

A facile access to substituted benzo[a]fluorenes from *o*-alkynylbenzaldehydes via *in situ* formed acetals

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Electronic Supplementary Information

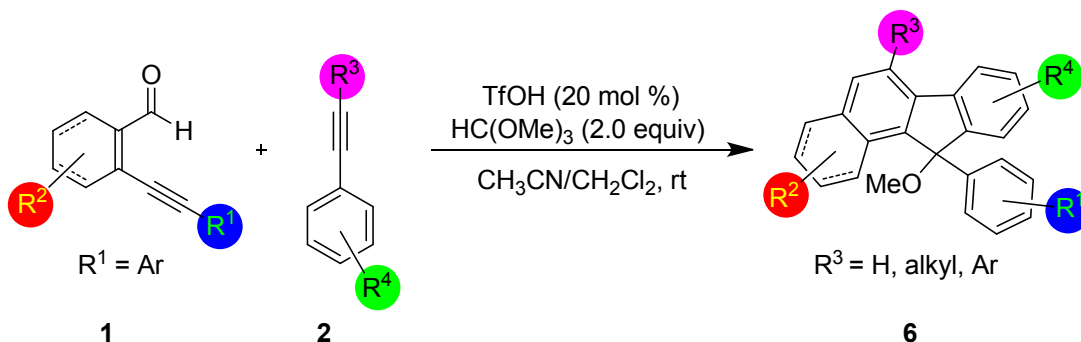
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1. General information:

Chemicals and solvents were obtained from various commercial sources. All starting materials were prepared by following known literature procedures. Trimethyl orthoformate and nitromethane were obtained from SD-Fine chemicals. Triflic acid were purchased from Sigma-Aldrich. THF was dried over sodium and freshly distilled before use. ^1H and ^{13}C spectra were recorded on a Bruker Avance 400 MHz and 500 MHz using solution in CDCl_3 with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on JASCO FT/IR-5300 spectrometer. High-resolution mass spectra (HRMS) were recorded using electrospray ionization on a Bruker Maxis machine. Melting points were determined by using MR-VIS visual melting range apparatus and are uncorrected. For TLC, silica gel plates 60 F254 were used and compounds were visualized by UV light and/or by treatment with Seebach solution (phosphomolibdic acid (2.5 g), $\text{Ce}(\text{SO}_4)_2$ (1 g), Conc. H_2SO_4 (6 mL), H_2O (94 mL)) followed by heating. Column chromatography was performed on silicagel (100-200 mesh) using ethyl acetate and hexanes mixture as eluent. All the *o*-alkynylaldehydes were prepared by following the standard Sonogashira coupling reaction of corresponding bromo or iodo compounds and arylalkynes. All the *o*-alkynylaldehydes are reported in the literatures and our prepared *o*-alkynylaldehyde data are matching with those literatures.

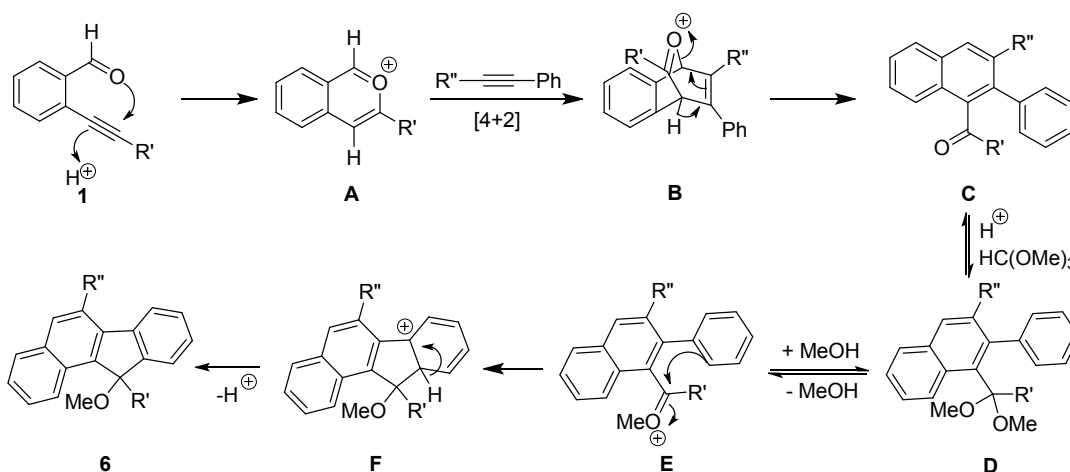
2. General procedure for the synthesis of benzo[a]fluorene derivatives 6a – 6x:



Triflic acid (20 mol %) was charged into a solution of compound **1** (1.0 equiv), compound **2** (1.2 equiv) and trimethyl orthoformate (2.0 equiv) in acetonitrile solvent (5 mL/1 mmol) at room temperature. The resulting mixture was stirred at room temperature under nitrogen atmosphere. The reaction was monitored by TLC. After the completion of the reaction, ether was added and then organic layer was separated and washed with brine solution and dried over anhydrous sodium sulfate. Then the organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/EtOAc) to furnish the pure compound **6**.

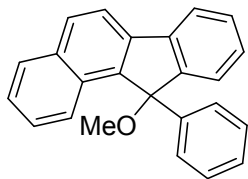
For internal alkynes (**2**), dichloromethane was used as a solvent. After completion of the reaction, solvent was evaporated under pressure. Then, crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to furnish the pure compound **6**.

3. Alternate mechanism for the benzo[a]fluorene formation



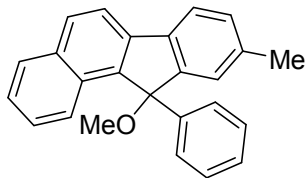
4. Analytical data of compounds 6a – 6x:

11-Methoxy-11-phenyl-11H-benzo[a]fluorene 6a:



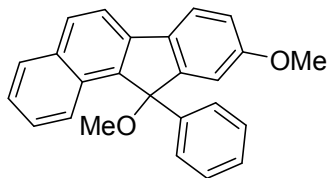
Light yellow solid; mp 126-128 °C; $R_f = 0.6$ (in 10% EtOAc/Hexane); IR (neat): 3063, 2931, 1594, 1490, 1454, 1178, 1101, 1073, 821, 756, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.95 (d, $J = 8.0$ Hz, 1H), 7.90-7.86 (m, 3H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.38-7.33 (m, 5H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 6.8$ Hz, 1H), 7.19-7.15 (m, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.7, 143.2, 141.0, 140.6, 139.4, 133.8, 130.5, 129.9, 128.7, 128.2, 127.8, 126.9, 126.8, 125.6, 125.2, 124.6, 119.7, 118.1, 90.1, 51.3. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{18}\text{O}$ $[M+H]^+$ 323.1436; found 323.1437.

11-Methoxy-9-methyl-11-phenyl-11H-benzo[a]fluorene 6b:



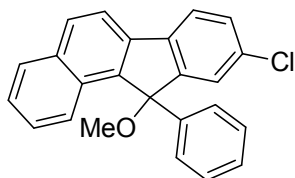
Yellow solid; mp 142-144 °C; $R_f = 0.6$ (in 10% EtOAc/Hexane); IR (neat): 2931, 2816, 1615, 1484, 1276, 1177, 1100, 1078, 1029, 815, 739, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 8.4$ Hz, 1H), 7.88-7.82 (m, 3H), 7.60 (d, $J = 7.6$ Hz, 1H), 7.36-7.30 (m, 4H), 7.18 (d, $J = 6.0$ Hz, 2H), 7.14 (d, $J = 8.8$ Hz, 2H), 7.09 (s, 1H), 2.89 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.9, 143.4, 140.6, 139.6, 138.0, 137.8, 133.5, 130.4, 130.0, 129.4, 129.1, 128.9, 128.7, 128.2, 126.8, 126.7, 125.3, 124.4, 119.5, 118.0, 89.9, 51.3, 21.6. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{O}$ $[M+Na]^+$ 359.1412; found 359.1408.

9,11-Dimethoxy-11-phenyl-11H-benzo[a]fluorene 6c:



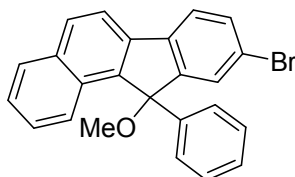
Light brown solid; mp 136-138 °C; $R_f = 0.4$ (in 20% EtOAc/Hexane); IR (neat): 2936, 2827, 1610, 1577, 1484, 1429, 1281, 1226, 1106, 1078, 1034, 821, 733, 706 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.37-7.29 (m, 4H), 7.20-7.14 (m, 3H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.84 (s, 1H), 3.78 (s, 3H), 2.91 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.1, 150.8, 143.3, 140.2, 139.5, 133.4, 133.1, 130.5, 130.0, 128.7, 128.2, 126.9, 126.7, 125.2, 125.1, 124.2, 120.5, 117.8, 114.2, 110.5, 89.9, 55.5, 51.4. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{O}_2$ $[M+\text{H}]^+$ 353.1542; found 353.1539.

9-Chloro-11-methoxy-11-phenyl-11H-benzo[a]fluorene 6d:



Light yellow solid; mp 158-160 °C $R_f = 0.65$ (in 10% EtOAc/Hexane); IR (KBr): 2986, 2827, 1572, 1495, 1101, 1073, 986, 805, 734, 701 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.89 (q, $J = 8.4$ Hz, 3H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.45-7.43 (m, 1H), 7.41-7.35 (m, 4H), 7.29 (d, $J = 1.6$ Hz, 1H), 7.24-7.20 (m, 3H), 2.94 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 150.6, 142.4, 140.9, 139.1, 138.4, 133.8, 133.6, 130.7, 129.8, 129.0, 128.8, 128.3, 127.2, 127.0, 125.8, 125.2, 125.0, 124.5, 120.7, 118.0, 89.9, 51.5. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{ClO}$ $[M+\text{Na}]^+$ 379.0866; found 379.0866.

9-Bromo-11-methoxy-11-phenyl-11H-benzo[a]fluorene 6e:



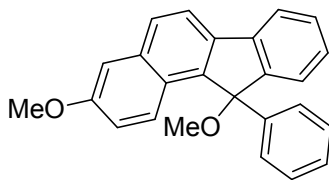
Light yellow solid; mp 178-180 °C; $R_f = 0.6$ (in 10% EtOAc/Hexane); IR (KBr): 2990, 2820, 1469, 1164, 1096, 1070, 988, 821, 716 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.96 (d, $J = 8.4$ Hz, 1H), 7.89-7.83 (m, 3H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.48 (dd, $J = 1.6, 8.0$ Hz, 1H), 7.42-7.39 (m, 2H), 7.36-7.30 (m, 3H), 7.21-7.18 (m, 3H), 2.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 150.8, 142.4, 140.8, 139.5, 138.4, 133.9, 131.9, 130.8, 129.8, 128.8, 128.3, 127.9, 127.2, 127.0, 125.9, 125.2, 124.5, 121.7, 121.1, 117.9, 89.9, 51.5. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{BrO}$ [$M+\text{Na}$] $^+$ 423.0360; found 423.0360.

12-Methoxy-12-phenyl-12H-benzo[7,8]fluoreno[2,3-d][1,3]dioxole 6f:



Yellow solid; mp 205-207 °C; $R_f = 0.4$ (in 20% EtOAc/Hexane); IR (KBr): 2925, 2832, 1582, 1478, 1440, 1319, 1259, 1237, 1073, 1040, 947, 865, 695 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.29-7.21 (m, 4H), 7.15-7.08 (m, 4H), 6.68 (s, 1H), 5.87 (d, $J = 24.0$ Hz, 2H), 2.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 148.4, 147.9, 143.2, 143.0, 140.9, 139.3, 134.5, 133.1, 130.4, 129.7, 128.7, 128.2, 126.9, 126.8, 125.2, 124.1, 117.5, 105.7, 101.4, 100.7, 89.6, 51.2. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{18}\text{O}_3$ [$M+\text{H}$] $^+$ 367.1334; found 367.1333.

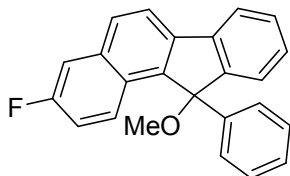
3,11-Dimethoxy-11-phenyl-11H-benzo[a]fluorene 6g:



Light yellow solid; mp 153-155 °C; $R_f = 0.4$ (in 20% EtOAc/Hexane); IR (KBr): 2936, 1627, 1594, 1490, 1375, 1243, 1167, 1073, 1019, 865, 832, 750, 706 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.84 (s, 2H), 7.80 (d, $J = 9.2$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.35-7.32 (m, 3H), 7.27-7.24 (m, 1H), 7.20-7.14 (m, 5H), 7.02 (dd, $J = 2.4, 9.2$ Hz, 1H), 3.88 (s, 3H), 2.89 (s, 3H);

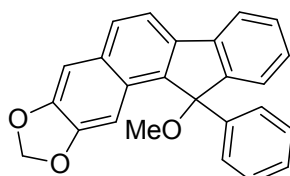
^{13}C NMR (100 MHz, CDCl_3): δ 157.4, 148.3, 143.3, 141.2, 140.8, 137.3, 135.1, 129.1, 128.7, 128.2, 127.3, 126.9, 126.1, 125.4, 125.2, 124.5, 119.5, 119.4, 118.7, 106.9, 90.0, 55.2, 51.3. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{O}_2$ $[M+H]^+$ 353.1542; found 353.1543.

3-Fluoro-11-methoxy-11-phenyl-11H-benzo[a]fluorene 6h:



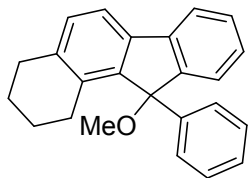
Yellow oil; R_f = 0.5 (in 20% EtOAc/Hexane); IR (neat): 2936, 2821, 1600, 1528, 1479, 1358, 1079, 953, 871, 821, 756 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.92-7.90 (m, 1H), 7.88 (s, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.47 (dd, J = 2.4, 9.6 Hz, 1H), 7.36-7.32 (m, 3H), 7.27 (d, J = 7.2 Hz, 1H), 7.22-7.09 (m, 5H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.4 (d, J = 245.0 Hz), 148.3, 143.0, 141.4, 140.3, 138.7, 134.7 (d, J = 9.0 Hz), 129.7 (d, J = 5.0 Hz), 128.8, 128.2, 127.8, 127.0, 126.9, 125.2, 124.6, 119.7, 119.3, 117.1 (d, J = 25.0 Hz), 111.8 (d, J = 20.0 Hz), 90.0, 51.3. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{FO}$ $[M+H]^+$ 341.1342; found 341.1343.

11-Methoxy-11-phenyl-11H-indeno[2',1':5,6]naphtho[2,3-d][1,3]dioxole 6i:



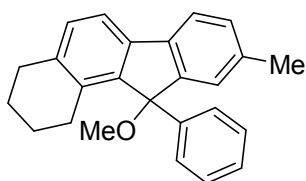
Light yellow solid; mp 195-197 $^\circ\text{C}$; R_f = 0.4 (in 30% EtOAc/Hexane); IR (KBr): 2980, 2893, 1495, 1457, 1221, 1046, 942, 860, 745, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.67 (m 3H), 7.34-7.31 (m, 3H), 7.25-7.14 (m, 7H), 5.92 (d, J = 22.0 Hz, 2H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 148.1, 147.4, 143.1, 140.6, 140.2, 138.0, 130.9, 129.1, 128.7, 128.2, 127.5, 127.1, 126.9, 125.2, 124.5, 119.5, 116.5, 104.7, 101.0, 100.9, 90.0, 51.2. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{18}\text{O}_3$ $[M+H]^+$ 367.1334; found 367.1333.

11-Methoxy-11-phenyl-2,3,4,11-tetrahydro-1H-benzo[a]fluorene 6j:



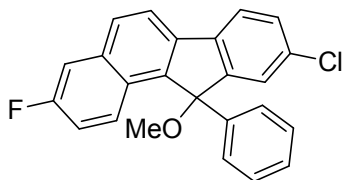
Brown oil; $R_f = 0.6$ (in 10% EtOAc/Hexane); IR (neat): 2931, 2821, 1599, 1495, 1451, 1171, 1100, 1078, 1035, 760, 706 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, $J = 7.2$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.32-7.27 (m, 3H), 7.24-7.12 (m, 6H), 2.95 (s, 3H), 2.79-2.73 (m, 3H), 2.14-2.10 (m, 1H), 1.73-1.59 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.8, 143.2, 142.7, 140.5, 139.1, 137.5, 136.0, 130.3, 128.6, 128.0, 127.4, 126.6, 125.3, 124.5, 119.3, 116.9, 89.7, 51.0, 29.9, 24.9, 22.9, 22.6. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{22}\text{O}$ [$M+\text{H}$] $^+$ 327.1749; found 327.1745.

11-Methoxy-9-methyl-11-phenyl-2,3,4,11-tetrahydro-1H-benzo[a]fluorene 6k:



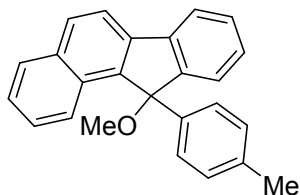
Light yellow oil; $R_f = 0.65$ (in 20% EtOAc/Hexane); IR (neat): 2962, 2821, 1490, 1463, 1101, 1079, 805, 739, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 6.8$ Hz, 2H), 7.24-7.16 (m, 3H), 7.10 (t, $J = 8.0$ Hz, 2H), 6.94 (s, 1H), 2.94 (s, 3H), 2.77-2.71 (m, 3H), 2.27 (s, 3H), 2.13-2.06 (m, 1H), 1.72-1.59 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.0, 143.1, 142.9, 139.2, 137.9, 137.3, 136.9, 135.9, 130.2, 129.4, 129.1, 128.0, 126.5, 125.3, 125.2, 119.1, 116.6, 89.7, 51.0, 29.8, 24.9, 22.9, 22.7, 21.5. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{O}$ [$M+\text{Na}$] $^+$ 363.1725; found 363.1722.

9-Chloro-3-fluoro-11-methoxy-11-phenyl-11H-benzo[a]fluorene 6l:



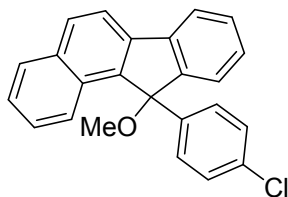
Colorless solid; mp 147-149 °C; $R_f = 0.6$ (in 10% EtOAc/Hexane); IR (KBr): 2936, 2821, 1600, 1523, 1473, 1161, 1079, 879, 805, 723 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.84 (m 3H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.49 (dd, $J = 2.0, 9.6$ Hz, 1H), 7.33 dd, $J = 1.6, 8.0$ Hz, 1H), 7.31-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.21-7.19 (m, 3H), 7.13 (td, $J = 2.4, 8.8$ Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.5 (d, $J = 246.0$ Hz), 150.3, 142.3, 141.3, 138.9, 137.7, 134.7 (d, $J = 9.0$ Hz), 133.7, 133.0 (d, $J = 5.0$ Hz), 129.1, 128.4, 127.4, 127.0, 126.9, 125.1, 125.0, 120.7, 119.1, 117.4 (d, $J = 25.0$ Hz), 111.9 (d, $J = 21.0$ Hz), 89.8, 51.5. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{16}\text{ClFO}$ [$M+\text{H}$] $^+$ 375.0952; found 375.0947.

11-Methoxy-11-p-tolyl-11H-benzo[a]fluorene 6m:



Light yellow oil; $R_f = 0.6$ (in 20% EtOAc/Hexane); IR (neat): 2926, 2821, 1627, 1517, 1479, 1178, 1095, 1073, 821, 767 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.90 (m, 2H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.39-7.32 (m, 3H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 3H), 6.98 (d, $J = 8.0$ Hz, 2H), 2.88 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.9, 141.0, 140.5, 140.2, 139.3, 136.4, 133.7, 130.4, 130.0, 128.9, 128.7, 128.6, 127.8, 126.7, 125.5, 125.1, 124.6, 124.5, 119.7, 118.1, 90.0, 51.3, 21.0. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{O}$ [$M+\text{H}$] $^+$ 337.1592; found 337.1590.

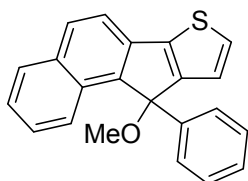
11-(4-Chlorophenyl)-11-methoxy-11H-benzo[a]fluorene 6n:



Colorless solid; mp 138-140 °C; $R_f = 0.5$ (in 10% EtOAc/Hexane); IR (KBr): 2926, 1495, 1342, 1178, 1128, 1079, 832, 761, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.95 (d, $J = 8.0$ Hz, 1H),

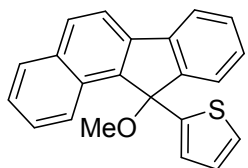
7.88-7.84 (m, 3H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.39-7.33 (m, 3H), 7.29-7.21 (m, 4H), 7.13 (d, $J = 8.8$ Hz, 2H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 141.9, 140.5, 140.4, 139.4, 133.8, 132.6, 130.7, 129.7, 128.9, 128.8, 128.3, 127.9, 126.9, 126.8, 125.7, 124.4, 124.3, 119.9, 118.1, 89.6, 51.4. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{ClO}$ [$M+\text{Na}$] $^+$ 379.0866; found 379.0865.

10-Methoxy-10-phenyl-10H-benzo[4,5]indeno[1,2-b]thiophene 6o:



Light brown solid; mp 122-124 °C; $R_f = 0.45$ (in 10% EtOAc/Hexane); IR (KBr): 2920, 2816, 1616, 1523, 1441, 1095, 1068, 821, 701, 679 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.37-7.30 (m, 4H), 7.24-7.21 (m, 1H), 7.20-7.16 (m, 3H), 6.91 (d, $J = 4.8$ Hz, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.5, 143.5, 143.1, 142.0, 136.2, 132.6, 130.4, 129.8, 128.8, 128.3, 127.8, 127.1, 126.8, 125.4, 125.1, 123.9, 122.2, 118.0, 87.9, 51.7. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{16}\text{OS}$ [$M+\text{H}$] $^+$ 329.1000; found 329.1002.

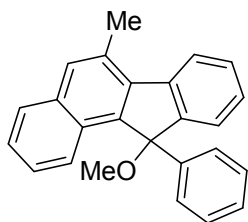
2-(11-Methoxy-11H-benzo[a]fluoren-11-yl)thiophene 6p:



Light yellow oil; $R_f = 0.65$ (in 10% EtOAc/Hexane); IR (neat): 2931, 1698, 1627, 1473, 1227, 1156, 1101, 1063, 821, 761, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.06 (m, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.91-7.89 (m, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 7.2$ Hz, 1H), 7.45-7.40 (m, 2H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.16 (d, $J = 4.8$ Hz, 1H), 6.73 (t, $J = 4.8$ Hz, 1H), 6.42 (d, $J = 3.2$ Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.6, 147.4, 139.9, 139.6, 139.0, 133.8, 130.9, 130.0, 128.9, 128.7, 127.8,

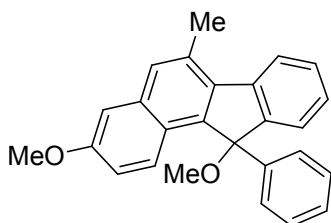
126.9, 126.4, 125.7, 124.8, 124.4, 124.2, 122.9, 119.9, 118.2, 88.7, 51.7. HRMS (ESI): calcd for $C_{22}H_{16}OS$ $[M+H]^+$ 329.1000; found 329.1001.

11-Methoxy-6-methyl-11-phenyl-11H-benzo[a]fluorene 6q:



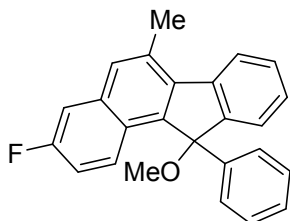
Light yellow solid; mp 128-130 °C; $R_f = 0.5$ (in 20% EtOAc/Hexane); IR (KBr): 2931, 2821, 1600, 1501, 1446, 1174, 1073, 1030, 745, 695 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.90 (t, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.70 (s, 1H), 7.38-7.30 (m, 5H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.25-7.22 (m, 1H), 7.18-7.13 (m, 3H), 2.91 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 143.5, 141.6, 141.4, 138.8, 133.6, 131.1, 130.9, 128.6, 128.3, 128.1, 127.7, 127.2, 126.8, 125.8, 125.7, 125.2, 124.5, 122.9, 89.5, 51.2, 21.6. HRMS (ESI): calcd for $C_{25}H_{20}O$ $[M+H]^+$ 337.1592; found 337.1591.

3,11-Dimethoxy-6-methyl-11-phenyl-11H-benzo[a]fluorene 6r:



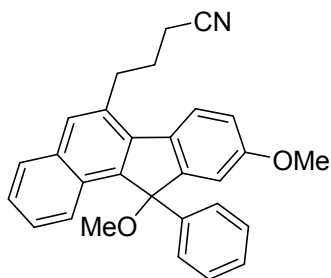
Light yellow solid; mp 166-168 °C; $R_f = 0.5$ (in 20% EtOAc/Hexane); IR (KBr): 2931, 2821, 1621, 1599, 1484, 1452, 1386, 1320, 1172, 1079, 1030, 882, 838, 761, 695 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 9.2$ Hz, 1H), 7.60 (s, 1H), 7.36-7.30 (m, 4H), 7.25-7.11 (m, 5H), 6.95 (dd, $J = 2.8, 9.2$ Hz, 1H), 3.87 (s, 3H), 2.89 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 148.7, 143.6, 141.8, 141.6, 136.6, 135.0, 131.7, 129.7, 128.6, 128.1, 128.0, 126.82, 126.78, 126.1, 125.2, 124.5, 123.9, 122.5, 118.5, 105.8, 89.4, 55.2, 51.2, 21.6. HRMS (ESI): calcd for $C_{26}H_{22}O_2$ $[M+H]^+$ 367.1698; found 367.1701.

3-Fluoro-11-methoxy-6-methyl-11-phenyl-11H-benzo[a]fluorene 6s:



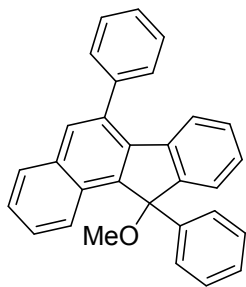
Yellow solid; mp 131-133 °C; $R_f = 0.6$ (in 20% EtOAc/Hexane); IR (KBr): 2925, 2821, 1637, 1517, 1473, 1456, 1221, 1144, 1078, 1034, 749, 700 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.92-7.87 (m, 2H), 7.61 (s, 1H), 7.39-7.29 (m, 5H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.18-7.12 (m, 3H), 7.03 (td, $J = 2.0, 8.8$ Hz, 1H), 2.88 (s, 3H), 2.85 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.6 (d, $J = 245.0$ Hz), 148.8, 143.3, 141.9, 141.2, 138.1, 134.5 (d, $J = 9.0$ Hz), 132.4, 130.1, 128.7, 128.2, 127.2, 127.1, 127.0, 125.4, 125.1, 124.6, 122.8, 116.2 (d, $J = 25.0$ Hz), 110.7 (d, $J = 21.0$ Hz), 89.4, 51.2, 21.6. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{19}\text{FO}$ [$M+\text{H}$] $^+$ 355.1498; found 355.1498.

4-(9,11-Dimethoxy-11-phenyl-11H-benzo[a]fluoren-6-yl)butanenitrile 6t:



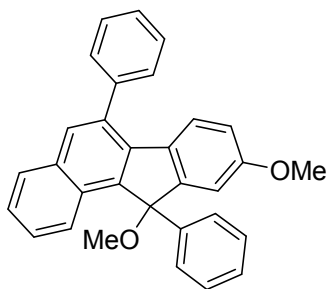
Light yellow oil; $R_f = 0.3$ (in 40% EtOAc/Hexane); IR (neat): 2942, 2827, 2252, 1605, 1484, 1293, 1227, 1073, 1030, 734 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.88 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.72-7.69 (m, 2H), 7.37-7.27 (m, 4H), 7.25-7.13 (m, 3H), 6.91-6.87 (m, 2H), 3.77 (s, 3H), 3.44-3.31 (m, 2H), 2.88 (s, 3H), 2.49 (t, $J = 7.2$ Hz, 2H), 2.22 (pentet, $J = 7.2$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.6, 151.5, 143.3, 141.8, 137.8, 132.9, 132.8, 132.2, 130.3, 128.7, 128.2, 127.8, 126.9, 126.3, 125.6, 125.1, 124.2, 123.2, 119.5, 114.0, 110.8, 89.1, 55.4, 51.2, 32.9, 25.3, 16.7. HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{25}\text{NO}_2$ [$M+\text{Na}$] $^+$ 442.1783; found 442.1787.

