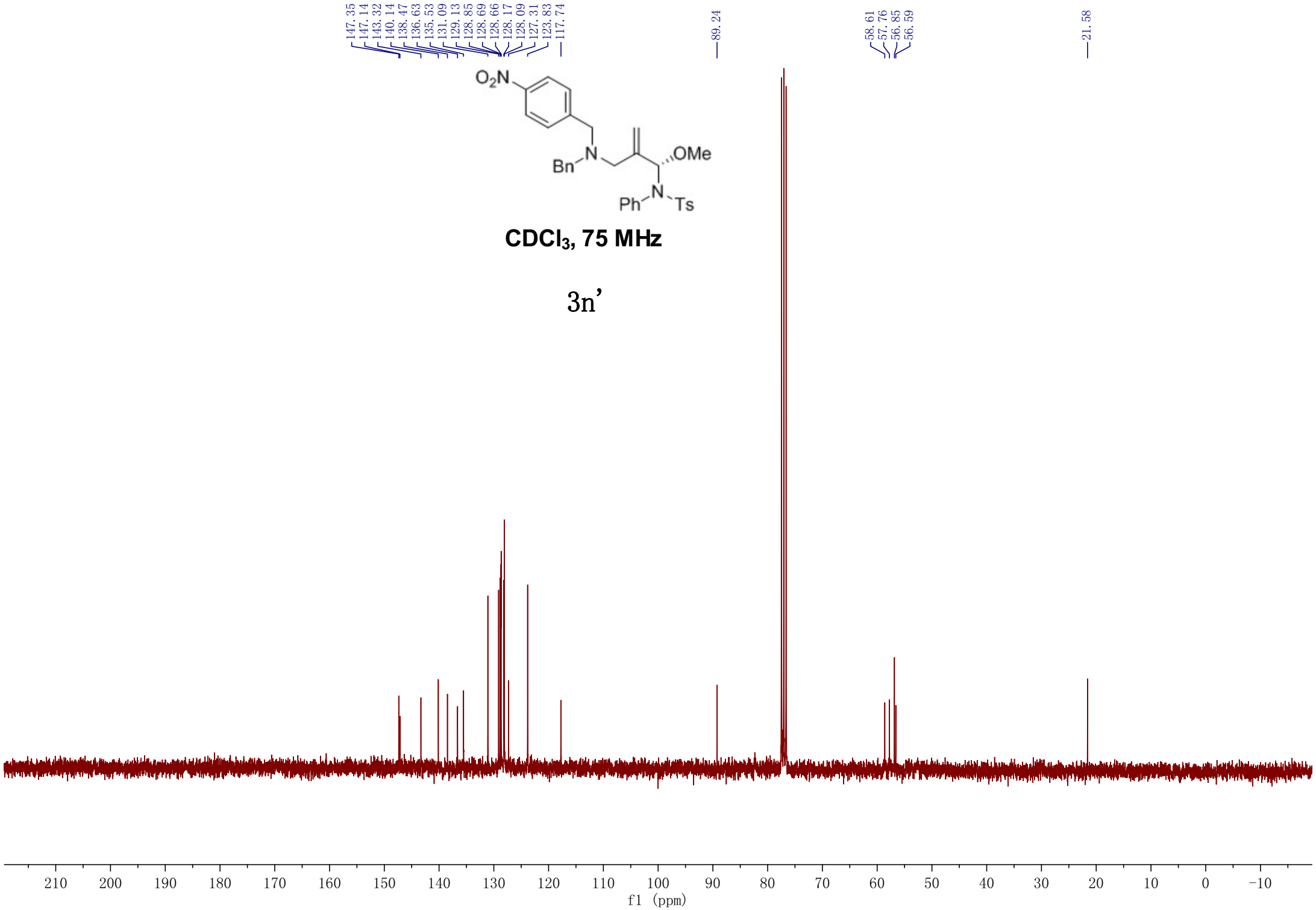


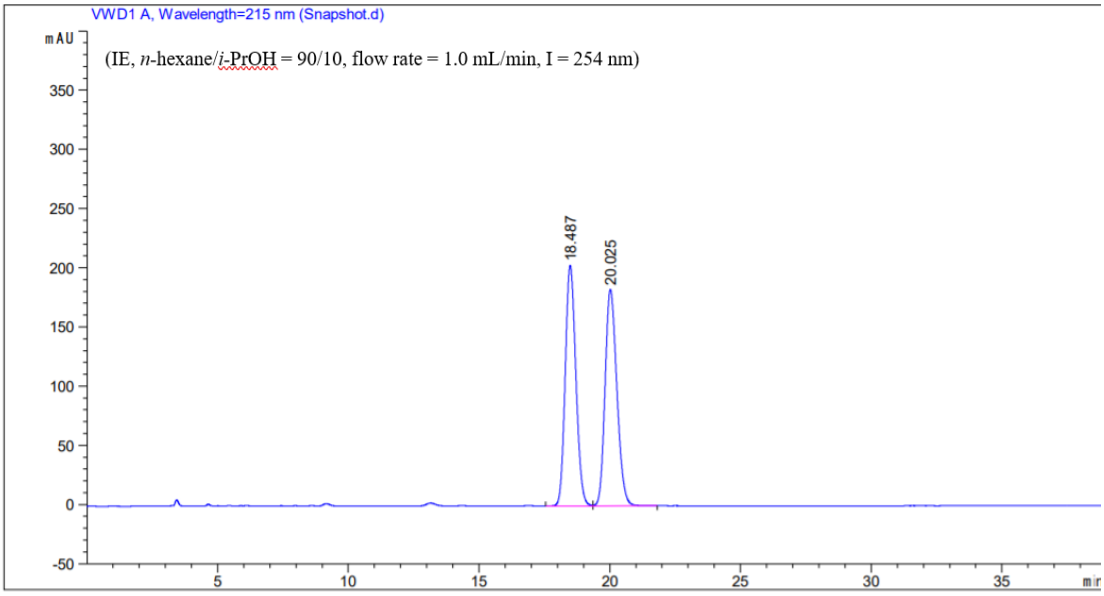
$CDCl_3$, 75 MHz

3m'



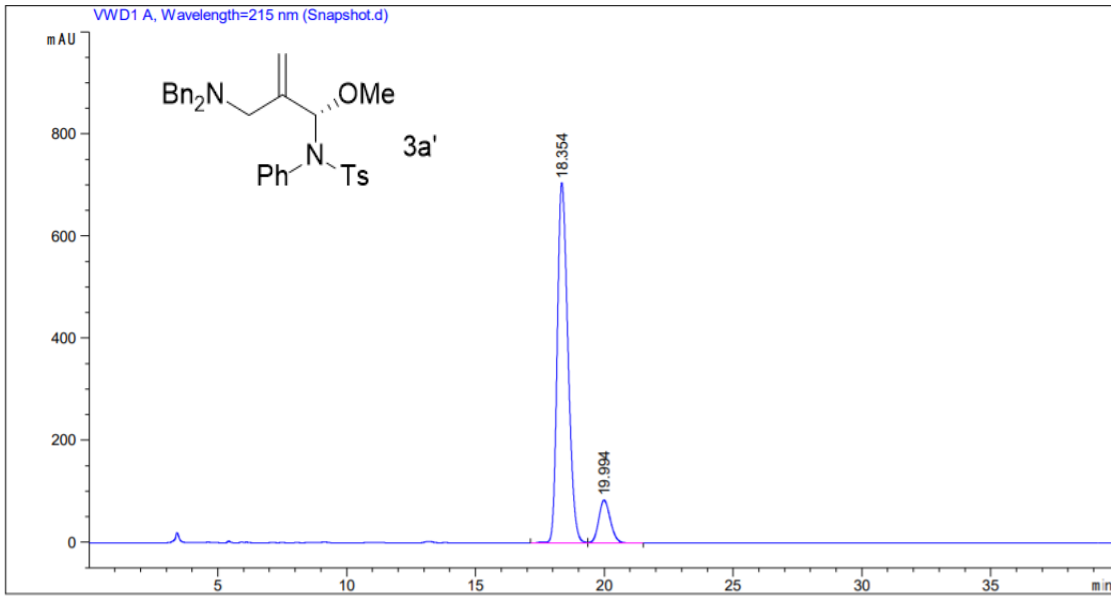

8.25
8.23
7.65
7.63
7.45
7.43
7.40
7.38
7.37
7.26
7.16
7.14
7.07
6.77
6.75
6.12
5.17
5.04
3.81
3.78
3.78
3.75
3.39
3.34
3.30
3.27
3.13
3.09
2.72
2.69
2.39
1.60
0.00
O2N
Bn
N
OMe
Ph
N
Ts
CDCl3, 400 MHz
3n'
2.04
2.02
6.02
1.01
3.01
2.03
2.00
1.01
1.01
1.04
2.00
3.05
2.04
1.00
1.02
3.00
f1 (ppm)


147.35
147.14
143.32
140.14
138.47
136.63
135.53
131.09
129.13
128.85
128.69
128.66
128.17
128.09
127.31
123.83
117.74
89.24
58.61
57.76
56.85
56.59
21.58
O2N
Bn
N
OMe
Ph
N
Ts
CDCl3, 75 MHz
3n'
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)



