Supporting Information for:

Synthesis of Tailored Hydrodipyrrins and Examination in Directed Routes to Bacteriochlorins and Tetradehydrocorrins

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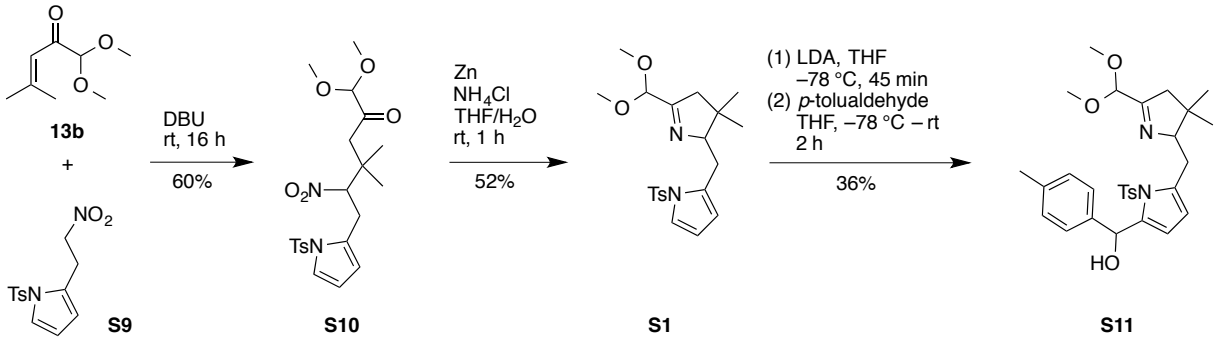
Table of Contents **Pages**

I. Synthesis of hydrodipyrrins

The eight hydrodipyrrins that were prepared and tested but found not to afford a viable macrocycle are shown in Chart 1. We first describe the synthesis and characterization of the eight hydrodipyrrins (Schemes S1–S6), followed by exploratory routes to several desired hydrodipyrrins (Scheme S7). The examination of the eight hydrodipyrrins in exploratory routes to macrocycles is described in the subsequent section.

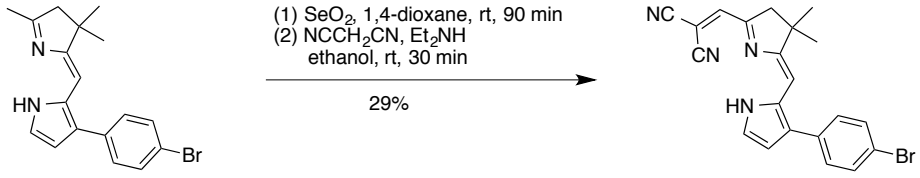


Scheme S1. Route to a protected tetrahydrodipyrrin–acetal and use in α-lithiation.

1,1-Dimethoxy-4,4-dimethyl-5-nitro-6-(*N*-*p*-tosylpyrrol-2-yl)hexan-2-one (S10). Following a general procedure,[20] a mixture of **S9** (0.937 g, 3.19 mmol), **13b** (1.01 g, 6.37 mmol) and DBU (1.0 mL, 6.4 mmol) was stirred at room temperature for 16 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (3 × 50 mL). The organic phase was dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a yellow solid (0.86 g, 60%): ^{1}H NMR δ 1.15 (s, 3H), 1.23 (s, 3H), 2.42 (s, 3H), 2.59, 2.70 (AB, ^2J = 18.9 Hz, 2H), 3.21 (ABX, ^3J = 2.0 Hz, ^2J = 13.1 Hz, 1H), 3.36 (ABX, ^3J = 4.5 Hz, ^2J = 13.1 Hz, 1H), 3.42 (s, 6H), 4.37(s, 1H), 5.17 (ABX, ^3J = 2.0 Hz, ^2J = 11.7 Hz, 1H), 6.02 (m, 1H), 6.16 (m, 1H), 7.26 (m, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 21.9, 23.9, 26.7, 36.6, 44.7, 55.2, 94.1, 104.8, 112.1, 114.8, 123.8, 126.7, 128.3, 130.4, 138.3, 145.5, 203.3; ESI-MS obsd 453.1189, calcd 453.1690 [(M + H)$^+$, M = $C_{21}H_{28}N_2O_7S$].

2,3,4,5-Tetrahydro-1-(1,1-dimethoxymethyl)-3,3-dimethyl-N^{11}-*p*-tosyldipyrrin (S1). Following a general procedure,[25] a mixture of **S10** (0.862 g, 1.91 mmol) and NH_4Cl (0.303 g, 5.72 mmol) in THF/H_2O (20 mL, 1:1) was treated with fresh zinc dust (1.25 g, 19.1 mmol) in one portion and stirred at room temperature for 1 h. The reaction mixture was filtered through filter paper. The filtrate was diluted with ethyl acetate (50 mL). The organic layer was washed with brine, dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (4:1)] to afford a yellow oil (0.40 g, 52%): ^{1}H NMR δ 0.90 (s, 3H), 1.08 (s, 3H), 2.40 (s, 3H), 2.37–2.49 (m, 2H), 2,72 (ABX, ^3J = 9.6 Hz, ^2J = 16.0 Hz, 1H), 2.98 (ABX, ^3J = 4.8 Hz, ^2J = 16.0 Hz, 1H), 3.38 (s, 3H), 3.39 (s, 3H), 3,81–3.85 (m, 1H), 4,79 (s, 1H), 6.21–6.24 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.29–7.31 (m, 1H), 7.65 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 21.8, 22.8, 27.2, 28.2, 41.8, 48.7, 54.8, 78.2, 103.1, 111.9, 113.9, 122.6, 127.0, 130.2, 133.8, 136.6, 145.0, 174.2; ESI-MS obsd 405.1845, calcd 405.1842 [$(M + H)^+$, M = $C_{21}H_{28}N_2O_4S$].

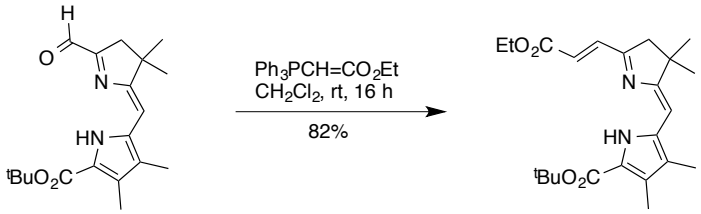
2,3,4,5-Tetrahydro-9-(hydroxy(*p*-tolyl)methyl)-1-(1,1-dimethoxymethyl)-3,3-dimethyl-N^{11}-*p*-tosyldipyrrin (S11). In an oven-dried flask, a solution of **S1** (42.8 mg, 0.106 mmol) in dry THF (4.0 mL) was bubbled with argon for at least 45 min. Then the solution was cooled to –78 °C (dry ice/acetone bath) and treated dropwise with LDA solution (2.0 M in heptanes/THF/ethylbenzene, 106 μL, 0.212 mmol) under argon. The reaction mixture was stirred at –78 °C for 45 min. Then, *p*-tolualdehyde (22 μL, 0.21 mmol) was added via syringe. After 30 min, the dry ice/acetone bath was removed and the reaction mixture was stirred at room temperature for 2 h. The mixture was quenched by the addition of water and extracted with ethyl acetate (3 × 50 mL). The organic extract was washed, dried and concentrated. Purification by gradient chromatography [silica, hexanes/ethyl acetate (3:1 to 1:1)] afforded a yellow oil (20 mg, 36%): ^{1}H NMR δ 0.88 (s, 3H), 1.09 (s, 3H), 2.34 (s, 3H), 2.41 (m, 5H), 2.75 (m, 1H), 3.02 (m, 1H), 3.37 (m, 6H), 3.47 (br, 1H), 3.82 (m, 1H), 4.78 (s, 1H), 5.68 (m, 1H), 6.12 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H); ESI-MS obsd 525.2409, calcd 525.2353 [$(M + H)^+$, M = $C_{29}H_{36}N_2O_5S$].



Scheme S2. Synthesis of a dihydrodipyrrin bearing a 1-dicyanovinyl group.

7-(4-Bromophenyl)-1-(2,2-dicyanovinyl)-2,3-dihydro-3,3-dimethyldipyrrin (S2). A sample of **21** (78 mg, 0.20 mmol) was treated with SeO_2 (67 mg, 0.60 mmol) in 1,4-dioxane at room temperature for 90 min. The reaction mixture was diluted with ethyl acetate. The organic phase was washed (saturated aqueous $NaHCO_3$ solution then brine), dried (Na_2SO_4) and concentrated. The residue was dissolved in ethanol (8.0 mL) and then treated with malononitrile (20. mg, 0.30 mmol) and Et_2NH (10. μL, 0.10 mmol) at room temperature. After 30 min, the reaction mixture was concentrated and then diluted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), concentrated and chromatographed (silica, CH_2Cl_2) to afford a blue solid (24 mg, 29%): ^{1}H NMR (300 MHz) δ 1.24 (s, 6H), 2.91 (s, 2H), 6.34 (s, 1H), 6.35 (m, 1H),

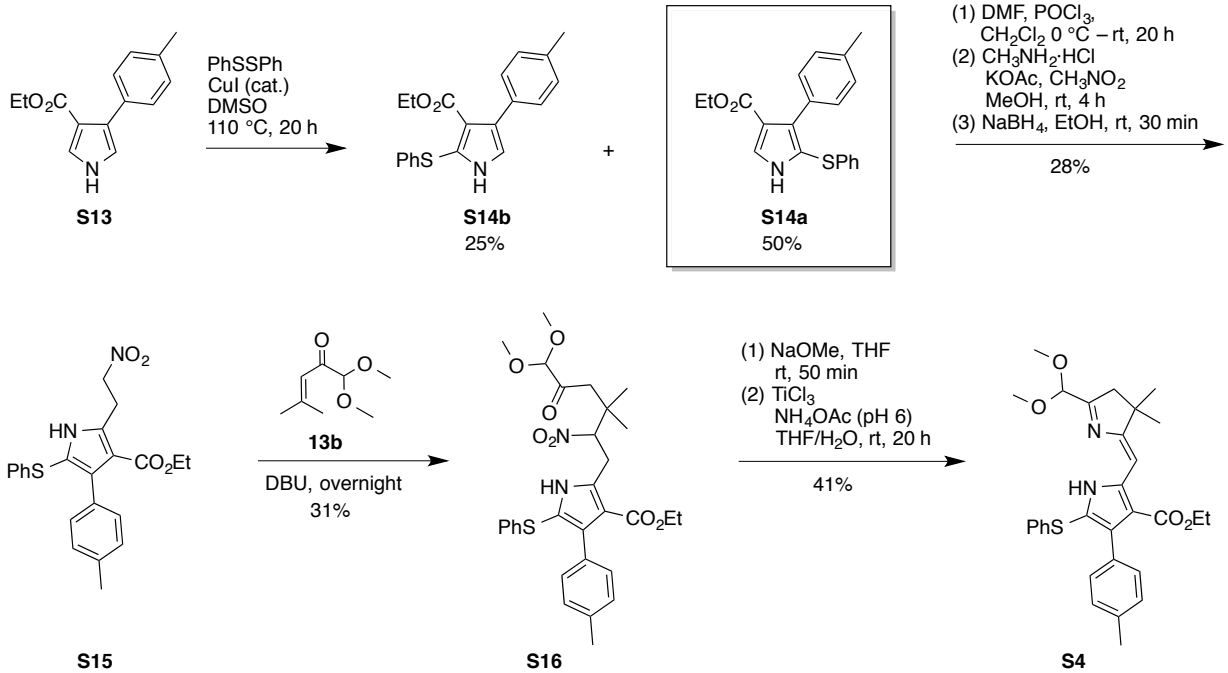
7.05 (m, 1H), 7.28 (d, J = 6.3 Hz, 2H), 7.54–7.57 (m, 3H), 10.88 (br, 1H); ESI-MS obsd 405.0706, calcd 405.0709 [$(M + H)^+$, M = $C_{21}H_{17}BrN_4$]; λ_{abs} (CH_2Cl_2) 608 nm.



S12 **S3**

Scheme S3. Synthesis of a dihydrodipyrrin bearing an ethyl acrylate group at the 1-position.

9-*tert*-Butoxycarbonyl-1-(3-ethoxy-3-oxoprop-1-enyl)-2,3-dihydro-3,3,7,8-tetramethyldipyrrin (S3). A mixture of **S12** (34.4 mg, 0.100 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (38.3 mg, 0.110 mmol) in dry CH_2Cl_2 (1.0 mL) was stirred at room temperature for 16 h. The resulting mixture was concentrated and chromatographed (silica, CH_2Cl_2) to give an orange solid (34.0 mg, 82%): ^{1}H NMR (300 MHz) δ 1.26 (s, 6H), 1.34 (t, J = 6.9 Hz, 3H), 1.61 (s, 9H), 2.06 (s, 3H), 2.26 (s, 3H), 2.59 (s, 2H), 4.27 (q, J = 6.9 Hz, 2H), 5.93 (s, 1H), 6.28 (d, J = 16.2 Hz, 1H), 7.58 (d, J = 16.2 Hz, 1H), 10.98 (br, 1H); ESI-MS obsd 401.2436, calcd 401.2435 [$(M + H)^+$, M = $C_{23}H_{32}N_2O_4$].



S13 **S14b** 25% **S14a** 50%

S15 **S16** **S4**

Scheme S4. Synthesis of a dihydrodipyrrin bearing a 9-phenylthio group.

4-Ethoxycarbonyl-3-*p*-tolyl-2-(phenylthio)pyrrole (S14a). Following a general procedure,[30] a mixture of **S13** (6.90 g, 50.0 mmol), PhSSPh (5.45 g, 25.0 mmol) and CuI (0.47 g, 2.5 mmol) was treated with DMSO (50 mL). The reaction mixture was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (400 mL) and washed with water (300 mL × 4). The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2), which afforded two isomers. The title compound was isolated

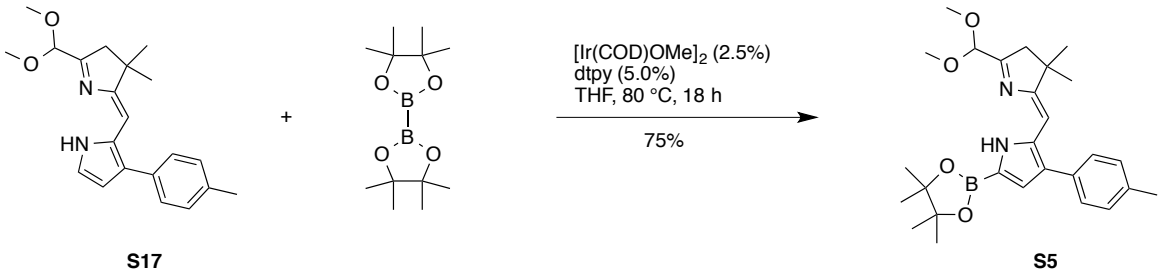
as a brown solid (6.03 g, 50%): ^{1}H NMR (300 MHz) δ 1.21 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.96–6.99 (m, 2H), 7.10–7.22 (m, 7H), 7.61 (d, J = 3.0 Hz, 1H), 8.6 (br, 1H); ESI-MS obsd 338.1209, calcd 338.1209 [(M + H)$^+$, M = $C_{20}H_{19}NO_2S$]. Isomer **S14b** was isolated as a yellow solid (3.01 g, 25%): ^{1}H NMR (300 MHz) δ 1.11 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.96–7.52 (m, 10H), 7.96 (br, 1H); ESI-MS obsd 338.1209, calcd 338.1216 [(M + H)$^+$, M = $C_{20}H_{19}NO_2S$].

4-Ethoxycarbonyl-5-(2-nitroethyl)-3-*p*-tolyl-2-(phenylthio)pyrrole (S15). Following a general procedure,[19] a solution of **S14a** (6.0 g, 25 mmol) in CH_2Cl_2 (50 mL) and DMF (7.7 mL) was treated dropwise with $POCl_3$ (3.5 mL, 38 mmol) under argon at 0 °C (ice bath). After 1 h, the ice-bath was removed and the reaction mixture was allowed to warm to room temperature. The mixture was stirred for 20 h and then cooled to 0 °C again, whereupon aqueous NaOH solution (2M, 50 mL) was added. The mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, dried and concentrated. Chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a brown solid. The brown solid was dissolved in methanol (125 mL) along with CH_3NH_2·HCl (2.0 g, 30 mmol) and KOAc (2.9 g, 30 mmol), and treated with nitromethane (4.0 mL) at room temperature. After 4 h, the reaction mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (200 mL × 2). The combined organic layer was washed, dried, and concentrated. The residue was dissolved in ethanol (120 mL) in a 500 mL-round bottom flask, treated with $NaBH_4$ (1.9 g, 50 mmol), and stirred vigorously for 30 min. Then the solvent was evaporated. The residue was taken up in water (500 mL) and neutralized with saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate. The organic extract was filtered. The filtrate was washed, dried, concentrated, and chromatographed [silica, hexanes/ethyl acetate (1:1)] to afford a yellow solid (2.82 g, 28%): ^{1}H NMR (300 MHz) δ 1.08 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 3.59 (t, J = 6.0 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 4.78 (t, J = 6.0 Hz, 2H), 7.0–7.50 (m, 9H), 8.60 (br, 1H); ESI-MS obsd 411.1375, calcd 411.1373 [(M + H)$^+$, M = $C_{22}H_{22}N_2O_4S$].

6-(4-Ethoxycarbonyl-3-*p*-tolyl-2-(phenylthio)pyrrol-5-yl)-1,1-dimethoxy-4,4-dimethyl-5-nitrohexan-2-one (S16). Following a general procedure,[19] a mixture of **S15** (1.42 g, 3.46 mmol) and **13b** (1.64 g, 10.4 mmol) was treated with DBU (1.7 mL, 10.4 mmol) and stirred overnight at room temperature. The mixture was then diluted with ethyl acetate (200 mL). The organic layer was washed with brine and water (200 mL × 4), dried (Na_2SO_4) and concentrated. Chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow oil (0.61 g, 31%): ^{1}H NMR (300 MHz) δ 1.07 (t, J = 6.9 Hz, 3H), 1.17 (s, 3H), 1.30 (s, 3H), 2.33 (s, 3H), 2.68 (AB, 2H), 3.36 (ABX, ^3J = 2.4 Hz, ^2J = 14.0 Hz, 1H), 3.41 (s, 6H), 3.68–3.73 (ABX, ^3J = 4.8 Hz, ^2J = 14.0 Hz, 1H), 4.10 (q, J = 6.9 Hz, 2H), 4.41 (s, 1H), 5.29 (ABX, ^3J = 2.4 Hz, ^2J = 11.4 Hz, 1H), 6.83–7.31 (m, 9H), 8.92 (br, 1H); ESI-MS obsd 569.2313, calcd 569.2316 [(M + H)$^+$, M = $C_{30}H_{36}N_2O_7S$].

7-Ethoxycarbonyl-2,3-dihydro-1-(1,1-dimethoxymethyl)-3,3-dimethyl-9-(phenylthio)-8-*p*-tolyldipyrrin (S4). Following a general procedure,[19] in a first flask, a solution of **S16** (0.610 g, 1.07 mmol) in THF (10 mL) was bubbled with argon for 10 min and then treated with $NaOCH_3$ (0.290 g, 5.35 mmol). The mixture was stirred at room temperature for 50 min. In a second flask, $TiCl_3$ solution (20 wt% in 3% HCl, 5.4 mL, 8.6 mmol) and water (40 mL) were mixed and bubbled with argon for 15 min. Then NH_4OAc (8.2 g, 107 mmol) was added to adjust the pH to 6, followed by 3.0 mL of THF. The resulting mixture was bubbled with argon for further 30 min. The solution in the first flask was transferred via cannula into the second one.

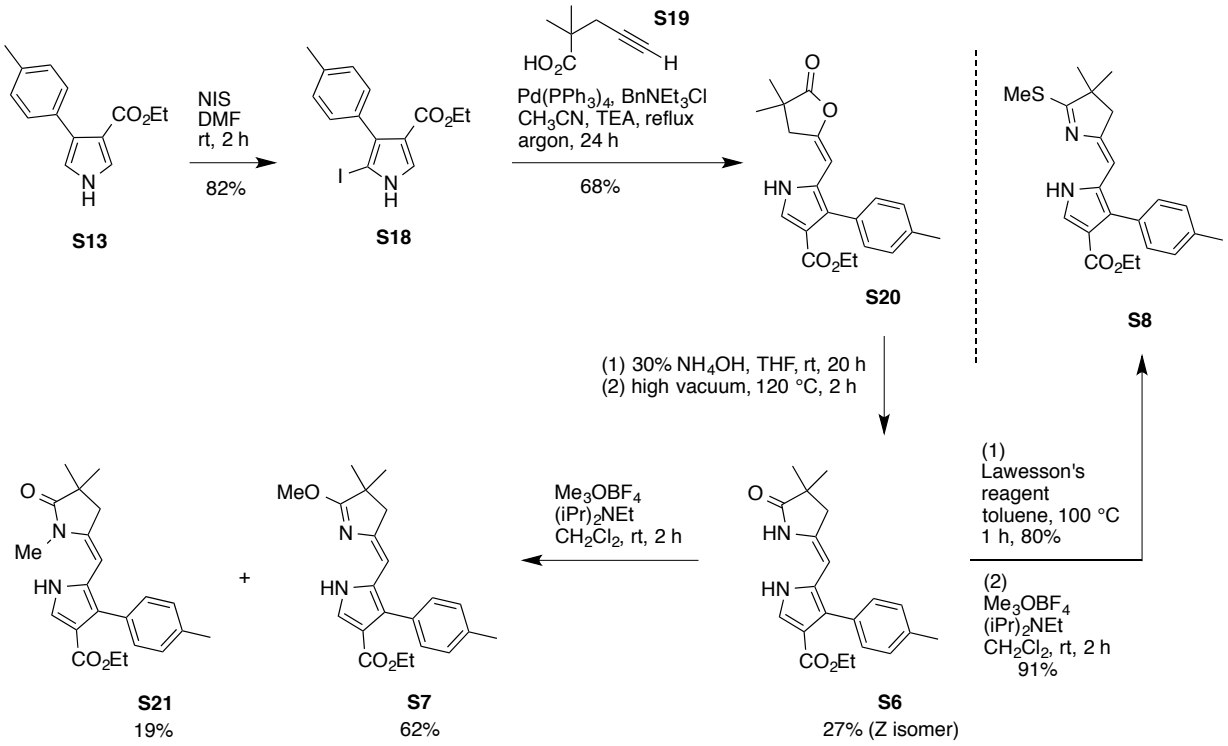
After 20 h, saturated aqueous $NaHCO_3$ solution (300 mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The extract was washed with brine and water, dried (Na_2SO_4) and concentrated. Chromatography (silica, CH_2Cl_2) afforded a yellow oil (230 mg, 41%): ^{1}H NMR (300 MHz) δ 1.10 (t, J = 7.2 Hz, 3H), 1.26 (s, 6H), 2.34 (s, 3H), 2.64 (s, 2H), 3.37 (s, 6H), 4.12 (q, J = 7.2 Hz, 2H), 4.90 (s, 1H), 6.86 (s, 1H), 7.07–7.20 (m, 9H), 11.3 (br, 1H); ESI-MS obsd 519.2322, calcd 519.2312 [$(M + H)^+$, M = $C_{30}H_{34}N_2O_4S$].



S17 **S5**

Scheme S5. Synthesis of a dihydrodipyrrin–acetal bearing a pinacol boronate at the 9-position.

2,3-Dihydro-1-(1,1-dimethoxymethyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethyl-7-*p*-tolyldipyrrin (S5). Following a reported procedure,[31] samples of **S17** (339 mg, 1.00 mmol), $B_2(pin)_2$ (152 mg, 0.598 mmol), $[Ir(cod)(OMe)]_2$ (6.6 mg, 0.010 mmol) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtpy) (5.4 mg, 0.020 mmol) were placed in a Schlenk flask, which then was evacuated and purged with argon, and then charged with dried THF (3.0 mL). The mixture was stirred at 80 °C for 18 h. The resulting mixture was concentrated to a green oil. The green oil was dissolved in CH_2Cl_2 and filtered through a short silica column (2 cm high, eluent CH_2Cl_2) to remove the catalyst and salts. The filtrate was concentrated, and the resulting residue was dried in vacuum to give a yellow solid (265 mg, 75%): ^{1}H NMR (300 MHz) δ 1.19 (s, 6H), 1.32 (s, 12H), 2.38 (s, 3H), 2.63 (s, 2H), 3.53 (s, 6H), 5.06 (s, 1H), 6.09 (s, 1H), 6.86 (d, J = 2.7 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 11.13 (br, 1H); ESI-MS obsd 465.2919, calcd 465.2922 [$(M + H)^+$, M = $C_{27}H_{37}N_2O_4B$].



Scheme S6. Synthesis of dihydrodipyrrins bearing 1-methoxy or 1-methylthio groups.

4-Ethoxycarbonyl-2-iodo-3-*p*-tolylpyrrole (S18). Following a general procedure,[21] a stirred solution of **S13** (2.29 g, 10.0 mmol) in dry DMF (25 mL) was treated dropwise with a solution of NIS (2.25 g, 10.0 mmol) in DMF (25 mL) at room temperature. The reaction mixture was stirred for 2 h. Then, the mixture was diluted with ethyl acetate (200 mL) and washed with brine and water. The organic layer was dried (Na_2SO_4), concentrated and chromatographed (silica, CH_2Cl_2) to give a bright-white solid (2.90 g, 82%): ^{1}H NMR (300 MHz) δ 1.18 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 4.10 (q, J = 7.2 Hz, 2H), 7.21 (m, 4H), 7.56 (d, J = 3.0 Hz, 1H), 8.40 (br, 1H); ESI-MS obsd 356.0141, calcd 356.0142 [$(M + H)^+$, M = $C_{14}H_{14}INO_2$].

4-Ethoxycarbonyl-2-[(4,4-dimethyl-5-oxodihydrofuran-2(*3H*)-ylidene)methyl]-3-*p*-tolylpyrrole (S20). Following a general procedure,[21] a solution of **S18** (1.78 g, 5.00 mmol), **S19** (1.26 g, 10.0 mmol) and $BnNEt_3Cl$ (1.14 g, 5.00 mmol) in dry acetonitrile (20.0 mL) and Et_3N (5.0 mL) was degassed by three freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (289 mg, 0.250 mmol) was added under argon. The reaction mixture was refluxed for 24 h, and then concentrated under high vacuum. The residue was dissolved in CH_2Cl_2. The resulting solution was washed with brine and water, dried (Na_2SO_4), concentrated, and chromatographed [silica, hexanes/ethyl acetate (2:1)] to afford a yellow solid (1.20 g, 68%): ^{1}H NMR (300 MHz) δ 1.18 (s, 6H), 1.21 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 2.48 (d, J = 2.4 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 6.07 (m, 1H), 7.16 – 7.19 (m, 4H), 7.41 (d, J = 3.3 Hz, 1H), 8.8 (br, 1H); ^{13}C NMR (100 MHz) δ 179.8, 165.0, 148.3, 136.5, 131.4, 130.7, 128.7, 125.2, 124.8, 124.6, 115.1, 97.6, 59.9, 40.2, 40.0, 31.2, 25.1, 21.4, 14.5; ESI-MS obsd 354.1703, calcd 354.1700 [$(M + H)^+$, M = $C_{21}H_{23}NO_4$].

8-Ethoxycarbonyl-1,10,2,3,-tetrahydro-2,2-dimethyl-7-*p*-tolyldipyrrin-1-one (S6). Following a general procedure,[28] a solution of **S20** (704 mg, 2.00 mmol) in THF (4.0 mL) was treated with 30% NH_4OH (4.0 mL, ~30 mmol) at room temperature for 20 h. The solution was

then concentrated to dryness at 50 °C under reduced pressure. The resulting residue was placed in a 20-mL vial, which was then heated to 120 °C under high vacuum to effect dehydration. After 2 h, the residue was allowed to cool to room temperature. Chromatography [silica, hexanes/ethyl acetate (1:1)] gave the unsaturated lactams as a mixture of geometric isomers (molar ratio *Z:E* = 1:1); the *Z* and *E* isomers exhibited TLC (silica, ethyl acetate) R_f values of 0.70 and 0.84, respectively. The title compound (*Z*-isomer) was isolated as a white solid (190 mg, 27%): ^{1}H NMR (300 MHz) δ 1.14 (s, 6H), 1.18 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 2.53 (d, *J* = 2.1 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 5.63 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 3.0 Hz, 1H), 7.95 (br, 1H), 8.66 (br, 1H); ESI-MS obsd 353.1860, calcd 353.1860 [$(M + H)^+$, M = $C_{21}H_{24}N_2O_3$]. Data for the *E*-isomer of **S6**: ^{1}H NMR (300 MHz) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 6H), 2.39 (s, 3H), 2.64 (d, *J* = 1.5 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.36 (m, 1H), 7.20 – 7.23 (m, 4H), 7.48 (d, *J* = 3.3 Hz, 1H), 10.08 (br, 1H), 10.13 (br, 1H); ESI-MS obsd 353.1862, calcd 353.1860 [$(M + H)^+$, M = $C_{21}H_{24}N_2O_3$].

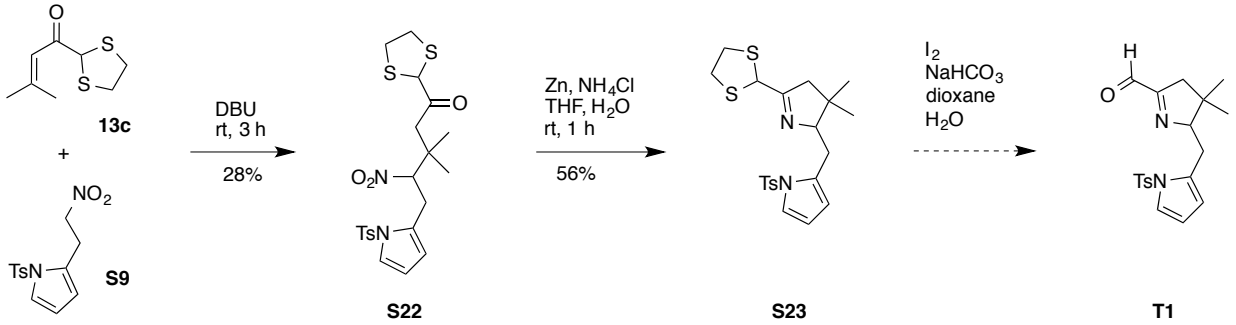
8-Ethoxycarbonyl-2,3-dihydro-1-methoxy-2,2-dimethyl-7-*p*-tolyldihydrodipyrrin (S7). Following a general procedure,[47] a stirred solution of **S6** (100 mg, 0.285 mmol) in CH_2Cl_2 (20 mL) was treated at room temperature under argon with Hünig's base (990 μL, 5.70 mmol) and trimethyloxonium tetrafluoroborate (841 mg, 5.70 mmol). After 2 h, the mixture was diluted with CH_2Cl_2 (50 mL), washed twice with water (50 mL), dried (Na_2SO_4) and concentrated. Column chromatography [silica, CH_2Cl_2/ethyl acetate (1:1)] gave a byproduct (**S21**) followed by the title compound. The title compound exhibited a TLC [silica, hexanes/ethyl acetate (1:1)] R_f value of 0.50 and was isolated as a yellow solid (63 mg, 62%): ^{1}H NMR (300 MHz) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 6H), 2.34 (s, 3H), 2.71 (d, *J* = 1.8 Hz, 2H), 3.86 (s, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 6.25 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* =3.3 Hz, 1H), 8.5 (br, 1H); ^{13}C NMR (100 MHz) δ 182.7, 147.8, 135.9, 131.7, 130.8, 128.9, 128.4, 124.2, 124.0, 115.3, 104.7, 59.5, 56.6, 44.6, 44.3, 25.8, 25.7, 21.3, 14.4; ESI-MS obsd 367.2015, calcd 367.2016 [$(M + H)^+$, M = $C_{22}H_{26}N_2O_3$].

8-Ethoxycarbonyl-1,10,2,3,-tetrahydro-2,2,N^{10}-trimethyl-7-*p*-tolyldipyrrin-1-one (S21). This byproduct exhibited a TLC (silica, CH_2Cl_2) R_f value of 0.50 and was isolated as a solid (19 mg, 19%): ^{1}H NMR (300 MHz) δ 1.19 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 6H), 2.38 (s, 3H), 2.64 (d, *J* = 1.8 Hz, 2H), 4.01 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 5.59 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 3.0 Hz, 1H), 11.03 (br, 1H); ESI-MS obsd 367.2015, calcd 367.2016 [$(M + H)^+$, M = $C_{22}H_{26}N_2O_3$].

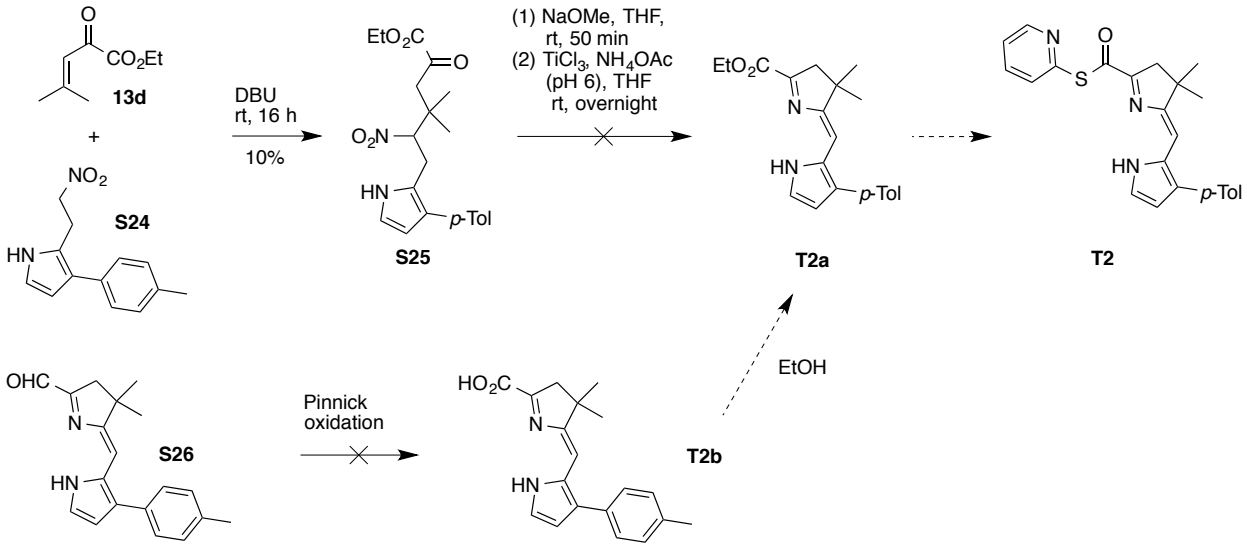
8-Ethoxycarbonyl-2,3-dihydro-2,2-dimethyl-1-methylthio-7-*p*-tolyldihydrodipyrrin (S8). Following a general procedure,[25] a solution of **S6** (100 mg, 0.285 mmol) and Lawesson's reagent (70 mg, 0.17 mmol) in toluene (10 mL) was stirred for 1 h at 100 °C under argon. An additional 20 mg of Lawesson's reagent was added and stirring was continued for 20 min. Then, the reaction mixture was cooled down. It was portioned between ethyl acetate and water. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (1:1)] afforded 8-ethoxycarbonyl-1,10,2,3-tetrahydro-2,2-dimethyl-7-*p*-tolyldipyrrin-1-thione as a brown solid (76 mg, 71%). A stirred solution of the brown solid (34 mg, 0.092 mmol) in CH_2Cl_2 (9.2 mL) was treated under argon, with the Hünig's base (320 μL, 1.84 mmol) and trimethyloxonium tetrafluoroborate (272 mg, 1.84 mmol). After 2h, the mixture was diluted with CH_2Cl_2, washed with brine and water, dried (Na_2SO_4) and concentrated. Chromatography [silica, CH_2Cl_2/ethyl acetate (3:1)] afforded a pale-

yellow solid (32 mg, 91%): ^{1}H NMR (300 MHz) δ 1.18 (t, *J* = 6.9 Hz, 3H), 1.26 (s, 6H), 2.36 (s, 3H), 2.46 (s, 3H), 2.73 (d, *J* = 2.1 Hz, 2H), 4.1 (q, *J* = 6.9 Hz, 2H), 6.41 (m, 1H), 7.15–7.24 (m, 4H), 7.48 (d, J = 3.0 Hz, 1H), 8.40 (br, 1H); ESI-MS obsd 383.1786, calcd 383.1788 [$(M + H)^+$, M = $C_{22}H_{26}N_2O_2S$].

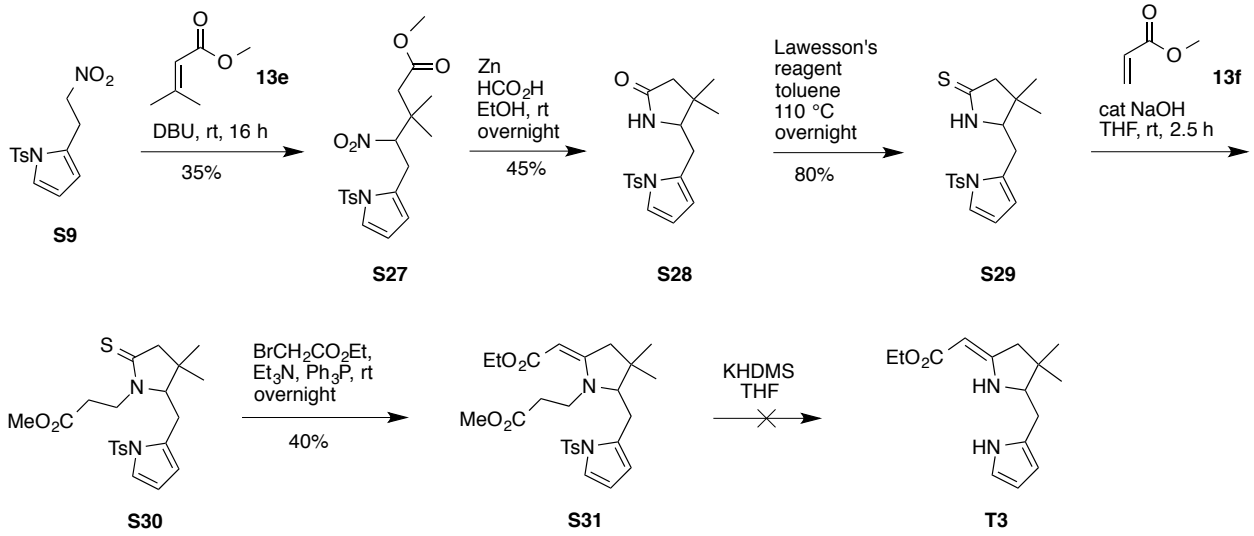
Exploratory routes to hydrodipyrrin targets **T1**–**T3** are shown in Schemes S7–S9.



Scheme S7. Exploratory route to hydrodipyrrin **T1**.



Scheme S8. Exploratory route to hydrodipyrrin **T2**.



Scheme S9. Exploratory route to hydrodipyrrins **T3**.

3,3-Dimethyl-4-nitro-1-(1,3-dithiolan-2-yl)-5-(*N*-*p*-tosylpyrrol-2-yl)pentan-1-one (S22). Following a general procedure,[19] a mixture of **S9** (0.925 g, 3.15 mmol) and **13c** (0.887 g, 4.72 mmol) was treated with DBU (2.60 mL, 9.45 mmol) at room temperature. The progress of the reaction was monitored by TLC analysis. After 3 h, the reaction mixture was diluted with ethyl acetate. The organic phase was washed (brine and water), dried (Na_2SO_4), and concentrated to a brown oil. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow oil (0.431 mg, 28%): ^{1}H NMR δ 1.19 (s, 3H), 1.24 (s, 3H), 2.42 (s, 3H), 2.75 (AB, J = 17.6 Hz, 1H), 2.82 (AB, J = 17.6 Hz, 1H), 3.23–3.40 (m, 7H), 5.06 (ABX, ^3J = 2.0 Hz, ^2J = 11.6 Hz, 1H), 6.02 (m, 1H), 6.17 (m, 1H), 7.24 (m, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 202.3, 201.6, 145.5, 145.1, 136.3, 130.5, 130.4, 129.4, 129.2, 127.3, 126.6, 124.0, 123.8, 122.7, 115.1, 114.9, 112.4, 112.2, 94.9, 94.7, 59.1, 58.9, 58.6, 58.4, 46.8, 46.6, 45.5, 43.9, 41.9, 41.7, 39.2, 39.2, 38.9, 38.0, 37.2, 27.8, 26.9, 24.4, 23.8, 23.5, 22.0; ESI-MS obsd 483.1072, calcd 483.1077 [$(M + H)^+$, M = $C_{21}H_{26}N_2O_5S_3$].

2,3,4,5-Tetrahydro-3,3-dimethyl-1-(1,3-dithiolan-2-yl)-*N*^{11}-*p*-tosyldipyrrin (S23). Following a general procedure,[25] a sample of **S22** (0.43 g, 0.89 mmol) in THF/H_2O (4.5 mL/4.5 mL) was treated with NH_4Cl followed by zinc dust. The reaction mixture was stirred vigorously at room temperature for 1 h. Then ethyl acetate (10 mL) was added and the resulting mixture was filtered. The filtrate was washed (brine), dried (Na_2SO_4), concentrated and chromatographed [silica, CH_2Cl_2/ethyl acetate (1:1)] to afford a white solid (219 mg, 56%): ^{1}H NMR δ 1.00 (s, 3H), 1.08 (s, 3H), 2.40 (s, 3H), 2,54 (AB, J = 18 Hz, 1H), 2.61 (AB, J = 18 Hz, 1H), 3.08 (ABX, ^3J = 9.9 Hz, ^2J = 15.9 Hz, 1H), 3.31 (m, 4H), 3.45 (ABX, ^3J = 3.9 Hz, ^2J = 15.9 Hz, 1H), 4.12 (m, 1H), 5.95 (s, 1H), 6.11 (m, 1H), 6.21 (m, 1H), 7.27 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 146.0, 136.0, 130.7, 130.3, 127.1, 126.9, 123.3, 123.2, 115.0, 114.9, 111.9, 80.3, 44.6, 44.5, 42.0, 40.1, 40.0, 37.3, 28.2, 27.3, 24.7, 22.8, 21.9; ESI-MS obsd 434.1151, calcd 434.1151 [M^+, M = $C_{21}H_{26}N_2O_2S_3$].

1-Ethoxy-4,4-dimethyl-5-nitro-6-[3-(*p*-tolyl)pyrrol-2-yl]hexan-1,2-dione (S25). Following a general procedure,[19] a mixture of **S24** (380 mg, 1.64 mmol) and **13d** (635 mg, 4.96

mmol) in DBU (0.50 mL, 3.3 mmol) was stirred for 16 h at room temperature. The reaction mixture was diluted with ethyl acetate and then washed with brine and water. The organic phase was dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a yellow oil (51 mg, 10%): ^{1}H NMR (300 MHz) δ 1.12 (s, 3H), 1.21 (s, 3H), 1.38 (t, 3H), 2.37 (s, 3H), 2.79, 3.01 (AB, ^2J = 18.4 Hz, 2H), 3.28 (ABX, ^3J = 3.0 Hz, ^2J = 15.8 Hz, 1H), 3.36 (ABX, ^3J = 11.6 Hz, ^2J = 15.8 Hz, 1H), 4.12 (m, 2H), 5.02 (ABX, ^3J = 3.0 Hz, ^2J = 11.2 Hz, 1H), 6.24 (m, 1H), 6.68 (m, 1H), 7.20 (m, 4H), 8.80–8.08 (br, 1H); ^{13}C NMR (100 MHz) δ 192.2, 129.4, 128.4, 122.3, 117.8, 109.7, 95.1, 63.0, 46.7, 37.3, 25.4, 24.4, 24.0, 21.3, 14.20; ESI-MS obsd 387.1908, calcd 387.1914 [$(M + H)^+$, M = $C_{21}H_{26}N_2O_5$].

Methyl 3,3-dimethyl-4-nitro-5-(*N*-*p*-tosyl-2-pyrrolyl)pentanoate (S27). Following a general procedure,[19] a mixture of **S9** (270 mg, 0.918 mmol) and methyl 3,3-dimethylacrylate (**13e**, 0.67 mL, 5.5 mmol) was treated with DBU (0.54 mL, 2.8 mmol) and stirred at room temperature under argon for 24 h. The crude reaction mixture was diluted with ethyl acetate. The organic phase was washed (water and brine), dried (Na_2SO_4), and concentrated to a dark brown oil. Column chromatography [silica, CH_2Cl_2/hexanes (2:1)] afforded a yellow oil (132 mg, 35%): ^{1}H NMR δ 1.18 (s, 3H), 1.22 (s, 3H), 2.36, 2.46 (AB, ^2J = 15.1 Hz, 2H), 2.42 (s, 3H), 3.22 (ABX, ^3J = 2.5 Hz, ^2J = 15.8 Hz, 1H), 3.36 (ABX, ^3J = 11.6 Hz, ^2J = 15.8 Hz, 1H), 3.68 (s, 3H), 5.01 (ABX, ^3J = 2.5 Hz, ^2J = 11.6 Hz, 1H), 6.03–6.05 (m, 1H), 6.16–6.19 (m, 1H), 7.24–7.27 (m 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 21.8, 24.0, 26.9, 36.6, 42.6, 51.7, 95.1, 112.2, 115.1, 123.9, 126.5, 129.0, 130.4, 136.2, 145.4, 171.2; ESI-MS obsd 431.1250, calcd 431.1247 [$(M + Na)^+$, M = $C_{19}H_{24}N_2O_6S$].

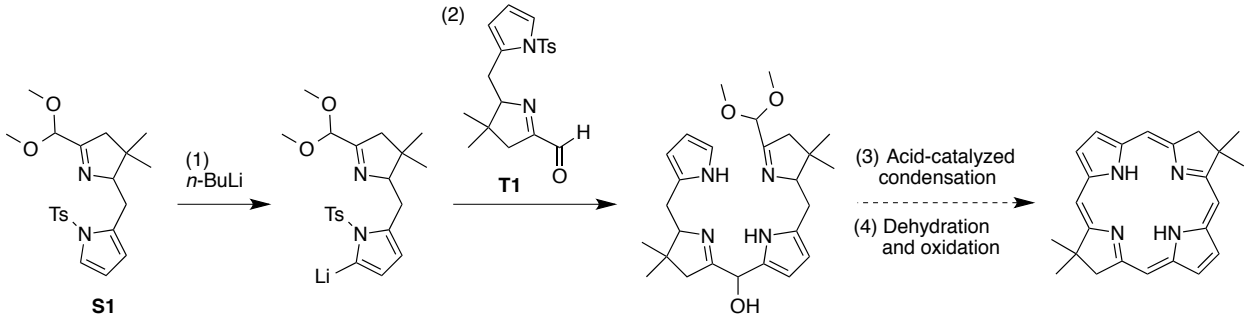
1,10,2,3,4,5-Hexahydro-3,3-dimethyl-N^{11}-*p*-tosyldipyrrin-1-one (S28). Following a general procedure,[25] a solution of **S27** (215 mg, 0.527 mmol) in ethanol/formic acid (4.8 mL, 4:1) was treated with zinc dust (856 mg, 13.2 mmol) and stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through Celite. The filtrate was washed (saturated aqueous $NaHCO_3$, water, and brine), dried (Na_2SO_4) and concentrated to a light pink solid. Chromatography (silica, ethyl acetate) afforded a white solid (45 mg, 25%): mp 124–126 °C; ^{1}H NMR δ 1.08 (s, 3H), 1.20 (s, 3H), 2.12–2.23 (m, 2H), 2.42 (s, 3H), 2.51 (ABX, ^3J = 11.0 Hz, ^2J = 15.0 Hz, 1H), 3.01 (ABX, ^3J = 2.6 Hz, ^2J = 15.0 Hz, 1H), 3.56 (ABX, ^3J = 2.6 Hz, ^2J = 11.0 Hz, 1H), 5.36 (br, 1H), 6.04–6.06 (m, 1H), 6.22–6.23 (m, 1H), 7.30 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 22.1, 23.2, 27.7, 29.5, 38.9, 46.5, 62.7, 112.3, 114.4, 124.1, 127.0, 130.7, 132.1, 136.7, 145.8, 176.8.

1,10,2,3,4,5-Hexahydro-3,3-dimethyl-N^{11}-*p*-tosyldipyrrin-1-thione (S29). Following a literature procedure,[25] a mixture of **S28** (89 mg, 0.26 mmol) and Lawesson's reagent (120 mg, 0.300 mmol) in toluene (5.2 mL) was stirred overnight at 100 °C. The reaction mixture was diluted with ethyl acetate. The organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated to a yellow oil, which solidified on standing. Chromatography (silica, CH_2Cl_2) afforded a white solid (75 mg, 80%): mp 149–152 °C; ^{1}H NMR δ 1.06 (s, 3H), 1.20 (s, 3H), 2.42 (s, 3H), 2.61 (ABX, ^3J = 11.3 Hz, ^2J = 15.1 Hz, 1H), 2.72 (s, 2H), 3.00 (ABX, ^3J = 2.5 Hz, ^2J = 15.1 Hz, 1H), 3.85 (ABX, ^3J = 2.5 Hz, ^2J = 11.3 Hz, 1H), 6.09–6.12 (m, 1H), 6.24–6.27 (m, 1H), 7.30–7.34 (m, 3H), 7.62 (d, J = 8.5 Hz, 2H), the N–H signal was missing; ^{13}C NMR δ 21.9, 22.3, 26.5, 28.1, 41.5, 58.4, 69.3, 112.2, 114.7, 124.2, 126.7, 130.5, 130.9, 136.3, 145.7, 204.9; Calcd for $C_{18}H_{22}N_2O_2S_2$: C, 59.64; H, 6.12; N, 7.73; Found: C, 60.01; H, 6.14; N, 7.40.

1-(2-Ethoxy-2-oxoethylidene)-2,3,4,5-hexahydro-N^{10}-(3-methoxy-3-oxopropyl)-N^{11}-*p*-tosyldipyrrin (S31). Following a literature procedure,[29] samples of **S29** (30 mg, 0.10 mmol), methyl acrylate (**13f**, 0.027 mL, 0.30 mmol) and a catalytic amount of NaOH were stirred in THF (1.4 mL) at room temperature for 2.5 h. The reaction mixture was diluted with ethyl acetate, and water was added. The organic extract was dried (Na_2SO_4) and concentrated to a colorless oil that was dried overnight under high vacuum. The resulting crude product (1,10,2,3,4,5-hexahydro-N^{10}-(3-methoxy-3-oxopropyl)-3,3-dimethyl-N^{11}-*p*-tosyldipyrrin-1-thione, **S30**) was dissolved in CH_3CN (1.4 mL) and treated with ethyl bromoacetate (0.033 mL, 0.30 mmol). The reaction mixture was stirred overnight at room temperature. A solution of Et_3N (0.016 mL, 0.12 mmol) and Ph_3P (31 mg, 0.12 mmol) in CH_2Cl_2 (0.3 mL) was added. The reaction mixture was stirred at room temperature under argon for 2 h. Concentration of the reaction mixture followed by chromatography [silica, CH_2Cl_2/hexanes (3:1) then CH_2Cl_2, then CH_2Cl_2/ethyl acetate (10:1)] afforded a light yellow oil (20 mg, 40%): ^{1}H NMR δ 0.94 (s, 3H), 0.98 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H), 2.41 (s, 3H), 2.36–2.48 (m, 2H), 2.59 (ABX, ^3J = 8.4 Hz, ^2J = 15.2 Hz, 1H), 2.68 (d, J = 17.2 Hz, 1H), 2.79 (m, 1H), 2.88 (ABX, ^3J = 5.4 Hz, ^2J = 15.2 Hz, 1H), 3.12 (d, J = 17.2 Hz, 1H), 3.23 (m, 1H), 3.57 (ABX, ^3J = 5.4 Hz, ^2J = 8.4 Hz, 1H), 3.66 (s, 3H), 4.09 (q, J = 6.8 Hz, 2H), 4.46 (s, 1H), 6.00 (m, 1H), 6.22 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.32 (m, 1H), 7.61 (d, J = 8.4 Hz, 2H); LD-MS obsd 503.5, calcd 503.2 [$(M + H)^+$, M = $C_{26}H_{34}N_2O_6S$].

II. Exploration of directed routes to bacteriochlorins

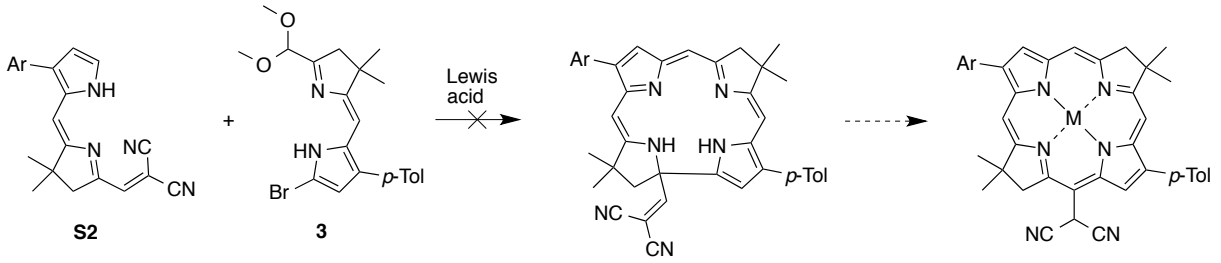
Possible routes to unsymmetrically unsubstituted-bacteriochlorins were proposed and explored as outlined in the following schemes. In Scheme S10, the condensation between the respective hydrodipyrrin halves was envisaged to proceed via an organometallic reagent. The initial approach employed β-unsubstituted hydrodipyrrins, hence leading to a symmetrical bacteriochlorin. Each half is a tetrahydrodipyrrin and contains an *N*-*p*-tosyl protected pyrrolic unit. One hydrodipyrrin half contains a 9-carboxaldehyde unit whereas the other half contains an α-lithiated pyrrole (derived from **S1**). The required tetrahydrodipyrrin–carboxaldehyde (**T1**) was not reliably obtained. Exploratory reaction with the putative hydrodipyrrin derived from **S1**, envisaged to entail nucleophilic attack on the carboxaldehyde, failed to give the expected linear tetrapyrrole.



Scheme S10. Bacteriochlorin synthesis via an α-lithio pyrrolic species derived from **S1**.

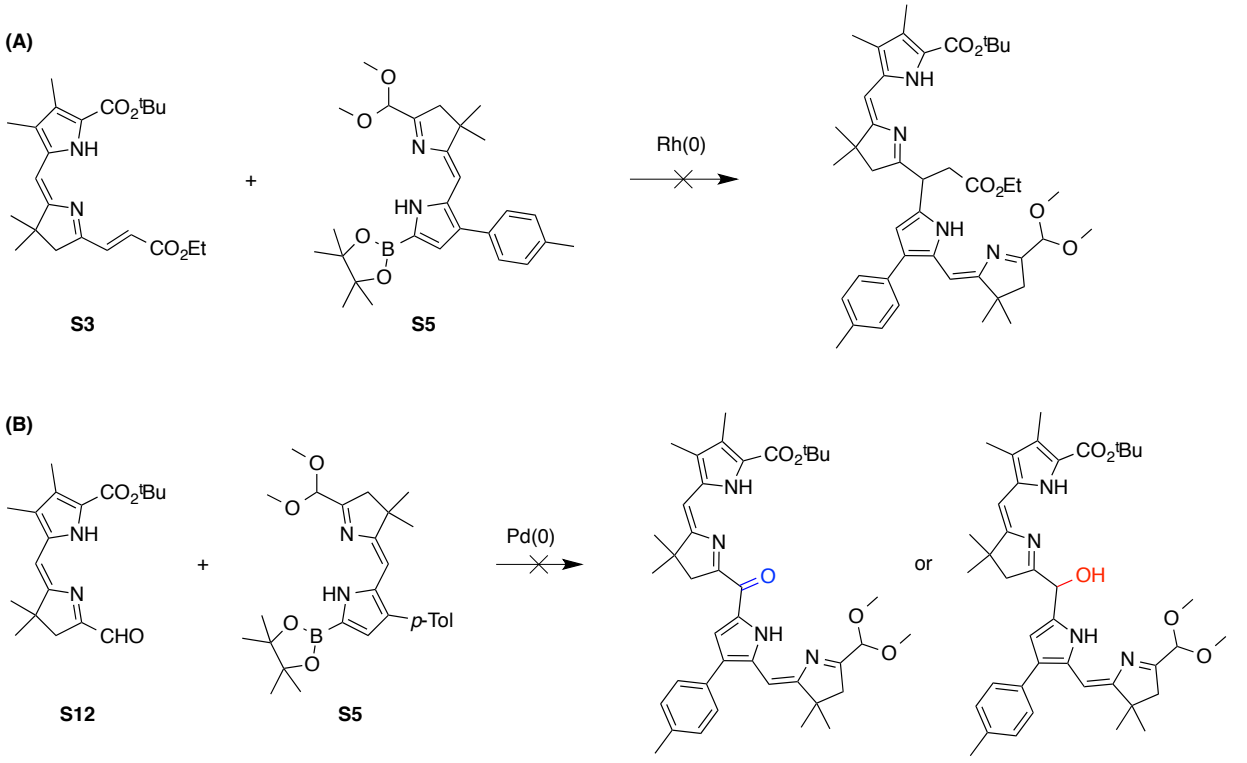
In Scheme S11, a dihydrodipyrrin bears a Michael-like acceptor at the 1-position (**S2**). The Michael acceptor is the dicyanovinyl unit, akin to the ethyl acrylate **8** described in the body

of the paper. The reactant **3** is a 9-bromodihydrodipyrrin-1-acetal. On the basis of the outcome of the reaction of **8** + **3** (Scheme 9, left), we anticipated the isolable product would be a tetradehydrocorrin bearing a dicyanovinyl moiety at the 19-position; such a macrocycle could also be expected to rearrange to give the corresponding 15-malonylbacteriochlorin. The route failed to give a characterizable macrocycle.



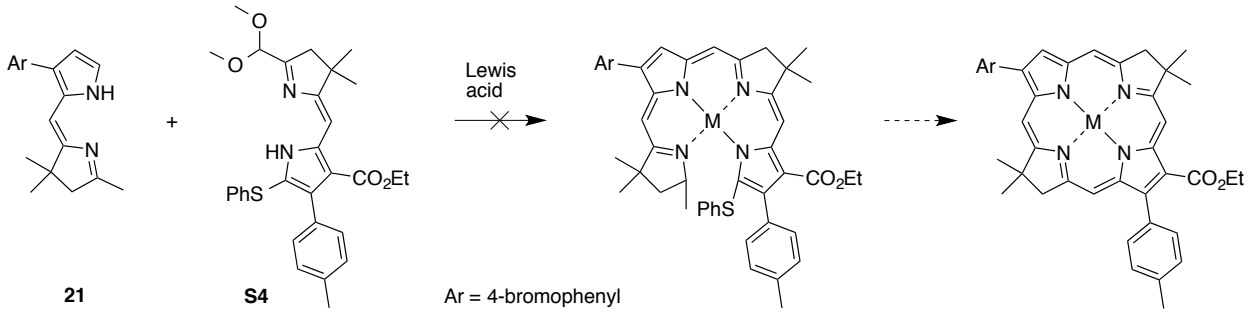
Scheme S11. Bacteriochlorin synthesis using a hydrodipyrrin bearing a Michael acceptor.

In Scheme S12, two routes to link the two hydrodipyrrin halves were explored using Rh or Pd catalyzed coupling reactions. In each case, one half (**S5**) is a dihydrodipyrrin bearing a pinacol boronate ester at the α-pyrrole position, whereas the pyrroline α-substituent of the other half varies from ethyl acrylate (**S3**, route A) to carboxaldehyde (**S12**, route B). No bacteriochlorin was formed in any case.



