Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

Construction of tetrahydro-β-carboline skeleton *via* Brønsted acid activation of imide carbonyl group: Syntheses of indole alkaloids (±)-harmicine and (±)-10-desbromoarborescidine-A

Selvaraj Mangalaraj and Chinnasamy Ramaraj Ramanathan*

Department of Chemistry, Pondicherry University, Puducherry-605014, India.

crrnath.che@pondiuni.edu.in.

Supporting Information

This journal is © The Royal Society of Chemistry 2012

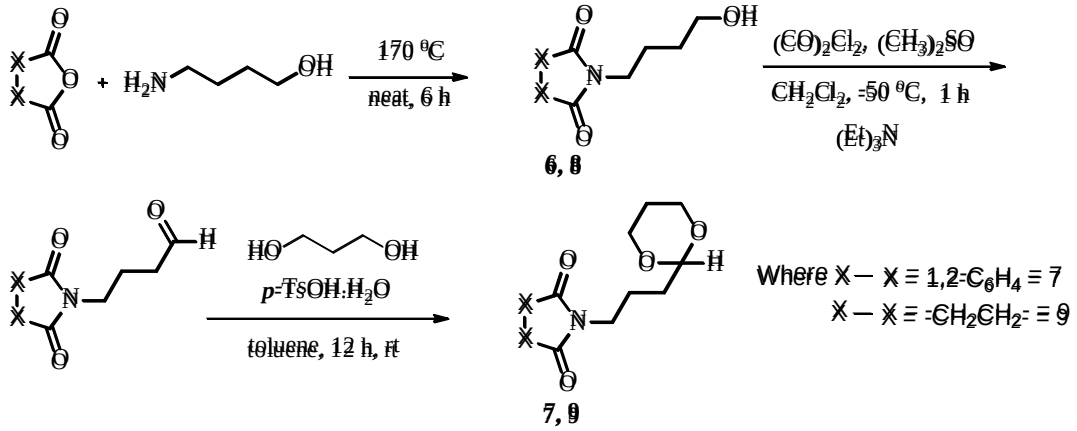
(A) General Information

Instrumentation. All reactions were performed in oven-dried round bottom flasks. Stainless steel syringes or cannulae were used to transfer air and moisture sensitive liquids. Melting points reported in this paper are uncorrected and were determined using EZ Melt, Stanford Research Systems, USA. Infrared spectra were recorded on Thermo Nicolet 6700 FT-IR Spectrophotometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Q-TOF Micro mass spectrometer. ^{1}H and ^{13}C NMR were recorded on Brucker AVANCE 400 spectrometer. NMR spectra for all the samples were measured either in $CDCl_3$ or DMSO-d_6 or acetone-d_6 a using TMS as an internal standard. The chemical shifts are expressed in δ ppm down field from the signal of internal TMS. Data are represented as follows : chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublet, ddd = doublet of doublet of doublet, td = triplet of doublet, dt = doublet of triplet, sep = septet, m = multiplet), coupling constants in Hertz (Hz), and integration. Trifluromethanesulphonic acid, 4-amino-1-butanol, oxalyl chloride, substituted phenyl hydrazine hydrochloride were purchased from Aldrich; remaining from local products and used without further purification. Column chromatography was performed on Merck silica gel 100-200 mesh, neutral alumina 70-230 mesh and TLC analysis was facilitated using phosphomolybdic acid stain in addition to UV light with Merck 60 F_{254} pre-coated silica plates.

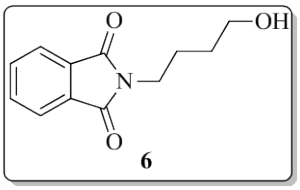
Abbreviations used: EtOAc – ethyl acetate, THF – tetrahydrofuran, MeOH – methanol, TEA – triethylamine, MS – molecular sieves, LAH – lithium aluminum hydride, TLC – thin layer chromatography.

Representative Experimental procedures

(B) Synthesis of 6, 7, 8, 9

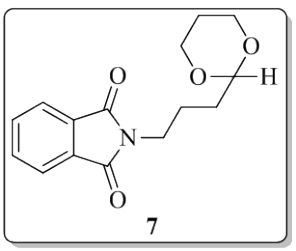


2-(4-Hydroxybutyl)isoindoline-1,3-dione (6)[1]



A mixture of finely powdered phthalic anhydride (8.308 g, 56.092 mmol) and 4-amino-1-butanol (5.000 g, 56.092 mmol) were heated at 170 °C with vigorous stirring under nitrogen atmosphere. After 6 h the reaction mixture was cooled to 80 °C and it was poured to 100 mL of ice-cold water. The product was extracted with $CHCl_3$ (4 x 100 mL), and the combined organic layer was washed with 5% $NaHCO_3$ solution (3 x 100 mL), and with water (3 x 100 mL). Organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum to give the mixture, which was purified through silica gel column chromatography using ethyl acetate : hexane as eluent (2:5) to give 2-(4-hydroxybutyl)isoindoline-1,3-dione in 92% yield (11.314 g) as colorless solid. (m.p. : 45-46 °C, lit.[1] 47-49 °C); IR (KBr, cm^{-1}) : 3471, 2938, 1771, 1710, 1399; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.74 (t, *J* = 7.2 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 1.82-1.75 (m, 2H), 1.66-1.59 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz): 168.63, 134.06, 132.23, 123.34, 62.43, 37.84, 29.90, 25.23.

2-(3-(1,3-Dioxan-2-yl)propyl)isoindoline-1,3-dione (7)



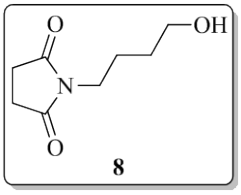
To a well stirred solution of oxalyl chloride (2.8 mL, 33.56 mmol) in 20 mL of CH_2Cl_2, a solution of anhydrous $(CH_3)_2SO$ (5.7 mL, 80.24 mmol) in 20 mL of CH_2Cl_2 was added under nitrogen atmosphere at -50 °C at such a rate that temperature was maintained

This journal is © The Royal Society of Chemistry 2012

at -50 °C. Stirring was continued for additional 15 min, then a solution of 2-(4-hydroxybutyl)isoindoline-1,3-dione (5.00 g, 22.82 mmol) in 40 mL of CH_2Cl_2 was added while keeping the temperature at -50 °C. The reaction mixture was stirred for another 1 h at -50 °C, and triethylamine (21.42 mL, 153.56 mmol) was added. The mixture is allowed to warm to room temperature, and 200 mL of water was added and stirred for 30 min. The organic layer was separated and washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude 4-(1,3-dioxoisoindolin-2-yl)butanal was obtained as viscous oil in 98% yield (4.84 g) and was stored under nitrogen atmosphere and used without further purification for the next step.

Propane-1,3-diol (4.2 g, 55.28 mmol) was added to a solution of 4-(1,3-dioxoisoindolin-2-yl)butanal (4.0 g, 18.4 mmol) and *p*-toluenesulphonic acid monohydrate (0.348 g, 0.92 mmol) in toluene (200 mL) at room temperature. The solution was stirred for 12 h, then diluted with ethyl acetate (200 mL) and washed with saturated $NaHCO_3$ (60 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (4 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography using silica gel and ethyl acetate : hexane as eluent (1:1) to give 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione in 84% yield (4.256 g) as colorless solid. (m.p. : 86-87 °C); IR (KBr, cm^{-1}) : 3064, 2949, 2843, 1764, 1715, 1613, 1143; ^{1}H-NMR ($CDCl_3$, 400 MHz) : 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 4.55 (t, *J* = 5.0 Hz, 1H), 4.07 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.03 (dd, *J* = 5.0, 1.2 Hz, 1H), 3.76 (dd, *J* = 2.4, 1.6 Hz, 1H), 3.73 (d, *J* = 2.4 Hz, 1H), 3.70 (t, *J* = 7.2 Hz, 2H), 2.10-1.98 (m, 1H), 1.84-1.76 (m, 2H), 1.65 (d, *J* = 5.0 Hz, 1H), 1.63-1.61 (m, 1H), 1.30 (d of sep, *J* = 13.2, 1.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.50, 133.97, 132.29, 123.27, 101.69, 66.97, 37.84, 32.49, 25.89, 23.24.

1-(4-Hydroxybutyl)pyrrolidine-2,5-dione (8)

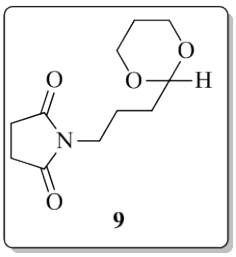


8

A mixture of finely powdered succinic anhydride (4.491 g, 44.873 mmol) and 4-amino-1-butanol (4.000 g, 44.873 mmol) were heated at 170 °C with vigorous stirring under nitrogen atmosphere. After 6 h the reaction mixture was cooled to room temperature and distilled under reduced pressure to give 1-(4-hydroxybutyl)pyrrolidine-2,5-dione in 70% yield (5.377 g) as

colorless viscous liquid. IR (KBr, cm^{-1}) : 3448, 2942, 1764, 1695, 1250; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 3.67-3.62 (m, 2H), 3.56-3.51 (m, 2H), 2.69-2.68 (m, 4H), 1.69-1.61 (m, 2H), 1.58-1.51 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.44, 62.16, 38.54, 29.69, 28.17, 24.24.

1-(3-(1,3-Dioxan-2-yl)propyl)pyrrolidine-2,5-dione (9)



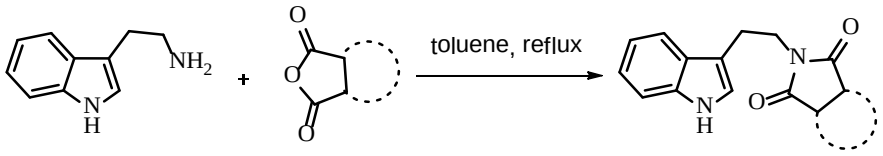
9

To a well stirred solution of oxalyl chloride (2.9 mL, 34.36 mmol) in 20 mL of CH_2Cl_2, a solution of anhydrous $(CH_3)_2SO$ (5.8 mL, 82.16 mmol) in 20 mL of CH_2Cl_2 was added under nitrogen atmosphere at -50 °C at such a rate that temperature was maintained at -50 °C. Stirring was continued for additional 15 min, then a solution of 1-(4-hydroxybutyl)pyrrolidine-2,5-dione (4.00 g, 23.37 mmol) in 40 mL of CH_2Cl_2 was added while keeping the temperature at -50 °C. The reaction mixture was stirred for another 1 h at -50 °C, and triethylamine (21.93 mL, 157.23 mmol) was added. The mixture is allowed to warm to room temperature, and 200 mL of water was added and stirred for 30 min. The organic layer was separated and washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude 4-(2,5-dioxopyrrolidin-1-yl)butanal was obtained as viscous oil in 98% yield (3.87 g) and was stored under nitrogen atmosphere and used without further purification for the next step.

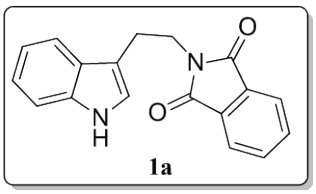
Propane-1,3-diol (4.73 g, 62.15 mmol) was added to a solution of 4-(2,5-dioxopyrrolidin-1-yl)butanal (3.5 g, 20.69 mmol) and *p*-toluenesulphonic acid monohydrate (0.196 g, 1.0344 mmol) in toluene (200 mL) at room temperature. The solution was stirred for 12 h, then diluted with ethyl acetate (200 mL) and washed with saturated $NaHCO_3$ (60 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (4 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through column chromatography using silica gel and ethyl acetate : hexane as eluent (1:1) to give 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione in 84% yield (4.256 g) as colorless solid. (m.p. : 112-113 °C); IR (KBr, cm^{-1}) : 2861, 1763, 1695, 1238, 1145; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 4.51 (t, *J* = 5.0 Hz, 1H), 4.05 (ddd, *J* = 12.4, 5.0, 1.2 Hz, 2H), 3.72 (td, *J* = 12.4, 2.4 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 2H), 2.66 (s, 4H), 2.09-1.97 (m, 1H), 1.73-1.64 (m, 2H), 1.56 (dd, *J* = 8.8, 5.0 Hz, 2H), 1.30 (d of sep, *J* = 13.5, 1.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.17, 101.47, 66.82, 38.50, 32.28, 28.11, 25.72, 22.20.

This journal is © The Royal Society of Chemistry 2012

(C) General procedure for the synthesis of imide derivative of tryptamine

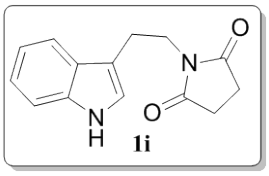


2-(2-(1*H*-Indol-3-yl)ethyl)isoindoline-1,3-dione (1a)[2]



A suspension of phthalic anhydride (2.773 g, 18.725 mmol) in toluene in an oven dried round bottom flask fitted with Dean-Stark set up was heated at reflux until complete dissolution of the anhydride and no additional water was removed. To this solution was added tryptamine (3.000 g, 18.725 mmol) and refluxing was continued until the water evolution was completed (12 h). Reaction mixture was concentrated under reduced pressure to give a residue which was purified through neutral alumina column chromatography using ethyl acetate : hexane as eluent (1:4) to give 2-(2-(1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 78% yield (4.240 g) as yellow solid. (m.p. : 166-167 °C, lit.[2] 166-168 °C); IR (KBr, cm^{-1}) : 3383, 3044, 2942, 2858, 1767, 1703, 1233; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.05 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.34 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 8.0, 1.2 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 4.04-3.99 (m, 2H), 3.19-3.15 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.51, 136.37, 134.00, 132.34, 127.55, 123.31, 122.27, 122.14, 119.66, 119.01, 112.59, 111.24, 38.66, 24.60.

1-(2-(1*H*-Indol-3-yl)ethyl)pyrrolidine-2,5-dione (1i)[3]

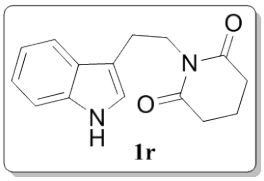


A suspension of succinic anhydride (1.874 g, 18.725 mmol) in toluene in an oven dried round bottom flask fitted with Dean-Stark set up was heated at reflux until complete dissolution of the anhydride and no additional water was removed. To this solution was added tryptamine (3.000 g, 18.725 mmol) and refluxing was continued until the water evolution was completed (12 h). Reaction mixture was concentrated under reduced pressure to give a residue which was purified through neutral alumina column chromatography using ethyl acetate : hexane as eluent (1:4) to give 1-(2-(1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 71% yield (3.211 g) as tan solid. (m.p. : 166-167 °C, lit.[3] 163-166 °C); IR (KBr, cm^{-1}) : 3265, 3052, 2925, 1764, 1694, 1401, 1339; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.04 (br s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H),

This journal is © The Royal Society of Chemistry 2012

7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 3.83 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.38, 136.29, 127.64, 122.27, 122.23, 119.67, 118.77, 112.41, 111.30, 39.65, 28.29, 23.45.

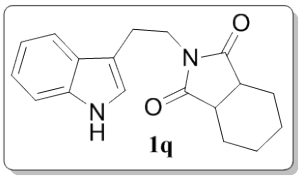
1-(2-(1*H*-Indol-3-yl)ethyl)piperdine-2,6-dione (1r)[4]



1r

A suspension of glutaric anhydride (2.136 g, 18.725 mmol) in toluene in an oven dried round bottom flask fitted with Dean-Stark set up was heated at reflux until complete dissolution of the anhydride and no additional water was removed. To this solution was added tryptamine (3.000 g, 18.725 mmol) and refluxing was continued until the water evolution was completed (12 h). Reaction mixture was concentrated under reduced pressure to give a residue which was purified through neutral alumina column chromatography using ethyl acetate : hexane as eluent (1:4) to give 1-(2-(1*H*-indol-3-yl)ethyl)piperdine-2,6-dione in 67% yield (3.215 g) as tan solid. (m.p. : 174-175 $^{\circ}$C), IR (KBr, cm^{-1}) : 3333, 2971, 2958, 1718, 1665, 1456, 1354; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.02 (br s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.20-7.12 (m, 2H), 7.06 (d, *J* = 1.7 Hz, 1H), 4.07 (t, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 4H), 1.87 (p, 6.4 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 172.67, 136.27, 127.78, 122.25, 122.13, 119.56, 119.25, 113.06, 111.17, 40.45, 32.99, 23.84, 17.26.

2-(2-(1*H*-Indol-3-yl)ethyl)hexahydro-1*H*-isoindole-1,3(2*H*)-dione (1q)

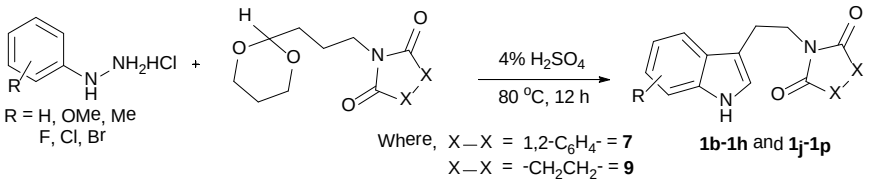


1q

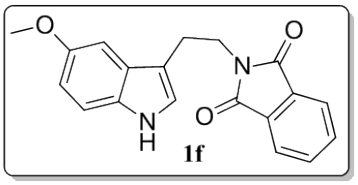
A suspension of hexahydrophthalic anhydride (2.887 g, 18.725 mmol) in toluene in an oven dried round bottom flask fitted with Dean-Stark set up was heated at reflux until complete dissolution of the anhydride and no additional water was removed. To this solution was added tryptamine (3.000 g, 18.725 mmol) and refluxing was continued until the water evolution was completed (12 h). Reaction mixture was concentrated under reduced pressure to give a residue which was purified through neutral alumina column chromatography using ethyl acetate : hexane as eluent (1:4) to give 2-(2-(1*H*-indol-3-yl)ethyl)hexahydro-1*H*-isoindole-1,3(2*H*)-dione in 63% yield (3.496 g) as pale orange solid. (m.p. : 145-146 $^{\circ}$C); IR (KBr, cm^{-1}) : 3364, 2944, 2860, 1766, 1694, 1401, 1341; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.02 (br s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.15-7.11 (m, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 3.82 (t, *J* = 7.6 Hz, 2H), 3.07

(t, *J* = 7.6 Hz, 2H), 2.78-2.72 (m, 2H), 1.79-1.77 (m, 2H), 1.64-1.61 (m, 2H), 1.42-1.31 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 179.98, 136.25, 127.63, 122.28, 122.13, 119.55, 118.93, 112.17, 111.21, 39.73, 39.12, 23.69, 23.37, 21.62.

(D) General procedure for the synthesis of imide derivative of substituted tryptamine

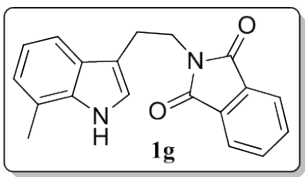


2-(2-(5-Methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1f)[5]



A mixture of (4-methoxyphenyl)hydrazine hydrochloride (349 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5-methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 67% yield (429 mg) as yellow solid. (m.p. : 160-161 °C); IR (KBr, cm^{-1}) : 3390, 2999, 2939, 2835, 1765, 1704, 1579, 1398, 1211, 1097; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.95 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.02-3.98 (m, 2H), 3.86 (s, 3H), 3.14-3.10 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.39, 154.08, 133.87, 132.19, 131.30, 127.81, 123.16, 122.74, 112.57, 112.20, 111.89, 100.31, 55.82, 38.44, 24.50.

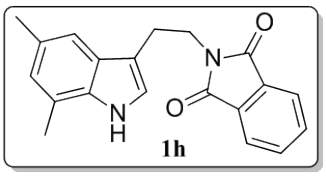
2-(2-(7-Methyl-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1g)



A mixture of *o*-tolylhydrazine hydrochloride (317 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with

CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(7-methyl-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 64% yield (389 mg) as orange solid. (m.p. : 208-209 $^{\circ}$C); IR (KBr, cm^{-1}) : 3391, 3045, 2931, 2857, 1760, 1703, 1438, 1072; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.95 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 1H), 4.03-3.99 (m, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.48 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.52, 135.97, 134.00, 132.35, 127.08, 123.32, 122.82, 121.86, 120.39, 119.90, 116.76, 113.08, 38.68, 24.75, 16.71.

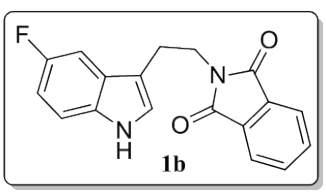
2-(2-(5,7-Dimethyl-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1h)



1h

A mixture of (2,4-dimethylphenyl)hydrazine hydrochloride (345 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5,7-dimethyl-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 59% yield (375 mg) as pale brown solid. (m.p. : 221-222 $^{\circ}$C); IR (KBr, cm^{-1}) : 3380, 2919, 2856, 1766, 1705, 1608, 1442, 1086; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.87 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.34 (s, 1H), 7.06 (d, *J* = 1.7 Hz, 1H), 6.82 (s, 1H), 3.99 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.53, 134.27, 133.96, 132.35, 129.12, 127.33, 124.54, 123.27, 122.02, 120.05, 116.25, 112.55, 38.79, 24.73, 21.54, 16.64.

2-(2-(5-Fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1b)[6]



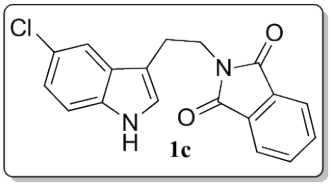
1b

A mixture of (4-fluorophenyl)hydrazine hydrochloride (325 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room

This journal is © The Royal Society of Chemistry 2012

temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5-fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 75% yield (462 mg) as pale yellow solid. (m.p. : 125-126 °C, lit.[6] 122-124 °C); IR (KBr, cm^{-1}) : 3390, 3048, 2934, 1766, 1702, 1448, 1402, 1247, 716; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.04 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.34 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.24 (t, *J* = 4.4 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 6.91 (td, *J* = 9.0, 2.4 Hz, 1H), 3.98 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.33, 157.81 (d, *J* = 233.5 Hz, 1C), 133.90, 132.68, 132.12, 127.82 (d, *J* = 9.8 Hz, 1C), 123.79, 123.19, 112.63 (d, *J* = 4.6 Hz, 1C), 111.72 (d, *J* = 9.5 Hz, 1C), 110.52 (d, *J* = 26.2 Hz, 1C), 103.75 (d, *J* = 23.3 Hz, 1C), 38.33, 24.33.

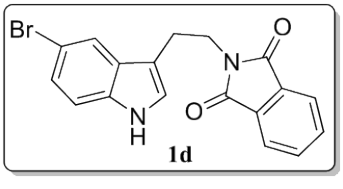
2-(2-(5-Chloro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1c)



1c

A mixture of (4-chlorophenyl)hydrazine hydrochloride (358 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5-chloro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 62% yield (402 mg) as pale yellow solid. (m.p. : 195-196 °C); IR (KBr, cm^{-1}) : 3340, 1769, 1702, 1610, 1450, 1402, 1238, 721; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.05 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.64 (d, *J* = 1.3 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.13-7.11 (m, 2H), 3.98 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.47, 134.67, 134.06, 132.24, 128.70, 125.46, 123.56, 123.35, 122.57, 118.48, 112.47, 112.26, 38.56, 24.35.

2-(2-(5-Bromo-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1d)

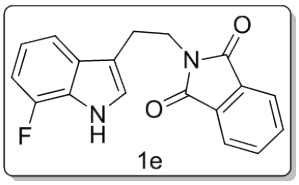


1d

This journal is © The Royal Society of Chemistry 2012

A mixture of (4-bromophenyl)hydrazine hydrochloride (430 mg, 1.943 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (535 mg, 1.943 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5-bromo-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 72% yield (517 mg) as pale orange solid. (m.p. : 212-213 $^{\circ}$C); IR (KBr, cm^{-1}) : 3318, 3048, 2934, 2860, 1764, 1695, 1458, 1389, 1230, 719; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.05 (br s, 1H), 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.79-7.78 (m, 1H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.23 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.19 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 4.00-3.96 (m, 2H), 3.13-3.09 (m, 2H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 167.75, 134.82, 134.33, 131.52, 128.90, 124.77, 123.36, 122.95, 120.31, 113.42, 111.00, 110.53, 38.16, 23.52.

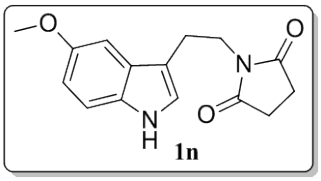
2-(2-(7-Fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (1e)



1e

A mixture of (2-fluorophenyl)hydrazine hydrochloride (325 mg, 1.998 mmol) and 2-(3-(1,3-dioxan-2-yl)propyl)isoindoline-1,3-dione (550 mg, 1.998 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 2-(2-(5-fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione in 68% yield (419 mg) as orange solid. (m.p. : 199-200 $^{\circ}$C); IR (KBr, cm^{-1}) : 3358, 2944, 1768, 1704, 1429, 1228, 715; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.24 (br s, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.01 (td, *J* = 8.0, 4.8 Hz, 1H), 6.91-6.86 (m, 1H), 4.02-3.98 (m, 2H), 3.16-3.13 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.48, 149.69 (d, *J* = 242.3 Hz, 1C), 134.05, 132.26, 131.31 (d, *J* = 5.2 Hz, 1C), 124.68 (d, *J* = 13.2 Hz, 1C), 123.34, 122.85, 119.90 (d, *J* = 6.3 Hz, 1C), 114.76 (d, *J* = 3.5 Hz, 1C), 113.41 (d, *J* = 2.2 Hz, 1C), 107.08 (d, *J* = 15.9 Hz, 1C), 38.52, 24.57.

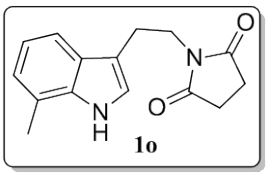
1-(2-(5-Methoxy-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1n)[4]



1n

A mixture of (4-methoxyphenyl)hydrazine hydrochloride (231 mg, 1.320 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (300 mg, 1.320 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(5-methoxy-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 61% yield (219 mg) as pale tan solid. (m.p. : 169-170 $^{\circ}$C); IR (KBr, cm^{-1}) : 3424, 2951, 1761, 1696, 1487, 1404, 1227, 1153; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.98 (br s, 1H), 7.28 (d, *J* = 6.1 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.93 (s, 3H), 3.85 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.67 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.31, 154.08, 131.24, 127.86, 122.84, 112.49, 111.95, 111.91, 100.24, 55.87, 39.29, 28.18, 23.40.

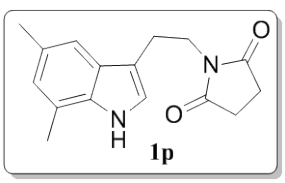
1-(2-(7-Methyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1o)[4]



1o

A mixture of *o*-tolylhydrazine hydrochloride (349 mg, 2.200 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (500 mg, 2. 200 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(7-methyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 66% yield (372 mg) as colorless solid. (m.p. : 172-173 $^{\circ}$C); IR (KBr, cm^{-1}) : 3272, 1770, 1694, 1405, 1343; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.97 (br s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 3.85-3.81 (m, 2H), 3.07-3.03 (m, 2H), 2.62 (s, 4H), 2.47 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.39, 135.88, 127.15, 122.76, 121.96, 120.45, 119.86, 116.47, 112.83, 39.67, 28.27, 23.58, 16.69.

1-(2-(5,7-Dimethyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1p)

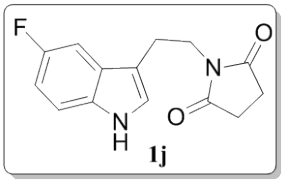


1p

This journal is © The Royal Society of Chemistry 2012

A mixture of (2,4-dimethylphenyl)hydrazine hydrochloride (380 mg, 2.200 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (500 mg, 2.200 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(5,7-dimethyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 55% yield (327 mg) as pale yellow solid. (m.p. : 192-193 $^{\circ}$C); IR (KBr, cm^{-1}) : 3348, 3125, 2860, 1769, 1691, 1405, 1264; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.84 (br s, 1H), 7.28 (s, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 6.83 (s, 1H), 3.83-3.79 (m, 2H), 3.03-3.00 (m, 2H), 2.62 (s, 4H), 2.43 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.26, 134.09, 128.98, 127.27, 124.42, 121.95, 119.97, 115.88, 112.25, 39.58, 28.15, 23.47, 21.45, 16.51.

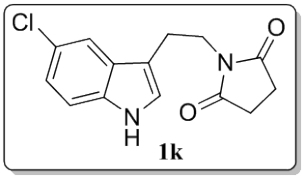
1-(2-(5-Fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1j)[4]



1j

A mixture of (4-fluorophenyl)hydrazine hydrochloride (122 mg, 0.748 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (170 mg, 0.748 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(5-fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 73% yield (142 mg) as tan solid. (m.p. : 136-137 $^{\circ}$C); IR (KBr, cm^{-1}) : 3344, 2935, 2860, 1773, 1697, 1486, 1404, 1260, 1152, 805; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.14 (br s, 1H), 7.30-7.23 (m, 2H), 7.10 (d, *J* = 1.4 Hz, 1H), 6.92 (td, *J* = 9.0, 2.2 Hz, 1H), 3.79 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.63 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.35, 157.96 (d, *J* = 234.0 Hz, 1C), 132.77, 128.03 (d, *J* = 9.0 Hz, 1C), 124.03, 112.60 (d, *J* = 4.0 Hz, 1C), 111.97 (d, *J* = 9.0 Hz, 1C), 110.66 (d, *J* = 27.0 Hz, 1C), 103.64 (d, *J* = 23.0 Hz, 1C), 39.46, 28.27, 23.38.

1-(2-(5-Chloro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1k)

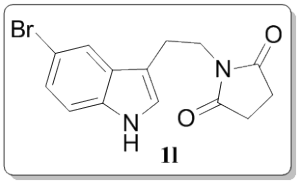


1k

This journal is © The Royal Society of Chemistry 2012

A mixture of (4-chlorophenyl)hydrazine hydrochloride (197 mg, 1.100 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (250 mg, 1.100 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(5-chloro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 71% yield (216 mg) as pale yellow solid. (m.p. : 145-146 °C); IR (KBr, cm^{-1}) : 3420, 2922, 1763, 1686, 1462, 1409, 1267; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.20 (br s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 0.8 Hz, 1H), 7.14 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 3.82 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.64 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.39, 134.58, 128.77, 125.38, 123.67, 122.52, 118.14, 112.38, 112.28, 39.59, 28.24, 23.22.

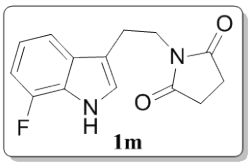
1-(2-(5-Bromo-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1l)[4]



1l

A mixture of (4-bromophenyl)hydrazine hydrochloride (171 mg, 0.770 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (175 mg, 0.770 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12 h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(5-bromo-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 53% yield (131 mg) as tan solid. (m.p. : 138-139 °C); IR (KBr, cm^{-1}) : 3318, 2919, 2854, 1767, 1699, 1336, 666; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.28 (br s, 1H), 7.71 (s, 1H), 7.25-7.18 (m, 2H), 7.04 (s, 1H), 3.78 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.61 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.43, 134.84, 129.42, 124.97, 123.54, 121.15, 112.86, 112.80, 112.13, 39.65, 28.22, 23.17.

1-(2-(7-Fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (1m)



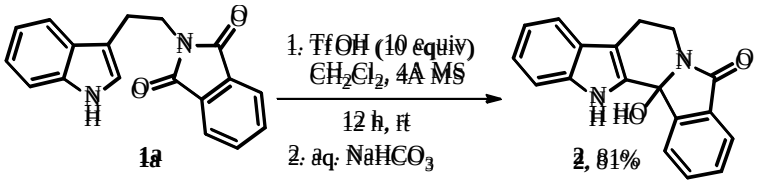
1m

A mixture of (2-fluorophenyl)hydrazine hydrochloride (122 mg, 0.748 mmol) and 1-(3-(1,3-dioxan-2-yl)propyl)pyrrolidine-2,5-dione (170 mg, 0.748 mmol) in 100 mL of 4% H_2SO_4 was heated at reflux for 12

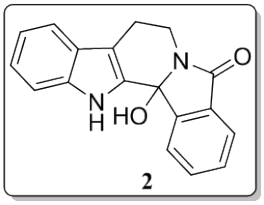
This journal is © The Royal Society of Chemistry 2012

h. The reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The tryptamine product was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was purified through neutral alumina column chromatography using ethyl acetate : hexane (1:4) as eluent to give 1-(2-(7-fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione in 69% yield (98 mg) as pale yellow solid. (m.p. : 170-171 $^{\circ}$C); IR (KBr, cm^{-1}) : 3282, 2943, 1770, 1699, 1448, 1336, 796; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.29 (br s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 7.03 (td, *J* = 8.0, 4.8 Hz, 1H), 6.92-6.87 (m, 1H), 3.84-3.80 (m, 2H), 3.06-3.03 (m, 2H), 2.62 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 177.33, 149.73 (d, *J* = 243.0 Hz, 1C), 131.39 (d, *J* = 5.0 Hz, 1C), 124.65 (d, *J* = 13.0 Hz, 1C), 122.93, 119.97 (d, *J* = 6.0 Hz, 1C), 114.57 (d, *J* = 4.0 Hz, 1C), 113.30 (d, *J* = 2.0 Hz, 1C), 107.08 (d, *J* = 16.0 Hz, 1C), 39.51, 28.29, 23.46.

(E) General procedure for the synthesis of benzindolizino indolones.

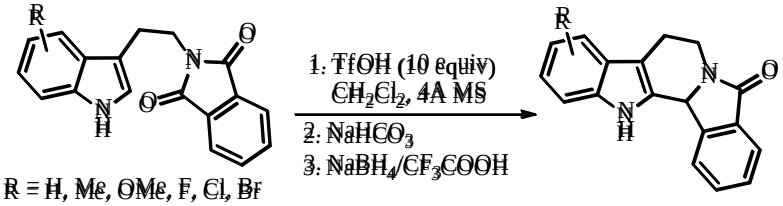


13b-Hydroxy-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2)

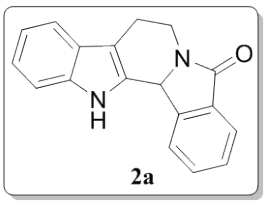


A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (110 mg, 0.379 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (335 µL, 3.789 mmol) with stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate as eluent to give 13b-hydroxy-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 81% yield (86 mg) as colorless solid. (m.p. : 163-

164 °C); IR (KBr, cm^{-1}) : 3350, 3226, 2924, 1682, 1409, 1300; ^{1}H-NMR (DMSO-d_6, 400 MHz) : δ 11.51 (br s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.13-7.09 (m, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 4.41 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.47 (td, *J* = 12.1, 4.4 Hz, 1H), 2.79 (dd, *J* = 15.6, 4.4 Hz, 1H), 2.73-2.65 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 166.70, 147.07, 136.56, 133.14, 132.64, 130.38, 129.76, 125.64, 123.78, 122.92, 122.42, 119.12, 118.99, 111.71, 109.06, 84.23, 35.10, 21.63; HRMS (ESI) (m/z) : $[M+Na]^+$ Found 313.0958; Calculated 313.0953; for $C_{18}H_{14}N_2O_2Na$.



7,8,13,13b-Tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2a)[3]

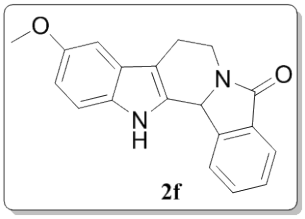


A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (110 mg, 0.379 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (335 µL, 3.789 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (350 mg, 4.168 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (64 mg, 1.705 mmol) and CF_3COOH (392 µL, 5.115 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 83% yield (86 mg) as pale yellow solid. (m.p. : 215-216 °C, lit.[3] 212-214 °C); IR (KBr, cm^{-1}) : 3225, 2932, 2841, 1670, 1461; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.51 (br s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.6, 1.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.18 (td,

This journal is © The Royal Society of Chemistry 2012

J = 8.0, 1.0 Hz, 1H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 5.84 (s, 1H), 4.87 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.41 (ddd, *J* = 13.2, 11.2, 5.2 Hz, 1H), 3.02-2.93 (m, 1H), 2.87 (dd, *J* = 15.2, 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.36, 143.07, 136.72, 132.68, 132.04, 130.18, 129.04, 126.92, 124.61, 122.75, 122.33, 120.20, 118.82, 111.24, 109.59, 57.22, 38.36, 21.83.

10-Methoxy-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2f)

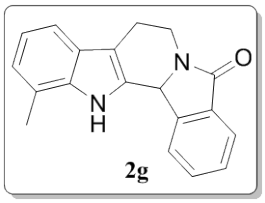


2f

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(5-methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (100 mg, 0.312 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. After 15 min to this mixture was added trifluoromethanesulfonic acid (276 µL, 3.121 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (288 mg, 3.433 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (53 mg, 1.404 mmol) and CF_3COOH (323 µL, 4.213 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 10-methoxy-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 74% yield (70 mg) as pale yellow solid. (m.p. : 230-231 $^{\circ}$C); IR (KBr, cm^{-1}) : 3246, 3057, 2838, 1674, 1473, 1405, 1206, 861; ^{1}H-NMR (DMSO-d_6, 400 MHz) : δ 11.18 (br s, 1H), 8.27 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.03 (s, 1H), 4.58 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.73 (s, 3H), 3.37 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.80 (dd, *J* = 15.2, 4.8 Hz, 1H), 2.71-2.64 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 167.05, 153.27, 143.62, 131.81, 131.63, 131.43, 131.40, 128.55, 126.46, 123.71, 123.06, 111.88, 111.36, 106.94, 100.11, 56.61, 55.28, 37.67, 21.42; HRMS (ESI) (m/z) : $[M+H]^+$ Found 305.1302; Calculated 305.1290; for $C_{19}H_{17}N_2O_2$.

This journal is © The Royal Society of Chemistry 2012

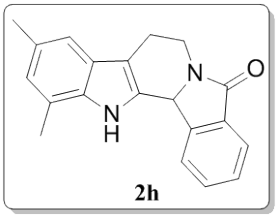
12-Methyl-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2g)



2g

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(7-methyl-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (120 mg, 0.394 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (349 µL, 3.943 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (364 mg, 4.337 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (67 mg, 1.774 mmol) and CF_3COOH (408 µL, 5.323 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 12-methyl-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 66% yield (75 mg) as pale yellow solid. (m.p. : 204-205 $^{\circ}$C); IR (KBr, cm^{-1}) : 3266, 3046, 2848, 2788, 1666, 1464, 1407; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.09 (br s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H),7.83 (d, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 1H), 5.85 (s, 1H), 4.86 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.42-3.36 (m, 1H), 3.02-2.93 (m, 1H), 2.86 (dd, *J* = 15.4, 4.8 Hz, 1H), 2.52 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.26, 143.09, 136.23, 132.76, 132.03, 129.93, 129.03, 126.56, 124.70, 123.50, 122.20, 120.53, 120.33, 116.58, 110.39, 57.20, 38.35, 21.93, 16.84; HRMS (ESI) (m/z) : $[M+H]^+$ Found 289.1355; Calculated 289.1341; for $C_{19}H_{17}N_2O$.

10,12-Dimethyl-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2h)



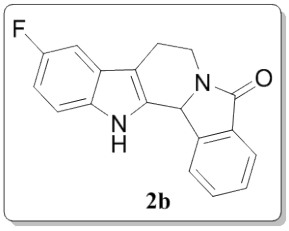
2h

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(5,7-dimethyl-1*H*-indol-3-

This journal is © The Royal Society of Chemistry 2012

yl)ethyl)isoindoline-1,3-dione (120 mg, 0.377 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (334 µL, 3.769 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (348 mg, 4.146 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (64 mg, 1.696 mmol) and CF_3COOH (390 µL, 5.088 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 10,12-dimethyl-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 60% yield (68 mg) as pale yellow solid. (m.p. : 200-201 °C); IR (KBr, cm^{-1}) : 3271, 2851, 1666, 1409; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.03 (br s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.12 (s, 1H), 6.84 (s, 1H), 5.83 (s, 1H), 4.85 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.42-3.34 (m, 1H), 2.98-2.90 (m, 1H), 2.83 (dd, *J* = 15.4, 4.8 Hz, 1H), 2.48 (s, 3H), 2.39 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 168.29, 143.20, 134.59, 132.74, 132.00, 130.02, 129.81, 128.96, 126.84, 125.16, 124.61, 122.30, 119.99, 116.20, 109.87, 57.30, 38.39, 21.94, 21.49, 16.78; HRMS (ESI) (m/z) : $[M+H]^+$ Found 303.1498; Calculated 303.1497; for $C_{20}H_{19}N_2O$.

10-Fluoro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2b)



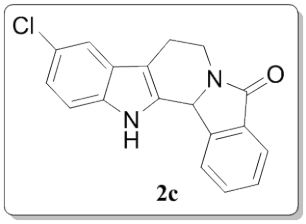
2b

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(5-fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (125 mg, 0.405 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (359 µL, 4.054 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (375 mg, 4.460 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (69 mg, 1.824 mmol) and CF_3COOH (419 µL, 5.473 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic

This journal is © The Royal Society of Chemistry 2012

layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 10-fluoro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 79% yield (94 mg) as pale yellow solid. (m.p. : 251-252 $^{\circ}$C); IR (KBr, cm^{-1}) : 3216, 2949, 1671, 1471, 1419, 727; ^{1}H-NMR (DMSO-d_6, 400MHz) : δ 11.46 (br s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 14.0, 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 10.0, 5.0 Hz, 1H), 7.18 (dd, *J* = 11.2, 4.0 Hz, 1H), 6.93 (td, *J* = 10.0, 3.0 Hz, 1H), 6.06 (s, 1H), 4.58 (dd, *J* = 13.2, 5.0 Hz, 1H), 3.40-3.36 (m, 1H) [to assign this proton the compound was recorded in acetone-d_6, the value obtained was 3.27 (ddd, *J* = 13.2, 10.8, 5.6 Hz, 1H)], 2.81 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.71-2.62 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100MHz) : 167.03, 156.80 (d, *J* = 230.4 Hz, 1C), 143.37, 132.98 (d, *J* = 4.3 Hz, 1C), 131.86, 131.63, 128.63, 126.38 (d, *J* = 10.0 Hz, 1C), 123.60, 123.09, 112.16 (d, *J* = 9.7 Hz, 1C), 109.55, 109.29, 107.47 (d, *J* = 4.6 Hz, 1C), 103.03 (d, *J* = 23.2 Hz, 1C), 56.52, 37.54, 21.29; HRMS (ESI) (m/z) : $[M+H]^+$ Found 293.1099; Calculated 293.1090; for $C_{18}H_{14}N_2OF$.

10-Chloro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2c)

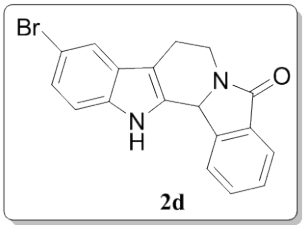


2c

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(5-chloro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (120 mg, 0.370 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (330 µL, 3.695 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (341 mg, 4.065 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (63 mg, 1.663 mmol) and CF_3COOH (382 µL, 4.988 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl

acetate : hexane (4:1) mixture as eluent to give 10-chloro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 78% yield (89 mg) as pale yellow solid. (m.p. : 242-243 °C), IR (KBr, cm^{-1}) : 3220, 2939, 1671, 1468, 1413, 725; ^{1}H-NMR (DMSO-d_6, 400MHz) : δ 11.57 (br s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.72 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.08 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.07 (s, 1H), 4.58 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.45-3.39 (m, 1H), [to assign this proton the compound was recorded in acetone-d_6, the value obtained was 3.45 (ddd, *J* = 13.2, 11.2, 5.2 Hz, 1H)], 2.82 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.71-2.63 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 167.12, 146.36, 134.92, 132.78, 131.97, 131.69, 128.75, 127.34, 123.77, 123.53, 123.21, 121.44, 117.58, 112.82, 107.24, 56.54, 37.58, 21.27; HRMS (ESI) : $[M+H]^+$ Found 309.0780; Calculated 309.0795; for $C_{18}H_{14}N_2OCl$.

10-Bromo-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2d)



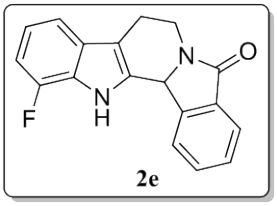
2d

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(5-bromo-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (120 mg, 0.389 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (344 µL, 3.892 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (360 mg, 4.281 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (66 mg, 1.751 mmol) and CF_3COOH (402 µL, 5.254 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 10-bromo-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 73% yield (100 mg) as pale brown solid. (m.p. : 238-239 °C); IR (KBr, cm^{-1}) : 3235, 2844, 1672, 1466, 1414, 726; ^{1}H-NMR (DMSO-d_6, 400 MHz) : δ 11.59 (br s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.72 (dd, *J* = 14.5, 7.6 Hz, 2H), 7.61 (d, *J* = 1.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.20 (dd, *J* = 8.6, 1.7 Hz,

This journal is © The Royal Society of Chemistry 2012

1H), 6.07 (s, 1H), 4.57 (dd, *J* = 13.1, 6.0 Hz, 1H), 3.40-3.38 (m, 1H), [to assign this proton the compound was recorded again in acetone-d_6, the value obtained was 3.36 (ddd, *J* = 12.8, 11.2, 4.8 Hz)], 2.83 (dd, *J* = 15.5, 4.0 Hz, 1H), 2.70-2.64 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 167.11, 143.34, 135.16, 132.60, 131.97, 131.68, 128.75, 128.02, 123.97, 123.76, 123.20, 120.59, 113.29, 111.43, 107.14, 56.50, 37.57, 21.25; HRMS (ESI) (m/z) : $[M+H]^+$ Found 353.0307; Calculated 353.0289; for $C_{18}H_{14}N_2OBr$.

