Electronic Supplementary Information

Synthesis of multisubstituted phenols by formal [4+2] cycloaddition of nucleophilic alkynes with 3-ethoxycyclobutanones

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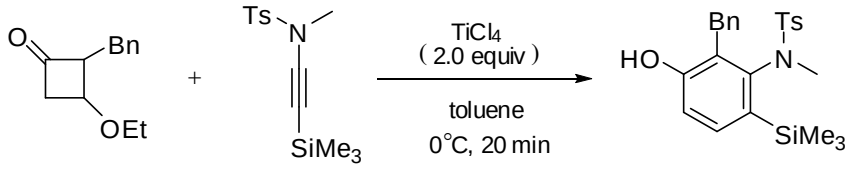
1. General

All melting points were determined on Yanagimoto micro melting point apparatus. Infrared spectra (IR) were recorded on Horiba IR-710. ^{1}H NMR spectra were recorded on a JOEL JNM ECA600 (600 MHz) or a JOEL JNM ECS400 (400 MHz) spectrometer at room temperature; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting pattern are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JOEL JNM ECA600 (150 MHz) or a JOEL JNM ECS400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard $CDCl_3$. HRMS data were recorded on JEOL JMS-T100TD. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel Column chromatography was carried out on silica gel 60 N (Kanto Kagaku Co., Ltd., spherical, neutral, 63-210 μm or 40-50 μm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. All reactions were carried out under nitrogen in dried glassware with magnetic stirring. Cyclobutanones **5a-e**[1] and **5f**[2] were prepared by reported procedures. Ynamides **6a,c**,[3] **6b**,[4] **6d**[5], **10a,c**[6] **10b**[7], and **10d**[8] were prepared by a reported procedure. A solution of $TiCl_4$ in CH_2Cl_2 was purchased from Aldrich.

2. Experimental procedures and characterization data

2.1. Typical experimental procedure for $TiCl_4$-mediated formal [4+2] cycloaddition of 3-ethoxycyclobutanones with ynamides (Table 1, entry 4)



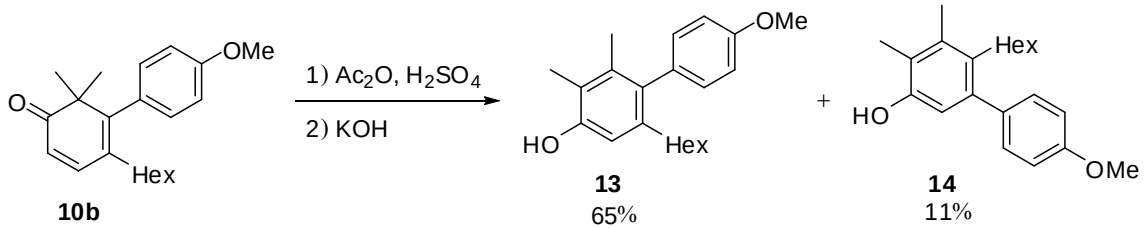
5d (1.0 equiv) + **6a** (1.2 equiv) → **7d**

To a stirred solution of **5d** (40.9 mg, 0.200 mmol) and ynamide **6a** (67.5 mg, 0.240 mmol) in dry toluene (2.0 mL) was added 1.0M $TiCl_4$ (0.40 ml, 0.40 mmol) at 0 ˚C, and the reaction mixture was

1 Matsuo, J.; Okuno, R.; Takeuchi, K.; Kawano, M.; Ishibashi, H. *Tetrahedron Lett.* **2010**, *51*, 3736.
2 Samuel, S. P.; Niu, T.-q.; Erickson, K. L. *J. Am. Chem. Soc*. **1989**, *111*, 1429.
3 Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 833.
4 Mansfield, S. J.; Campbell, C. D.; Jones, M. W.; Anderson, E. A. *Chem. Comm.* **2015,** *51*, 3316.
5 Alford, J. S.; Davis, H. M. L. *Org. Lett*. **2012**, *14*, 6020.
6 Nishikawa, D.; Hirano, K.; Miura, M. *J. Am. Chem. Soc*. **2015**, *137*, 15620.
7 Rasolofonjatovo, E.; Treguier, B.; Provot, O.; Hamze, A.; Brion, J.-D.; Alami, M. *Eur. J. Org. Chem*. **2012**, 1603.
8 Jiao, J.; Hyodo, K.; Hu, H.; Nakajima, K.; Nishikawa, Y. *J. Org. Chem*. **2014**, *79*, 285.

stirred at the same temperature for 20 min. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (10 g, hexane/ethyl acetate = 10:1) to afford **7d** (65.6 mg, 75%).

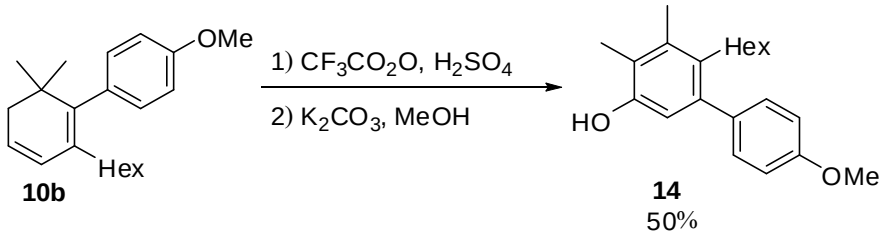
2.2. Dienone-phenol rearrangement using acetic anhydride and sulfuric acid



10b **13** 65% **14** 11%

Dienone **10b** (110mg, 0.350 mmol) was treated with 1ml of acetic anhydride containing 1 drop of sulfuric acid at room temperature for overnight. The reaction was quenched with sodium carbonate solution, and the mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was dissolved in 3 ml. of methanol and treated with 3ml of 10% potassium hydroxide solution for 3 h at room temperature. The mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 5:1) to afford **13** (71.5 mg, 65%) and **14** (12.7 mg, 11%) .

2.3. Dienone-phenol rearrangement using trifluoroacetic anhydride and sulfuric acid

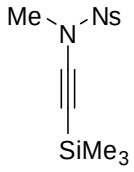


10b **14** 50%

To a stirred solution of **10b** (110mg, 0.350 mmol) and trifluoroacetic anhydride (0.1 ml, 0.700 mmol) in dry dichloromethane (1.0 mL) was added 1 drop of sulfuric acid at room temperature, and the reaction mixture was stirred at the same temperature for overnight. The reaction was quenched with sodium carbonate solution, and the mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was dissolved in 3 ml. of methanol and treated with 3ml of 10% potassium carbonate solution for 2 hr at room temperature. The mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by thin-layer chromatography on silica gel

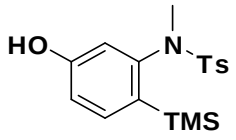
(hexane/ethyl acetate = 5:1) to afford **14** (55.0 mg, 50%) .

2.4. Characterization data of new compounds



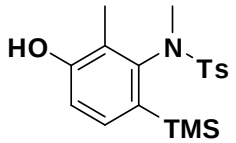
6c

Compound **6c**: white solid; mp 113.5–114.0 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.44 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 3.13 (s, 3H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 150.7, 141.4, 129.0, 124.3, 95.1, 72.5, 39.3, -0.1; IR (CH_3Cl, cm^{-1}) 3103, 2976, 2171, 1941, 1807, 1739, 1687, 1605, 1533, 1454, 1400, 1369, 1303, 1248, 1180, 1107, 1086, 985, 841, 752, 702, 640, 602, 571, 467; HRMS (EI^+) calcd for $C_{12}H_{17}N_2O_4SSi$ (m/z) 313.06783, found 313.06729.



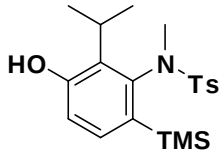
7a

Compound **7a**: colorless crystals; mp 203.0–203.5 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.65 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 2.4, 8.4 Hz, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 4.74 (s, 1H), 3.06 (s, 3H), 2.47 (s, 3H), 0.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 156.7, 148.5, 143.8, 137.2, 134.1, 133.0, 129.5, 128.7, 115.2, 113.1, 40.4, 21.6, 0.4; IR (CH_3Cl, cm^{-1}) 3589, 3032, 2954, 1599, 1576, 1348, 1165, 1093, 1043, 962, 843, 586, 554; Anal. Calcd for $C_{17}H_{23}NO_3SSi$: C, 58.42; H, 6.63; N, 4.01; found: C, 58.14; H, 6.24; N, 4.03.



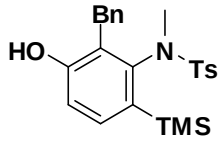
7b

Compound **7b**: colorless crystals; mp 203.5–204.0 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.63 (d, *J* = 8.4 Hz, 2H), 7.31-7.26 (m, 3H), 6.75 (d, *J* = 7.6, 1H), 4.98 (s, 1H), 3.23 (s, 3H), 2.43 (s, 3H), 1.33 (s, 3H), 0.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 155.6, 145.0, 143.2, 137.5, 134.6, 134.2, 129.6, 127.5, 123.7, 114.5, 39.1, 21.5, 11.2, 0.8; IR (CH_3Cl, cm^{-1}) 3597, 3032, 2954, 1583, 1396, 1344, 1288, 1248, 1209, 1153, 1026, 941, 885, 843; Anal. Calcd for $C_{18}H_{25}NO_3SSi$: C, 59.47; H, 6.93; N, 3.85; found: C, 59.19; H, 6.78; N, 3.87.



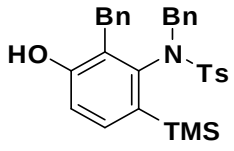
7c

Compound **7c**: colorless crystals; mp 200.0–200.5 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.71 (d, *J* = 8.4 Hz, 2H), 7.31-7.26 (m, 3H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.13 (s, 1H), 3.25 (s, 3H), 2.43 (s, 3H), 2.35-2.32 (m, 1H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 156.7, 144.6, 143.0, 137.6, 134.6, 134.1, 133.7, 129.5, 127.6, 116.5, 40.1, 28.1, 21.5, 20.7, 20.3, 0.9; IR (CH_3Cl, cm^{-1}) 3593, 3030, 2958, 1579, 1454, 1398, 1340, 1286, 1248, 1174, 1151, 1115, 1088, 1059, 970, 908, 850, 586, 549; Anal. Calcd for $C_{20}H_{29}NO_3SSi$: C, 61.34; H, 7.64; N, 3.58; found: C, 65.11; H, 7.84; N, 3.88.



7d

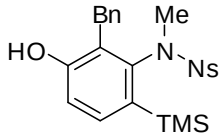
Compound **7d**: colorless crystals; mp 222.5–223.0 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.16-7.12 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 4.82 (s, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 3.06 (s, 3H), 2.91 (d, *J* = 17.2 Hz, 1H), 2.45 (s, 3H), 0.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 156.2, 145.6, 143.4, 138.5, 137.2, 135.7, 135.0, 129.6, 128.5, 127.5, 127.3, 126.3, 125.1, 115.9, 39.8, 31.2, 21.5, 0.8; IR (CH_3Cl, cm^{-1}) 3587, 3029, 2954, 1583, 1495, 1400, 1344, 1290, 1153, 993, 843; Anal. Calcd for $C_{24}H_{29}NO_3SSi$: C, 65.57; H, 6.65; N, 3.19; found: C, 65.29; H, 6.72; N, 3.16.



7e

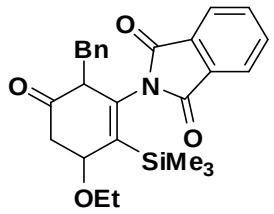
Compound **7e**: colorless crystals; mp 203.5–204.0 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.26-7.11 (m, 8H), 7.05 (d, *J* = 6.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 6.8 Hz, 2H), 4.77 (d, *J* = 14.8 Hz, 1H), 4.61 (s, 1H), 4.29 (d, *J* = 14.8 Hz, 1H), 3.14 (d, *J* = 17.6 Hz, 1H), 2.79 (d, J = 17.2 Hz, 1H), 2.45 (s, 3H), 0.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 156.0, 143.4, 143.2, 138.1, 137.6, 137.5, 135.9, 135.8, 130.3, 129.7, 128.7, 128.4, 128.1, 127.6, 127.4, 126.5, 124.3, 115.9, 56.2, 31.6, 21.6, 1.1; IR (CH_3Cl, cm^{-1}) 3587, 3033, 2954, 1732,

1581, 1495, 1344, 1250, 1157, 1080, 1039, 953, 923, 843, 754, 700, 586, 538; Anal. Calcd for $C_{30}H_{33}NO_3SSi$: C, 69.87; H, 6.45; N, 2.74; found: C, 69.67; H, 6.84; N, 2.57.



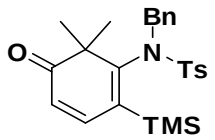
7f

Compound **7f**: colorless crystals; mp 178.0–178.5 ˚C; ^{1}H NMR ($CDCl_3$, 600MHz) δ: 8.19 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.16-7.15 (m, 3H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.67 (s, 2H), 4.71 (s, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.21 (s, 3H), 3.03 (d, *J* = 16.8 Hz, 1H), 0.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 156.2, 149.8, 145.5, 144.8, 137.6, 136.1, 134.9, 128.7, 128.5, 127.3, 126.7, 124.6, 124.1, 116.3, 40.3, 31.4, 0.8; IR (CH_3Cl, cm^{-1}) 3436, 2943, 2900, 2848, 1583, 1529, 1464, 1350, 1248, 1153, 1103, 995, 901, 843, 735, 688, 607, 463; Anal. Calcd for $C_{23}H_{26}N_2O_5SSi$: C, 58.70; H, 5.57; N, 5.95; found: C, 58.71; H, 5.68; N, 5.95.



7g'

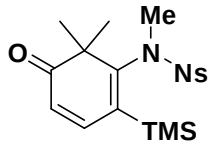
Compound **7g'**: colorless oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.84 (d, *J* = 7.2 Hz, 1H), 7.75-7.67 (m, 3H), 7.00-6.87 (m, 5H), 4.33-4.27 (m, 1H), 4.14 (d, *J* = 16.0 Hz, 1H), 3.62-3.53 (m, 2H), 3.18 (d, *J* = 16.4 Hz, 1H), 3.12 (d, *J* = 4.8 Hz, 1H), 2.88 (dd, J = 4.0, 16.4 Hz, 1H), 2.68 (dd, *J* = 12.0, 17.2 Hz, 1H), 1.21 (d, J = 7.2 Hz, 3H) 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 196.7, 166.0, 164.2, 149.0, 138.3, 135.5, 134.1, 133.8, 131.3, 131.0, 127.7, 127.6, 125.4, 123.4, 123.1, 75.6, 63.8, 42.9, 38.8, 30.6, 14.9, 0.0; IR (CH_3Cl, cm^{-1}) 2976, 2937, 2900, 2871, 1782, 1714, 1622, 1464, 1412, 1358, 1325, 1248, 1188, 1115, 1074, 1022, 885, 841, 762, 715, 629, 532; HRMS (EI^+) calcd for $C_{26}H_{30}NO_4Si$ (m/z) 448.19441, found 448.19435.



8a

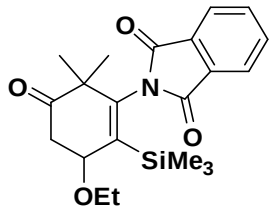
Compound **8a**: yellow crystals; mp 193.5–194.0 ˚C; ^{1}H NMR ($CDCl_3$, 600MHz) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.32-7.30 (m, 7H), 7.11 (d, *J* = 10.2 Hz, 1H), 6.01 (d, *J* = 9.6 Hz, 1H), 4.92 (d, *J* = 9.6 Hz,

1H), 4.62 (d, *J* = 15.0 Hz, 1H), 2.43 (s, 3H), 1.24 (s, 3H), 0.84 (s, 3H), -0.02 (s, 9H); ^{13}C NMR ($CDCl_3$, 150MHz) δ: 206.5, 155.5, 144.7, 143.6, 139.4, 138.8, 135.6, 130.4, 129.8, 128.5, 128.4, 127.3, 122.5, 54.9, 53.8, 28.0, 24.2, 21.5, -0.7; IR (CH_3Cl, cm^{-1}) 3033, 3008, 2956, 1668, 1599, 1525, 1496, 1456, 1348, 1252, 1157, 1090, 1028, 845, 700, 663, 546; Anal. Calcd for $C_{25}H_{31}NO_3SSi$: C, 66.19; H, 6.89; N, 3.09; found: C, 66.00; H, 6.93; N, 3.07.



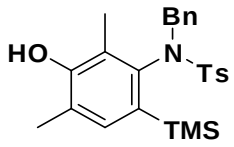
8b

Compound **8b**: yellow crystals; mp 149.5–150.0 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.39 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 10.4 Hz, 2H), 6.08 (d, *J* = 9.6 Hz, 2H), 3.34 (s, 3H), 1.10 (s, 3H), 0.90 (s, 3H), 0.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 158.5, 149.9, 146.4, 144.3, 136.4, 128.5, 124.3, 124.0, 54.8, 40.4, 25.5, 25.1, -0.7; IR (CH_3Cl, cm^{-1}) 3018, 2401, 1670, 1535, 1352, 1215, 1084, 1011, 845, 785, 721, 673, 600, 463; Anal. Calcd for $C_{18}H_{24}N_2O_5SSi$: C, 52.92; H, 5.92; N, 6.86; found: C, 52.86; H, 5.94; N, 6.76.



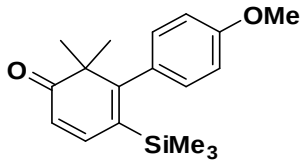
8c'

Compound **7g'**: colorless crystals; mp 104.5–105.0 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.93-7.90 (m, 2H), 7.81-7.77 (m, 2H), 4.38 (t, *J* = 4.4 Hz, 1H), 3.70-3.63 (m, 1H), 3.40-3.32 (m, 1H), 2.89 (dd, *J* = 2.4, 4.4 Hz, 2H), 1.28 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.16 (s, 3H), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 210.9, 168.5, 167.9, 143.7, 143.4, 134.4, 134.4, 131.8, 131.8, 123.8, 123.7, 74.2, 64.0, 51.6, 41.2, 24.7, 24.5, 15.5, -0.7; IR (CH_3Cl, cm^{-1}) 3477, 2978, 2941, 2941, 2898, 2873, 1782, 1720, 1610, 1466, 1414, 1358, 1331, 1250, 1190, 1101, 1074, 1022, 960, 918, 883, 841, 762, 715, 629, 590, 530, 459; Anal. Calcd for $C_{21}H_{27}NO_4Si$: C, 65.42; H, 7.06; N, 3.63; found: C, 65.25; H, 7.11; N, 3.63.



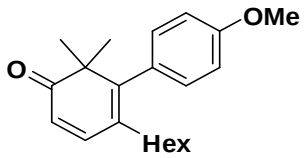
9

Compound **9**: colorless crystals; mp 203.5–204.0 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J* = 8.4 Hz, 2H), 7.25-7.18 (m, 6H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.72 (d, *J* = 14.4 Hz, 1H) 4.67 (d, *J* = 14.0 Hz, 1H), 4.55 (s, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.09 (s, 3H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 153.5, 143.1, 140.1, 138.6, 136.0, 135.6, 135.6, 130.4, 129.6, 128.2, 128.0, 127.6, 122.8, 122.3, 54.5, 21.5, 16.0, 12.0, 1.2; IR (CH_3Cl, cm^{-1}) 3604, 3031, 2952, 1574, 1473, 1342, 1250, 1157, 1110, 1049, 916, 840, 740, 701, 551; Anal. Calcd for $C_{25}H_{31}NO_3SSi$: C, 66.19; H, 6.89; N, 3.09.



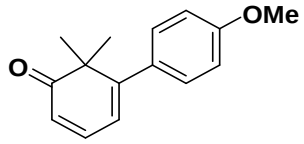
11a

Compound **11a**: yellow crystals; mp 50.0–50.5 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.22 (d, *J* = 10.0 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.10 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 1.18 (s, 6H), -0.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 205.8, 168.3, 159.0, 145.2, 132.0, 130.8, 129.0, 123.1, 112.8, 55.2, 51.4, 24.9, 0.3; IR (CH_3Cl, cm^{-1}) 3008, 2958, 2839, 1649, 1610, 1504, 1464, 1286, 1248, 1176, 1086, 1036, 831, 785, 690; HRMS (EI^+) calcd for $C_{18}H_{25}O_2Si$ (m/z) 301.16238, found 301.16336.



11b

Compound **11b**: yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.04 (d, *J* = 9.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.834(s, 3H), 1.87 (t, *J* = 7.8 Hz, 2H), 1.31-1.08 (m, 14H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150MHz) δ: 206.1, 158.5, 152.7, 145.8, 130.4, 130.3, 129.7, 124.2, 113.2, 55.2, 49.8, 32.7, 31.4, 29.2, 28.8, 25.0, 22.2, 14.0; IR (CH_3Cl, cm^{-1}) 3020, 2958, 2929, 2858, 1732, 1657, 1626, 1564, 1508, 1464, 1410, 1375, 1284, 1246, 1207, 1176, 1132, 1109, 1038, 835, 775, 727, 665, 590, 538; HRMS (EI^+) calcd for $C_{21}H_{29}O_2$ (m/z) 313.21675, found 313.21637.

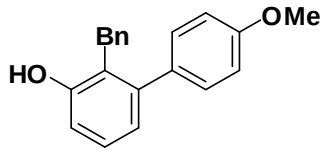


11c

Compound **11c**: yellow powder; mp 50.0–50.5 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.17 (d, *J* = 8.8 Hz, 2H), 7.11-7.07 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.09 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.30 (s, 6H); ^{1}H NMR (400 MHz, C_6D_6) δ: 6.91 (2H, d, *J* = 8.4 Hz), 6.69 (2H, d, *J* = 8.4 Hz), 6.41 (1H, dd, *J* = 6.0 and 9.6 Hz), 6.04 (1H, d, *J* = 9.6 Hz), 5.72 (1H, d, *J* = 6.0 Hz), 3.30 (3H, s), 1.29 (6H, s); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 206.0, 159.6, 159.2, 141.5, 132.3, 130.0, 123.9, 120.1, 113.3, 55.2, 50.9, 25.0; IR (CH_3Cl, cm^{-1}) 3010, 2933, 2839, 1658, 1608, 1562, 1510, 1464, 1377, 1286, 1246, 1178, 1126, 1036, 964, 822, 754, 710, 569, 484; HRMS (EI^+) calcd for $C_{15}H_{17}O_2$ (m/z) 229.12285, found 229.12380.

11d

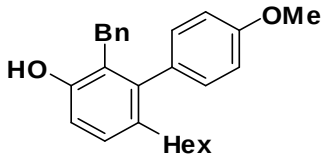
Compound **11d**: yellow powder; mp 62.0–62.5 ˚C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.33 (m, 3H), 7.23 (d, *J* = 9.6 Hz, 1H), 7.01-7.07 (m, 2H), 6.12 (d, *J* = 10.4 Hz, 1H), 1.19 (s, 6H), -0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 205.6, 168.2, 145.1, 139.6, 129.7, 128.7, 127.6, 127.5, 123.2, 51.1, 24.9, -0.4; IR (CH_3Cl, cm^{-1}) 3010, 2956, 1649, 1533, 1489, 1252, 1138, 1032, 841, 768, 708; Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20; N, 2.07; found: C, 75.18; H, 6.84; N, 8.30.



12a

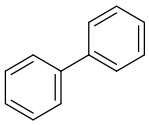
Compound **12a**: yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.27-7.16 (m, 6H), 7.09 (d, J = 7.6 Hz, 2H), 6.92-6.81 (m, 4H), 4.74 (s, 1H), 4.00 (s, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 158.7, 154.4, 143.9, 140.1, 133.8, 130.1, 128.6, 128.0, 127.3, 126.2, 124.1, 123.0, 114.7, 113.4, 55.2, 33.0; IR (CH_3Cl, cm^{-1}) 3545, 2972, 2947, 2895, 2873, 2841, 1610, 1583, 1516, 1462, 1377, 1290, 1246, 1174, 1090, 1032, 947, 841, 781, 725, 696, 669, 557, 492, 455; HRMS (EI^+) calcd for

$C_{20}H_{19}O_2$ (m/z) 291.13580, found 291.13845.



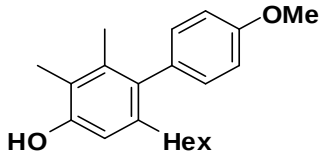
12b

Compound **12b**: yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.21-7.11 (m, 3H), 7.07 (d, J = 8.4 Hz, 1H), 7.00-6.97 (m, 4H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.60 (s, 1H), 3.81 (s, 3H), 3.77 (s, 2H) 2.25 (t, *J* = 7.8 Hz, 2H), 1.38-1.32 (m, 2H), 1.21-1.12 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 158.3, 151.2, 142.8, 140.3, 140.2, 134.1, 132.3, 130.5, 128.4, 128.1, 127.9, 126.0, 125.2, 114.8, 113.3, 55.2, 33.5, 33.3, 31.5, 31.4, 29.1, 22.5, 14.0; IR (CH_3Cl, cm^{-1}) 3597, 3020, 2958, 2929, 2858, 1732, 1610, 1514, 1468, 1441, 1375, 1282, 1246, 1174, 1105, 1043, 949, 829, 793, 783, 775, 739, 700, 573, 499; HRMS (EI^+) calcd for $C_{26}H_{31}O_2$ (m/z) 375.23240, found 375.23321.



12c

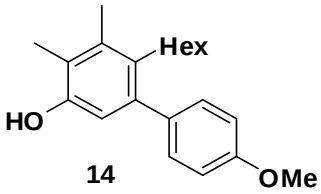
Compound **12c**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.16 (3H, s), 3.85 (3H, s), 4.90 (1H, s), 6.78 (1H, d, *J* = 7.8 Hz), 6.83 (1H, d, *J* = 7.8 Hz), 6.95 (2H, d, *J* = 9.2 Hz), 7.10 (1H, dd, *J* = 7.8 Hz), 7.24 (2H, d, *J* = 9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.0, 55.3, 113.4, 113.5, 121.7, 122.6, 126.2, 130.3, 134.0, 143.3, 154.0, 158.5. IR: (CHCl3, cm^{-1}) 3340, 3010, 1610, 1515. HRMS (DART/CH_2Cl_2): $[M+H]^+$ Calcd for $C_{14}H_{15}O_2$: 215.10720; Found 215.10692.



13

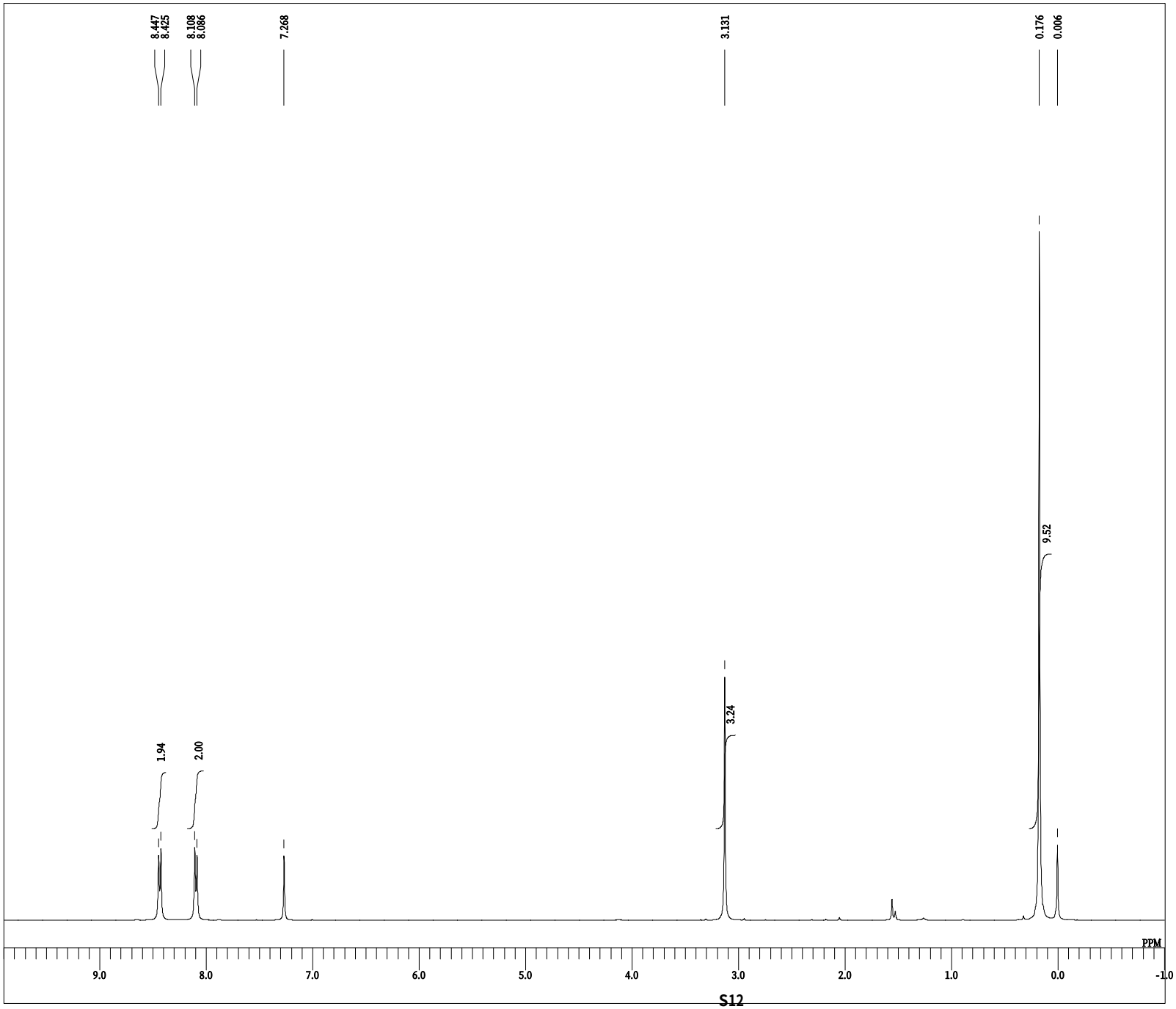
Compound **13**: yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.02 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.58 (s, 1H), 4.73 (s, 1H), 3.86 (s, 3H), 2.23 (t, *J* = 8.0 Hz, 2H), 2.18 (s, 3H), 1.93 (s, 3H), 1.37-1.32 (m, 2H), 1.21-1.10 (m, 6H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 158.0, 152.3, 140.0, 136.8, 134.1, 133.7, 131.0, 131.0, 120.0, 113.5, 112.6, 55.2, 33.5, 31.5, 31.1, 29.1, 22.4, 17.8, 14.0, 11.9; IR (CH_3Cl, cm^{-1}) 3600, 3003, 2956, 2922, 2858, 2062, 1990, 1705, 1608, 1514, 1466, 1415, 1282, 1246, 1174, 1082, 1036, 908, 835, 602, 553, 526; HRMS (EI^+) calcd for $C_{21}H_{29}O_2$

(m/z) 313.21675, found 313.21598.



14

Compound **14**: yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.15 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.45 (s, 1H), 4.90 (s, 1H), 3.83 (s, 3H), 2.45 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.34-1.1.15 (m, 8H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ: 158.1, 150.7, 140.1, 136.5, 135.2, 131.6, 130.2, 122.0, 114.4, 113.2, 55.2, 31.3, 30.7, 30.0, 29.4, 22.5, 16.1, 14.0, 12.1; IR (CH_3Cl, cm^{-1}) 3602, 3006, 2956, 2929, 2857, 1731, 1610, 1583, 1514, 1466, 1375, 1327, 1284, 1244, 1174, 1105, 1076, 1038, 837, 779, 768, 727, 665, 588, 523; HRMS (EI^+) calcd for $C_{21}H_{29}O_2$ (m/z) 313.21675, found 313.21671.



