Supplementary Material (ESI) for Chemical Communications

Supporting Information

Efficient Synthetic Method of 2,4,5-Trisubstituted 2,5-Chiral Tetrahydropyridines by One-pot Asymmetric Azaelectrocyclization Protocol

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Experimental section

All commercially available reagents were used without further purification. All solvents were used after distillation. Diethylether, Dioxane, and benzene were refluxed over and distilled from sodium. Dichloromethane and acetonitrile were refluxed over and distilled from P_2O_5. Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Preparative separation was usually performed by column chromatography on silica gel and on aluminum oxide deactivated with 5 w/% of H_2O. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer and chemical shifts were represented as δ-values relative to the internal standard TMS. IR spectra were recorded on a FT/IR Spectrometer. High resolution mass spectra (HRMS) were measured on an ESI-TOF MS. Melting point was uncorrected.

Data for (*Z*)-methyl 3-formyl-2-iodopent-2-enoate 5: IR (KBr disk, cm^{-1}) 2976, 1730, 1689, 1593, 1435, 1265, 1205, 1086; ^1H NMR (400 MHz $CDCl_3$) δ 9.60 (s, 1H), 3.87 (s, 3H), 2.41 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.5, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 196.5, 165.6, 146.7, 101.8, 53.5, 23.9, 12.6.

One-pot reaction by using (a), 5 and 6: To a suspension of the vinyliodide **5** (70 mg, 0.261 mmol) and molecular sieve 4Å (162 mg) in 1,4-dioxane (2 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (50 mg, 0.261 mmol) at room temperature, and the mixture was stirred for 30 min at 80 °C. Then to this suspension was added lithium chloride (22 mg, 0.523 mmol), Tri(2-furyl)phosphine (5 mg, 0.021 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (5 mg, 0.005 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane **6** (206 mg, 0.523 mmol) in 1,4-dioxane (2.0 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated *in vacuo* to give a crude products which were purified by column chromatography on silica gel (from 5% to 9% ethyl acetate in hexane) gave the 1,2,5,6-tetrahydropyridine derivative **8** (84 mg, 77%) as a yellow oil; IR (neat, cm^{-1}) 1755, 1595, 1377, 1289, 1053; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H), 7.18 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.01 (d, 1H, *J* = 8.0), 6.99 (d, 1H, *J* = 7.6 Hz), 6.80 (d, 1H, *J* = 2.5 Hz), 4.95-4.92 (m, 1H), 4.89-4.88 (m, 1H), 4.26 (brs, 1H), 3.72 (s, 3H), 3.19 (d, 2H,

J = 3.2 Hz), 2.95-2.92 (m, 1H), 2.69 (qq, 1H, 6.9, 6.9 Hz), 1.65-1.57 (m, 3H), 1.01 (d, 3H, *J* = 6.9 Hz), 0.86 (t, 3H, *J* = 7.6 Hz), 0.61 (d, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.7, 143.1, 141.0, 138.6, 136.0, 129.1, 128.7, 128.4, 127.9, 127.3, 123.5, 121.6, 91.0 74.8, 74.7, 57.1, 39.5, 35.9, 27.9, 26.7, 23.5.

One-pot reaction by using (a), 5 and 9: To a suspension of the vinyl iodide **5** (100 mg, 0.373 mmol) and molecular sieve 4Å (373 mg) in 1,4-dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (78 mg, 0.410 mmol) at room temperature, and the mixture was stirred for 30 min at 80 ºC. Then to this suspension was added lithium chloride (32 mg, 0.746 mmol), Tri(2-furyl)phosphine (7 mg, 0.03 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (7 mg, 0.007 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane **9** (427 mg, 0.746 mmol) in 1,4-dioxane (3.0 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated *in vacuo* to give a crude products which were purified by column chromatography on silica gel (from 5% to 25% ethyl acetate in hexane) gave the 1,2,5,6-tetrahydropyridine derivative **10** (108 mg, 48%) as a yellow oil and **11** (58 mg, 28%) as a yellow oil: Data for **10**; IR (KBr disk, cm^{-1}) 1719, 1449, 1371, 1256, 1173, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, 1H, *J* = 8.2 Hz), 7.72-7.69 (m, 2H), 7.54-7.50 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 1H), 7.19 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.02 (d, 1H, *J* = 7.6 Hz), 6.99 (d, 1H, *J* = 7.6 Hz), 6.91 (brs, 1H), 6.68 (d, 1H, *J* = 3.0 Hz), 5.13 (dd, 1H, *J* = 2.6, 2.6 Hz), 4.86-4.83 (m, 1H), 4.62 (d, 1H, *J* =5.3 Hz), 4.25 (brs, 1H), 3.71 (s, 3H), 3.16-3.14 (m, 2H), 3.05 (qq, 1H, *J* = 6.9 Hz), 2.90 (dd, 1H, *J* = 5.8, 5.8 Hz), 1.59-1.51 (m, 3H), 1.05 (d, 3H, *J* = 6.6 Hz), 0.81 (t, 3H, *J* = 7.6), 0.59 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 147.4, 143.2, 141.1, 139.1, 137.9, 136.3, 135.8, 134.1, 129.5, 129.3, 128.9, 127.3, 126.1, 126.0, 125.0, 124.2, 123.5, 121.8, 120.7, 115.4, 113.6, 91.1, 76.0, 75.3, 55.5, 51.7, 39.2, 35.8, 28.0, 26.4, 23.5, 21.0, 11.4. Data for **11** (R = iPr); IR (KBr disk, cm^{-1}) 1711, 1447, 1373, 1177, 1049; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 16.3 Hz, 1H), 8.24-8.22 (m, 1H), 7.86-7.83 (m, 2H), 7.52-7.45 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.86 (s, 1H), 6.77 (d, *J* = 16.3 Hz, 1H), 5.75 (d, *J* = 6.2 Hz, 1H), 5.35 (s, 1H), 5.26 (ddd, *J* = 6.0, 6.0, 3.0 Hz, 1H), 3.65 (qq, *J* = 6.9, 6.9 Hz, 1H), 3.31-3.20 (m, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.33 (d, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.23 (t,

J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 156.3, 147.9, 141.4, 139.4, 138.4, 137.6, 136.1, 133.7, 129.8, 129.6, 129.1, 128.6, 126.8, 126.1, 125.1, 124.5, 124.0, 123.8, 122.3, 120.8, 120.0, 115.1, 108.9, 91.1, 85.6, 62.6, 39.1, 28.8, 23.7, 20.8, 12.1; ESI-HRMS m/z calcd for $C_{34}H_{32}N_2O_4S$ $[M + H]^+$ 587.1980, found 587.1985.

One-pot reaction by using (b), 5 and 9: To a suspension of the vinyliodide **5** (50 mg, 0.187 mmol) and molecular sieve 4Å (260 mg) in 1,4-dioxane (2 mL) was added *cis*-1-aminoindan-2-ol **(-)-b** (28 mg, 0.187 mmol) at room temperature, and the mixture was stirred for 30 min at 80 ºC. Then to this solution was added lithium chloride (16 mg, 0.373 mmol), Tri(2-furyl)phosphine (4 mg, 0.015 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (4 mg, 0.004 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane **9** (243 mg, 0.373 mmol) in 1,4-dioxane (1.5 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated *in vacuo* to give a crude products which were purified by column chromatography on silica gel (from 5% to 25% ethyl acetate in hexane) gave the compound **11** (76 mg, 72%) as yellow oil: Data for **11**(R = H); IR (KBr disk, cm^{-1}) 1711, 1447, 1375, 1177, 1049; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 16.3 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.88-7.85 (m, 2H), 7.55-7.45 (m, 3H), 7.43-7.39 (m, 2H), 7.35-7.22 (m, 5H), 6.88 (s, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 5.32 (s, 1H), 5.22 (ddd, *J* = 6.0, 6.0, 2.3 Hz, 1H), 3.31-3.19 (m, 2H), 2.66-2.56 (m, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 156.6, 141.4, 139.4, 139.3, 138.5, 137.6, 133.7, 129.7, 129.1, 128.9, 128.7, 127.6, 126.8, 126.1, 125.2, 125.1, 124.5, 124.0, 120.8, 119.8, 115.1, 108.7, 91.4, 85.8, 63.4, 39.0, 20.7, 12.2; ESI-HRMS m/z calcd for $C_{31}H_{26}N_2O_4S$ $[M + H]^+$ 545.1511, found 545.1485.

Data for (*Z*)-*tert*-butyl 3-formyl-2-iodopent-2-enoate 15: IR (neat, cm^{-1}) 1720, 1688, 1460, 1372, 1261, 1152; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 2.53 (q, *J* = 7.8 Hz, 2H), 1.56 (s, 9H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 164.4, 144.4, 105.1, 27.8, 23.2, 13.3, 10.9; ESI-HRMS m/z calcd for $C_{10}H_{15}INNaO_3$ $[M+ Na]^+$ 332.9964, found 332.9951.

One-pot reaction by using (a), 15 and 9. To a suspension of the vinyl iodide **15** (50

mg, 0.162 mmol) and molecular sieve 5Å (162 mg) in Dioxane (1 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (31 mg, 0.162 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (14 mg, 0.324 mmol), Tri(2-furyl)phosphine (3 mg, 13 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (3 mg, 3 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **9** (185 mg, 0.324 mmol) in Dioxane (1 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 10 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (from 3% to 9% ethyl acetate in hexane) to gave the tetracyclic product **16T** (79 mg, 77%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3449, 2964, 1709, 1448, 1369 ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.51 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.41-7.36 (m, 3H), 7.31 (dd, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.00 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.89 (brs, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 5.14 (dd, *J* = 2.5, 2.5 Hz, 1H), 4.89-4.86 (m, 1H), 4.73 (d, *J* = 5.3 Hz, 1H), 4.23 (brs, 1H), 3.20-3.11 (m, 2H), 2.98 (qq, *J* = 6.9, 6.9 Hz, 1H), 2.86-2.83 (m, 1H), 1.55-1.47 (m, 2H), 1.44 (s, 9H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.58 (d, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 147.9, 143.2, 141.5, 139.1, 137.9, 136.0, 134.9, 134.1, 129.7, 129.3, 129.0, 128.8, 126.1, 124.9, 124.2, 123.5, 121.8, 120.7, 115.5, 113.8, 91.3, 80.7, 75.7, 75.3, 55.3, 39.3, 35.9, 28.0, 26.7, 23.5, 23.0 ; ESI-HRMS m/z calcd for $C_{38}H_{42}N_2NaO_5S$ $[M + Na]^+$ 661.2712, found 661.2729.

One-pot reaction by using (a), 15 and 17. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **17** (377 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 2.5 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **17T** (174 mg, 83%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3449, 2964,

1709, 1369, 1174; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.65 (s, 1H), 7.64 (d, *J* = 9.4 Hz, 1H), 7.34 (td, *J* = 8.5, 1.0 Hz, 1H), 7.24-7.20 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.0Hz, 1H), 6.92 (d, *J* = 7.5Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 4.97 (td, *J* = 5.0, 2.0 Hz, 1H), 4.93 (d, *J* = 5.6 Hz, 1H), 4.33 (t, *J* = 2.5 Hz, 1H), 4.27 (d, *J* = 0.5 Hz, 1H), 3.20 (m, 2H), 2.83-2.81 (m, 1H), 2.65 (sep, *J* = 7.0 Hz, 1H), 2.31 (s, 3H), 1.70-1.55 (m, 2H), 1.45 (s, 9H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H), 0.15 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 147.6, 145.0, 143.0, 135.9, 135.8, 136.6, 135.2, 130.8, 129.9, 129.5, 128.7, 126.8, 124,9, 124.8, 123.4, 122.9, 121.7, 121.6, 121.3, 113.3, 91.1, 80.7, 74.7, 74.4, 55.3, 39.4, 36.5, 28.0, 27.7, 27.0, 22.8, 22.4, 21.5, 12.3; ESI-HRMS m/z calcd for $C_{39}H_{44}N_2NaO_5S$ $[M + Na]^+$ 675.2869, found 675.2848.

One-pot reaction by using (a), 15 and 18. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **18** (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 1 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **18T** (94 mg, 63%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3416, 2964, 1668, 1591, 1473 ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56-8.54 (m, 1H), 7.76 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.52 (dt, *J* = 7.5, 1.0Hz, 1H), 7.28-7.25 (m, 1H), 7.16 (t, *J* = 7.5Hz, 1H), 6.99 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.76 (d, *J* = 2.5 Hz, 1H), 5.09 (d, *J* = 5.5 Hz, 1H), 4.98-4.95 (m, 1H), 4.38 (t, *J* = 3.0 Hz, 1H), 4.25 (d, *J* = 1.0 Hz, 1H), 3.17-3.16 (m, 2H), 2.89-2.88 (m, 1H), 2.57 (sep, *J* = 7.0 Hz, 1H), 1.62-1.52 (m, 2H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.67 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 161.3, 148.5, 147.2, 143.2, 136.5, 136.1, 135.3, 129.8, 128.7, 123.8, 123.4, 122.7, 121.7, 90.9, 80.6, 75.0, 74,9, 65.6, 39.4, 36.0, 28.1, 28.0, 27.0, 23.5, 22.9, 11.7 ; ESI-HRMS m/z calcd for $C_{29}H_{37}N_2O_3$ $[M + H]^+$ 461.2804, found 461.2798.

One-pot reaction by using (a), 15 and 19. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **19** (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **19T** (130 mg, 88%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3449, 2964, 1709, 1255, 1163 ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.0 Hz, 1H), 8.61 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.77 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.35 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 4.96-4.93 (m, 2H), 4.81 (d, *J* = 5.0 Hz, 1H), 4.25 (d, *J* = 1.0 Hz, 1H), 4.13 (brt, *J* = 3.0 Hz, 1H), 3.19-3.18 (m, 2H), 2.89-2.86 (m, 1H), 2.58 (sep, *J* = 7.0 Hz, 1H), 1.64-1.53 (m, 2H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.64 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ , 165.1, 150.1, 149.4, 147.4, 136.9, 136.8, 135.6, 130.0, 128.9, 123.5, 123.3, 121.7, 90.9, 80.8, 74.8, 74.8, 61.2, 39.4, 36.0, 28.1, 28.0, 27.0, 23.4, 22.7, 11.7 ; ESI-HRMS m/z calcd for $C_{29}H_{37}N_2O_3$ $[M+H]^+$ 461.2804, found 461.2797.

One-pot reaction by using (a), 15 and 20. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **20** (285 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4.5 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **20T** (133 mg, 81%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3449, 2964,

1711, 1253, 1163 ; ^{1}H NMR (400 Mhz, $CDCl_3$) δ 9.00 (d, *J* = 2.5 Hz, 1H), 8.19 (d, *J* = 1.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.75 (dt, *J* = 7.0, 1.5 Hz, 1H), 7.59 (dt, *J* = 8.0, 1.0Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 6.5 Hz, 2H), 6.69 (d, *J* = 3.0 Hz, 1H), 5.02-4.99 (m, 1H), 4.88 (d, *J* = 5.5 Hz, 1H), 4.33 (t, *J* = 3.0 Hz, 1H), 4.31 (s, 1H), 3.22-3.21 (m, 1H), 2.94 (m, 1H), 2.55 (sep, *J* = 7.0 Hz, 1H), 1.67-1.61 (m, 2H), 1.01(d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.35 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 147.7, 143.0, 142.2, 136.6, 136.1, 129.0, 128.7, 128.0, 125.8, 123.5, 122.9, 121.6, 91.1, 80.5, 74.9, 74.6, 58.6, 39.5, 35.9, 28.0, 26.8, 23.6, 23.0, 11.5 ; ESI-HRMS m/z calcd for $C_{33}H_{39}N_2O_3$ $[M+H]^+$ 511.2961, found 511.2953.

One-pot reaction by using (a), 15 and 21. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **21** (257 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **21T** (109 mg, 73%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3449, 2964, 1709, 1253, 1167 ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 5.0, 3.0 Hz, 1H) , 7.28 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 4.93-4.89 (m, 2H), 4.25 (t, *J* = 3.0 Hz, 1H), 4.16 (d, *J* = 3.5 Hz, 1H), 3.19-3.18 (m, 2H), 2.89-2.87 (m, 1H), 2.78 (sep, *J* = 7.0 Hz, 1H), 1.65-1.52 (m, 2H), 1.46 (s, 9H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 151.9, 147.5, 143.1, 135.6, 135.5, 130.1, 129.5, 129.3, 128.9, 127.5, 126.9, 123.5, 121.7, 91.0, 80.8, 74.8, 61.7, 39.4, 36.0, 28.2, 28.0, 27.0, 23.4, 22.5, 11.7 ; ESI-HRMS m/z calcd for $C_{28}H_{35}NNaO_3S$ $[M+Na]^+$ 488.2235, found 488.2240.

One-pot reaction by using (a), 15 and 6. To a suspension of the vinyl iodide **15** (100

mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **6** (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **22T** (120 mg, 81%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3462, 2928, 1664, 1454, 1369; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33(m, 5H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 4.97-4.93 (m, 1H), 4.89 (d, *J* = 5.0 Hz, 1H), 4.26 (s, 1H), 4.10 (t, *J* = 2.0 Hz, 1H), 3.20-3.19 (m, 2H), 2.88 (m, 1H), 2.68 (sep, *J* = 7.0 Hz, 1H), 1.65-1.55 (m, 2H), 1.47 (s, 9H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 147.7, 143.0, 141.2, 137.1, 136.1, 129.2, 128.9, 128.7, 128.3, 127.8, 123.5, 121.6, 91.1, 80.4, 74.7, 74.7, 63.6, 39.5, 36.0, 28.0, 27.8, 27.1, 23.5, 22.8, 11.7; ESI-HRMS m/z calcd for $C_{30}H_{37}NNaO_3$ $[M + Na]^+$ 482.2695, found 482.2671.

One-pot reaction by using (a), 15 and 23. To a suspension of the vinyl iodide **15** (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added *cis*-1-amino-7-isopropylindan-2-ol **(a)** (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 ºC for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 μmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 μmol) at 80 ºC, and the mixture was stirred for 10 min at this temperature then vinyl stannane **23** (314 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 1.5 h, cooled to room temperature, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to gave the tetracyclic product **23T** (118 mg, 66%) as a yellow amorphous: IR (KBr disk, cm^{-1}) 3508, 2959, 2858, 1711, 1253 ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 3.0 Hz, 1H), 5.85 (dt, *J* = 15.0, 4.5 Hz,

1H), 5.72 (ddt, *J* = 15.0, 9.0, 1.5 Hz, 1H), 4.88 (d, *J* = 5.0 Hz, 1H), 4.79-4.77 (m, 1H), 4.25 (dd, *J* = 5.0, 1.5 Hz, 2H), 4.14 (d, *J* = 1.0 Hz, 1H), 3.63-3.56 (m, 2H), 3.15 (m, 1H), 2.82-2.80 (m, 1H), 1.25 (m, 11H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.15 (d, *J* = 7.0 Hz, 3H), 0.93 (s, 9H), 0.74 (t, *J* = 7.5 Hz, 3H), 0.10 (s, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 147.6, 143.1, 136.9, 132.4, 130.0, 129.2, 128.7, 123.5, 121.7, 91.0, 80.4, 74.4, 74.7, 63.0, 61.6, 39.4, 35.8, 28.4, 26.4, 25.9, 23.5, 23.5, 11.1, -5.2, -5.2 ; ESI-HRMS m/z calcd for $C_{33}H_{52}NO_4Si$ $[M + H]^+$ 554.3666, found 554.3652.

4-Hydroxymethyl-2-(*N*-benzensulfonylindol-2-yl)-1,2,5,6-tetrahydropyridine 16P : To a solution of compound **16T** (22 mg, 34.4 μmol) in CH_2Cl_2 (3 mL) was slowly added diisobutylaluminium hydride (0.44 mL. 0.44 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 30 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (20% to 50% ethyl acetate in hexane) gave the diol (15 mg, 76%).