11-Methoxy-6,11-diphenyl-11H-benzo[a]fluorene 6u:



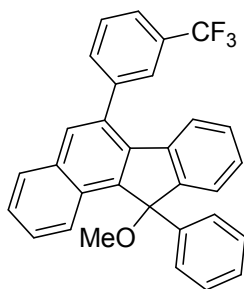
Light yellow solid; mp 161-163 °C; $R_f = 0.65$ (in 10% EtOAc/Hexane); IR (KBr): 2986, 2821, 1588, 1490, 1462, 1441, 1183, 1101, 1073, 1035, 893, 750, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.82 (s, 1H), 7.64-7.56 (m, 5H), 7.47-7.42 (m, 3H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.31-7.23 (m, 3H), 7.21-7.13 (m, 2H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.1, 143.4, 142.1, 140.7, 140.4, 137.3, 135.9, 133.2, 131.3, 129.0, 128.4, 128.2, 127.7, 127.4, 126.9, 126.6, 126.1, 125.2, 124.6, 124.3, 122.9, 89.5, 51.3. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{22}\text{O}$ [$M+\text{Na}$] $^+$ 421.1568; found 421.1570.

9,11-Dimethoxy-6,11-diphenyl-11H-benzo[a]fluorene 6v:



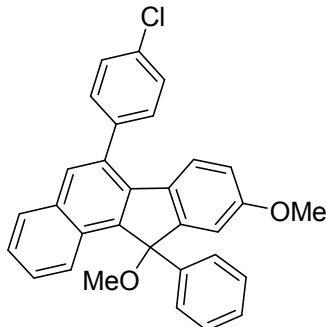
Light yellow oil; $R_f = 0.4$ (in 20% EtOAc/Hexane); IR (neat): 2931, 2832, 1621, 1489, 1287, 1221, 1073, 1029, 739, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.75 (s, 1H), 7.59-7.52 (m, 5H), 7.42-7.30 (m, 4H), 7.24-7.16 (m, 3H), 6.81 (s, 1H), 6.71 (d, $J = 8.8$ Hz, 1H), 6.55 (d, $J = 8.4$ Hz, 1H), 3.71 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.6, 151.3, 143.4, 141.2, 140.8, 137.4, 135.4, 133.2, 132.6, 131.1, 129.1, 128.4, 128.2, 127.7, 126.9, 126.6, 125.6, 125.2, 124.3, 123.7, 113.5, 110.3, 89.3, 55.4, 51.4. HRMS (ESI): calcd for $\text{C}_{31}\text{H}_{24}\text{O}_2$ [$M+\text{Na}$] $^+$ 451.1674; found 451.1675.

11-Methoxy-11-phenyl-6-(3-(trifluoromethyl)phenyl)-11H-benzo[a]fluorene 6w:



Light yellow oil; $R_f = 0.55$ (in 10% EtOAc/Hexane); IR (neat): 2931, 2827, 1627, 1495, 1402, 1172, 1084, 1013, 821, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 3H), 7.74 (d, $J = 7.2$ Hz, 1H), 7.40-7.28 (m, 8H), 7.25 (s, 1H), 7.22-7.14 (m, 4H), 2.90 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.7, 143.2, 141.0, 140.6, 139.4, 133.8, 130.5, 129.9, 128.7, 128.2, 127.8, 126.9, 126.8, 125.6, 124.6, 119.7, 118.1, 90.1, 51.3; ^{19}F NMR (376 MHz, CDCl_3): δ -62.40. HRMS (ESI): calcd for $\text{C}_{31}\text{H}_{21}\text{F}_3\text{O}$ [$M+\text{Na}$] $^+$ 489.1442; found 489.1440.

6-(4-Chlorophenyl)-9,11-dimethoxy-11-phenyl-11H-benzo[a]fluorene 6x:



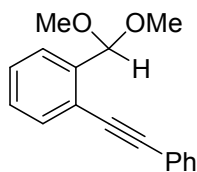
Yellow solid; mp 70-72 $^{\circ}\text{C}$; $R_f = 0.55$ (in 20% EtOAc/Hexane); IR (KBr): 2925, 2832, 1604, 1489, 1347, 1292, 1089, 1035, 832, 739, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 1H), 7.56-7.50 (m, 4H), 7.39 (d, $J = 7.2$ Hz, 3H), 7.36-7.32 (m, 1H), 7.25-7.16 (m, 3H), 6.81 (d, $J = 2.0$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.60 (dd, $J = 2.0, 8.8$ Hz, 1H), 3.72 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 151.3, 143.3, 141.5, 139.2, 137.1, 134.0, 133.7, 132.9, 132.6, 131.2, 129.2, 128.4, 128.2, 126.9, 126.8, 125.8, 125.2, 124.3, 123.5, 113.6, 110.4, 89.3, 55.4, 51.4. HRMS (ESI): calcd for $\text{C}_{31}\text{H}_{23}\text{ClO}_2$ [$M+\text{Na}$] $^+$ 485.1284; found 485.1285.

Data of compounds 6a and 9a (mixture)

Light yellow oil; $R_f = 0.6$ (in 10% EtOAc/Hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97-7.93 (m, 2.6H), 7.89-7.85 (m, 3.4H), 7.74-7.71 (m, 1.5H), 7.37-7.32 (m, 8H), 7.29 (d, $J = 7.2$ Hz, 2H), 7.23-7.13 (m, 7.3H), 3.08-3.01 (m, 1H), 2.95-2.88 (m, 1H), 2.89 (s, 1.3H), 1.08 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 149.5, 148.7, 143.4, 143.2, 141.8, 141.0, 140.6, 140.3, 139.4, 139.0, 133.7, 131.1, 130.5, 130.3, 129.9, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 126.9, 126.8, 126.7, 125.5, 125.3, 124.62, 124.56, 124.4, 119.7, 118.1, 90.0, 89.4, 58.9, 51.3, 15.6. HRMS (ESI) for **6a**: calcd for $\text{C}_{24}\text{H}_{18}\text{O}$ $[M+H]^+$ 323.1436; found 323.1437. HRMS (ESI) for **9a**: calcd for $\text{C}_{25}\text{H}_{20}\text{O}$ $[M+H]^+$ 337.1592; found 337.1601.

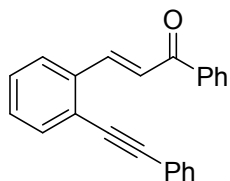
5. Analytical data of compounds 7 and 8

1-(Dimethoxymethyl)-2-(phenylethynyl)benzene 7:¹



$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.62 (d, $J = 7.6$ Hz, 1H), 7.55 (dd, $J = 1.6, 7.2$ Hz, 3H), 7.38-7.29 (m, 5H), 5.76 (s, 1H), 3.45 (s, 6H).

(E)-1-Phenyl-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one 8:²

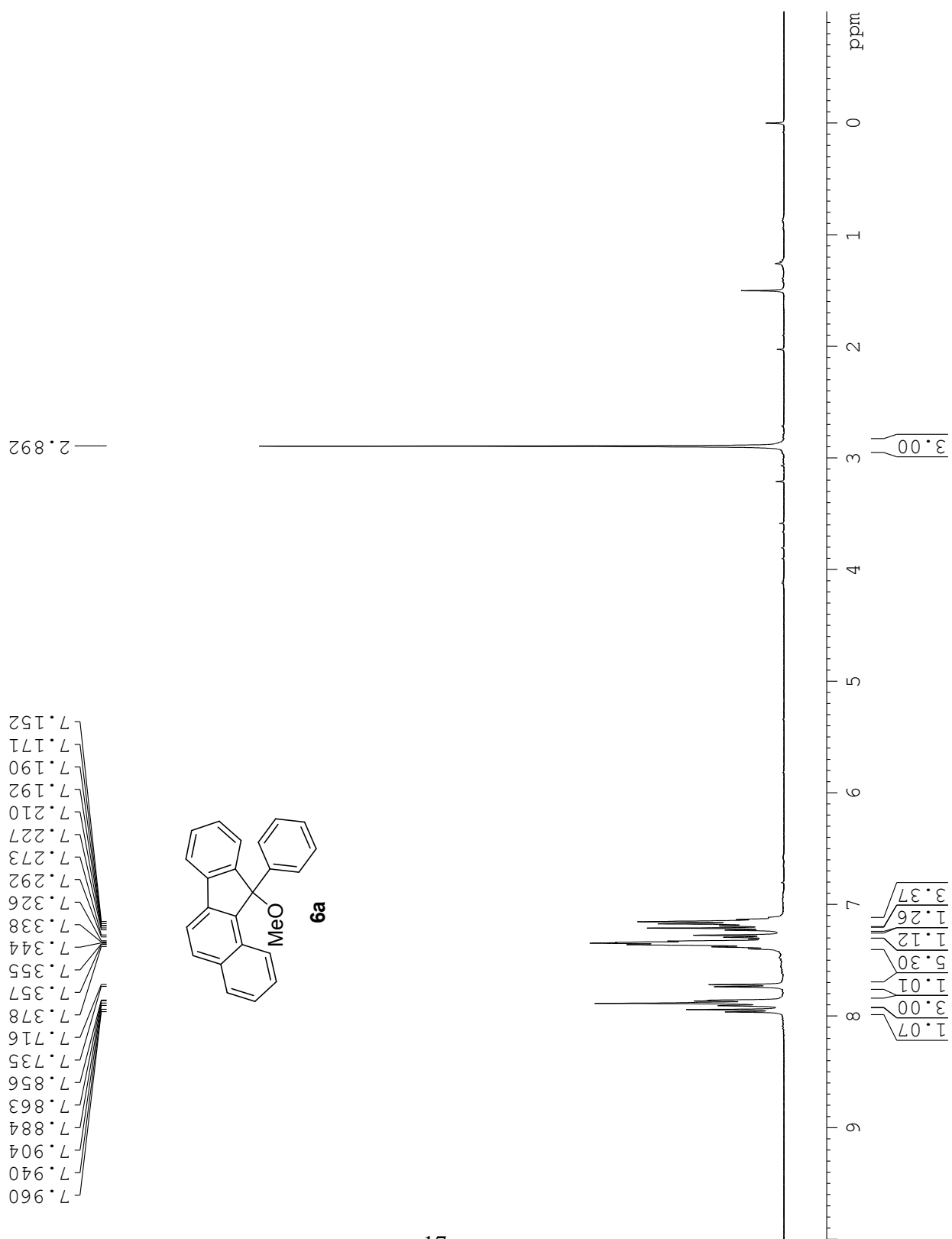


The compound was prepared by the following the reported procedure.² Yield 76%. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.35 (d, $J = 16.0$ Hz, 1H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.78-7.75 (m, 1H), 7.64 (d, $J = 16.0$ Hz, 1H), 7.60-7.58 (m, 1H), 7.55-7.51 (m, 3H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.39-7.34 (m, 6H).

6. References

1. I. Nakamura, G. B. Bajracharya, Y. Mizushima, Y. Yamamoto, Y. *Angew. Chem., Int. Ed.*, 2002, **41**, 4328.
2. X. Du, S. Yang, J. Yang, Y. Liu, *Chem. -Eur. J.*, 2011, **17**, 4981.

7. Copies of ^1H and ^{13}C spectra of all new compounds

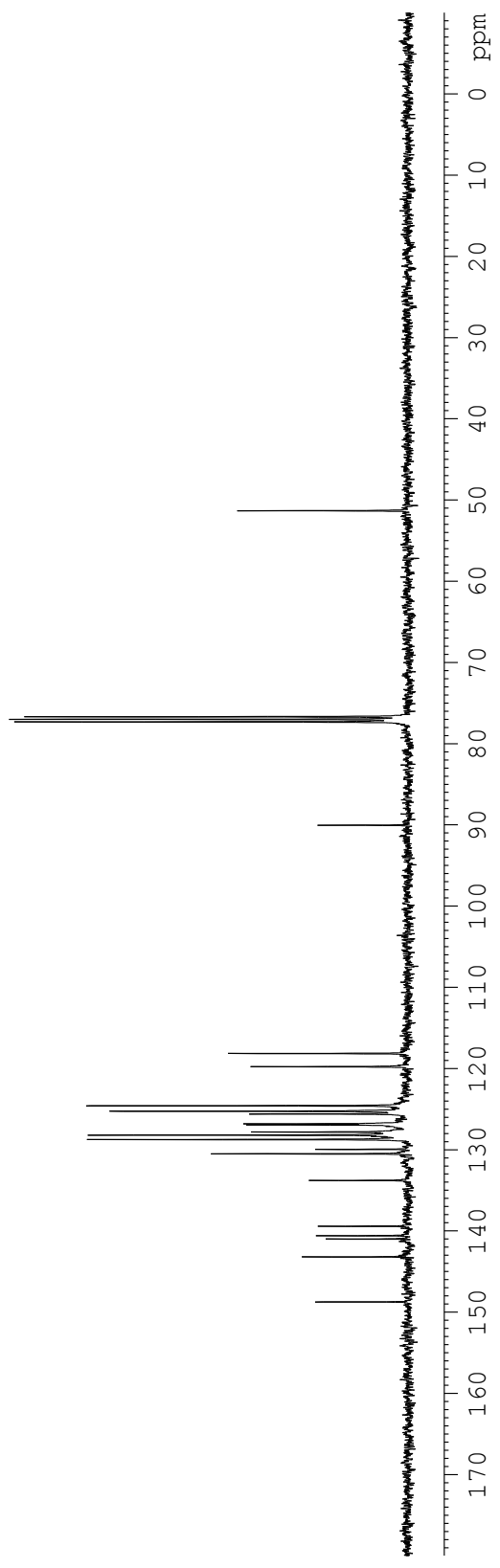
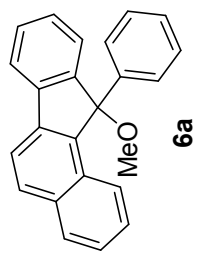


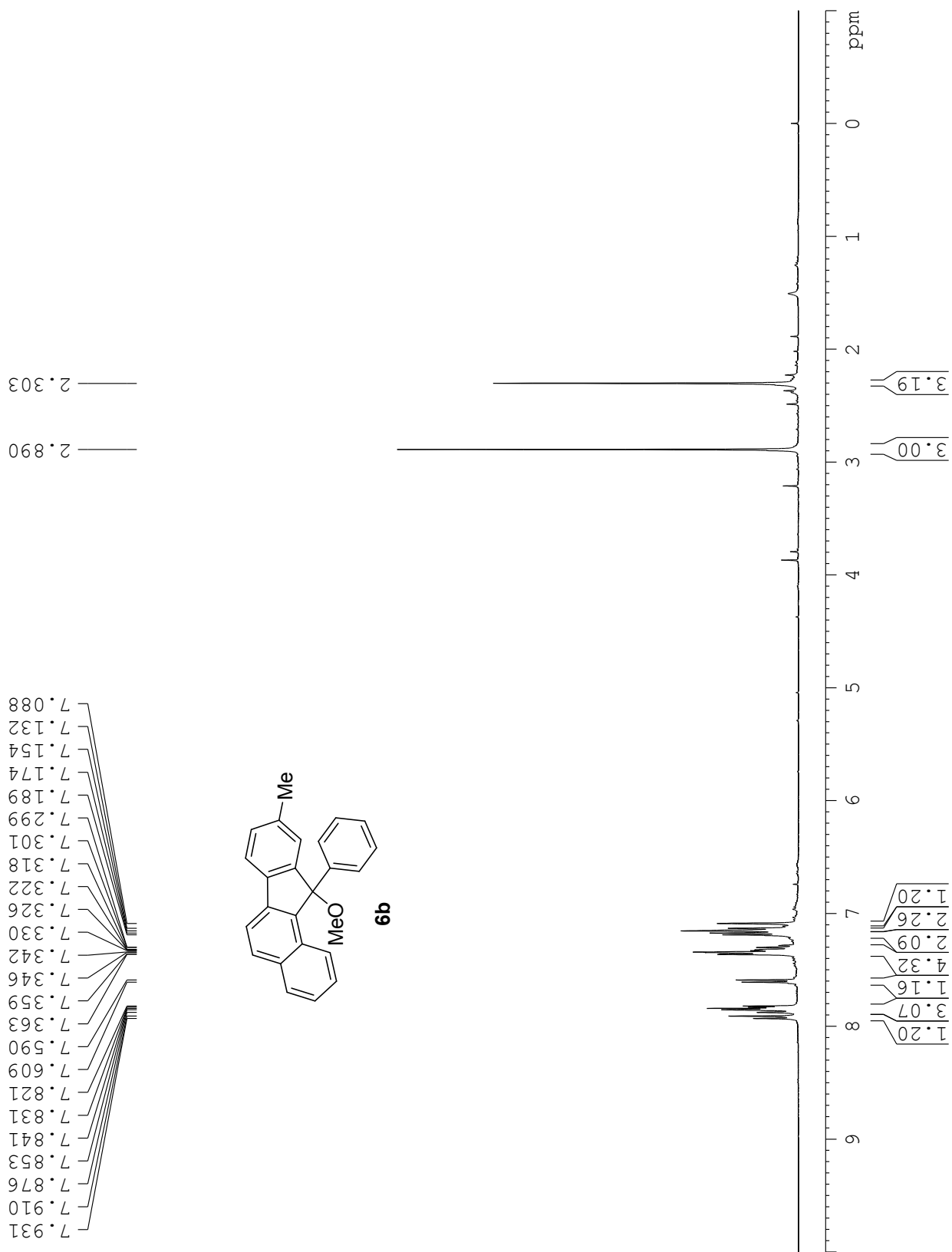
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118.12

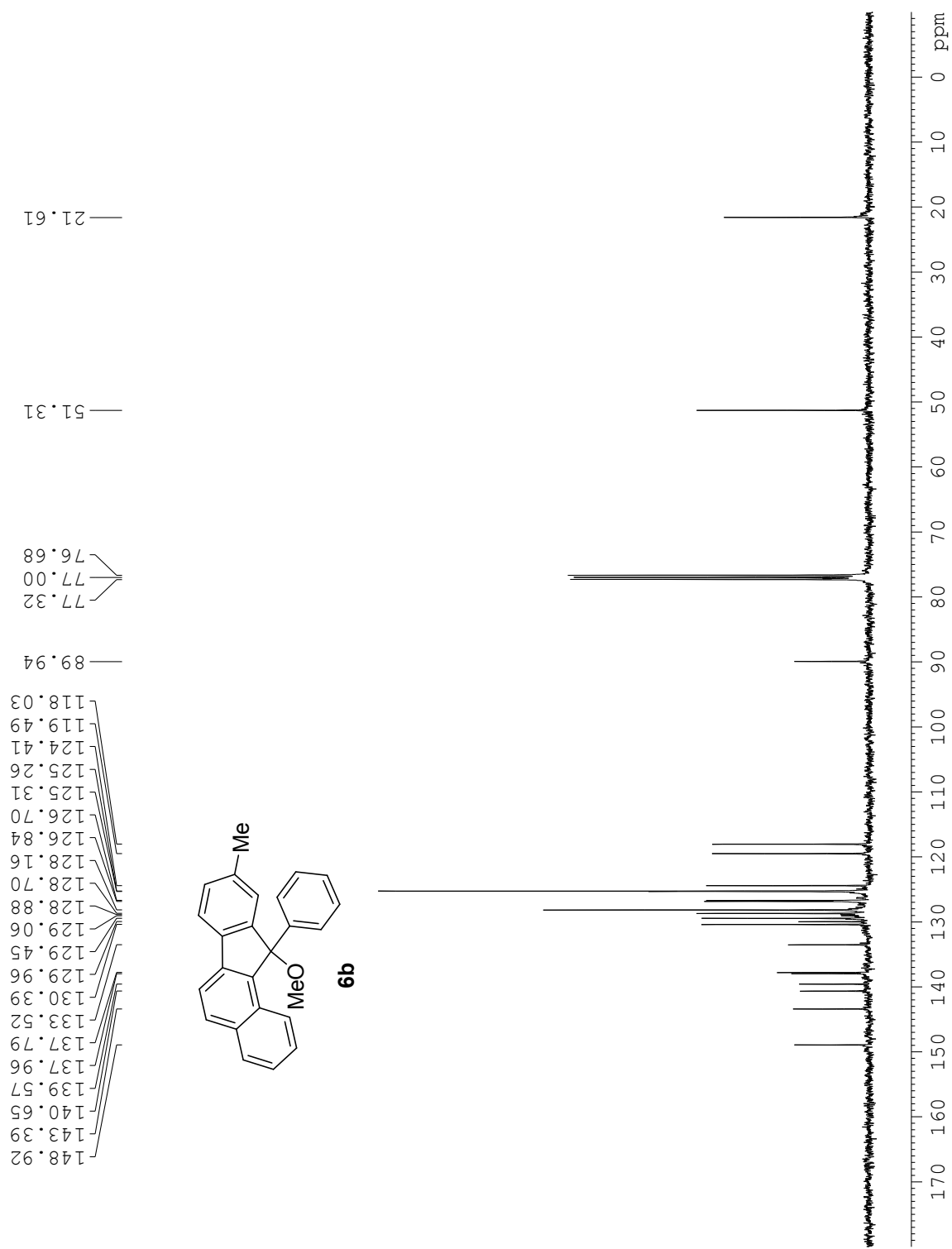
90.05

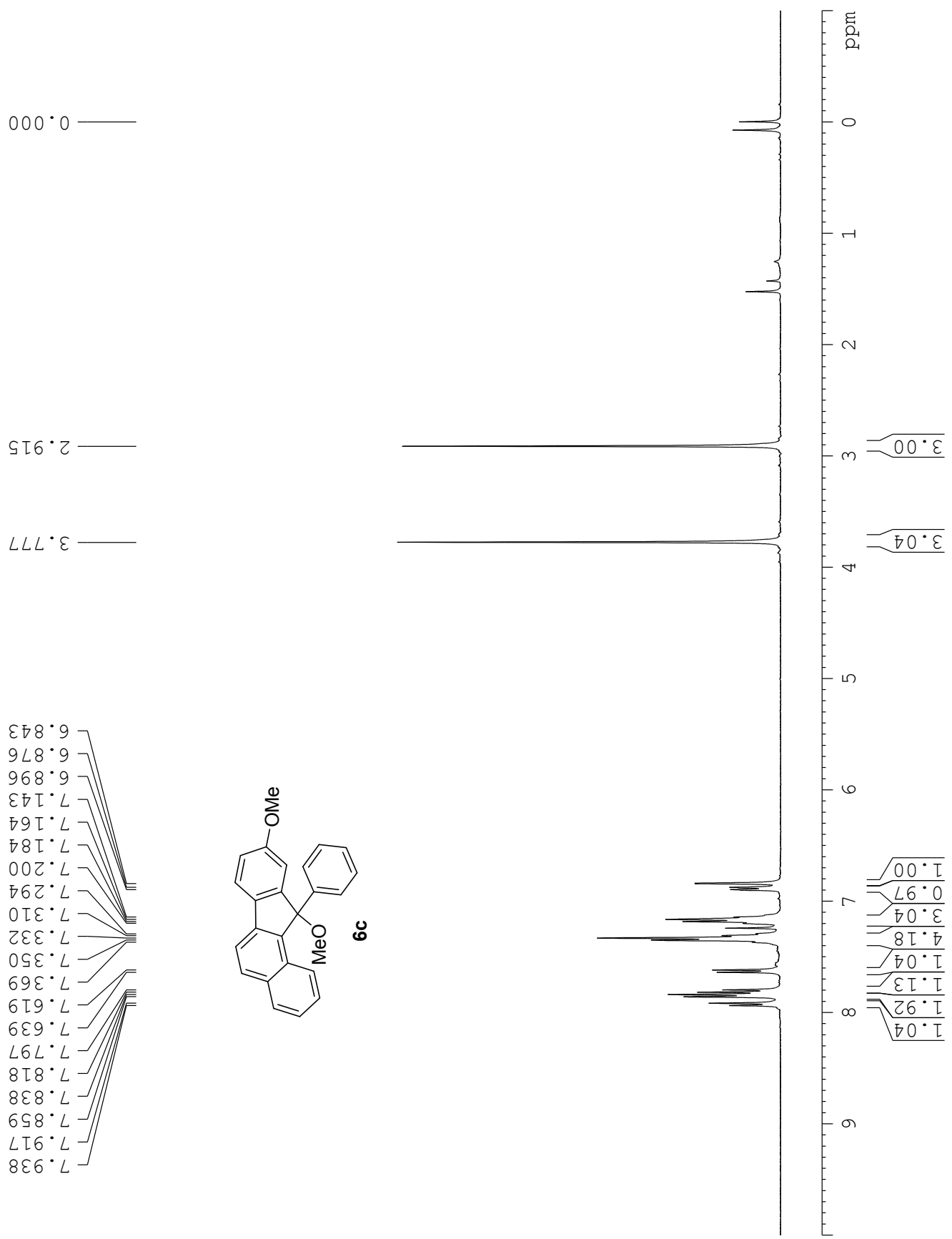
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77.00
76.68