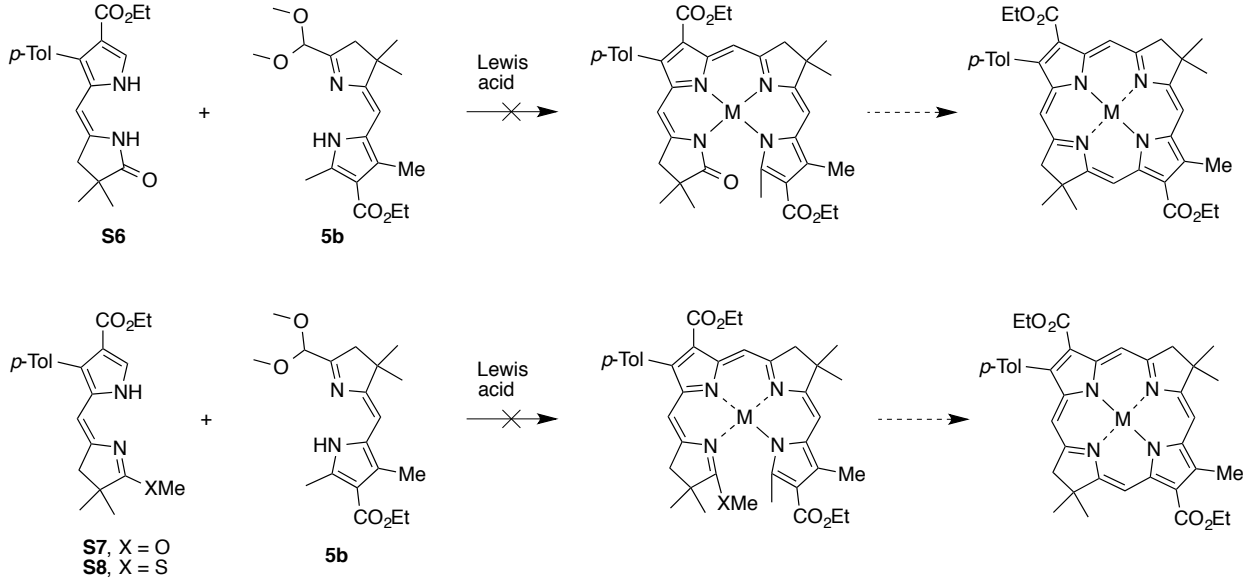
Scheme S12. Organometallic coupling to form linear tetrapyrrole precursors to bacteriochlorins.

In Scheme S13, the hydrodipyrrin **S4** contains a phenylthio group as the blocking unit at the α-pyrrolic position, whereas the other half (**21**) is a 1-methyldihydrodipyrrin. The acid-catalyzed condensation failed to afford the expected linear intermediate or any macrocycle.



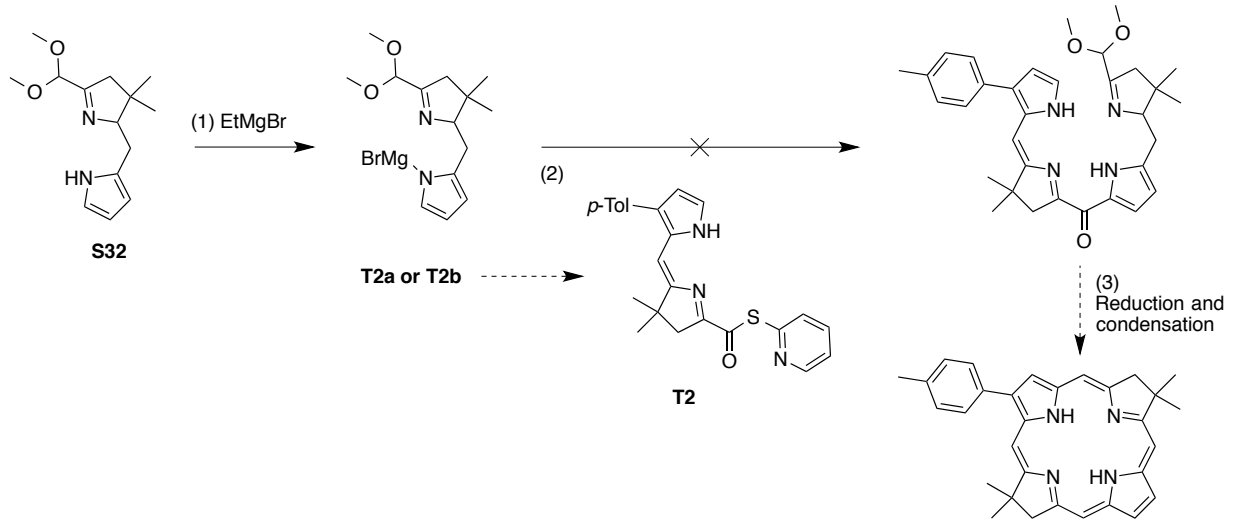
Scheme S13. Bacteriochlorin synthesis with a 9-(phenylthio)dihydrodipyrrin.

In Scheme S14, one half (**5b**) is a 9-methyldihydrodipyrrin-1-acetal whereas the other half contains a 1-oxo (**S6**), 1-methoxy (**S7**), or 1-methylthio (**S8**) group. The hydrodipyrrins described to this point all contain the gem-dimethyl unit at the 3-position, whereas the hydrodipyrrins here contain the gem-dimethyl unit at the 2-position. The latter were prepared via a new synthetic approach.[21] Regardless, none of the approaches led to the corresponding linear tetrapyrrole, a precursor to the desired bacteriochlorin.



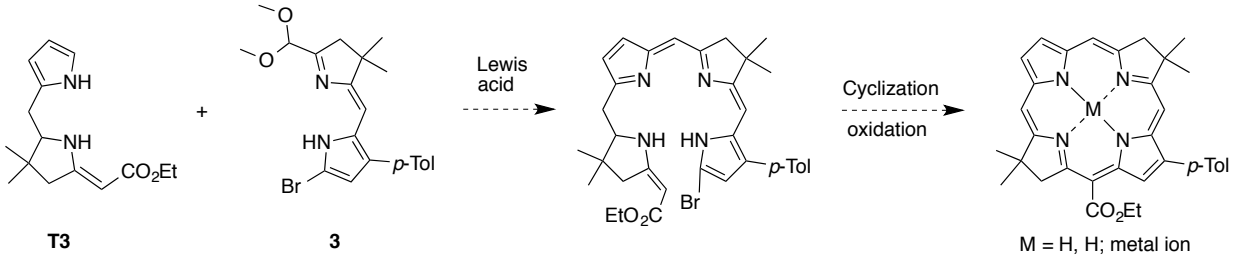
Scheme S14. Bacteriochlorin routes via 2,2-dimethyl-substituted hydrodipyrrins.

In Scheme S15, like that in Scheme S10, the condensation between the respective hydrodipyrrin halves was envisaged to proceed via an organometallic reagent. The Grignard-mediated α-acylation of a pyrrole unit of a dipyrromethane is a well established approach in the synthesis of porphyrins bearing distinct patterns of meso-substituents.[32] The acylation entails reaction of the pyrrole Grignard reagent of the tetrahydrodipyrrin (derived from **S32**) and an *S*-2-pyridyl thioester. Synthesis of the desired *S*-2-pyridyl thioester (**T2**) failed, however.



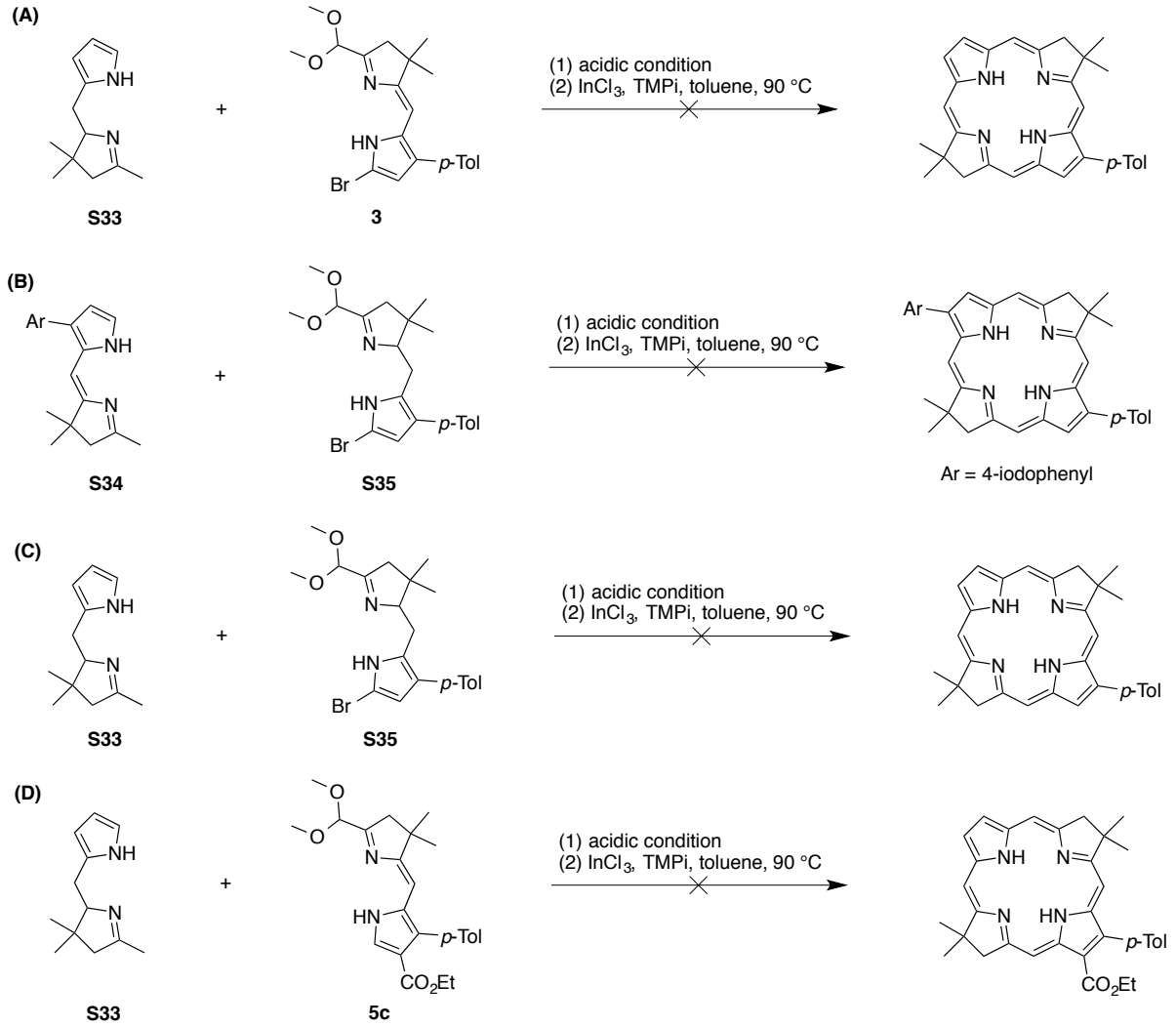
Scheme S15. Bacteriochlorin synthesis via α-acylation of a pyrrolic unit.

In Scheme S16, a 1-(ethoxycarbonylmethylene)hexahydrodipyrrin (**T3**) was desired for reaction with a 9-bromo-dihydrodipyrrin-1-acetal (**3**). The exocyclic α,β-unsaturated ester in **T3** was envisaged as a means to shift the imine-enamine equilibrium to favor the enamine, whereas the bromo group served as a displaceable blocking group to thwart self-condensation of hydrodipyrrin **3**. The resulting 15-ethoxycarbonyl group on the bacteriochlorin would serve as a convenient handle for subsequent elaboration, such as bioconjugation. The ethylidene embedded in the pyrrolidine motif of the hexahydrodipyrrin **T3** is quite different from the Michael acceptor located at the 1-position of the dihydrodipyrrin **S2** in Scheme S11 (or **8** in Scheme 9); the ethylidene moiety is attached to, and conjugated with, with pyrrolidine motif of the hexahydrodipyrrin **T3**, whereas the Michael acceptor is designed to promote attack at the β-carbon of the Michael acceptor. However, attempts to prepare **T3** failed (Scheme S9); hence, the condensation and macrocyclization were not explored.



Scheme S16. Route to bacteriochlorins via a stabilized enamine-containing hydrodipyrrin.

In Scheme S17, a 1-methyltetrahydrodipyrrin (**S33**) or 1-methyldihydrodipyrrin (**S34**) was used as one half whereas a dihydrodipyrrin-1-acetal (**3**, **5c**) or tetrahydrodipyrrin-1-acetal (**S35**) was used as the other half. In route A, one half was a dihydrodipyrrin–acetal bearing a 9-bromo group (**3**); in routes B and C, the corresponding half was a tetrahydrodipyrrin–acetal bearing a 9-bromo group (**S35**); and in route D, a dihydrodipyrrin–acetal lacking any blocking group at the 9-position (**5c**) was used. No bacteriochlorin was formed in any case (routes A–D).

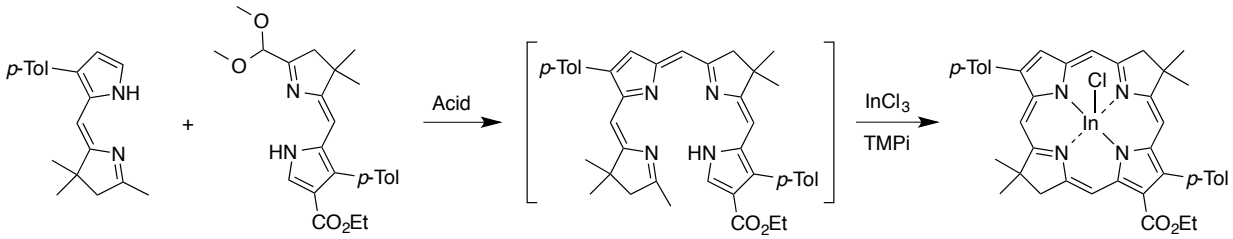


Scheme S17. Chlorin-inspired routes to bacteriochlorins.

III. Screening of reaction parameters

Screening of reaction parameters was performed with analysis by absorption spectroscopy and LD-MS of crude reaction mixtures for the reaction of **22** + **5c**. The results are shown in Table S1. During this process, attempts to isolate the linear tetrapyrrole intermediate failed, and the second reaction (cyclization) was performed directly using crude products from the first step (condensation). The best result (entry 8) was obtained using $InCl_3$ and 2,2,6,6-tetramethylpiperidine (TMPi) in toluene at 90 °C whereupon the bacteriochlorin **InBC-1** was obtained in 8% yield (the isolated yield was determined spectroscopically). Some amount of tetradehydrocorrin and a trace of a free base A_2-bacteriochlorin, a side-product obtained from self-condensation of **5c**, were also observed. Various metal salts screened in addition to $InCl_3$ included $NiCl_2$, $Zn(OAc)_2$, $Pd(OAc)_2$, $CdCl_2$, $MgBr_2$, $YbCl_3 \cdot 6H_2O$, $CoCl_2$, $Cu(OAc)_2$, $ErCl_3$ and $SnCl_2 \cdot H_2O$.

Table S1. Survey of conditions to prepare bacteriochlorin **InBC-1**[a]

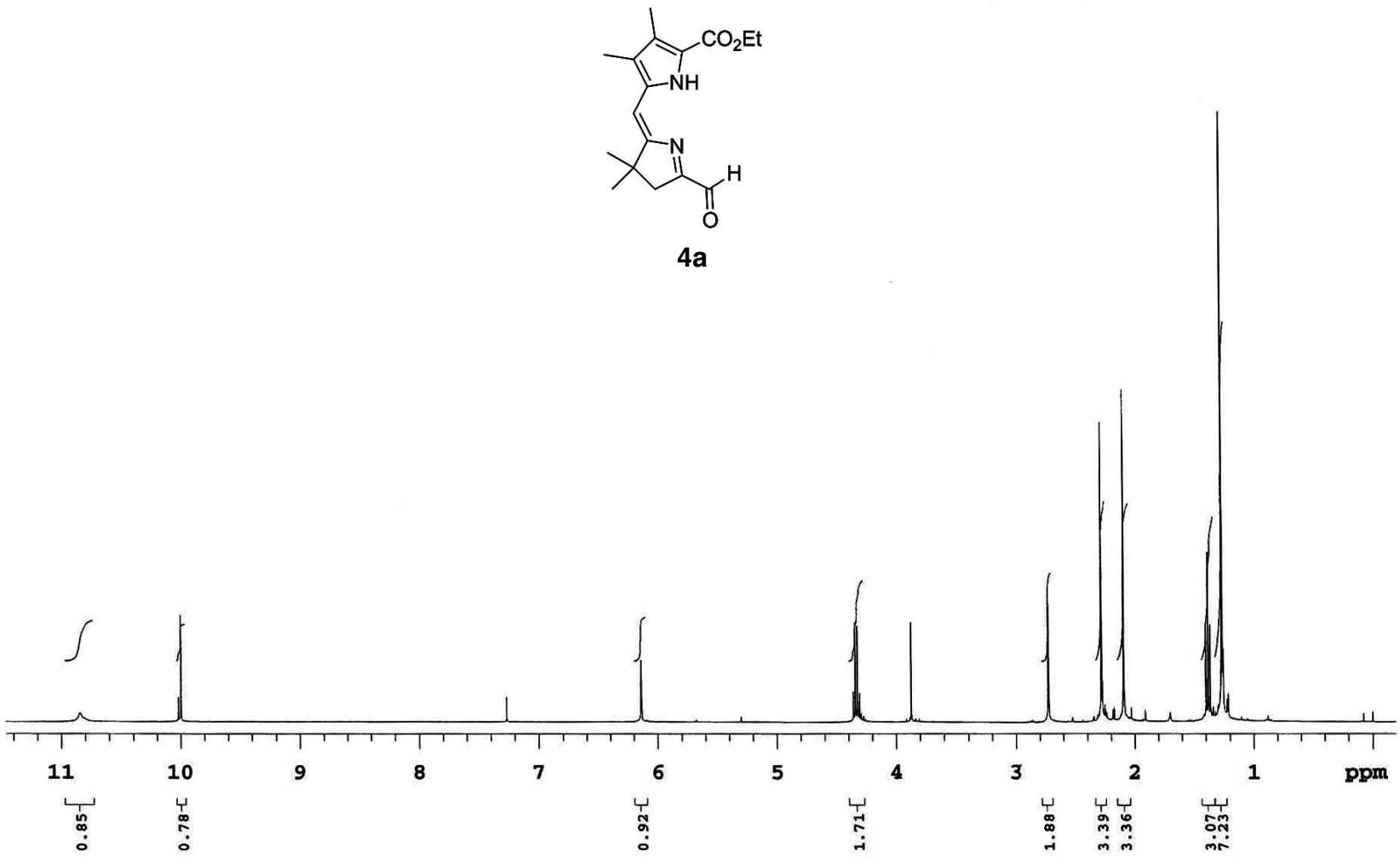


22 **5c** **InBC-1**

Entry	condensation conditions		cyclization conditions			
	LA	Molar equiv	solvent	base	T, °C	Yield,[b] %
1	$InCl_3$[c]	5	CH_3CN	TMPi	83	0.8
2	$In(OTf)_3$	5	CH_3CN	TMPi	83	trace
3	$Sc(OTf)_3$[d]	2	CH_3CN	TMPi	83	trace
4	$Ga(OTf)_3$	2	CH_3CN	TMPi	83	2
5	$Bi(OTf)_3$	2	CH_3CN	TMPi	83	2
6	$Yb(OTf)_3$[d]	5	CH_3CN	TMPi	83	0
7	$HfCl_4$	2	CH_3CN	TMPi	83	0
8	$Bi(OTf)_3$	2	toluene	TMPi	90	8
9	$Bi(OTf)_3$	2	toluene/EtOH [3:1]	TMPi	90	5
10	$Bi(OTf)_3$	2	EtOH	TMPi	68	trace
11	$Bi(OTf)_3$	2	1,2-dichloroethane	TMPi	84	4
12	$Bi(OTf)_3$	2	nitromethane	TMPi	90	0
13	$Bi(OTf)_3$	2	DMF	TMPi	90	0
14	$Bi(OTf)_3$	2	THF	TMPi	68	trace
15	$Bi(OTf)_3$	2	CH_2Br_2	TMPi	90	0
16	$Bi(OTf)_3$	2	toluene	TMG[e]	90	trace
17	$Bi(OTf)_3$	2	toluene	piperidine	90	1
18	$Bi(OTf)_3$	2	toluene	Et_3N	90	1.5
19	$Bi(OTf)_3$	2	toluene	collidine	90	trace
20	$Bi(OTf)_3$	2	toluene	KOH	90	0
21	$Bi(OTf)_3$	2	toluene	Cs_2CO_3	90	0

[a]The condensation was performed for 20 min using **22** (10 mM) and **5c** (10 mM) in the presence of Lewis acid in CH_2Cl_2 at room temperature. Then the reaction was neutralized with 2.2 molar equiv of Et_3N and concentrated to a solid. The crude solid was treated with $InCl_3$ (10 mol equiv) and base (10 mol equiv) in 0.5 mL of solvent for 1.5–2 h. [b]Isolated yield determined by absorption spectroscopy ($\varepsilon_{\blacktriangleleft\blacktriangleleft\blacktriangleleft\blacktriangle\,nm}$ = 100,000 $M^{-1}cm^{-1}$) in toluene. [c]The condensation was carried out for 40 min. [d]The condensation was carried out for 150 min. [e]Tetramethylguanidine.

IV. Spectral data for new compounds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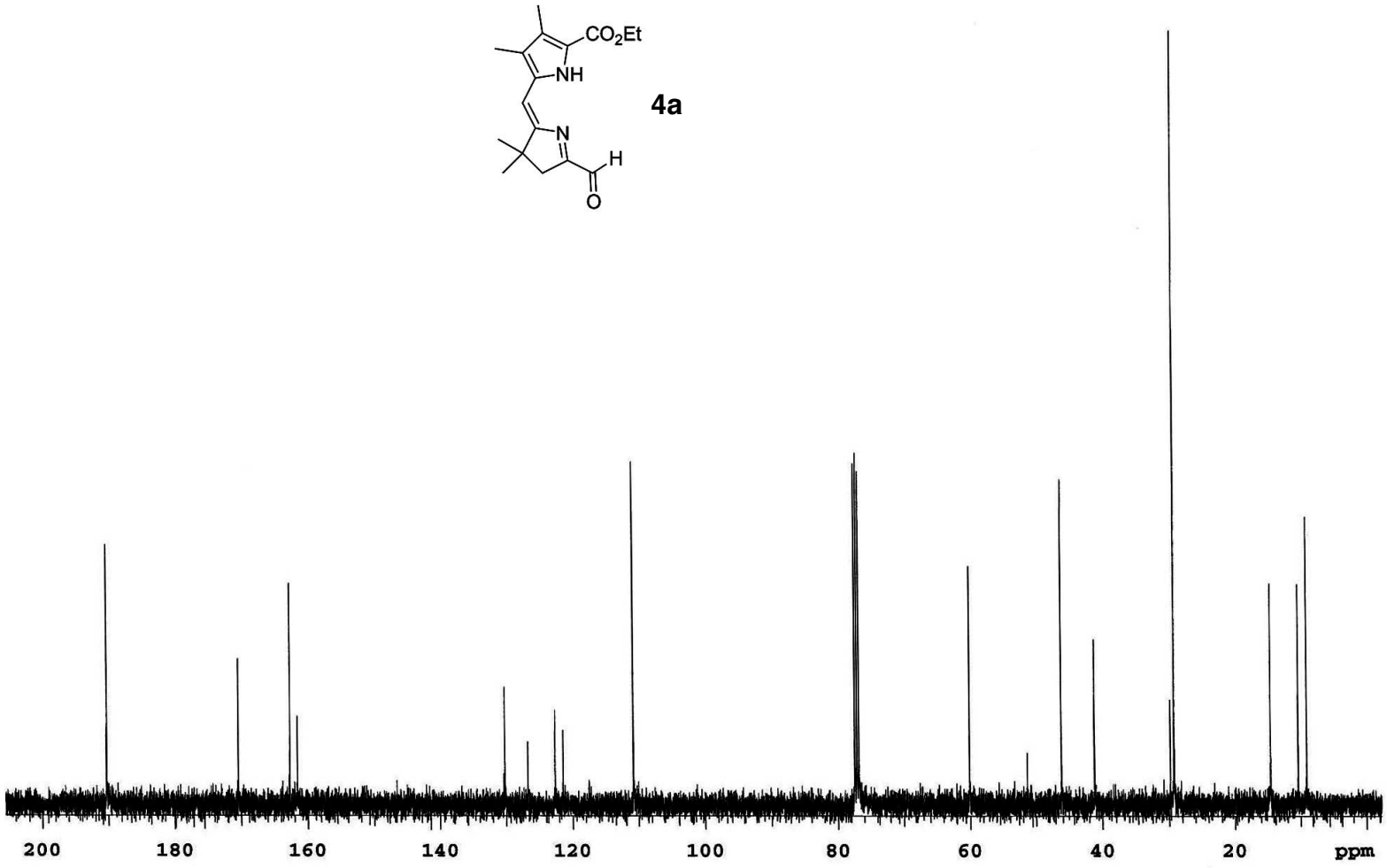
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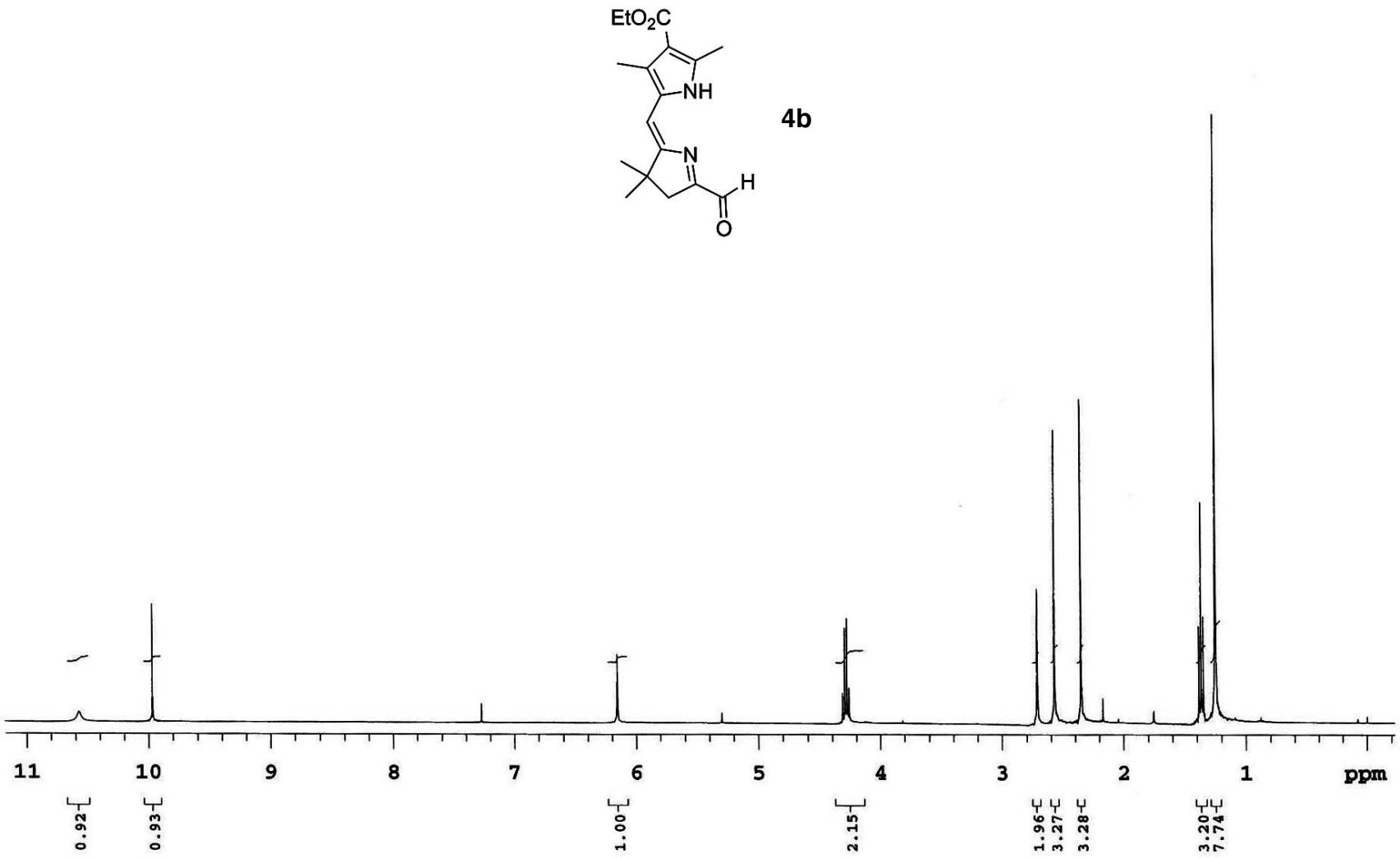
20
ppm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H
O
4b
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10
9
8
7
6
5
4
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1.96
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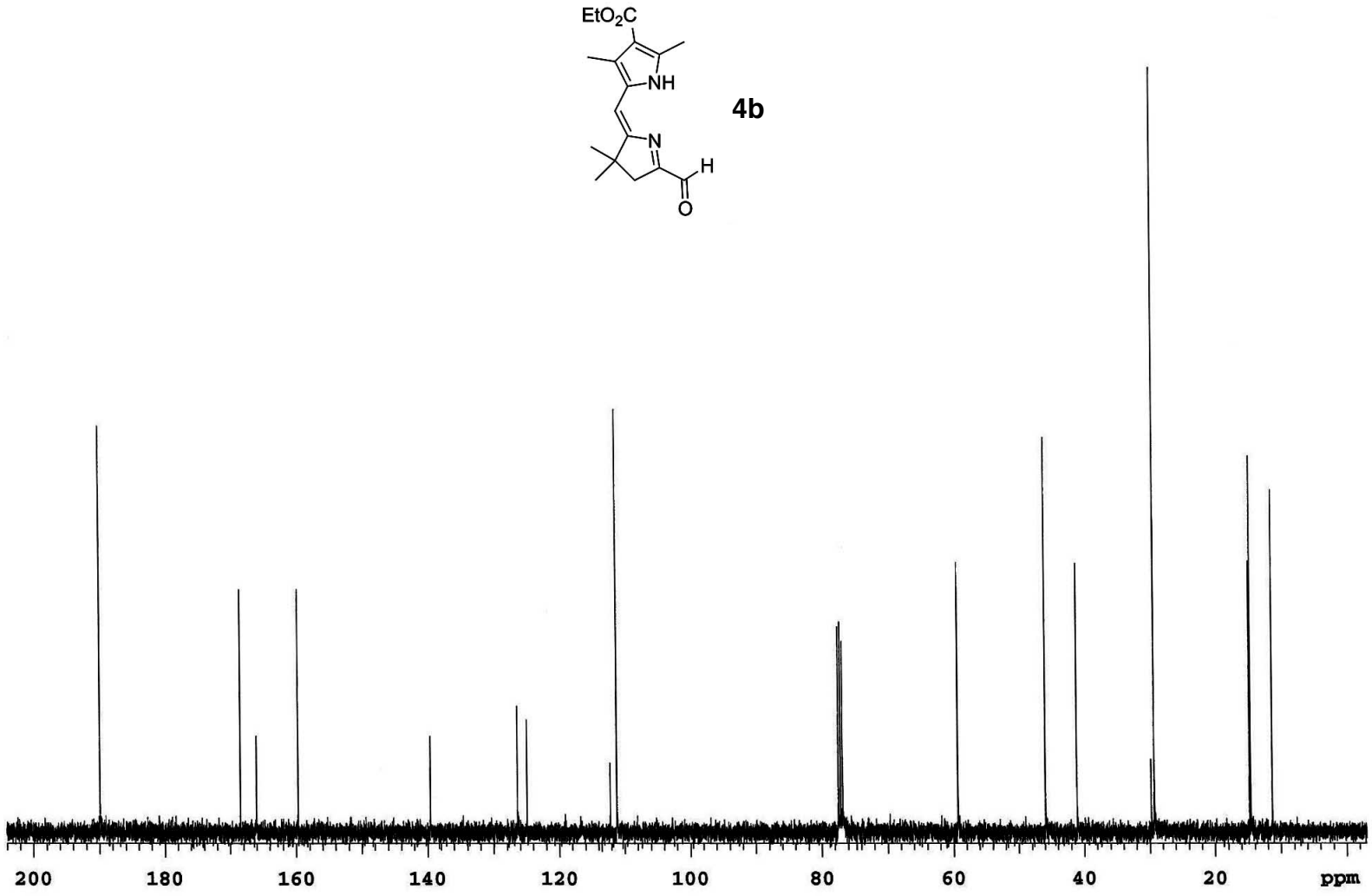
3.28
3.20
7.74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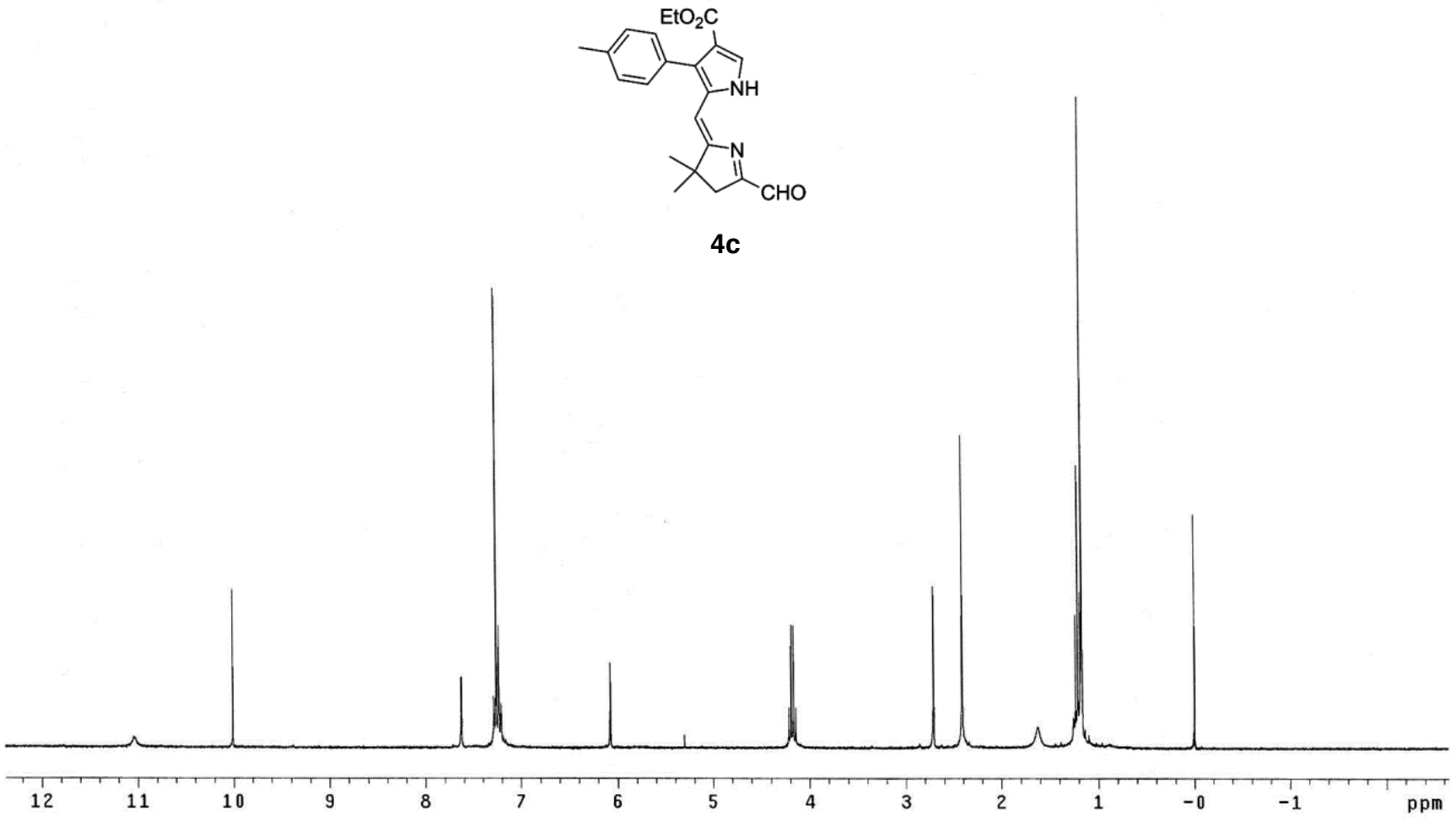
60
40
20
ppm



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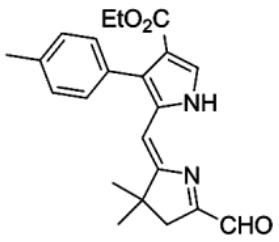

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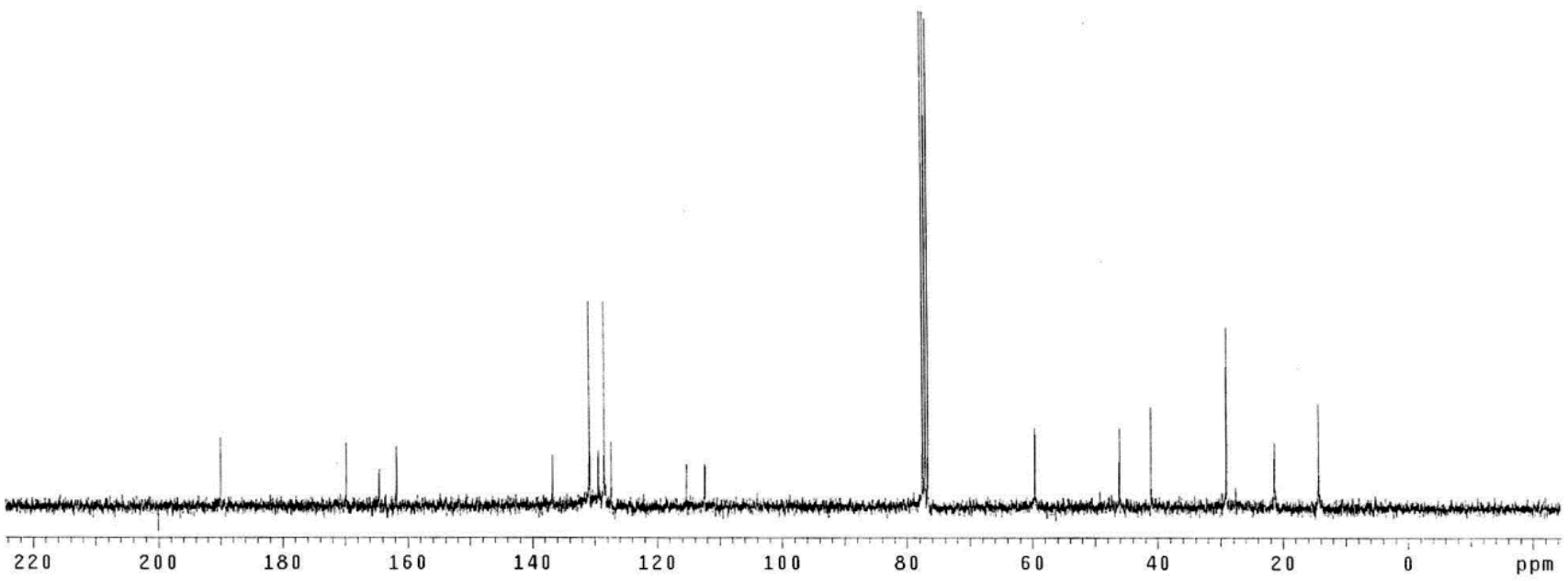
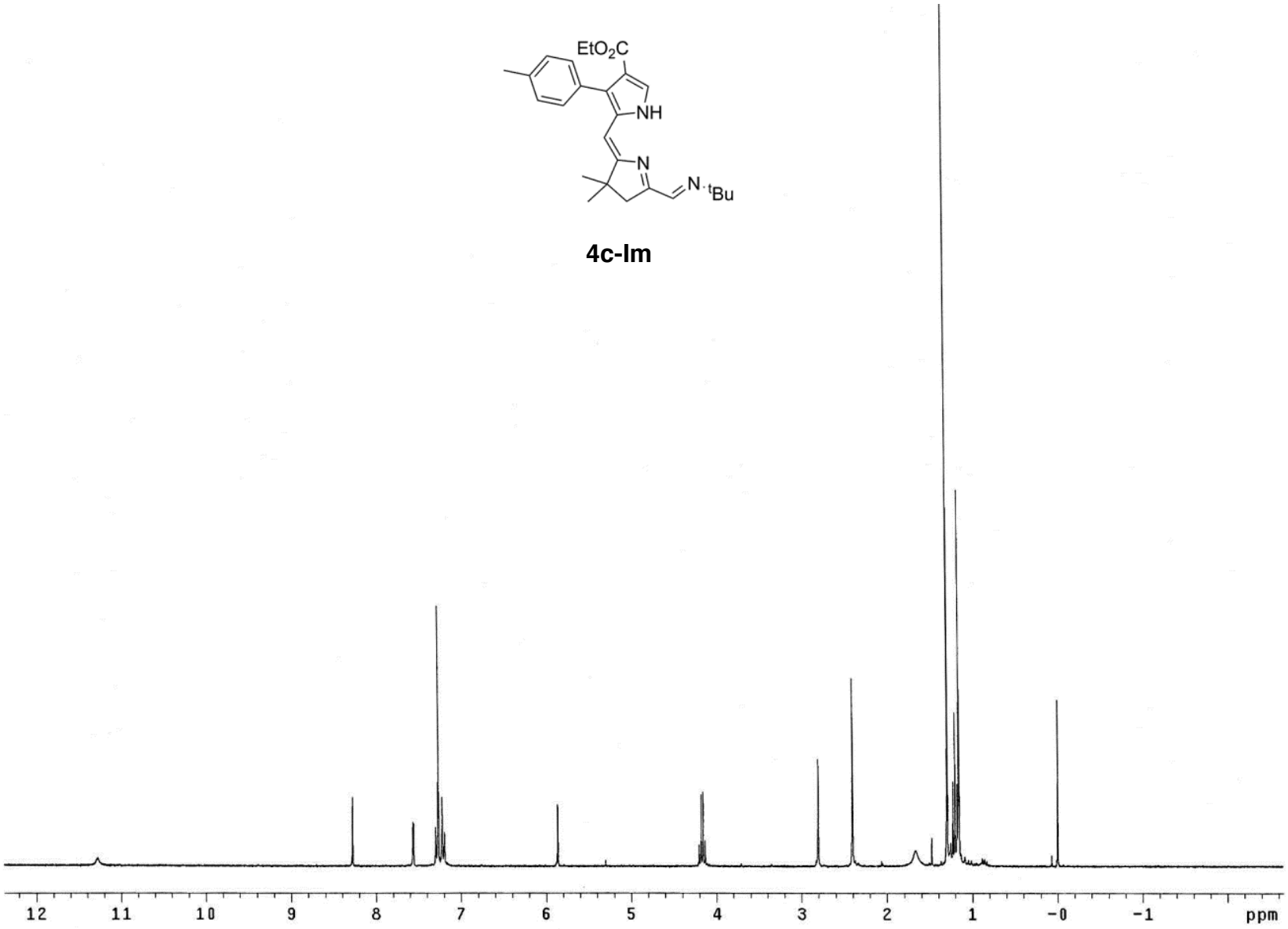
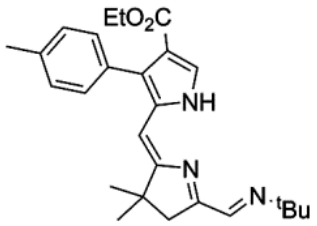




4c-Im



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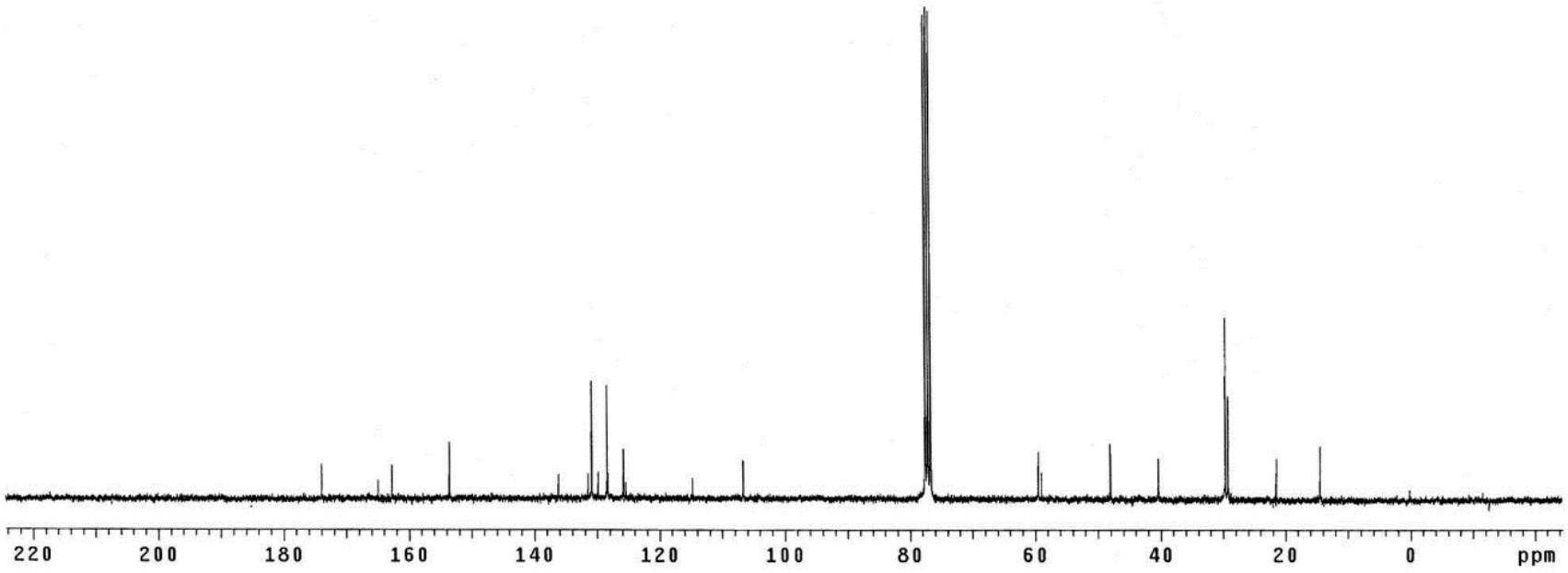

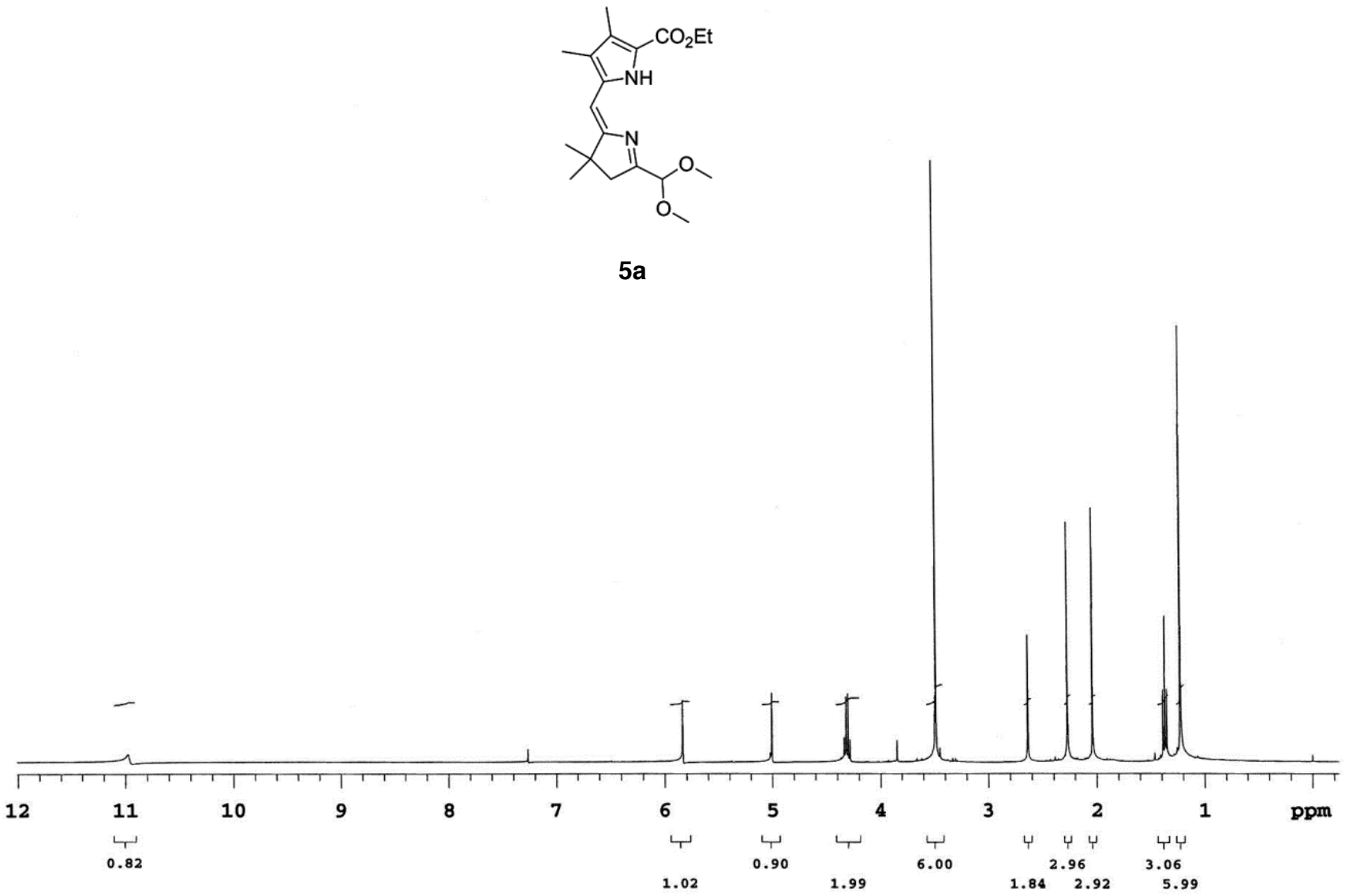
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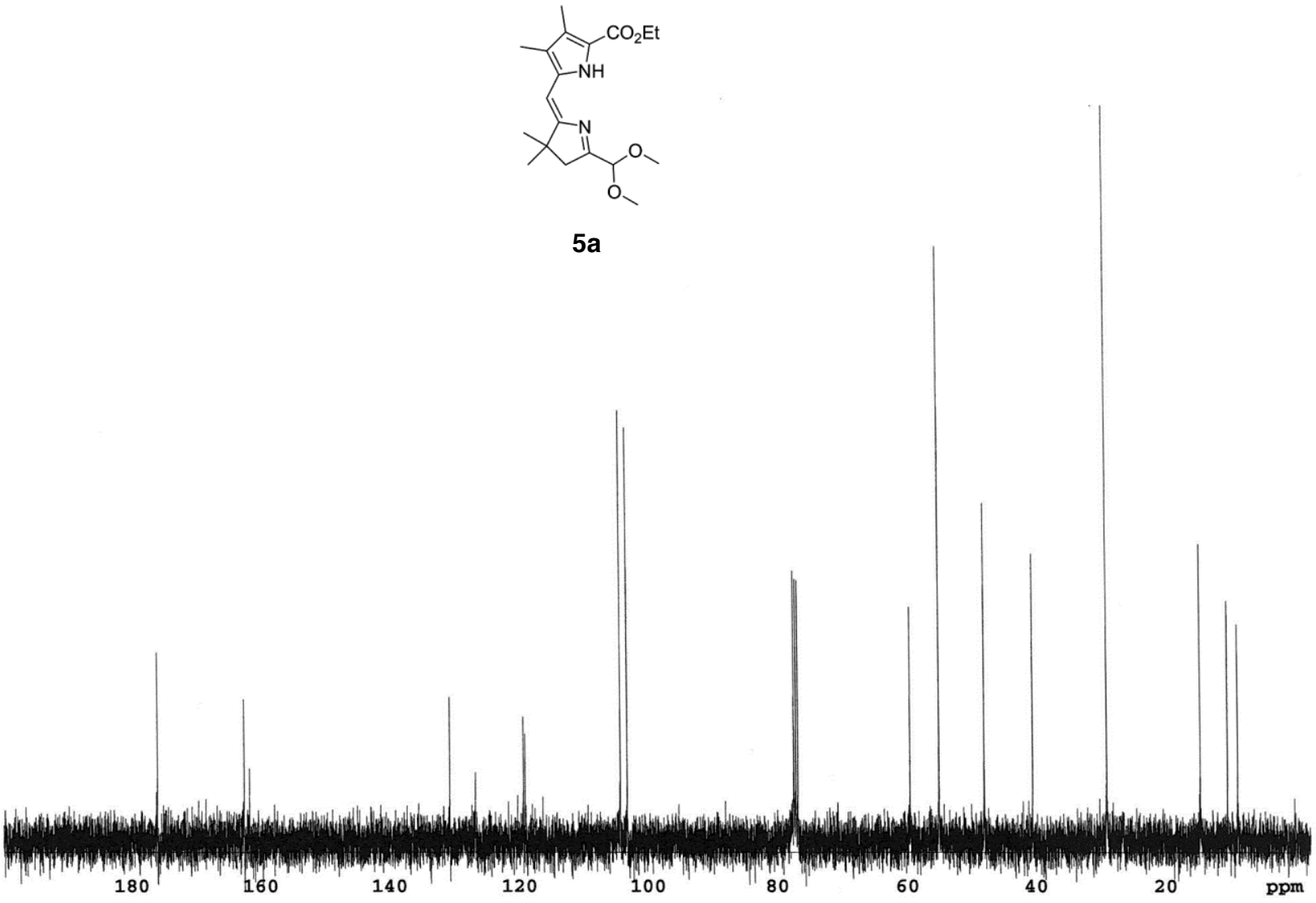
3.06
5.99



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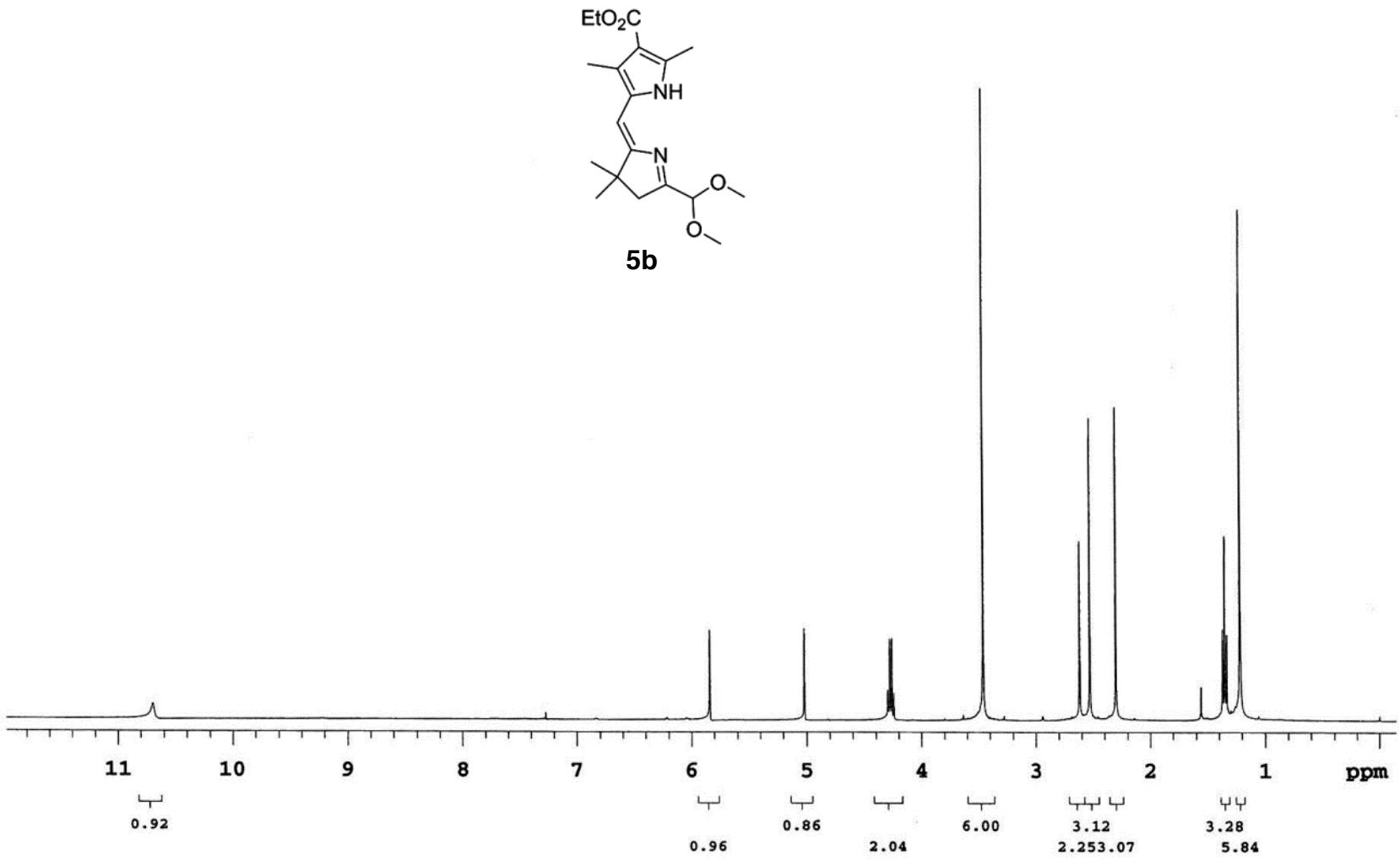
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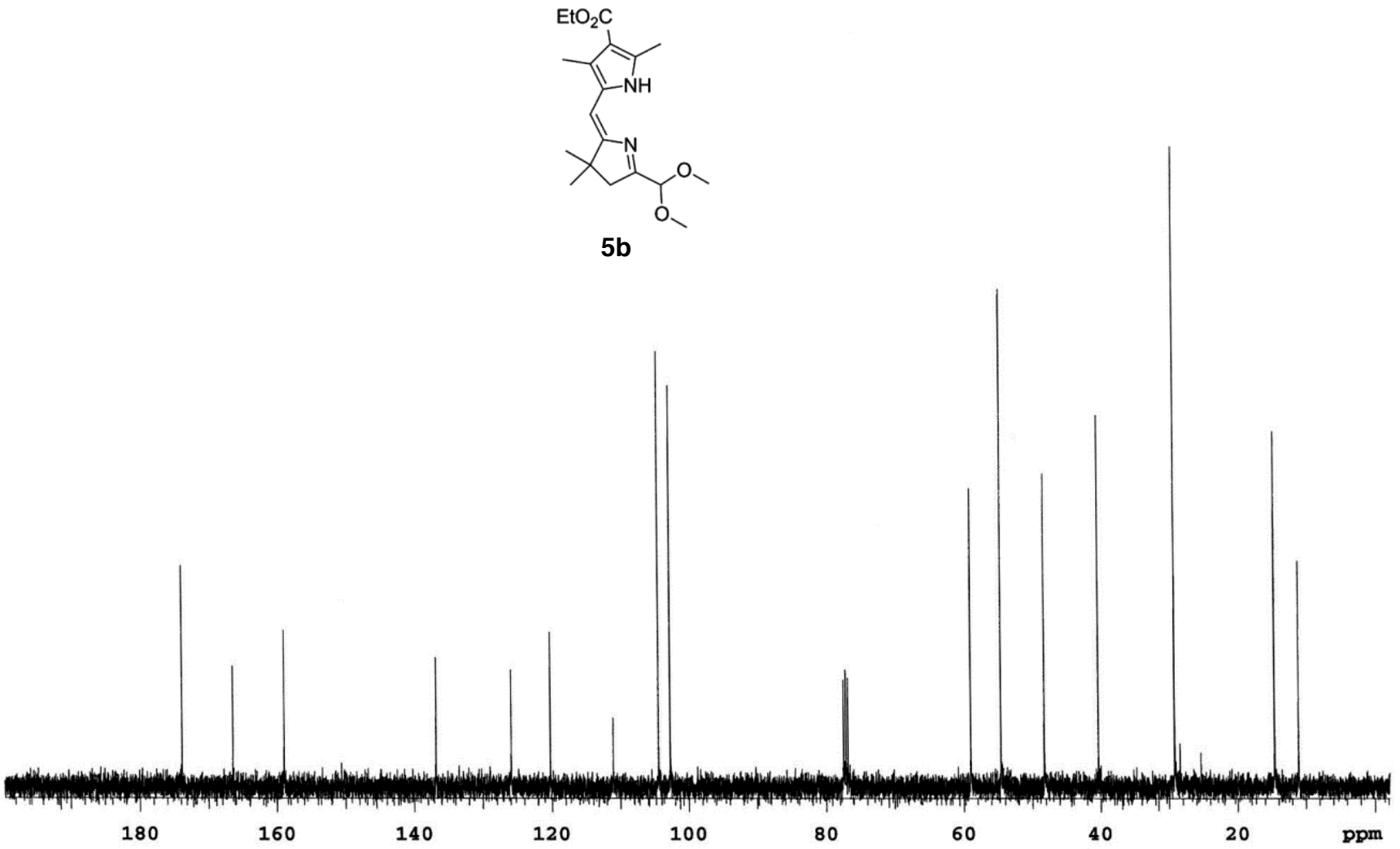