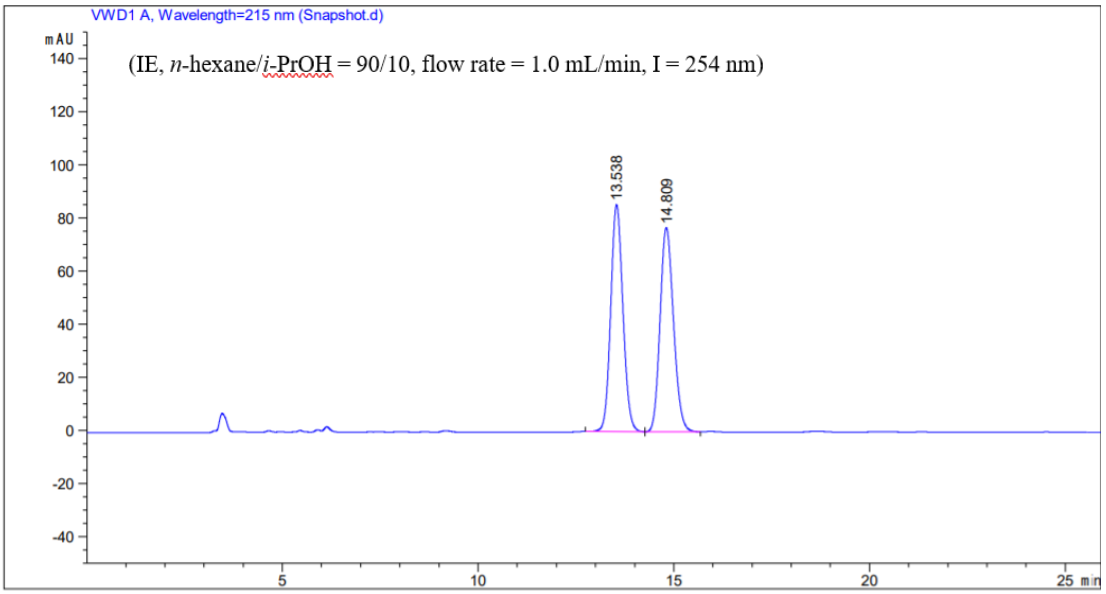
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.487	BV	0.4390	5734.35156	203.34953	49.9923
2	20.025	VB	0.4879	5736.12402	182.91193	50.0077

总量 : 1.14705e4 386.26146

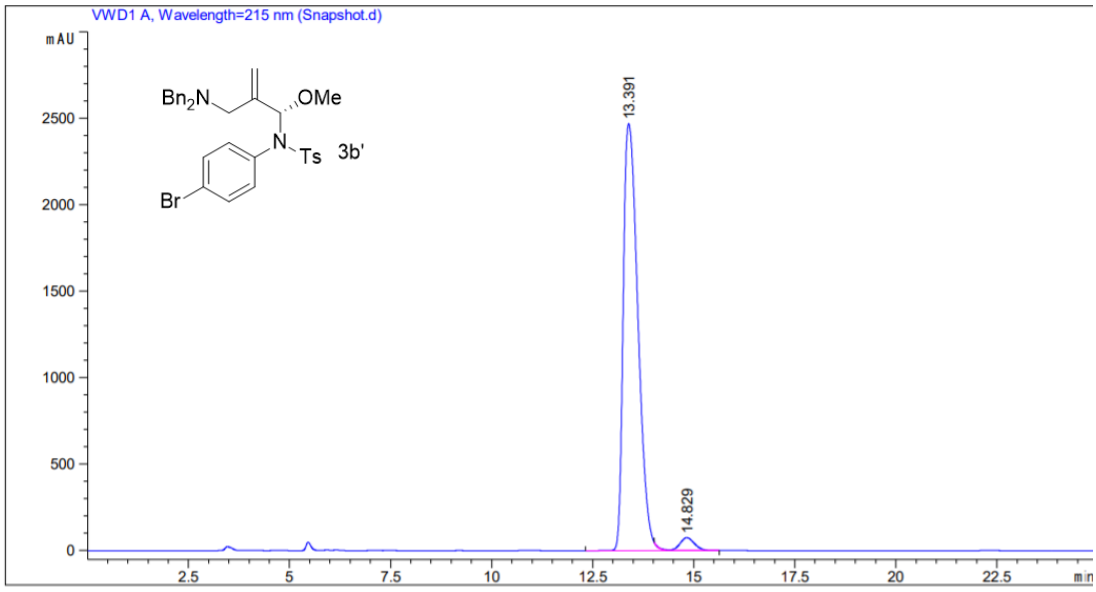


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.354	VV R	0.4462	2.03382e4	706.16089	88.5076
2	19.994	VB	0.4861	2640.84644	84.14775	11.4924

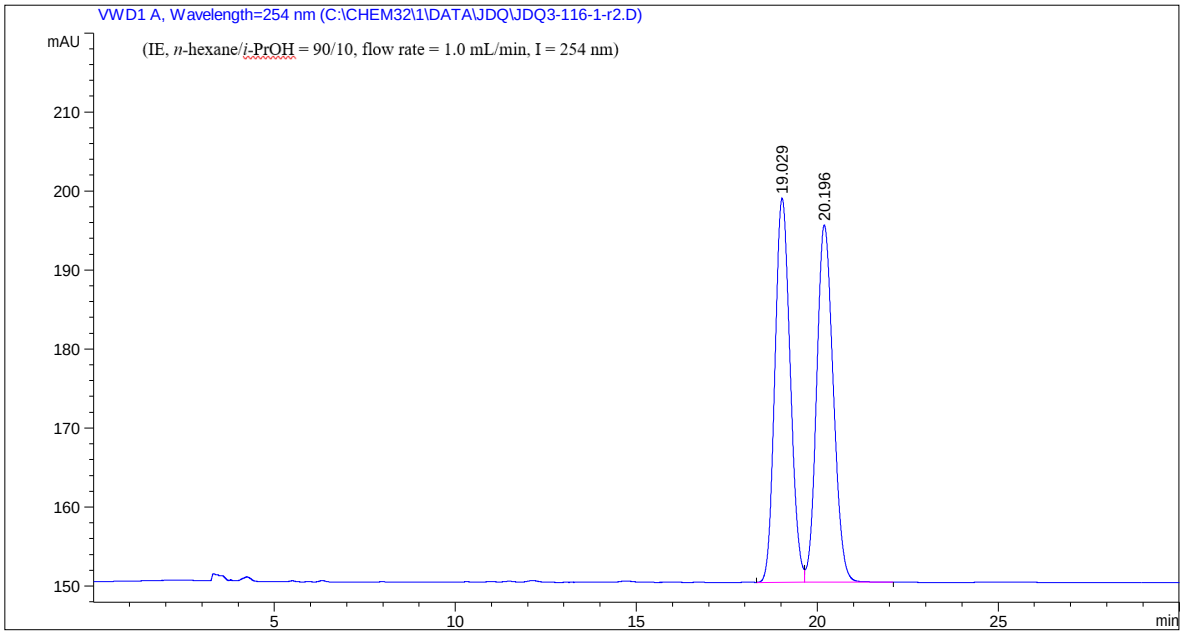
总量 : 2.29790e4 790.30864



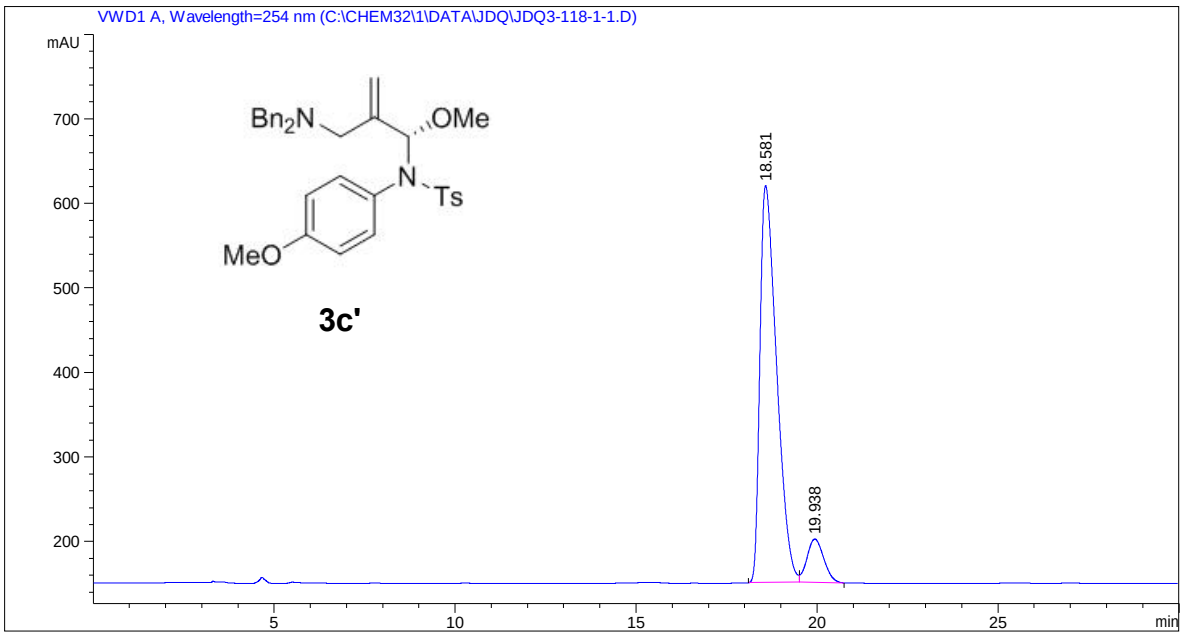
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.538	BB	0.3359	1850.92090	85.38480	50.2395
2	14.809	BB	0.3702	1833.27380	76.87555	49.7605
总量：				3684.19470	162.26035	



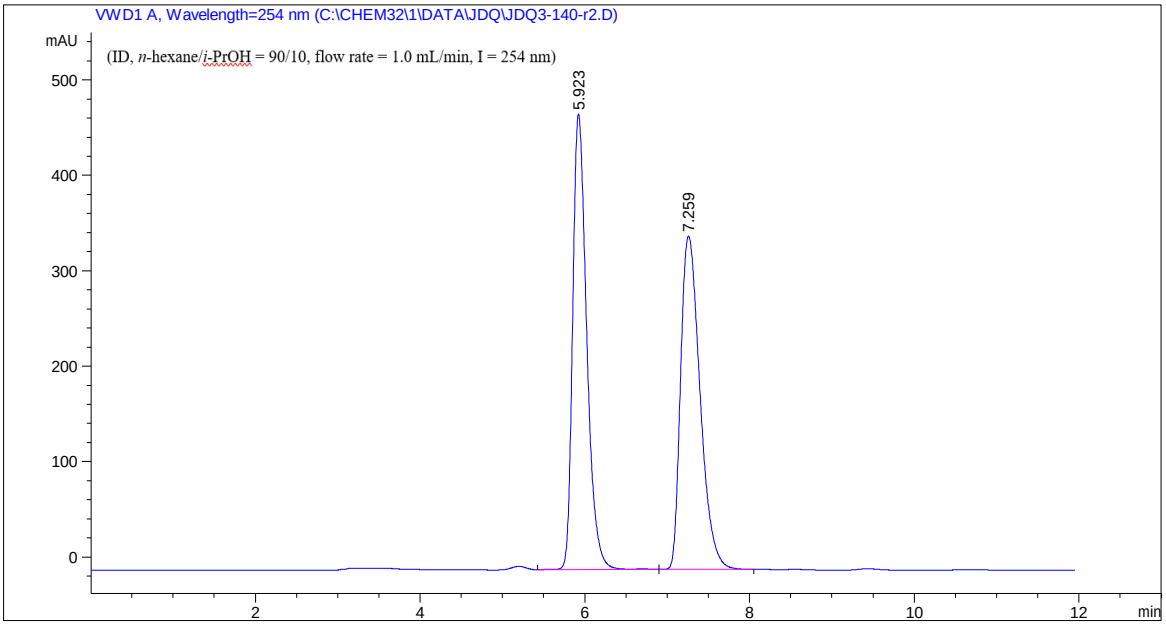
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.391	BV R	0.3964	6.22506e4	2466.70728	97.0337
2	14.829	VB E	0.3910	1903.00684	74.74831	2.9663
总量：				6.41536e4	2541.45558	



