Supporting Information

For

Synthesis of Cycloalkanes/Steroidal Heteroaryl Sulfides Using Rhodium-Catalyzed Heteroaryl Exchange Reaction

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Supplimentary Materials

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury (400 MHz) and tetramethylsilane were used as standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotomer. 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. Kanto Chemical. Co. Inc. silica gel 60 (63-210 μm) was employed for flash column chromatography.

Typical procedures for synthesis of the 2-(6-chlorobenzoxazolyl) cyclopentyl sulfide (3c)

In a two-necked flask were placed $RhH(PPh_3)_4$ (28.8 mg, 10 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz, 22.3 mg, 20 mol%), benzenecarbothioic acid *S*-cyclopentyl ester (0.25 mmol, 51.5 mg), and 6-chloro-2-(4-chlorophenoxy)benzoxazole **2c** (0.25 mmol, 69.8 mg) in chlorobenzene (1 mL) under an argon atomosphere, and the mixture was heated at reflux for 6 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2-(6-chlorobenzoxazolyl) cyclopentyl sulfide **3c** (57.7 mg, 91%). **3c**: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.68-1.83 (6H, m), 2.27-2.33 (2H, m), 4.10 (1H, quintet, J = 6.4 Hz), 7.25 (1H, dd, J = 8.4, 1.6 Hz), 7.44 (1H, d, J = 1.6 Hz), 7.49 (1H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.7, 33.7, 45.4, 110.5, 118.7, 124.7, 129.3, 140.9, 151.7, 166.1. IR (neat) 2961, 2869, 1498, 1461, 1257, 1214, 1134, 915 cm^{-1}. MS (EI) *m/z* 253 (M^+, 16%), 185 (M^+-68, 100%). HRMS Calcd for $C_{12}H_{12}ClNOS$: 253.0318. Found: 253.0354.

2-(4,6-Diphenyl-1,3,5-triazyl) cyclopentyl sulfide (3a)

Colorless solid. Mp 98.0-99.0 °C (Hexane:EtOAc = 4:1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.72-1.86 (6H, m), 2.32-2.39 (2H, m), 4.26 (1H, quintet, J = 6.0 Hz), 7.53 (1H, td, J = 8.8, 1.6 Hz), 7.58 (2H, t, J = 7.2 Hz), 8.61 (4H, dd, J = 7.2, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.0, 33.2, 43.5, 128.6, 128.9, 132.5, 135.7, 169.9, 183.4. IR (KBr) 2961, 2869, 1498, 1461, 1257, 1214, 1134, 915 cm^{-1}. MS (EI) *m/z* 333 (M^+, 34%), 300 (M^+-33, 100%). HRMS Calcd for $C_{20}H_{19}N_3S$: 333.1300. Found: 333.1302.

2-Benzoxazolyl cyclopentyl sulfide (3b)

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.67-1.82 (6H, m), 2.23-2.31 (2H, m), 4.11 (1H, quintet, J = 7.6 Hz), 7.21 (1H, td, J = 7.6, 1.6 Hz), 7.26 (1H, td, J = 7.6, 1.6 Hz), 7.41 (1H, dd, J = 7.6, 0.8 Hz), 7.59 (1H, dd, J = 7.2, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.7, 33.7, 45.3, 109.8, 118.4, 123.7, 124.2, 142.0, 151.6, 165.3. IR (neat) 2960, 2870, 1498, 1454, 1128, 1095, 742 cm^{-1}. MS (EI) *m/z* 219 (M^+, 16%), 151 (M^+-68, 100%). HRMS Calcd for $C_{12}H_{13}NOS$: 219.0717. Found: 219.0719.

2-Benzothiazolyl cyclopentyl sulfide (3d)[1)]

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.67-1.82 (6H, m), 2.26-2.30 (2H, m), 4.12 (1H, quintet, J = 7.6 Hz), 7.28 (1H, td, J = 8.0, 1.2 Hz), 7.41 (1H, td, J = 8.0, 1.2 Hz), 7.75 (1H, dd, J = 8.0, 0.8 Hz), 7.87 (1H, d, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.8, 33.7, 46.6, 120.8, 121.5, 124.1, 125.9, 135.2, 153.4, 167.5. IR (neat) 3060, 2958, 2867, 1456, 992 cm^{-1}. MS (EI) *m/z* 235 (M^+, 21%), 180 (M^+-68, 100%). HRMS Calcd for $C_{12}H_{13}NS_2$: 235.0489. Found: 235.0506.

2-(5-Acetylthienyl) cyclopentyl sulfide (3e)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.61-1.68 (4H, m), 1.75-1.79 (2H, m), 2.02-2.06 (2H, m), 2.46 (3H, s), 3.64 (1H, quintet, J = 6.4 Hz), 6.49 (1H, d, *J* = 3.6 Hz), 7.15 (1H, d, *J* = 3.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.6, 25.8, 33.6, 47.3, 116.1, 118.5, 153.4, 154.2, 185.9. IR (neat) 2959, 2868, 1681, 1565, 1454, 1291, 1025 cm^{-1}. MS (EI) *m/z* 210 (M^+, 22%), 142 (M^+-68, 100%). HRMS Calcd for $C_{11}H_{14}O_2S$: 210.0714. Found: 210.0740.

2-(4,6-Diphenyl-1,3,5-triazyl) cyclohexyl sulfide (3a')

Colorless solid. Mp 119.0-120.0 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38-1.44 (1H, m), 1.52-1.72 (5H, m), 1.84-1.88 (2H, m), 2.21-2.26 (2H, m), 4.06 (1H, quintet, *J* = 6.8 Hz), 7.53 (4H, td, *J* = 7.2, 1.6 Hz), 7.59 (2H, t, *J* = 6.8 Hz), 8.61 (4H, dd, *J* = 6.8, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.7, 26.0, 32.7, 43.6, 128.6, 128.9, 132.5, 135.7, 170.0, 182.8. IR (KBr) 2928, 2852, 1507, 1362, 1250 cm^{-1}. MS (EI) *m/z* 347 (M^+, 73%), 104 (M^+-243, 100%). HRMS Calcd for $C_{21}H_{21}N_3S$: 347.1456. Found: 347.1432.

2-(4,6-Diphenyl-1,3,5-triazyl) octyl sulfide (3a")

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.4 Hz), 1.30-1.40 (8H, m), 1.53 (2H, quintet, *J* = 7.2 Hz), 1.86 (2H, quintet, *J* = 7.2 Hz), 3.32 (2H, t, *J* = 7.2 Hz), 7.53 (4H, td, *J* = 7.6, 1.6 Hz), 7.61 (2H, td, *J* = 7.2, 1.6 Hz), 8.62 (4H, dd, *J* = 7.2, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.21, 29.22, 30.5, 31.8, 128.5, 128.9, 132.6, 135.6, 170.0, 182.9. IR (KBr) 3064, 2925, 1508, 1362, 1252 cm^{-1}. MS (EI) *m/z* 377 (M^+, 21%), 265 (M^+-112, 100%). HRMS Calcd for $C_{23}H_{27}N_3S$: 377.1926. Found: 377.1920. One carbon peak of aliphatic region was piled up in ^{13}C-NMR.

4-Chlorophenyl benzoate (4)[2)]

Colorless solid. Mp 91.0-92.0°C (Hexane:Ethyl acetate = 4:1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, d, *J* = 8.8 Hz), 7.40 (2H, d, *J* = 9.2 Hz), 7.52 (2H, t, *J* = 7.6 Hz), 7.65 (1H, t, *J* = 7.6 Hz), 8.19 (2H, dd, *J* = 7.2, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 123.1, 128.6, 129.1, 129.5, 130.2, 131.3, 133.8, 149.4, 165.0. IR (KBr) 2925, 1735, 1450, 1060 cm^{-1}. MS (EI) *m/z* 232 (M^+, 5%), 105 (M^+-127, 100%). HRMS Calcd for $C_{13}H_9Cl_2O$: 232.0291. Found: 232.0276.

(3ß,17ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thiol (7)

Colorless solid. Mp 133.0-133.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.71 (3H, s), 0.88 (9H, s), 0.91-0.98 (2H, m), 1.01 (3H, s), 1.05 (1H, td, *J* = 13.2, 3.6 Hz), 1.64-1.27 (1H, m), 1.21 (1H, d, *J* = 8.4 Hz), 1.39-1.64 (7H, m), 1.66-1.73 (2H, m), 1.78-1.84 (2H, m), 1.98-2.21 (2H, m), 2.27 (1H, t, *J* = 13.2 Hz), 2.61 (1H, q, *J* = 8.8 Hz), 3.47 (1H, septet, *J* = 6.4 Hz), 5.31 (1H, d, *J* = 5.2Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 12.3, 18.2, 19.4, 20.8, 24.5, 25.9, 31.8, 32.0, 32.7, 33.0, 36.4, 36.7, 37.4, 42.7, 43.3, 49.4, 50.2, 54.4, 72.5, 120.8, 141.6. IR (KBr) 2926, 2851, 1469, 1246, 1076, 832 cm^{-1}. MS (EI) *m/z* 420 (M^+, 1%), 363 (M^+-57, 100%). HRMS Calcd. for $C_{25}H_{44}OSSi$: 420.2882, M^+-H $C_{25}H_{43}OSSi$: 419.2804. Found: 419.2808.

3ß-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thione (8)

Colorless solid. Mp 135.5-136.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.89 (9H, s), 0.90 (3H, s), 0.92-1.09 (2H, m), 1.04 (3H, s), 1.20-1.35 (2H, m), 1.49-1.57 (2H, m), 1.58-1.77 (5H, m), 1.81-1.85 (1H, m), 1.98-2.06 (2H, m), 2.11-2.21 (2H, m), 2.28 (1H, t, *J* = 11.2 Hz), 2.64 (1H, dt, *J* = 22.0, 8.4 Hz), 2.97 (1H, dd, *J* = 22.0, 8.8 Hz), 3.48 (1H, septet, *J* = 6.0 Hz), 5.34 (1H, d, *J* = 5.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 17.5, 18.2, 19.5, 21.0, 24.5, 25.9, 31.5, 32.0, 32.3, 35.4, 36.7, 37.3, 42.7, 49.1, 49.8, 53.3, 59.0, 72.4, 120.5, 141.7, 273.8. IR (KBr) 2925, 2851, 1461, 1252, 1092, 836, 774 cm^{-1}. MS (EI) *m/z* 418 (M^+, 2%), 361 (M^+-57, 100%). HRMS Calcd. for $C_{25}H_{42}OSSi$: 418.2726. Found: 418.2698.

(3ß,17ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (9)
Colorless solid. Mp 144.0-144.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.80 (3H, s), 0.89 (9H, s), 0.97-1.11 (2H, m), 1.01 (3H, m), 1.21-1.33 (3H, m), 1.42 (1H, ddd, *J* = 26.0, 12.8, 4.0 Hz), 1.47-1.64 (3H, m), 1.68-1.84 (5H, m), 1.99-2.07 (1H, m), 2.19 (1H, ddd, *J* = 13.6, 6.4, 2.8 Hz), 2.25-2.37 (2H, m), 3.49 (1H, septet, *J* = 6.4 Hz), 3.63 (1H, t, *J* = 9.6 Hz), 5.33-5.34 (1H, m), 7.44 (2H, t, *J* = 8.0 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.98 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 14.1, 18.3, 19.5, 20.7, 24.6, 25.9, 29.5, 31.7, 32.0, 32.4, 36.5, 36.7, 37.4, 42.8, 43.5, 50.2, 52.6, 54.3, 72.5, 120.8, 127.2, 128.5, 133.1, 137.4, 141.7, 192.3. IR (KBr) 2958, 2936, 2856, 1656, 1205, 1088, 905 cm^{-1}. MS (EI) *m/z* 524 (M^+, 1%), 467 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{48}O_2SSi$: 524.3144. Found: 524.3110.

(3ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5,16-dien (10)
Colorless solid. Mp 145.0-146.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.86 (3H, s), 0.89 (9H, s), 1.10-1.08 (2H, m), 1.04 (3H, s), 1.45-1.57 (3H, m), 1.60-1.70 (6H, m), 1.79 (1H, dt, *J* = 13.2, 3.2 Hz), 2.03-2.22 (3H, m), 2.28 (1H, td, *J* = 10.8, 2.0 Hz), 2.39 (1H, ddd, *J* = 16.0, 6.0, 3.2 Hz), 3.50 (1H, septet, *J* = 6.0 Hz), 5.35 (1H, d, *J* = 5.6 Hz), 6.32 (1H, dd, *J* = 3.2, 1.6 Hz), 7.46 (2H, t, *J* = 8.0 Hz), 7.58 (1H, t, *J* = 7.6 Hz), 7.99 (2H, dd, *J* = 8.4, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 15.8, 18.3, 19.4, 20.6, 25.9, 30.8, 31.4, 32.0, 32.7, 33.9, 36.8, 37.2, 42.8, 49.3, 50.5, 55.8, 72.5, 120.7, 127.4, 128.6, 133.4, 137.0, 140.0, 141.4, 141.9, 190.7. IR (KBr) 2958, 2927, 1857, 1681, 1255, 1203, 1085, 897 cm^{-1}. MS (EI) *m/z* 522 (M^+, 1%), 465 (M^+-57, 38%), 105 (M^+-417, 100%). HRMS Calcd. for $C_{32}H_{46}O_2SSi$: 522.2988. Found: 522.2993.

Typical procedures for synthesis of the (3ß,17ß)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy] -17-[2- (4,6-diphenyl-1,3,5-triazyl)thio]androst-5-ene (11a)
In a two-necked flask were placed $RhH(PPh_3)_4$ (14.4 mg, 10 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz, 11.1 mg, 20 mol%), (3ß,17ß)-17-(benzoylthio)-3-[[(1,1-dimethyl)dimethylsilyl]oxy]androst-5-ene **9** (0.125 mmol, 65.5 mg) and 4,6-diphenyl-2-(4-chlorophenoxy)triazine **2a** (0.125 mmol, 44.9 mg) in chlorobenzene (0.5 mL) under an argon atomosphere, and the mixture was heated at reflux for 6 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving (3ß,17ß)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androst-5-ene **11a** (66.1 mg, 81%) and **4** (23.2 mg, 80%). **11a**: Colorless solid. Mp 196.0-196.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.07 (6H, s), 0.90 (12H, s), 1.03 (3H, s), 1.06-1.11 (1H, m), 1.25-1.43 (4H, m), 1.48-1.66 (4H, m), 1.71 (2H, t, *J* =

13.2 Hz), 1.78-1.96 (4H, m), 2.07 (1H, dd, *J* = 17.2, 2.0 Hz), 2.20 (1H, dd, *J* = 13.2, 3.2 Hz), 2.29 (1H, t, *J* = 11.2 Hz), 2.54-2.64 (1H, m), 3.50 (1H, septet, *J* = 4.8 Hz), 4.00 (1H, t, *J* = 9.2 Hz), 5.36 (1H, d, *J* = 4.8 Hz), 7.53 (4H, t, *J* = 7.2 Hz), 7.58 (2H, d, *J* = 7.2 Hz), 8.61 (4H, d, *J* = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 13.9, 18.3, 19.4, 20.7, 24.8, 25.9, 30.1, 31.8, 32.0, 32.4, 36.7, 36.9, 37.4, 42.8, 43.7, 50.2, 53.6, 54.6, 72.5, 120.8, 128.6, 128.9, 132.5, 135.7, 141.7, 169.9, 183.5. IR (KBr) 2928, 2854, 1504, 1362, 1253, 1083 cm^{-1}. MS (EI) *m/z* 651 (M^+, 26%), 594 (M^+-57, 100%). HRMS Calcd. for $C_{40}H_{53}N_3OSSi$: 651.3679. Found: 651.3668.

(3ß,17ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11c)

Colorless solid. Mp 142.5-143.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.84 (3H, s), 0.89 (9H, s), 0.98-1.01 (1H, m), 1.01 (3H, s), 1.01-1.10 (1H, m), 1.17-1.40 (3H, m), 1.45-1.62 (5H, m), 1.73 (1H, bd, *J* = 12.8 Hz), 1.76-1.86 (4H, m), 2.01-2.06 (1H, m), 2.18 (1H, bddd, *J* = 13.2, 4.8, 2.0 Hz), 2.28 (1H, td, *J* = 11.2, 2.0 Hz), 2.50-2.59 (1H, m), 3.49 (1H, septet, *J* = 4.8 Hz), 3.74 (1H, t, *J* = 9.2 Hz), 5.33 (1H, d, *J* = 4.8 Hz), 7.24 (1H, dd, *J* = 8.4, 1.6 Hz), 7.43 (1H, d, *J* = 1.6 Hz), 7.74 (1H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 13.5, 18.3, 19.4, 20.7, 24.6, 25.9, 30.5, 31.7, 32.0, 32.4, 36.6, 37.3, 42.7, 43.8, 50.1, 54.1, 56.3, 72.5, 110.4, 118.6, 120.7, 124.7, 129.3, 140.8, 141.7, 151.8, 166.5. IR (KBr) 2930, 2854, 1498, 1461, 1256, 1094, 836 cm^{-1}. MS (EI) *m/z* 571 (M^+, 10%), 514 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{47}NOS_2Si$: 571.2707. Found: 571.2708. One carbon peak of aliphatic region was piled up in ^{13}C-NMR.

(3ß,17ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11d)

Colorless solid. Mp 112.5-113.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.85 (3H, s), 0.89 (9H, s), 1.01 (3H, s), 0.95-1.09 (1H, m), 1.20-1.38 (4H, m), 1.45-1.61 (6H, m), 2.02-2.05 (1H, m), 2.16-2.21 (1H, m), 2.25 (1H, t, *J* = 11.2 Hz), 2.50-2.60 (1H, m), 3.49 (1H, septet, *J* = 6.4 Hz), 3.80 (1H, t, *J* = 9.2 Hz), 5.33 (1H, bd, *J* = 5.2 Hz), 7.28 (1H, td, *J* = 7.2, 0.8 Hz), 7.40 (1H, td, *J* = 8.0, 0.8 Hz), 7.74 (1H, d, *J* = 8.4 Hz), 7.40 (1H, td, *J* = 8.0, 0.8 Hz), 7.74 (1H, d, *J* = 8.4 Hz), 7.84 (1H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 13.5, 18.3, 19.4, 20.7, 24.7, 25.9, 30.5, 31.7, 32.0, 32.4, 36.7, 36.9, 37.4, 42.7, 44.1, 50.1, 54.2, 57.5, 72.5, 120.7, 120.8, 121.4, 124.1, 125.9, 135.3, 141.7, 153.3, 167.7. IR (KBr) 2940, 2854, 1459, 1428, 1255, 1086 cm^{-1}. MS (EI) *m/z* 553 (M^+, 20%), 496 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{47}NOS_2Si$: 553.2868. Found: 553.2860.

(3ß,17ß)-17-[4-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11f)

Colorless solid. Mp 183.0-184.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.07 (6H, s), 0.90 (9H, s), 0.92 (3H, s), 1.03 (3H, s), 0.99-1.11 (1H, m), 1.25-1.38 (3H, m), 1.41-1.66 (6H, m), 1.72-1.77 (1H, m), 1.80-1.84 (2H, m), 2.03-2.09 (1H, m), 2.19 (1H, ddd, *J* = 12.4, 5.2, 2.0 Hz), 2.26 (1H, td, *J* = 11.2, 2.0 Hz), 2.50-2.56 (1H, m), 3.50 (1H, septet, *J* = 5.2 Hz), 4.04 (3H, s), 4.05 (3H, s), 4.16 (1H, t, *J* = 9.6 Hz), 5.34-5.36 (1H, m), 7.26 (1H, s), 7.27 (1H, s), 8.81 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 14.2, 18.2, 19.5, 20.7, 24.7, 25.9, 30.2, 31.7, 32.0, 32.4, 36.66, 36.69, 37.4, 42.8, 43.5, 50.2, 52.8, 54.3, 56.27, 56.33, 72.5, 101.8, 106.9, 119.3, 120.8, 141.6, 145.3, 149.8, 152.3,

155.3, 168.5. IR (KBr) 2930, 2853, 1506, 1344, 1252, 1100, 835 cm^{-1}. MS (EI) *m/z* 608 (M^+, 100%), 222 (M^+-386, 90%). HRMS Calcd. for $C_{35}H_{52}N_2O_3SSi$: 608.3468. Found: 608.3470.

(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11g)

Colorless solid. Mp 96.0-97.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.07 (6H, s), 0.80 (3H, s), 0.88 (9H, s), 1.00 (3H, s), 1.00-1.18 (2H, m), 1.23-1.30 (2H, m), 1.41 (1H, dd, *J* = 13.2, 4.0 Hz), 1.49-1.62 (5H, m), 1.64-1.74 (4H, m), 1.80 (1H, dd, *J* = 13.2, 3.2 Hz), 1.96-2.03 (1H, m), 2.16 (2H, dd, *J* = 14.8, 4.8 Hz), 2.26 (1H, bt, *J* = 13.2 Hz), 3.14 (1H, t, *J* = 9.2 Hz), 3.47 (1H, septet, *J* = 4.8 Hz), 5.31 (1H, dd, *J* = 5.2, 2.0 Hz), 6.44 (1H, d, *J* = 3.6 Hz), 7.03 (1H, d, *J* = 3.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 13.0, 18.3, 19.4, 20.7, 24.4, 25.9, 30.0, 31.7, 32.0, 32.4, 36.6, 36.8, 37.3, 42.7, 44.0, 50.0, 54.3, 58.5, 72.5, 111.4, 114.6, 120.7, 123.5, 127.0, 141.6, 154.4. IR (KBr) 2959, 2941, 2856, 2228, 1463, 1259, 1085 cm^{-1}. MS (EI) *m/z* 511 (M^+, 2%), 454 (M^+-57, 100%). HRMS Calcd. for $C_{30}H_{45}NO_2SSi$: 511.2940. Found: 511.2917.

(3ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androsta-5,16-diene (12a)

Colorless solid. Mp 158.5-159.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.89 (9H, s), 0.95 (3H, s), 1.04 (3H, s), 1.46-1.62 (6H, m), 1.65-1.82 (6H, m), 2.11-2.21 (3H, m), 2.29 (1H, bt, *J* = 11.2 Hz), 2.48 (1H, ddd, *J* = 15.6, 5.6, 3.2 Hz), 3.50 (1H, septet, *J* = 6.0 Hz), 5.38 (1H, d, *J* = 4.8 Hz), 6.49 (1H, dd, *J* = 3.2, 1.6 Hz), 7.53 (4H, td, *J* = 7.6, 1.2 Hz), 7.59 (2H, tt, *J* = 7.2, 1.6 Hz), 8.61 (4H, d, *J* = 7.2, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 16.1, 18.3, 19.4, 20.7, 25.9, 30.9, 31.6, 32.0, 32.7, 33.8, 36.8, 37.2, 42.8, 49.7, 50.7, 56.2, 72.5, 120.6, 128.6, 129.0, 132.6, 135.5, 141.0, 141.4, 142.1, 170.1, 183.4. IR (KBr) 2933, 2845, 1507, 1361, 1247 cm^{-1}. MS (EI) *m/z* 649 (M^+, 100%), 592 (M^+-57, 77%). HRMS Calcd. for $C_{40}H_{51}N_3OSSi$: 649.3522. Found: 649.3524.

(3ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12c)

Colorless solid. Mp 103.0-104.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.89 (9H, s), 0.93 (3H, s), 1.02 (3H, s), 1.00-1.07 (1H, m), 1.40 (1H, ddd, *J* = 21.6, 12.0, 4.8 Hz), 1.47-1.78 (8H, m), 2.02-2.11 (2H, m), 2.18 (1H, ddd, *J* = 13.6, 5.2, 2.0 Hz), 2.27 (1H, td, *J* = 13.2, 2.0 Hz), 2.39 (1H, ddd, *J* = 15.6, 6.0, 3.2 Hz), 3.48 (1H, septet, *J* = 6.0 Hz), 5.34 (1H, d, *J* = 5.2 Hz), 6.43 (1H, dd, *J* = 2.8, 1.6 Hz), 7.28 (1H, dd, *J* = 8.8, 2.0 Hz), 7.48 (1H, d, *J* = 1.6 Hz), 7.53 (1H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 15.9, 18.3, 19.3, 20.6, 25.9, 30.8, 31.3, 32.0, 32.5, 33.7, 36.8, 37.2, 42.8, 49.5, 50.3, 55.8, 72.5, 110.7, 119.4, 120.5, 125.0, 130.0, 139.6, 139.8, 140.8, 141.9, 151.7, 163.7. IR (KBr) 2926, 2901, 2855, 1503, 1462, 1258, 1084, 839 cm^{-1}. MS (EI) *m/z* 569 (M^+, 9%), 512 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{44}ClNO_2SSi$: 569.2551. Found: 569.2557.

(3ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12d)

Colorless solid. Mp 170.0-170.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.88 (9H,

s), 0.93 (3H, s), 1.02 (3H, s), 0.98-1.09 (1H, m), 1.38-1.57 (4H, m), 1.60-1.77 (7H, m), 2.04-2.11 (2H, m), 2.19 (1H, ddd, *J* = 13.6, 4.8, 2.0 Hz), 2.27 (1H, td, *J* = 11.6, 1.2 Hz), 2.39 (1H, ddd, *J* = 15.6, 6.0, 2.8 Hz), 3.47 (1H, septet, *J* = 5.2 Hz), 5.34 (1H, d, *J* = 5.2 Hz), 6.45 (1H, d, *J* = 1.2 Hz), 7.30 (1H, td, *J* = 7.2, 0.8 Hz), 7.41 (1H, td, *J* = 7.6, 0.2 Hz), 7.74 (1H, d, *J* = 7.6 Hz), 7.88 (1H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 16.0, 18.2, 19.3, 20.6, 25.9, 30.9, 31.3, 32.0, 32.5, 33.9, 36.8, 37.2, 42.8, 49.6, 50.4, 56.3, 72.5, 120.5, 120.8, 122.0, 124.4, 126.1, 135.7, 141.6, 142.0, 143.8, 154.0, 168.4. IR (KBr) 2926, 1424, 1253, 1084, 1004 cm^{-1}. MS (EI) *m/z* 551 (M^+, 100%), 494 (M^+-57, 90%). HRMS Calcd. for $C_{32}H_{45}NOS_2Si$: 551.2712. Found: 551.2698.

(3ß)-17-[4-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12f)

Pale yellow solid. Mp 202.0-203.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.89 (9H, s), 0.93 (3H, s), 1.02 (3H, s), 1.05-1.09 (2H, m), 1.19-1.23 (1H, m), 1.47-1.57 (5H, m), 1.66-1.79 (4H, m), 2.07-2.13 (2H, m), 2.19 (1H, dd, *J* = 13.2, 3.2 Hz), 2.28 (1H, t, J = 11.2 Hz), 2.45 (1H, ddd, *J* = 16.0, 6.0, 3.2 Hz), 3.49 (1H, septet, *J* = 6.0 Hz), 4.04 (3H, s), 4.06 (3H, s), 5.35 (1H, t, *J* = 5.2 Hz), 6.42 (1H, dd, *J* = 3.2, 2.0 Hz), 7.27 (1H, s), 7.36 (1H, s), 8.85 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 16.2, 18.3, 19.3, 20.7, 25.9, 31.0, 31.4, 31.9, 32.8, 34.1, 36.8, 37.2, 42.8, 50.0, 50.4, 55.5, 56.3, 56.4, 72.5, 101.9, 107.1, 119.3, 120.7, 141.3, 141.4, 141.9, 146.2, 150.1, 152.7, 155.6, 167.7. IR (KBr) 2928, 2857, 1505, 1342, 1231, 1157, 1094 cm^{-1}. MS (EI) *m/z* 606 (M^+, 97%), 260 (M^+-346, 100%). HRMS Calcd. for $C_{35}H_{50}N_2O_3SSi$: 606.3311. Found: 606.3328.

(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12g)

Colorless solid. Mp 144.0-145.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.88 (9H, s), 0.89 (3H, s), 1.02 (3H, s), 0.96-1.08 (1H, m), 1.19-1.31 (3H, m), 1.42-1.55 (3H, m), 1.59-1.70 (4H, m), 1.77 (1H, dt, *J* = 12.8, 3.6 Hz), 1.93 (1H, ddd, *J* = 15.2, 11.6, 2.0 Hz), 1.98-2.03 (1H, m), 2.15-2.22 (2H, m), 2.26-2.30 (1H, m), 3.47 (1H, septet, *J* = 4.8 Hz), 5.32 (1H, d, *J* = 5.2 Hz), 5.67 (1H, dd, *J* = 2.8, 1.6 Hz), 6.59 (1H, d, *J* = 3.6 Hz), 7.07 (1H, d, *J* = 3.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.6, 15.8, 18.2, 19.3, 20.6, 25.9, 30.6, 31.3, 31.8, 32.0, 33.9, 36.7, 37.2, 42.8, 48.9, 50.3, 56.4, 72.5, 111.1, 116.8, 120.6, 123.5, 128.6, 131.5, 141.9, 144.5, 151.2. IR (neat) 2928, 2856, 2238, 1465, 1256, 1098 cm^{-1}. MS (EI) *m/z* 509 (M^+, 2%), 452 (M^+-57, 100%). HRMS Calcd. for $C_{30}H_{43}NO_2SSi$: 509.2784. Found: 509.2783.

Typical procedures for synthesis of the (17ß)-[2-(6-Chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14c)

In a two-necked flask were placed $RhH(PPh_3)_4$ (28.8 mg, 20 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz, 22.3 mg, 40 mol%), (17ß)-17-(benzoylthio)-3-[[(1,1-dimethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene **13** (0.125 mmol, 63.3 mg), and 6-chloro-2-(4-chlorophenoxy)benzoxazole **2c** (0.125 mmol, 34.9 mg) in chlorobenzene (0.5 mL) under an argon atomosphere, and the mixture was heated at reflux for 5 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving (17ß)-[2-(6-chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate **14c** (43.0 mg, 63%) and 1-chloro-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene (24.5

mg, 81%). **14c**: Pale yellow solid. Mp 76.0-77.5 ℃ (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, s), 1.42-1.57 (6H, m), 1.84-1.99 (4H, m), 2.30-2.40 (2H, m), 2.55-2.65 (1H, m), 2.92 (2H, br s), 3.86 (1H, t, J = 9.2 Hz), 6.94 (1H, d, J = 2.4 Hz), 6.97 (1H, dd, J = 8.4, 2.4 Hz), 7.26 (1H, dd, J = 8.4, 2.0 Hz), 7.33 (1H, d, J = 8.4 Hz), 7.45 (1H, d, J = 2.0 Hz), 7.48-7.53 (3H, m), 7.63 (1H, t, J = 7.2 Hz), 8.20 (2H, dd, J = 7.2, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.7, 24.2, 26.1, 27.4, 29.5, 30.5, 36.7, 38.8, 43.9, 44.3, 52.9, 56.3, 110.5, 118.6, 118.7, 121.6, 124.8, 126.5, 128.5, 129.3, 129.6, 130.1, 133.5, 137.7, 138.2, 140.8, 148.7, 151.8, 165.4, 166.3. IR (KBr) 2925, 1736, 1496, 1260, 1062, 706 cm^{-1}. MS (EI) *m/z* 543 (M^+, 8%), 105 (M^+-438, 100%). HRMS Calcd. for $C_{32}H_{30}ClNO_3$: 543.1635. Found: 543.1638.

(17ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (13)
Colorless solid. Mp 142.5-143.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.19 (6H, s), 0.83 (3H, s), 0.98 (9H, s), 1.34-1.46 (6H, m), 1.59-1.79 (1H, m), 1.85-1.91 (3H, m), 2.25-2.38 (3H, m), 2.80-2.85 (2H, m), 3.72 (1H, t, J = 9.6 Hz), 6.56 (1H, d, J = 2.4 Hz), 6.61 (1H, dd, J = 8.4, 2.8 Hz), 7.12 (1H, d, J = 8.4 Hz), 7.44 (2H, td, J = 8.0, 1.6 Hz), 7.55 (1H, t, J = 7.6 Hz), 7.99 (2H, d, J = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.4, 14.3, 18.2, 24.3, 25.7, 26.2, 27.6, 29.5, 29.6, 36.7, 39.2, 43.8, 44.1, 52.7, 53.1, 117.1, 119.9, 126.1, 127.2, 128.5, 132.9, 133.1, 137.4, 137.7, 153.3, 192.2. IR (KBr) 2933, 2857, 1658, 1496, 1255, 907, 842 cm^{-1}. MS (EI) *m/z* 506 (M^+, 59%), 449 (M^+-57, 67%), 105 (M^+-401, 100%). HRMS Calcd. for $C_{31}H_{42}O_2SSi$: 506.2675. Found: 506.2652.

(17ß)-[2-(4,6-Diphenyl-1,3,5-triaziyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a)
Colorless solid. Mp 236.0-238.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (3H, s), 1.46-1.59 (6H, m), 1.85-1.93 (1H, m), 1.95-2.01 (2H, m), 2.06 (1H, bd, J = 9.2 Hz), 2.36 (2H, bd, J = 6.0 Hz), 2.52-2.68 (1H, m), 2.94 (2H, br s), 4.11 (1H, t, J = 9.2 Hz), 6.95 (1H, s), 6.97 (1H, dd, J = 8.4, 3.6 Hz), 7.34 (1H, d, J = 8.8 Hz), 7.49-7.65 (9H, m), 8.20 (2H, dd, J = 7.2, 0.9 Hz), 8.63 (4H, dd, J = 6.8, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 24.4, 26.1, 27.5, 29.6, 30.2, 37.0, 38.8, 44.06, 44.14, 53.4, 53.7, 118.7, 121.6, 126.5, 128.5, 128.6, 128.9, 129.6, 130.1, 132.5, 133.5, 135.7, 137.8, 138.2, 148.7, 165.5, 169.9, 183.4. IR (KBr) 3061, 2925, 1738, 1506, 1249, 755 cm^{-1}. MS (EI) *m/z* 623 (M^+, 32%), 105 (M^+-518, 100%). HRMS Calcd. for $C_{40}H_{37}N_3O_2S$: 623.2606. Found: 623.2608.

(17ß)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]-3-[2-(4,6-diphenyl-1,3,5-triazyl)oxy]estra-1,3,5(10)-triene (15a)
Colorless solid. Mp 145.0-146.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.49-1.68 (6H, m), 1.91 (1H, bq, J = 14.0 Hz), 2.01-2.10 (3H, m), 2.40-2.44 (2H, m), 2.61-2.71 (1H, m), 2.95-3.00 (2H, m), 4.14 (1H, t, J = 9.6 Hz), 7.07 (1H, d, J = 2.8 Hz), 7.12 (1H, dd, J = 8.4, 2.8 Hz), 7.39 (1H, d, J = 8.4 Hz), 7.40-7.62 (12H, m), 8.57 (4H, d, J = 6.8 Hz), 8.63 (4H, d, J = 6.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 24.5, 26.2, 27.6, 29.7, 30.2, 37.1, 38.9, 44.1, 44.2, 53.5, 53.7, 118.8, 121.3, 126.2, 128.58, 128.60, 129.0, 129.1, 132.6, 132.8, 135.4, 135.7, 137.5, 138.1, 149.9, 169.9, 171.7, 174.0, 183.5. IR (KBr) 2933, 2878, 1542, 1507, 1361 cm^{-1}. MS (EI) *m/z* 750 (M^+, 13%), 44 (M^+-706, 100%). HRMS Calcd. for $C_{48}H_{42}N_6OS$: 750.3141. Found: 750.3123.

1-Chloro-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene[3)]

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.18 (6H, s), 0.97 (9H, s), 6.76 (2H, d, J = 8.8 Hz), 7.17 (2H, d, J = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.5, 18.2, 25.6, 121.3, 126.2, 129.3, 154.3. IR (KBr) 2929, 2858, 1490, 1257, 912 cm^{-1}. MS (EI) *m/z* 242 (M^+, 44%), 185 (M^+-57, 100%). HRMS Calcd. for $C_{12}H_{19}ClOSi$: 242.0894. Found: 242.0895.

(17ß)-[2-(Benzothiazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14d)

Colorless solid. Mp 166.5-168.0 ℃ (EtOAc). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, s), 1.42-1.56 (6H, m), 1.81-2.00 (4H, m), 2.30-2.38 (2H, m), 2.57-2.65 (1H, m), 2.91 (2H, br s), 3.94 (1H, t, J = 9.2 Hz), 6.94 (1H, s), 6.97 (1H, dd, J = 8.8, 2.0 Hz), 7.29 (1H, t, J = 7.6 Hz), 7.33 (1H, d, J = 8.4 Hz), 7.41 (1H, t, J = 8.0 Hz), 7.50 (2H, t, J = 7.6 Hz), 7.63 (1H, t, J = 7.6 Hz), 7.75 (1H, d, J = 7.6 Hz), 7.86 (1H, d, J = 8.0 Hz), 8.20 (2H, d, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.7, 24.3, 26.2, 27.4, 29.5, 30.5, 37.0, 38.9, 44.0, 44.6, 53.0, 57.5, 118.7, 120.8, 121.4, 121.6, 124.1, 125.9, 126.5, 128.5, 129.7, 130.1, 133.5, 135.3, 137.8, 138.2, 148.7, 153.3, 165.4, 167.5. IR (KBr) 2923, 1734, 1426, 1263, 1064, 752, 713 cm^{-1}. MS (EI) *m/z* 525 (M^+, 24%), 105 (M^+-420, 100%). HRMS Calcd. for $C_{32}H_{31}NO_2S_2$: 525.1796. Found: 525.1782.

(17ß)-[4-(6,7-Dimethoxyquinazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14f)

Colorless solid. Mp 118.5-119.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, s), 1.44-1.61 (6H, m), 1.81 (1H, bq, J = 10.8 Hz), 1.91-2.01 (3H, m), 2.30-2.41 (2H, m), 2.54-2.64 (1H, m), 2.88-2.96 (2H, br s), 4.04 (3H, s), 4.06 (3H, s), 4.29 (1H, t, J = 9.6 Hz), 6.95 (1H, s), 6.97 (1H, d, J = 8.4 Hz), 7.25 (1H, s), 7.28 (1H, s), 7.34 (1H, d, J = 8.4 Hz), 7.50 (2H, t, J = 7.2 Hz), 7.63 (1H, t, J = 7.2 Hz), 8.20 (2H, d, J = 7.2 Hz), 8.83 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.3, 24.3, 26.1, 27.4, 29.6, 30.2, 36.7, 38.9, 44.0, 52.8, 53.1, 56.27, 56.32, 101.8, 107.1, 118.7, 119.3, 121.6, 126.5, 128.5, 129.6, 130.1, 133.5, 137.9, 138.2, 145.5, 148.6, 149.8, 152.4, 155.3, 165.4, 168.2. IR (KBr) 2927, 1735, 1504, 1228, 1156, 1061 cm^{-1}. MS (EI) *m/z* 580 (M^+, 35%), 105 (M^+-475, 100%). HRMS Calcd. for $C_{35}H_{36}N_2O_4S$: 580.2396. Found: 580.2396. One carbon peak of aliphatic region was piled up in ^{13}C-NMR.

(17ß)-[4-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16f)

Colorless solid. Mp 121.0-121.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.19 (6H, s), 0.95 (3H, s), 0.98 (9H, s), 1.42-1.58 (6H, m), 1.79 (1H, bq, J = 10.0 Hz), 1.88-1.96 (3H, m), 2.24-2.34 (2H, m), 2.54-2.59 (1H, m), 2.80-2.88 (2H, m), 4.04 (3H, s), 4.05 (3H, s), 4.27 (1H, t, J = 9.6 Hz), 6.57 (1H, s), 6.61 (1H, d, J = 8.4 Hz), 7.13 (1H, d, J = 8.4 Hz), 7.25 (1H, s), 7.28 (1H, s), 8.82 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.4, 14.4, 18.2, 24.3, 25.7, 26.2, 27.6, 29.6, 30.2, 36.8, 39.2, 43.9, 44.1, 52.9, 53.1, 56.27, 56.33, 101.8, 107.1, 117.2, 119.3, 119.9, 126.1, 132.9, 137.8, 145.5, 149.8, 152.4, 153.3, 155.3, 168.3. IR (KBr) 2927, 2856, 1504, 1251, 1231, 1157, 846 cm^{-1}. MS (EI) *m/z* 590 (M^+, 100%), 249 (M^+-341, 55%). HRMS Calcd. for $C_{34}H_{46}N_2O_3SSi$: 590.2998. Found: 590.2985.

