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Supporting Information

For

Synthesis of Thiiranes by Rhodium-catalyzed Sulfur Addition Reaction to Reactive Alkenes

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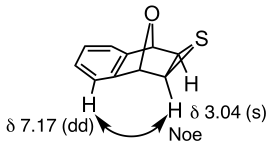
CONTENTS

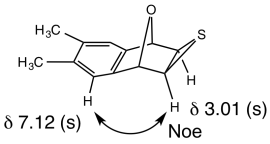
Supplementary Materials

^{1}H-, ^{13}C-, ^{31}P-NMR spectra were recorded on a Varian Mercury (400 MHz) and tetramethylsilane, triphenylphosphine were used as standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotometer. Melting points were determined with a Yanagimoto micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. Elemental analyses were conducted with Yanako CHN CORDER MT-6 and Yanako YHS-11. Merck silica gel 60 (63-200 mm) was employed for flash column chromatography.

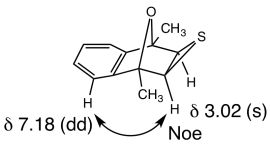
Typical experimental procedures for the synthesis of *exo*-1,2,7,8-tetrahydro-2,7- epoxynaphtho [2.3-*b*] thiirane 4a : In a two-necked flask equipped with a reflux condenser were placed 1,4-epoxy-1,4-tetrahydronaphthalene (0.250 mmol, 36.0 mg), $RhH(PPh_3)_4$ (5 mol%, 14.4 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 10.0 mg), and 4-ethynyltoluene (50 mol%, 15.2 μL) in acetone (0.25 mL) under an argon atmosphere, and the solution was stirred at room temperature for 30 min. Then, sulfur (1.5 eq., 14.4 mg) was added, and the solution was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving *exo*-1,2,7,8-tetrahydro-2,7-epoxynaphtho- [2.3-*b*]thiilane **4a** (40.1mg, 91%). **4a:** Colorless needles. Mp. 103.0-103.5 ^{o}C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.04 (2H, s), 5.18 (2H, s), 7.17 (2H, dd, J = 5.2, 3.2 Hz), 7.34 (2H, dd, J = 5.2, 3.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 37.1, 77.8, 120.7, 127.0, 145.0. IR (KBr) 3024, 1451, 1246, 1055, 981, 879, 838, 766, 670, 648, 523 cm^{-1}. MS (EI) *m/z* 176 (M^+, 15%), 147 (M^+-CHO, 100%). HRMS Calcd for $C_{10}H_8OS$: 176.0296. Found:176.0289. **4a** exhibited NOE between aromatic proton at δ 7.17(dd) and thiirane proton at δ 3.04 (s).



***exo*-5,6-Dimethyltetrahydro-2,7-epoxynaphtho[2.3-*b*]thiirane 4b:** Colorless crystals. Mp. 98.5-99.0 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.25 (6H, s), 3.01 (2H, s), 5.11 (2H, s), 7.12 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.9, 37.3, 77.7, 122.1, 135.0, 142.7. IR (KBr) 3055, 3007, 2938, 2919, 1456, 1244, 1049, 979, 867, 677, 650 cm^{-1}. MS (EI) *m/z* 204 (M^+, 11%), 175 (M^+- CHO, 100%). HRMS Calcd for $C_{12}H_{12}OS$: 204.0609 Found: 204.0605. **4b** exhibited NOE between aromatic proton at δ 7.12 (s) and thiirane proton at δ 3.01 (s).

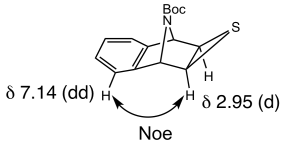


***exo*-2,7-Dimethy-1,8-dihydro-2,7-epoxynaphtho[2.3-*b*]thiirane 4c:** Colorless crystals. Mp. 90.5-91.0 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.80 (6H, s), 3.02 (2H, s), 7.18 (2H, dd, *J* = 5.2, 3.2 Hz), 7.24 (2H, dd, *J* = 5.2, 3.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.9, 44.1, 84.0, 119.4, 126.9, 148.2. IR (KBr) 3040, 2976, 2928, 1924, 1820, 1405, 1385, 1270, 1137, 1028, 899, 871, 765, 655 cm^{-1}. MS (EI) *m/z* 204 (M^+, 2%), 161 (M^+- C_2H_3O, 100%), 128 (M^+-C_2H_3OS, 17%). HRMS Calcd for $C_{12}H_{12}OS$: 204.0609 Found: 204.0626. **4c** exhibited NOE between aromatic proton at δ 7.18 (dd) and thiirane proton at δ 3.02 (s).

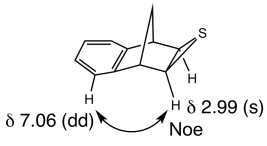


1,1-Dimethylethyl-1a,2,7,7a-tetrahydronaphtho[2.3-*b*]thiirane-2,7-imine-8-carboxylate 4d: Colorless crystals. Mp. 96.0-96.5 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.47 (9H, s), 2.91 (1H,

d, J = 5.2 Hz), 2.95 (1H, d, J = 5.2 Hz), 5.08 (1H, s), 5.22 (1H, s), 7.14 (2H, dd, J = 5.6, 3.2 Hz), 7.29-7.33 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.2, 37.6, 38.3, 61.5 (d, J = 2.3 Hz), 62.2, 80.1, 120.8, 121.0, 126.7, 144.3, 144.6, 154.6. IR (KBr) 2977, 2928, 1689, 1452, 1364, 1298, 1161, 1084, 1043, 945, 864, 741, 681, 654 cm^{-1}. MS (EI) *m/z* 275 (M^+, 1%), 219 (M^+- C_4H_8, 100%), 175 (M^+- $C_5H_8O_2$, 91%), 130 (M^+- $C_6H_{10}O_2S$, 44%), 57 (^{t}Bu, 72%). HRMS Calcd for $C_{15}H_{17}NO_2S$: 275.0980. Found:275.0970. **4d** exhibited NOE between aromatic proton at δ 7.14 (dd) and thiirane proton at δ 2.95 (d).

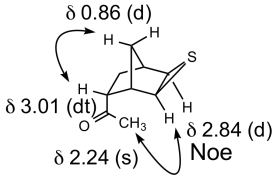


***exo*-2,7-Methanonaphtho[2.3-*b*]thiirane 4e:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.56 (1H, dt, J = 10.0, 1.6 Hz), 2.16 (1H, dt, J = 10.0, 1.6 Hz), 2.99 (2H, s), 3.40 (2H, s), 7.06 (2H, dd, J = 4.8, 2.8 Hz), 7.23 (2H, dd, J = 4.8, 2.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 39.8, 40.6, 44.6, 122.2, 125.9, 148.3. IR (KBr) 3049, 2914, 1694, 1484, 1432, 1246, 1093, 871, 812, 741, 695, 525 cm^{-1}. MS (EI) *m/z* 174 (M^+, 96%), 173 (M^+-H, 100%), 141 (M^+-HS, 65%). HRMS Calcd for $C_{11}H_{10}S$: 174.0503. Found:174.0499. **4e** exhibited NOE between aromatic proton at δ 7.06 (dd) and thiirane proton at δ 2.99 (s).

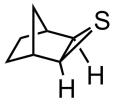


***exo*-1-(3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-yl)-ethanone 4f:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.86 (1H, d, J = 10.0 Hz), 1.69 (1H, ddd, J = 12.8, 10.0, 4.0 Hz), 1.76 (1H, d, J = 10.0 Hz), 1.89 (1H, ddd, J = 12.8, 4.8, 2.8 Hz), 2.24 (3H, s), 2.52 (1H, d, J = 2.8 Hz), 2.63 (1H, d, J = 5.2 Hz), 2.84

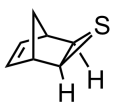
(1H, d, J = 5.2 Hz), 2.89 (1H, s), 3.01 (1H, dt, J = 10.0, 4.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.3, 29.3, 29.6, 33.7, 37.1, 38.2, 41.2, 54.6, 208.1. IR (neat) 2971, 1705, 1359, 1173, 1070, 651 cm^{-1}. MS (EI) *m/z* 168 (M^+, 100%), 125 (M^+- C_2H_3O, 37%), 98 (M^+- C_4H_6O, 69%), 43 (C_2H_3O, 31%). HRMS Calcd for $C_9H_{12}OS$: 168.0609. Found:168.0592. **4f** exhibited NOE between thiirane proton at δ 2.84 (d) and acetyl proton at δ 2.24 (s).



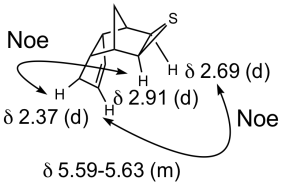
***exo*-3-Thiatricyclo[3.2.1.0^{2,4}]octane[1] 4g:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.65 (1H, d, J = 10.0 Hz), 1.25 (2H, dd, J = 8.0, 2.4 Hz), 1.53 (1H, d, J = 10.0 Hz), 1.63 (2H, d, J = 8.0 Hz), 2.44 (2H, s), 2.74 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.5 (2 peaks), 37.4, 37.6. IR (neat) 2921, 2868, 1724, 1364, 1224, 1103 cm^{-1}. MS (EI) *m/z* 126 (M^+, 100%), 93 (M^+- HS, 73%). HRMS Calcd for $C_7H_{10}S$: 126.0503. Found:12.0509.



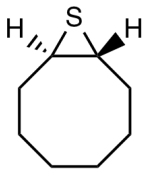
***exo*-3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-ene[2] 4h:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28 (1H, d, J = 9.2 Hz), 1.85 (1H, d, J = 9.2 Hz), 2.97 (2H, s), 3.03 (2H, s), 6.38 (2H, t, J = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 41.5, 41.6, 43.4, 140.1. IR (neat) 2991, 1441, 1313, 1192, 1053, 715 cm^{-1}. MS (EI) *m/z* 124 (M^+, 99%), 123 (M^+- H, 100%), 91 (M^+- HS, 71%). HRMS Calcd for C_7H_8S: 124.0347. Found:124.0357.



***exo*-1a,2a,3,5a,6,6a-Hexahydro-2,6-methano-2*H*-indeno[5.6-*b*]thiirane[3] 4i:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.86 (1H, d, *J* = 10.4 Hz), 1.70 (1H, d, *J* = 10.4 Hz), 2.28 (1H, ddq, *J* = 18.0, 10.0, 2.4 Hz), 2.37 (1H, d, *J* = 18.0 Hz), 2.46 (1H, d, *J* = 4.0 Hz), 2.56 (1H, dd, *J* = 4.0, 1.6 Hz), 2.69 (1H, d, *J* = 5.2 Hz), 2.75 (1H,tt, *J* = 10.0, 4.0 Hz), 2.91 (1H, d, *J* = 5.2 Hz), 3.25-3.30 (1H, m), 5.59-5.63 (1H, m), 5.67-5.69 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.9, 31.0, 34.5, 37.6, 39.6, 41.2, 42.5, 54.3, 130.2, 132.2. IR (neat) 2925, 2852, 1450, 1320, 1261, 1060, 653 cm^{-1}. MS (EI) *m/z* 164 (M^+, 43%), 131 (M^+- HS, 10%), 98 (M^+- C_5H_6, 100%), 66 (M^+- C_5H_6S, 16%). HRMS Calcd for $C_{10}H_{12}S$: 164.0660. Found:164.0678. **4i** exhibited NOE between thiirane proton at δ 2.69 (d) and alkene proton at δ 5.59-5.63 (m).

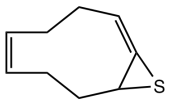


***trans*-10-Thiabicyclo[7.1.0]nonane 6**: Colorless crystals. Mp.57.5-58.0 °C (Hexane) Lit[4] 58.0-59.0 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.98-1.08 (2H, m), 1.15 (2H, t, *J* = 12.0 Hz), 1.64 (2H, q, *J* = 12.0 Hz), 1.94 (2H, d, *J* = 14.4 Hz), 2.08 (2H, dt, *J* = 10.0, 4.0 Hz), 2.45 (2H, dt, *J* = 14.4, 2.0 Hz), 2.66 (2H, d, *J* = 10.0 Hz). The *trans* structure was confirmed by referred thiirane proton[4] [^{1}H-$CDCl_3$ δ 2.68(2H, m)] ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.3, 31.9, 36.9, 43.3. IR (KBr) 2926, 2855, 1450, 1412, 1220, 982, 636 cm^{-1}. MS (EI) *m/z* 142 (M^+, 8%), 109 (M^+- HS, 4%), 85 (M^+- C_2HS, 68%), 83 (M^+- C_2H_3S, 100%). HRMS Calcd for $C_8H_{14}S$: 142.0816. Found:142.0826.

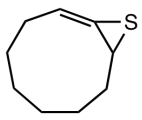


Typical experimental procedures for the synthesis of 10-thiabicyclo[7.1.0]dec-1,5-diene 10: In a

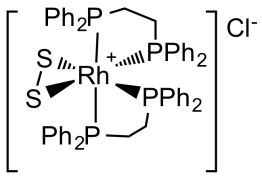
two-necked flask equipped with a reflux condenser were placed 1,2,6-cyclononatriene (1.50 mmol, 180.3 mg), $RhH(PPh_3)_4$ (5 mol%, 28.8 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 20.0 mg), and 4-ethynyltoluene (50 mol%, 31.2 μL) in acetone (0.25 mL) and DMF (0.25 mL) under an argon atmosphere, and the solution was stirred at room temperature for 30 min. Then, sulfur (0.6 mmol, 19.2 mg) was added, and the solution was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 10-thiabicyclo[7.1.0]dec-1,5-diene **10** (26.3 mg, 35%). **10**: Colorless needles. Mp. 58.0-58.5 ^{o}C (Hexane). Lit.[5] 54.0-55.0 ^{o}C (Petroleum ether). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.14 (1H, q, *J* = 12.0 Hz), 2.14 (2H, dt, *J* = 14.0, 6.4 Hz), 2.25 (1H, t, J = 12.0 Hz), 2.37-2.46 (1H, m), 2.55 (1H, d, *J* = 18.0 Hz), 2.62-2.70 (2H, m), 3.36 (1H, ddd, *J* = 10.4, 4.0, 1.6 Hz), 5.39 (1H,dt, *J* = 11.2, 4.0 Hz), 5.55-5.64 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.6, 24.4, 30.2, 37.1, 37.2, 114.1, 127.3, 127.9, 131.0. IR (KBr) 3000, 2941, 2912, 2899, 2880, 2851, 1650 cm^{-1}. MS (EI) *m/z* 152 (M^+, 100%), 119 (M^+- HS, 96%). HRMS Calcd for $C_9H_{12}S$: 152.0660. Found:152.0659.



10-Thiabicyclo[7.1.0]dec-1-ene 8[5]: Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20-1.77 (8H, m), 1.80-1.91 (1H, m), 2.05-2.15 (1H, m), 2.45-2.60 (2H, m), 3.29 (1H, d, *J* = 12.0 Hz), 5.62 (1H, d, *J* = 4.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.3, 24.1, 24.2, 25.1, 29.5, 34.7, 38.0, 114.0, 128.7. IR (neat) 2931, 2866, 2360, 2342, 1716, 1463, 1443, 1336, 964, 781, 616 cm^{-1}. MS (EI) *m/z* 154 (M^+, 81%), 121 (M^+- HS, 62%), 57 (M^+- C_5H_5S, 100%). HRMS Calcd for $C_9H_{14}S$: 154.0816. Found:154.0818.



Typical experimental procedure for the synthesis of [$RhS_2(dppe)_2$]Cl complex 12: In a two-necked flask were placed sulfur (0.5 mmol atom, 16 mg), $RhH(PPh_3)_4$ (5 mol%, 28.8 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 20.0 mg) in acetone (0.5 mL). The solution was stirred under an argon atmosphere at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was washed with $CHCl_3$ and hexane, concentrated gave [$RhS_2(dppe)_2$]Cl complex **12** as purple crystals. **12**: Mp. 205.0-206.0 ^oC (Hexane/CH_2Cl_2 = 3). Lit[7] 200 ℃(decompt., MeCN). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.28-2.75 (8H, m), 6.04 (4H,dd, *J* = 9.2, 8.8 Hz), 7.00 (4H, t, *J* = 7.2 Hz), 7.12 (4H, t, *J* = 7.2 Hz), 7.18 (4H, t, *J* = 7.2 Hz), 7.29-7.40 (12H, m), 7.49 (6H, dd, *J* = 7.6, 6.8 Hz), 7.58 (2H, dd, *J* = 7.6, 6.4 Hz), 7.70 (4H, dd, *J* = 6.8, 5.6 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 50.1 (dt, *J* = 126.7, 16.8 Hz), 52.1 (dt, *J* = 87.0, 16.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.6 (q, *J* = 15.0 Hz), 31.5 (dt, *J* = 32.2, 10.5 Hz), 125.2 (t, *J* = 28.4 Hz), 126.3, 129.0 (t, *J* = 44.0 Hz), 129.2 (t, *J* = 40.9 Hz), 130.3, 131.5, 131.6, 133.0 (dd, *J* = 74.5, 60.3 Hz). IR (KBr) 3431, 3050, 2915, 1694, 1432, 1093, 742, 685, 526 cm^{-1}. LC-MS(ESI^+) $C_{52}H_{48}P_4RhS_2$ Calcd for 963.1203. Found: 963.1222. Elemental analysis ($C_{52}H_{48}ClP_4RhS_2$) Calcd for: C, 62.50%; H, 4.84%; Cl, 3.55%; S, 6.42%, Found: C, 62.39%; H, 4.97%; Cl, 3.46%; S, 6.42%



Typical experimental procedure for the analysis of complex 11: In a two-necked flask equipped with a reflux condenser were placed sulfur (0.5 mmol atom, 16 mg), $RhH(PPh_3)_4$ (5 mol%, 28.8 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 20.0 mg), in acetone (0.5 mL). The solution was stirred under an argon atmosphere at room temperature for 3 h. The reaction mixture was sampling by a syringe and diluted by degassed toluene-d_8. ^{31}P-NMR analysis showed formation of a rhodium

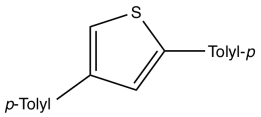
intermediate **11**. **11**: ^{31}P-NMR (Toluene-d_8) δ 49.4 (bs), 50.1 (dd, *J* = 38.2, 15.2 Hz). LC-MS(ESI$^+$) $C_{52}H_{48}P_4RhS_2$ Calcd for 963.1203. Found: 963.1175.

Typical experimental procedure for the synthesis of RhH(dppe)$_2$ 13: In a two-necked flask were placed $RhH(PPh_3)_4$ (0.05 mmol, 57.6 mg) and 1,2-bis(diphenylphosphino)ethane (0.10 mmol , 40.0 mg) in acetone (1.0 mL). The solution was stirred under an argon atmosphere at room temperature for 30 min. The precipitated solid was filted, and the solid washed with hexane, gave $RhH(dppe)_2$ complex **13** as red crystals (36.2 mg, 80%). **13**: ^{1}H-NMR (400 MHz, C_6D_6) δ -10.19 (1H, dpent, *J* = 17.6, 10.8 Hz), 2.09 (8H, brs), 6.90-6.97 (24H, m), 7.48 (16H, brs). ^{31}P-NMR (162 MHz, C_6D_6) δ 56.4 (dd, *J* = 143.4, 6.1 Hz). IR (KBr) 3045, 2887, 1896, 1431, 1095, 738, 692, 521, 491 cm^{-1}. LC-MS(ESI$^+$) $C_{52}H_{48}P_4Rh$ Calcd for 899.1762. Found: 899.1799.

The reaction using RhH(dppe)$_2$ complex 13: In a two-necked flask equipped with a reflux condenser were placed 1,4-epoxy-1,4-tetrahydronaphthalene (0.250 mmol, 36.0 mg), $RhH(dppe)_2$ **13** (5 mol%, 11.3 mg), and 4-ethynyltoluene (50 mol%, 15.2 μL) in acetone (0.25 mL) under an argon atmosphere, and the solution was stirred at room temperature for 30 min. Then, sulfur (1.5 eq., 14.4 mg) was added, and the solution was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving **4a** (17.6 mg, 91%).

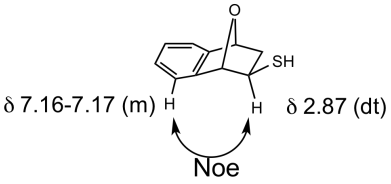
Typical experimental procedures for the synthesis of 2,4-bis(4-tolyl)thiophene 15: In a two-necked flask equipped with a reflux condenser were placed 4-ethynyltoluene **3** (1.5 mmol, 188.4 μL), sulfur (0.5 mmol atom, 16 mg), $RhH(PPh_3)_4$ (5 mol%, 28.8 mg), 1,2-bis(diphenylphosphino)-ethane (10 mol%, 20.0 mg) in acetone (0.5 mL). The solution was heated at reflux under an argon

atmosphere for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2,4-bis(4-tolyl)thiophene **15** (3.0 mg, 2%). **15**: Colorless crystals. Mp. 146.5-147.0 ^{o}C (Hexane/Toluene = 1) Lit[6] 144.0-145.0 ^{o}C (Ethanol). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.38 (6H, s), 7.20 (2H, d, *J* = 10.8 Hz), 7.22 (2H, d, *J* = 10.8 Hz), 7.31 (1H, d, *J* = 2.0 Hz), 7.51 (2H, d, *J* = 10.8 Hz), 7.52 (1H, d, *J* = 2.0 Hz), 7.54 (2H, d, *J* = 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 21.2, 118.6, 121.8, 125.7, 126.2, 129.5 (2 peaks), 131.6, 133.1, 136.9, 137.5, 143.0, 145.0. IR (KBr) 3096, 3021, 2911, 2854, 1908 1499, 1307, 1123, 809, 748 cm^{-1}. MS (EI) *m/z* 264.1 (M^+, 100%). HRMS Calcd for $C_{18}H_{16}S$: 264.0982. Found:264.0973.

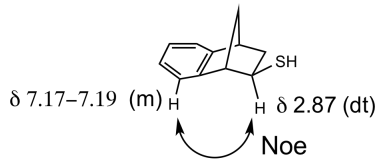


Typical experimental procedures for the synthesis of *exo*-1,2,7,8-Tetrahydro-2,7-epoxynaphthalene-1-thiol 16a: In a two-necked flask equipped with a reflux condenser were placed $LiAlH_4$ in THF (0.5 mL), to which *exo*-1,2,7,8-tetrahydro-2,7-epoxynaphtho[2,3-*b*]thiirane **4a** (0.1 mmol, 18.0 mg) in THF (0.5 mL) was added dropwise. The mixture was heated at reflux under an argon atmosphere for 3 h. A small amount of cold water was added slowly, and the solution was diluted with ether. Then a small amount of 2 M HCl solution was added. The organic layer was washed with brine twice. The aqueous layer was extracted with ether. The combined organic layer was dried with $MgSO_4$ and concentrated. Purified by flash column chromatography afforded *exo*-1,2,7,8-tetrahydro-2,7-epoxynaphthalene-1-thiol **16a** (11.6 mg, 65%): Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.96 (1H, ddd, *J* = 12.4, 4.8, 4.0 Hz), 2.07 (1H, d, *J* = 8.0 Hz), 2.11 (1H, dd, *J* = 12.4, 4.0 Hz), 2.87 (1H, dt *J* = 8.0, 4.0 Hz), 5.18 (1H, s), 5.44 (1H, d, *J* = 4.8 Hz), 7.16-7.29 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 38.0, 40.5, 79.5, 87.3, 119.1, 119.6, 126.9, 127.3, 143.9, 145.2. IR (neat) 3069, 2968, 1468, 1276, 1155, 1000, 756, 514 cm^{-1}. MS (EI) *m/z* 178 (M^+, 2%), 118 (M^+-

CH_2CHSH, 100%). HRMS Calcd for $C_{10}H_{10}OS$: 178.0452. Found:178.0431. **16a** exhibited NOE between *endo* proton at δ 2.87 (dt) and aryl proton at δ 7.16-7.17 (m).