To a solution of diol obtained above (15 mg, 26.3 μmol) in $CHCl_3$ (2 mL) was added *n*-propylamine (22 μL, 0.263 mmol) and lead tetraacetate (70 mg, 0.158 mmol) at –50 °C. After the mixture was stirred at this temperature for 43 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 5% methanol in chloroform containing 0.5% triethylamine) gave the **16P** (8 mg, 77%) as a pale yellow amorphous: IR (thin film) 3339, 2963, 2929, 2874, 1655, 1449, 1368, 1173, 1092, 1046 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.74-7.77 (m, 2H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.19-7.44 (m, 5H), 6.49 (s, 1H), 5.79 (d, *J* = 2.5 Hz, 1H), 5.11 (s, 1H), 4.74 (s, 1H), 4.19 (d, *J* = 14.0 Hz, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 2.95 (dd, *J* = 12.0, 5.0 Hz, 1H), 2.66 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.20 (m, 1H), 1.60-1.70 (m, 1H), 1.28-1.41 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.7, 141.1, 138.8, 137.6, 133.8, 129.7, 129.3, 129.0, 128.5, 126.2, 124.9, 123.8, 121.7, 120.9, 115.0, 64.6, 50.5, 43.0, 36.7, 23.5, 11.3; ESI-HRMS m/z calcd for $C_{22}H_{25}N_2O_3S$ $(M + H)^+$ 397.1586, found 397.1587

4-Hydroxymethyl-2-(*N*-*p*-toluenesulfonylindol-3-yl)-1,2,5,6-tetrahydropyridine 17P : To a solution of compound **17T** (30 mg, 46.0 μmol) in CH_2Cl_2 (3 mL) was slowly added diisobutylaluminium hydride (0.46 mL. 0.46 mmol, 1M in toluene) at -78 ºC. After the mixture was stirred at this temperature for 40 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 1 h. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (20% to 50% ethyl acetate in hexane) gave the diol (19 mg, 79%).

To a solution of diol obtained above (12 mg, 20.5 μmol) in $CHCl_3$ (1.8 mL) was added *n*-propylamine (25 μL, 0.308 mmol) and lead tetraacetate (82 mg, 0.185 mmol) at –50 ºC. After the mixture was stirred at this temperature for 42 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 5% methanol in chloroform containing 0.5% triethylamine) gave the **17P** (7 mg, 83%) as a pale yellow amorphous: IR (thin film) 3318, 2965, 2932, 2874, 1655, 1447, 1373, 1175, 1125, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.17-7.33 (m, 5H), 5.81 (s, 1H), 4.73 (s, 1H), 4.18 (d, *J* = 13.0 Hz, 1H), 4.12 (d, *J* = 13.0 Hz, 1H), 2.88-2.98 (m, 2H), 2.32 (s, 3H), 2.11 (m, 1H), 1.62-1.75 (m, 1H), 1.45-1.57 (m, 1H), 0.94 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 141.7, 135.6, 135.2, 129.8, 129.5, 126.8, 124.8, 124.1, 124.0, 123.4, 123.2, 120.1, 113.8, 65.0, 50.6, 44.6, 36.4, 23.9, 21.5, 11.9; ESI-HRMS m/z calcd for $C_{23}H_{27}N_2O_3S$ $(M + H)^+$ 411.1742, found 411.1755

4-Hydroxymethyl-2-(2-pyridyl)-1,2,5,6-tetrahydropyridine 18P : To a solution of compound **18T** (35 mg, 76.0 μmol) in CH_2Cl_2 (4 mL) was slowly added diisobutylaluminium hydride (0.76 mL. 0.76 mmol, 1M in toluene) at -78 ºC. After the mixture was stirred at this temperature for 50 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 33 min. The organic layers were extracted

with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (67% to 100% ethyl acetate in hexane and then 17% methanol in chloroform) gave the diol (21 mg, 70%).

To a solution of diol obtained above (18 mg, 45.9 μmol) in $CHCl_3$ (3.0 mL) was added *n*-propylamine (57 μL, 0.688 mmol) and lead tetraacetate (122 mg, 0.275 mmol) at –50 °C. After the mixture was stirred at this temperature for 50 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 33% methanol in chloroform containing 0.5% triethylamine) gave the **18P** (6 mg, 60%) as a yellow amorphous: IR (thin film) 3373, 2965, 2926, 1655, 1590, 1460, 1437, 1380, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.64 (td, *J* = 7.5, 2.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 7.5, 4.5 Hz, 1H), 5.80 (s, 1H), 4.68 (s, 1H), 4.14 (d, *J* = 13.0 Hz, 1H), 4.09 (d, *J* = 13.0 Hz, 1H), 3.07 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.02 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.07 (m, 1H), 1.48-1.71 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.2, 141.6, 136.9, 122.5, 122.4 122.0, 65.0, 59.2, 44.3, 35.9, 24.3, 12.1; ESI-HRMS m/z calcd for $C_{13}H_{19}N_2O$ $(M + H)^+$ 219.1497, found 219.1499

4-Hydroxymethyl-2-(3-pyridyl)-1,2,5,6-tetrahydropyridine 19P : To a solution of compound **19T** (33 mg, 71.6 μmol) in CH_2Cl_2 (4 mL) was slowly added diisobutylaluminium hydride (0.716 mL. 0.716 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 34 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (50% to 100% ethyl acetate in hexane) gave the diol (22 mg, 78%).

To a solution of diol obtained above (12 mg, 30.6 μmol) in $CHCl_3$ (2.5 mL) was added *n*-propylamine (25 μL, 0.306 mmol) and lead tetraacetate (81 mg, 0.183 mmol) at –50 °C. After the mixture was stirred at this temperature for 23 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The

organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the **19P** (5 mg, 75%) as a pale yellow amorphous: IR (thin film) 3350, 2963, 2928, 1458, 1428, 1217, 1030, 874 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.58 (s, 1H), 8.49 (brs, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.23-7.27 (m, 1H), 5.67 (s, 1H), 4.62 (s, 1H), 4.11-4.19 (m, 2H), 3.01 (d, *J* = 4.0 Hz, 2H), 2.14 (m, 1H), 1.52-1.73 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 149.2, 142.4, 136.9, 136.2, 123.6, 121.9, 64.5, 55.8, 43.9, 35.8, 24.1, 11.9; ESI-HRMS m/z calcd for $C_{13}H_{19}N_2O$ $(M + H)^+$ 219.1497, found 219.1487

4-Hydroxymethyl-2-(3-quinolyl)-1,2,5,6-tetrahydropyridine 20P : To a solution of compound **20T** (28 mg, 54.8 μmol) in CH_2Cl_2 (4 mL) was slowly added diisobutylaluminium hydride (0.548 mL. 0.548 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 45 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (33% to 100% ethyl acetate in hexane) gave the diol (20 mg, 82%).

To a solution of diol obtained above (20 mg, 45.2 μmol) in $CHCl_3$ (3 mL) was added *n*-propylamine (37 μL, 0.451 mmol) and lead tetraacetate (120 mg, 0.271 mmol) at –50 °C. After the mixture was stirred at this temperature for 40 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 17% methanol in chloroform containing 0.5% triethylamine) gave the **20P** (8 mg, 66%) as a yellow amorphous: IR (thin film) 3390, 2965, 2928, 1622, 1499, 1462, 1379, 1217, 1046 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.89 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.66 (td, *J* = 8.5, 1.5 Hz, 1H), 7.51 (td, *J* = 8.0, 1.0 Hz, 1H), 5.73 (s, 1H), 4.68 (s, 1H), 4.12-4.21 (m, 2H), 3.07 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.00 (dd, *J* = 12.5, 4.5 Hz, 1H) 2.05 (m, 1H), 1.60-1.70 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 147.6,

143.2, 136.3, 130.0, 128.8, 128.0, 127.6, 127.1, 120.1, 64.1, 55.0, 42.7, 35.2, 23.7, 11.4; ESI-HRMS m/z calcd for $C_{17}H_{21}N_2O$ $(M + H)^+$ 269.1654, found 269.1659

4-Hydroxymethyl-2-(3-thienyl)-1,2,5,6-tetrahydropyridine 21P : To a solution of compound **21T** (35 mg, 75.2 μmol) in CH_2Cl_2 (4 mL) was slowly added diisobutylaluminium hydride (0.752 mL. 0.752 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 31 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 36 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (25% to 40% ethyl acetate in hexane) gave the diol (23 mg, 77%).

To a solution of diol obtained above (21 mg, 52.8 μmol) in $CHCl_3$ (3.5 mL) was added *n*-propylamine (43 μL, 0.528 mmol) and lead tetraacetate (141 mg, 0.317 mmol) at –50 °C. After the mixture was stirred at this temperature for 20 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the **21P** (9 mg, 76%) as a yellow amorphous: IR (thin film) 3384, 2963, 2928, 1649, 1458, 1217, 1046, 857 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 5.77 (s, 1H), 4.59 (s, 1H), 4.14 (d, *J* = 13.5 Hz, 1H), 4.08 (d, *J* = 13.5 Hz, 1H), 2.90-3.00 (m, 2H), 2.06 (m, 1H), 1.58-1.69 (m, 1H), 1.40-1.53 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 141.1, 128.5, 127.1, 126.0, 124.4, 121.9, 65.0, 53.8, 44.5, 36.1, 24.2, 12.0; ESI-HRMS m/z calcd for $C_{12}H_{18}NOS$ $(M + H)^+$ 224.1109, found 224.1099

4-Hydroxymethyl-2-phenyl-1,2,5,6-tetrahydropyridine 22P: To a solution of compound **22T** (65 mg, 0.141 mmol) in CH_2Cl_2 (5 mL) was slowly added diisobutylaluminium hydride (1.13 mL. 1.13 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 34 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 30 min. The organic layers were extracted

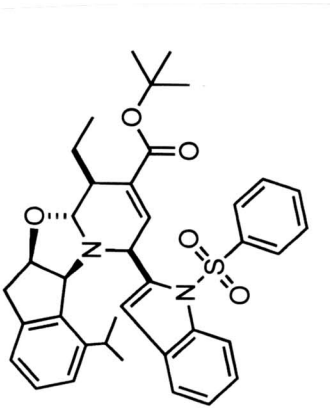
with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (17% to 25% ethyl acetate in hexane) gave the diol (45 mg, 81%).

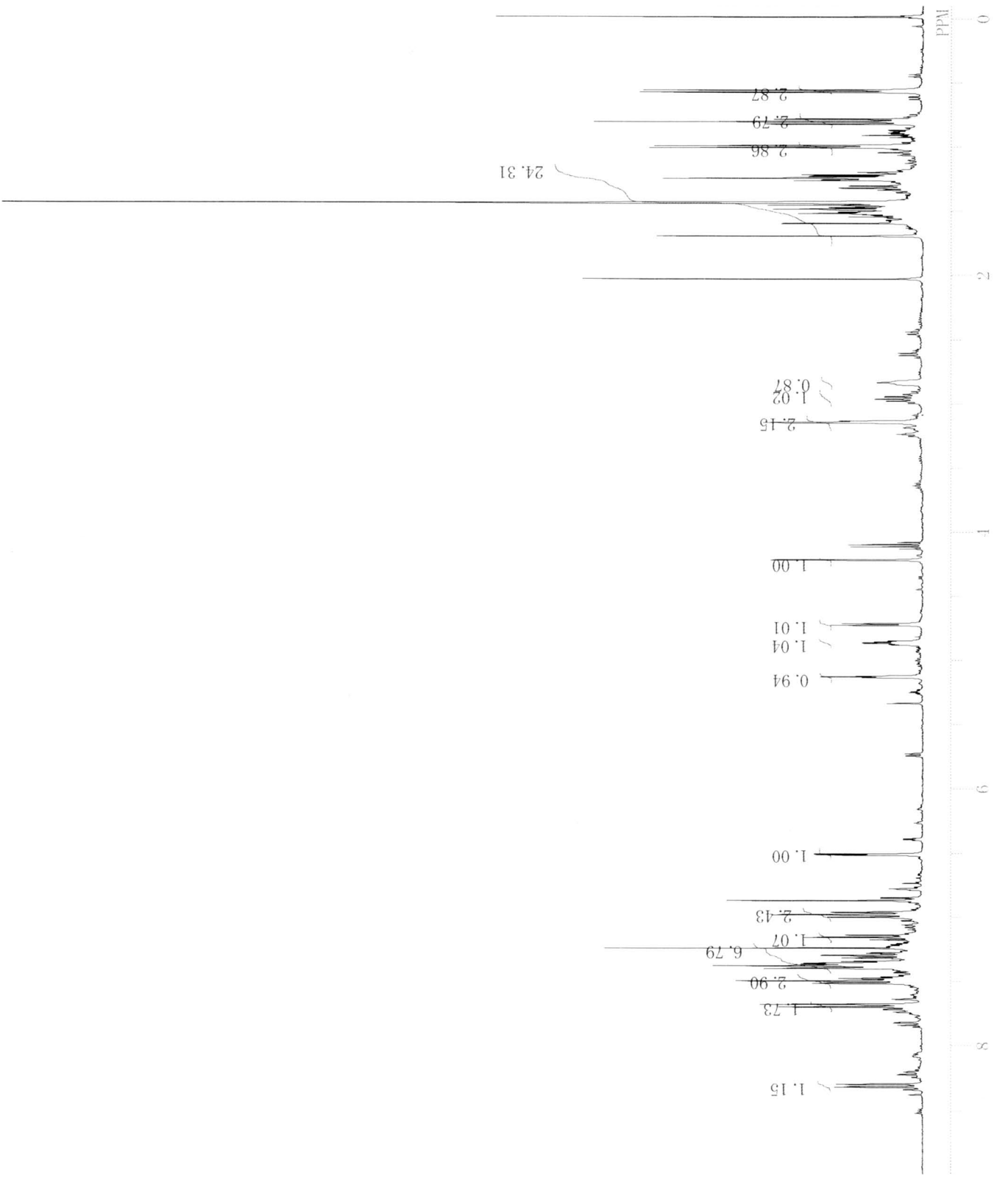
To a solution of diol obtained above (19 mg, 39.1 μmol) in $CHCl_3$ (3 mL) was added *n*-propylamine (48 μL, 0.587 mmol) and lead tetraacetate (104 mg, 0.235 mmol) at –50 °C. After the mixture was stirred at this temperature for 30 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the **22P** (9 mg, 86%) as a pale yellow amorphous: IR (thin film) 3377, 2961, 1637, 1491, 1217, 1121, 1028, 874 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.14-7.26 (m, 5H), 5.60 (s, 1H), 4.39 (s, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 4.01 (d, *J* = 13.0 Hz, 1H), 2.96 (dd, *J* = 12.0, 2.5 Hz, 1H), 2.87 (dd, *J* = 12.0, 4.0 Hz, 1H), 1.95 (m, 1H), 1.42-1.64 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 141.1, 128.5, 127.7, 127.4, 125.2, 65.2, 58.9, 45.1, 36.3, 24.5, 12.3; ESI-HRMS m/z calcd for $C_{14}H_{20}NO$ $(M + H)^+$ 218.1545, found 218.1539

4-Hydroxymethyl-2-(3-*tert*-butyldimethylsilyloxy)prop-1-enyl-1,2,5,6-tetrahydropyridine 23P: To a solution of compound **23T** (31 mg, 56.0 μmol) in CH_2Cl_2 (3 mL) was slowly added diisobutylaluminium hydride (0.560 mL. 0.560 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 1 h, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 33 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel (17% to 33% ethyl acetate in hexane) gave the diol (19 mg, 70%).

To a solution of diol obtained above (15 mg, 30.9 μmol) in $CHCl_3$ (2.5 mL) was added *n*-propylamine (38 μL, 0.463 mmol) and lead tetraacetate (82 mg, 0.185 mmol) at –50 °C. After the mixture was stirred at this temperature for 28 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude products. Column chromatofraphy on silica gel

(from 0% to 17% methanol in chloroform containing 0.5% triethylamine) gave the **23P** (7 mg, 73%) as a brown amorphous: I IR (thin film) 3423, 2959, 2930, 2855, 1671, 1472, 1256, 1123, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.64-5.76 (m, 2H), 5.62 (s, 1H), 3.96-4.15 (m, 5H), 2.72-3.13 (m, 2H), 2.12 (m, 1H), 1.54-1.65 (m, 1H), 1.34-1.44 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.88 (s, 9H), 0.041 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.1, 133.0, 129.3, 123.2, 64.7, 63.2, 54.7, 43.3, 35.5, 29.7, 25.9, 23.6, 18.4, 11.4, -5.2; ESI-HRMS m/z calcd for $C_{17}H_{34}NO_2Si$ $(M + H)^+$ 312.2359, found 312.2347

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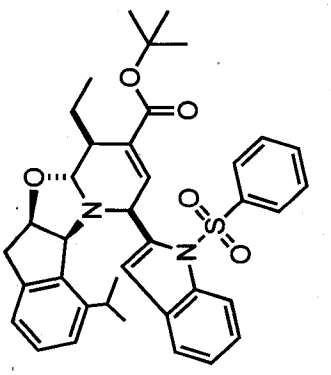