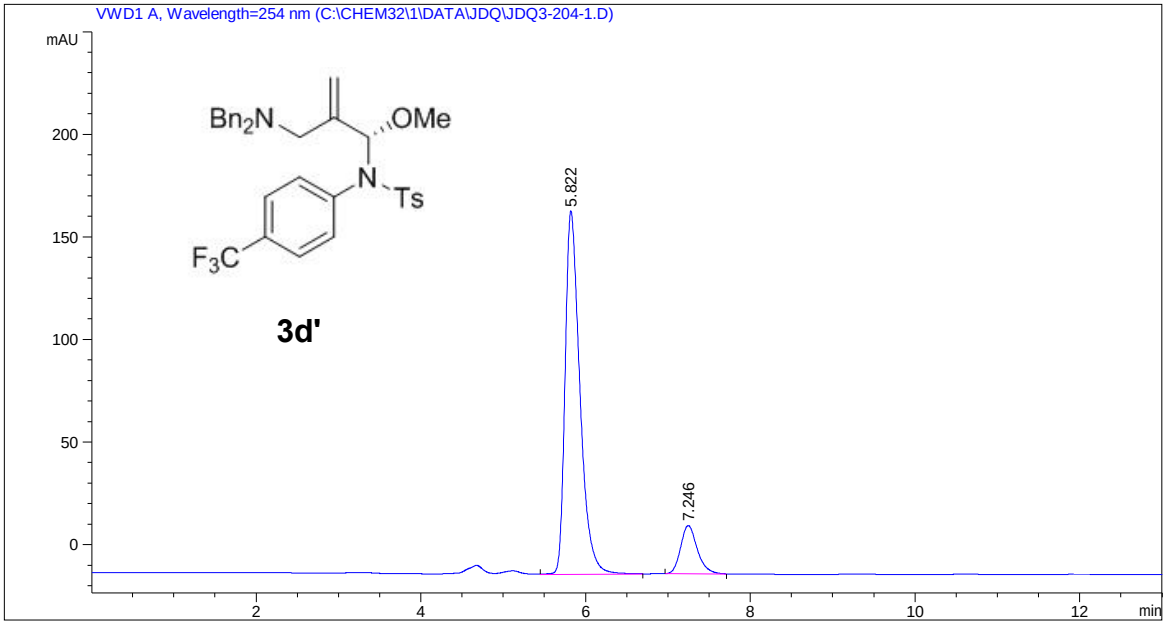
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.029	BV	0.4611	1434.24731	48.62281	49.8157
2	20.196	VB	0.4977	1444.85803	45.22926	50.1843



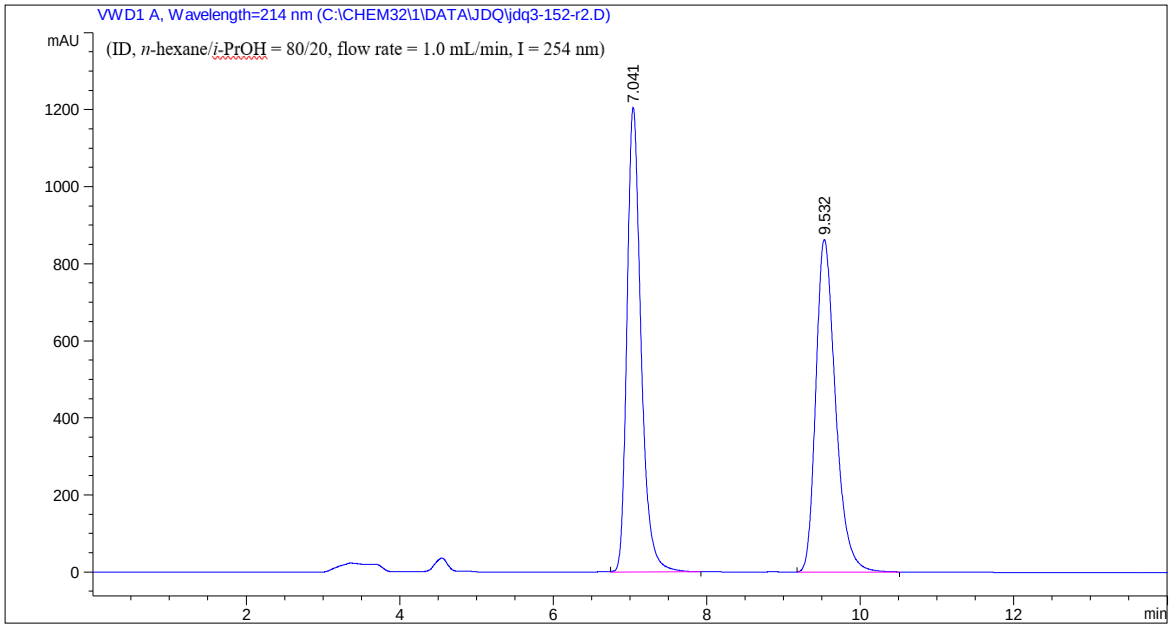
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.581	MM	0.5340	1.50357e4	469.30423	90.1427
2	19.938	MM	0.5357	1644.18652	51.15065	9.8573



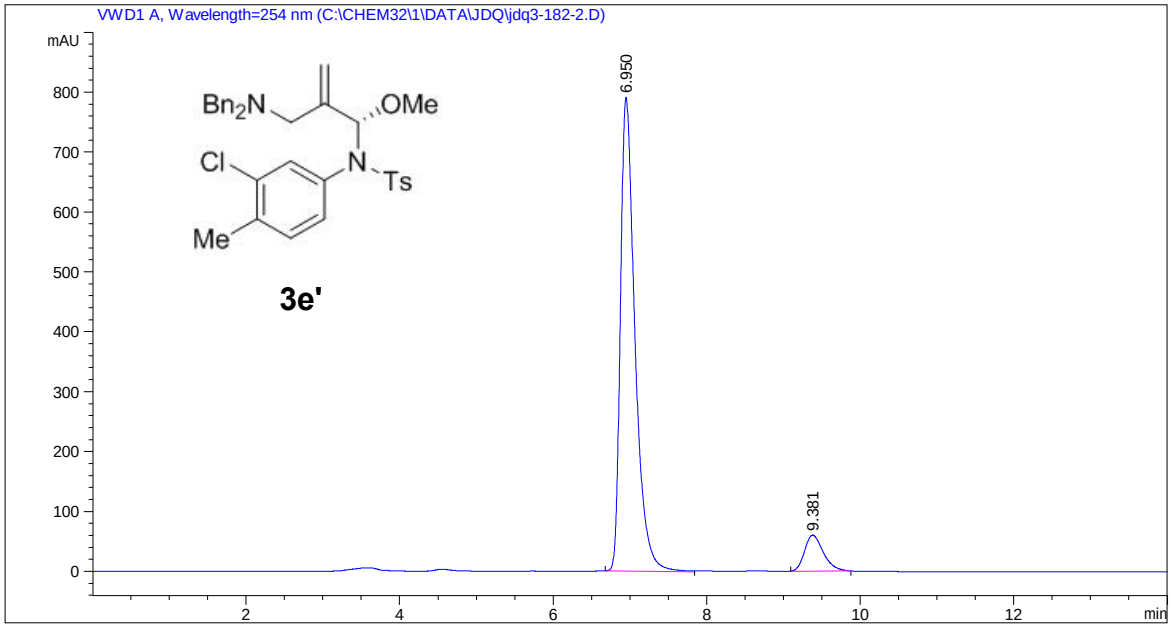
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.923	VV R	0.1824	5663.89063	477.58734	49.7988
2	7.259	BB	0.2567	5709.65186	349.23334	50.2012



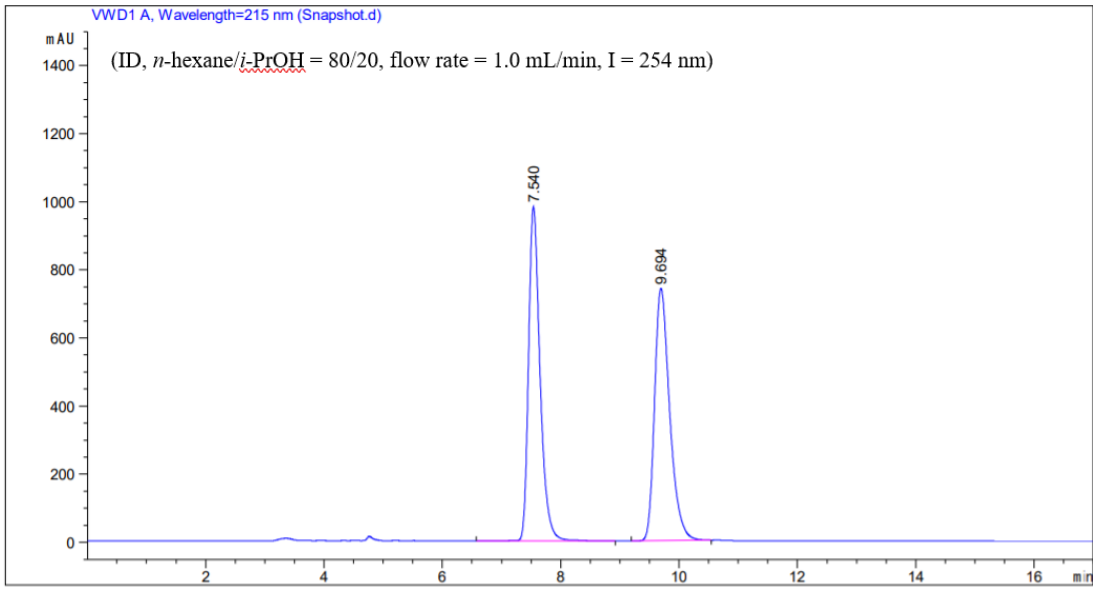
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.822	MM	0.2077	2207.93042	177.13953	87.0718
2	7.246	MM	0.2332	327.82834	23.43088	12.9282