12-Fluoro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one (2e)



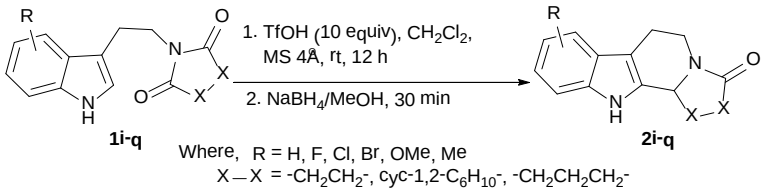
2e

A 50 mL two neck round bottom flask fitted with condenser and rubber septum was charged with 2-(2-(7-fluoro-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (125 mg, 0.405 mmol), 4Å molecular sieves (50 mg), magnetic stir bar and anhydrous dichloromethane (20 mL) under nitrogen atmosphere. To this mixture was added trifluoromethanesulfonic acid (359 µL, 4.054 mmol) with stirring at room temperature. After 12 h the reaction mixture was neutralized with solid $NaHCO_3$ (375 mg, 4.460 mmol). After 15 min., to this crude reaction mixture was added $NaBH_4$ (69 mg, 1.824 mmol) and CF_3COOH (419 µL, 5.473 mmol) under nitrogen atmosphere with vigorous stirring at room temperature. After 12 h the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) mixture as eluent to give 12-fluoro-7,8,13,13b-tetrahydro-5*H*-benzo[1,2]indolizino[8,7-*b*]indol-5-one in 71% yield (84 mg) as pale yellow solid. (m.p. : 230-231 $^{\circ}$C); IR (KBr, cm^{-1}) : 3185, 3046, 1674, 1471, 1237, 719; ^{1}H-NMR (DMSO-d_6, 400 MHz) : δ 11.81 (br s, 1H), 8.45 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 6.4, 2.0 Hz, 1H), 6.99-6.91 (m, 2H), 6.06 (s, 1H), 4.59 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.40-3.37 (m, 1H), [to assign this proton the compound was recorded again in acetone-d_6, the value obtained was 3.54 (ddd, *J* = 13.2, 11.2, 5.2 Hz, 1H)], 2.84 (dd, *J* = 15.6, 4.4 Hz, 1H), 2.74-2.65 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 167.31, 149.04 (d, *J* = 241.3 Hz, 1C), 143.50, 132.33, 132.04, 131.62, 130.16 (d, *J* = 5.9 Hz, 1C), 128.73, 124.11, 123.96, 123.11, 119.39 (d, *J* = 6.1 Hz, 1C), 114.47 (d, *J* = 3.0 Hz, 1C), 108.60 (d, *J* = 2.0 Hz, 1C), 106.63 (d, *J* = 16.2 Hz, 1C),

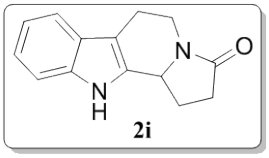
This journal is © The Royal Society of Chemistry 2012

56.66, 37.68, 21.60; HRMS (ESI) (m/z) : $[M+H]^+$ Found 293.1087; Calculated 293.1090; for $C_{18}H_{14}N_2OF$.

(F) General procedure for the synthesis of indoloindolizinones and indoloquinolizinones

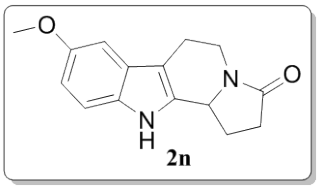


5,6,11,11b-Tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2i)[7]



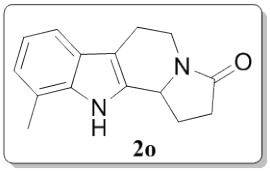
A 50 mL two neck round bottom flask was charged with 1-(2-(1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (150 mg, 0.619 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (548 µL, 6.191 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (105 mg, 2.786 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 82% yield (113 mg) as off white solid. (m.p. : 251-252 °C, lit[7] 250 °C); IR (KBr, cm^{-1}) : 3444, 3076, 2853, 1659, 1450, 1304; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.13 (br s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 4.96-4.92 (m, 1H), 4.57-4.52 (m, 1H), 3.08-3.01 (m, 1H), 2.92-2.80 (m, 2H), 2.65-2.48 (m, 3H), 1.99-1.93 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 173.33, 136.39, 133.28, 126.92, 122.37, 120.01, 118.57, 111.09, 108.45, 54.38, 37.72, 31.75, 25.81, 21.14.

8-Methoxy-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2n)[4]



A 50 mL two neck round bottom flask was charged with 1-(2-(5-methoxy-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (100 mg, 0.367 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (325 µL, 3.672 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (63 mg, 1.653 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 8-methoxy-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 80% yield (75 mg) as off white solid. (m.p. : 220-221 $^{\circ}$C); IR (KBr, cm^{-1}) : 3255, 2983, 2909, 2838, 1669, 1441, 1303, 1134; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.91 (br s, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.56-4.51 (m, 1H), 3.85 (s, 3H), 3.07-3.00 (m, 1H), 2.89-2.75 (m, 2H), 2.67-2.48 (m, 3H), 2.02-1.89 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 173.37, 154.48, 134.17, 131.42, 127.40, 112.30, 111.84, 108.33, 100.72, 56.07, 54.47, 37.75, 31.77, 25.83, 21.23.

10-Methyl-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2o)[4]



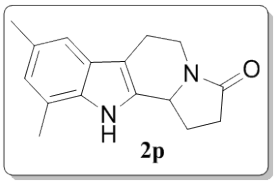
2o

A 50 mL two neck round bottom flask was charged with 1-(2-(7-methyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (125 mg, 0.488 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (432 µL, 4.877 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (83 mg, 2.195 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 10-methyl-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 70% yield (82 mg) as

This journal is © The Royal Society of Chemistry 2012

colorless solid. (m.p. : 278-279 °C); IR (KBr, cm^{-1}) : 3248, 2971, 2920, 2837, 1665, 1440, 1305; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.92 (br s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 4.98-4.94 (m, 1H), 4.53 (ddd, *J* = 13.2, 5.2, 2.0 Hz, 1H), 3.07-3.00 (m, 1H), 2.88 (ddd, *J* = 15.2, 5.2, 2.0 Hz, 1H), 2.85-2.79 (m, 1H), 2.68-2.51 (m, 3H), 2.49 (s, 3H), 2.03-1.93 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 172.43, 135.61, 134.46, 126.09, 121.68, 120.29, 118.84, 115.49, 106.39, 53.81, 36.95, 31.13, 25.74, 20.91, 16.92.

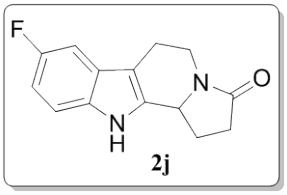
8,10-Dimethyl-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2p)



2p

A 50 mL two neck round bottom flask was charged with 1-(2-(5,7-dimethyl-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (100 mg, 0.370 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (327 µL, 3.699 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (63 mg, 1.665 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 8,10-dimethyl-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 65% yield (61 mg) as pale blue solid. (m.p. : 252-253 °C); IR (KBr, cm^{-1}) : 3264, 2907, 2719, 1665, 1431, 1368; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.83 (br s, 1H), 7.13 (s, 1H), 6.84 (s, 1H), 4.96-4.92 (m, 1H), 4.52 (ddd, *J* = 12.8, 5.5, 1.6 Hz, 1H), 3.06-2.98 (m, 1H), 2.84 (ddd, *J* = 15.6, 5.5, 1.6 Hz, 1H), 2.80-2.79 (m, 1H), 2.65-2.57 (m, 2H), 2.54-2.50 (m, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 1.98-1.91 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 173.24, 134.09, 133.02, 129.48, 126.65, 124.61, 119.81, 115.83, 108.43, 54.39, 37.66, 31.69, 25.86, 21.36, 21.15, 16.65; HRMS (ESI) : $[M+H]^+$ Found 255.1509; Calculated 255.1497; for $C_{16}H_{19}N_2O$.

8-Fluoro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2j)[4]

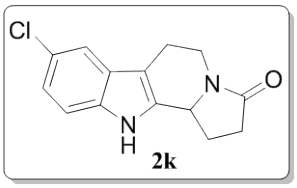


2j

This journal is © The Royal Society of Chemistry 2012

A 50 mL two neck round bottom flask was charged with 1-(2-(5-fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (100 mg, 0.384 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (340 µL, 3.842 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (65 mg, 1.729 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 8-fluoro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 65% yield (61 mg) as off white solid. (m.p. : 276-277 $^{\circ}$C); IR (KBr, cm^{-1}) : 3244, 2978, 2924, 2865, 1658, 1439, 1306, 799; ^{1}H-NMR (acetone-d_6, 400 MHz) : δ 10.3 (br s, 1H), 7.38 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.20 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.91 (td, *J* = 9.0, 2.4 Hz, 1H), 5.02-4.98 (m, 1H), 4.44 (ddd, *J* = 12.8, 5.6, 1.2 Hz, 1H), 3.08-3.00 (m, 1H), 2.81-2.70 (m, 2H), 2.69-2.64 (m, 1H), 2.58-2.49 (m, 1H), 2.35 (ddd, *J* = 16.4, 9.6, 2.4 Hz, 1H), 2.01-1.93 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 172.33, 156.82 (d, *J* = 230.0 Hz, 1C), 136.82, 132.74, 126.69 (d, *J* = 9.8 Hz, 1C), 112.00 (d, *J* = 9.7 Hz, 1C), 108.82 (d, *J* = 25.7 Hz, 1C), 106.36 (d, *J* = 4.4 Hz, 1C), 102.79 (d, *J* = 23.1 Hz, 1C), 53.60, 36.80, 31.00, 25.30, 20.69.

8-Chloro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2k)



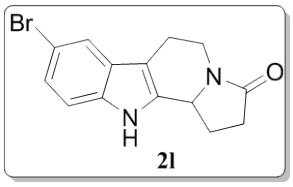
2k

A 50 mL two neck round bottom flask was charged with 1-(2-(5-chloro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (140 mg, 0.506 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (448 µL, 5.059 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (86 mg, 2.277 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was

This journal is © The Royal Society of Chemistry 2012

purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 8-chloro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 88% yield (116 mg) as pale brown solid. (m.p. : 241-242 °C); IR (KBr, cm^{-1}) : 3256, 2978, 2913, 2852, 2353, 1659, 1438, 1262, 641; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.88 (br s, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.14 (dd, *J* = 8.6, 1.6 Hz, 1H), 4.94-4.90 (m, 1H), 4.53 (ddd, *J* = 13.2, 6.0, 1.6 Hz, 1H), 3.03 (td, *J* = 11.6, 6.0 Hz, 1H), 2.84 (ddd, *J* = 15.4, 6.0, 2.0 Hz, 1H), 2.81-2.74 (m, 1H), 2.68-2.49 (m, 3H), 2.04-1.90 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 172.38, 136.57, 134.61, 127.63, 123.29, 120.88, 117.26, 112.68, 106.06, 53.55, 36.77, 31.01, 25.26, 20.60; HRMS (ESI) : $[M+H]^+$ Found 261.0784; Calculated 261.0795; for $C_{14}H_{14}N_2OCl$.

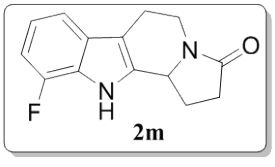
8-Bromo-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2l)[4]



2l

A 50 mL two neck round bottom flask was charged with 1-(2-(5-bromo-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (80 mg, 0.249 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (220 µL, 2.491 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (42 mg, 1.121 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 8-bromo-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 85% yield (65 mg) as off white solid. (m.p. : 260-261 °C); IR (KBr, cm^{-1}) : 3260, 2966, 2844, 1661, 1437, 1304, 793; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 8.10 (br s, 1H), 7.61 (s, 1H), 7.27 (d, *J* = 5.6 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 4.94-4.90 (m, 1H), 4.52 (dd, *J* = 13.6, 5.6 Hz, 1H), 3.02 (td, *J* = 11.2, 5.6 Hz, 1H), 2.83 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.79-2.74 (m, 1H), 2.67-2.48 (m, 3H), 1.99-1.89 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 172.32, 136.37, 134.83, 128.32, 123.40, 120.27, 113.15, 111.20, 105.96, 53.50, 36.74, 31.00, 25.25, 20.58.

10-Fluoro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (2m)

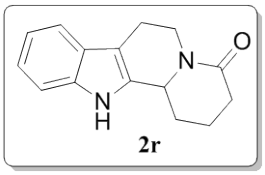


2m

This journal is © The Royal Society of Chemistry 2012

A 50 mL two neck round bottom flask was charged with 1-(2-(7-fluoro-1*H*-indol-3-yl)ethyl)pyrrolidine-2,5-dione (100 mg, 0.384 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (340 µL, 3.842 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (65 mg, 1.729 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 10-fluoro-5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one in 81% yield (76 mg) as pale brown solid. (m.p. : 219-220 $^{\circ}$C); IR (KBr, cm^{-1}) : 3221, 2924, 2855, 1672, 1437, 1352, 726; ^{1}H-NMR (acetone-d_6, 400 MHz) : δ 10.3 (br s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.85 (td, *J* = 7.8, 4.7 Hz, 1H), 6.73 (dd, *J* = 11.5, 7.8 Hz, 1H), 4.87-4.83 (m, 1H), 4.27 (ddd, *J* = 13.0, 5.8, 1.0 Hz, 1H), 2.91-2.83 (m, 1H), 2.65-2.52 (m, 3H), 2.41-2.32 (m, 1H), 2.17 (ddd, *J* = 16.3, 9.4, 2.4 Hz, 1H), 1.84-1.76 (m, 1H); ^{13}C-NMR (DMSO-d_6, 100 MHz) : 172.41, 149.13 (d, *J* = 239.1 Hz, 1C), 135.95, 130.43, 123.61 (d, *J* = 12.8 Hz, 1C), 119.07, 114.17, 107.15, 106.08 (d, *J* = 15.8 Hz, 1C), 53.61, 36.74, 31.04, 25.48, 20.89; HRMS (ESI) (m/z) : $[M+H]^+$ Found 245.1100; Calculated 245.1090; for $C_{14}H_{14}N_2OF$.

1,2,3,6,7,12b-Hexahydroindolo[2,3-*a*]quinolizin-4(12*H*)-one (2r)[8]



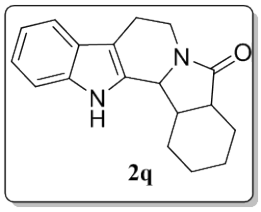
2r

A 50 mL two neck round bottom flask was charged with 1-(2-(1*H*-indol-3-yl)ethyl)piperdine-2,6-dione (150 mg, 0.585 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (518 µL, 5.853 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (100 mg, 2.634 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column

This journal is © The Royal Society of Chemistry 2012

chromatography using ethyl acetate : hexane (4:1) as eluent to give1,2,3,6,7,12b-hexahydroindolo[2,3-*a*]quinolizin-4(12*H*)-one in 87% yield (122 mg) as off white solid. (m.p. : 239-240 °C, lit.[8] 240-241 °C); IR (KBr, cm^{-1}) : 3265, 3052, 1596, 1434, 1262; ^{1}H-NMR (DMSO-d_6, 400 MHz) : δ 10.92 (br s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 4.91 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.78 (dd, *J* = 10.4, 4.4 Hz, 1H), 2.78 (td, *J* = 12.0, 4.0 Hz, 1H), 2.71-2.54 (m, 3H), 2.39-2.22 (m, 2H), 1.82-1.75 (m, 2H), 1.67-1.57 (m,1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 169.19, 136.23, 133.32, 126.93, 122.18, 119.87, 118.43, 110.93, 109.67, 54.39, 40.15, 32.45, 29.10, 21.01, 19.42.

2,3,4,4a,7,8,13b,13c-Octahydro-1*H*-benzo[1,2]indolizino[8,7-*b*]indol-5(13*H*)-one (2q)



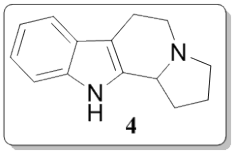
2q

A 50 mL two neck round bottom flask was charged with 2-(2-(1*H*-indol-3-yl)ethyl)hexahydro-1*H*-isoindole-1,3(2*H*)-dione (80 mg, 0.270 mmol), 4Å molecular sieves (50 mg), anhydrous CH_2Cl_2 (20 mL), and a stir bar. The flask was capped with a rubber septum and maintained in nitrogen atmosphere. Trifluoromethanesulfonic acid (239 µL, 2.699 mmol) was added and stirred at room temperature for 12 h. To this reaction mixture was added $NaBH_4$ (46 mg, 1.215 mmol), methanol (3 mL) and stirred for 0.5 h under nitrogen atmosphere. Then the reaction mixture was quenched with aqueous $NaHCO_3$. Organic layer was separated and aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude mixture was purified through neutral alumina column chromatography using ethyl acetate : hexane (4:1) as eluent to give 2,3,4,4a,7,8,13b,13c-octahydro-1*H*-benzo[1,2]indolizino[8,7-*b*]indol-5(13*H*)-one in 62% yield (47 mg) as pale yellow solid. (m.p. : 248-249 °C); IR (KBr, cm^{-1}) : 3293, 2929, 2851, 1668, 1430, 1250; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.94 (br s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 4.8 Hz, 1H), 4.54 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.98 (td, *J* = 11.6, 4.4 Hz, 1H), 2.88 (dd, *J* = 15.2, 4.4 Hz, 1H), 2.84-2.80 (m, 1H), 2.76 (t, *J* = 5.6 Hz, 1H), 2.68-2.64 (m, 1H), 2.32 (d, *J* = 14.0 Hz, 1H), 1.56-1.46 (m, 3H), 1.28-1.24 (m, 1H), 1.12-1.01 (m, 2H), 0.83-0.74 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 173.87, 136.53, 130.20, 127.02, 122.27, 119.93, 118.46, 111.02, 110.43,

56.47, 43.13, 38.25, 37.45, 29.84, 23.85, 23.19, 22.77, 21.25; HRMS (ESI) (m/z) : $[M+H]^+$ Found 281.1652; Calculated 281.1654; for $C_{18}H_{21}N_2O$.

(G) Synthesis of (±)-harmicine

2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-b]indole (4)[9]

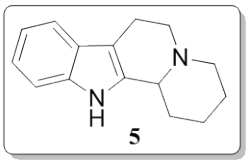


4

Lithium aluminium hydride (252 mg, 6.629 mmol) was weighed into a pre-dried two neck round bottom flask fitted with a condenser under nitrogen atmosphere. 5,6,11,11b-tetrahydro-1*H*-indolizino[8,7-*b*]indol-3(2*H*)-one (100 mg, 0.442 mmol) was added to the reaction flask under nitrogen atmosphere. Anhydrous tetrahydrofuran was added to the reaction mixture at 0 °C and the reaction mixture was stirred at room temperature for 24 h. After checking TLC, *tert*-butyl methyl ether (25.0 mL) was added and the reaction was quenched by careful addition of saturated aqueous sodium potassium tartrate solution. The mixture was stirred for 1 h before the addition of anhydrous Na_2SO_4 prior to filtration through celite pad. The filtrate was evaporated under reduced pressure to give of 2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-b]indole, 73 mg (78%), as colorless solid. (m.p. : 171-172 °C, lit.[9] 174-175 °C); IR (KBr, cm^{-1}) : 3433, 3054, 2940, 2842, 1453, 1305, 743; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.85 (br s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 7.2, 1.0 Hz, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 4.26-4.23 (m, 1H), 3.33 (ddd, *J* = 13.2, 5.6, 2.4 Hz, 1H), 3.12-3.05 (m, 1H), 2.99-2.87 (m, 3H), 2.69-2.64 (m, 1H), 2.31-2.28 (m, 1H), 1.96-1.83 (m, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 136.10, 135.57, 127.52, 121.57, 119.55, 118.27, 110.84, 108.03, 57.09, 49.41, 46.10, 29.55, 23.58, 17.95.

Synthesis of (±)-10-desbromoarborescidine-A

1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-a]quinolizine (5)[10]



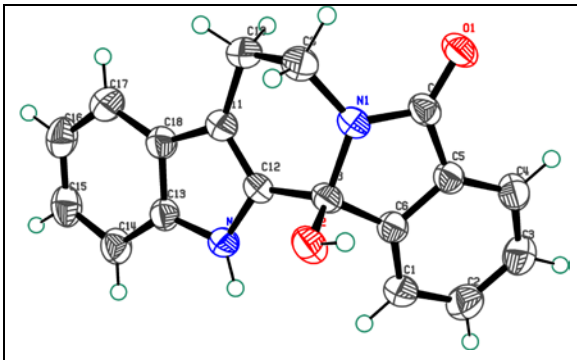
5

Lithium aluminium hydride (710 mg, 18.727 mmol) was weighed into a pre-dried two neck round bottom flask fitted with a condenser under nitrogen atmosphere. 1,2,3,6,7,12b-hexahydroindolo[2,3-*a*]quinolizin-4(12*H*)-one (300 mg, 1.248 mmol) was added to the reaction flask under nitrogen atmosphere. Anhydrous tetrahydrofuran was added to the reaction mixture at 0 °C and the reaction mixture was heated to reflux for 24 h. After checking TLC, tert-butyl methyl ether (25.0 mL) was added and the reaction was quenched by careful addition of

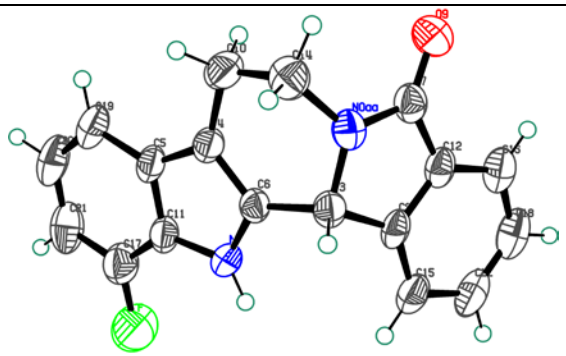
This journal is © The Royal Society of Chemistry 2012

saturated aqueous sodium potassium tartrate solution. The mixture was stirred for 1 h before the addition of anhydrous Na_2SO_4 prior to filtration through celite pad. The filtrate was evaporated under reduced pressure to give 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-a]quinolizine, 178 mg (63%), as colorless solid. (m.p. : 144-145 °C, lit.[10] 146-148 °C); IR (KBr, cm^{-1}) : 3191, 2922, 2848, 1448, 1321, 735; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ 7.72 (br s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.15-7.07 (m, 2H), 3.24 (d, *J* = 11.0 Hz, 1H), 3.10-2.98 (m, 3H), 2.75-2.59 (m, 2H), 2.39 (td, *J* = 11.0, 4.0 Hz, 1H), 2.07 (dd, *J* = 12.0, 2.4 Hz, 1H), 1.91 (dt, *J* = 12.0, 3.2 Hz, 1H), 1.80-1.71 (m, 2H), 1.60 (ddd, *J* = 24.0, 12.0, 3.2 Hz, 1H), 1.55-1.45 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 136.09, 135.27, 127.64, 121.37, 119.47, 118.23, 110.83, 108.26, 60.37, 55.89, 53.69, 30.13, 25.88, 24.46, 21.73.

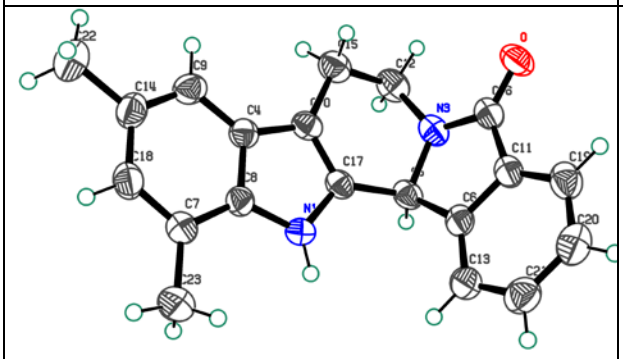
(H) Crystal structures



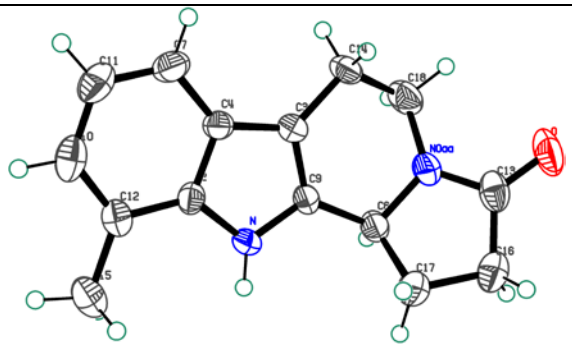
2, CCDC 876038



2e, CCDC 876034

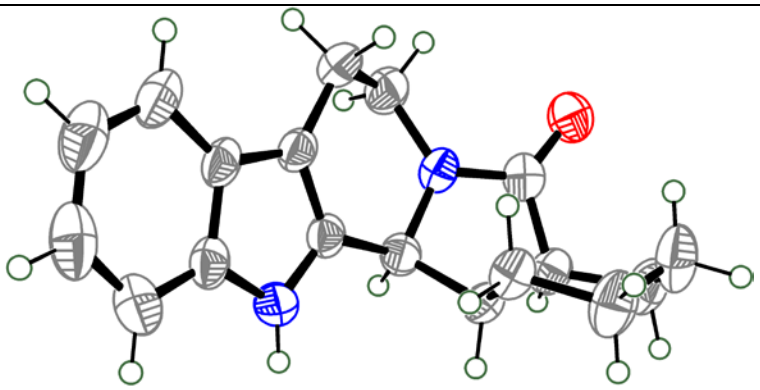


2h, CCDC 876035



2o, CCDC 876036

This journal is © The Royal Society of Chemistry 2012



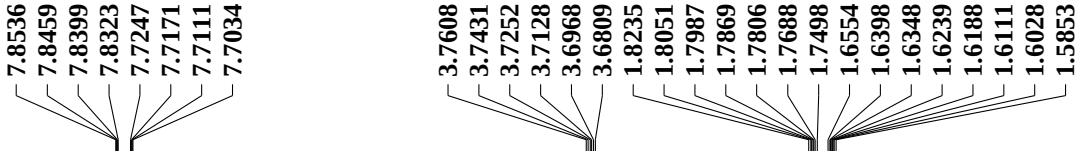
2q, 876037

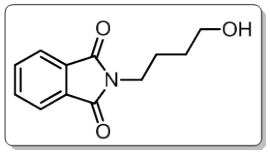
(I) References

1. J. C. Eriks, H. Van der Goot, G. J. Sterk, H. Timmerman, *J. Med.Chem.*, 1992, **35**, 3239.
2. Y. Liu, S. Luo, X. Fu, F. Fang, Z. Zhuang, W. Xiong, X. Jia, H. Zhai, *Org. Lett.*, 2006, **8**, 115.
3. B. Hoefgen, M. Decker, P. Mohr, A. M. Schramm, S. A. F. Rostom, H. E. Subbagh, P. M. Schweikert, D. R. Rudolf, M. U. Kassack, J. Lehmann, *J. Med. Chem.*, 2006, **49**, 760.
4. I. T. Raheem, P. S. Thiara, E. A. Peterson, E. N. Jacobsen, *J. Am. Chem. Soc.*, 2007, **129**, 13404.
5. A. M. Schmidt, P. Eilbracht, *Org. Biomol. Chem.*, 2005, **3**, 2333.
6. C. Hu, H. Qin, Y. Cui, Y. Jia, *Tetrahedron.* 2009, **65**, 9075.
7. W. A. da Silva, M. T. Rodrigues. Jr, N. Shankaraiah, R. B. Ferreira, C. K. Z. Andrade, R. A. Pilli, L. S. Santos, *Org. Lett.*, 2009, **11**, 3238.
8. E. Airiau, N. Girard, A. Mann, J. Salvadori, M. Taddei, *Org. Lett.*, 2009, **11**, 5314.
9. (a) W.-H. Chiou, G.-H. Lin, C.-C. Hsu, S. J. Chaterpaul, I. Ojima, *Org. Lett.*, 2009, **11**, 2659. (b) T. S. Kam, K. M. Sim, *Phytochemistry*. 1998, **47**, 145.
10. (a) S. M. Allin, C. I. Thomas, J. E. Allard, K. Doyle, M. R. J. Elsegood, *Eur. J. Org. Chem.*, 2005, 4179. (b) M. Chbani, M. Pais, *J. Nat. Prod.*, 1993, **56**, 99.

This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} crr 1



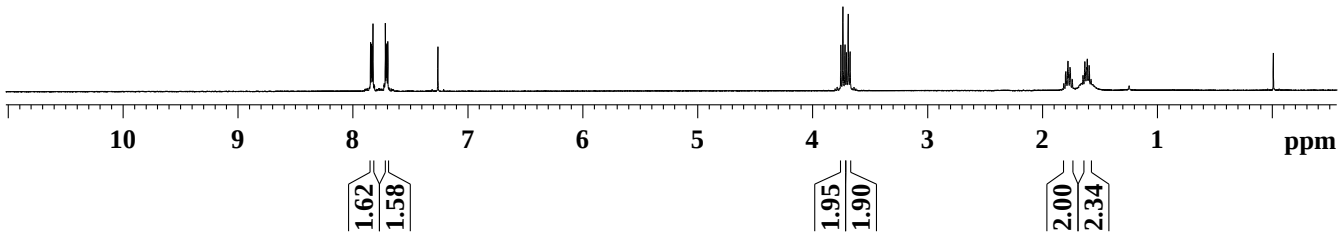


Current Data Parameters
NAME SMR-I-53-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100321
Time 18.14
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 362
DW 60.800 usec
DE 6.00 usec
TE 296.7 K
D1 2.00000000 sec
TD0 1

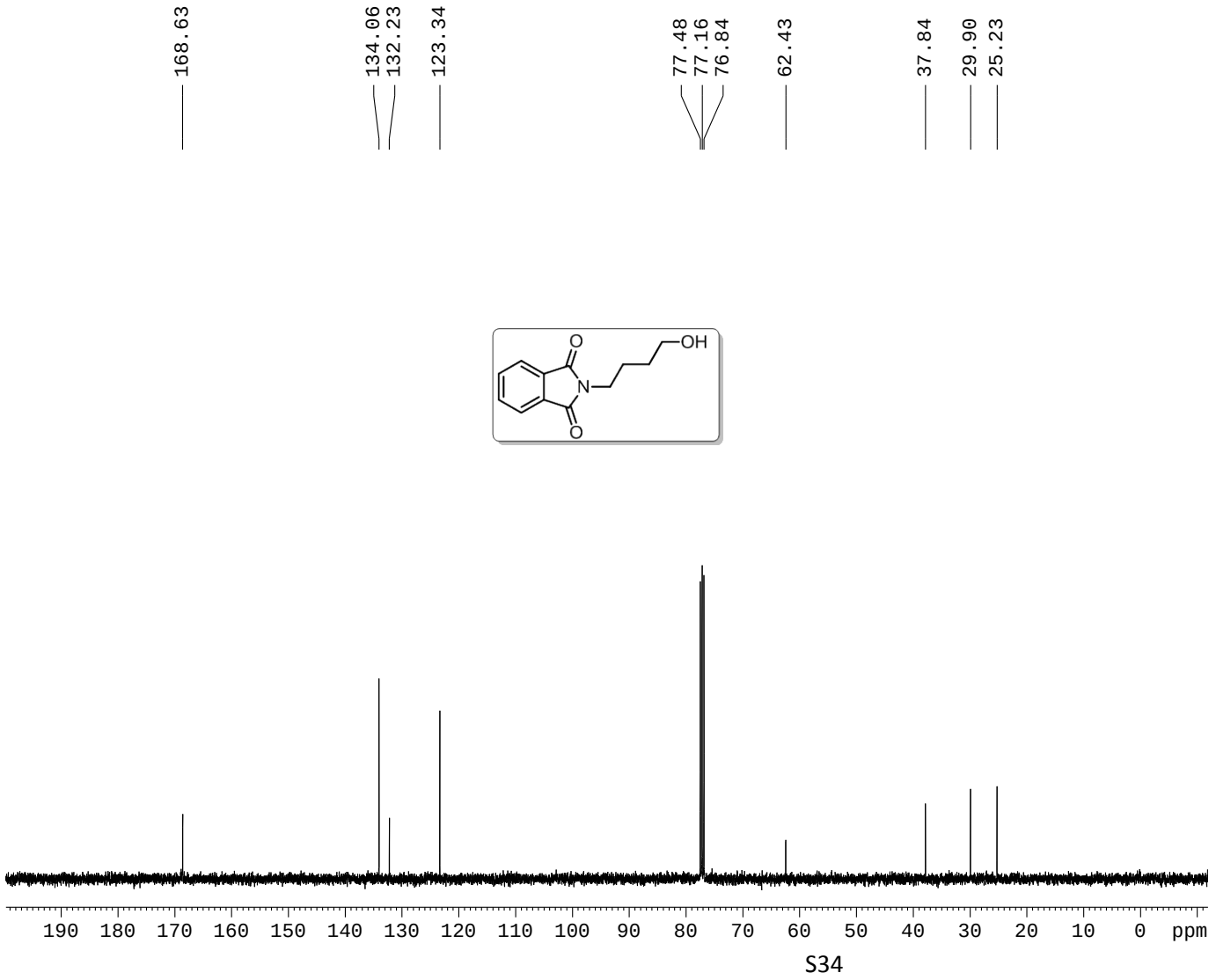
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -0.90 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300045 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



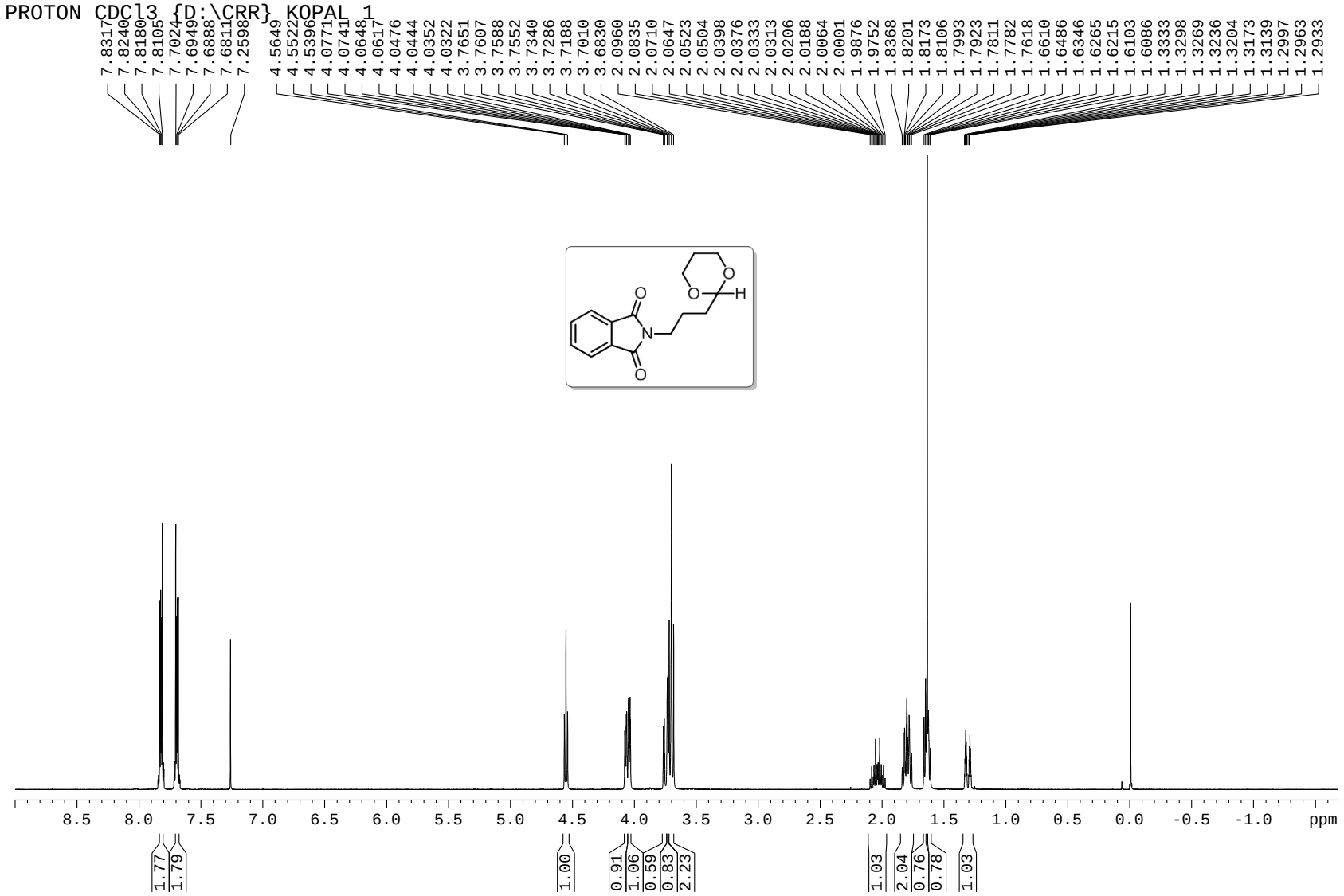
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



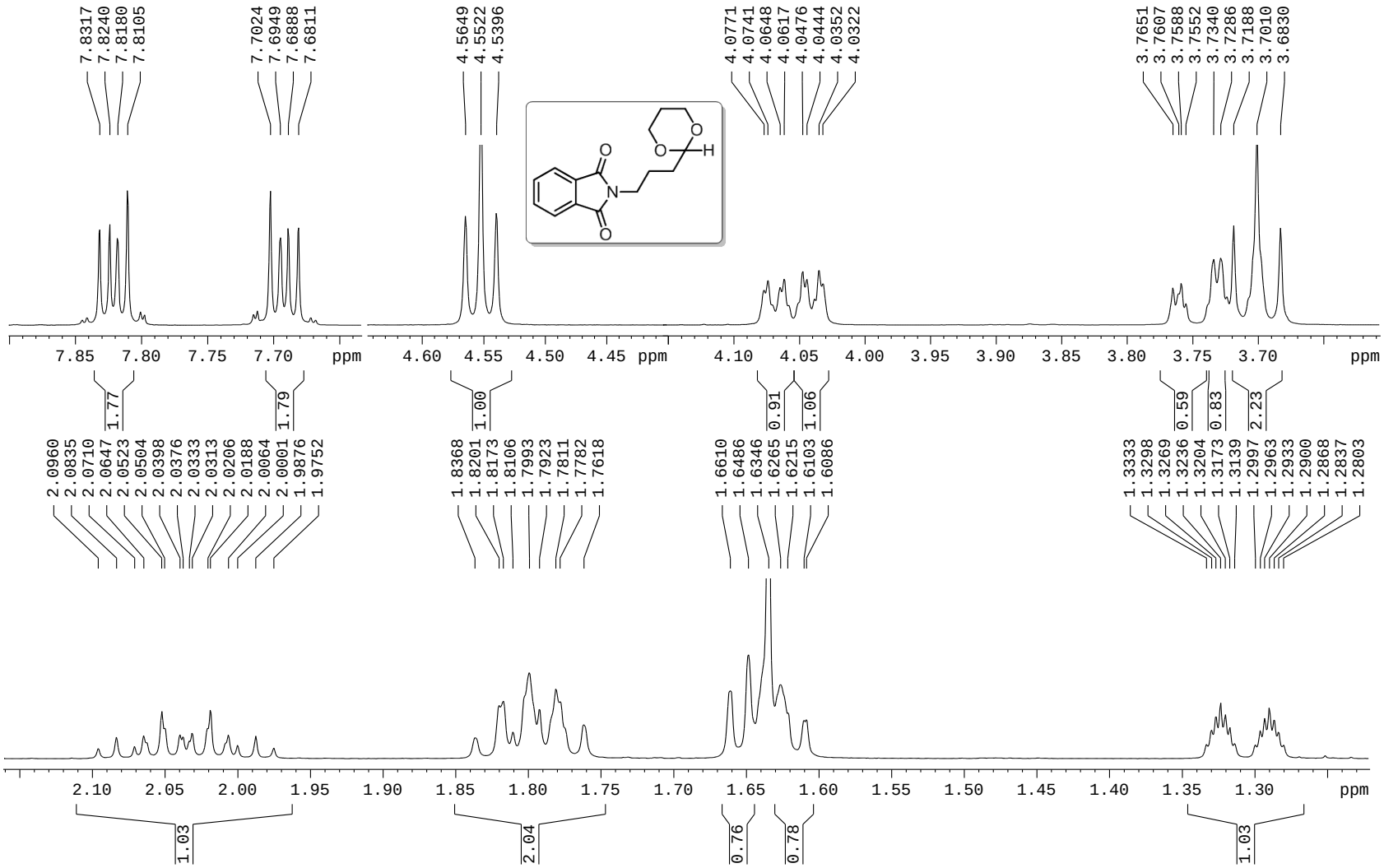

```
Current Data Parameters
NAME           SMR-PHOH
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20101102
Time              13.15
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   87
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   57
DW                20.800 usec
DE                 6.00 usec
TE                298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127546 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



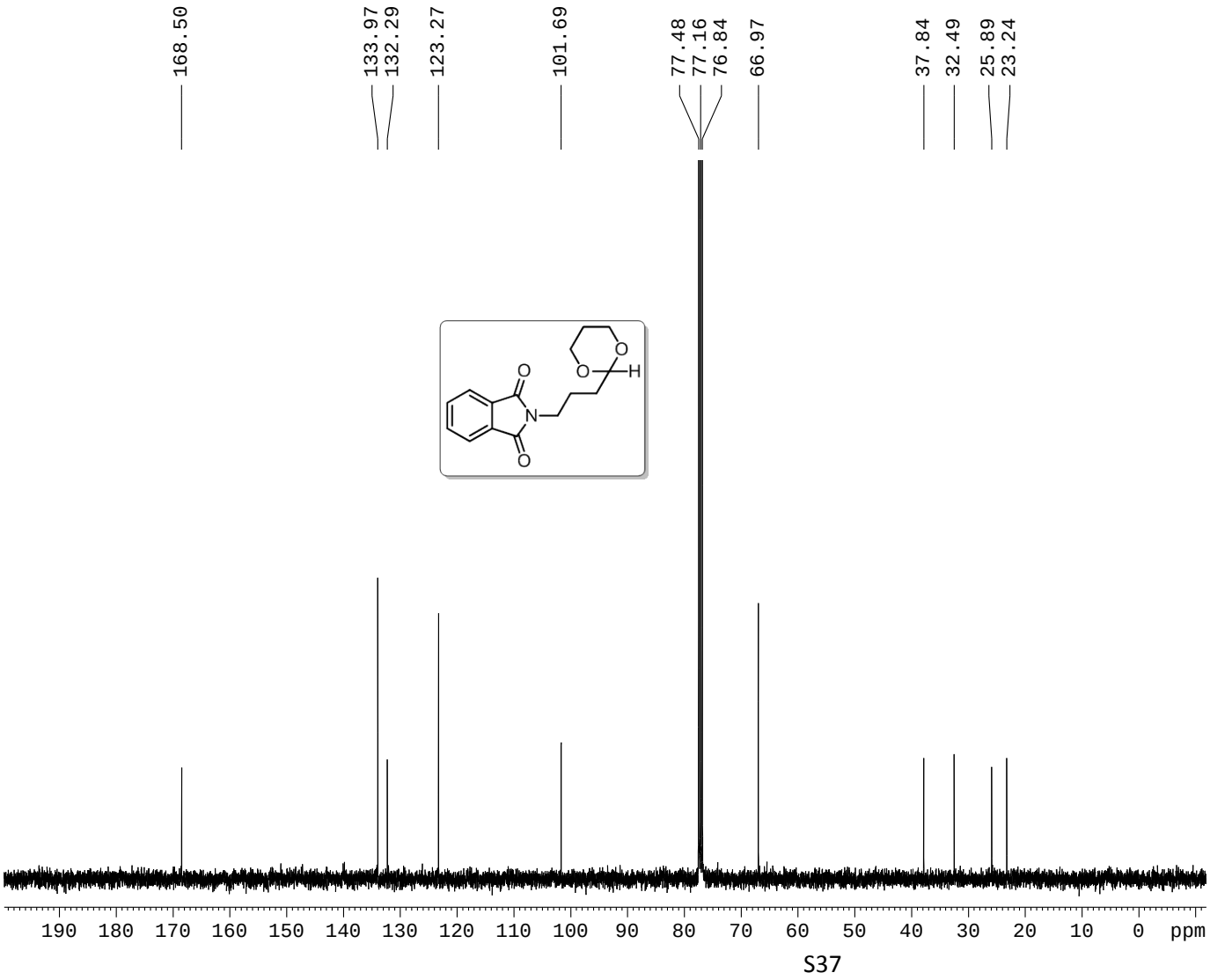
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



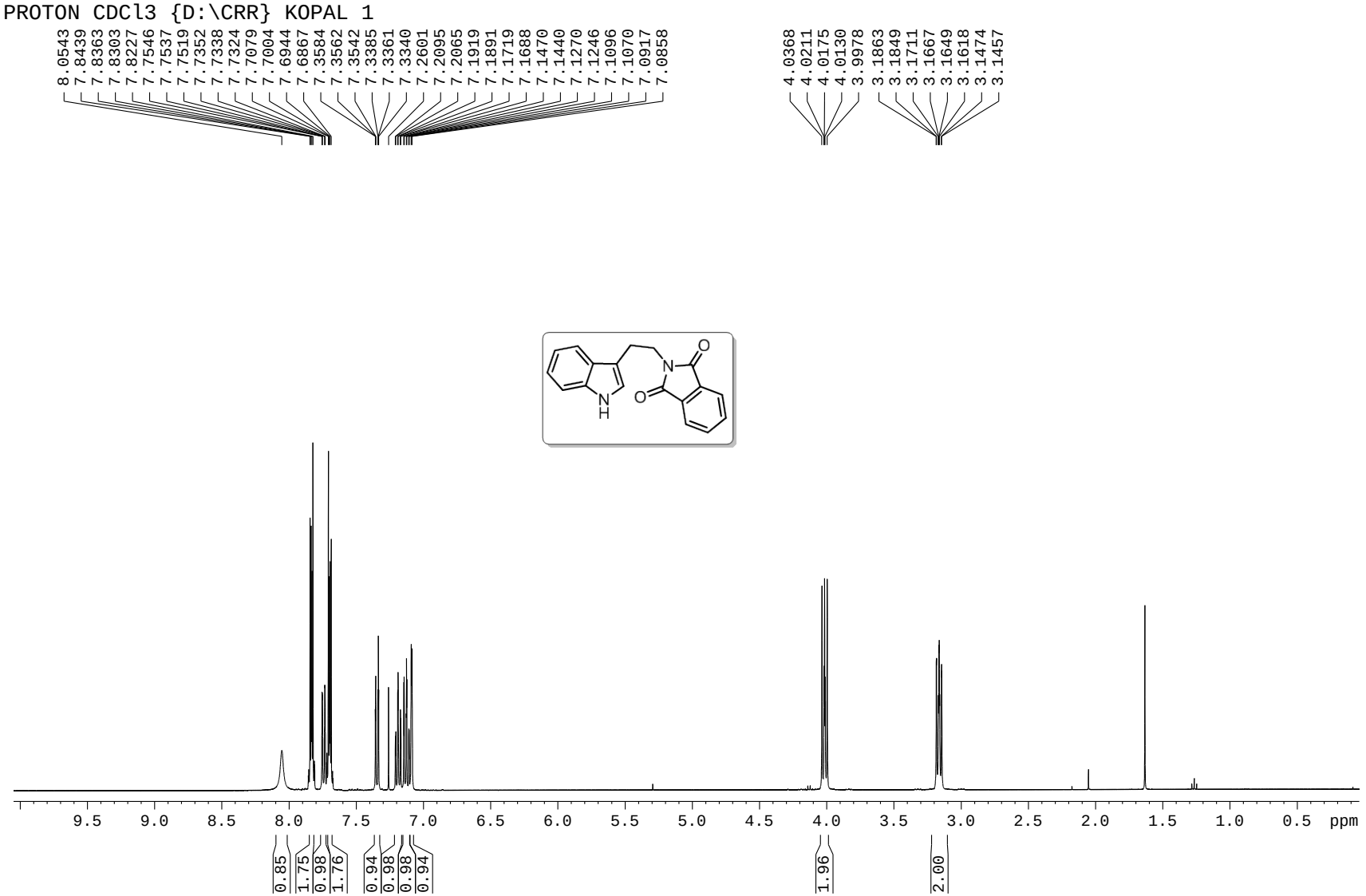
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



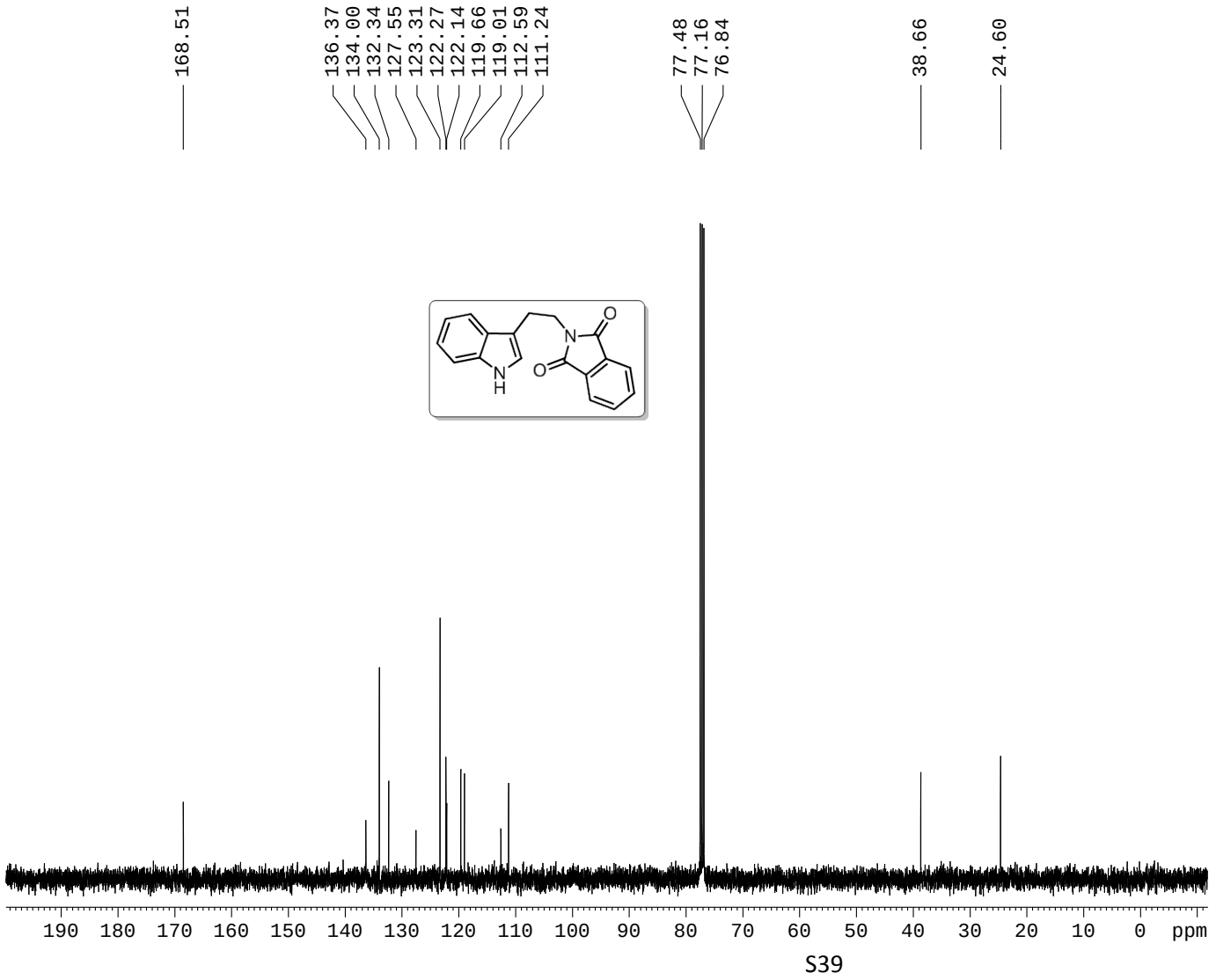