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OBFIN 7.29 Hz
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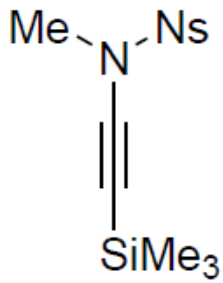
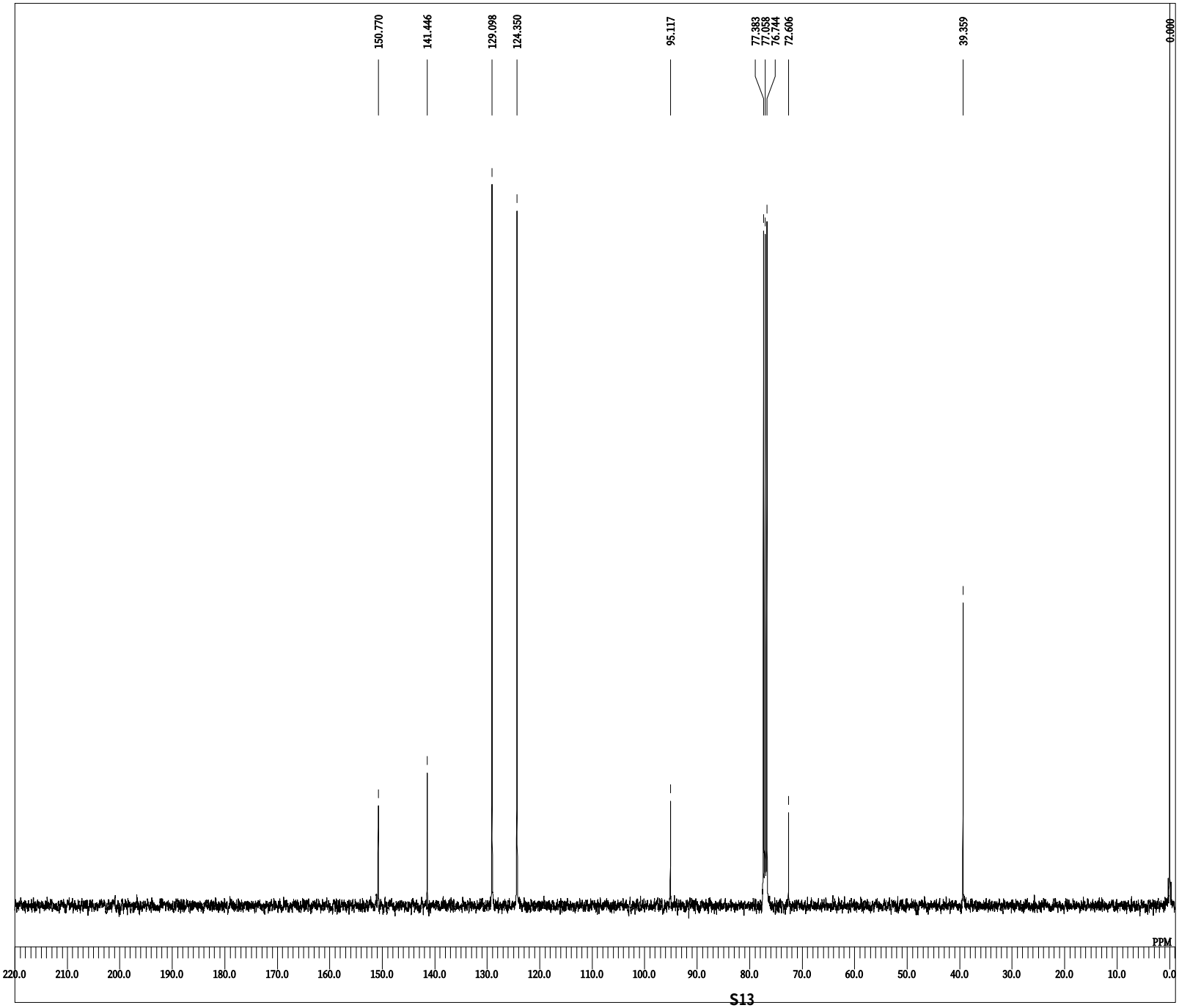
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 3.00 Hz
RGAIN 48



6c



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CTEMP	20.6 c
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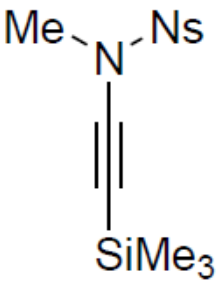
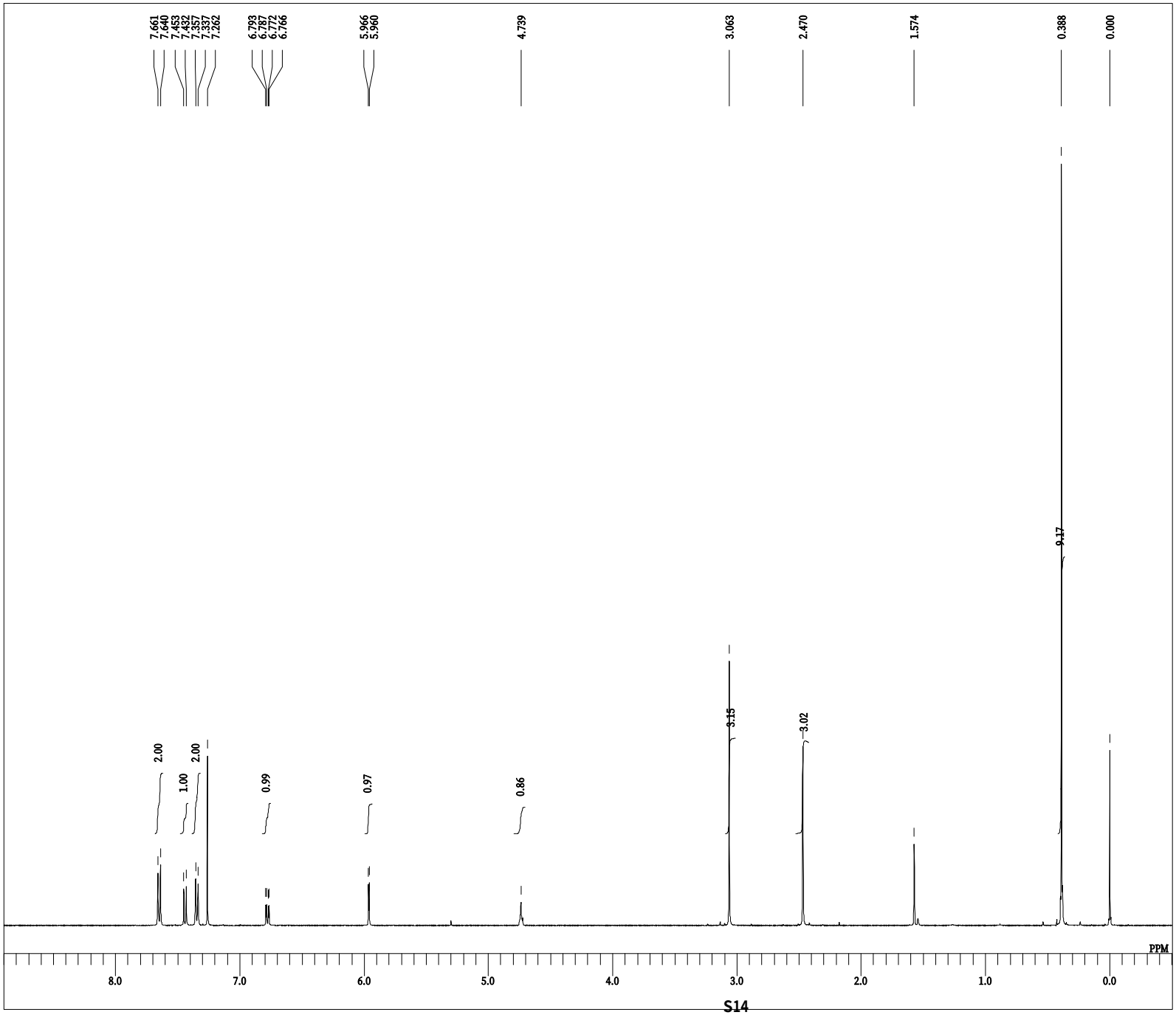
EXREF	0.00 ppm
BF	3.00 Hz
RGAIN	60



6c



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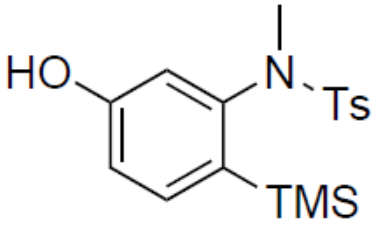
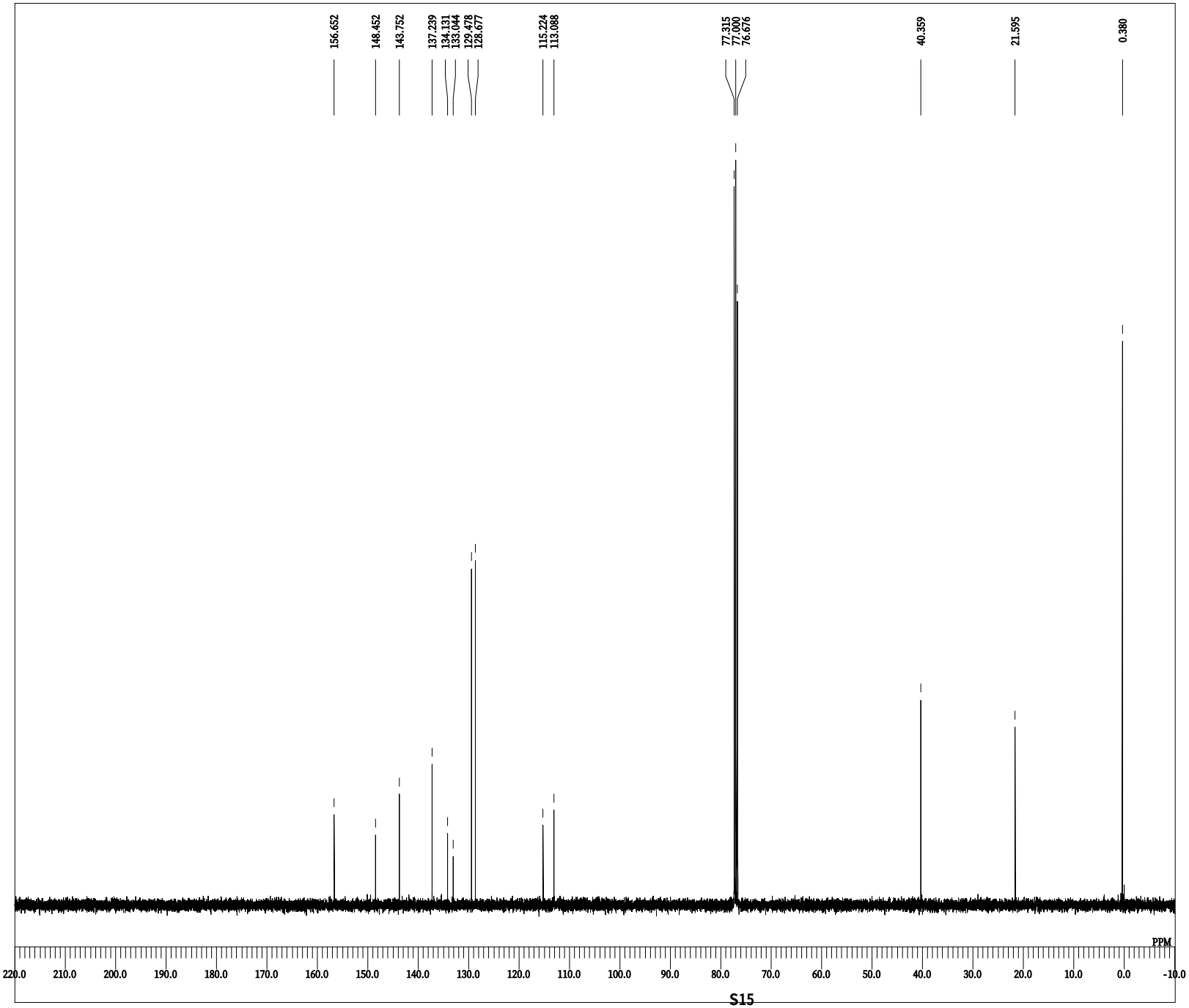
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 50



7a



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OBSET 5.35 KHz
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FREQU 25125.24 Hz
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PD 1.2000 sec
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IRNUC 1H
CTEMP 20.6 c
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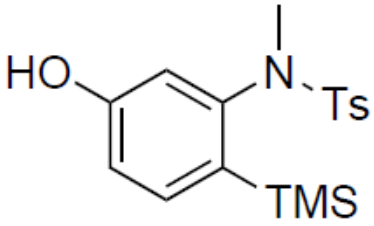
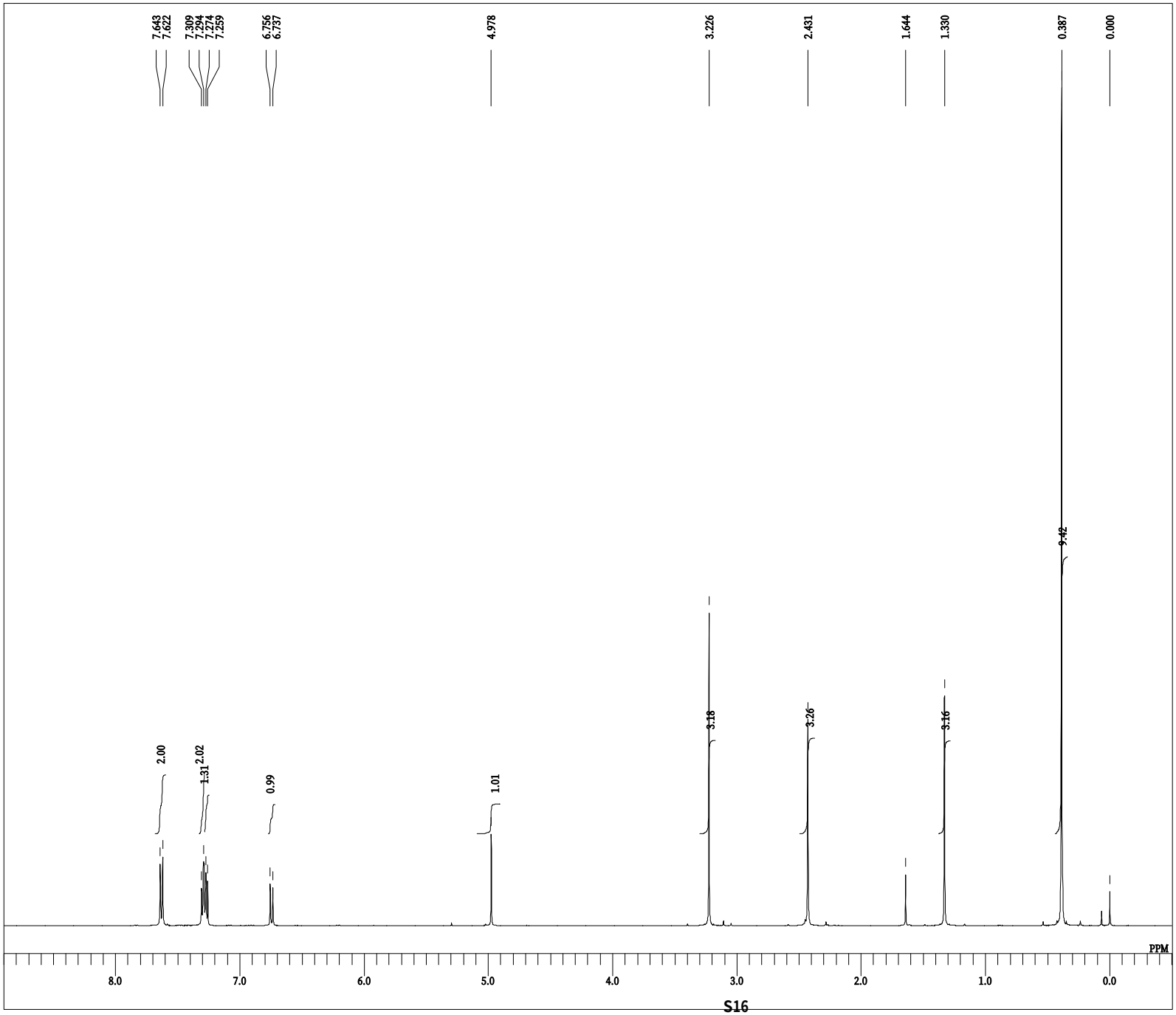
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



7a



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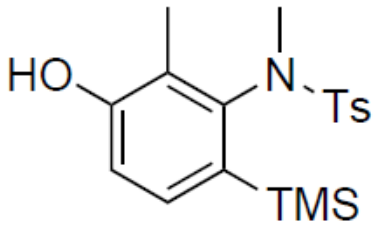
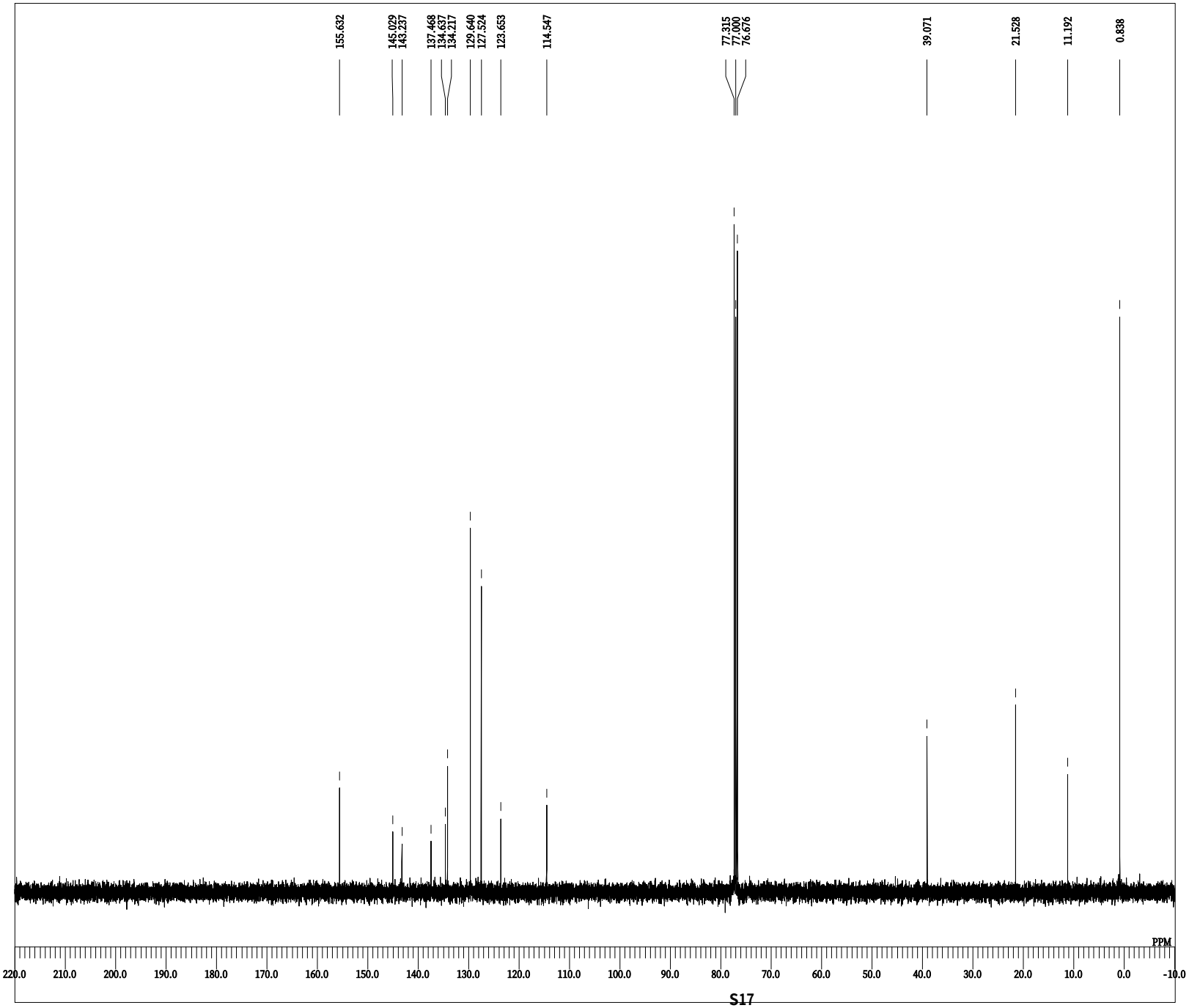
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 38



7b



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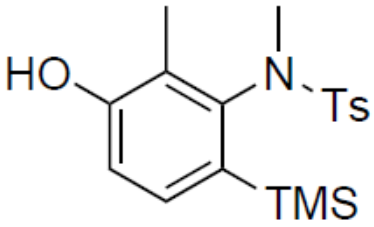
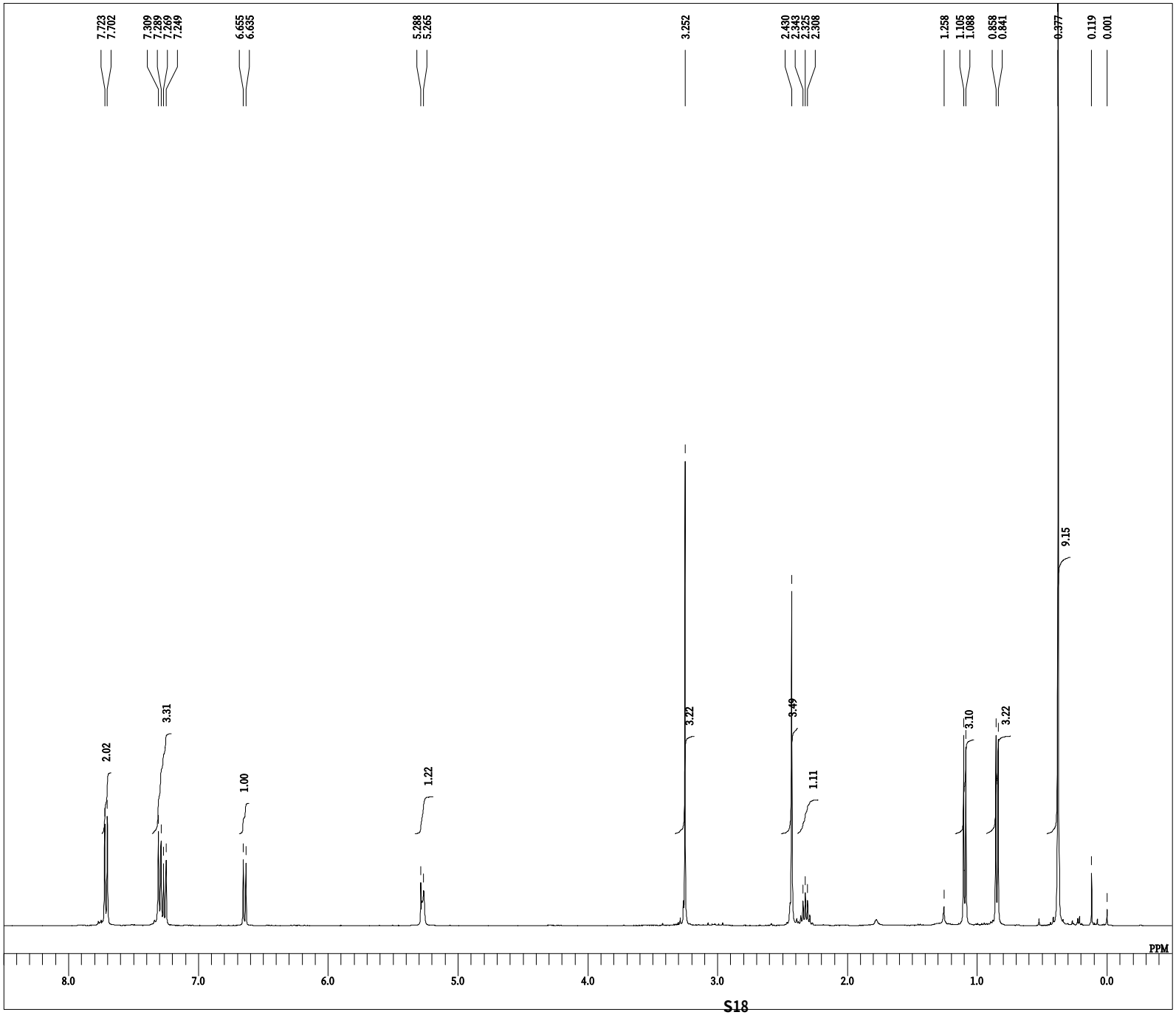
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	222
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.87 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



7b



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OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
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ACQTM 2.1837 sec
PD 2.0000 sec
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IRNUC 1H
CTEMP 20.9 c
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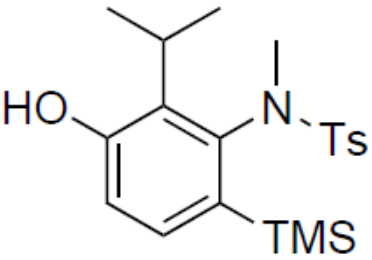
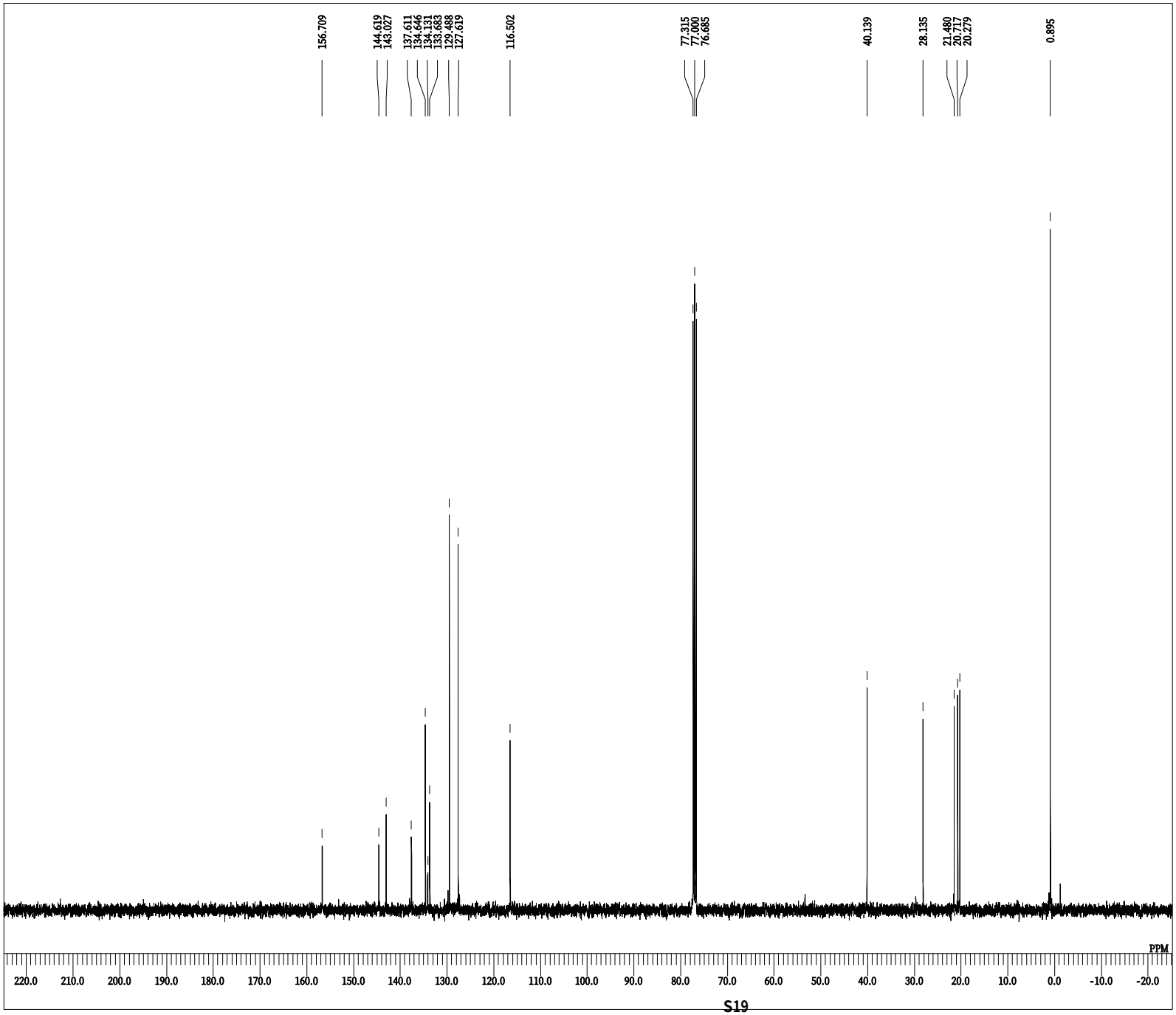
BF 0.20 Hz
RGAIN 30



