

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

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Supplementary Materials

¹H- and ¹³C-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 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. 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(PPh₃)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 atmosphere, 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. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₂H₁₂ClNOS: 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). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₀H₁₉N₃S: 333.1300. Found: 333.1302.

2-Benzoxazolyl cyclopentyl sulfide (**3b**)

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₂H₁₃NOS: 219.0717. Found: 219.0719.

2-Benzothiazolyl cyclopentyl sulfide (**3d**)¹⁾

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₂H₁₃NS₂: 235.0489. Found: 235.0506.

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

Yellow oil. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₁H₁₄O₂S: 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). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₁H₂₁N₃S: 347.1456. Found: 347.1432.

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

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₃H₂₇N₃S: 377.1926. Found: 377.1920. One carbon peak of aliphatic region was piled up in ¹³C-NMR.

4-Chlorophenyl benzoate (4)²

Colorless solid. Mp 91.0-92.0°C (Hexane:Ethyl acetate = 4:1). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₃H₉Cl₂O: 232.0291. Found: 232.0276.

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

Colorless solid. Mp 133.0-133.5 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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* = 5.2 Hz). ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₅H₄₄OSSi: 420.2882, M⁺-H C₂₅H₄₃OSSi: 419.2804. Found: 419.2808.

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

Colorless solid. Mp 135.5-136.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₅H₄₂OSSi: 418.2726. Found: 418.2698.

(3β,17β)-17-(Benzoylthio)-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5-ene (9)

Colorless solid. Mp 144.0-144.5 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₂H₄₈O₂SSi: 524.3144. Found: 524.3110.

(3β)-17-(Benzoylthio)-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5,16-dien (10)

Colorless solid. Mp 145.0-146.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₂H₄₆O₂SSi: 522.2988. Found: 522.2993.

Typical procedures for synthesis of the (3β,17β)-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(PPh₃)₄ (14.4 mg, 10 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz, 11.1 mg, 20 mol%), (3β,17β)-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 atmosphere, 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 (3β,17β)-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 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{40}\text{H}_{53}\text{N}_3\text{OSSi}$: 651.3679. Found: 651.3668.

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

Colorless solid. Mp 142.5-143.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{32}\text{H}_{47}\text{NOS}_2\text{Si}$: 571.2707. Found: 571.2708. One carbon peak of aliphatic region was piled up in ^{13}C -NMR.

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

Colorless solid. Mp 112.5-113.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{32}\text{H}_{47}\text{NOS}_2\text{Si}$: 553.2868. Found: 553.2860.

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

Colorless solid. Mp 183.0-184.0 $^\circ\text{C}$ (Hexane). ^1H -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 $\text{C}_{35}\text{H}_{52}\text{N}_2\text{O}_3\text{SSi}$: 608.3468. Found: 608.3470.

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

Colorless solid. Mp 96.0-97.0 $^{\circ}\text{C}$ (Hexane). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{30}\text{H}_{45}\text{NO}_2\text{SSi}$: 511.2940. Found: 511.2917.

(3 β)-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 $^{\circ}\text{C}$ (Hexane). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{40}\text{H}_{51}\text{N}_3\text{OSSi}$: 649.3522. Found: 649.3524.

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

Colorless solid. Mp 103.0-104.0 $^{\circ}\text{C}$ (Hexane). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{32}\text{H}_{44}\text{ClNO}_2\text{SSi}$: 569.2551. Found: 569.2557.

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

Colorless solid. Mp 170.0-170.5 $^{\circ}\text{C}$ (Hexane). $^1\text{H-NMR}$ (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 ($\text{M}^+ - 57$, 90%). HRMS Calcd. for $\text{C}_{32}\text{H}_{45}\text{NOS}_2\text{Si}$: 551.2712. Found: 551.2698.

(3 β)-17-[4-(6,7-Dimethoxyquinazoly)thio]-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5,16-diene (12f)

Pale yellow solid. Mp 202.0-203.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 346$, 100%). HRMS Calcd. for $\text{C}_{35}\text{H}_{50}\text{N}_2\text{O}_3\text{SSi}$: 606.3311. Found: 606.3328.

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

Colorless solid. Mp 144.0-145.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{30}\text{H}_{43}\text{NO}_2\text{SSi}$: 509.2784. Found: 509.2783.

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

In a two-necked flask were placed $\text{RhH}(\text{PPh}_3)_4$ (28.8 mg, 20 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz, 22.3 mg, 40 mol%), (17 β)-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 atmosphere, 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 (17 β)-[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 °C (Ethyl acetate). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₂H₃₀ClNO₃: 543.1635. Found: 543.1638.

(17B)-17-(Benzoylthio)-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]estra-1,3,5(10)-triene (13)

Colorless solid. Mp 142.5-143.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₁H₄₂O₂SSi: 506.2675. Found: 506.2652.

(17B)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a)

Colorless solid. Mp 236.0-238.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₄₀H₃₇N₃O₂S: 623.2606. Found: 623.2608.

(17B)-[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 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₄₈H₄₂N₆OS: 750.3141. Found: 750.3123.

1-Chloro-4-[[1,1-dimethylethyl]dimethylsilyl]oxy]benzene³

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₂H₁₉ClOSi: 242.0894. Found: 242.0895.

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

Colorless solid. Mp 166.5-168.0 °C (EtOAc). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₂H₃₁NO₂S₂: 525.1796. Found: 525.1782.

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

Colorless solid. Mp 118.5-119.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₅H₃₆N₂O₄S: 580.2396. Found: 580.2396. One carbon peak of aliphatic region was piled up in ¹³C-NMR.

(17B)-[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 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₄H₄₆N₂O₃SSi: 590.2998. Found: 590.2985.

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

Colorless solid. Mp 138.0-139.5 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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 ($\text{M}^+ - 378$, 100%). HRMS Calcd. for $\text{C}_{30}\text{H}_{29}\text{NO}_3\text{S}$: 483.1868. Found: 483.1880.

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

Colorless solid. Mp 101.0-102.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 82%). HRMS Calcd. for $\text{C}_{29}\text{H}_{39}\text{NO}_2\text{SSi}$: 493.2471. Found: 493.2477.

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

Colorless solid. Mp 138.5-139.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{32}\text{H}_{50}\text{O}_2\text{SSi}$: 526.3301. Found: 526.3290.

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

Colorless solid. Mp 42.0-43.0 $^\circ\text{C}$ (Hexane). ^1H -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 ($\text{M}^+ - 57$, 100%). HRMS Calcd. for $\text{C}_{32}\text{H}_{50}\text{O}_2\text{SSi}$: 526.3301. Found: 526.3297.

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

Colorless solid. Mp 216.0-217.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₅H₅₄N₂O₃SSi: 610.3624. Found: 610.3615.

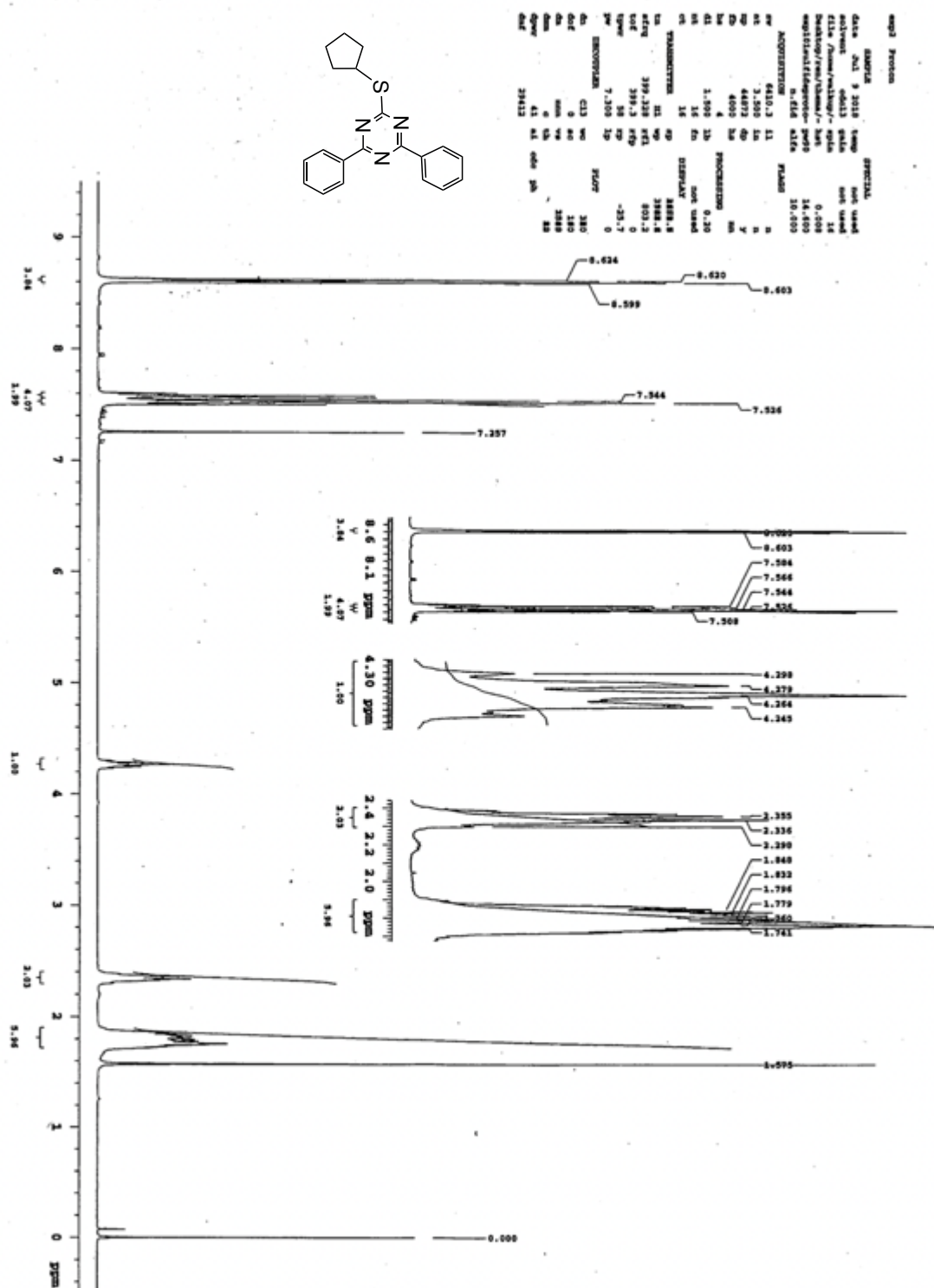
(3α,17β)-3-[2-(6,7-Dimethoxyquinazoly)thio]-17-[(1,1-dimethylethyl)dimethylsilyloxy]-5α-androstane (18f')

Colorless solid. M.p. 104.0-105.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) 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). ¹³C-NMR (100 MHz, CDCl₃) 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 C₃₅H₅₄N₂O₃SSi: 610.3624. Found: 610.3626.

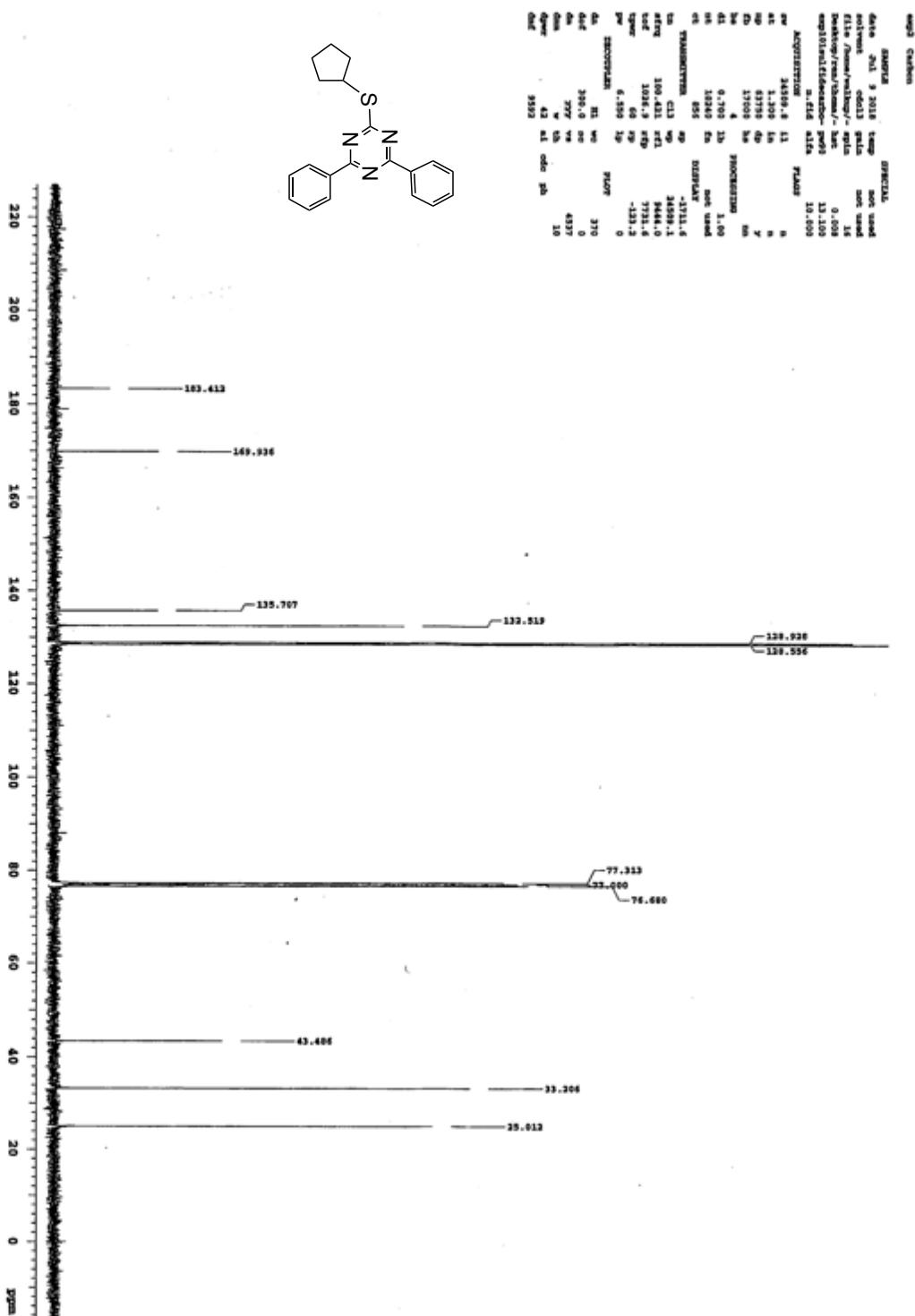
References

- 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.
- 3) Iwao, M., *J. Org. Chem.*, **1990**, *55*, 3622-3627.

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



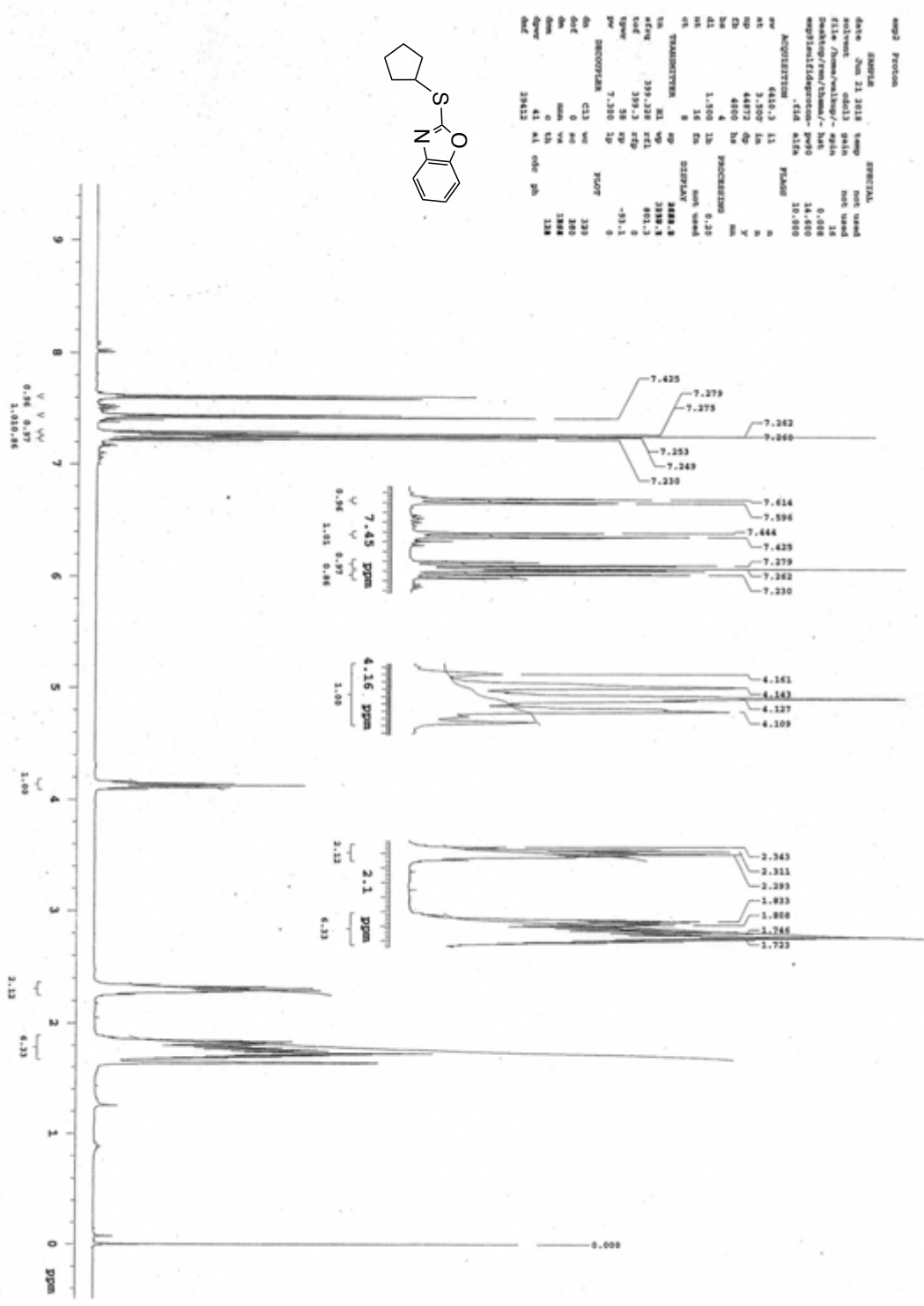
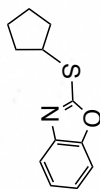
2-(4,6-Diphenyl-1,3,5-triazyl) cyclopentyl sulfide (3a) ¹³C-NMR



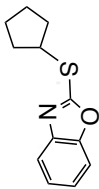
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exp101/multiscan/	psd	not used			
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2-Benzoxazolyl cyclopentyl sulfide (3b) ¹H-NMR



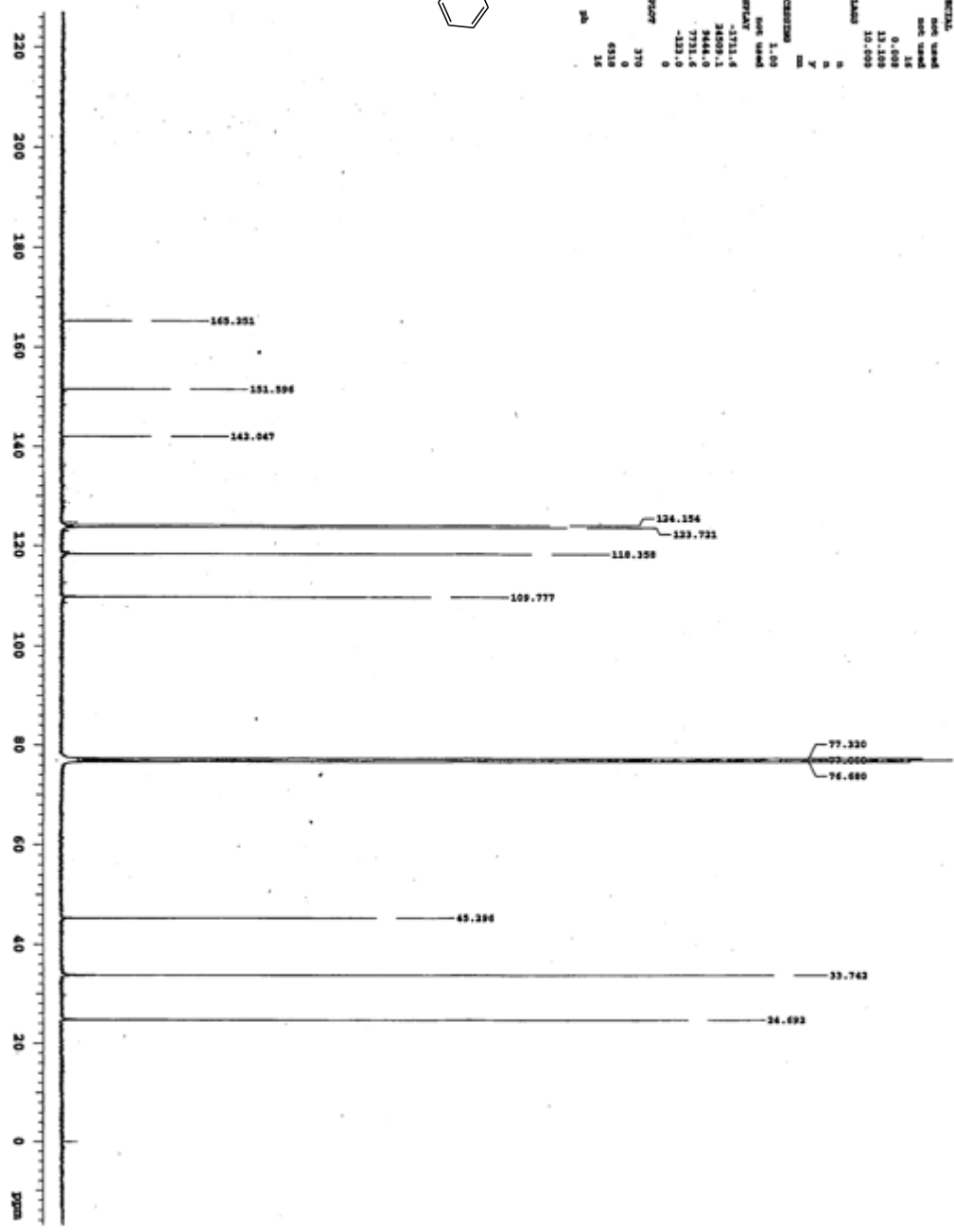
2-Benzoxazolyl cyclopentyl sulfide (3b) ¹³C-NMR



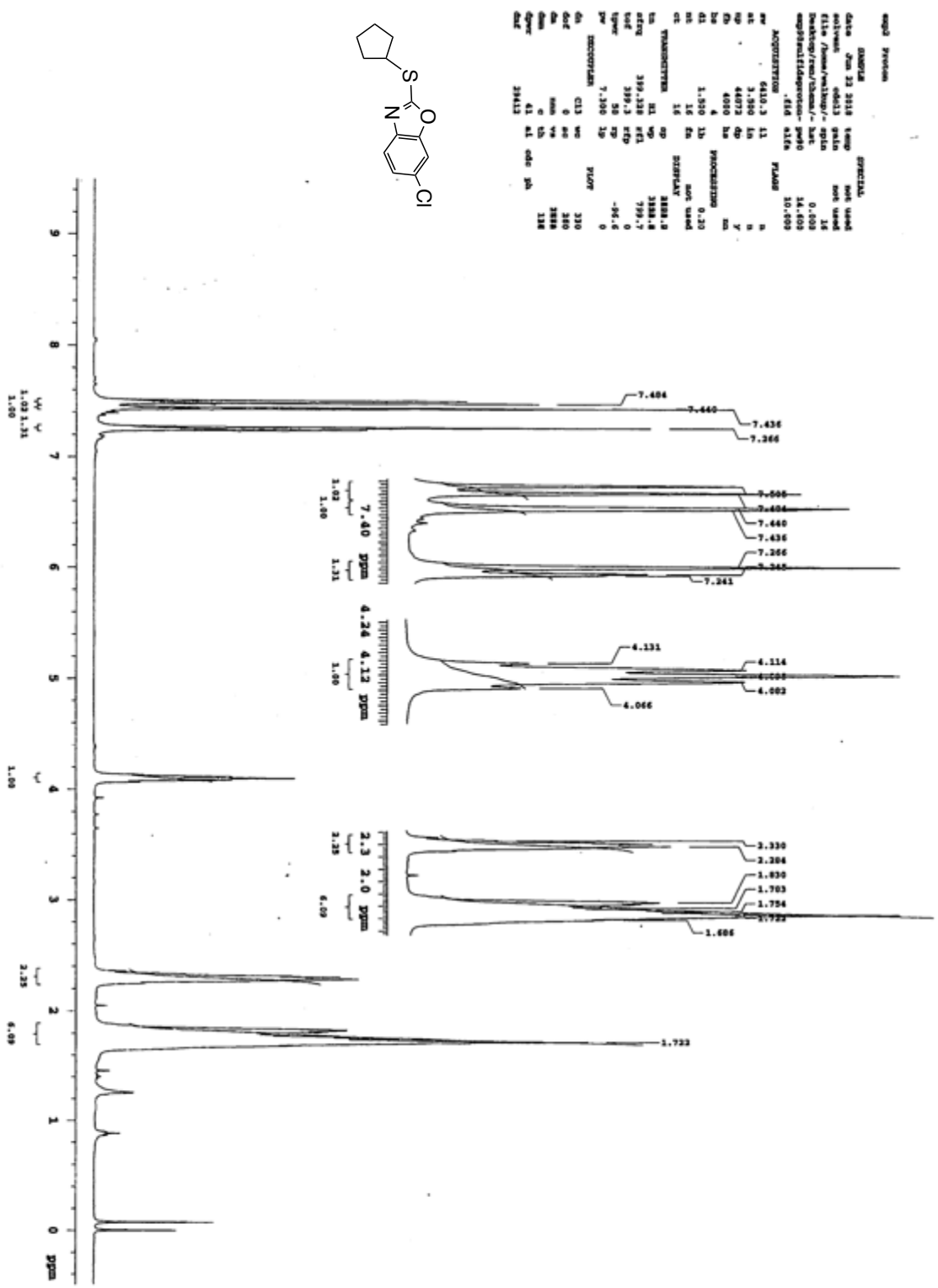
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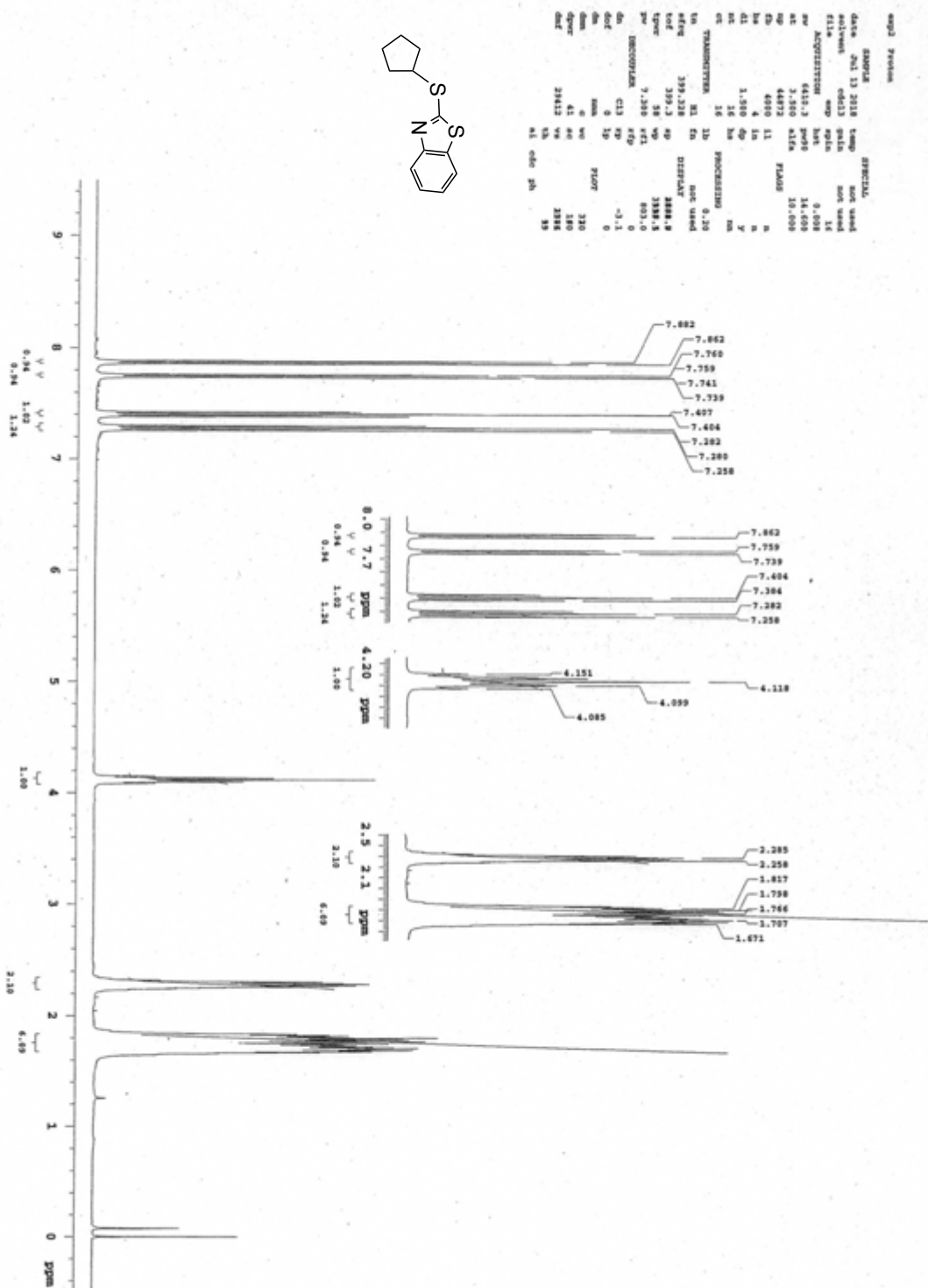
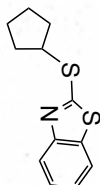
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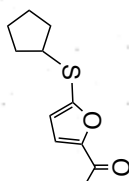
2-(6-Chlorobenzoxazolyl) cyclopentyl sulfide (3c) ¹H-NMR



