Supporting Information

The Effect of Alkynyl Groups on Torquoselectivity. Highly Stereoselective Olefination of Alkynyl Ketones with Ynolates

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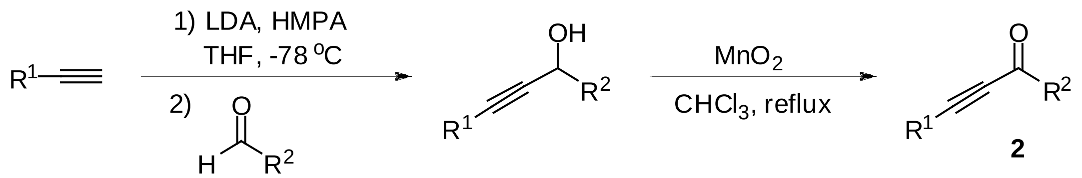
EXPERIMENTAL

Materials. *tert*-Butyllithium was titrated with diphenylacetic acid.

General Procedures. ^{1}H-NMR spectra were measured in $CDCl_3$ solution and referenced to TMS (0.00 ppm) using JEOL JNM-LA 400 (400 MHz) and JNM-ECA 600 (600 MHz) spectrometers, unless otherwise noted. ^{13}C-NMR spectra were measured in $CDCl_3$ solution and referenced to $CDCl_3$ (77.0 ppm) using JEOL JNM-LA 400 (100 MHz). IR spectra were recorded on SHIMADZU FTIR-8300 spectrometer. Mass spectra were obtained on a JEOL JMS-700. Column chromatography was performed on silica gel (Kanto Chemical Co.). Thin-layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck 60 F_{254}). All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. Reaction mixtures were stirred magnetically. Solutions of alkyllithium reagents were transferred by syringe of cannula and were introduced into reaction vessels through rubber septa. The stereochemistry was determined by nOe experiments, unless otherwise noted.

The known compounds (1-phenylhept-1-yn-3-one **2a**,[1] 1-(4-methoxybenzyloxy)-buty-3-yn,[2] 1,3-diphenylpropynone **2h**,[4] and 4,4-dimethyl-1-phenylpent-2-yn-1-one **2i**[5]) were prepared according to the literatures.

Preparation of alkynylketones (2) (Table 1)



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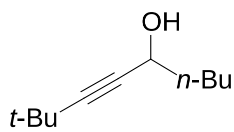
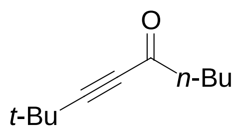
General procedure for preparation of alkynyl alcohol. A solution of lithium diisopropylamide (1.1 eq) was generated in THF (12 ml) from diisopropylamine (0.463 ml, 3.3 mmol) and *n*-BuLi (1.33 ml, 3.3 mmol, 2.48 M in Hex.) at –78 °C. To this solution, the alkyne (246 mg, 3.0 mmol) in HMPA (1.96 ml, 11.3 mmol) was added dropwise and the mixture was stirred at –78 °C for 1.5 h, at which time the aldehyde (350 mg, 3.3 mmol) in THF (3 ml) was added. The mixture was stirred at same temperature for 1.5 h, and then warmed to room temperature over 1 h, quenched with saturated NH_4Cl solution, and extracted with Et_2O. The organic phase was washed with 1 M HCl solution, a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, filtered and concentrated to give residue, which was purified by column chromatography to afford the alcohol.

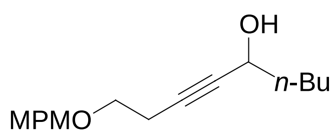
General procedure for oxidation of alkynyl alcohol with MnO_2. A mixture of the alcohol (1.15 mmol), manganese dioxide (3.54g, 34.6 mmol), and $CHCl_3$ (11.5 ml) was stirred under reflux. The resulting mixture was filtered and concentrated to give a residue, which was purified by column chromatography to afford the ketone.



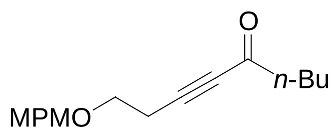
2,2-Dimethylnon-3-yn-5-ol : According to the *preparation of alkynyl alcohol*, the alkynyl alcohol (72%) was obtained from 3,3-dimethyl-1-butyne and valeraldehyde as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, *J* = 7.2 Hz, 3H), 1.12 (s, 9H), 1.30-1.46 (m, 4H), 1.61-1.70 (m, 3H), 4.34 (q, *J* = 6.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9 (q), 22.3 (t), 27.2 (s), 27.3 (t), 30.9 (q x 3), 37.8 (t), 62.4 (d), 79.8 (s), 93.5 (s); IR (Neat): 3335 cm^{-1}, 2237 cm^{-1}; MS (EI) *m/z* 168 (M^+), 111 (100%); HRMS (EI) calcd for $C_{11}H_{20}O$: 168.1514, found: 168.1516.



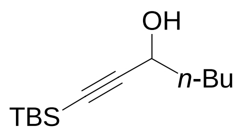
2,2-Dimethylnon-3-yn-5-one (2b): According to the *oxidation of alkynyl alcohol with MnO_2*, the alkynyl ketone **2b** (47%) was obtained from the alkynyl alcohol as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 9H), 1.30-1.40 (m, 2H), 1.60-1.68 (m, 2H), 2.52 (q, *J* = 7.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.7 (q), 22.0 (t), 26.1 (t), 27.6 (s), 30.0 (q x 3), 45.1 (t), 79.2 (s), 101.2 (s), 188.5 (s); IR (Neat): 2212 cm^{-1}, 1674 cm^{-1}; MS (EI) *m/z* 166 (M^+), 109 (100%); HRMS (EI) calcd for $C_{11}H_{18}O$: 166.1358, found: 166.1359.



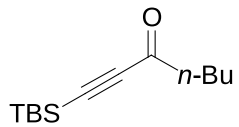
1-(4-Methoxybenzyloxy)non-3-yn-5-ol : According to *preparation of alkynyl alcohol*, the alkynyl alcohol (42%) was obtained from 1-(4-methoxybenzyloxy)-buty-3-yn[2] and valeraldehyde as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 1.32-1.45 (m, 4H), 1.62-1.72 (m, 3H), 2.52 (dt, *J* = 2.0 Hz, 7.2 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 4.34 (q, *J* = 5.2 Hz, 2H), 4.48 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0 (q), 20.1 (t), 22.4 (t), 27.3 (t), 37.7 (t), 55.2 (q), 62.6 (d), 68.1 (t), 72.6 (t), 82.0 (s), 82.4 (s), 113.8 (d x 2), 129.3 (d x 2), 130.1 (s), 159.2 (s) IR (Neat): 3418 cm^{-1}, 2230 cm^{-1}; MS (EI) *m/z* 276 (M^+), 121 (100%); HRMS (EI) calcd for $C_{17}H_{24}O_3$: 276.1725, found: 276.1723.



1-(4-Methoxybenzyloxy)non-3-yn-5-one (2c): According to *oxidation of alkynyl alcohol with MnO₂*, the alkynyl ketone **2c** (53%) was obtained from the alkynyl alcohol as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 1.29-1.39 (m, 2H), 1.59-1.68 (m, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.81 (s, 3H), 4.49 (s, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.6 (q), 20.2 (t), 21.9 (t), 25.9 (t), 45.0 (t), 55.0 (q), 66.7 (t), 72.5 (t), 81.2 (s), 90.4 (s), 113.6 (d x 2), 114.1 (s), 129.1 (d x 2), 129.6 (s), 159.2 (s), 188.0 (s); IR (Neat): 2216 cm^{-1}, 1674 cm^{-1}; MS (EI) *m/z* 274 (M^+), 121 (100%); HRMS (EI) calcd for $C_{17}H_{22}O_3$: 274.1569, found: 274.1571.

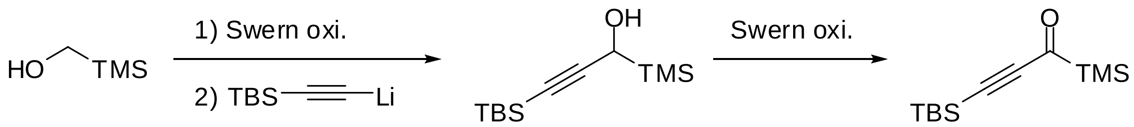


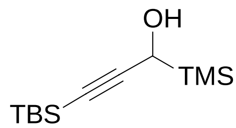
1-(*tert*-Butyldimethylsilanyl)hept-1-yn-3-ol : According to *preparation of alkynyl alcohol*, the alkynyl alcohol (90%) was obtained from *tert*-butyldimethylsilyl acetylene and valeraldehyde as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.11 (s, 6H), 0.92 (t, *J* = 7.6 Hz, 3H), 0.94 (s, 9H), 1.31-1.55 (m, 4H), 1.64-1.77 (m, 3H), 4.36 (q, *J* = 6.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: –4.7 (q x 2), 13.9 (q), 16.4 (s), 22.3 (t), 26.0 (q x 3), 27.3 (t), 37.5 (t), 62.8 (d), 87.4 (s), 107.7 (s); IR (Neat): 3323 cm^{-1}, 2172 cm^{-1}; MS (EI) *m/z* 226 (M^+), 75 (100%); HRMS (EI) calcd for $C_{13}H_{26}OSi$: 226.1753, found: 226.1756.



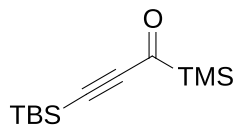
1-(*tert*-Butyldimethylsilanyl)hept-1-yn-3-one (2d): According to *oxidation of alkynyl alcohol with MnO₂*, the alkynyl ketone **2d** (77%) was obtained from the alkynyl alcohol as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.18 (s, 6H), 0.92 (t, *J* = 4.9 Hz, 3H), 0.97 (s, 9H), 1.31-1.41 (m, 2H), 1.63-1.70 (m, 2H), 2.55 (q, J = 4.9 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: −5.2 (q x 2), 13.7 (q), 16.5 (s), 22.0 (t), 25.9 (q x 3), 26.1 (t), 45.1 (t), 96.4 (s), 102.8 (s), 187.9 (s); IR (Neat): 2151 cm^{-1}, 1682 cm^{-1}; MS (EI) *m/z* 224 (M^+), 168 (100%); HRMS (EI) calcd for $C_{13}H_{24}OSi$: 224.1596, found: 224.1595.

Synthesis of acylsilane 2f[3]



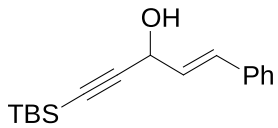


3-(*tert*-Butyldimethylsilanyl)-1-trimethylsilanylprop-2-yn-1-ol : To a solution of oxalyl chloride (0.456 ml, 5.25 mmol) in Et_2O (50 ml) was added dimethyl sulfoxide (0.390 ml, 5.5 mmol) dropwise at -78 °C. The mixture was warmed to -40 °C and stirred for 0.5 h. The reaction mixture was then cooled to -78 °C, and (trimethylsilyl)methanol (0.631 ml, 5.0 mmol) was added dropwise. The mixture was warmed to -40 °C and stirred for 1.5 h. After cooling to -78 °C, triethylamine (3.48 ml, 25 mmol) was added dropwise. The mixture was stirred for 1 h at -78 ^{o}C and warmed to 0 ^{o}C for 2 h. The mixture was then cooled to -78 ^{o}C, and 10 mmol of lithium *tert*-butyldimethylsilyl acetylide (prepared from *tert*-butyldimethylsilyl acetylene and lithium diisopropylamide) was added. After the mixture was stirred for 1 h at -78 ^{o}C, 30 ml of water and ether were added and the mixture was allowed to warm to room temperature. The solution was extracted with Et_2O and washed with brine, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 85/15) to afford the alcohol (809 mg, 67%) as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.11 (d, J = 1.2 Hz, 6H), 0.15 (s, 9H), 0.93 (s, 9H), 1.42 (d, J = 4.4 Hz, 1H), 4.10 (d, J = 4.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.5 (q), -4.5 (q), -4.3 (q x 3), 16.5 (s), 26.1 (q x 3), 57.2 (d), 90.4 (s), 107.3 (s); IR (Neat): 3383 cm^{-1}, 2154 cm^{-1}; MS (EI) *m/z* 242 (M^+), 73 (100%); HRMS (EI) calcd for $C_{12}H_{26}OSi_2$: 242.1522, found: 242.1516.

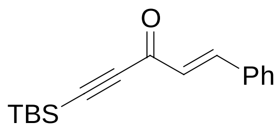


3-(*tert*-Butyldimethylsilanyl)-1-trimethylsilanylpropynone (2f): To a solution of oxalyl chloride (0.395 ml, 4.55 mmol) in CH_2Cl_2 (25 ml) was added dimethyl sulfoxide (0.366 ml, 5.15 mmol) dropwise at -78 ^{o}C. After 0.5 h, 3-(*tert*-butyldimethylsilanyl)-1-trimethylsilanylprop-2-yn-1-ol (736, 3.03 mmol) in CH_2Cl_2 (5 ml) was added dropwise. The mixture was stirred for 0.5 h, triethylamine

(2.11 ml, 15.2 mmol) was added dropwise. After the mixture was stirred for 4 h at -78 °C, water was added and the mixture was allowed to warmed to room temperature. The solution was concentrated in vacuo and extracted with Et_2O. Organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 90/10) to afford the ketone **2f** (565 mg, 78%) as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.19 (s, 6H), 0.27 (s, 9H), 0.98 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -5.1 (q x 2), -3.7 (q x 3), 16.5 (s), 26.0 (q x 3), 105.5 (s), 106.0 (s), 227.0 (s); IR (Neat): 2131 cm^{-1}, 1601 cm^{-1}; MS (EI) *m/z* 240 (M^+), 155 (100%); HRMS (EI) calcd for $C_{12}H_{24}OSi_2$: 240.1366, found: 240.1363.

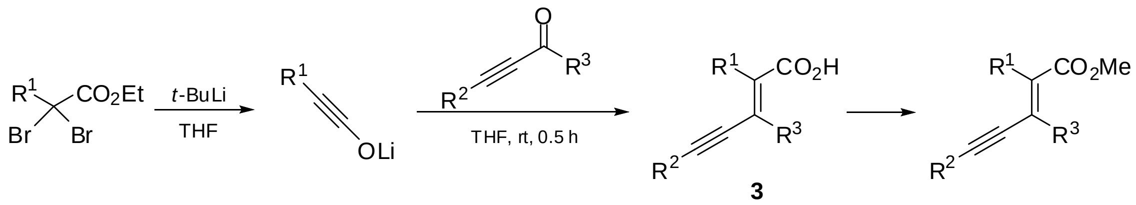


5-(*tert*-Butyldimethylsilanyl)-1-phenylpent-1-en-4-yn-3-ol : To a *tert*-butyldimethylsilyl acetylene (982 mg, 7.0 mmol) in THF (15 ml) was added *n*-BuLi (2.82 ml, 7.0 mmol, 2.48 M in Hex.) at –78 °C. After 1.5 h, *trans*-cinnamaldehyde (925 mg, 7.0 mmol) in THF (3 ml) was added. The mixture was stirred at same temperature for 1.5 h, quenched with saturated NH_4Cl solution and the mixture was allowed to warmed to room temperature. The mixture was extracted with Et_2O, washed with brine, dried over $MgSO_4$, filtered and concentrated to give residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 90/10) to afford the alcohol (1.69 g, 89%) as a pale yellow needle: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H), 0.97 (s, 9H), 1.94 (d, *J* = 6.4 Hz, 1H), 5.06 (d, *J* = 6.4 Hz, 1H), 6.30 (dd, *J* = 6.0 Hz, 12.0 Hz, 1H), 6.81 (d, *J* = 16.4 Hz, 1H), 7.26-7.42 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.7 (q x 2), 16.4 (s), 26.0 (q x 3), 63.2 (d), 89.6 (s), 104.9 (s), 126.8 (d), 127.9 (d), 128.0 (d), 128.6 (d), 132.0 (d), 136.1 (s); IR (KBr): 3281 cm^{-1}, 2168 cm^{-1}; MS (EI) *m/z* 272 (M^+), 215 (100%); HRMS (EI) calcd for $C_{17}H_{24}OSi$: 272.1596, found: 272.1600.



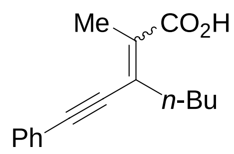
5-(*tert*-Butyldimethylsilanyl)-1-phenylpent-1-en-4-yn-3-one (2g): According to *oxidation of alkynyl alcohol with MnO_2*, the alkynyl ketone **2g** (86%) was obtained from the alkynyl alcohol as a green oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.25 (s, 6H), 1.04 (s, 9H), 6.79 (d, *J* = 16.0 Hz, 1H), 7.43-7.57 (m, 5H), 7.88 (d, *J* = 16.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -5.1 (q x 2), 16.6 (s), 26.0 (q x 3), 97.4 (s), 101.2 (s), 128.3 (d), 128.6 (d), 129.0 (d), 131.2 (d), 133.9 (s), 148.9 (d), 177.9 (s); IR (KBr): 2154 cm^{-1}, 1636 cm^{-1}; MS (EI) *m/z* 270 (M^+), 213 (100%); HRMS (EI) calcd for $C_{17}H_{22}OSi$: 270.1440, found: 270.1441.

Olefination of alkynylketones with lithium ynolate

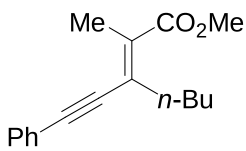


General procedure for the olefination of alkynylketone (preparation of ynolate by lithium-halogen exchange using tert-butyllithium). To a solution of ethyl 2,2-dibromopropionate (156 mg, 0.6 mmol) in THF (3 ml), cooled to –78 °C under argon, was added dropwise a solution of *tert*-butyllithium (1.53 mL, 2.4 mmol, 1.57 M in pentane). The yellow solution was stirred for 10 min at –78 °C and allowed to warm to 0 °C. After 30 min, a solution of the alkynylketone (0.5 mmol) in THF (1 ml) was added. After 0.5 h, the solution was concentrated in vacuo, and then diluted with hexane. The resulting solution was washed with water (x 3). The combined water phase was acidified with 1 M HCl solution and extracted with CH_2Cl_2 (x 3). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give residue, which was purified by column chromatography to afford the carboxylic acid.

General procedure for esterification of the carboxylic acid. To a solution of the carboxylic acid (1.0 eq.) and MeOH in CH_2Cl_2 was added EDC (1.2 eq.) and DMAP (0.1 eq.) at room temperature. After 20 h, a saturated NH_4Cl solution was added and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by column chromatography followed by HPLC to afford the methyl ester.

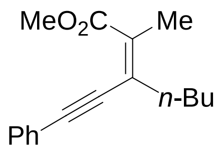


3-Butyl-2-methyl-5-phenylpent-2-en-4-ynoic acid (3a): According to *the general procedure for the olefination of alkynylketon*, the pentenynoic acid **3a** (69%) was obtained from **2a** as a pale yellow needle: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 1.36-1.67 (m, 4H), 2.24 (s, 3H), 2.71 (t, J = 7.6 Hz, 2H).

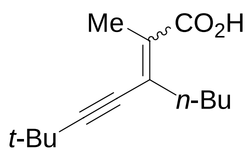


(*E*)-Methyl 3-butyl-2-methyl-5-phenylpent-2-en-4-ynoate : According to *the general procedure for esterification of the carboxylic acid*, the methyl pentenynoate (86%) was obtained from **3a** as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 1.36-1.44 (m, 2H), 1.59-1.66 (m, 2H), 2.20 (s, 3H), 2.62 (t, J = 7.6 Hz, 2H), 3.76 (s, 3H), 7.32-7.47 (m, 5H); ^{13}C-NMR (100 MHz,

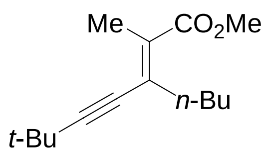
$CDCl_3$) δ: 13.9 (q), 18.9 (q), 22.4 (t), 31.1 (t), 33.5 (t), 51.5 (q), 89.2 (s), 98.8 (s), 123.0 (s), 128.3 (d), 128.6 (d), 131.5 (d), 132.1 (s), 133.5 (s), 168.7 (s); IR (Neat): 2191 cm^{-1}, 1715 cm^{-1}; MS (EI) *m/z* 256 (M^+), 227 (100%); HRMS (EI) calcd for $C_{17}H_{20}O_2$: 256.1463, found: 256.1465.



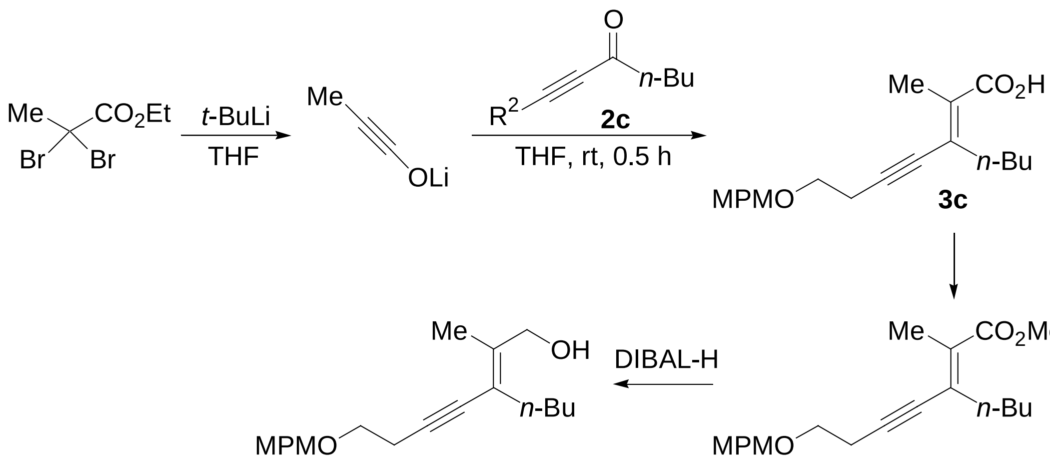
(*Z*)-Methyl 3-butyl-2-methyl-5-phenylpent-2-en-4-ynoate : colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, *J* = 7.2 Hz, 3H), 1.36-1.46 (m, 2H), 1.59-1.67 (m, 2H), 2.01 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H), 3.82 (s, 3H), 7.31-7.48 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.0 (q), 15.4 (q), 22.4 (t), 30.1 (t), 34.1 (t), 51.7 (q), 89.6 (s), 96.3 (s), 123.5 (s), 128.3 (d), 128.4 (d), 130.8 (s), 131.7 (d), 132.4 (s), 168.6 (s); IR (Neat): 2195 cm^{-1}, 1705 cm^{-1}; MS (EI) *m/z* 256 (M^+), 199 (100%); HRMS (EI) calcd for $C_{17}H_{20}O_2$: 256.1463, found: 256.1461.

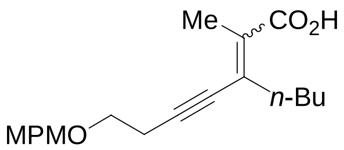


3-Butyl-2,6,6-trimethylhept-2-en-4-ynoate (3b): According to *the general procedure for the olefination of alkynylketone*, the heptenynoic acid **3b** (88%) was obtained from **2b** as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H), 1.31-1.39 (m, 2H), 1.50-1.58 (m, 2H), 2.10 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H).

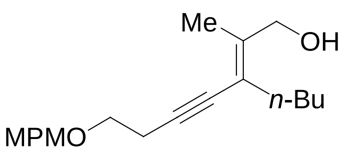


(*E*)-Methyl 3-butyl-2,6,6-trimethylhept-2-en-4-ynoate : According to *the general procedure for esterification of the carboxylic acid*, the methyl heptenynoate (77%) was obtained from **3b** as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 9H), 1.31-1.38 (m, 2H), 1.49-1.55 (m, 2H), 2.06 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 3.73 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9 (q), 18.6 (q), 22.4 (t), 28.4 (s), 30.9 (q x 3), 30.9 (t), 33.7 (t), 51.4 (q), 79.1 (s), 109.1 (s), 130.4 (s), 134.4 (s), 169.0 (s); IR (Neat): 2203 cm^{-1}, 1717 cm^{-1}; MS (EI) *m/z* 236 (M^+), 179 (100%); HRMS (EI) calcd for $C_{15}H_{24}O_2$: 236.1776, found: 236.1780.



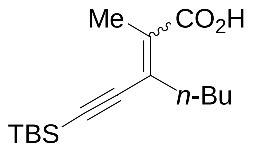


3-Butyl-7-(4-methoxybenzyloxy)-2-methyl-hept-2-en-4-ynoic acid (3c): To a solution of ethyl 2,2-dibromopropionate (156 mg, 0.6 mmol) in THF (3 ml), cooled to –78 °C under argon, was added dropwise a solution of *tert*-butyllithium (1.58 mL, 2.4 mmol, 1.52 M in pentane). The yellow solution was stirred for 10 min at –78 °C and allowed to warm to 0 °C. After 30 min, a solution of the alkynylketone **2c** (137 mg, 0.5 mmol) in THF (1 ml) was added. After 0.5 h, the solution was concentrated in vacuo, and then diluted with hexane. The resulting solution was washed with water (x 3). The combined water phase was acidified with 1 M HCl solution and extracted with CH_2Cl_2 (x 3). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 70/30 to 50/50) to afford the carboxylic acid **3c** (141.2 mg, 85%) as a pale brown solid: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.90 (t, J = 7.2 Hz, 3H), 1.29-1.68 (m, 4H), 2.11 (s, 3H), 2.58 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H), 3.63 (t, J = 7.2 Hz, 2H), 3.81 (s, 3H), 4.50 (s, 2H), 6.88 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H).

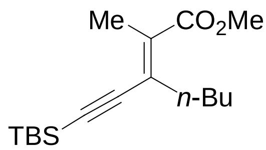


(*E*)-3-Butyl-7-(4-methoxybenzyloxy)-2-methylhept-2-en-4-yn-1-ol : To a solution of the carboxylic acid **3c** (140 mg) and MeOH (0.1 ml) in CH_2Cl_2 (4 ml) was added EDC (97.5 mg, 0.508 mmol) and DMAP (5.2 mg, 0.0424 mmol) at room temperature. After 13 h, a saturated NH_4Cl solution was added and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 80/20) to afford the methyl ester (123 mg, 84%).

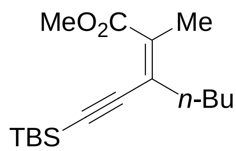
To a solution of diisobutyl alminium hydride (1.54 ml, 1.50 mmol, 0.97 M in hexane) in THF (1.5 ml), cooled to –78 °C, was added a solution of the methyl ester (103 mg) in THF (1.5 ml). After 1.5 h, the mixture was added water and allowed to warm to room temperature over 1 h. The mixture was filtered through celite and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 70/30 to 50/50) followed by HPLC (hexane/AcOEt = 77/23) to afford the alcohol (90.6 mg, 96%) as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.90 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 6.4 Hz, 1H), 1.25-1.35 (m, 2H), 1.43-1.50 (m, 2H), 1.99 (s, 3H), 2.17 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 4.18 (d, *J* = 6.0 Hz, 2H), 4.50 (s, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9 (q), 19.2 (q), 20.9 (t), 22.3 (t), 31.3 (t), 31.6 (t), 55.2 (q), 62.2 (t), 68.5 (t), 72.6 (t), 81.7 (s), 90.4 (s), 113.7 (d), 121.3 (s), 129.3 (d), 130.2 (s), 139.9 (s), 159.2 (s); IR (Neat): 3404 cm^{-1}, 2214 cm^{-1}; MS (EI) *m/z* 316 (M$^+$), 121 (100%); HRMS (EI) calcd for $C_{20}H_{28}O_3$: 316.2038, found: 316.2035.



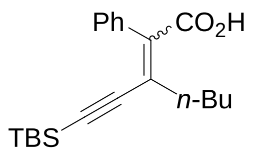
3-Butyl-5-(*tert*-butyldimethylsilanyl)-2-methylpent-2-en-4-ynoic acid (3d): According to *the general procedure for the olefination of alkynylketone*, the pentenynoic acid **3d** (69%) was obtained from **2d** as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.16 (s, 6H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.97 (s, 9H), 1.32-1.41 (m, 2H), 1.53-1.59 (m, 2H), 2.15 (s, 3H), 2.59 (t, *J* = 8.0 Hz, 2H).



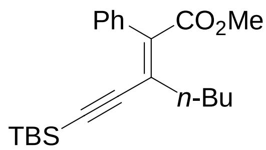
(*E*)-Methyl 3-butyl-5-(*tert*-butyldimethylsilanyl)-2-methylpent-2-en-4-ynoate : According to *the general procedure for esterification of the carboxylic acid*, the methyl pentenynoate (72%) was obtained from **3d** as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.96 (s, 9H), 1.29-1.39 (m, 2H), 1.54-1.58 (m, 2H), 2.11 (s, 3H), 2.49 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.7 (q x 2), 13.9 (q), 15.4 (q), 16.6 (s), 22.3 (t), 26.1 (q x 3), 30.0 (t), 33.8 (t), 51.6 (q), 99.9 (s), 104.9 (s), 129.7 (s), 133.6 (s), 168.9 (s); IR (Neat): 2141 cm^{-1}, 1732 cm^{-1}; MS (EI) *m/z* 294 (M$^+$), 237 (100%); HRMS (EI) calcd for $C_{17}H_{30}O_2Si$: 294.2015, found: 294.2019.



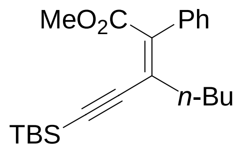
(*Z*)-Methyl 3-butyl-5-(*tert*-butyldimethylsilanyl)-2-methylpent-2-en-4-ynoate : colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.14 (s, 6H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.96 (s, 9H), 1.32-1.41 (m, 2H), 1.53-1.62 (m, 2H), 1.94 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; -4.6 (q x 2), 13.9 (q), 16.6 (s), 18.9 (q), 22.3 (t), 26.1 (q x 3), 30.9 (t), 33.3 (t), 51.5 (q), 103.0 (s), 105.0 (s), 133.1 (s), 133.1 (s), 168.8 (s); IR (Neat): 2139 cm^{-1}, 1717 cm^{-1}; MS (EI) *m/z* 294 (M$^+$), 237 (100%); HRMS (EI) calcd for $C_{17}H_{30}O_2Si$: 294.2015, found: 294.2017.



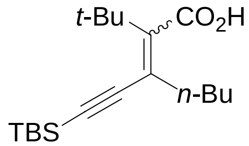
3-Butyl-5-(*tert*-butyldimethylsilanyl)-2-phenylpent-2-en-4-ynoic acid (3e): To a solution of ethyl dibromophenylacetate (193 mg, 0.6 mmol) in THF (3 ml), cooled to –78 °C under argon, was added dropwise a solution of *tert*-butyllithium (1.55 mL, 2.4 mmol, 1.55 M in pentane). The yellow solution was stirred for 10 min at –78 °C and allowed to warm to 0 °C. After 30 min, a solution of the alkynylketone **2d** (112 mg, 0.5 mmol) in THF (1 ml) was added. After 0.5 h, the solution was concentrated in vacuo, and then diluted with hexane. The resulting solution was washed with water (x 3). The combined water phase was acidified with 1 M HCl solution and extracted with CH_2Cl_2 (x 3). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford the carboxylic acid **3e** (196 mg) as a orange oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: -0.03 (s, 6H), 0.78 (s, 9H), 0.84-1.70 (m, 7H), 2.64 (t, *J* = 7.6 Hz, 2H), 7.26-7.40 (m, 5H).



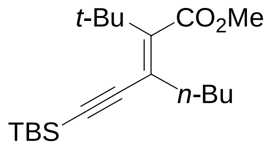
(*E*)-Methyl 3-butyl-5-(*tert*-butyldimethylsilanyl)-2-phenylpent-2-en-4-ynoate : To a solution of the carboxylic acid **3e** (190 mg) in acetonitrile (3 ml) was added DBU (0.248 ml, 1.66 mmol) and iodomethane (0.103 ml, 1.66 mmol) at room temperature. After 12.5 h, the reaction mixture was concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 95/5 to 90/10) followed by HPLC (hexane/AcOEt = 99/1) to afford the methyl ester (89 mg, 50% over 2 steps) as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: -0.01 (s, 6H), 0.80 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H), 1.36-1.45 (m, 2H), 1.62-1.69 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 7.27-7.33 (m, 3H), 7.44 (dd, *J* = 1.6 Hz, 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; -5.0 (q x 2), 13.9 (q), 16.5 (s), 22.2 (t), 25.9 (q x 3), 30.7 (t), 34.3 (t), 52.0 (q), 102.3 (s), 104.6 (s), 127.8 (d), 127.8 (d), 129.0 (d), 131.0 (s), 136.8 (s), 138.6 (s), 168.6 (s); IR (Neat): 2143 cm^{-1}, 1732 cm^{-1}; MS (EI) *m/z* 356 (M$^+$, 100%); HRMS (EI) calcd for $C_{22}H_{32}O_2Si$: 356.2172, found: 356.2177.



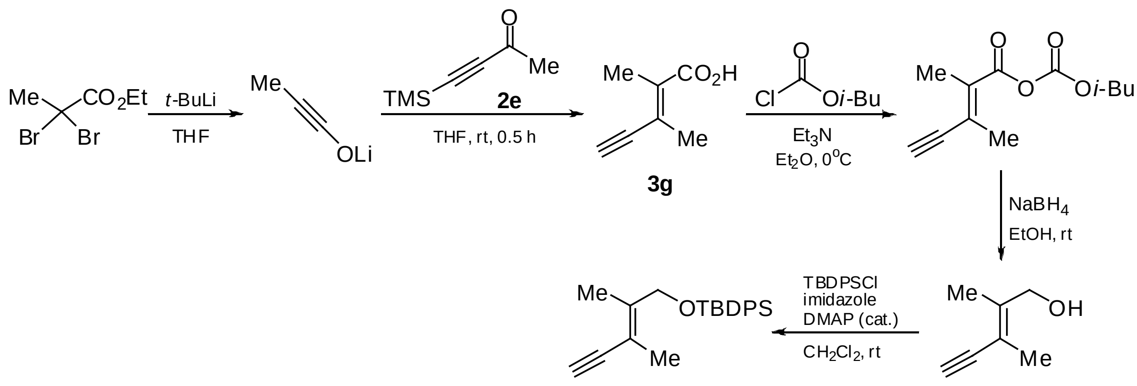
(*Z*)-Methyl 3-butyl-5-(*tert*-butyldimethylsilanyl)-2-phenylpent-2-en-4-ynoate : pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.17 (s, 6H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.99 (s, 9H), 1.19-1.28 (m, 2H), 1.52-1.59 (m, 2H), 2.13 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.31-7.38 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.6 (q x 2), 13.8 (q), 16.7 (s), 22.1 (t), 26.1 (q x 3), 30.4 (t), 33.3 (t), 52.1 (q), 101.7 (s), 104.0 (s), 127.9 (d), 128.3 (d), 128.9 (d), 130.2 (s), 135.5 (s), 139.4 (s), 168.1 (s); IR ($CHCl_3$): 2139 cm^{-1}, 1719 cm^{-1}; MS (EI) *m/z* 356 (M^+), 299 (100%); HRMS (EI) calcd for $C_{22}H_{32}O_2Si$: 356.2172, found: 356.2164.

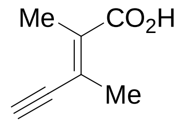


3-Butyl-2-*tert*-butyl-5-(*tert*-butyldimethylsilanyl)-pent-2-en-4-ynoic acid (3f): According to *the general procedure for the olefination of alkynylketone*, the pentenynoic acid **3f** was obtained from **2d** as a yellow oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.14 (s, 6H), 0.86-0.92 (m, 3H), 0.96 (s, 9H), 1.23-1.30 (m, 2H), 1.35 (s, 9H), 1.50-1.70 (m, 2H), 2.14 (t, *J* = 7.6 Hz, 2H)

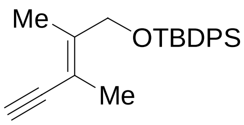


(*E*)-Methyl 3-butyl-2-*tert*-butyl-5-(*tert*-butyldimethylsilanyl)-pent-2-en-4-ynoate : According to *the general procedure for esterification of the carboxylic acid*, the methyl pentenynoate (39% over 2 steps) was obtained from **3f** as a colorless oil: ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.13 (s, 6H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.95 (s, 9H), 1.25-1.32 (m, 2H), 1.30 (s, 9H), 1.50-1.57 (m, 2H), 2.01 (t, *J* = 7.2 Hz, 2H), 3.72 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.9 (q x 2), 13.9 (q), 16.8 (s), 21.9 (t), 26.1 (q x 3), 29.1 (q x 3), 30.6 (t), 34.3 (s), 36.0 (t), 51.2 (q), 103.4 (s), 104.3 (s), 121.5 (s), 149.1 (s), 170.4 (s); IR (Neat): 2141 cm^{-1}, 1732 cm^{-1}; MS (EI) *m/z* 336 (M^+), 279 (100%); HRMS (EI) calcd for $C_{20}H_{36}O_2Si$: 336.2485, found: 336.2481.





2,3-Dimethylpent-2-en-4-ynoic acid (3g): To a solution of ethyl 2,2-dibromopropionate (312 mg, 1.2 mmol) in THF (6 ml), cooled to –78 °C under argon, was added dropwise a solution of *tert*-butyllithium (3.16 mL, 4.8 mmol, 1.52 M in pentane). The yellow solution was stirred for 10 min at –78 °C and allowed to warm to 0 °C. After 30 min, the mixture was recooled to –78 °C and added a solution of the alkynylketone **2e** (1.0 mmol) in THF (2 ml). After 0.5 h, the solution was allowed to warm to room temperature. After 0.5 h, concentrated in vacuo, and then diluted with hexane. The resulting solution was washed with water (x 3). The combined water phase was acidified with 1 M HCl solution and extracted with CH_2Cl_2 (x 3). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to afford the carboxylic acid **3g** (89 mg, 72%) as a yellow solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.16 (d, J = 1.2 Hz, 3H), 2.24 (d, J = 1.2 Hz, 3H), 3.55 (s, 1H).

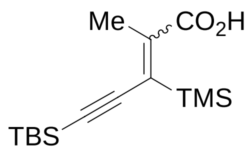


(*E*)-1-(*tert*-Butyldiphenylsiloxy)-2,3-dimethylpent-2-en-4-yn : To a solution of the carboxylic acid (93.5 mg, 0.735 mmol) and triethylamine (0.331 ml, 2.37 mmol) in Et_2O (7.5 ml), cooled to 0 °C, was added isobutyl chloroformate (0.294 ml). After 0.5 h, the mixture was filtered, and then washed with 1 M HCl solution, water, a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, filtered and concentrated to afford the mixed anhydride (205 mg).

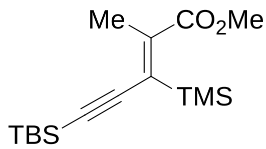
To a solution of the mixed anhydride (205 mg) in ethanol (3.8 ml) was added $NaBH_4$ (74.1 mg, 1.96 mmol) at room temperature. After 0.5 h, the mixture was concentrated in vacuo. The residue was diluted with water, extracted $CHCl_3$, dried over $MgSO_4$, filtered and concentrated to afford the alkynyl alcohol (115 mg).

To a solution of the alkynyl alcohol (115 mg) in CH_2Cl_2 (1.8 ml) was added imidazole (123 mg, 1.81 mmol), a solution of *tert*-butyldiphenylsilyl chloride (414 mg, 1.51 mmol) in CH_2Cl_2 (2 ml) and

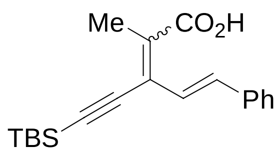
DMAP (9.2 mg, 0.0753 mmol) at room temperature. After 0.5 h, the mixture was added water, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 100/0 to 99/1) followed by HPLC (hexane) to afford the silyl ether (152 mg, 58% over 3 steps) as a pale yellow oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.05 (s, 9H), 1.60 (s, 3H), 2.06 (s, 3H), 3.06 (s, 1H), 4.23 (s, 2H), 7.38-7.69 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; 17.8 (q), 18.7 (q), 19.3 (s), 26.7 (q x 3), 26.8 (s), 63.2 (d), 79.3 (s), 85.2 (s), 112.3 (s), 127.7 (d), 129.7 (d), 133.5 (s), 135.6 (d), 144.0 (s); IR (Neat): 2091 cm^{-1}; MS (EI) *m/z* 348 (M^+), 199 (100%); HRMS (EI) calcd for $C_{23}H_{28}OSi$: 348.1909, found: 348.1913.



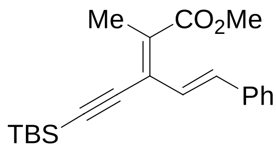
5-(*tert*-Butyldimethylsilanyl)-2-methyl-3-trimethylsilanylpent-2-en-4-ynoic acid (3h): According to *the general procedure for the olefination of alkynylketone*, the pentenynoic acid **3h** (75%) was obtained from **2f** as a orange oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.16 (s, 6H), 0.23 (s, 9H), 0.97 (s, 9H), 2.24 (s, 3H).



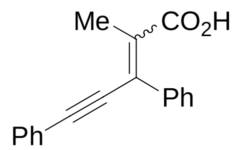
(*E*)-Methyl 5-(*tert*-butyldimethylsilanyl)-2-methyl-3-trimethylsilanylpent-2-en-4-ynoate : According to *the general procedure for esterification of the carboxylic acid*, the methyl pentenynoate (65%) was obtained from **3h** as a orange oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.15 (s, 6H), 0.22 (s, 9H), 0.96 (s, 9H), 2.21 (s, 3H), 3.75 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.5 (q x 2), -0.0 (qx3), 16.6 (s), 19.7 (q), 26.1 (q x 3), 51.8 (q), 106.8 (s), 109.9 (s), 137.2 (s), 147.6 (s), 168.7 (s); IR (Neat): 2120 cm^{-1}, 1717 cm^{-1}; MS (EI) *m/z* 310 (M^+), 295 (100%); HRMS (EI) calcd for $C_{16}H_{30}O_2Si_2$: 310.1784, found: 310.1780.



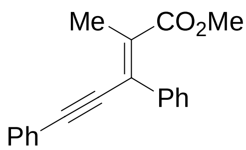
3-[(*tert*-Butyldimethylsilanyl)-ethynyl]-2-methyl-5-phenylpenta-2,4-dienoic acid (3i): According to *the general procedure for the olefination of alkynylketone*, the heptenynoic acid **3i** (81%) was obtained from **2g** as a pale yellow needle: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.24 (s, 6H), 1.04 (s, 9H), 2.33 (s, 3H), 7.23-7.37 (m, 4H), 7.49 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 15.6 Hz, 1H).



