

A New Synthetic Approach to 6-Unsubstituted Phenanthridine and Phenanthridine-like Compounds under Mild and Metal-Free Conditions

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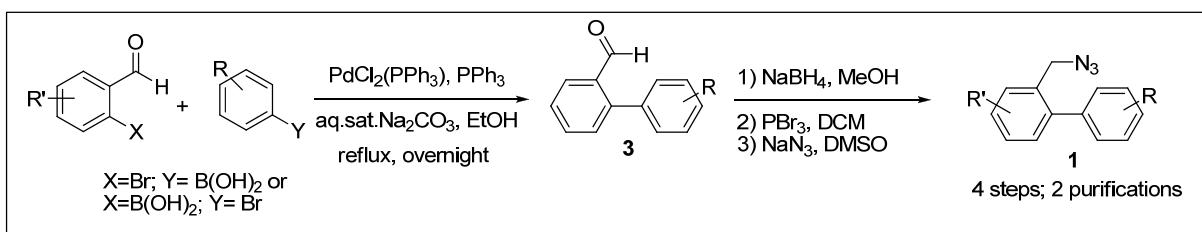
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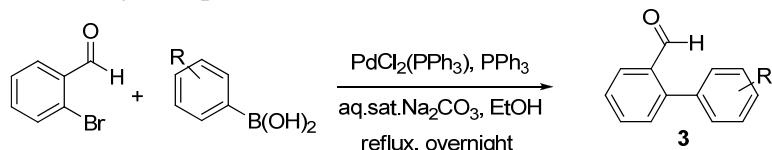
Experimental Section

1. General Information. Commercial grade reagents and solvents were used as received from the supplier except where indicated otherwise. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene were purified by pressure filtration through activated alumina. All glassware was oven-dried at 110 °C for two hours or more. ¹H and ¹³C NMR spectra were recorded in CDCl₃ with 300 MHz NMR spectrometers. ¹H NMR and ¹³C NMR chemical shifts (δ) were reported in units of part per million (ppm), relative to tetramethylsilane (TMS) at δ equal to zero ppm. Coupling constants (J) were reported in Hertz (Hz). Infrared spectra measured using an FT-IR spectrometer and were reported in cm⁻¹. High resolution mass spectra (HRMS) was measured on a mass spectrometer.

2. Synthesis of 2-(azidomethyl)biaryl (1):

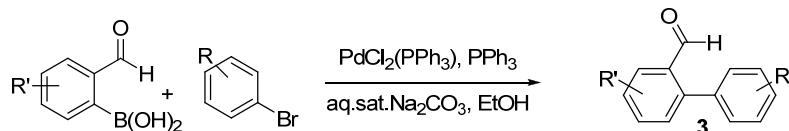


Synthesis of compound **3b**-**3j**, **3o**-**3p** and **3r**:

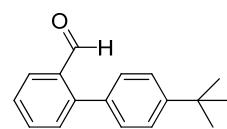


A solution of 2-bromobenzoaldehyde (1.0 equiv), phenylboronic acid (1.2 equiv), PdCl₂(PPh₃)₂ (5 mol%), and PPh₃ (10 mol%) in EtOH (5.0 mL/mmol) was refluxed for 30 min and then Na₂CO₃ (1.2 equiv) in water (0.5 mL/mmol) was added into the reaction mixture. The resulting solution was stirred under refluxing conditions for overnight. The solvent was removed, and the crude material was diluted with water, extracted with EtOAc (2x 20 mL), washed with water (2x 10 mL), and dried over Na₂SO₄. After rotary evaporation, the crude product was purified on silica gel to yield the biphenyl-2-carbaldehyde (**3**).

Synthesis of compound **3k**-**3n**:

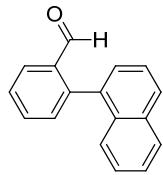


Prepared according to general procedure with a slight modification: 2-formylphenylboronic acid (1.2 equiv) and bromophenyl compound (1.0 equiv) was used for the synthesis of compound **3k**-**3n**.



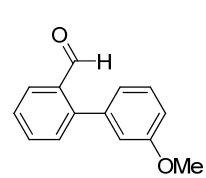
4'-tert-butylbiphenyl-2-carbaldehyde (3b): Yield 316.1 mg (82%, colorless oil); IR (neat): ν_{max} 2962, 1690, 1597, 1475, 1392, 1255, 1195 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.00 (s, 1H), 8.01 (d, 1H, J = 8.1 Hz), 7.60 (td, 1H, J = 7.5, 1.5 Hz), 7.49-7.42 (m, 4H), 7.33-7.28 (m, 2H), 1.37 (s, 9H); ¹³C NMR (75 MHz,

CDCl_3) δ 192.6, 151.1, 145.9, 134.6, 133.7, 133.4, 130.7, 129.8, 127.44, 127.40, 125.3, 34.6, 31.3. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{NaO} (\text{M}+\text{Na})^+$ 261.1250, found 261.1246.

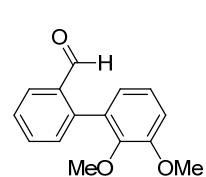


2-(naphthalen-1-yl)benzaldehyde (3c**):** Yield 359.9 mg (96%, white solid); 86-87 °C. IR (neat): ν_{max} 2844, 1963, 1596, 1197 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.63 (s, 1H), 8.11 (dd, 1H, J = 7.8, 1.5 Hz), 7.94 (app d, 2H, J = 8.1 Hz), 7.70 (td, 1H, J = 7.2, 1.5 Hz), 7.61-7.39 (m, 7H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.0, 144.2, 135.4, 134.8, 133.6, 133.4, 132.7, 131.7, 128.6, 128.3, 128.1, 127.0, 126.7, 126.2, 125.7, 125.0. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{12}\text{NaO} (\text{M}+\text{Na})^+$ 255.0780, found 255.0787.

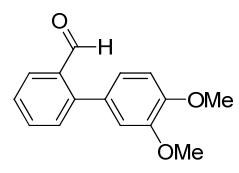
2-(naphthalen-2-yl)benzaldehyde (3d**):** Yield 309.8 mg (81%, yellow oil); IR (neat): ν_{max} 2844, 2752, 1691, 1595, 1195 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 10.03 (d, 1H, J = 0.6 Hz), 8.08-8.05 (m, 1H), 7.49-7.86 (m, 3H), 7.81 (s, 1H), 7.66 (td, 1H, J = 7.9, 1.5 Hz), 7.57-7.49 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.3, 145.8, 135.1, 133.8, 133.5, 132.9, 132.6, 130.9, 129.3, 128.1, 128.0, 127.8, 127.6, 126.7, 126.6. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{12}\text{NaO} (\text{M}+\text{Na})^+$ 255.0780, found 255.0772.



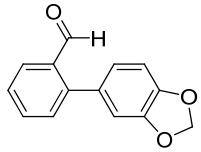
3'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (3e**):** Yield 197.2 mg (58%, colorless oil); IR (neat): ν_{max} 2838, 1692, 1597, 1213, 763 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 10.02 (d, 1H, J = 0.6 Hz), 8.04 (dd, 1H, J = 7.8, 1.2 Hz), 7.64 (td, 1H, J = 7.5, 1.5 Hz), 7.53-7.45 (m, 2H), 7.39 (t, 1H, J = 7.8 Hz), 7.02-6.94 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.3, 159.4, 145.7, 139.1, 133.7, 133.4, 130.5, 129.3, 127.7, 127.4, 122.6, 115.6, 113.5, 55.2. ESI-HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{NaO}_2 (\text{M}+\text{Na})^+$ 235.0729, found 235.0721.



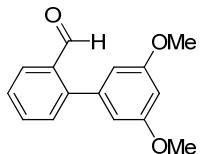
2',3'-dimethoxy-[1,1'-biphenyl]-2-carbaldehyde (3f**):** Yield 233.1 mg (88%, colorless oil); IR (neat): ν_{max} 2936, 2838, 1694, 1261, 1002 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.85 (d, 1H, J = 0.6 Hz), 8.02 (dd, 1H, J = 7.8, 1.2 Hz), 7.63 (td, 1H, J = 7.5, 1.2 Hz), 7.49 (t, 1H, J = 7.5 Hz), 7.40 (dd, 1H, J = 7.8, 0.9 Hz), 7.16 (t, 1H, J = 7.8 Hz), 7.01 (dd, 1H, J = 8.1, 1.5 Hz), 6.89 (dd, 1H, J = 7.8, 1.5 Hz), 3.92 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 191.8, 152.4, 146.1, 141.2, 133.5, 133.2, 131.9, 130.8, 127.6, 126.5, 124.1, 122.8, 121.5, 60.0, 55.6. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{NaO}_3 (\text{M}+\text{Na})^+$ 265.0835, found 265.0837.



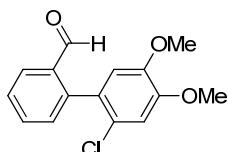
3',4'-dimethoxy-[1,1'-biphenyl]-2-carbaldehyde (3g**):** Yield 303.3 mg (74%, colorless oil); IR (neat): ν_{max} 2836, 1688, 1518, 1246, 1025, 760 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 10.00 (s, 1H), 7.99 (dd, 1H, J = 8.4, 1.8 Hz), 7.61 (td, 1H, J = 7.5, 1.2 Hz), 7.47 (app t, 2H, J = 7.8 Hz), 6.99-6.89 (m, 3H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.5, 149.0, 148.7, 145.6, 133.7, 133.3, 130.6, 130.2, 127.4, 127.3, 122.7, 113.0, 110.9, 55.9. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{NaO}_3 (\text{M}+\text{Na})^+$ 265.0835, found 265.0828.



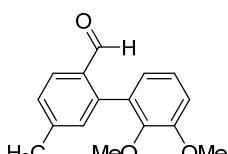
2-(benzo[d][1,3]dioxol-5-yl)benzaldehyde (3h): Yield 228.8 mg (62%, colorless oil); IR (neat): ν_{max} 2891, 1691, 1473, 1223, 1038 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.99 (d, 1H, $J = 0.3$ Hz), 7.98 (dd, 1H, $J = 7.5, 1.2$ Hz), 7.59 (td, 1H, $J = 7.5, 1.2$ Hz), 7.45 (t, 1H, $J = 7.5$ Hz), 7.39 (dd, 1H, $J = 7.5, 0.6$ Hz), 6.90-6.86 (m, 2H), 6.78 (dd, 1H, $J = 7.8, 1.8$ Hz), 6.02 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.2, 147.7, 147.6, 145.3, 133.7, 133.4, 131.4, 130.5, 127.44, 127.40, 123.9, 110.1, 108.0, 101.3. ESI-HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 249.0522, found 249.0520.



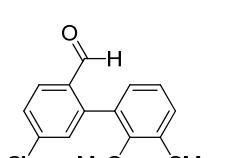
3',5'-dimethoxybiphenyl-2-carbaldehyde (3i): Yield 357.3 mg (71%, colorless oil); IR (neat): ν_{max} 2939, 2839, 1692, 1590, 1456, 1203, 1153 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 10.01 (d, 1H, $J = 0.6$ Hz), 8.01 (dd, 1H, $J = 7.5, 0.9$ Hz), 7.62 (td, 1H, $J = 7.5, 1.5$ Hz), 7.52-7.44 (m, 2H), 6.55-6.50 (m, 3H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.4, 160.6, 145.9, 139.8, 133.8, 133.5, 130.4, 127.9, 127.3, 108.4, 100.0, 55.4. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 265.0835, found 265.0847.



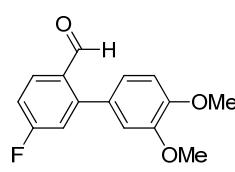
2'-chloro-4',5'-dimethoxy-[1,1'-biphenyl]-2-carbaldehyde (3j): Yield 192.7 mg (58%, white solid); mp 105-106 °C; IR (neat): ν_{max} 2842, 1694, 1508, 1210 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.83 (d, 1H, $J = 0.6$ Hz), 8.03 (dd, 1H, $J = 7.8, 1.2$ Hz), 7.66 (td, 1H, $J = 7.5, 1.5$ Hz), 7.53 (app td, 1H, $J = 7.5, 0.9$ Hz), 7.35 (dd, 1H, $J = 7.5, 0.9$ Hz), 6.98 (s, 1H), 6.80 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 191.7, 149.6, 147.8, 142.7, 134.0, 133.6, 131.1, 128.4, 128.3, 127.2, 124.8, 114.1, 112.4, 56.24, 56.20. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{ClNaO}_3$ (Cl-35) ($\text{M}+\text{Na}$) $^+$ 299.0455, found 299.0450.



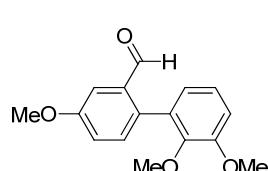
2',3'-dimethoxy-5-methyl-[1,1'-biphenyl]-2-carbaldehyde (3k): Yield 384.2 mg (99%, colorless oil); IR (neat): ν_{max} 2936, 2838, 1691, 1603, 1467, 1262 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.80 (d, 1H, $J = 0.6$ Hz), 7.93 (d, 1H, $J = 7.8$ Hz), 7.29 (d, 1H, $J = 7.8$ Hz), 7.20 (s, 1H), 7.14 (t, 1H, $J = 7.8$ Hz), 7.00 (dd, 1H, $J = 8.1, 1.2$ Hz), 6.87 (dd, 1H, $J = 7.5, 1.5$ Hz), 3.91 (s, 3H), 3.49 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 191.8, 152.6, 146.4, 144.1, 141.5, 132.2, 131.5, 131.4, 128.7, 126.9, 124.1, 123.0, 112.5, 60.3, 55.8, 21.7. ESI-HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 279.0992, found 279.0994.



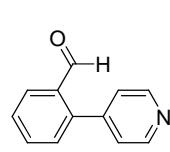
5-chloro-2',3'-dimethoxybiphenyl-2-carbaldehyde (3l): Yield 305.5 mg (81%, colorless oil); IR (neat): ν_{max} 2973, 2838, 1694, 1588, 1475, 1262 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.78 (d, 1H, $J = 0.6$ Hz), 7.96 (d, 1H, $J = 8.4$ Hz), 7.47 (ddd, 1H, $J = 8.4, 2.1, 0.9$ Hz), 7.40 (d, 1H, $J = 2.1$ Hz), 7.18 (t, 1H, $J = 7.8$ Hz), 7.03 (dd, 1H, $J = 8.1, 1.5$ Hz), 6.88 (dd, 1H, $J = 7.5, 1.5$ Hz), 3.92 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 190.7, 152.6, 146.2, 142.8, 139.4, 132.1, 130.8, 130.6, 128.2, 128.1, 124.3, 122.6, 113.1, 60.3, 55.8. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{ClNaO}_3$ (Cl-35) ($\text{M}+\text{Na}$) $^+$ 299.0445, found 299.0456.



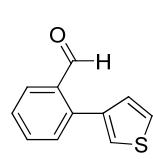
5-fluoro-3',4'-dimethoxybiphenyl-2-carbaldehyde (3m): Yield 351.9 mg (79%, white solid); mp 85-86 °C; IR (neat): ν_{max} 2936, 2893, 1687, 1486, 1249 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.93 (d, 1H, *J* = 3.3 Hz), 7.67 (dd, 1H, *J* = 8.7, 2.7 Hz), 7.44 (dd, 1H, *J* = 8.4, 5.1 Hz), 7.32 (td, 1H, *J* = 7.8, 2.7 Hz), 6.96 (d, 1H, *J* = 9.3 Hz), 6.89 (d, 1H, *J* = 2.1 Hz), 6.86 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 191.2, 161.9 (d, *J*_{CF} = 247 Hz), 149.2, 148.9, 141.8 (d, *J*_{CF} = 12 Hz), 135.2 (d, *J*_{CF} = 7 Hz), 132.6 (d, *J*_{CF} = 8 Hz), 129.3, 122.9, 120.6 (*J*_{CF} = 22 Hz), 113.4 (d, *J*_{CF} = 26 Hz), 113.0, 111.0, 55.9. ESI-HRMS calcd for C₁₅H₁₃FNaO₃ (M+Na)⁺ 283.0741, found 283.0748.



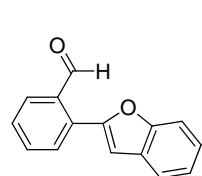
2',3',4-trimethoxy-[1,1'-biphenyl]-2-carbaldehyde (3n): Yield 375.0 mg (98%, colorless solid); mp 65-66 °C; IR (neat): ν_{max} 2935, 2838, 1687, 1468, 1018 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.81 (s, 1H), 7.52 (d, 1H, *J* = 2.7 Hz), 7.32 (d, 1H, *J* = 8.4 Hz), 7.19 (dd, 1H, *J* = 8.4, 2.7 Hz), 7.13 (t, 1H, *J* = 7.8 Hz), 6.99 (dd, 1H, *J* = 8.4 Hz), 6.87 (dd, 1H, *J* = 7.5, 1.5 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 3.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 191.9, 159.1, 152.6, 146.4, 134.5, 134.0, 132.2, 131.8, 124.1, 123.2, 120.8, 112.4, 109.4, 60.1, 55.8, 55.4. ESI-HRMS calcd for C₁₆H₁₆NaO₄ (M+Na)⁺ 295.0941, found 195.0940.



2-(pyridin-4-yl)benzaldehyde (3o): Yield 290.6 mg (89%, white solid); mp 67-68 °C; IR (neat): ν_{max} 3030, 2848, 1693, 1593, 1408, 1258, 1195 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.98 (s, 1H), 8.72 (dd, 2H, *J* = 4.4, 1.4 Hz), 8.06 (d, 1H, *J* = 7.7 Hz), 7.71 (dd, 1H, *J* = 7.5, 1.4 Hz), 7.59 (dd, 1H, *J* = 7.6, 0.8 Hz), 7.44 (d, 1H, *J* = 7.6 Hz), 7.33 (dd, 2H, *J* = 4.4, 1.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 191.0, 149.7, 145.7, 142.6, 133.8, 133.3, 130.2, 128.9, 128.3, 124.6. ESI-HRMS calcd for C₁₂H₁₀NO (M+H)⁺ 184.0757, found 184.0762.

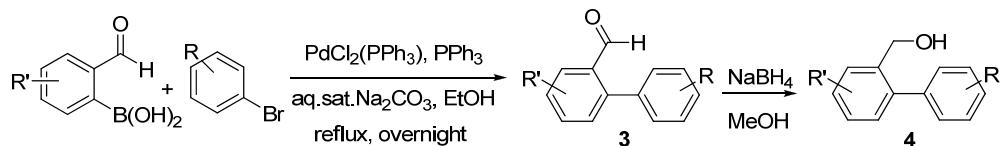


2-(thiophen-3-yl)benzaldehyde (3p): Yield 74.5 mg (73%, yellow oil); IR (neat): ν_{max} 2848, 1686, 1597, 1196, 759 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.10 (s, 1H), 8.99 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.61 (td, 1H, *J* = 7.8, 1.5 Hz), 7.49-7.43 (m, 3H), 7.29 (dd, 1H, *J* = 3.0, 1.2 Hz), 7.19 (dd, 1H, *J* = 4.8, 1.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 192.3, 140.4, 138.3, 133.9, 133.6, 130.5, 129.3, 127.7, 127.5, 126.2, 125.0. ESI-HRMS calcd for C₁₁H₈NaOS (M+Na)⁺ 211.0188, found 211.0185.



2-(benzofuran-2-yl)benzaldehyde (3r): Yield 223.4 mg (62%, colorless oil); IR (neat): ν_{max} 2854, 1686, 1257, 1021, 748 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.46 (d, 1H, *J* = 0.6 Hz), 8.02 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.81 (dd, 1H, *J* = 7.8, 0.9 Hz), 7.64 (td, 2H, *J* = 7.5, 1.2 Hz), 7.55-7.47 (m, 2H), 7.34 (td, 1H, *J* = 8.1, 1.5 Hz), 7.27 (dd, 1H, *J* = 7.5, 1.2 Hz), 6.95 (d, 1H, *J* = 0.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 192.0, 155.5, 152.8, 133.8, 133.5, 133.0, 129.1, 128.9, 128.5, 128.1, 125.2, 123.2, 121.3, 111.4, 107.8. ESI-HRMS calcd for C₁₅H₁₀NaO₂ (M+Na)⁺ 245.0573, found 245.0576.

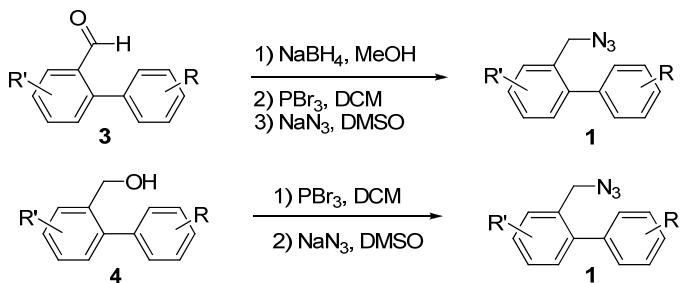
General procedure for the synthesis of biphenylmethanol (**4q**):



Biphenyl-2-carbaldehydes were prepared using the general procedure. However the products (**3e** and **3q**) were unable to isolate from the impurities. Therefore, the mixture was subjected to the reduction reaction using NaBH₄ (1.0 equiv) in MeOH. The reaction was quenched with water, extracted with EtOAc (2x 20 mL), washed with water (2x 10 mL), and dried over Na₂SO₄. After rotary evaporation, the crude product was purified on silica gel to yield biphenylmethanol (**4q**).

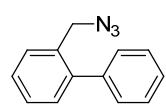
*(2-(benzo[b]thiophen-2-yl)phenyl)methanol (**4q**):* Yield 386.4 mg (65%, white solid); mp 108-109 °C; IR (neat): ν_{max} 3344, 3058, 2884, 1598, 1431, 1306, 1191, 1015 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.86-7.78 (m, 2H), 7.56 (dd, 1H, *J* = 7.5, 1.6 Hz), 7.52 (dd, 1H, *J* = 7.5, 1.6 Hz), 7.44-7.31 (m, 5H), 4.79 (s, 2H), 1.83 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 141.7, 140.2, 140.1, 138.8, 133.6, 130.9, 128.9, 128.7, 127.8, 124.5, 124.3, 123.7, 123.6, 122.0, 63.3. ESI-HRMS calcd for C₁₅H₁₂NaOS (M+Na)⁺ 263.0501, found 263.0496.

General procedure for the synthesis of 2-(azidomethyl)biphenyl (**1**):

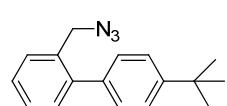


To a solution of biphenyl-2-carbaldehyde (1.0 equiv) in MeOH (3.8 mL/mmol) was added NaBH₄ (1.0 equiv) at 0 °C and then warmed to room temperature, stirred for another 30 min. The reaction was quenched with water, extracted with EtOAc, dried with Na₂SO₄ and concentrated under reduced pressure. The crude of benzyl alcohol was dissolved in DCM (3.8 mL/mmol) and then added PBr₃ (0.34 equiv) at room temperature. The reaction mixture was stirred for 1 h and the solvent was removed under reduce pressure. The residue was used for next step without further purification. The crude product was dissolved in DMSO (3.0 mL/mmol) followed by addition of NaN₃ (2.0 equiv) at 0°C. The reaction mixture was stirred at 0°C for 0.5 h and allowed to stir at room temperature for 16 h. The mixture was diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na₂SO₄) and concentrated under reduced pressure to obtain the crude material which was purified on silica gel to yield 2-(azidomethyl)biphenyl (**1**). **(Note:** Safety precaution should be taken seriously. DCM from the first step should be removed completely when

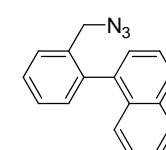
preparing the benzylic azides using NaN_3 . See: R. E. Conrow, W. D. Dean, *Org. Proc. Res. Dev.* **2008**, *12*, 1285-1286.)



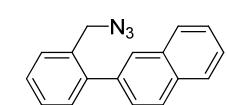
2-(azidomethyl)biphenyl (1a**):** Yield 529.2 mg (91%, colorless oil); IR (neat): ν_{\max} 2090, 1598, 1480, 1254 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.30 (m, 9H), 4.28 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.2, 140.2, 132.8, 130.4, 129.5, 129.2, 128.3, 127.8, 127.4, 52.6. ESI-HRMS calcd for $\text{C}_{13}\text{H}_{12}\text{N} (\text{MH-N}_2)^+$ 182.0964, found 182.0956.



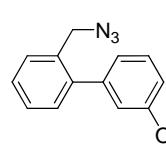
2-(azidomethyl)-4'-tert-butylbiphenyl (1b**):** Yield 252.3 mg (78%, colorless oil); IR (neat): ν_{\max} 2963, 2094, 1483, 1268 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.42 (m, 3H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 1H), 7.29-7.25 (m, 2H), 4.31 (s, 2H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.2, 142.0, 137.2, 132.8, 130.4, 129.4, 128.8, 128.2, 127.5, 125.2, 52.5, 34.5, 31.3. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{N} (\text{MH-N}_2)^+$ 238.1590, found 238.1593.



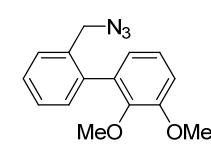
1-(2-(azidomethyl)phenyl)naphthalene (1c**):** Yield 242.2 mg (63%, colorless oil) IR (neat): ν_{\max} 2926, 2093, 1592, 1394, 1259 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 8.00-7.96 (m, 2H), 7.64-7.39 (m, 9H), 4.18 (d, 1H, $J = 13.8$ Hz), 4.10 (d, 1H, $J = 13.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 139.9, 137.5, 134.3, 133.4, 132.0, 130.9, 128.7, 128.2, 128.01, 127.99, 127.0, 126.2, 125.9, 125.6, 125.2, 52.3. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{N} (\text{MH-N}_2)^+$ 232.1121, found 232.1125.



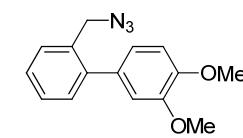
2-(2-(azidomethyl)phenyl)naphthalene (1d**):** Yield 110.2 mg (82%, colorless oil); IR (neat): ν_{\max} 2928, 2090, 1597, 1489, 1246 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.91-7.85 (m, 3H), 7.80 (s, 1H), 7.52-7.40 (m, 7H), 4.31 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.1, 137.7, 133.2, 133.0, 132.5, 130.6, 129.6, 128.4, 128.1, 128.0, 127.91, 127.88, 127.7, 127.4, 126.4, 126.2, 52.6. ESI-HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{N} (\text{MH-N}_2)^+$ 232.1121, found 232.1118.



(3'-methoxy-[1,1'-biphenyl]-2-yl)methanol (1e**):** Yield 167.5 mg (78%, colorless oil); IR (neat): ν_{\max} 3749, 2938, 2836, 2093, 1598, 1475, 1213, 758 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.28 (m, 5H), 6.93-6.89 (m, 3H), 4.27 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.5, 142.1, 141.7, 132.8, 130.3, 129.6, 129.4, 128.4, 127.9, 121.6, 114.8, 113.2, 55.3, 52.6. ESI-HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{NaO} (\text{M+Na})^+$ 262.0951, found 262.0962.

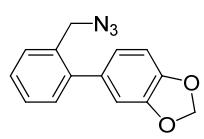


2'-(azidomethyl)-2,3-dimethoxybiphenyl (1f**):** Yield 316.8 mg (81%, colorless oil); IR (neat): ν_{\max} 2935, 2093, 1580, 1466, 1262 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.53 (dd, 1H, $J = 9.0, 3.0$ Hz), 7.46-7.30 (m, 3H), 7.15 (t, 1H, $J = 9.0$ Hz), 7.00 (dd, 1H, $J = 9.0, 3.0$ Hz), 6.85 (dd, 1H, $J = 9.0, 3.0$ Hz), 4.39 (d, 1H, $J = 13.8$ Hz), 4.27 (d, 1H, $J = 13.8$ Hz), 3.92 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.5, 145.8, 137.5, 134.5, 134.0, 130.1, 128.1, 127.6, 127.5, 123.9, 122.6, 116.7, 60.2, 55.5, 52.3. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{N}_3\text{NaO}_2 (\text{M+Na})^+$ 292.1057, found 292.1056.

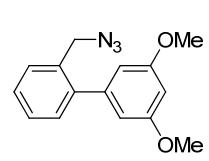


2-(azidomethyl)-3',4'-dimethoxybiphenyl (1g**):** Yield 229.7 mg (82%, colorless oil); IR (neat): ν_{\max} 2935, 2090, 1519, 1245, 1218, 1026 cm^{-1} . ^1H NMR (300

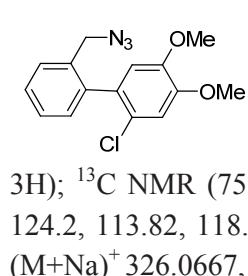
MHz, CDCl₃) δ 7.38-7.30 (m, 4H), 6.90 (d, 1H, *J* = 1.2 Hz), 6.88 (s, 1H), 6.87 (d, 1H, *J* = 1.5 Hz), 4.24 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.2, 148.0, 141.6, 132.4, 130.0, 129.3, 127.9, 127.1, 121.0, 112.2, 110.6, 55.3, 52.2. ESI-HRMS calcd for C₁₅H₁₅N₃NaO₂ (M+Na)⁺ 292.1057, found 292.1052.



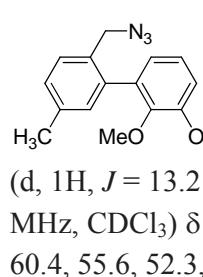
5-(2-(azidomethyl)phenyl)benzo[d][1,3]dioxole (Ih): Yield 180.5 mg (87%, colorless oil); IR (neat): ν_{max} 2890, 2089, 1503, 1475, 1220, 1037 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.24 (m, 4H), 6.85-8.81 (m, 2H), 6.76 (d, 1H, *J* = 6.0 Hz), 5.94 (s, 2H), 4.26 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 147.4, 146.9, 141.7, 133.9, 132.8, 130.4, 129.5, 128.2, 127.5, 122.5, 109.6, 108.0, 101.0, 52.5. ESI-HRMS calcd for C₁₄H₁₁N₃NaO₂ (M+Na)⁺ 276.0744, found 276.0736.



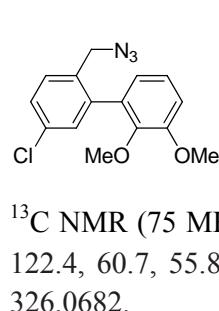
2-(azidomethyl)-3',5'-dimethoxybiphenyl (Ii): Yield 138.7 mg (73%, colorless oil); IR (neat): ν_{max} 2938, 2092, 1590, 1456, 1419, 1203, 1152 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.30 (m, 4H), 6.49 (s, 3H), 4.29 (s, 2H), 3.81 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 142.1, 132.7, 130.0, 129.5, 128.2, 127.8, 107.3, 99.5, 55.4, 52.5. ESI-HRMS calcd for C₁₅H₁₅N₃NaO₂ (M+Na)⁺ 292.1056, found 292.1047.



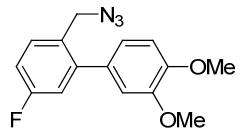
2'-(azidomethyl)-2-chloro-4,5-dimethoxy-1,1'-biphenyl (Ij): Yield 146.1 mg (69%, colorless oil); IR (neat): ν_{max} 2936, 2094, 1486, 1211 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.49-7.37 (m, 3H), 7.26-7.23 (m, 1H), 6.96 (s, 1H), 6.77 (s, 1H), 4.24 (d, 1H, *J* = 13.8 Hz), 4.15 (d, 1H, *J* = 13.5 Hz), 3.92 (s, 3H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.2, 147.7, 139.1, 134.0, 130.6, 130.5, 129.0, 128.4, 128.2, 124.2, 113.82, 118.79, 112.38, 112.35, 56.16, 52.5. ESI-HRMS calcd for C₁₅H₁₄ClN₃NaO₂ (Cl-35) (M+Na)⁺ 326.0667, found 326.0663.



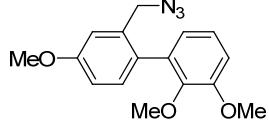
2'-(azidomethyl)-2,3-dimethoxy-5'-methylbiphenyl (Ik): Yield 271.3 mg (64%, colorless oil); IR (neat): ν_{max} 2934, 2093, 1578, 1468, 1262 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (d, 1H, *J* = 7.8 Hz), 7.21 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.14-7.08 (m, 2H), 6.96 (dd, 1H, *J* = 8.2, 1.5 Hz), 6.80 (dd, 1H, *J* = 7.6, 1.2 Hz), 4.29 (d, 1H, *J* = 13.2 Hz), 4.19 (d, 1H, *J* = 13.6 Hz), 3.91 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.6, 146.0, 137.6, 137.3, 134.6, 131.0, 130.9, 128.44, 128.35, 123.9, 122.9, 111.7, 60.4, 55.6, 52.3, 20.9. ESI-HRMS calcd for C₁₆H₁₇N₃NaO₃ (M+Na)⁺ 306.1213, found 306.1217.



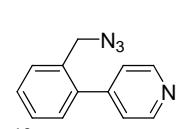
2'-(azidomethyl)-5'-chloro-2,3-dimethoxybiphenyl (Il): Yield 195.0 mg (62%, colorless oil); IR (neat): ν_{max} 2936, 2835, 2098, 1579, 1467, 1264, 1110 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.28 (m, 2H), 7.29 (d, 1H, *J* = 2.1 Hz), 7.10 (t, 1H, *J* = 8.1 Hz), 6.96 (dd, 1H, *J* = 8.1, 1.2 Hz), 6.79 (dd, 1H, *J* = 7.5, 1.5 Hz), 4.31 (d, 1H, *J* = 10.5 Hz), 4.16 (d, 1H, *J* = 13.8 Hz), 3.88 (s, 3H), 3.52 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.8, 146.0, 139.4, 133.3, 133.2, 133.0, 129.6, 127.9, 124.3, 122.6, 122.4, 60.7, 55.8, 52.0. ESI-HRMS calcd for C₁₅H₁₄ClN₃NaO₂ (Cl-35) (M+Na)⁺ 326.0667, found 326.0682.



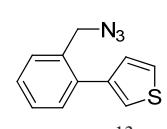
2-(azidomethyl)-4-fluoro-3',4'-dimethoxybiphenyl (1m**):** Yield 219.2 mg (63%, color oil); IR (neat): ν_{max} 2937, 2096, 1605, 1588, 1489, 1246 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.28 (dd, 1H, J = 8.4, 5.7 Hz), 7.16 (dd, 1H, J = 9.3, 2.7 Hz), 7.06 (td, 1H, J = 8.1, 2.7 Hz), 6.94-6.91 (m, 1H), 6.85-6.81 (m, 2H), 4.27 (s, 2H), 3.93 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.9 (d, J_{CF} = 246 Hz), 148.6, 148.5, 137.8 (d, J_{CF} = 3 Hz), 135.1 (d, J_{CF} = 7 Hz), 131.9 (d, J_{CF} = 8 Hz), 131.8, 121.4, 115.9 (d, J_{CF} = 22 Hz), 115.0 (d, J = 21 Hz), 112.5, 110.0, 55.8, 52.32, 52.30. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$ 260.1018, found 260.1076.



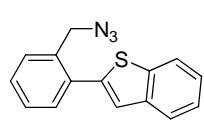
2'-(azidomethyl)-2,3,4'-trimethoxybiphenyl (In**):** Yield 203.6 mg (54%, colorless oil); IR (neat): ν_{max} 2936, 2097, 1609, 1467, 1262 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.19 (d, 1H, J = 4.2 Hz), 7.09 (t, 1H, J = 8.1 Hz), 7.02 (d, 1H, J = 2.7 Hz), 6.94 (dd, 1H, J = 8.4, 2.7 Hz), 6.90 (dd, 1H, J = 8.4, 2.7 Hz), 6.78 (dd, 1H, J = 6.8 Hz), 4.33 (d, 1H, J = 11.4 Hz), 4.19 (d, 1H, J = 12.3 Hz), 3.89 (s, 3H), 3.85 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.1, 152.6, 146.2, 135.4, 134.2, 131.3, 129.8, 124.0, 123.2, 113.3, 113.2, 111.6, 60.4, 55.7, 55.2, 52.6. ESI-HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 322.1162, found 322.1160.



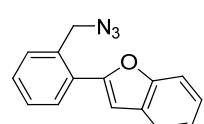
4-(2-(azidomethyl)phenyl)pyridine (Io**):** Yield 164.5 mg (50%, colorless oil); IR (neat): ν_{max} 3029, 2095, 1594, 1479, 1408, 1251 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 8.68 (dd, 2H, J = 4.5, 1.5 Hz), 7.48-7.43 (m, 3H), 7.31-7.28 (m, 3H), 4.26 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.8, 148.0, 139.4, 132.4, 130.0, 129.9, 128.8, 128.7, 124.0, 52.3. ESI-HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{N}_4$ ($\text{M}+\text{H}$) $^+$ 211.0978, found 211.0970.



3-(2-(azidomethyl)phenyl)thiophene (Ip**):** Yield 203.6 mg (35%, colorless oil); IR (neat): ν_{max} 3102, 2929, 2090, 1482, 1449, 1256 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.36 (m, 5H), 7.32 (dd, 1H, J = 3.0, 1.2 Hz), 7.17 (dd, 1H, J = 4.8, 1.2 Hz), 4.32 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.2, 136.7, 132.7, 130.2, 129.8, 128.7, 128.3, 127.6, 125.5, 123.2, 52.7. ESI-HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{NS}$ ($\text{M}-\text{N}_2$) $^+$ 118.0528, found 188.0528.

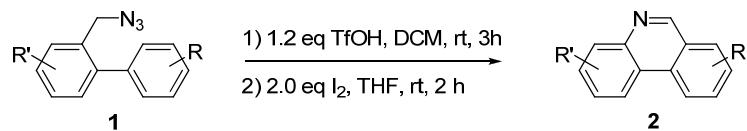


2-(2-(azidomethyl)phenyl)benzo[b]thiophene (Iq**):** Yield 270.7 mg (71%, colorless oil); IR (neat): ν_{max} 2928, 2093, 1724, 1431, 1250 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.92-7.87 (m, 2H), 7.64-7.61 (m, 1H), 7.55-7.41 (m, 6H), 4.52 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.1, 140.2, 140.0, 134.3, 133.5, 131.3, 130.0, 128.7, 128.4, 124.4, 123.8, 123.7, 122.0, 52.7. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{NS}$ ($\text{M}-\text{N}_2$) $^+$ 238.0685, found 238.0686.

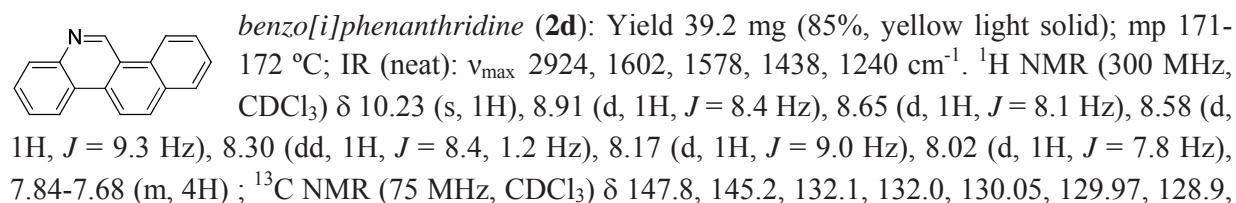
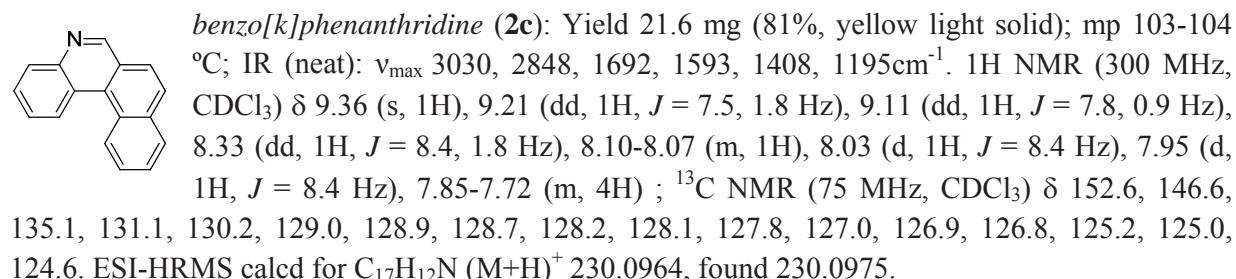
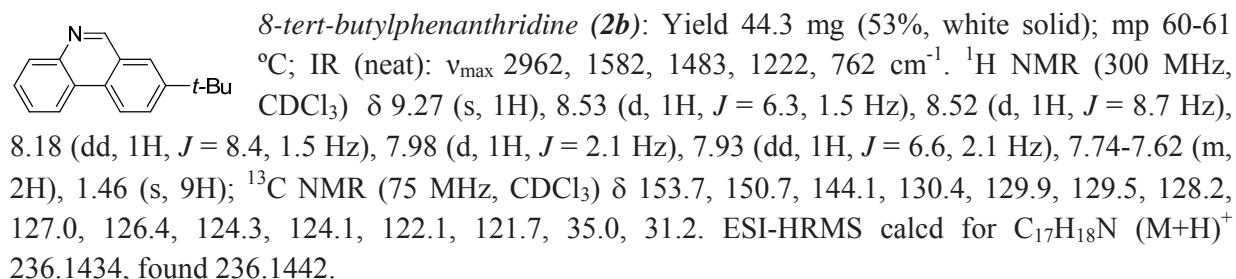
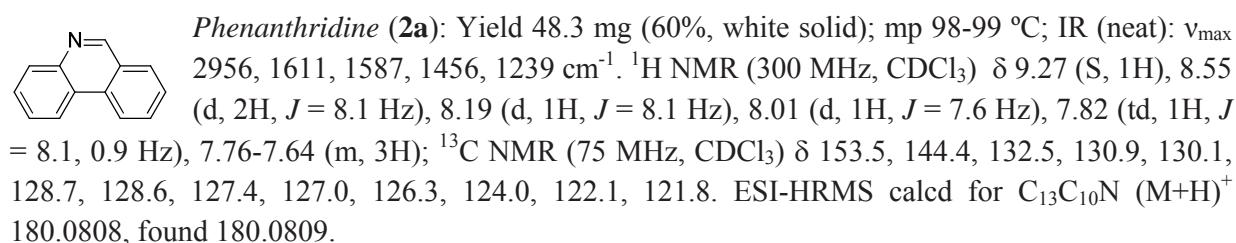


2-(2-(azidomethyl)phenyl)benzofuran (Ir**):** Yield 350.0 mg (67%, colorless oil); IR (neat): ν_{max} 2933, 2093, 1449, 1255 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, 1H, J = 7.2 Hz), 7.73 (d, 1H, J = 7.5 Hz), 7.68 (d, 1H, J = 7.5 Hz), 7.56-7.36 (m, 5H), 7.11 (d, 1H, J = 0.6 Hz), 4.68 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.7, 154.1, 132.4, 130.3, 129.9, 128.9, 128.8, 128.5, 124.5, 122.9, 121.1, 111.1, 105.5, 53.2. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{NaO}$ ($\text{M}+\text{Na}$) $^+$ 272.0794, found 272.0796.

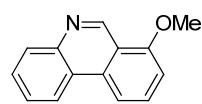
3. General procedure for the synthesis of phenanthridine (2):



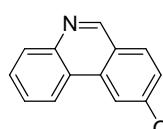
To a solution of 2-(azidomethyl)biphenyl **1** (1.0 equiv) in DCM (6.0 mL/mmol) was added TfOH (1.2 equiv) at room temperature. The reaction mixture was stirred for 3 h and then added with sat. NaHCO₃ to dilute the reaction. The mixture was extracted with EtOAc (2×20 mL), and the combined organic layers were washed with water (10 mL) and brine (10 mL), dried over Na₂SO₄, filtered, concentrated under reduced pressure. The residue was used in the next step without further purification. The crude product in THF (18.0 mL/mmol) was then added with I₂ (2.0 equiv) and stirred for 2 h. The reaction mixture was added aq. Na₂S₂O₈ (mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na₂SO₄) and concentrated under reduced pressure to obtain the crude material which was purified on silica gel to yield phenanthridine (**2**).



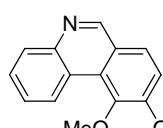
128.8, 128.0, 127.1, 127.0, 124.2, 122.6, 122.1, 121.7, 119.7. ESI-HRMS calcd for C₁₇H₁₂N (M+H)⁺ 230.0964, found 230.0959.



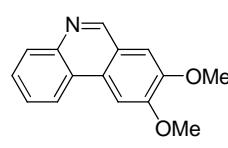
7-methoxyphenanthridine (2e-A): Yield 6.5 mg (14%, yellow solid); mp 116-117 °C; IR (neat): ν_{max} 2926, 1587, 1254, 1019, 751 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.74 (s, 1H), 8.55 (dd, 1H, *J* = 8.1, 1.2 Hz), 8.21-8.14 (m, 2H), 7.79-7.72 (m, 2H), 7.66 (td, 1H, *J* = 6.9, 1.2 Hz), 7.05 (d, 1H, *J* = 7.8 Hz), 4.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.5, 148.3, 144.6, 133.9, 131.6, 130.0, 128.7, 126.8, 123.7, 122.7, 117.4, 113.8, 106.7, 55.8. ESI-HRMS calcd for C₁₄H₁₂NO (M+H)⁺ 210.0913, found 210.0920.



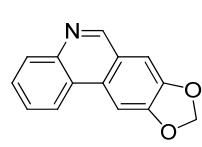
9-methoxyphenanthridine (2e-B): Yield 31.4 mg (65%, yellow solid); mp 84-85 °C; IR (neat): ν_{max} 2835, 1617, 1232, 760 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.07 (s, 1H), 8.39 (dd, 1H, *J* = 8.1, 0.9 Hz), 8.08 (dd, 1H, *J* = 8.1, 0.9 Hz), 7.85 (d, 1H, *J* = 8.7 Hz), 7.79 (d, 1H, *J* = 2.1 Hz), 7.65 (td, 1H, *J* = 6.9, 1.2 Hz), 7.55 (td, 1H, *J* = 8.4, 1.5 Hz), 7.20 (dd, 1H, *J* = 8.7, 2.4 Hz), 3.94 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.7, 152.7, 144.6, 134.5, 130.5, 130.0, 128.7, 126.5, 123.8, 122.1, 121.4, 117.8, 102.4, 55.5. ESI-HRMS calcd for C₁₄H₁₂NO (M+H)⁺ 210.0913, found 210.0914.



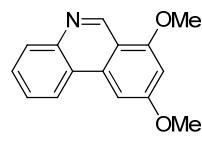
9,10-dimethoxyphenanthridine (2f): Yield 70.7 mg (99%, white solid); mp 106-107 °C; IR (neat): ν_{max} 2936, 1602, 1497, 1280, 1113 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.43 (dd, 1H, *J* = 8.1, 1.2 Hz), 9.12 (s, 1H), 8.15 (dd, 1H, *J* = 8.1, 1.8 Hz), 7.83 (d, 1H, *J* = 8.7 Hz), 7.74 (td, 1H, *J* = 7.2, 1.5 Hz), 7.66 (td, 1H, *J* = 6.9, 1.5 Hz), 7.42 (d, 1H, *J* = 8.7 Hz), 4.01 (s, 3H), 4.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 154.7, 153.2, 145.7, 144.8, 129.6, 128.5, 127.2, 126.9, 126.6, 125.9, 123.4, 122.5, 113.3, 59.8, 56.3. ESI-HRMS calcd for C₁₅H₁₄NO₂ (M+H)⁺ 240.1019, found 240.1018.



8,9-dimethoxyphenanthridine (2g): Yield 61.6 mg (83%, white solid); mp 163-164 °C; IR (neat): ν_{max} 2998, 2832, 1609, 1504, 1264, 1160 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.13 (s, 1H), 8.42 (d, 1H, *J* = 7.8 Hz), 8.15 (d, 1H, *J* = 7.8 Hz), 7.84 (s, 1H), 7.71-7.62 (m, 2H), 7.32 (s, 1H), 4.12 (s, 3H), 4.06 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.8, 151.6, 149.9, 143.8, 130.0, 128.1, 127.7, 126.5, 123.7, 121.7, 121.6, 107.7, 101.7, 56.1, 56.0. ESI-HRMS calcd for C₁₅H₁₄NO₂ (M+H)⁺ 240.1019, found 240.1028.

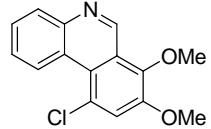


[1,3]dioxolo[4,5-j]phenanthridine (2h): Yield 41.8 mg (49%, white solid); mp 139-140 °C; IR (neat): ν_{max} 2910, 1621, 1461, 1251, 1036, 939 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.07 (s, 1H), 8.34 (d, 1H, *J* = 8.1 Hz), 8.14 (d, 1H, *J* = 8.4 Hz), 7.87 (s, 1H), 7.70-7.58 (m, 2H), 7.30 (s, 1H), 6.14 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 151.7, 151.4, 148.1, 144.1, 130.1, 130.0, 127.9, 126.6, 124.2, 123.0, 121.9, 105.4, 101.8, 99.8. ESI-HRMS calcd for C₁₄H₁₀NO₂ (M+H)⁺ 224.0706, found 224.0705.

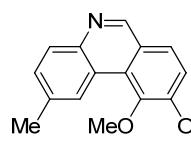


7,9-dimethoxyphenanthridine (2i): Yield 52.9 mg (97%, white solid); mp 138-139 °C; IR (neat): ν_{max} 2830, 1614, 1594, 1208 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 9.45 (s, 1H), 8.40 (d, 1H, *J* = 8.2 Hz), 8.14 (dd, 1H, *J* = 8.2, 1.0 Hz), 7.71 (td, 1H, *J* = 7.0, 1.4 Hz), 7.59 (td, 1H, *J* = 8.2, 1.3 Hz), 7.40 (d, 1H, *J* = 1.6 Hz), 6.59 (d,

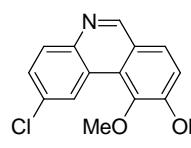
1H, $J = 2.0$ Hz), 3.99 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.6, 158.8, 147.6, 145.1, 135.4, 130.0, 128.7, 126.2, 123.6, 122.5, 113.2, 98.2, 94.0, 55.7, 55.5. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 240.1019, found 240.1023.



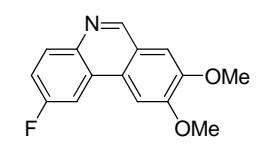
10-chloro-7,8-dimethoxyphenanthridine (2j-A): Yield 192.7 mg (58%, white solid); mp 140-141 °C; IR (neat): ν_{max} 3749, 2946, 1586, 1306, 1076, 755 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.71 (dd, 1H, $J = 8.7, 1.2$ Hz), 9.64 (s, 1H), 8.19 (dd, 1H, $J = 8.1, 1.5$ Hz), 7.74 (td, 1H, $J = 6.9, 1.5$ Hz), 7.66 (app. td, 1H, $J = 6.9, 1.2$ Hz), 7.60 (s, 1H), 4.08 (s, 3H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.4, 148.2, 144.8, 144.6, 130.3, 128.3, 126.8, 125.9, 125.3, 123.6, 123.04, 123.01, 121.1, 62.0, 56.6. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{ClNO}_2$ (Cl-35) ($\text{M}+\text{H}$) $^+$ 274.0629, found 274.0637.



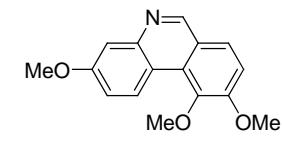
9,10-dimethoxy-2-methylphenanthridine (2k): Yield 97.4 mg (99%, white solid); mp 75-76 °C; IR (neat): ν_{max} 2934, 2835, 1603, 1499, 1279, 1111 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.22 (s, 1H), 9.04 (s, 1H), 8.04 (d, 1H, $J = 8.1$ Hz), 7.76 (d, 1H, 1H, $J = 8.7$ Hz), 7.55 (dd, 1H, $J = 8.1, 1.8$ Hz), 7.35 (d, 1H, $J = 8.7$ Hz), 4.04 (s, 3H), 3.99 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.6, 152.4, 145.9, 143.2, 136.7, 130.1, 129.5, 126.9, 126.5, 125.8, 123.3, 122.9, 113.4, 59.8, 56.4, 22.2. ESI-HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 254.1176, found 254.1181.



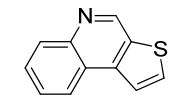
2-chloro-9,10-dimethoxyphenanthridine (2l): Yield 80.7 mg (86%, yellow light solid); mp 121-122 °C; IR (neat): ν_{max} 2941, 1609, 1495, 1281, 1116 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.43 (d, 1H, $J = 2.1$ Hz), 9.09 (s, 1H), 8.06 (d, 1H, $J = 8.7$ Hz), 7.81 (d, 1H, $J = 6.0$ Hz), 7.67 (dd, 1H, $J = 9.0, 2.4$ Hz), 7.43 (d, 1H, $J = 8.7$ Hz) 4.07 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.8, 153.5, 145.8, 143.5, 132.4, 131.0, 128.9, 126.7, 125.8, 125.6, 124.4, 122.6, 114.1, 59.8, 56.4. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{ClNO}_2$ (Cl-35) ($\text{M}+\text{H}$) $^+$ 247.0624, found 274.0624.



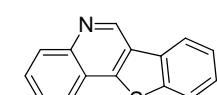
2-fluoro-8,9-dimethoxyphenanthridine (2m): Yield 87.1 mg (99%, yellow light solid); mp 161-162 °C; IR (neat): ν_{max} 1618, 1503, 1467, 1265, 1158 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.11 (s, 1H), 8.36 (dd, 1H, $J = 9.3, 5.7$ Hz), 7.77 (dd, 1H, $J = 9.9, 2.7$ Hz), 7.74 (s, 1H), 7.42-7.34 (m, 1H), 7.31 (s, 1H), 4.12 (s, 3H), 4.05 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.0 (d, $J_{\text{CF}} = 246$), 153.2, 152.8, 149.8, 145.1 (d, $J_{\text{CF}} = 12$ Hz), 128.0, 123.5 (d, $J_{\text{CF}} = 9$ Hz), 121.3, 120.5, 115.7 (d, $J_{\text{CF}} = 24$), 114.3 (d, $J_{\text{CF}} = 20$ Hz), 107.7, 101.5, 56.14, 56.07. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$ 258.0925, found 258.0926.



