1,6-Stannatropic Strategy : Effective Generation and Cyclization of 1,5-Dipoles from *o*-Stannylmethylated Thioanilides or Phenyl Isothiocyanates

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Contents

General Methods.: Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and

chloroform as an eluent. Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel glass plates (silica gel 60 F254, 0.25 mm thickness) (MERCK Co.). Visualization was accomplished with UV light and ethanolic phosphomolybdic acid followed by heating. All reactions were carried out under an atmosphere of nitrogen. Organic solvents were dried and distilled prior to use.

Experimental Procedure and Spectral Data

2-Benzylbenzenamine, 2-benzyl-4-chlorobenzenamine, 2-benzyl-4-methoxy-benzenamine, and 2-(4-chlorophenylmethyl)benzenamine were produced by reduction of the corresponding ketones.[1]

General procedure of preparation of *o*-tributylstannylmethylated aniline derivatives

n-Butyllithium (1.6 M hexane solution, 7.5 mL, 12 mmol) was slowly added to a THF solution (50 mL) of a 2-benzylbenzenamine derivative (10 mmol) over 5 min at -78 ºC, and was stirred for 1 h at -78 ºC. To the solution was added trimethylsilyl chloride (1.5 mL, 12 mmol) over 5 min. After the solution was stirred for 1 h at -78 ºC, *sec*-butyllithium (1.3 M cyclohexane solution, 11.5 mL, 15 mmol) was added over 10 min. Then, the reaction mixture was stirred for 1 h at -78 ºC, and tributylstannyl chloride (7.3 mL, 27 mmol) was added. The reaction mixture was warmed to room temperature, and was stirred for 1 h. After the solvents were removed from the mixture in vacuo, diethyl ether (50 mL) was added to the residue. The solution was washed with water (50 mL), and was dried over anhydrous potassium carbonate. The organic layer was concentrated and purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to give the corresponding *o*-tributylstannylmethylated

aniline derivative.

2-(α-Tributylstannylbenzyl)benzenamine: 89% yield; yellow oil; IR (neat) ν_{max} 3435, 2956, 2924, 1618, 1491, 1452, 1271 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.95 (m, 15H), 1.15-1.46 (m, 12H), 3.46 (brs, 2H), 4.00 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 35 Hz), 6.67-6.81 (m, 2H), 7.00-7.47 (m, 7H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.2, 13.7, 27.4, 29.0, 38.2, 116.3, 118.9, 124.0, 126.4, 128.4, 128.5, 131.2, 144.0, 144.5; EI-MS *m/z* 473 (M^+, 3), 416 (M^+ - Bu, 100), 182 (M^+ - Bu_3Sn, 83); Anal. Calcd for $C_{25}H_{39}NSn$: C, 63.58; H, 8.32; N, 2.97. Found: C, 63.46; H, 8.40; N, 2.96.

4-Chloro-2-(α-tributylstannylbenzyl)benzenamine: 80% yield; yellow oil; IR (neat) ν_{max} 3439, 2956, 2924, 1620, 1491, 1279, 1074, 806, 752, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.95 (m, 15H), 1.16-1.49 (m, 12H), 3.44 (brs, 2H), 3.95 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 35 Hz), 6.60 (d, 1H, *J* = 8.4 Hz), 6.96-7.08 (m, 5H), 7.19-7.25 (m, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.4, 13.7, 27.4, 29.0, 38.3, 117.3, 123.4, 124.3, 126.0, 126.6, 128.6, 130.3, 130.6, 142.87, 142.93; EI-MS *m/z* 507 (M^+, 2), 450 (M^+- Bu, 100), 291 (Bu_3Sn^+, 50), 216 (M^+ - Bu_3Sn, 80); Anal. Calcd for $C_{25}H_{38}ClNSn$: C, 59.25; H, 7.56; N, 2.76. Found: C, 59.14 H, 7.67; N, 2.83.

4-Methoxy-2-(α-tributylstannylbenzyl)benzenamine: 73% yield; yellow oil; IR (neat) ν_{max} 3419, 2924, 1601, 1498, 1460, 1246, 1043, 806, 758, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.70-0.95 (m, 15H), 1.15-1.44 (m, 12H), 3.77 (brs, 2H), 3.75 (s, 3H), 4.01 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 35 Hz), 6.62-6.71 (m, 3H), 6.99-7.05 (m, 3H), 7.17-7.24 (m, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.4, 13.7, 27.4, 29.0, 38.8, 55.7, 111.4, 116.7, 117.5, 124.0,

126.5, 128.5, 130.7, 137.9, 143.7, 153.0; CI-MS *m/z* 504 (MH^+, 22), 446 (M^+ - Bu, 94), 291 (Bu_3Sn^+, 42), 212 (M^+ - Bu_3Sn, 20), 87 (100); Anal. Calcd for $C_{26}H_{41}NOSn$: C, 62.17; H, 8.23; N, 2.79. Found: C, 61.89; H, 8.21; N, 2.87.

2-[(4-Chlorophenyl)-tributylstannylmethyl]benzenamine: yellow oil; 78% yield; IR (neat) ν_{max} 3439, 2924, 1618, 1487, 1456, 1375, 1281, 1171, 1092, 1011, 960, 829, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.95 (m, 15H), 1.16-1.42 (m, 12H), 3.43 (brs, 2H), 3.94 (t, 1H, $^2J_{H\text{-}Sn}$ = 35 Hz), 6.68-6.81 (m, 2H), 6.92-7.18 (m, 6H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.2, 13.7, 27.4, 29.0, 37.5, 116.5, 119.0, 126.7, 127.6, 128.0, 128.5, 129.4, 131.3, 142.8, 144.4; EI-MS *m/z* 507 (M^+, 2), 450 (M^+ - Bu, 100), 291 (Bu_3Sn^+, 49), 216 (M^+ - Bu_3Sn, 86); Anal. Calcd for $C_{25}H_{38}ClNSn$: C, 59.25; H, 7.56; N, 2.76. Found: C, 59.10; H, 7.38; N, 2.76.

Preparation of a *o*-tributylstannylmethylated aniline derivative

n-Butyllithium (1.6 M hexane solution, 7.5 mL, 12 mmol) was slowly added to a THF solution (50 ml) of *o*-toluidine (1.1 mL, 10 mmol) over 5 min at -78 ºC, and was stirred for 1 h at -78 ºC. To the solution was added trimethylsilyl chloride (1.5 mL, 12 mmol) over 5 min, and the mixture was stirred for 1 h at room temperature. THF was removed from the solution under reduced pressure, and to the residue was added hexane (50 mL). *n*-Butyllithium (1.6 M hexane solution, 7.5 mL, 12 mmol) was added to the mixture over 5 min at 0 ºC and was stirred for 1 h. *sec*-Butyllithium (1.3 M cyclohexane solution, 11.5 mL, 12 mmol) was added to the solution over 10 min at 0 ºC and was refluxed for 6 h. To the solution was added tributylstannyl chloride (7.3 mL, 27 mmol) at room temperature and the mixture was stirred for 1 h. After the solvent

was removed from the mixture in vacuo, diethyl ether (50 ml) was added to the residue. The solution was washed with water (50 ml) and dried over potassium carbonate. The organic layer was concentrated and purified by silica gel column chromatography (eluent: hexane / ethyl acetate) and gel permeation column chromatography (JAIGEL-2H, Japan Analytical Industry, eluent: chloroform) to give 2-(tributylstannylmethyl)benzenamine (1.35 g, 34%).

2-Tributylstannylmethylbenzenamine: orange colored oil; IR (neat) ν_{max} 2924, 1620, 1495, 1456, 1076, 864, 743 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.69-0.95 (m, 15H), 1.18-1.48 (m, 12H), 2.11 (t, 2H, $^{2}J_{H\text{-}Sn}$ = 27 Hz), 3.41 (brs, 2H), 6.60-6.68 (m, 2H), 6.82-6.92 (m, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.1, 13.8, 13.9, 27.4, 29.1, 115.0, 118.9, 124.2, 128.0, 128.2, 142.0; Anal. Calcd for $C_{19}H_{35}NSn$: C, 57.60; H, 8.90; N, 3.54. Found: C, 57.42 H, 8.83; N, 3.64.

General procedure of preparation of *o*-tributylstannylmethylated thioanilide derivatives

An acid chloride (2 mmol) was added to a THF solution (5 mL) of an *o*-tributylstannylmethylated aniline derivative and triethylamine (0.279 ml, 2 mmol) at 0 ºC, and was stirred for 3 h at room temperature. The solvent was removed from the solution and diethyl ether (30 mL) was added to the residue. The mixture was washed with a saturated ammonium chloride aqueous solution (10 mL) and dried over potassium carbonate. The organic layer was concentrated and was purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to give the corresponding *o*-tributylstannylmethylated anilide derivative.

A benzene solution (15 mL) of an *o*-tributylstannylmethylated anilide

derivative (2 mmol) with Lawesson's reagent (0.61 g, 1.5 mmol) was heated at 60 ºC for 3 h. The solution was cooled to room temperature and the white precipitate was removed by filtration. After the filtrate was concentrated the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to give the corresponding *o*-tributylstannylmethylated thioanilide derivative.

N-[2-(α-Tributylstannylbenzyl)phenyl]benzamide: 96% yield; colorless solid; mp 52-53 ºC; IR (KBr) ν_{max} 2954, 2925, 1666 (C=O), 1521, 1450, 1303, 752 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.77-0.86 (m, 15H), 1.11-1.41 (m, 12H), 4.08 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 34 Hz), 7.04-7.49 (m, 13H), 7.73 (brs, 1H), 8.19 (d, 1H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.6, 27.3, 28.8, 38.3, 123.0, 124.4, 124.9, 126.7, 128.4, 128.5, 129.0, 131.5, 131.7, 133.3, 134.7, 136.5, 143.4, 164.8; EI-MS *m/z* 577 (M^+, 34), 520 (M^+ - Bu, 83), 105 ($PhCO^+$, 100); Anal. Calcd for $C_{32}H_{43}NOSn$: C, 66.68; H, 7.52; N, 2.43. Found: C, 66.42; H, 7.42; N, 2.42.

N-[2-(α-Tributylstannylbenzyl)phenyl]thiobenzamide (**1a**): 95% yield; yellow solid; mp 76-77 ºC; IR (KBr) ν_{max} 3255, 2927, 1506, 1486, 1448, 1358 (C=S), 1213, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.78-0.97 (m, 15H), 1.13-1.41 (m, 12H), 4.12 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 33 Hz), 6.98-7.45 (m, 11H), 7.64 (d, 2H, *J* = 7.3 Hz), 7.89 (d, 1H, *J* = 6.8 Hz), 8.71 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.8, 13.7, 27.4, 29.0, 37.5, 124.4, 126.1, 126.5, 126.6, 126.9, 127.3, 128.3, 128.7, 131.1, 132.1, 137.7, 138.6, 141.8, 143.9, 197.9; CI-MS *m/z* 594 (MH^+, 40), 302 (M^+ - Bu_3Sn, 92), 270 (M^+ - Bu_3Sn - S, 100); Anal. Calcd for $C_{32}H_{43}NSSn$: C, 64.87; H, 7.32; N, 2.36. Found: C, 64.76; H, 7.25; N, 2.31.

N-[2-(α-Tributylstannylbenzyl)phenyl]-4-methoxybenzamide: 88% yield; colorless solid; mp 45-47 °C; IR (KBr) ν_{max} 3352, 2956, 1643 (C=S), 1502, 1253 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.95 (m, 15H), 1.11-1.39 (m, 12H), 3.83 (s, 3H), 4.08 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 35 Hz,), 6.81 (d, 2H, *J* = 8.9 Hz), 7.04-7.35 (m, 10H), 7.64 (brs, 1H), 8.16 (d, 1H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.6, 27.4, 29.0, 38.3, 55.4, 113.4, 122.9, 124.2, 124.9, 126.7, 126.8, 127.0, 128.7, 129.0, 131.7, 133.1, 136.7, 143.5, 162.1, 164.3; EI-MS *m/z* 607 (M^+, 37), 550 (M^+ - Bu, 88), 135 (4-$CH_3OC_6H_4CO^+$, 100); Anal. Calcd for $C_{33}H_{45}NO_2Sn$: C, 65.36; H, 7.48; N, 2.31. Found: C, 65.28; H, 7.36; N, 2.28.

N-[2-(α-Tributylstannylbenzyl)phenyl]-4-methoxythiobenzamide (**1b**): 98% yield; yellow solid; mp 85-88 °C; IR (KBr) ν_{max} 3216, 2927, 1606, 1498, 1352 (C=S), 1245, 1182 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.73-0.97 (m, 15H), 1.13-1.41 (m, 12H), 3.83 (s, 3H), 4.11 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 33 Hz), 6.79-6.82 (m, 2H), 6.97-7.09 (m, 3H), 7.18-7.37 (m, 5H), 7.60-7.62 (m, 2H), 7.85 (brs, 1H), 8.63 (brs 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.8, 13.7, 27.3, 29.0, 37.5, 55.5, 113.4, 124.4, 126.1, 126.5, 126.97, 127.04, 128.5, 128.7, 132.0, 134.0, 137.9, 138.4, 143.9, 162.1, 196.6; EI-MS *m/z* 624 (MH^+, 35), 566 (M^+ - Bu, 14), 332 (M^+ - Bu_3Sn, 68), 300 (M^+ - Bu_3Sn - S, 100); Anal. Calcd for $C_{33}H_{45}NOSSn$: C, 63.67; H, 7.29; N, 2.25. Found: C, 63.58; H, 7.11; N, 2.27.

N-[2-(α-Tributylstannylbenzyl)phenyl]-4-trifluoromethylbenzamide: 96% yield; pale yellow solid; mp 65-67 °C; IR (KBr) ν_{max} 3315, 2925, 1649 (C=O), 1531, 1502, 1332, 1128, 1068 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.95 (m, 15H), 1.02-1.45 (m, 12H), 4.07 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 34 Hz,), 7.00-7.76 (m, 12H), 7.88 (brs, 1H), 8.20 (d, 1H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.6, 27.3, 28.9, 38.3, 122.7, 123.5 (q, *J* = 272 Hz), 124.8, 125.1, 125.3, 125.4, 125.5, 126.7, 127.2, 131.8, 132.3 (q, *J* = 32 Hz),

133.2, 136.2, 138.0, 143.2, 163.3; EI-MS *m/z* 645 (M^+, 78), 588 (M^+ - Bu, 100), 291 (Bu_3Sn^+, 72), 173 (4-$CF_3C_6H_4CO^+$, 69); Anal. Calcd for $C_{33}H_{42}F_3NOSn$: C, 61.51; H, 6.57; N, 2.17. Found: C, 61.50; H, 6.63; N, 2.18.

N-[2-(α-Tributylstannylbenzyl)phenyl]-4-trifluoromethylthiobenzamide (**1c**): 90% yield; yellow solid; mp 86-88 °C; IR (KBr) ν_{max} 3218, 2929, 1491, 1325 (C=S), 1164, 1128, 1068 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.73-0.97 (m, 15H), 1.13-1.43 (m,12H), 4.08 (t, 1H, $^2J_{H\text{-}Sn}$ = 33 Hz), 6.95-7.37 (m, 8H), 7.56-7.67 (m, 4H), 7.95 (d, 1H, *J* = 6.5 Hz), 8.74 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.5, 27.2, 28.9, 37.5, 123.5 (q, *J* = 272 Hz), 124.4, 125.1, 126.1, 126.3, 126.4, 126.8, 127.4, 128.7, 132.1, 132.3 (q, *J* = 33 Hz), 137.3, 138.2, 143.6, 144.6, 195.8; EI-MS *m/z* 661 (M^+, 1), 604 (M^+ - Bu, 7), 370 (M^+ - Bu_3Sn, 100), 338 (M^+ - Bu_3Sn - S, 88); Anal. Calcd for $C_{33}H_{42}F_3NSSn$: C, 60.01; H, 6.41; N, 2.12. Found: C, 59.96; H, 6.40; N, 2.21.

N-[2-(α-Tributylstannylbenzyl)phenyl]cinnamamide: 76% yield; colorless solid; mp 56-57 °C; IR (KBr) ν_{max} 3232, 2954, 1657 (C=O), 1622, 1535, 1448, 1344, 1191, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.78-1.00 (m, 15H), 1.15-1.42 (m, 12H), 4.10 (t, 1H, $^2J_{H\text{-}Sn}$ = 34 Hz), 6.22 (d, 1H, *J* = 16 Hz), 7.06-7.50 (m, 15H), 8.06 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.8, 13.6, 27.3, 28.9, 37.8, 121.2, 123.5, 124.6, 126.4, 126.6, 126.7, 127.6, 128.6, 128.8, 129.6, 131.4, 134.5, 136.0, 141.2, 143.6, 163.5; CI-MS *m/z* 604 (MH^+, 100), 546 (M^+ - Bu, 46); Anal. Calcd for $C_{34}H_{45}NOSn$: C, 67.79; H, 7.53; N, 2.33. Found: C, 67.70; H, 7.52; N, 2.25.

N-[2-(α-Tributylstannylbenzyl)phenyl]thiocinnamamide (**1d**): 78% yield; yellow solid; mp 104-105 °C; IR (KBr) ν_{max} 2937, 1637, 1392 (C=S), 1176, 756 m^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz, 45 °C) δ 0.76-0.93 (m, 15H), 1.05-1.32 (m, 12H), 4.06 (t, 0.53H,

$^{2}J_{H\text{-}Sn}$ = 33 Hz), 4.14 (t, 0.47H, $^{2}J_{H\text{-}Sn}$ = 31 Hz), 6.73 (d, 0.47H, *J* = 15 Hz), 6.87 (d, 0.53H, *J* = 16 Hz), 7.00-7.68 (m, 14.53H), 8.09 (d, 0.47H, *J* = 15 Hz), 8.68 (brs, 0.53H), 9.30 (brs, 0.47H); ^{13}C-NMR ($CDCl_3$, 68 MHz, 45 °C) δ 10.2, 10.3, 13.8, 13.9, 27.36, 27.43, 28.7, 28.9, 36.2, 36.6, 122.0, 124.1, 124.2, 126.0, 126.2, 127.1, 127.8, 127.9, 128.1, 128.2, 128.4, 128.5, 128.7, 129.9, 130.1, 131.5, 131.9, 134.0, 134.2, 135.1, 136.9, 138.5, 139.0, 141.6, 142.4, 143.8, 147.3, 193.4, 195.9; CI-MS *m/z* 619 (M^+, 58), 327 (M^+ - H - Bu_3Sn, 81), 131 (100); Anal. Calcd for $C_{34}H_{45}NSSn$: C, 66.02; H, 7.33; N, 2.26. Found: C, 65.85; H, 7.21; N, 2.25.

N-{2-[4-Chlorophenyl(tributylstannyl)methyl]phenyl}benzamide: yield 70%; colorless solid; mp 72-74 °C; IR (KBr) ν_{max} 3236, 2923, 1643 (C=O), 1483, 1315, 754, 713 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.73-0.99 (m, 15H), 1.12-1.42 (m, 12H), 4.03 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 34 Hz), 6.96-6.99 (m, 2H), 7.14-7.52 (m, 10H), 7.65 (brs, 1H), 8.11 (d, 1H, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.6, 27.3, 28.9, 37.3, 123.5, 124.7, 126.7, 126.8, 127.8, 128.5, 128.9, 130.2, 131.6, 131.7, 133.2, 134.6, 136.2, 142.3, 164.9; CI-MS *m/z* 612 (MH^+, 66), 554 (M^+ - Bu, 24), 322 (100), 291 (Bu_3Sn^+, 32), 105 ($PhCO^+$, 14); Anal. Calcd for $C_{32}H_{42}ClNOSn$: C, 62.92; H, 6.93; N, 2.29. Found: C, 62.79; H, 6.79; N, 2.32.

N-{2-[4-Chlorophenyl(tributylstannyl)methyl]phenyl}thiobenzamide (**1e**): 88% yield; yellow solid; IR (KBr) ν_{max} 2926, 1487, 1348 (C=S), 774 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.74-0.98 (m, 15H), 1.14-1.42 (m, 12H), 4.09 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 32 Hz), 6.92 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 8.4 Hz), 7.34-7.51 (m, 6H), 7.67-7.74 (m, 3H), 8.62 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.9, 13.7, 27.4, 29.0, 36.8, 126.4, 126.5, 127.3, 127.4, 127.6, 128.4, 128.6, 129.7, 131.3, 132.0, 137.6, 138.7, 141.7, 142.9,

198.5; CI-MS *m/z* 628 (MH^+, 18), 338 (100), 304 (M^+ - Bu_3Sn - S, 87); Anal. Calcd for $C_{32}H_{42}ClNSSn$: C, 61.31; H, 6.75; N, 2.23. Found: C, 61.17; H, 6.59; N, 2.44.

N-[2-(α-Tributylstannylbenzyl)phenyl]formamide: 53% yield: yellow oil; IR (neat) ν_{max} 3251, 2956, 1689 (C=O), 1596, 1492, 1294, 752 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.74-0.98 (m, 15H), 1.15-1.46 (m, 12H), 4.03 (t, 0.35H, $^2J_{H-Sn}$ = 34 Hz), 4.07 (t, 0.65H, $^2J_{H-Sn}$ = 33 Hz), 6.89 (brs, 0.35H), 6.89-7.32 (m, 9.3H), 7.98-8.01 (m, 0.35H), 8.262 and 8.268 (s x 2, 0.35H), 8.40 (s, 0.33H), 8.44 (s, 0.33H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.9, 11.0, 13.7, 27.1, 28.9, 37.0, 37.4, 122.2, 123.8, 124.6, 125.0, 126.1, 126.3, 126.4, 128.4, 128.5, 128.7, 128.8, 131.7, 132.0, 133.5, 134.6, 134.8, 135.8, 143.0, 143.4, 158.7, 162.6; CI-MS *m/z* 501 (M^+, 100), 444 (M^+ - Bu, 86), 291 (Bu_3Sn^+, 61); Anal. Calcd for $C_{26}H_{39}NOSn$: C, 62.42; H, 7.86; N, 2.80. Found: C, 62.55; H, 7.58; N, 2.86.

N-[2-(α-Tributylstannylbenzyl)phenyl]thioformamide (**1f**): 91% yield; pale yellow solid; mp 50-51 °C; IR (KBr) ν_{max} 2923, 1647, 1551, 1357 (C=S), 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.71-0.93 (m, 15H), 1.04-1.36 (m,12H), 4.02 (t, 1H, $^2J_{H-Sn}$ = 33 Hz), 6.93-7.01 (m, 3H), 7.11-7.23 (m, 6H), 9.10 + 9.15 (2brs, 1H), 9.44 + 9.49 (2s, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.9, 13.6, 27.2, 28.8, 36.9, 120.7, 124.8, 126.4, 126.5, 126.6, 128.8, 131.7, 134.3, 137.3, 142.5, 188.8; CI-MS *m/z* 518 (MH^+, 66), 460 (M^+ - Bu, 96), 226 (M^+ - Bu_3Sn, 32), 194 (M^+ - Bu_3Sn - S, 100); Anal. Calcd for $C_{26}H_{39}NSSn$: C, 60.48; H, 7.61; N, 2.71. Found: C, 60.45; H, 7.42; N, 2.73.

N-[2-(α-Tributylstannylbenzyl)phenyl]acetamide: 74% yield; colorless solid; mp 65-66 °C; IR (KBr) ν_{max} 3274, 2927, 1653 (C=O), 1535, 1452, 1305, 744, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.77-1.06 (m, 15H), 1.16-1.43 (m,12H), 1.92 (s, 3H), 4.03 (t,

1H, $^{2}J_{H\text{-}Sn}$ = 34 Hz,), 7.01-7.23 (m, 9H), 7.84 (brd, 1H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.6, 13.6, 24.2, 27.3, 28.9, 37.7, 123.9, 124.4, 124.5, 126.2, 126.4, 128.6, 131.0, 133.9, 135.9, 143.7, 167.8; CI-MS *m/z* 515 (M^+, 25), 458 (M^+ - Bu, 56), 179 (M^+ - Bu_3Sn - CH_3CO, 100); Anal. Calcd for $C_{27}H_{41}NOSn$: C, 63.05; H, 8.03; N, 2.72. Found: C, 63.05; H, 7.93; N, 2.72.

N-[2-(α-Tributylstannylbenzyl)phenyl]thioacetamide (**1g**): 86% yield; pale yellow solid; mp 45-47 °C; IR (KBr) ν_{max} 3142, 2939, 1595, 1527, 1491, 1448, 1377 (C=S), 1165, 754, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.75-0.96 (m, 15H), 1.05-1.46 (m,12H), 2.18 (s, 1.59H), 2.59 (s, 1.41H), 4.03 (t, 0.47H, $^{2}J_{H\text{-}Sn}$ = 32 Hz), 4.05 (t, 0.53H, $^{2}J_{H\text{-}Sn}$ = 31 Hz), 7.00-7.44 (m, 8.47H), 7.59 (d, 0.53H, *J* = 7.3 Hz), 8.22 (brs, 0.47H), 8.96 (brs, 0.53H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.7, 13.66, 13.71, 27.33, 27.37, 28.89, 28.96, 29.8, 35.0, 36.9, 37.4, 124.3, 124.5, 126.1, 126.2, 126.3, 126.5, 127.5, 127.6, 127.8, 128.47, 128.55, 128.61, 131.8, 132.0, 136.3, 137.4, 138.9, 140.4, 142.9, 144.1, 200.7, 205.1; CI-MS *m/z* 532 (MH^+, 16), 474 (M^+- Bu, 30), 240 (M^+- Bu_3Sn, 66), 208 (M^+- Bu_3Sn - S, 100); Anal. Calcd for $C_{27}H_{41}NSSn$: C, 61.14; H, 7.79; N, 2.64. Found: C, 60.91; H, 7.61; N, 2.62.

N-[2-(α-Tributylstannylmethyl)phenyl]benzamide: 5% yield; colorless solid; mp 43-44 °C; IR (KBr) ν_{max} 2919, 2360, 1647 (C=O), 1521, 1270 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.68-0.90 (m, 15H), 1.02-1.47 (m, 12H), 2.26 (t, 2H, $^{2}J_{H\text{-}Sn}$ = 26 Hz), 7.00-7.09 (m, 3H), 7.44-7.57 (m, 4H), 7.86-7.89 (m, 3H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 9.9, 13.7, 14.2, 27.3, 29.0, 123.3, 124.0, 125.2, 126.8, 128.2, 128.6, 131.6, 133.1, 134.9, 135.1, 165.1; CI-MS *m/z* 502 (MH^+, 100), 444 (M^+- Bu, 48), 105 ($PhCO^+$, 3); Anal. Calcd for $C_{26}H_{39}NOSn$: C, 62.42; H, 7.86; N, 2.80. Found: C, 62.70; H, 7.69; N, 2.83.

N-[2-(α-Tributylstannylmethyl)phenyl]thiobenzamide (**1h**): 77% yield; yellow oil; IR (neat) ν_{max} 2923, 1601, 1448, 1351 (C=S) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.67-0.93 (m, 15H), 1.13-1.45 (m, 12H), 2.27 (t, 2H, $^2J_{H\text{-}Sn}$ = 26 Hz), 7.06-7.21 (m, 3H), 7.40-7.53 (m, 3H), 7.64 (d, 1H, *J* = 7.6 Hz), 7.88 (d, 2H, *J* = 7.3 Hz), 8.66 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 10.0, 13.7, 14.3, 27.3, 29.0, 123.7, 126.4, 126.5, 127.7, 128.5, 128.8, 131.1, 134.8, 139.3, 142.3, 198.4; CI-MS *m/z* 518 (MH^+, 75), 460 (M^+ - Bu, 52), 226 (M^+ - Bu_3Sn, 100), 194 (M^+ - Bu_3Sn-S, 37); Anal. Calcd for $C_{26}H_{39}NSSn$: C, 60.48; H, 7.61; N, 2.71. Found: C, 60.64; H, 7.41; N, 2.66.

General procedure of thermal reaction of thioanilide **1**

A benzene solution (1.5 mL) of thioanilide **1** (0.15 mmol) in a sealed tube was heated at reaction temperature. After the reaction, the solution was concentrated, and the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to give the corresponding indole derivative **2**.

Indoles **2a**,**c**,**e**-**h** was confirmed by comparison of the spectral data with those reported in the reference.[2]

2-(4'-Methoxyphenyl)-3-phenylindole (**2b**): 84% yield; yellow solid; IR (KBr) ν_{max} 3406, 1603, 1510, 1489, 1456, 1250, 1176, 1030, 833, 746, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 3.79 (s, 3H), 6.81-6.86 (m, 2H), 7.10-7.45 (m, 10H), 7.66 (d, 1H, *J* = 7.8 Hz), 8.11 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 55.3, 110.7, 114.0, 119.3, 120.2, 122.3, 125.0, 126.0, 128.4, 128.6, 129.3, 130.0, 134.0, 135.1, 135.6, 159.0; EI-MS *m/z* 299 (M^+, 100), 284 (M^+ - Me, 19).

3-(4'-Chlorophenyl)-2-phenylindole (**2d**): 82% yield; colorless needle; mp 152-154 °C; IR (KBr) ν_{max} 3398, 1500, 1450, 1325, 1248, 1093, 1014, 968, 841, 746 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.13-7.44 (m, 12H), 7.63 (d, 1H, *J* = 7.8 Hz), 8.23 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 110.9, 113.7, 119.3, 120.5, 122.8, 127.8, 128.1, 128.3, 128.6, 128.7, 131.2, 131.9, 132.2, 133.5, 134.2, 135.7; EI-MS *m/z* 303 (M^+, 100), 267 (M^+ - HCl, 38); Anal. Calcd for $C_{20}H_{14}ClN$: C, 79.07; H, 4.65; N, 4.61. Found: C, 78.90; H, 4.61; N, 4.60.

General procedure of preparation of *o*-tributylstannylmethylated aryl isothiocyanate derivatives[3]

A chloroform (6 mL) solution of an *o*-tributylstannylmethylated aniline derivative (5 mmol) was added to a suspension of thiophosgen (7.5 mmol) and calcium carbonate (0.75 g, 7.5 mmol) in chloroform (6 mL) and water (2 mL) at 0 °C and stirred for 30 min. After the reaction, to the mixture was added a saturated sodium chloride aqueous solution. The organic layer was separated from the mixture, and the aqueous layer was extracted with chloroform (5 mL). The combined organic layers were combined, and dried over anhydrous magnesium sulfate. The solution was concentrated, and the residue was purified by silica gel column chromatography (eluent: hexane / ethyl acetate) to give the corresponding *o*-tributylstannylmethylated phenyl isocyanate derivative **3**.

2-[α-(Tributylstannyl)benzyl]phenyl isothiocyanate (**3a**): 80% yield; pale yellow oil; IR (neat) ν_{max} 2925, 2089 (N=C=S), 1591, 1448, 752 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.75-0.96 (m, 15H), 1.04-1.45 (m, 12H), 4.33 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 32 Hz,), 7.00-7.30 (m,

9H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.0, 13.7, 27.3, 28.9, 38.0, 124.6, 125.3, 127.1, 127.3, 127.9, 128.3, 128.6, 129.1, 136.7, 140.7, 142.8; CI-MS *m/z* 516 (MH^+, 78), 458 (M^+ - Bu, 100), 291 (Bu_3Sn^+, 27), 224 (M^+ - Bu_3Sn, 10); Anal. Calcd for $C_{26}H_{37}NSSn$: C, 60.71; H, 7.25; N, 2.72. Found: C, 60.57; H, 7.26; N, 2.80.

4-Chloro-2-[α-(tributylstannyl)benzyl]phenyl isothiocyanate (**3b**): 77% yield; pale yellow oil; IR (neat) ν_{max} 2924, 2079 (N=C=S), 1470, 939 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.75-1.00 (m, 15H), 1.15-1.43 (m, 12H), 4.26 (t, 1H, $^2J_{H\text{-}Sn}$ = 32 Hz,), 6.99-7.05 (m, 1H), 7.10-7.18 (m, 4H), 7.24-7.31 (m, 3H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.2, 13.7, 27.4, 28.9, 38.3, 125.1, 125.3, 126.9, 128.27, 128.37, 128.39, 128.6, 132.8, 141.9, 142.8; EI-MS *m/z* 549 (M^+, 1), 492 (M^+ - Bu, 100), 291 (Bu_3Sn^+, 22), 258 (M^+ - Bu_3Sn, 23); Anal. Calcd for $C_{26}H_{36}ClNSSn$: C, 56.90; H, 6.61; N, 2.55. Found: C, 56.80 H, 6.76; N, 2.59.

4-Methoxy-2-[α-(tributylstannyl)benzyl]phenyl isothiocyanate (**3c**): 71% yield; pale yellow oil; IR (neat) ν_{max} 2926, 2096 (N=C=S), 1598, 1488 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.80-1.00 (m, 15H), 1.15-1.42 (m, 12H), 3.75 (s, 3H), 4.26 (t, 1H, $^2J_{H\text{-}Sn}$ = 32 Hz,), 6.59 (dd, 1H, *J* = 3.0, 8.6 Hz), 6.82 (d, 1H, *J* = 3.0 Hz), 7.07-7.29 (m, 6H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.0, 13.7, 27.4, 28.9, 38.2, 55.4, 110.6, 114.3, 121.1, 124.8, 128.1, 128.26, 128.32, 128.4, 142.4, 142.5, 158.3; CI-MS *m/z* 546 (MH^+, 100), 488 (M^+ - Bu, 70), 291 (Bu_3Sn^+, 38), 256 (M^+ - Bu_3Sn, 35); Anal. Calcd for $C_{27}H_{39}NOSSn$: C, 59.57; H, 7.22; N, 2.57. Found: C, 59.39; H, 7.01; N, 2.57.

2-[4-Chlorophenyl(tributylstannyl)methyl]phenyl isothiocyanate (**3d**): 83% yield; pale

yellow oil; IR (neat) ν_{max} 2085 (N=C=S) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.75-1.02 (m, 15H), 1.15-1.41 (m, 12H), 4.26 (t, 1H, $^{2}J_{H\text{-}Sn}$ = 32 Hz,), 7.04-7.26 (m, 8H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.0, 13.7, 27.4, 28.9, 37.3, 125.7, 127.2, 127.5, 128.4, 128.8, 128.9, 129.2, 130.1, 140.1, 141.6; CI-MS *m/z* 550 (MH^+, 65), 492 (M^+ - Bu, 63), 291 (Bu_3Sn^+, 100); Anal. Calcd for $C_{26}H_{36}ClNSSn$: C, 56.90; H, 6.61; N, 2.55. Found: C, 57.17 H, 6.47; N, 2.59.