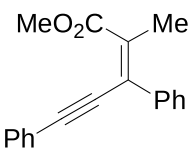
(*E*)-Methyl 3-[(*tert*-butyldimethylsilanyl)-ethynyl]-2-methyl-5-phenylpenta-2,4-dienoate : According to *the general procedure for the olefination of alkynylketone* and *esterification of the carboxylic acid* the methyl heptenynoate (72%) was obtained from **3i** as a pale yellow needle: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.26 (s, 6H), 1.03 (s, 9H), 2.29 (s, 3H), 3.82 (s, 3H), 7.24-7.28 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 16.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: -4.6 (q x 2), 16.7 (s), 19.5 (q), 26.2 (q x 3), 51.9 (q), 101.4 (s), 104.9 (s), 124.8 (d), 127.3 (d), 128.3 (d), 128.6 (d), 130.7 (s), 132.5 (s), 136.6 (d), 136.8 (s), 168.3 (s); IR (KBr): 2149 cm^{-1}, 1701 cm^{-1}; MS (EI) *m/z* 340 (M^+), 283 (100%); HRMS (EI) calcd for $C_{21}H_{28}O_2Si$: 340.1859, found: 340.1859.



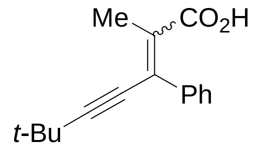
2-Methyl-3,5-diphenylpent-2-en-4-ynoic acid (3j): According to *the general procedure for the olefination of alkynylketone*, the pentenynoic acid **3j** (98%) was obtained from **2h** as a orange oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.04 (s, 3H), 2.40 (s, 3H), 7.26-7.48 (m, 10H).



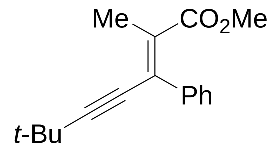
(*E*)-Methyl 2-methyl-3,5-diphenylpent-2-en-4-ynoate: According to *the general procedure for* ***e****sterification of the carboxylic acid*, the methyl pentenynoate (52% over 2 steps) was obtained from **3j** as a yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 3.52 (s, 3H), 7.26-7.48 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 19.6 (q), 51.7 (q), 88.3 (s), 99.3 (s), 122.8 (s), 127.8 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.8 (d), 129.1 (s), 131.6 (d), 135.3 (s), 138.6 (s), 169.8 (s); IR (Neat): 2201 cm^{-1}, 1715 cm^{-1}; MS (EI) *m/z* 276 (M^+, 100%); HRMS (EI) calcd for $C_{19}H_{16}O_2$: 276.1150, found: 276.1150.



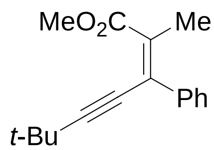
(*Z*)-Methyl 2-methyl-3,5-diphenylpent-2-en-4-ynoate: yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 3.89 (s, 3H), 7.28-7.46 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 19.6 (q), 51.7 (q), 88.3 (s), 99.3 (s), 122.8 (s), 127.8 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.8 (d), 129.1 (s), 131.6 (d), 135.3 (s), 138.6 (s), 169.8 (s); IR (Neat): 2197 cm^{-1}, 1717 cm^{-1}; MS (EI) *m/z* 276 (M^+), 205 (100%); HRMS (EI) calcd for $C_{19}H_{16}O_2$: 276.1150, found: 276.1151.



2,6,6-Trimethyl-3-phenylhept-2-en-4-ynoic acid (3k): According to *the general procedure for the olefination of alkynylketone*, the heptenynoic acid **3k** (97%) was obtained from **2i** as a yellow oil: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.28 (s, 9H), 2.27 (s, 3H), 7.22-7.40 (m, 5H).

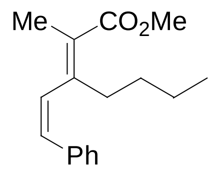


(*E*)-Methyl 2,6,6-trimethyl-3-phenylhept-2-en-4-ynoate: According to *the general procedure for esterification of the carboxylic acid*, the methyl heptenynoate (66%) was obtained from **3k** as a pale yellow oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.28 (s, 9H), 2.23 (s, 3H), 3.48 (s, 3H), 7.26-7.33 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; 19.3 (q), 28.4 (s), 30.8 (q x 3), 51.5 (q), 78.4 (s), 109.3 (s), 127.7 (d), 127.8 (d), 127.9 (d), 129.5 (s), 133.9 (s), 139.2 (s), 170.2 (s); IR (Neat): 2212 cm^{-1}, 1732 cm^{-1}; MS (EI) *m/z* 256 (M^+), 199 (100%); HRMS (EI) calcd for $C_{17}H_{20}O_2$: 256.1463, found: 256.1468.

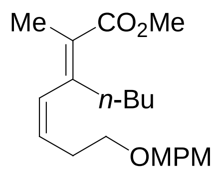


(*Z*)-Methyl 2,6,6-trimethyl-3-phenylhept-2-en-4-ynoate: pale yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.25 (s, 9H), 1.94 (s, 3H), 3.84 (s, 3H), 7.24-7.40 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; 17.1 (q), 28.3 (s), 30.7 (q x 3), 51.7 (q), 79.3 (s), 106.6 (s), 127.8 (d), 128.1 (d), 128.6 (d), 129.4 (s), 133.3 (s), 139.0 (s), 169.5 (s); IR (Neat): 2208 cm^{-1}, 1732 cm^{-1}; MS (EI) *m/z* 256 (M^+), 199 (100%); HRMS (EI) calcd for $C_{17}H_{20}O_2$: 256.1463, found: 256.1465.

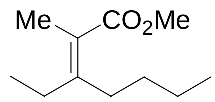
Reduction of the triple bond of the conjugate enyne compounds[6], [7]



Methyl 3-butyl-2-methyl-5-phenylpenta-2,4-dienoante: To a solution of alkyne (7.7 mg, 0.030 mmol) in hexane (0.3 ml) at room temperature was added quinoline (0.77 μl) and Pd on $CaCO_3$ / poisoned with lead (1.9 mg). The atmosphere was purged with hydrogen gas and the reaction was stirred under a hydrogen balloon for 45 min. Upon completion, the reaction was filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, hexane/AcOEt = 90/10) provided the diene (7.0 mg, 90%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, *J* = 7.2 Hz, 3H), 1.25-1.34 (m, 2H), 1.43-1.51 (m, 2H), 1.76 (s, 3H), 2.46 (t, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 6.11 (d, *J* = 12.0 Hz, 1H), 6.47 (d, *J* = 12.8 Hz, 1H), 7.19-7.35 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9 (q), 16.9 (q), 23.0 (t), 31.3 (t), 34.0 (t), 51.4 (q), 124.2 (s), 127.5 (d), 128.3 (d), 128.4 (d), 130.1 (d), 130.7 (d), 136.9 (s), 147.3 (s), 169.7 (s); IR (Neat): 1717 cm^{-1}; MS (EI) *m/z* 258 (M^+), 143 (100%); HRMS (EI) calcd for $C_{17}H_{22}O_2$: 258.1620, found: 258.1619.

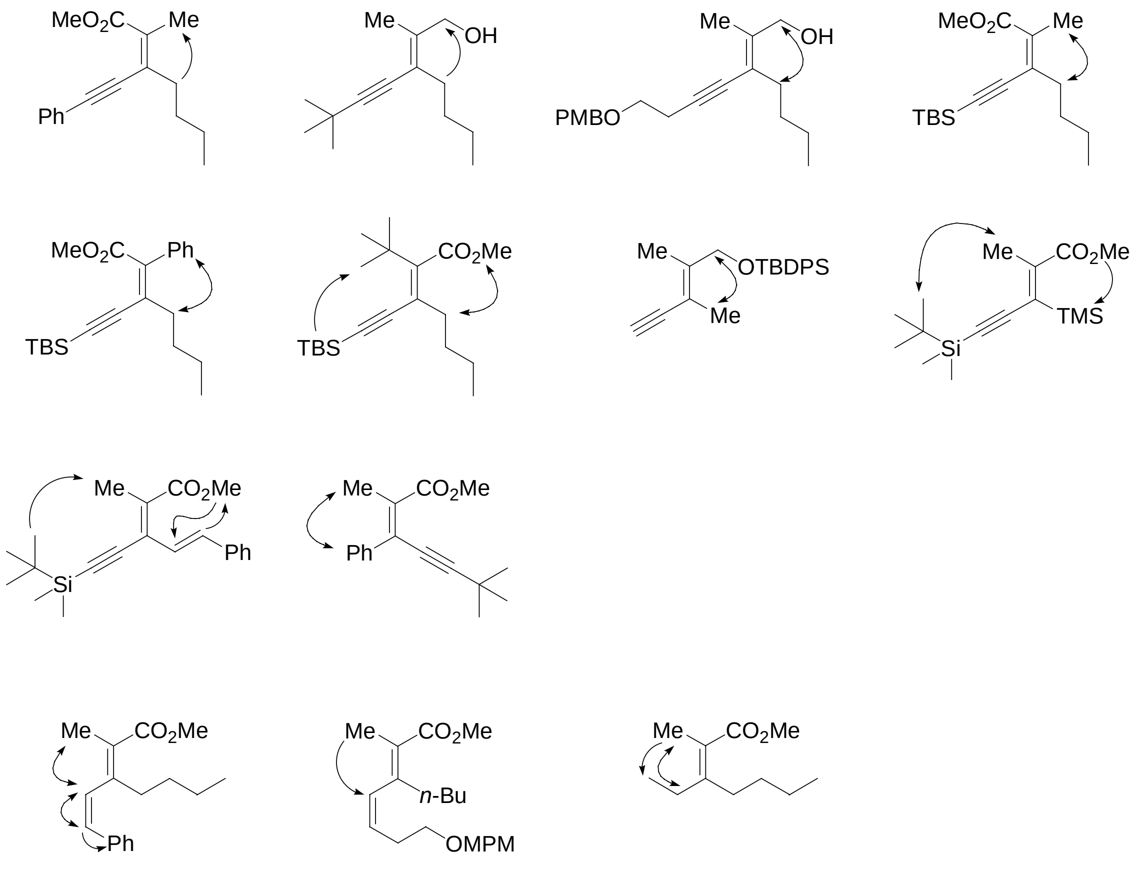


Methyl 3-butyl-7-(4-methoxybenzyloxy)-2-methylhepta-2,4-dienoate: To a solution of alkyne (21.2 mg, 0.0615 mmol) in hexane (1.6 ml) at room temperature was added quinoline (2.1 μl) and Pd on $CaCO_3$ / poisoned with lead (5.3 mg). The atmosphere was purged with hydrogen gas and the reaction was stirred under a hydrogen balloon for 45 min. Upon completion, the reaction was filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, hexane/AcOEt = 85/15) provided the diene (18.9 mg, 89%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, *J* = 7.2 Hz, 3H), 1.24-1.40 (m, 4H), 1.80 (s, 3H), 2.23 (dq, *J* = 1.2 Hz, 6.8 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.74 (s, 3H), 3.81 (s, 3H), 4.44 (s, 2H), 5.60 (dt, *J* = 7.2 Hz, 11.6 Hz, 1H), 5.88 (d, *J* = 12.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.9 (q), 17.2 (q), 22.8 (t), 29.8 (t), 30.5 (t), 34.1 (t), 51.3 (q), 55.2 (q), 69.1 (t), 72.5 (t), 113.7 (d), 124.0 (s), 128.8 (d), 129.2 (d), 130.4 (d), 130.4 (s), 146.5 (s), 159.1 (s), 169.9 (s); IR (Neat): 1717 cm^{-1}; MS (FAB) *m/z* 346 (M^+), 121 (100%); HRMS (FAB) calcd for $C_{21}H_{30}O_4$:346.2144, found:346.2141.



Methyl 3-ethyl-2-methylhept-2-enoate: A thick-walled pressure tube was charged with alkyne (14.0 mg, 0.0777 mmol) and 0.9 ml of a 2:1 THF/H_2O solution. To this mixture were added *p*-toluenesulfonyl hydrazide (54.0 mg, 0.290 mmol, 3.7 eq.) and sodium acetate (38.1 mg, 0.464 mmol, 6.0 eq.). After sealing the tube with a threaded Teflon stopper, the reaction vessel was submerged in an oil bath preheated to 100 ^oC. The reaction mixture was stirred for 1 h then cooled to room temperature prior to removing carefully the Teflon plug. A second portion of *p*-toluenesulfonyl hydrazide (54.0 mg, 0.290 mmol, 3.7 eq.) and sodium acetate (38.1 mg, 0.464 mmol, 6.0 eq.) were added, the reaction vessel was sealed, and the solution was stirred at 100 ^{o}C. Following a 1 h period, the contents were cooled to room temperature and the Teflon stopper was carefully removed. A third portion of *p*-toluenesulfonyl hydrazide (54.0 mg, 0.290 mmol, 3.7 eq.) and sodium acetate (38.1 mg, 0.464 mmol, 6.0 eq.) were added, the reaction vessel was sealed, and the solution was stirred at 100 ^{o}C for 1 h. Upon cooling to room temperature, the reaction mixture was quenched with a saturated $NaHCO_3$ solution and extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 90/10) to afford the alkene (9.1 mg, 64%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H), 1.25-1.52 (m, 4H), 1.86 (s, 3H), 2.14 (q, *J* = 8.0 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 3.71 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ; 12.1 (q), 14.0 (q), 15.2 (q), 23.0 (t), 26.7 (t), 31.0 (t), 33.8 (t), 51.2 (q), 121.9 (s), 152.6 (s), 170.3 (s) ; IR (Neat): 1717 cm^{-1}; MS (EI) *m/z* 184 (M^+, 100%); HRMS (EI) calcd for $C_{11}H_{20}O_2$:184.1463, found:184.1469.

NOE experiments



Computational Details

All calculations in the present study were performed with the Gaussian 03 program (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision D.02; Gaussian Inc.: Wallingford, CT, 2004.) and by using the restricted Becke-three-parameter plus Lee-Yang-Parr (B3LYP) DFT method with the 6-31G(d) basis set (Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley; New York, 1986. References cited therein.). Stationary points were optimized without any symmetry assumption unless noted otherwise.

Normal coordination analyses were performed for all transition states, and one imaginary frequency was confirmed at each optimized structure.

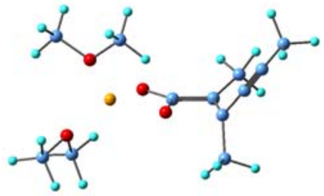
The origin of the stereoelectronic effects of the ring-opening of the β-lactone enolate derivative was examined with the aid of Natural Bond Orbital (NBO) analysis. The transition states of the ring opening are reactant-like rather than product-like by the optimal Lewis structure search. Second-order perturbation analysis of bonding NBOs and antibonding NBOs was carried out for these transition states. The second order interaction energy is expressed as follows.

$$E^{(2)}_{\phi\phi*} = -2\frac{\langle\phi|F|\phi*\rangle^2}{\varepsilon_{\phi*}-\varepsilon_{\phi}} = -2\frac{F_{ij}{}^2}{\Delta\varepsilon}$$

The ϕ/ϕ^* and F refer to the filled/vacant NBO and Fock matrices, respectively. The ε_ϕ and $\varepsilon_{\phi*}$ refer to the NBO energies of the bonding/lone pair and those of antibonding/Rydberg, respectively. NBOs are mutually orthogonal.

Cartesian coordinates of TSE and TSZ

TSE1



E(RB+HF-LYP) = -778.288356382 A.U.

Value of imaginary frequency = 517.0465*i* cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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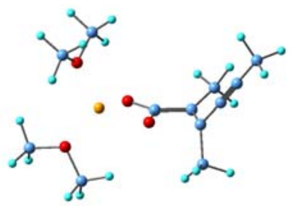
2	6	0	-2.035056	-0.976281	-0.468843
3	6	0	-3.074471	0.007367	-0.538648
4	8	0	-0.210122	-0.345900	-0.487522
5	3	0	1.620987	0.111061	0.135583
6	8	0	0.777888	-0.991292	1.452155
7	1	0	-2.890503	-2.706360	2.034409
8	1	0	-3.193065	-0.977007	2.230663
9	1	0	-1.748159	-1.712071	2.947233
10	8	0	1.795572	2.066526	0.183495
11	6	0	0.555781	2.777922	0.137719
12	6	0	2.805667	2.749108	0.913314
13	6	0	-1.891112	-1.827859	-1.716755
14	1	0	-2.797494	-2.443611	-1.815800
15	1	0	-1.030500	-2.492253	-1.621236
16	1	0	-1.799272	-1.219414	-2.622916
17	8	0	3.342819	-0.657727	-0.397794
18	6	0	4.096214	-0.335857	-1.557406
19	6	0	3.534245	-2.003196	0.049064
20	6	0	-1.582704	-1.419260	0.849570
21	6	0	-2.397743	-1.721865	2.064623
22	6	0	-3.924146	0.875865	-0.572851
23	6	0	-4.959142	1.901991	-0.610278
24	1	0	-5.057036	2.340529	-1.610859
25	1	0	-5.933641	1.475210	-0.340564
26	1	0	-4.749851	2.713390	0.097717
27	1	0	-0.166123	2.107354	-0.330180
28	1	0	0.220385	3.027248	1.153500
29	1	0	0.668810	3.701827	-0.445890
30	1	0	3.827671	-0.994433	-2.395191
31	1	0	3.860342	0.698241	-1.819269
32	1	0	5.173962	-0.426846	-1.361788
33	1	0	2.818528	-2.162324	0.857022
34	1	0	3.332349	-2.708992	-0.768087
35	1	0	4.564191	-2.143298	0.404385
36	1	0	2.489542	2.923347	1.951164
37	1	0	3.693822	2.113232	0.906962
38	1	0	3.042272	3.713826	0.442924

TSE2



E(RB+HF-LYP) = -778.287980383 A.U.

Value of imaginary frequency = 515.5331*i* cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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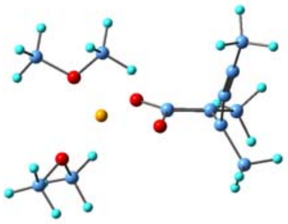
2	6	0	-2.077006	-0.998082	-0.066157
3	6	0	-3.018987	-0.087796	-0.644105
4	8	0	-0.200849	-0.590517	-0.270741
5	3	0	1.621395	0.066531	0.178131
6	8	0	0.687037	-0.313209	1.801426
7	1	0	-3.134398	-1.277491	2.901482
8	1	0	-3.265348	0.360327	2.251741
9	1	0	-1.909838	-0.069716	3.310193
10	8	0	2.172079	1.947413	0.129747
11	6	0	2.541925	2.672089	-1.034328
12	6	0	1.534353	2.756767	1.122170
13	1	0	2.999815	1.960804	-1.725606
14	1	0	3.265928	3.461896	-0.789244
15	1	0	1.661808	3.127131	-1.509603
16	1	0	0.672217	3.282999	0.690616
17	1	0	1.193729	2.073157	1.901298
18	1	0	2.243785	3.490878	1.527789
19	6	0	-1.994816	-2.344502	-0.762136
20	1	0	-2.953845	-2.863379	-0.616415
21	1	0	-1.205194	-2.949964	-0.313173
22	1	0	-1.830685	-2.243008	-1.840542
23	8	0	3.024463	-1.000041	-0.682327
24	6	0	4.396347	-0.984830	-0.311844
25	6	0	2.574548	-2.280766	-1.130314
26	1	0	4.626080	0.026223	0.031761
27	1	0	4.590623	-1.699172	0.500014
28	1	0	5.035142	-1.233704	-1.170794
29	1	0	1.494526	-2.196026	-1.259006
30	1	0	2.796703	-3.050445	-0.378900
31	1	0	3.060985	-2.545836	-2.078902
32	6	0	-1.689314	-0.808573	1.331311
33	6	0	-2.546473	-0.438365	2.497755
34	6	0	-3.787026	0.721902	-1.125283
35	6	0	-4.719214	1.689288	-1.691268
36	1	0	-5.020639	1.418319	-2.710356
37	1	0	-5.627952	1.755167	-1.079719
38	1	0	-4.276532	2.692688	-1.725325

TSZ1

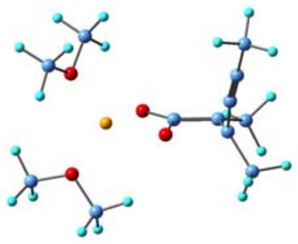


E(RB+HF-LYP) = -778.283847051 A.U.

Value of imaginary frequency = 518.5337*i* cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.382517	-0.970349	-0.758942
2	6	0	2.182658	-0.916953	0.417291
3	6	0	2.728403	0.412370	0.446647
4	8	0	0.315614	-0.324462	0.453260
5	3	0	-1.526857	0.094701	-0.162713
6	8	0	-0.656277	-0.987987	-1.486892
7	1	0	3.140409	-2.422834	-2.137526
8	1	0	2.414956	-3.541821	-0.978319
9	1	0	1.465664	-2.948828	-2.347269
10	8	0	-1.839878	2.026619	-0.274422
11	6	0	-0.635777	2.795555	-0.349189
12	6	0	-2.927333	2.621473	-0.969013
13	1	0	0.147010	2.190661	0.110740
14	1	0	-0.759480	3.746835	0.186405
15	1	0	-0.375691	2.997631	-1.396864
16	1	0	-2.687744	2.753628	-2.033206
17	1	0	-3.781033	1.947056	-0.870668
18	1	0	-3.180479	3.598284	-0.533544
19	6	0	2.677095	-1.798445	1.545961
20	1	0	2.077856	-2.710110	1.613797
21	1	0	3.721337	-2.081910	1.353097
22	1	0	2.654322	-1.265669	2.500887
23	8	0	-3.146388	-0.782068	0.502254
24	6	0	-3.851048	-0.469813	1.694916
25	6	0	-3.243559	-2.159651	0.129518
26	1	0	-3.471442	-1.059372	2.541040
27	1	0	-4.926204	-0.664648	1.576064
28	1	0	-3.694080	0.592754	1.894424
29	1	0	-4.278065	-2.408125	-0.143971
30	1	0	-2.922055	-2.803708	0.959232
31	1	0	-2.573252	-2.293706	-0.720990
32	6	0	1.669152	-1.498311	-0.816903
33	6	0	2.208443	-2.652294	-1.598075
34	6	0	3.336334	1.464070	0.462424
35	6	0	4.052205	2.735748	0.458590
36	1	0	4.129553	3.152446	-0.553417
37	1	0	3.548194	3.481209	1.087631
38	1	0	5.071689	2.618910	0.847649

TSZ2



E(RB+HF-LYP) = -778.283623731 A.U.

Value of imaginary frequency = 512.0443*i* cm^{-1}

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3	6	0	-2.646382	0.559509	-0.640344
4	8	0	-0.350064	-0.467448	-0.370826
5	3	0	1.517298	-0.052828	0.182446
6	8	0	0.533083	-0.676713	1.708794
7	1	0	-3.422107	-1.363697	2.607674
8	1	0	-2.846927	-2.848160	1.840639
9	1	0	-1.828900	-2.011230	3.018339
10	8	0	2.315475	1.690939	0.593641
11	6	0	2.797435	2.640538	-0.345388
12	6	0	1.803804	2.287238	1.789997
13	6	0	-2.898759	-1.859870	-1.078329
14	1	0	-2.386653	-2.810867	-0.908655
15	1	0	-3.953727	-1.982811	-0.795966
16	1	0	-2.870690	-1.603661	-2.141180
17	8	0	2.756775	-1.069170	-0.945640
18	6	0	2.156957	-2.154104	-1.657261
19	6	0	4.133144	-1.275848	-0.661343
20	6	0	-1.843729	-1.042779	1.134582
21	6	0	-2.527691	-1.850983	2.189566
22	6	0	-3.103443	1.637030	-0.965165
23	6	0	-3.626931	2.947015	-1.336990
24	1	0	-3.850941	3.558082	-0.453525
25	1	0	-2.904208	3.502974	-1.948499
26	1	0	-4.550163	2.857966	-1.923345
27	1	0	3.635885	3.214478	0.073917
28	1	0	3.139963	2.084997	-1.221627
29	1	0	2.000866	3.336265	-0.643731
30	1	0	1.038969	3.036347	1.544853
31	1	0	1.352775	1.477980	2.366271
32	1	0	2.616326	2.766093	2.353232
33	1	0	4.480221	-0.406127	-0.098999
34	1	0	4.276802	-2.182073	-0.056746
35	1	0	4.714055	-1.367561	-1.589837
36	1	0	1.088980	-1.935960	-1.702744
37	1	0	2.583326	-2.230289	-2.666861
38	1	0	2.318531	-3.099337	-1.121452

References

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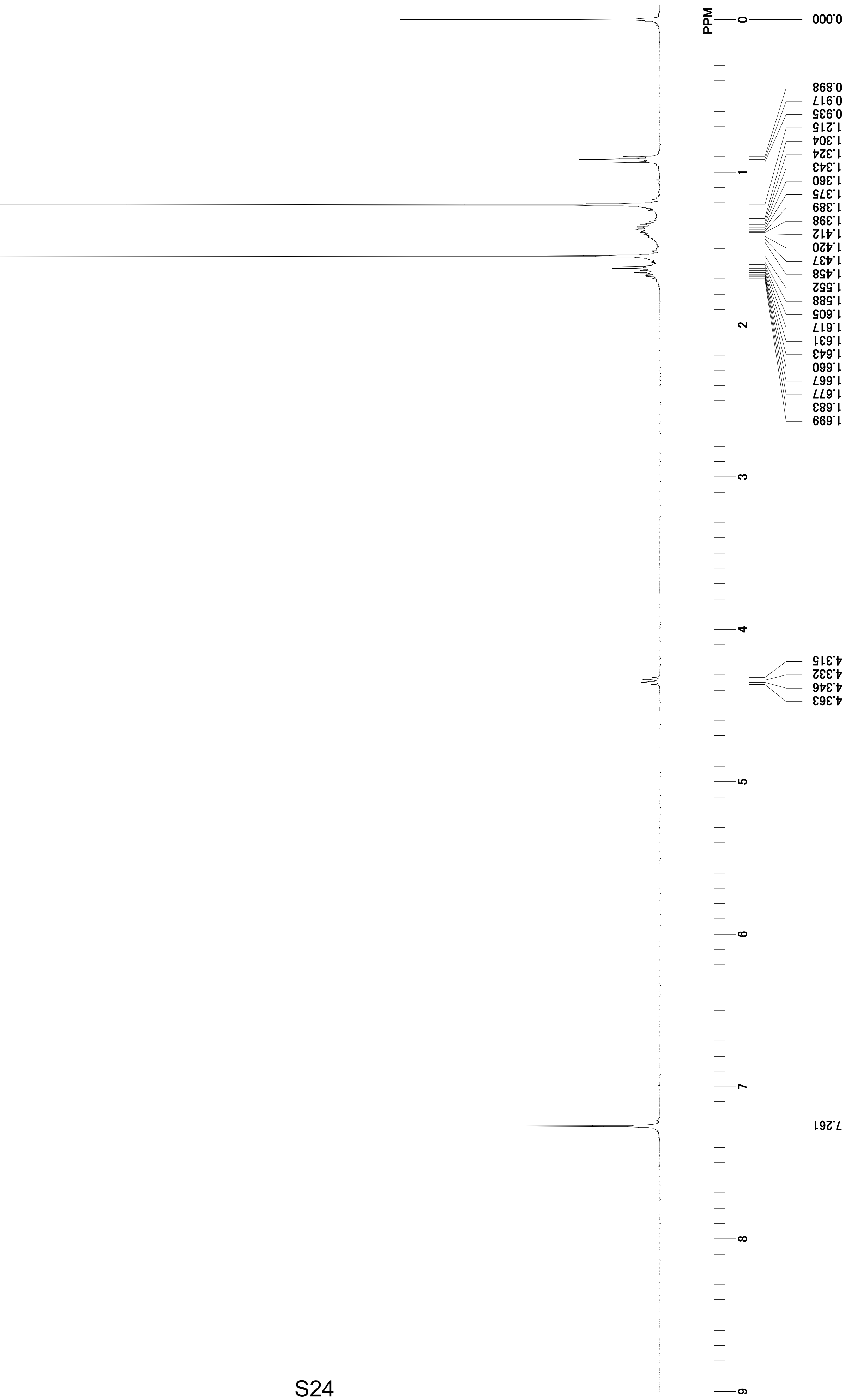
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1.420
1.437
1.458
1.552
1.588
1.605
1.617
1.631
1.643
1.660
1.667
1.677
1.683
1.699
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4.363
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2
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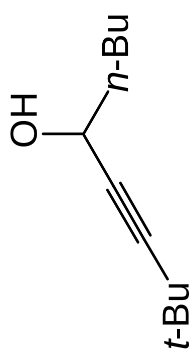
6
7
8
9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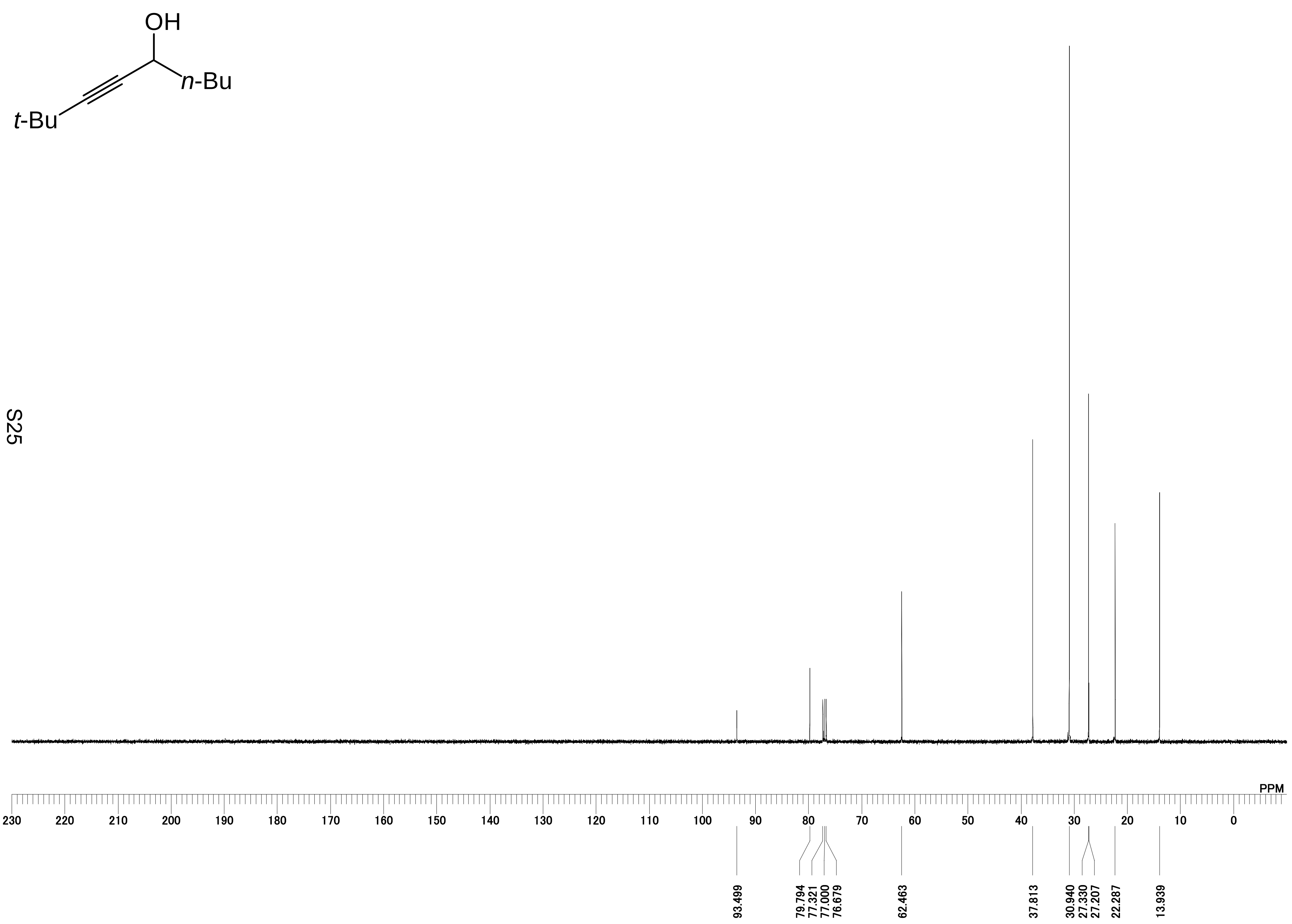
t-Bu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t-Bu
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80
70
60
50
40
30
20
10
0
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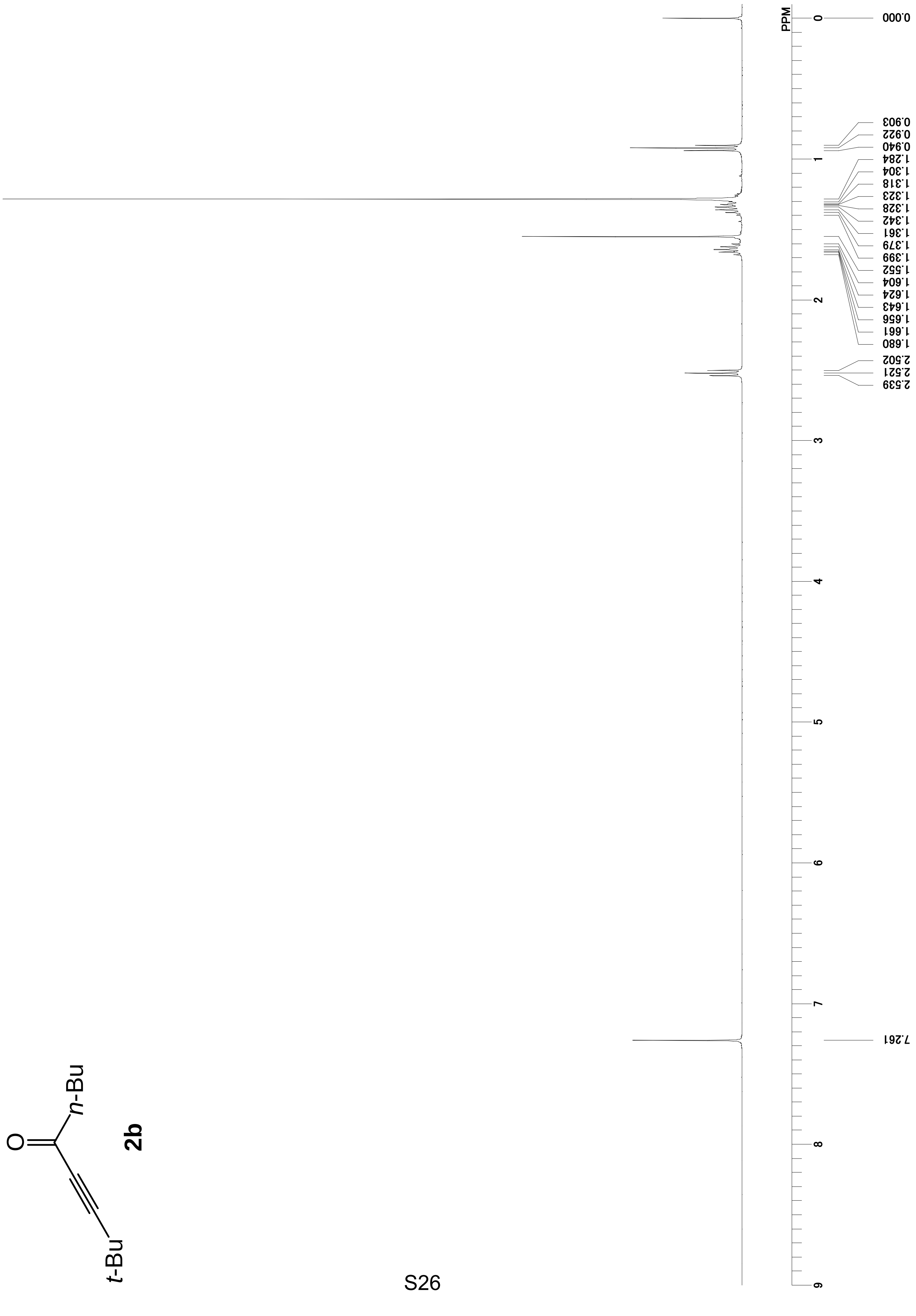
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O
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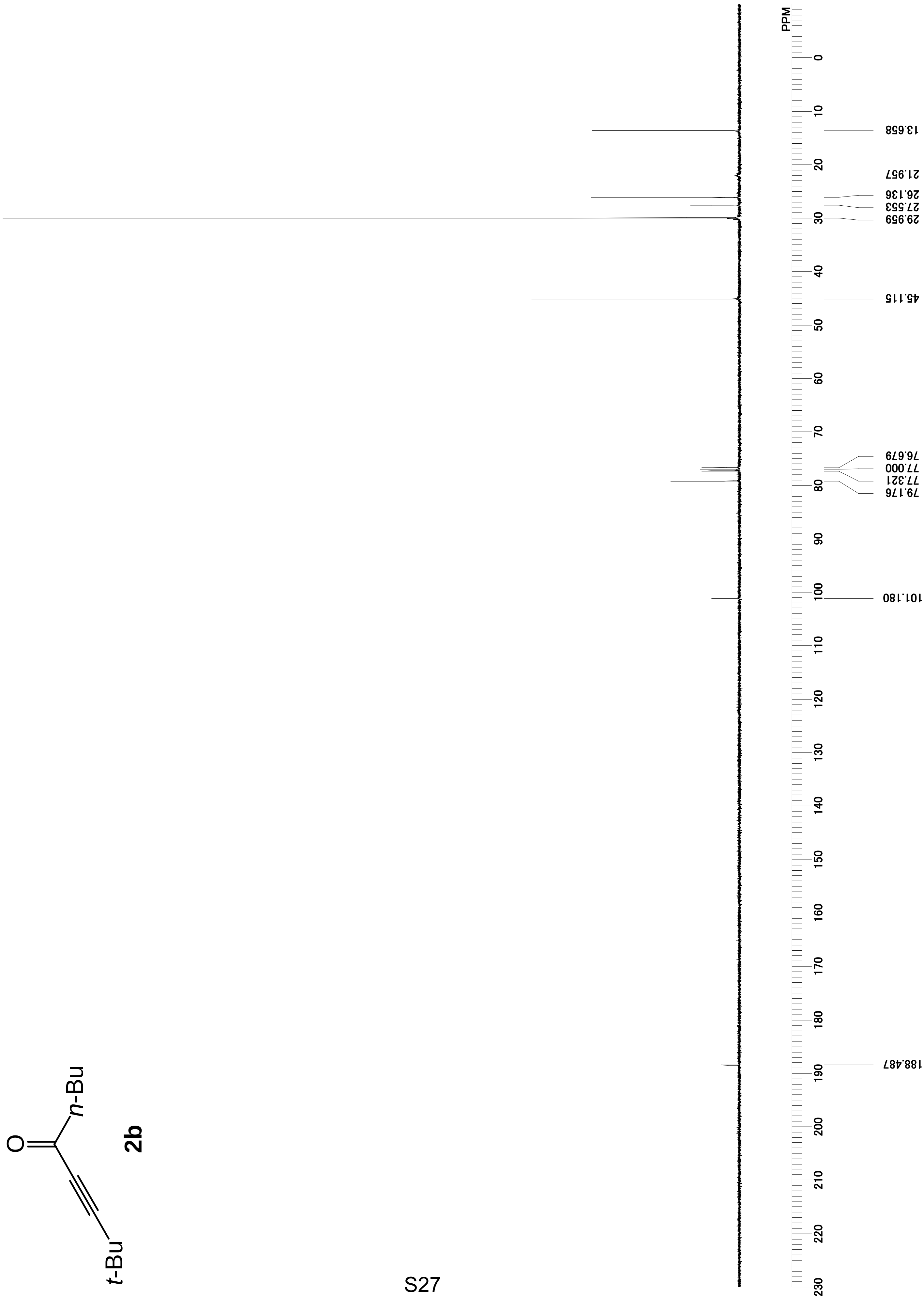
t-Bu