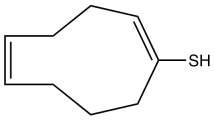


***exo*-1,2,7,8-Tetrahydro-2,7-methanonaphthalene-1-thiol 16e:** Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.68 (1H, dt, *J* = 12.8, 4.0 Hz), 1.82-1.88 (2H, m), 1.95 (1H, d, *J* = 5.6 Hz), 2.09 (1H, dt, *J* = 8.0, 1.2 Hz), 2.87 (1H, ddd, *J* = 8.0, 5.6 Hz), 3.21 (1H, s), 3.36 (1H, d, *J* = 2.4 Hz), 7.07-7.08 (2H, m), 7.13-7.15 (1H, m), 7.17-7.19 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 38.0, 39.5, 44.2, 46.1, 53.8, 120.9, 121.2, 125.9, 126.3, 146.3, 147.6. IR (neat) 3001, 2947, 1459, 1258, 1206, 985, 758, 626 cm^{-1}. MS (EI) *m/z* 176 (M^+, 25%), 143 (M^+- SH, 29%), 116 (M^+- CH_2CHSH, 100%). HRMS Calcd for $C_{11}H_{12}S$: 176.0660. Found:176.0662. **16e** exhibited NOE between *endo* proton at δ 2.87 (dt) and aryl proton at δ 7.17-7.19 (m).

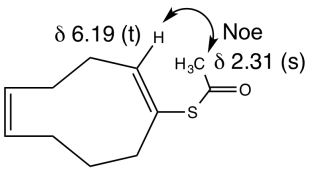


Typical experimental procedures for the synthesis of 1,5-cyclononadiene-1-thiol 17: In a two-necked flask were placed $LiAlH_4$ in THF (0.5 mL), to which 10-thiabicyclo[7.1.0]dec-1-ene **10** (0.1 mmol, 15.0 mg) in THF (0.5 mL) was added dropwise. The mixture was stirred under an argon atmosphere at room temperature for 2 h. A small amount of cold water was added slowly, and the solution was diluted with ether. Then a small amount of 2 M HCl solution was added. The organic layer was washed with brine twice. The aqueous layer was extracted with ether. The combined organic layer was dried with $MgSO_4$ and concentrated giving 1,5-cyclononadiene-1-thiol **17** (37%,

yield was determined by internal standard 1,1,2-trichloroethane). **17**: Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.73 (2H, s), 1.95-2.05 (4H, m), 2.13 (2H, s), 2.25-2.31 (2H, m), 2.60 (1H, s), 5.42 (1H, q, *J* = 8.8 Hz), 5.74 (1H, d, *J* = 8.0 Hz), 5.88(1H, t, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.0, 26.2, 27.2, 27.8, 31.6, 129.9, 130.1 (2 peaks), 130.9. IR (neat) 2949, 2869, 1729, 1703, 1454, 1260, 1092, 803, 754 cm^{-1}. MS (EI) *m/z* 154 (M^+, 14%), 121 (M^+- HS, 100%). HRMS Calcd for $C_9H_{14}S$: 154.0816. Found:154.0801.



Typical experimental procedures for the synthesis of 1-acetylthio-1,5-cyclononadiene 18: In a two-necked flask were placed 1,5-cyclononadiene-1-thiol **17** (0.04 mmol, 6.3 mg) and pyridine (0.1 mmol, 8.0 μL) in dichloromethane (0.25 mL) under an argon atmosphere. The mixture was cooled at 0 ^{o}C, and acetyl chloride (0.1 mmol, 7.0 μL) was added dropwise. The solution was warmed to room temperature for 1 h, when a small amount of water was added. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried with $MgSO_4$, and concentrated. Purification by flash column chromatography afforded 1-acetylthio-1,5-cyclononadiene **18** (6.0 mg, 88%). **18**: Colorless oils. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.63-1.65 (2H, m), 1.91-1.96 (2H, m), 2.04-2.09 (2H, m), 2.13-2.18 (2H, m), 2.29-2.32 (2H, m), 2.31 (3H, s), 5.44 (1H, dt, *J* = 10.8, 8.4 Hz), 5.75 (1H, dt, *J* = 10.8, 8.4 Hz), 6.19 (1H, t, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.3, 25.6, 27.4, 28.1, 29.3, 30.2, 130.3, 130.4, 130.7, 143.5, 195.8. IR (neat) 3006, 2933, 2859, 1697, 1460, 1352, 1110, 947, 728, 619 cm^{-1}. MS (EI) *m/z* 196 (M^+, 3%), 153 (M^+-CH_3CO, 27%), 121 (M^+- CH_3COS, 100%). HRMS Calcd for $C_{11}H_{16}OS$: 196.0922. Found: 196.0912. **18** exhibited NOE between alkene proton at δ 6.19 (t) and acetyl proton at δ 2.31 (s).



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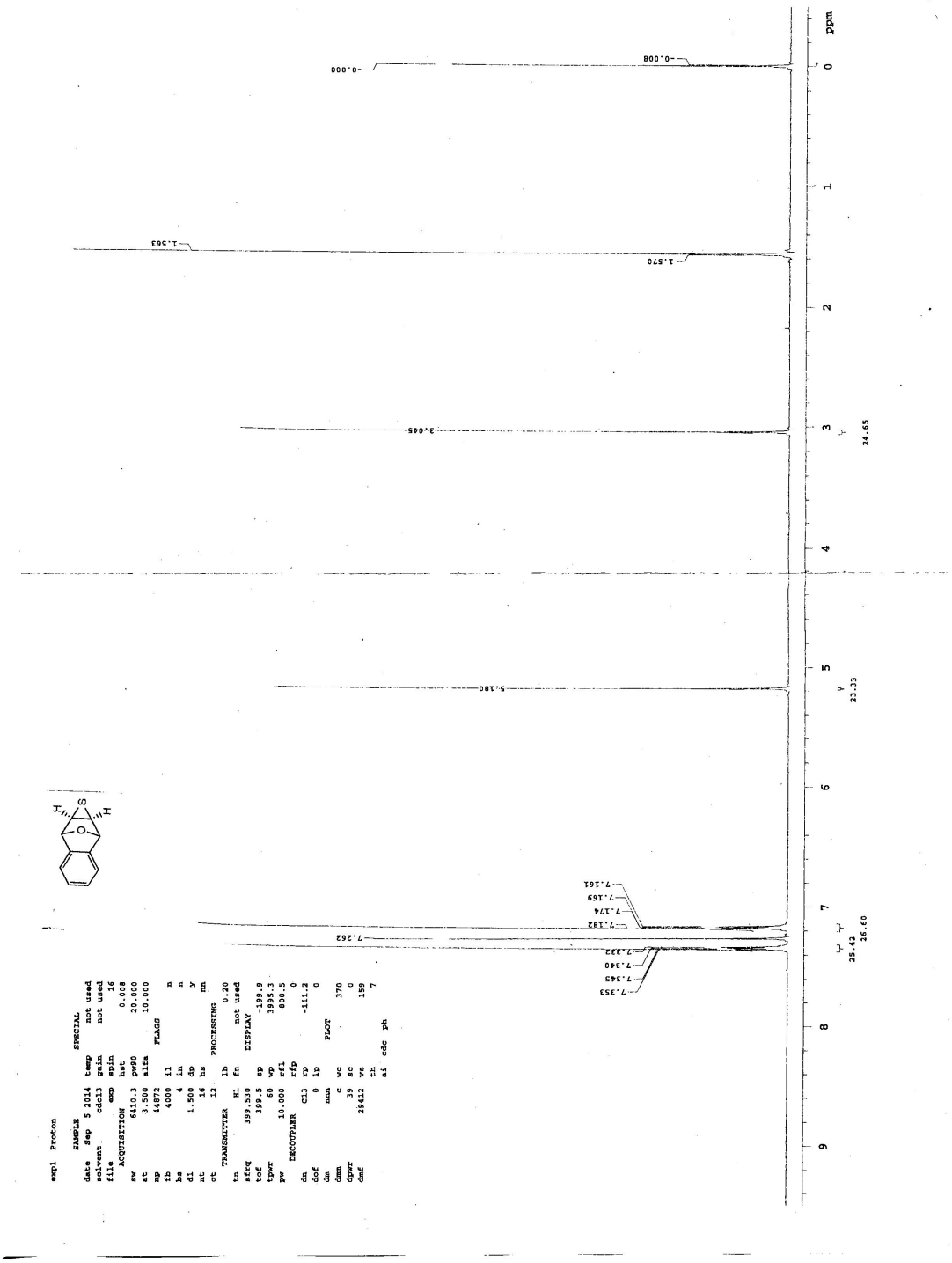
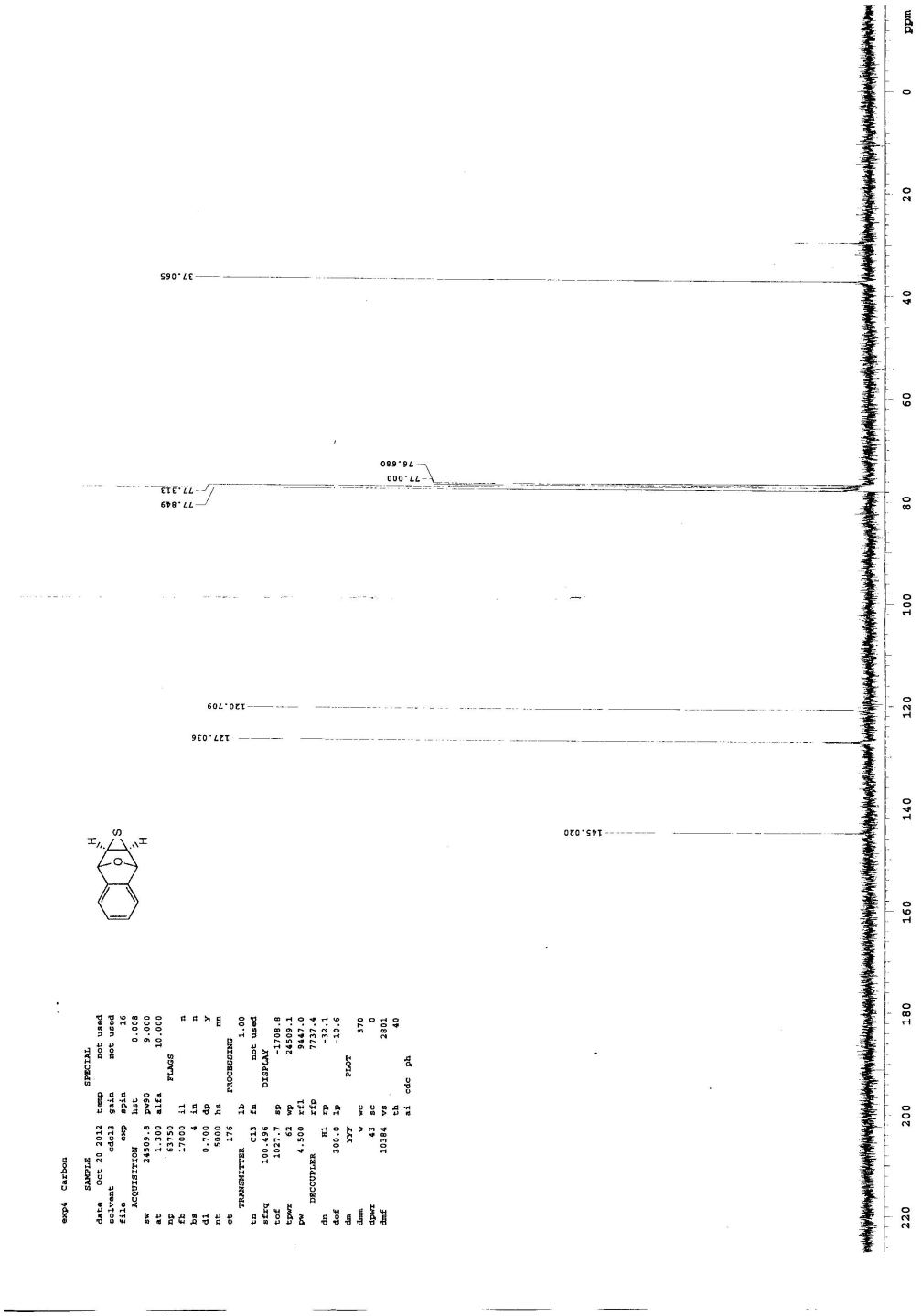
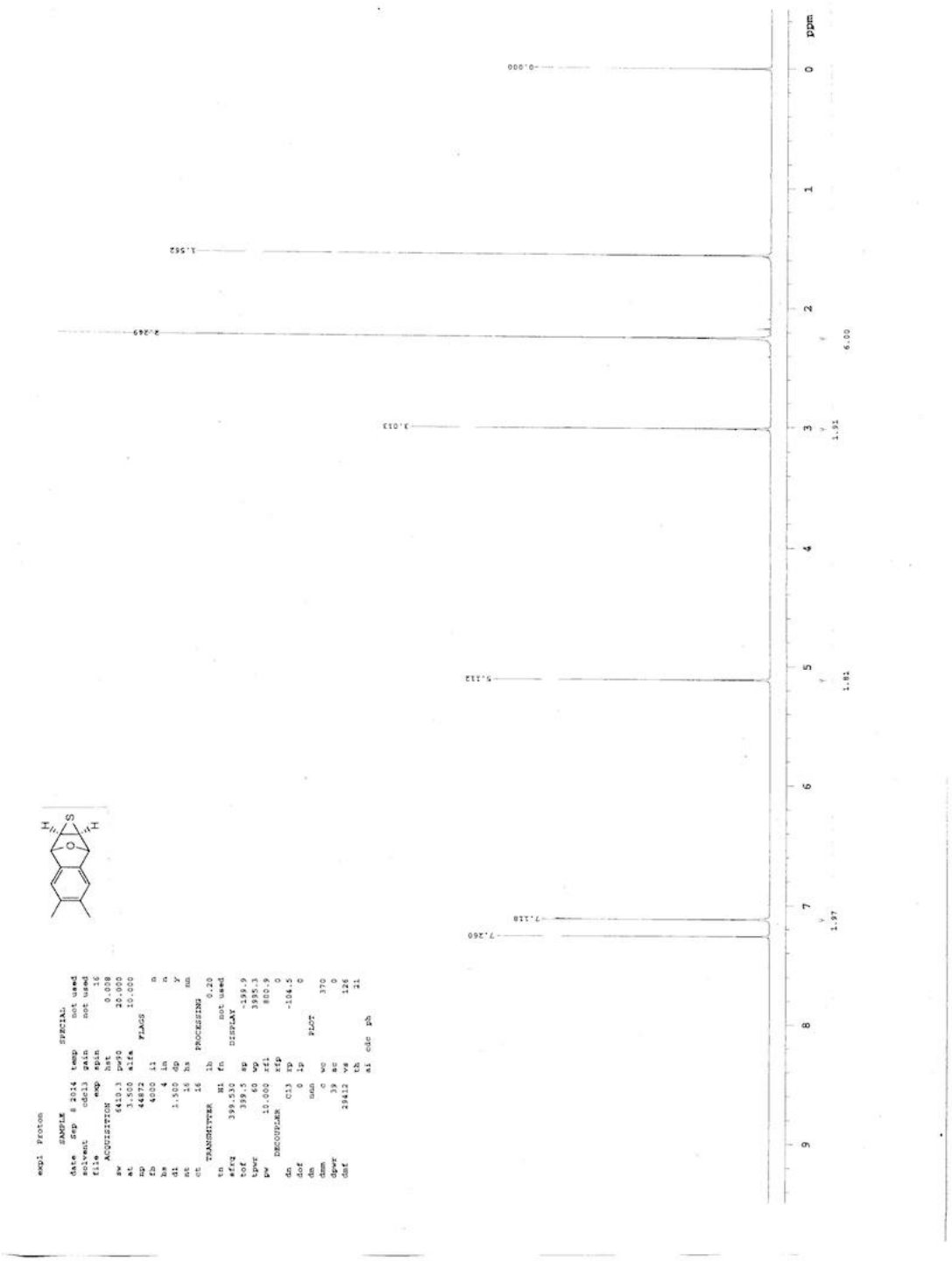
exo-1,2,7,8-Tetrahydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4a** (^{1}H-NMR)



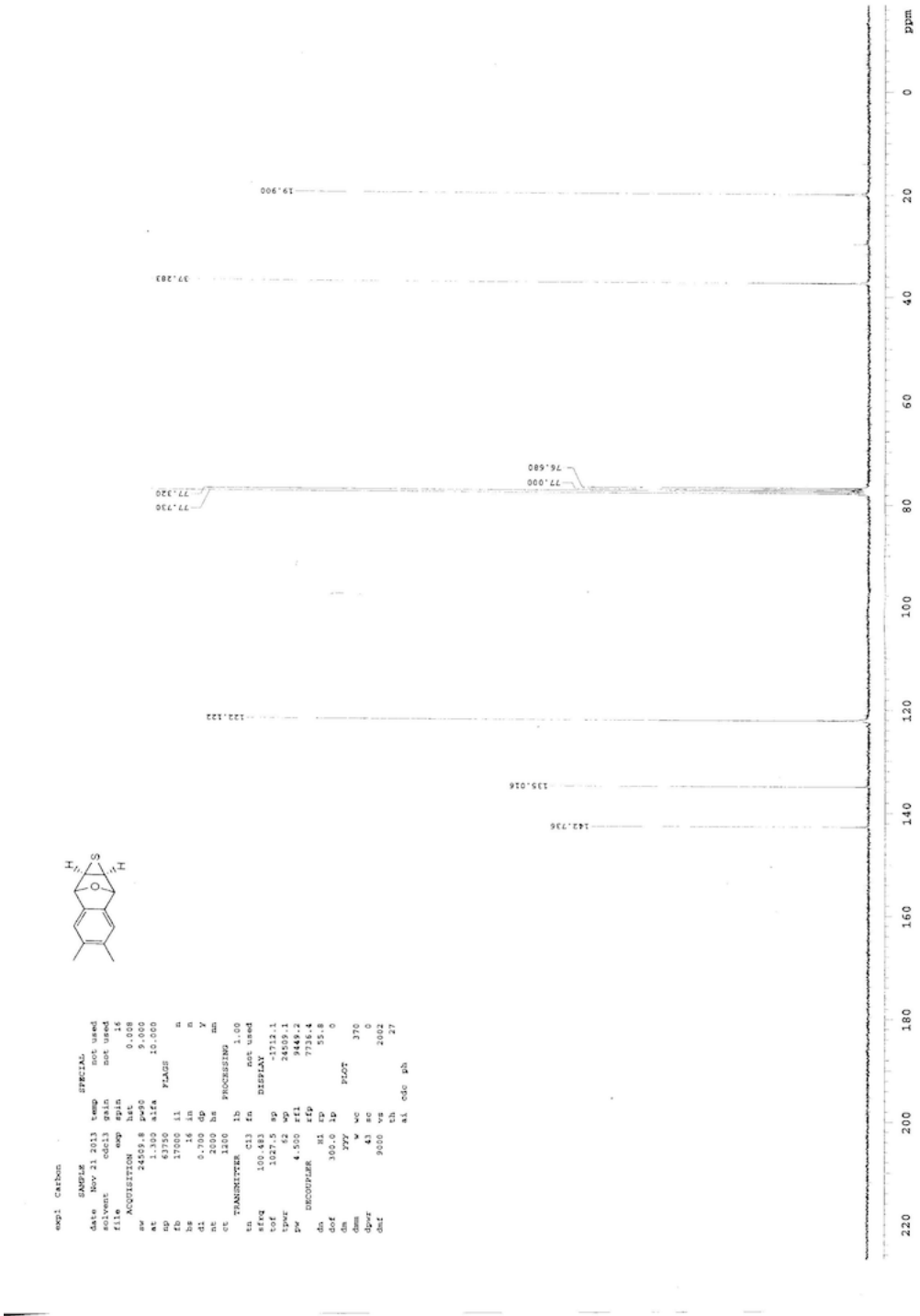
exo-1,2,7,8-Tetrahydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4a** (^{13}C-NMR)



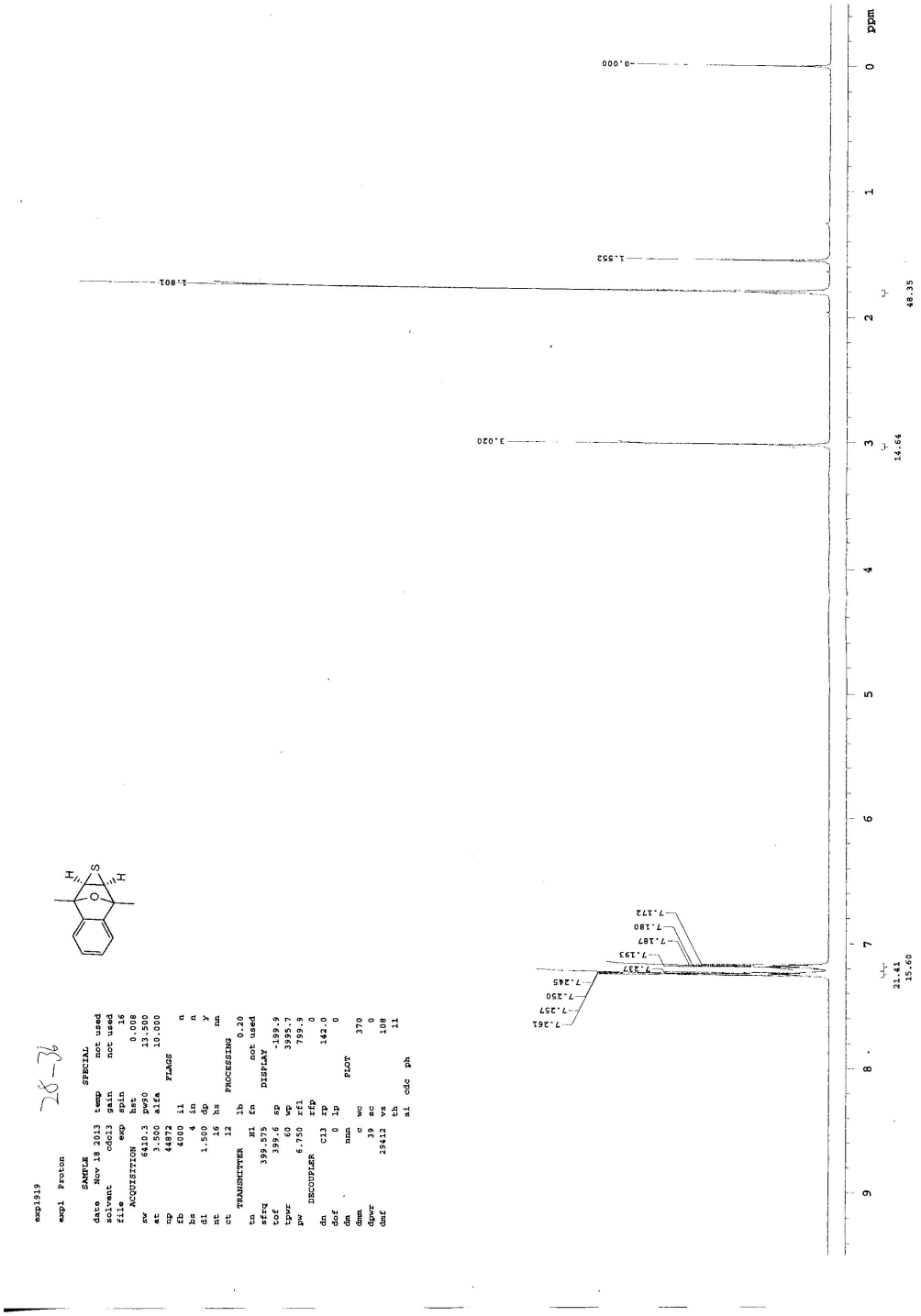
exo-5,6-Dimethyltetrahydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4b** (^{1}H-NMR)