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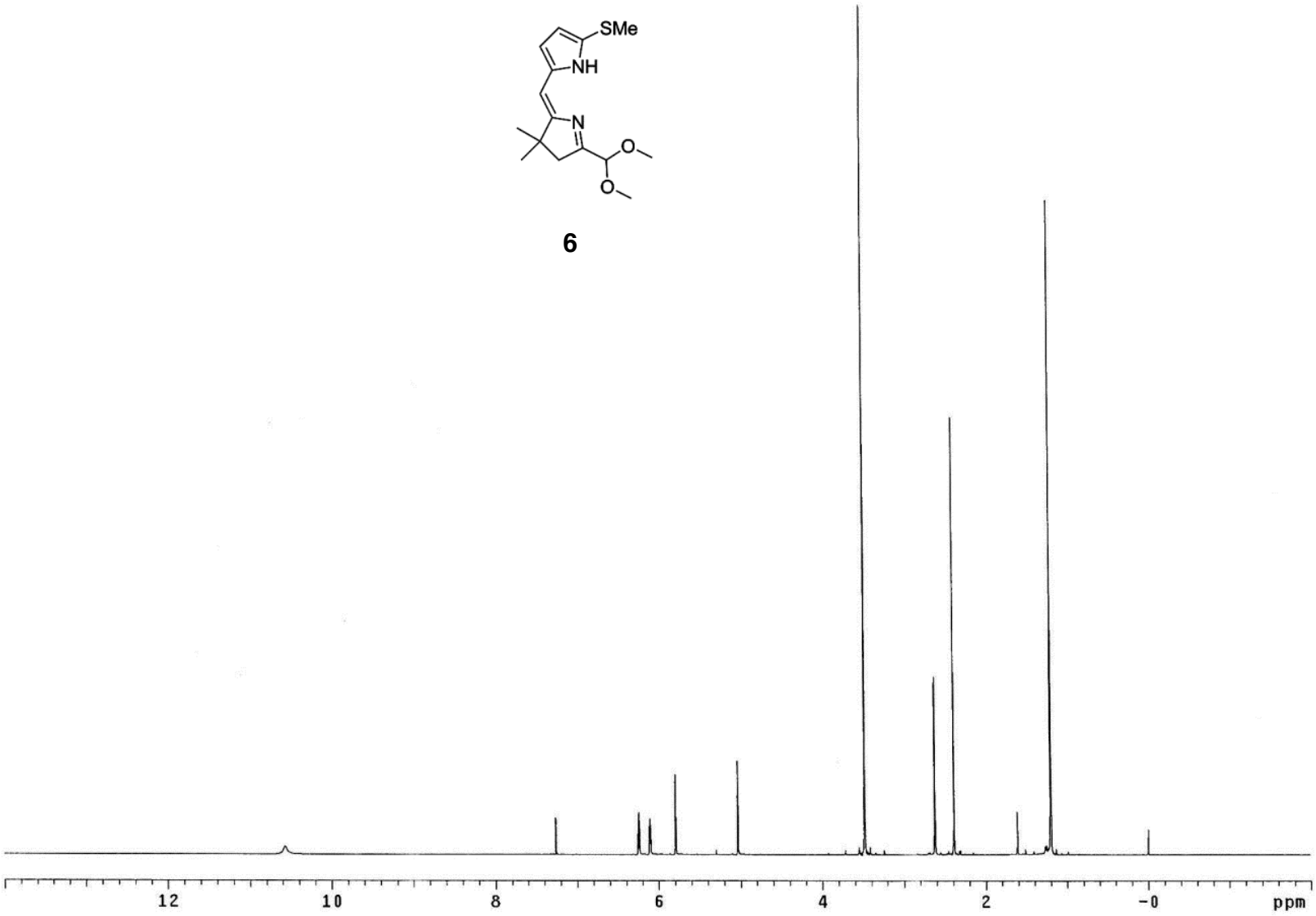

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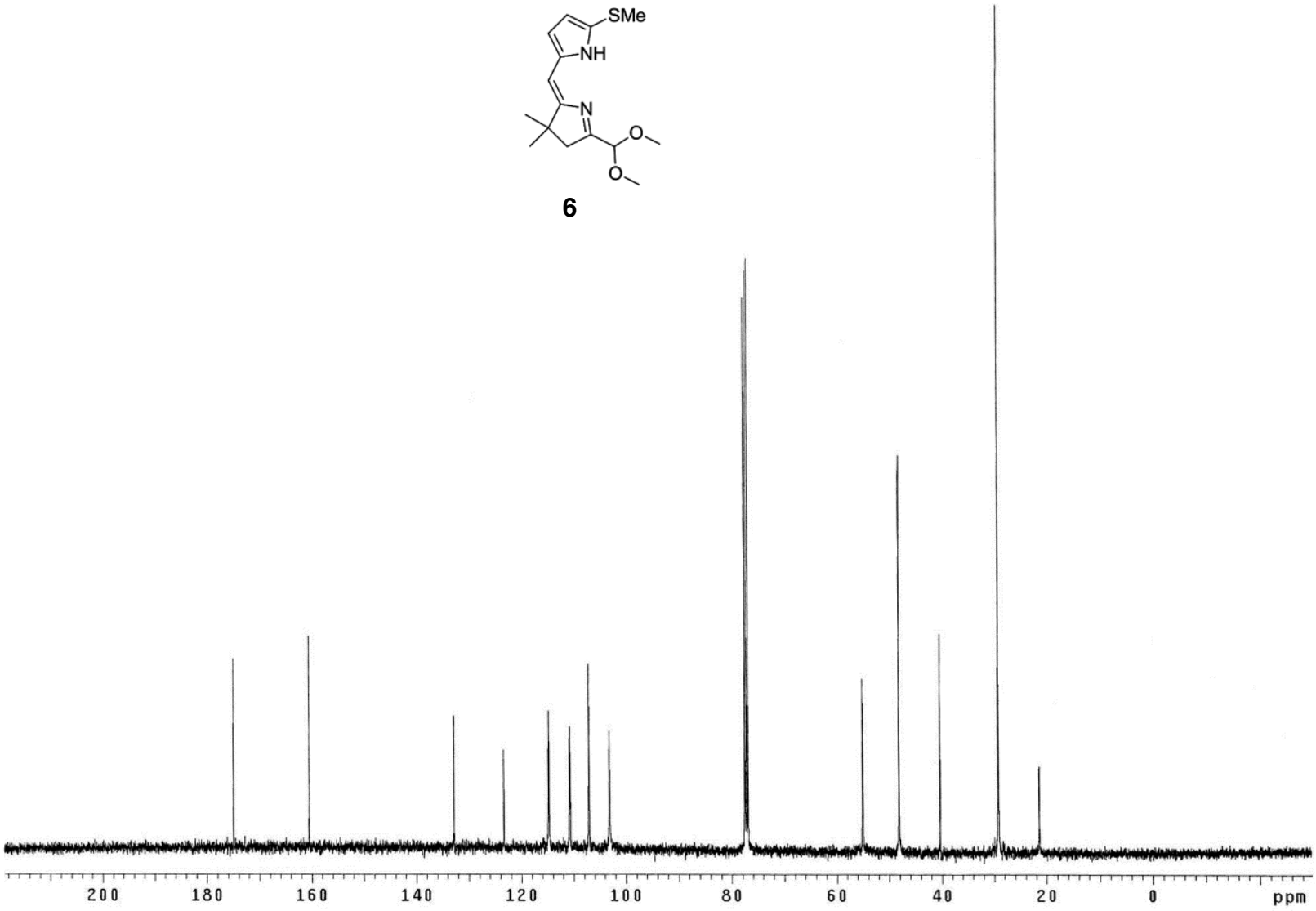
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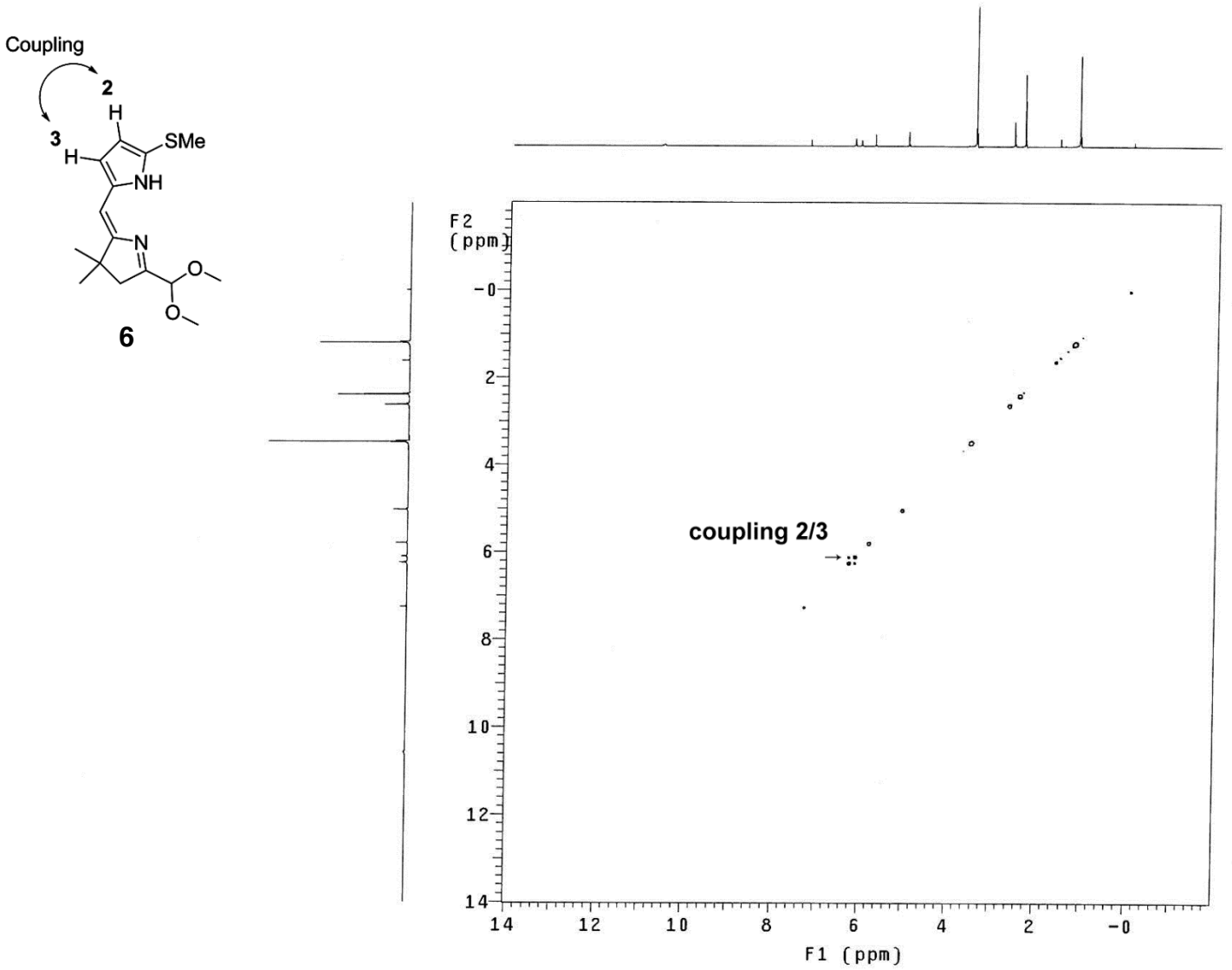
N
O
O
6
200
180
160
140
120
100
80
60
40
20
0
ppm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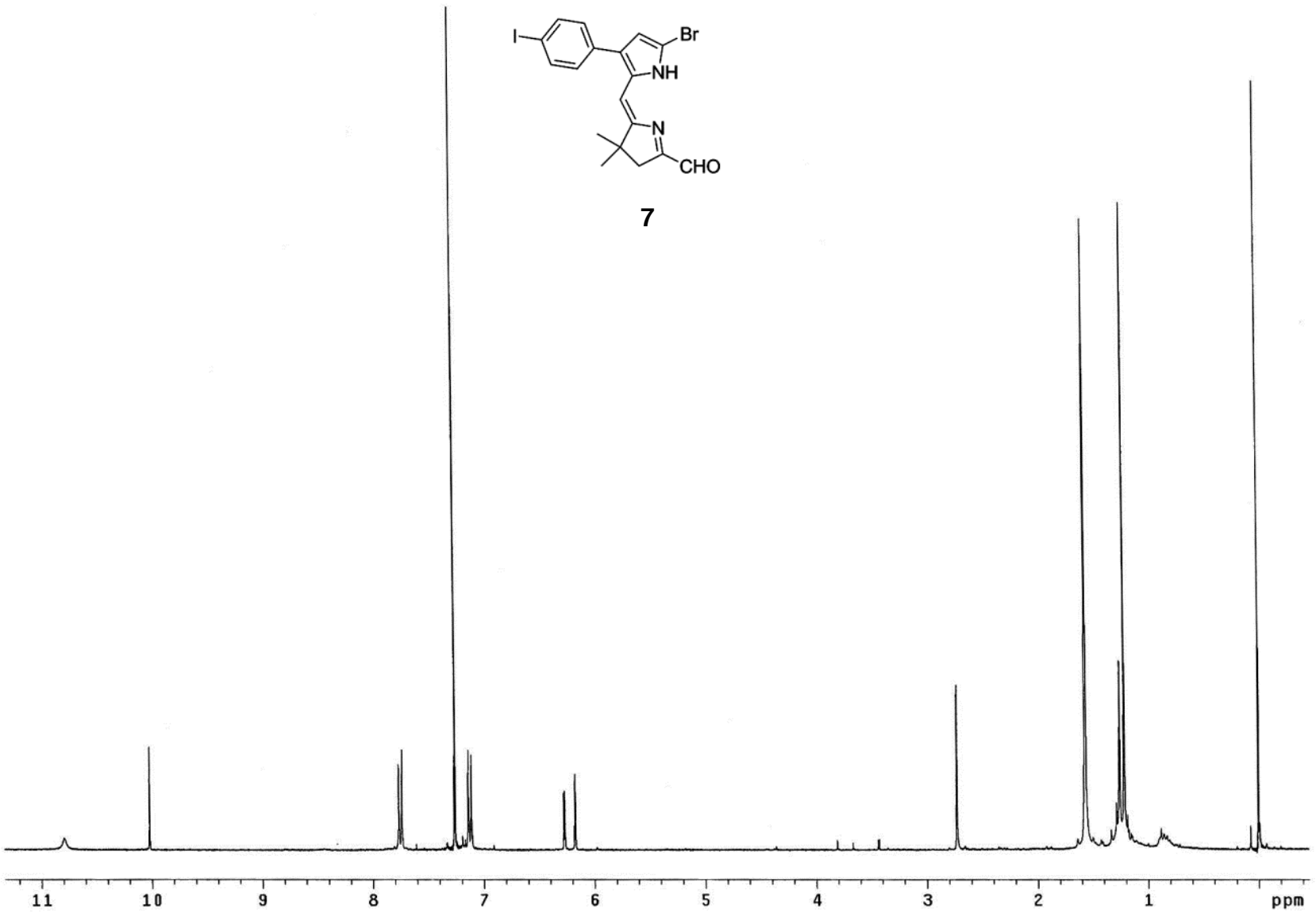
3
H
H
SMe
NH
N
O
O
6
F2
(ppm)
-0
2
4
6
8
10
12
14
coupling 2/3
14
12
10
8
6
4
2
-0
F1 (ppm)



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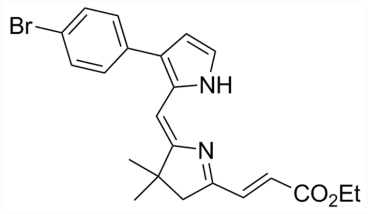
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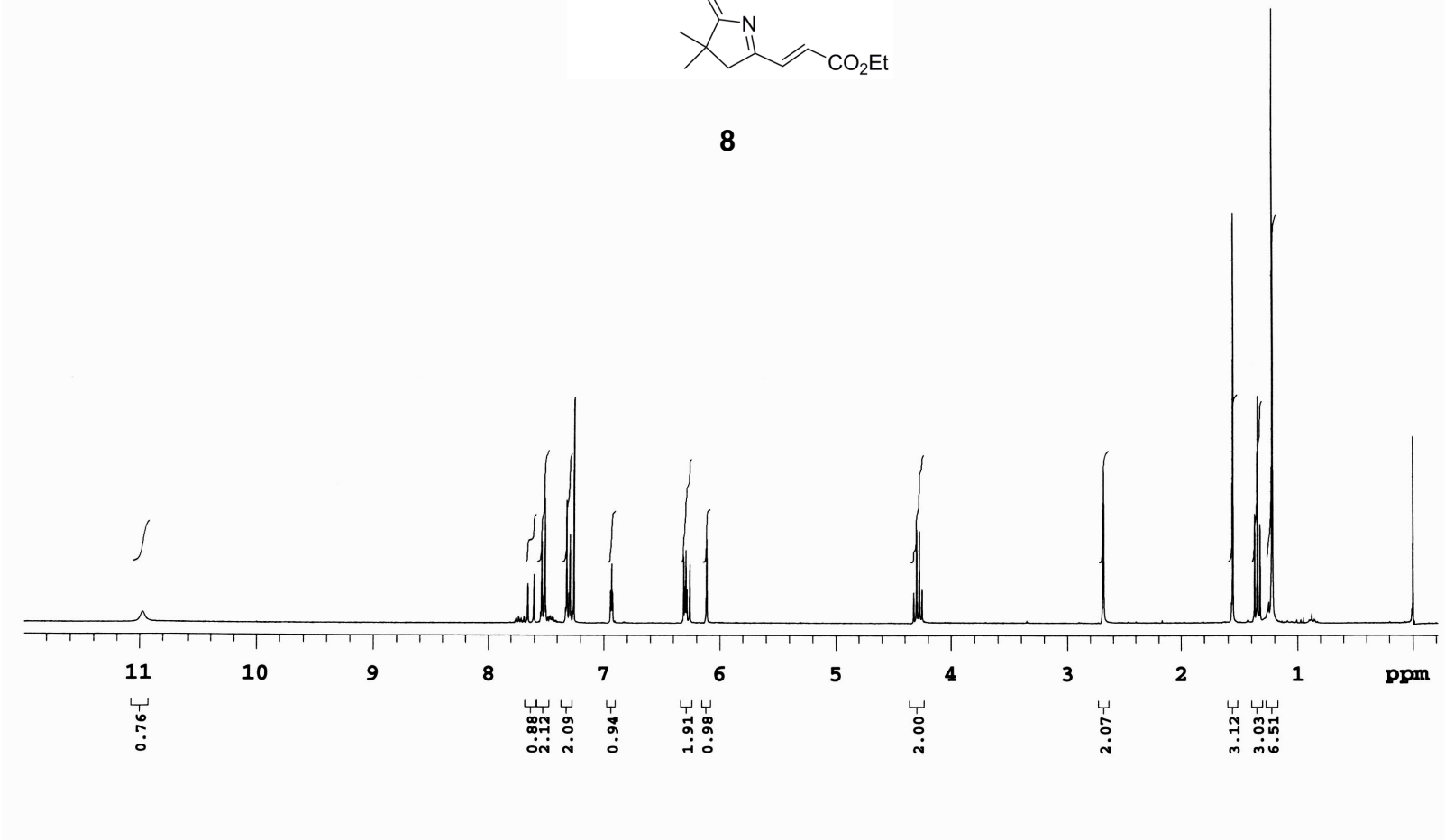
CO2Et

8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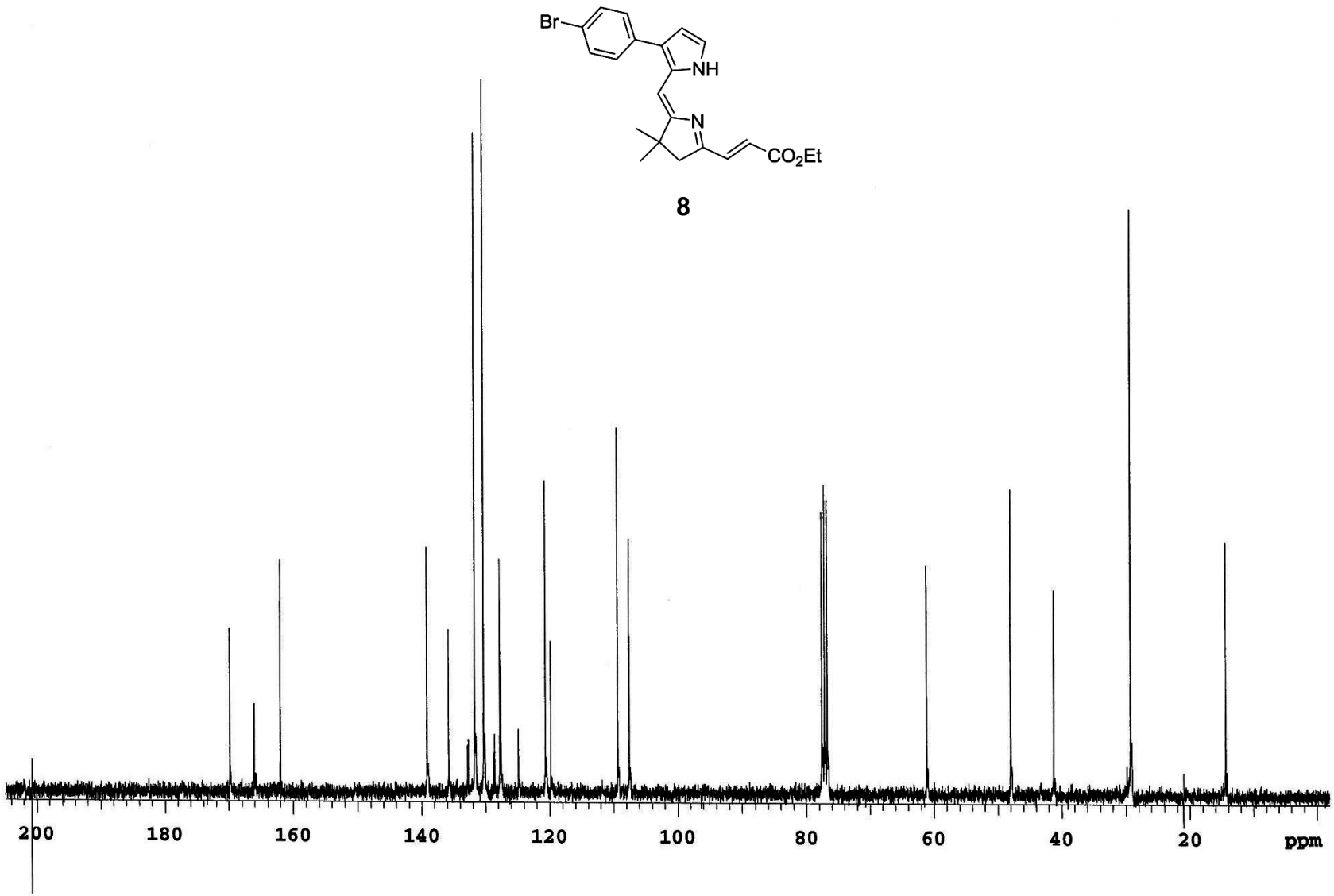

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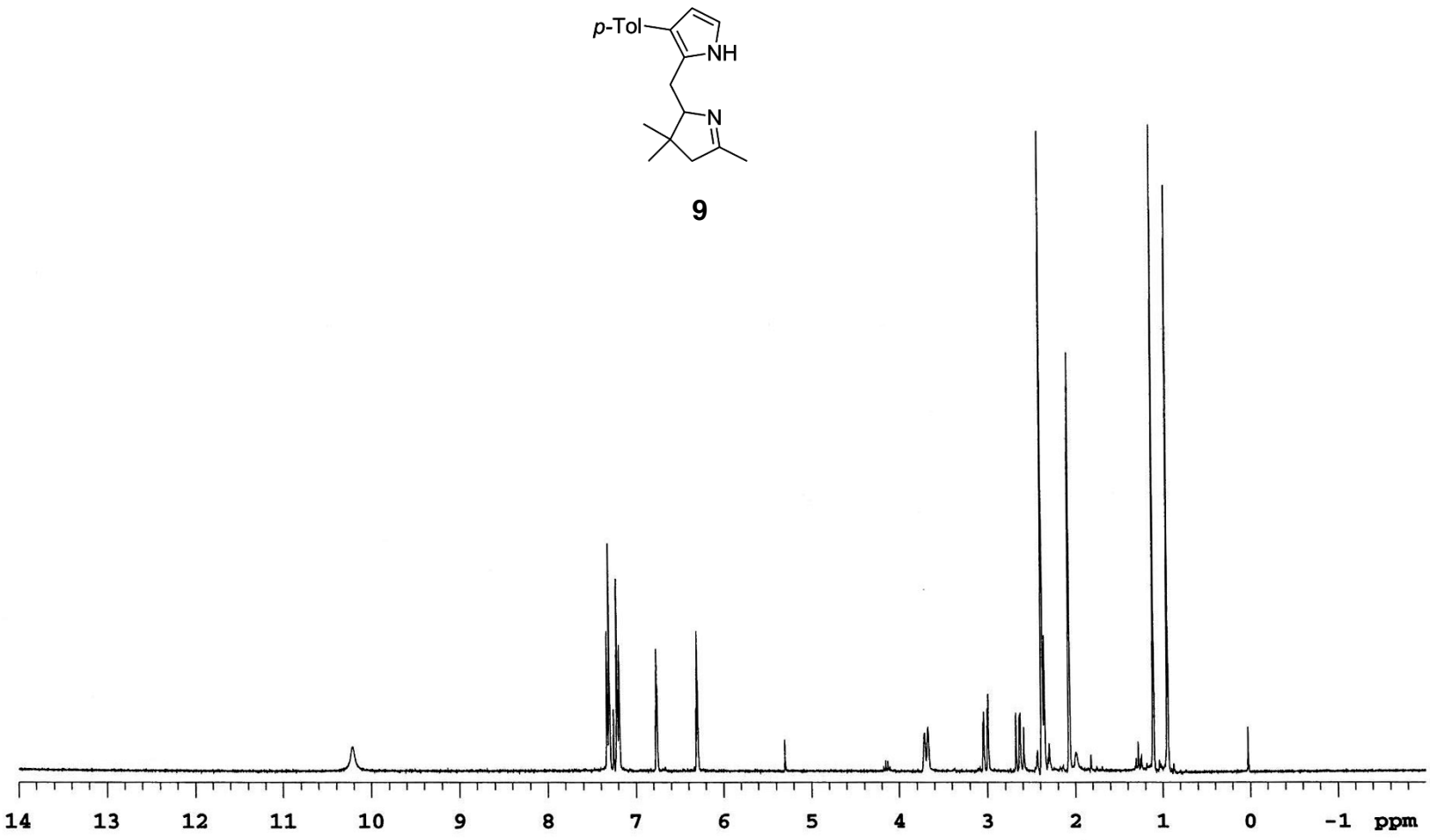

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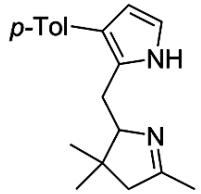

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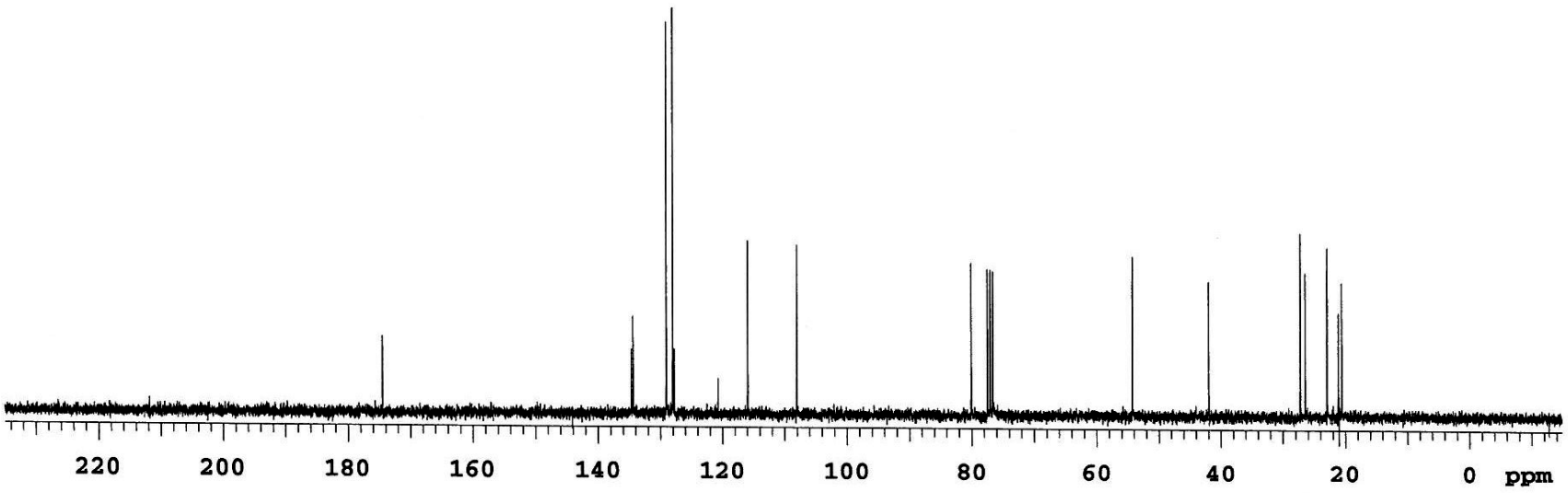

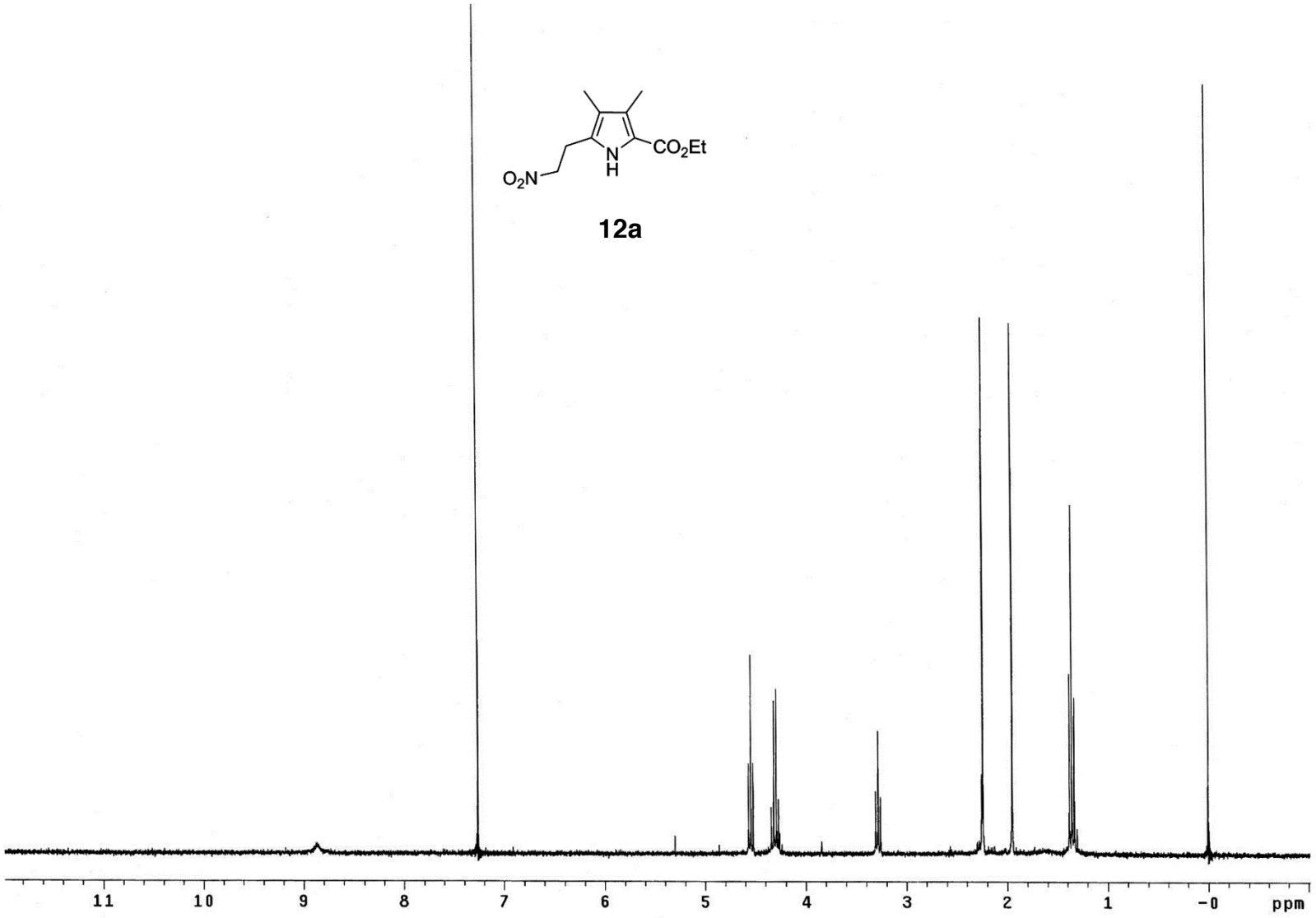

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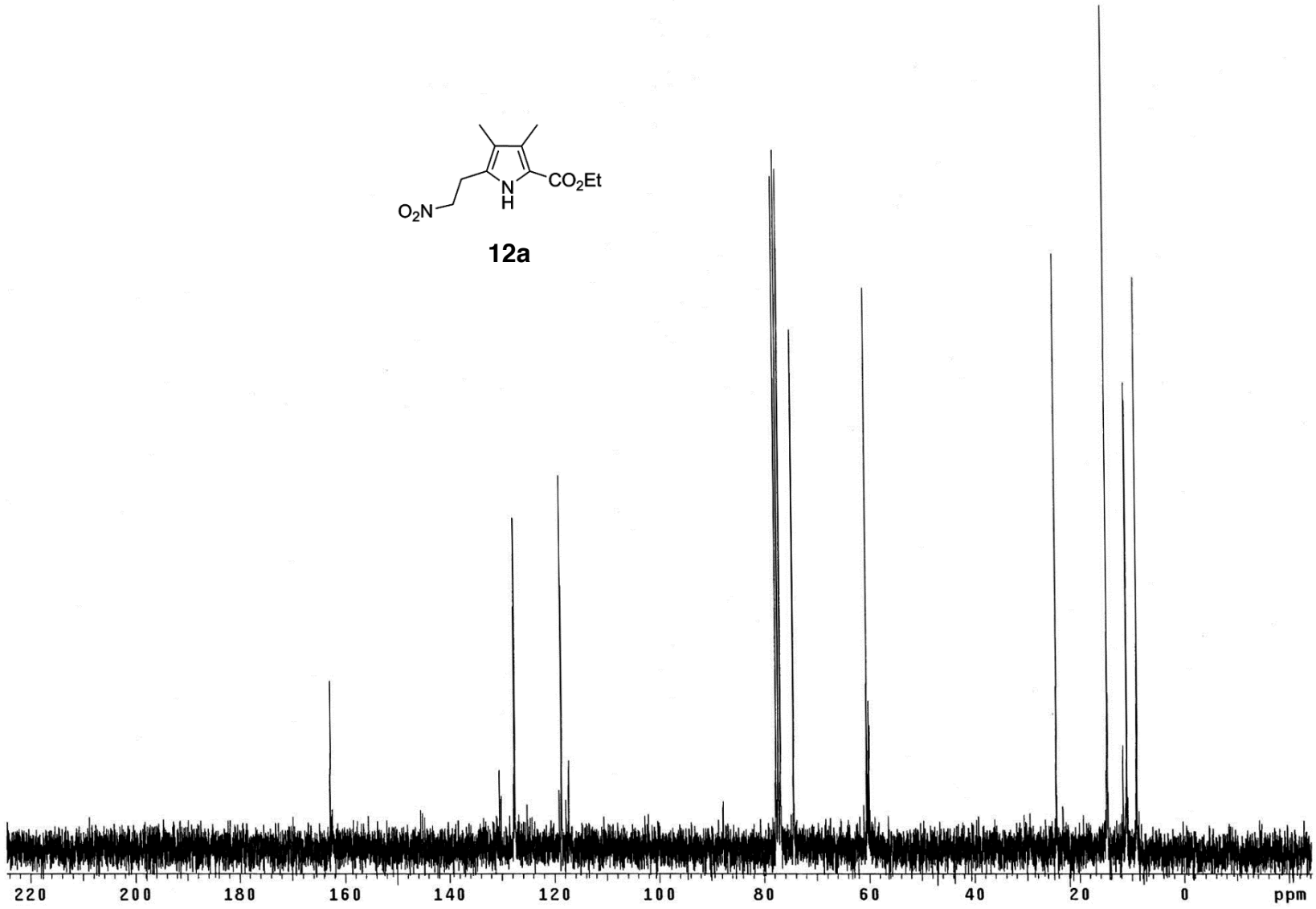

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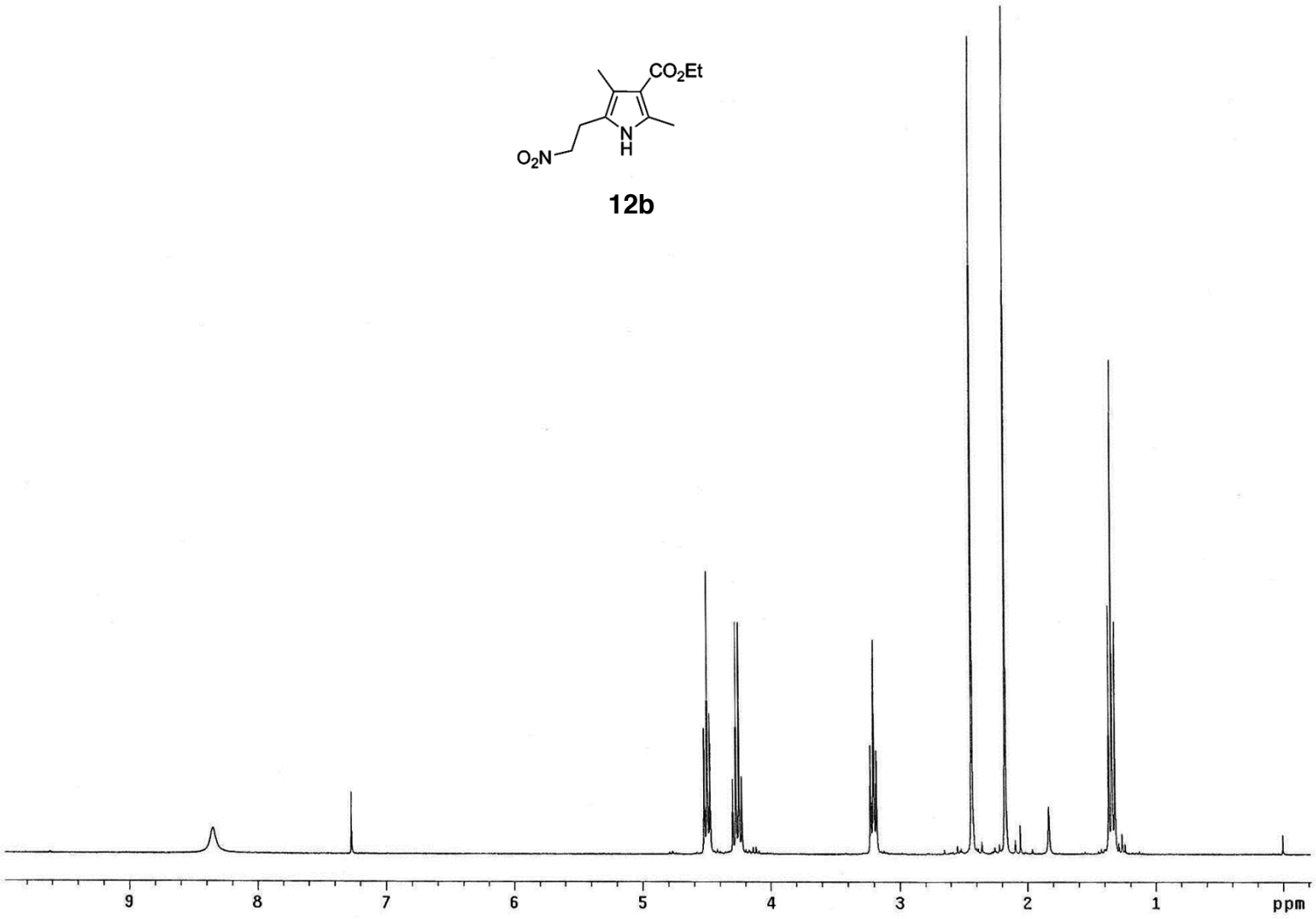
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O2N
N
H
12b
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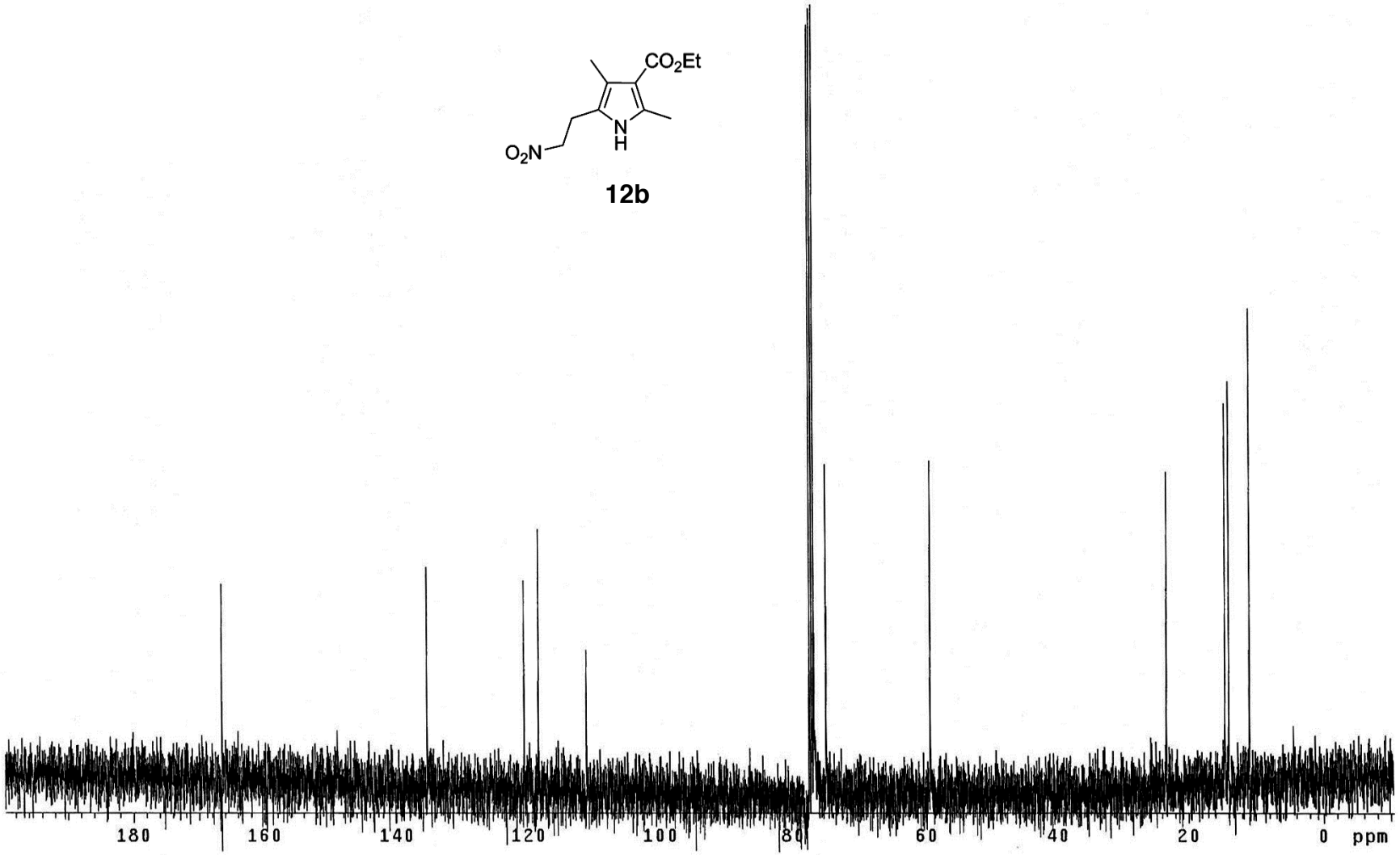
8
7
6
5
4
3
2
1
ppm



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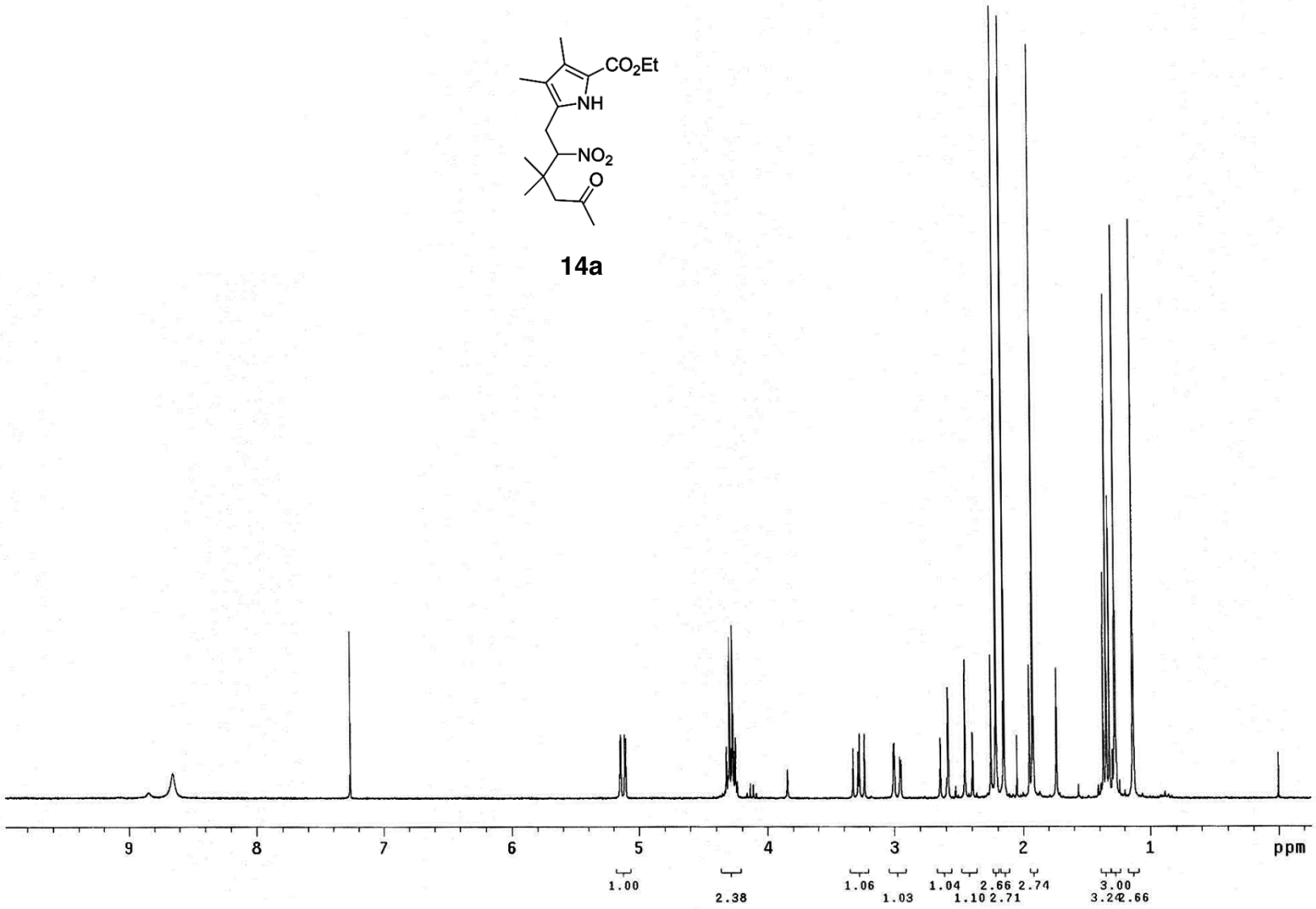
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4
3
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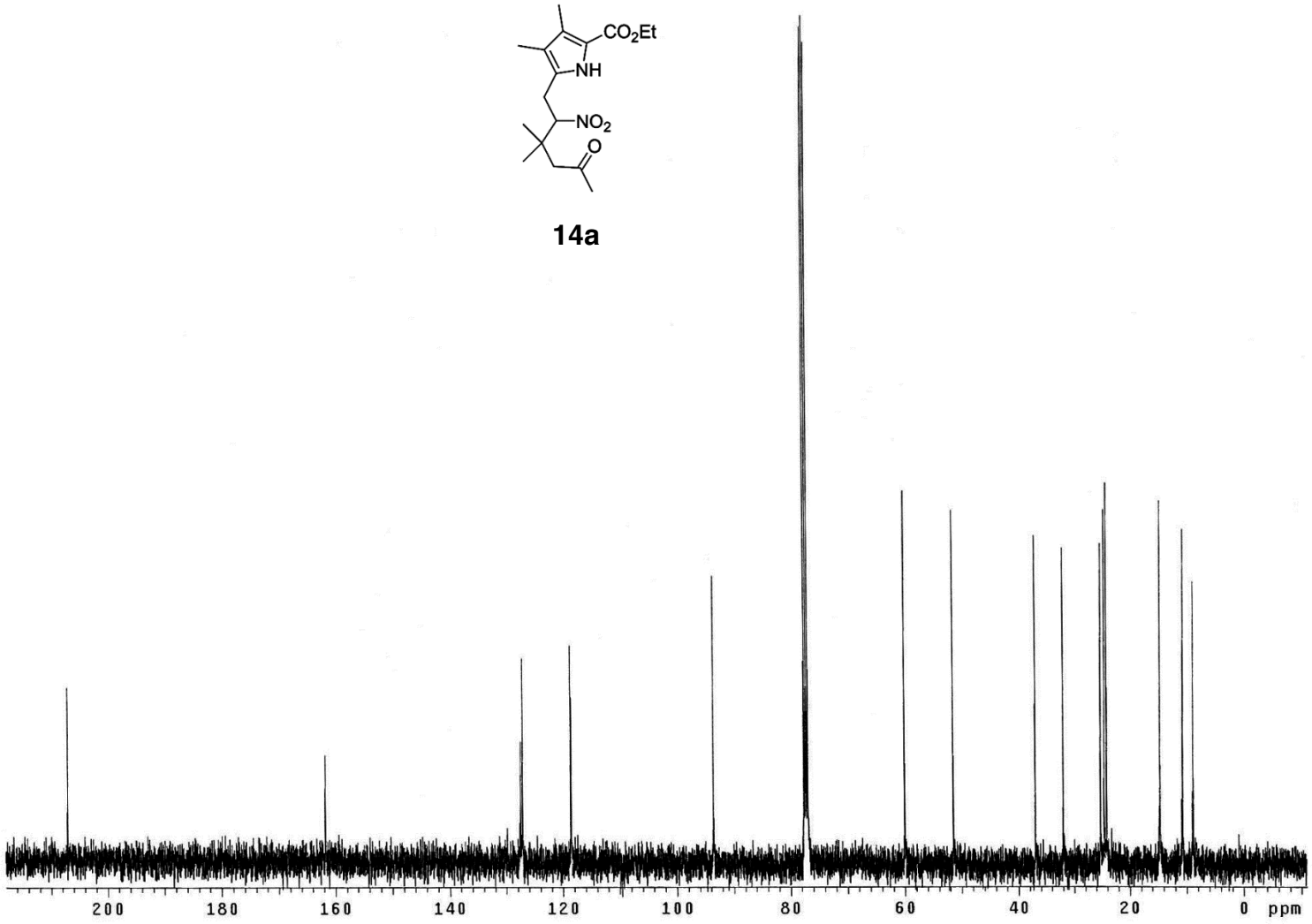

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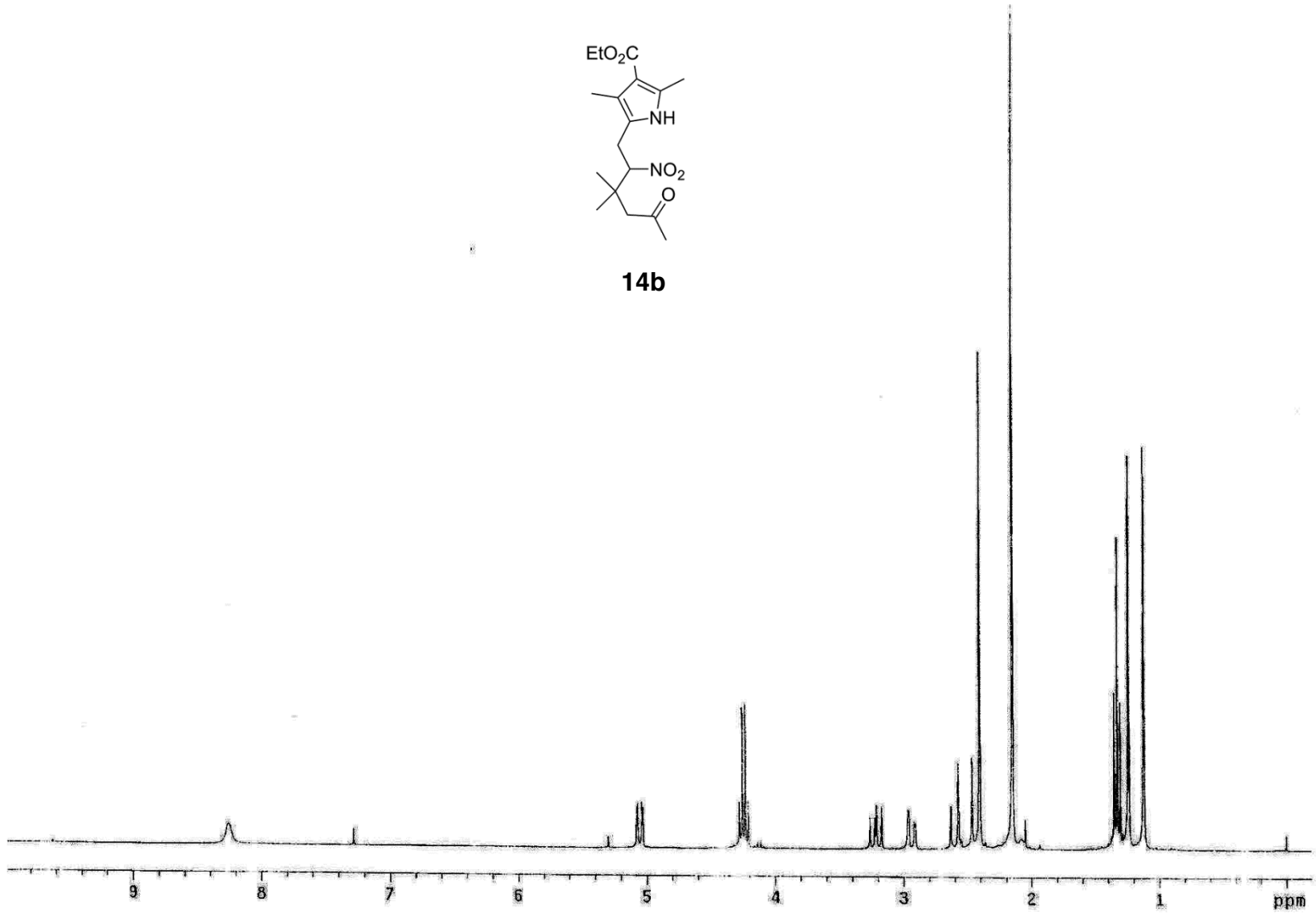

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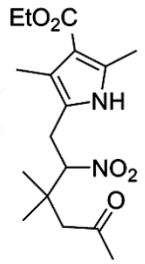

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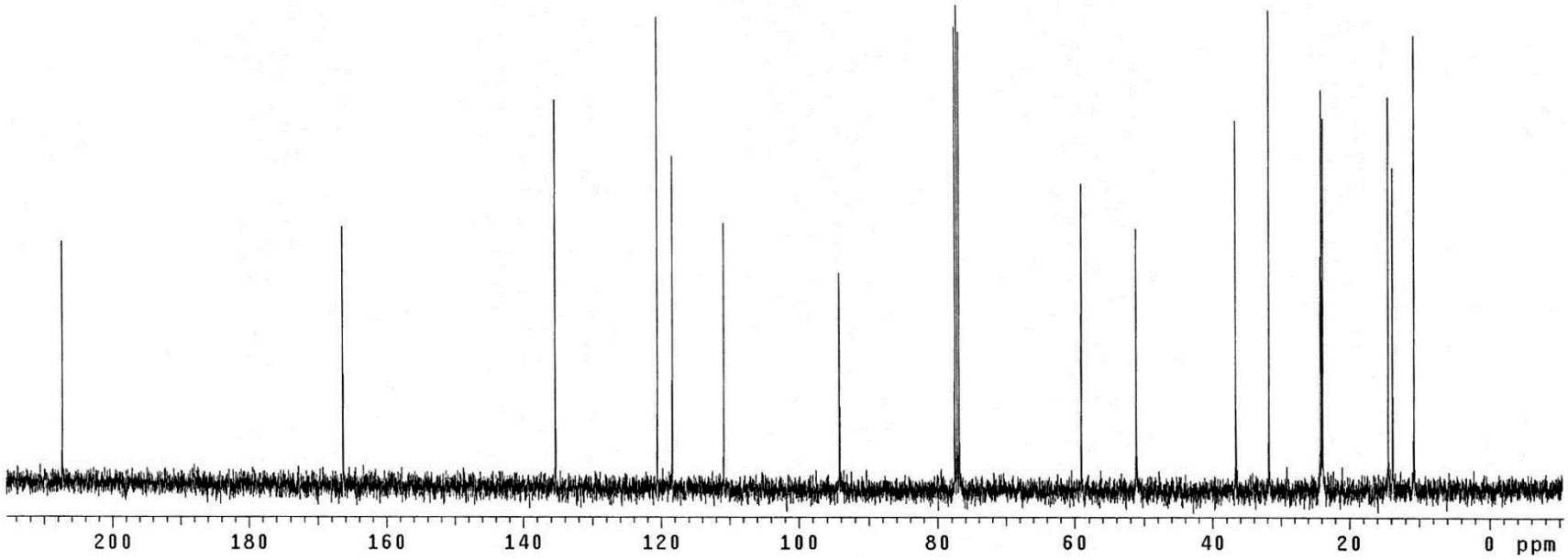