General procedure of thermal reaction of *o*-tributylstannylmethylated aryl isothiocyanate derivative **3**

A benzene solution (3 mL) of *o*-tributylstannylmethylated aryl isothiocyanate derivative **3** (0.3 mmol) in a sealed tube was heated at reaction temperature. After the reaction, the solution was concentrated, and the residue was purified by silica gel column chromatography (the silica gel dryied at 150 °C under reduced pressure, eluent: hexane / ethyl acetate) under nitrogen atmosphere to give the corresponding 2-indolyl sulufide **4**. When a undried silica gel was employed in the purification of the mixture under air, disulfide **5** was obtained.

2-Tributylstannylthio-3-phenylindole (**4a**): 91% yield; yellow solid; mp 30-32 °C; IR (KBr) ν_{max} 3404, 2937, 1521, 1439, 1406, 1346, 1244, 873, 770, 743 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.74-0.97 (m, 15H), 1.07-1.21 (m, 6H), 1.26-1.46 (m, 6H), 7.05-7.18 (m, 2H), 7.25-7.31 (m, 2H), 7.41-7.46 (m, 2H), 7.63-7.66 (m, 1H), 7.72-7.75 (m, 2H), 7.99 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 13.6, 14.9, 27.0, 28.4, 109.8, 118.6, 119.9, 120.5, 121.9, 125.4, 125.9, 127.8, 128.0, 129.8, 135.0, 135.6; CI-MS *m/z* 516 (MH^+, 100), 291 (Bu_3Sn^+, 52); Anal. Calcd for $C_{26}H_{37}NSSn$: C, 60.71; H, 7.25; N, 2.72.

Found: C, 60.87; H, 6.97; N, 2.82.

Bis(3-phenyl-2-indolyl) disulfide (**5a**): 88% yield; yellow soild; mp 196-198 °C (lit.[4] 196-197.5 °C); IR (KBr) ν_{max} 3388, 1521, 1479, 1439, 1402, 1352, 1329, 1244, 1151, 1012, 970, 829, 773, 744, 698, 671 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.09-7.30 (m, 16H), 7.59 (d, 2H, *J* = 8.1 Hz), 8.08 (brs, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 111.0, 120.2, 120.6, 124.3, 124.5, 125.0, 126.8, 127.0, 128.1, 129.8, 133.1, 137.0; EI-MS *m/z* 448 (M^+, 5), 416 (M^+ - S, 15), 224 (M^+/2, 96), 223 (M^+/2 - H, 100); Anal. Calcd for $C_{28}H_{20}N_2S_2$: C, 74.97; H, 4.49; N, 6.24. Found: C, 74.72; H, 4.59; N, 6.10.

Bis(5-chloro-3-phenyl-2-indolyl) disulfide (**5b**): 96% yield; yellow solid; mp 193-195 °C; IR (KBr) ν_{max} 3385, 1601, 1525, 1483, 1433, 1402, 1348, 1267, 1240, 1198, 1066, 939, 800, 771, 700, 673, 592 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.09-7.25 (m, 14H), 7.53-7.54 (m, 2H), 8.07 (brs, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 112.1, 119.5, 124.6, 124.7, 125.6, 126.4, 127.0, 127.8, 128.3, 129.6, 132.3, 135.1; EI-MS *m/z* 516 (M^+, 11), 259 (M^+/2 + H, 62), 223 (M^+/2 + H - S, 100); Anal. Calcd for $C_{28}H_{18}Cl_2N_2S_2$: C, 64.99; H, 3.51; N, 5.41. Found: C, 64.97; H, 3.54; N, 5.38.

Bis(5-methoxy-3-phenyl-2-indolyl) disulfide (**5c**): 94% yield; yellow solid; mp 172-174 °C; IR (KBr) ν_{max} 3415, 3317, 2951, 1620, 1493, 1450, 1433, 1292, 1257, 1221, 1134, 1117, 1034, 957, 839, 791, 764, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 3.79 (s, 6H), 6.93-7.01 (m, 4H), 7.12-7.26 (m, 12H), 8.00 (brs, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 55.8, 100.9, 111.9, 115.3, 124.7, 125.0, 126.7, 127.3, 128.2, 129.7, 132.2, 133.3, 154.7; EI-MS *m/z* 477 (M^+ - OMe, 28), 256 (M^+/2 + 2H, 100); Anal. Calcd for

$C_{30}H_{24}N_2O_2S_2$: C, 70.84; H, 4.76; N, 5.51. Found: C, 70.72; H, 4.76; N, 5.45.

Bis[3-(4-chlorophenyl)-2-indolyl] disulfide (**5d**): 85% yield; yellow solid; mp 201-204 °C; IR (KBr) ν_{max} 3383, 1522, 1477, 1329, 1149, 1090, 1014, 839, 743 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 6.97-7.35 (m, 14H), 7.50 (d, 2H, *J* = 8.1 Hz), 8.10 (brs, 2H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 111.1, 119.9, 120.9, 123.8, 124.89, 124.91, 126.5, 128.1, 130.7, 131.2, 132.5, 137.0; CI-MS *m/z* 517 (MH^+, 1), 485 (MH^+ - S, 41), 260 ($M^+/2$ + 2H, 100); Anal. Calcd for $C_{28}H_{18}Cl_2N_2S_2$: C, 64.99; H, 3.51; N, 5.41. Found: C, 65.10; H, 3.60; N, 5.29.

Procedure of one-pot reaction of phenyl isothiocyanate derivative **3a** to 2-methylthio-3-phenylindole (**6**)

A benzene solution (3 mL) of phenyl isothiocyanate derivative **3a** (154 mg, 0.3 mmol) was heated at 150 °C for 15 h, and was concentrated. Acetonitrile solution (3 mL) of methyl iodide (0.0187 mL) and tetrabutylammonium fluoride (1.0 M THF solution, 0.3 mL) were added to the residue. The mixture was stirred for 30 min at room temperature, and concentrated. Diethyl ether (20 mL) were added to the residue, and the mixture was washed with a saturated potassium fluoride aqueous solution (20 mL) and a saturated sodium chloride aqueous solution (20 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to give 2-methylthio-3-phenylindole (**6**, 88% yield).

2-Methylthio-3-phenylindole (**6**): colorless plate; mp 84-86 °C (lit.[5] 84-86 °C); IR (KBr) ν_{max} 3477, 1603, 1529, 1485, 1439, 1408, 1352, 1327, 1244, 1038, 970, 775, 754, 704,

679 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 2.30 (s, 3H), 7.09-7.19 (m, 1H), 7.22-7.25 (m, 1H), 7.29-7.36 (m, 2H), 7.43-7.49 (m, 2H), 7.63-7.70 (m, 3H), 8.11 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 19.5, 110.5, 119.4, 120.3, 121.1, 123.0, 126.4, 126.8, 127.4, 128.2, 129.6, 134.1, 136.1; CI-MS *m/z* 239 (M^+, 76), 224 (M^+ - Me, 100); Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.15; H, 5.28; N, 5.95.

Procedure of one-pot reaction of phenyl isothiocyanate derivative **3a** to 3-phenyl-2-indolyl 2-pyridyl sulfide (**7**)

A benzene solution (3 mL) of phenyl isothiocyanate derivative **3a** (168 mg, 0.33 mmol) was heated at 150 °C for 15 h in a sealed tube and was cooled to room temperature. The sealed tube was opened, and then tetrakis(triphenylphosphine)palladium (38.1 mg, 0.33 mmol) and 2-bromopyridine (0.0314 mL, 0.33 mmol) were added to the solution. The solution was heated for 24 h at 100 °C in a sealed tube and concentrated. Diethyl ether (20 mL) were added to the residue, and the mixture was washed with a saturated potassium fluoride aqueous solution (20 mL) and a saturated sodium chloride aqueous solution (20 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated. The mixture was purified by silica gel column chromatography (eluent: hexane / ethyl acetate) to give *S*-3-phenyl-2-indolyl 2-pyridyl sulfide (**7**, 86% yield).

3-Phenyl-2-indolyl 2-pyridyl sulfide (**7**): mp 159-160 °C; IR (KBr) ν_{max} 3199, 2918, 1603, 1576, 1448, 1416, 1356, 1246, 1128, 752, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 6.86 (dt, 1H, *J* = 0.8, 7.3 Hz), 6.98 (ddd, 1H, *J* = 1.0, 4.9, 7.4 Hz), 7.14-7.62 (m, 9H), 7.77 (d, 1H, *J* = 8.1 Hz), 8.40 (ddd, 1H, *J* = 0.8, 1.8, 4.9 Hz), 9.29 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 111.1, 120.0, 120.3, 120.4, 120.6, 121.2, 123.6, 126.7, 127.0, 128.3, 129.5, 133.6, 137.0, 149.3, 159.9; EI-MS *m/z* 302 (M^+, 100), 269 (M^+ - SH, 20), 223

(M^+-Py-H, 35); Anal. Calcd for $C_{19}H_{14}N_2S$: C, 75.47; H, 4.67; N, 9.26. Found: C, 75.43; H, 4.76; N, 9.30.

Procedure of one-pot reaction of phenyl isothiocyanate derivative **3a** to *S*-3-phenyl-2-indolyl benzothioate (**8**)

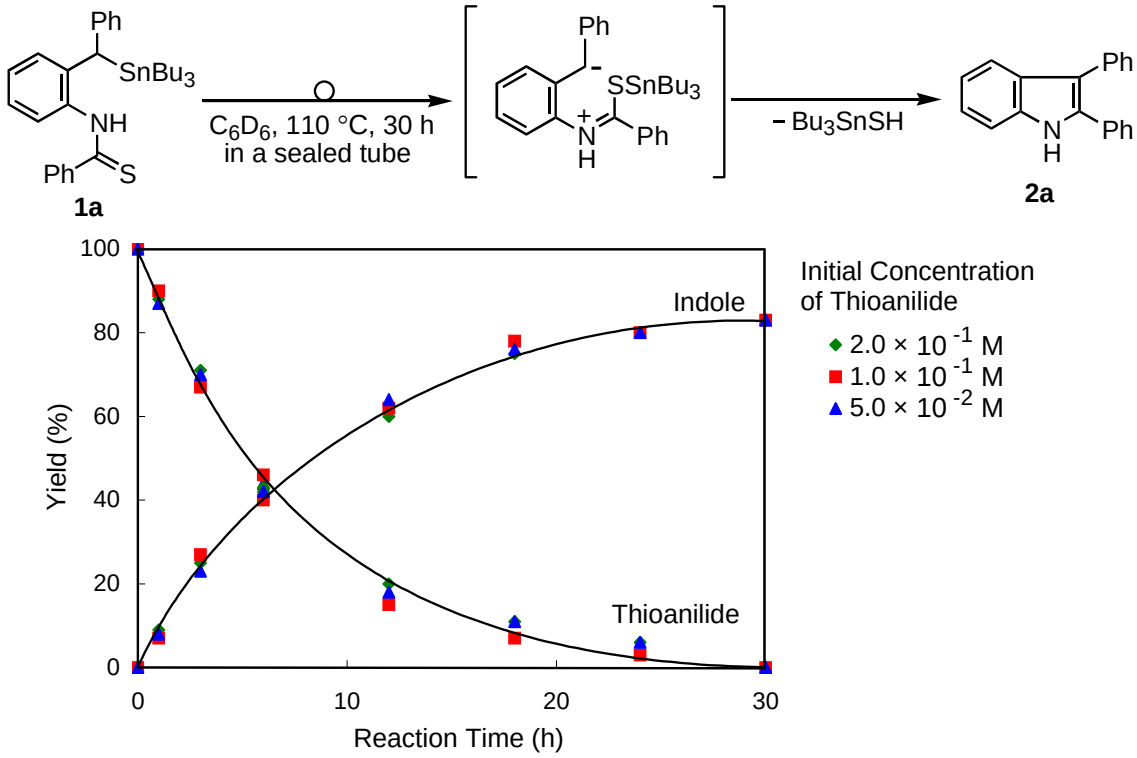
A benzene solution (3 mL) of phenyl isothiocyanate derivative **3a** (154 mg, 0.3 mmol) was heated at 150 °C for 15 h, and the solution was concentrated. Chloroform (3 mL) solution of benzoyl chloride (0.0348 mL, 0.3 mmol) was added to the residue. The mixture was refluxed for 8 h, and concentrated. Diethyl ether (20 mL) was added to the residue, and the mixture was washed with a saturated potassium fluoride aqueous solution (20 mL) and then a saturated sodium chloride aqueous solution (20 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated. The mixture was purified by silica gel column chromatography (eluent: hexane / ethyl acetate) to give *S*-3-phenyl-2-indolyl benzothioate (**8**, 74% yield).

S-3-phenyl-2-indolyl benzothioate (**8**): pale yellow needle; mp 153–154 °C; IR (KBr) ν_{max} 3369, 1672, 1485, 1444, 1400, 1331, 1246, 1209, 1174, 893, 773, 750, 687 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.14-7.74 (m, 12H), 7.99-8.03 (m, 2H), 9.02 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 111.1, 117.7, 119.7, 120.4, 123.5, 123.6, 126.8, 126.9, 127.5, 128.3, 128.8, 129.7, 133.5, 134.0, 136.0, 137.3, 190.2; EI-MS *m/z* 329 (M^+, 23), 105 ($PhCO^+$, 100).

Time Course of Thermal Reaction of Thioanilide 1a

d_6-Benzene solutions of thioanilide **1a** (initial concentrations : 2.0 x 10^{-1}, 1.0 x 10^{-1}, and

5.0 x 10^{-2} M) were heated in sealed NMR tubes, and yields were determined by ^{1}H NMR. Reaction rates of the reactions are the same.



Reference

(1) A. B. Smith III, R. Mewshaw, *J. Org. Chem.* **1984**, *49*, 3685-3689.

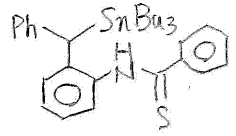
(2) A. Fürstner, D. N. Jumbam, *Tetrahedron* **1992**, *48*, 5991-6010.

(3) H. Tokuyama, T. Yamashita, M. T. Reding, Y. Kaburagi, T. Fukuyama, *J. Am. Chem. Soc.* **1999**, *121*, 3791-3792.

(4) B. D. Palmer, G. W. Rewcastle, A. M. Thompson, M. Boyd, H. D. H. Showalter, A. D. Sercel, D. W. Fry, A. J. Kraker, W. A. Denny, *J. Med. Chem.* **1995**, *38*, 58-67.

(5) D. Lednicer, E. Emmat, *J. Heterocyclic Chem.* **1971**, *8*, 903-910.

M1-OH-P11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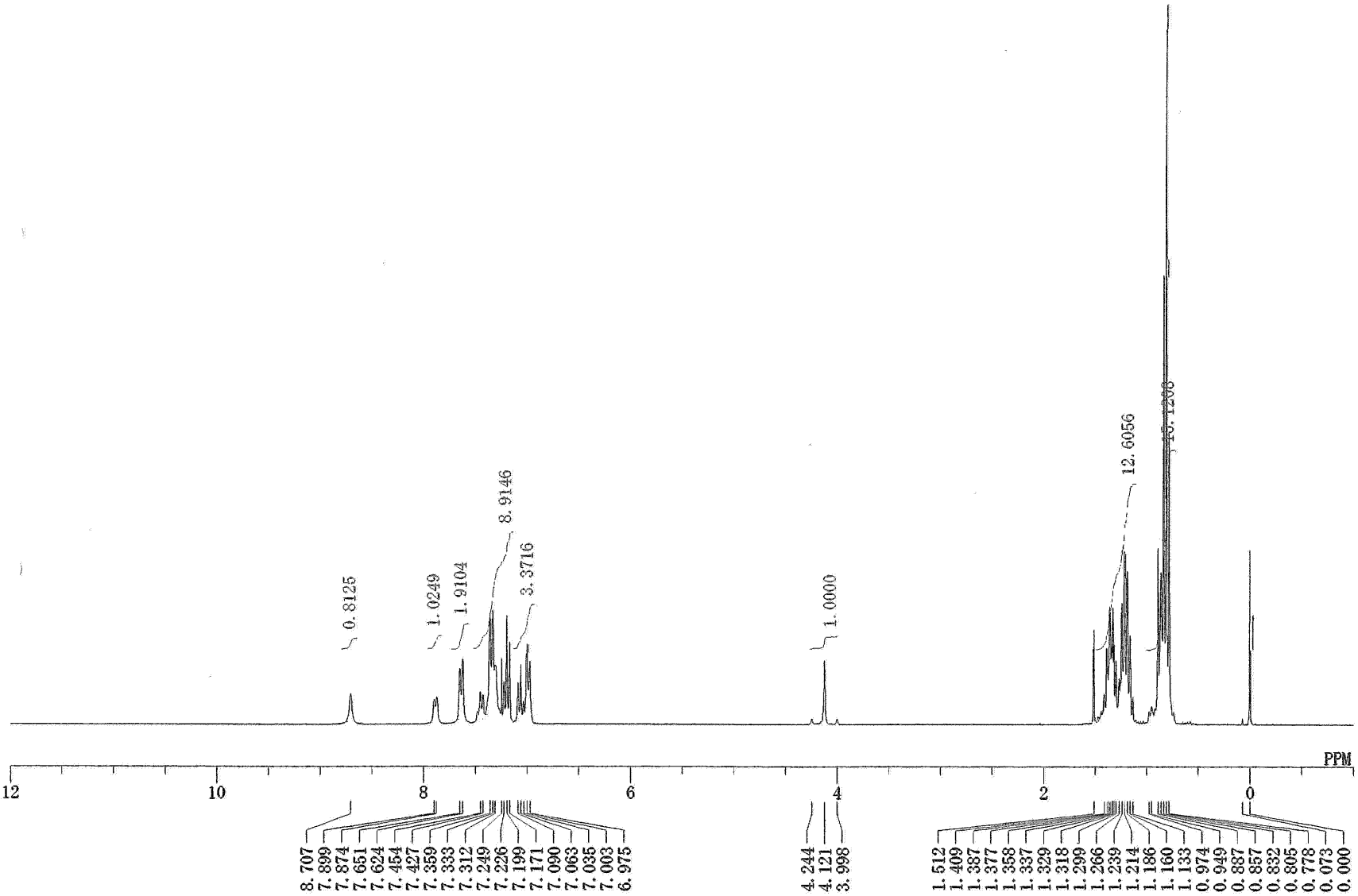
H
N
S

1a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PPM
12
10
8
6
4
2
0
8.707
7.899
7.874
7.651
7.624
7.454
7.427
7.359
7.333
7.312
7.249
7.226
7.199
7.171
7.090
7.063
7.035
7.003
6.975
4.244
4.121
3.998
1.512
1.409
1.387
1.377
1.358
1.337
1.329
1.318
1.299
1.266
1.239
1.214
1.186
1.160
1.133
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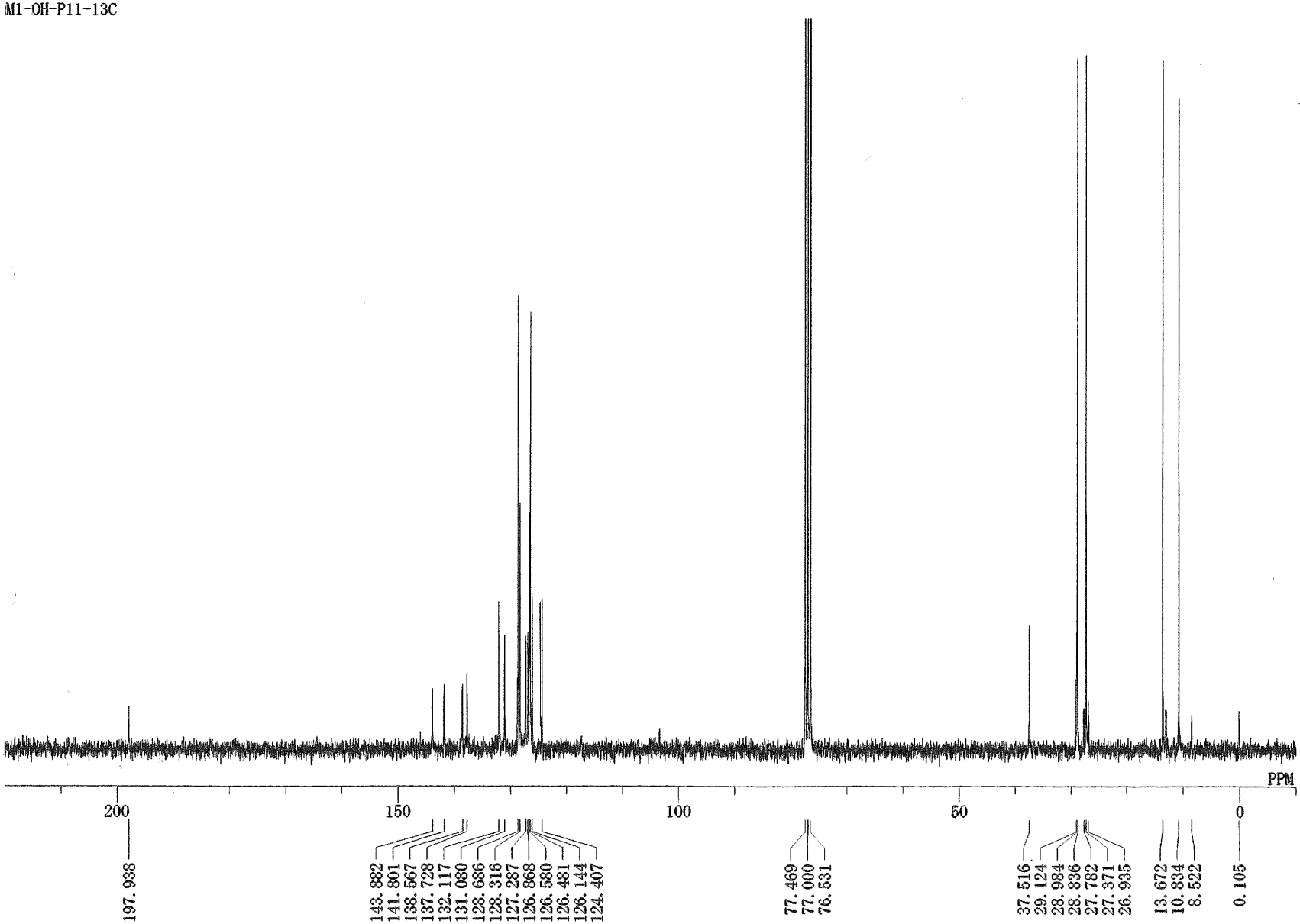
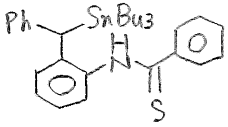
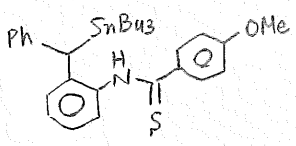
M1-OH-P11-13C





1a

M1-OH-P44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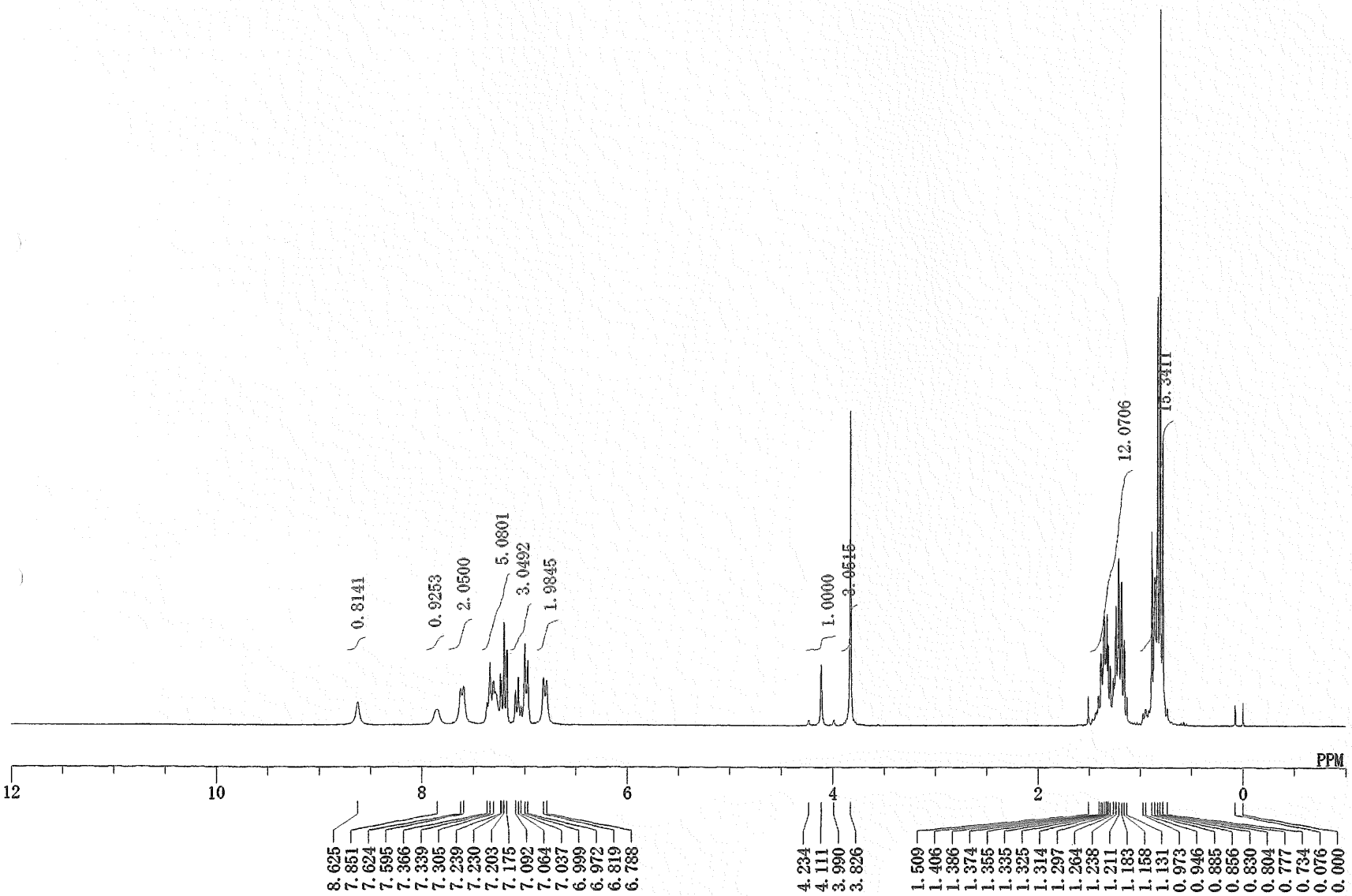
SnBu3
OMe
H
N
S

1b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PPM
12
10
8
6
4
2
0
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7.851
7.624
7.595
7.366
7.339
7.305
7.239
7.230
7.203
7.175
7.092
7.064
7.037
6.999
6.972
6.819
6.788
4.234
4.111
3.990
3.826
1.509
1.406
1.386
1.374
1.355
1.335
1.325
1.314
1.297
1.264
1.238
1.211
1.183
1.158
1.131
0.973
0.946
0.885
0.856
0.830
0.804
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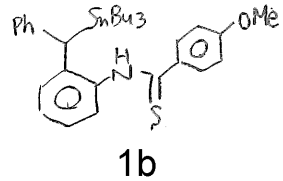
0.734
0.076
0.000

\\Komanmr\personal\ota\preparation\P44\P44-13C.als
M1-OH-P44



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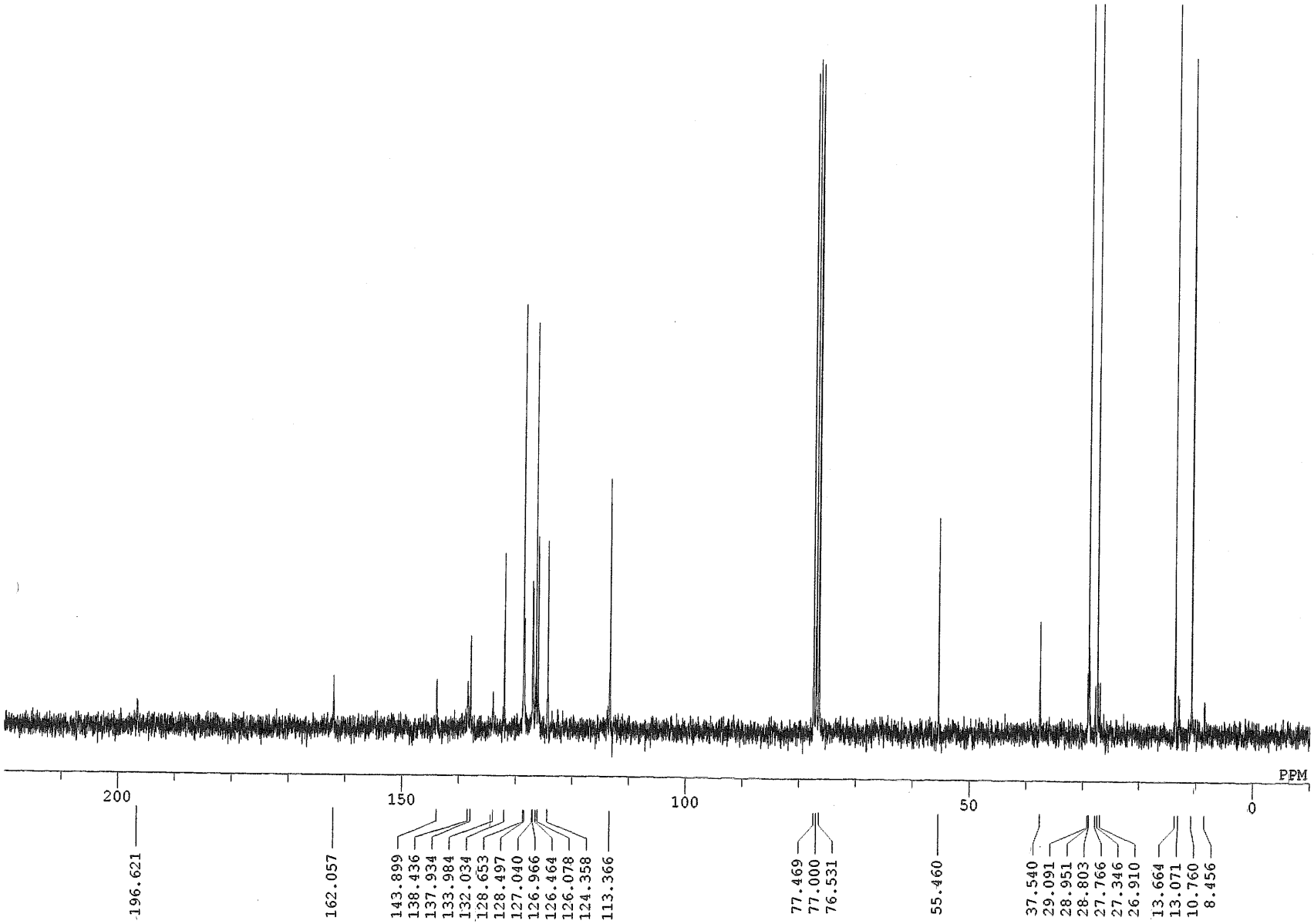
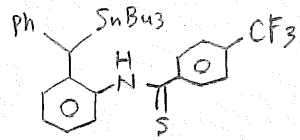
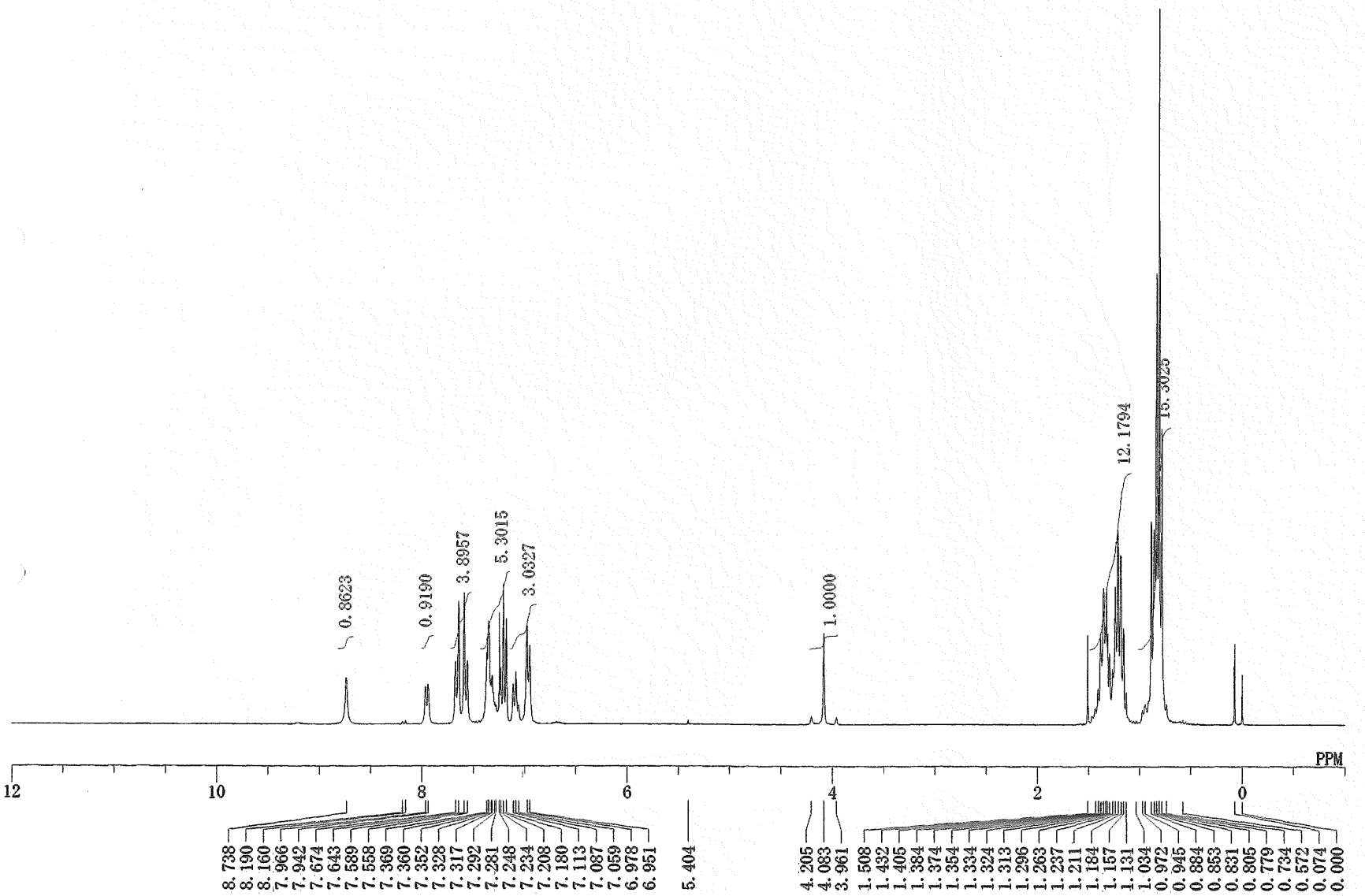