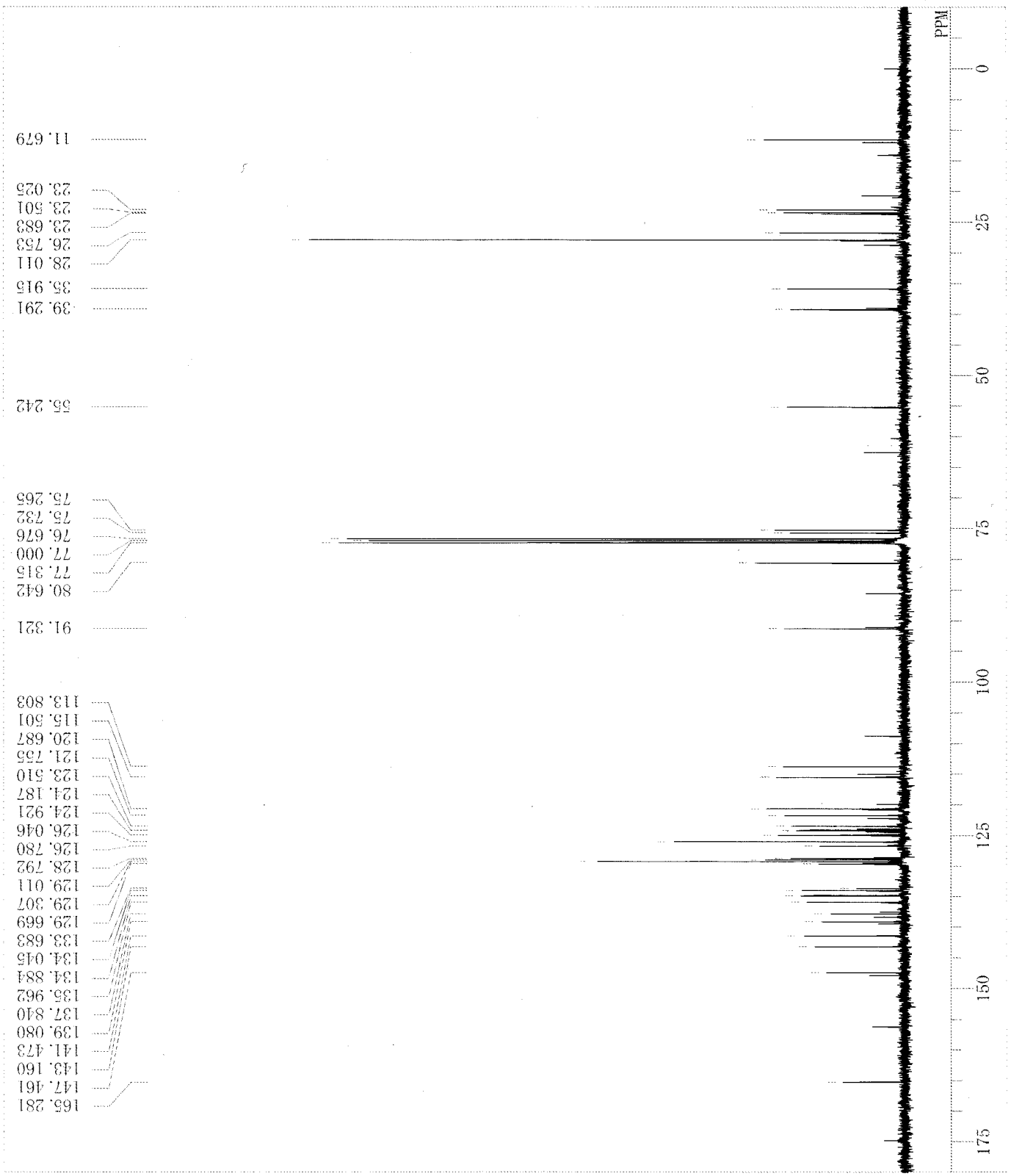
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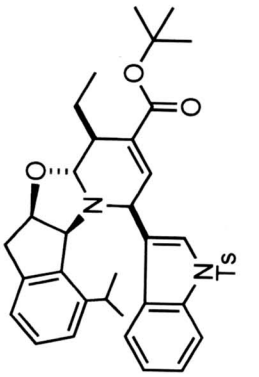
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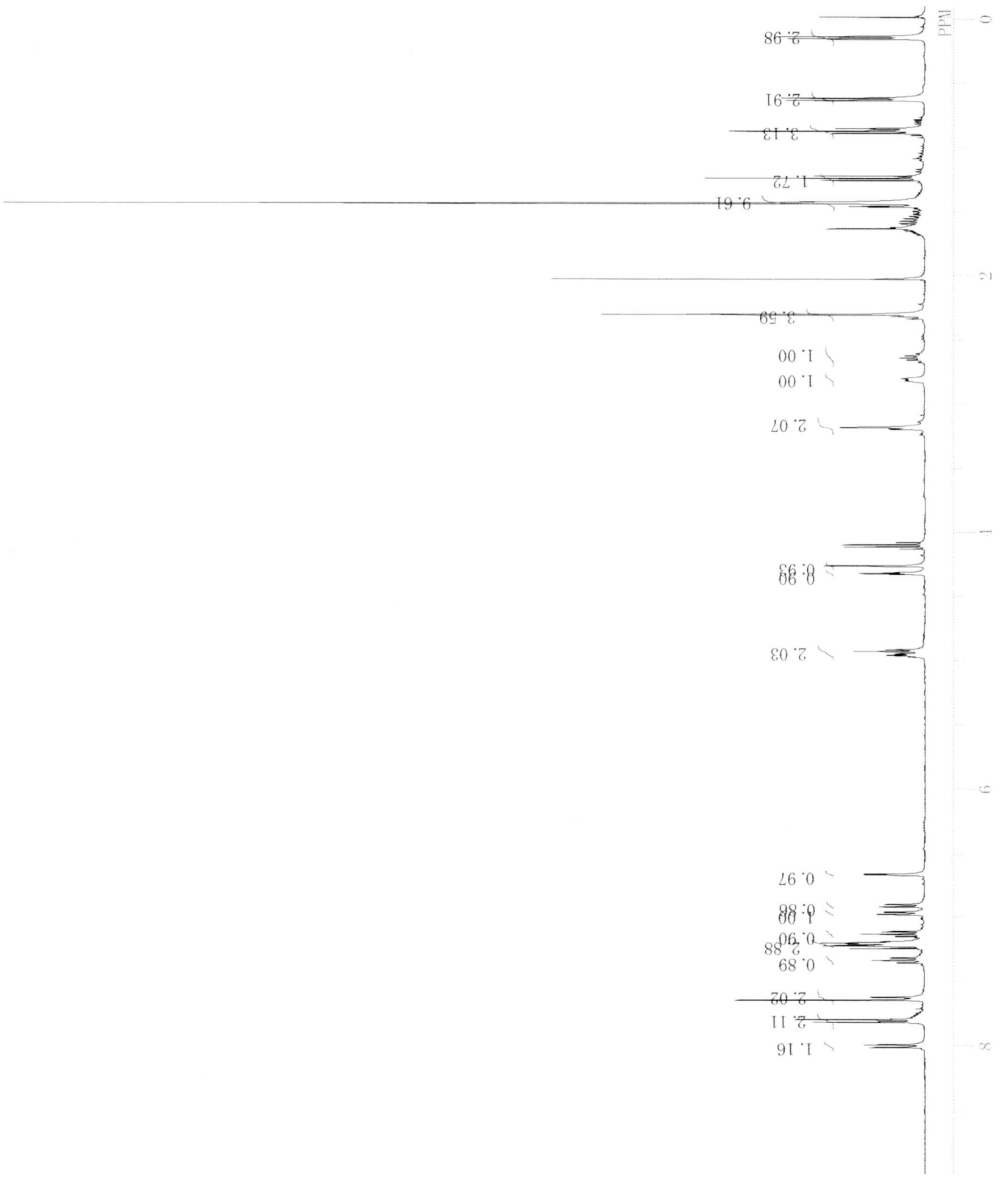
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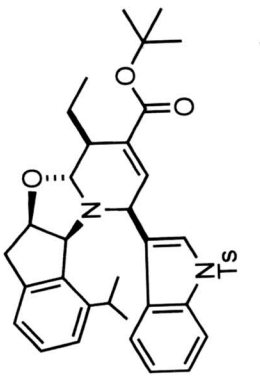
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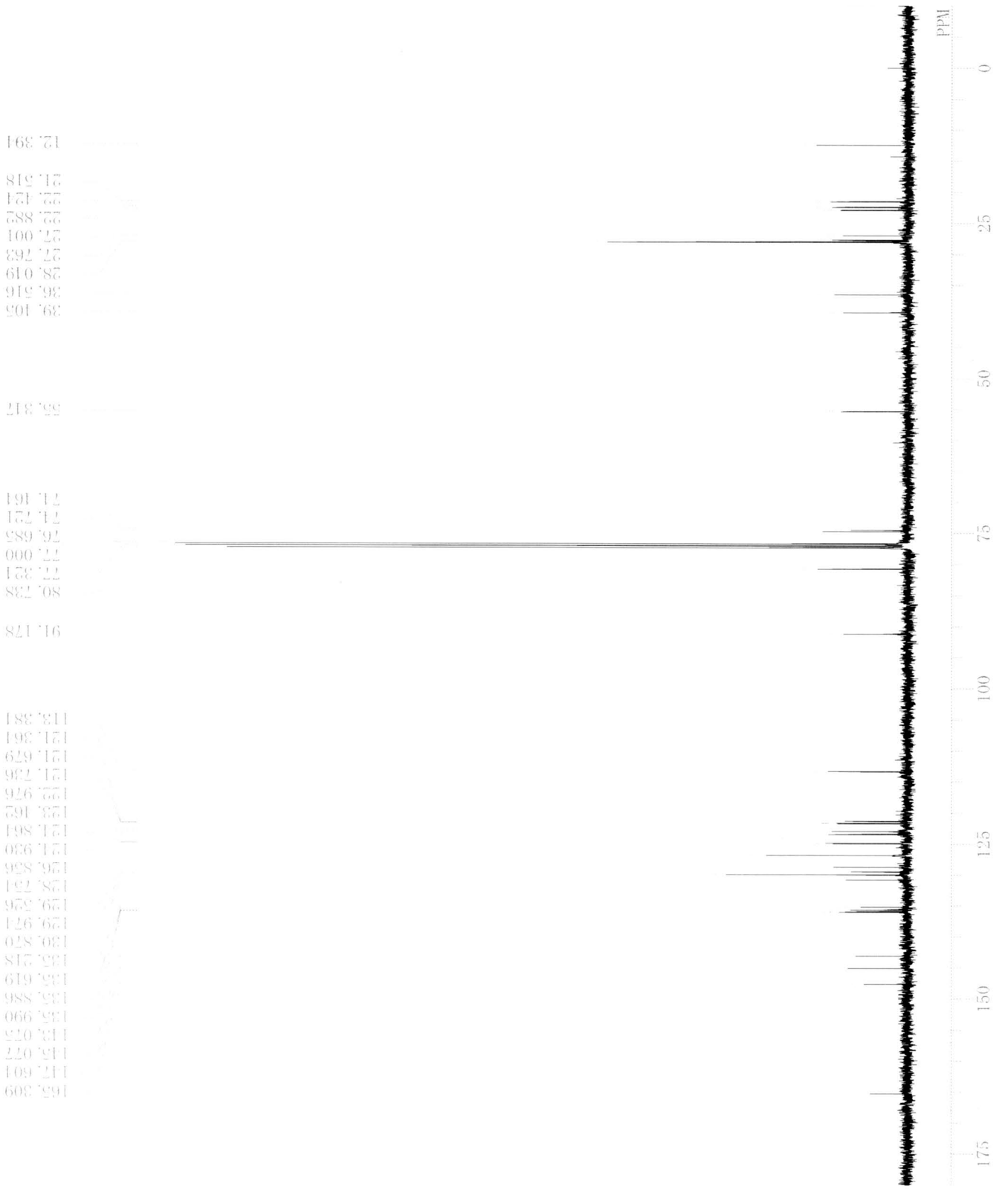
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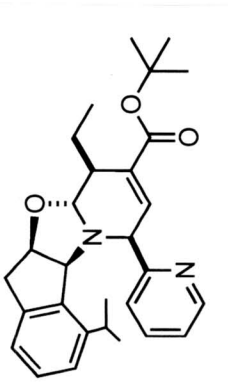

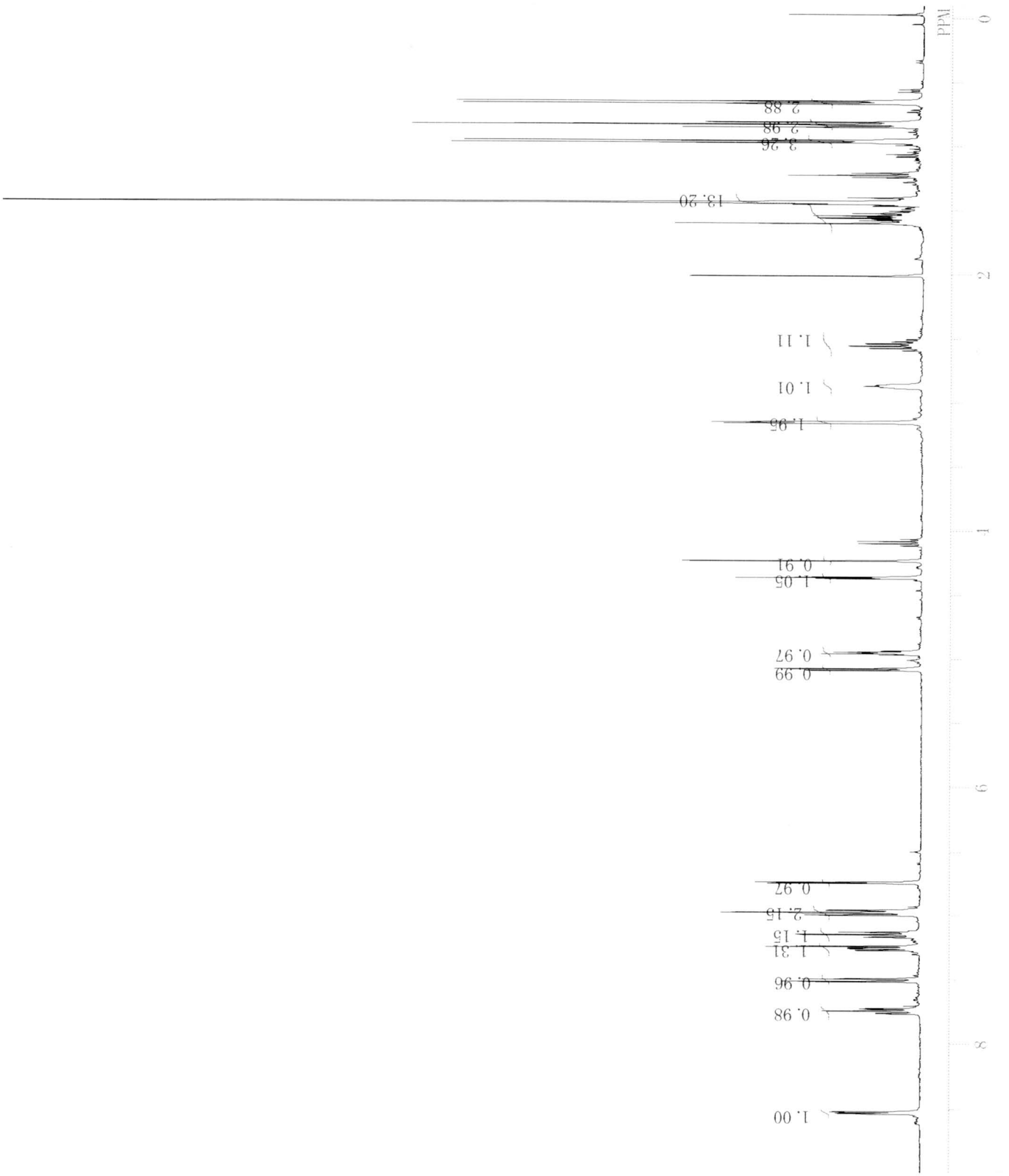
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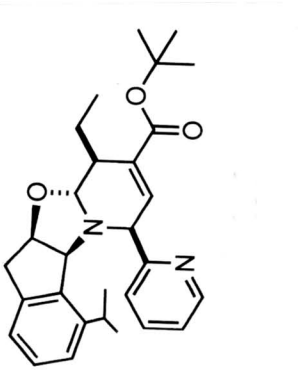

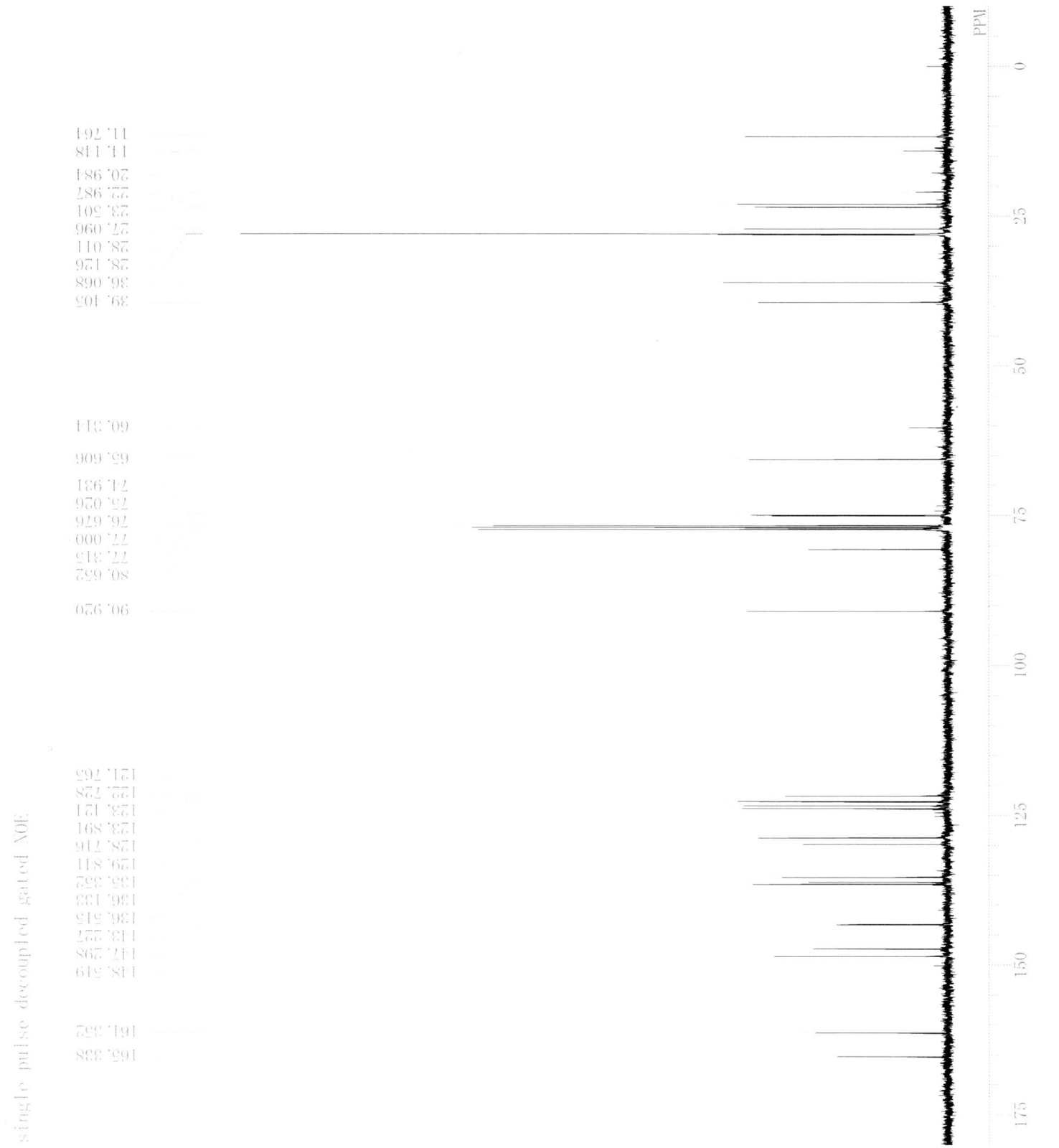
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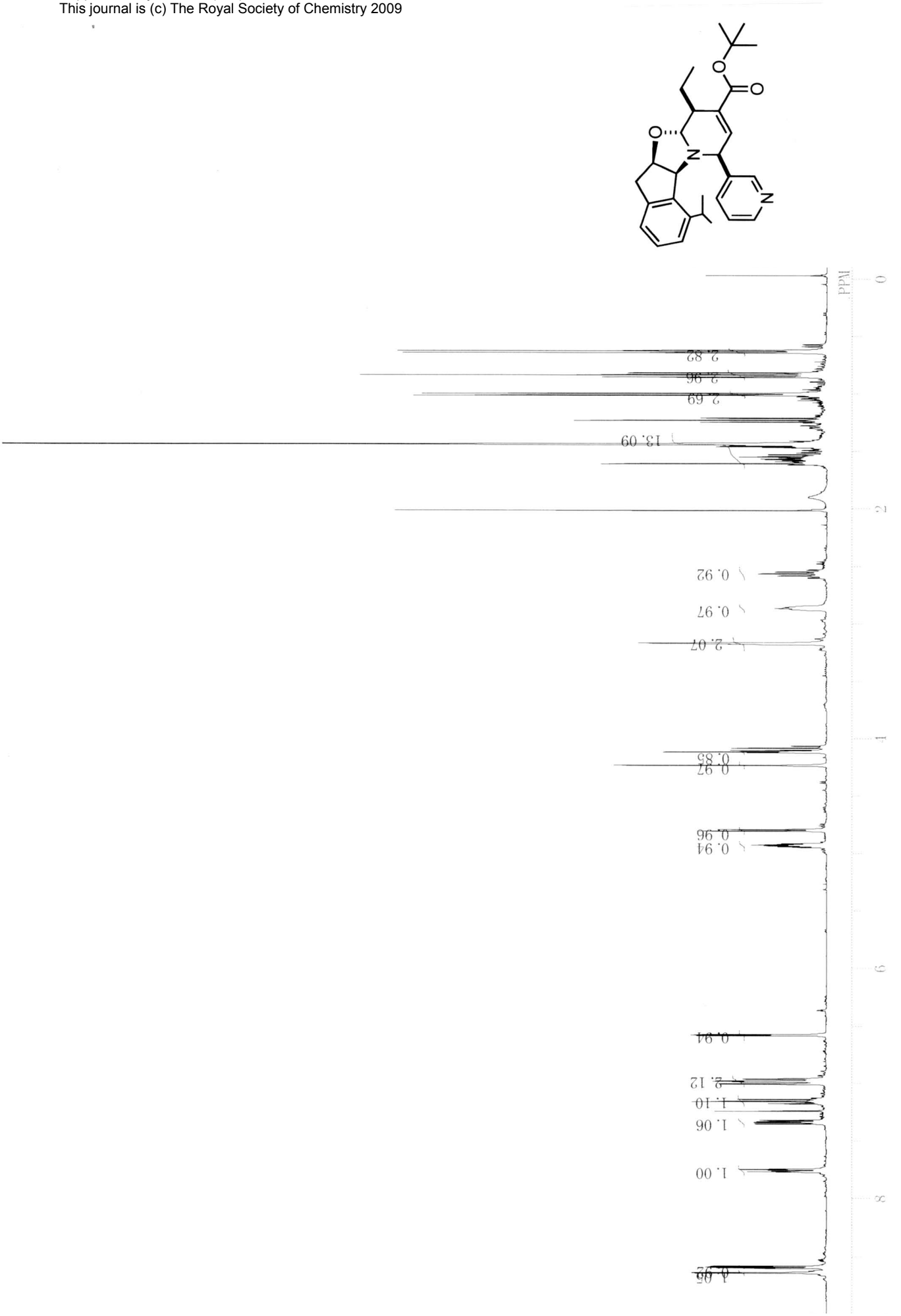
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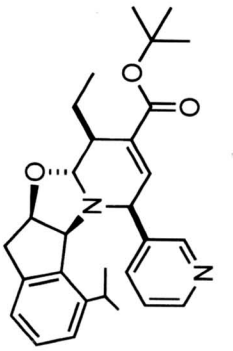