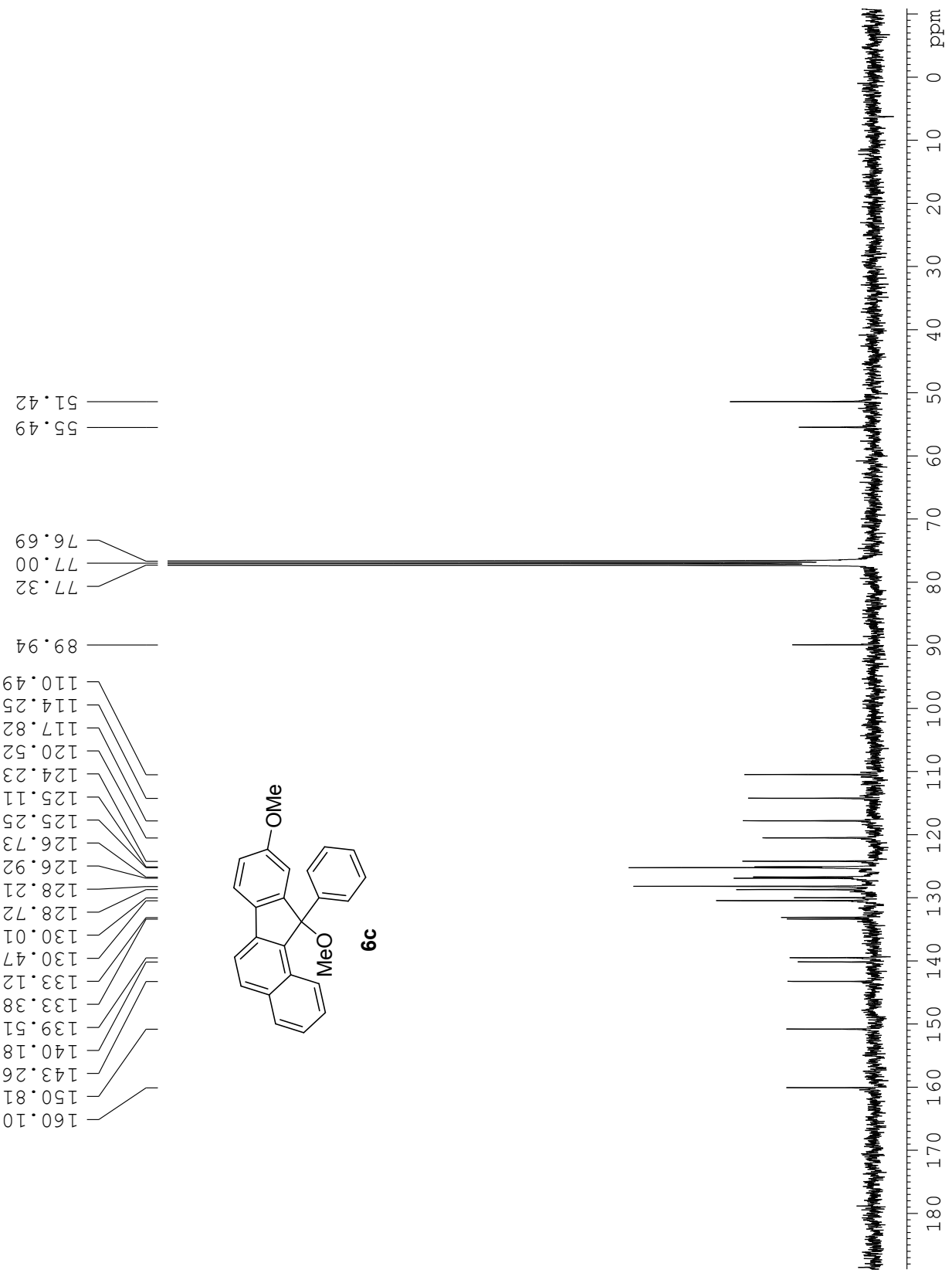
51.32

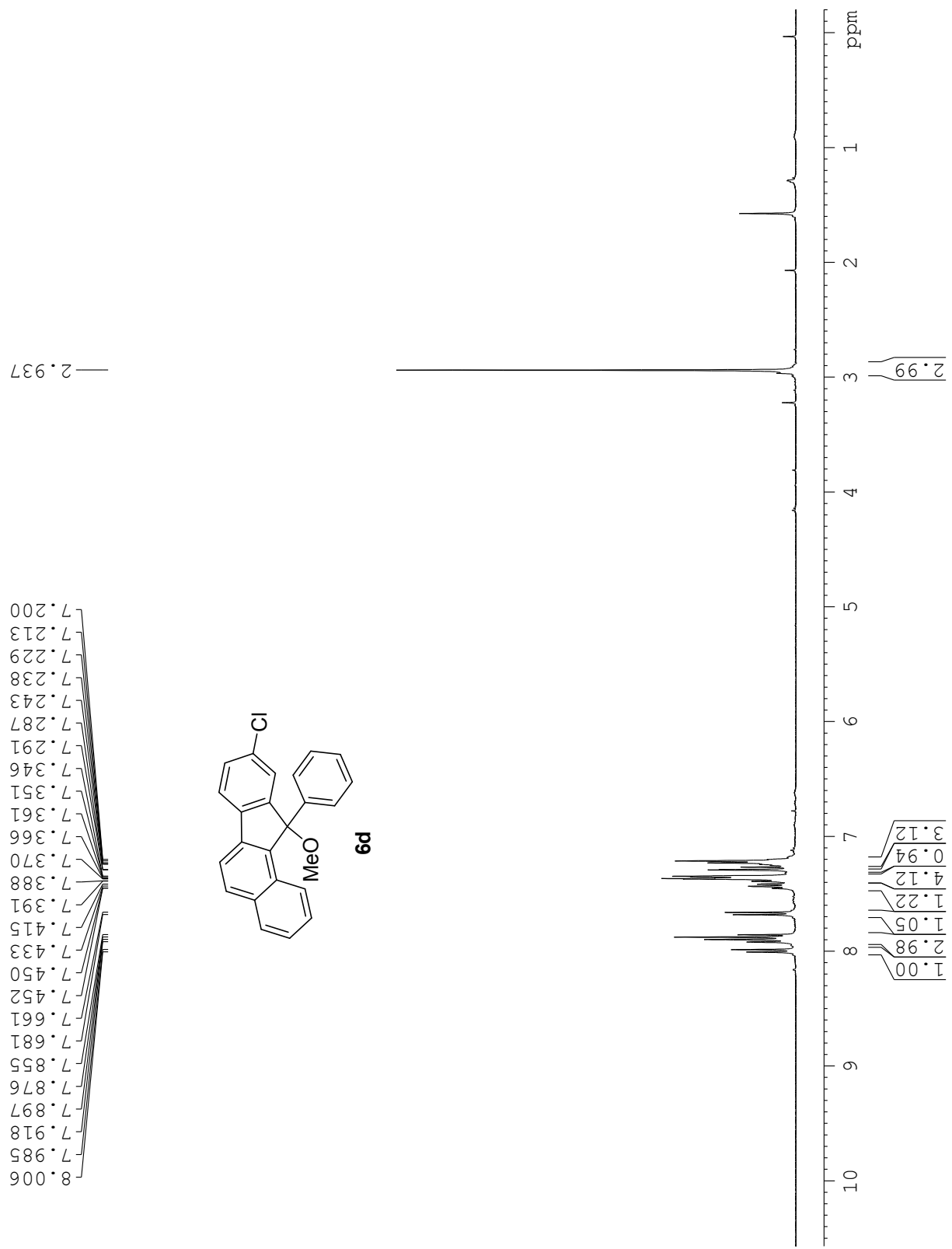


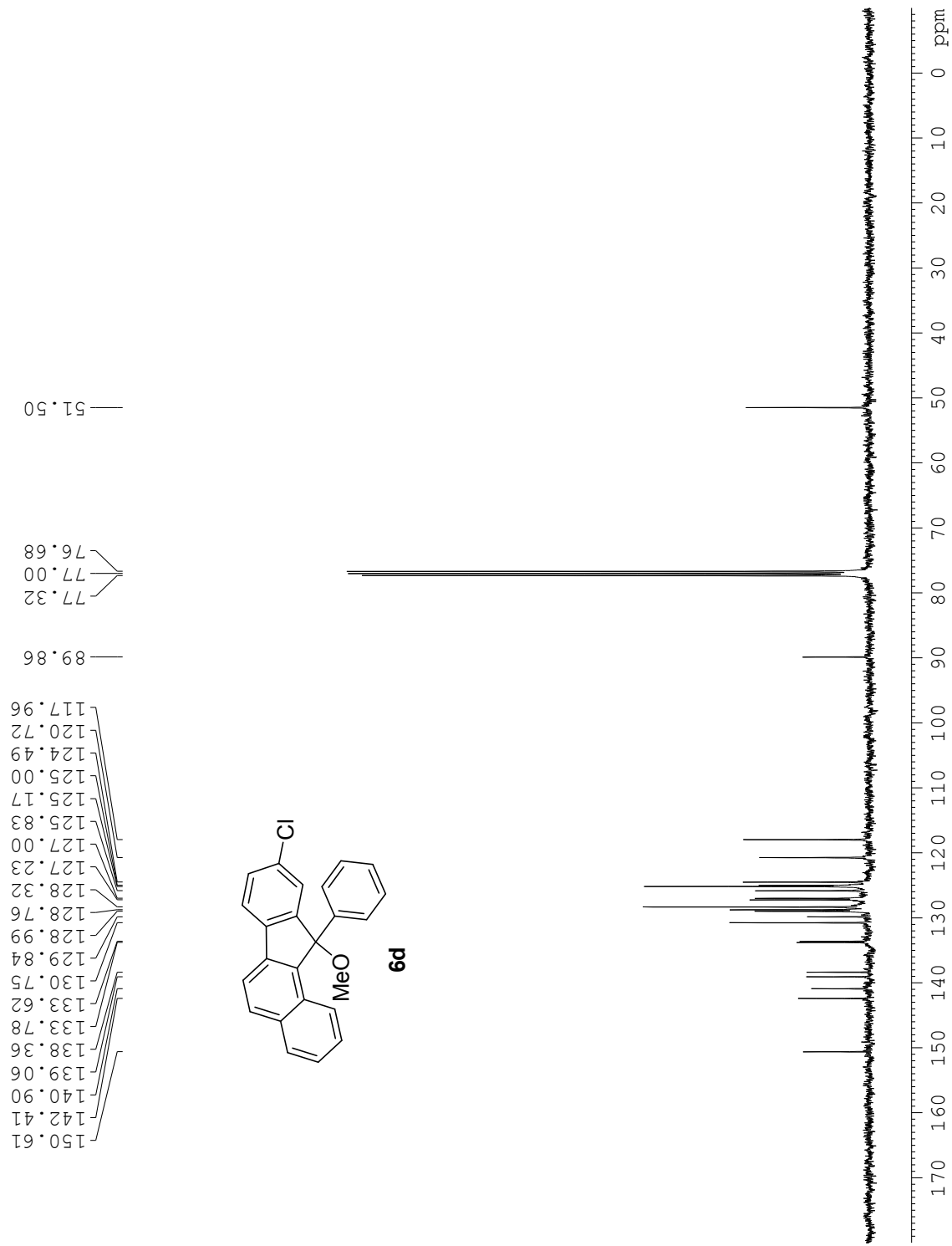


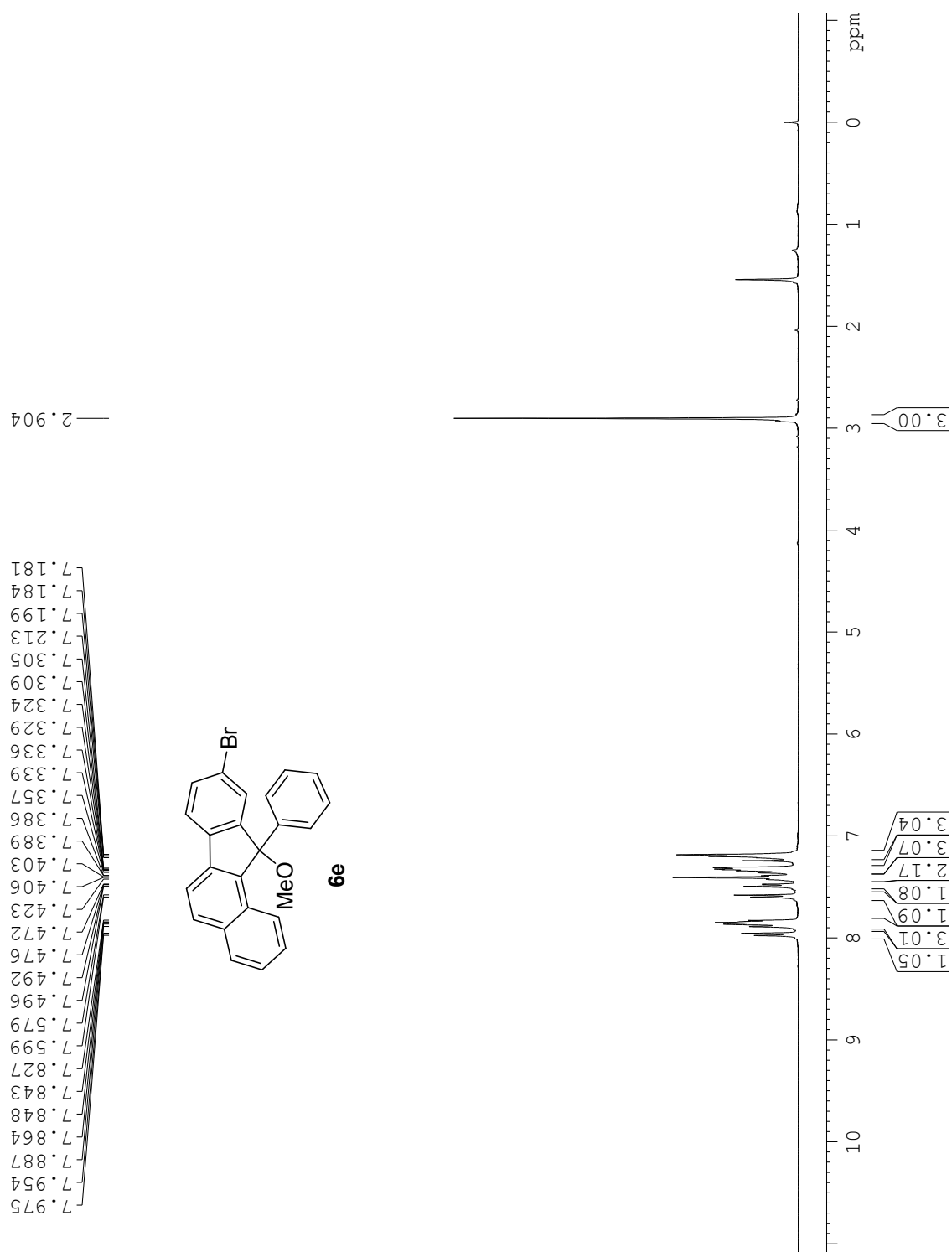


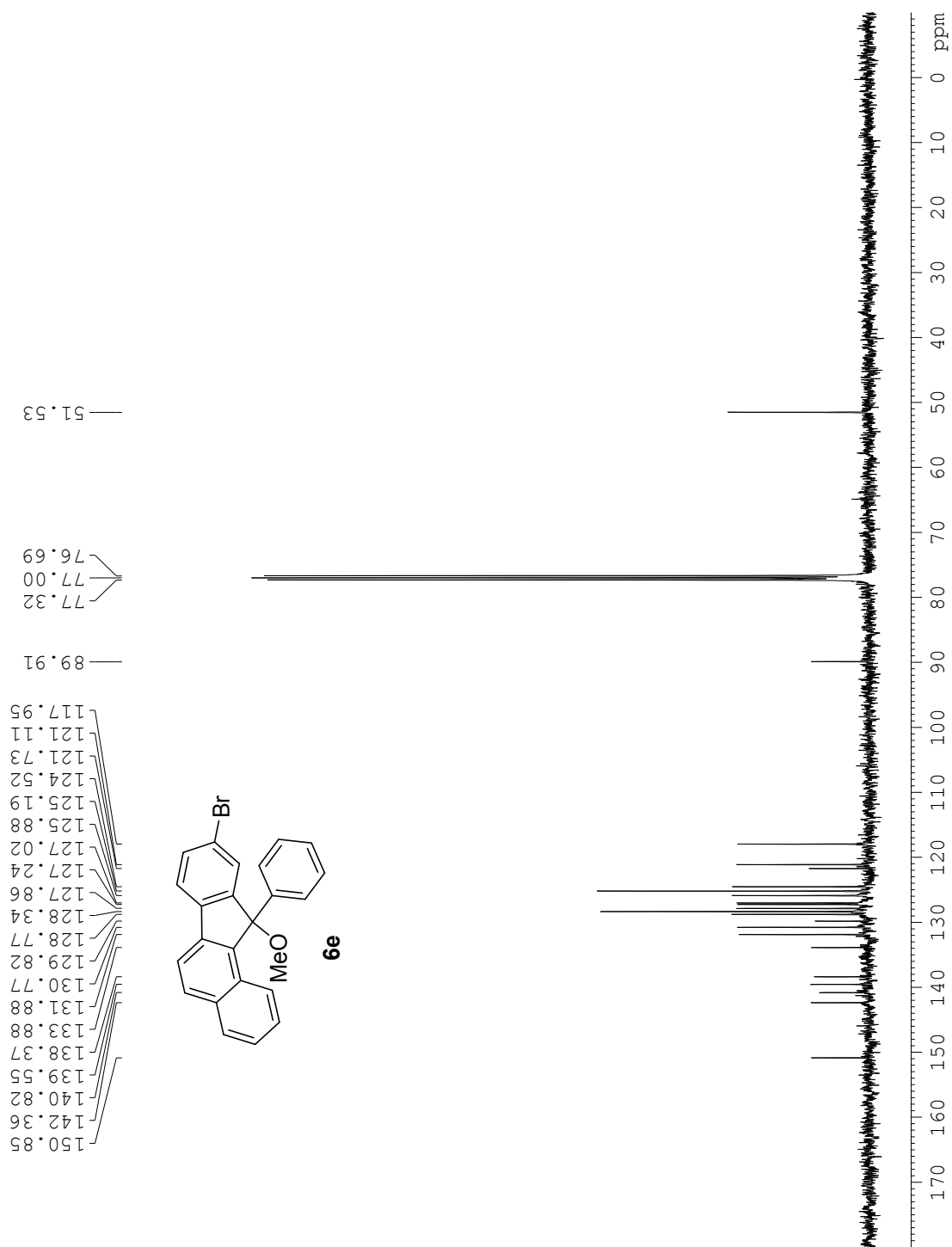


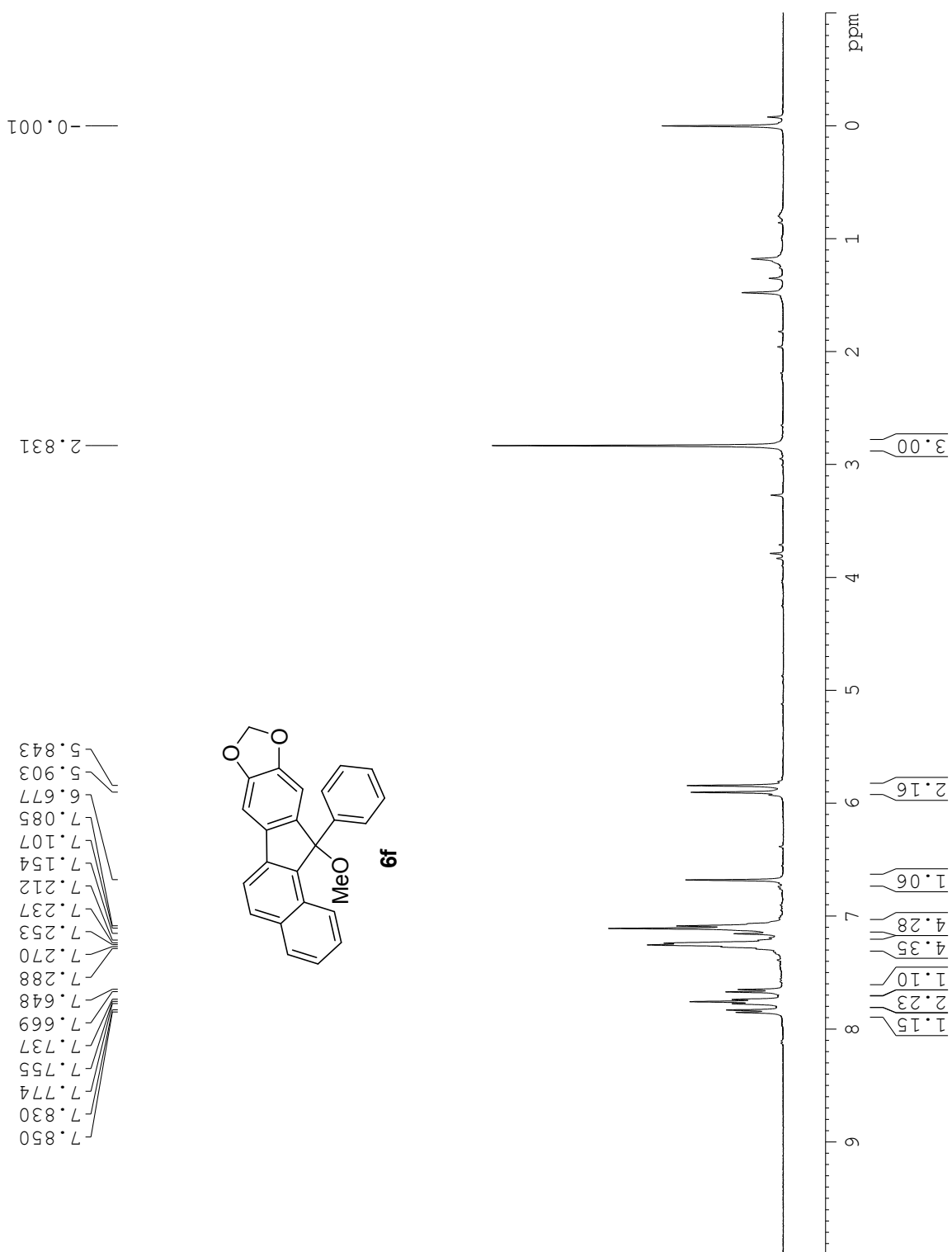


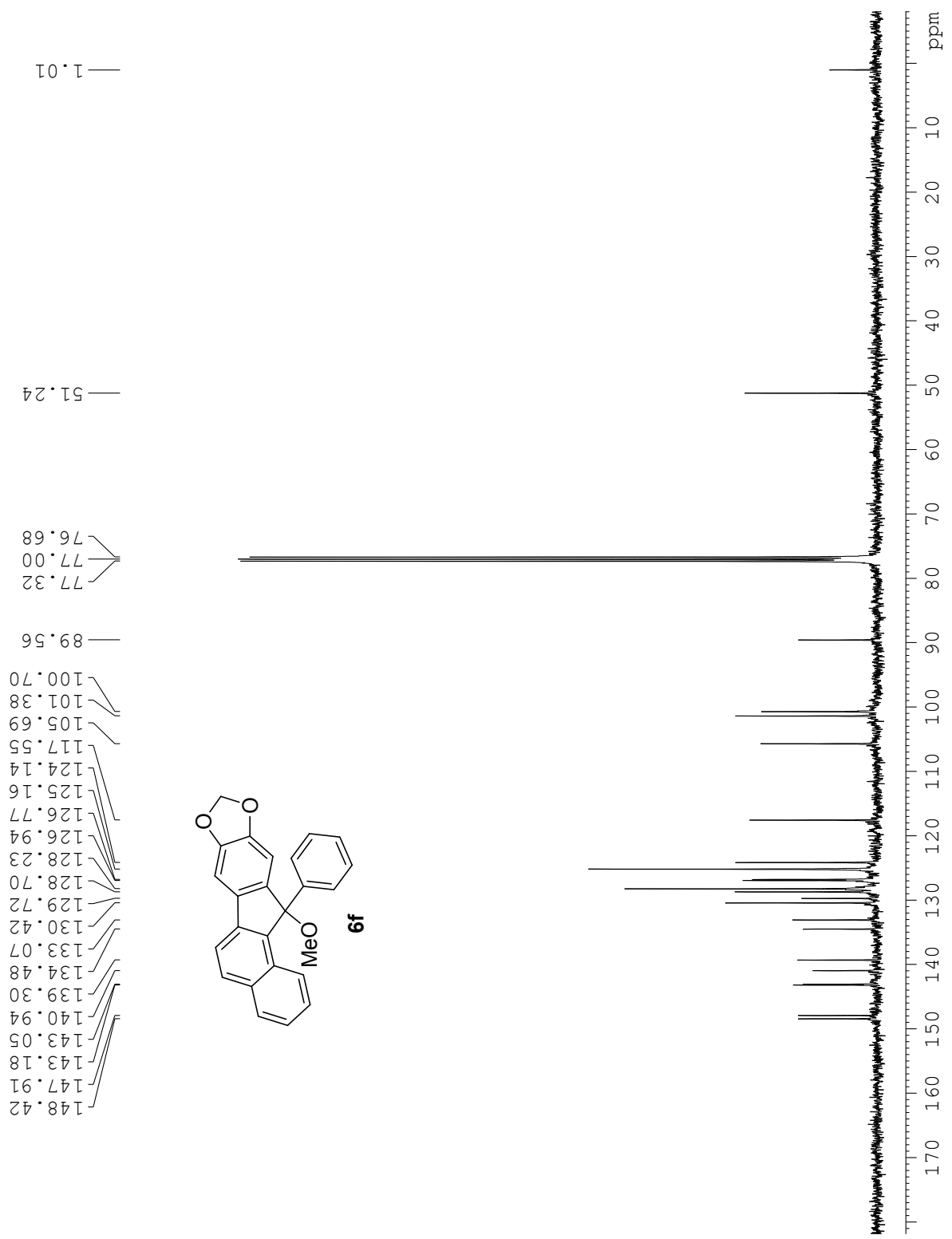


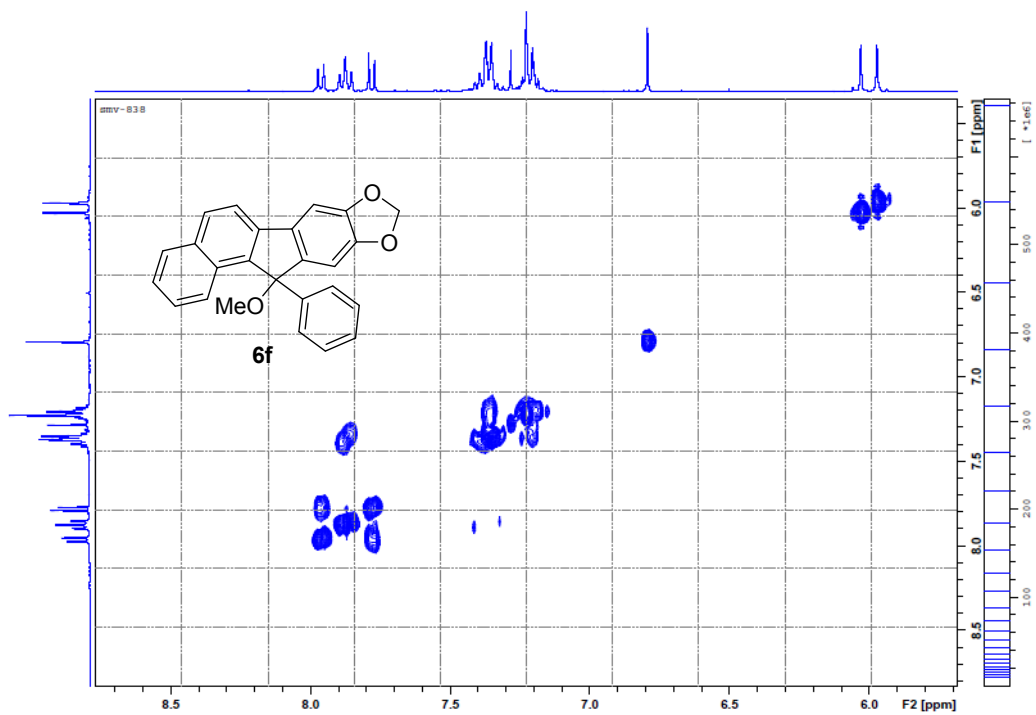




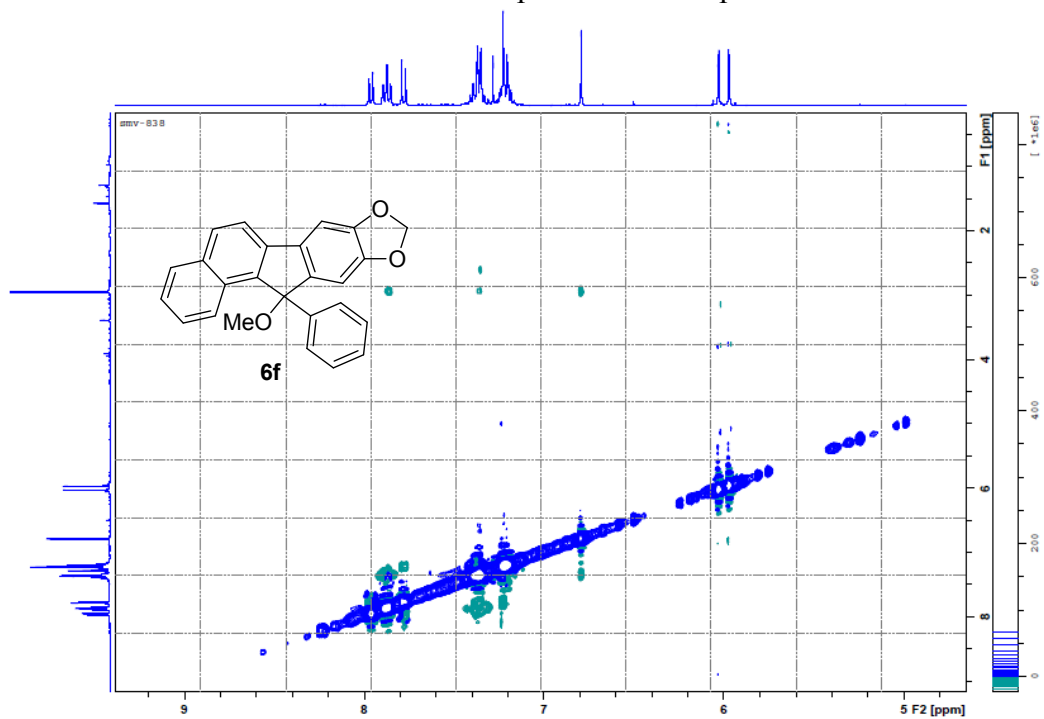




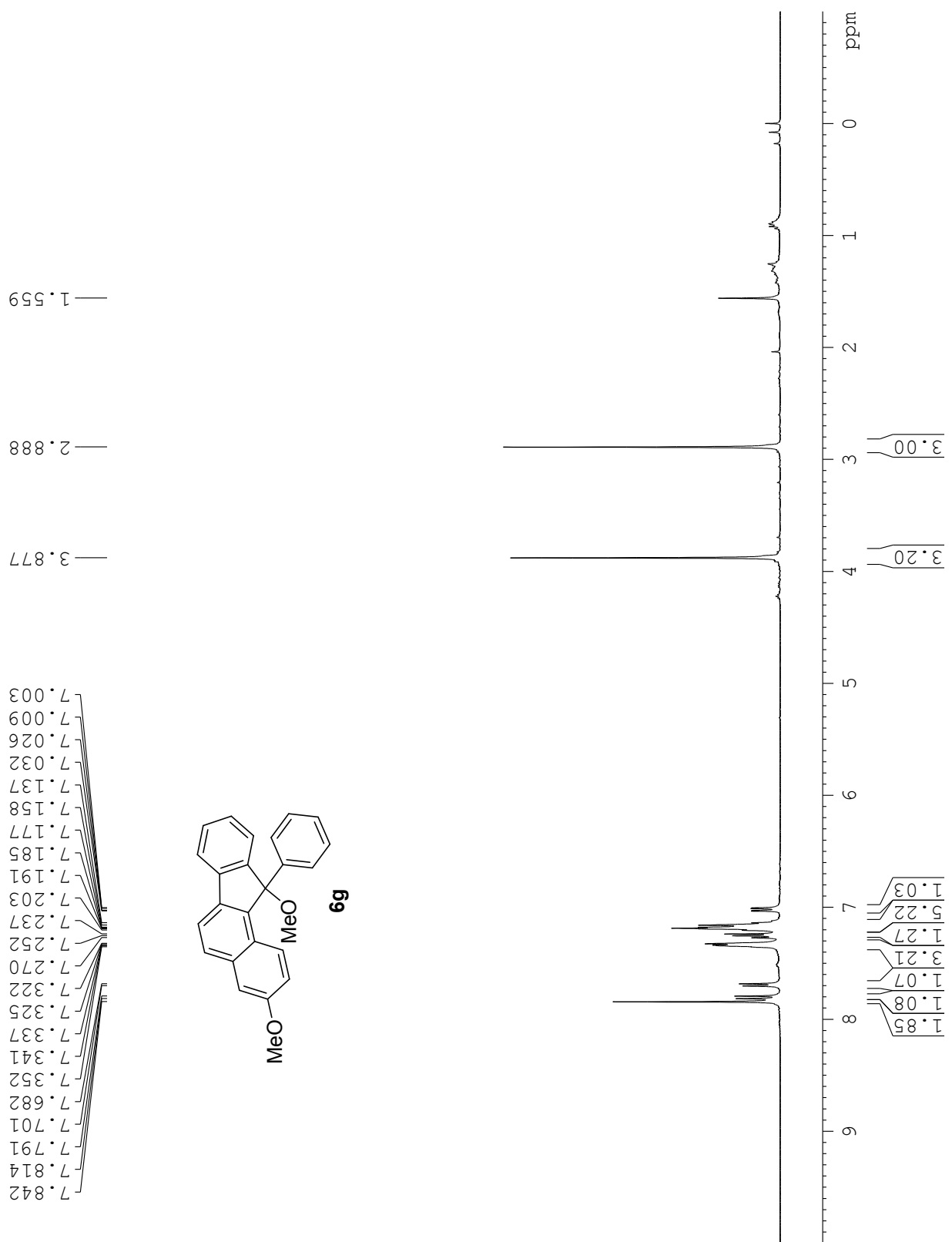


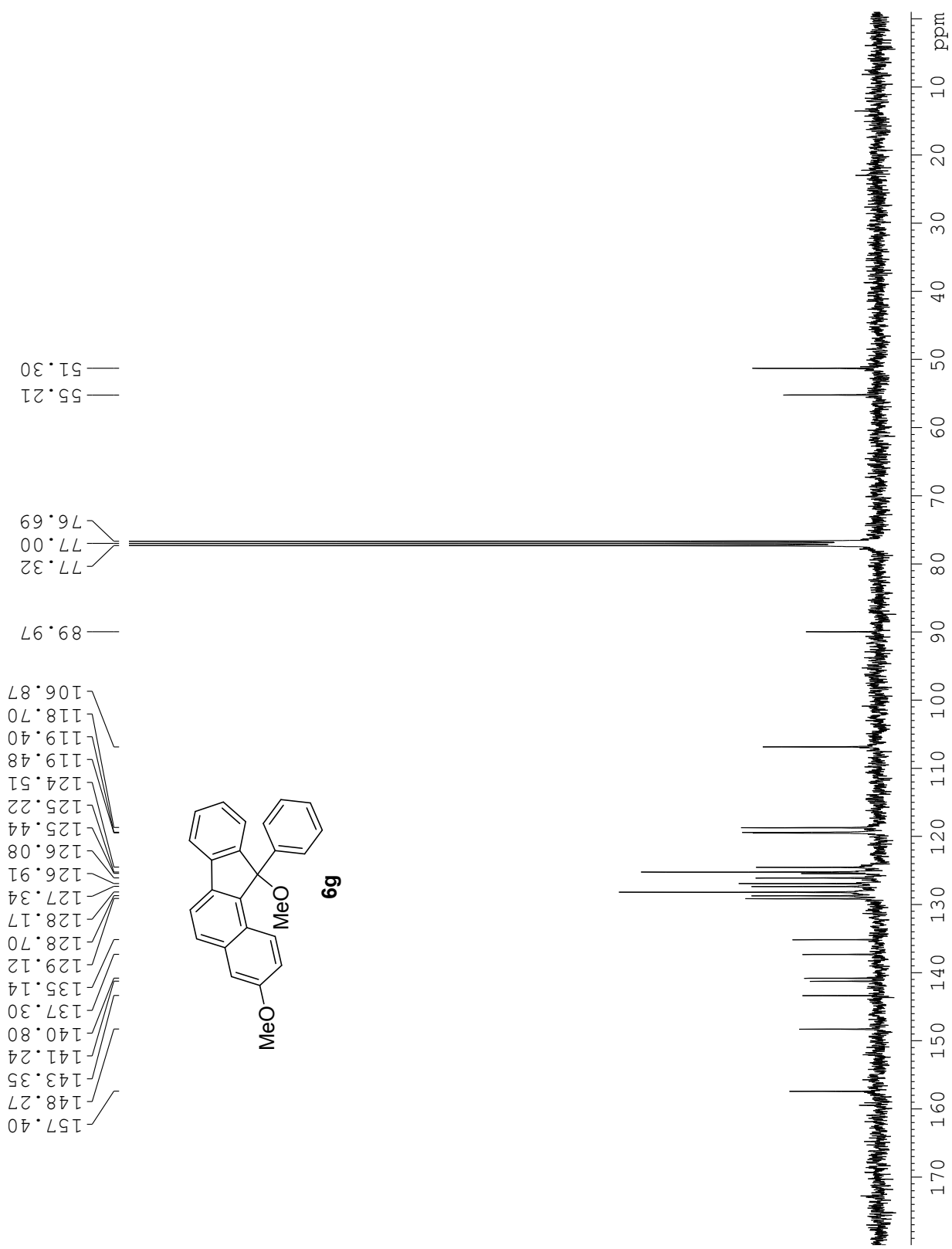


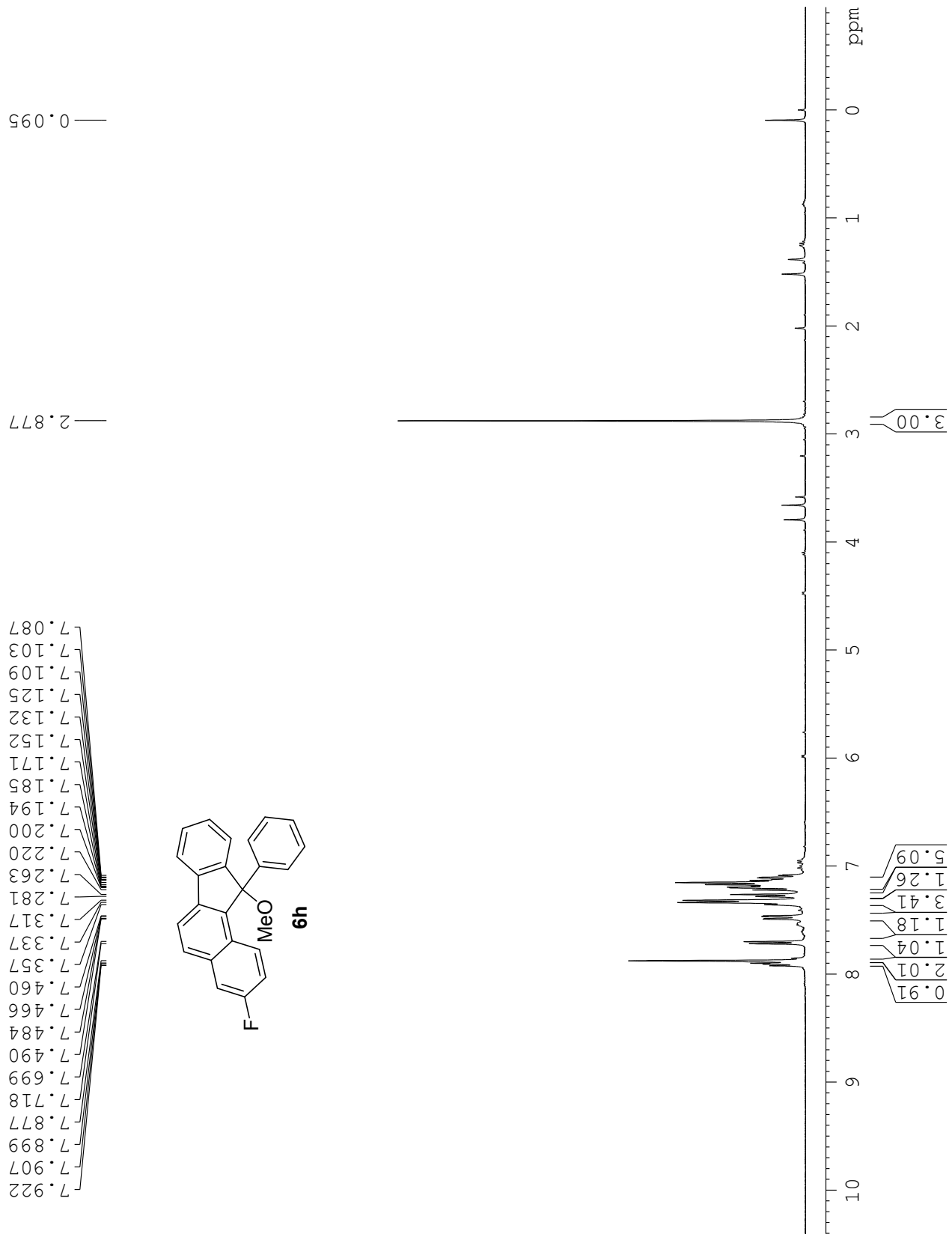
^1H - ^1H COSY spectrum of compound **6f**