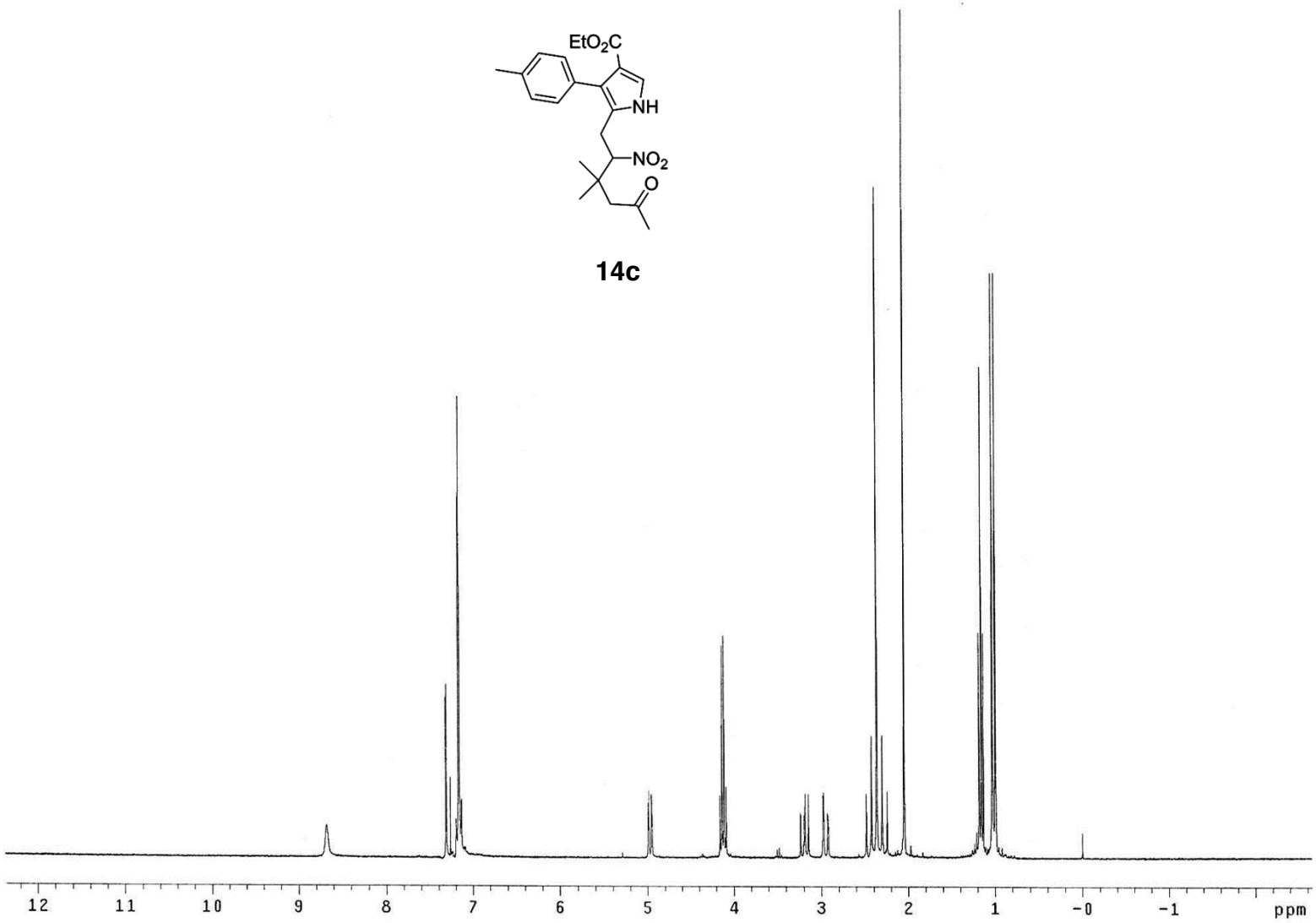

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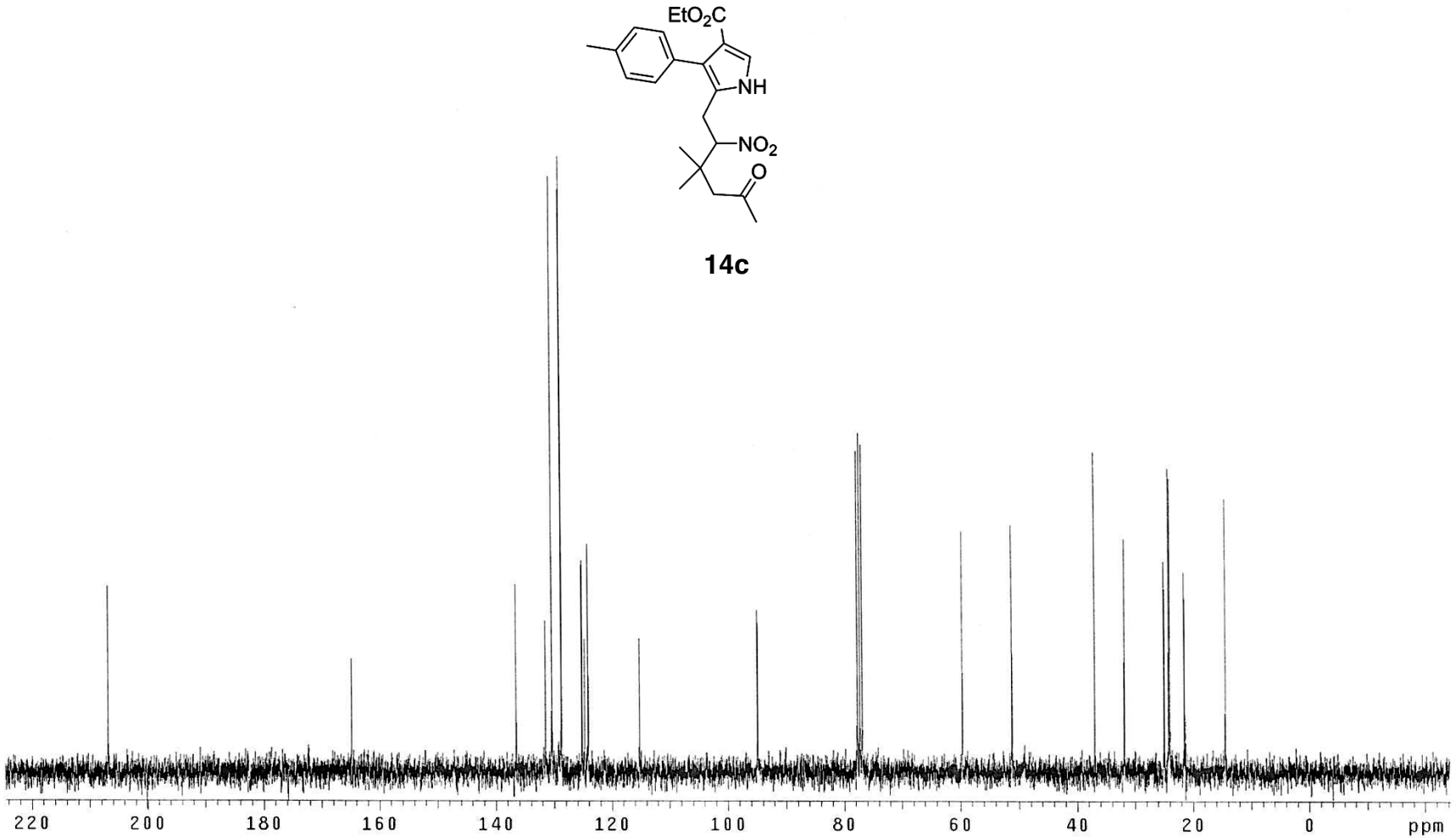

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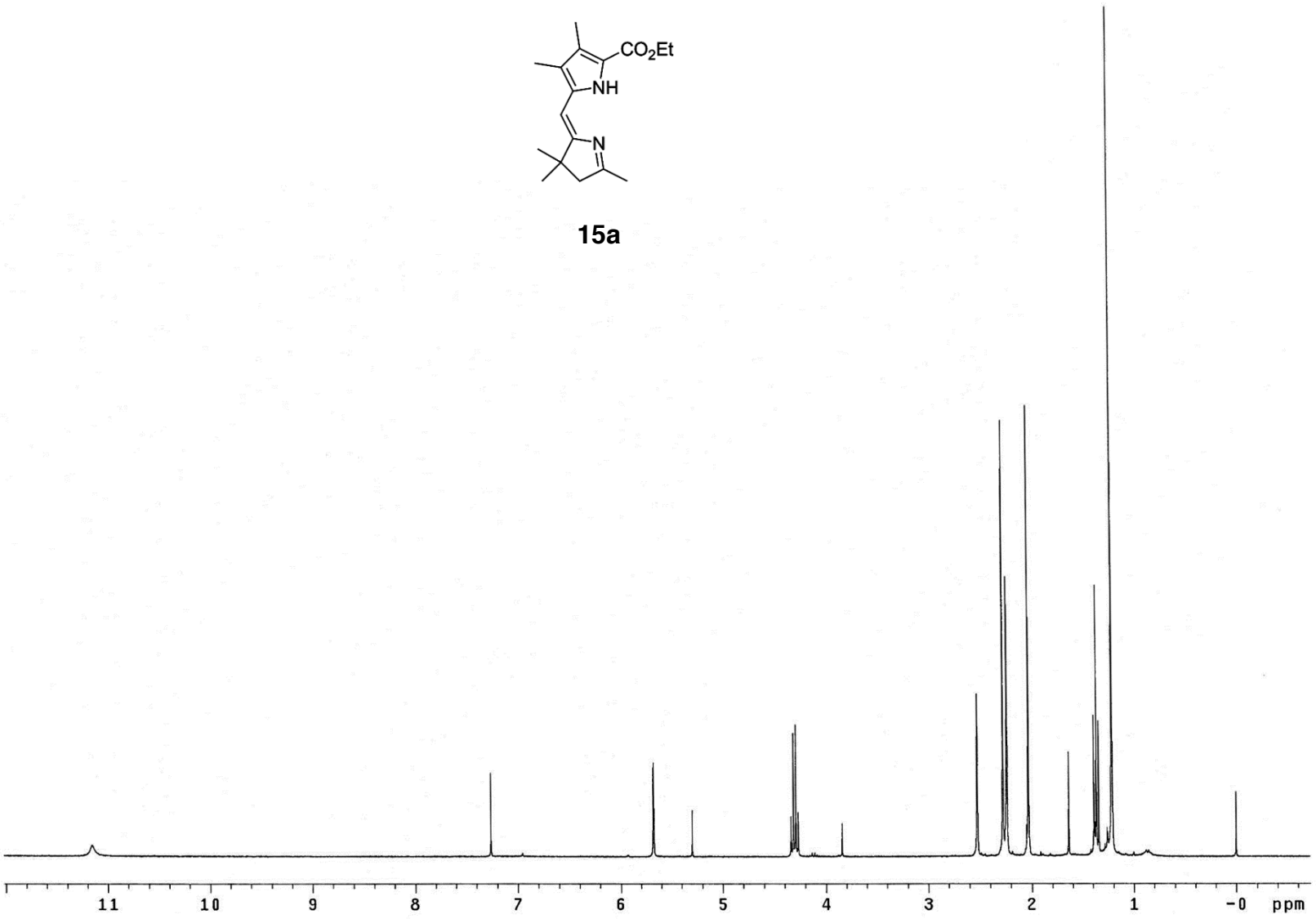

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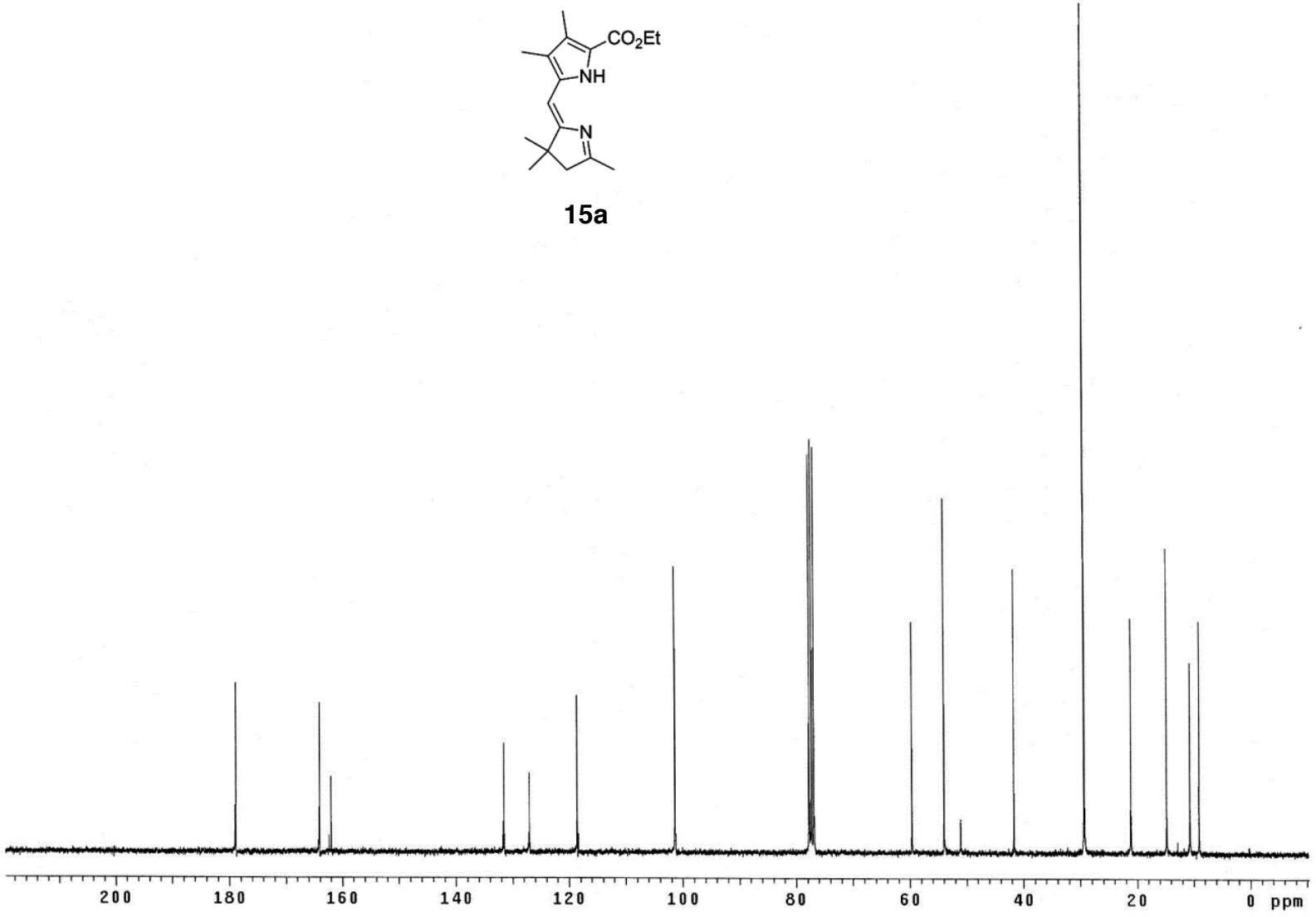
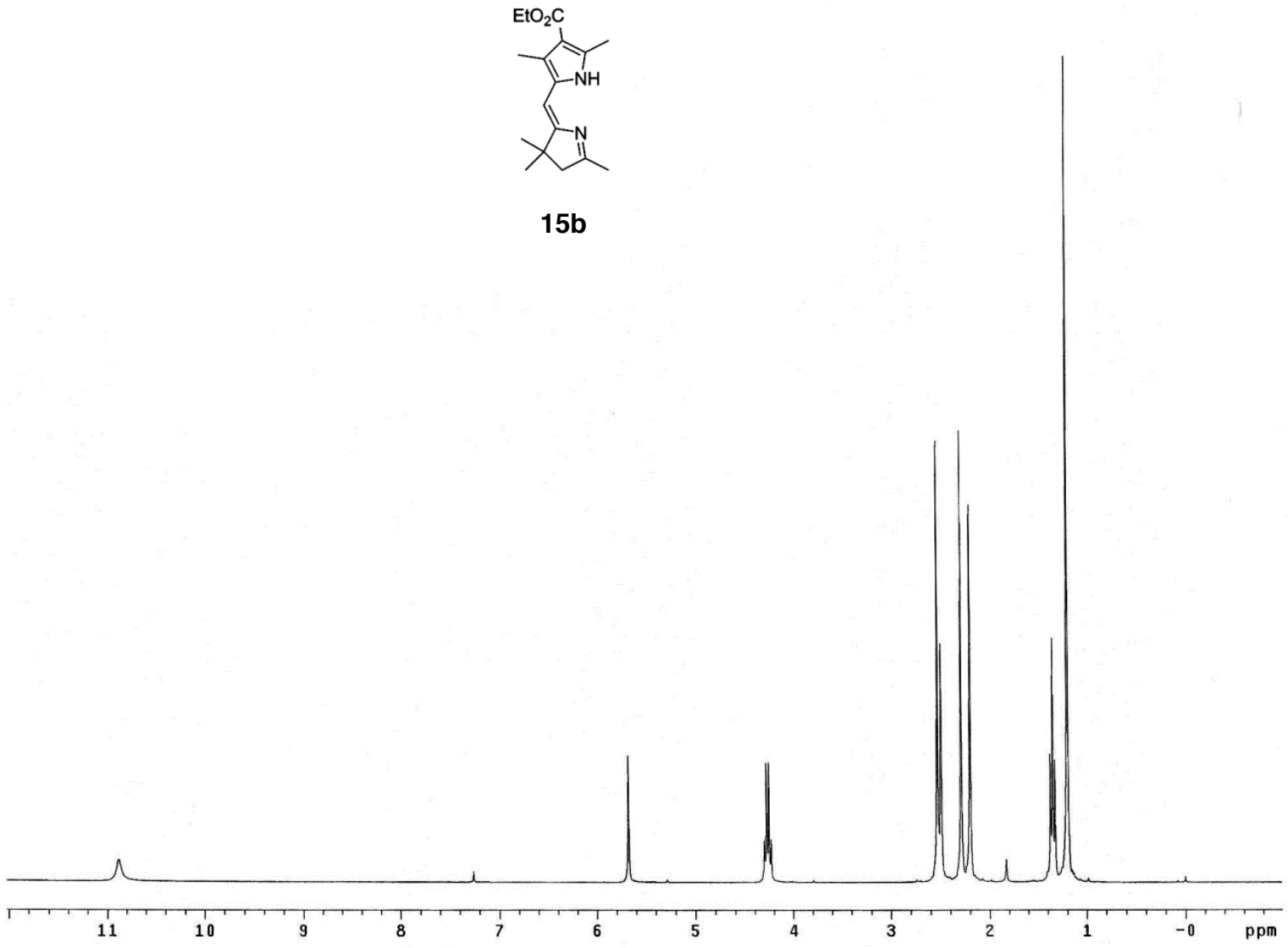
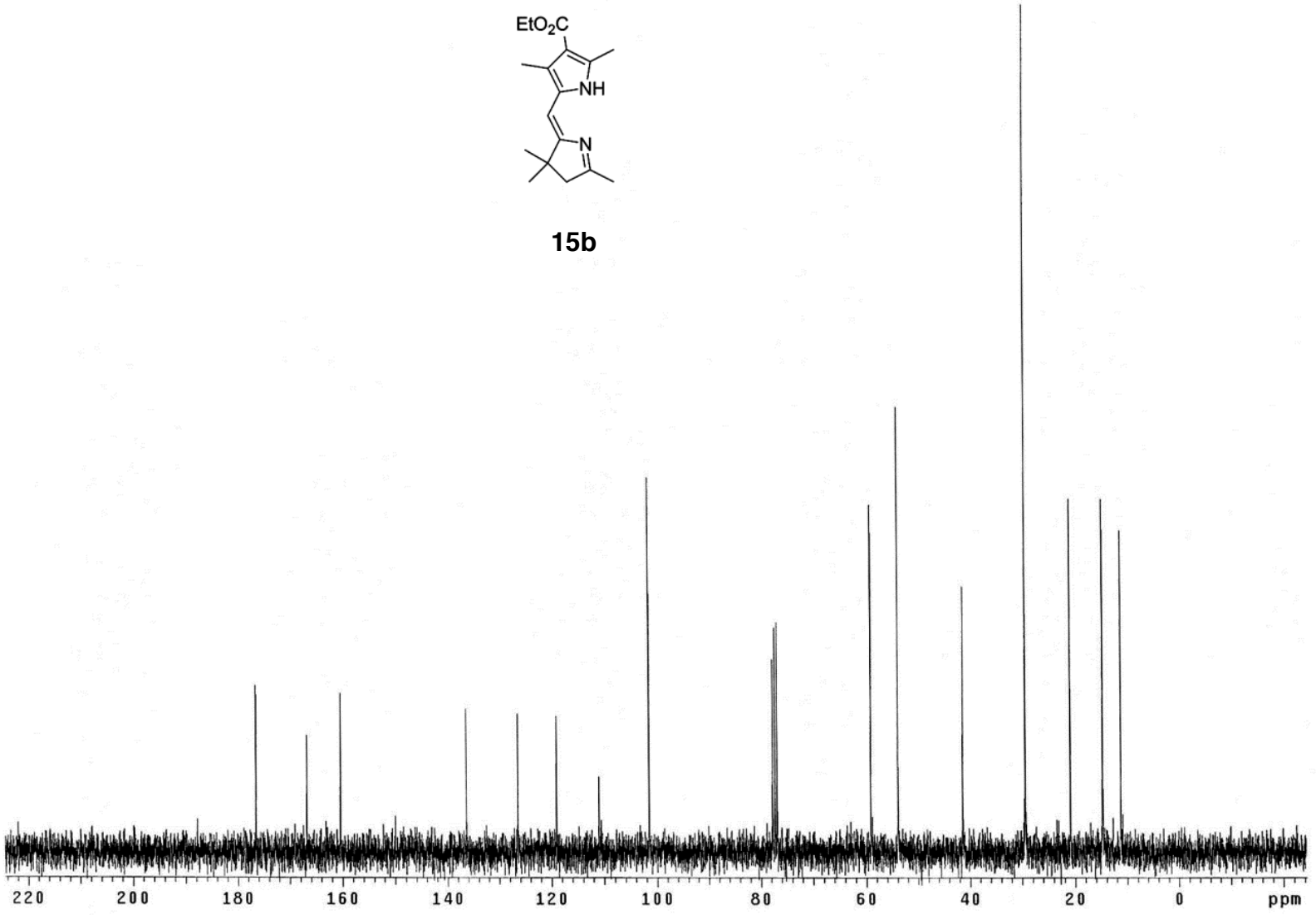


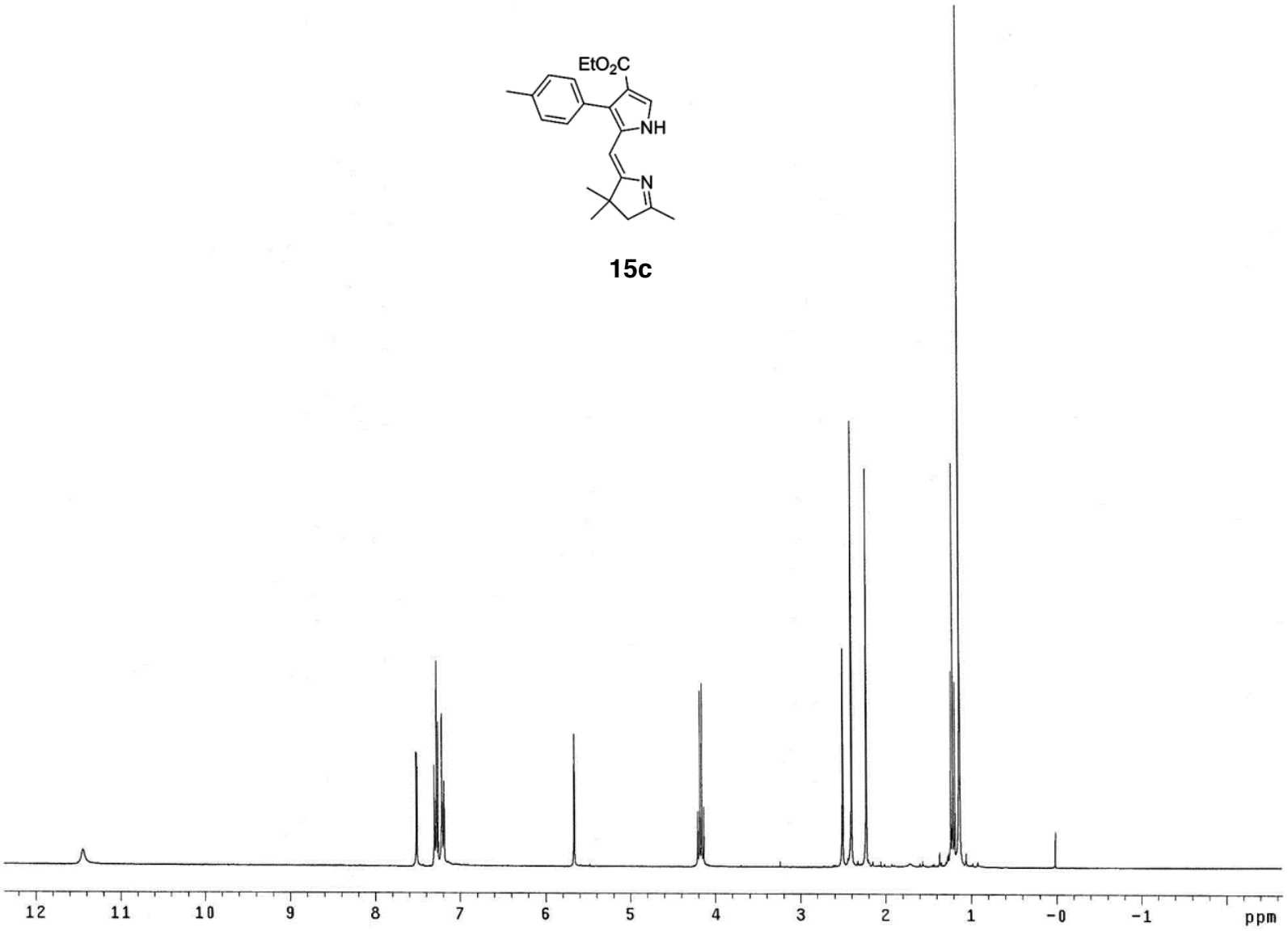
15a



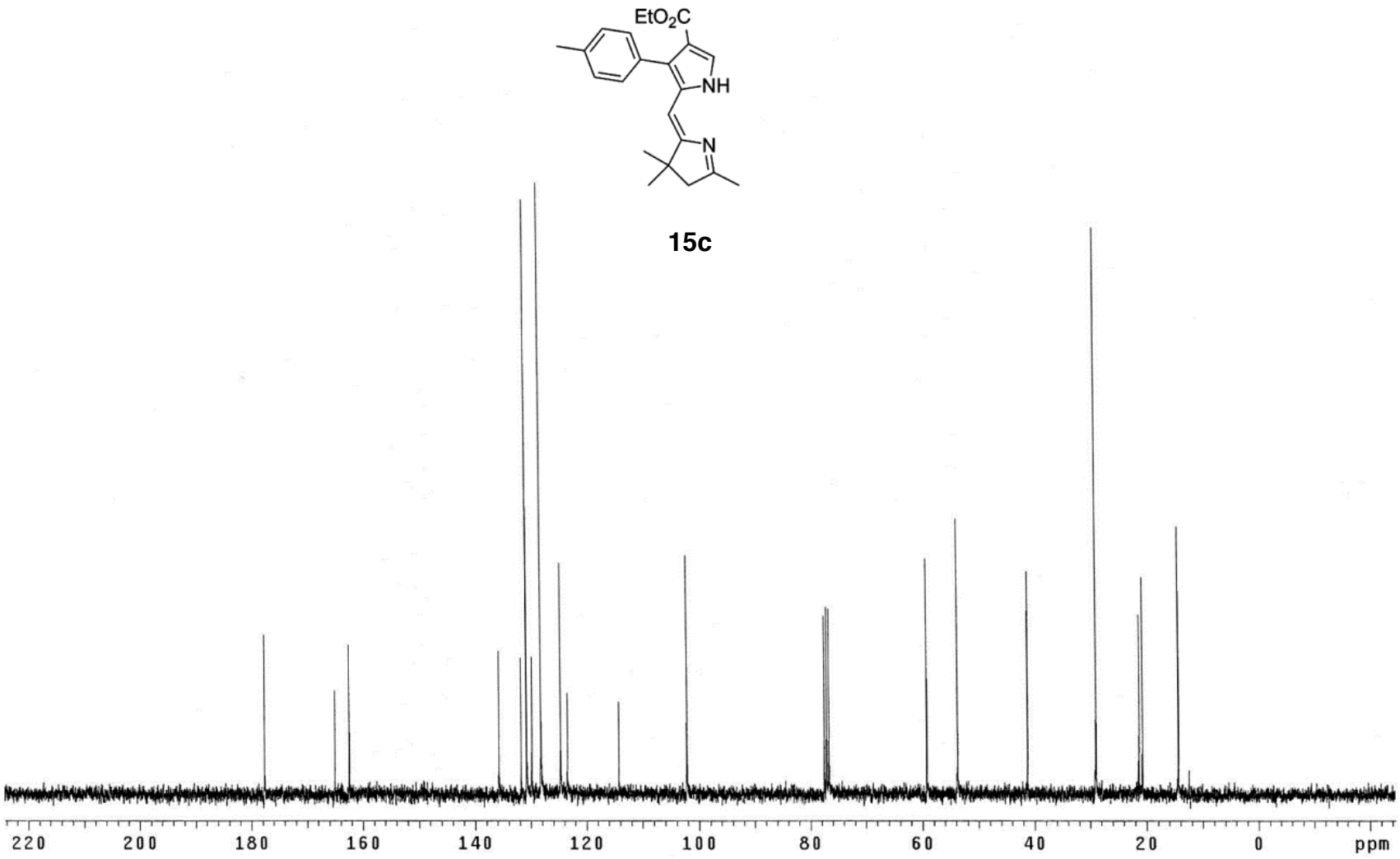
15b



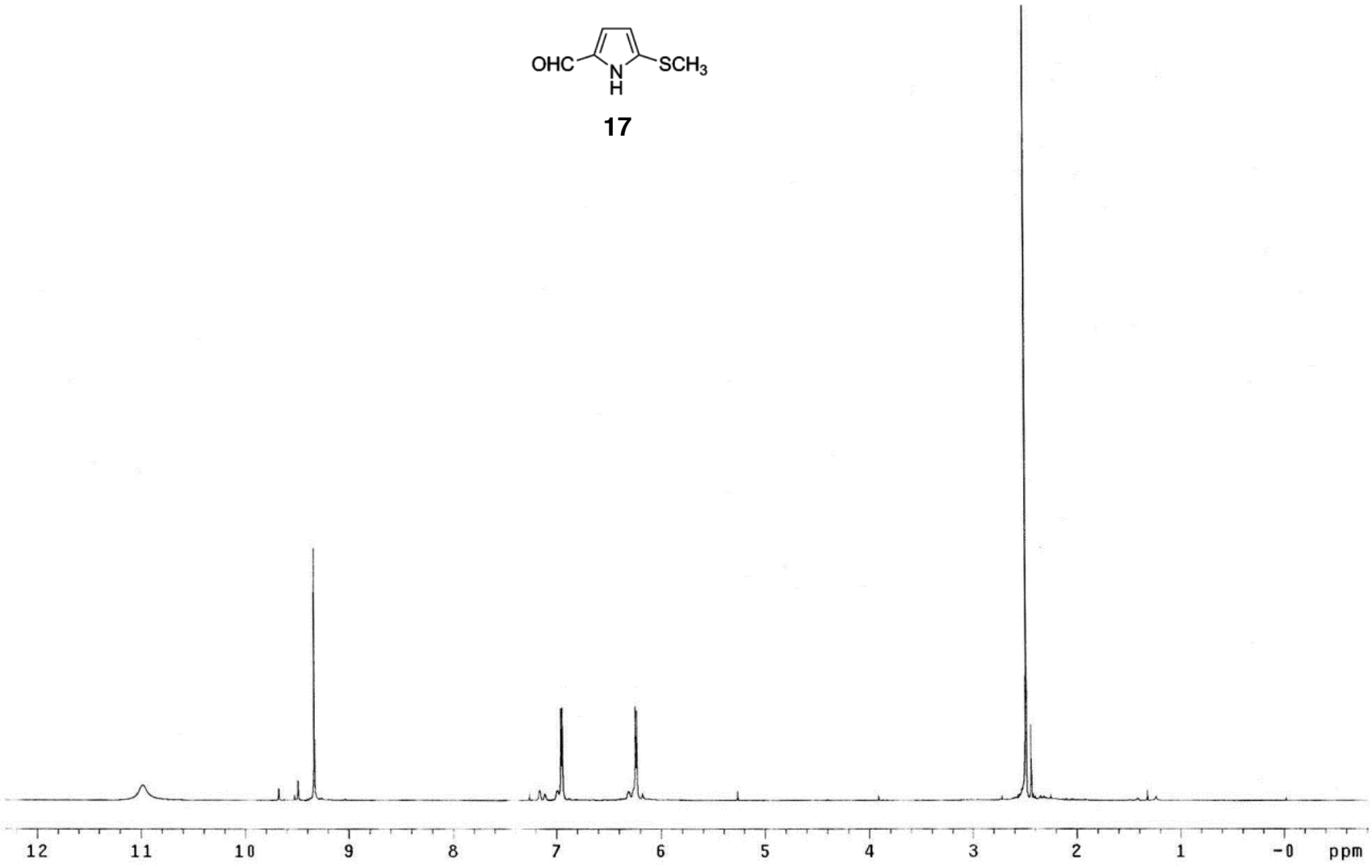
15b



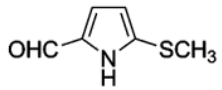
15c



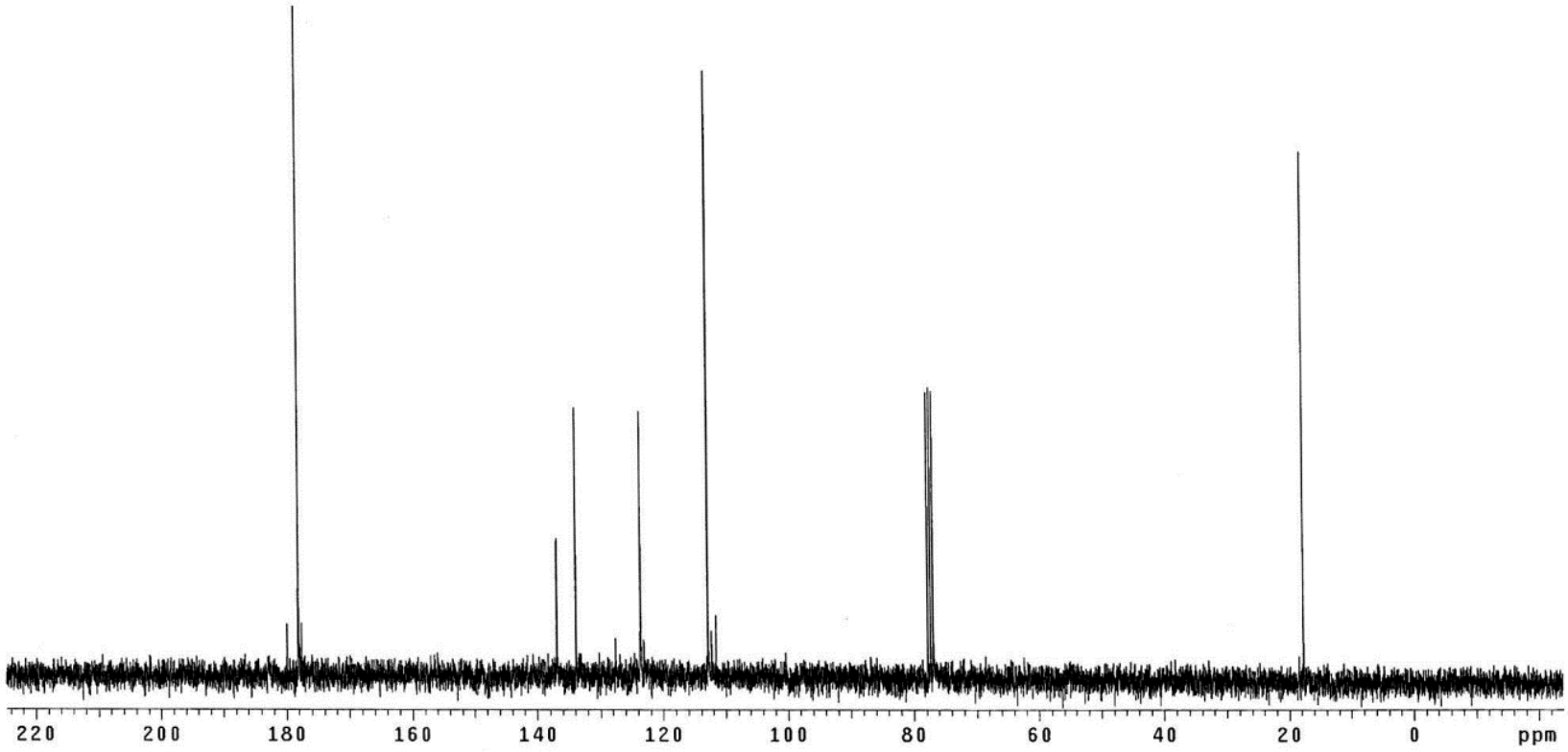
15c

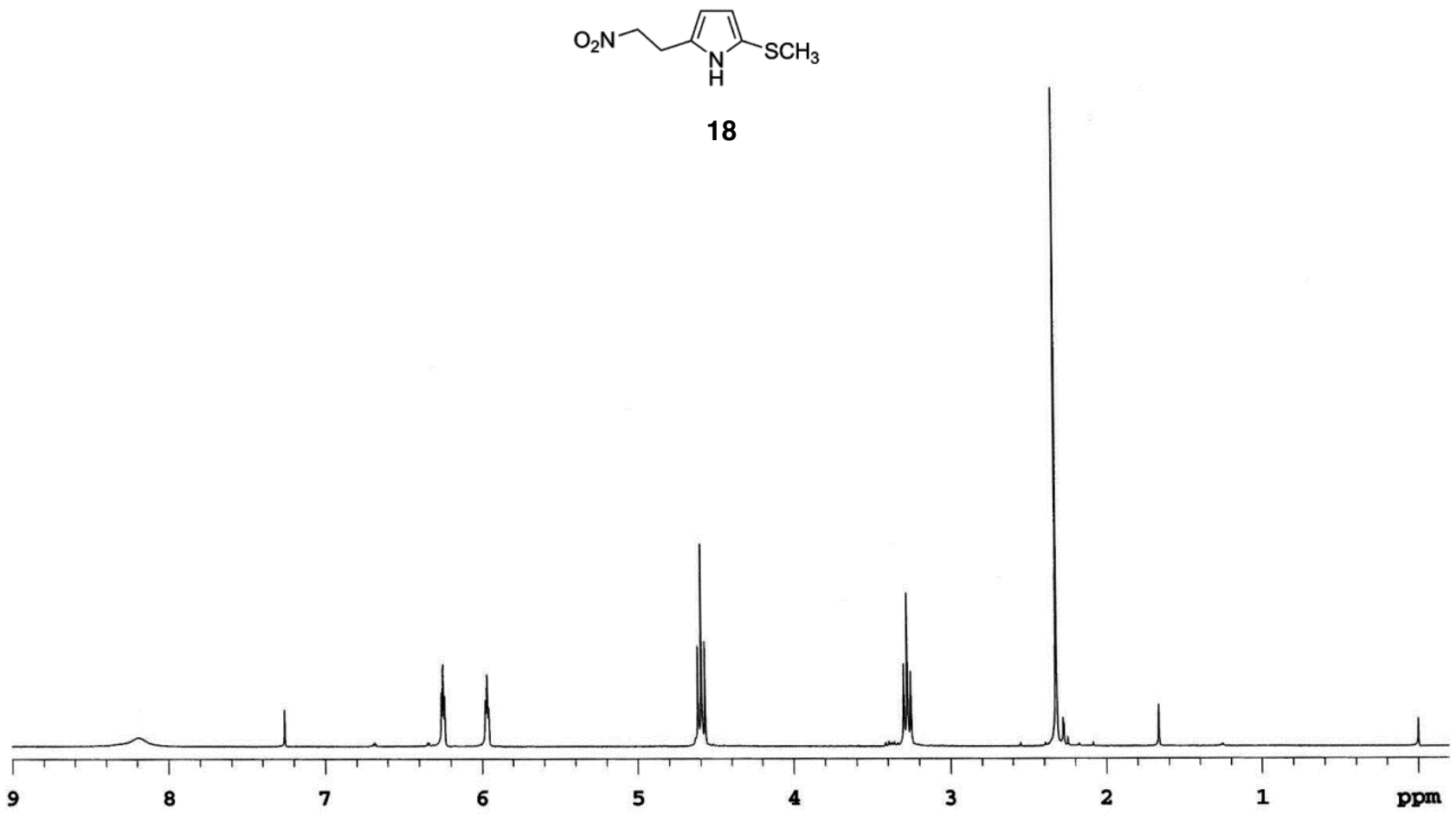


17

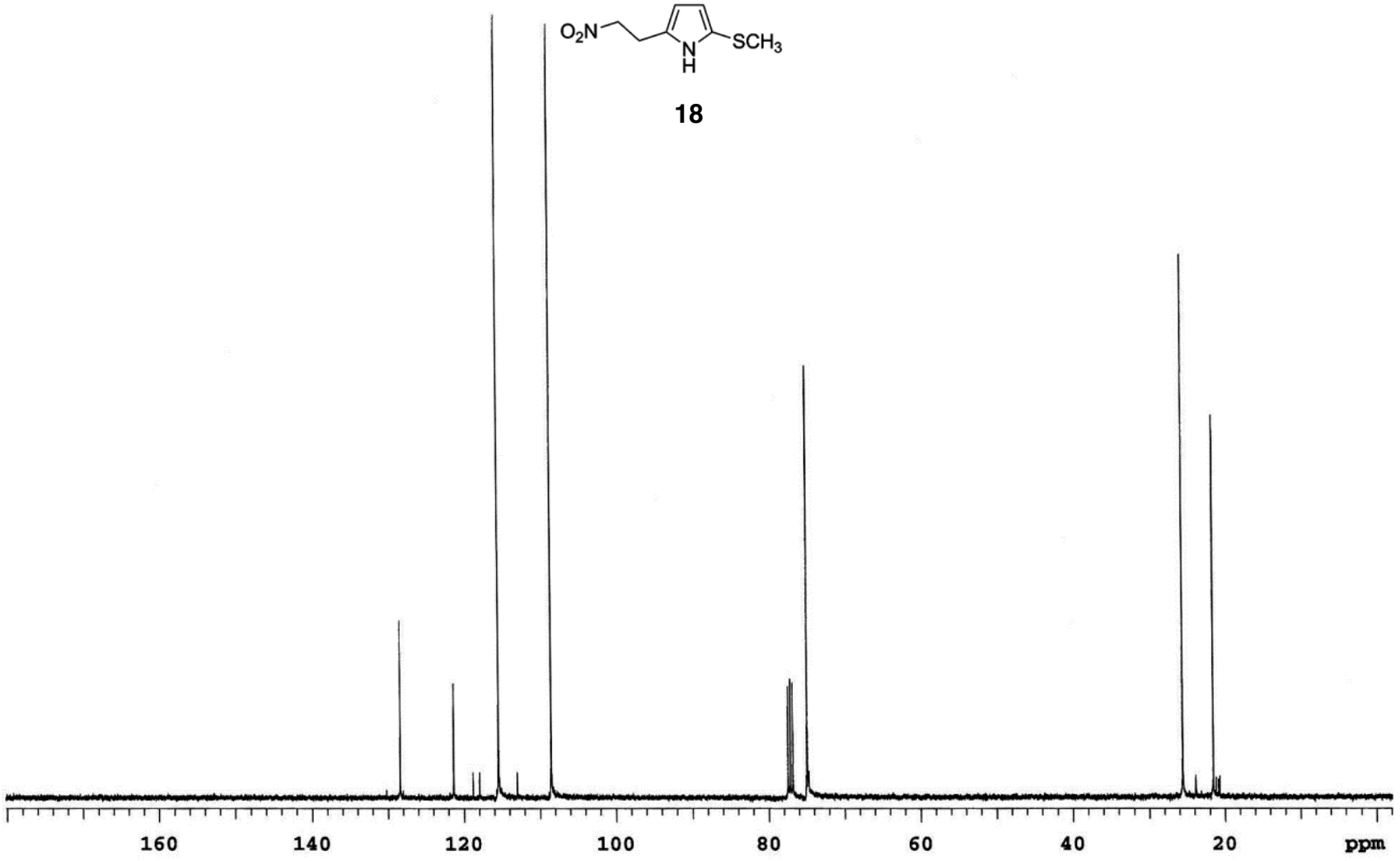


17

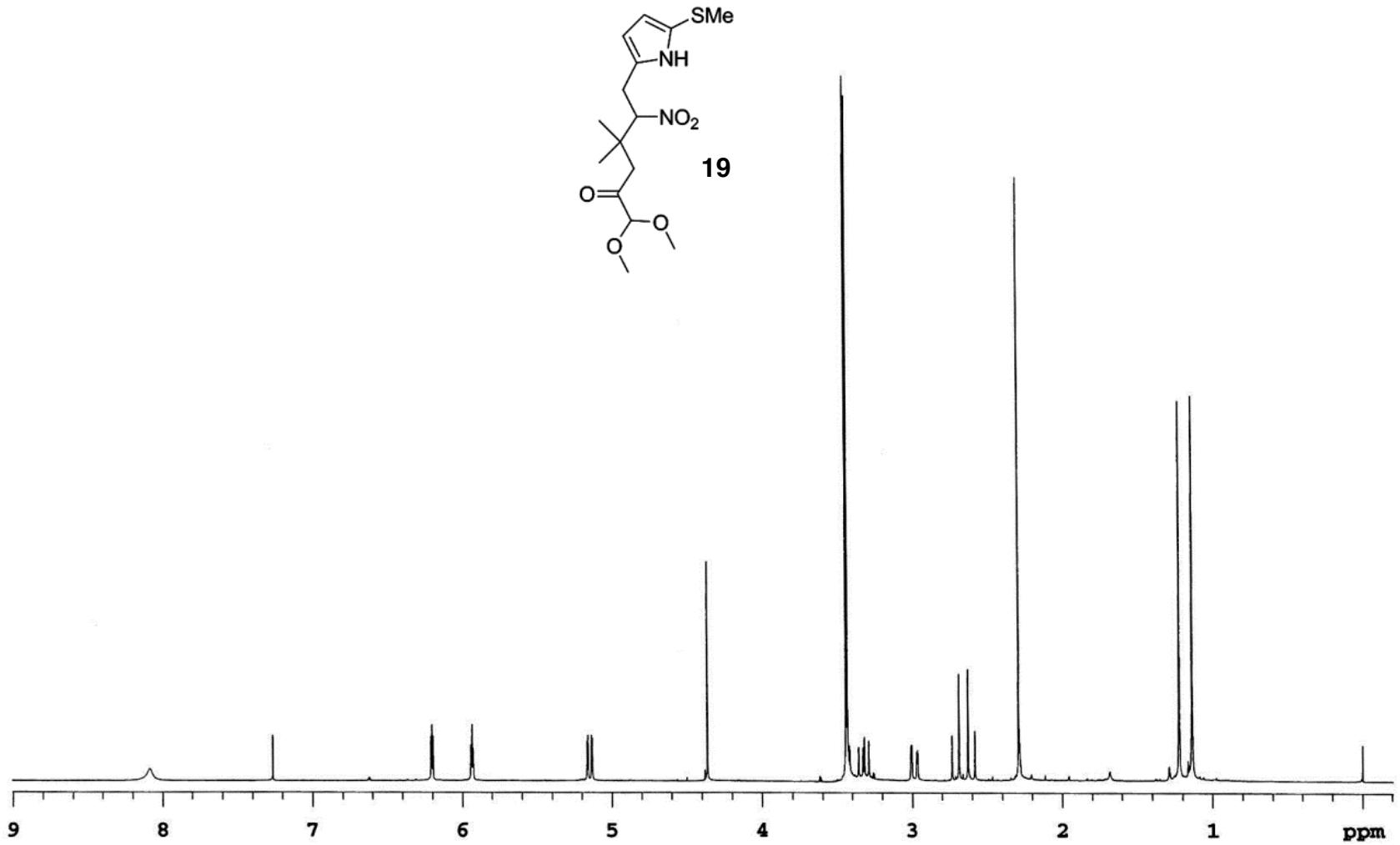


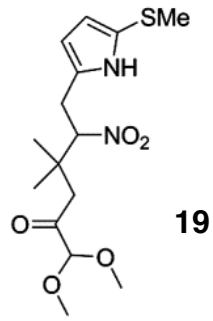


18

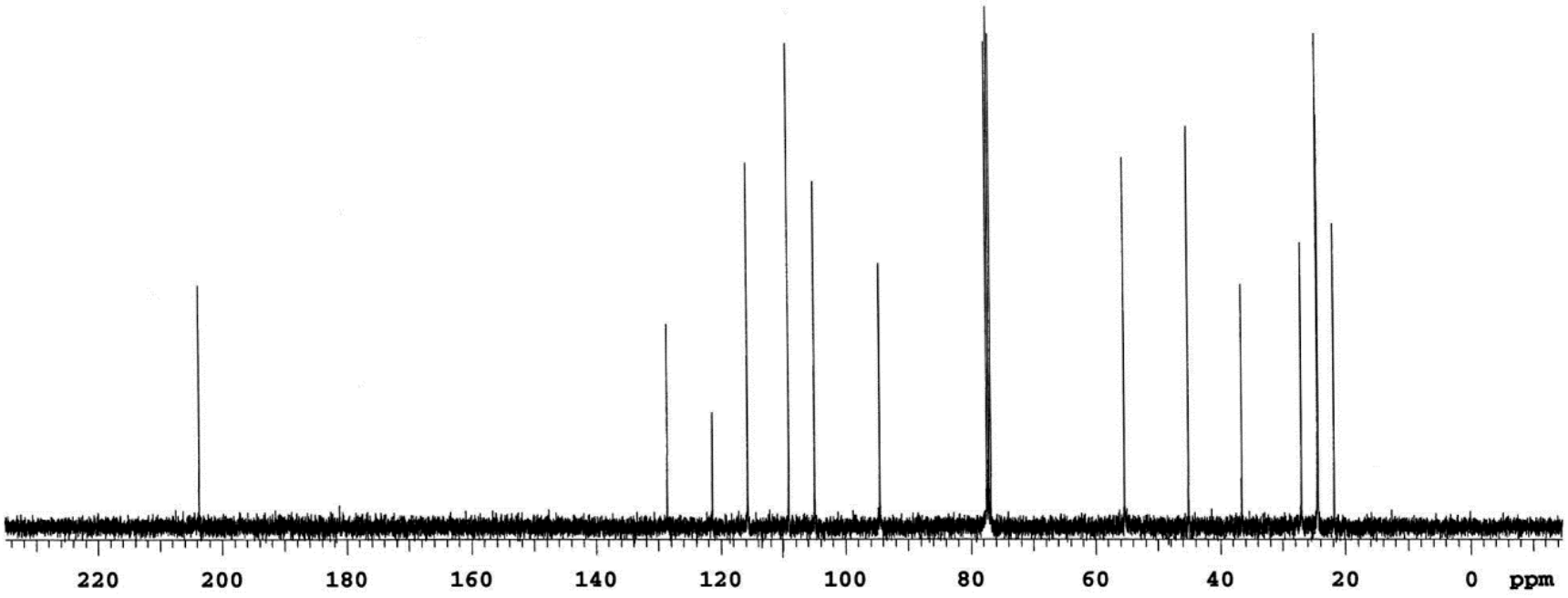


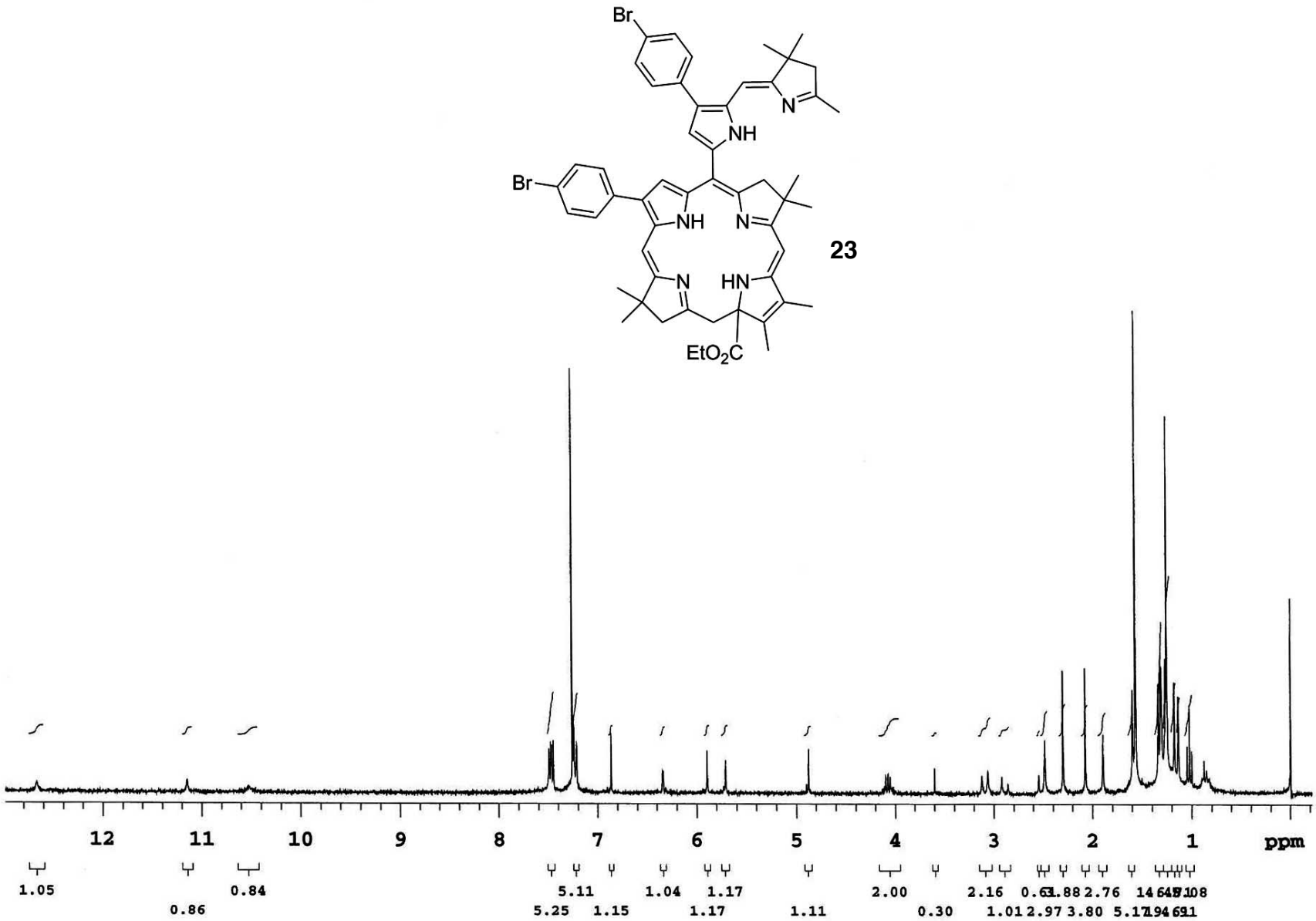
18

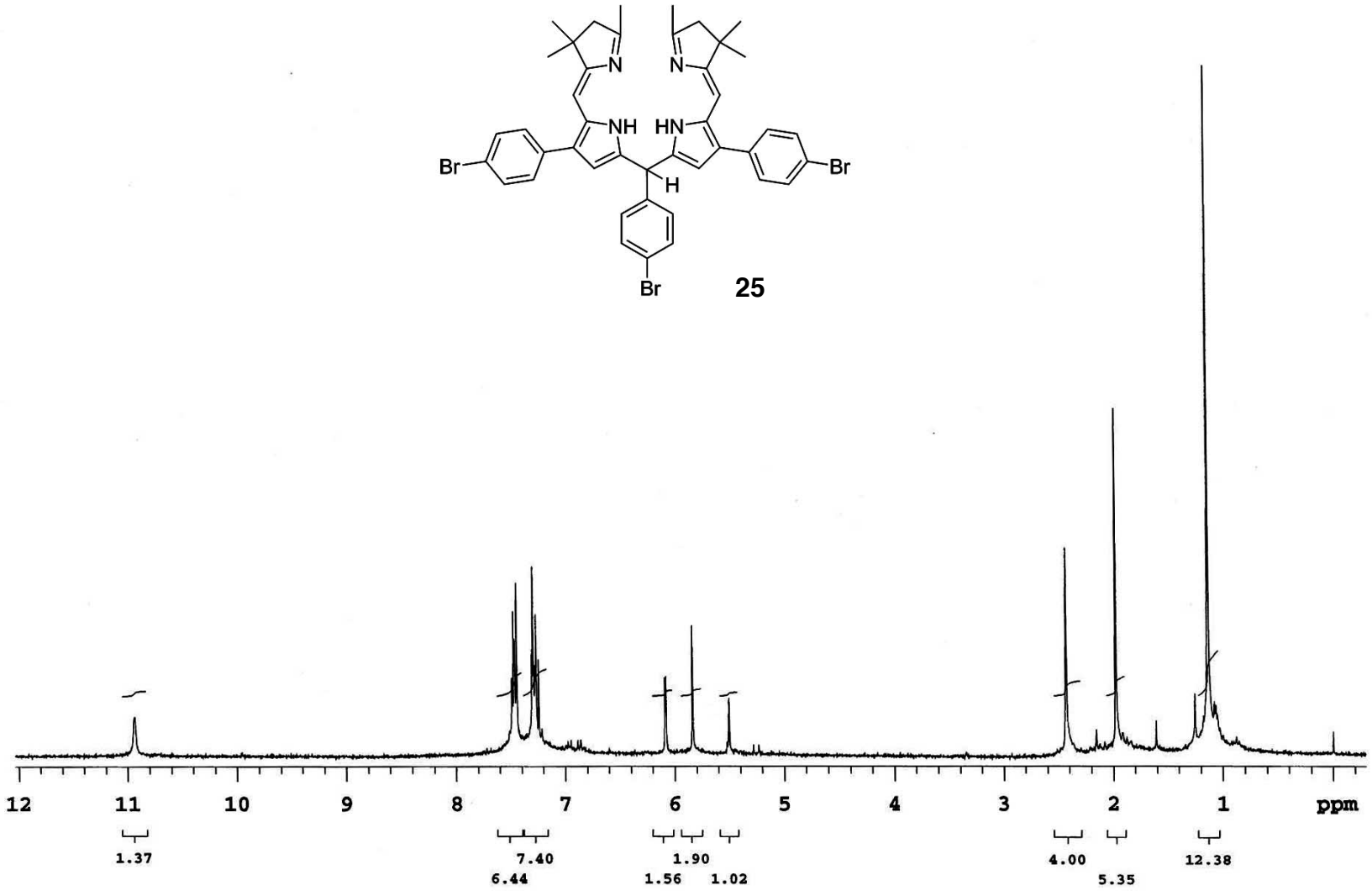

SMe
NH
NO2
19
O
O
O
9
8
7
6
5
4
3
2
1
ppm

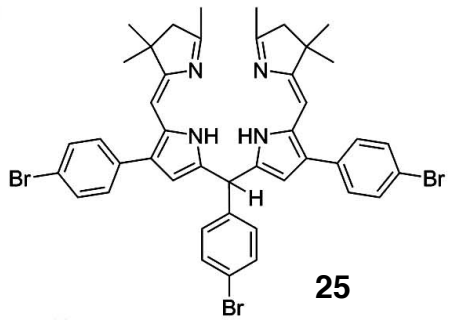


19

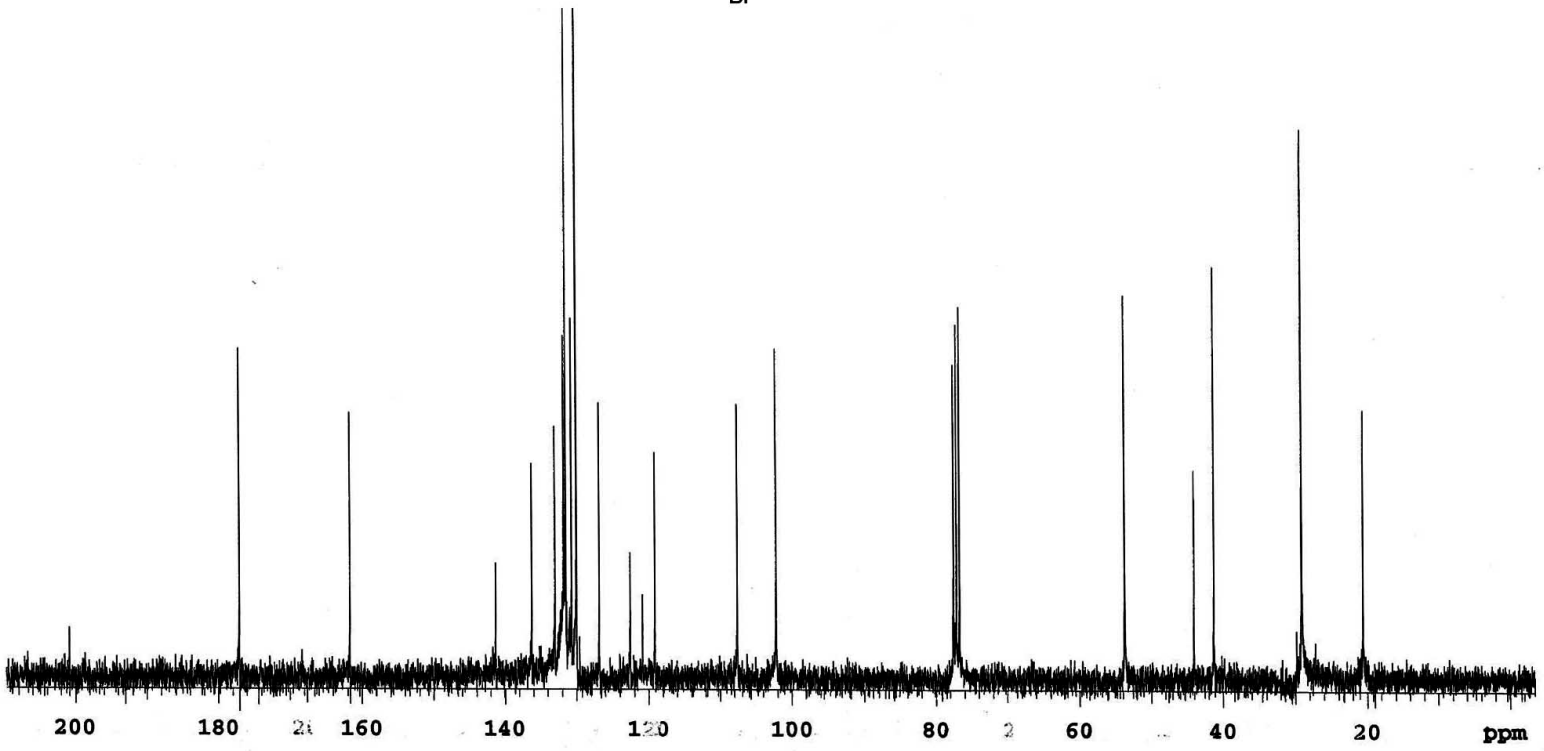


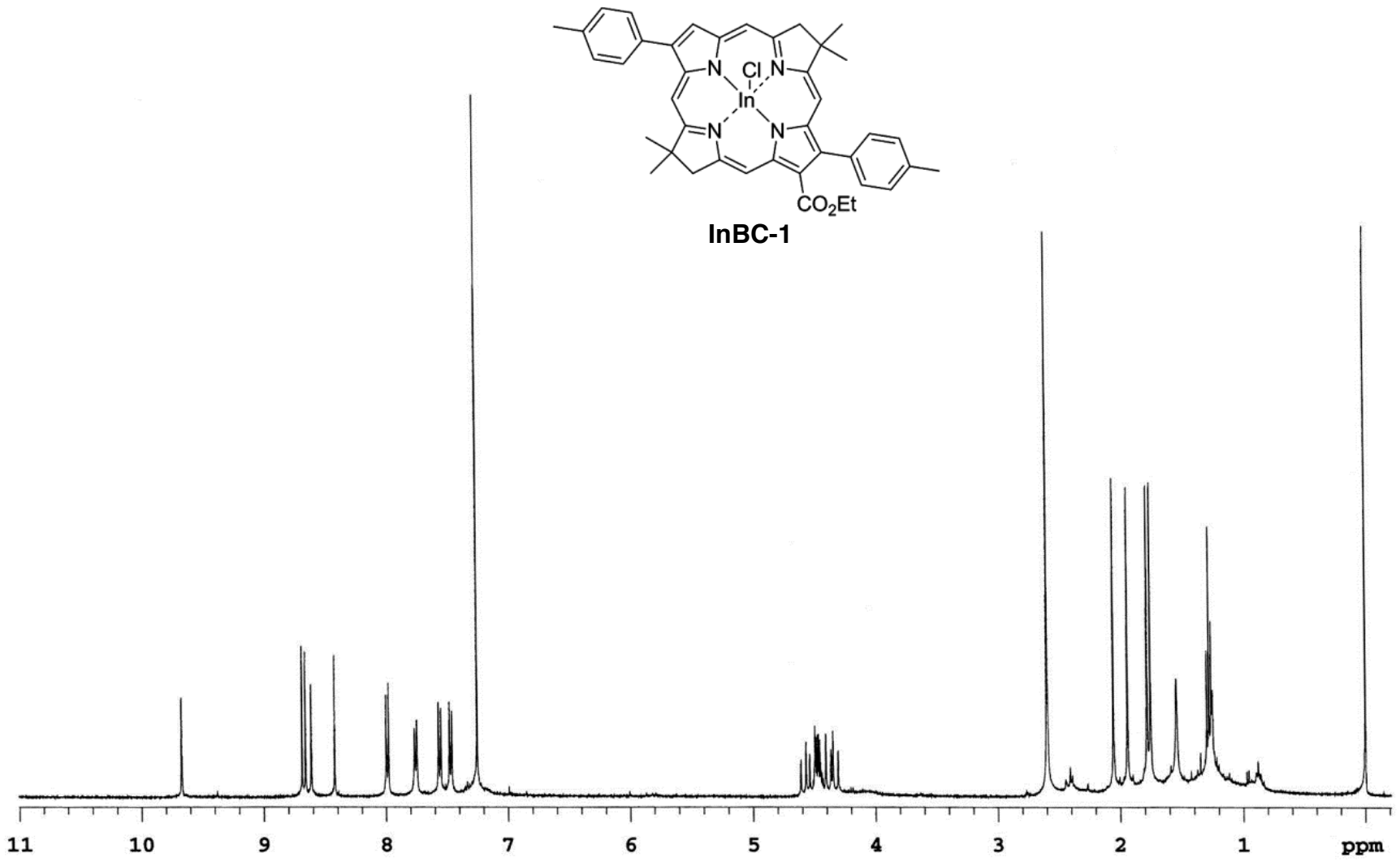

Br
NH
Br
NH
N
N
HN
EtO2C
23
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
0.86
0.84
5.11
5.25
1.15
1.04
1.17
1.17
1.11
2.00
0.30
2.16
1.01
0.63
2.97
1.88
3.80
2.76
5.17
14
19
64
46
97
91
08