#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.041	MM	0.2112	1.52689e4	1204.75647	49.7874
2	9.532	MM	0.2972	1.53993e4	863.48914	50.2126

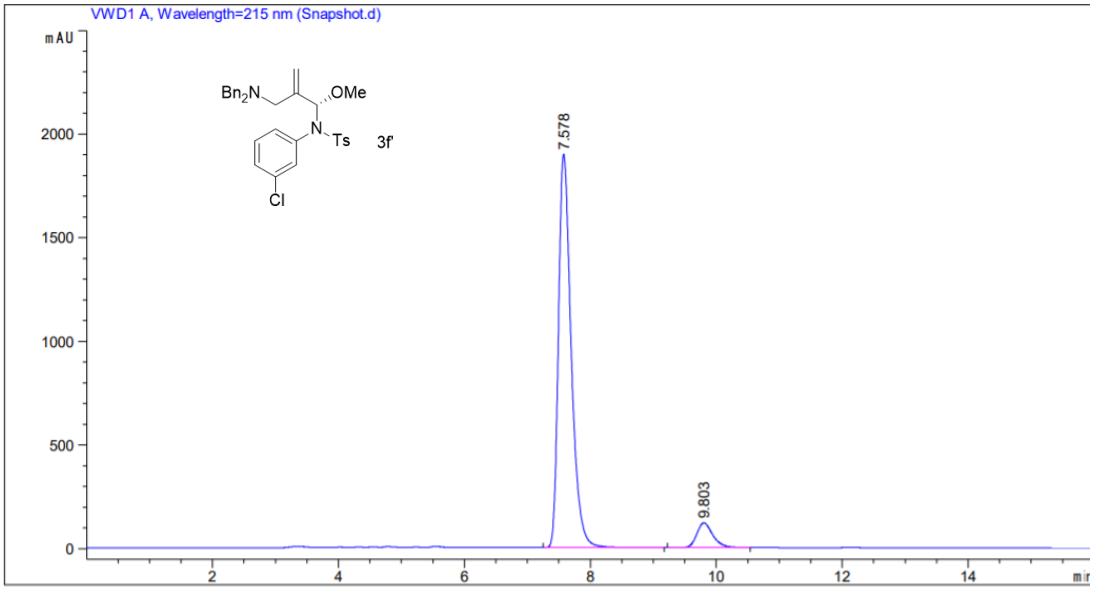


#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.950	MM	0.2197	1.04215e4	790.58722	90.9869
2	9.381	MM	0.2849	1032.34717	60.39630	9.0131



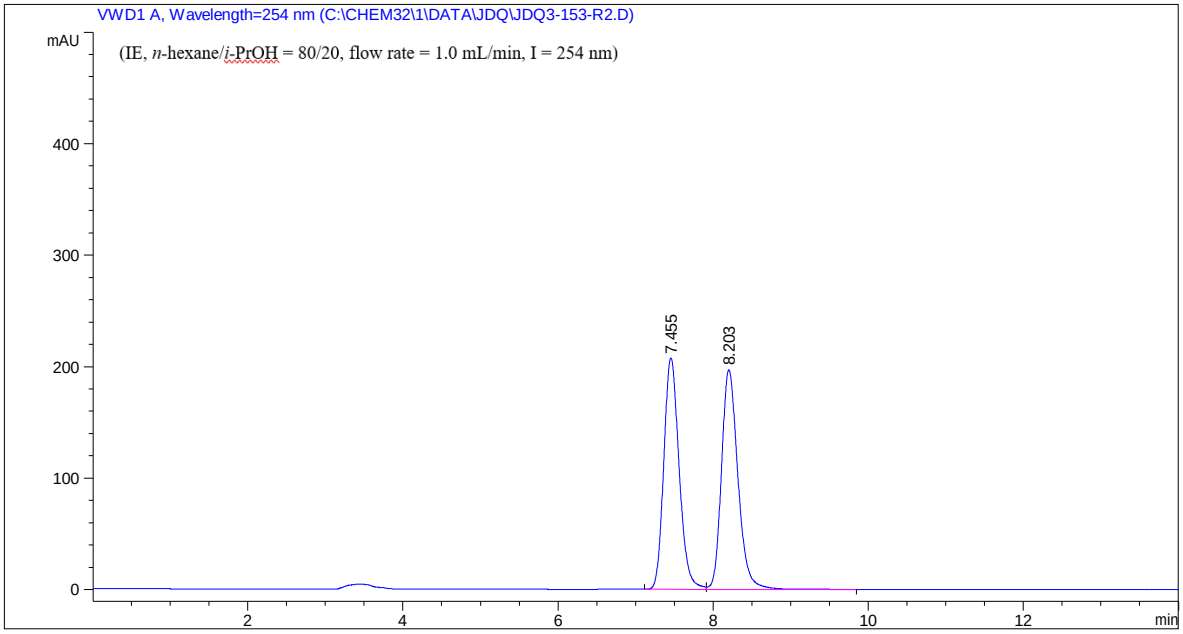
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.540	VB R	0.2045	1.32580e4	981.97534	50.1800
2	9.694	BB	0.2702	1.31629e4	741.12482	49.8200

总量 : 2.64209e4 1723.10016

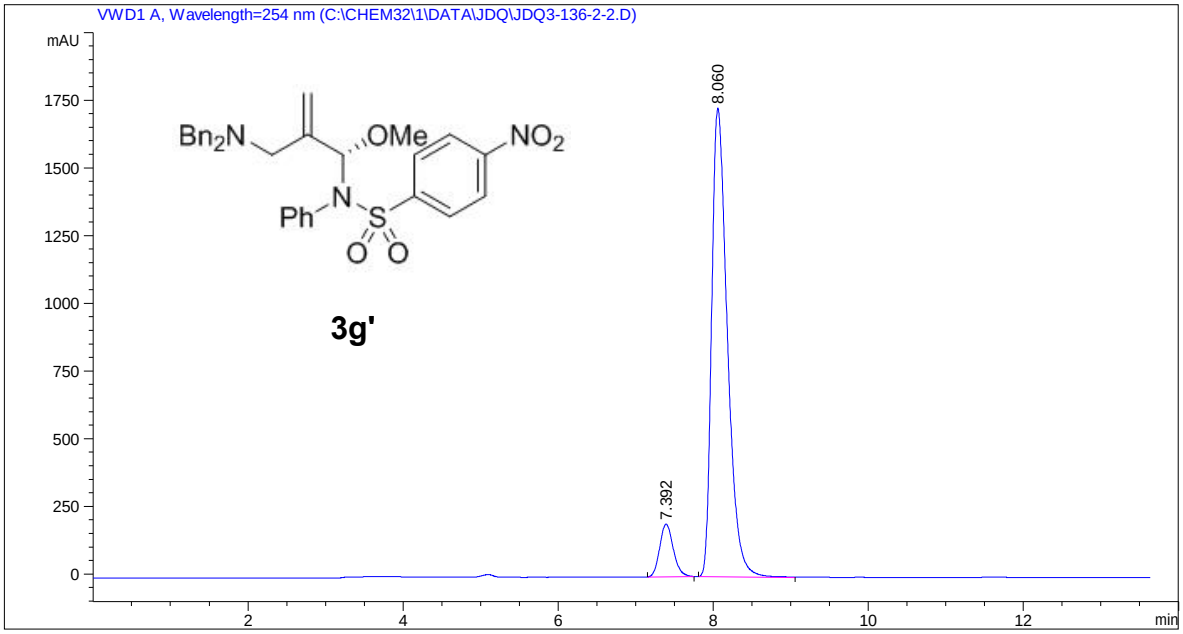


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.578	BB	0.2132	2.65455e4	1898.12756	92.7227
2	9.803	BB	0.2675	2083.40381	118.85362	7.2773