```
Current Data Parameters
NAME                  SMR-PR
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20120307
Time                   11.29
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        256
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                       50.8
DW                     20.800 usec
DE                      6.00 usec
TE                     295.5 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -0.60 dB
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                   90.00 usec
PL12                    15.60 dB
PL13                    15.60 dB
PL2                     -0.90 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF               100.6127546 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

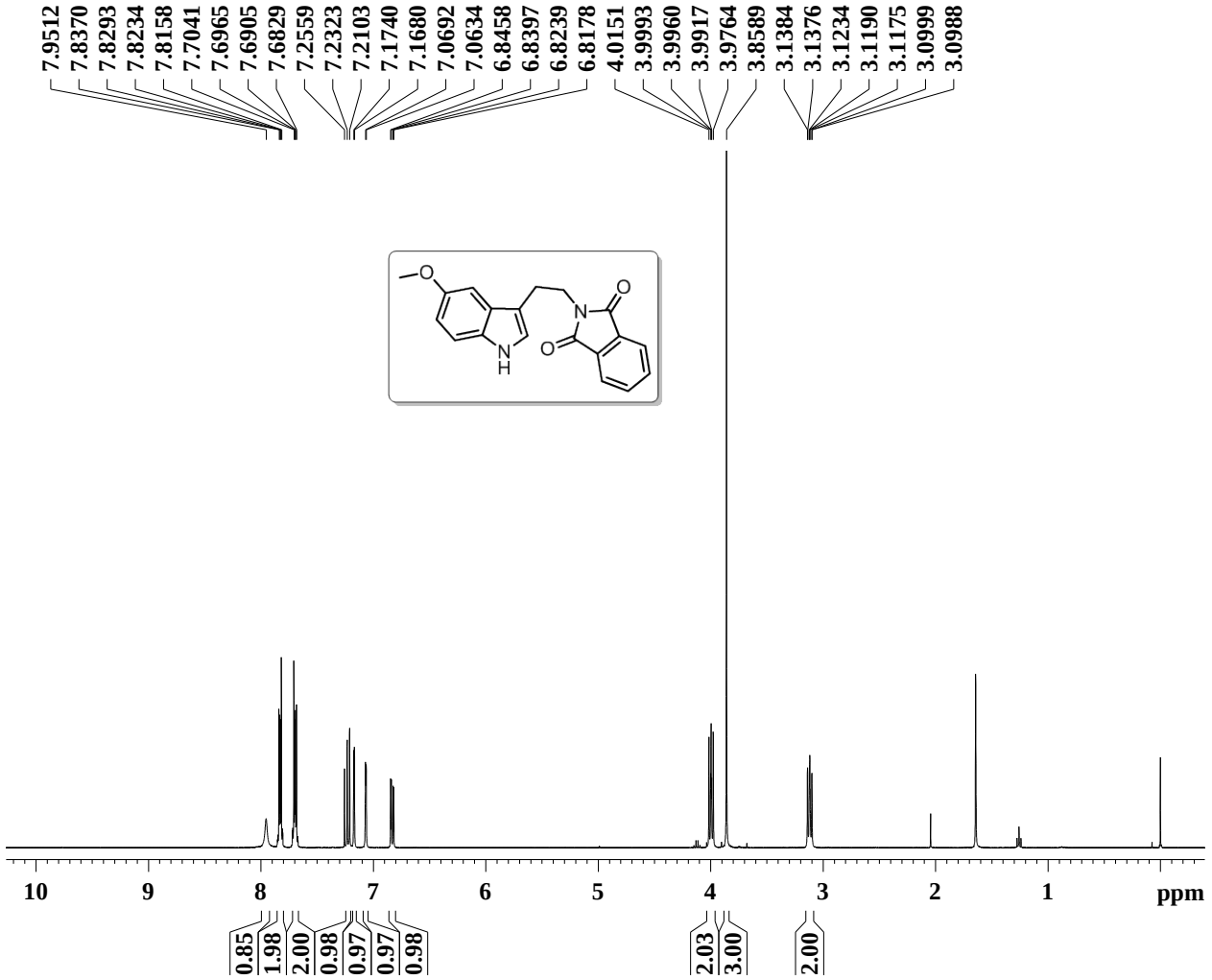
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME            SMR-PHIM
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20101102
Time               13.29
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   106
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   912
DW                20.800 usec
DE                 6.00 usec
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127547 MHz
WDW                  EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

This journal is © The Royal Society of Chemistry 2012

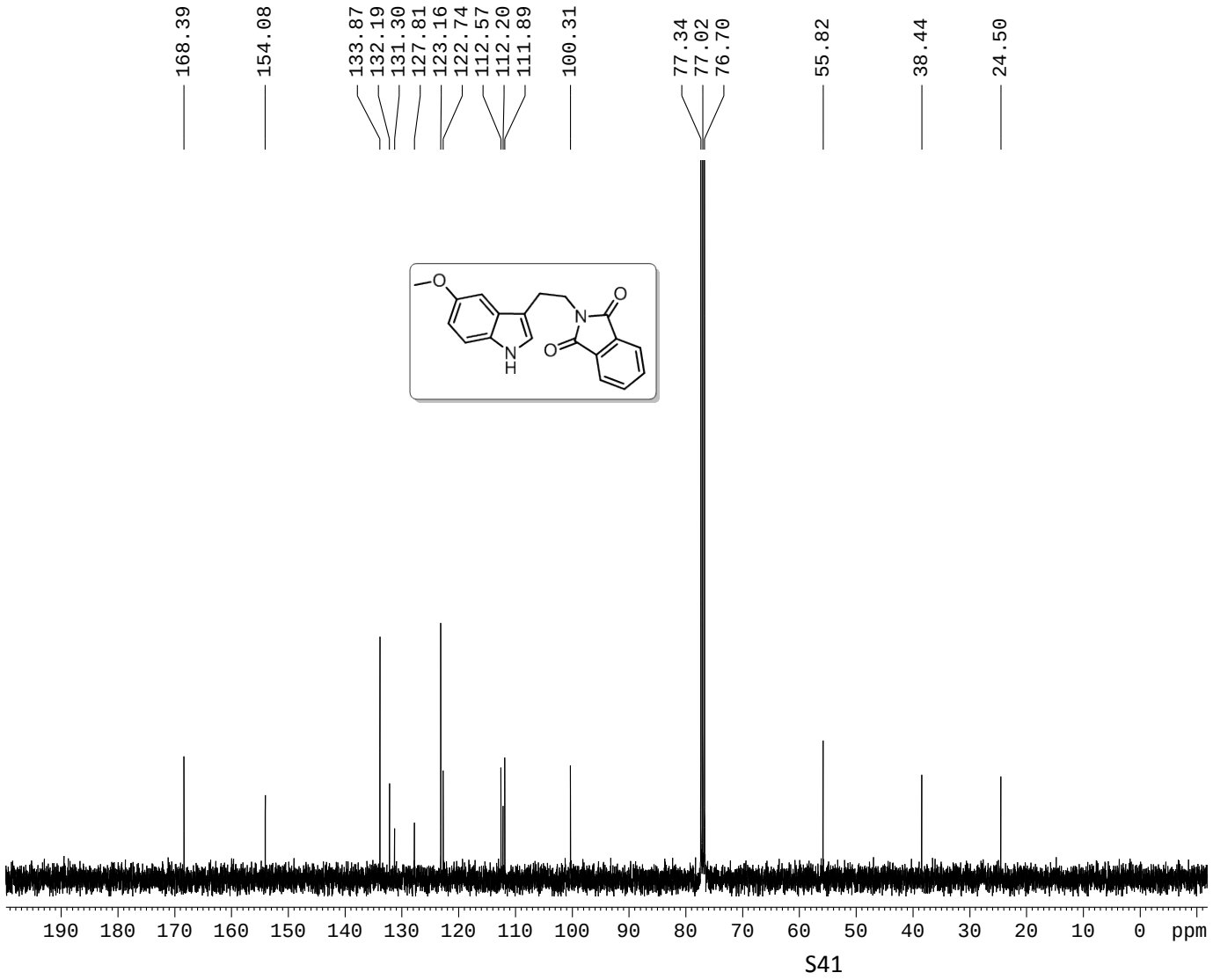
PROTON CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME         SMR-1-156-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20101229
Time               12.48
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    12
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   228
DW                60.800 usec
DE                 6.00 usec
TE                297.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.00 usec
PL1                -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300056 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

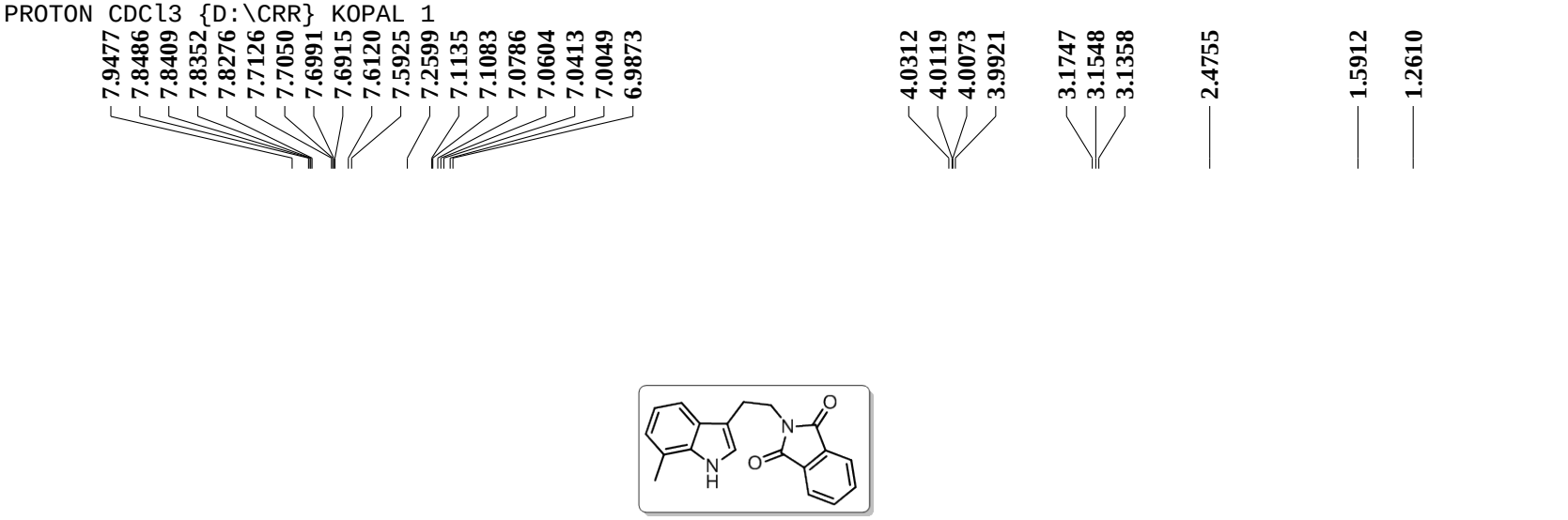
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



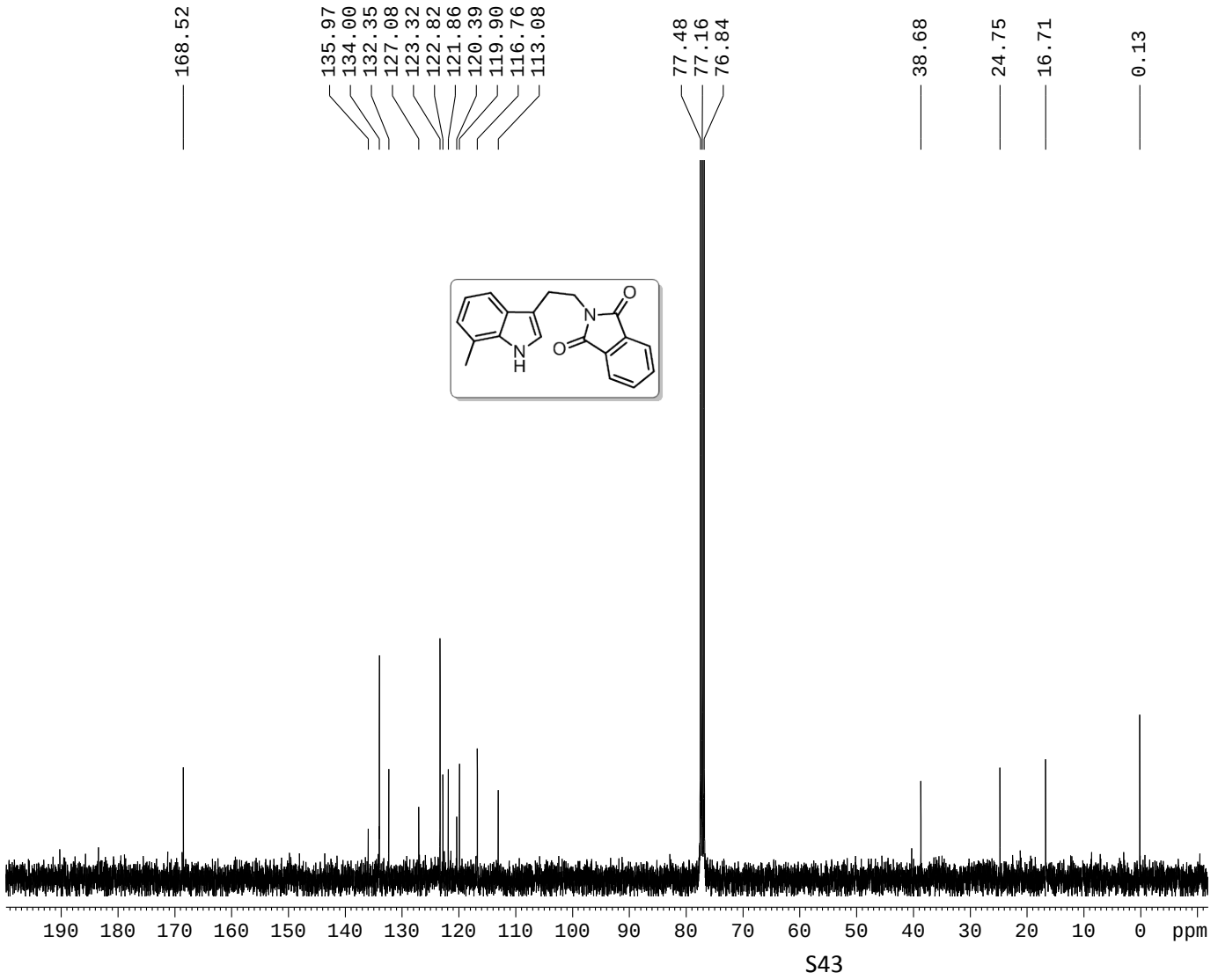

```
Current Data Parameters
NAME        SMR-1-156-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20101229
Time              12.53
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   63
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1440
DW               20.800 usec
DE                6.00 usec
TE                297.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



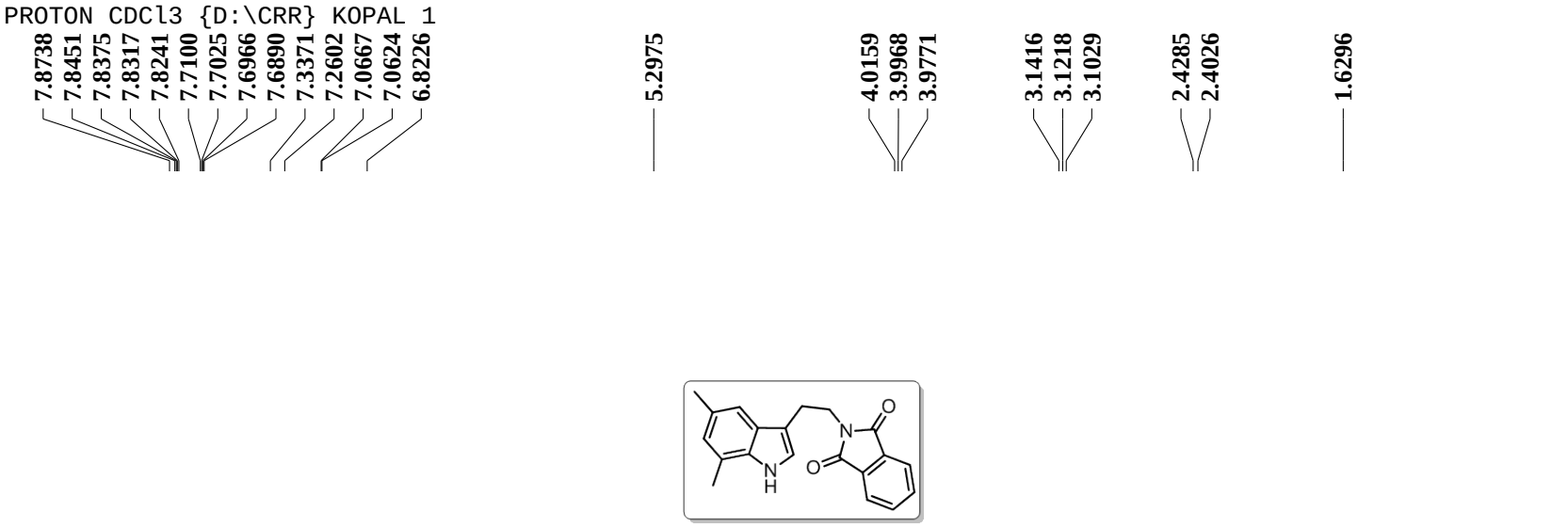
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



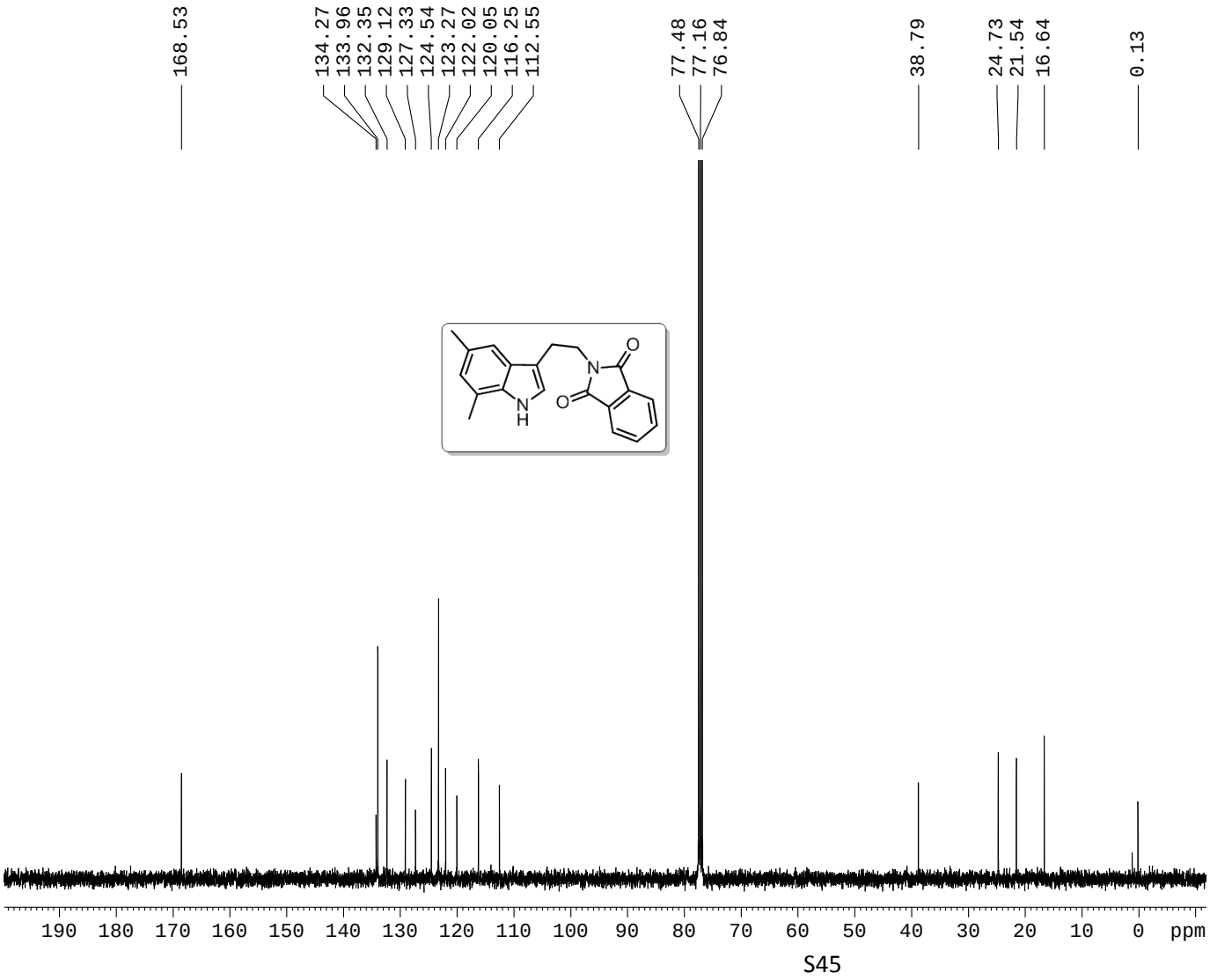

```
Current Data Parameters
NAME        SMR-I-10-Me
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20110621
Time              11.10
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  812
DW               20.800 usec
DE                6.00 usec
TE                296.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127540 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



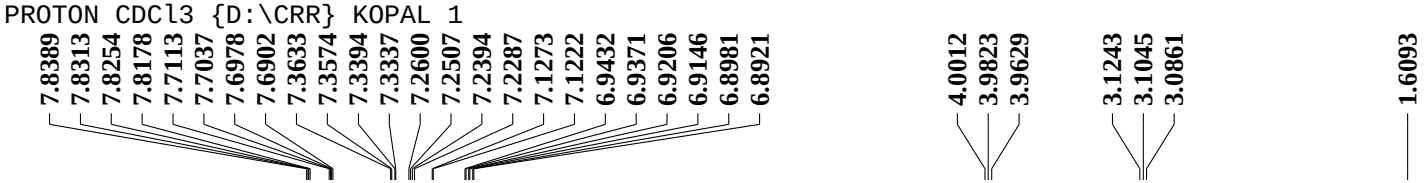
This journal is © The Royal Society of Chemistry 2012

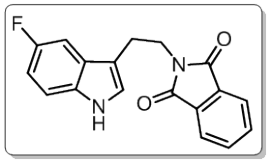
C13CPD CDCl3 {D:\CRR} KOPAL 1

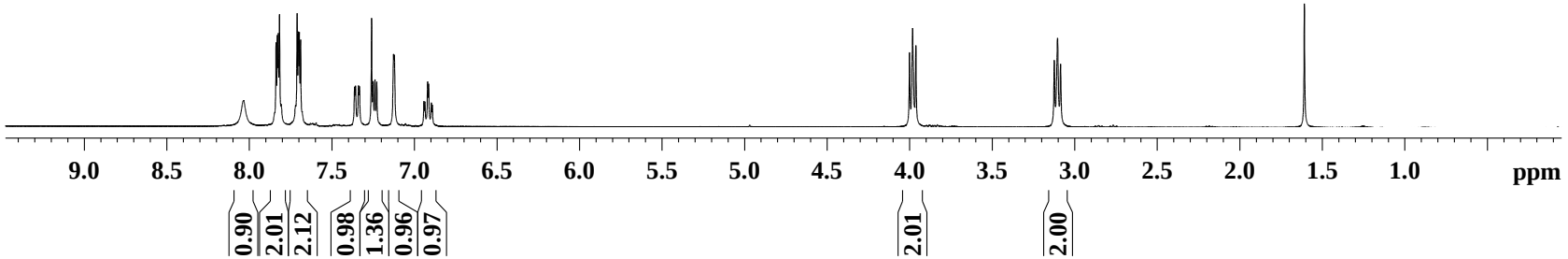



```
Current Data Parameters
NAME       SMR-I-100-Di
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20110621
Time              11.30
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 45.2
DW                20.800 usec
DE                 6.00 usec
TE                296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127561 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012

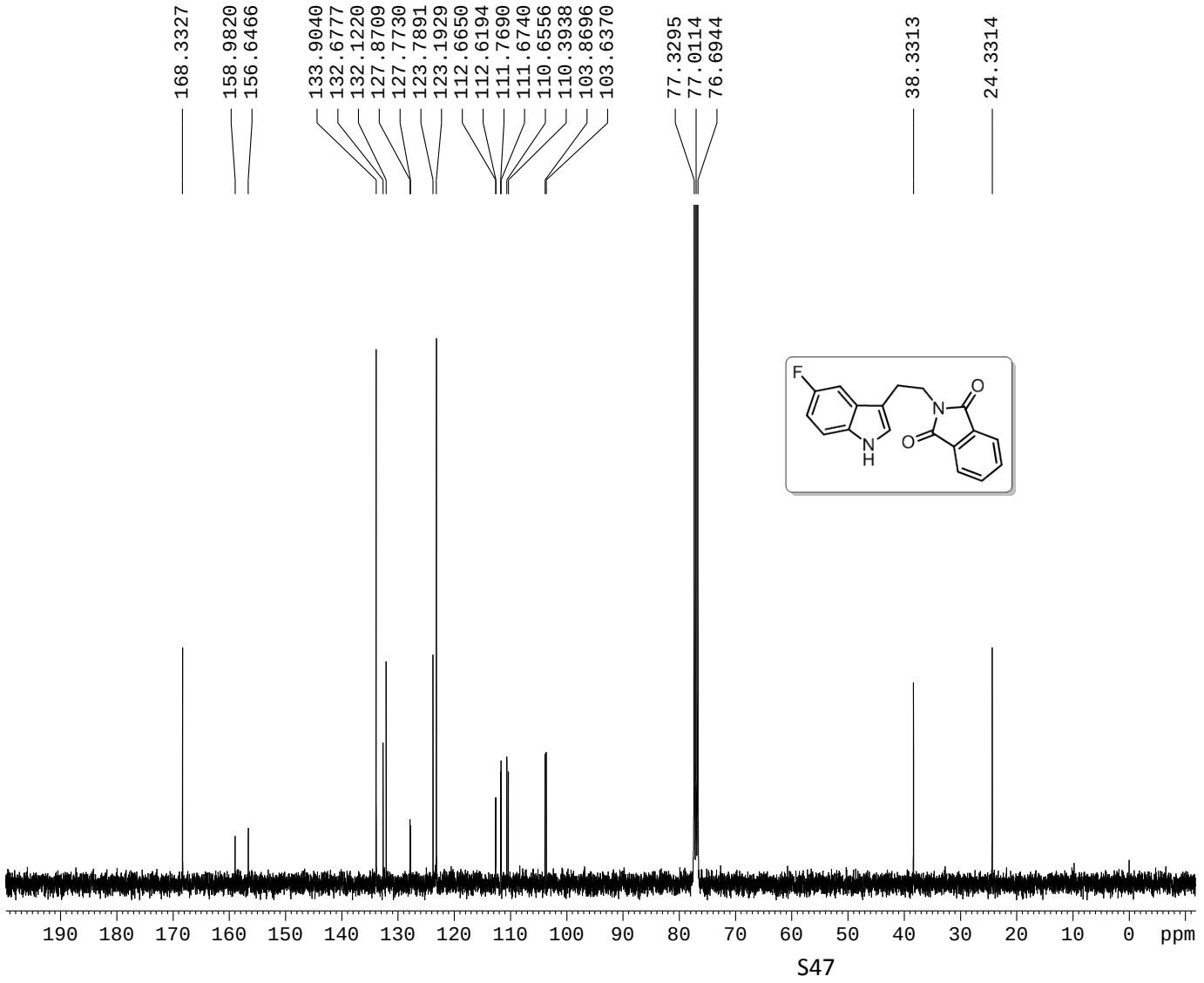






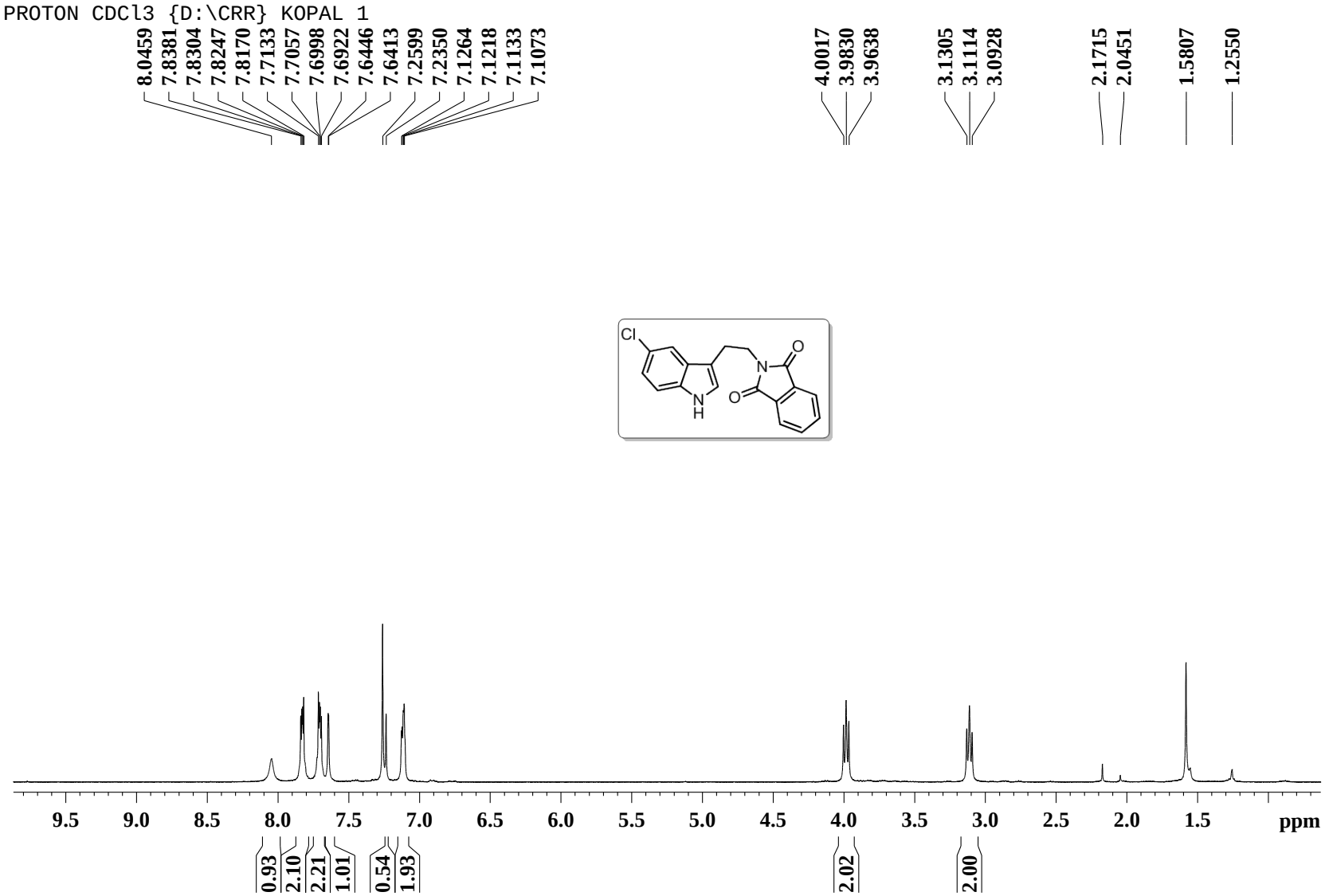
Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



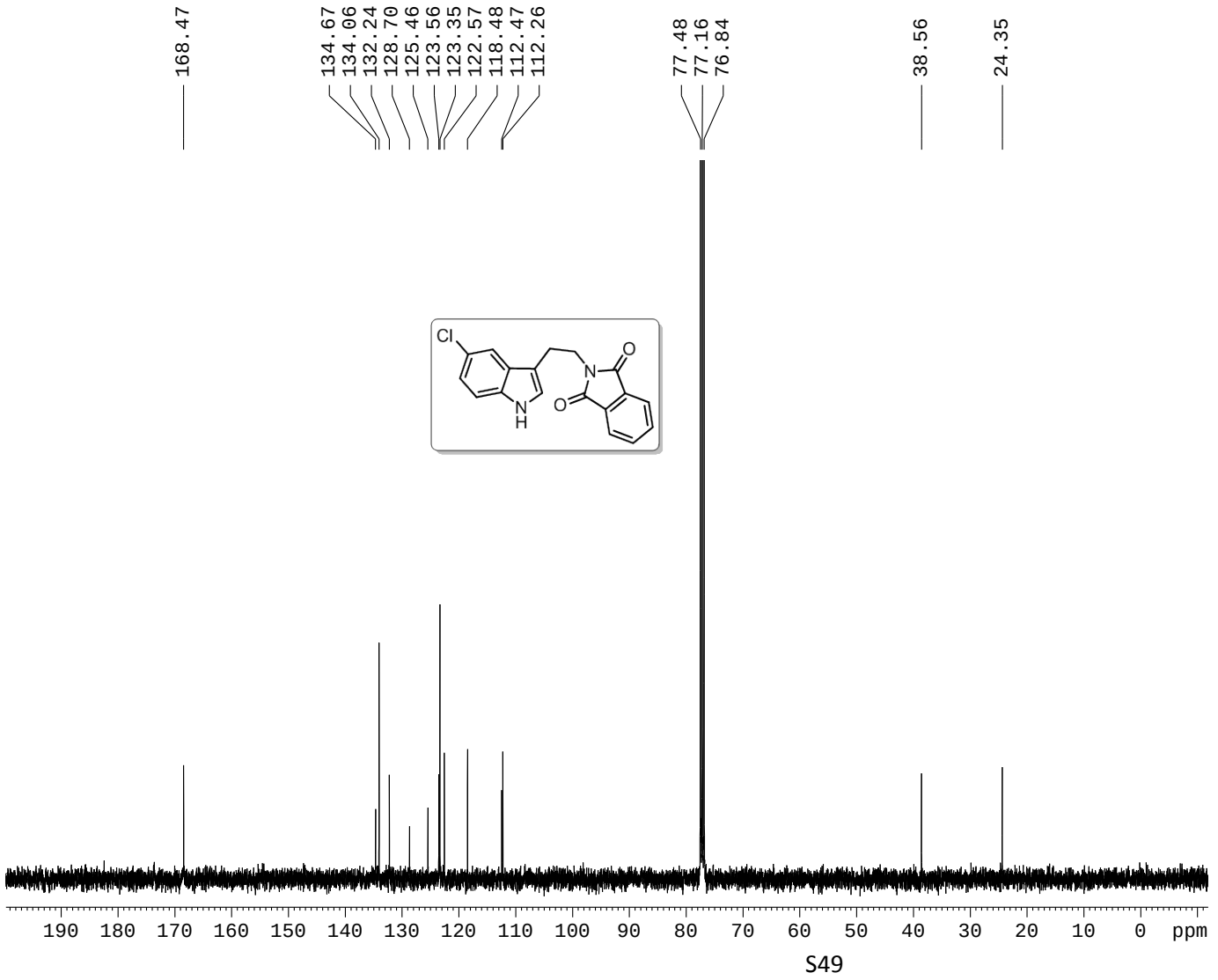

```
Current Data Parameters
NAME          SMR-Con-A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120130
Time              18.32
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                297.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



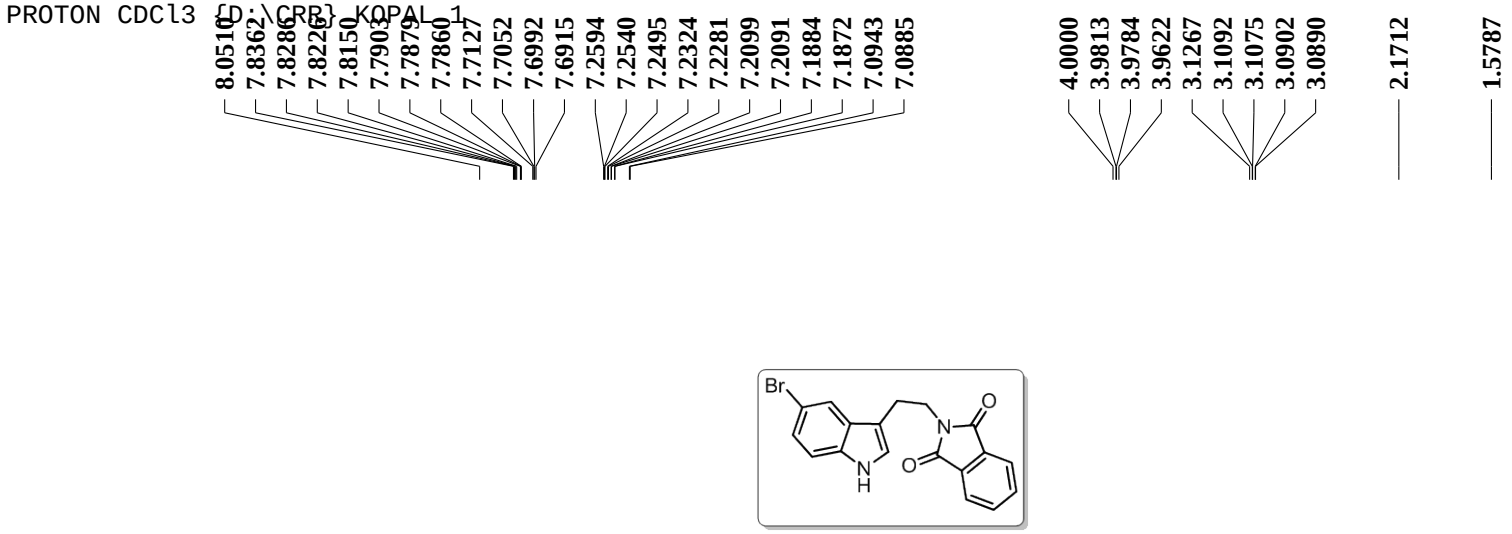
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