N
N
NH
HN
Br
Br
H
Br
25
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.37
7.40
6.44
1.90
1.56
1.02
4.00
5.35
12.38

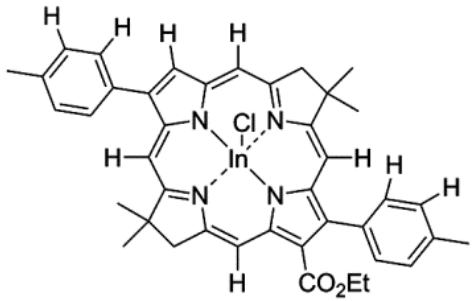


25



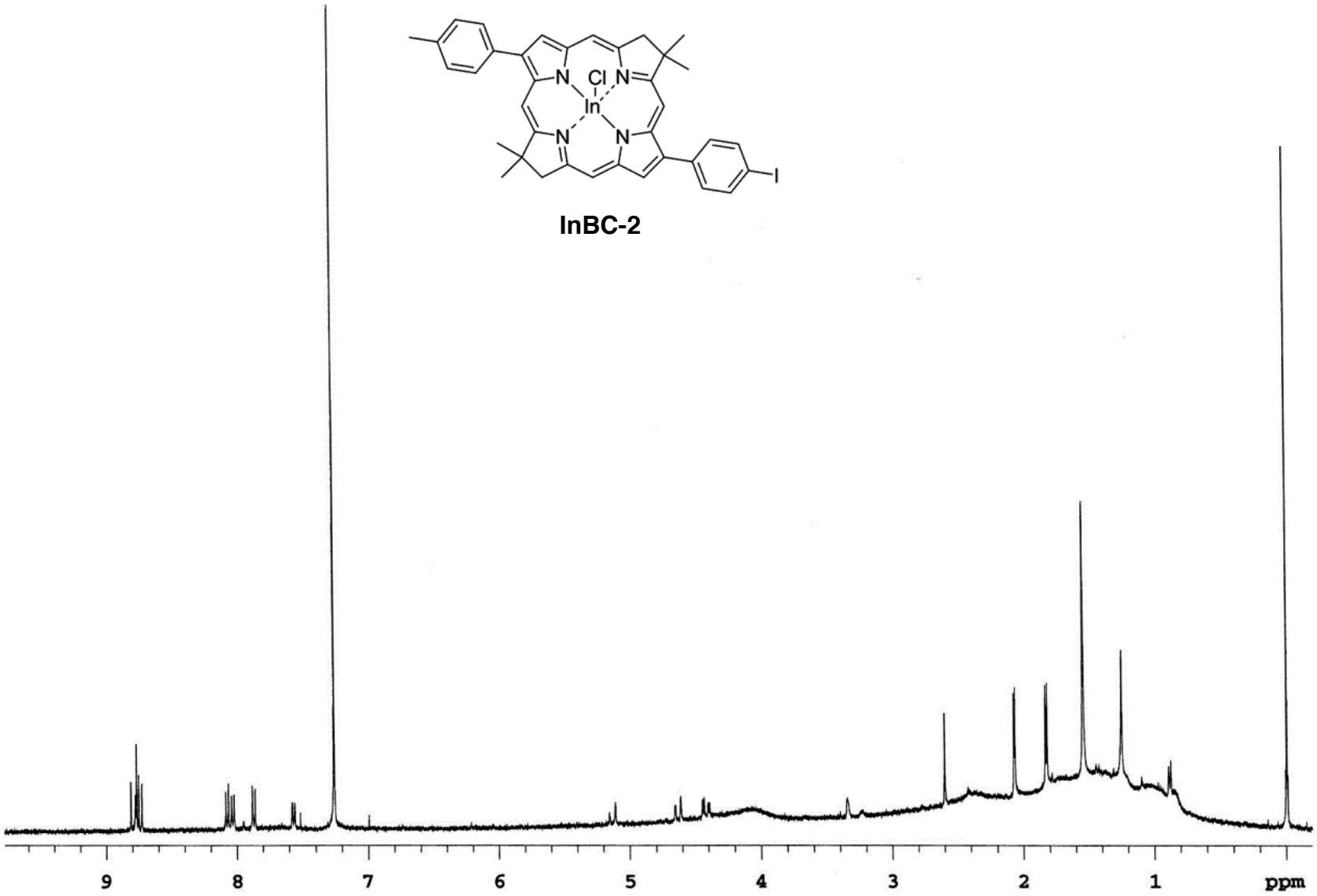


InBC-1

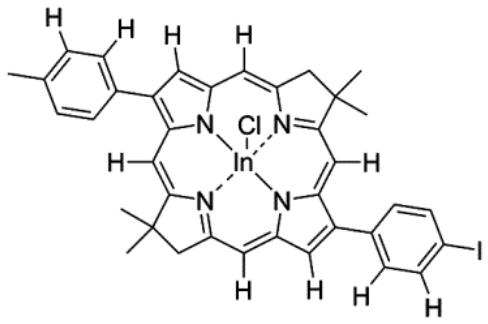

H
H
H
H
N
Cl
N
In
H
H
H
H
N
N
H
CO2Et

InBC-1

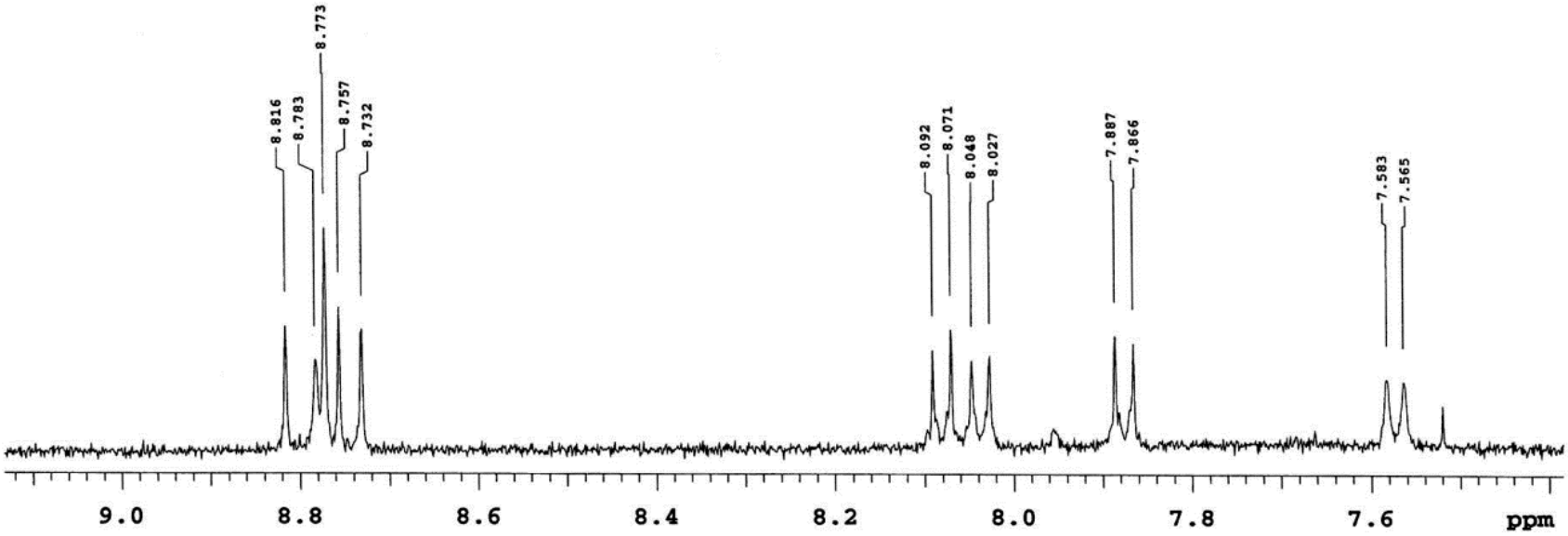
9.676
8.693
8.665
8.618
8.427
8.003
7.983
7.771
7.751
7.574
7.555
7.484
7.464
7.259
10.0
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm

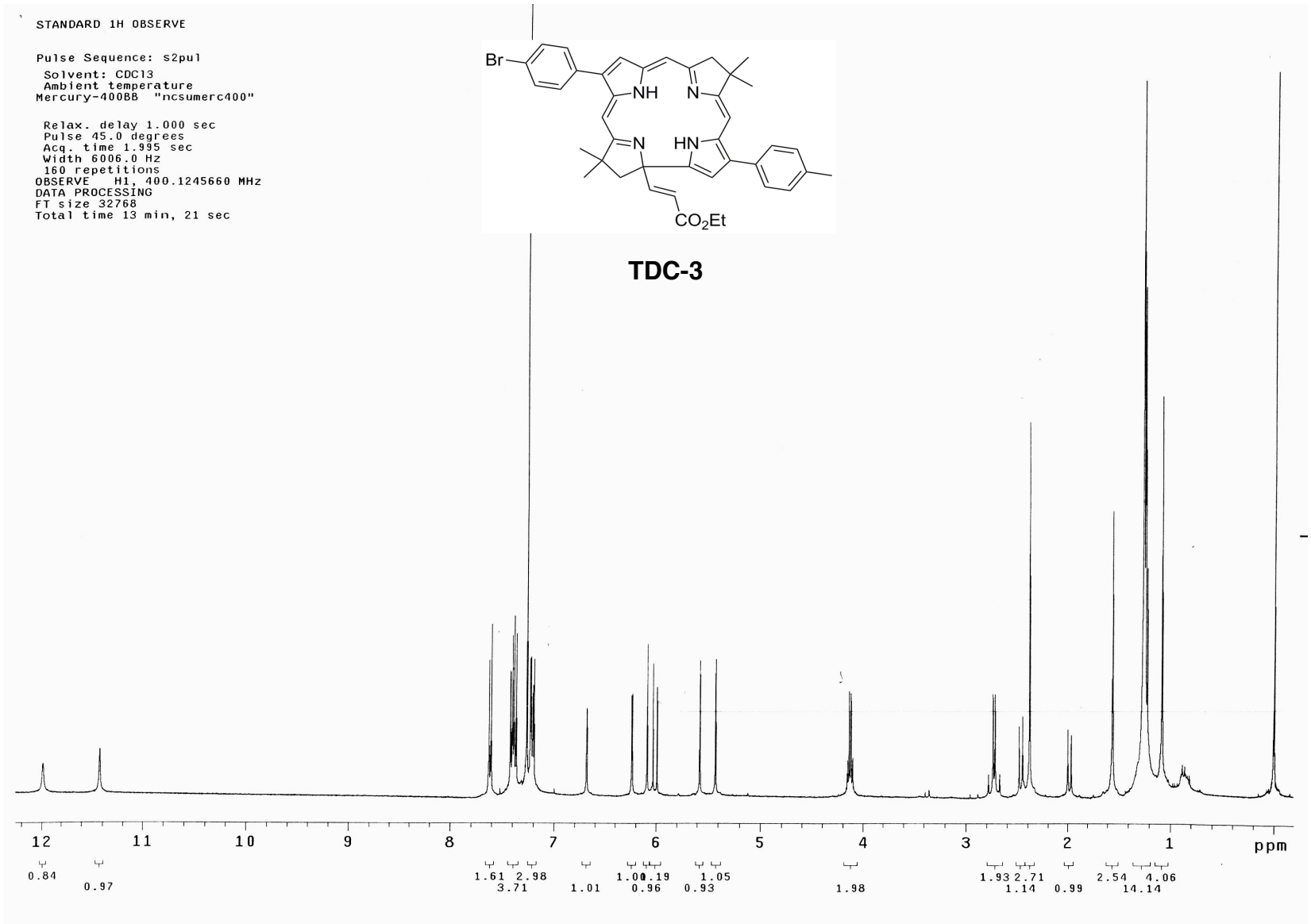


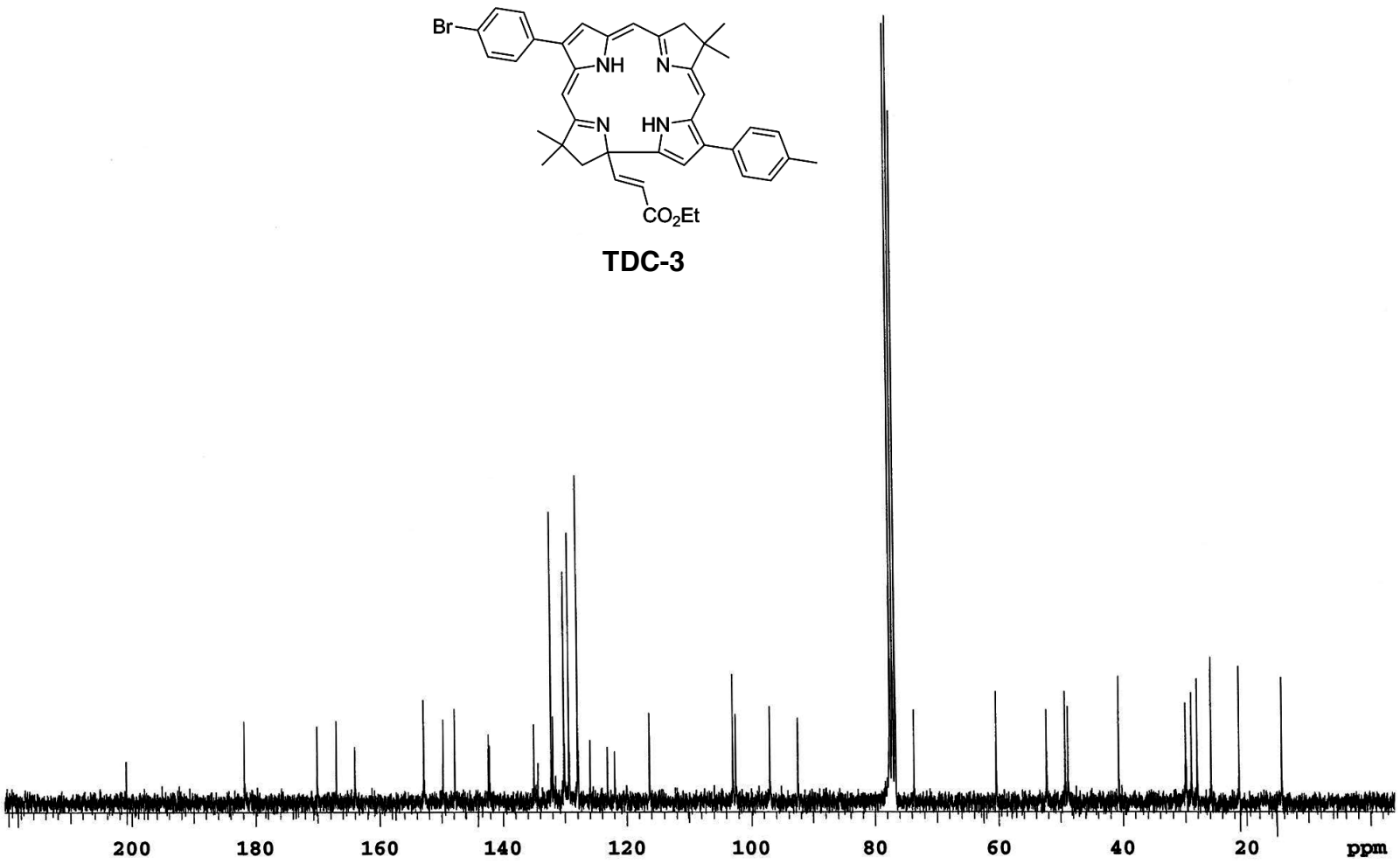
InBC-2


H
H
H
H
N
Cl
N
In
H
H
N
N
I
H
H
H
H

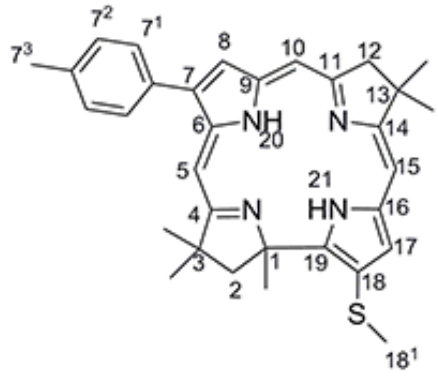
InBC-2


8.816
8.783
8.773
8.757
8.732
8.092
8.071
8.048
8.027
7.887
7.866
7.583
7.565
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm

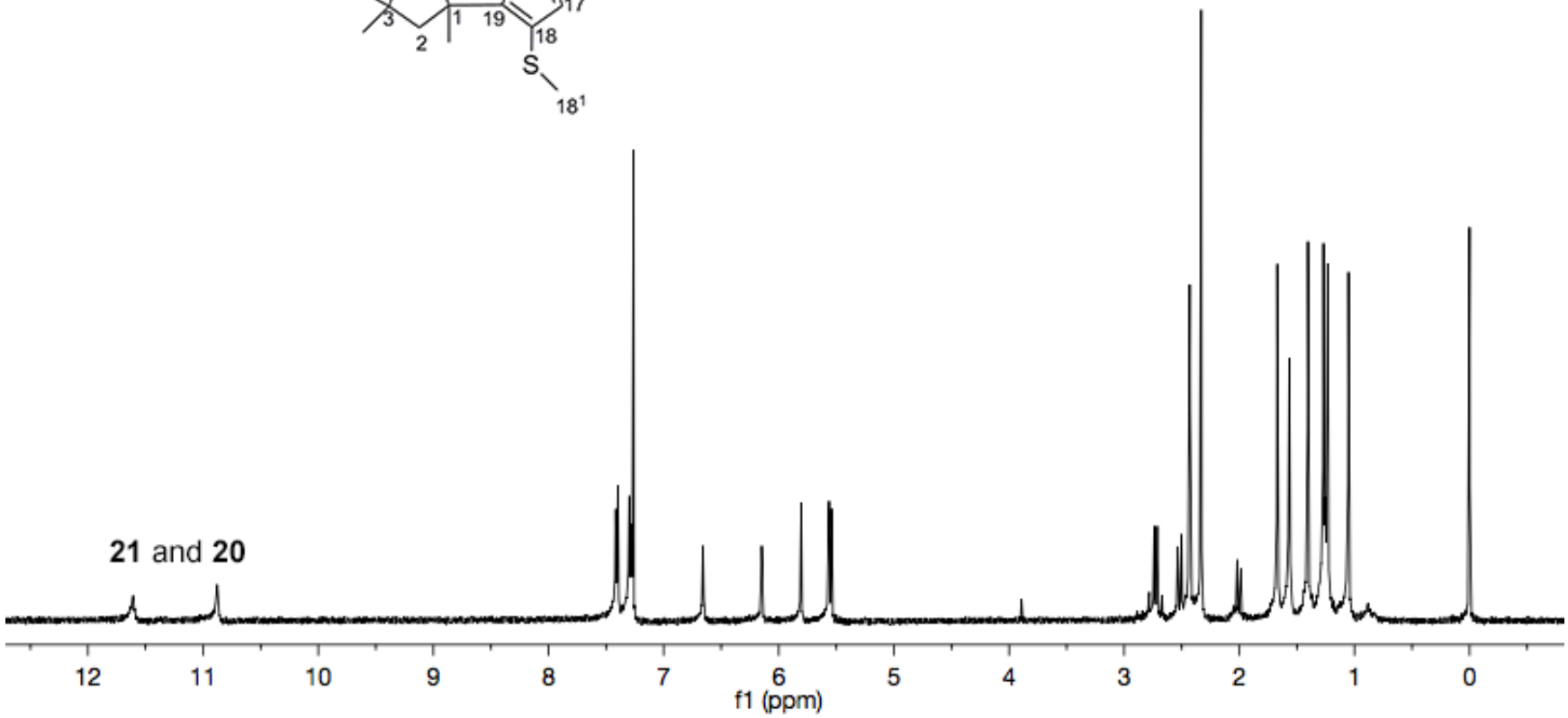

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
160 repetitions
OBSERVE H1, 400.1245660 MHz
DATA PROCESSING
FT size 32768
Total time 13 min, 21 sec
Br
NH
N
N
HN
CO2Et
TDC-3
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.84
0.97
1.61
2.98
3.71
1.01
1.00
1.19
0.96
1.05
0.93
1.98
1.93
2.71
1.14
0.99
2.54
4.06
14.14

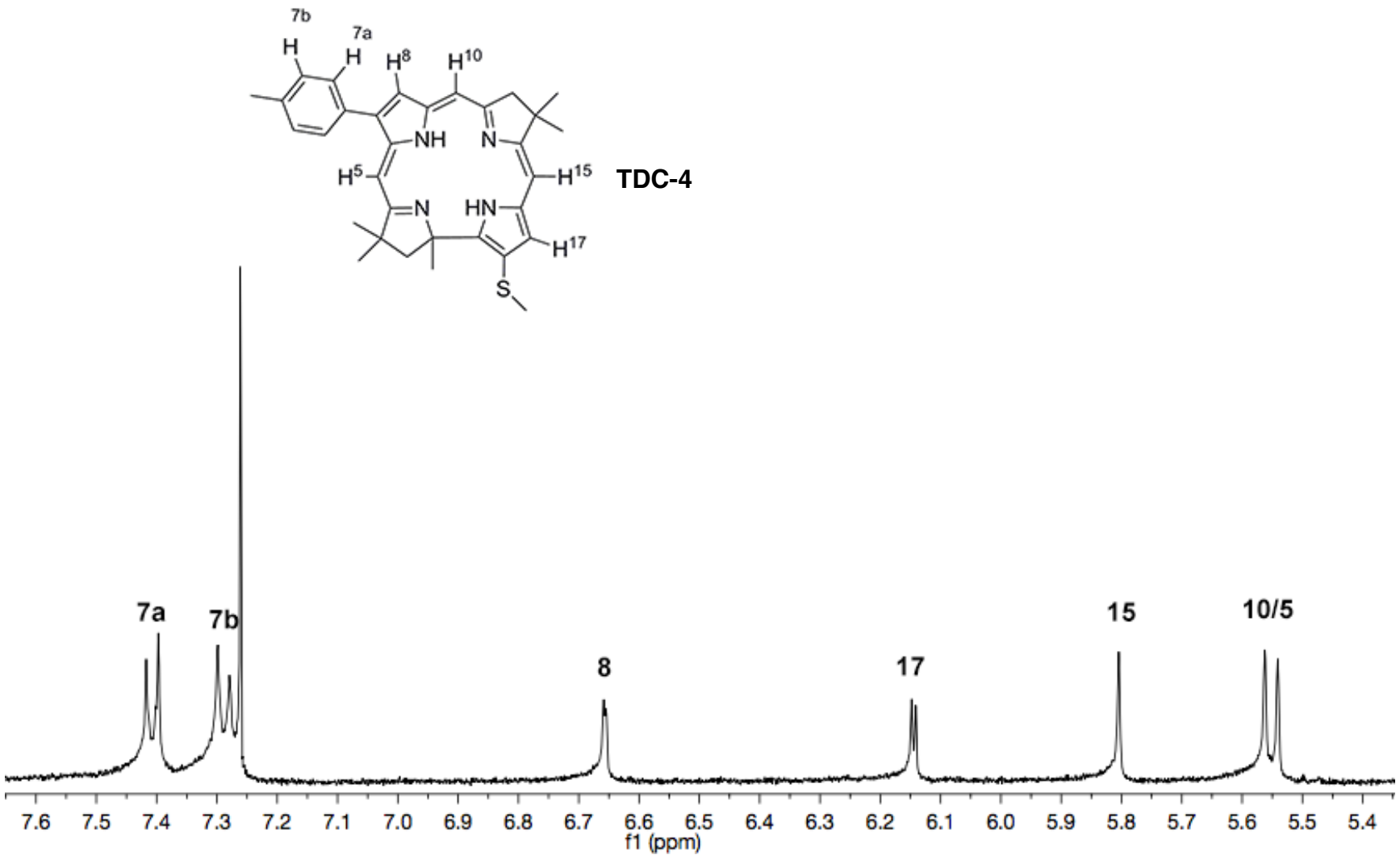


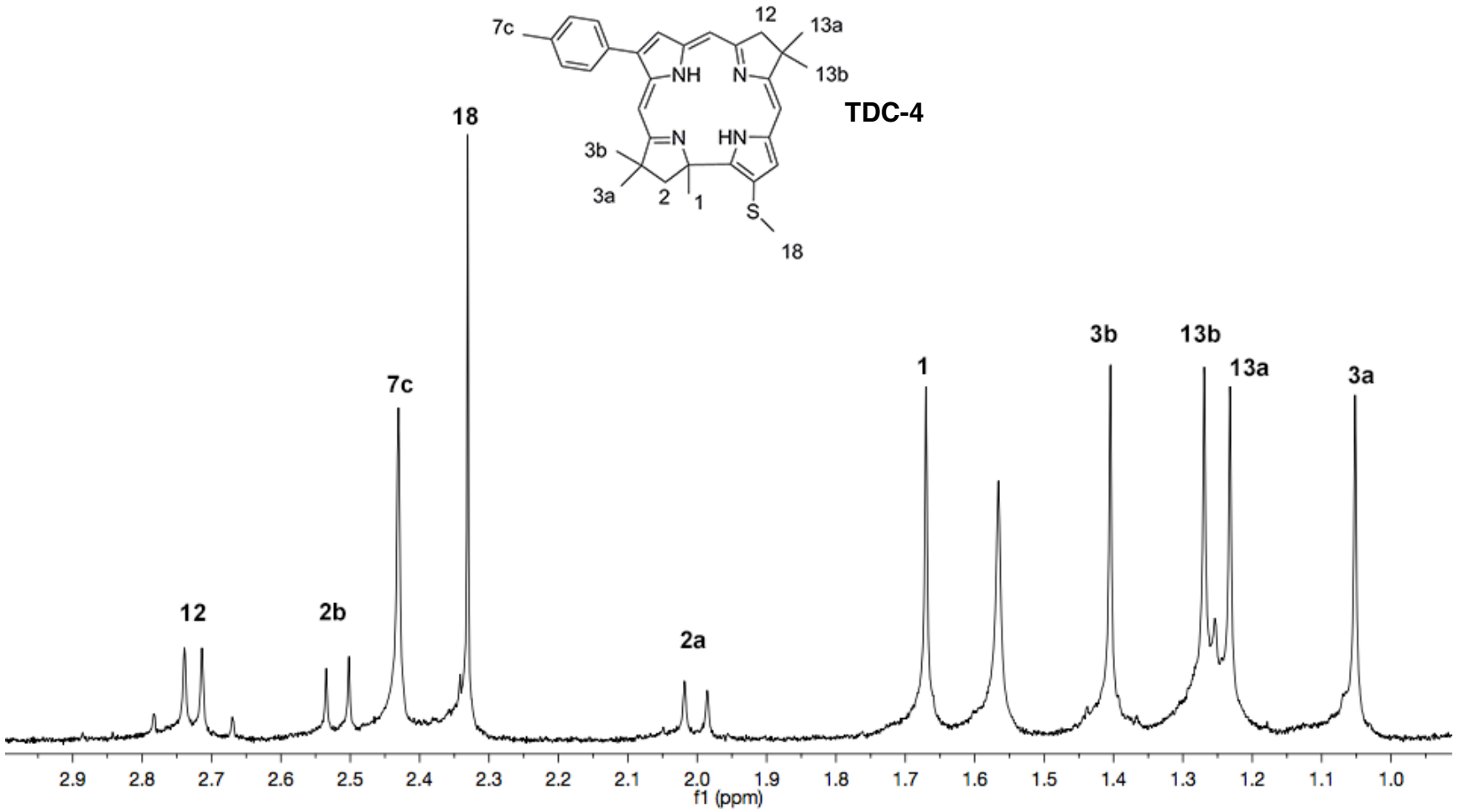
TDC-3

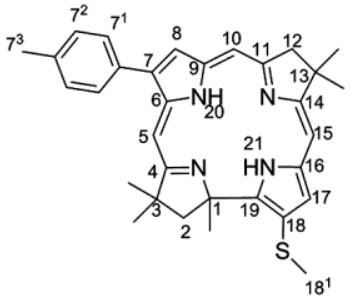

7²
7¹
7³
8
10
11
12
7
9
13
6
NH
20
N
14
5
15
21
4
N
HN
16
3
1
19
17
2
18
S
18¹

TDC-4

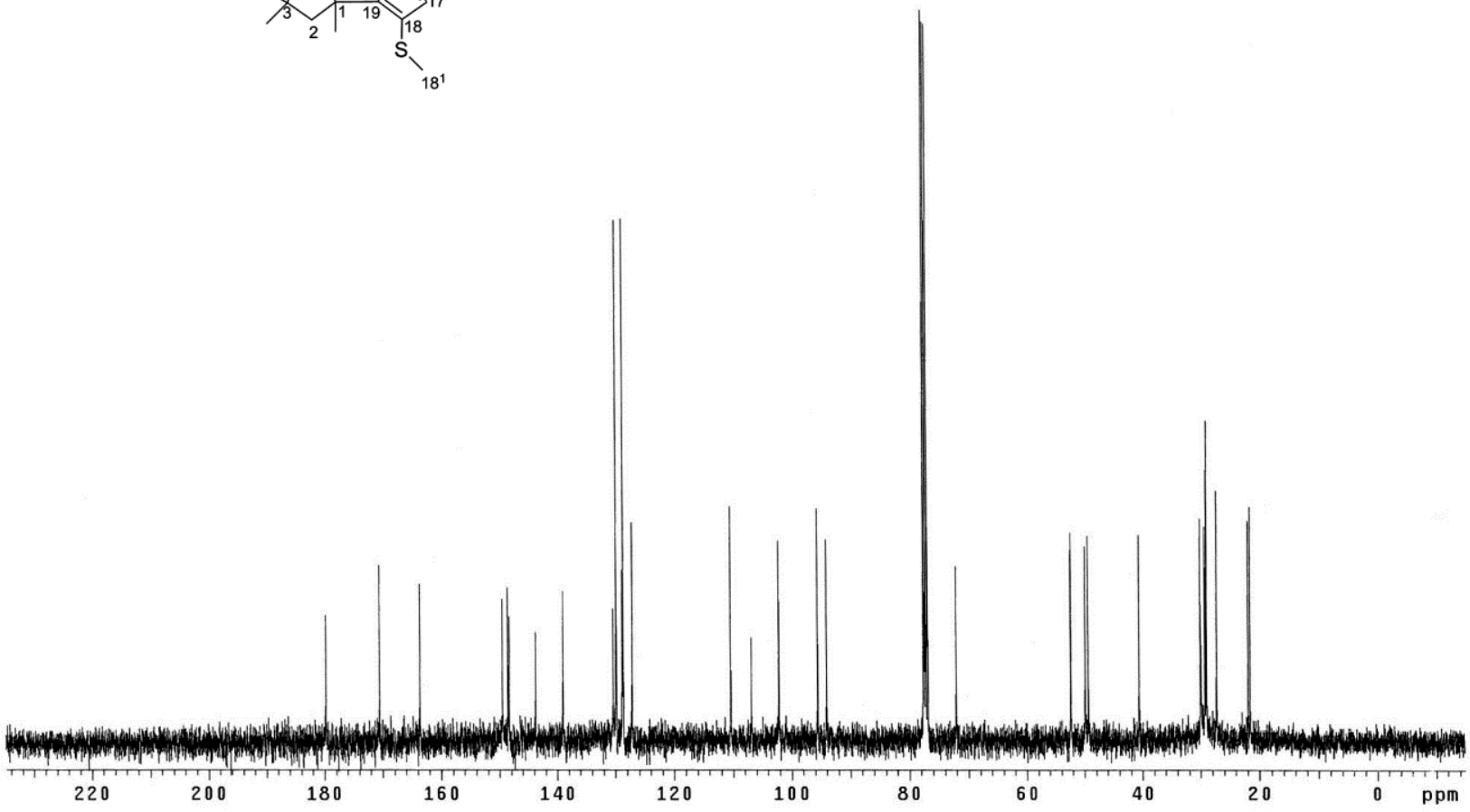

21 and 20
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

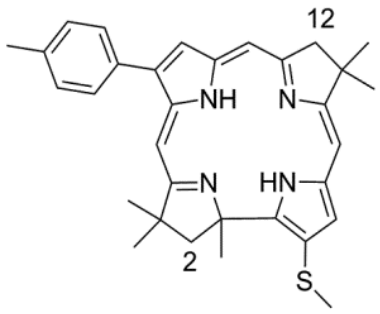

7b
7a
H
H
H8
H10
NH
N
H5
H15
N
HN
H17
S
TDC-4
7a
7b
8
17
15
10/5
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
f1 (ppm)


7c
12
13a
13b
NH
N
18
3b
N
HN
3a
2
1
S
18
TDC-4
12
2b
7c
18
2a
1
3b
13b
13a
3a
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
f1 (ppm)

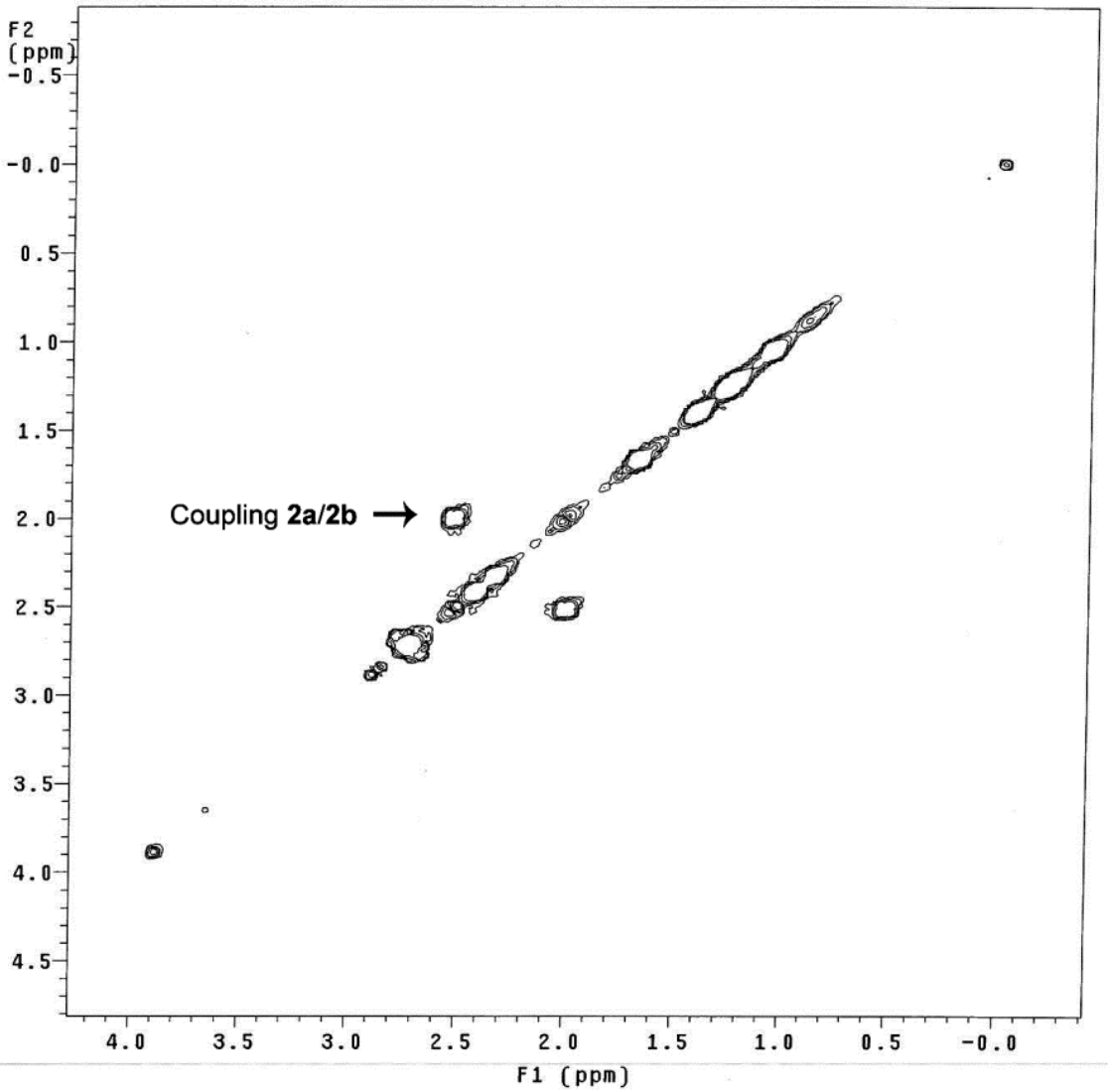

7²
7¹
7³
8
10
11
12
7
9
13
6
NH
20
N
14
5
21
15
4
N
HN
16
3
1
19
17
2
18
S
18¹

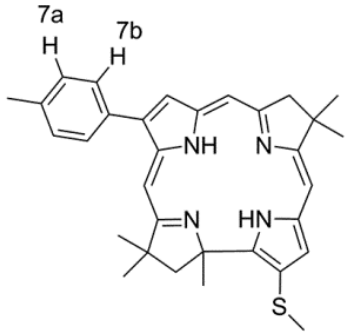
TDC-4


220
200
180
160
140
120
100
80
60
40
20
0
ppm

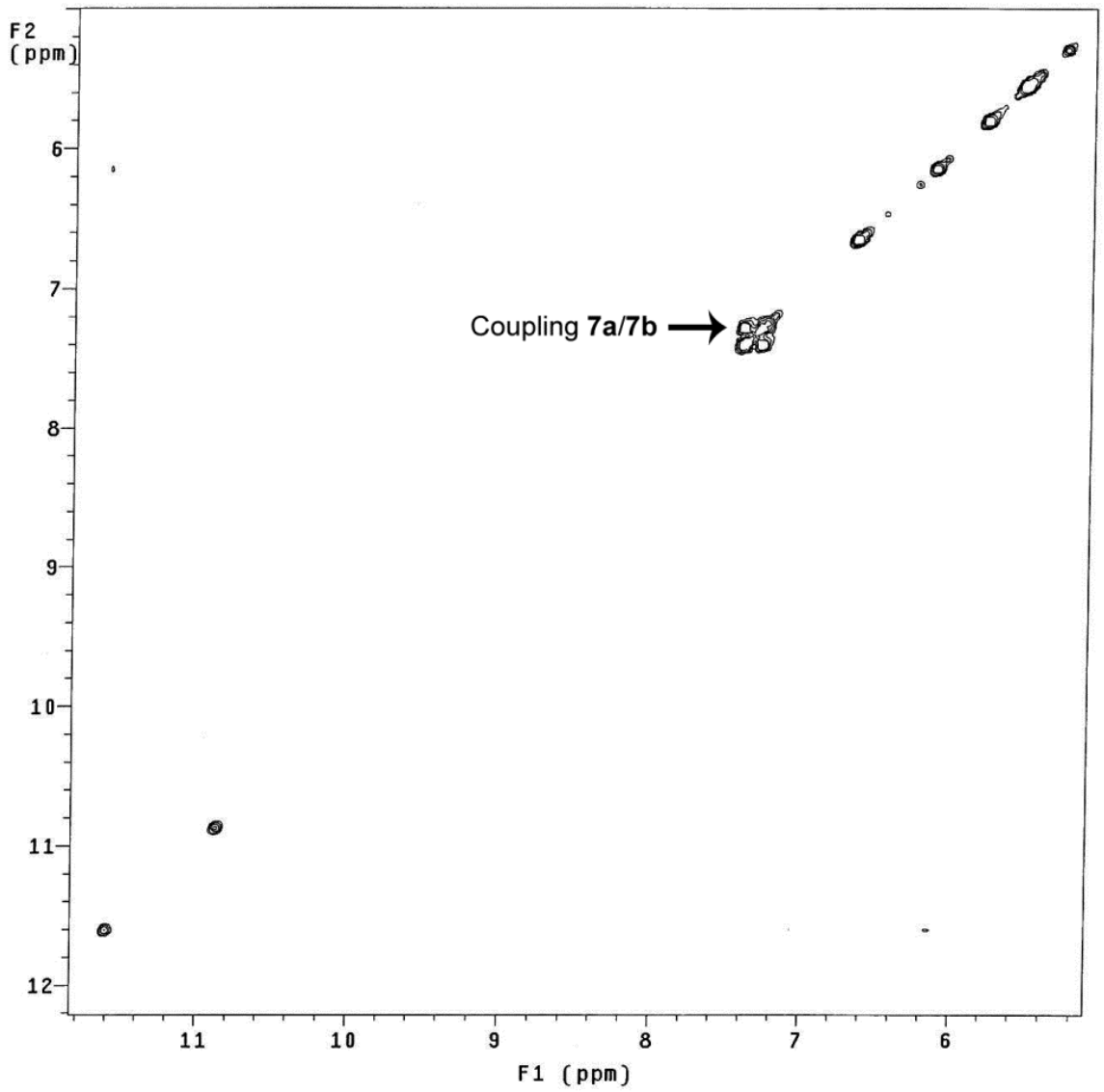

12
NH
N
N
HN
2
S

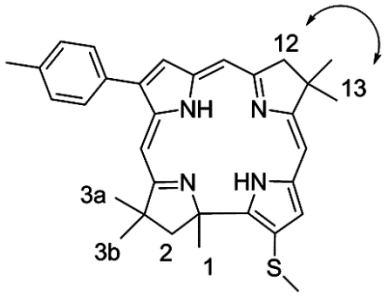
TDC-4


F2 (ppm)
-0.5
-0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Coupling 2a/2b
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
F1 (ppm)

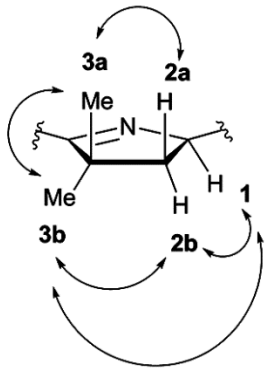

7a
H
7b
H
NH
N
N
HN
S

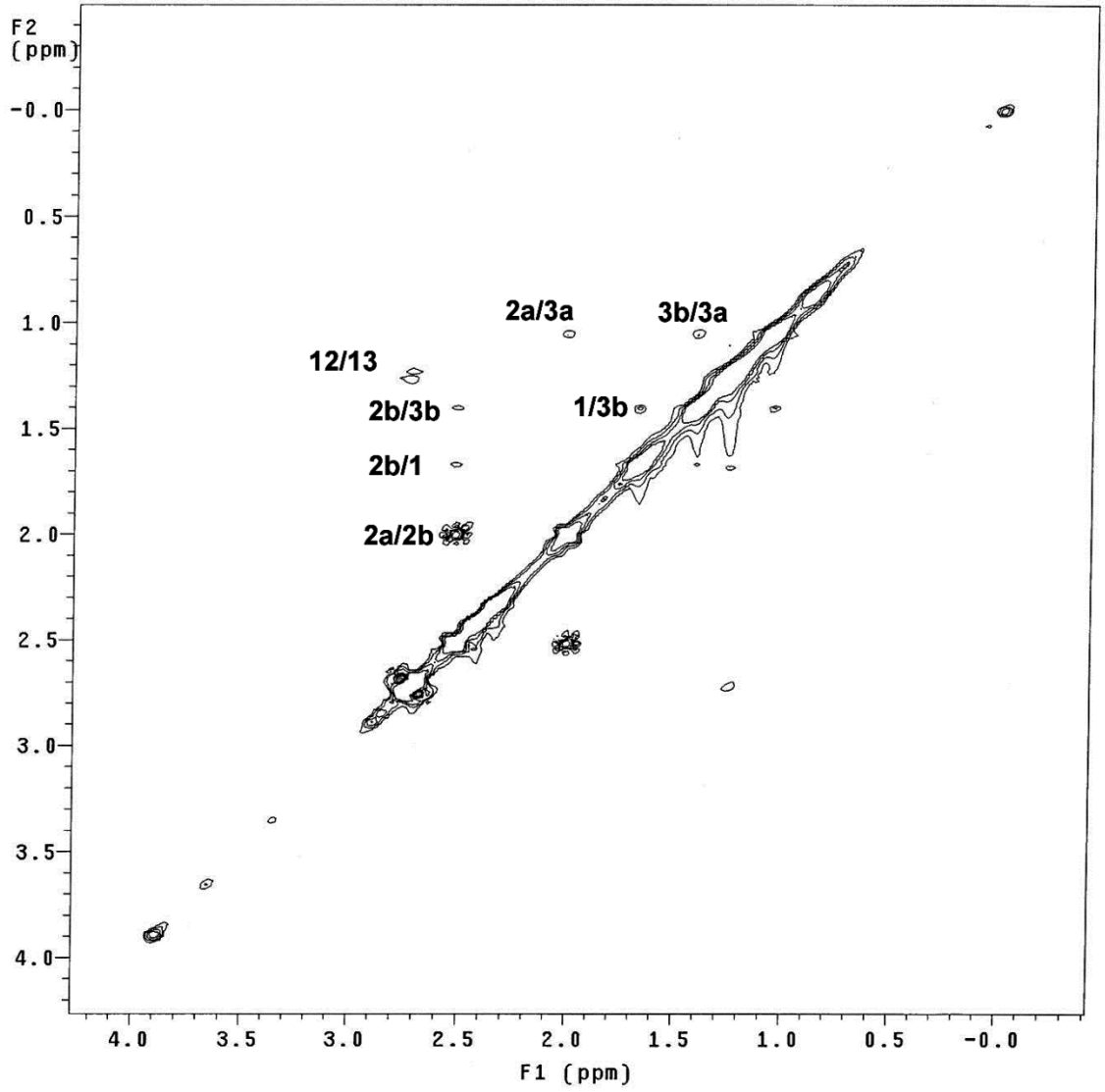
TDC-4

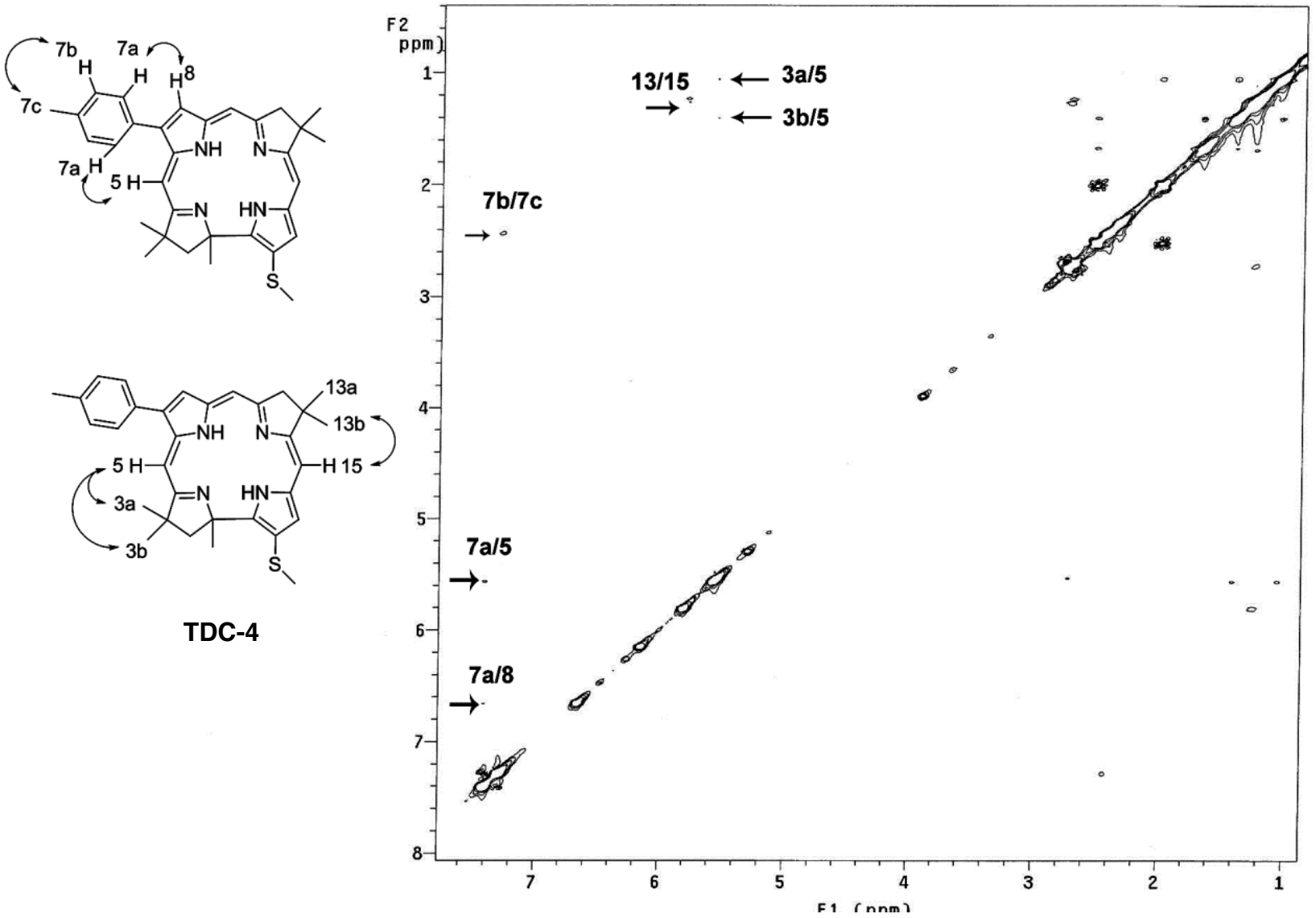

F2
(ppm)
6
7
8
9
10
11
12
Coupling 7a/7b
11
10
9
8
7
6
F1 (ppm)

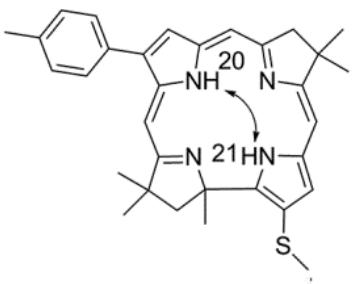

12
13
NH
N
3a
N
HN
3b
2
1
S

TDC-4

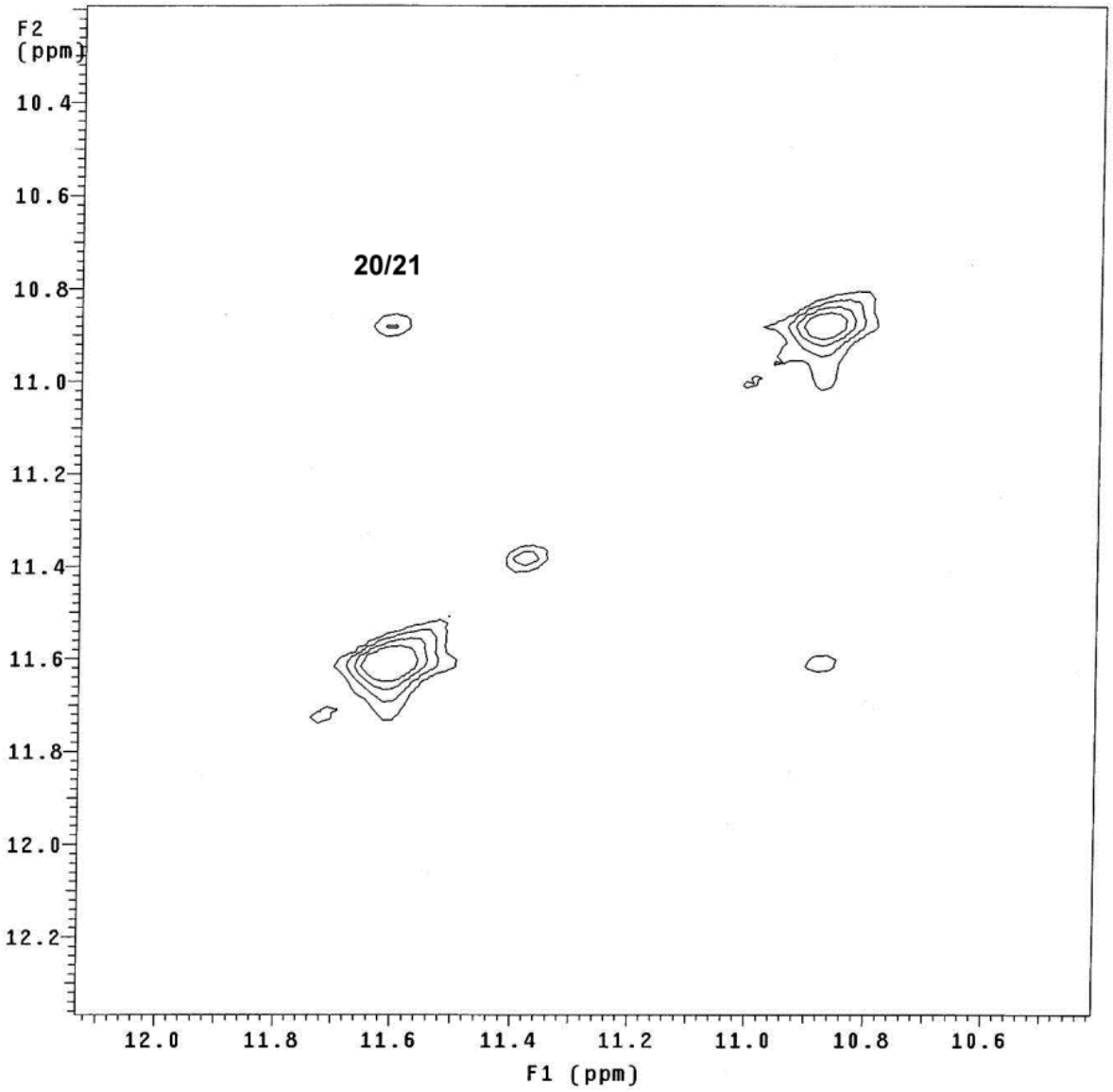

3a
2a
Me
H
N
Me
H
H
1
3b
2b

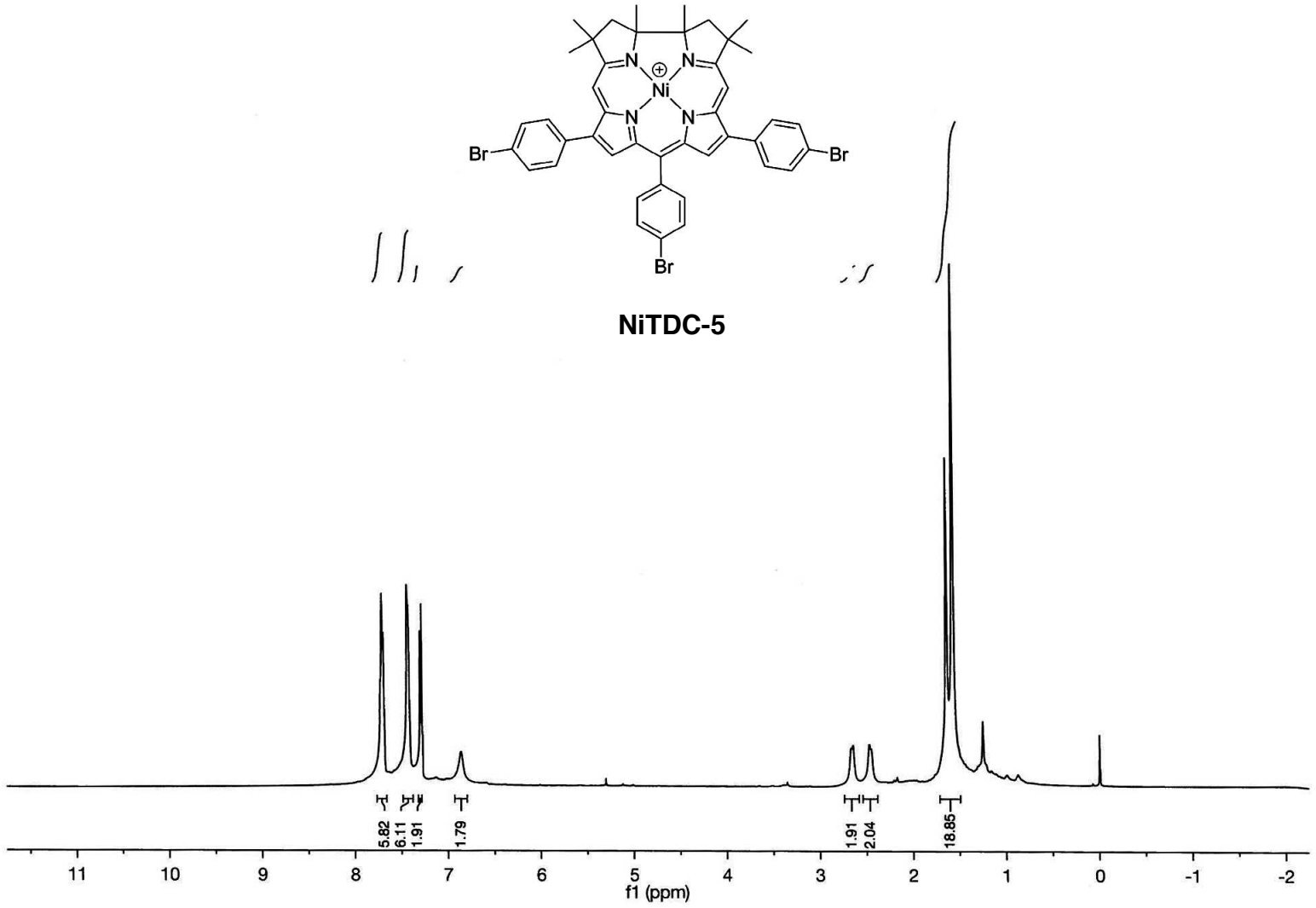

F2 (ppm)
-0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
2a/3a
3b/3a
12/13
2b/3b
1/3b
2b/1
2a/2b
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
F1 (ppm)