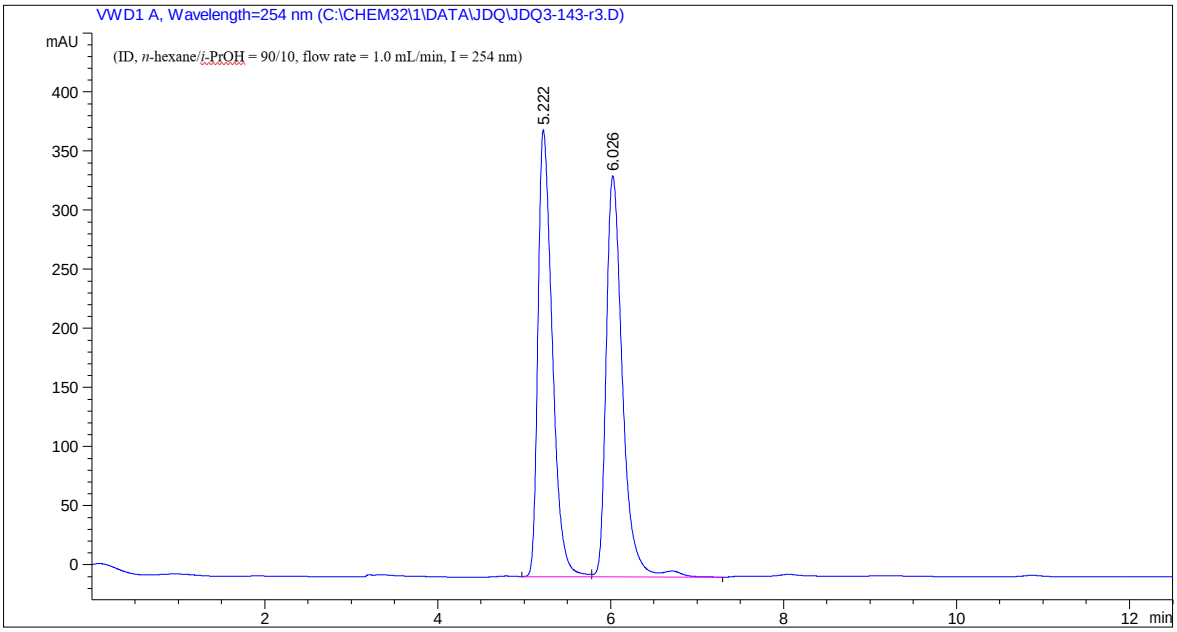
总量 : 2.86289e4 2016.98119



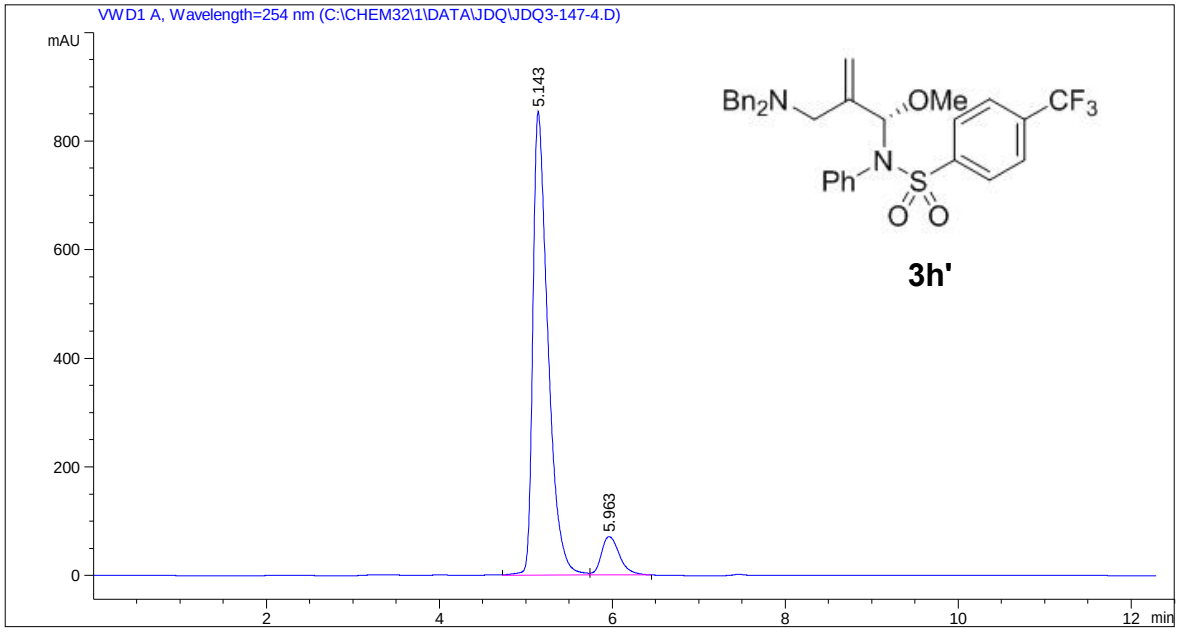
#	[min]	[min]	[mAU*s]	[mAU]	%
1	7.455 BV	0.2122	2850.96387	207.56659	49.5758
2	8.203 VB	0.2269	2899.75049	196.75731	50.4242



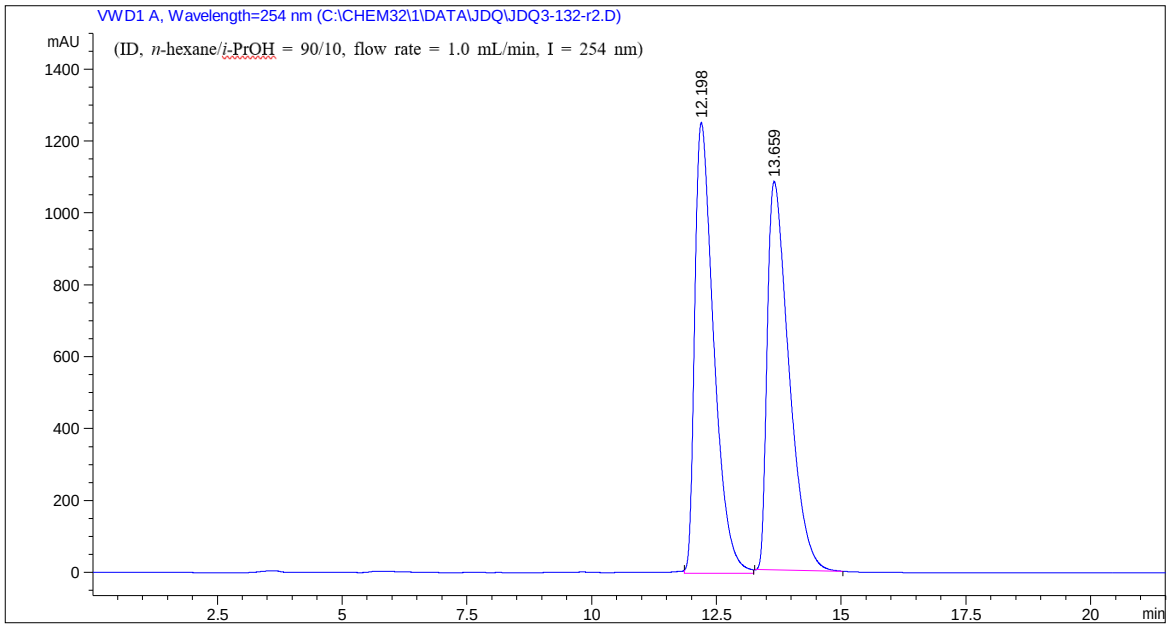
#	[min]	[min]	[mAU*s]	[mAU]	%
1	7.392 MM	0.2038	2389.98560	195.46638	8.9439
2	8.060 MM	0.2344	2.43321e4	1729.99744	91.0561



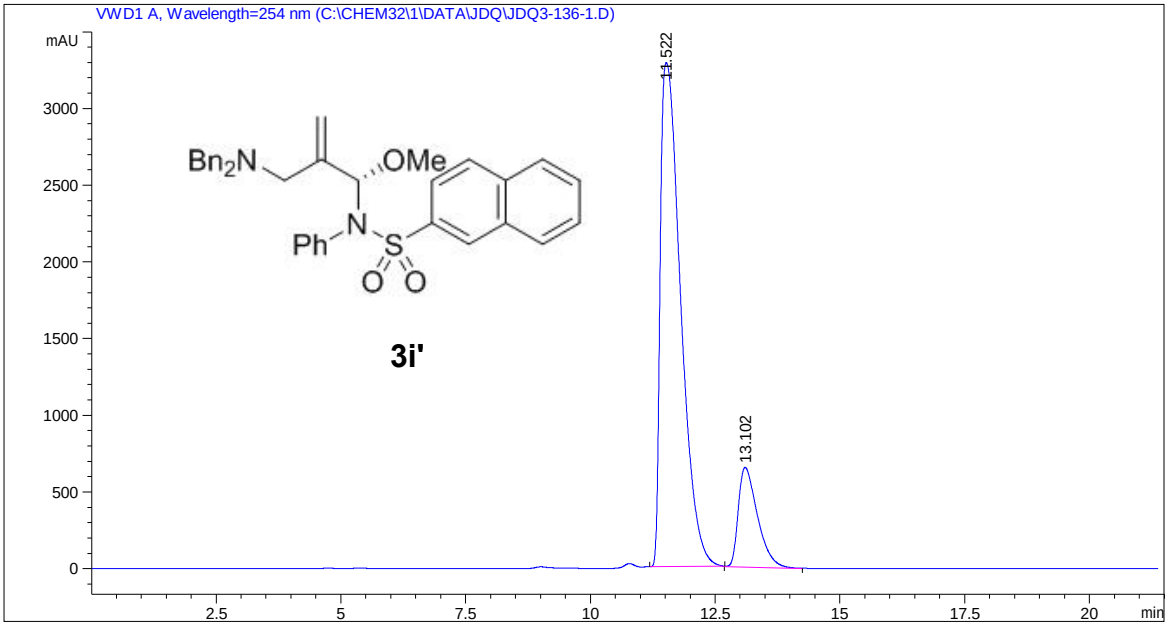
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.222	BV	0.1813	4349.80420	378.00122	49.3998
2	6.026	VV R	0.1985	4455.50684	339.35486	50.6002



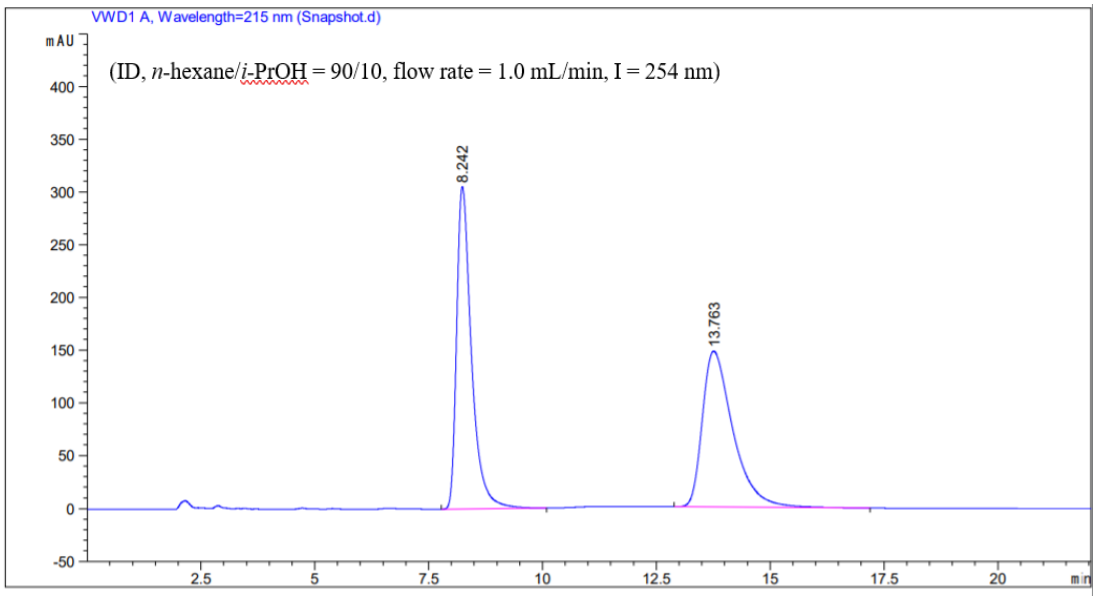
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.143	MM	0.2015	1.03185e4	853.42346	91.0659
2	5.963	MM	0.2406	1012.30774	70.12303	8.9341