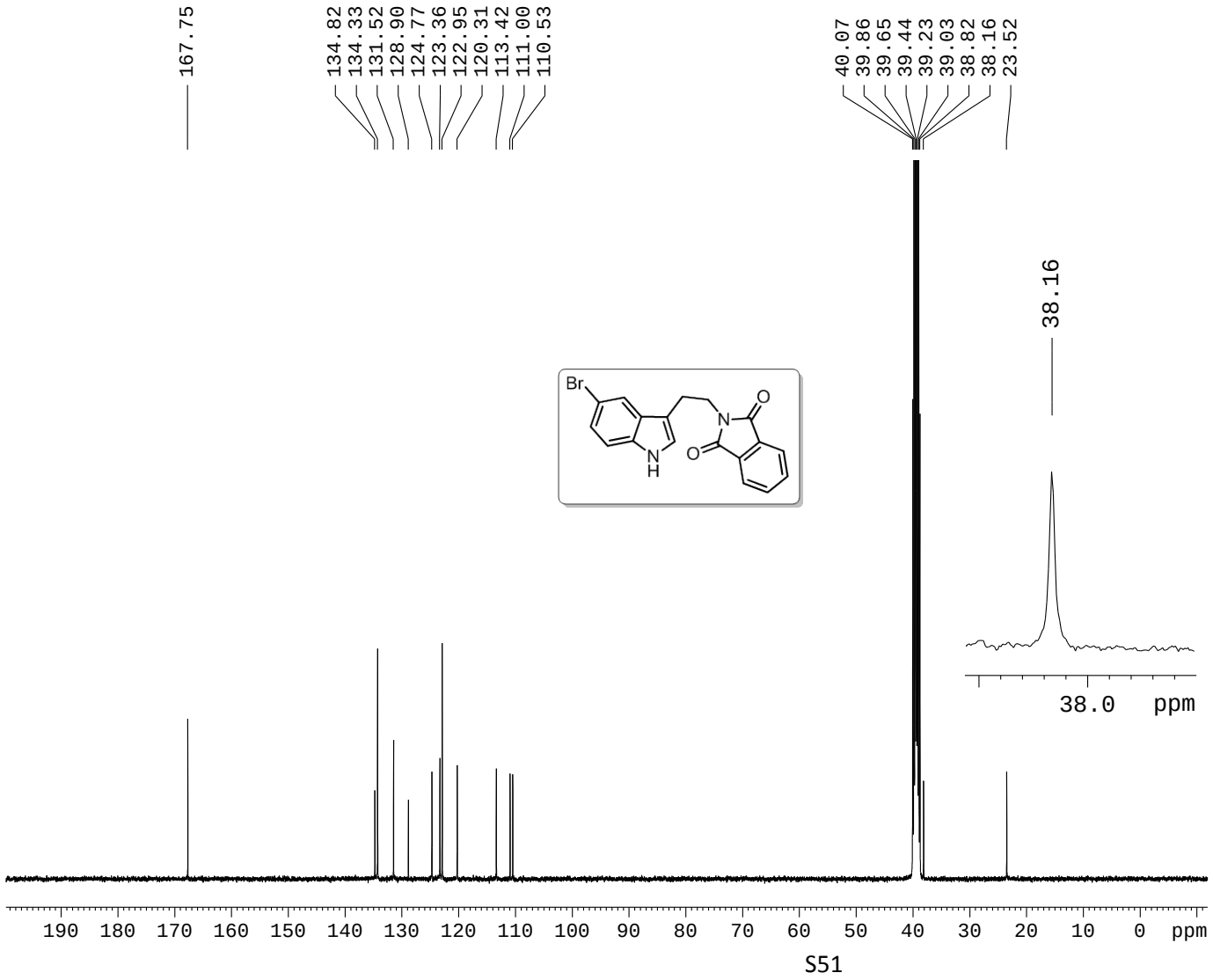

```
Current Data Parameters
NAME          SMR-CHLORO
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20111208
Time               11.28
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1290
DW                20.800 usec
DE                 6.00 usec
TE                298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127543 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

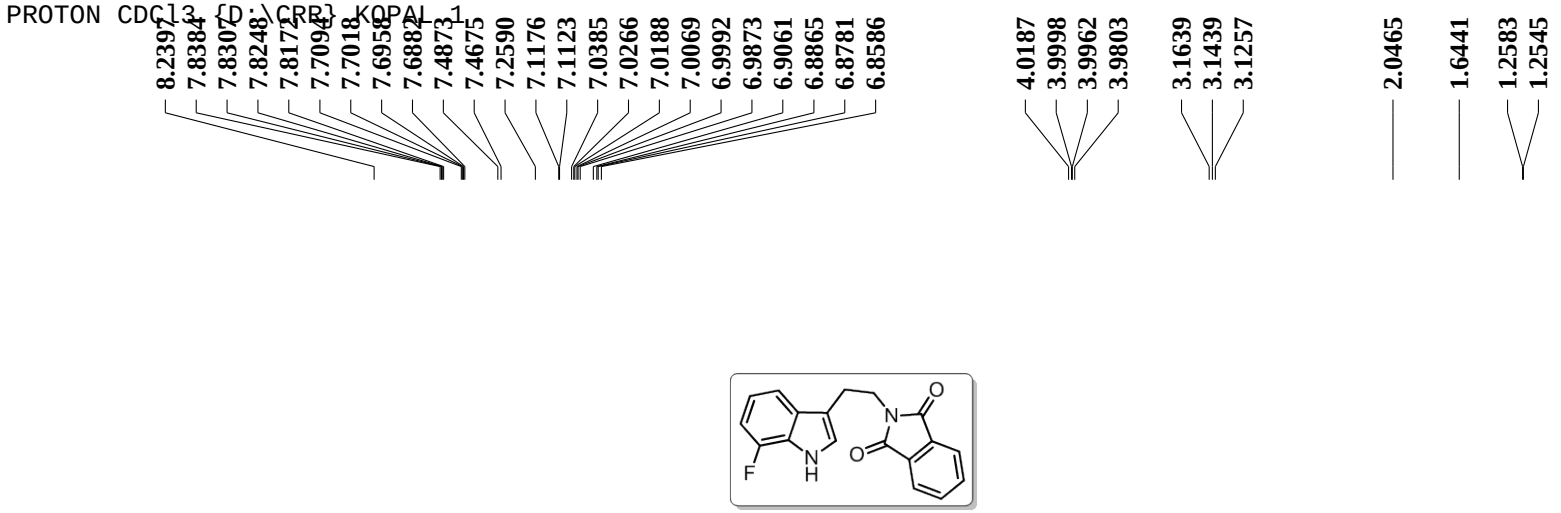
C13CPD DMSO {D:\CRR} KOPAL 1



S51

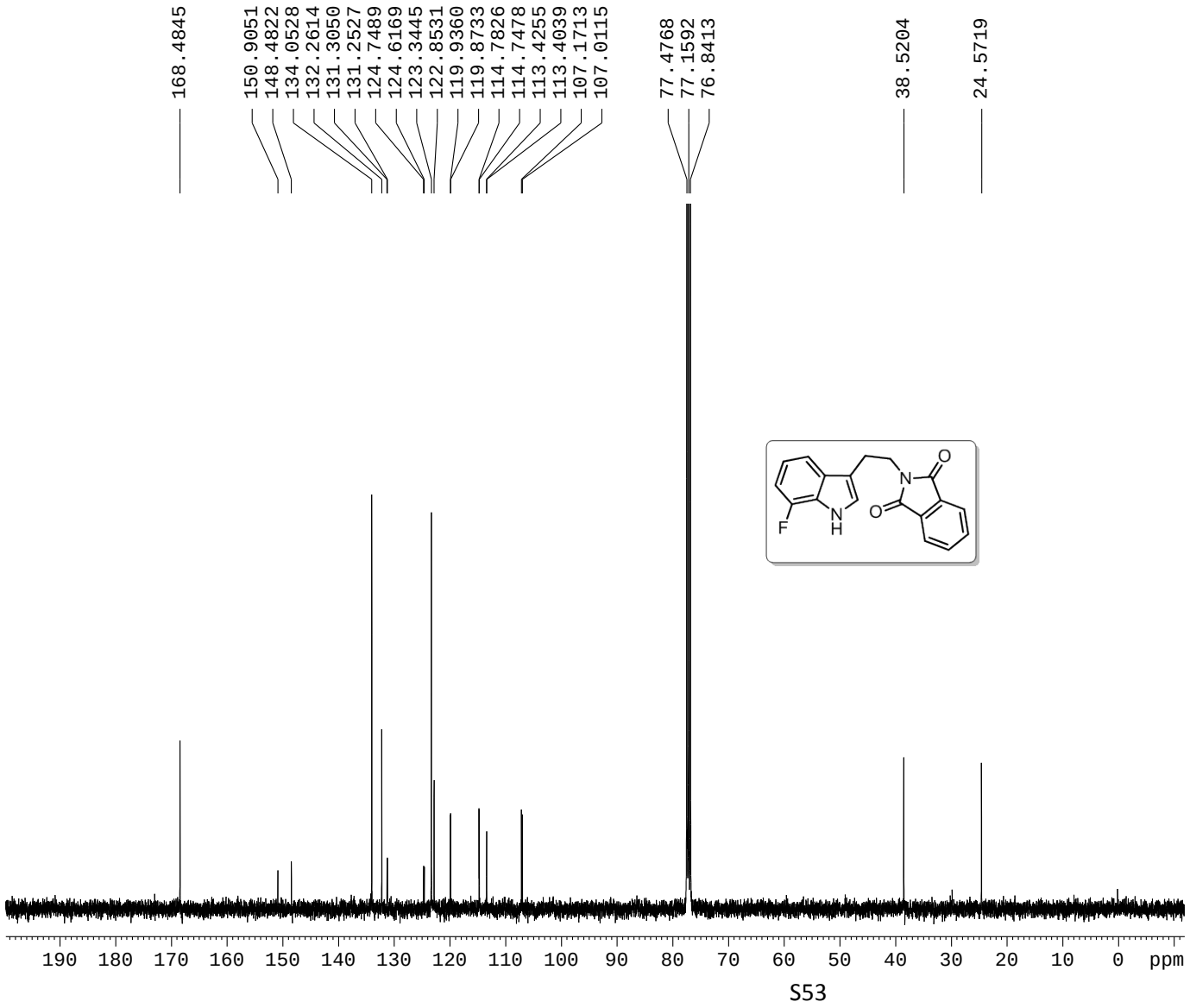
```
Current Data Parameters
NAME          SMR-con-G
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120225
Time               9.15
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD                65536
SOLVENT             DMSO
NS                18000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                292.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6128193 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



Current Data Parameters
NAME SMR-con-B
EXPNO 1
PROCNO 1

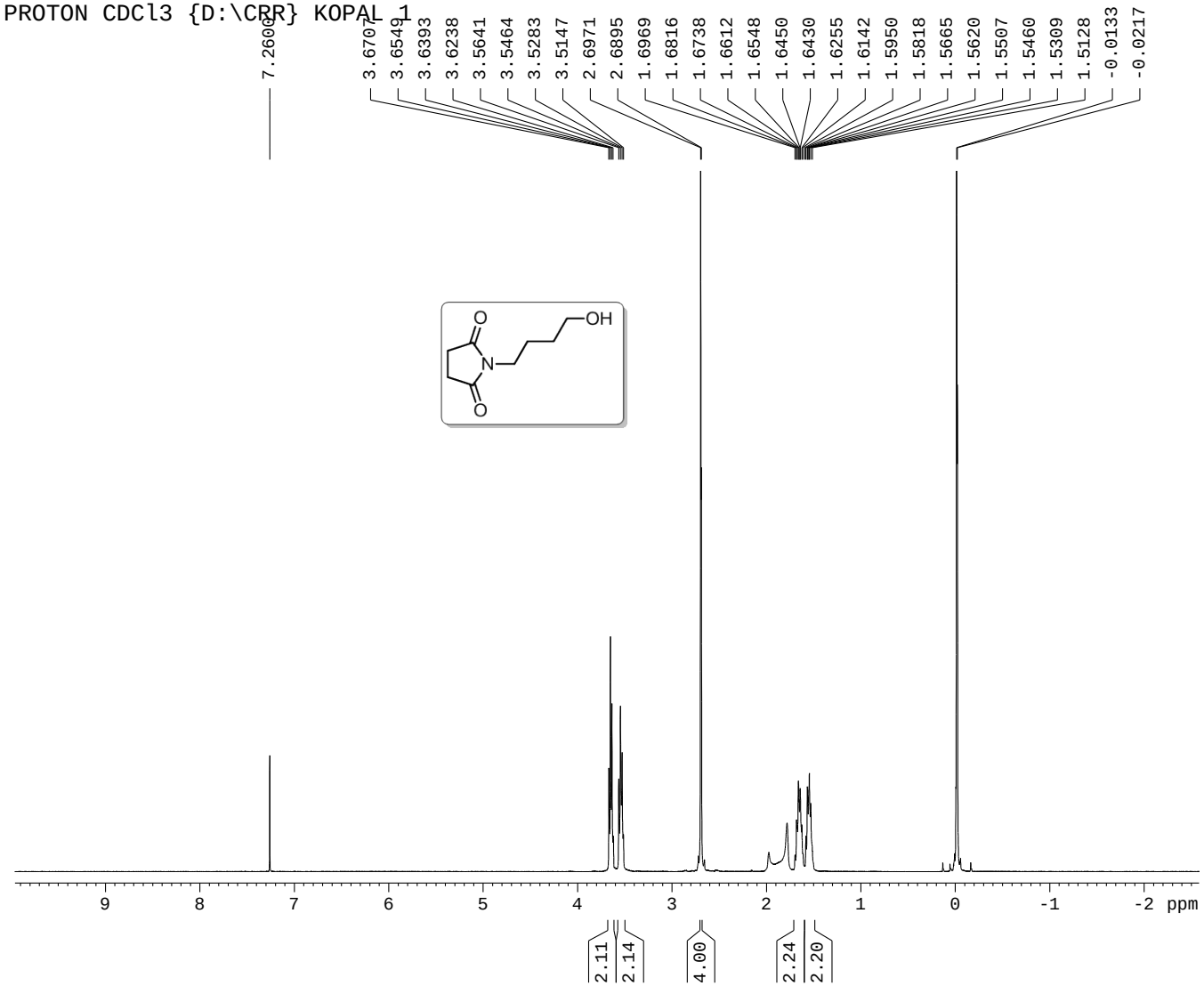
F2 - Acquisition Parameters
Date_ 20120130
Time 13.53
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.00 usec
TE 295.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.60 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 15.60 dB
PL13 15.60 dB
PL2 -0.90 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127546 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

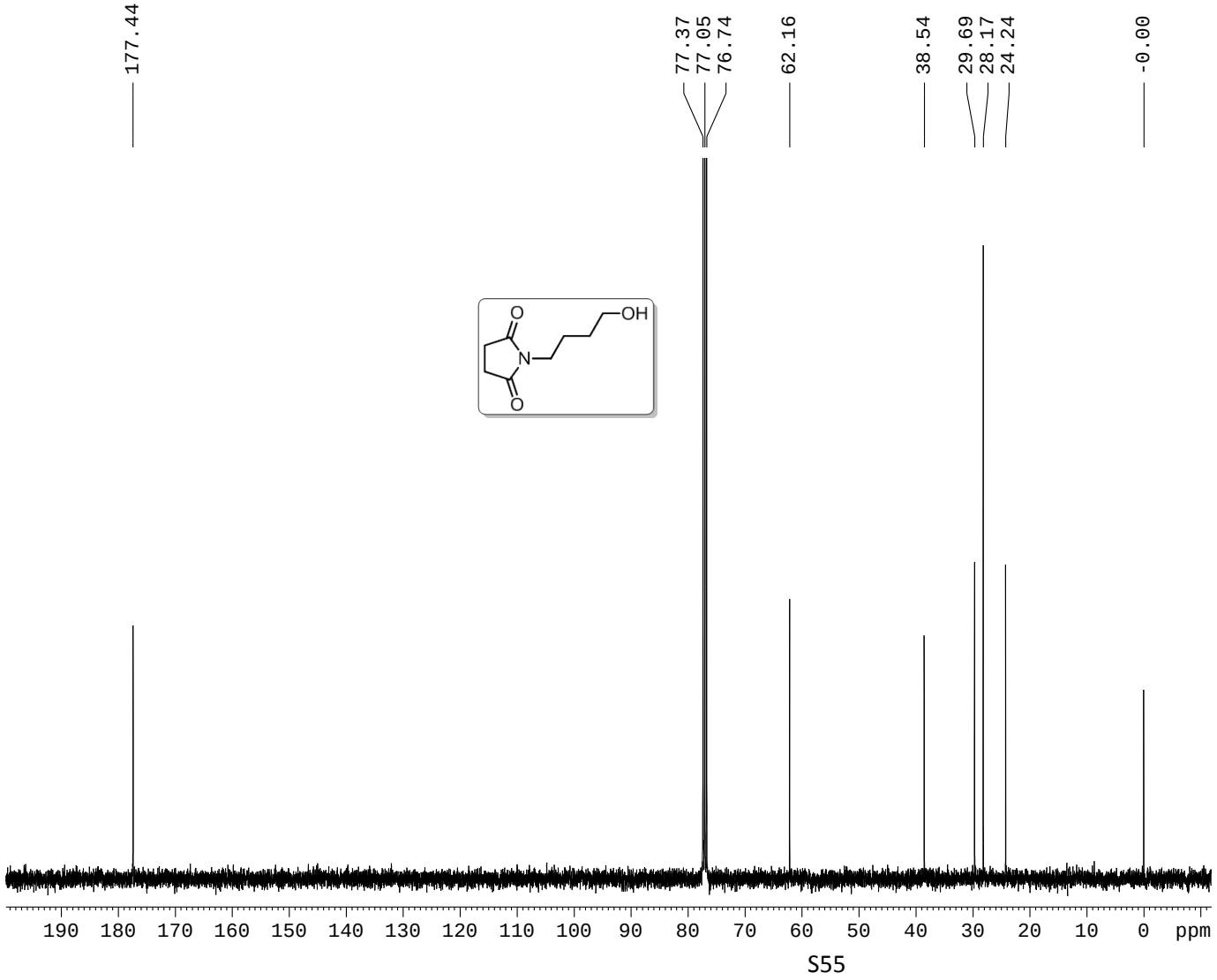
This journal is © The Royal Society of Chemistry 2012




```
Current Data Parameters
NAME         SMR-I-230-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110624
Time               16.15
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   181
DW                60.800 usec
DE                 6.00 usec
TE                294.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300039 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

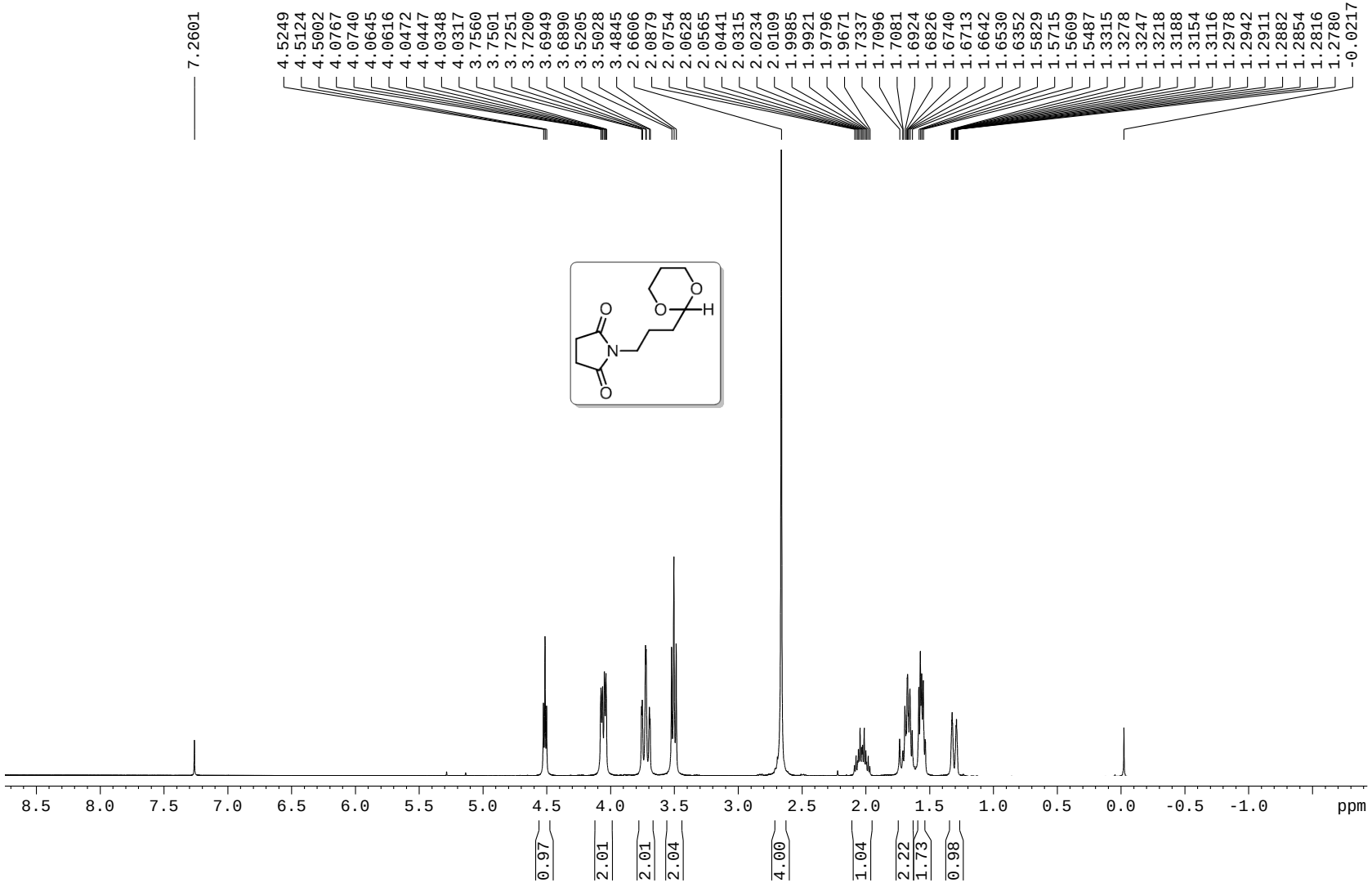
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME        SMR-I-230-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110713
Time              14.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  269
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                295.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127664 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

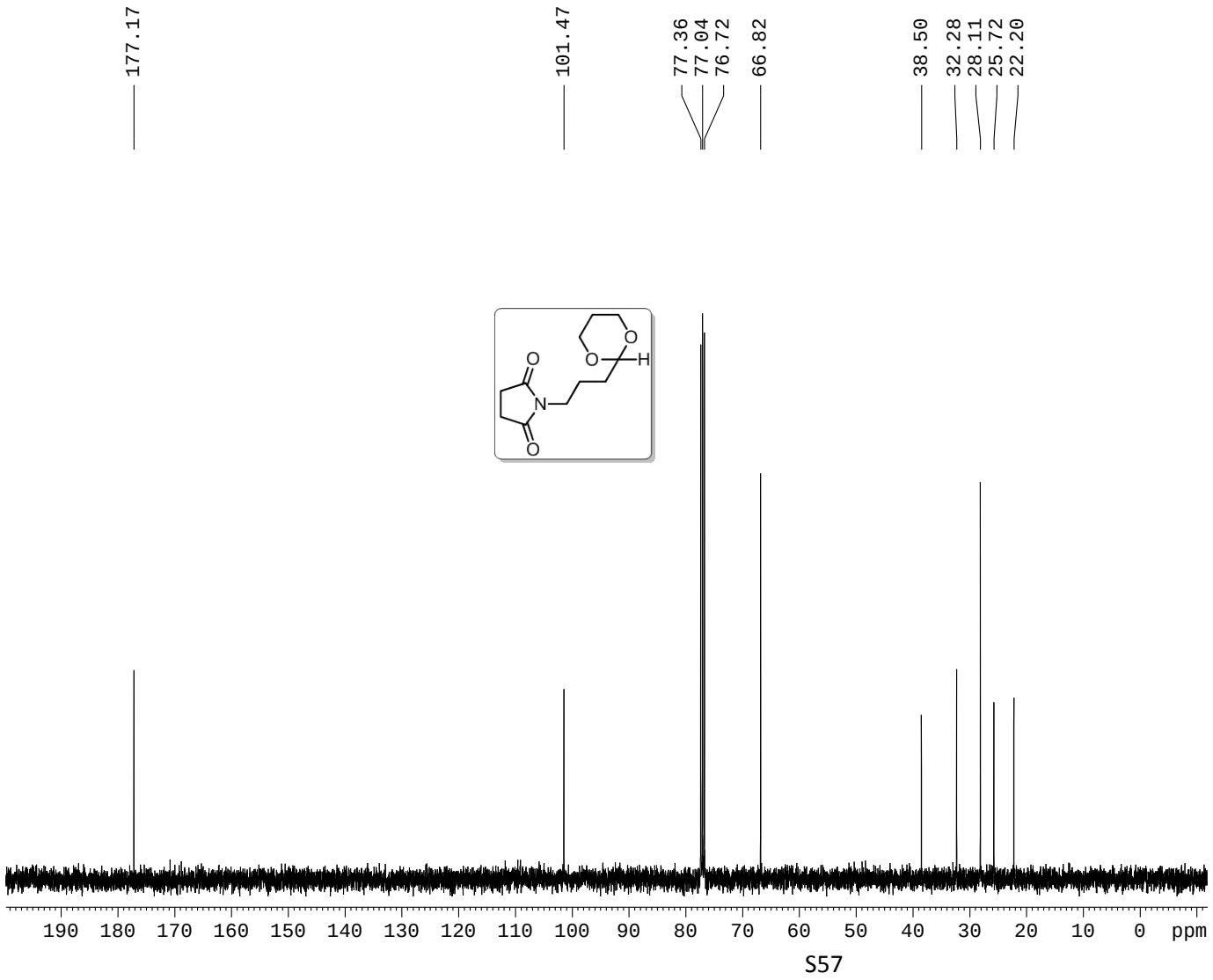
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



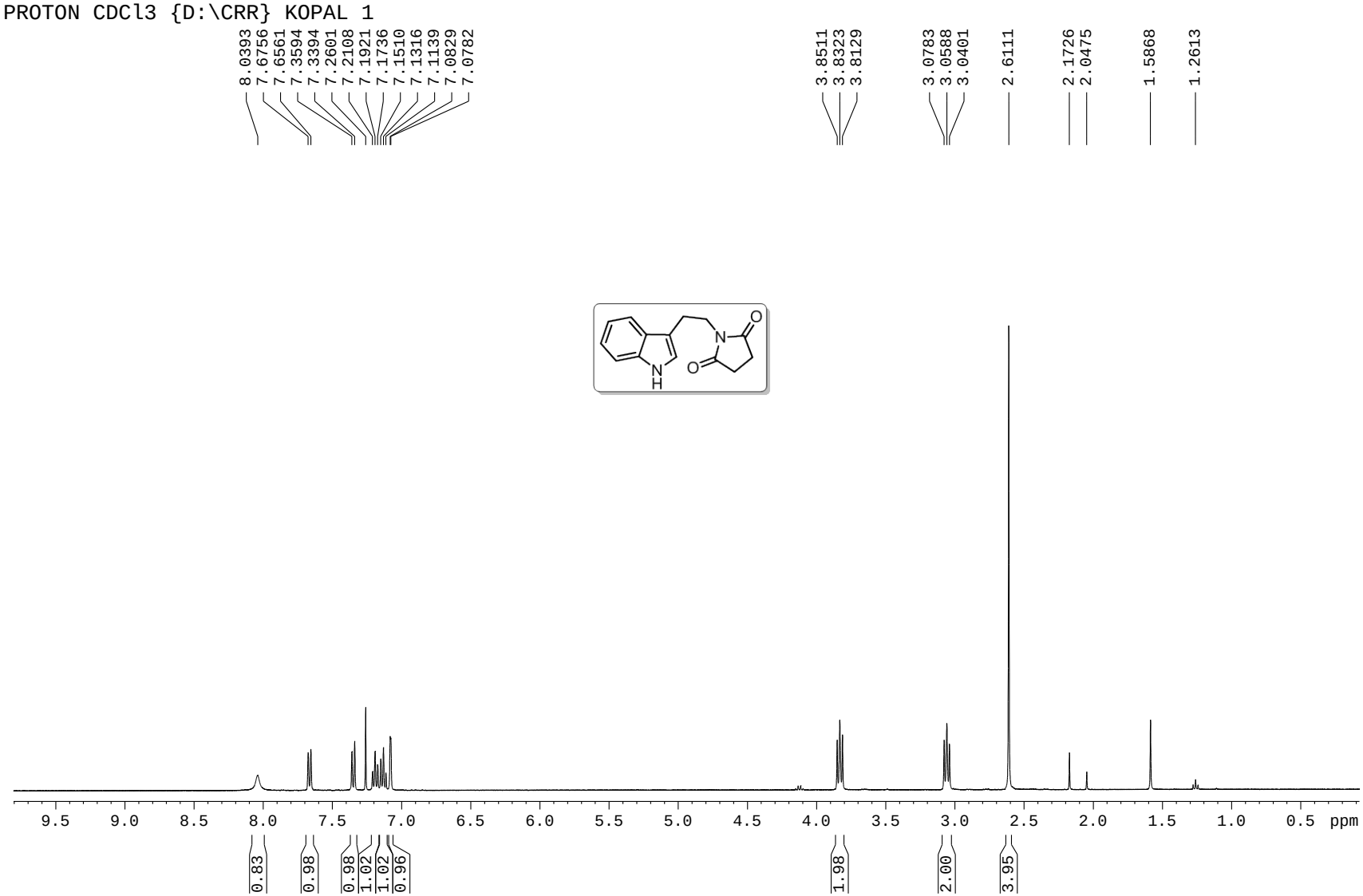
Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



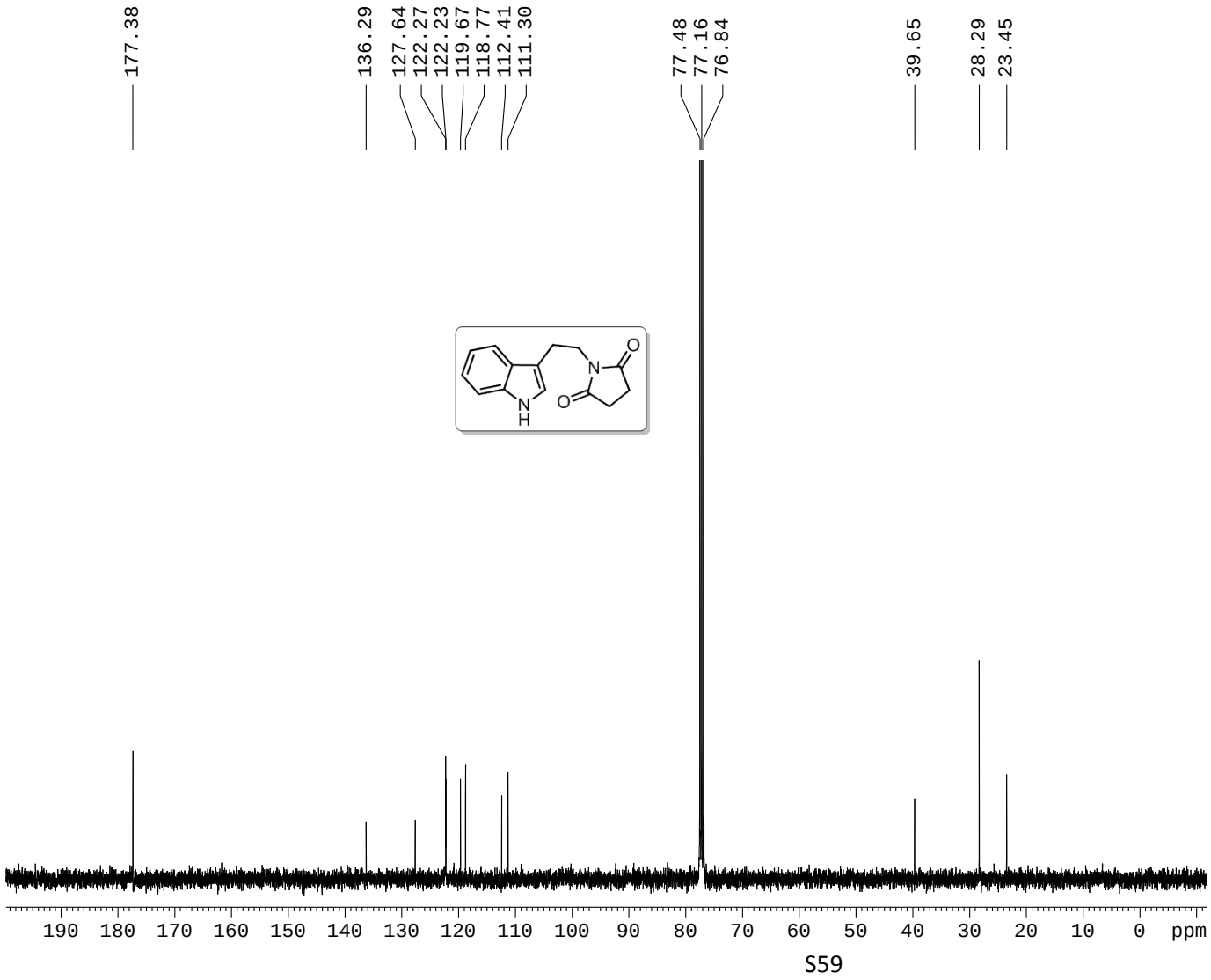

```
Current Data Parameters
NAME        SMR-I-185-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110310
Time              10.39
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   57
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1290
DW                20.800 usec
DE                 6.00 usec
TE                295.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

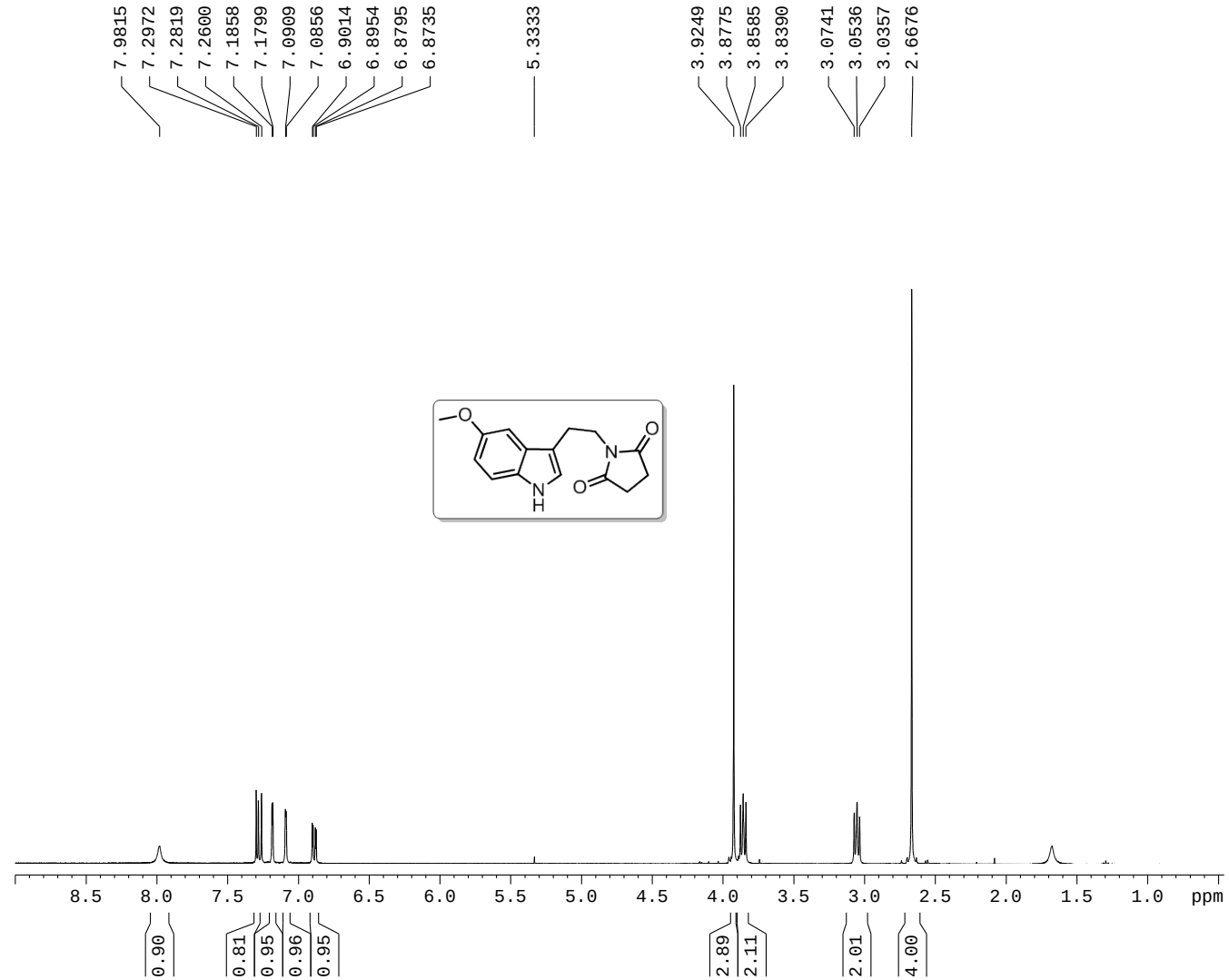
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME            SMR-CUI
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20111220
Time              16.16
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1290
DW                20.800 usec
DE                 6.00 usec
TE                296.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

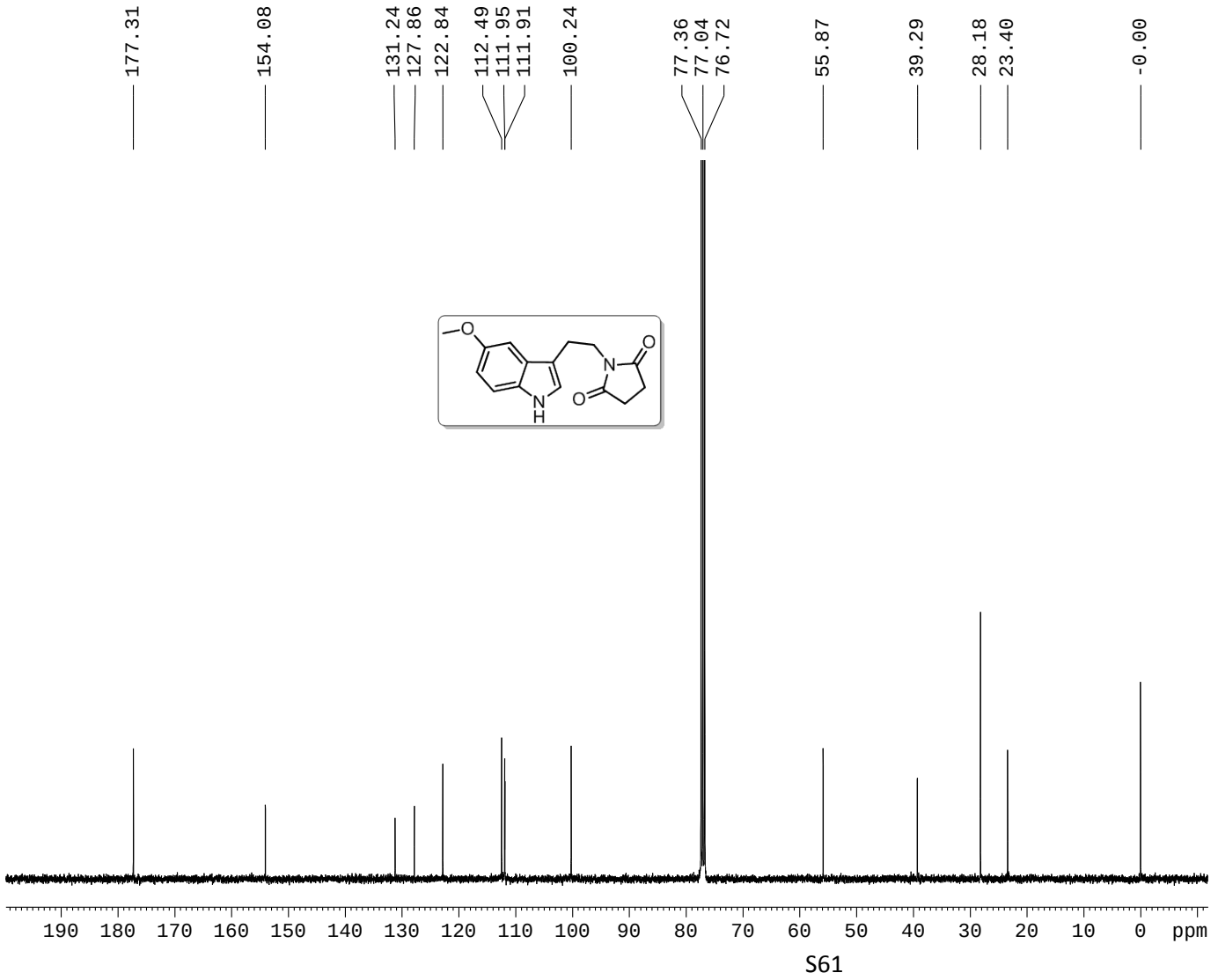
PROTON CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME         SMR-I-235-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110708
Time               12.15
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   228
DW                60.800 usec
DE                 6.00 usec
TE                295.7 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1299888 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

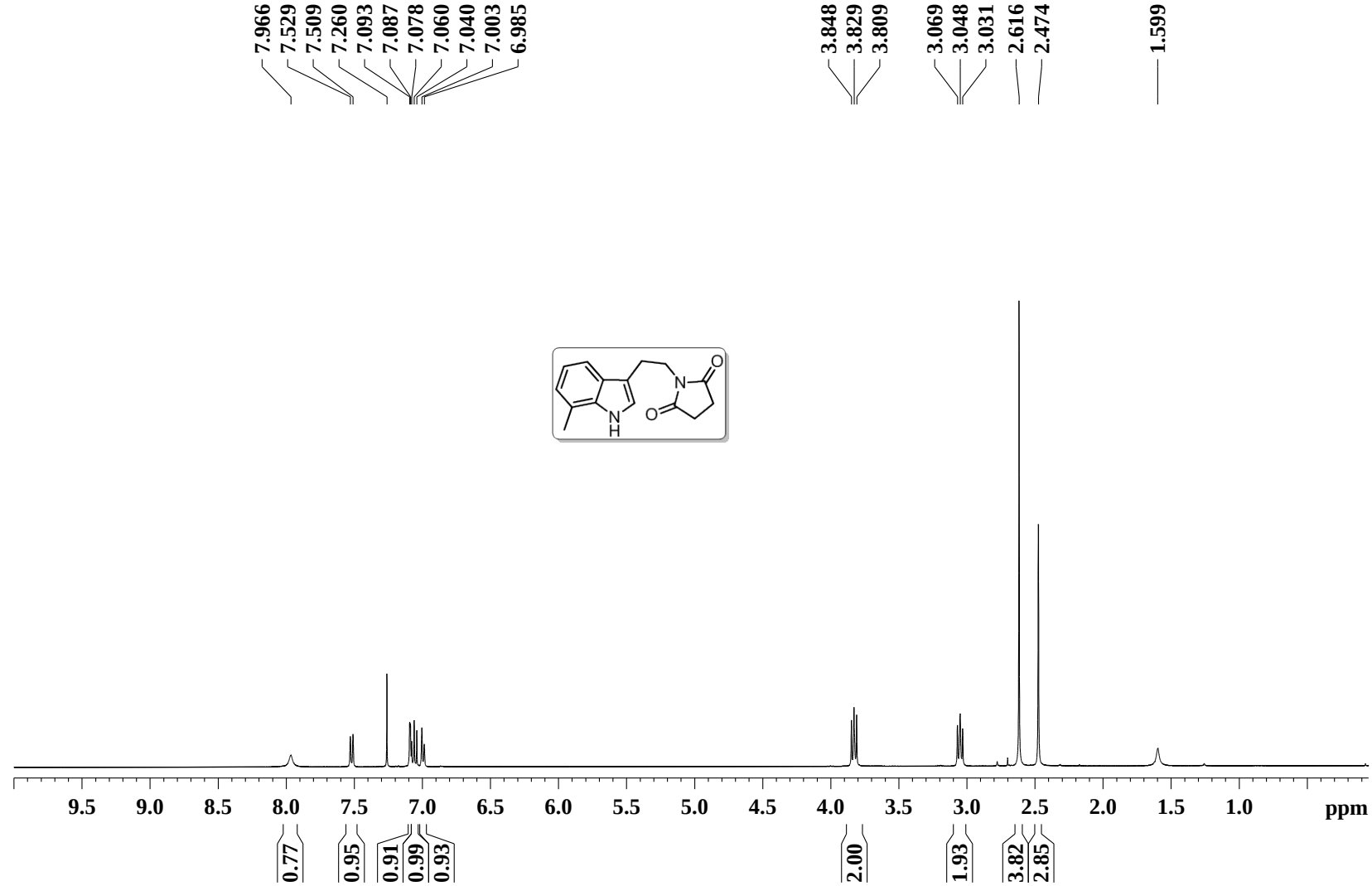
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