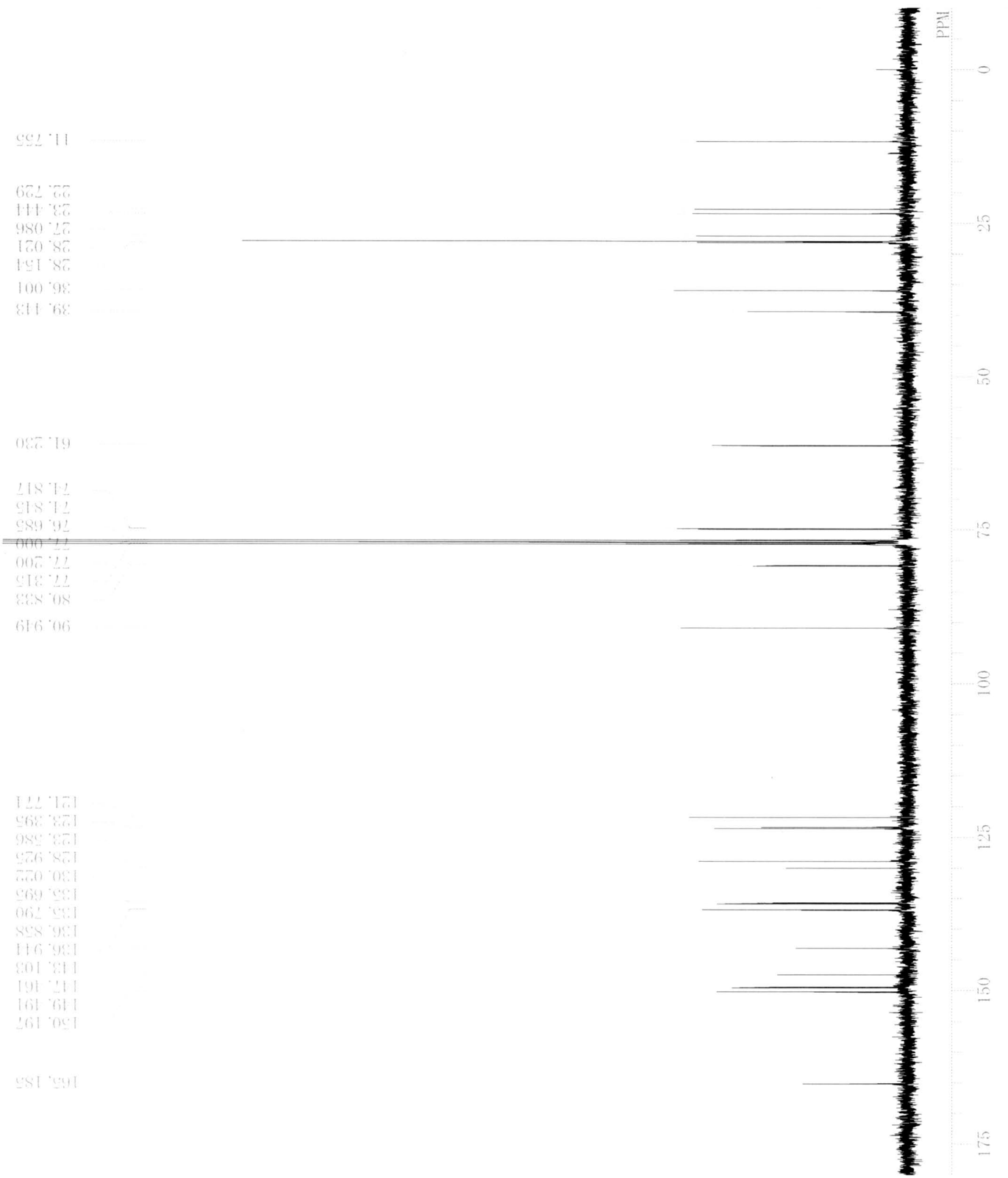
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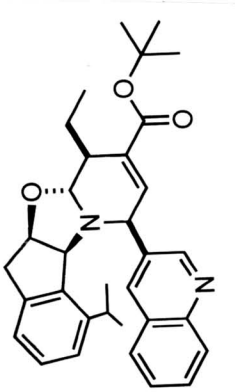

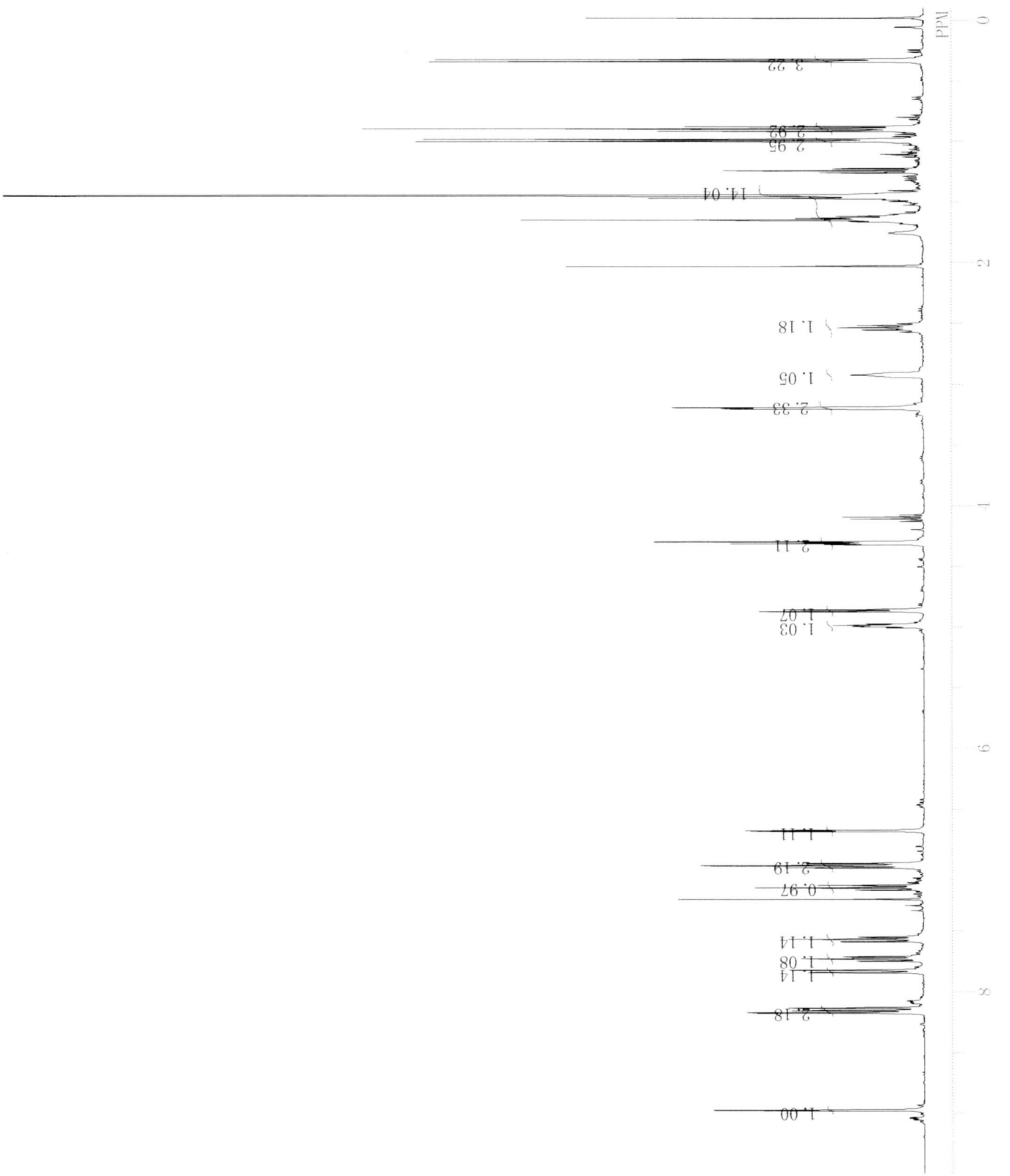
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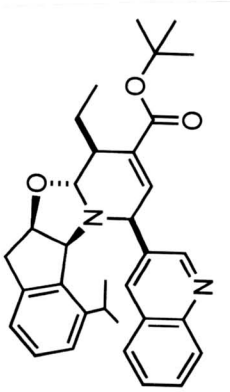

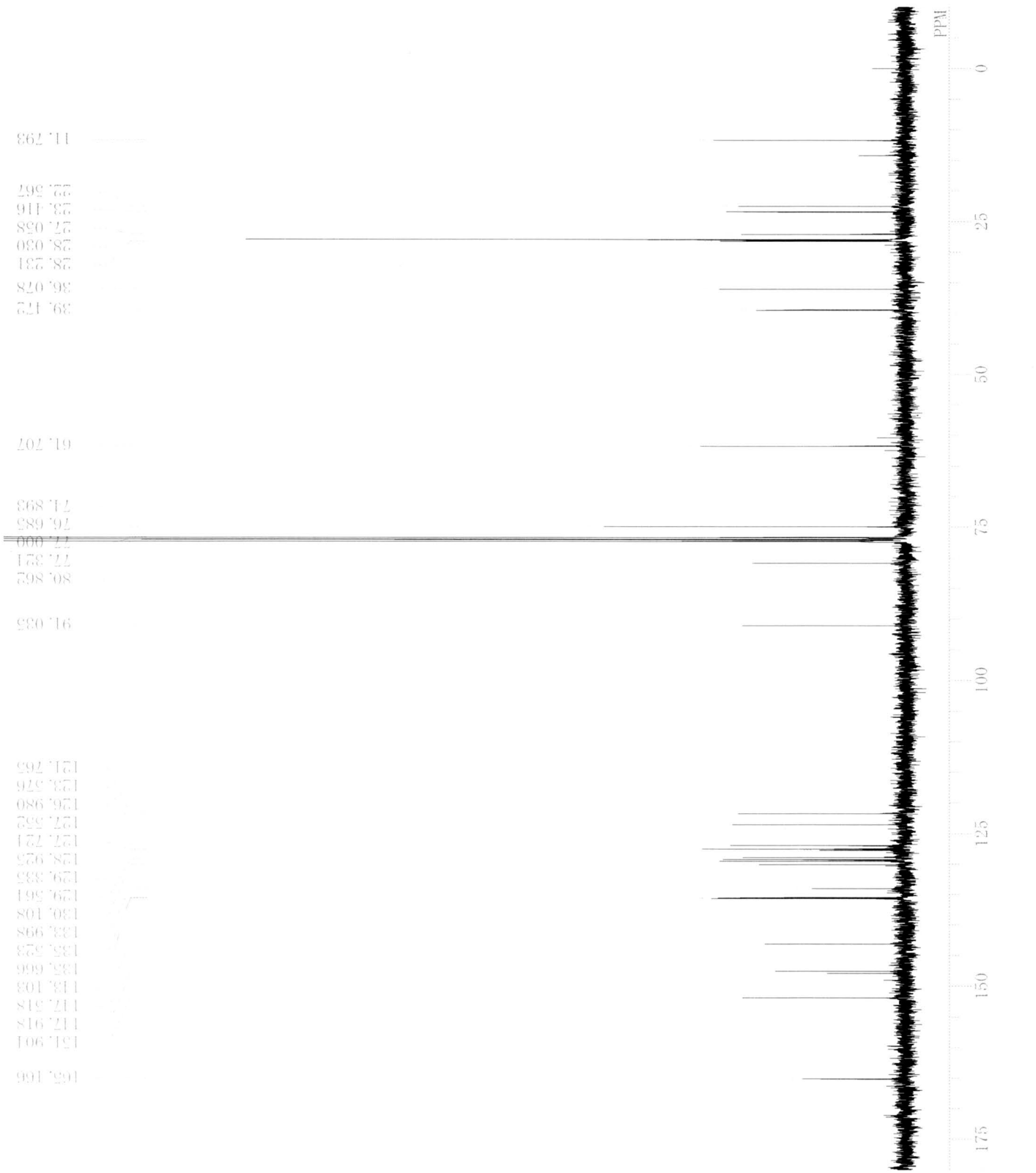
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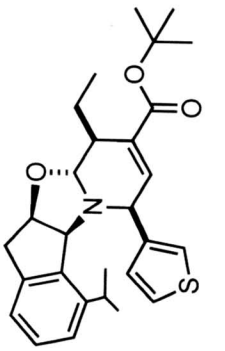

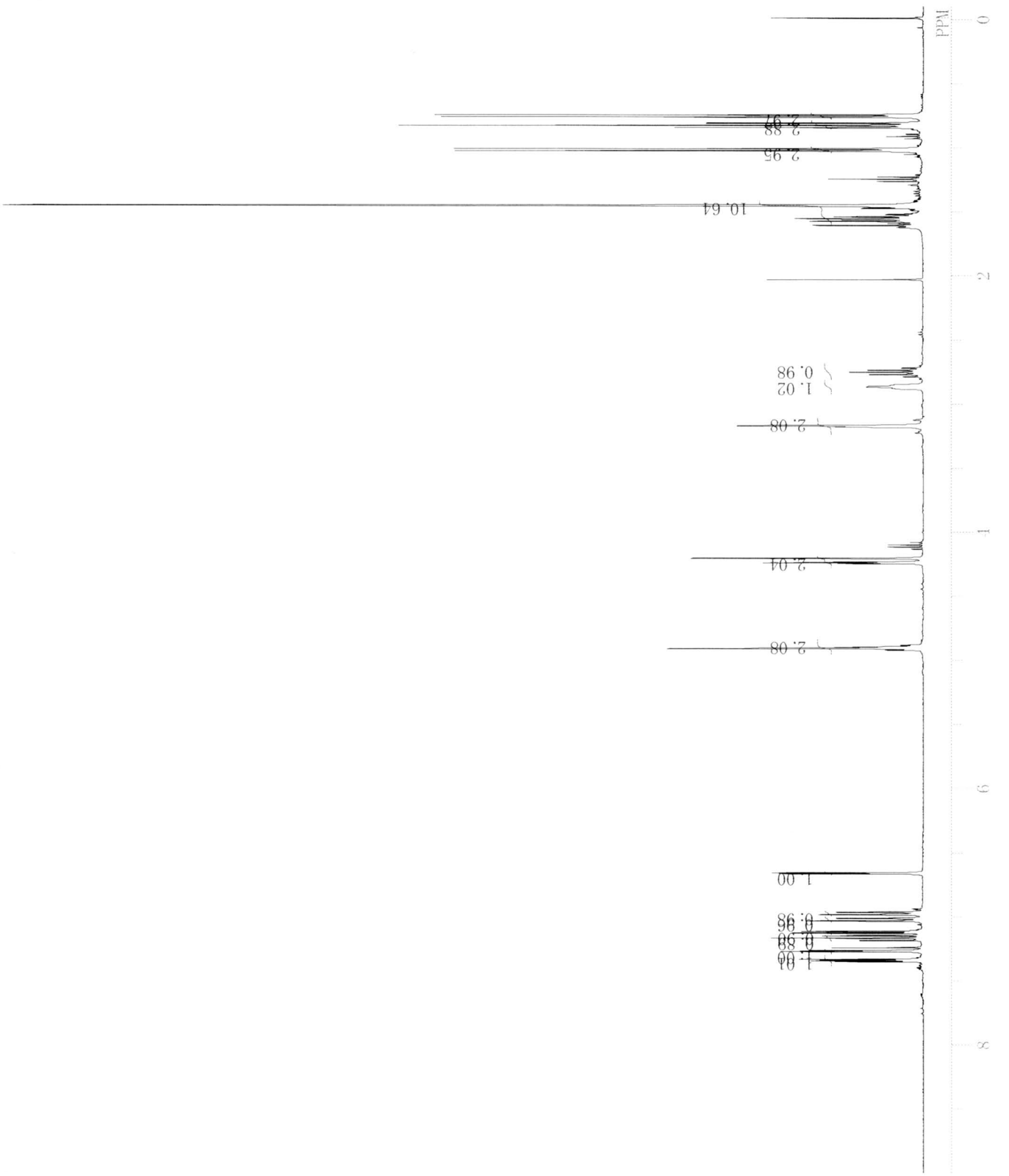
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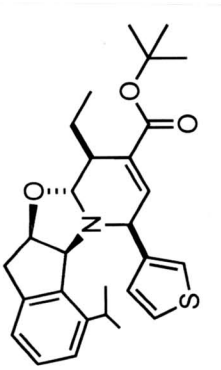