M1-OH-P38


Ph
SnBu3
CF3
H
N
O
S

1c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7.369
7.360
7.352
7.328
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7.292
7.281
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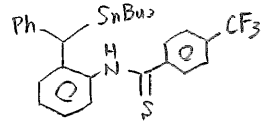
\\Komanmr\personal\ota\preparation\P38\P38-13C'.als
M1-OH-P38-13C



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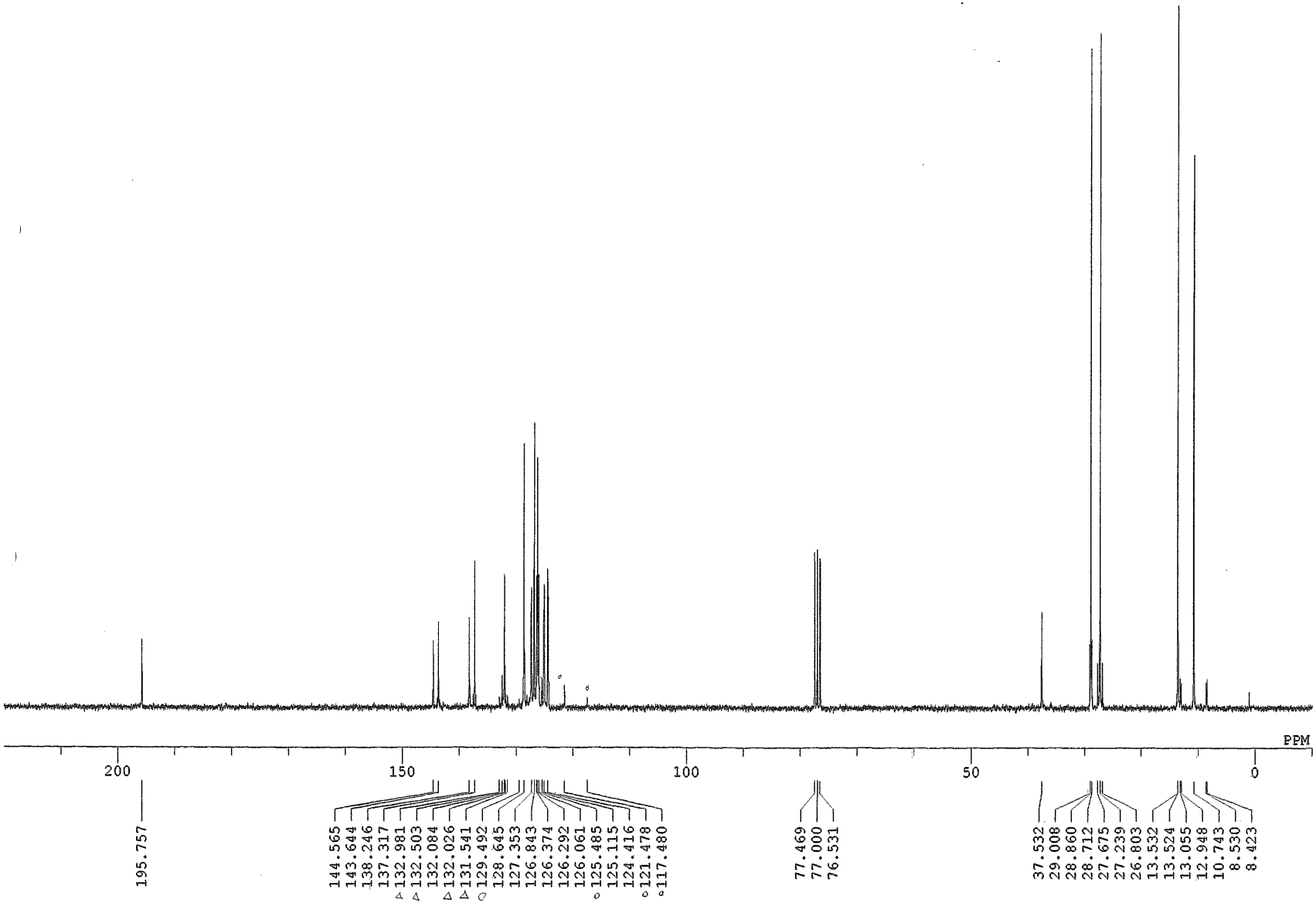

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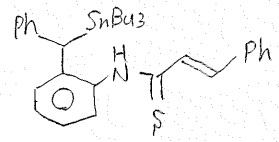

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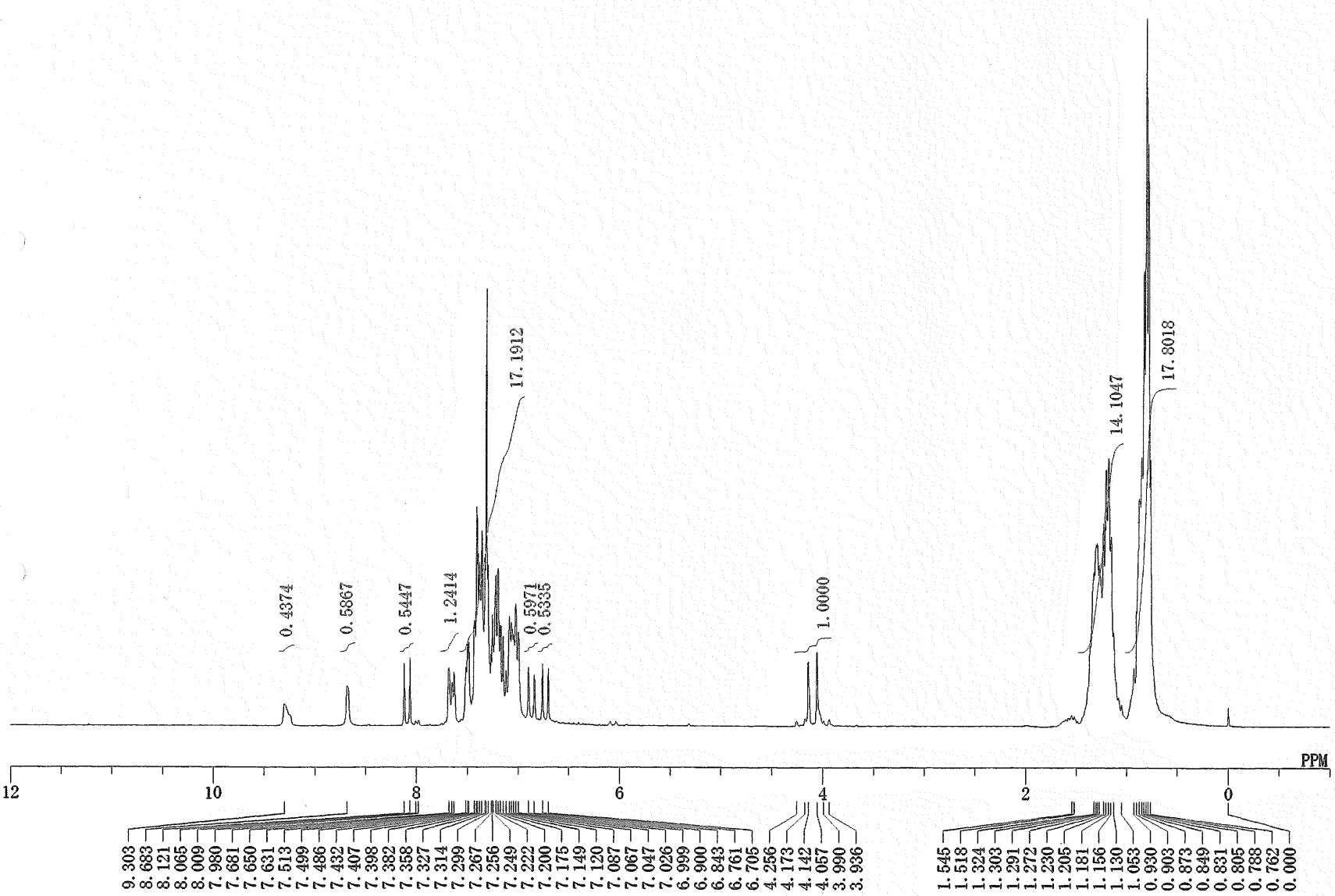
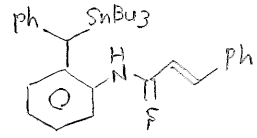
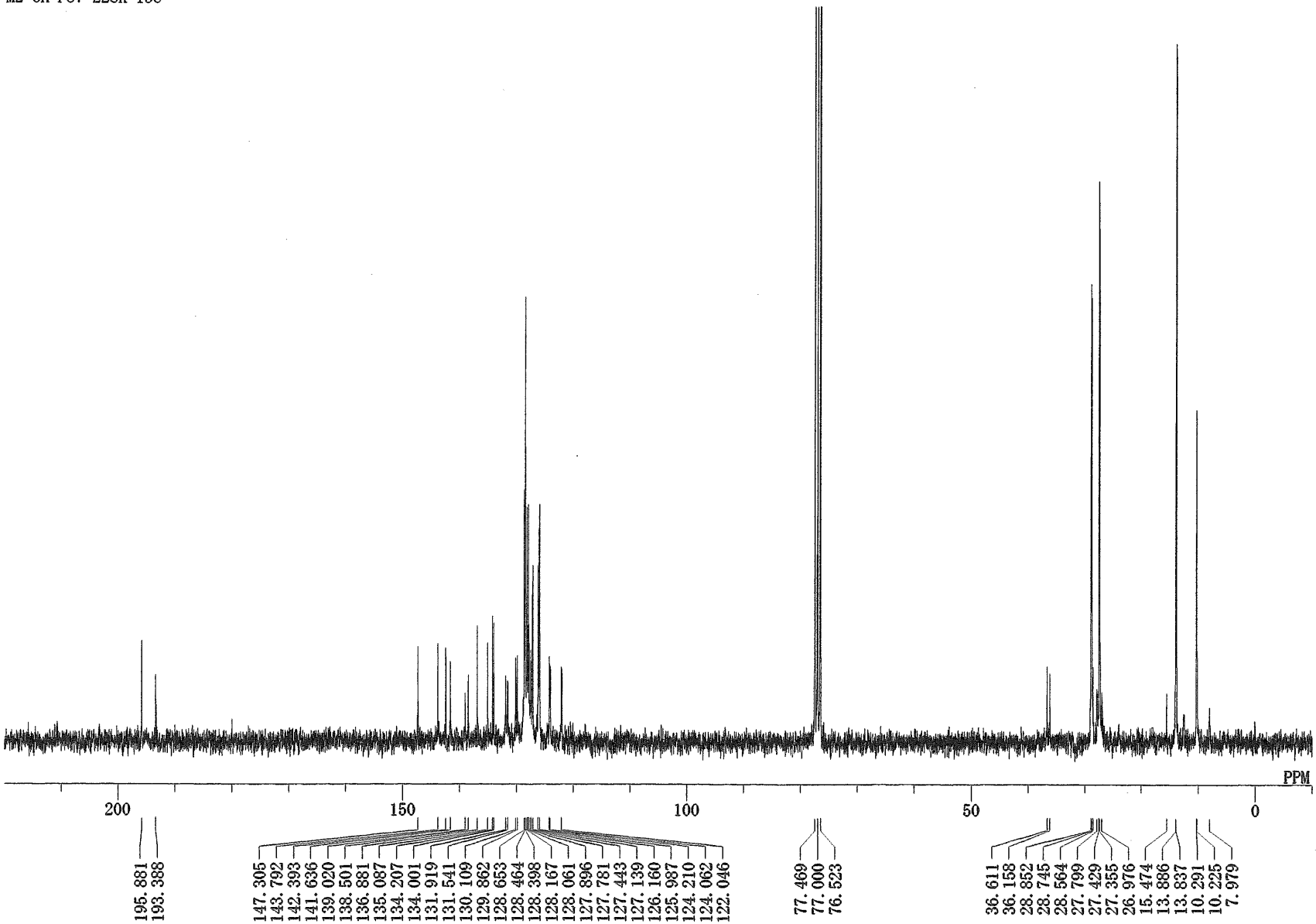


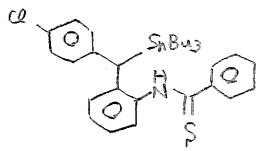


1d

M2-OH-P87-228K-13C



M2-OH-P124



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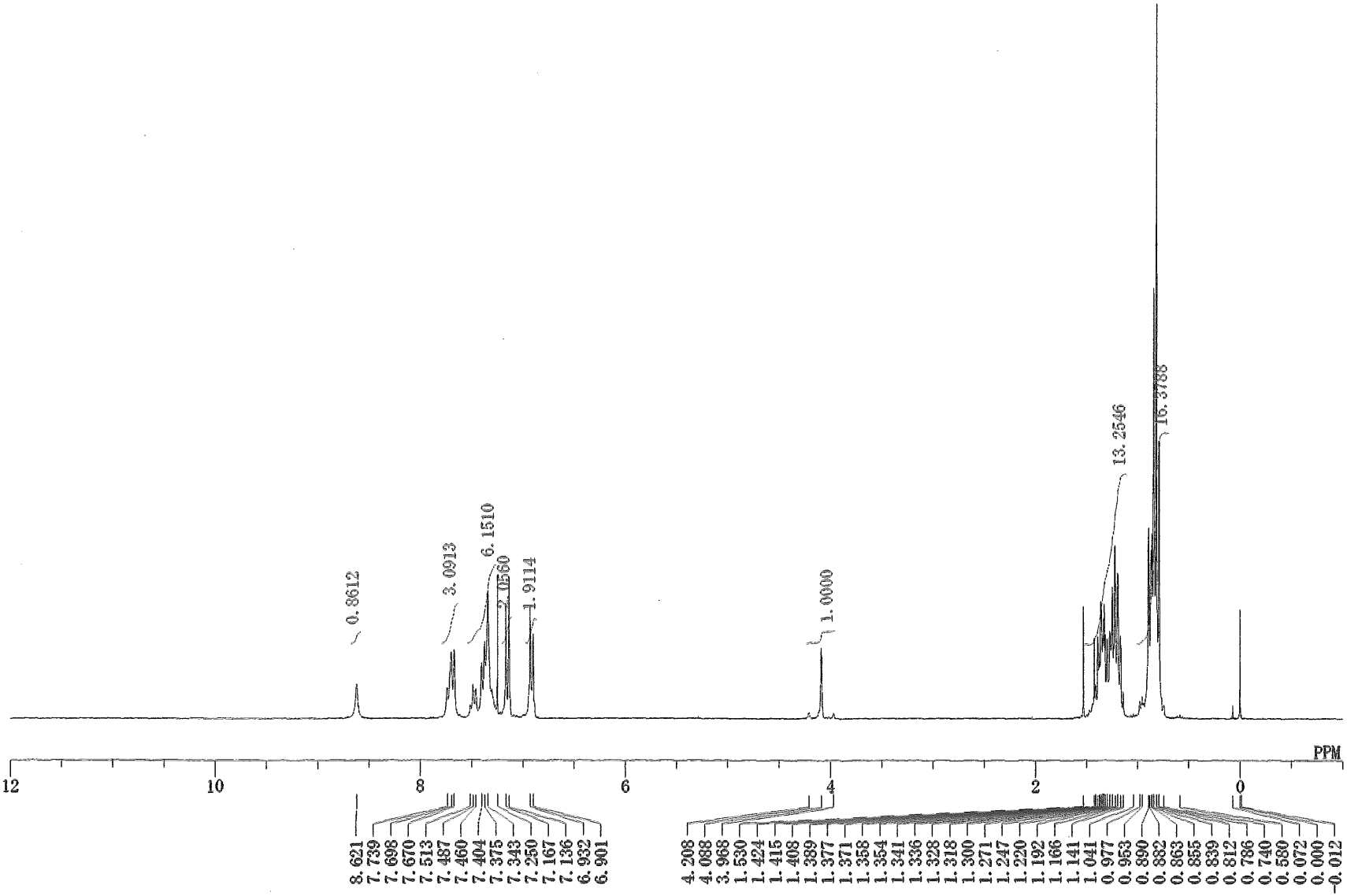
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PPM
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10
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6
4
2
0
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7.739
7.698
7.670
7.513
7.487
7.460
7.404
7.375
7.343
7.250
7.167
7.136
6.932
6.901
4.208
4.088
3.968
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1.415
1.408
1.389
1.377
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1.358
1.354
1.341
1.336
1.328
1.318
1.300
1.271
1.247
1.220
1.192
1.166
1.141
1.041
0.977
0.953
0.890
0.882
0.863
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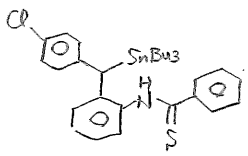
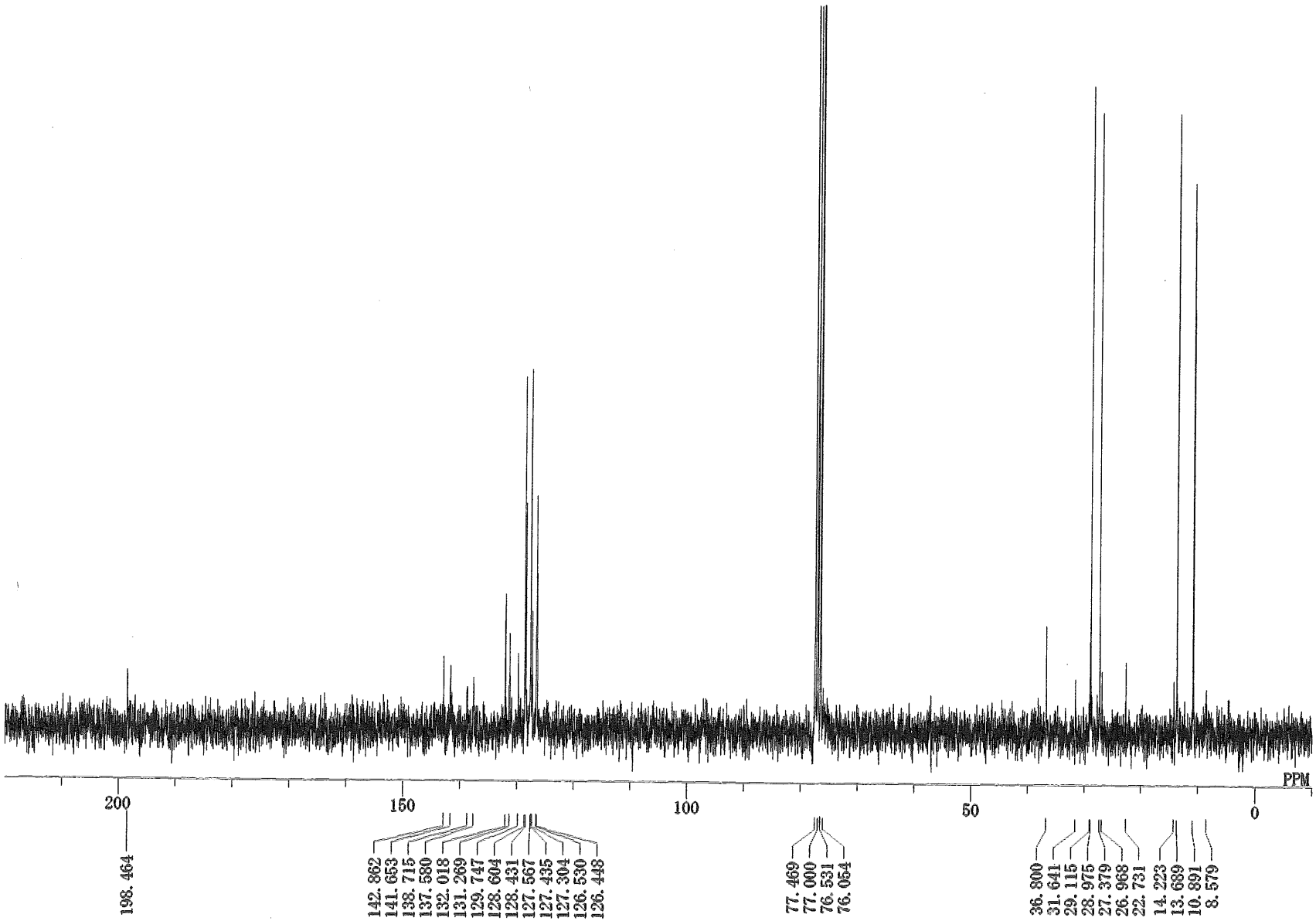
0.000
-0.012

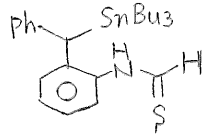
M2-OH-P124-13C



1e



M2-OH-P73


Ph
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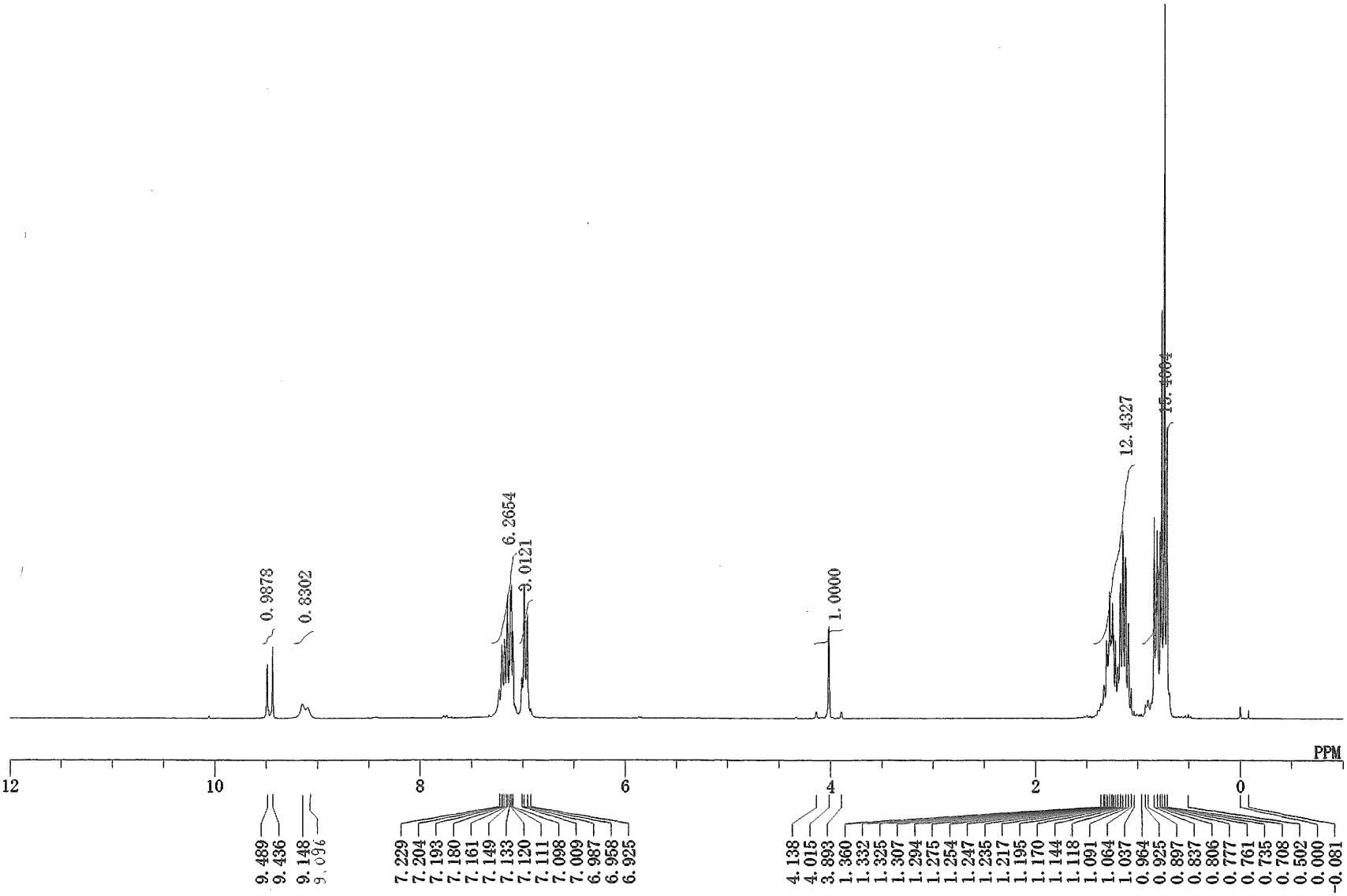
H
N
H
O
S

1f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6
4
2
0
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9.436
9.148
9.096
7.229
7.204
7.193
7.180
7.161
7.149
7.133
7.120
7.111
7.098
7.009
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6.925
4.138
4.015
3.893
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1.325
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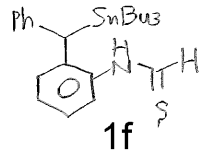
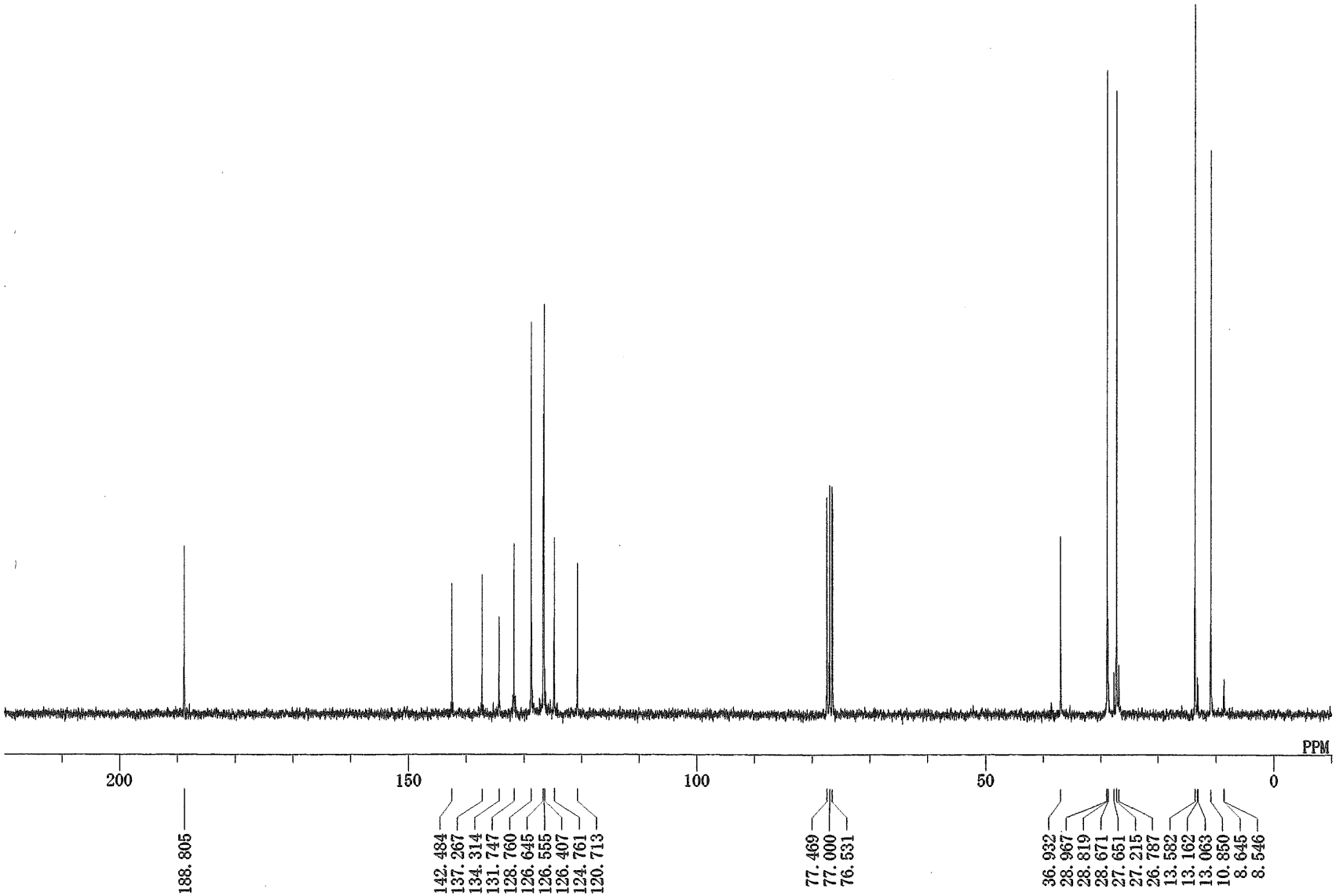
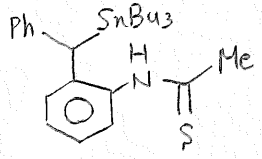
M2-OH-P73-13C



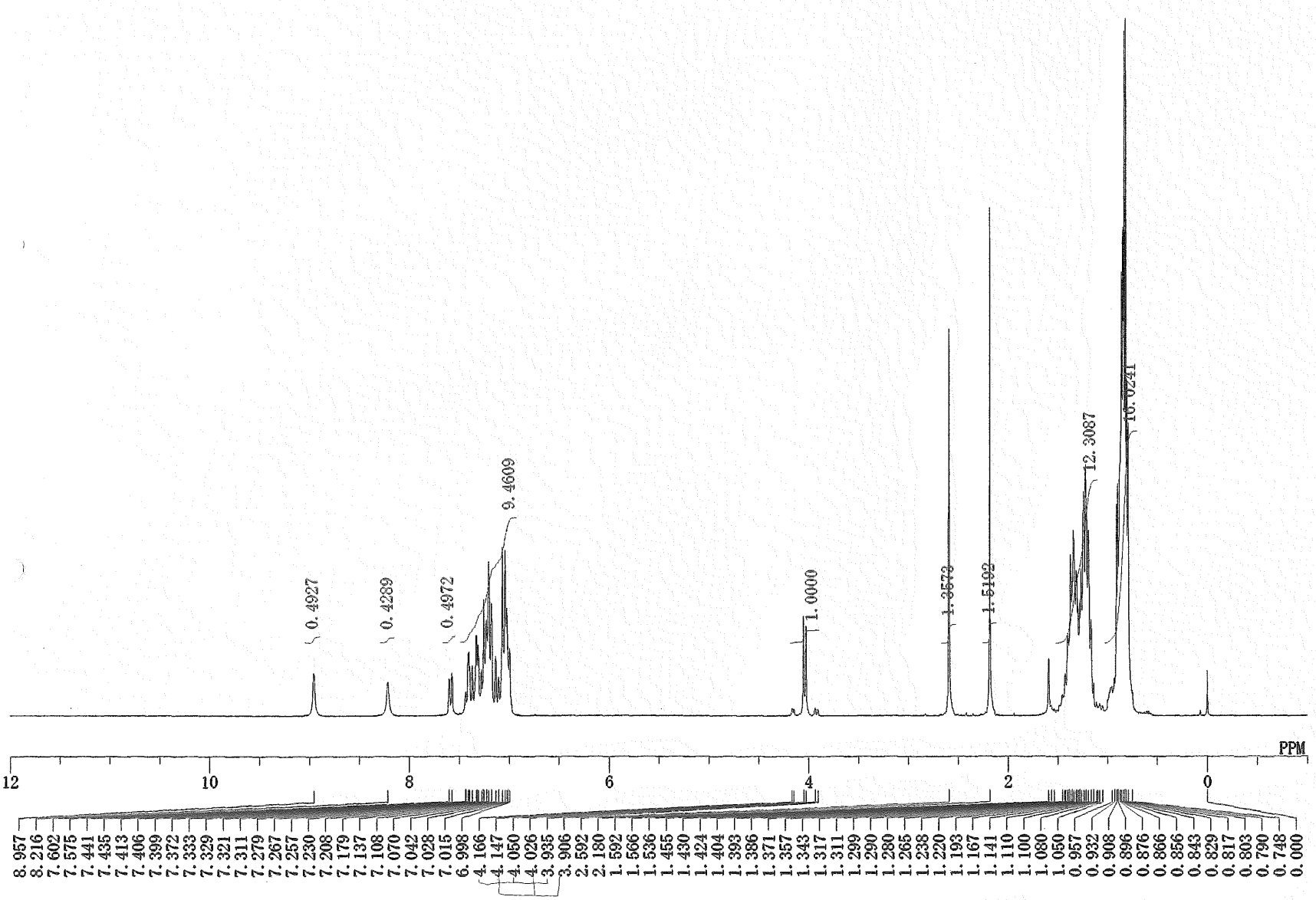
1f



M1-OH-P50


Ph
SnBu3
H
N
Me
S

1g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16.0241
PPM
12
10
8
6
4
2
0
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8.216
7.602
7.575
7.441
7.435
7.413
7.406
7.399
7.372
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7.015
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1.455
1.430
1.424
1.404
1.393
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1.371
1.357
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1.317
1.311
1.299
1.290
1.280
1.265
1.238
1.220
1.193
1.167
1.141
1.110
1.100
1.080
1.050
0.957
0.932
0.908
0.896
0.876
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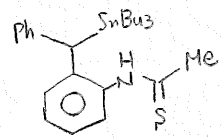
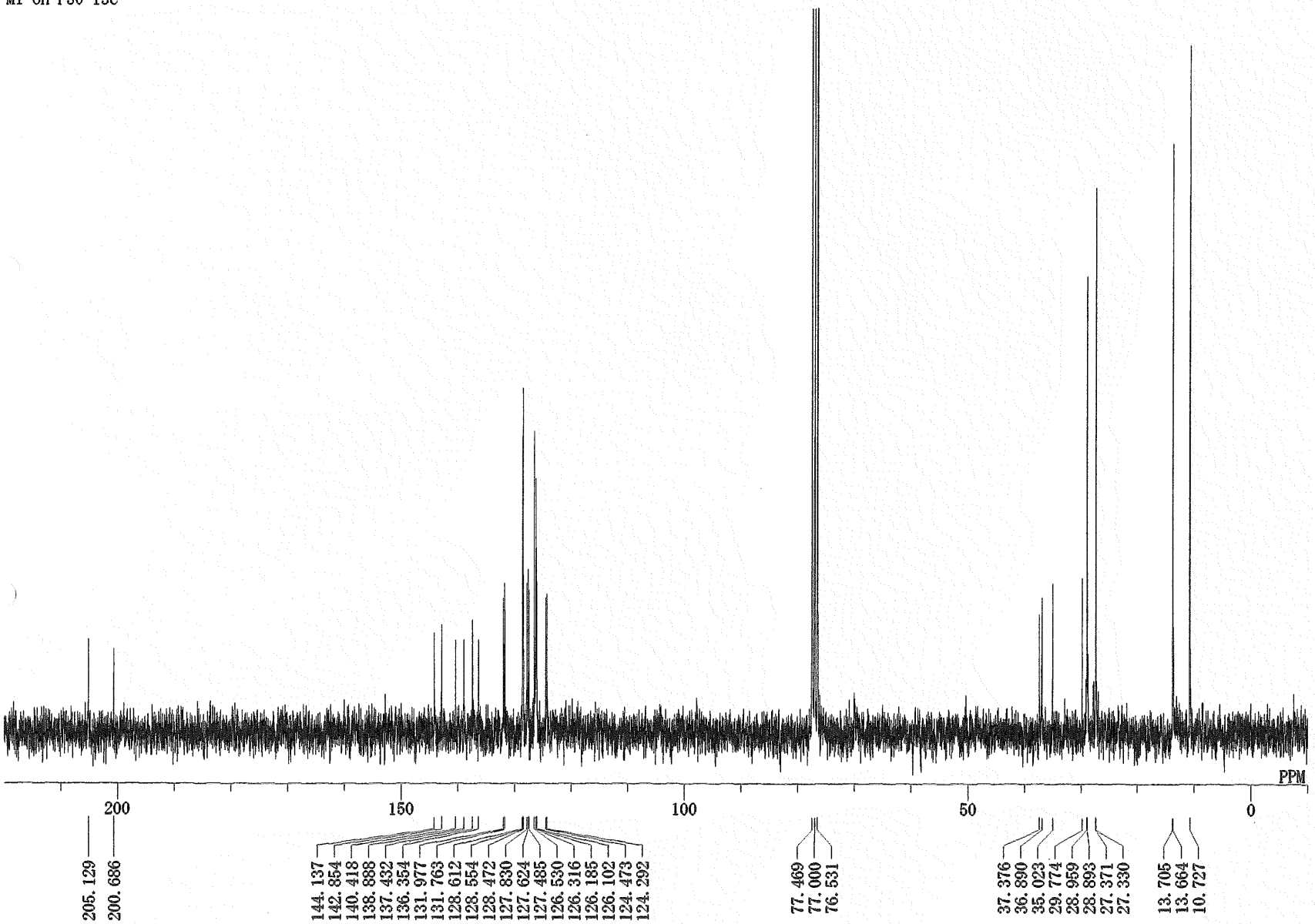
0.000