2b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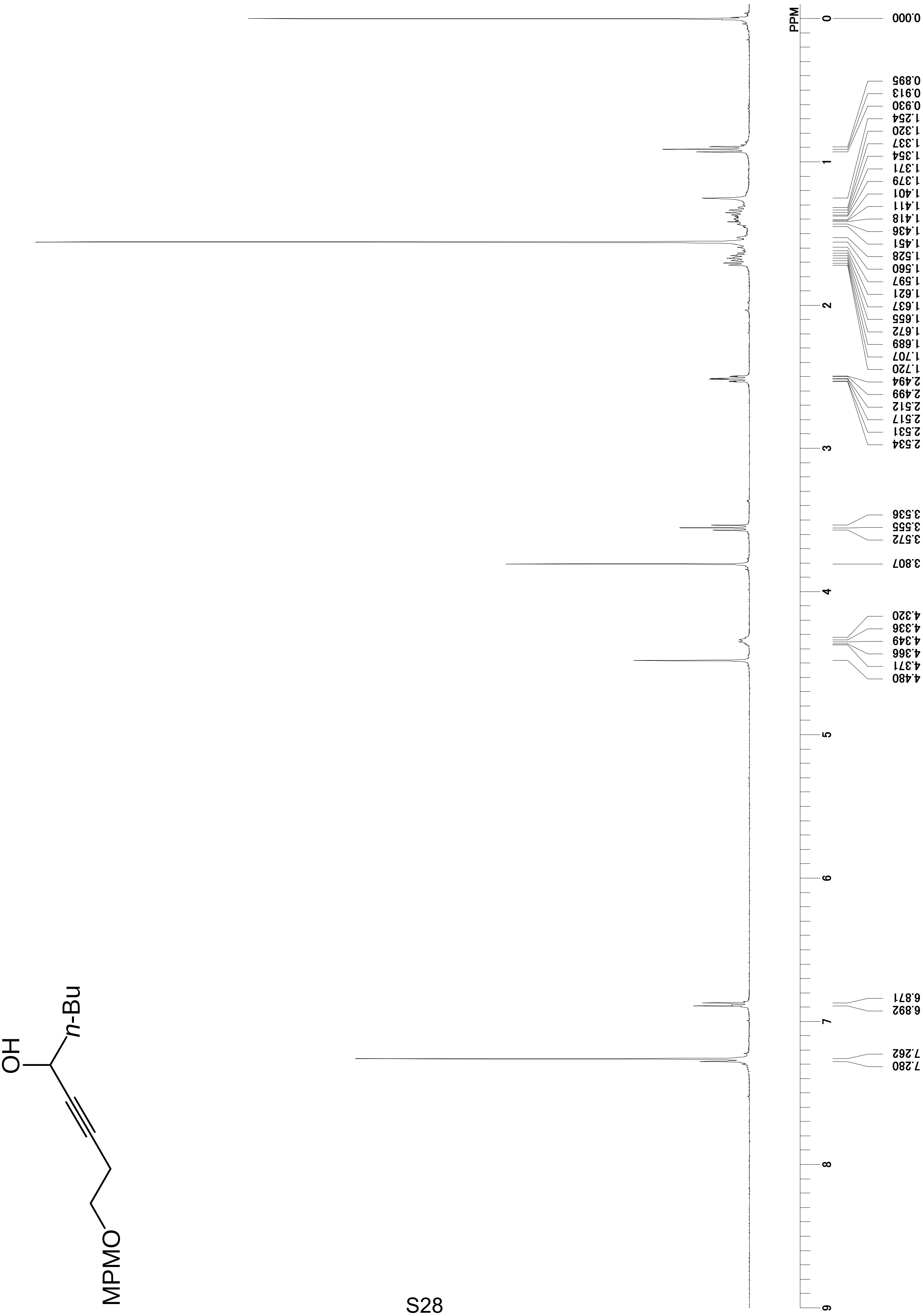
t-Bu
2b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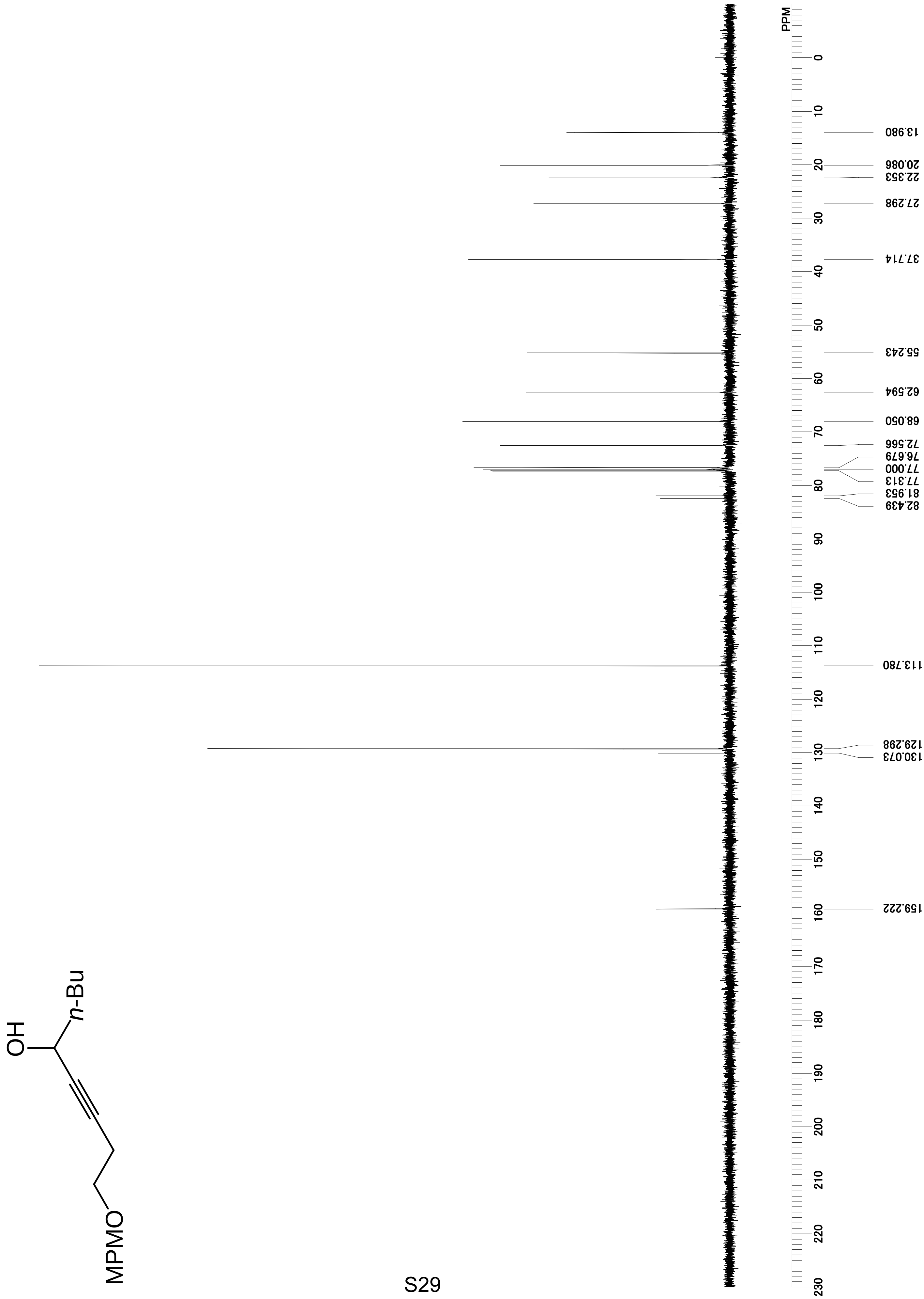
7.262 7.280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n-Bu
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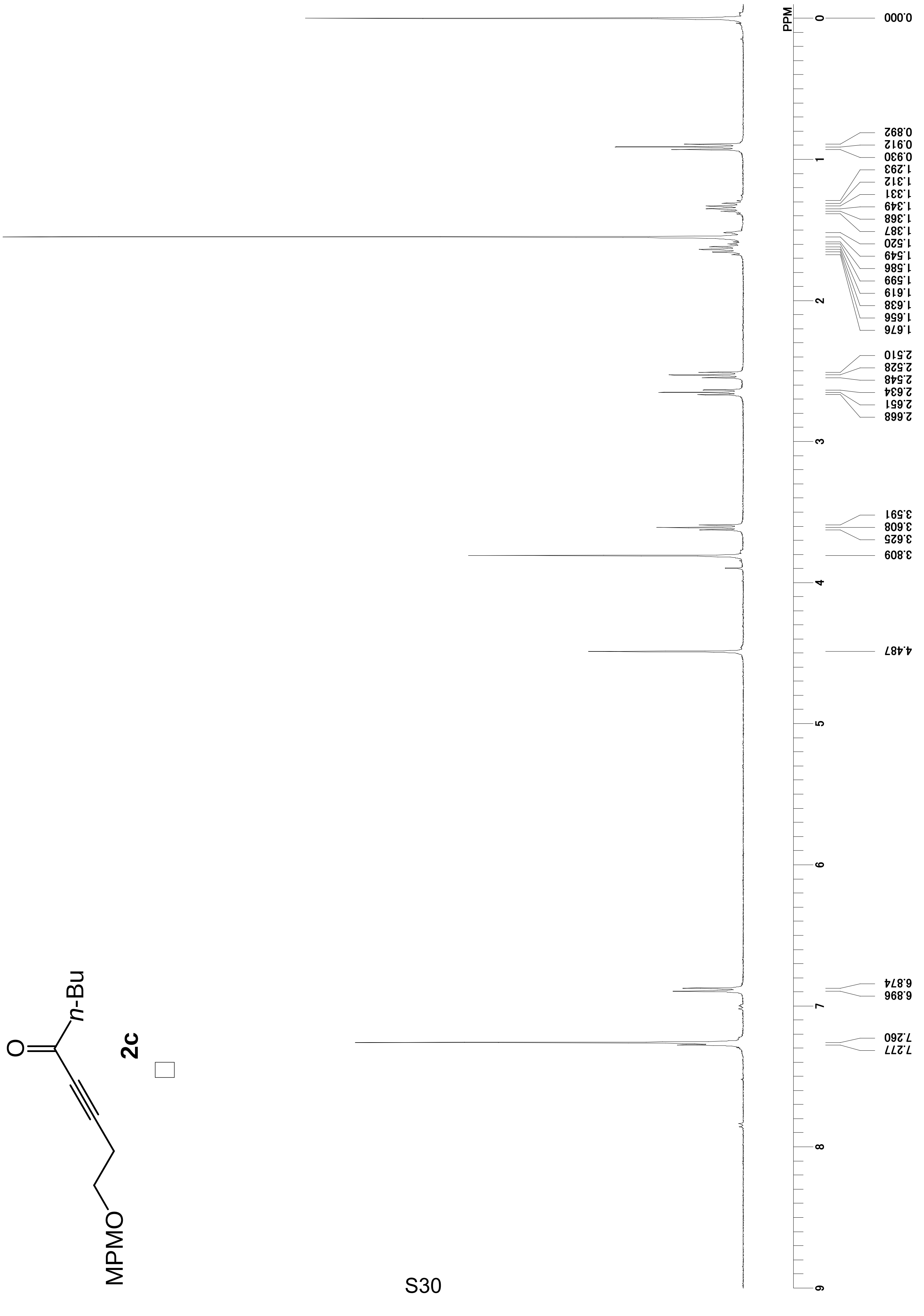
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2c
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0.930
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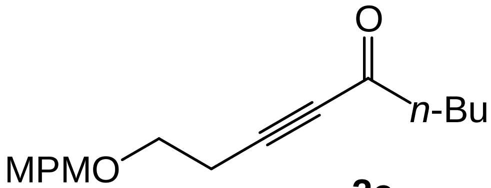

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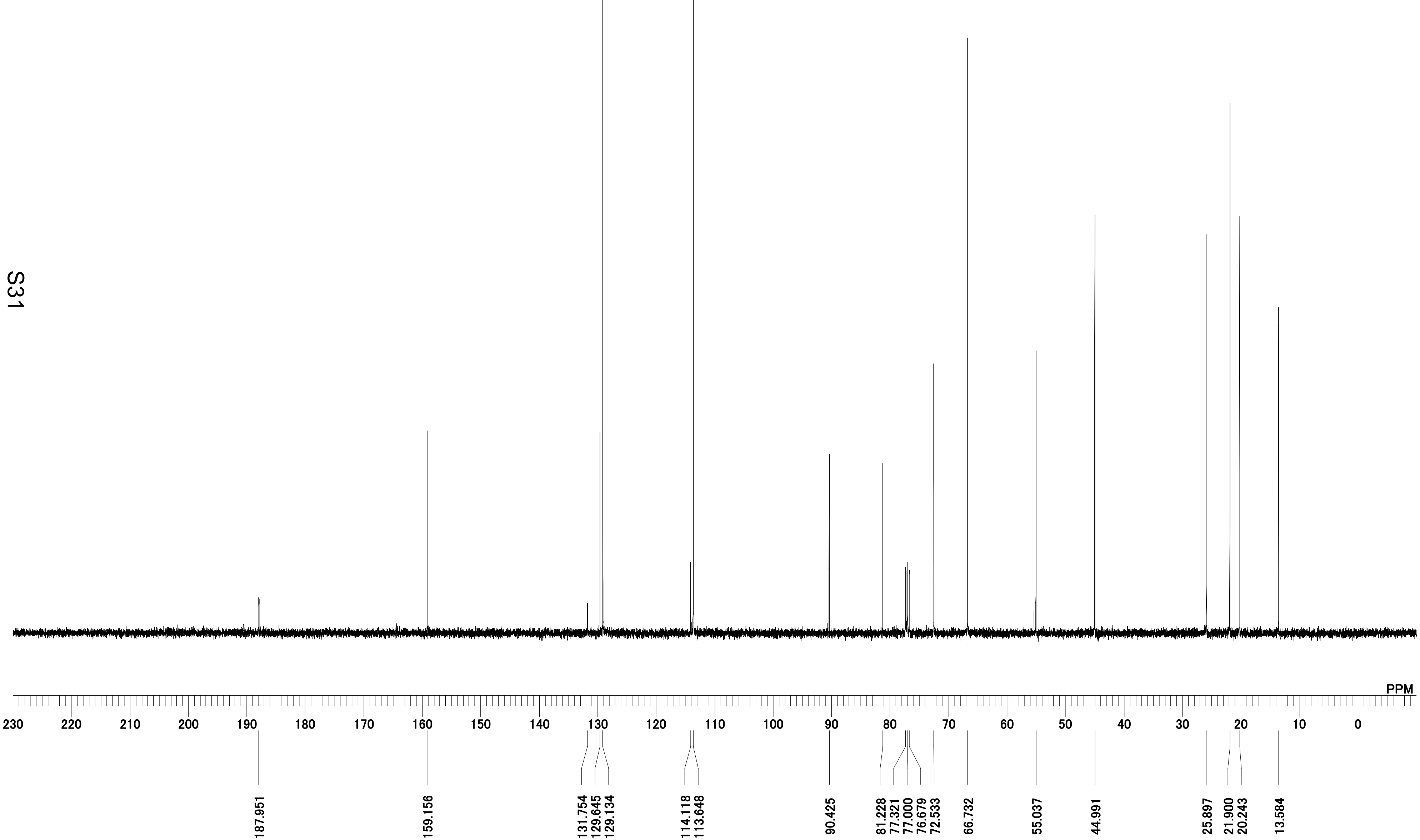

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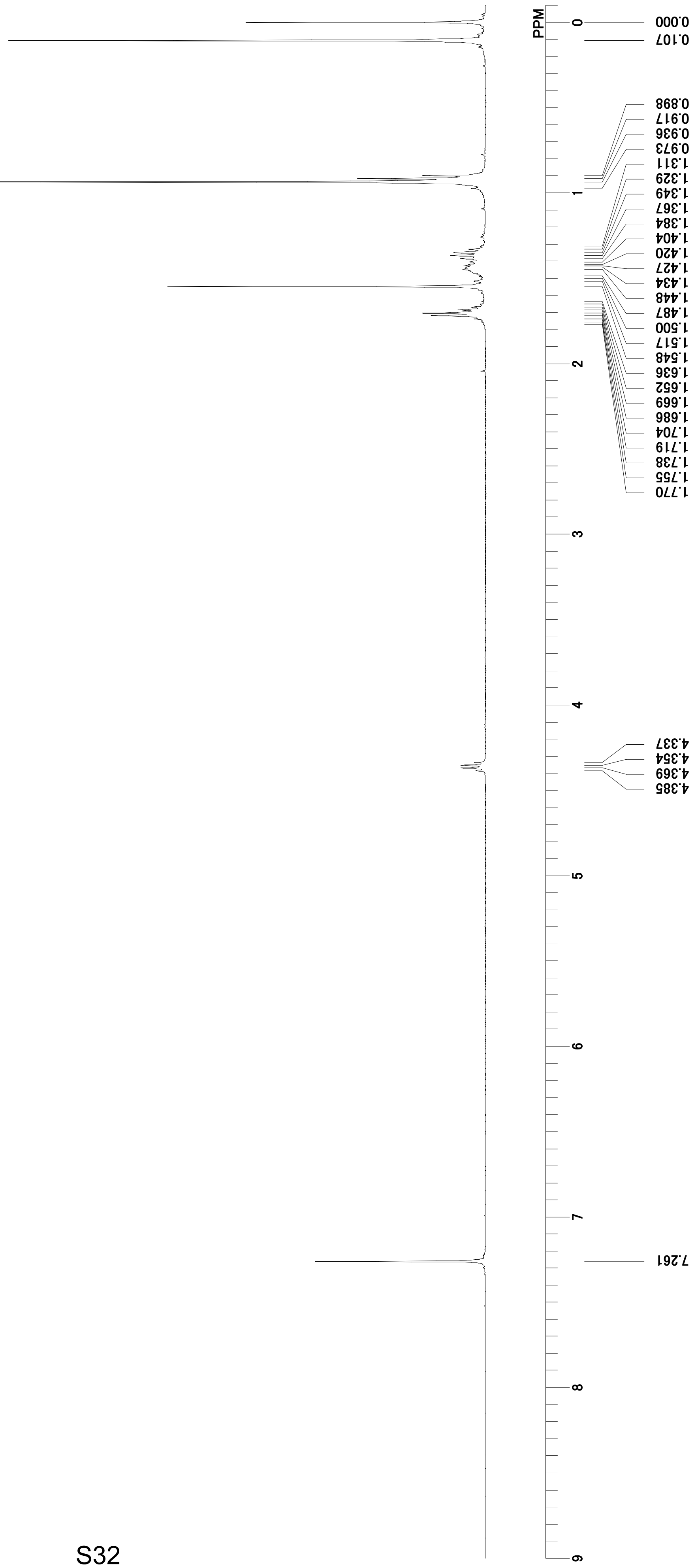
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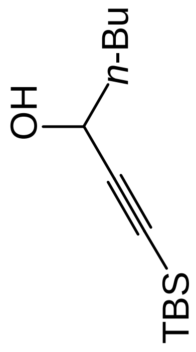
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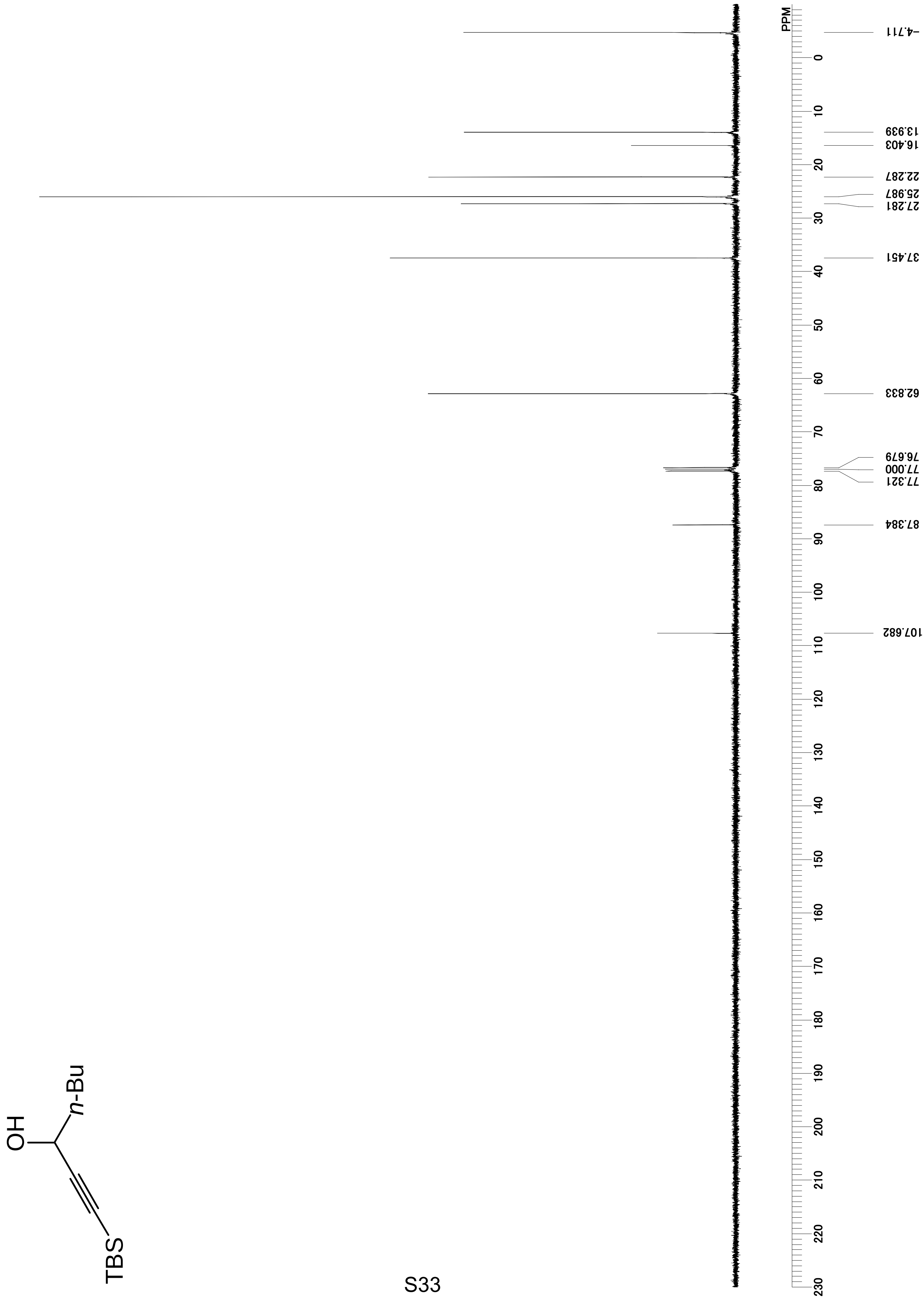
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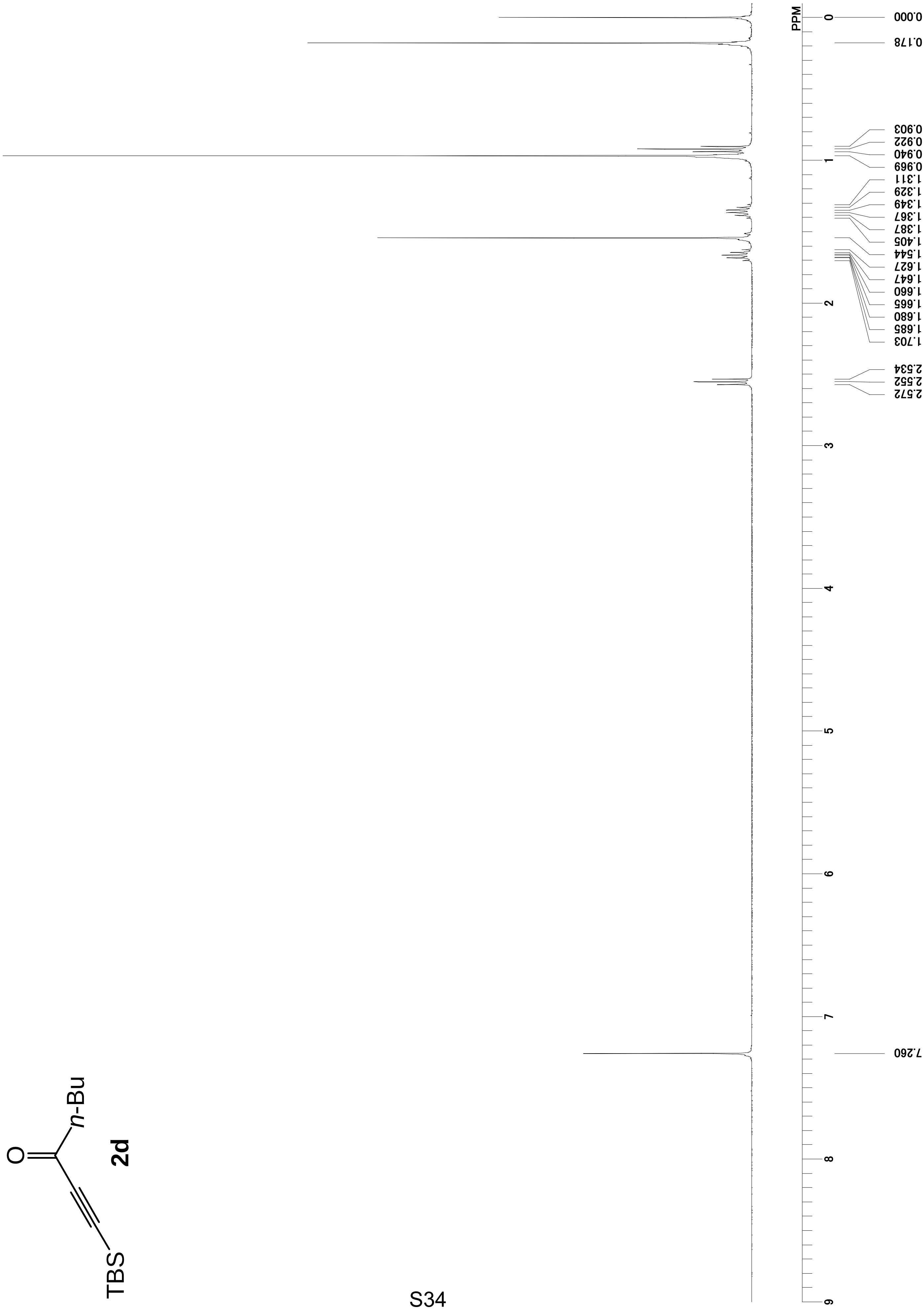
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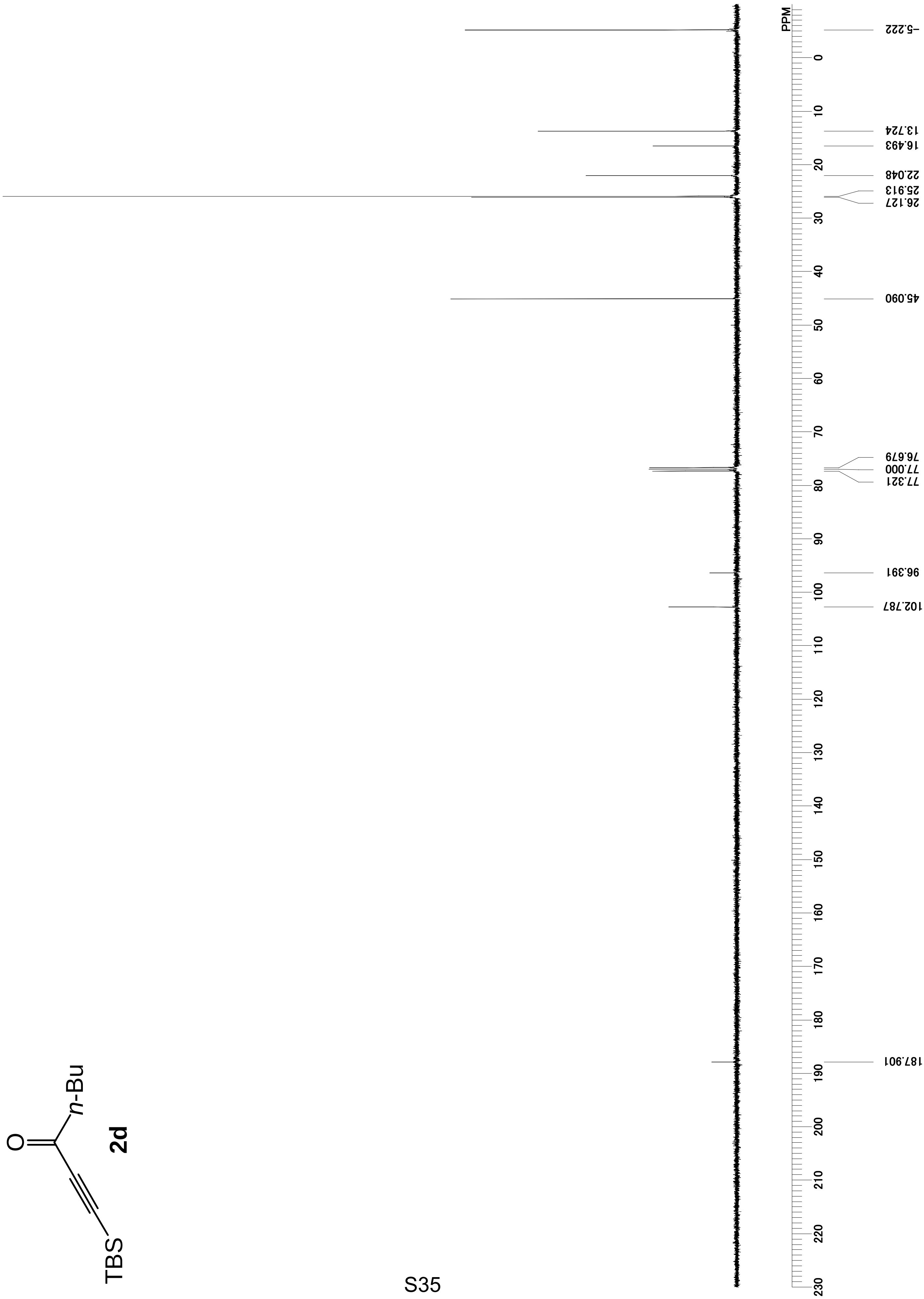
2d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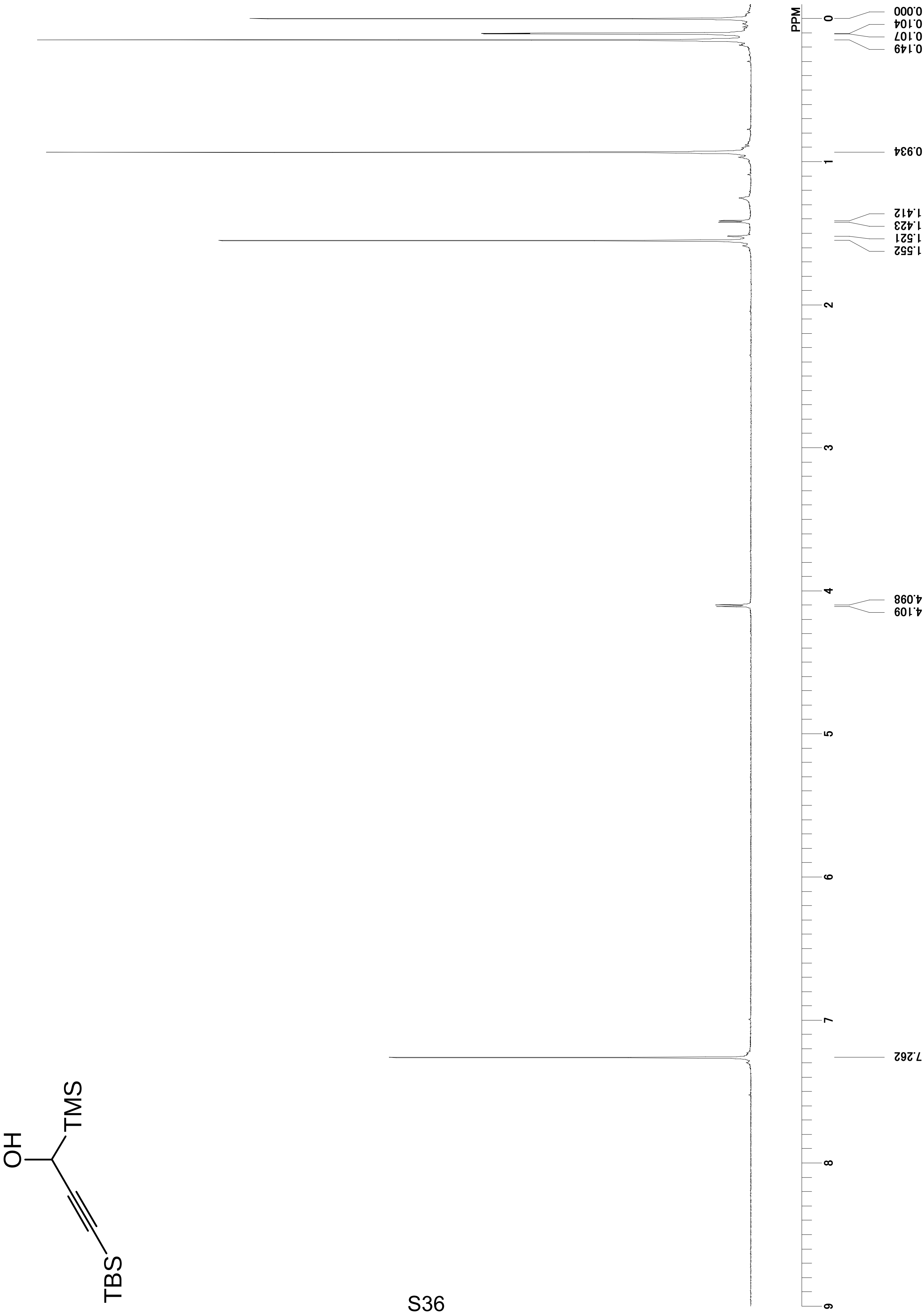
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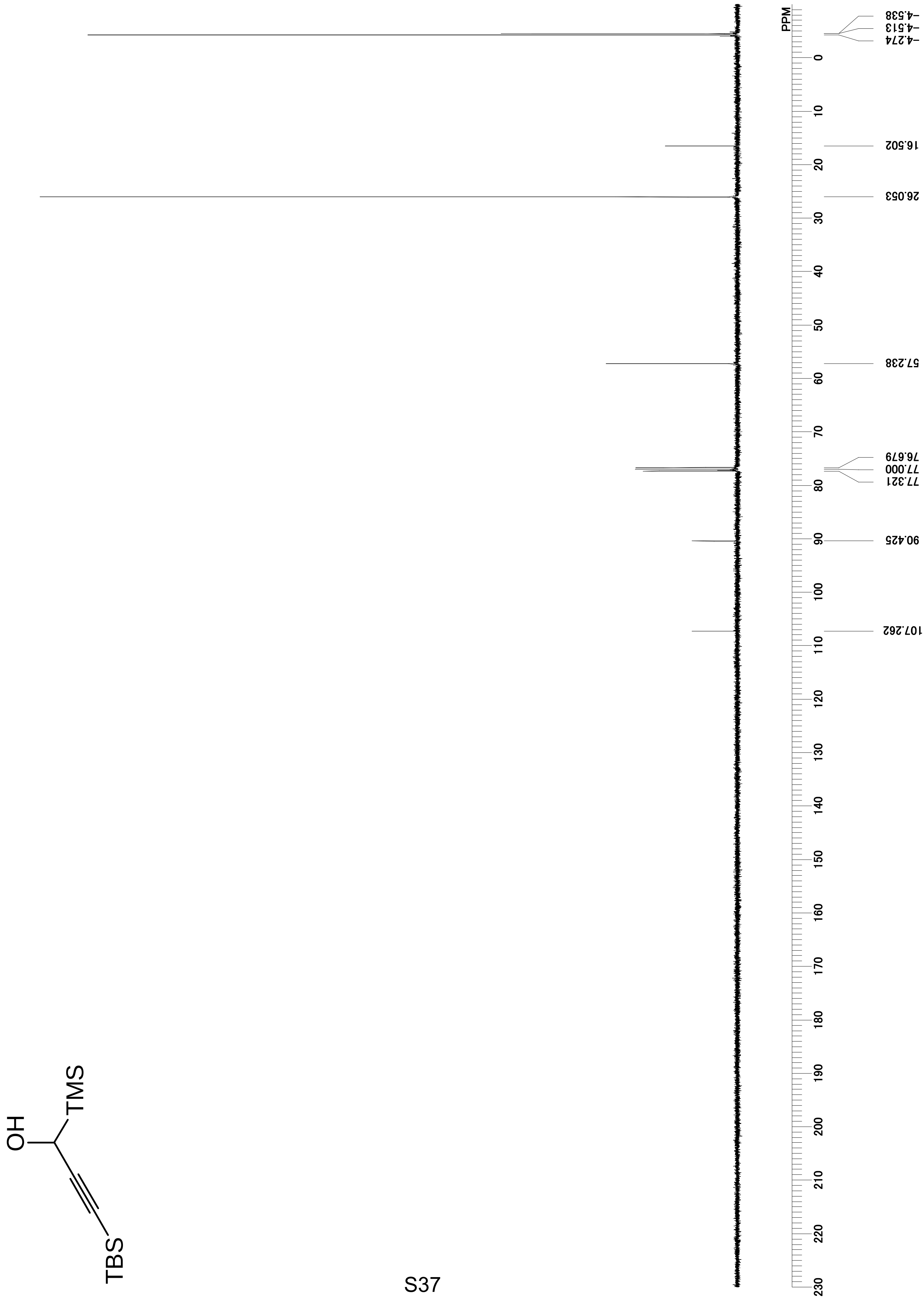
OH
TMS
TBS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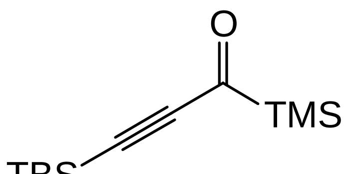
TBS



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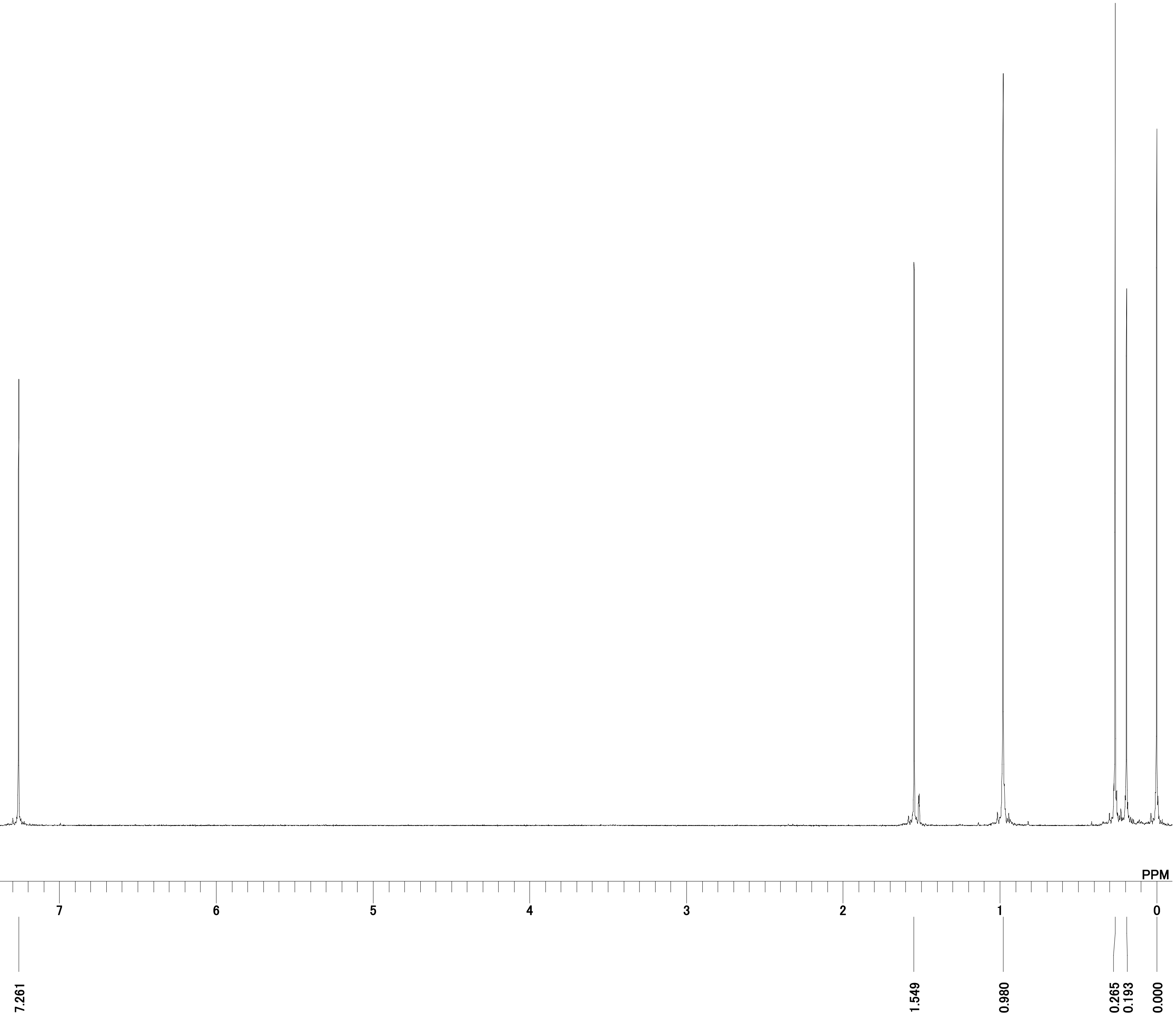

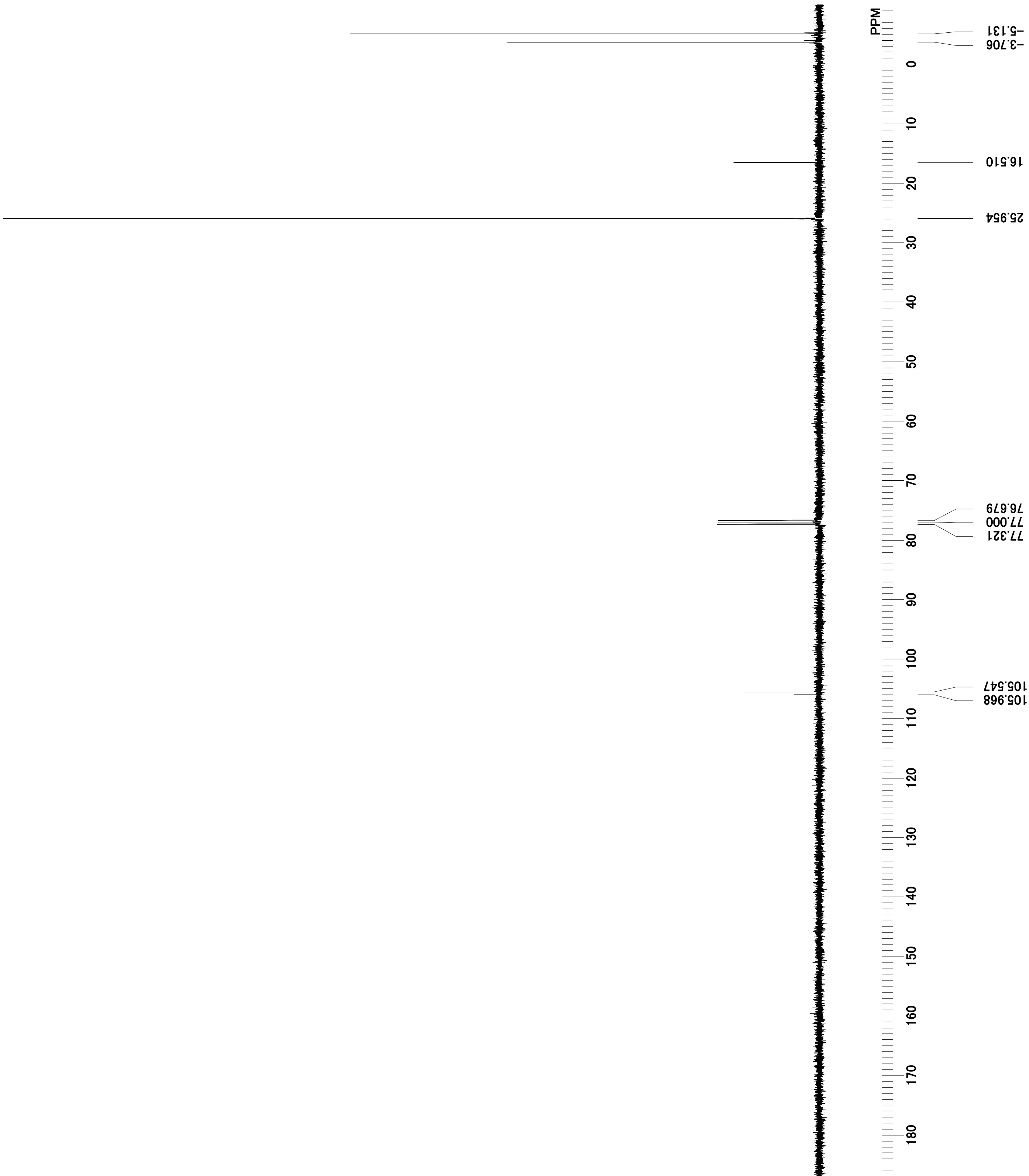
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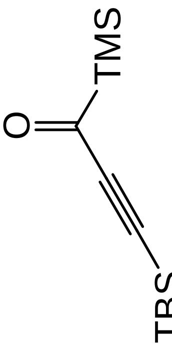
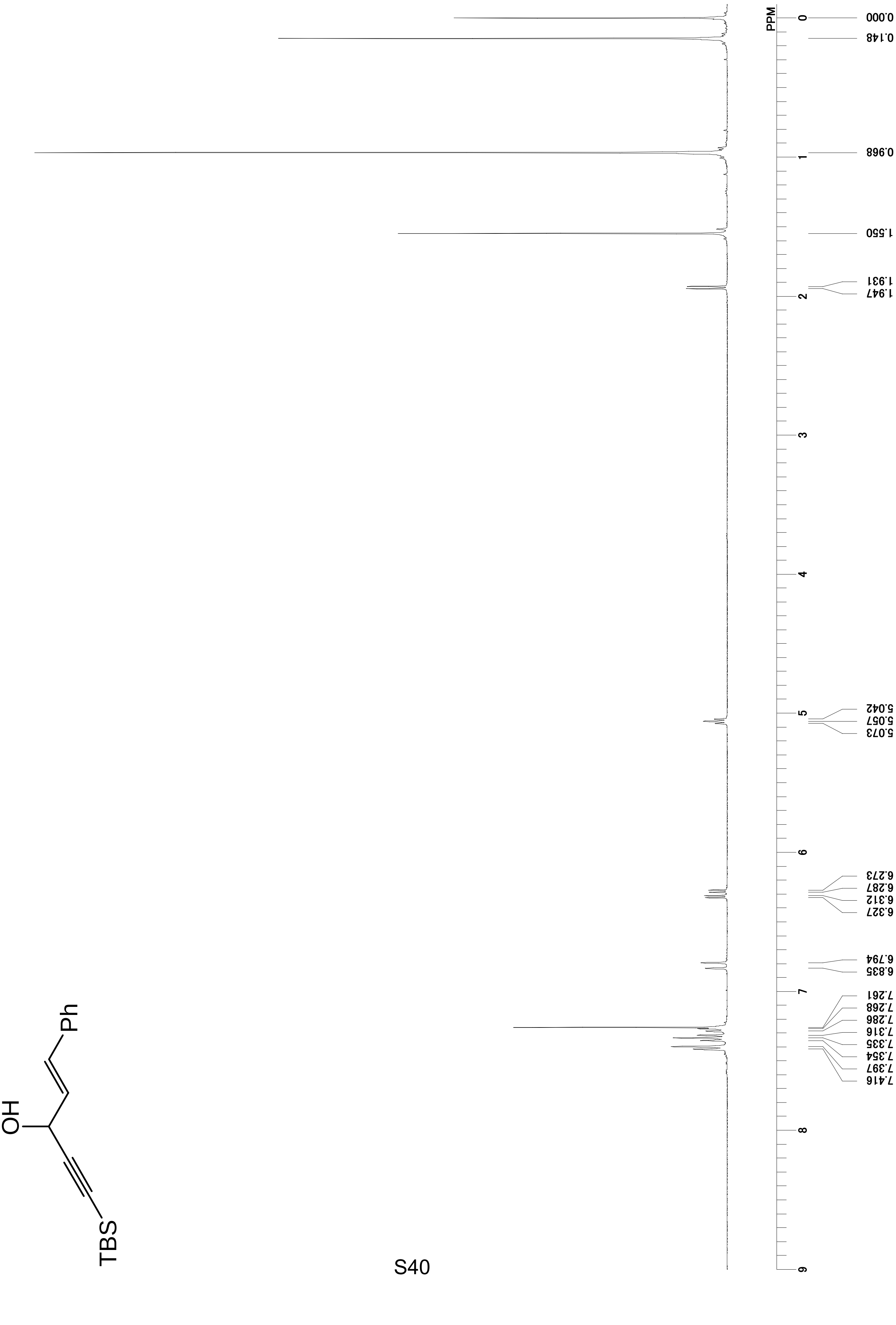