(17ß)-[2-(5-Cyanofuranyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14g)

Colorless solid. Mp 138.0-139.5 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85 (3H, s),

1.25-1.54 (6H, m), 1.73-1.93 (4H, m), 2.21-2.34 (3H, m), 2.89 (2H, br s), 3.24 (1H, t, *J* = 9.2 Hz), 6.47 (1H, t, J = 9.2 Hz), 6.93 (1H, s), 6.97 (1H, d, *J* = 8.4 Hz), 7.06 (1H, d, *J* = 3.6 Hz), 7.32 (1H, d, *J* = 8.4 Hz), 7.50 (2H, t, *J* = 8.0 Hz), 7.63 (1H, t, *J* = 7.6 Hz), 8.19 (2H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.1, 24.0, 26.1, 27.3, 29.5, 30.1, 36.8, 38.8, 43.9, 44.5, 53.1, 58.6, 111.4, 114.7, 118.7, 121.6, 123.5, 126.4, 127.0, 128.5, 129.6, 130.1, 133.5, 137.6, 138.1, 148.7, 154.3, 165.4. IR (KBr) 2926, 2225, 1734, 1457, 1263, 1063 cm^{-1}. MS (EI) *m/z* 483 (M^+, 21%), 105 (M^+-378, 100%). HRMS Calcd. for $C_{30}H_{29}NO_3S$: 483.1868. Found: 483.1880.

(17ß)-[2-(5-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16g)

Colorless solid. Mp 101.0-102.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.18 (6H, s), 0.84 (3H, s), 0.97 (9H, s), 1.24-1.47 (6H, m), 1.71-1.88 (4H, m), 2.20-2.29 (3H, m), 2.81 (2H, bd, *J* = 4.4 Hz), 3.23 (1H, t, *J* = 9.2 Hz), 6.46 (1H, d, *J* = 3.6 Hz), 6.55 (1H, d, *J* = 2.0 Hz), 6.61 (1H, dd, *J* = 8.8, 2.4 Hz), 7.05 (1H, d, *J* = 3.6 Hz), 7.10 (1H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.4, 13.2, 18.2, 24.0, 25.7, 26.2, 27.6, 29.5, 30.1, 36.9, 39.2, 43.7, 44.5, 53.1, 58.7, 111.4, 114.6, 117.2, 119.9, 123.5, 126.1, 127.0, 132.6, 137.7, 153.4, 154.4. IR (KBr) 2928, 2225, 1496, 1460, 1255, 842 cm^{-1}. MS (EI) *m/z* 493 (M^+, 100%), 436 (M^+-57, 82%). HRMS Calcd. for $C_{29}H_{39}NO_2SSi$: 493.2471. Found: 493.2477.

(3ß,17ß)-3-benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17)

Colorless solid. Mp 138.5-139.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.003 (3H, s), 0.01 (3H, s), 0.69 (3H, s), 0.83 (3H, s), 0.88 (9H, s), 1.00 (1H, dd, J = 12.8, 3.6 Hz), 1.13-1.32 (8H, m), 1.40 (3H, ddd, *J* = 21.2, 11.2, 3.6 Hz), 1.47 (1H, d, *J* = 12.4 Hz), 1.54-1.58 (2H, m), 1.61-1.70 (3H, m), 1.75 (2H, ddt, *J* = 24.0, 13.2, 4.0 Hz), 1.84-1.94 (2H, m), 3.55 (1H, t, *J* = 8.0 Hz), 3.62 (1H, tt, *J* = 12.4, 4.4 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.54 (1H, t, *J* = 7.6 Hz), 7.93 (2H, d, *J* = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.8, -4.5, 11.4, 12.2, 18.1, 20.6, 23.5, 25.8, 28.5, 28.8, 30.9, 31.5, 35.4, 35.5, 35.6, 37.1, 38.9, 42.6, 43.3, 47.1, 50.6, 54.5, 81.8, 127.1, 128.5, 133.1, 137.4, 192.0. IR (KBr) 2925, 2853, 1660, 1447, 1204, 1093, 910 cm^{-1}. MS (EI) *m/z* 526 (M^+, 1%), 469 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{50}O_2SSi$: 526.3301. Found: 526.3290.

(3α,17ß)-3-benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17')

Colorless solid. Mp 42.0-43.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.002 (3H, s), 0.01 (3H, s), 0.69 (3H, s), 0.84 (3H, s), 0.87 (9H, s), 0.94 (1H, ddd, *J* = 22.4, 12.4, 3.6 Hz), 1.15-1.32 (6H, m), 1.34-1.44 (4H, m), 1.45-1.58 (4H, m), 1.64 (2H, t, *J* = 13.6 Hz), 1.74 (2H, t, *J* = 13.6 Hz), 1.86 (2H, dt, *J* = 14.4, 4.0 Hz), 2.04 (1H, tt, *J* = 14.4, 4.0 Hz), 3.53 (1H, t, *J* = 8.4 Hz), 4.22 (1H, br s), 7.43 (2H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.99 (2H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.8, -4.5, 11.4, 11.9, 18.1, 20.4, 23.5, 25.8, 27.6, 28.3, 30.9, 31.5, 34.8, 35.5, 36.3, 37.1, 42.2, 42.8, 43.3, 50.7, 54.5, 81.8, 127.1, 128.5, 133.1, 137.5, 191.9. IR (KBr) 2924, 2853, 1660, 1447, 1204, 1093, 910 cm^{-1}. MS (EI) *m/z* 526 (M^+, 1%), 469 (M^+-57, 100%). HRMS Calcd. for $C_{32}H_{50}O_2SSi$: 526.3301. Found: 526.3297.

(3ß,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f)

Colorless solid. Mp 216.0-217.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.003 (3H, s), 0.01 (3H, s), 0.69 (3H, s), 0.86 (3H, s), 0.88 (9H, s), 0.90-1.02 (2H, m), 1.16-1.27 (5H, m), 1.32 (2H, d, J = 13.2 Hz), 1.35-1.44 (3H, m), 1.54 (3H, t, *J* = 0.4 Hz), 1.65-1.76 (3H, m), 1.81-1.90 (3H, m), 2.07 (1H, d, *J* = 12.8 Hz), 3.54 (1H, t, *J* = 8.0 Hz), 4.02 (3H, s), 4.03 (3H, s), 4.11 (1H, tt, *J* = 12.4, 4.4 Hz), 7.19 (1H, s), 7.25 (1H, s), 8.83 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.8, -4.5, 11.4, 12.3, 18.1, 20.6, 23.5, 25.8, 28.5, 28.8, 30.9, 31.6, 35.4, 35.6, 35.7, 37.2, 38.9, 42.7, 43.3, 47.1, 50.6, 54.6, 56.2, 56.3, 81.8, 101.7, 107.0, 119.1, 145.5, 149.8, 152.5, 155.4, 167.9. IR (KBr) 2929, 2854, 1505, 1342, 1230, 1158, 1094 cm^{-1}. MS (EI) *m/z* 610 (M^+, 6%), 222 (M^+-388, 100%). HRMS Calcd. for $C_{35}H_{54}N_2O_3SSi$: 610.3624. Found: 610.3615.

(3α,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f')

Colorless solid. M.p. 104.0-105.0 ℃ (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ -0.01 (3H, s), 0.001 (3H, s), 0.70 (3H, s), 0.87 (9H, s), 0.88 (3H, s), 0.96-0.99 (1H, m), 1.19-1.31 (6H, m), 1.38-1.46 (3H, m), 1.50-1.60 (3H, m), 1.64-1.70 (3H, m), 1.74 (2H, d, *J* = 12.0 Hz), 1.85-1.94 (3H, m), 2.09 (1H, dt, *J* = 14.0, 4.0 Hz), 3.53 (1H, t, *J* = 8.0 Hz), 4.03 (3H, s), 4.06 (3H, s), 4.72 (1H, br s), 7.24 (1H, s), 7.25 (1H, s), 8.83 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.8, -4.5, 11.4, 11.9, 18.1, 20.4, 23.5, 25.8, 27.4, 28.4, 30.9, 31.5, 34.0, 34.6, 35.5, 36.4, 37.2, 42.3, 42.6, 43.3, 50.7, 54.5, 56.30, 56.34, 81.8, 101.7, 107.0, 119.1, 145.5, 149.8, 152.5, 155.3, 167.9. IR (KBr) 2927, 2853, 1505, 1260, 1093 cm^{-1}. MS (EI) *m/z* 610 (M^+, 12%), 222 (M^+-388, 100%). HRMS Calcd. for $C_{35}H_{54}N_2O_3SSi$: 610.3624. Found: 610.3626.

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1) a) Lian, Z.; Bhawal, B. N.; Yu, P.; Morandi, B. *Science*, **2017**, *356*, 1059-1063. b) Zhao, J.; Fang, H.; Han, J.; Pan, Y.; Li, G. *Adv. Synth. Catal.*, **2014**, *356*, 2719-2774.

2) Arisawa, M.; Tazawa, T.; Tanii, S.; Horiuchi, K.; Yamaguchi, M. *J. Org. Chem*., **2017**, *82*, 804-810.

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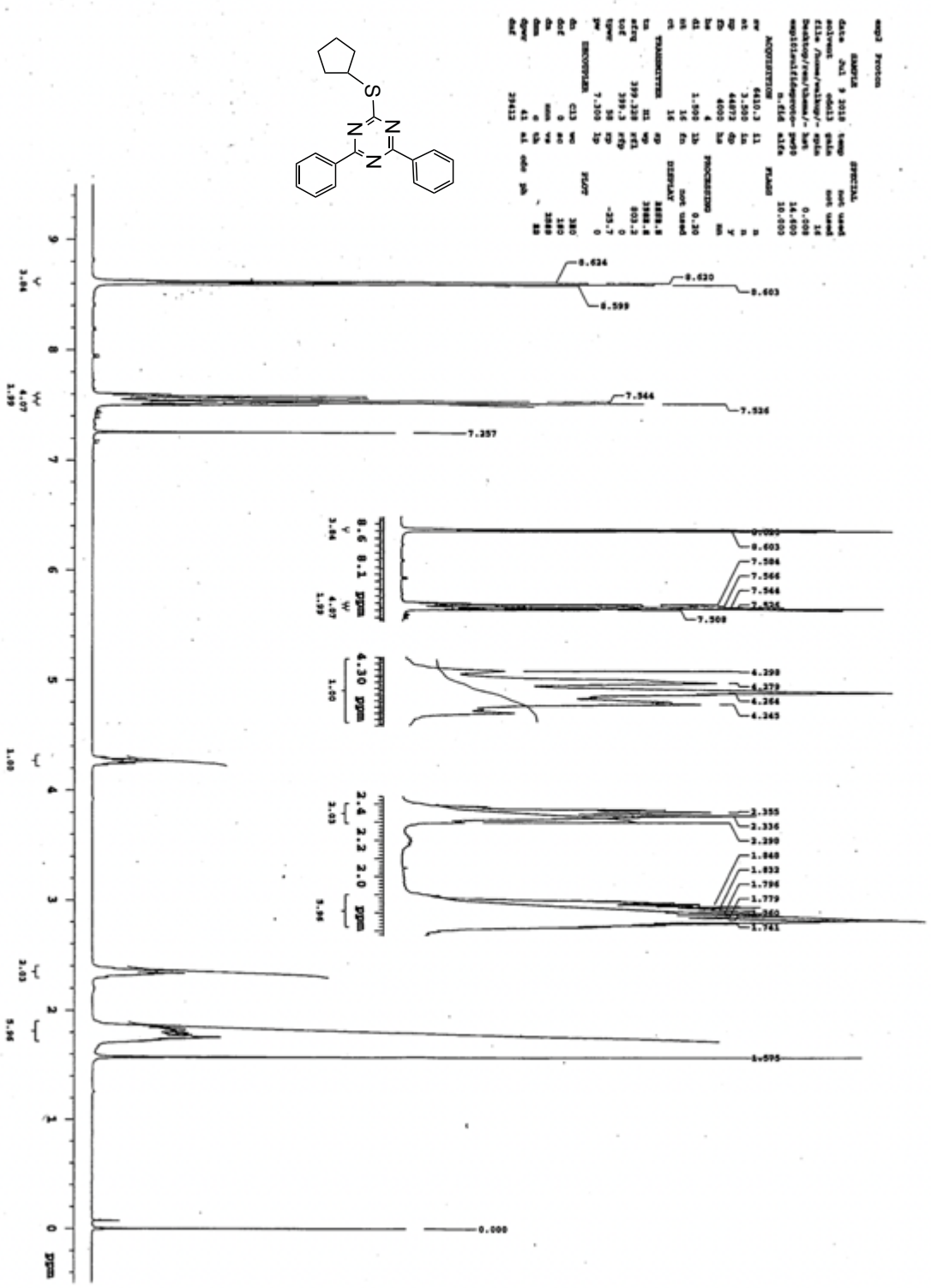
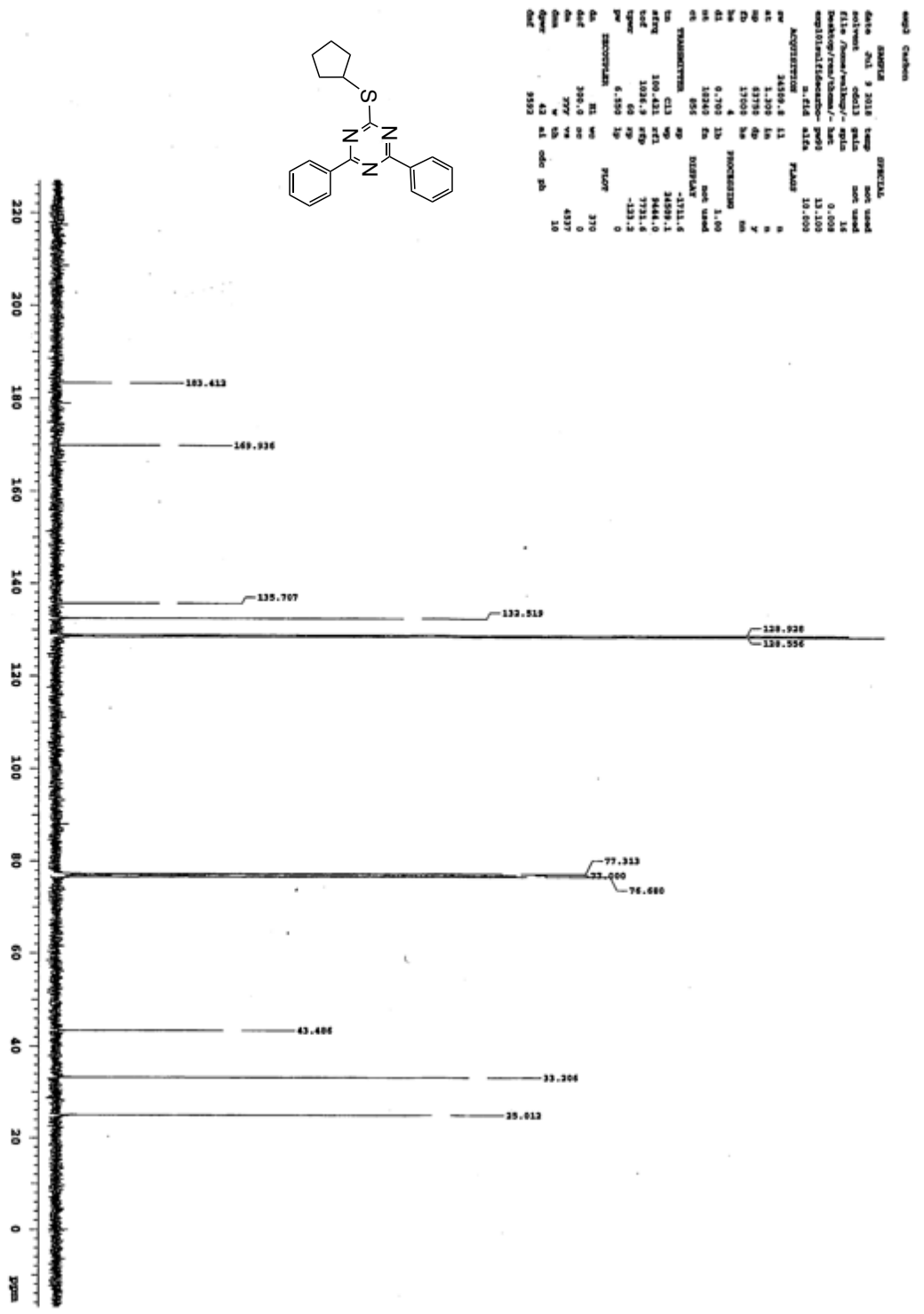
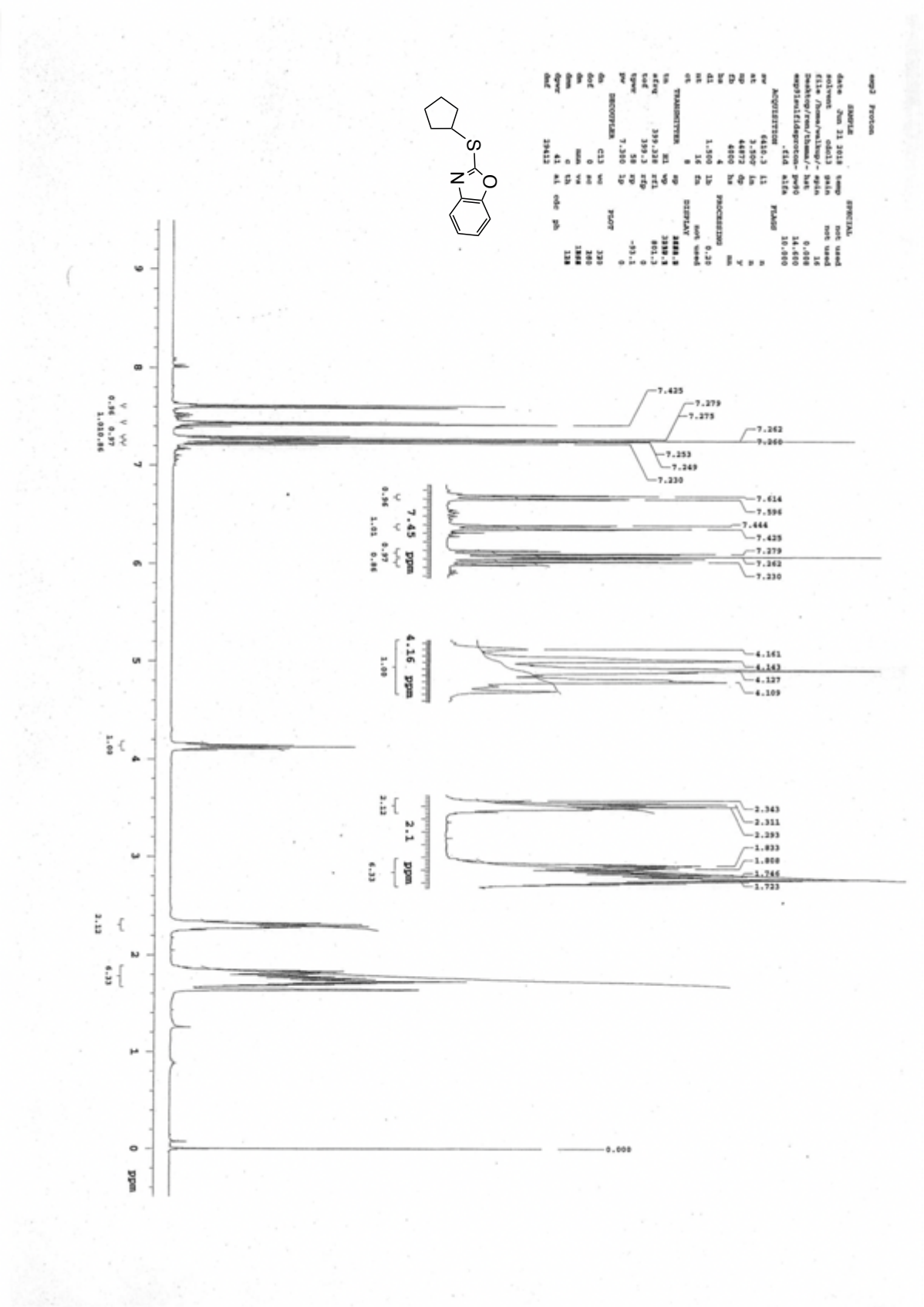
2-(4,6-Diphenyl-1,3,5-triazyl) cyclopentyl sulfide (3a) ^{1}H-NMR



2-(4,6-Diphenyl-1,3,5-triazyl) cyclopentyl sulfide (3a) ^{13}C-NMR



2-Benzoxazolyl cyclopentyl sulfide (3b) ^{1}H-NMR



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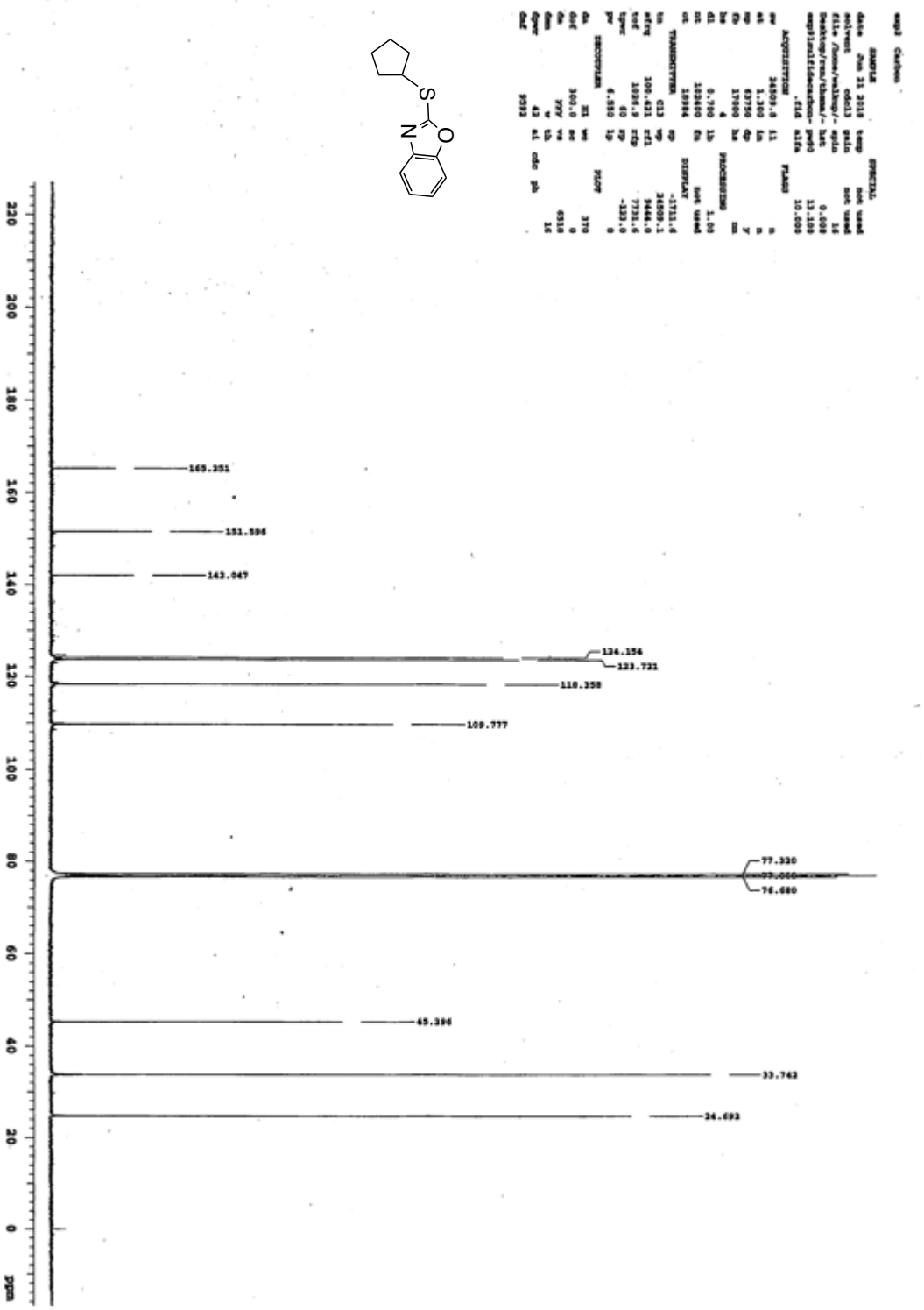

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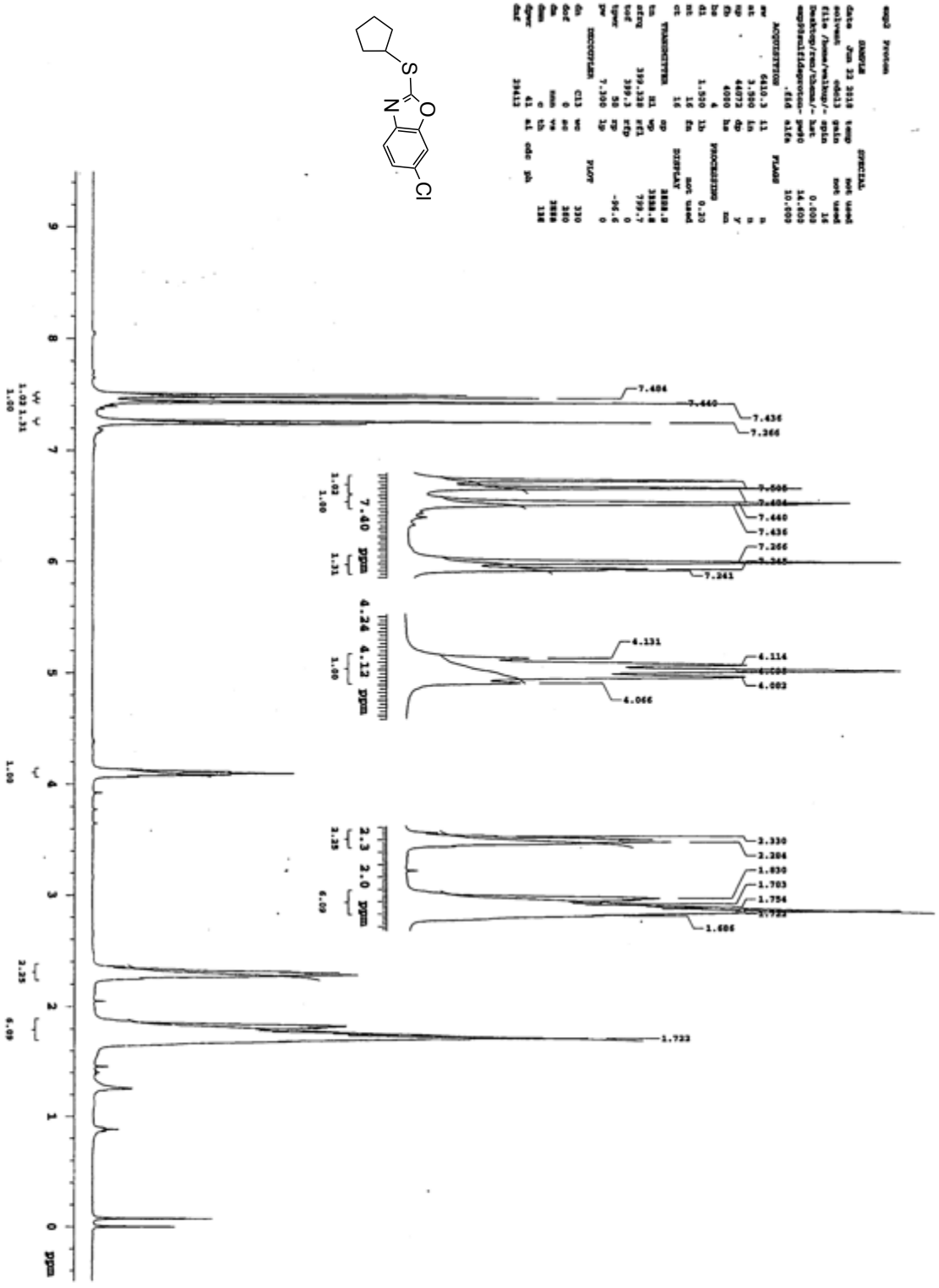
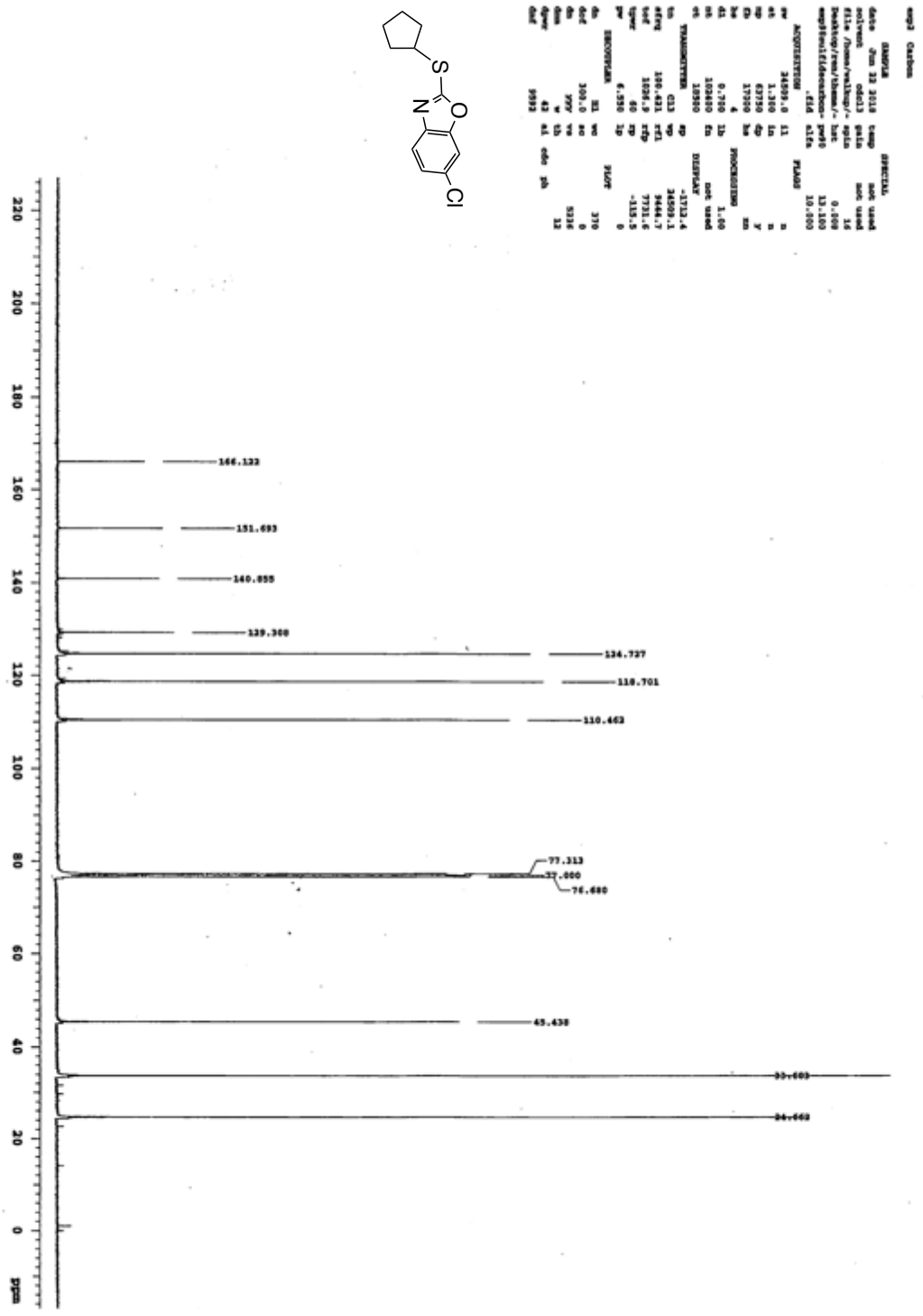
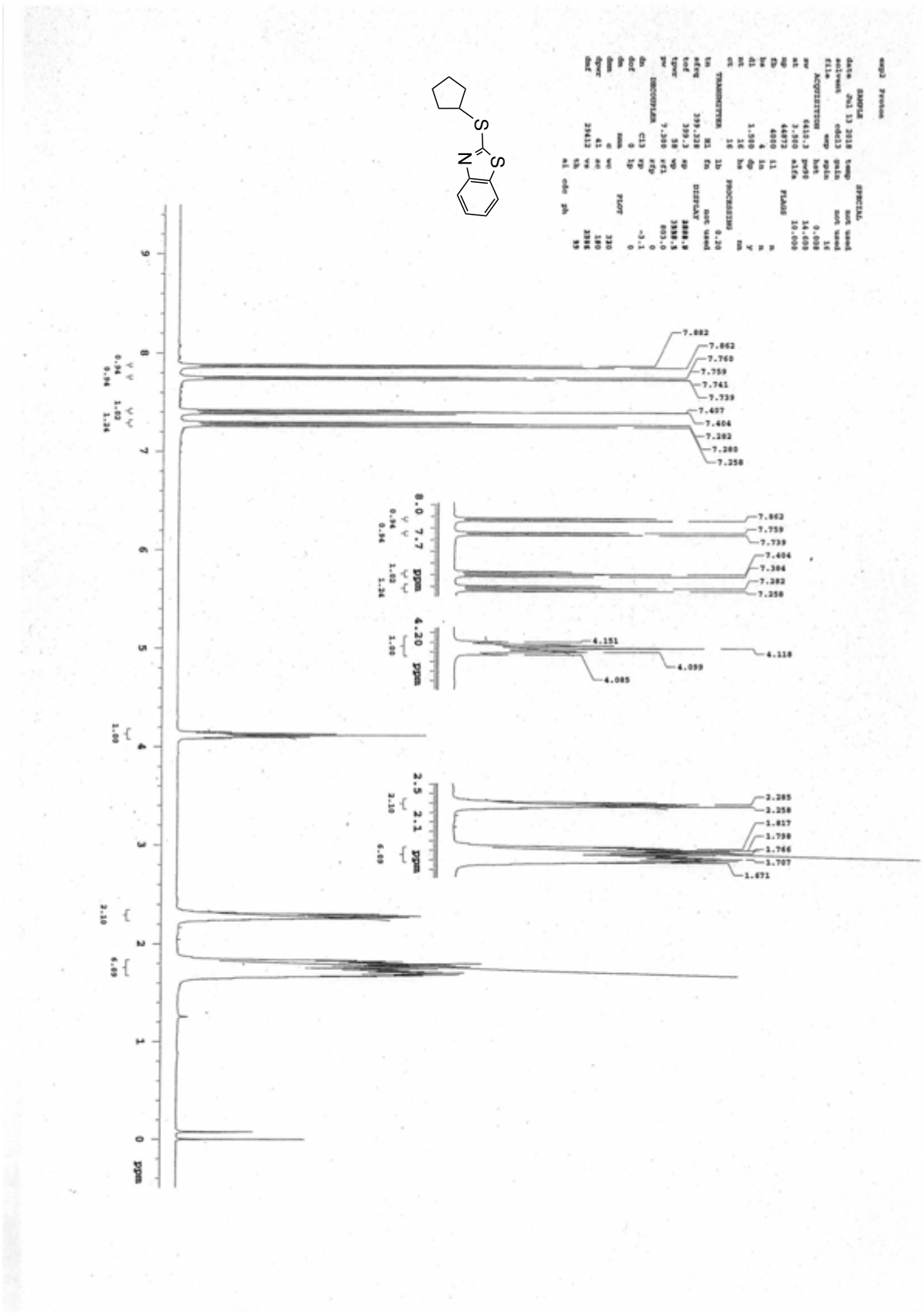


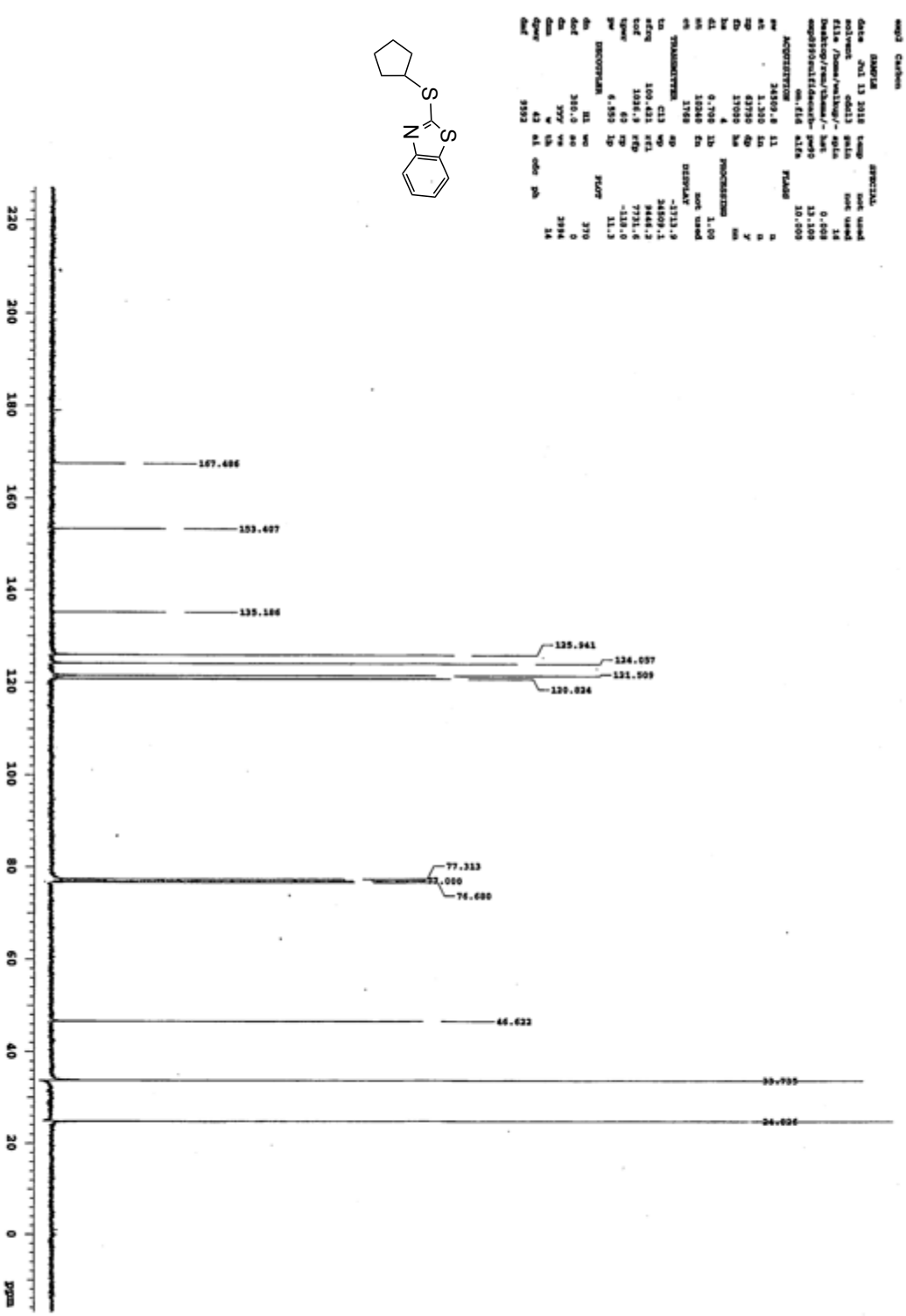
2-(6-Chlorobenzoxazolyl) cyclopentyl sulfide (3c) ^{13}C-NMR