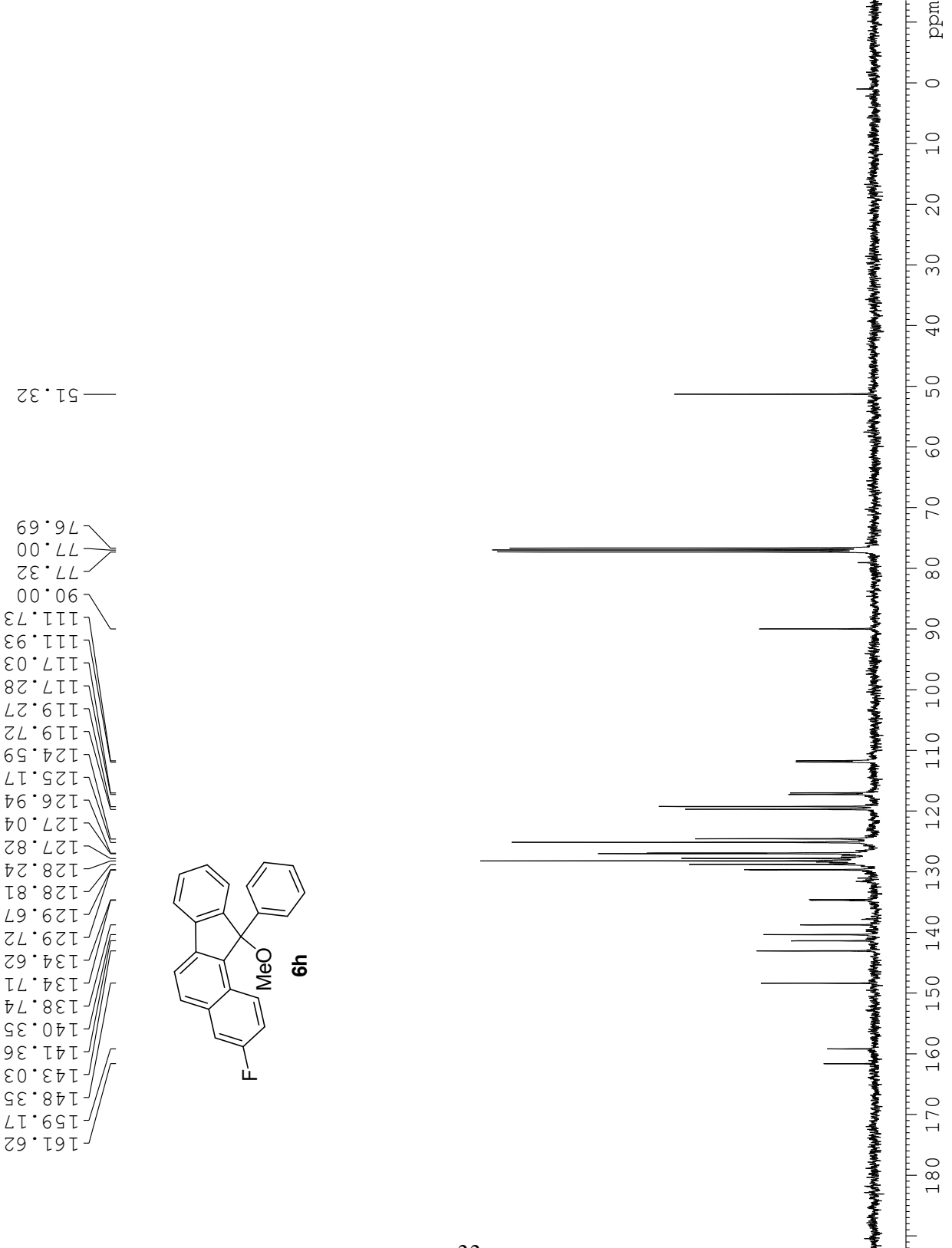


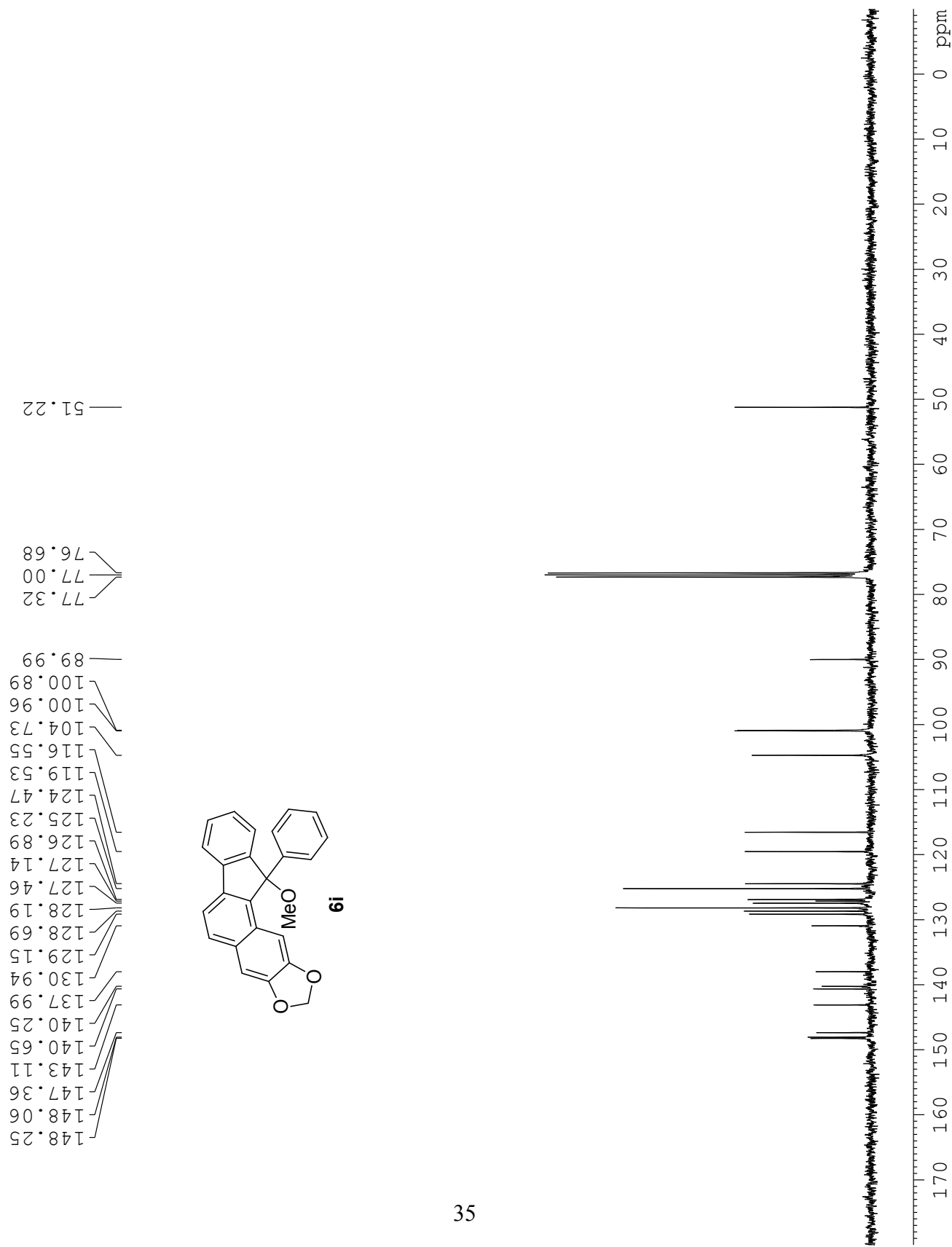
NOESY spectrum of compound **6f**

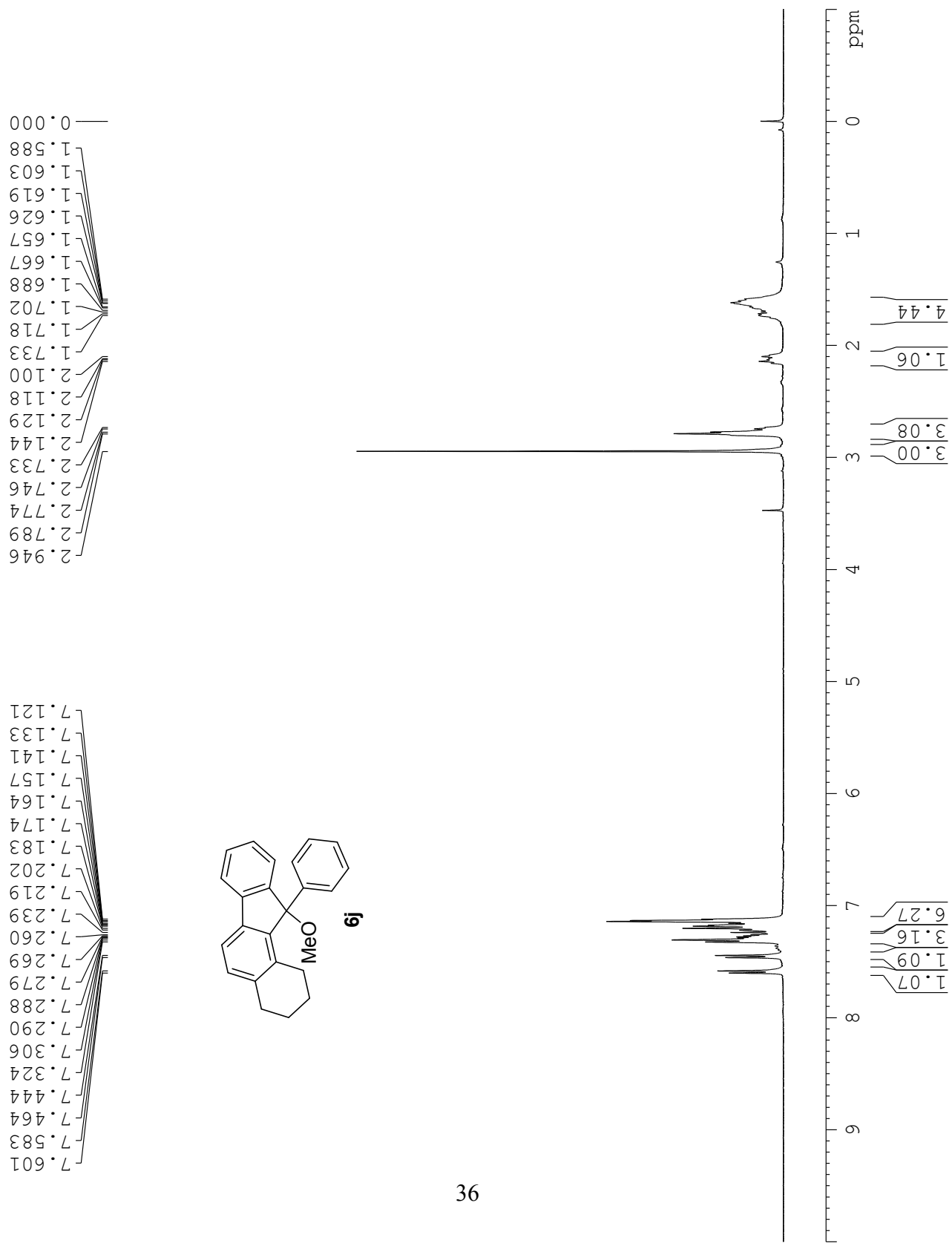


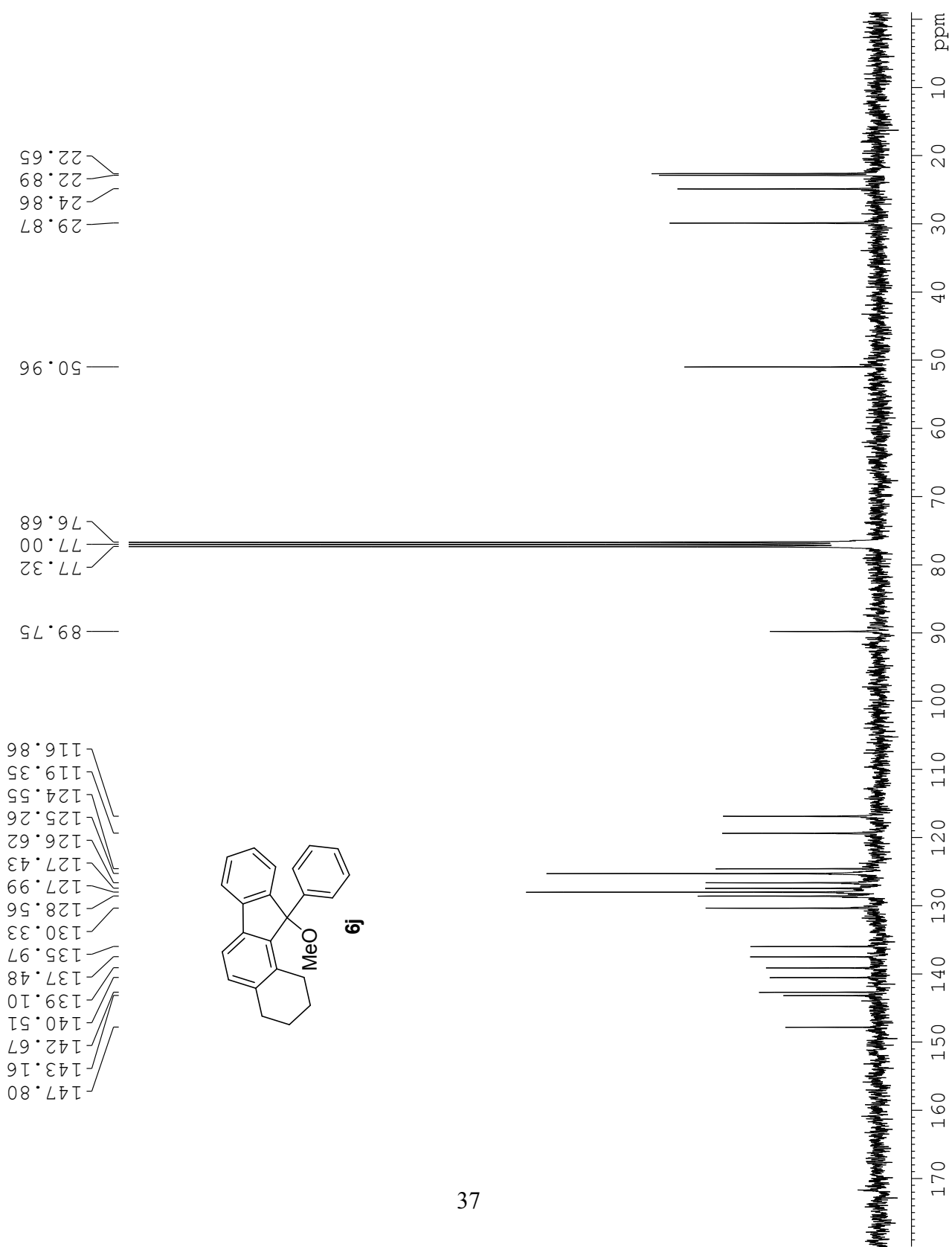


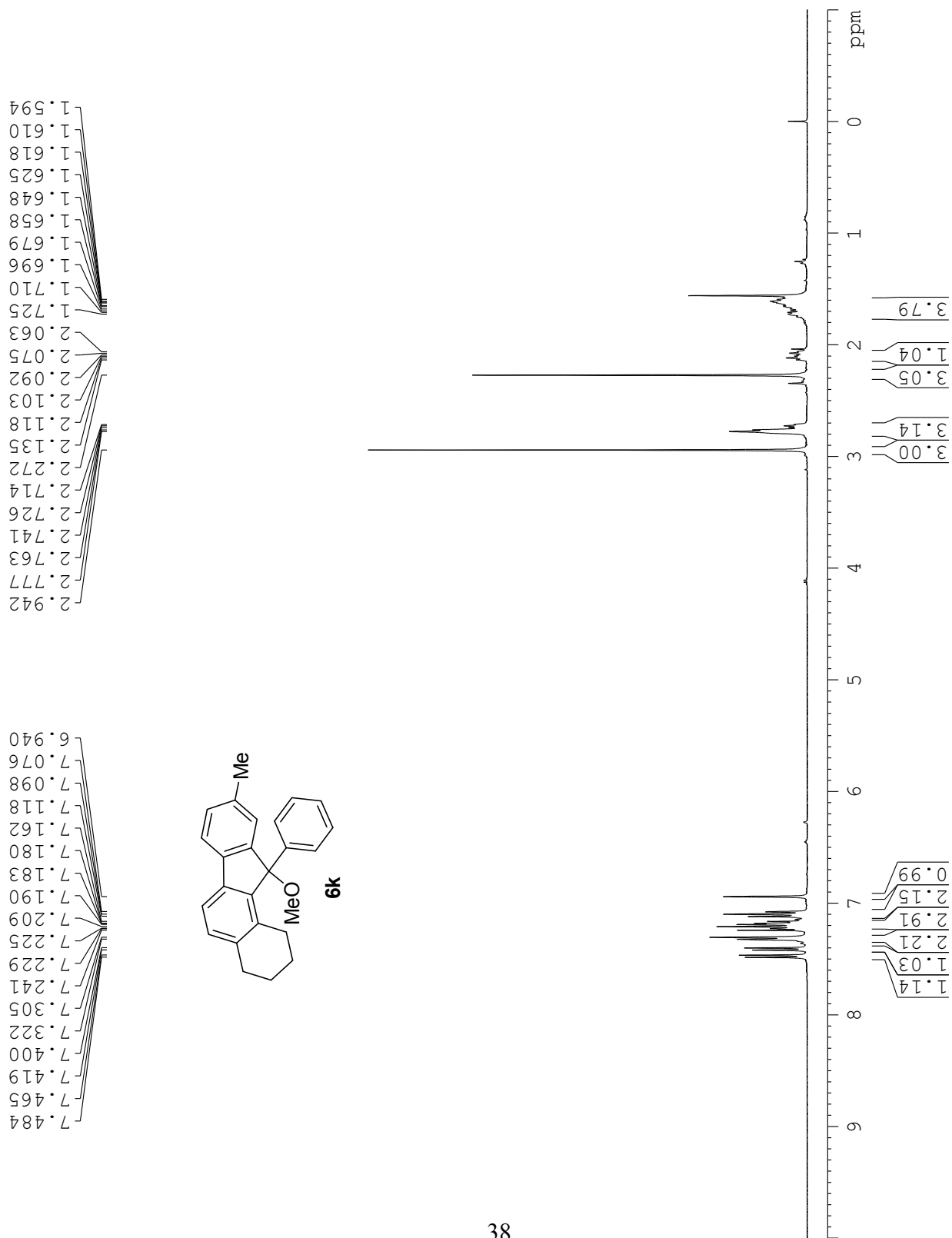


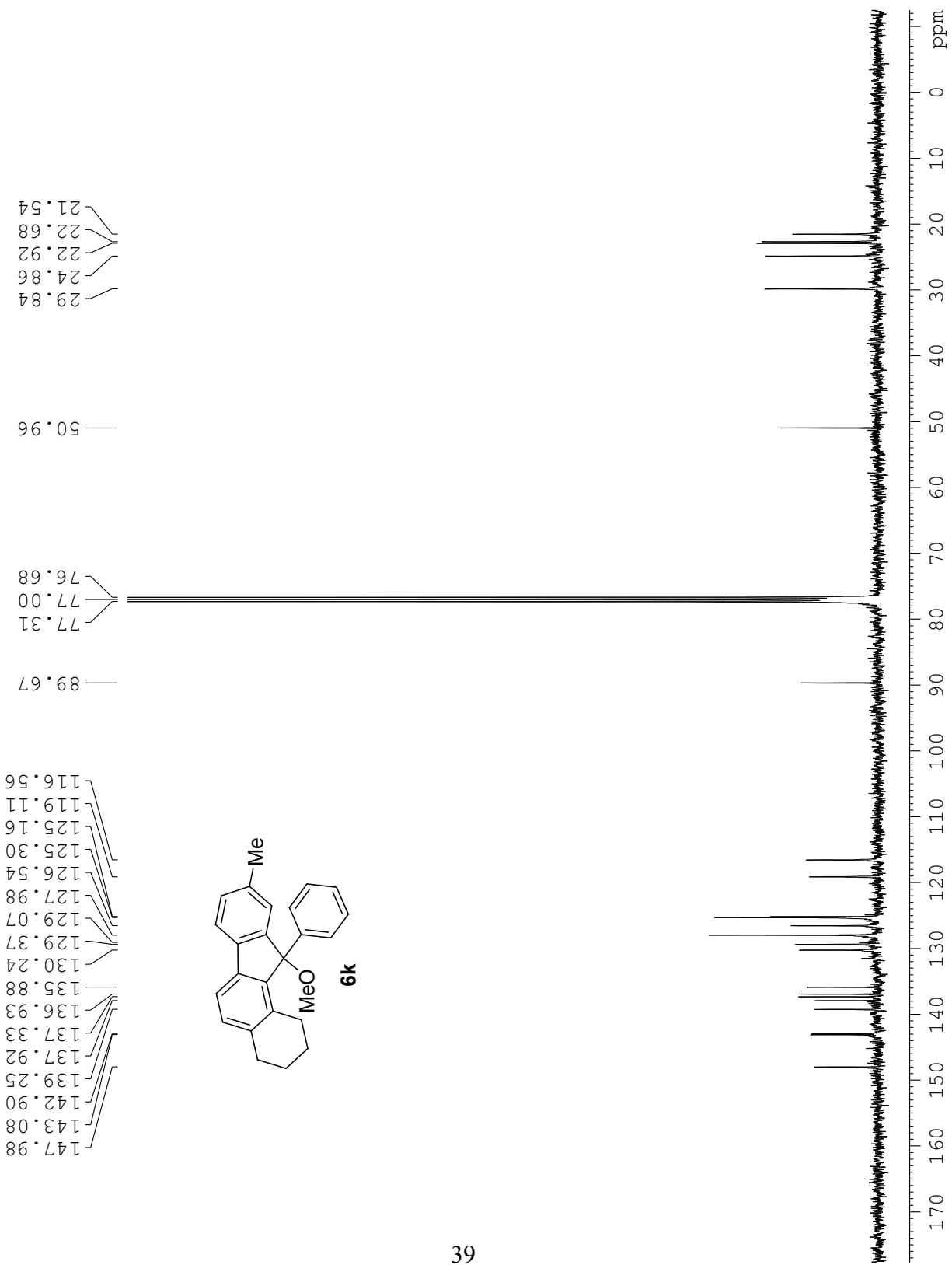


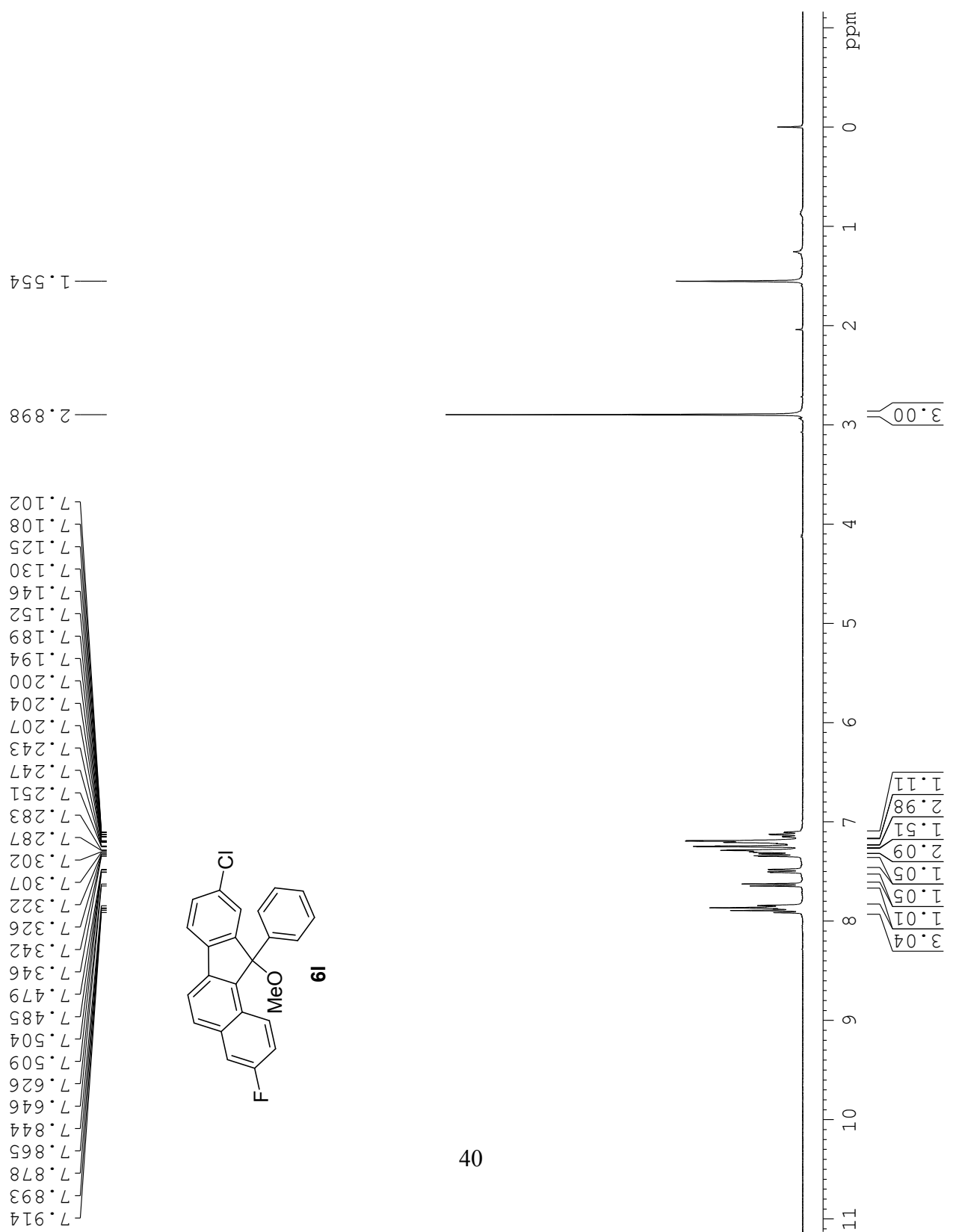


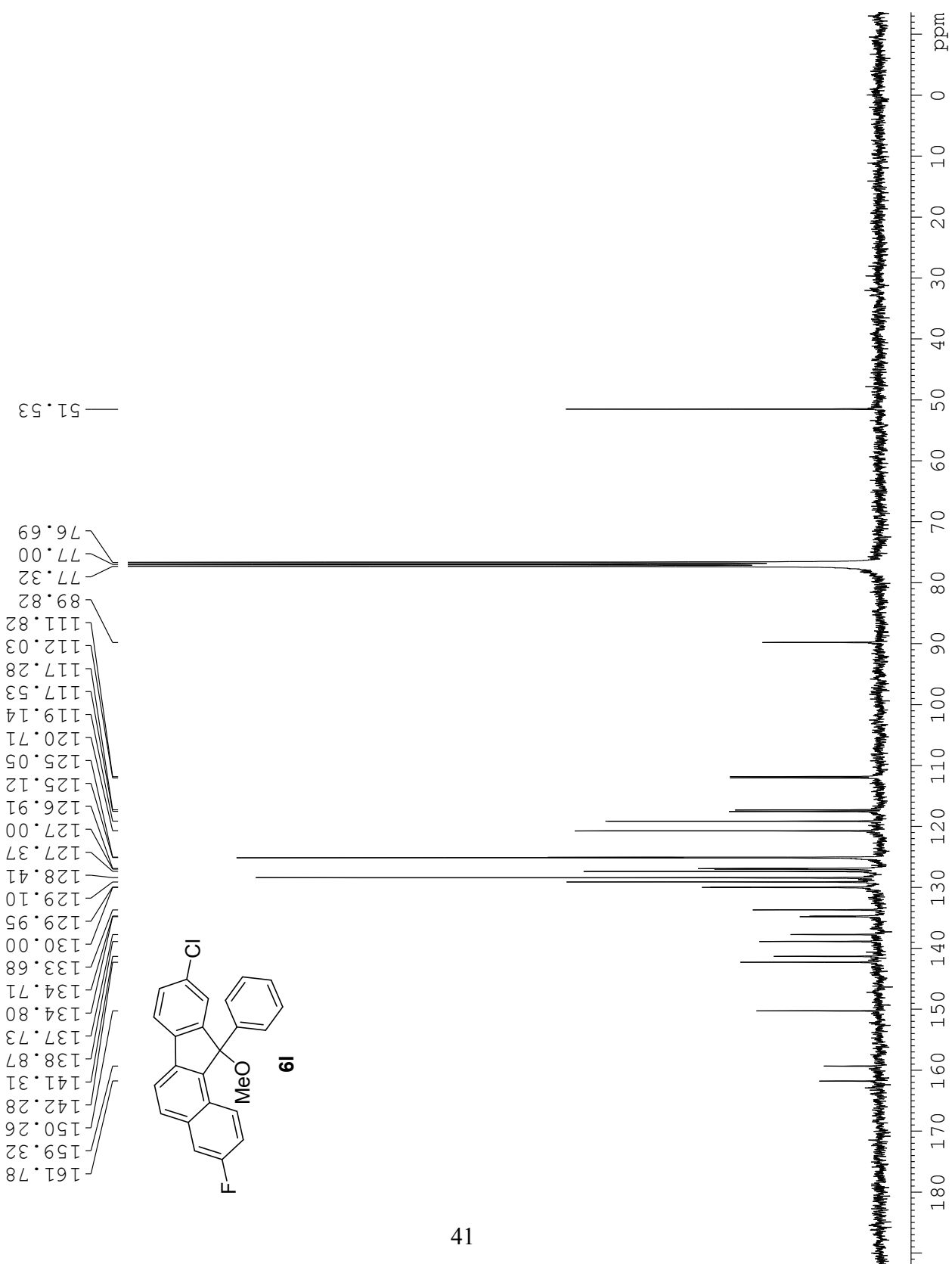