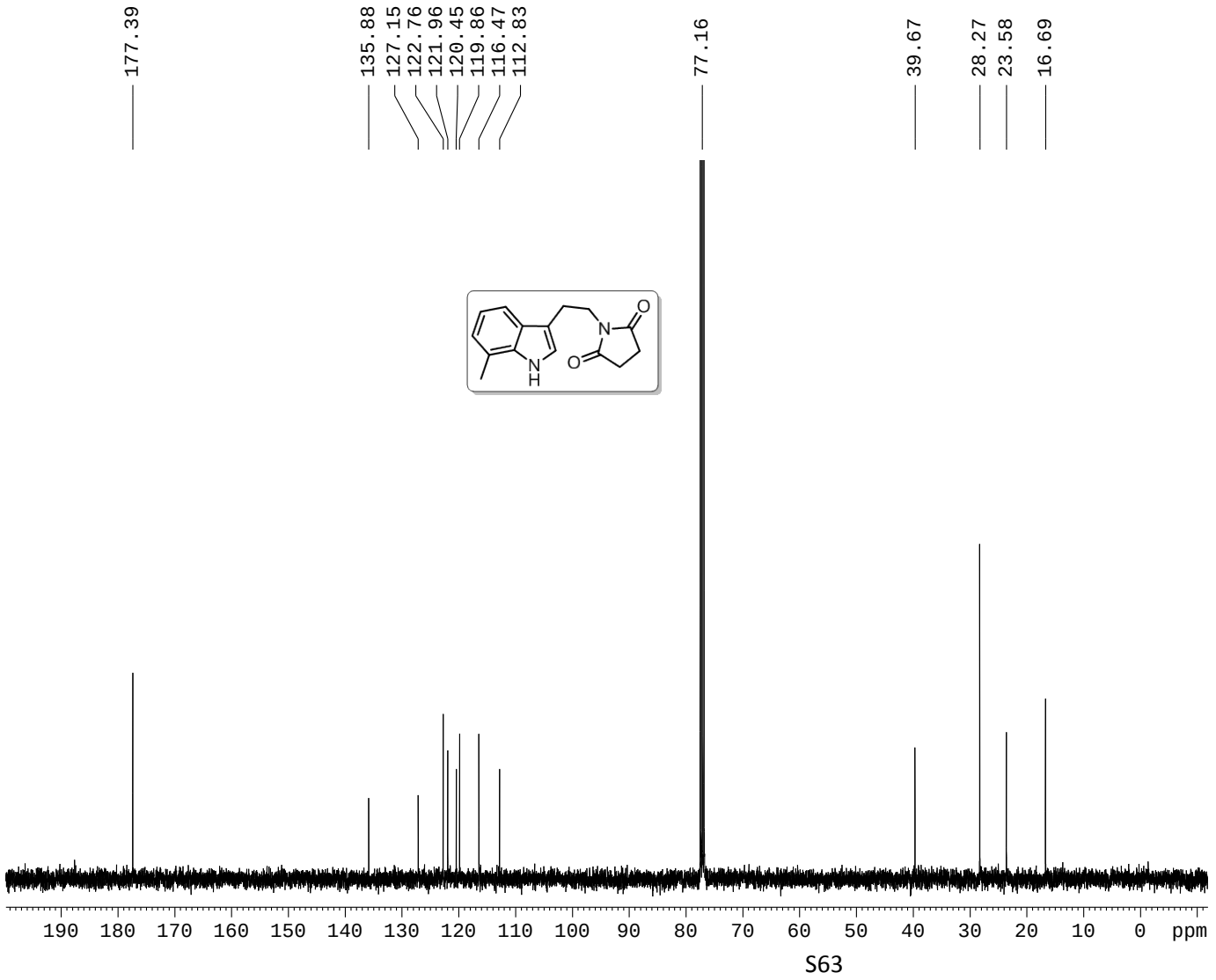

```
Current Data Parameters
NAME        SMR-I-235-2
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20110713
Time              12.45
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                295.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



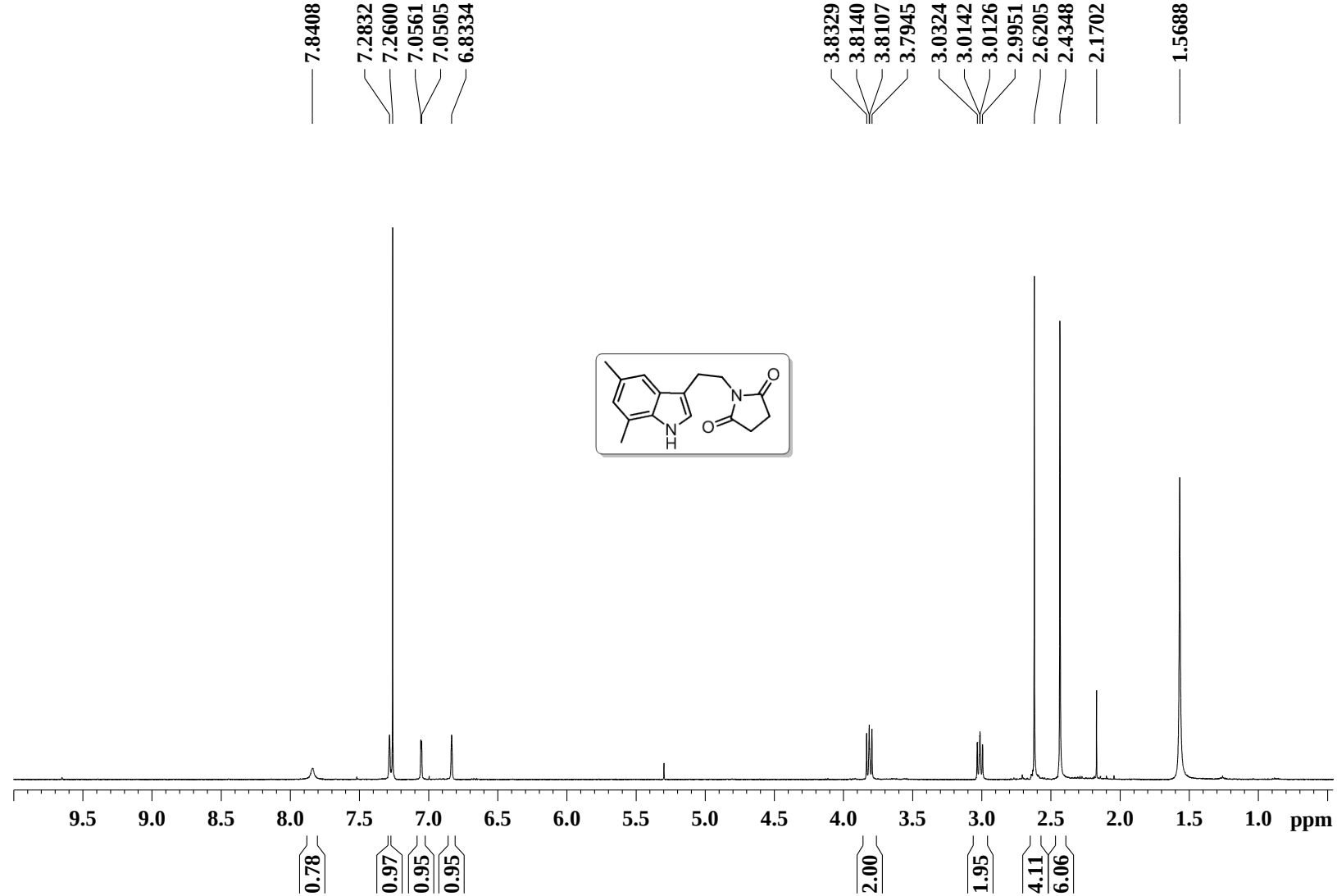
Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



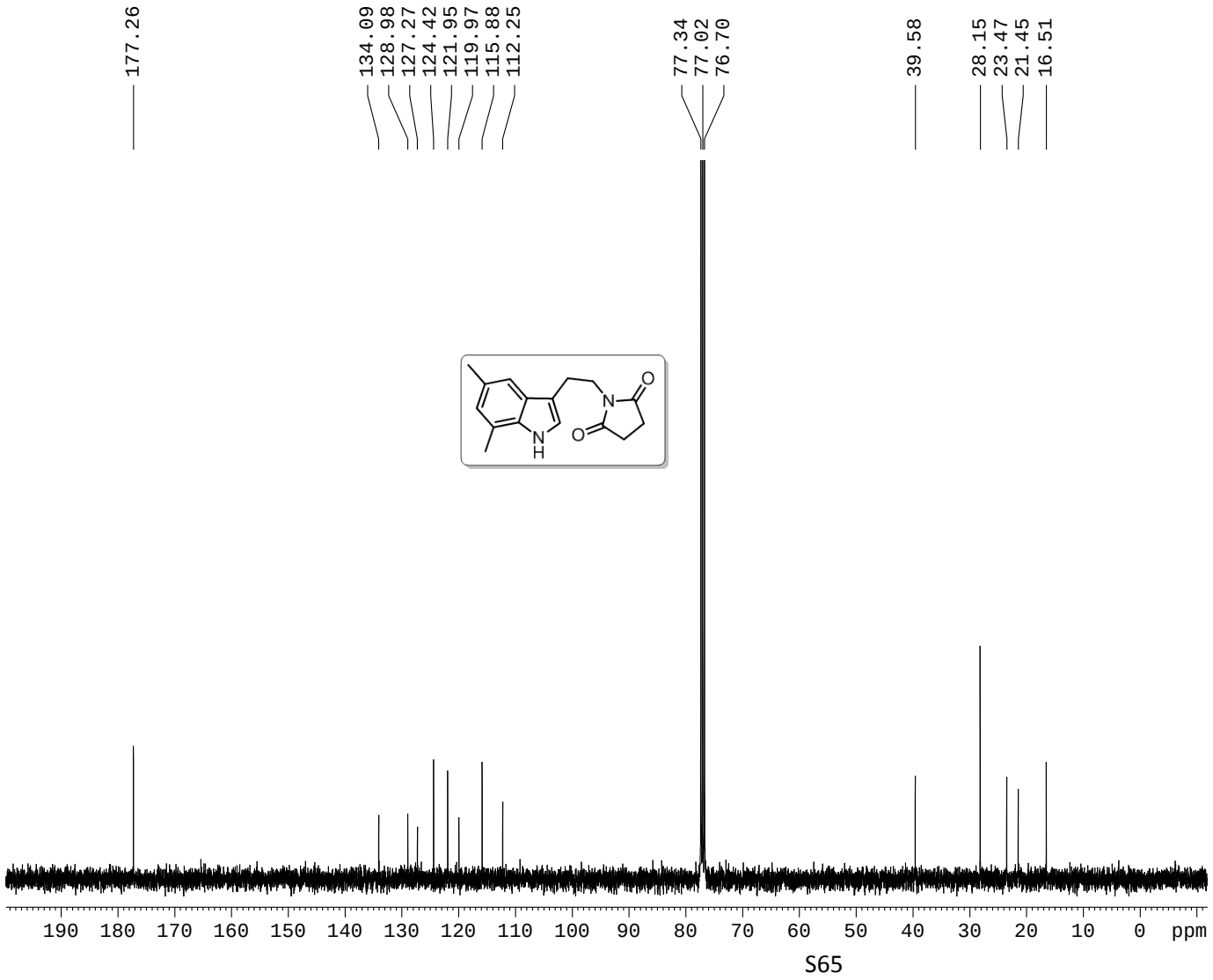

```
Current Data Parameters
NAME       SMR-I-100-10
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110802
Time              11.42
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  175
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                297.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL12             15.60 dB
PL13             15.60 dB
PL2              -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127564 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



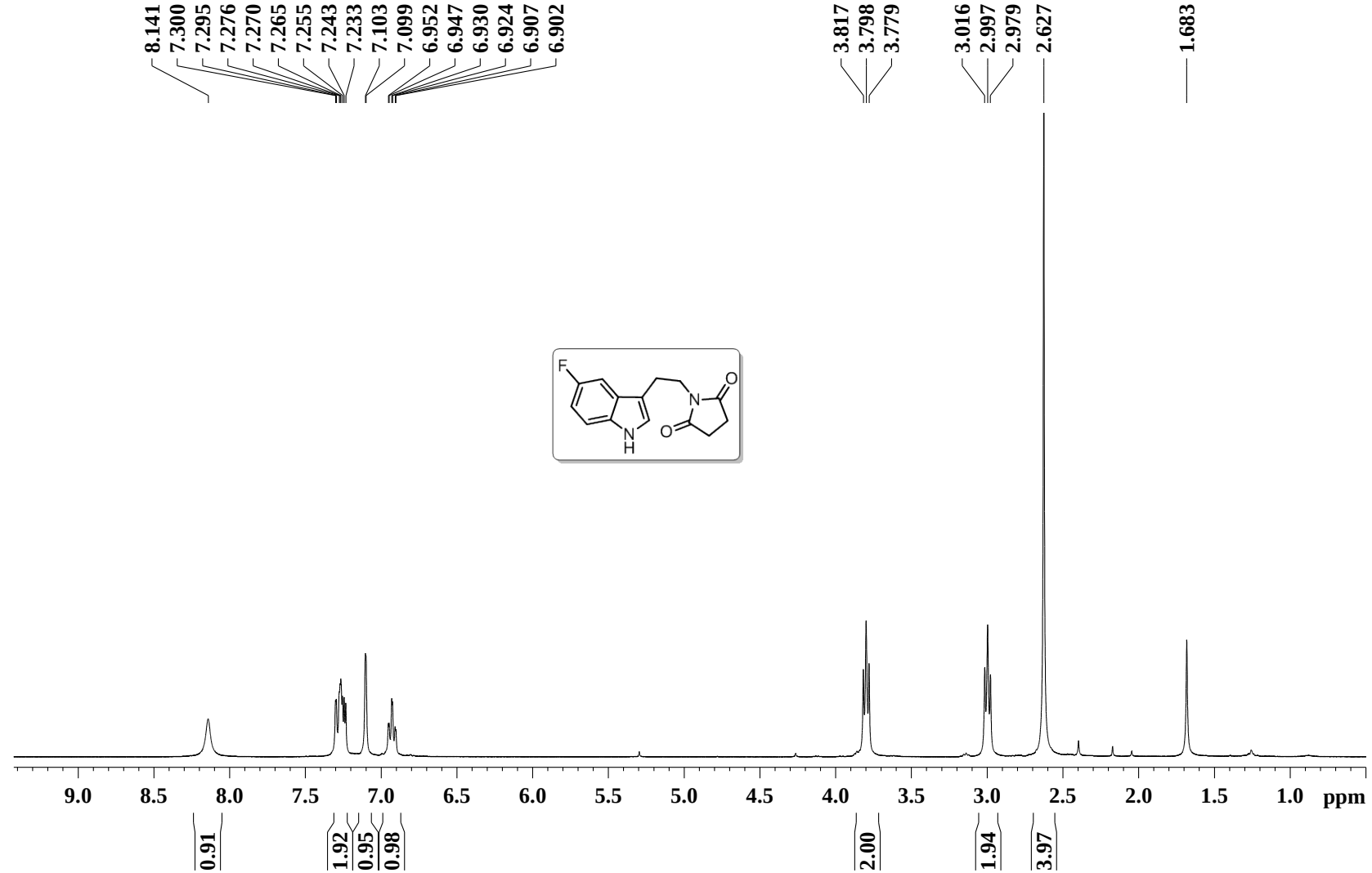
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



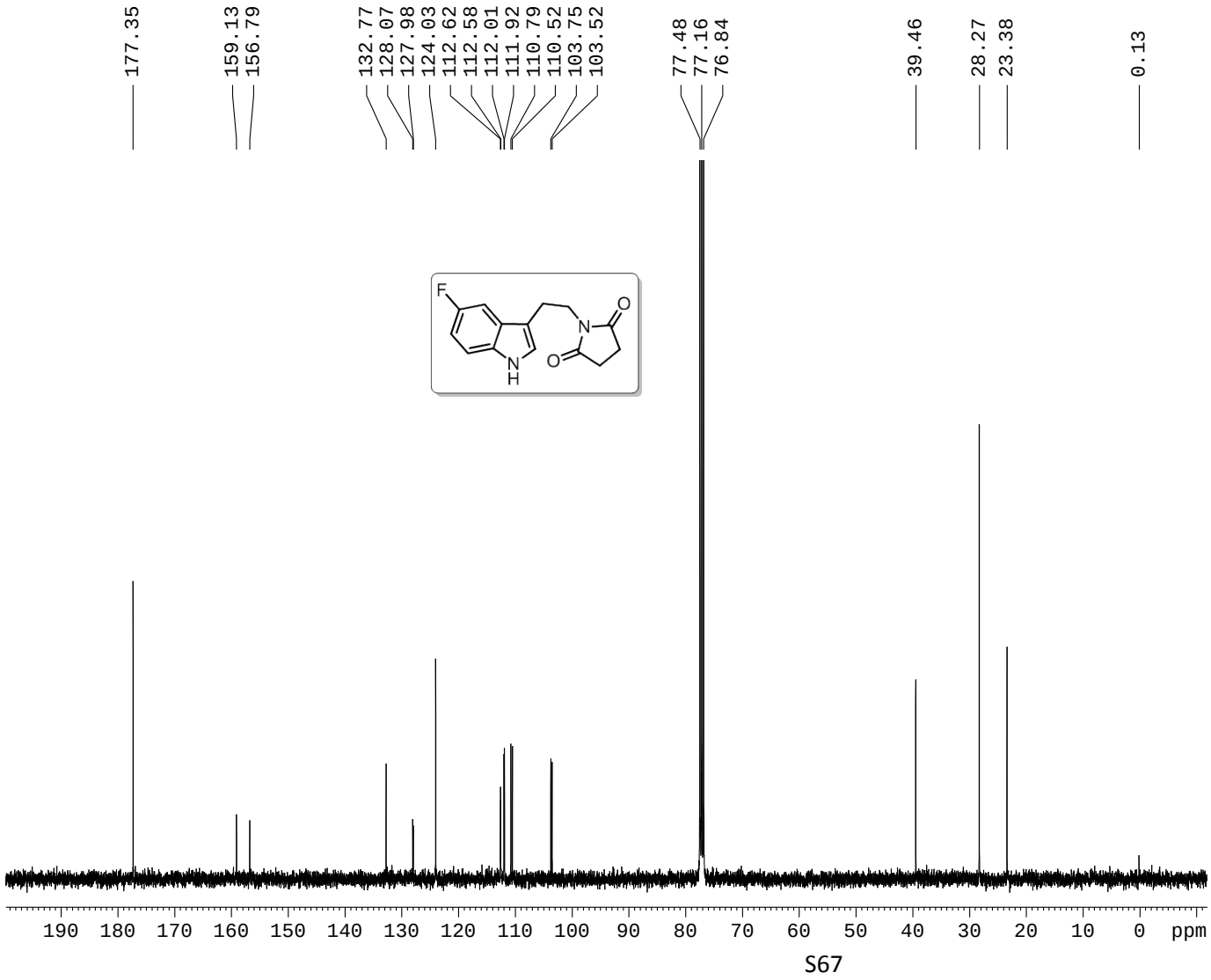

```
Current Data Parameters
NAME      SMR-2,4-D1-IMI
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110727
Time               12.02
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

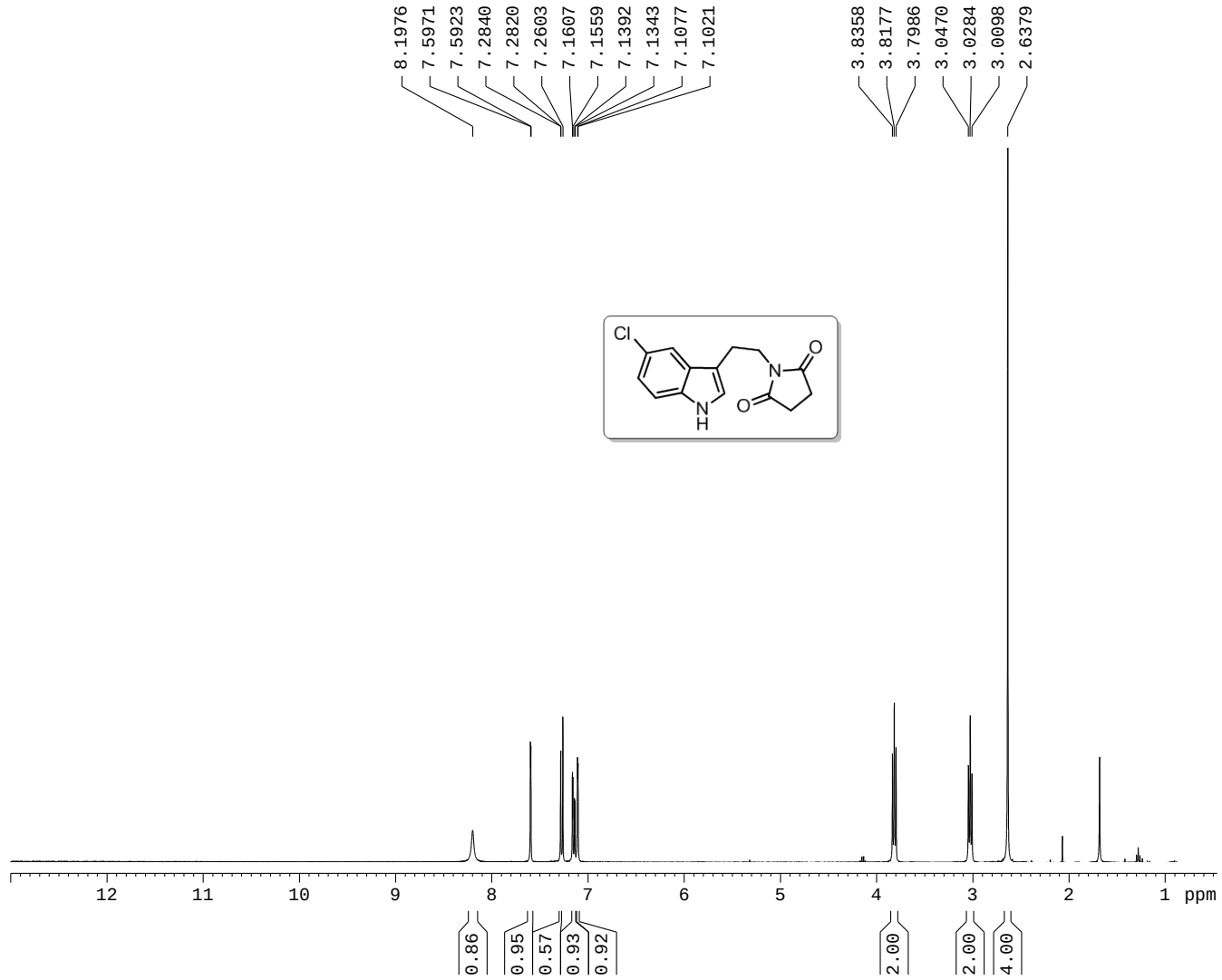
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME            SMR-4DS
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120216
Time              18.14
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                297.7 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL12             15.60 dB
PL13             15.60 dB
PL2              -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127547 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

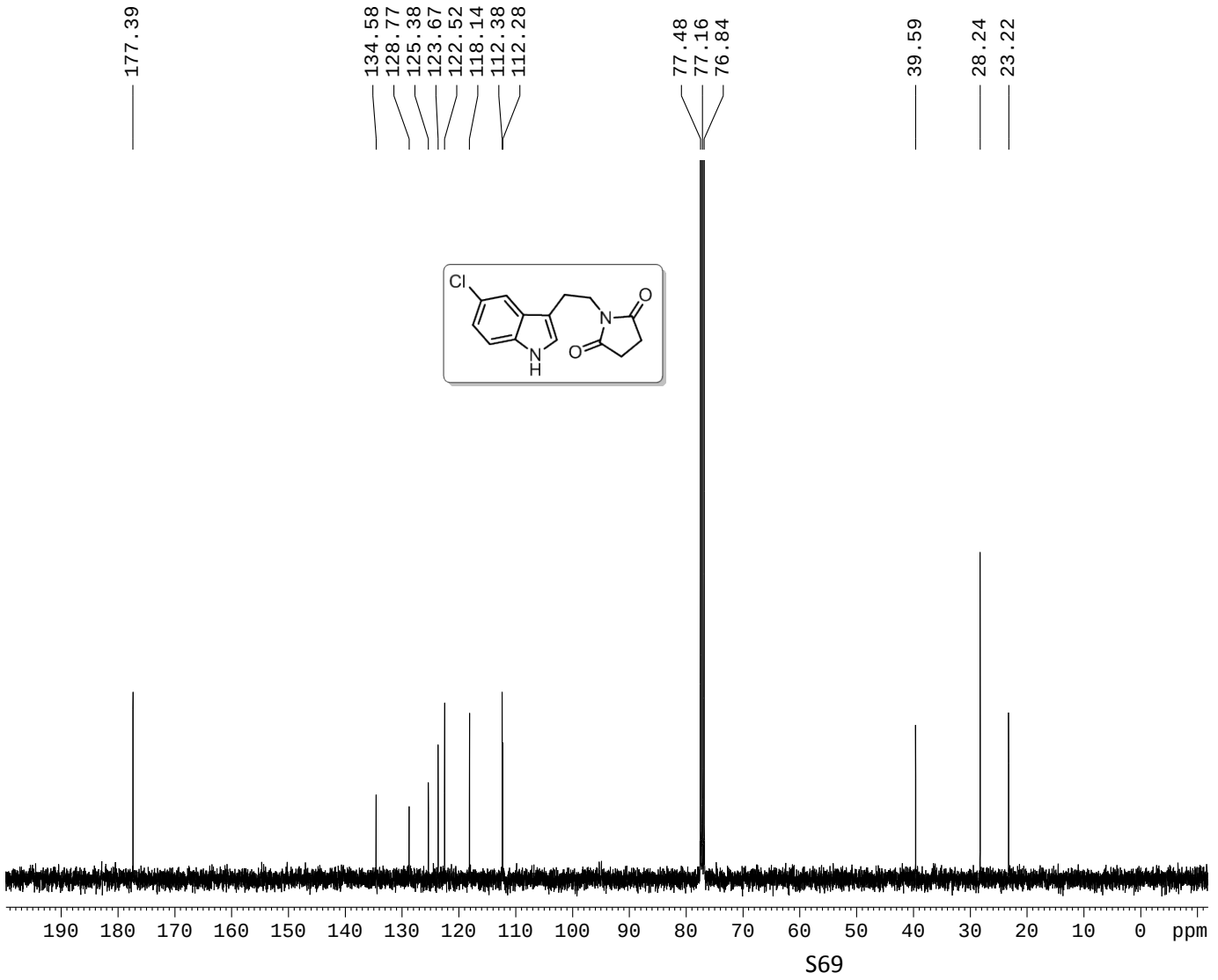
PROTON CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME         SMR-I-192-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110324
Time               11.48
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.00 usec
TE                294.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1299939 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

This journal is © The Royal Society of Chemistry 2012

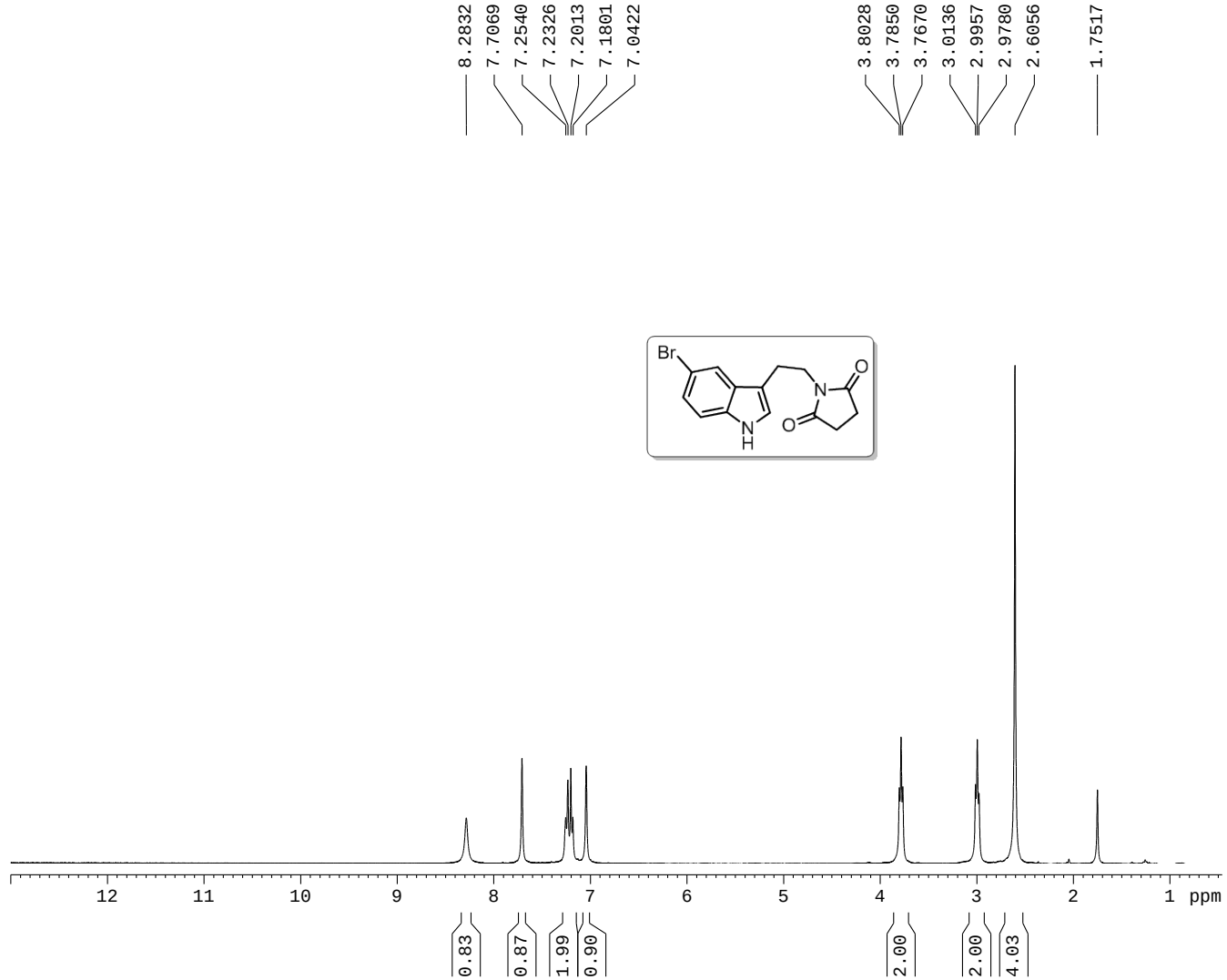
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME        SMR-I-192-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110324
Time              12.04
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1030
DW               20.800 usec
DE                6.00 usec
TE                294.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127561 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

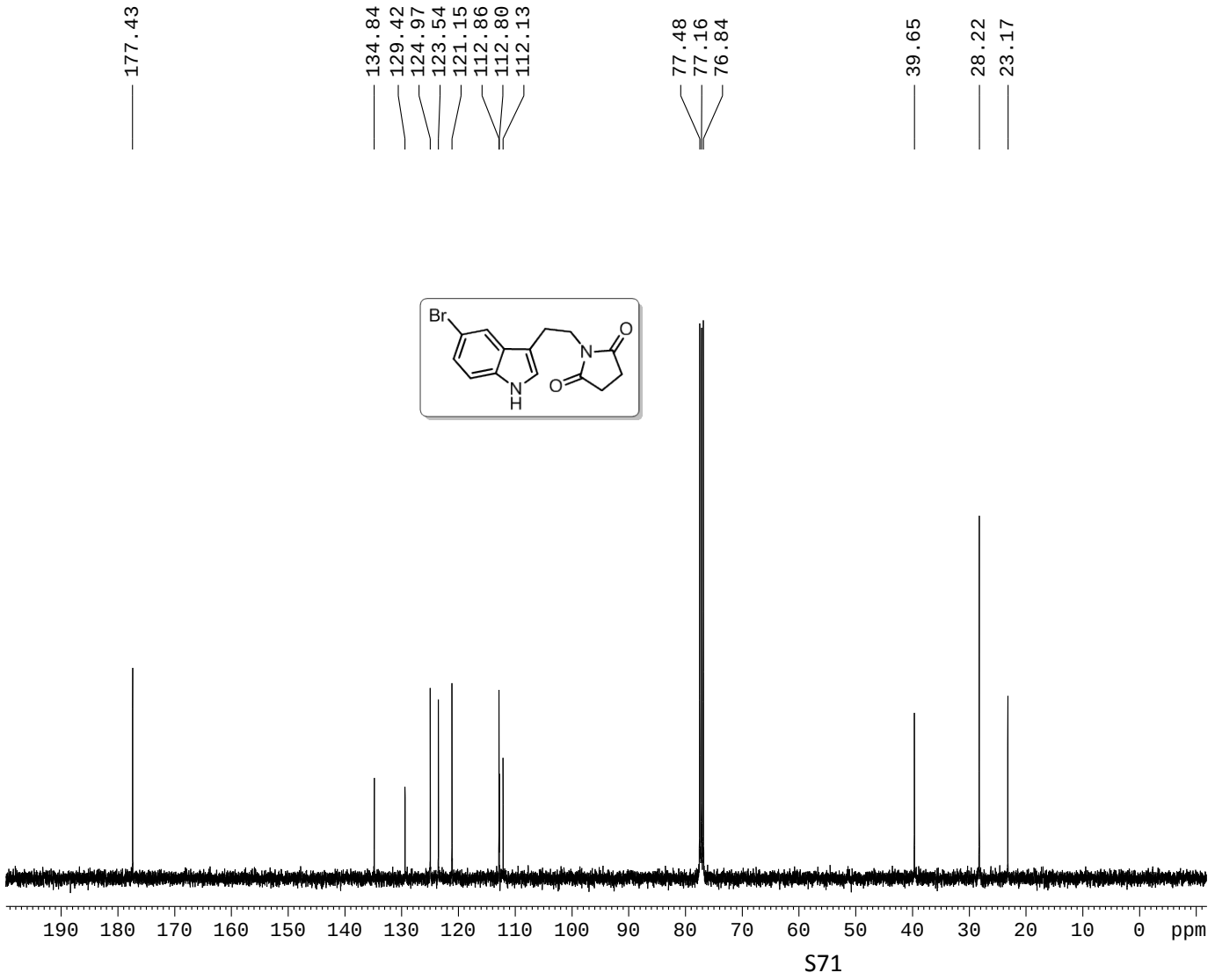
PROTON CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME         SMR-1-187-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110314
Time               12.08
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   161
DW                60.800 usec
DE                 6.00 usec
TE                294.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300002 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

This journal is © The Royal Society of Chemistry 2012

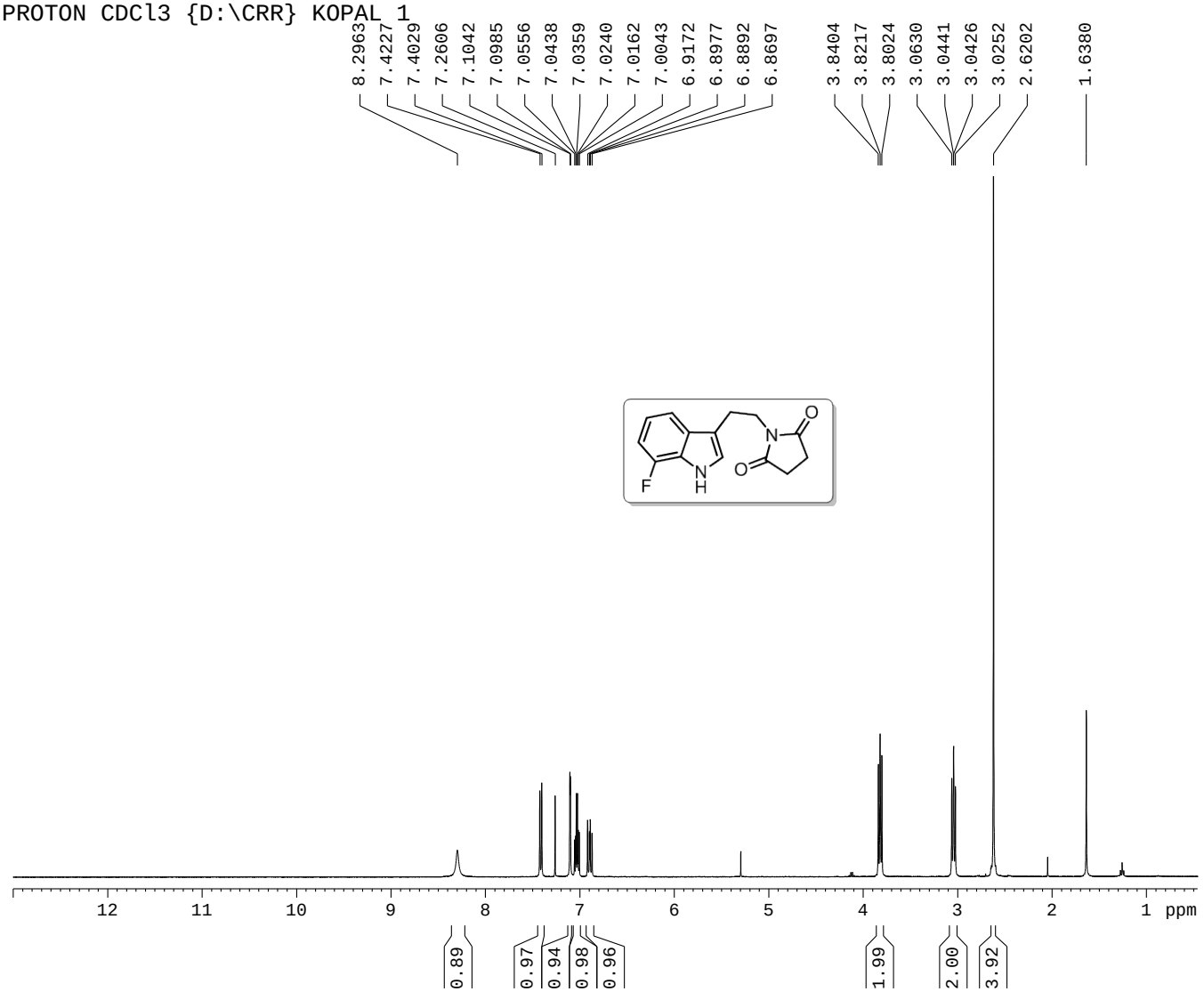
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME        SMR-1-187-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110314
Time              12.17
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  199
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  645
DW               20.800 usec
DE                6.00 usec
TE                295.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127584 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012

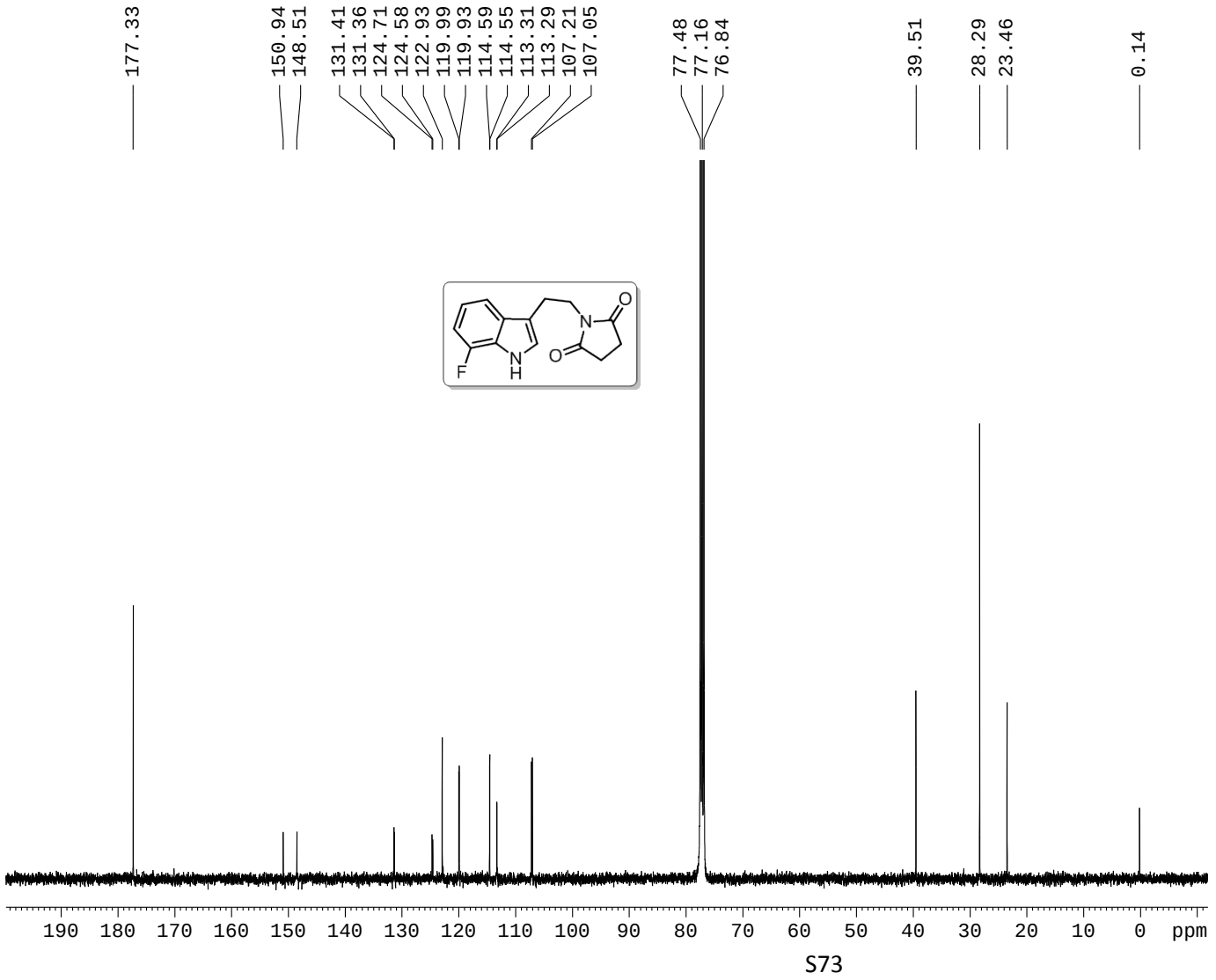
PROTON CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME         SMR-I-194-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110324
Time               15.40
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.00 usec
TE                294.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -0.90 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300034 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

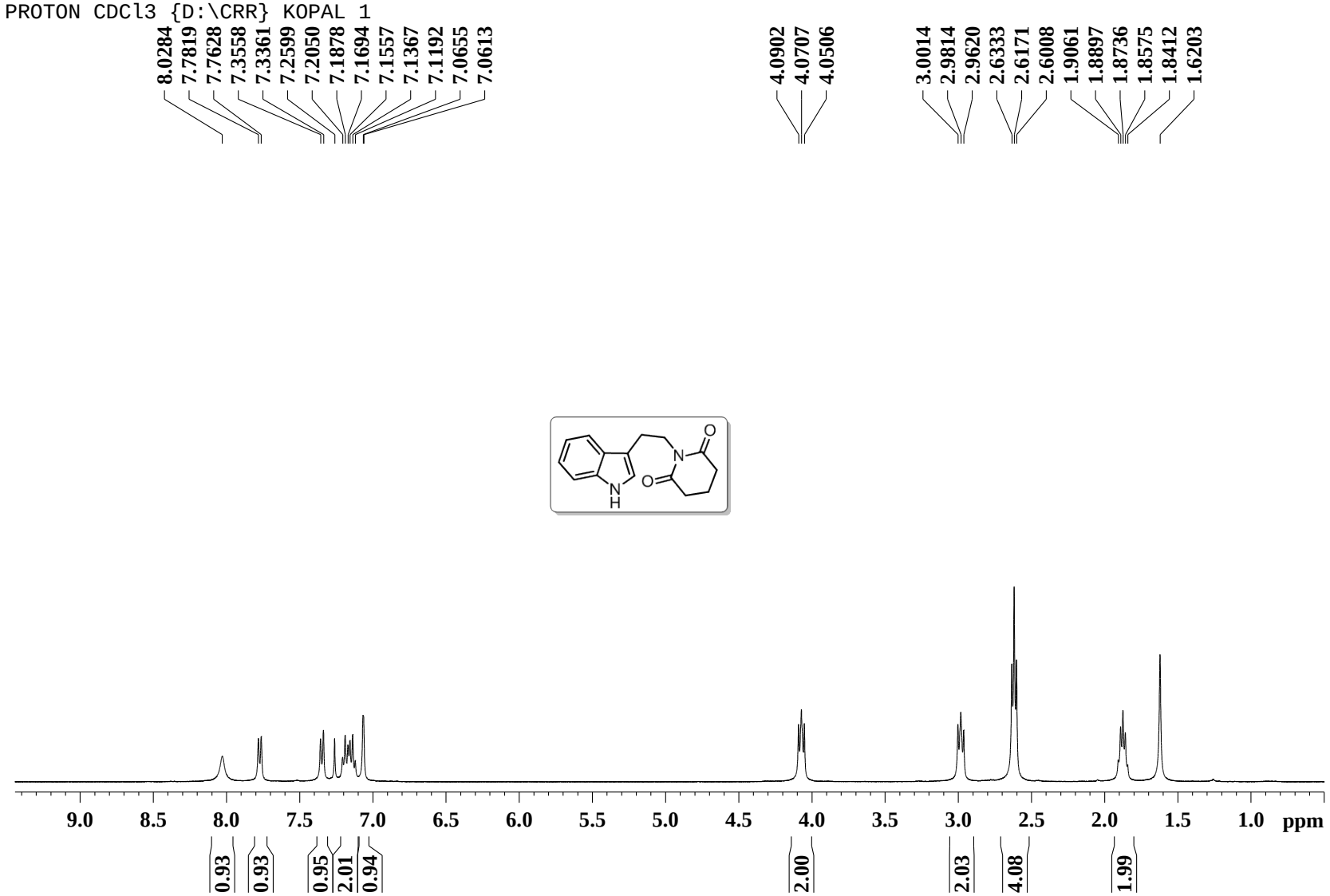
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



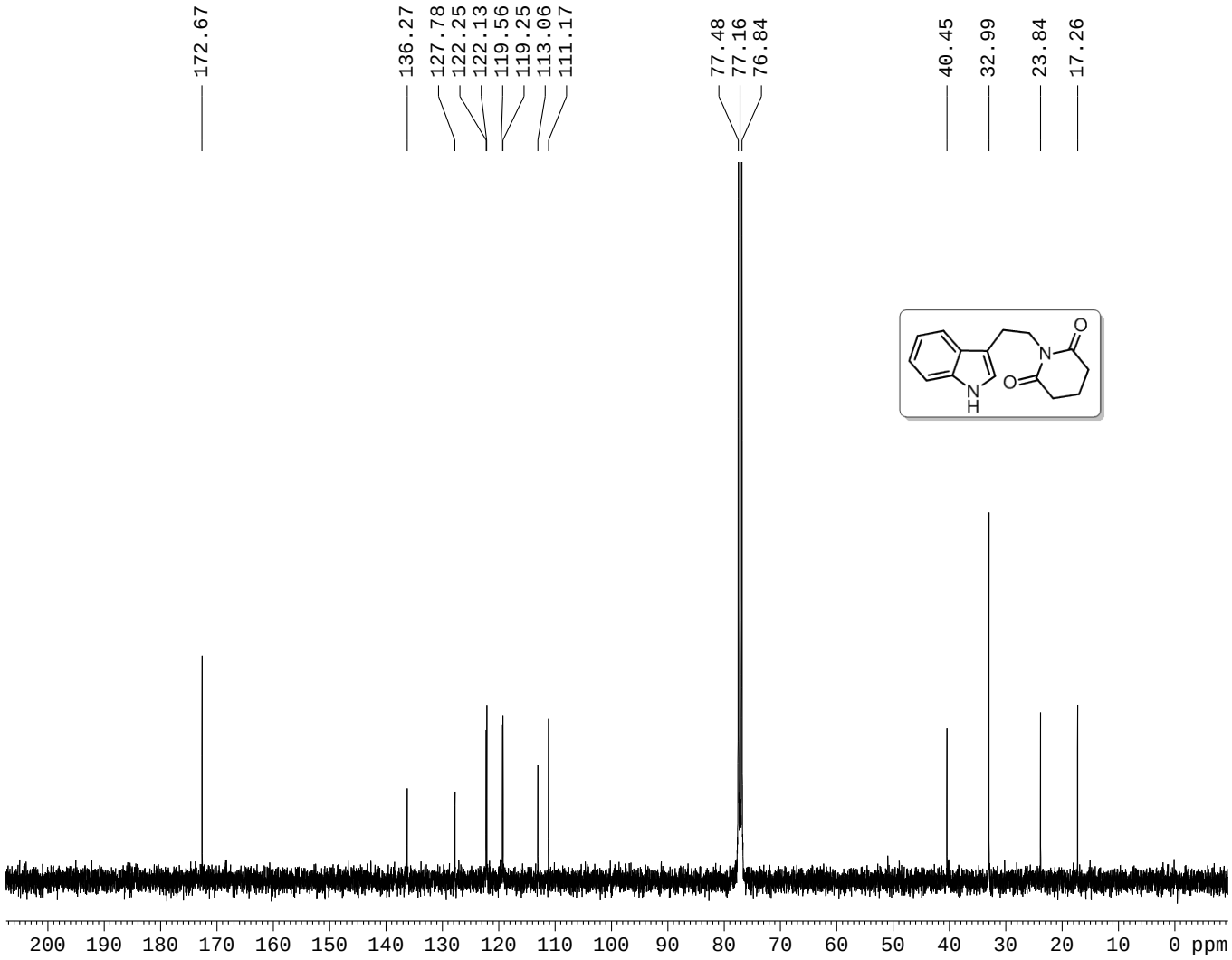