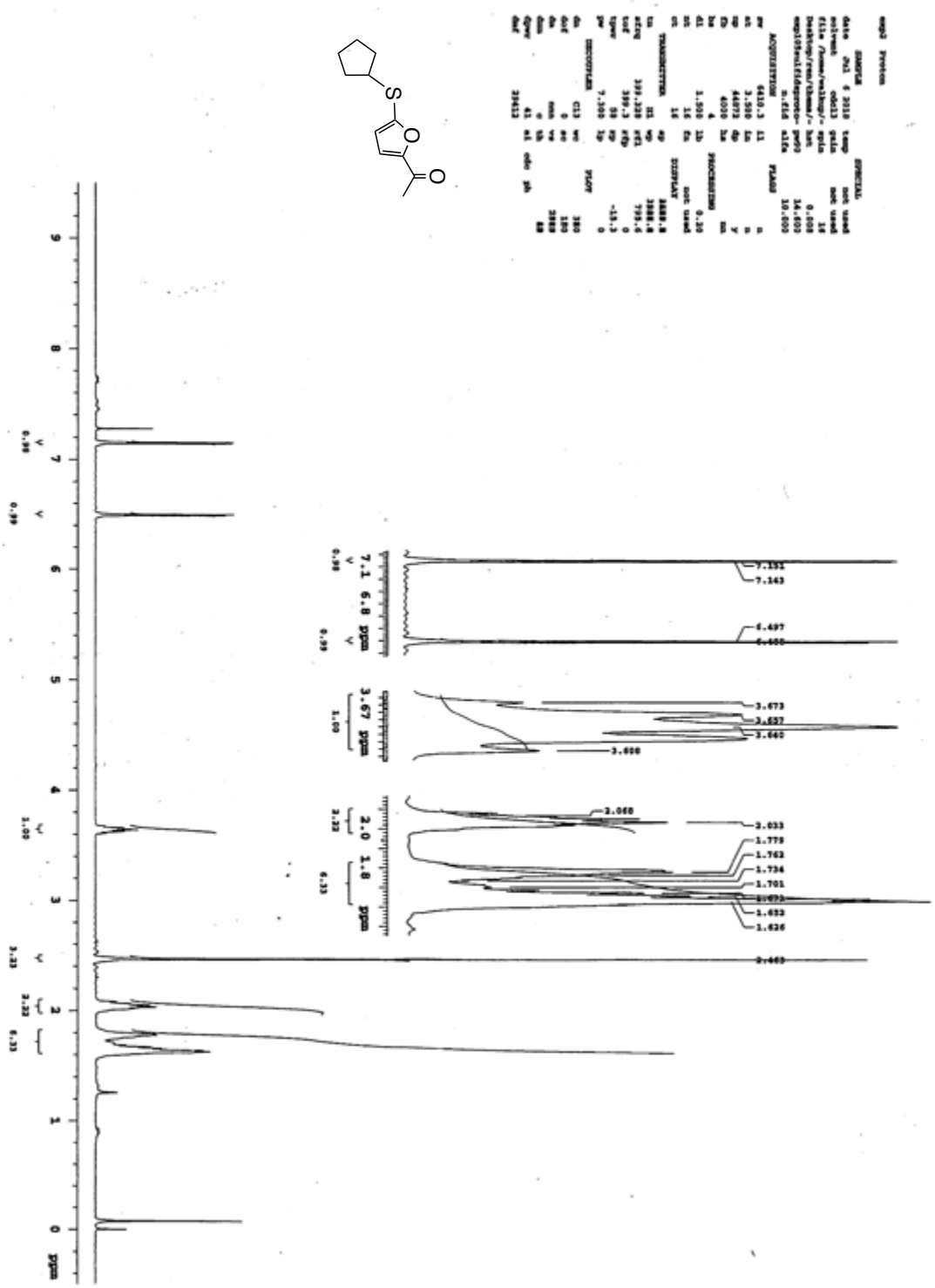
2-Benzothiazolyl cyclopentyl sulfide (3d) ^{1}H-NMR



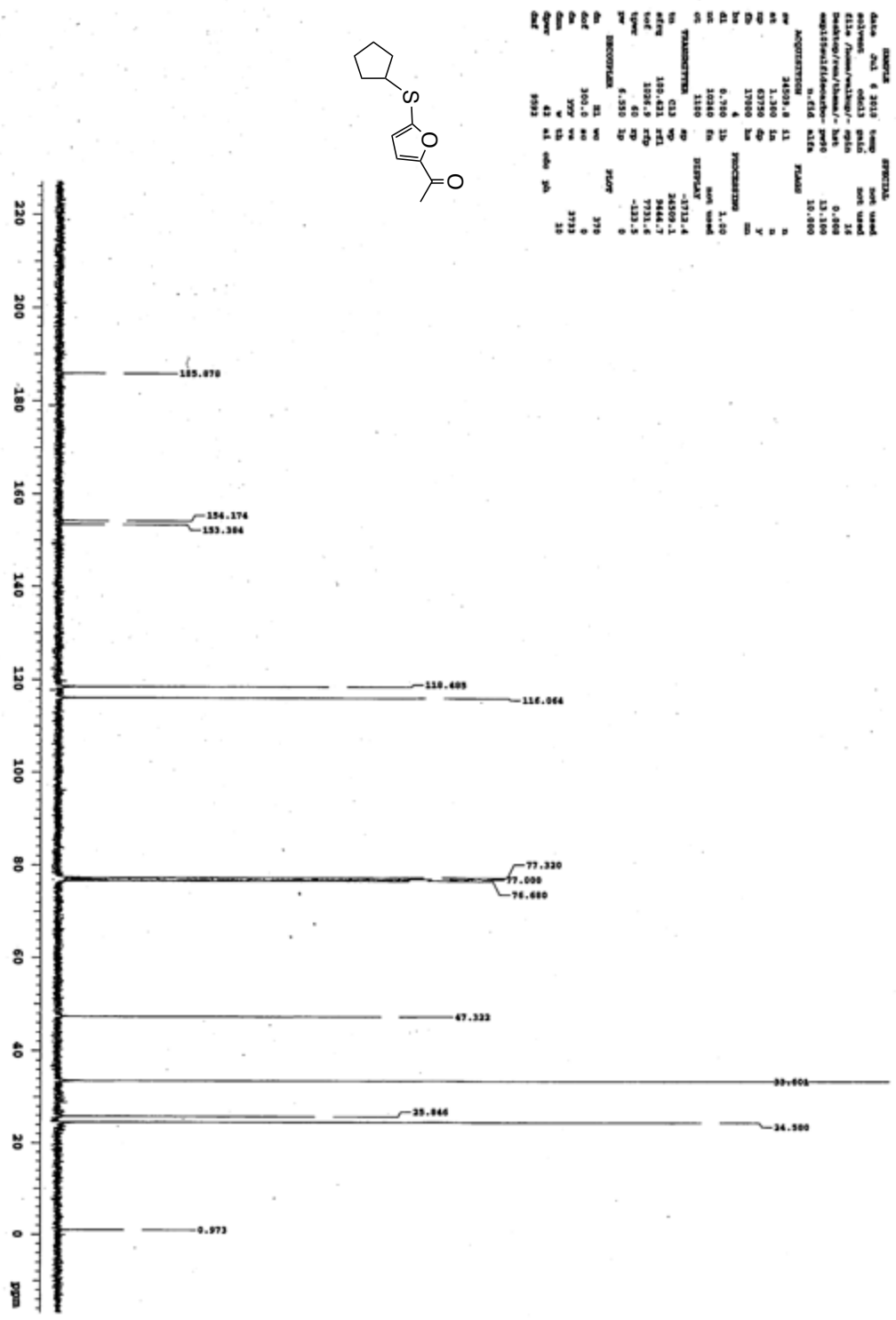
2-Benzothiazolyl cyclopentyl sulfide (3d) ^{13}C-NMR



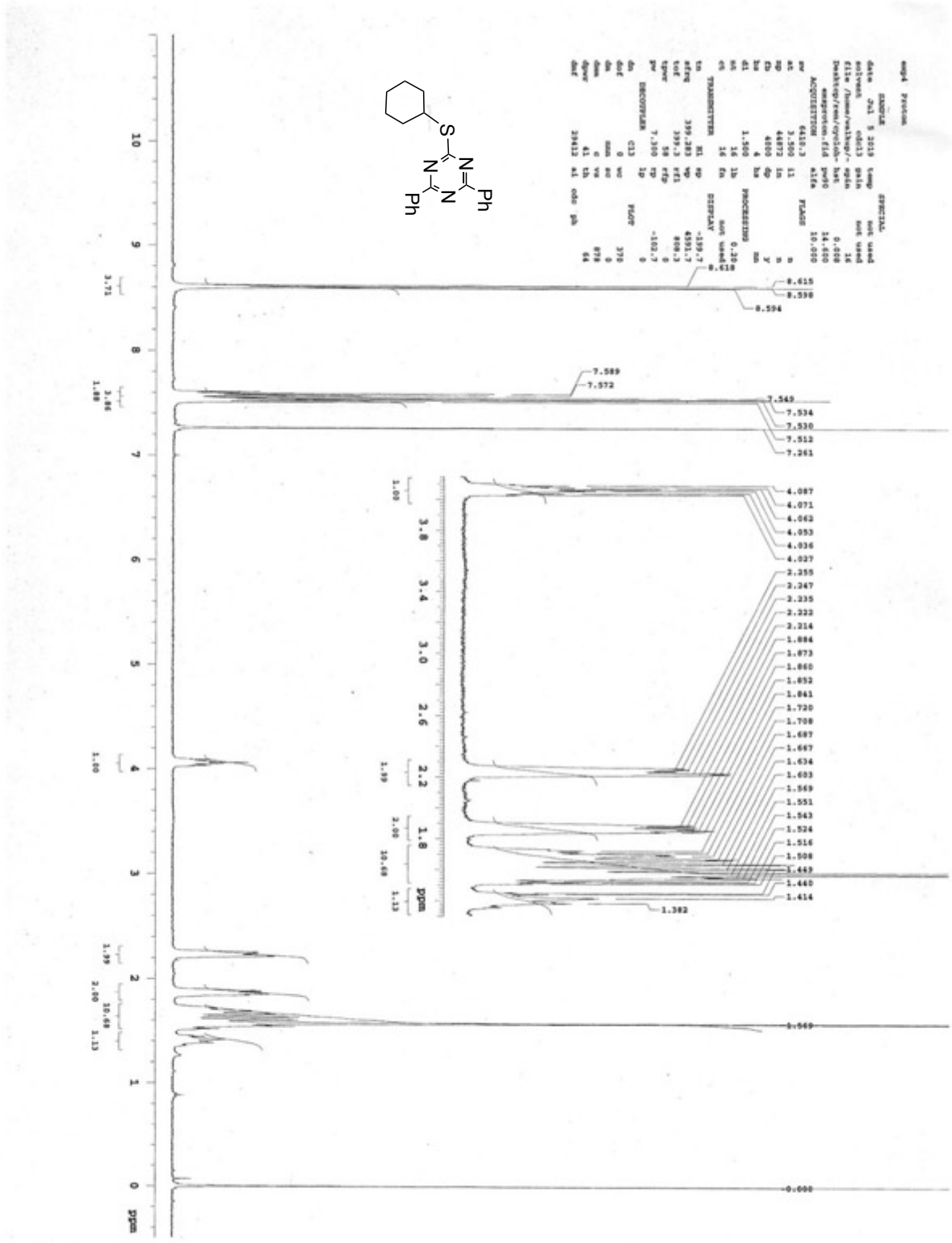
2-(5-Acetylthienyl) cyclopentyl sulfide (3e) ^{1}H-NMR



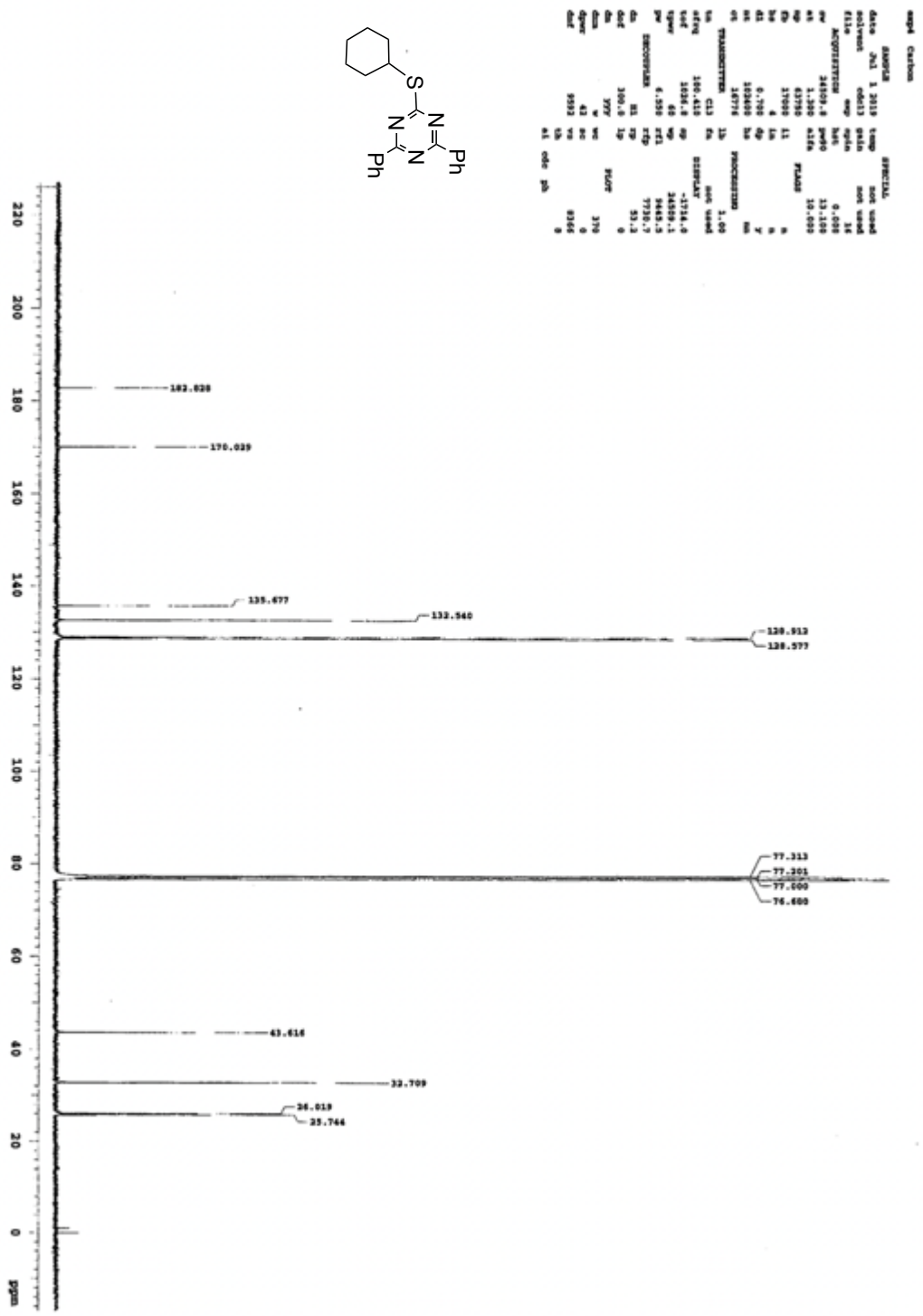
2-(5-Acetylthienyl) cyclopentyl sulfide (3e) ^{13}C-NMR



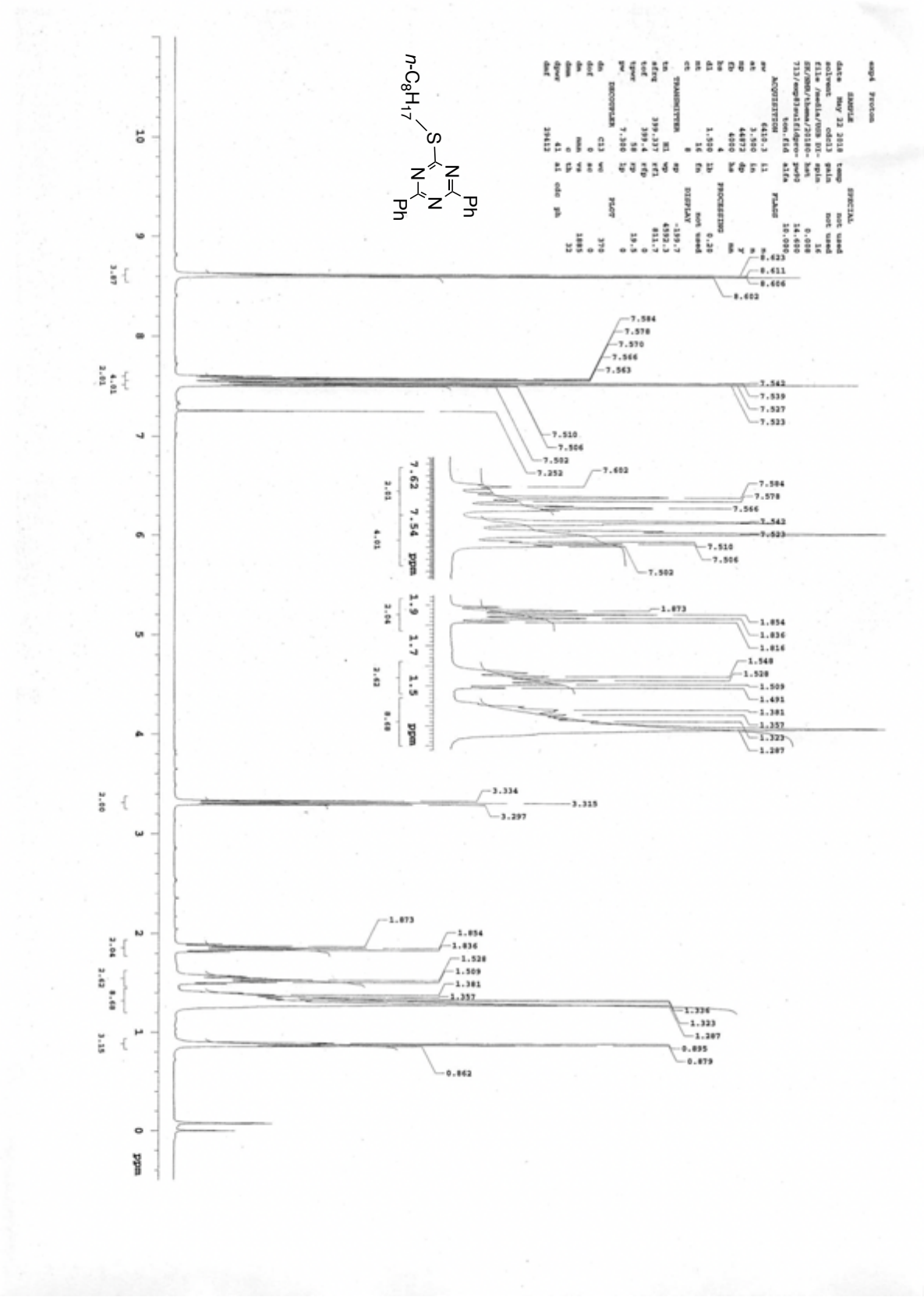
2-(4,6-Diphenyl-1,3,5-triazyl) cyclohexyl sulfide (3a') ^{1}H-NMR



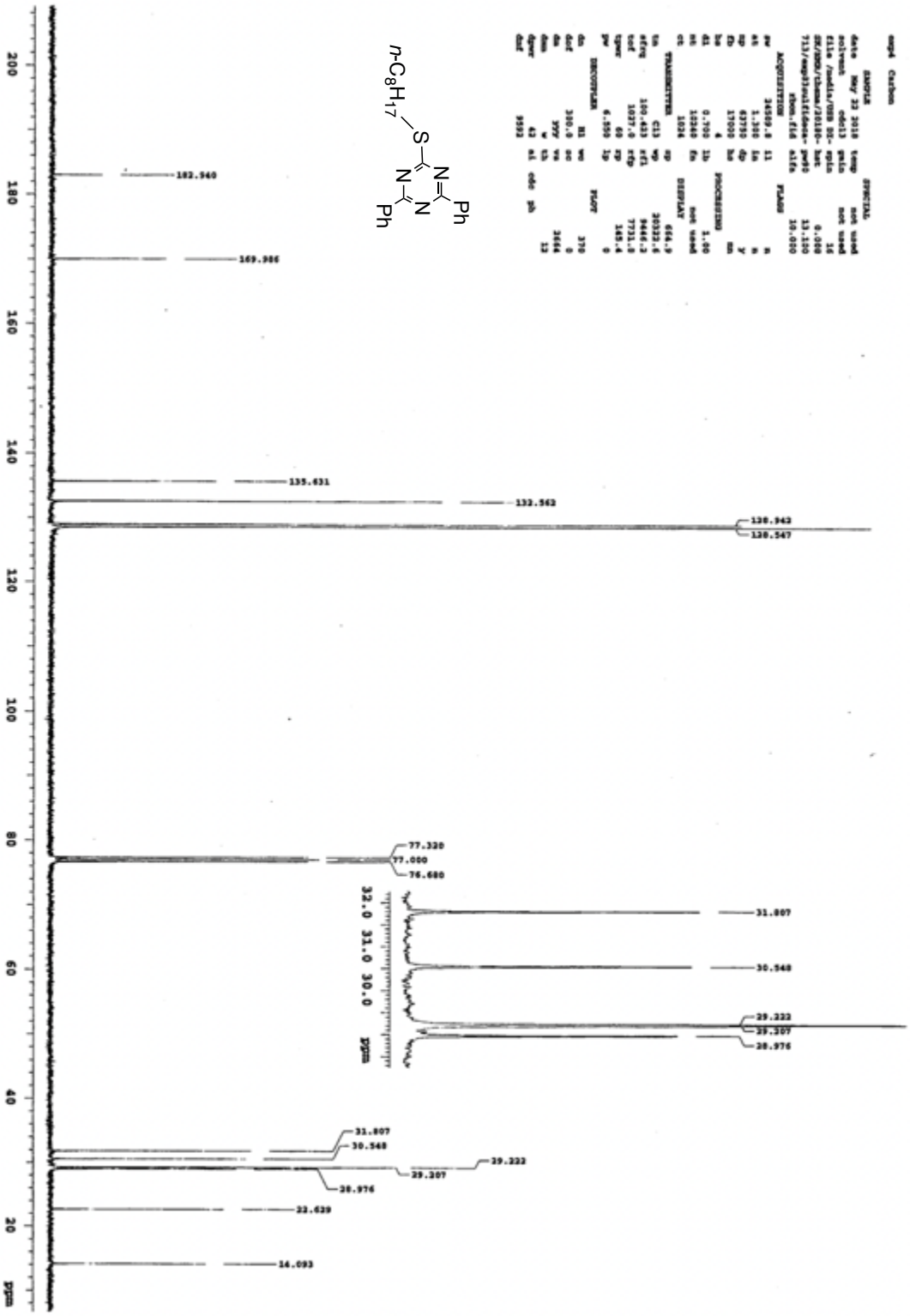
2-(4,6-Diphenyl-1,3,5-triazyl) cyclohexyl sulfide (3a') ^{13}C-NMR



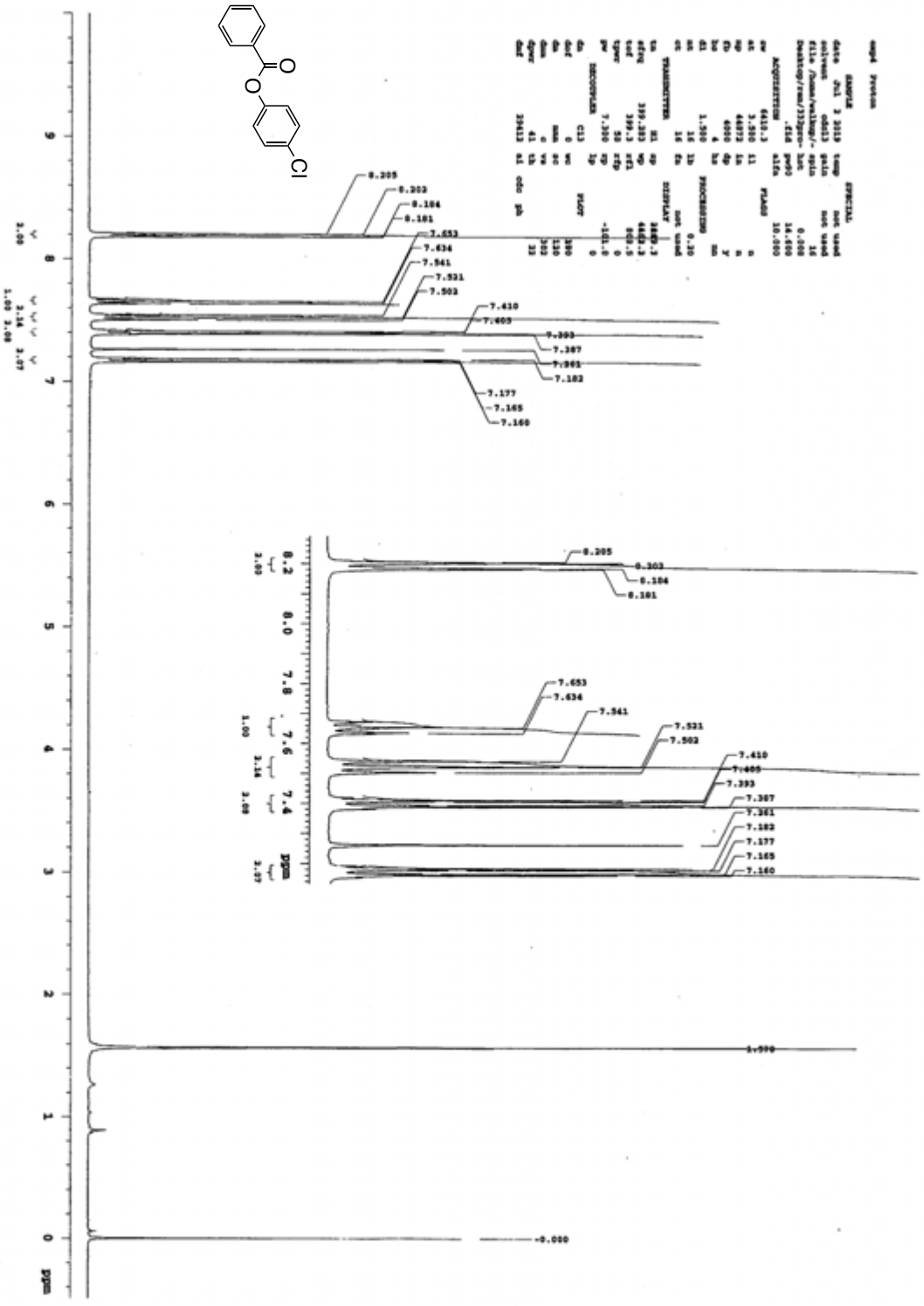
2-(4,6-Diphenyl-1,3,5-triazyl) octyl sulfide (3a”) ^{1}H-NMR



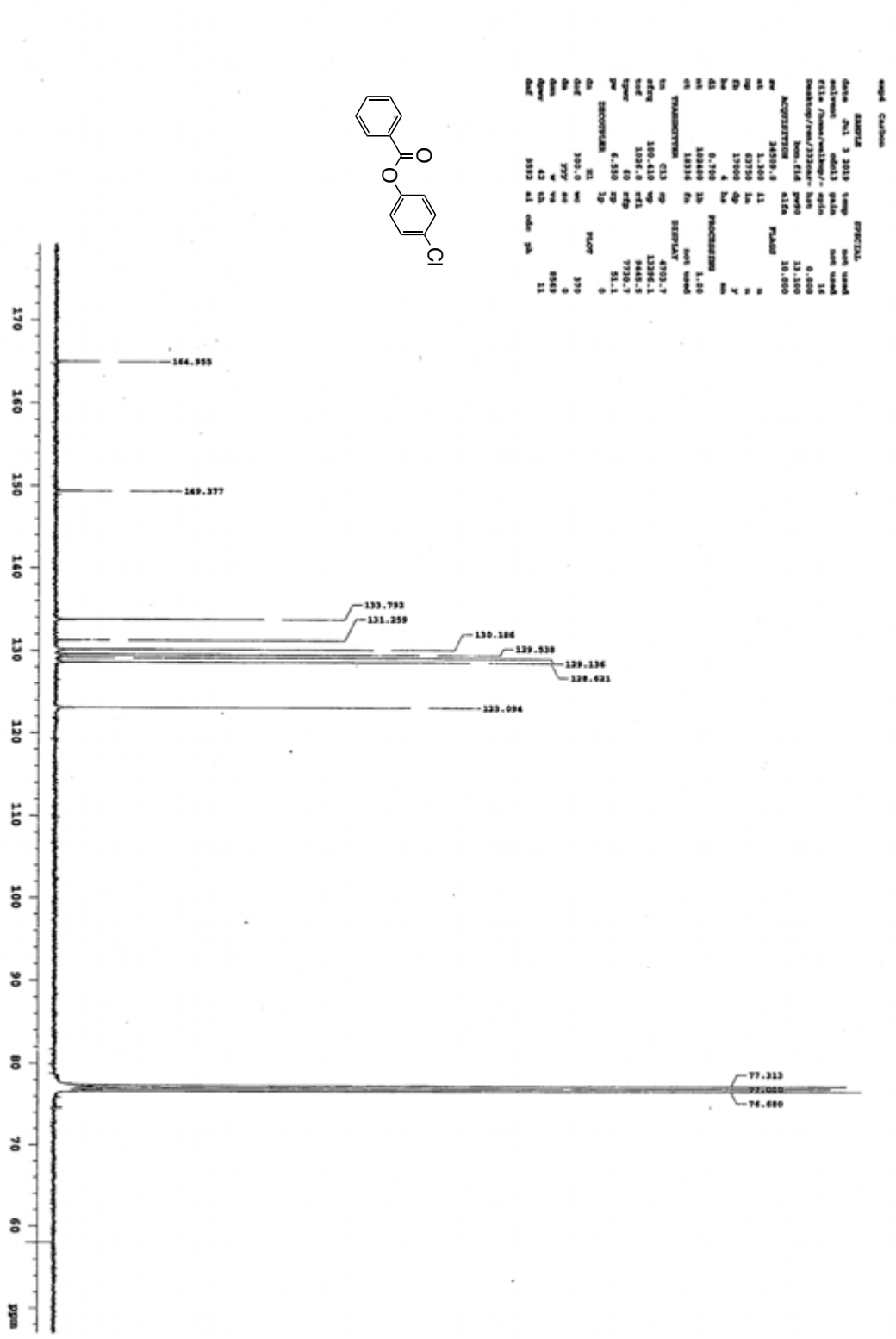
2-(4,6-Diphenyl-1,3,5-triazyl) octyl sulfide (3a”) ^{13}C-NMR



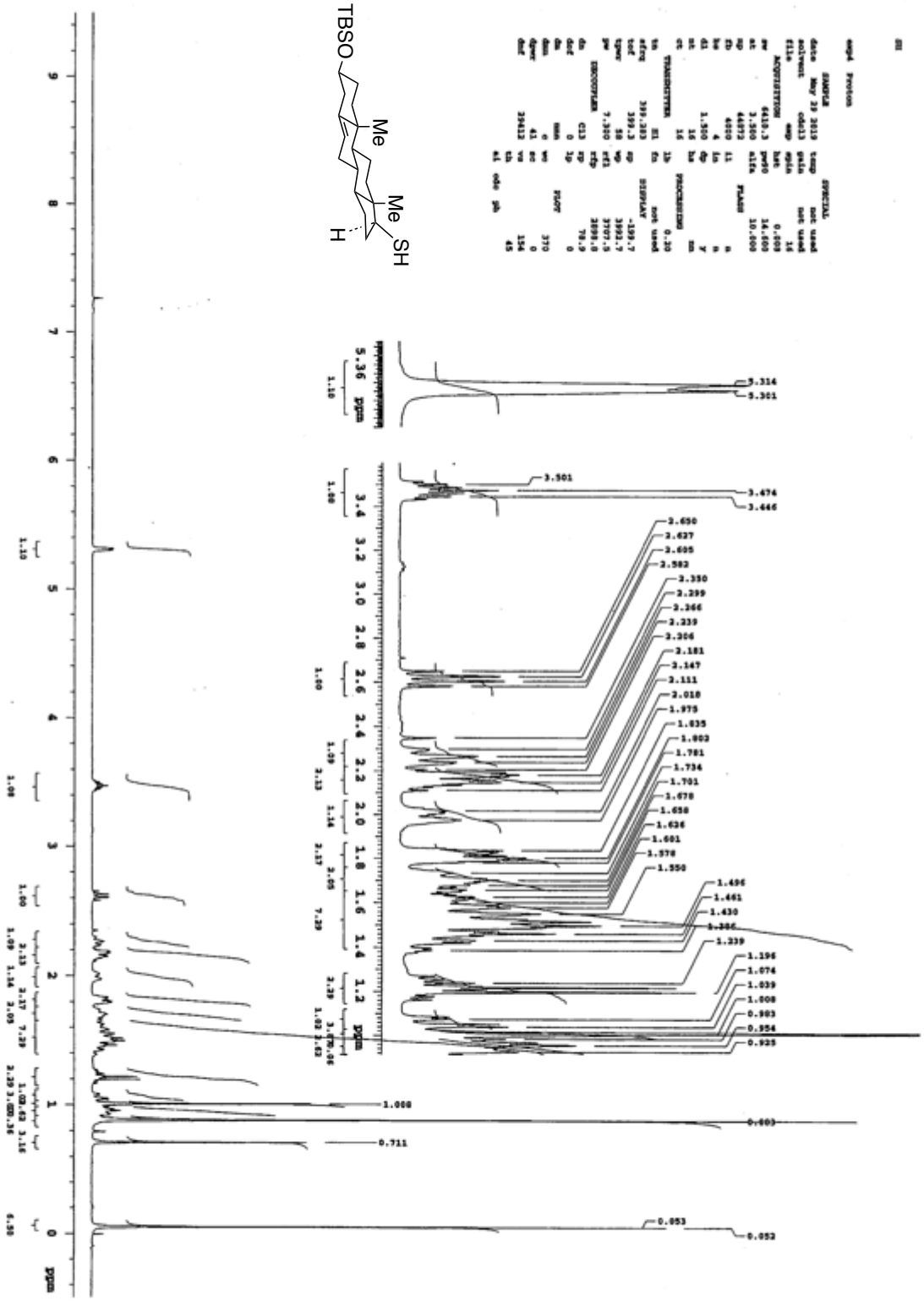
4-Chlorophenyl benzoate (4) ^{1}H-NMR



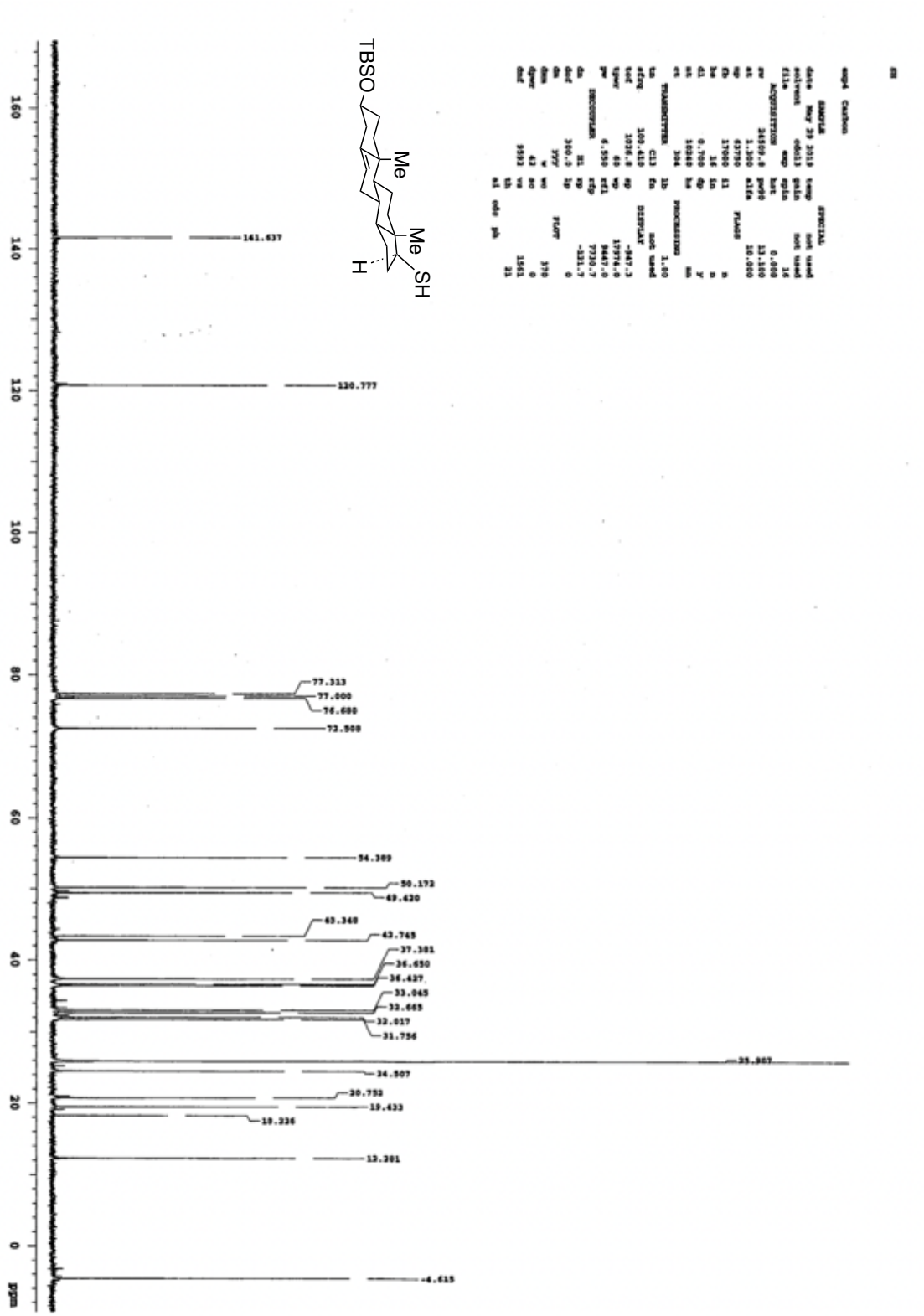
4-Chlorophenyl benzoate (4) ^{13}C-NMR



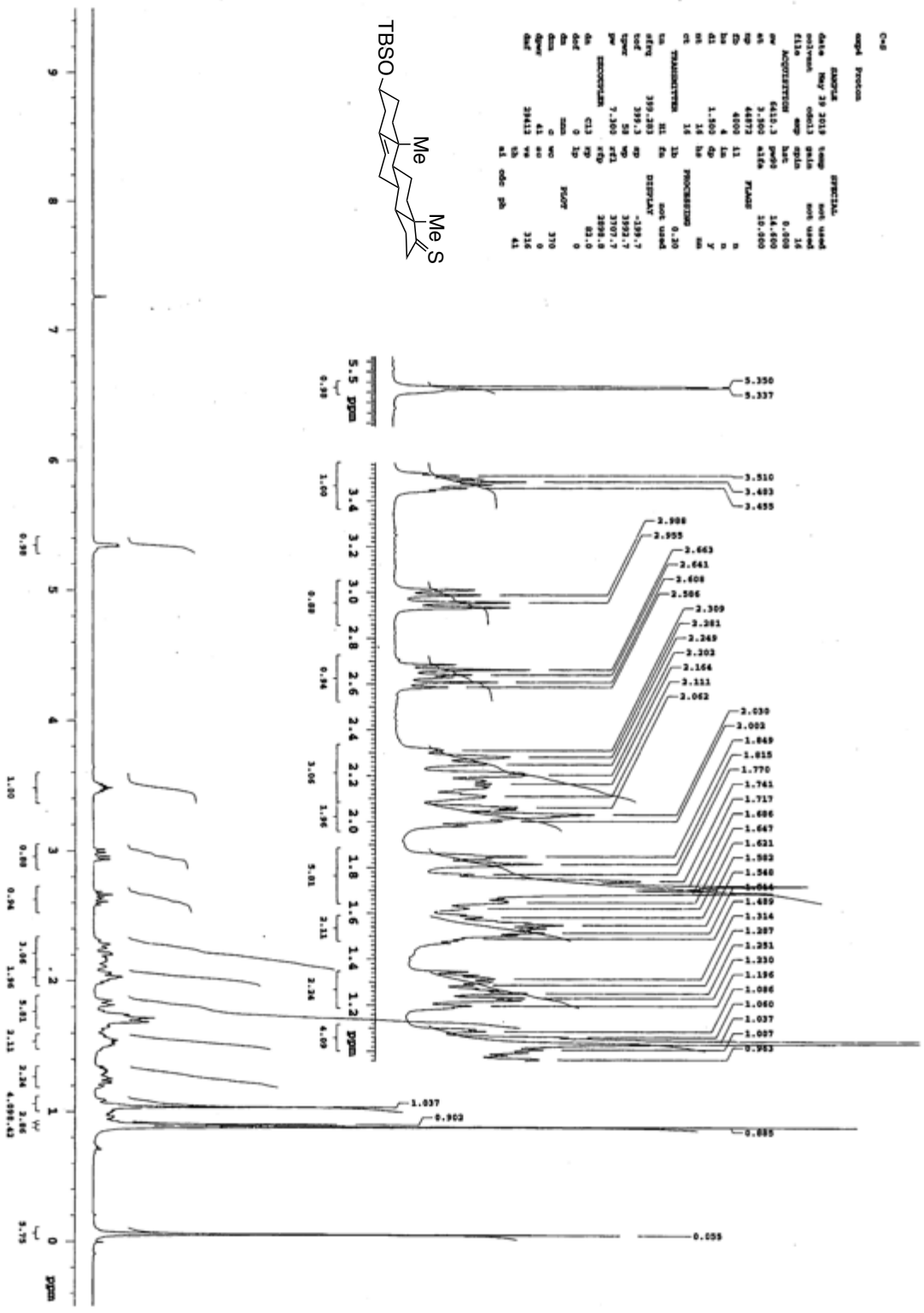
(3ß,17ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thiol (7) ^{1}H-NMR