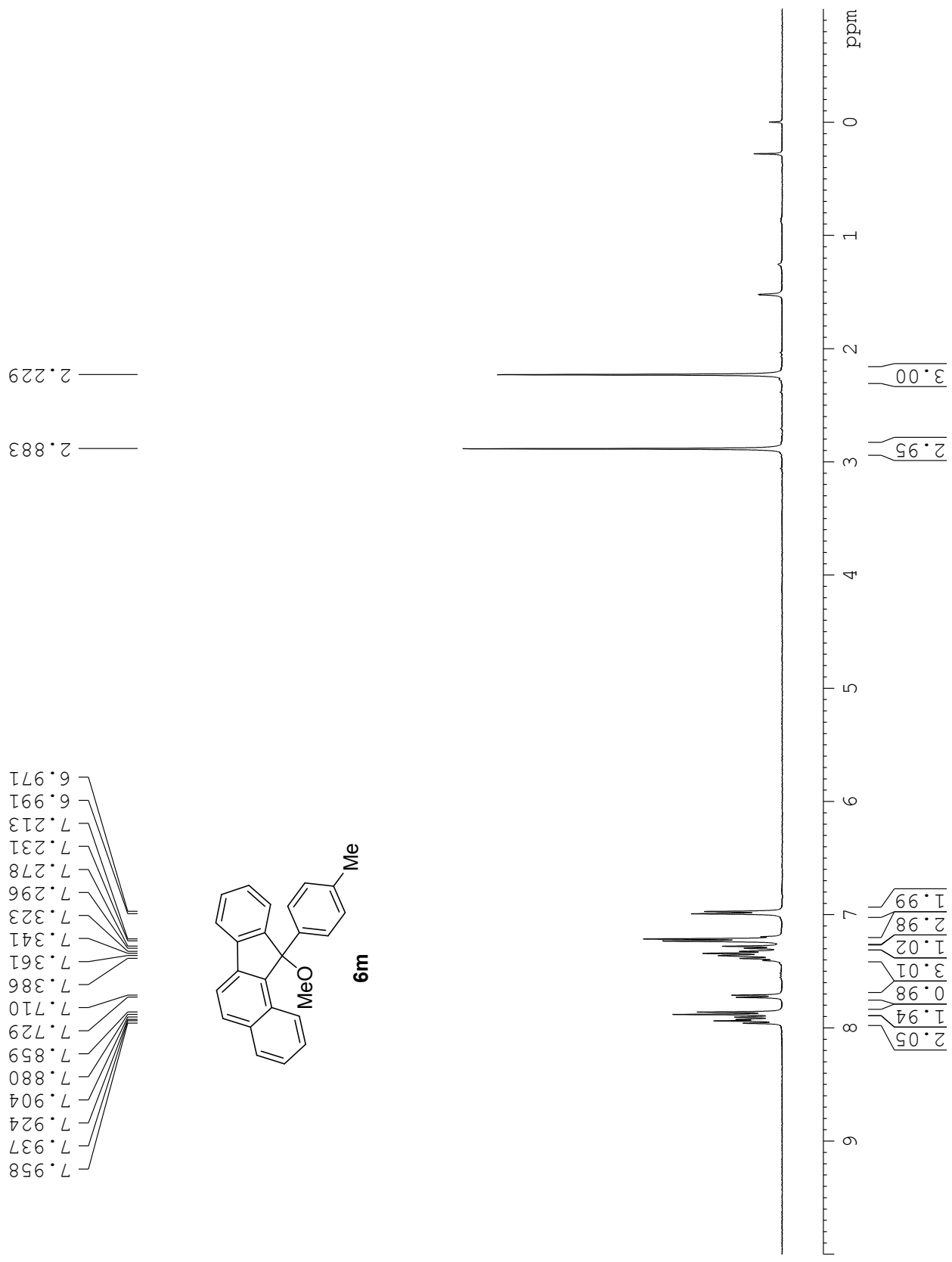


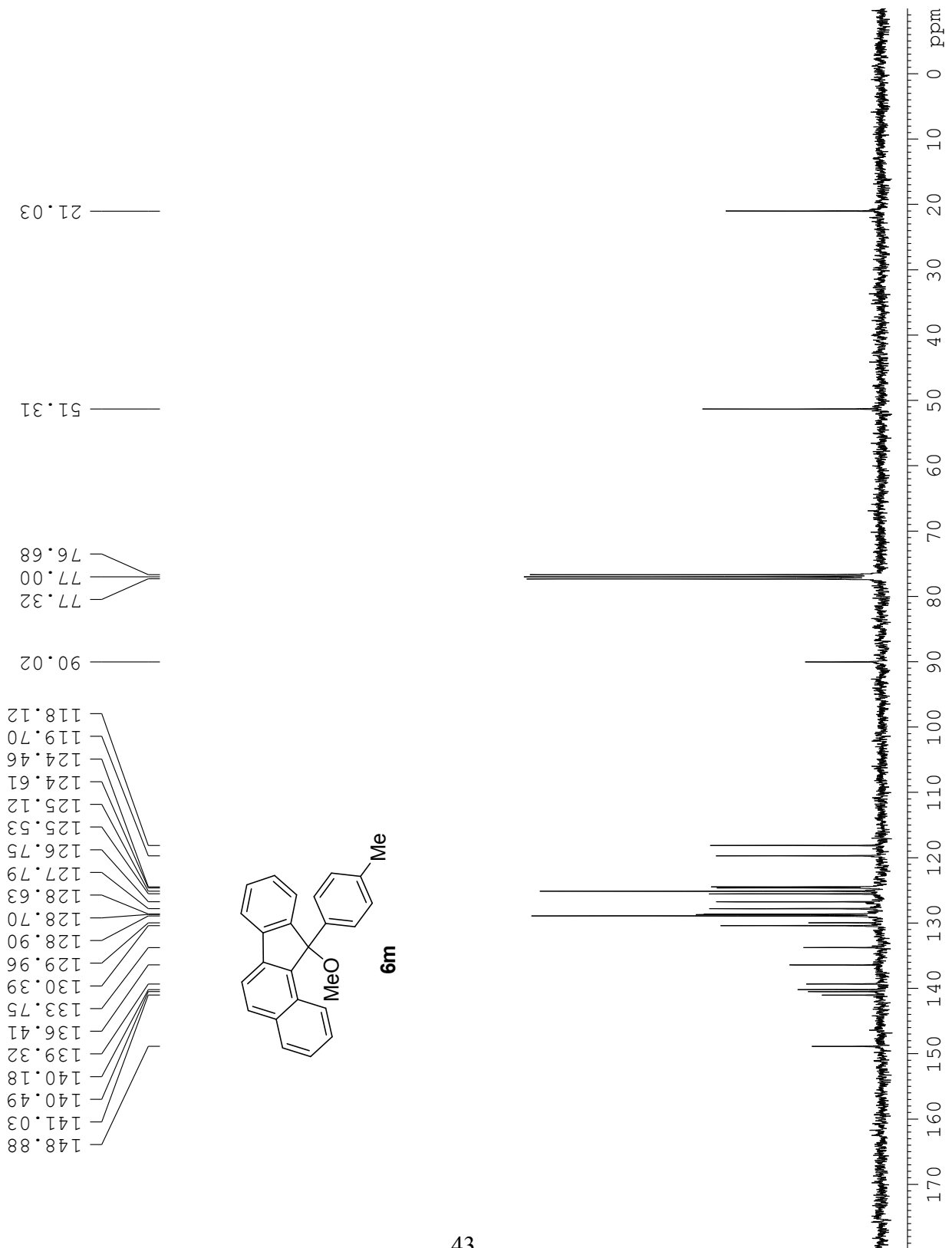


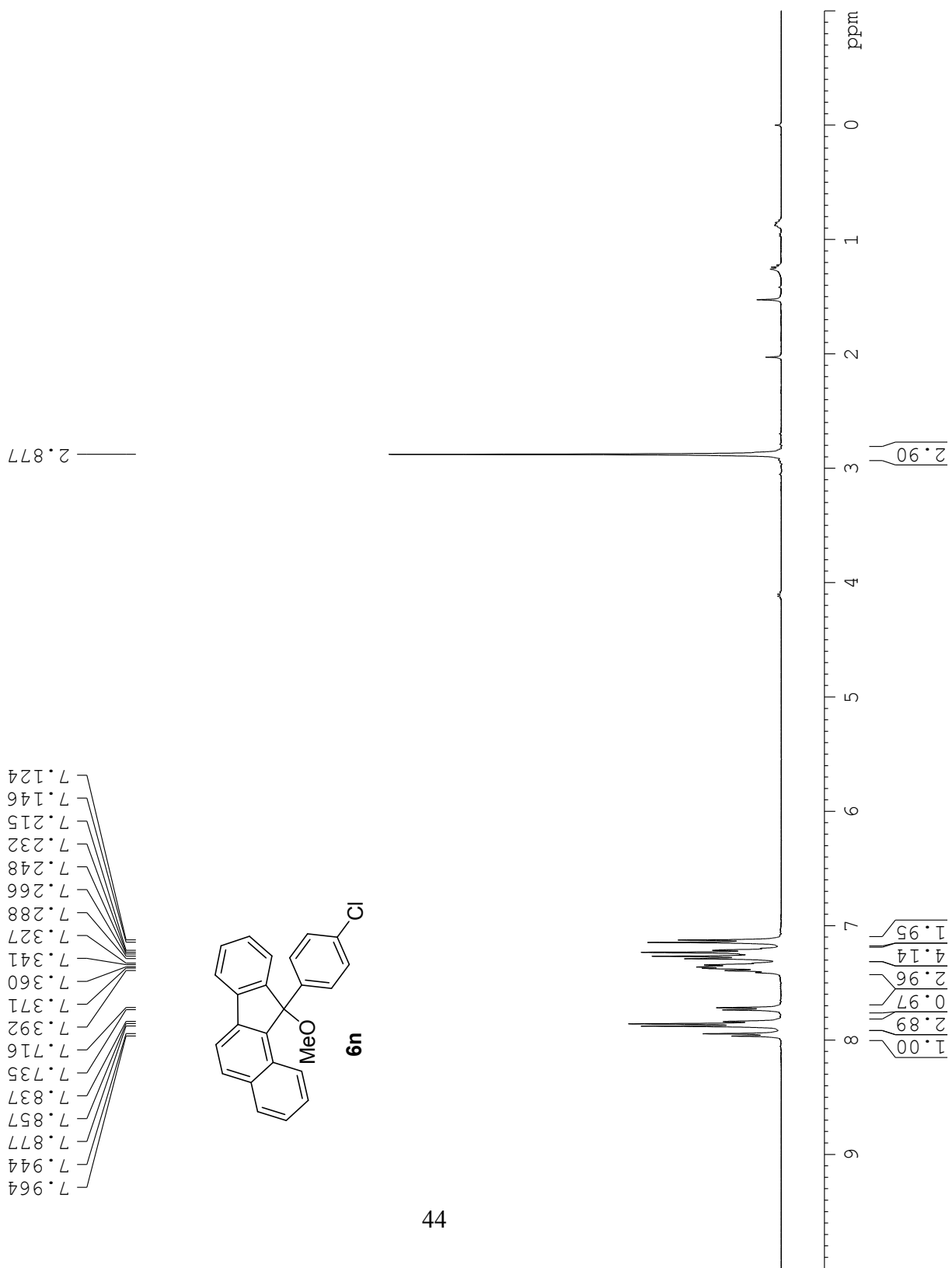


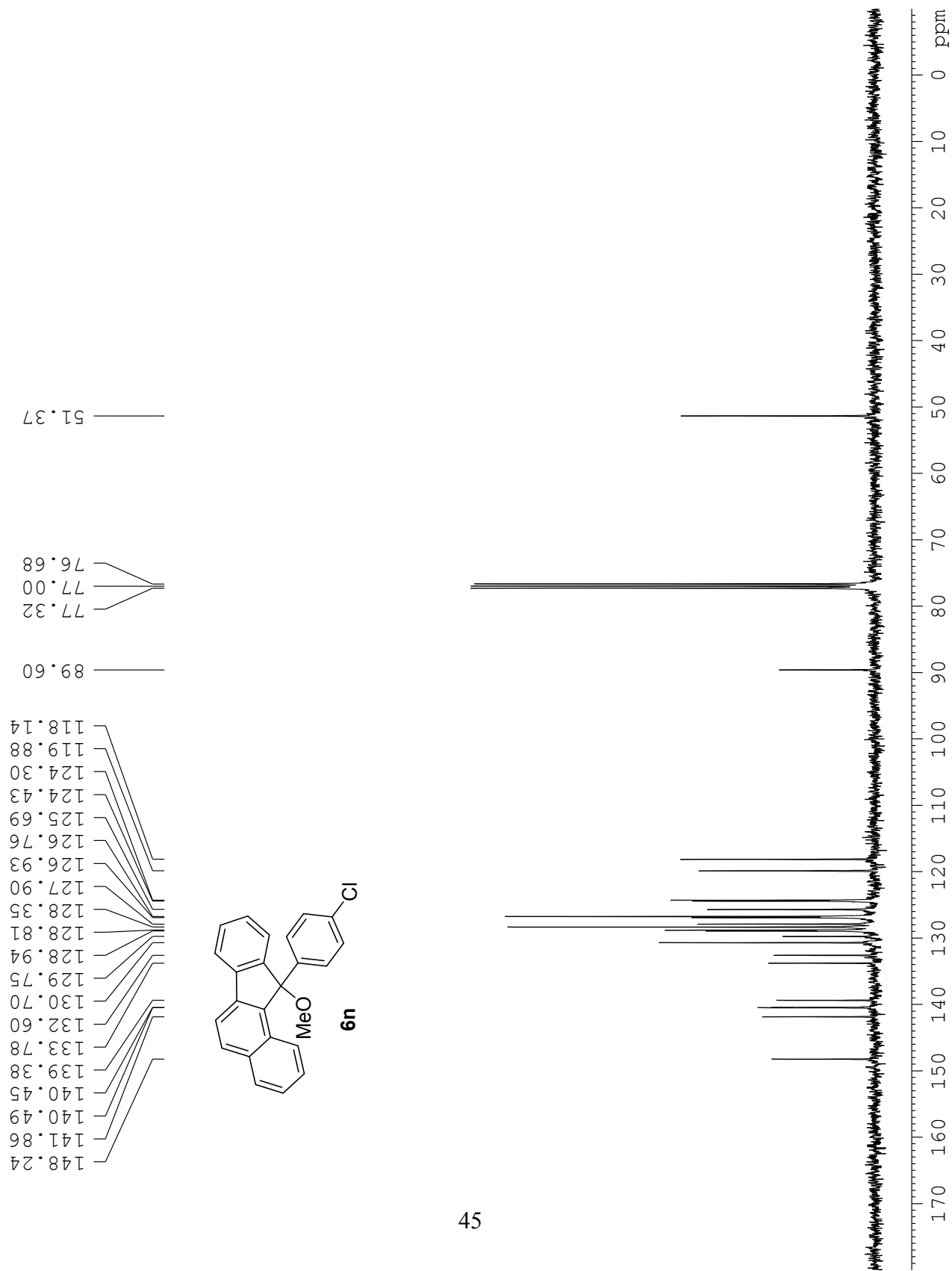


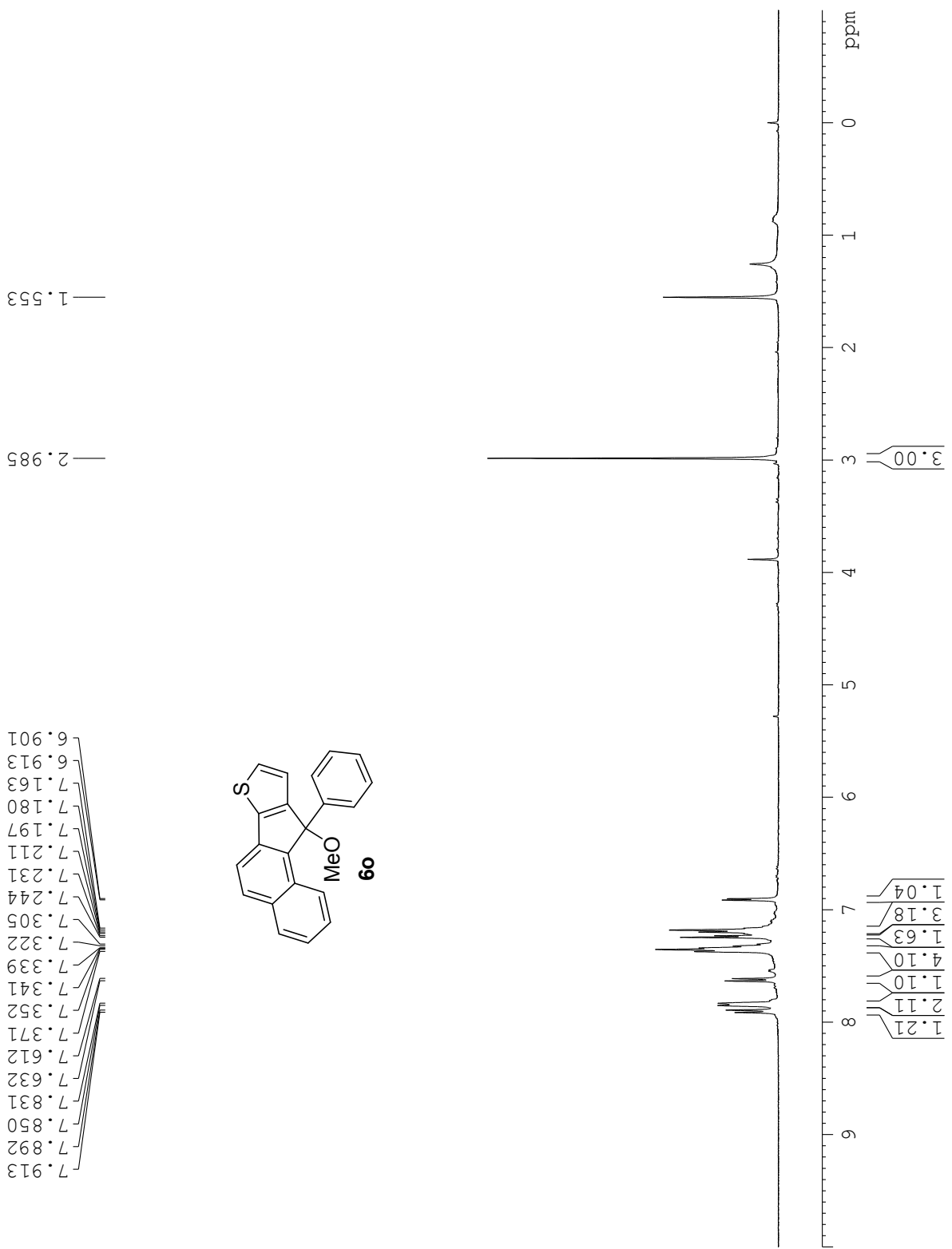


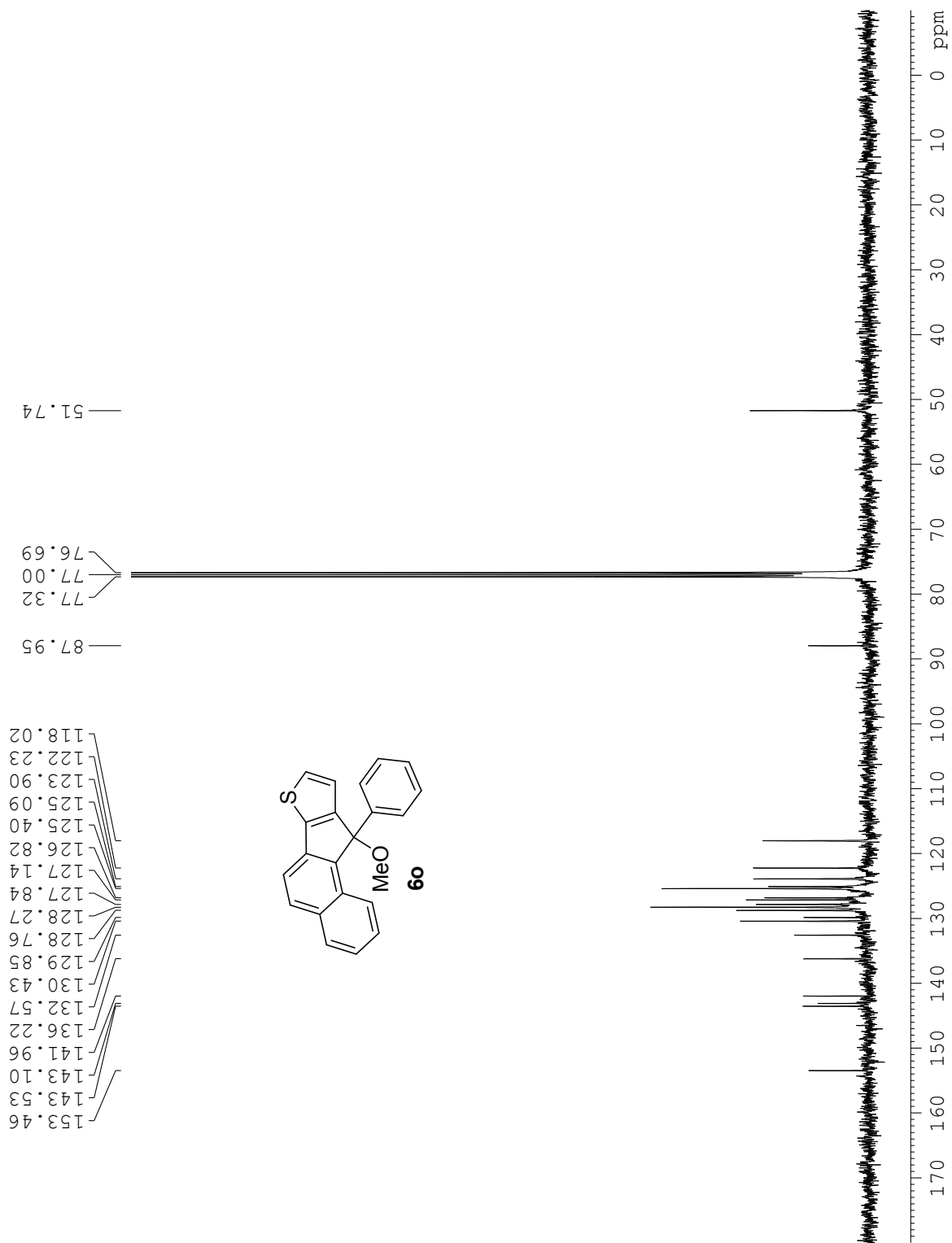


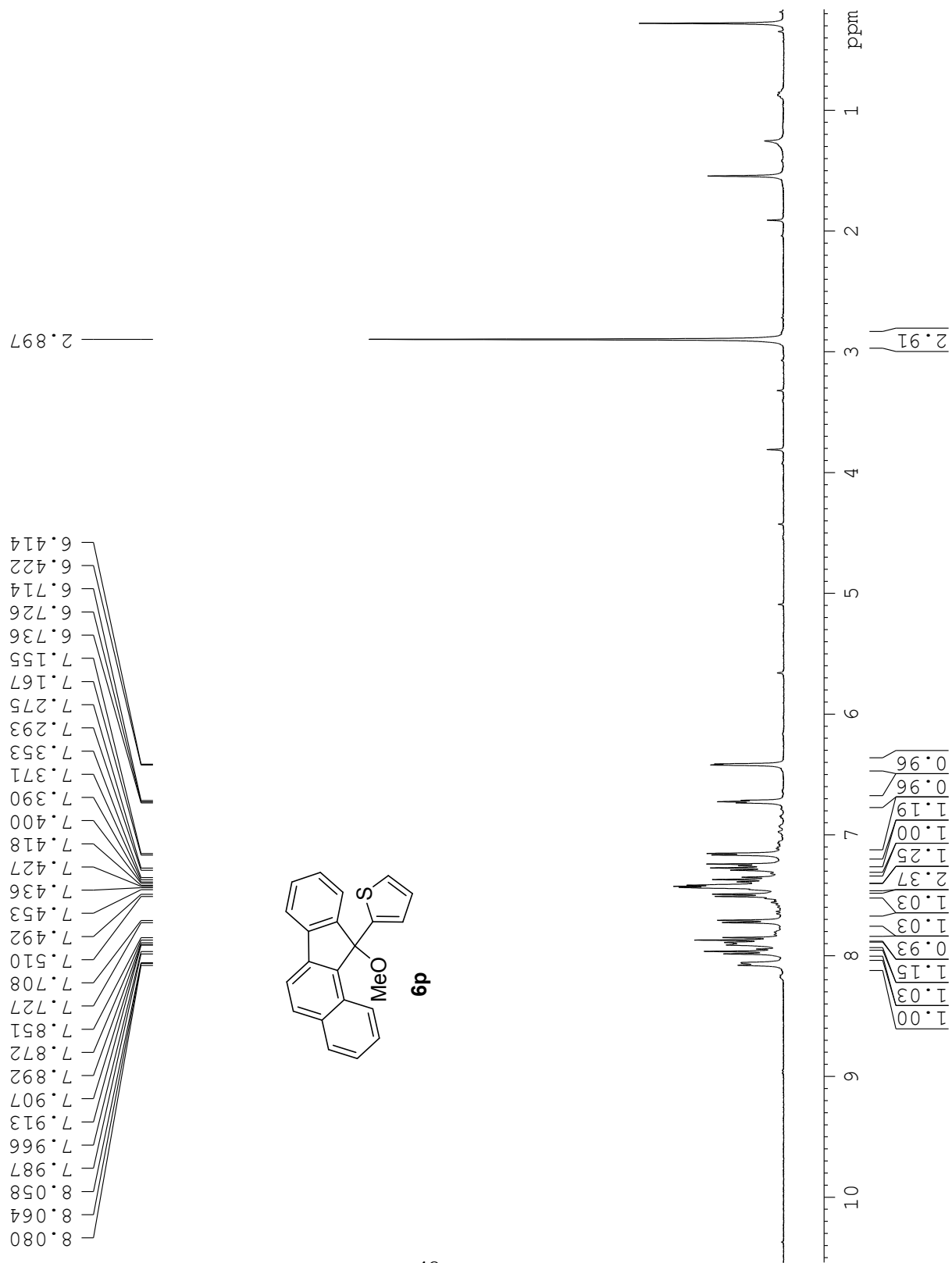


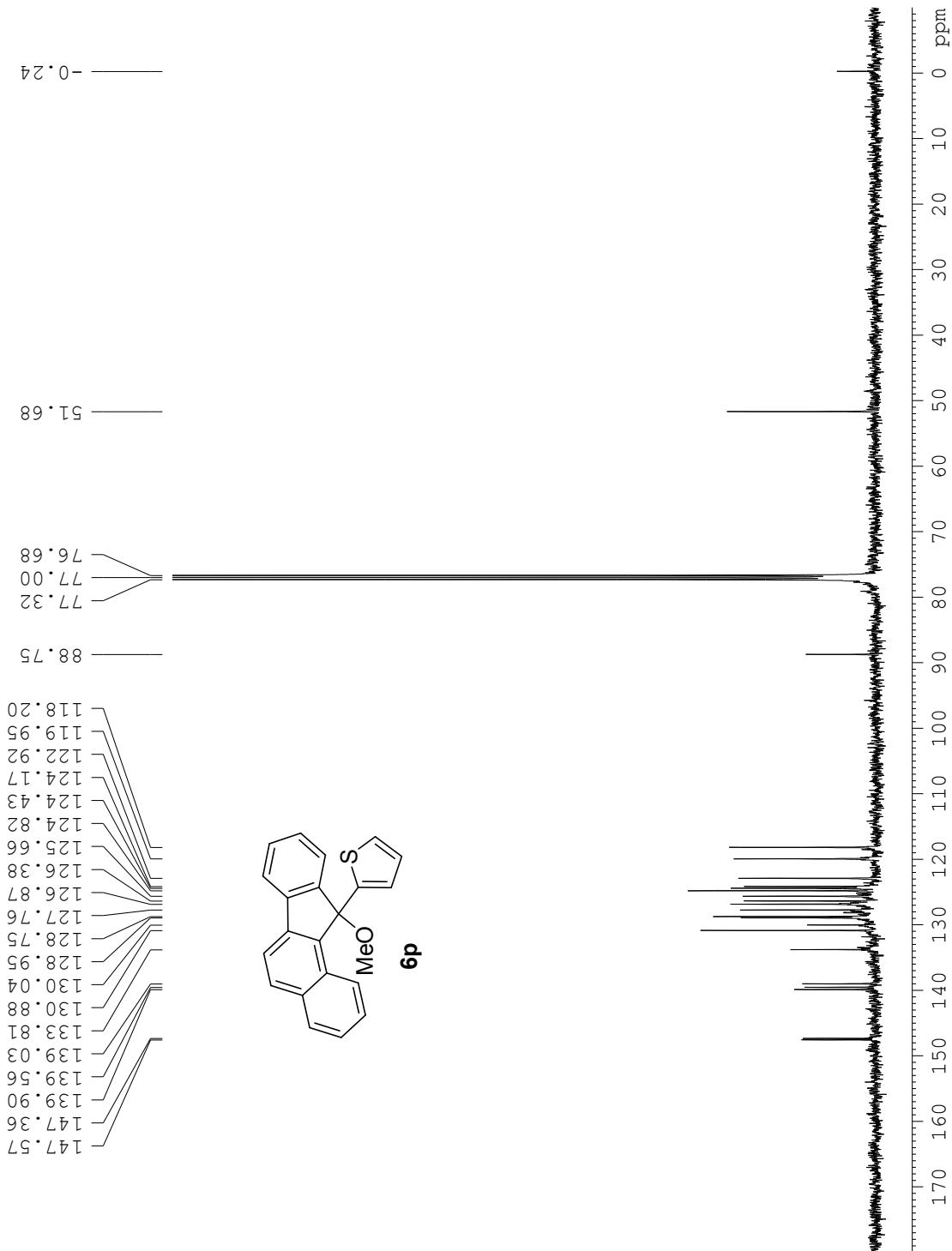