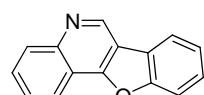
3,9,10-trimethoxyphenanthridine (2n): Yield 87.6 mg (76%, white solid); mp 125-126 °C; IR (neat): ν_{max} 2932, 1603, 1467, 1281, 1106 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.31 (d, 1H, $J = 9.3$ Hz), 9.07 (s, 1H), 7.77 (d, 1H, $J = 8.1$ Hz), 7.75 (d, 1H, $J = 2.7$ Hz), 7.33 (d, 1H, $J = 8.7$ Hz), 7.28 (dd, 1H, $J = 9.3, 3.0$ Hz), 4.05 (s, 3H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.6, 154.6, 153.7, 146.9, 145.0, 128.3, 126.8, 125.8, 122.0, 117.2, 117.0, 112.5, 110.2, 59.7, 56.3, 55.3. ESI-HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 270.1125, found 270.1128.



thieno[2,3-c]quinoline (2p): Yield 104.7mg (99%, white solid); mp 86-87 °C; IR (neat): ν_{max} 1499, 1363, 1220 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.30 (s, 1H), 8.25 (app td, 2H, J = 7.8, 0.6 Hz), 7.95 (d, 1H, J = 5.1 Hz), 7.83 (dd, 1H, J = 4.8, 0.3 Hz), 7.71 (td, 1H, J = 7.2, 1.5 Hz), 7.63 (td, 1H, J = 8.1, 1.2 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 144.1, 141.5, 133.0, 131.6, 129.7, 127.9, 126.8, 124.2, 123.2, 121.4. ESI-HRMS calcd for $\text{C}_{14}\text{H}_8\text{NS}$ ($\text{M}+\text{H}$) $^+$ 186.0372, found 186.0368.



compond (2q): Yield 28.5 mg (62%, white solid); mp 160-161 °C; IR (neat): ν_{max} 3052, 1560, 1499, 1359, 1243 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.55 (s, 1H), 8.31 (dd, 1H, J = 8.4, 1.5 Hz), 8.24 (d, 1H, J = 8.4 Hz), 8.08 (d, 1H, J = 7.8 Hz), 7.96 (dd, 1H, J = 7.2, 1.8 Hz), 7.75 (td, 1H, J = 7.8, 0.9), 7.63 (t, 1H, J = 7.8 Hz), 7.58-7.49 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.0, 145.5, 144.2, 138.9, 134.9, 130.3, 129.2, 128.6, 127.1, 126.9, 125.4, 124.2, 124.1, 123.0, 121.5. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{10}\text{NS}$ ($\text{M}+\text{H}$) $^+$ 236.0528, found 236.0537.



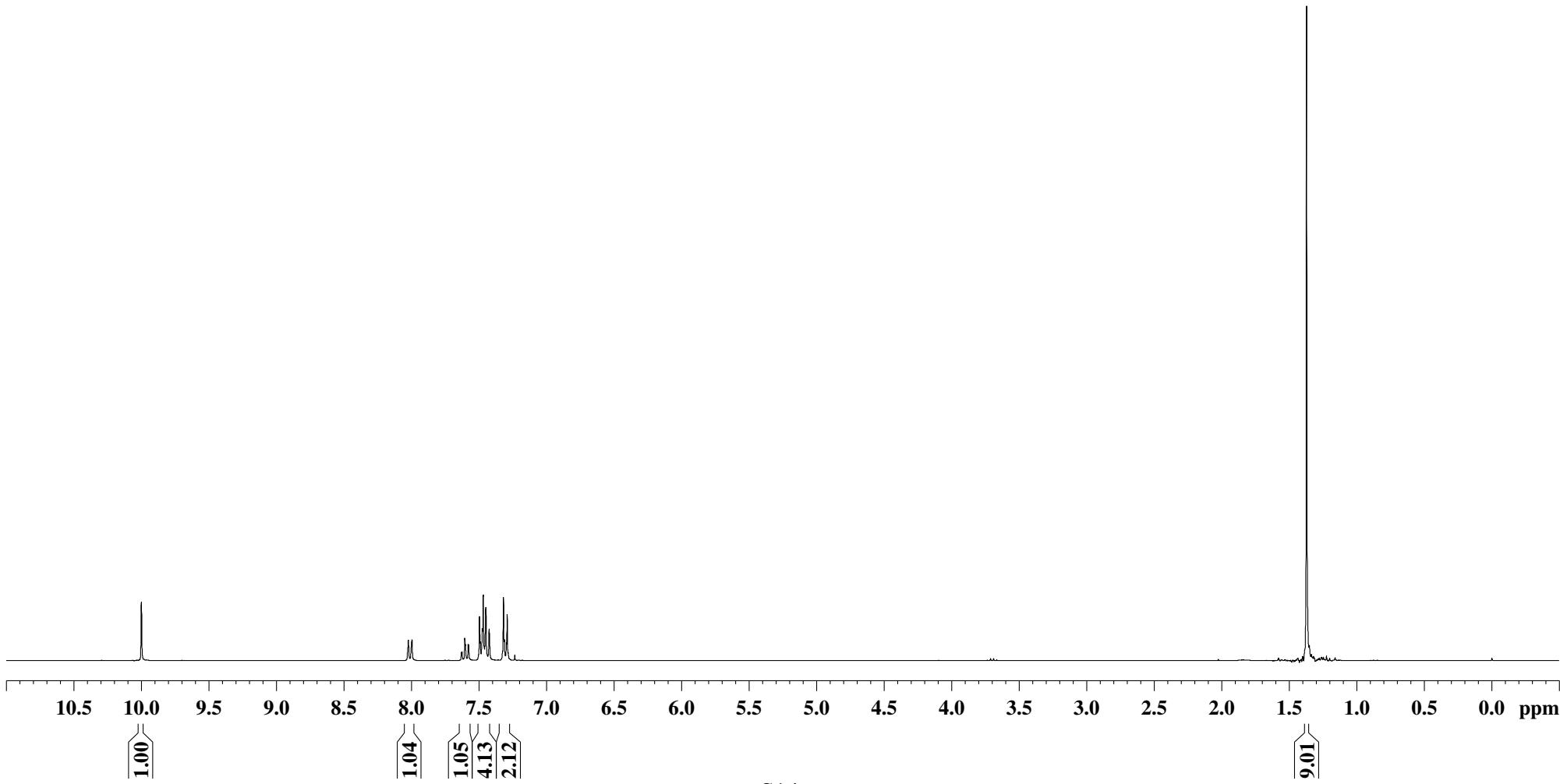
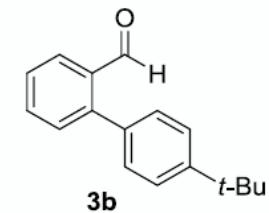
benzofuro[3,2-c]quinoline (2r): Yield 68.6 mg (80%, white solid); mp 130-131 °C; IR (neat): ν_{max} 2916, 2308, 2136, 1565, 1190 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.41 (s, 1H), 8.32 (dd, 1H, J = 8.1, 1.5 Hz), 8.23 (d, 1H, J = 8.4), 8.00 (dd, 1H, J = 7.5, 1.2 Hz), 7.76-7.60 (m, 3H), 7.48 (td, 1H, J = 7.2, 1.2 Hz), 7.40 (td, 1H, J = 7.5, 1.2 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 157.3, 155.8, 147.2, 144.1, 129.6, 129.2, 127.1, 126.9, 123.9, 122.5, 120.7, 120.5, 117.0, 116.2, 112.0. ESI-HRMS calcd for $\text{C}_{15}\text{H}_{10}\text{NO}$ ($\text{M}+\text{H}$) $^+$ 220.0757, found 220.0750.

SK-1-098

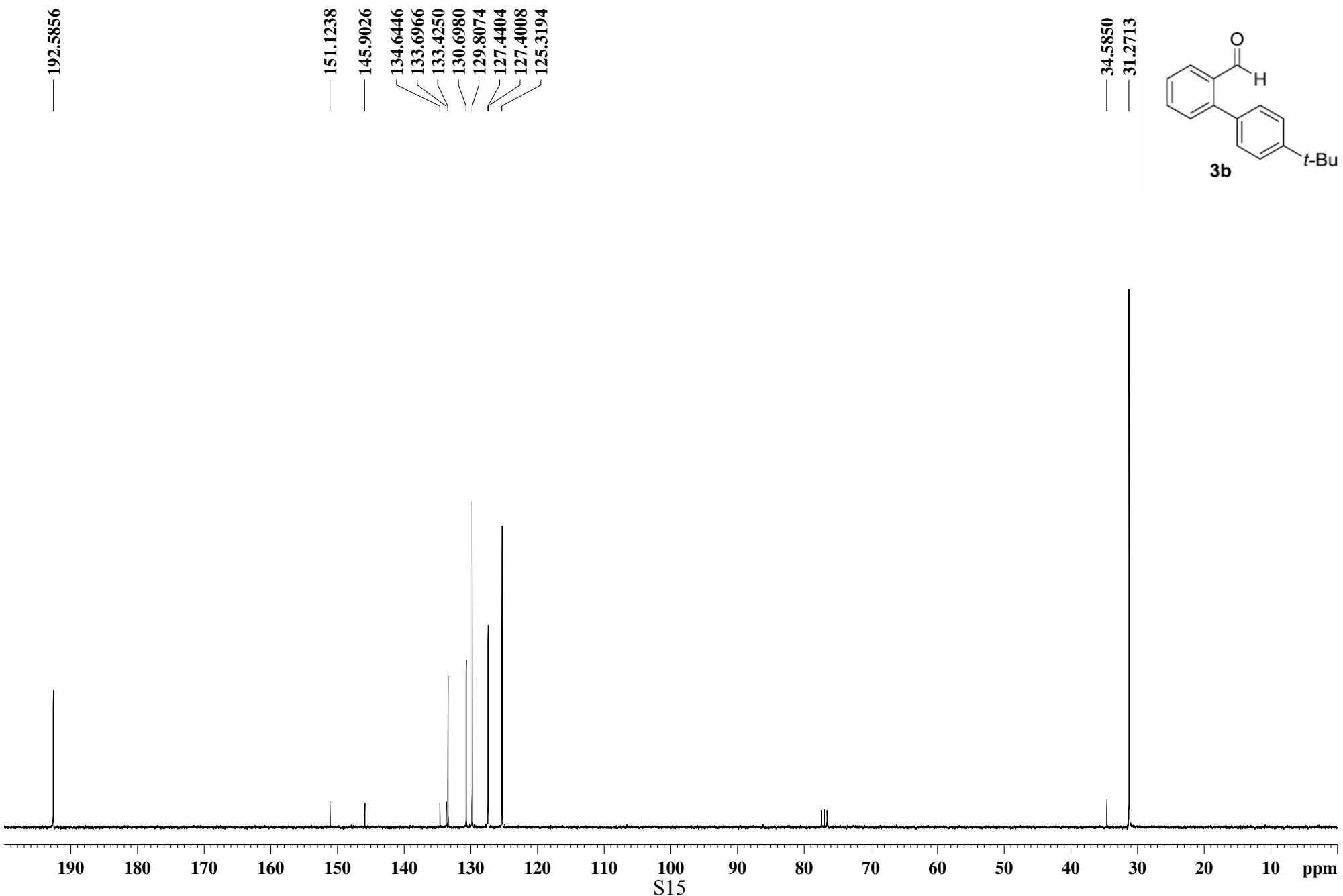
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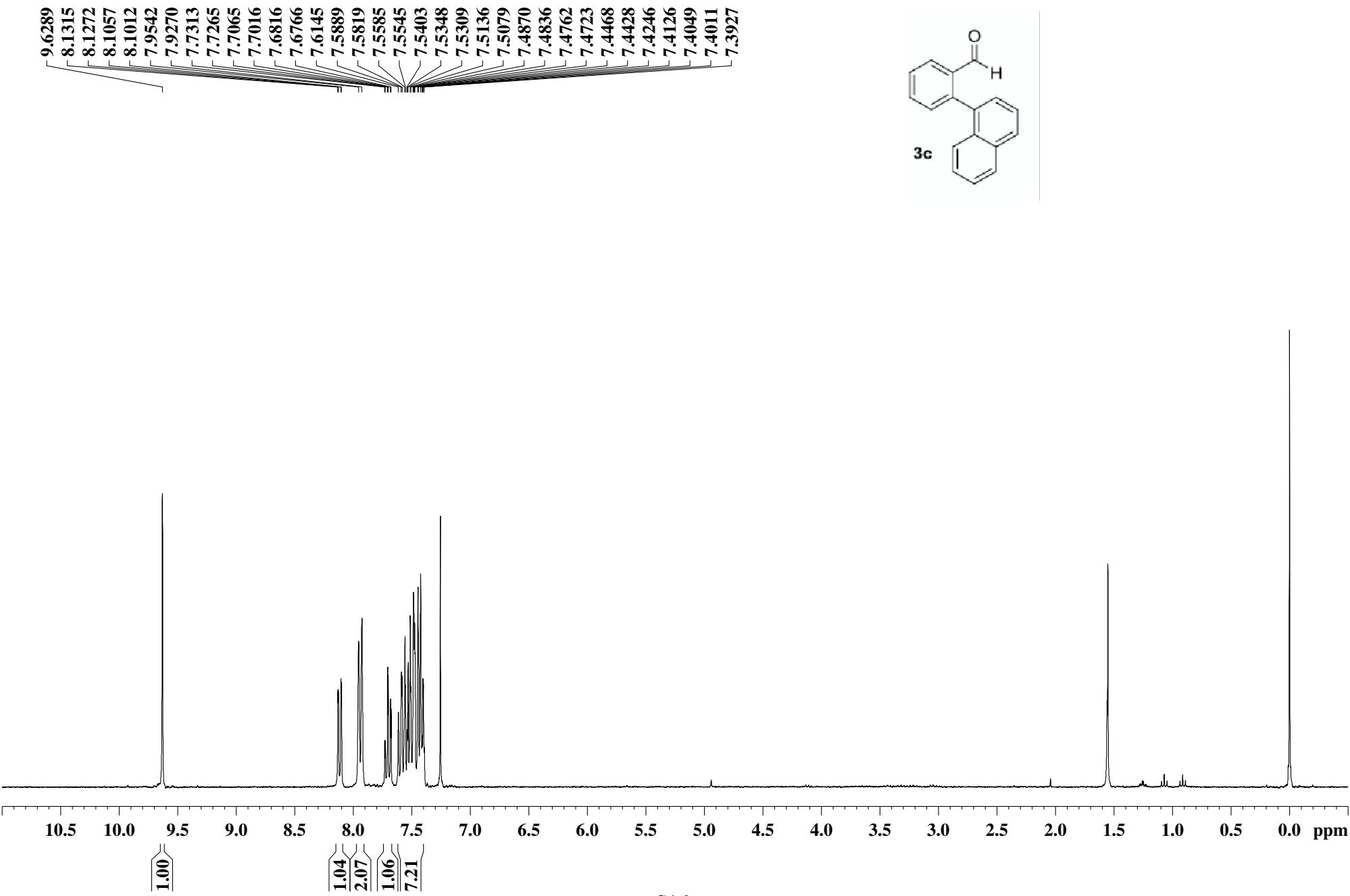
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SK-1-098

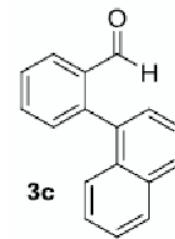
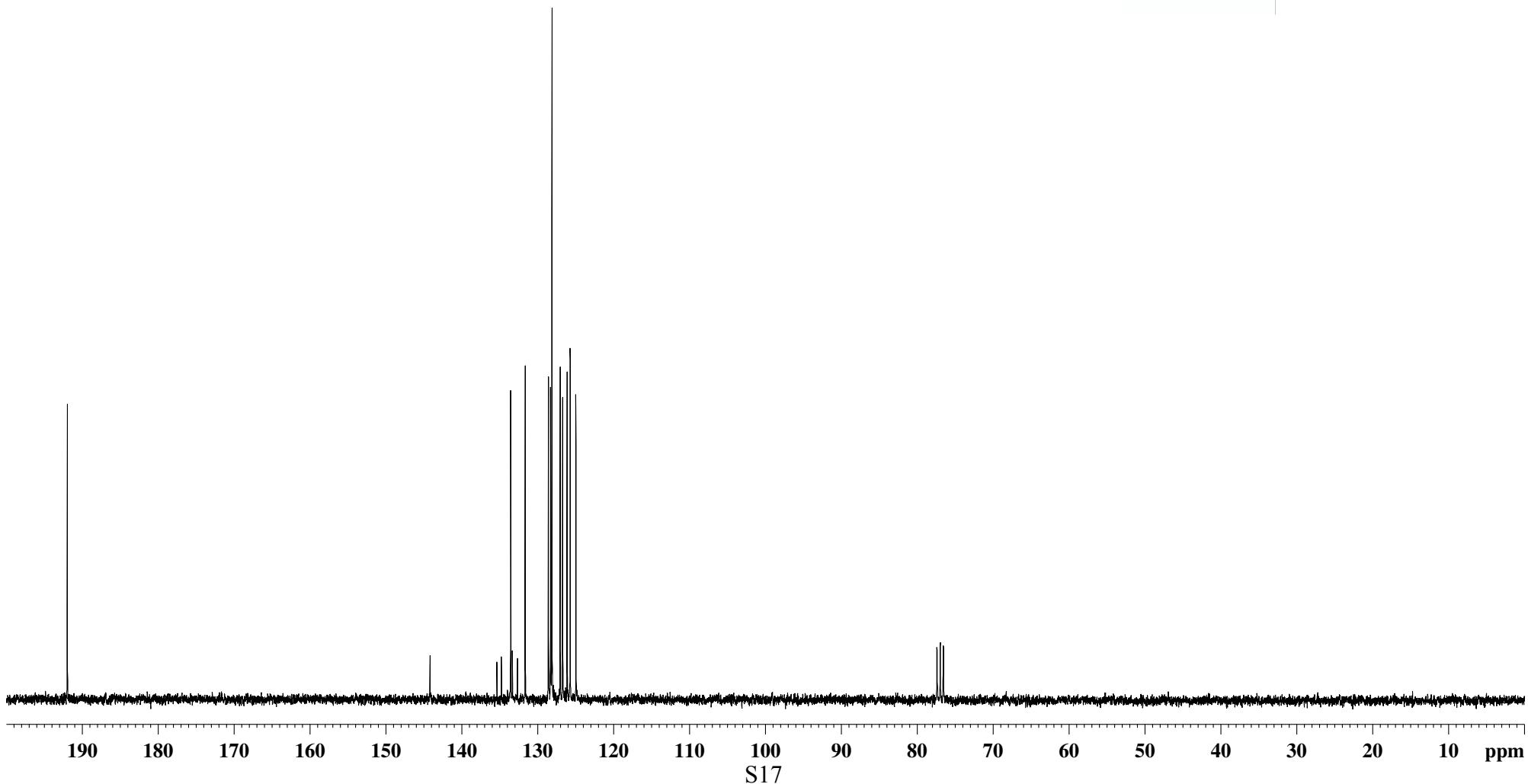


SK-1-125

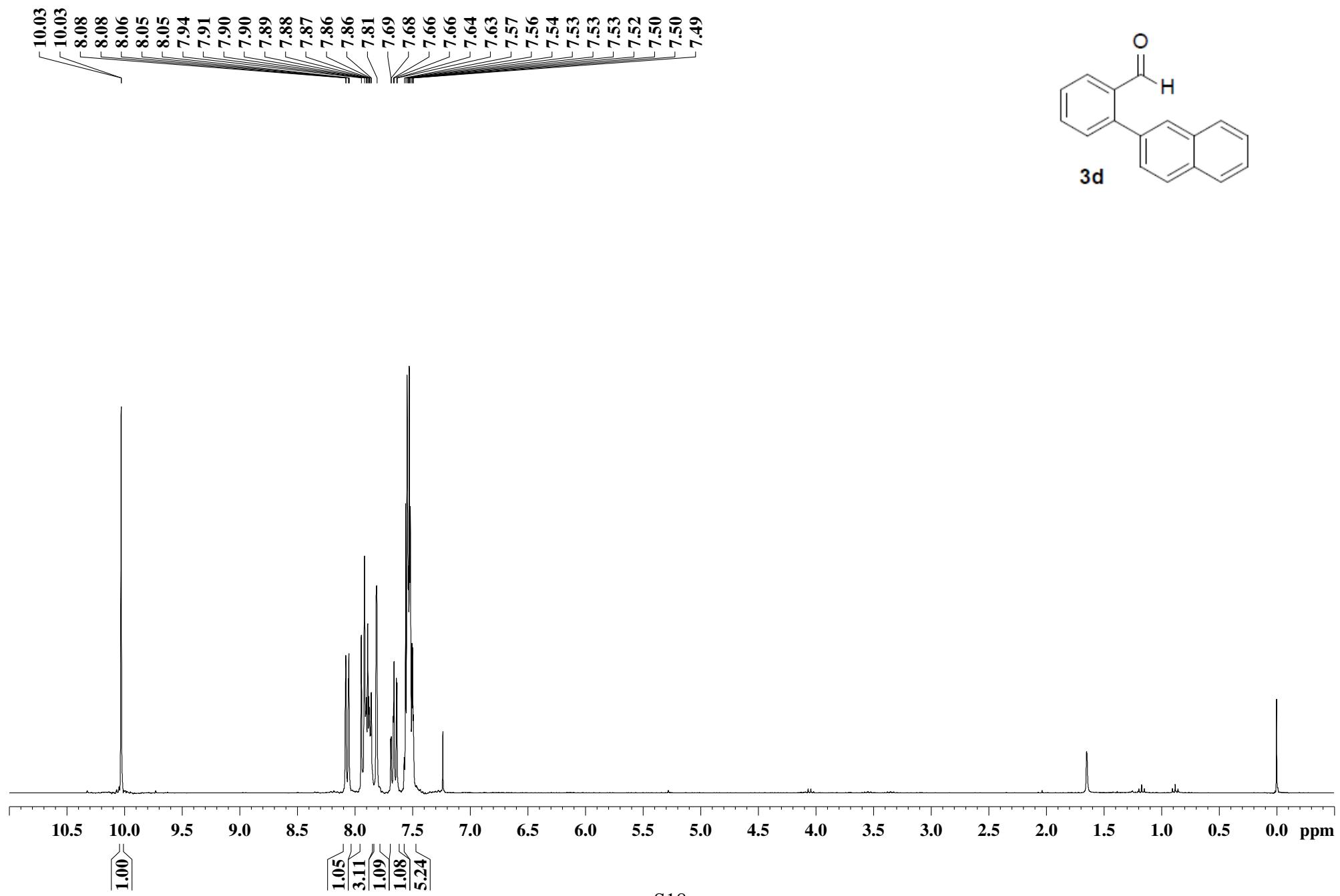


SK-1-125

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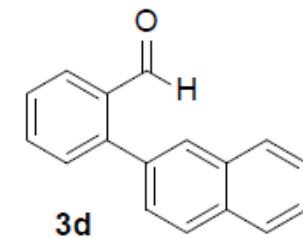
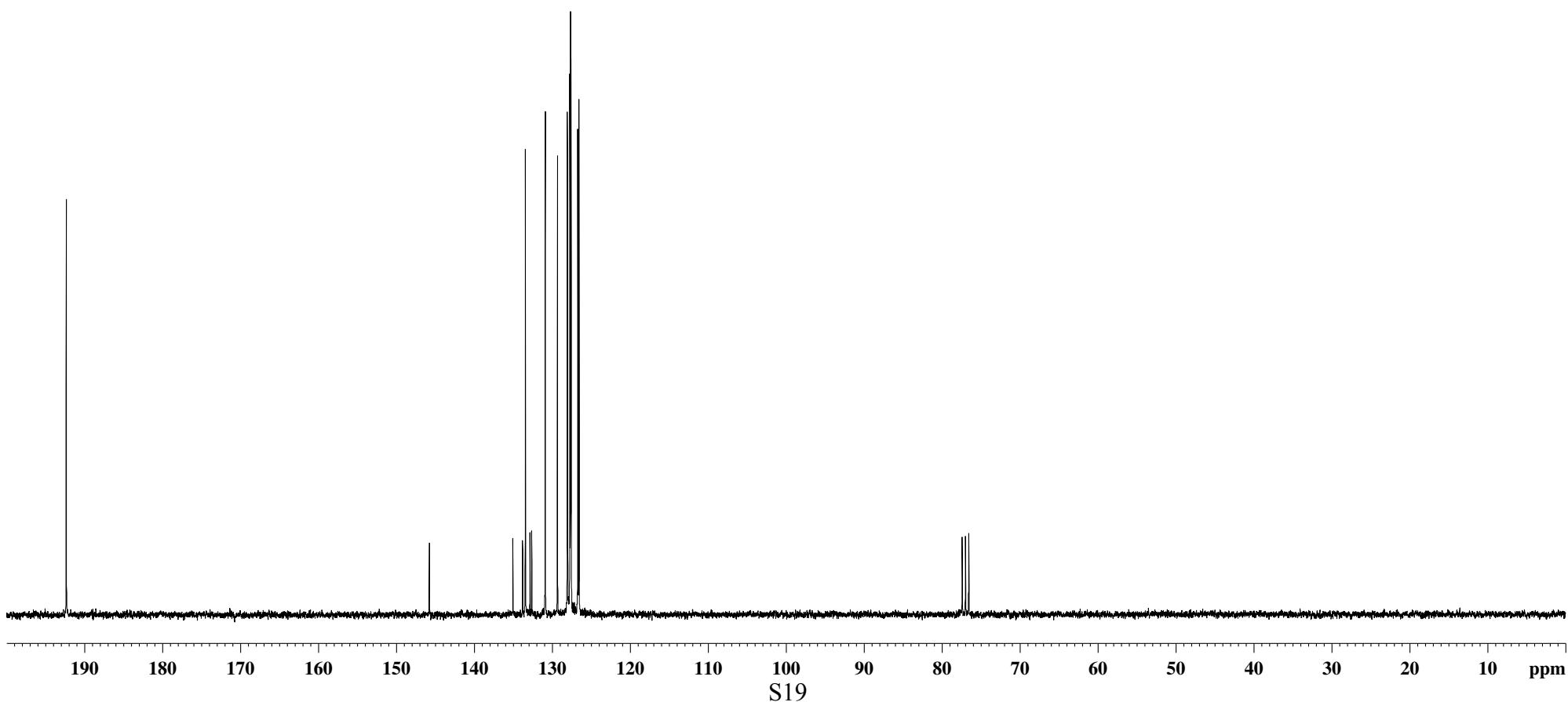


KN-1-004

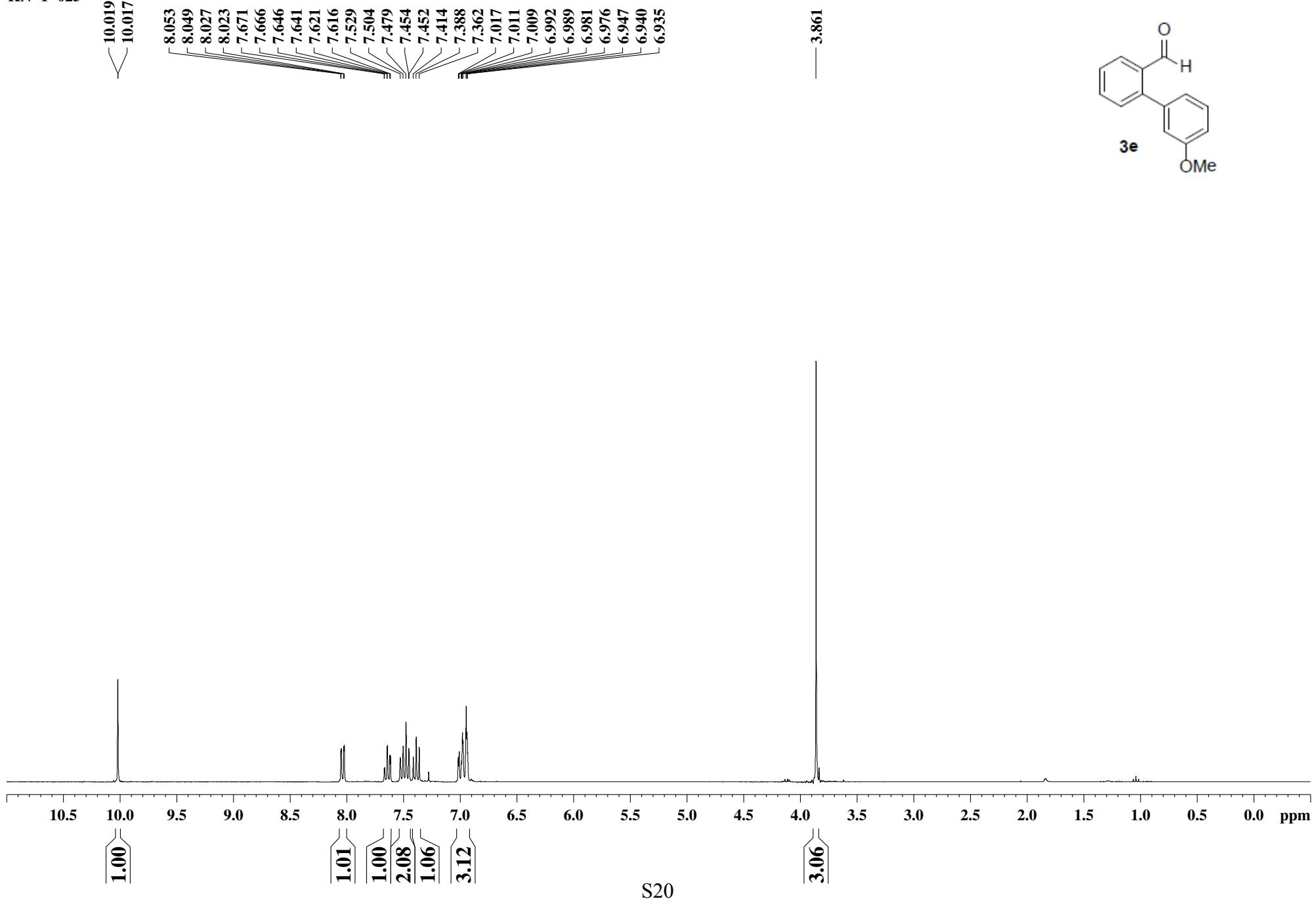


KN-1-004

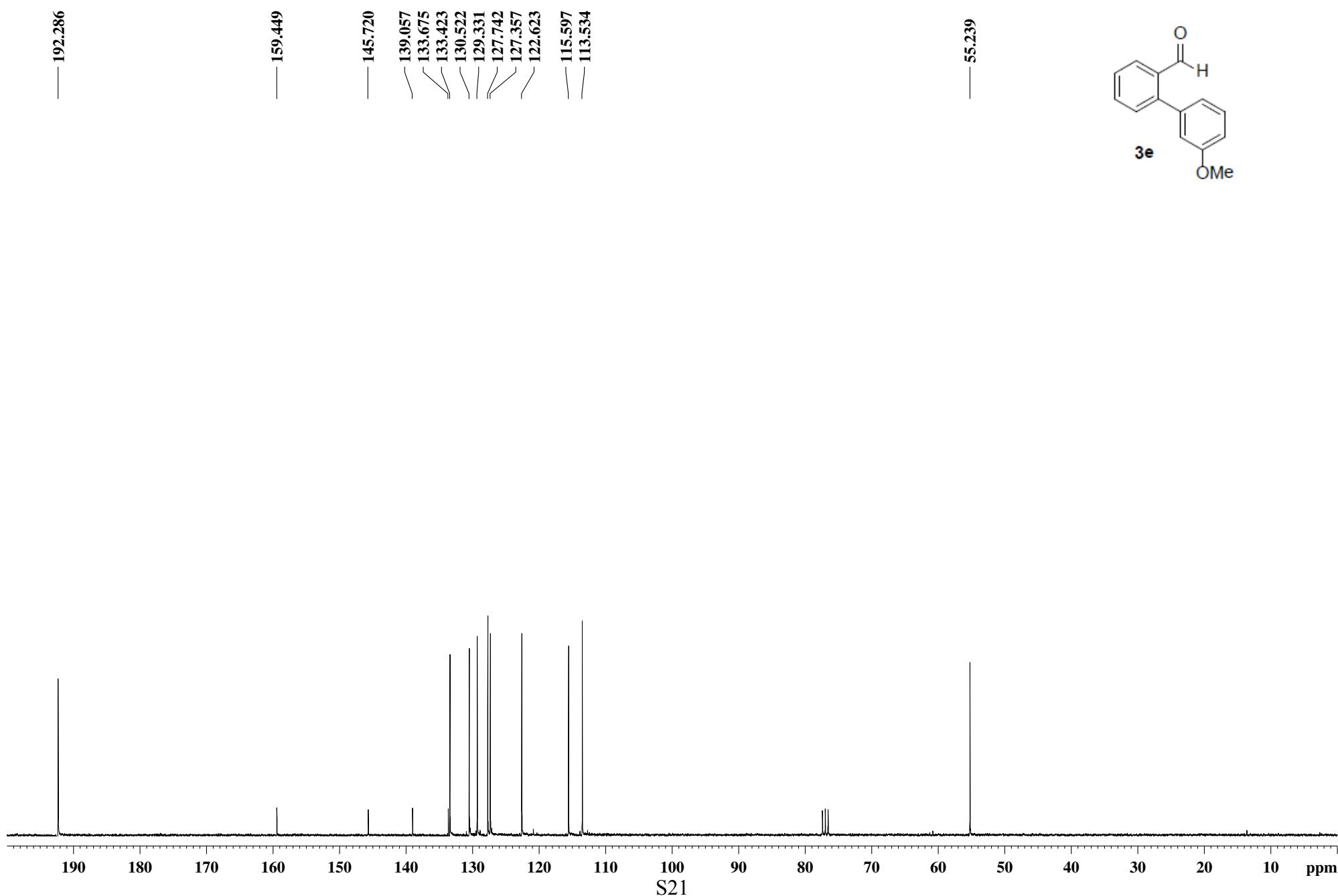
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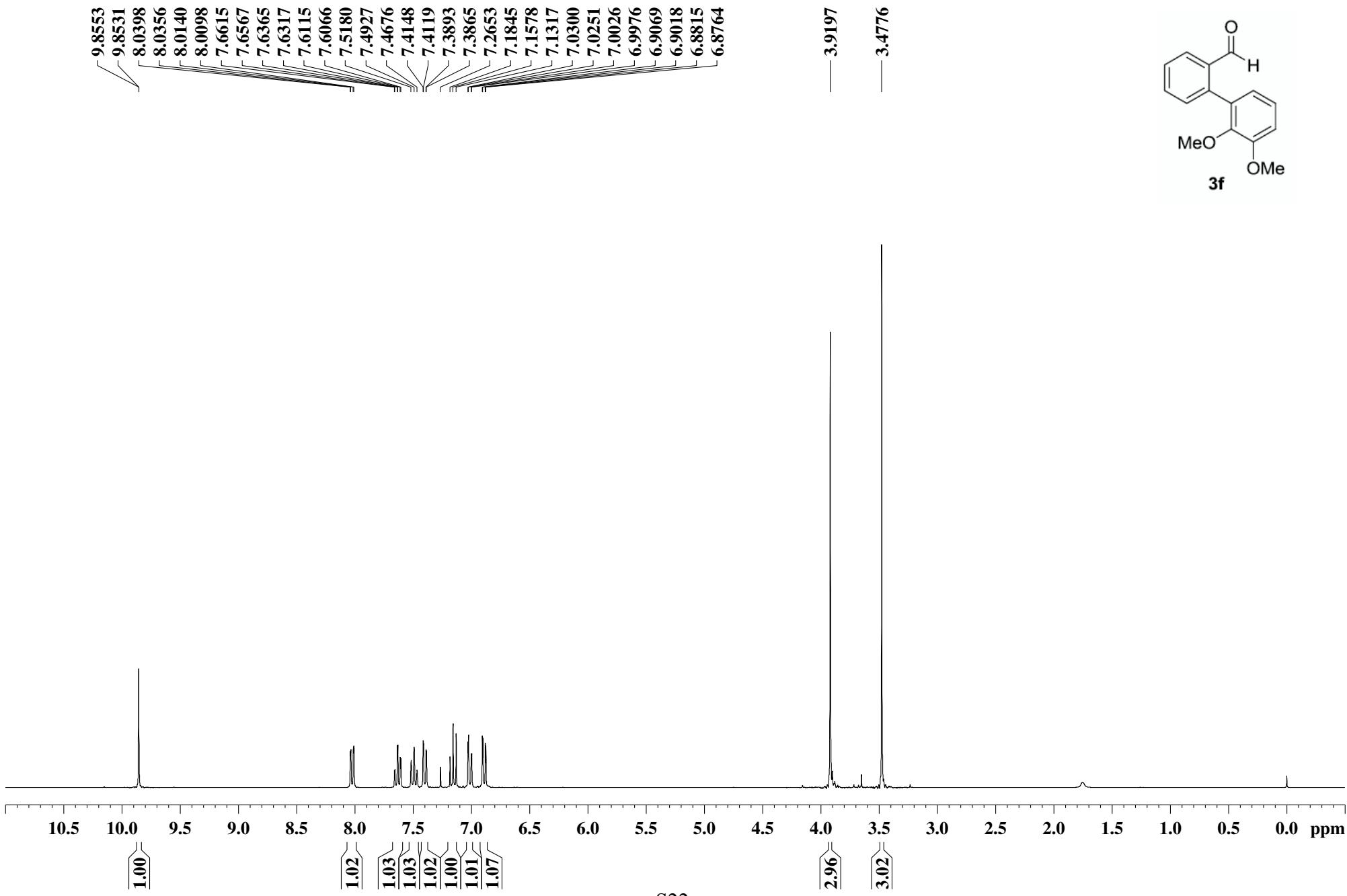
KN-1-025



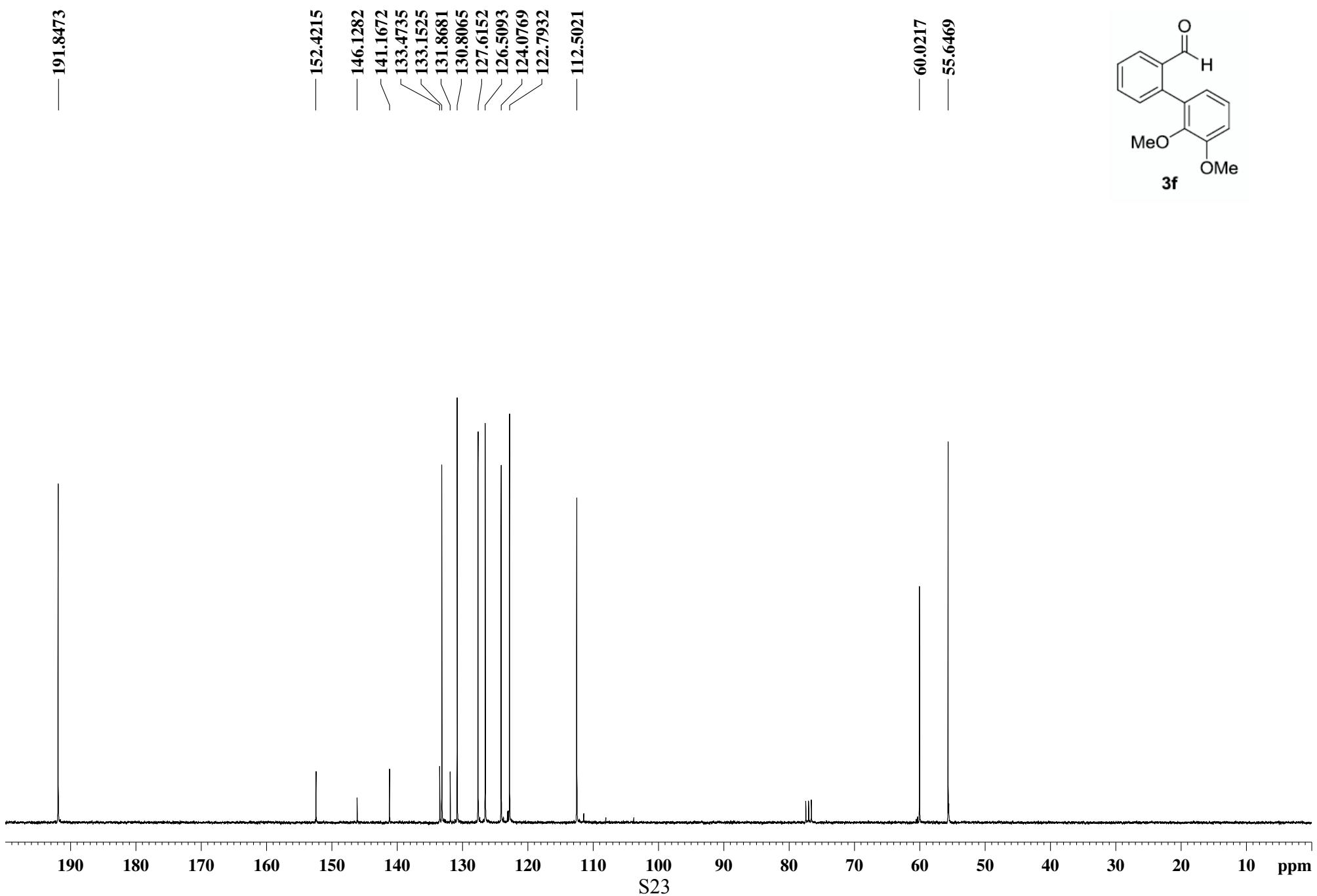
KN-1-025



SK-1-058B

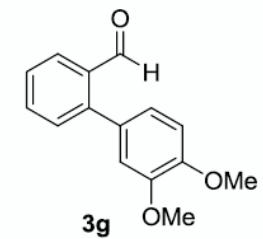
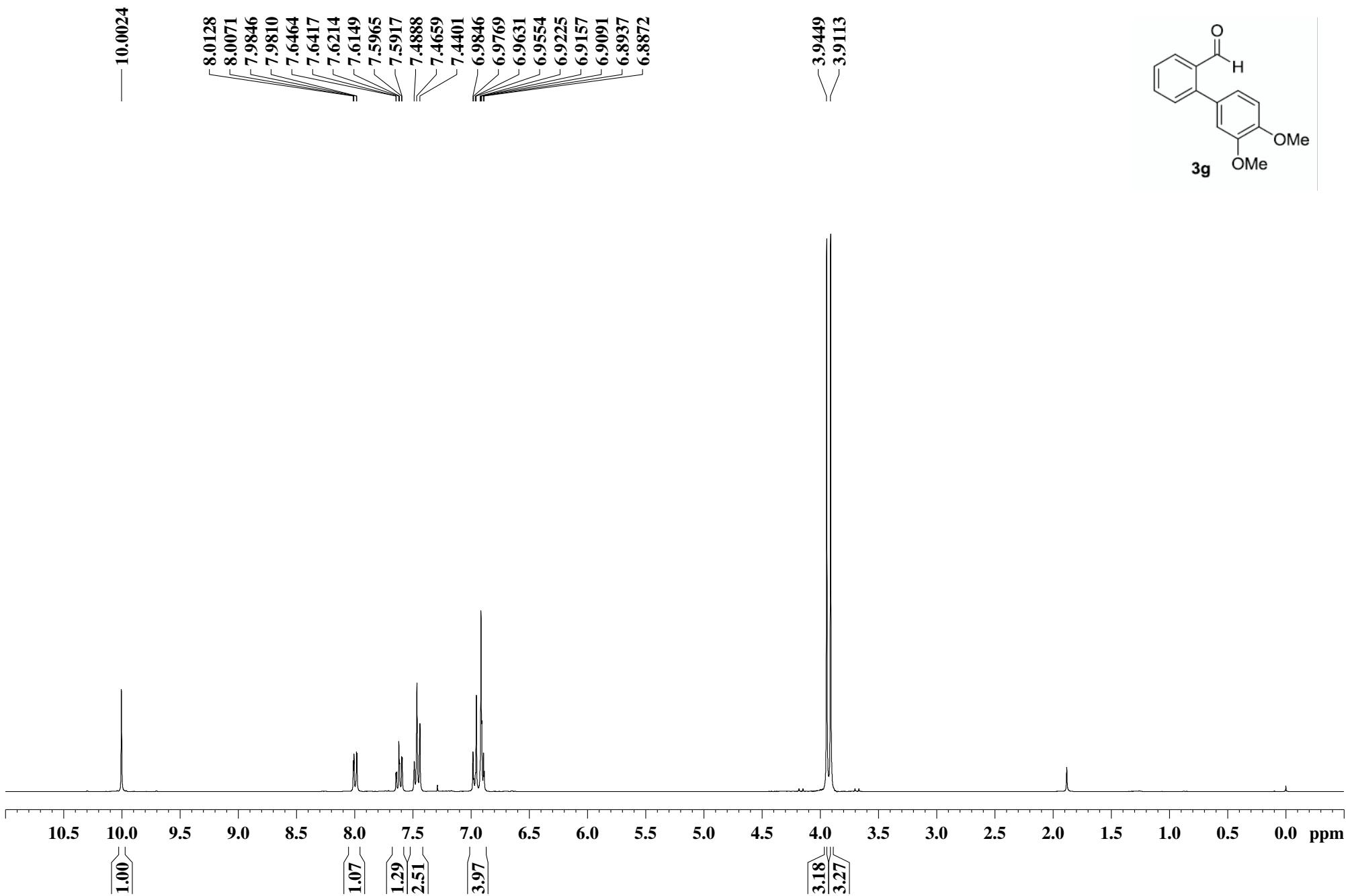


SK-1-058A



SK-1-060

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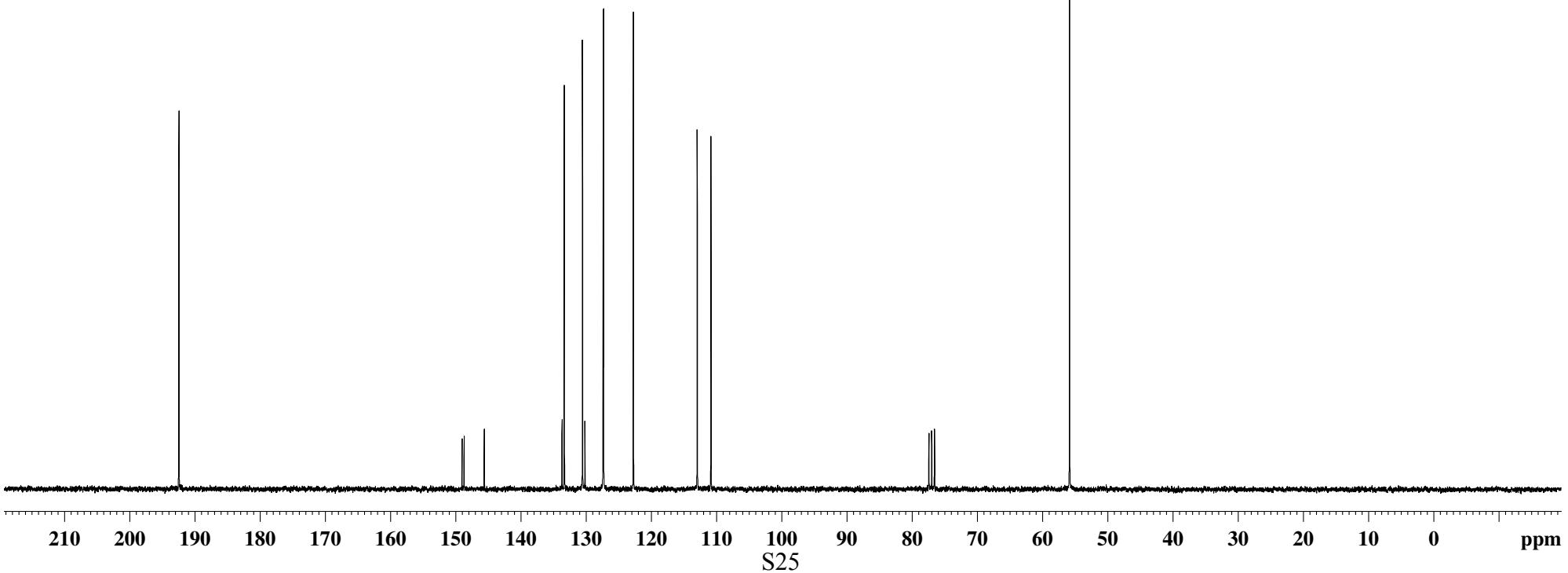
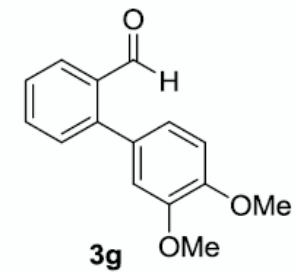


SK-1-060

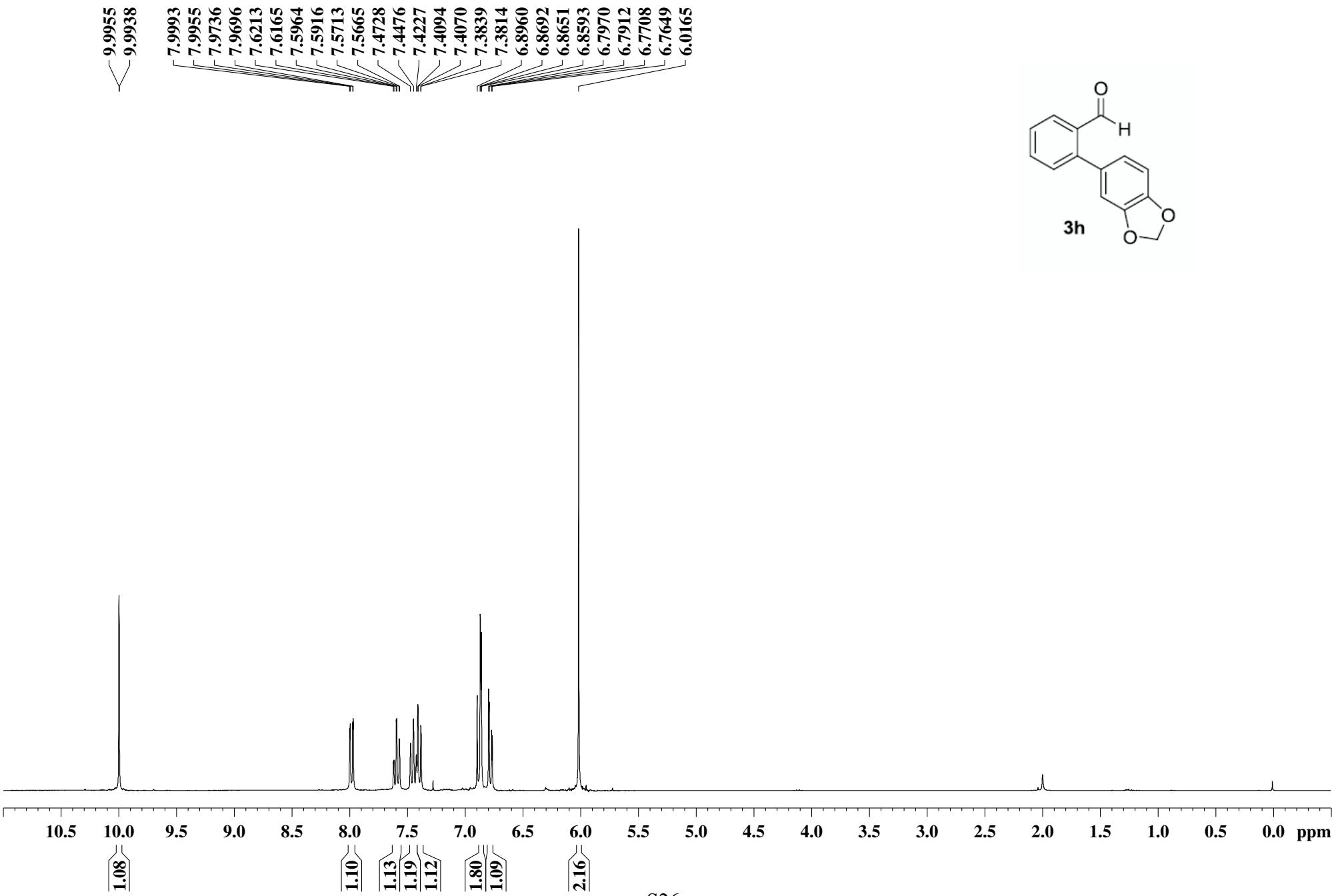
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— 55.8568



SK-1-059



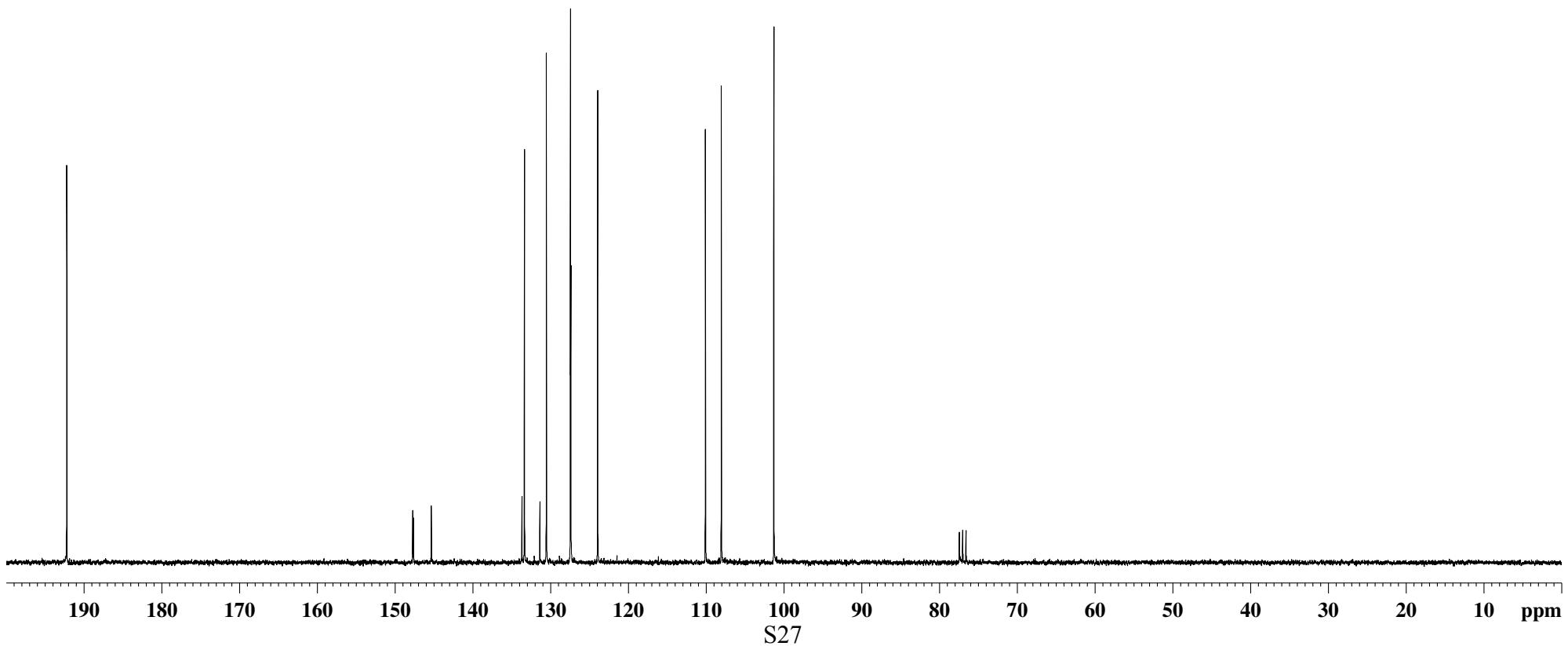
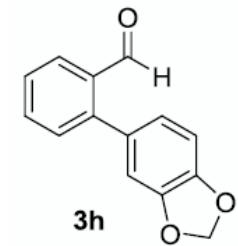
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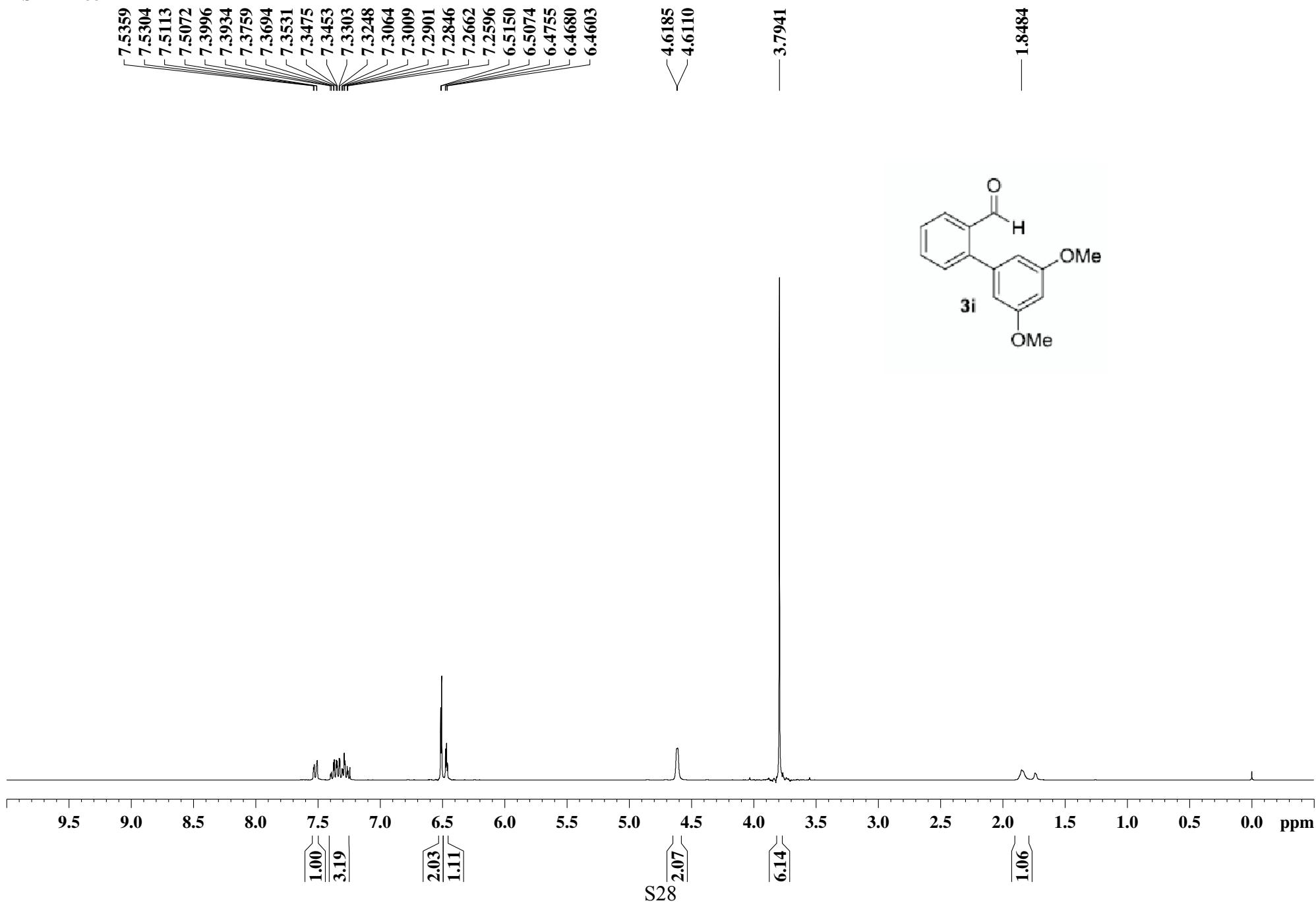
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— 101.2838