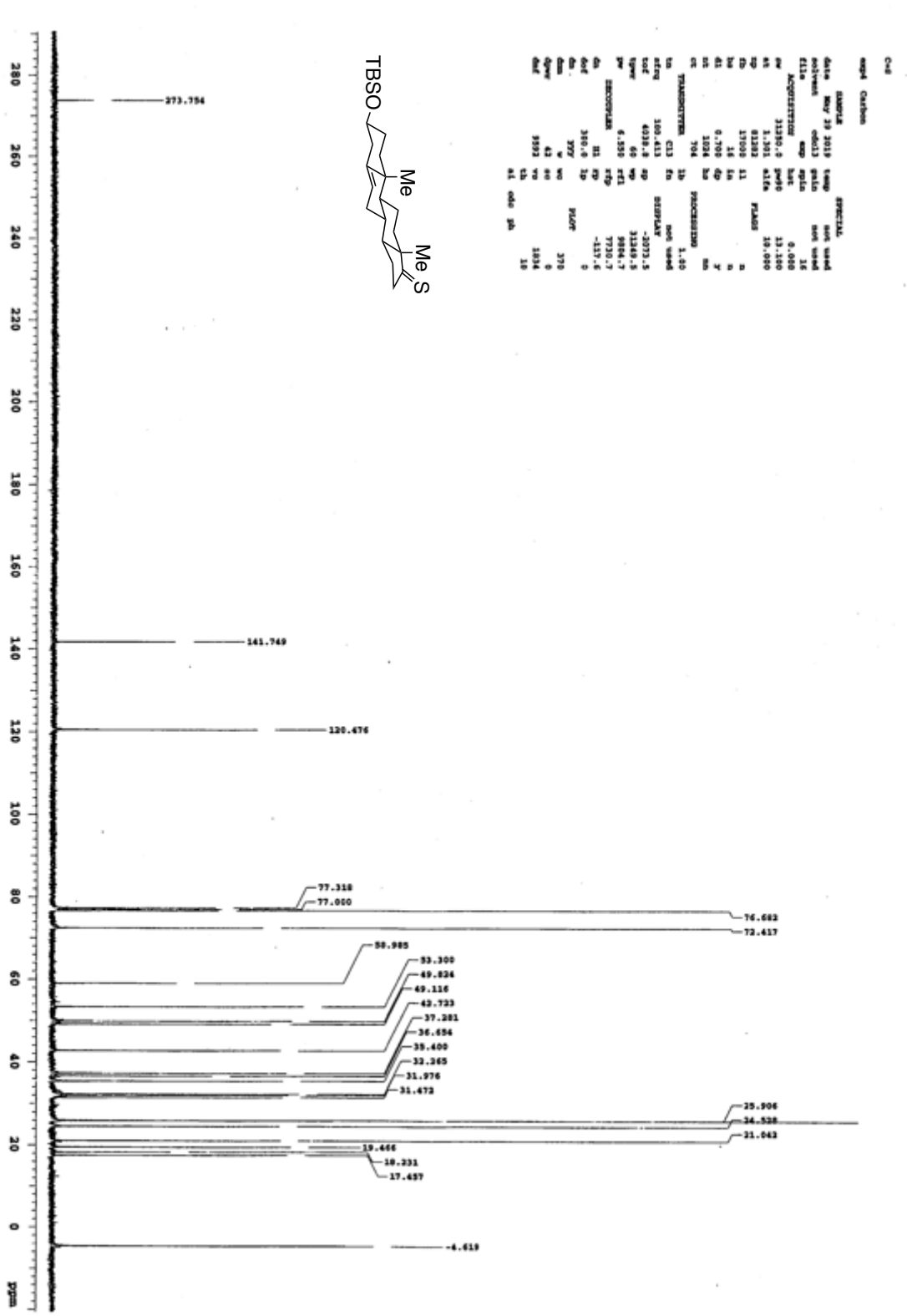
(3ß,17ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thiol (7) **^{13}C-NMR**



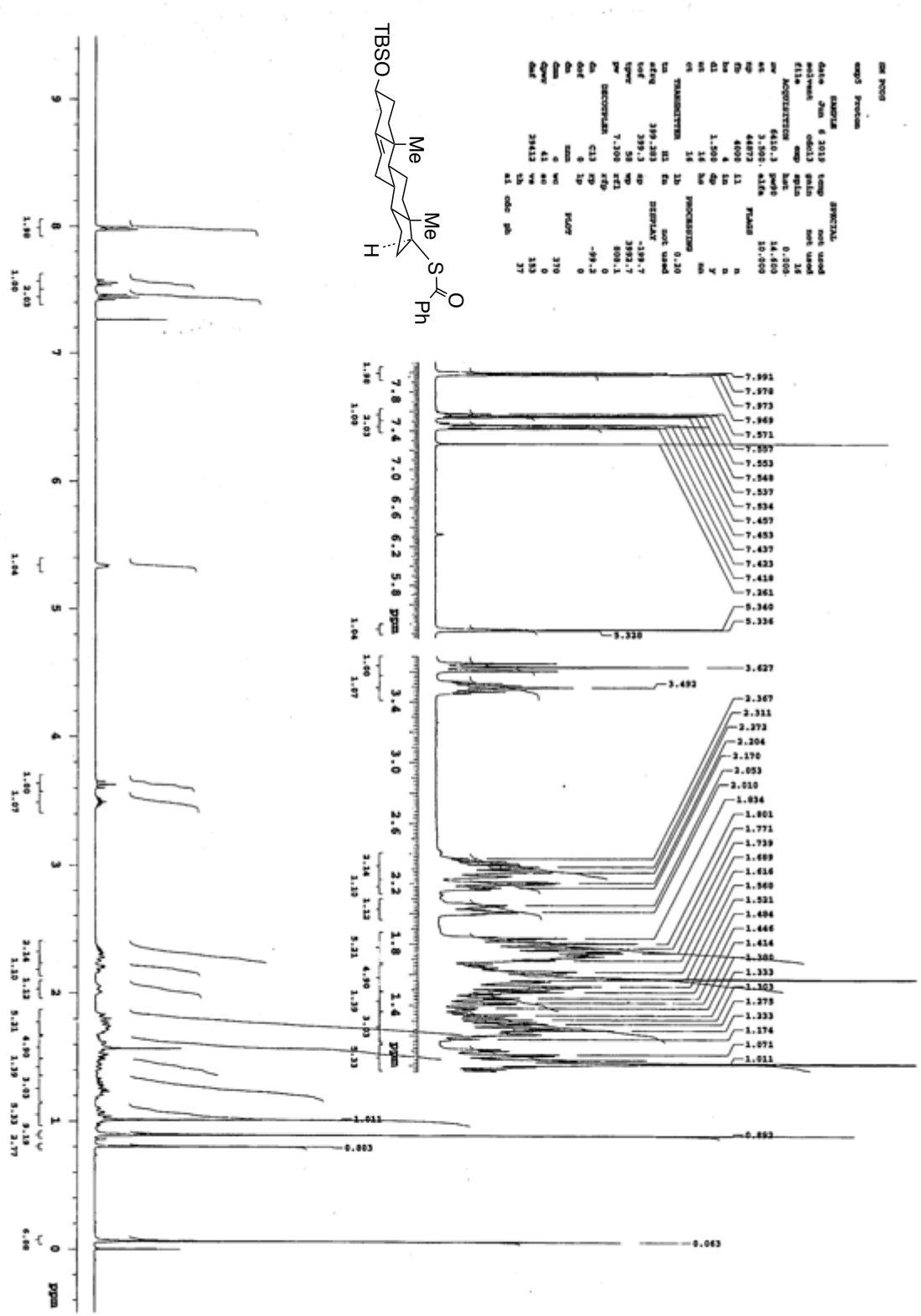
3ß-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thione (8) ^{1}H-NMR



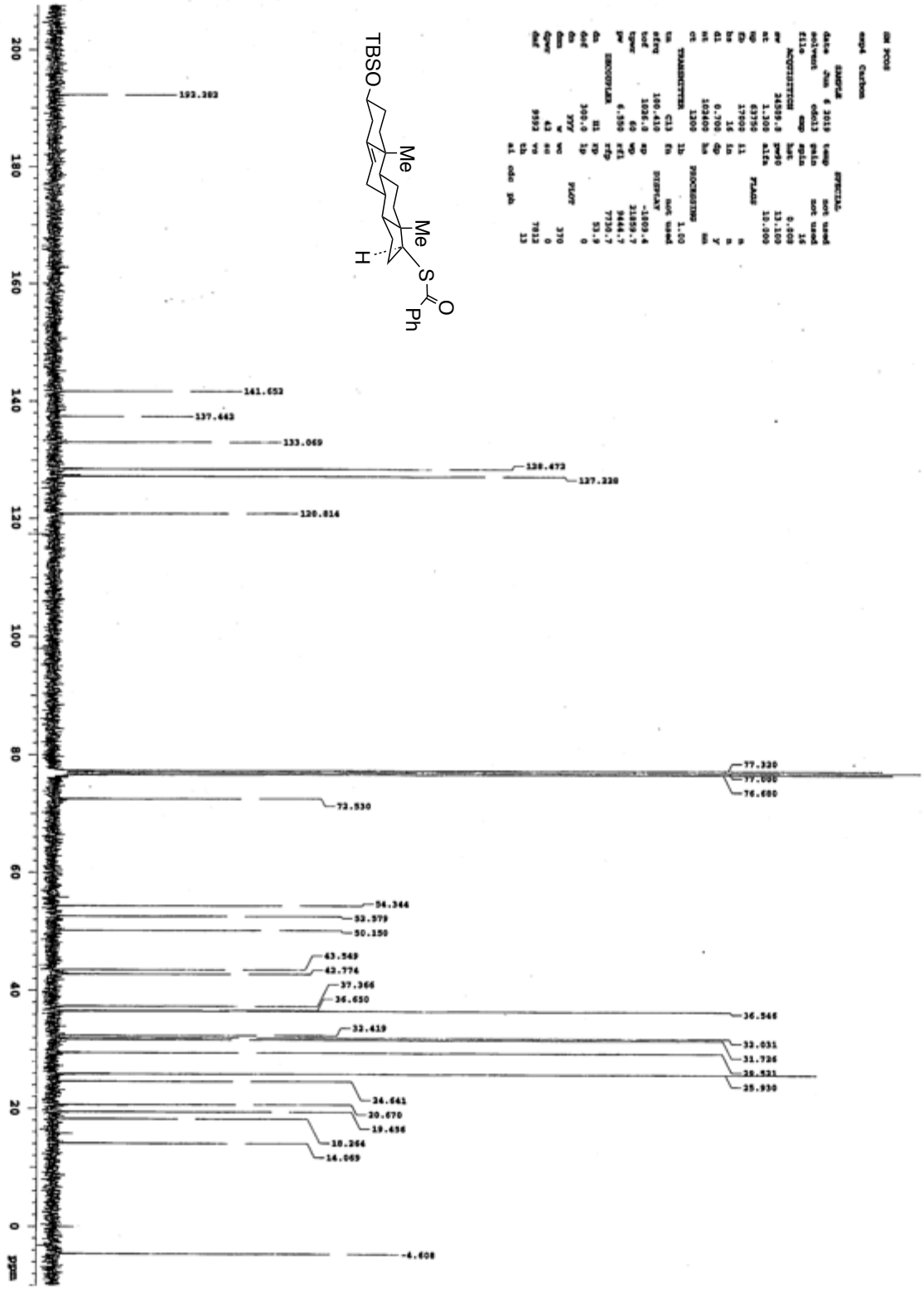
3ß-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thione (8) ^{13}**C-NMR**



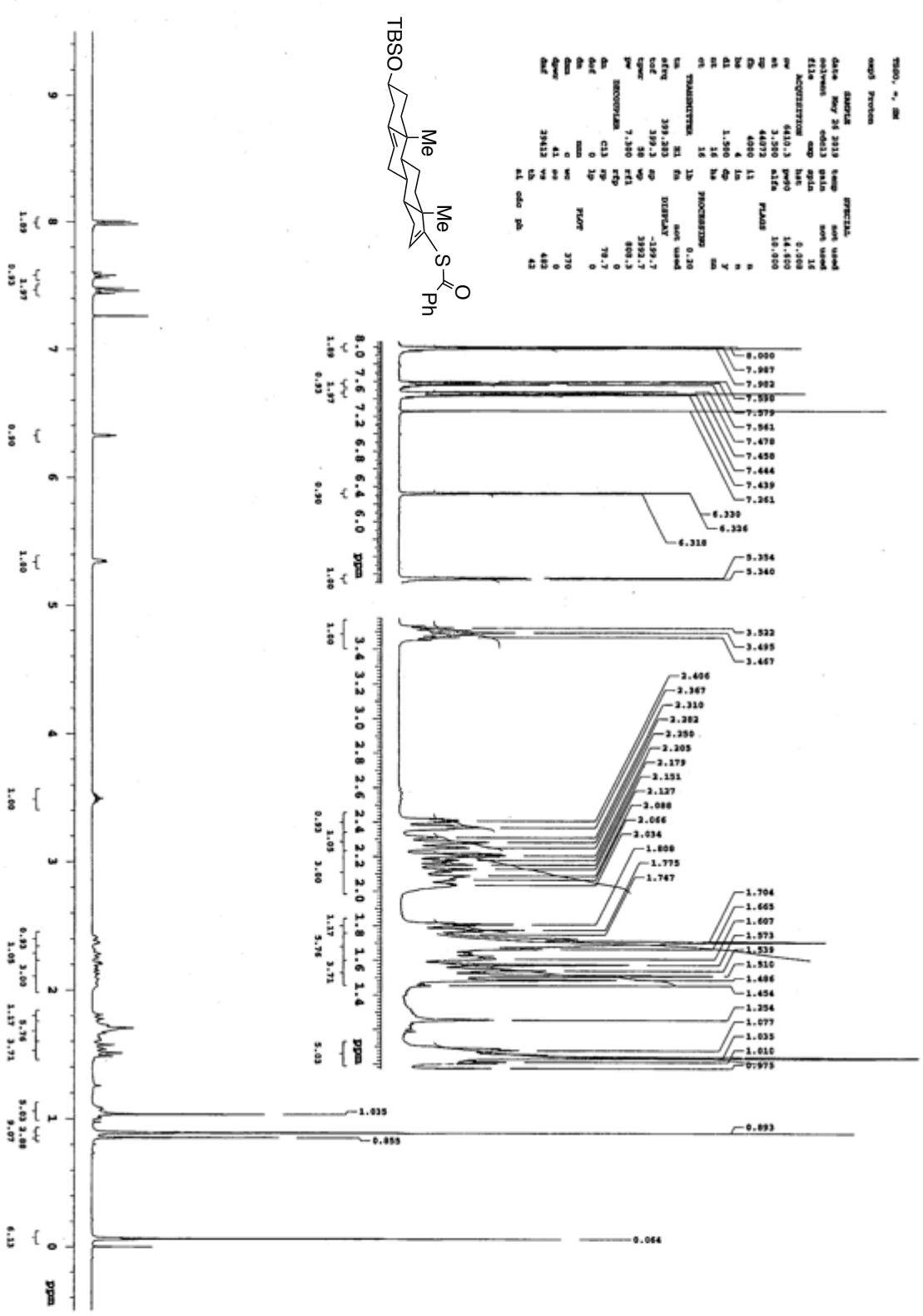
(3ß,17ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (9) **^{1}H-NMR**



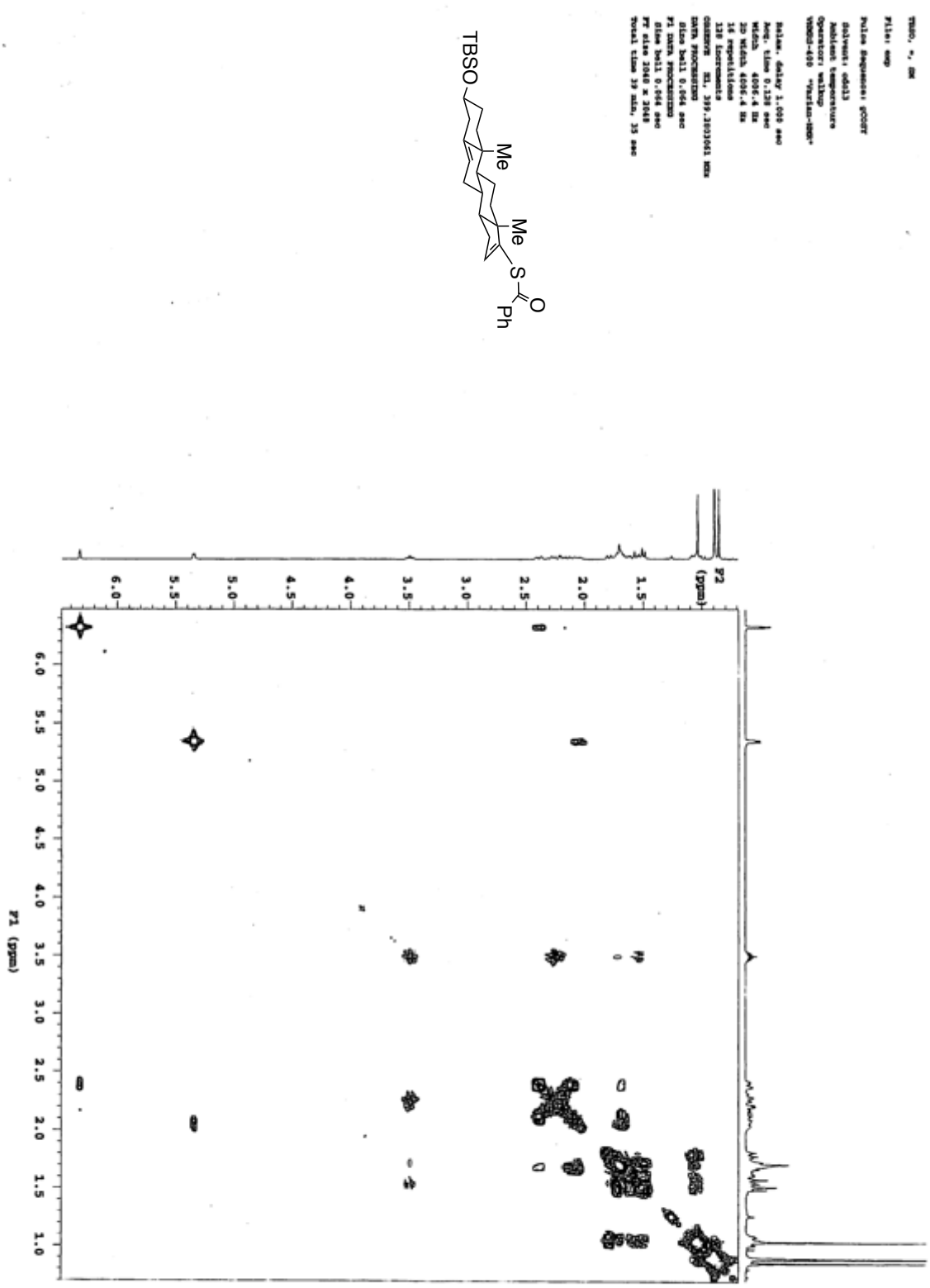
(3ß,17ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (9) **^{13}C-NMR**



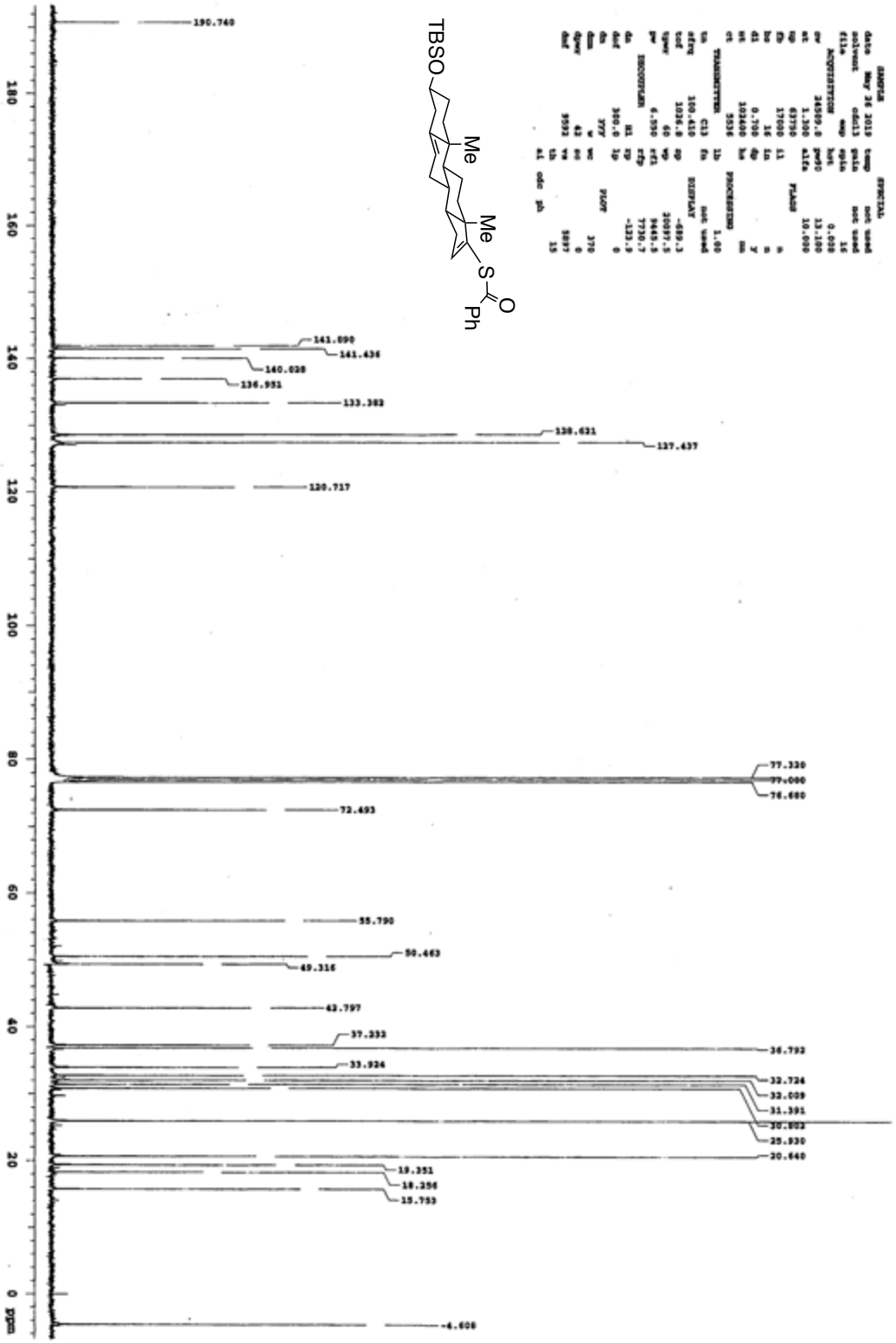
(3ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (10) ^{1}**H-NMR**



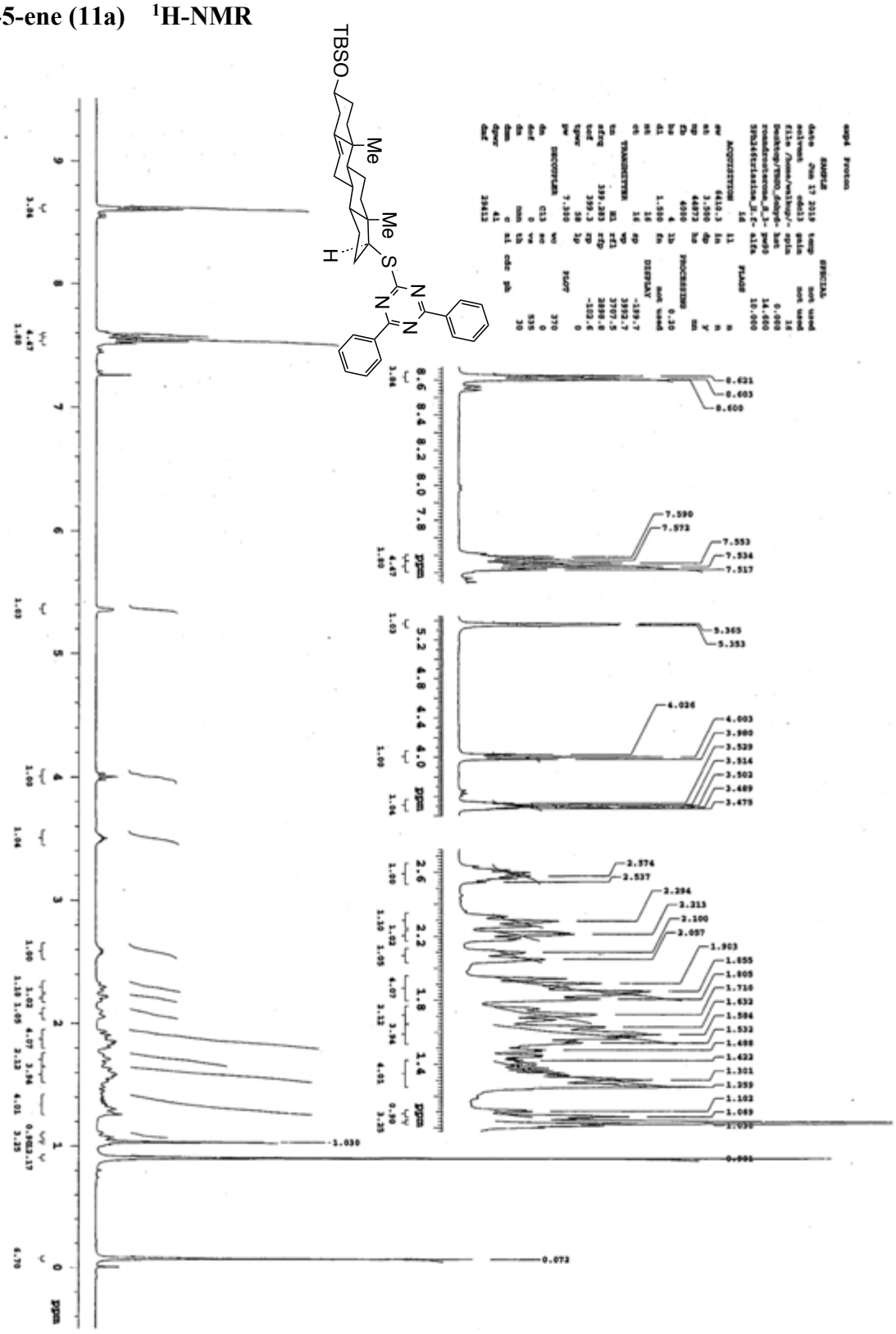
(3ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (10) HH-COSY



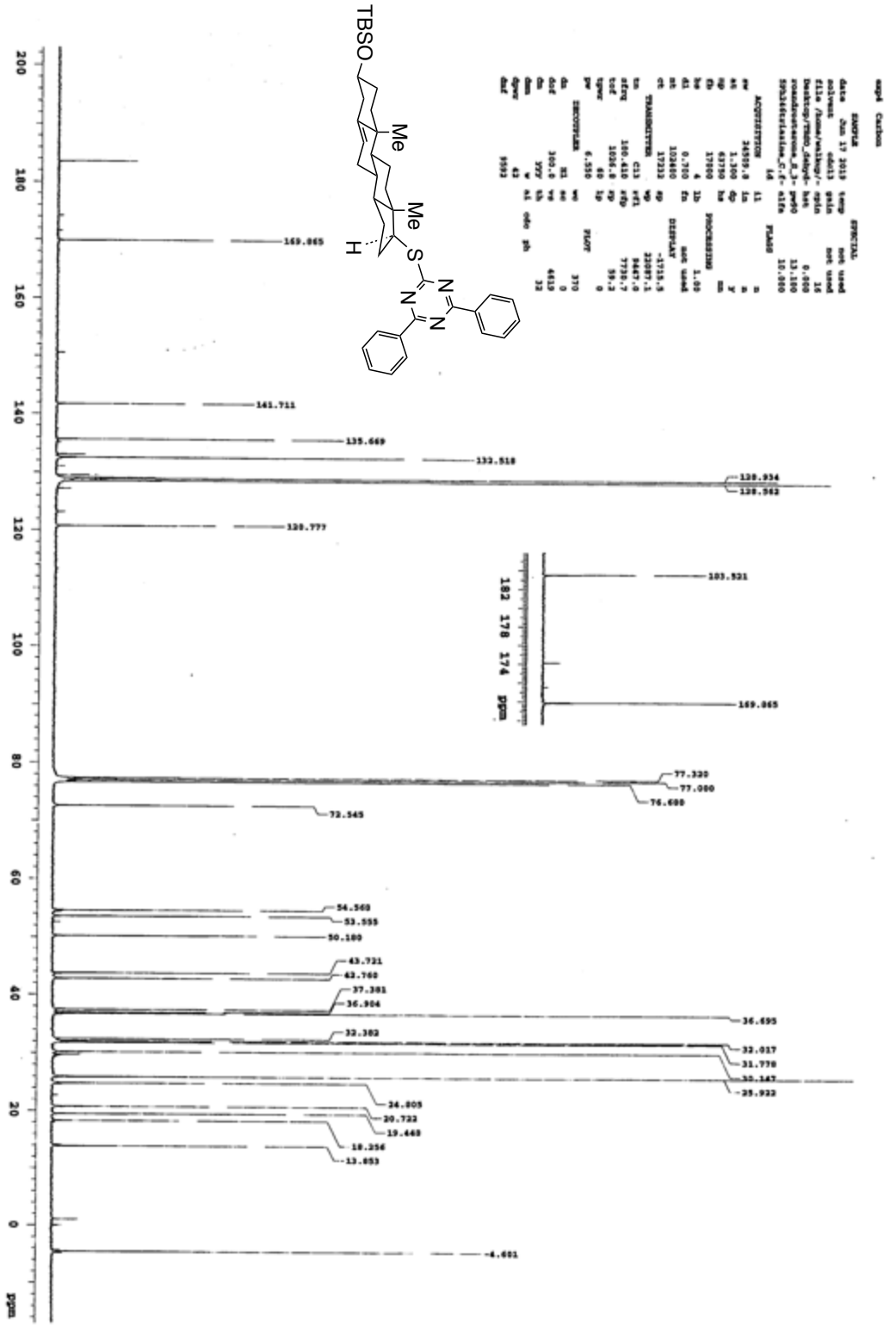
(3ß)-17-(Benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (10) ^{13}**C-NMR**



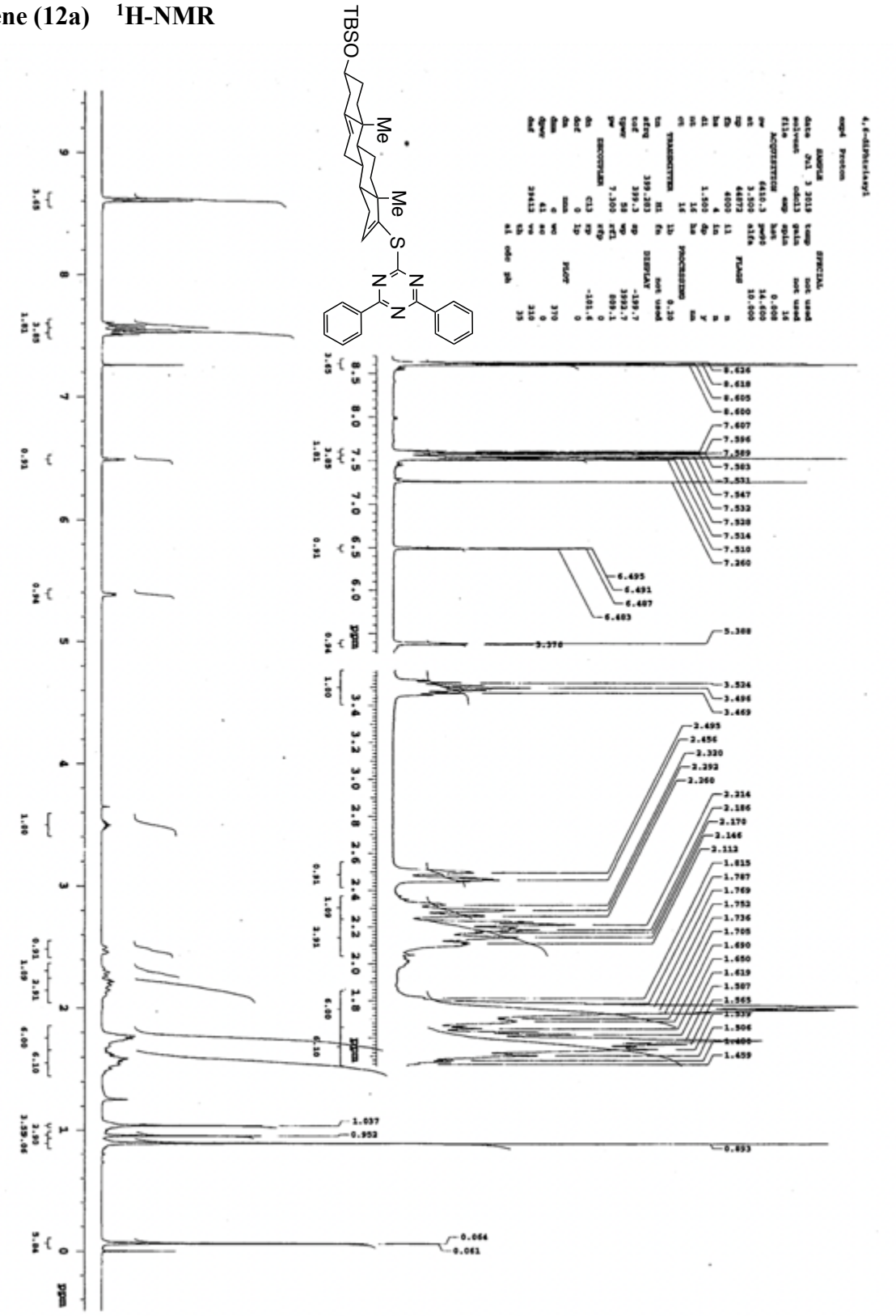
(3ß,17ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2- (4,6-diphenyl-1,3,5-triazyl)thio] androst-5-ene (11a) **^{1}H-NMR**



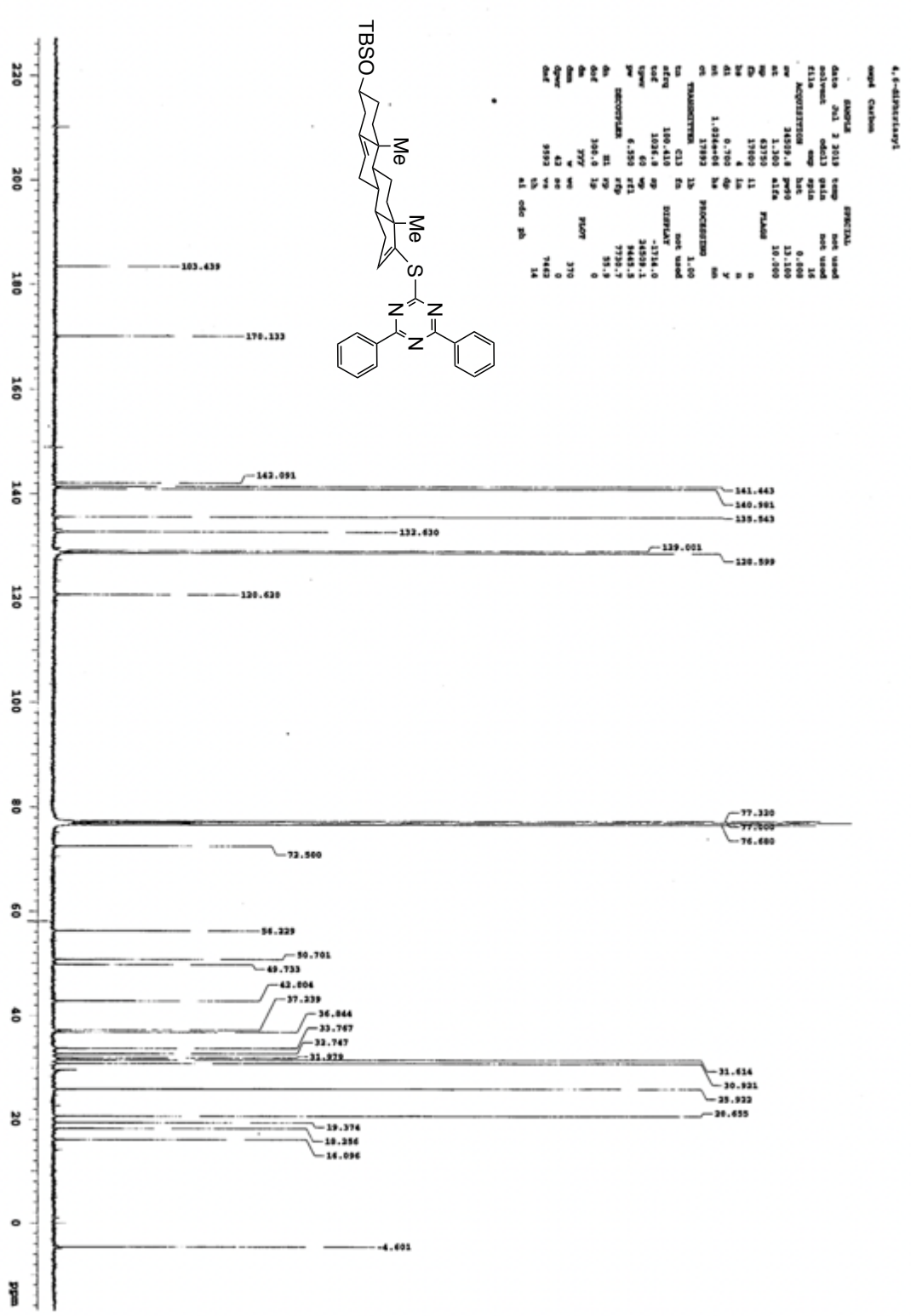
(3ß,17ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2- (4,6-diphenyl-1,3,5-triazyl)thio] androst-5-ene (11a) ^{13}**C-NMR**



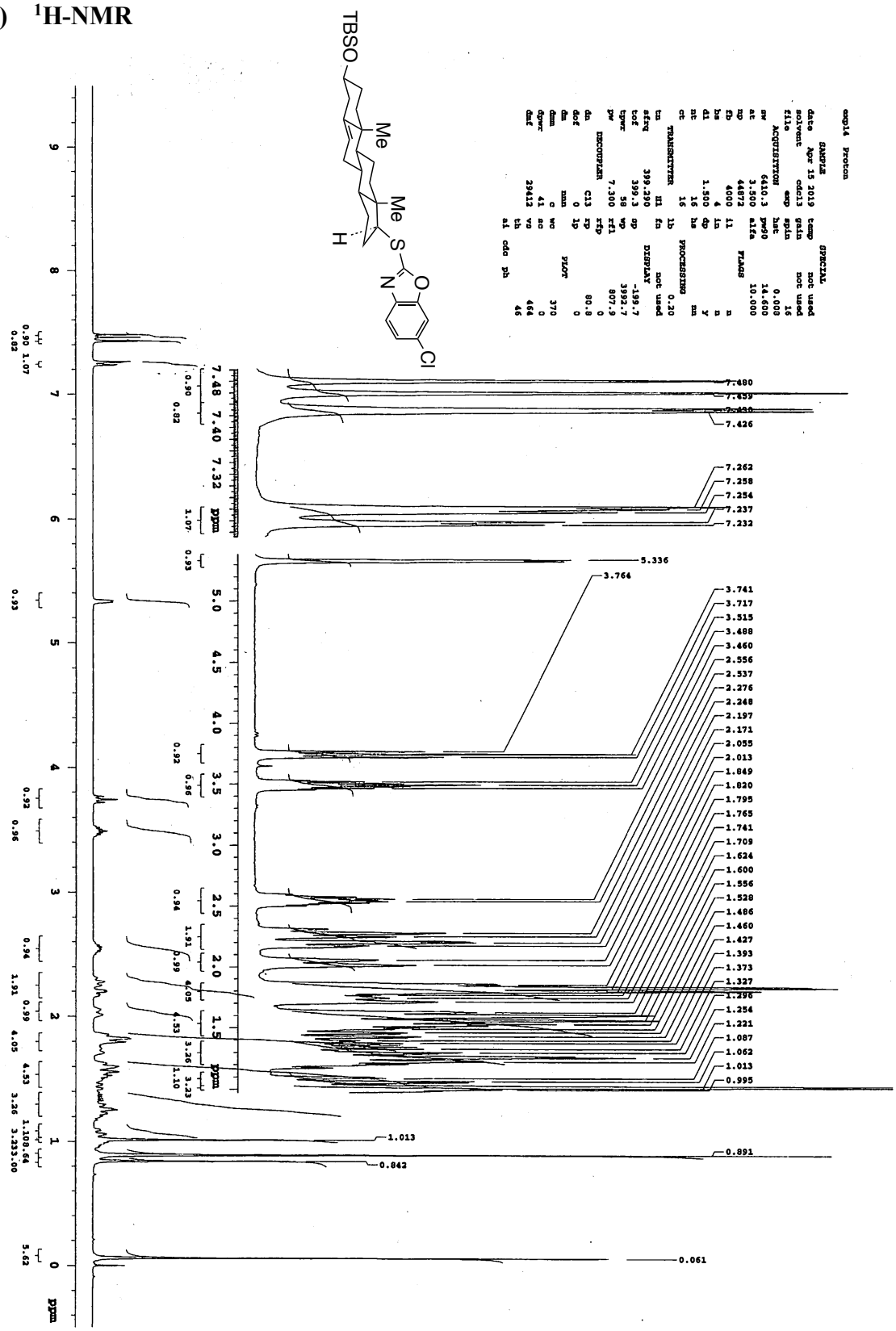
(3ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androsta-5,16-diene (12a) ^{1}**H-NMR**