7c



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OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 152
ACQTM 1.0433 sec
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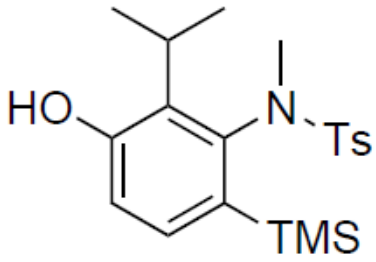
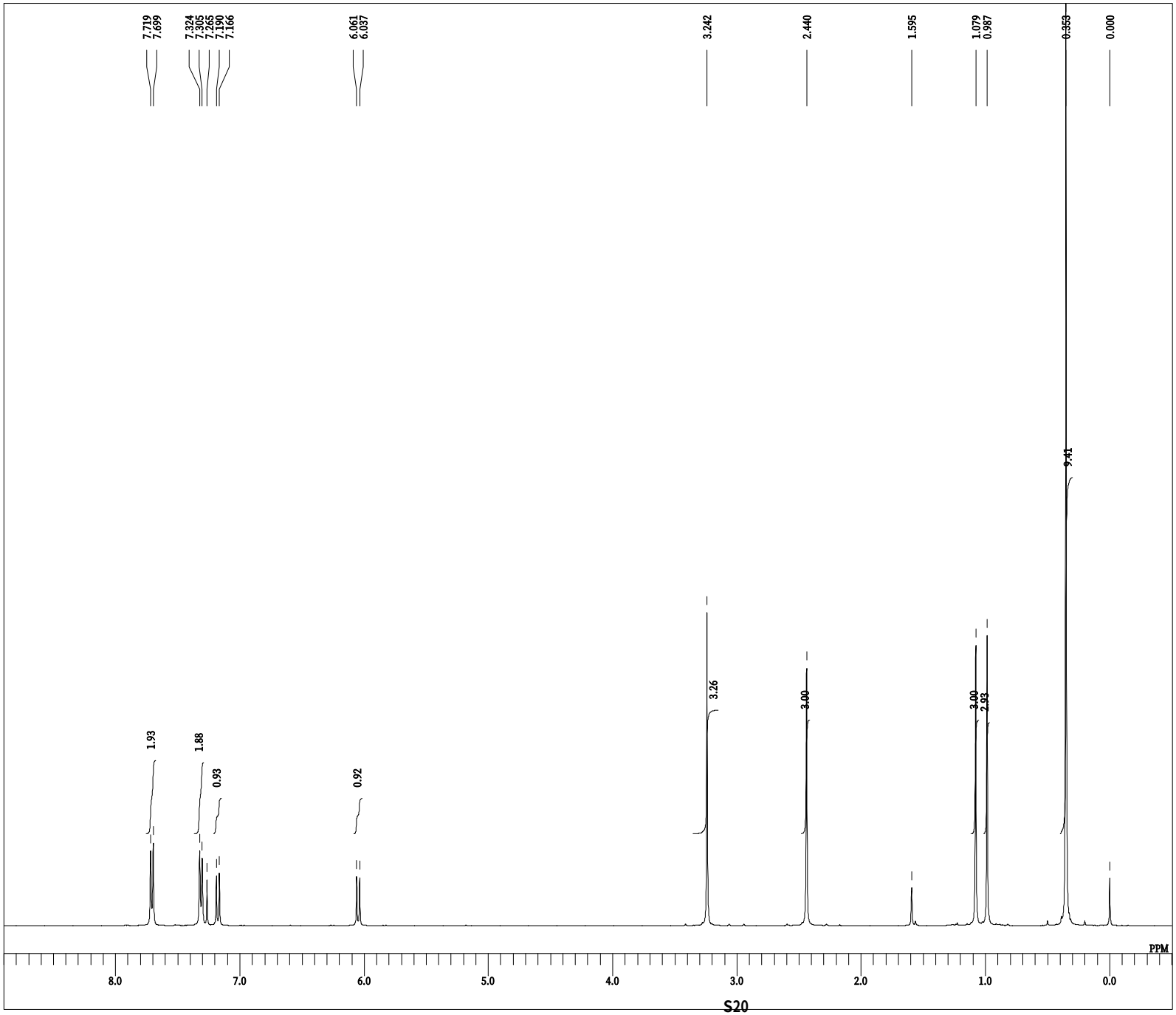
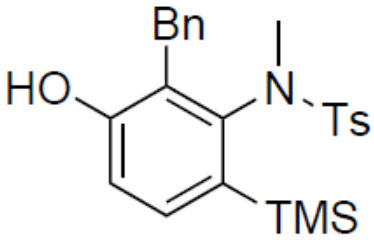
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.40 Hz
RGAIN 60



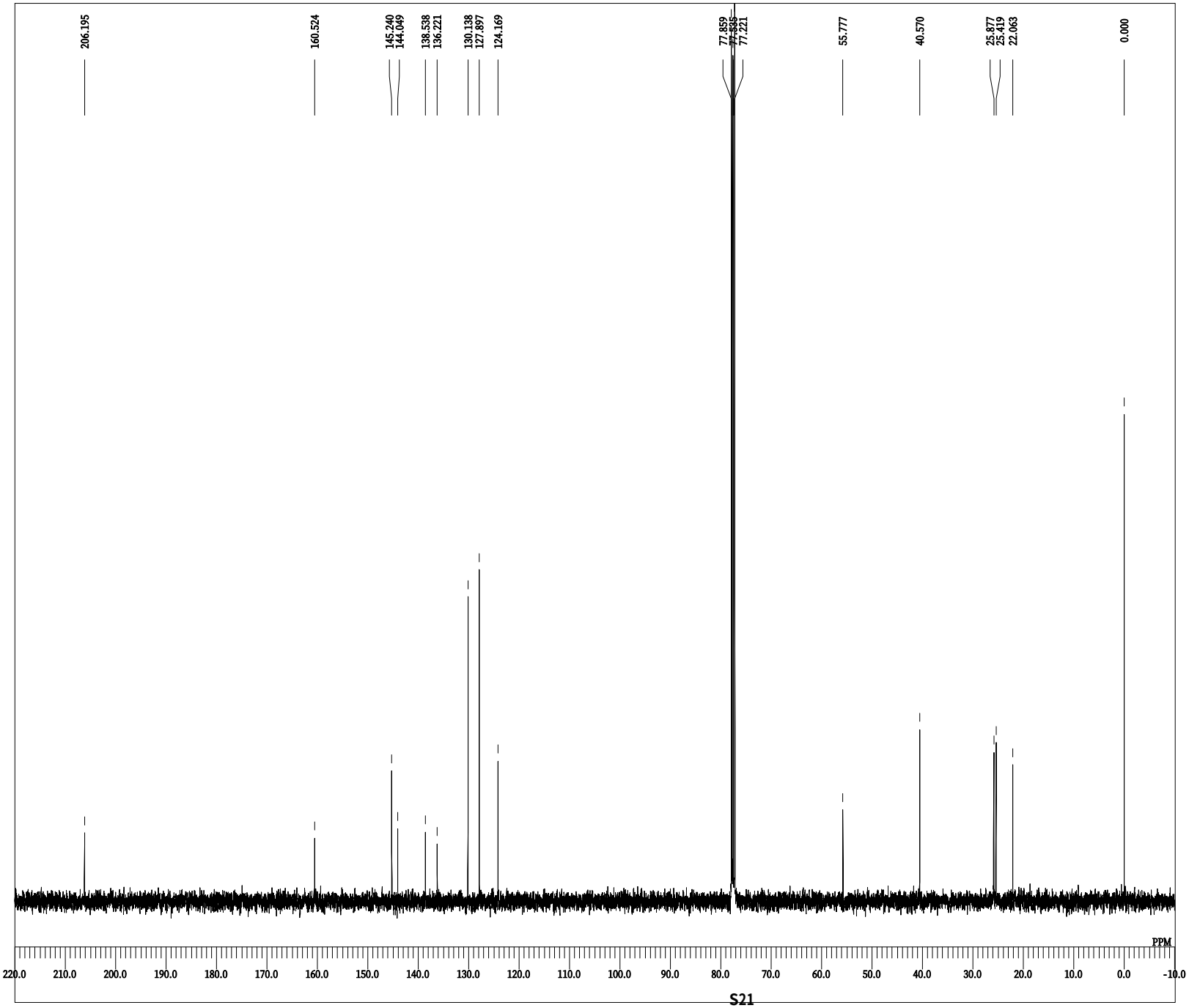
7c



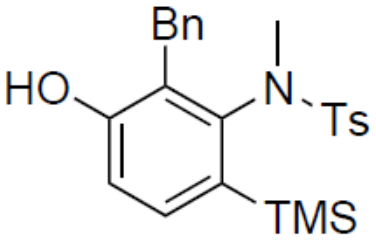

```
DFILE     sample-1-1.als
COMNT
DATIM     2016-10-12 18:39:01
OBNUC     1H
EXMOD     single_pulse.ex2
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      6002.31 Hz
SCANS            8
ACQTM         2.1837 sec
PD            2.0000 sec
PW1           4.70 usec
IRNUC     1H
CTEMP        22.1 c
SLVNT     CDCL3
EXREF         0.00 ppm
BF            1.40 Hz
RGAIN           38
```



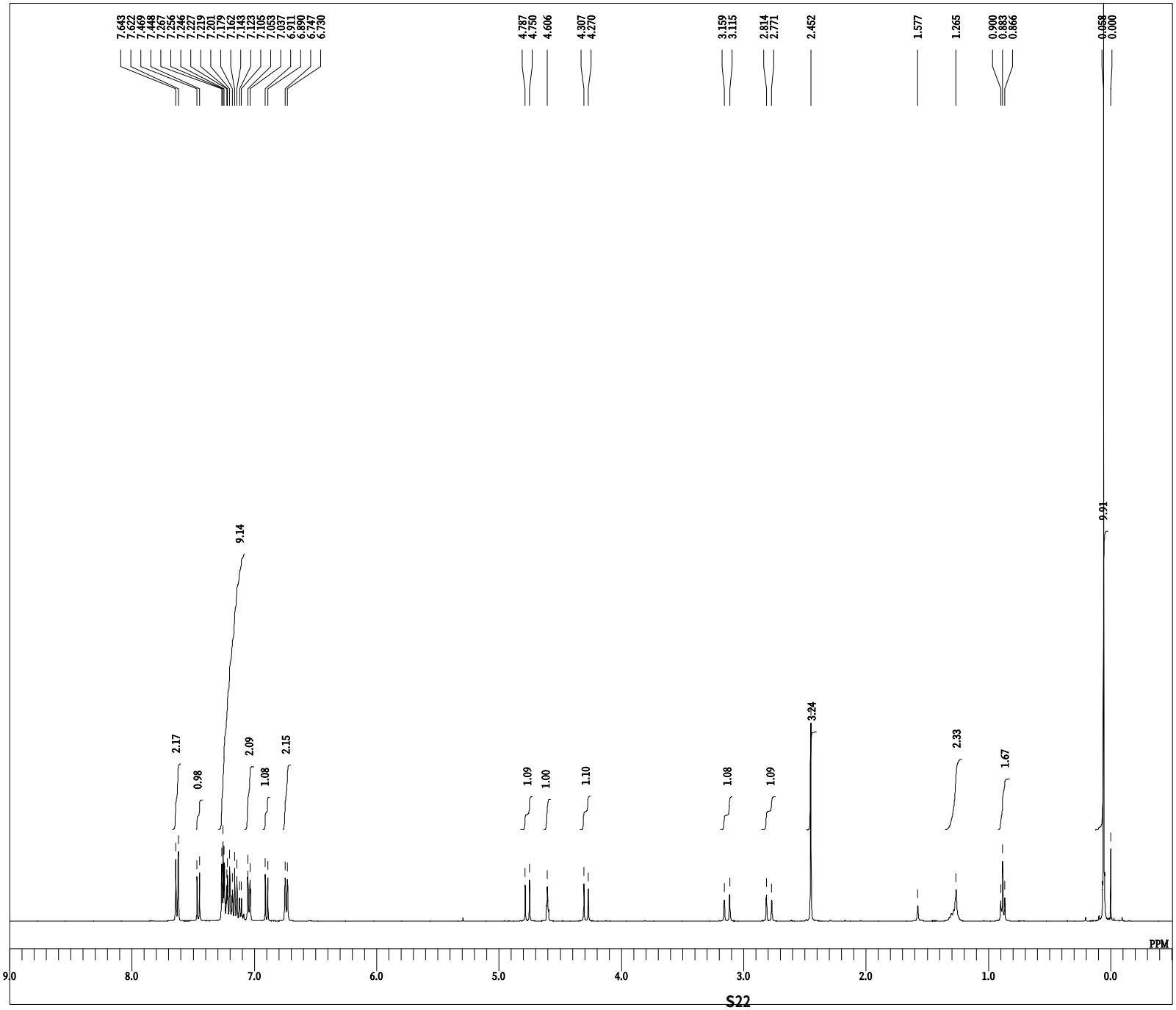
7d



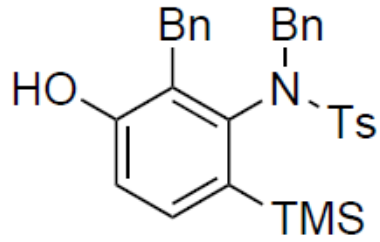
DFILE sample-1 c13-1.als
COMNT
DATIM 2016-10-12 18:47:51
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 215
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 60



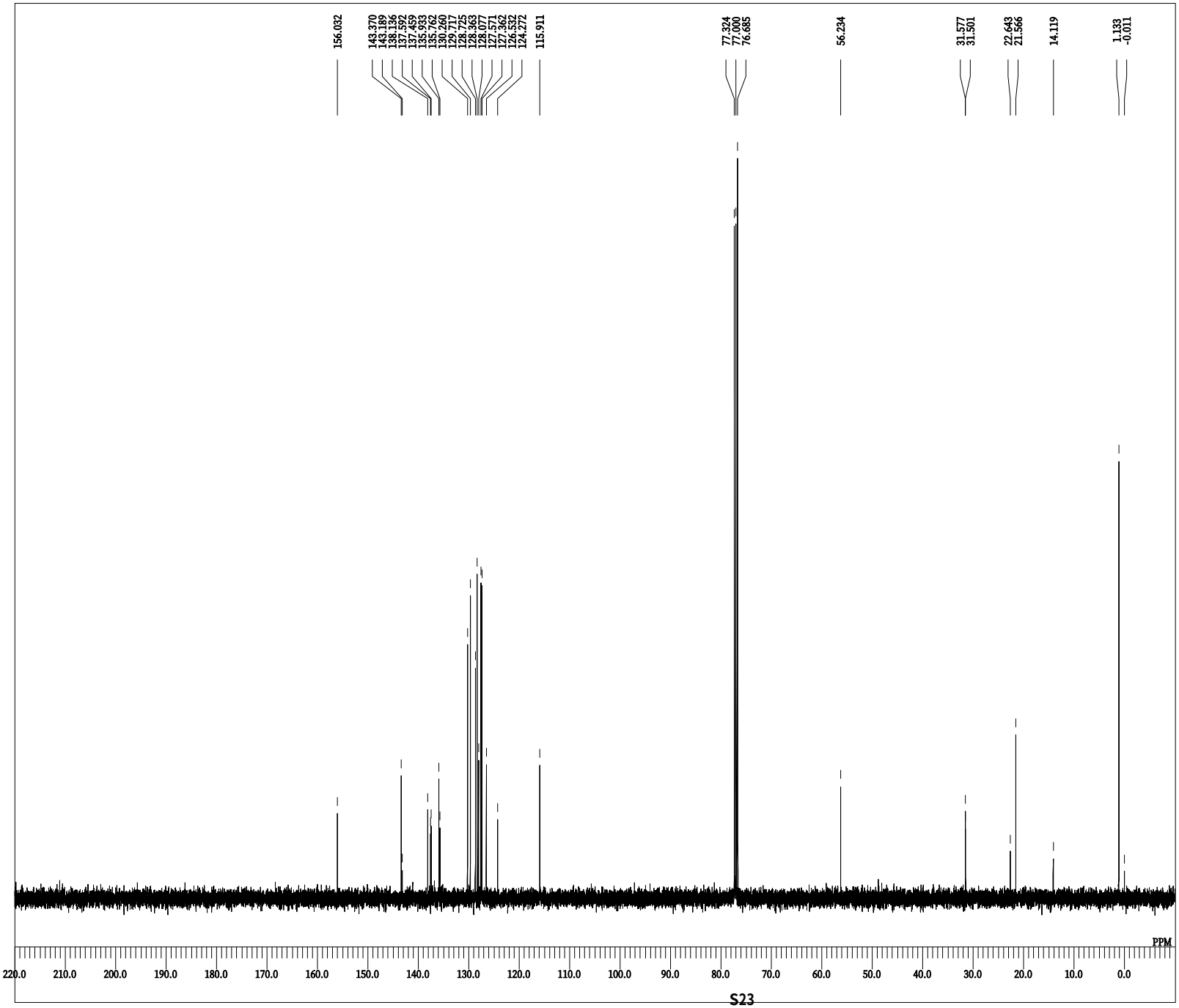
7d



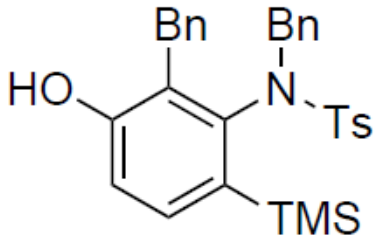
DFILE 7e-proton-1.als
COMNT
DATIM 2016-12-08 13:06:21
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



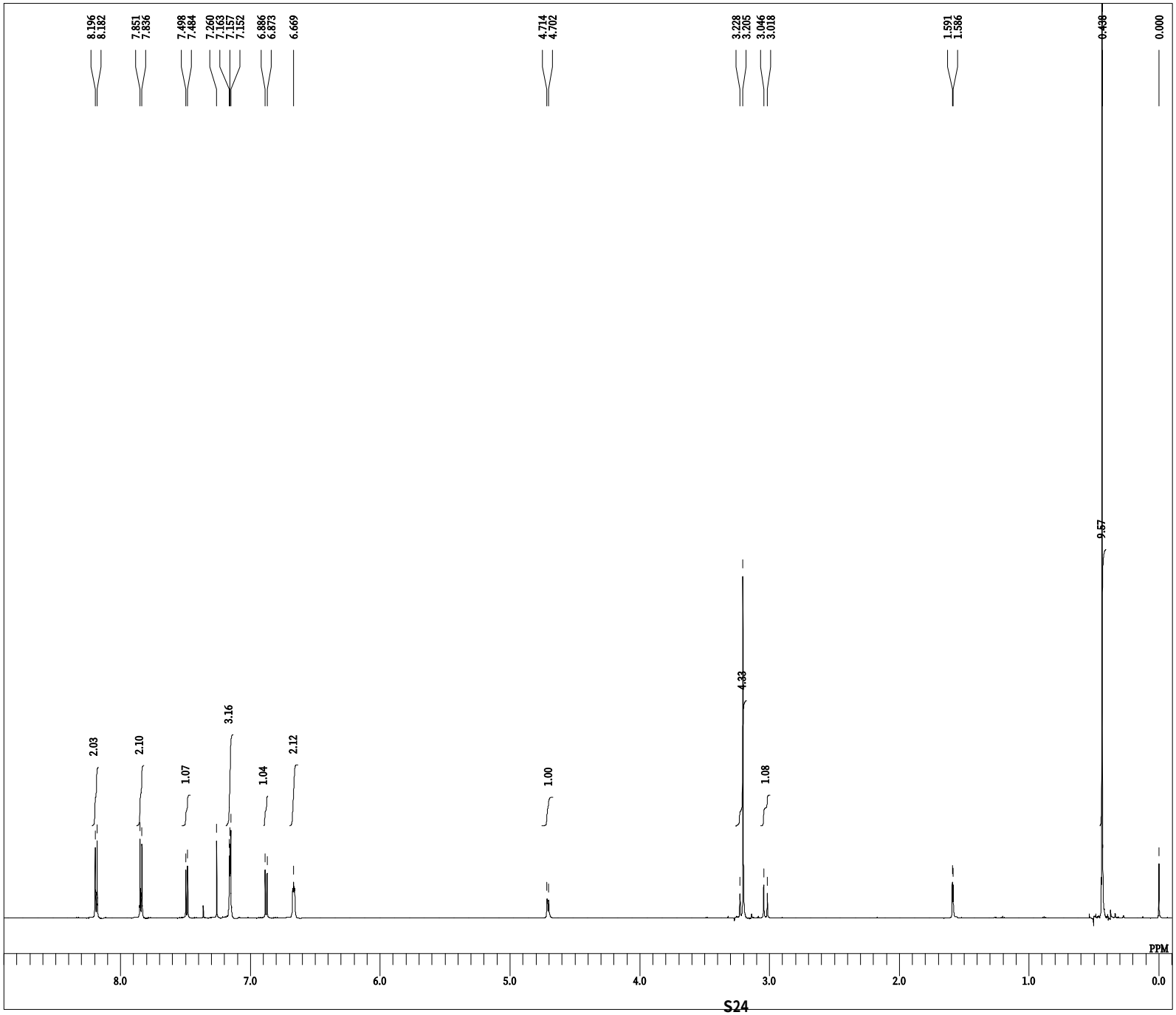
7e



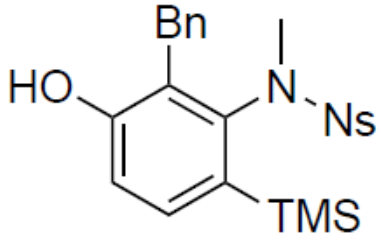
DFILE 7e-carbon-1.als
COMNT
DATIM 2016-12-08 13:21:02
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 369
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



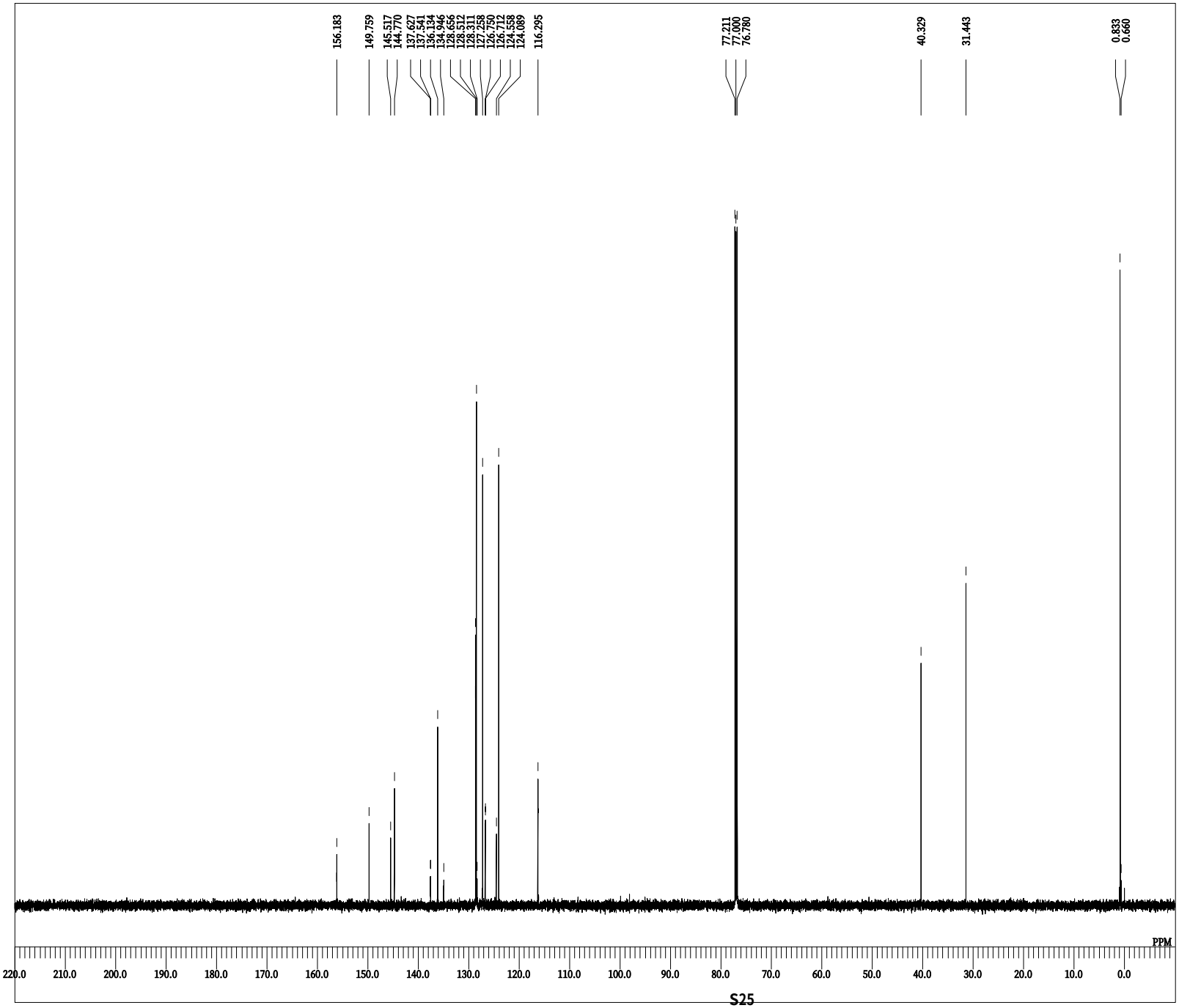
7e



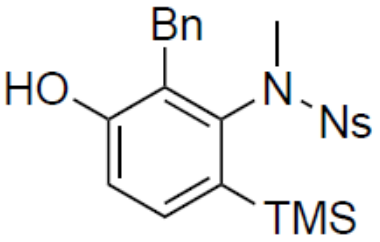

```
DFILE     7f proton-1.als
COMNT
DATIM     2016-12-19 15:33:48
OBNUC     1H
EXMOD     single_pulse.ex2
OBFRQ       600.17 MHz
OBSET         5.30 KHz
OBFIN         5.47 Hz
POINT        26214
FREQU      9008.87 Hz
SCANS            8
ACQTM        2.9098 sec
PD           2.0000 sec
PW1             6.85 usec
IRNUC     1H
CTEMP        19.6 c
SLVNT     CDCL3
EXREF        0.00 ppm
BF           0.20 Hz
RGAIN           44
```



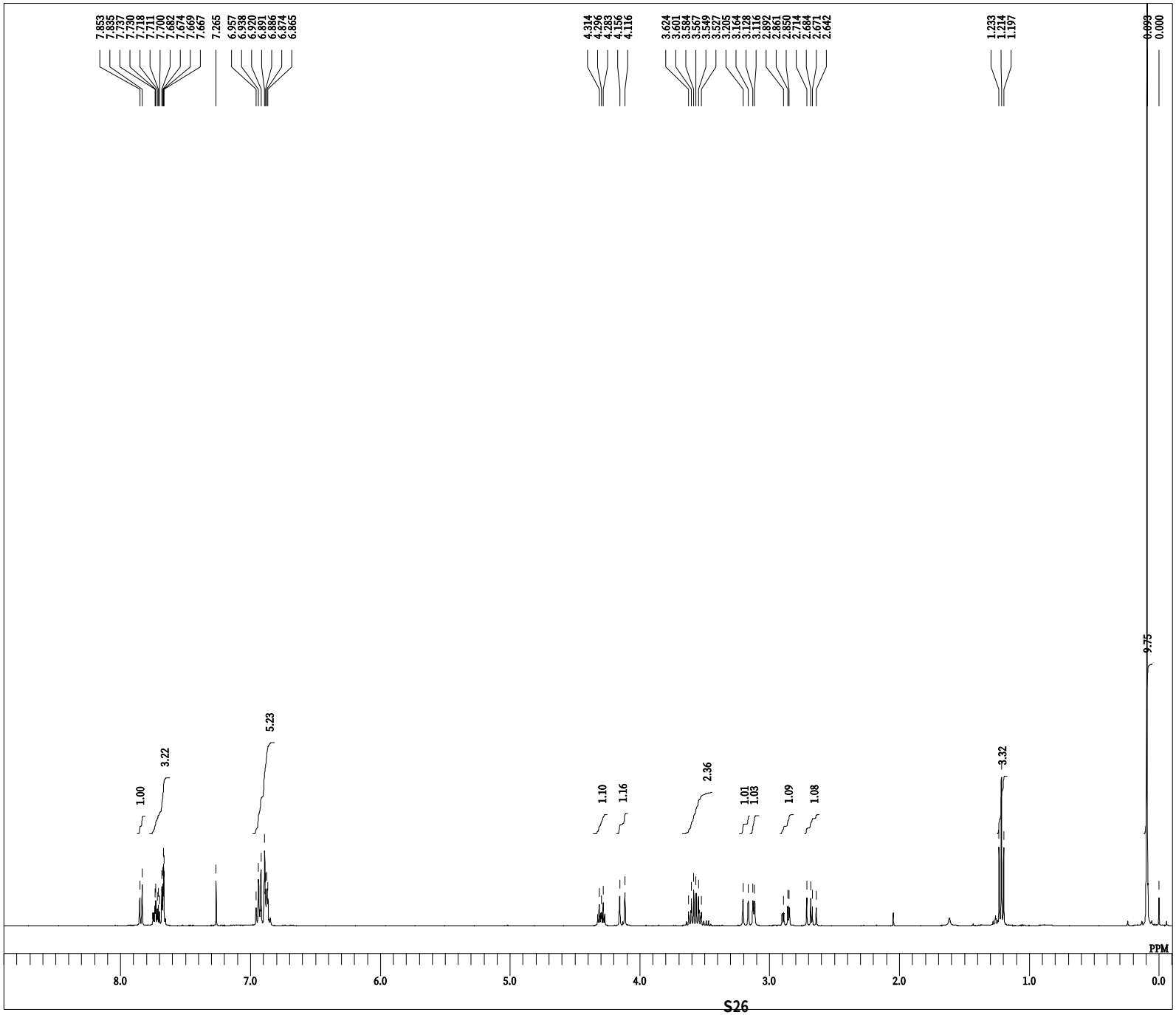
7f



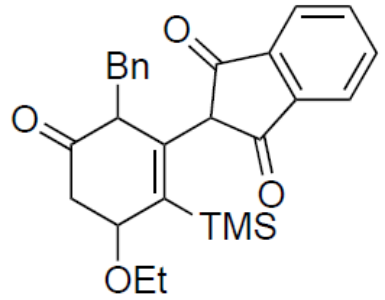
DFILE 7f carbon-1.als
COMNT
DATIM 2016-12-19 16:13:60
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26214
FREQU 37878.21 Hz
SCANS 905
ACQTM 0.6921 sec
PD 1.2000 sec
PW1 3.43 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 56



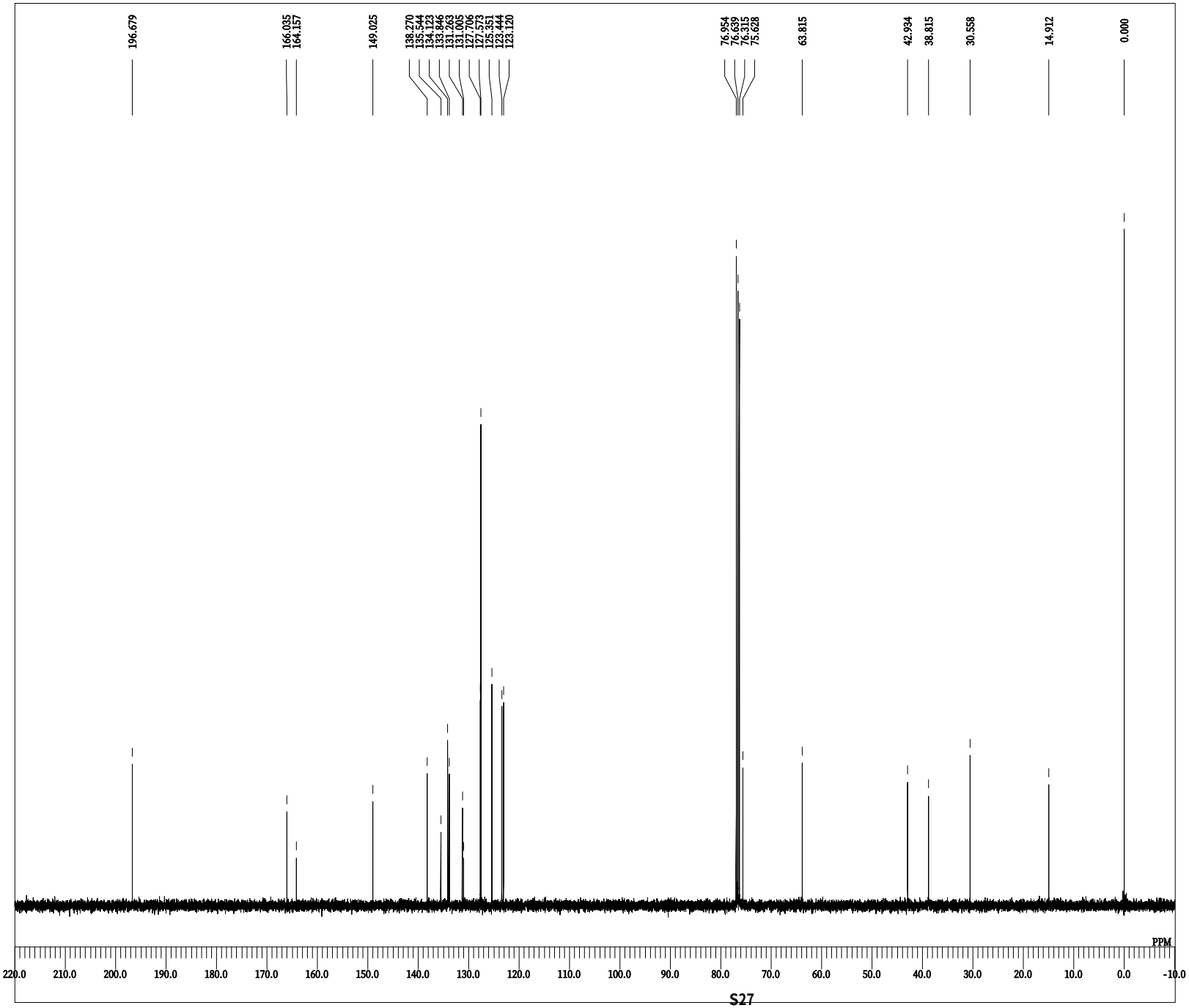
7f



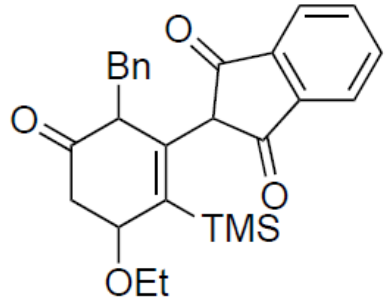
DFILE 7g` proton-1.als
COMNT
DATIM 2016-12-15 17:17:35
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 36