SK-1-188



SK-1-188

— 160.4742

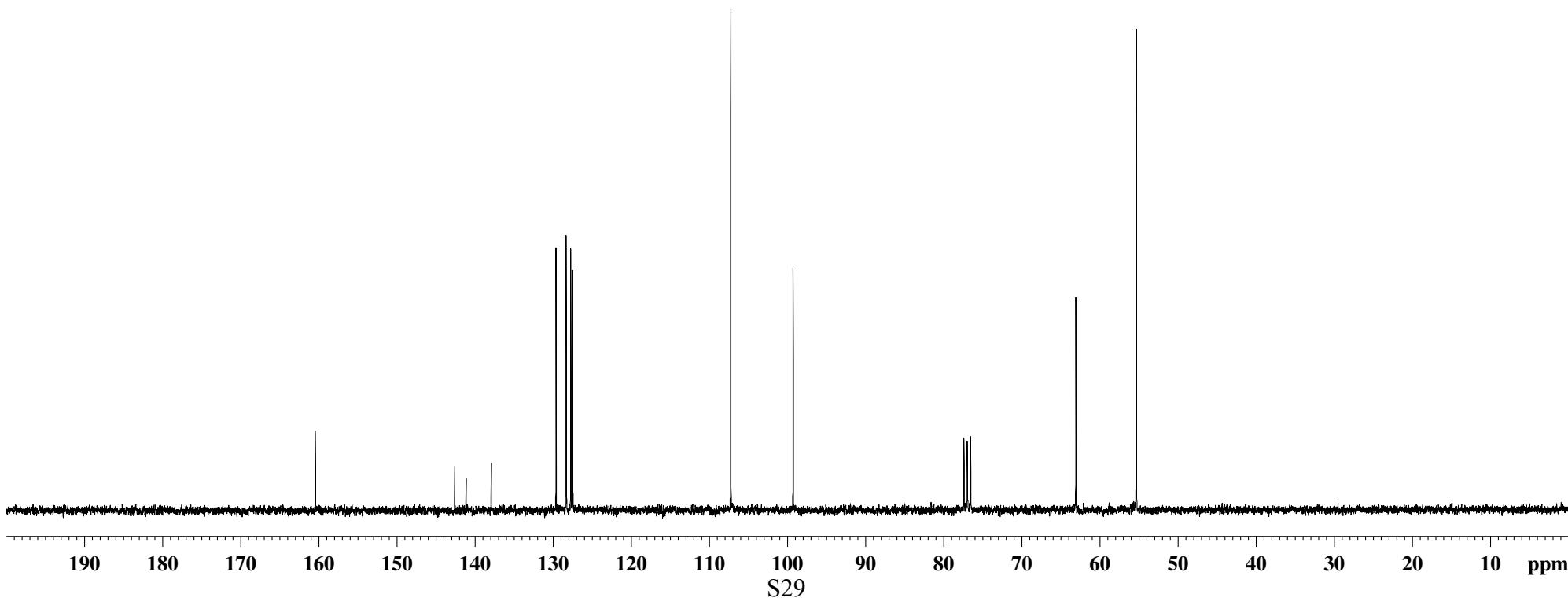
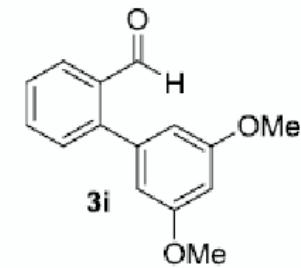
142.6074
141.1624
137.9433
129.6454
128.3417
127.7527
127.5200

— 107.2730

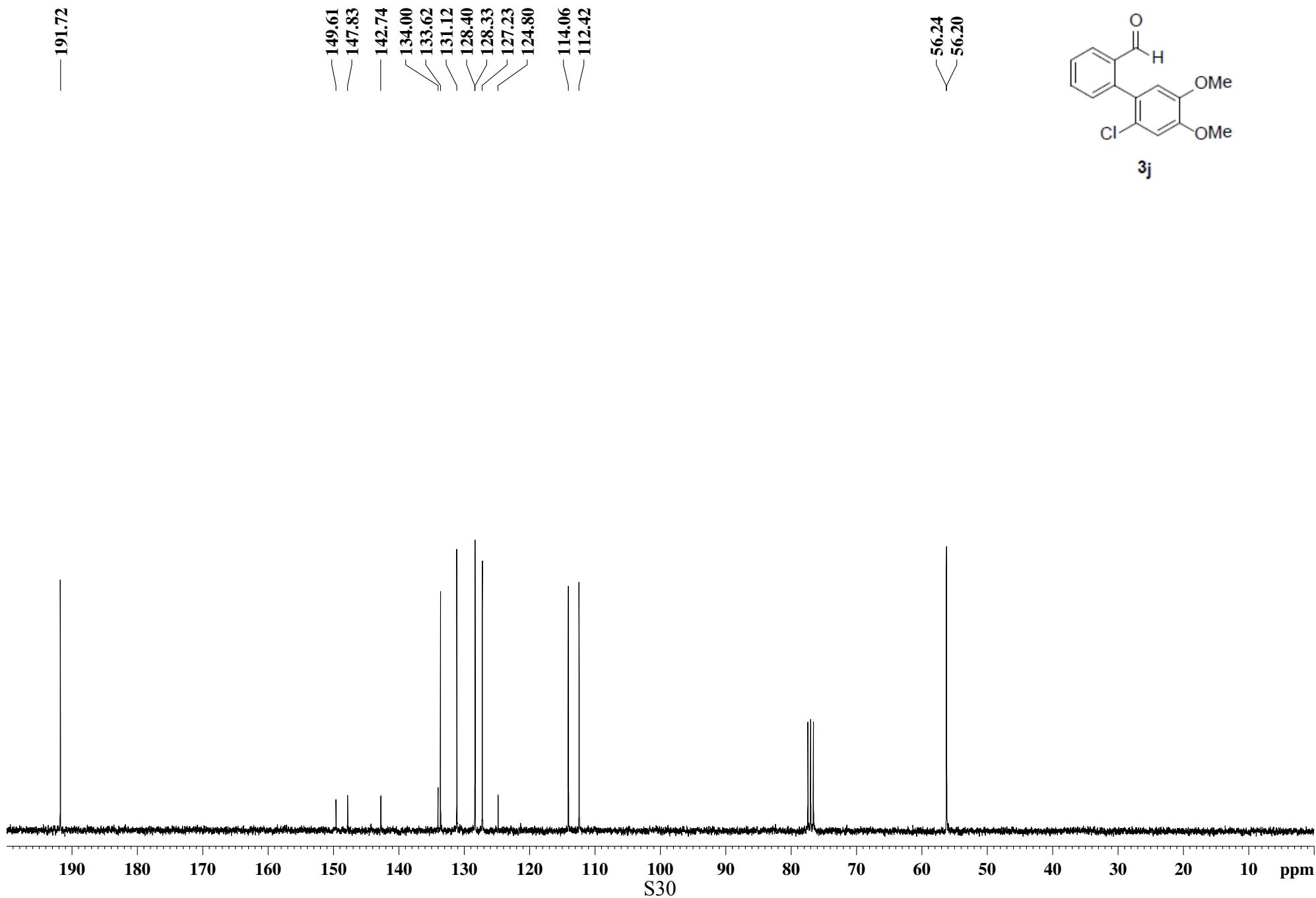
— 99.2833

— 63.0818

— 55.3279



KN-1-035R

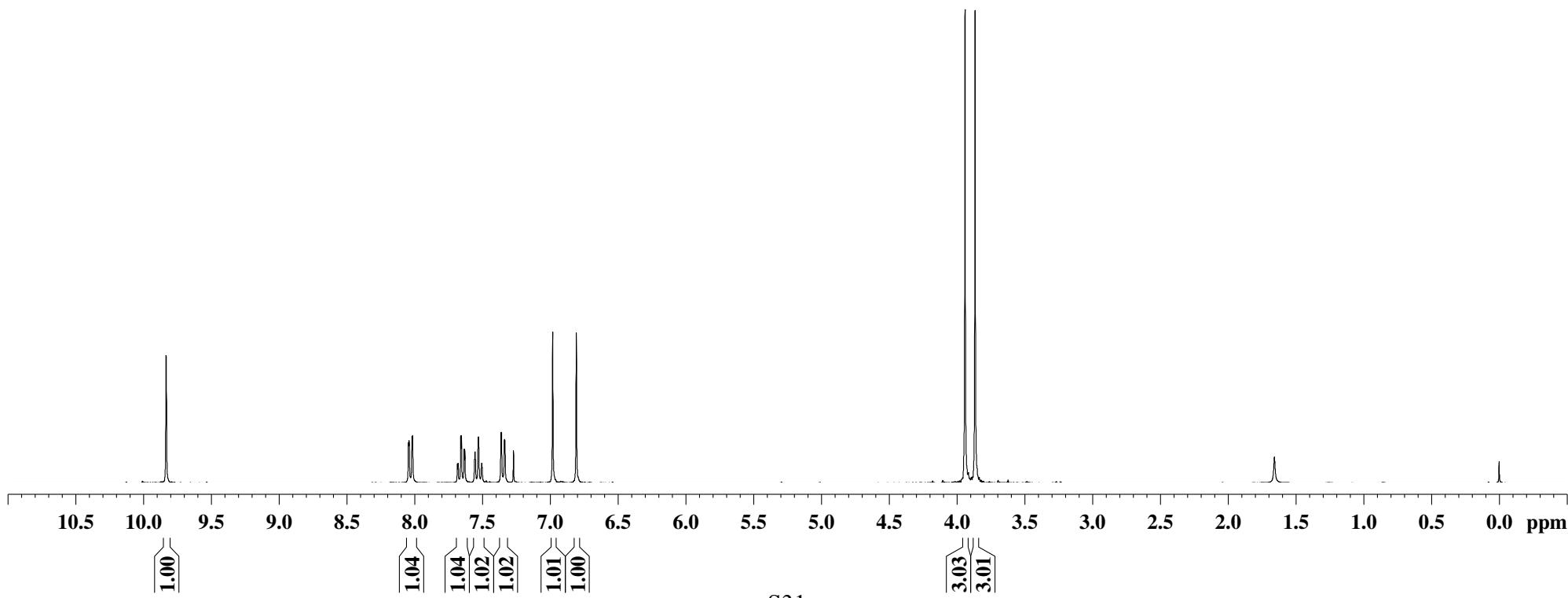
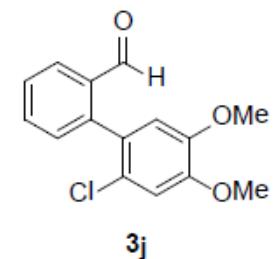


KN-1-035R

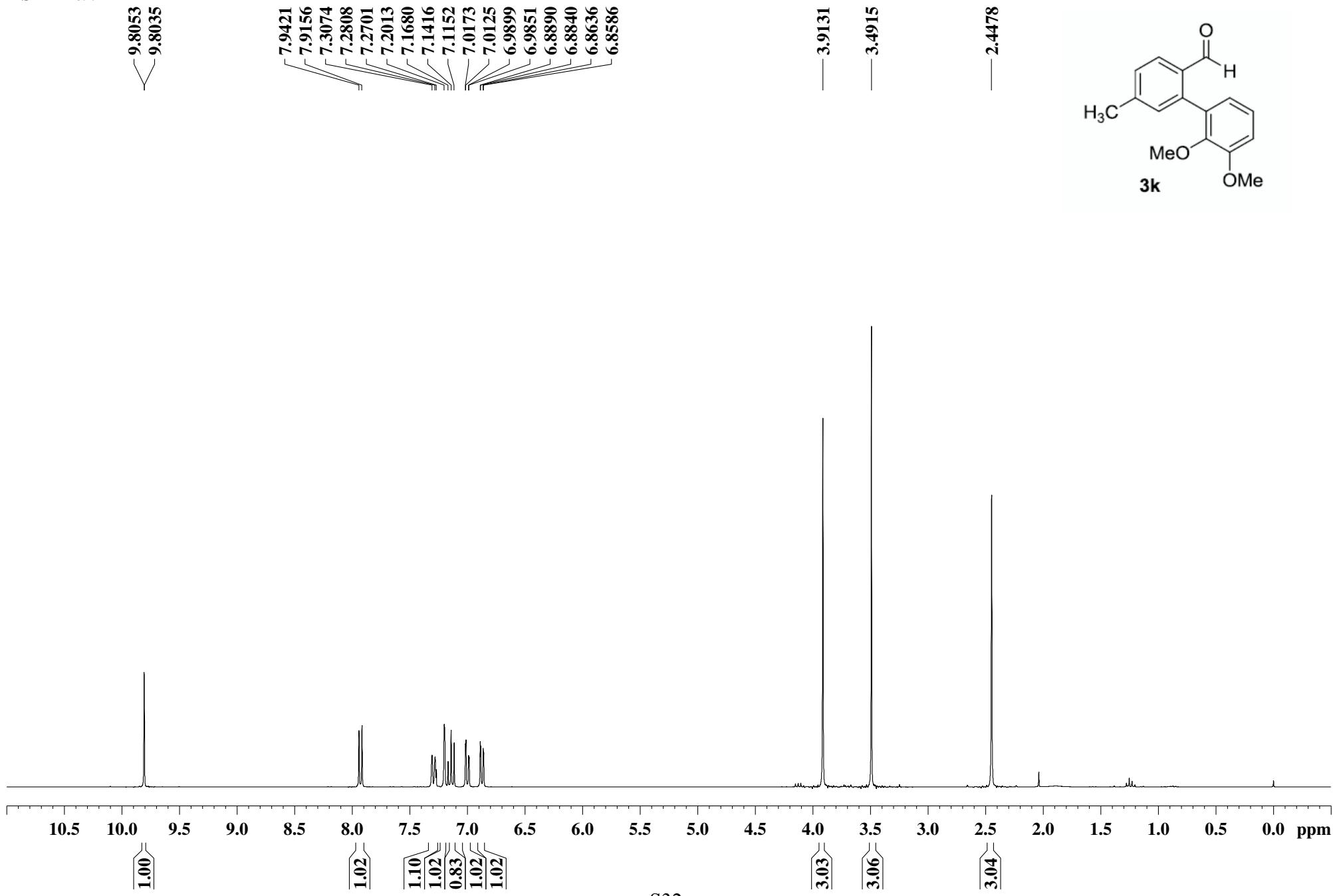
9.83
9.83

8.04
8.04
8.02
8.01
7.68
7.68
7.66
7.65
7.63
7.63
7.55
7.53
7.50
7.36
7.36
7.34
7.33
6.98
6.81

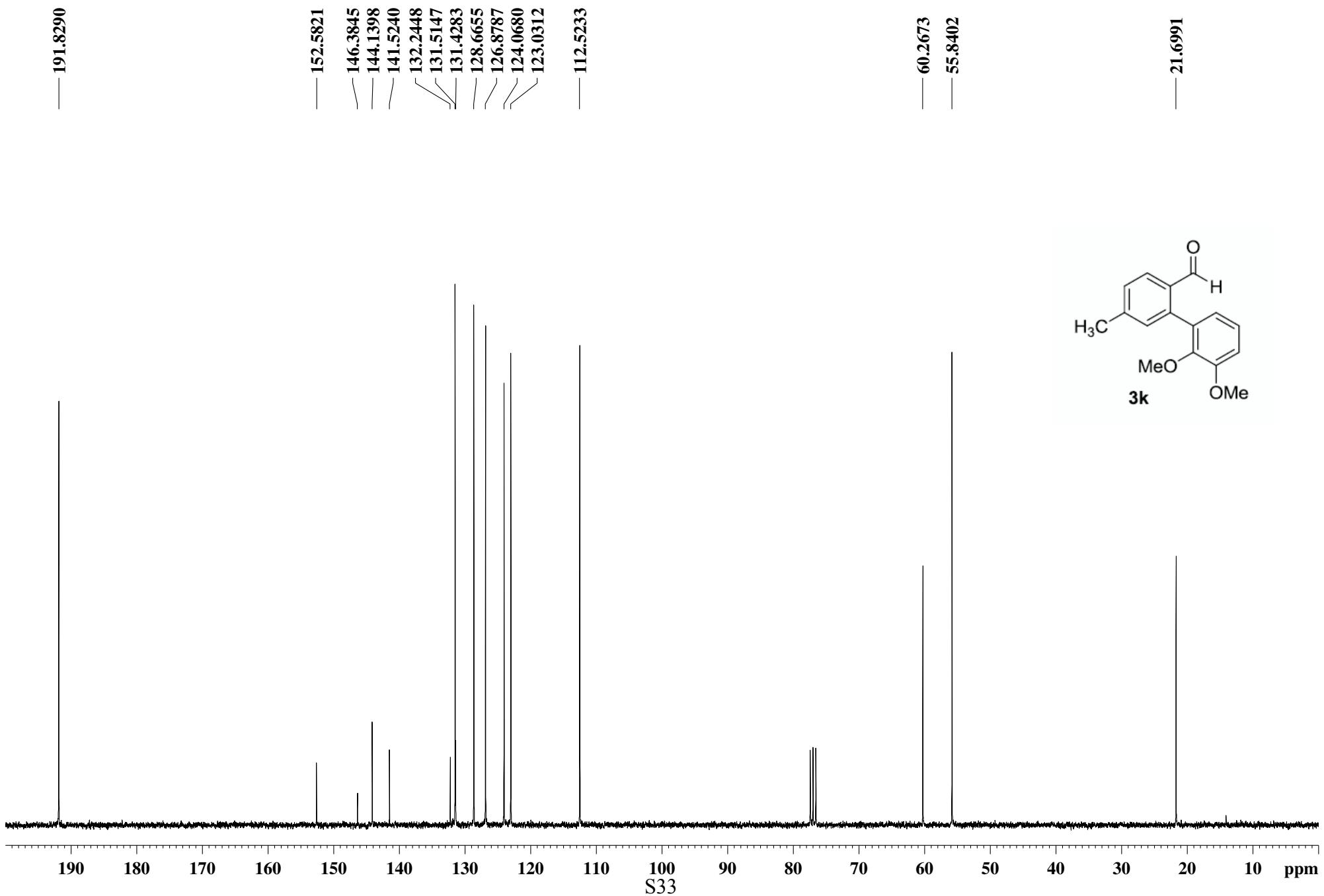
3.94
3.87



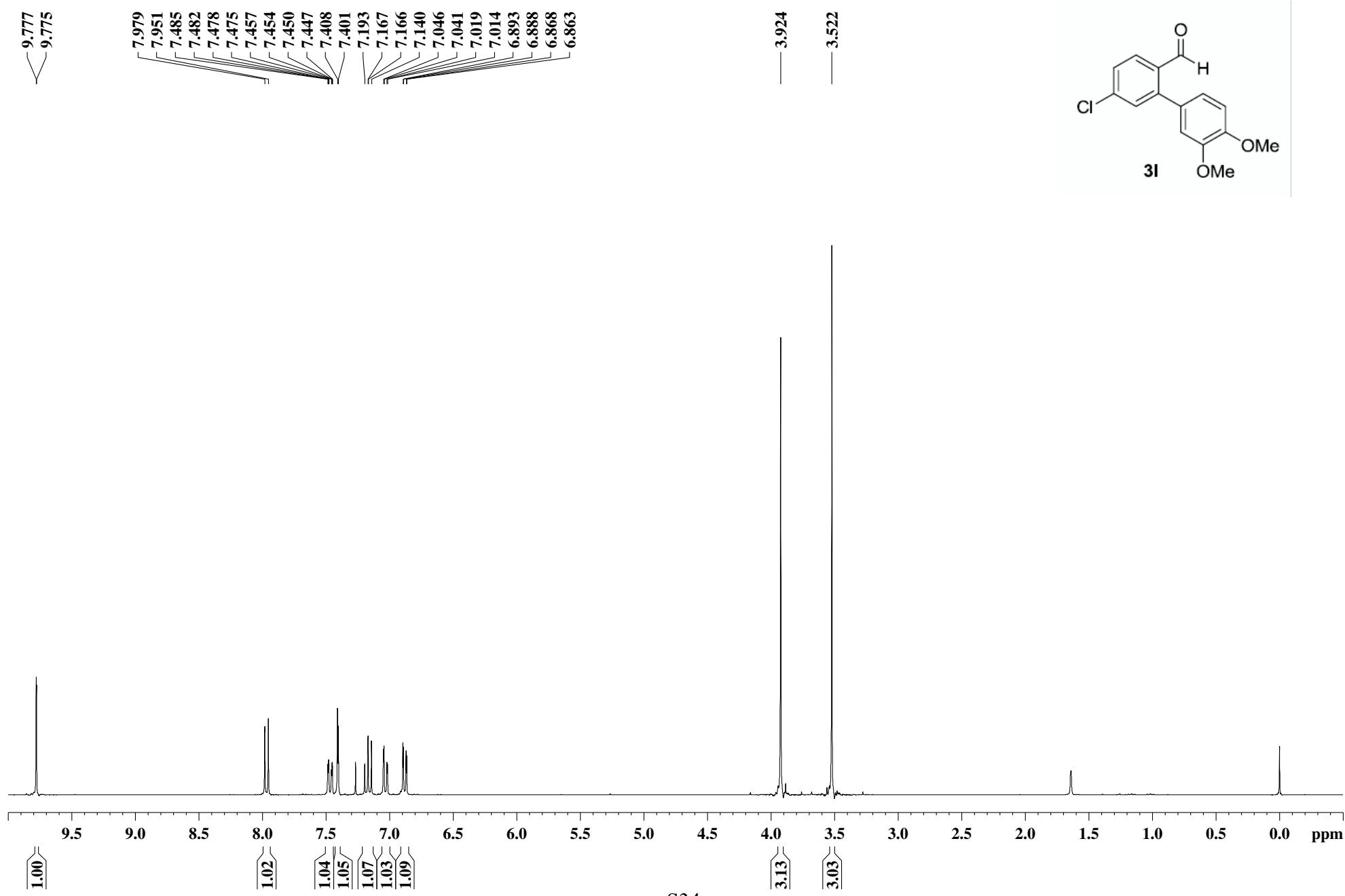
SK-1-099



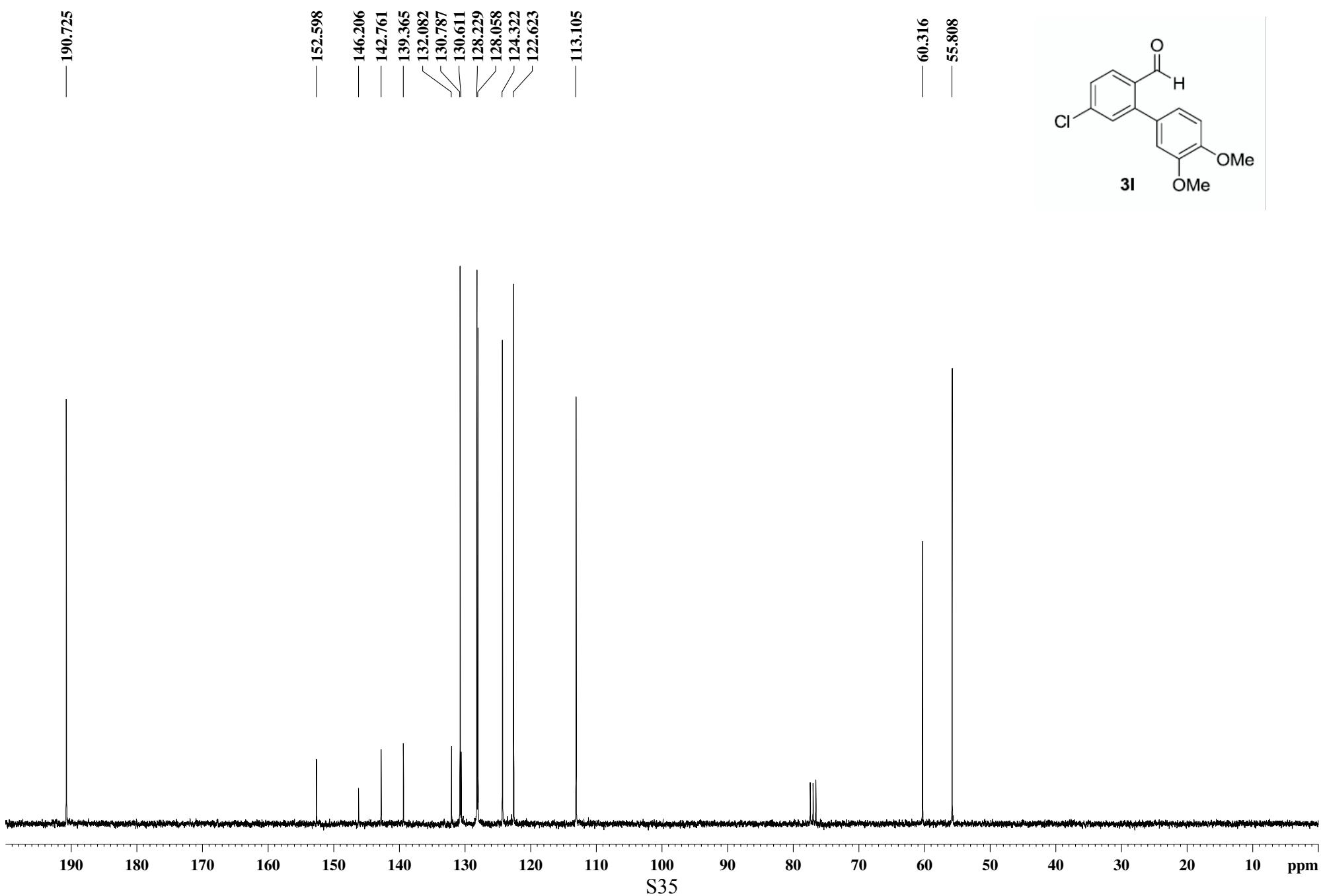
SK-1-099



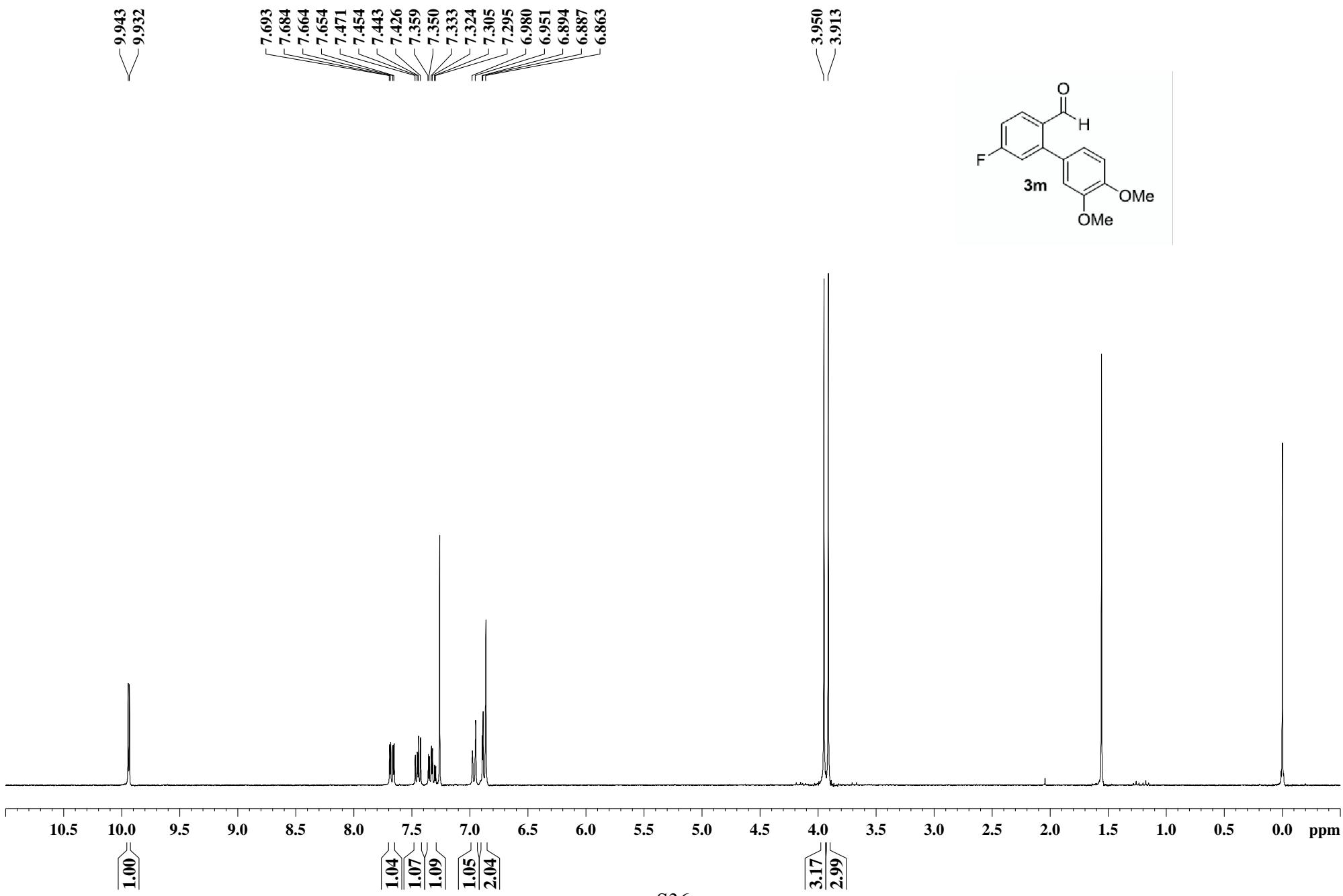
SK-1-122



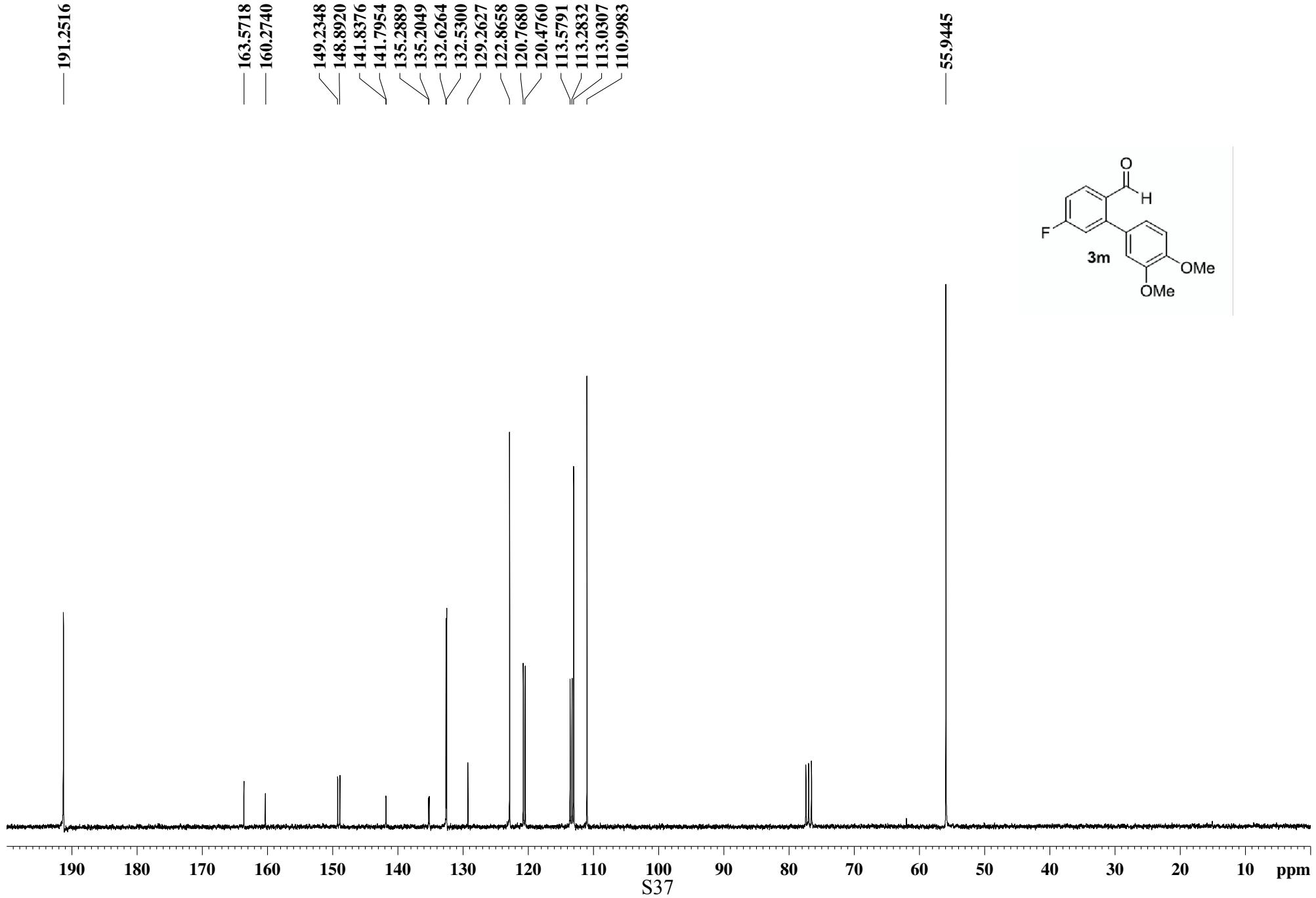
SK-1-122



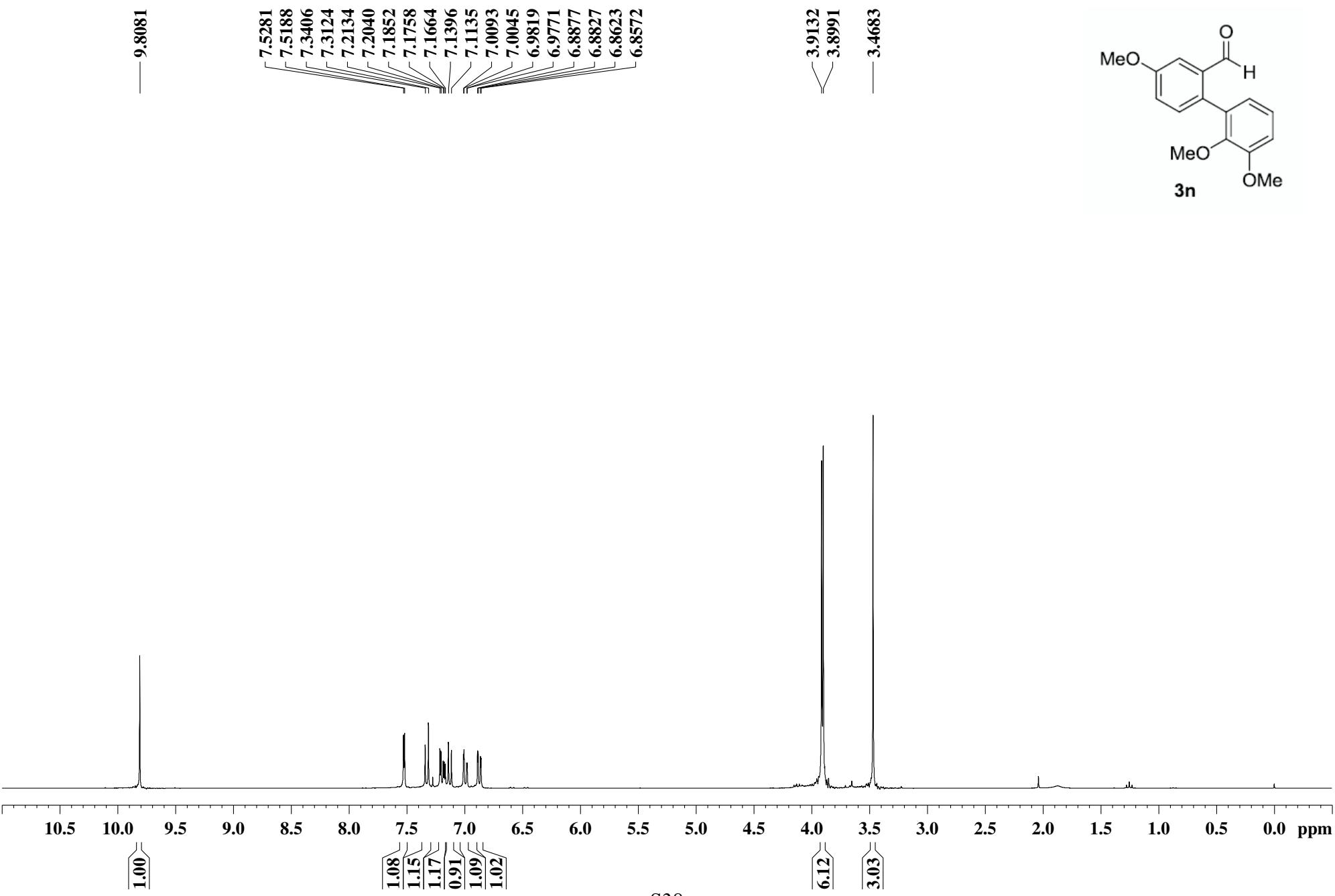
SK-1-129



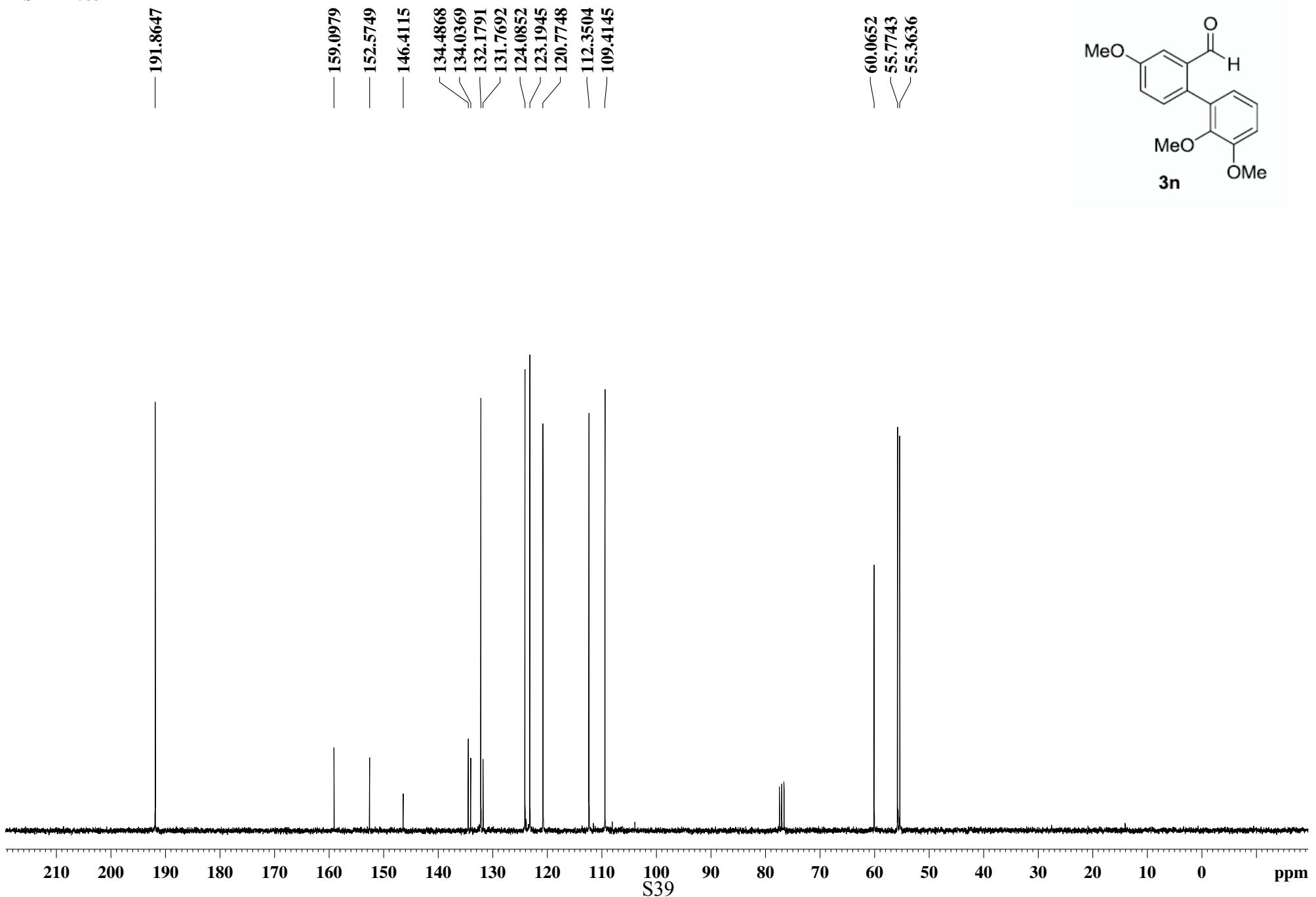
SK-1-129



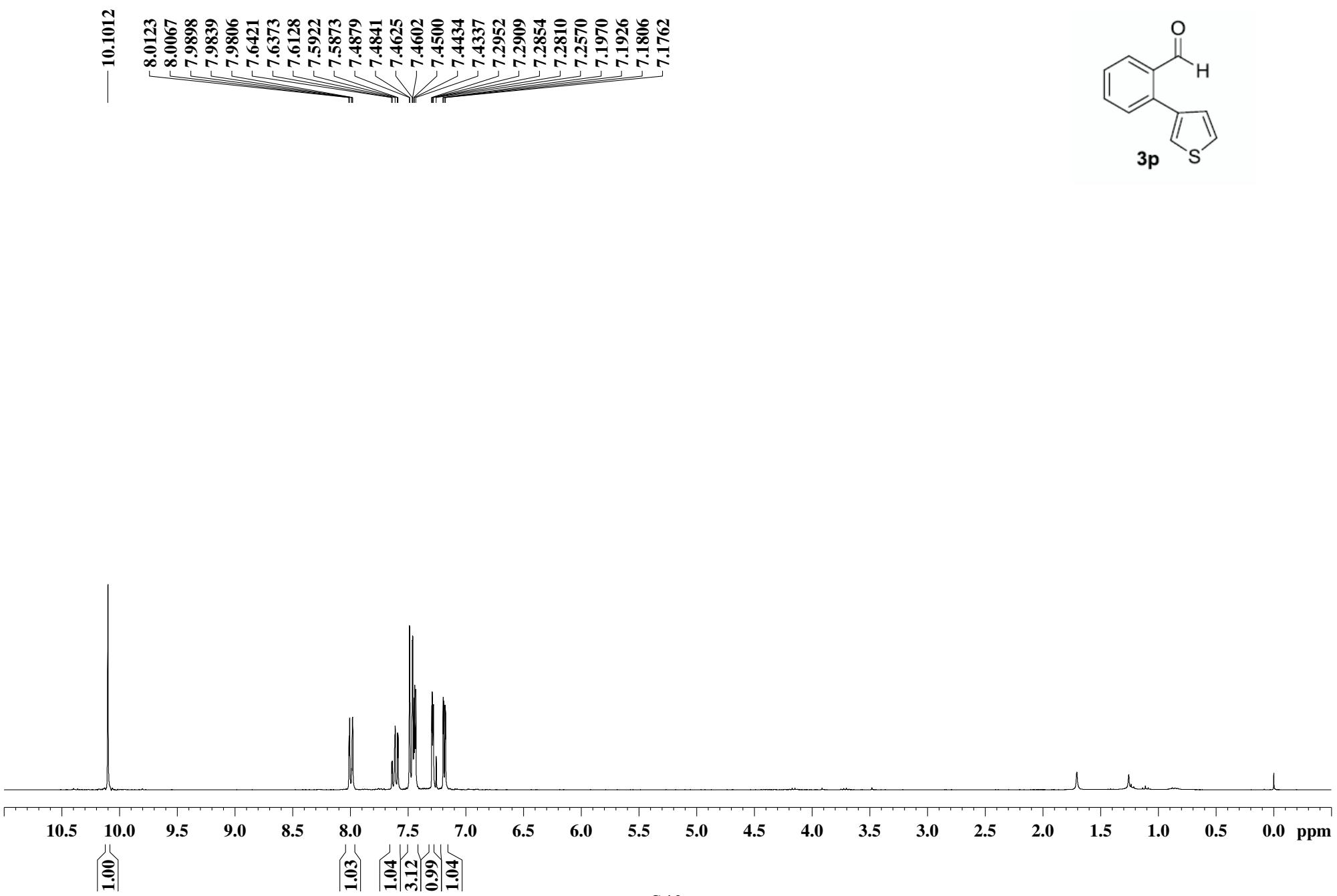
SK-1-083



SK-1-083



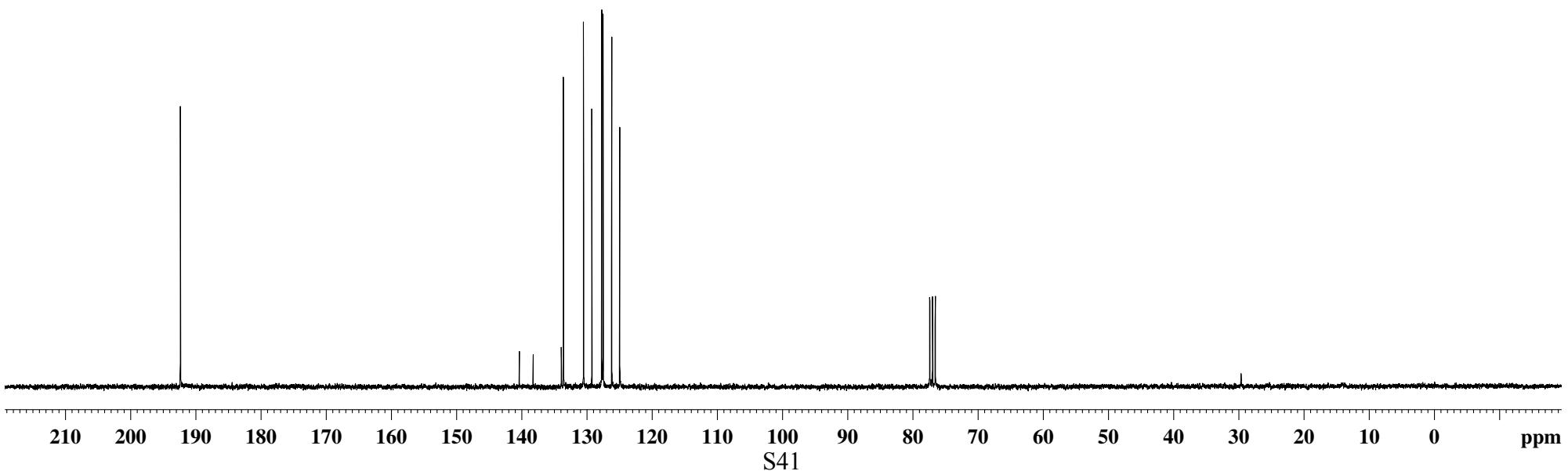
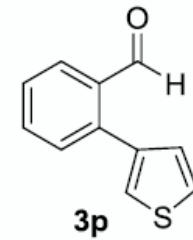
SK-1-096



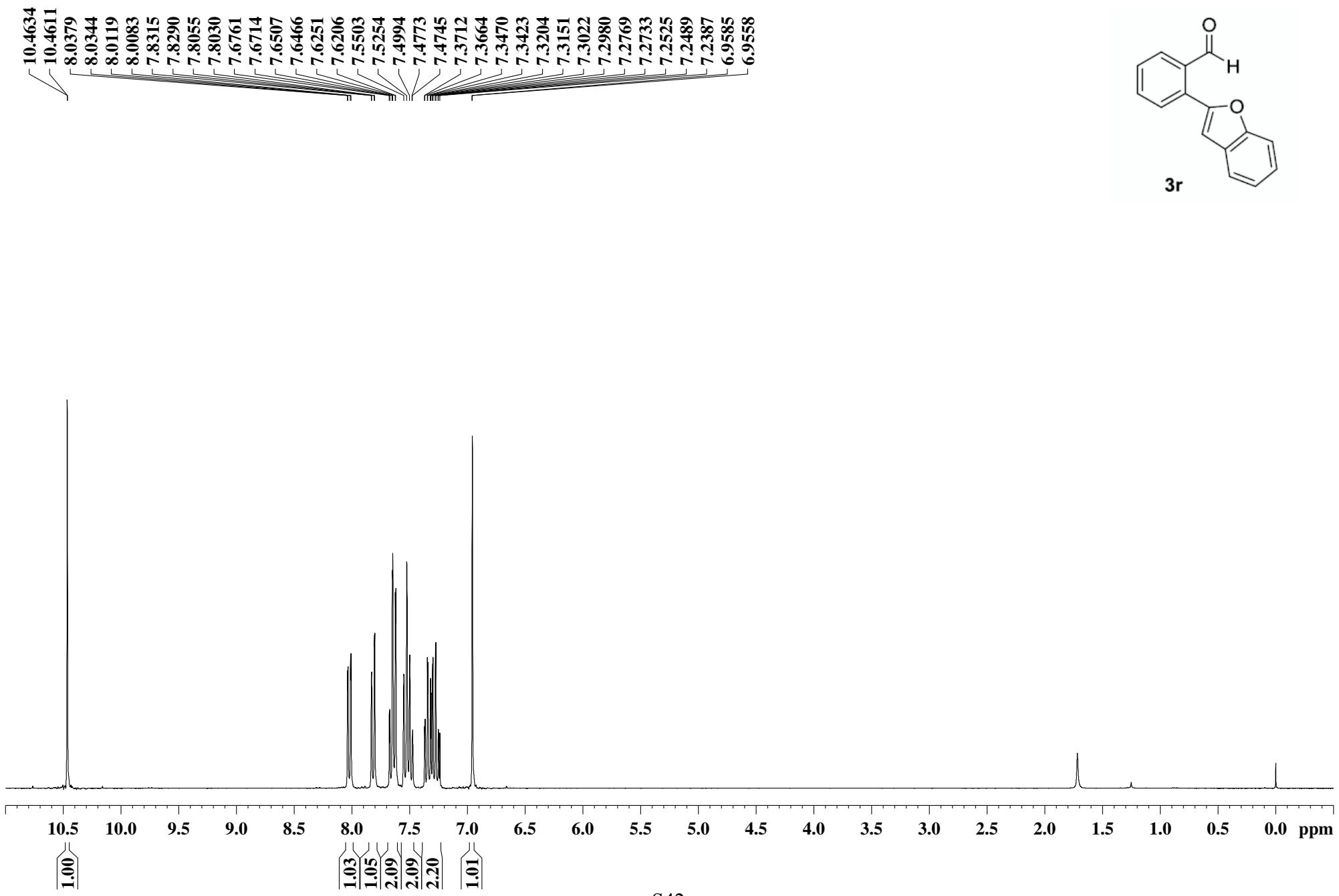
SK-1-096

— 192.3299

140.3807
138.2679
133.9387
133.6142
130.5350
129.2697
127.7460
127.5313
126.2181
124.9830