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

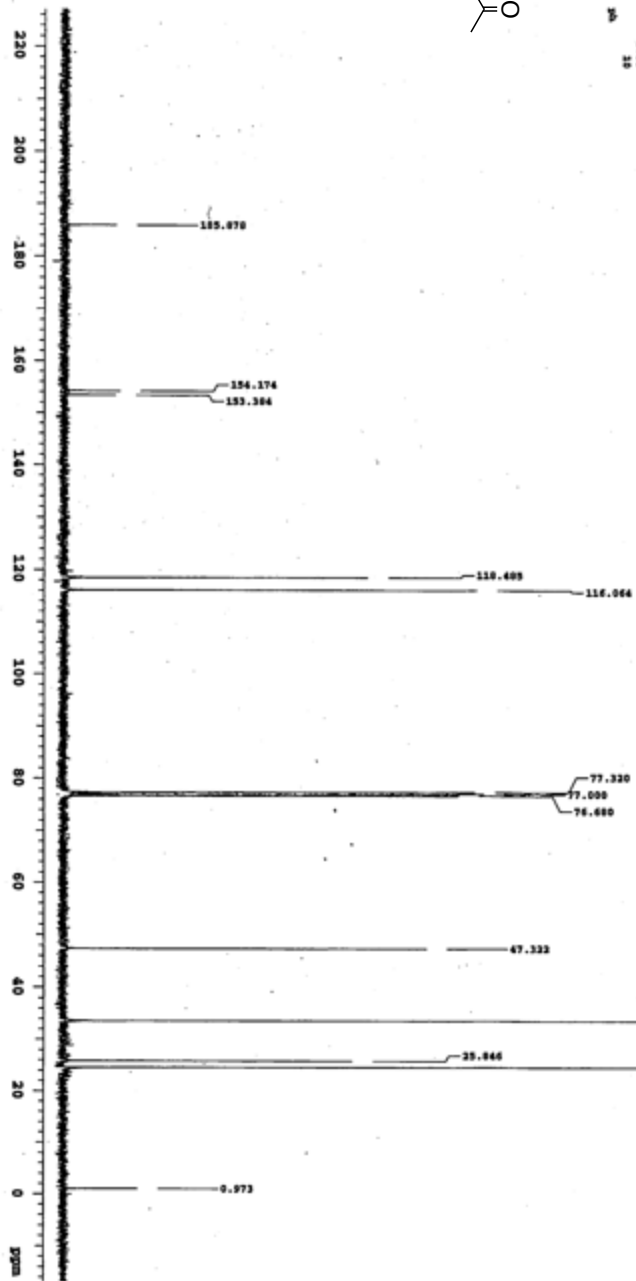


2-(5-Acetylthienyl) cyclopentyl sulfide (3e) ¹³C-NMR

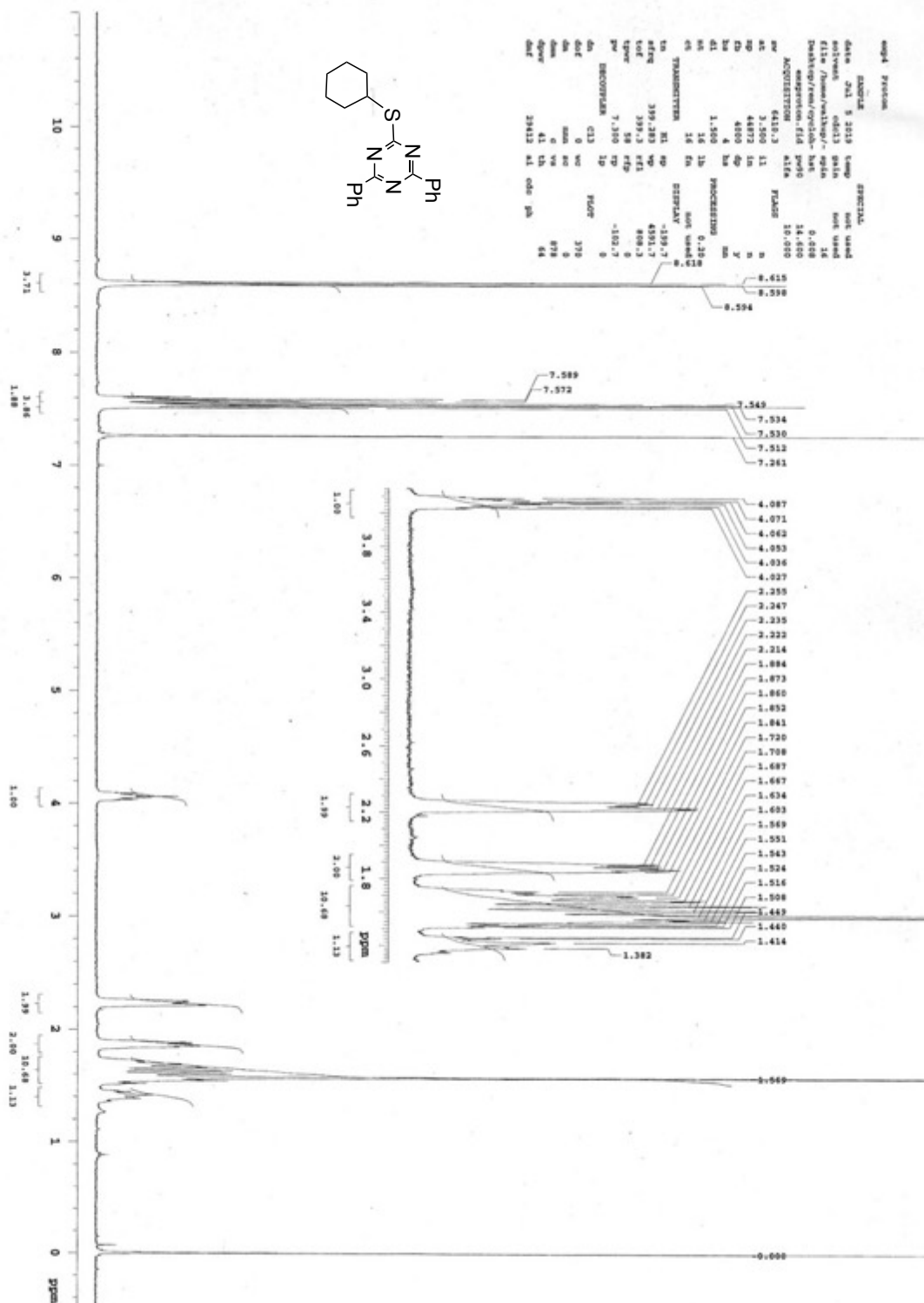


exp3 Carbon

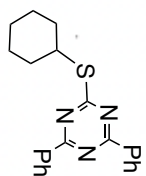
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CDCl3	116.064	AROMATIC					13C	0	100	100	
CDCl3	110.400	AROMATIC					13C	0	100	100	
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CDCl3	154.374	AROMATIC					13C	0	100	100	
CDCl3	153.364	AROMATIC					13C	0	100	100	
CDCl3	47.323	ALIPHATIC					13C	0	100	100	
CDCl3	39.601	ALIPHATIC					13C	0	100	100	
CDCl3	29.846	ALIPHATIC					13C	0	100	100	
CDCl3	24.300	ALIPHATIC					13C	0	100	100	
CDCl3	0.973	ALIPHATIC					13C	0	100	100	



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

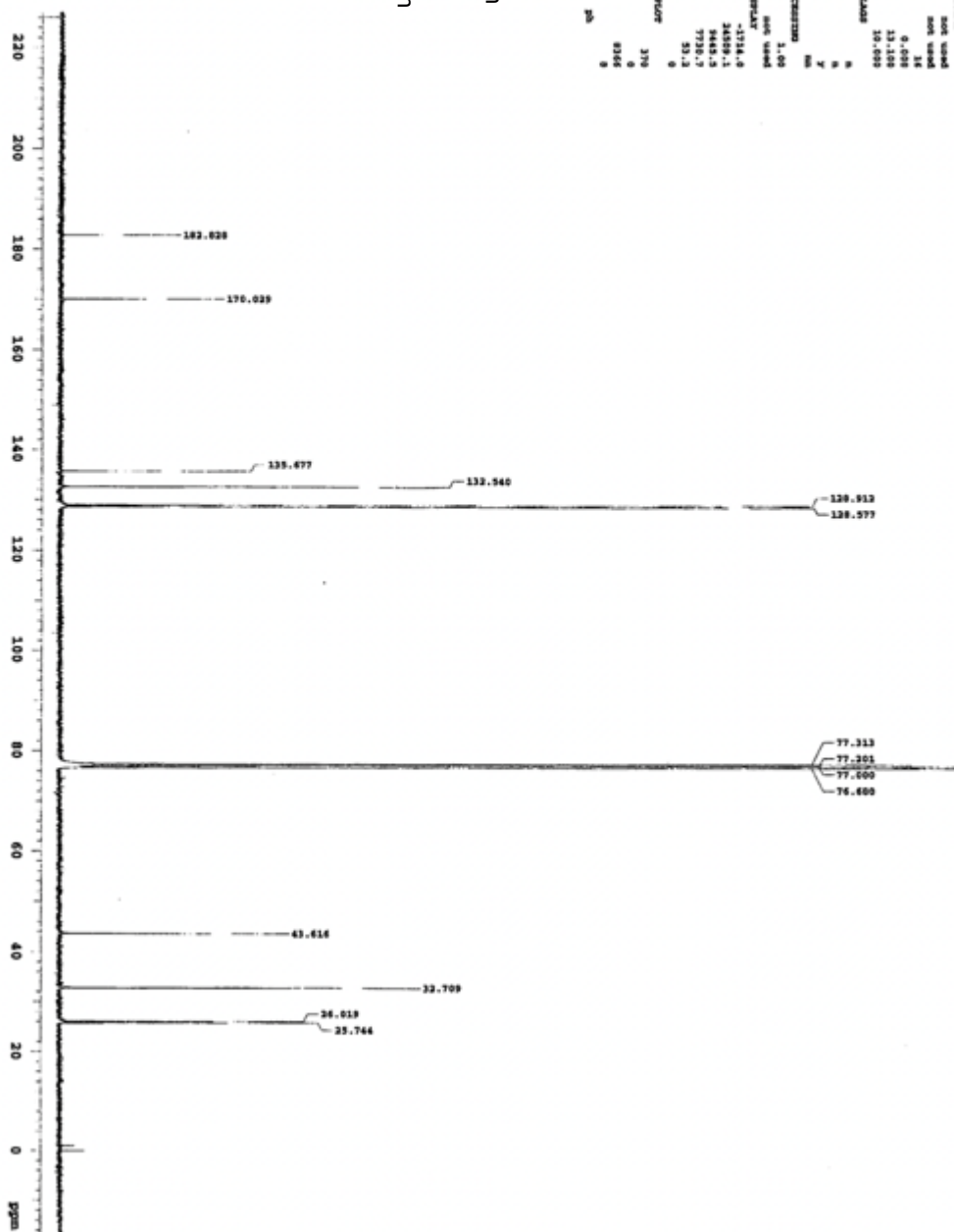


2-(4,6-Diphenyl-1,3,5-triazyl) cyclohexyl sulfide (3a') ¹³C-NMR

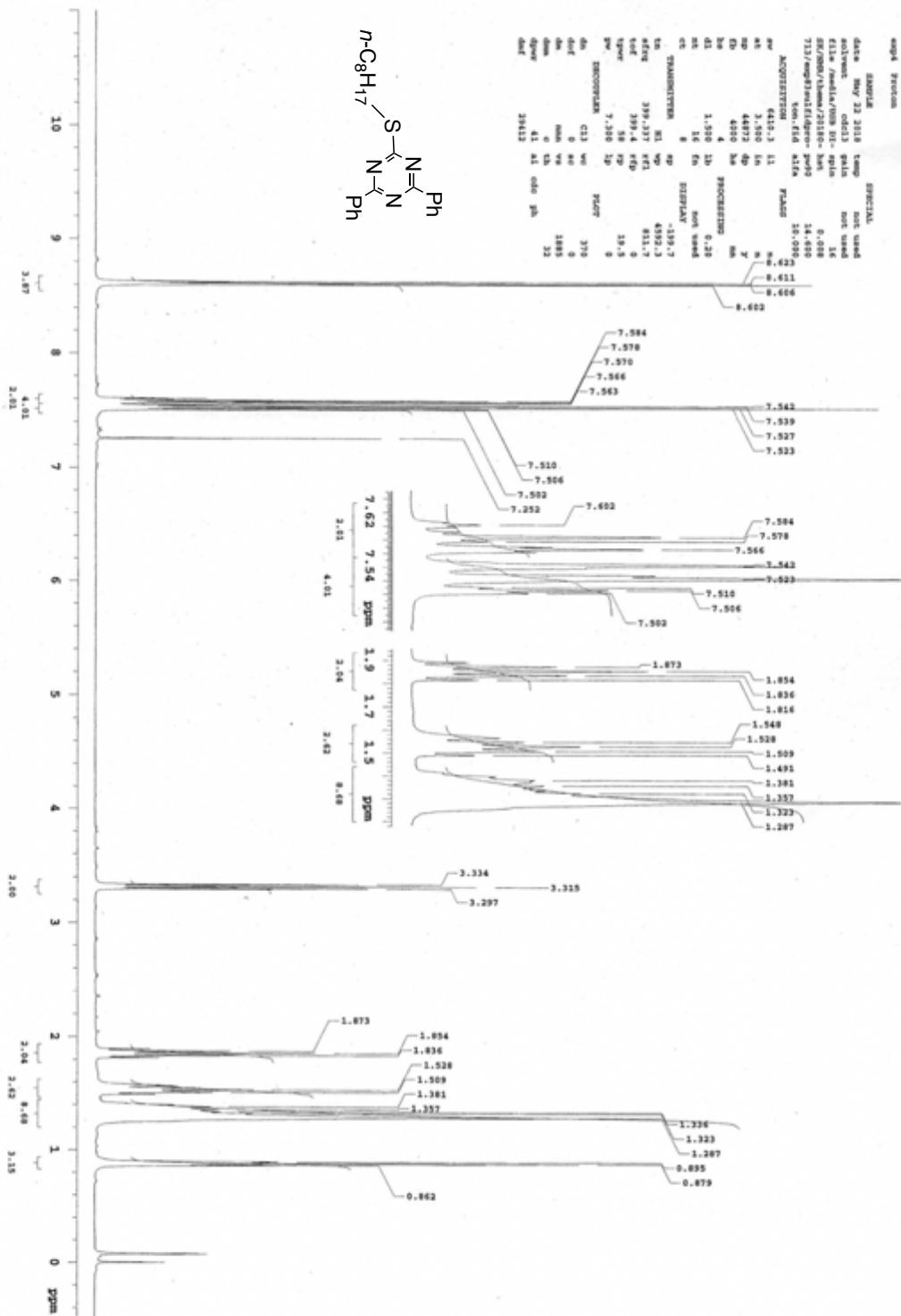


Sample Carbon

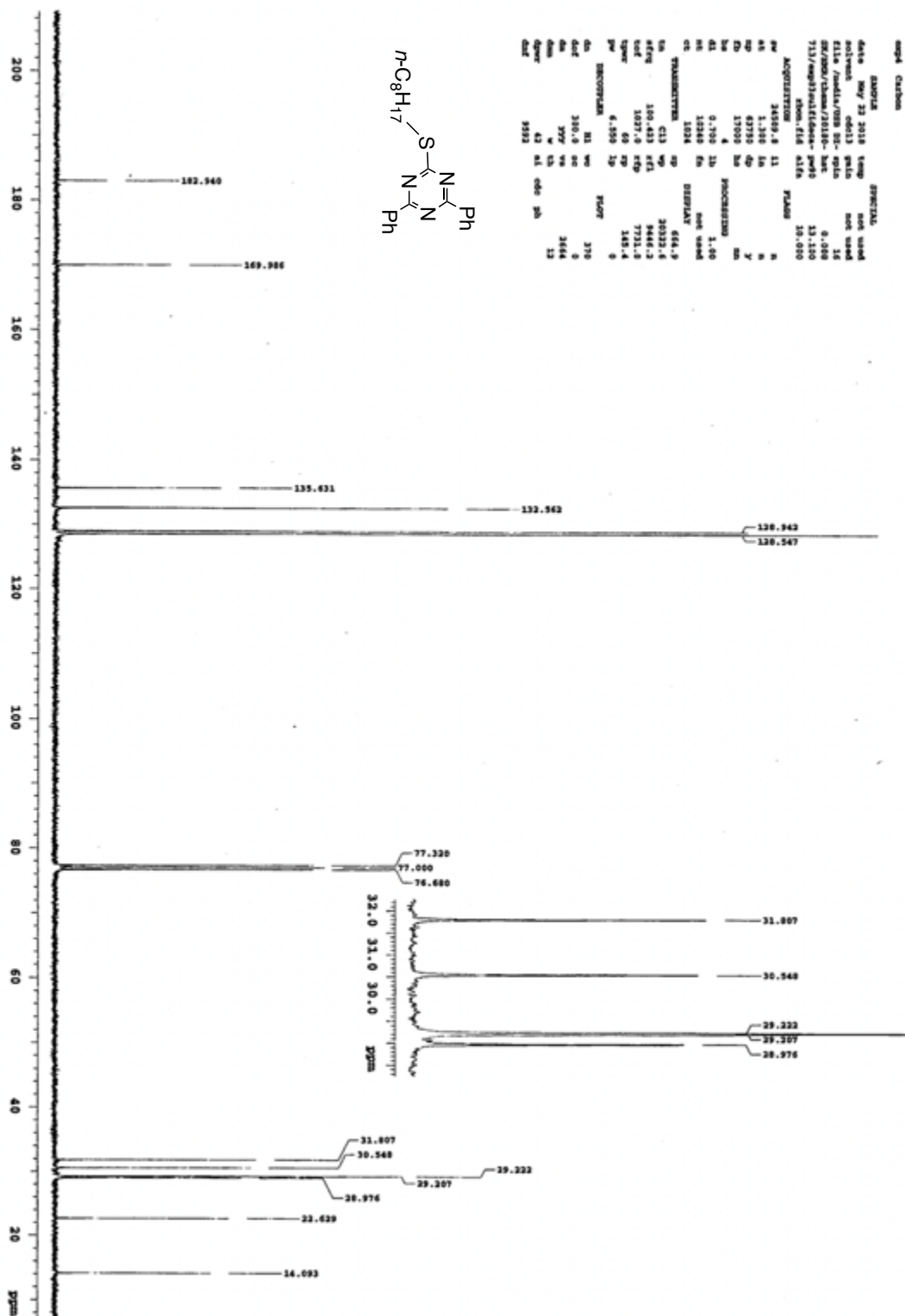
DATE	TIME	TEMP	SOLVENT	PROBHD	PULP	NUC1	NUC2	ACQ	PROG
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CH									
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2	179.2	11							
3	132.4	11							
4	132.4	11							
5	132.4	11							
6	132.4	11							
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8	132.4	11							
9	132.4	11							
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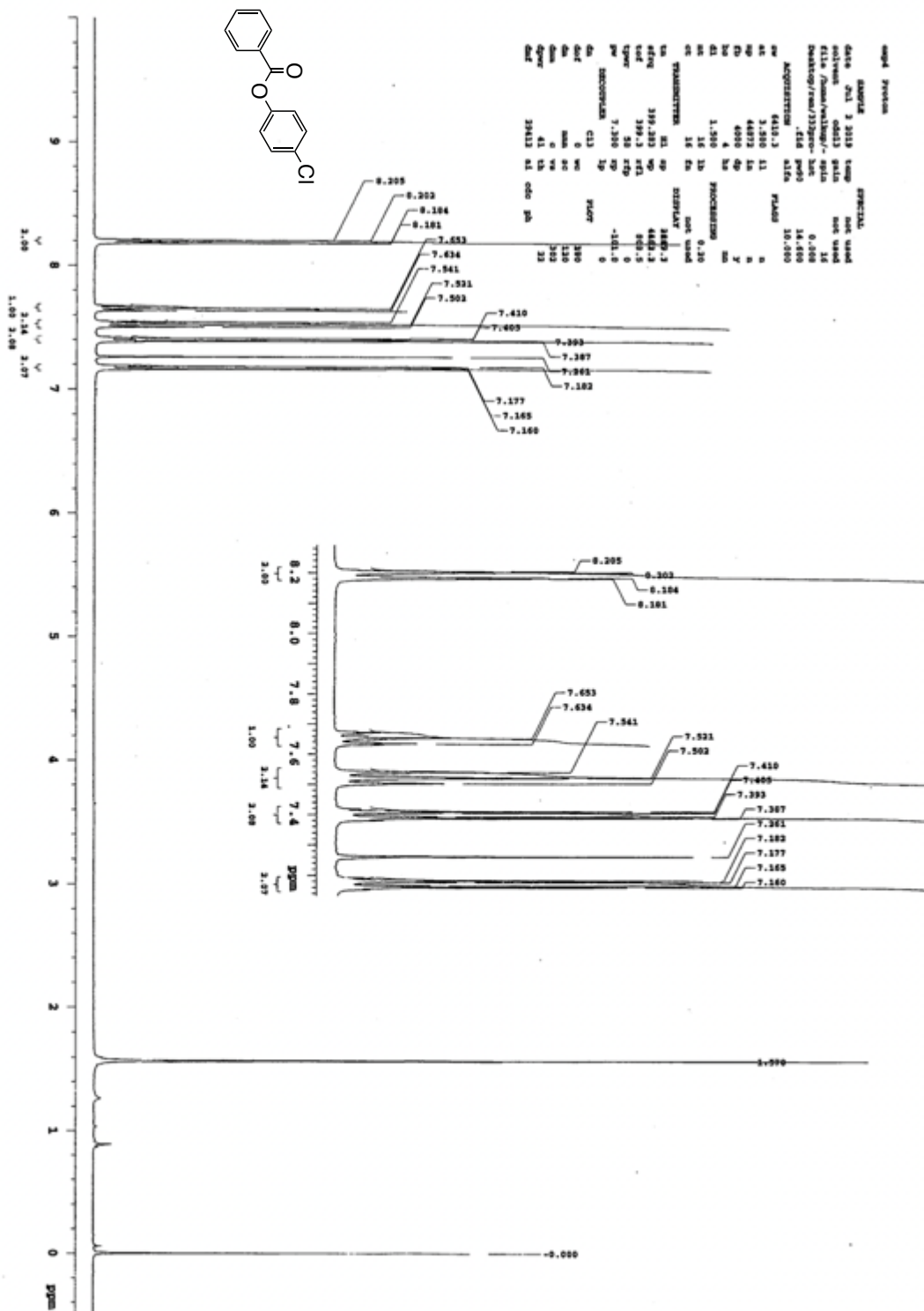
2-(4,6-Diphenyl-1,3,5-triazyl) octyl sulfide (3a'') ¹H-NMR



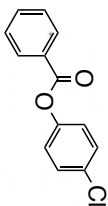
2-(4,6-Diphenyl-1,3,5-triazyl) octyl sulfide (3a'') ¹³C-NMR