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.198	MM	0.4428	3.33104e4	1253.81787	50.5123
2	13.659	MM	0.5034	3.26348e4	1080.45850	49.4877

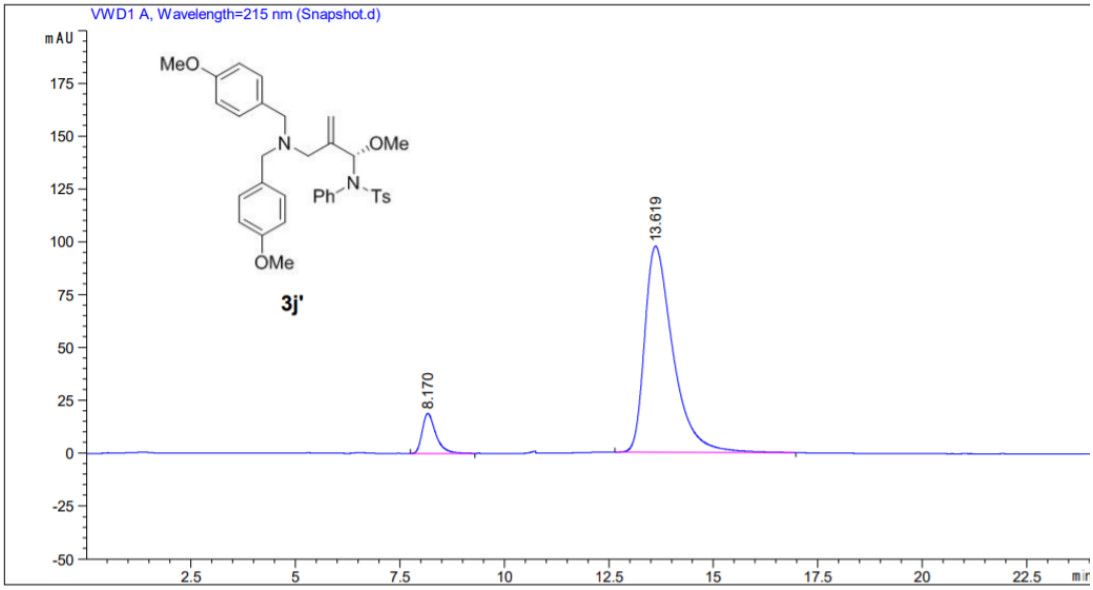


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.522	MM	0.4712	9.28572e4	3284.28125	84.1353
2	13.102	MM	0.4482	1.75094e4	651.04510	15.8647



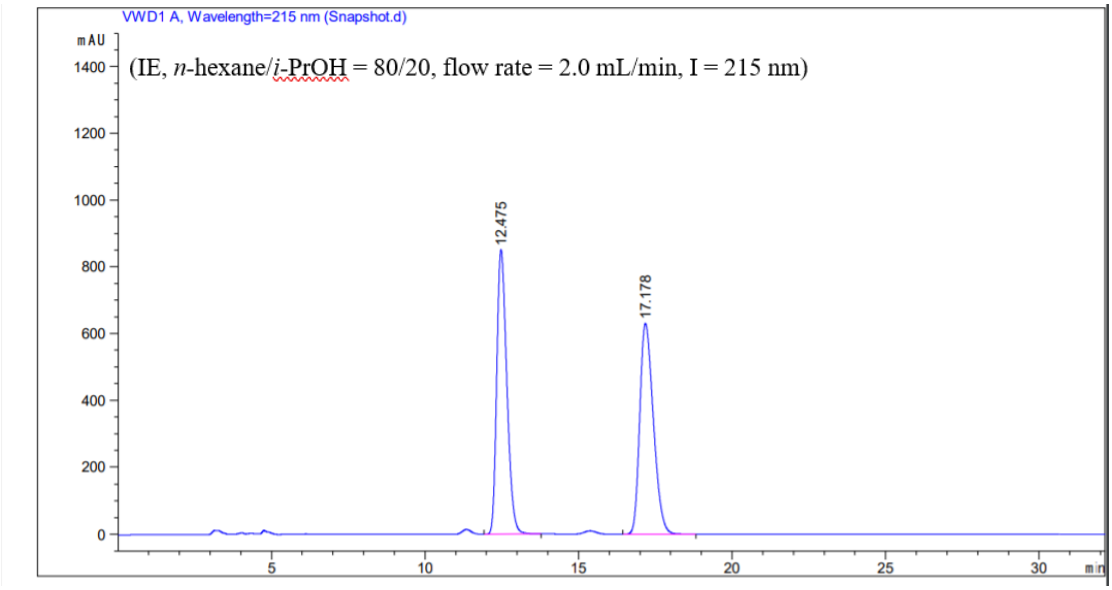
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.242	BB	0.3365	6870.56494	305.39972	49.9665
2	13.763	BB	0.7035	6879.78662	147.41821	50.0335

总量 : 1.37504e4 452.81793



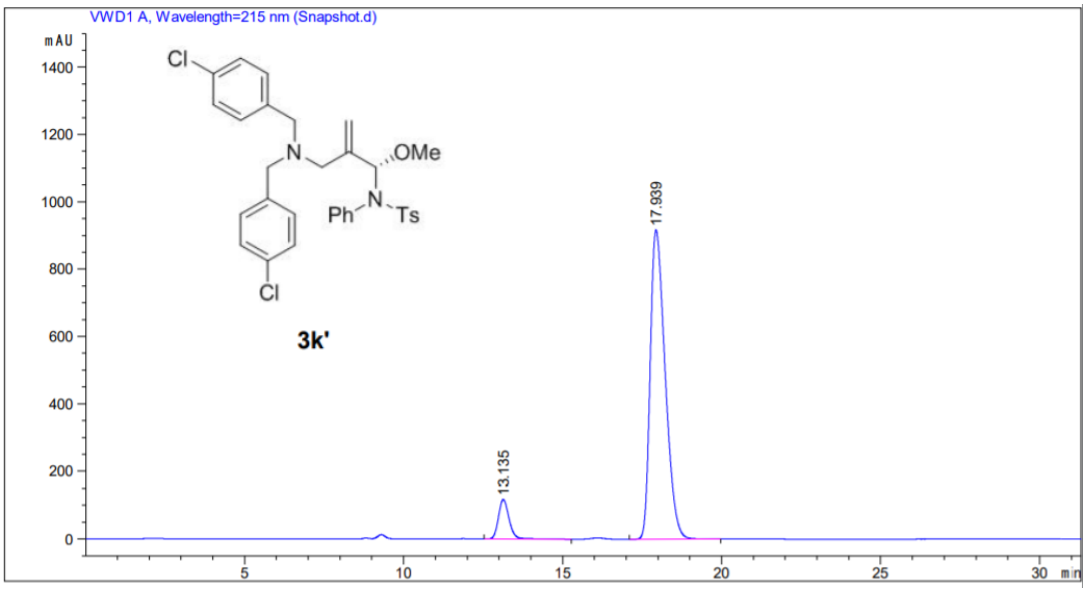
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.170	BB	0.3410	432.00006	19.01640	8.5874
2	13.619	BB	0.7088	4598.60010	97.58299	91.4126

总量 : 5030.60016 116.59939



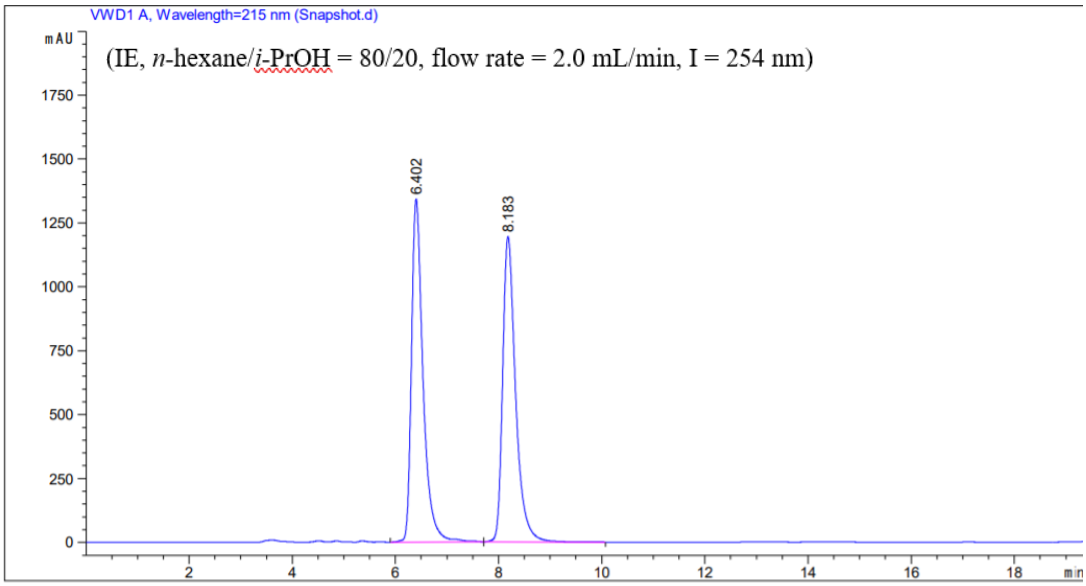
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.475	BB	0.3525	1.93650e4	851.03528	49.9052
2	17.178	BB	0.4785	1.94386e4	630.80719	50.0948