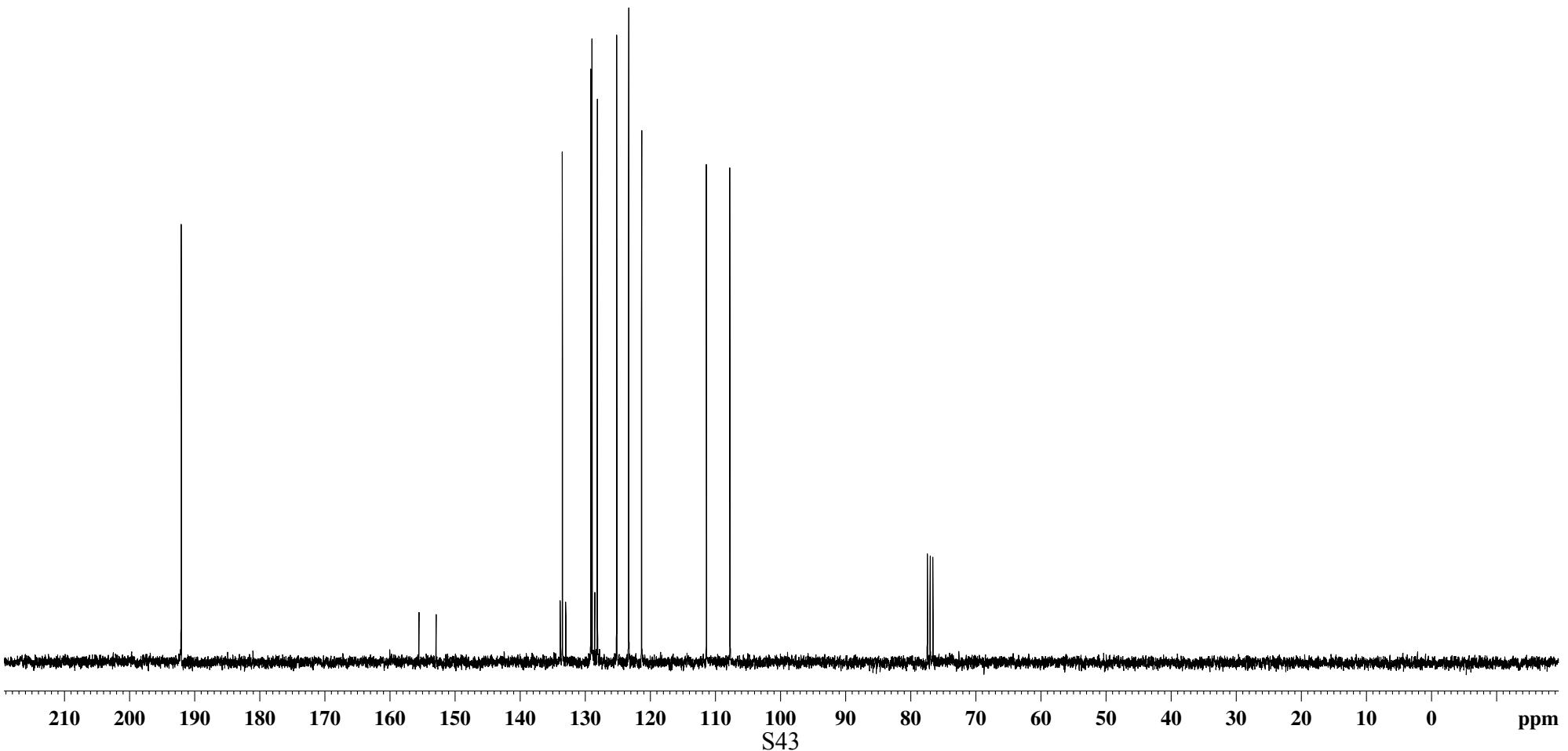
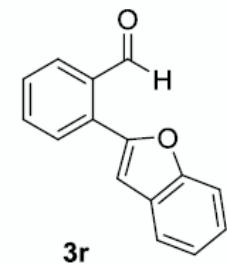
SK-1-104



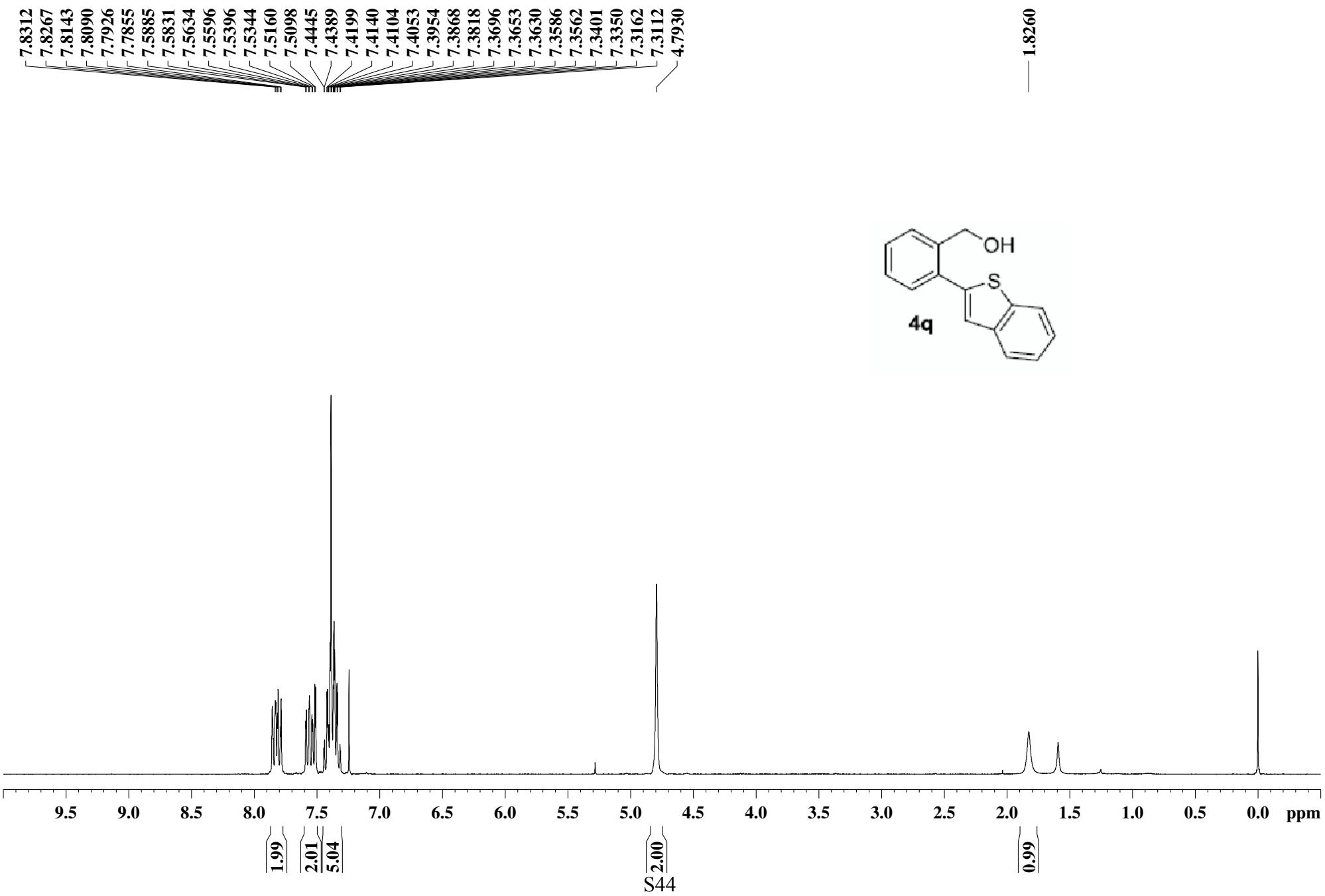
SK-1-104

— 191.9748

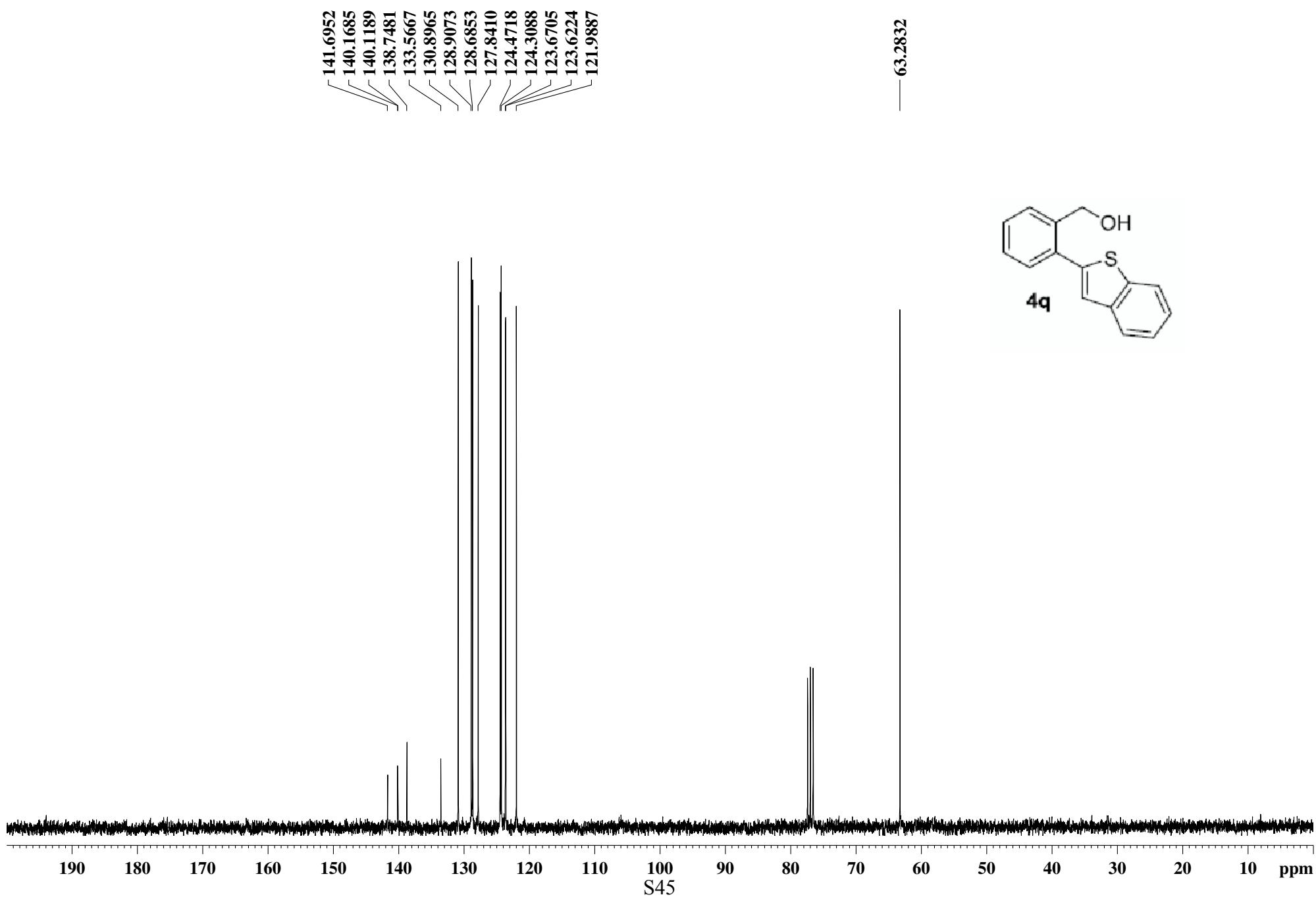
— 155.4696
— 152.8293
— 133.8473
— 133.4967
— 132.9766
— 129.1278
— 128.9447
— 128.5314
— 128.1244
— 125.1553
— 123.3249
— 121.3282
— 111.3776
— 107.7742

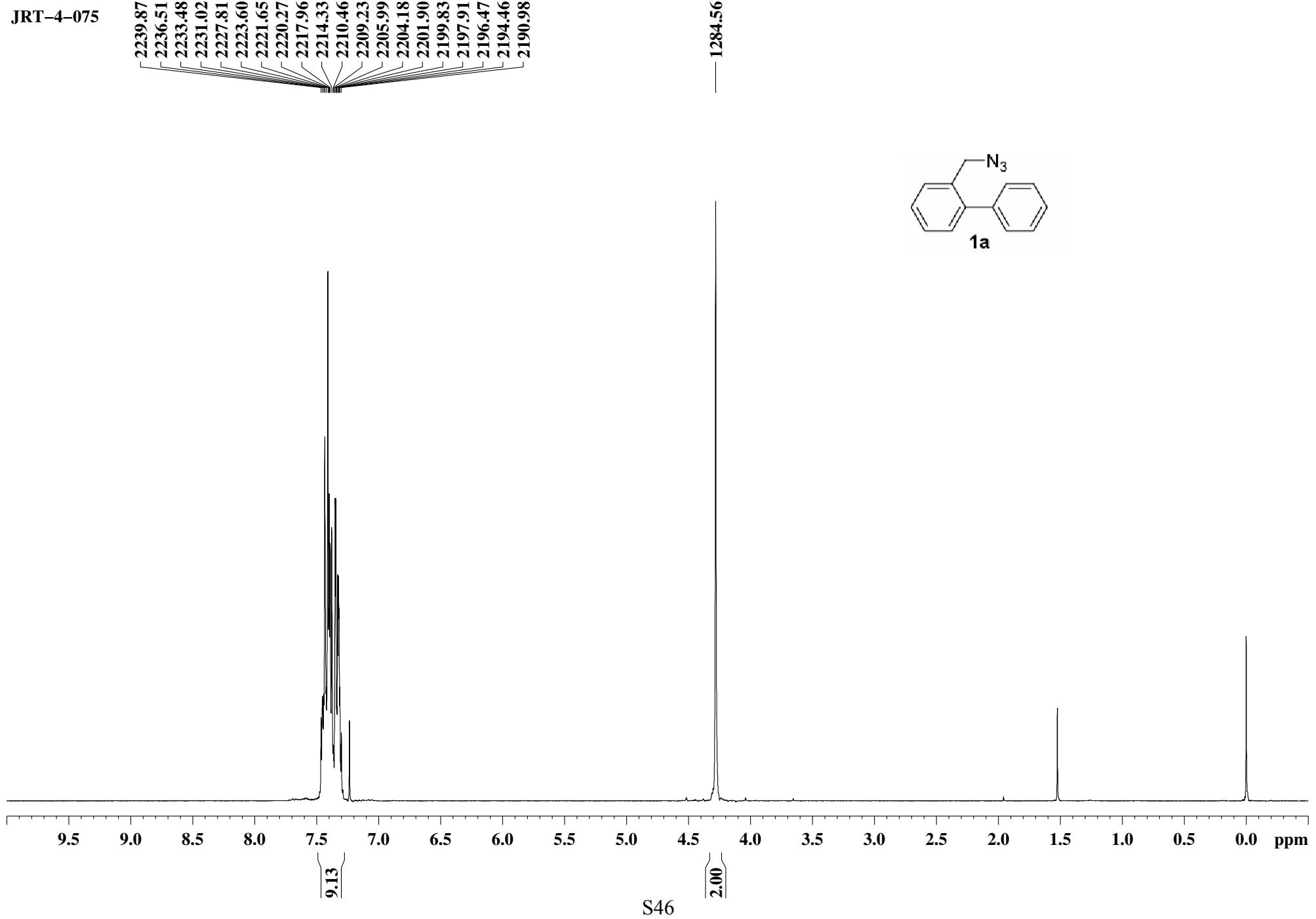


SK-1-161

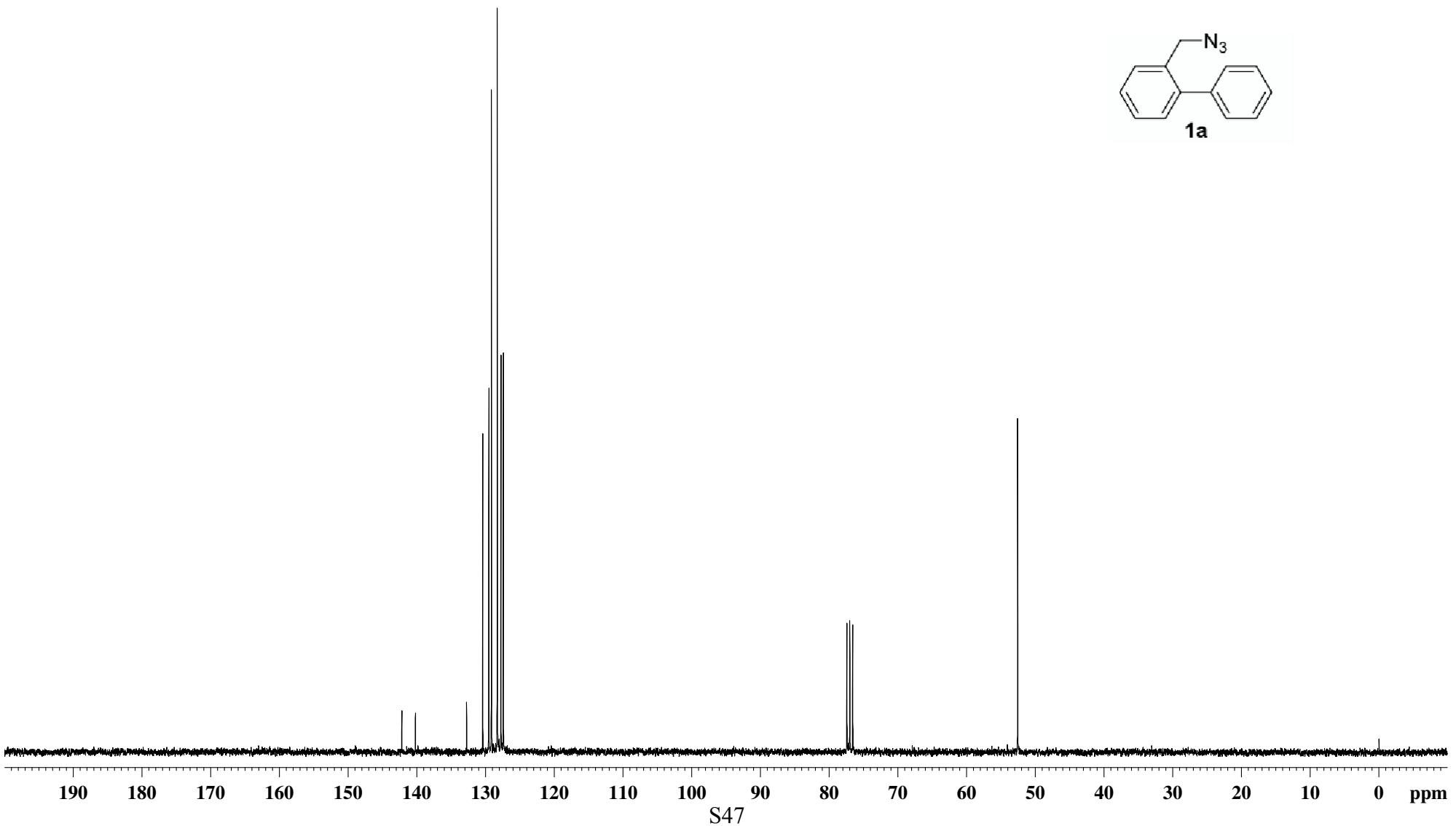


SK-1-161

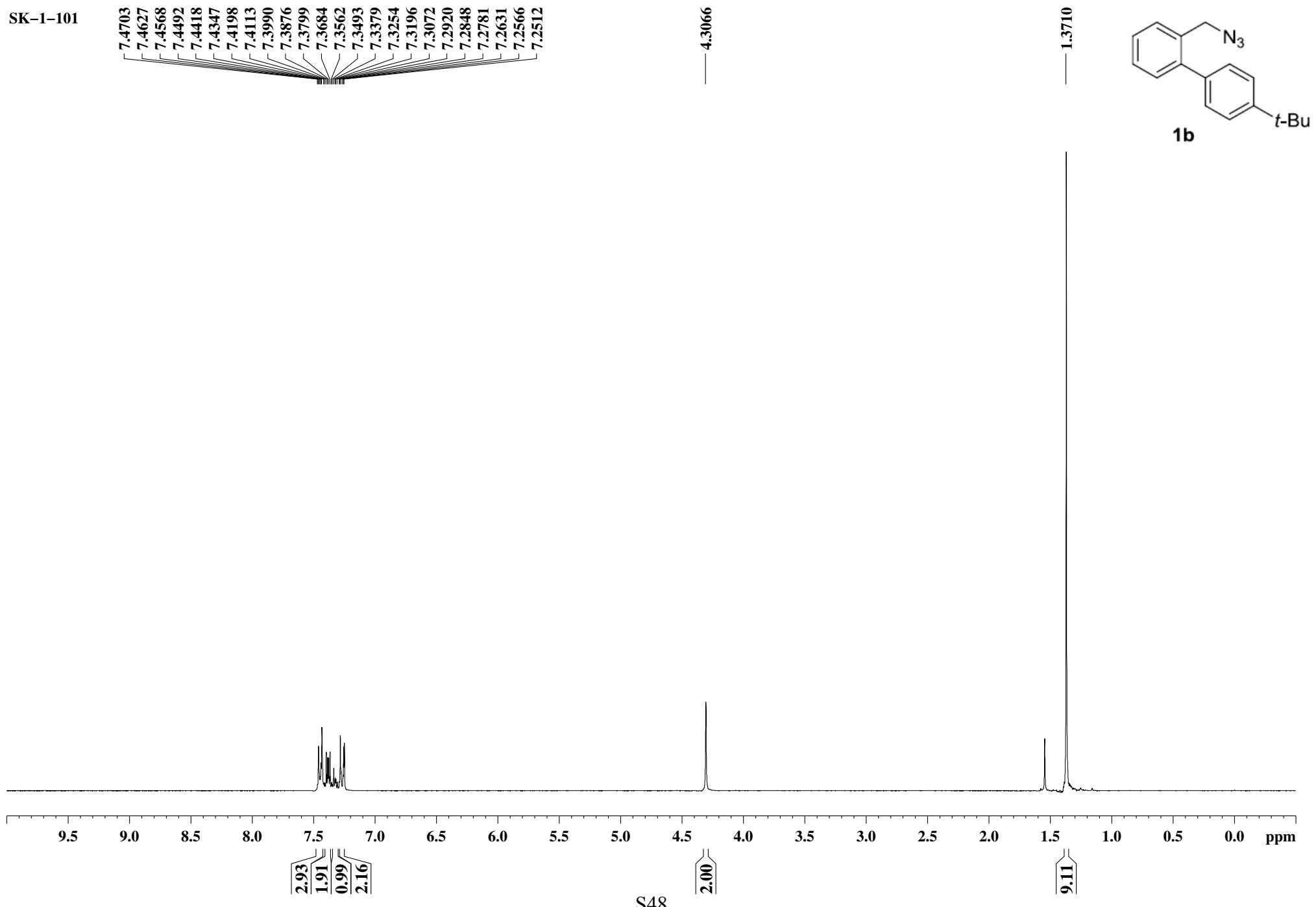




JRT-4-075



SK-1-101

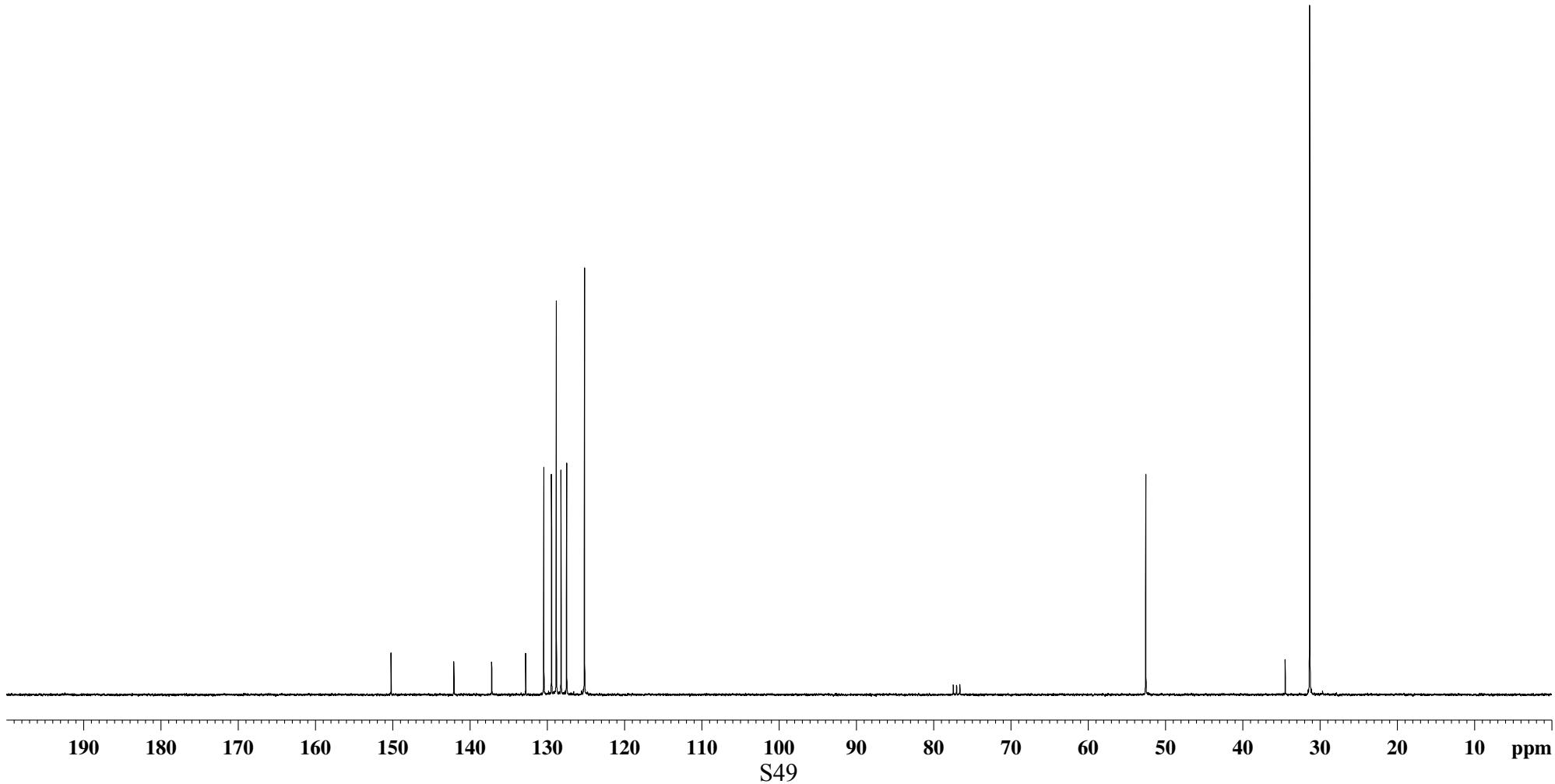
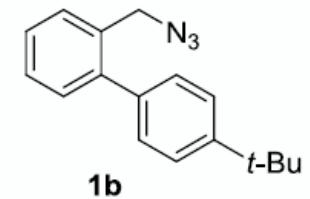


SK-1-101

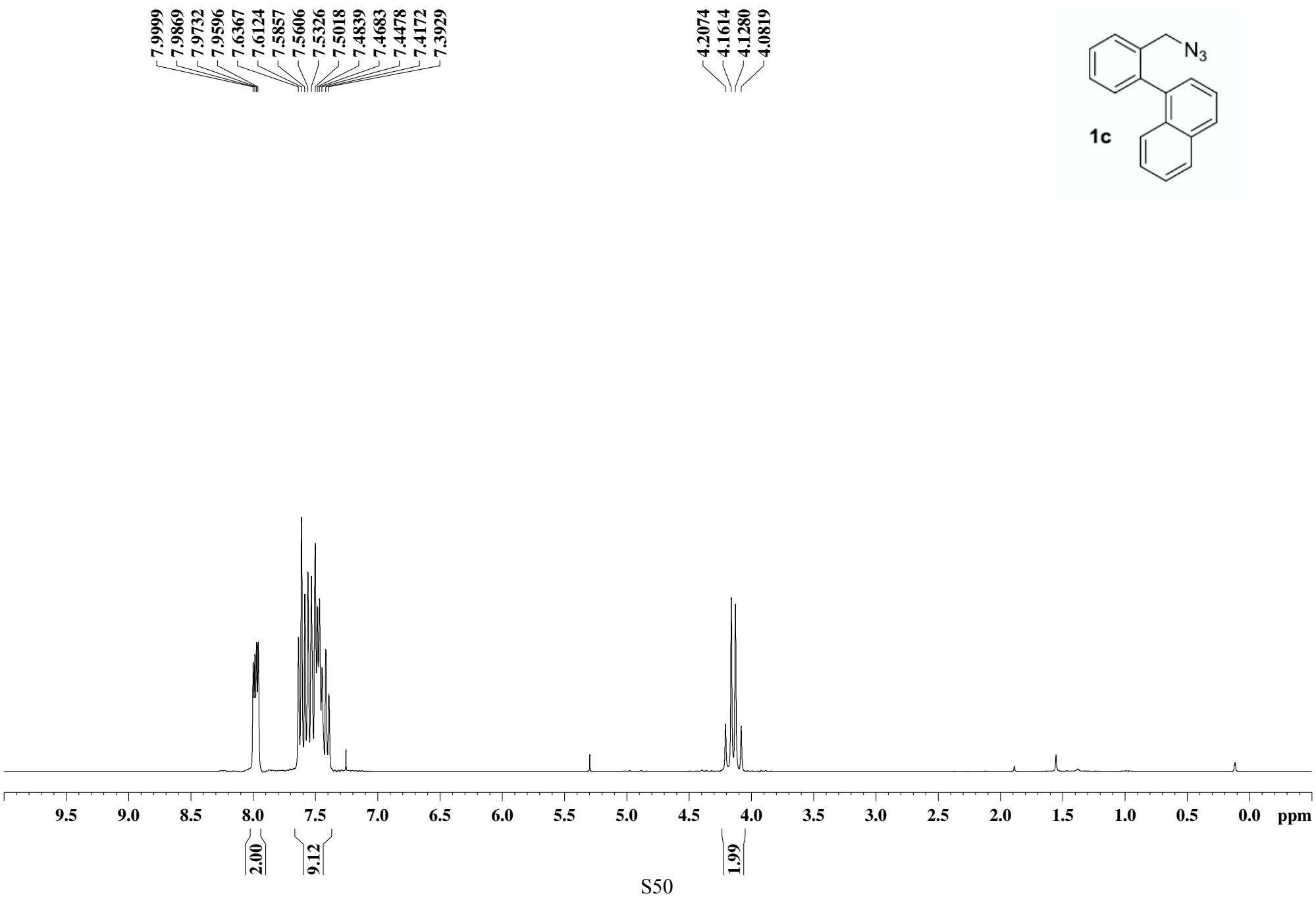
150.18
142.05
137.15
132.76
130.41
129.41
128.79
128.18
127.46
125.15

52.51

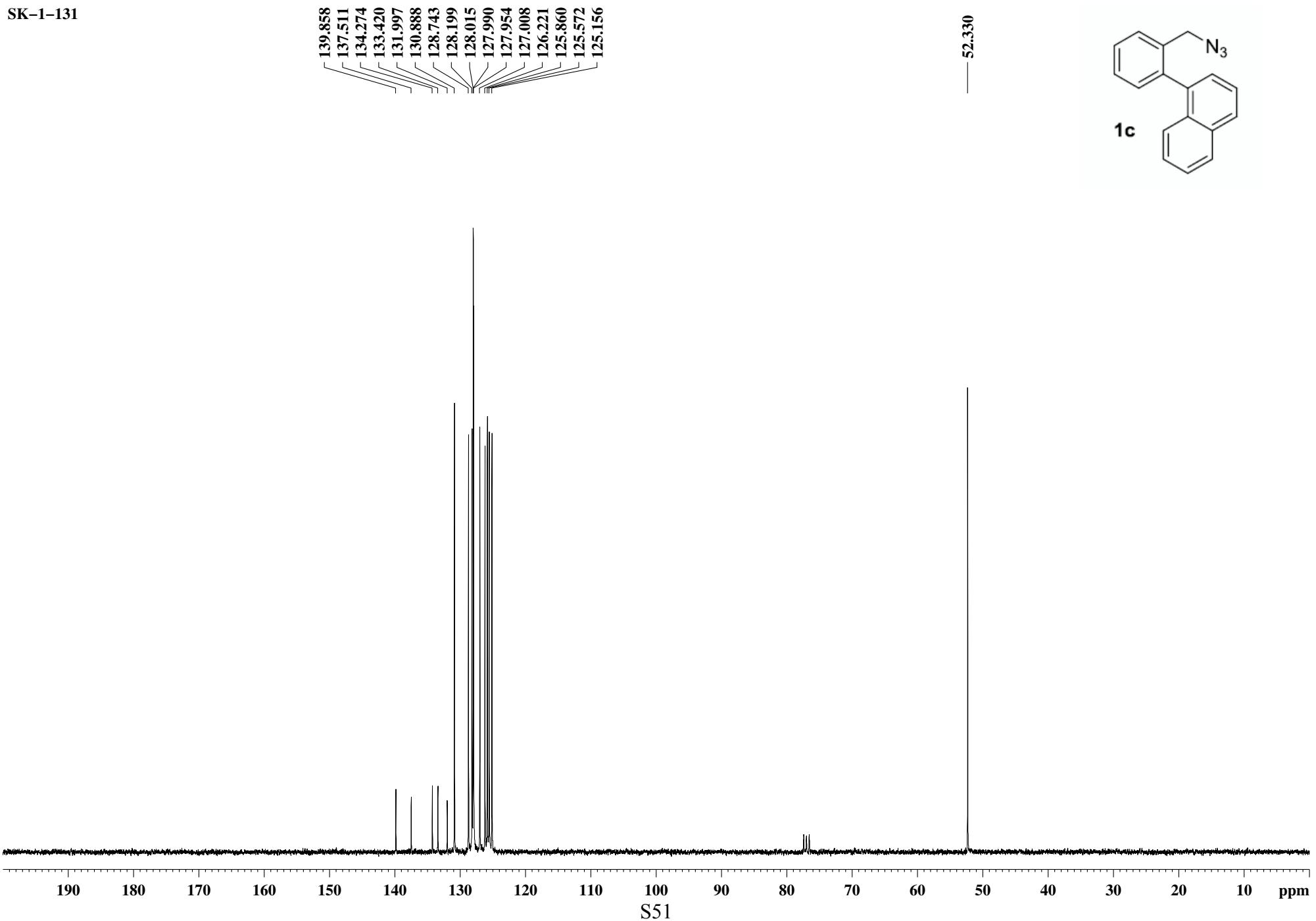
34.46
31.29



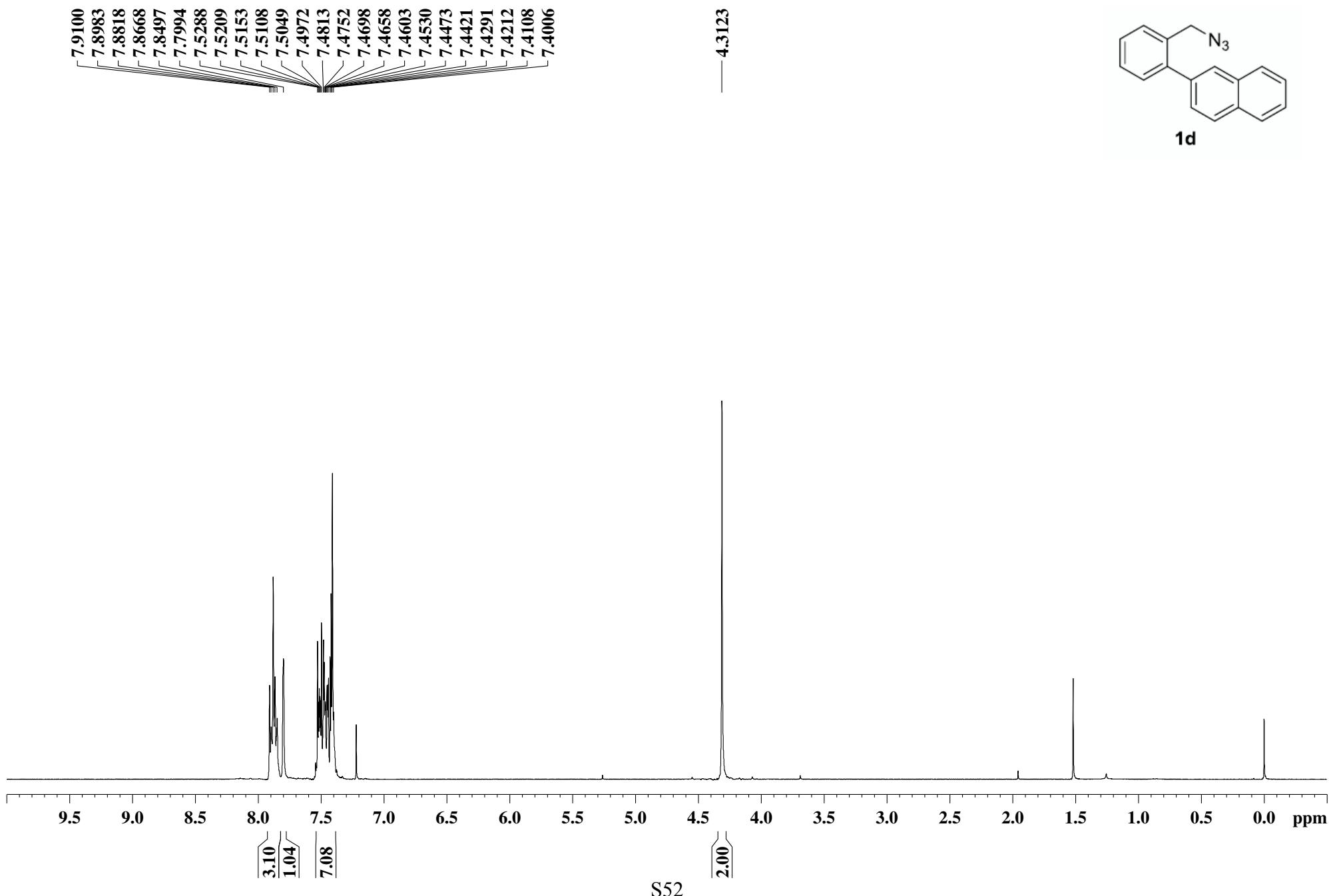
SK-1-131



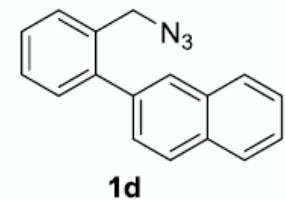
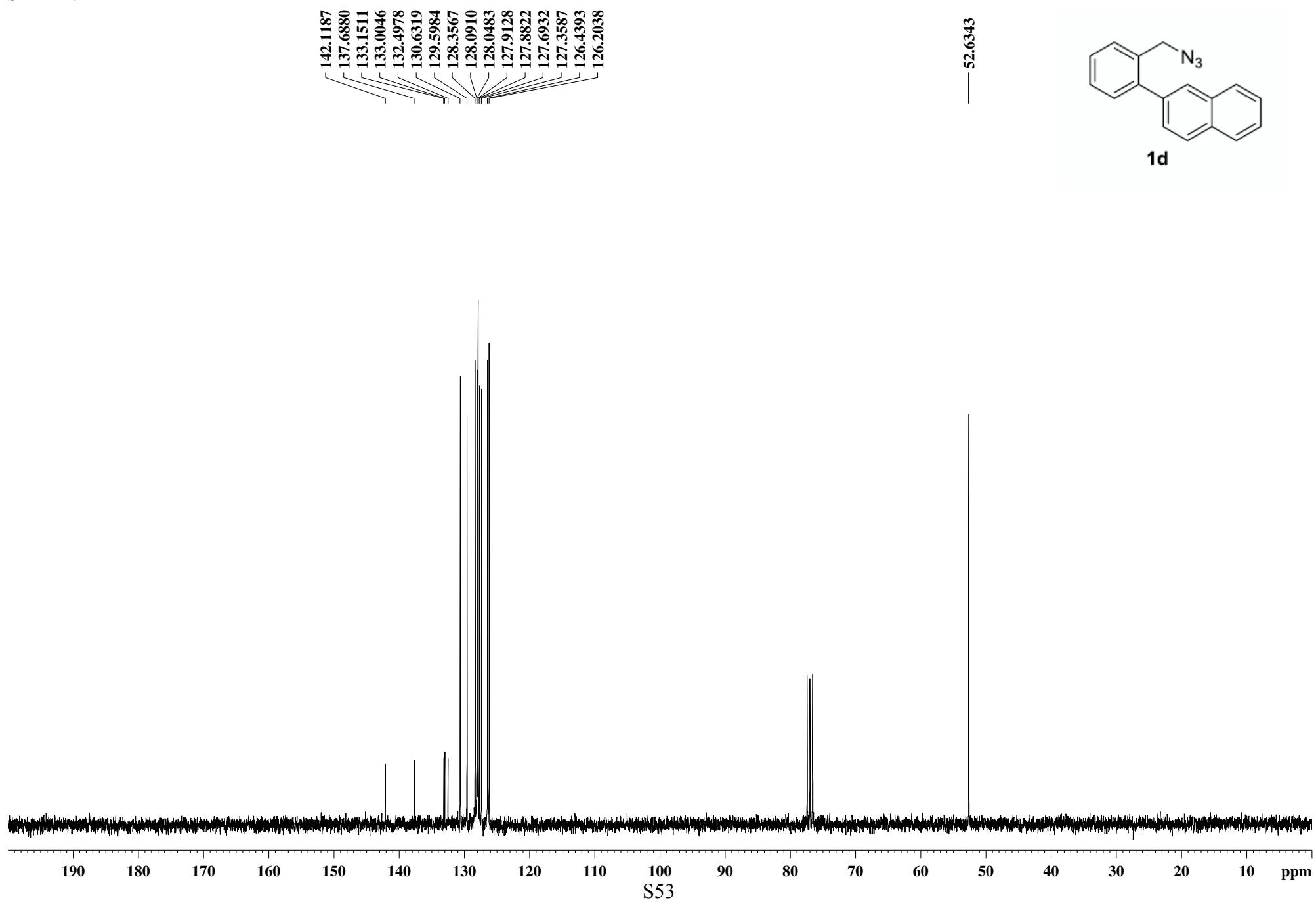
SK-1-131



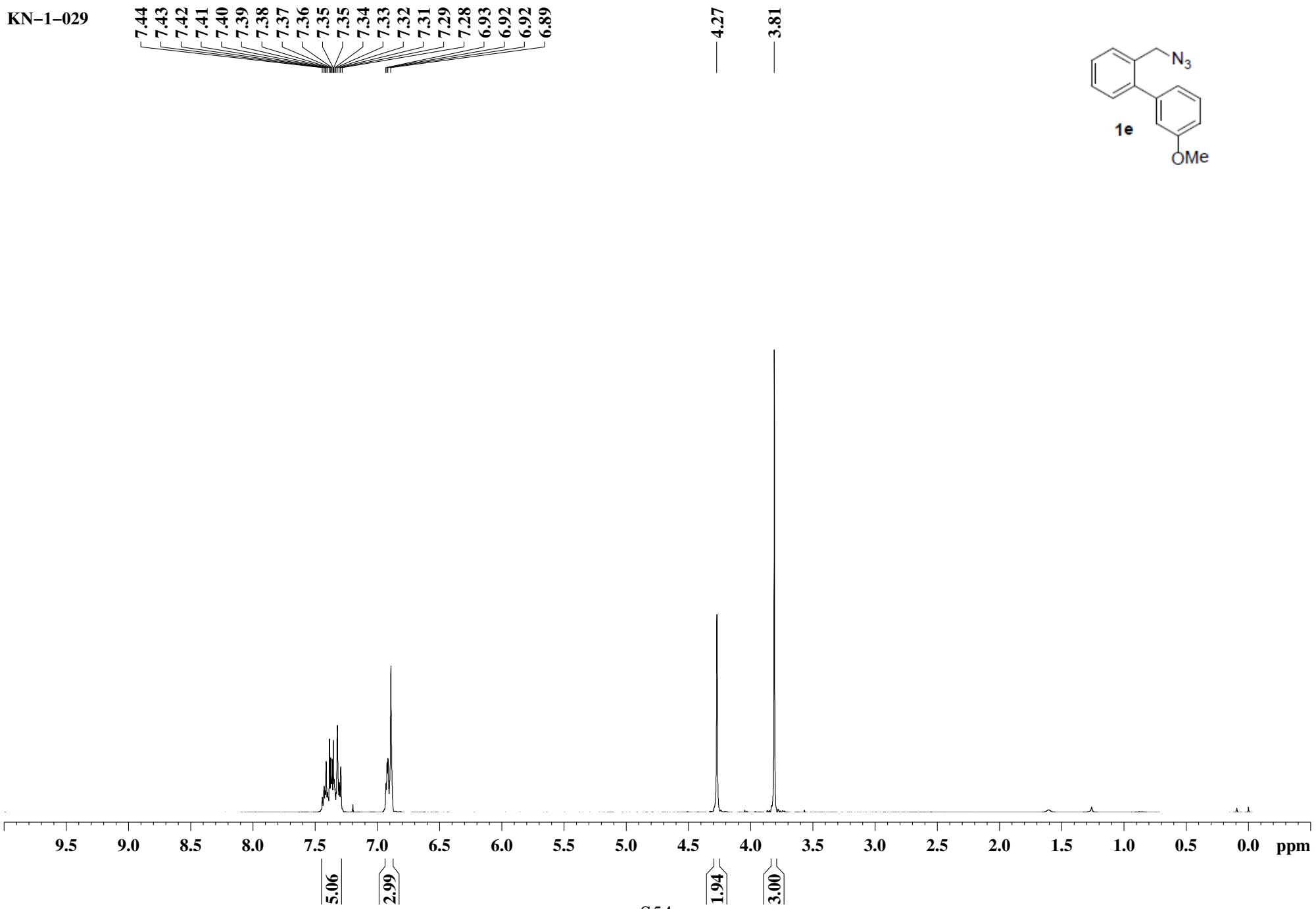
SK-1-170



SK-1-170



KN-1-029

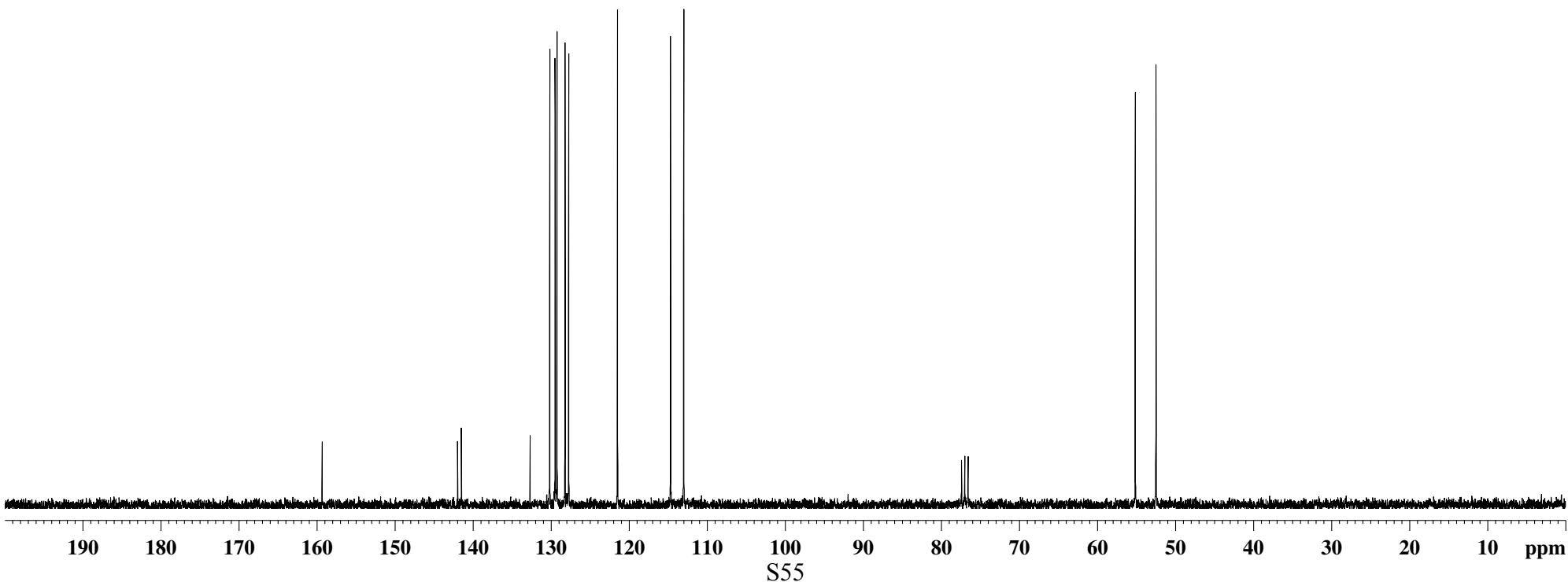
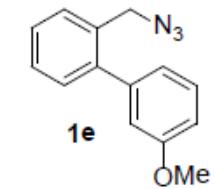


KN-1-029

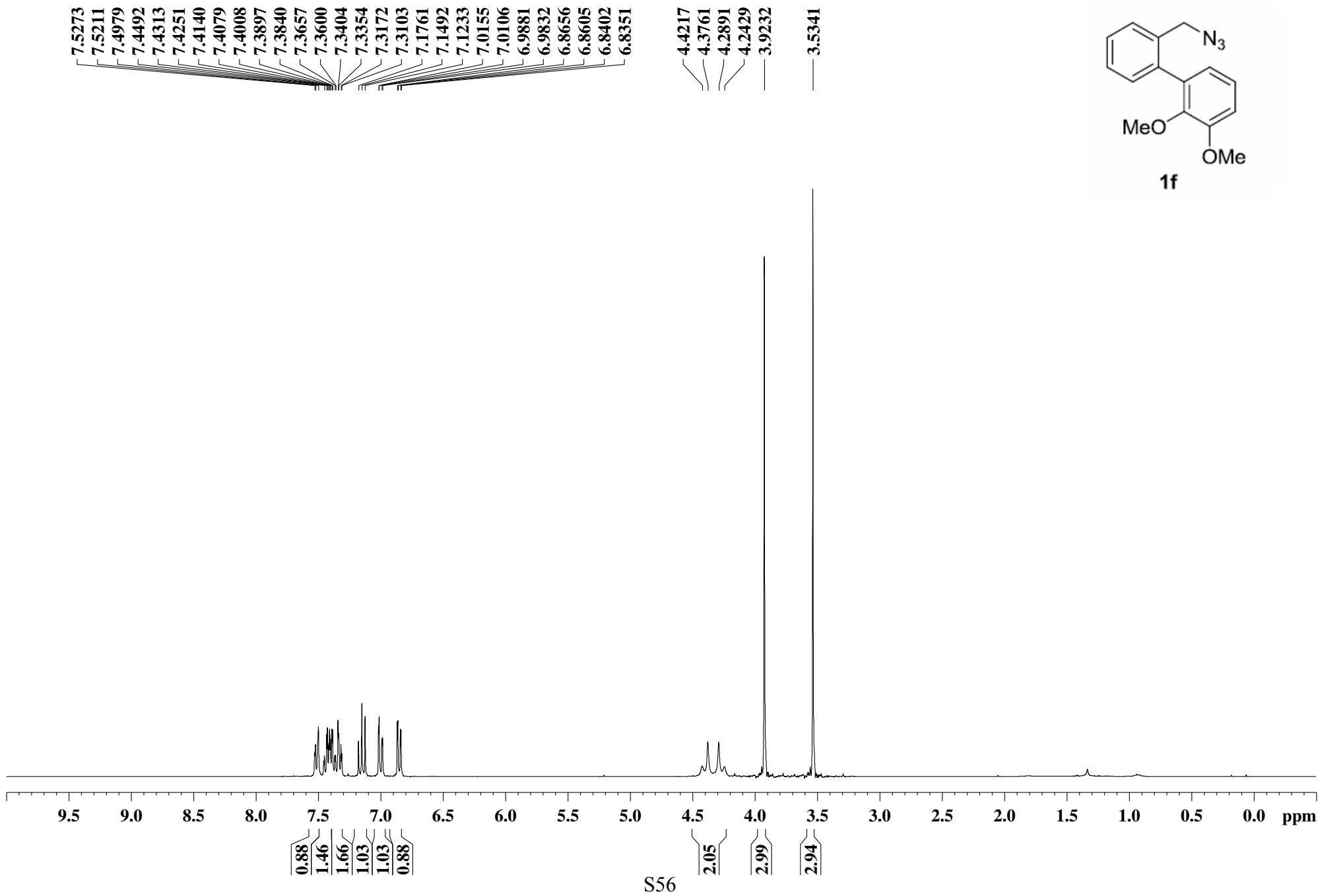
— 159.49 —

142.14
141.66
132.84
130.33
129.64
129.40
128.37
127.90
121.65
114.84
113.16

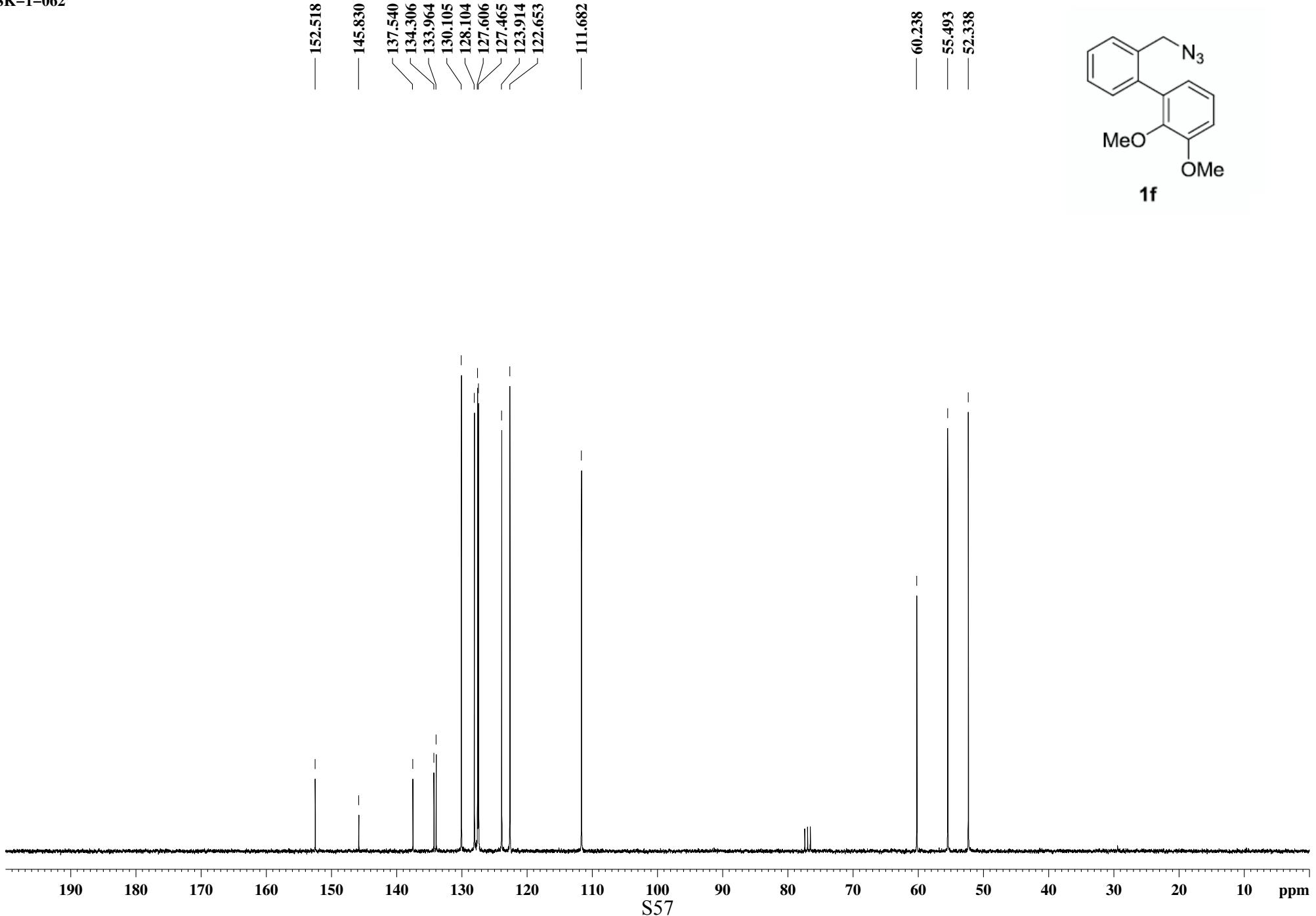
— 55.30 —
— 52.64 —



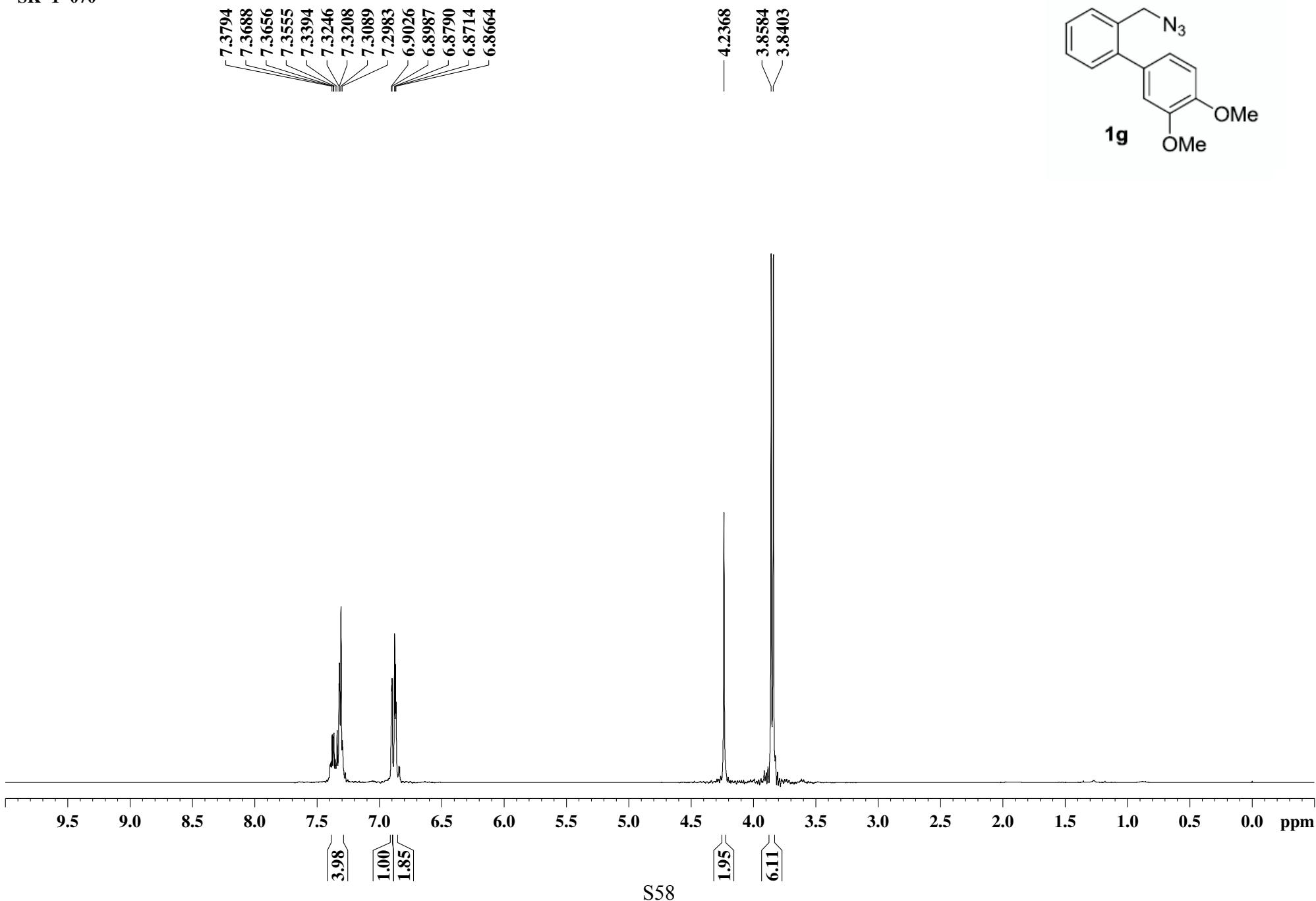
SK-1-062



SK-1-062



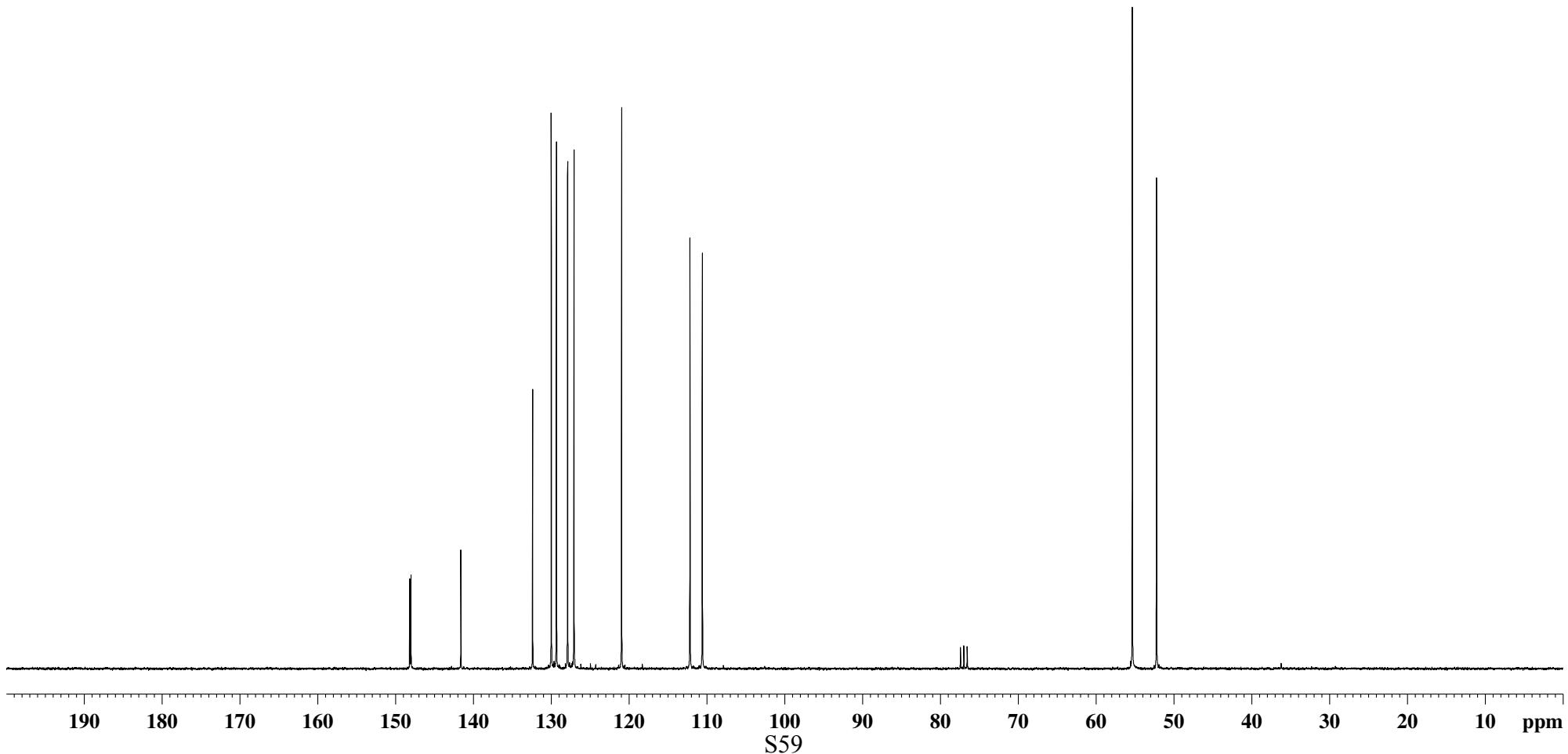
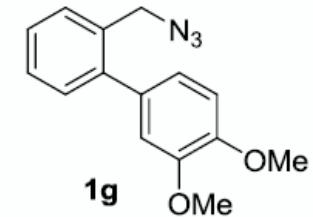
SK-1-070