```
Current Data Parameters
NAME                 SMR-ON
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_             20120221
Time                  9.25
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    17000
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                       57
DW                  20.800 usec
DE                   6.00 usec
TE                   297.8 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -0.60 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                90.00 usec
PL12                 15.60 dB
PL13                 15.60 dB
PL2                  -0.90 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127526 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

This journal is © The Royal Society of Chemistry 2012



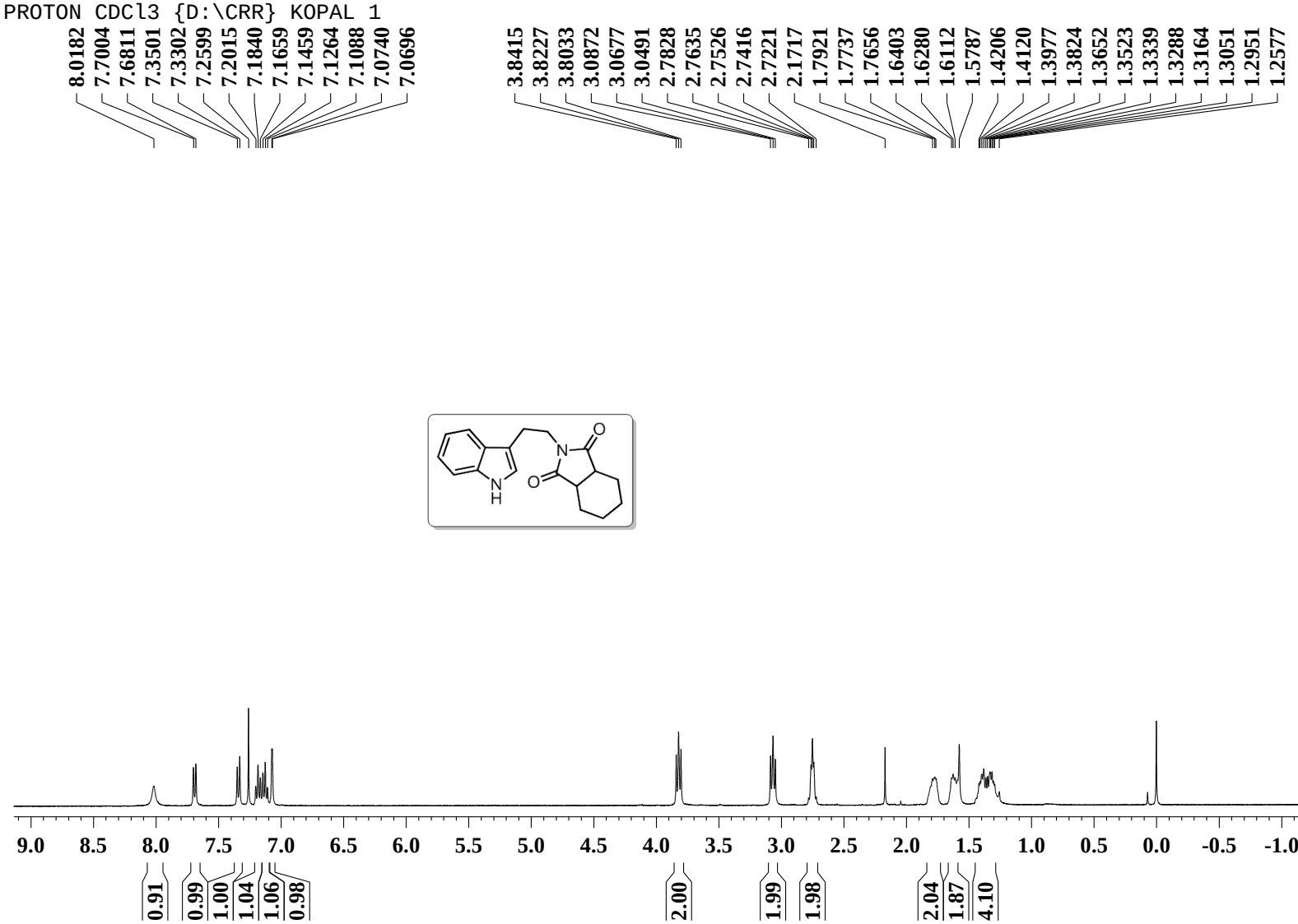
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



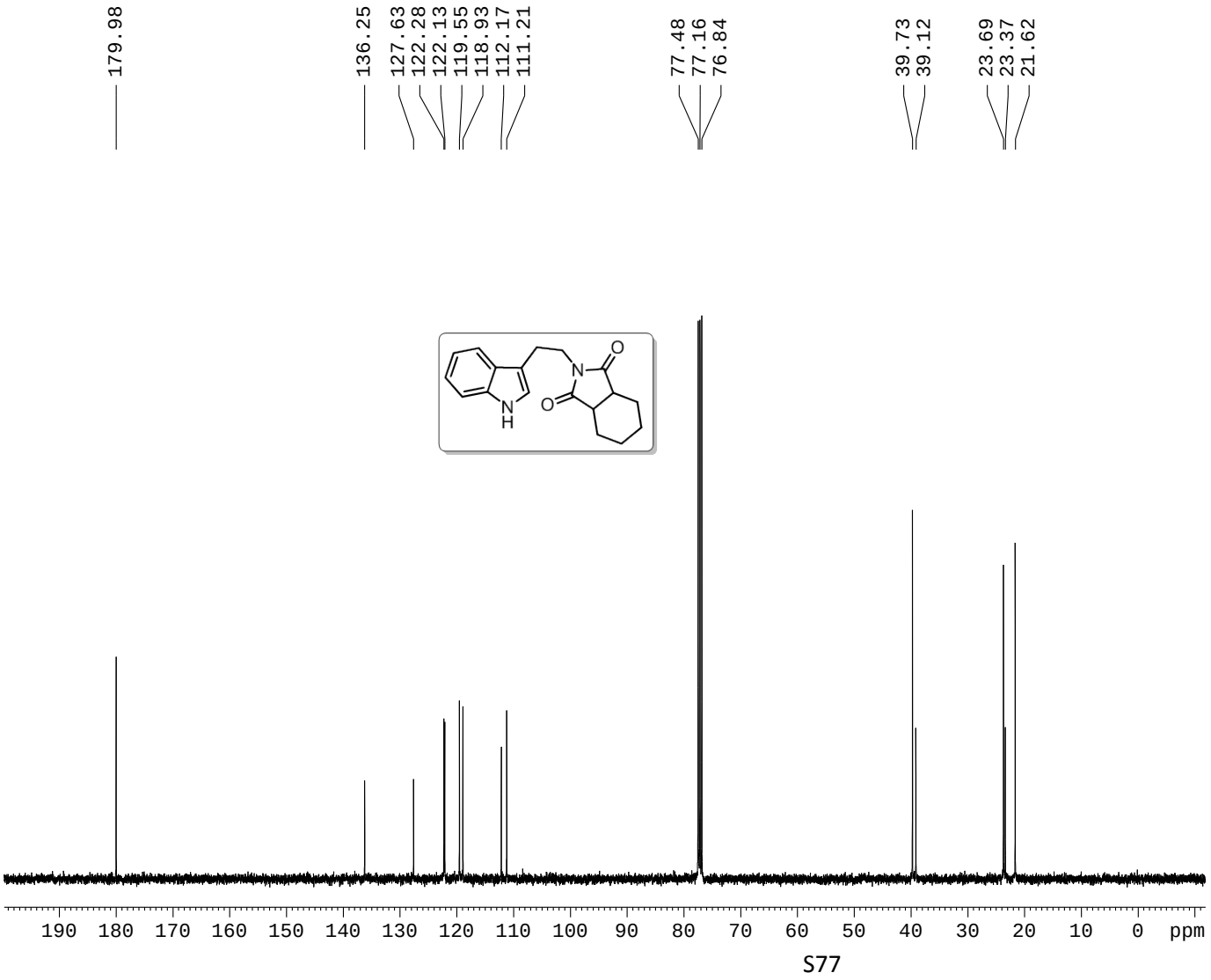

```
Current Data Parameters
NAME         SMR-I-200-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110406
Time                9.54
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                295.5 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127549 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1

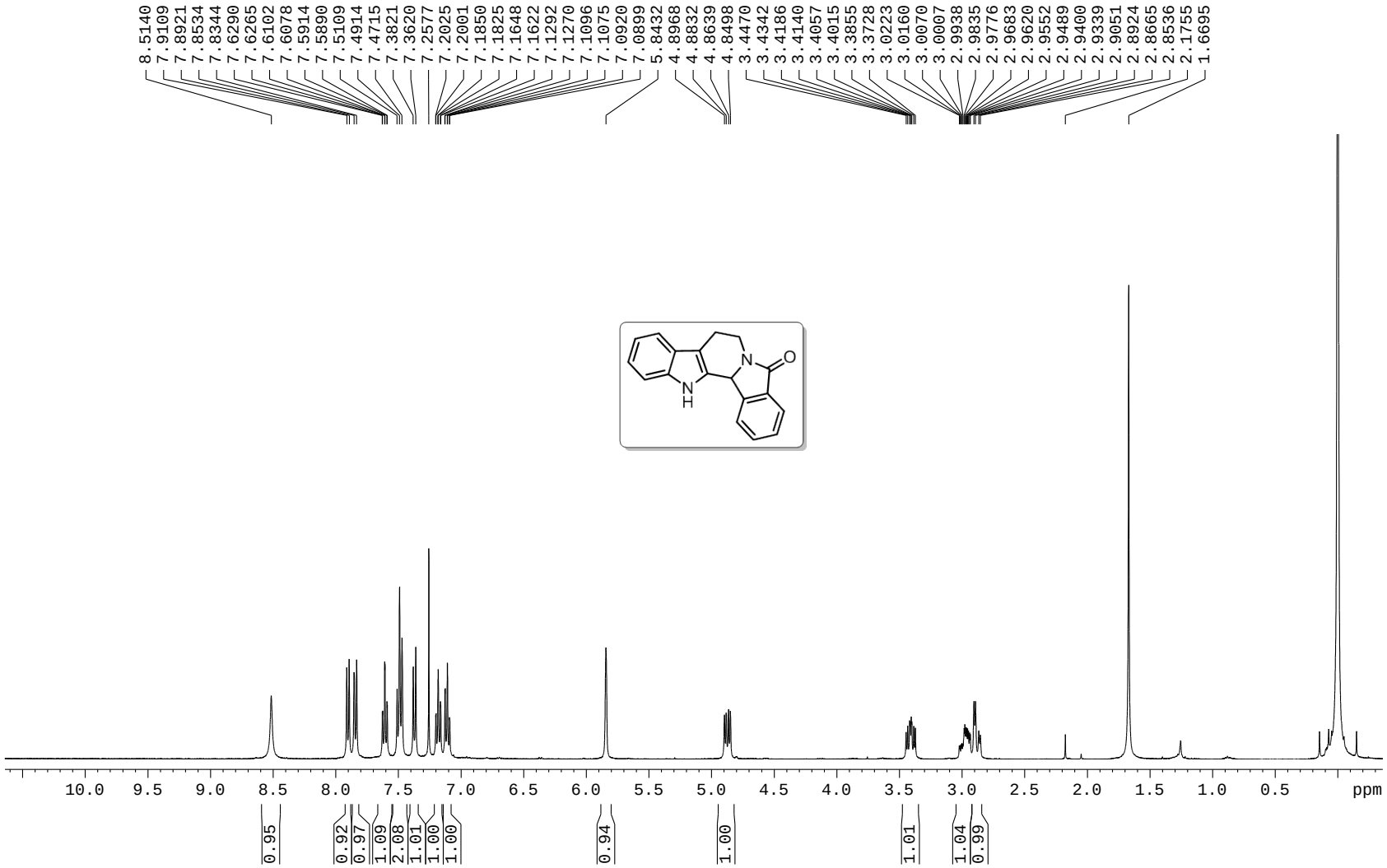


S77

```
Current Data Parameters
NAME          SMR-ALPHA
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20111221
Time              11.46
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   57
DW                20.800 usec
DE                 6.00 usec
TE                297.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127594 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

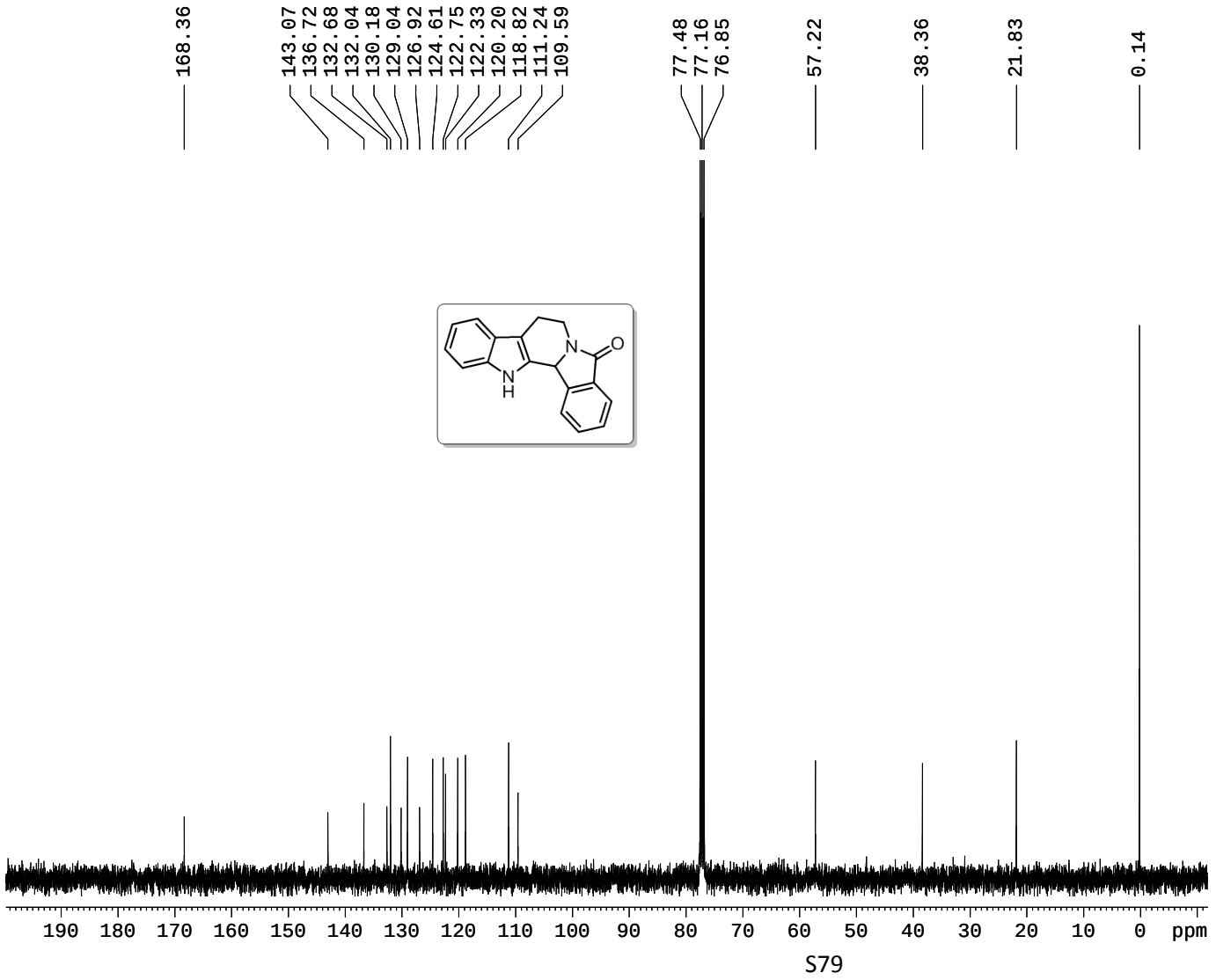
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



This journal is © The Royal Society of Chemistry 2012

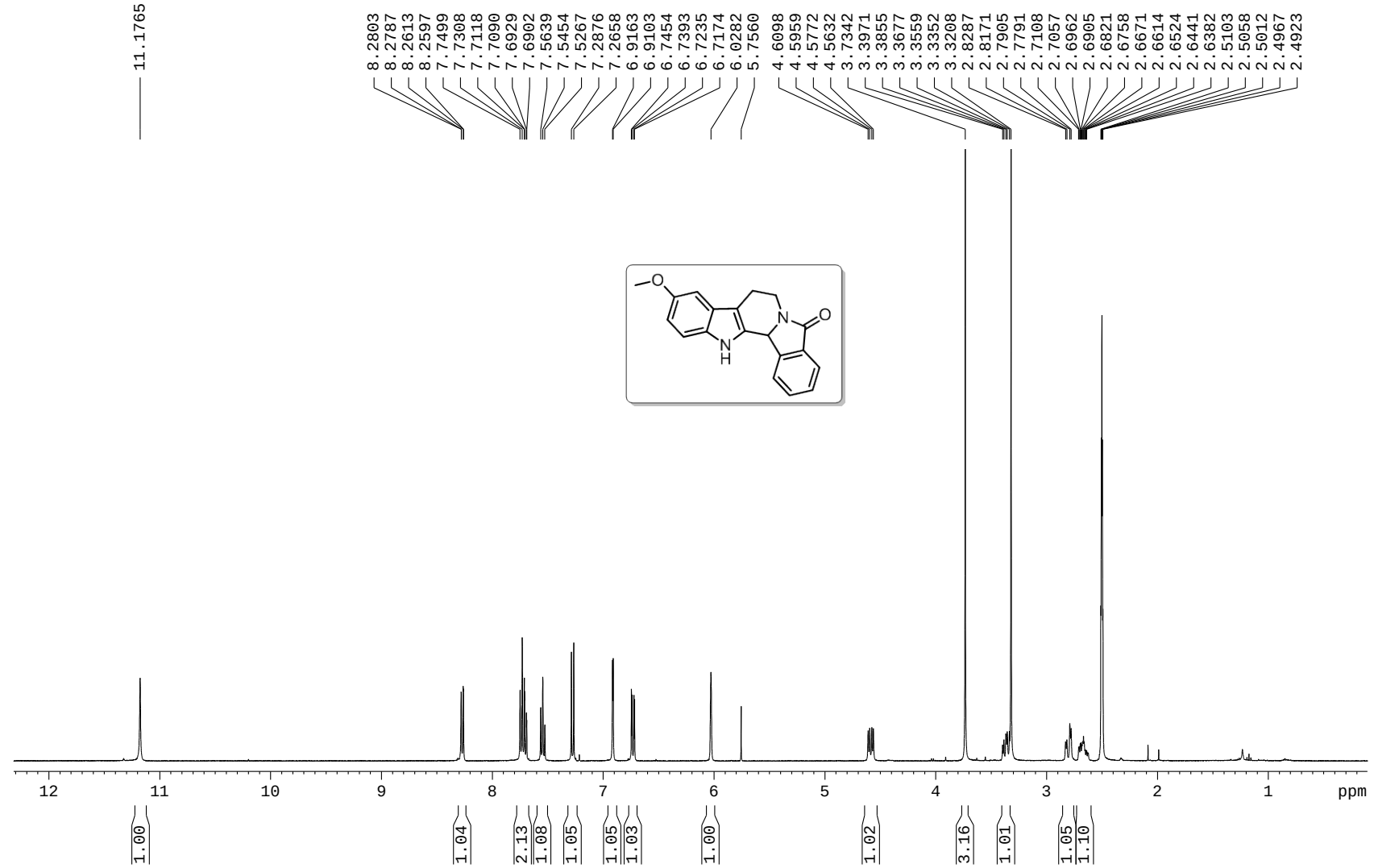
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME        SMR-I-206-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110420
Time              12.22
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                295.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

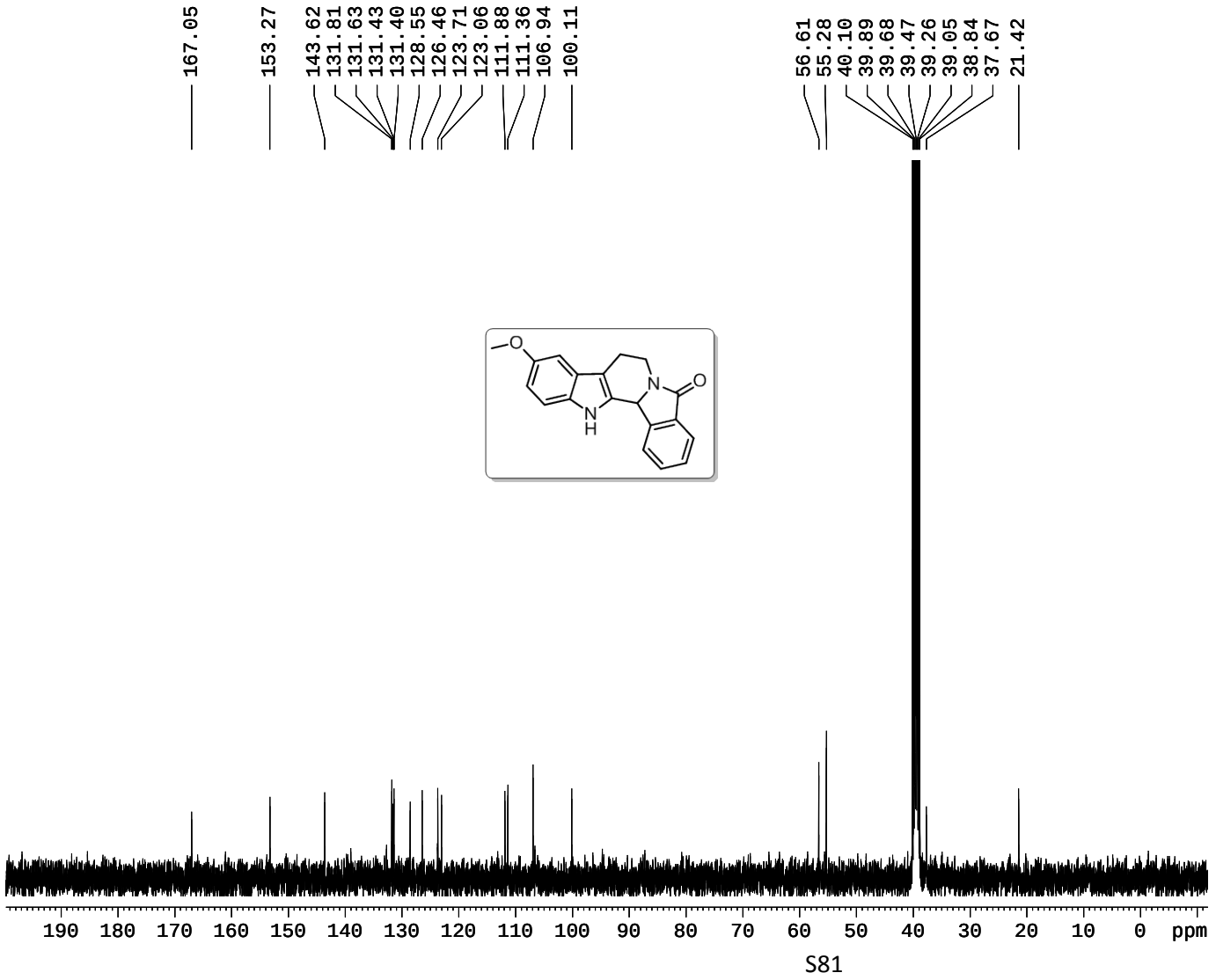
This journal is © The Royal Society of Chemistry 2012

PROTON DMSO {D:\CRR} crr 1



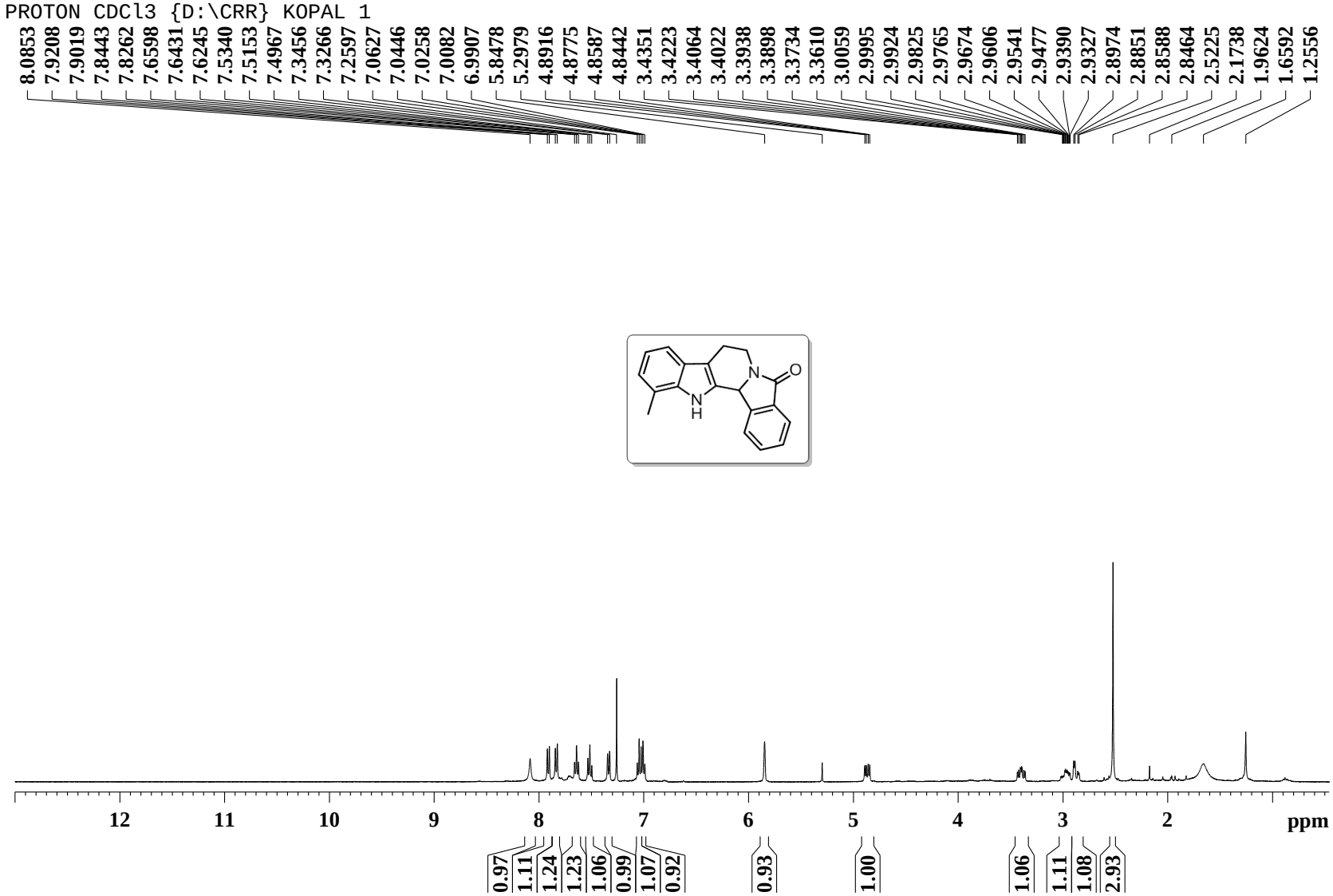
This journal is © The Royal Society of Chemistry 2012

C13CPD DMSO {D:\CRR} KOPAL 1



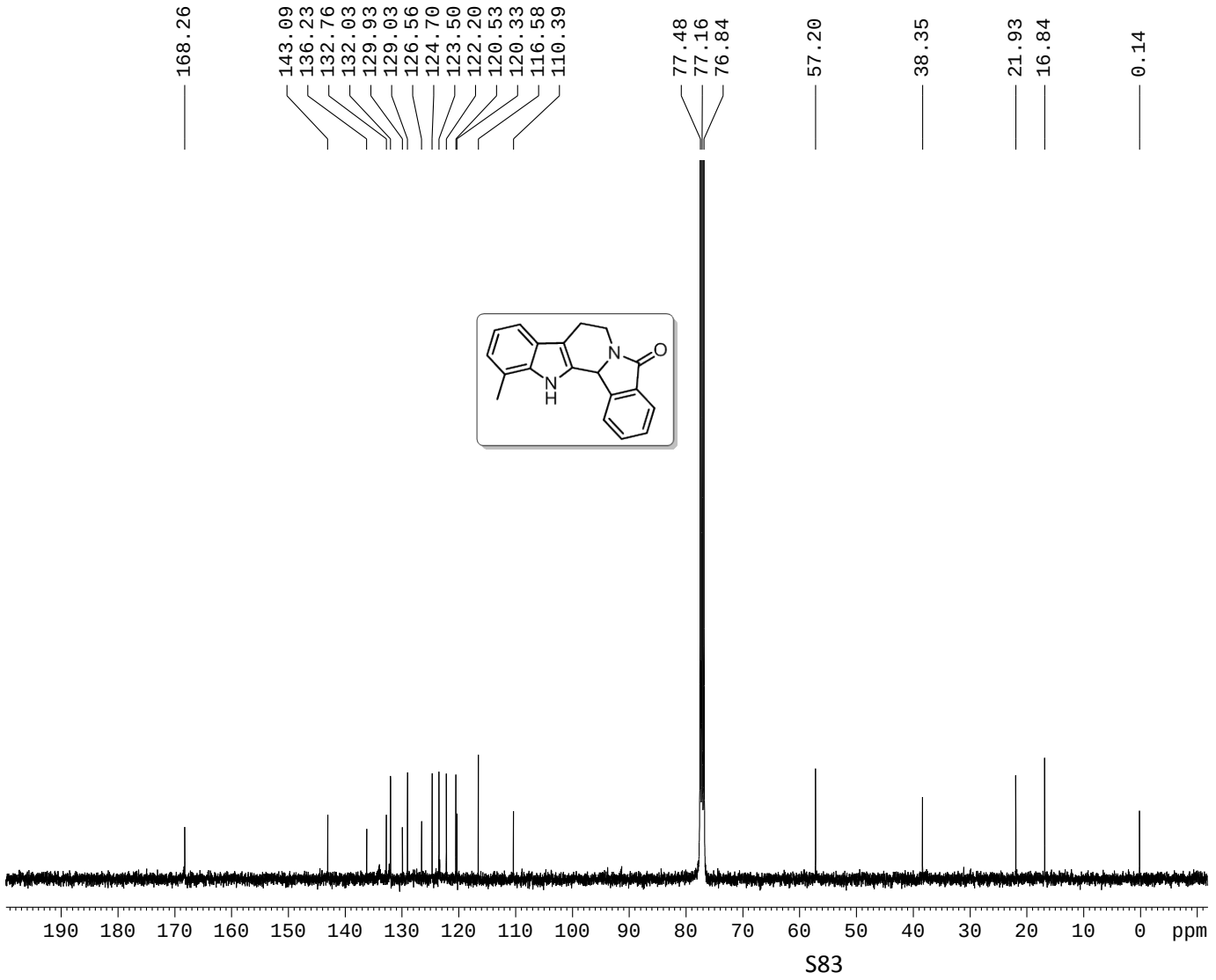

```
Current Data Parameters
NAME        SMR-I-237-2
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20110721
Time              16.52
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   876
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



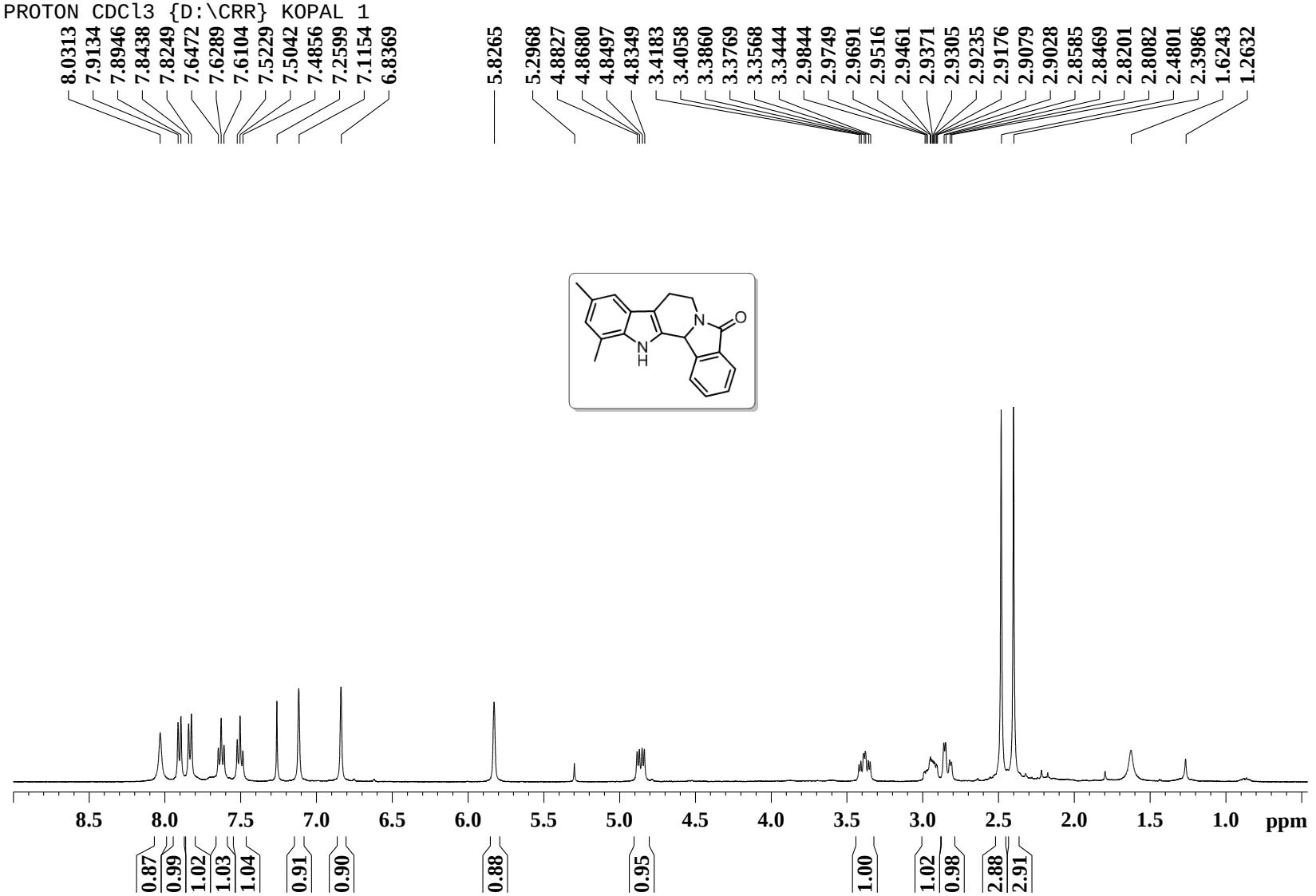
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



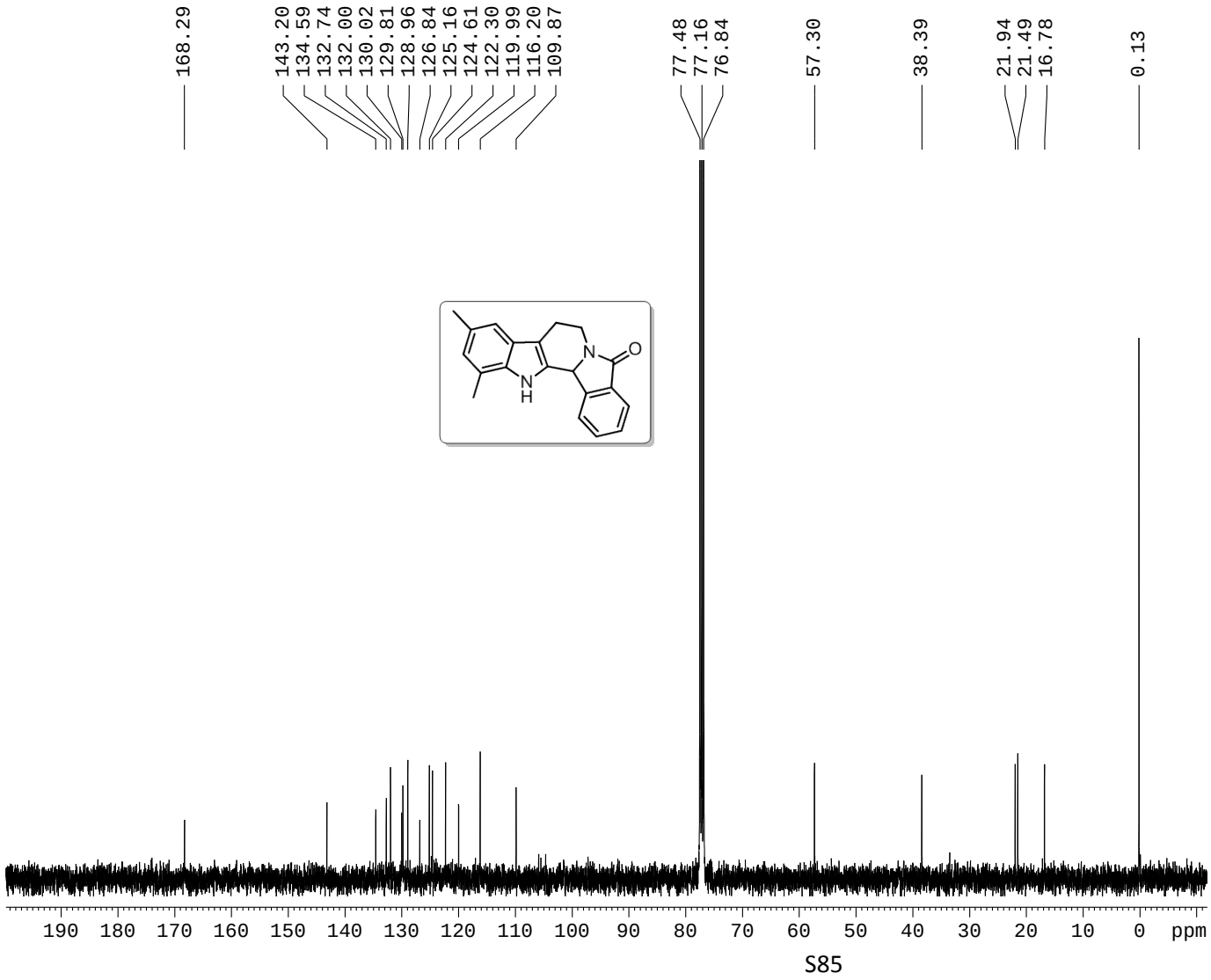

```
Current Data Parameters
NAME            SMR-OTPh
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120215
Time                9.24
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 17000
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.8 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127525 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