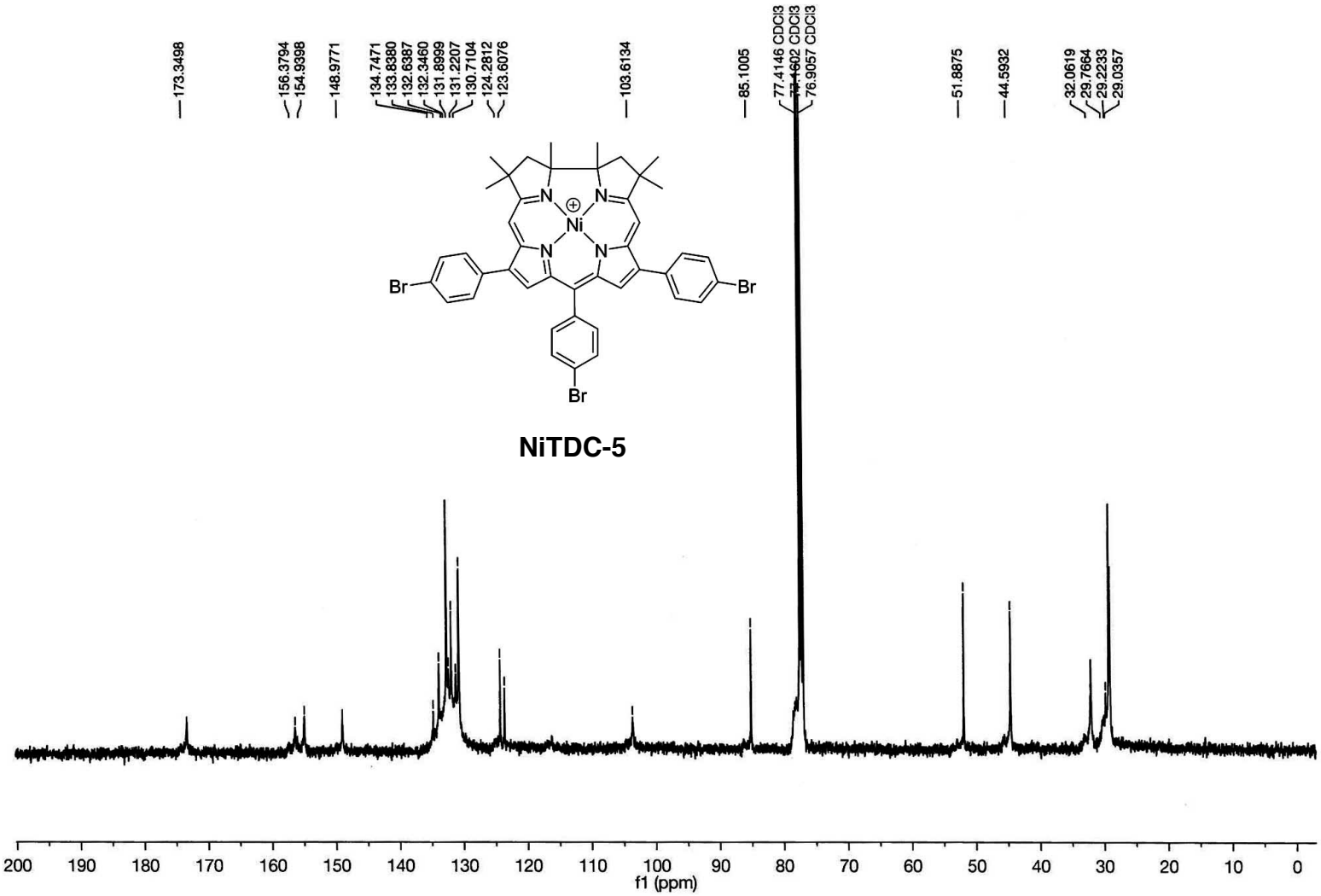

7b
7a
H
H
H8
7c
NH
N
7a H
5 H
N
HN
S
13a
13b
NH
N
5 H
H 15
3a
N
HN
3b
S
TDC-4
F2
ppm)
13/15
3a/5
3b/5
7b/7c
7a/5
7a/8
F1 (ppm)

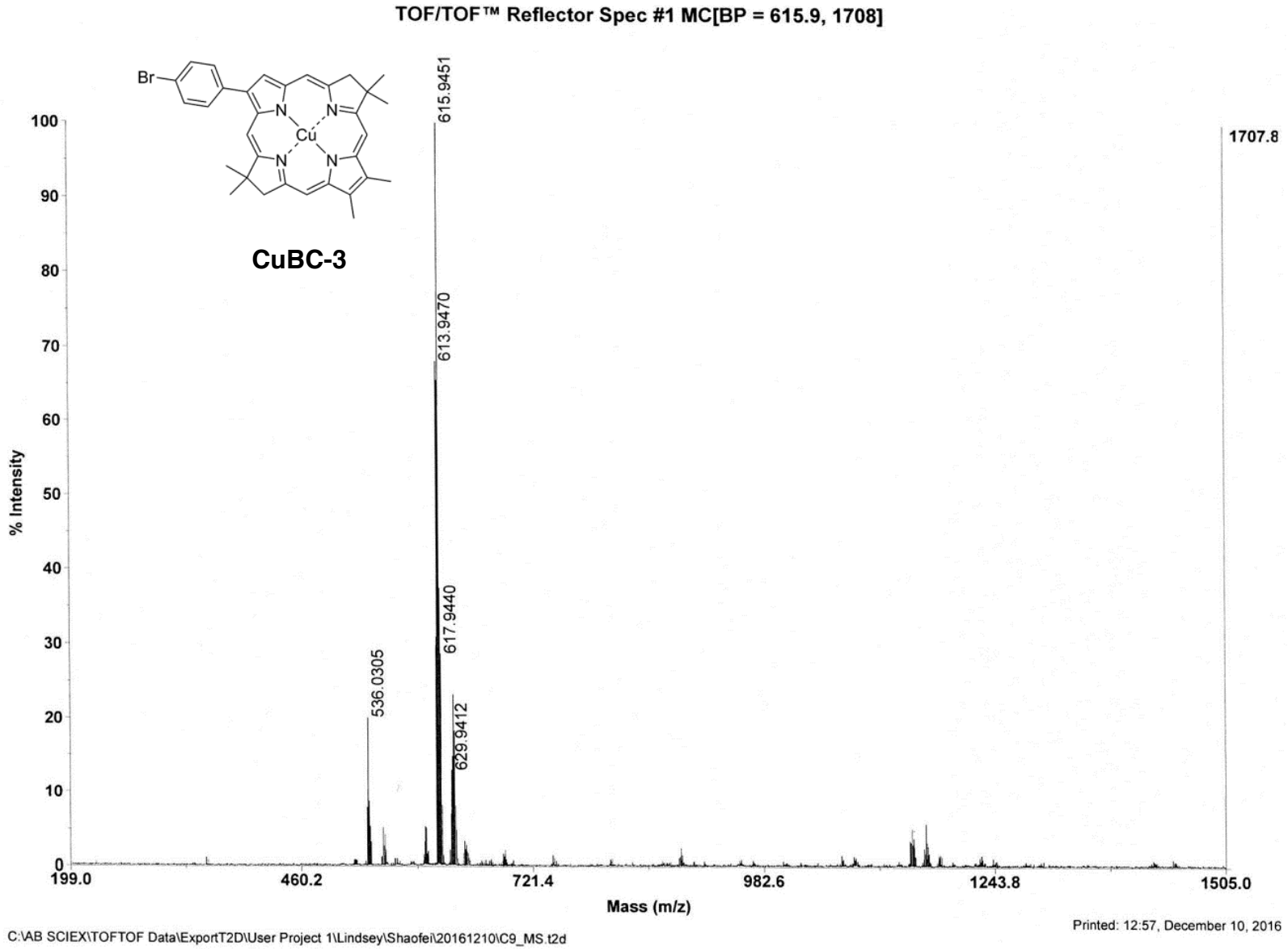

NH
20
N
N
21
HN
S

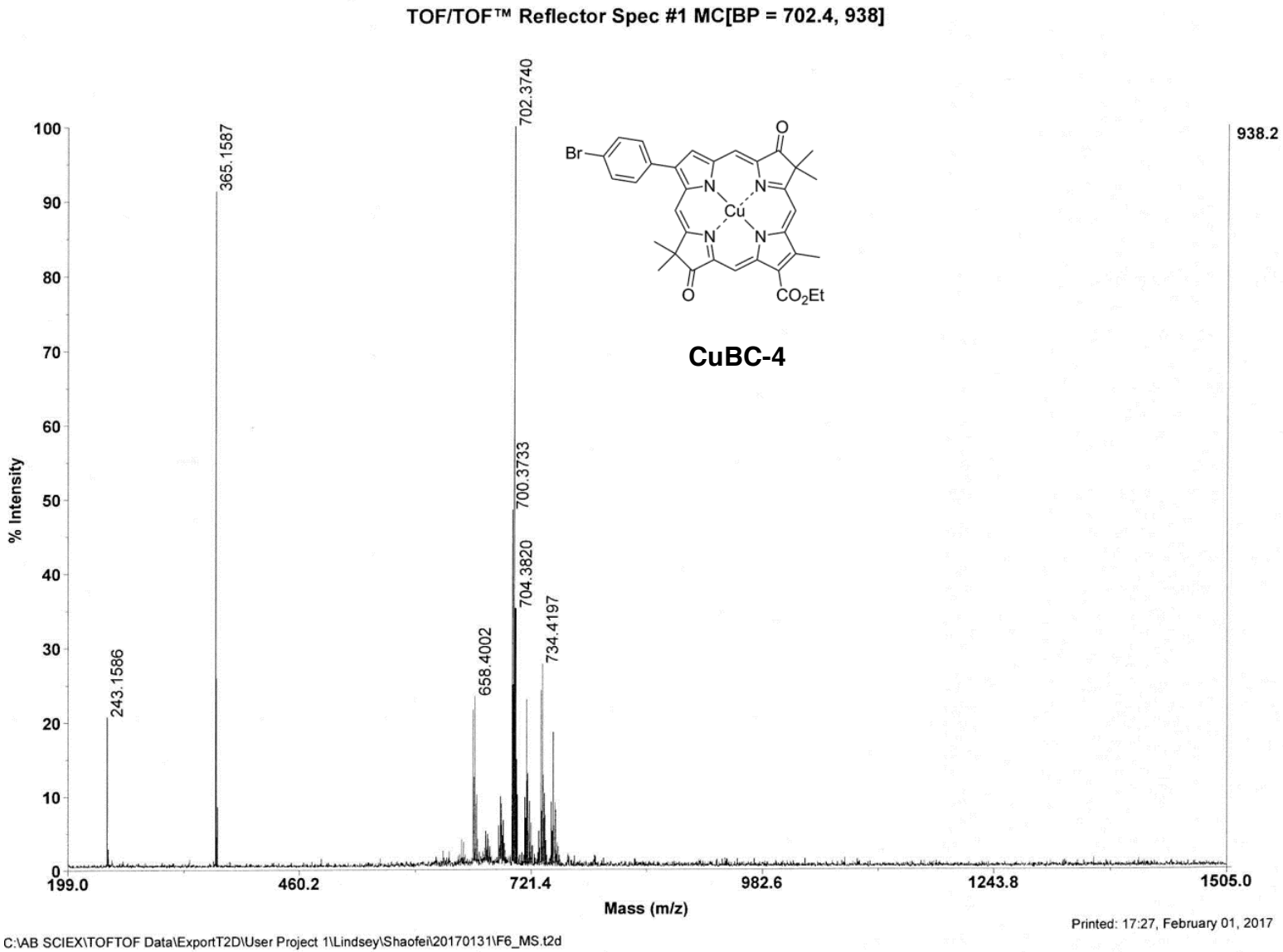
TDC-4

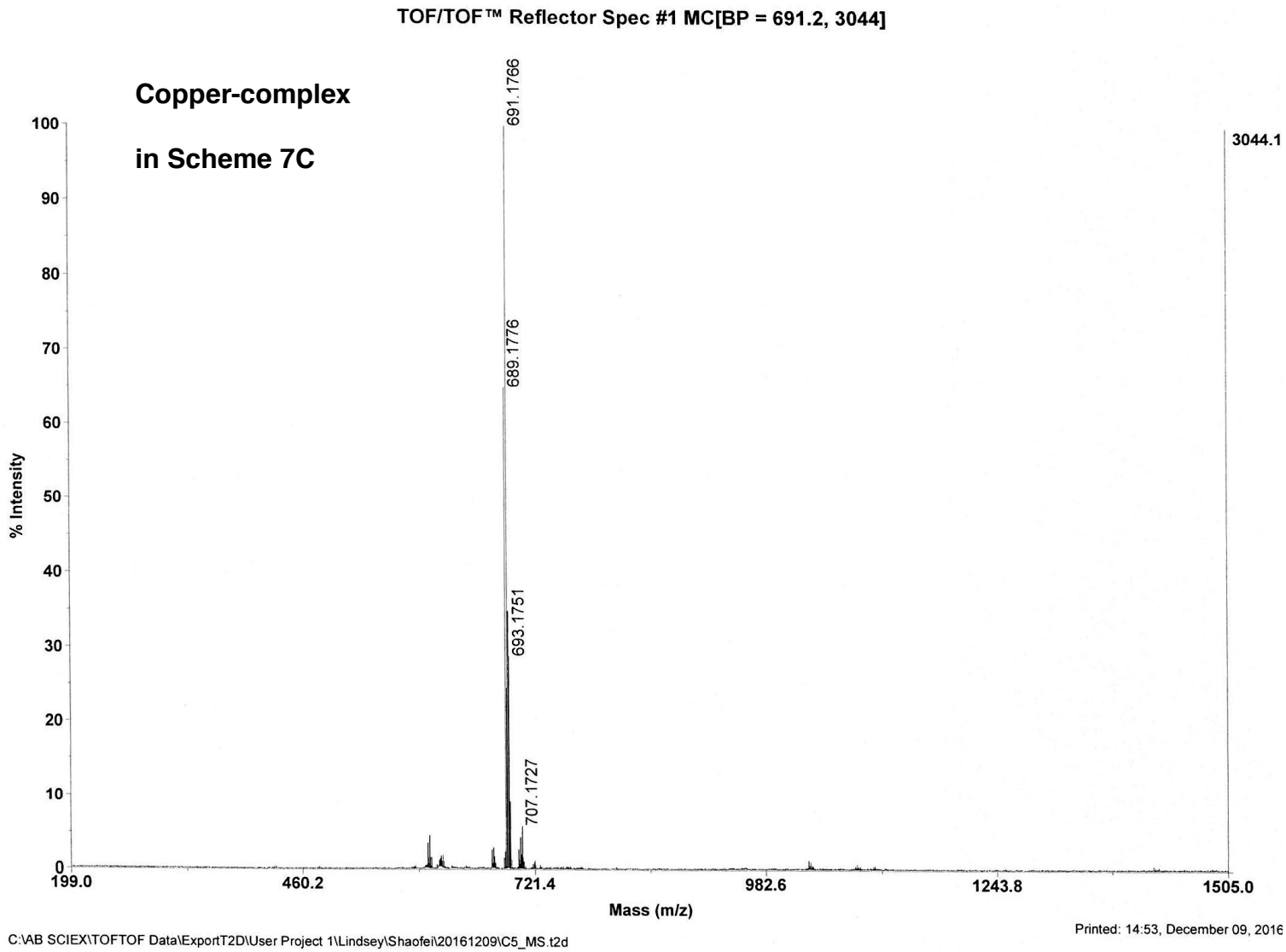

F2
(ppm)
10.4
10.6
10.8
11.0
11.2
11.4
11.6
11.8
12.0
12.2
20/21
12.0
11.8
11.6
11.4
11.2
11.0
10.8
10.6
F1 (ppm)


Br
Br
Br
Ni
N
N
N
N
NiTDC-5
5.82
6.11
1.91
1.79
1.91
2.04
18.85
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


173.3498
156.3794
154.9398
148.9771
134.7471
133.8380
132.6387
132.3460
131.8999
131.2207
130.7104
124.2812
123.6076
103.6134
85.1005
77.4146 CDCl3
77.1602 CDCl3
76.9057 CDCl3
51.8875
44.5932
32.0619
29.7664
29.2233
29.0357
Ni
Br
Br
Br
NiTDC-5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TOF/TOF™ Reflector Spec #1 MC[BP = 615.9, 1708]
Br
N
N
Cu
N
N
CuBC-3
615.9451
613.9470
617.9440
536.0305
629.9412
1707.8
% Intensity
100
90
80
70
60
50
40
30
20
10
0
199.0
460.2
721.4
982.6
1243.8
1505.0
Mass (m/z)
C:\AB SCIEX\TOFTOF Data\ExportT2D\User Project 1\Lindsey\Shaofei\20161210\C9_MS.t2d
Printed: 12:57, December 10, 2016


TOF/TOF™ Reflector Spec #1 MC[BP = 702.4, 938]
702.3740
365.1587
938.2
700.3733
704.3820
734.4197
658.4002
243.1586
% Intensity
Mass (m/z)
199.0
460.2
721.4
982.6
1243.8
1505.0
Br
Cu
N
O
CO2Et
CuBC-4
Printed: 17:27, February 01, 2017
C:\AB SCIEX\TOFTOF Data\ExportT2D\User Project 1\Lindsey\Shaofei\20170131\F6_MS.t2d


TOF/TOF™ Reflector Spec #1 MC[BP = 691.2, 3044]
Copper-complex
in Scheme 7C
691.1766
3044.1
689.1776
693.1751
707.1727
% Intensity
100
90
80
70
60
50
40
30
20
10
0
199.0
460.2
721.4
982.6
1243.8
1505.0
Mass (m/z)
C:\AB SCIEX\TOFTOF Data\ExportT2D\User Project 1\Lindsey\Shaofei\20161209\C5_MS.t2d
Printed: 14:53, December 09, 2016

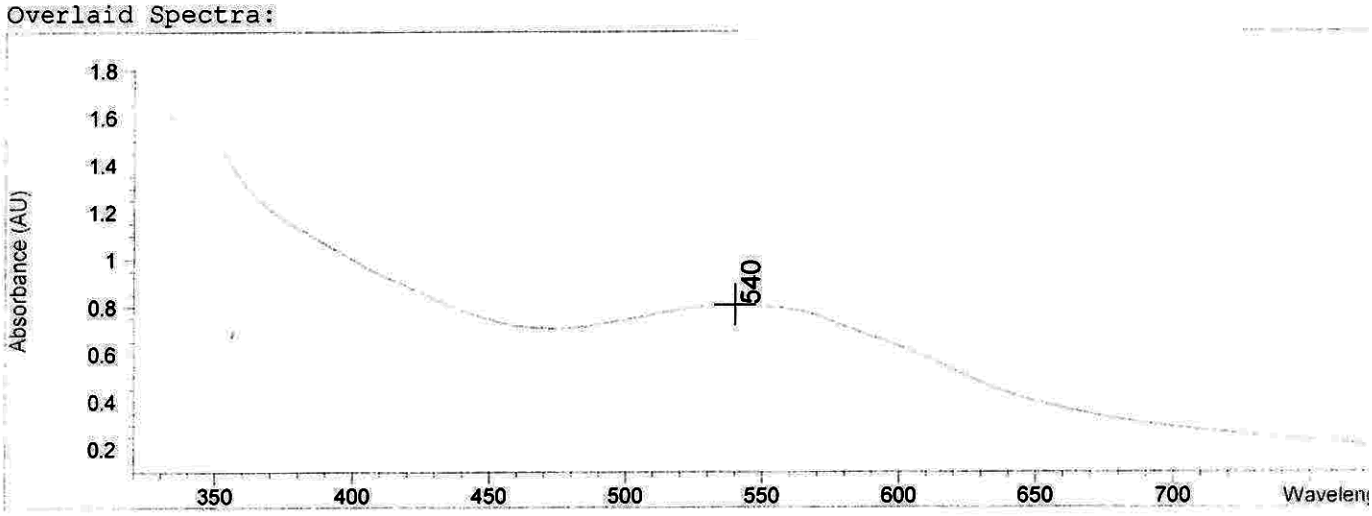
Spectrum/Peak Report Date 12/9/2016 Time 13:39:12 Page 1 o

Copper-complex

in Scheme 7C

Method file : <untitled>
Information : Default Method
Data File : <untitled>

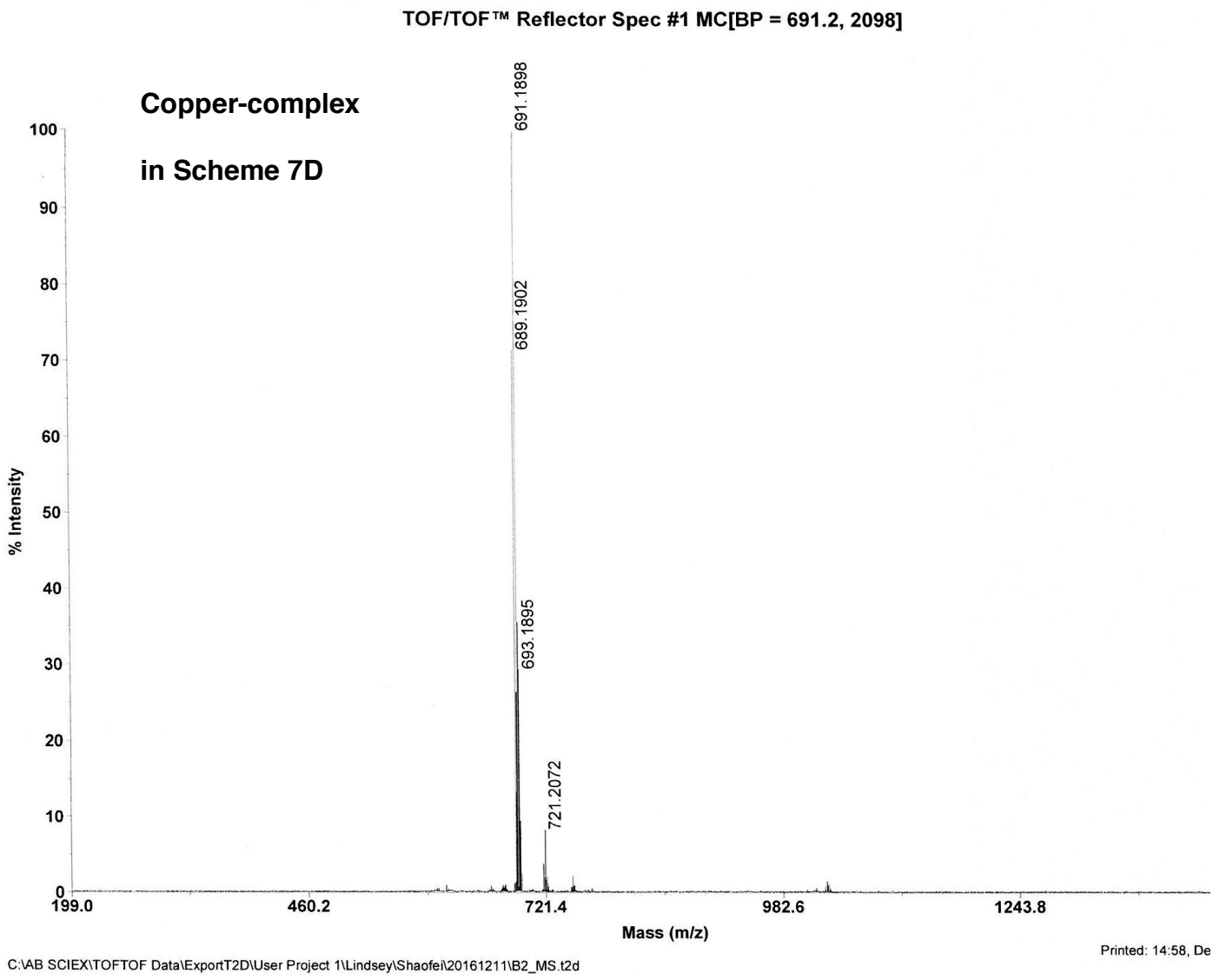
Overlaid Spectra:



#	Name	Peaks(nm)	Abs(AU)
1		540.0	0.80701

Report generated by : Lindsey Lab

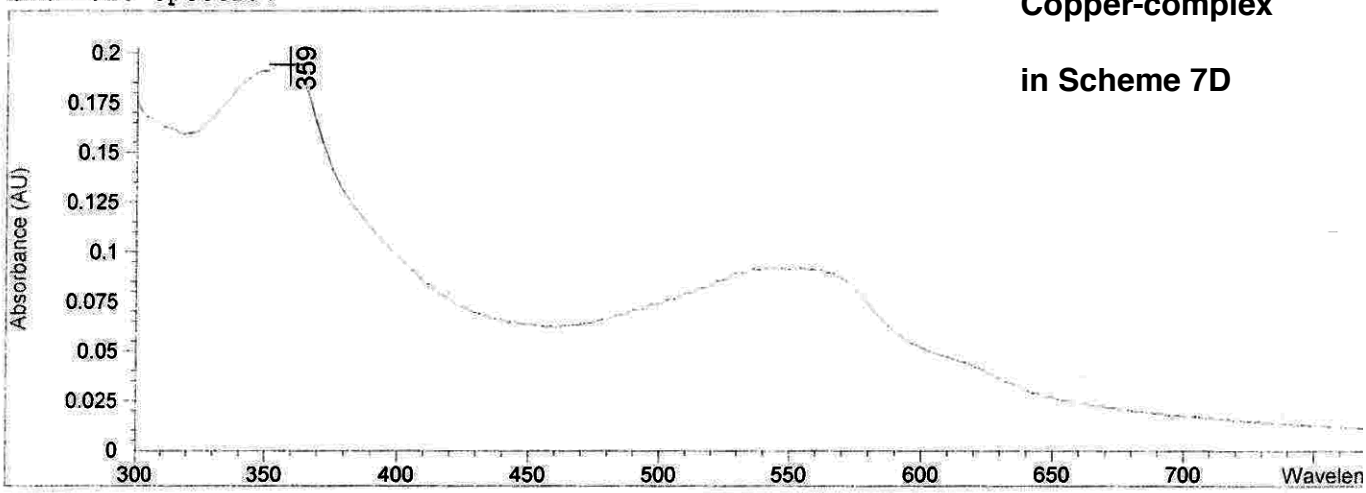
Signature: .....


TOF/TOF™ Reflector Spec #1 MC[BP = 691.2, 2098]
Copper-complex
in Scheme 7D
691.1898
689.1902
693.1895
721.2072
% Intensity
100
90
80
70
60
50
40
30
20
10
0
199.0
460.2
721.4
982.6
1243.8
Mass (m/z)
Printed: 14:58, De
C:\AB SCIEX\TOFTOF Data\ExportT2D\User Project 1\Lindsey\Shaofei\20161211\B2_MS.t2d

Spectrum/Peak Report Date 12/12/2016 Time 14:42:01 Page 1

Method file : <untitled>
Information : Default Method
Data File : C:\CHEM32\1\DATA\SHAOFEI\CUBILIN-2\CUBILIN-2.SD Created : 12/12/16 14:40:58

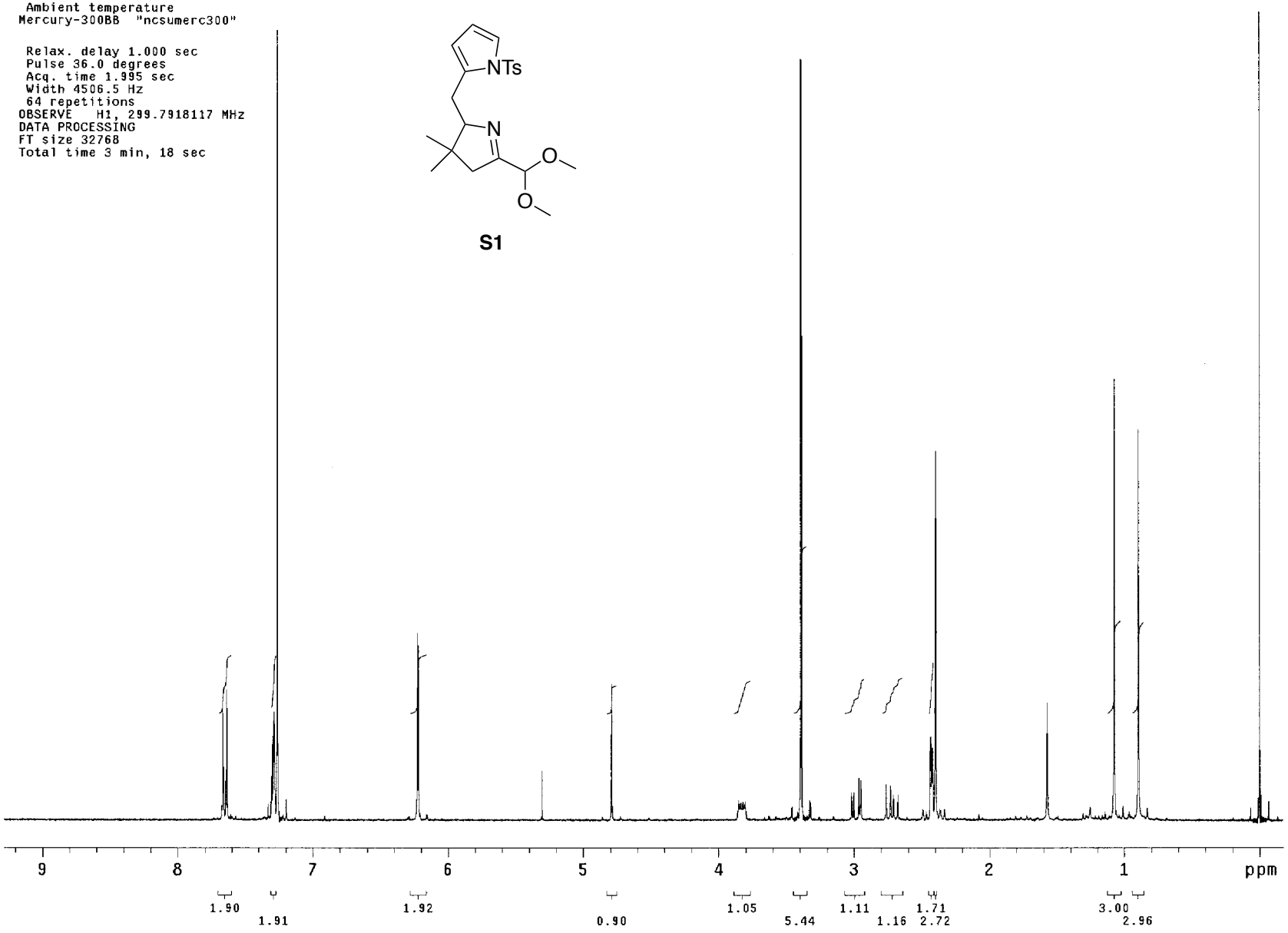
Overlaid Spectra:

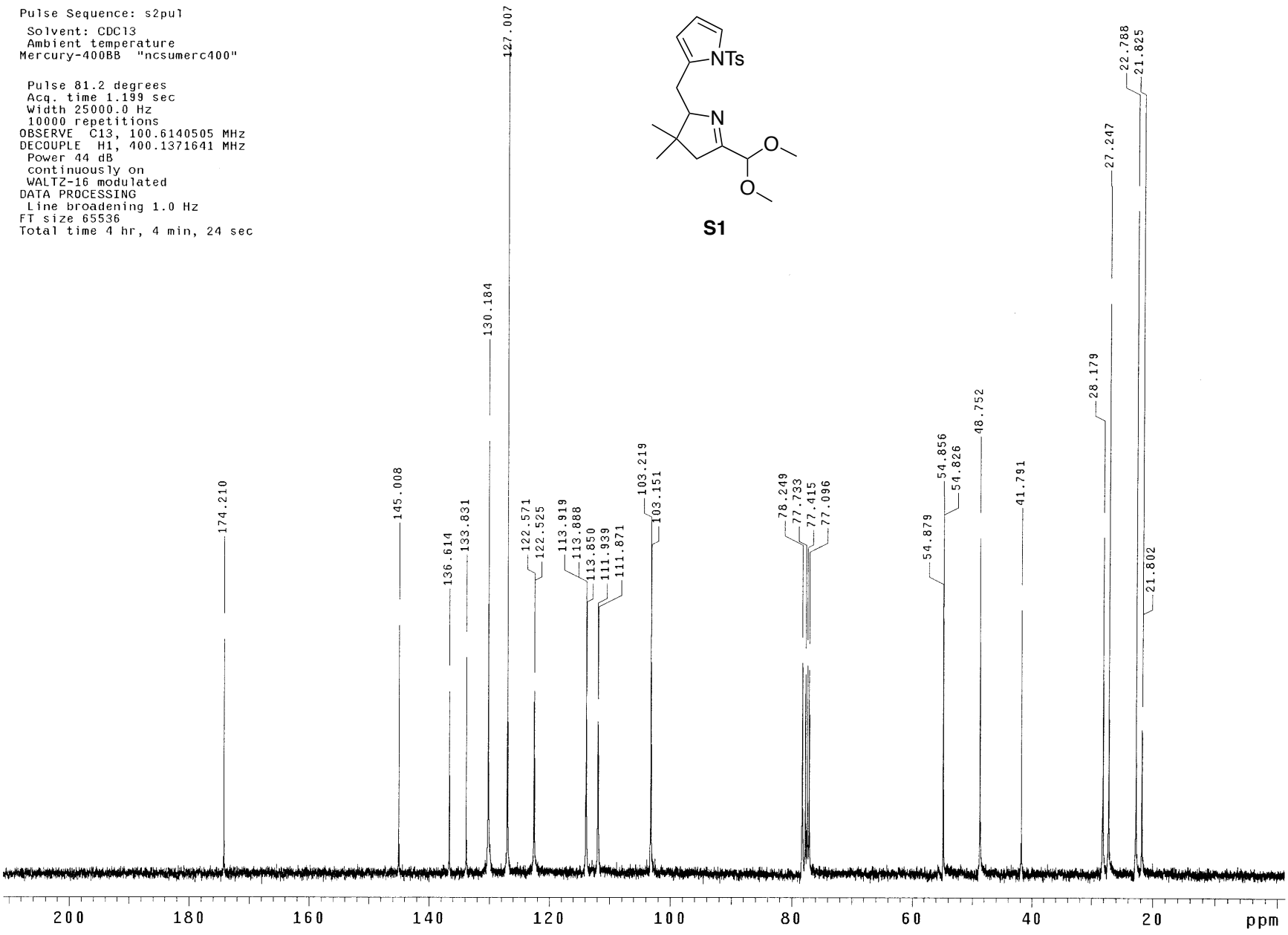


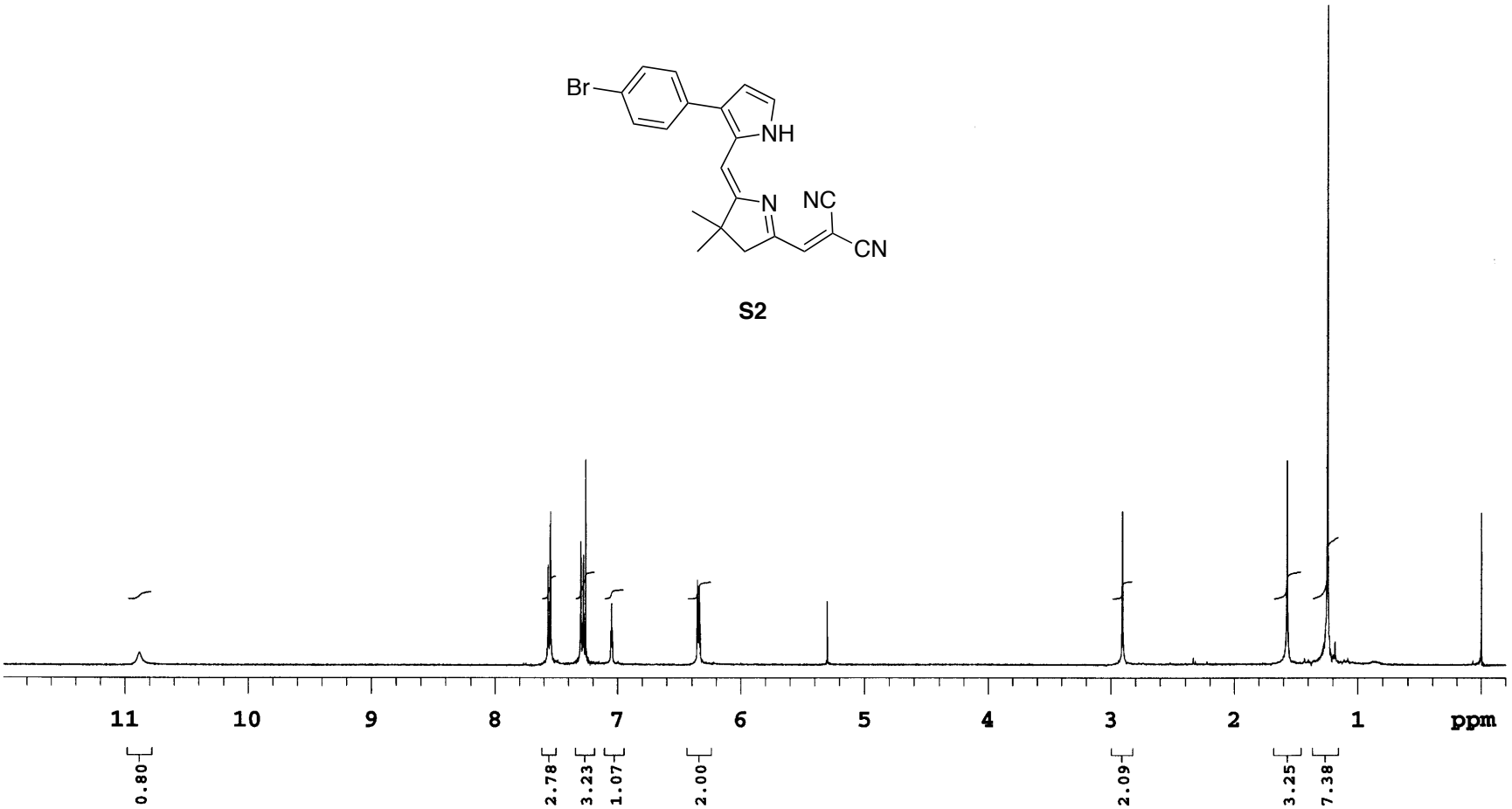
Copper-complex

in Scheme 7D

#	Name	Peaks(nm)	Abs(AU)
1		359.0	0.19407
1		000000000.0	-1.7977E308
1		000000000.0	-1.7977E308
1		000000000.0	-1.7977E308
1		000000000.0	-1.7977E308

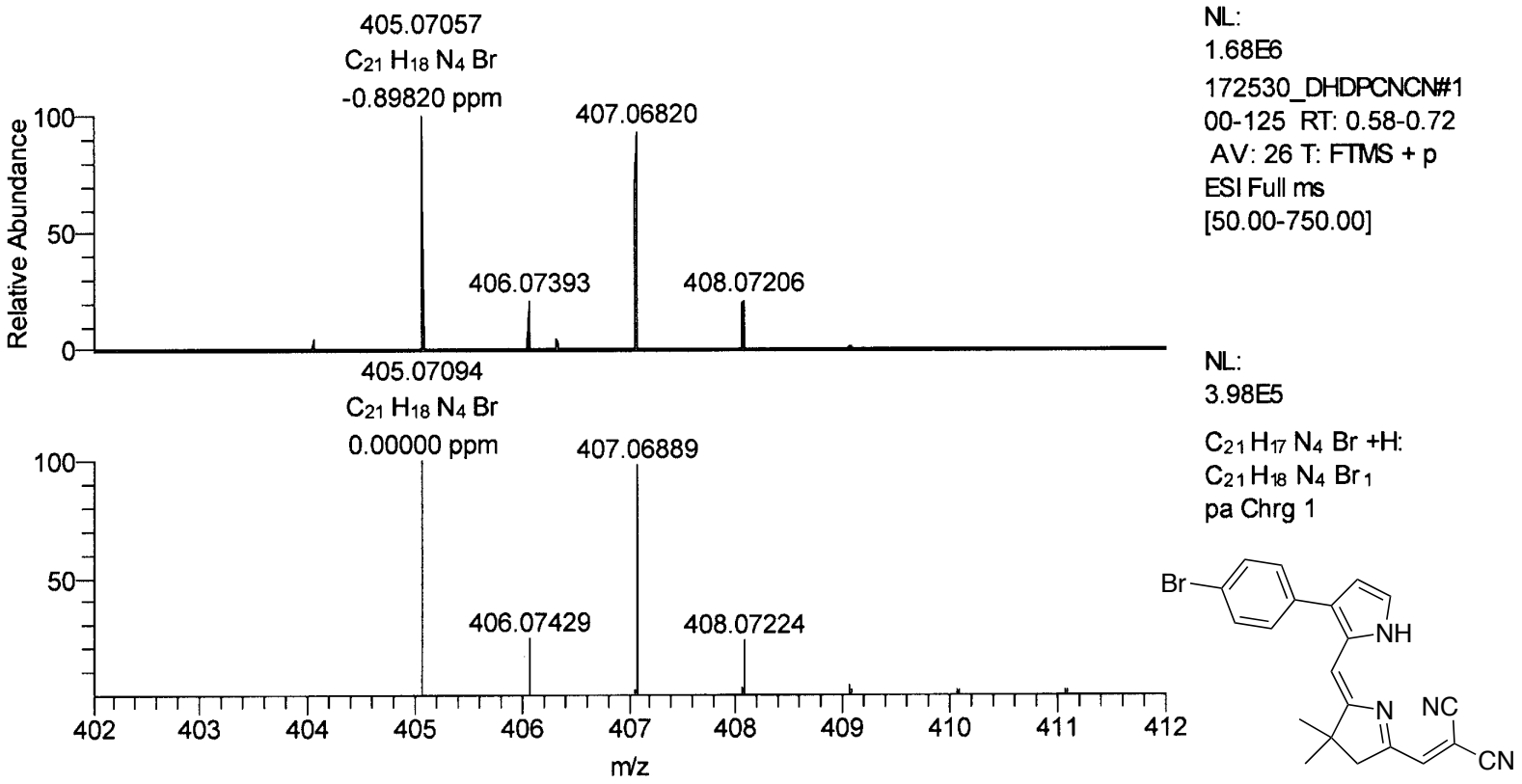

Ambient temperature
Mercury-300BB "ncsumerc300"
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 299.7918117 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec
NTs
N
O
O
S1
9
8
7
6
5
4
3
2
1
ppm
1.90
1.91
1.92
0.90
1.05
5.44
1.11
1.16
1.71
2.72
3.00
2.96


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
10000 repetitions
OBSERVE C13, 100.6140505 MHz
DECOUPLE H1, 400.1371641 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 hr, 4 min, 24 sec
NTs
N
O
O
S1
174.210
145.008
136.614
133.831
130.184
127.007
122.571
122.525
113.919
113.888
113.850
111.939
111.871
103.219
103.151
78.249
77.733
77.415
77.096
54.879
54.856
54.826
48.752
41.791
28.179
27.247
22.788
21.825
21.802
200
180
160
140
120
100
80
60
40
20
ppm

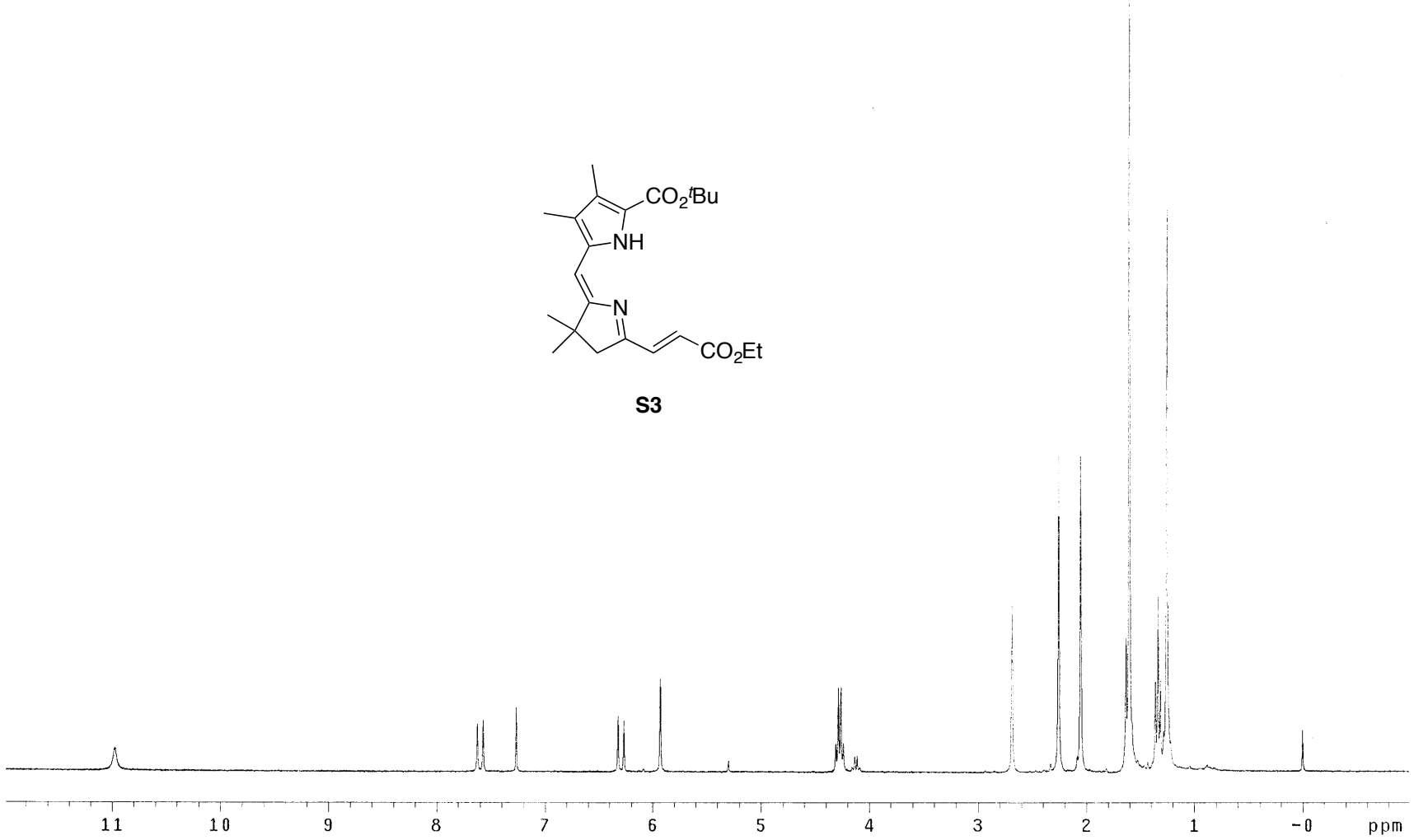


S2

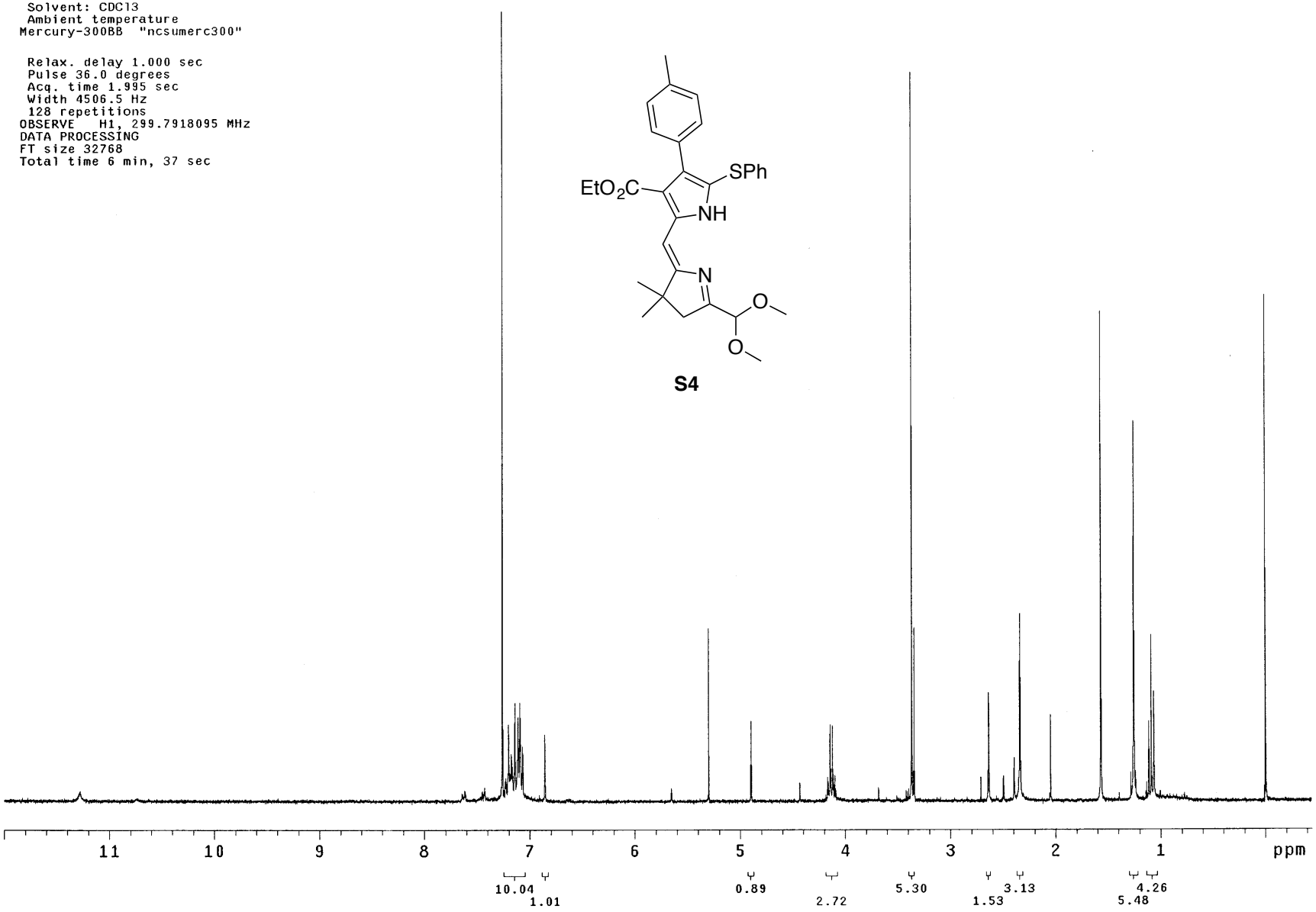
DHDP(CN)2. Experimental and Theoretical Isotopic Distribution $C_{21}H_{18}BrN_4$ $[M+H]^+$

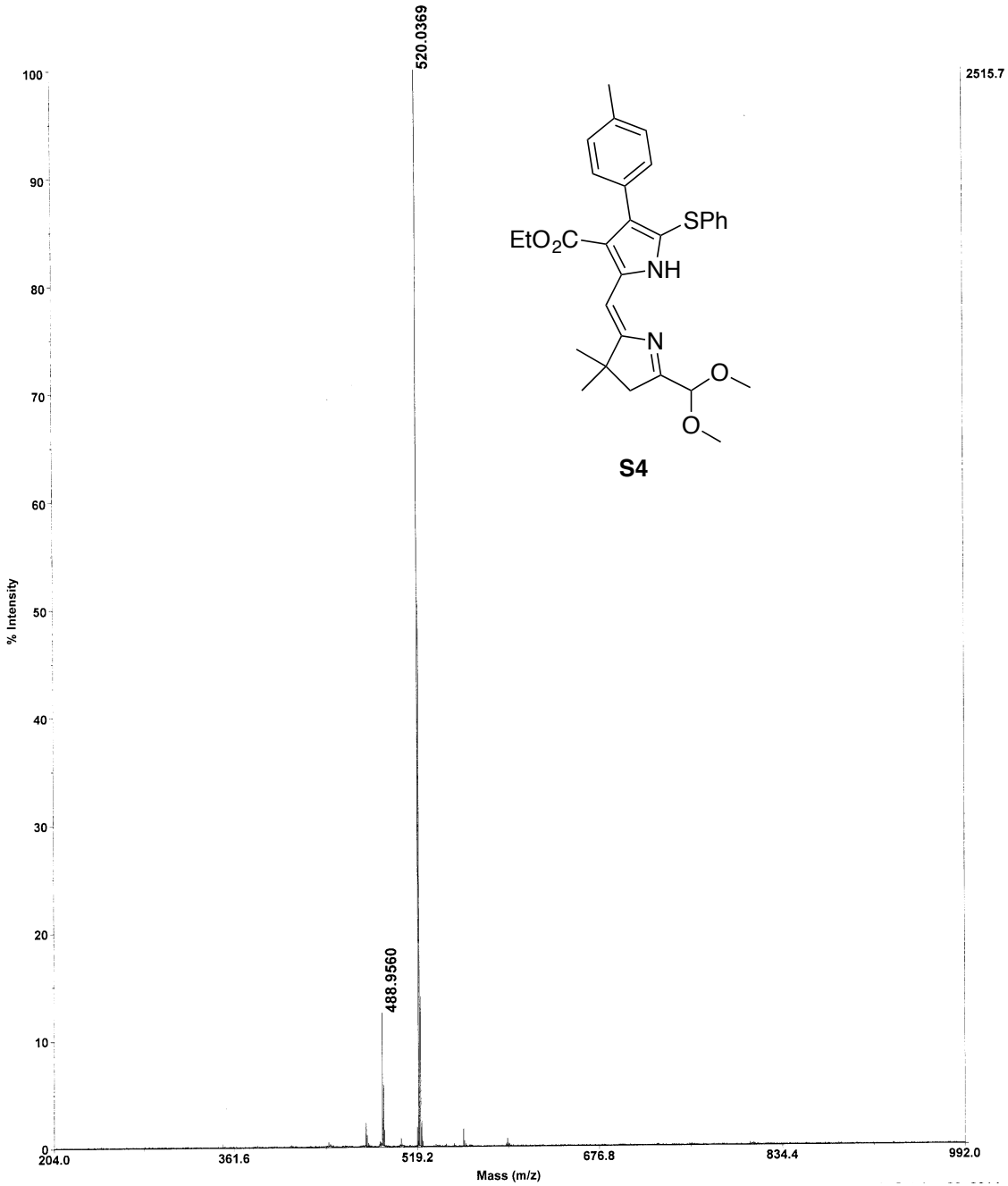


The characteristic "A+2" peak at ~97% is added confirmation of the presence of 1 Br atom. S2