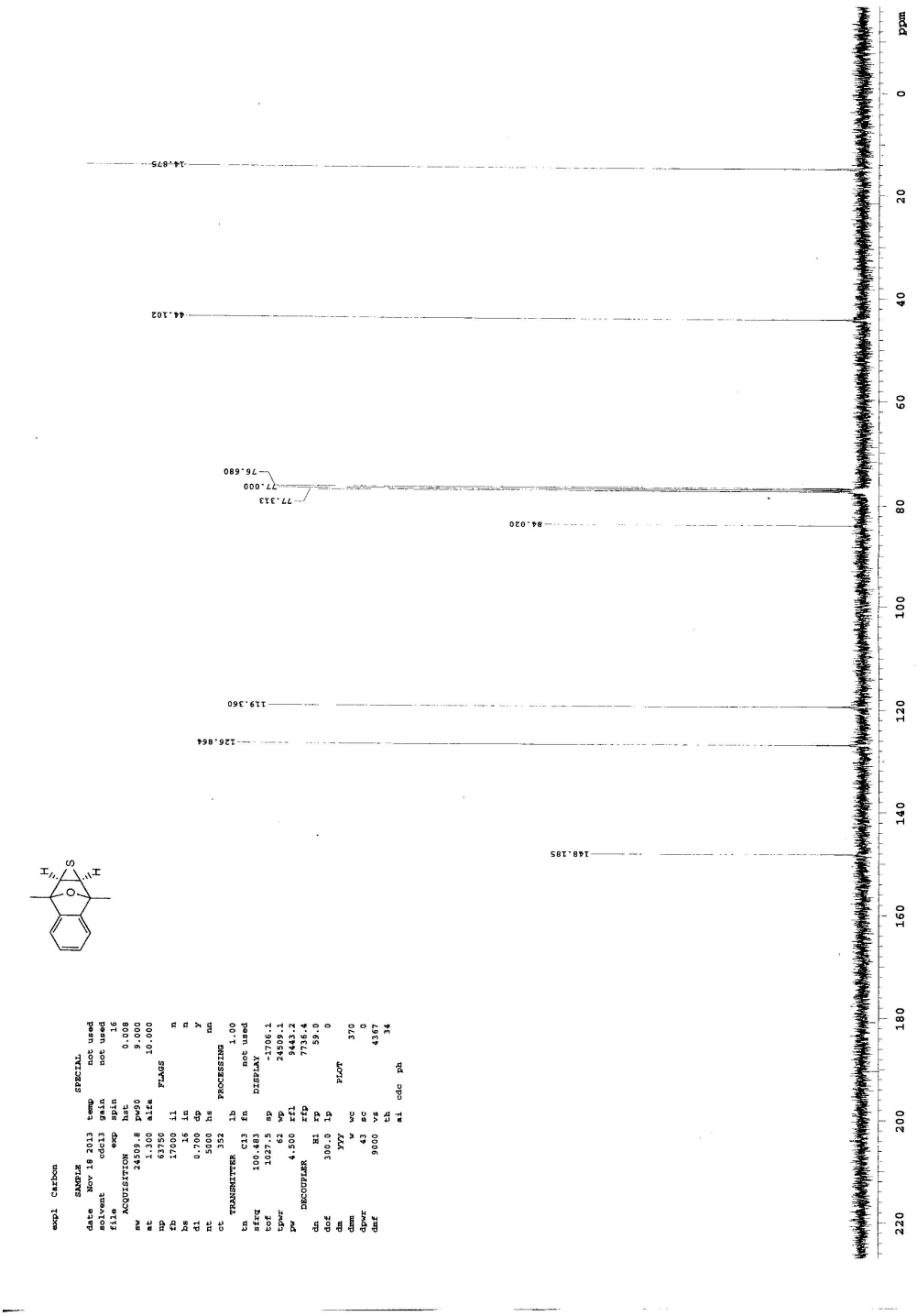
exo-5,6-Dimethyltetrahydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4b** (^{13}C-NMR)



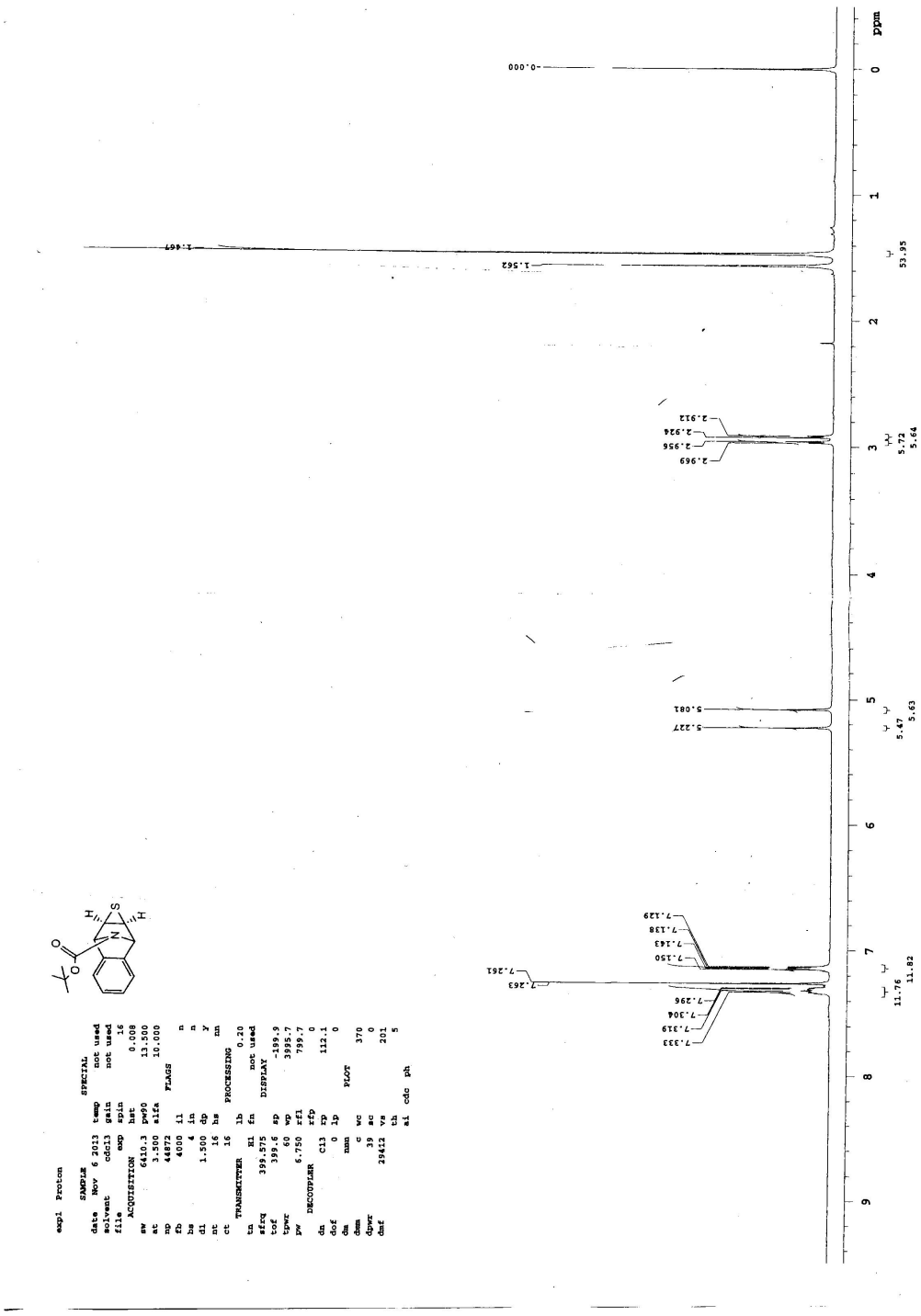
exo-2,7-Dimethyl-1,8-dihydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4c** (^{1}H-NMR)



exo-2,7-Dimethyl-1,8-dihydro-2,7-epoxynaphtho[2.3-*b*] thiirane **4c** (^{13}C-NMR)

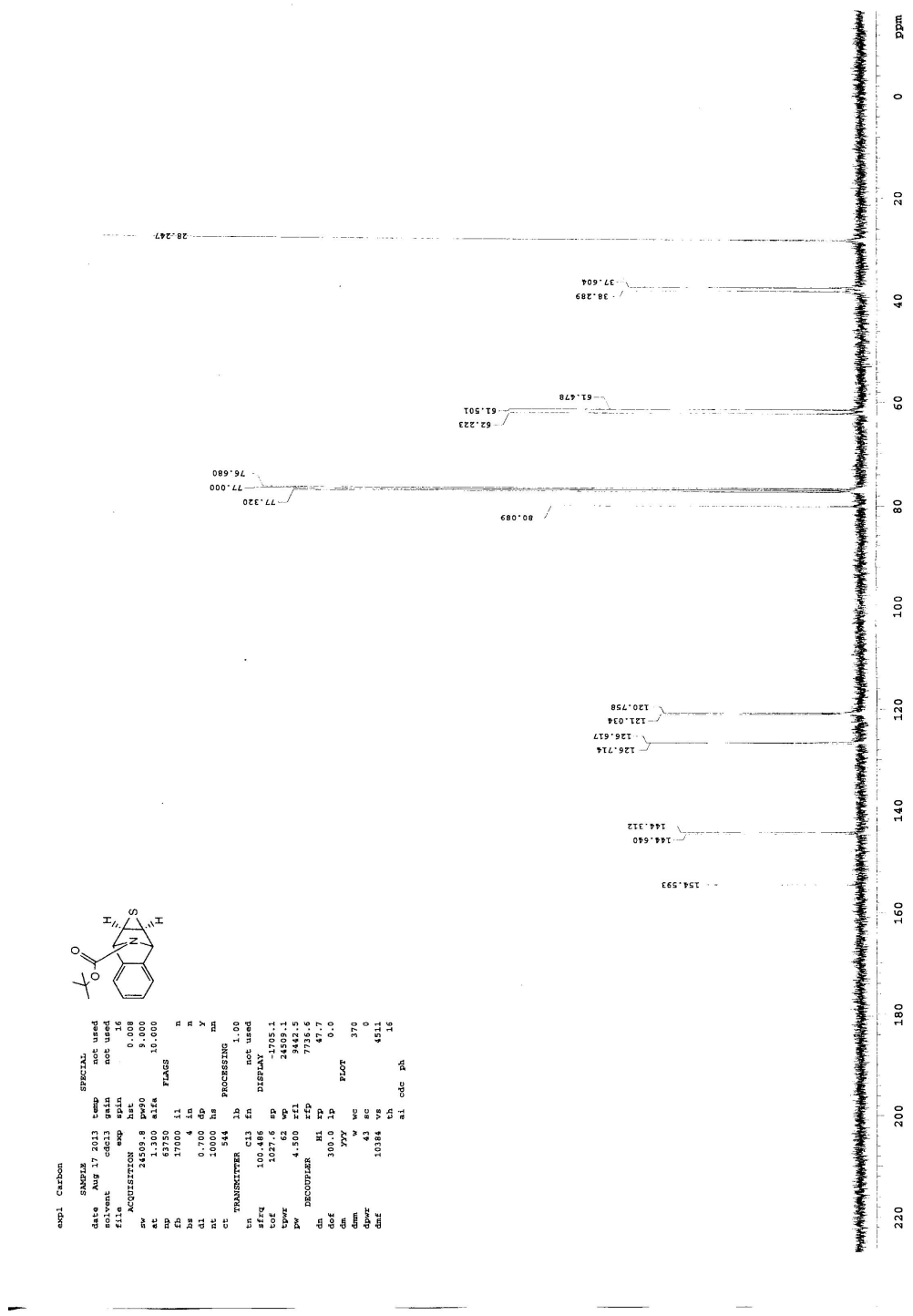


1,1-Dimethylethyl-1a,2,7,7a-tetrahydronaphtho[2.3-*b*] thiirane-2,7-imine-8-carboxylate **4d** (^{1}H-NMR)

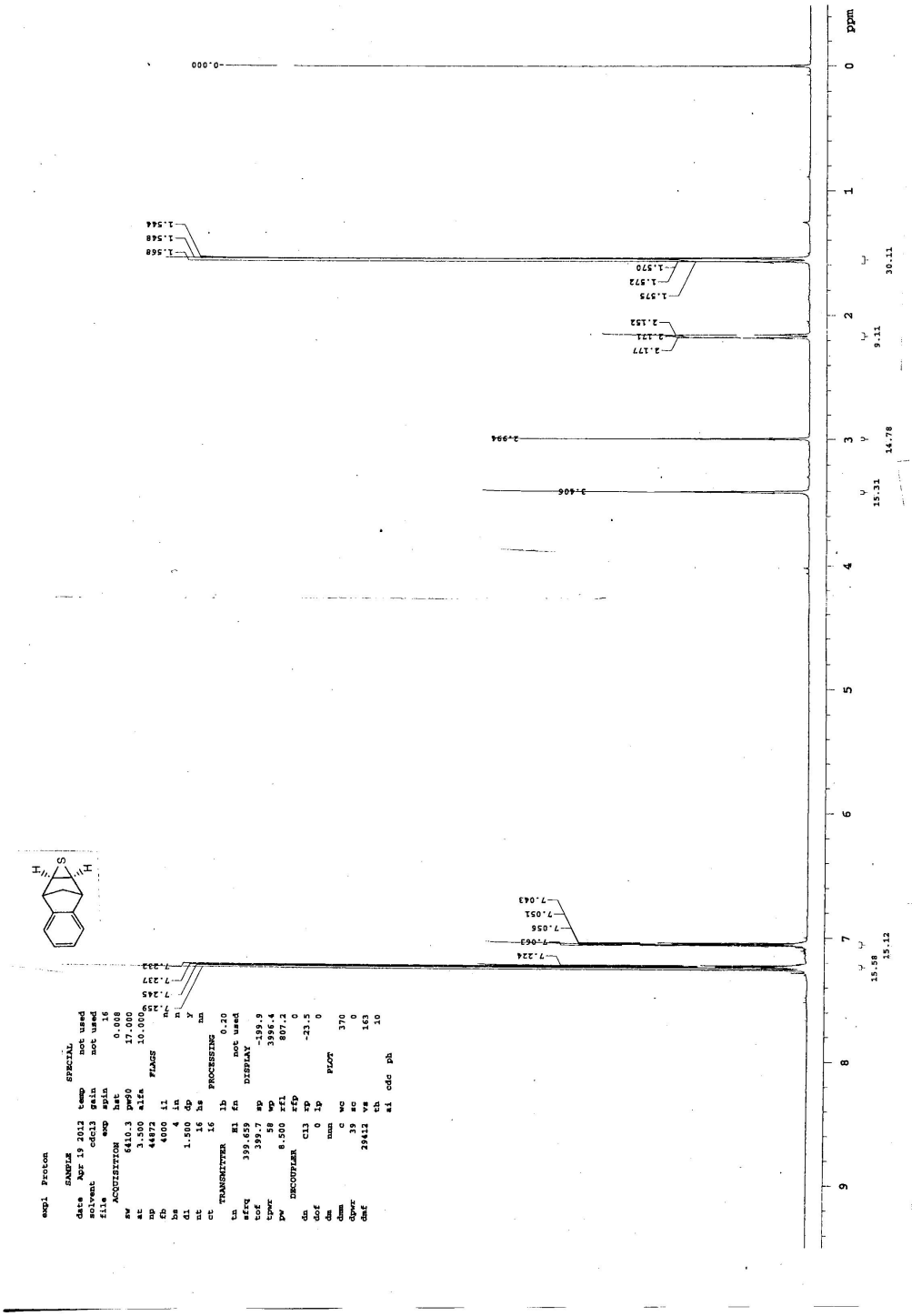


1,1-Dimethylethyl-1a,2,7,7a-tetrahydronaphtho[2.3-*b*] thiirane-2,7-imine-8-carboxylate **4d**

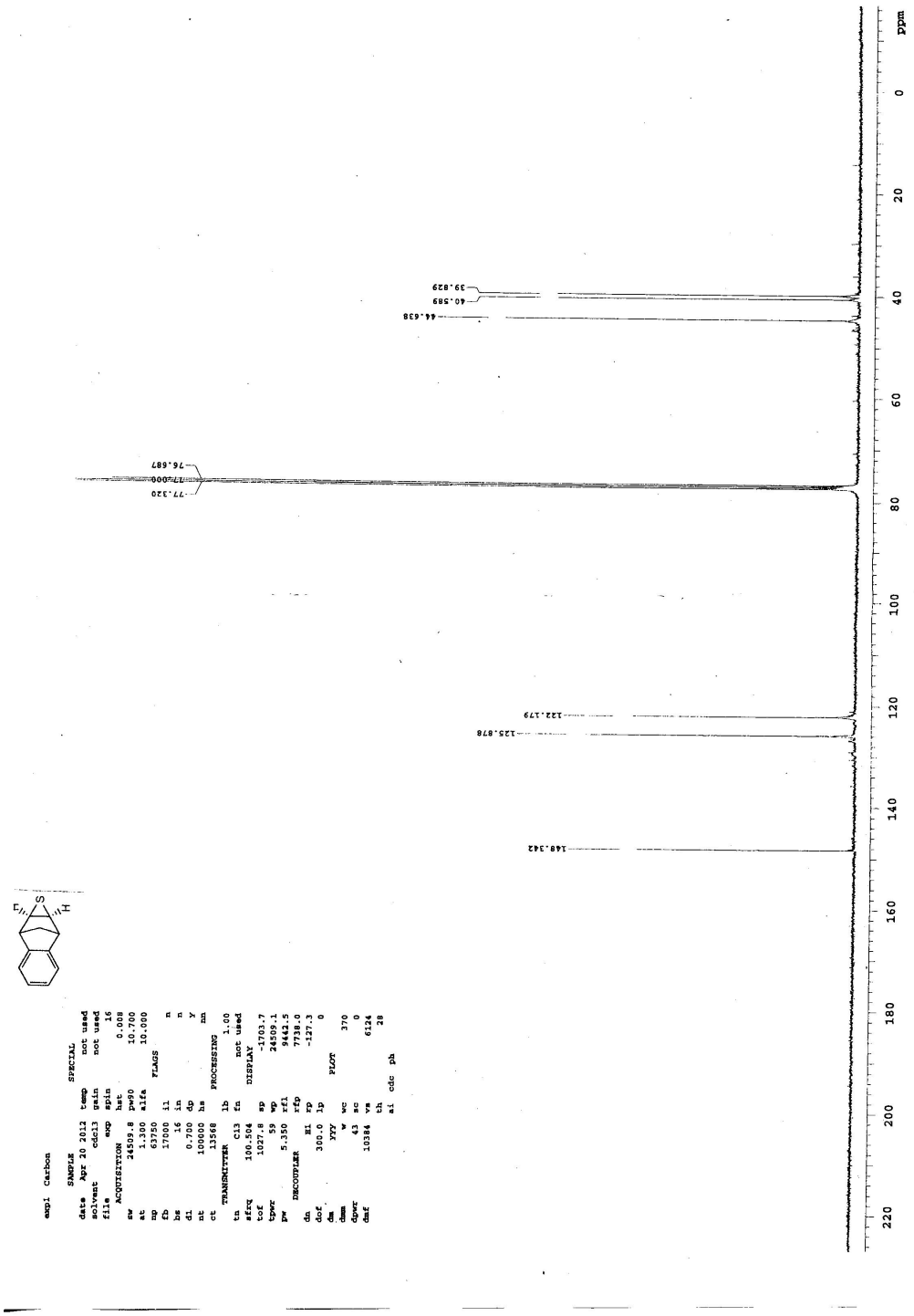
(^{13}C-NMR)



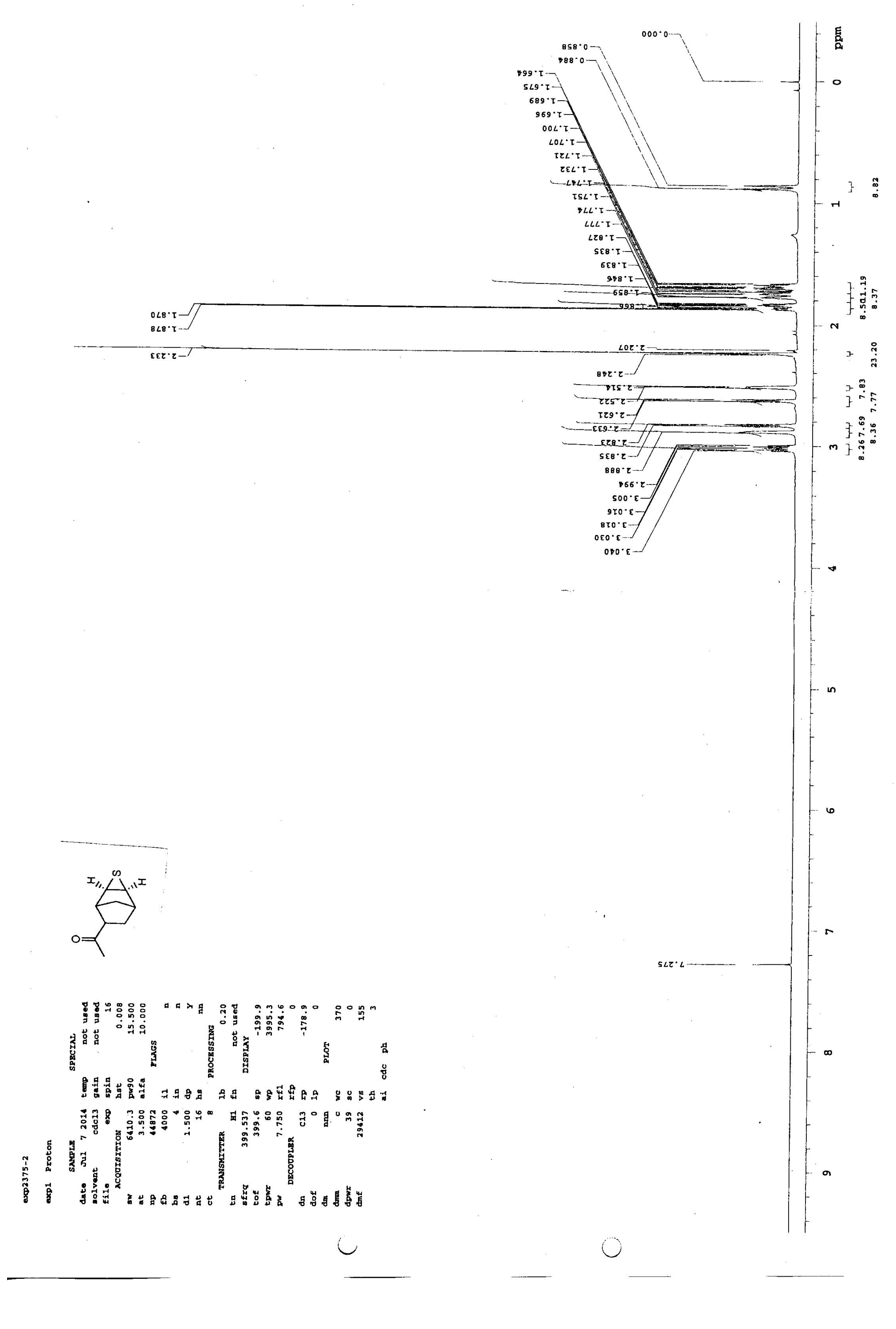
exo-2,7-Methanonaphtho[2.3-*b*] thiirane **4e** (^{1}H-NMR)