总量 : 3.88035e4 1481.84247

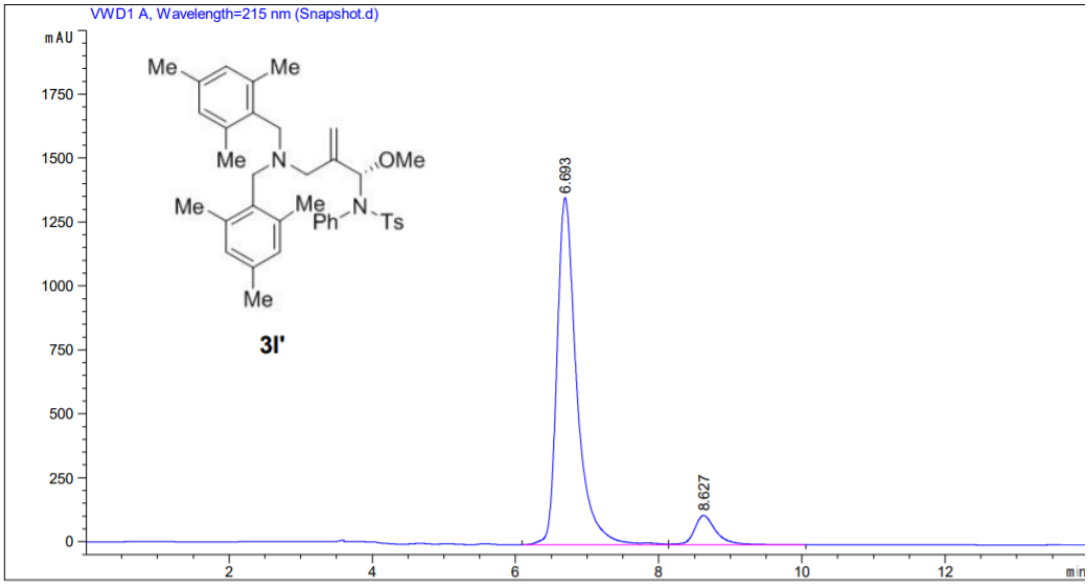


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.135	BB	0.3581	2728.44824	117.41451	8.3682
2	17.939	BB	0.5032	2.98766e4	916.78821	91.6318

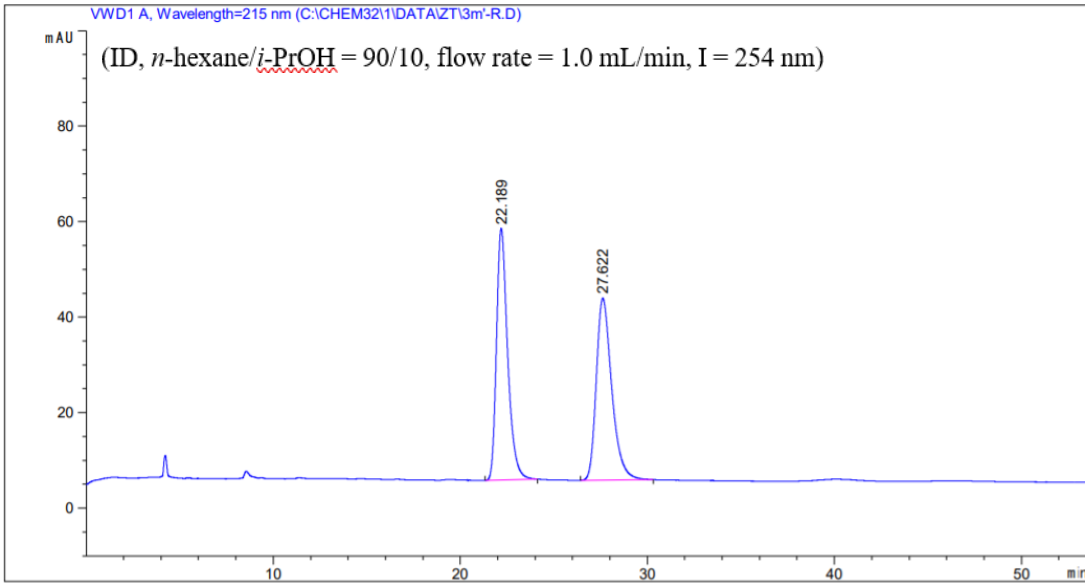
总量 : 3.26051e4 1034.20271



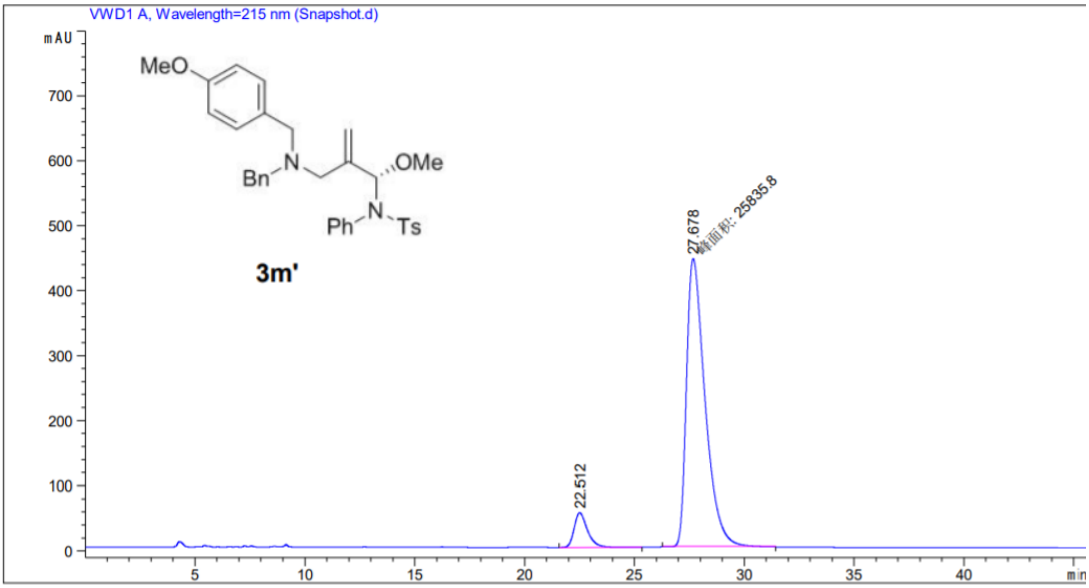
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.402	BB	0.2327	2.09074e4	1342.25476	50.1229
2	8.183	BB	0.2632	2.08048e4	1194.75684	49.8771
总量：				4.17122e4	2537.01160	



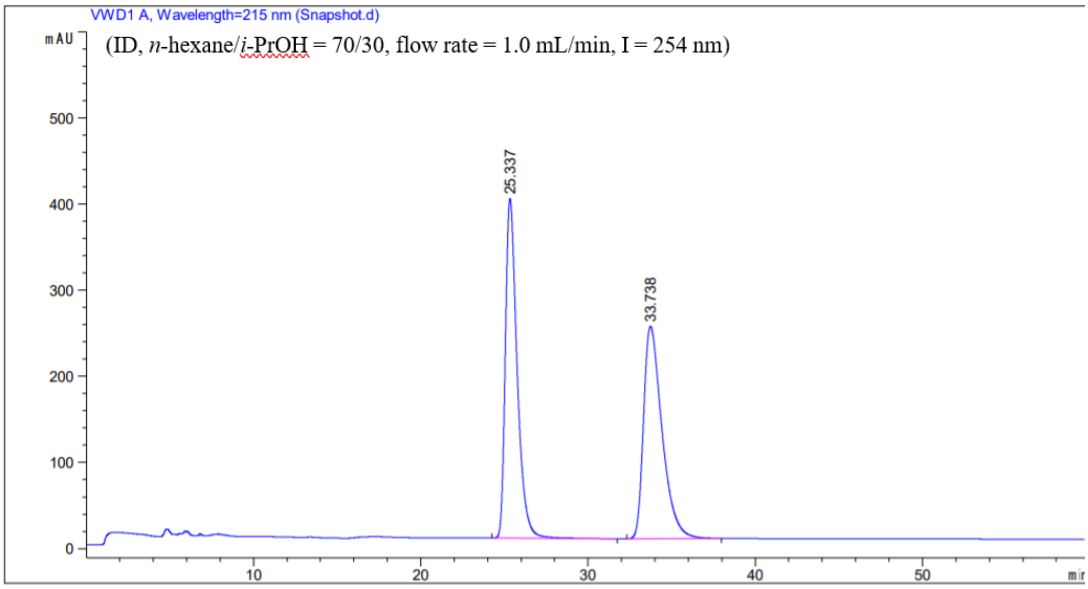
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.693	BV R	0.2849	2.60084e4	1357.76782	91.4616
2	8.627	VB	0.3148	2428.00879	114.78346	8.5384
总量：				2.84364e4	1472.55128	



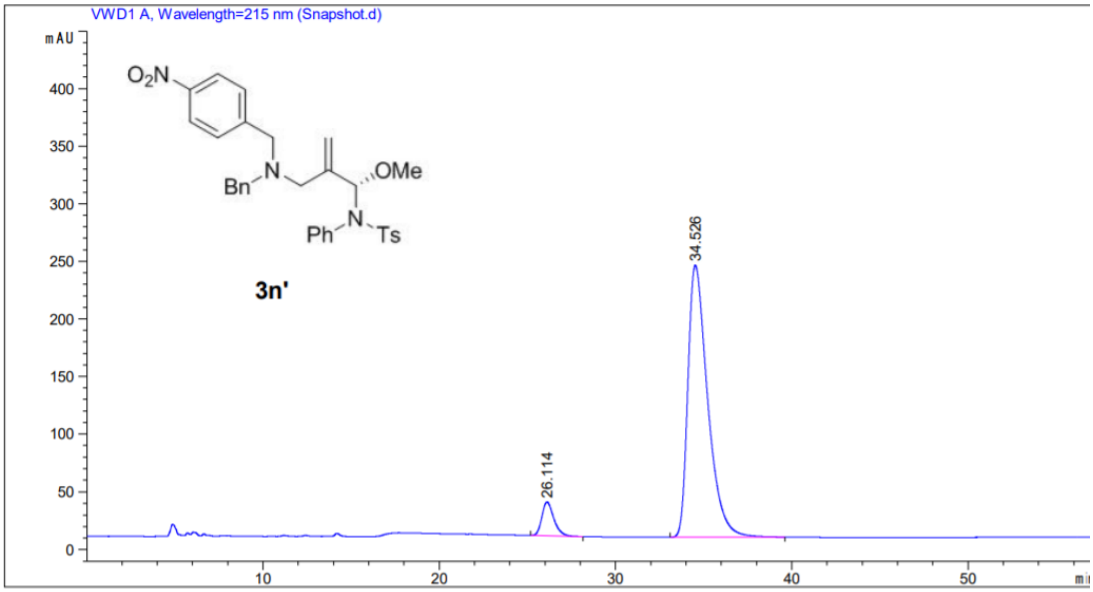
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.189	BB	0.6276	2181.51709	52.73207	49.9320
2	27.622	BB	0.8678	2187.45630	38.10400	50.0680
总量：				4368.97339	90.83607	