O
TMS
TBS

2f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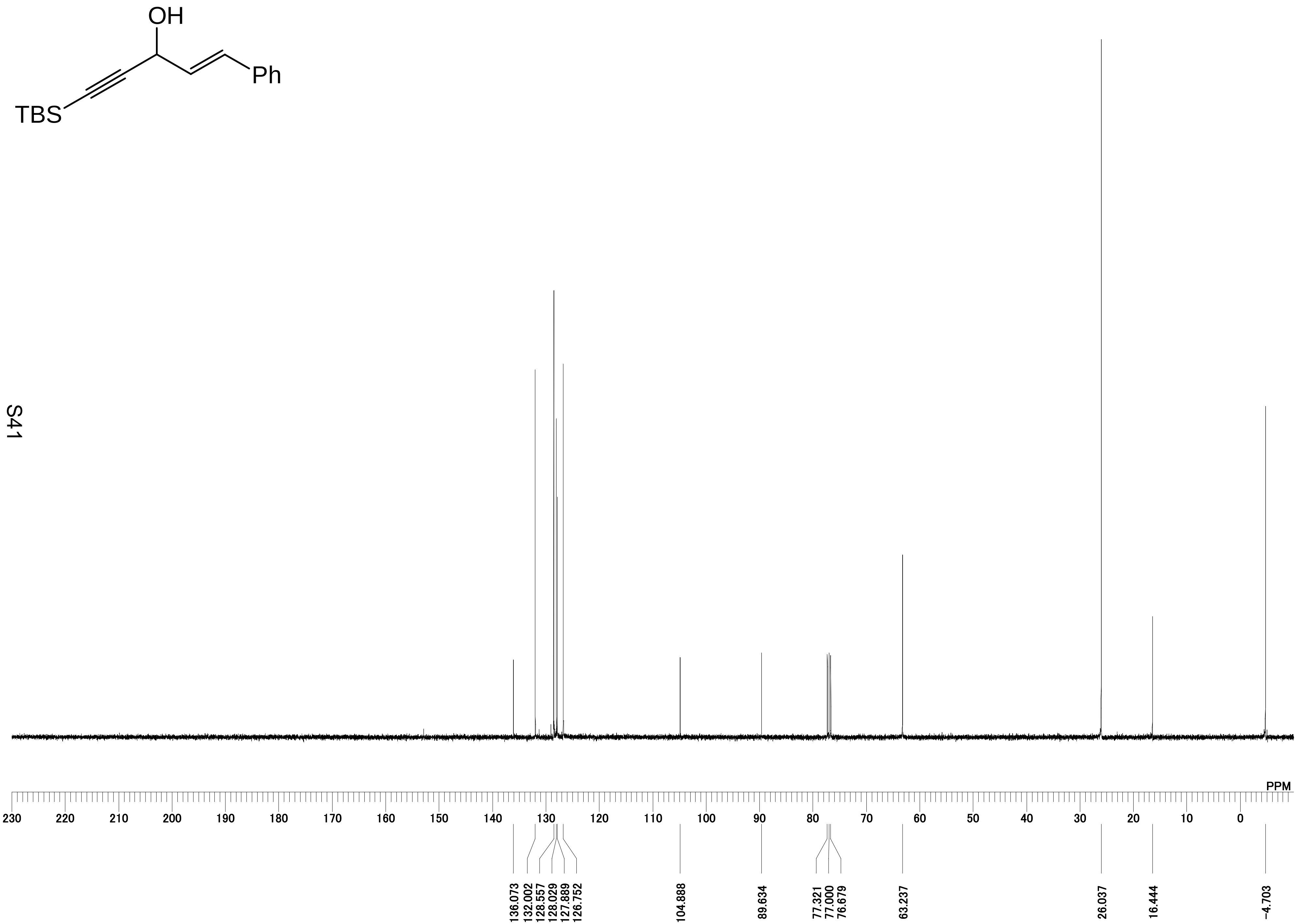
Ph
TBS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TBS
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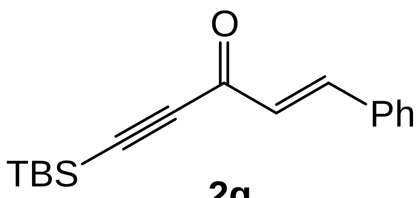
PPM



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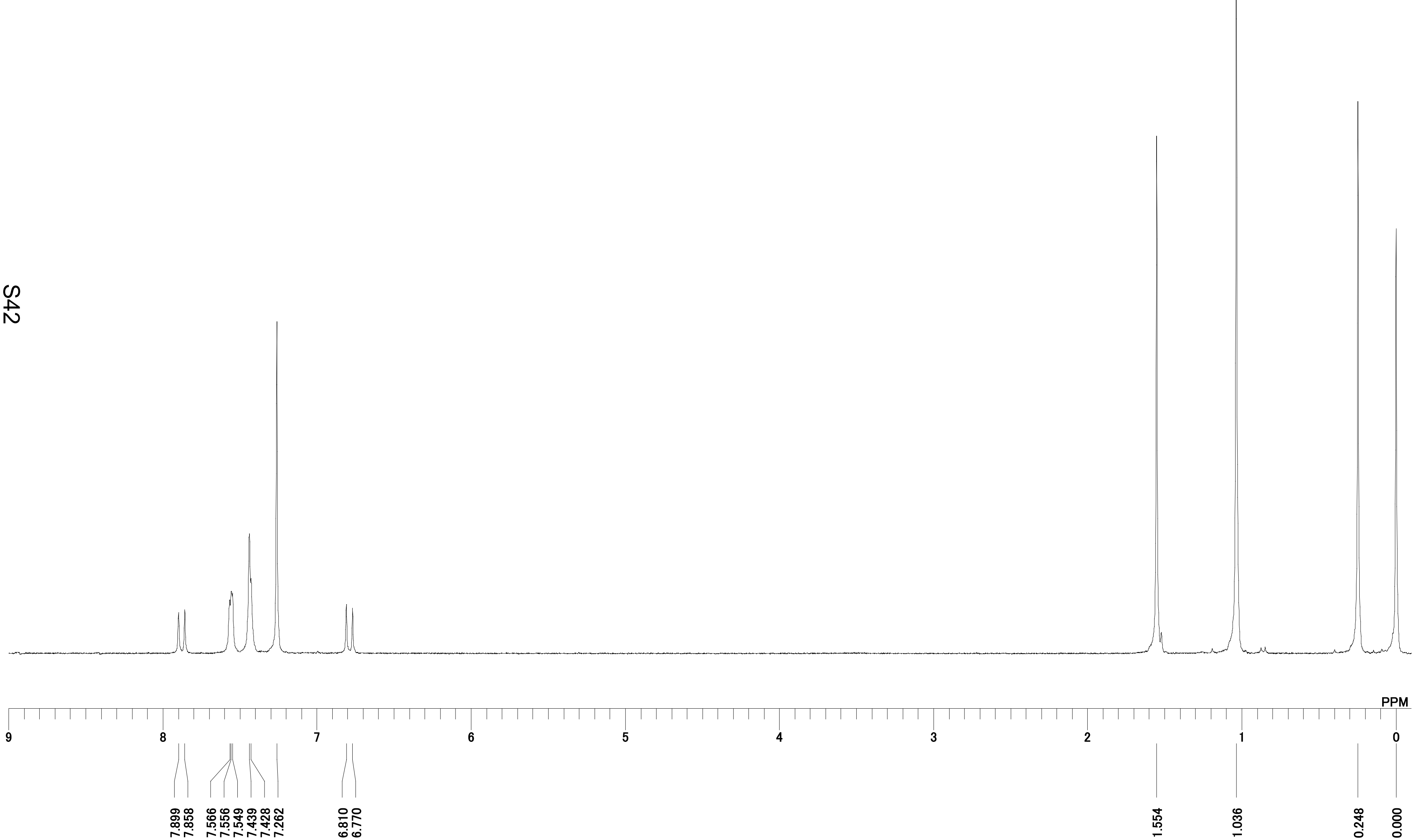
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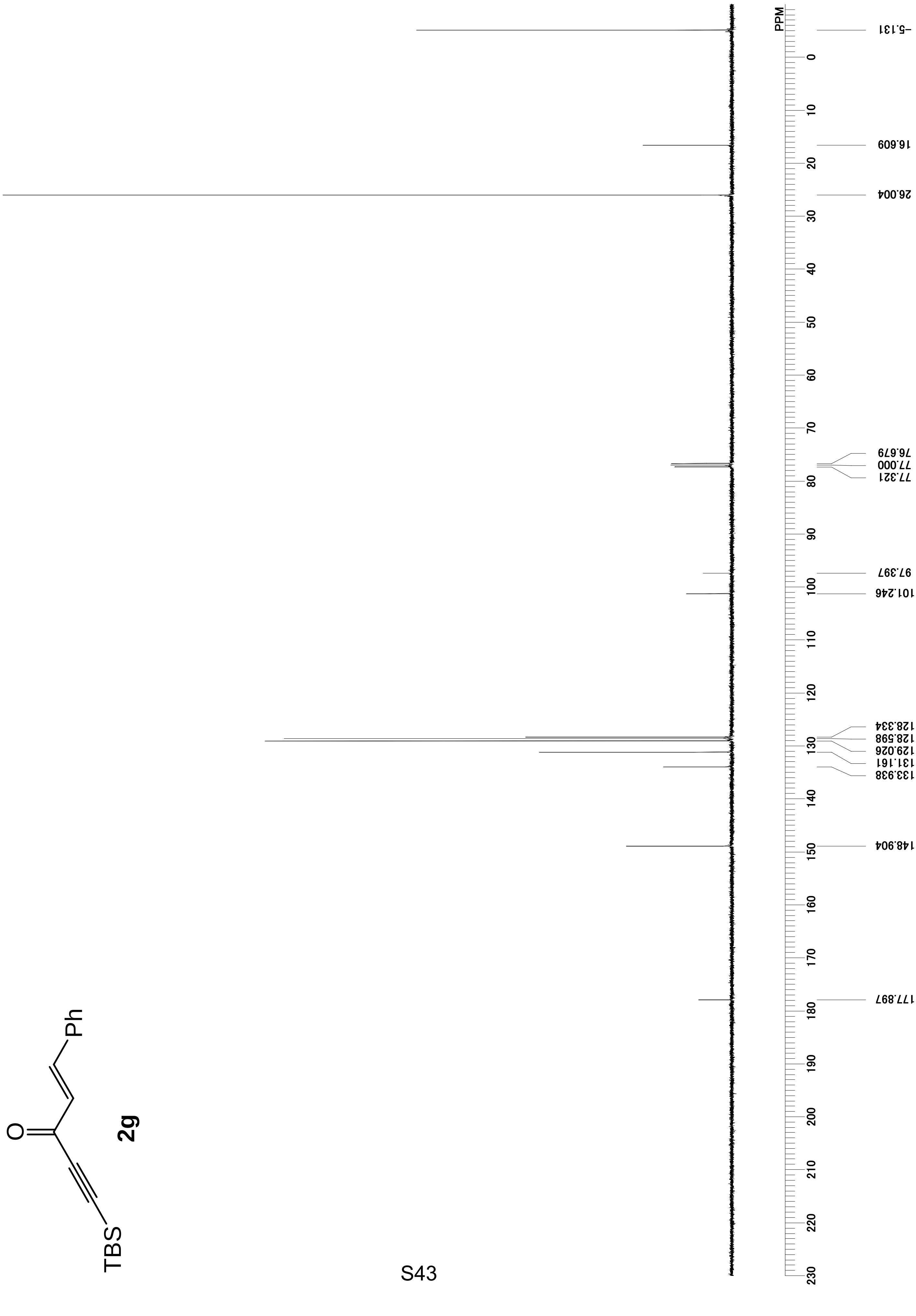
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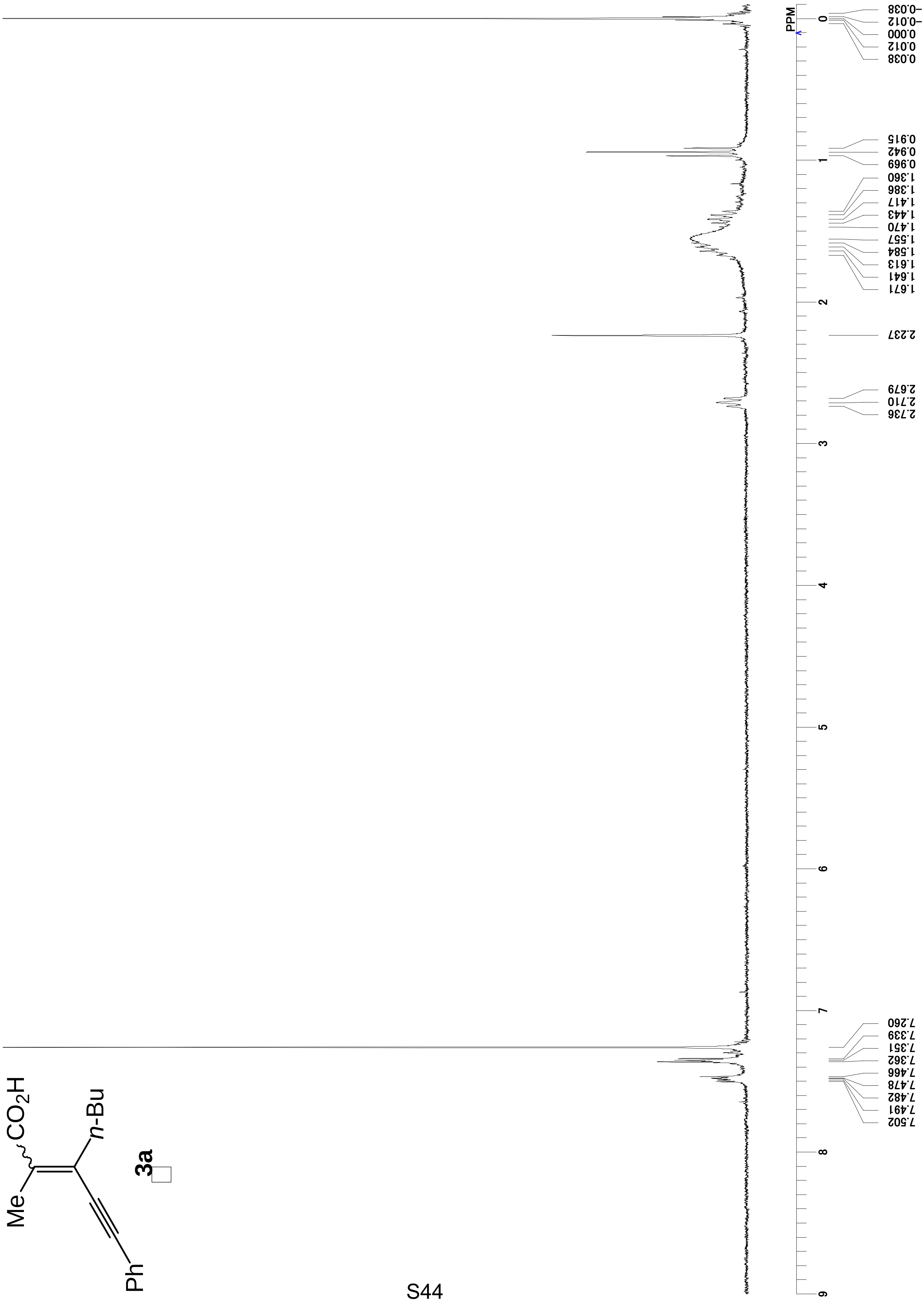
Ph
TBS
2g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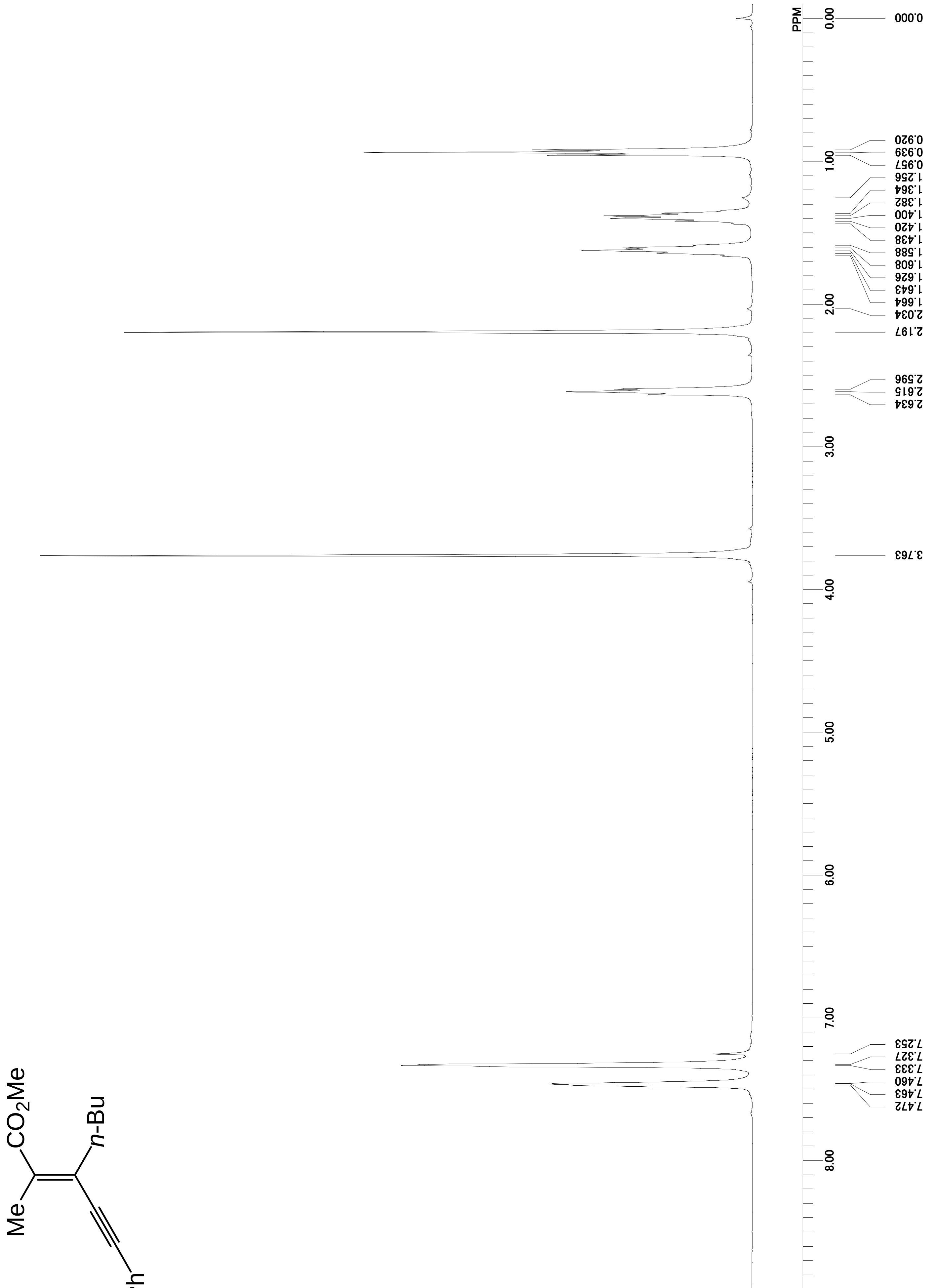
1.417
1.443
1.470
1.557
1.584
1.613
1.641
1.671
2.237
2.679
2.710
2.736
7.260
7.339
7.351
7.362
7.466
7.478
7.482
7.491
7.502



CO2Me
Me
n-Bu
Ph
PPM
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
0.000
0.920
0.939
0.957
1.256
1.364
1.382
1.400
1.420
1.438
1.588
1.608
1.626
1.643
1.664
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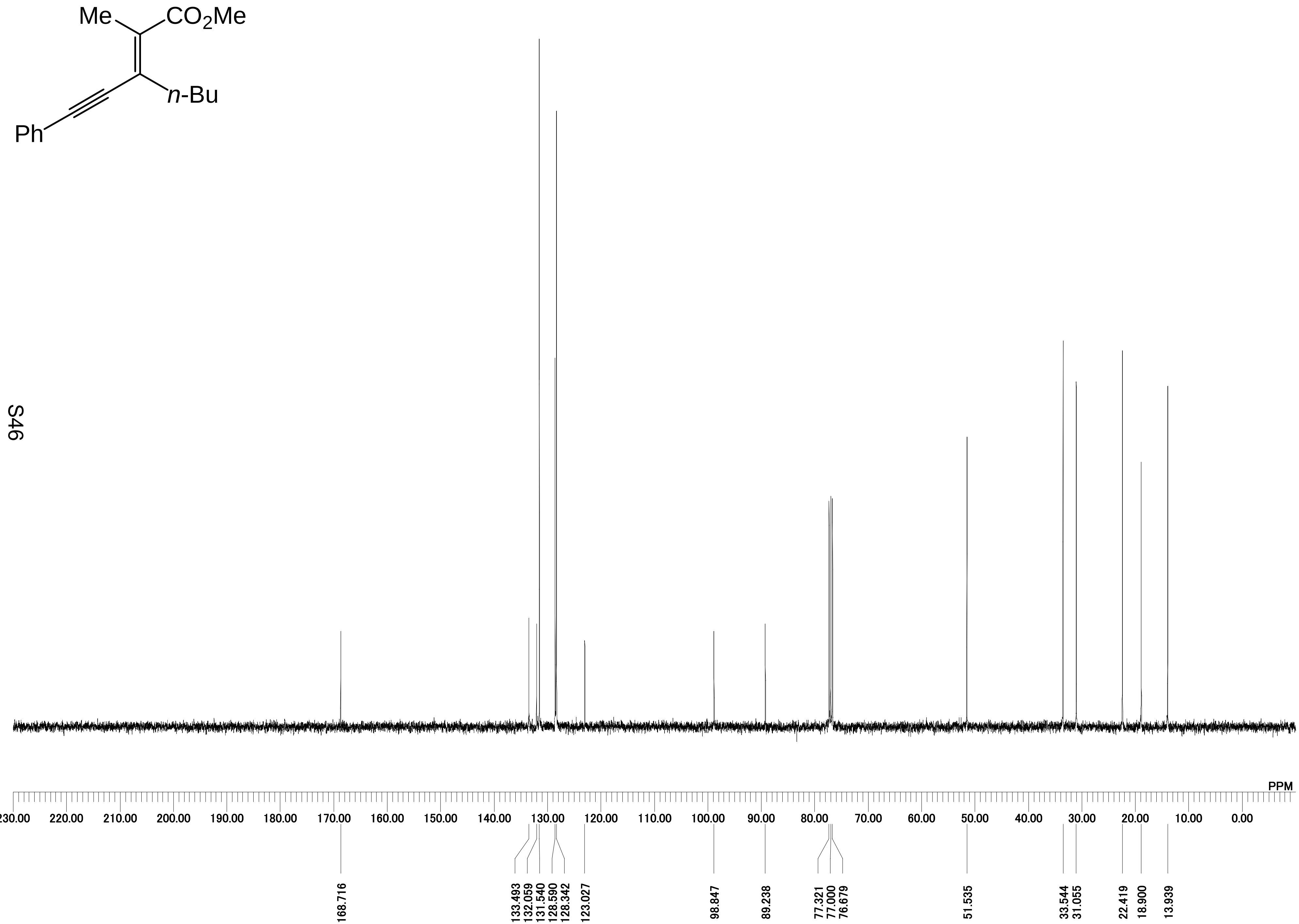
2.197
2.596
2.615
2.634
3.763
7.253
7.327
7.333
7.460
7.463
7.472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200.00
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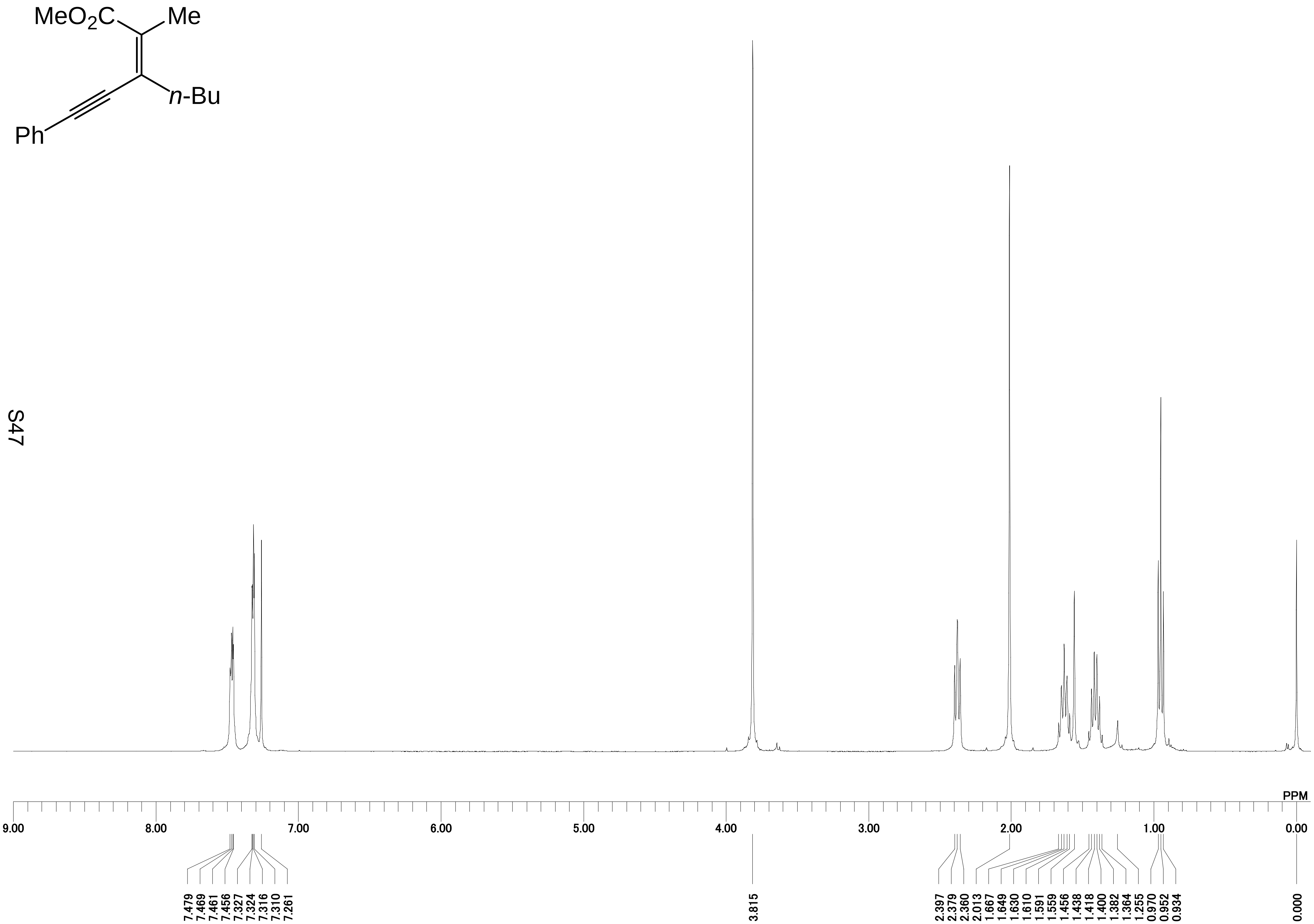
180.00
170.00
160.00
150.00
140.00
130.00
120.00
110.00
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
168.716
133.493
132.059
131.540
128.590
128.342
123.027
98.847
89.238
77.321
77.000
76.679
51.535
33.544
31.055
22.419
18.900
13.939



MeO2C
Me
n-Bu
Ph
PPM
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
7.479
7.469
7.461
7.456
7.327
7.324
7.316
7.310
7.261
3.815
2.397
2.379
2.360
2.013
1.667
1.649
1.630
1.610
1.591
1.559
1.456
1.438
1.418
1.400
1.382
1.364
1.255
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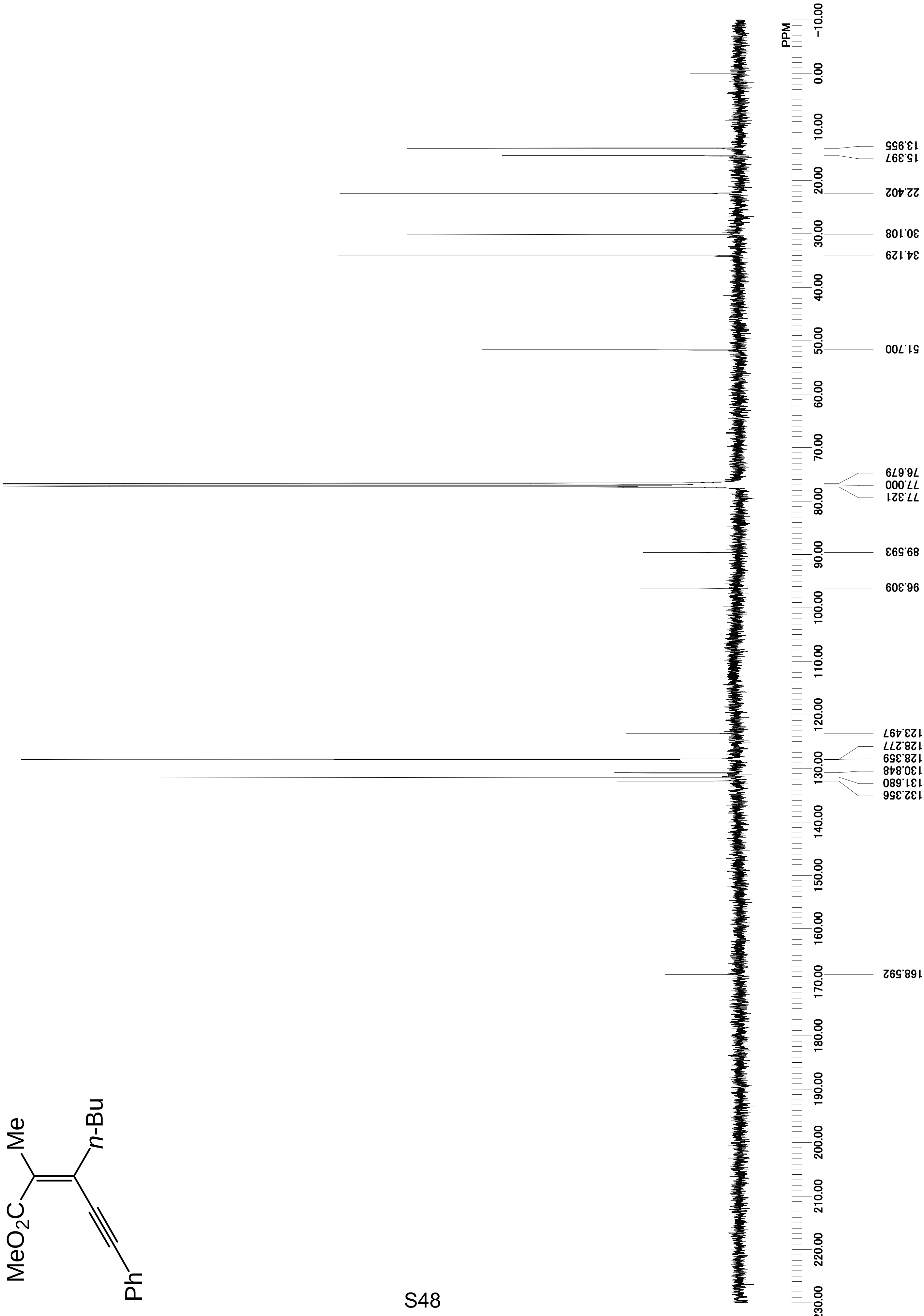
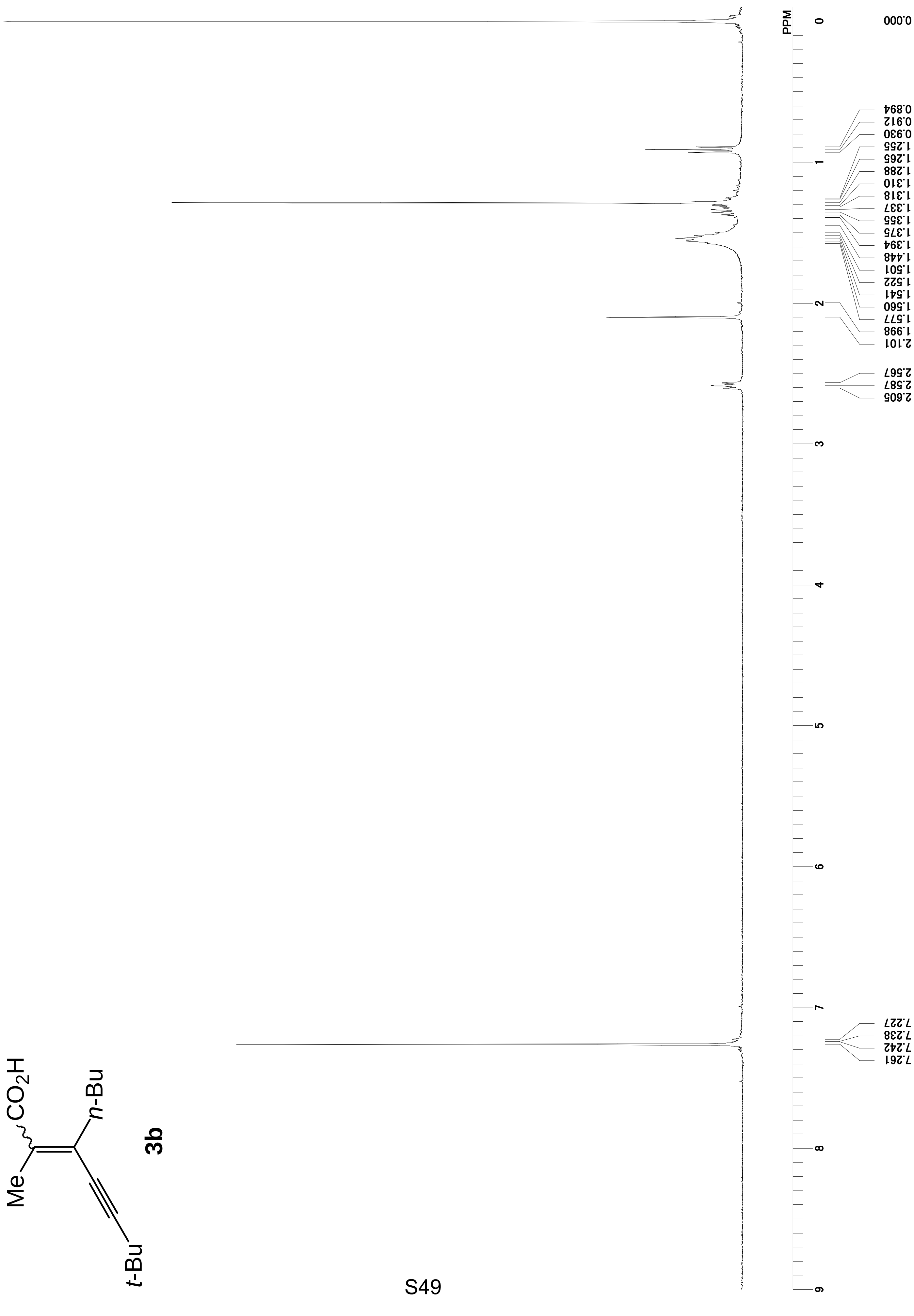
0.952
0.934
0.000



PPM
13.955
15.397
22.402
30.108
34.129
51.700
76.679
77.000
77.321
89.593
96.309
123.497
128.277
128.359
130.848
131.680
132.356
168.592
MeO2C
Me
n-Bu
Ph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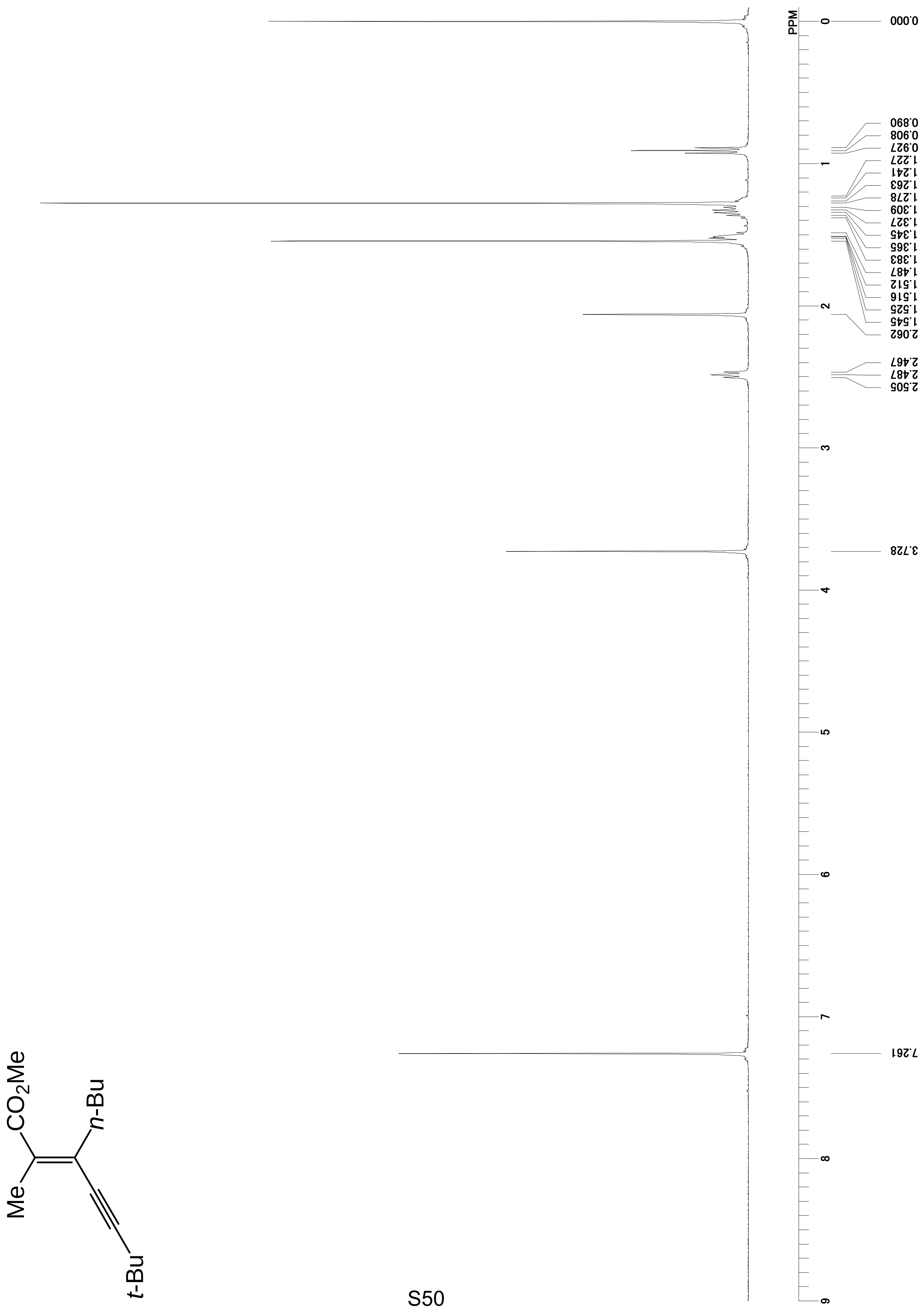
0.912
0.930
1.255
1.265
1.288
1.310
1.318
1.337
1.355
1.375
1.394
1.448
1.501
1.522
1.541
1.560
1.577
1.998
2.101
2.567
2.587
2.605
7.227
7.238
7.242
7.261
Me
CO2H
n-Bu
t-Bu
3b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1.241
1.263
1.278
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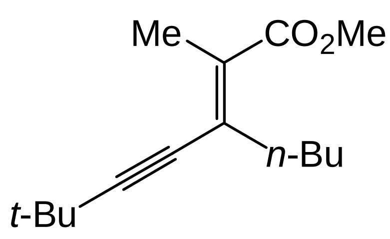
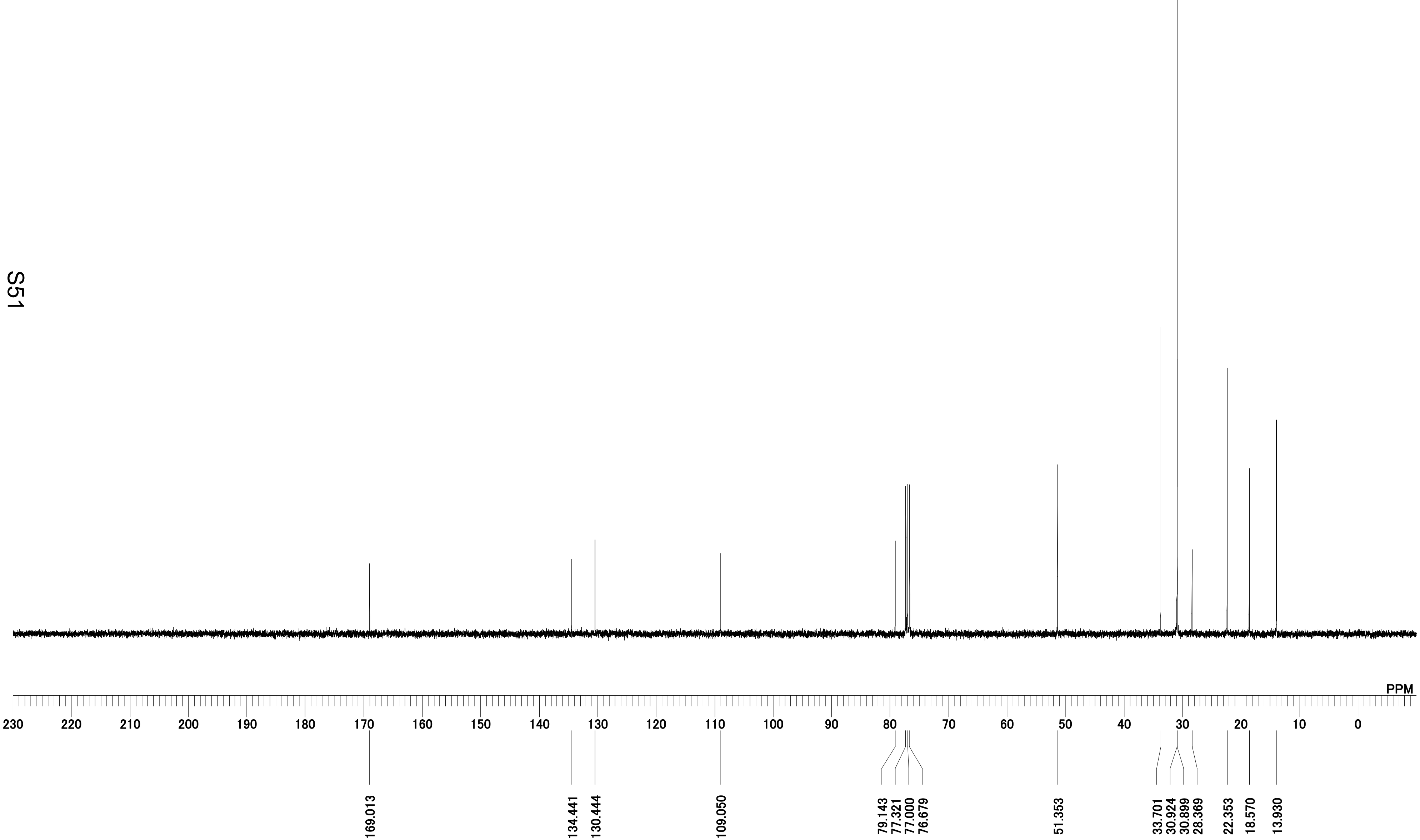
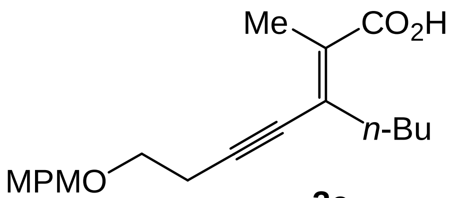
1.327
1.345
1.365
1.383
1.487
1.512
1.516
1.525
1.545
2.062
2.467
2.487
2.505
3.728
7.261
PPM
0
1
2
3
4
5
6
7
8
9
Me
CO_2Me
n-Bu
t-Bu