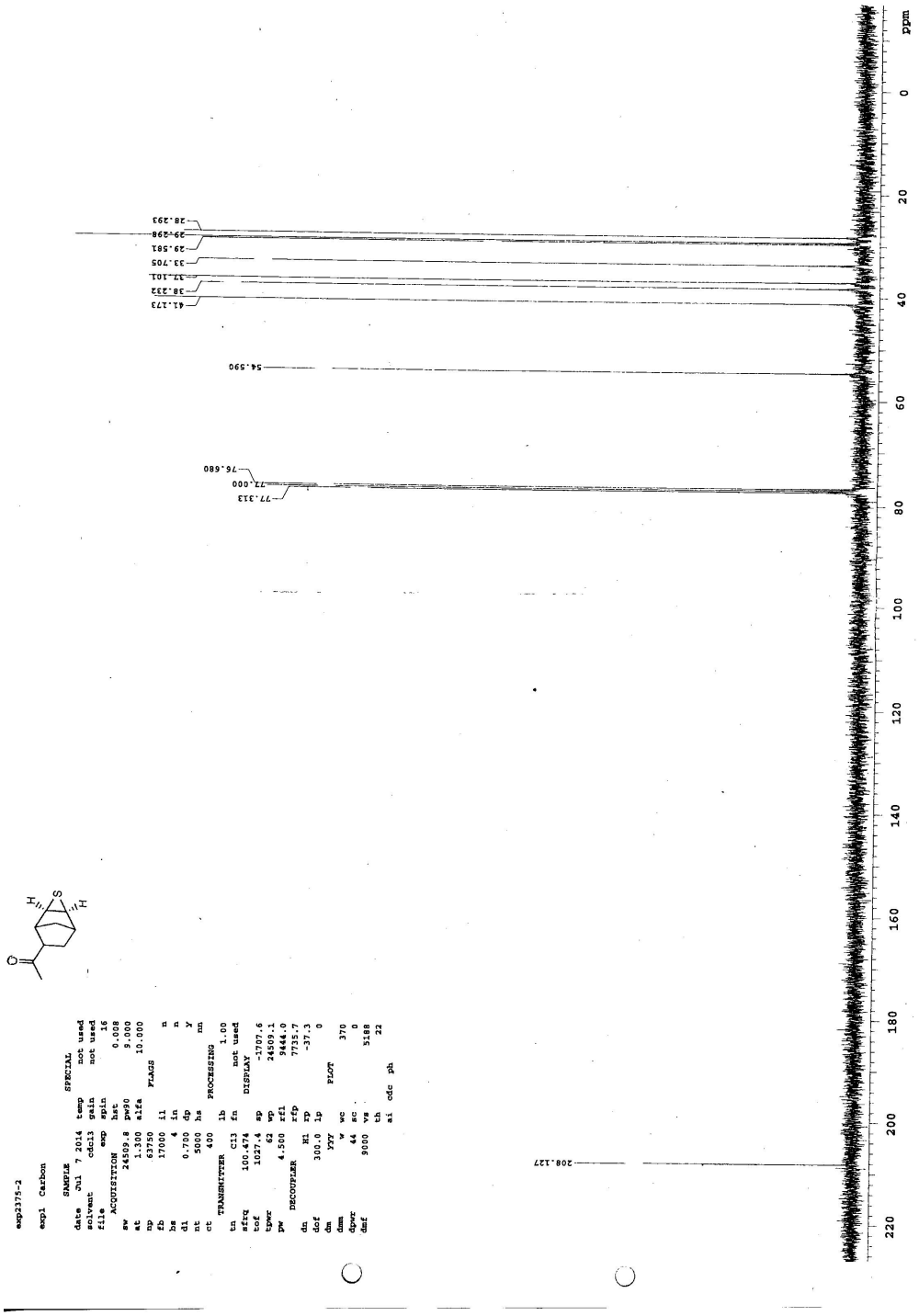
exo-2,7-Methanonaphtho[2.3-*b*] thiirane **4e** (^{13}C-NMR)



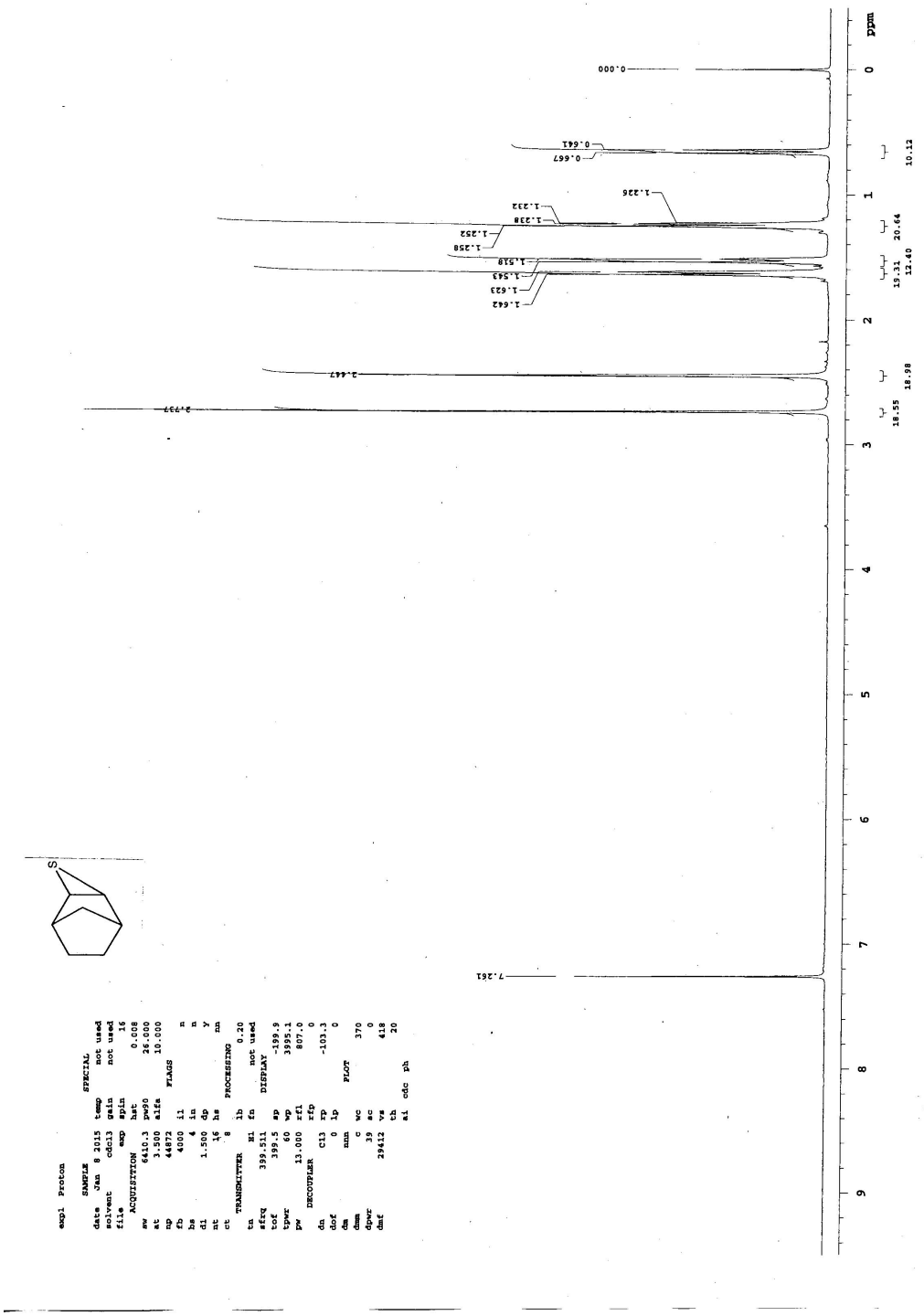
exo-1-(3-Thiatricyclo[3.2.1.0$^{2.4}$]oct-6-yl) ethanone **4f** (^{1}H-NMR)



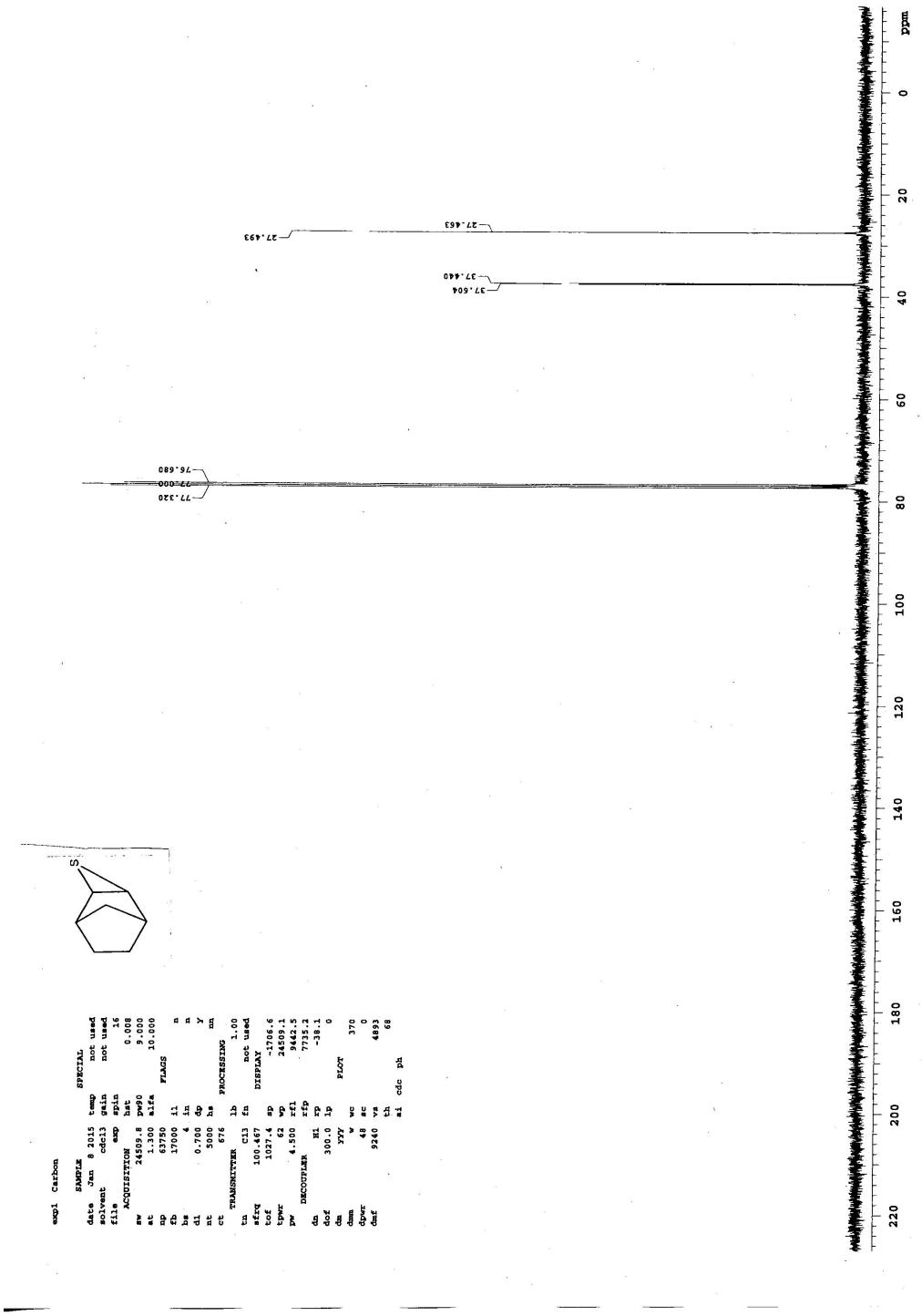
exo-1-(3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-yl) ethanone **4f** (^{13}C-NMR)



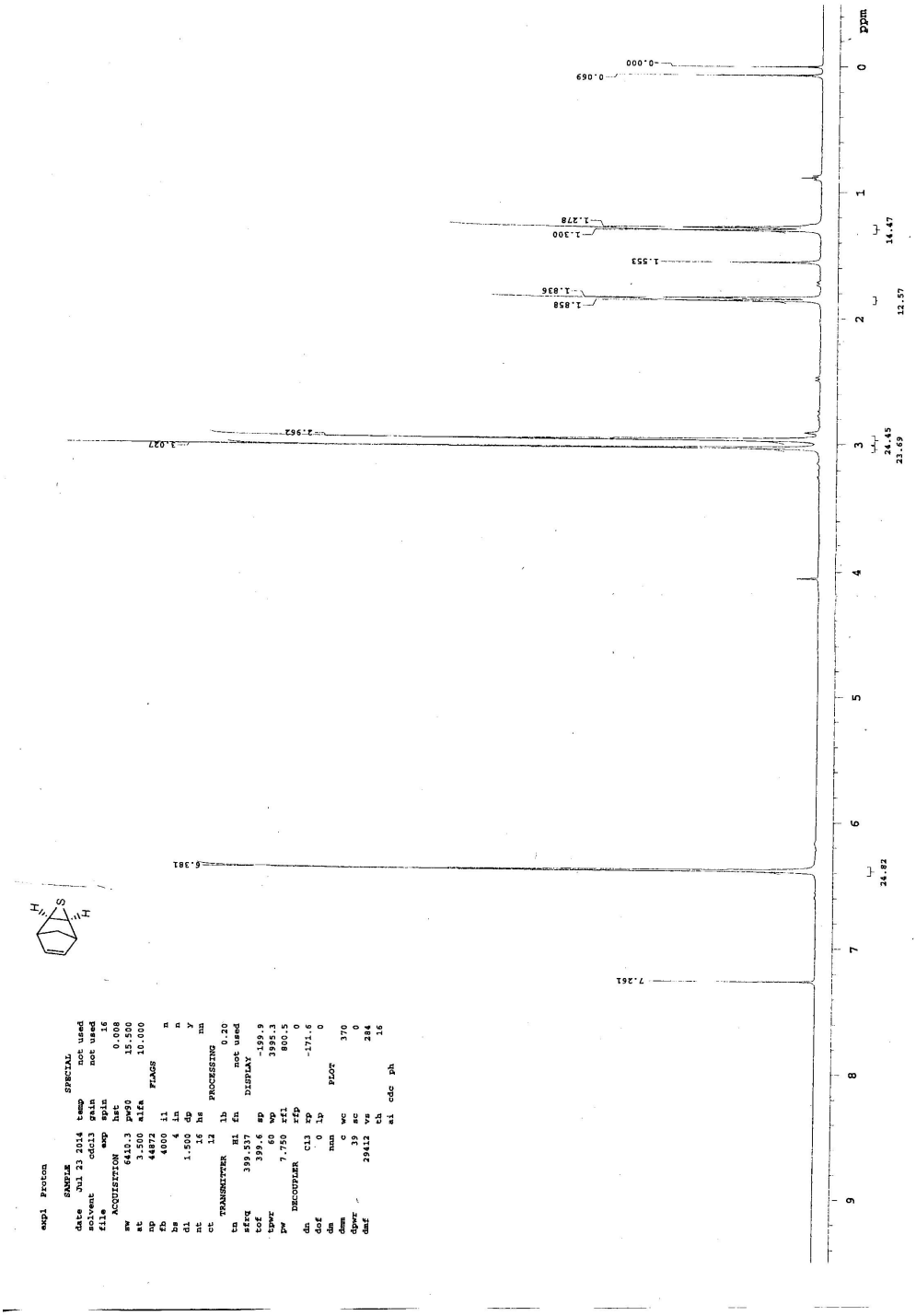
exo-3-Thiatricyclo[3.2.1.0$^{2.4}$]octane **4g** (^{1}H-NMR)



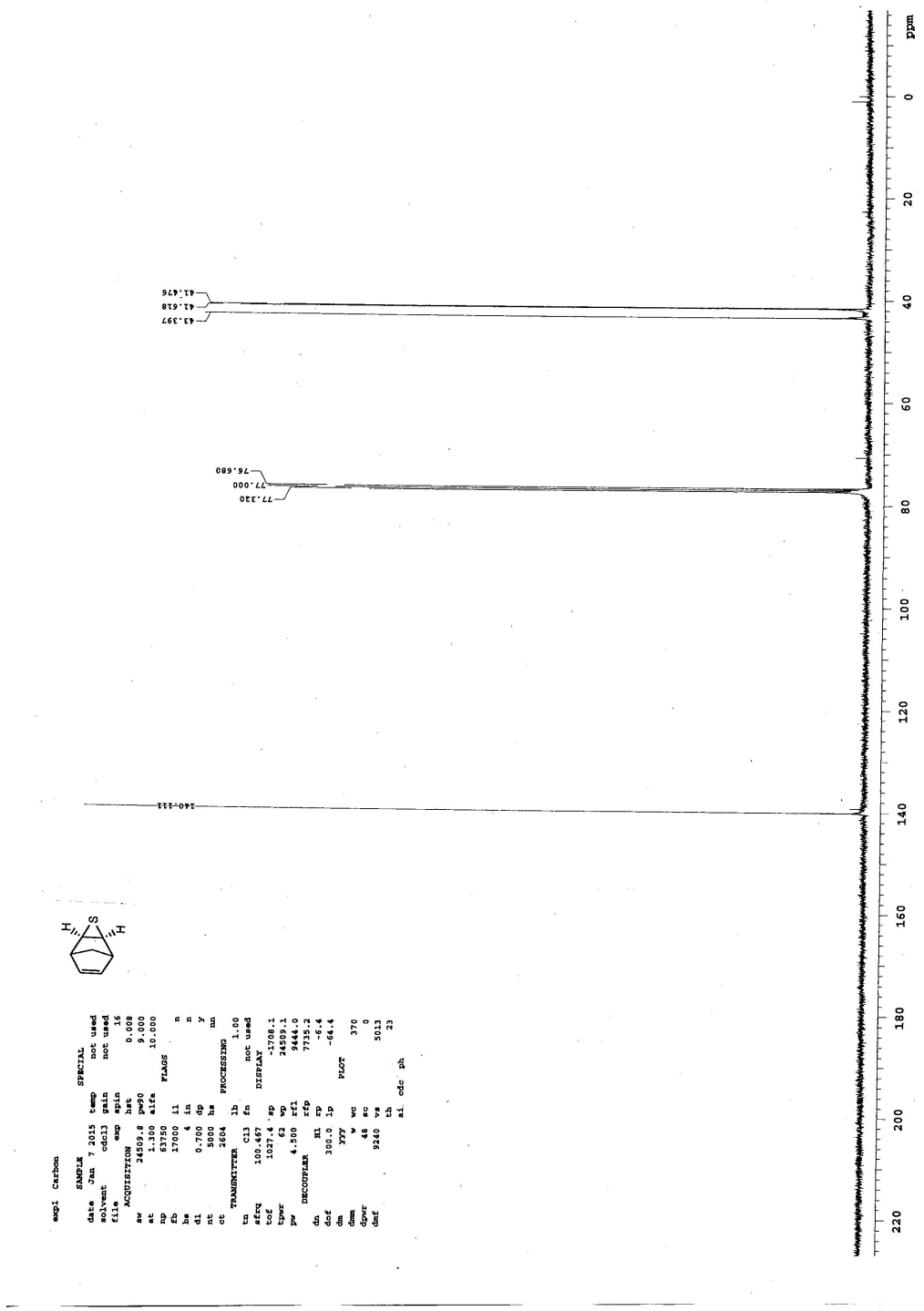
exo-3-Thiatricyclo[3.2.1.0$^{2.4}$]octane **4g** (^{13}C-NMR)



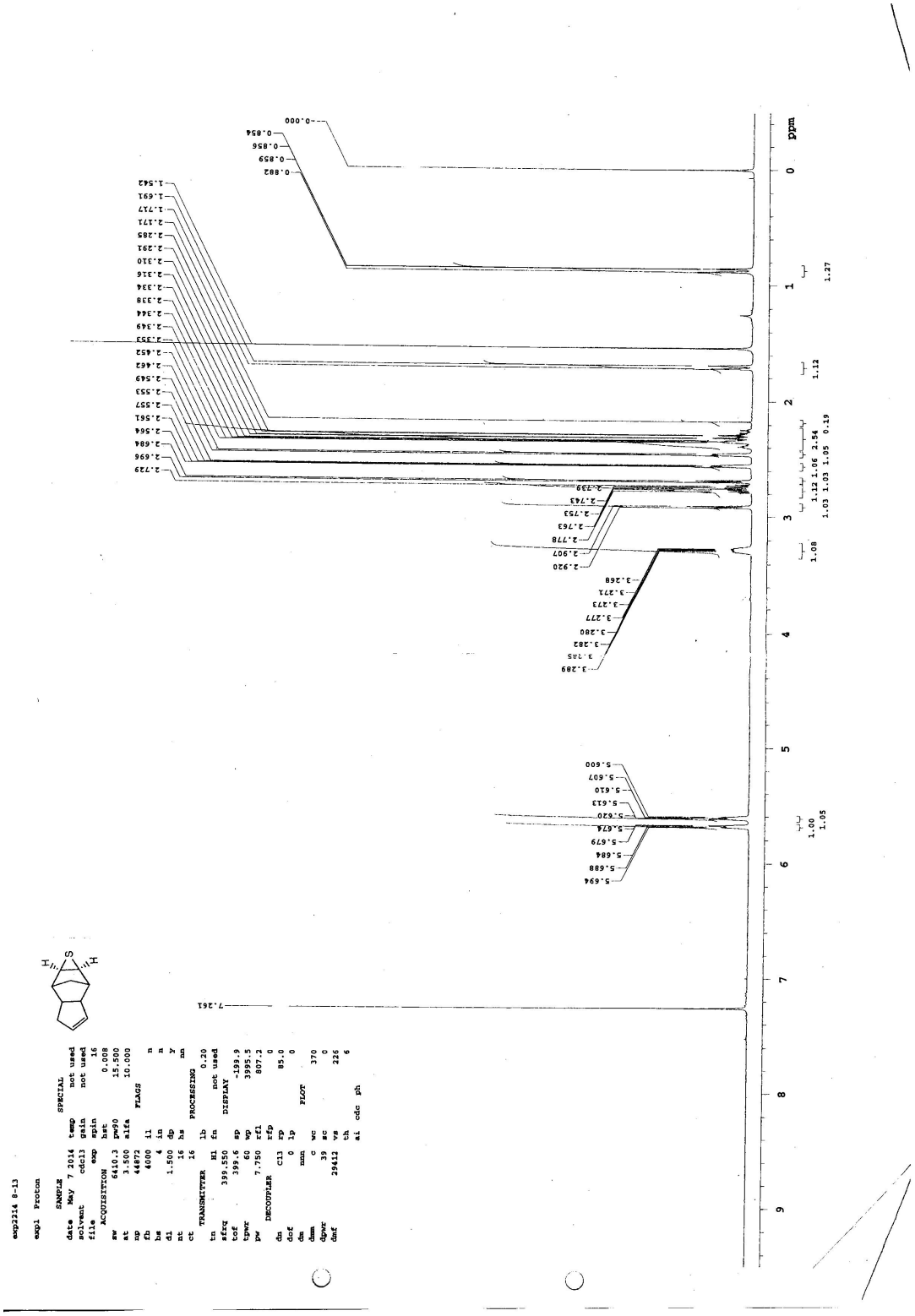
exo-3-Thiatricyclo[3.2.1.0$^{2.4}$]oct-6-ene **4h** (^{1}H-NMR)