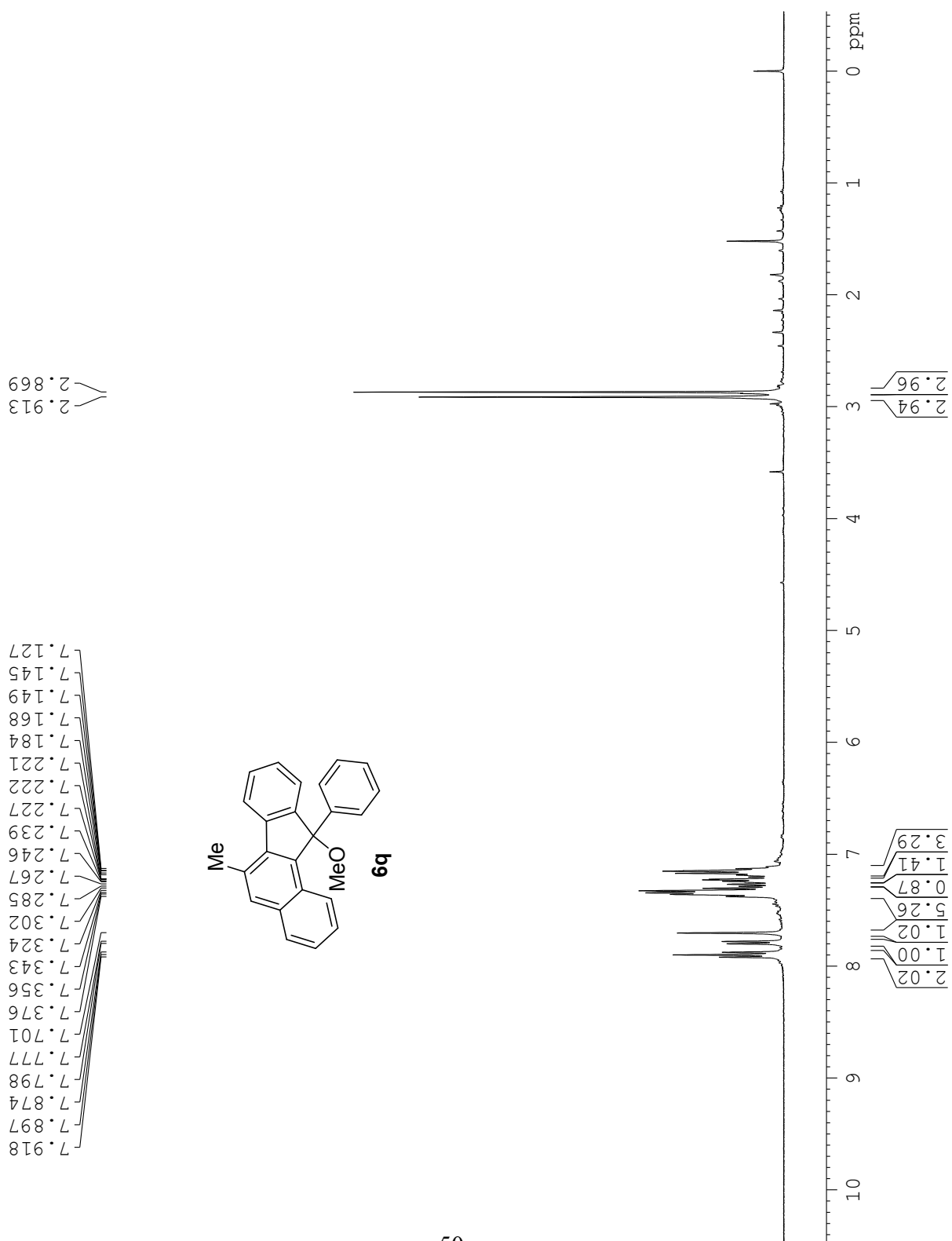


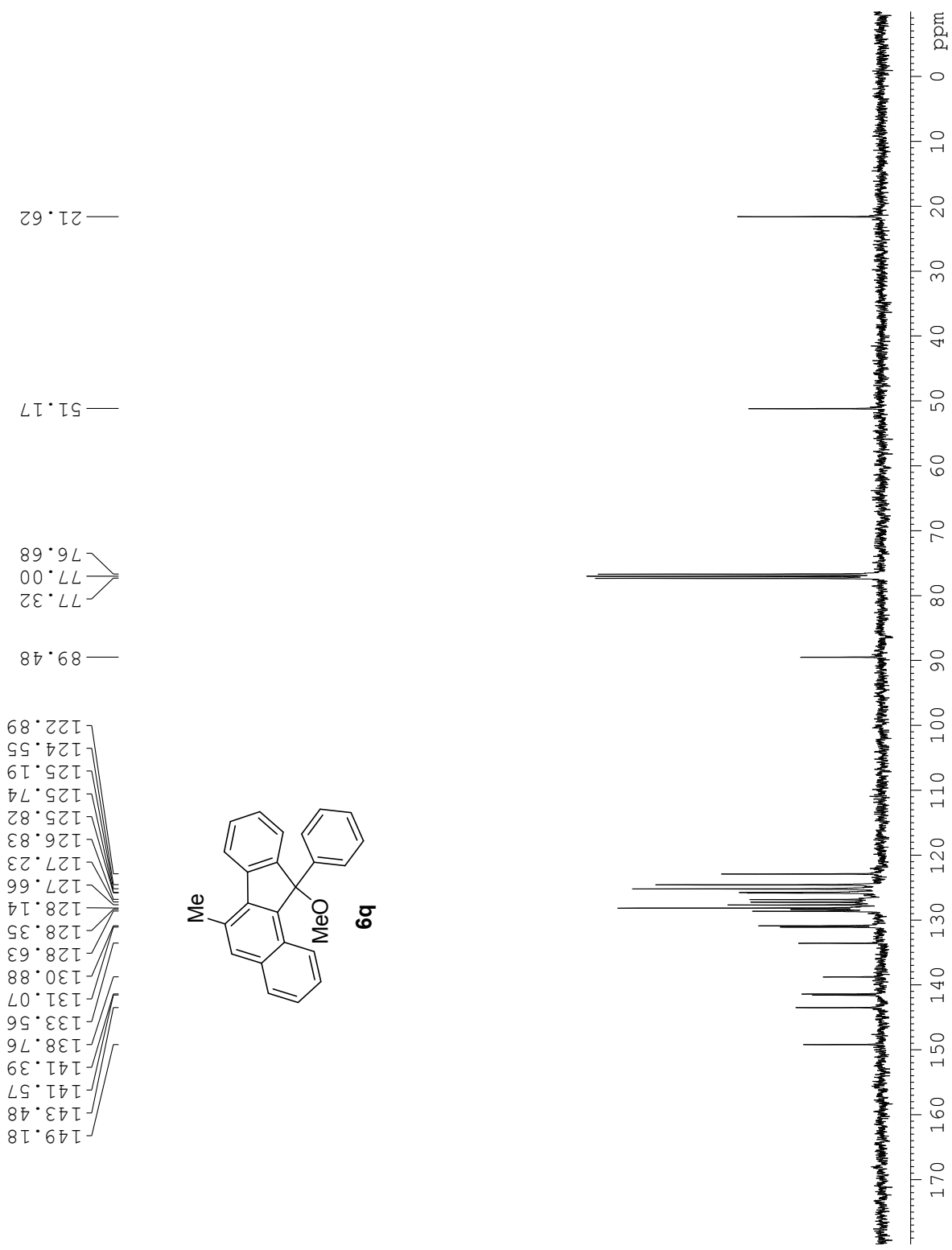


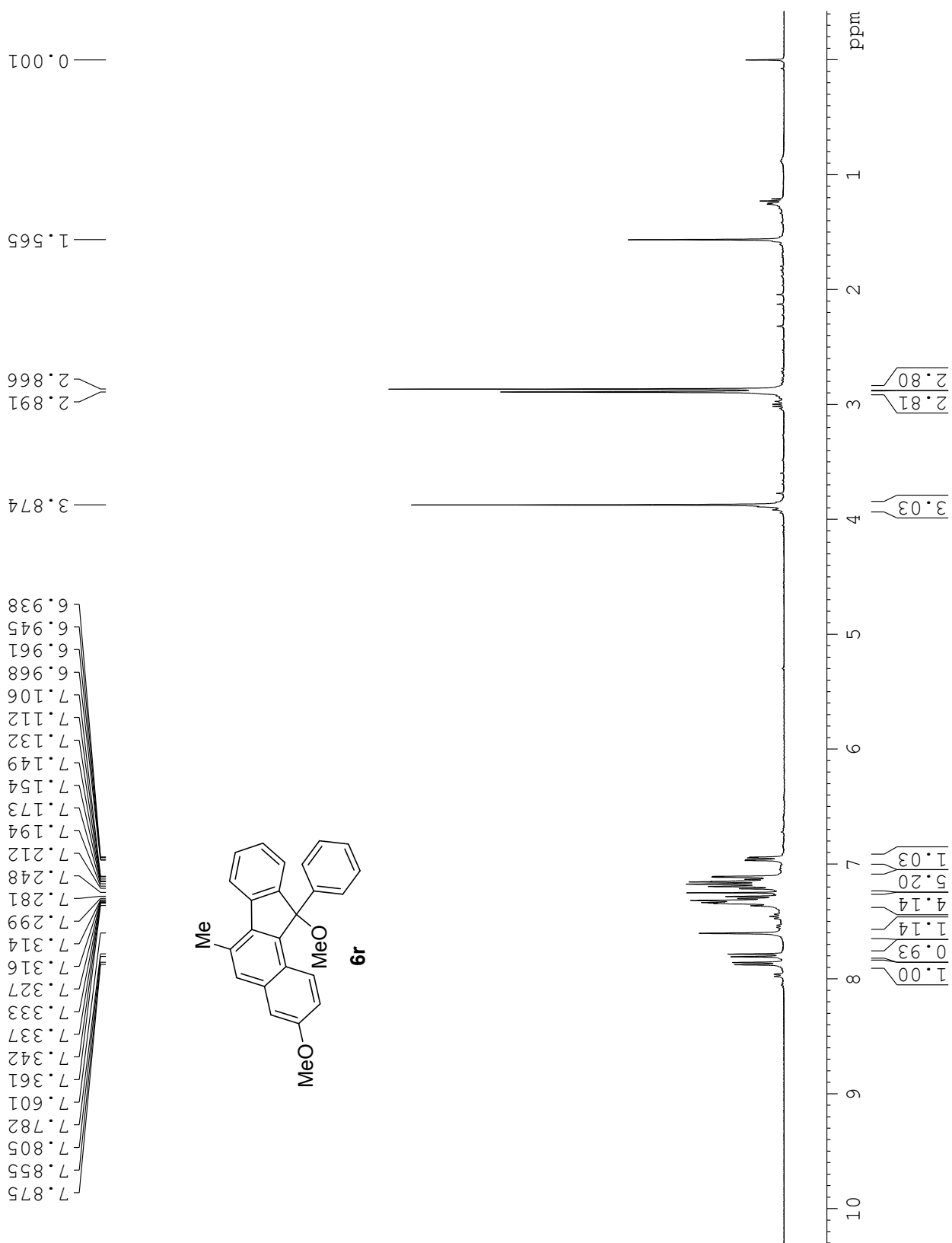


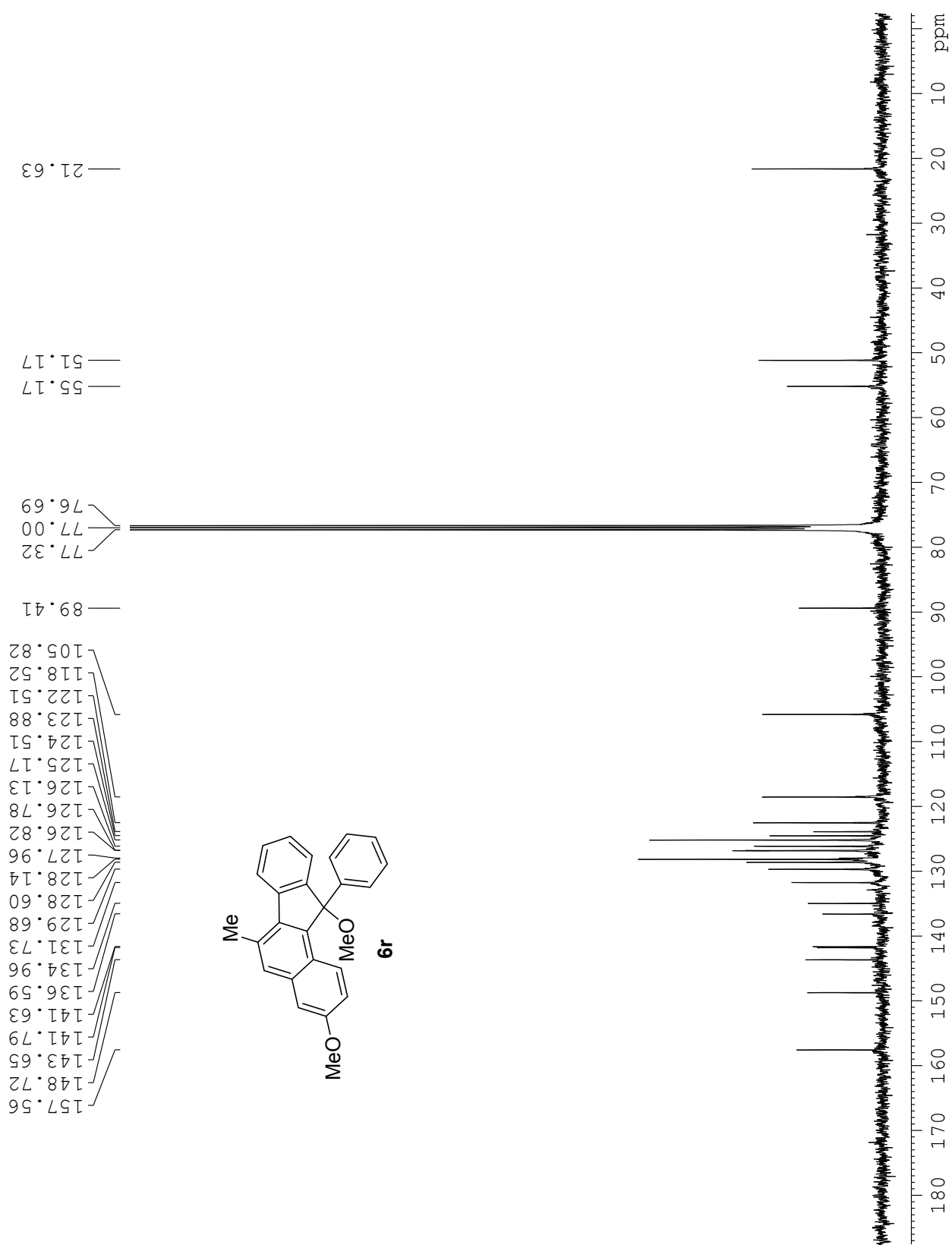


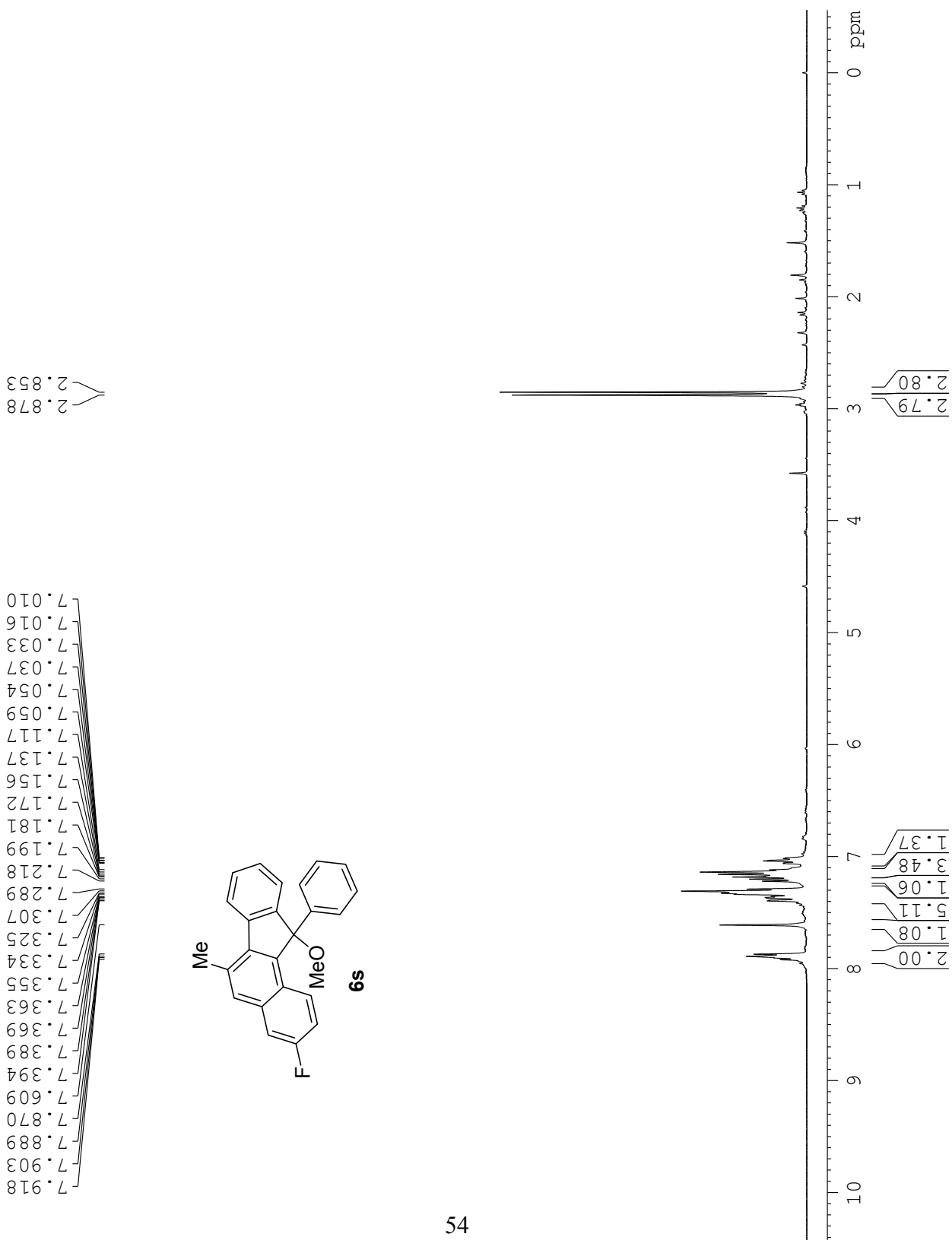


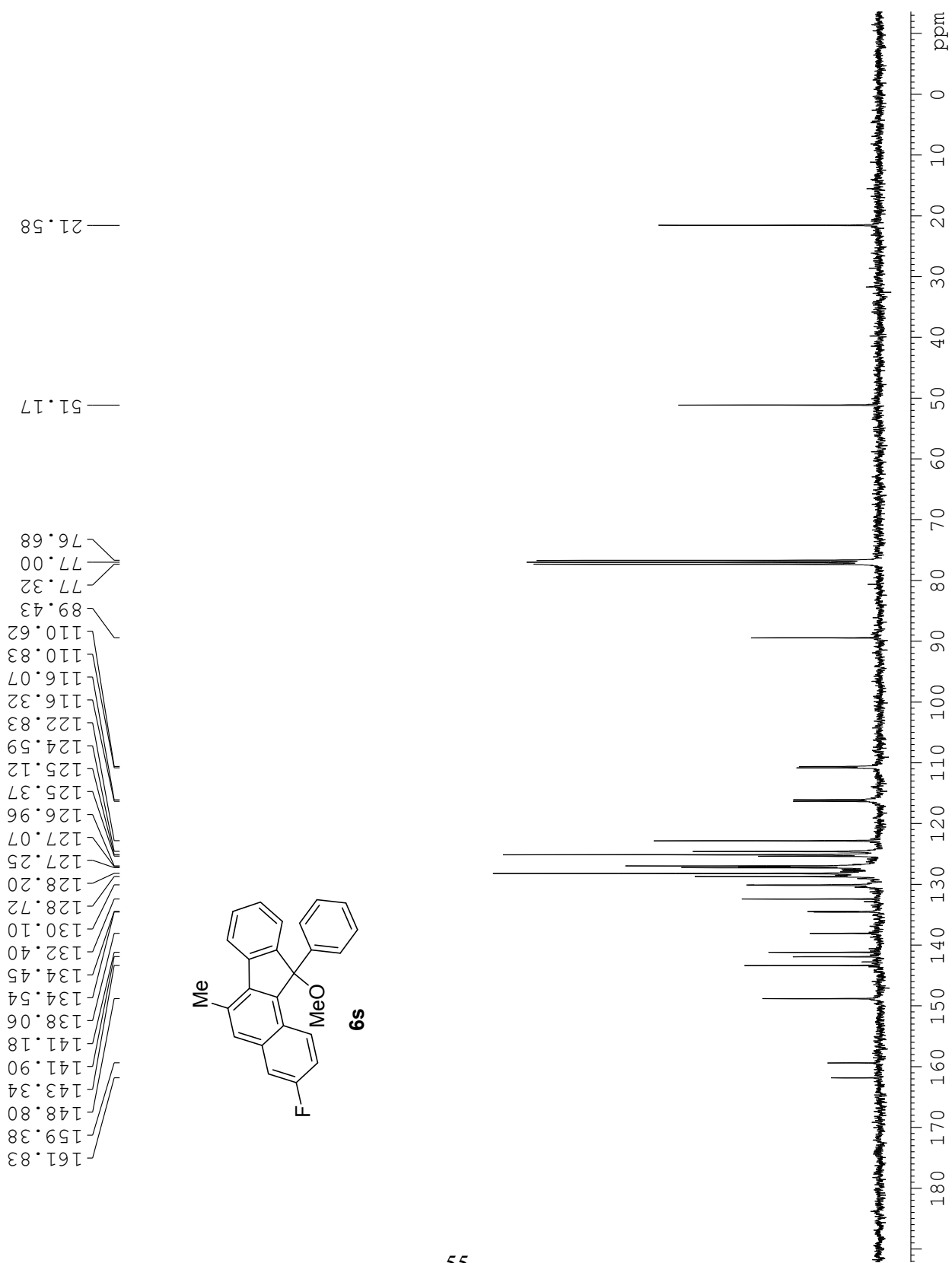




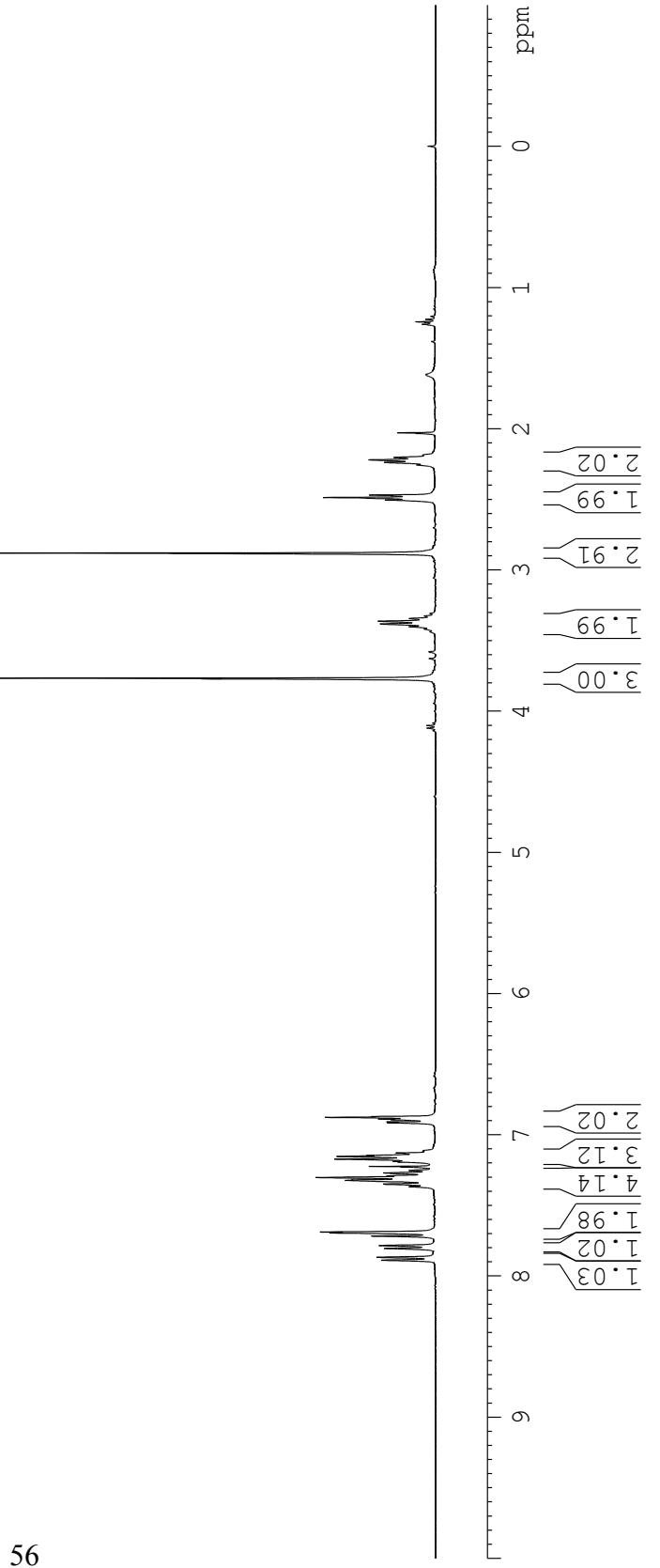
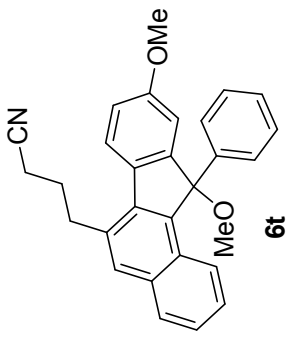


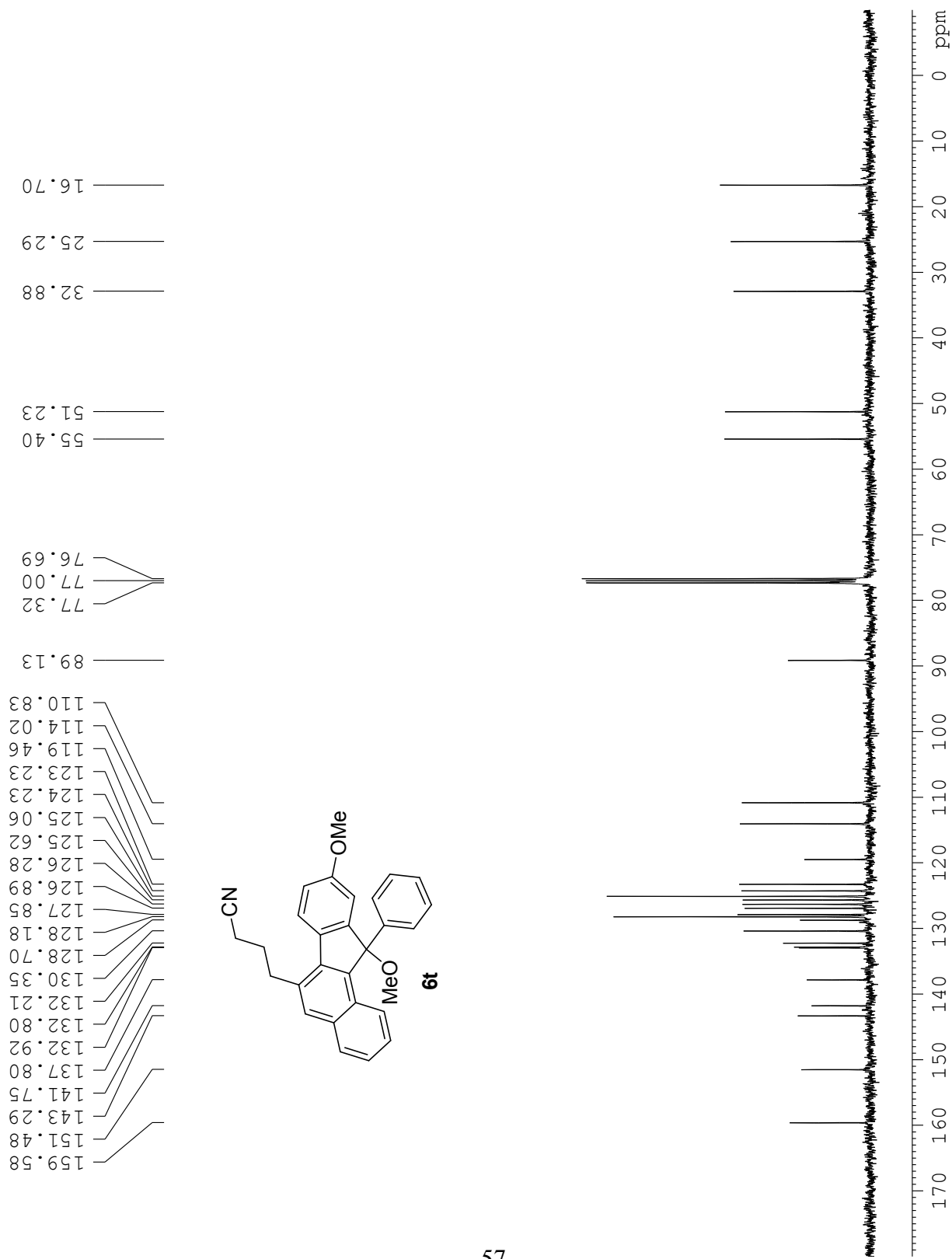