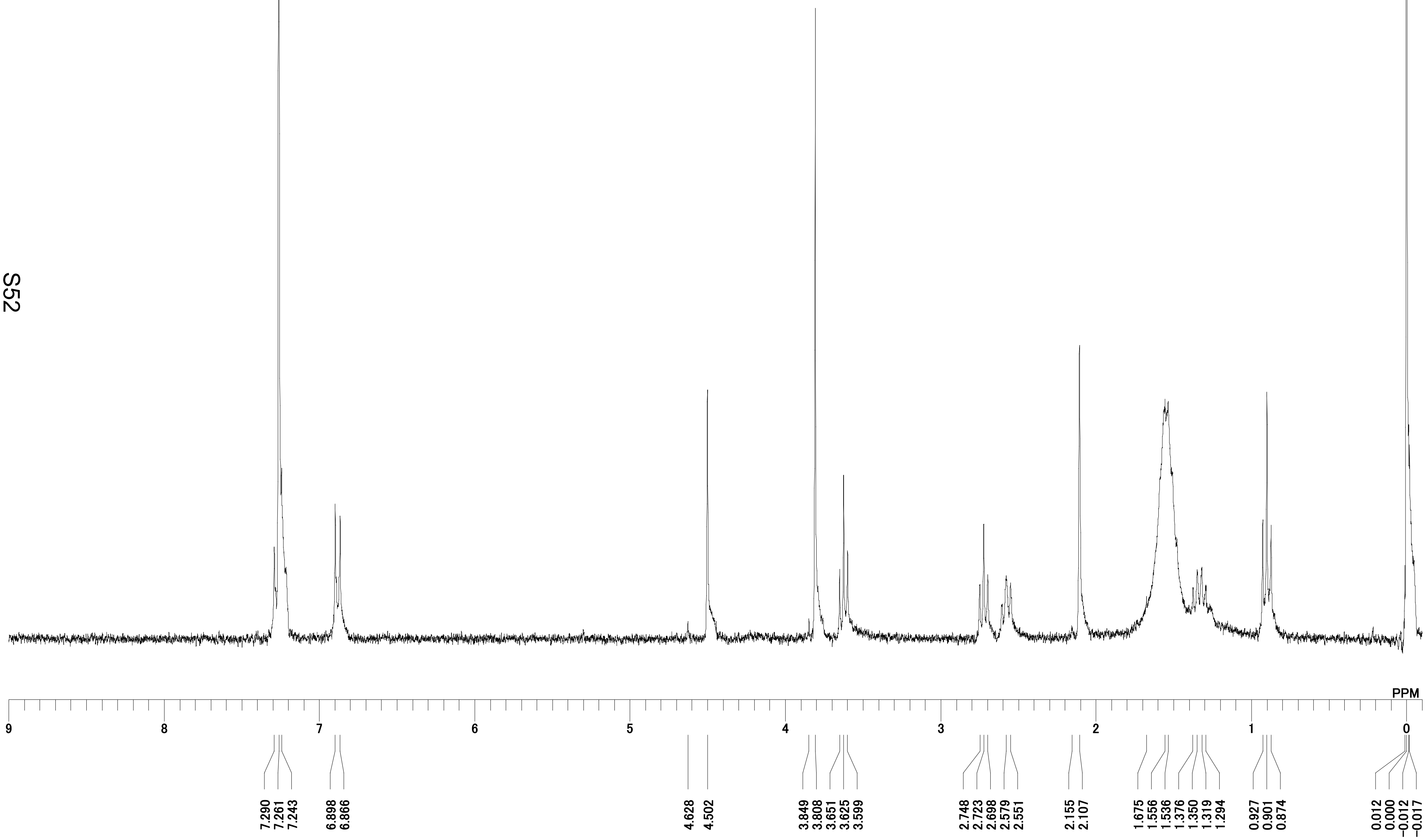

Me
CO_2Me
n-Bu
t-Bu


PPM
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
169.013
134.441
130.444
109.050
79.143
77.321
77.000
76.679
51.353
33.701
30.924
30.899
28.369
22.353
18.570
13.930



Me
CO2H
n-Bu
MPMO

3c



PPM
9
8
7
6
5
4
3
2
1
0
7.290
7.261
7.243
6.898
6.866
4.628
4.502
3.849
3.808
3.651
3.625
3.599
2.748
2.723
2.698
2.579
2.551
2.155
2.107
1.675
1.556
1.536
1.376
1.350
1.319
1.294
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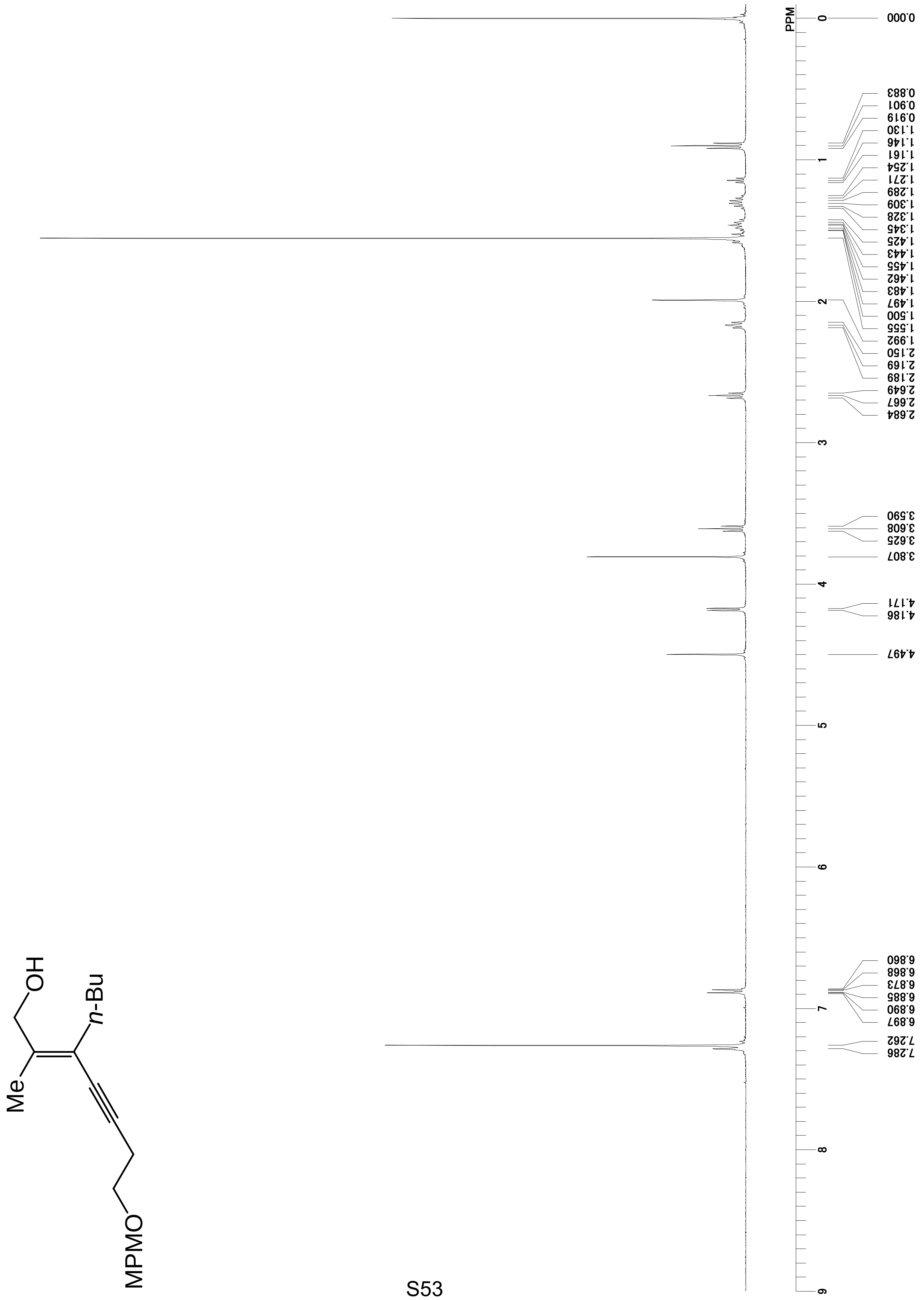
0.901
0.874
0.012
0.000
−0.012
−0.017


PPM
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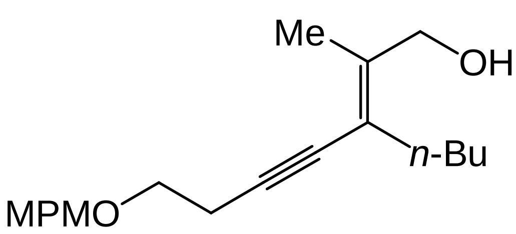
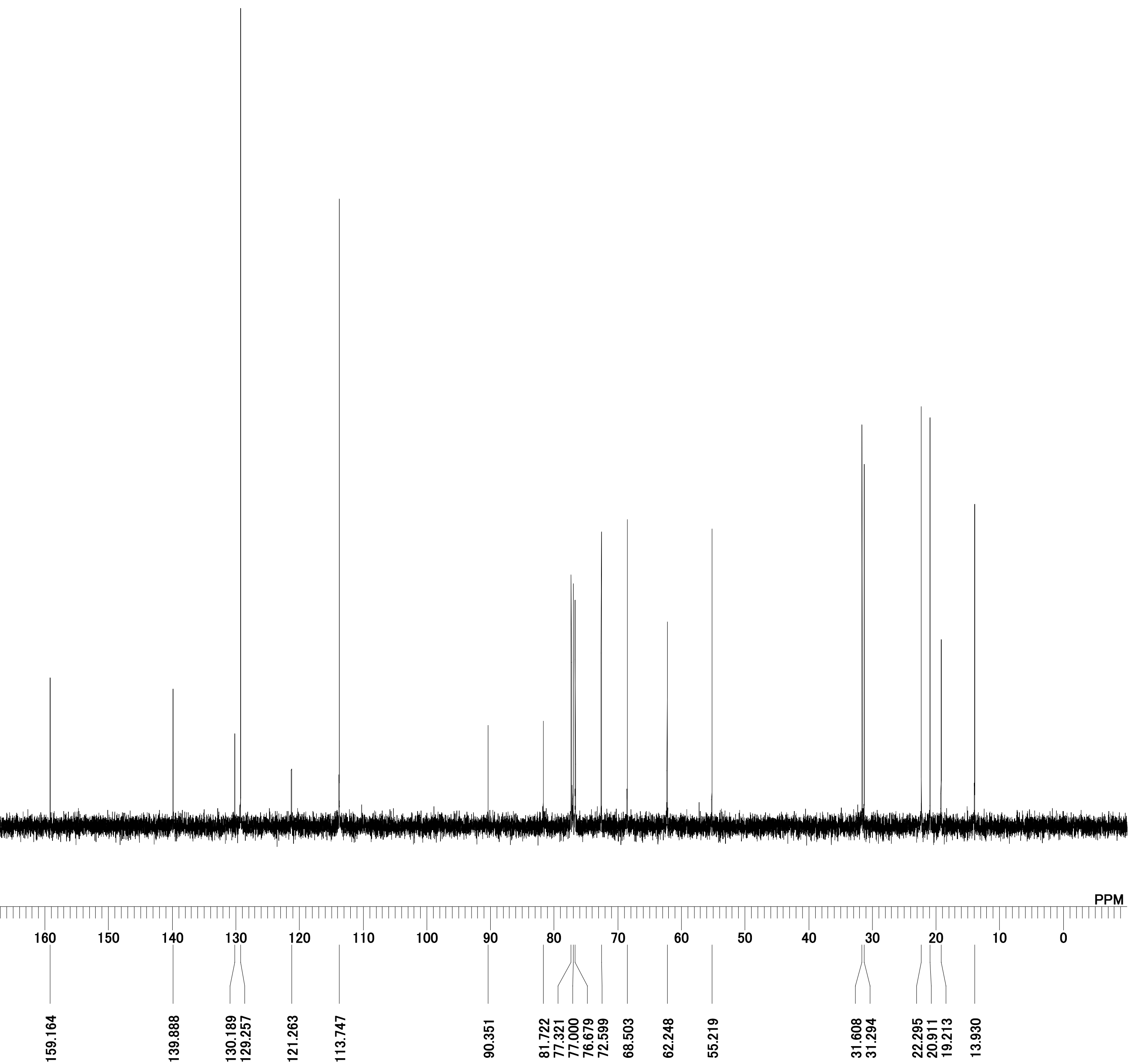
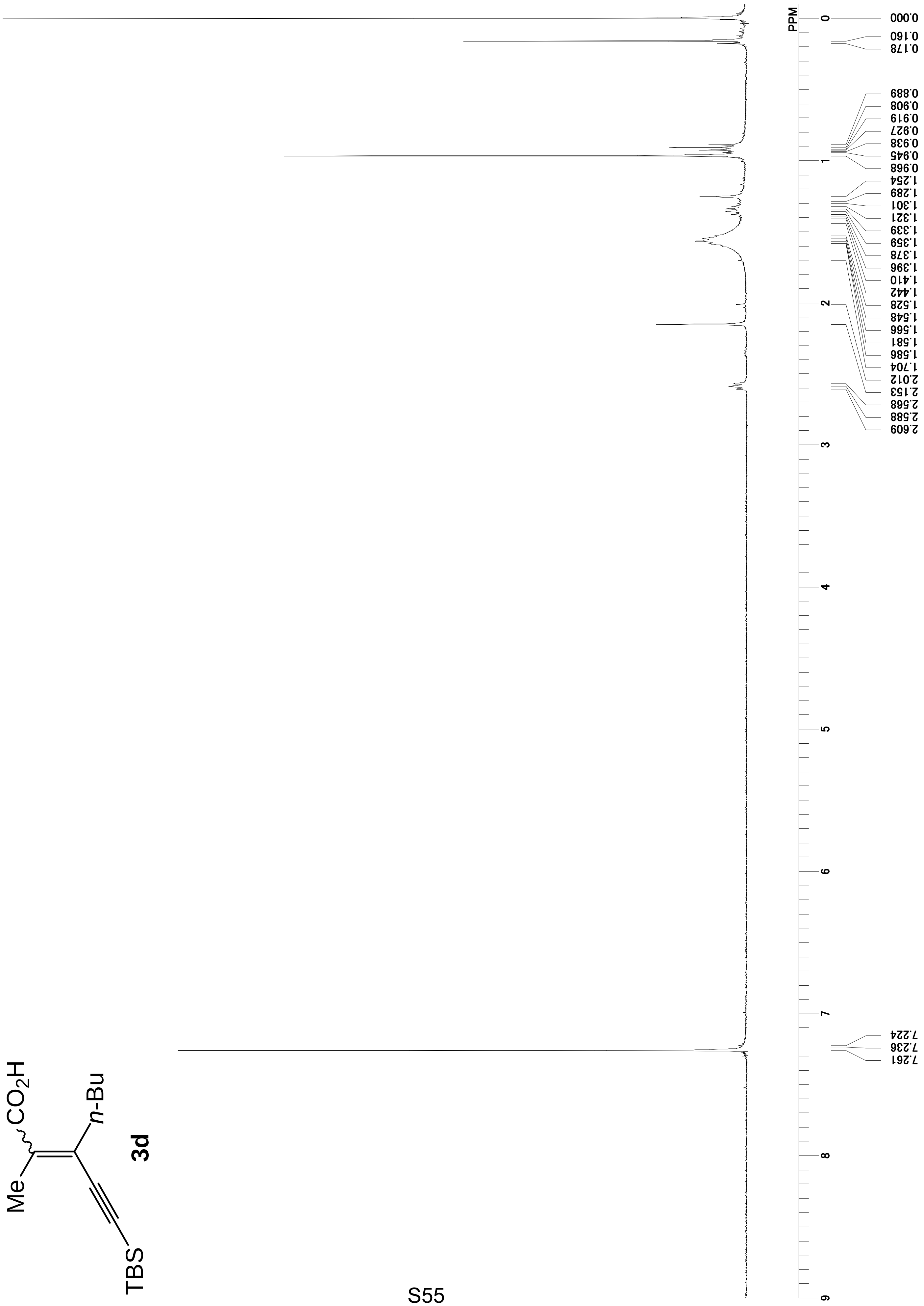
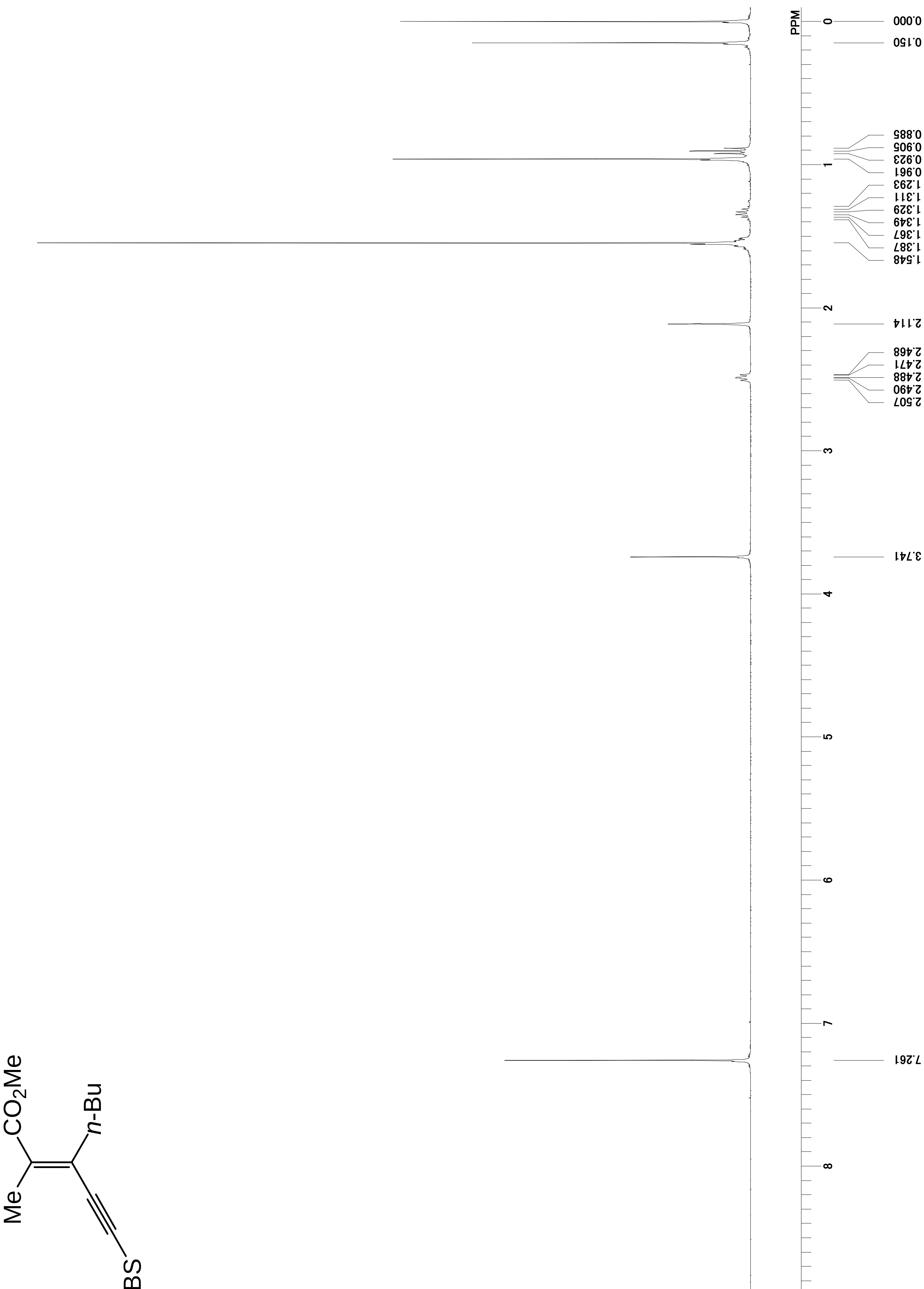
1
2
3
4
5
6
7
8
9
0.000
0.883
0.901
0.919
1.130
1.146
1.161
1.254
1.271
1.289
1.309
1.328
1.345
1.425
1.443
1.455
1.462
1.483
1.497
1.500
1.555
1.992
2.150
2.169
2.189
2.649
2.667
2.684
3.590
3.608
3.625
3.807
4.171
4.186
4.497
6.860
6.868
6.873
6.885
6.890
6.897
7.262
7.286
OH
n-Bu
Me
MPMO


Me
OH
n-Bu
MPMO


PPM
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
159.164
139.888
130.189
129.257
121.263
113.747
90.351
81.722
77.321
77.000
76.679
72.599
68.503
62.248
55.219
31.608
31.294
22.295
20.911
19.213
13.930


Me
CO2H
n-Bu
TBS
3d
PPM
0.000
0.160
0.178
0.889
0.908
0.919
0.927
0.938
0.945
0.968
1.254
1.289
1.301
1.321
1.339
1.359
1.378
1.396
1.410
1.442
1.528
1.548
1.566
1.581
1.586
1.704
2.012
2.153
2.568
2.588
2.609
7.224
7.236
7.261
0
1
2
3
4
5
6
7
8
9


PPM
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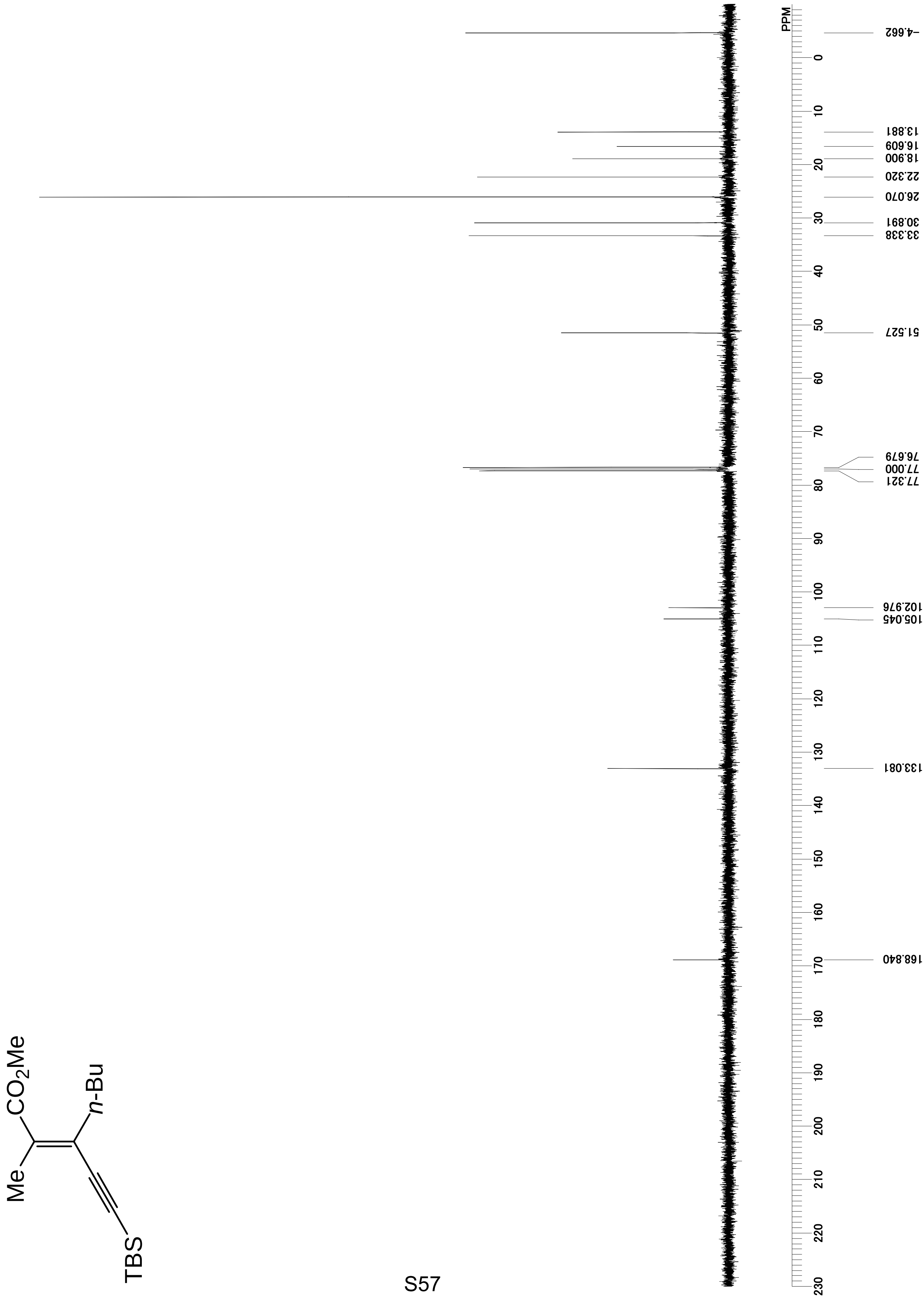
0.885
0.905
0.923
0.961
1.293
1.311
1.329
1.349
1.367
1.387
1.548
2.114
2.468
2.471
2.488
2.490
2.507
3.741
7.261
0
1
2
3
4
5
6
7
8
9
Me
CO_2Me
n-Bu
TBS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-4.662
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16.609
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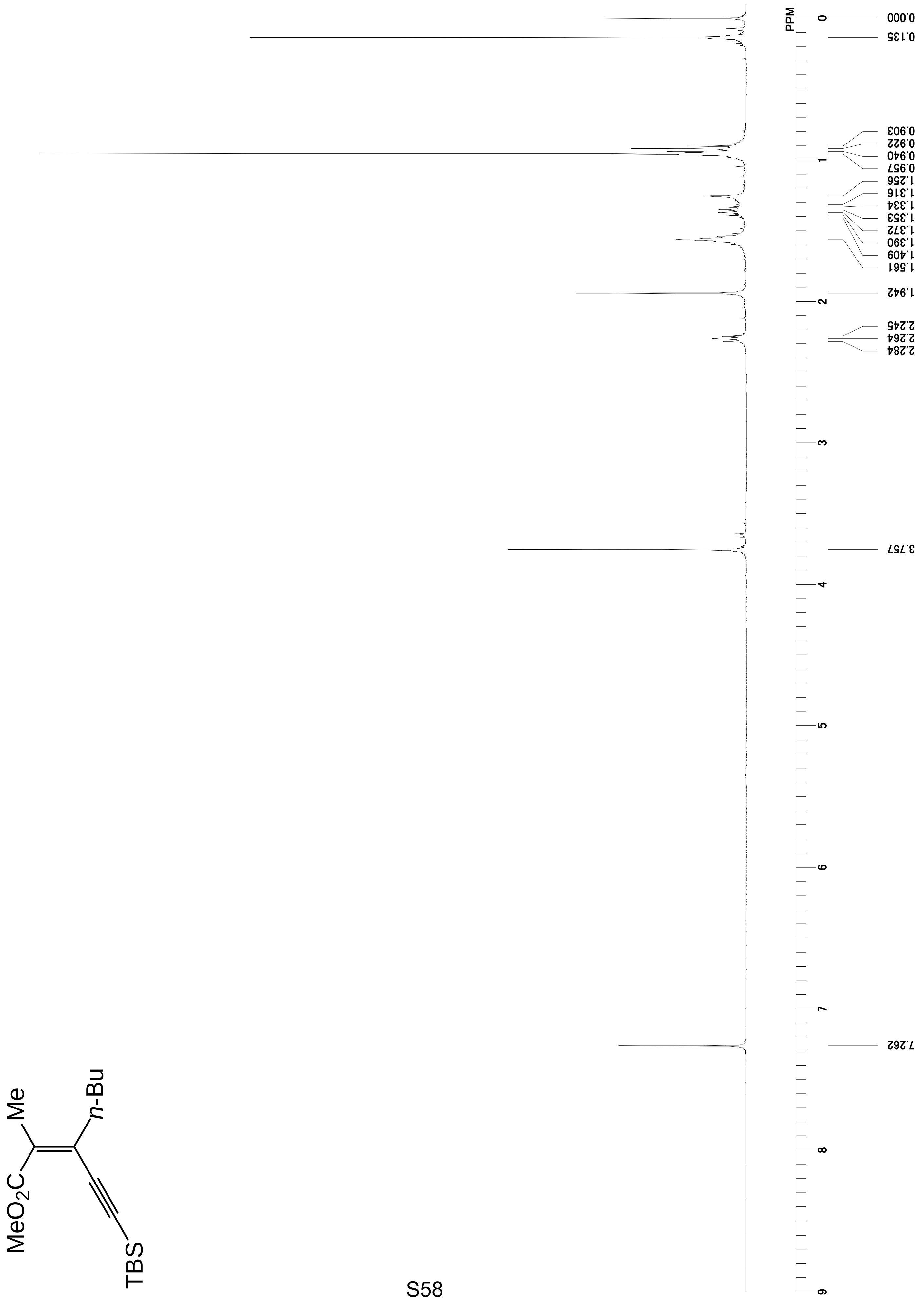
22.320
26.070
30.891
33.338
51.527
76.679
77.000
77.321
102.976
105.045
133.081
168.840
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
CO_2Me
Me
n-Bu
TBS


PPM
0.000
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0.922
0.940
0.957
1.256
1.316
1.334
1.353
1.372
1.390
1.409
1.561
1.942
2.245
2.264
2.284
3.757
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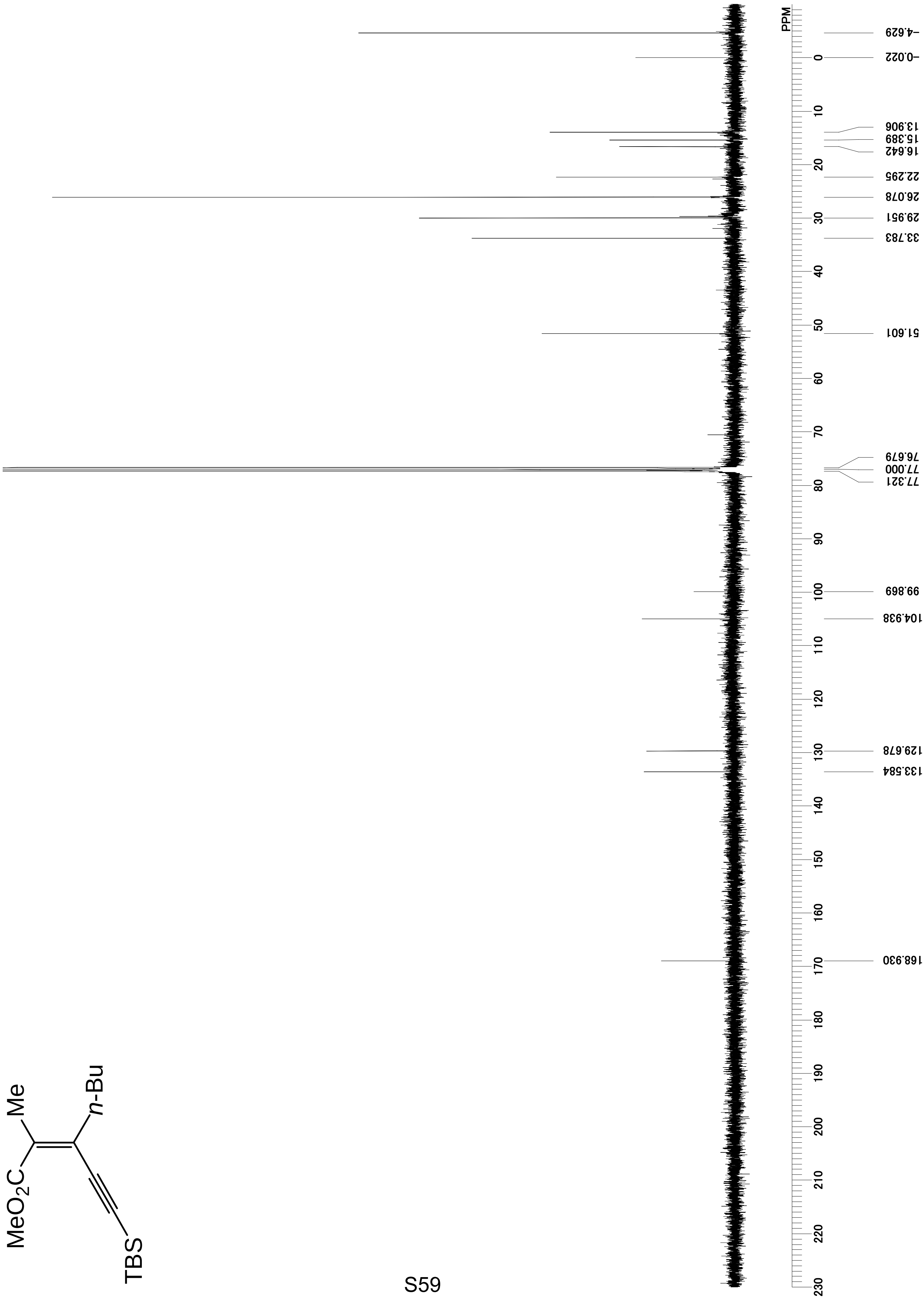
0
1
2
3
4
5
6
7
8
9
MeO2C
Me
n-Bu
TBS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-0.022
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16.642
22.295
26.078
29.951
33.783
51.601
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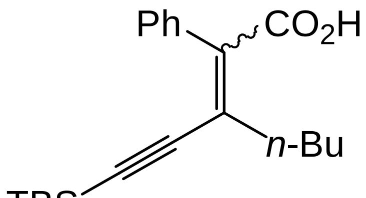
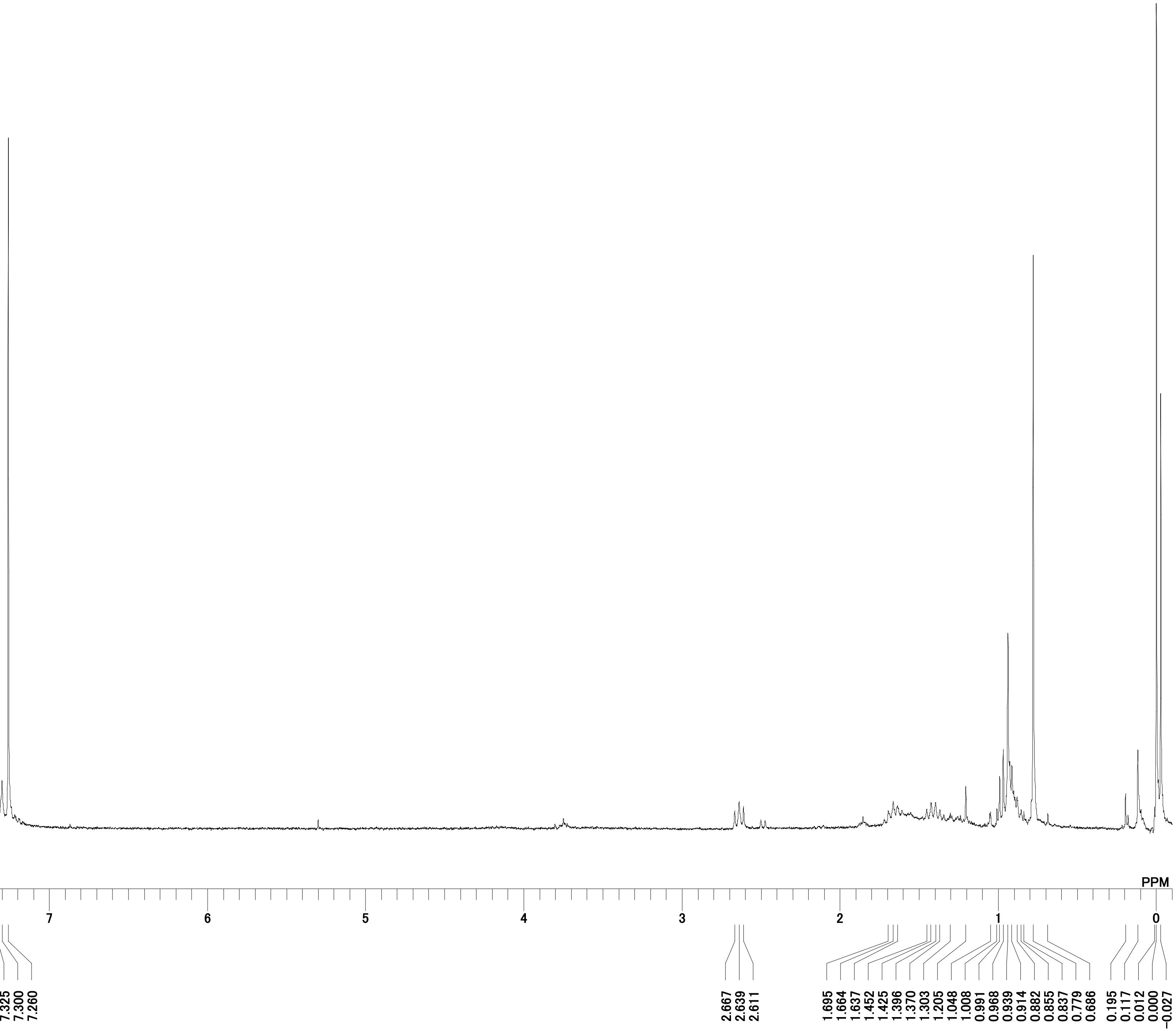
77.000
77.321
99.869
104.938
129.678
133.584
168.930
MeO2C
Me
n-Bu
TBS