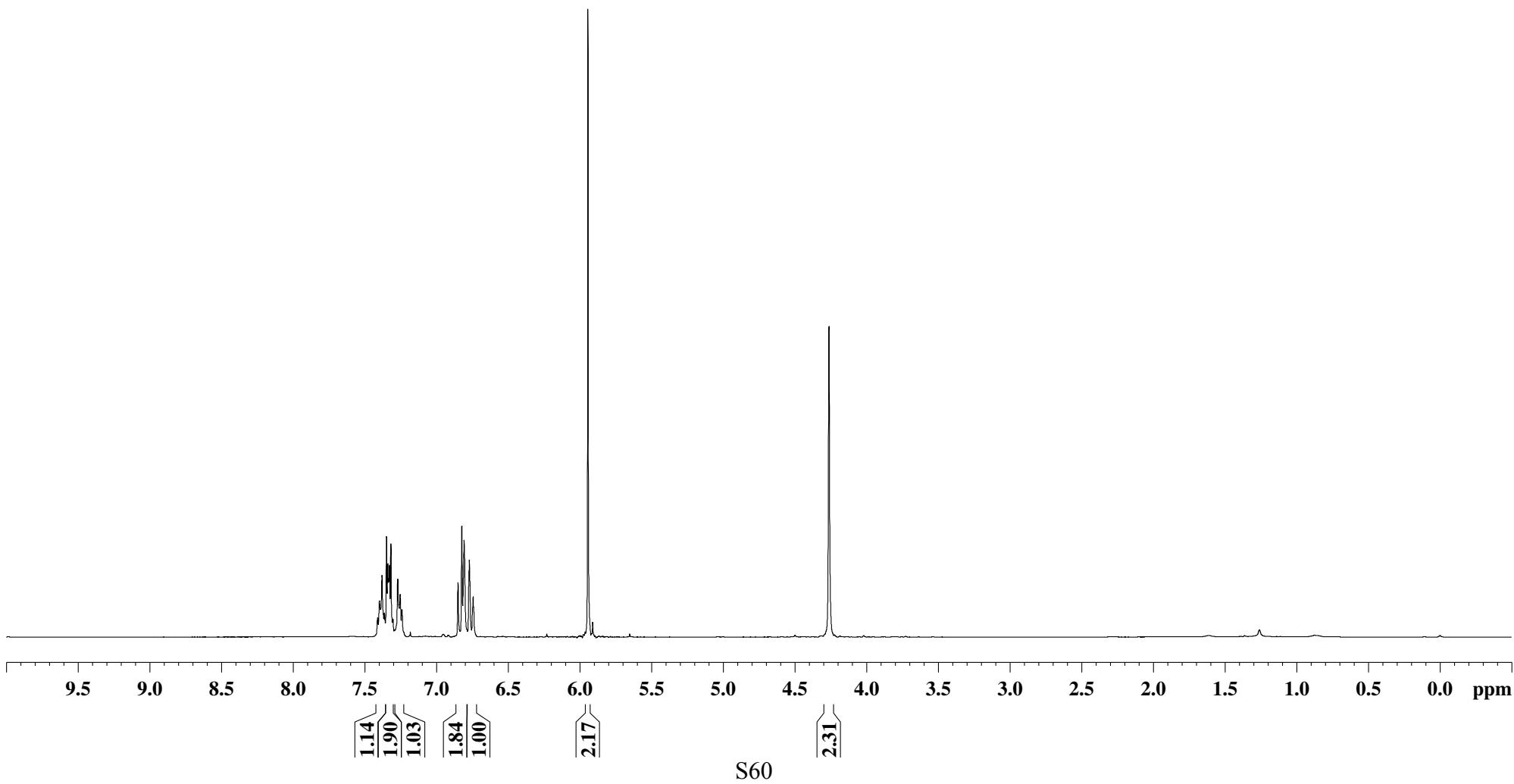
SK-1-070

148.1945
148.0322
141.6274
132.4043
130.0020
129.3451
127.9063
127.0865
120.9702
112.1913
110.6001

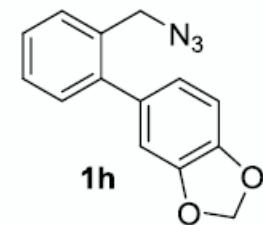
55.3485
52.2387



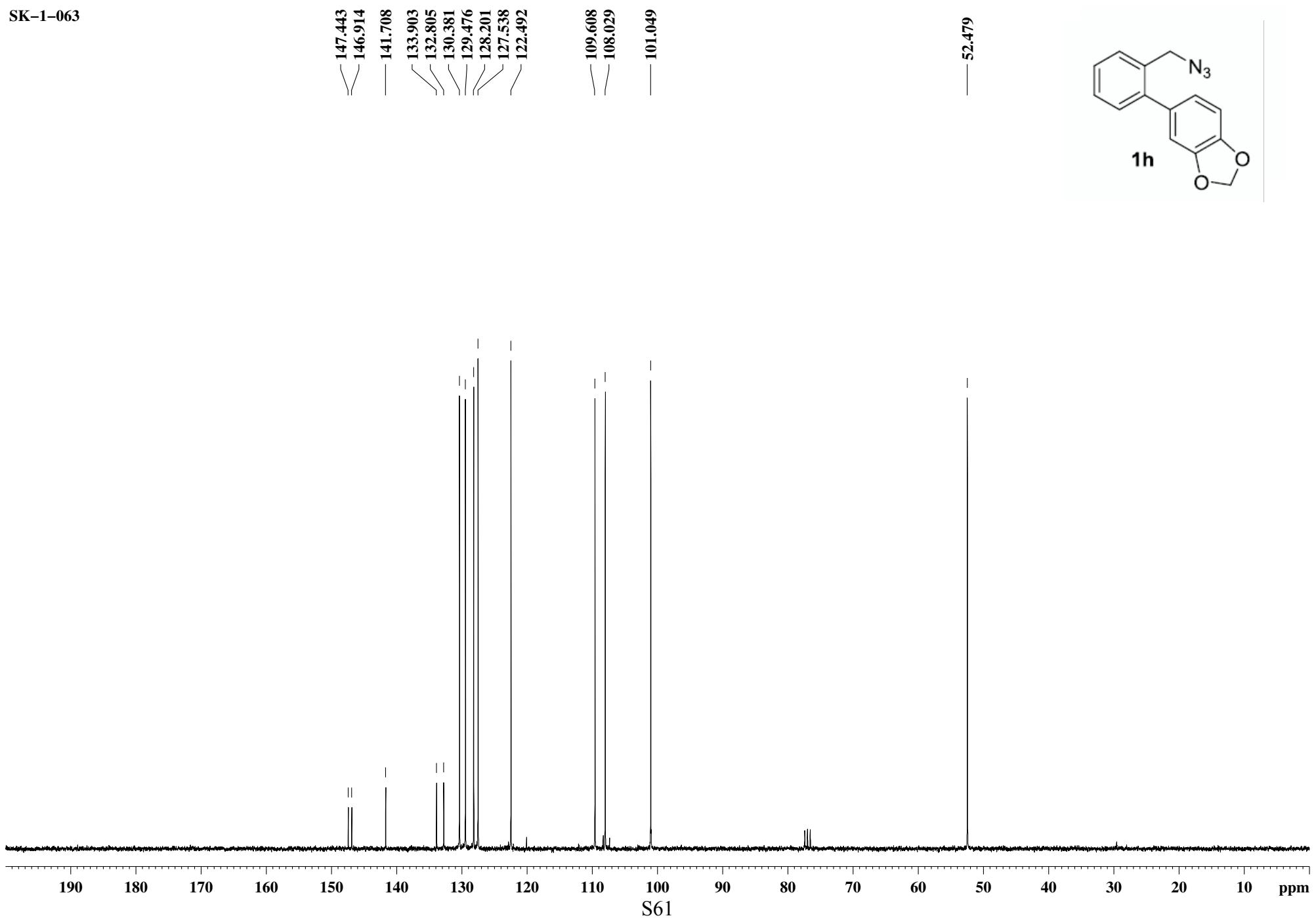
SK-1-063



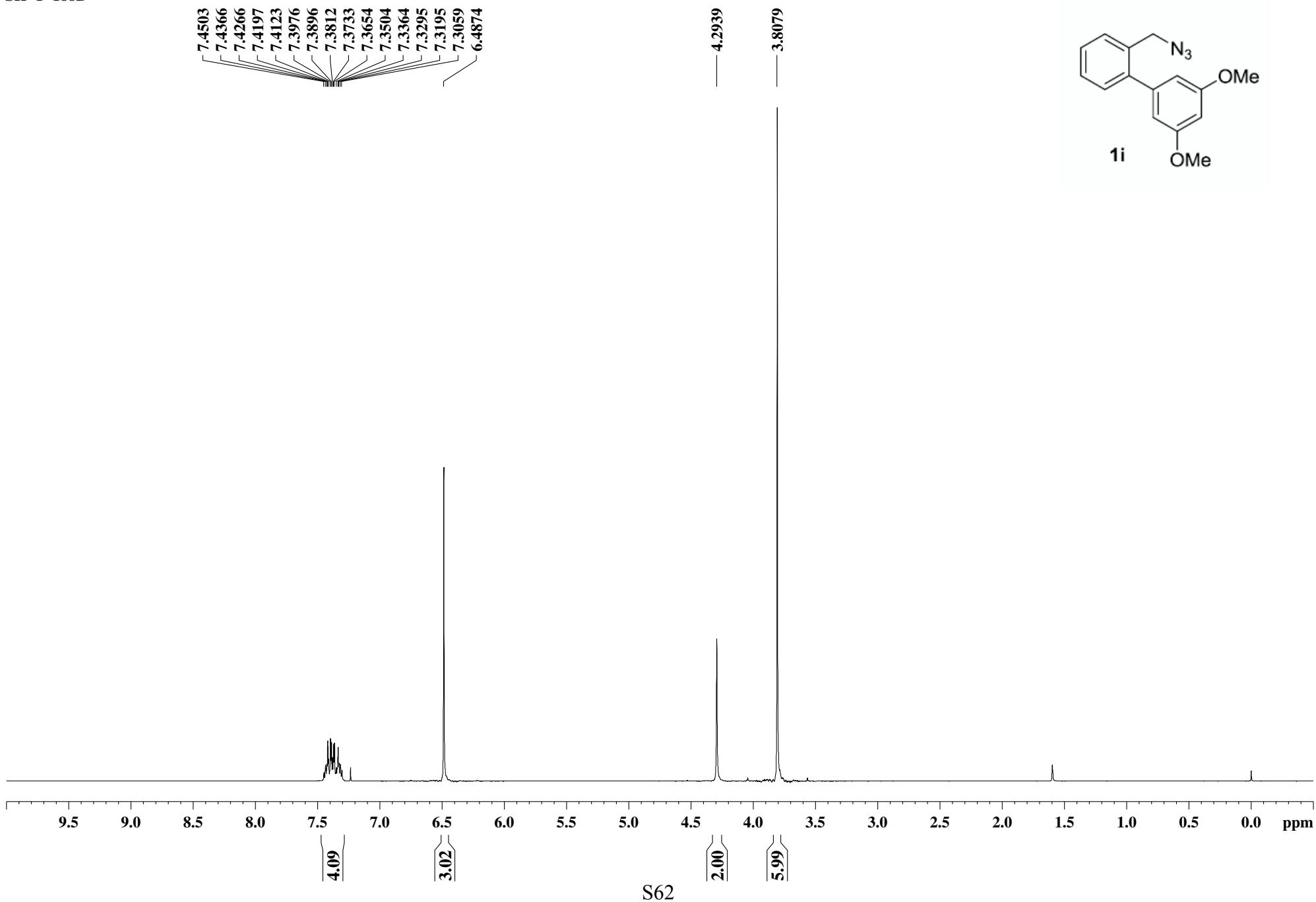
— 4.26 —



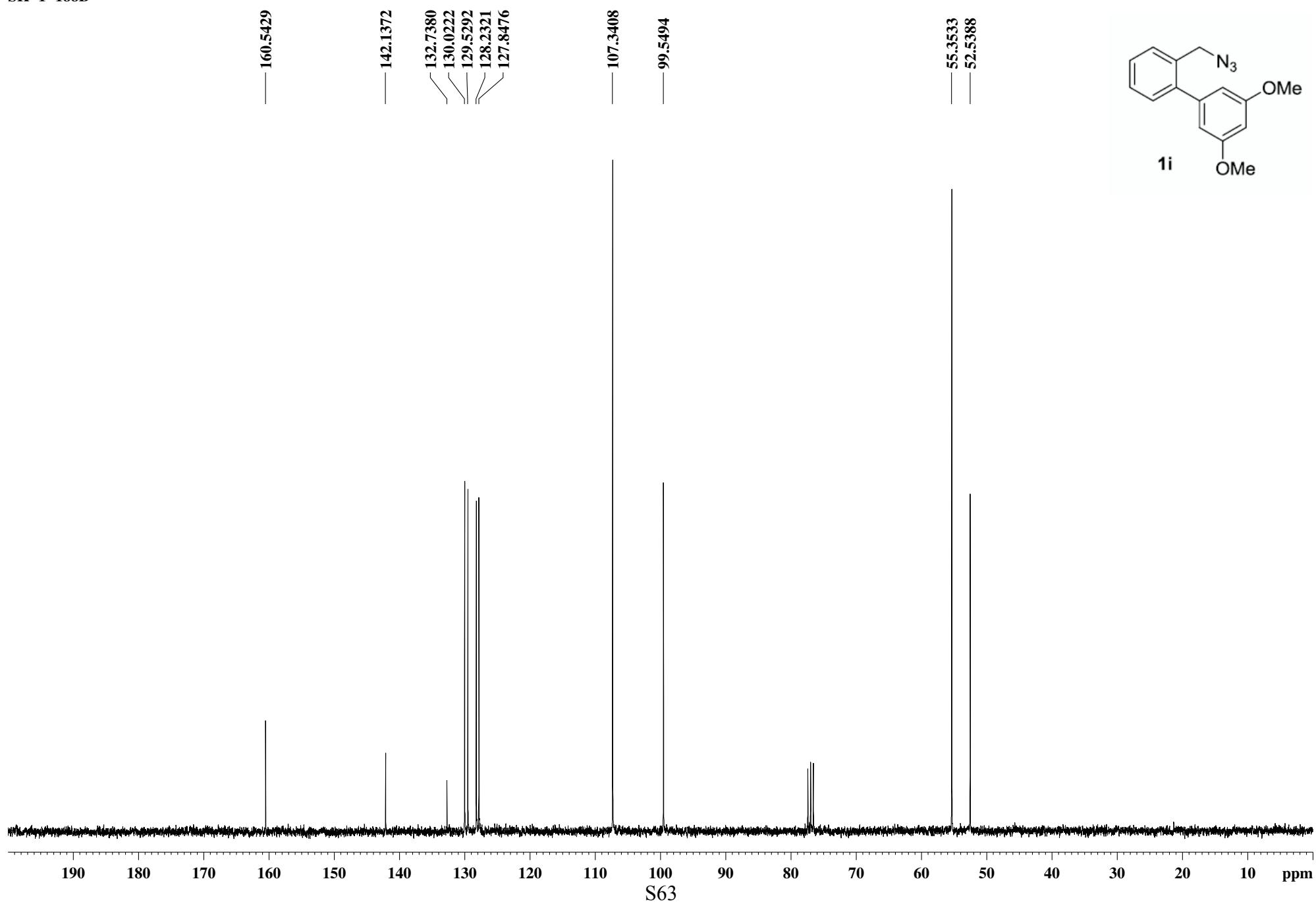
SK-1-063



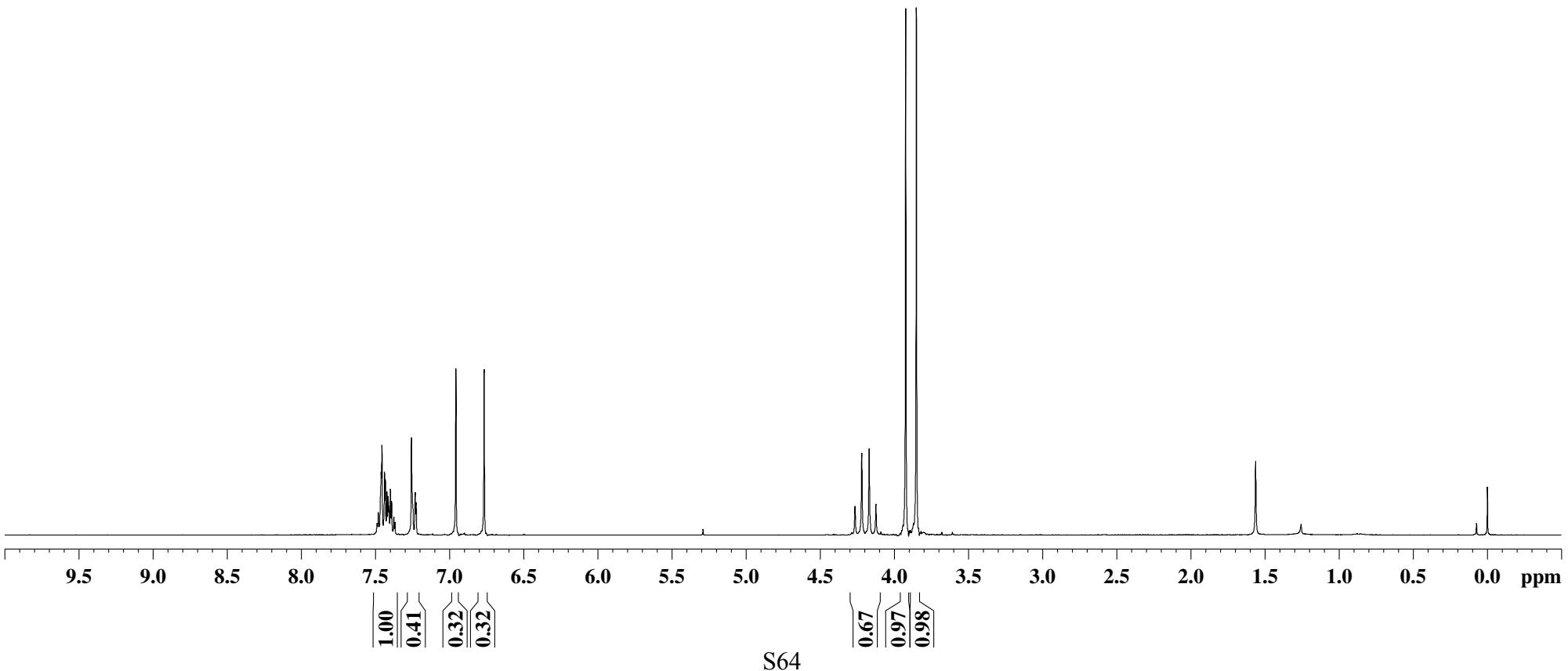
SK-1-188B



SK-1-188B



KN-1-039



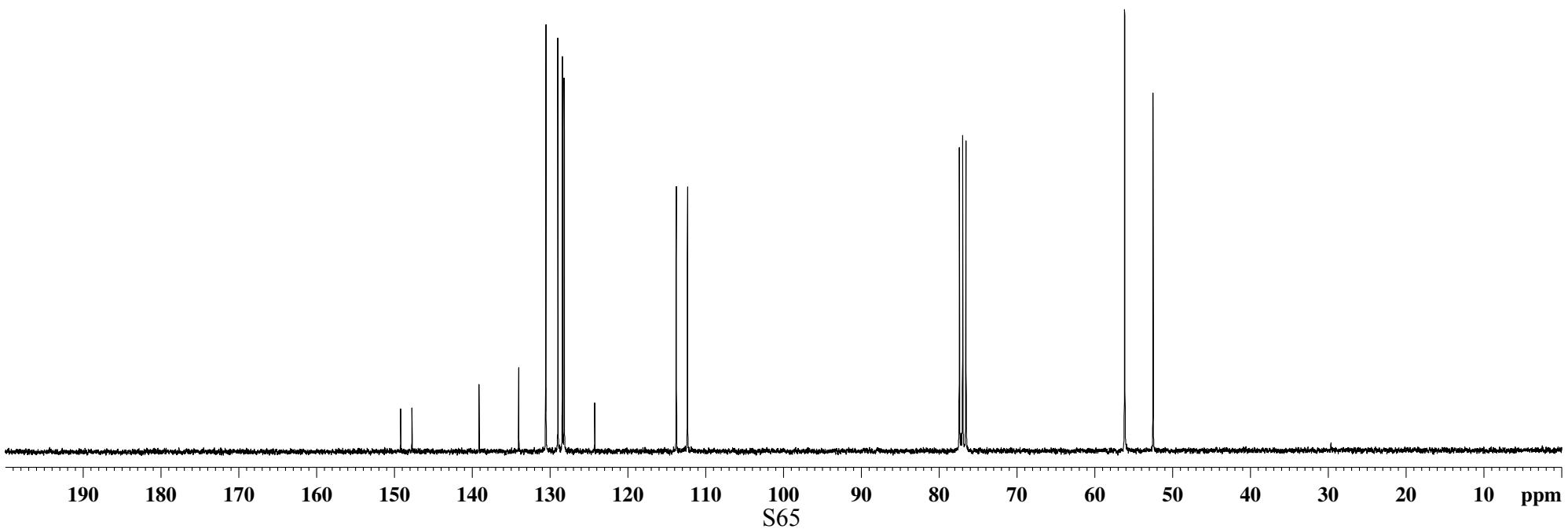
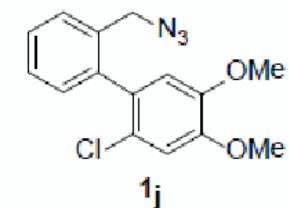
KN-1-039

149.174
147.717

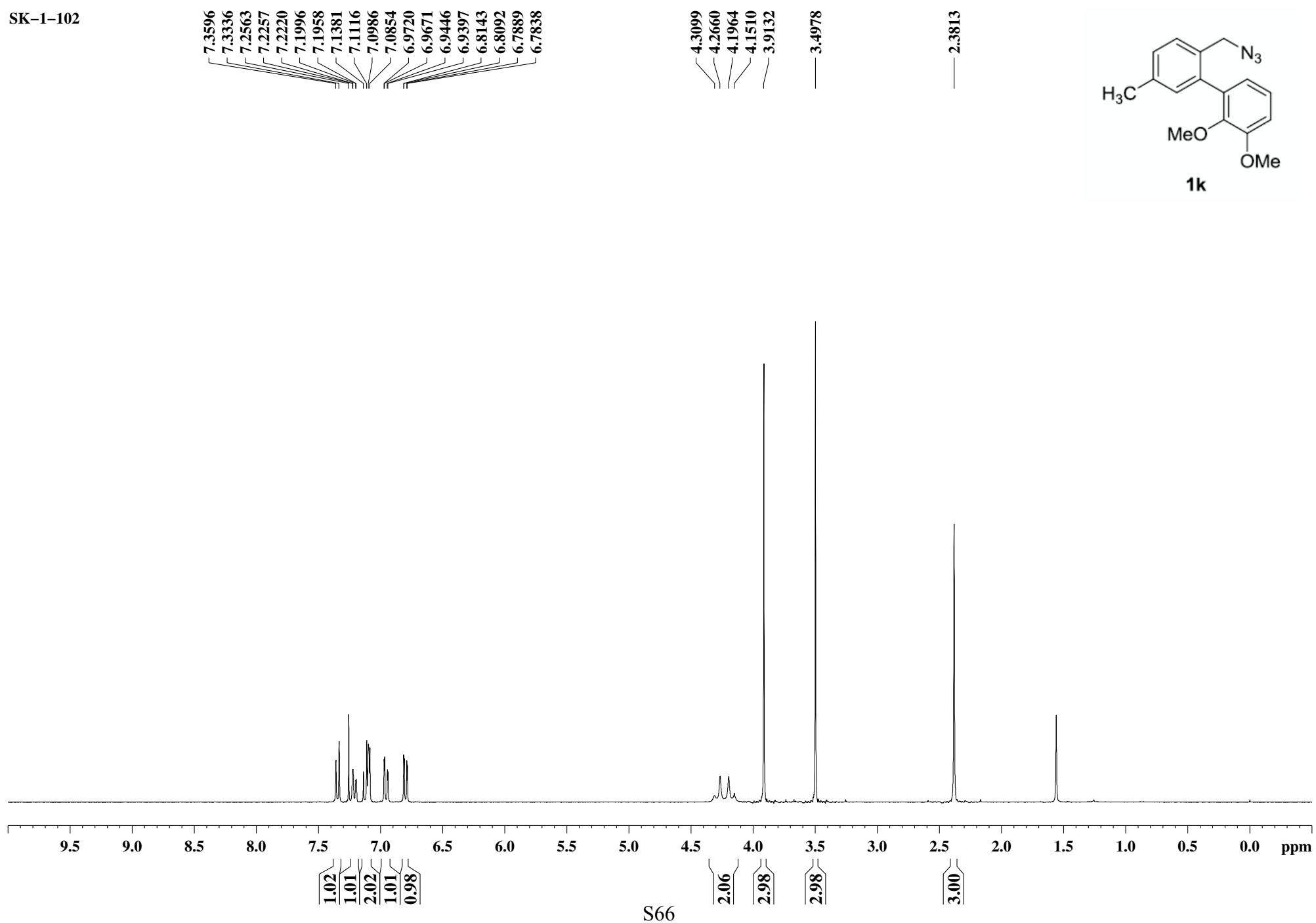
139.097
133.995
130.554
130.502
128.965
128.390
128.154
124.244

113.793
112.356

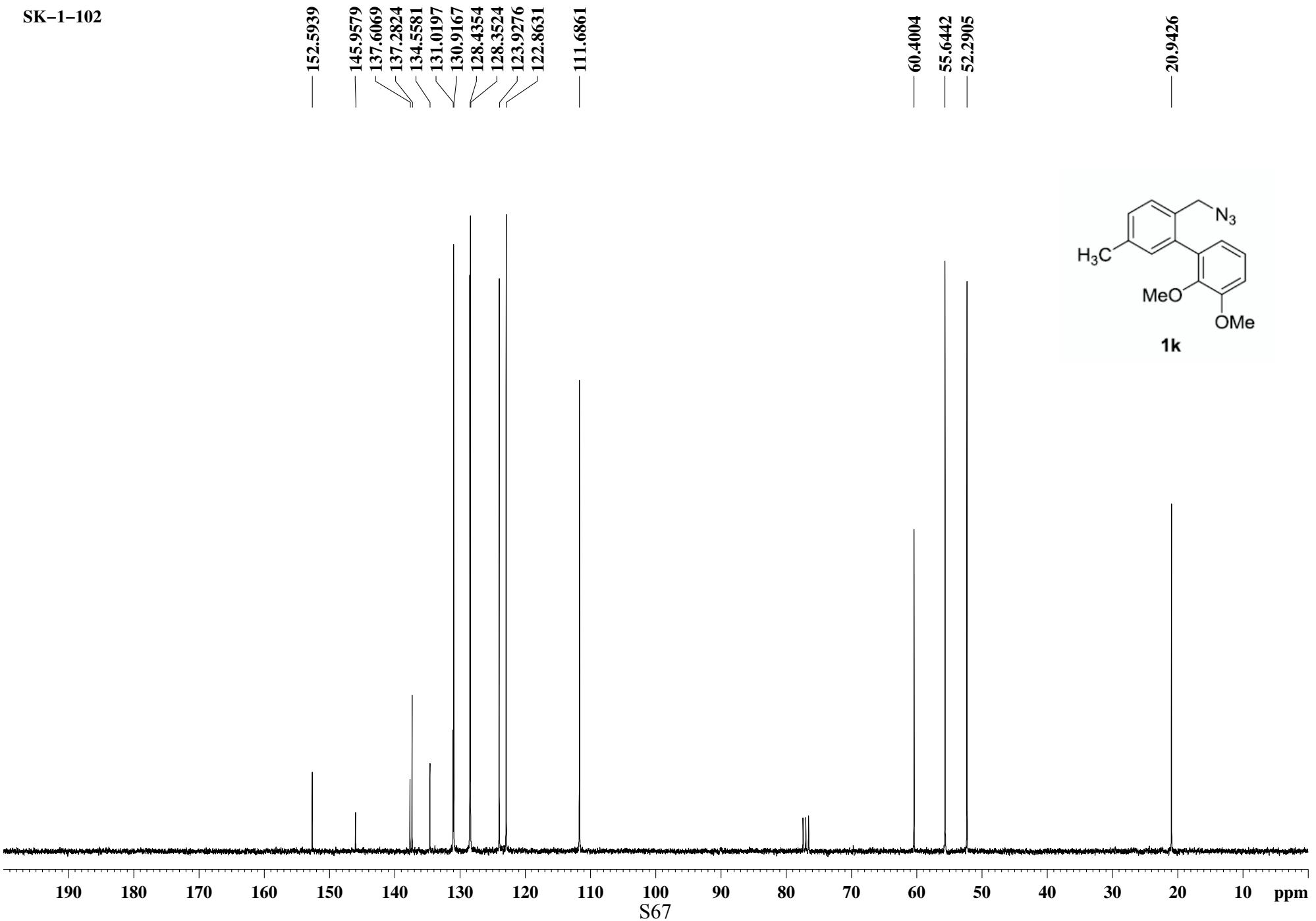
56.206
56.162
52.533



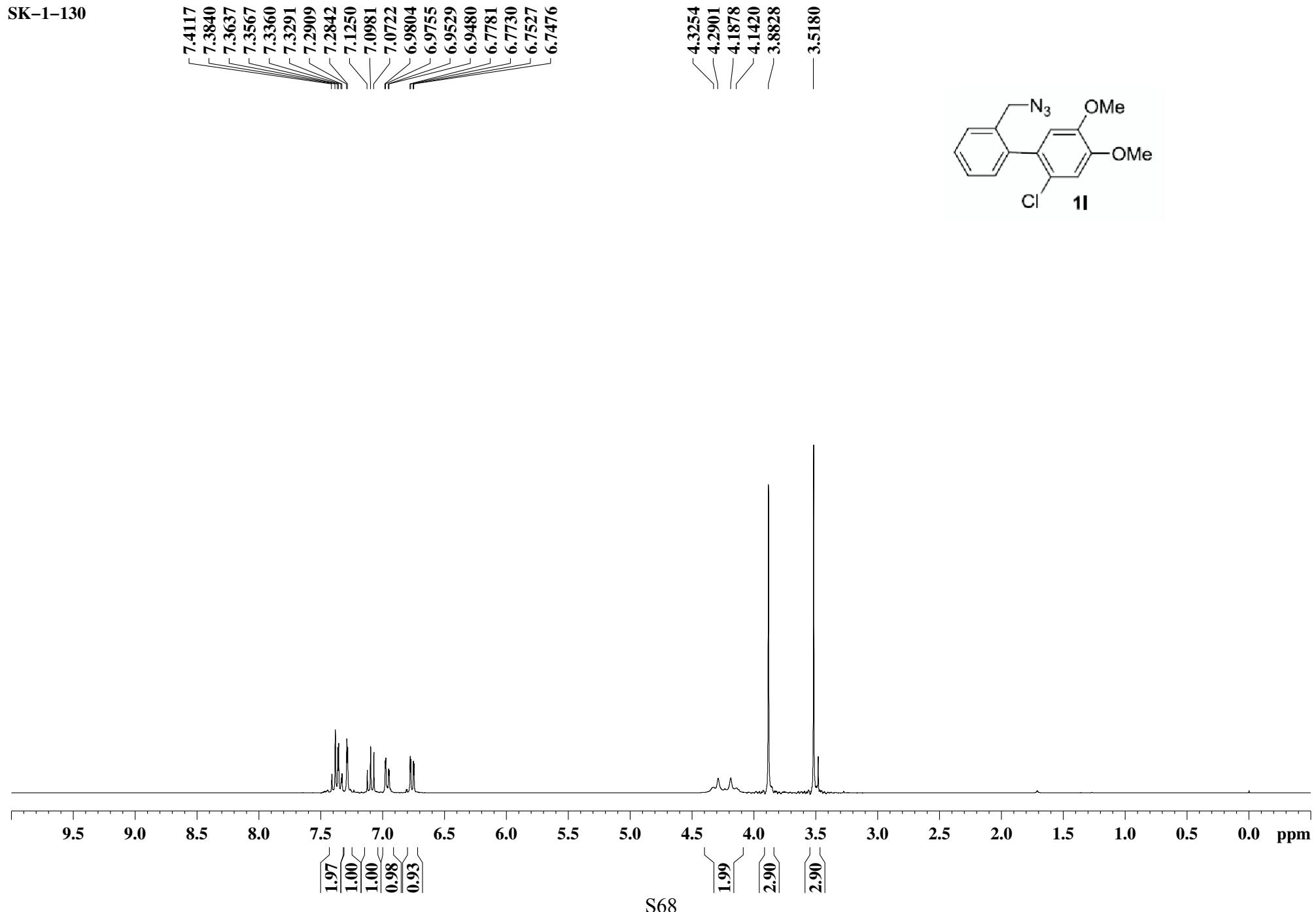
SK-1-102



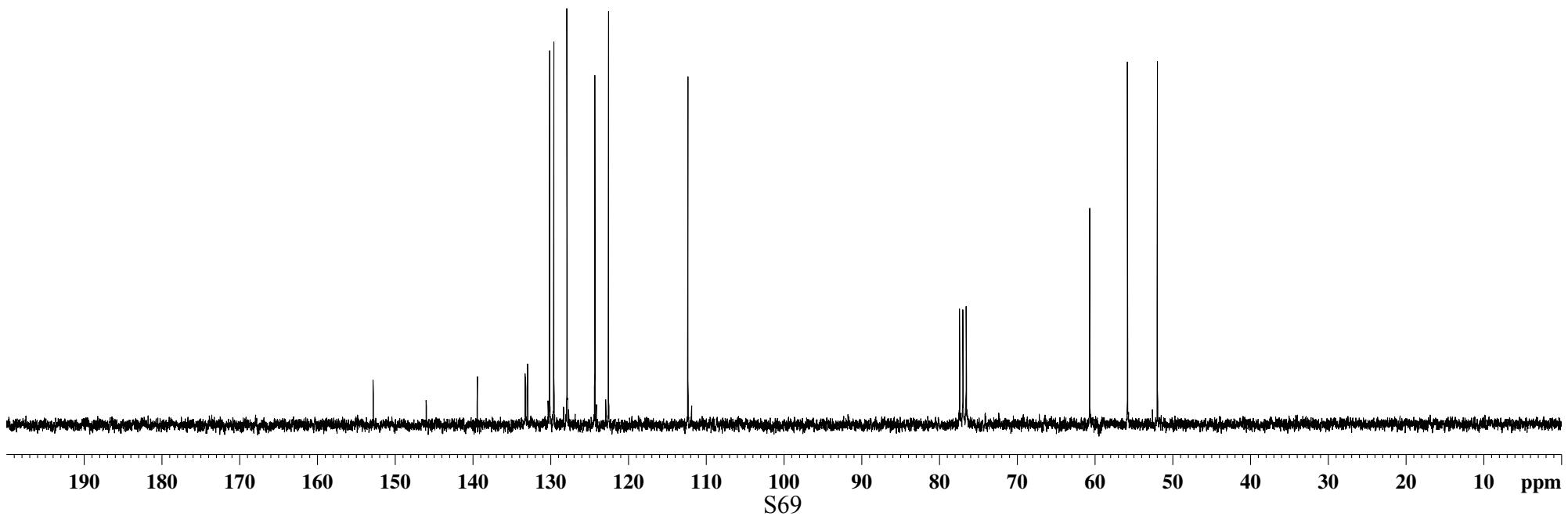
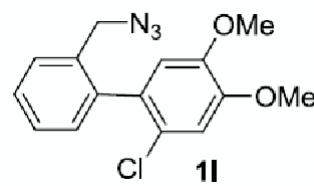
SK-1-102



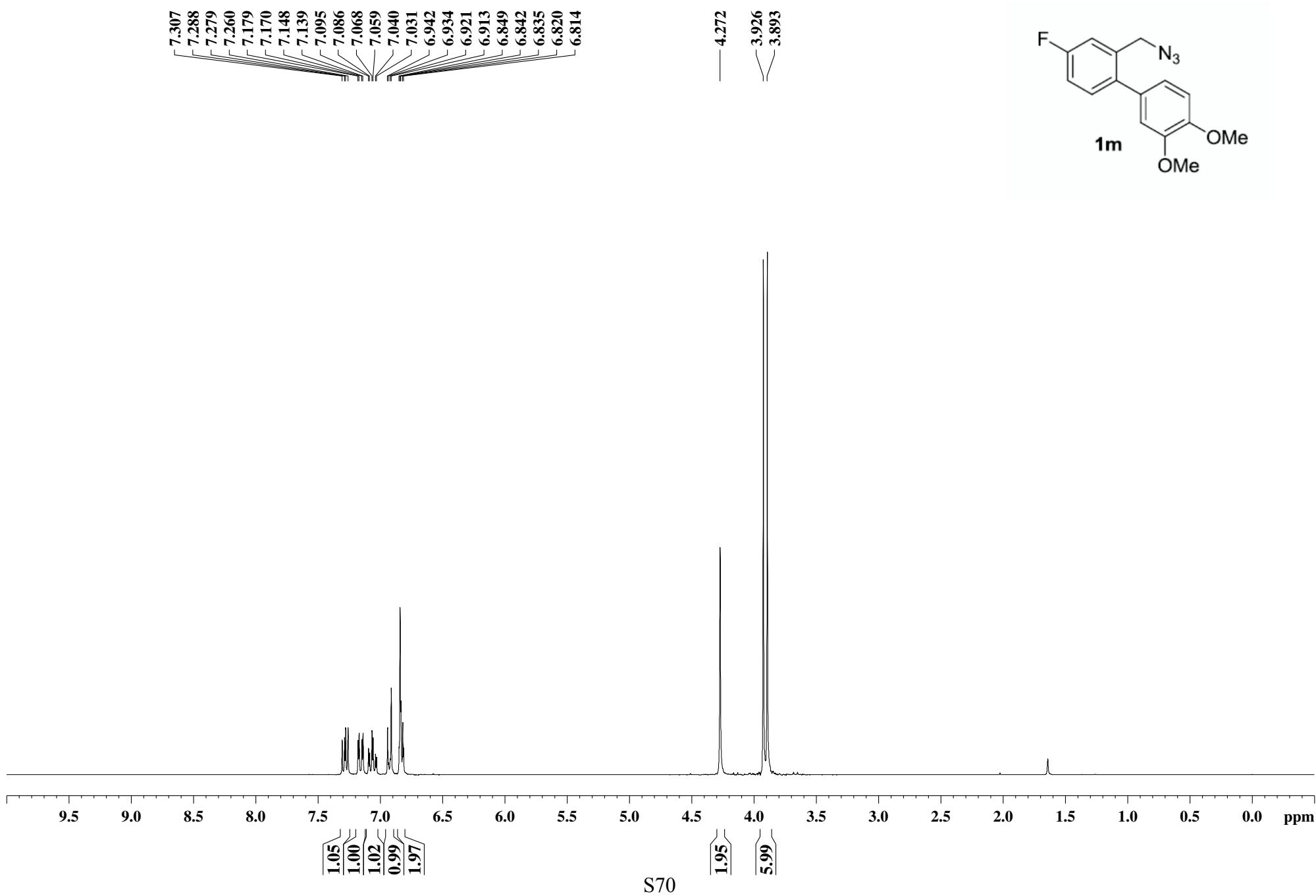
SK-1-130



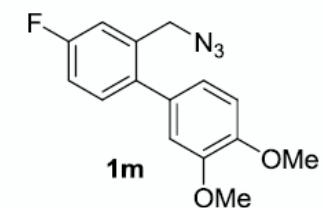
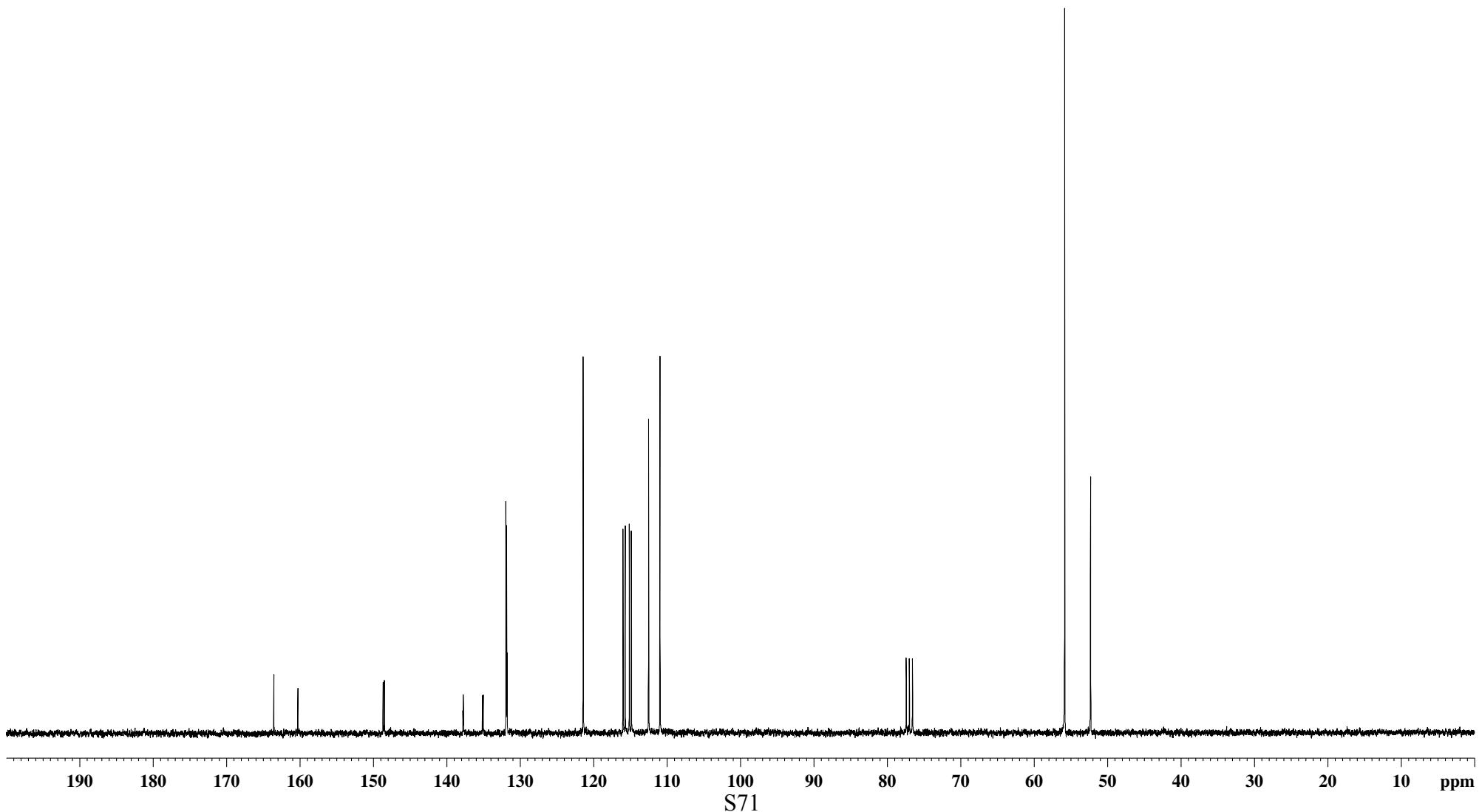
SK-1-130



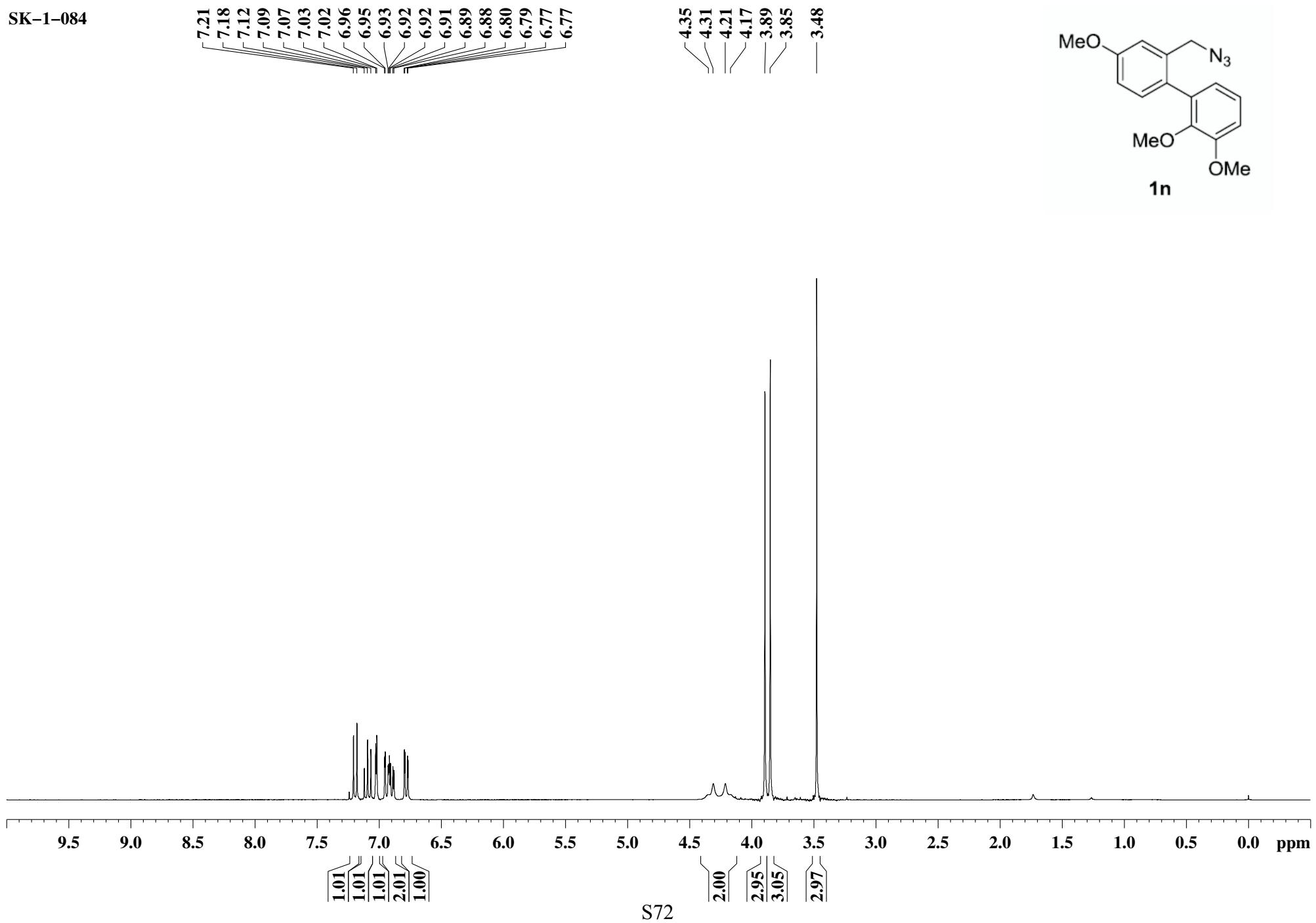
SK-1-136



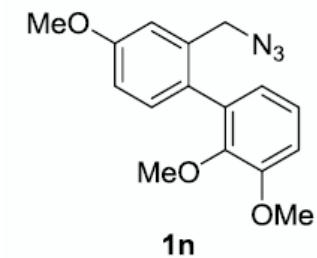
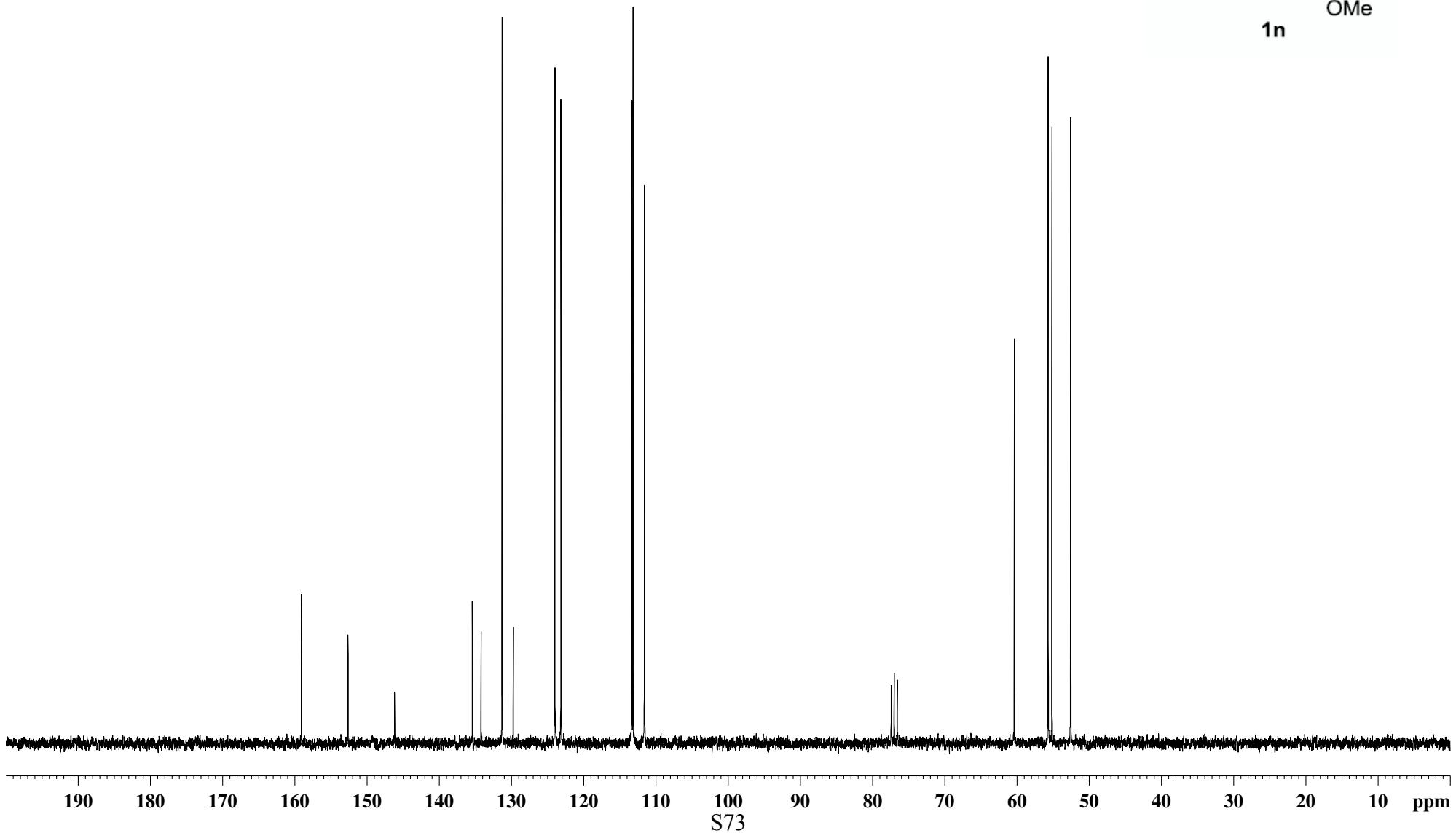
SK-1-136