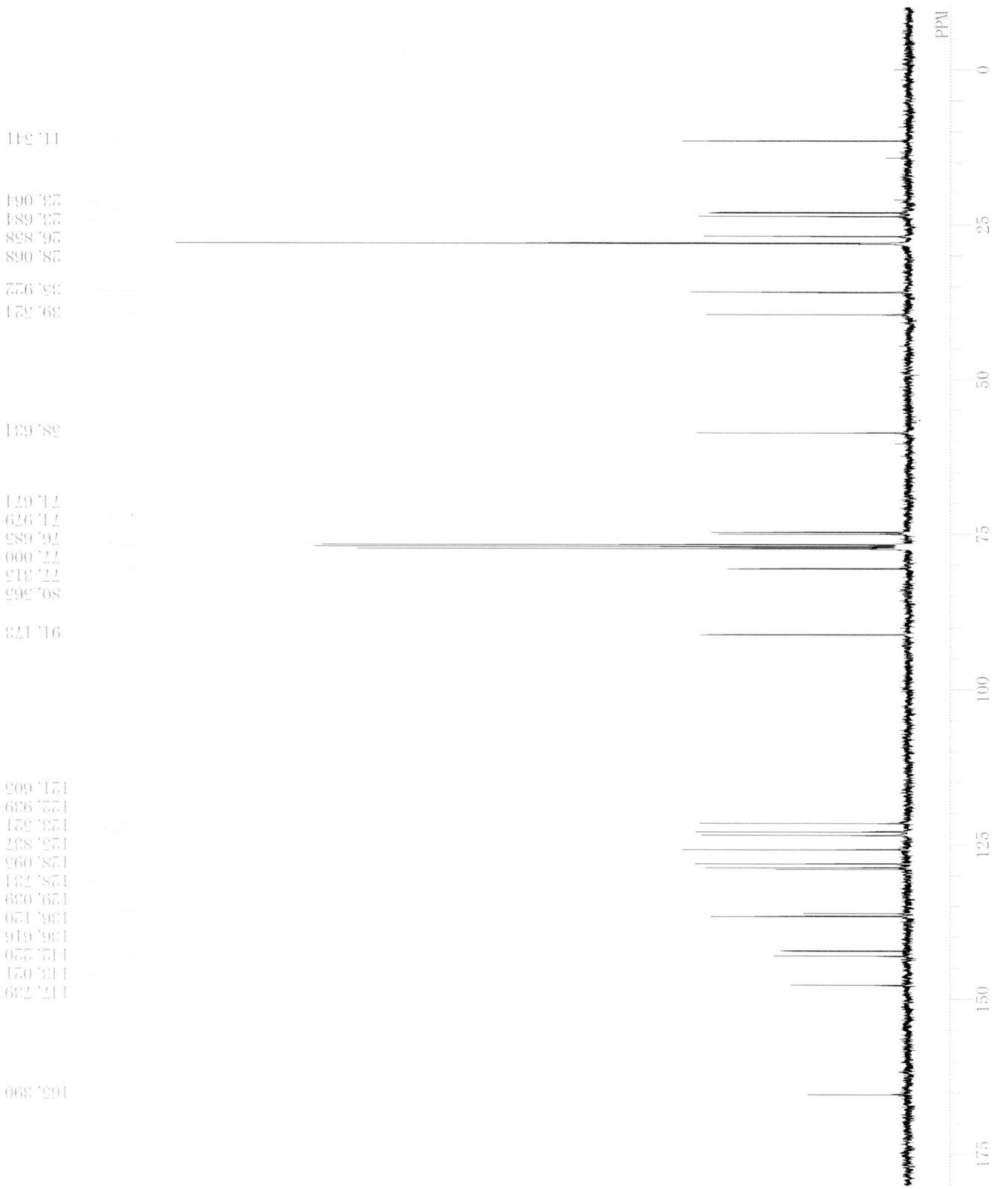
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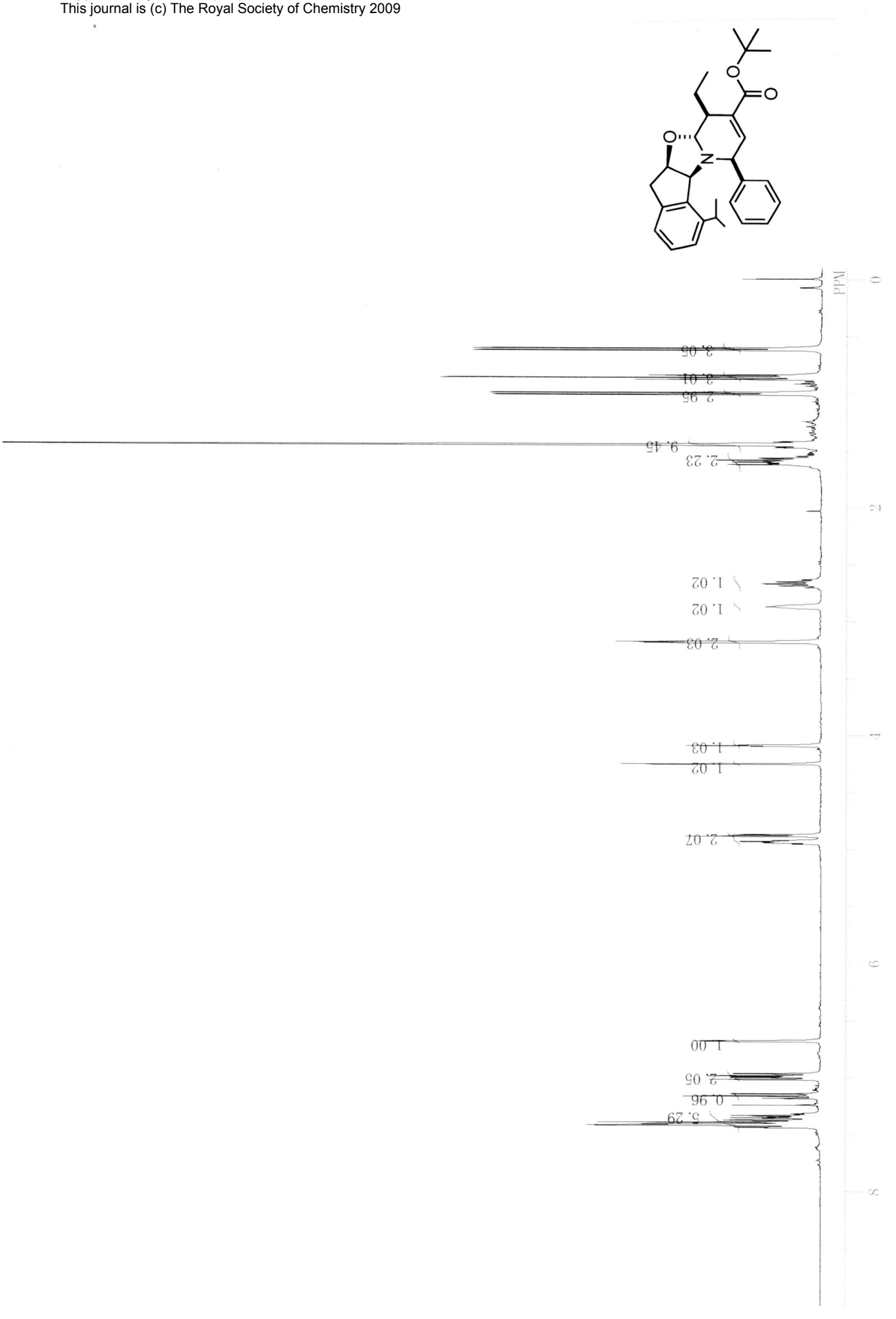
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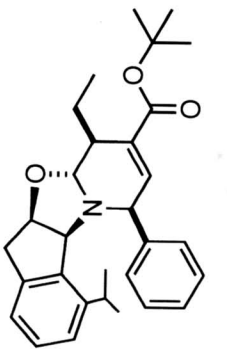
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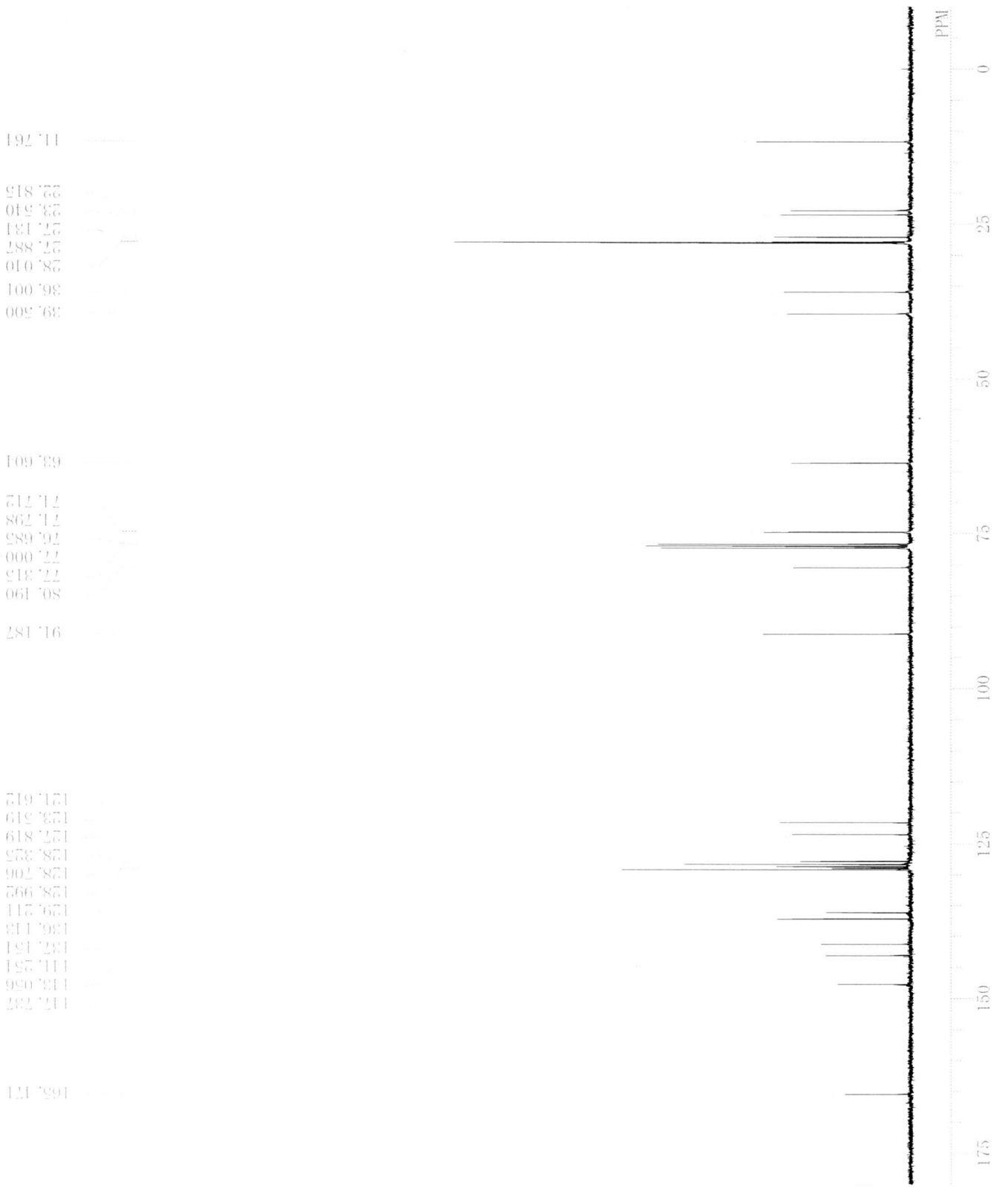
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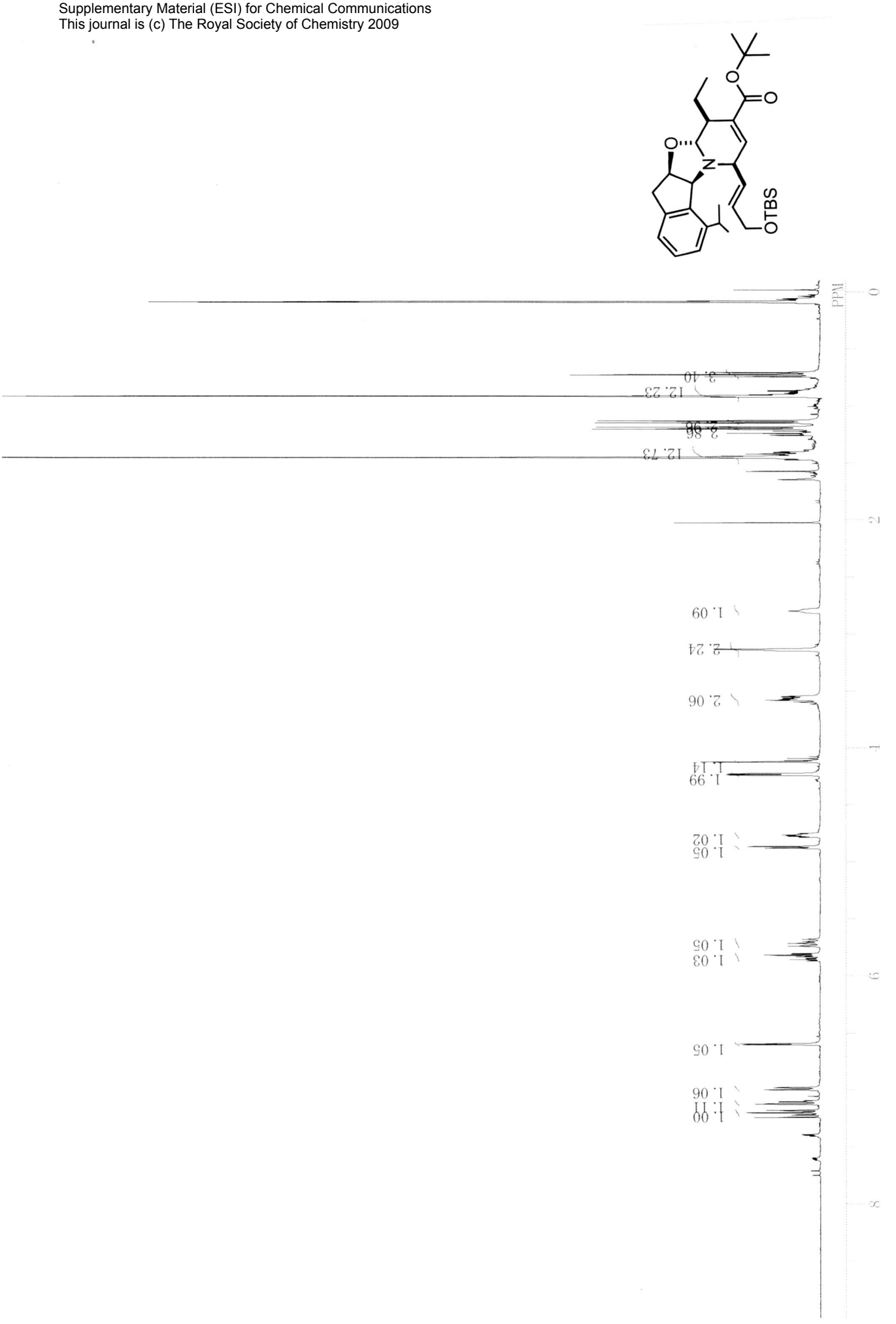
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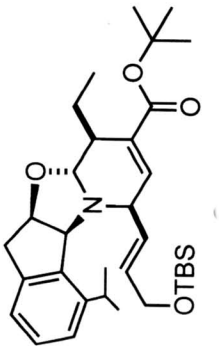
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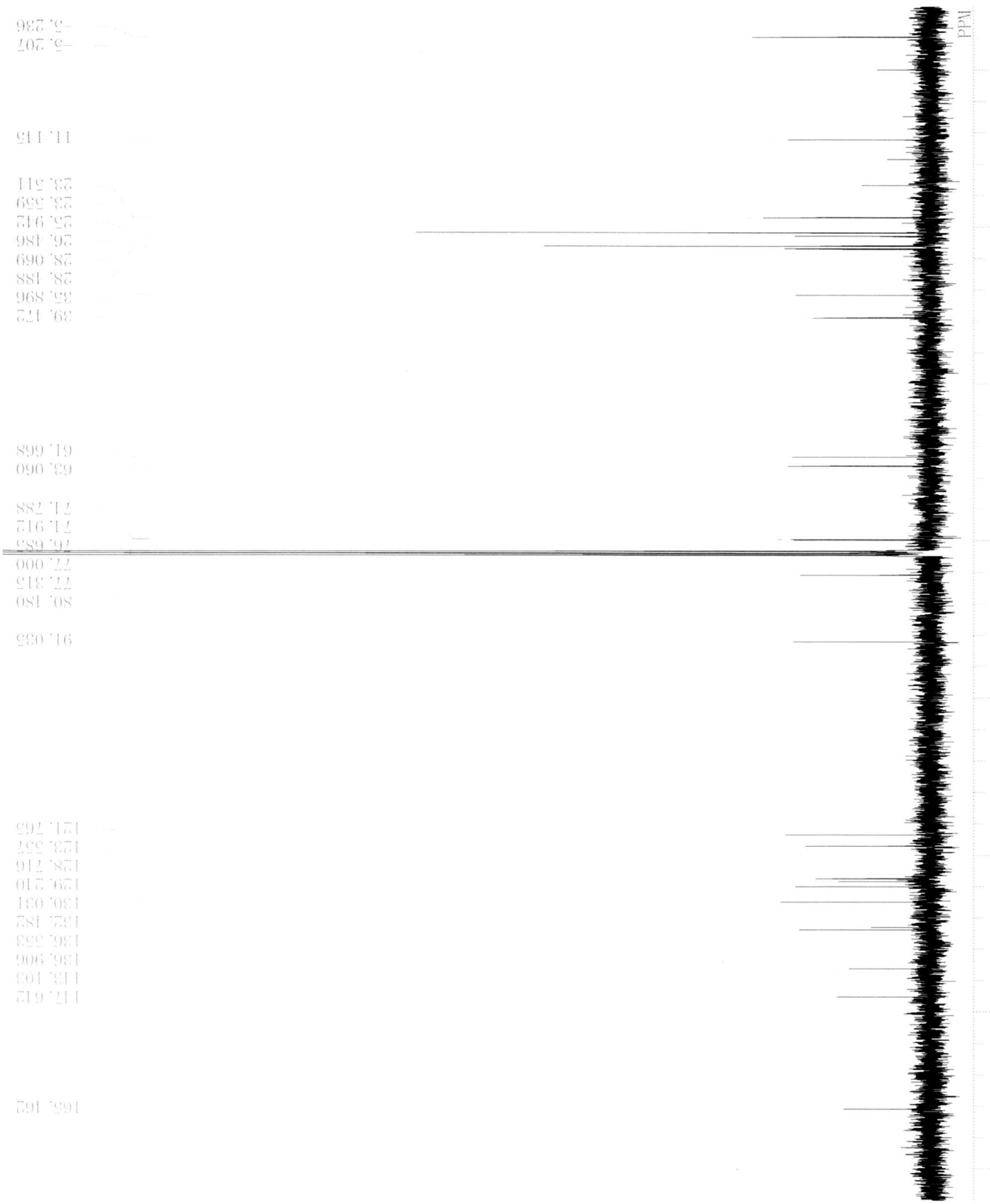