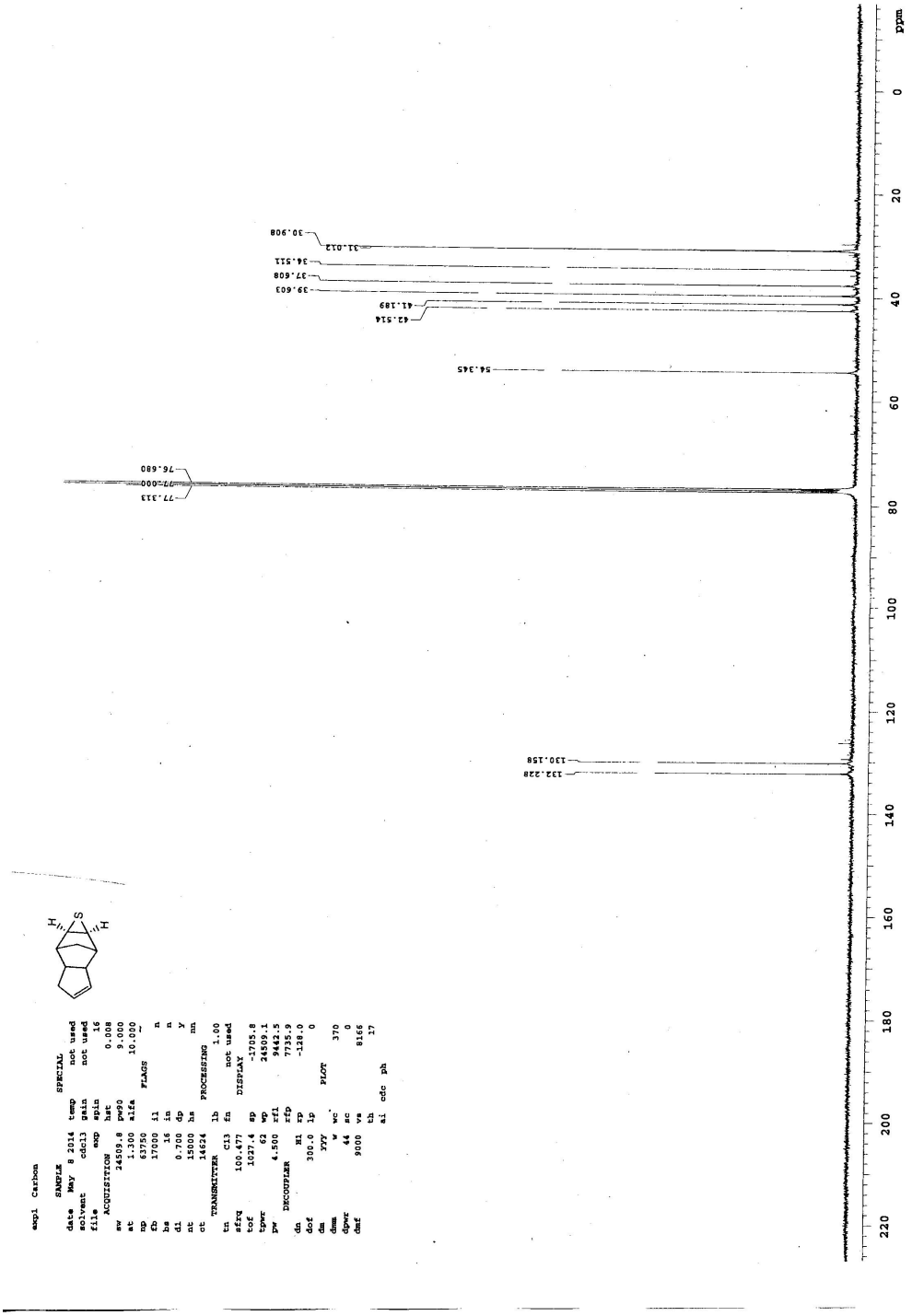
exo-3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-ene **4h** (^{13}C-NMR)



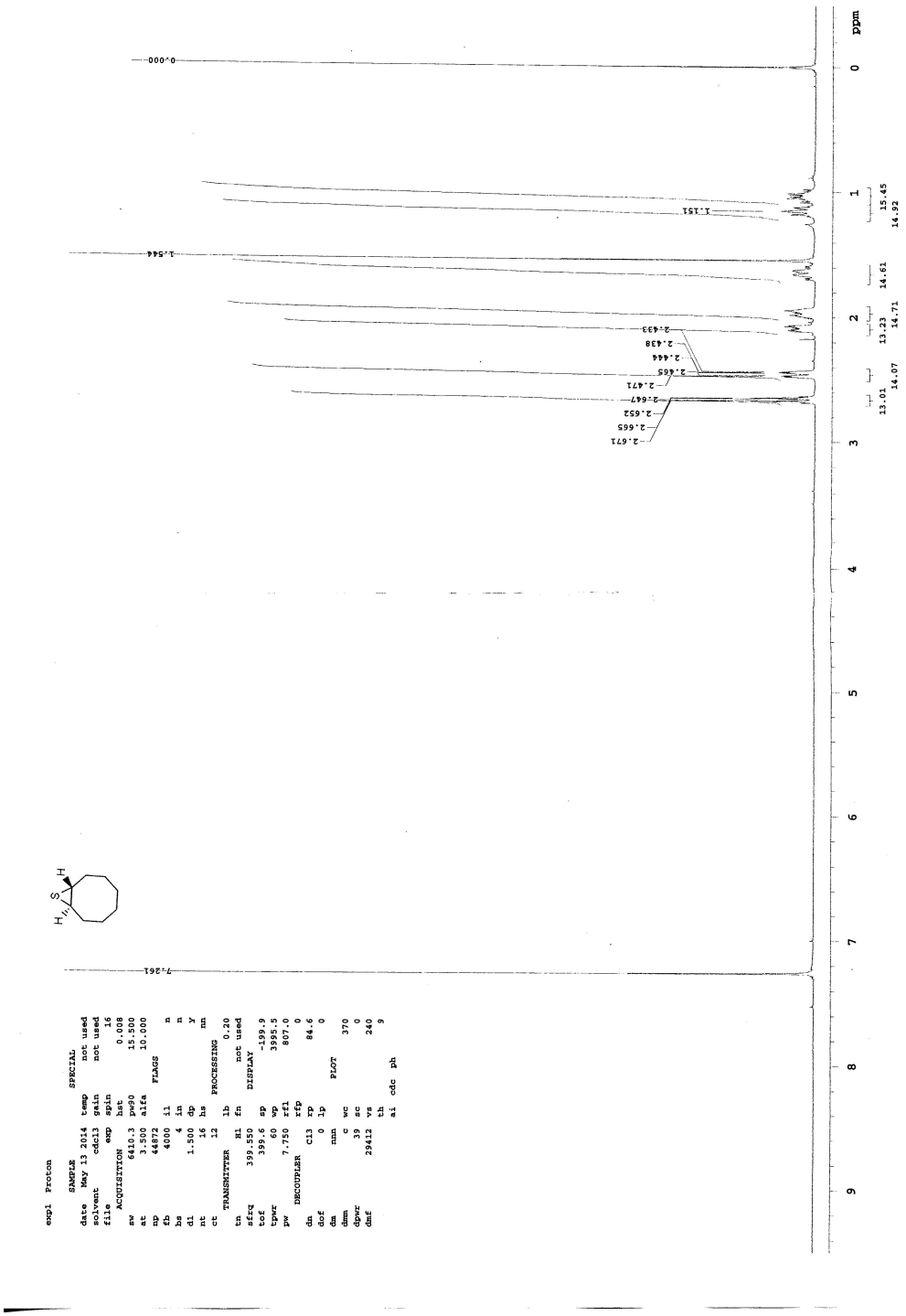
exo-1a,2a,3,5a,6,6a-Hexahydro-2,6-methano-2*H*-indeno[5.6-*b*]thiirane **4i** (^{1}H-NMR)



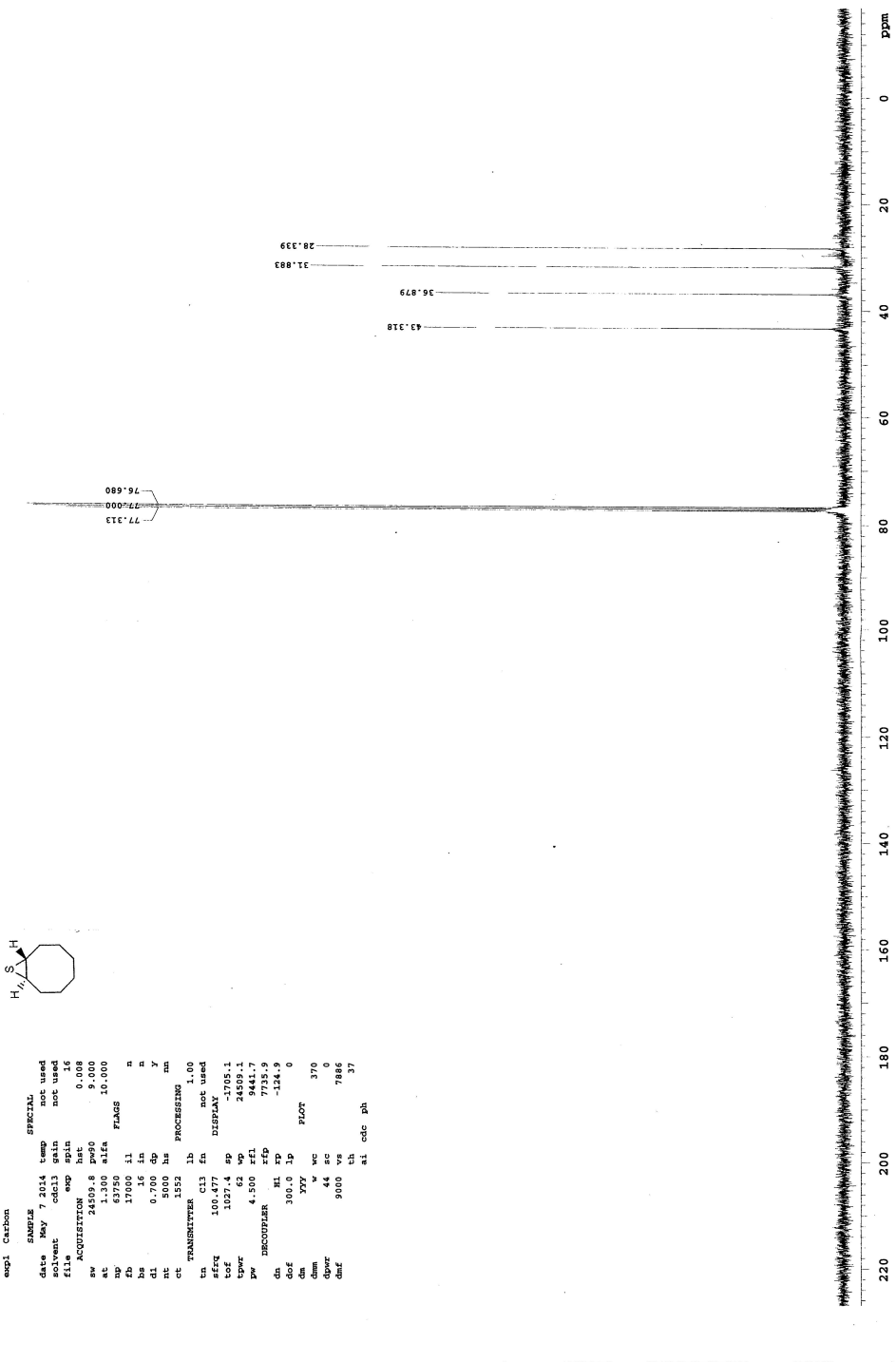
exo-1a,2a,3,5a,6,6a-Hexahydro-2,6-methano-2*H*-indeno[5.6-*b*]thiirane **4i** (^{13}C-NMR)



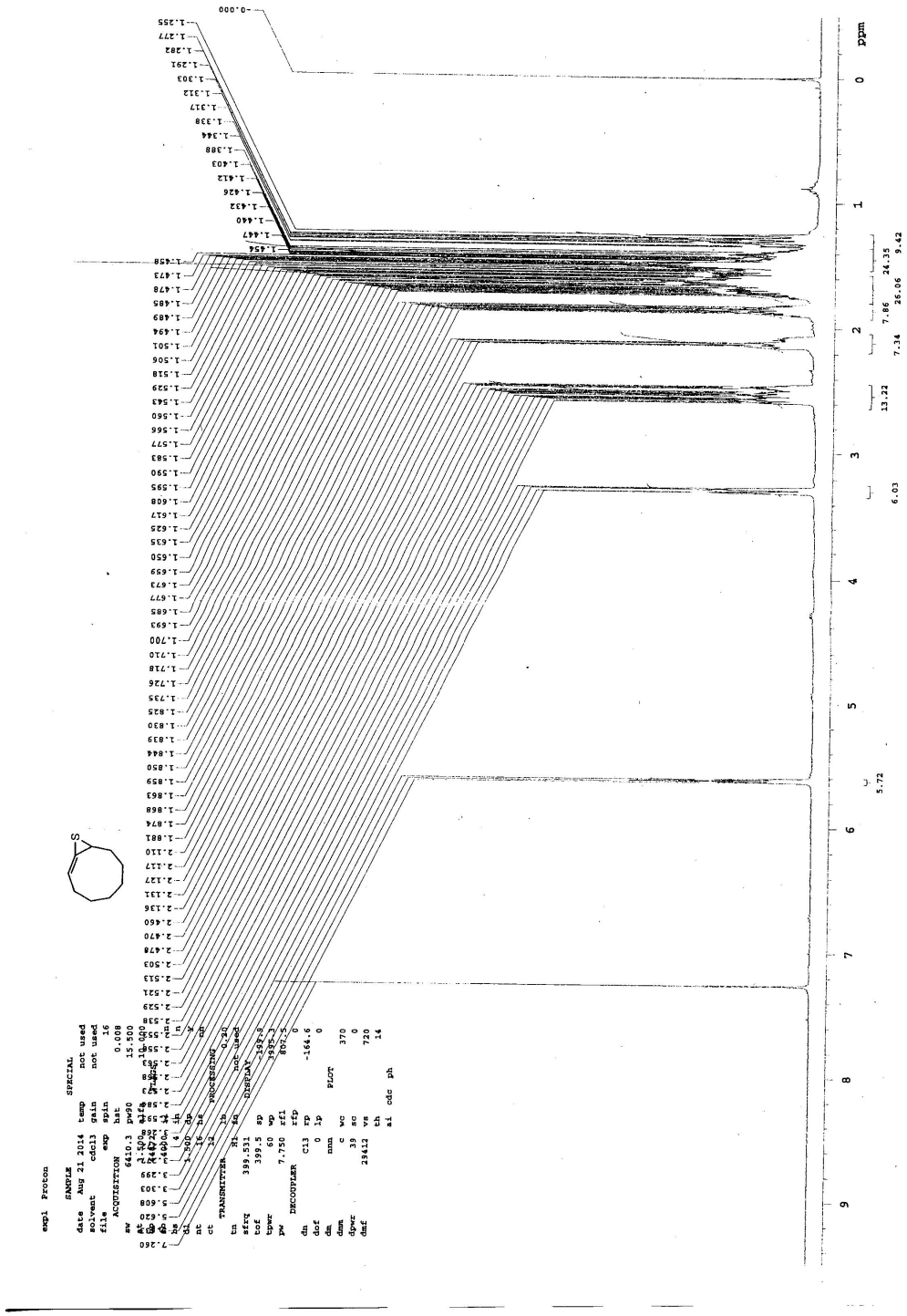
trans-10-Thiabicyclo[7.1.0]nonane **6** (^{1}H-NMR)



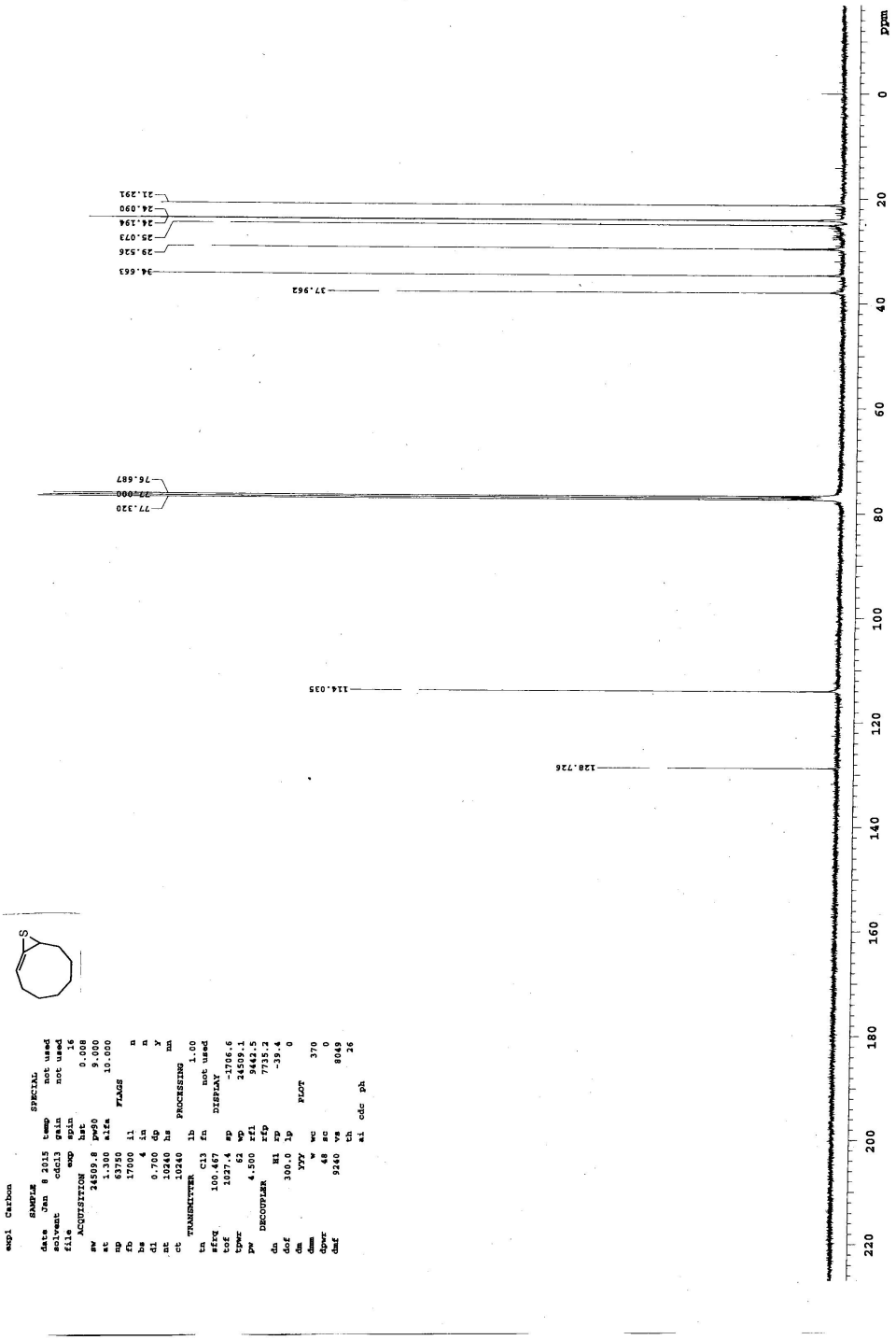
trans-10-Thiabicyclo[7.1.0]nonane **6** (^{13}C-NMR)



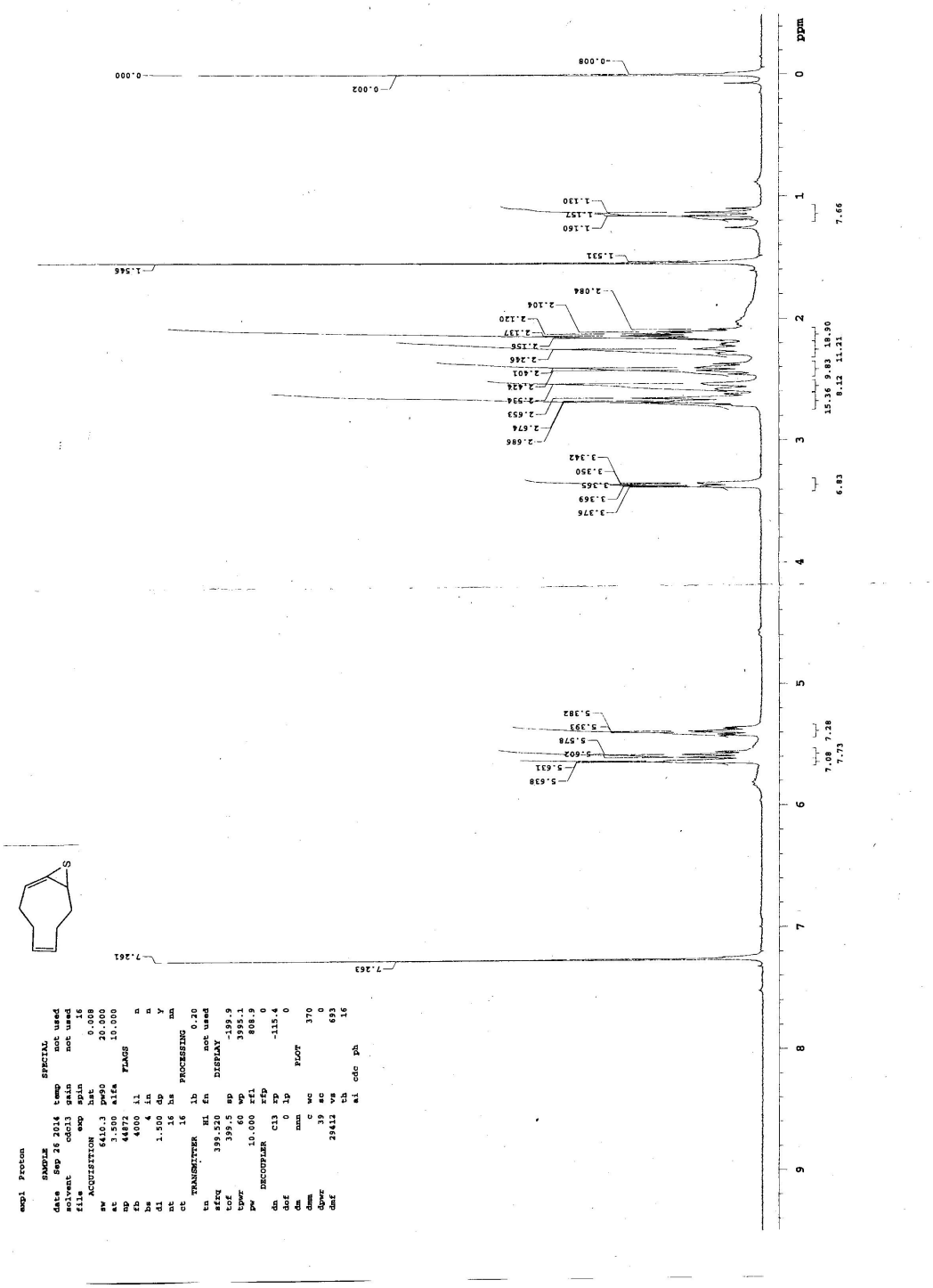
10-Thiabicyclo[7.1.0]dec-1-ene **8** (^{1}H-NMR)



10-Thiabicyclo[7.1.0]dec-1-ene **8** (^{13}C-NMR)



10-Thiabicyclo[7.1.0]dec-1,5-diene **10** (^{1}H-NMR)