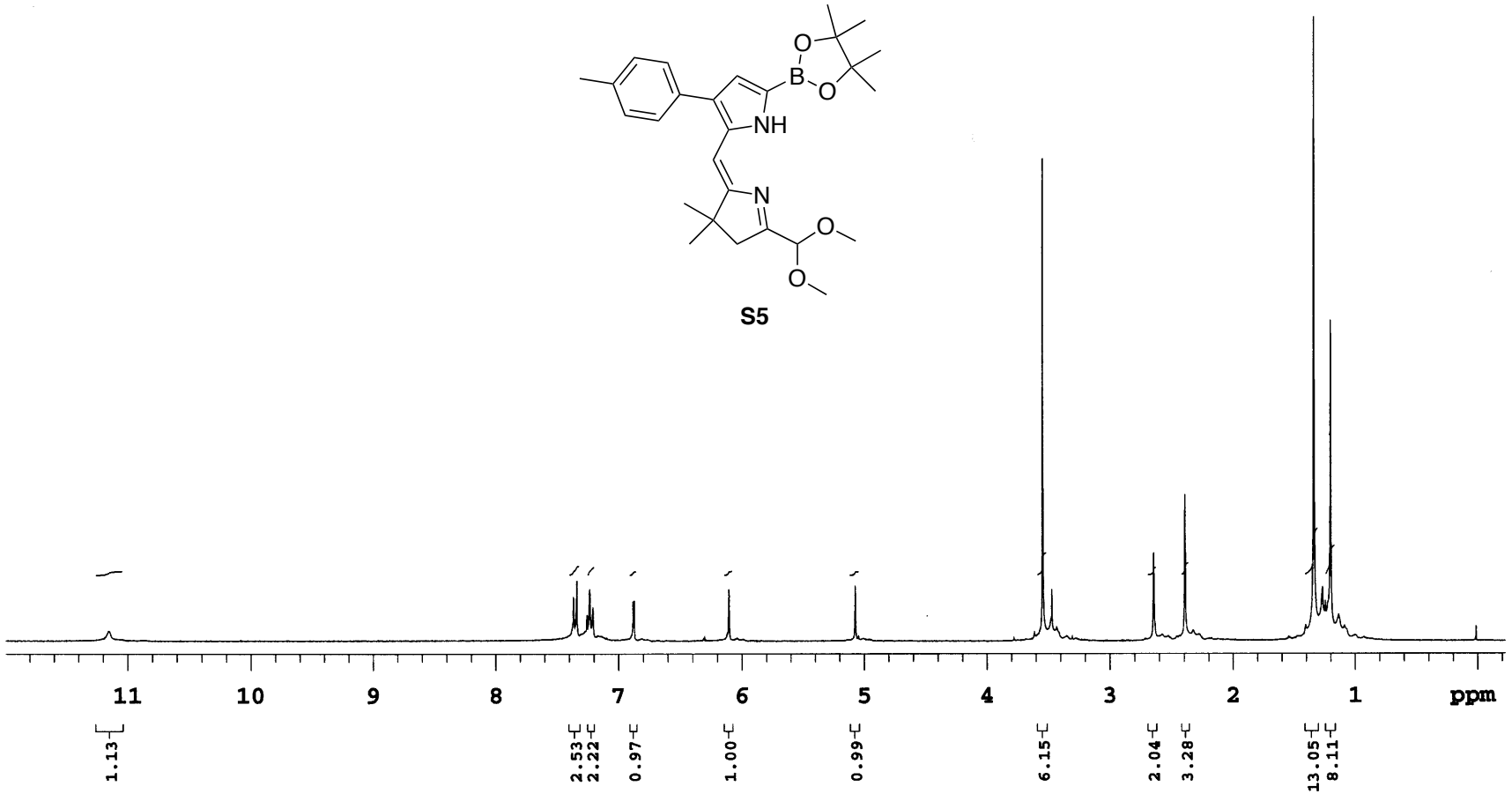


S3

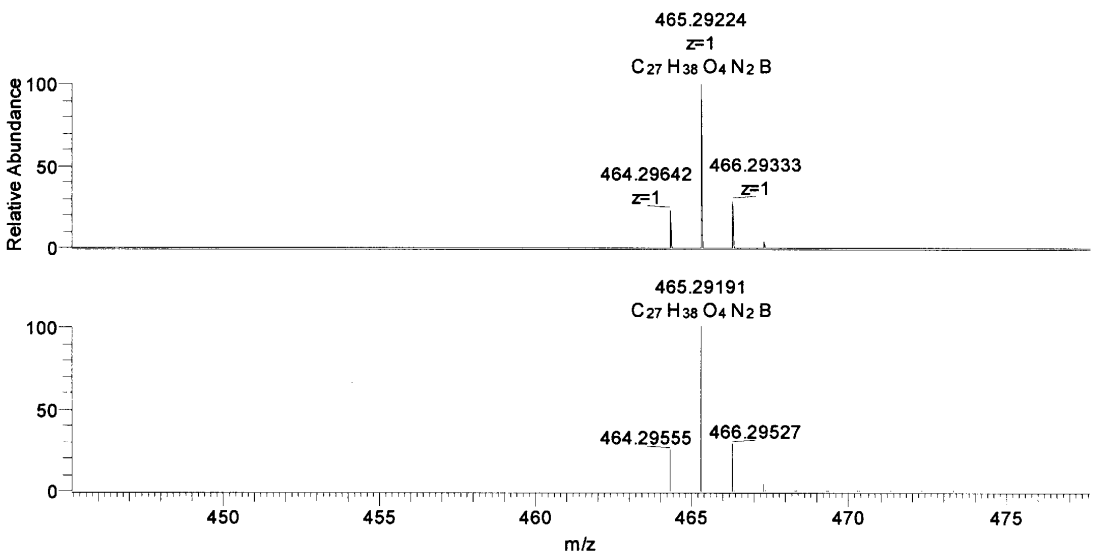

Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
128 repetitions
OBSERVE H1, 299.7918095 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 37 sec
EtO2C
SPh
NH
N
O
O
S4
11
10
9
8
7
6
5
4
3
2
1
ppm
10.04
1.01
0.89
2.72
5.30
1.53
3.13
4.26
5.48

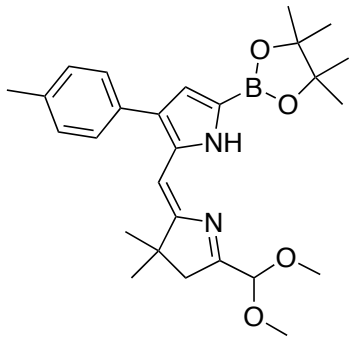

520.0369
2515.7
100
90
80
70
60
50
40
30
20
10
0
% Intensity
488.9560
204.0
361.6
519.2
676.8
834.4
992.0
Mass (m/z)
EtO2C
SPh
NH
N
O
O

S4


O
B
O
NH
N
O
O
11
10
9
8
7
6
5
4
3
2
1
ppm
1.13
2.53
2.22
0.97
1.00
0.99
6.15
2.04
3.28
13.05
8.11

S5

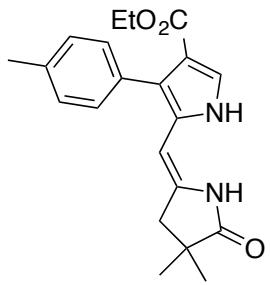

465.29224
z=1
C27 H38 O4 N2 B
464.29642
z=1
466.29333
z=1
Relative Abundance
100
50
0
NL:
8.22E9
DHDP-B(PIN)#213
RT: 1.11 AV: 1 T:
FTMS + p ESI Full
ms
[150.00-2000.00]
465.29191
C27 H38 O4 N2 B
464.29555
466.29527
NL:
5.86E5
C27 H38 BN2 O4:
C27 H38 B1N2 O4
pa Chrg 1
450
455
460
465
470
475
m/z


O
B
O
NH
N
O
O

S5

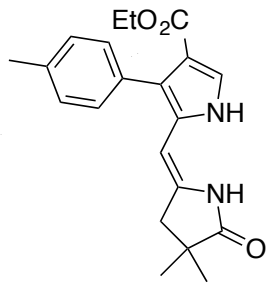
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.993 sec
Width 5065.9 Hz
8 repetitions
OBSERVE H1, 400.1245687 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 25 sec

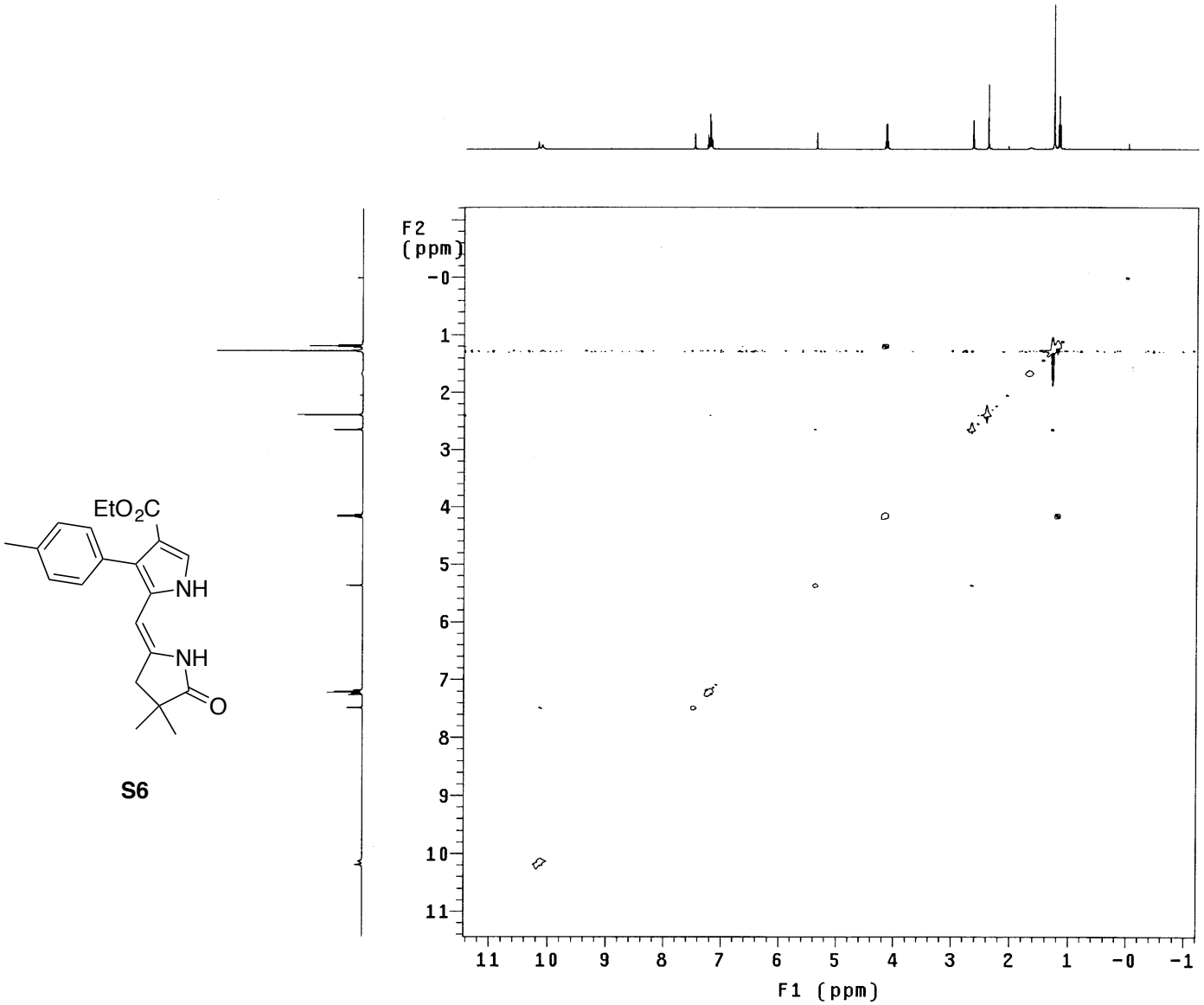


S6

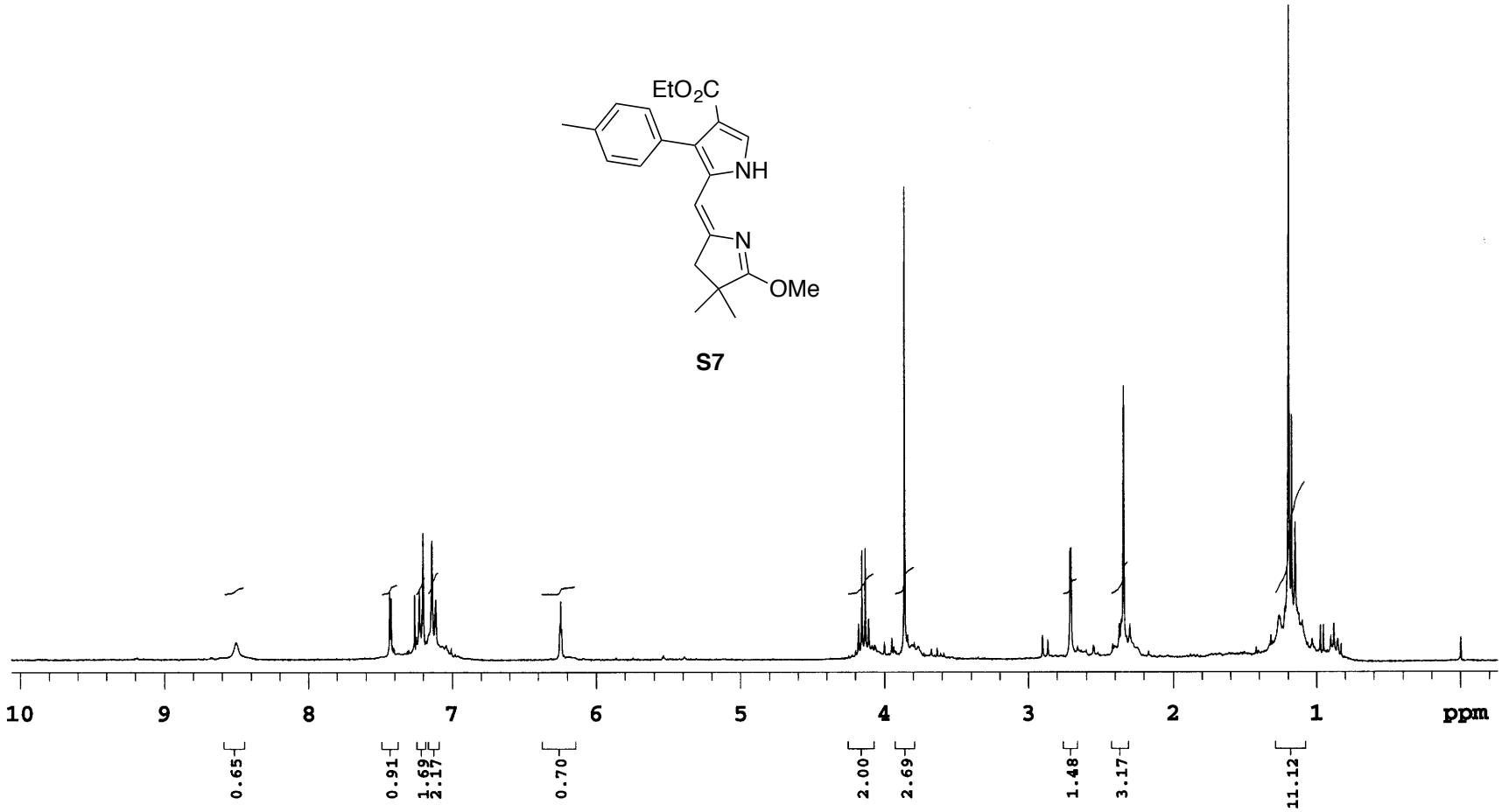
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
512 repetitions
OBSERVE C13, 100.6113782 MHz
DECOUPLE H1, 400.1266027 MHz
Power 44 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 19 min, 32 sec

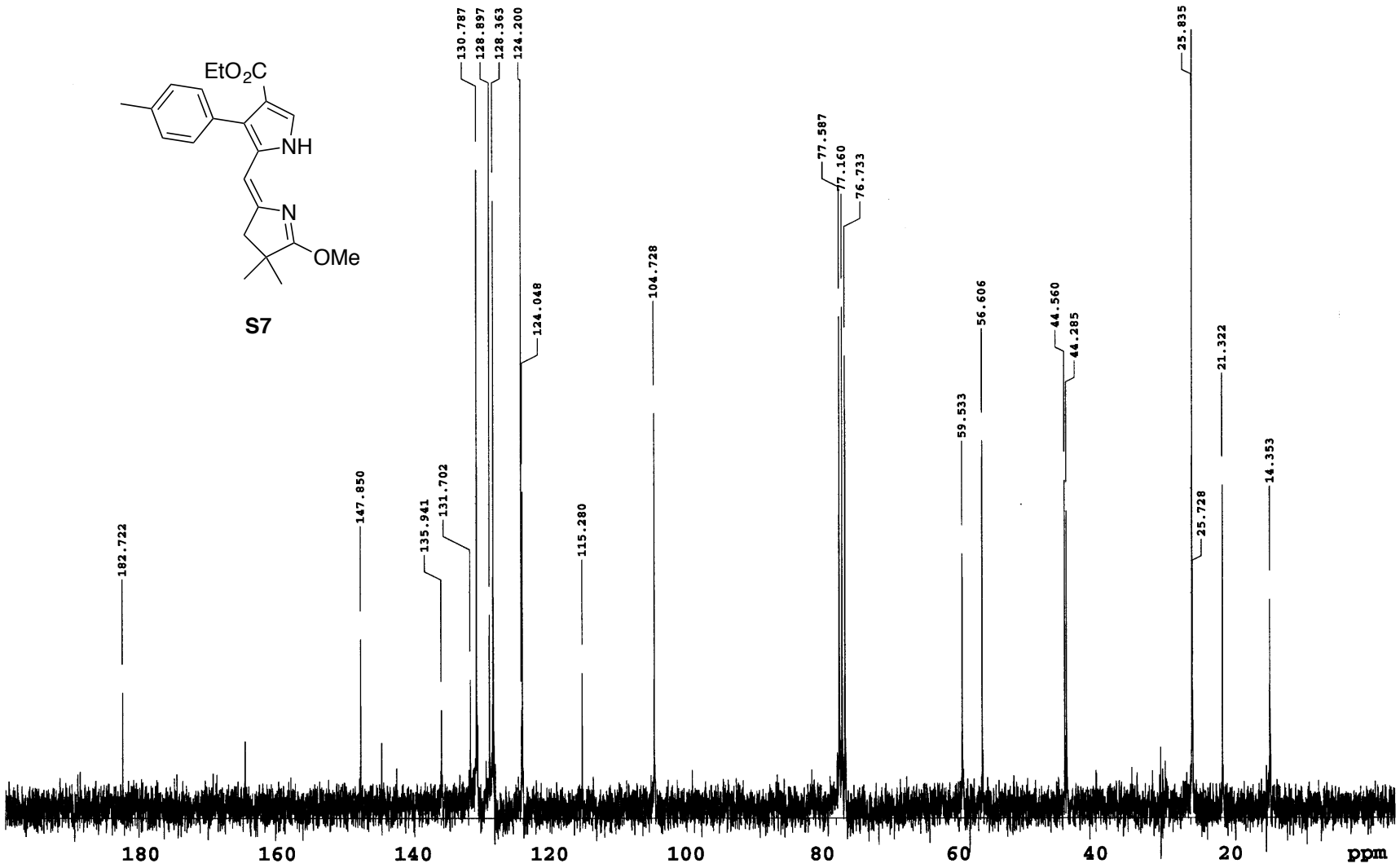


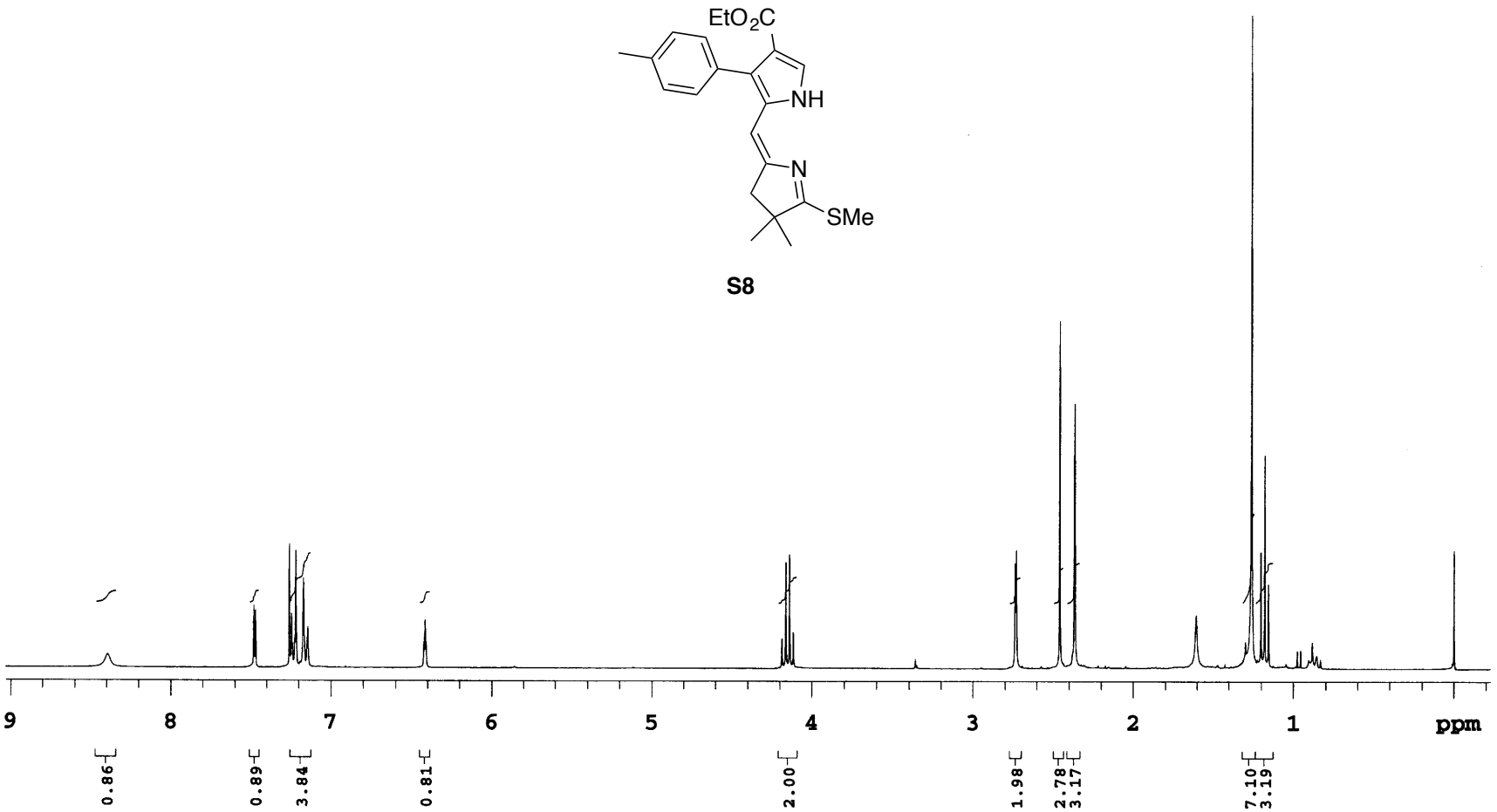
S6



S6


EtO2C
NH
N
OMe
S7
10
9
8
7
6
5
4
3
2
1
ppm
0.65
0.91
1.69
2.17
0.70
2.00
2.69
1.48
3.17
11.12

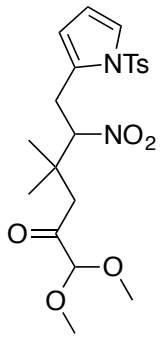

EtO2C
NH
N
OMe
S7
182.722
147.850
135.941
131.702
130.787
128.897
128.363
124.200
124.048
115.280
104.728
77.587
77.160
76.733
59.533
56.606
44.560
44.285
25.835
25.728
21.322
14.353
180
160
140
120
100
80
60
40
20
ppm


EtO2C
NH
N
SMe
9
8
7
6
5
4
3
2
1
ppm
0.86
0.89
3.84
0.81
2.00
1.98
2.78
3.17
7.10
3.19

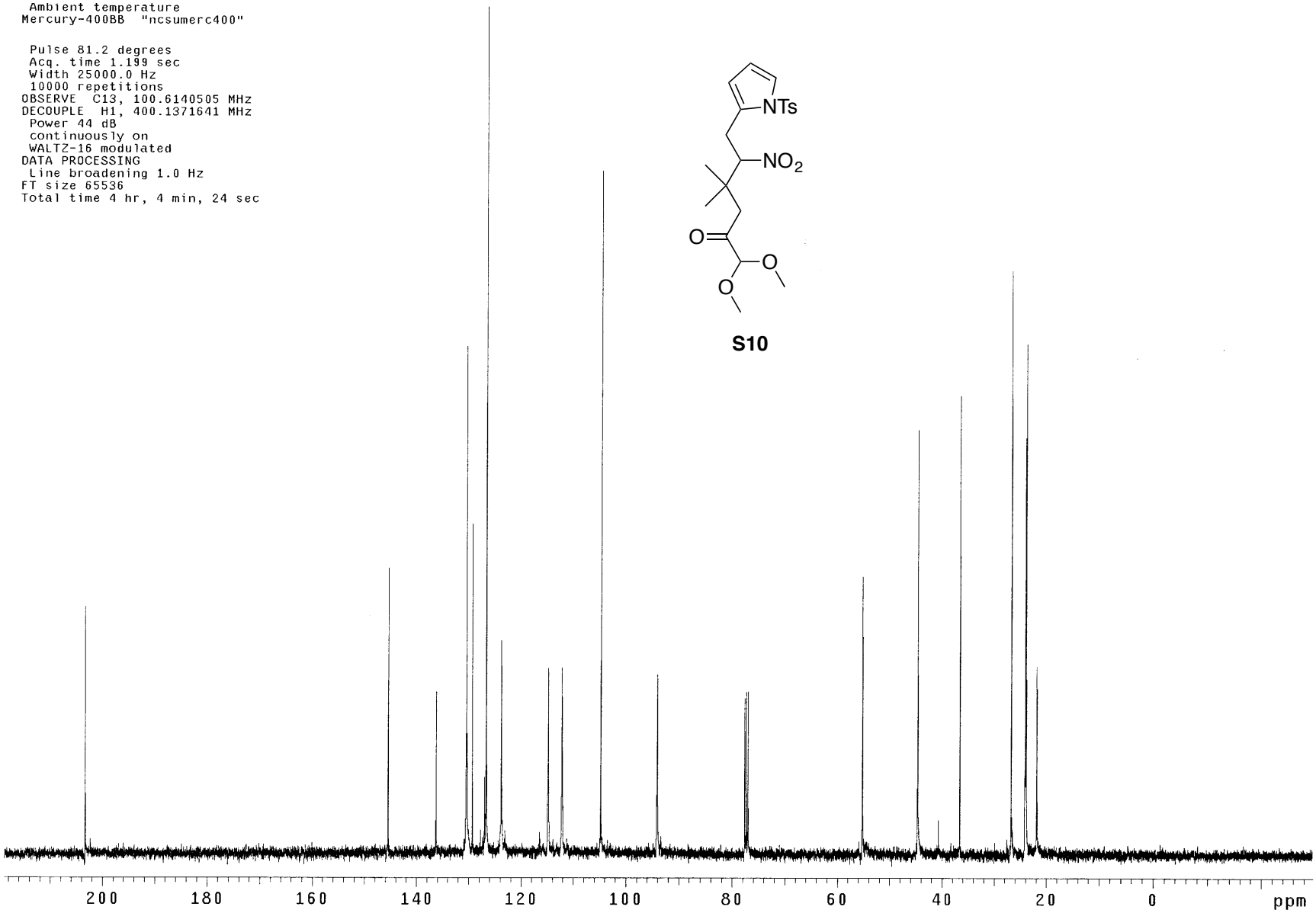
S8

Ambient temperature
Mercury-300BB "ncsumerc638"

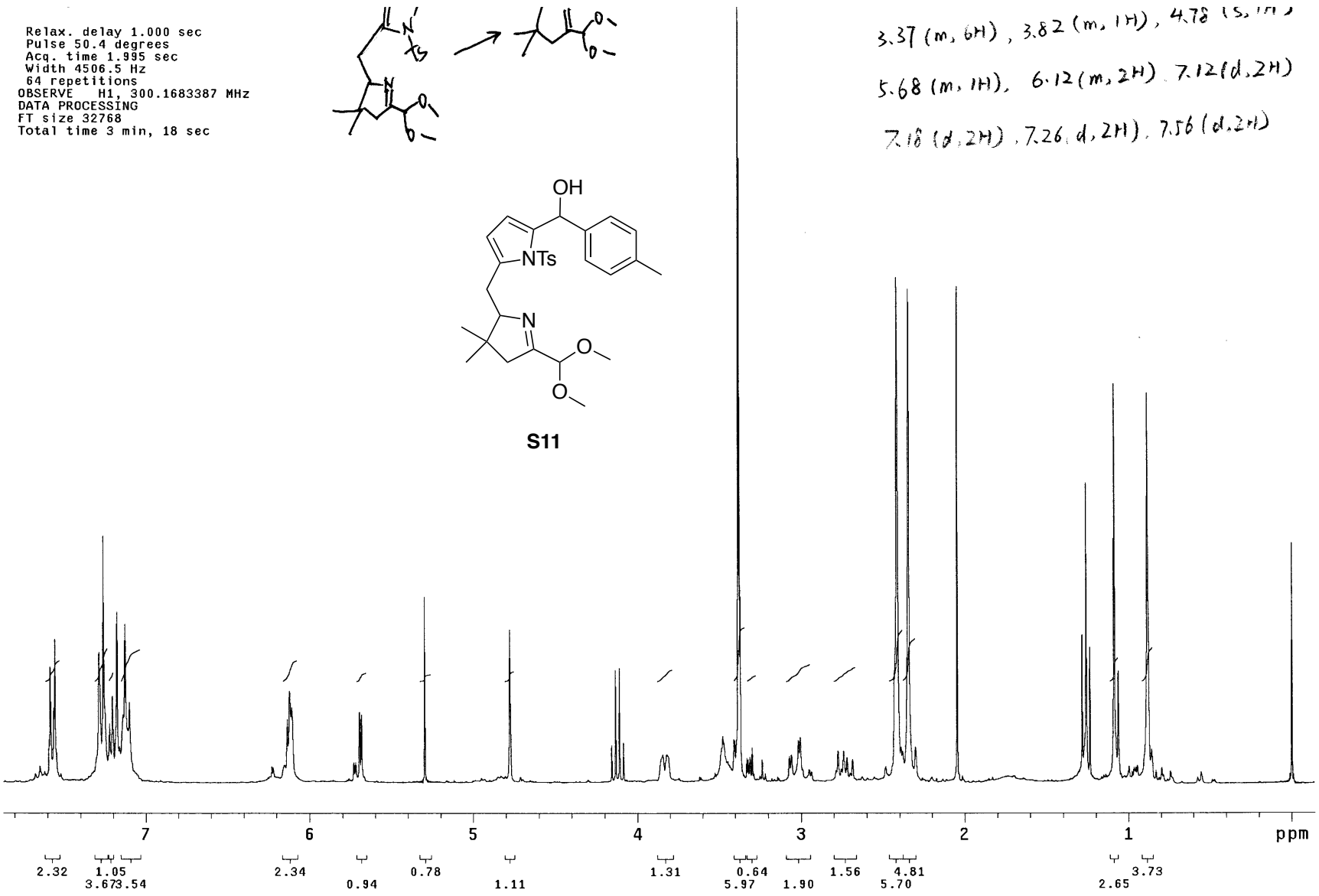
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 300.1683340 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec



S10

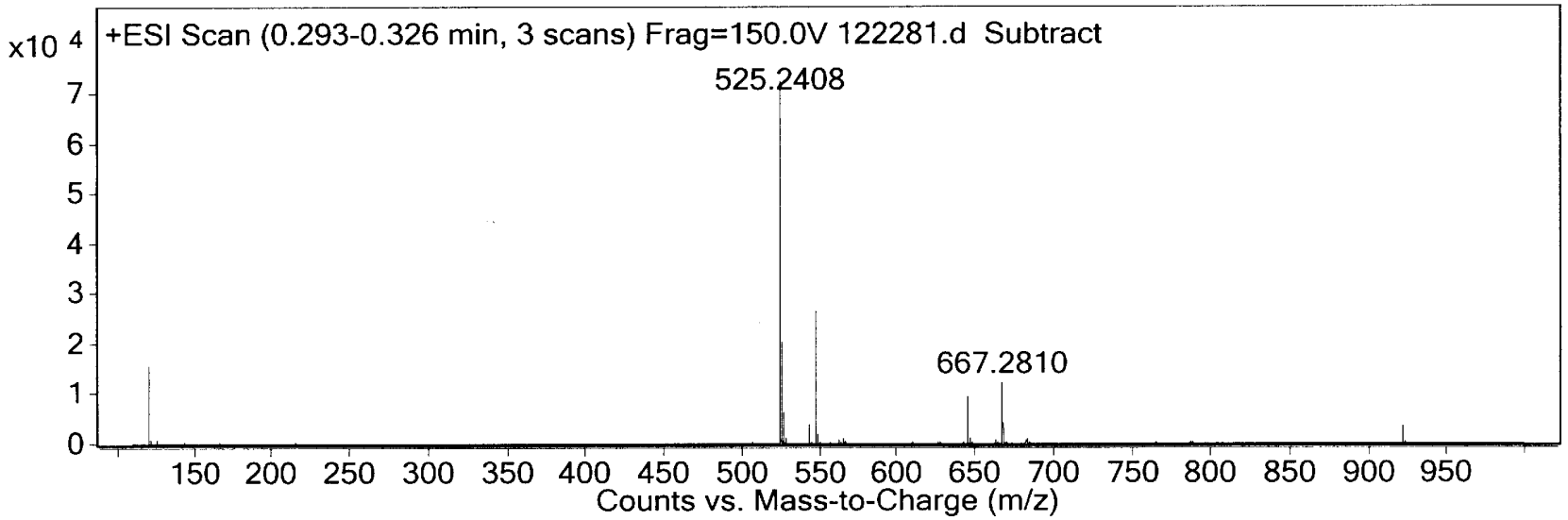

Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
10000 repetitions
OBSERVE C13, 100.6140505 MHz
DECOUPLE H1, 400.1371641 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 hr, 4 min, 24 sec
NTs
NO2
O
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm

S10


Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 300.1683387 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec
3.37 (m, 6H), 3.82 (m, 1H), 4.78
5.68 (m, 1H), 6.12 (m, 2H) 7.12 (d, 2H)
7.18 (d, 2H), 7.26 (d, 2H), 7.56 (d, 2H)
OH
NTs
N
O
O
S11
7
6
5
4
3
2
1
ppm
2.32
1.05
3.67
3.54
2.34
0.94
0.78
1.11
1.31
0.64
5.97
1.90
1.56
4.81
5.70
2.65
3.73

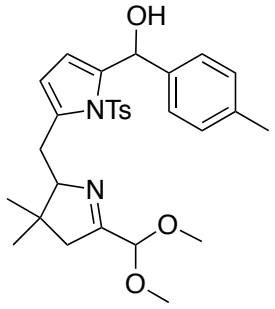
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
150	0	Esi

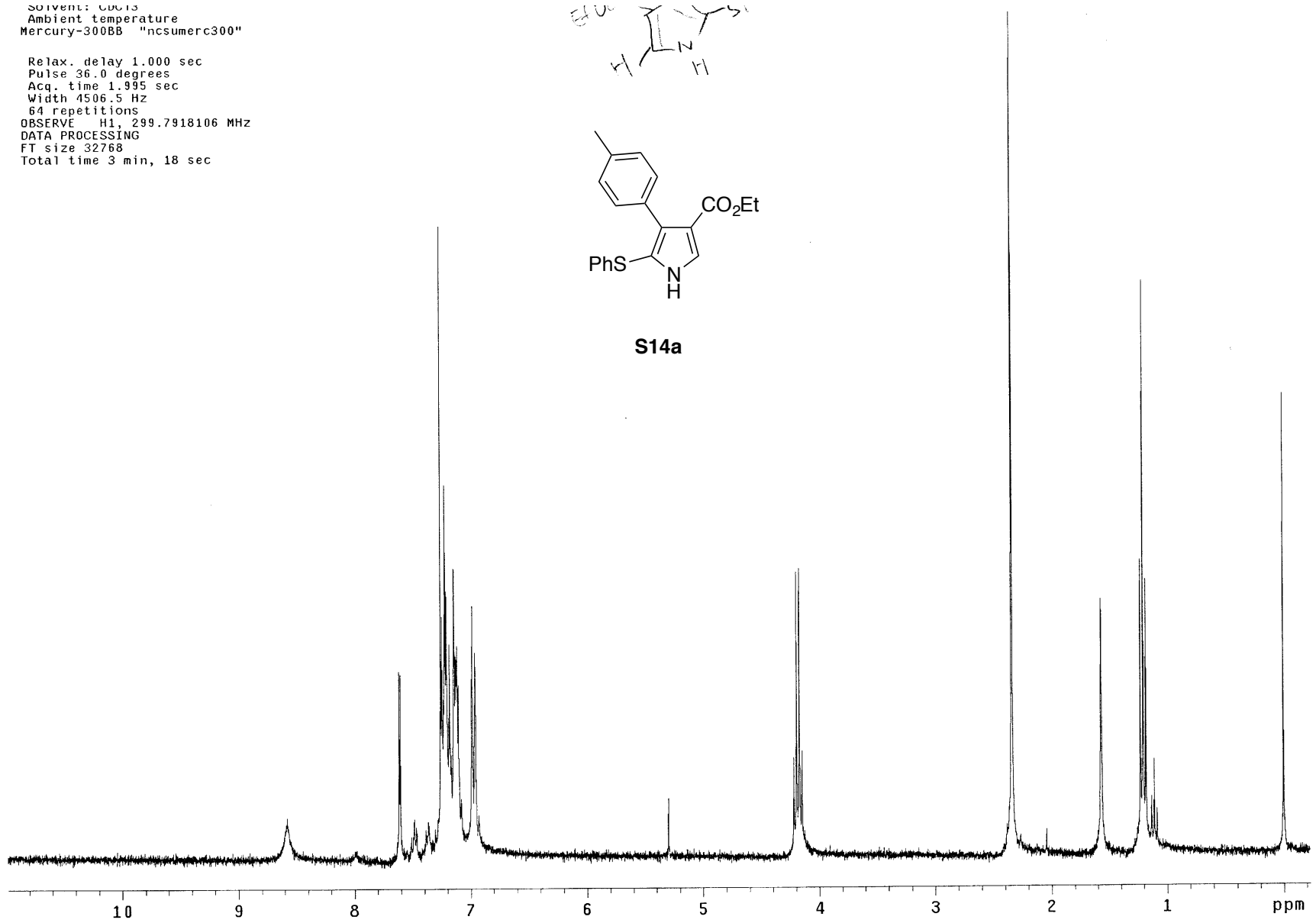


Peak List

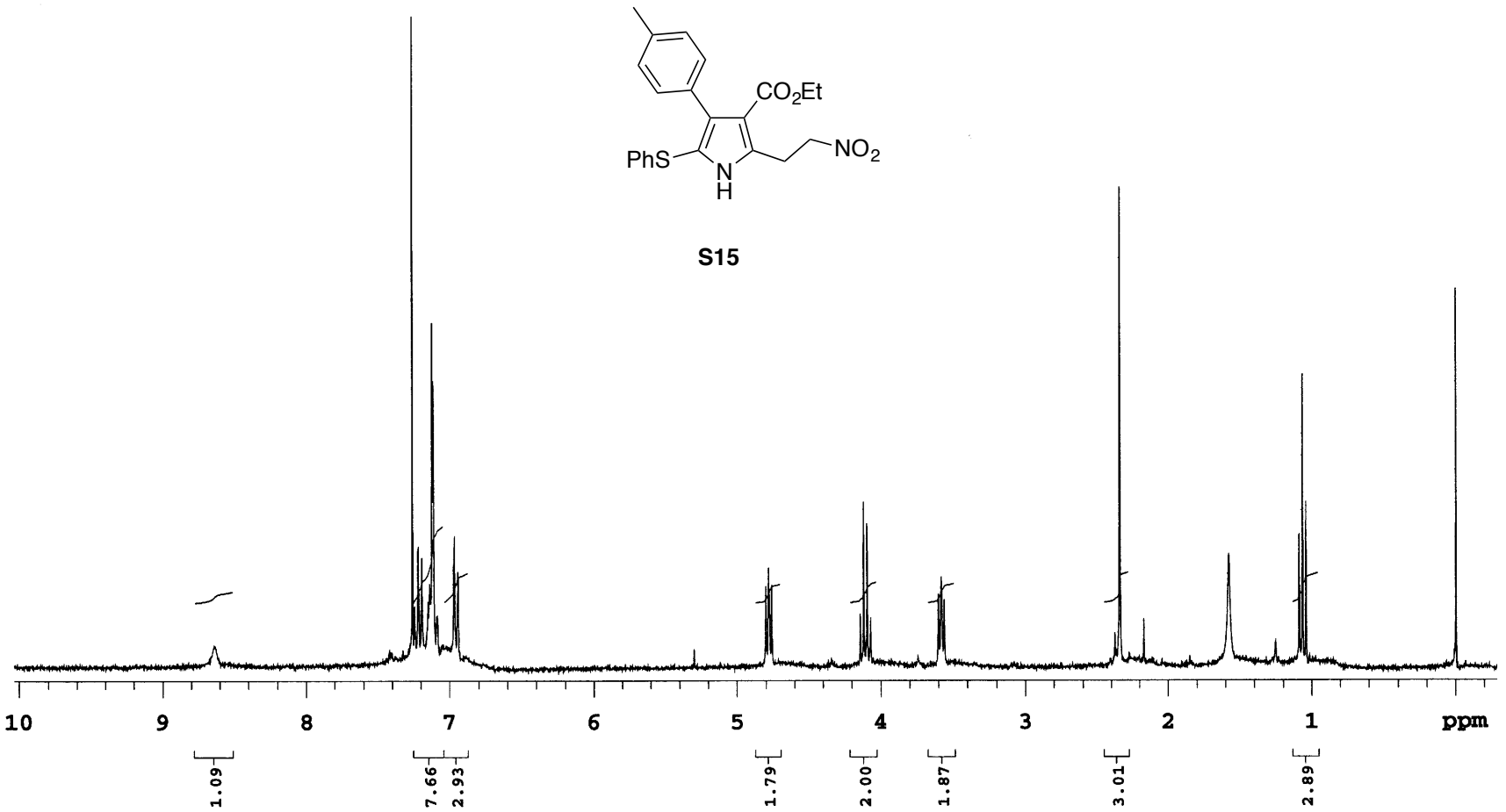
m/z	z	Abund
121.0512		15642
525.2408	1	75775
526.2444	1	21012
527.2432	1	6262
547.2234	1	27404
548.2265	1	8051
645.2991	1	9645
646.3018	1	4131
667.2810	1	12184
668.2843	1	4665



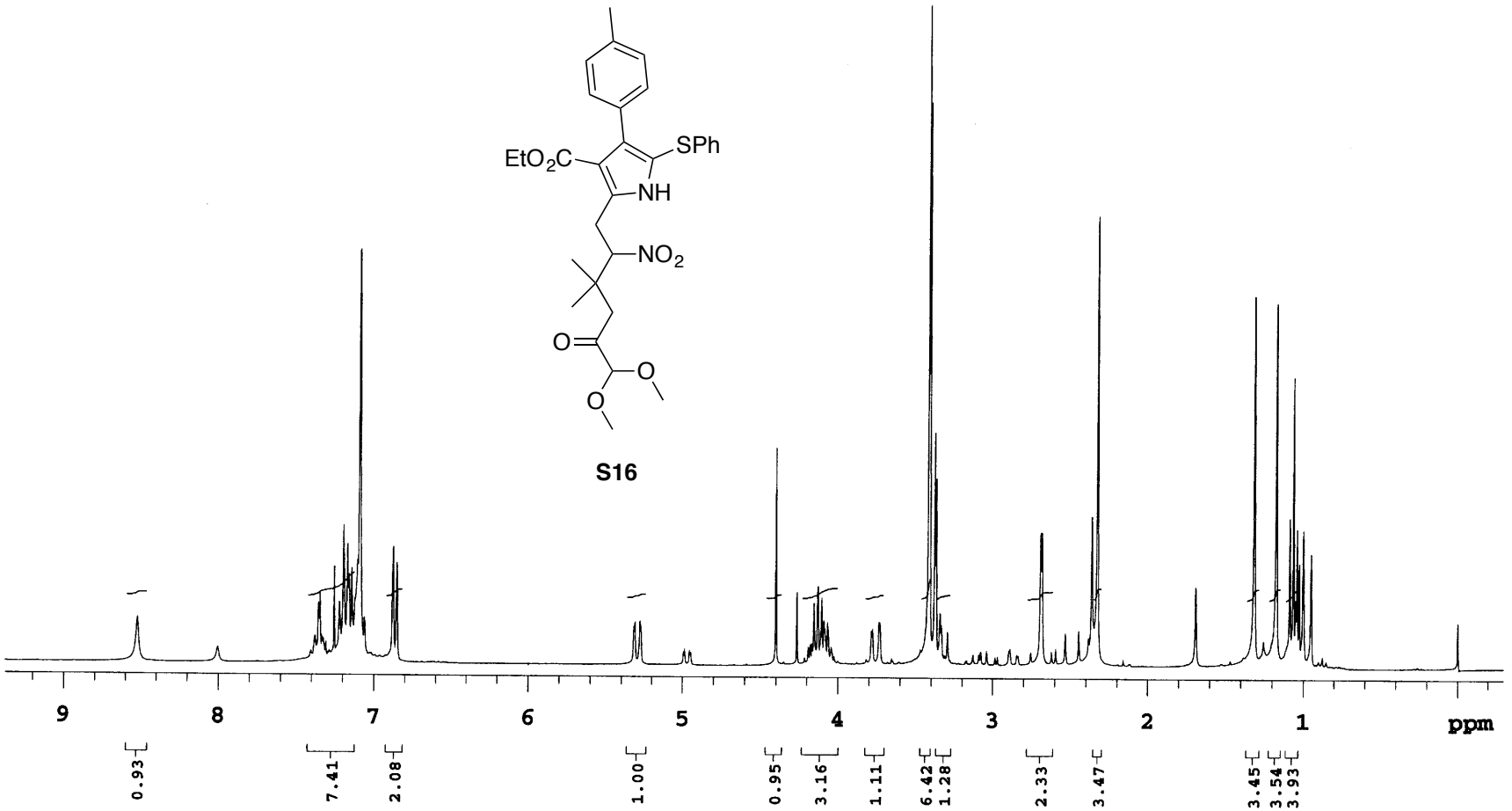
S11

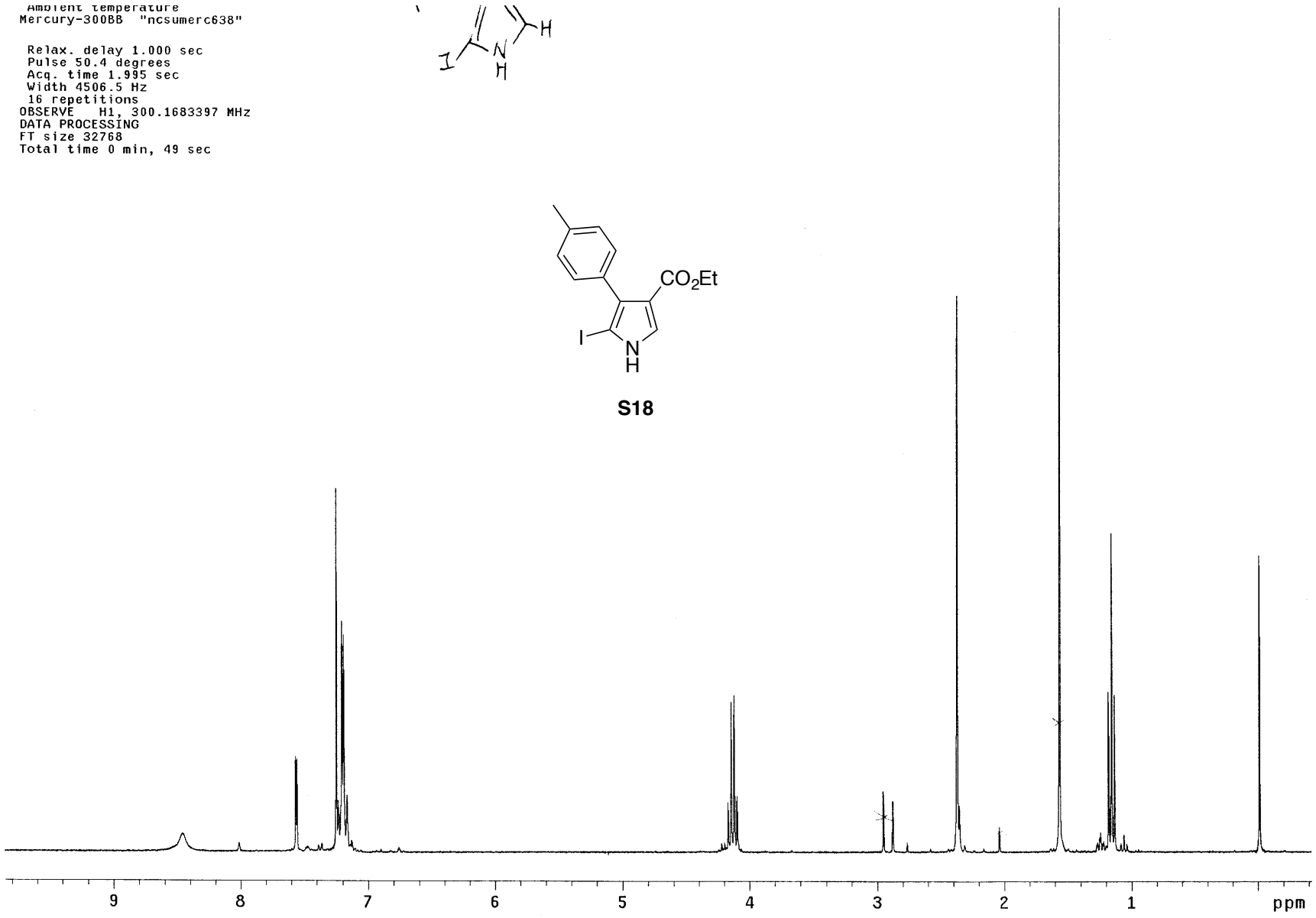

Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 299.7918106 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec
CO2Et
PhS
N
H
10
9
8
7
6
5
4
3
2
1
ppm

S14a


CO2Et
PhS
N
H
NO2
10
9
8
7
6
5
4
3
2
1
ppm
1.09
7.66
2.93
1.79
2.00
1.87
3.01
2.89

S15

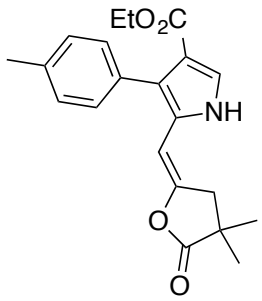

EtO2C
SPh
NH
NO2
O
O
O
S16
9
8
7
6
5
4
3
2
1
ppm
0.93
7.41
2.08
1.00
0.95
3.16
1.11
6.42
1.28
2.33
3.47
3.45
3.54
3.93


Ambient temperature
Mercury-300BB "ncsumerc638"
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 300.1683397 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
CO2Et
I
N
H
9
8
7
6
5
4
3
2
1
ppm

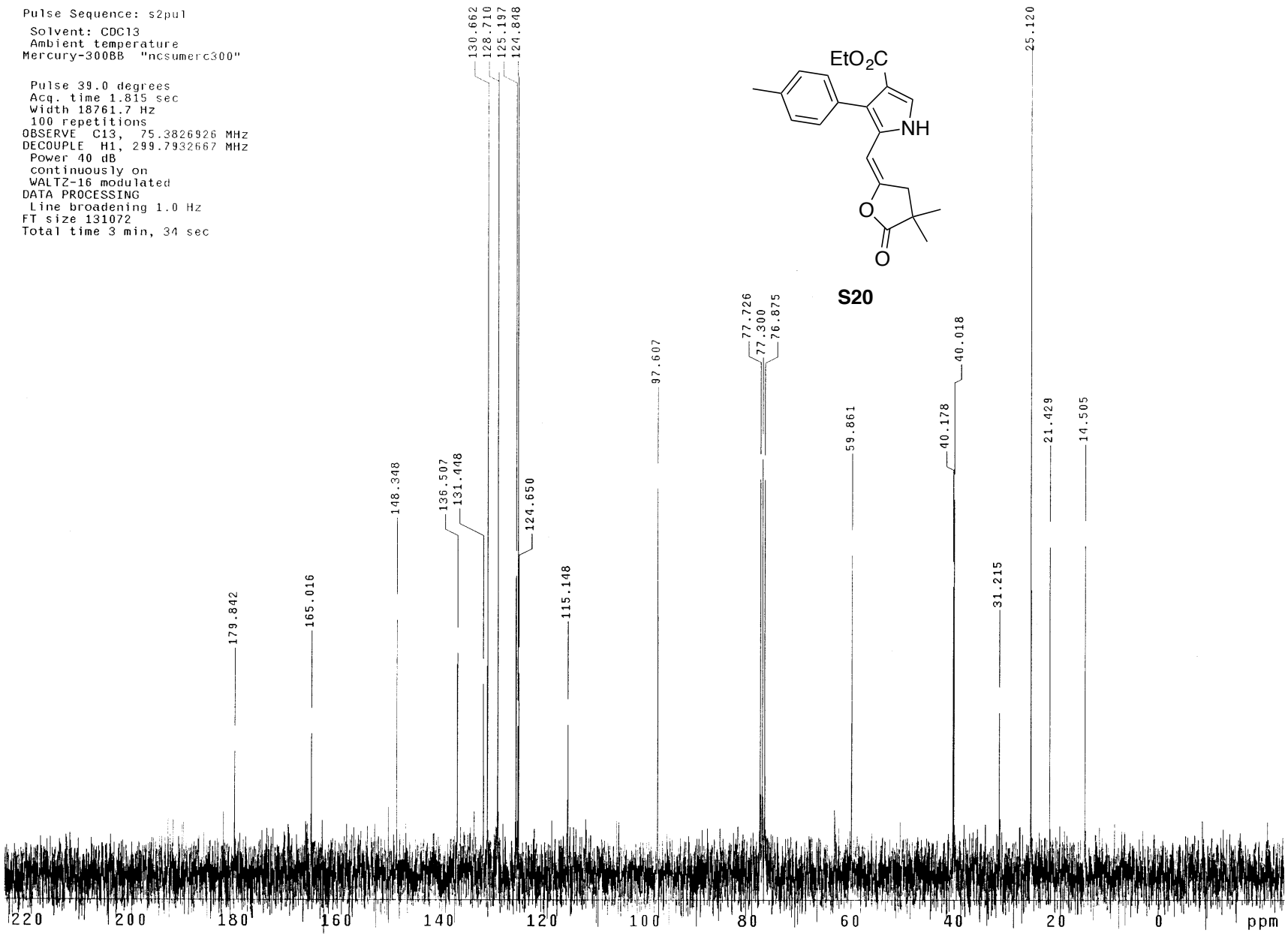
S18

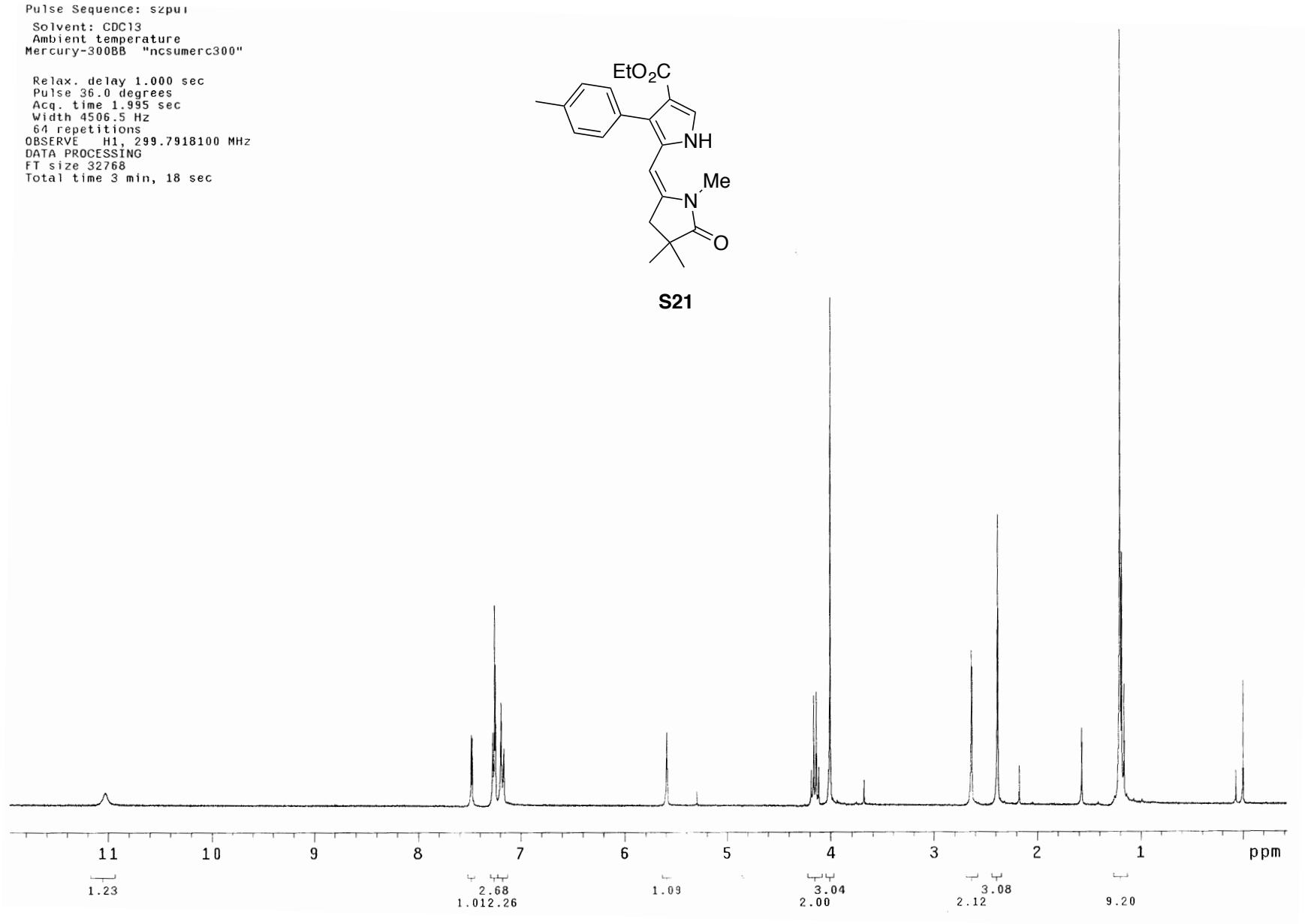
Ambient temperature
Mercury-300BB "ncsumerc300"

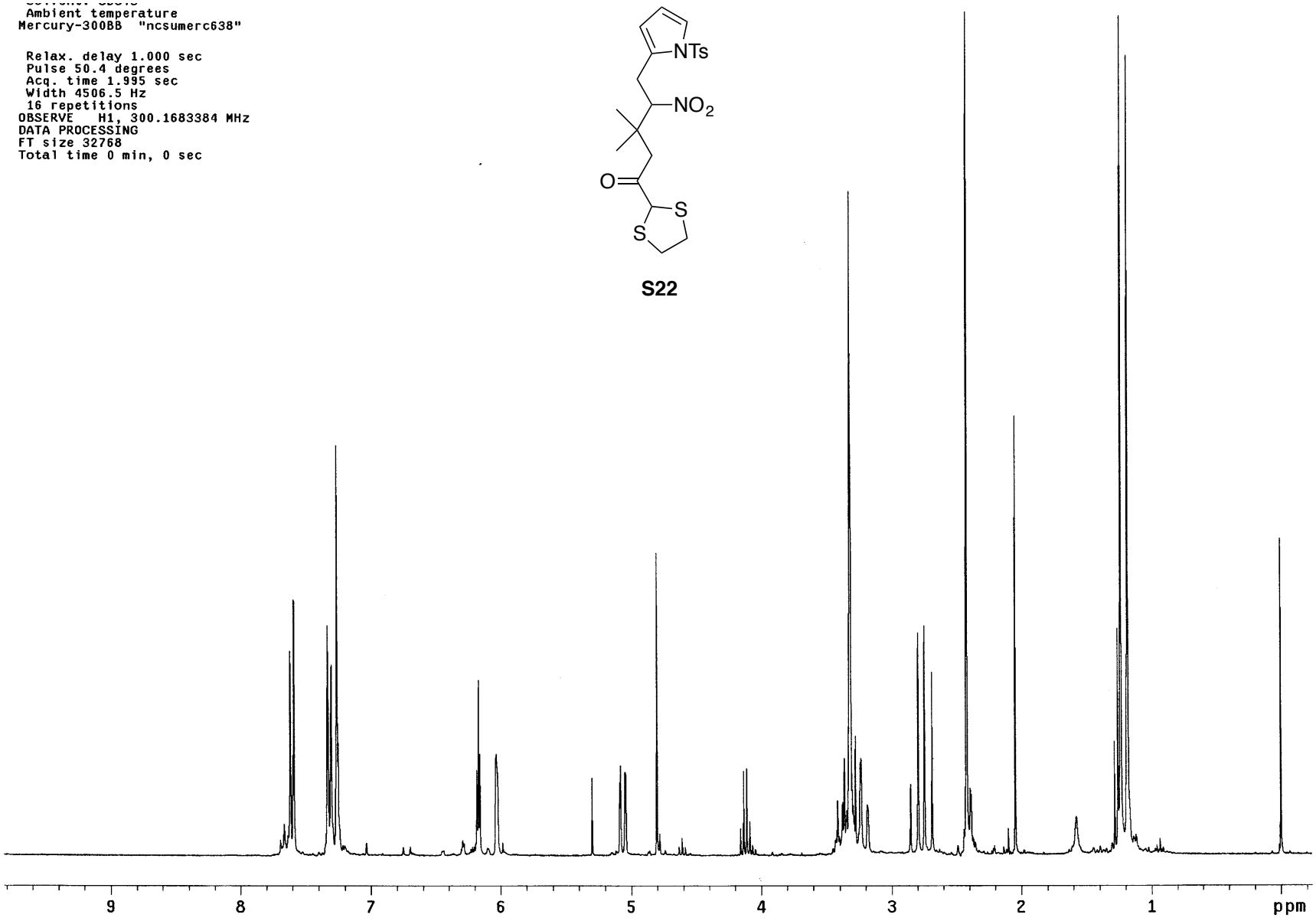
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 299.7918084 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