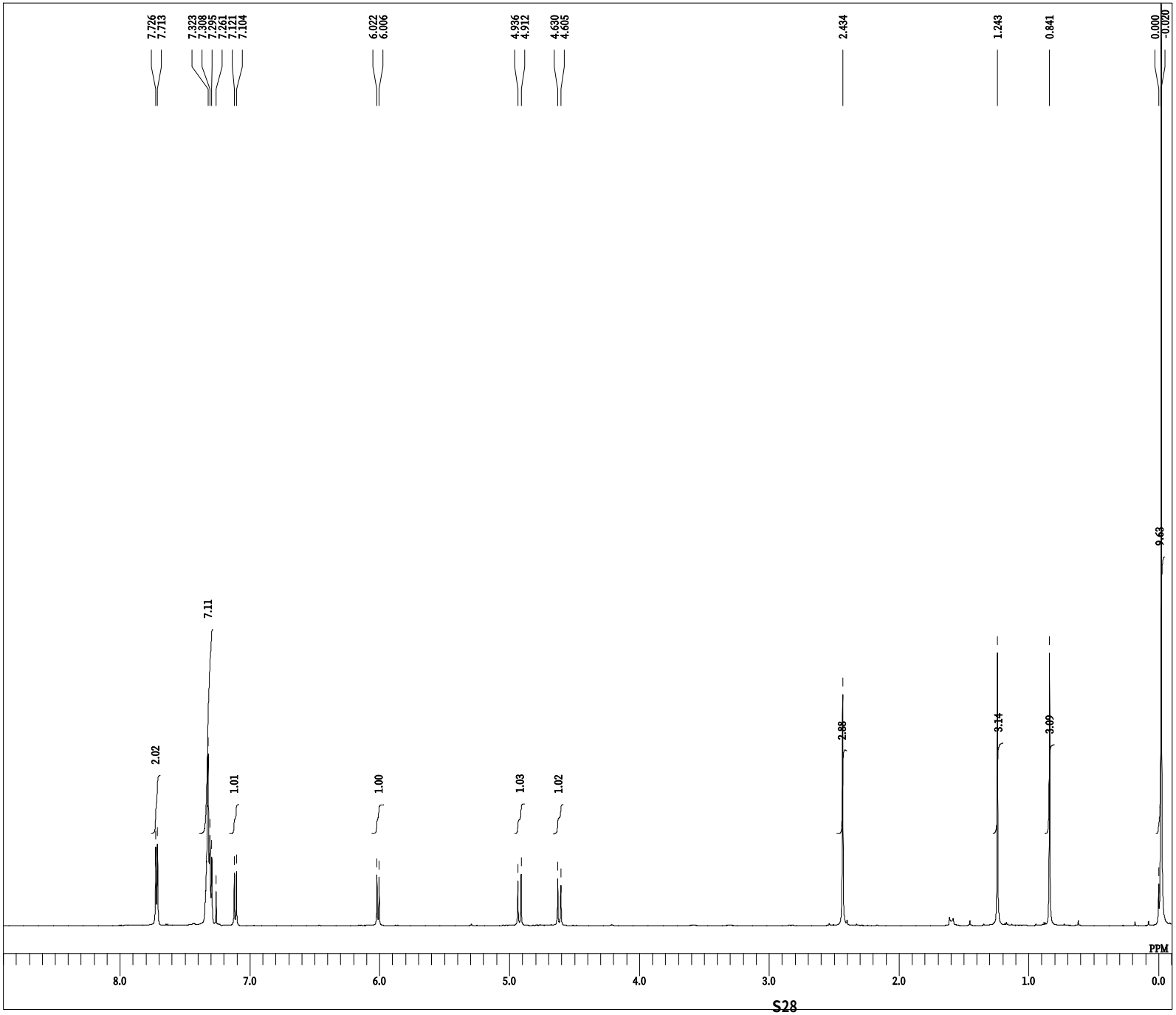
7g'



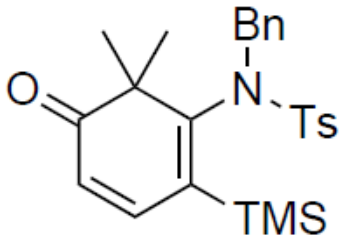
DFILE 7g` carbon-1.als
COMNT
DATIM 2016-12-15 17:39:31
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 565
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 60



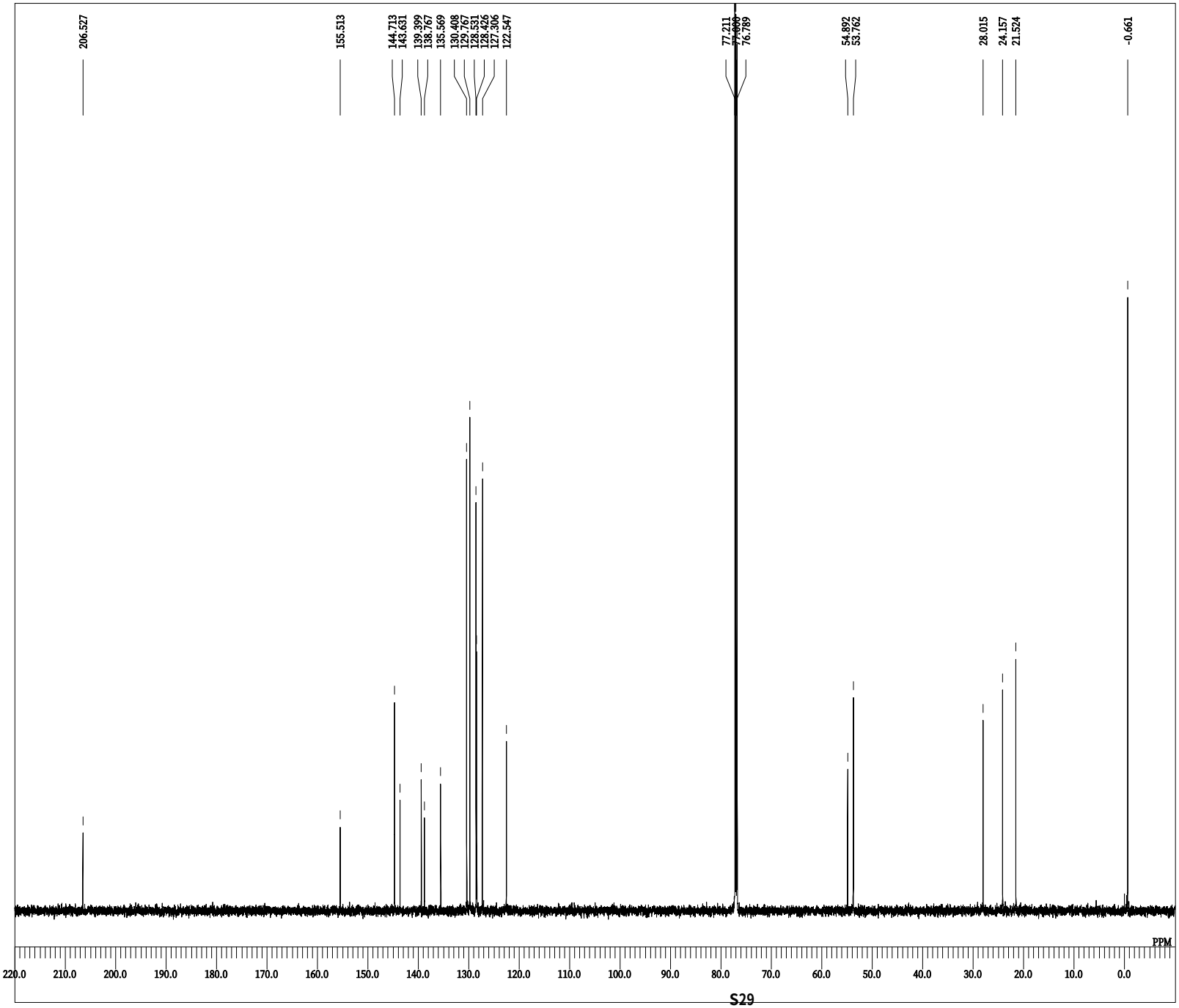
7g'



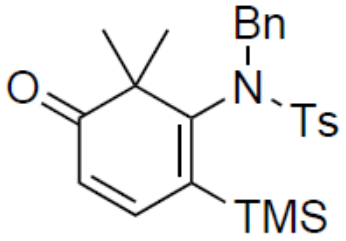
DFILE tk_sample2-1.als
COMNT
DATIM 2016-06-22 10:07:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 7.30 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 36



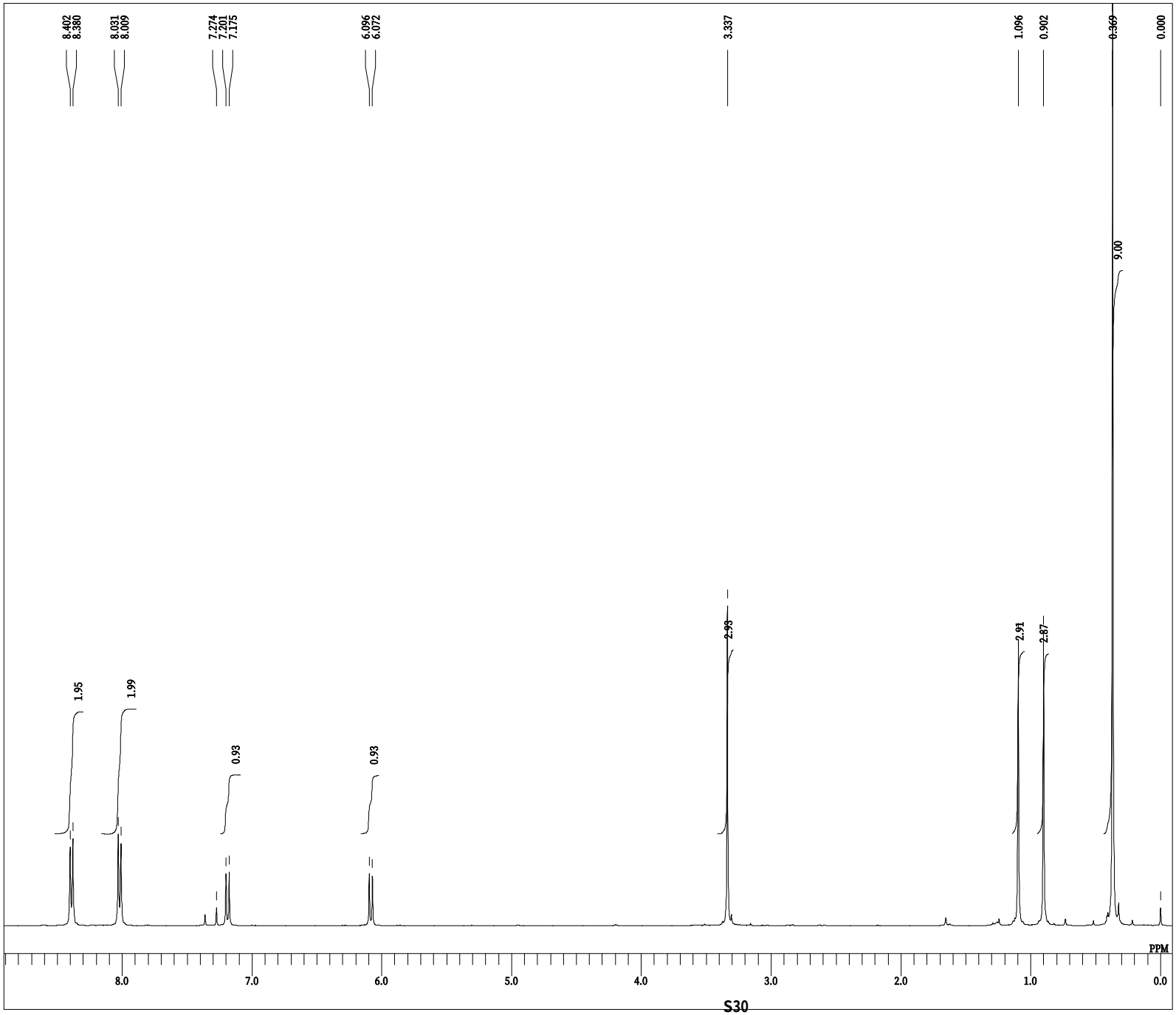
8a



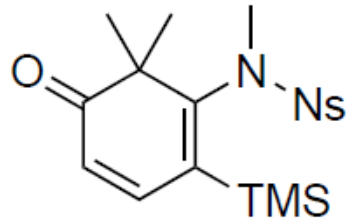
DFILE tk_sample2-carbon-1.als
COMNT
DATIM 2016-06-22 10:22:03
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26214
FREQU 37878.21 Hz
SCANS 416
ACQTM 0.6921 sec
PD 1.2000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.40 Hz
RGAIN 56



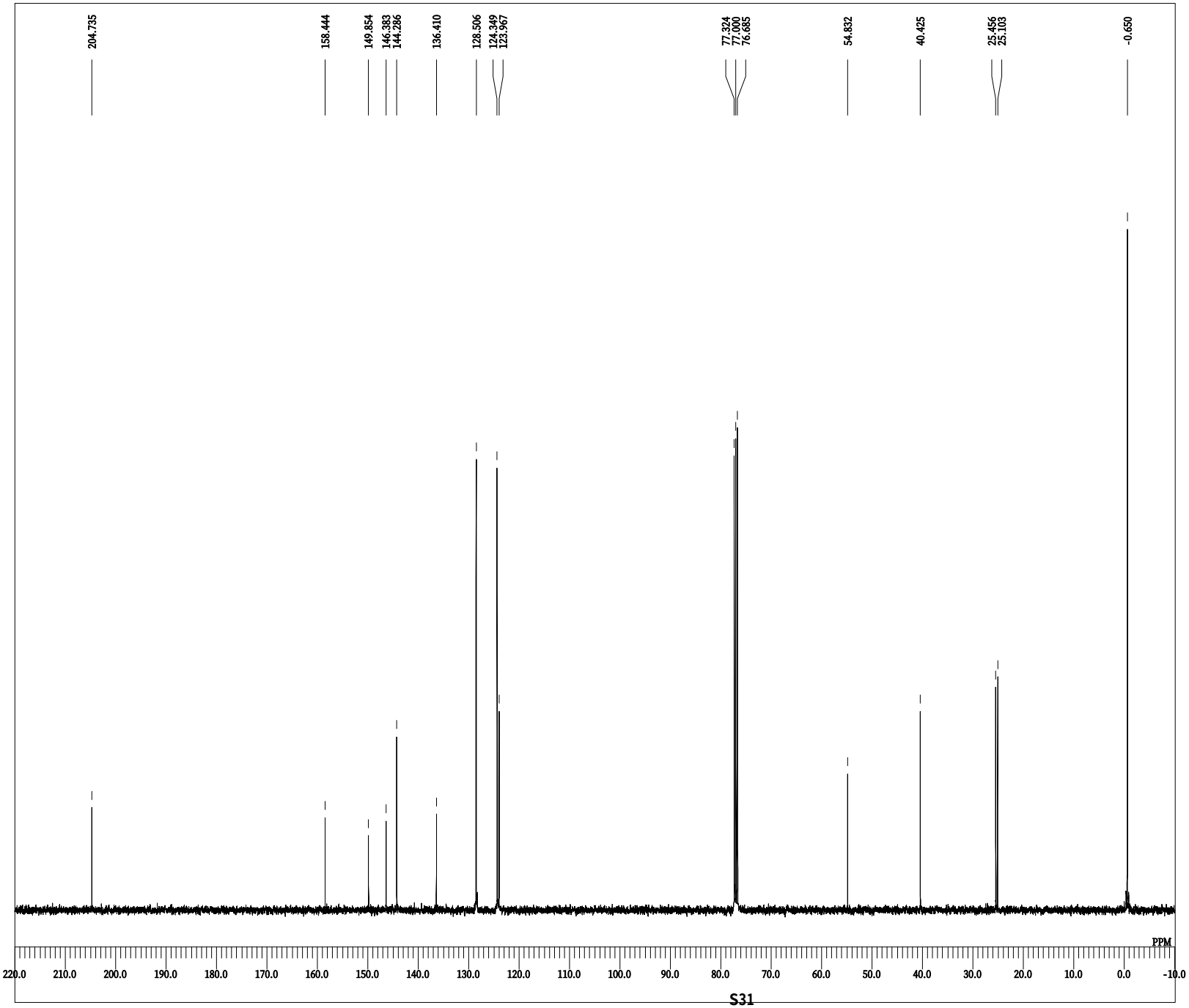
8a



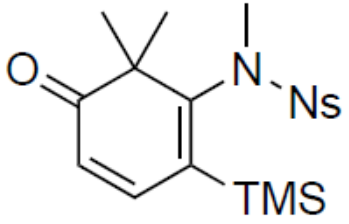
DFILE 8b-proton-1.als
COMNT
DATIM 2016-12-08 19:38:06
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 34



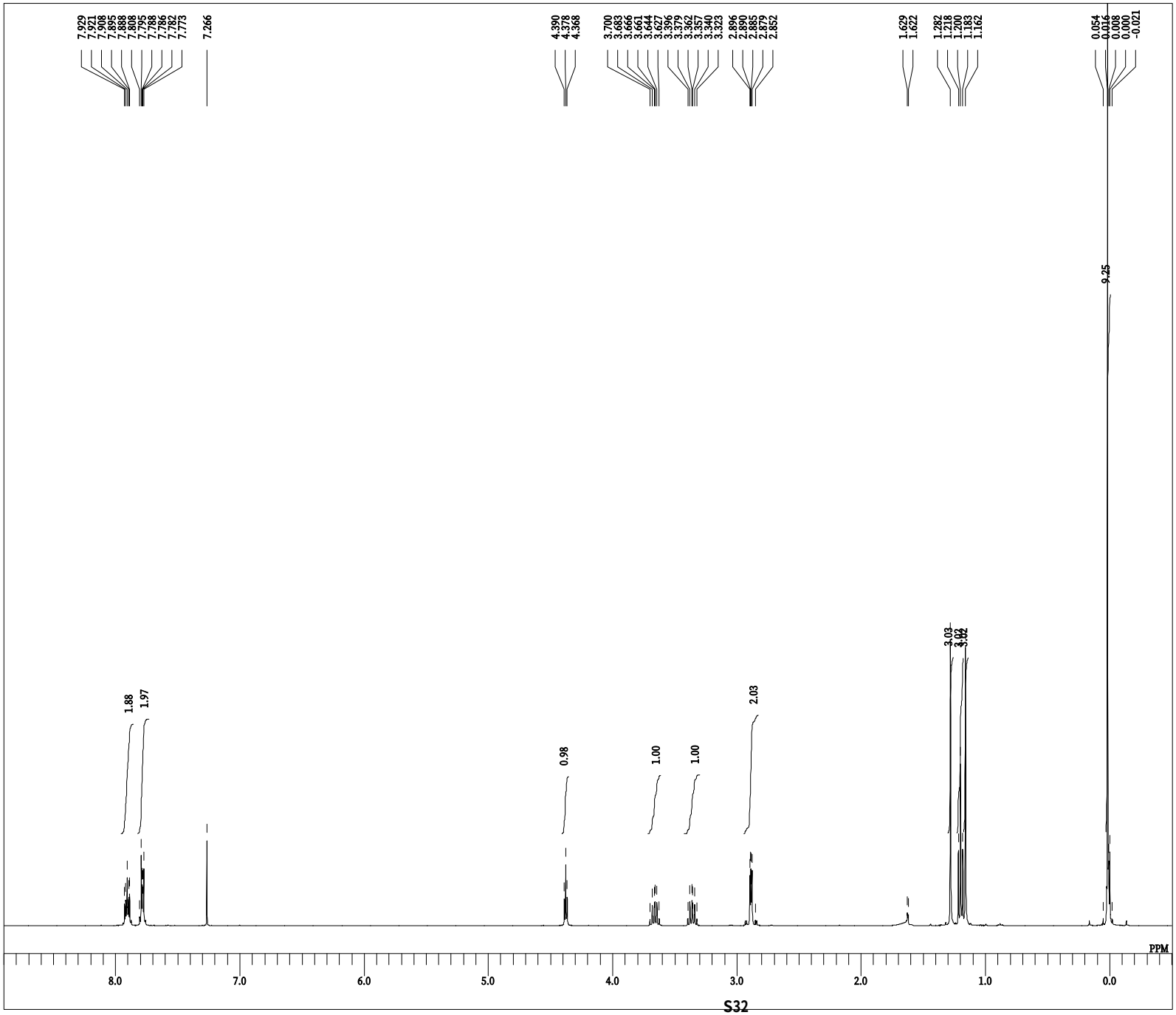
8b



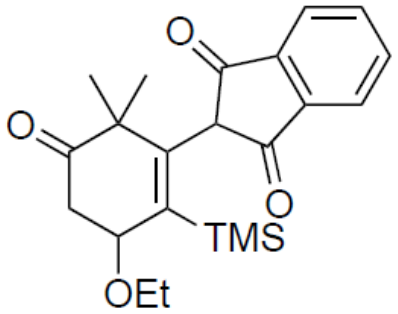
DFILE 8b-carbon-1.als
COMNT
DATIM 2016-12-08 19:53:53
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 390
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.40 Hz
RGAIN 60



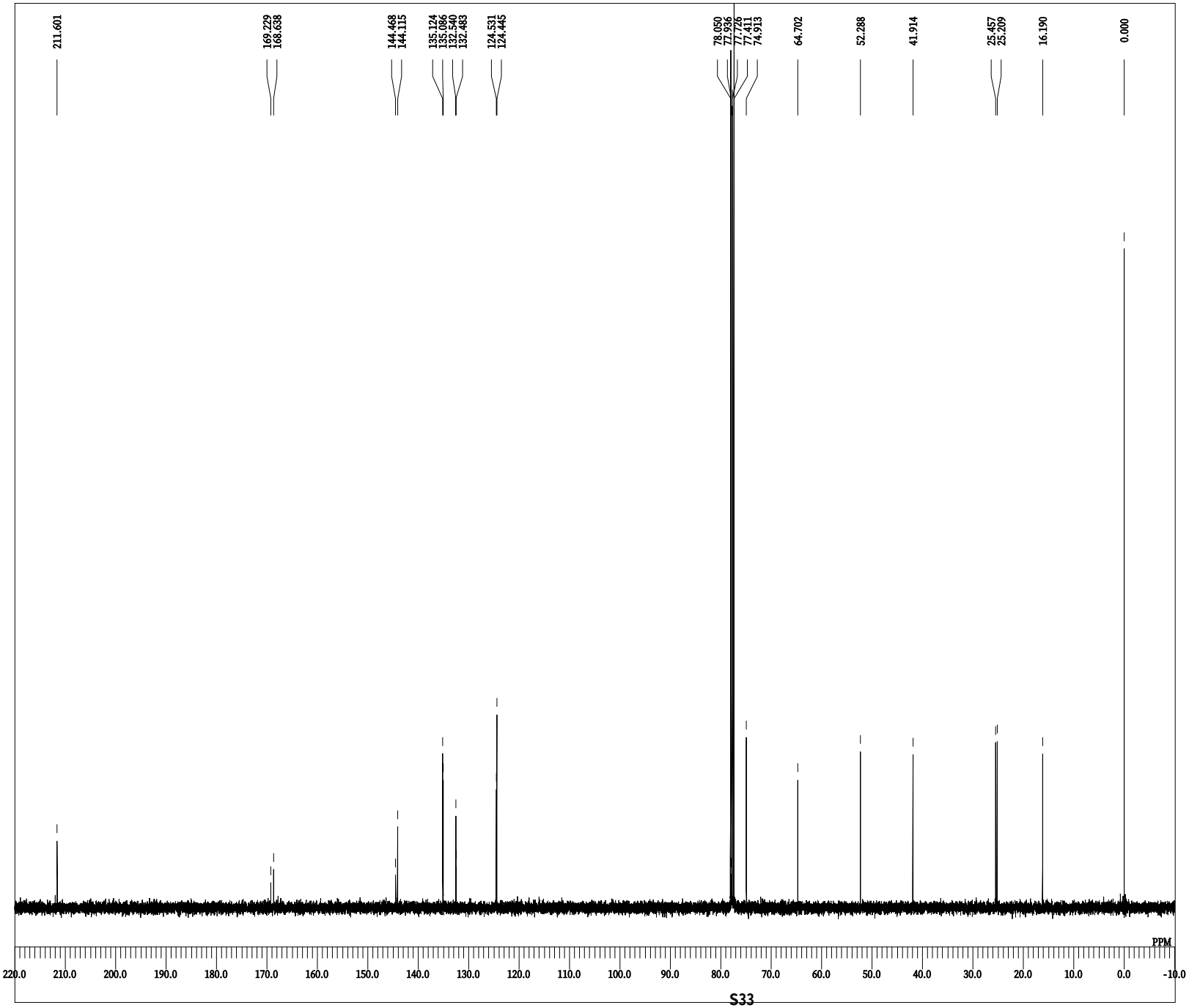
8b



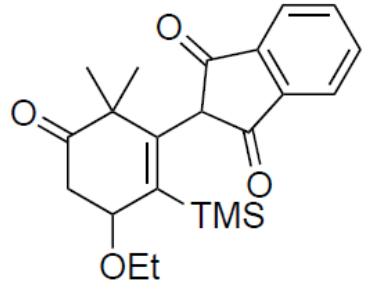
DFILE 8c proton-1.als
COMNT
DATIM 2016-12-21 16:30:43
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 40



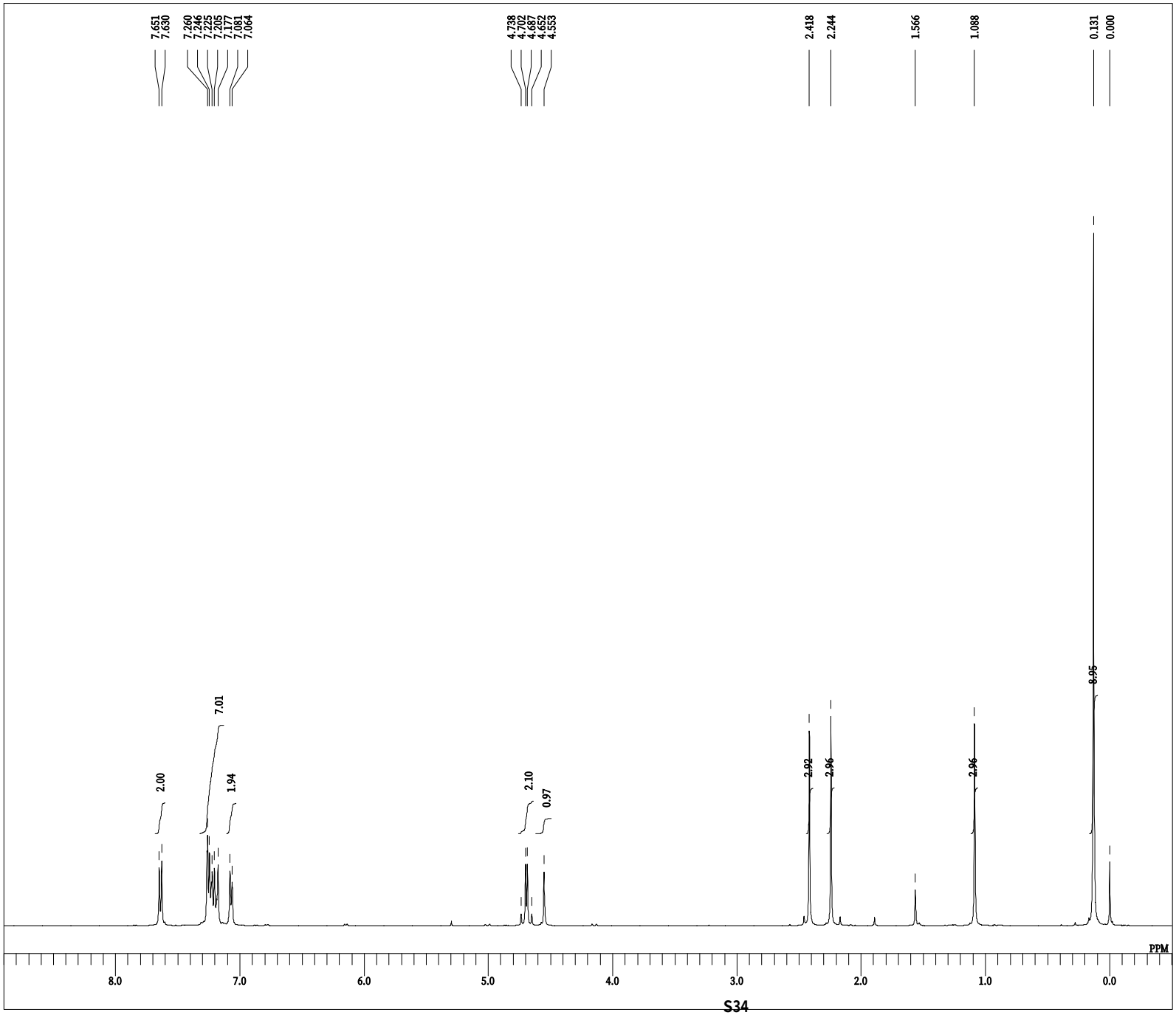
8c'



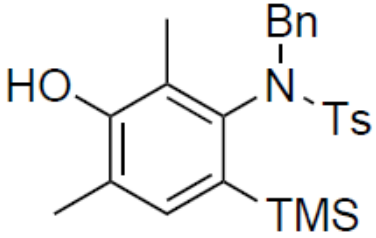
DFILE 8c carbon-1.als
COMNT
DATIM 2016-12-21 17:08:60
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 1000
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 60