SK-1-084



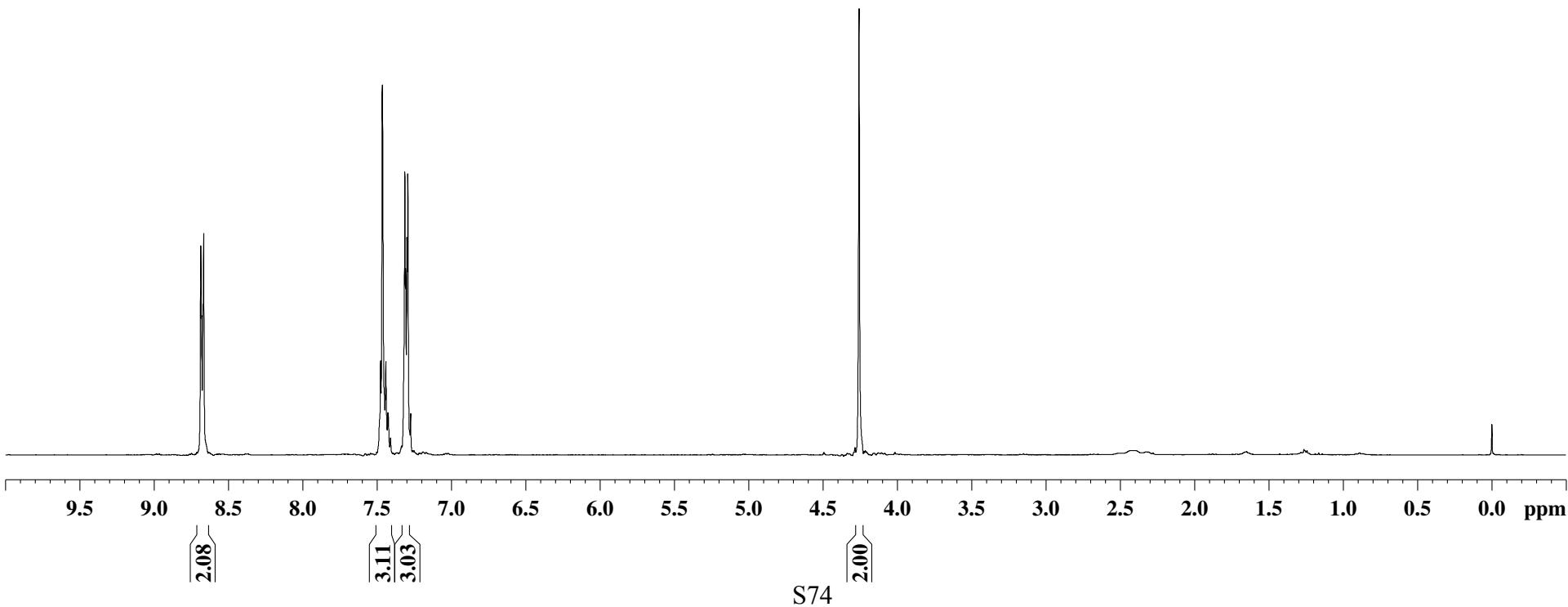
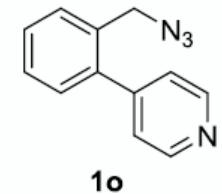
SK-1-084



SK-1-159

8.6882
8.6832
8.6733
8.6682
7.4780
7.4661
7.4423
7.4285
7.4110
7.3147
7.3091
7.3000
7.2944
7.2753

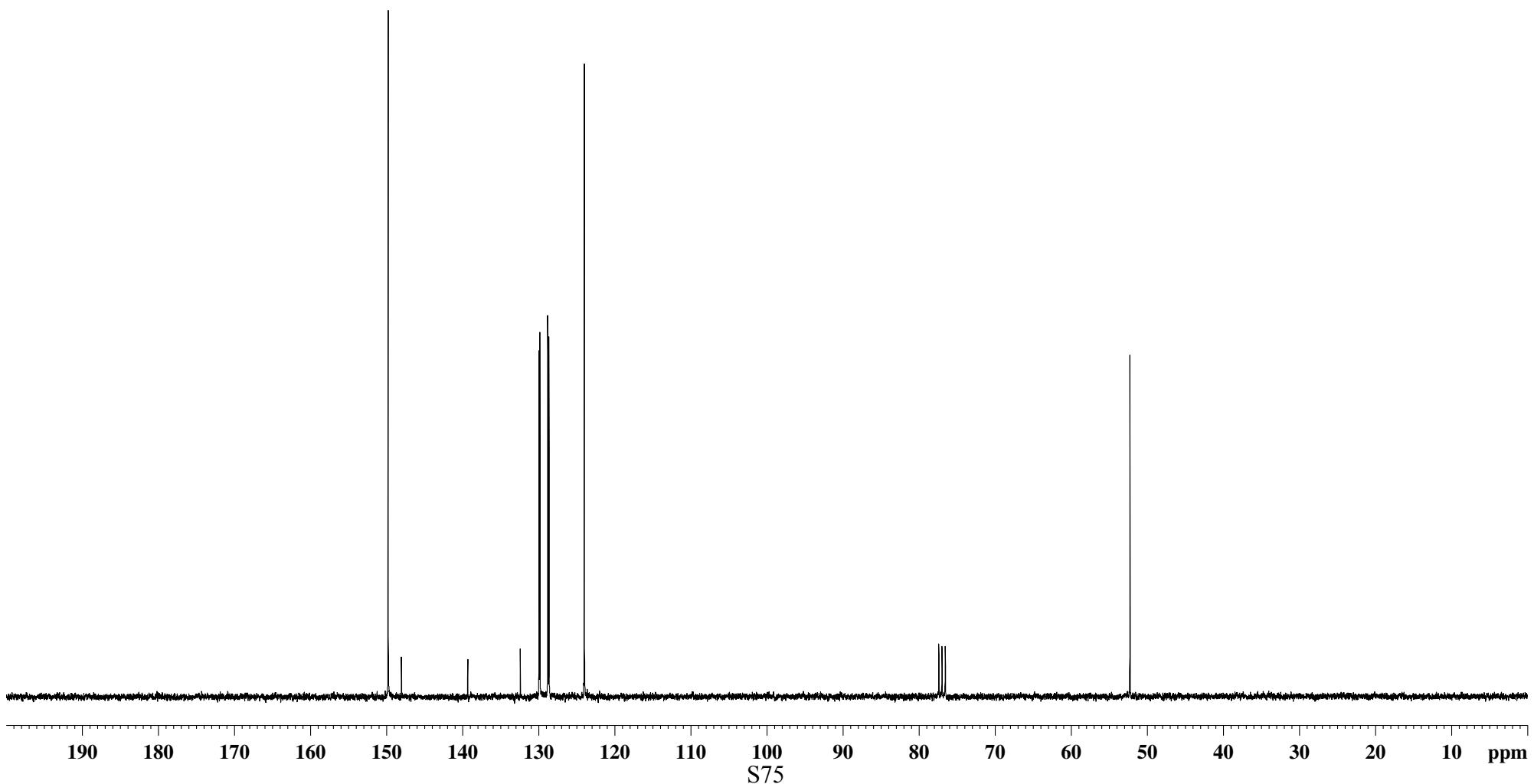
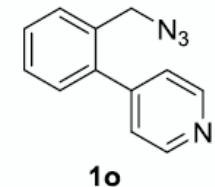
4.2582



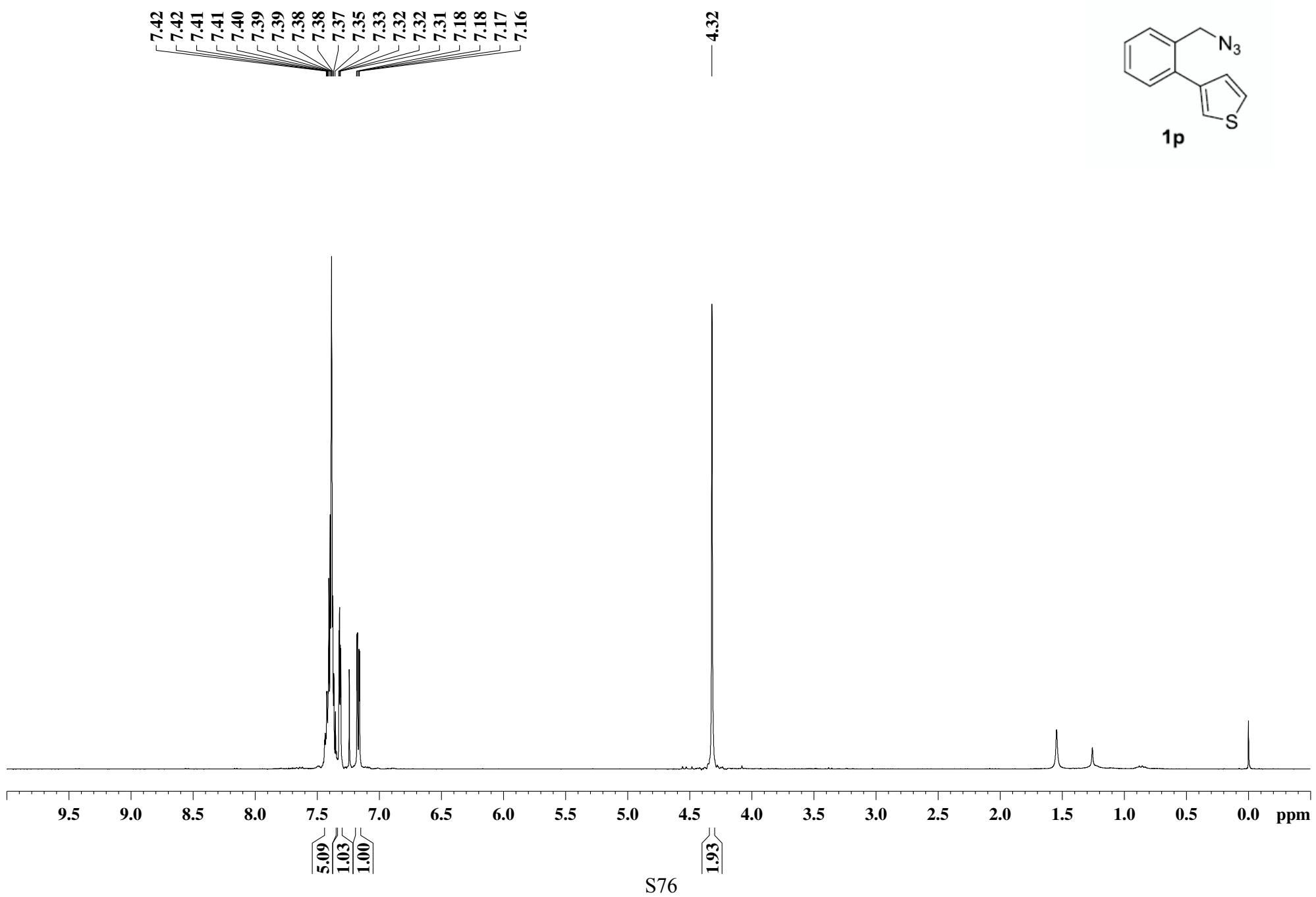
SK-1-159

149.7564
148.0124
139.3517
132.4480
129.9677
129.8596
128.8228
128.6642
124.0223

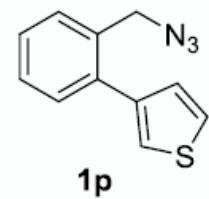
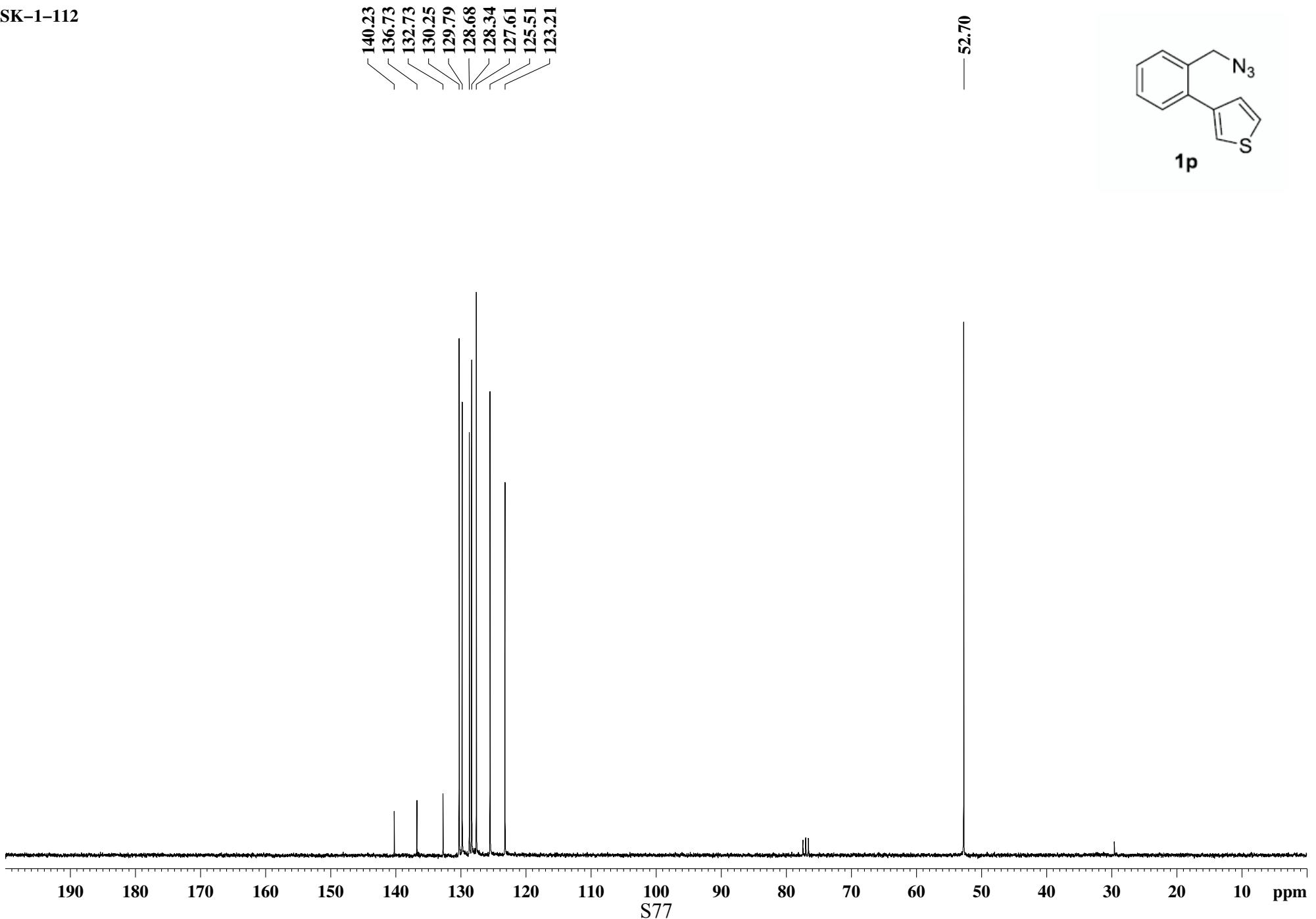
52.2892



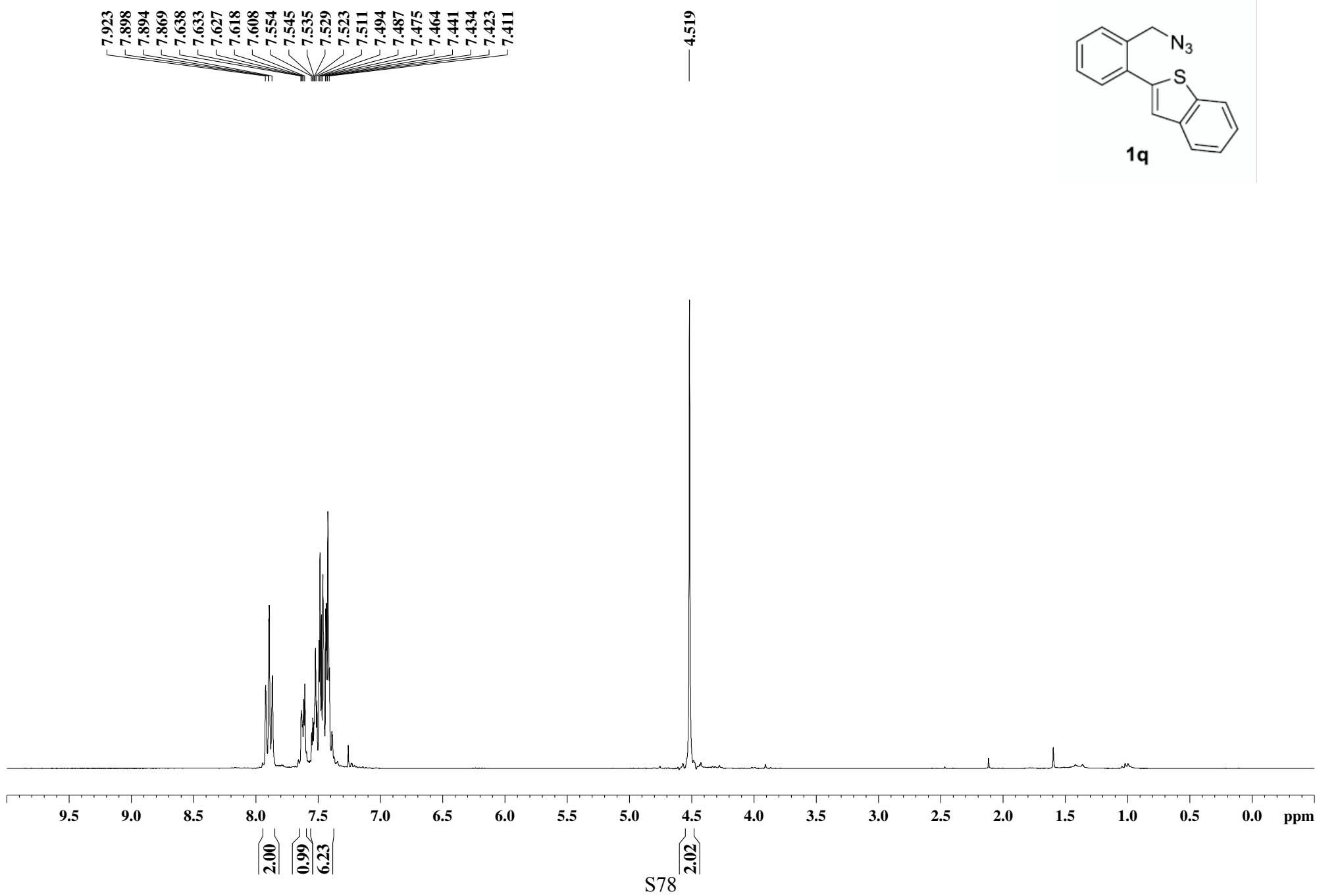
SK-1-112



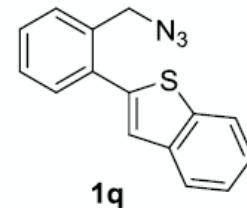
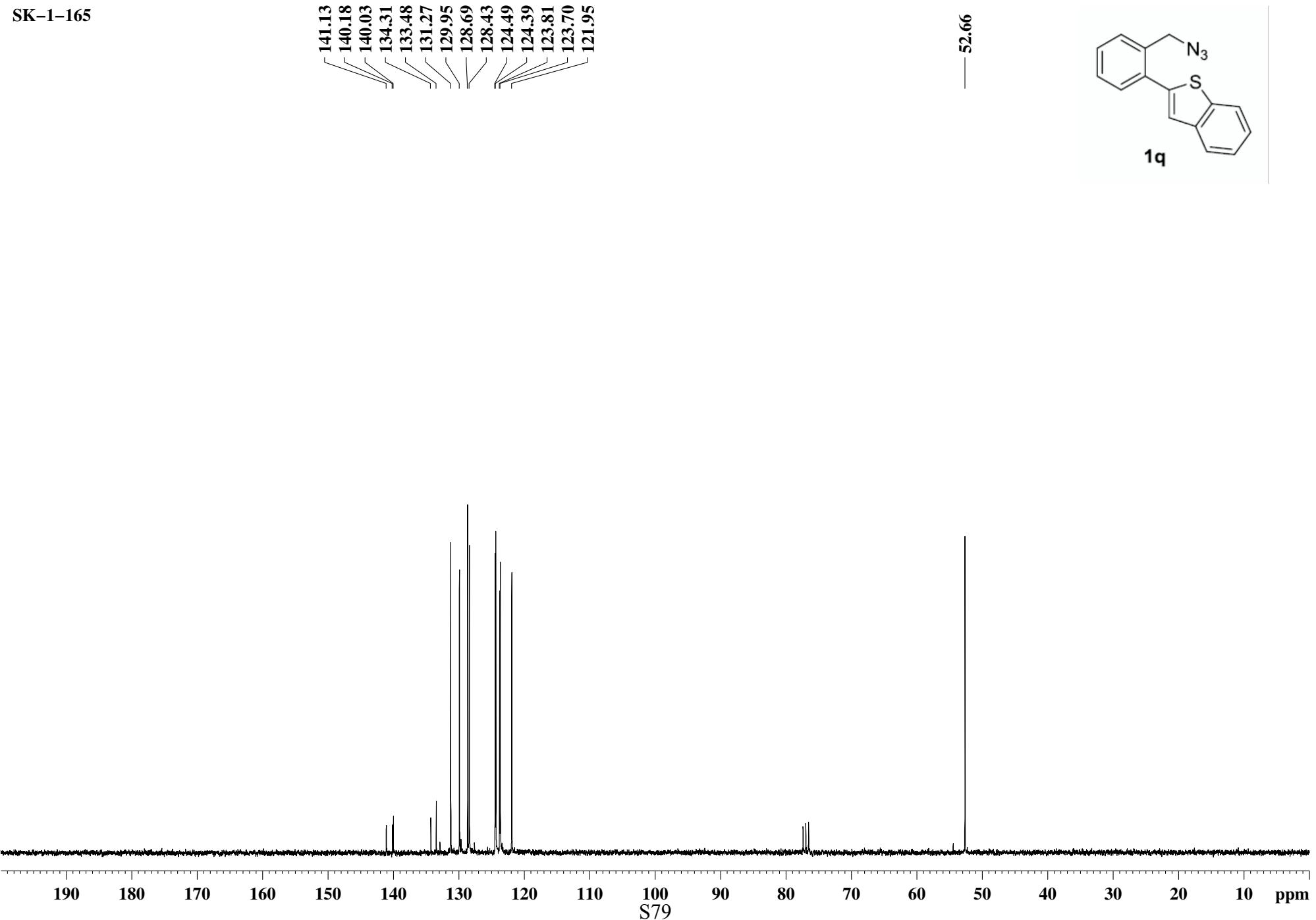
SK-1-112



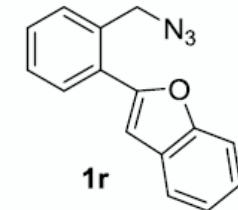
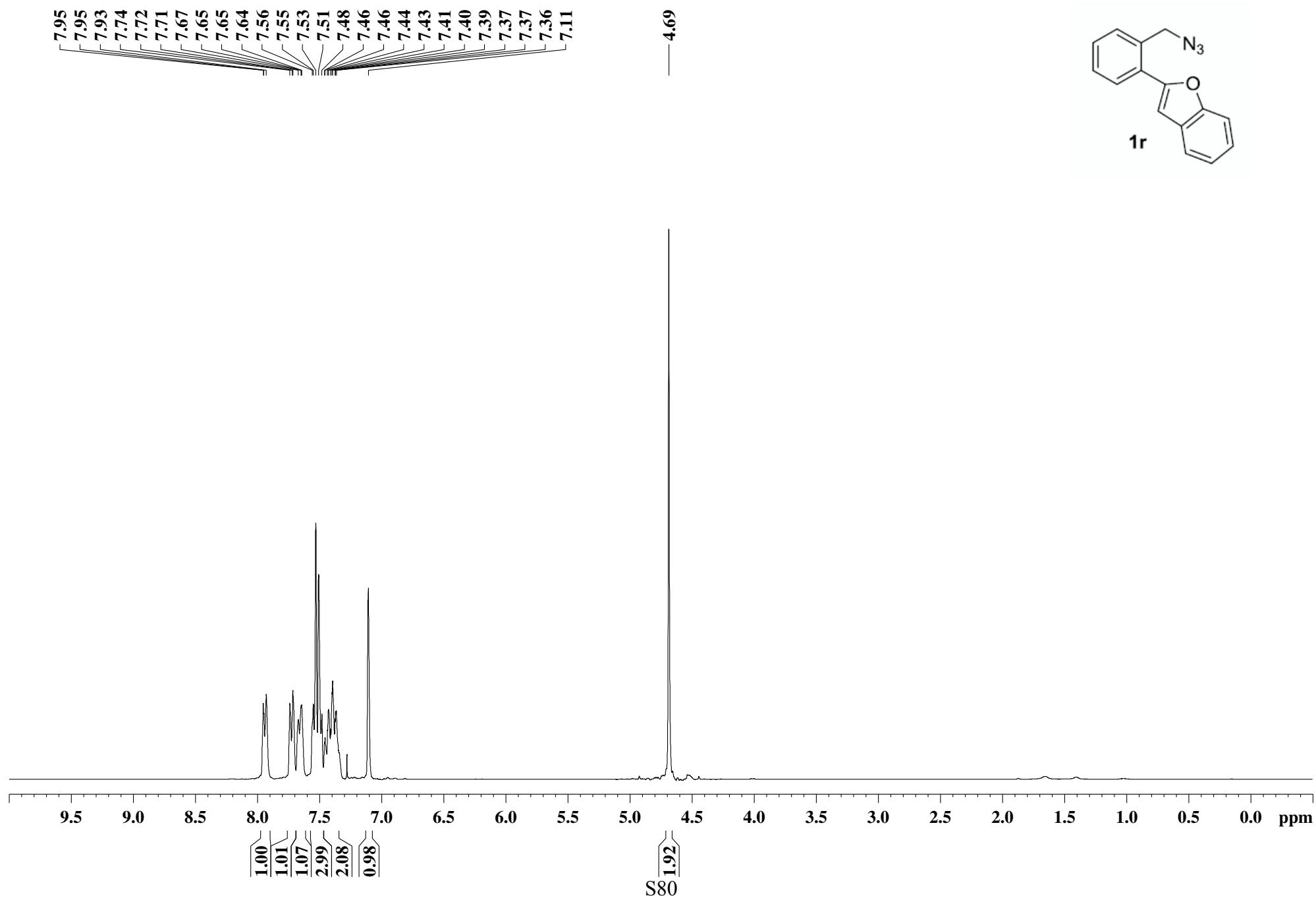
SK-1-165



SK-1-165



SK-1-109

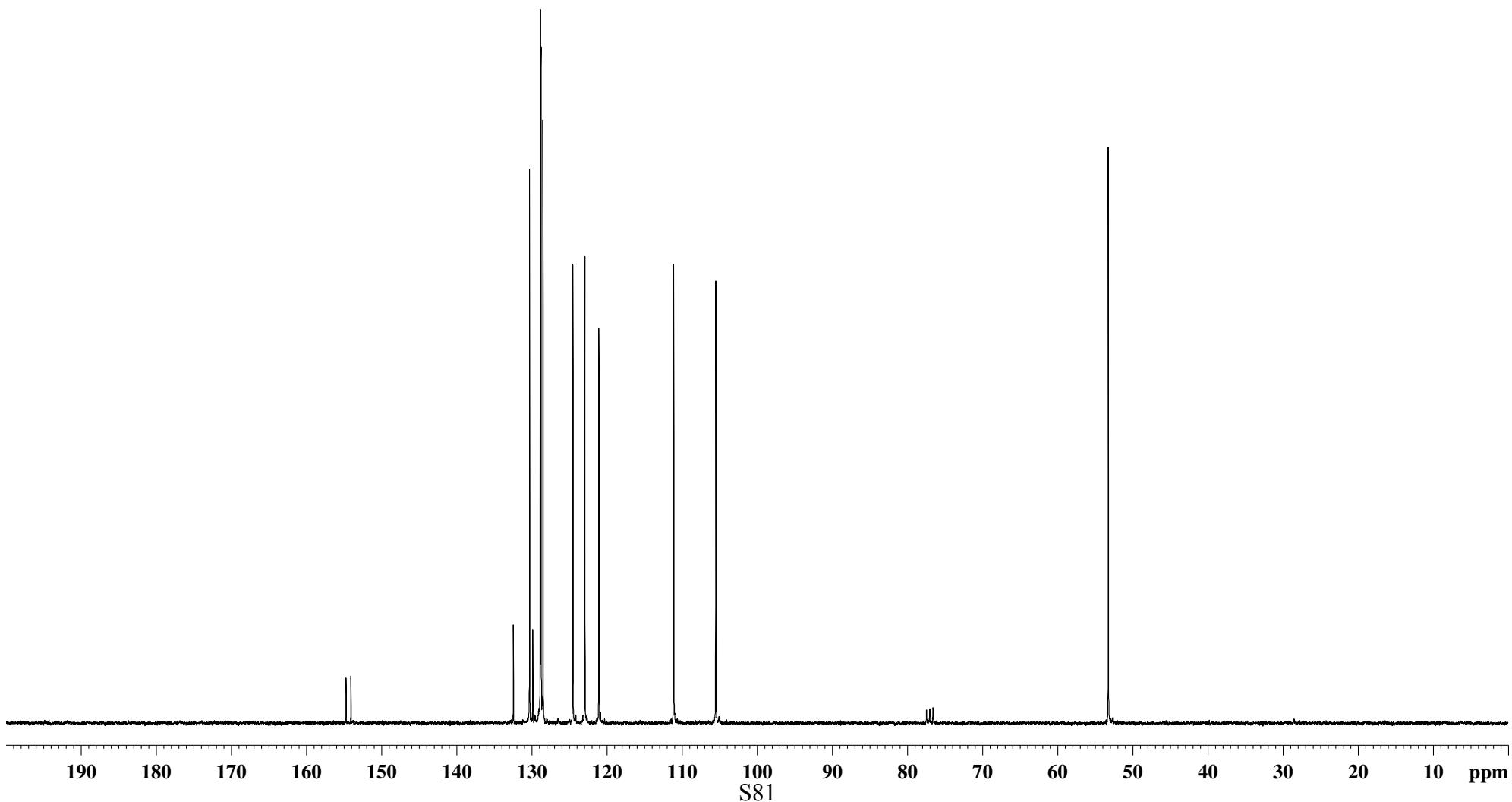
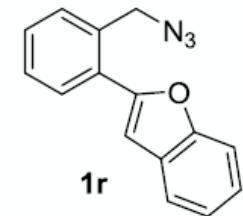


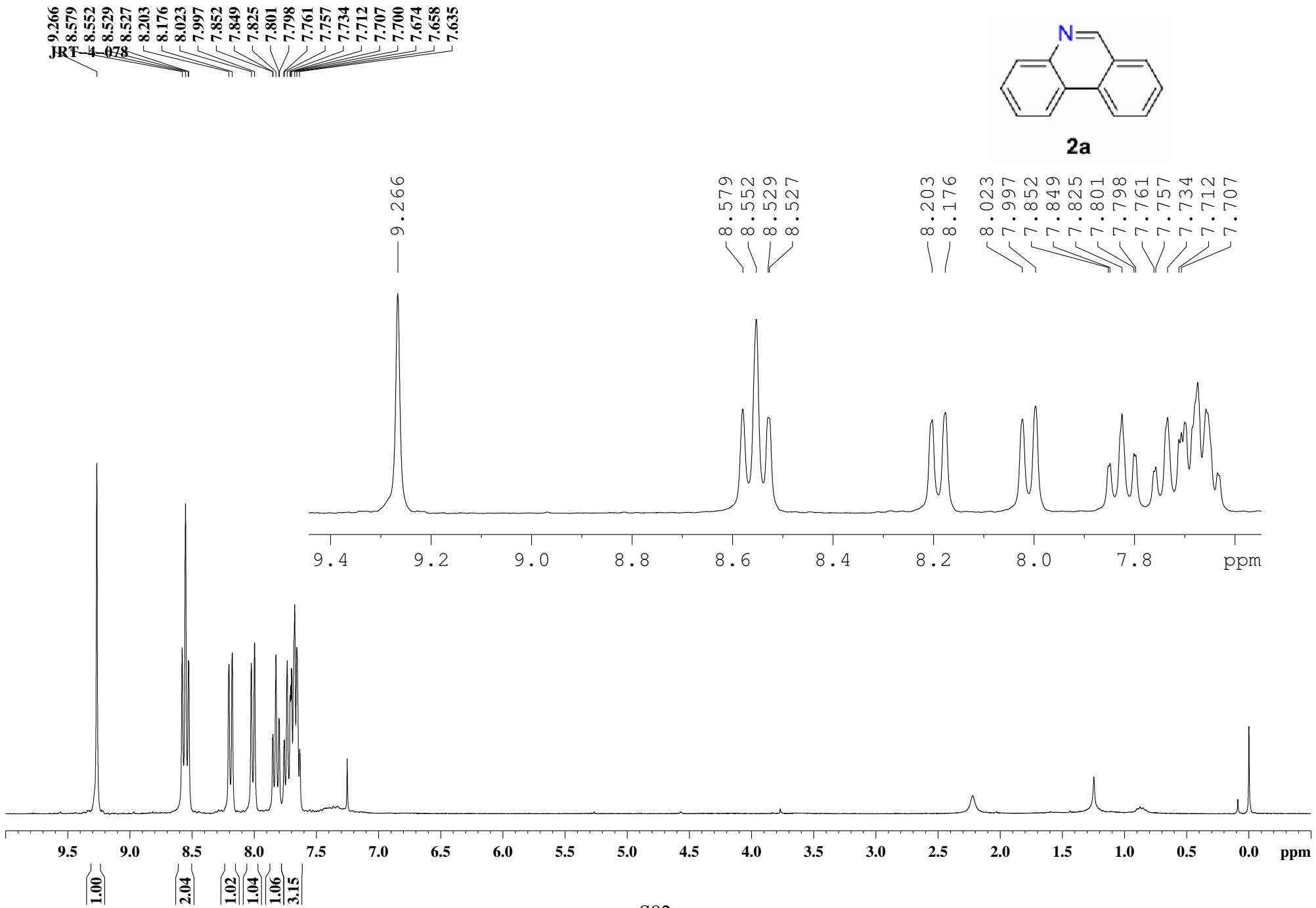
SK-1-109

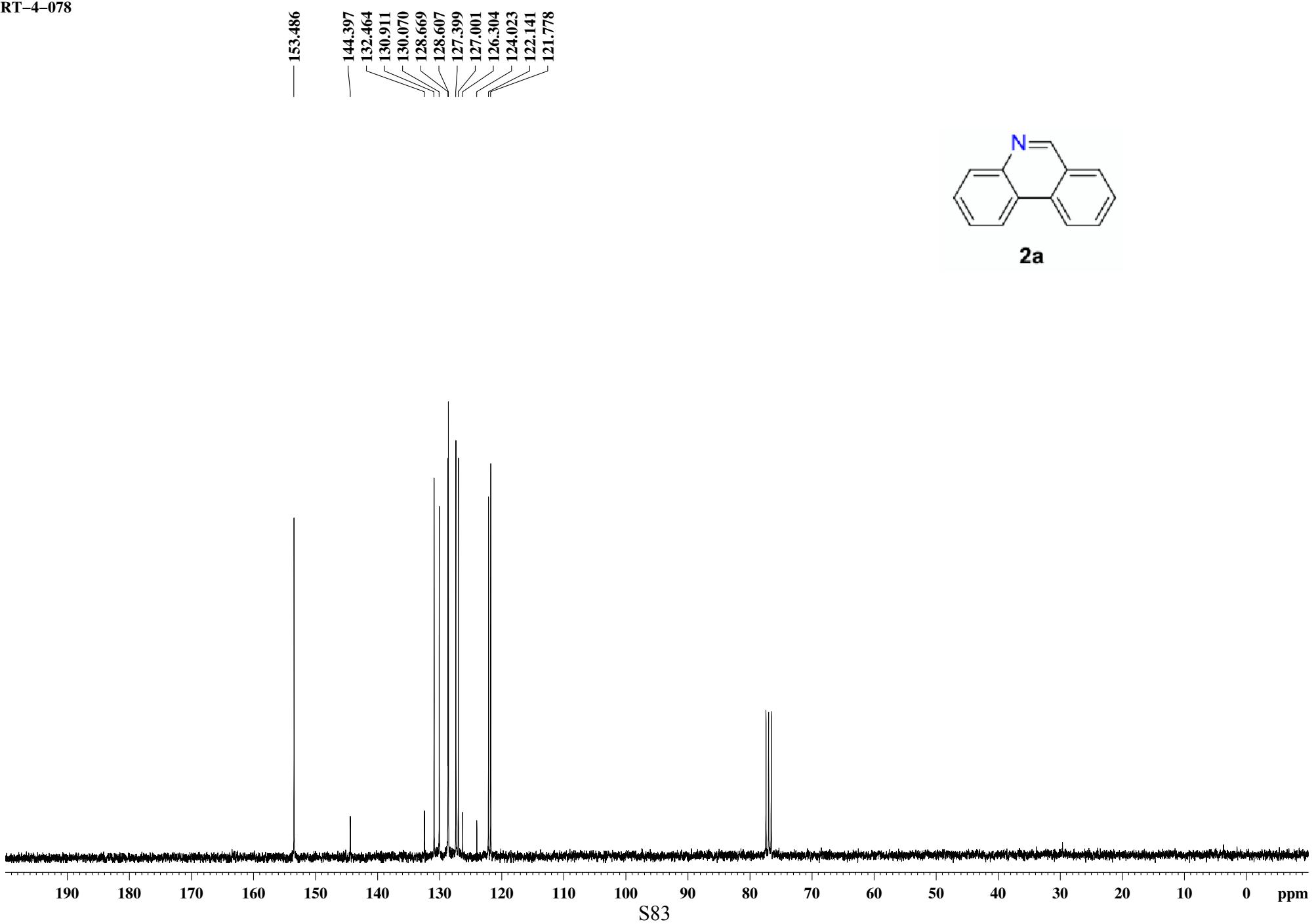
154.72
154.08

132.45
130.29
129.87
128.87
128.77
128.50
124.52
122.92
121.06
111.09
105.50

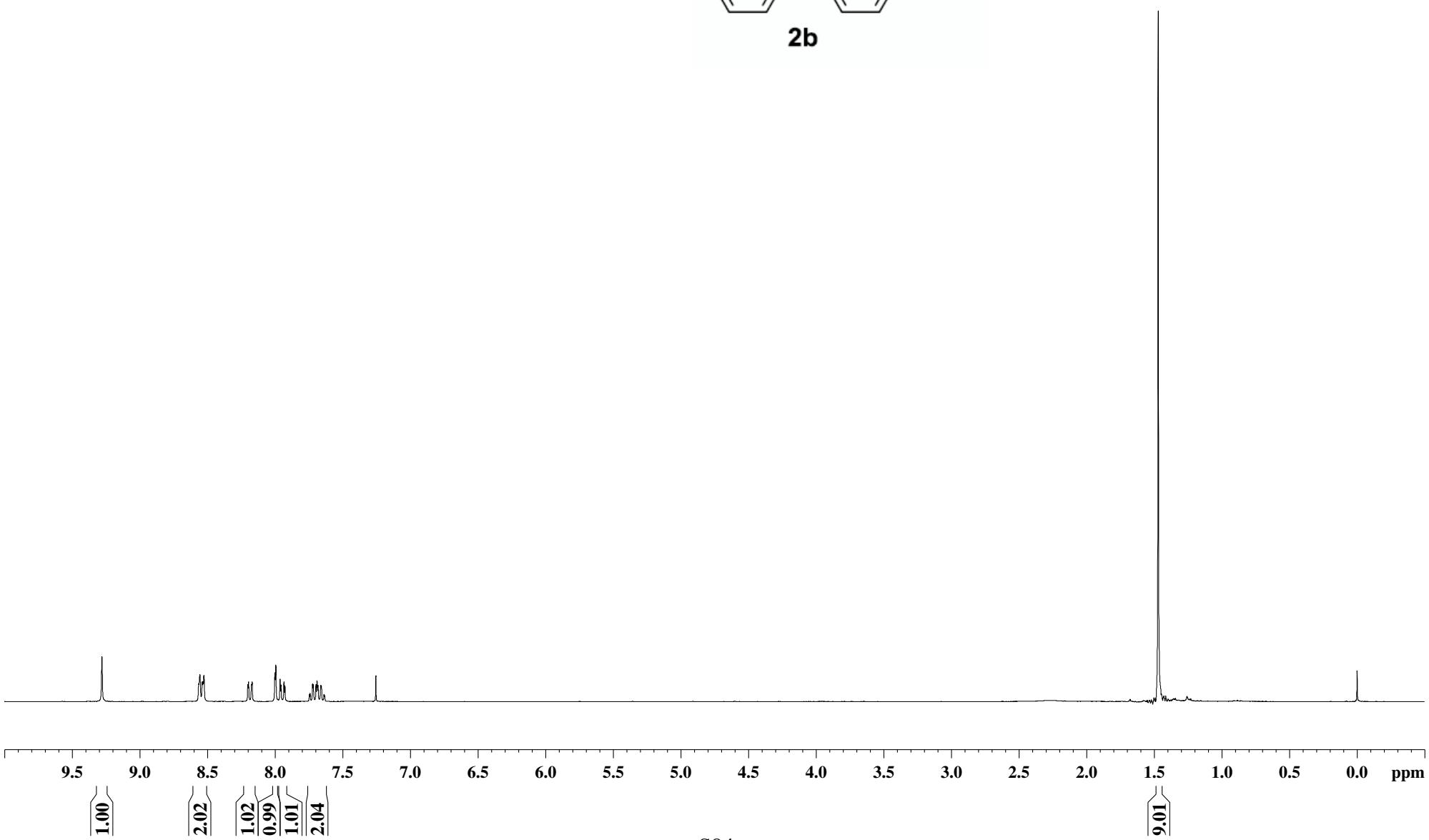
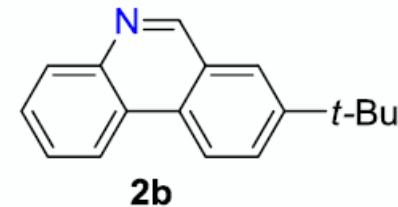
53.23





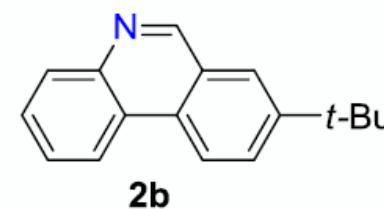


SK-1-114

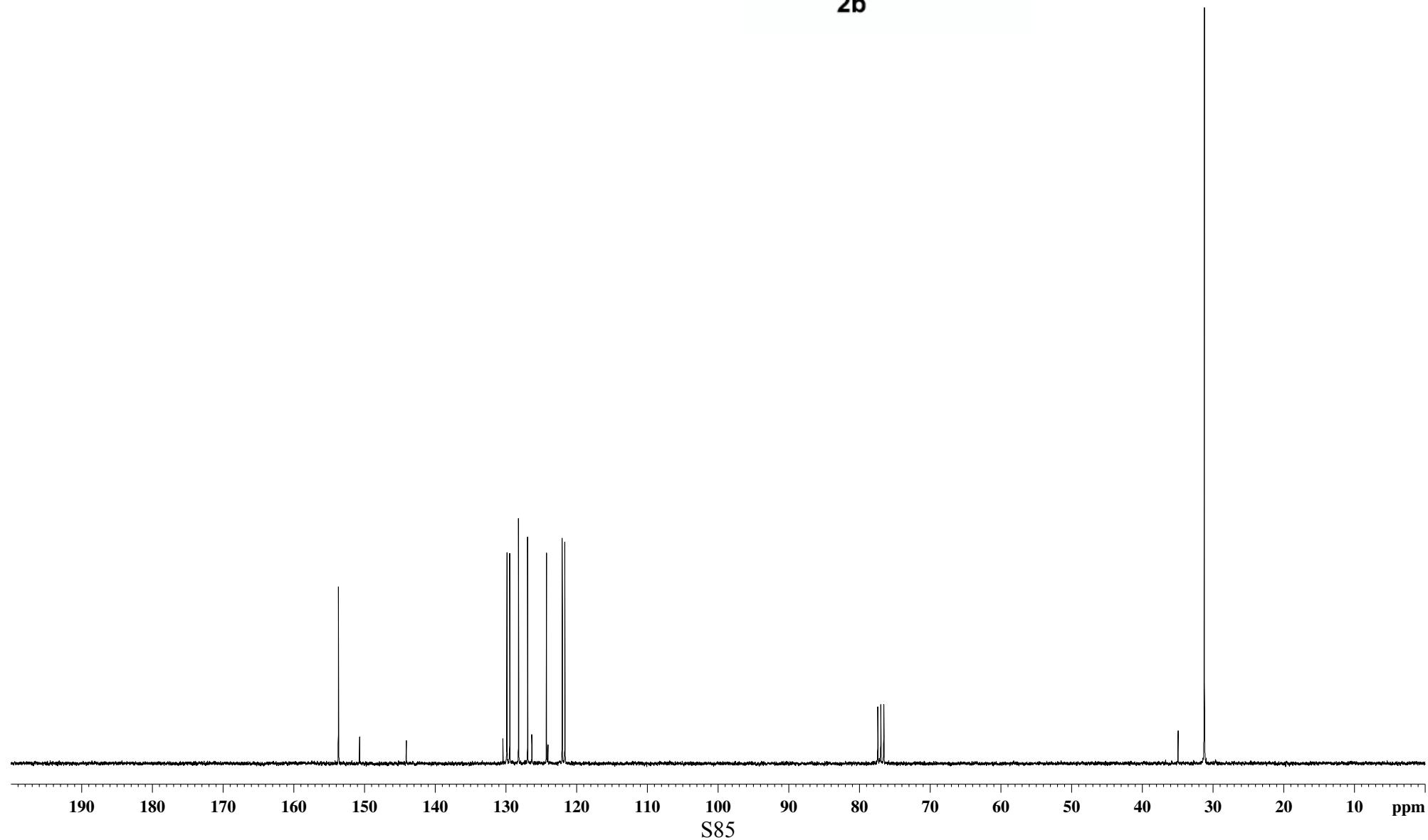


SK-1-114

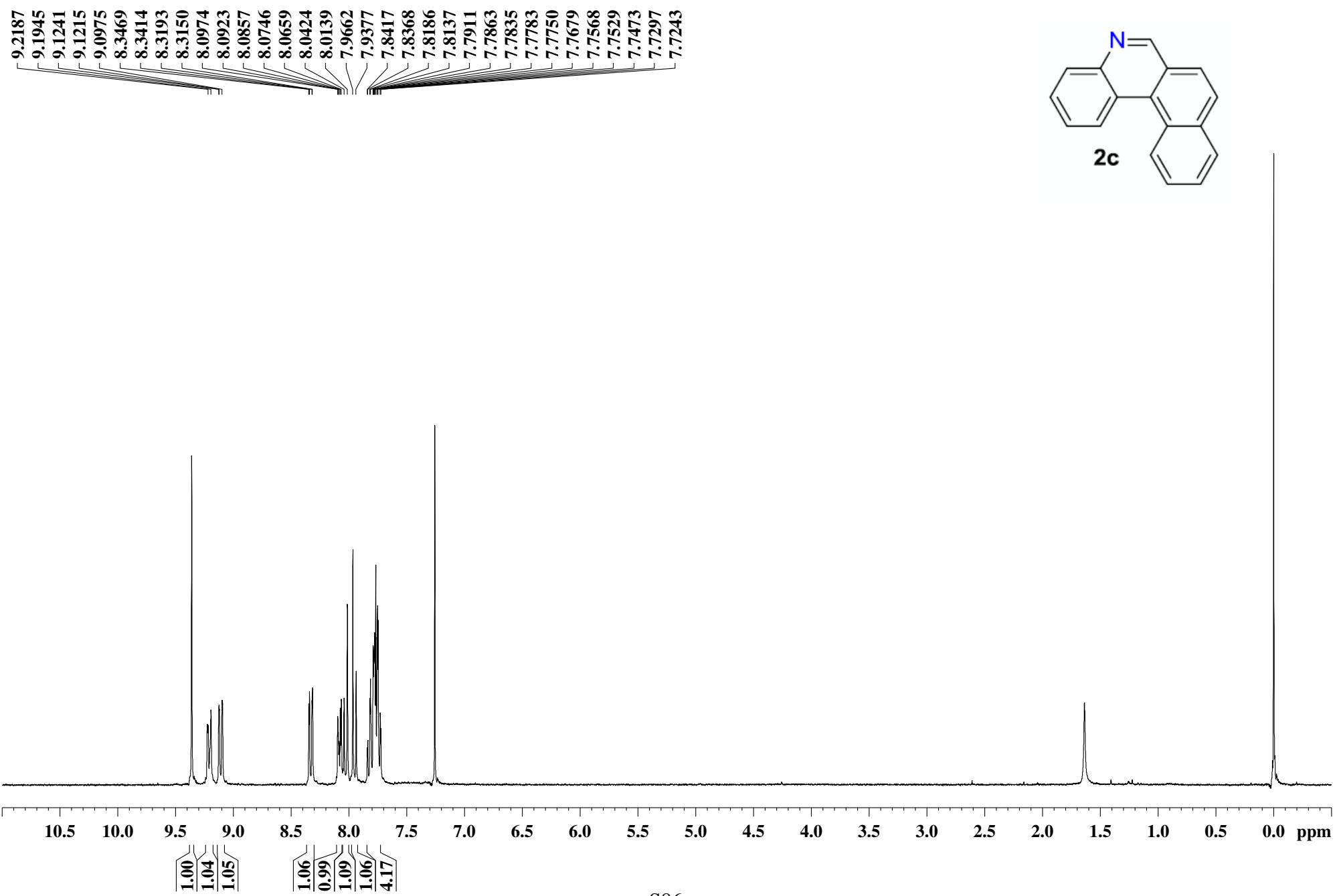
153.714
150.719
144.114
130.448
129.886
129.479
128.238
126.955
126.351
124.287
124.073
122.056
121.685



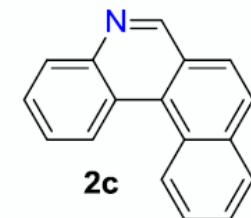
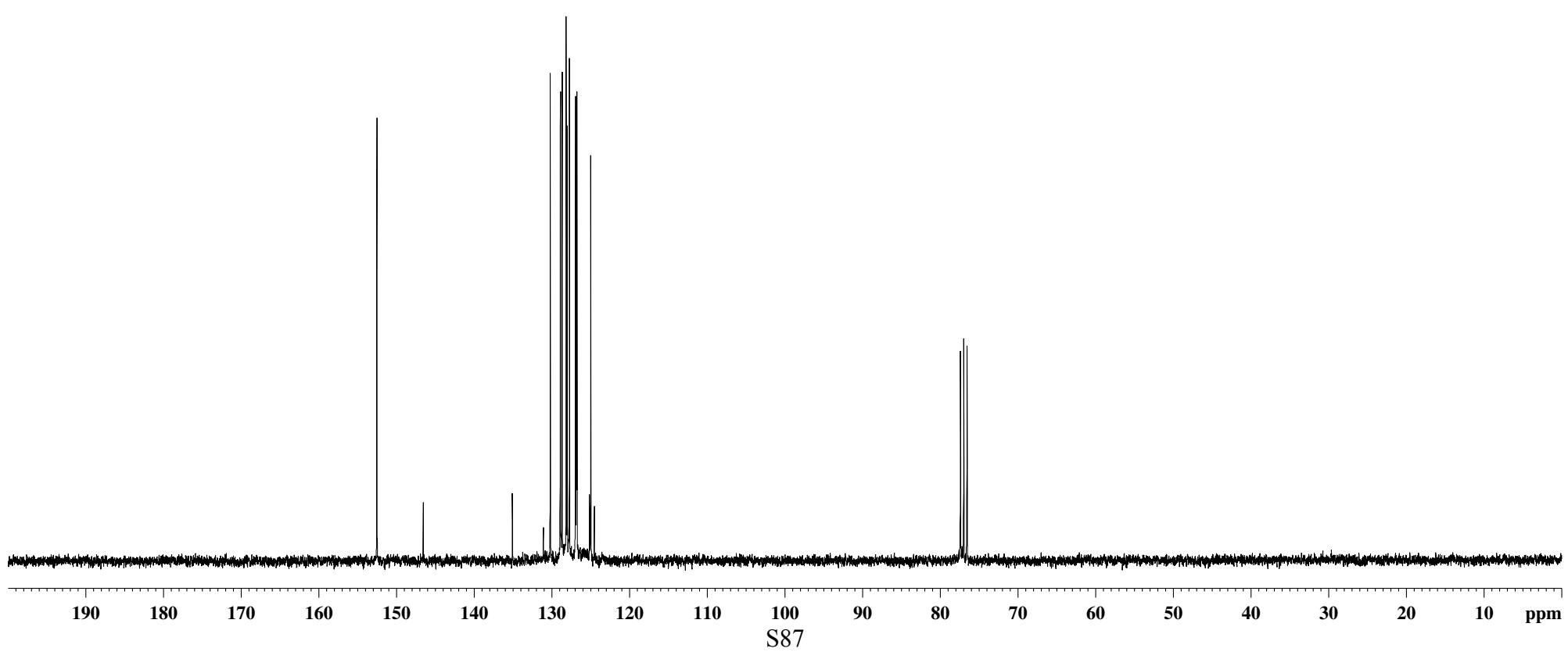
34.954
31.237