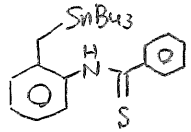
M1-OH-P50-13C



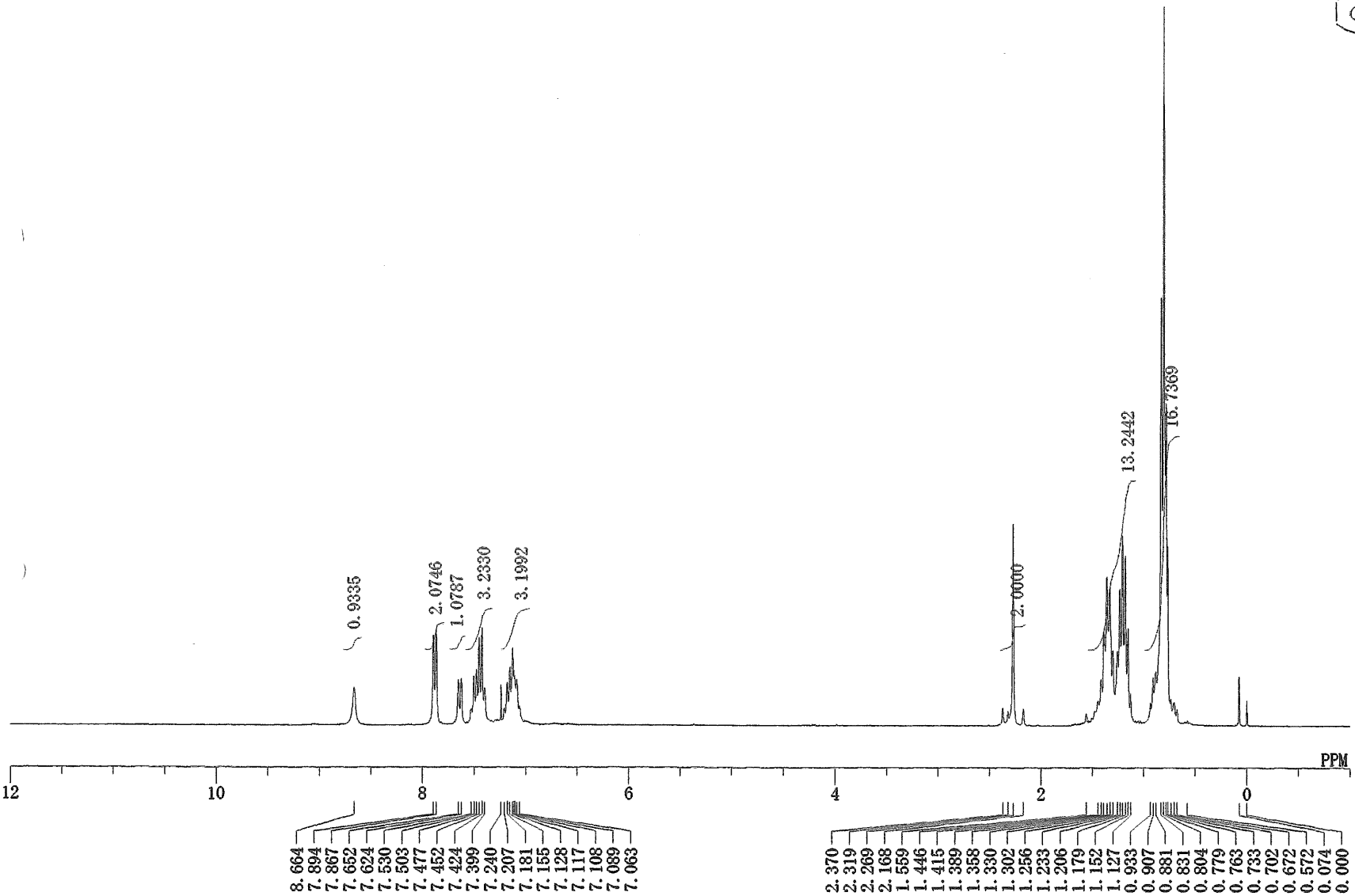
1g



M1-OH-P37


SnBu3
H
N
O
S

1h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PPM
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8
6
4
2
0
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7.894
7.867
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7.624
7.530
7.503
7.477
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7.424
7.399
7.240
7.207
7.181
7.155
7.128
7.117
7.108
7.089
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2.370
2.319
2.269
2.168
1.559
1.446
1.415
1.389
1.358
1.330
1.302
1.256
1.233
1.206
1.179
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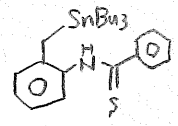
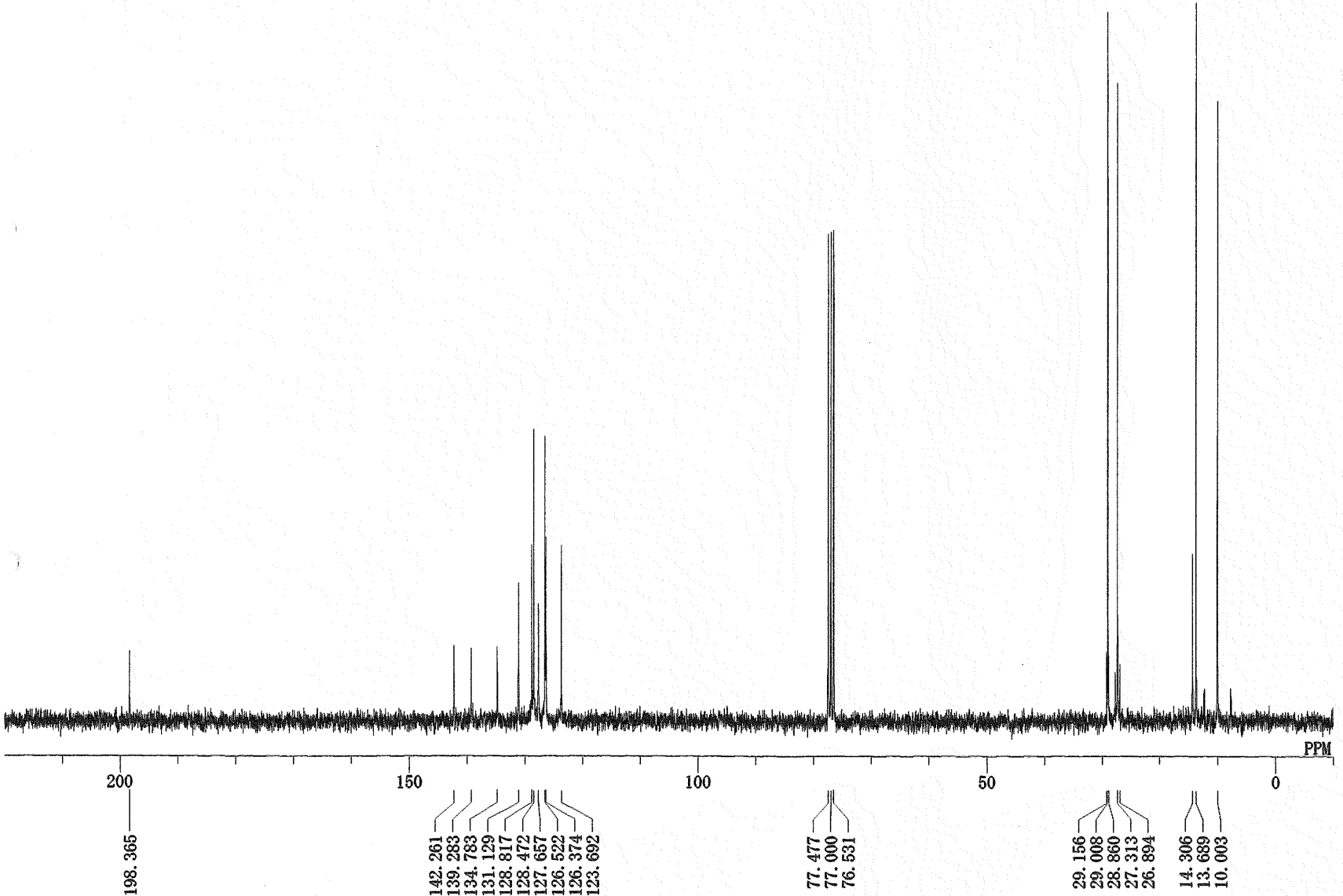
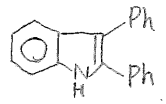
M1-OH-P37-13C



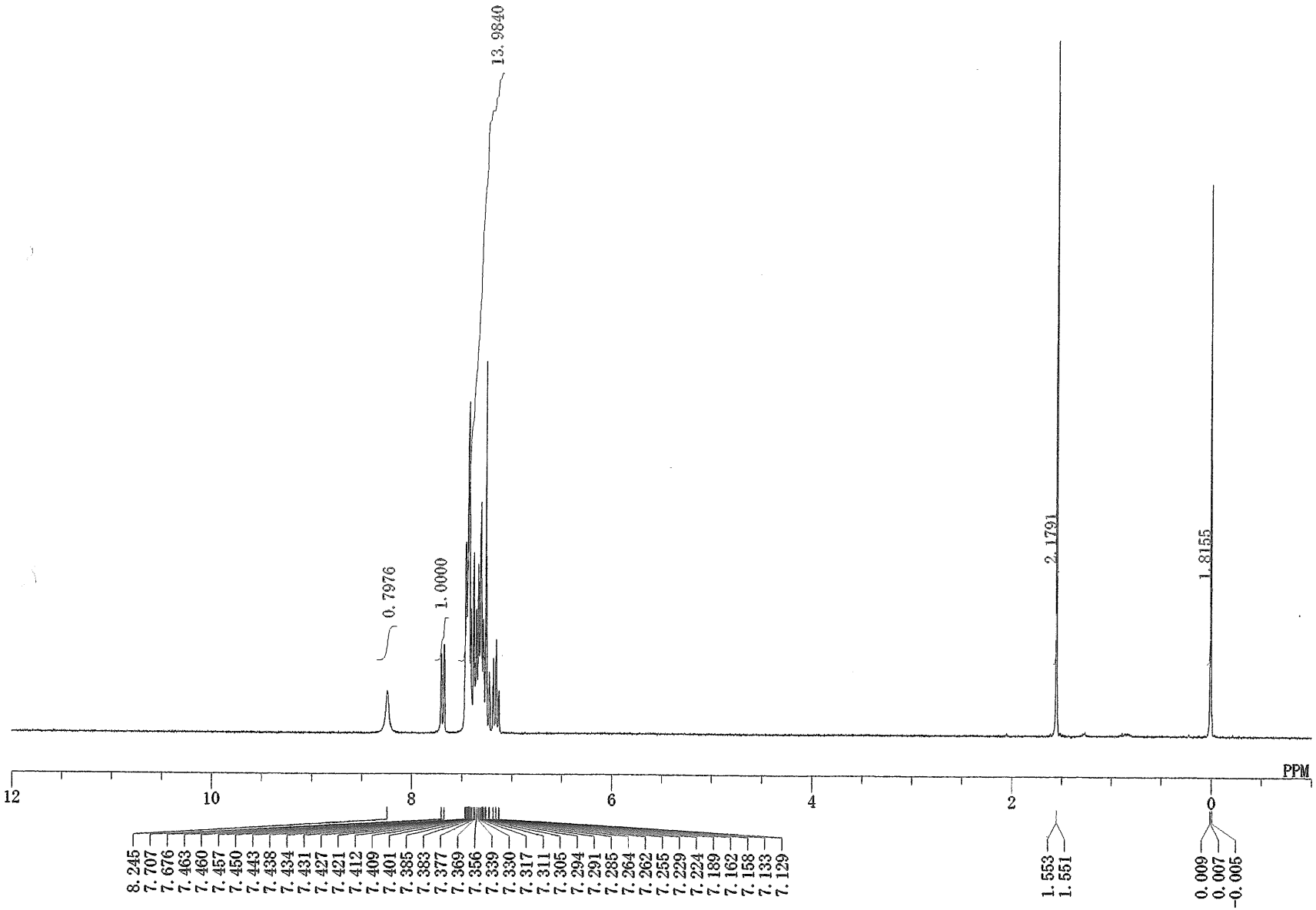
1h



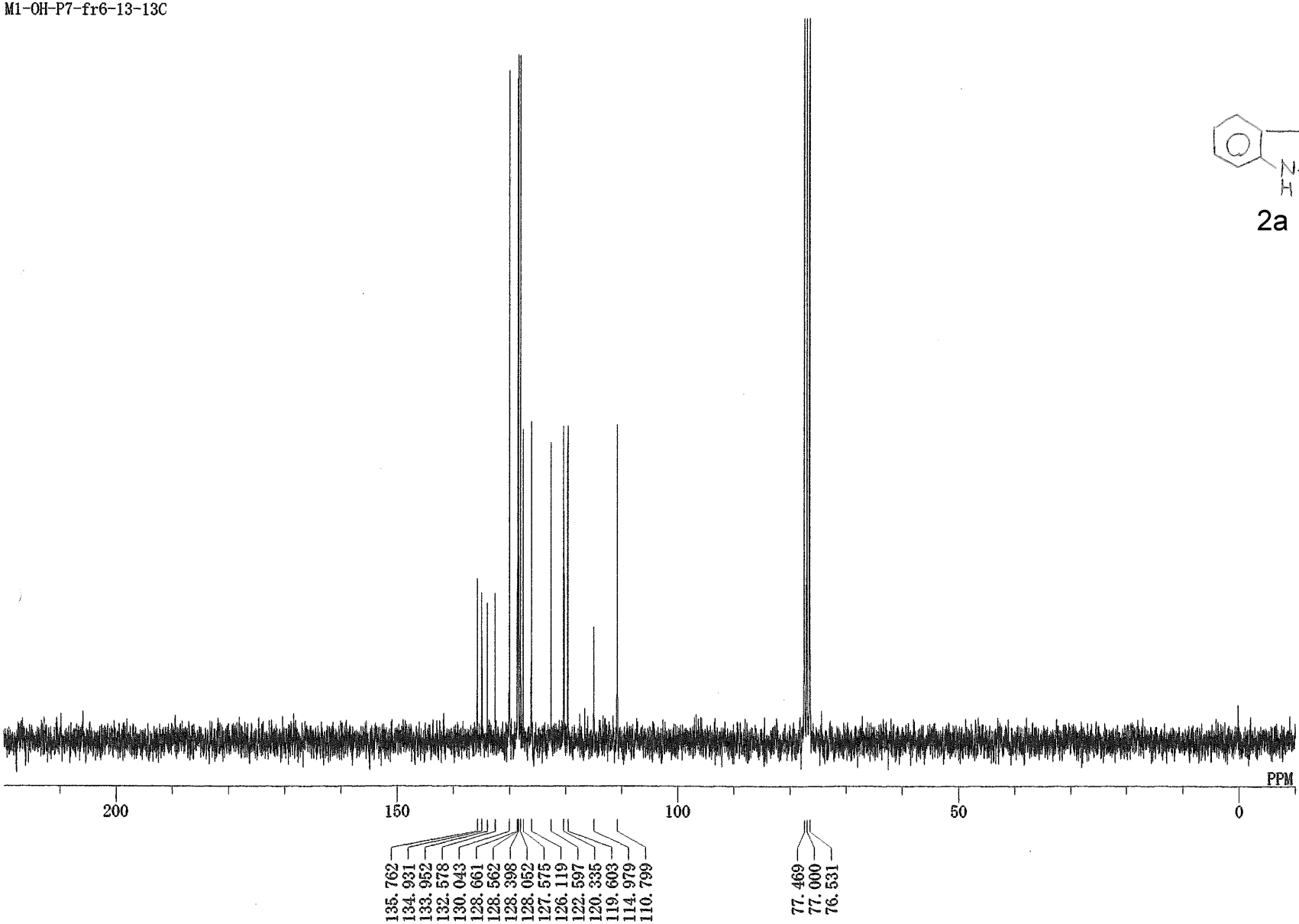
M1-OH-P7-fr6-13



2a



M1-OH-P7-fr6-13-13C



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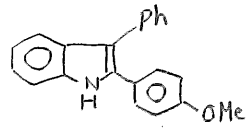
M1-OH-R47-fr8-12



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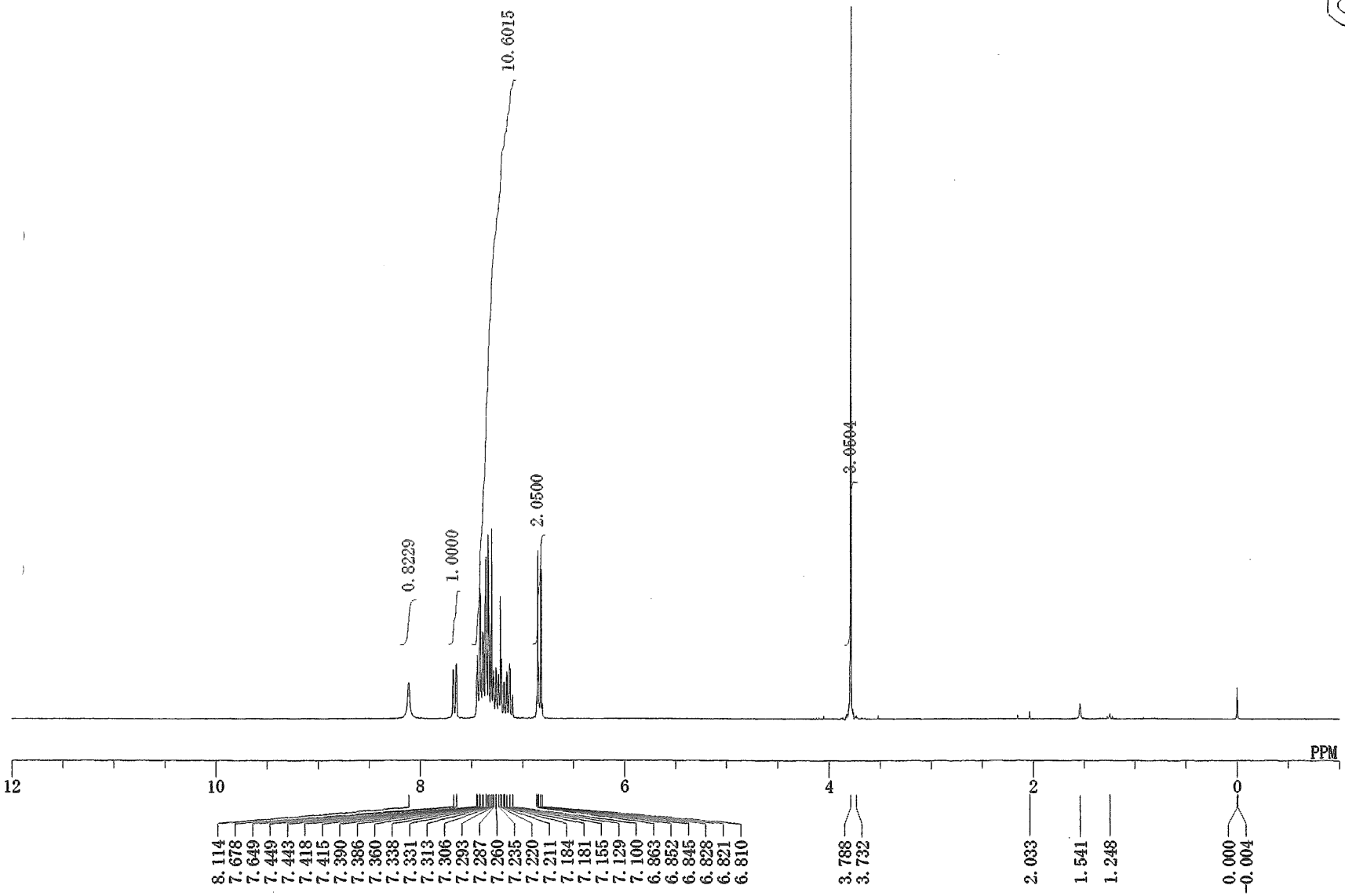
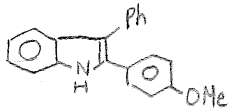


M2-OH-R47-13C



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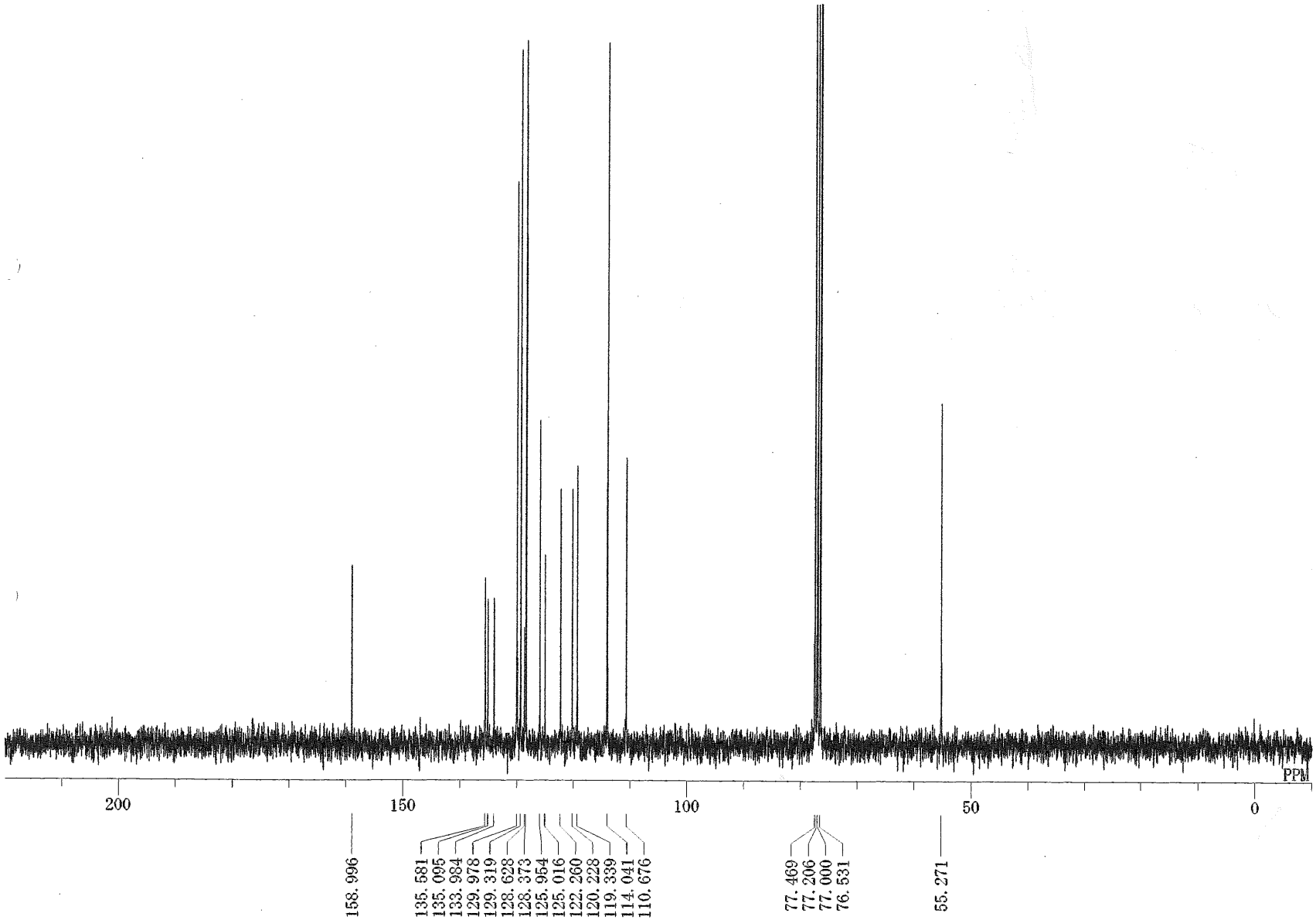
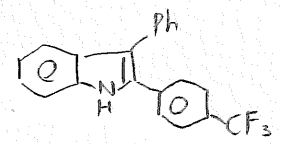


M1-OH-R50-fr5-13



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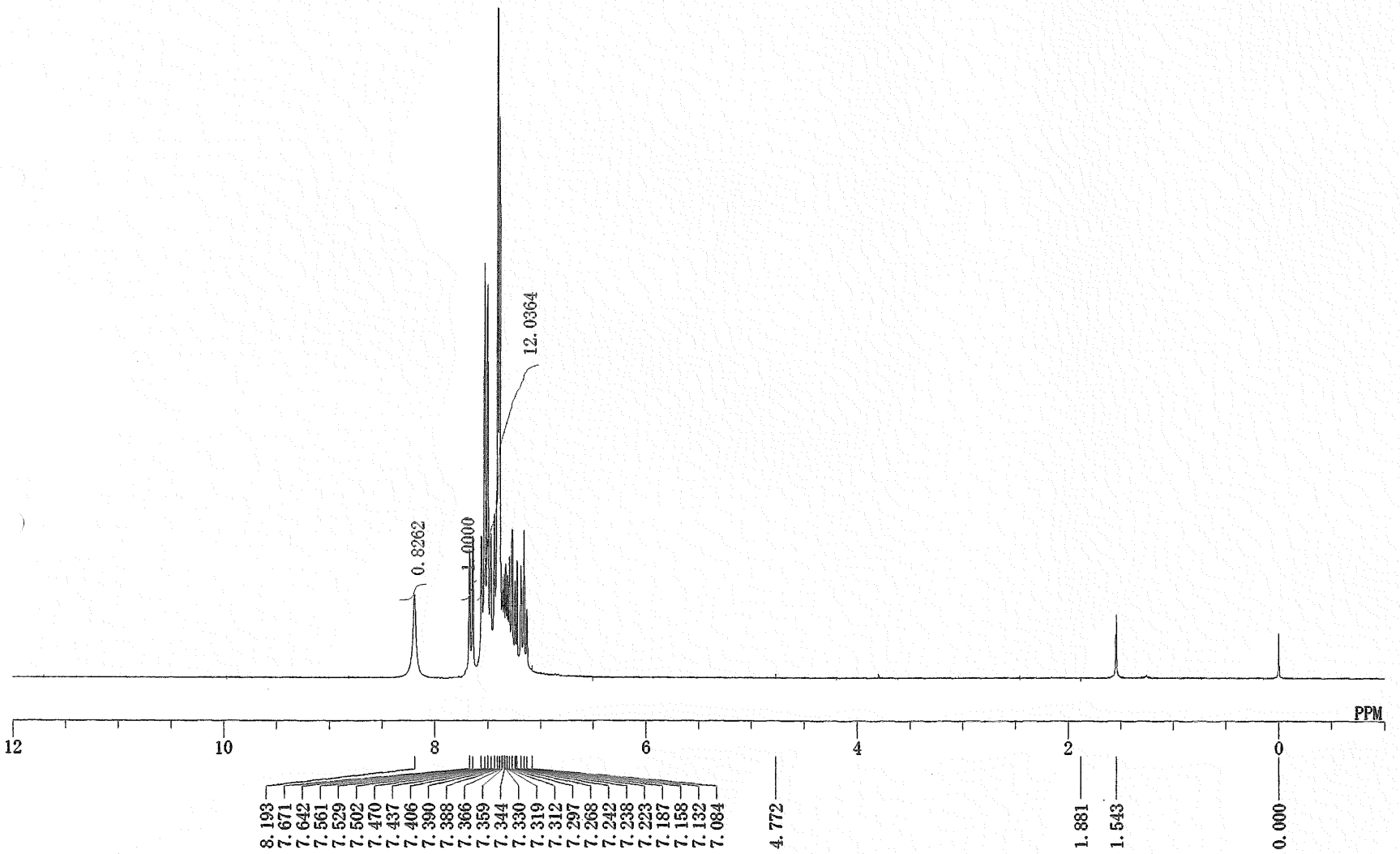
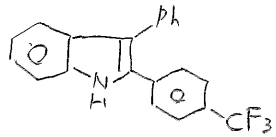


\\Komanmr\personal\ota\reaction\R50\R50-fr5-13-13C.als
M1-OH-R50-fr5-13-13C



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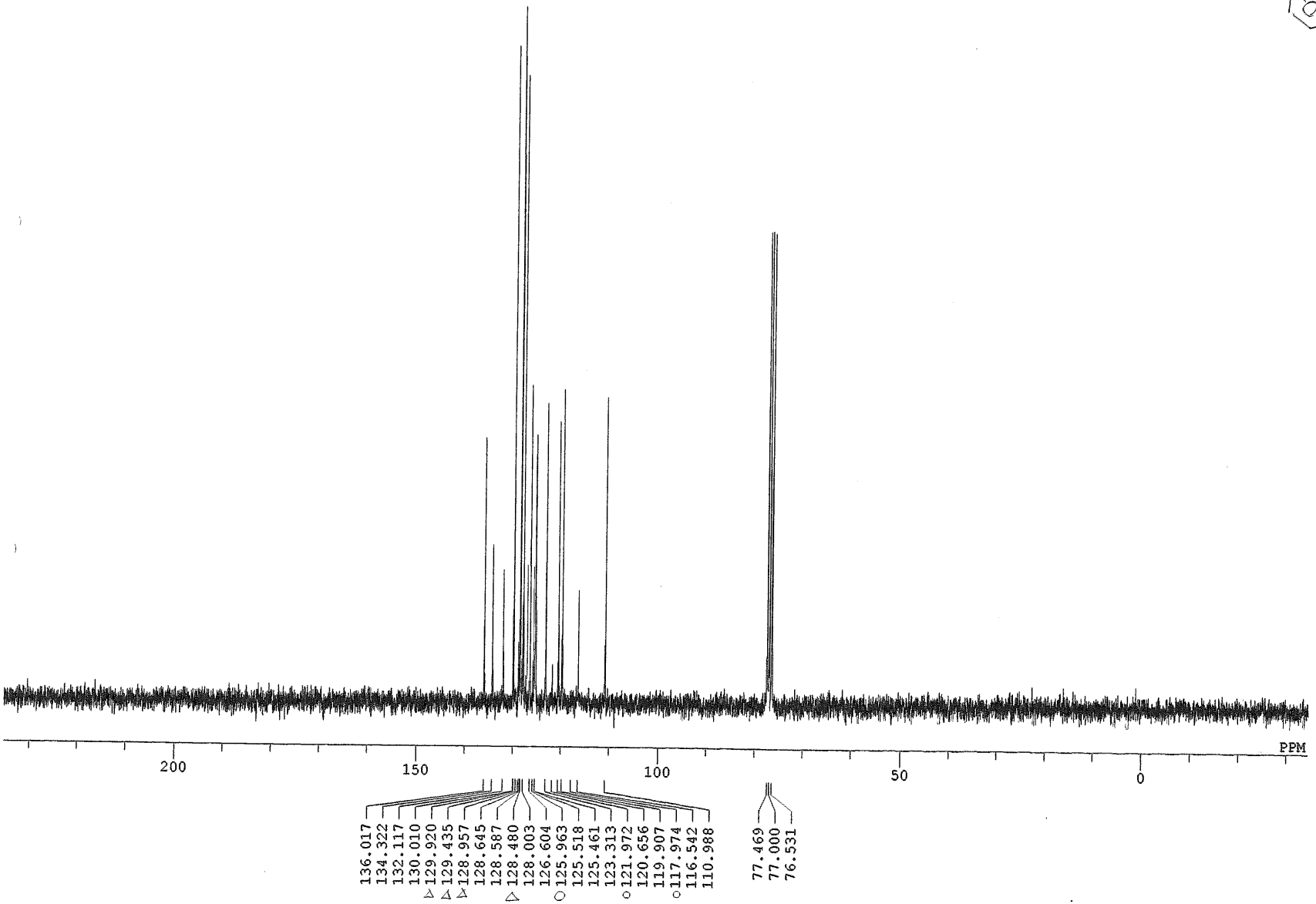
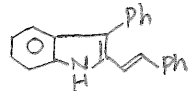
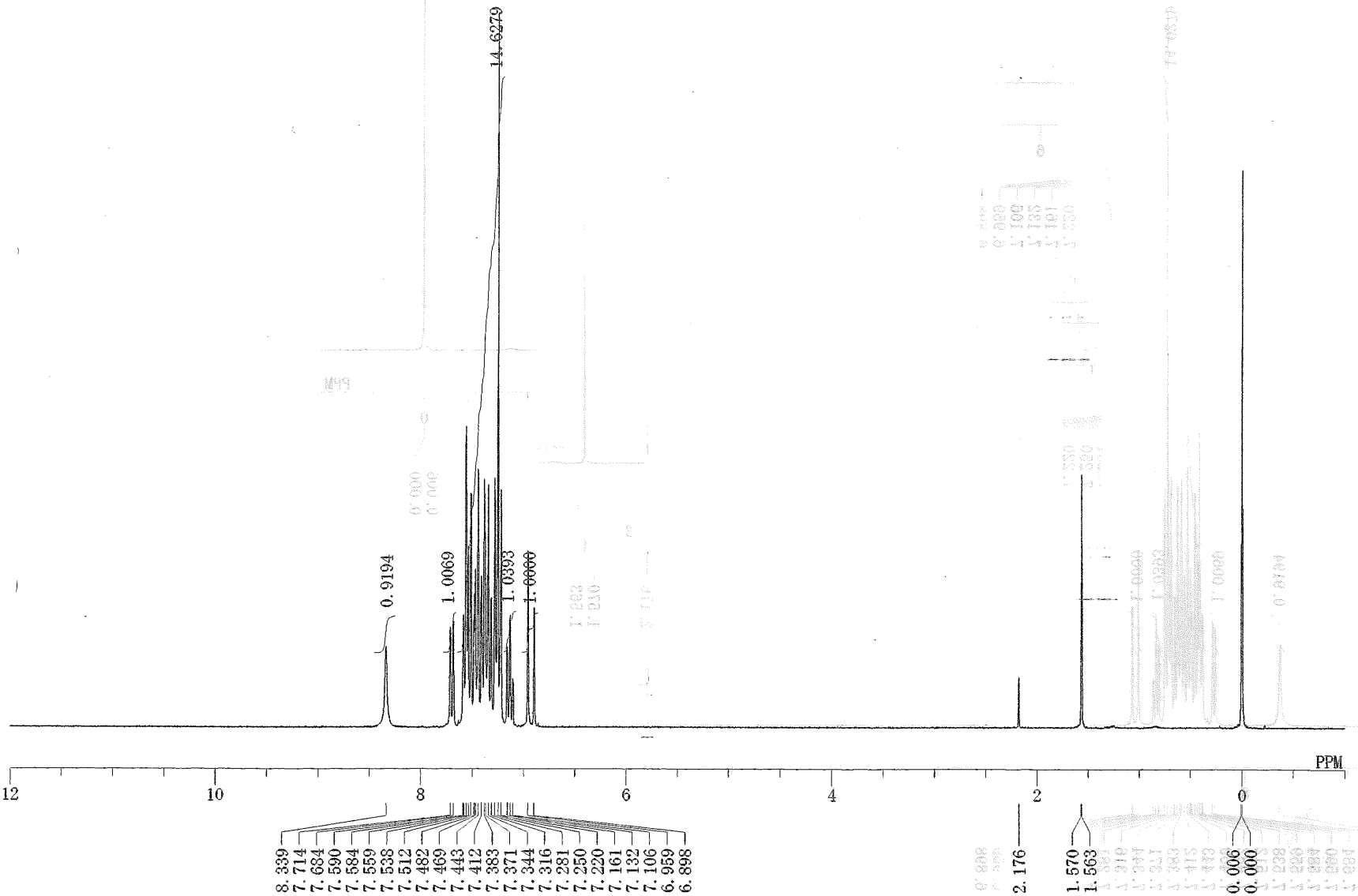