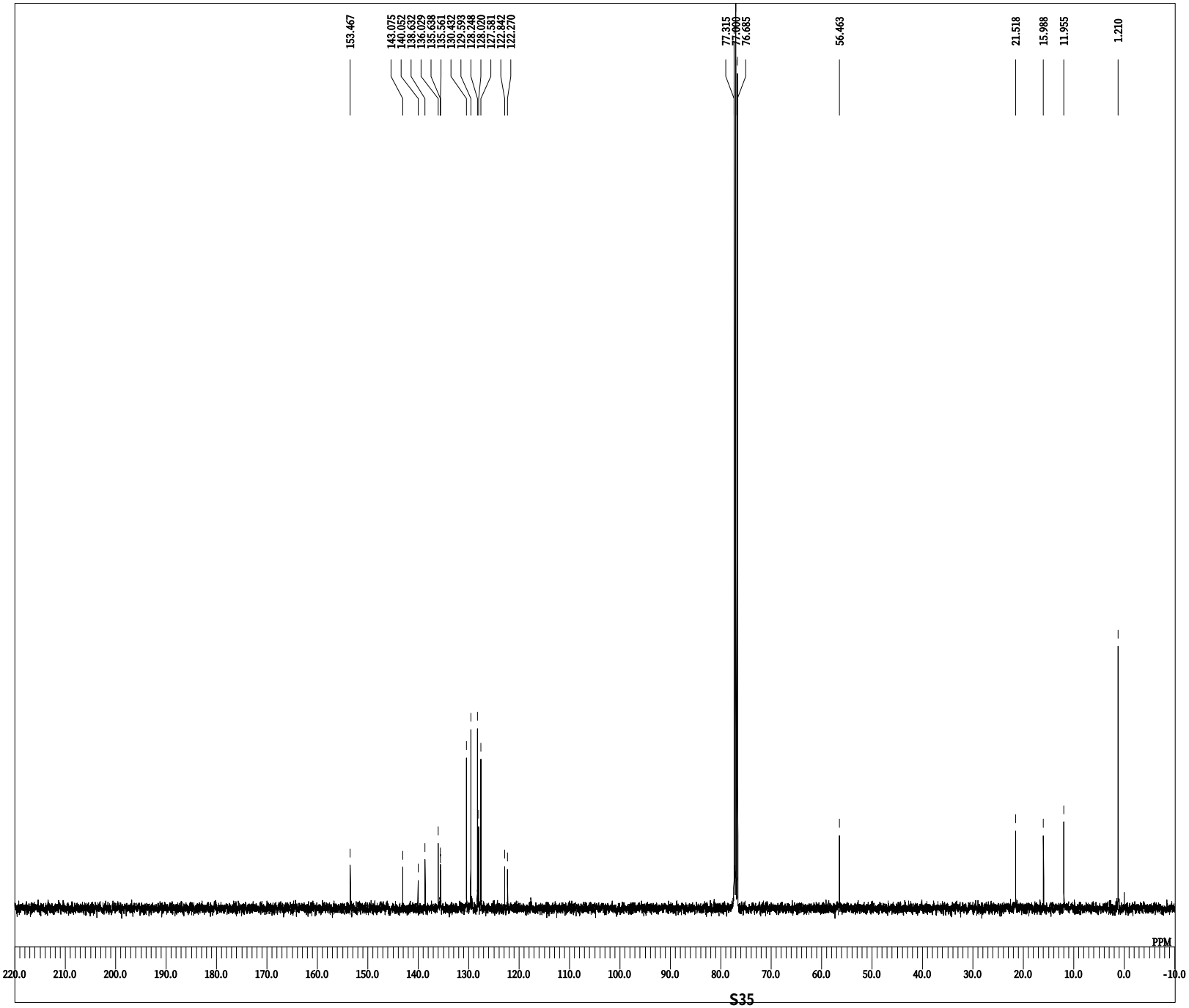
8c'



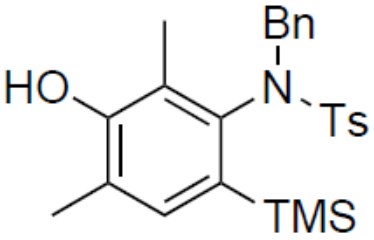
DFILE 9.als
COMNT
DATIM 2016-12-01 10:42:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 42



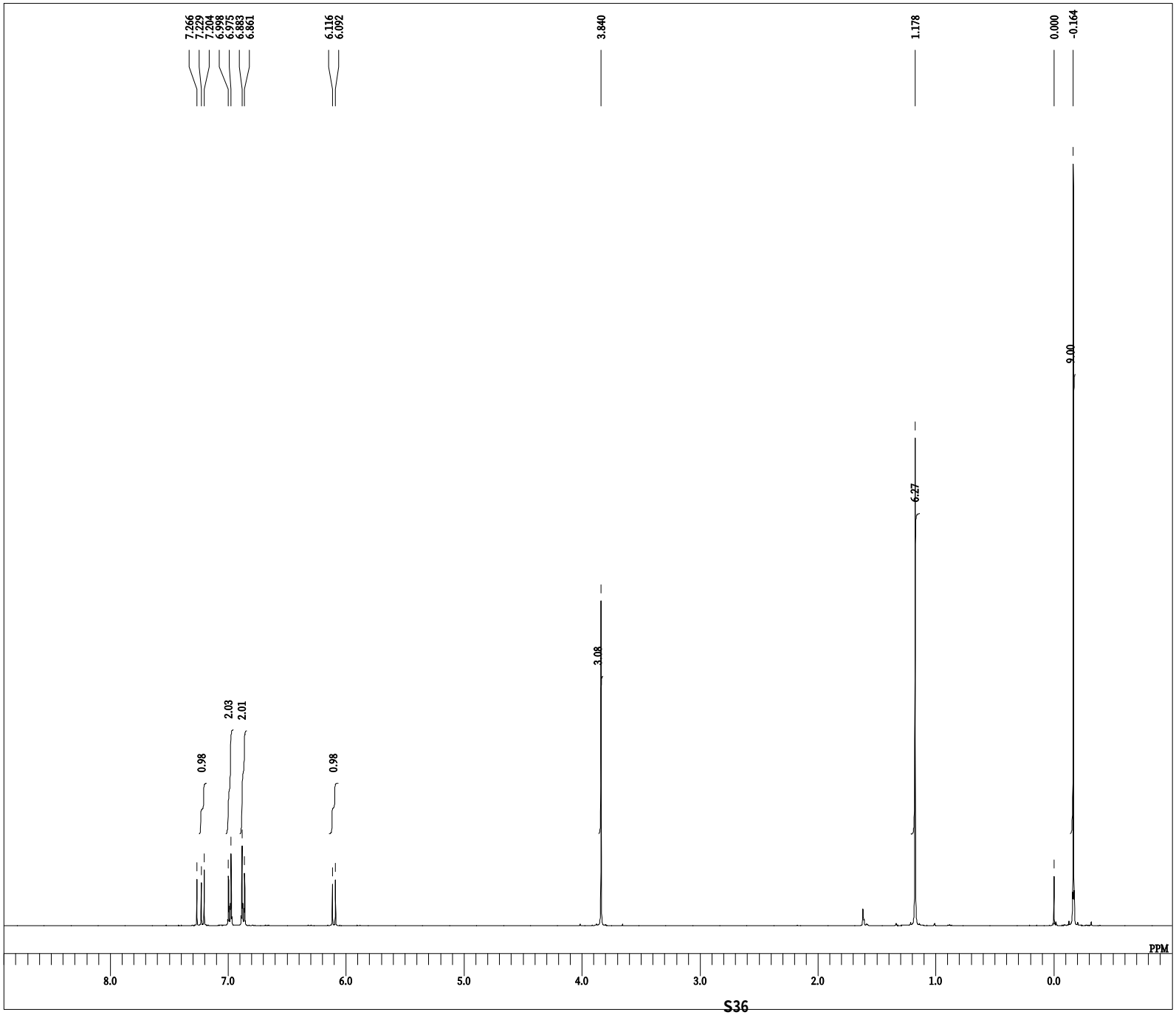
9



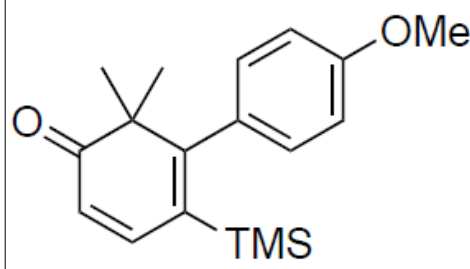
DFILE 9-carbon-1.als
COMNT
DATIM 2016-12-01 12:31:59
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 630
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.40 Hz
RGAIN 60



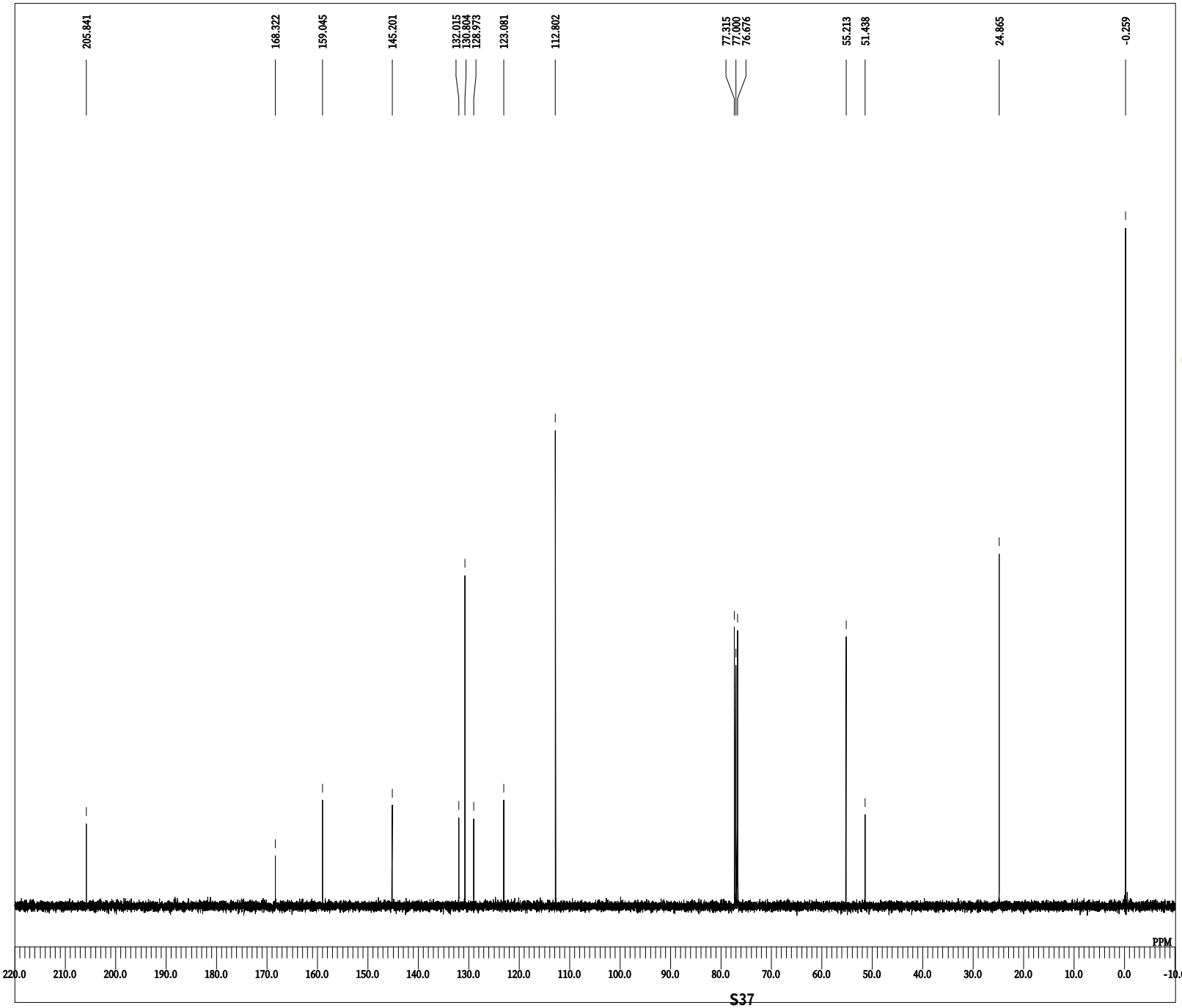
9



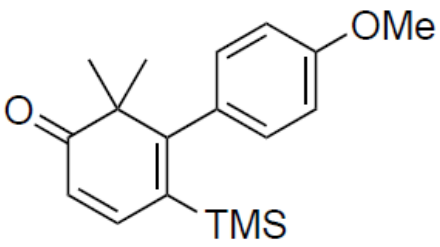
DFILE 11a-proton-1.als
COMNT
DATIM 2016-12-12 09:46:41
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



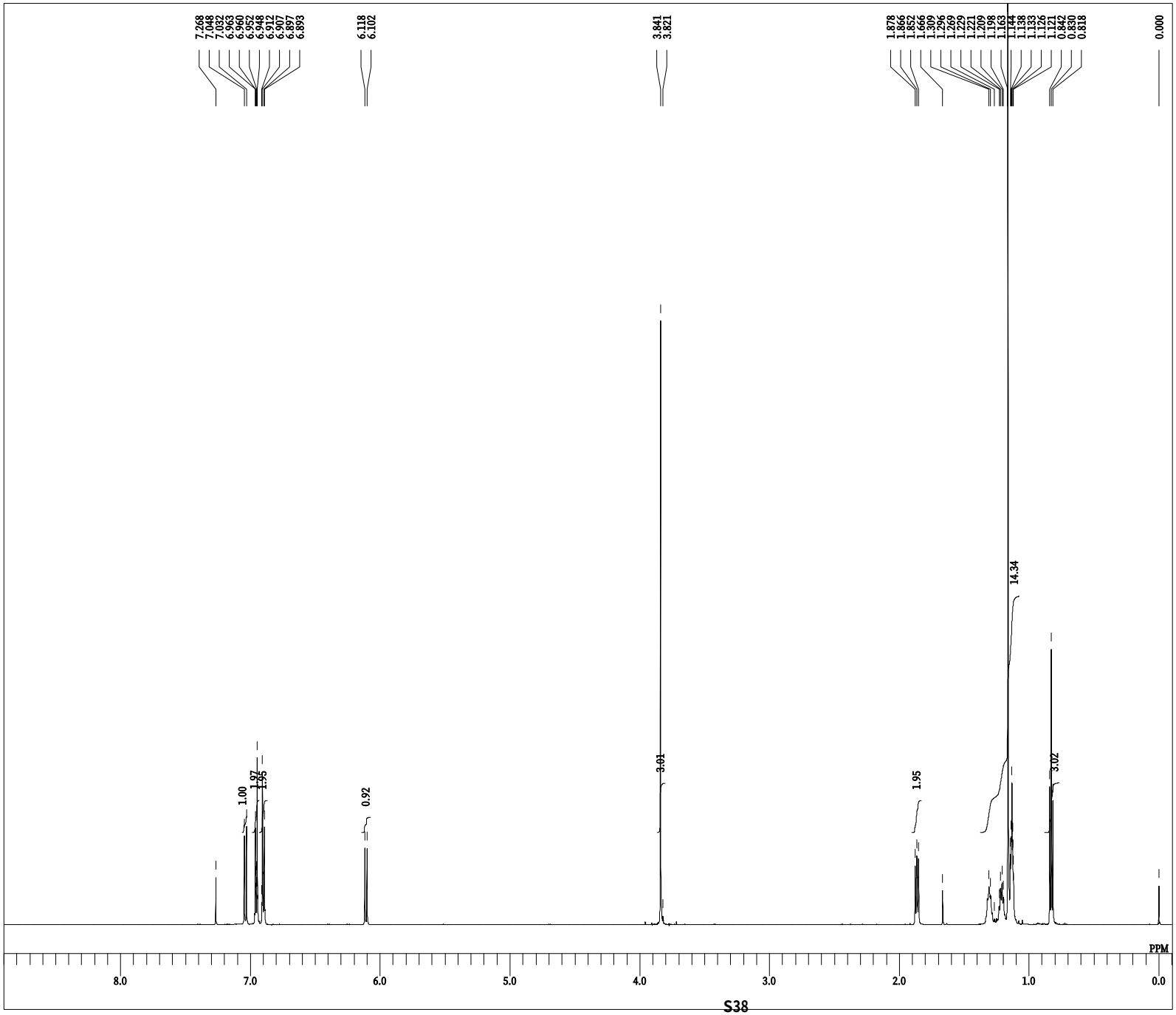
11a



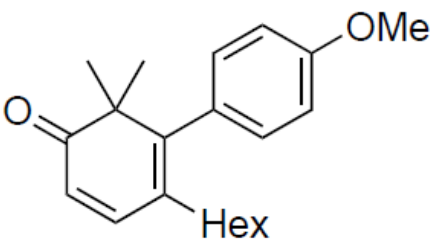
DFILE asmple-7 c13-1.als
COMNT
DATIM 2016-10-13 14:44:37
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 142
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



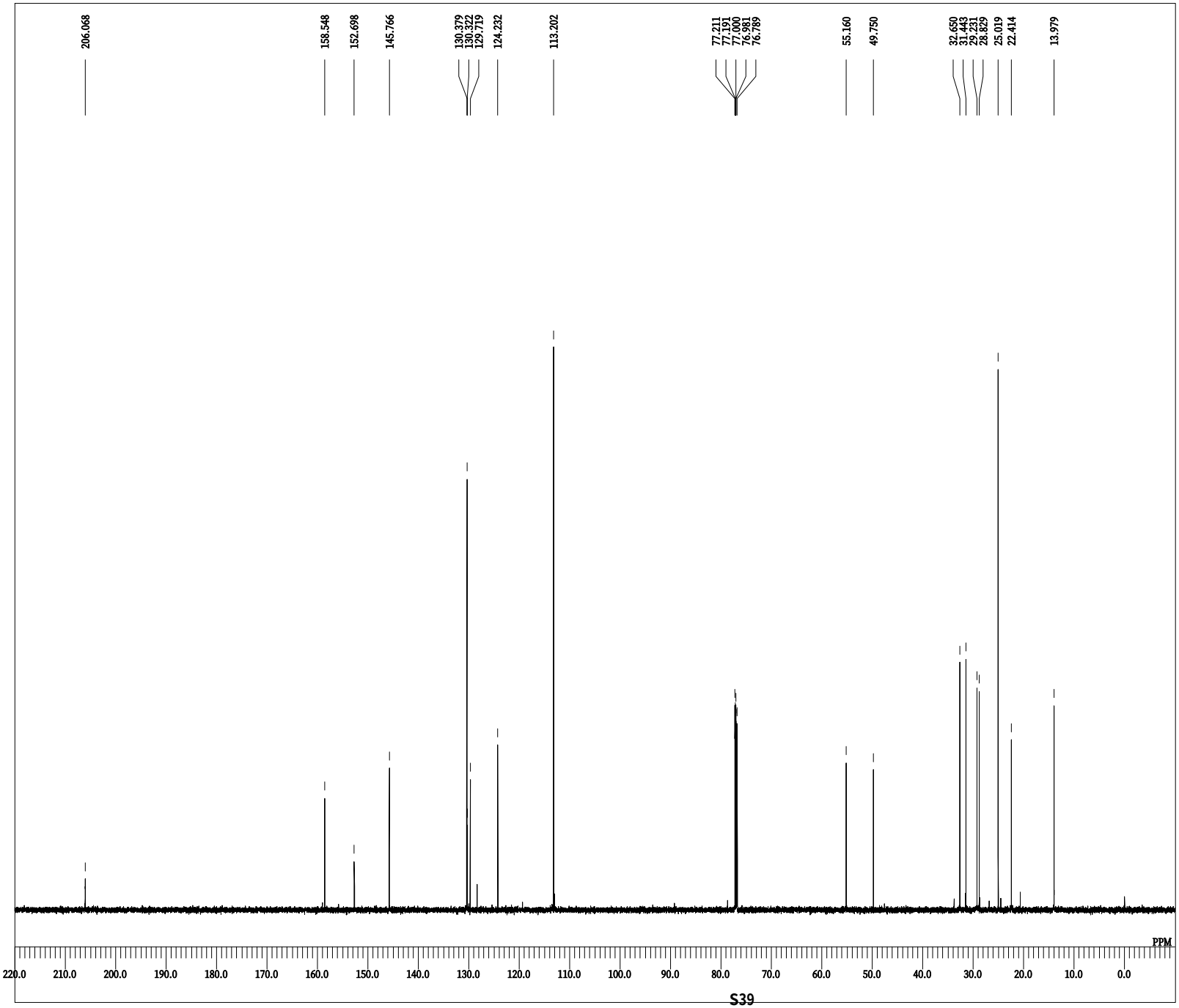
11a



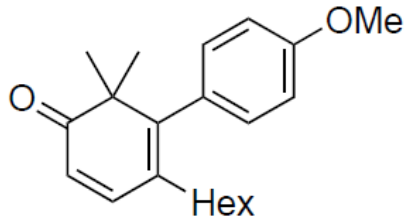
DFILE 11b proton-1.als
COMNT
DATIM 2016-12-15 16:17:20
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.85 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 36



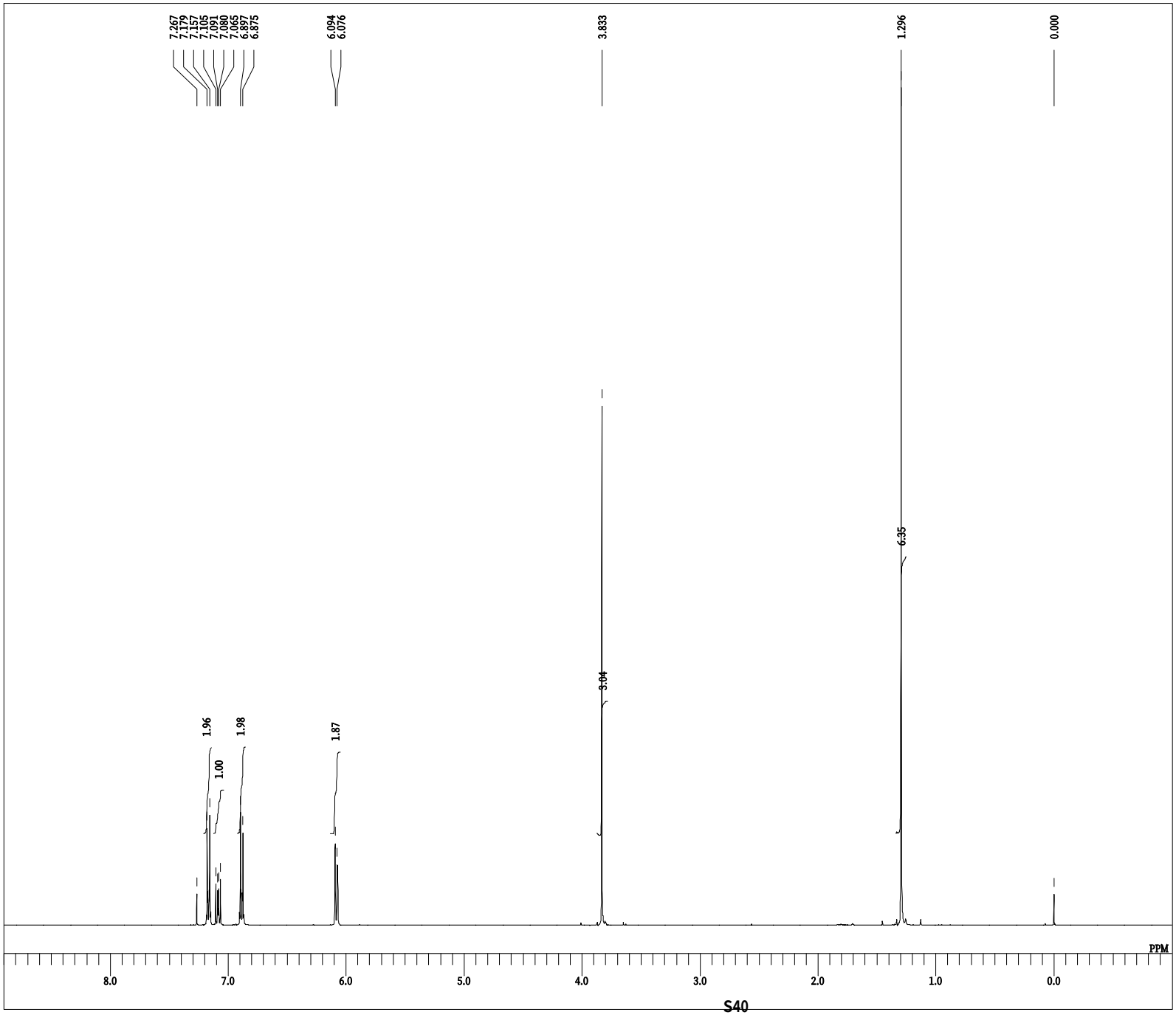
11b



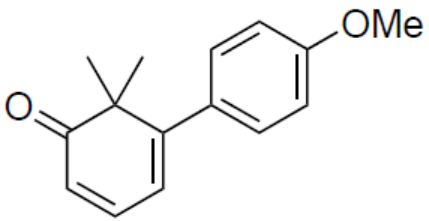
DFILE 11b-carbon-1.als
COMNT
DATIM 2016-12-13 19:30:41
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26214
FREQU 37878.21 Hz
SCANS 419
ACQTM 0.6921 sec
PD 1.2000 sec
PW1 3.43 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 54



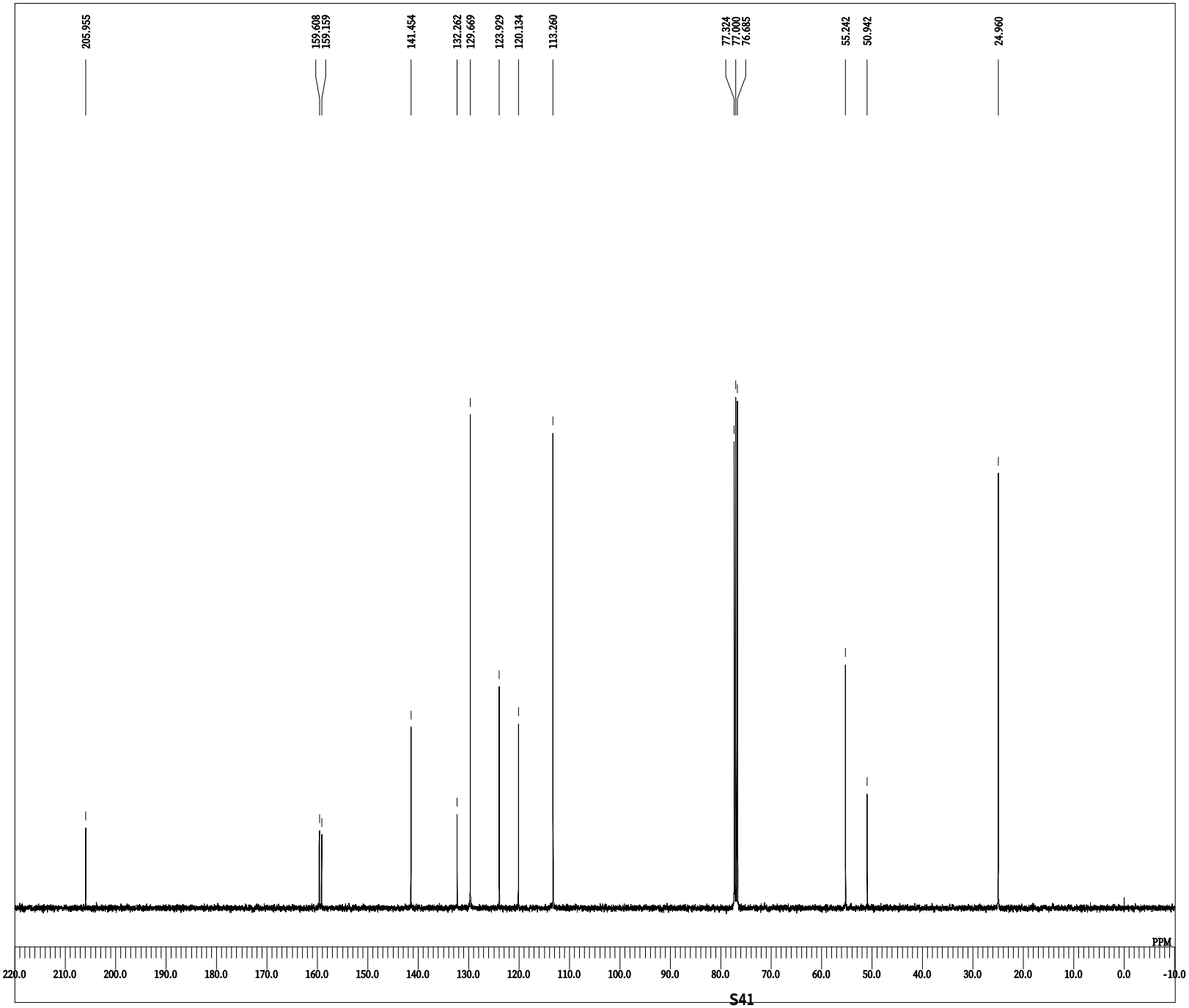
11b



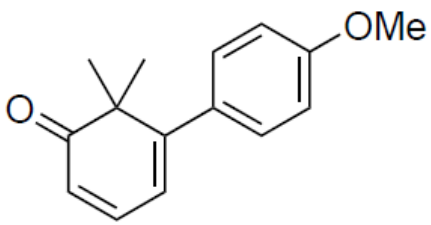
DFILE	11c-proton-1.als
COMNT	
DATIM	2016-12-12 09:51:57
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	4.70 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36



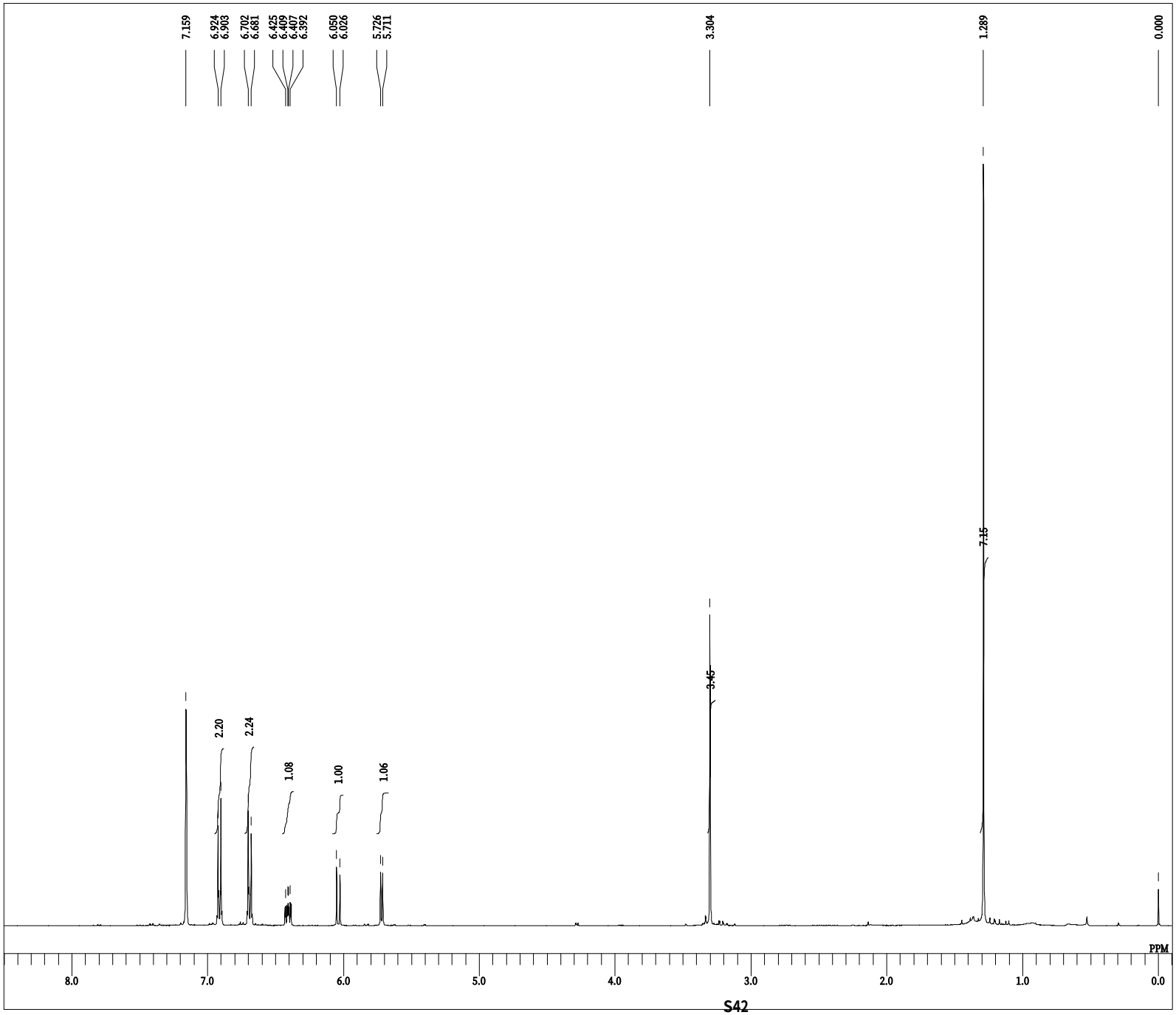
11c



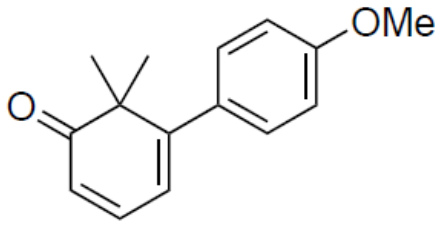
DFILE	11c carbon-1.als
COMNT	
DATIM	2016-12-12 15:34:32
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	760
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.87 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