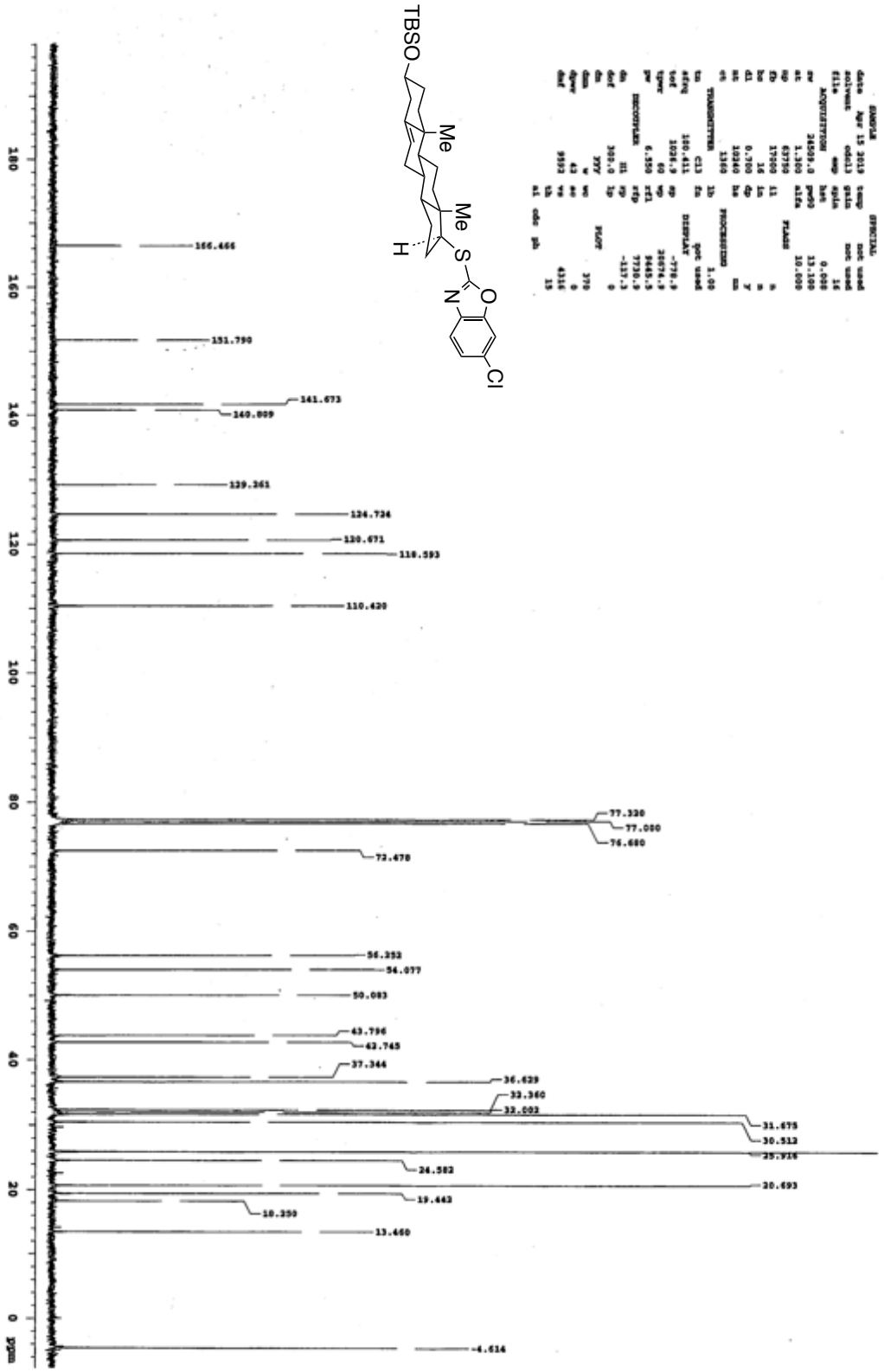
(3ß)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androsta-5,16-diene (12a) ^{13}**C-NMR**



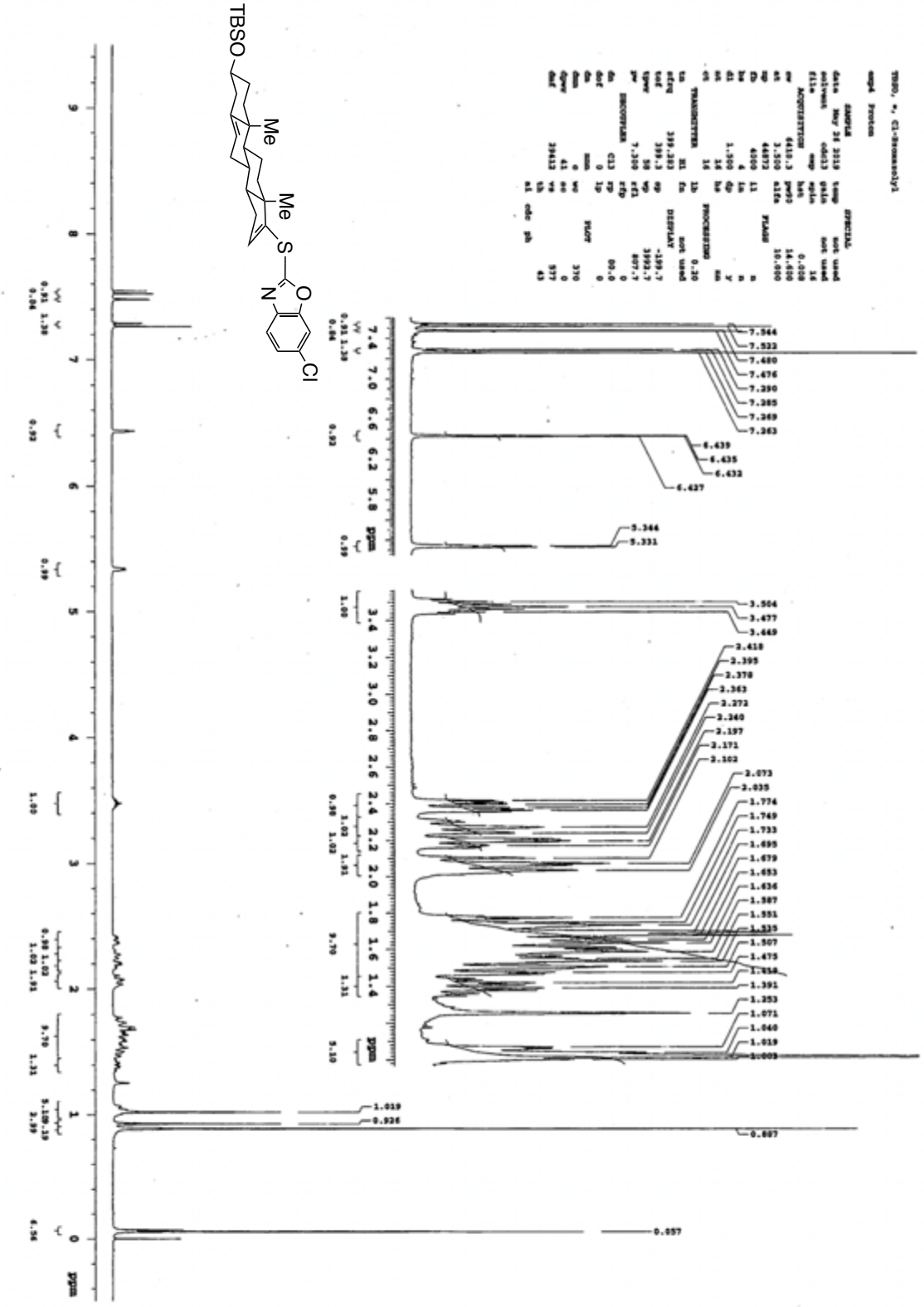
(3ß,17ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11c) ^{1}H-NMR



(3ß,17ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11c) ^{13}C-NMR

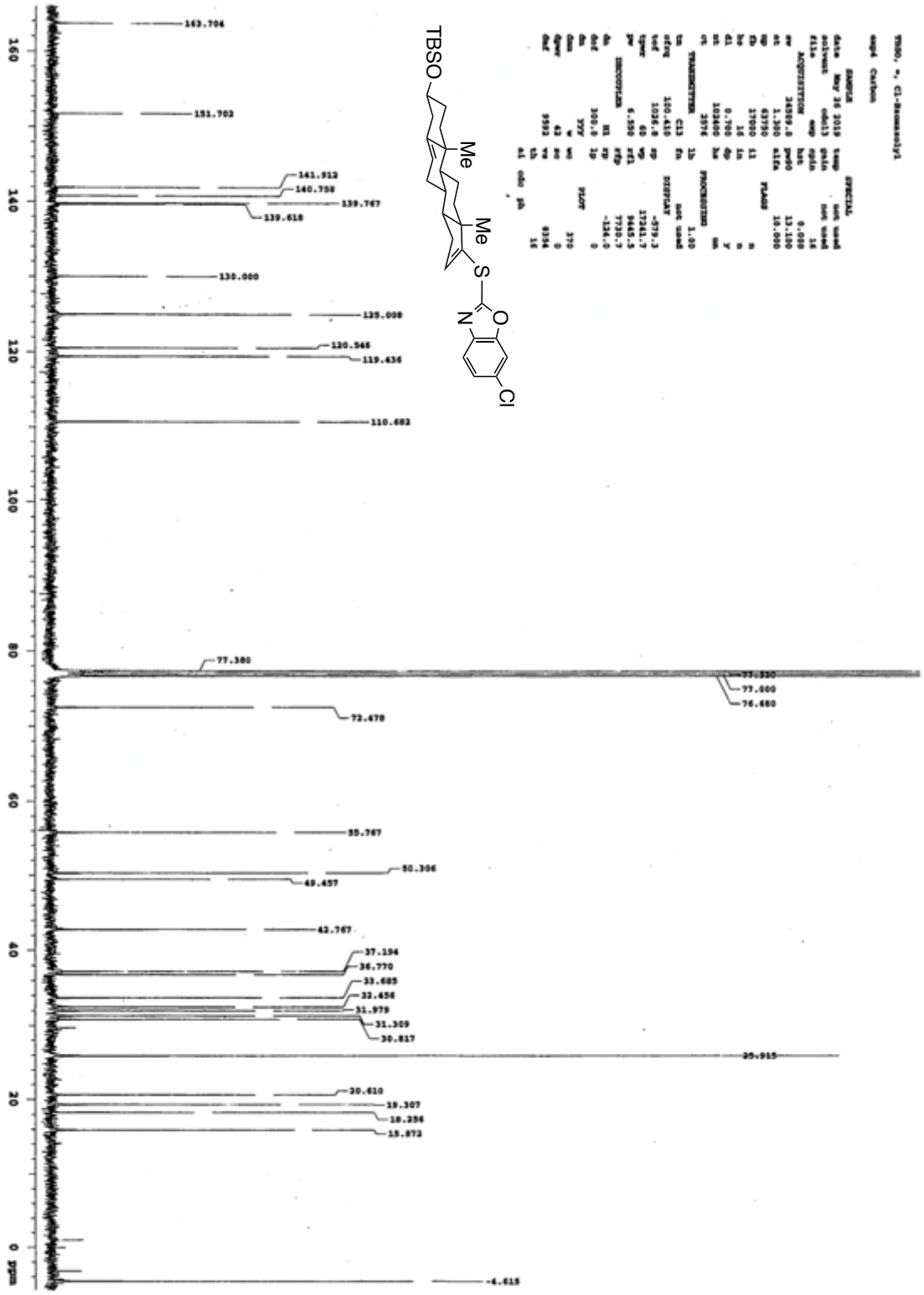


(3ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12c) **^{1}H-NMR**

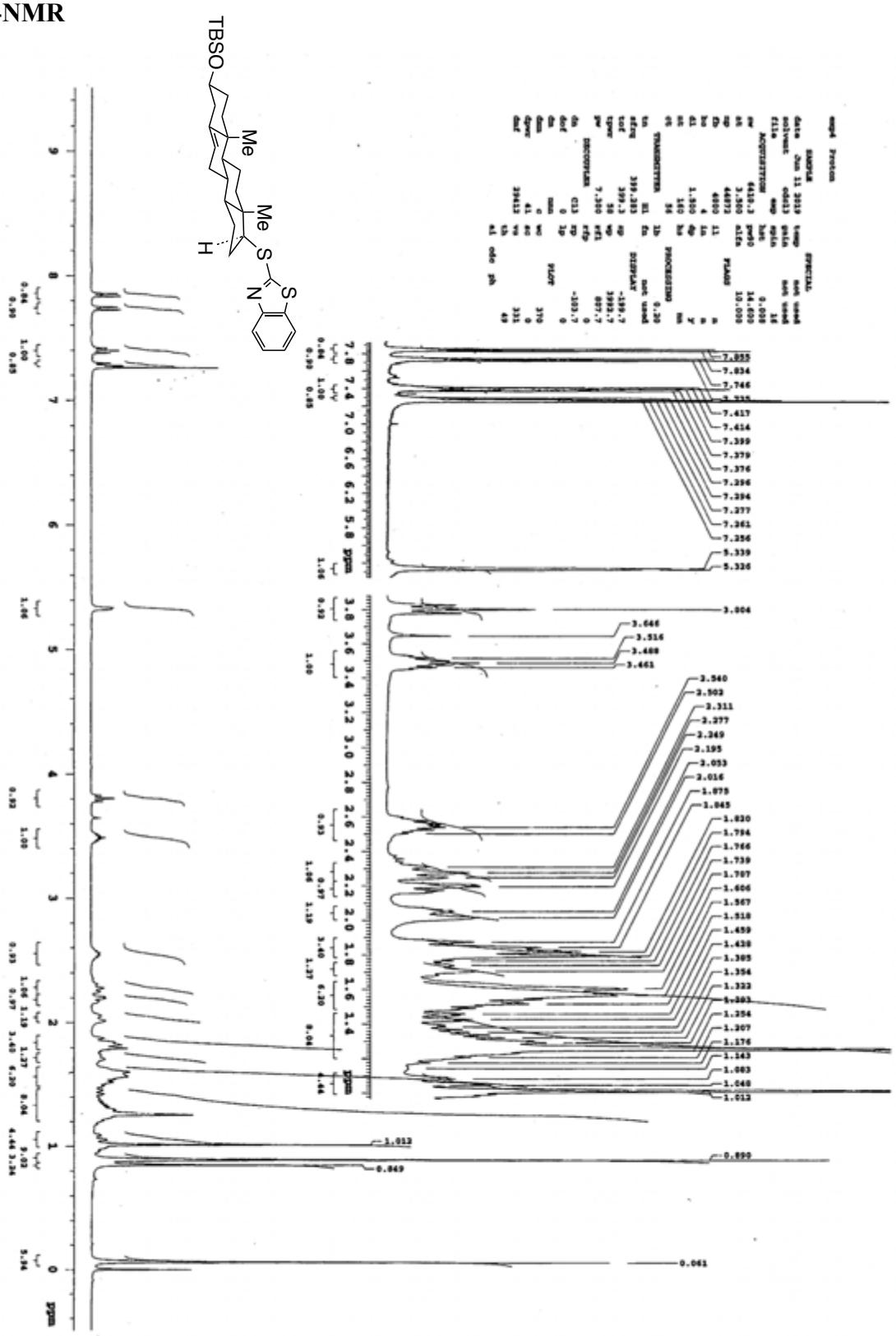


(3ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12c) HH-COSY

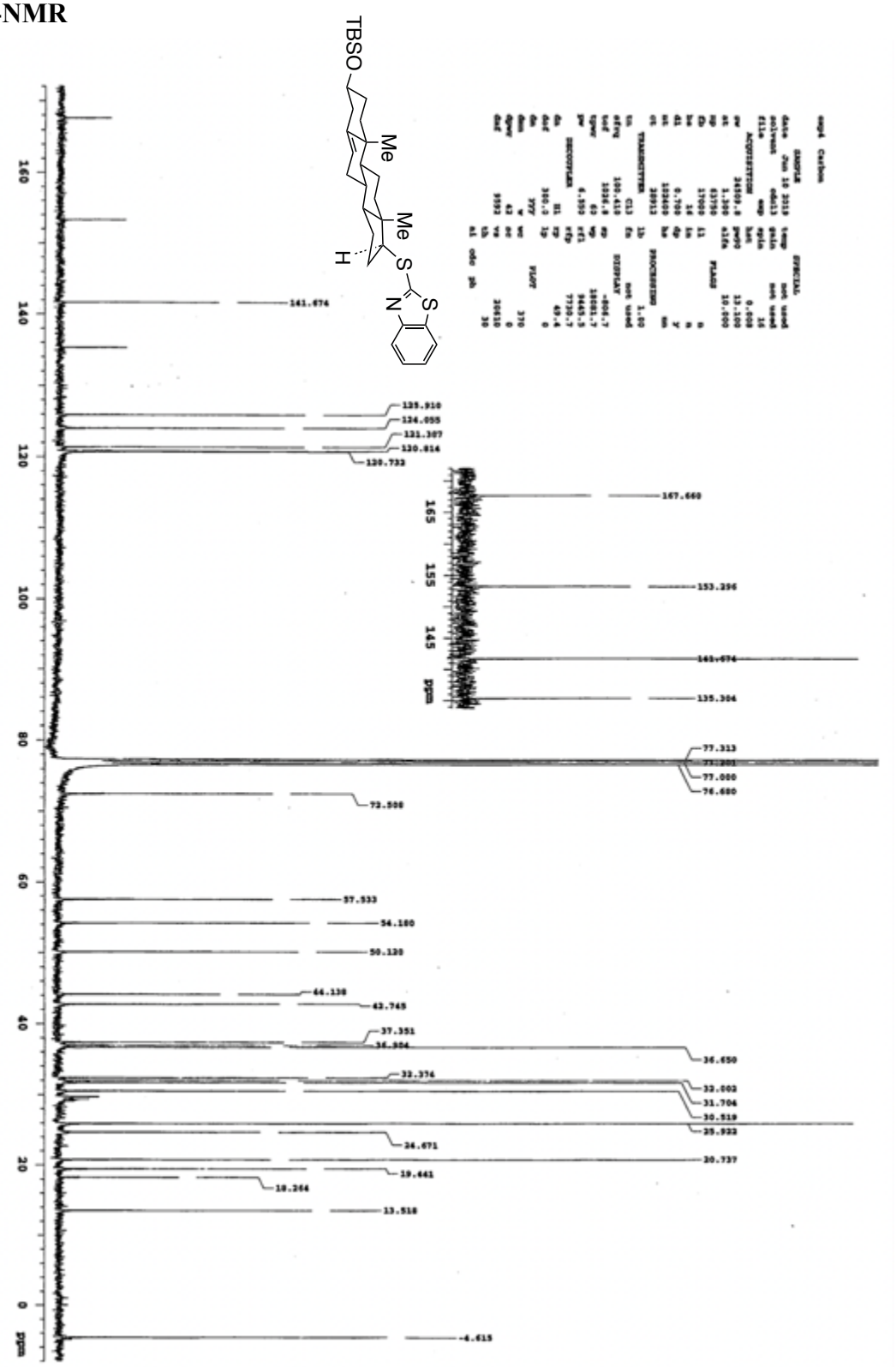
(3ß)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12c)
^{13}C-NMR



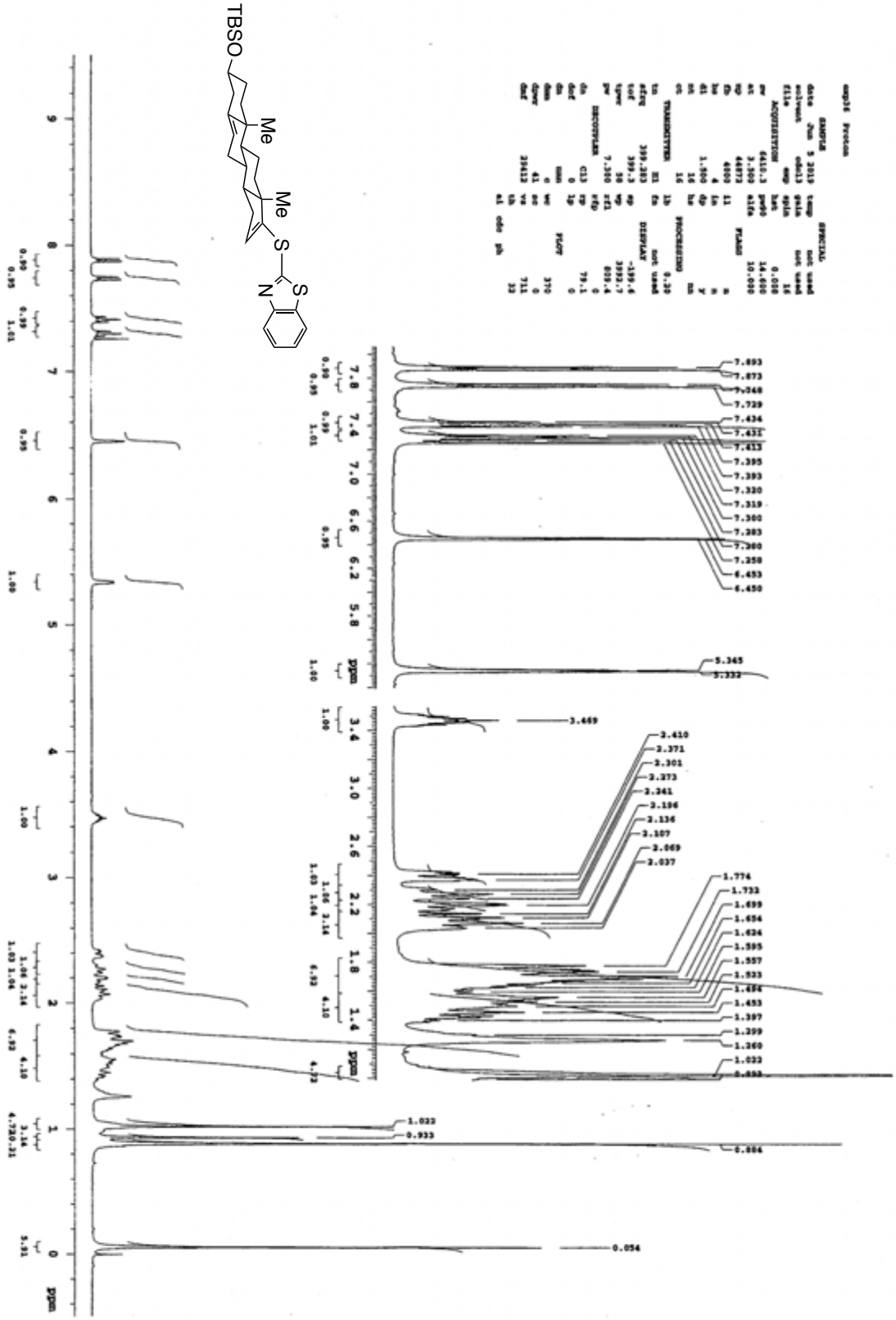
(3ß,17ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11d) ^{1}H-NMR



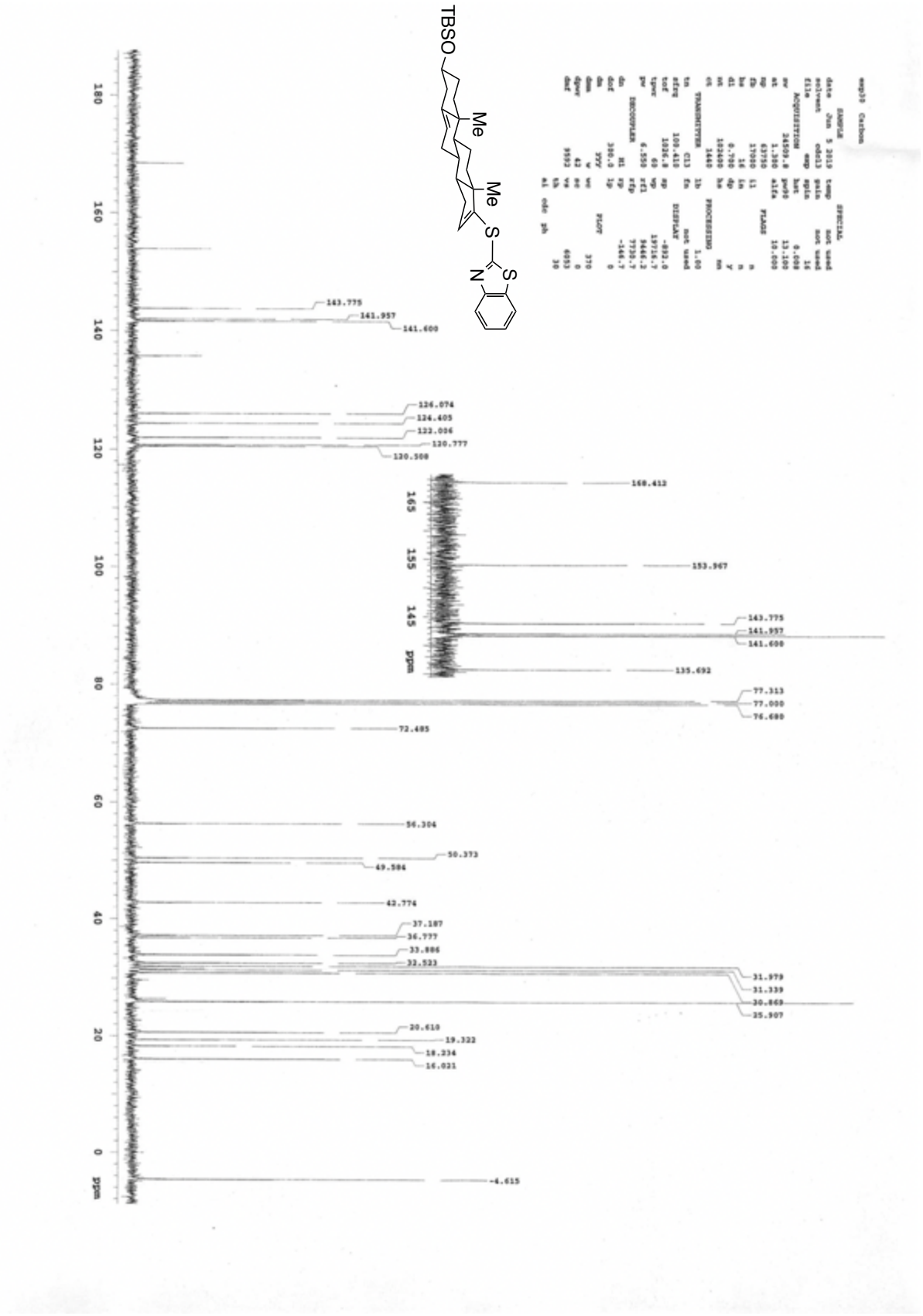
(3ß,17ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11d) ^{13}C-NMR



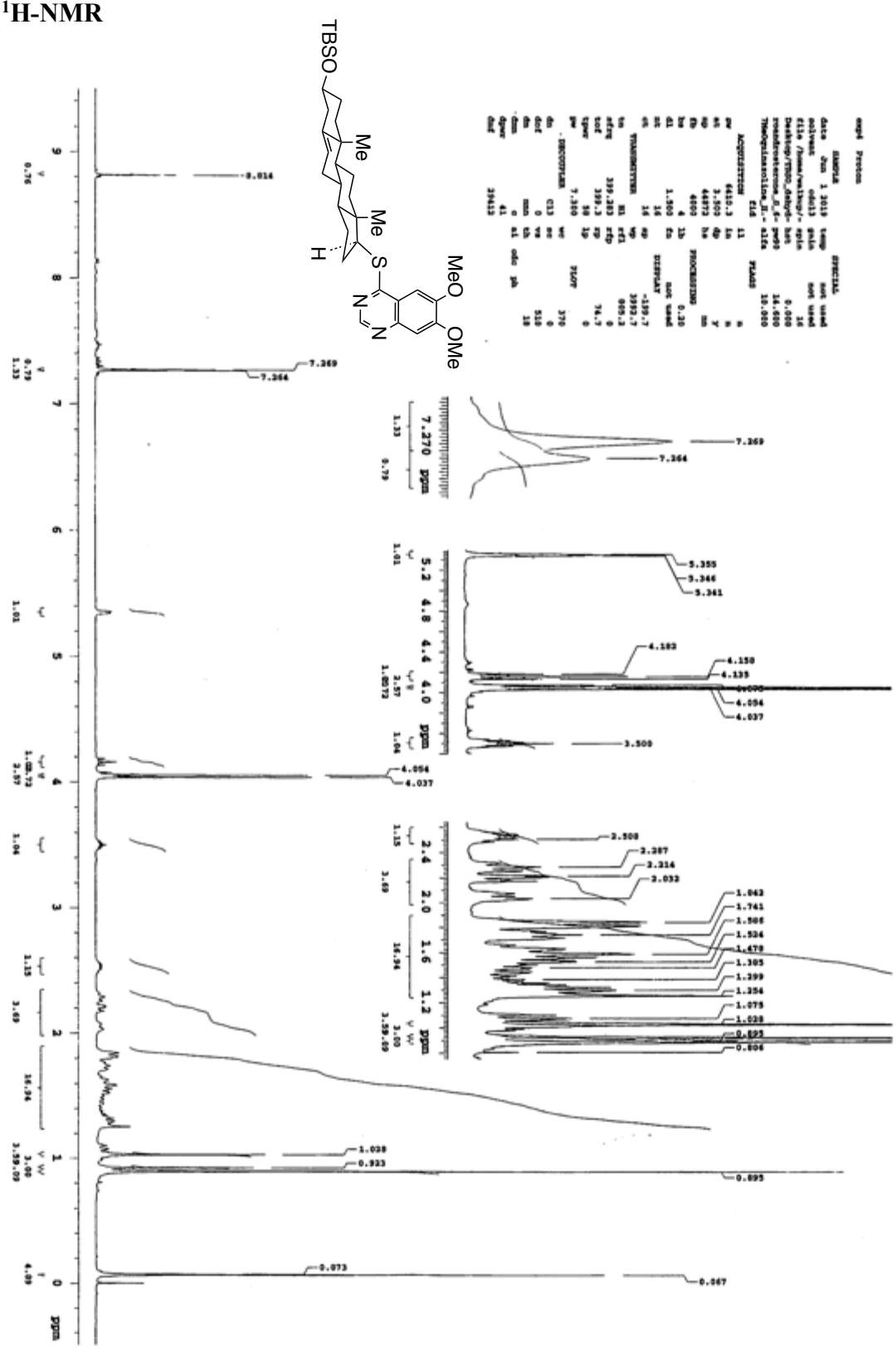
(3ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12d) ^{1}H-NMR



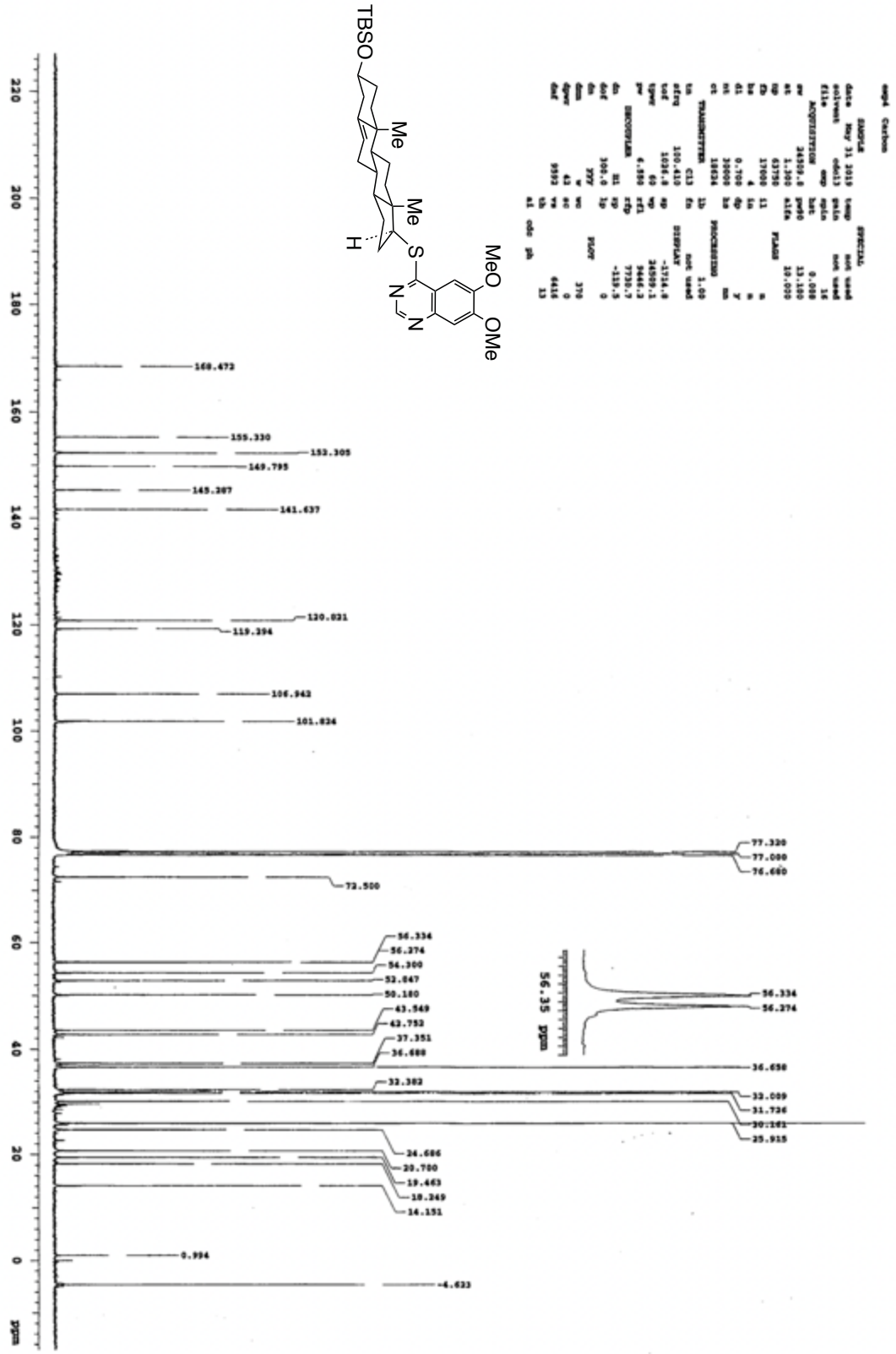
(3ß)-17-(2-Benzothiazolylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12d) ^{13}C-NMR



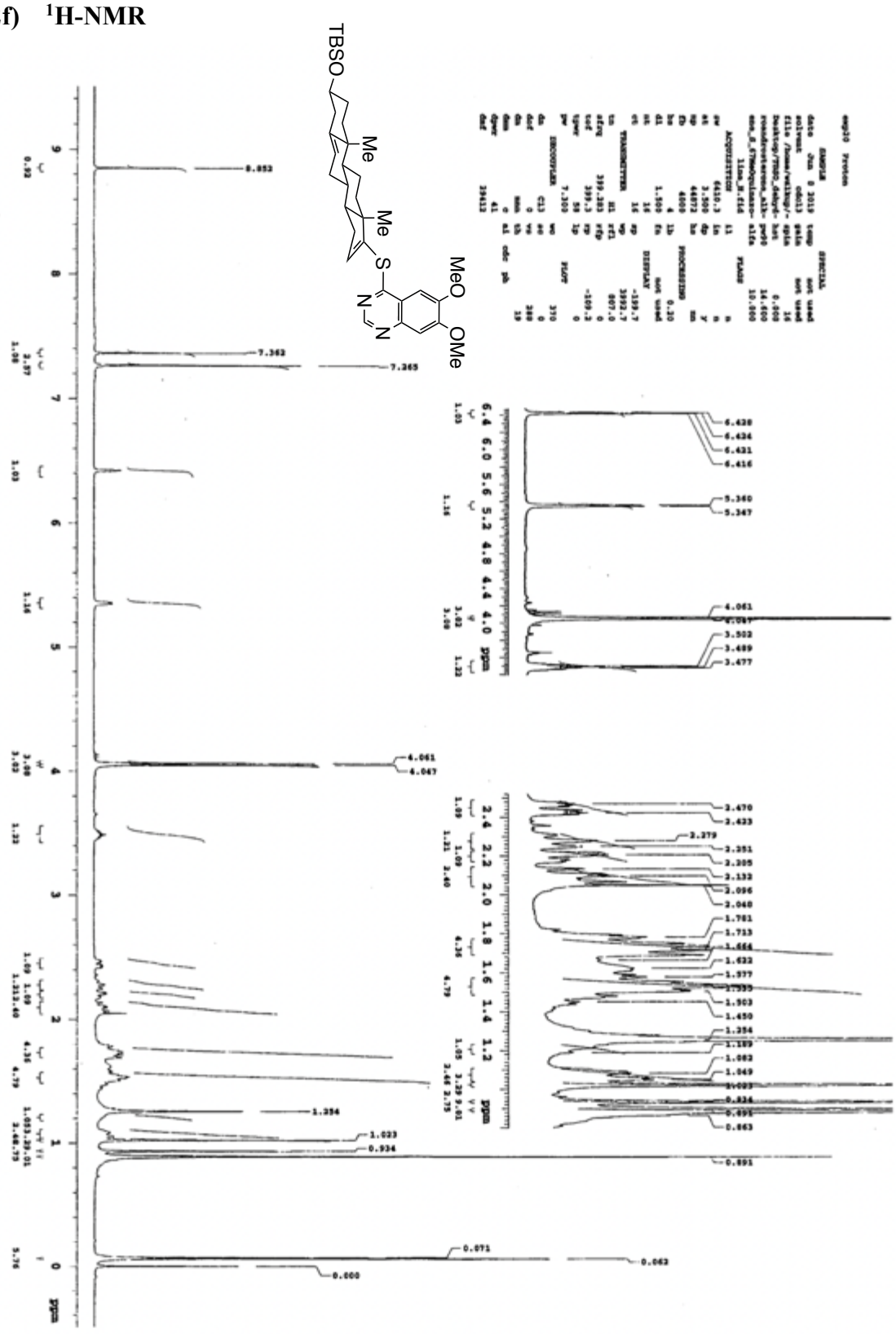
(3ß,17ß)-17-[2-(6,7-Dimethoxyqinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11f) **^{1}H-NMR**