M2-OH-R72


Ph
N
H
Ph

2d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1.0000
PPM
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10
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4
2
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7.714
7.684
7.590
7.584
7.559
7.538
7.512
7.482
7.469
7.443
7.412
7.383
7.371
7.344
7.316
7.281
7.250
7.220
7.161
7.132
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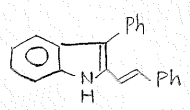
6.898
2.176
1.570
1.563
0.006
0.000

M2-OH-R72-fr6-8



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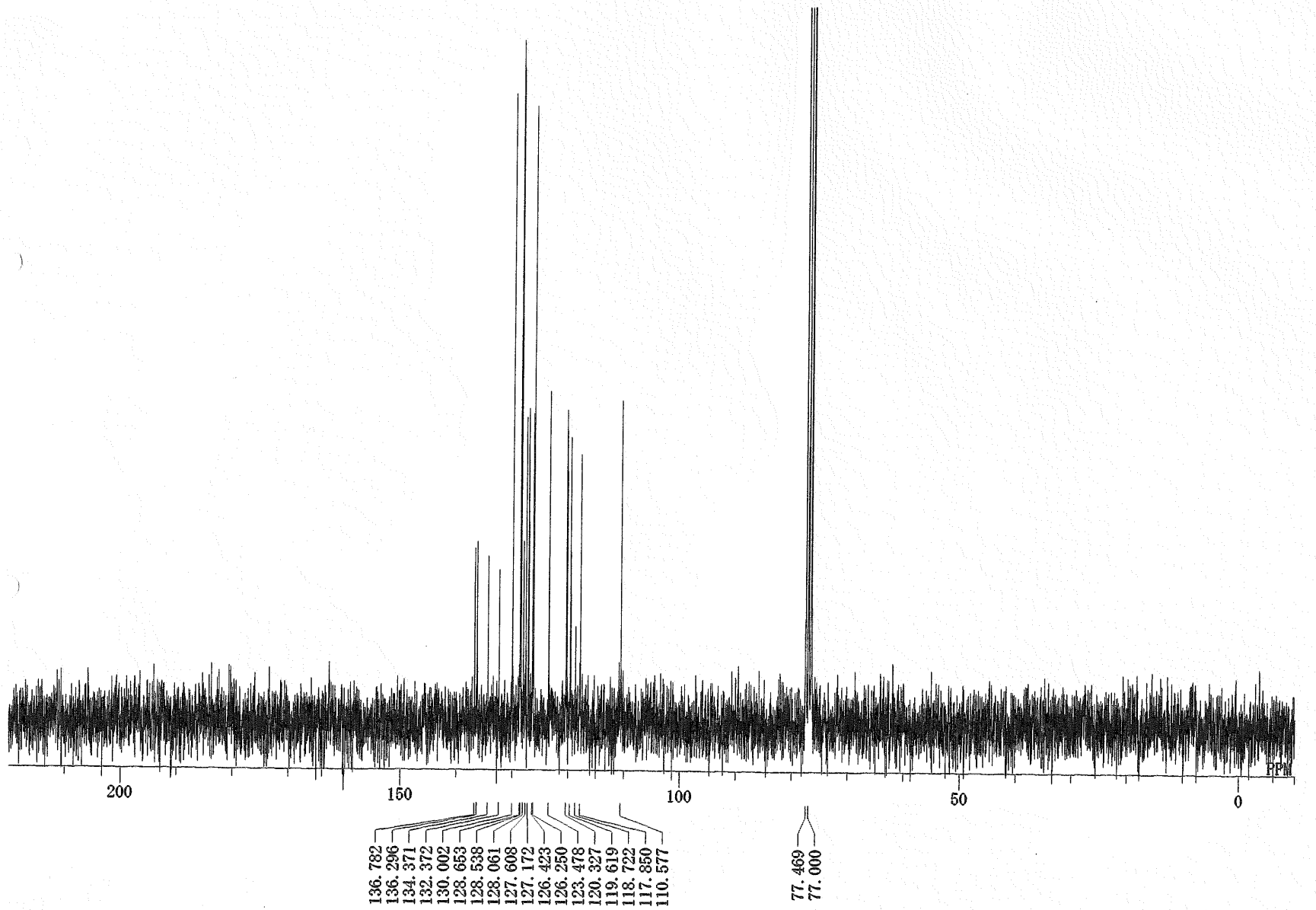
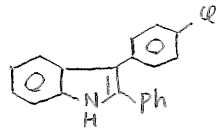


M2-OH-R88-fr6-15



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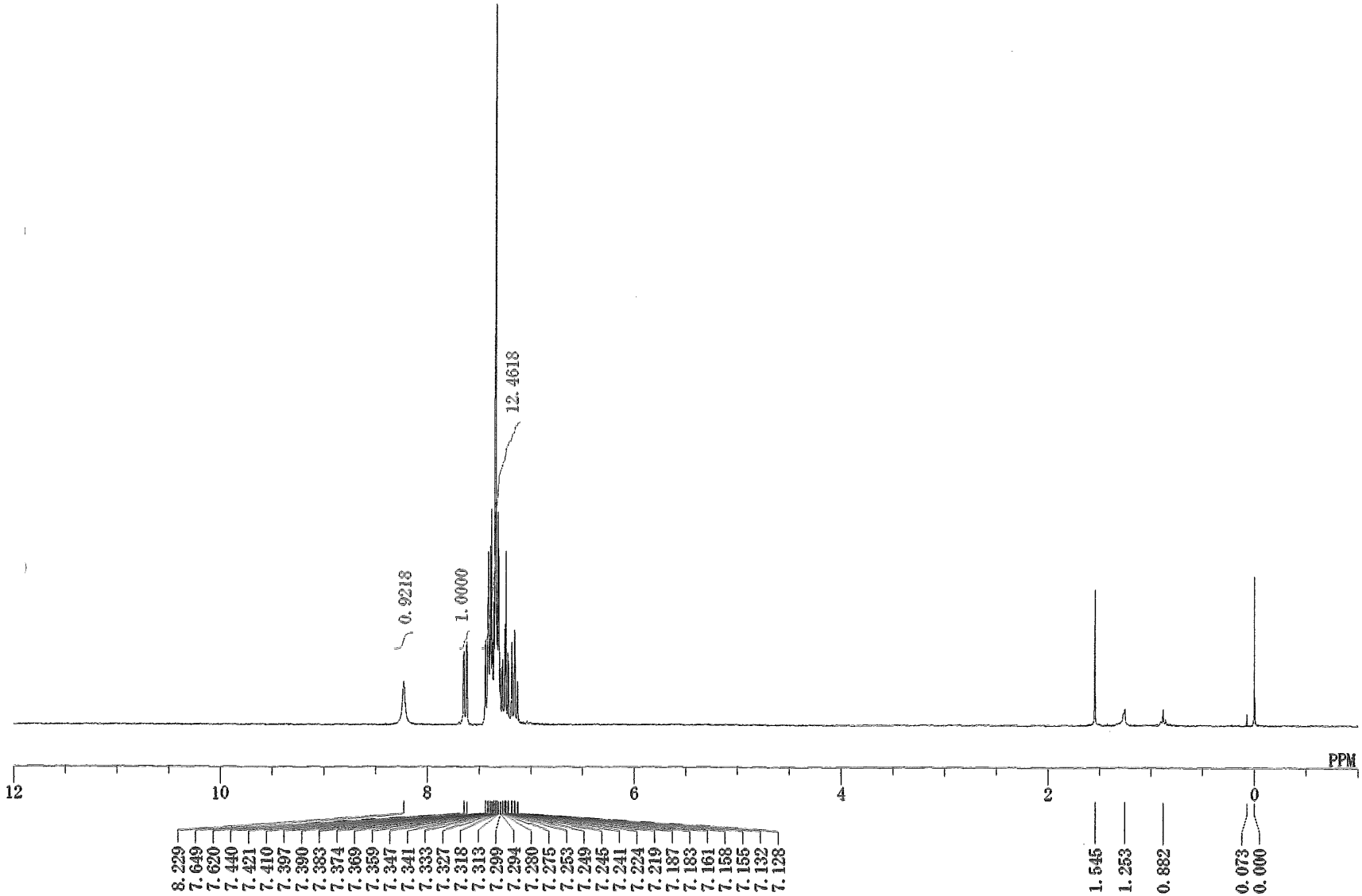
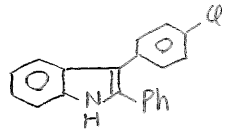


M2-OH-R88-fr6-15-13C



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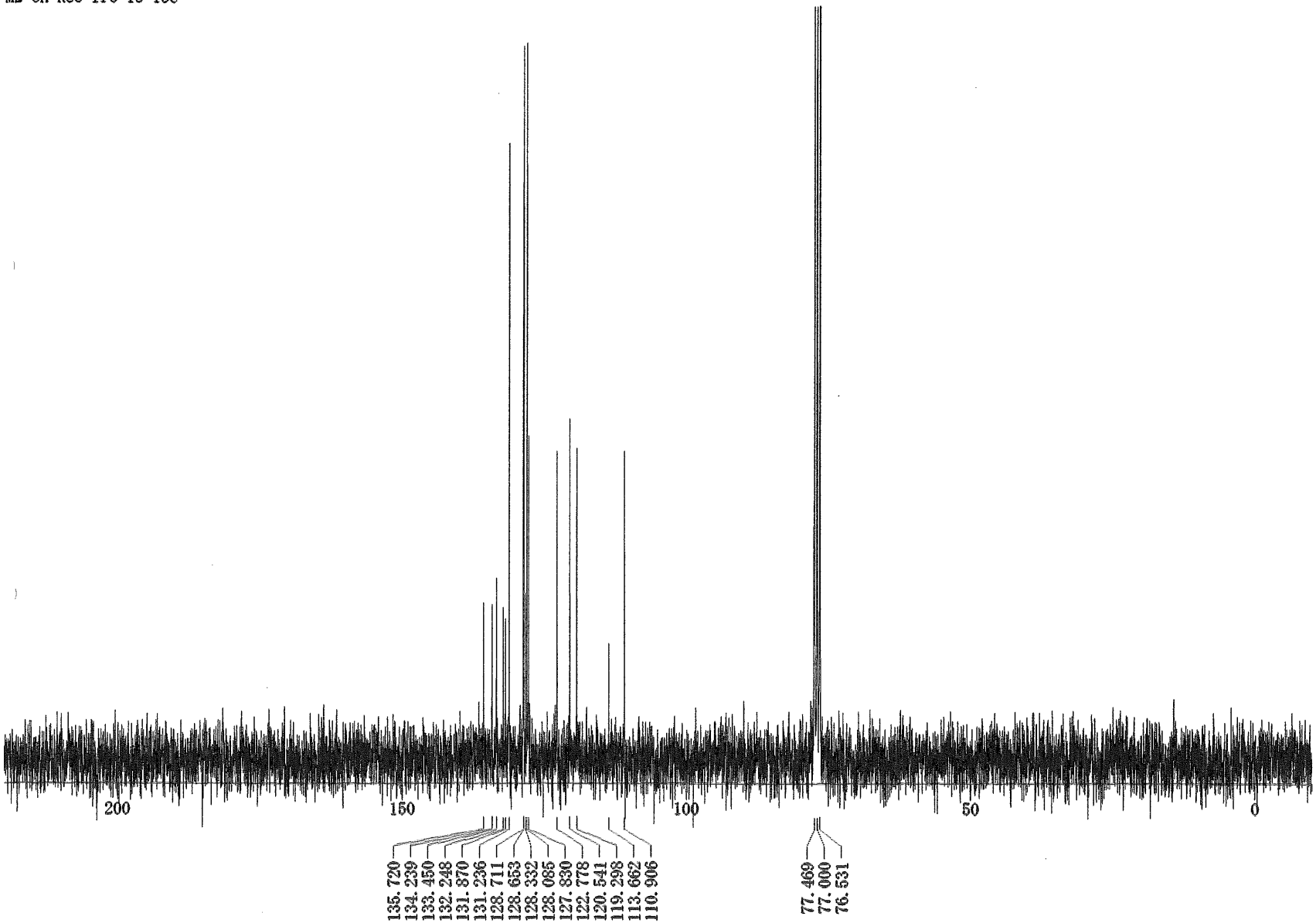
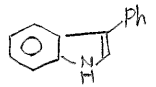


M2-OH-R65-fr14-19-GPC-3



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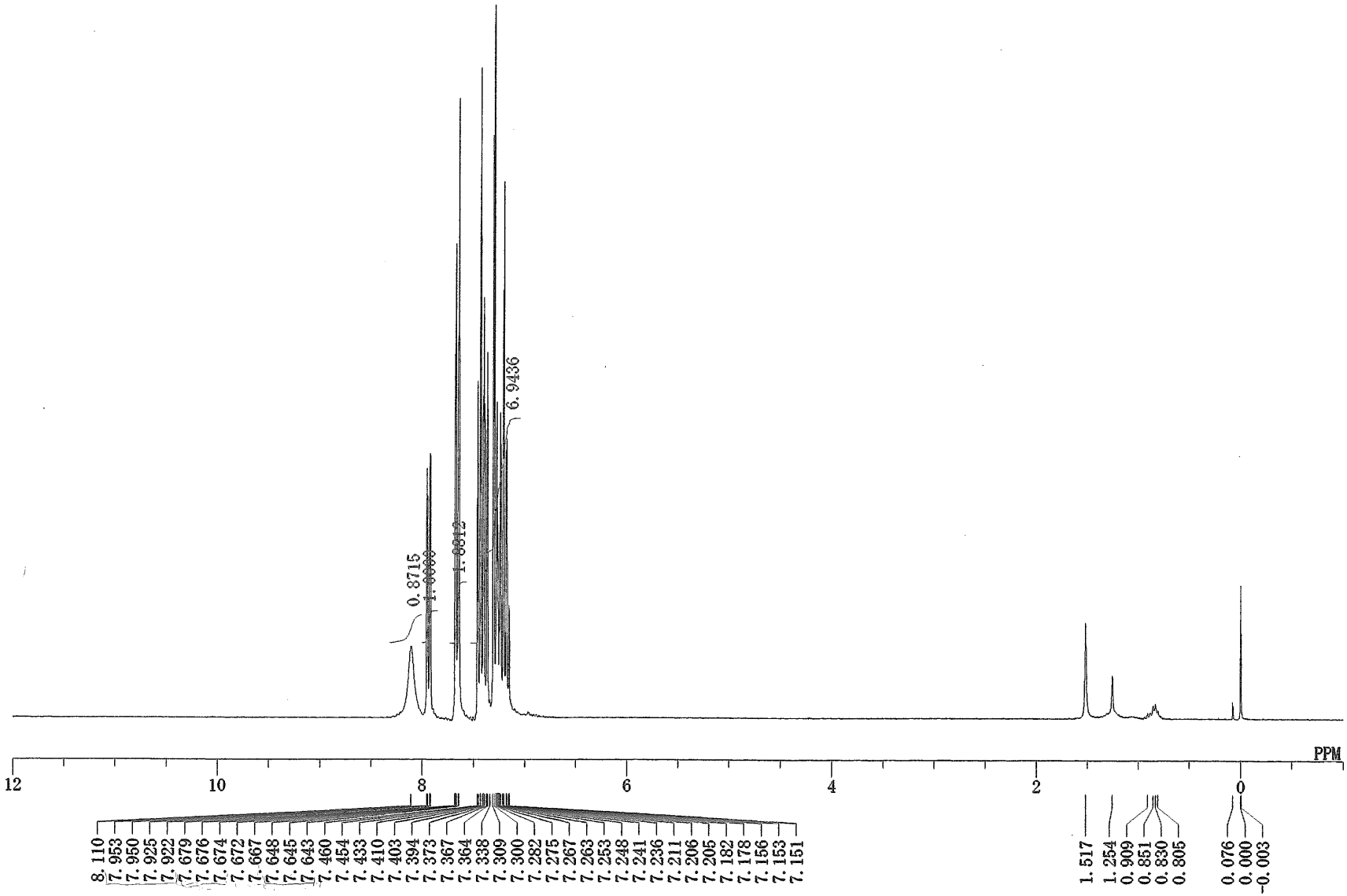
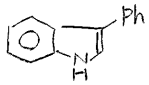
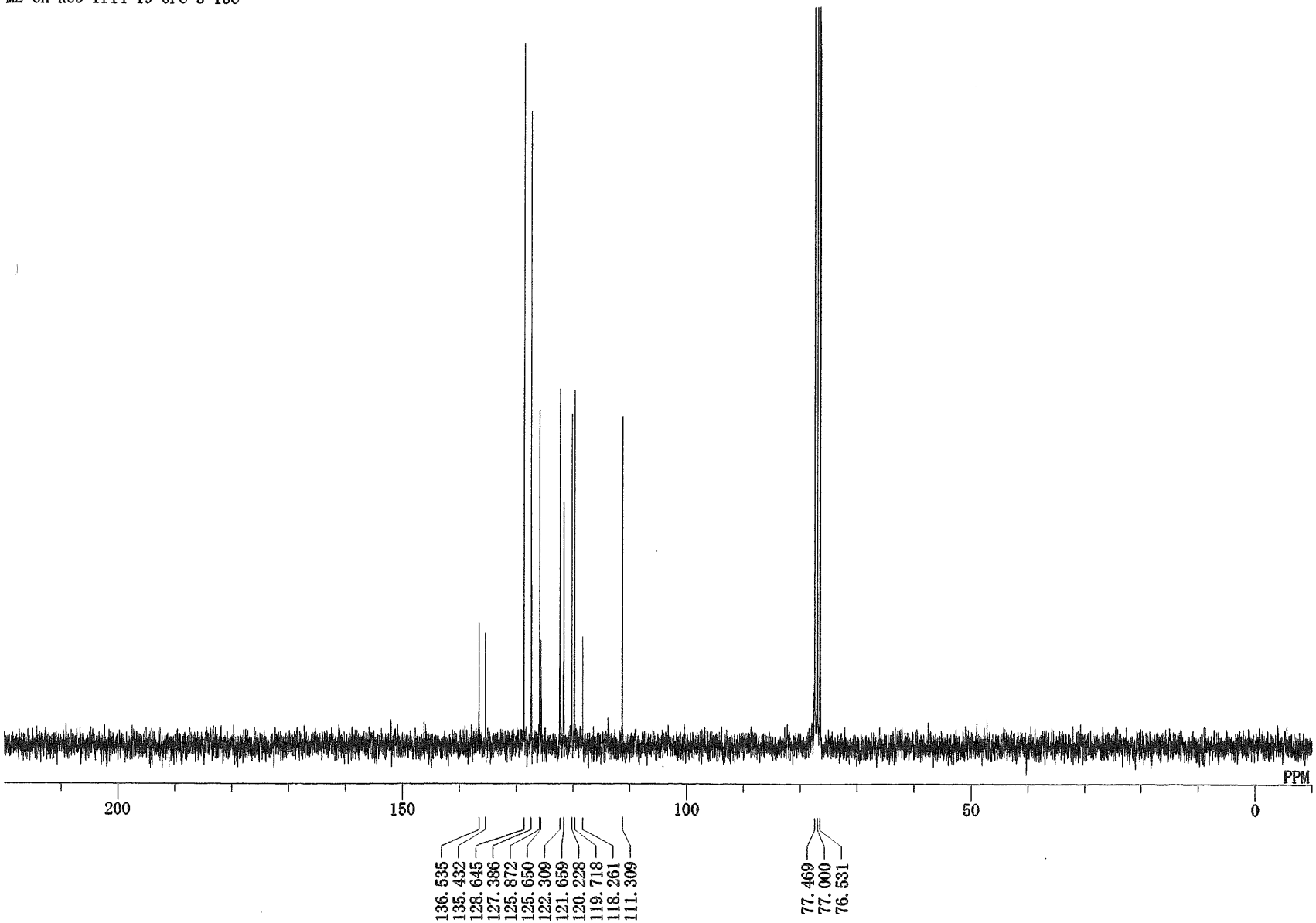