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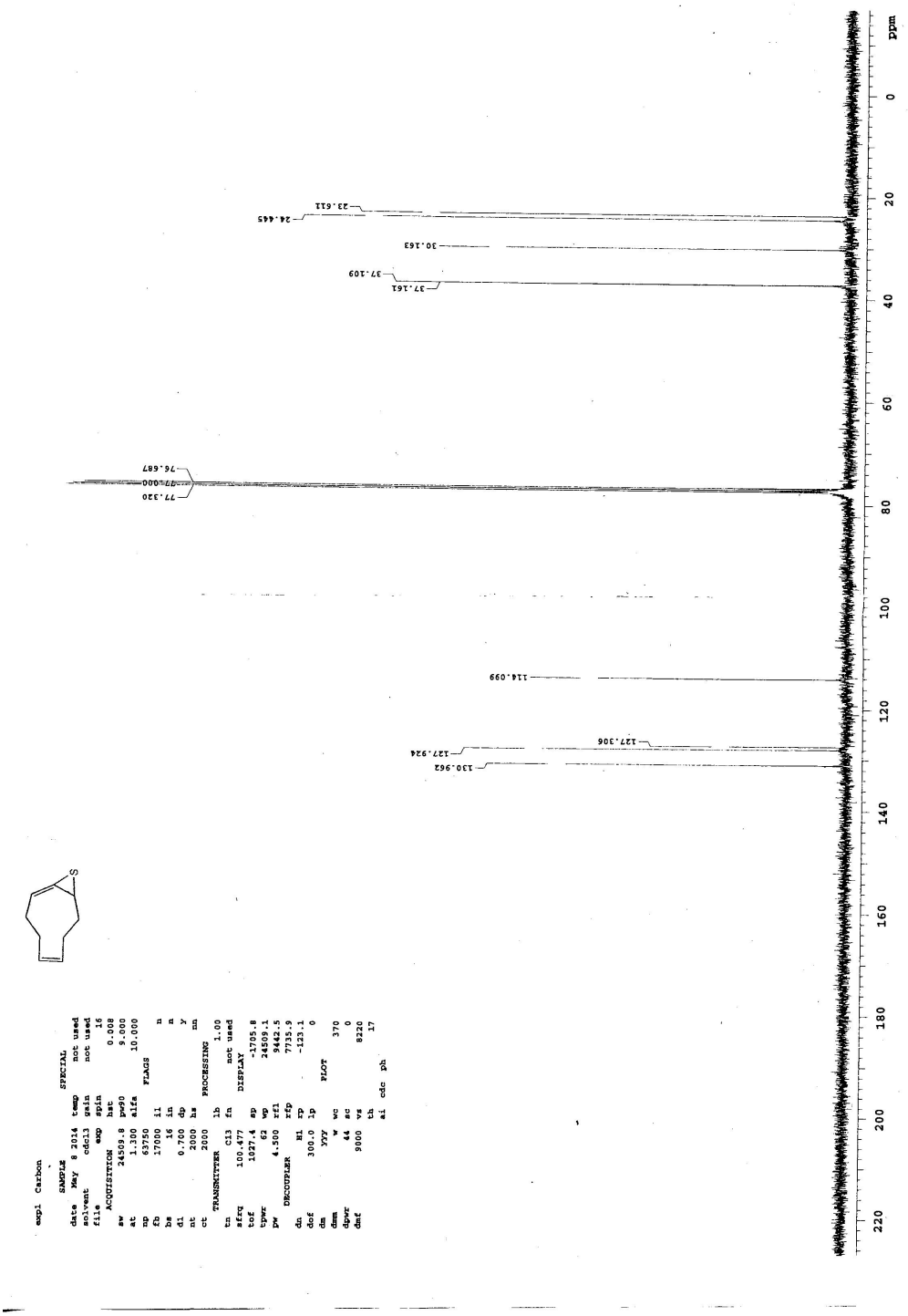
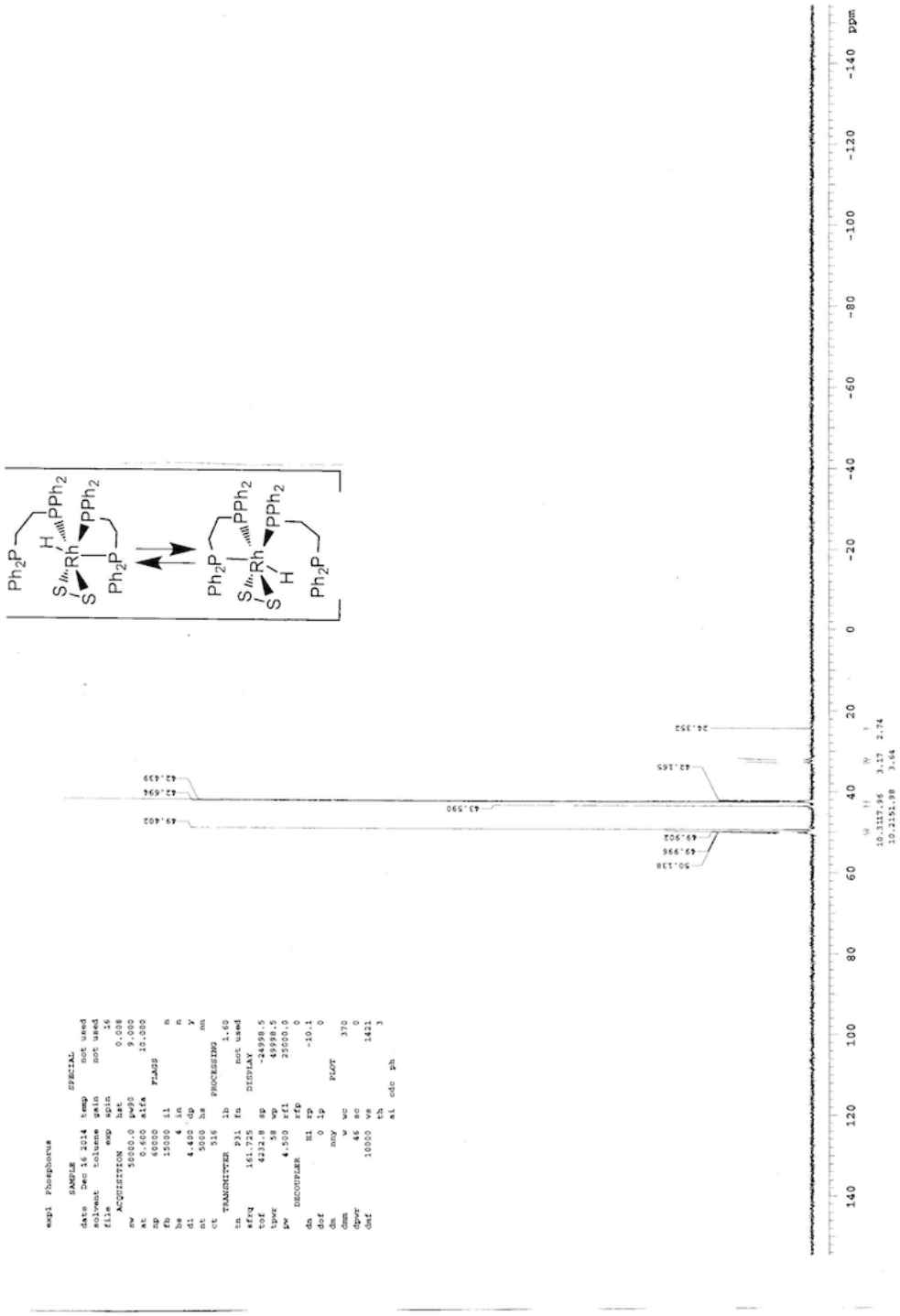
ct 16 PROCESSING
TRANSMITTER lb 0.20
tn H1 fn not used
sfrq 399.520 sp DISPLAY
tof 399.5 wp -199.9
tpwr 60 wp 3995.1
pw 10.000 rf1 808.3
DECOUPLER rfp 0
dn C13 rp -115.4
dof 0 lp 0
dm nnn PLOT
dmm c wc 370
dpwr 39 sc 0
dmf 29412 vs 693
th 16
ai cdc ph

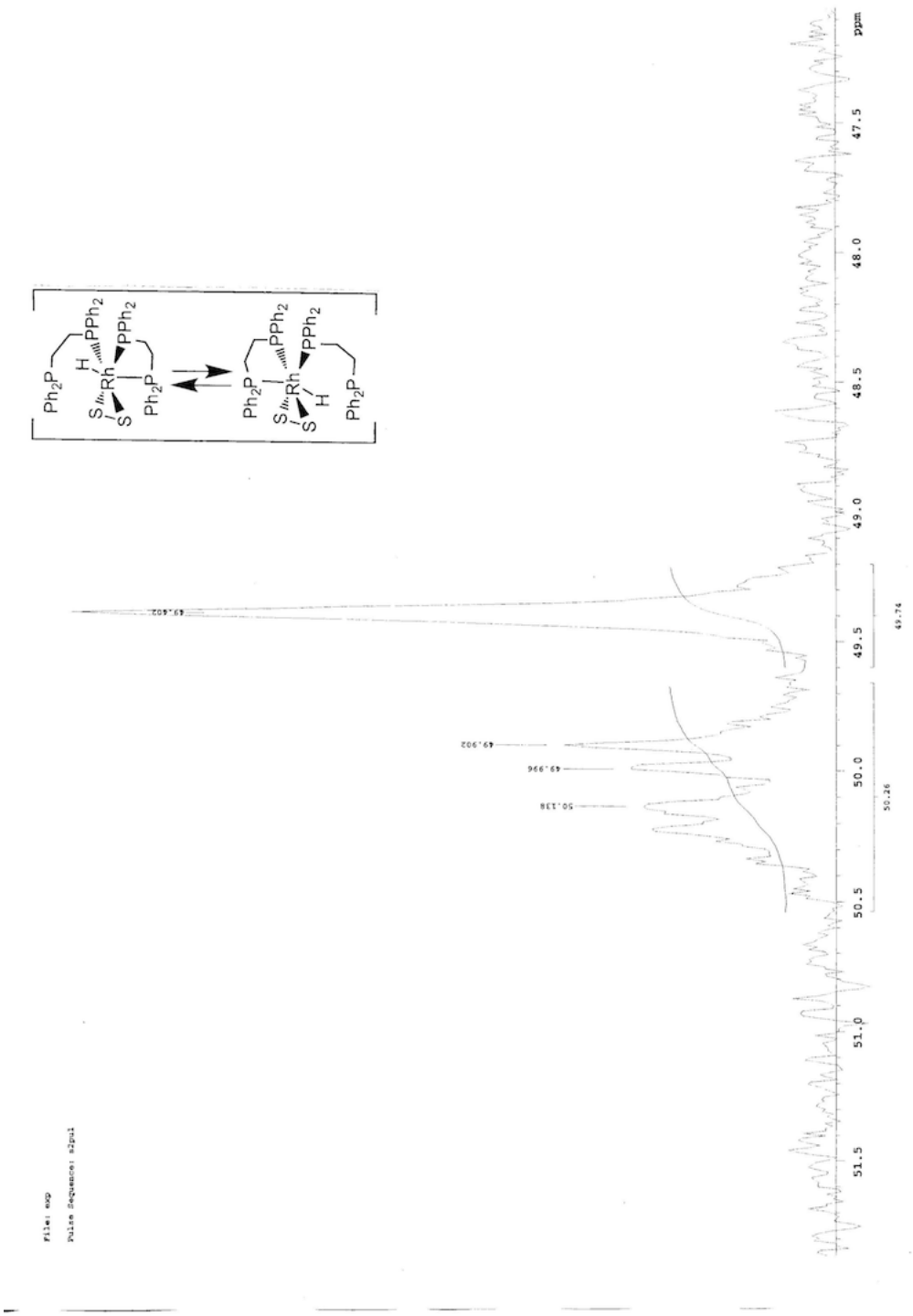
10-Thiabicyclo[7.1.0]dec-1,5-diene **10** (^{13}C-NMR)



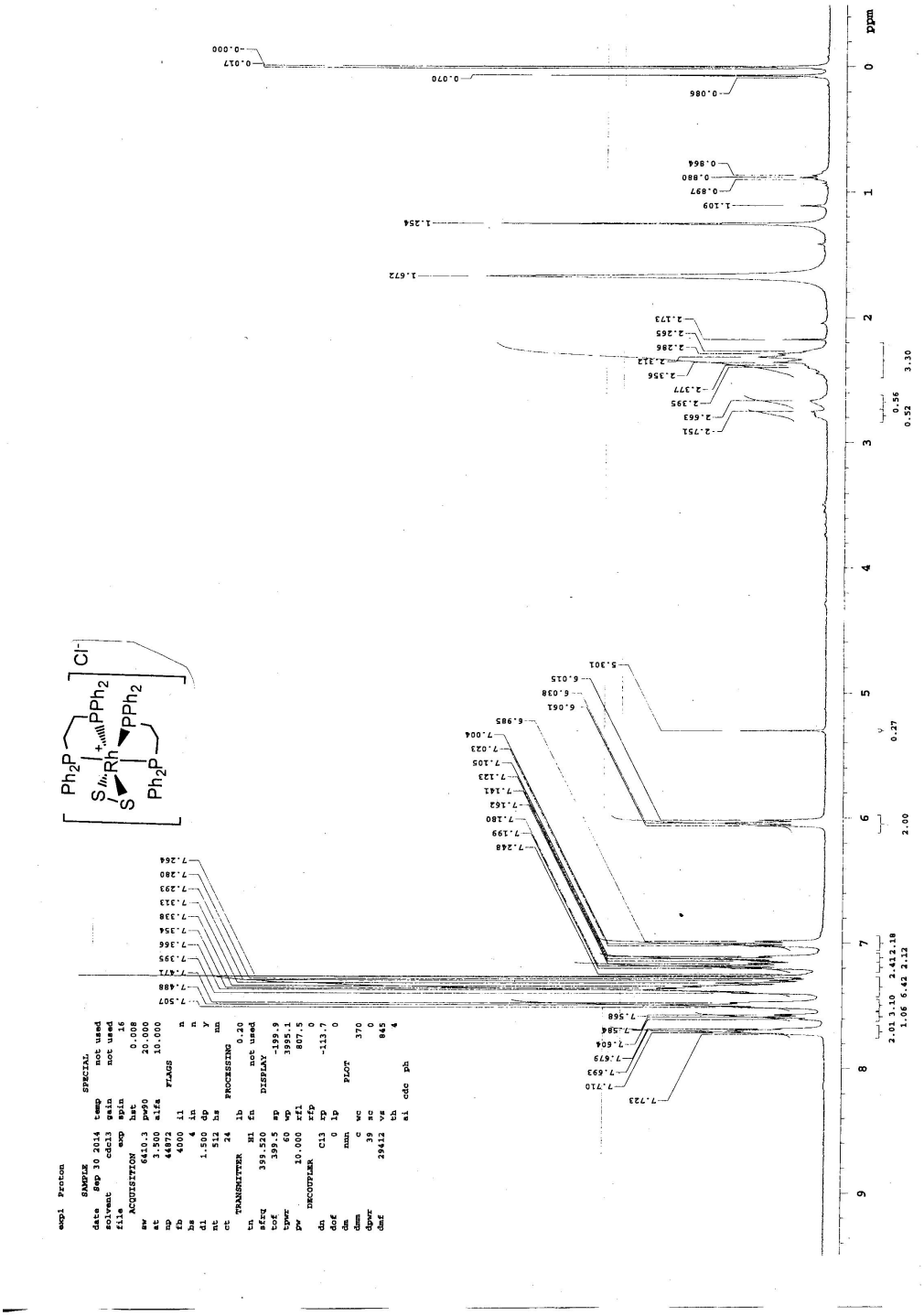
Rhodium intermediate **11** (^{31}P-NMR, $CD_3C_6D_5$)



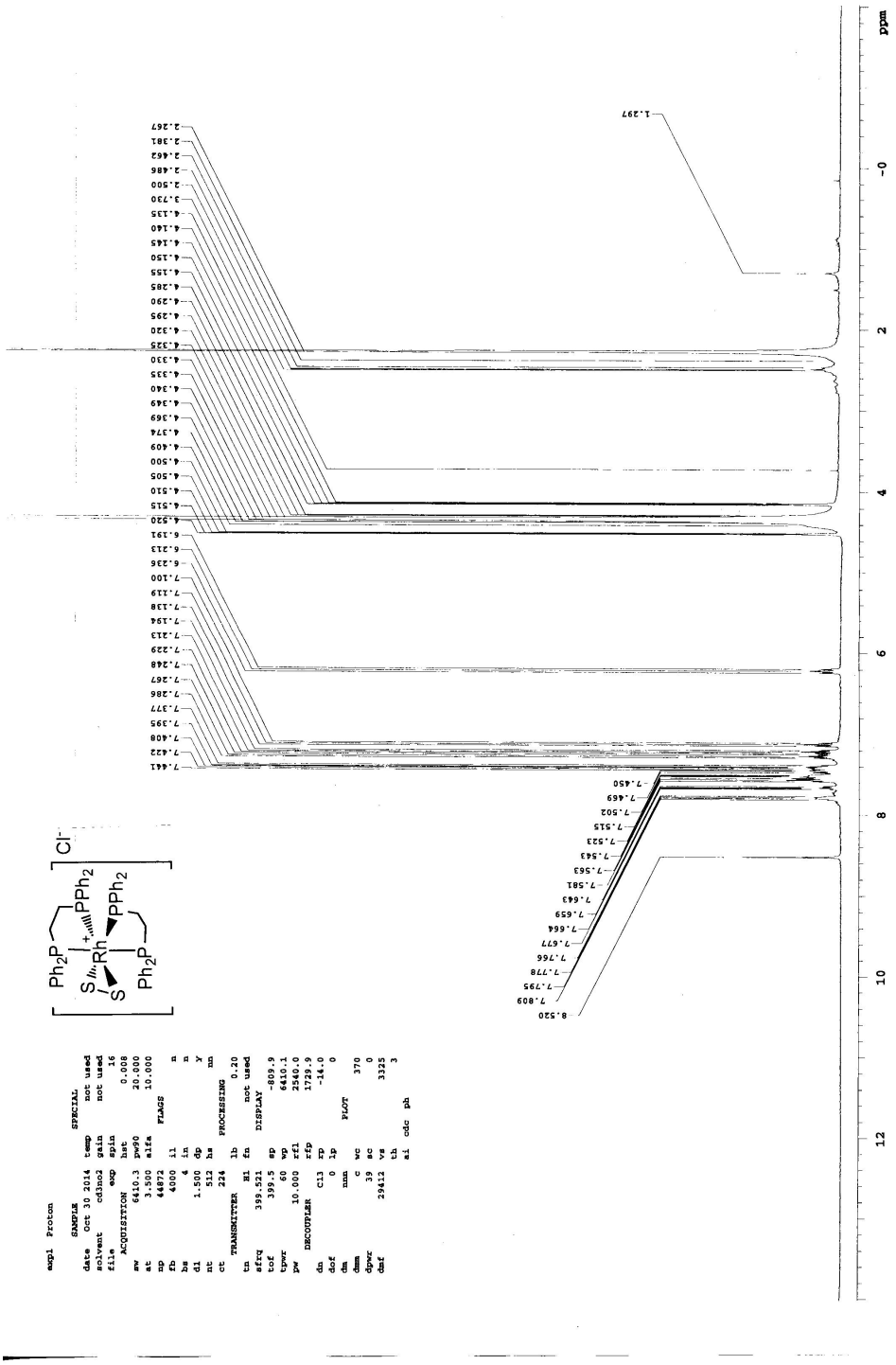
Rhodium intermediate **11** (^{31}P-NMR, $CD_3C_6D_5$)



[$RhS_2(dppe)_2$]Cl complex **12** (^{1}H-NMR, $CDCl_3$)



[$RhS_2(dppe)_2$]Cl complex **12** (^{1}H-NMR, CD_3NO_2)