4-Chlorophenyl benzoate (4) ¹H-NMR

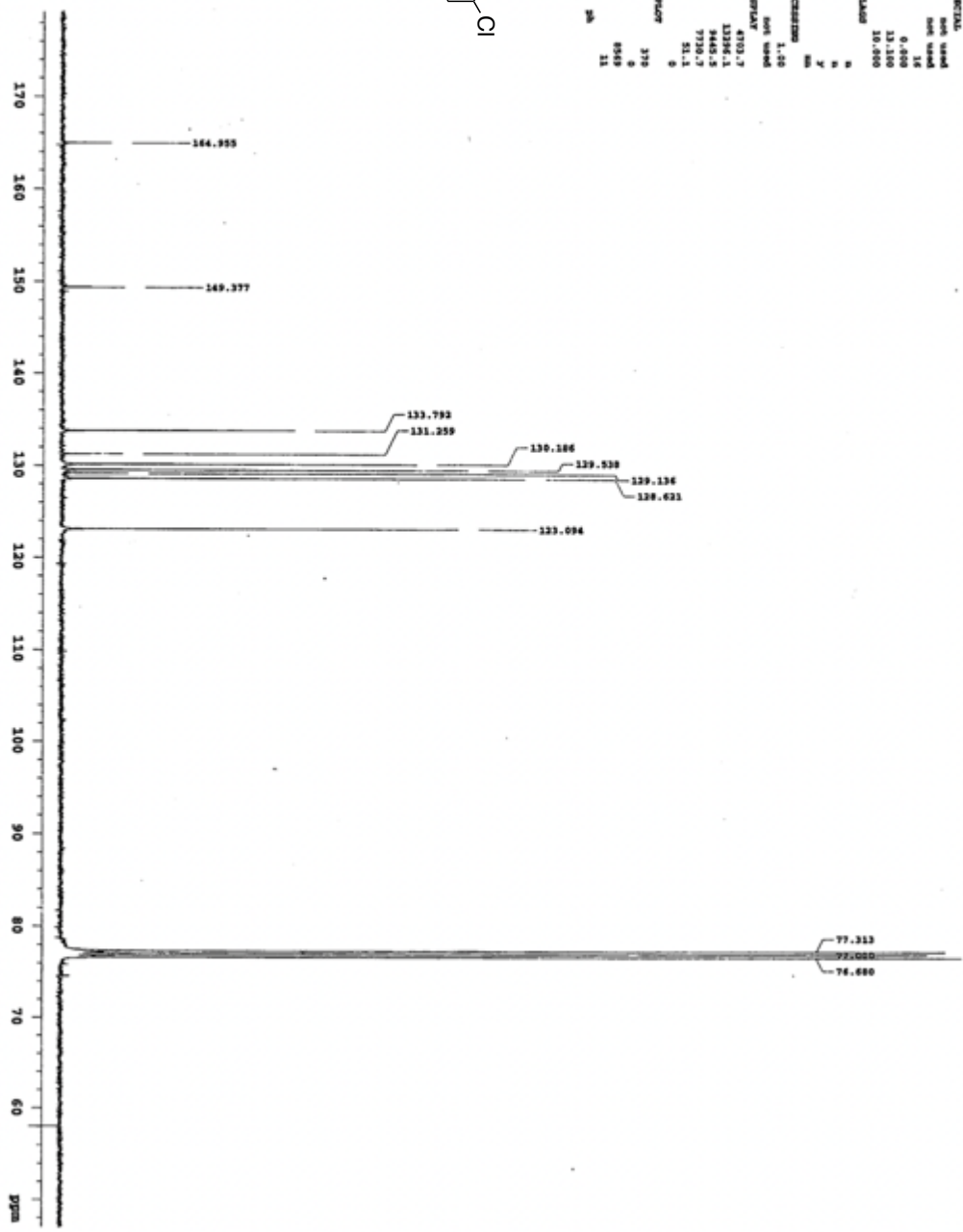


4-Chlorophenyl benzoate (4) ¹³C-NMR

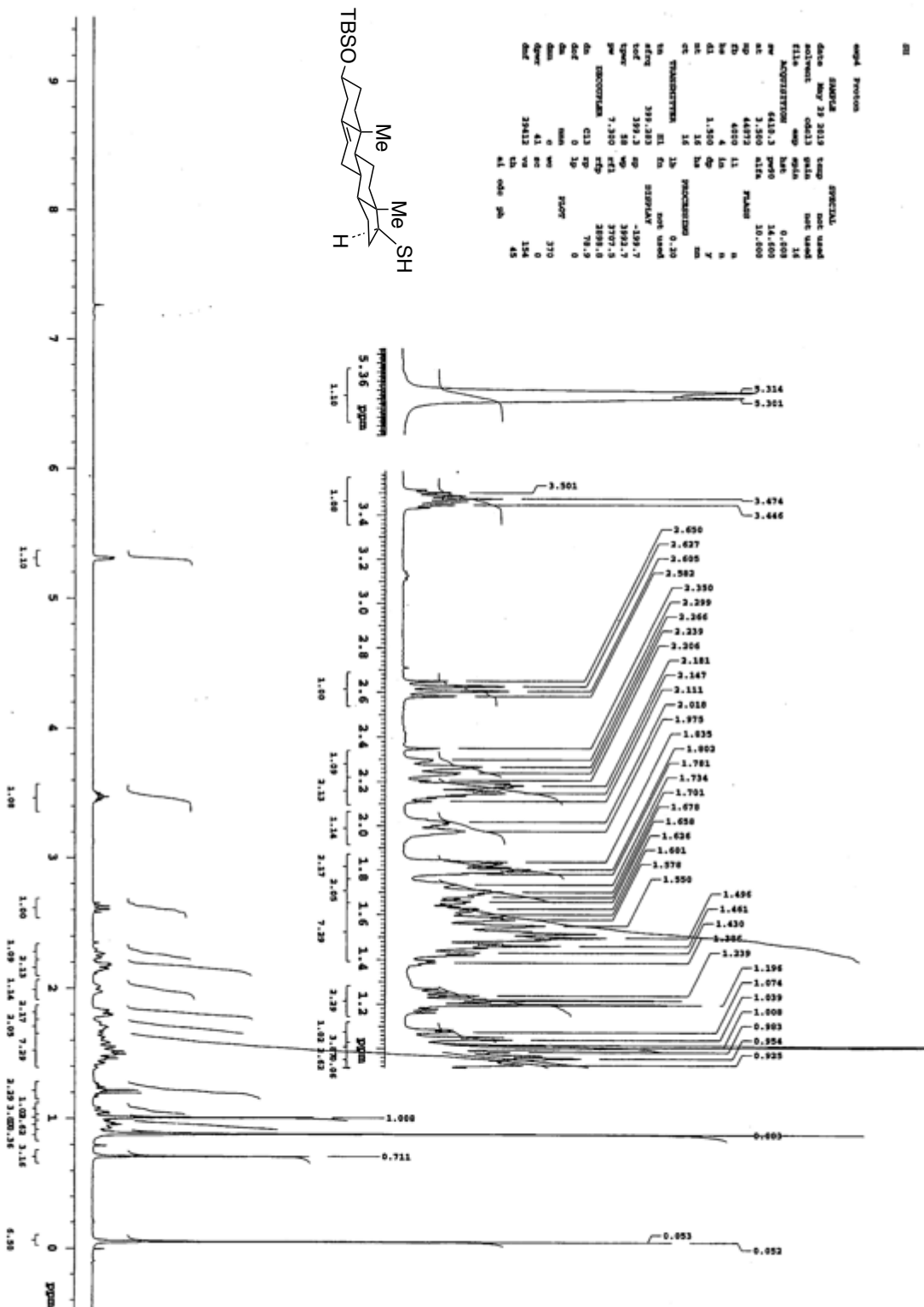


Signal Carbon

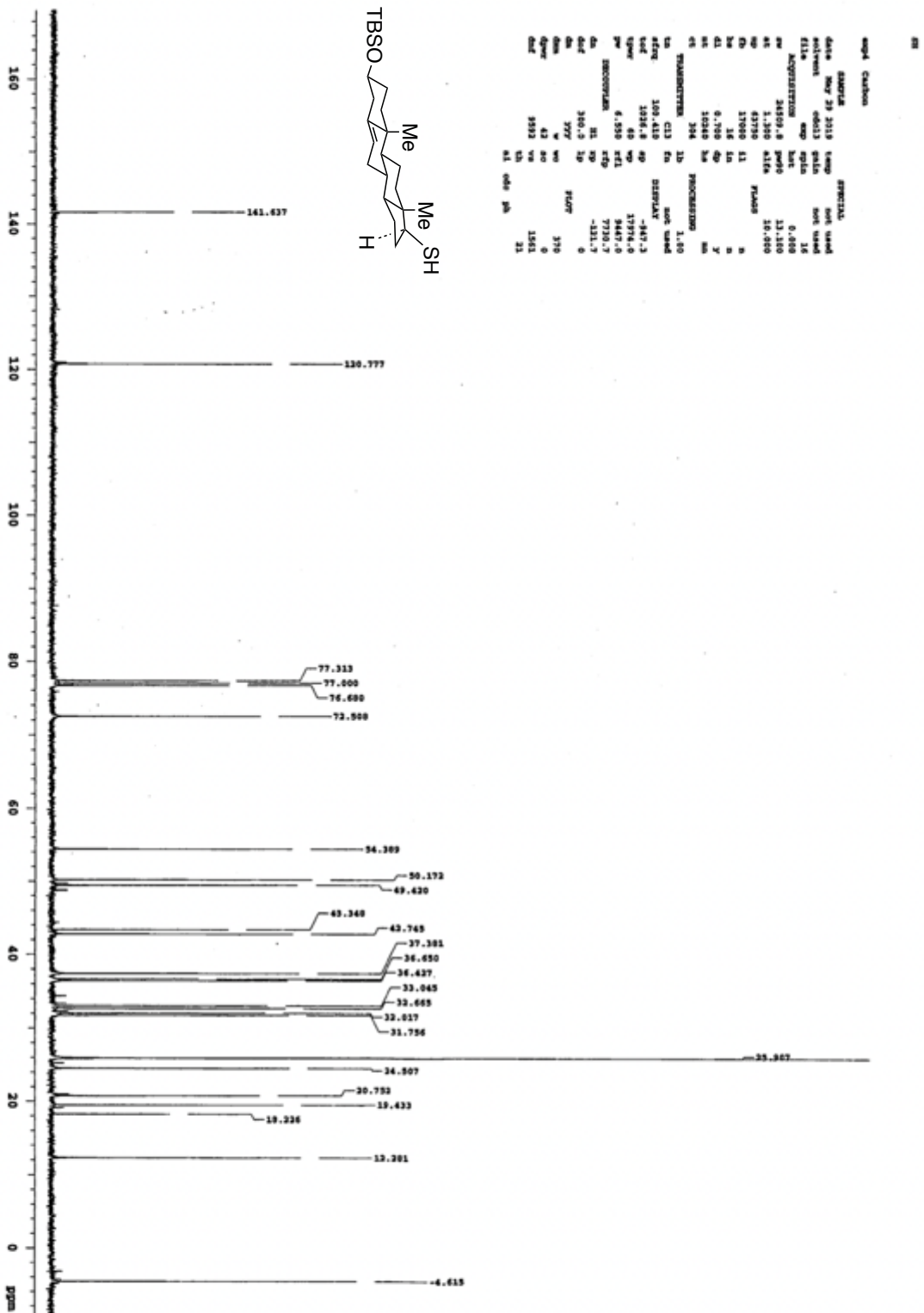
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CH	1	1308	LI	PLANS	1	1	1	1	1	1	1	1
CH	2	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	3	2700	CP	PROGCESS	1	1	1	1	1	1	1	1
CH	4	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	5	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	6	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	7	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	8	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	9	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	10	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	11	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	12	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	13	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	14	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	15	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	16	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	17	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	18	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	19	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	20	6379	LI	PLANS	1	1	1	1	1	1	1	1
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CH	22	6379	LI	PLANS	1	1	1	1	1	1	1	1
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CH	24	6379	LI	PLANS	1	1	1	1	1	1	1	1
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CH	38	6379	LI	PLANS	1	1	1	1	1	1	1	1
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CH	42	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	43	6379	LI	PLANS	1	1	1	1	1	1	1	1
CH	44	6379	LI	PLANS	1	1	1	1	1	1	1	1
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CH	48	6379	LI	PLANS	1	1	1	1	1	1	1	1
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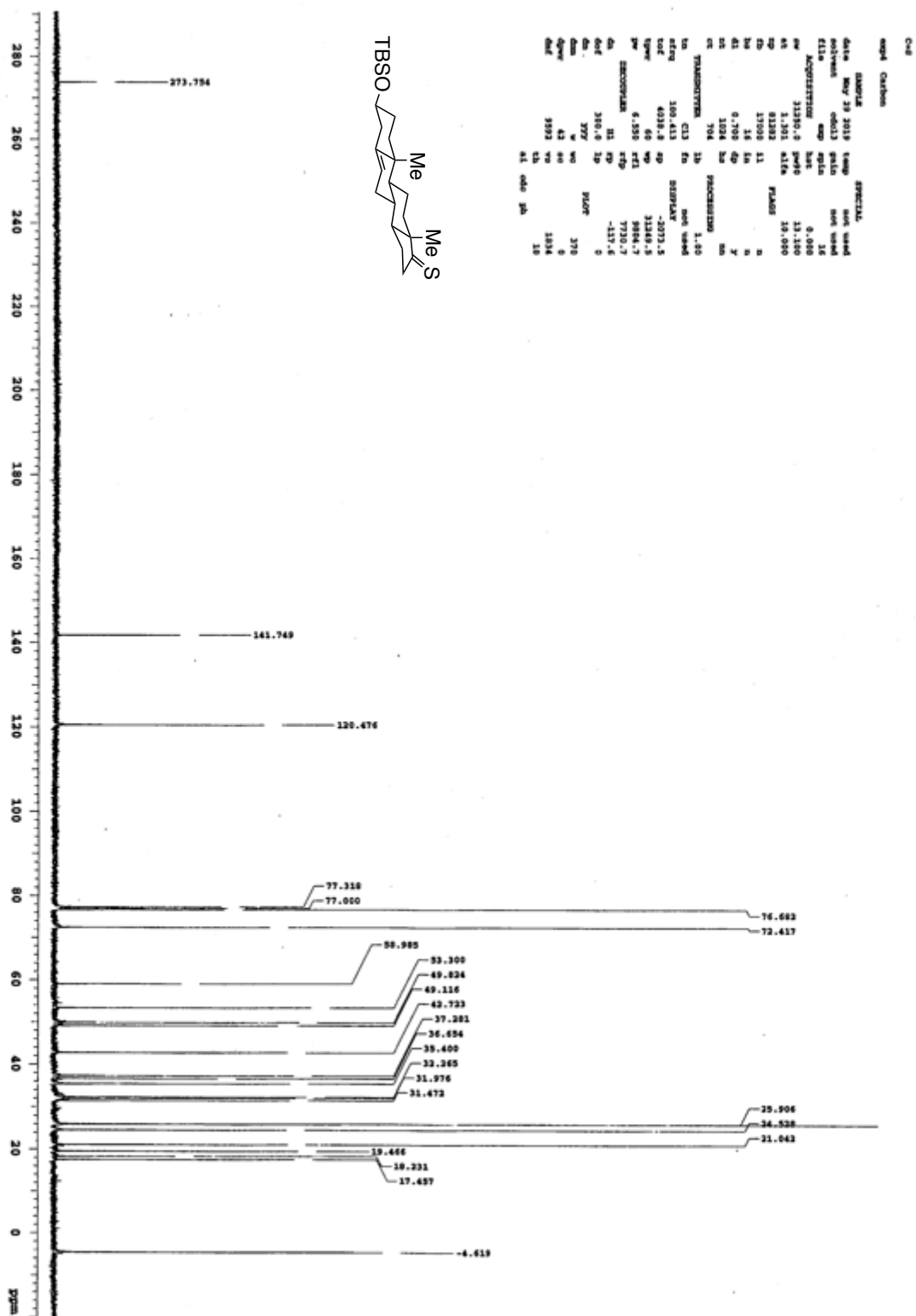
(3 β ,17 β)-3-[[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thiol (7) $^1\text{H-NMR}$



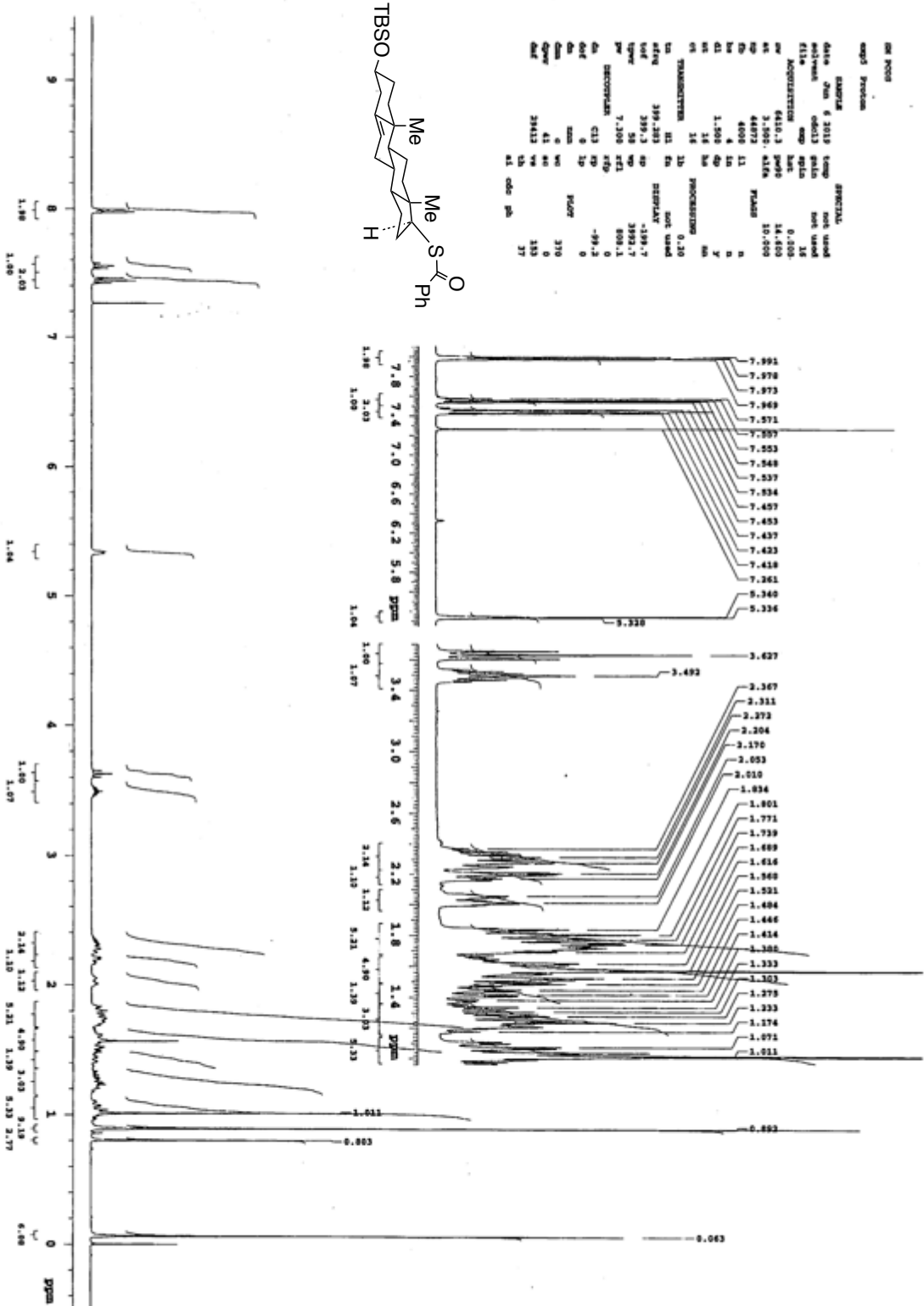
(3 β ,17 β)-3-[[1-(1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thiol (7) ¹³C-NMR



3B-[[[(1,1-Dimethylethyl)dimethylsilyl]oxy]androst-5-en-17-thione (8) ¹³C-NMR



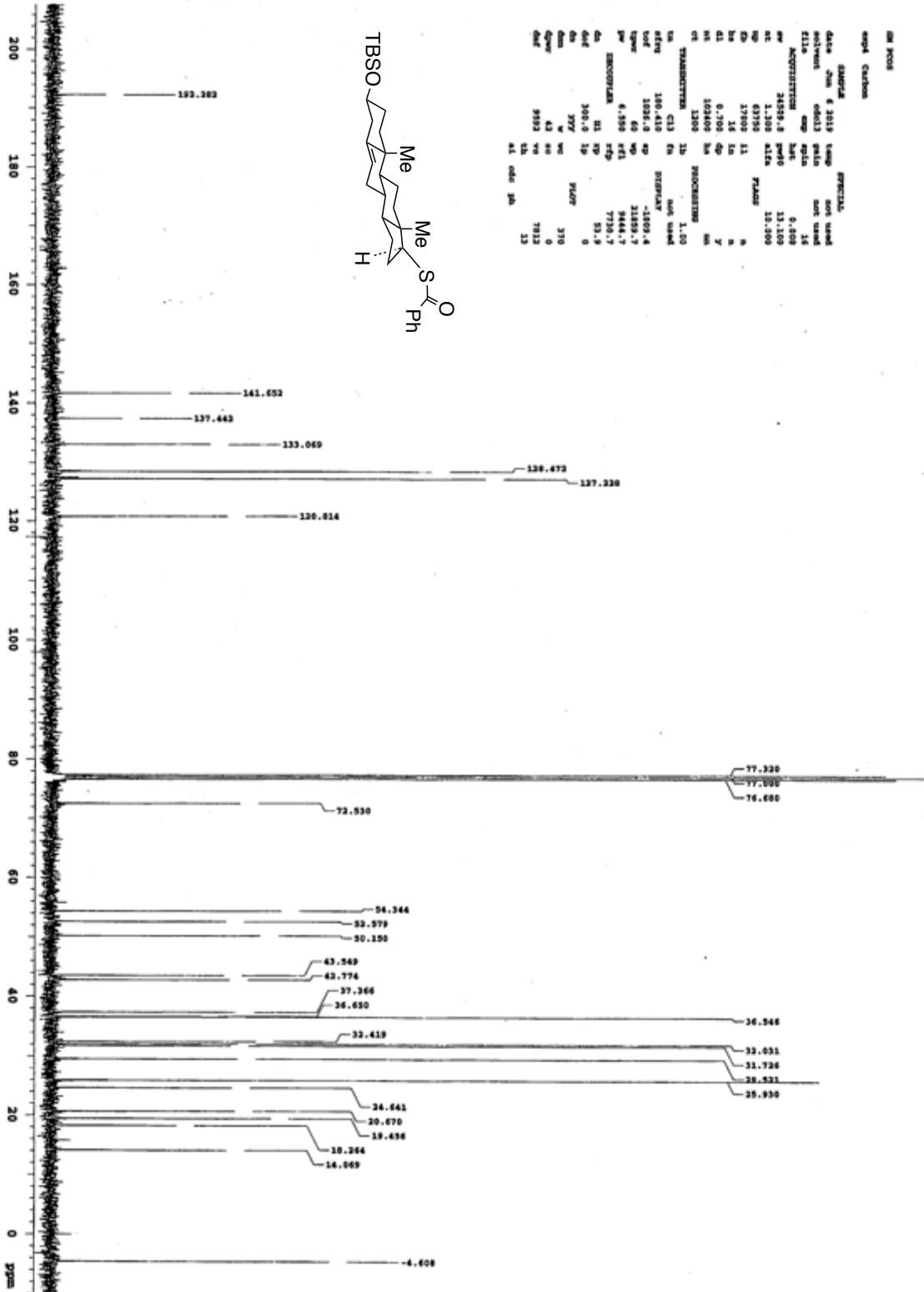
(3 β ,17 β)-17-(Benzoylthio)-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (9) ¹H-NMR



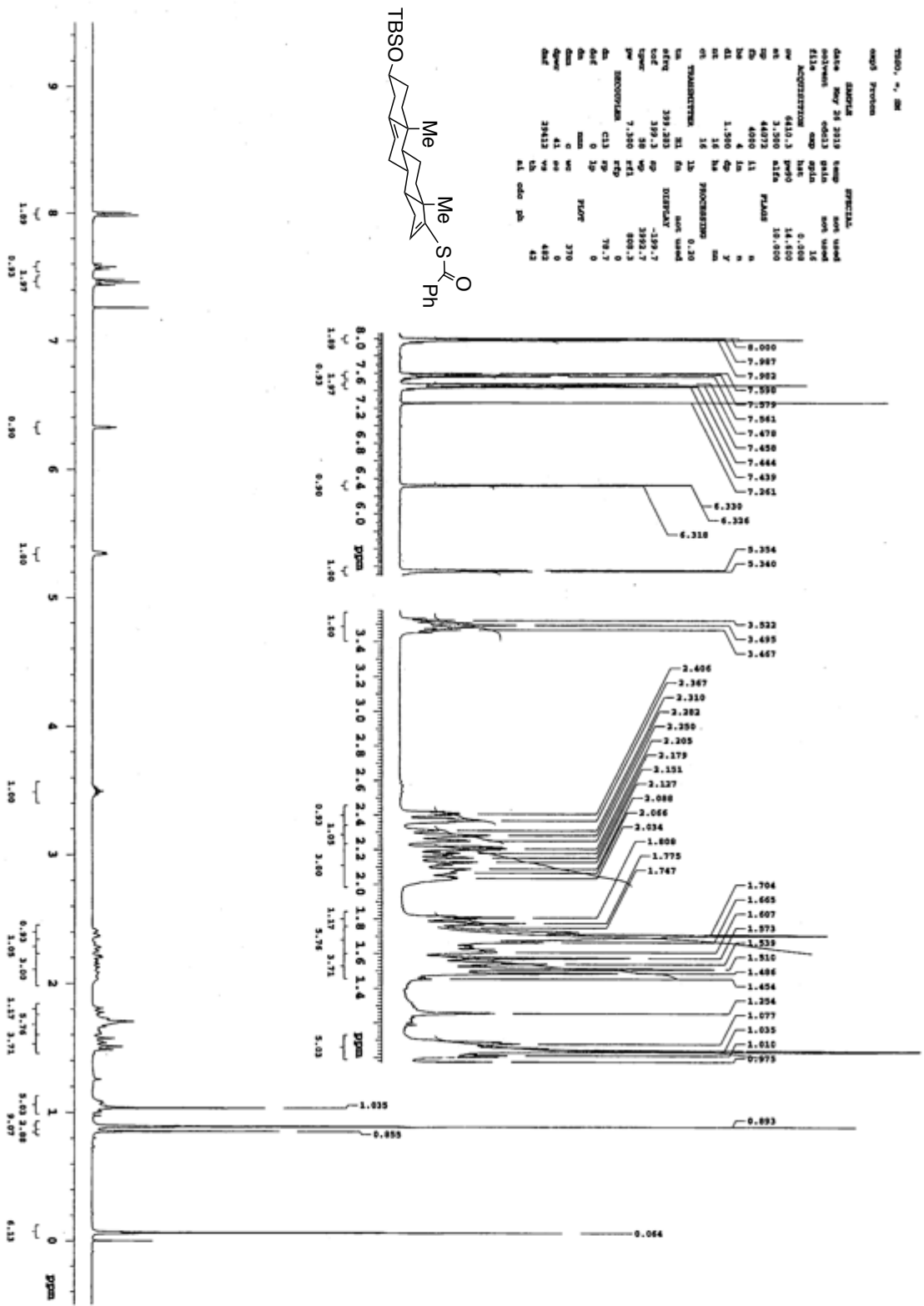
MR PROCS

NAME	DATE	TIME	TEMP	PROC
EXP1	2013	06	30	1
EXP2	2013	06	30	2
EXP3	2013	06	30	3
EXP4	2013	06	30	4
EXP5	2013	06	30	5
EXP6	2013	06	30	6
EXP7	2013	06	30	7
EXP8	2013	06	30	8
EXP9	2013	06	30	9
EXP10	2013	06	30	10
EXP11	2013	06	30	11
EXP12	2013	06	30	12
EXP13	2013	06	30	13
EXP14	2013	06	30	14
EXP15	2013	06	30	15
EXP16	2013	06	30	16
EXP17	2013	06	30	17
EXP18	2013	06	30	18
EXP19	2013	06	30	19
EXP20	2013	06	30	20
EXP21	2013	06	30	21
EXP22	2013	06	30	22
EXP23	2013	06	30	23
EXP24	2013	06	30	24
EXP25	2013	06	30	25
EXP26	2013	06	30	26
EXP27	2013	06	30	27

(3 β ,17 β)-17-(Benzoylthio)-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5-ene (9) ¹³C-NMR

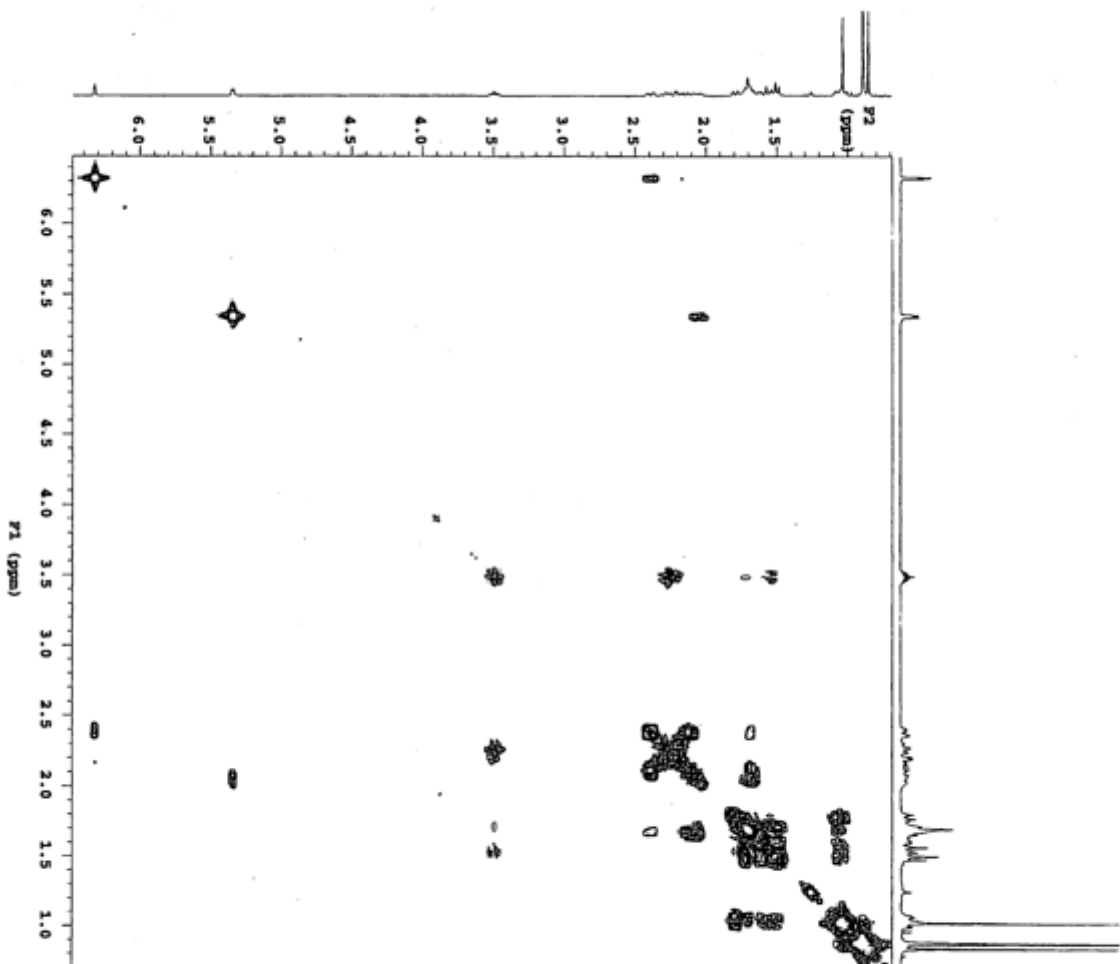
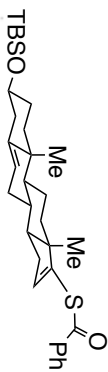


(3β)-17-(Benzoylthio)-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (10) ¹H-NMR

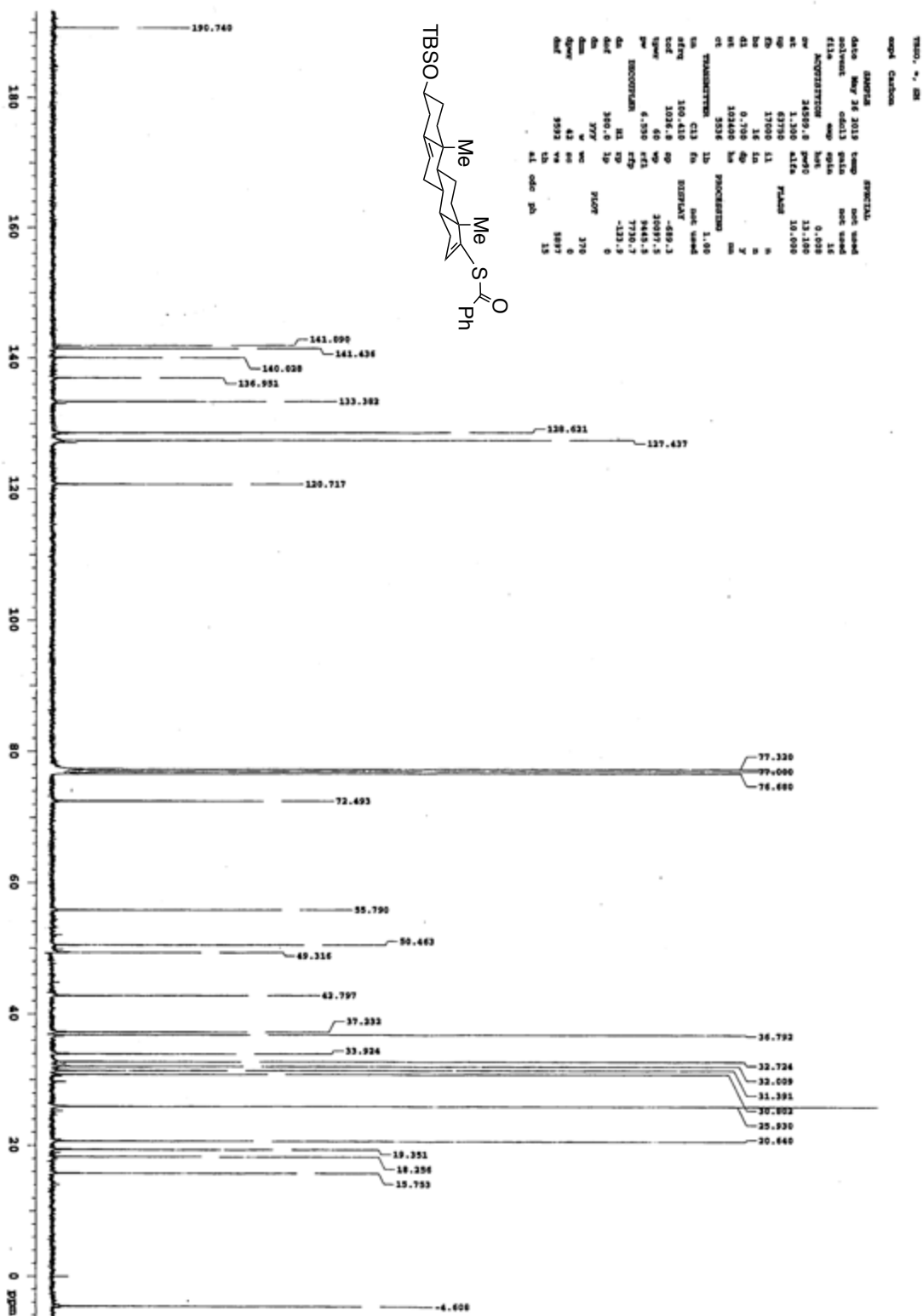


(3B)-17-(Benzoylthio)-3-[[[1,1-dimethylethyl]dimethylsilyl]oxy]androsta-5,16-diene (10) HH-COSY

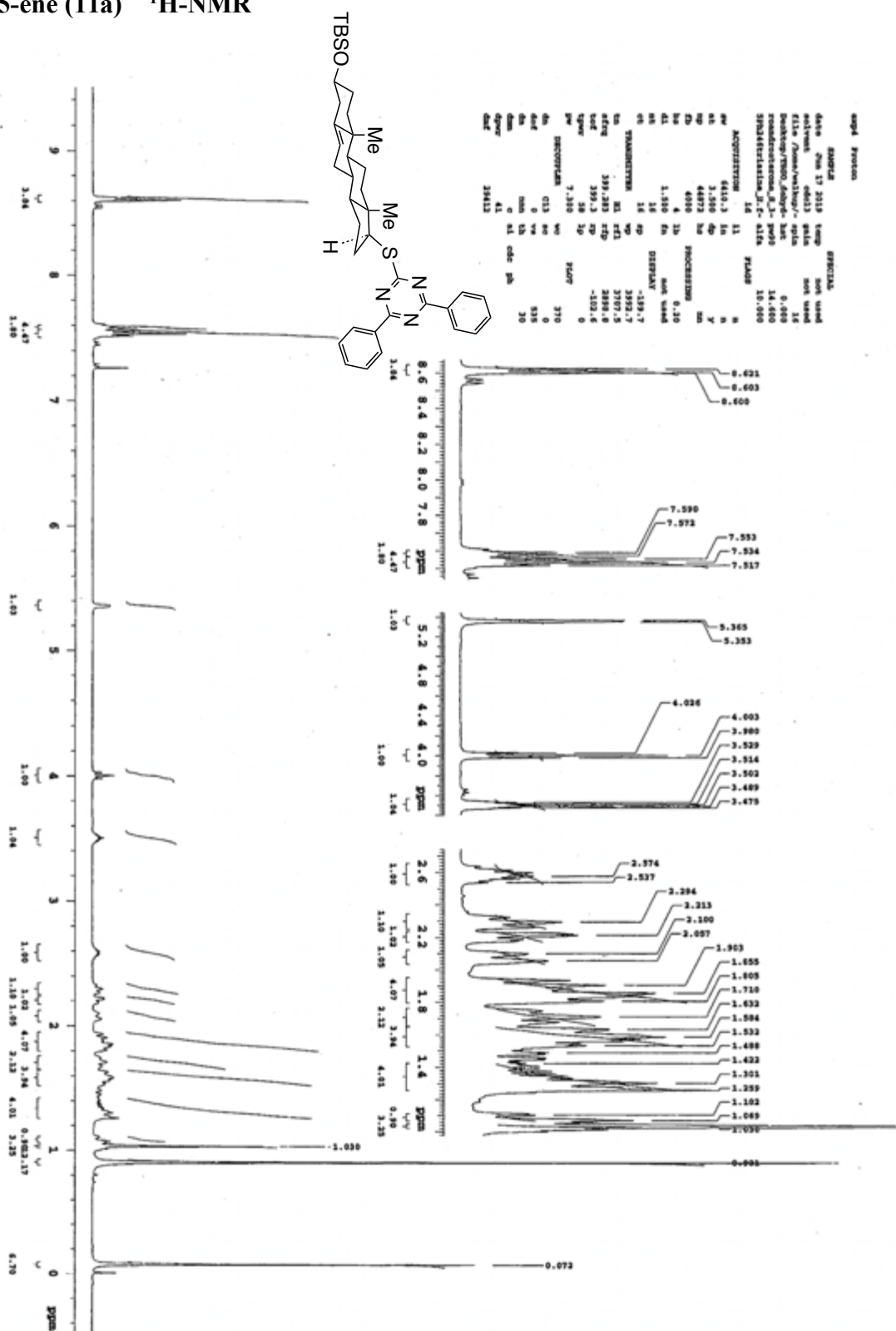
RUN: 4, 06
 FILE: 007
 Pulse Program: gpcor
 Solvent: cdcl3
 Nucleus: 13c
 Operator: waling
 VPROB: zgpg30
 VPPROG: zgpg30
 Date_Time: 2010.10.28 10:05:48
 Total Time: 39 min, 35 sec
 F2: delay 1.000 sec
 Acq. Time 0.238 sec
 Method 4000.4 Hz
 2D Method 4000.4 Hz
 16 repetitions
 128 Lockpoints
 Channel: 13, 200.1303001 MHz
 EXPT: zgpg30cor
 F1: 200.1303001 MHz
 F2: 200.1303001 MHz
 PR: 200.1303001 MHz
 Total Time 39 min, 35 sec