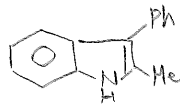
M2-OH-R65-fr14-19-GPC-3-13C



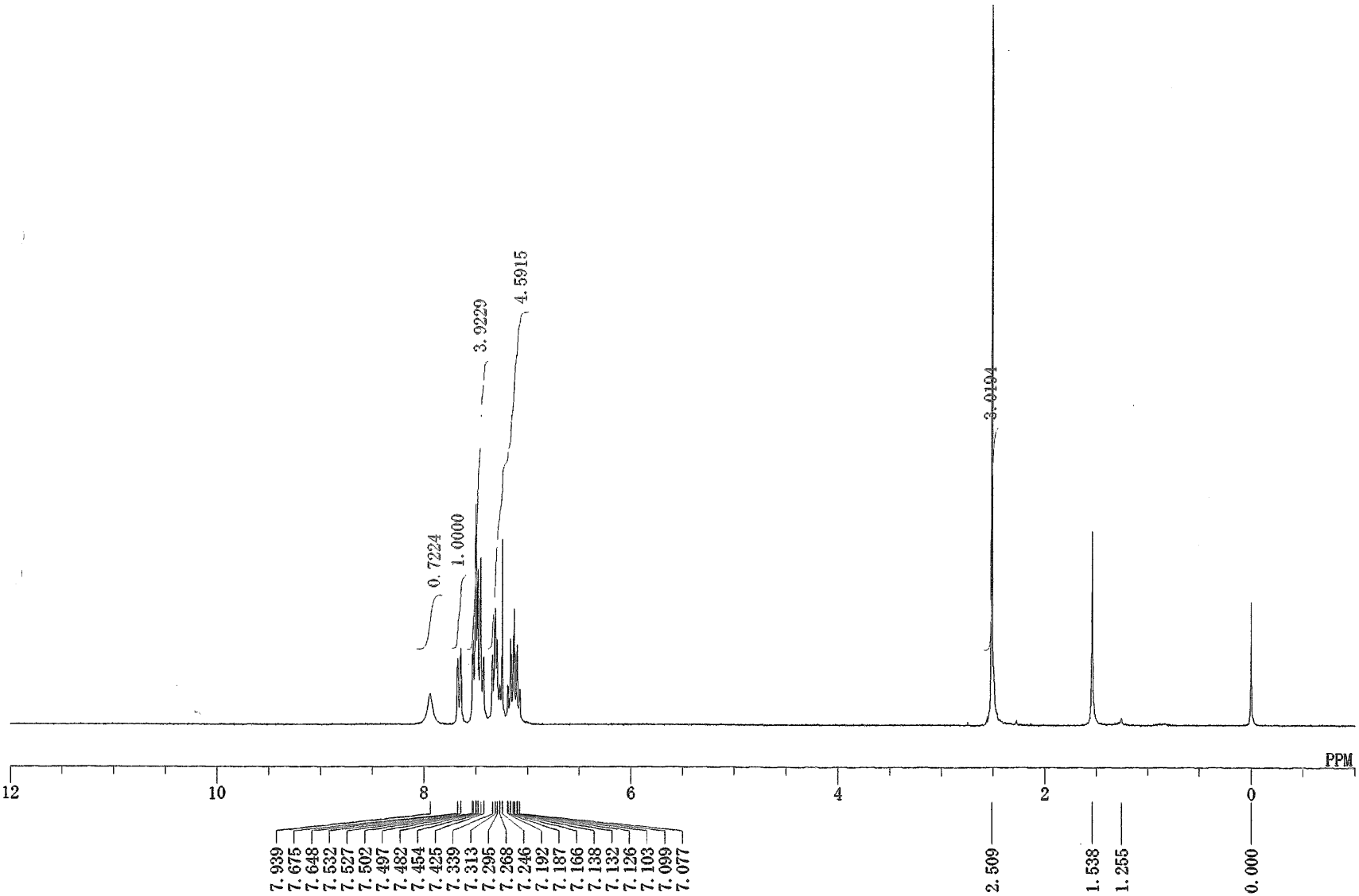
2f



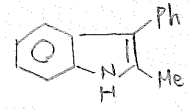
M1-OH-R55-fr9-12-GPC



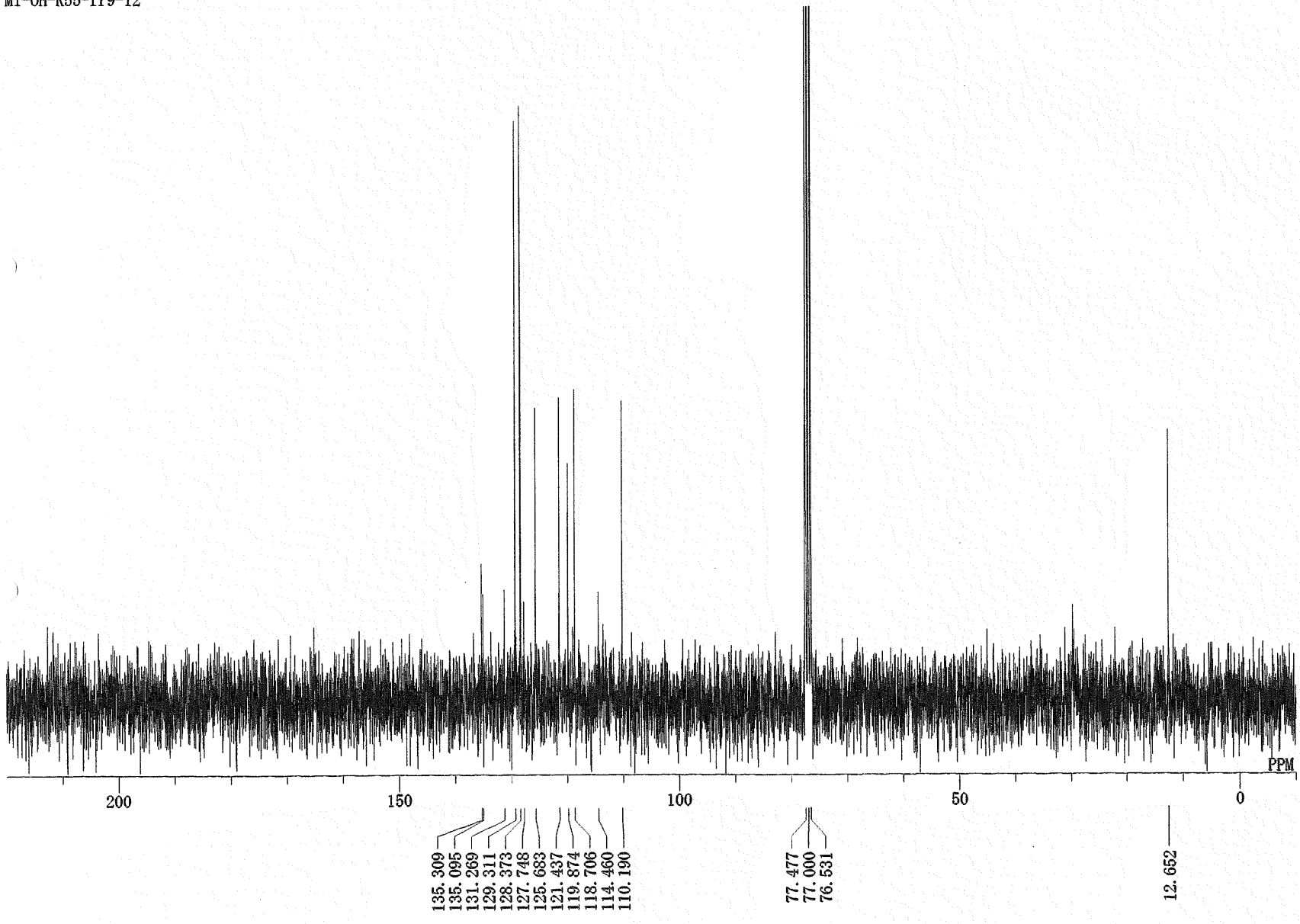
2g



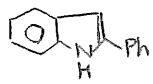
M1-OH-R55-fr9-12



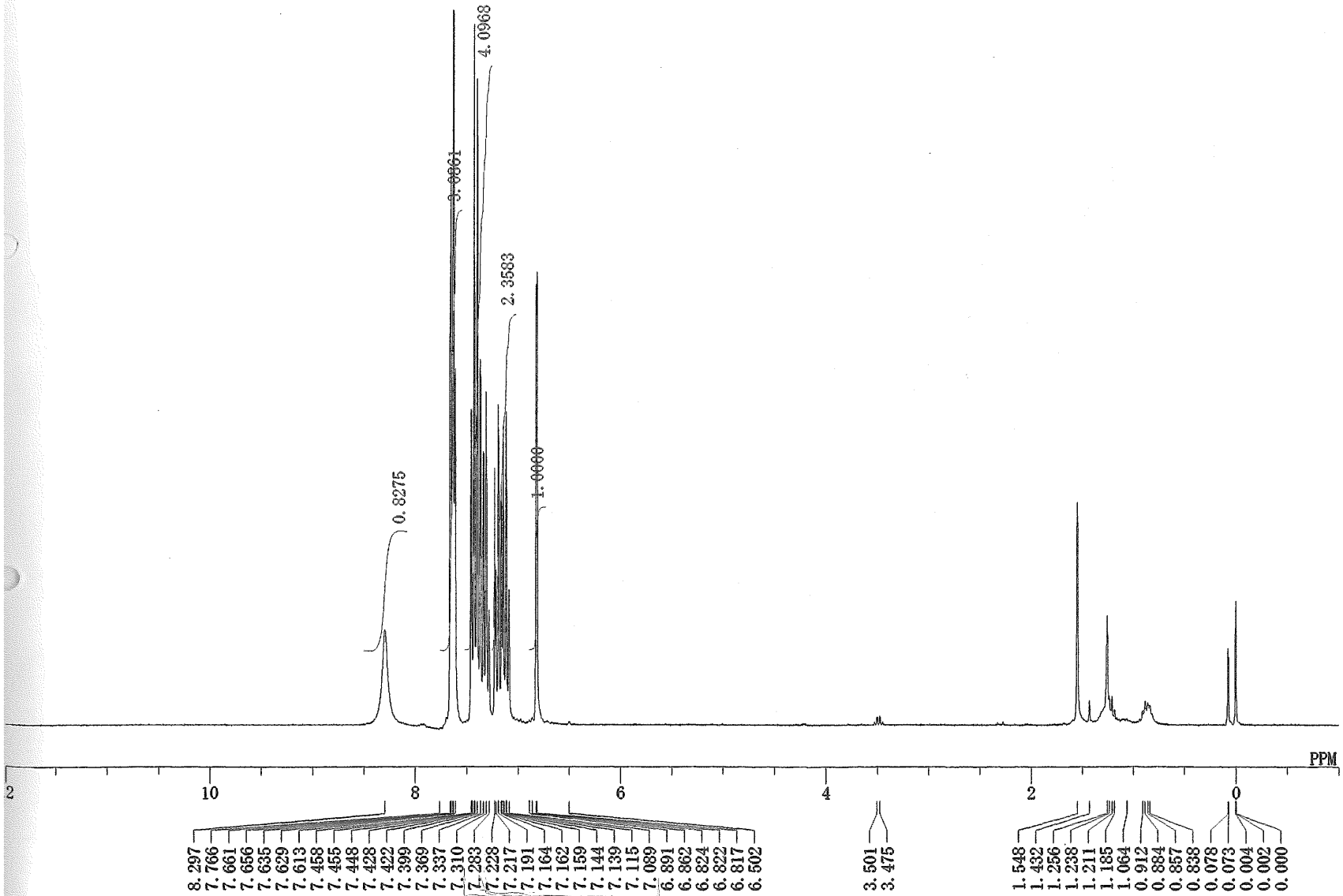
2g



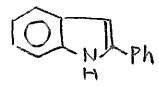
M1-OH-P23-indole



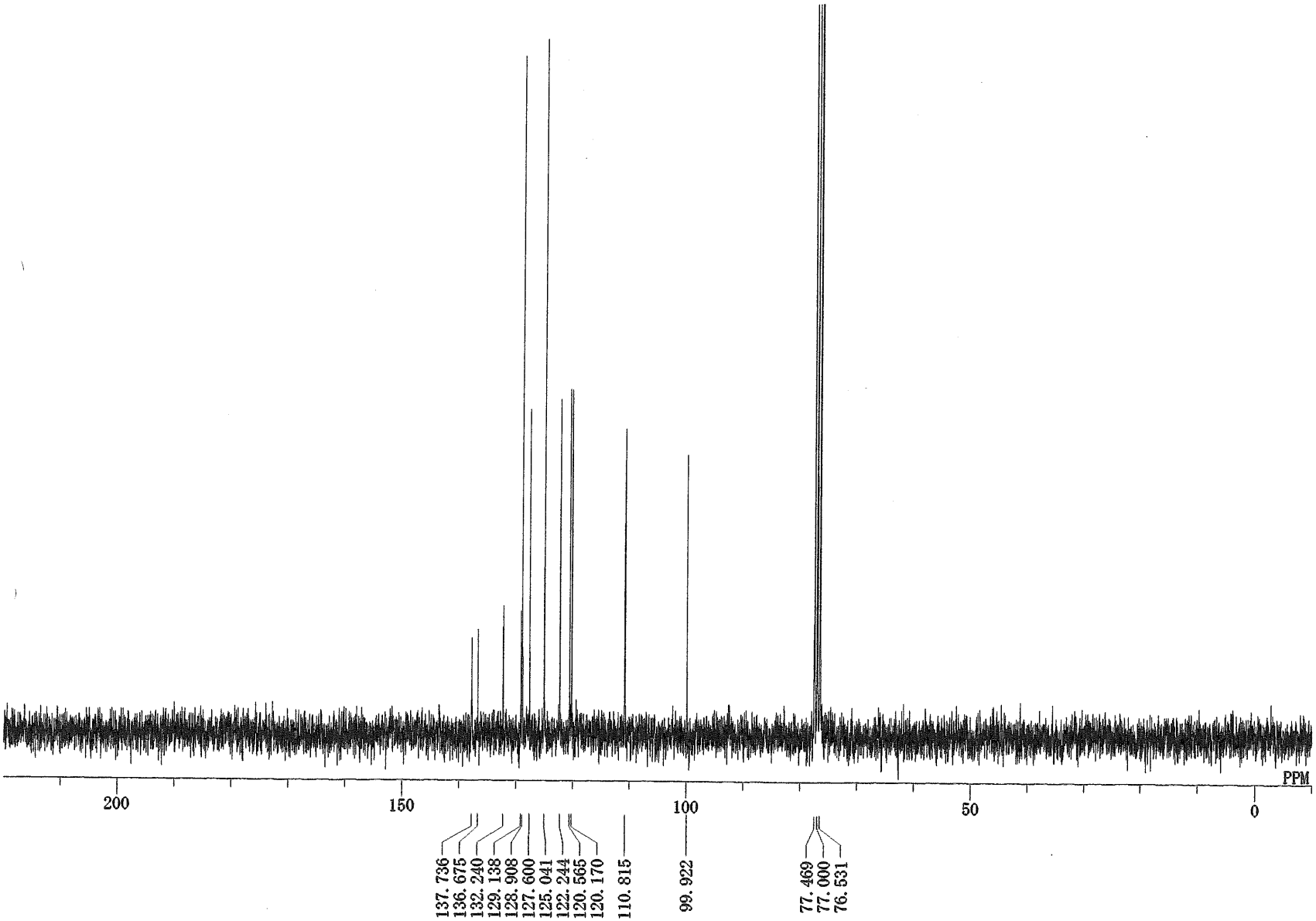
2h

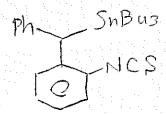


M1-OH-P23-indole



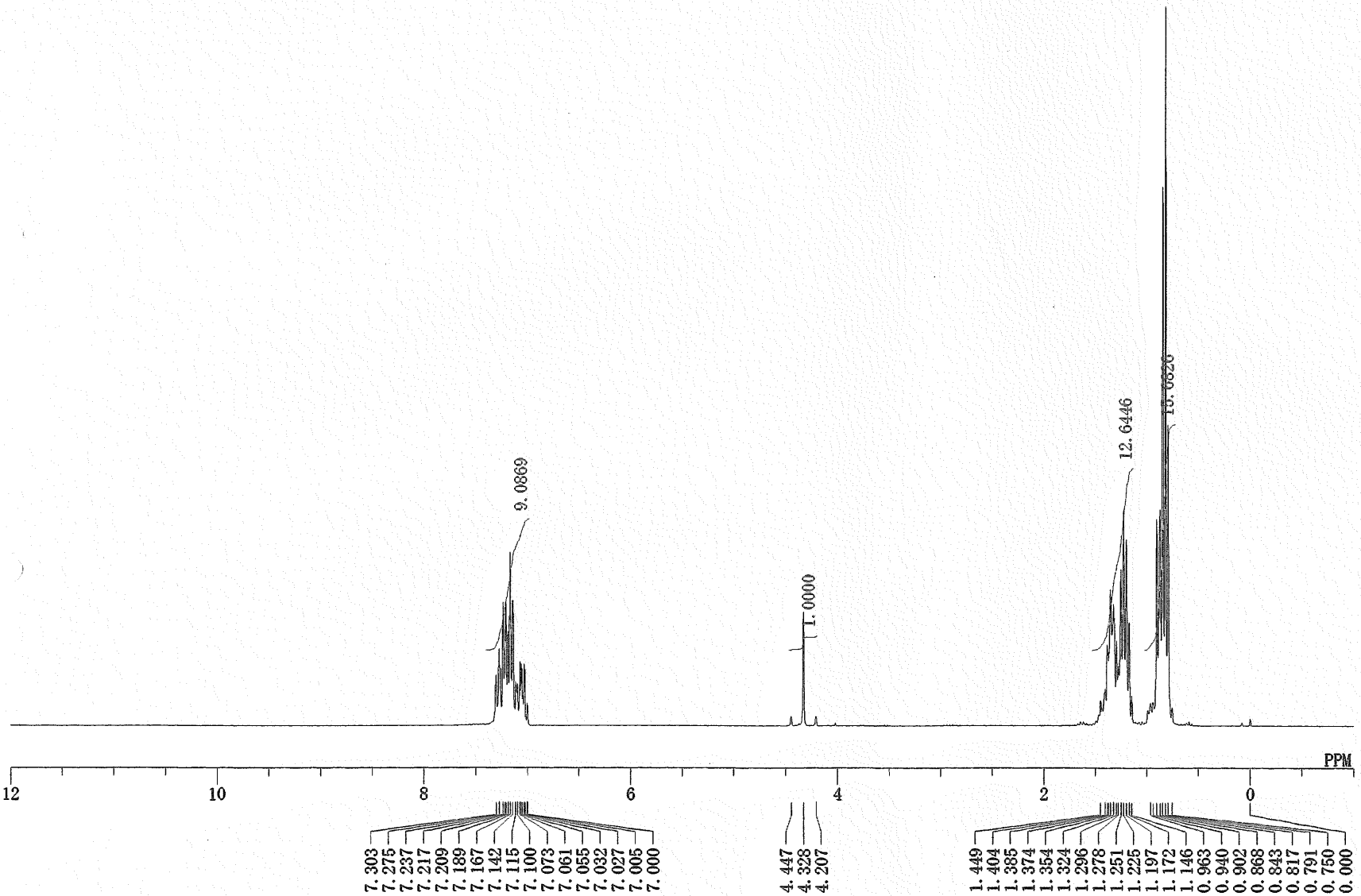
2h




Ph
SnBu3
NCS

3a

M2-OH-P76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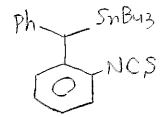
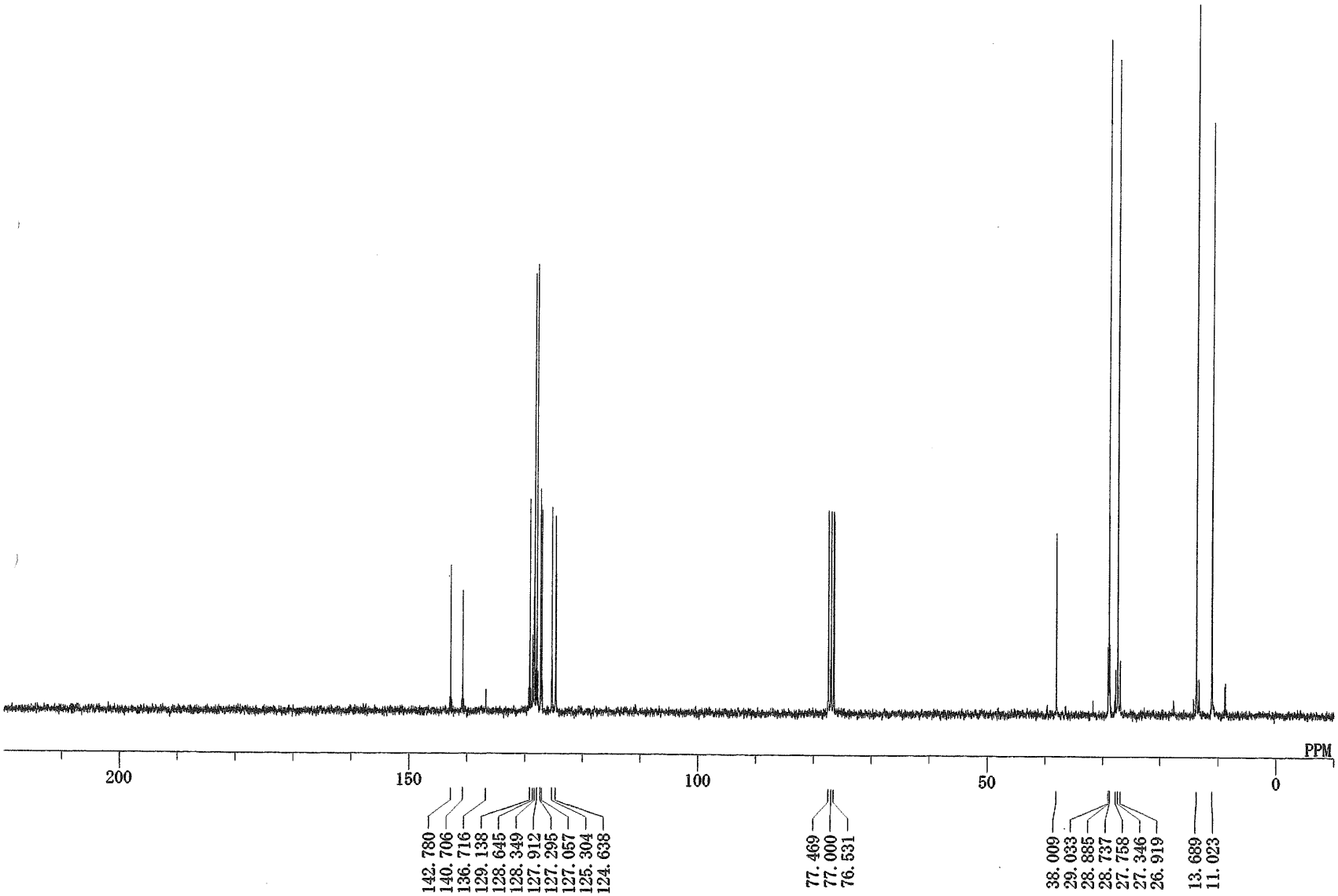
10.0820
PPM
12
10
8
6
4
2
0
7.303
7.275
7.237
7.217
7.209
7.189
7.167
7.142
7.115
7.100
7.073
7.061
7.055
7.032
7.027
7.005
7.000
4.447
4.328
4.207
1.449
1.404
1.385
1.374
1.354
1.324
1.296
1.278
1.251
1.225
1.197
1.172
1.146
0.963
0.940
0.902
0.868
0.843
0.817
0.791
0.750
0.000

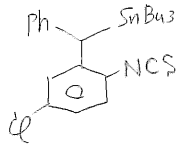
M2-OH-P76-13C



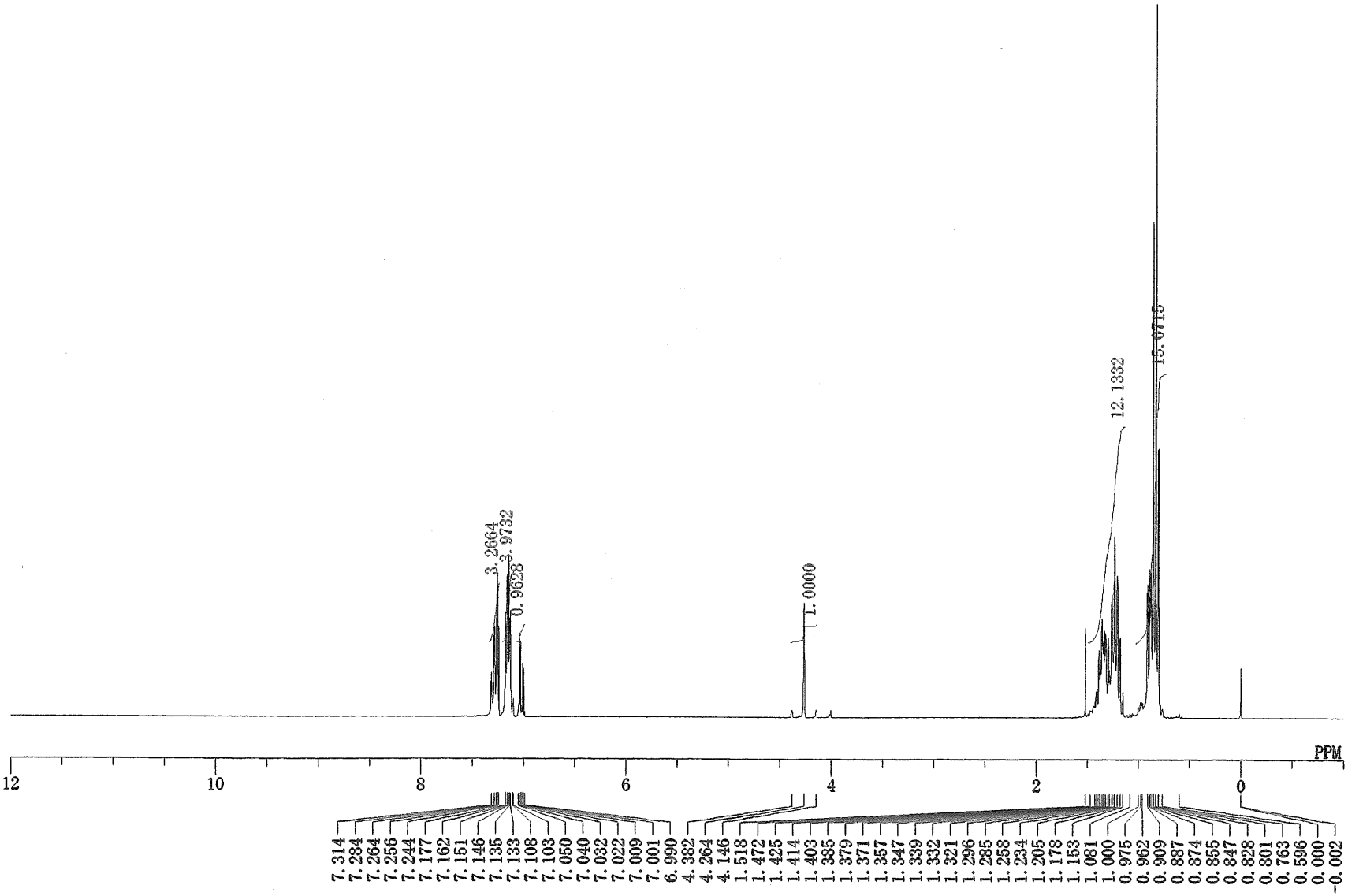
3a



M2-OH-P103


Ph
SnBu3
NCS
Cl

3b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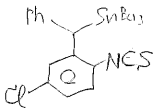
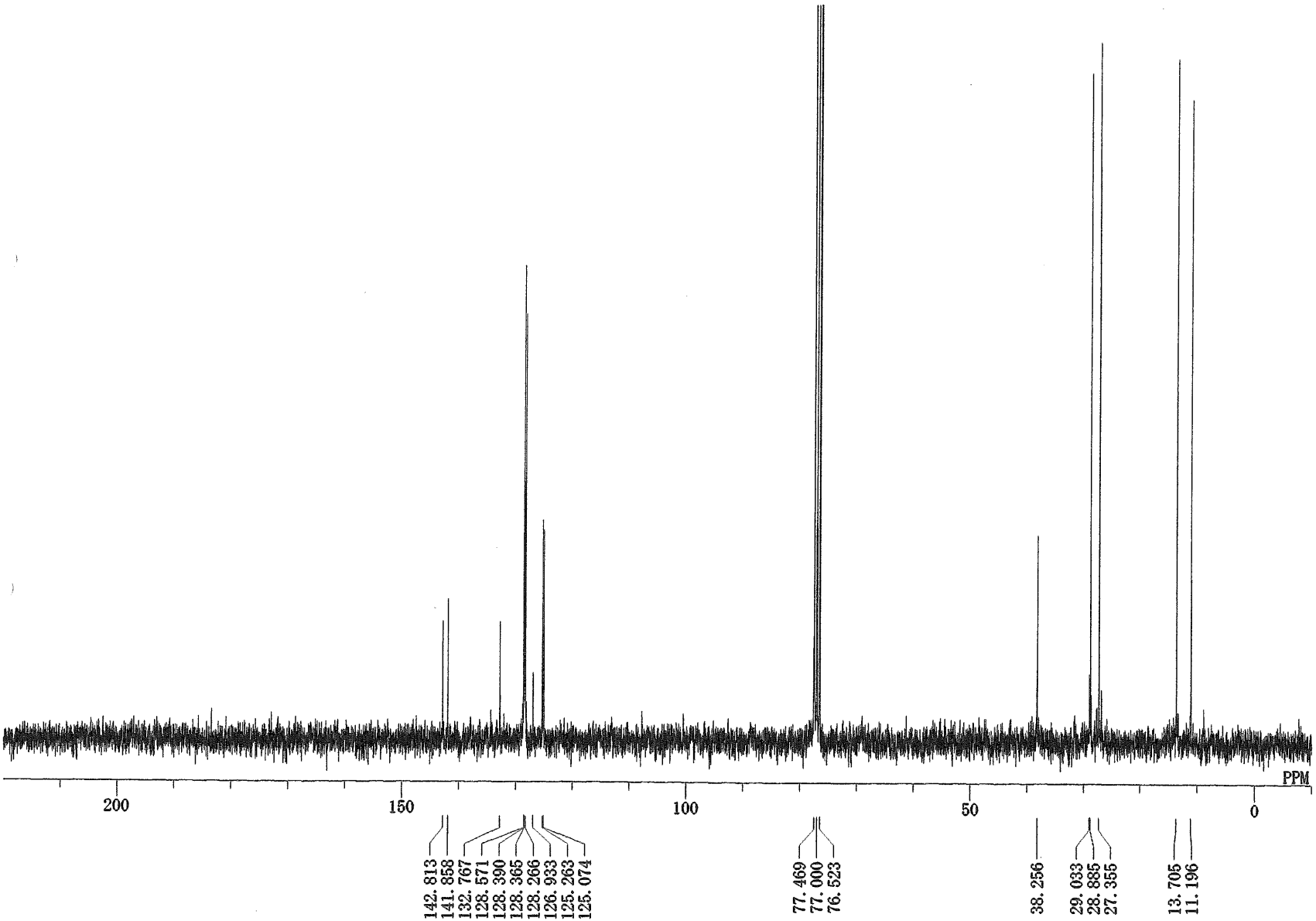
0.9628
1.0000
12.1332
15.6715
PPM
12
10
8
6
4
2
0
7.314
7.284
7.264
7.256
7.244
7.177
7.162
7.151
7.146
7.135
7.133
7.108
7.103
7.050
7.040
7.032
7.022
7.009
7.001
6.990
4.382
4.264
4.146
1.518
1.472
1.425
1.414
1.403
1.385
1.379
1.371
1.357
1.347
1.339
1.332
1.321
1.296
1.285
1.258
1.234
1.205
1.178
1.153
1.081
1.000
0.975
0.962
0.909
0.887
0.874
0.855
0.847
0.828
0.801
0.763
0.596
0.000
-0.002

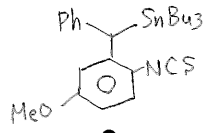
M2-OH-P103-13C



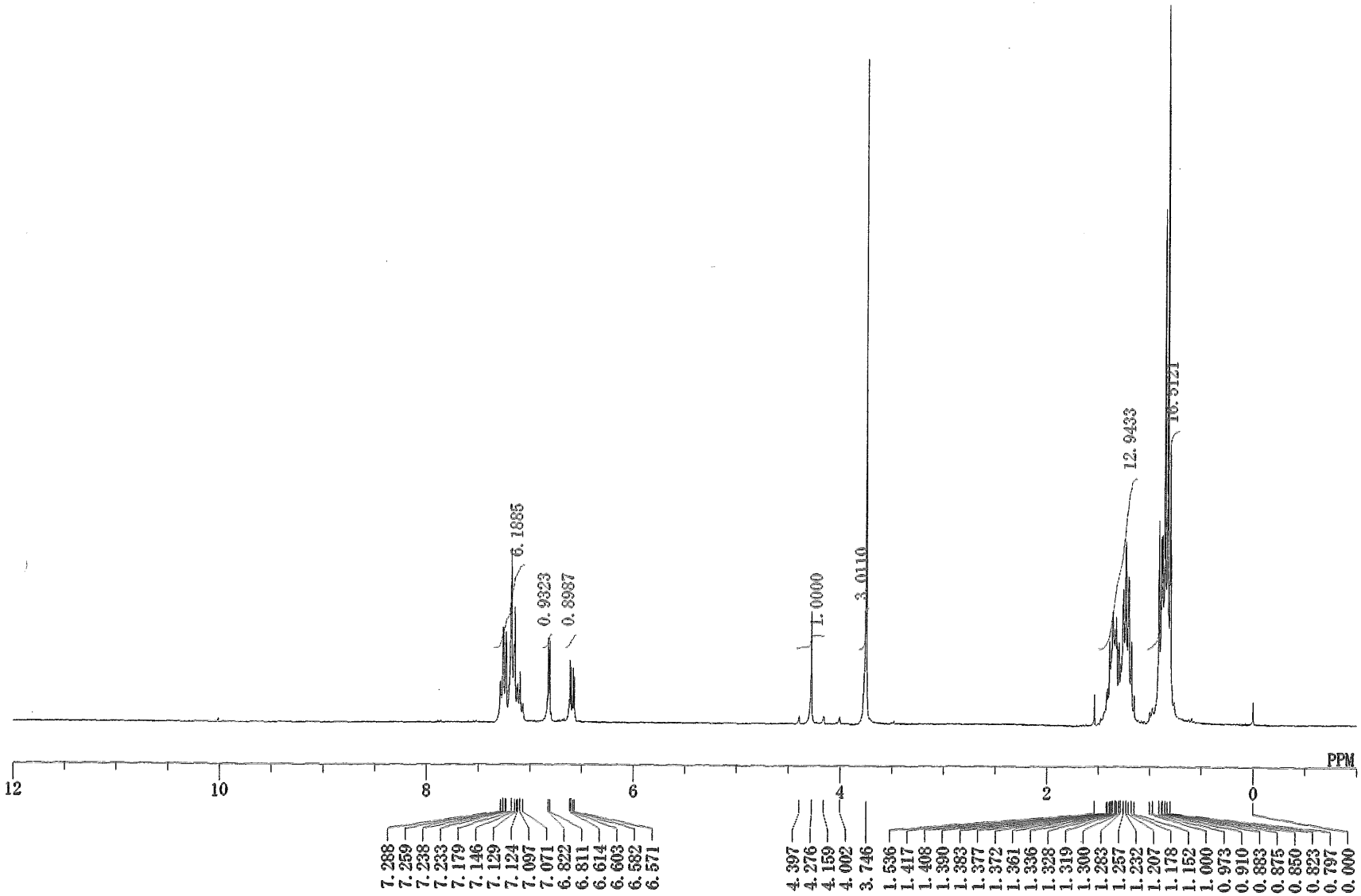
3b



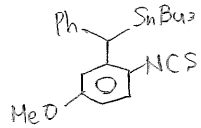
M2-OH-P115-13C



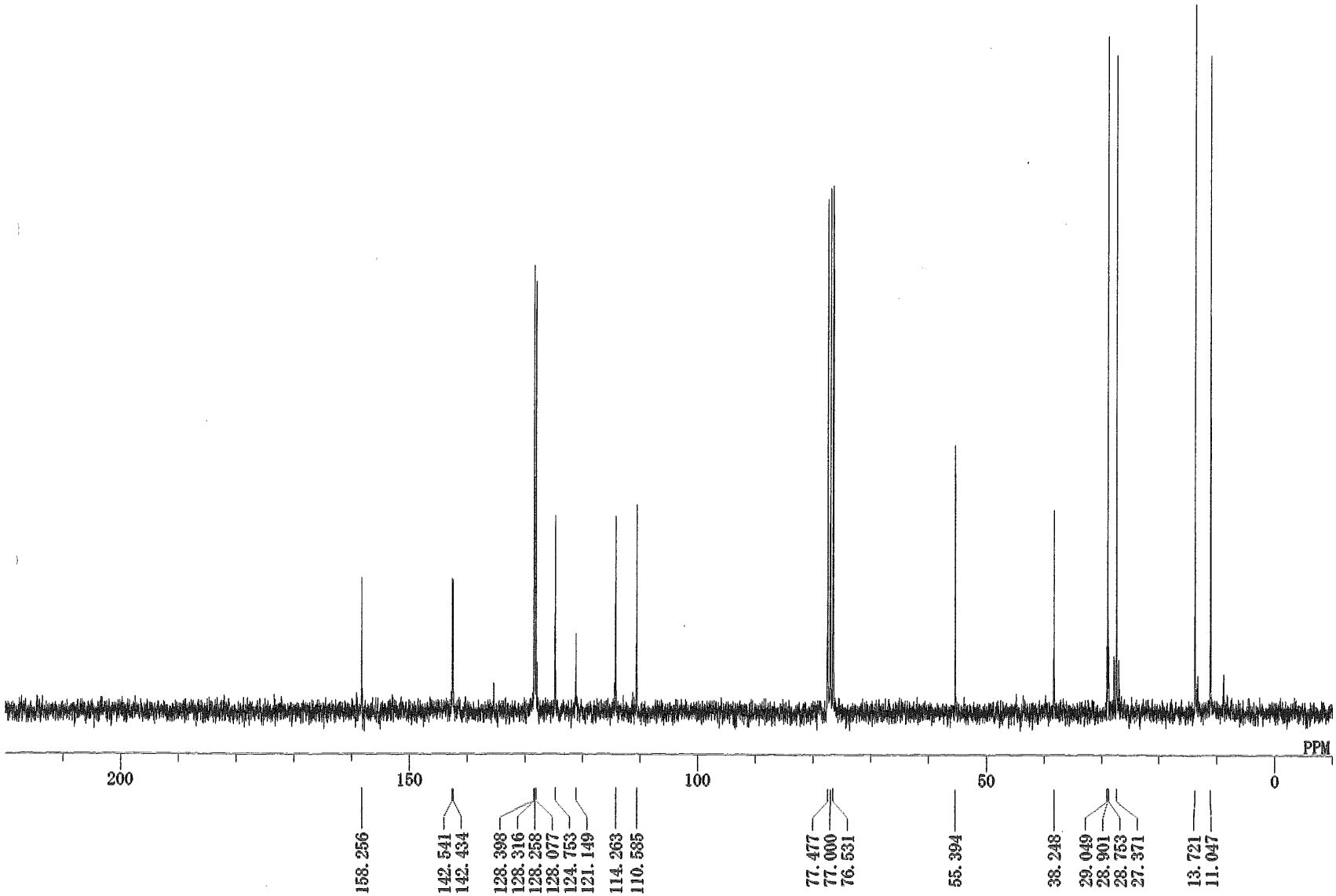
3c



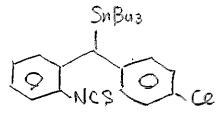
M2-OH-P115-13C



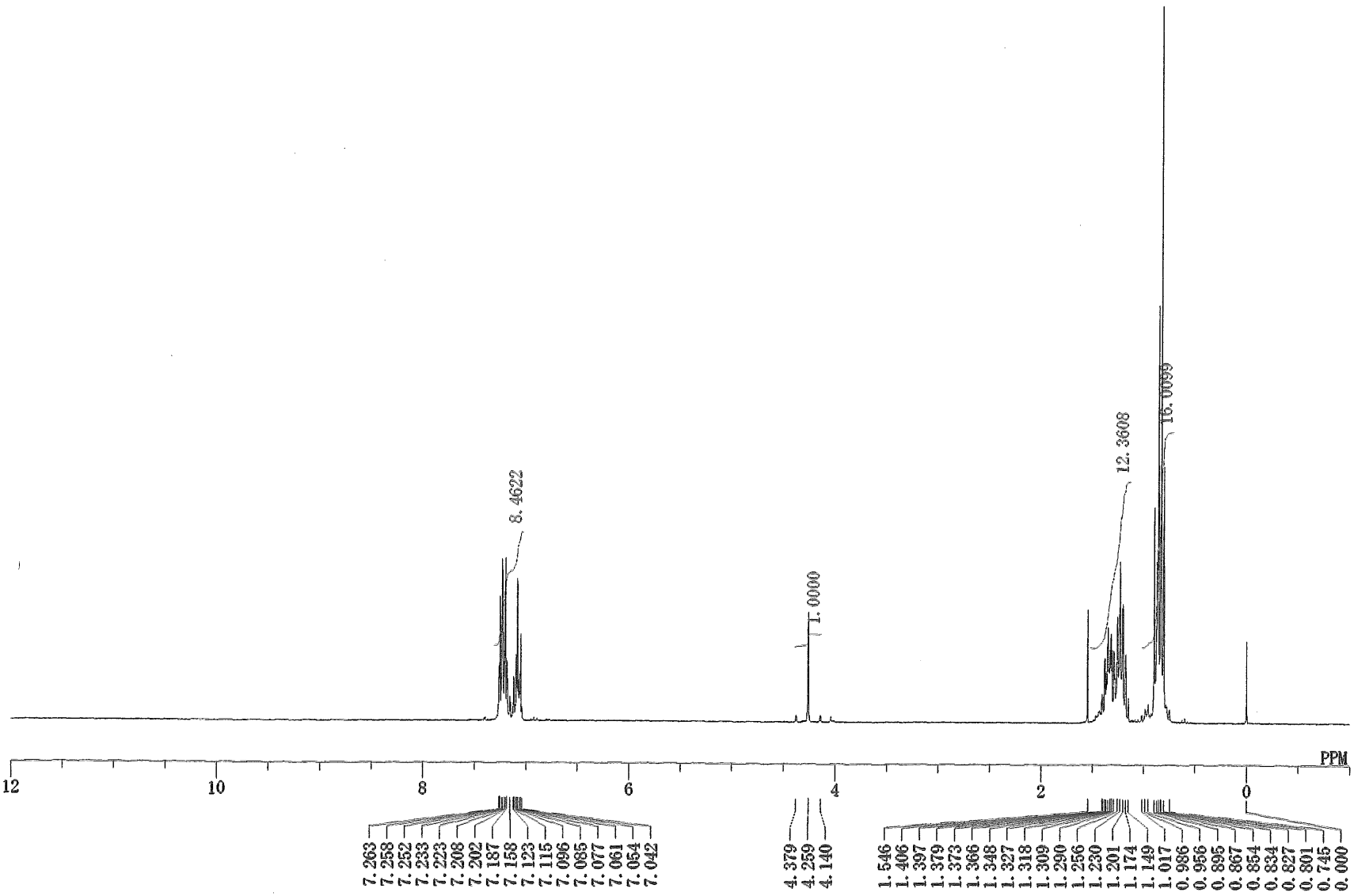
3c



M2-OH-P120


SnBu3
NCS
Ce

3d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12.3608
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PPM
12
10
8
6
4
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0
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7.252
7.233
7.223
7.208
7.202
7.187
7.158
7.123
7.115
7.096
7.085
7.077
7.061
7.054
7.042
4.379
4.259
4.140
1.546
1.406
1.397
1.379
1.373
1.366
1.348
1.327
1.318
1.309
1.290
1.256
1.230
1.201
1.174
1.149
1.017
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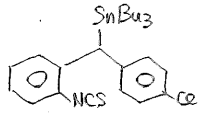
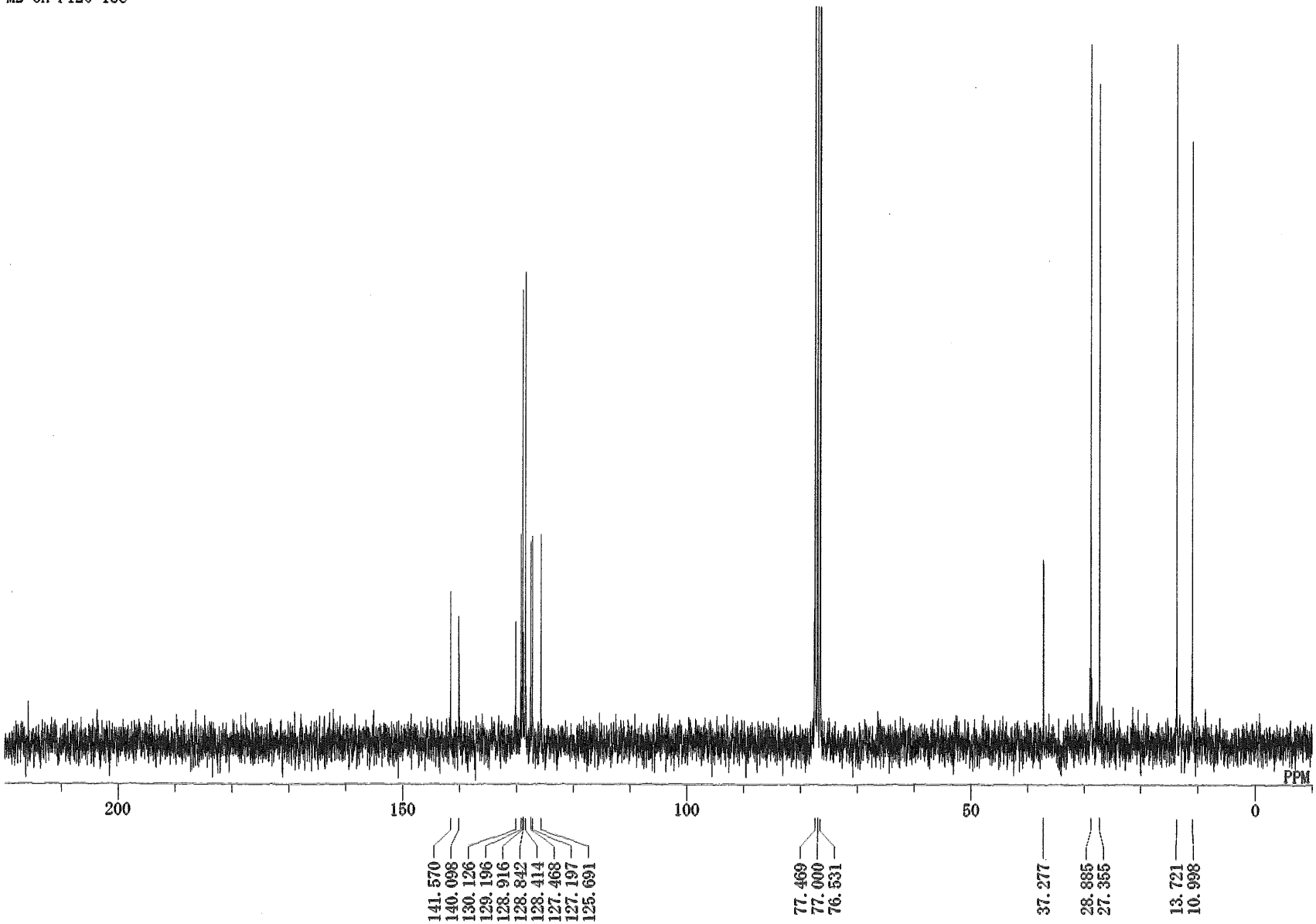
0.854
0.834
0.827
0.801
0.745
0.000