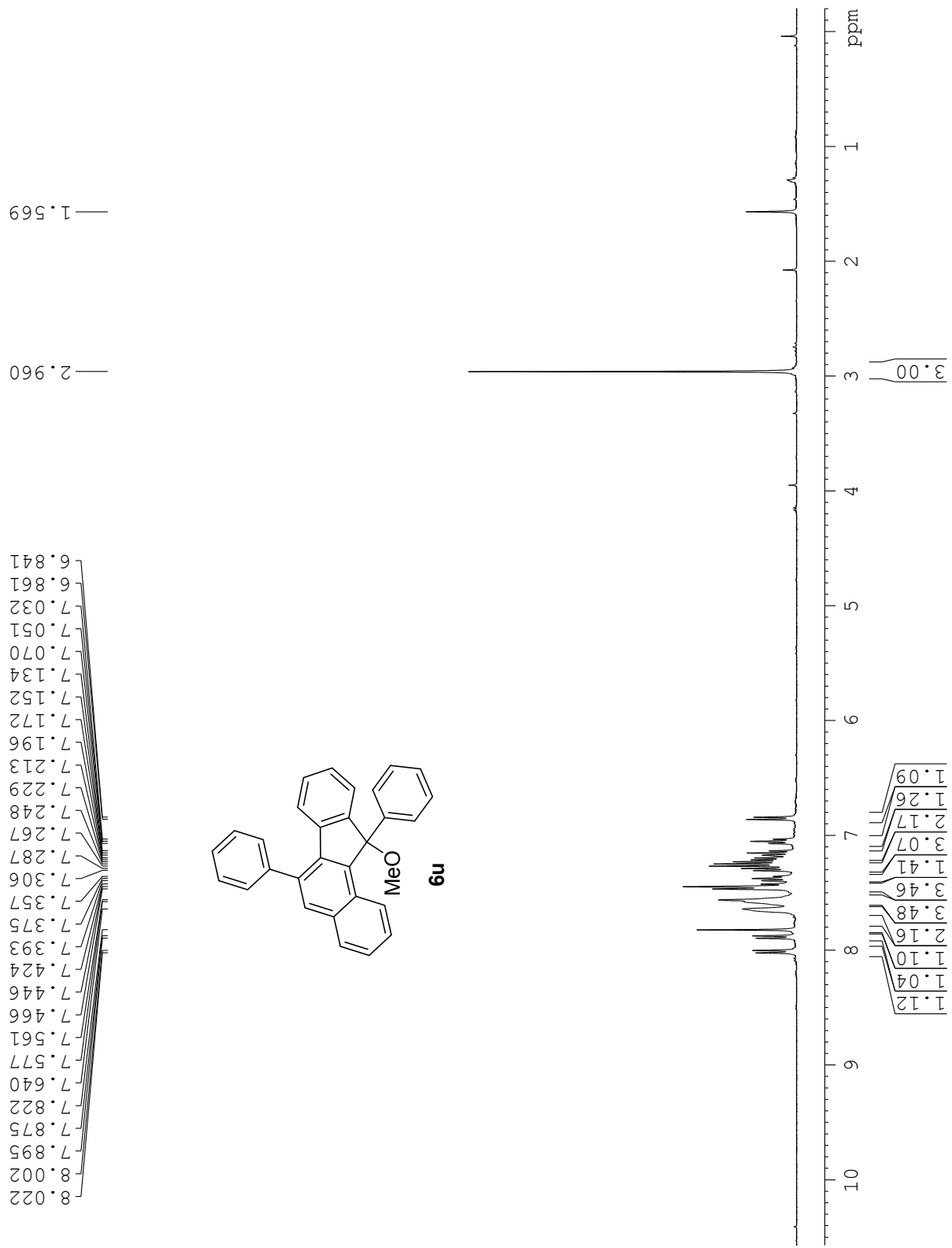


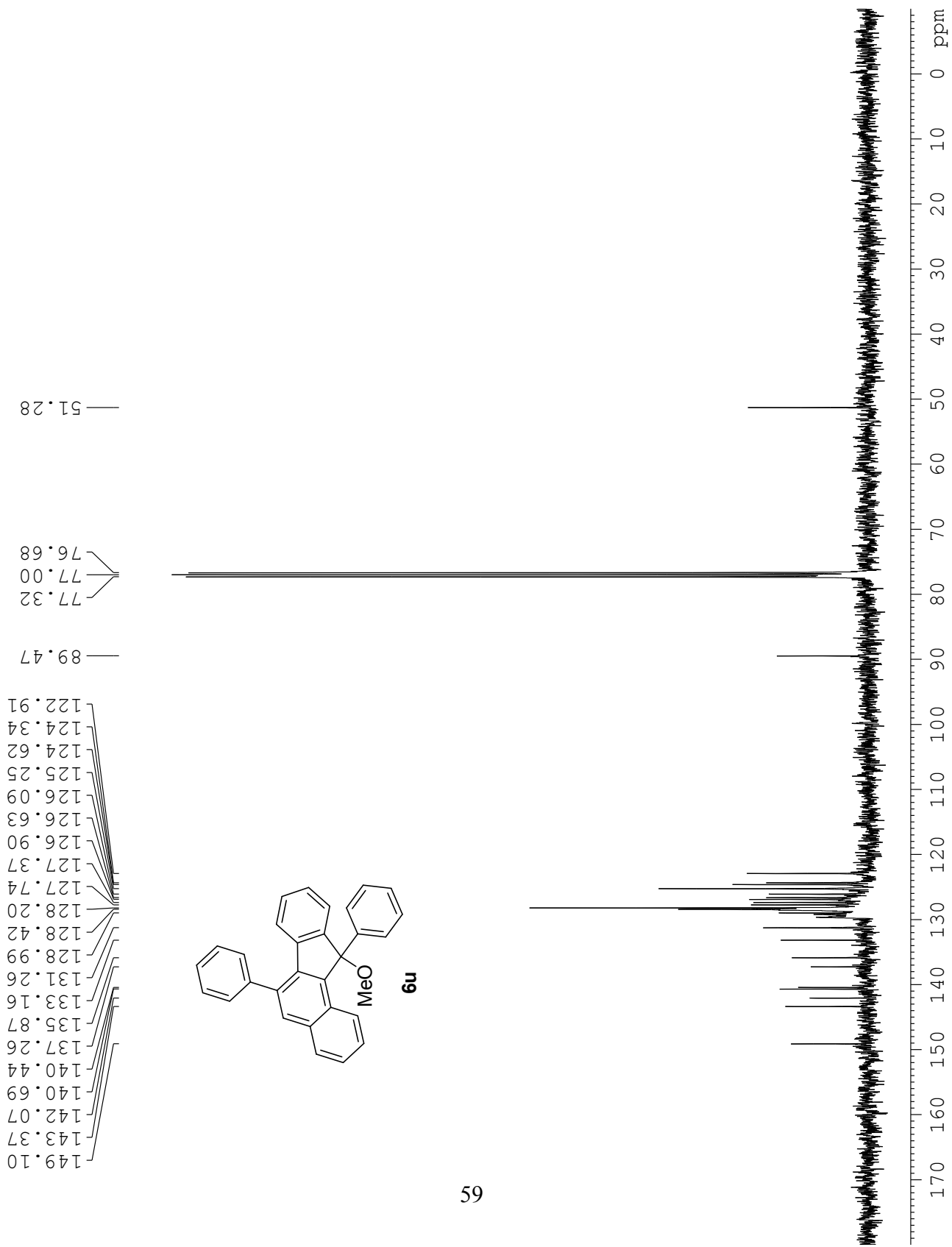


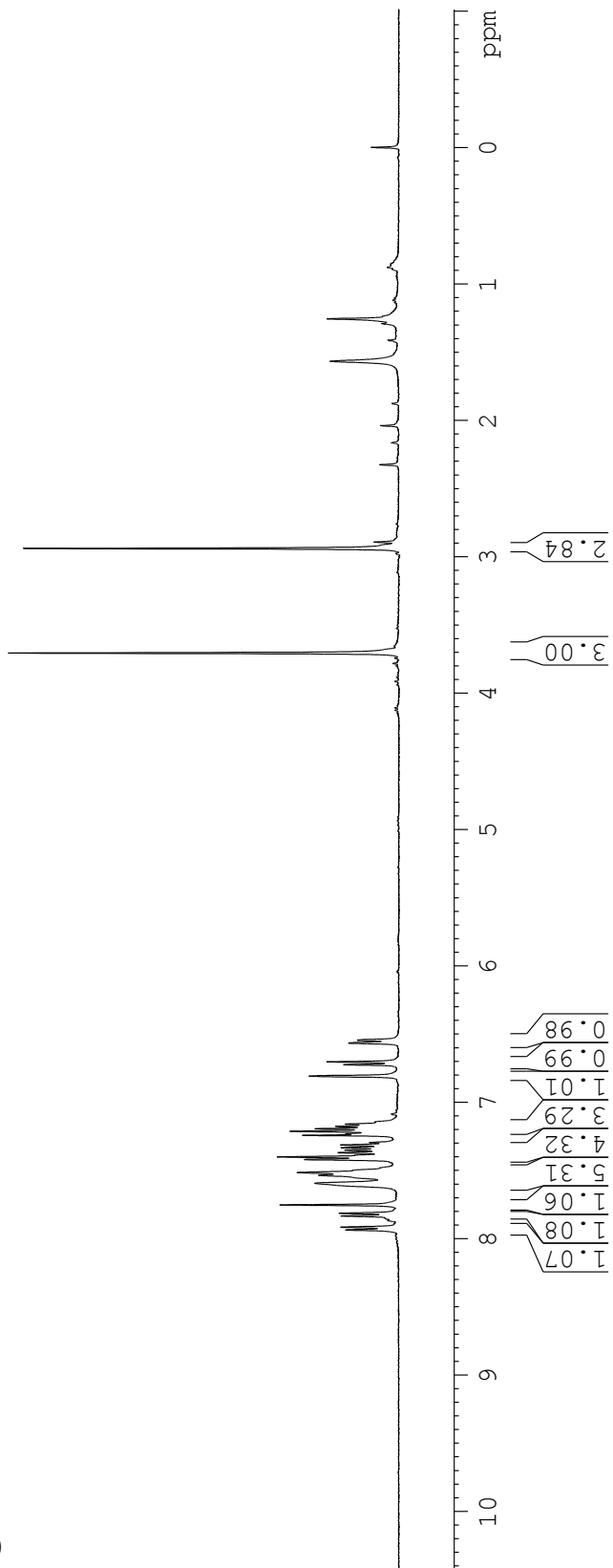
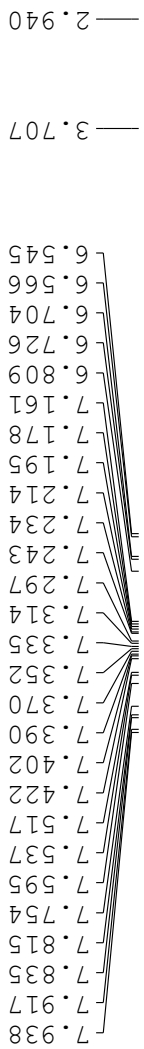
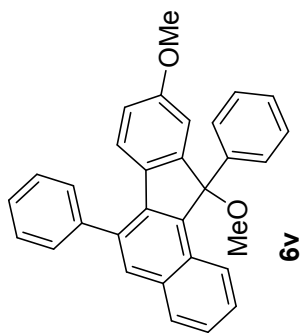
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 7.193
 7.188
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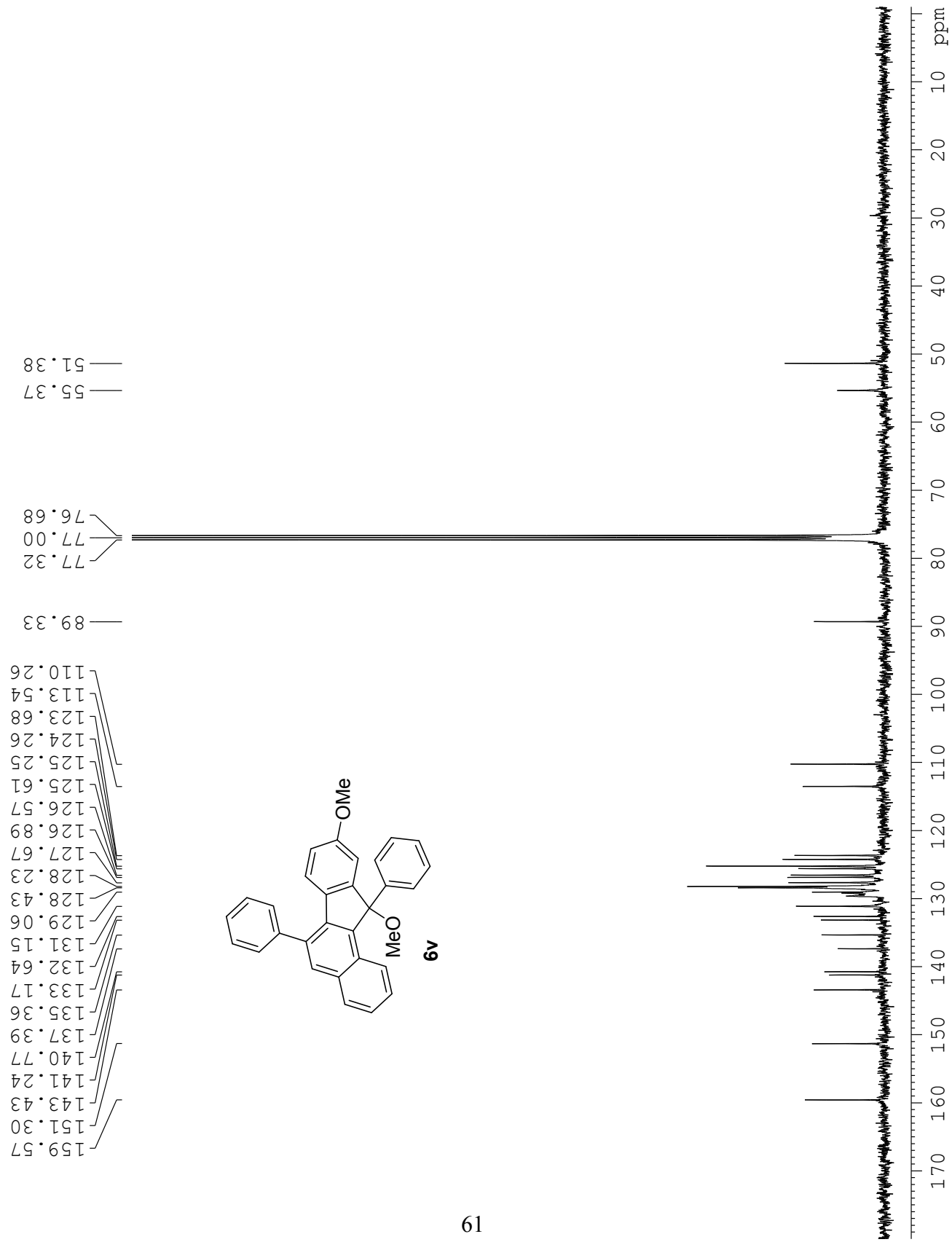