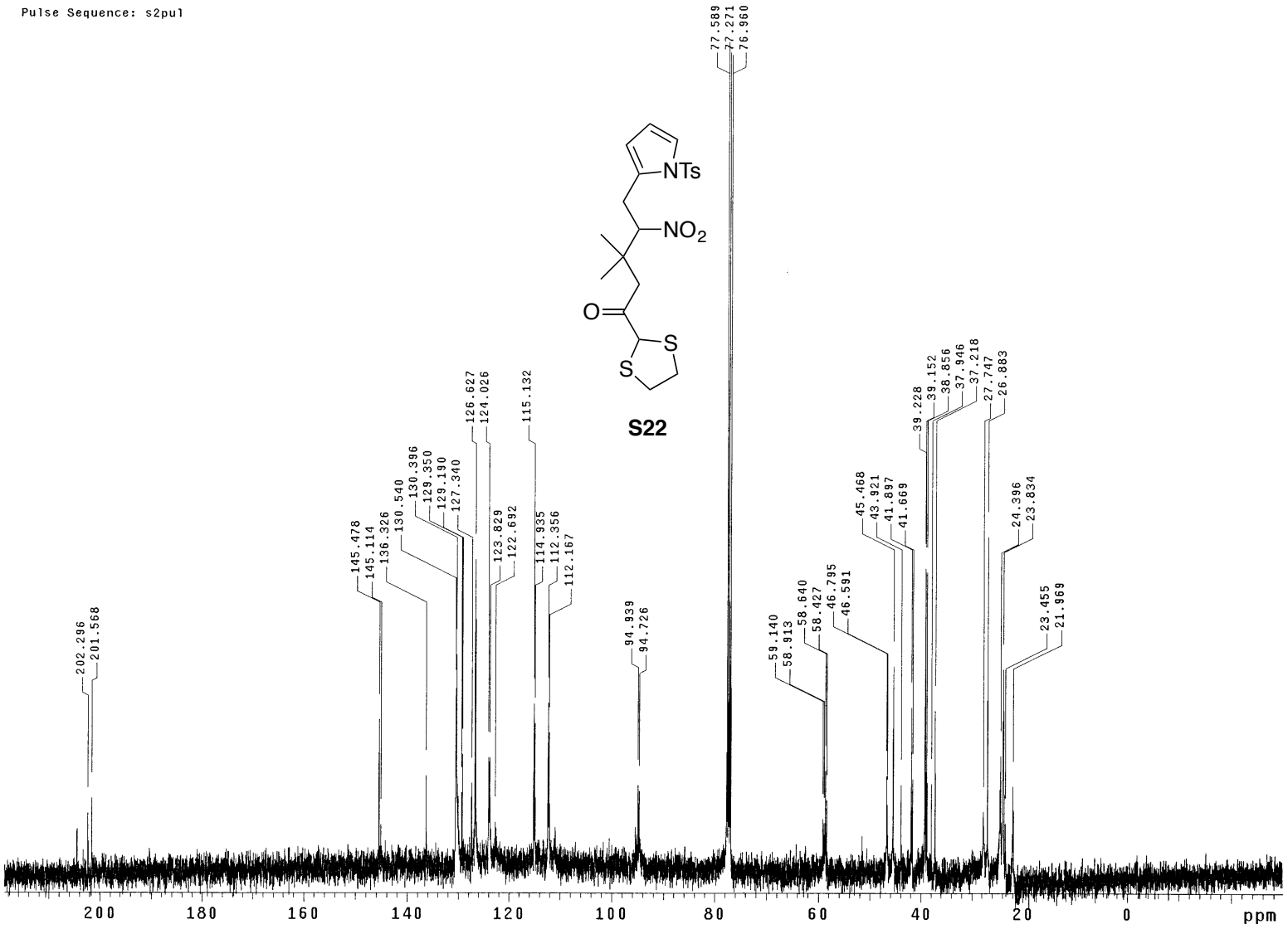


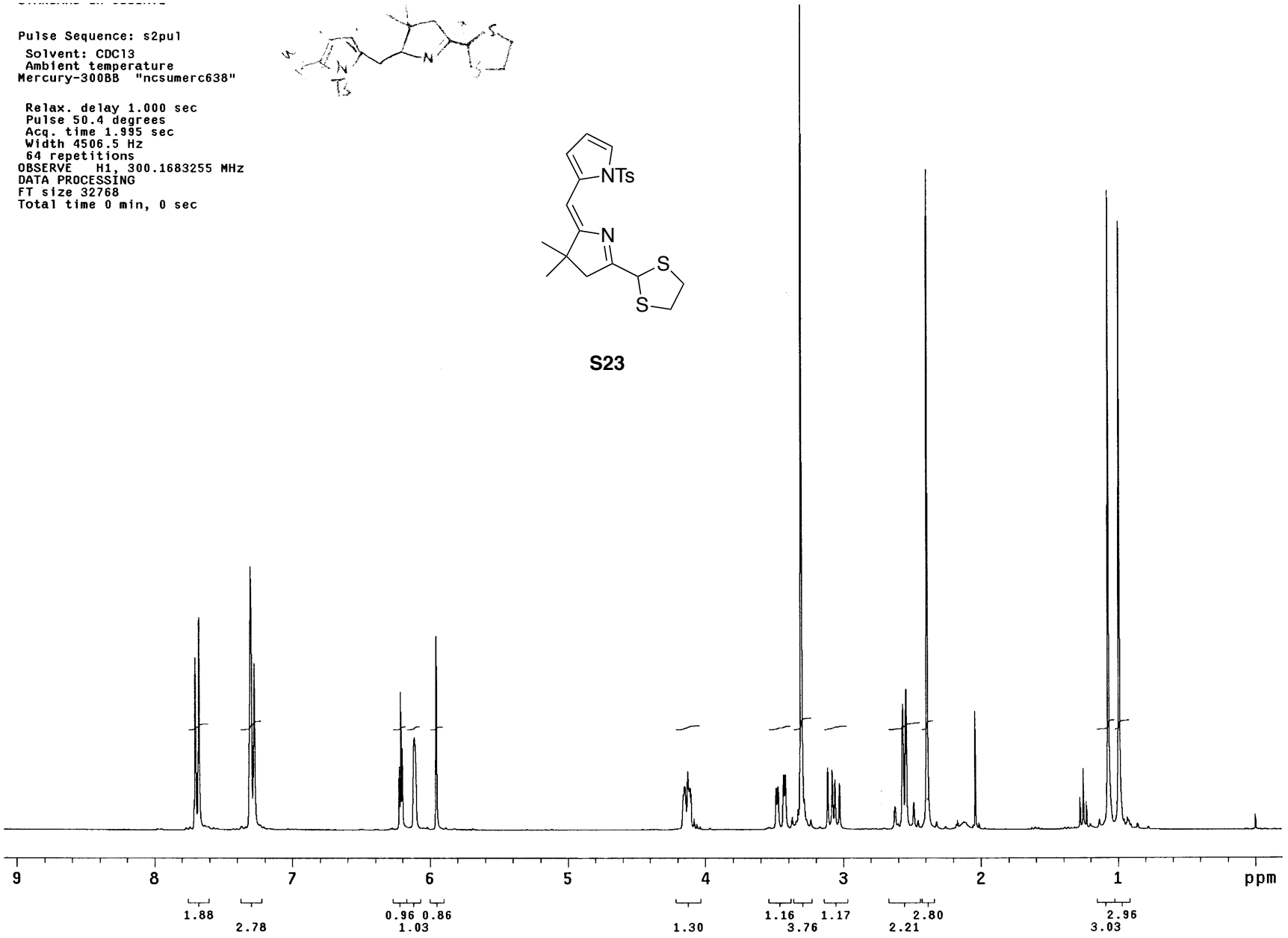
S20

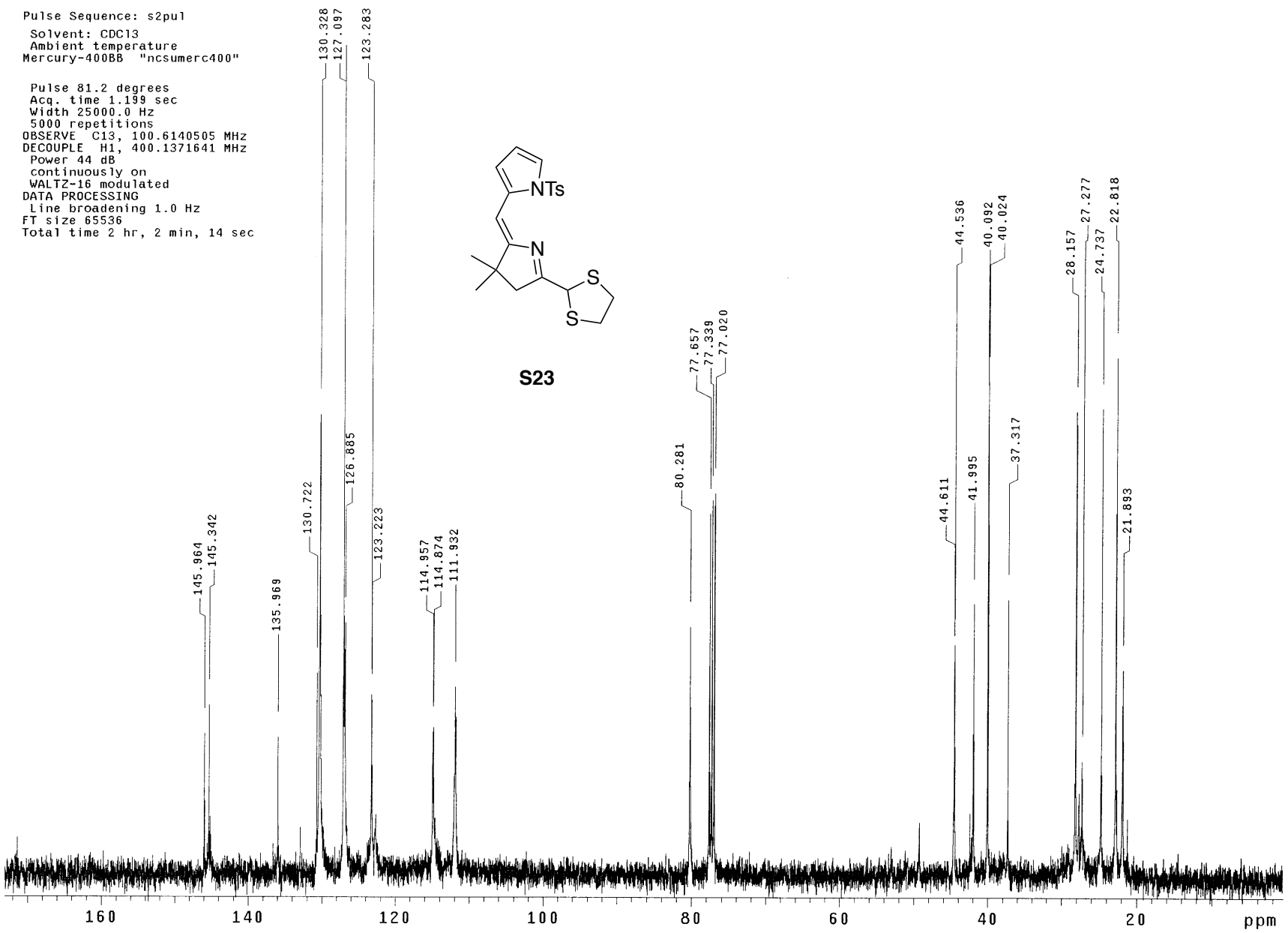

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"
Pulse 39.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
100 repetitions
OBSERVE C13, 75.3826926 MHz
DECOUPLE H1, 299.7932667 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min, 34 sec
EtO2C
NH
O
O
S20
130.662
128.710
125.197
124.848
25.120
179.842
165.016
148.348
136.507
131.448
124.650
115.148
97.607
77.726
77.300
76.875
59.861
40.178
40.018
31.215
21.429
14.505
220
200
180
160
140
120
100
80
60
40
20
0
ppm

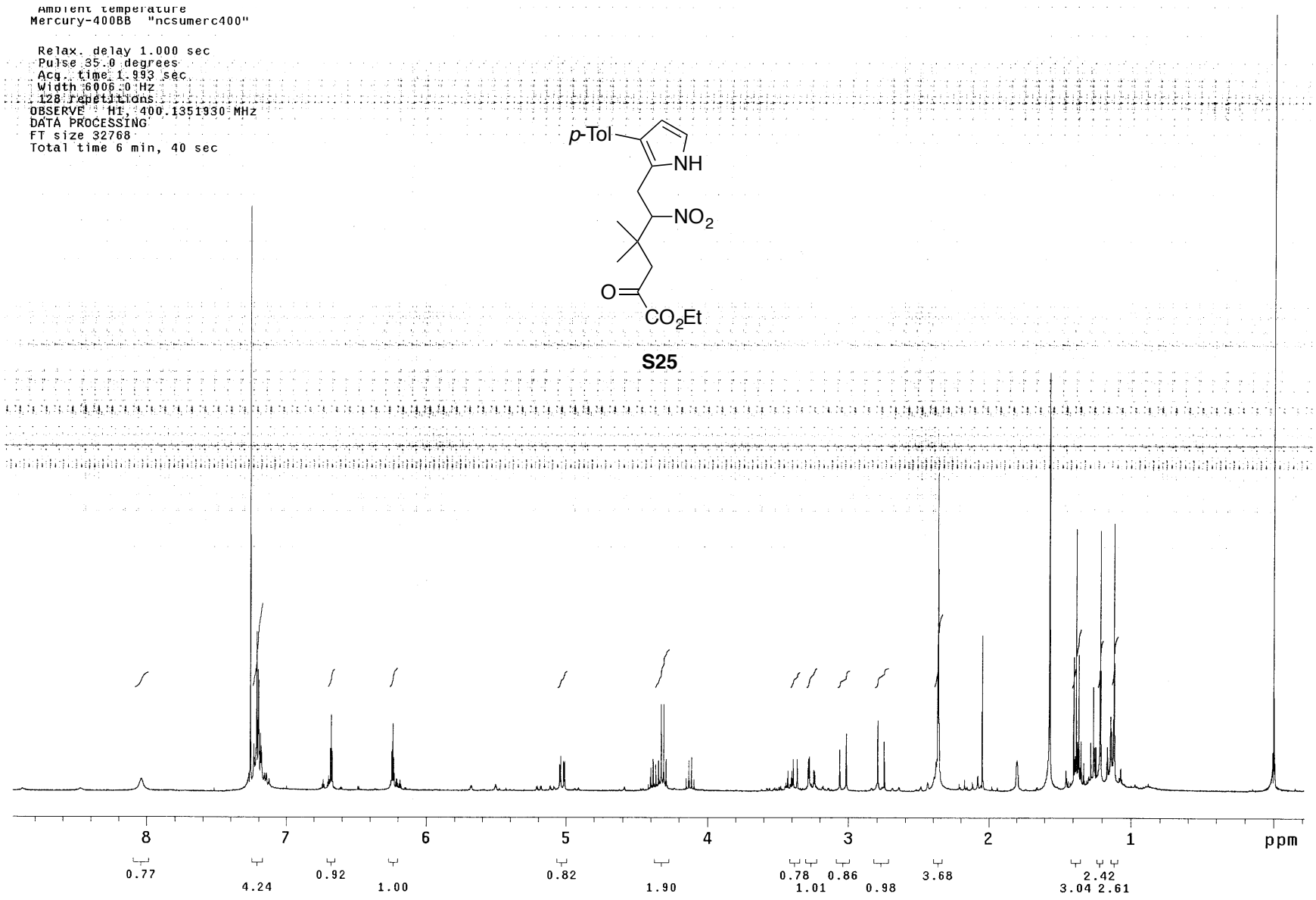

Pulse Sequence: szpul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"
Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 299.7918100 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec
EtO2C
NH
Me
N
O
S21
11
10
9
8
7
6
5
4
3
2
1
ppm
1.23
2.68
1.012.26
1.09
3.04
2.00
3.08
2.12
9.20

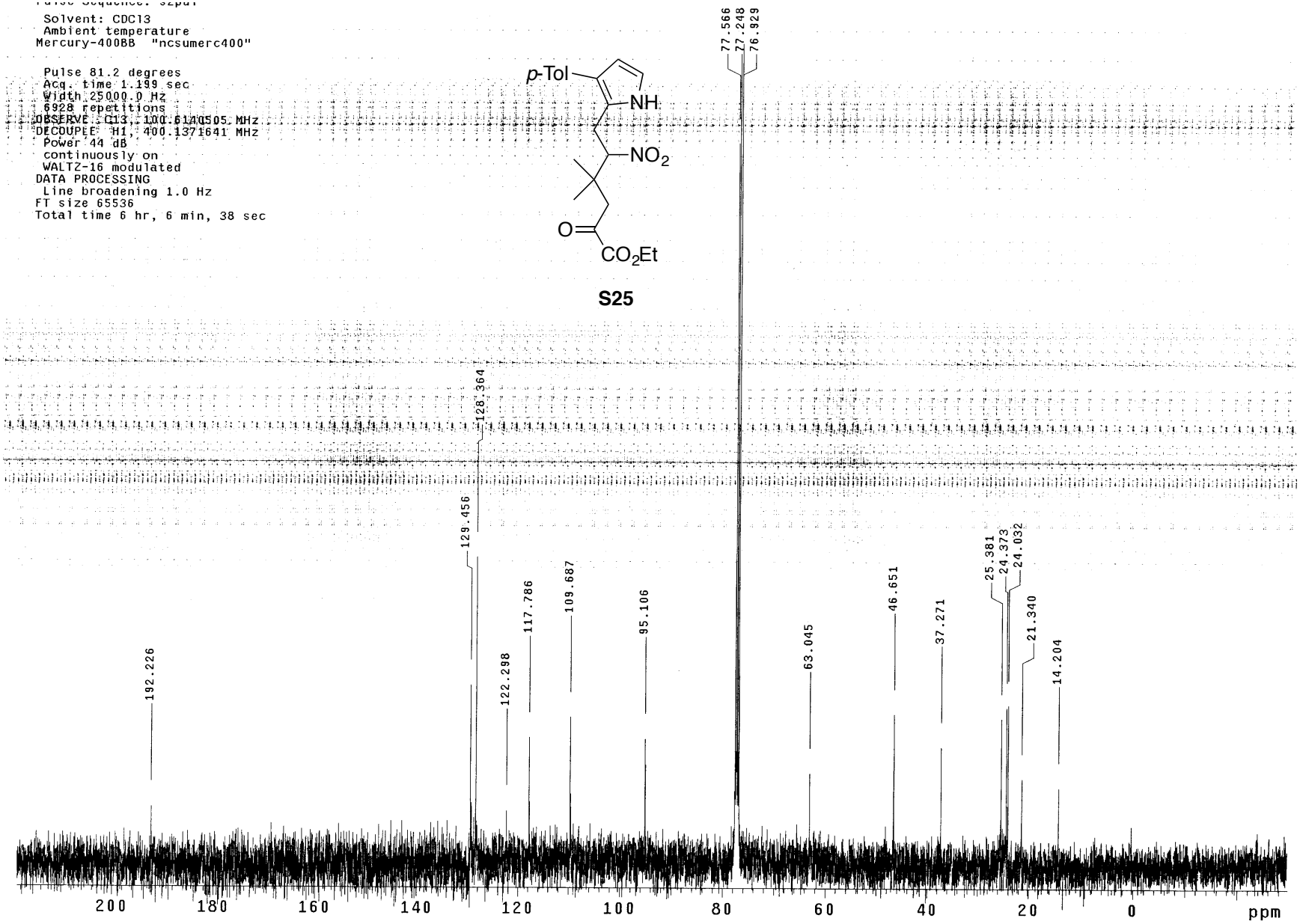

Ambient temperature
Mercury-300BB "ncsumerc638"
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 300.1683384 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
NTs
NO2
O
S
S
S22
9
8
7
6
5
4
3
2
1
ppm


Pulse Sequence: s2pul
NTs
NO2
O
S
S
S22
202.296
201.568
145.478
145.114
136.326
130.540
130.396
129.350
129.190
127.340
126.627
124.026
123.829
122.692
115.132
114.935
112.356
112.167
94.939
94.726
77.589
77.271
76.960
59.140
58.913
58.640
58.427
46.795
46.591
45.468
43.921
41.897
41.669
39.228
39.152
38.856
37.946
37.218
27.747
26.883
24.396
23.834
23.455
21.969
200
180
160
140
120
100
80
60
40
20
0
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc638"
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
64 repetitions
OBSERVE H1, 300.1683255 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
NTs
N
S
S
S23
9
8
7
6
5
4
3
2
1
ppm
1.88
2.78
0.96
0.86
1.03
1.30
1.16
3.76
1.17
2.80
2.21
2.96
3.03

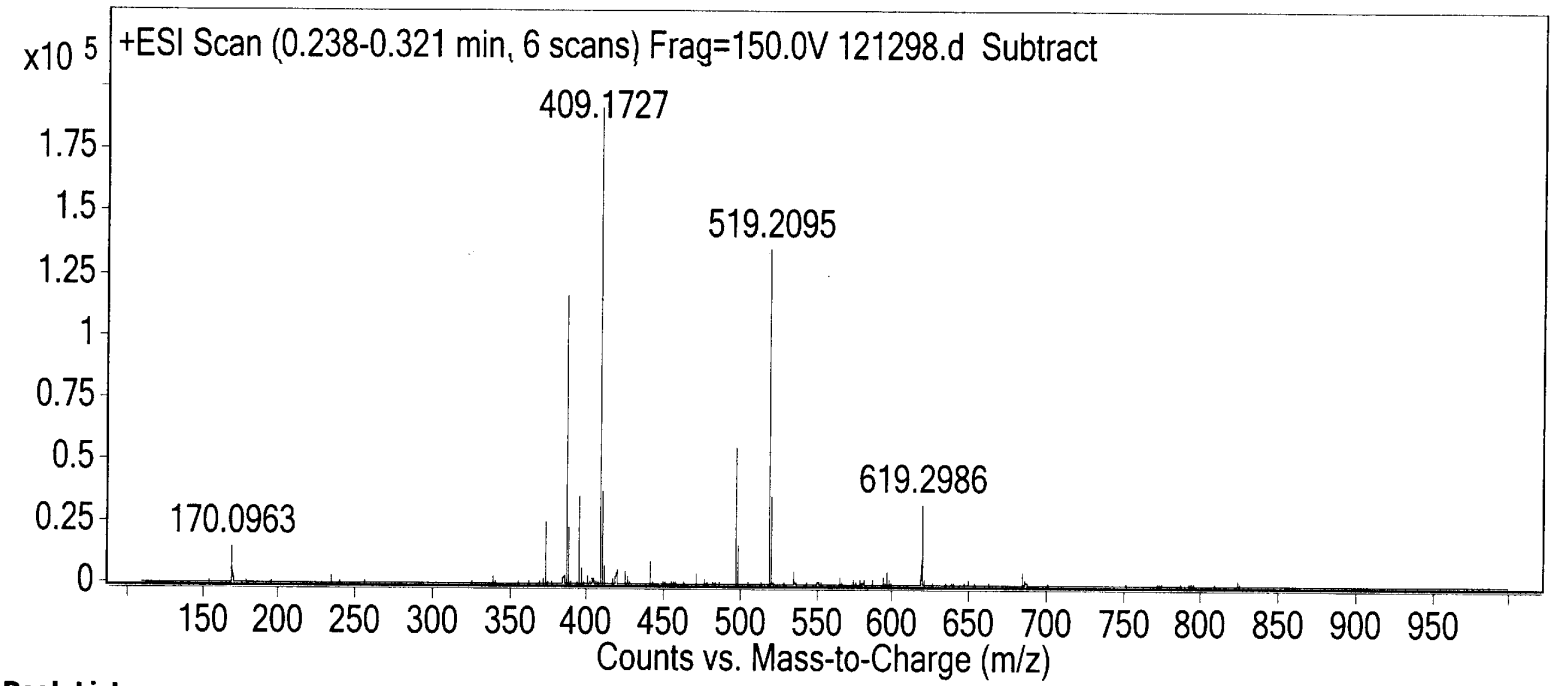

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
5000 repetitions
OBSERVE C13, 100.6140505 MHz
DECOUPLE H1, 400.1371641 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 2 min, 14 sec
NTs
N
S
S
S23
130.328
127.097
123.283
126.885
123.223
130.722
145.964
145.342
135.969
114.957
114.874
111.932
80.281
77.657
77.339
77.020
44.536
44.611
41.995
40.092
40.024
37.317
28.157
27.277
24.737
22.818
21.893
160
140
120
100
80
60
40
20
ppm


Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 35.0 degrees
Acq. time 1.993 sec
Width 6006.0 Hz
128 repetitions
OBSERVE H1, 400.1351930 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 40 sec
p-Tol
NH
NO2
O
CO2Et
S25
8
7
6
5
4
3
2
1
ppm
0.77
4.24
0.92
1.00
0.82
1.90
0.78
1.01
0.86
0.98
3.68
2.42
3.04
2.61


Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
6928 repetitions
OBSERVE C13, 100.6140505 MHz
DECOUPLE H1, 400.1371641 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 6 min, 38 sec
p-Tol
NH
NO2
O
CO2Et
S25
77.566
77.248
76.929
128.364
129.456
192.226
122.288
117.786
109.687
95.106
63.045
46.651
37.271
25.381
24.373
24.032
21.340
14.204
200
180
160
140
120
100
80
60
40
20
0
ppm

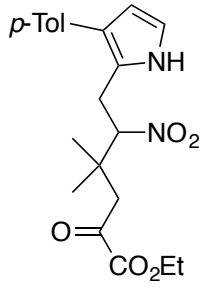
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
150	0	Esi

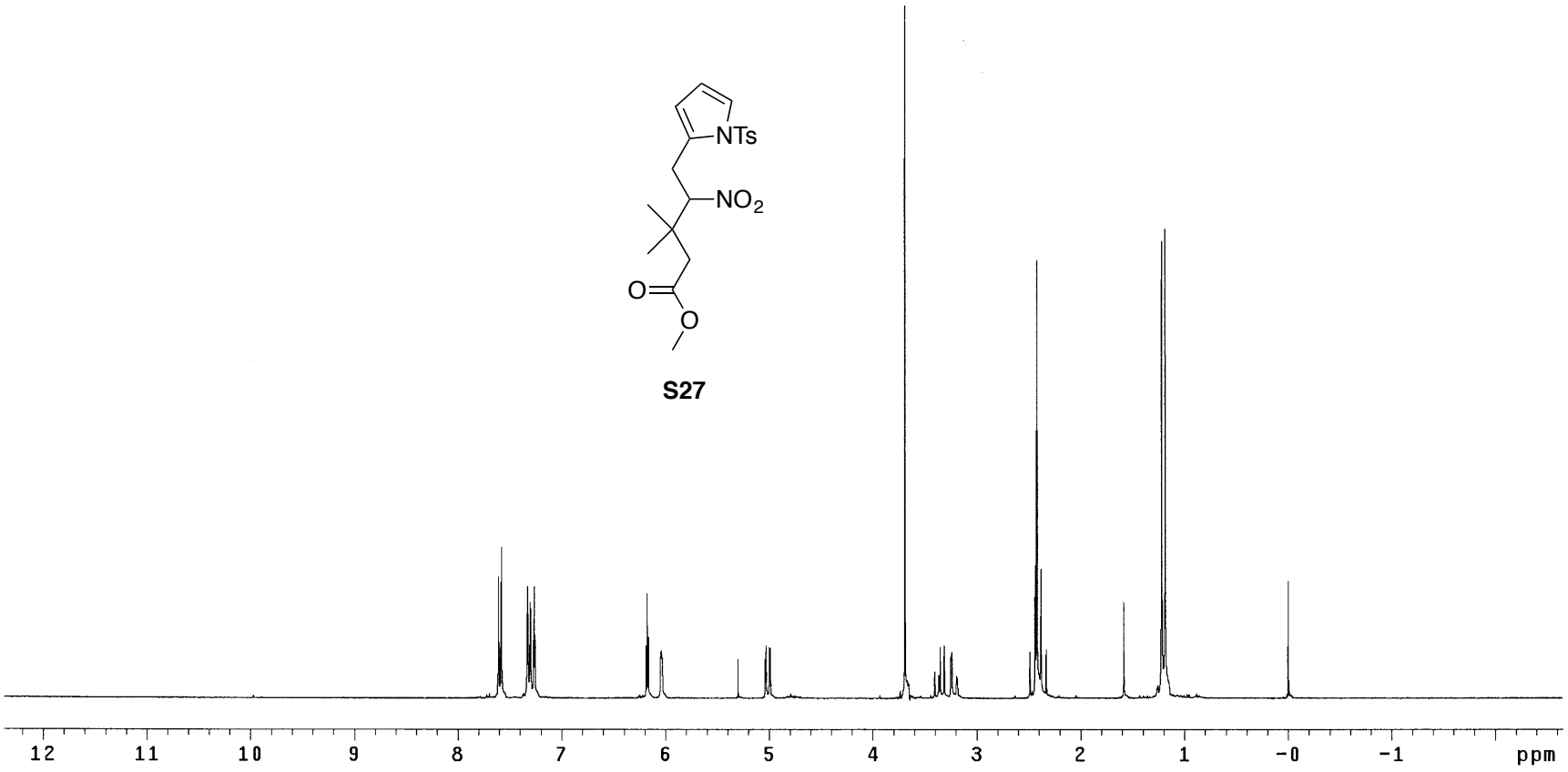


Peak List

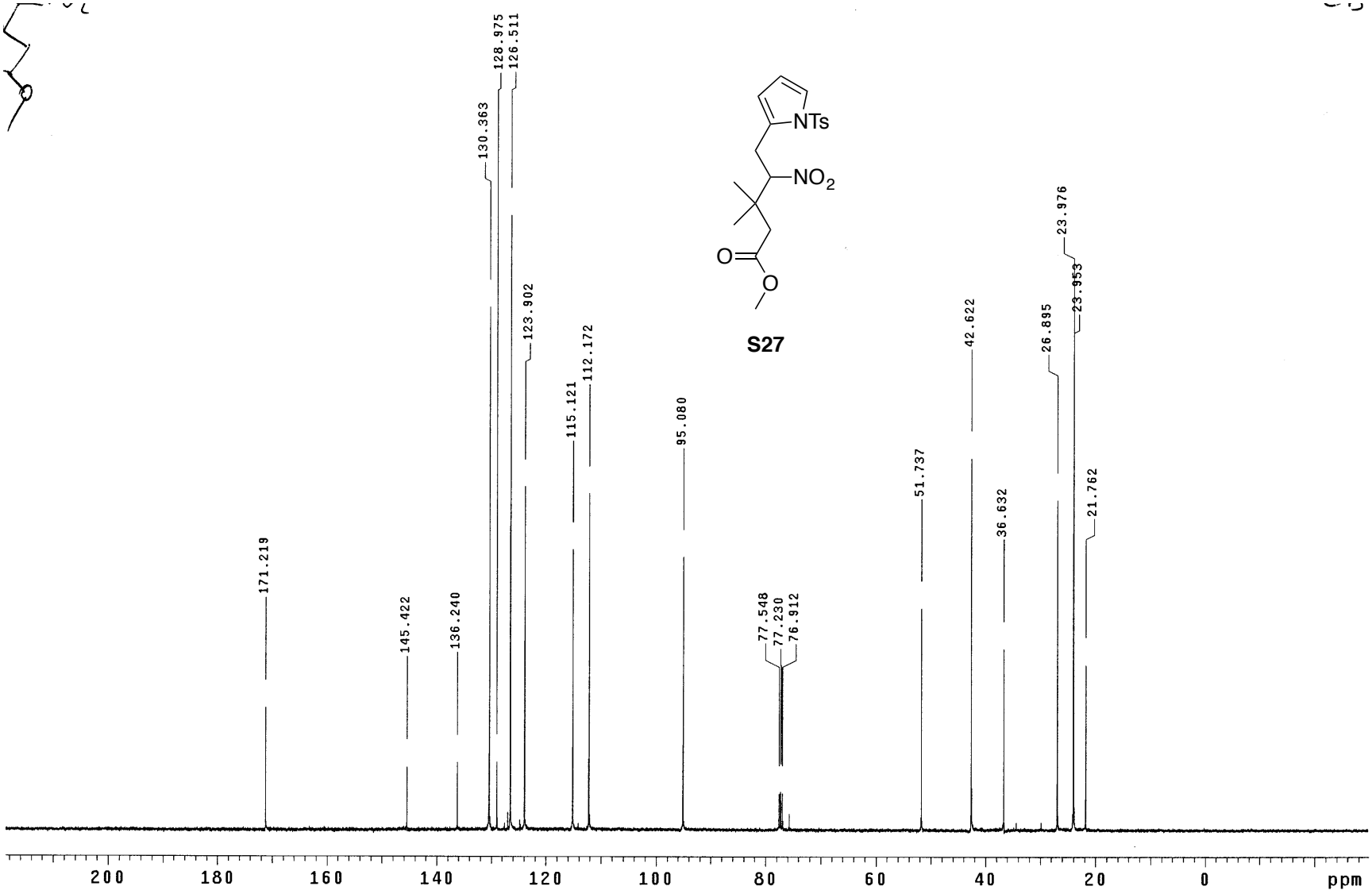
m/z	z	Abund	Formula	Ion
373.1753		25809		
387.1908	1	120614	C21 H27 N2 O5	(M+H)+
388.1937	1	23419	C21 H27 N2 O5	(M+H)+
395.1568		36887		
409.1727	1	199597		
410.1764	1	37646		
497.2275	1	59651		
519.2095	1	141651		
520.2132	1	34919		
619.2986		33066		



S25

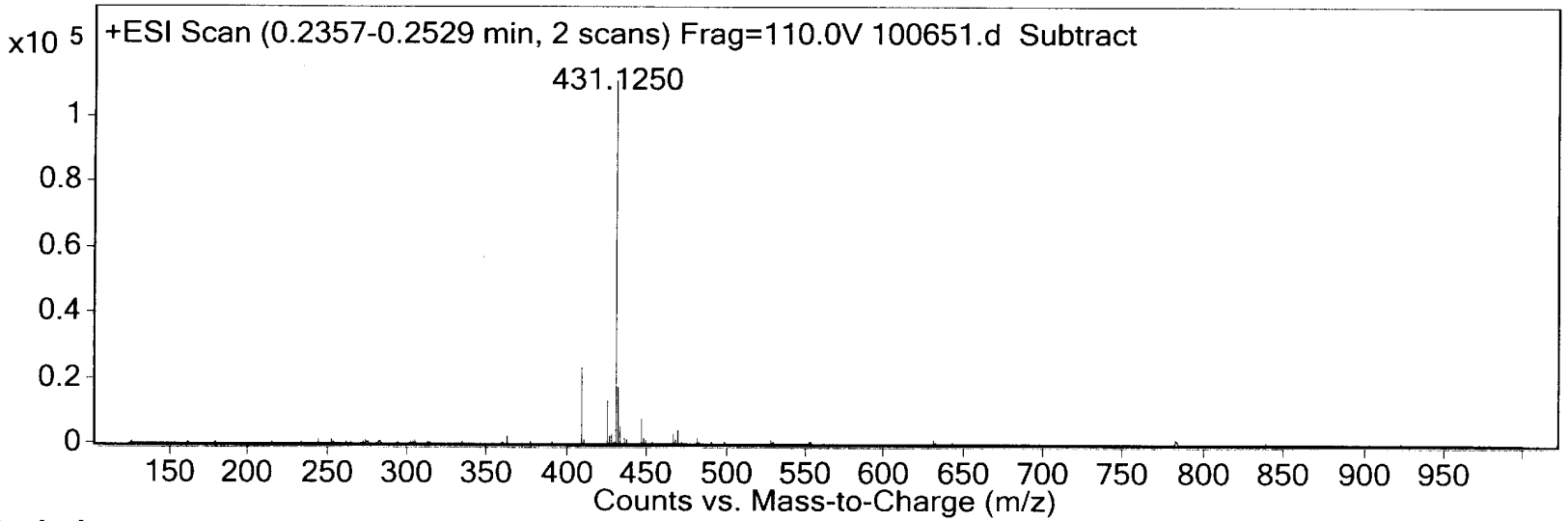


S27


NTs
NO2
O
O
S27
171.219
145.422
136.240
130.363
128.975
126.511
123.902
115.121
112.172
95.080
77.548
77.230
76.912
51.737
42.622
36.632
26.895
23.976
23.953
21.762
200
180
160
140
120
100
80
60
40
20
0
ppm

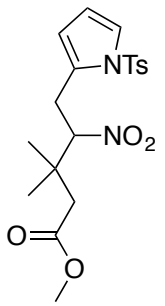
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
110	0	Esi

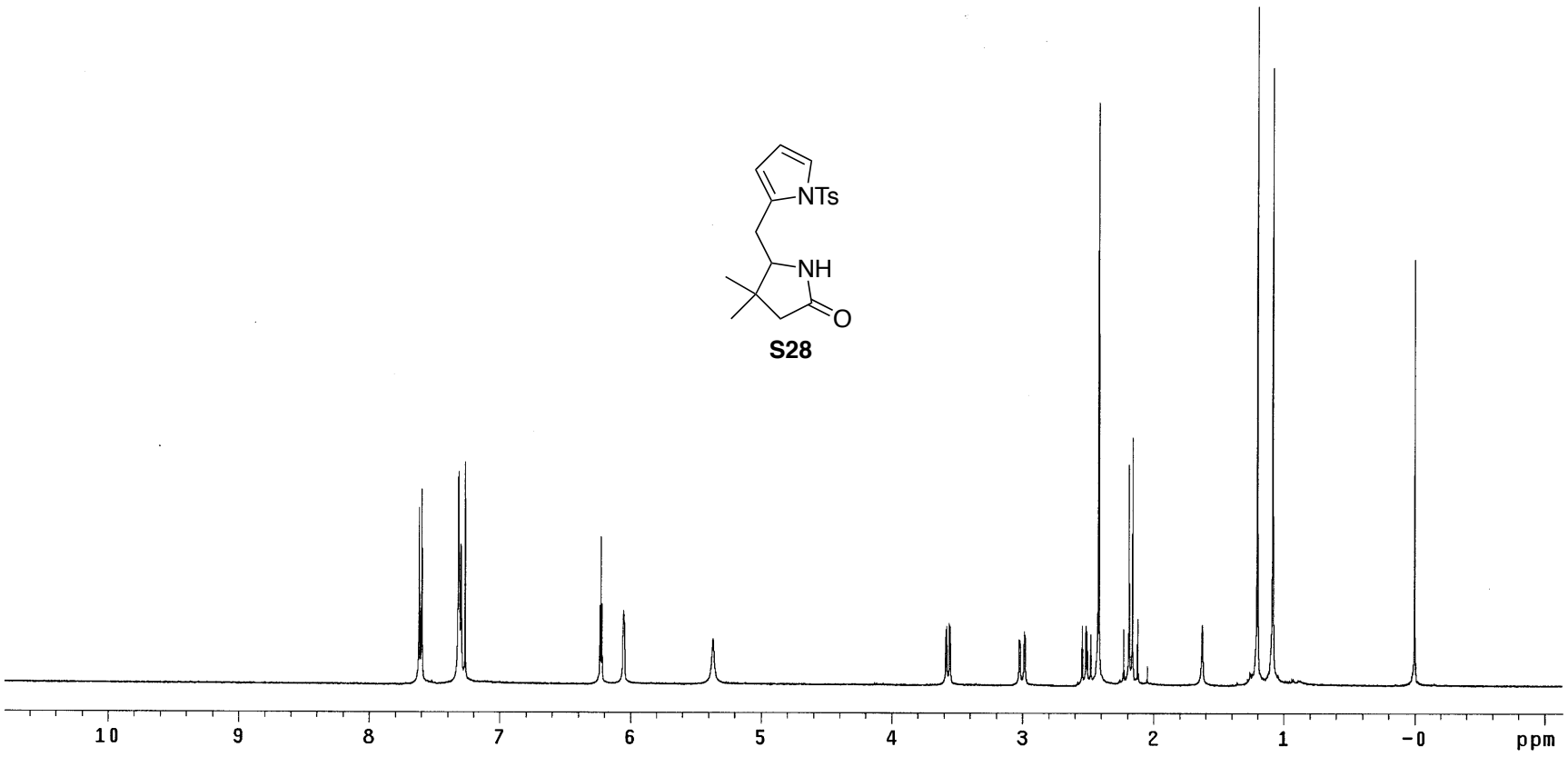


Peak List

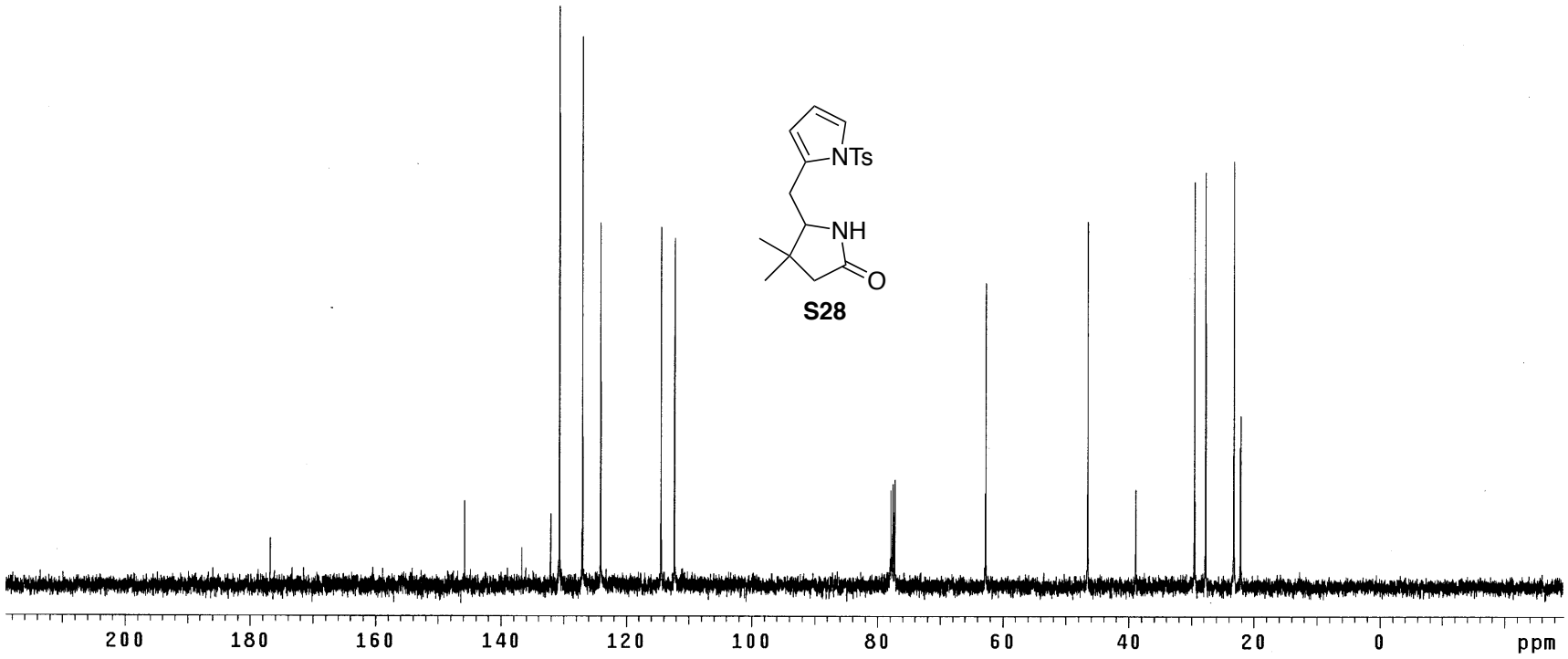
m/z	z	Abund	Formula	Ion
409.1435	1	23397	C19 H25 N2 O6 S	(M+H)+
426.1699	1	13760		
431.1250	1	111848		
432.1283	1	18445		
433.1251	1	5899		
447.0996	1	8009		



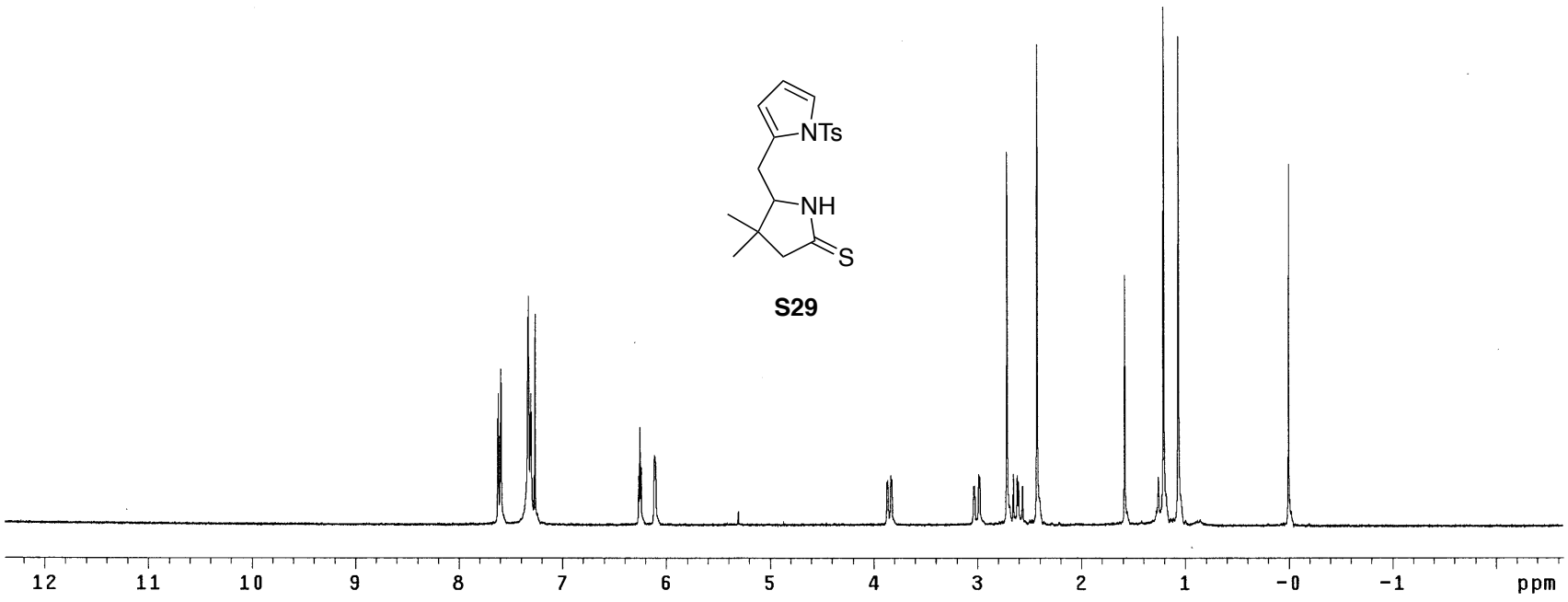
S27



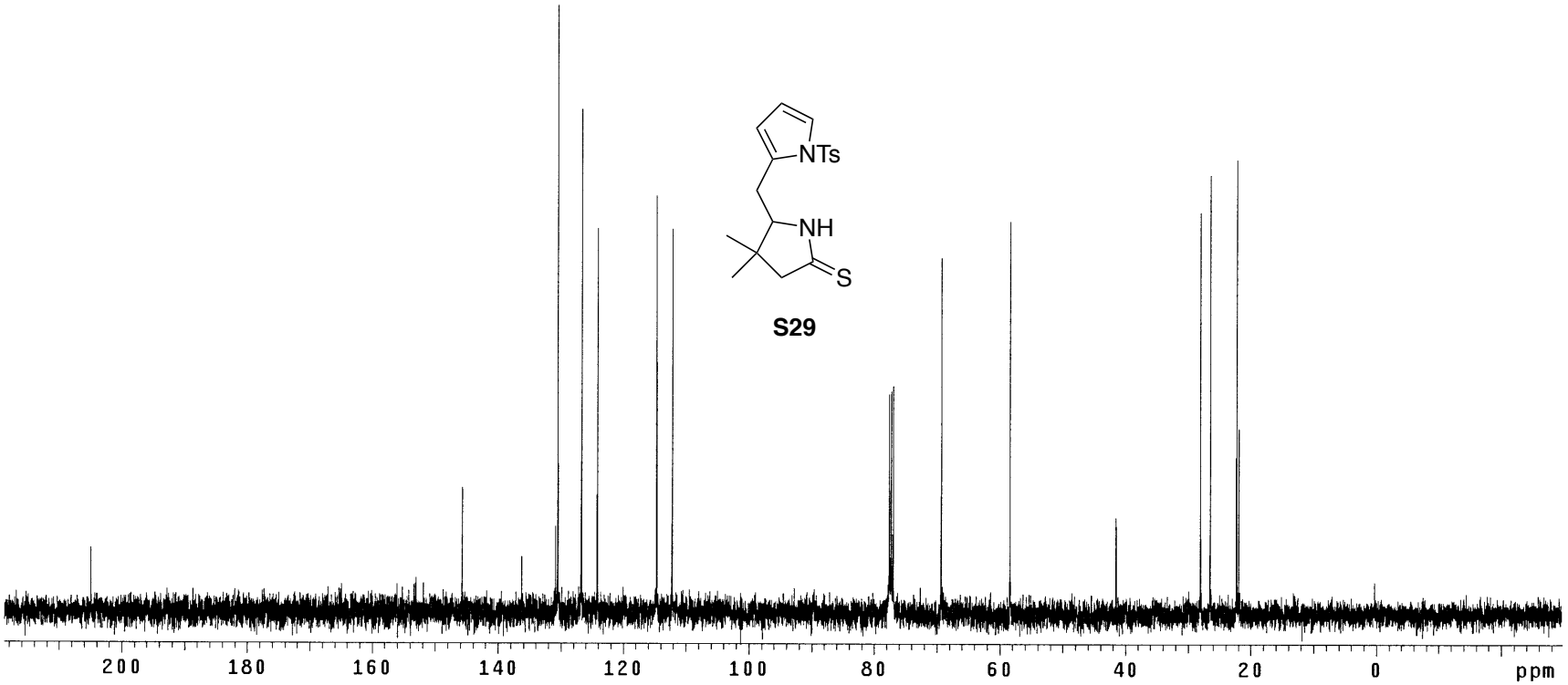
S28



S28



S29

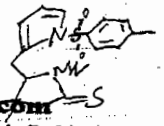


S29

ATLANTIC MICROLAB, INC.

Sample No. Ts-Pyr-Thiolac

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082
www.atlanticmicrolab.com



PROFESSOR/SUPERVISOR: J. S. Lindsey
P.O. #: 761361JSL

SUBMITTER

Company / School North Carolina State University
Address NCSU Dept of Chemistry
Campus Box 8204, 2620 Yarbrough Dr
Raleigh, NC 27695-8204
NAME Olga Mass DATE 5/25/10

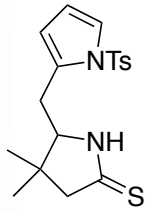
Element	Theory	Found	
C	59.64	60.01	
H	6.12	6.14	
N	7.73	7.40	

Single ☑ Duplicate ☐
Elements Present: C, H, N, O, S
Analyze for: C, H, N
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☐ No ☑
Temp. _____ Vac. _____ Time _____
FAX Service ☑ EMAIL Service ☑
FAX# /EMAIL 919-513-2830 fax
Rush Service ☐ (SEE CURRENT PRICE LIST)
~~Phone Service~~ ☐
Phone No. _____

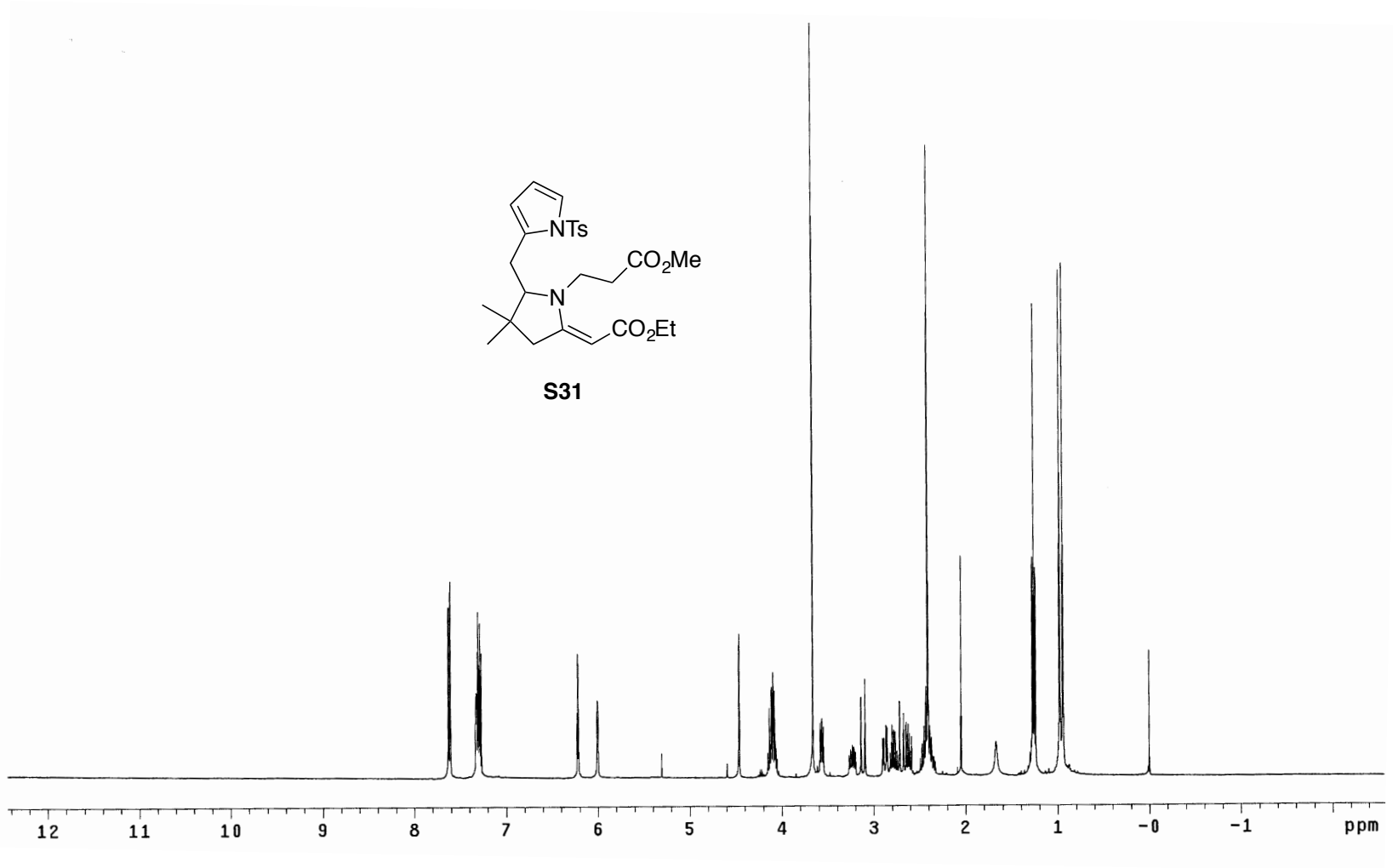
Date Received MAY 28 2010 Date Completed MAY 31 2010
Remarks:

email. oamass@ncsu.edu

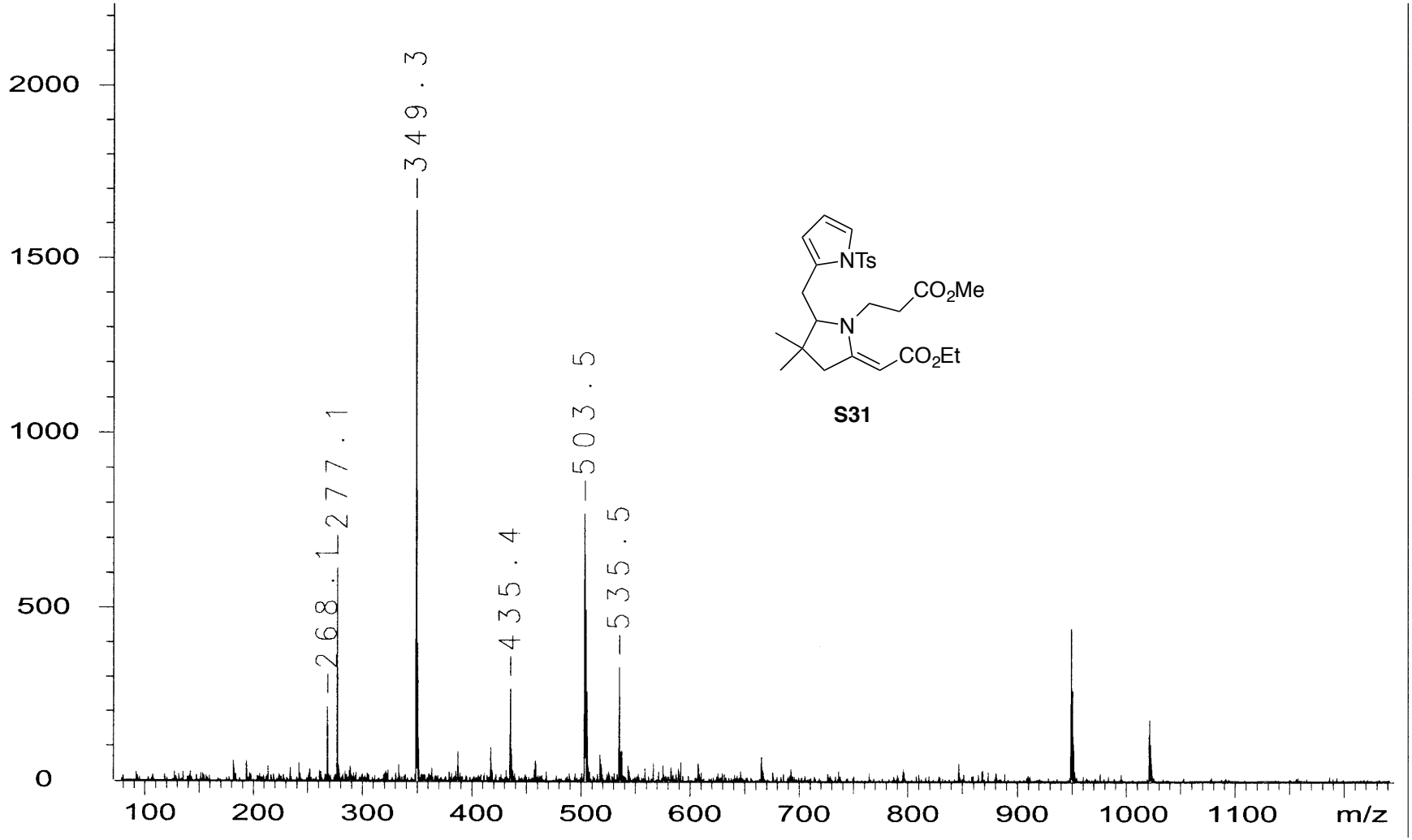
Billing Address:



S29



S31


2000
1500
1000
500
0
268.1
277.1
349.3
435.4
503.5
535.5
100
200
300
400
500
600
700
800
900
1000
1100
m/z
NTs
CO2Me
N
CO2Et

S31