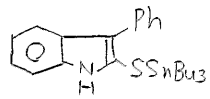
M2-OH-P120-13C



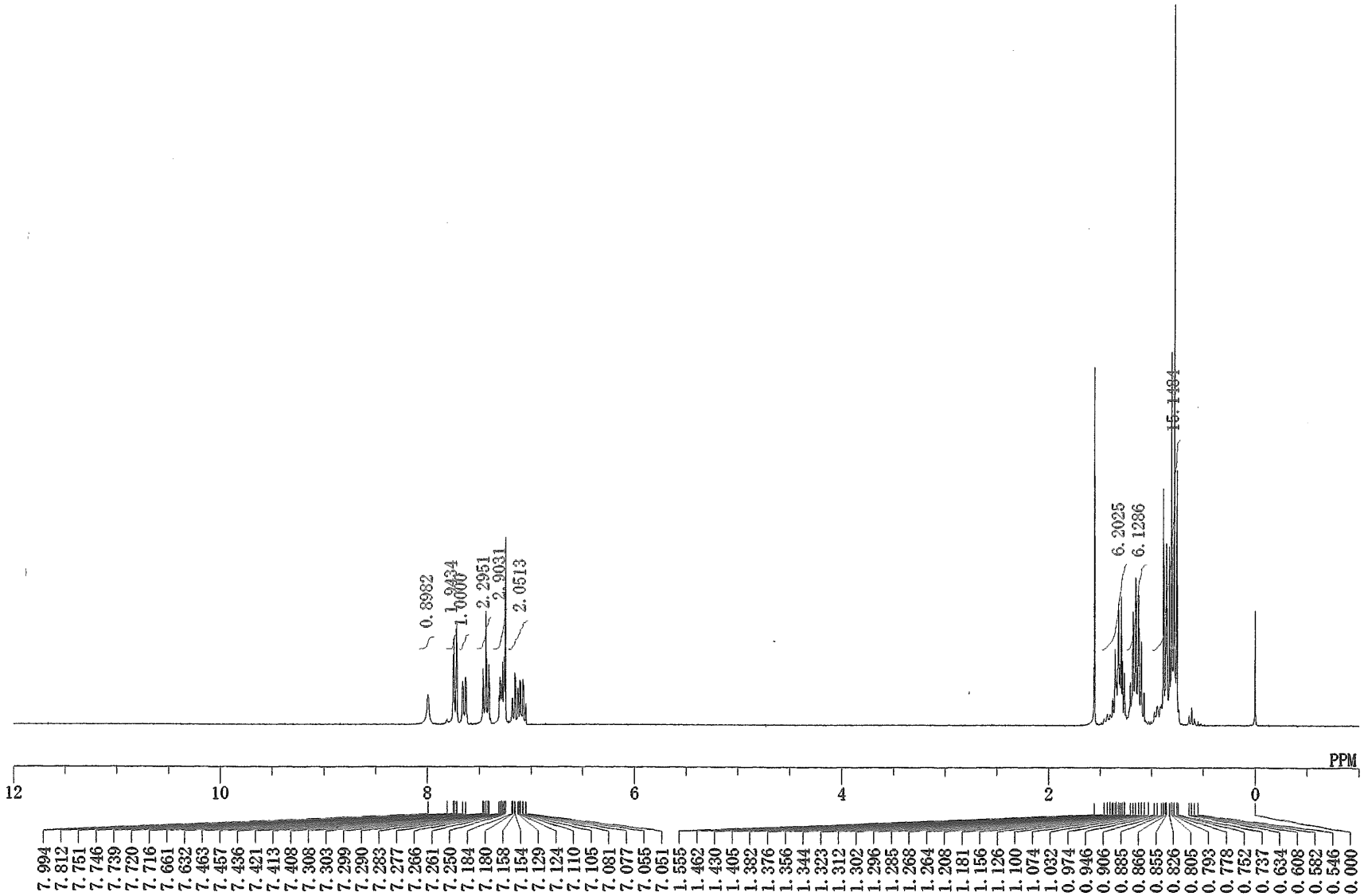
3d



M2-OH-R71


Ph
SSnBu3
N
H

4a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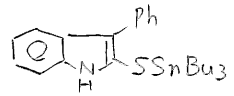
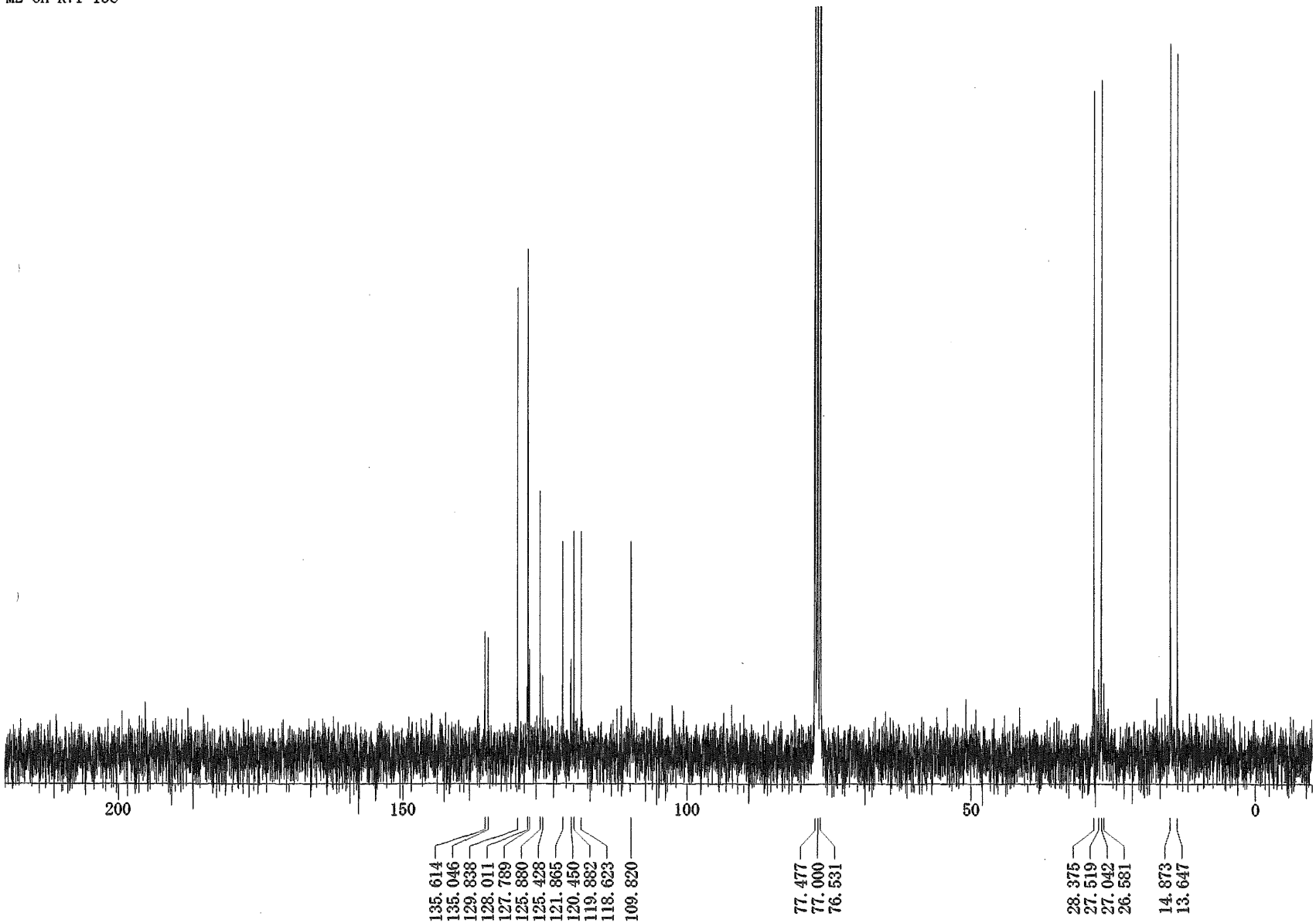
2.0513
6.2025
6.1286
15.1484
PPM
12
10
8
6
4
2
0
7.994
7.812
7.751
7.746
7.739
7.720
7.716
7.661
7.632
7.463
7.457
7.436
7.421
7.413
7.408
7.308
7.303
7.299
7.290
7.283
7.277
7.266
7.261
7.250
7.184
7.180
7.158
7.154
7.129
7.124
7.110
7.105
7.081
7.077
7.055
7.051
1.555
1.462
1.430
1.405
1.382
1.376
1.356
1.344
1.323
1.312
1.302
1.296
1.285
1.268
1.264
1.208
1.181
1.156
1.126
1.100
1.074
1.032
0.974
0.946
0.906
0.885
0.866
0.855
0.826
0.805
0.793
0.778
0.752
0.737
0.634
0.608
0.582
0.546
0.000

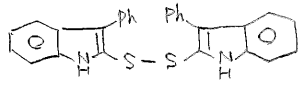
M2-OH-R71-13C



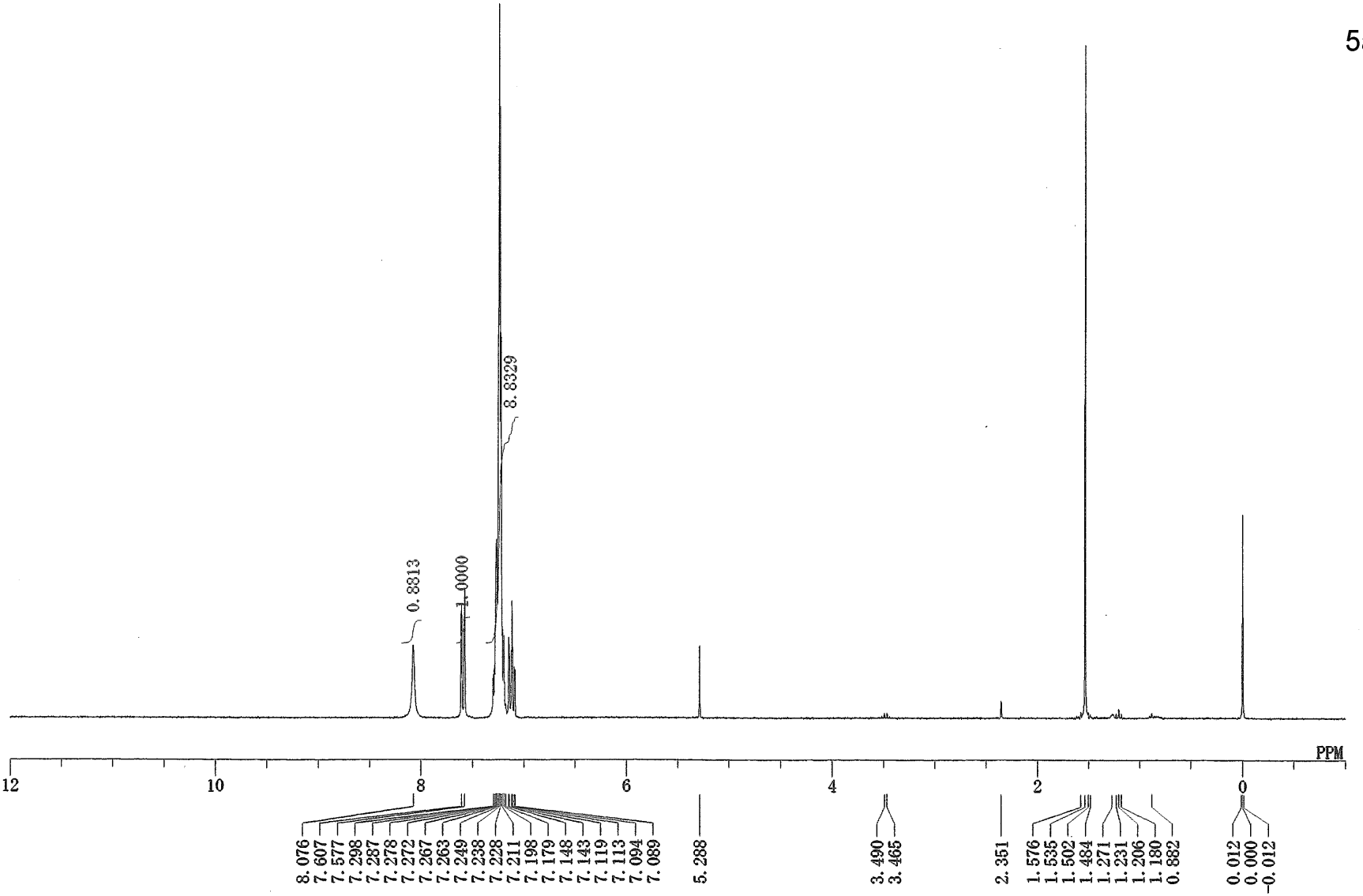
4a



M2-OH-R64-re~~~~
crys

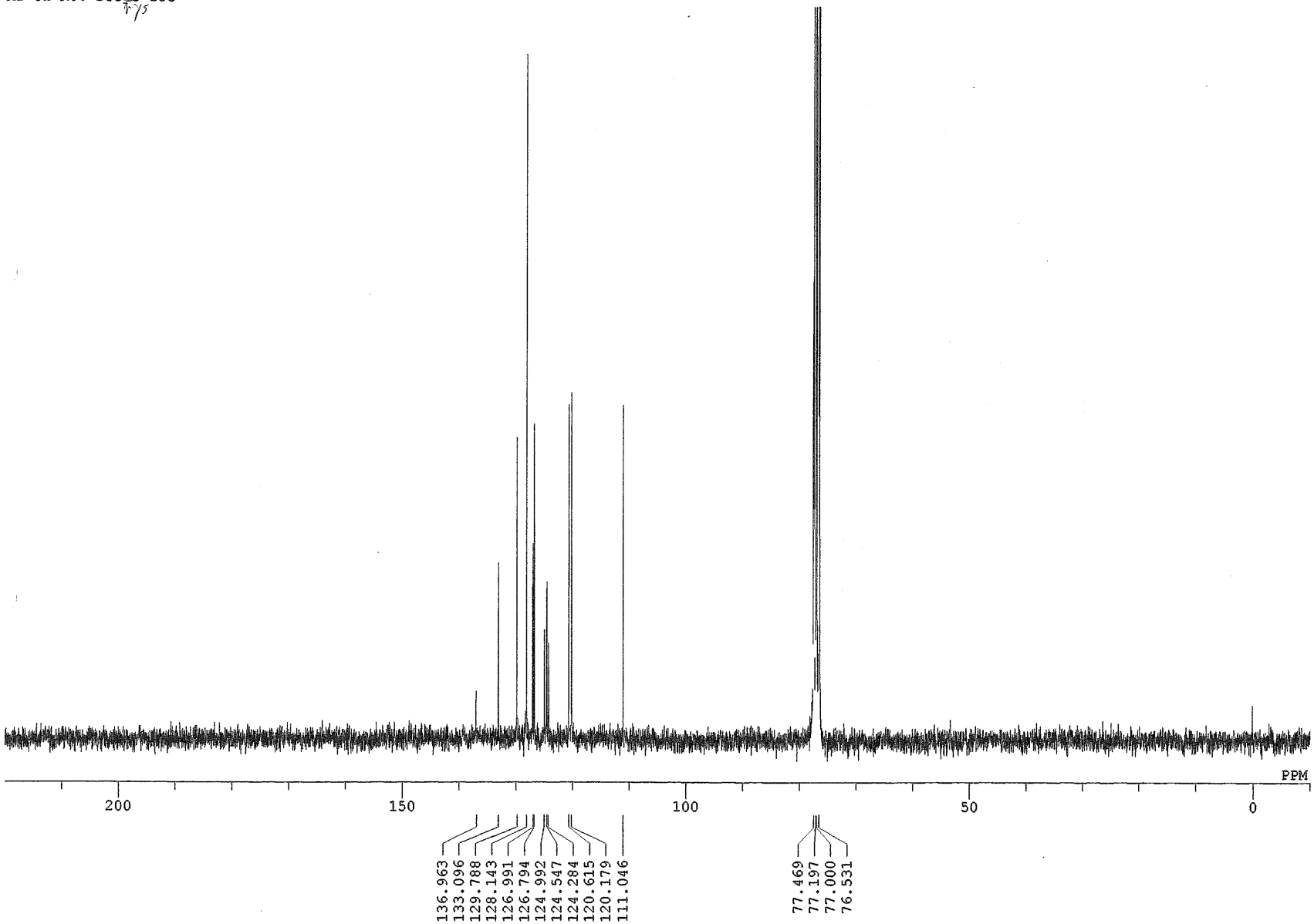


5a

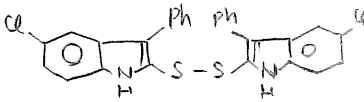


\\Komanmr\personal\ota\reaction\R64\M2-OH-R64-recyc-13C.als
M2-OH-R64-recyc-13C

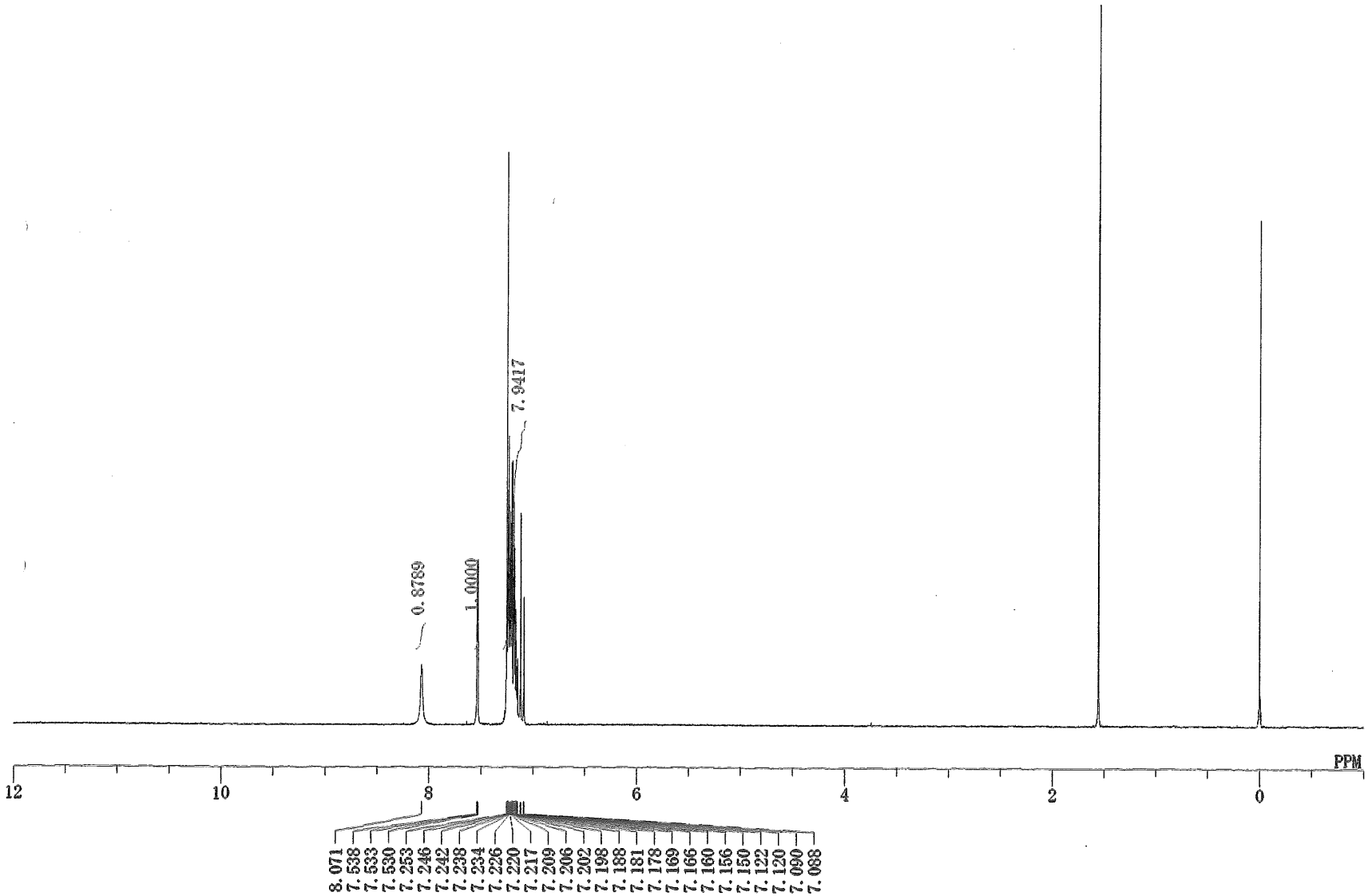
5a



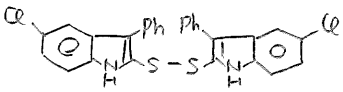
M2-OH-R83



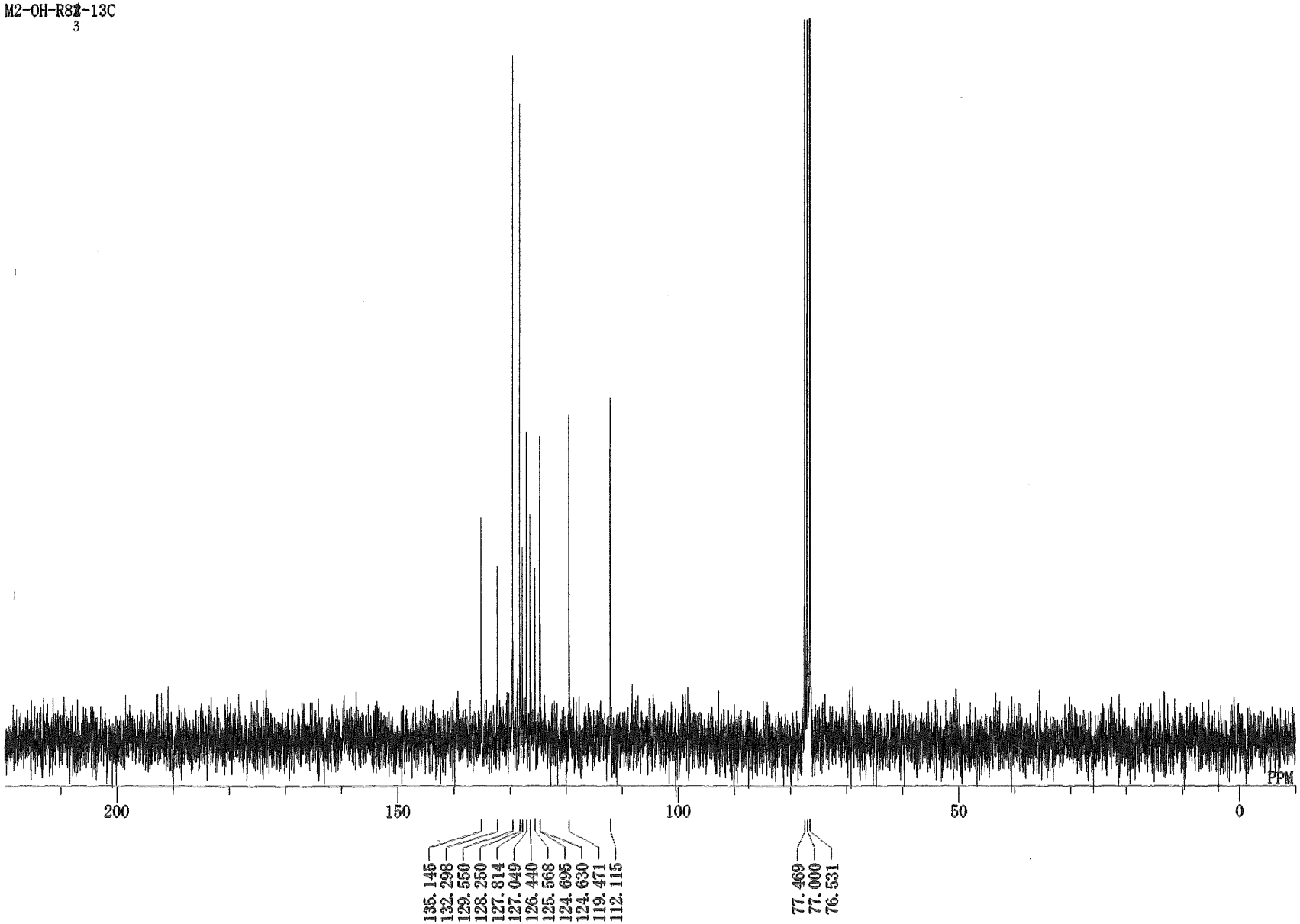
5b


0.8789
1.0000
7.9417
PPM
12
10
8
6
4
2
0
8.071
7.538
7.533
7.530
7.253
7.246
7.242
7.238
7.234
7.226
7.220
7.217
7.209
7.206
7.202
7.198
7.188
7.181
7.178
7.169
7.166
7.160
7.156
7.150
7.122
7.120
7.090
7.088

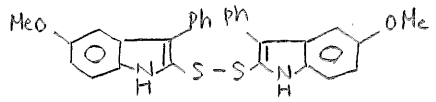
M2-OH-R8[illegible]-13C
3



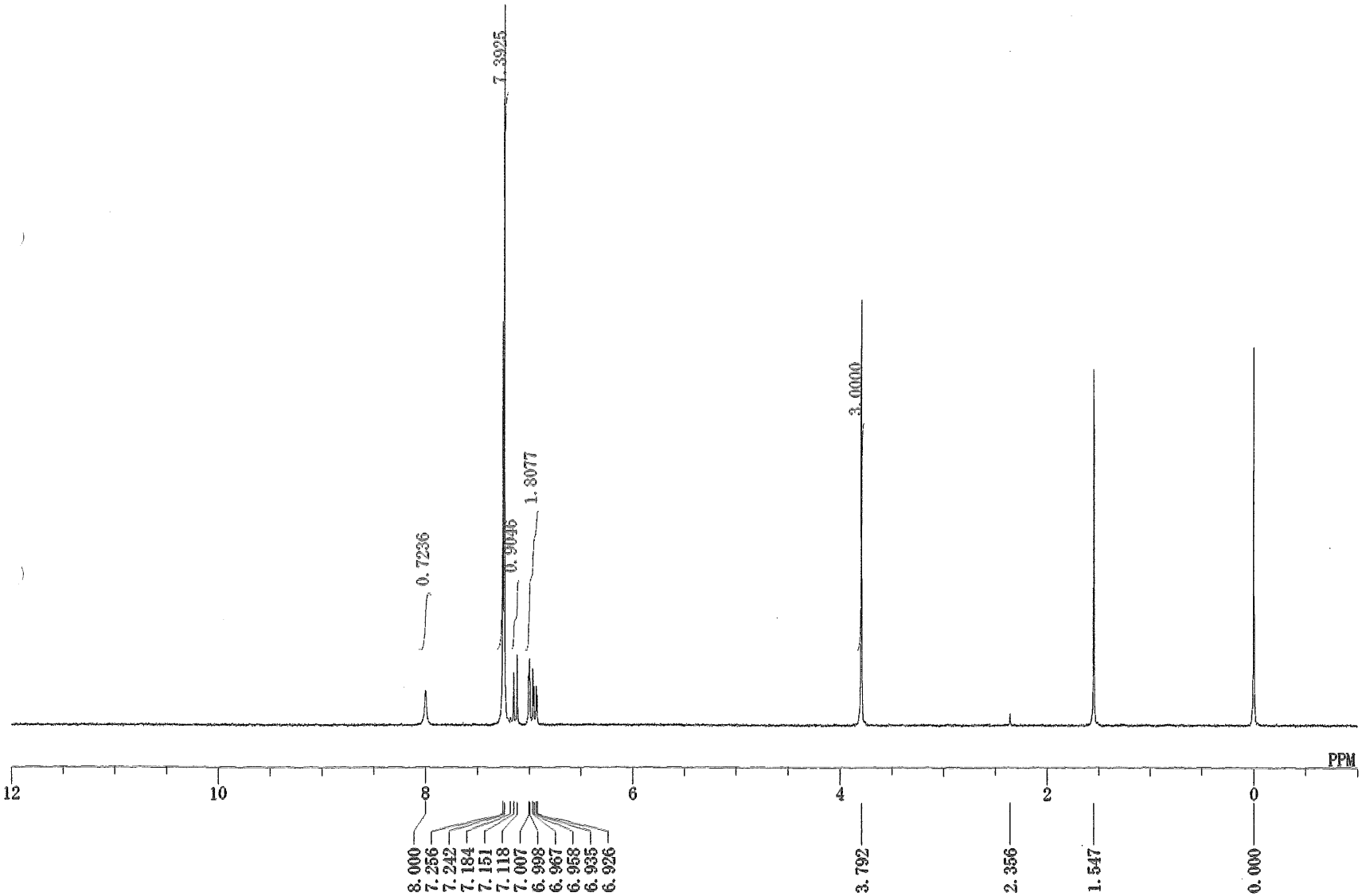
5b



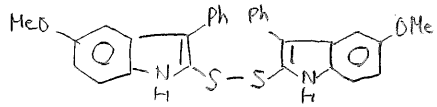
M2-OH-R85


MeO
Ph
Ph
OMe
S-S
N
H
N
H

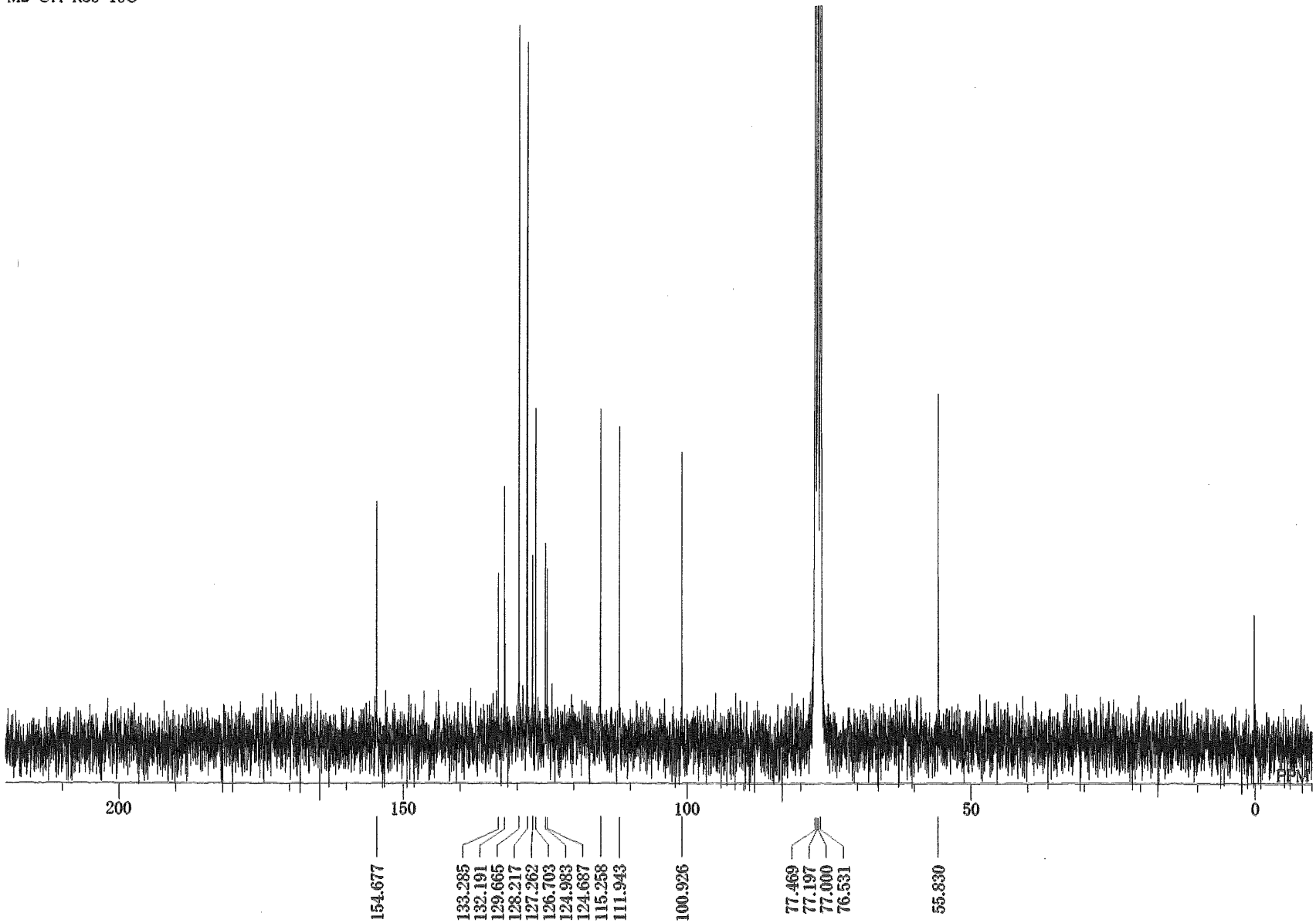
5c


7.3925
3.0000
1.8077
0.9096
0.7236
PPM
12
10
8
6
4
2
0
8.000
7.256
7.242
7.184
7.151
7.118
7.007
6.998
6.967
6.958
6.935
6.926
3.792
2.356
1.547
0.000