Ph
CO2H
n-Bu
TBS

3e


PPM
9
8
7
6
5
4
3
2
1
0
7.398
7.393
7.347
7.325
7.300
7.260
2.667
2.639
2.611
1.695
1.664
1.637
1.452
1.425
1.396
1.370
1.303
1.205
1.048
1.008
0.991
0.968
0.939
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0.855
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0.779
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0.000
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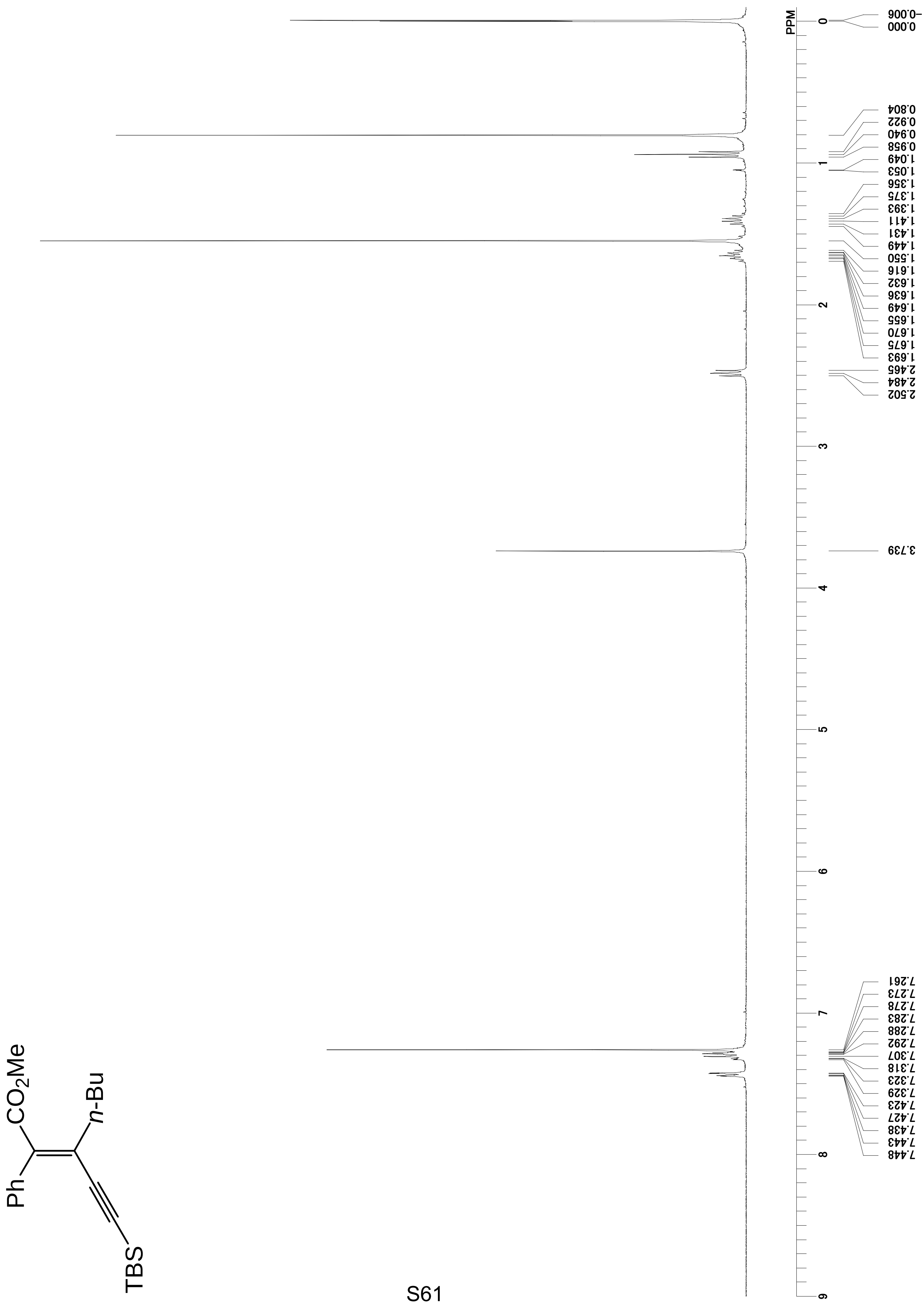

Ph
CO2Me
n-Bu
TBS
PPM
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1
2
3
4
5
6
7
8
9
-0.006
0.000
0.804
0.922
0.940
0.958
1.049
1.053
1.356
1.375
1.393
1.411
1.431
1.449
1.550
1.616
1.632
1.636
1.649
1.655
1.670
1.675
1.693
2.465
2.484
2.502
3.739
7.261
7.273
7.278
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7.288
7.292
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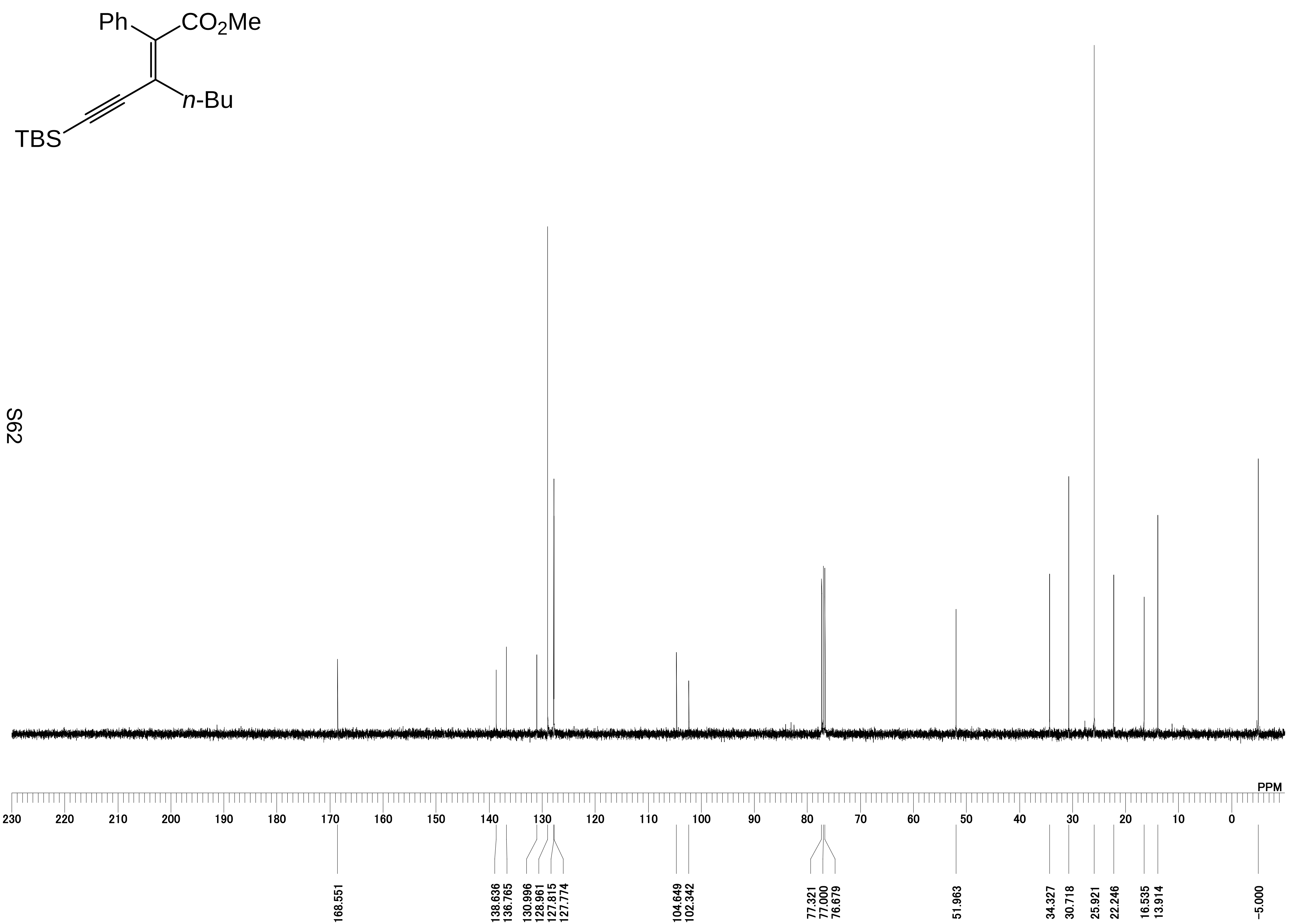
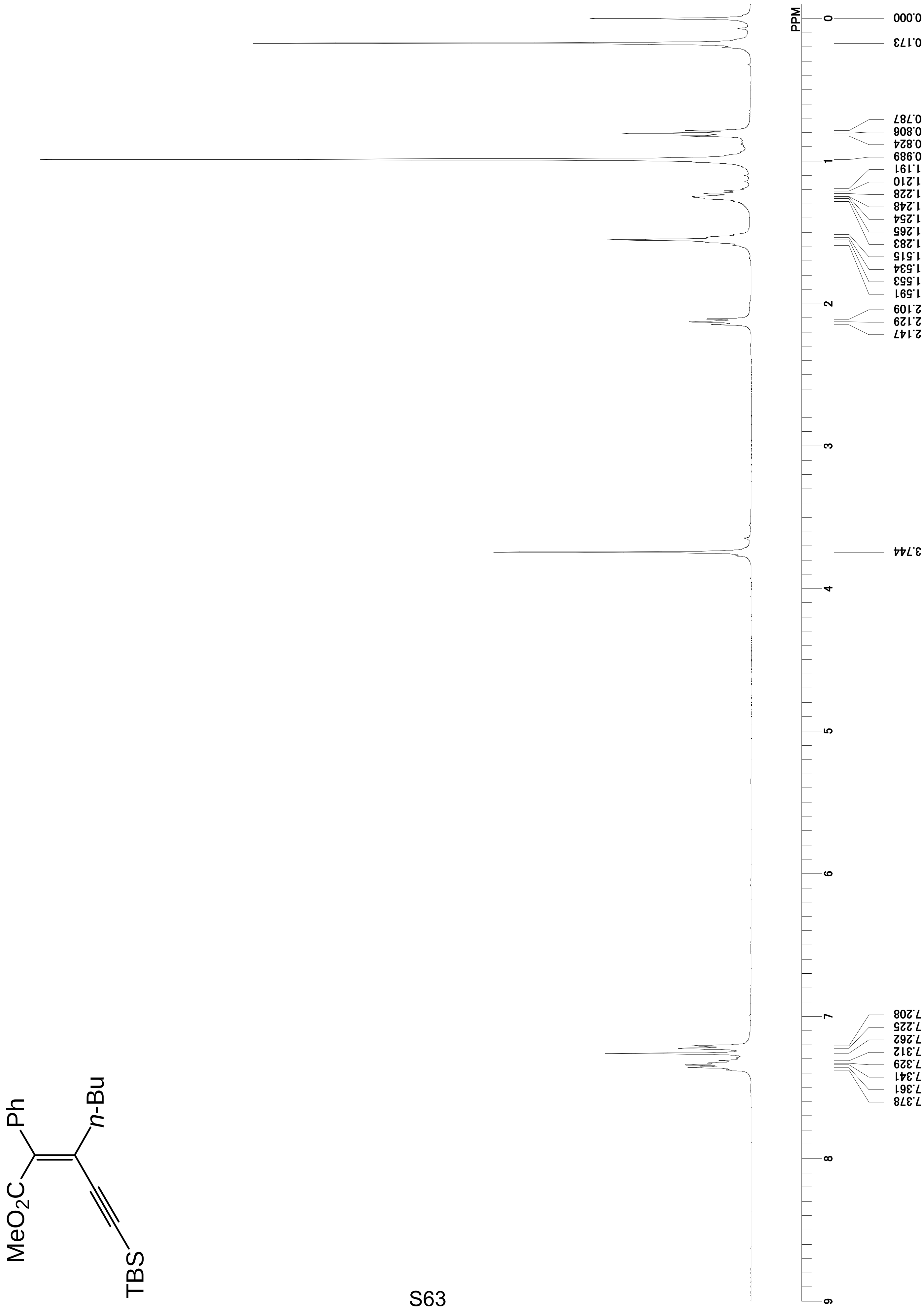
7.329
7.423
7.427
7.438
7.443
7.448


Ph
CO2Me
n-Bu
TBS
PPM
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
168.551
138.636
136.765
130.996
128.961
127.815
127.774
104.649
102.342
77.321
77.000
76.679
51.963
34.327
30.718
25.921
22.246
16.535
13.914
−5.000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1.191
1.210
1.228
1.248
1.254
1.265
1.283
1.515
1.534
1.553
1.591
2.109
2.129
2.147
3.744
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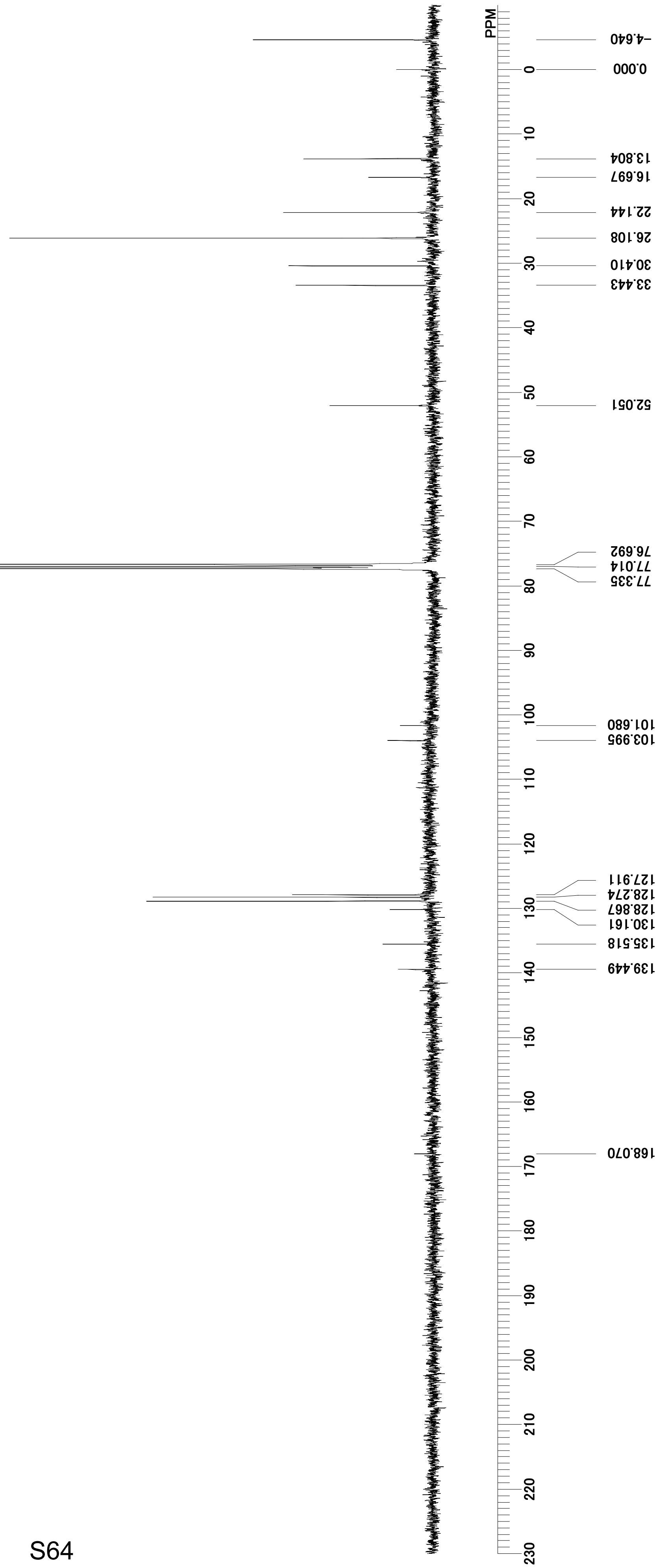
7.225
7.262
7.312
7.329
7.341
7.361
7.378
MeO2C
Ph
n-Bu
TBS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26.108
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33.443
52.051
76.692
77.014
77.335
101.680
103.995
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128.274
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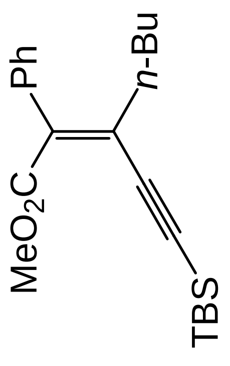
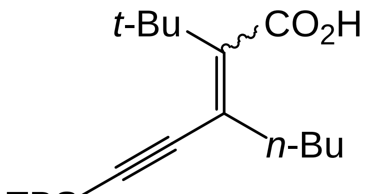
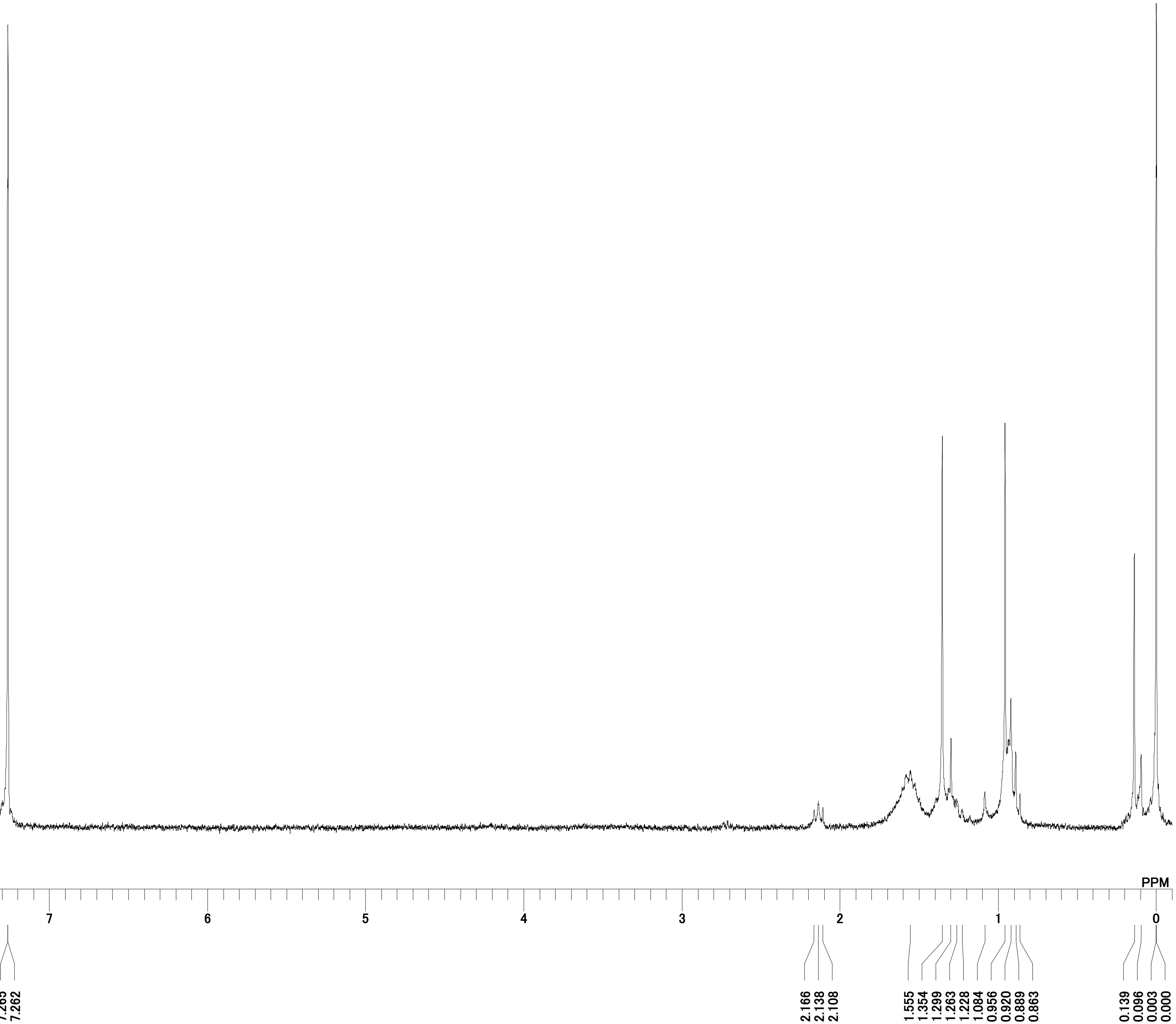
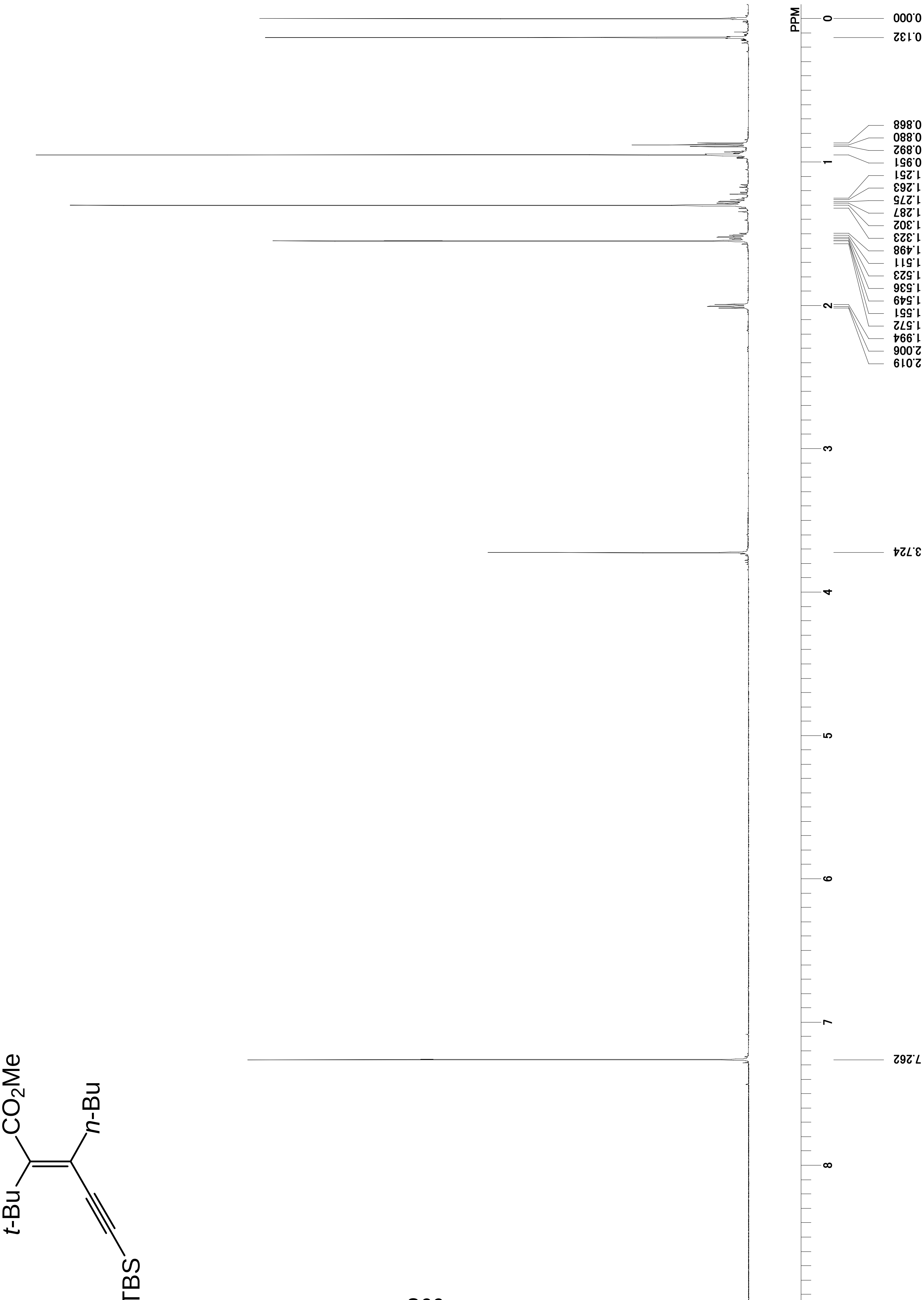
168.070


MeO2C
Ph
n-Bu
TBS


t-Bu
CO2H
n-Bu
TBS

3f


PPM
9
8
7
6
5
4
3
2
1
0
7.265
7.262
2.166
2.138
2.108
1.555
1.354
1.299
1.263
1.228
1.084
0.956
0.920
0.889
0.863
0.139
0.096
0.003
0.000



PPM
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0.132
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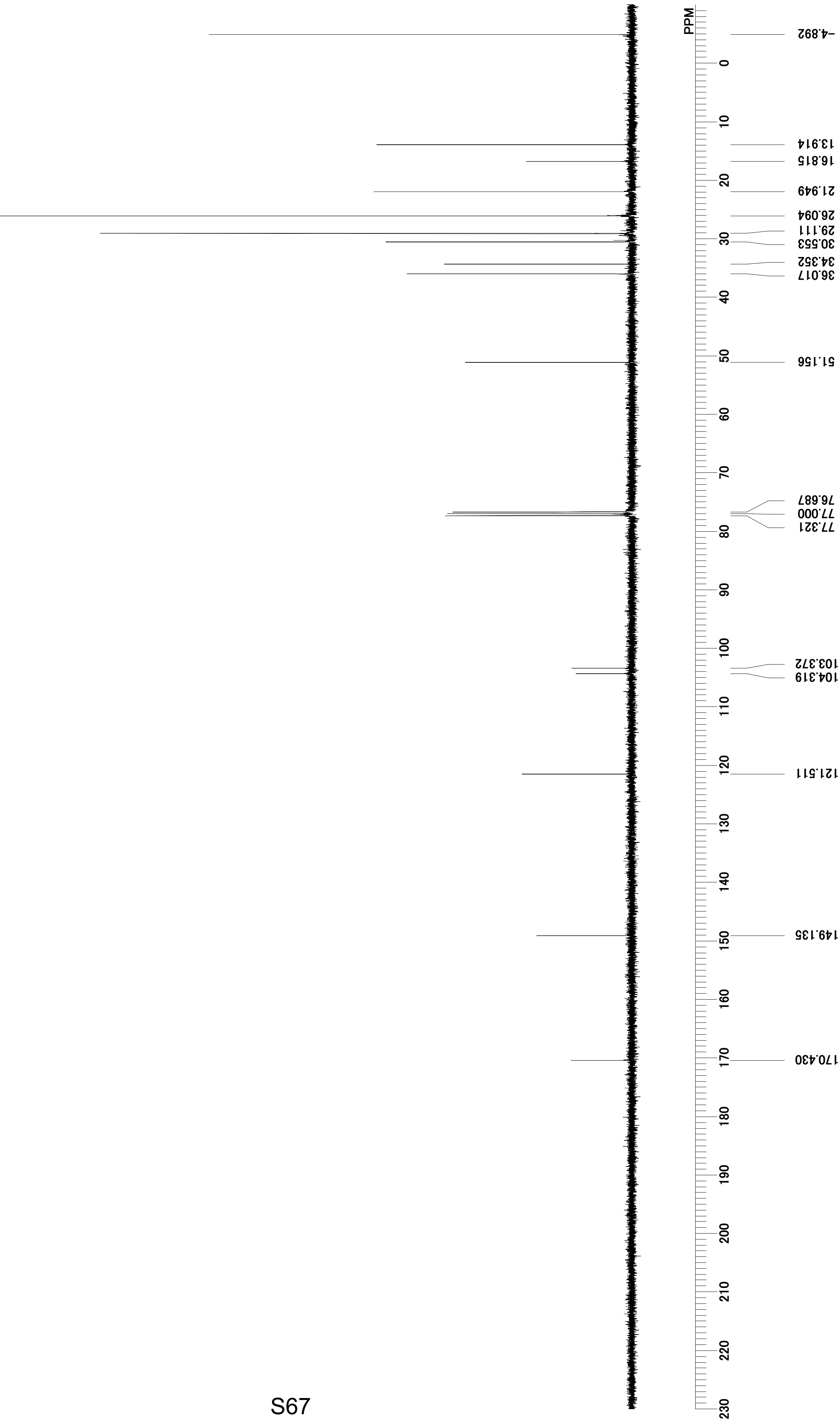
0.880
0.892
0.951
1.251
1.263
1.275
1.287
1.302
1.323
1.498
1.511
1.523
1.536
1.549
1.551
1.572
1.994
2.006
2.019
3.724
7.262
CO2Me
n-Bu
t-Bu
TBS


PPM
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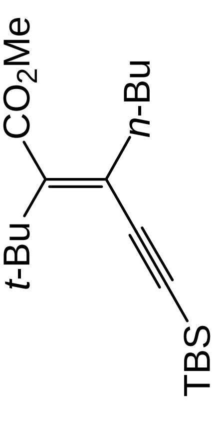
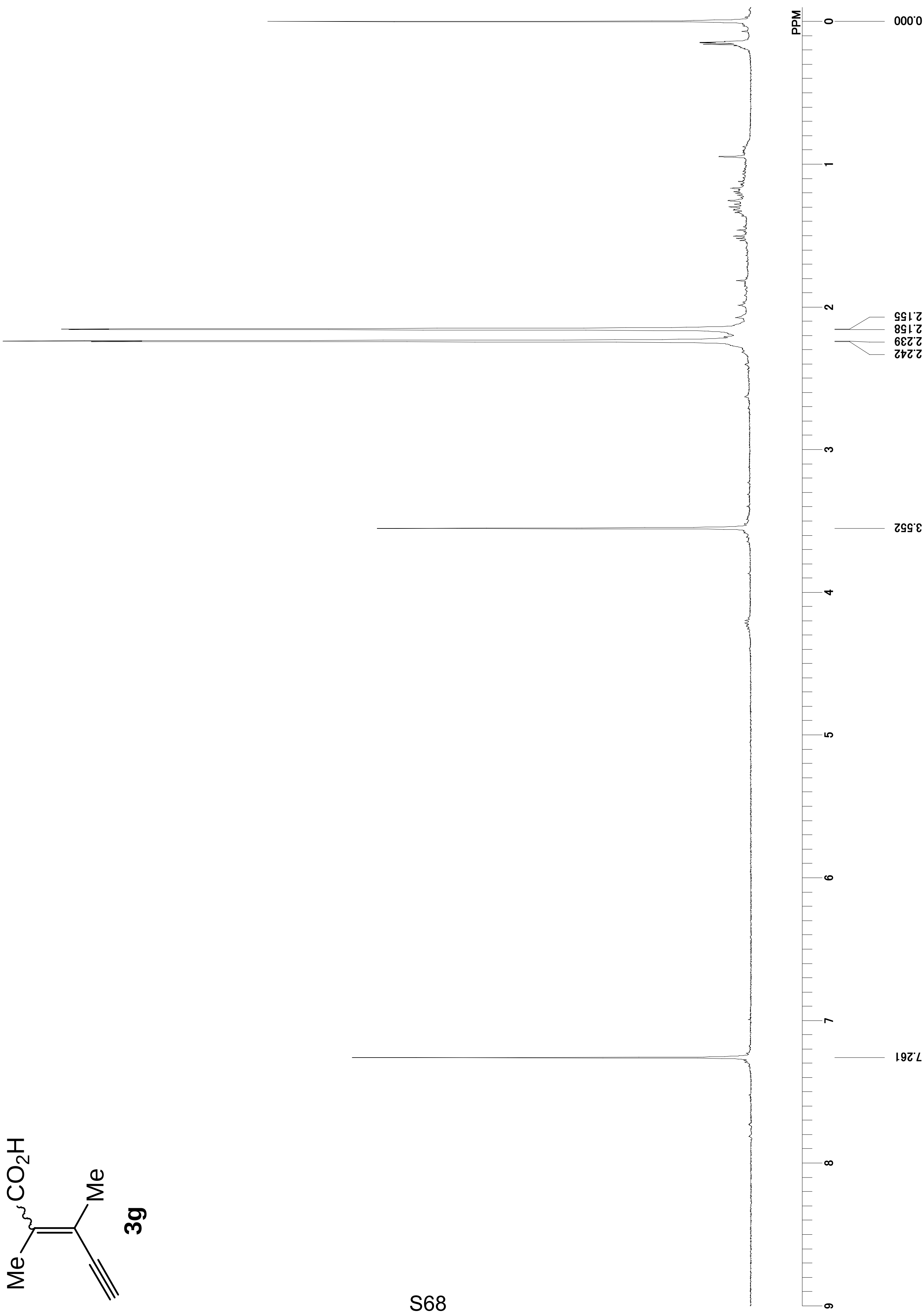
16.815
21.949
26.094
29.111
30.553
34.352
36.017
51.156
76.687
77.000
77.321
103.372
104.319
121.511
149.135
170.430


CO_2Me
n-Bu
t-Bu
TBS


PPM
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2.239
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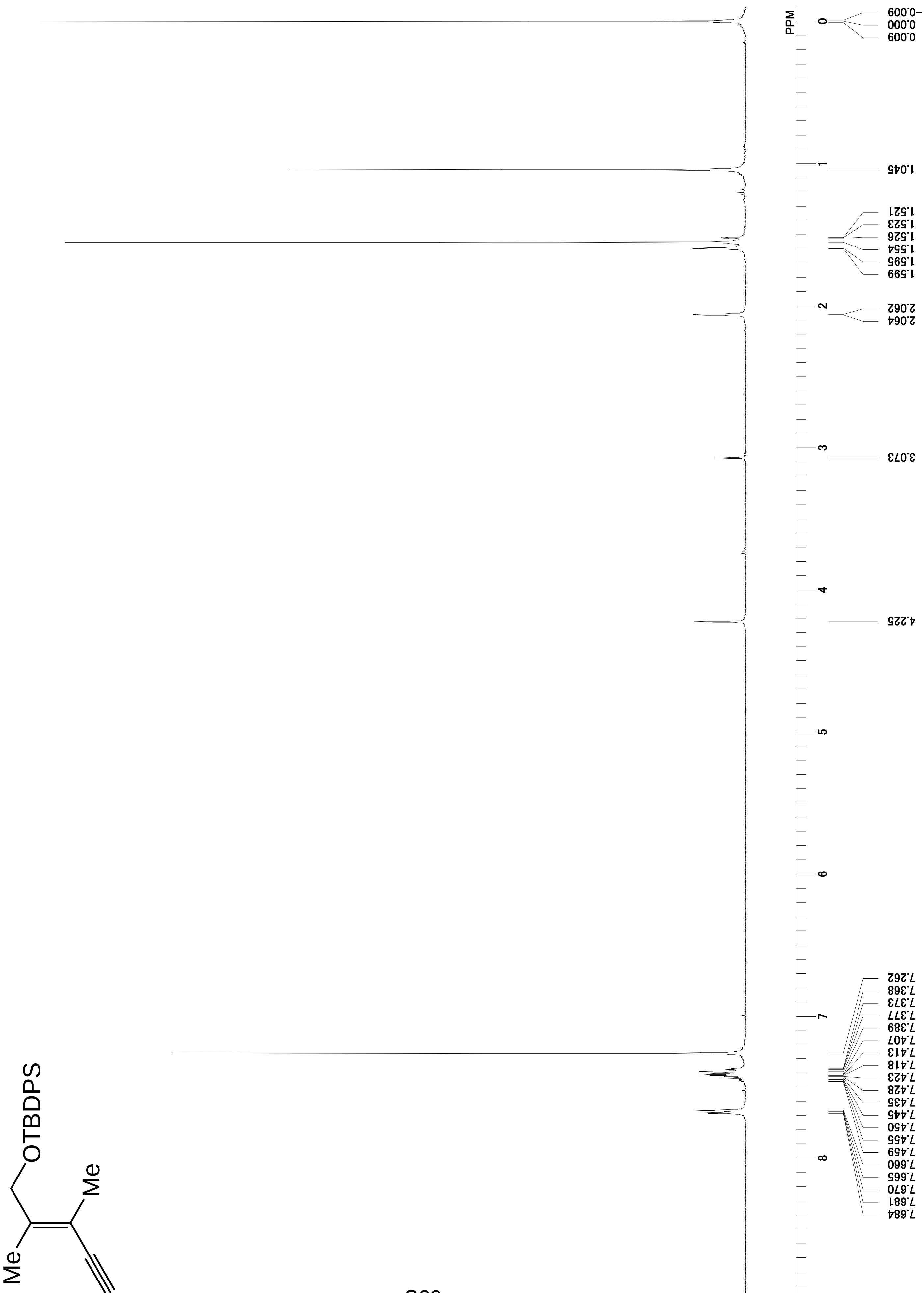
3.552
7.261
3g



OTBDPS
Me
Me
PPM
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0.000
0.009
1.045
1.521
1.523
1.526
1.554
1.595
1.599
2.062
2.064
3.073
4.225
7.262
7.368
7.373
7.377
7.389
7.407
7.413
7.418
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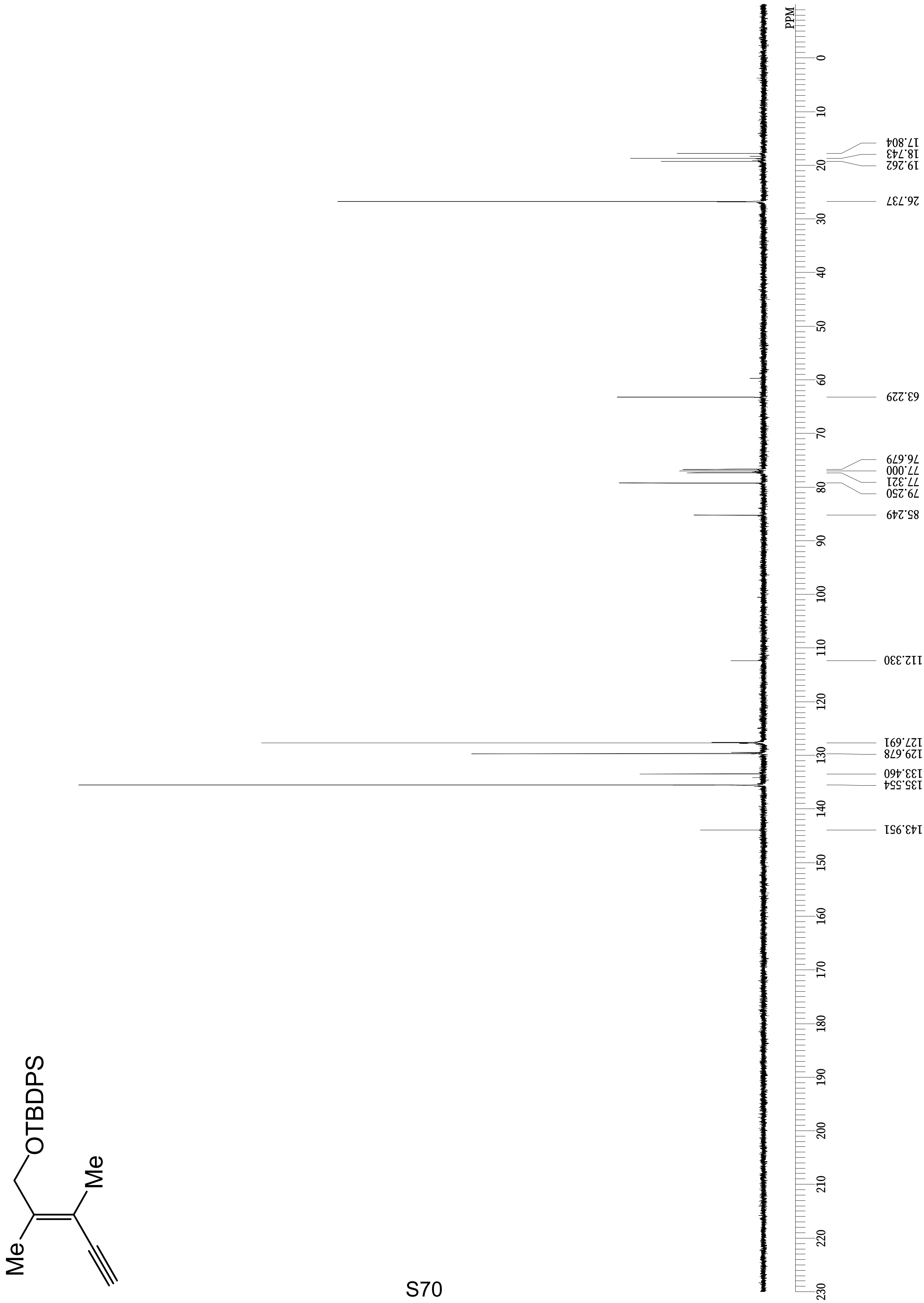
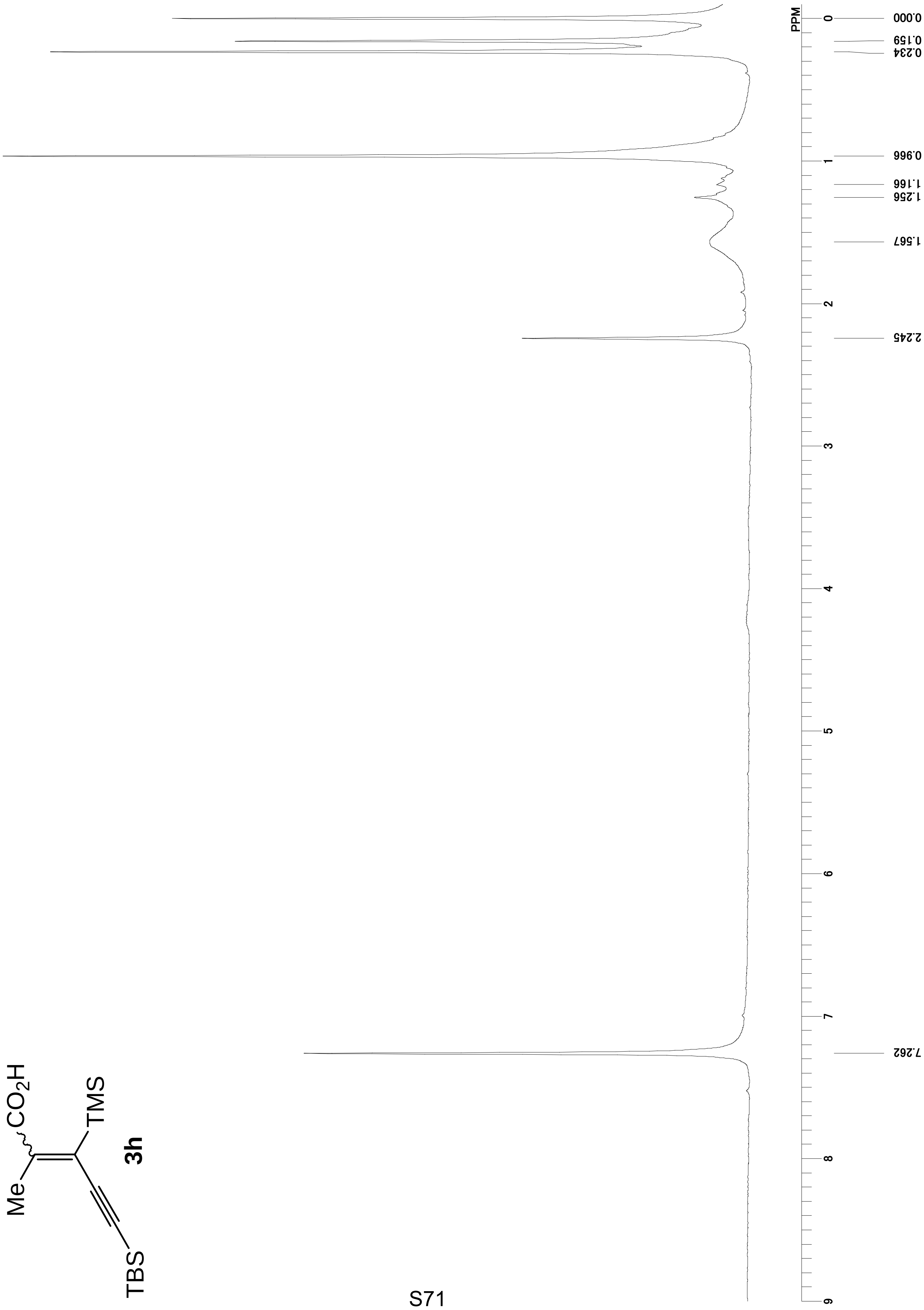
7.435
7.445
7.450
7.455
7.459
7.660
7.665
7.670
7.681
7.684


PPM
17.804
18.743
19.262
26.737
63.229
76.679
77.000
77.321
79.250
85.249
112.330
127.691
129.678
133.460
135.554
143.951
OTBDPS
Me
Me