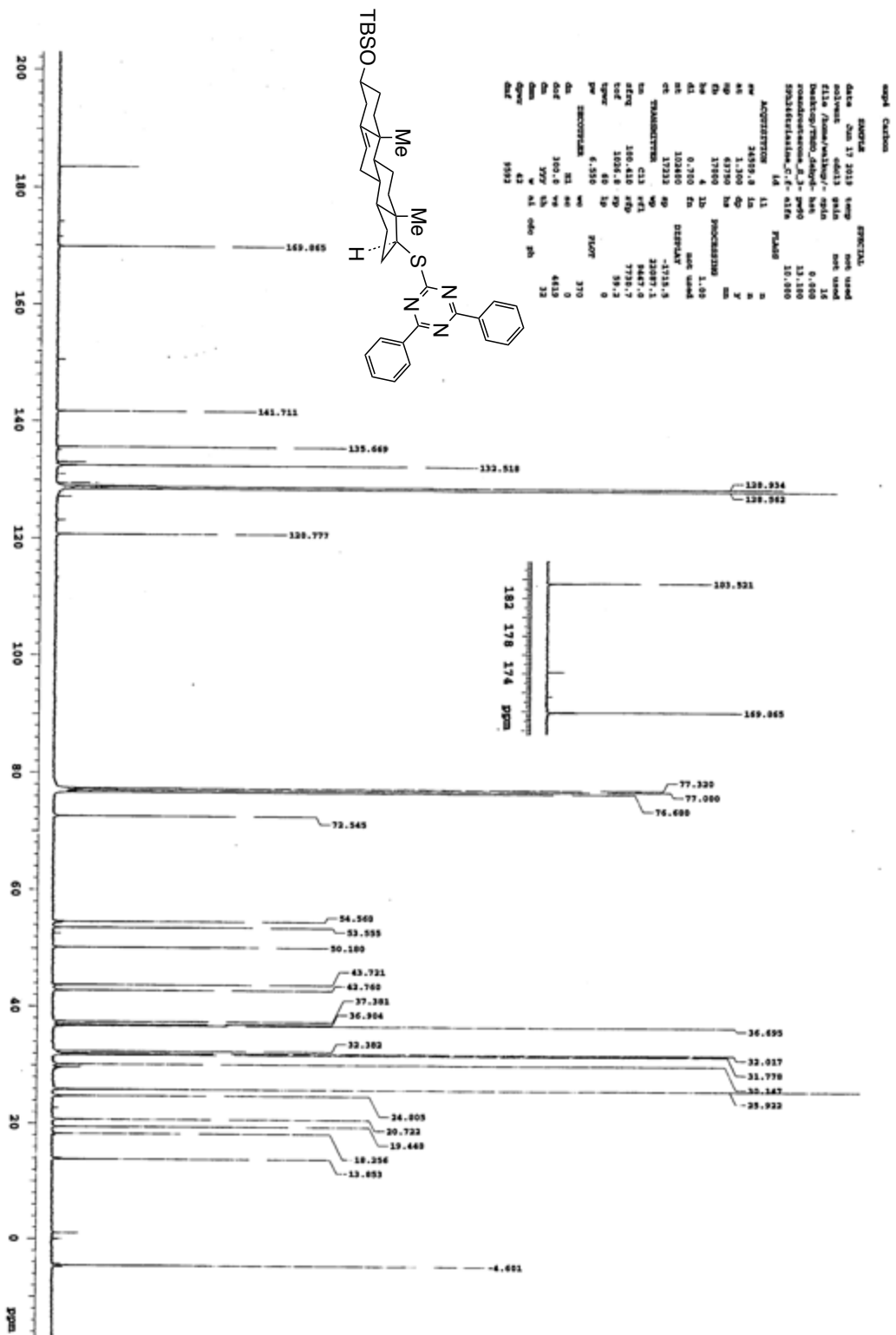
(3β)-17-(Benzoylthio)-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (10) ¹³C-NMR



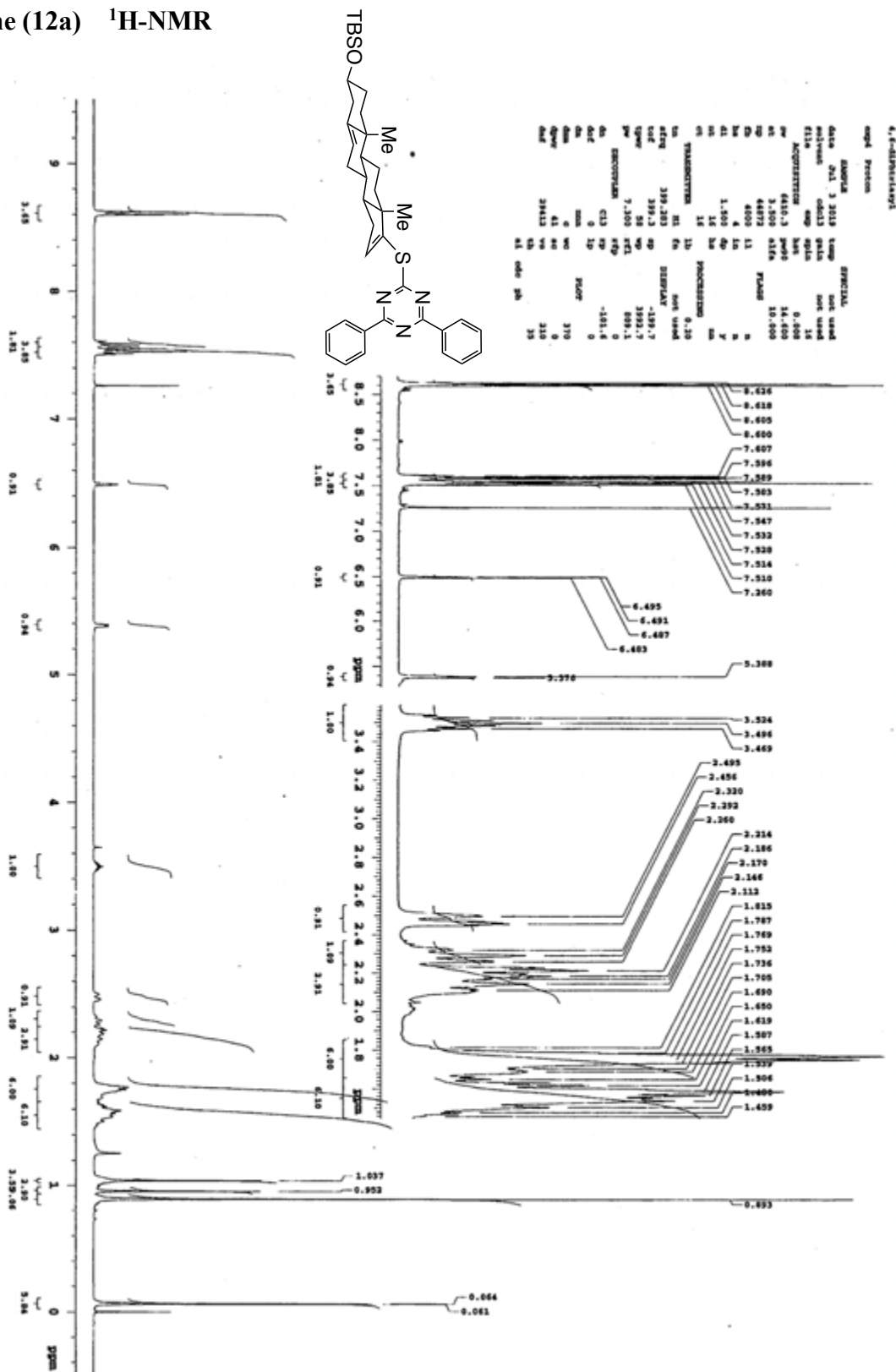
(3 β ,17 β)-3-[[1,1-Dimethylethyl]dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androst-5-ene (11a) ¹H-NMR



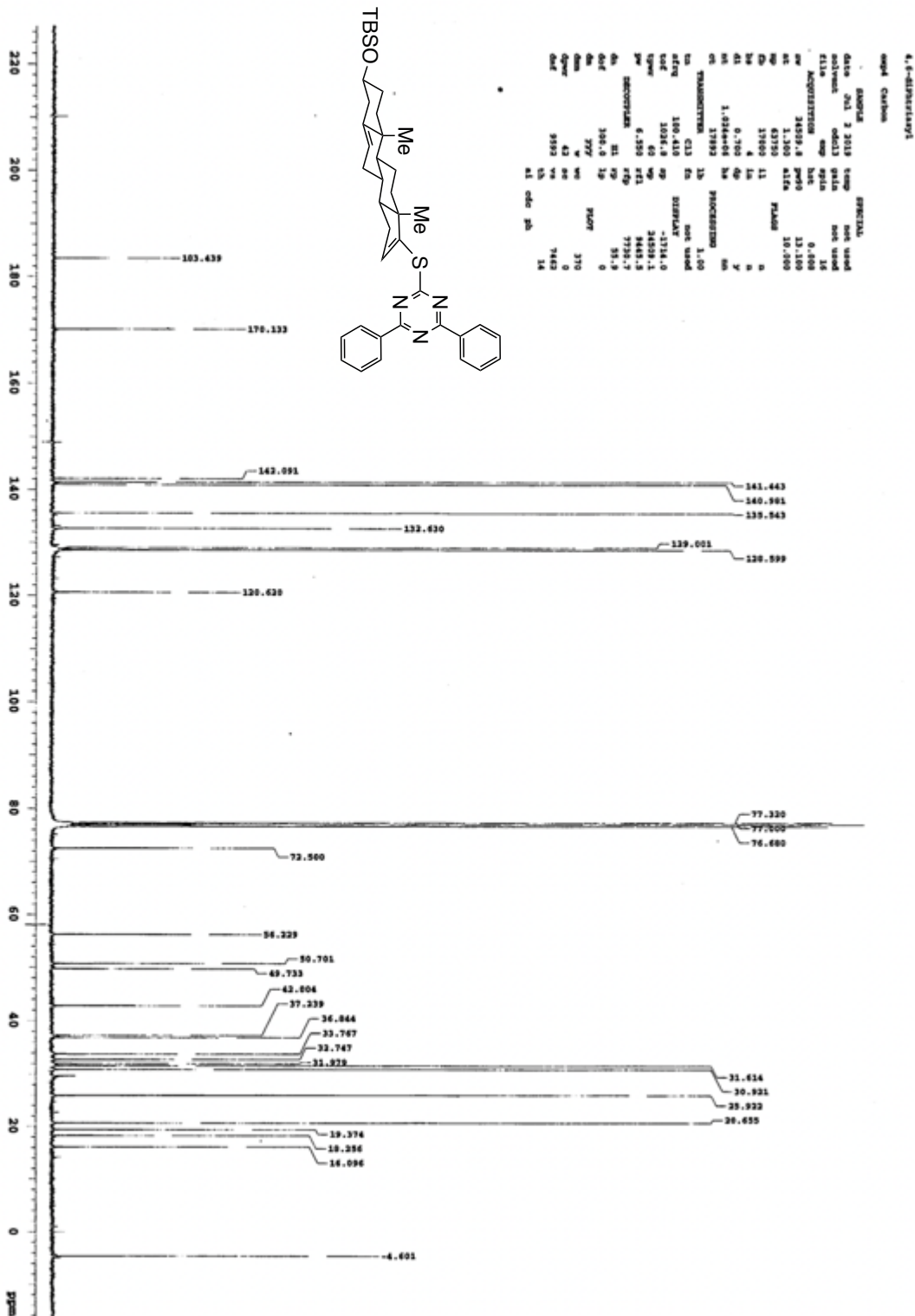
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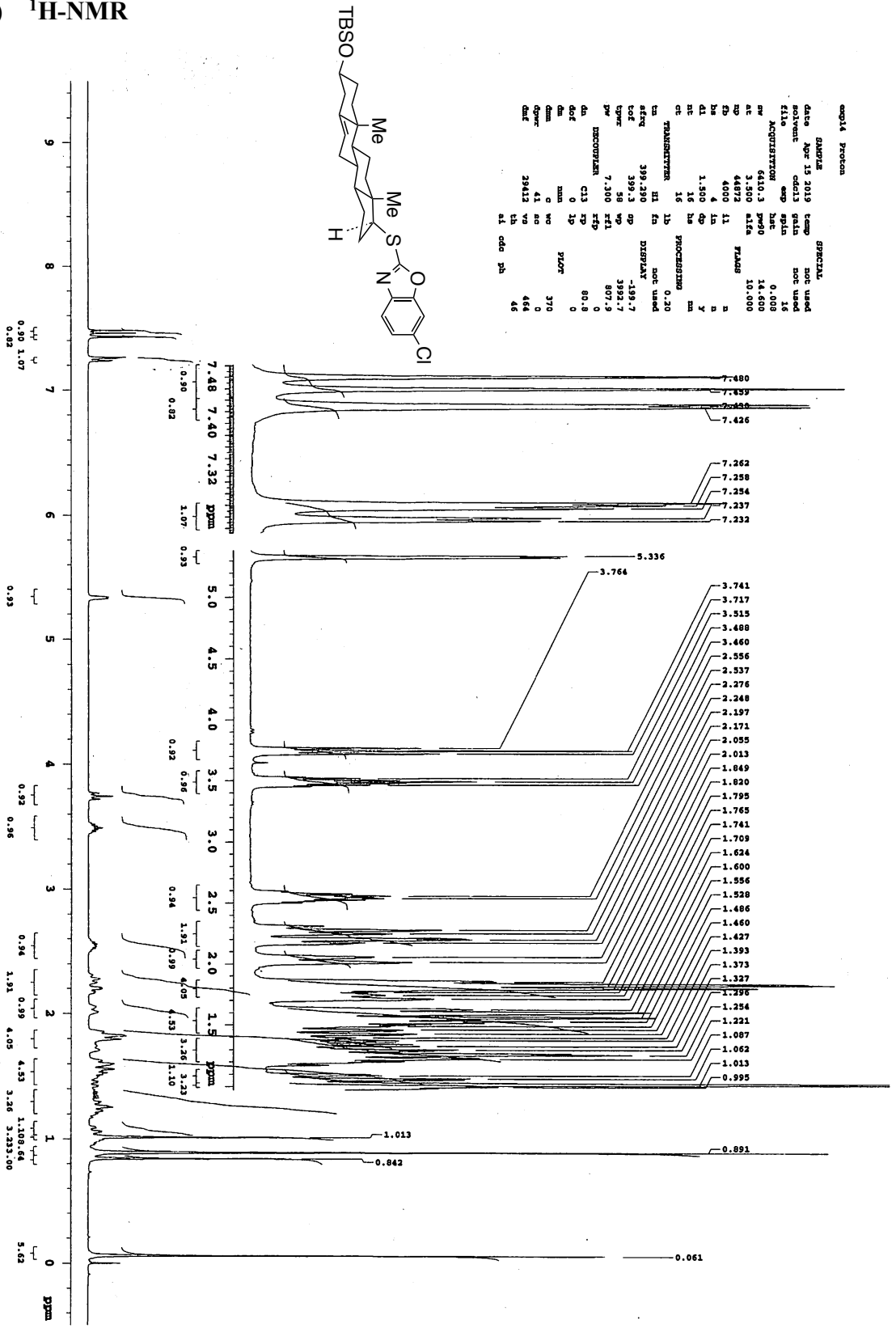
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(3 β)-3-[[[1,1-Dimethylethyl)dimethylsilyl]oxy]-17-[2-(4,6-diphenyl-1,3,5-triazyl)thio]androsta-5,16-diene (12a) ¹³C-NMR



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

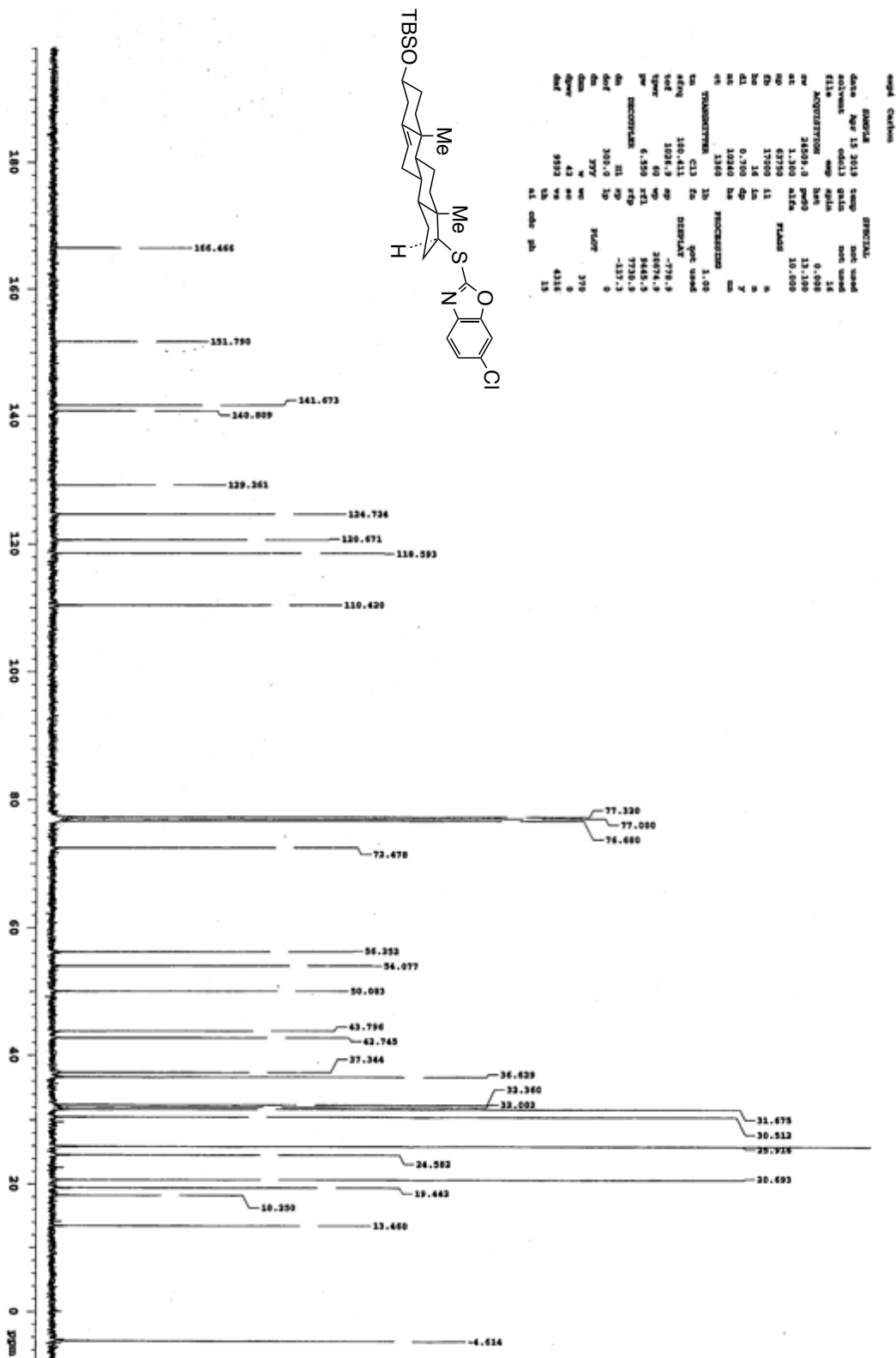


00014 Proton

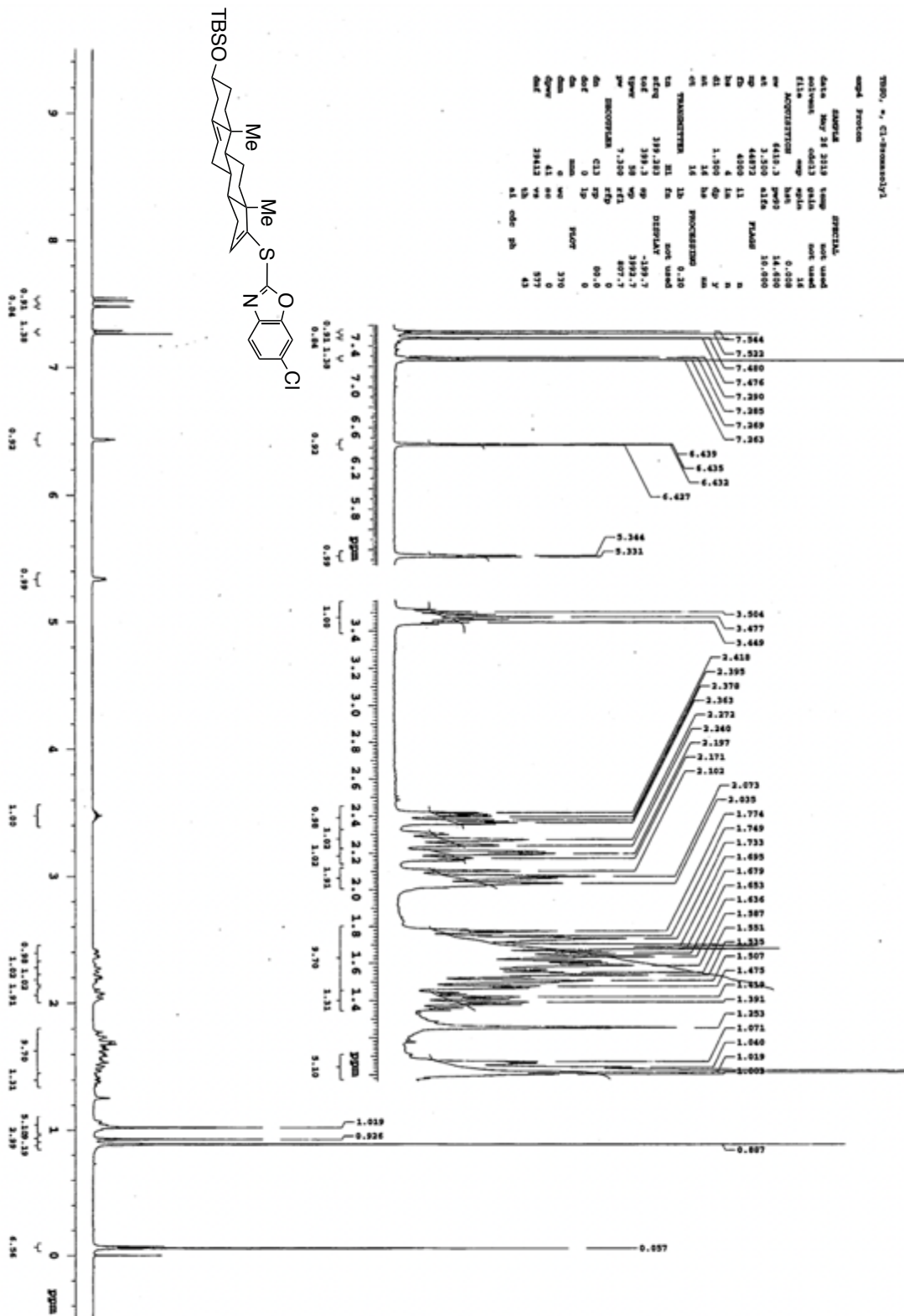
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SOLVENT	CDCL3	GAIN	NOT USED
FILE	ACQ0137704	IMP	16
NR	3.570	RTG	10.000
NP	4.000	11	
NS	4	1A	
NI	1.500	QP	
NT	16	1A	
CT	16	1B	
TS	399.290	SI	NOT USED
SCF	399.2	OP	DESIPTM
TCPE	7.100	RFI	3927.7
PCPE	7.100	RFI	807.9
DO	0	IP	80.8
DOF	0	IP	0
DM			
DMM			
OPAC	41	NO	370
DMF	29412	VO	464
		VA	46

AL ODO PH

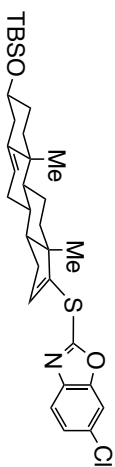
(3 β ,17 β)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5-ene (11c) ¹³C-NMR



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

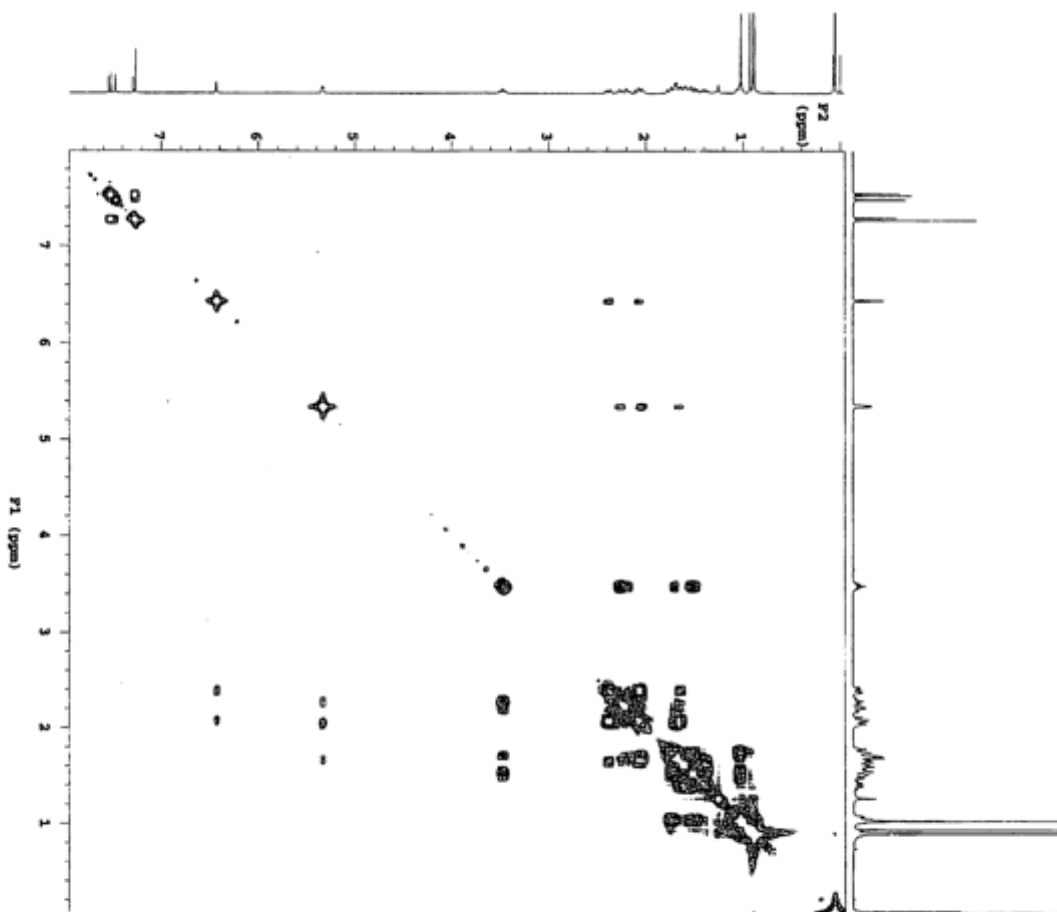


(3 β)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[1,(1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12c) HH-COSY

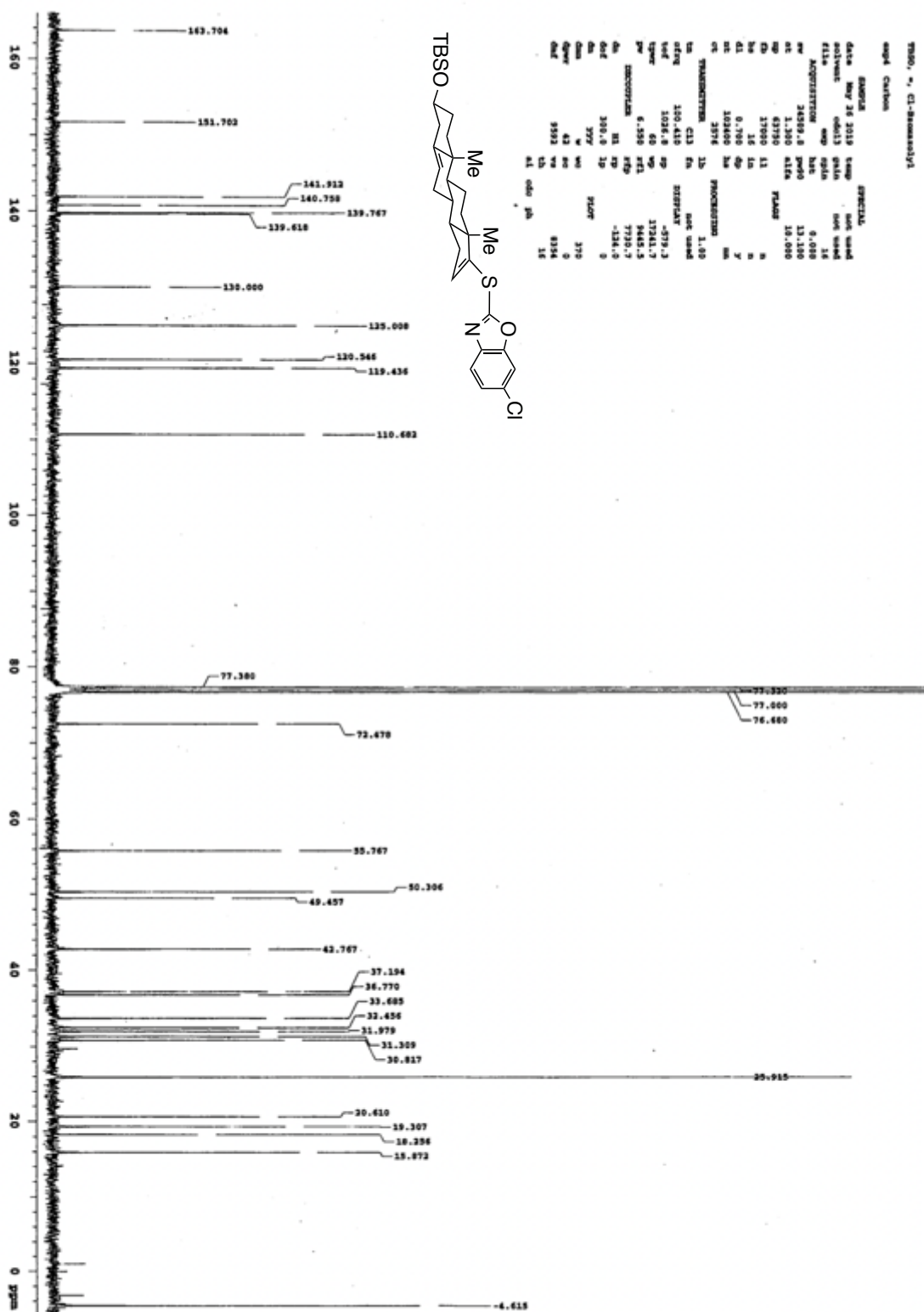


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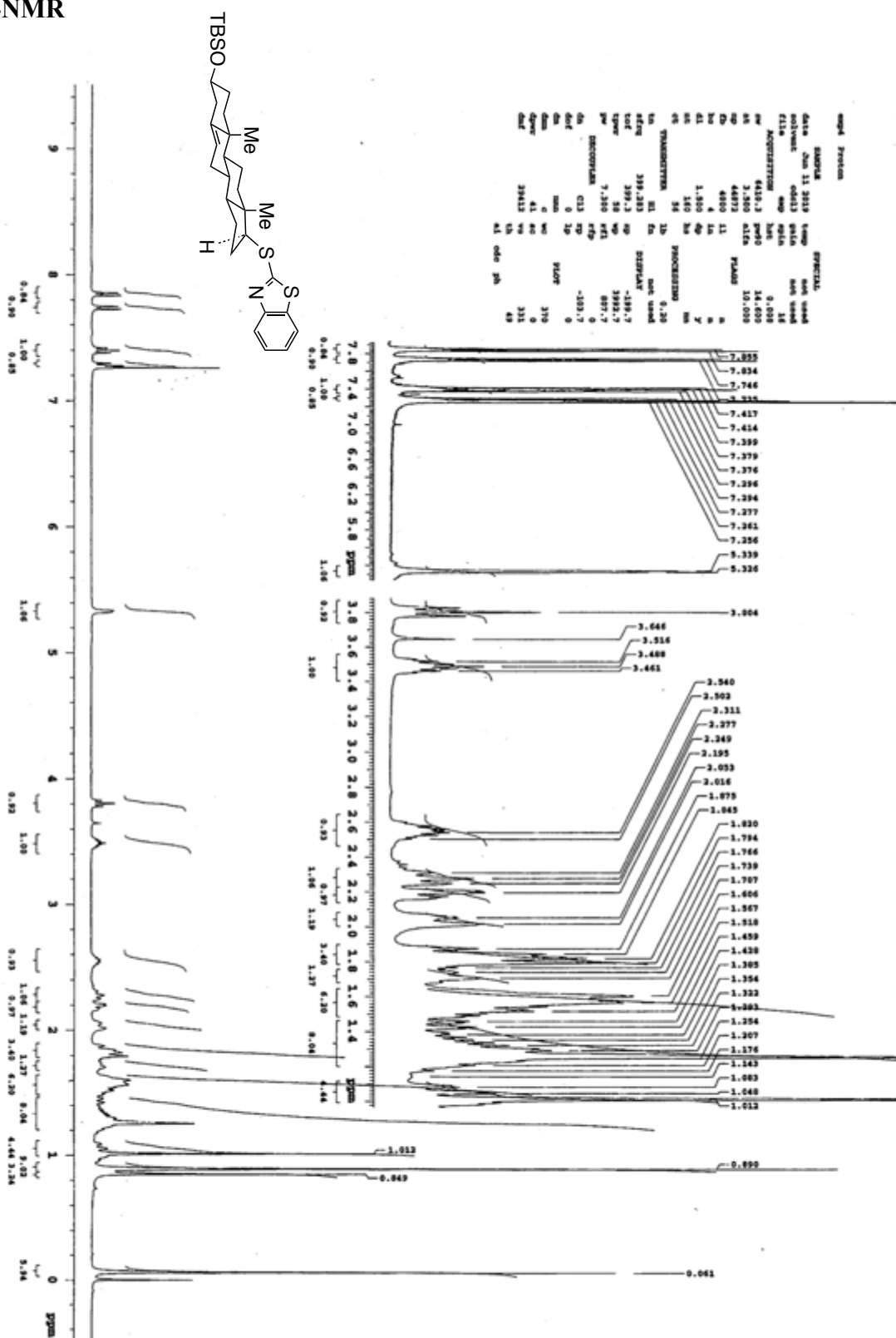
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F11a: exp
Pulse sequence: gpcpr
Solvent: cdcl3
Acquisition temperature:
Operator: waltng
INSTRUM: spect
PROBHD: 5mm
Date_ time: 04/17/00 09:23
Acq. time: 0:21:30
F2: 400.136 MHz
SI: 32768
SFO: 400.136 MHz
AQ: 1.00000000
RG: 655.36
DE: 0.00000000
TE: 300.2
D1: 1.50000000
DELTA: 1.00000000
DATA PROCESSING:
ORGANIC: 01_399_2803841.MK
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SI: 32768
F2: 400.136 MHz
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Total time: 43 min, 28 sec
  