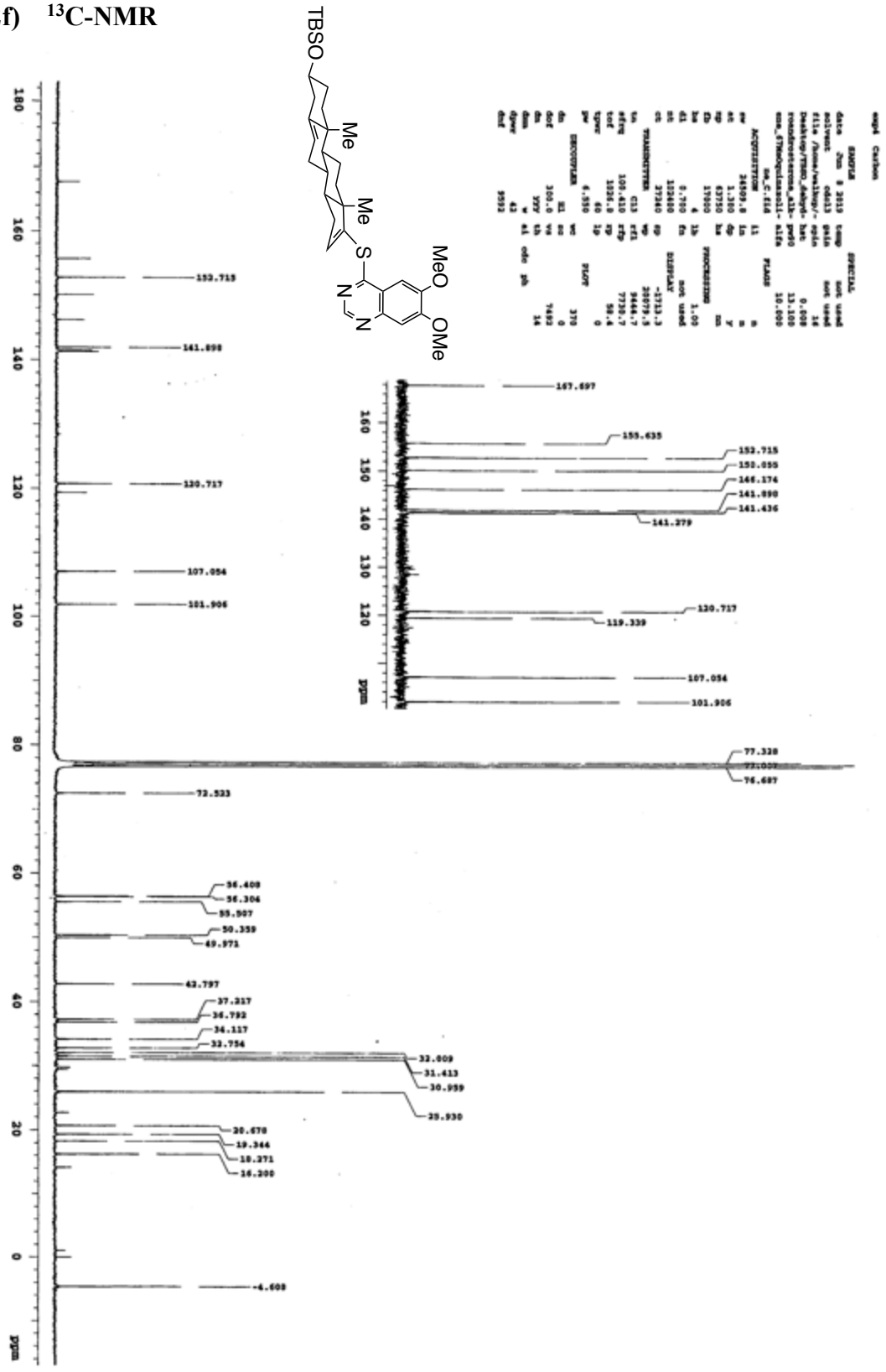
(3ß,17ß)-17-[2-(6,7-Dimethoxyqinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11f) ^{13}**C-NMR**



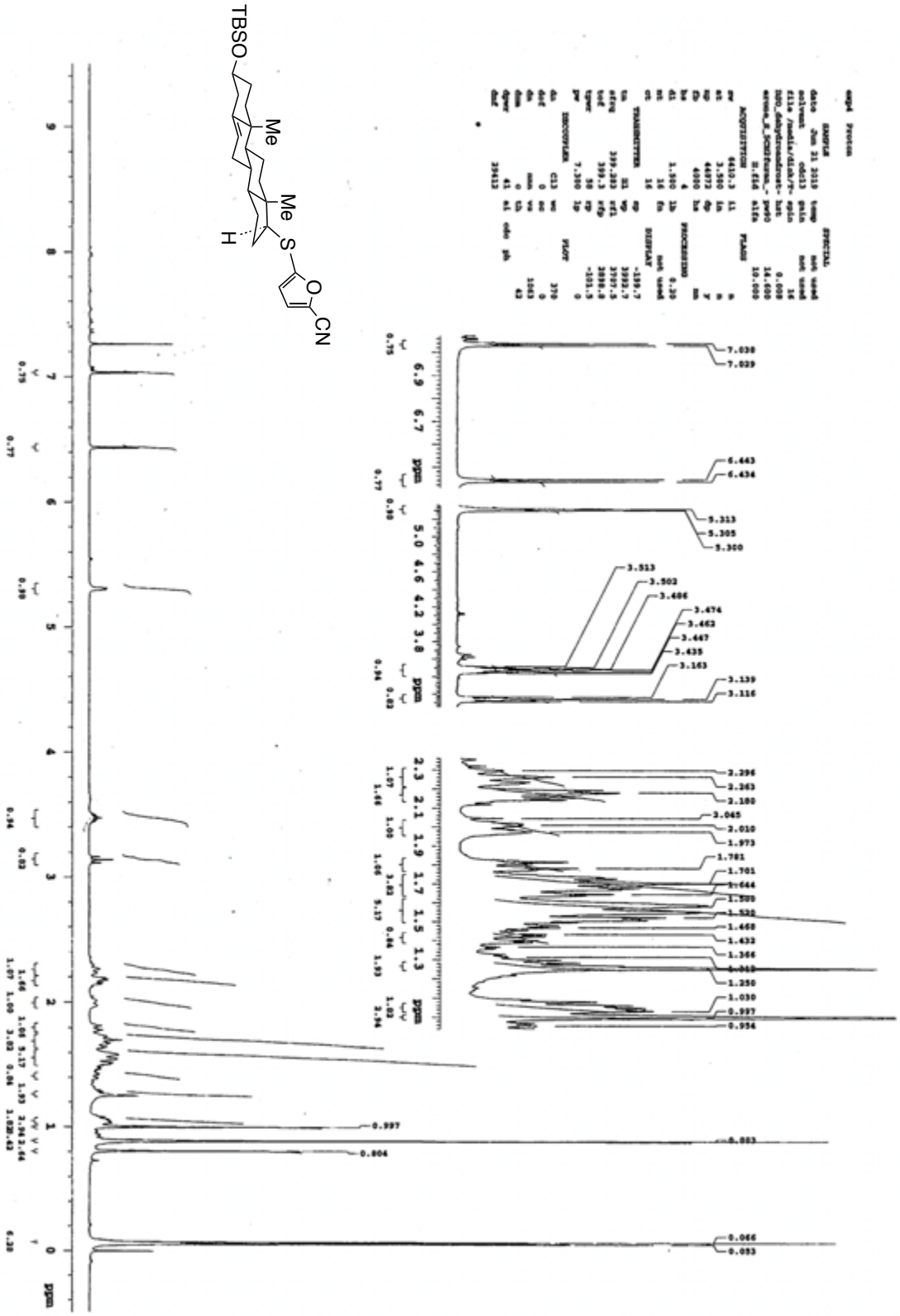
(3ß)-17-[2-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12f) ^{1}**H-NMR**



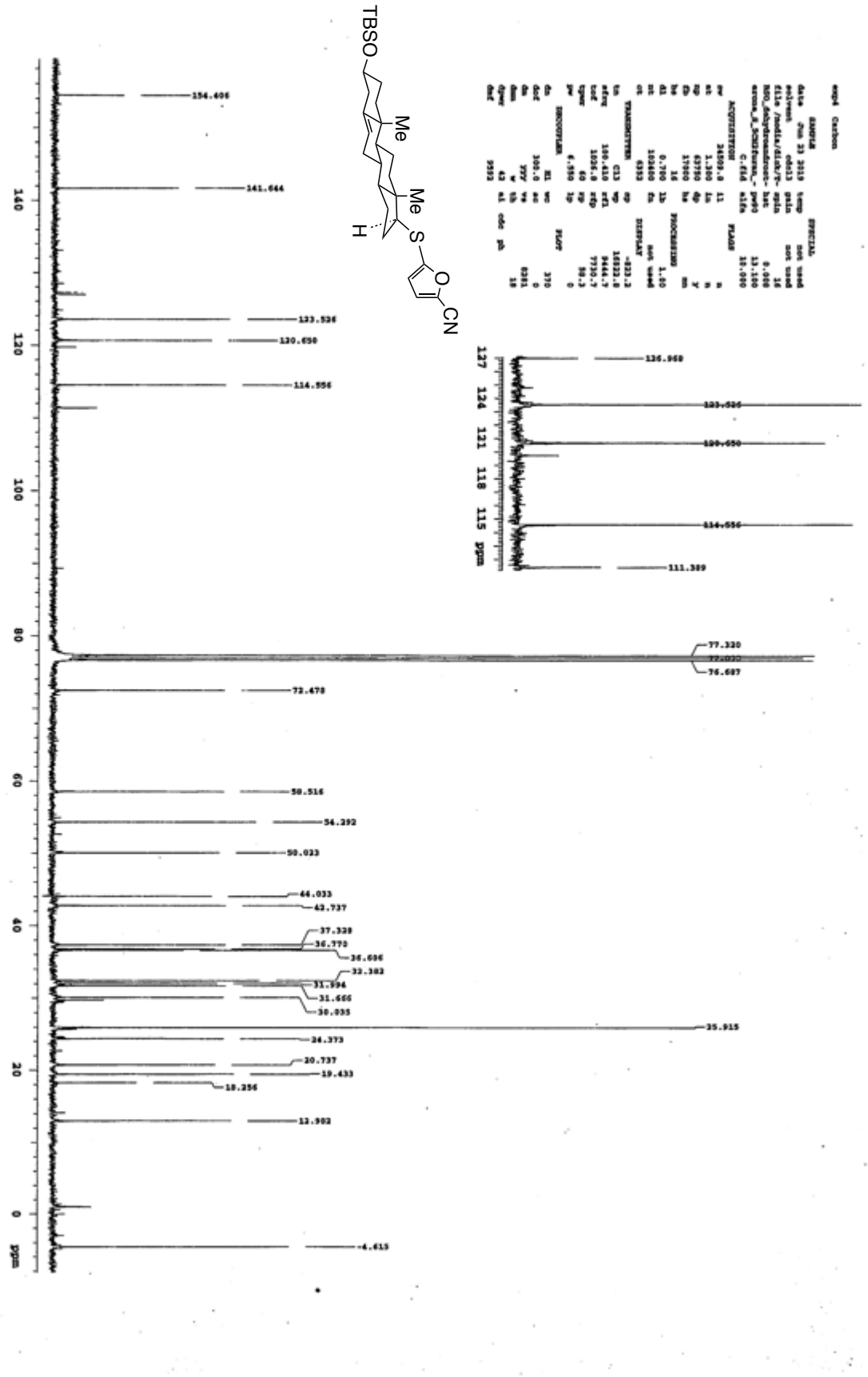
(3ß)-17-[2-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12f) ^{13}**C-NMR**



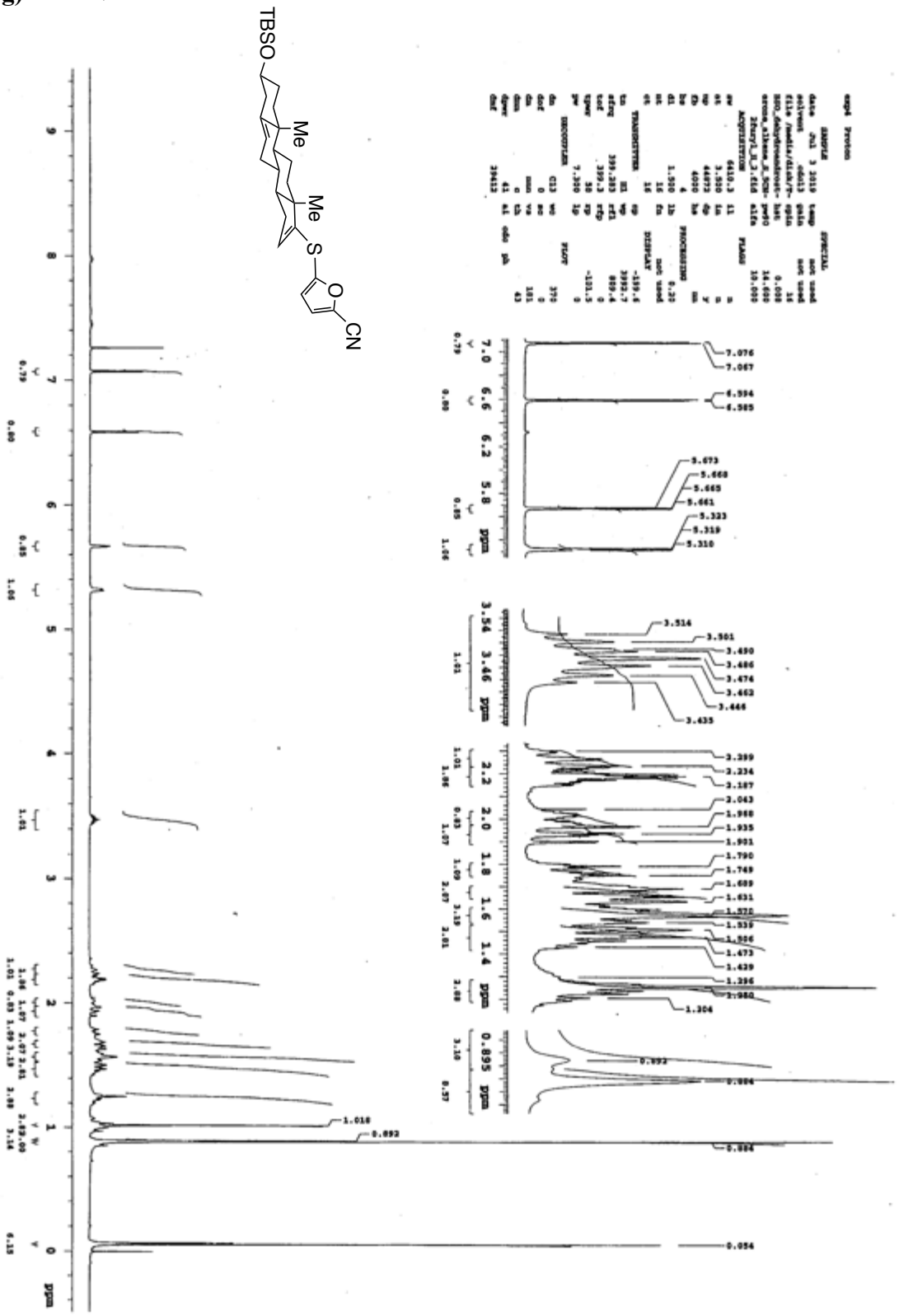
(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11g) ^{1}H-NMR



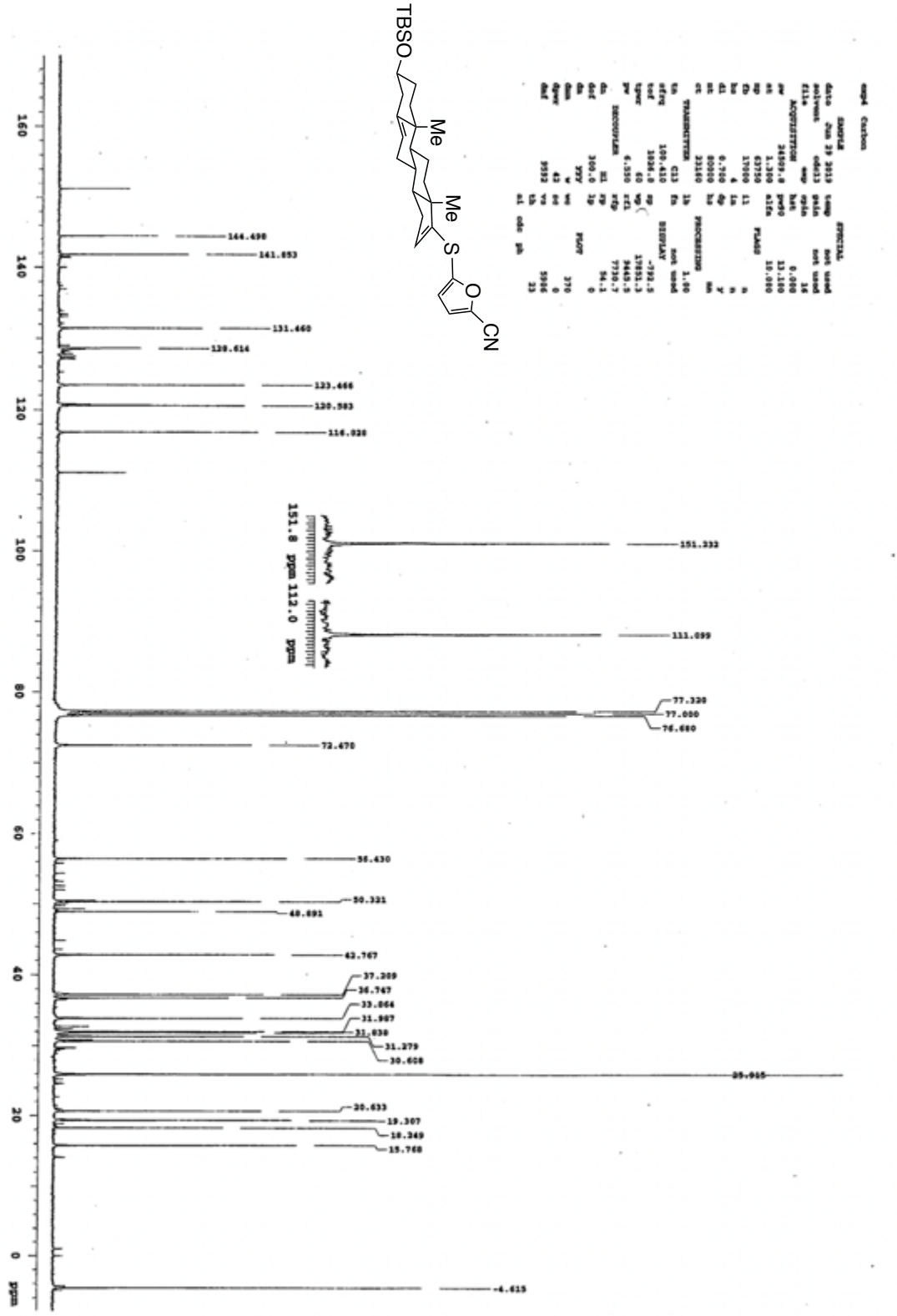
(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11g) ^{13}C-NMR



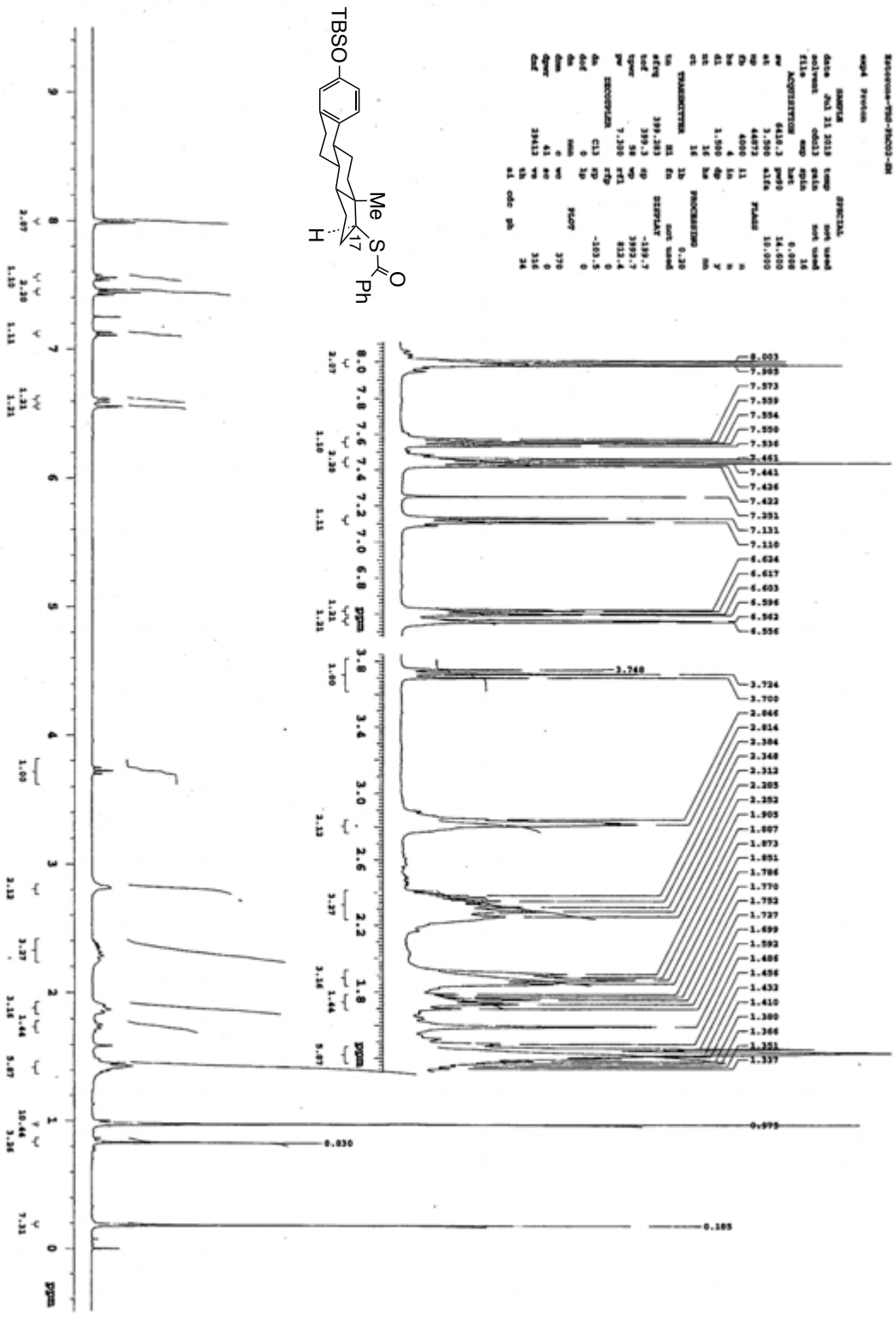
(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12g) ^{1}**H-NMR**



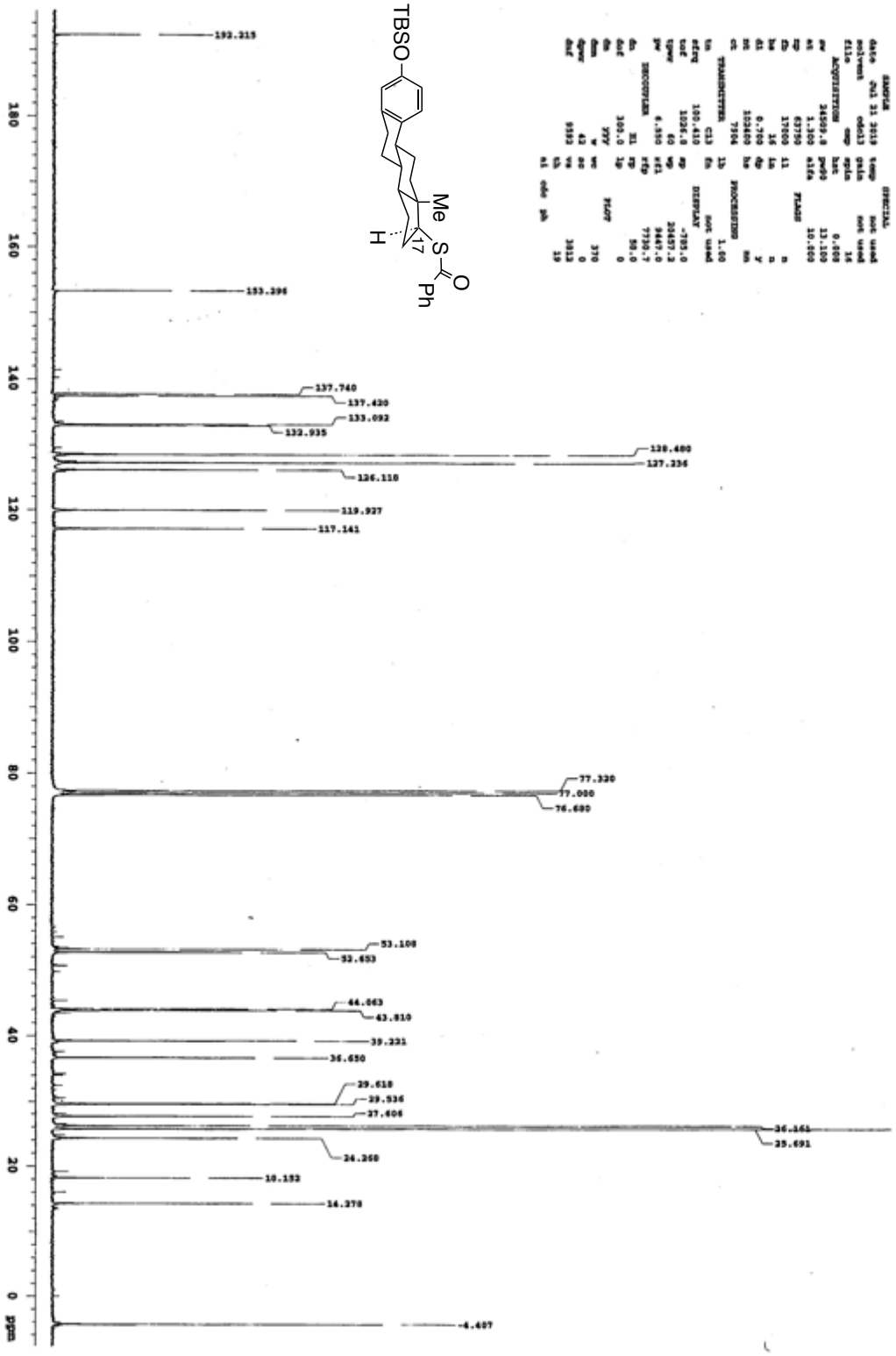
(3ß,17ß)-17-[5-(2-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12g) ^{13}**C-NMR**



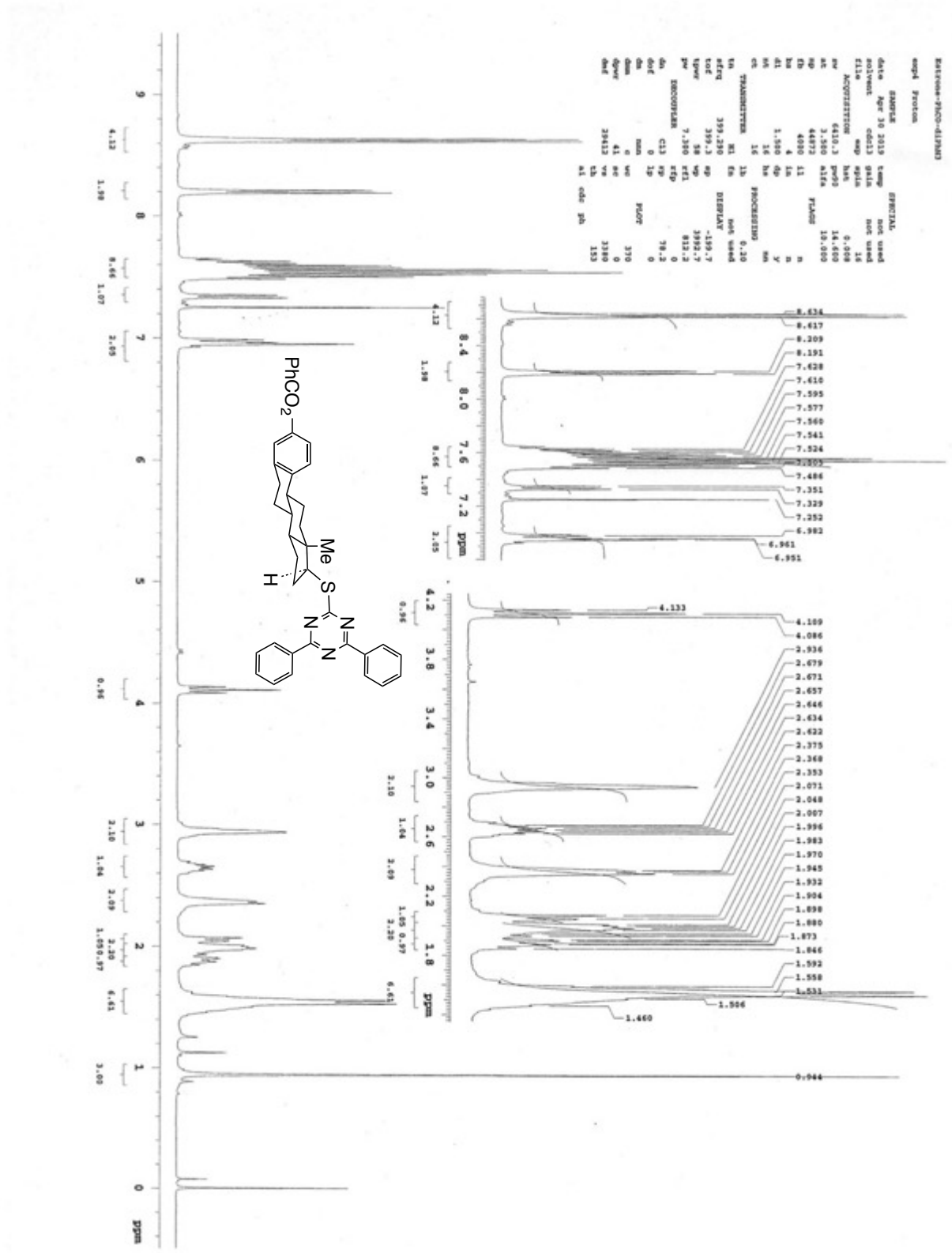
(17ß)-17-(benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (13) ^{1}H-NMR



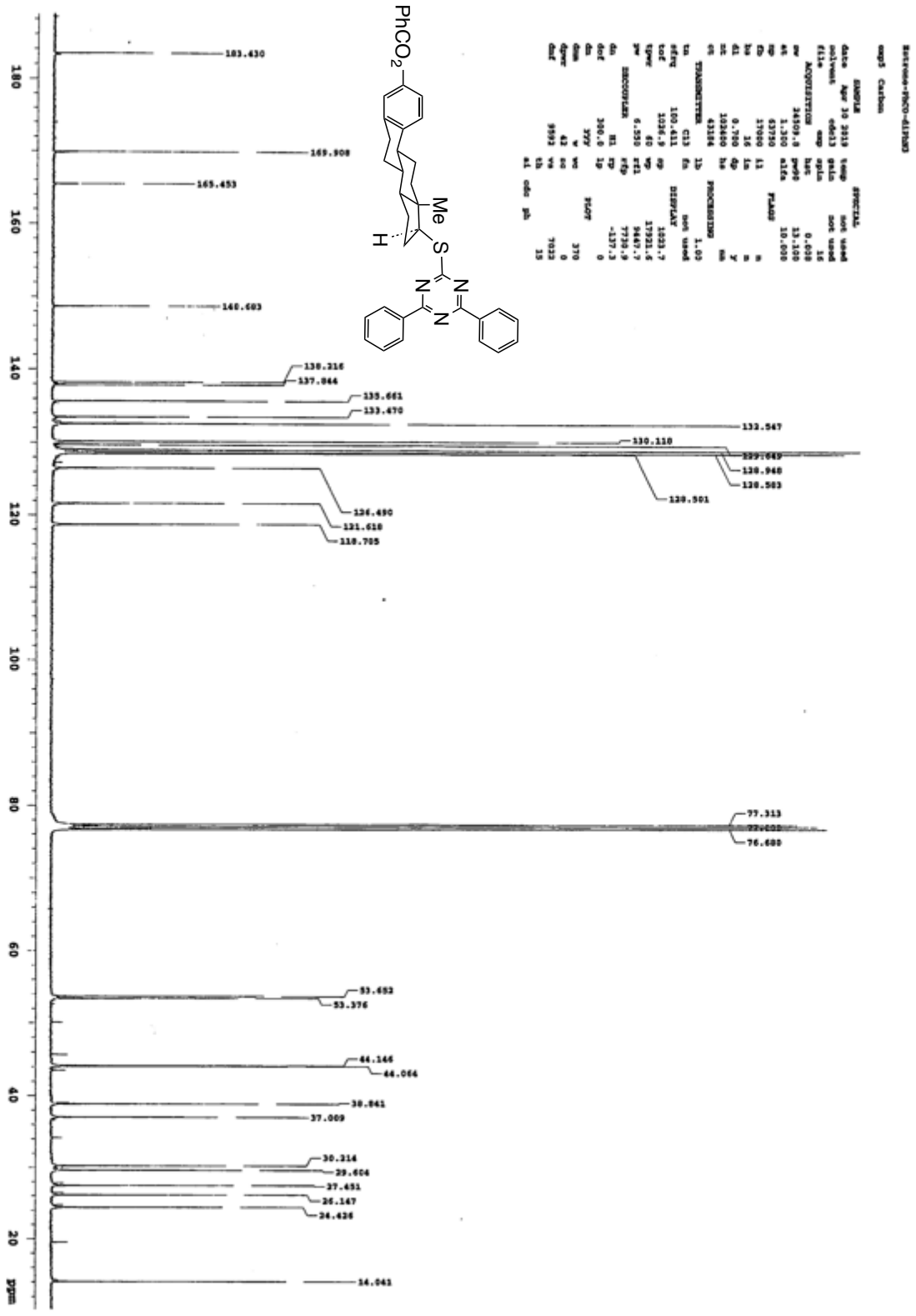
(17ß)-17-(benzoylthio)-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (13) ^{13}C-NMR



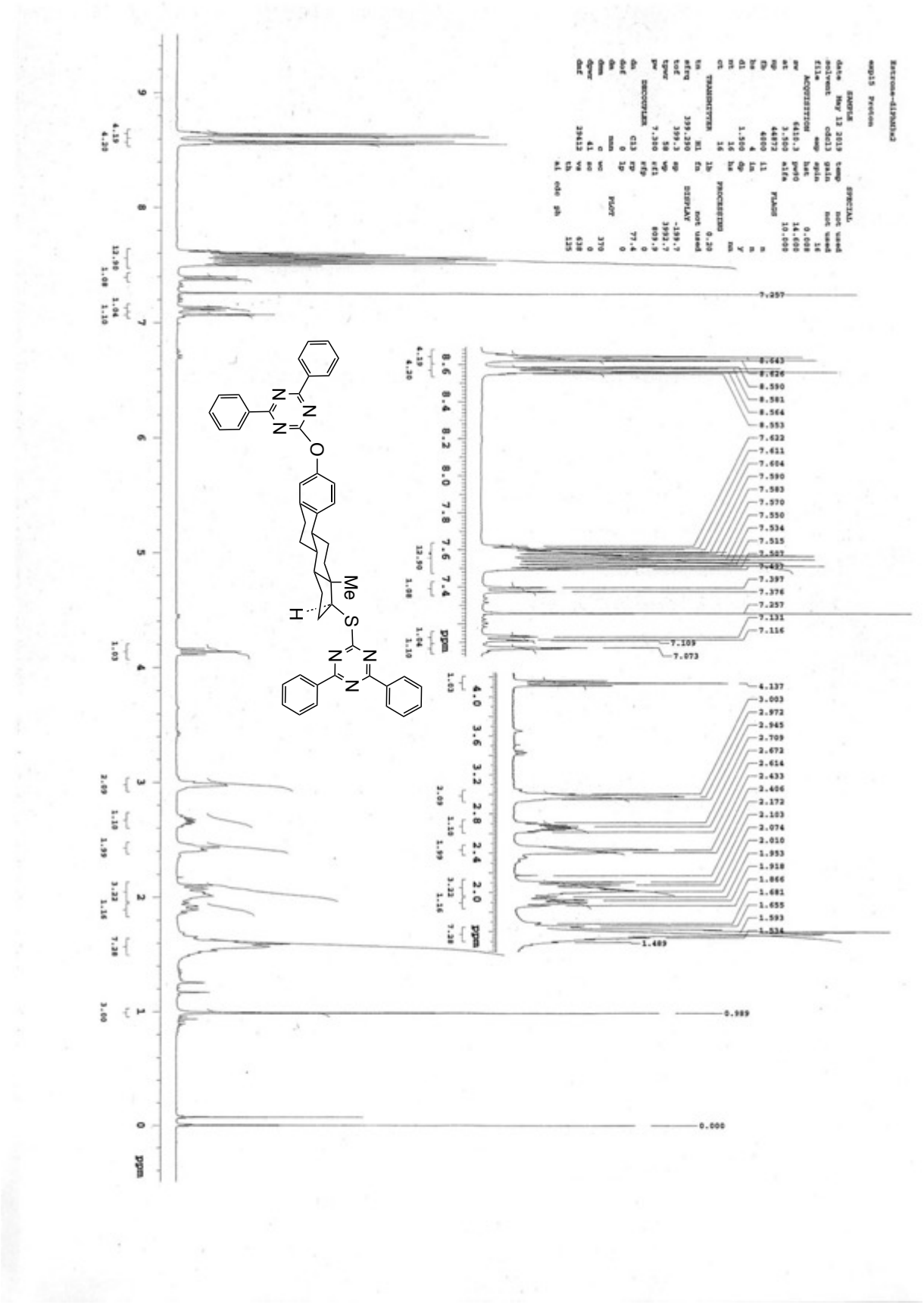
(17ß)-[2-(4,6-Diphenyl-1,3,5-triaziyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a) ^{1}**H-NMR**



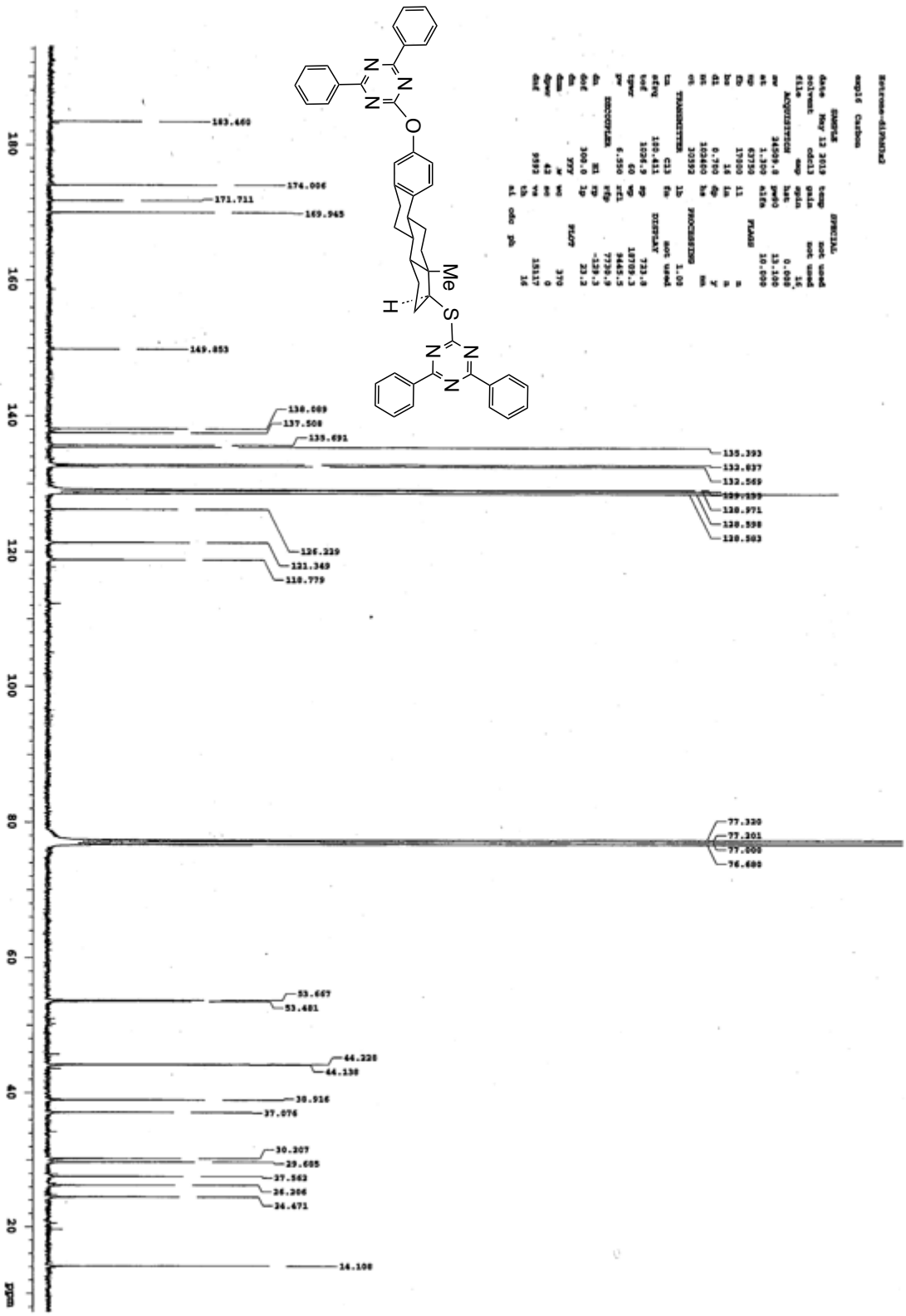
(17ß)-[2-(4,6-Diphenyl-1,3,5-triaziyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a) ^{13}C-NMR