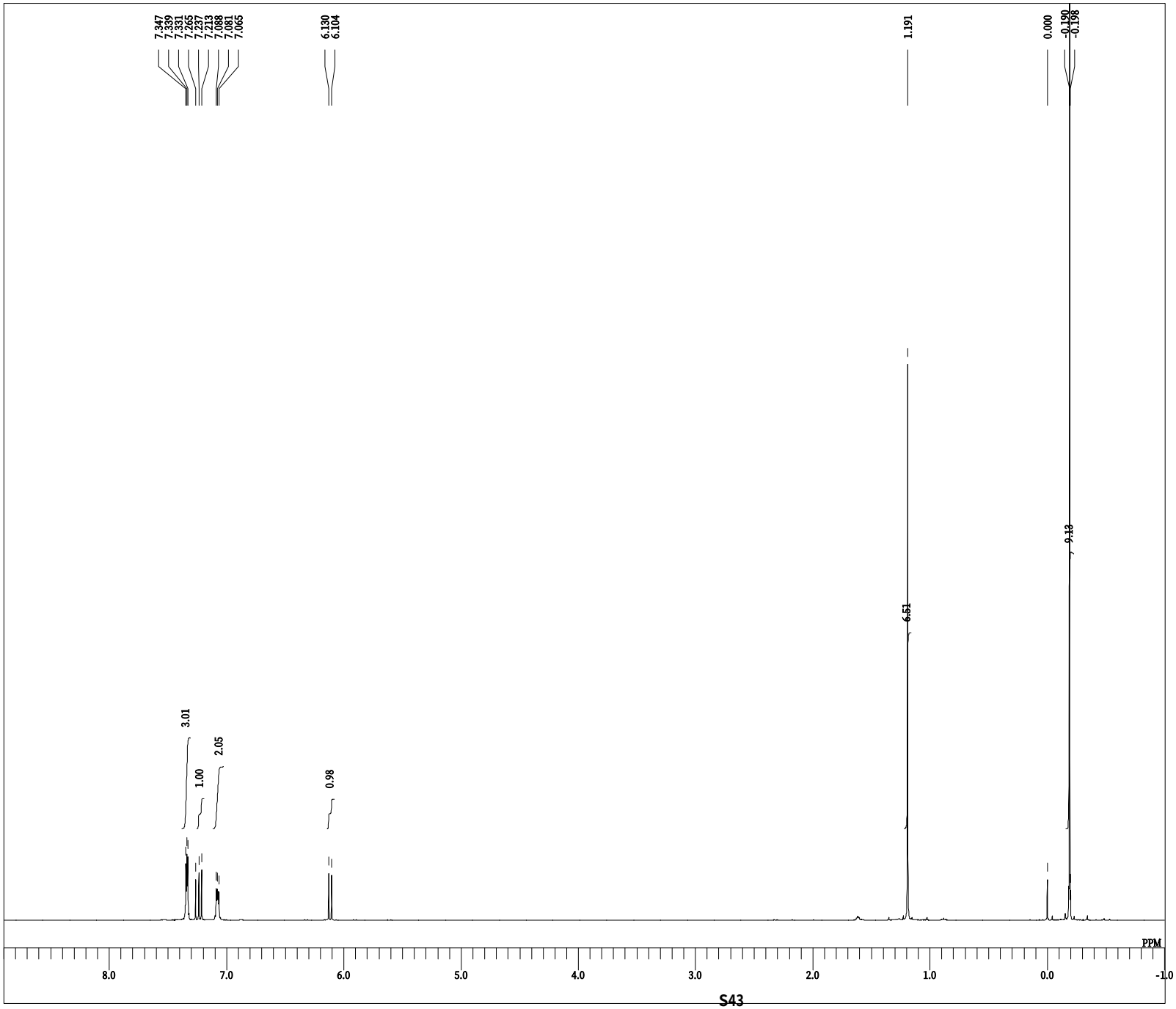
11c



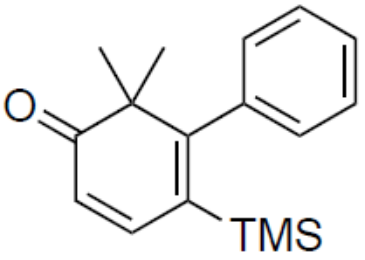
DFILE 238-re-1.als
COMNT
DATIM 2017-05-15 16:06:35
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 38



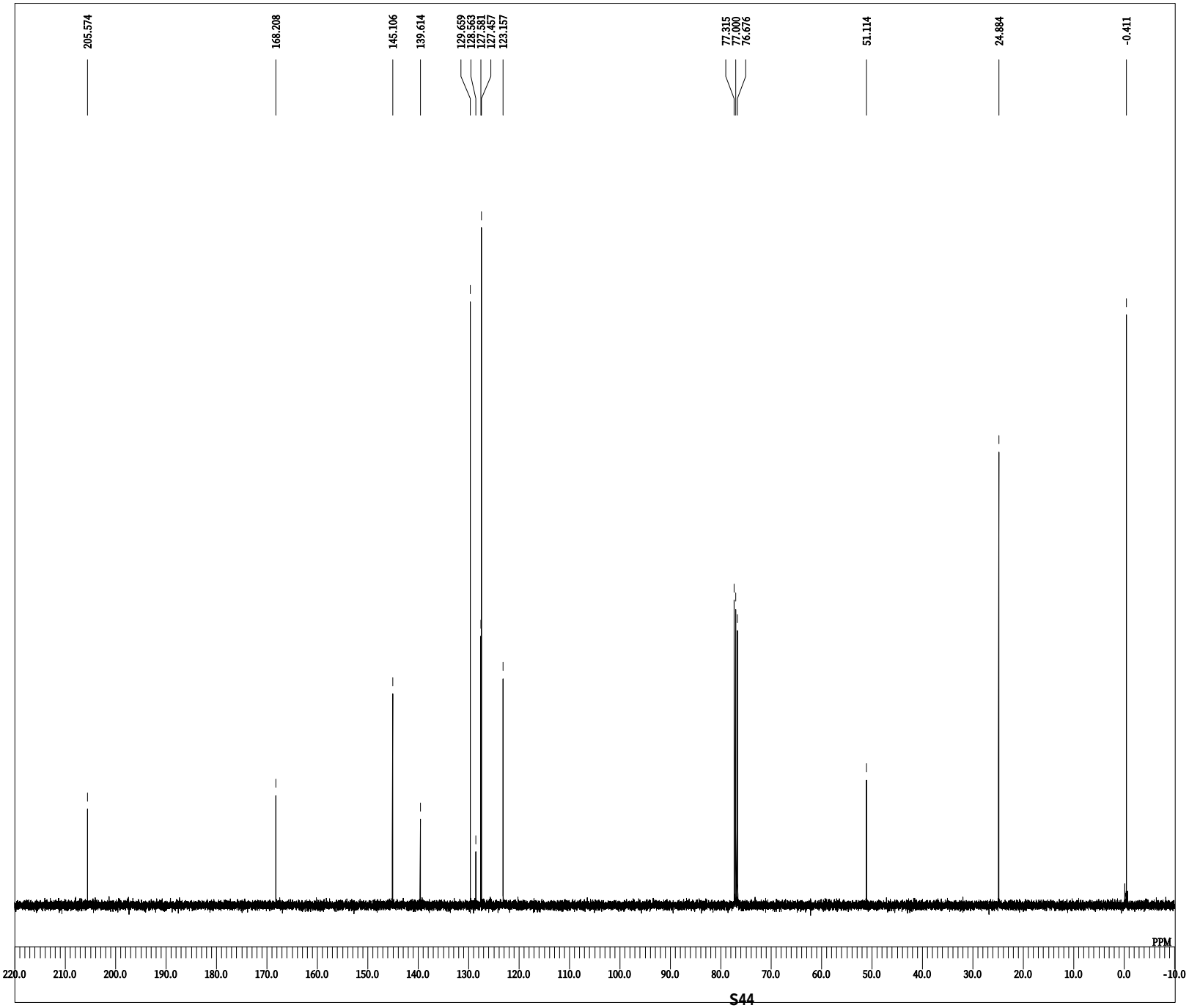
11c



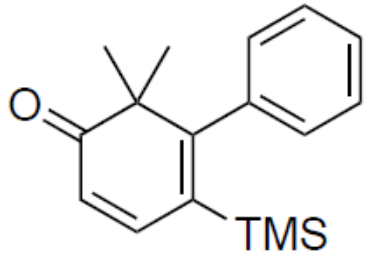
DFILE 11d-proton-1.als
COMNT
DATIM 2016-12-12 09:57:19
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



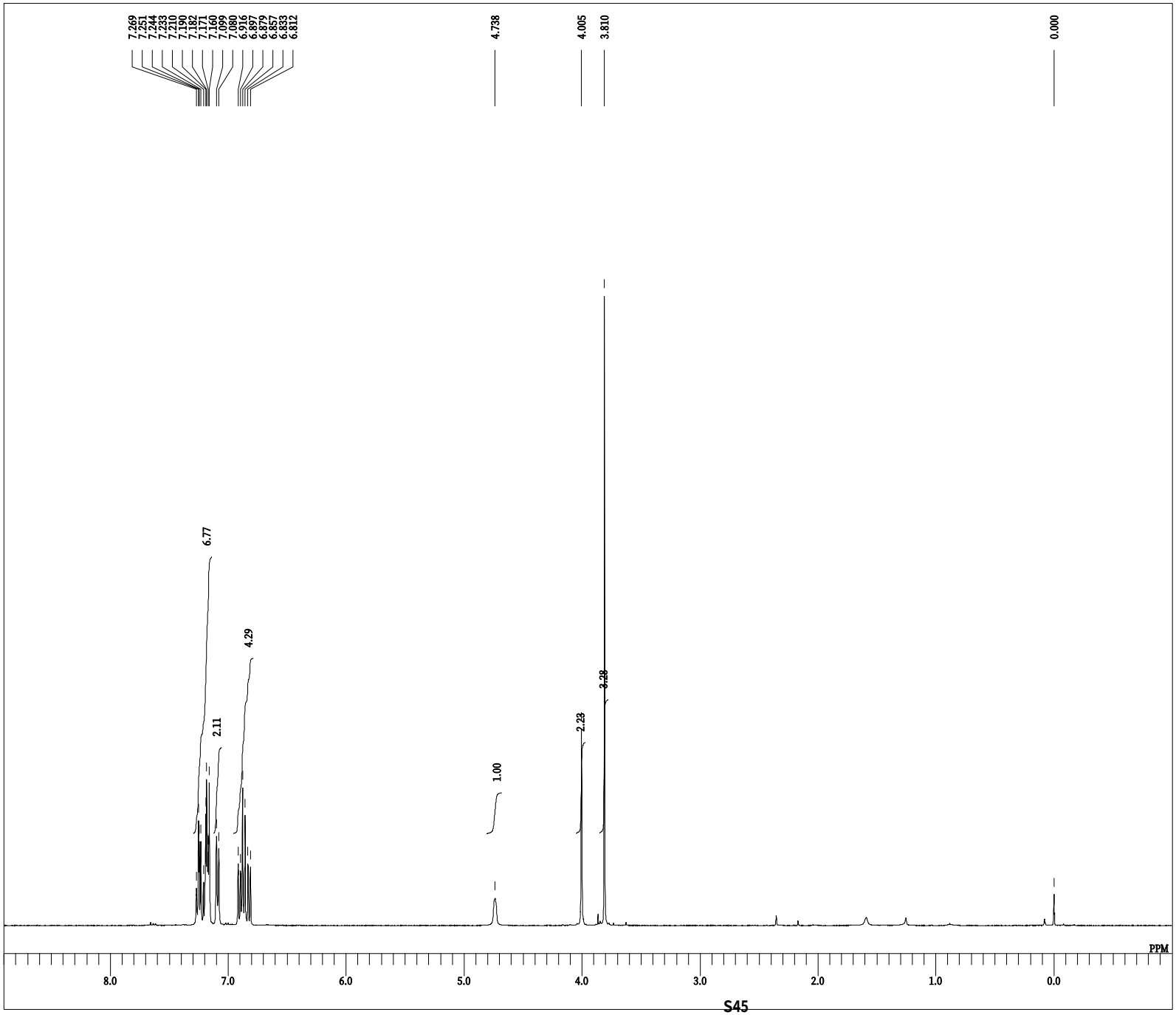
11d



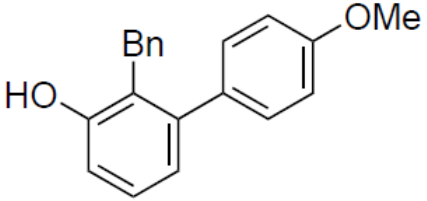
DFILE sample-8 c13-1.als
COMNT
DATIM 2016-10-13 14:58:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 205
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



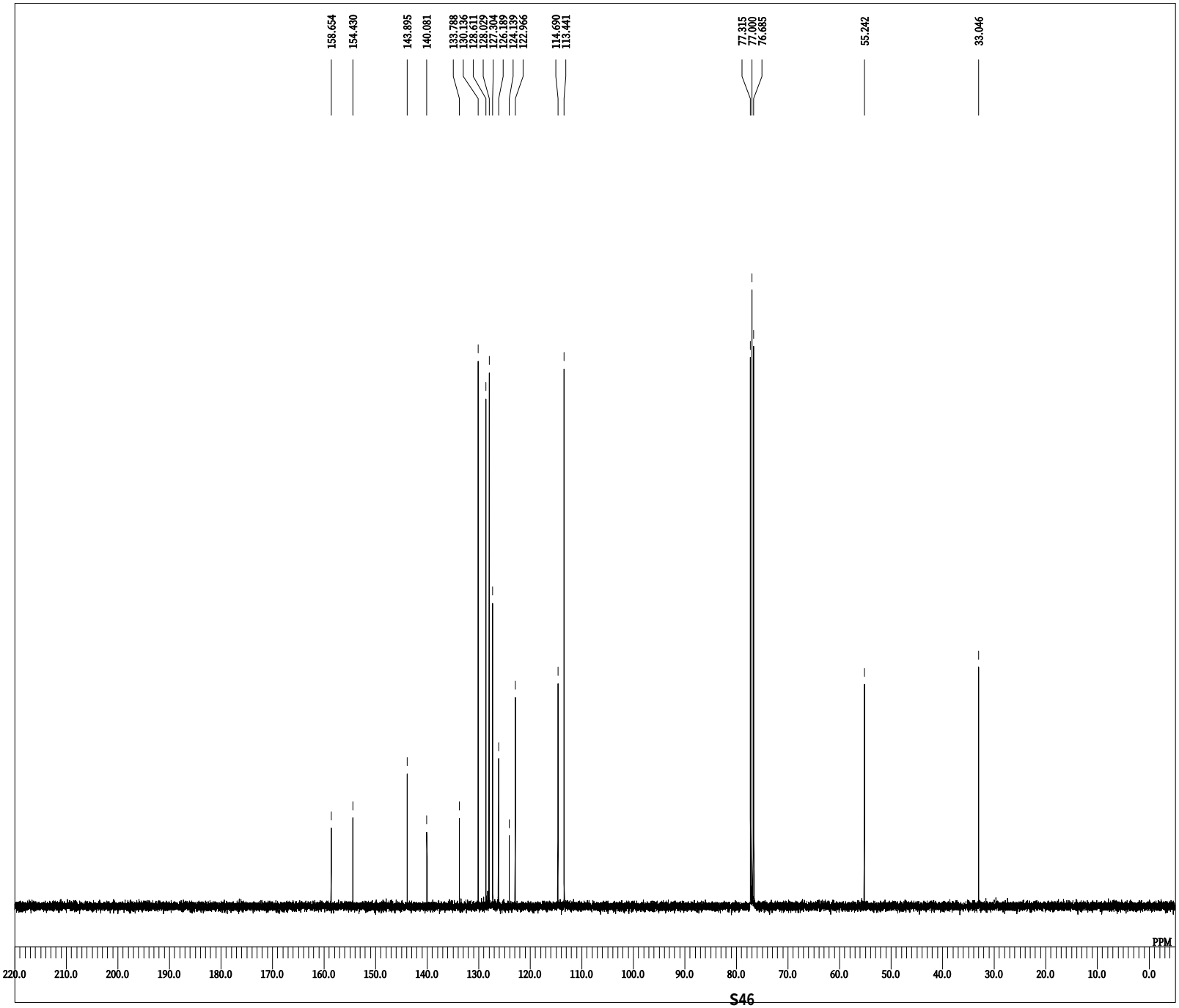
11d



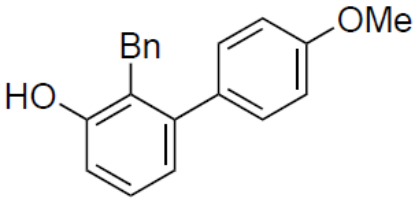

```
DFILE     12a proton-1.als
COMNT
DATIM     2016-12-17 16:03:34
OBNUC     1H
EXMOD     single_pulse.ex2
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      6002.31 Hz
SCANS            8
ACQTM       2.1837 sec
PD          2.0000 sec
PW1            4.70 usec
IRNUC     1H
CTEMP        20.4 c
SLVNT     CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           36
```



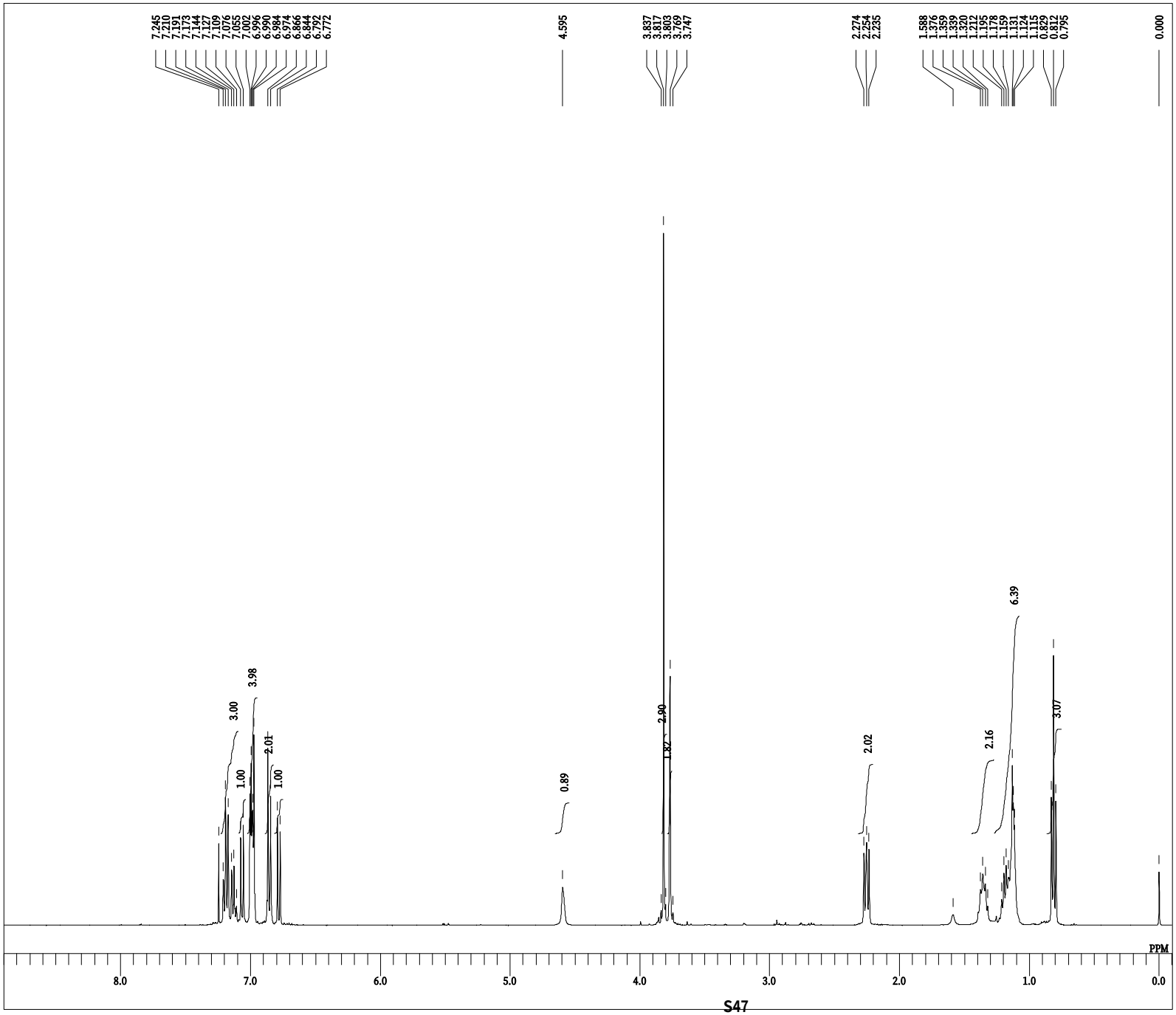
12a



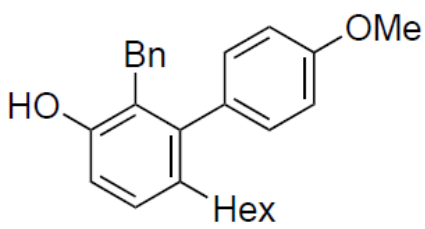
DFILE 12a carbon-1.jdf
COMNT
DATIM 2016-12-17 16:41:44
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 1000
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



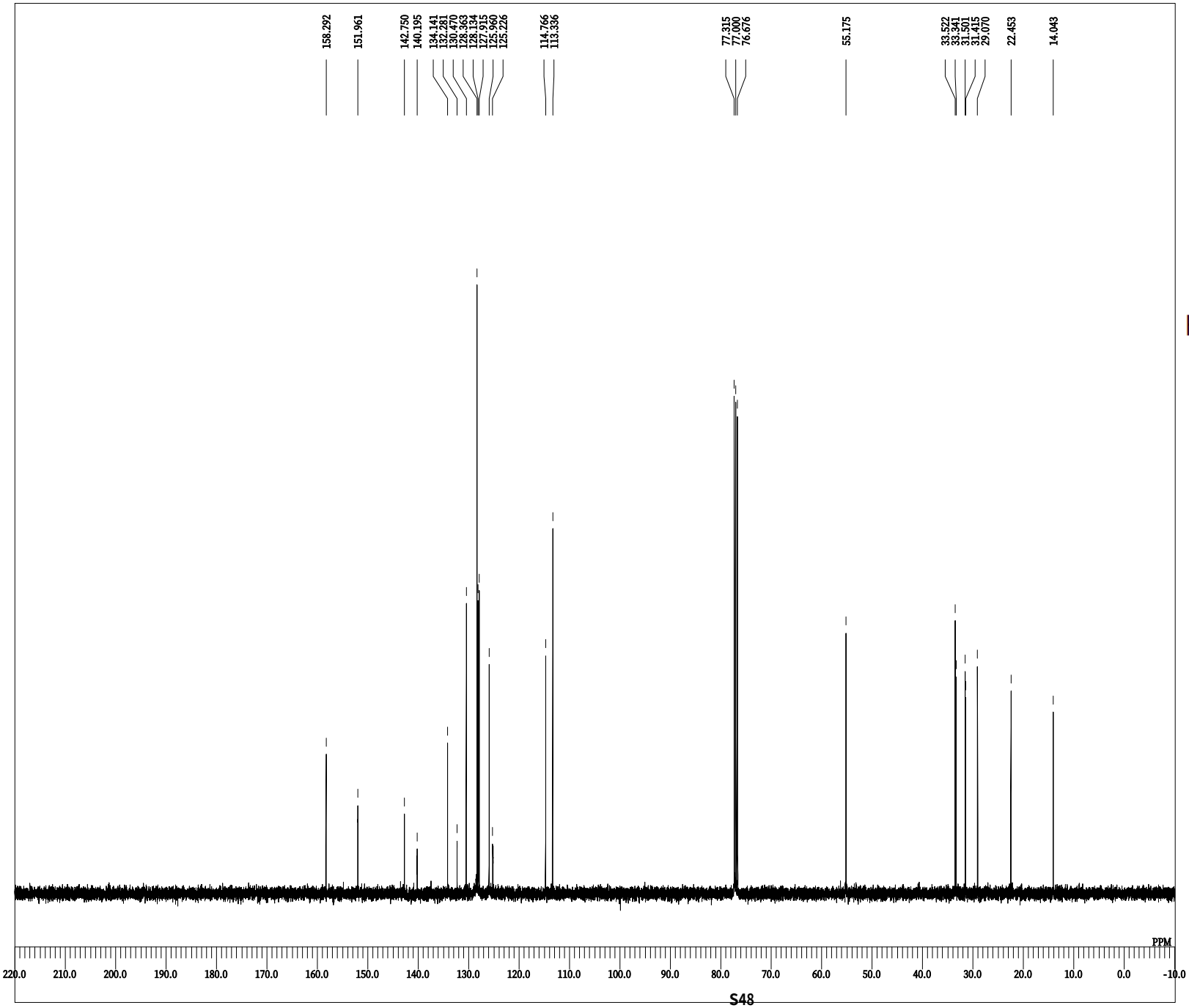
12a



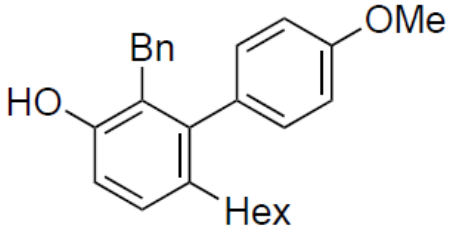
DFILE 12b-proton-1.als
COMNT
DATIM 2016-12-13 09:29:55
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 36



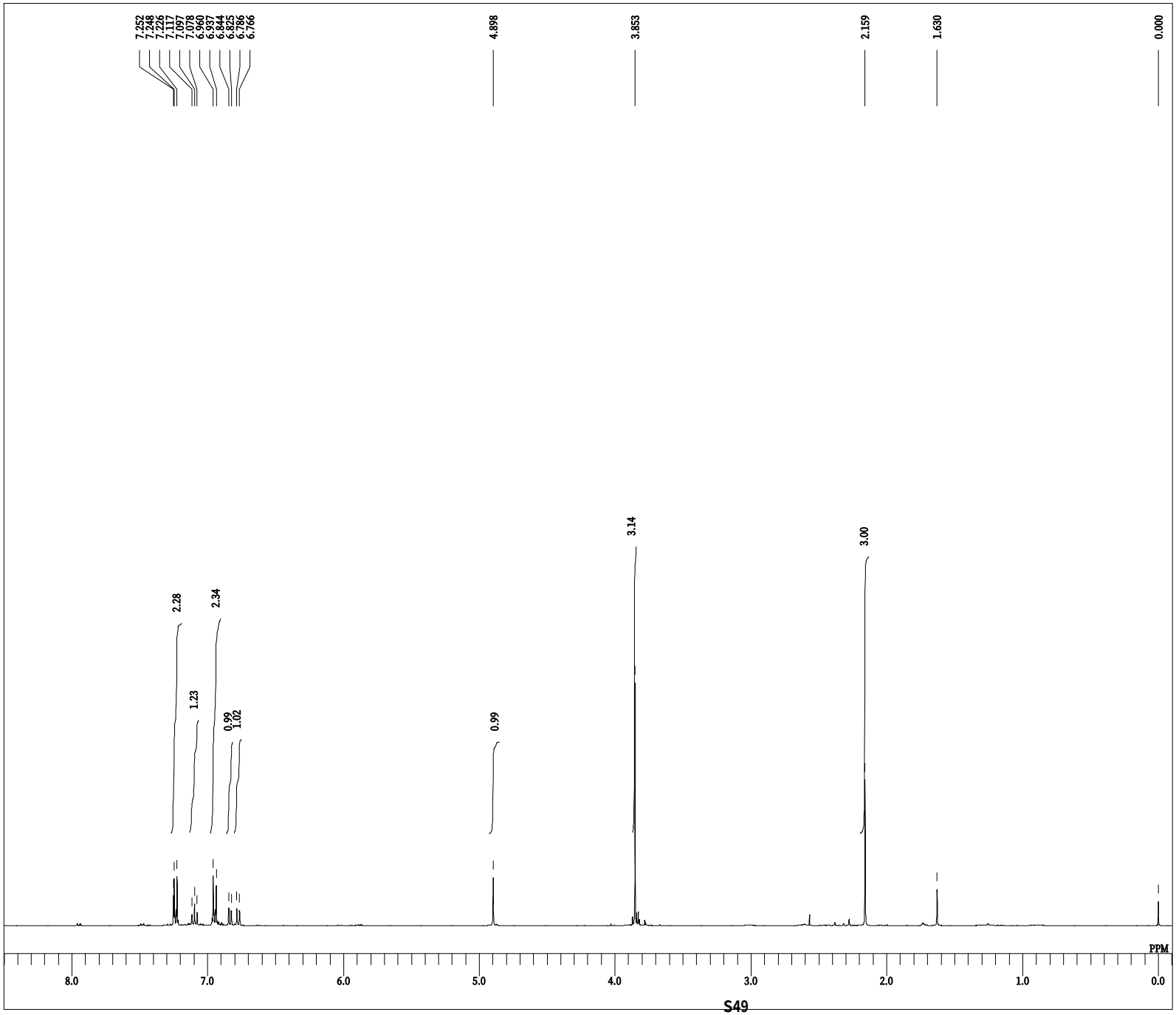
12b



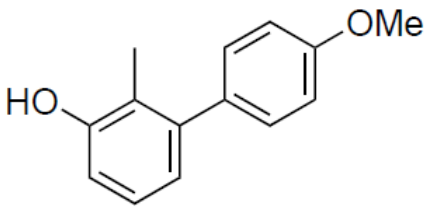
DFILE 12b-carbon-1.als
COMNT
DATIM 2016-12-13 13:26:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 601
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