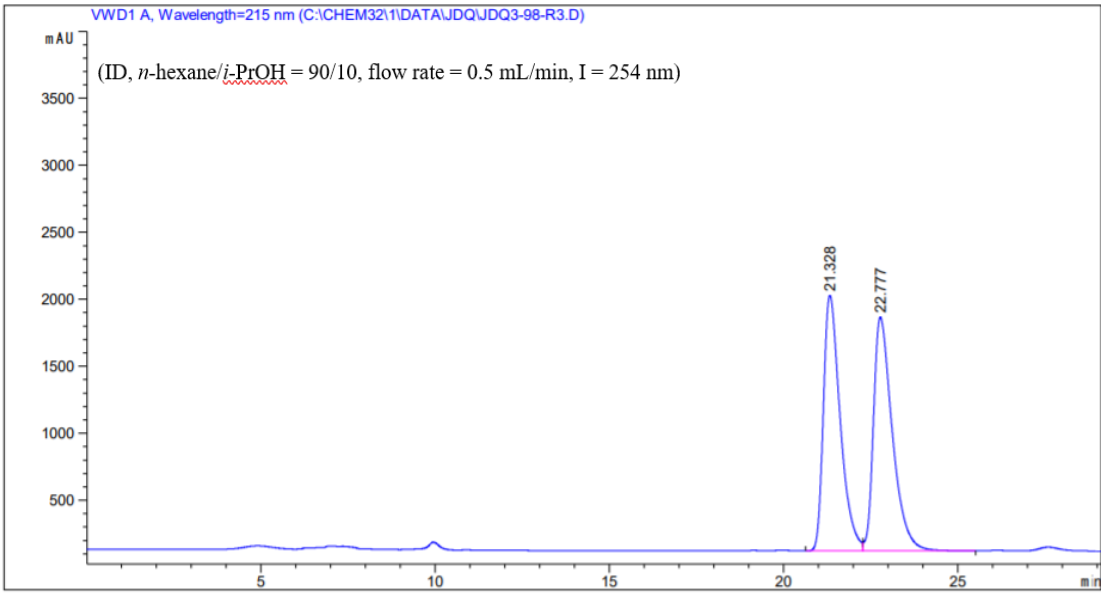
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.512	BB	0.6419	2264.04858	53.37036	8.0572
2	27.678	MM	0.9738	2.58358e4	442.19498	91.9428
总量：				2.80998e4	495.56533	



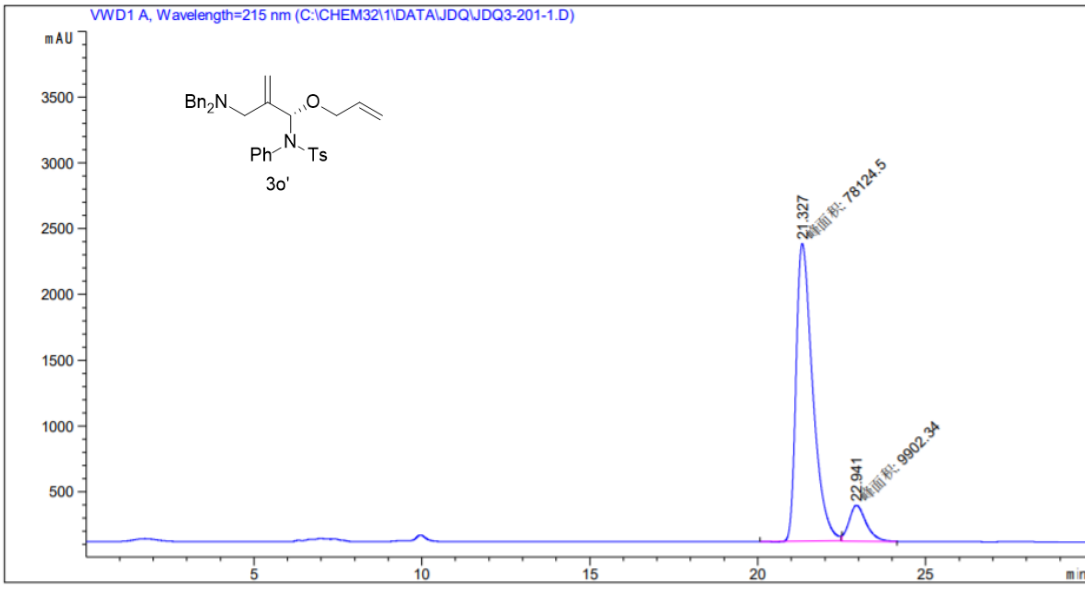
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.337	BB	0.7414	1.92477e4	393.65408	50.4789
2	33.738	BB	1.1660	1.88825e4	246.14005	49.5211
总量：				3.81301e4	639.79413	



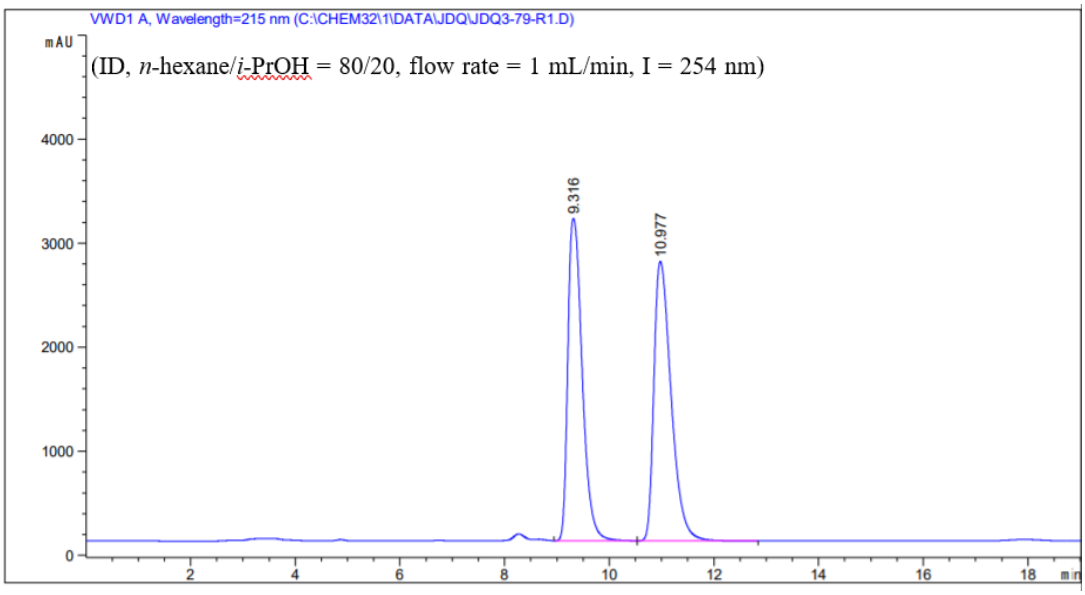
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.114	BB	0.7193	1395.99365	29.43606	7.0659
2	34.526	BB	1.1714	1.83607e4	235.80728	92.9341
总量：				1.97567e4	265.24334	



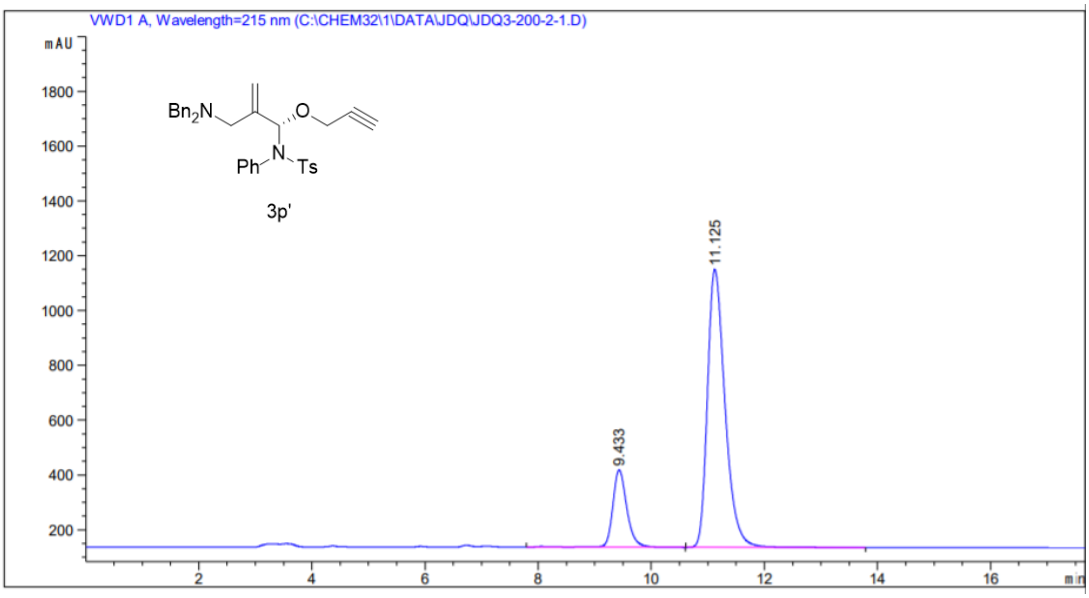
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.328	BV	0.5080	6.39255e4	1907.42773	49.3219
2	22.777	VB	0.5685	6.56832e4	1743.77600	50.6781
总量：				1.29609e5	3651.20374	



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.327	MM	0.5757	7.81245e4	2261.55444	88.7508
2	22.941	MM	0.6011	9902.34473	274.57123	11.2492
总量：				8.80269e4	2536.12567	



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.316	BB	0.2949	5.88934e4	3097.05908	49.0157
2	10.977	BB	0.3512	6.12588e4	2685.02271	50.9843
总量：				1.20152e5	5782.08179	



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.433	VB R	0.2632	4963.26855	282.69083	18.5066
2	11.125	BB	0.3295	2.18557e4	1013.81854	81.4934
总量：				2.68189e4	1296.50937	