PPM
0.000
0.159
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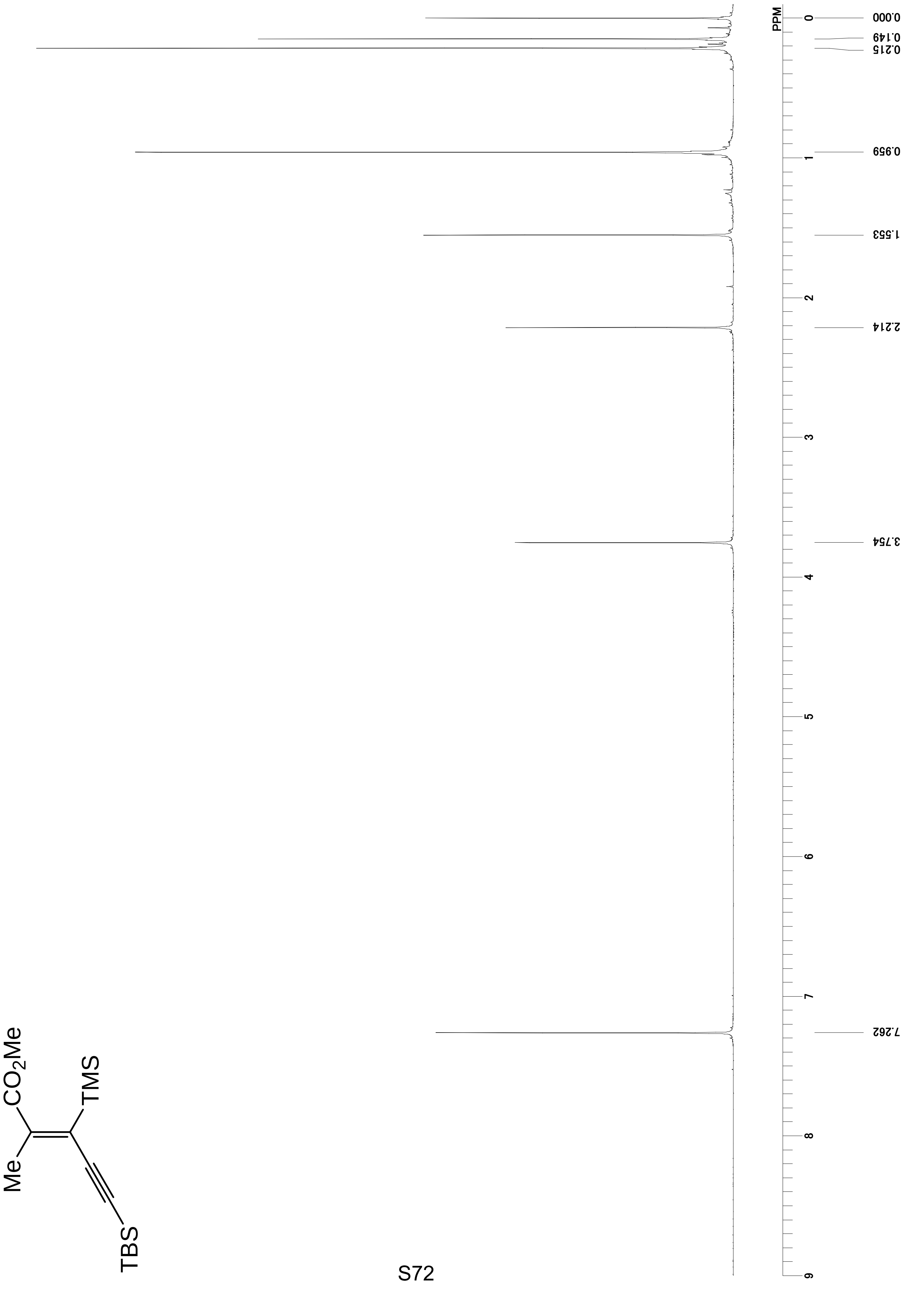
0.966
1.166
1.256
1.567
2.245
7.262
0
1
2
3
4
5
6
7
8
9
Me
CO_2H
TMS
TBS
3h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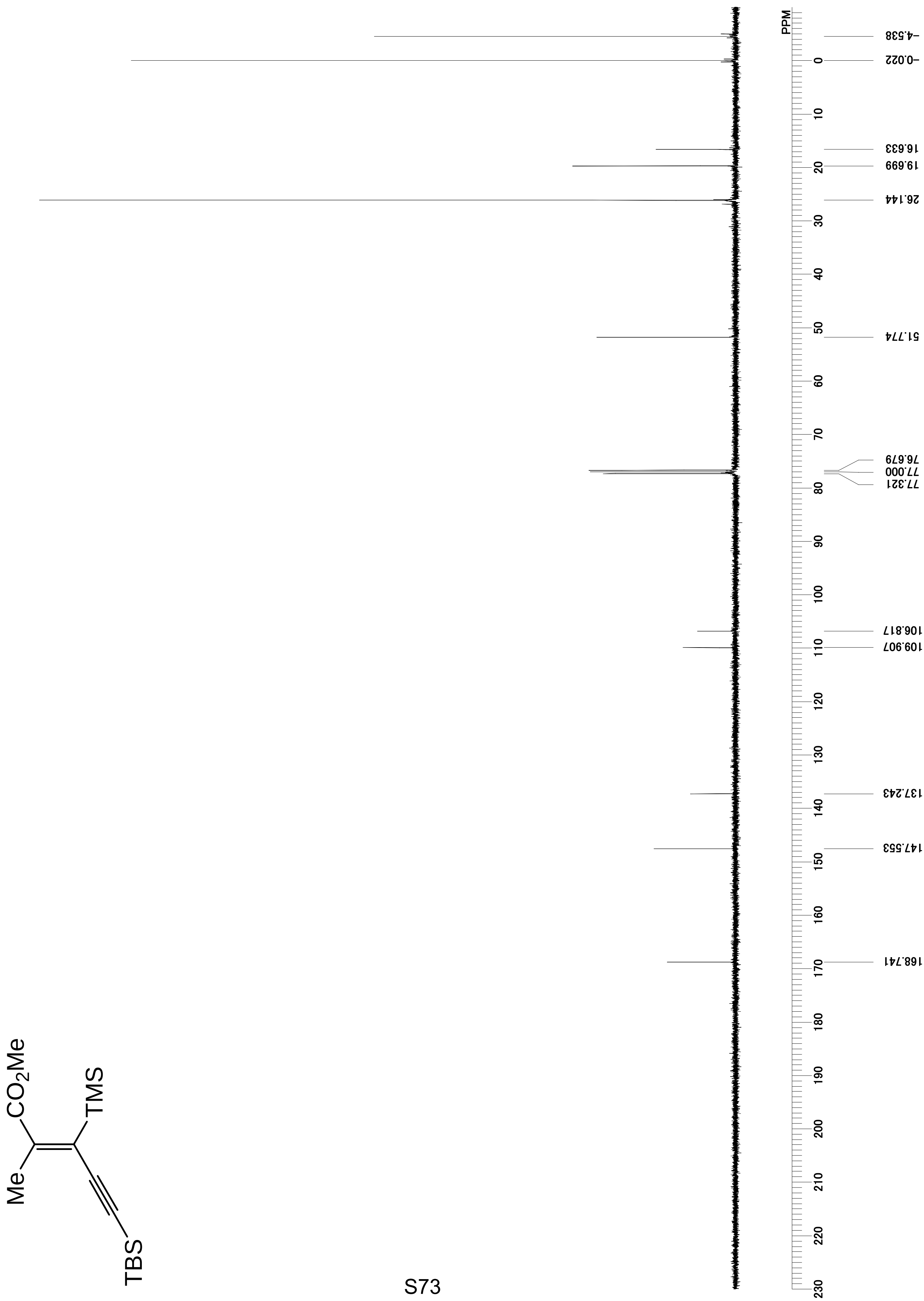
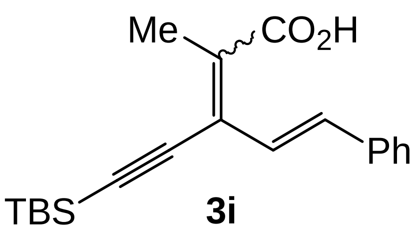
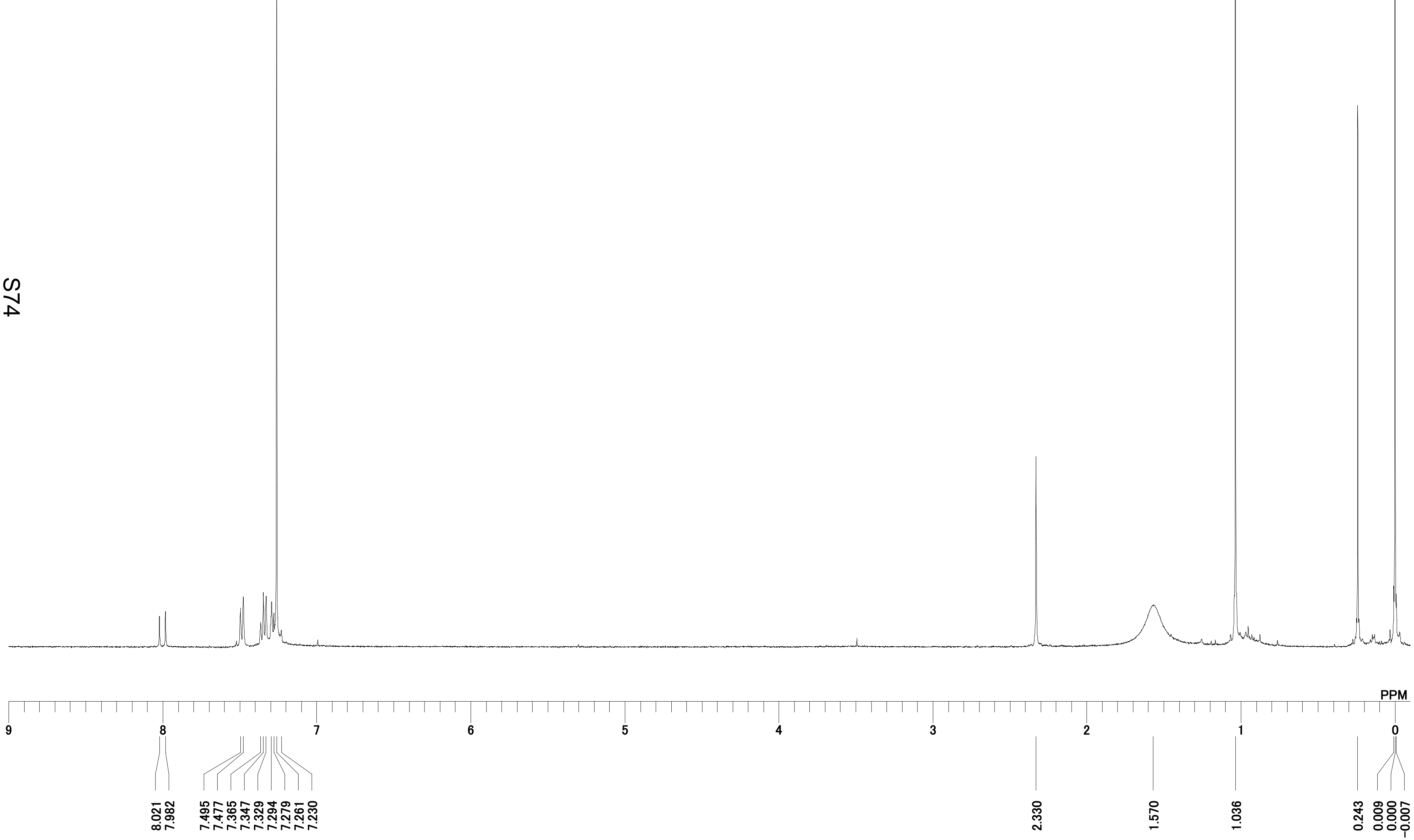
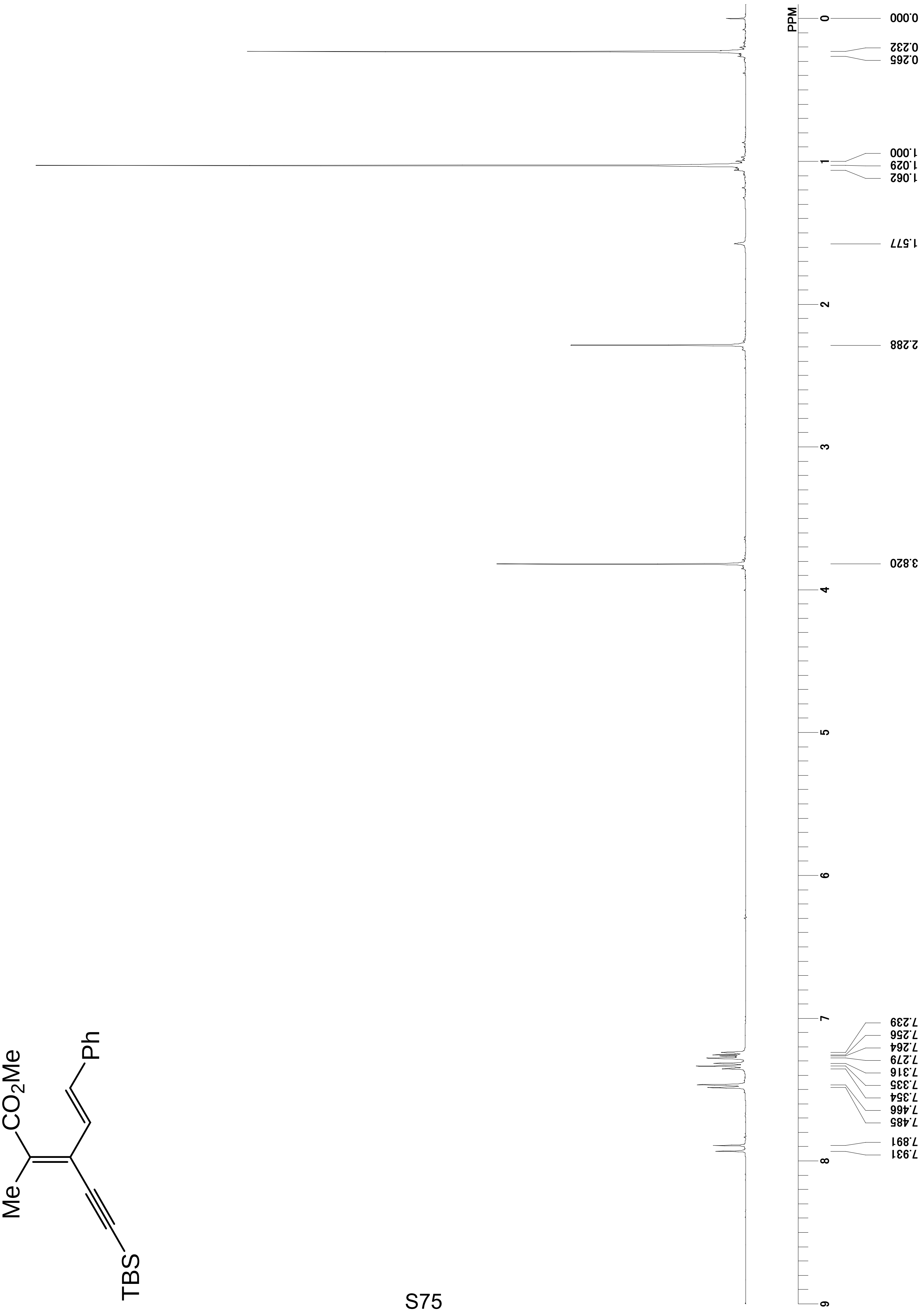
0.149
0.215
0.959
1.553
2.214
3.754
7.262
0
1
2
3
4
5
6
7
8
9
Me
CO2Me
TMS
TBS


PPM
-4.538
-0.022
16.633
19.699
26.144
51.774
76.679
77.000
77.321
106.817
109.907
137.243
147.553
168.741
CO2Me
Me
TMS
TBS



3i


8.021
7.982
7.495
7.477
7.365
7.347
7.329
7.294
7.279
7.261
7.230
2.330
1.570
1.036
0.243
0.009
0.000
−0.007
PPM
9
8
7
6
5
4
3
2
1
0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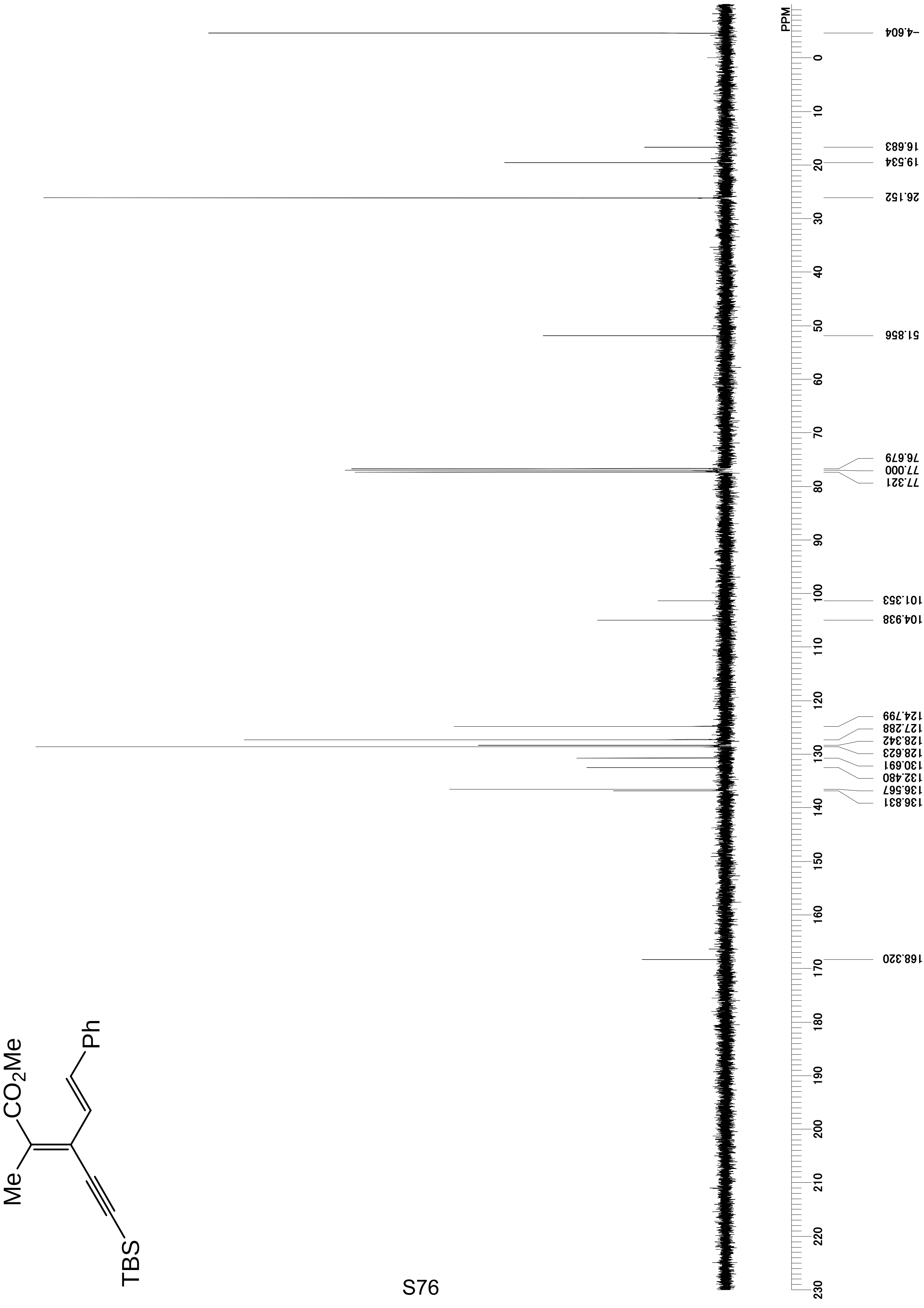
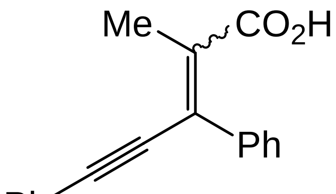
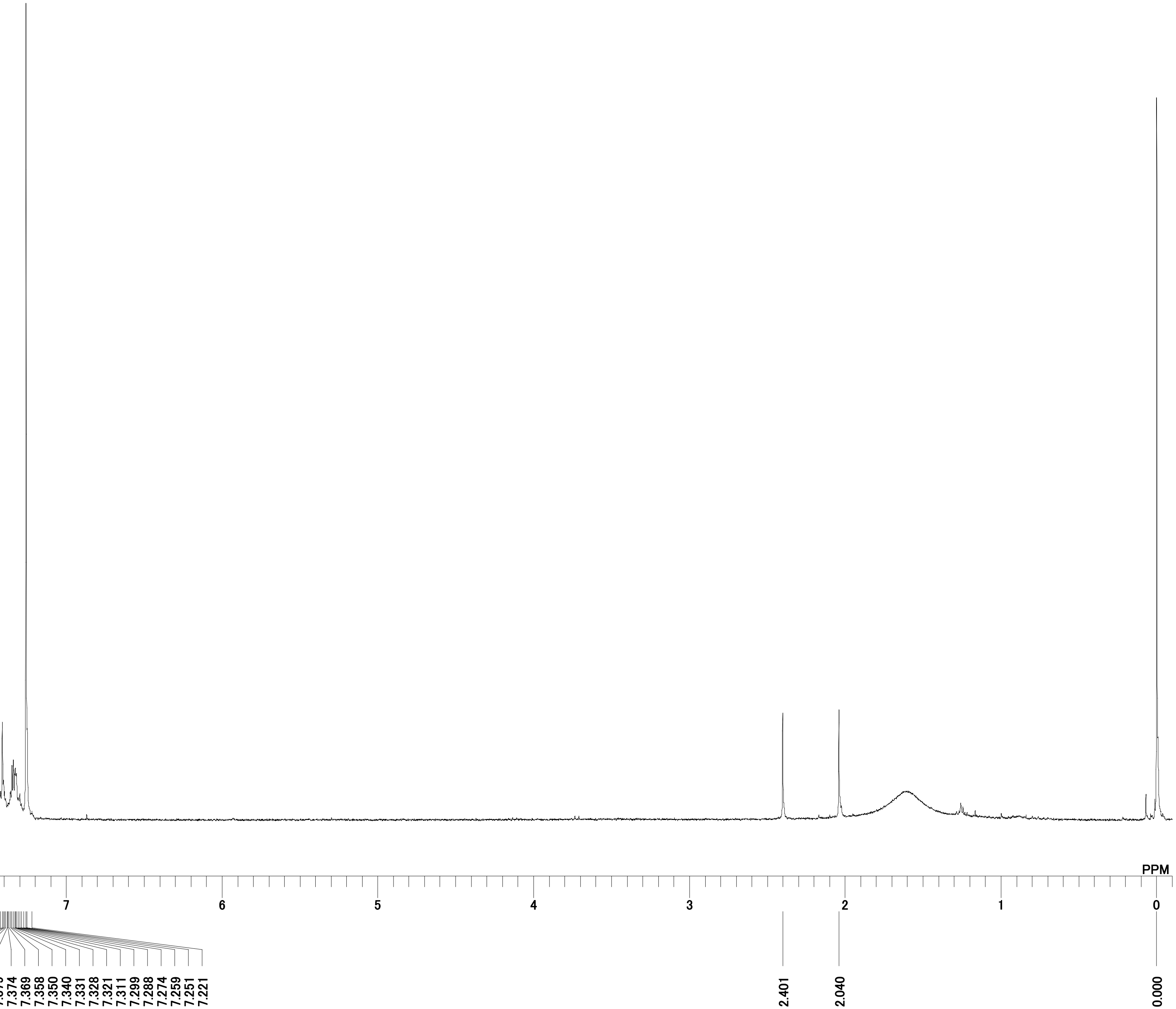
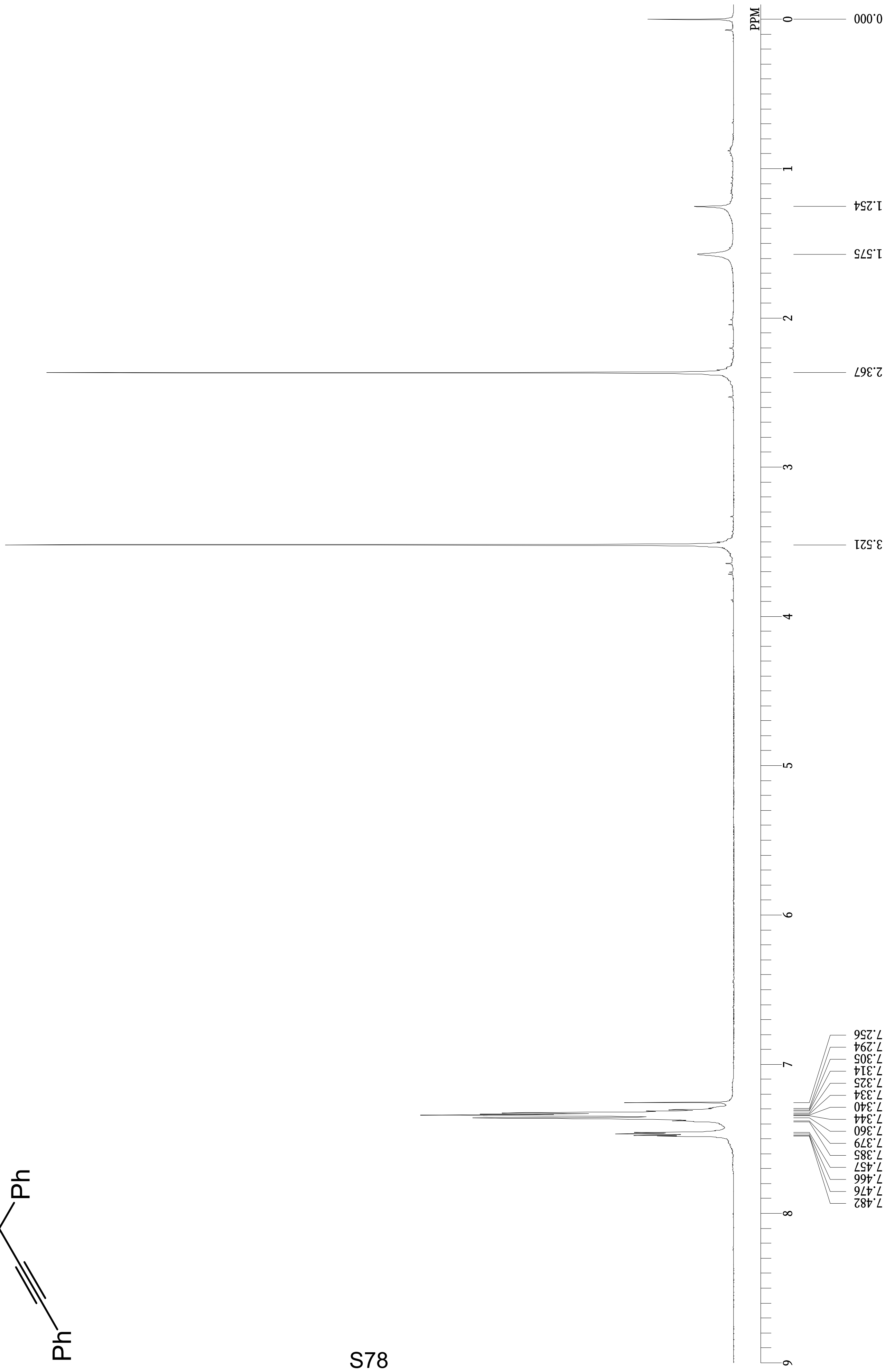
0.232
0.265
1.000
1.029
1.062
1.577
2.288
3.820
7.239
7.256
7.264
7.279
7.316
7.335
7.354
7.466
7.485
7.891
7.931
Me
CO_2Me
Ph
TBS

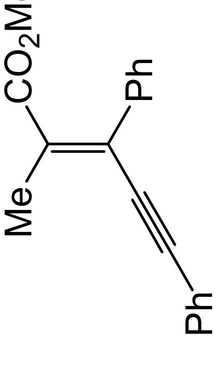

PPM
-4.604
16.683
19.534
26.152
51.856
76.679
77.000
77.321
101.353
104.938
124.799
127.288
128.342
128.623
130.691
132.480
136.567
136.831
168.320
Ph
CO_2Me
Me
TBS

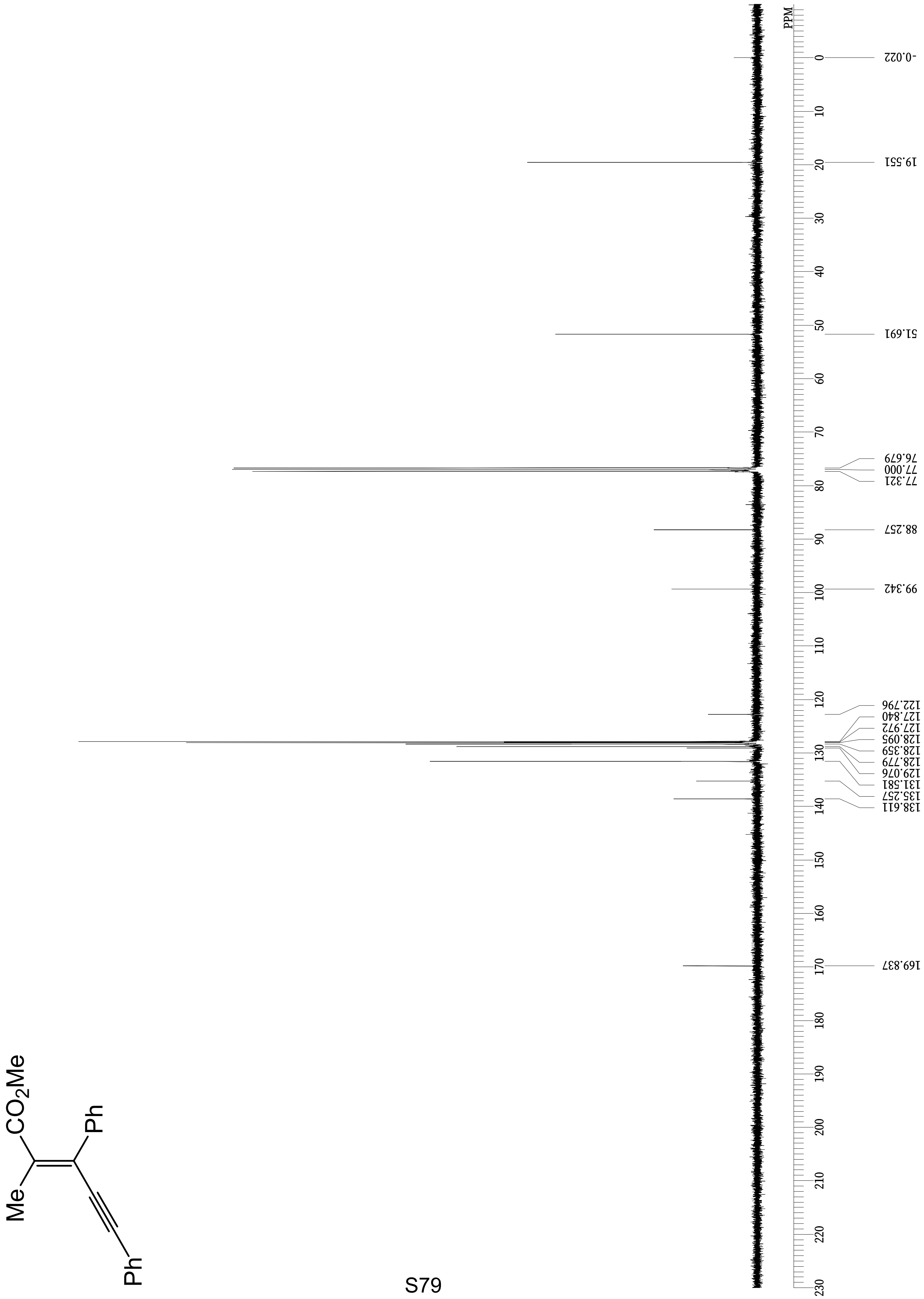


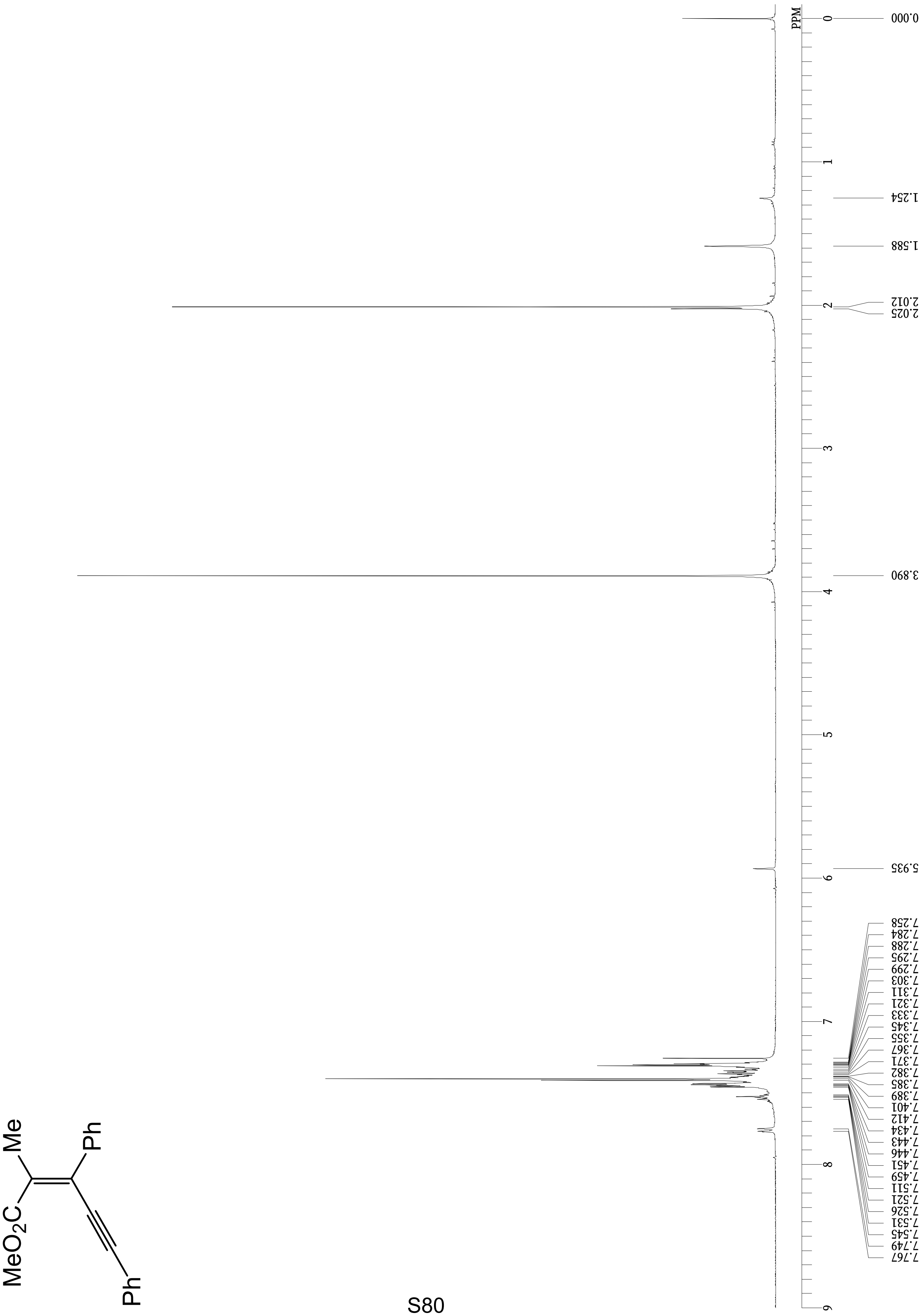
3j

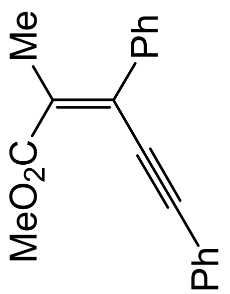

7.487
7.478
7.466
7.460
7.455
7.451
7.441
7.431
7.423
7.411
7.403
7.397
7.390
7.379
7.374
7.369
7.358
7.350
7.340
7.331
7.328
7.321
7.311
7.299
7.288
7.274
7.259
7.251
7.221
2.401
2.040
0.000
PPM
9
8
7
6
5
4
3
2
1
0

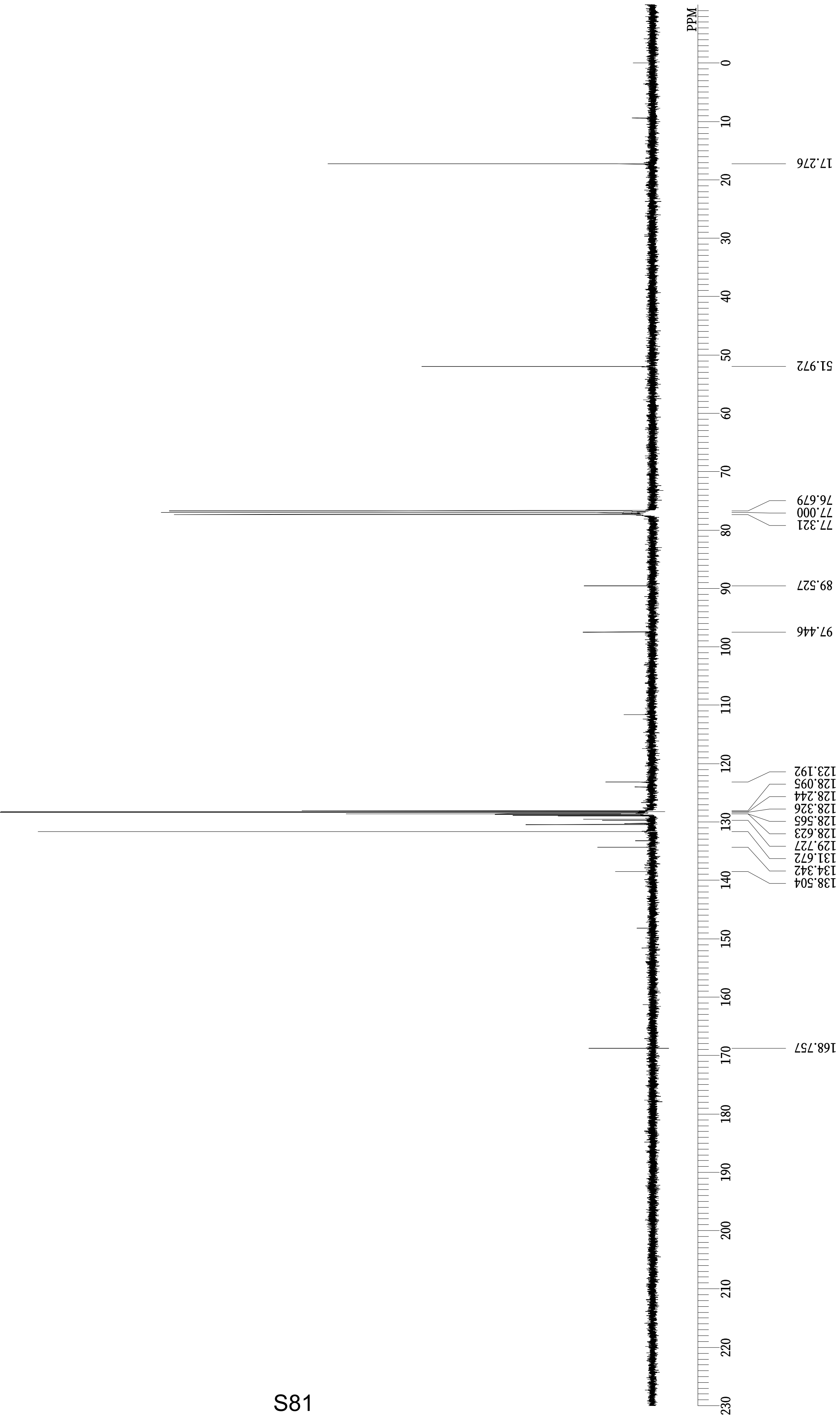

PPM
0
1
2
3
4
5
6
7
8
9
0.000
1.254
1.575
2.367
3.521
7.256
7.294
7.305
7.314
7.325
7.334
7.340
7.344
7.360
7.379
7.385
7.457
7.466
7.476
7.482

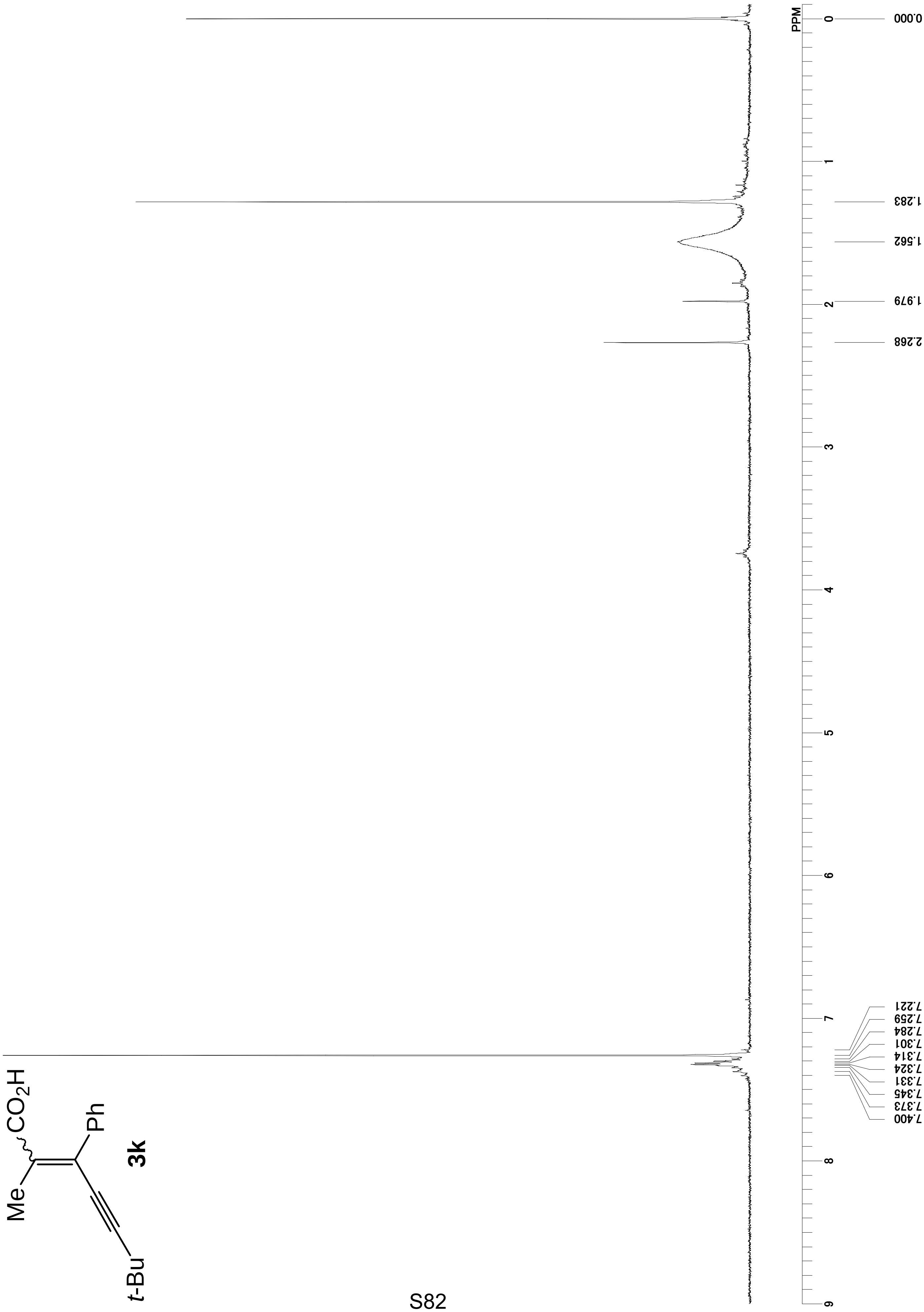

CO2Me
Me
Ph
Ph


PPM
-0.022
19.551
51.691
76.679
77.000
77.321
88.257
99.342
122.796
127.840
127.972
128.095
128.359
128.779
129.076
131.581
135.257
138.611
169.837
CO_2Me
Ph
Me
Ph