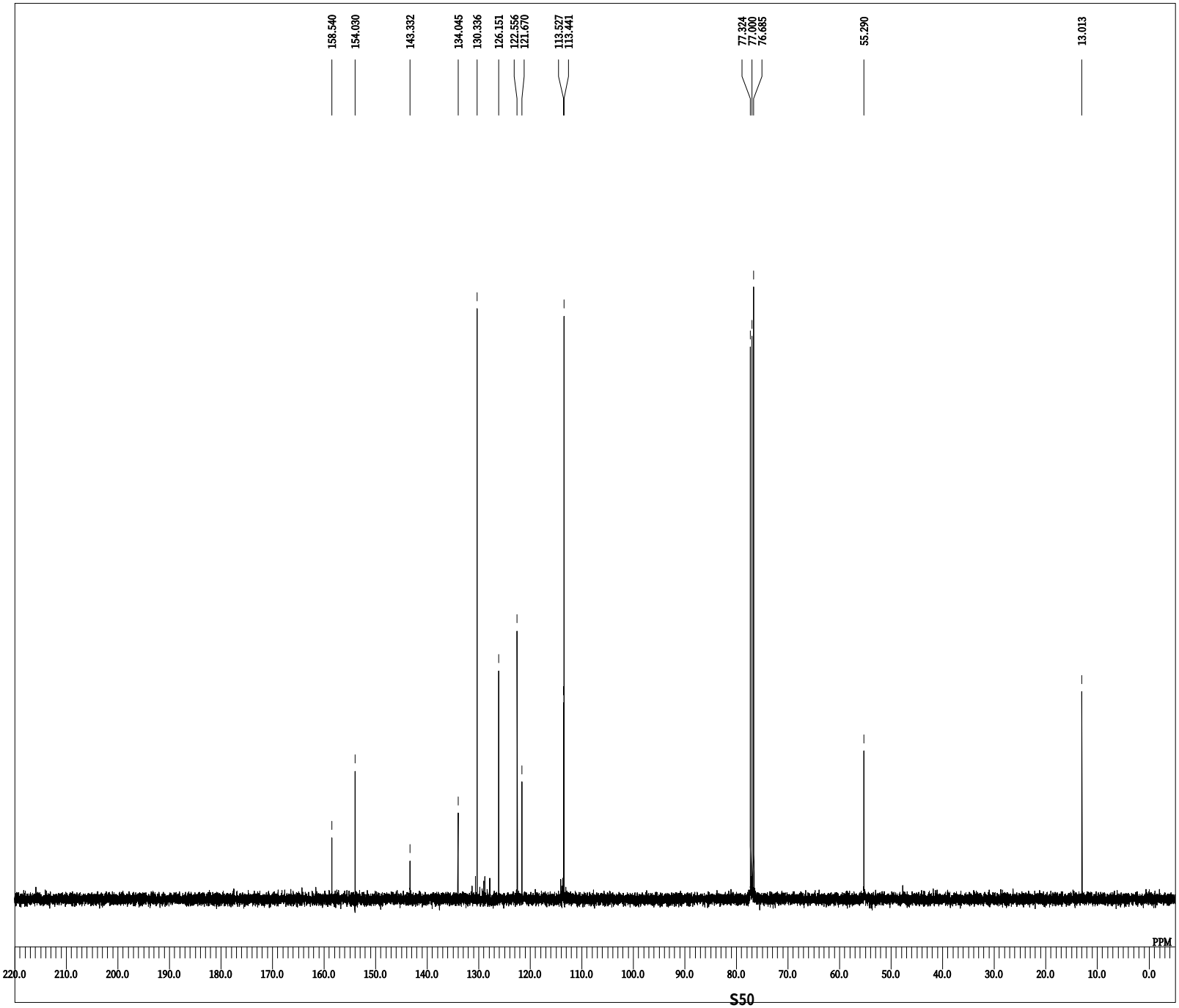
12b



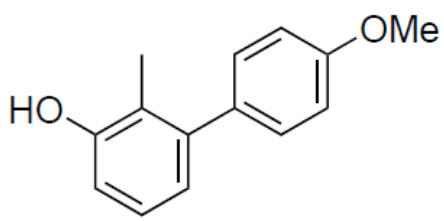
DFILE 241-1.als
COMNT
DATIM 2017-05-24 12:19:13
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 42



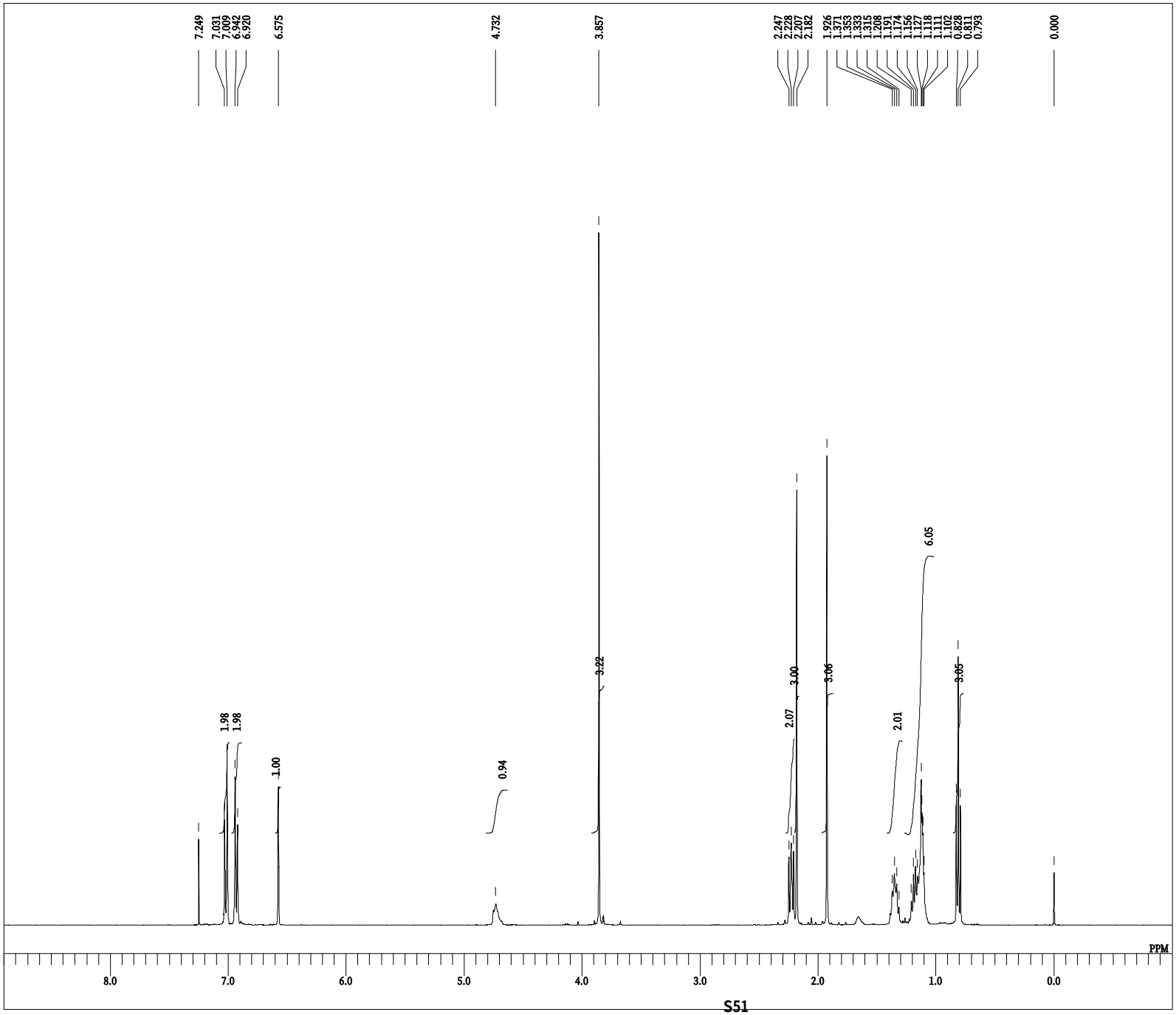
12c



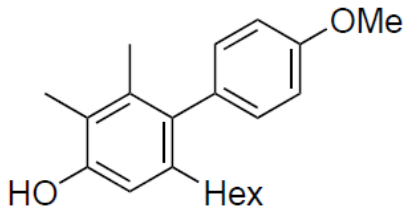
DFILE	241-13c-1.als
COMNT	
DATIM	2017-05-24 12:38:21
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	500
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.87 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



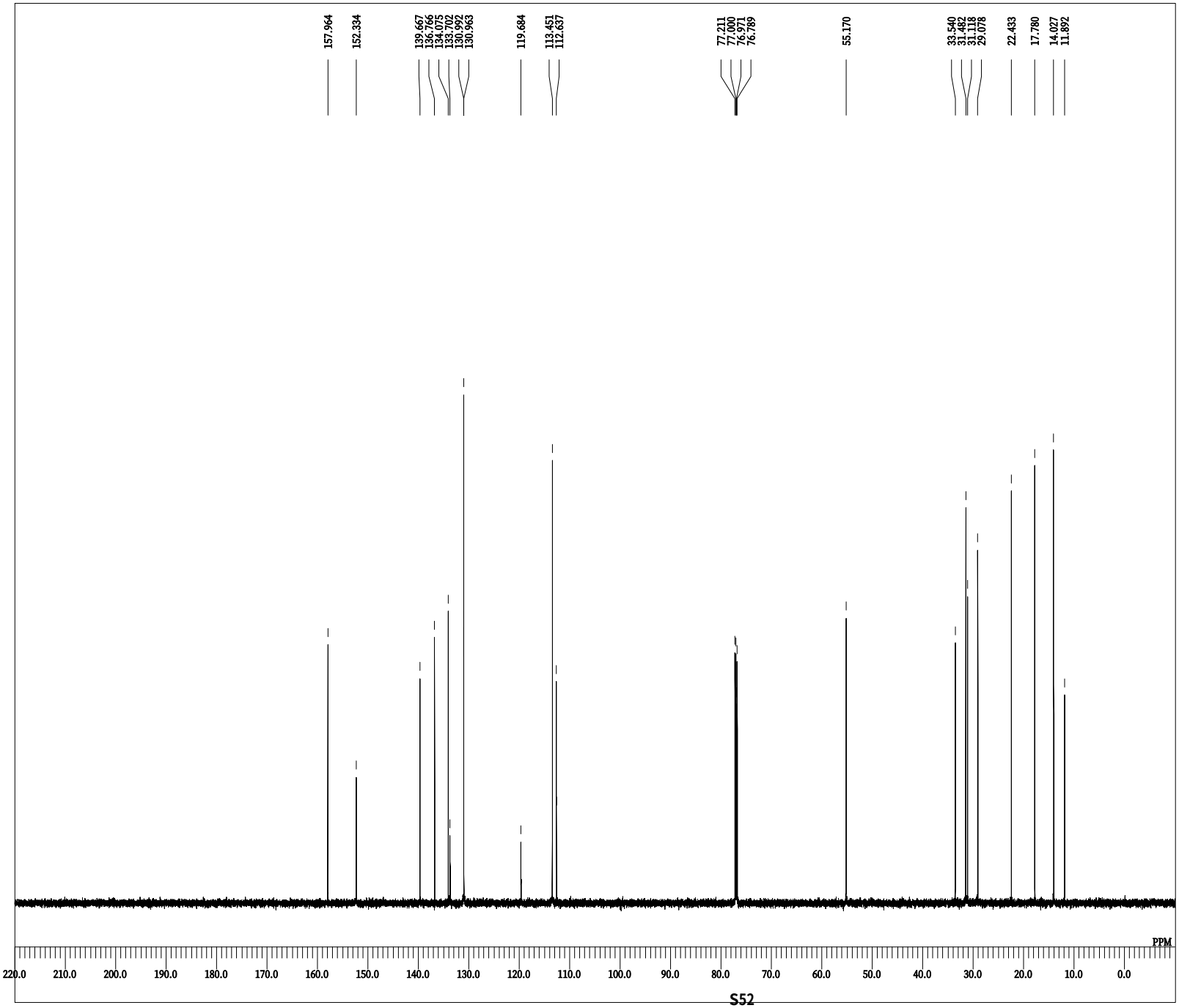
12c



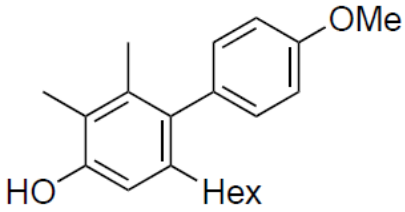
DFILE 13-proton-1.als
COMNT
DATIM 2016-12-12 10:02:37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32



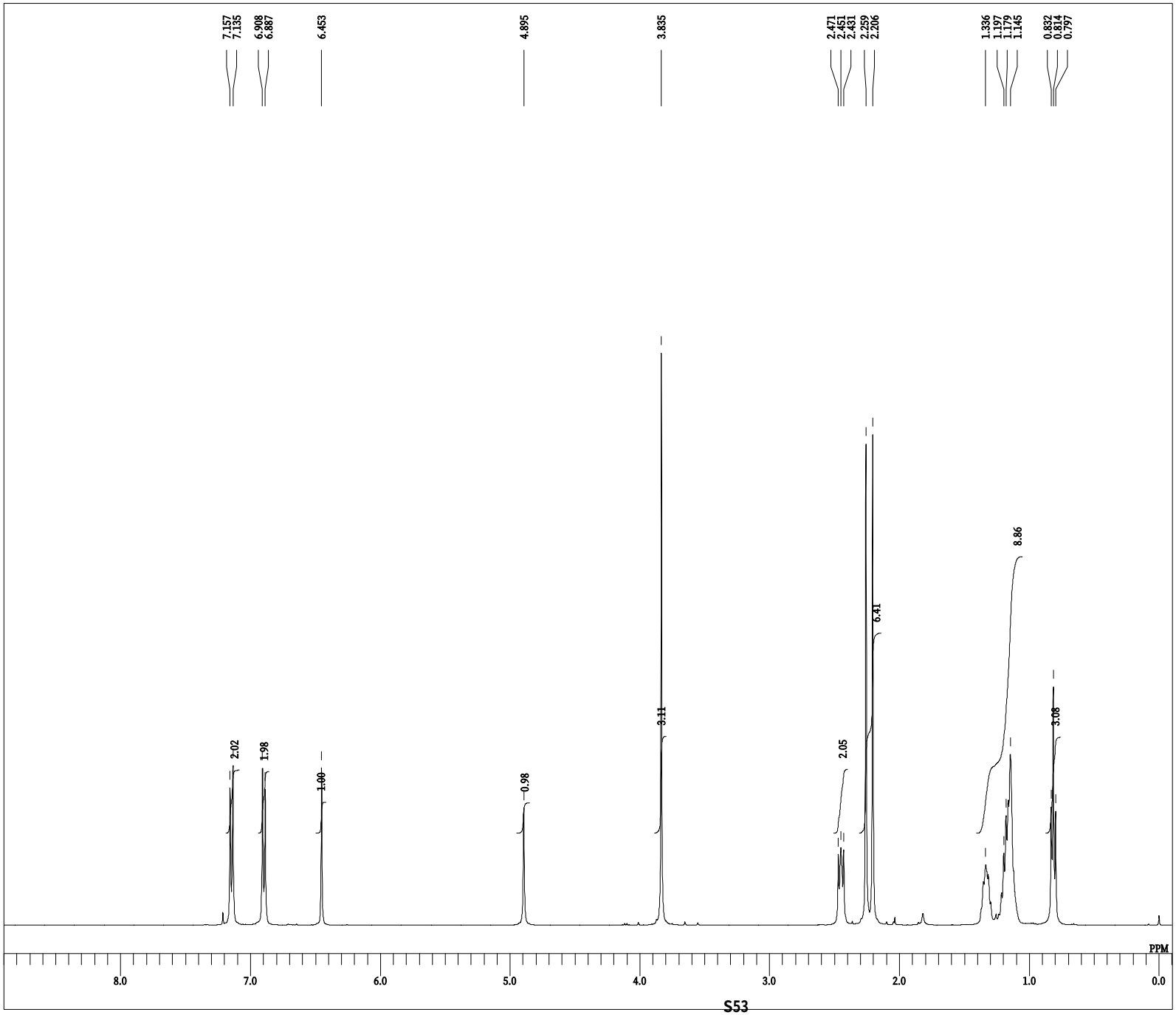
13



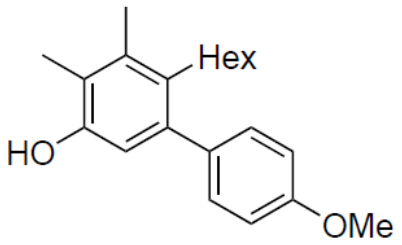
DFILE 13-carbon-1.als
COMNT
DATIM 2016-12-12 13:26:05
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26214
FREQU 37878.21 Hz
SCANS 591
ACQTM 0.6921 sec
PD 1.2000 sec
PW1 3.43 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



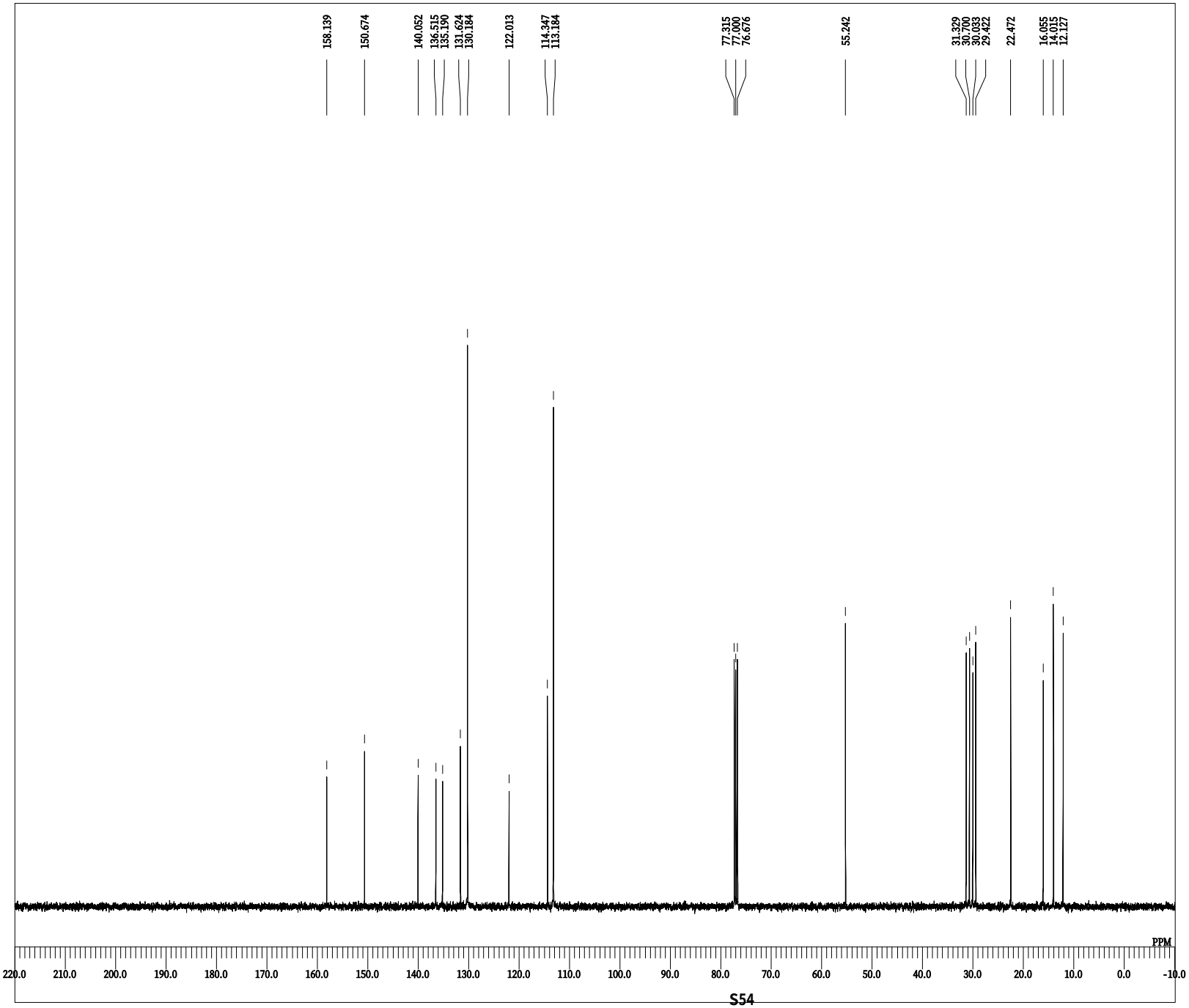
13



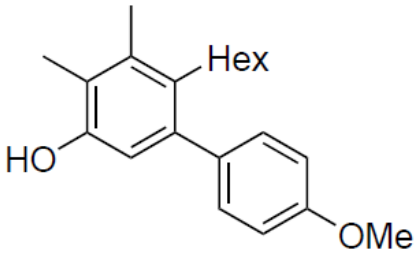
DFILE rea-TFAA-1.als
COMNT
DATIM 2016-09-29 20:57:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 24



14

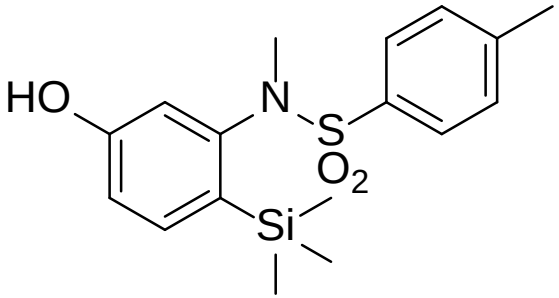


DFILE rea-TFAA-c13-1.als
COMNT
DATIM 2016-09-29 21:01:60
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 110
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.40 Hz
RGAIN 60