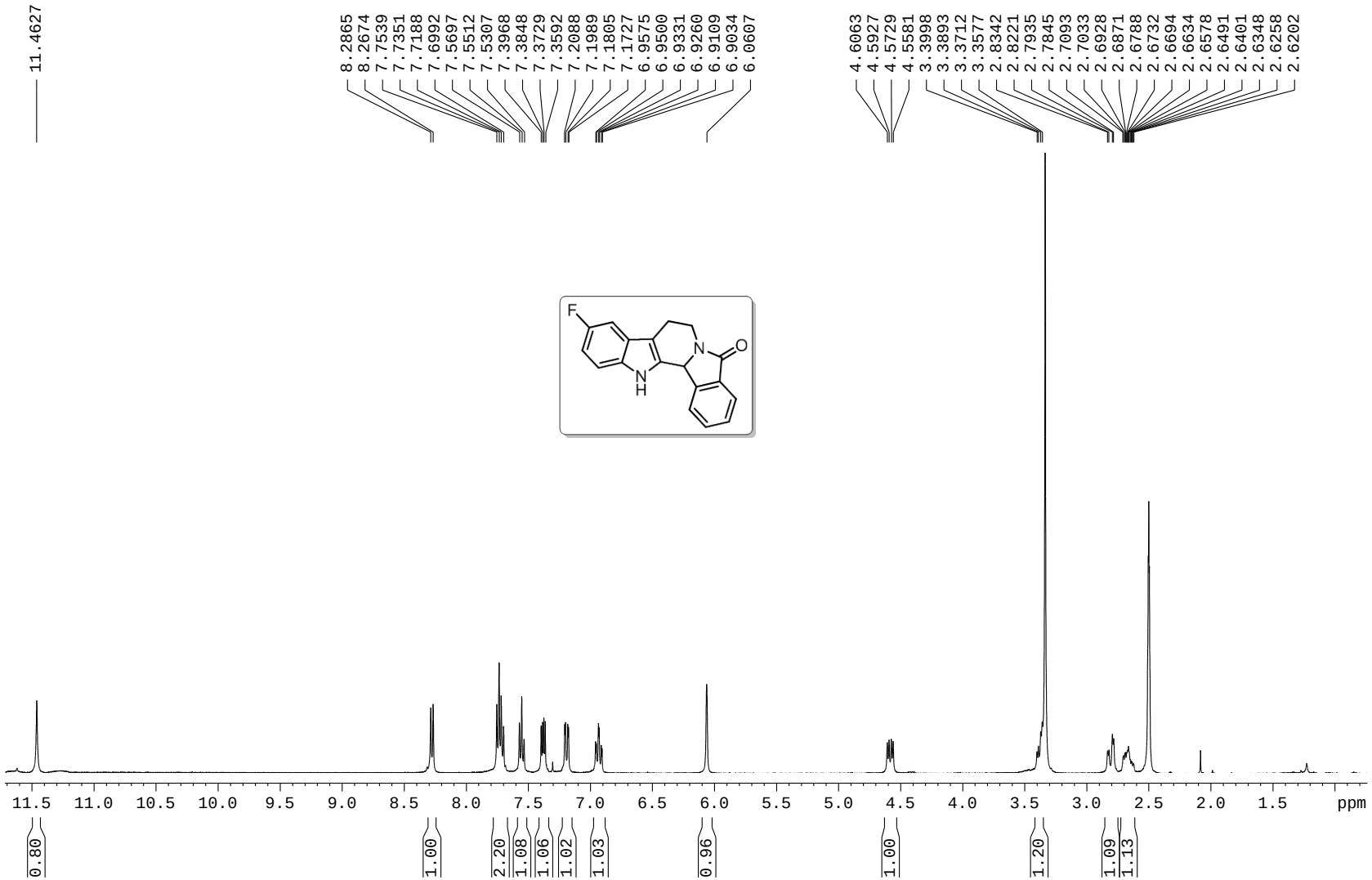
C13CPD CDCl3 {D:\CRR} KOPAL 1



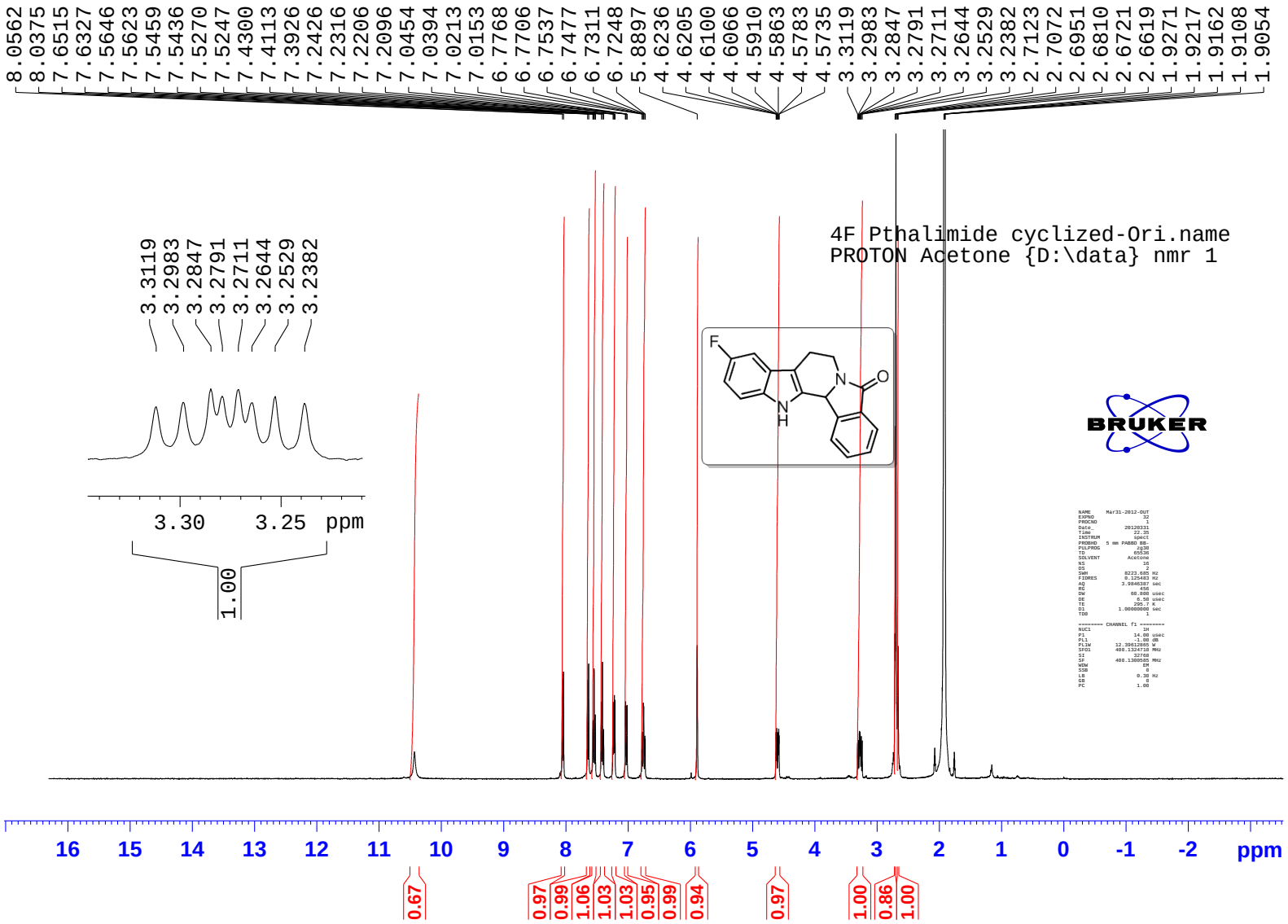

```
Current Data Parameters
NAME        SMR-I-228-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110622
Time              14.20
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1620
DW               20.800 usec
DE                6.00 usec
TE                298.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127524 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

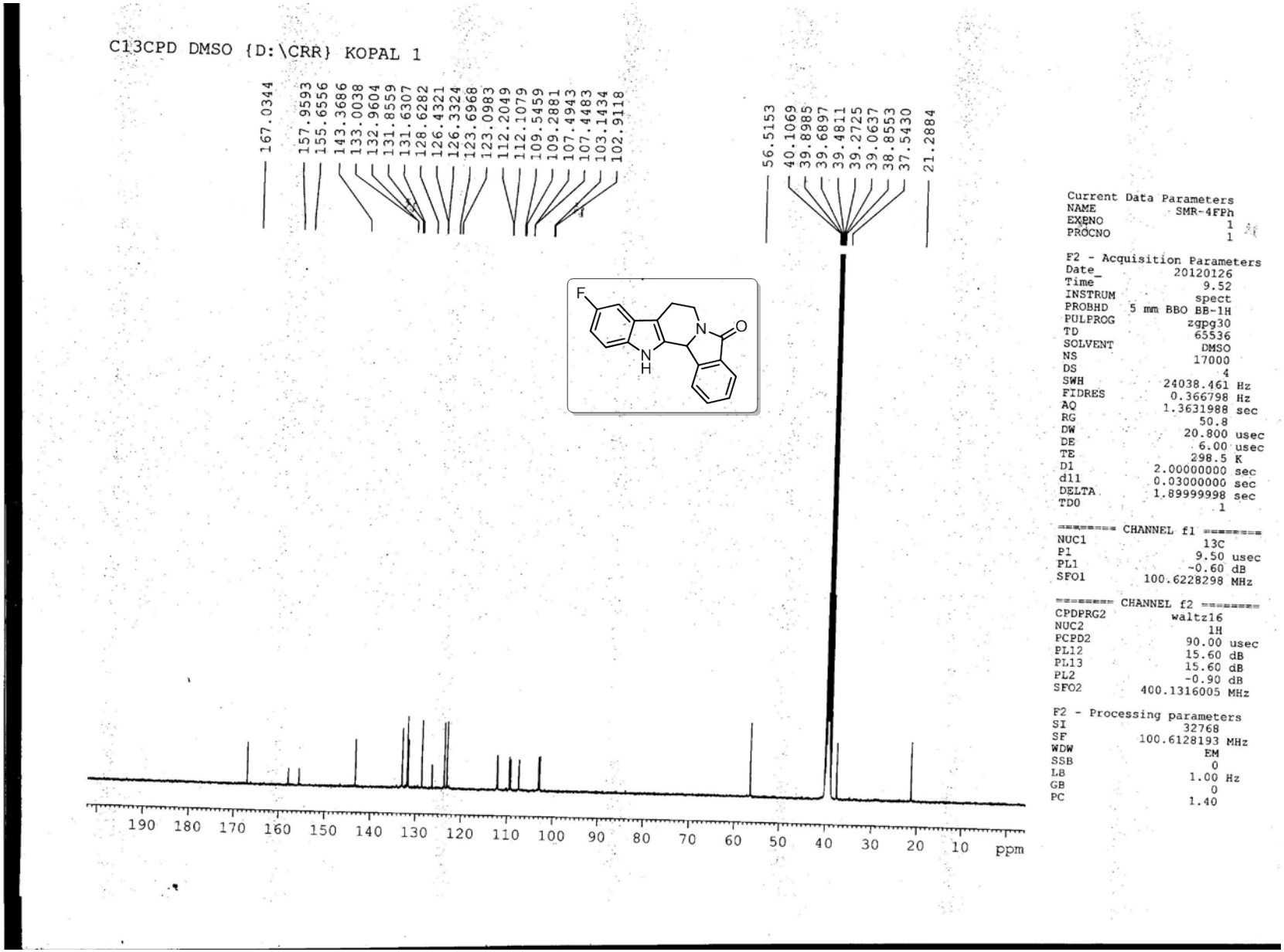
PROTON CDCl3 {D:\CRR} KOPAL 1



This journal is © The Royal Society of Chemistry 2012

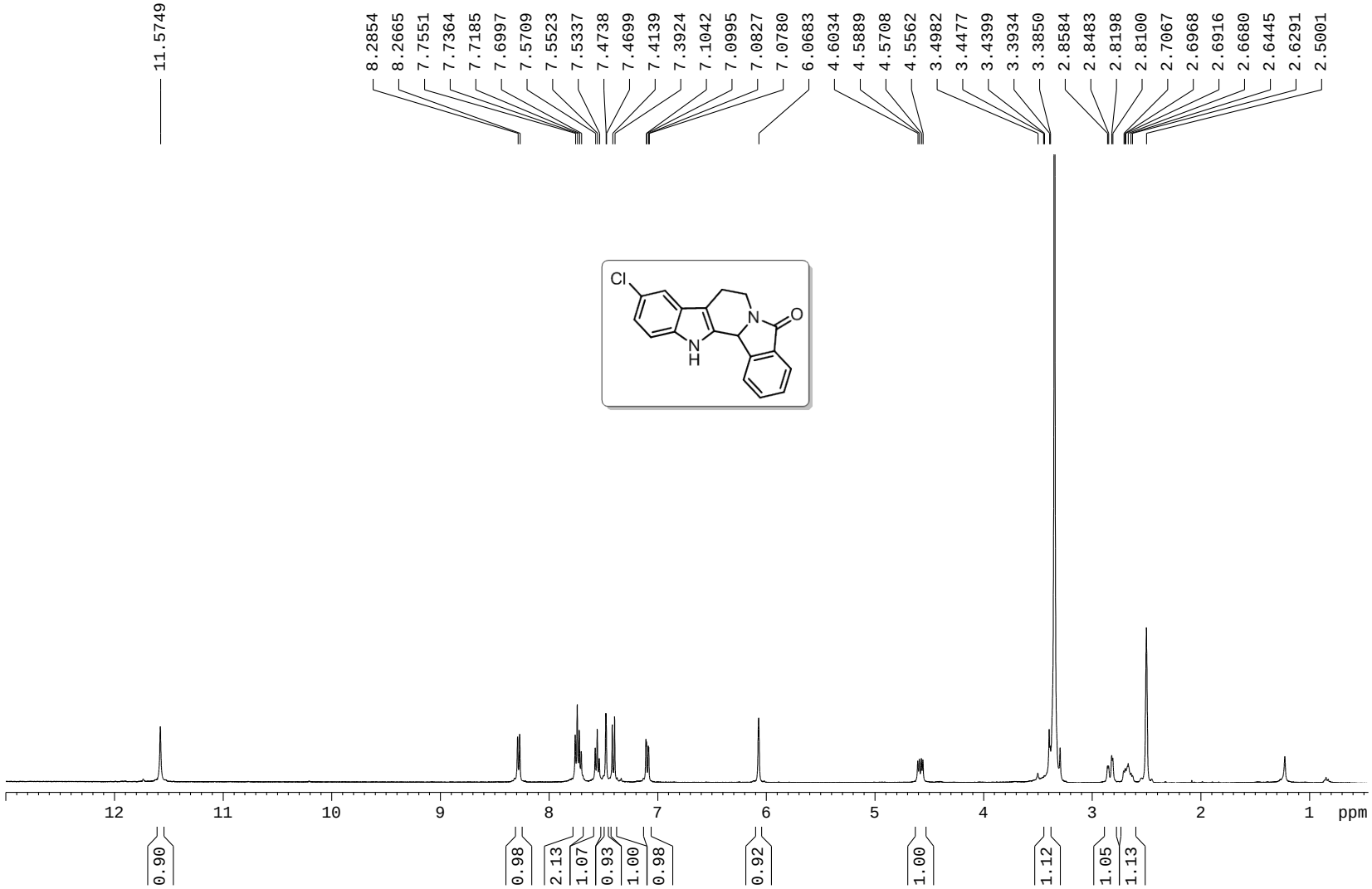


This journal is © The Royal Society of Chemistry 2012

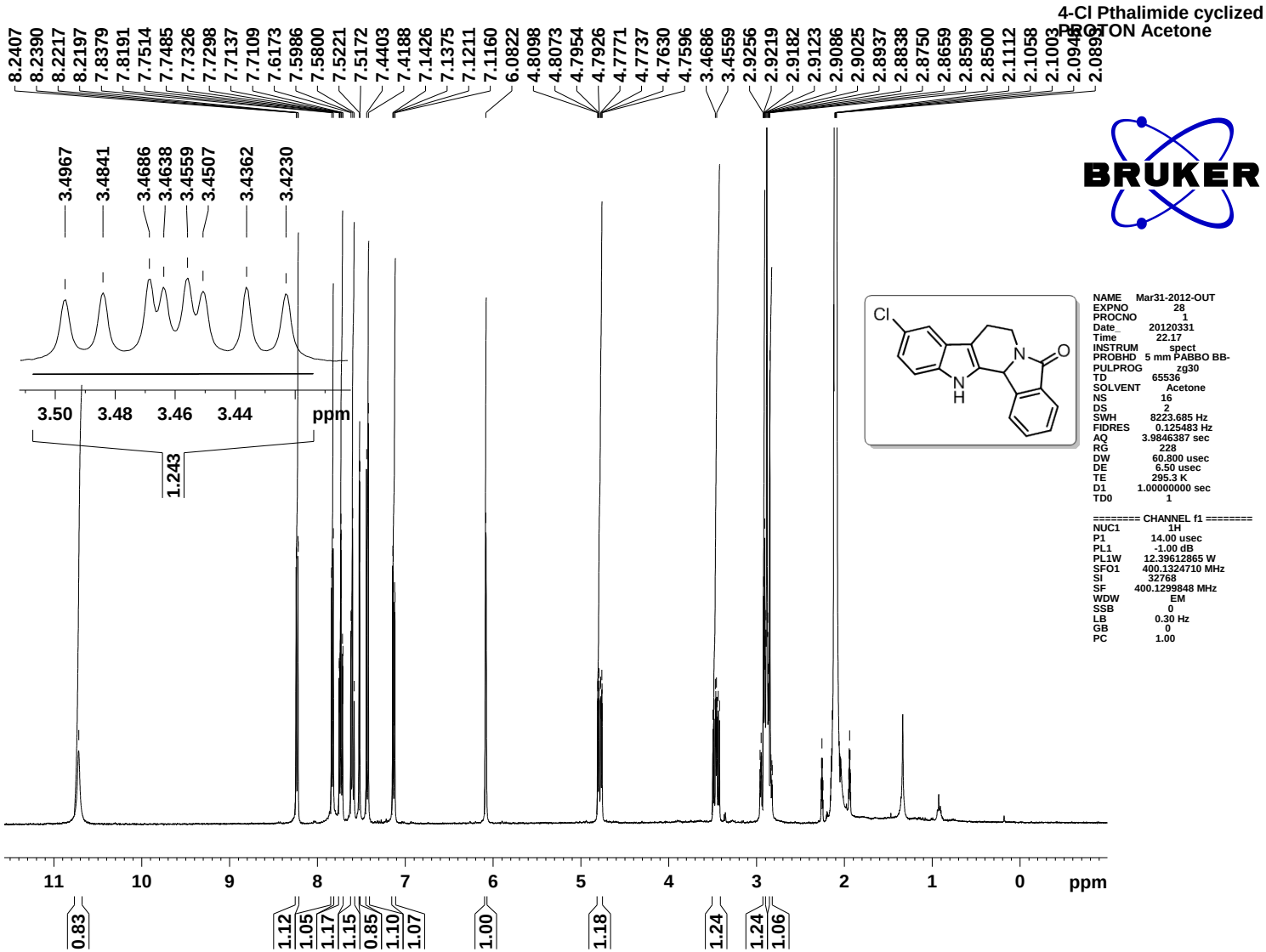


This journal is © The Royal Society of Chemistry 2012

PROTON DMSO {D:\CRR} KOPAL 1

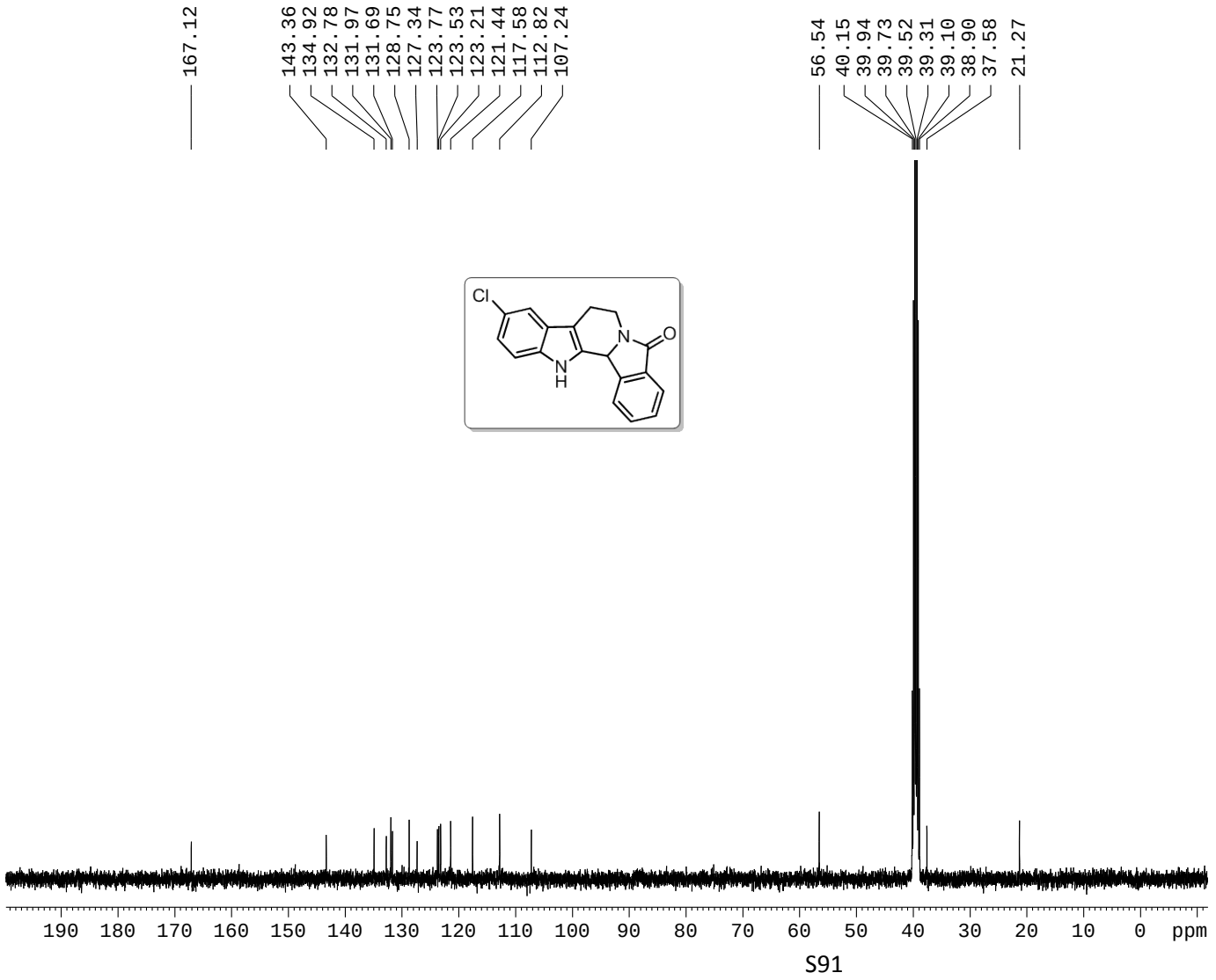


This journal is © The Royal Society of Chemistry 2012



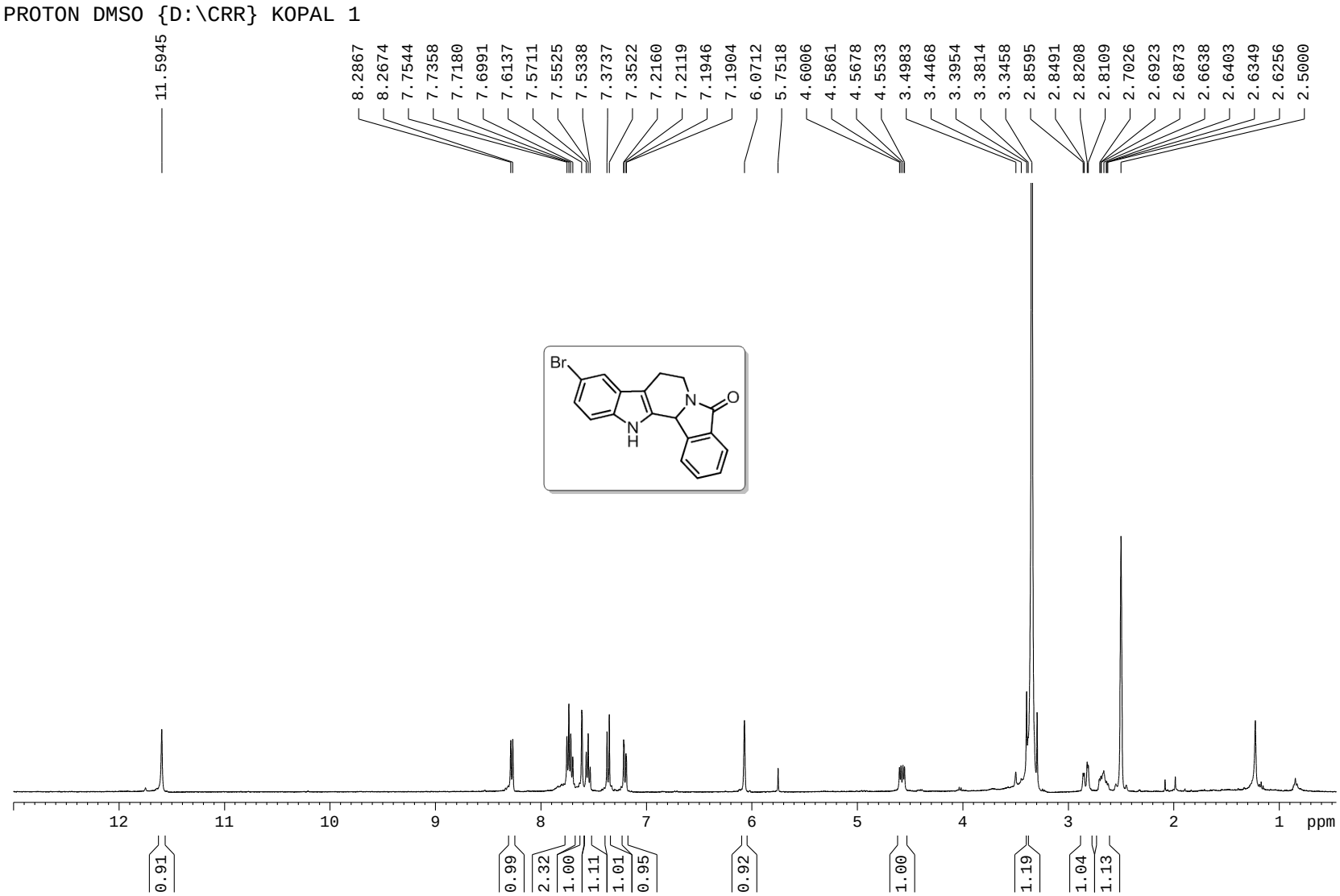
This journal is © The Royal Society of Chemistry 2012

C13CPD DMSO {D:\CRR} KOPAL 1

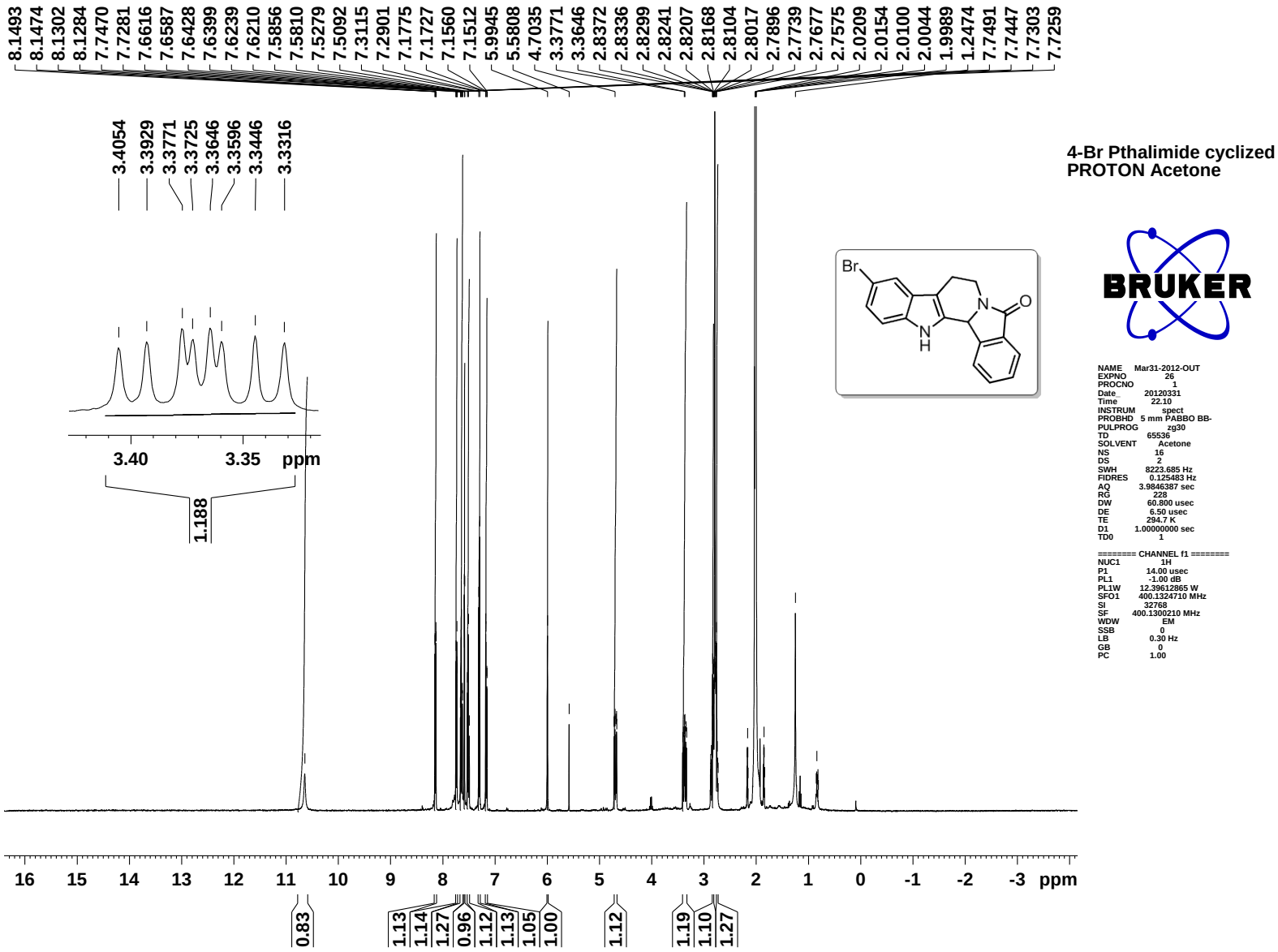



```
Current Data Parameters
NAME        SMR-I-214-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110525
Time              12.02
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128109 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

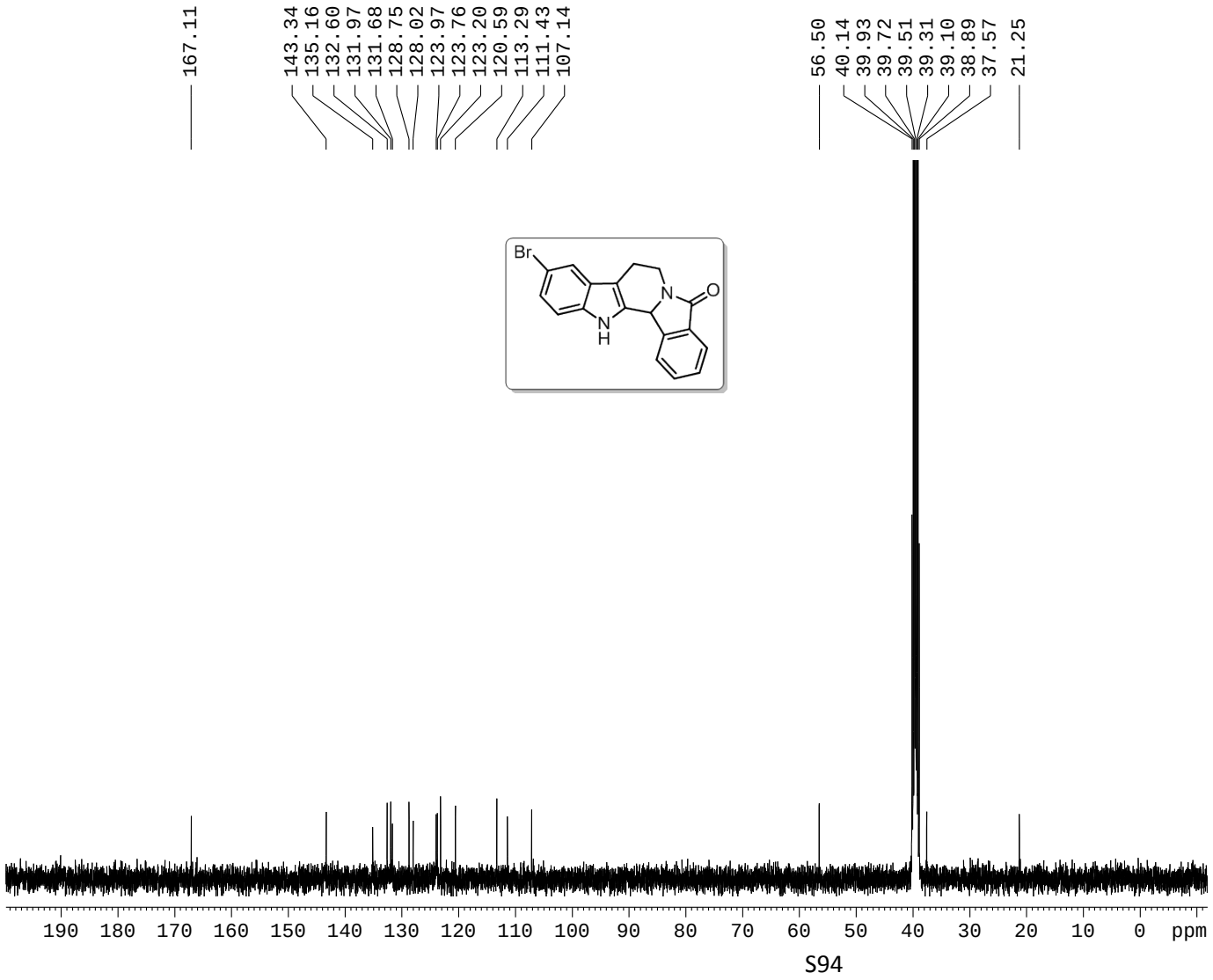


This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

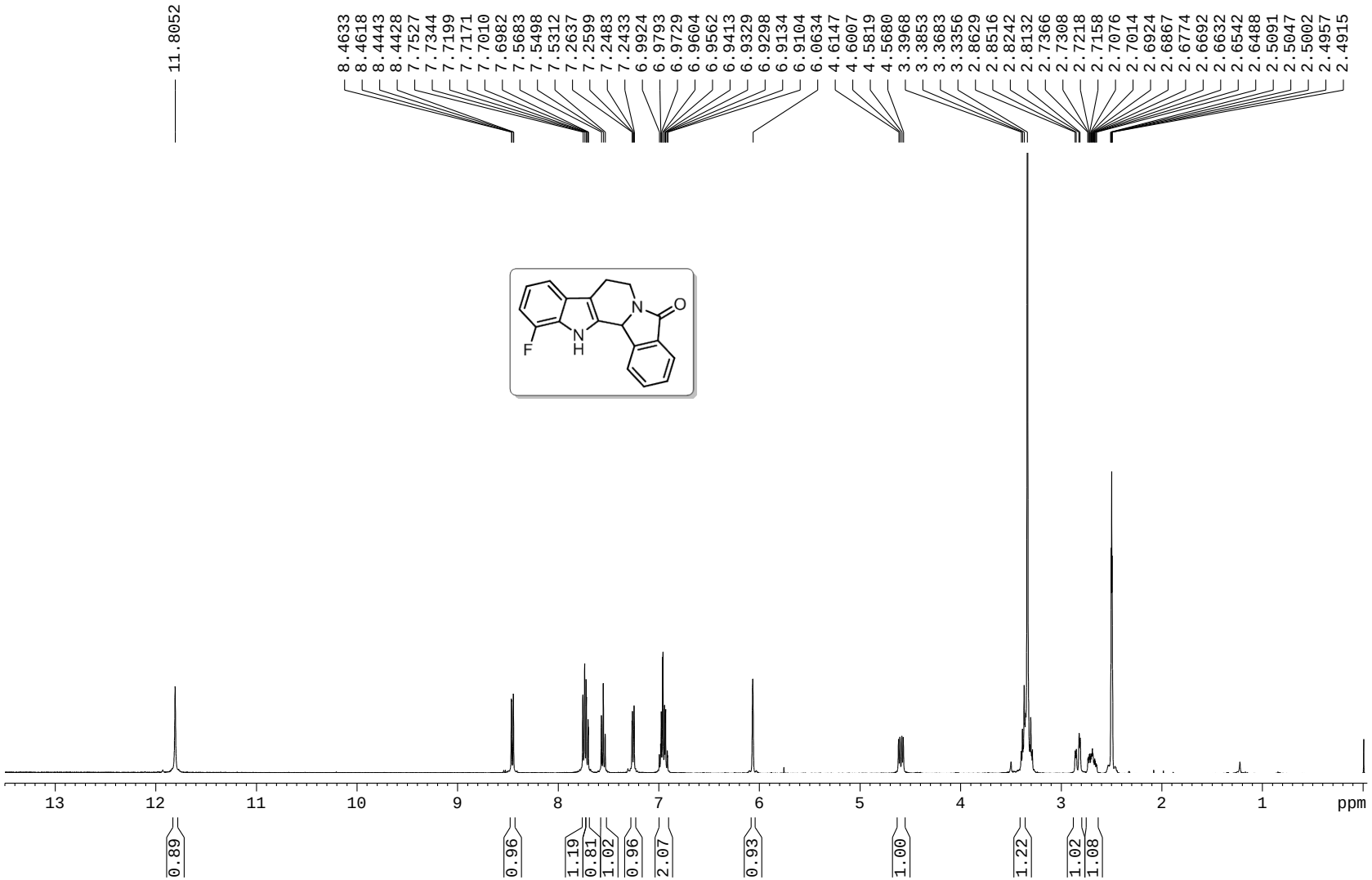
C13CPD DMSO {D:\CRR} KOPAL 1



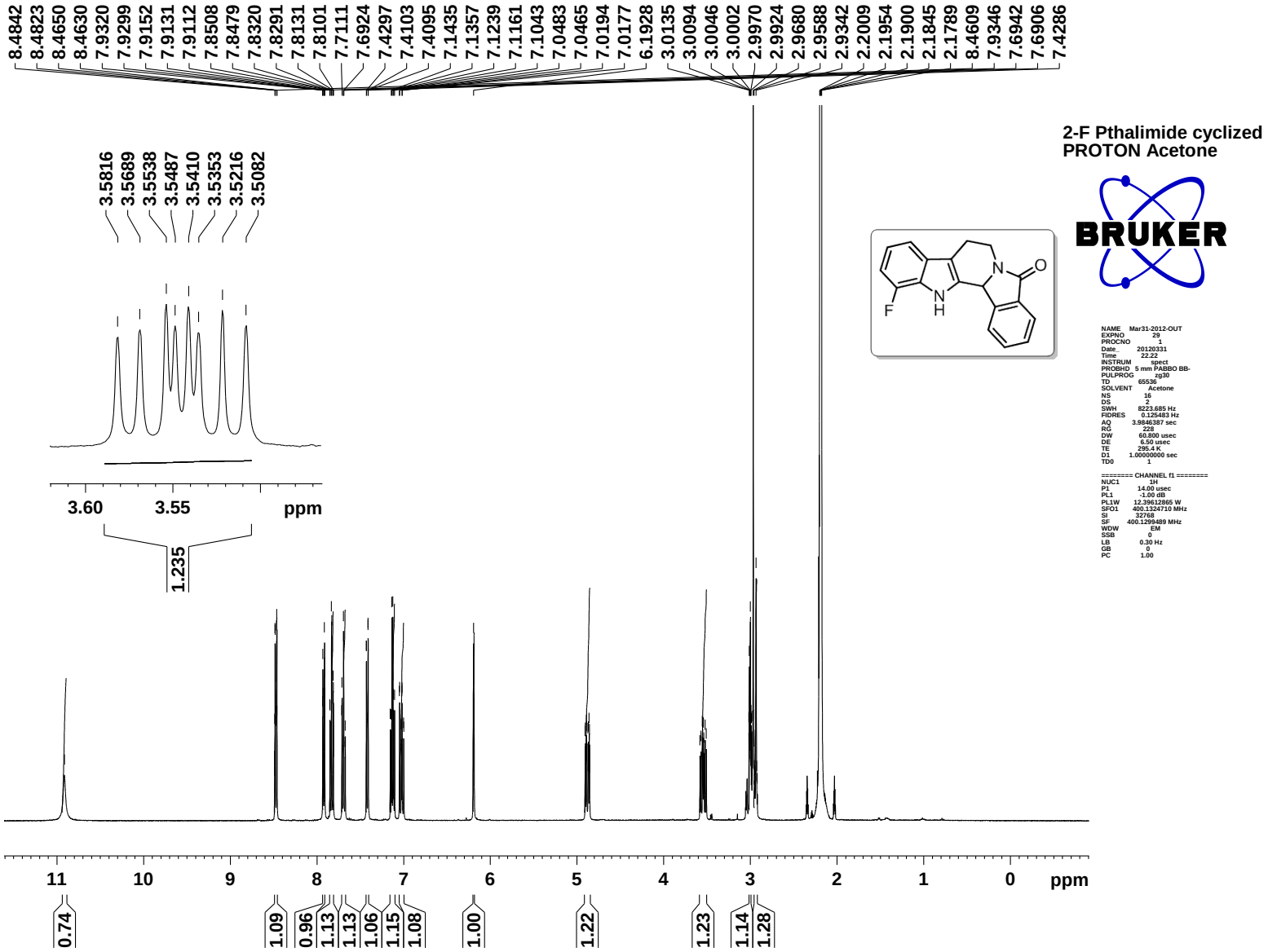

```
Current Data Parameters
NAME        SMR-I-215-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110525
Time              12.57
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD                65536
SOLVENT            DMSO
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                295.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128121 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012

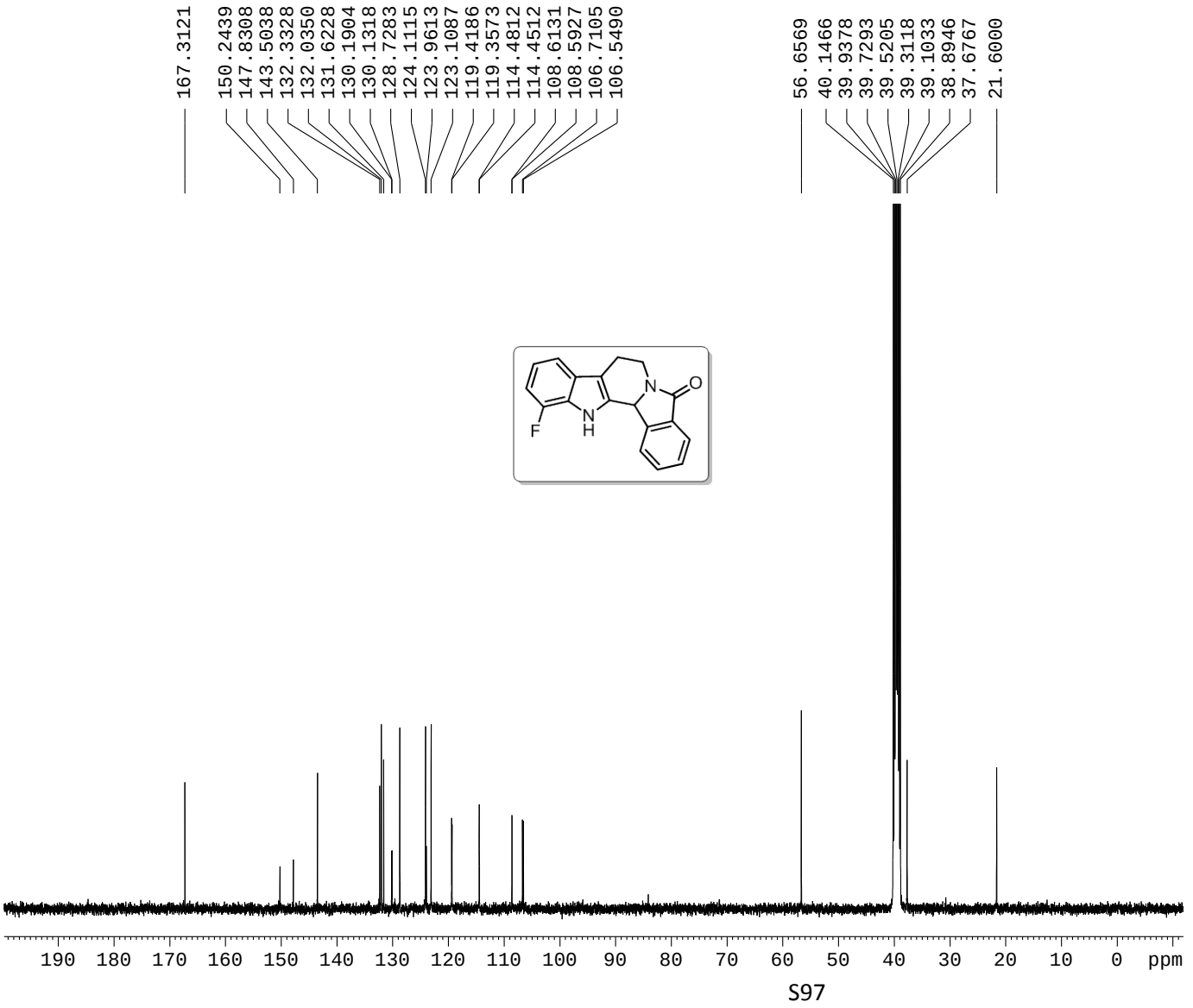
PROTON DMSO {D:\CRR} KOPAL 1



This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012



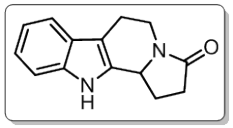

```
Current Data Parameters
NAME          SMR-BETCAR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120112
Time                9.30
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                 17000
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                 6.00 usec
TE                293.9 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128113 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

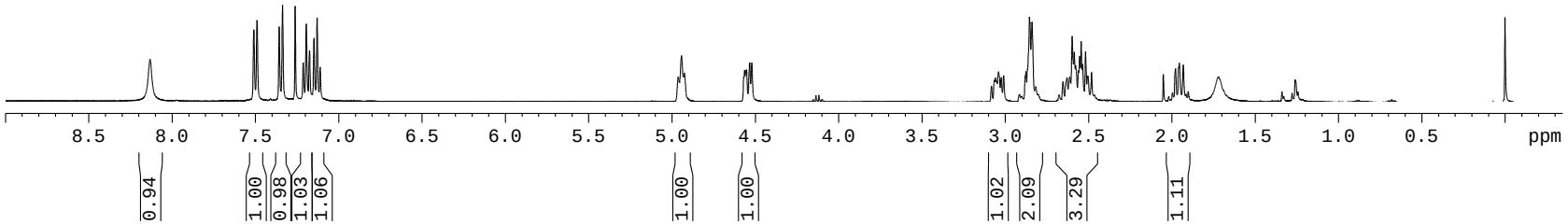
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1

8.1325 7.5083 7.4889 7.3559 7.3359 7.2601 7.2112 7.1933 7.1736 7.1483 7.1300 7.1118