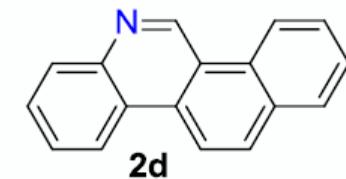
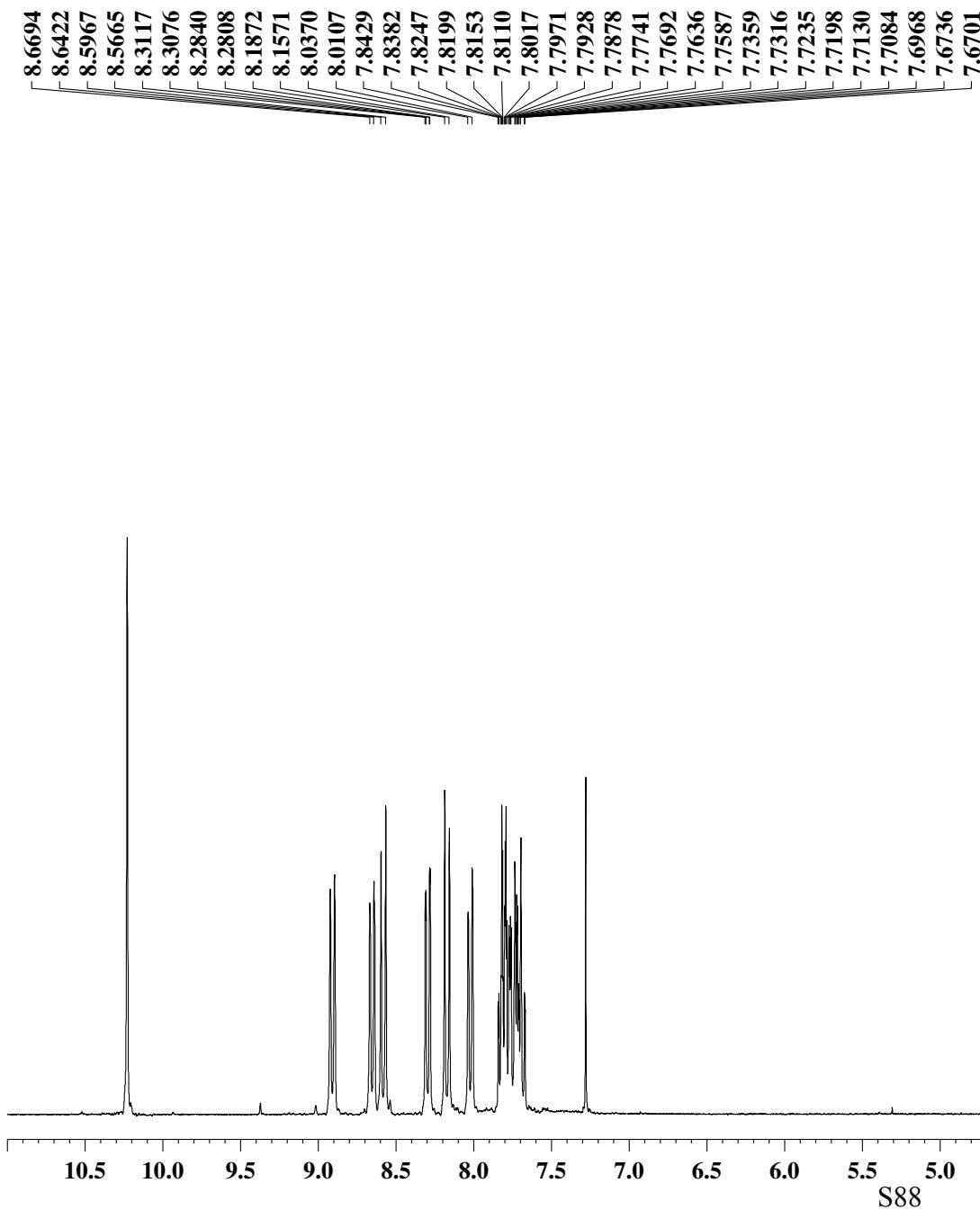
SK-1-139



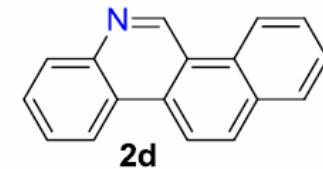
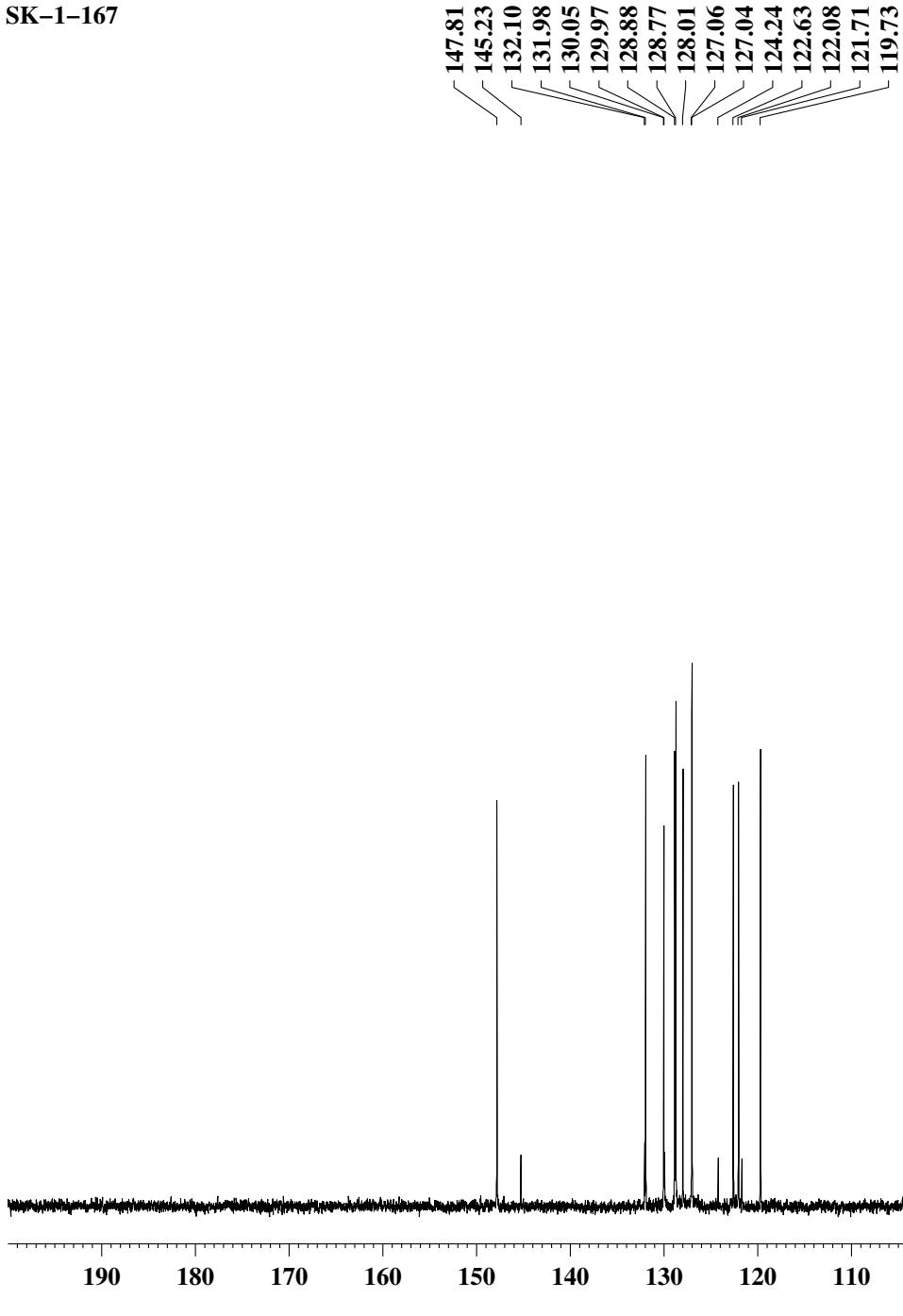
SK-1-135



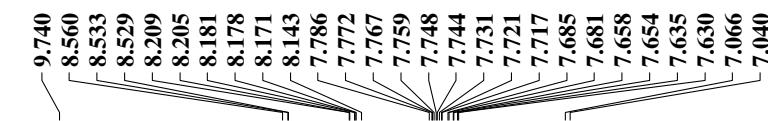
SK-1-167



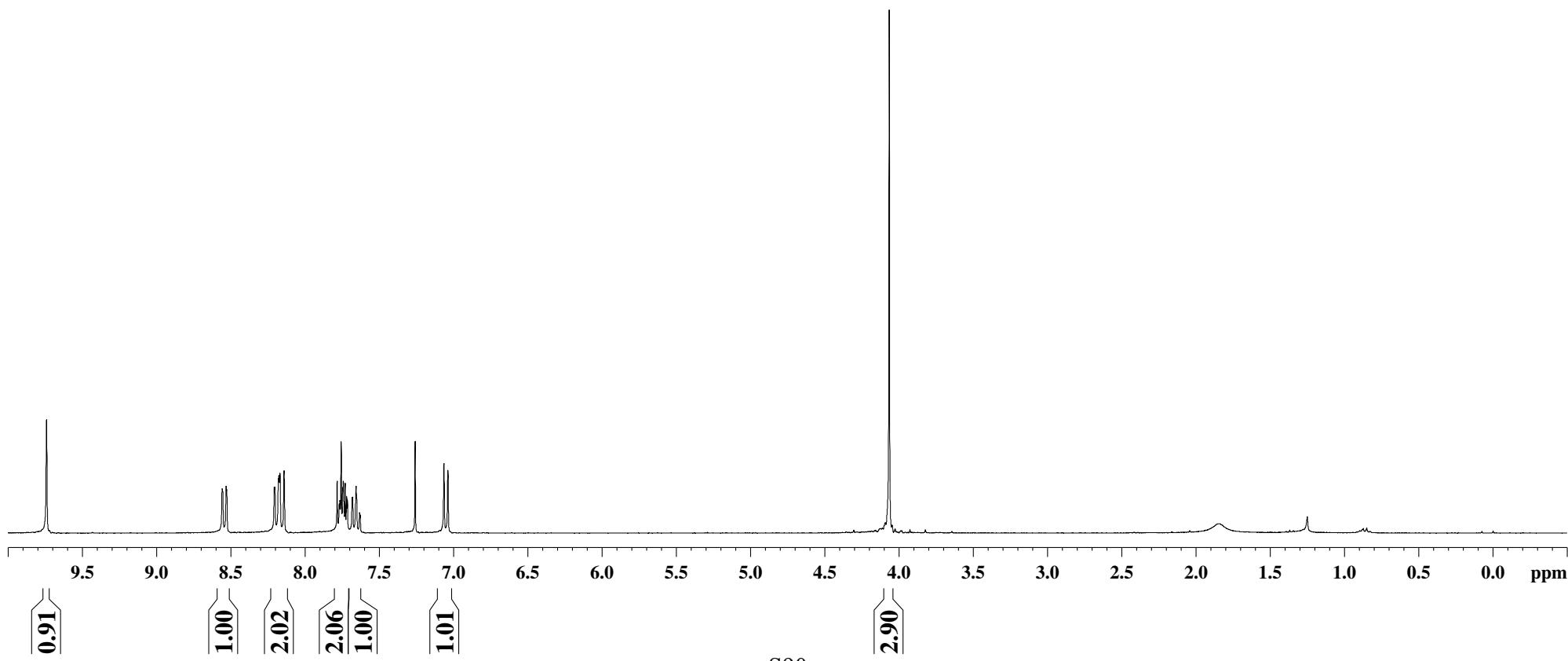
SK-1-167



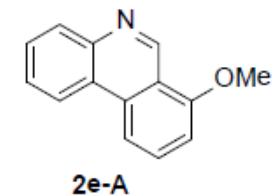
KN-1-031



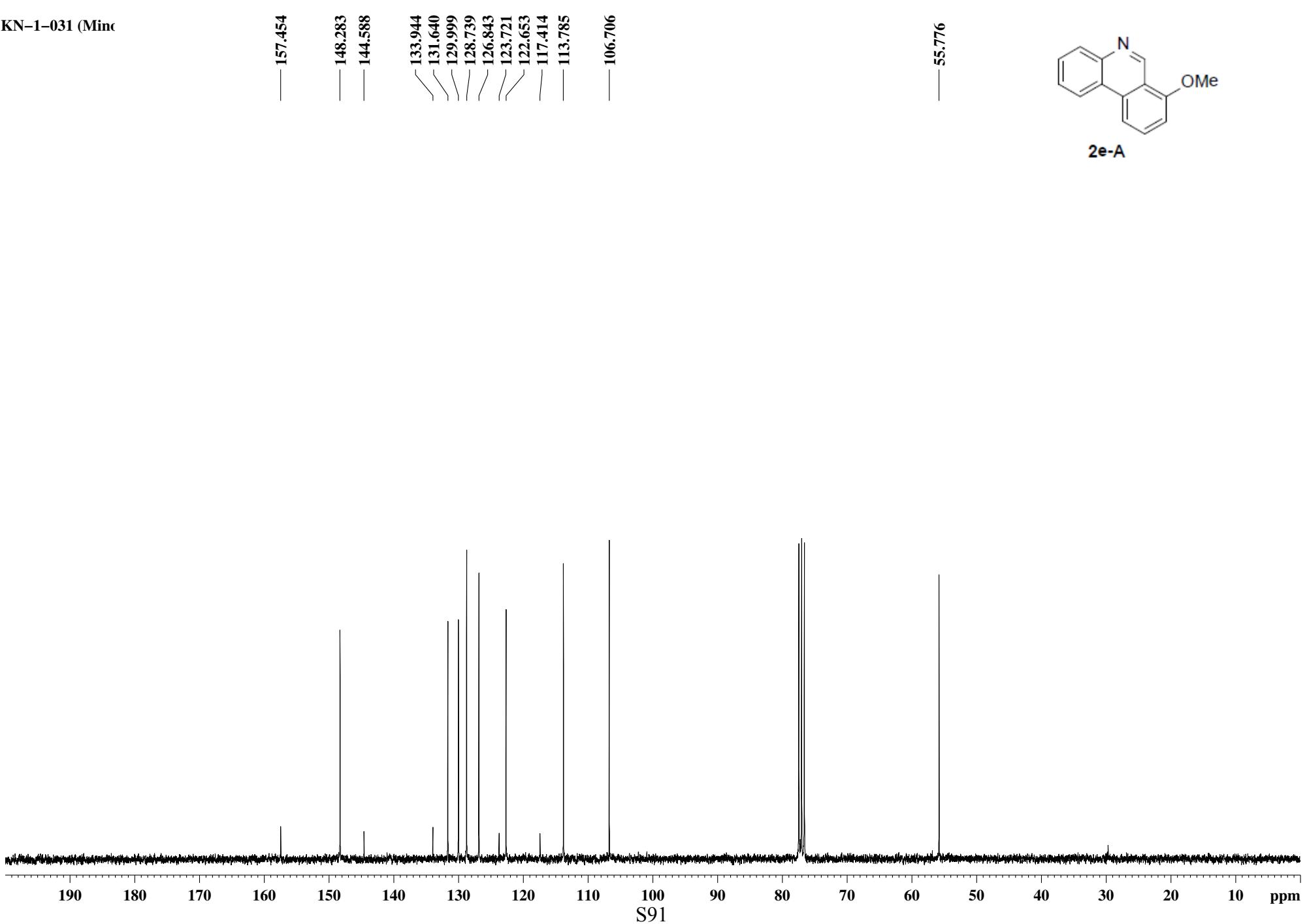
— 4.067 —



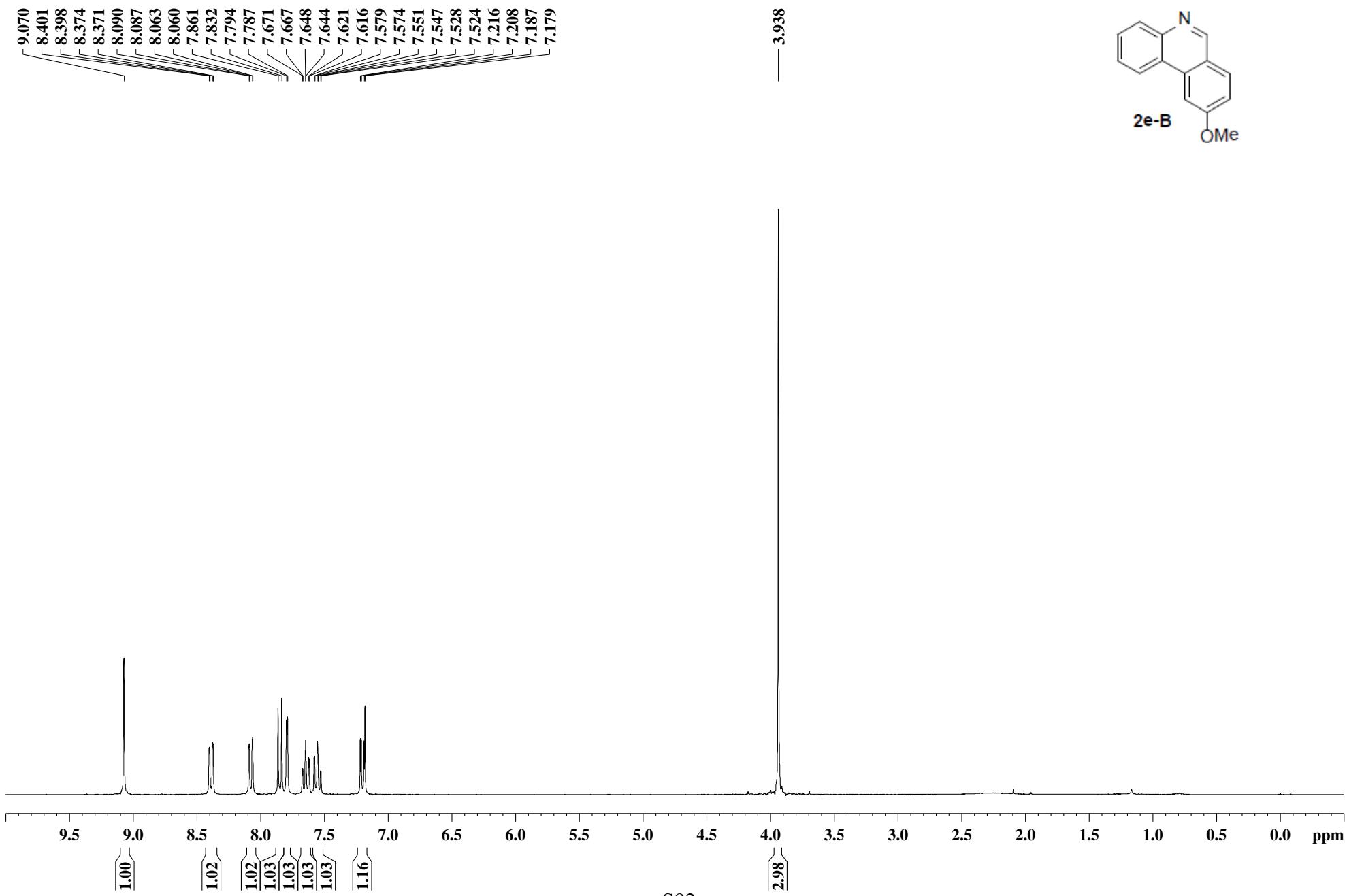
S90



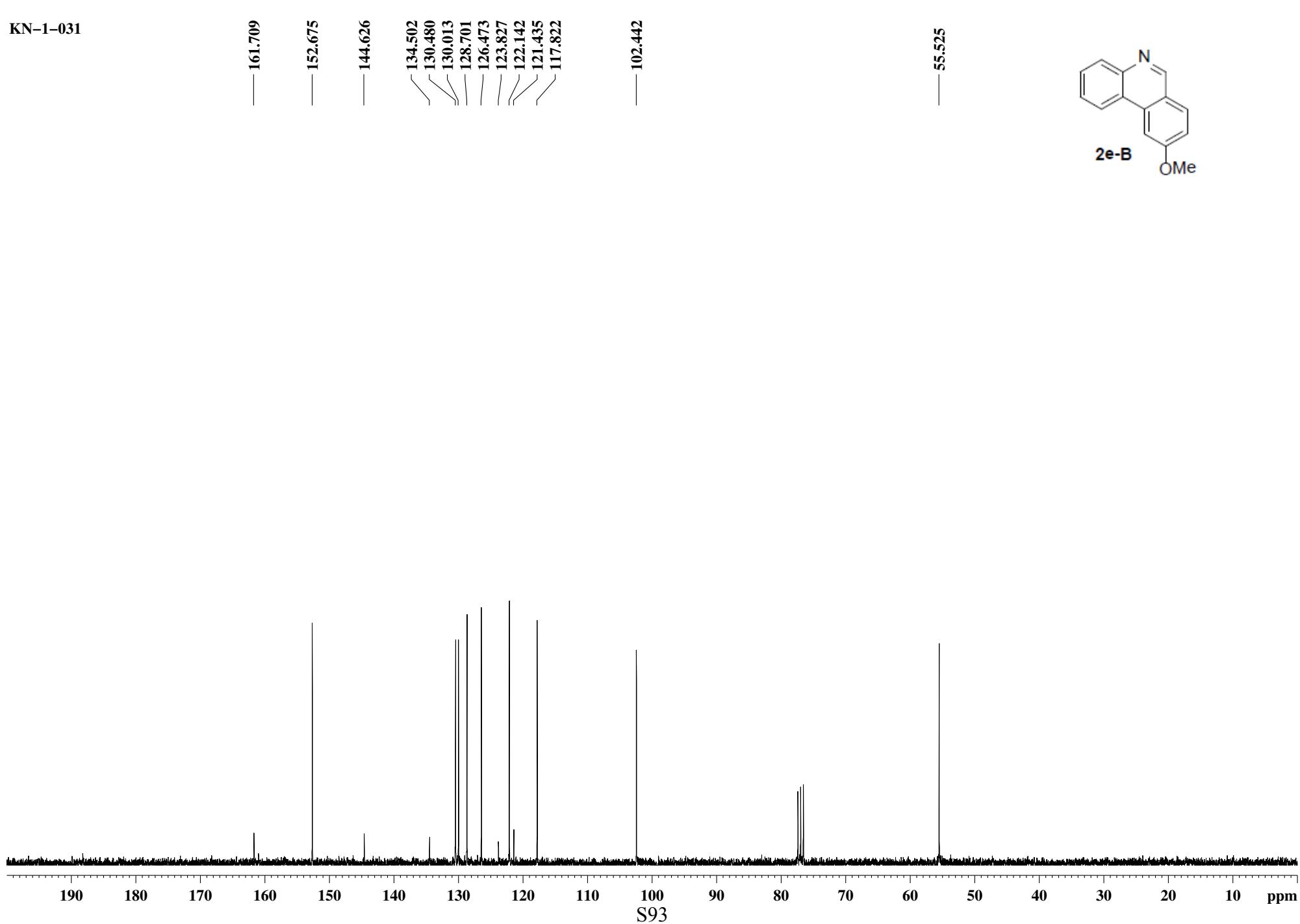
KN-1-031 (Minc)



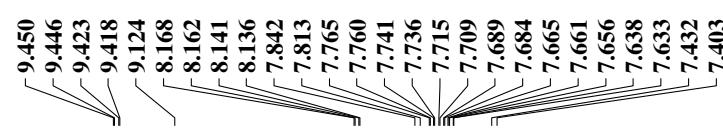
KN-1-031



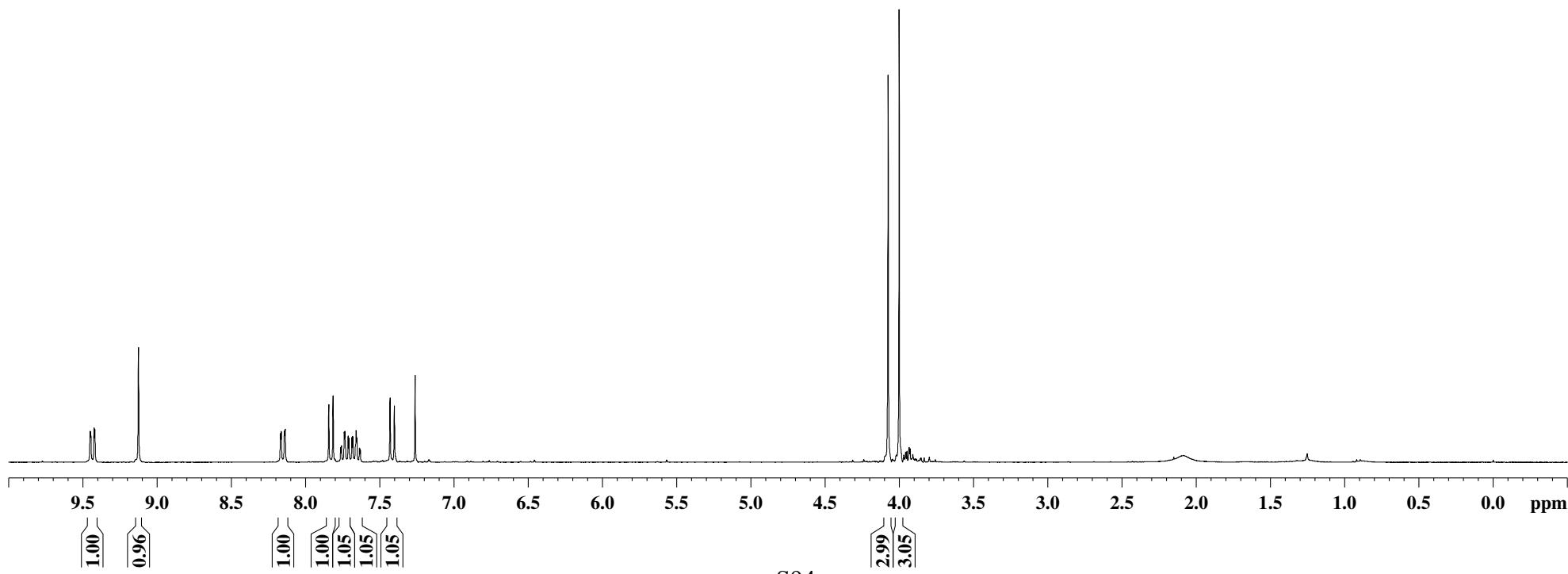
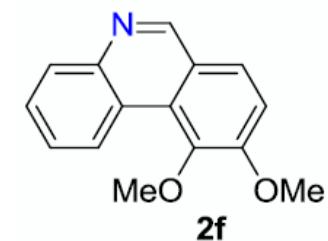
KN-1-031



SK-1-103



4.077
4.003

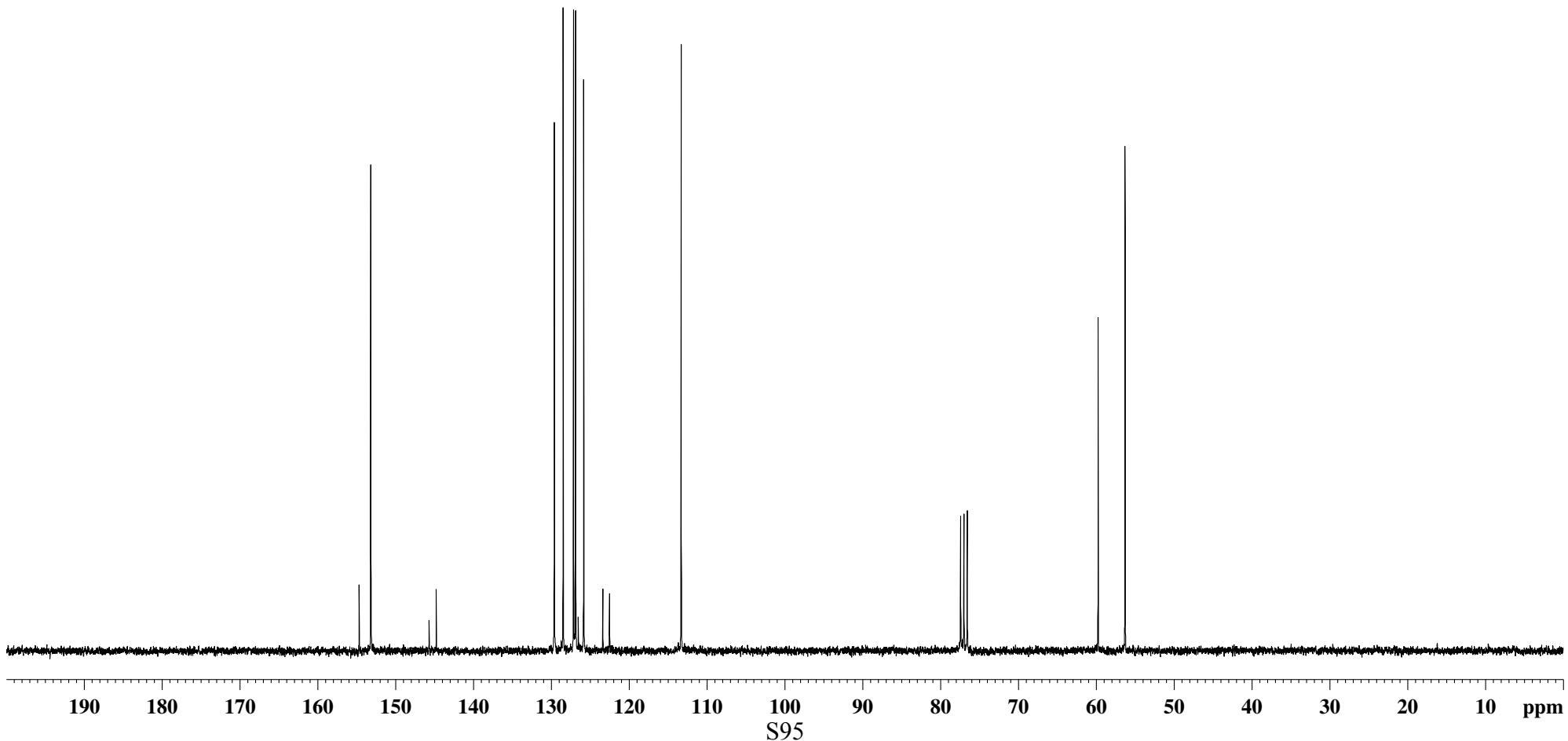
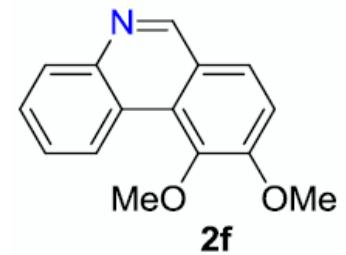


SK-1-103

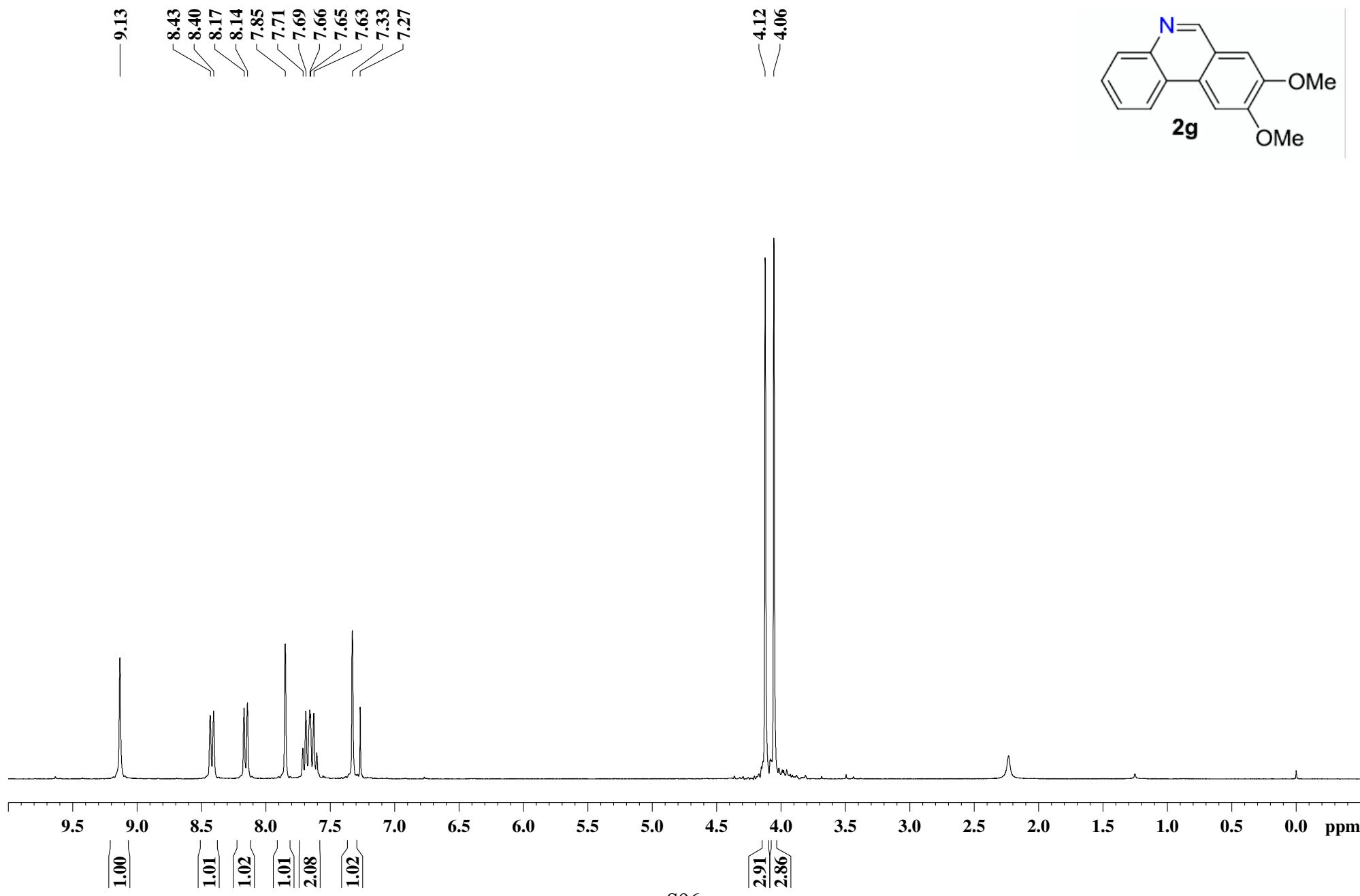
154.7018
153.2097
145.7210
144.8039

129.6314
128.4983
127.1588
126.8933
126.5640
125.8519
123.3865
122.5334
113.3314

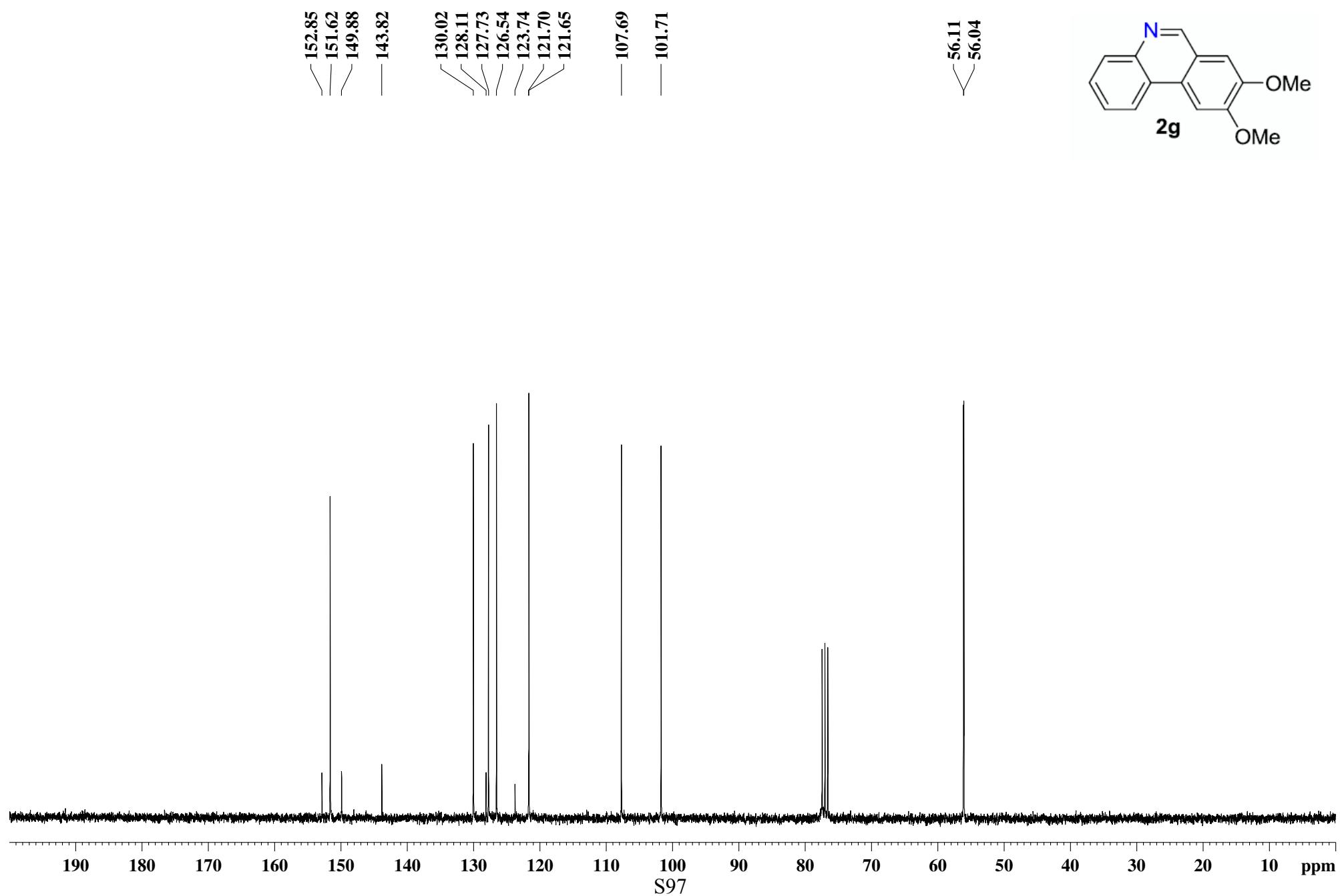
59.7650
56.2991

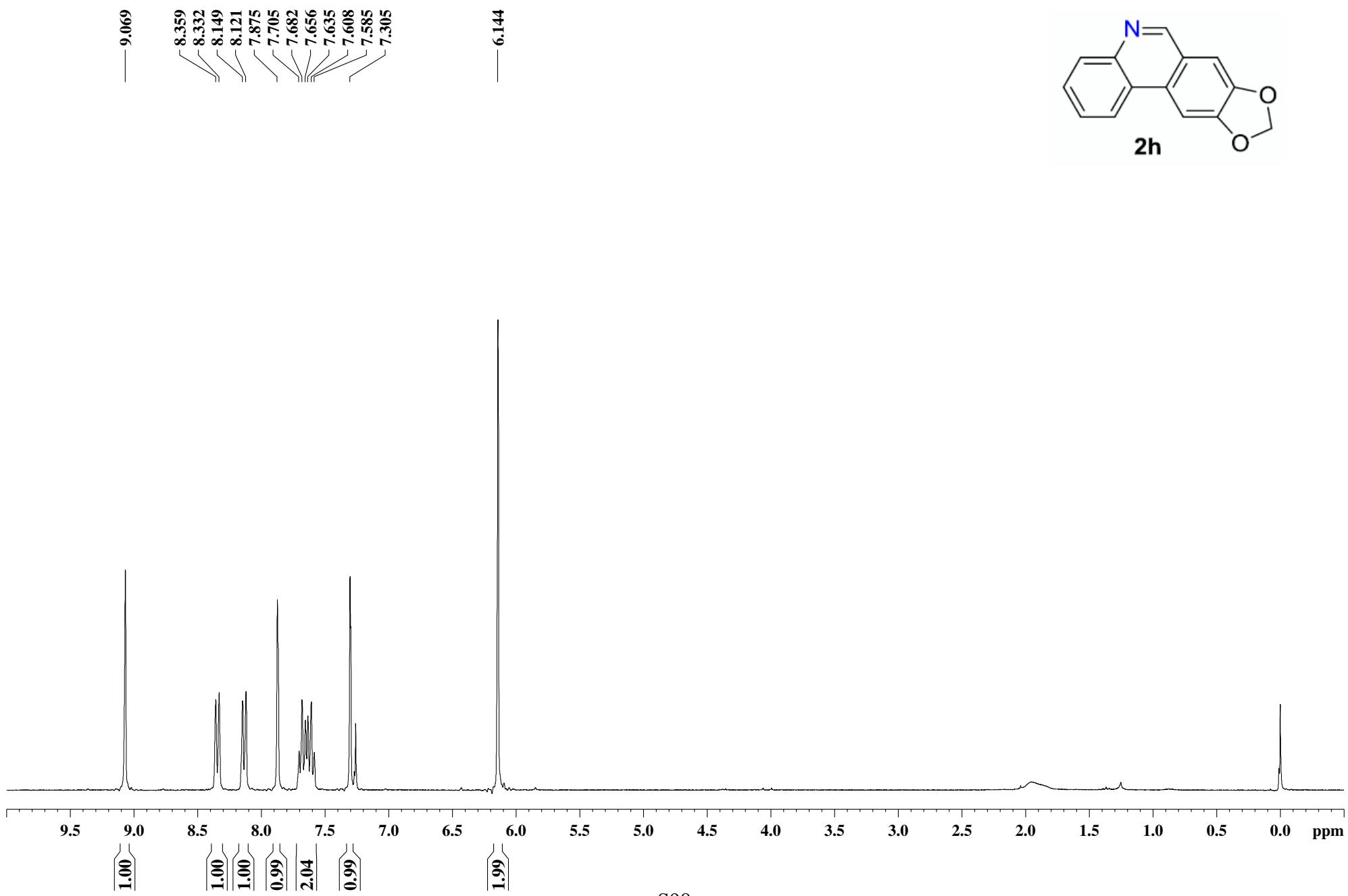


SK-1-106



SK-1-106



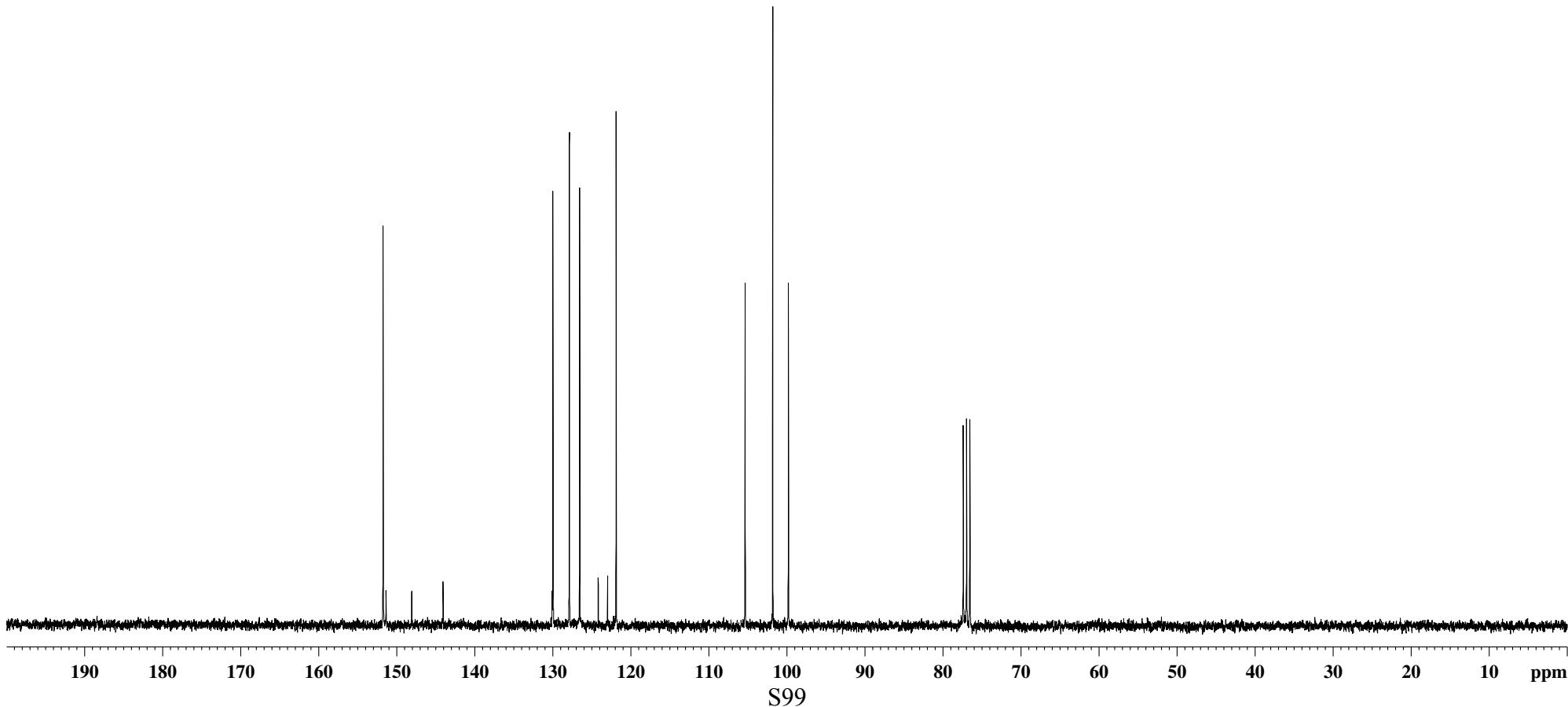
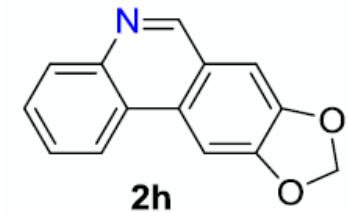


SK-1-117

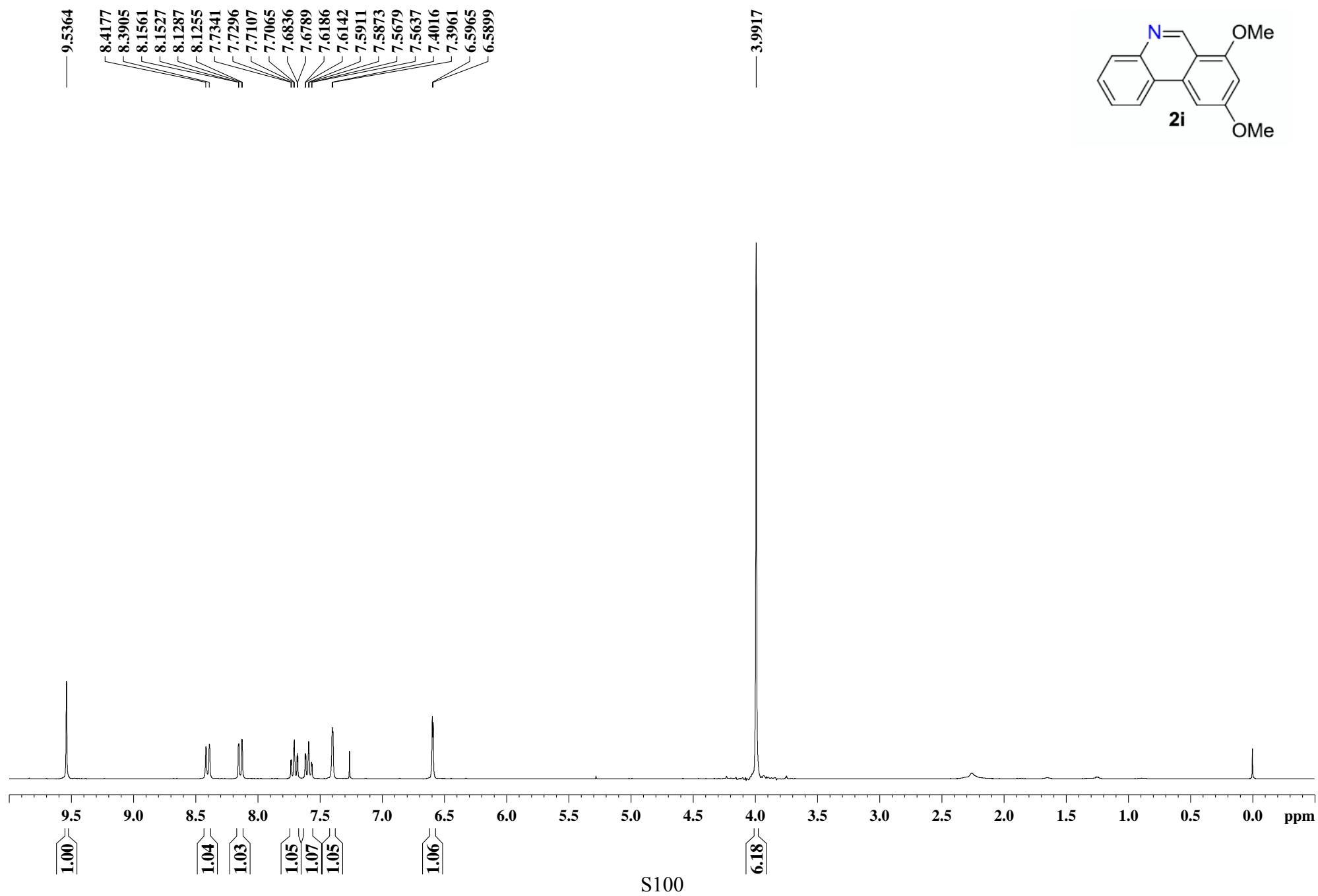
151.729
151.364
148.110
— 144.100

130.131
130.015
127.909
126.589
124.209
123.010
121.920

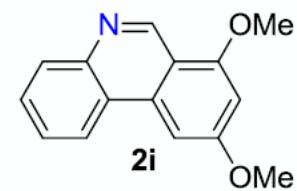
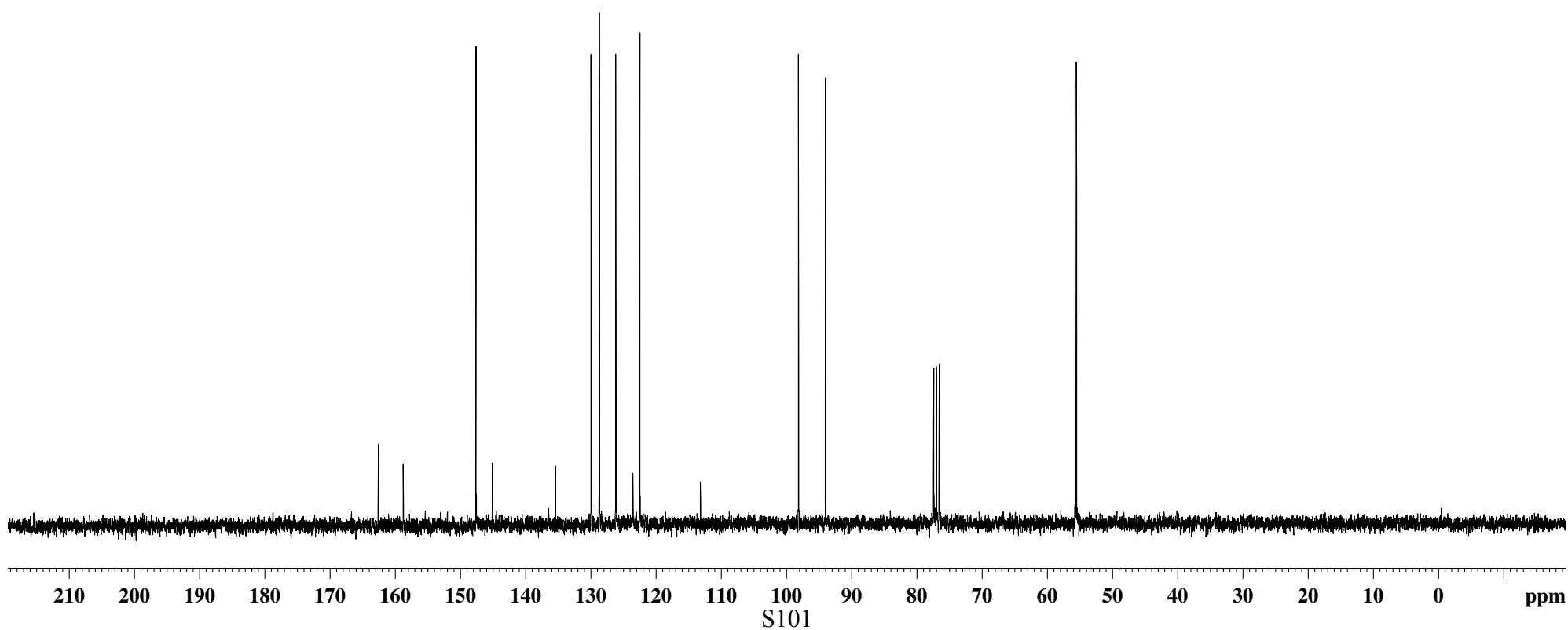
— 105.380
— 101.843
— 99.838