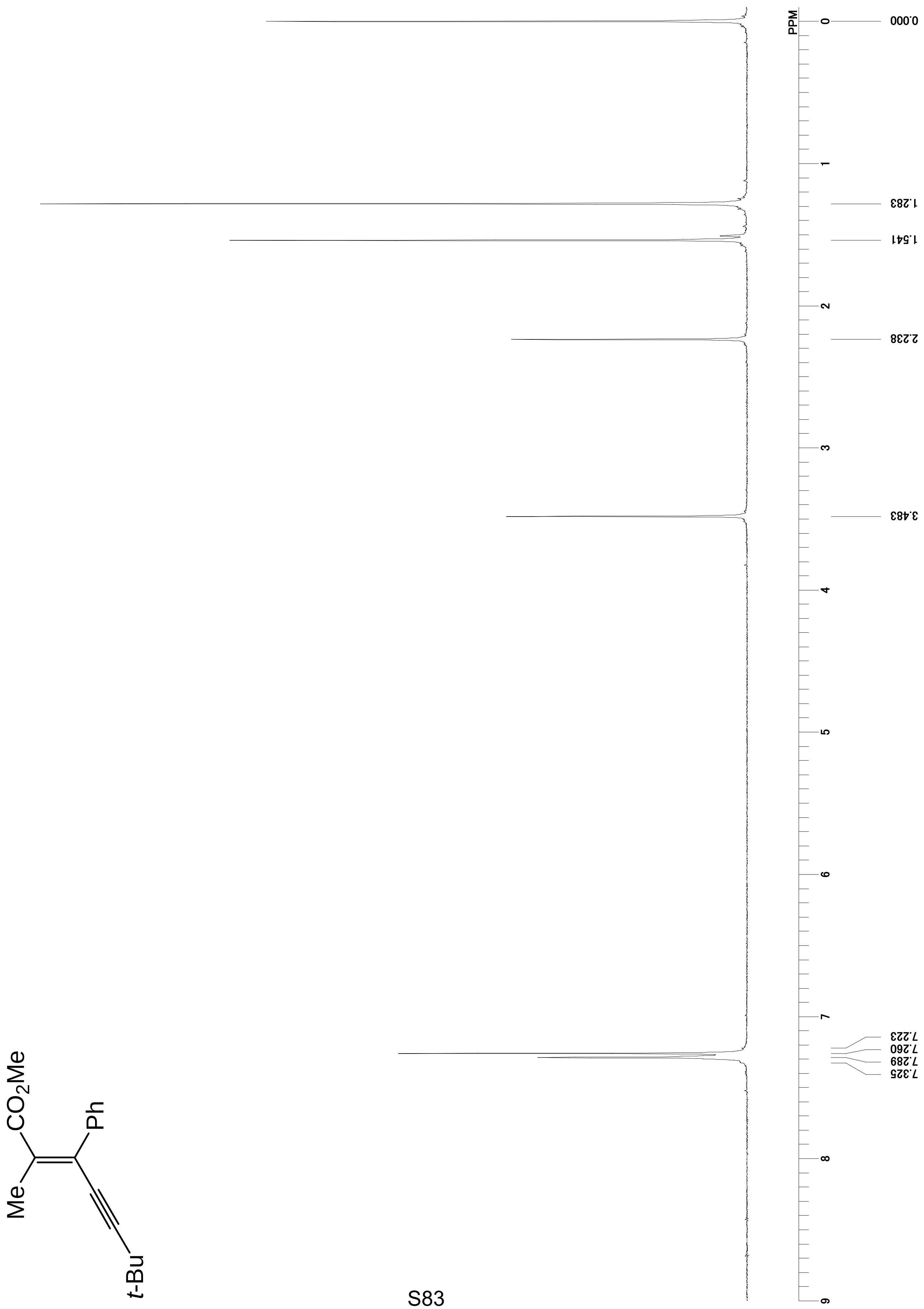

MeO2C
Me
Ph
Ph
PPM
0.000
1.254
1.588
2.012
2.025
3.890
5.935
7.258
7.284
7.288
7.295
7.299
7.303
7.311
7.321
7.333
7.345
7.355
7.367
7.371
7.382
7.385
7.389
7.401
7.412
7.434
7.443
7.446
7.451
7.459
7.511
7.521
7.526
7.531
7.545
7.749
7.767


MeO2C
Me
Ph
Ph

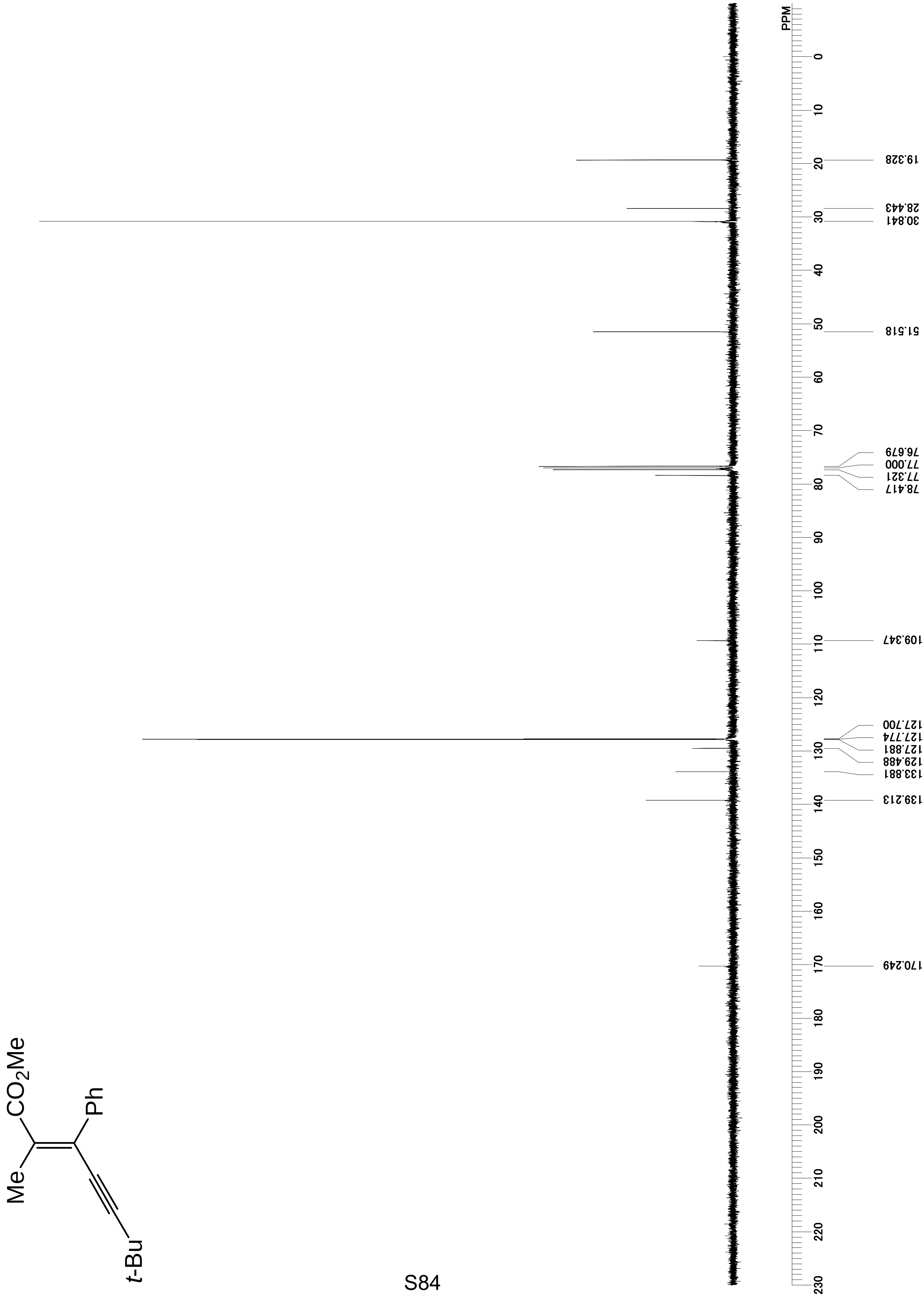

PPM
17.276
51.972
76.679
77.000
77.321
89.527
97.446
123.192
128.095
128.244
128.326
128.565
128.623
129.727
131.672
134.342
138.504
168.757

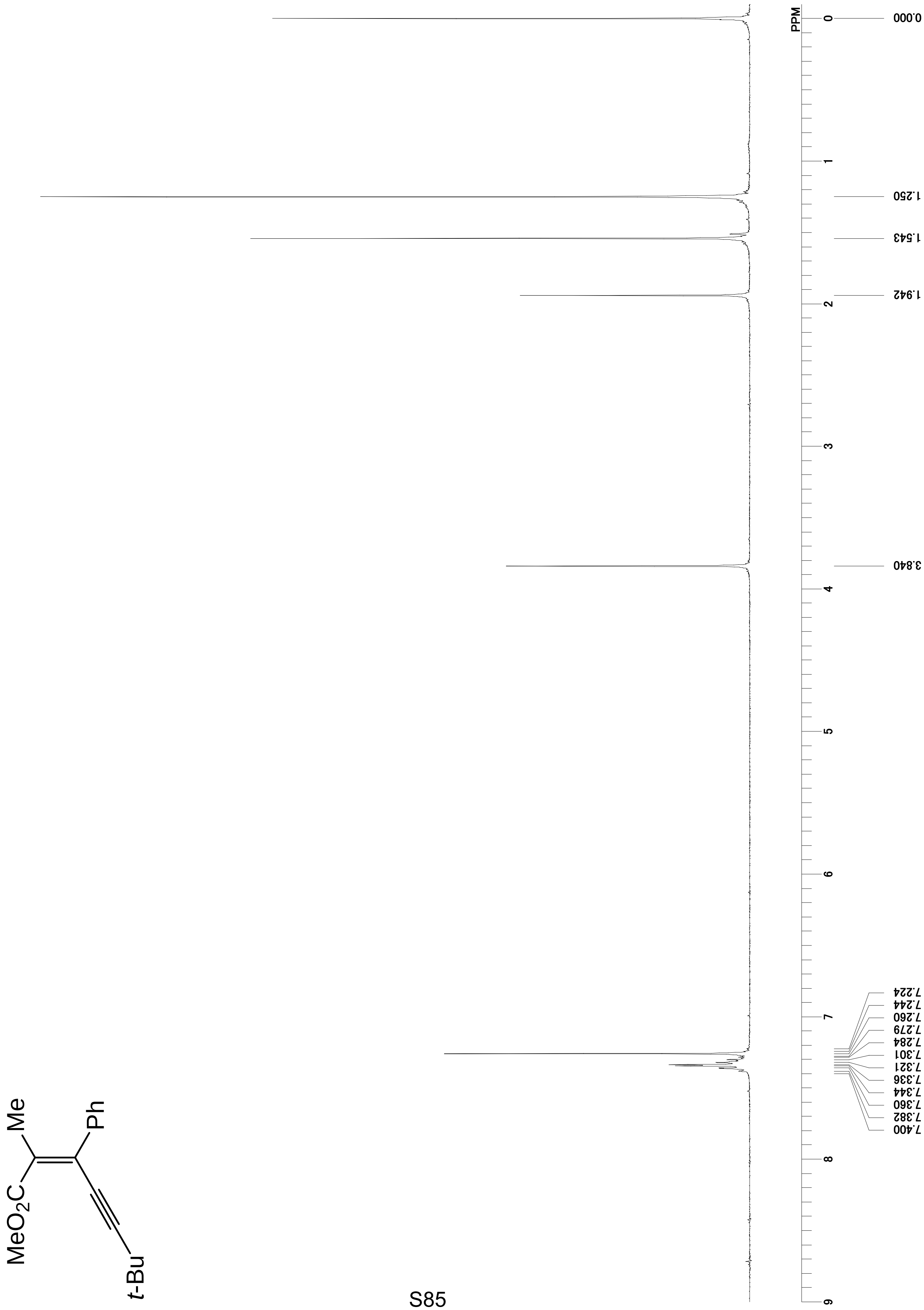

Me
CO_2H
Ph
t-Bu
PPM
0.000
1.283
1.562
1.979
2.268
7.221
7.259
7.284
7.301
7.314
7.324
7.331
7.345
7.373
7.400

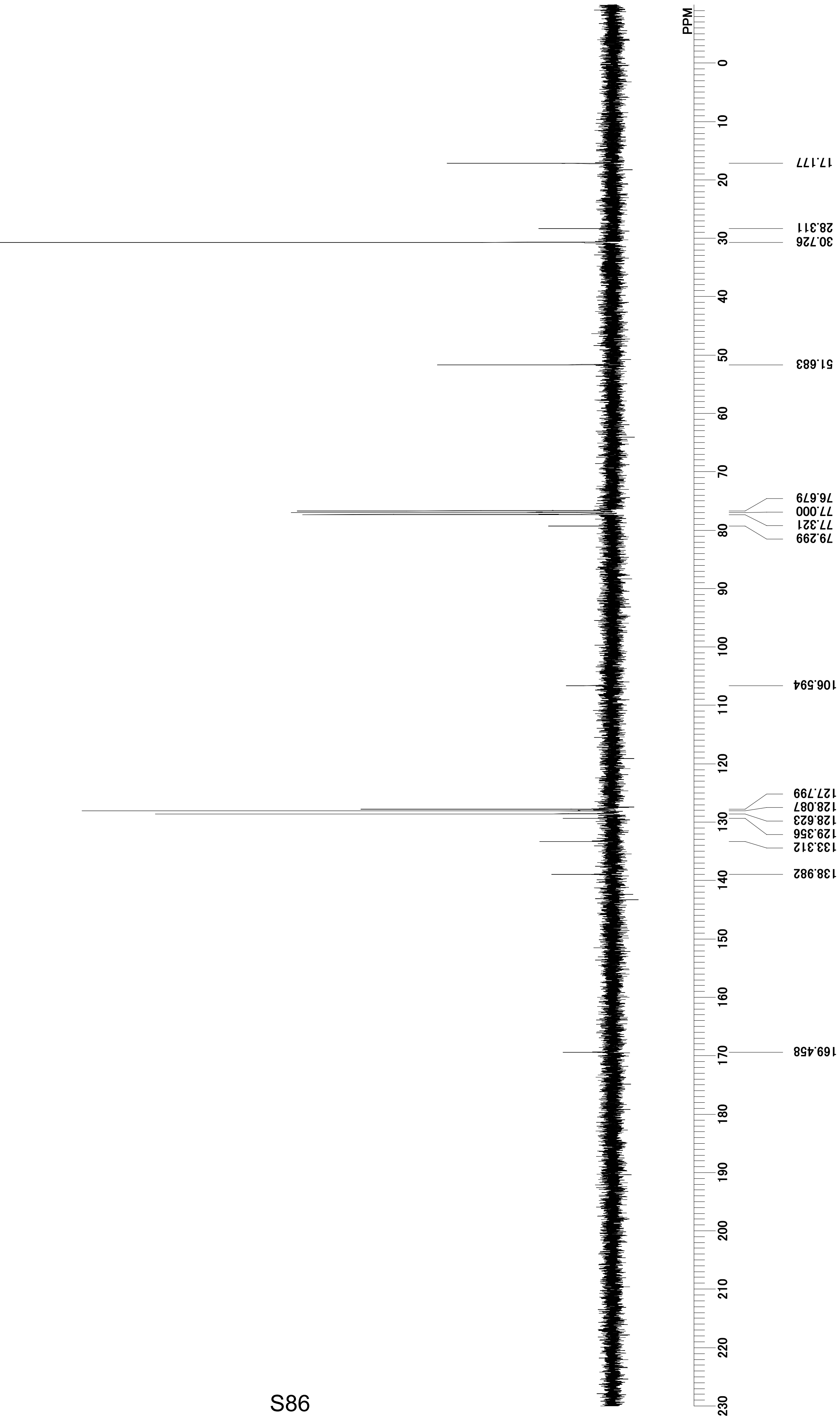
3k

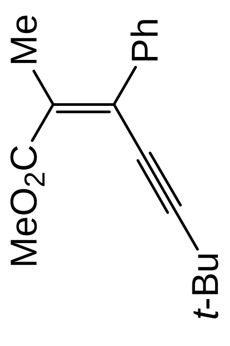


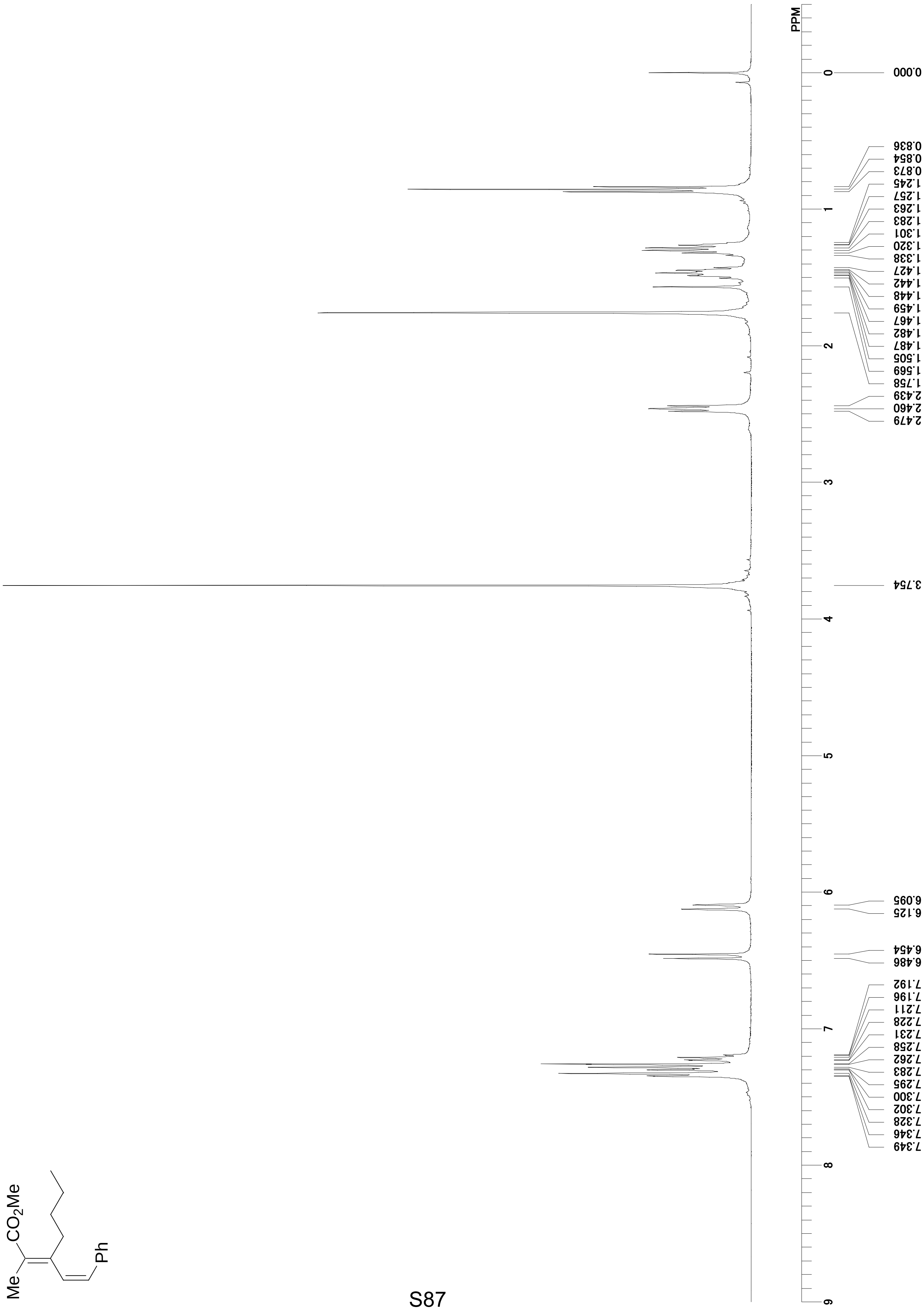
PPM
0
1
2
3
4
5
6
7
8
9
0.000
1.283
1.541
2.238
3.483
7.223
7.260
7.289
7.325
Me
CO_2Me
Ph
t-Bu

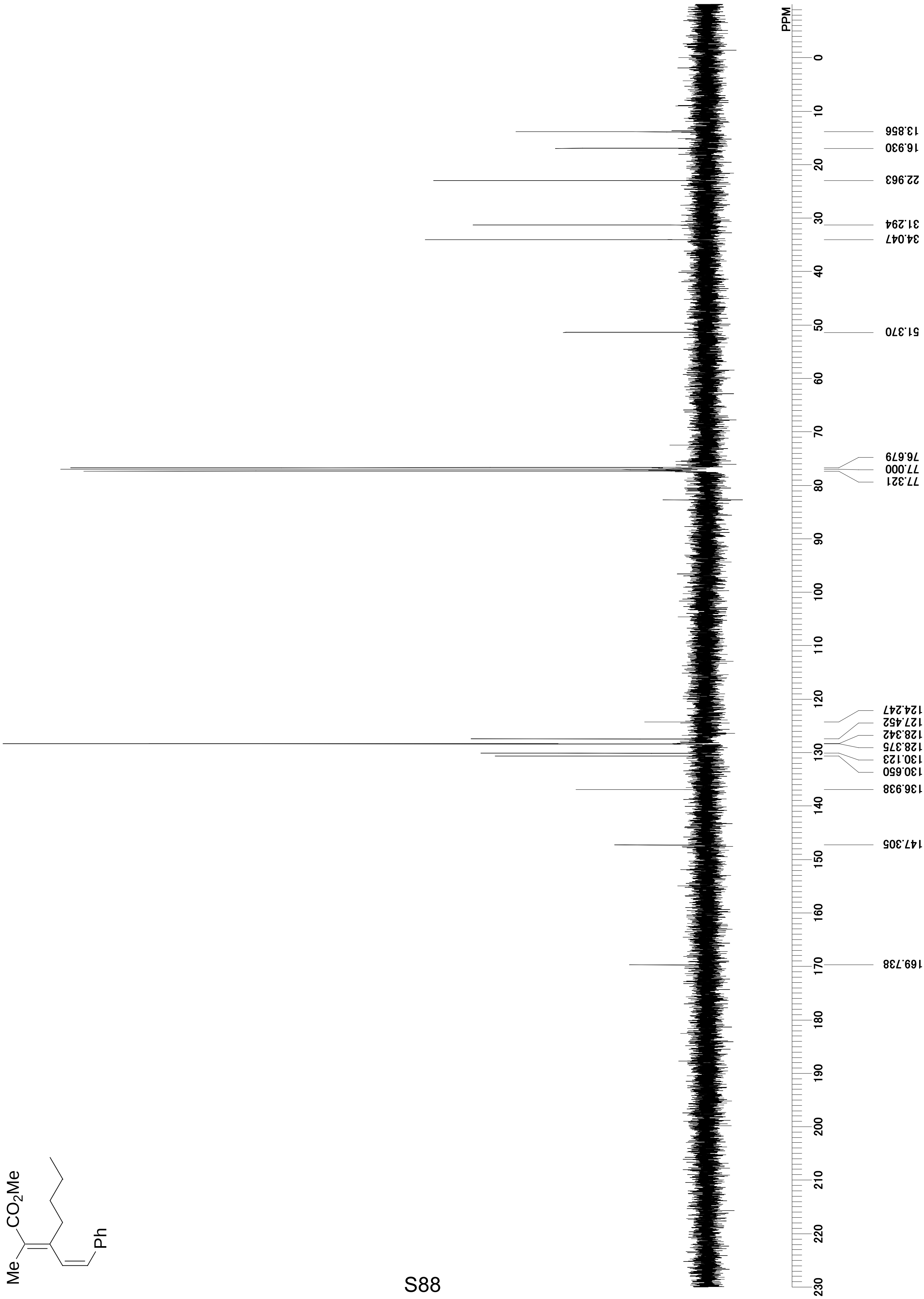

PPM
19.328
28.443
30.841
51.518
76.679
77.000
77.321
78.417
109.347
127.700
127.774
127.881
129.488
133.881
139.213
170.249
CO2Me
Me
Ph
t-Bu

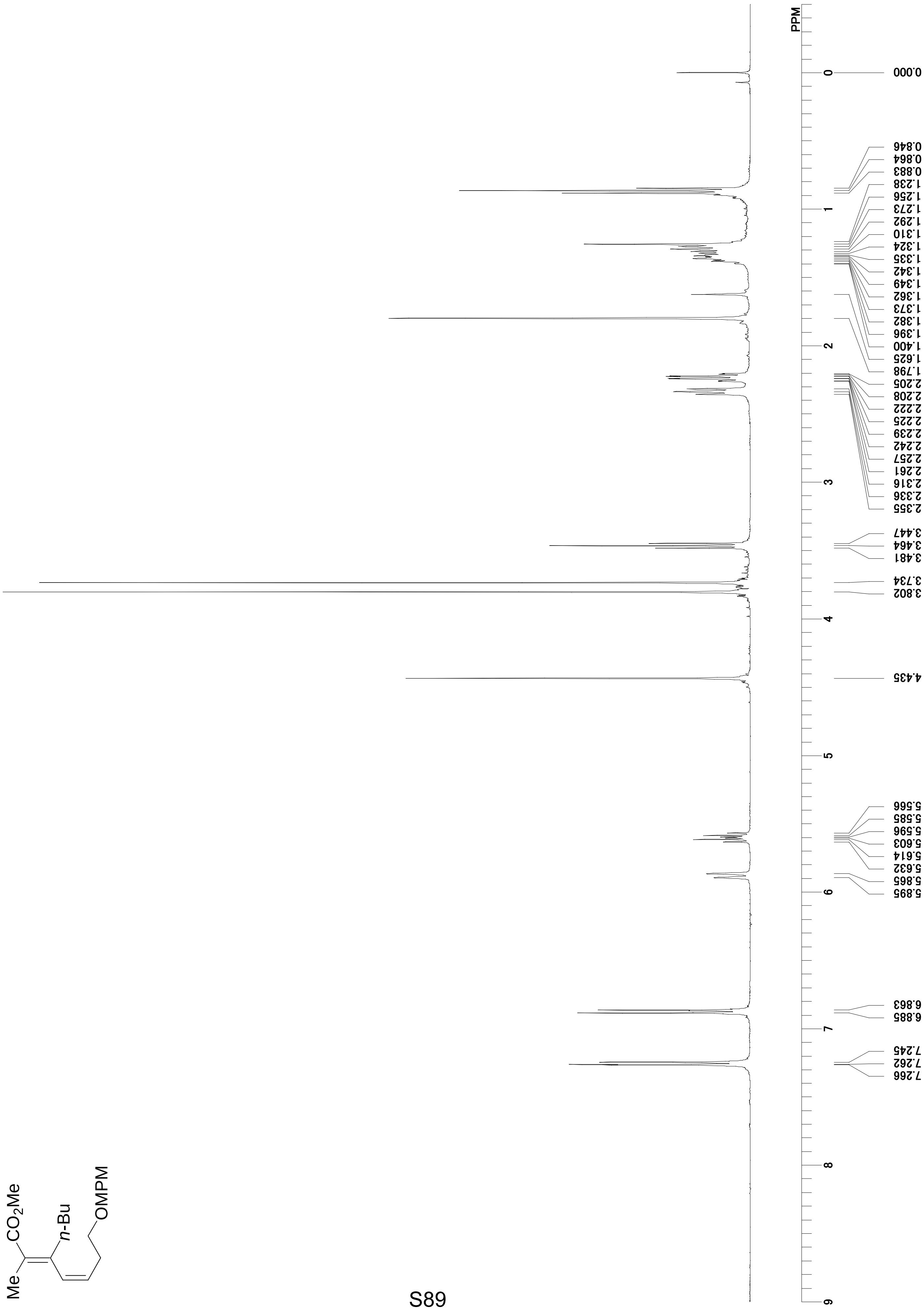

MeO2C
Me
Ph
t-Bu
PPM
0
1
2
3
4
5
6
7
8
9
0.000
1.250
1.543
1.942
3.840
7.224
7.244
7.260
7.279
7.284
7.301
7.321
7.336
7.344
7.360
7.382
7.400

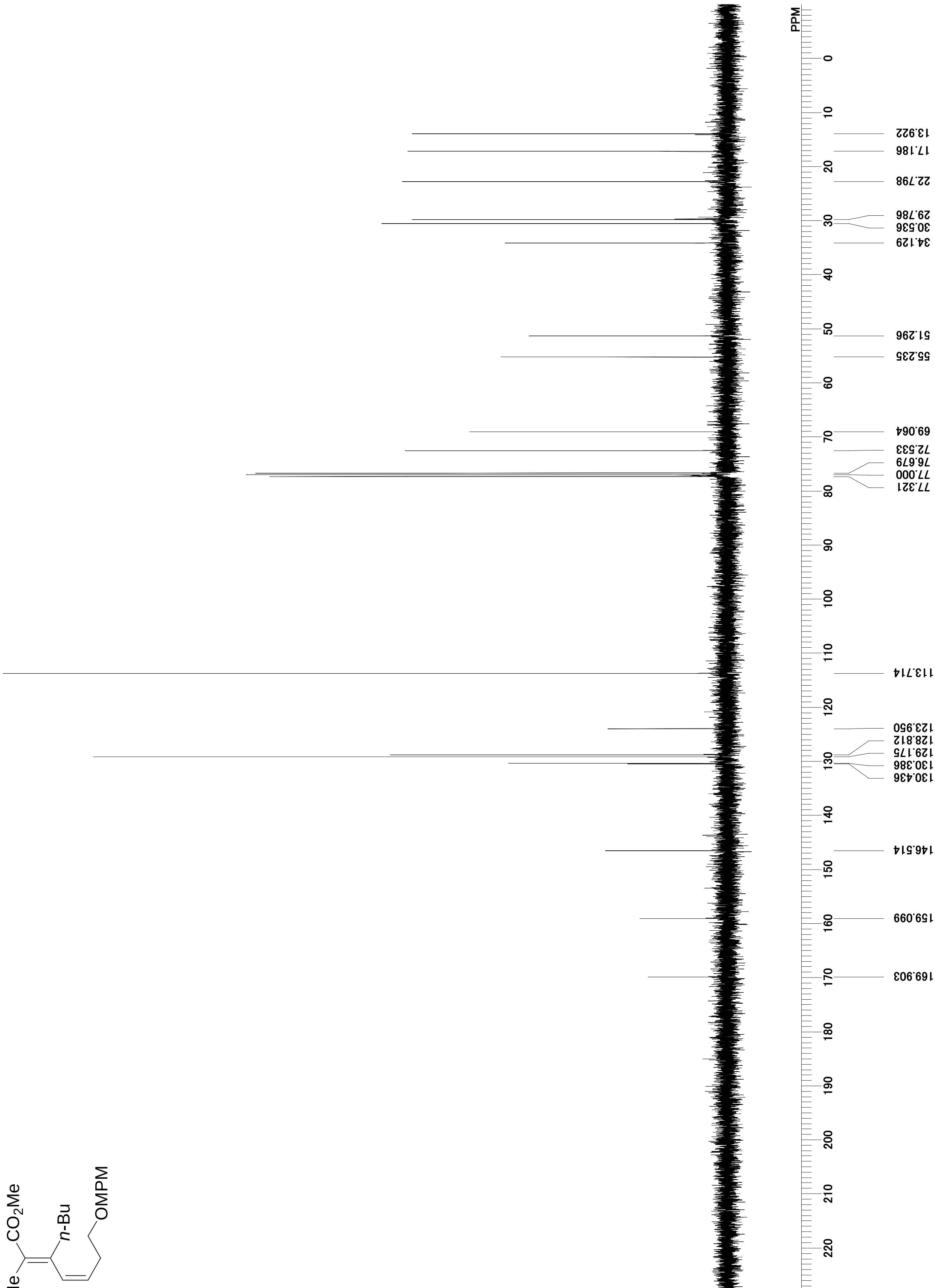

PPM
17.177
28.311
30.726
51.683
76.679
77.000
77.321
79.299
106.594
127.799
128.087
128.623
129.356
133.312
138.982
169.458


MeO2C
Me
Ph
t-Bu


PPM
0
1
2
3
4
5
6
7
8
9
0.000
0.836
0.854
0.873
1.245
1.257
1.263
1.283
1.301
1.320
1.338
1.427
1.442
1.448
1.459
1.467
1.482
1.487
1.505
1.569
1.758
2.439
2.460
2.479
3.754
6.095
6.125
6.454
6.486
7.192
7.196
7.211
7.228
7.231
7.258
7.262
7.283
7.295
7.300
7.302
7.328
7.346
7.349
Me
CO_2Me
Ph


PPM
13.856
16.930
22.963
31.294
34.047
51.370
76.679
77.000
77.321
124.247
127.452
128.342
128.375
130.123
130.650
136.938
147.305
169.738
Me
CO2Me
Ph


PPM
0 1 2 3 4 5 6 7 8 9
0.000
0.846
0.864
0.883
1.238
1.256
1.273
1.292
1.310
1.324
1.335
1.342
1.349
1.362
1.373
1.382
1.396
1.400
1.625
1.798
2.205
2.208
2.222
2.225
2.239
2.242
2.257
2.261
2.316
2.336
2.355
3.447
3.464
3.481
3.734
3.802
4.435
5.566
5.585
5.596
5.603
5.614
5.632
5.865
5.895
6.863
6.885
7.245
7.262
7.266
Me
CO_2Me
n-Bu
OMPM


PPM
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69.064
72.533
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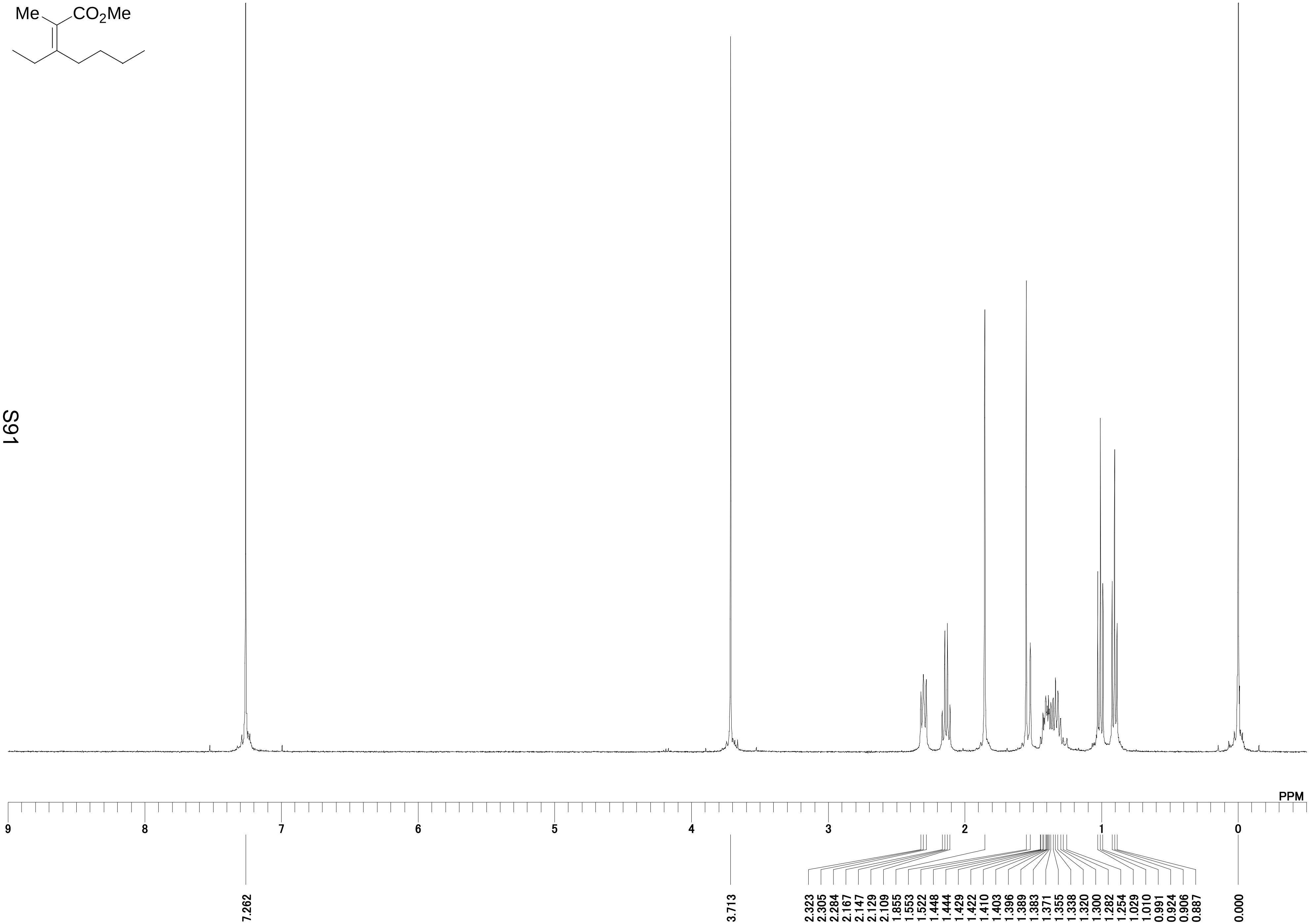
77.000
77.321
113.714
123.950
128.812
129.175
130.386
130.436
146.514
159.099
169.903
Me
CO_2Me
n-Bu
OMPM


Me
CO2Me
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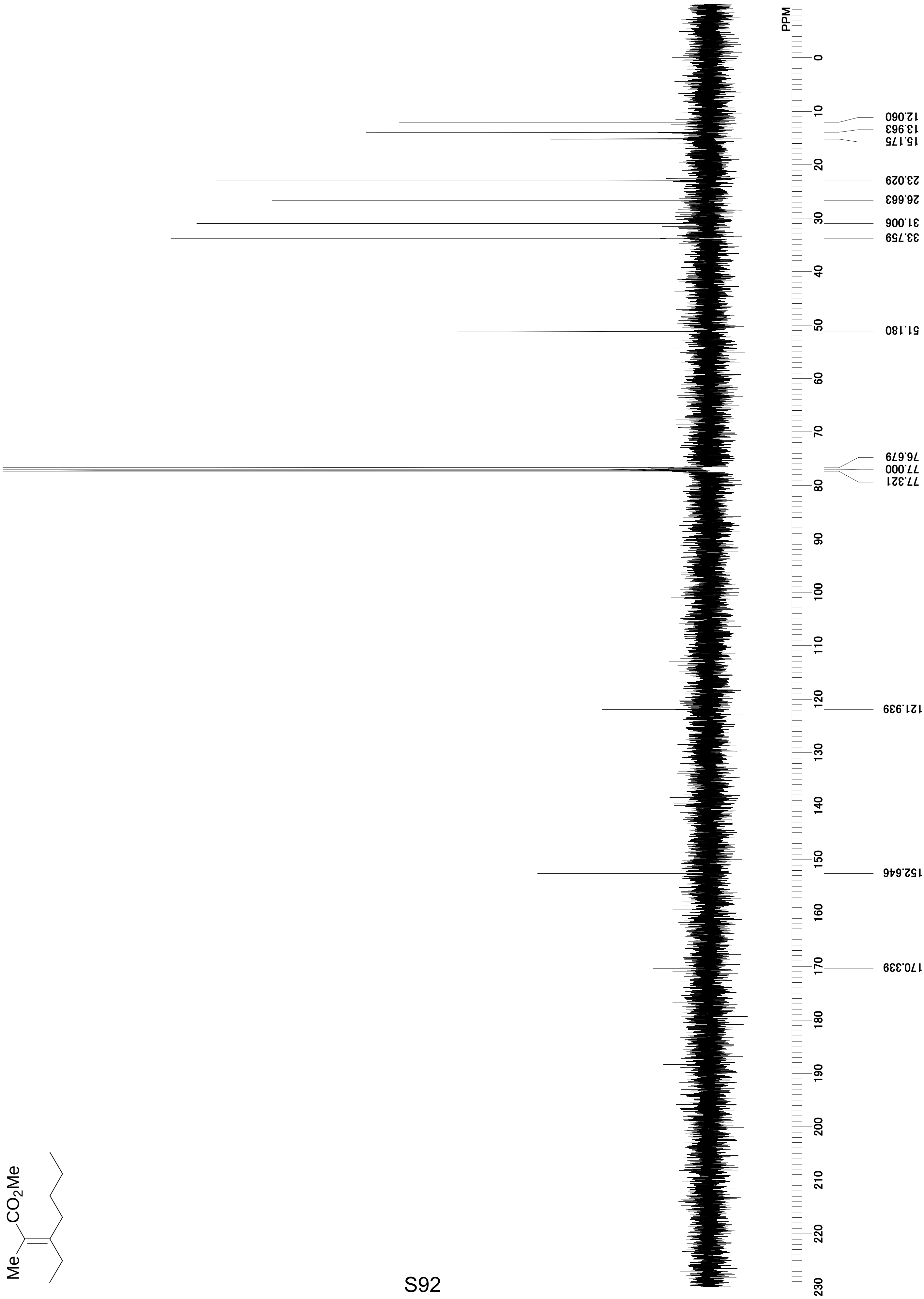
3.713
2.323
2.305
2.284
2.167
2.147
2.129
2.109
1.855
1.553
1.522
1.448
1.444
1.429
1.422
1.410
1.403
1.396
1.389
1.383
1.371
1.355
1.338
1.320
1.300
1.282
1.254
1.029
1.010
0.991
0.924
0.906
0.887
0.000
PPM
9
8
7
6
5
4
3
2
1
0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23.029
26.663
31.006
33.759
51.180
76.679
77.000
77.321
121.939
152.646
170.339
CO2Me
Me