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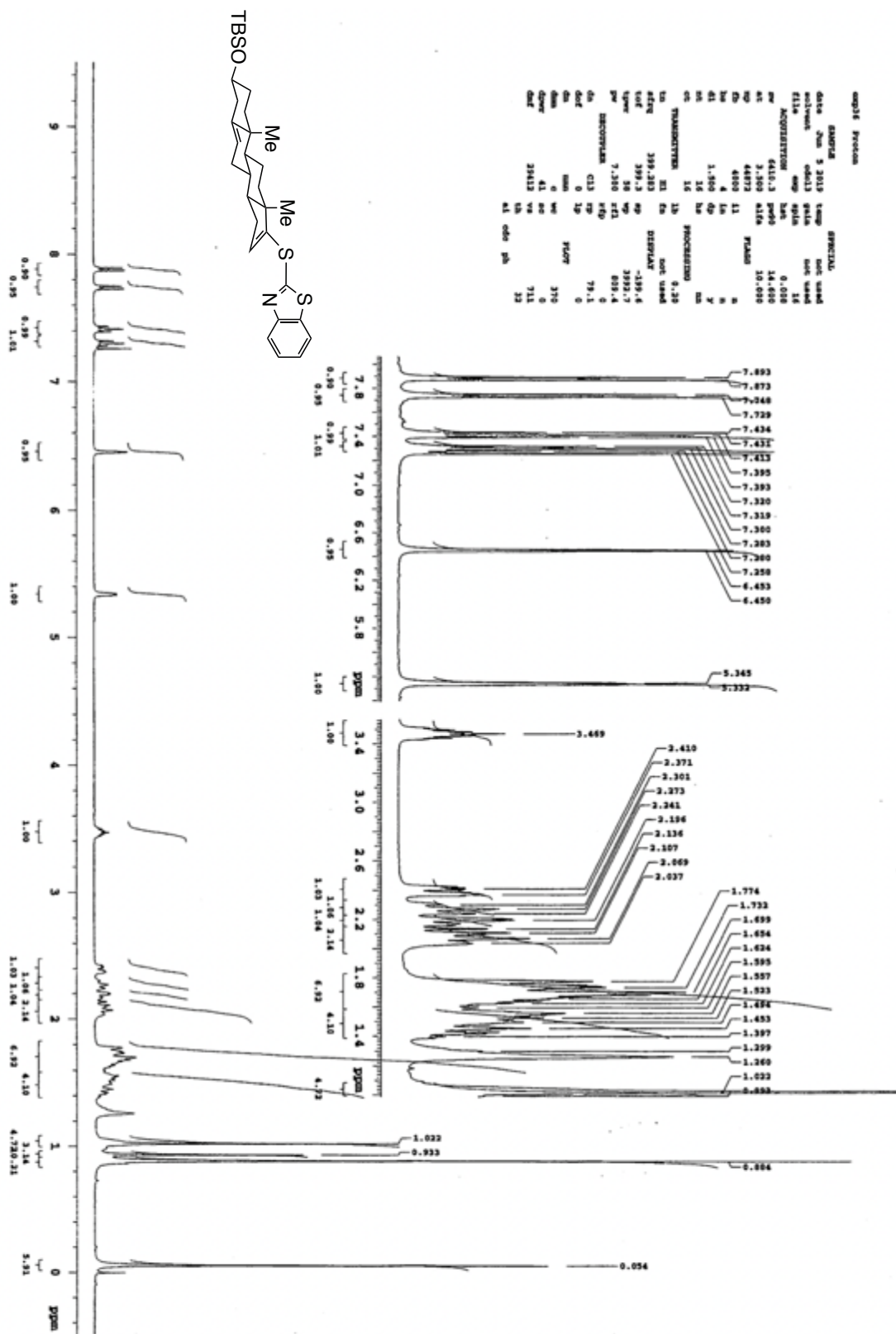
(3B)-17-[2-(6-Chlorobenzoxazolyl)thio]-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androsta-5,16-diene (12c)
¹³C-NMR



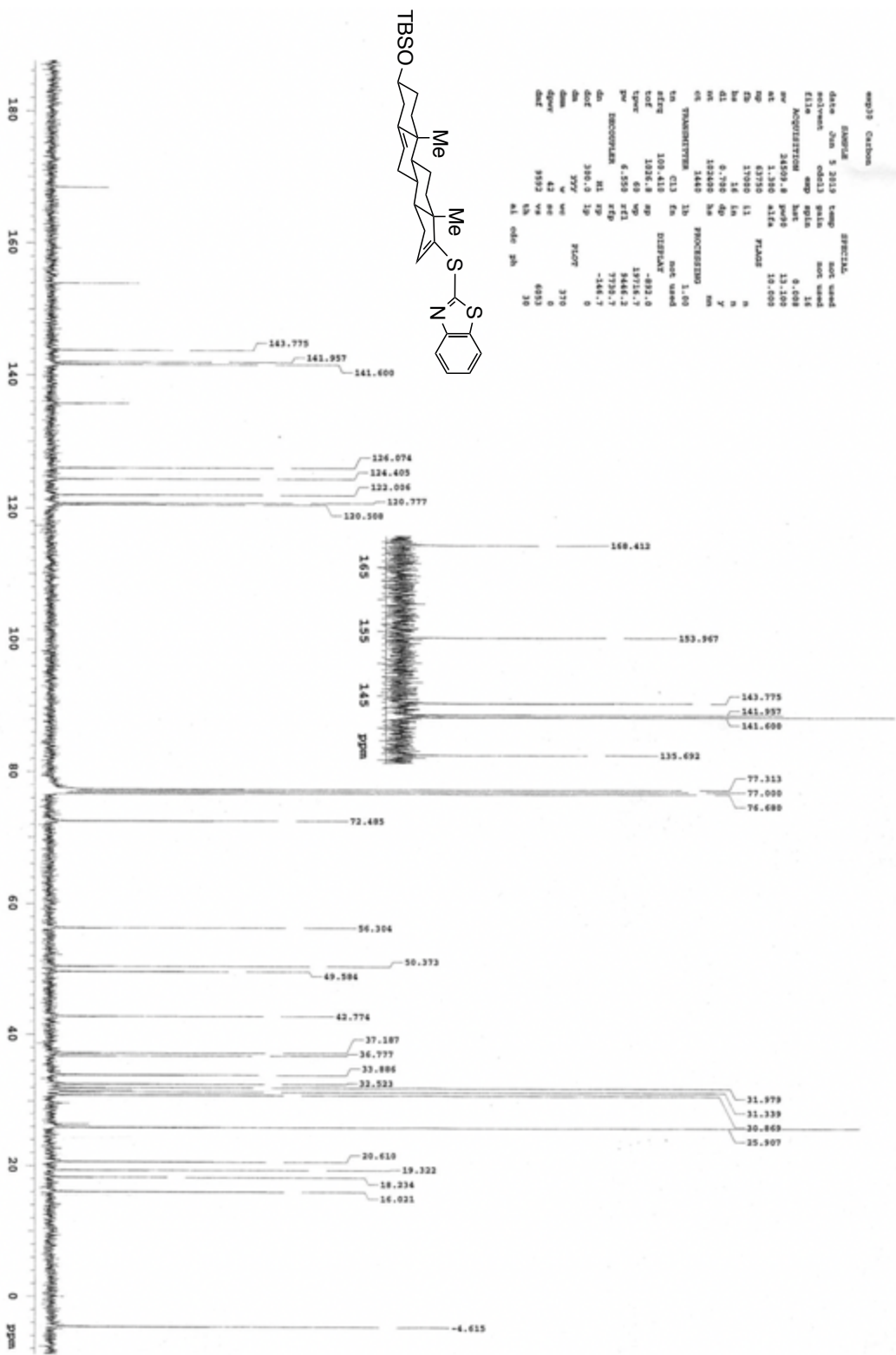
(3 β ,17 β)-17-(2-Benzothiazolylthio)-3-[[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5-ene (11d) $^1\text{H-NMR}$



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



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



NAME: 683916

DATE: 02/13/2013

TIME: 11:00

FILE: 683916

ACQUISITION: 28500.8

NUC1: 13C

NUC2: 13C

NUC3: 13C

NUC4: 13C

NUC5: 13C

NUC6: 13C

NUC7: 13C

NUC8: 13C

NUC9: 13C

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NUC12: 13C

NUC13: 13C

NUC14: 13C

NUC15: 13C

NUC16: 13C

NUC17: 13C

NUC18: 13C

NUC19: 13C

NUC20: 13C

NUC21: 13C

NUC22: 13C

NUC23: 13C

NUC24: 13C

NUC25: 13C

NUC26: 13C

NUC27: 13C

NUC28: 13C

NUC29: 13C

NUC30: 13C

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NUC32: 13C

NUC33: 13C

NUC34: 13C

NUC35: 13C

NUC36: 13C

NUC37: 13C

NUC38: 13C

NUC39: 13C

NUC40: 13C

NUC41: 13C

NUC42: 13C

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NUC44: 13C

NUC45: 13C

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NUC47: 13C

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NUC75: 13C

NUC76: 13C

NUC77: 13C

NUC78: 13C

NUC79: 13C

NUC80: 13C

NUC81: 13C

NUC82: 13C

NUC83: 13C

NUC84: 13C

NUC85: 13C

NUC86: 13C

NUC87: 13C

NUC88: 13C

NUC89: 13C

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NUC93: 13C

NUC94: 13C

NUC95: 13C

NUC96: 13C

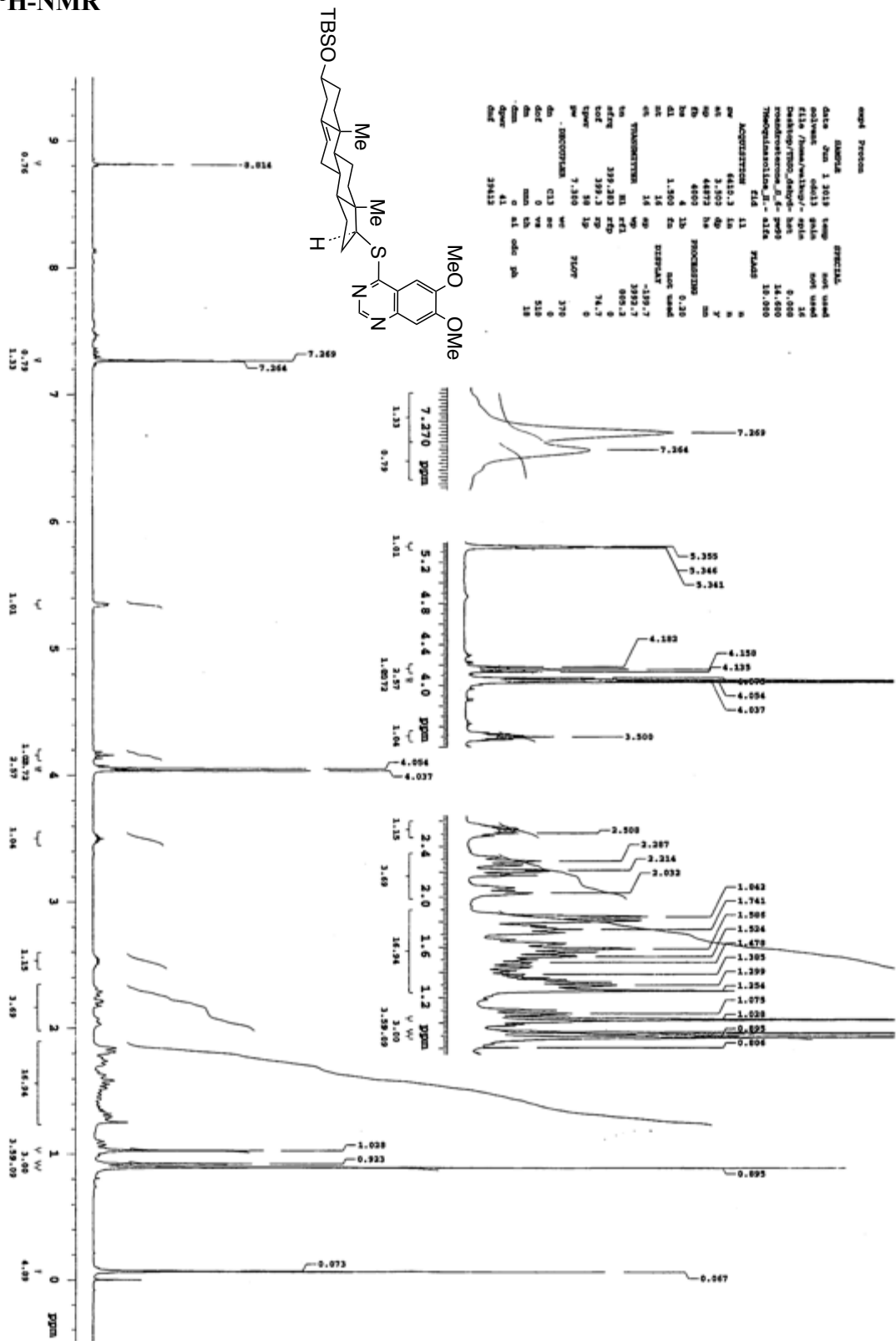
NUC97: 13C

NUC98: 13C

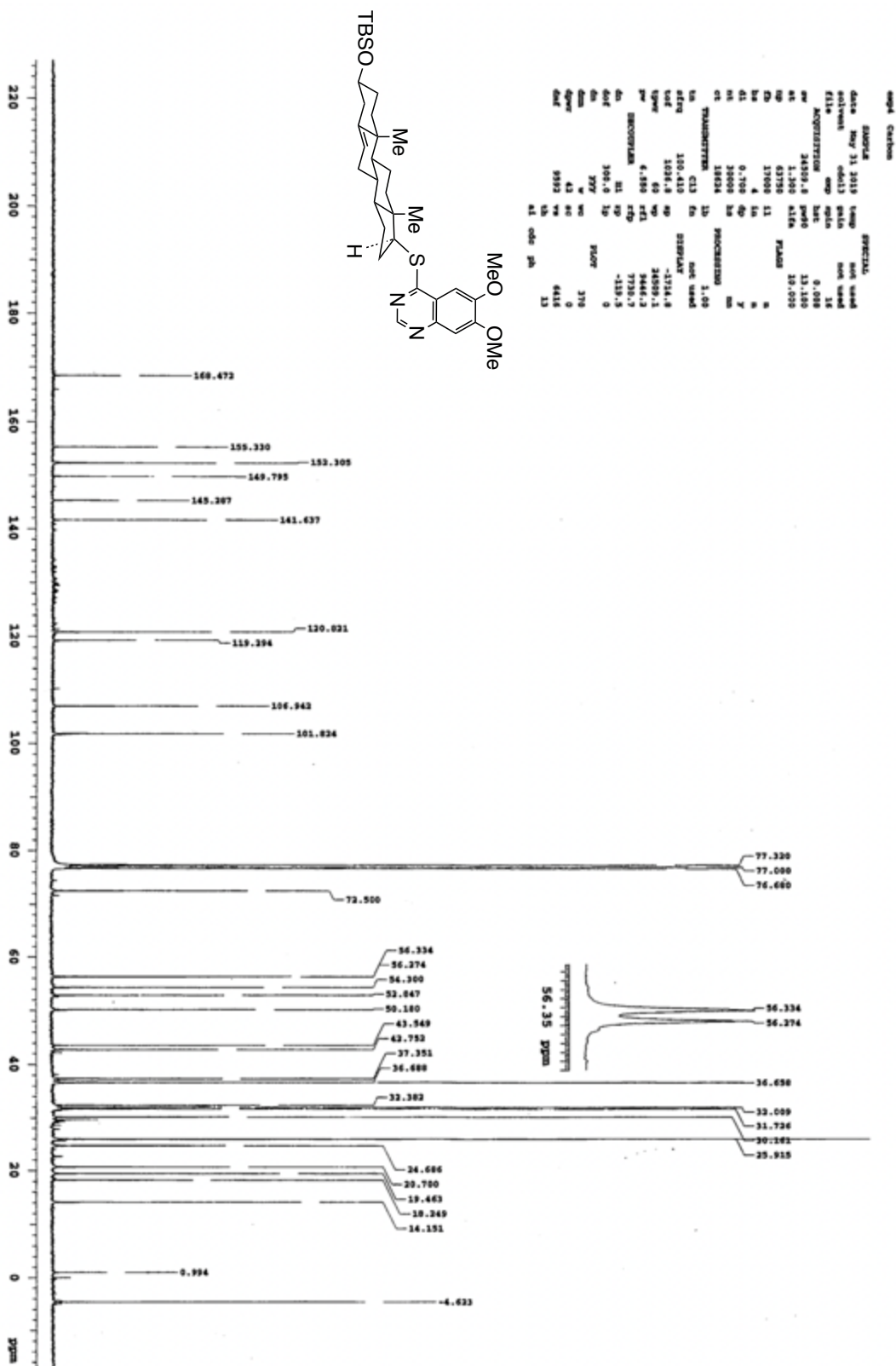
NUC99: 13C

NUC100: 13C

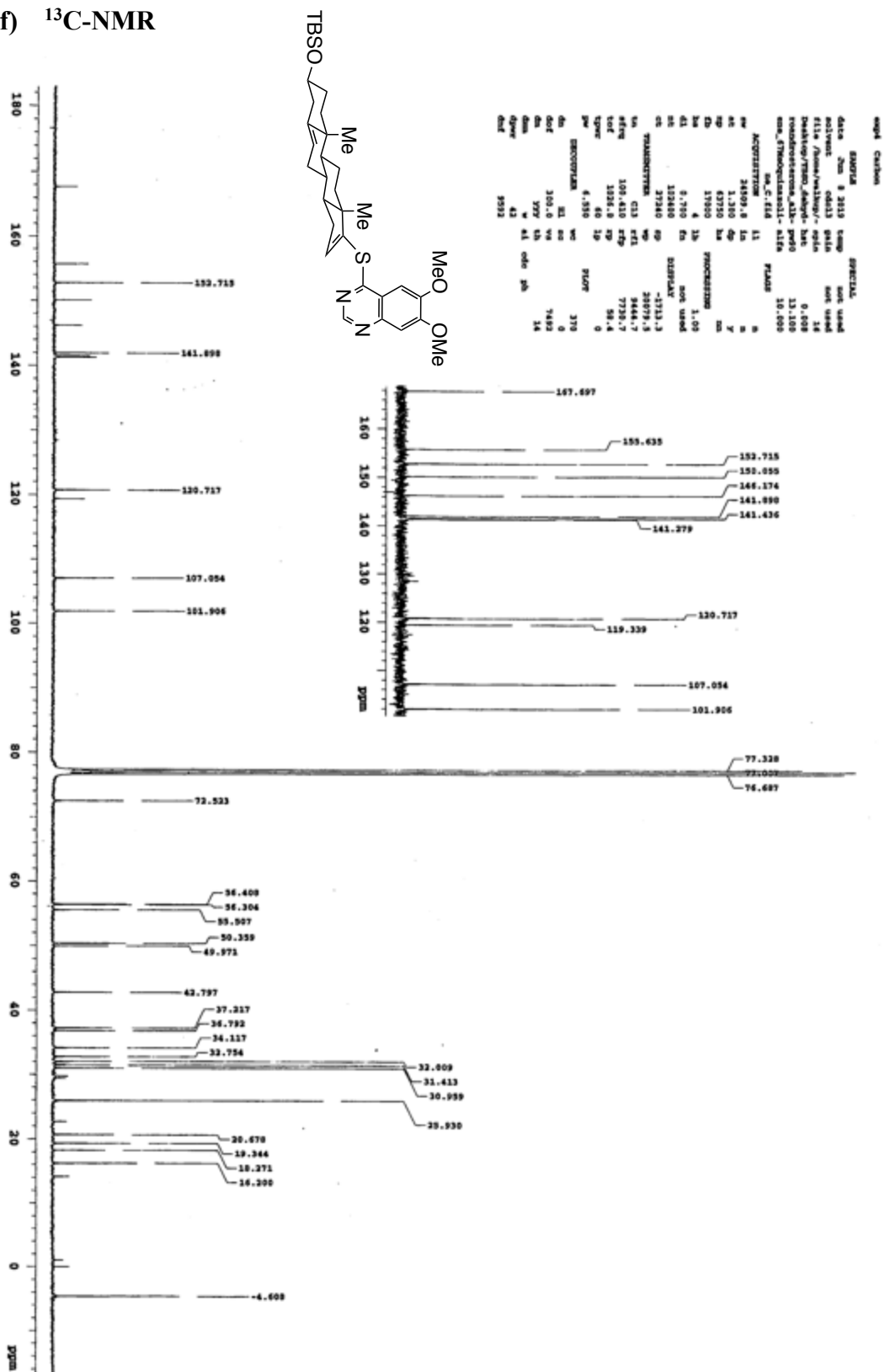
(3 β ,17 β)-17-[2-(6,7-Dimethoxyquinazoly)thio]-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11f) ¹H-NMR



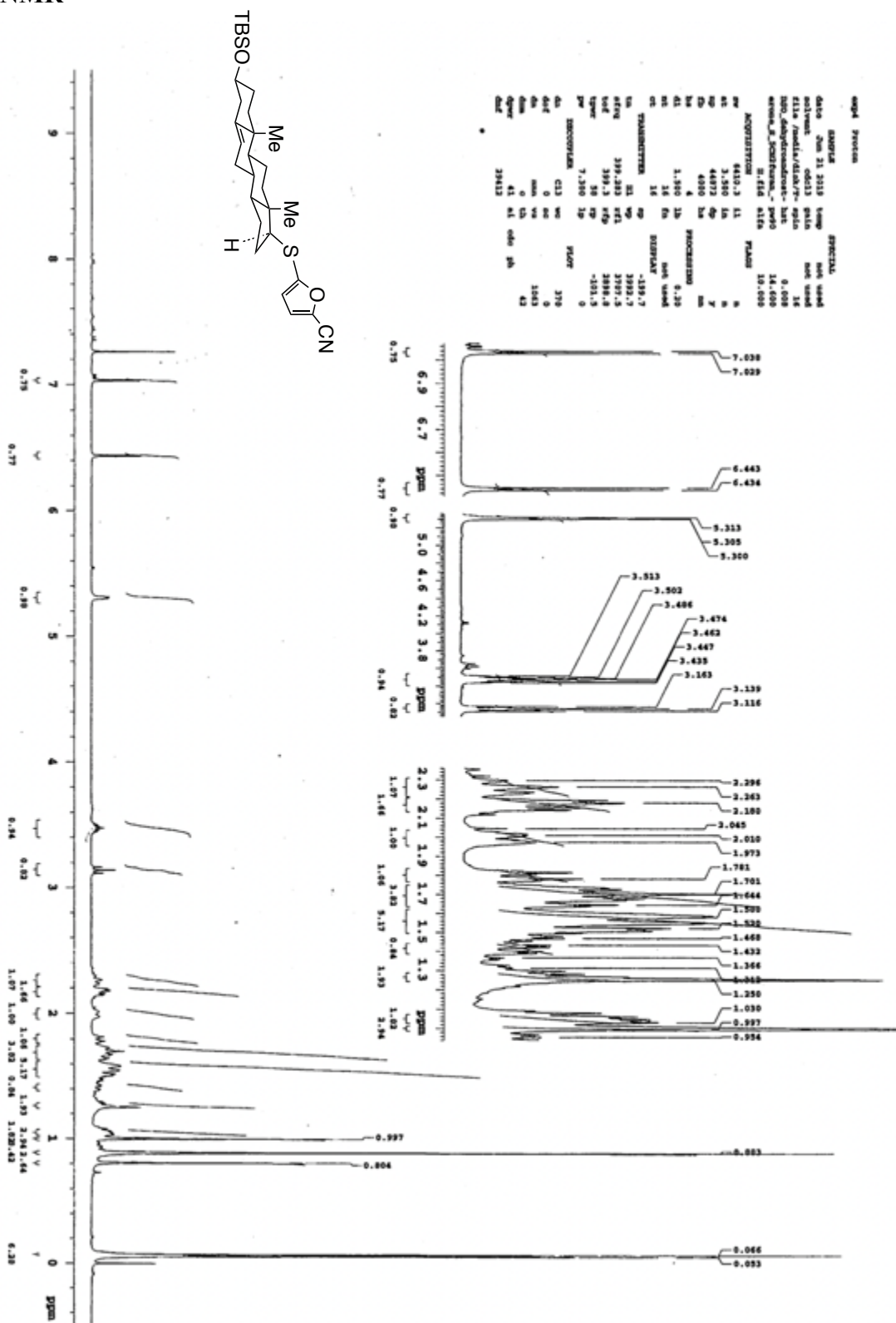
(3 β ,17 β)-17-[2-(6,7-Dimethoxyquinazoly)thio]-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11f) ^{13}C -NMR



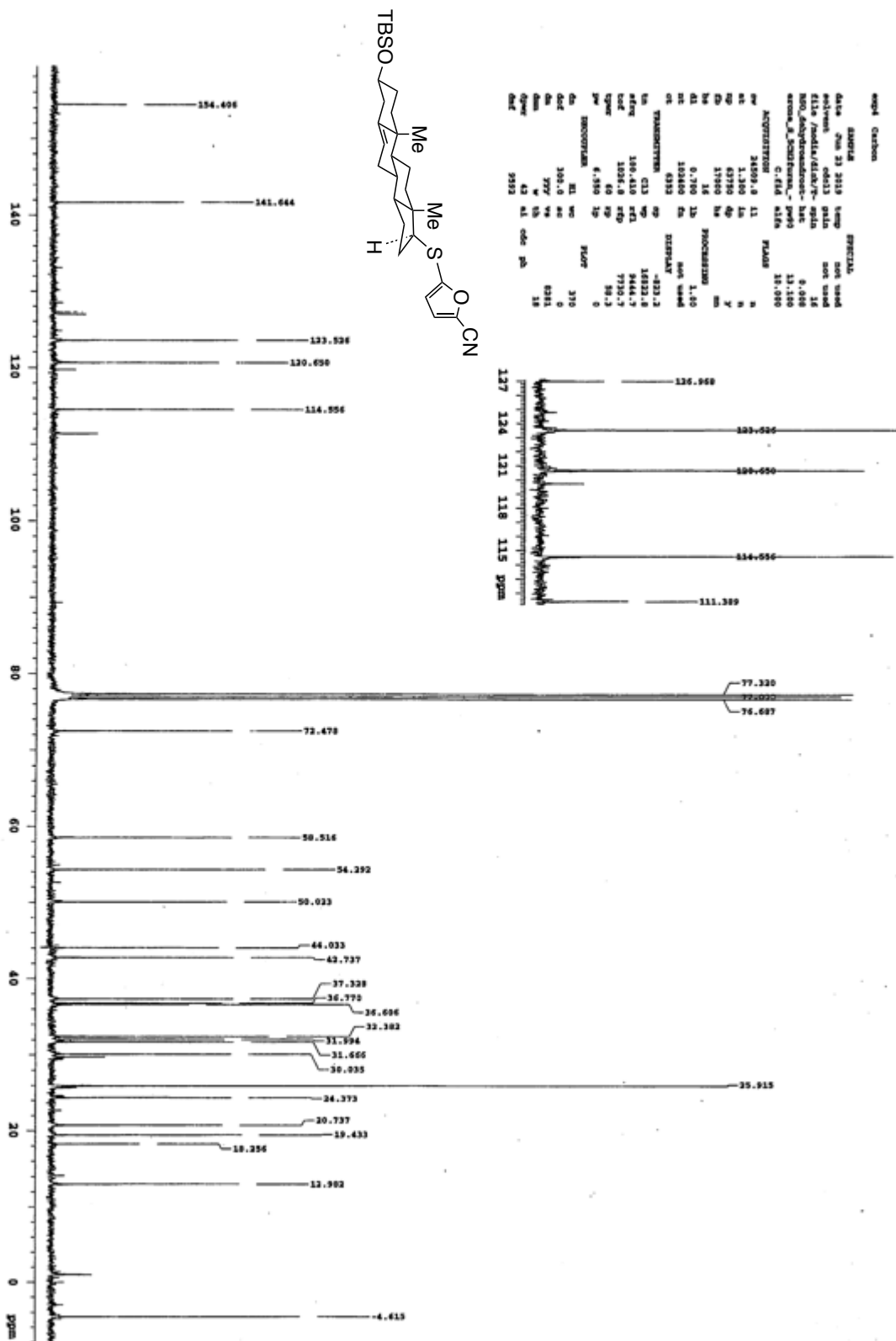
(3 β)-17-[2-(6,7-Dimethoxyquinazoly)thio]-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12f) ^{13}C -NMR