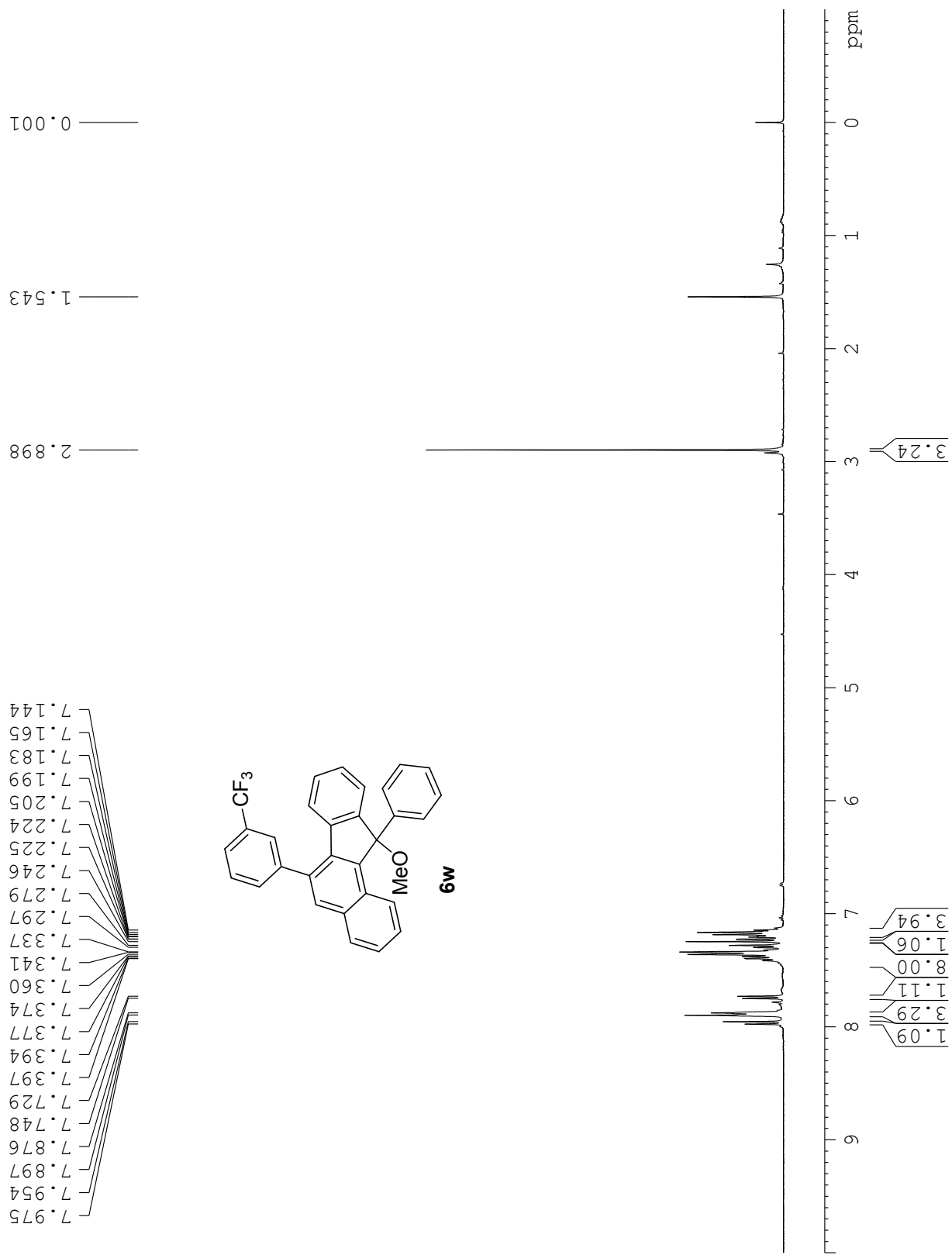


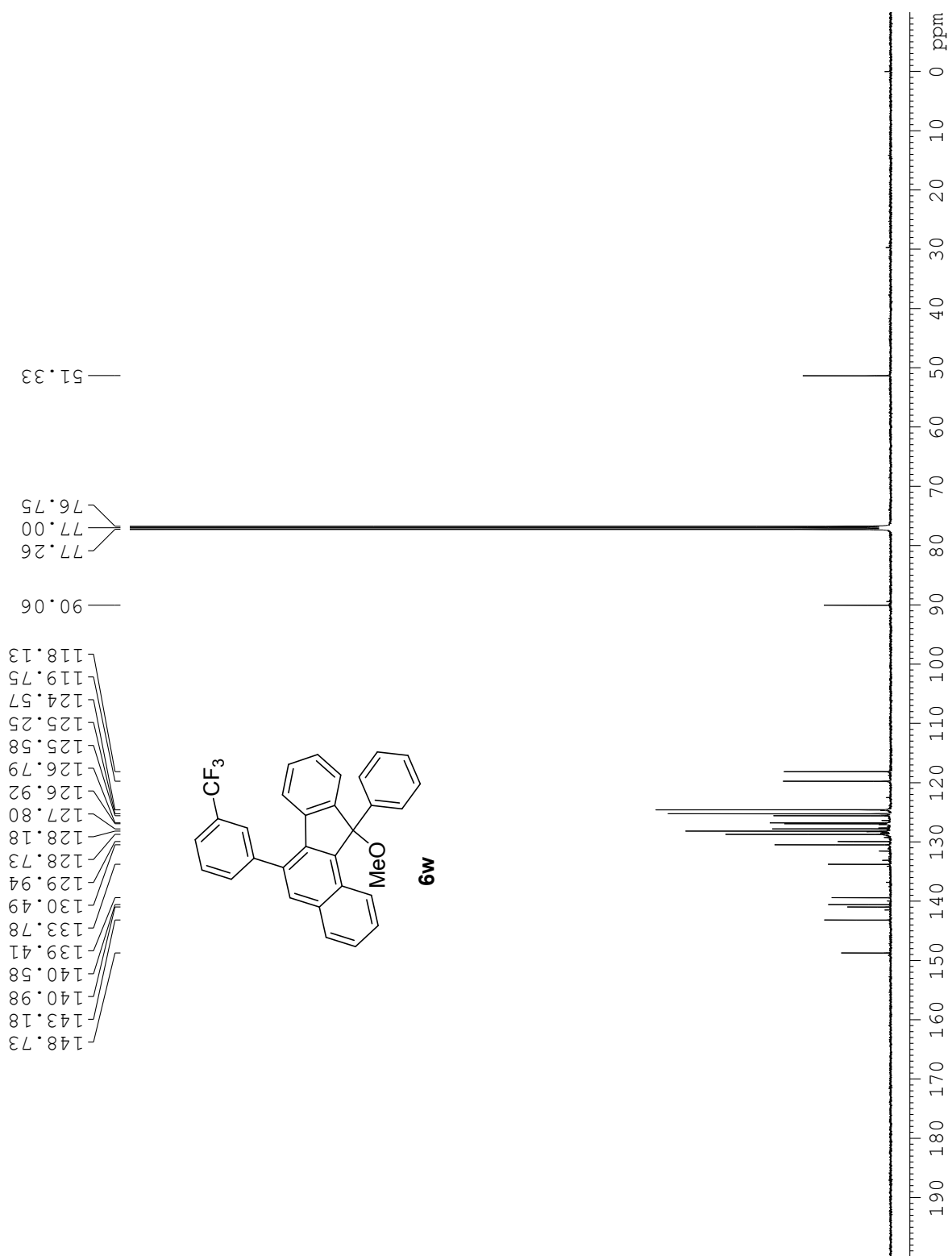






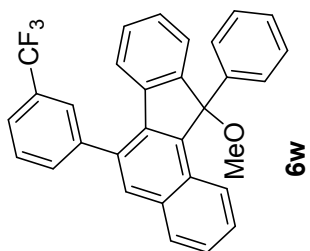




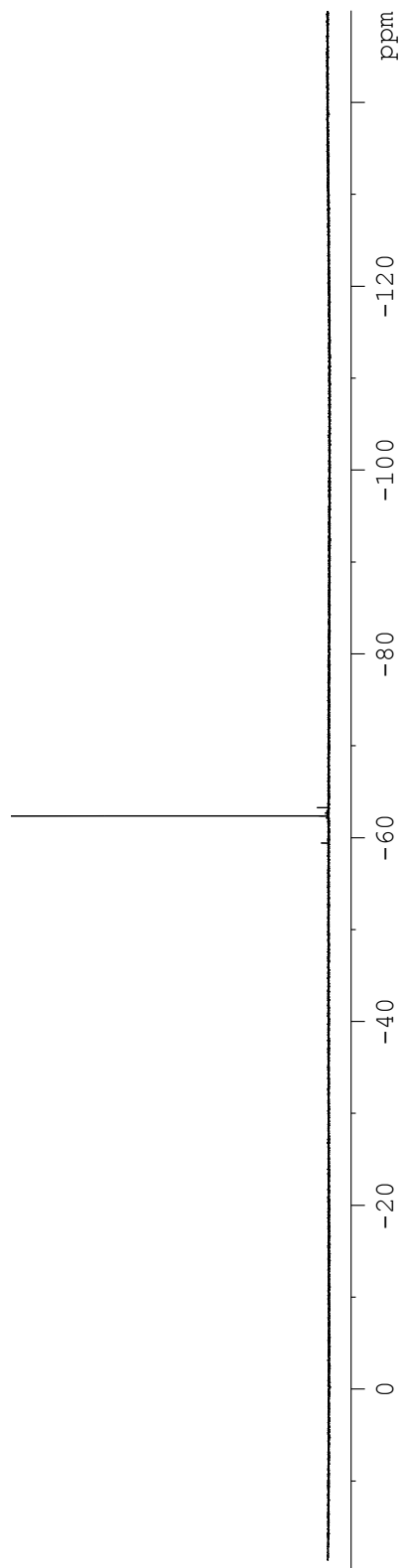


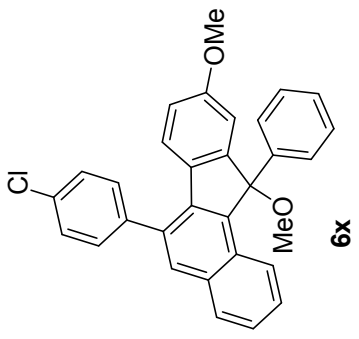
^{19}F NMR for compound 6w

— -62.399



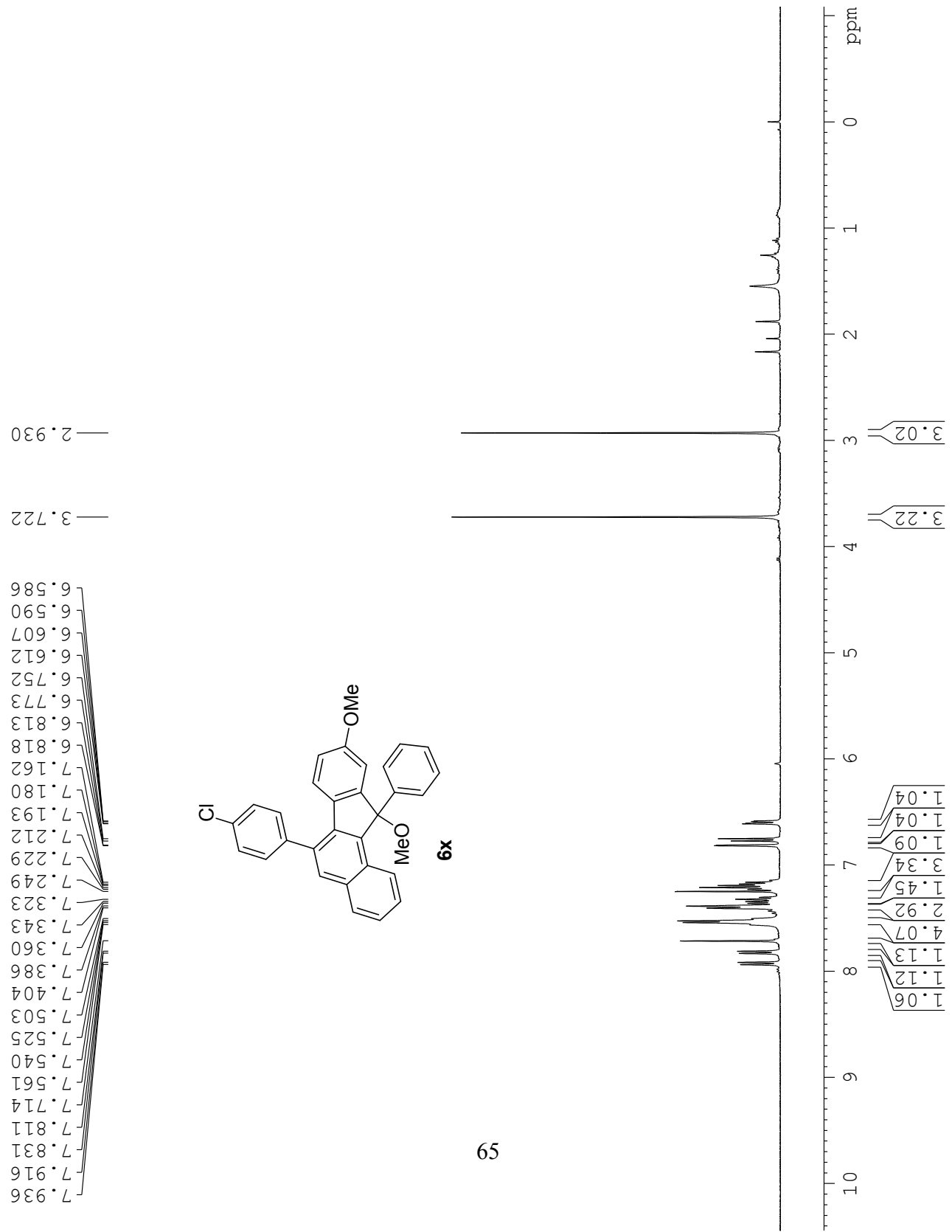
64

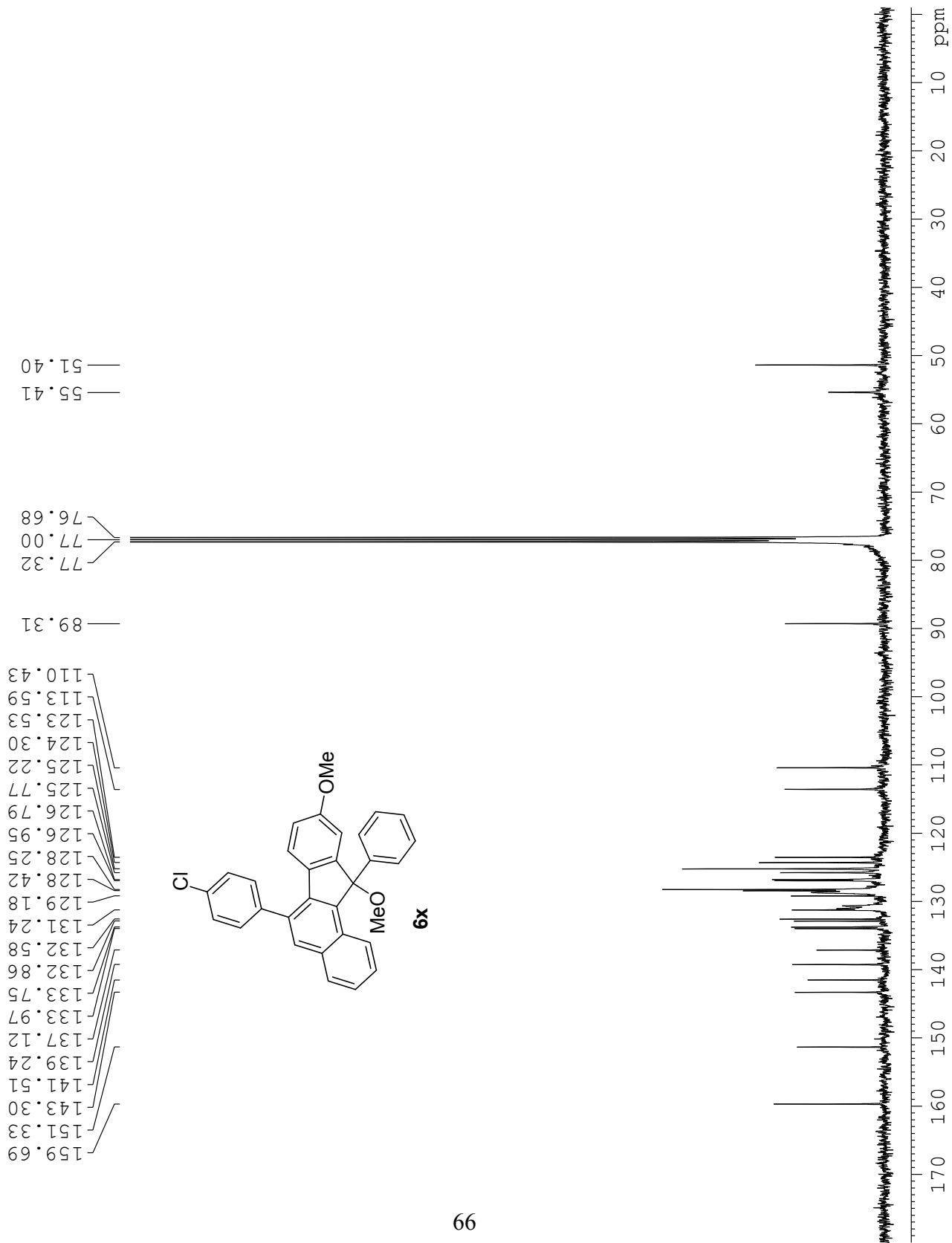


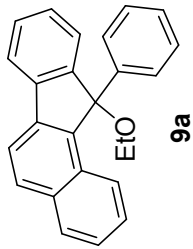
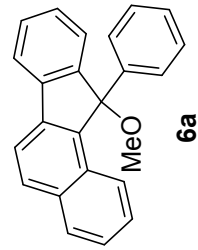
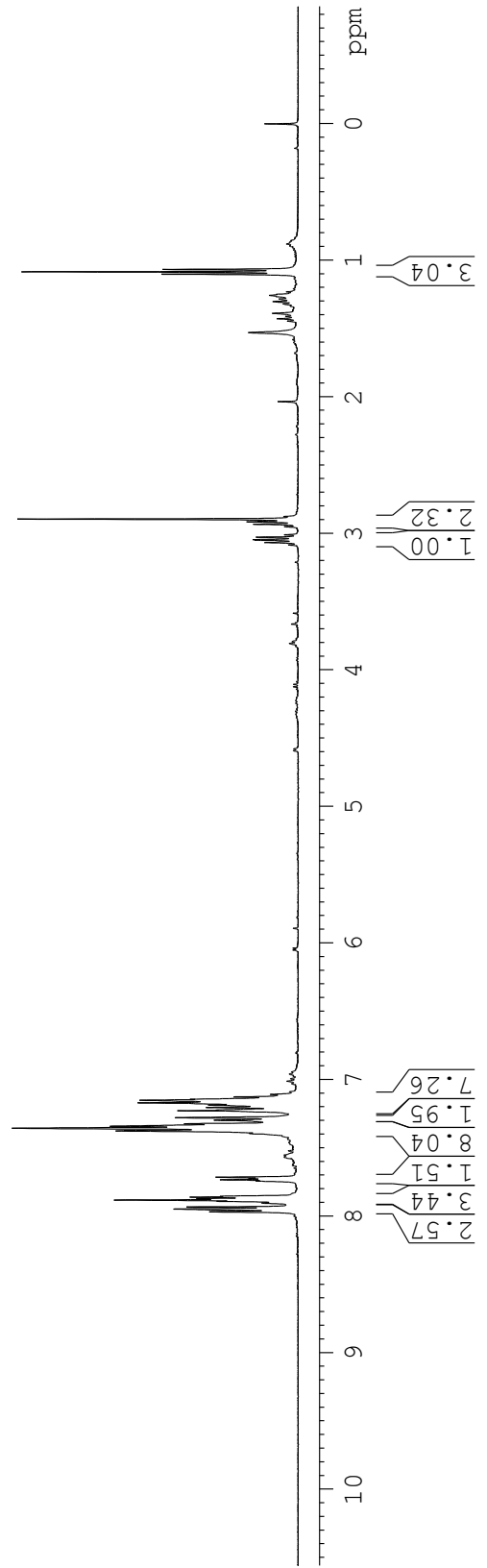


6x

59



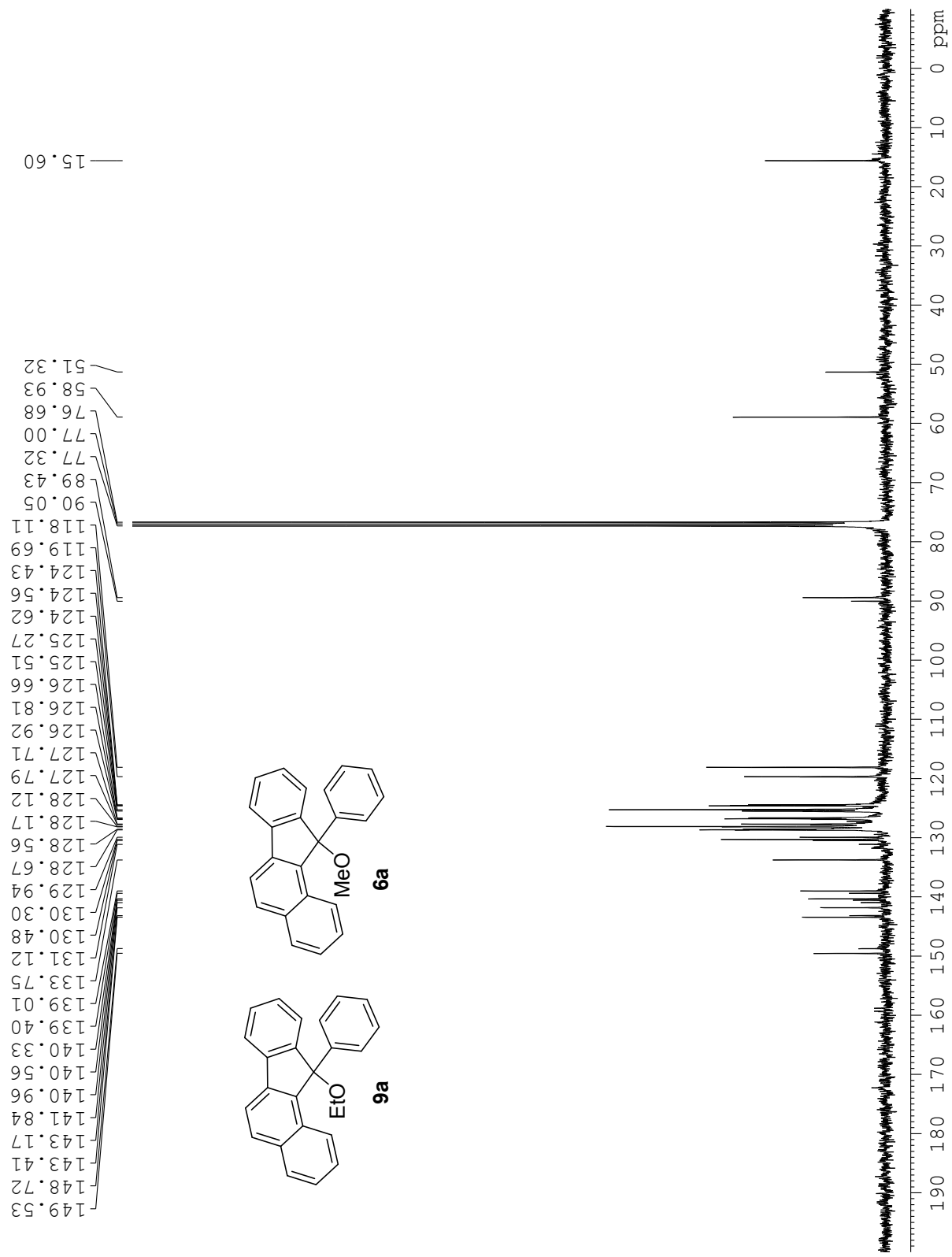




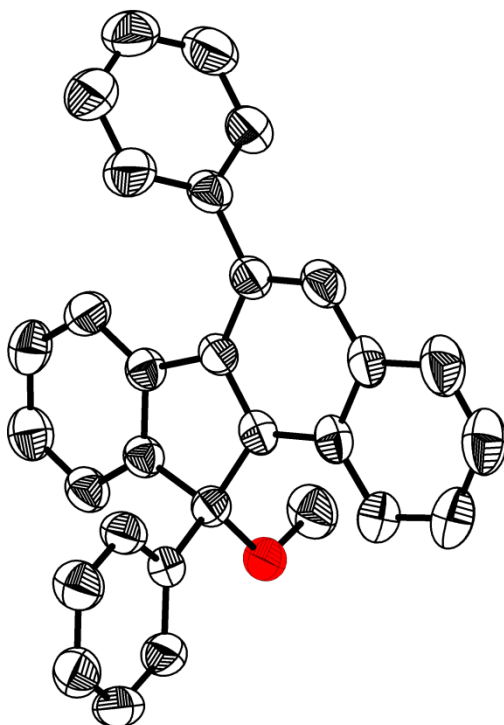
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3.045
3.049
3.067
3.085

7.128
7.145
7.152
7.171
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7.187
7.205
7.224
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7.871
7.881
7.881
7.890
7.890
7.932
7.932
7.947
7.947
7.967
7.967



8. ORTEP of compound 6u



9. Table 1. Crystal data and structure refinement for compound 6u.

Identification code	6u	
Empirical formula	$C_{30}H_{22}O$	
Formula weight	398.48	
Temperature	298 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.7885(9) Å	a = 90°.
	b = 8.7362(8) Å	b = 91.123(7)°.
	c = 22.4105(16) Å	g = 90°.
Volume	2111.8(3) Å ³	
Z	4	
Density (calculated)	1.346 Mg/m ³	
Absorption coefficient	0.125 mm ⁻¹	
F(000)	885	
Crystal size	0.20 x 0.20 x 0.15 mm ³	
Theta range for data collection	2.96 to 26.37°.	
Index ranges	-12 ≤ h ≤ 13, -10 ≤ k ≤ 10, -28 ≤ l ≤ 24	
Reflections collected	9034	
Independent reflections	4315 [R(int) = 0.0512]	
Completeness to theta = 26.37°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4315 / 0 / 281	
Goodness-of-fit on F ²	0.933	
Final R indices [I > 2σ(I)]	R1 = 0.0661, wR2 = 0.1603	
R indices (all data)	R1 = 0.1430, wR2 = 0.2122	
Largest diff. peak and hole	0.167 and -0.164 e.Å ⁻³	
CCDC	993937	