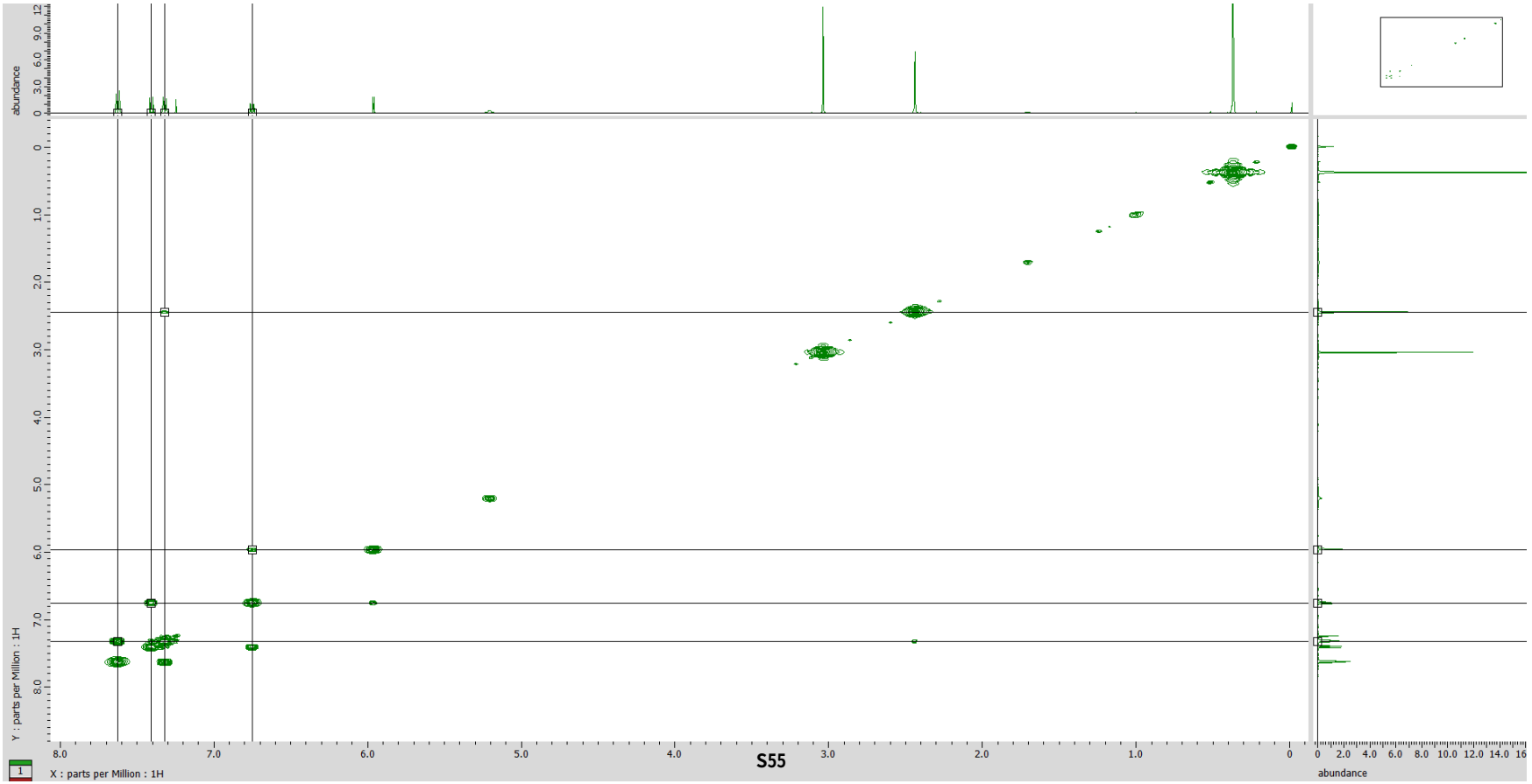


14

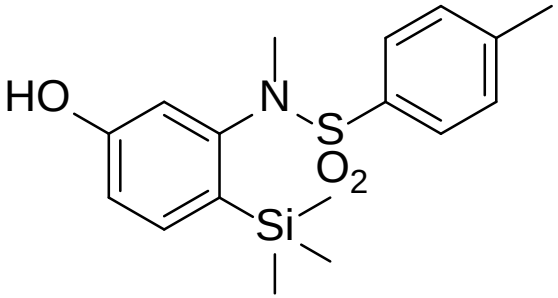
COSY


HO
N
S
O2
Si

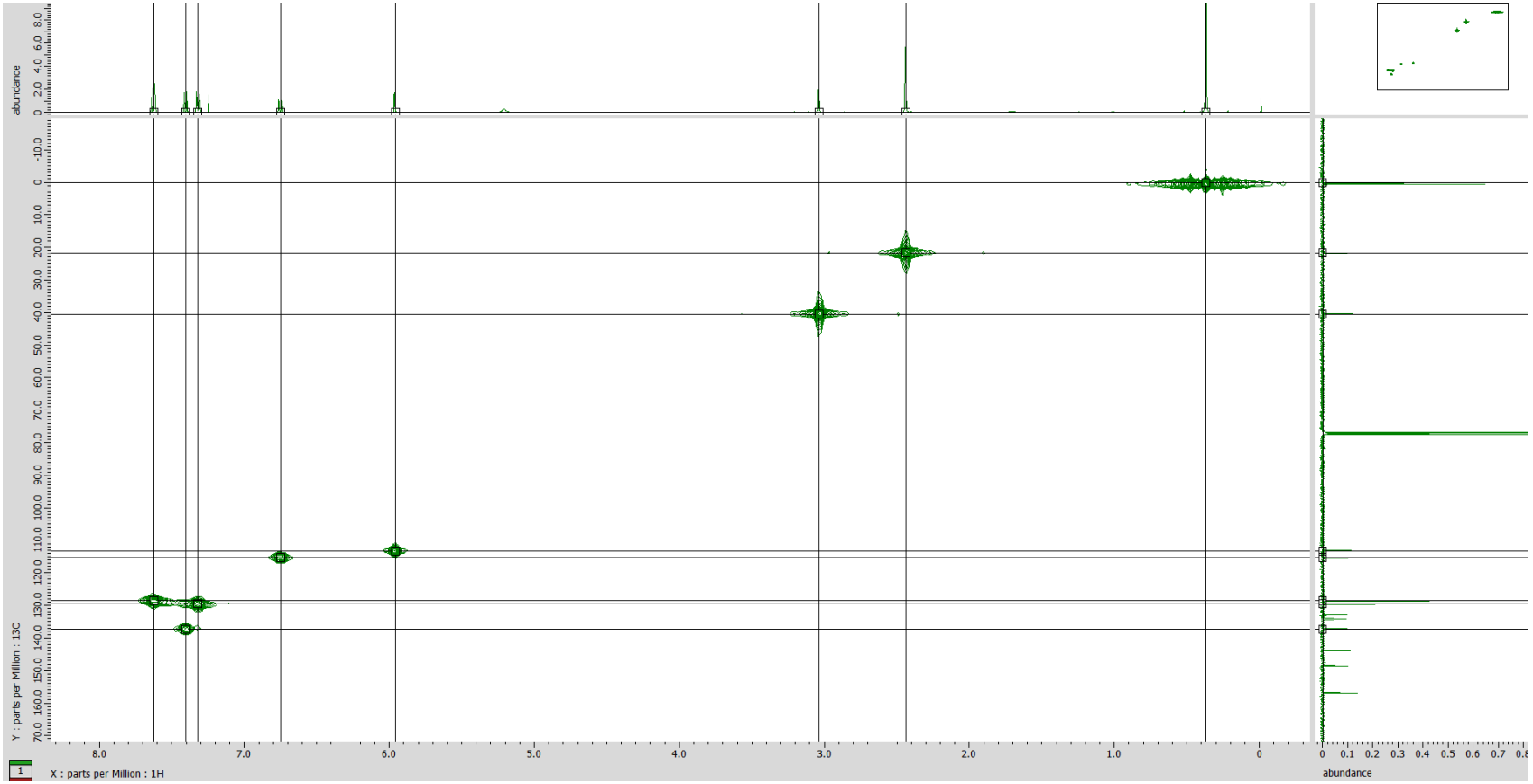
7a


abundance
Y : parts per Million : 1H
X : parts per Million : 1H
S55
abundance

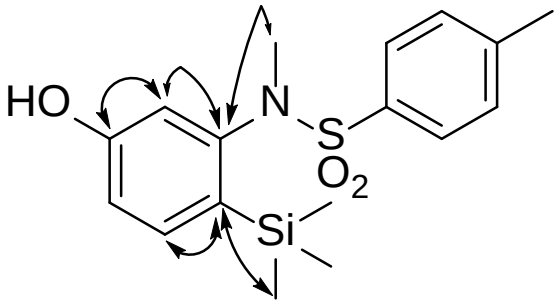
HMQC


HO
N
S
O2
Si

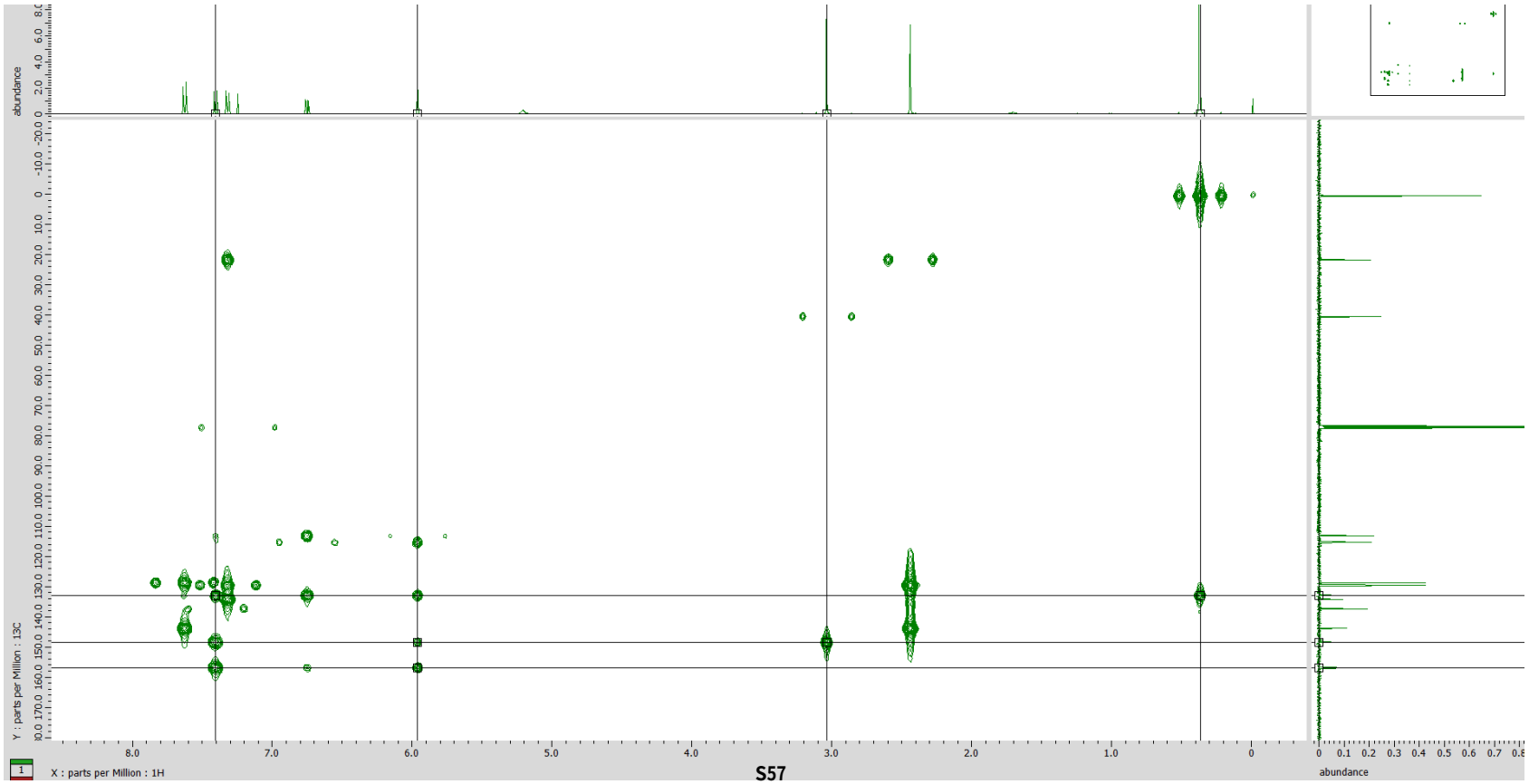
7a


abundance
Y : parts per Million : 13C
X : parts per Million : 1H
abundance

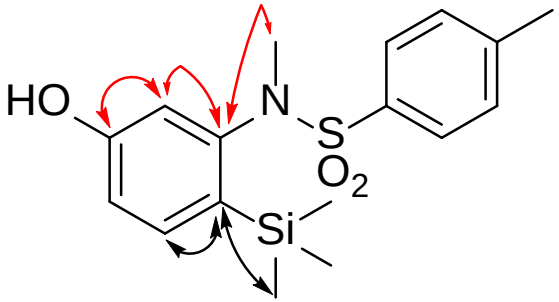
HMBC

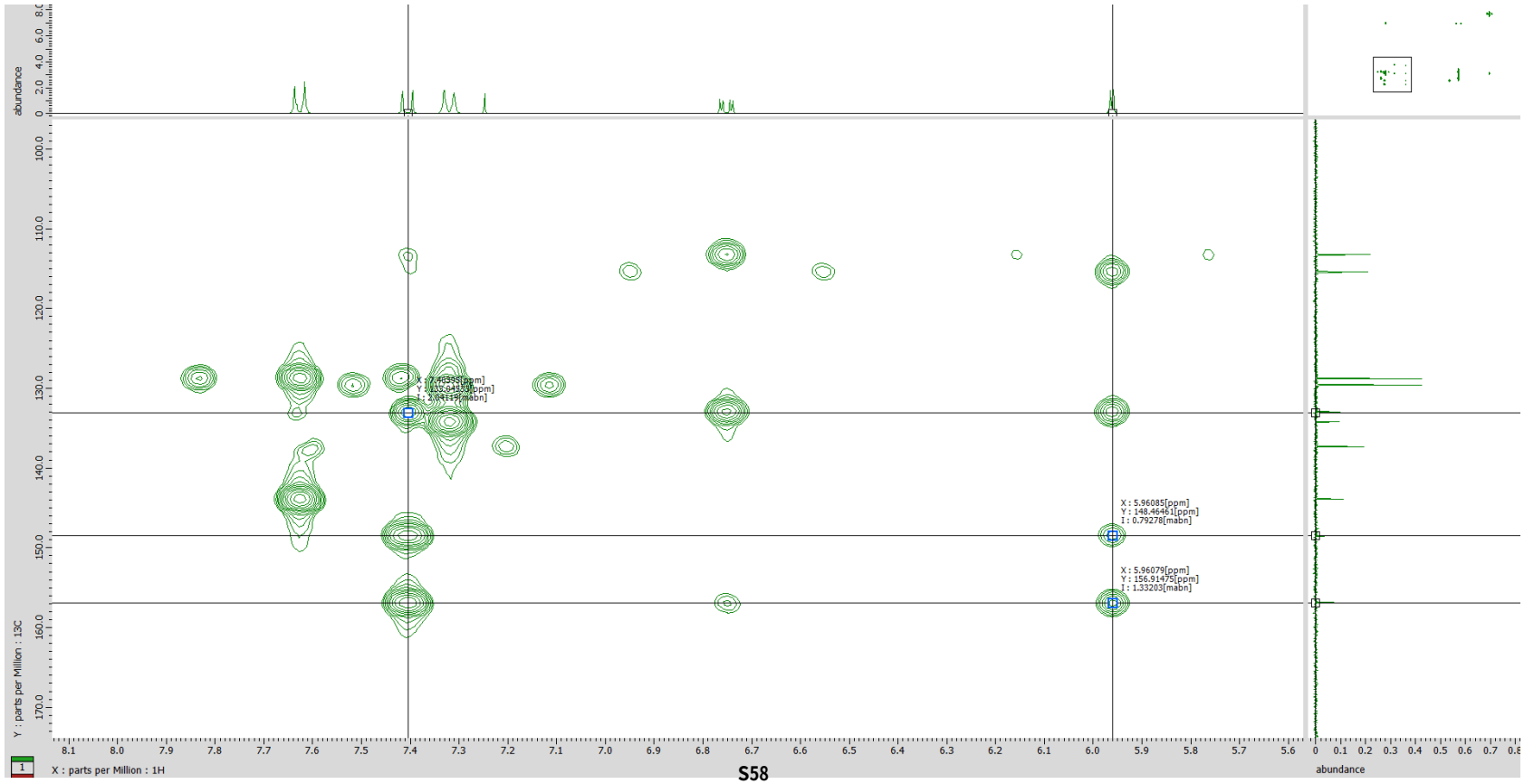

HO
N
S
O2
Si

7a

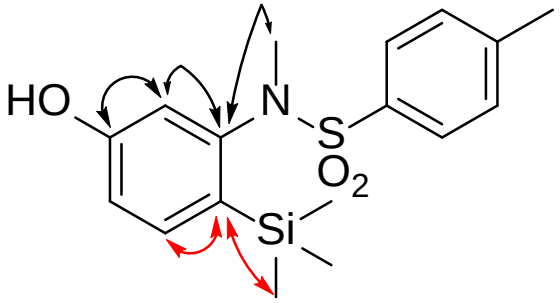

abundance
Y : parts per Million : 13C
X : parts per Million : 1H
S57
abundance

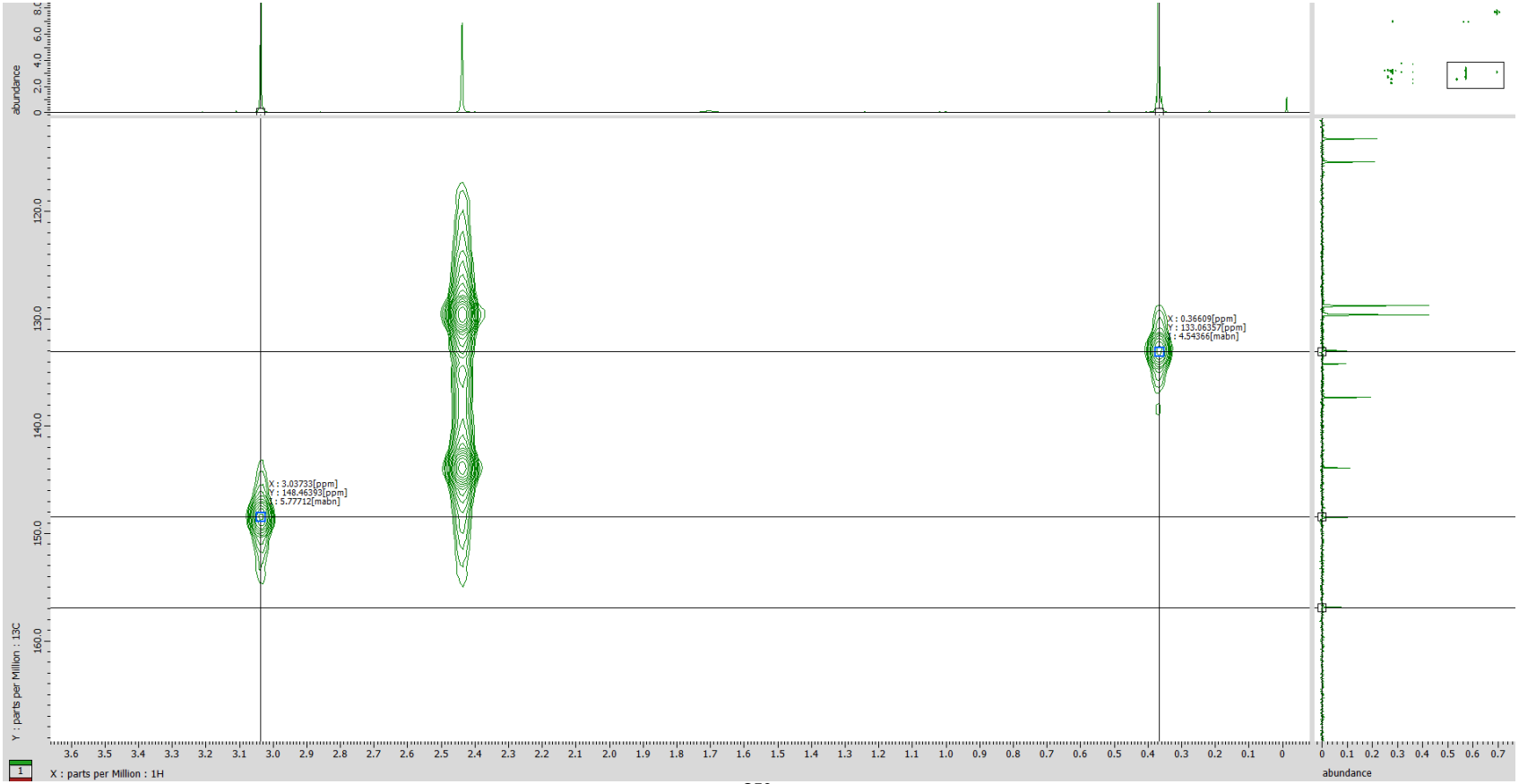
HMBC

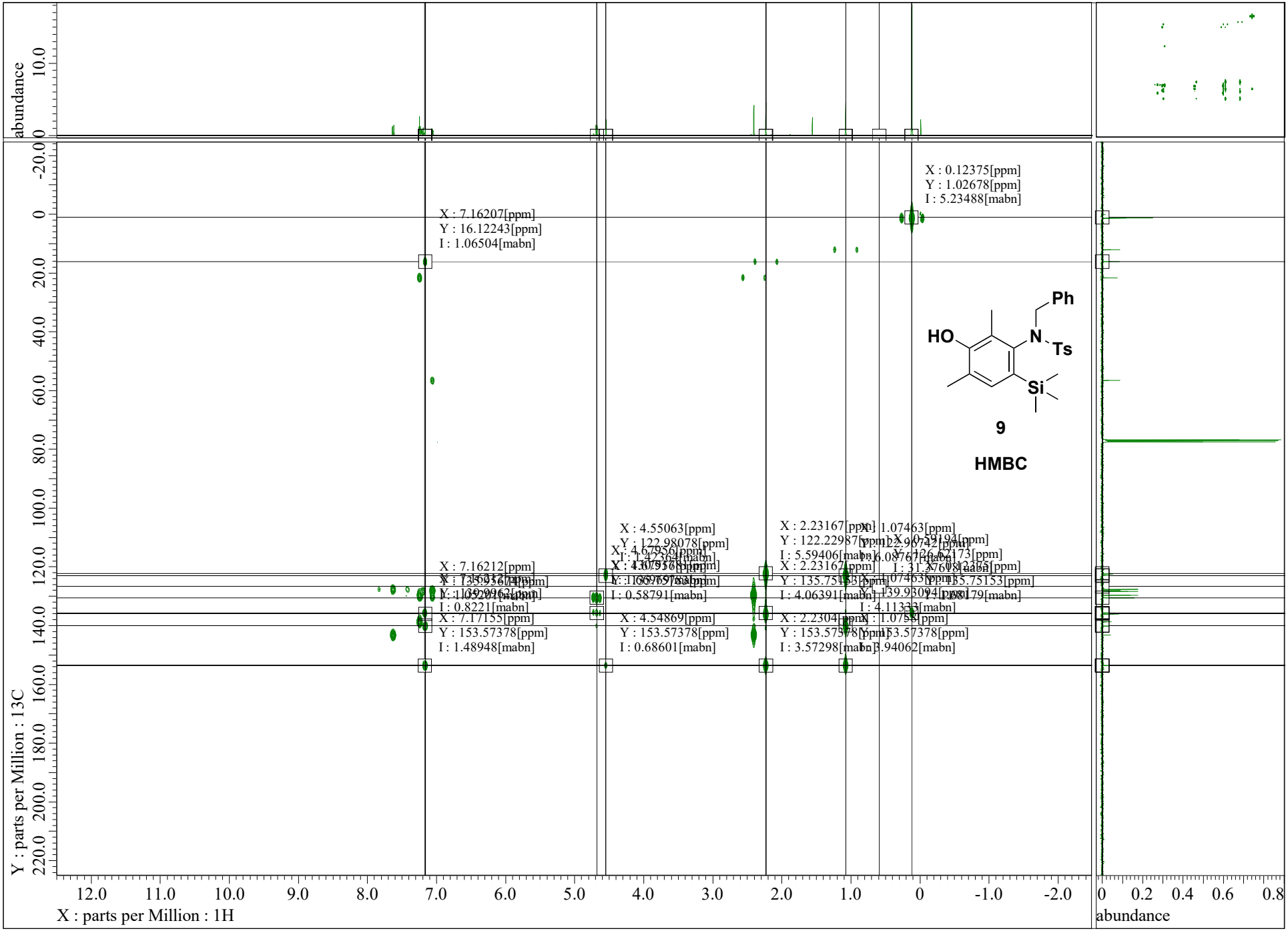

HO
N
S
O2
Si

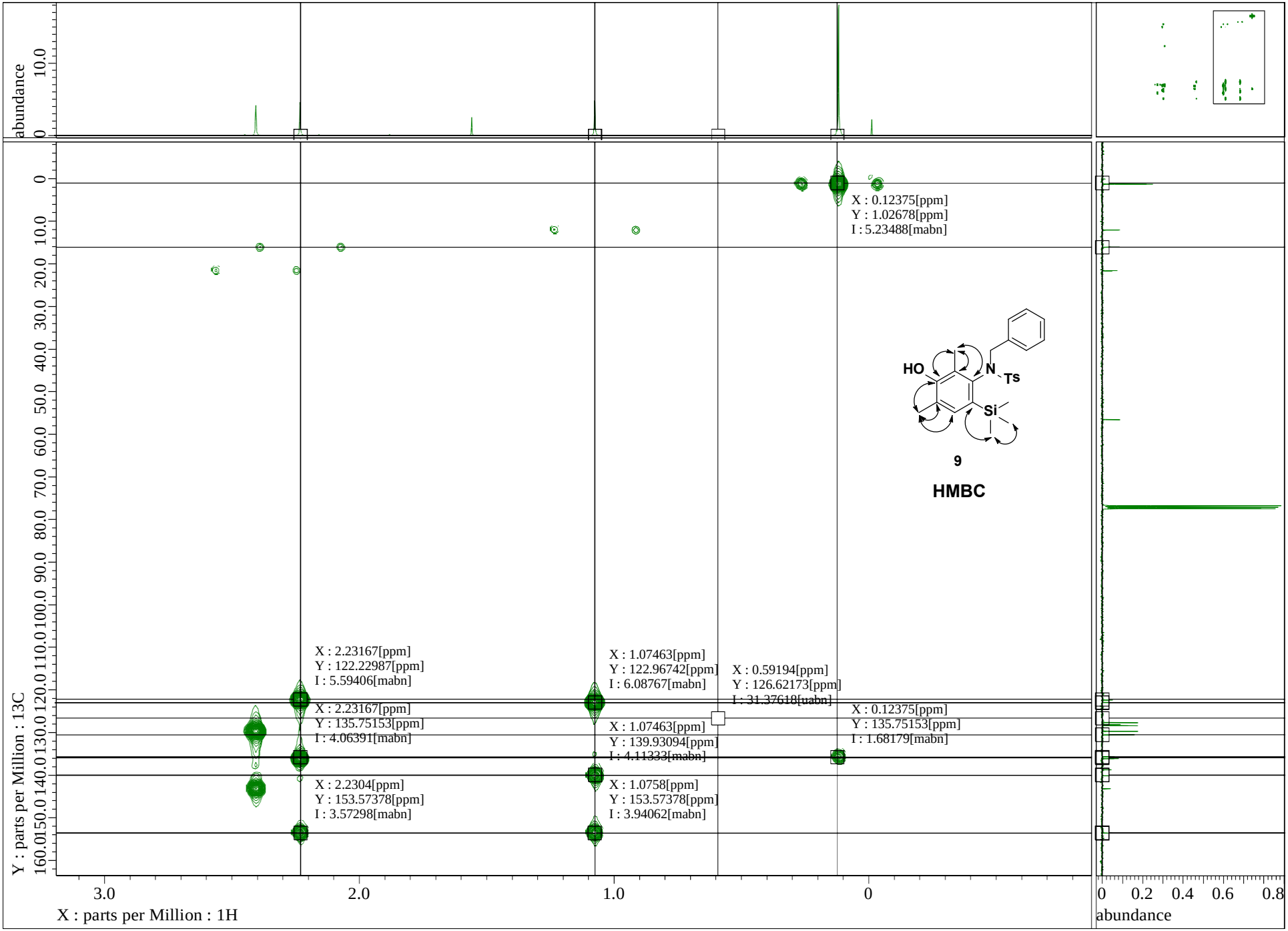

abundance
X : 5.96085[ppm]
Y : 148.46461[ppm]
I : 0.79278[mabn]
X : 5.96079[ppm]
Y : 156.91475[ppm]
I : 1.33203[mabn]
Y : parts per Million : 13C
X : parts per Million : 1H
abundance

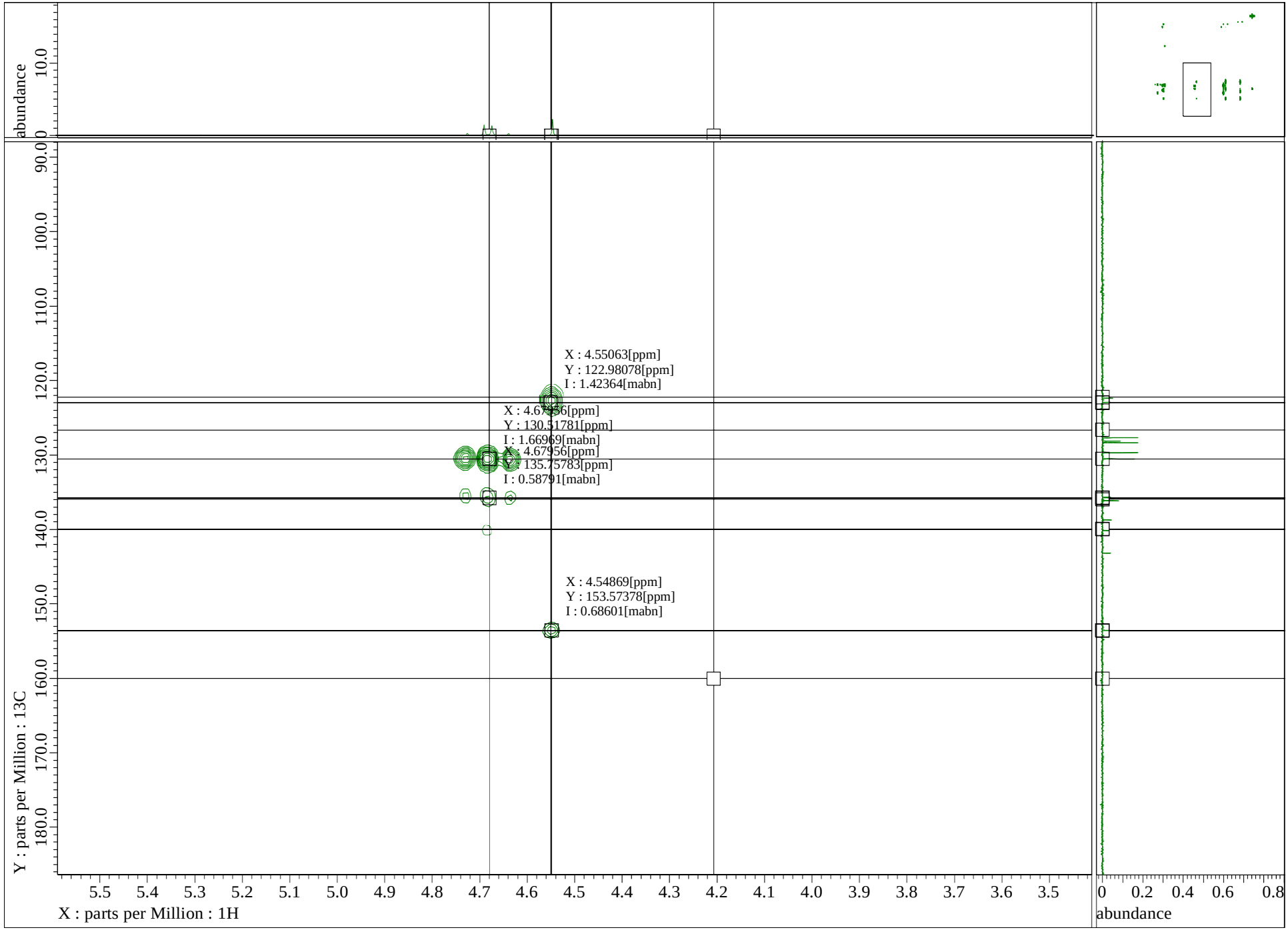
HMBC

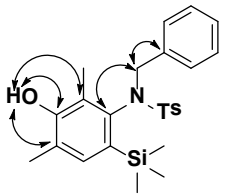

HO
N
S
O2
Si


abundance
X : 3.03733[ppm]
Y : 148.46393[ppm]
Z : 5.77712[mabn]
X : 0.36609[ppm]
Y : 133.06357[ppm]
Z : 4.54366[mabn]
Y : parts per Million : 13C
X : parts per Million : 1H
abundance


X : 0.12375[ppm]
Y : 1.02678[ppm]
I : 5.23488[mabn]
X : 7.16207[ppm]
Y : 16.12243[ppm]
I : 1.06504[mabn]
HO
N
Ph
Ts
Si
9
HMBC
X : 4.55063[ppm]
Y : 122.98078[ppm]
I : 0.58791[mabn]
X : 7.16212[ppm]
I : 0.8221[mabn]
X : 7.17155[ppm]
Y : 153.57378[ppm]
I : 1.48948[mabn]
X : 4.54869[ppm]
Y : 153.57378[ppm]
I : 0.68601[mabn]
X : 2.23167[ppm]
Y : 122.22987[ppm]
I : 5.59406[mabn]
X : 2.23167[ppm]
Y : 135.75153[ppm]
I : 4.06391[mabn]
X : 2.2304[ppm]
Y : 153.57378[ppm]
I : 3.57298[mabn]
X : 1.07463[ppm]
I : 4.11333[mabn]
X : 1.0758[ppm]
I : 3.94062[mabn]
Y : parts per Million : 13C
X : parts per Million : 1H
abundance
abundance

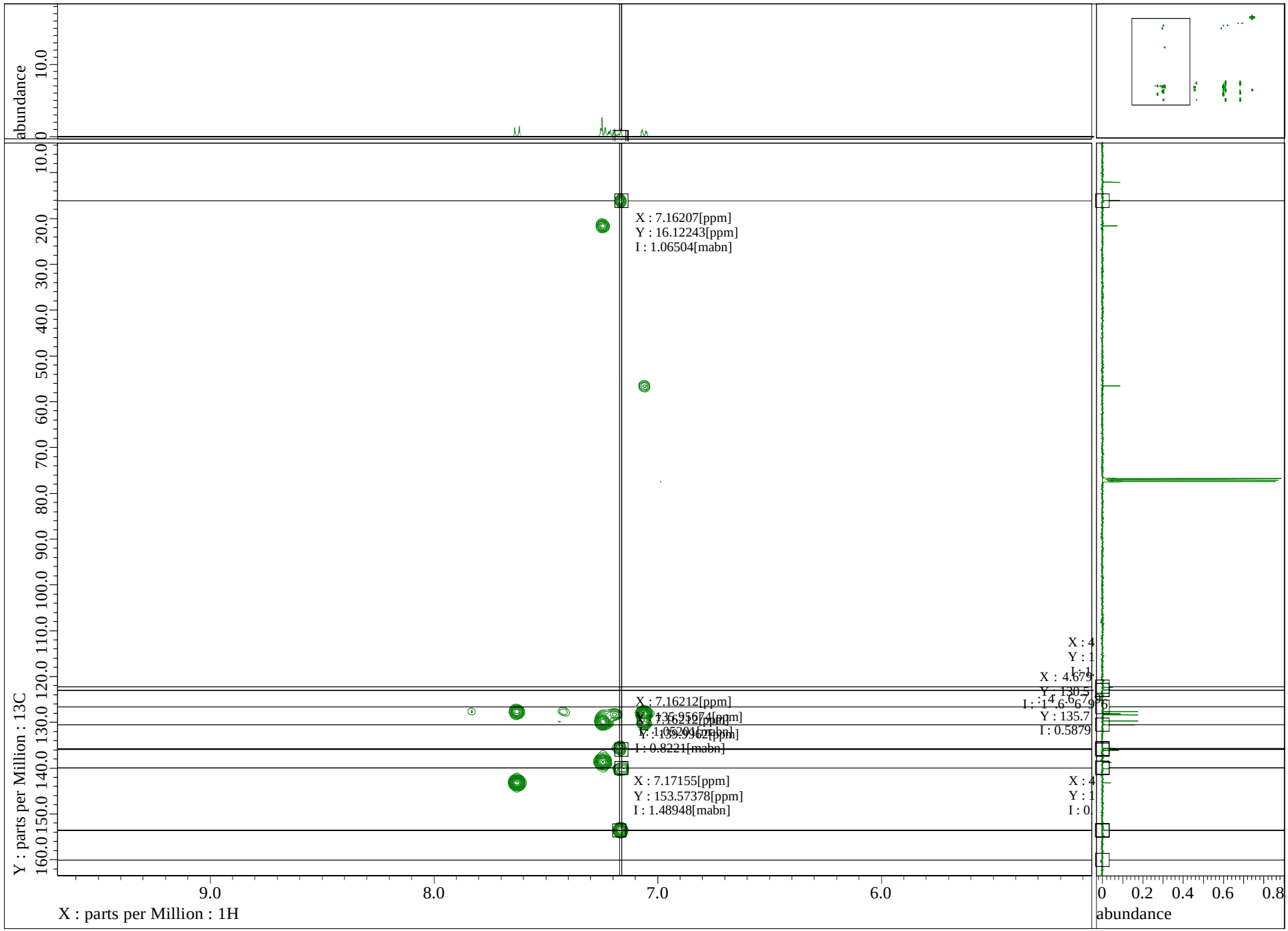

abundance
10.0
0
X : 0.12375[ppm]
Y : 1.02678[ppm]
I : 5.23488[mabn]
HO
N
Ts
Si
9
HMBC
X : 2.23167[ppm]
Y : 122.22987[ppm]
I : 5.59406[mabn]
X : 1.07463[ppm]
Y : 122.96742[ppm]
I : 6.08767[mabn]
X : 0.59194[ppm]
Y : 126.62173[ppm]
I : 31.37618[uabn]
X : 0.12375[ppm]
Y : 135.75153[ppm]
I : 1.68179[mabn]
X : 2.23167[ppm]
Y : 135.75153[ppm]
I : 4.06391[mabn]
X : 1.07463[ppm]
Y : 139.93094[ppm]
I : 4.11333[mabn]
X : 2.2304[ppm]
Y : 153.57378[ppm]
I : 3.57298[mabn]
X : 1.0758[ppm]
Y : 153.57378[ppm]
I : 3.94062[mabn]
Y : parts per Million : 13C
X : parts per Million : 1H
3.0
2.0
1.0
0
0 0.2 0.4 0.6 0.8
abundance

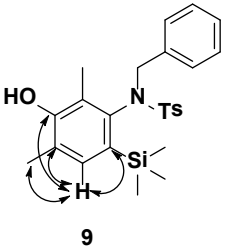

abundance
10.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
X : 4.55063[ppm]
Y : 122.98078[ppm]
I : 1.42364[mabn]
X : 4.67956[ppm]
Y : 130.51781[ppm]
I : 1.66969[mabn]
X : 4.67956[ppm]
Y : 135.75783[ppm]
I : 0.58791[mabn]
X : 4.54869[ppm]
Y : 153.57378[ppm]
I : 0.68601[mabn]
Y : parts per Million : 13C
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
X : parts per Million : 1H
0 0.2 0.4 0.6 0.8
abundance


HO
N
Ts
Si

9

HMBC


abundance
10.0
0
X : 7.16207[ppm]
Y : 16.12243[ppm]
I : 1.06504[mabn]
X : 7.16212[ppm]
I : 0.8221[mabn]
X : 7.17155[ppm]
Y : 153.57378[ppm]
I : 1.48948[mabn]
X : 4.679
Y : 135.7
I : 0.5879
Y : parts per Million : 13C
X : parts per Million : 1H
9.0
8.0
7.0
6.0
0 0.2 0.4 0.6 0.8
abundance


HO
N
Ts
Si
H

9

HMBC