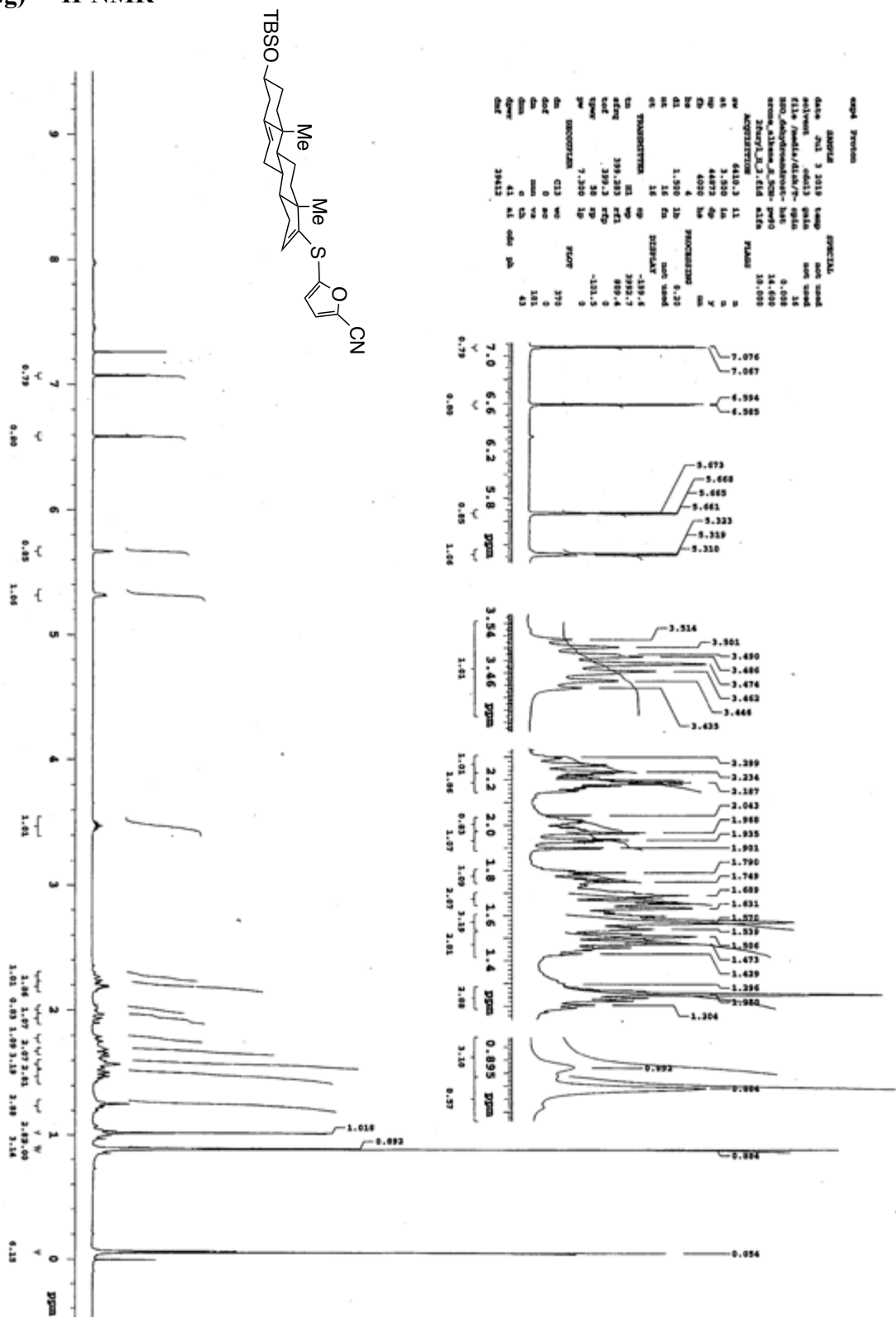
(3 β ,17 β)-17-[5-(2-Cyanofuranylthio)-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]androst-5-ene (11g) ¹H-NMR



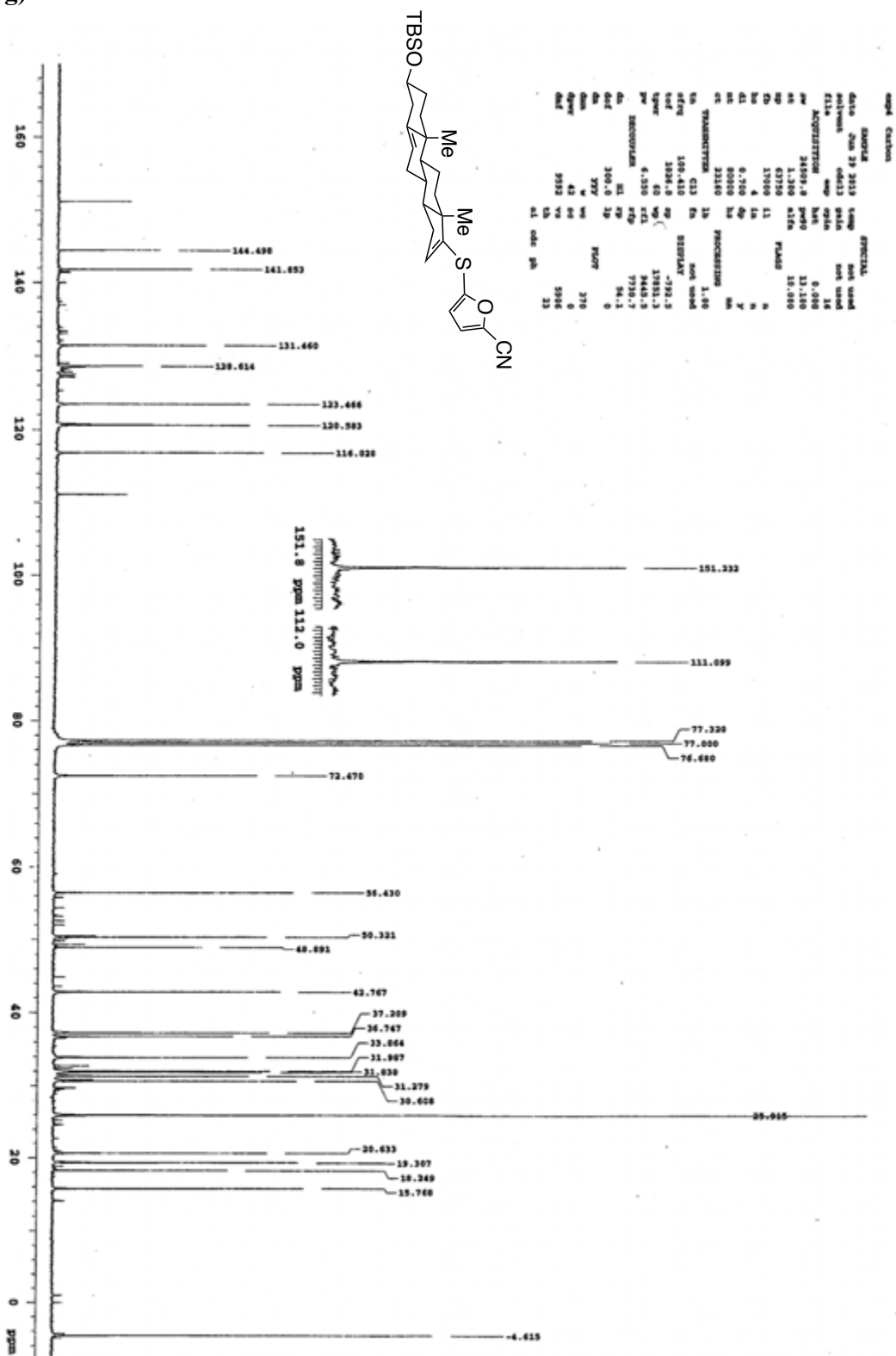
(3 β ,17 β)-17-[5-(2-Cyanofuranyl)thio]-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androst-5-ene
 (11g) ^{13}C -NMR



(3 β ,17 β)-17-[5-(2-Cyanofuranylthio)-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]androsta-5,16-diene (12g) $^1\text{H-NMR}$



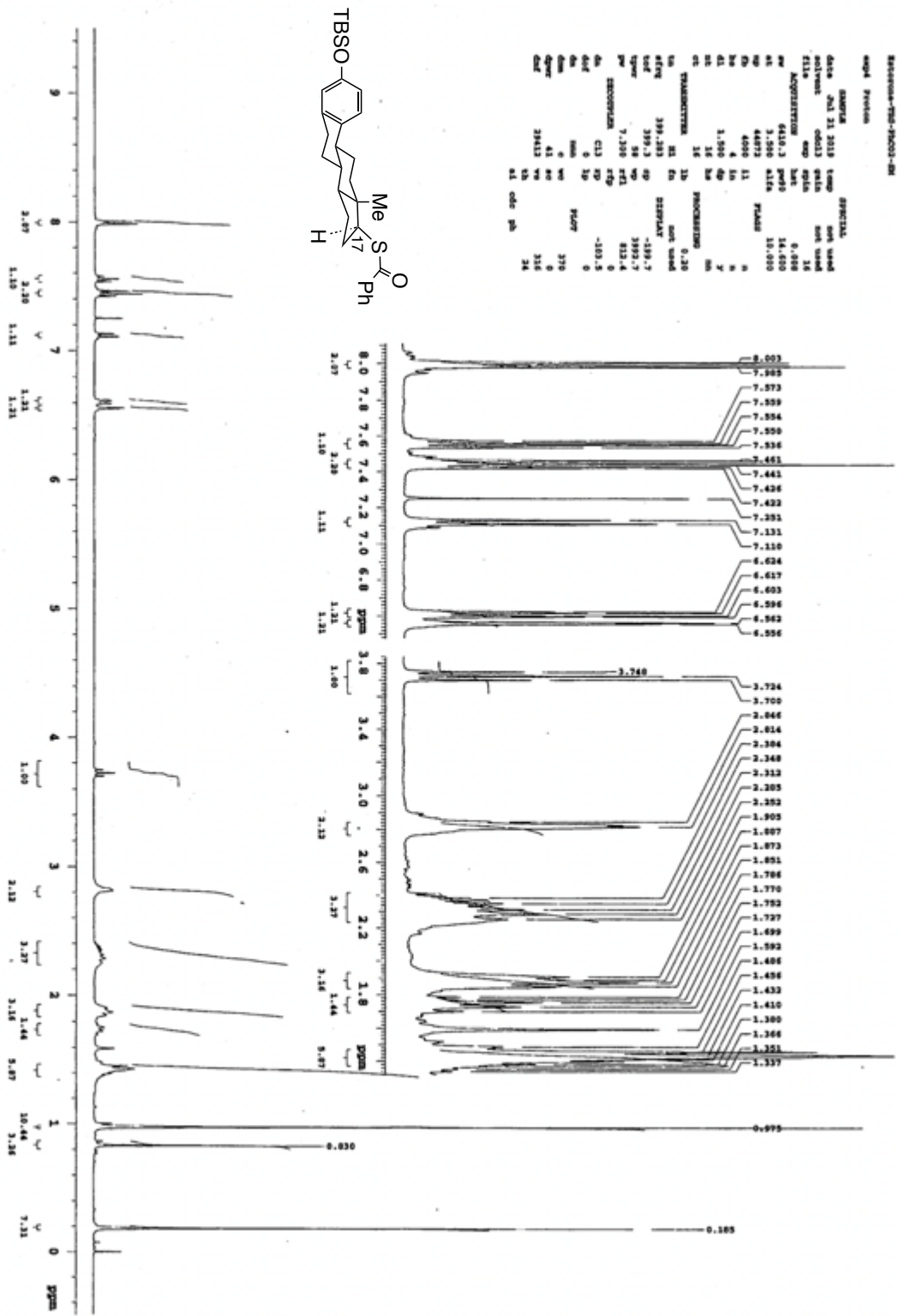
(3 β ,17 β)-17-[5-(2-Cyanofuranyl)thio]-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]androsta-5,16-diene (12g) ^{13}C -NMR



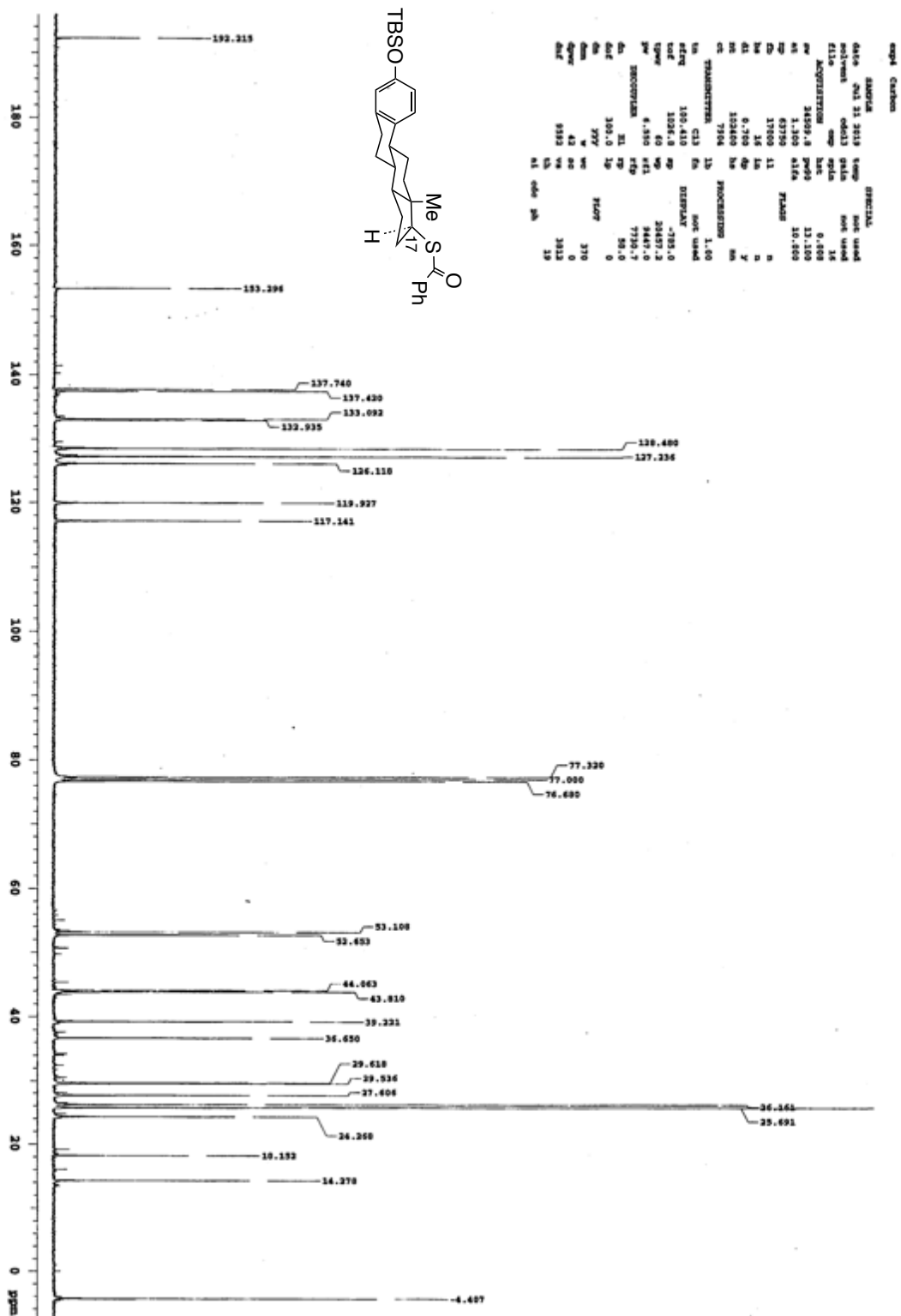
Sample Carbon

Sample	Chemical Shift (ppm)	Assignment
1	4.425	Me
2	15.768	Me
3	18.248	Me
4	20.632	Me
5	30.628	Me
6	31.279	Me
7	31.838	Me
8	31.987	Me
9	33.064	Me
10	36.747	Me
11	37.289	Me
12	42.767	Me
13	48.891	Me
14	50.321	Me
15	56.430	Me
16	72.470	Me
17	76.680	Me
18	77.000	Me
19	77.320	Me
20	111.099	Me
21	116.928	Me
22	130.583	Me
23	133.466	Me
24	138.614	Me
25	131.460	Me
26	141.853	Me
27	144.498	Me

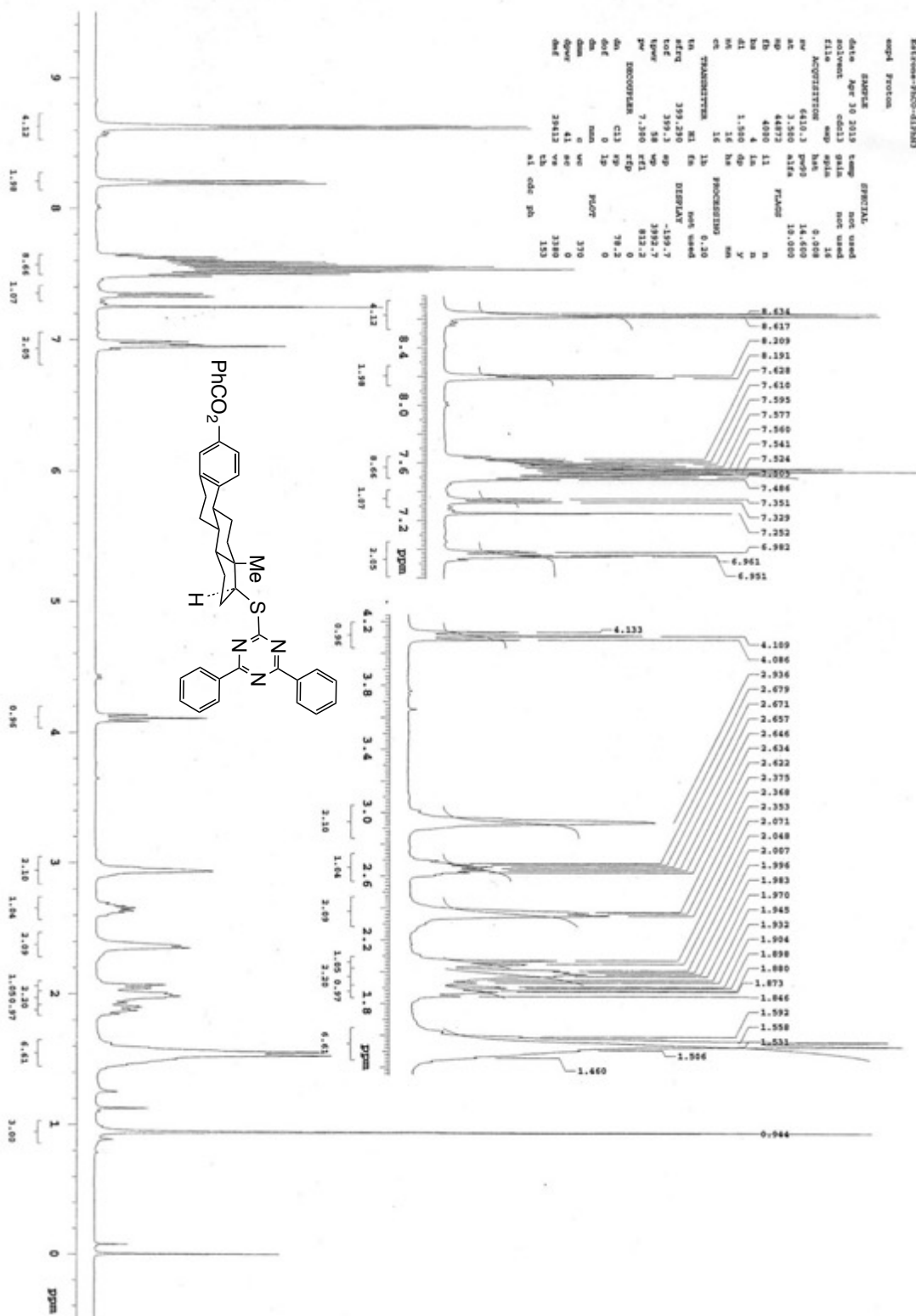
(17 β)-17-(benzoylthio)-3-[[1,1-dimethylethyl]dimethylsilyl]oxy]estra-1,3,5(10)-triene (13) ¹H-NMR



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

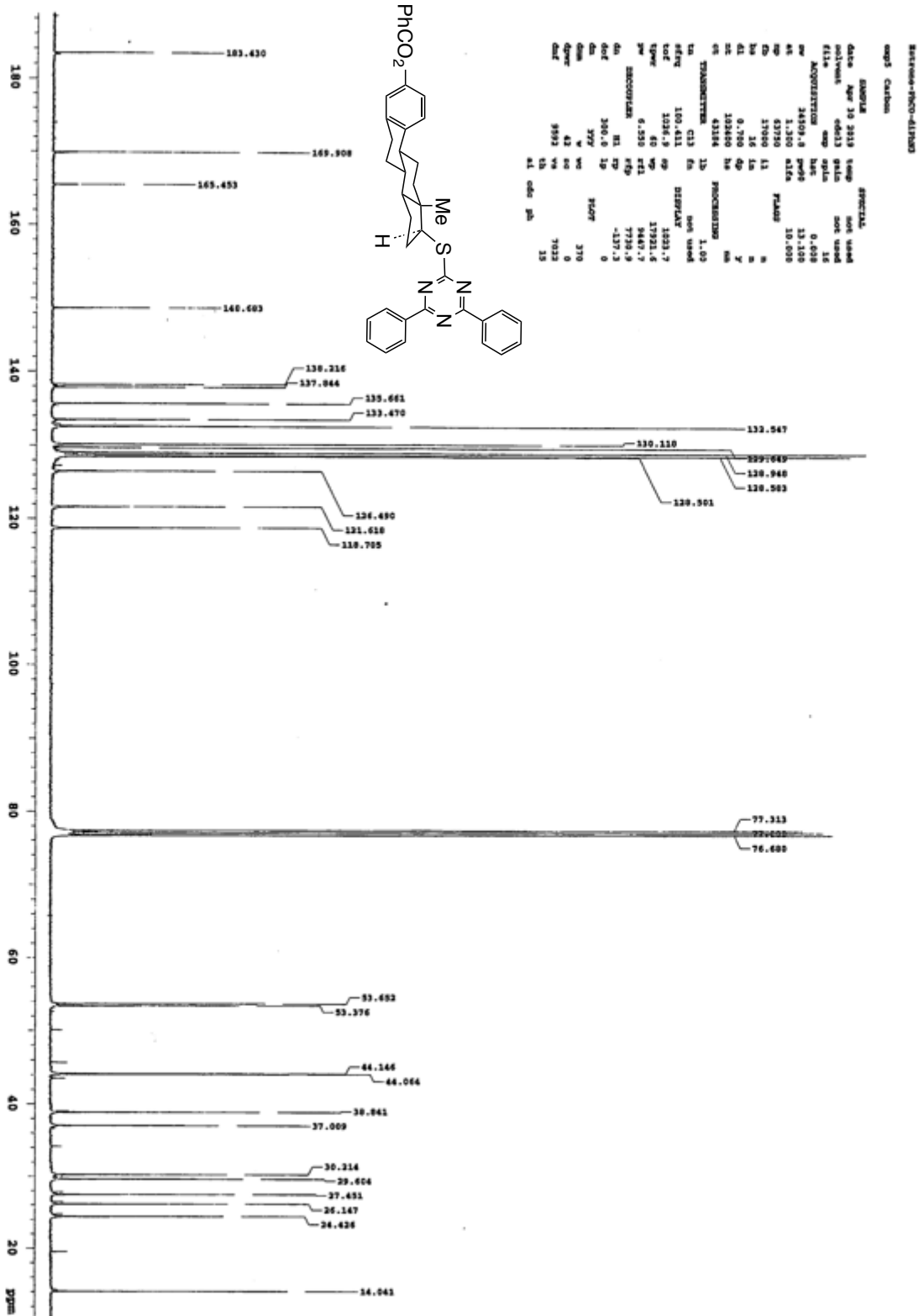


(17B)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a) ¹H-NMR

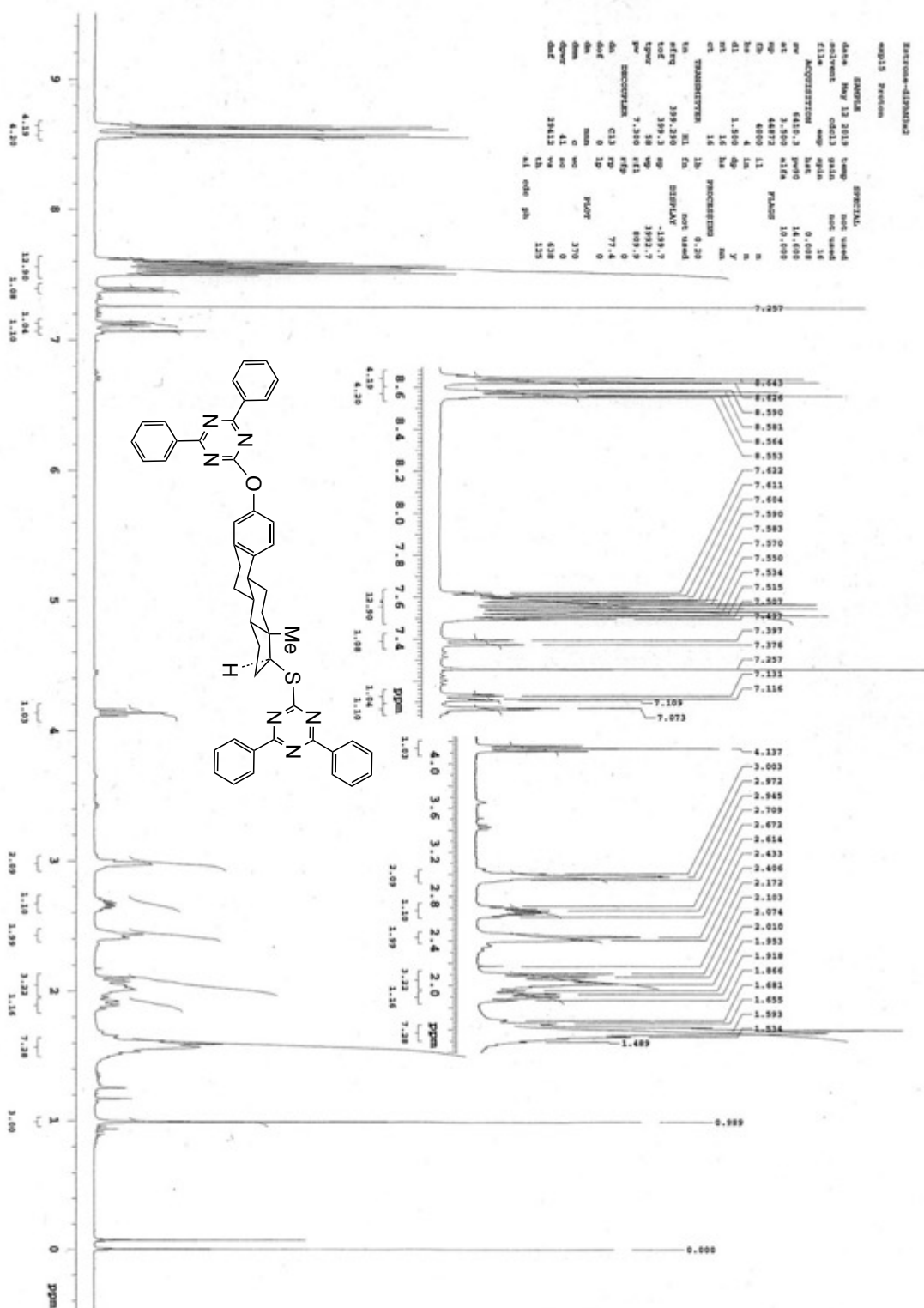


NAME: (17B)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a)
 EXP: 2019-04-18
 SOLVENT: CDCl3
 FILE: 14a_17B
 ACQ: 18.000
 PR: 18.000
 IN: 4.000
 DI: 1.000
 HI: 16.000
 CT: 16
 PROCESSED: 0.10
 EA: 393.290
 EC: 0.000
 REF: 393.290
 LAC: 393.290
 PR: 393.290
 DECOUPLER: C13
 DO: 0.15
 DDF: 0.15
 DM: 0.000
 DMC: 0.000
 DPC: 41.000
 DNF: 29812
 AL: 153
 CDCl3

(17B)-[2-(4,6-Diphenyl-1,3,5-triazyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14a) ¹³C-NMR



(17β)-[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) ¹H-NMR



NAME: (17β)-[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)

EXPNO: 1

PROCNO: 1

PROCFT: 1

PROCGB: 1

PROCIN: 1

PROCP1: 1

PROCP2: 1

PROCP3: 1

PROCP4: 1

PROCP5: 1

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PROCP7: 1

PROCP8: 1

PROCP9: 1

PROCP10: 1

PROCP11: 1

PROCP12: 1

PROCP13: 1

PROCP14: 1

PROCP15: 1

PROCP16: 1

PROCP17: 1

PROCP18: 1

PROCP19: 1

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PROCP29: 1

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PROCP96: 1

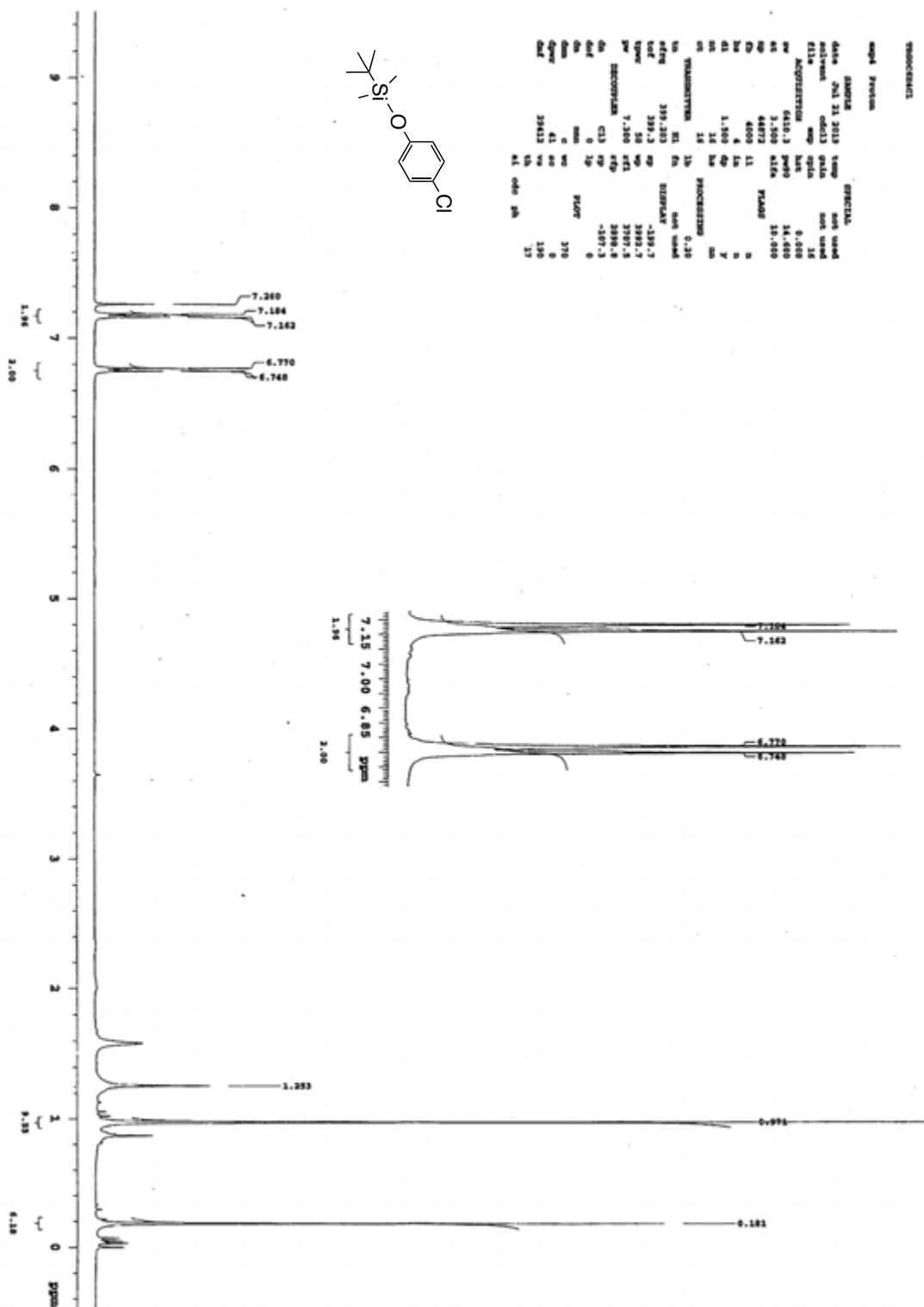
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PROCP98: 1