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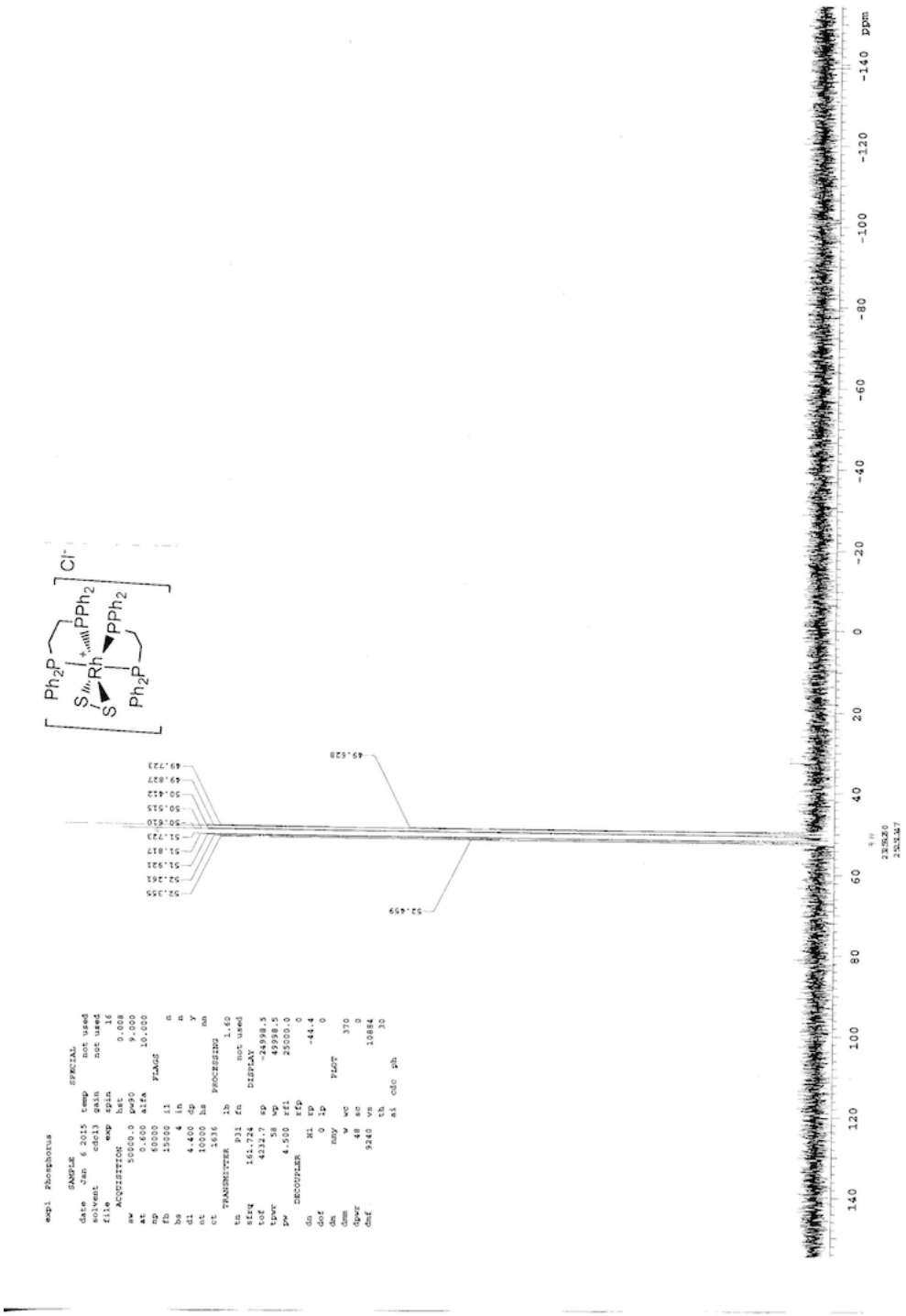
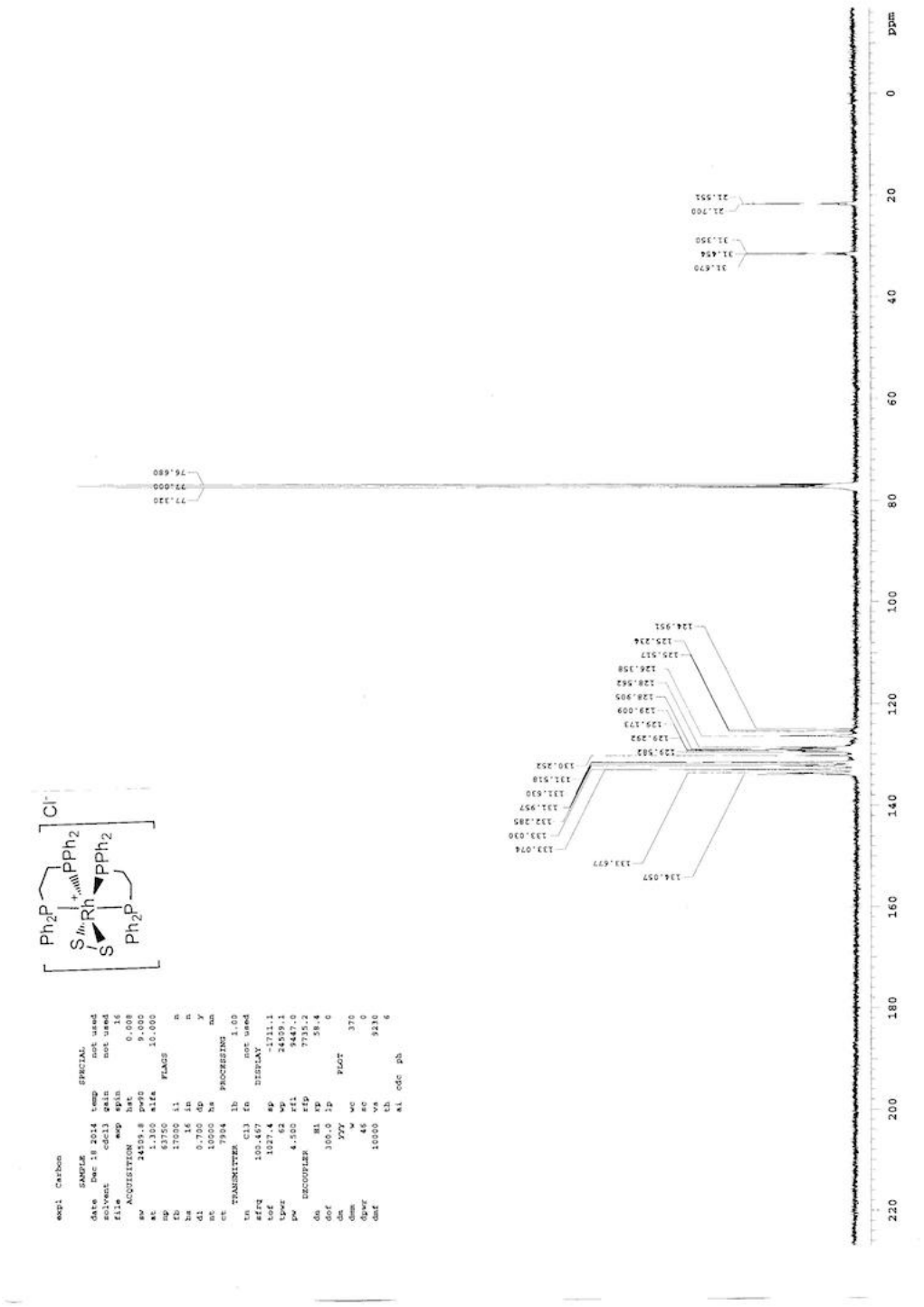
expl  Proton
      SAMPLE                  SPECIAL
date  Oct 30 2014   temp      not used
solvent  cd3no2     gain      not used
file                spin        16
  ACQUISITION       hst        0.008
sw        6410.3    pw90      20.000
at           3.500  alfa      10.000
np         44872          FLAGS
fb            4000  ii             n
bs               4  in             n
d1           1.500  dp             y
nt             512  hs            nn
ct             224          PROCESSING
tn     PRANSMITTER  lb           0.20
sfrq       399.521  fn       not used
tof        399.5    wp        -809.9
tpwr                sp        6410.1
pw           10.000  rf1       2540.0
     DECOUPLER      rfp       1729.9
dn                   rp        -14.0
dof                  lp            0
dm                 nm          PLOT
dmm                  c  wc        370
dpwr                39  sc          0
dmf            29412  vs       3325
                      th          3
                         al  cdc  ph
```

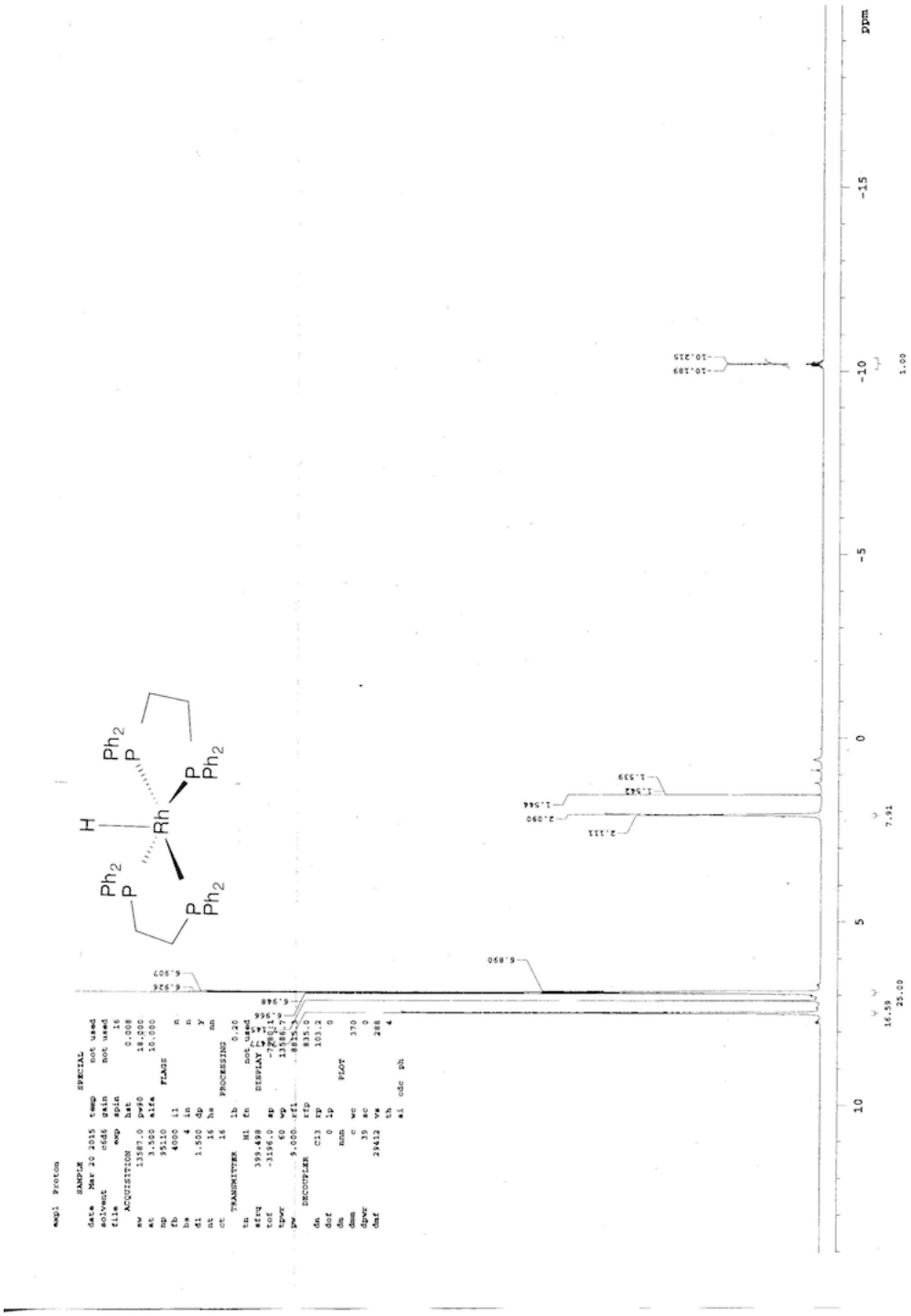
[$RhS_2(dppe)_2$]Cl complex **12** (^{31}P-NMR, $CDCl_3$)



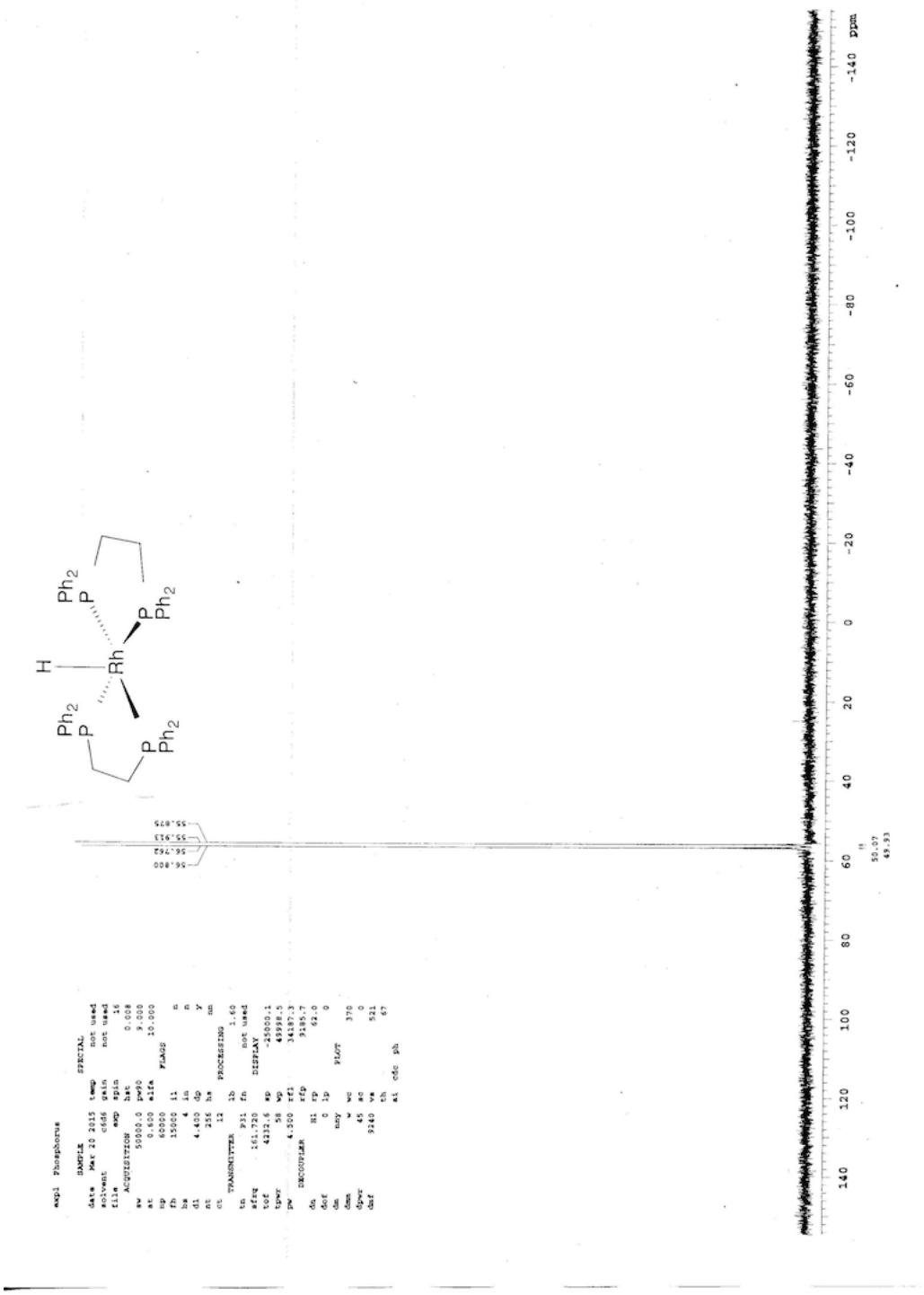
[$RhS_2(dppe)_2$]Cl complex **12** (^{13}C-NMR, $CDCl_3$)



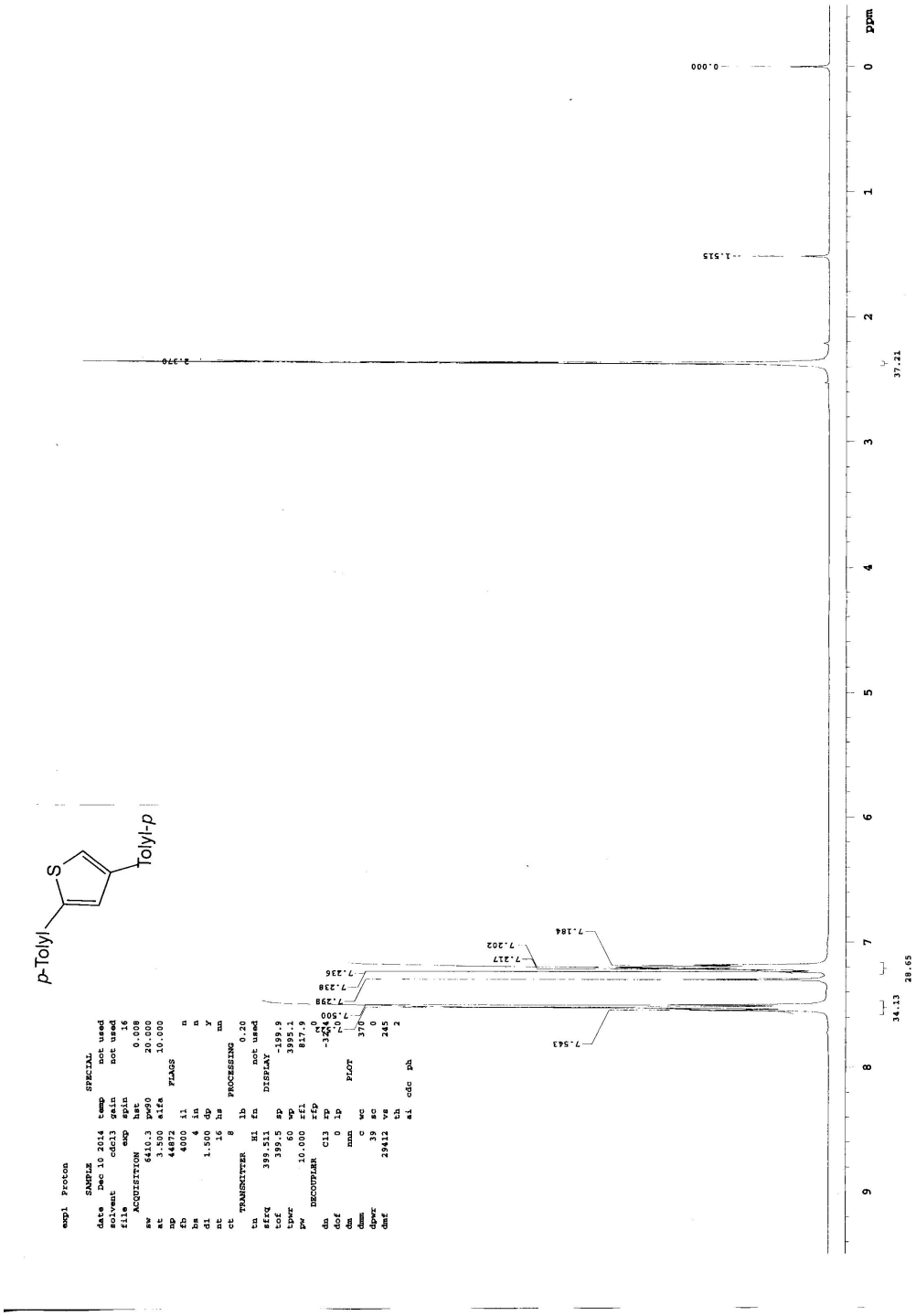
RhH(dppe)$_2$ complex **13** (^{1}H-NMR, C_6D_6)



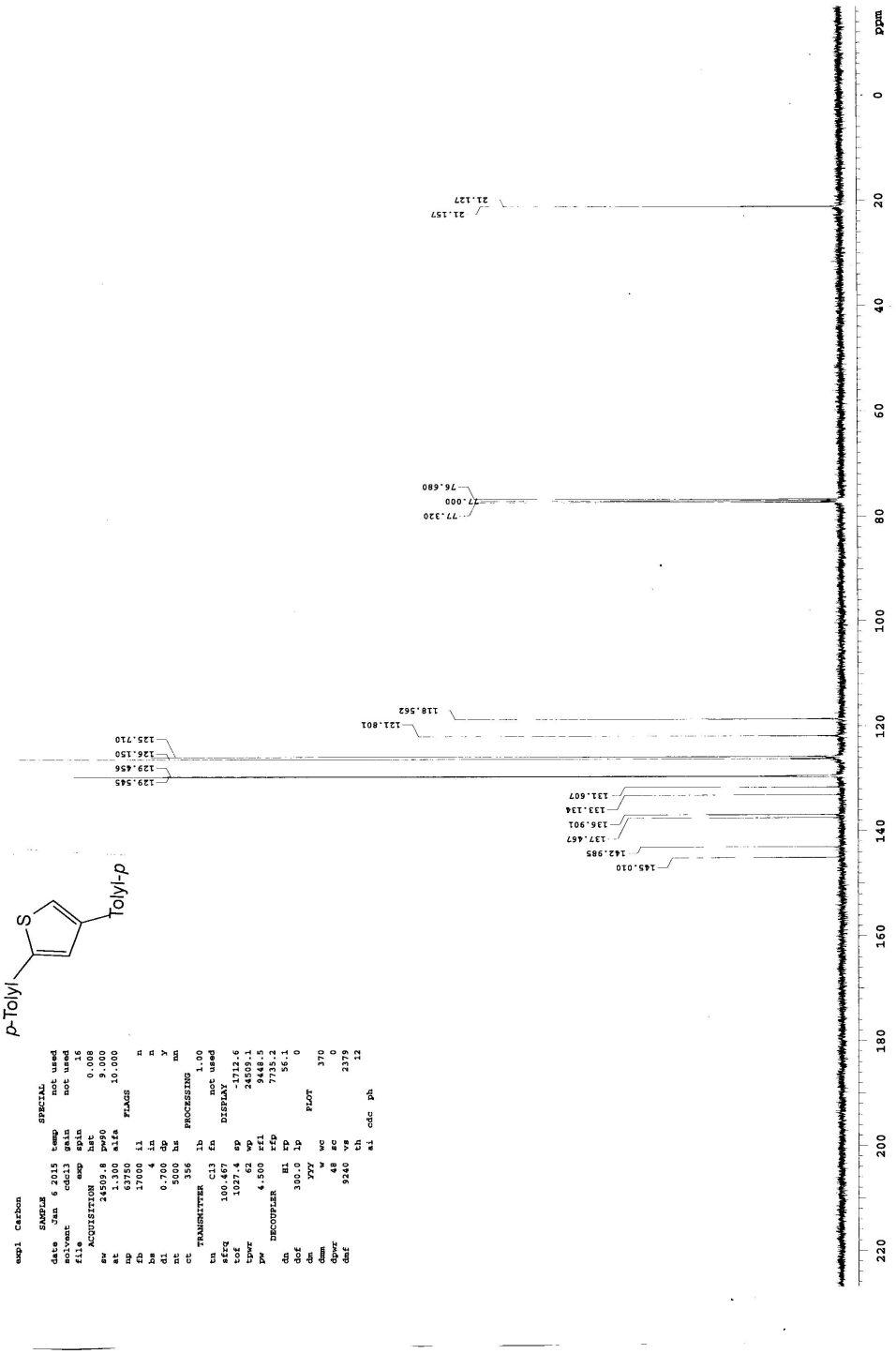
RhH(dppe)$_2$ complex **13** (^{31}P-NMR, C_6D_6)



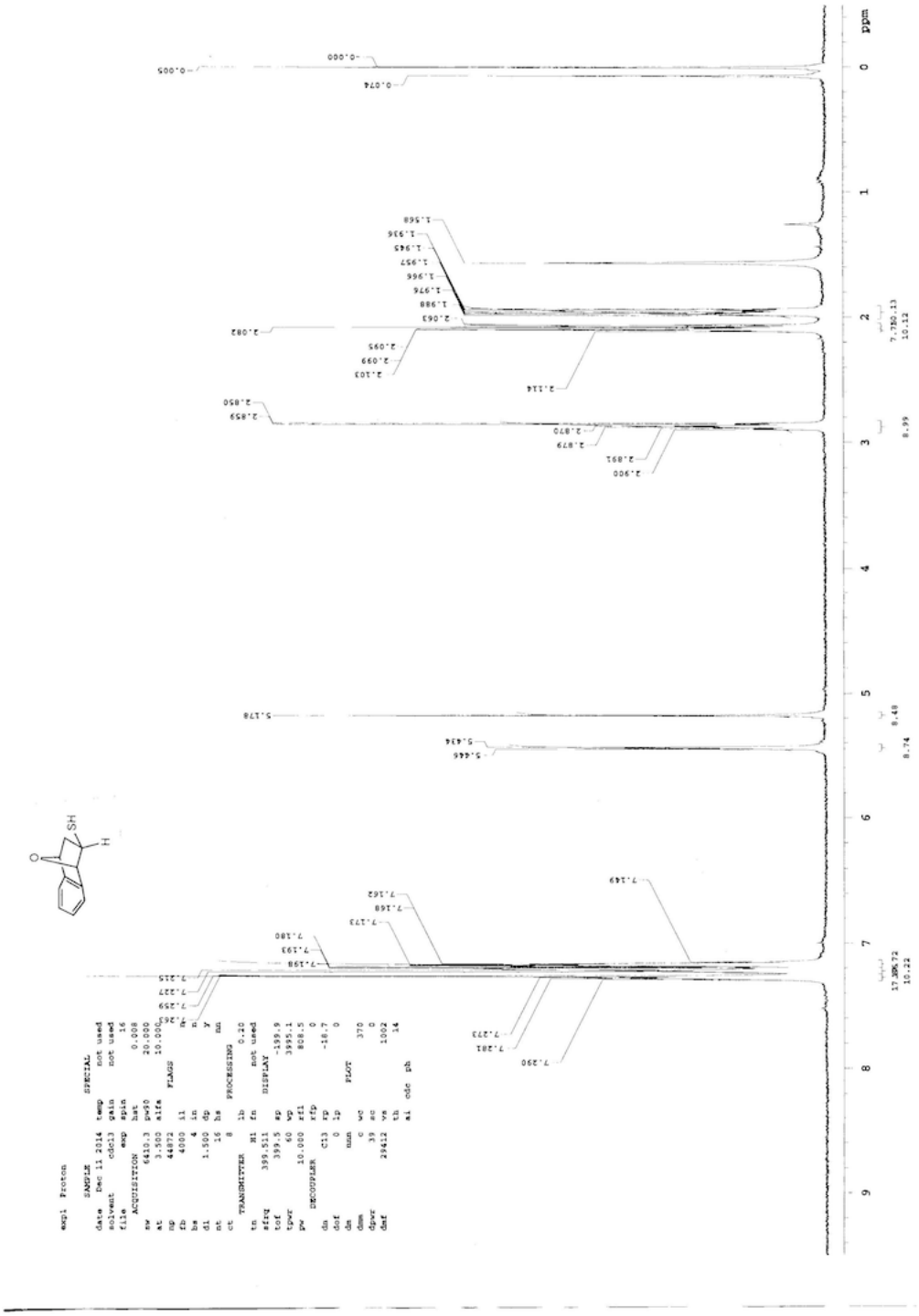
2,4-Bis(4-tolyl)thiophene **15** (^{1}H-NMR)



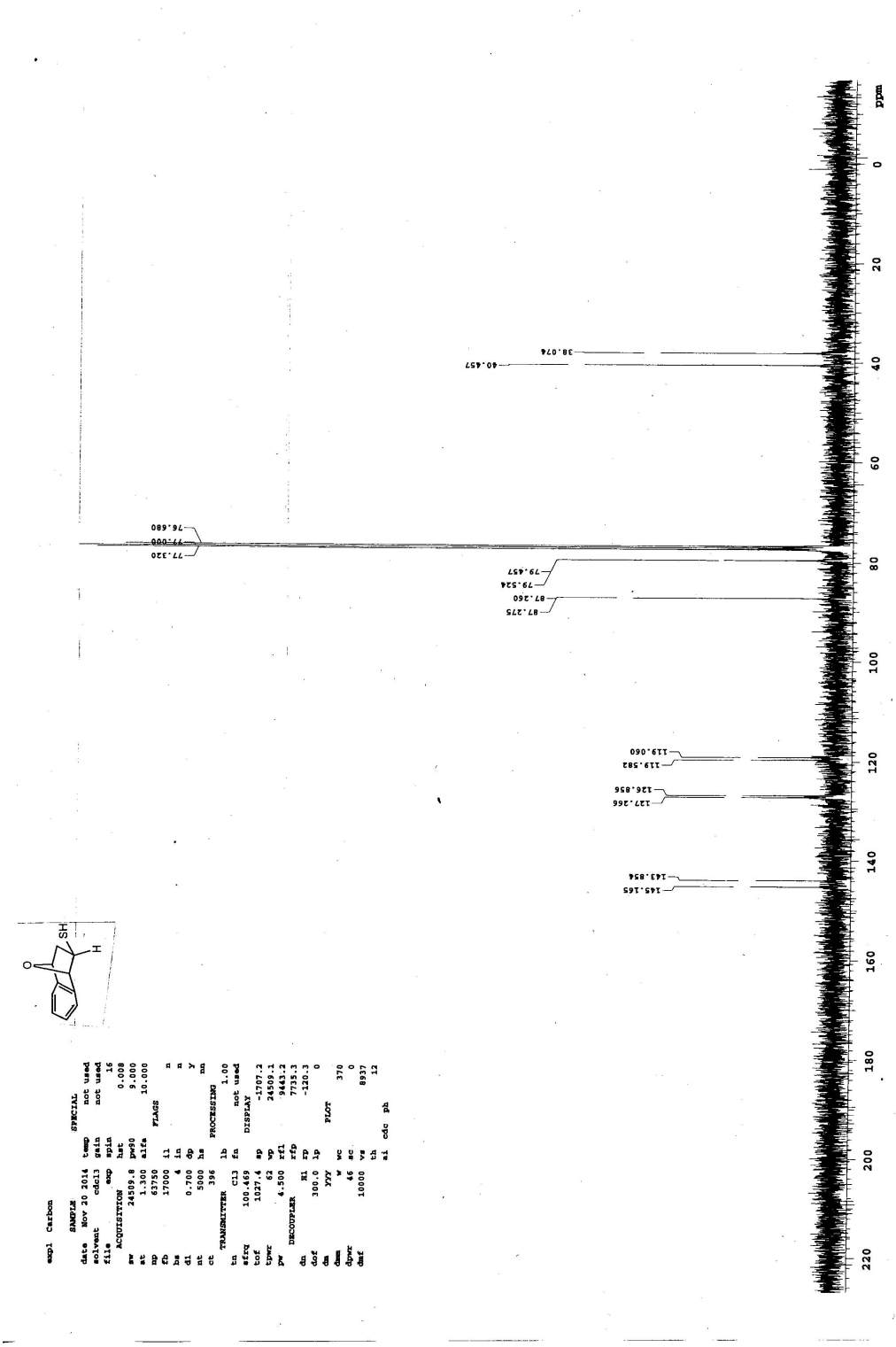
2,4-Bis(4-tolyl)thiophene **15** (^{13}C-NMR)



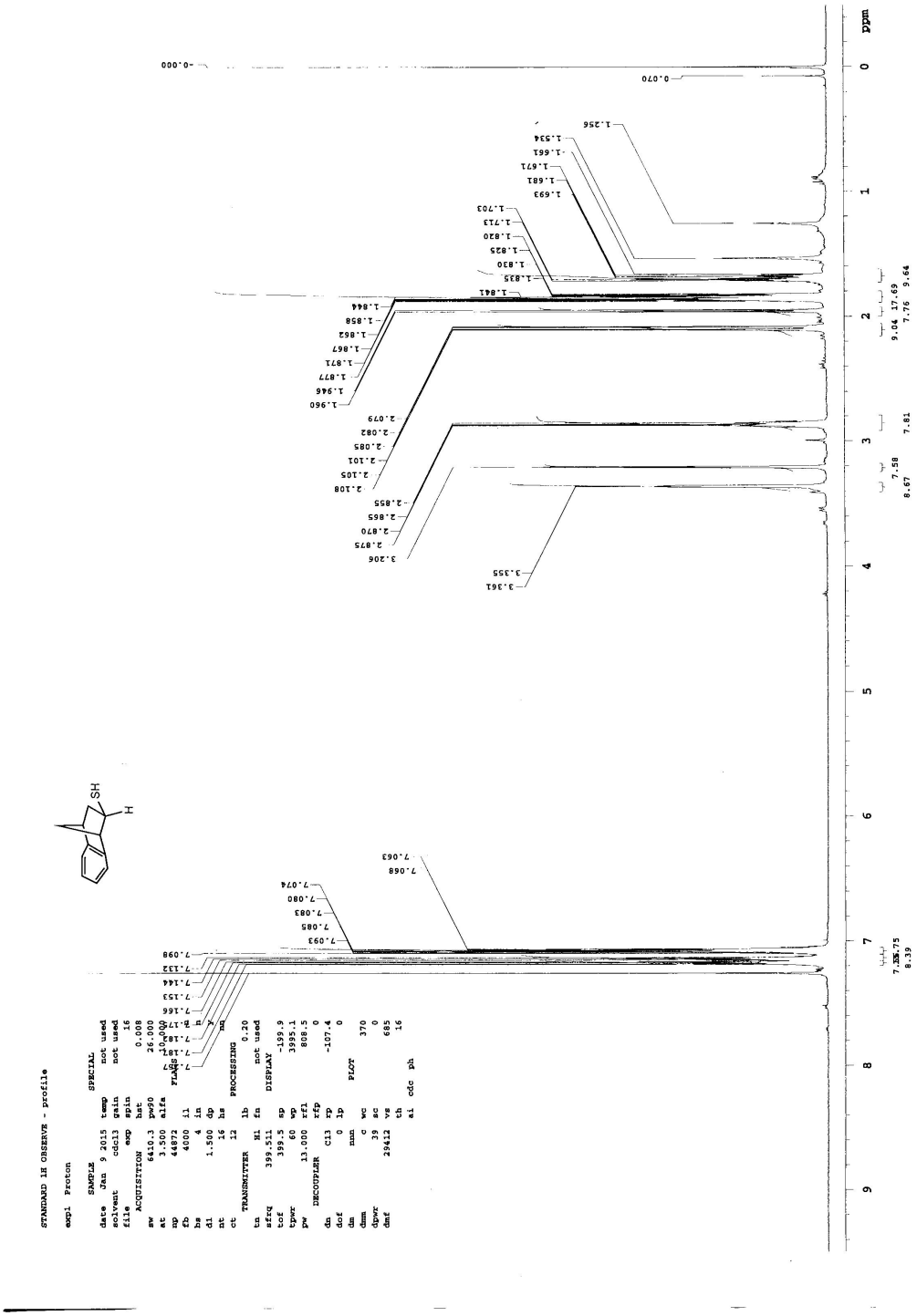
exo-1,2,7,8-Tetrahydro-2,7-epoxynaphthalene-1-thiol **16a** (^{1}H-NMR)



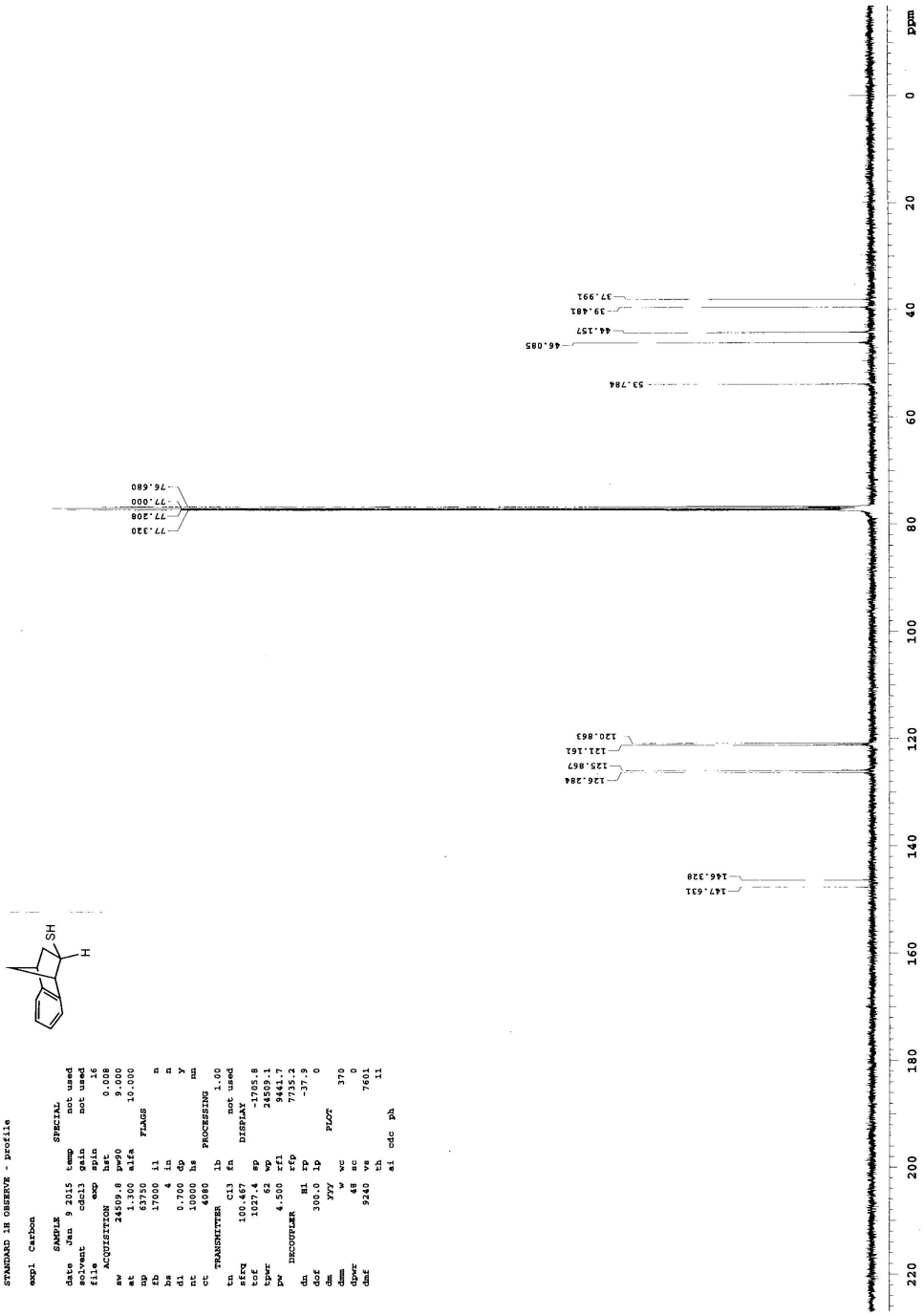
exo-1,2,7,8-Tetrahydro-2,7-epoxynaphthalene-1-thiol **16a** (^{13}C-NMR)



exo-1,2,7,8-Tetrahydro-2,7-methanonaphthalene-1-thiol **16e** (^{1}H-NMR)



exo-1,2,7,8-Tetrahydro-2,7-methanonaphthalene-1-thiol **16e** (^{13}C-NMR)



STANDARD 1H OBSERVE - profile

expl Carbon

SAMPLE

date Jan 9 2015
solvent cdcl3
file exp

SPECIAL

temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000

FLAGS

il n
in y
dp nn
hs

PROCESSING

lb 1.00
fn not used

DISPLAY

sw 24509.8
at 1.300
sp 63750
fb 17000
bs 4
d1 0.700
nt 10000
ct 4080

TRANSMITTER

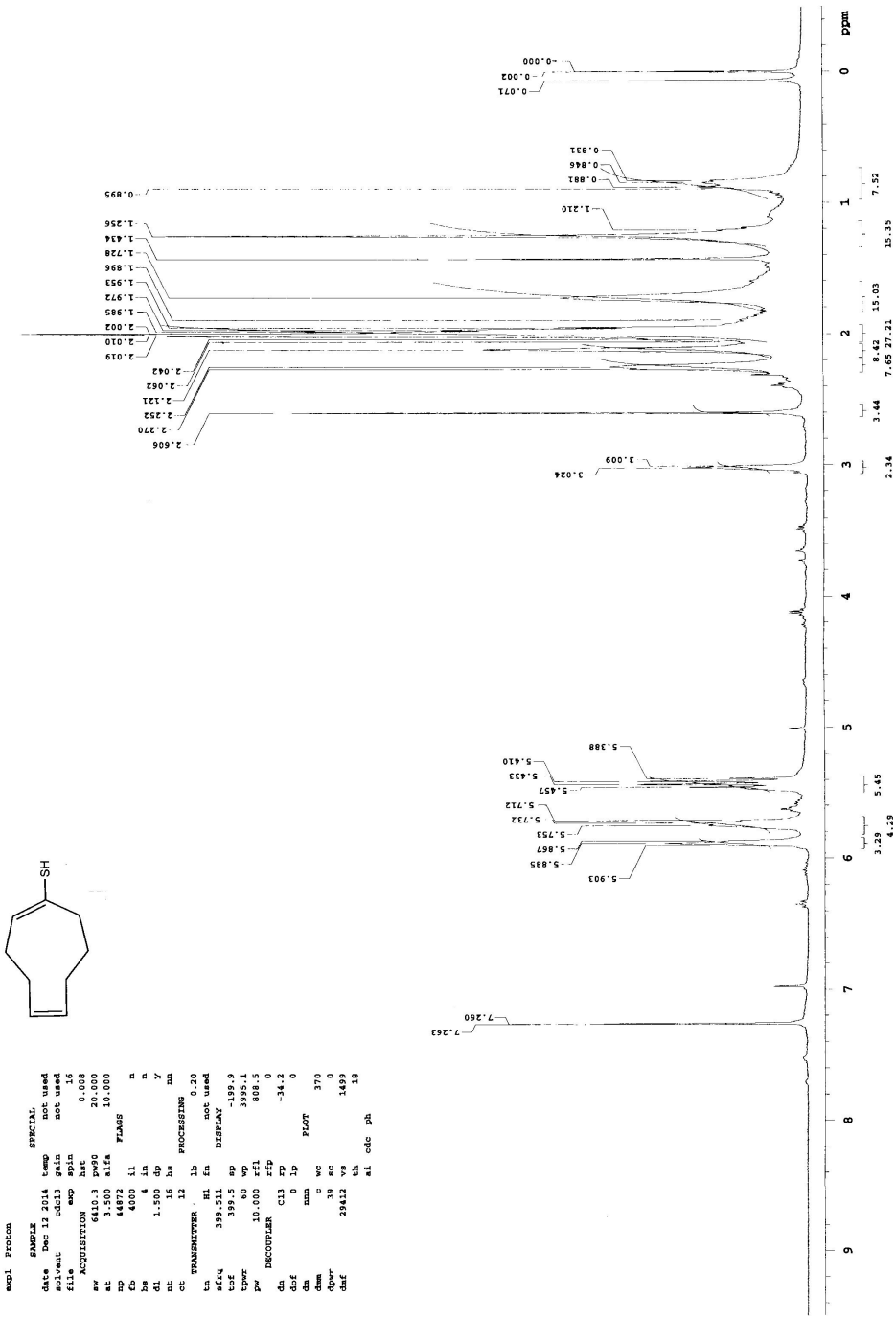
tn C13
sfrq 100.467
tof 1027.4
tpwr 62
pw 4.500

DECOUPLER

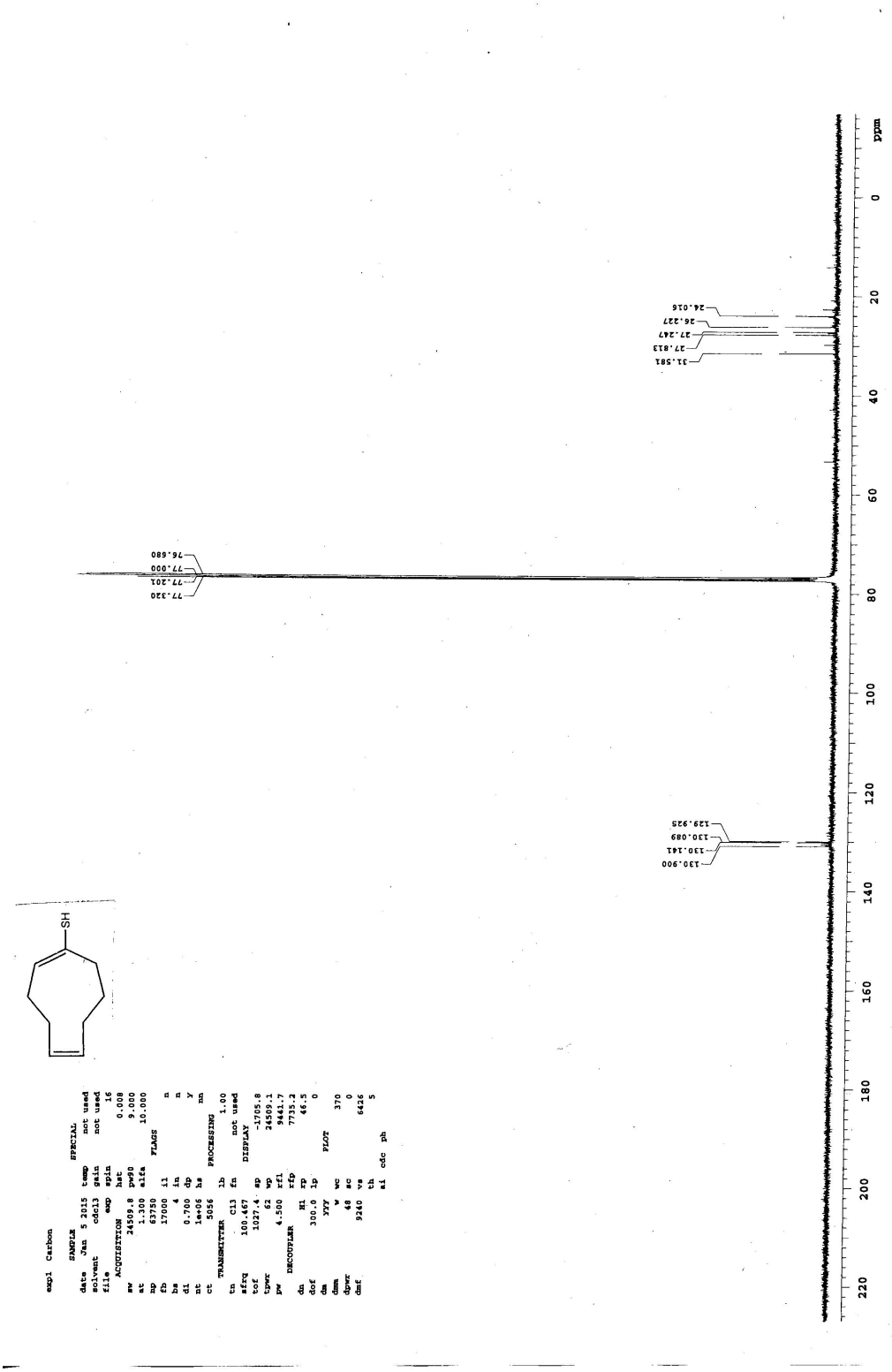
dn
dof
dm
dmm
dpwr
dmf

n1 sp wp sf fp
-1705.8
24509.1
9441.7
7733.2
-37.9
0
PLOT
370
0
7601
11
cdc ph

1,5-Cyclononadiene-1-thiol (*E*)-**17** (^{1}H-NMR)



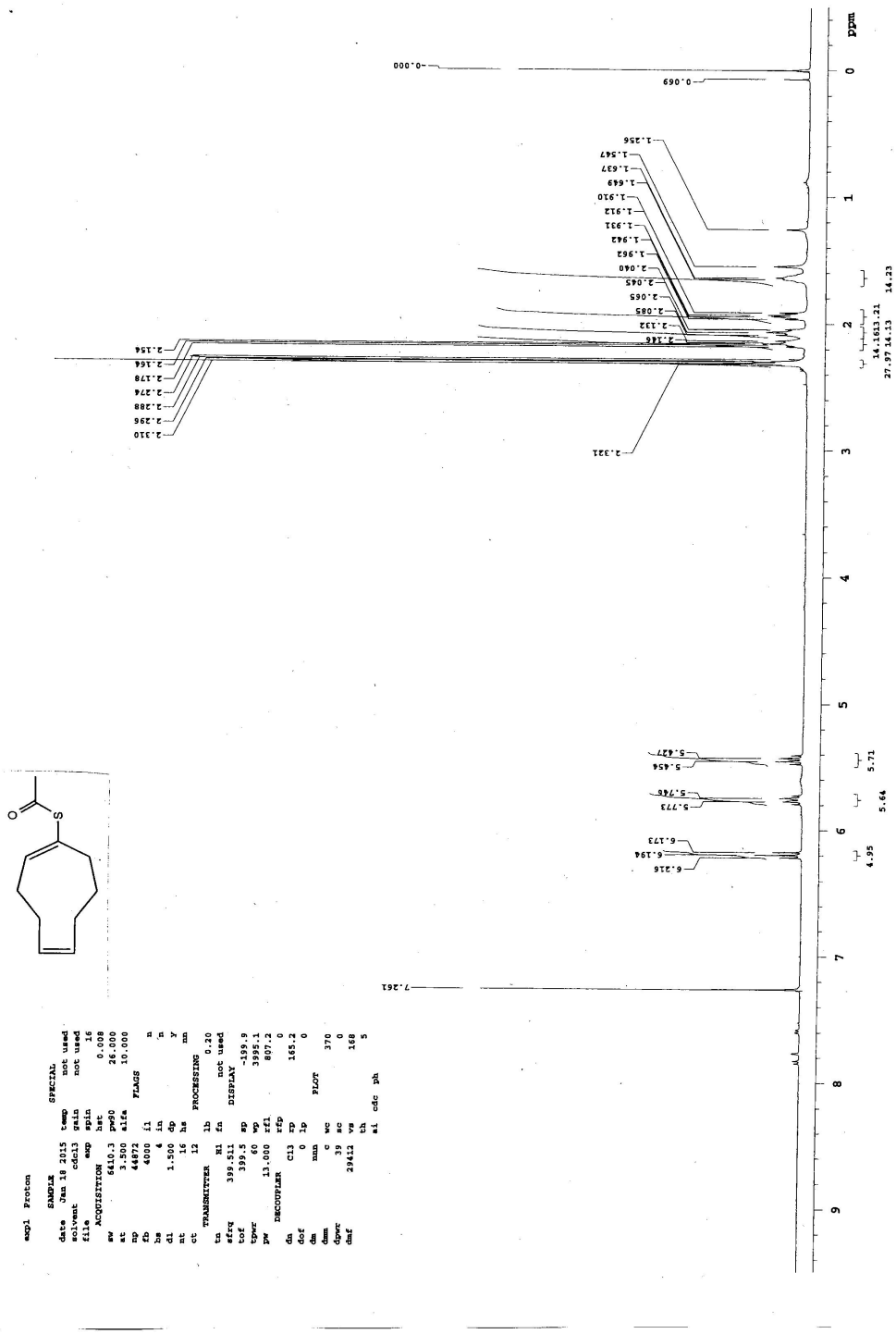
1,5-Cyclononadiene-1-thiol (*E*)-**17** (^{13}C-NMR)