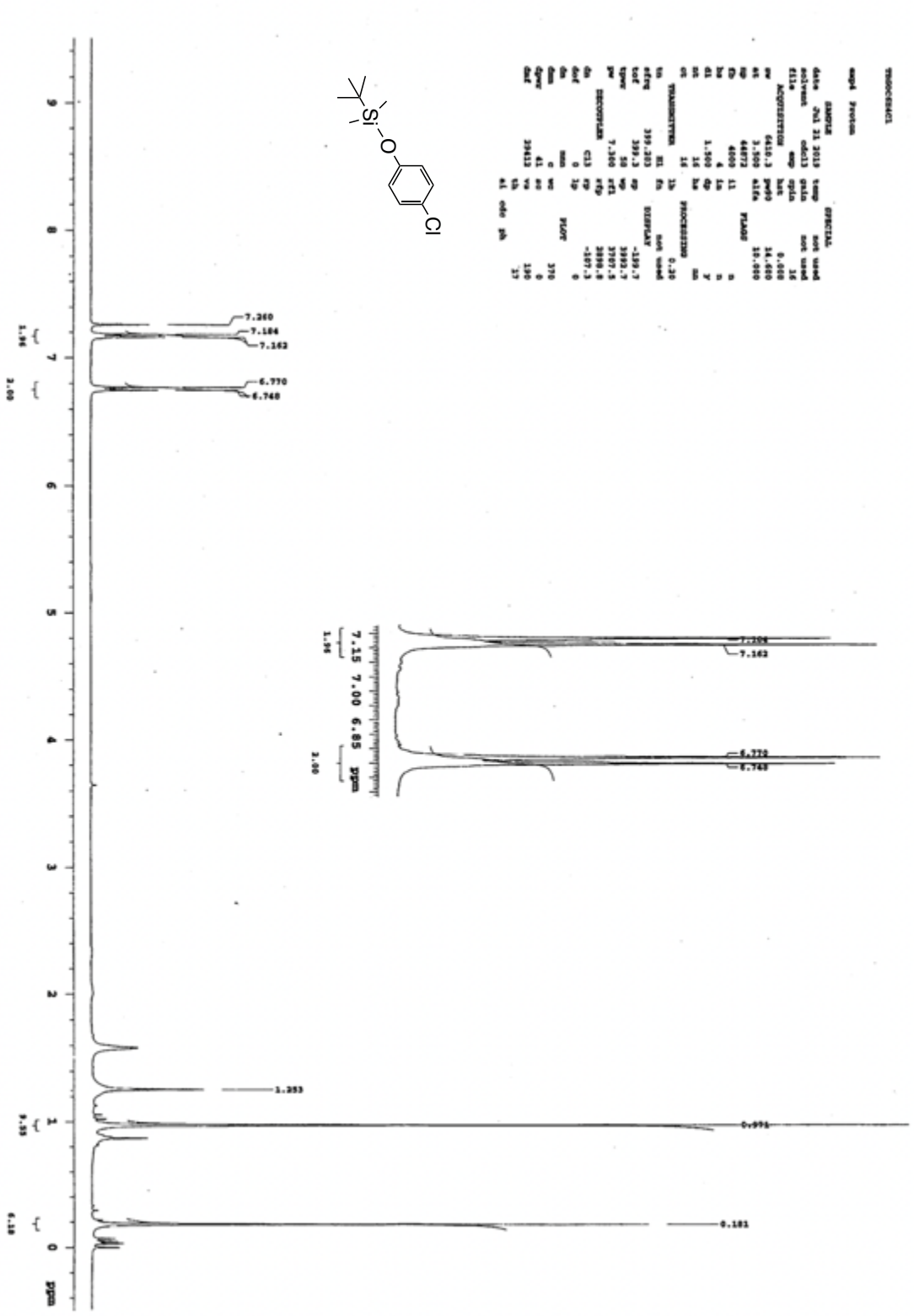
(17ß)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]-3-[2-(4,6-diphenyl-1,3,5-triazyl)oxy]estra-1,3,5(10)-triene (15a) ^{1}H-NMR



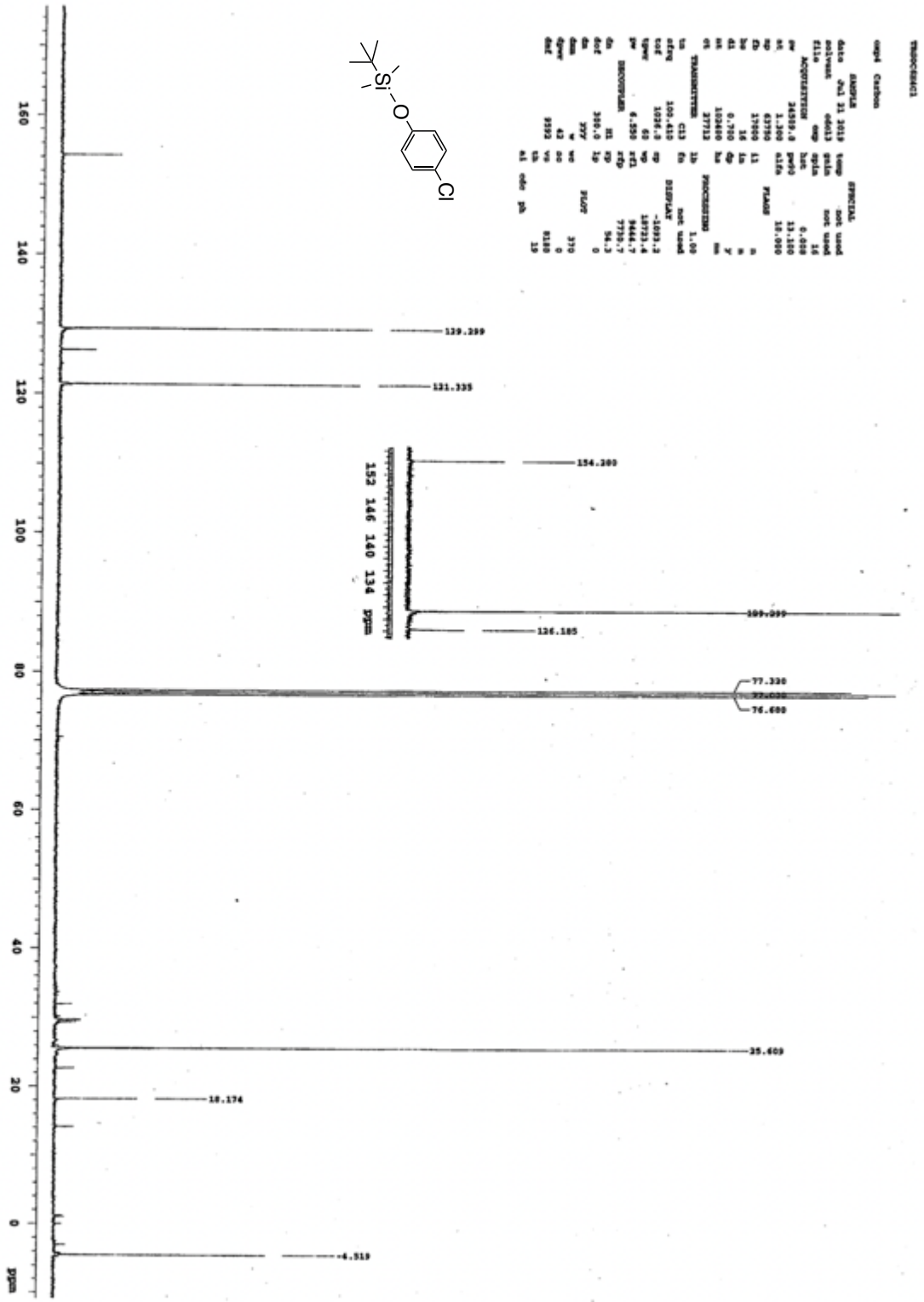
(17ß)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]-3-[2-(4,6-diphenyl-1,3,5-triazyl)oxy]estra-1,3,5(10)-triene (15a) ^{13}**C-NMR**



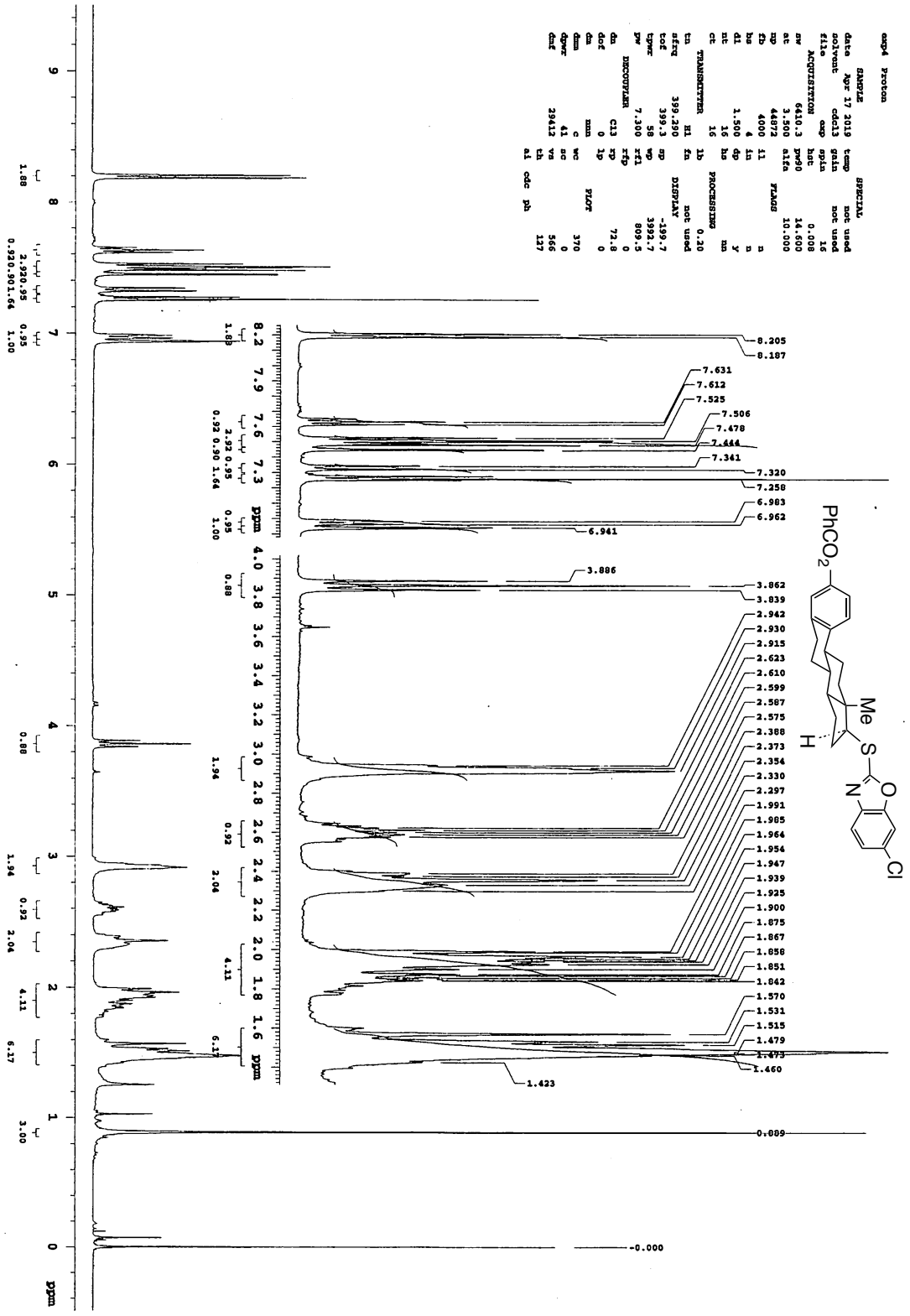
1-Chloro-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene ^{1}H-NMR



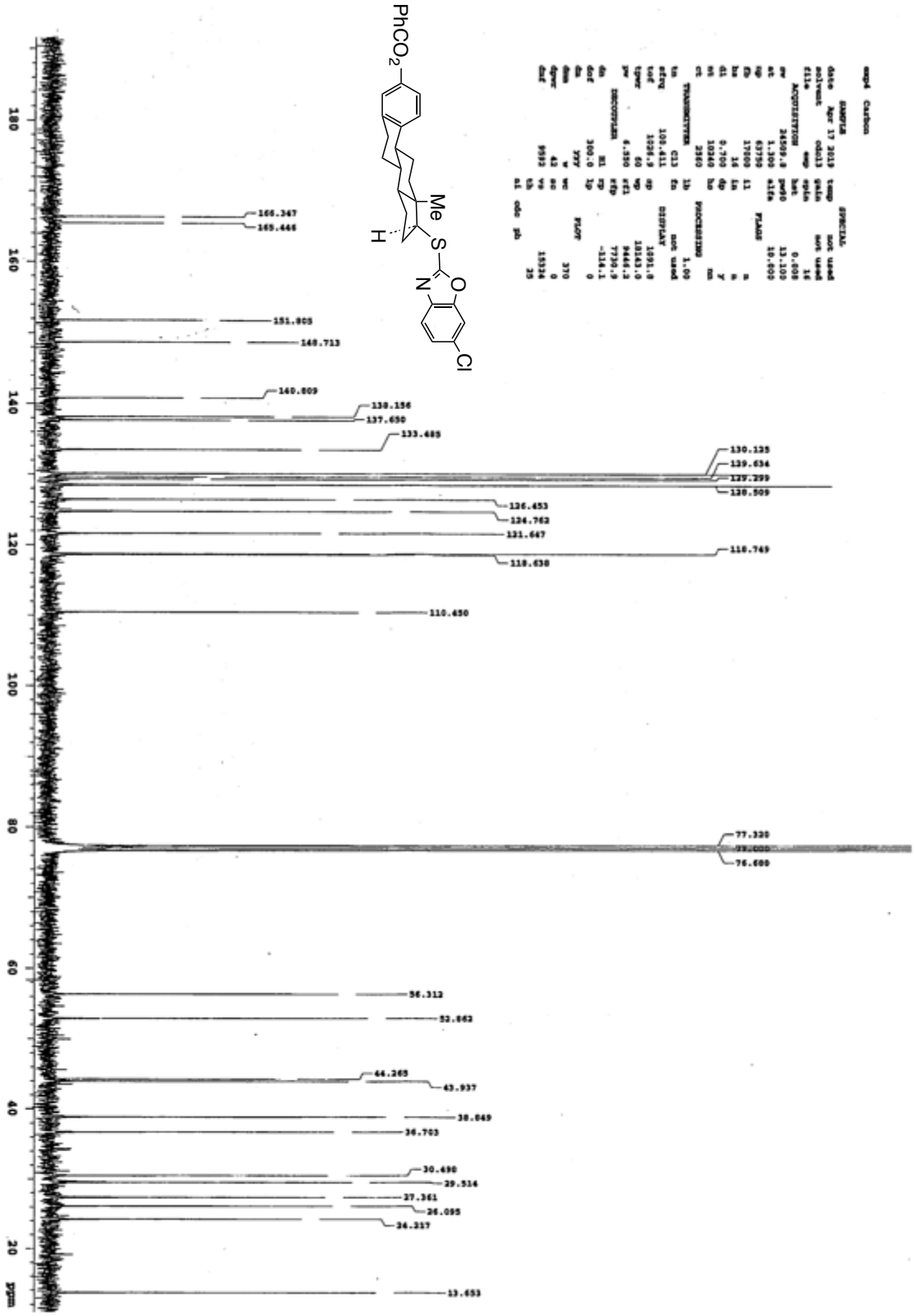
1-Chloro-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene ^{13}C-NMR



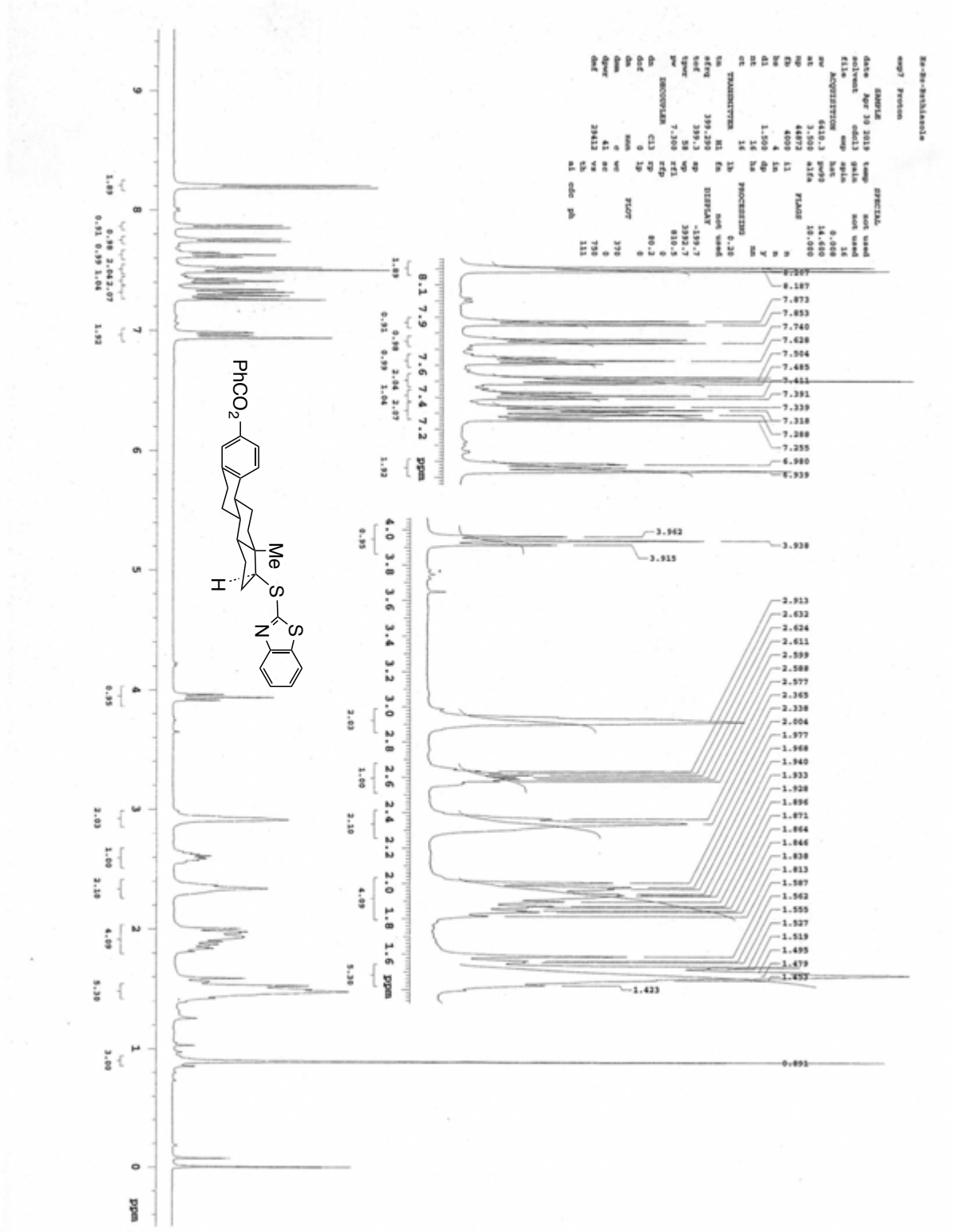
(17ß)-[2-(6-Chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14c) ^{1}H-NMR



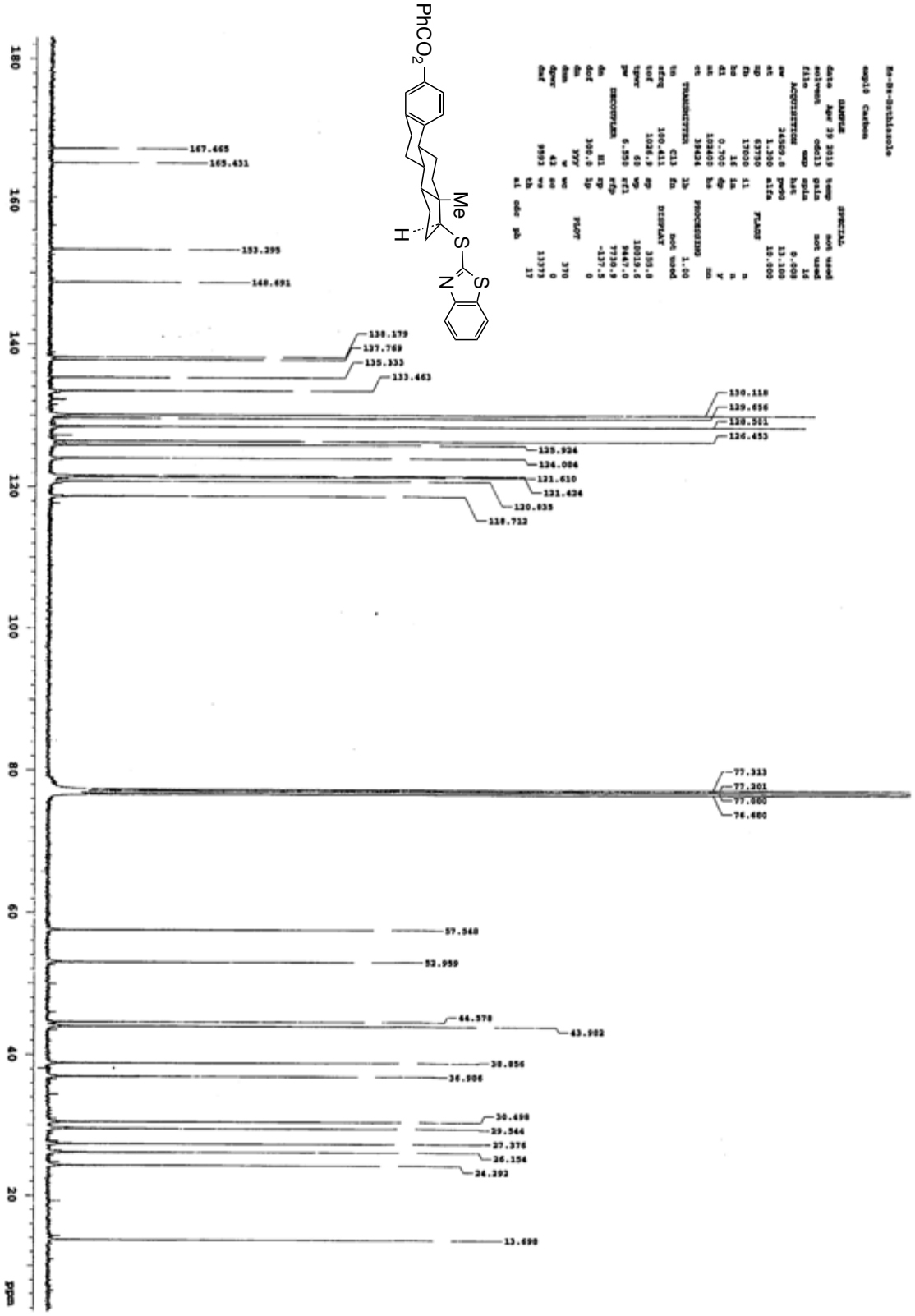
(17ß)-[2-(6-Chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14c) ^{13}C-NMR



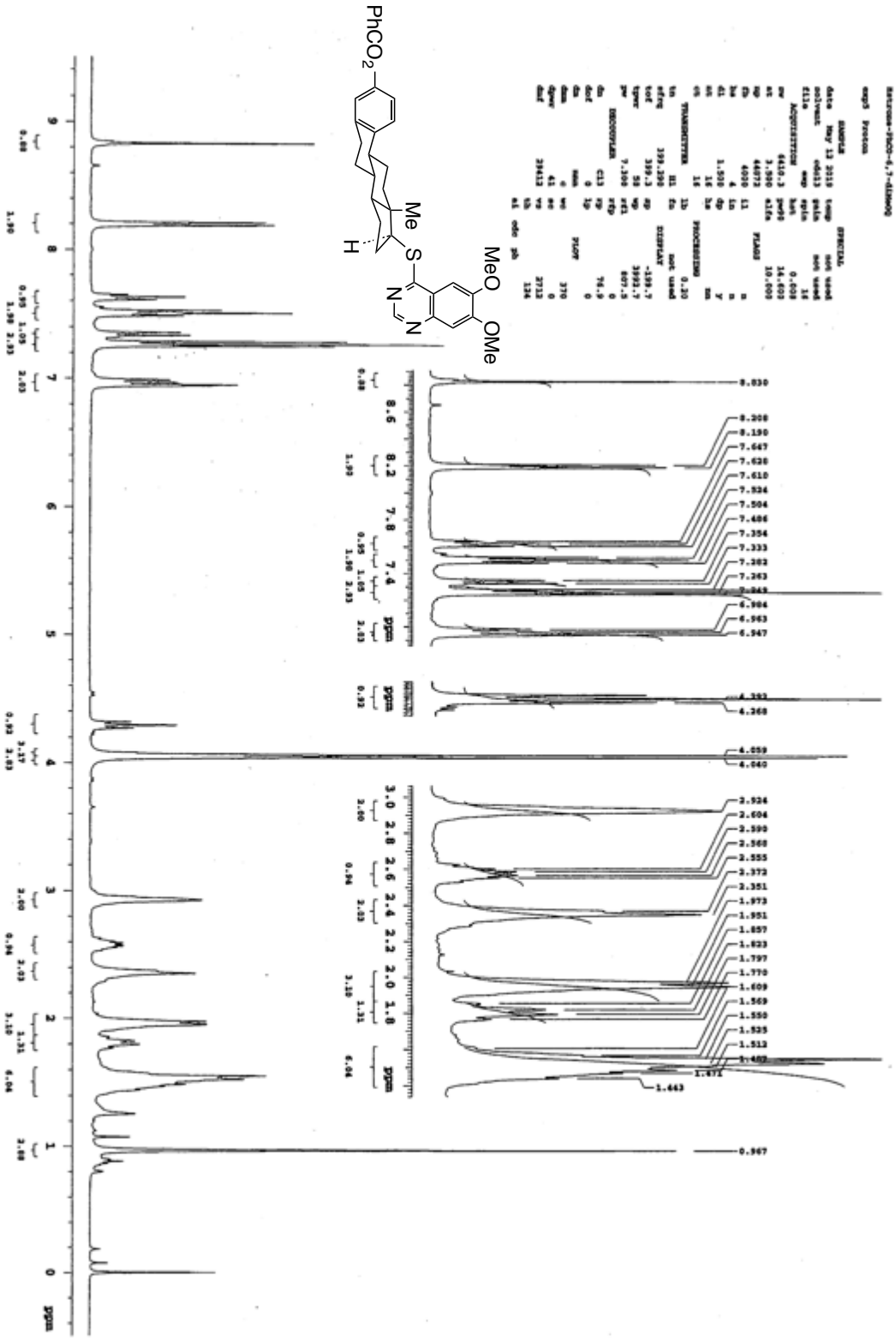
(17ß)-[2-(Benzothiazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14d) ^{1}H-NMR



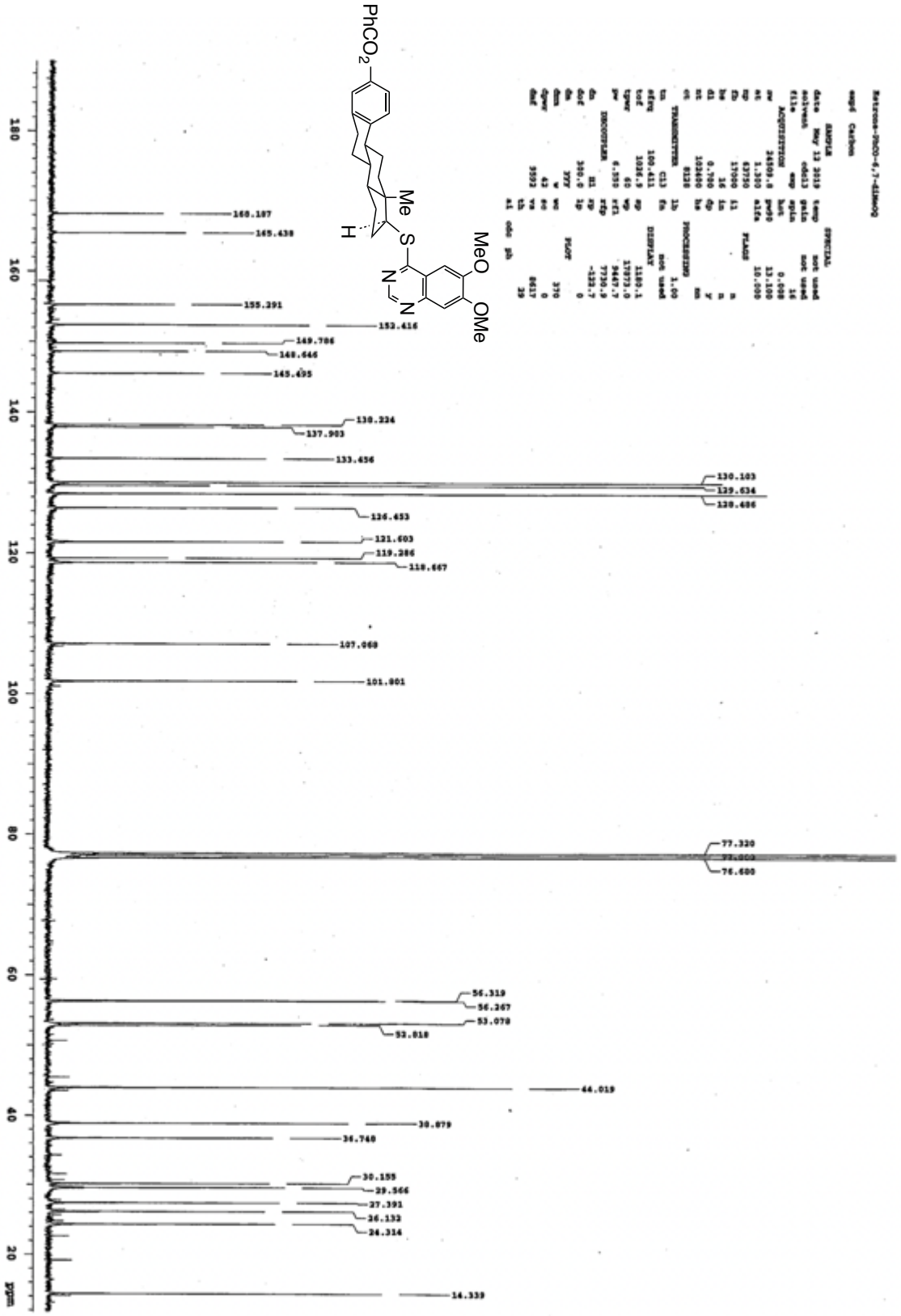
(17ß)-[2-(Benzothiazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14d) ^{13}C-NMR



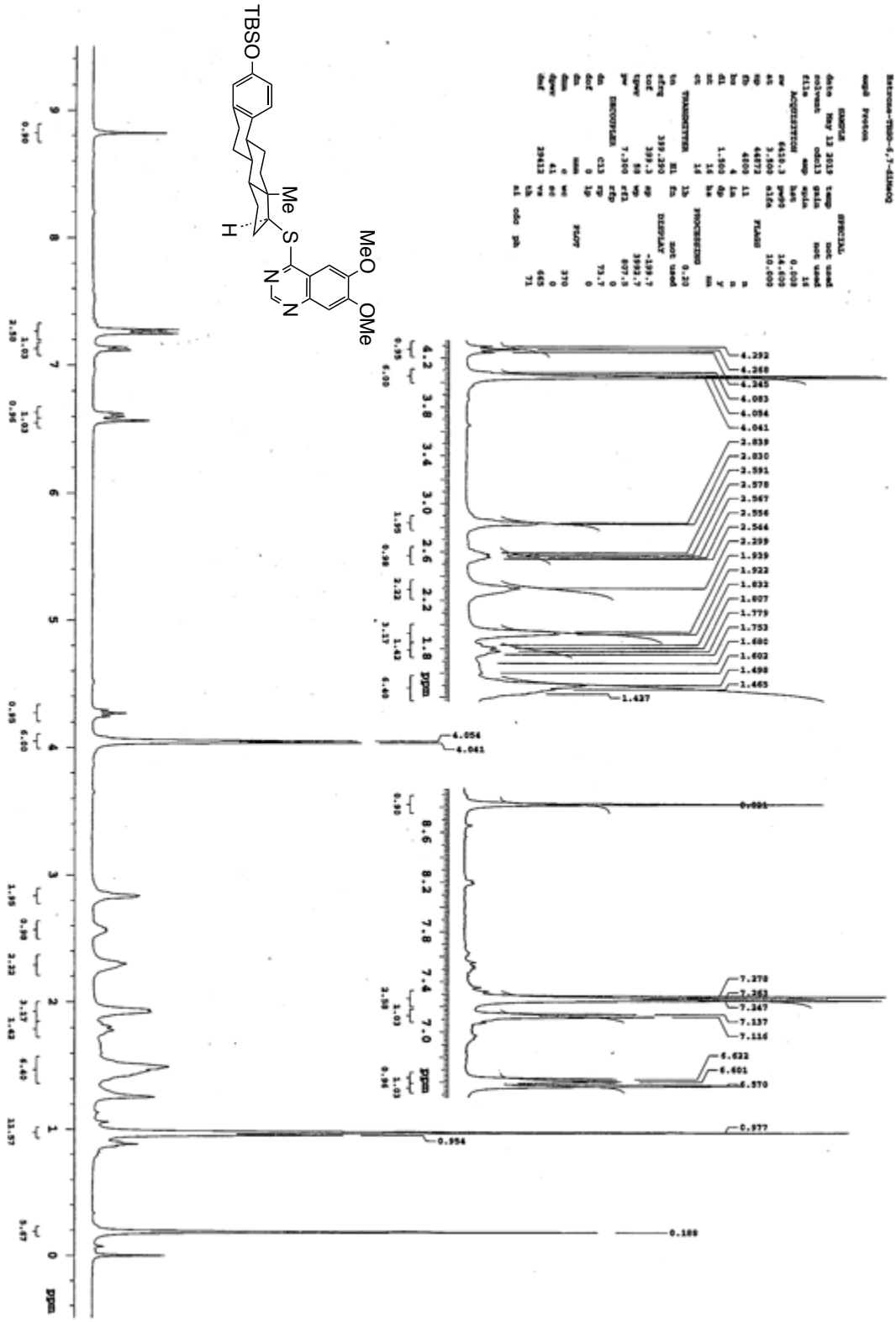
(17ß)-[2-(6,7-Dimethoxyquinazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14f) ^{1}H-NMR



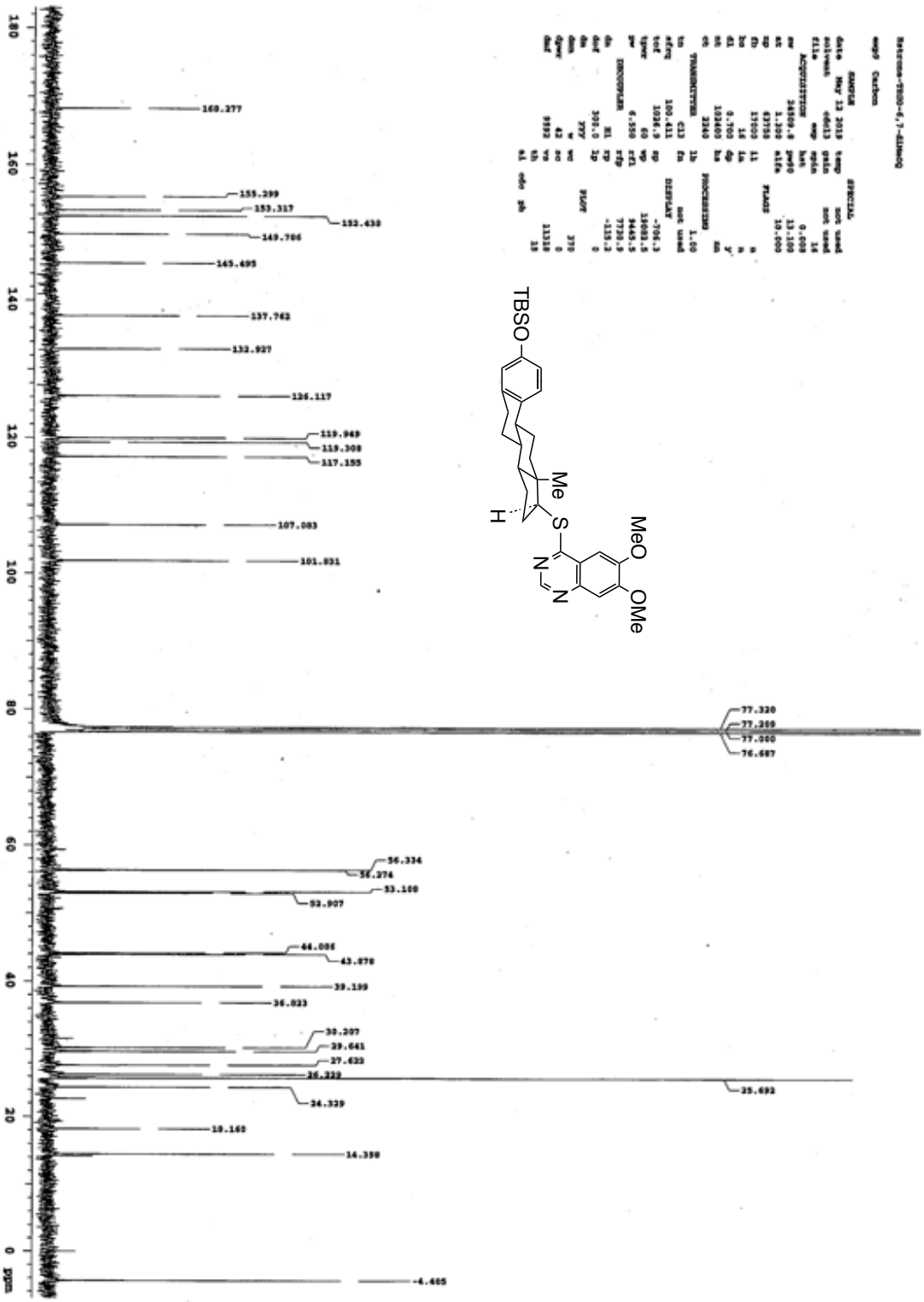
(17ß)-[2-(6,7-Dimethoxyquinazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14f) **^{13}C-NMR**