PROCP99: 1

PROCP100: 1

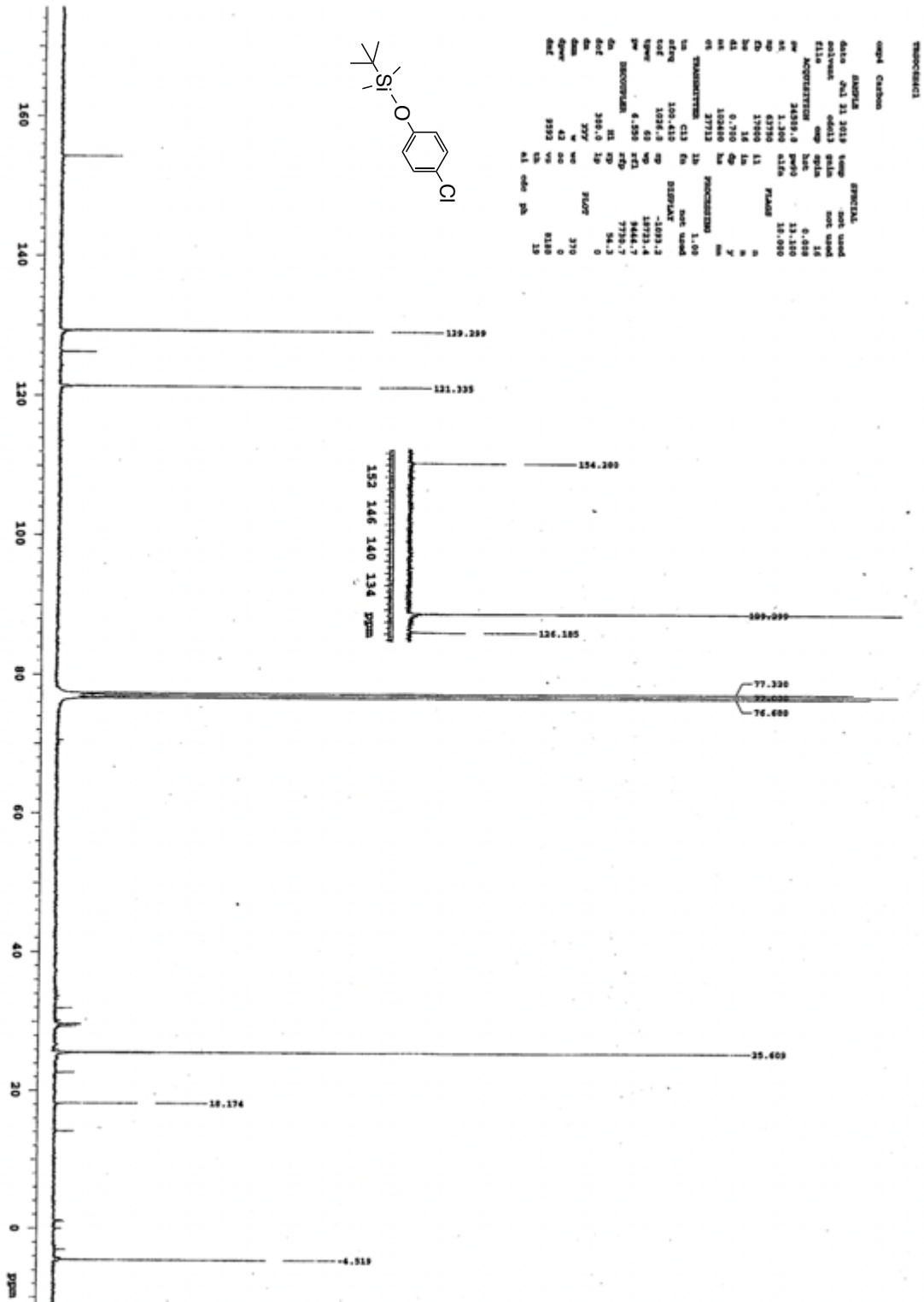
1-Chloro-4-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene ¹H-NMR



PROCESSED

DATE	TIME	TEMP	PROG
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SOLVENT	CDCl3	gala	not used
FILE	0001	gala	18
ACQUISITION	exp	gala	18
NAME	0001	gala	18
NO	48872	gala	18
NUC1	13C	gala	18
NUC2	1H	gala	18
NUC3	1H	gala	18
NUC4	1H	gala	18
NUC5	1H	gala	18
NUC6	1H	gala	18
NUC7	1H	gala	18
NUC8	1H	gala	18
NUC9	1H	gala	18
NUC10	1H	gala	18
NUC11	1H	gala	18
NUC12	1H	gala	18
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NUC96	1H	gala	18
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NUC98	1H	gala	18
NUC99	1H	gala	18
NUC100	1H	gala	18

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



NAME: 1-CHLORO-4-[[[(1,1-DIMETHYLETHYL)DIMETHYLSILYL]OXY]BENZENE

DATE: 01/21/2019

TIME: 10:00

PROBHD: 5mm QNP 1H/139

PULPROG: zgpg30

ACQRESOLUTION: 6.500

NUC1: 13C

NUC2: 13C

NUC3: 13C

NUC4: 13C

NUC5: 13C

NUC6: 13C

NUC7: 13C

NUC8: 13C

NUC9: 13C

NUC10: 13C

NUC11: 13C

NUC12: 13C

NUC13: 13C

NUC14: 13C

NUC15: 13C

NUC16: 13C

NUC17: 13C

NUC18: 13C

NUC19: 13C

NUC20: 13C

NUC21: 13C

NUC22: 13C

NUC23: 13C

NUC24: 13C

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NUC95: 13C

NUC96: 13C

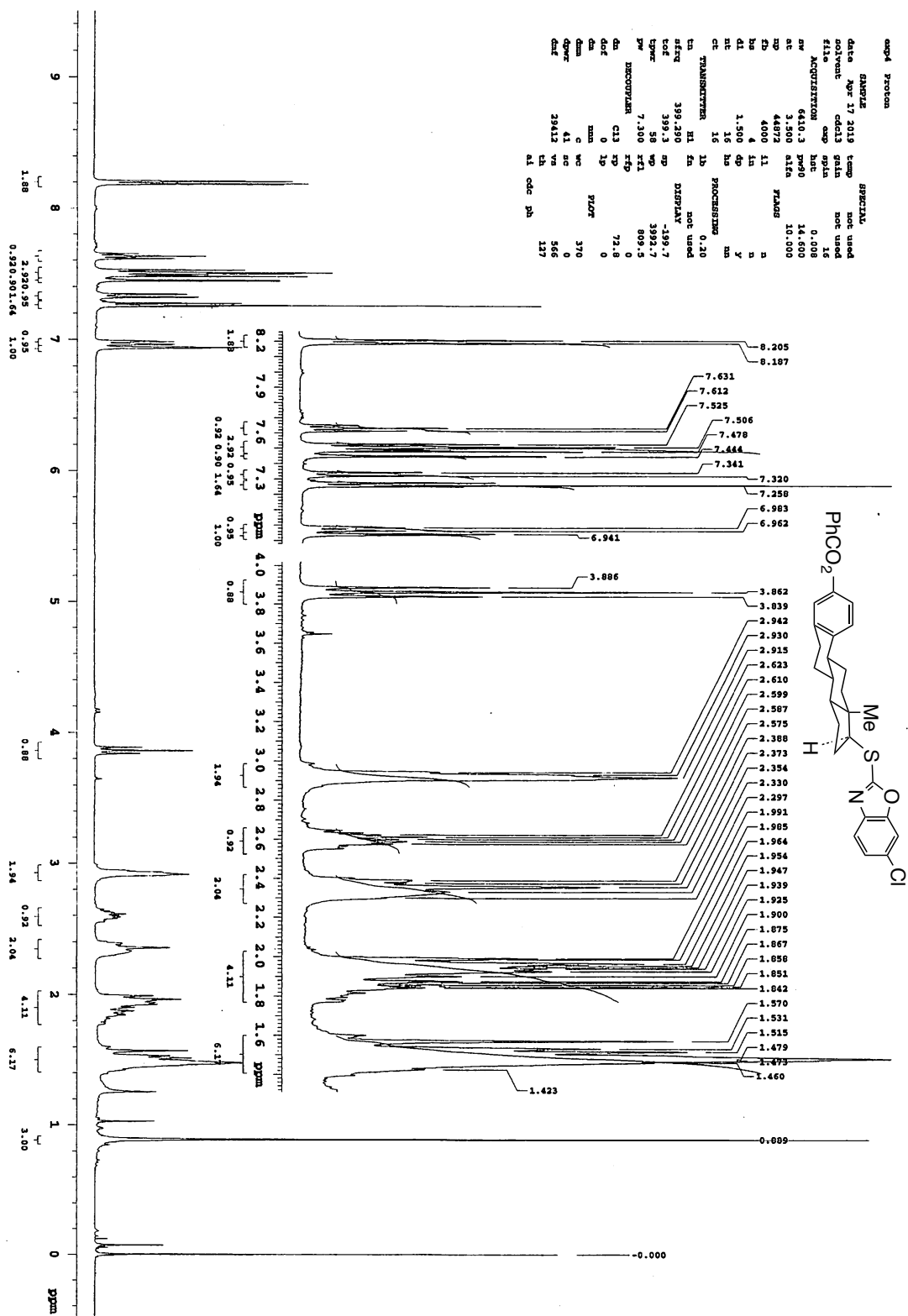
NUC97: 13C

NUC98: 13C

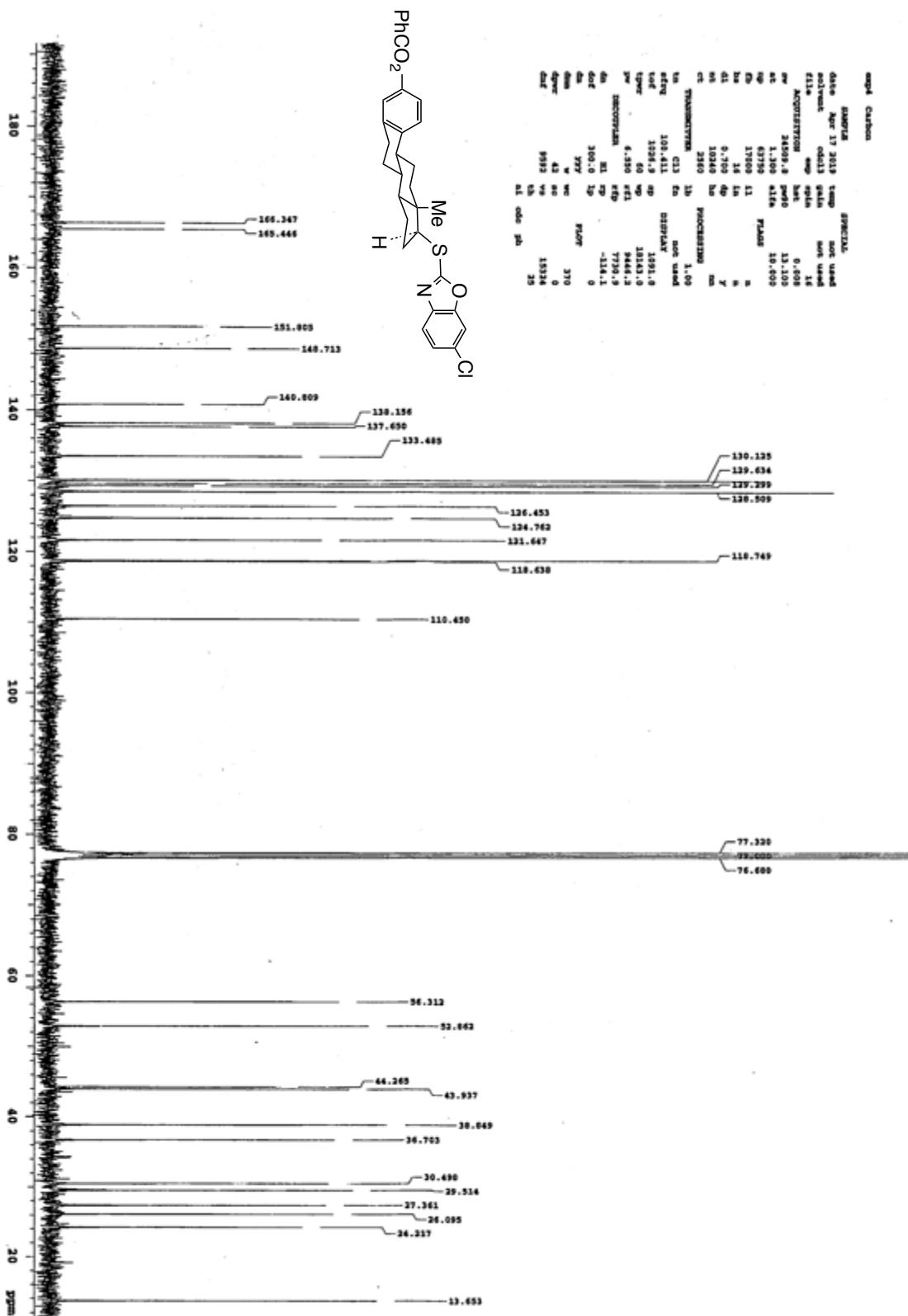
NUC99: 13C

NUC100: 13C

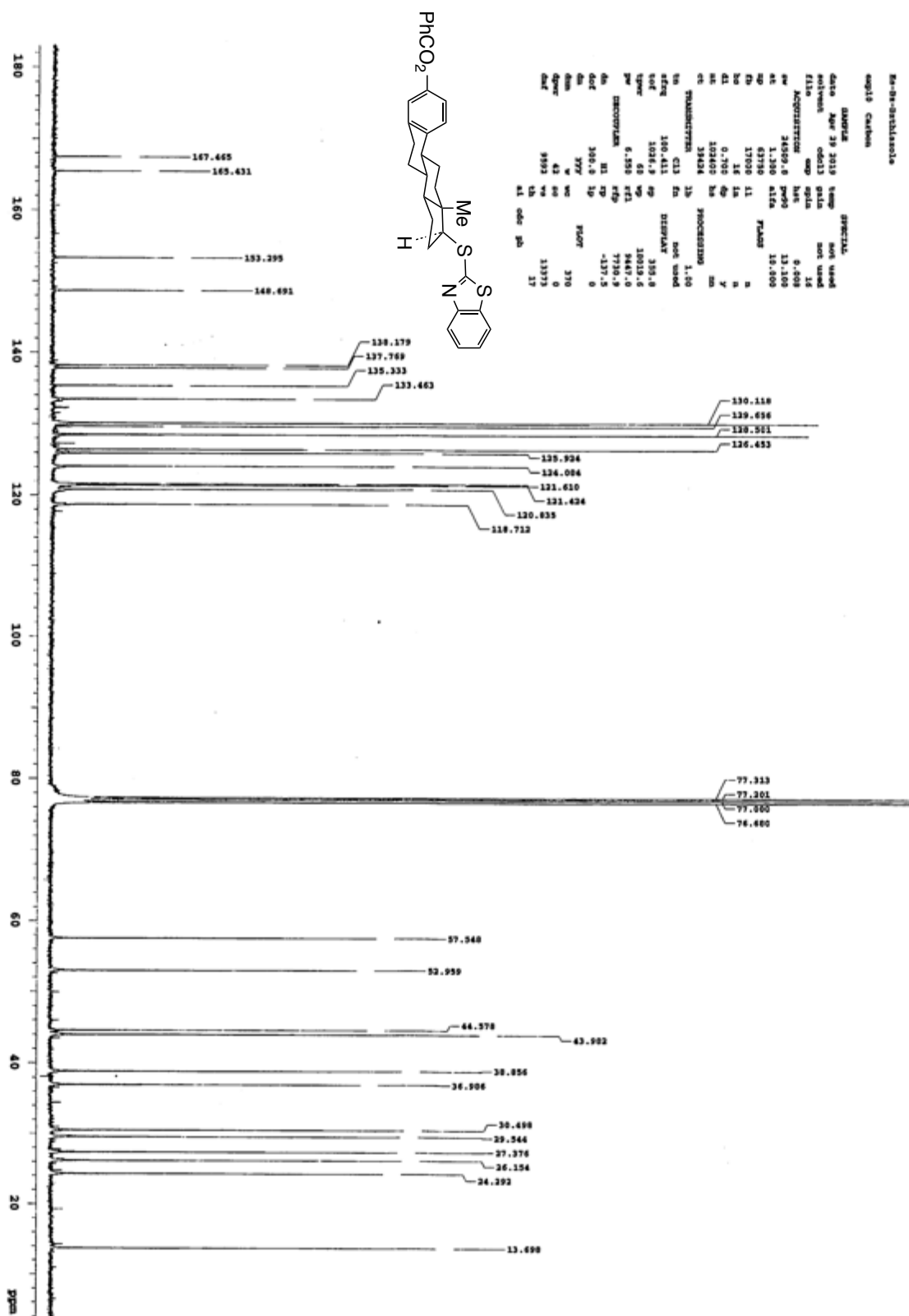
(17B)-[2-(6-Chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14c) ¹H-NMR



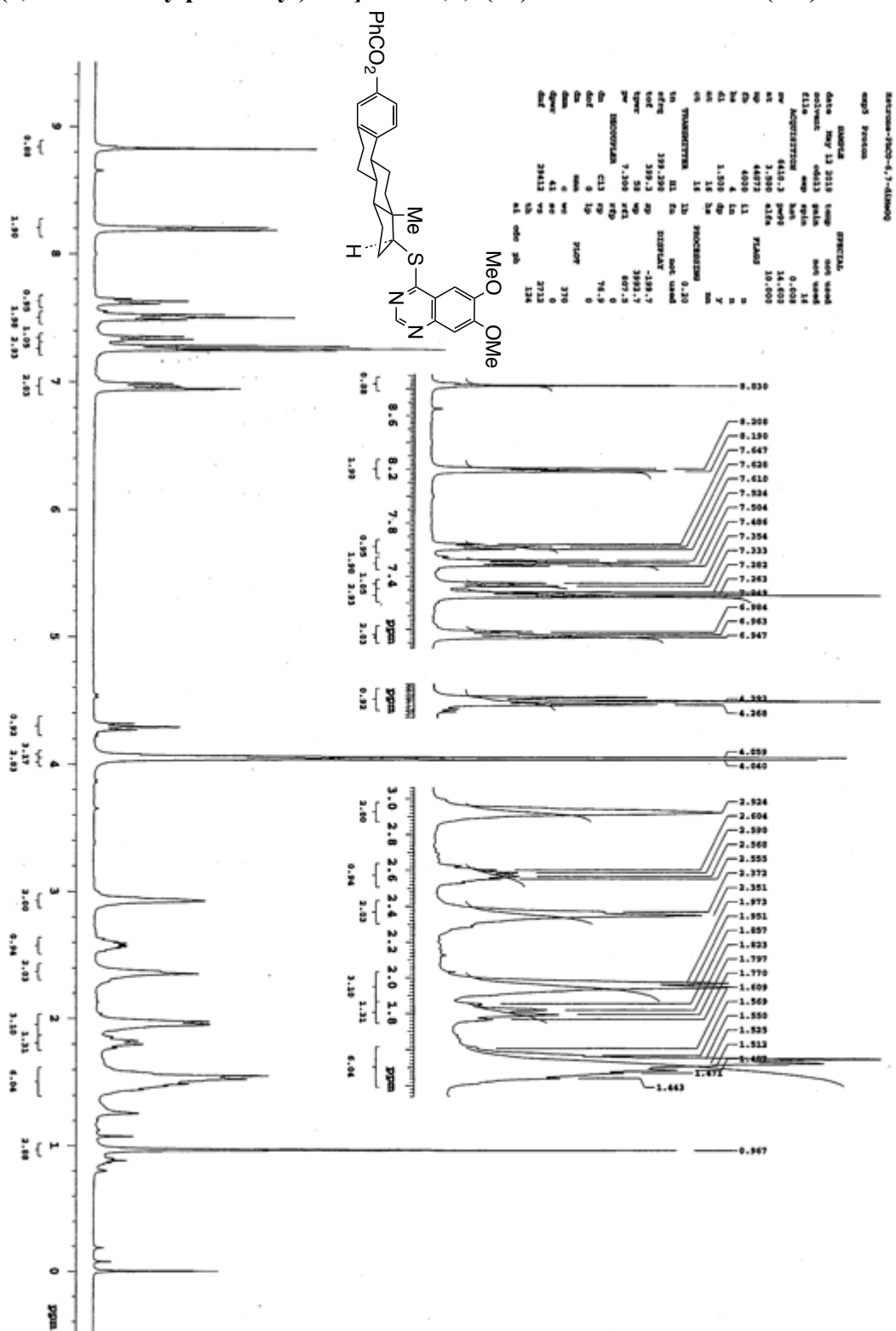
(17B)-[2-(6-Chlorobenzoxazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14c) ¹³C-NMR



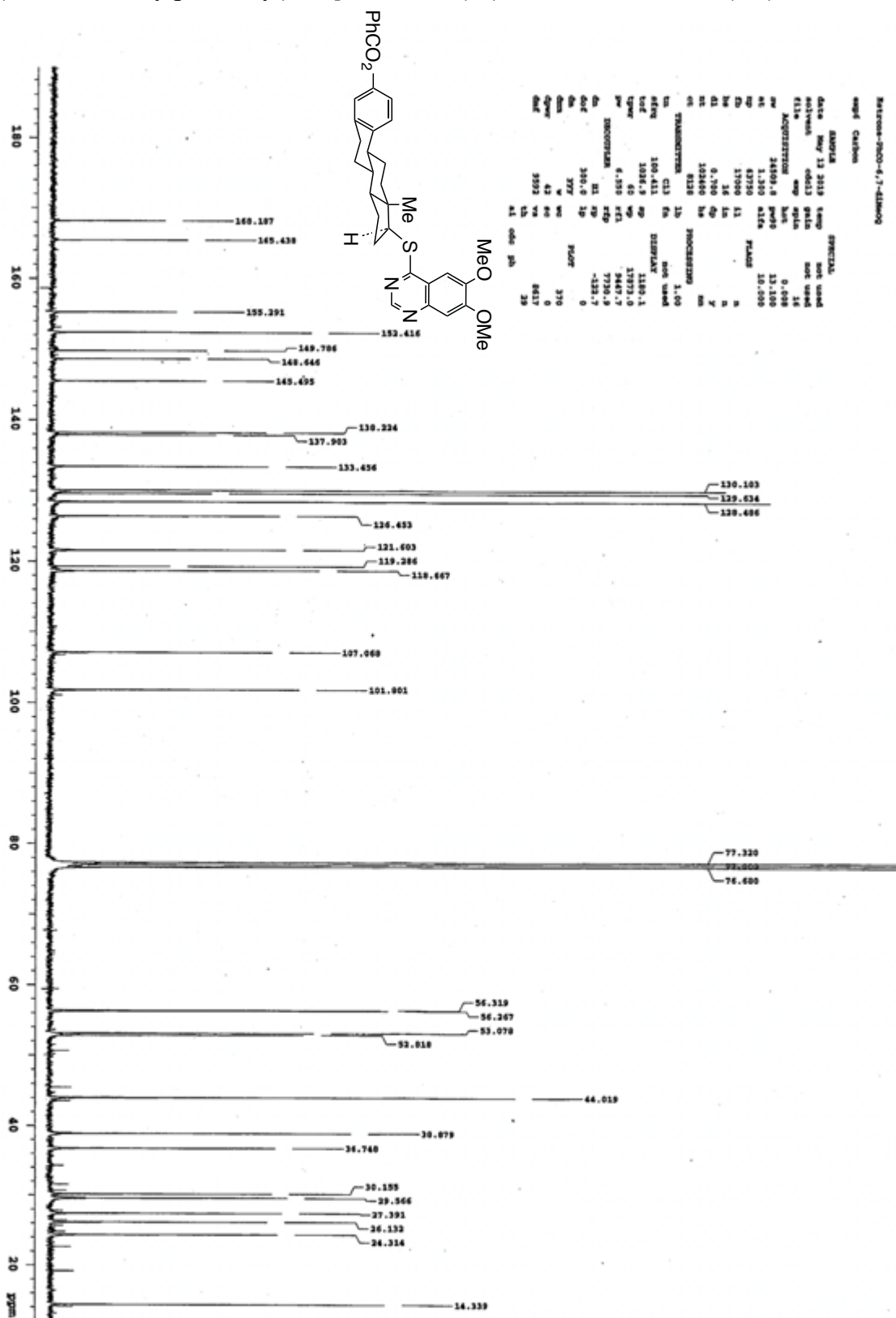
(17β)-[2-(Benzothiazolyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14d) ¹³C-NMR



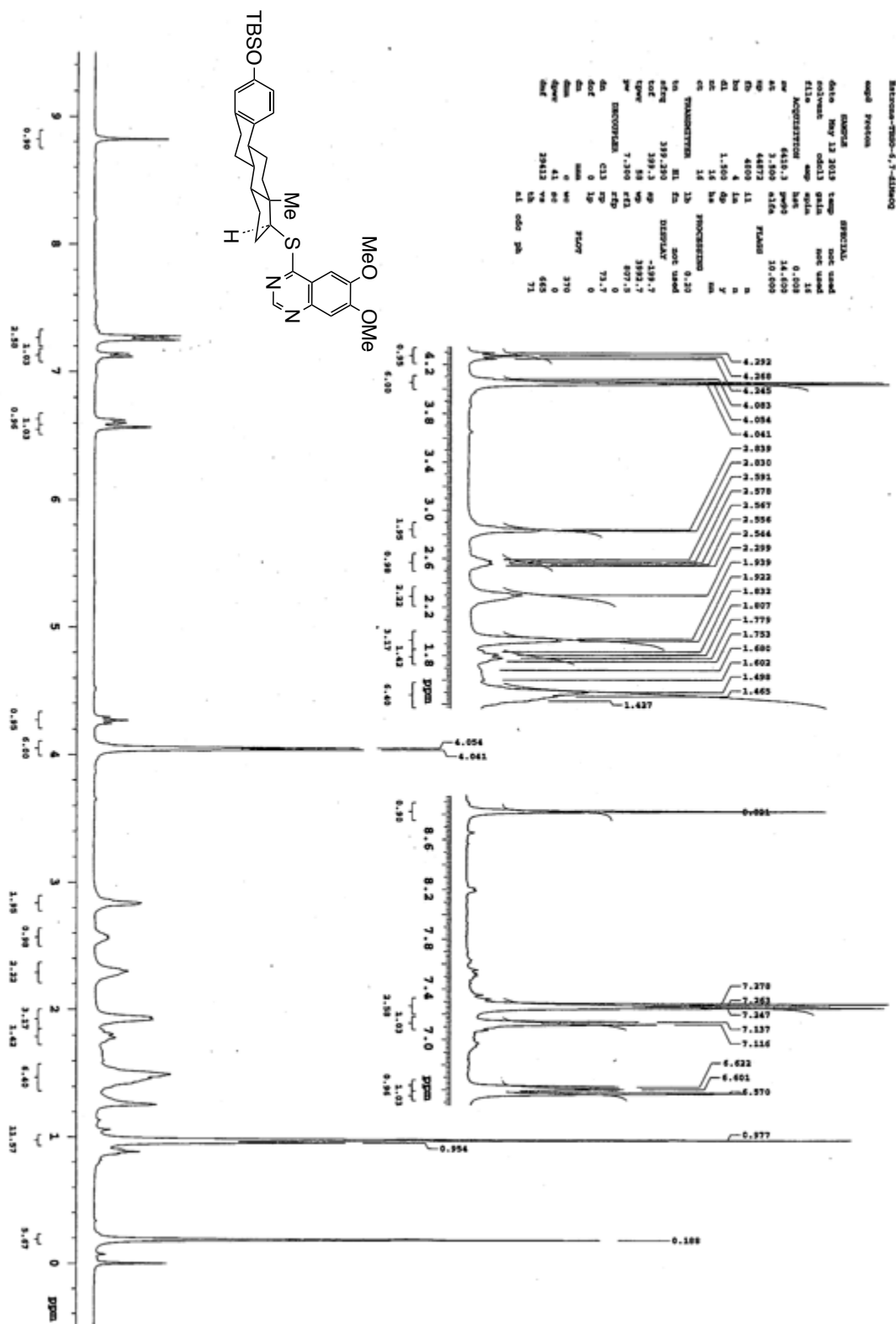
(17β)-[2-(6,7-Dimethoxyquinazoly)thio]estra-1,3,5(10)-trien-3-ol benzoate (14f) ¹H-NMR



(17B)-[2-(6,7-Dimethoxyquinazoly)thio]estra-1,3,5(10)-trien-3-ol benzoate (14f) ¹³C-NMR

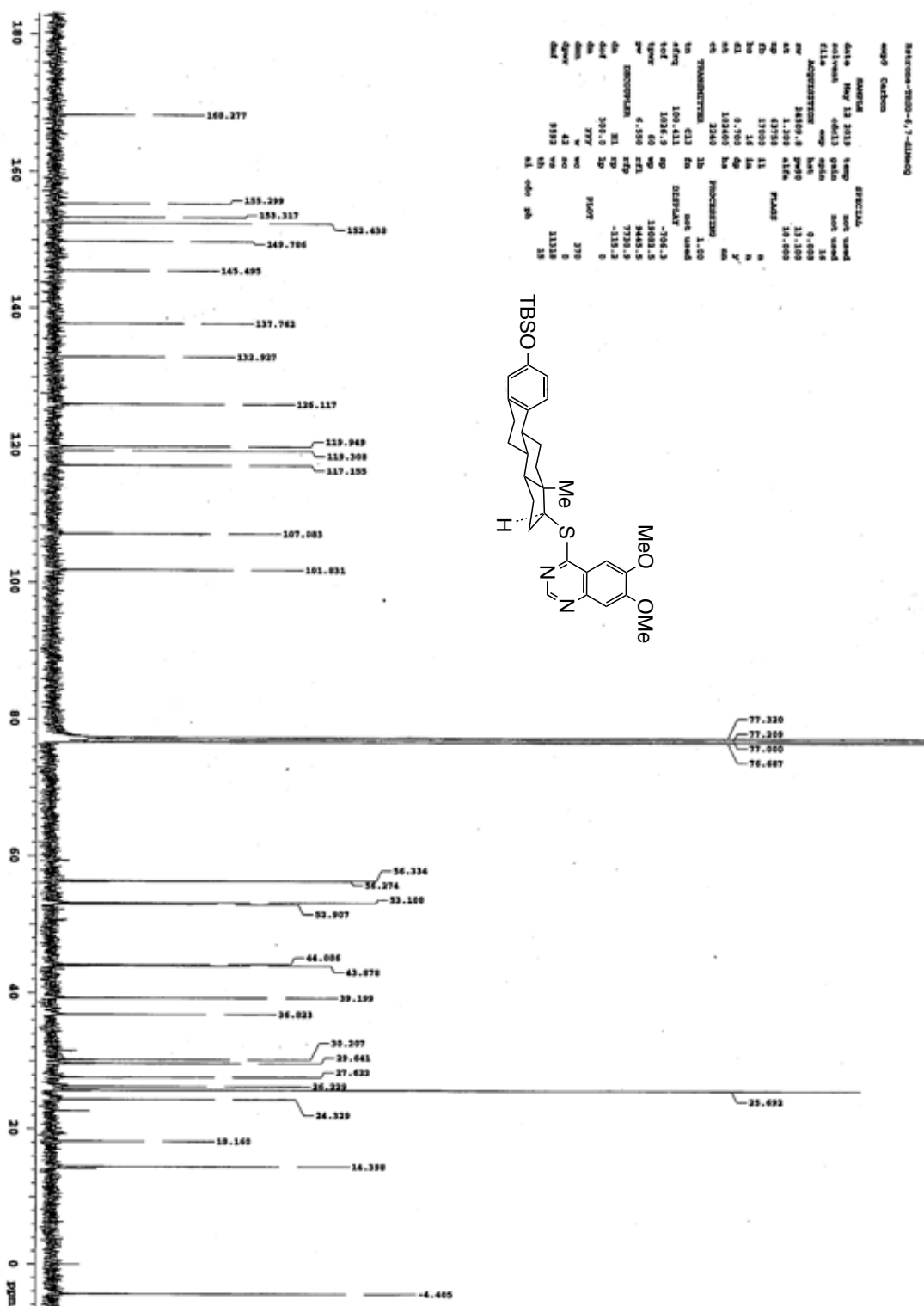


(17B)-[2-(6,7-Dimethoxyquinazoly)thio]-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16f) ¹H-NMR