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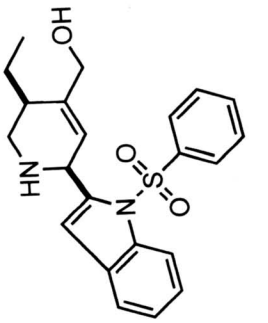
single pulse decoupled gated NOE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S
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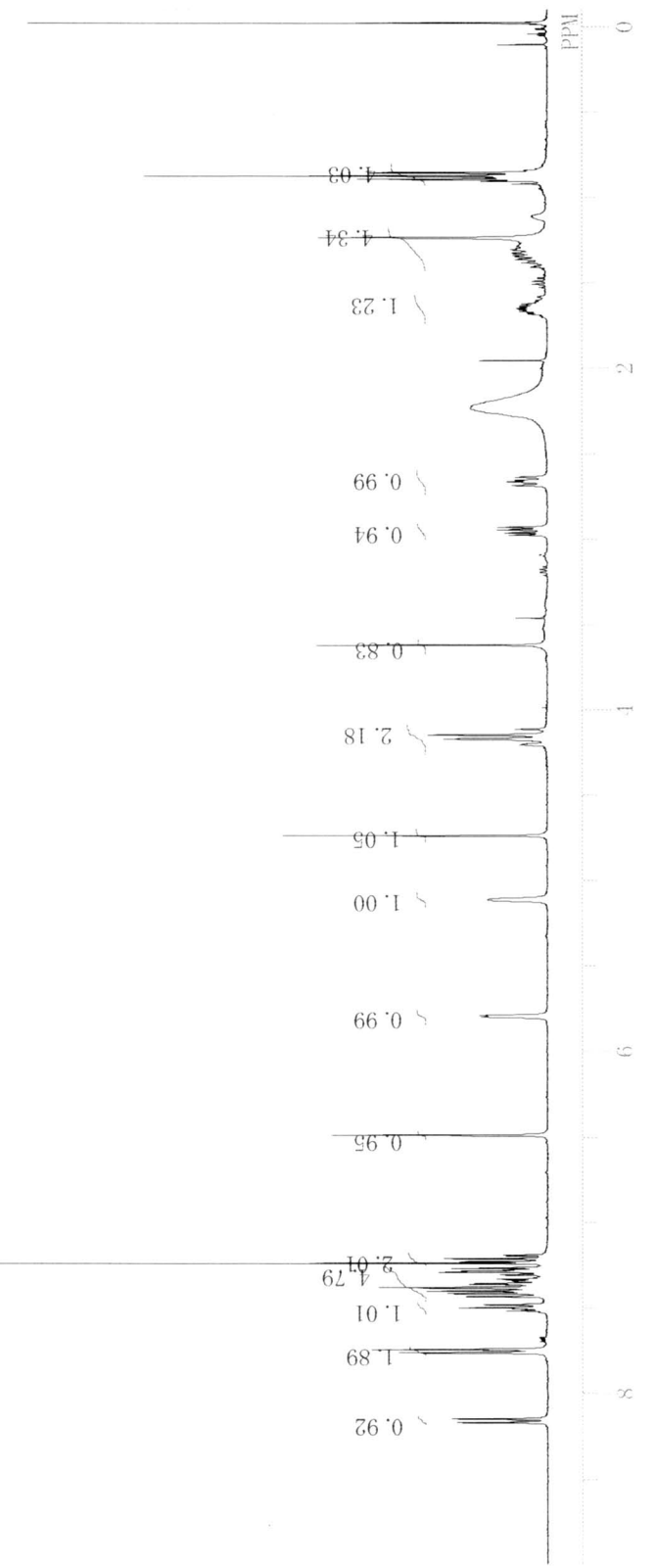
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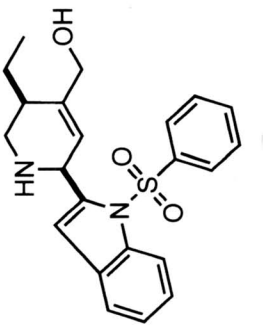
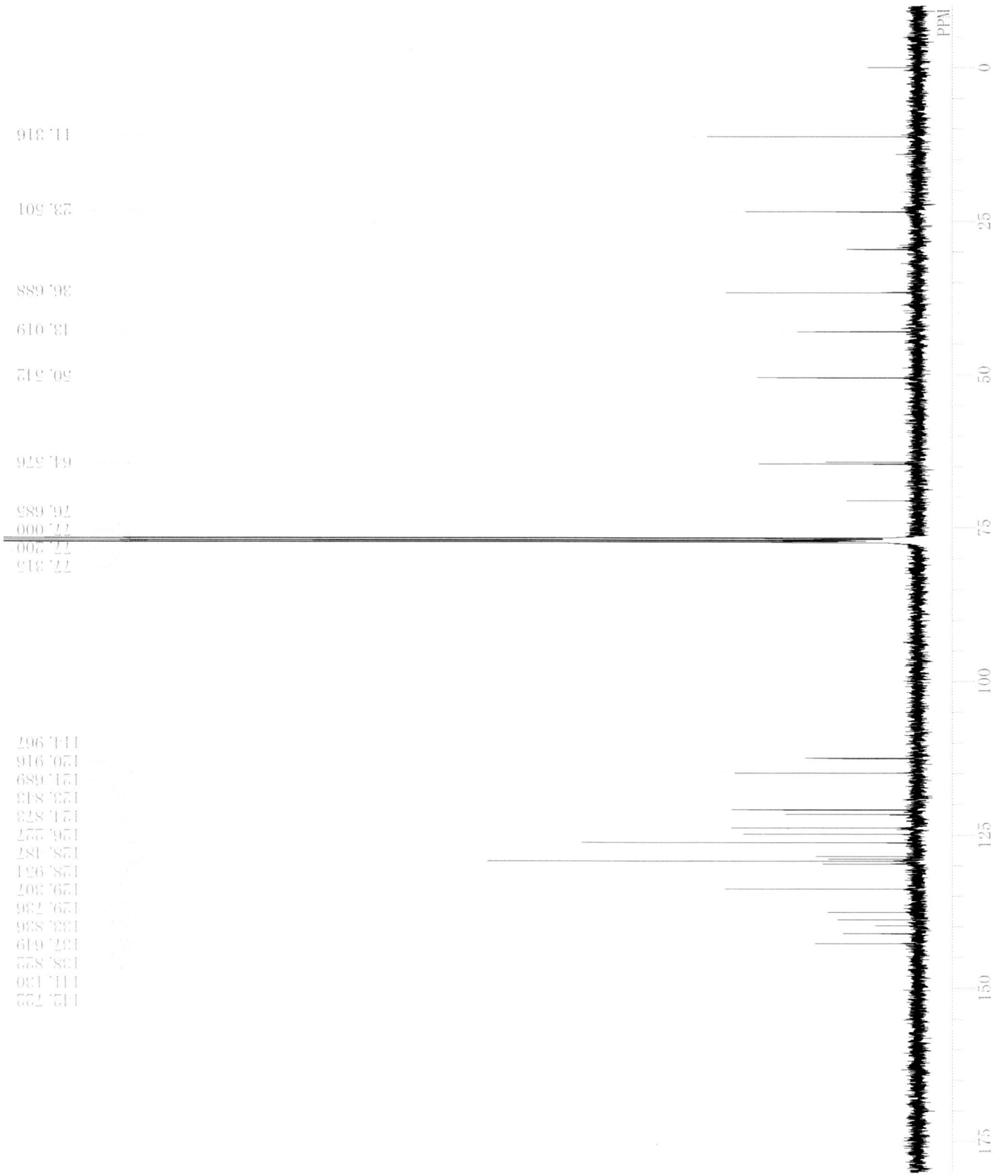
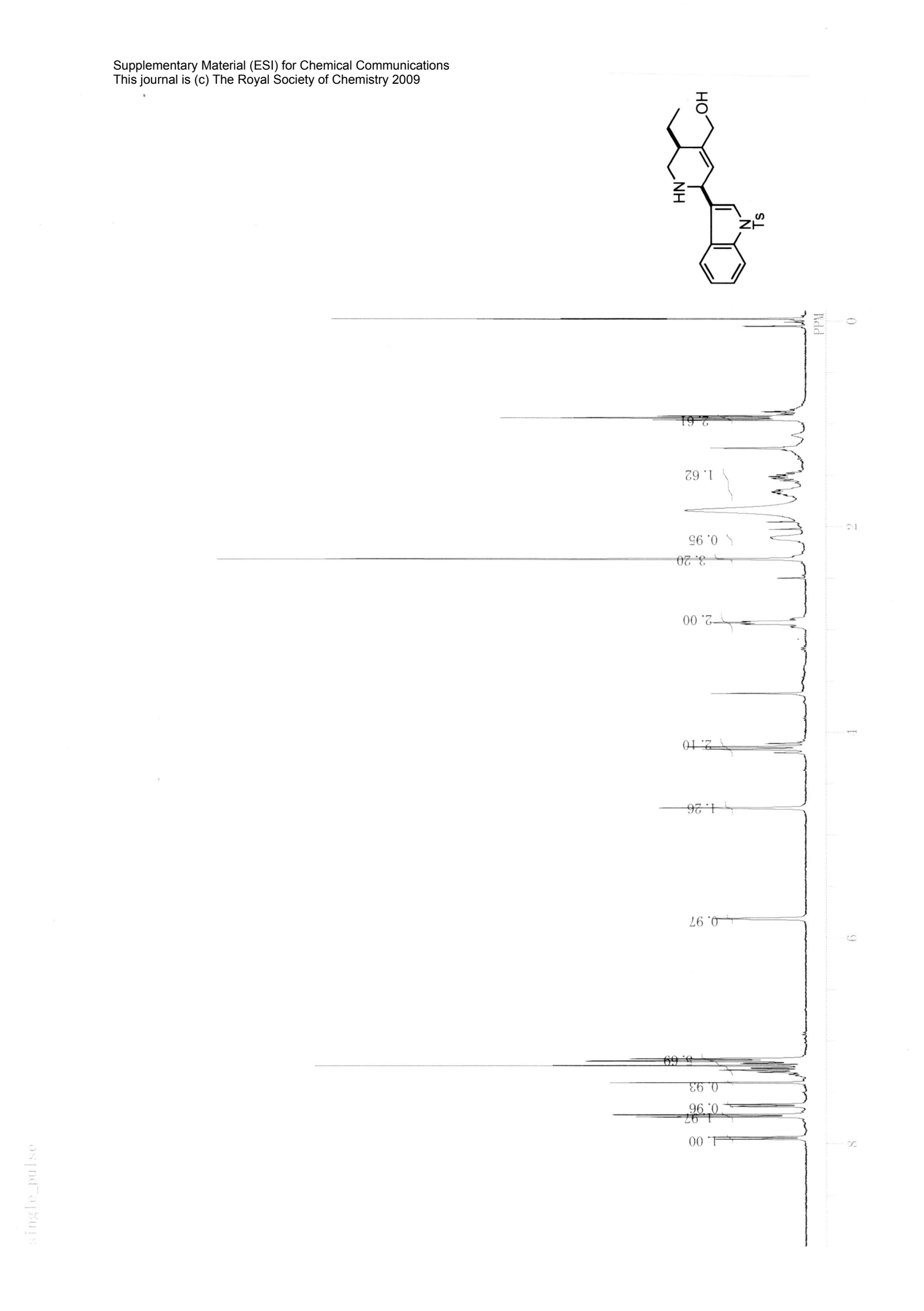
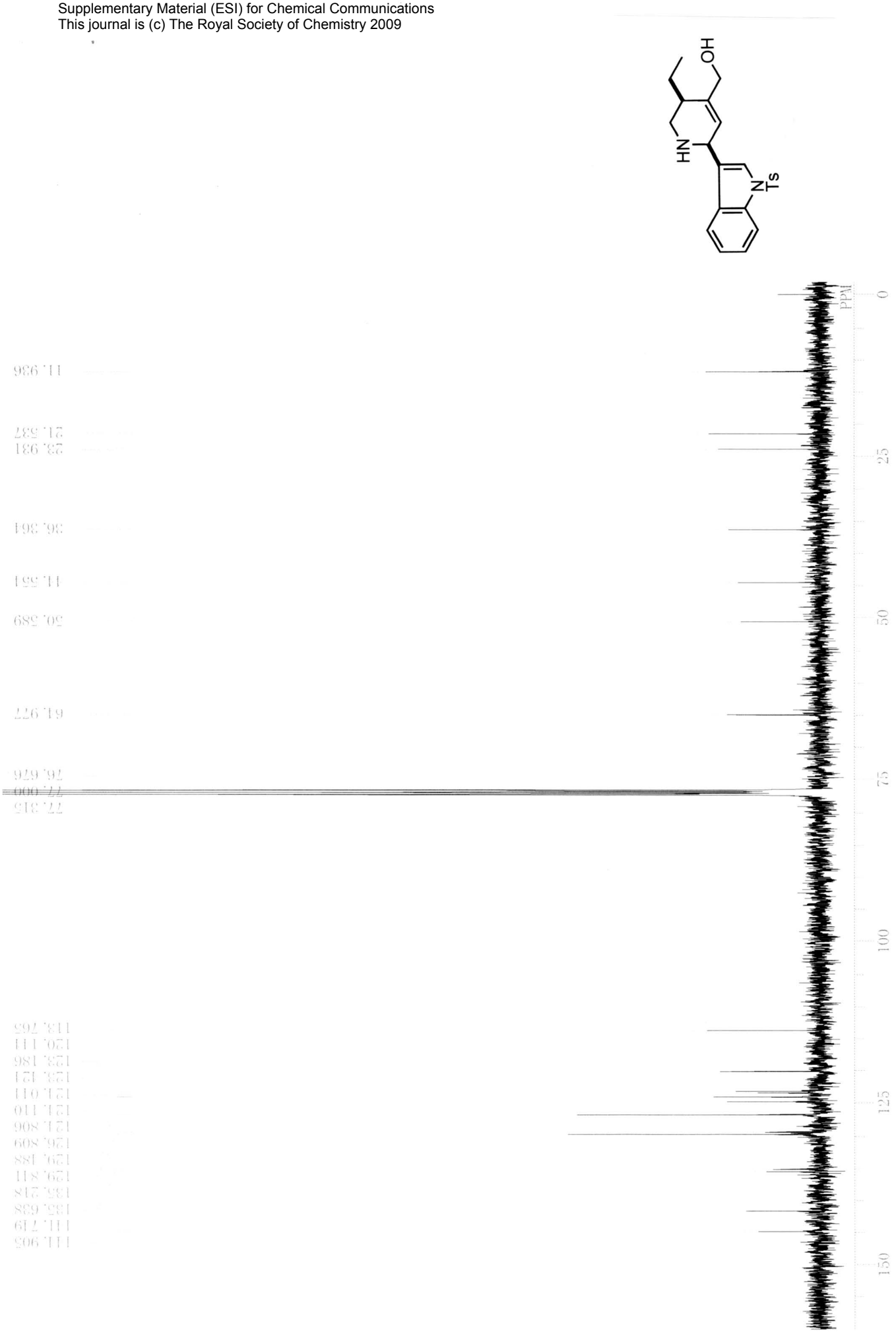
4.03
single_pulse