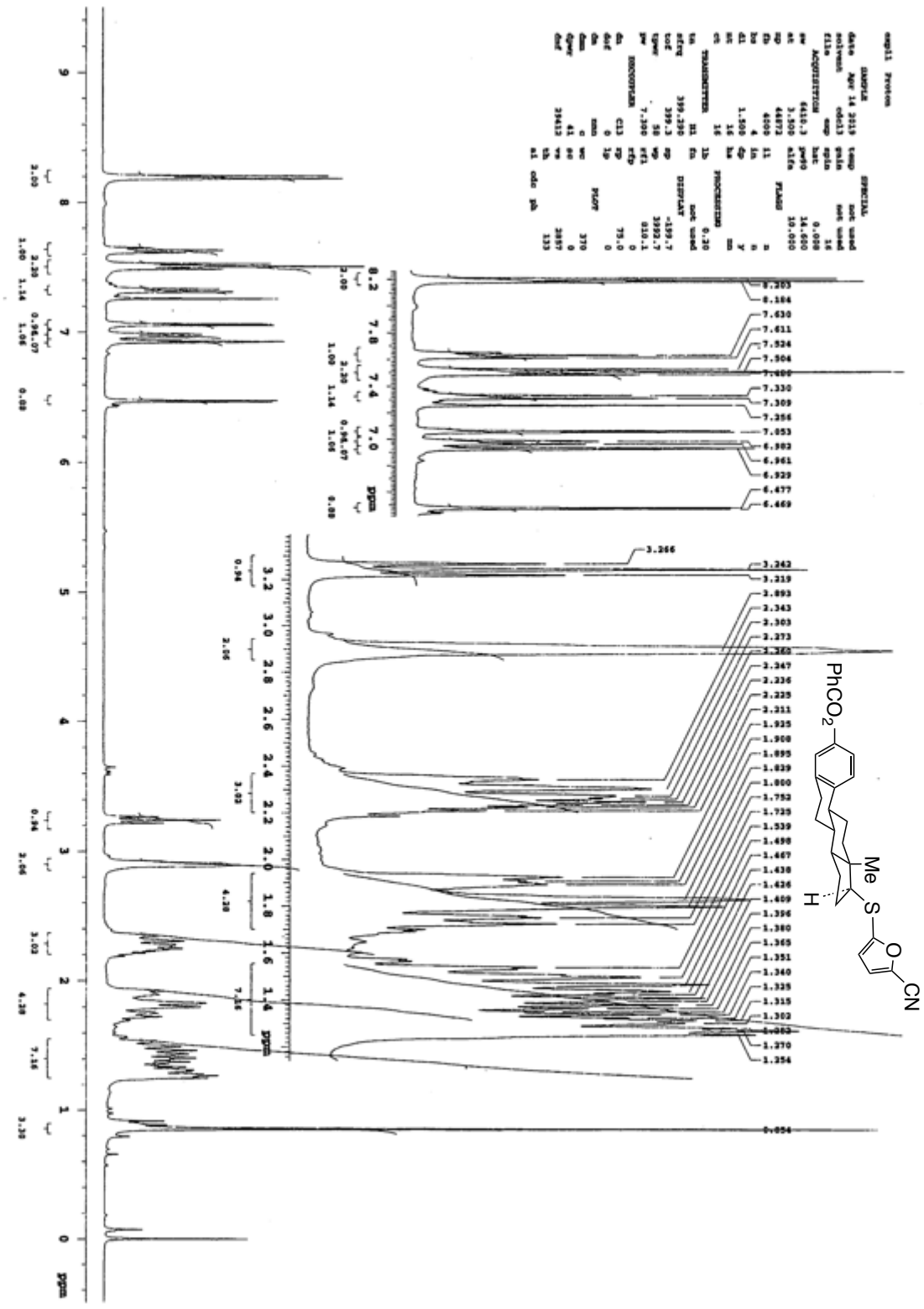
(17ß)-[2-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16f) ^{1}**H-NMR**



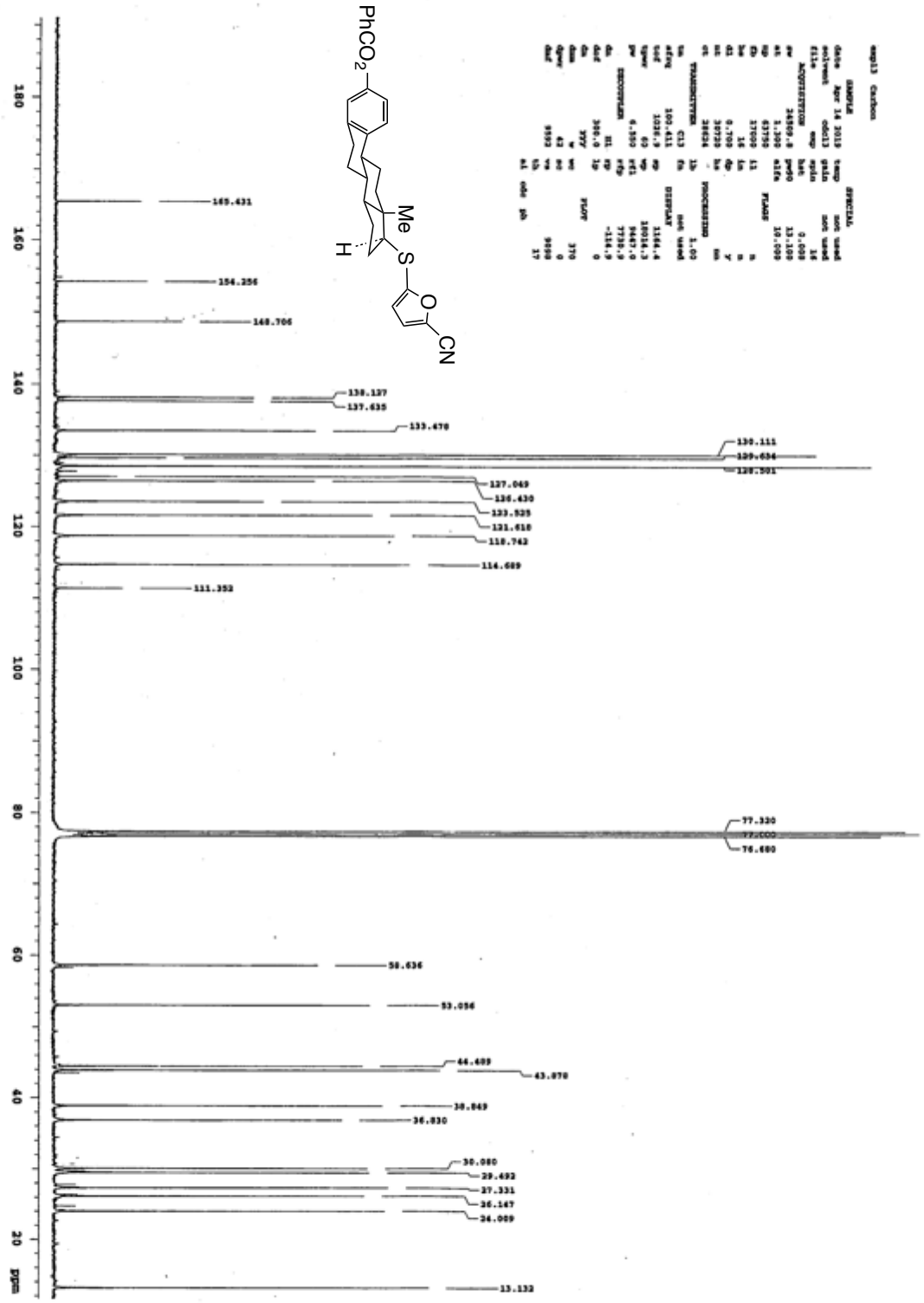
(17ß)-[2-(6,7-Dimethoxyquinazolyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16f) ^{13}**C-NMR**



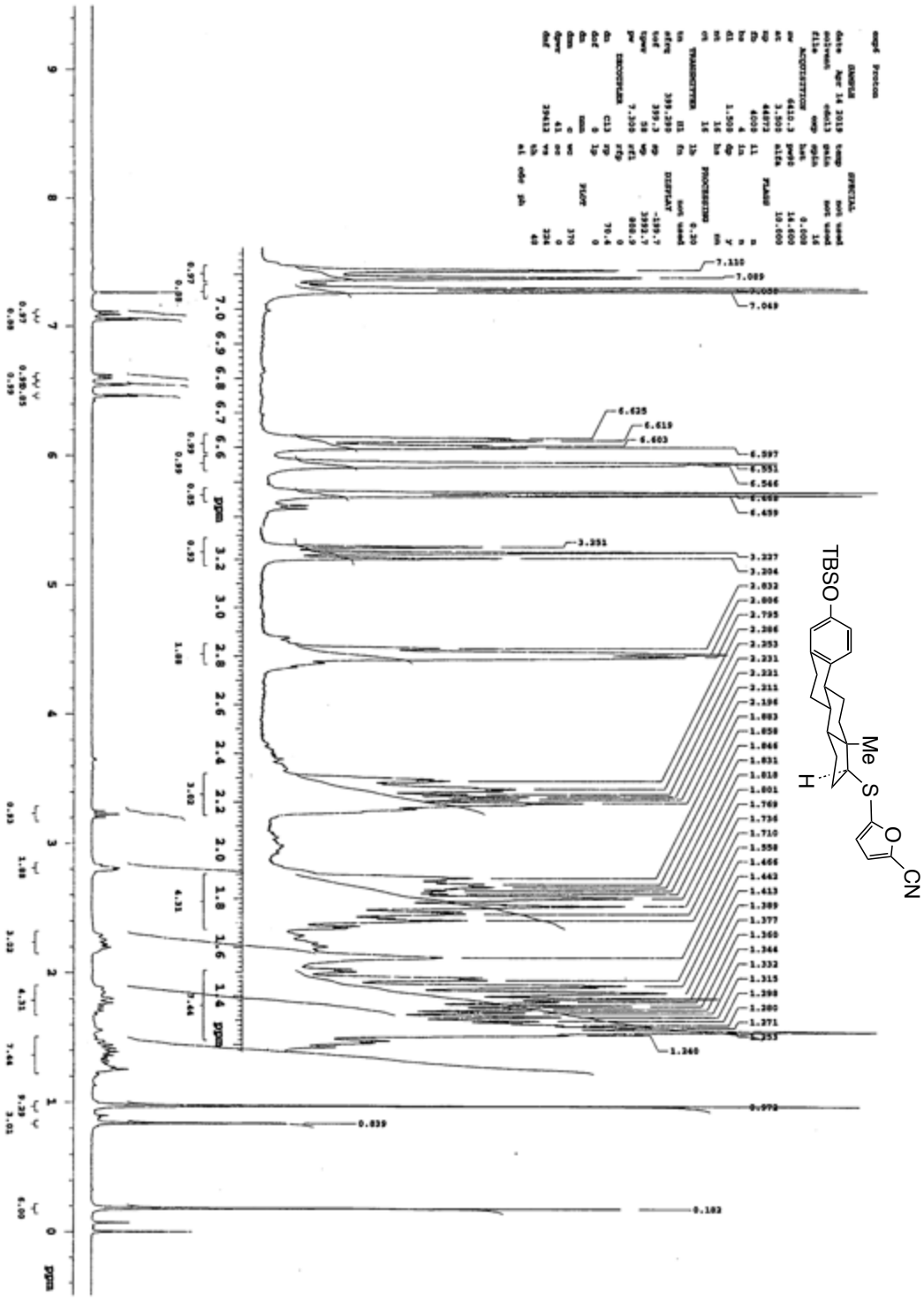
(17ß)-[2-(5-Cyanofuranyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14g) ^{1}**H-NMR**



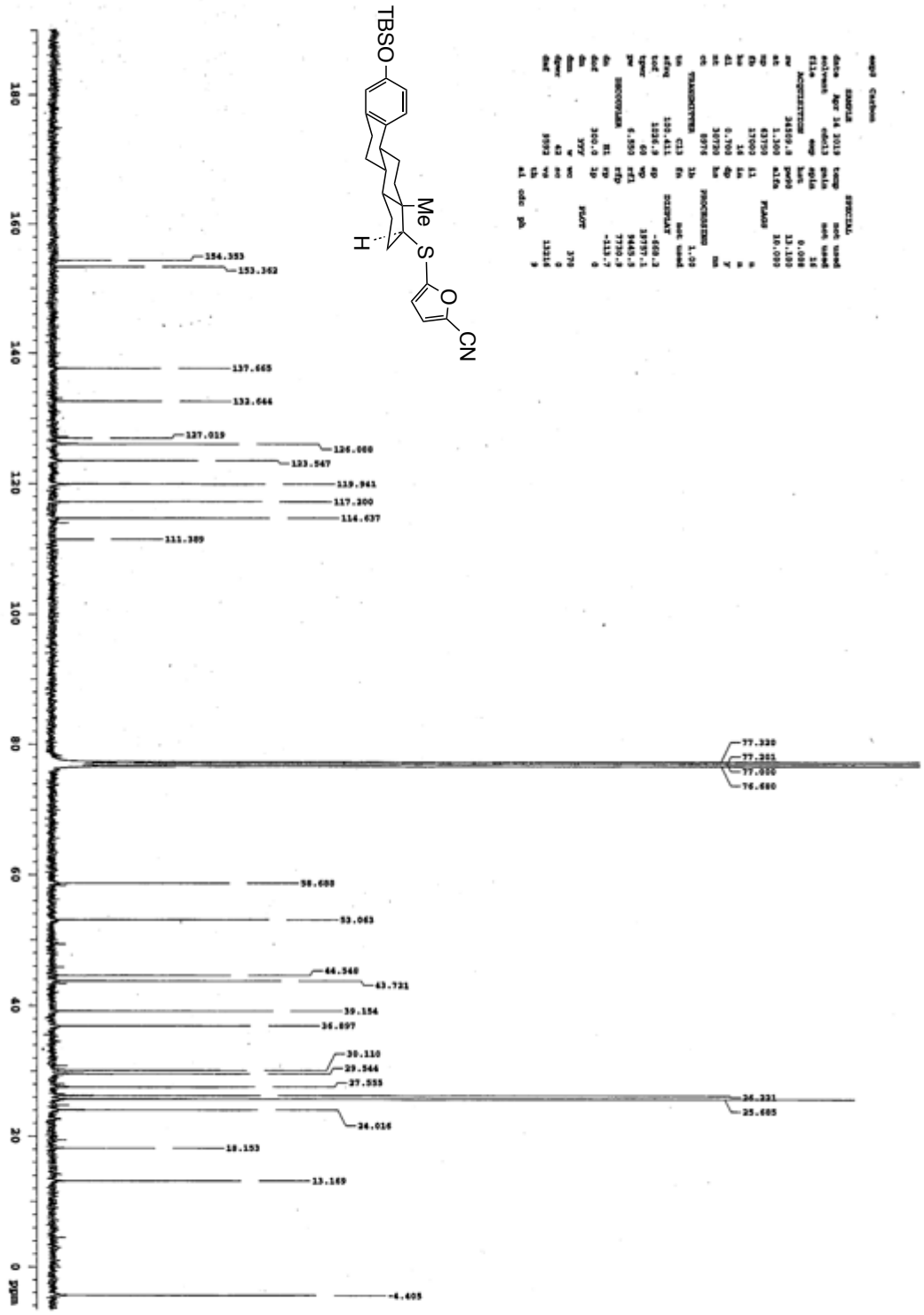
(17ß)-[2-(5-Cyanofuranyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14g) ^{13}**C-NMR**



(17ß)-[2-(5-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16g) ^{1}H-NMR

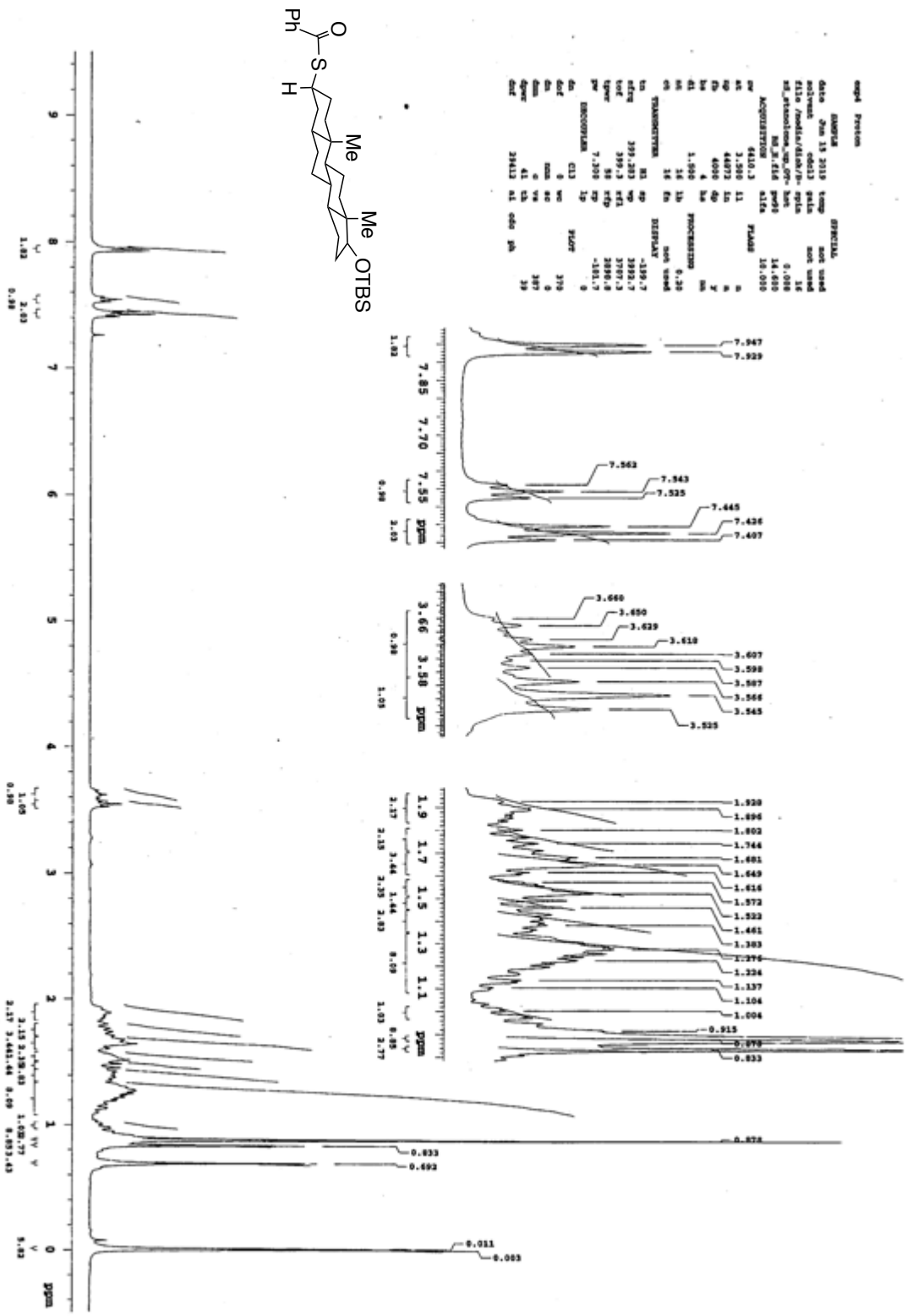


(17ß)-[2-(5-Cyanofuranyl)thio]-3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16g) ^{13}C-NMR

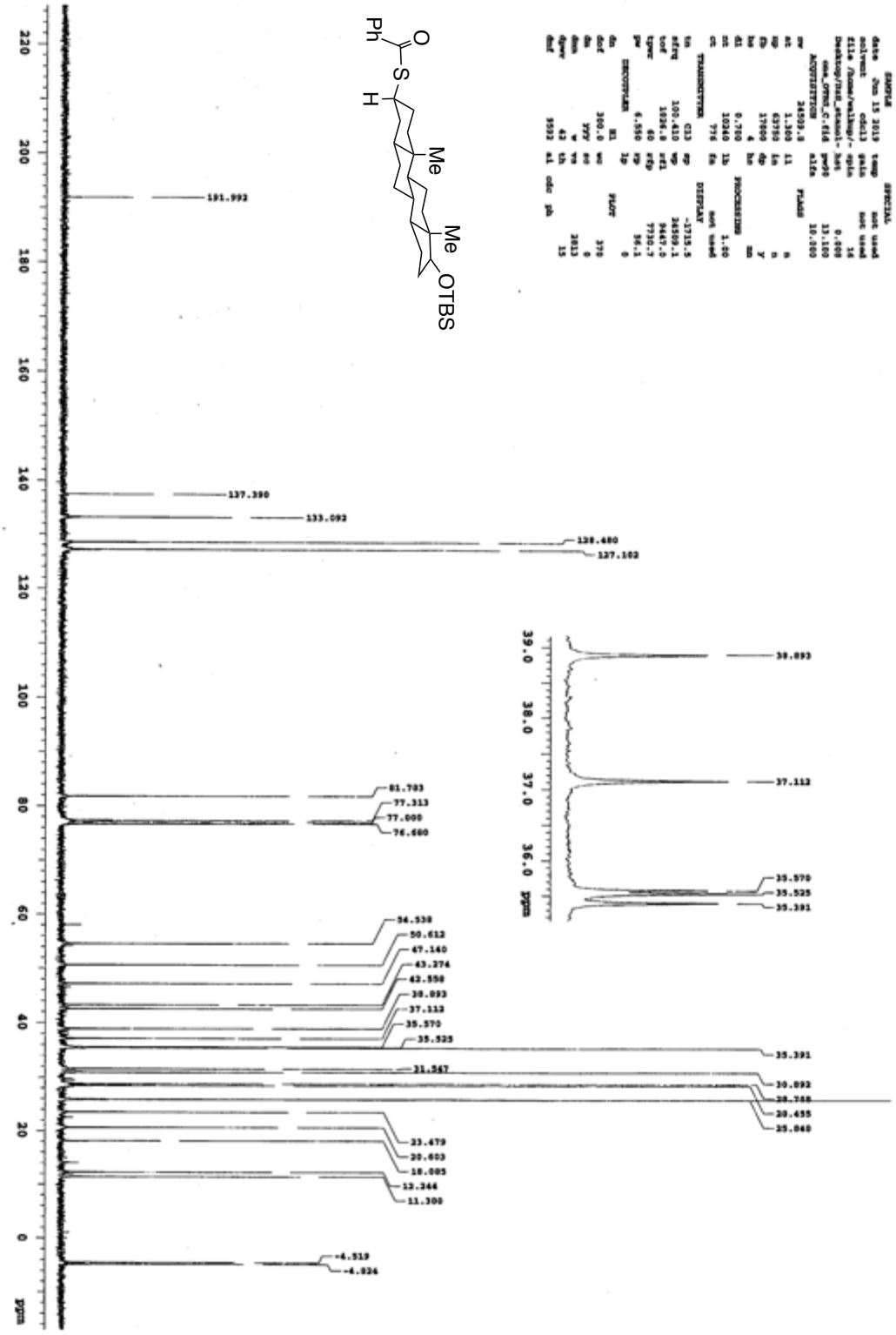


(3ß,17ß)-3-benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17)

^{1}H-NMR

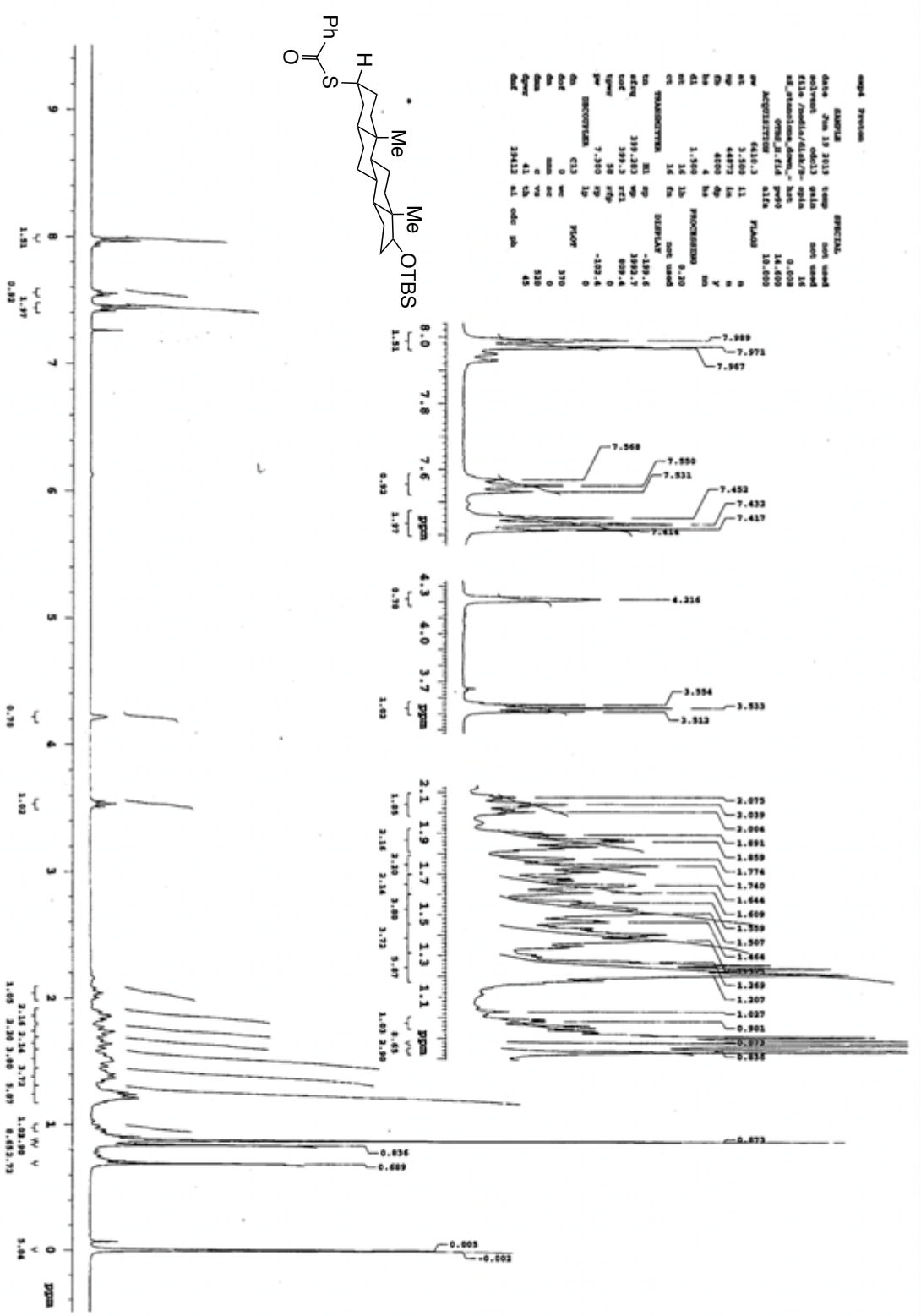


(3ß,17ß)-3-benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17)
^{13}C-NMR

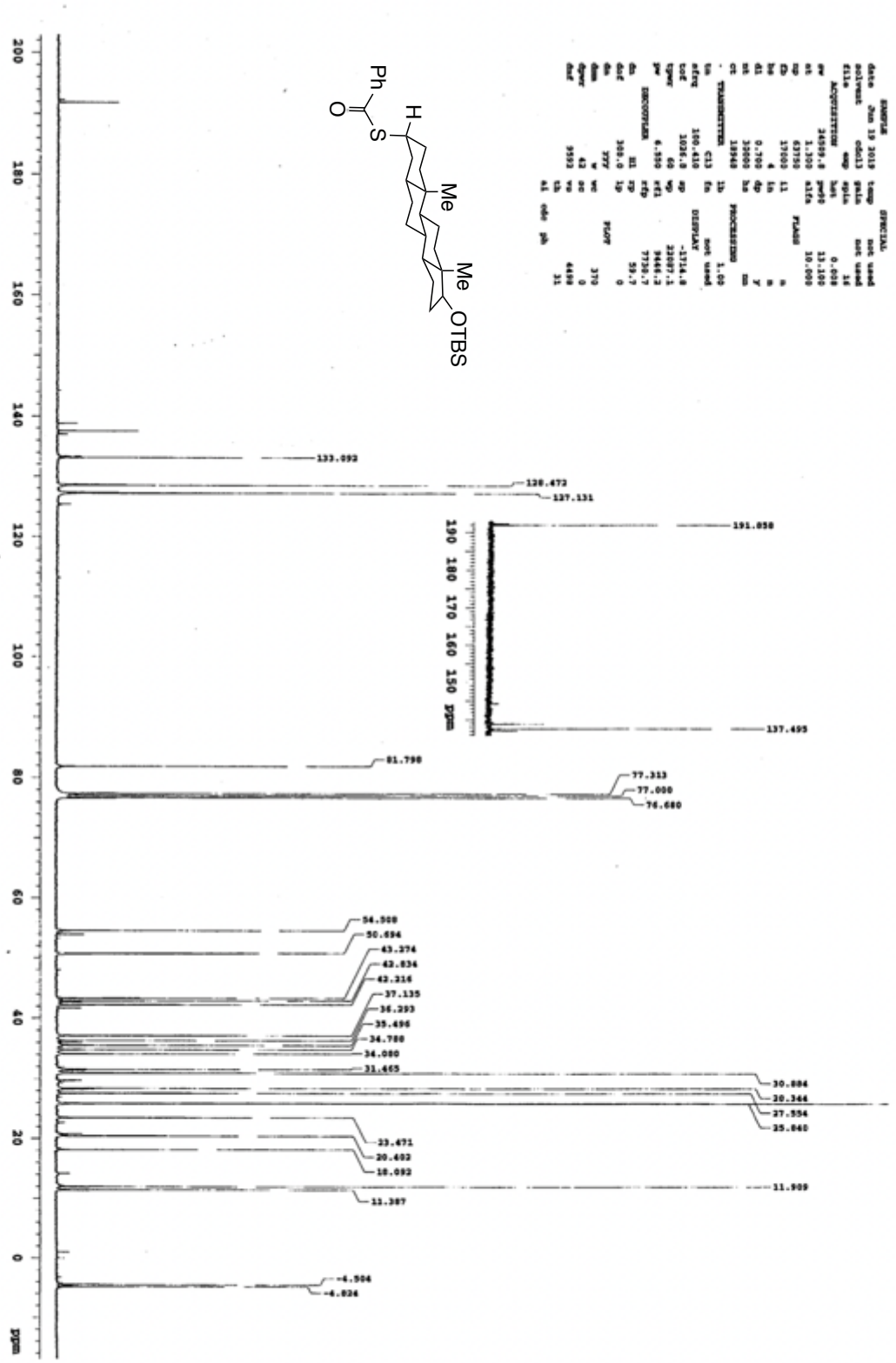


(3α,17ß)-3-Benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17')

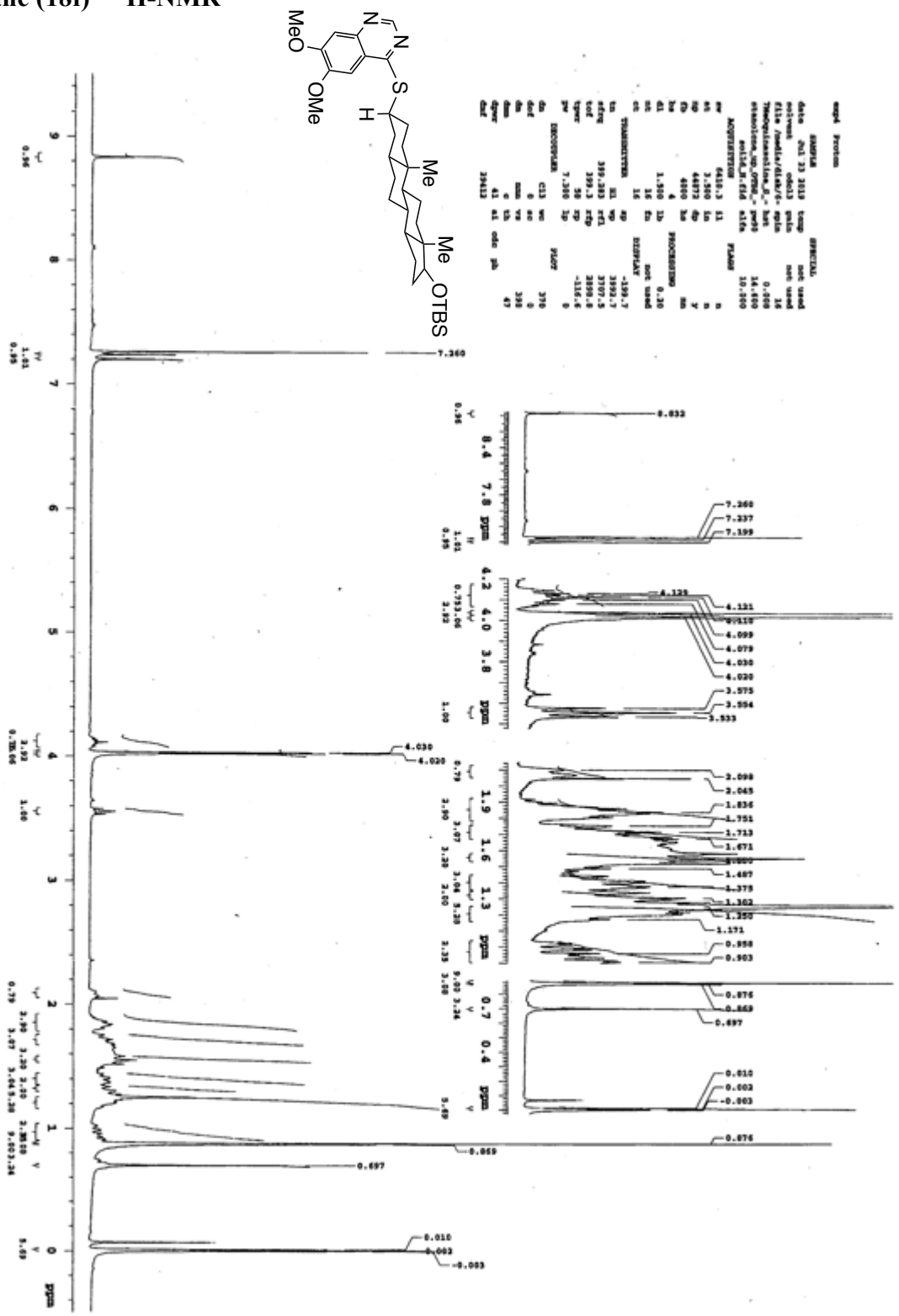
^{1}H-NMR



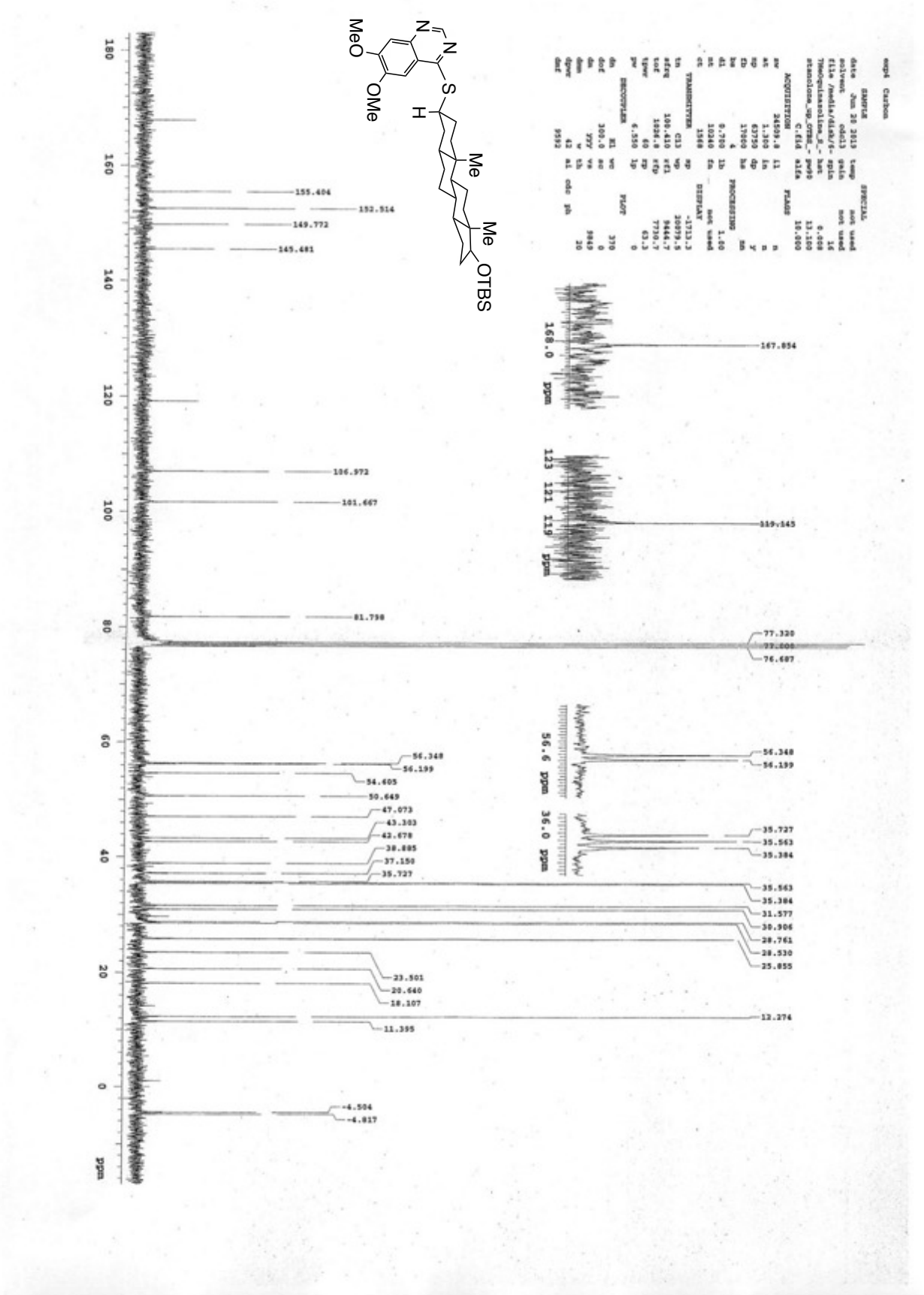
(3α,17ß)-3-Benzoylthio-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (17')
^{13}C-NMR



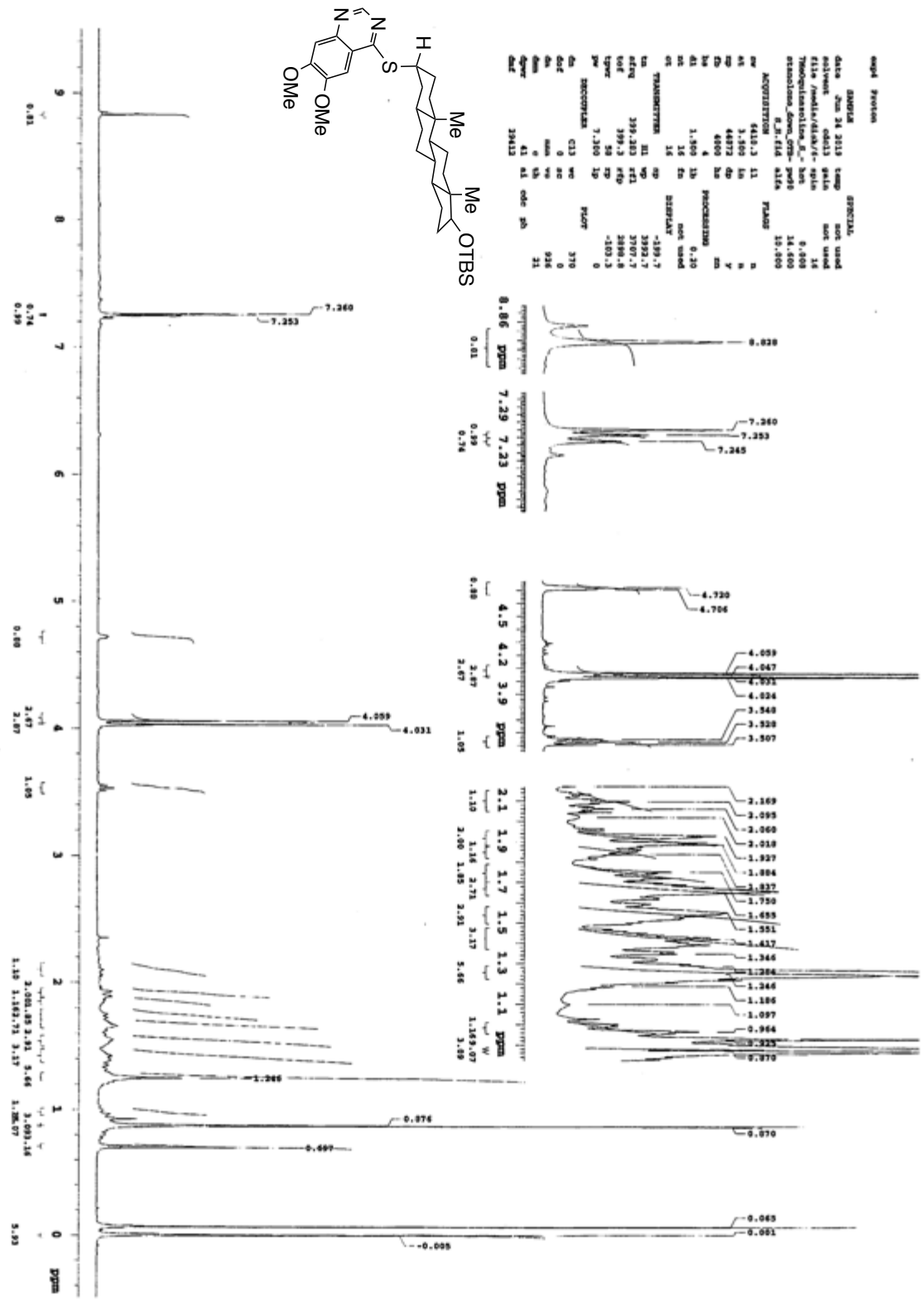
(3ß,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f) ^{1}**H-NMR**



(3ß,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f) ^{13}**C-NMR**



(3α,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f') ^{1}H-NMR



(3α,17ß)-3-[2-(6,7-Dimethoxyquinazolyl)thio]-17-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5α-androstane (18f') ^{13}C-NMR