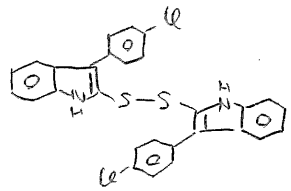
¥¥Komanmr¥personal¥ota¥M2-OH-R85-13C.als
M2-OH-R85-13C



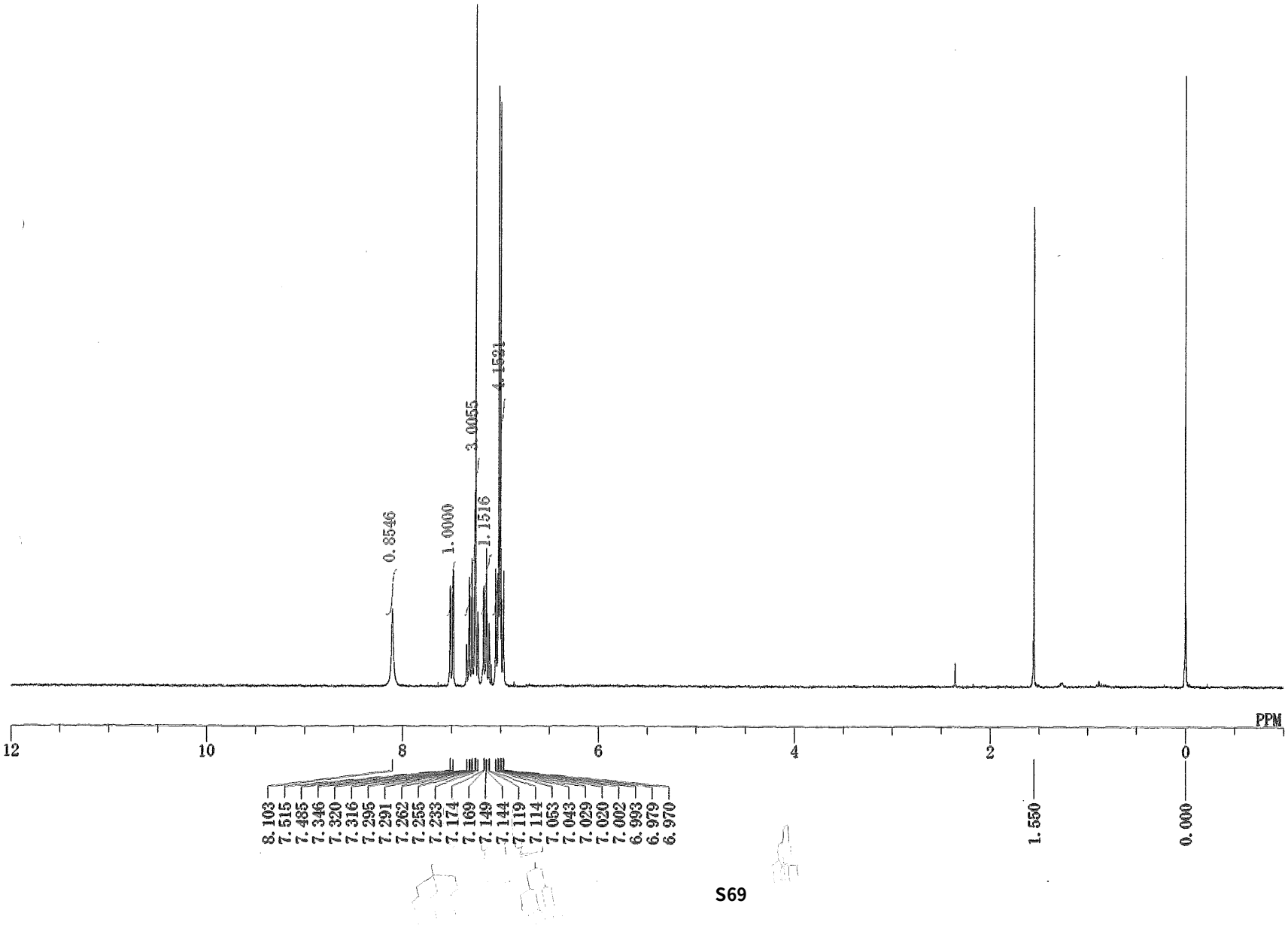
5c



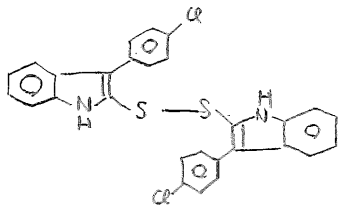
M2-OH-R87



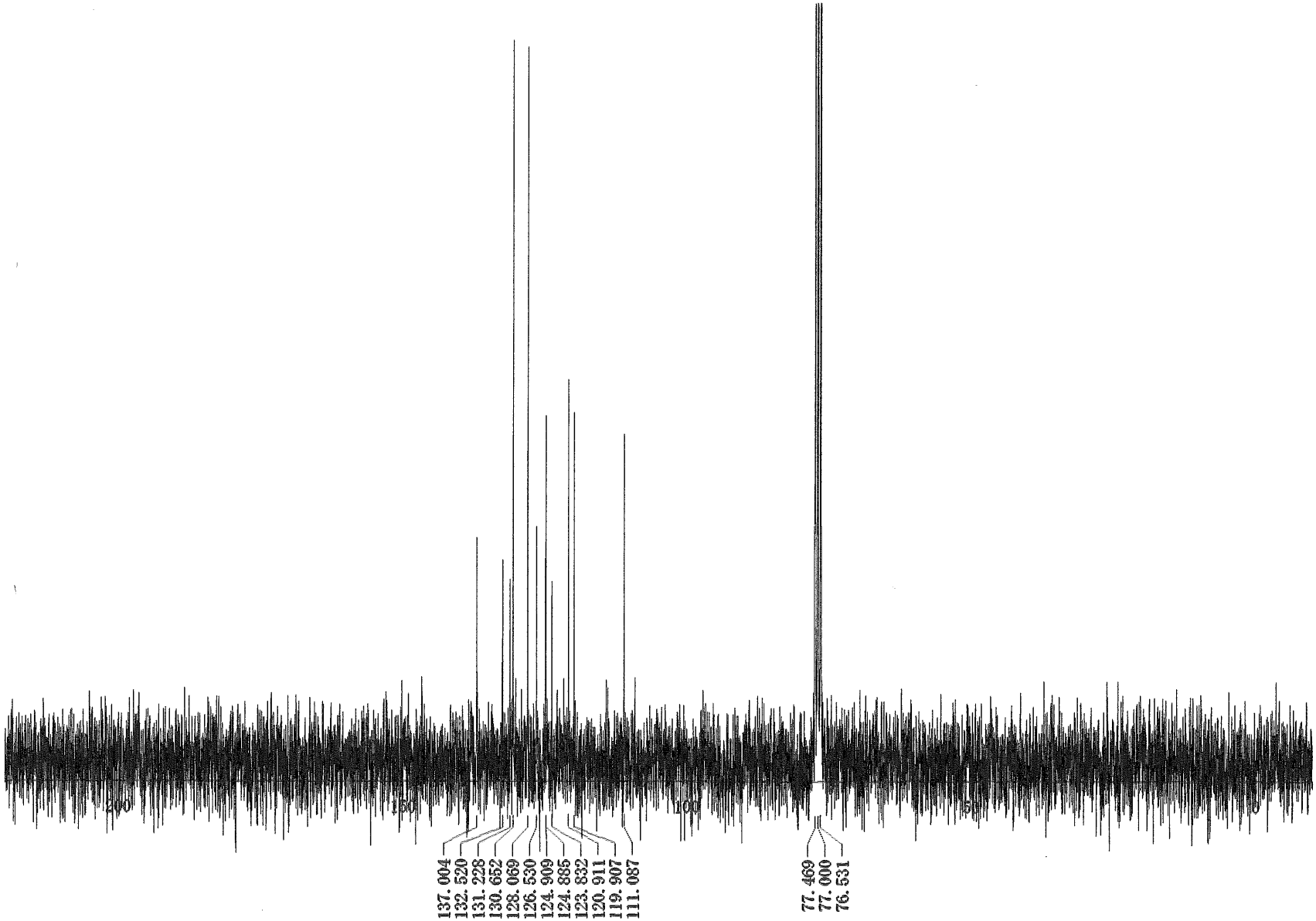
5d


0.8546
1.0000
3.0055
1.1516
4.1531
PPM
12
10
8
6
4
2
0
8.103
7.515
7.485
7.346
7.320
7.316
7.296
7.291
7.262
7.255
7.233
7.174
7.169
7.149
7.144
7.119
7.114
7.053
7.043
7.029
7.020
7.002
6.993
6.979
6.970
1.550
0.000

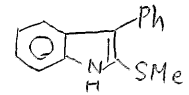
M2-OH-R87-13C



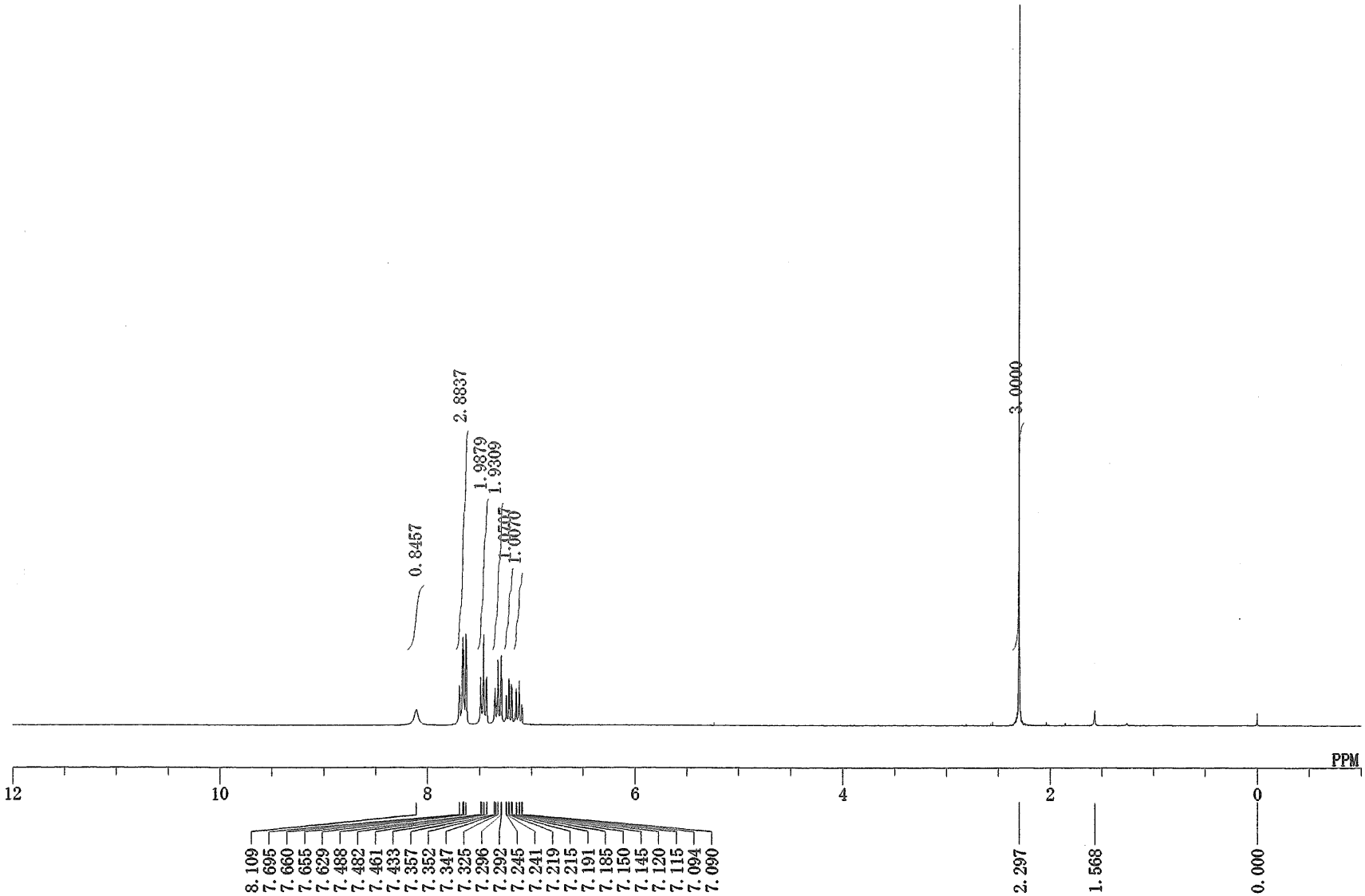
5d



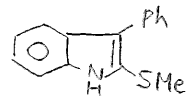
M2-OH-R75


Ph
N
H
SMe

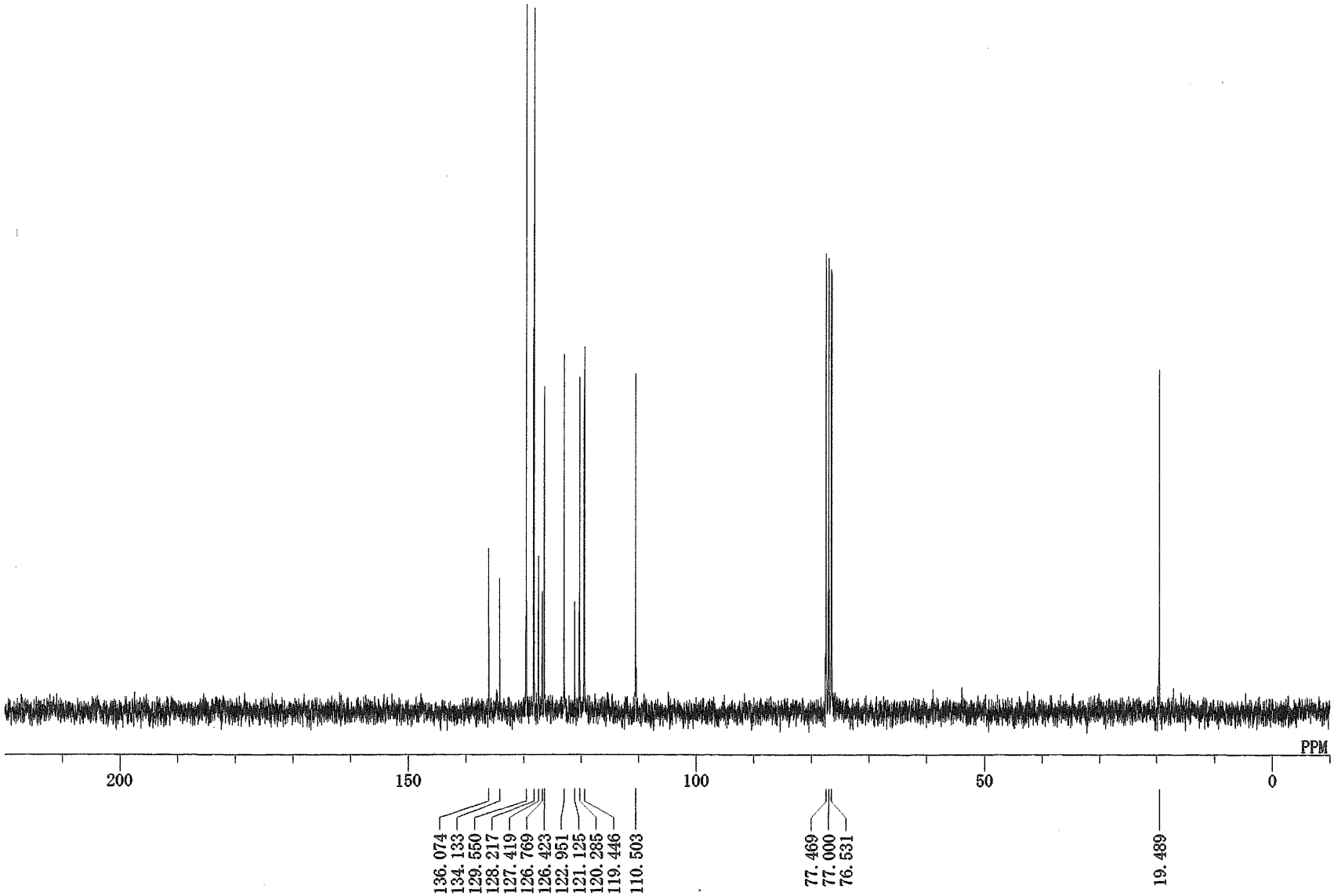
6


0.8457
2.8837
1.9879
1.9309
1.0707
1.0070
3.0000
PPM
12
10
8
6
4
2
0
8.109
7.695
7.660
7.655
7.629
7.488
7.482
7.461
7.433
7.357
7.352
7.347
7.325
7.296
7.292
7.245
7.241
7.219
7.215
7.191
7.185
7.150
7.145
7.120
7.115
7.094
7.090
2.297
1.568
0.000

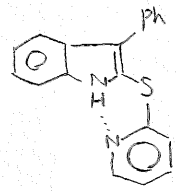
M2-OH-R75-13C



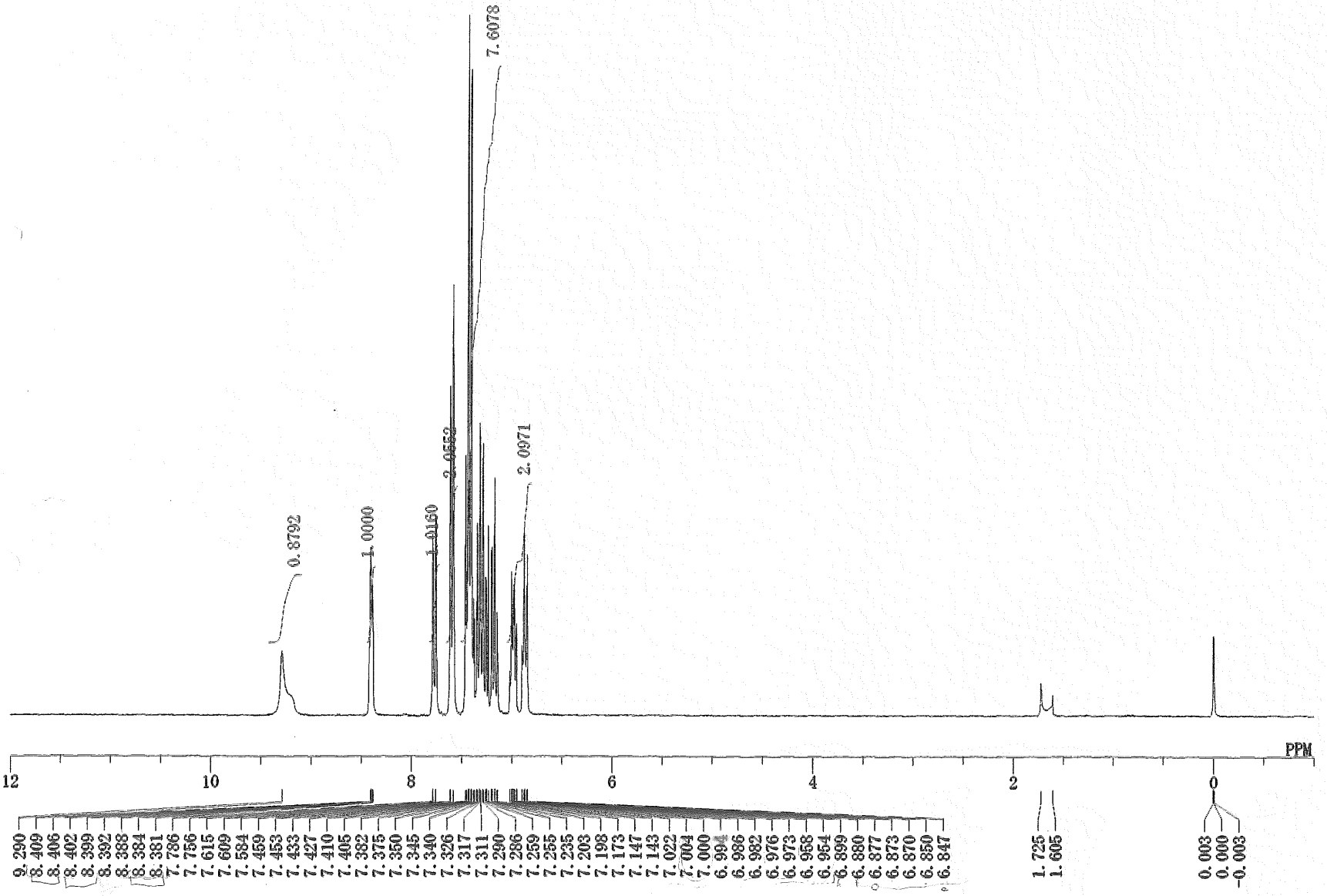
6



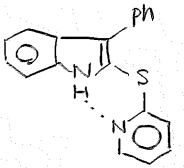
M2-OH-R90


Ph
S
N
H
N

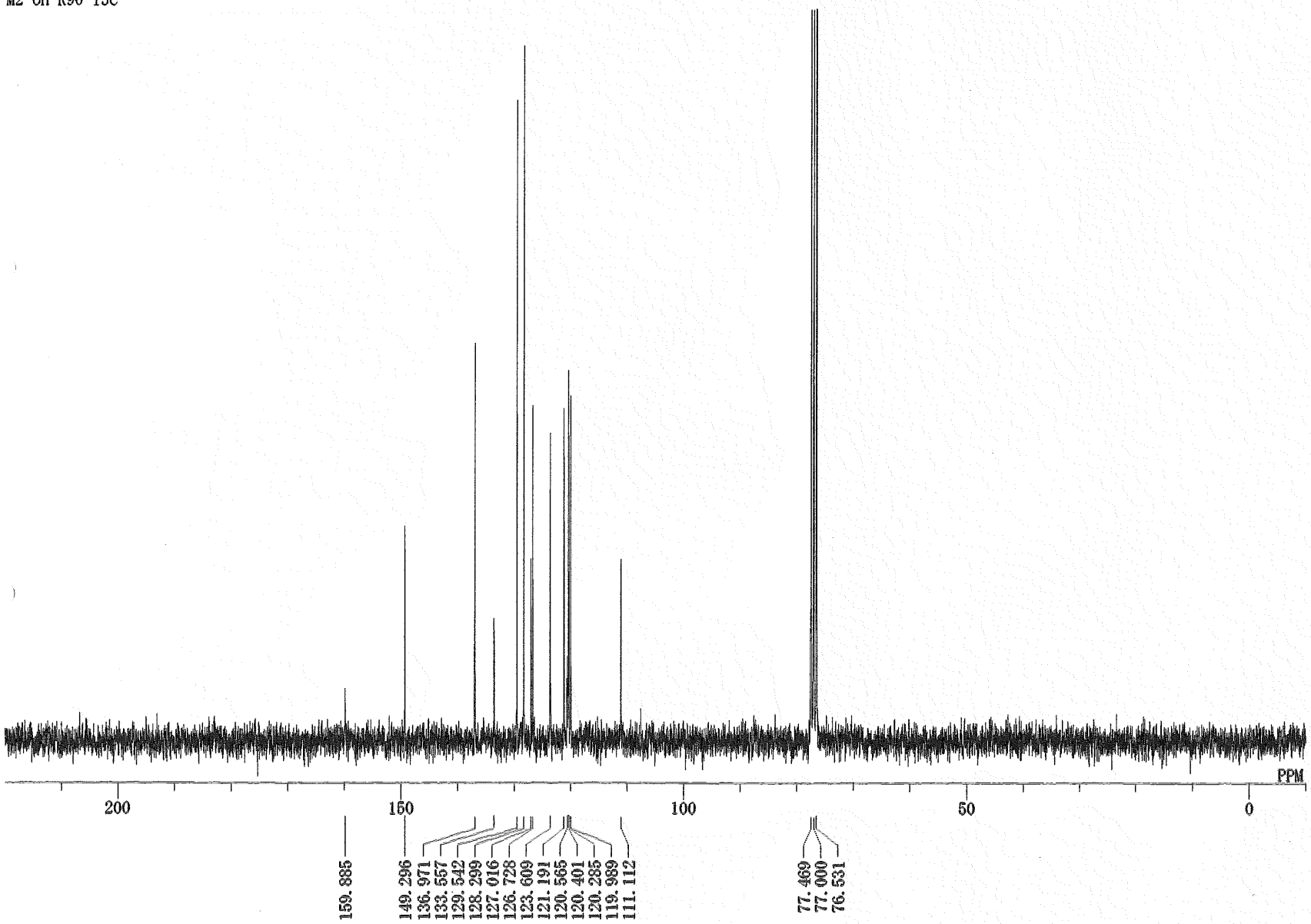
7


7.6078
2.0971
2.0552
1.0160
1.0000
0.8792
PPM
12
10
8
6
4
2
0
9.290
8.409
8.406
8.402
8.399
8.392
8.388
8.384
8.381
7.786
7.756
7.615
7.609
7.584
7.459
7.453
7.433
7.427
7.410
7.405
7.382
7.375
7.350
7.345
7.340
7.326
7.317
7.311
7.290
7.286
7.259
7.255
7.235
7.203
7.198
7.173
7.147
7.143
7.022
7.004
7.000
6.994
6.986
6.982
6.976
6.973
6.958
6.954
6.899
6.880
6.877
6.873
6.870
6.850
6.847
1.725
1.605
0.003
0.000
-0.003

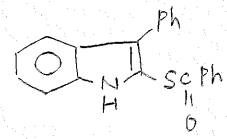
M2-OH-R90-13C



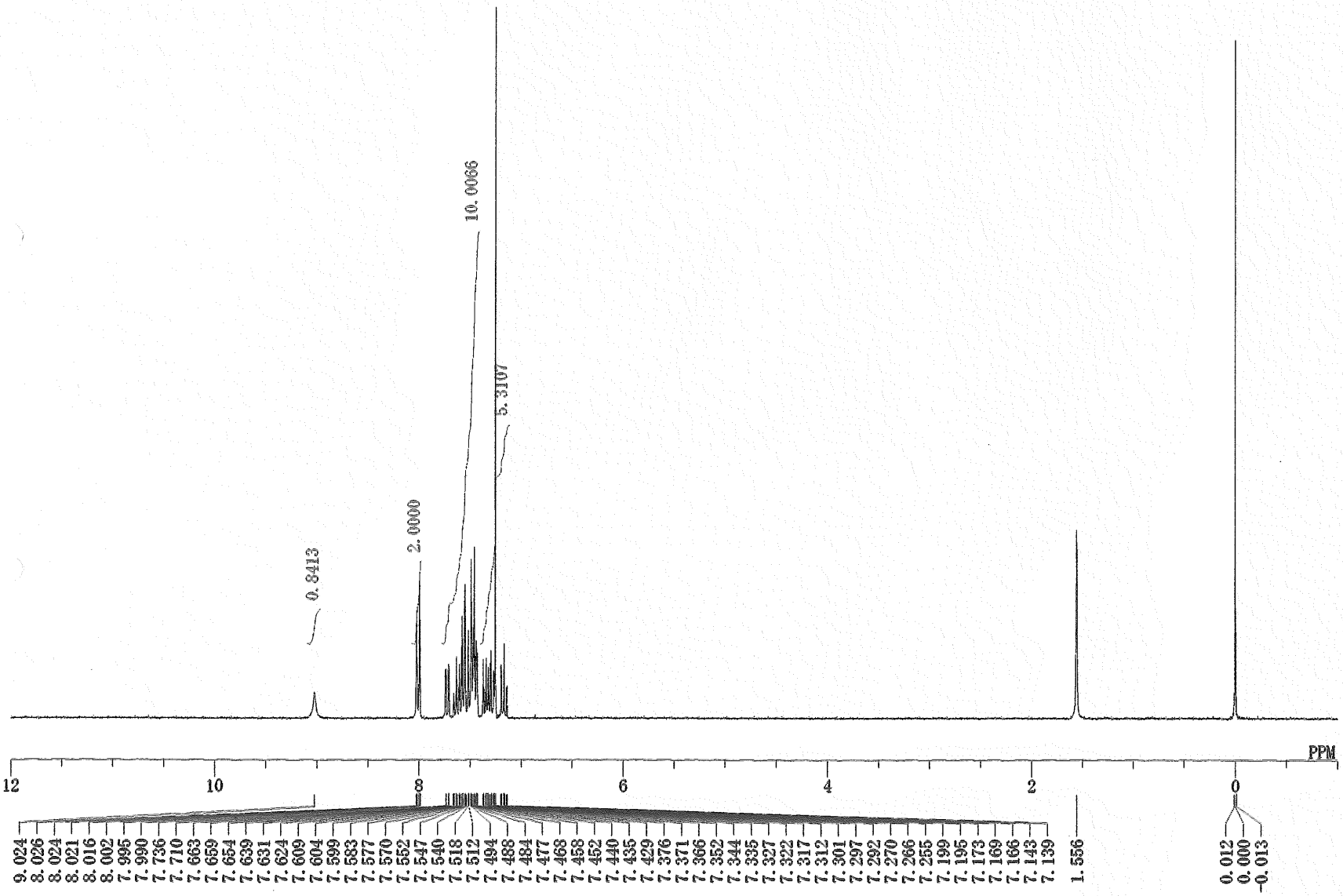
7



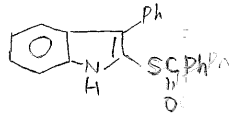
M2-OH-R76


Ph
N
H
S
Ph
O

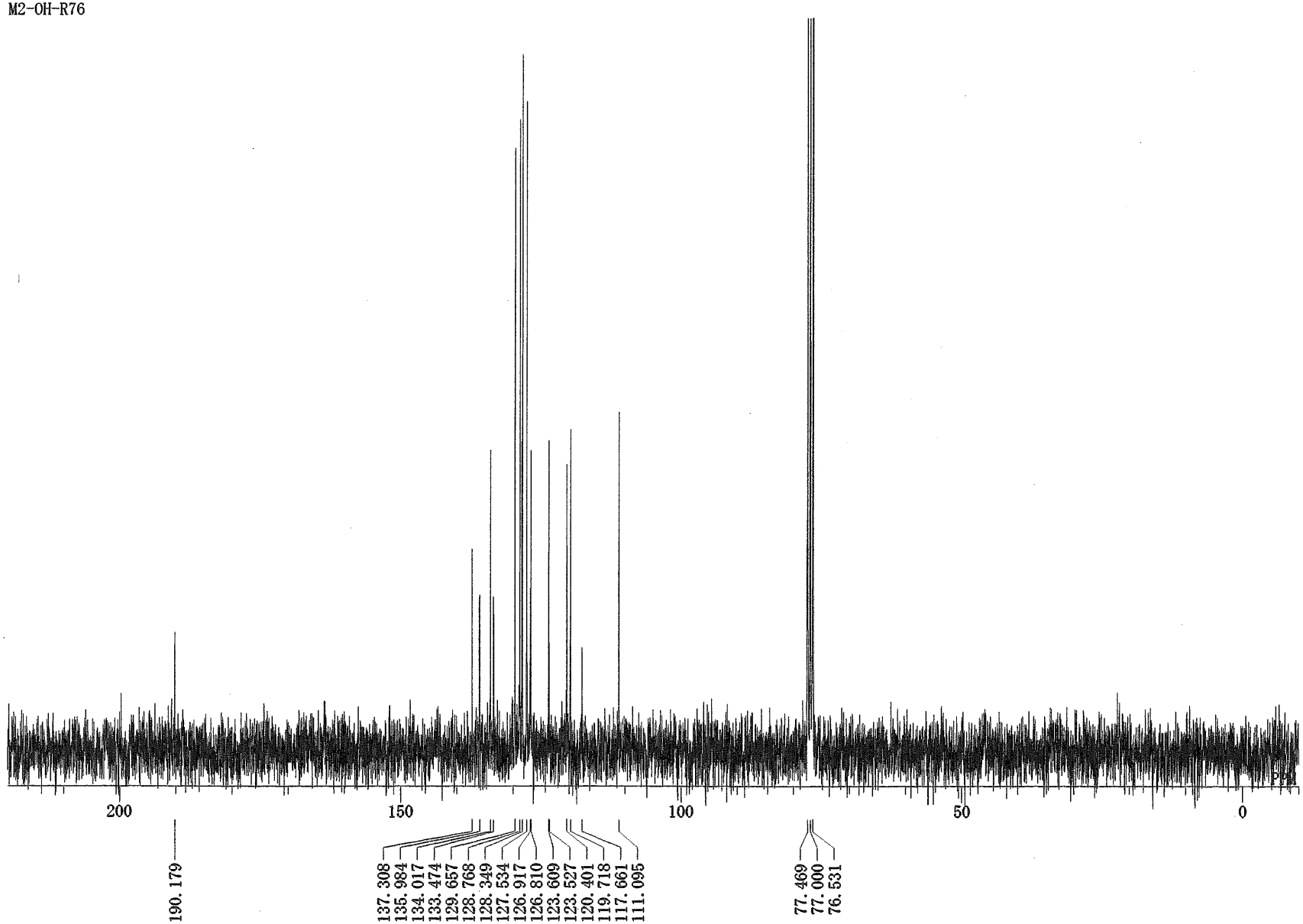
8


0.8413
2.0000
10.0066
5.3107
PPM
12
10
8
6
4
2
0
9.024
8.026
8.024
8.021
8.016
8.002
7.995
7.990
7.736
7.710
7.663
7.659
7.654
7.639
7.631
7.624
7.609
7.604
7.599
7.583
7.577
7.570
7.552
7.547
7.540
7.518
7.512
7.494
7.488
7.484
7.477
7.468
7.458
7.452
7.440
7.435
7.429
7.376
7.371
7.366
7.352
7.344
7.335
7.327
7.322
7.317
7.312
7.301
7.297
7.292
7.270
7.266
7.255
7.199
7.195
7.173
7.169
7.166
7.143
7.139
1.556
0.012
0.000
-0.013

M2-OH-R76



8


200
150
100
50
0
PPM
190.179
137.308
135.984
134.017
133.474
129.657
128.768
128.349
127.534
126.917
126.810
123.609
123.527
120.401
119.718
117.661
111.095
77.469
77.000
76.531