OH
HN
O
S
O
N


PPM
0
25
50
75
100
125
150
175
11.316
23.501
36.688
18.019
50.512
64.526
76.685
77.000
77.200
77.315
114.967
120.916
121.689
123.813
124.823
126.227
128.187
128.921
129.307
129.736
133.836
137.619
138.823
111.130
112.752
single pulse decoupled gated NOE


OH
HN
N
Ts
PPM
0
1
2
3
4
5
6
7
8
2.61
1.62
0.95
3.20
2.00
2.10
1.26
0.97
5.69
0.93
0.96
1.97
1.00
single_pulse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HN
N
Ts
PPM
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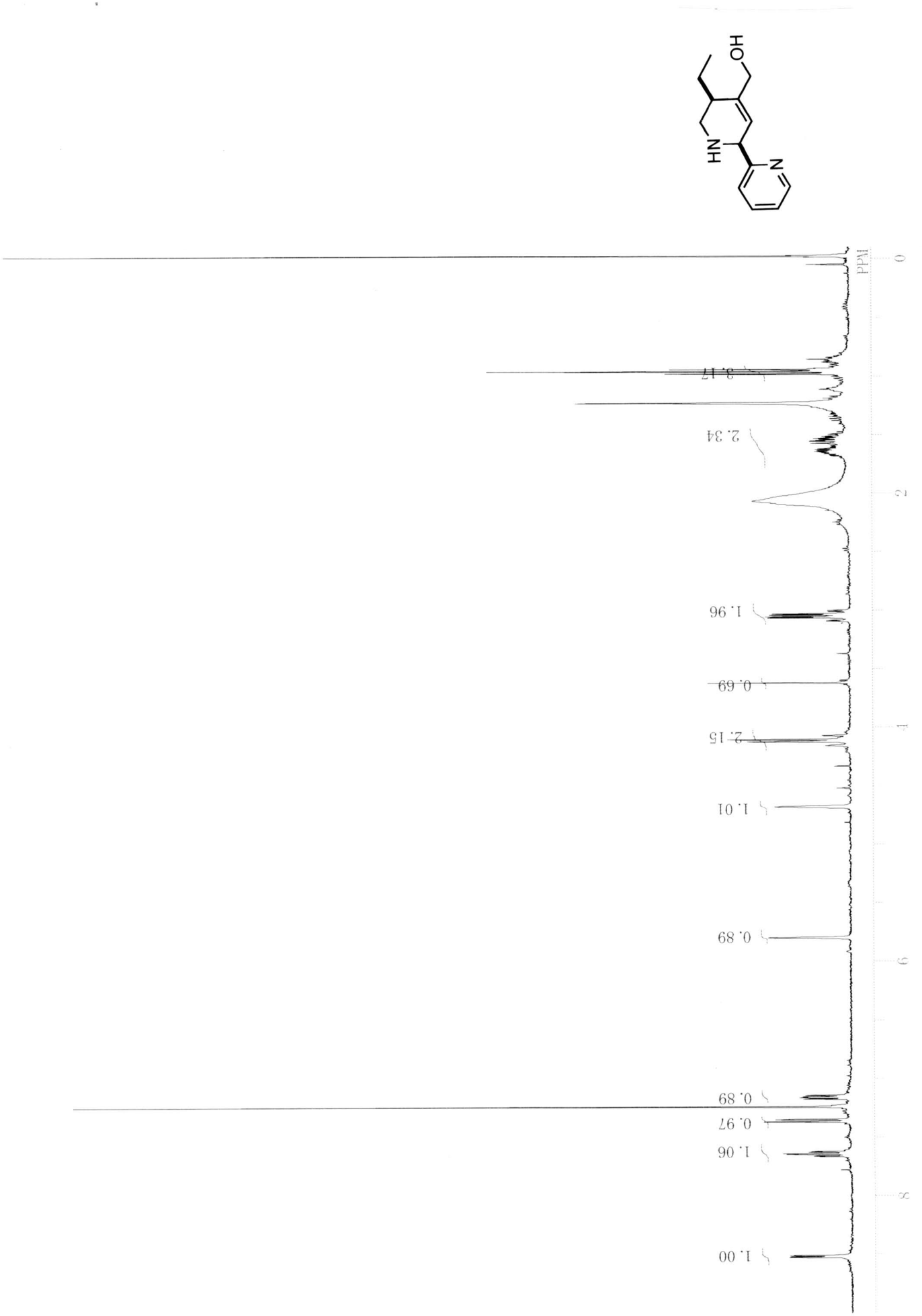
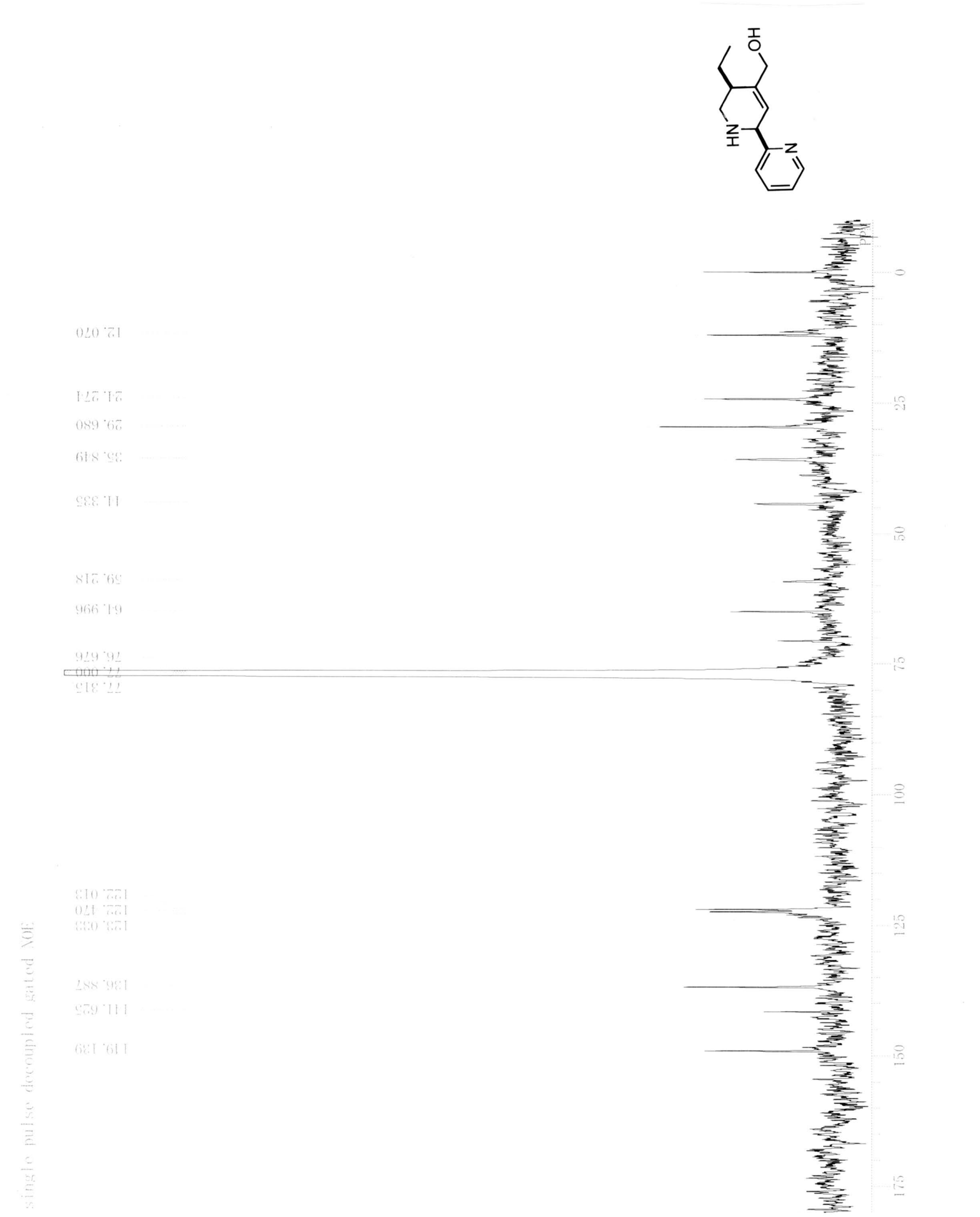
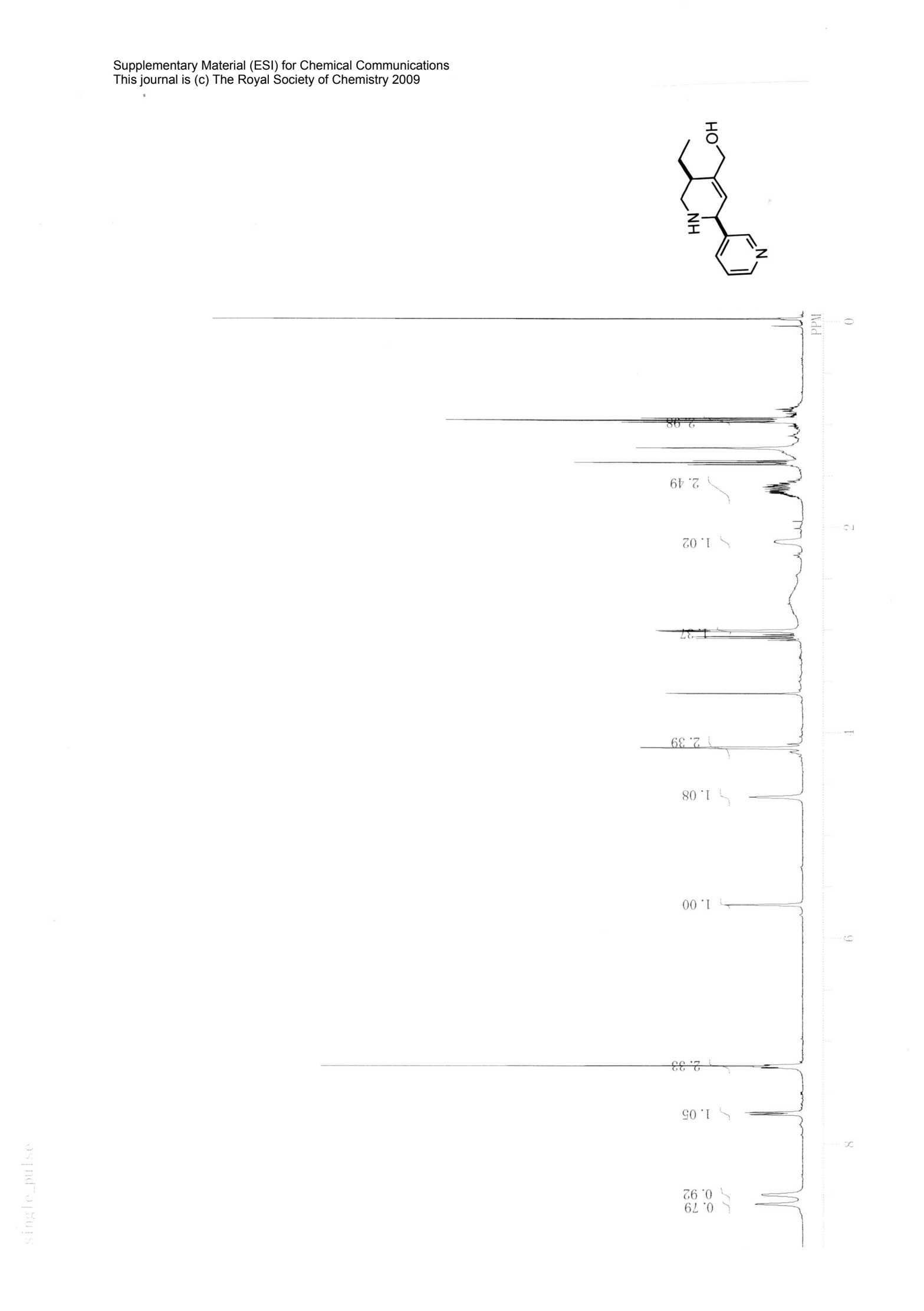
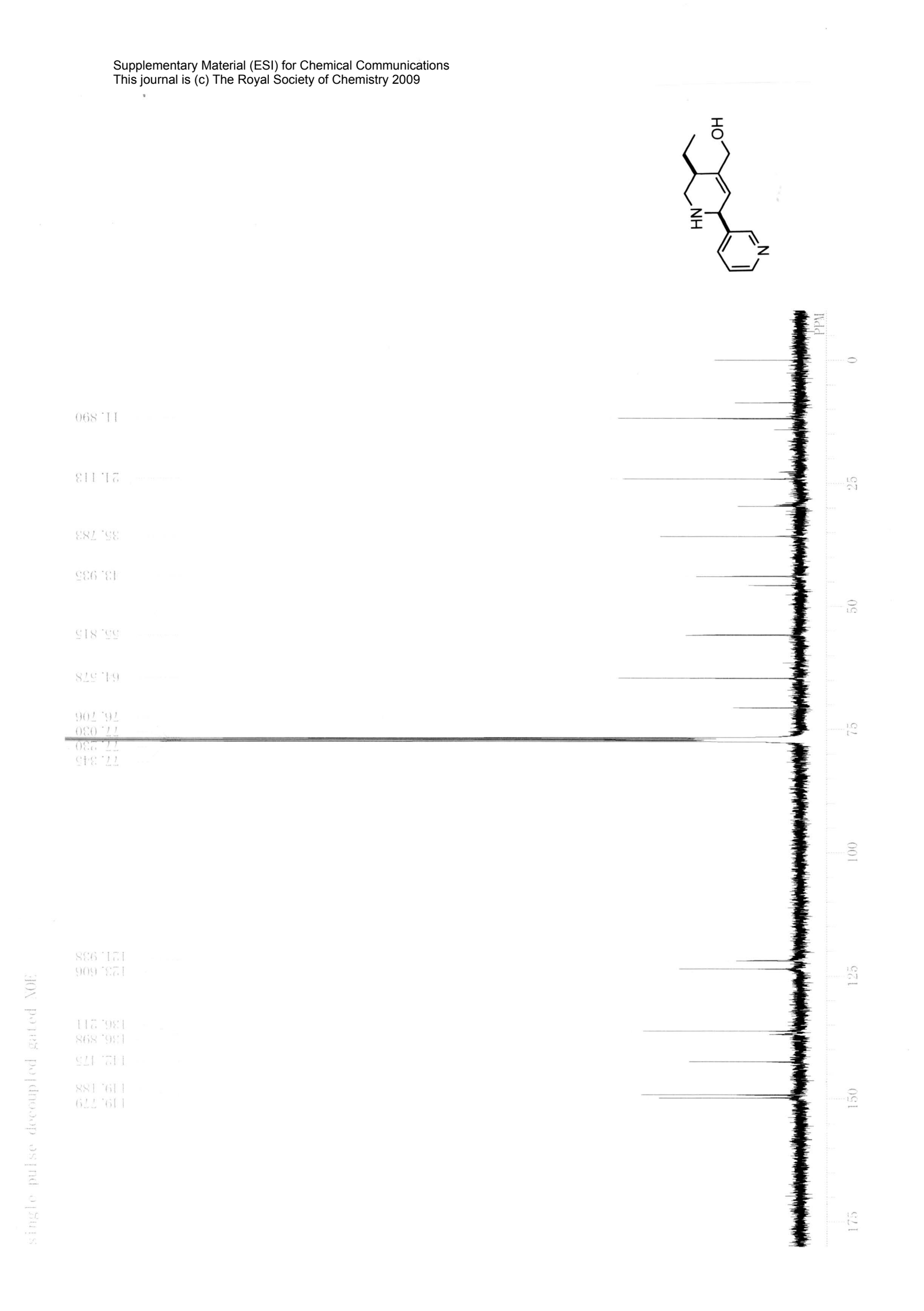
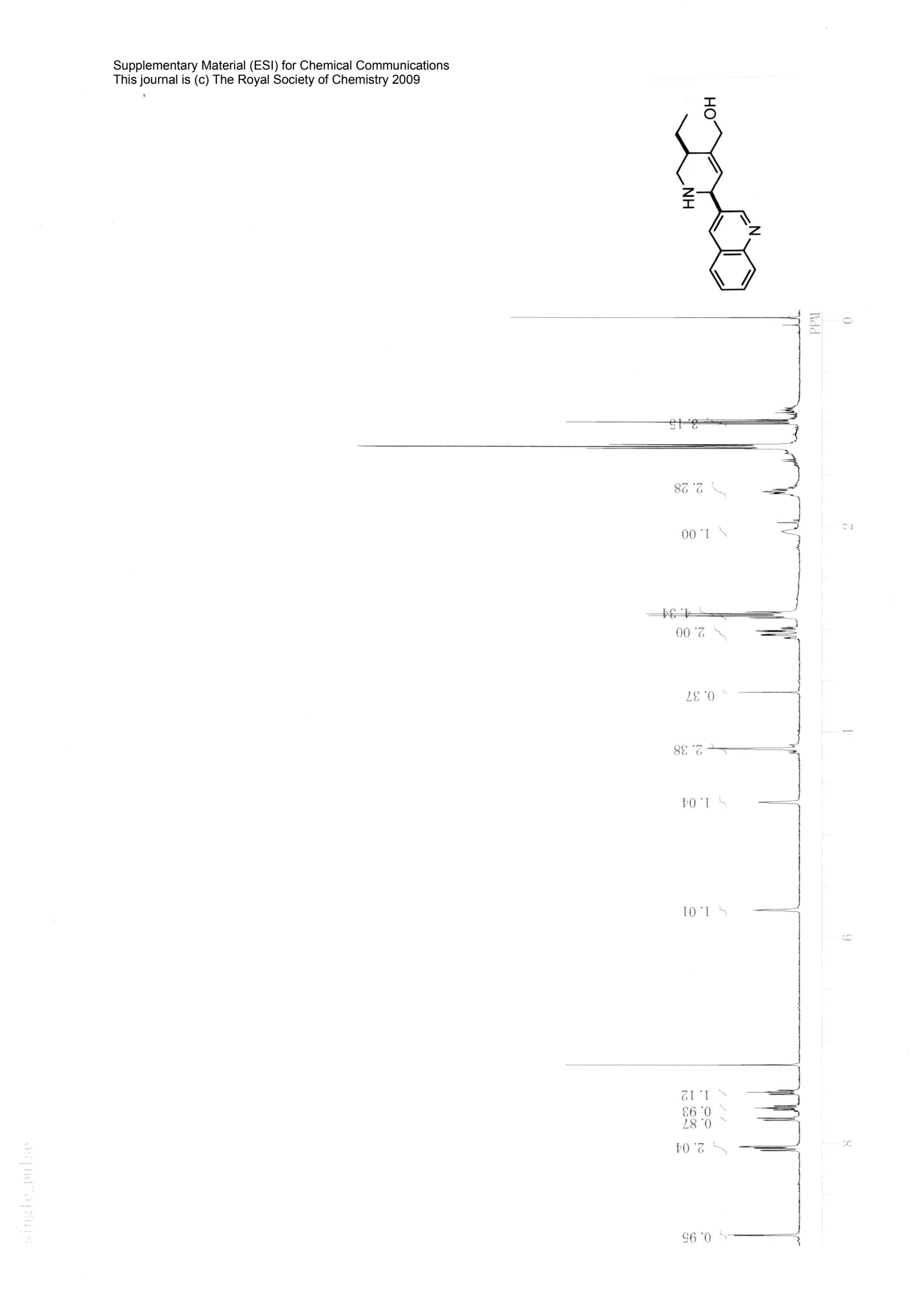
25
50
75
100
125
150
11.936
21.537
28.931
36.364
41.551
50.589
61.927
76.676
77.000
77.315
111.903
111.719
118.765
120.111
121.110
121.806
124.011
126.809
128.121
128.186
129.188
129.811
135.218
135.638
single pulse decoupled gated NOE

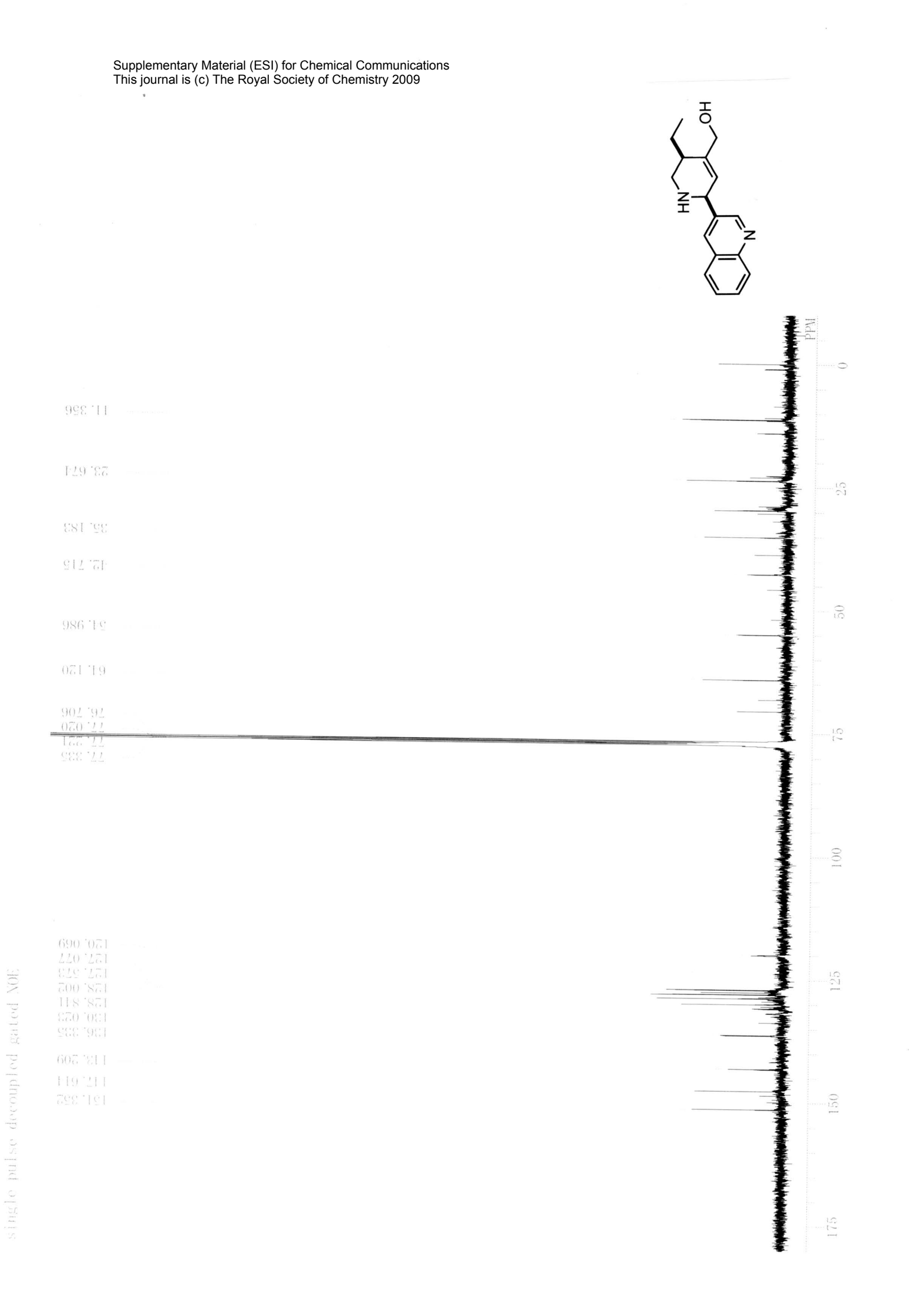

HO
HN
N
PPM
0
2
4
6
8
3.17
2.34
1.96
0.69
2.15
1.01
0.89
0.89
0.97
1.06
1.00
single_pulse

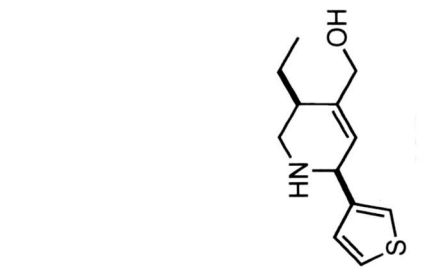

HO
HN
N
PPM
0
25
50
75
100
125
150
175
12.070
21.274
29.680
35.849
41.335
59.218
64.996
76.676
77.000
77.315
122.013
122.170
123.038
136.887
141.625
149.139
single pulse decoupled gated NOE

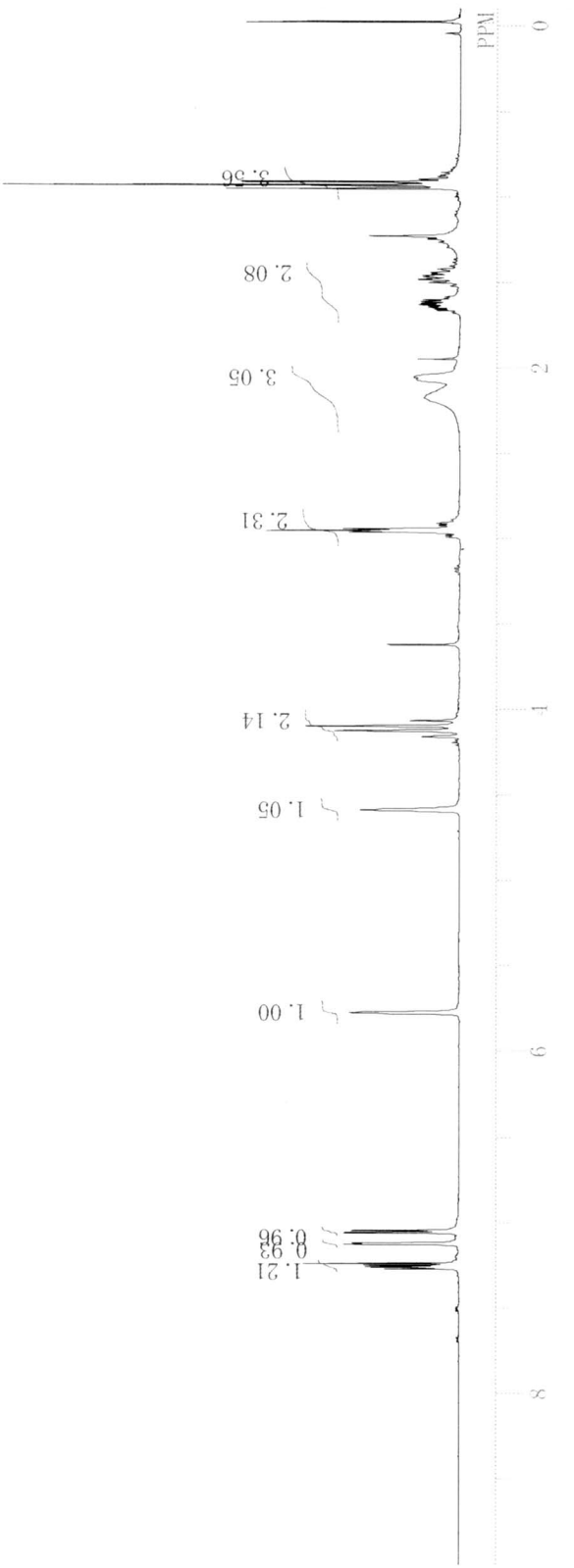

HO
HN
N
PPM
0
1
2
3
4
5
6
7
8
9
0.79
0.92
2.33
1.05
1.00
1.08
2.39
1.37
1.02
2.49
2.98
single_pulse