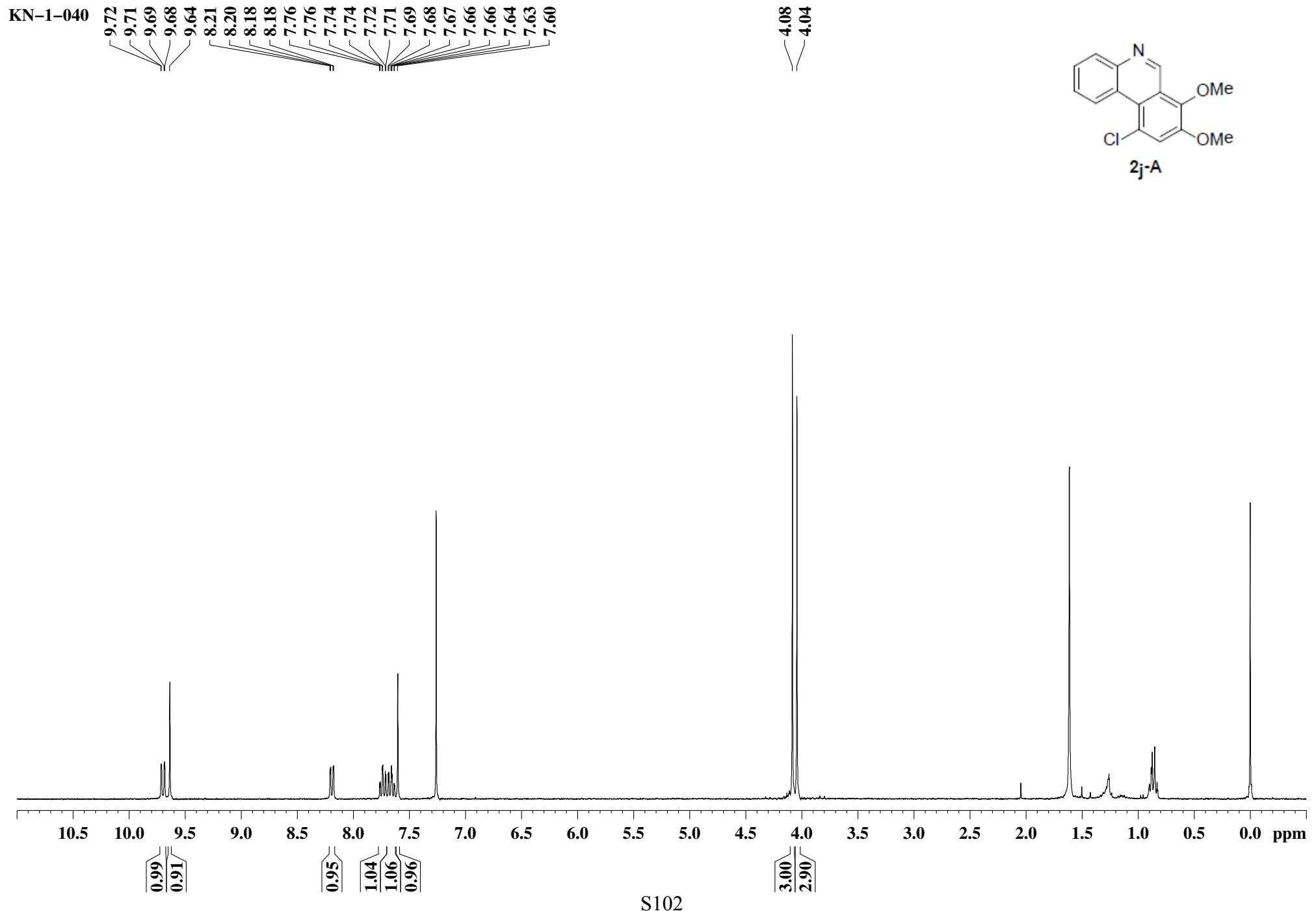


SK-1-190

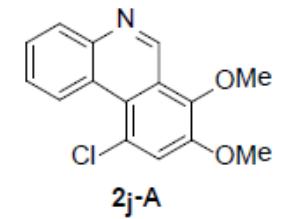
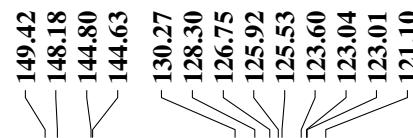
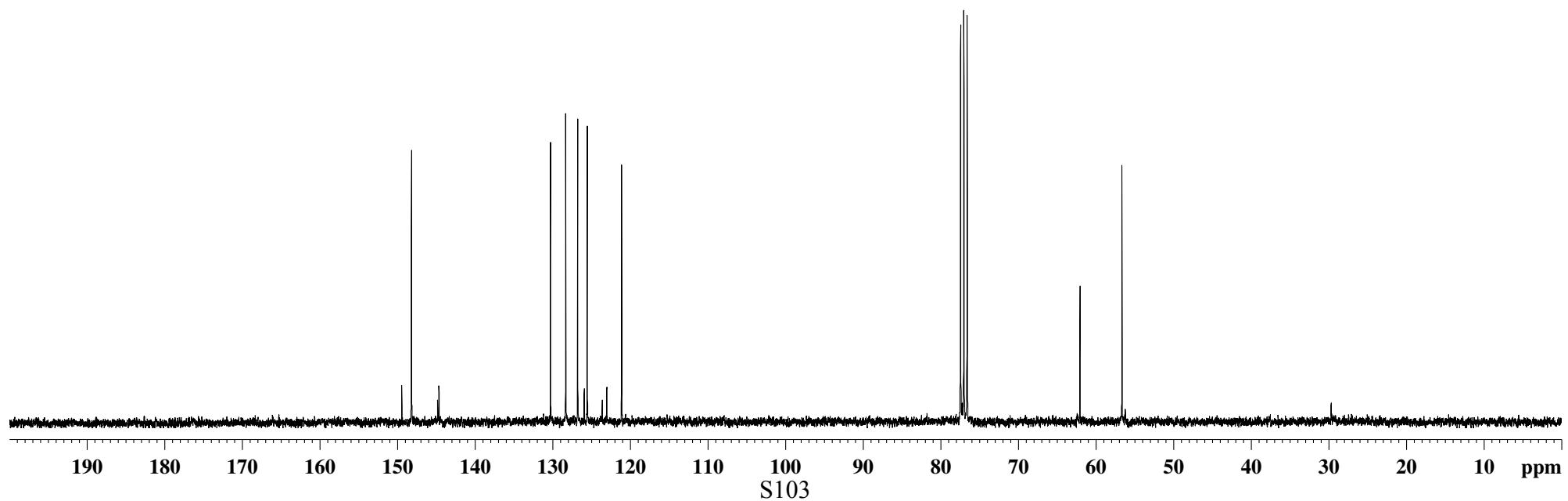


SK-1-190





KN-1-040



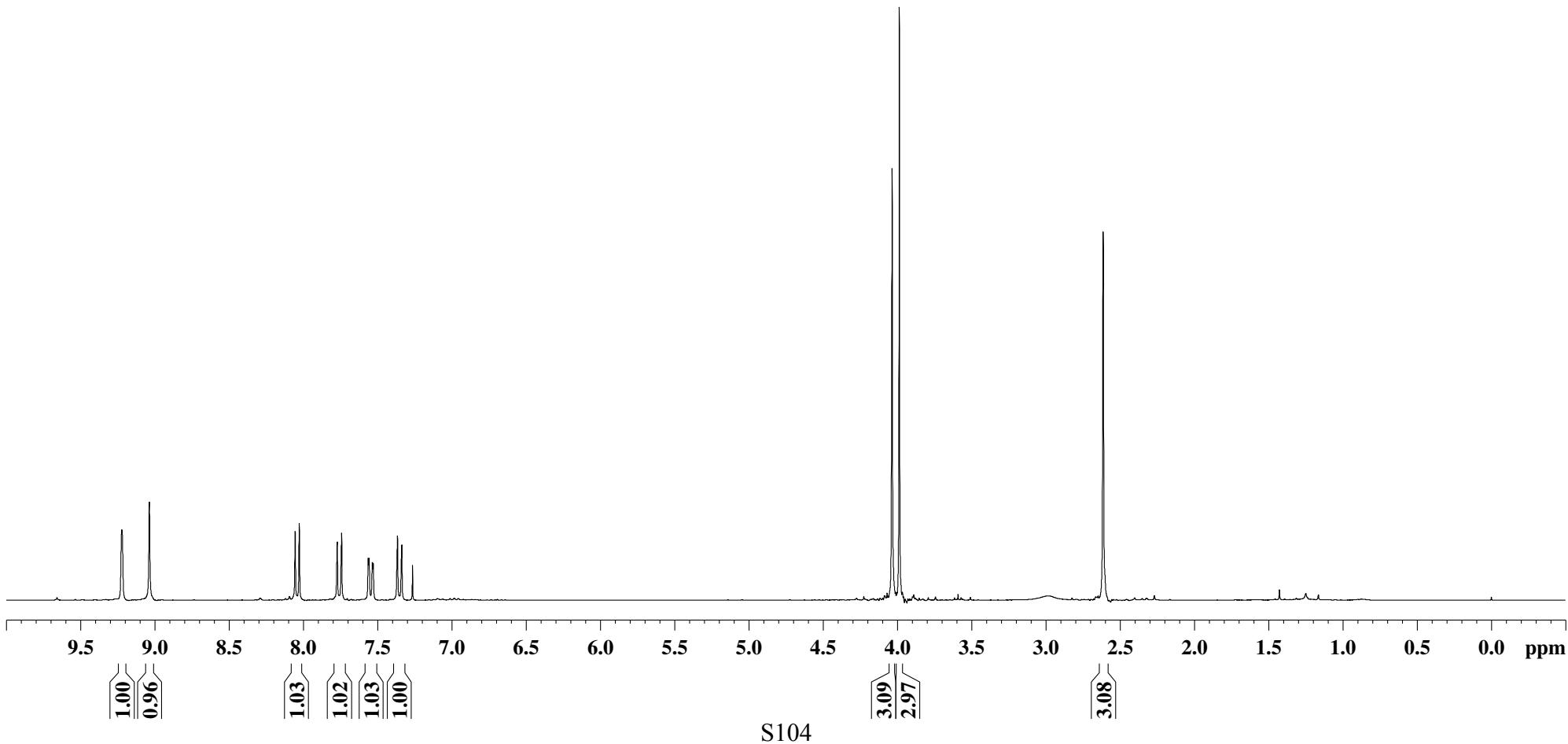
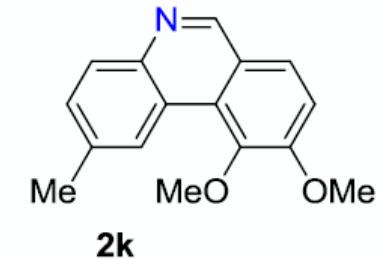
SK-1-111

— 9.2207
— 9.0353

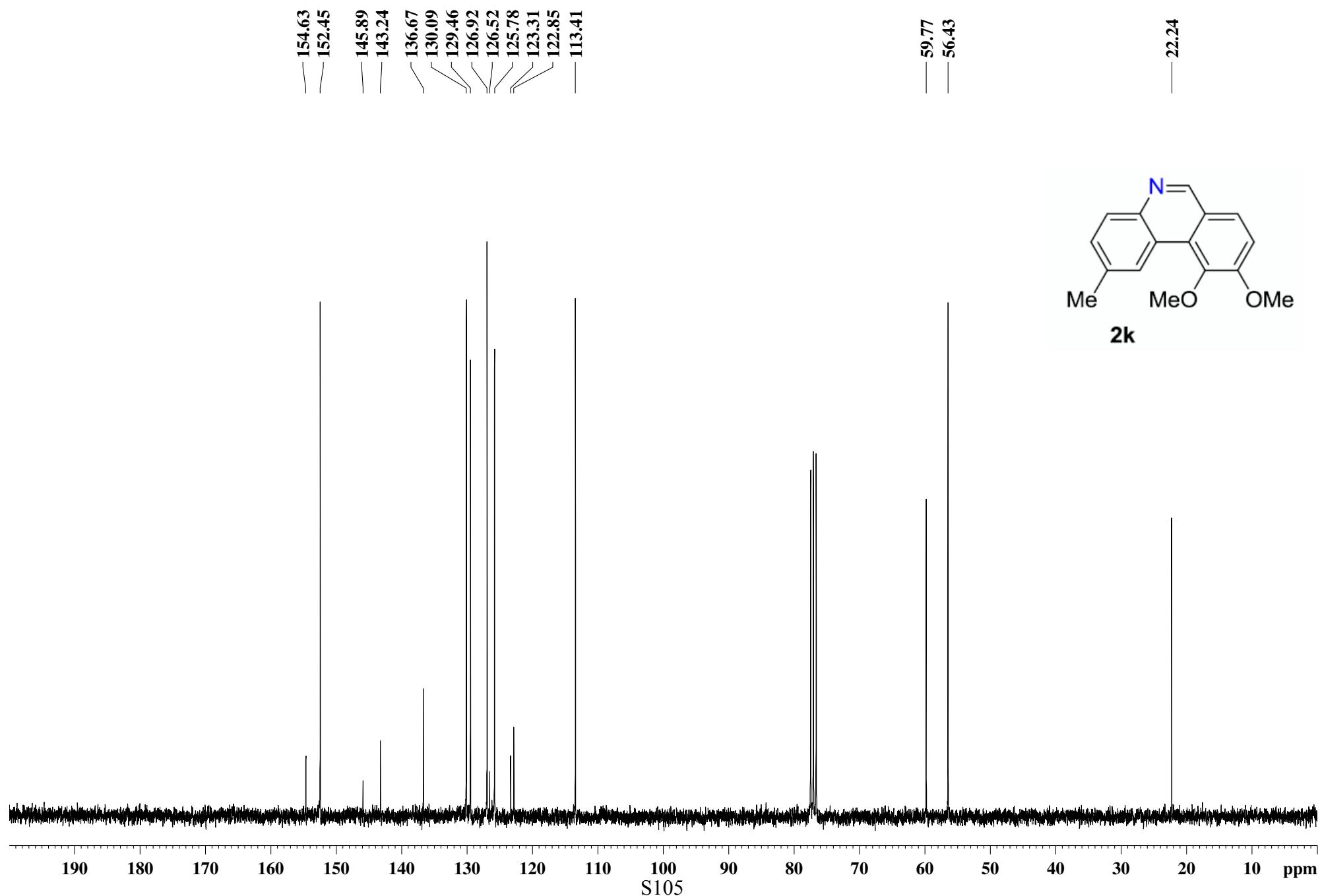
8.0565
8.0289
7.7725
7.7436
7.5644
7.5584
7.5369
7.5308
7.3672
7.3383

4.0359
3.9873

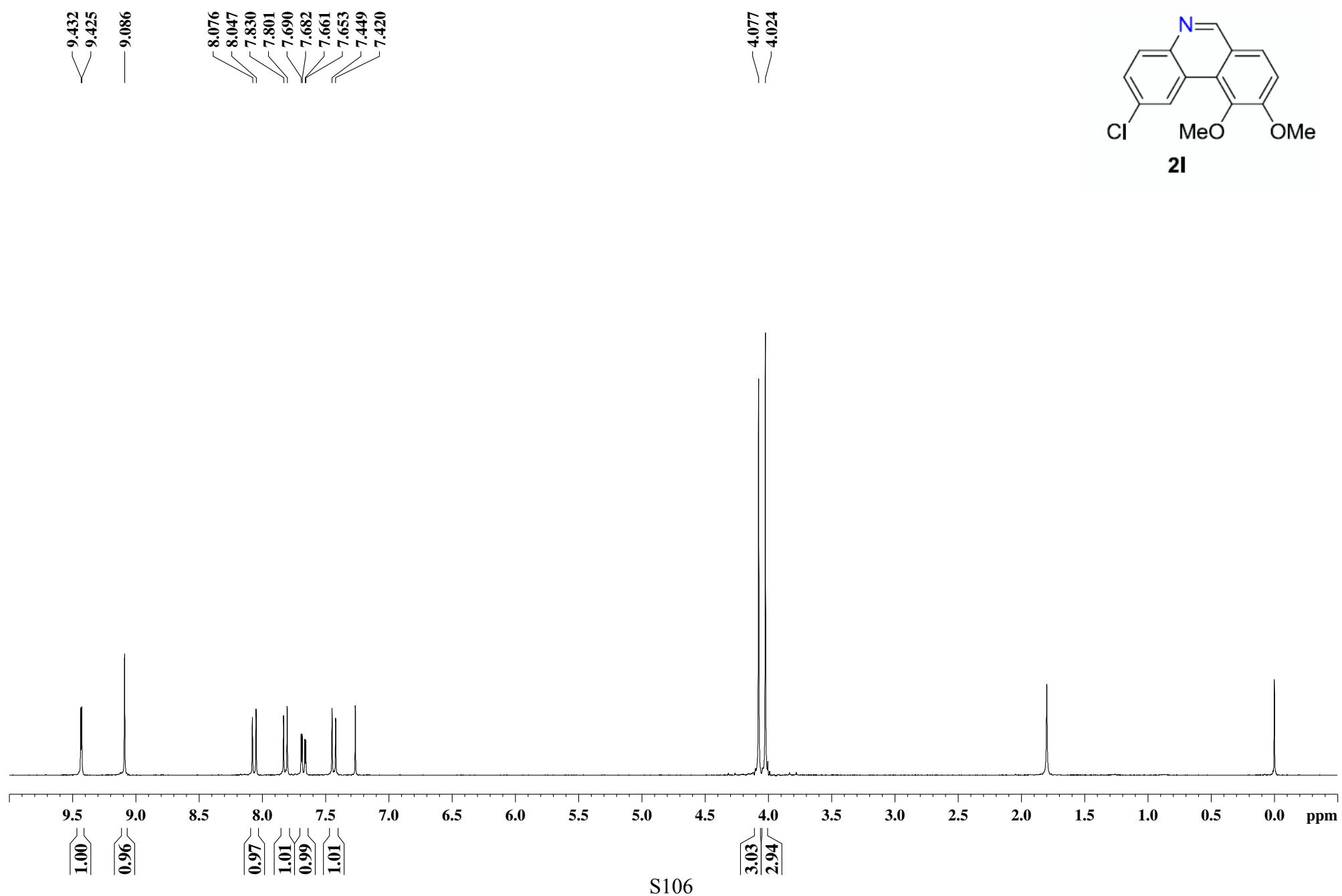
— 2.6149



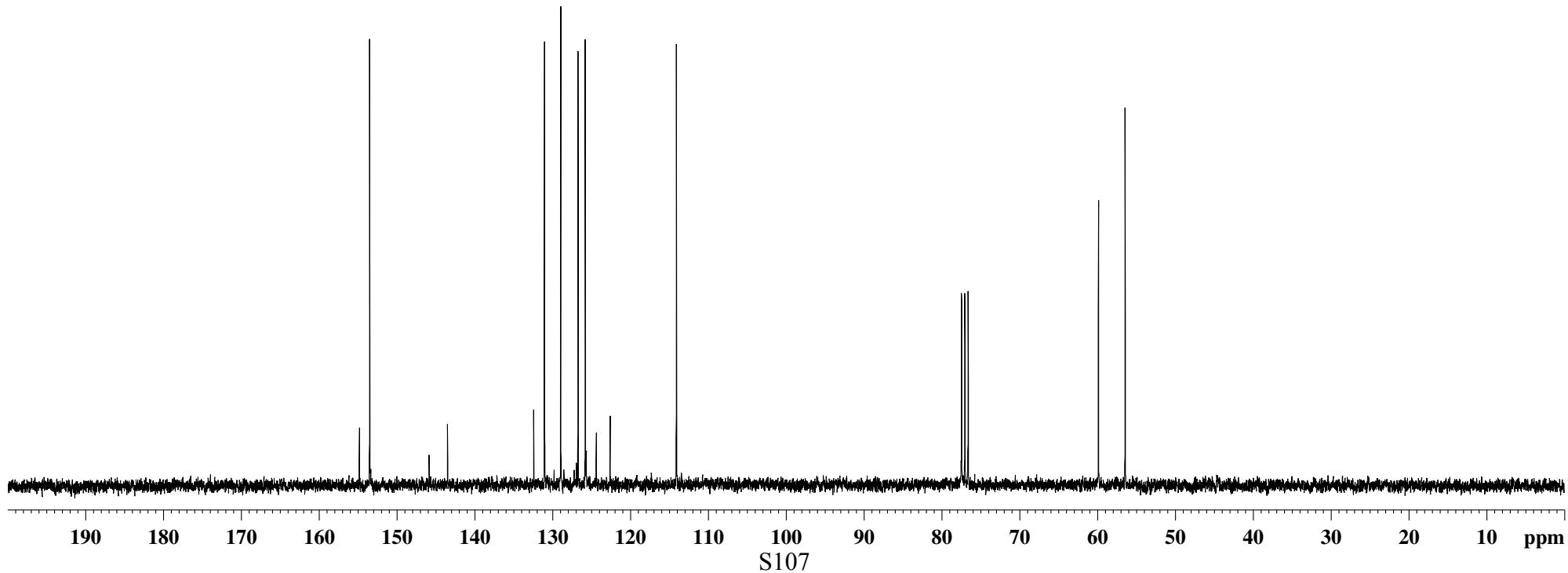
SK-1-111



SK-1-138

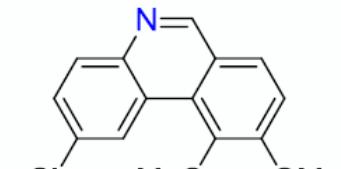


SK-1-138



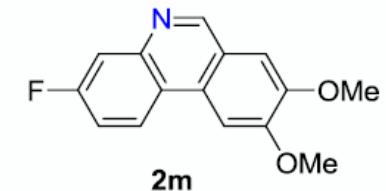
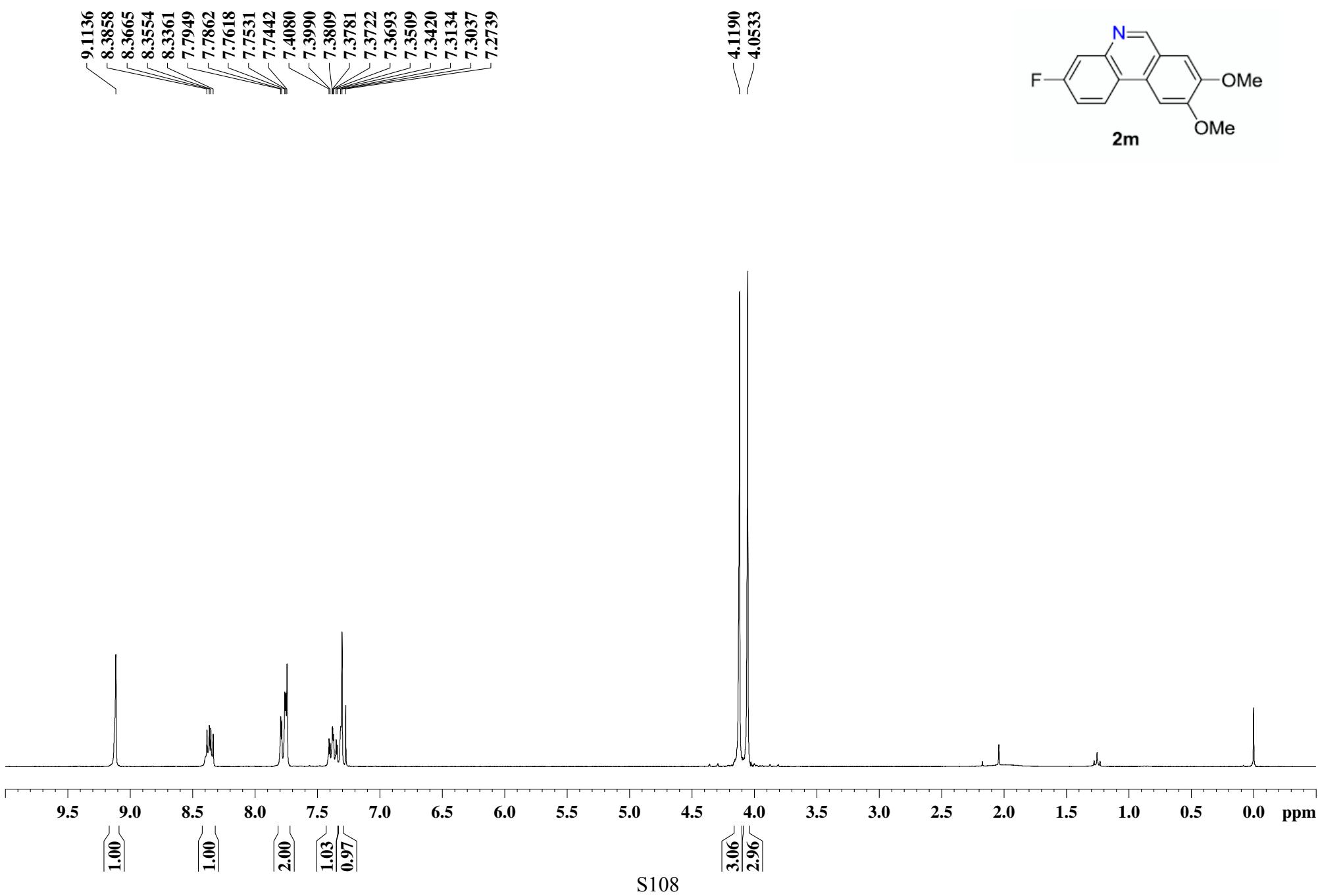
154.7852
153.4664
145.8342
143.4561
132.3918
131.0039
128.9121
126.6937
125.7643
125.6279
124.3547
122.5677
114.0624

59.8362
56.4060

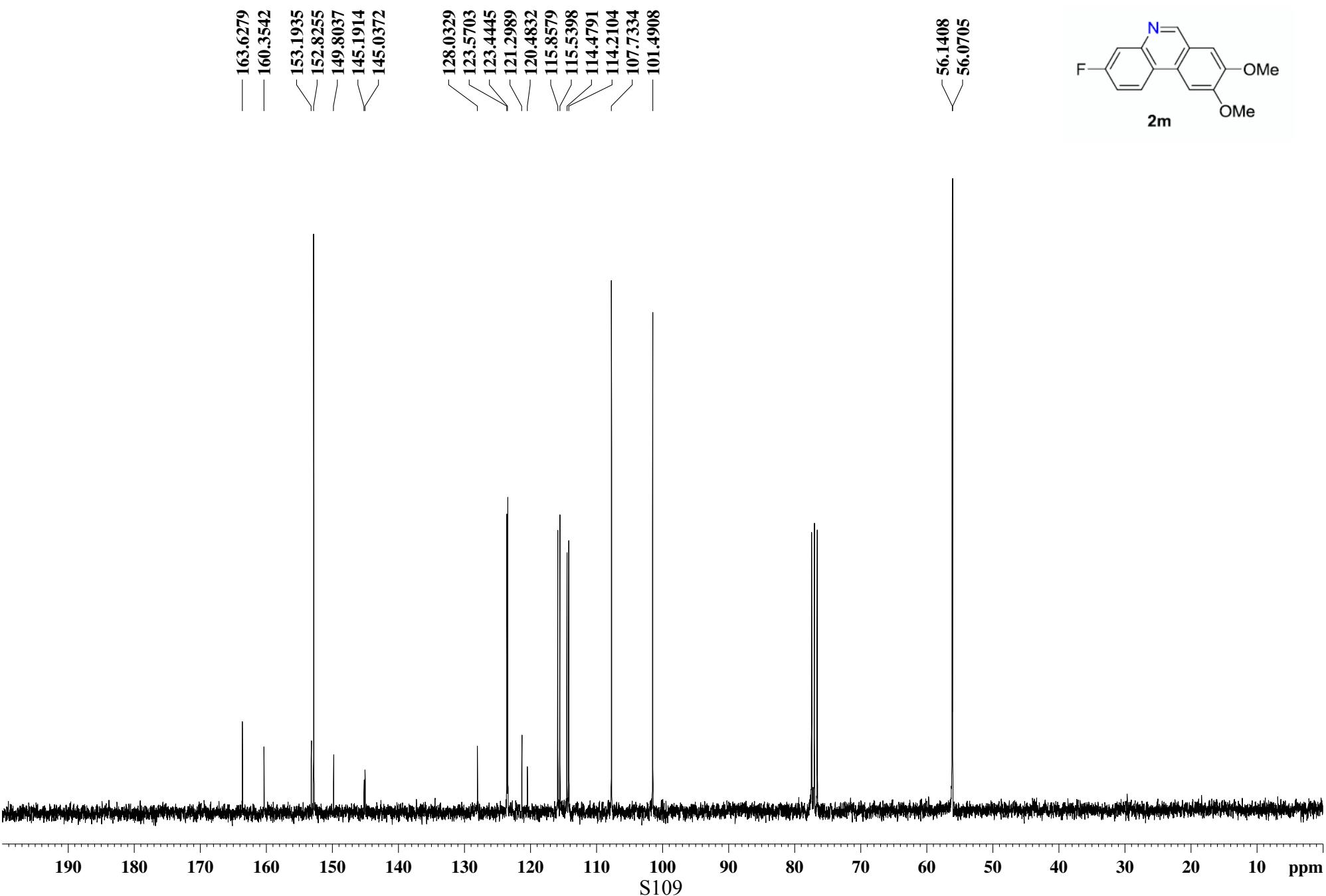


2I

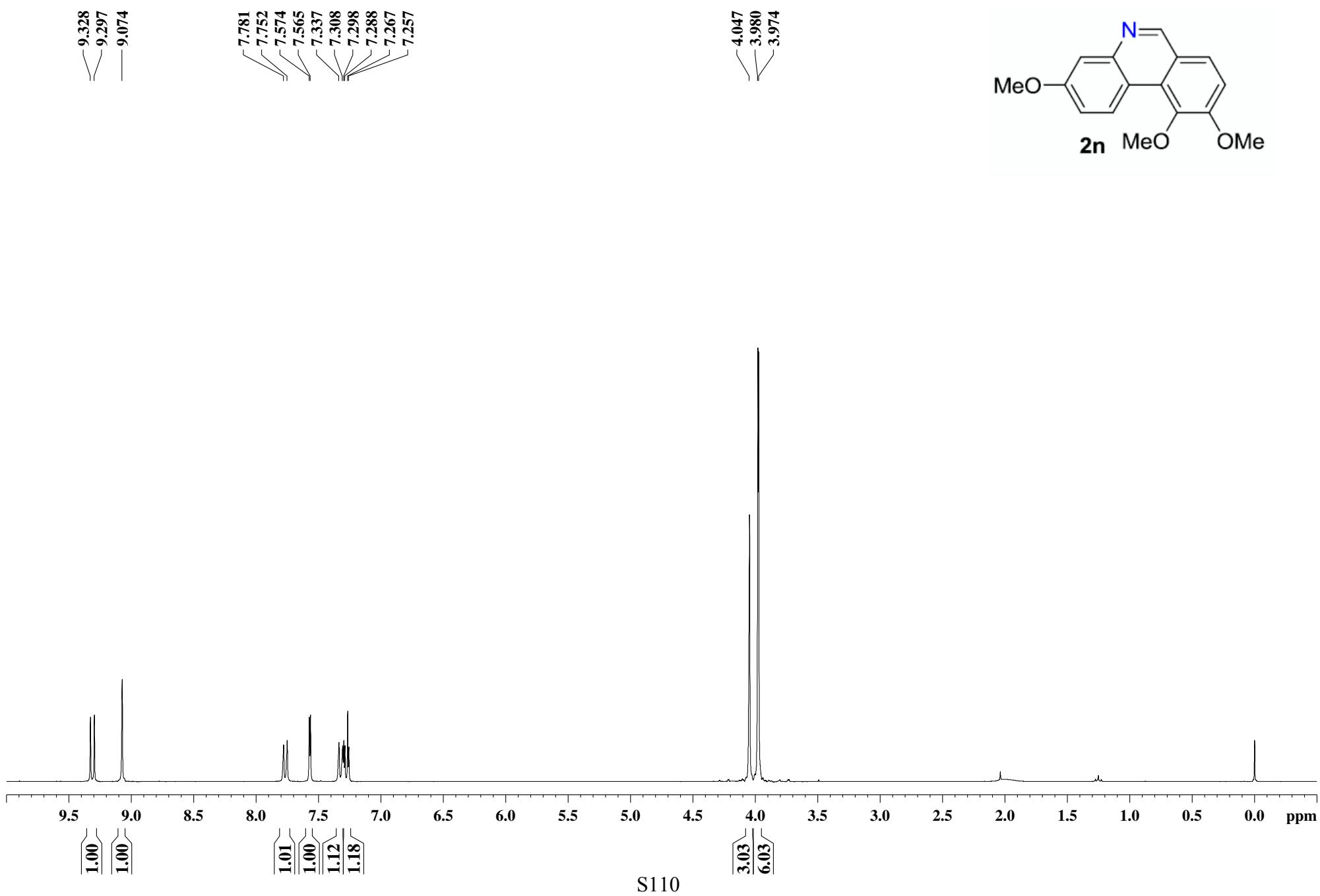
SK-1-146



SK-1-146



SK-1-118



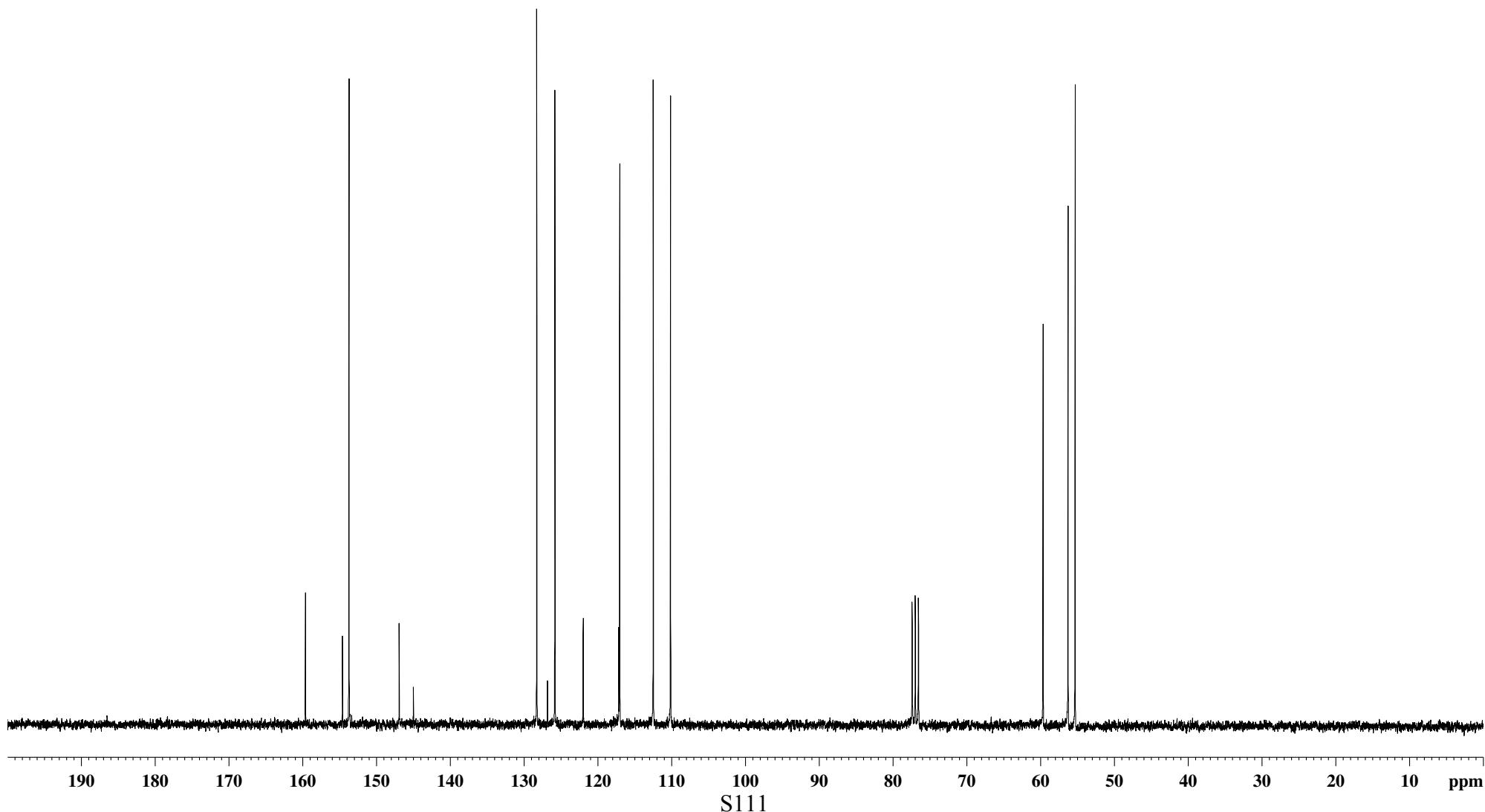
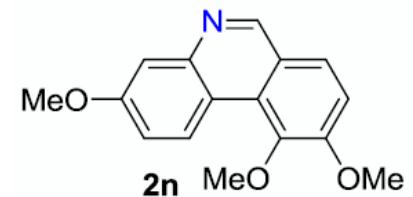
S110

SK-1-118

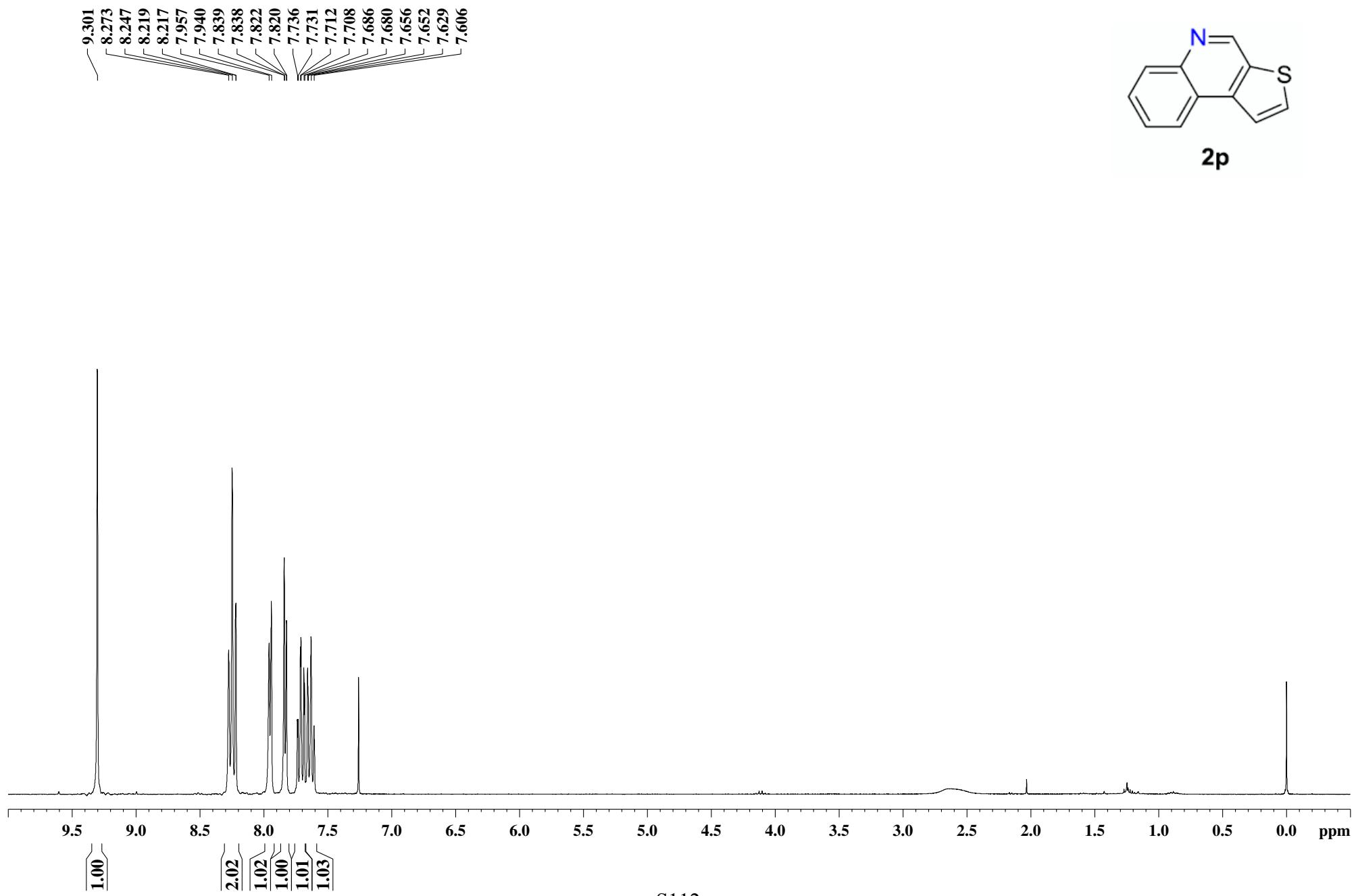
159.592
154.579
153.690
146.888
144.963

128.296
126.839
125.835
122.003
117.181
117.054
112.504
110.158

59.666
56.280
55.324



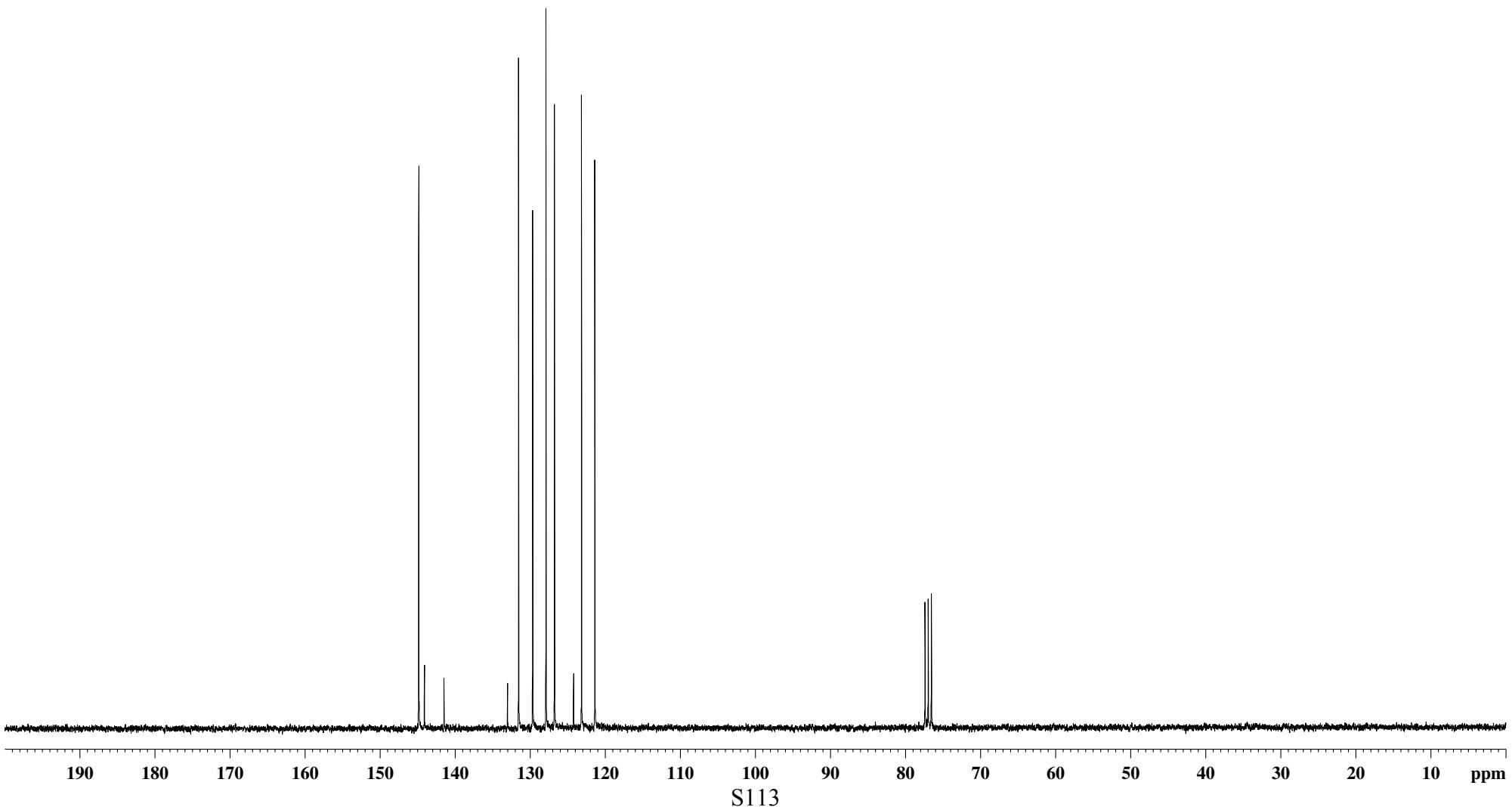
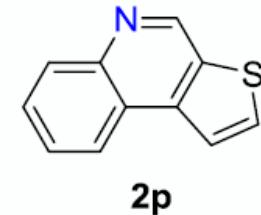
SK-1-116



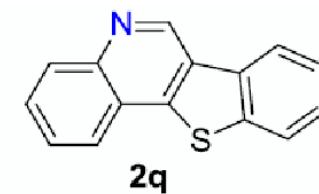
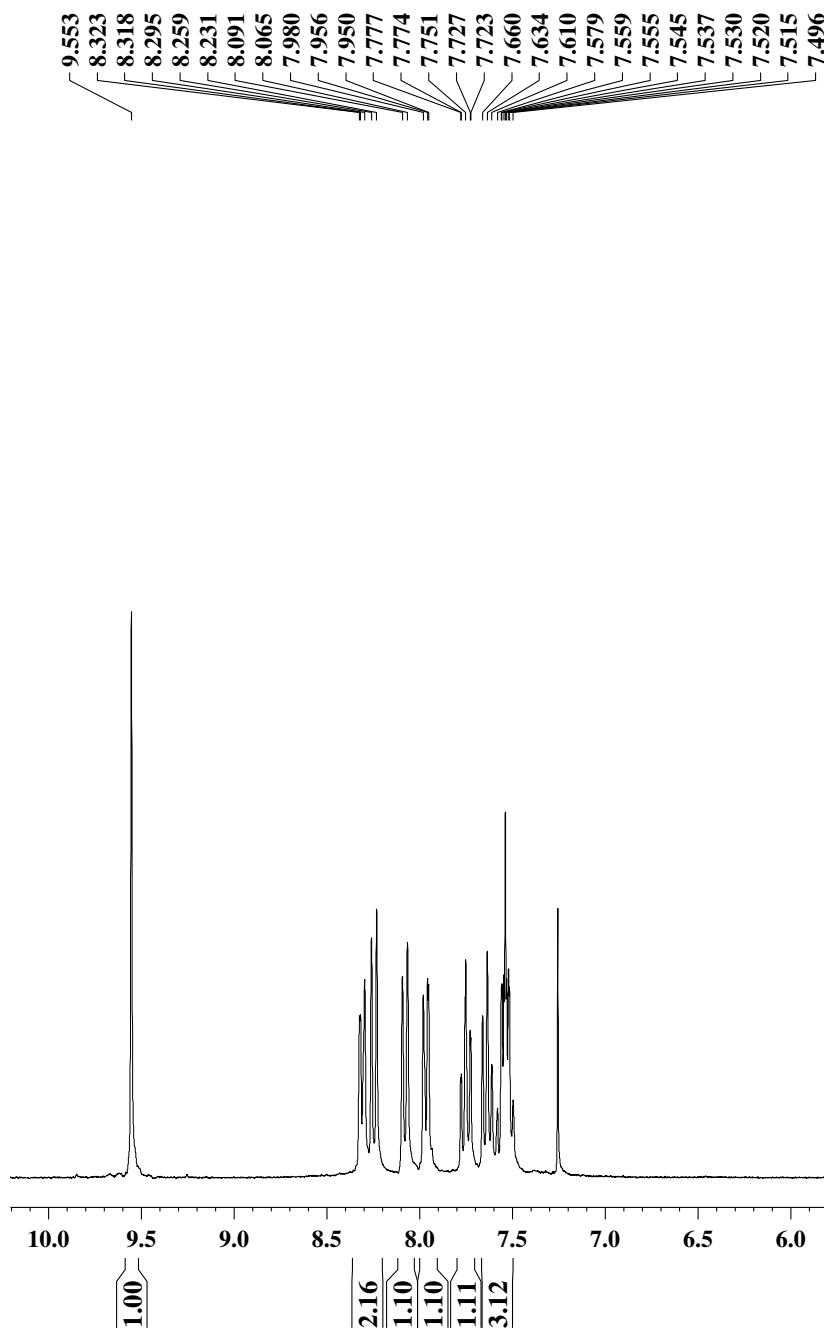
S112

SK-1-116

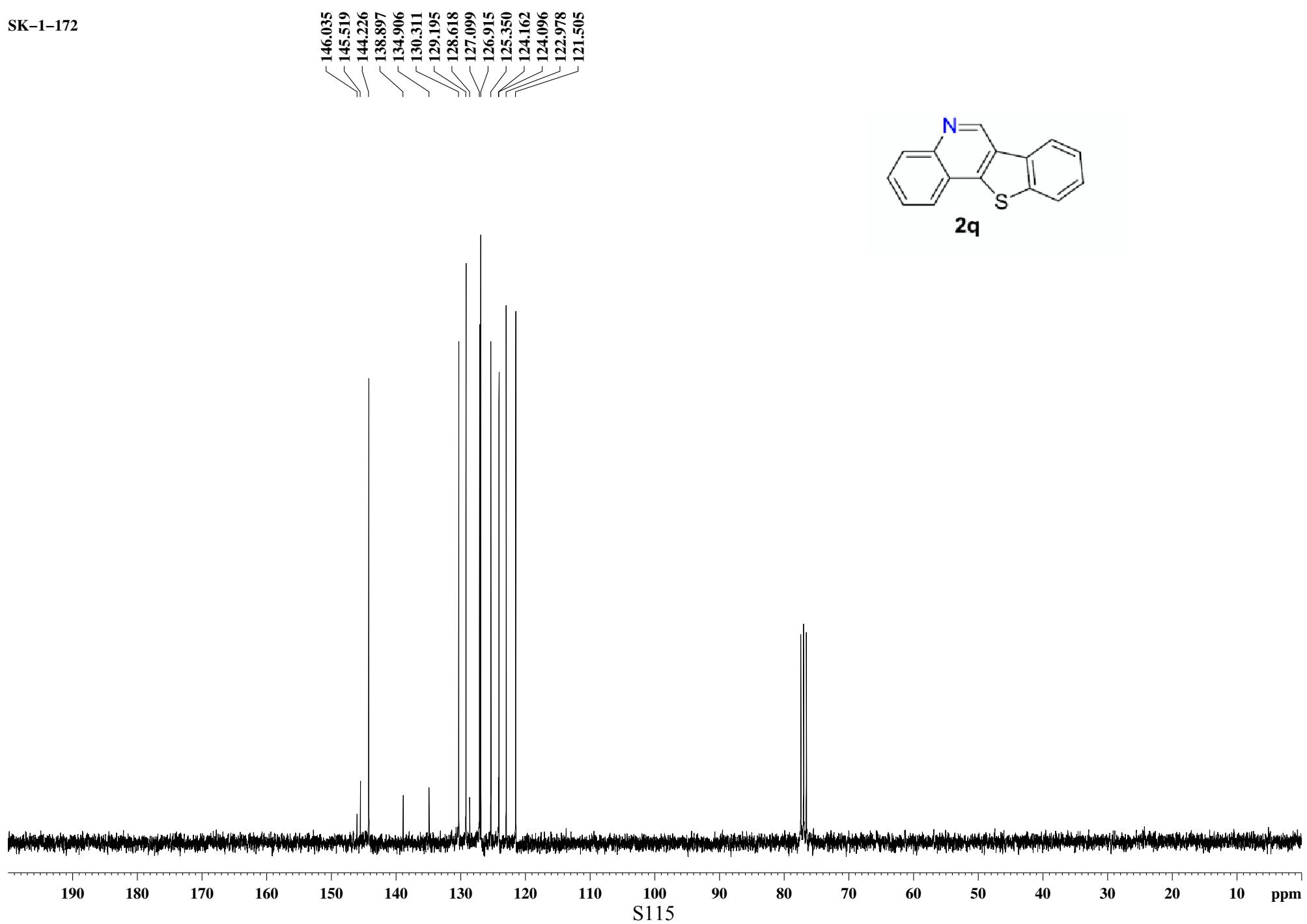
144.888
144.125
141.535
133.048
131.581
129.712
127.935
126.800
124.253
123.190
121.416



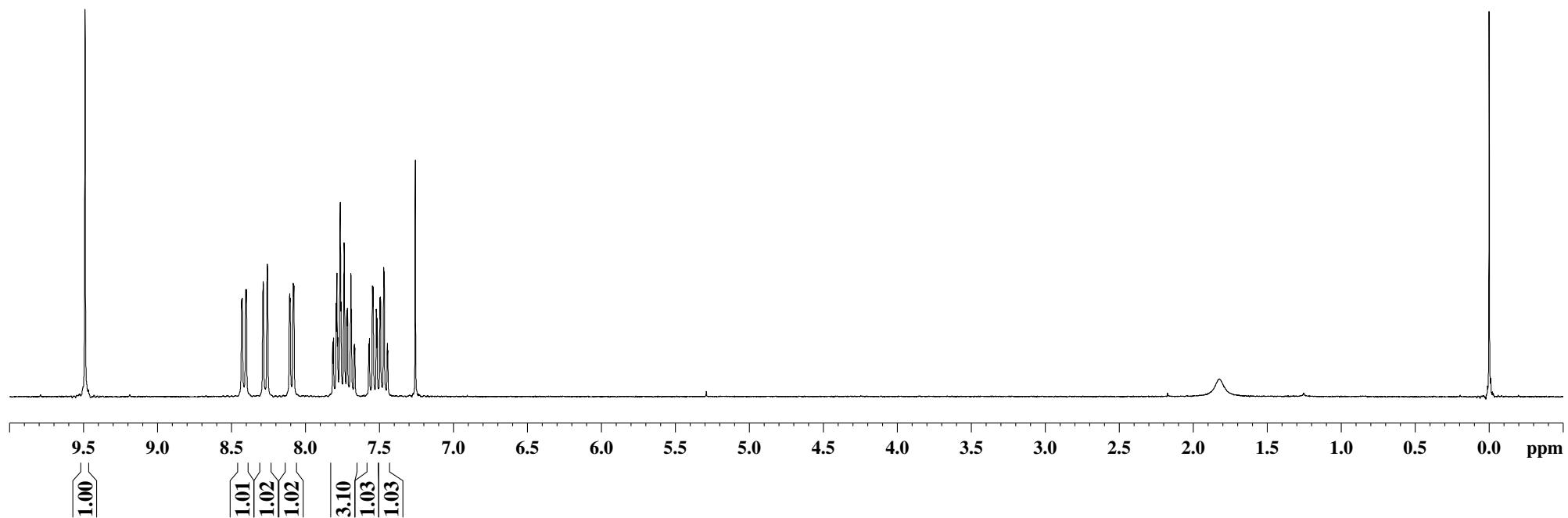
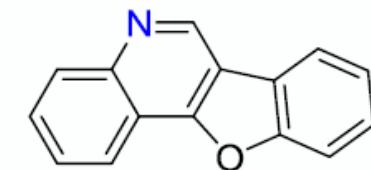
SK-1-175



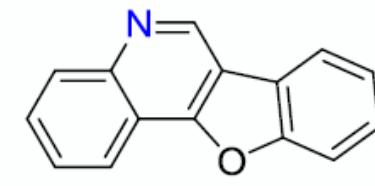
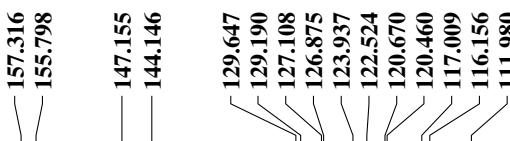
SK-1-172



SK-1-115



SK-1-115



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