```
exp1  Carbon

      SAMPLE                    SPECIAL
date  Jan 5 2015          temp      not used
solvent     cdcl3         gain      not used
file        exp           spin        16
      ACQUISITION           hst       0.008
sw          24509.8       pw90      9.000
at          1.300         alfa     10.000
np          63750       FLAGS
fb          17000         il          n
bs          4             in          n
d1          0.700         dp          y
nt          1e+06         hs         nn
ct          5056      PROCESSING
      TRANSMITTER           lb        1.00
tn          C13           fn      not used
sfrq        100.467     DISPLAY
tof         1027.4        sp      -1705.8
tpwr        52            wp       24509.1
pw          4.500         rfl      8441.7
      DECOUPLER             rfp      7771.2
dn          H1            rp         44.5
dof         300.0         lp            0
dm          yyy         PLOT
dmm         w             wc          370
dpwr        48            sc            0
dmf         9240          vs         6426
                          th            5
                          ai  cdc  ph
```

1- Acetylthio-1,5-cyclononadiene (*E*)-**18** (^{1}H-NMR)




```
exp1 Proton
    SAMPLE                  SPECIAL
  date  Jan 18 2015     temp      not used
solvent    cdcl3        gain      not used
  file        exp        spin        16
    ACQUISITION          hzpt       0.000
    sw       6410.3      pw90       26.000
    at        3.500      alfa       10.000
    np         44872           FLAGS
    fb          4000      il            n
    bs             4      in            n
    d1         1.500      dp            y
    nt            16      hs           nn
    ct            12           PROCESSING
                         lb         0.20
    TRANSMITTER          fn      not used
    sfrq     399.511          DISPLAY
    tof        399.5      sp       199.9
    tpwr          60      wp      3995.1
    pw        13.000      rfl       807.2
    DECOUPLER            rfp         0.0
    dn             C13    rp        165.2
    dof              0    lp            0
    dm             nnn           PLOT
    dmm              c    wc          370
    dpwr            39    sc            0
    dmf          29412    vs          168
                         th            5
                              ai  cdc  ph
```

1-Acetylthio-1,5-cyclononadiene (*E*)-**18** (^{13}C-NMR)