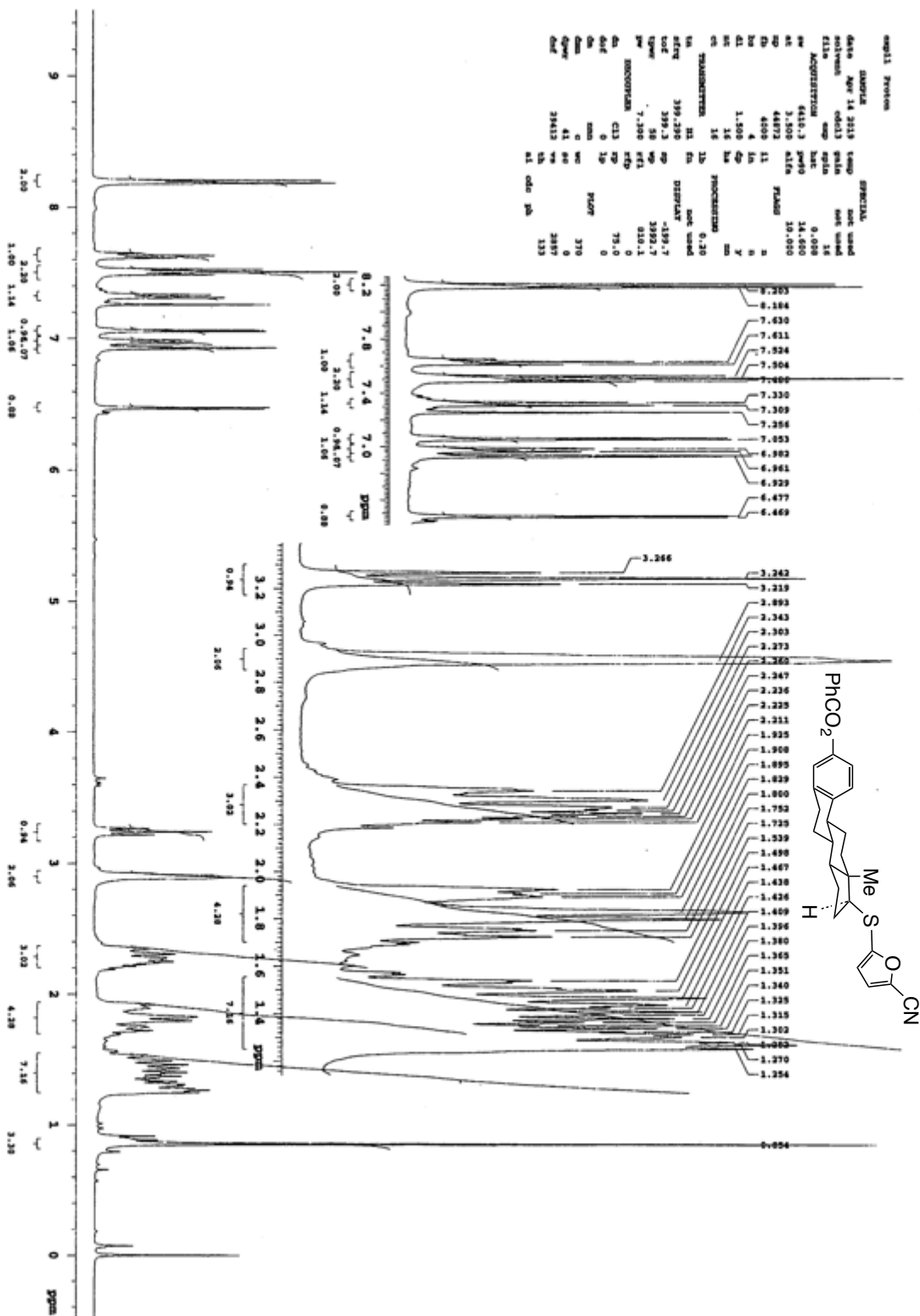


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 SF -> 125.13000000
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 AS -> 0
 RM -> 0.00000000
 GC -> 0
 PC -> 1.00000000
 PD -> 1.00000000
 RE -> 1.00000000
 RB -> 1.00000000
 RC -> 1.00000000
 RD -> 1.00000000
 RE -> 1.00000000
 RF -> 1.00000000
 RG -> 1.00000000
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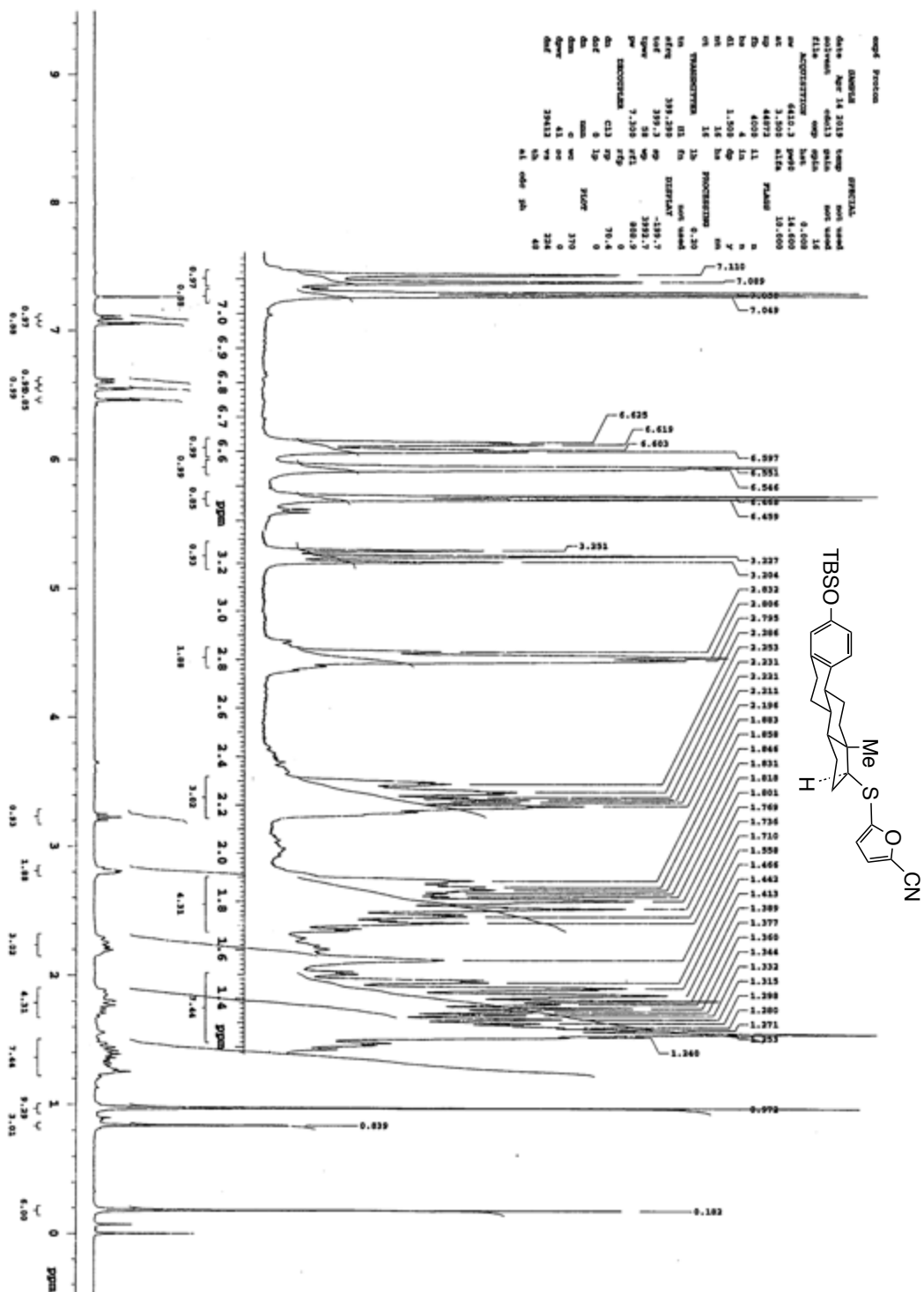
(17β)-[2-(6,7-Dimethoxyquinazoly)thio]-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16f) ¹³C-NMR



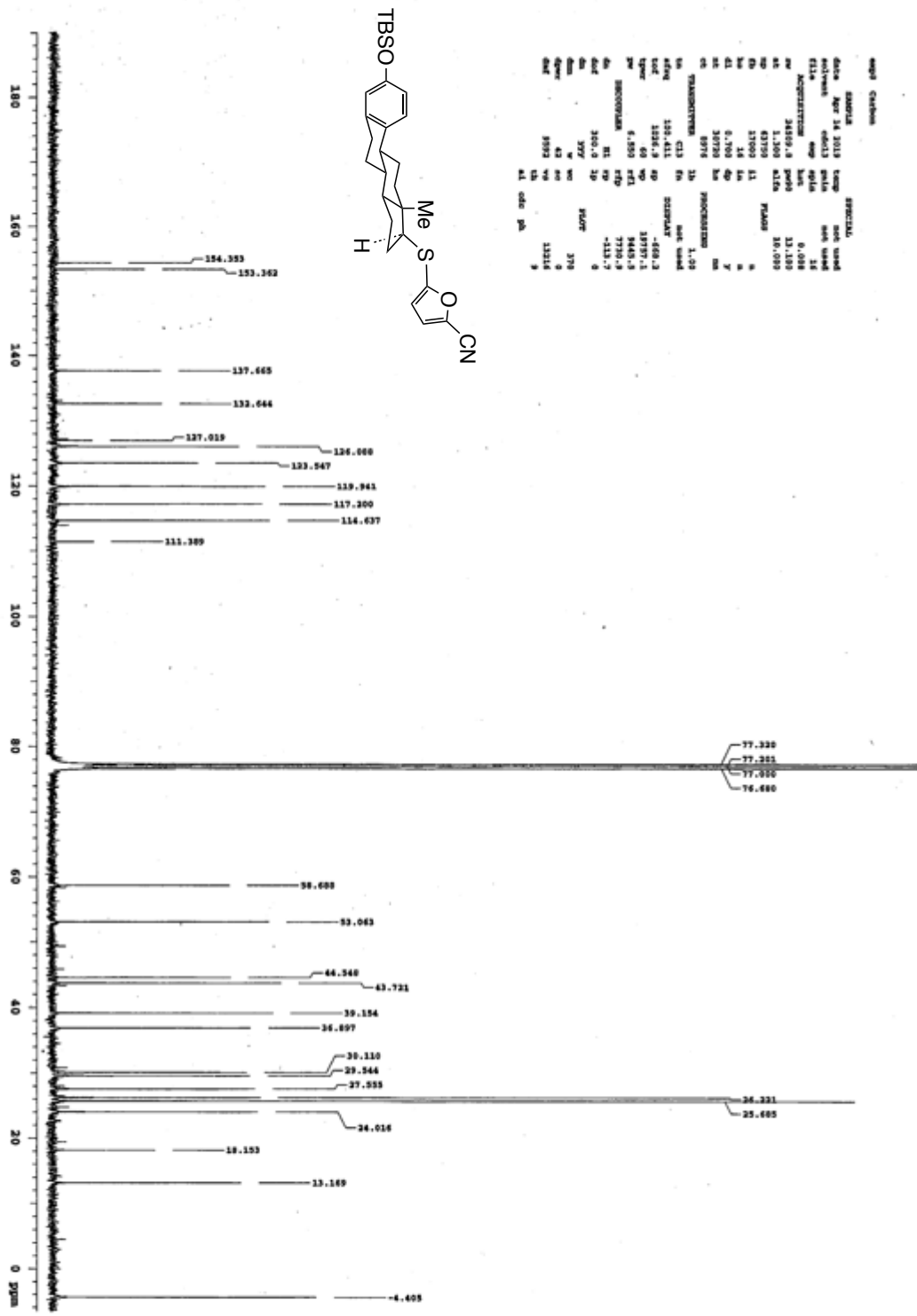
(17B)-[2-(5-Cyanofuranyl)thio]estra-1,3,5(10)-trien-3-ol benzoate (14g) ¹H-NMR



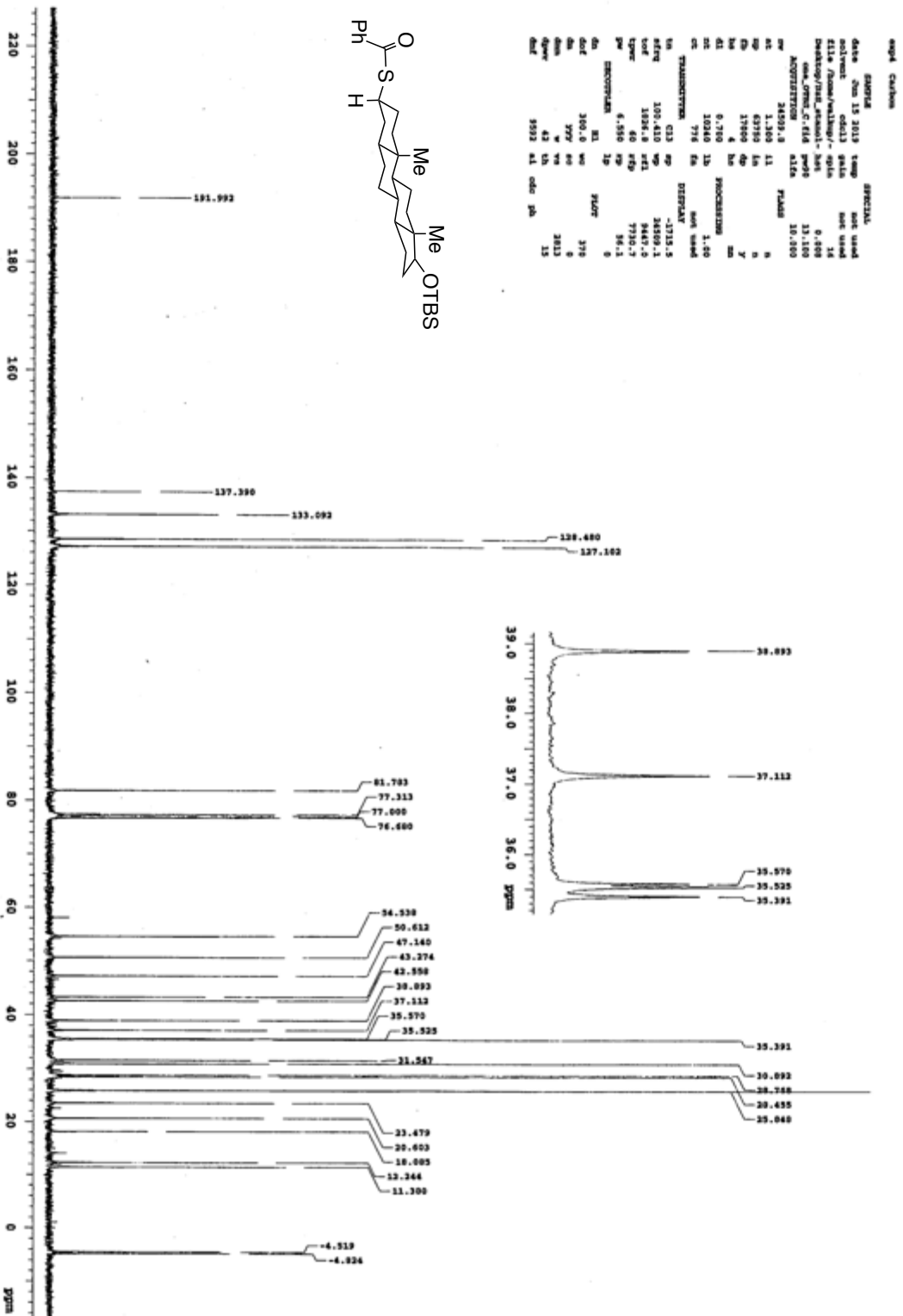
(17b)-[2-(5-Cyanofuranyl)thio]-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene (16g) ¹H-NMR



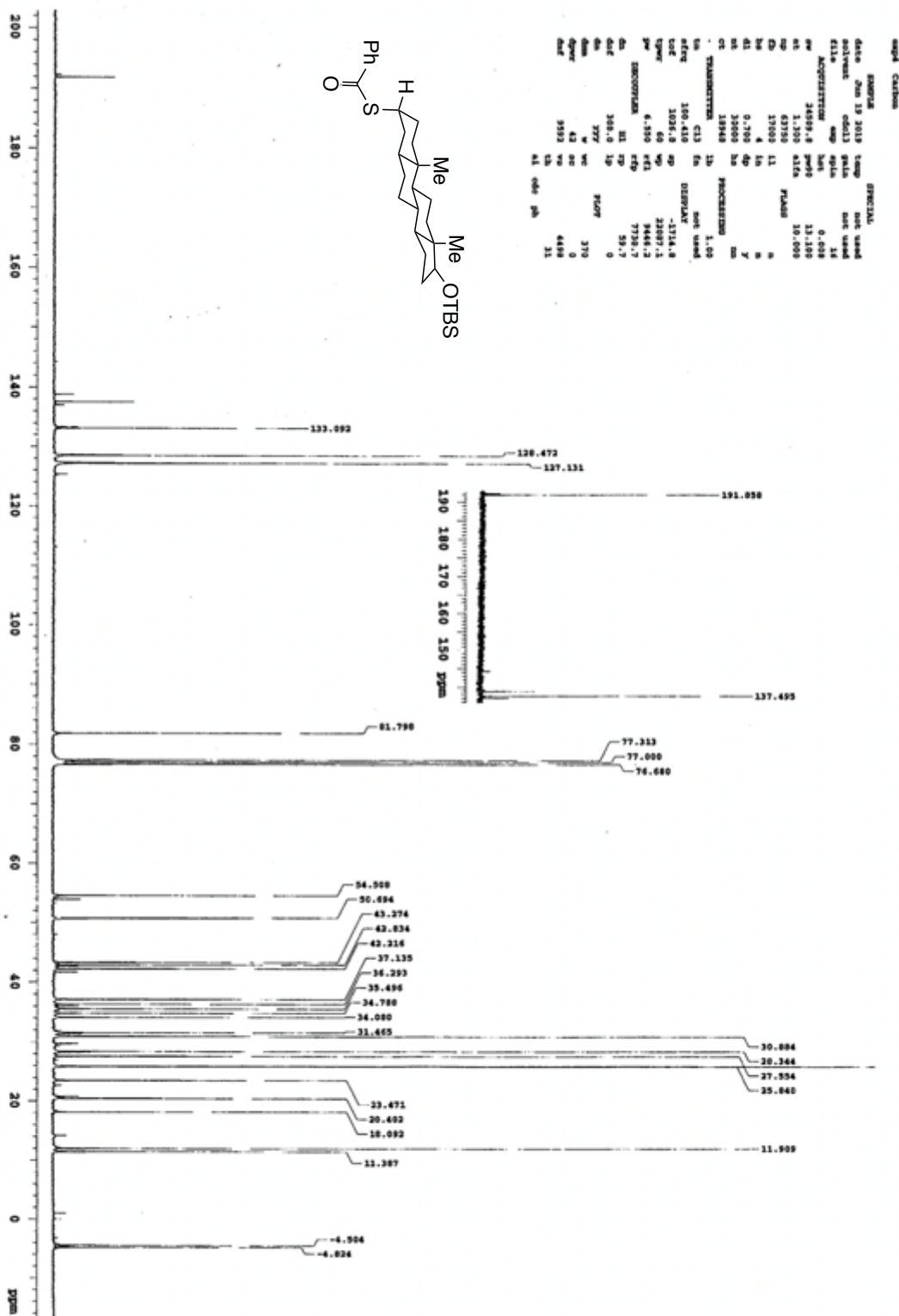
(17b)-[2-(5-Cyanofuranylthio)-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]estra-1,3,5(10)-triene
 (16g) ¹³C-NMR



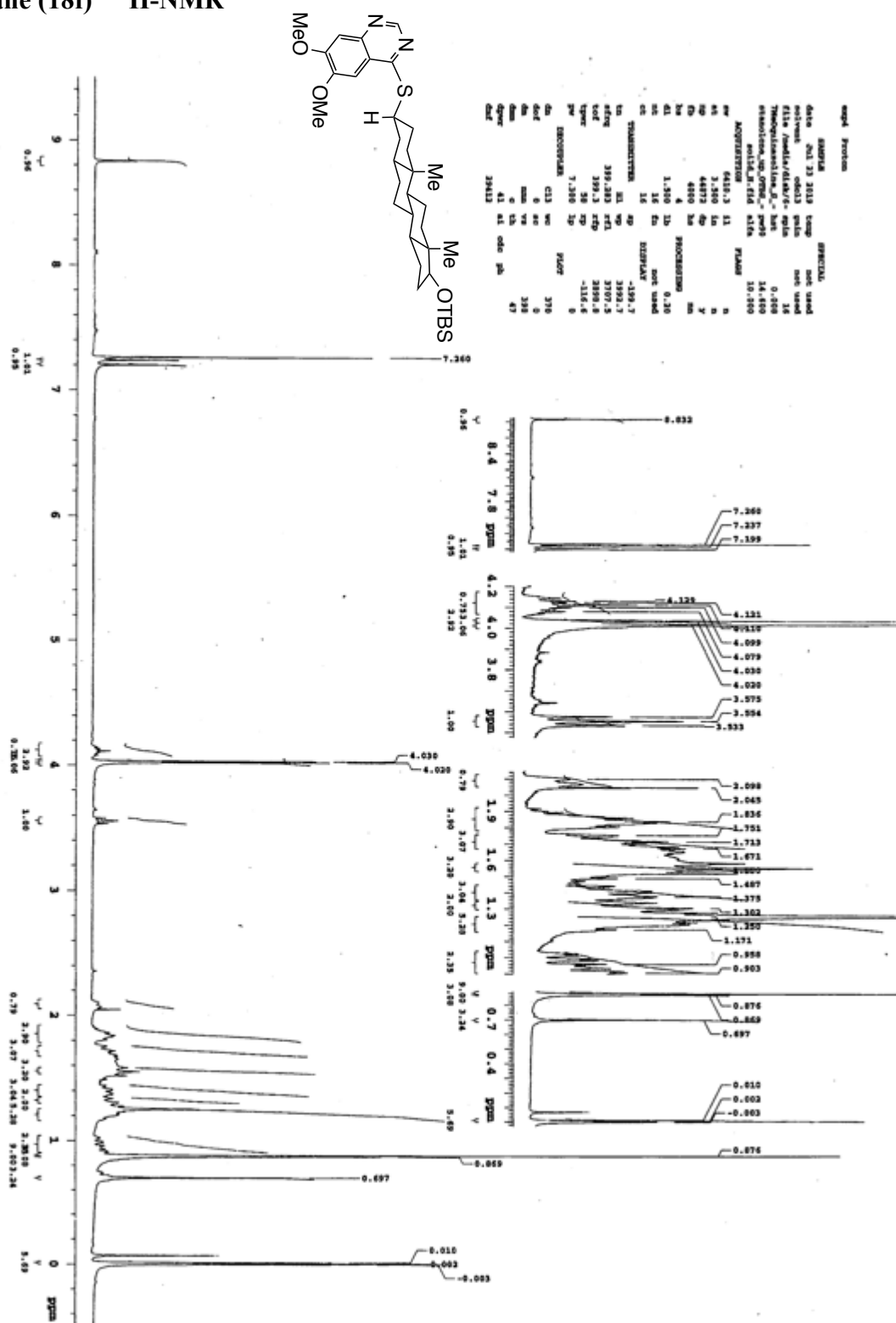
(3 β ,17 β)-3-benzoylthio-17-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5 α -androstane (17)
¹³C-NMR



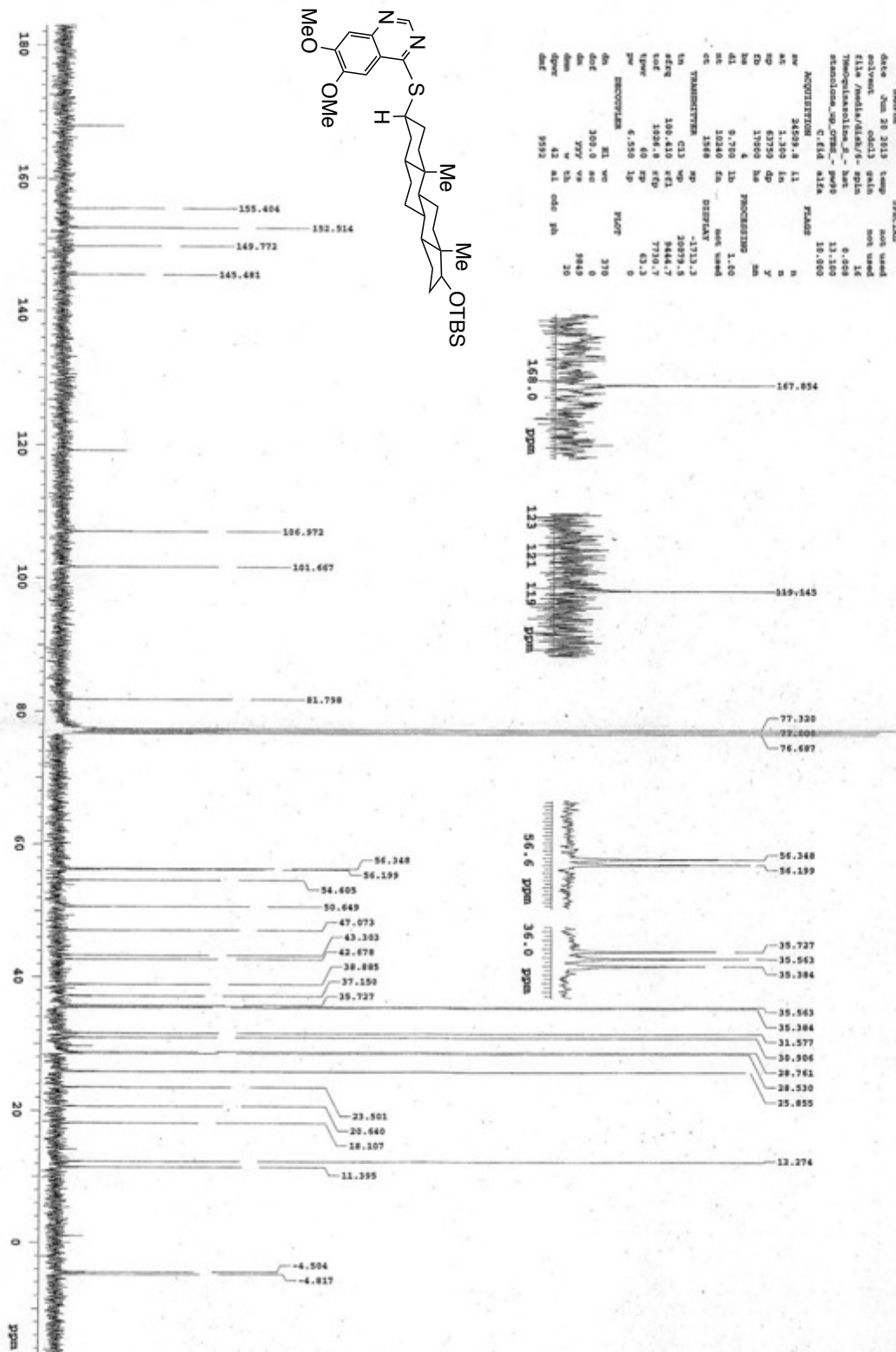
(3 α ,17 β)-3-Benzoylthio-17-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5 α -androstane (17')
¹³C-NMR



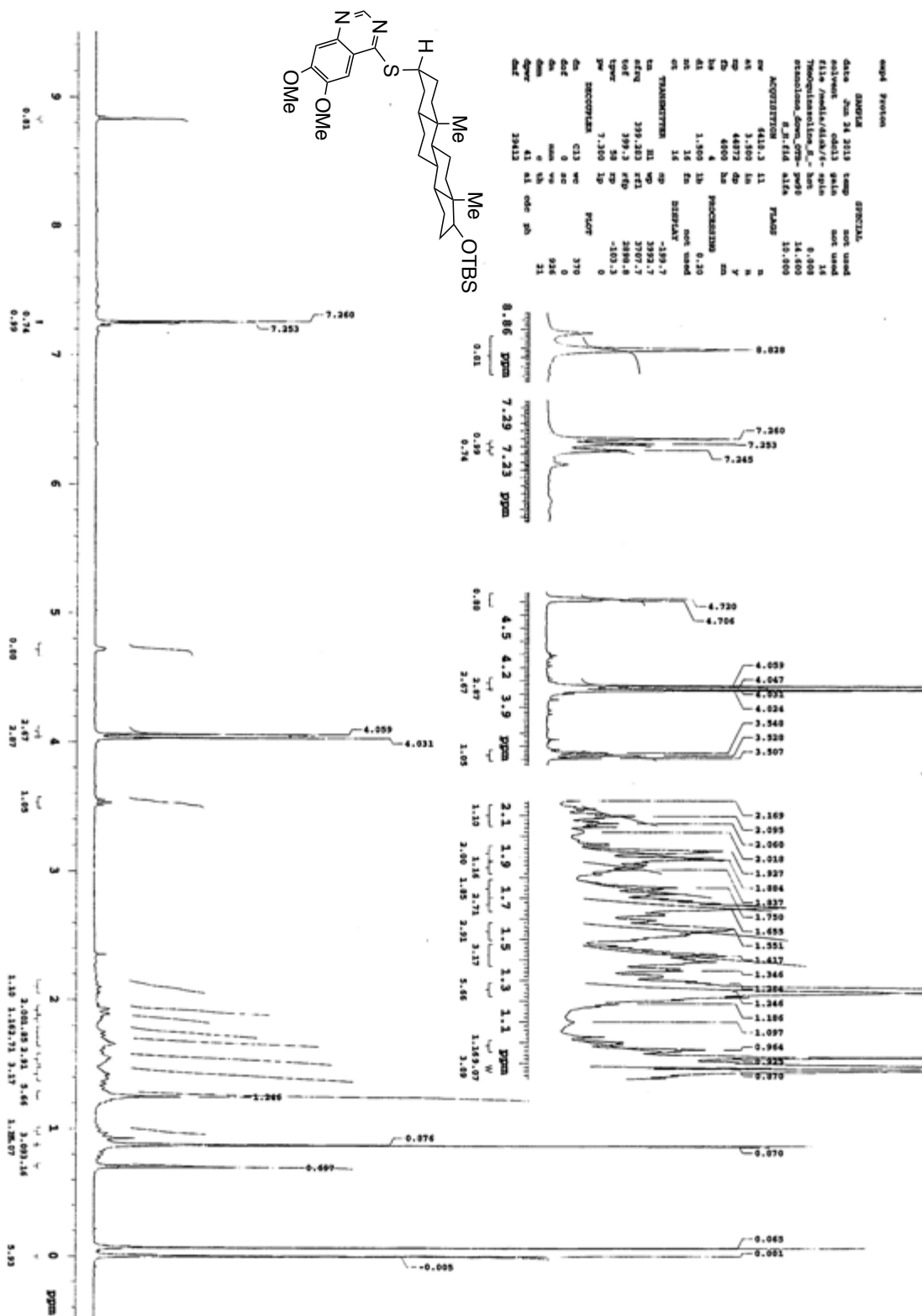
(3 β ,17 β)-3-[2-(6,7-Dimethoxyquinazoly)thio]-17-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5 α -androstane (18f) ¹H-NMR



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



(3 α ,17 β)-3-[2-(6,7-Dimethoxyquinazoly)thio]-17-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5 α -androstane (18f²) ¹H-NMR



(3 α ,17 β)-3-[2-(6,7-Dimethoxyquinazoly)thio]-17-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-5 α -androstane (18 f') 13 C-NMR