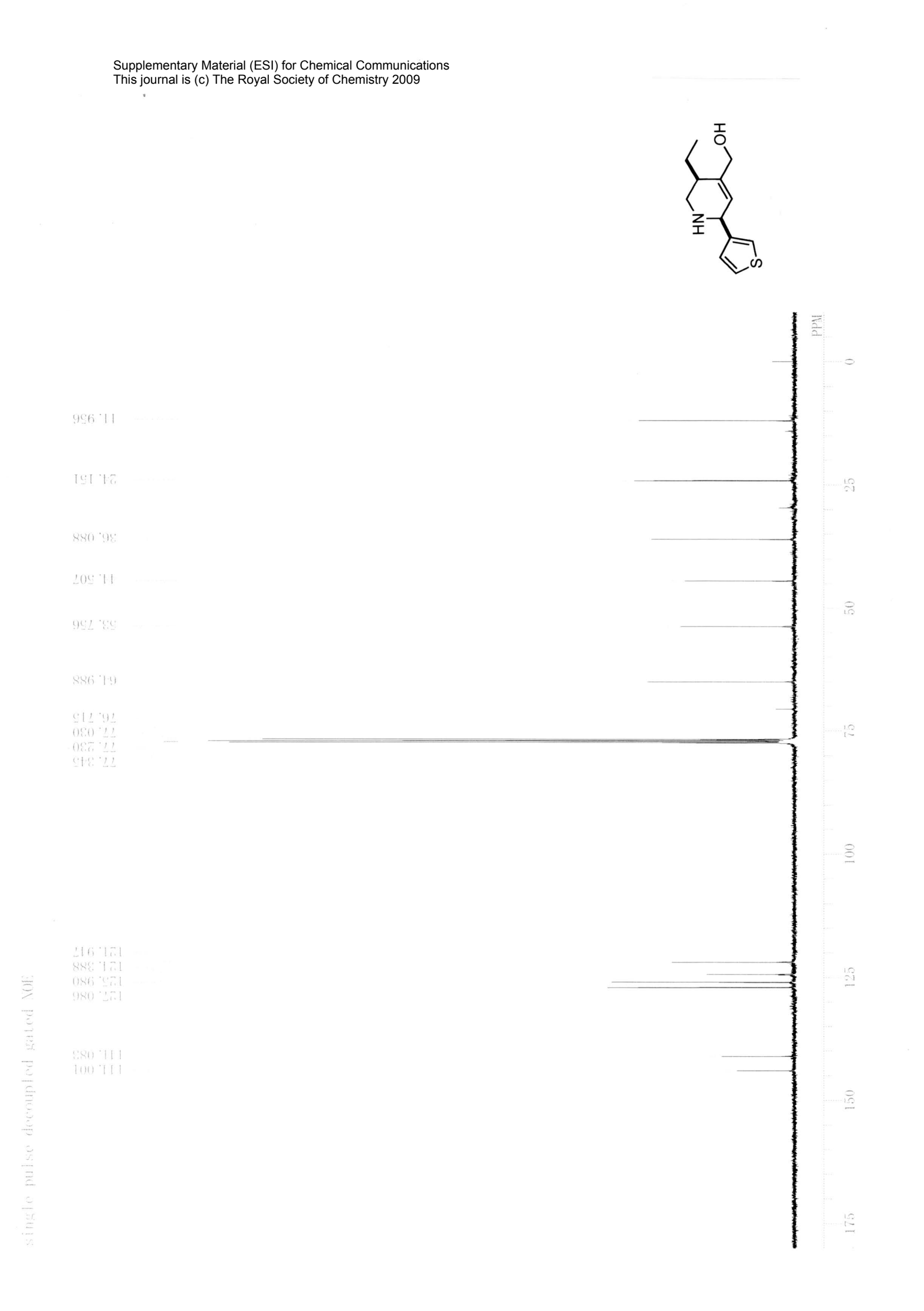

OH
HN
N
PPM
0
25
50
75
100
125
150
175
11.890
21.113
35.783
43.935
55.815
64.578
76.706
77.030
77.345
121.938
123.606
136.211
136.898
142.175
149.188
149.779
single pulse decoupled gated NOE

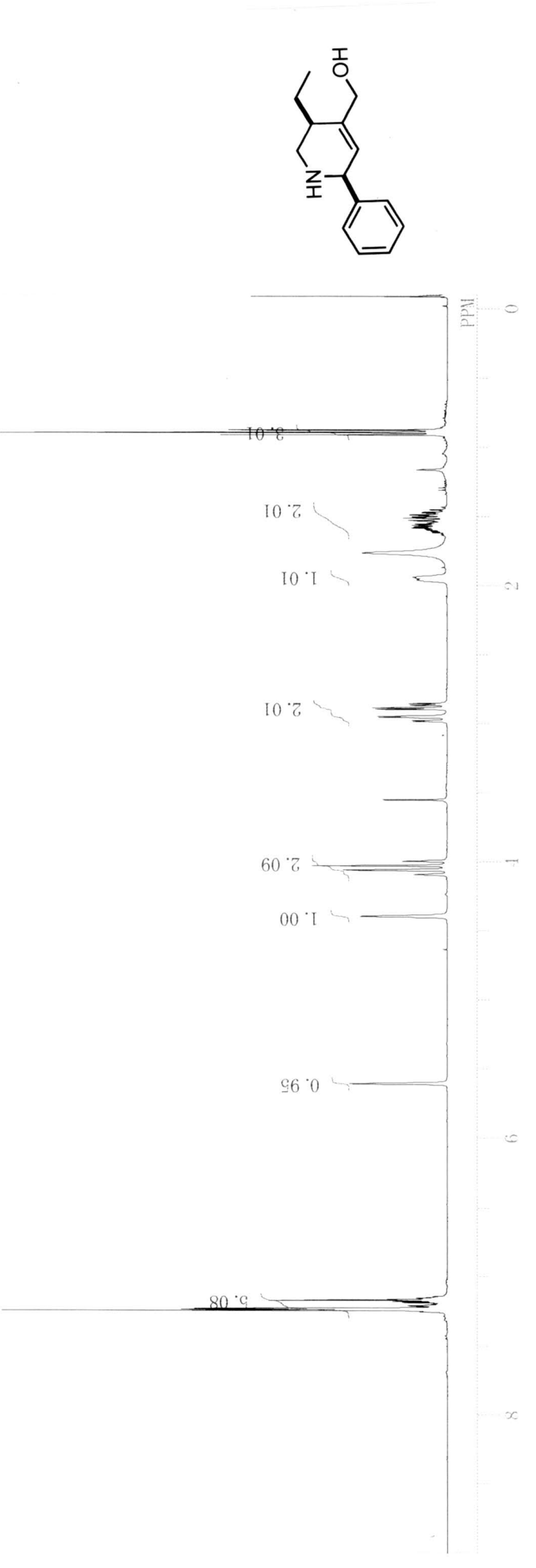

HO
HN
N
PPM
0
2
4
6
8
3.15
2.28
1.00
4.34
2.00
0.37
2.38
1.04
1.01
1.12
0.87
0.93
2.04
0.95
single_pulse

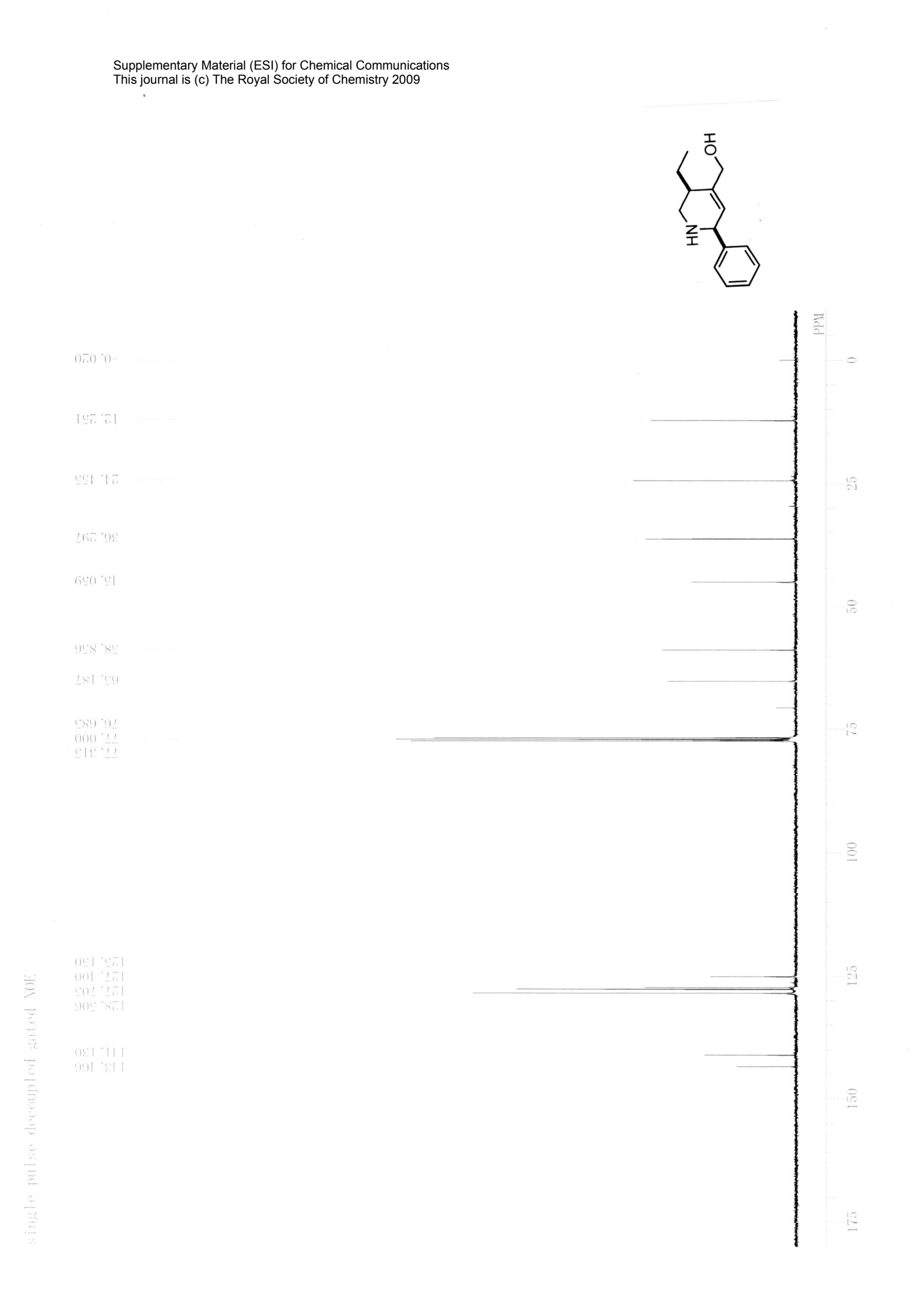

OH
HN
N
PPM
0
25
50
75
100
125
150
175
11.356
23.671
35.183
42.715
54.986
61.120
76.706
77.020
77.991
77.335
120.069
127.077
127.573
128.002
128.811
130.023
136.335
118.209
117.614
151.352
single pulse decoupled gated NOE


OH
HN
S


PPM
0
2
4
6
8
3.56
2.08
3.05
2.31
2.14
1.05
1.00
0.96
0.93
1.21
single_pulse


OH
HN
S
PPM
0
25
50
75
100
125
150
175
11.956
24.151
36.088
41.507
58.756
61.988
76.715
77.030
77.230
77.345
121.917
121.388
125.980
127.086
141.083
141.001
single pulse decoupled gated NOE


OH
HN
PPM
0
2
4
6
8
3.01
2.01
1.01
2.01
2.09
1.00
0.95
5.08


OH
HN
PPM
0
25
50
75
100
125
150
175
-0.020
12.251
21.155
36.297
15.059
58.856
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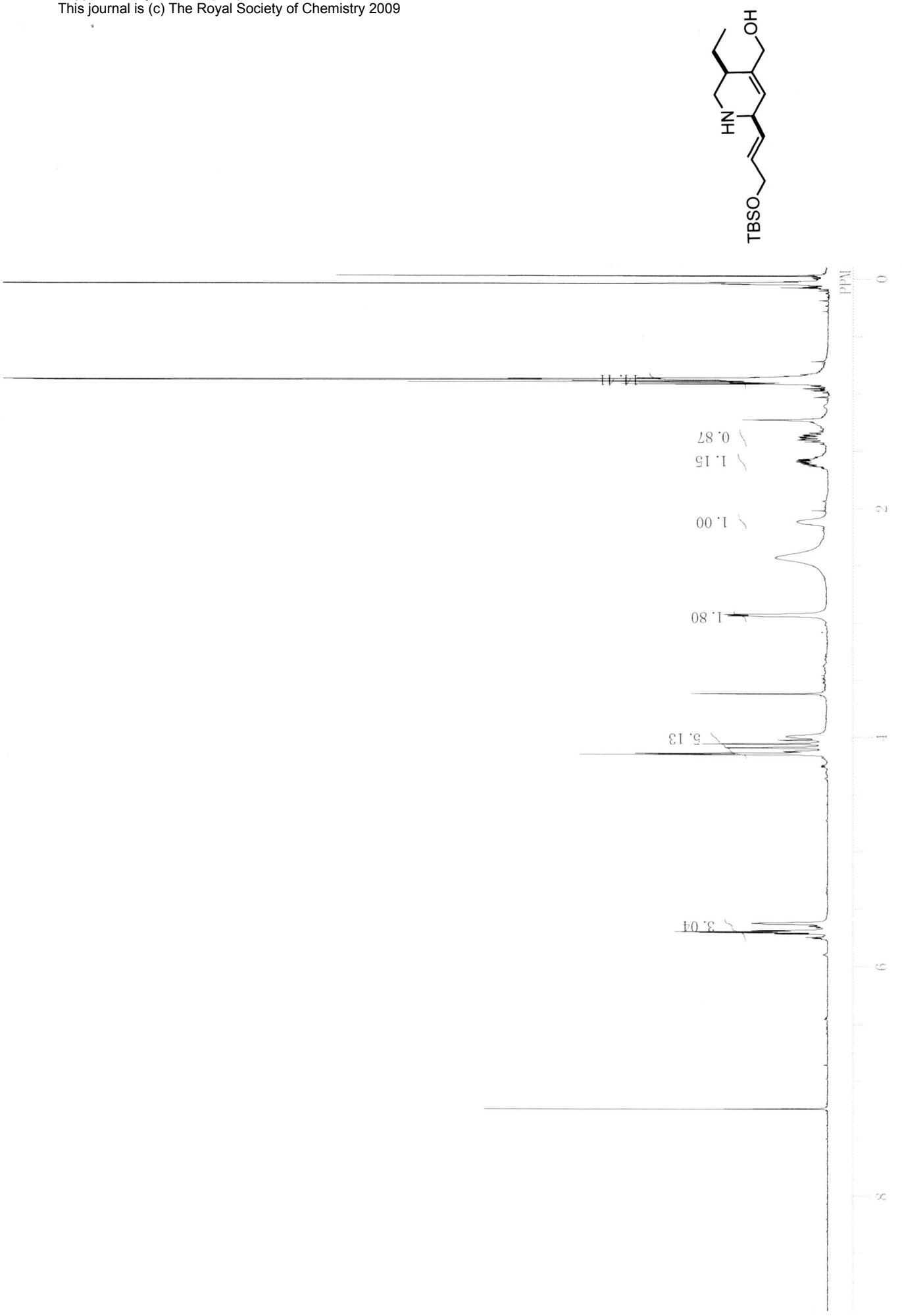
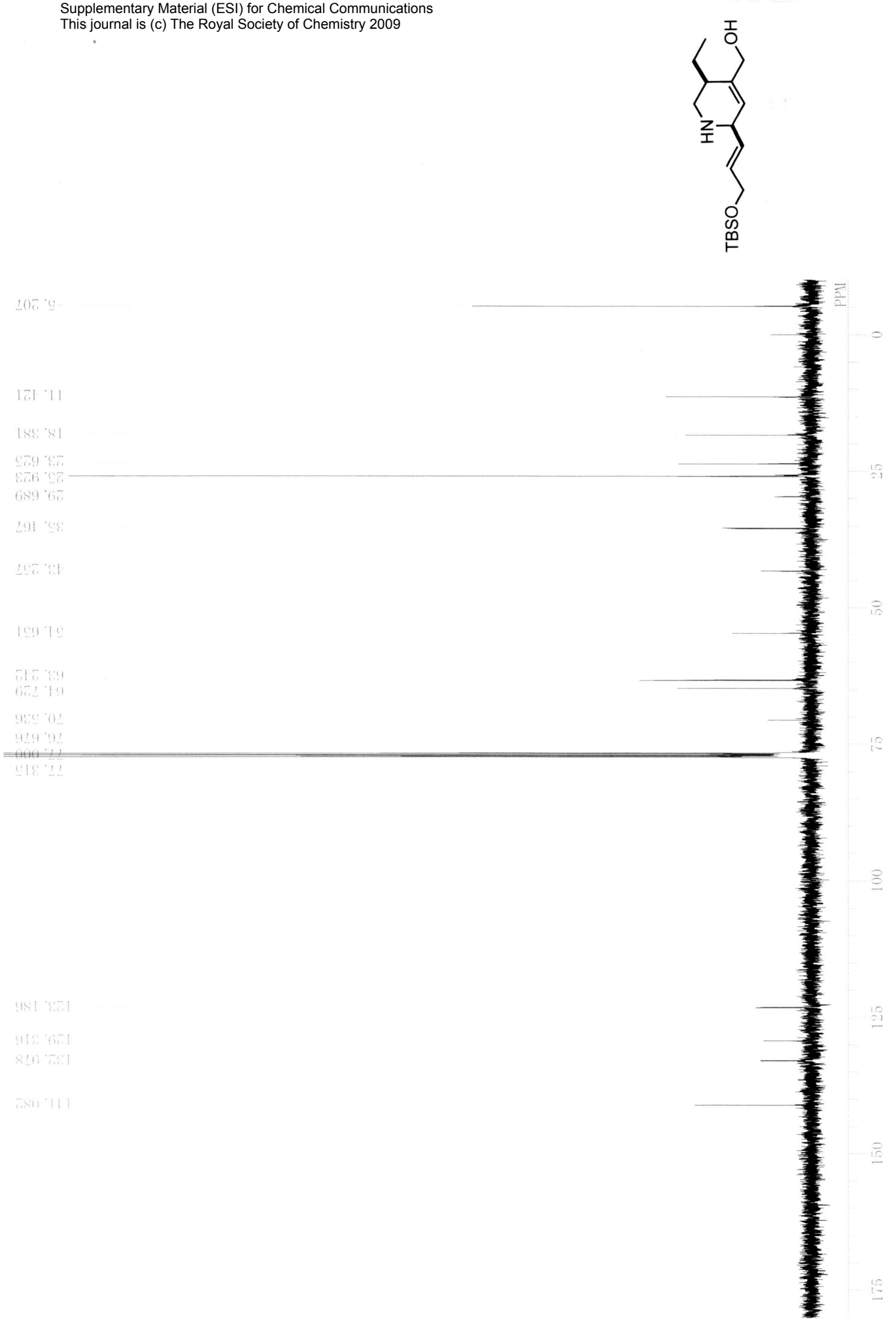
76.685
77.000
77.315
125.150
127.100
127.705
128.506
111.130
118.166
single pulse decoupled gated NOE


OH
HN
TBSO
PPM
0
2
4
6
8
14.11
0.87
1.15
1.00
1.80
5.13
3.04
simple_pulse


OH
HN
TBSO
PPM
0
25
50
75
100
125
150
175
-5.207
11.421
18.381
23.625
25.923
29.689
35.467
43.257
51.651
62.242
64.729
70.536
76.676
77.000
77.315
123.186
129.316
132.978
111.082
single pulse decoupled gated NOE