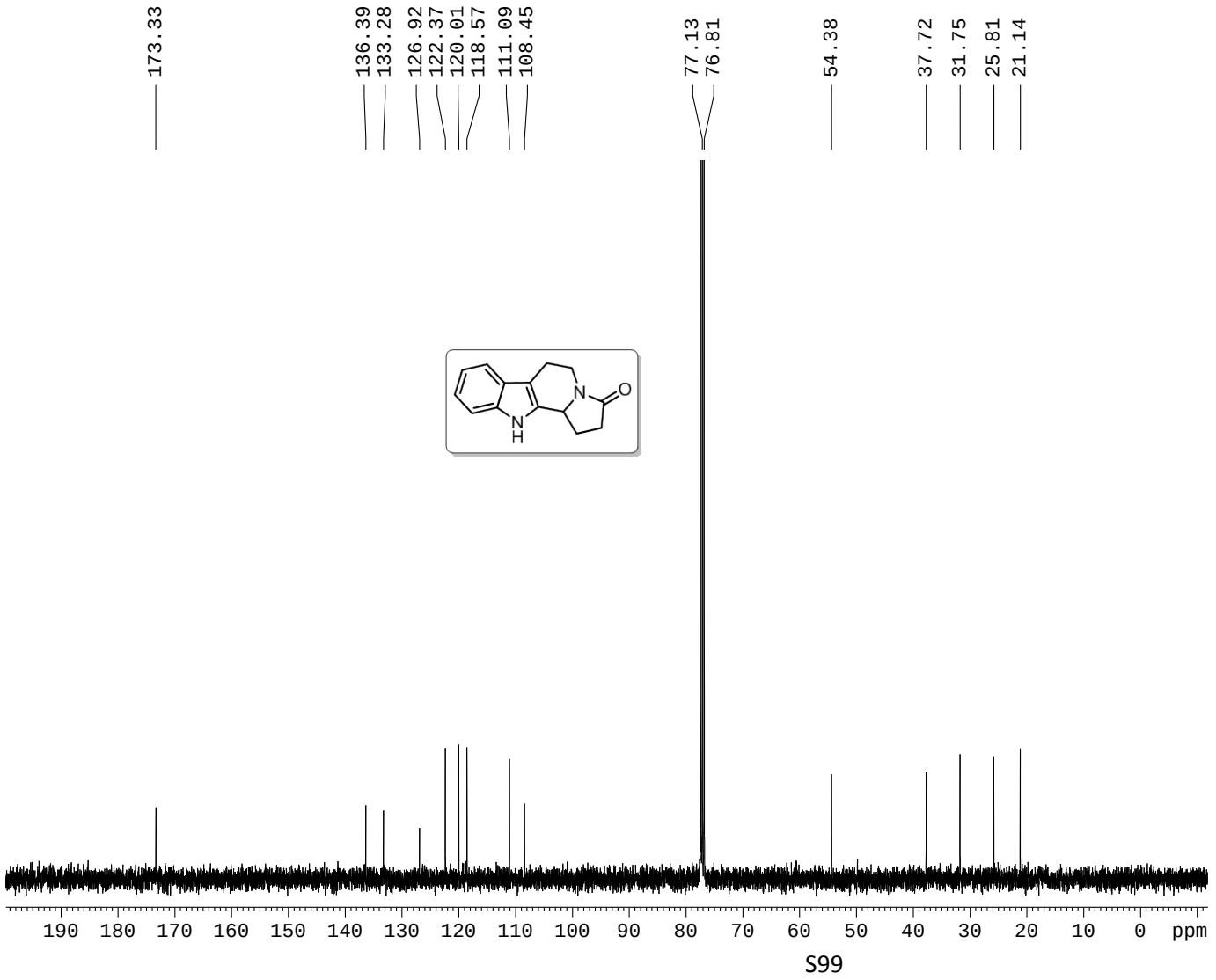
4.9621 4.9414 4.9239 4.5678 4.5628 4.5562 4.5512 4.5324 4.5194 4.1348 4.1170 3.0812 3.0640 3.0570 3.0493 3.0393 3.0230 3.0081 2.9174 2.9128 2.9043 2.8991 2.8792 2.8746 2.8655 2.8534 2.8375 2.8154 2.8007 2.6523 2.6277 2.6116 2.5971 2.5844 2.5762 2.5728 2.5585 2.5520 2.5431 2.5346 2.5166 2.5050 2.5014 2.4808 2.0499 1.9953 1.9766 1.9588 1.9539 1.9300 1.9007 1.7231 1.3410 1.3297 1.2802





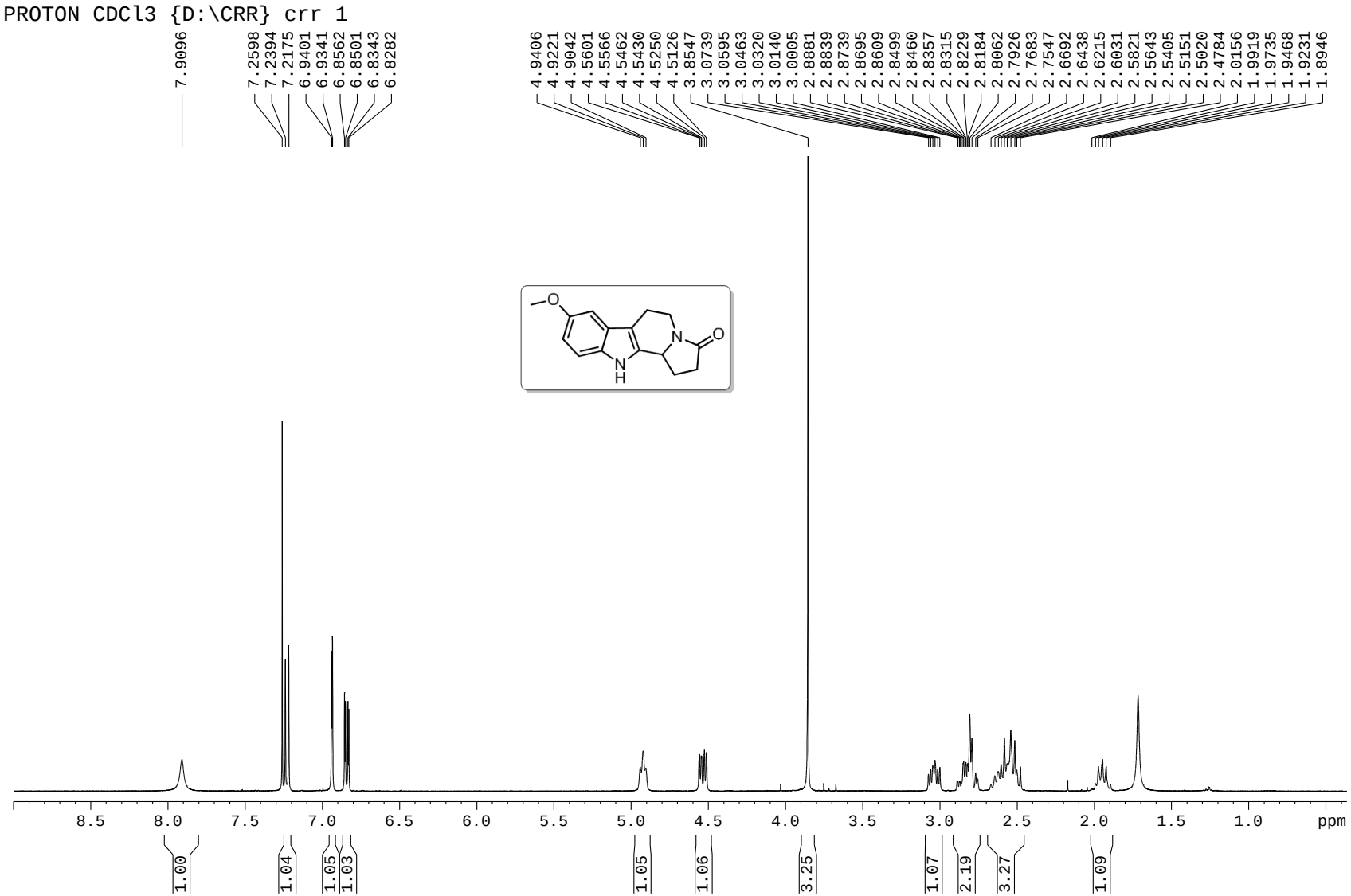
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



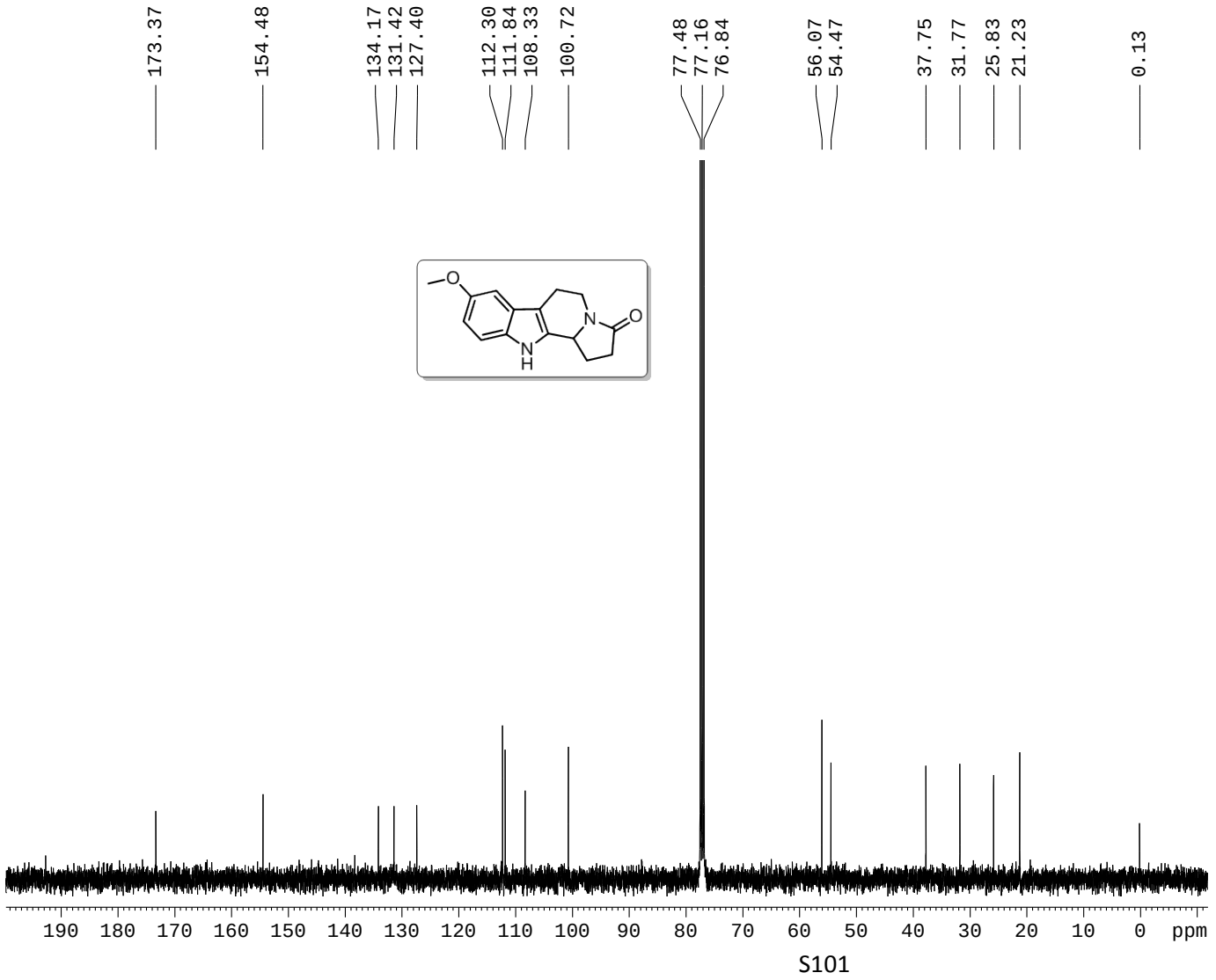

```
Current Data Parameters
NAME        SMR-1-109-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100817
Time              12.53
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127584 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



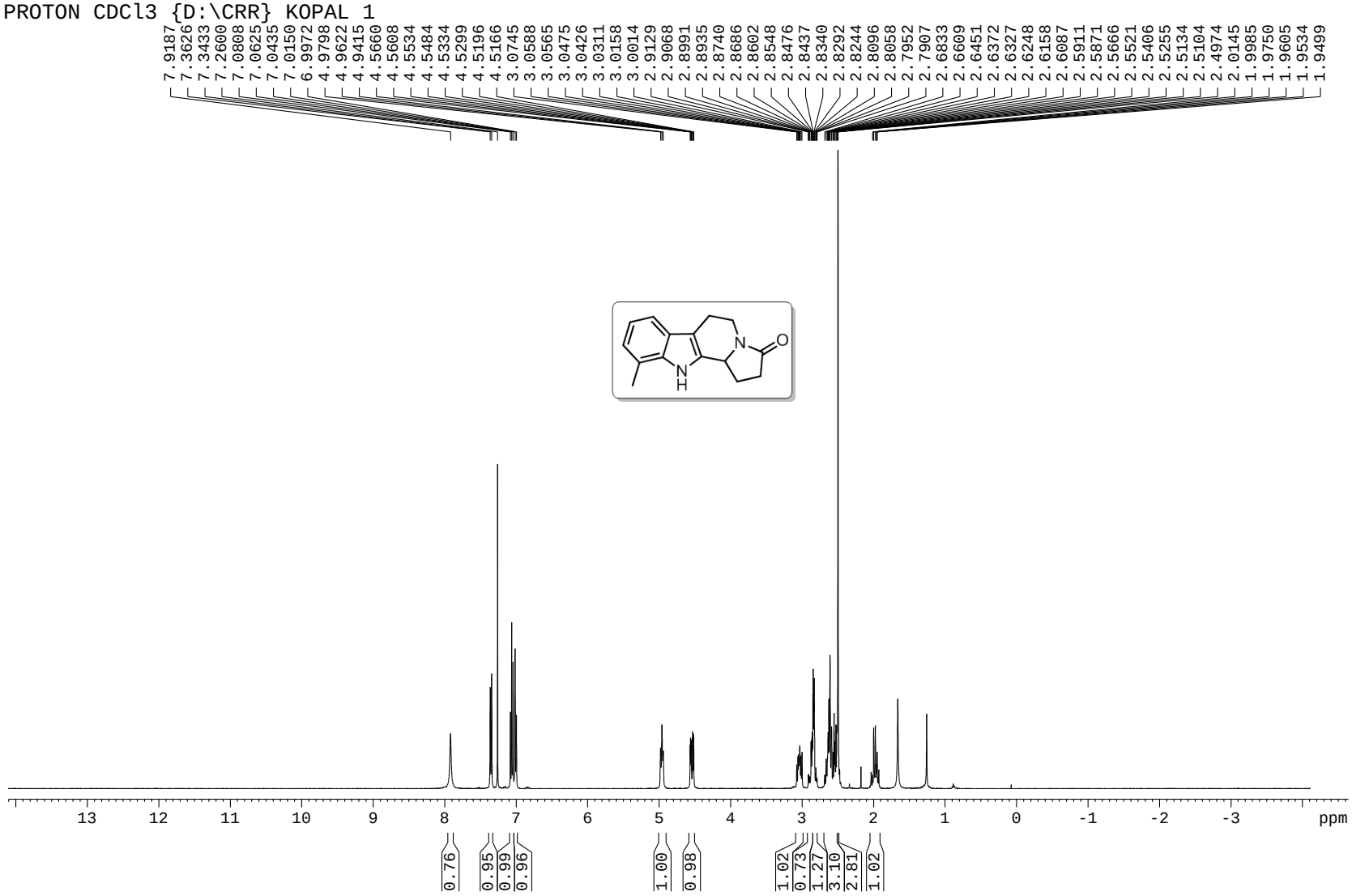
This journal is © The Royal Society of Chemistry 2012

C13CPD DMSO {D:\CRR} KOPAL 1



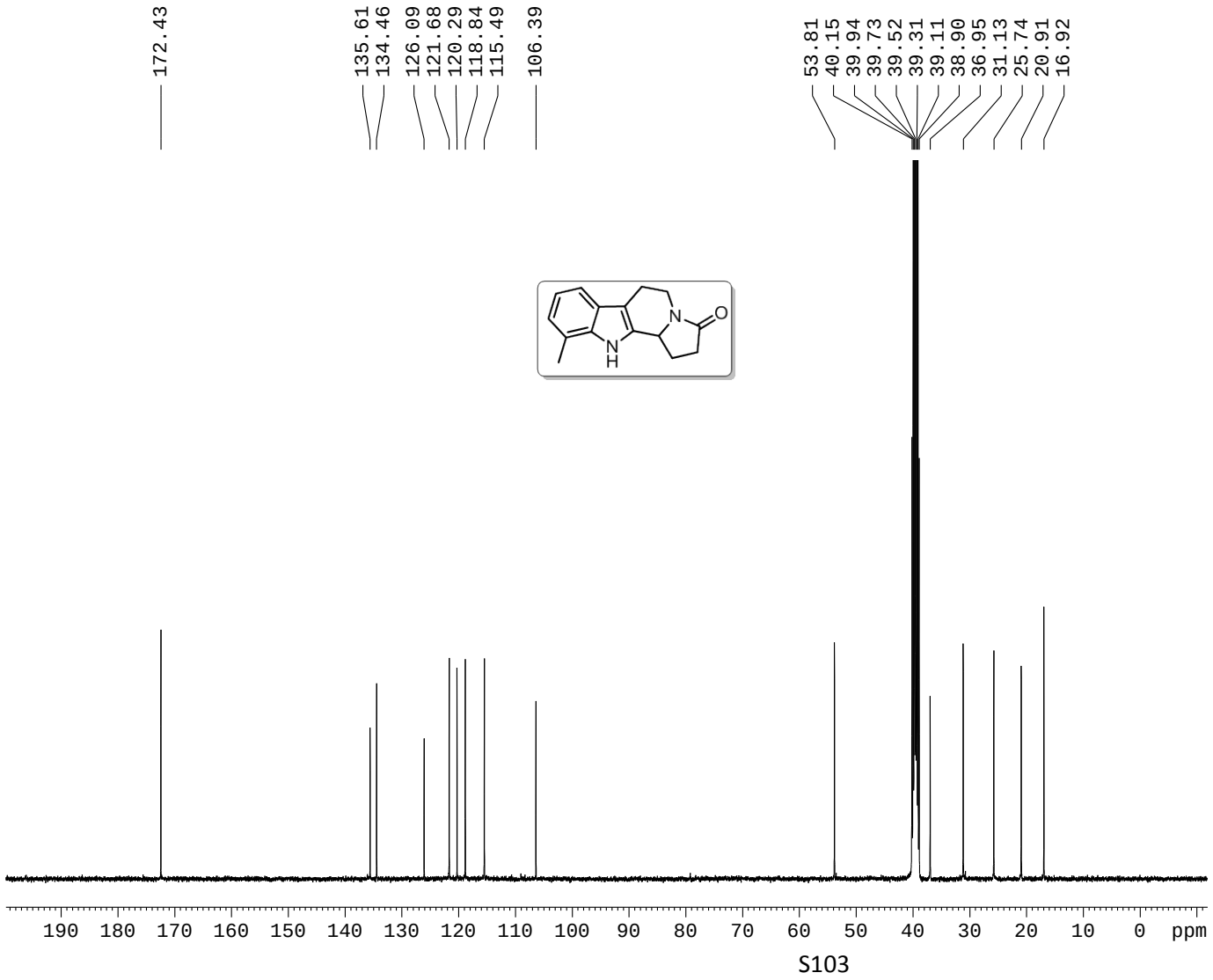

```
Current Data Parameters
NAME        SMR-I-236-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110719
Time              14.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   341
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  1150
DW                20.800 usec
DE                 6.00 usec
TE                296.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6122763 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



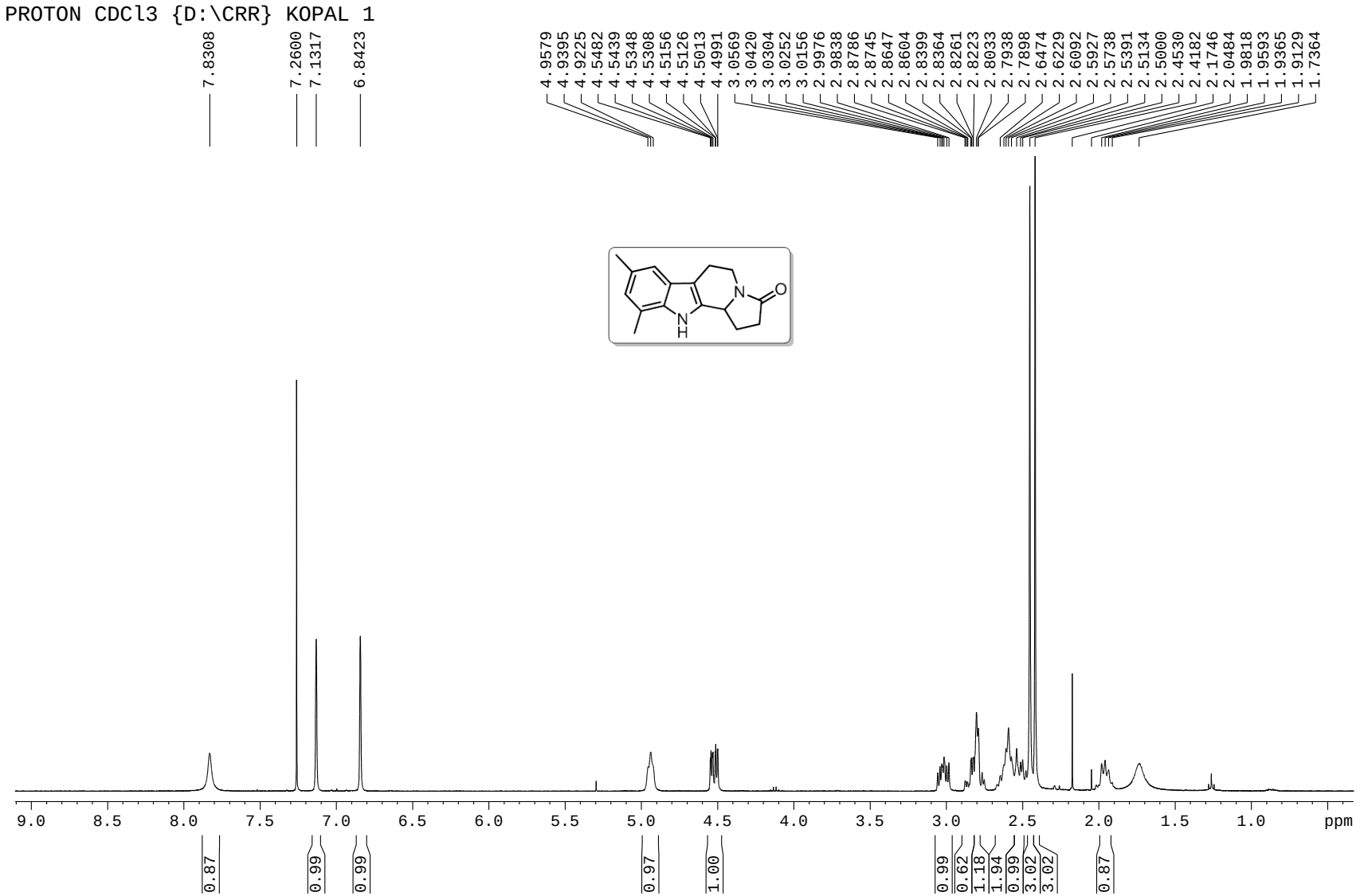
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



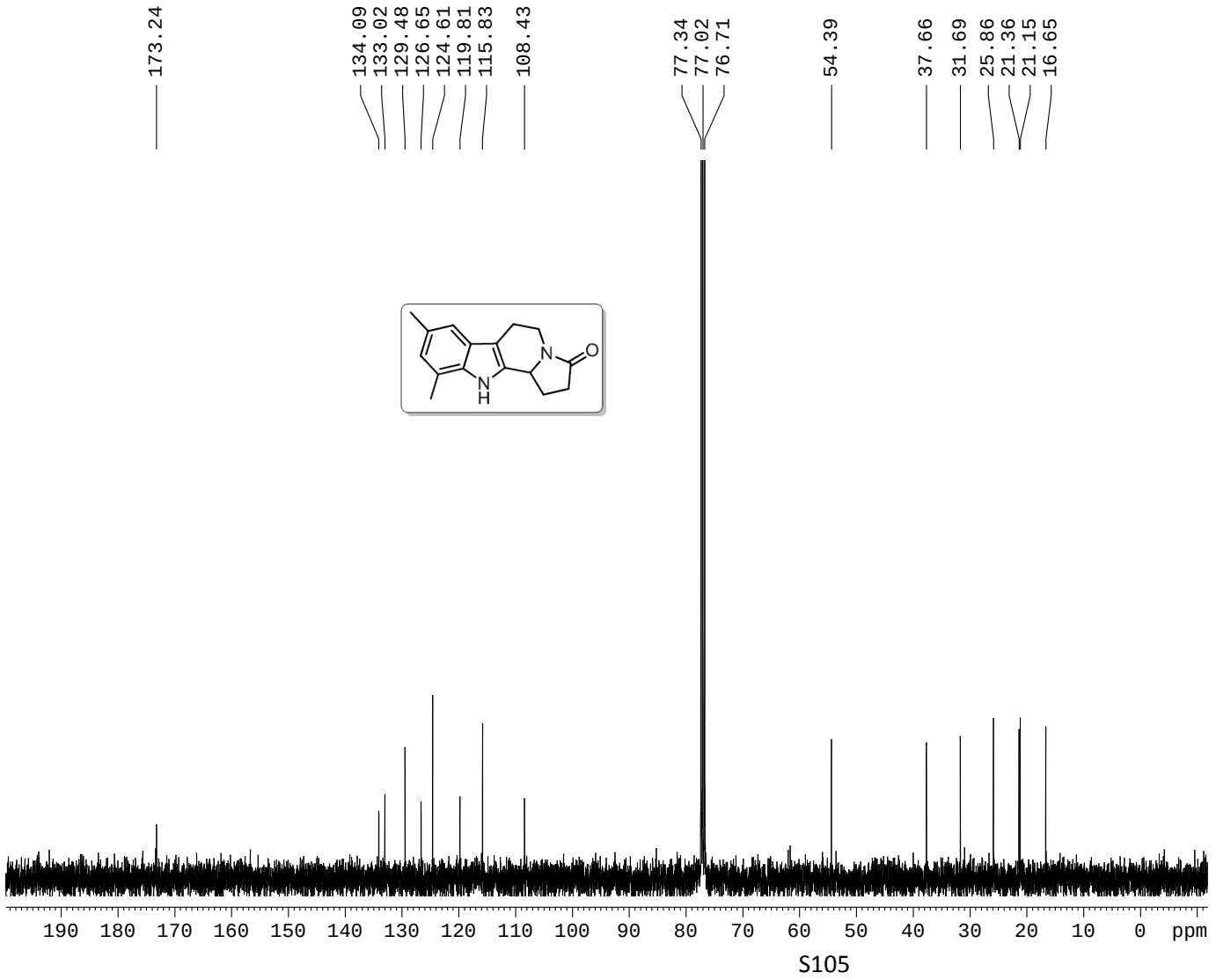

```
Current Data Parameters
NAME      CRR-SMR-CON-H
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20120229
Time               9.48
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                18000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                291.9 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6132881 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012



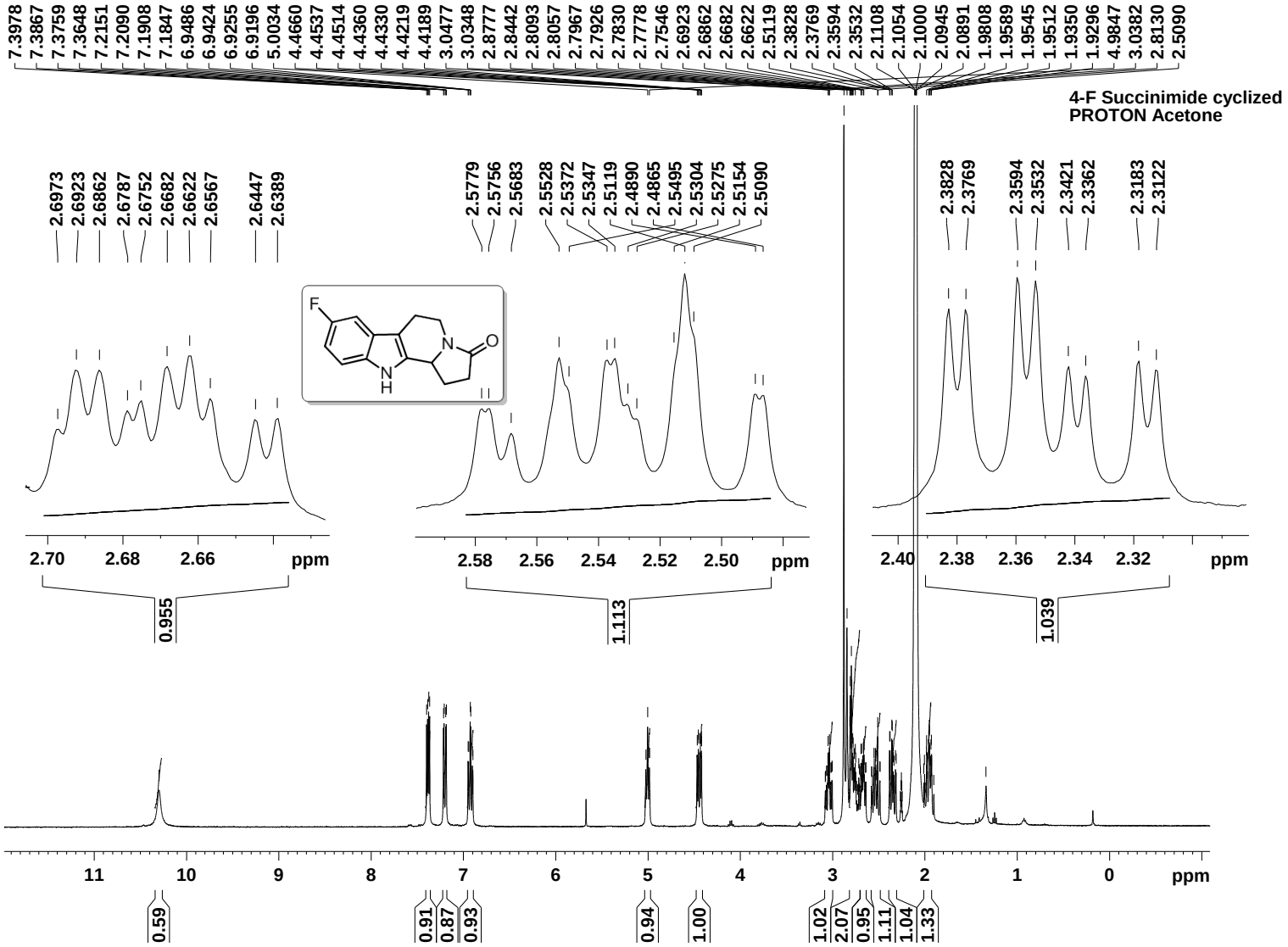
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1

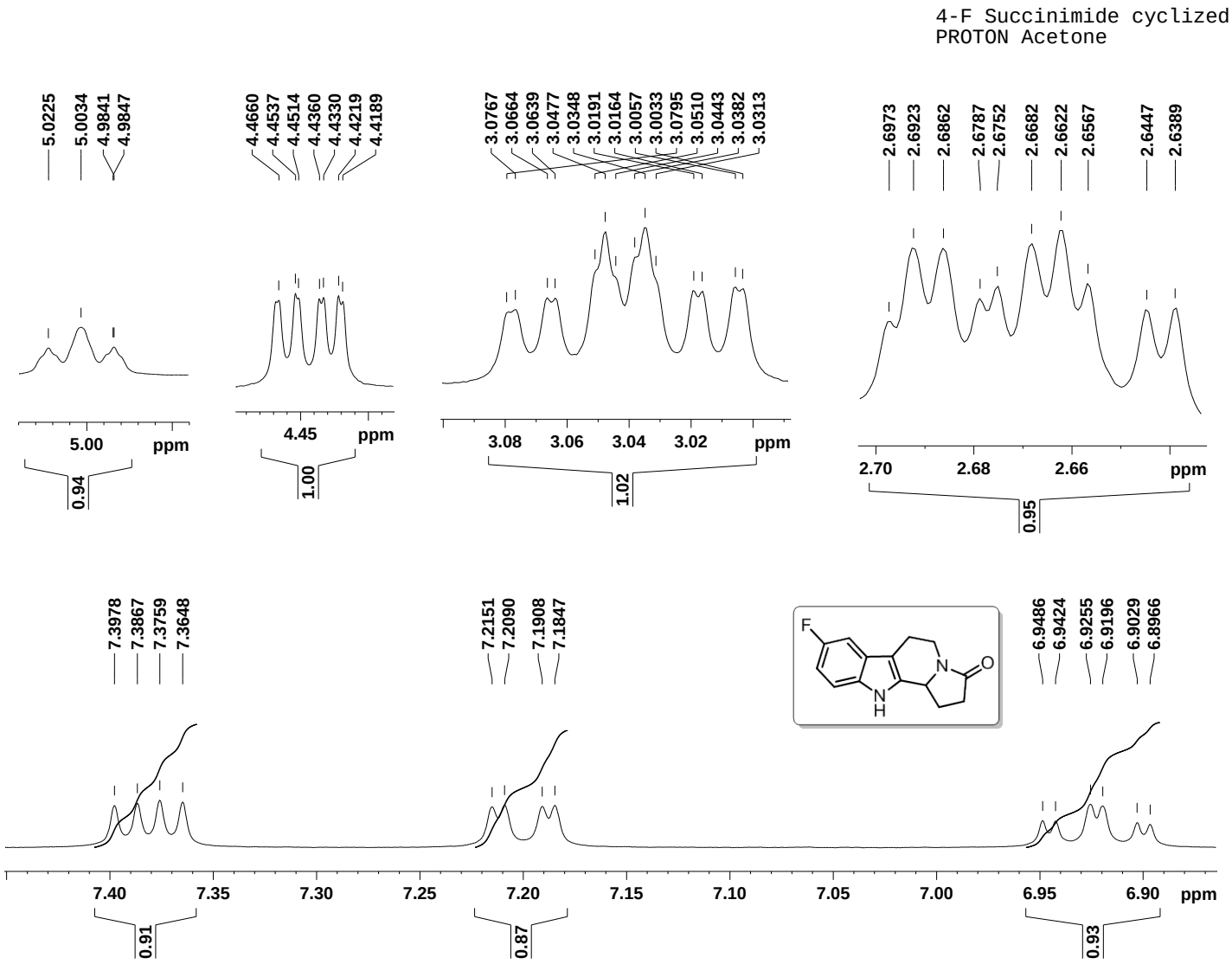



```
Current Data Parameters
NAME          SMR-239-2A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110722
Time               12.14
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  194
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                296.5 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

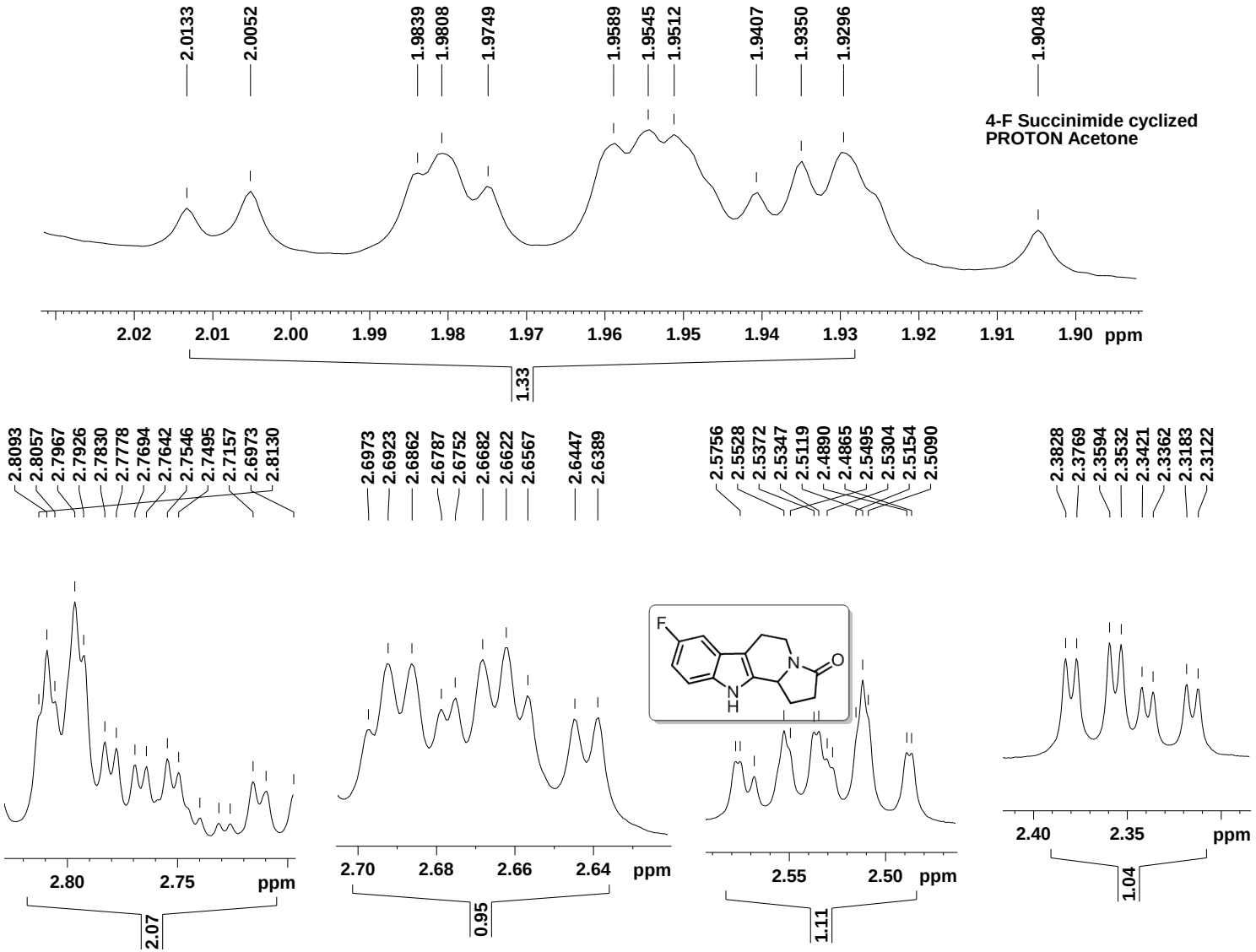
This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

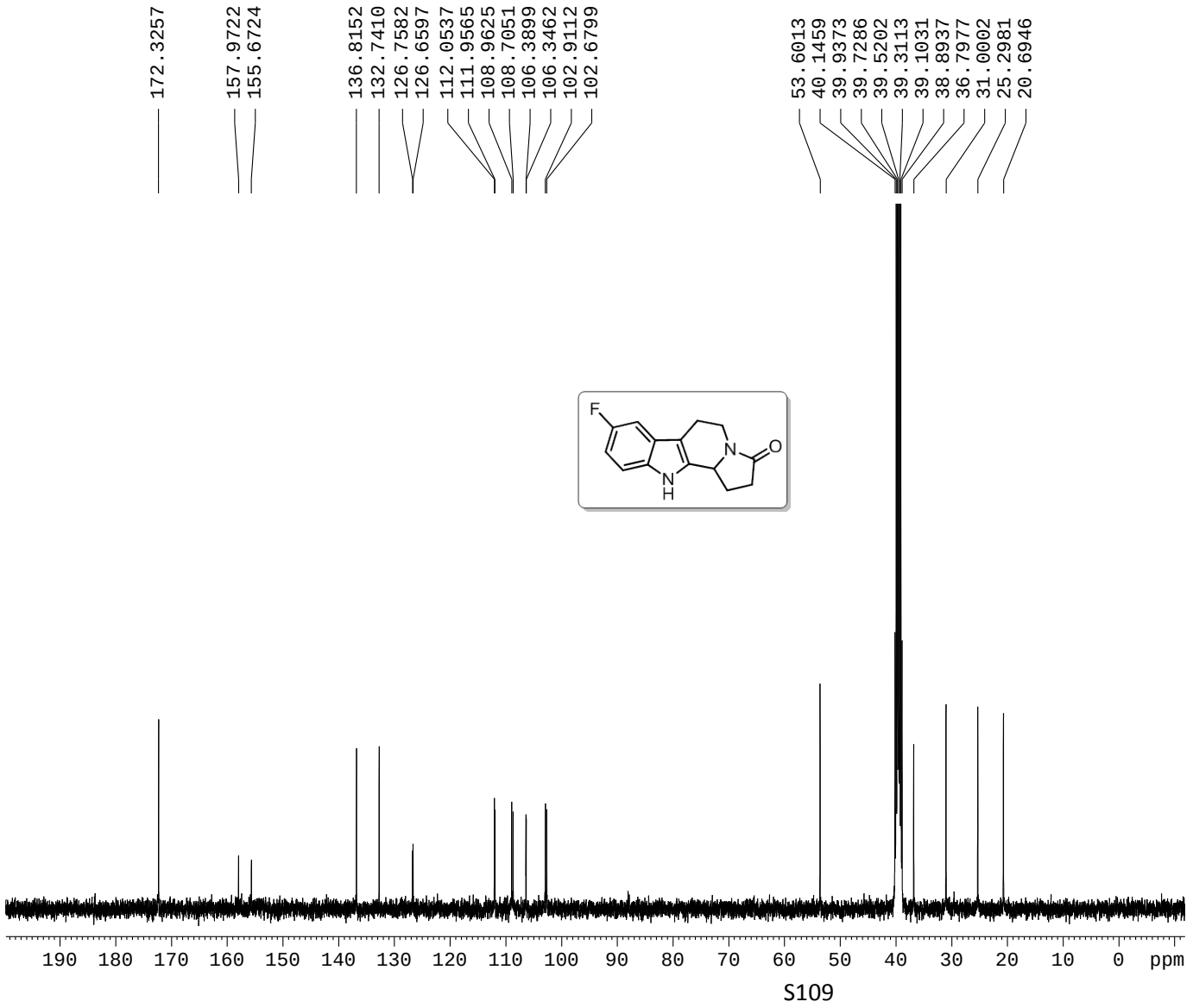


This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

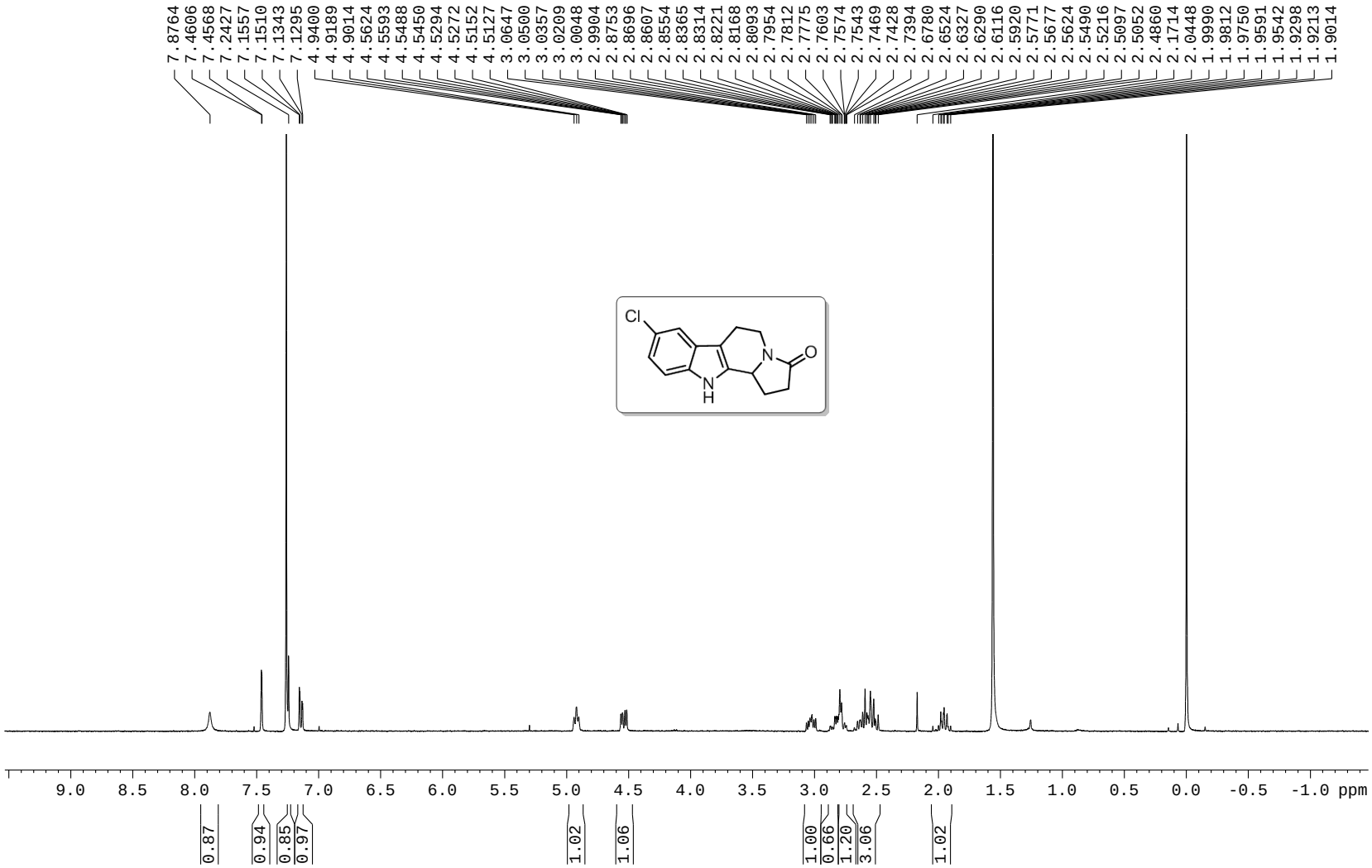
C13CPD DMSO {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME          SMR-I-188
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110321
Time              11.02
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  1290
DW                20.800 usec
DE                 6.00 usec
TE                295.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6128120 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

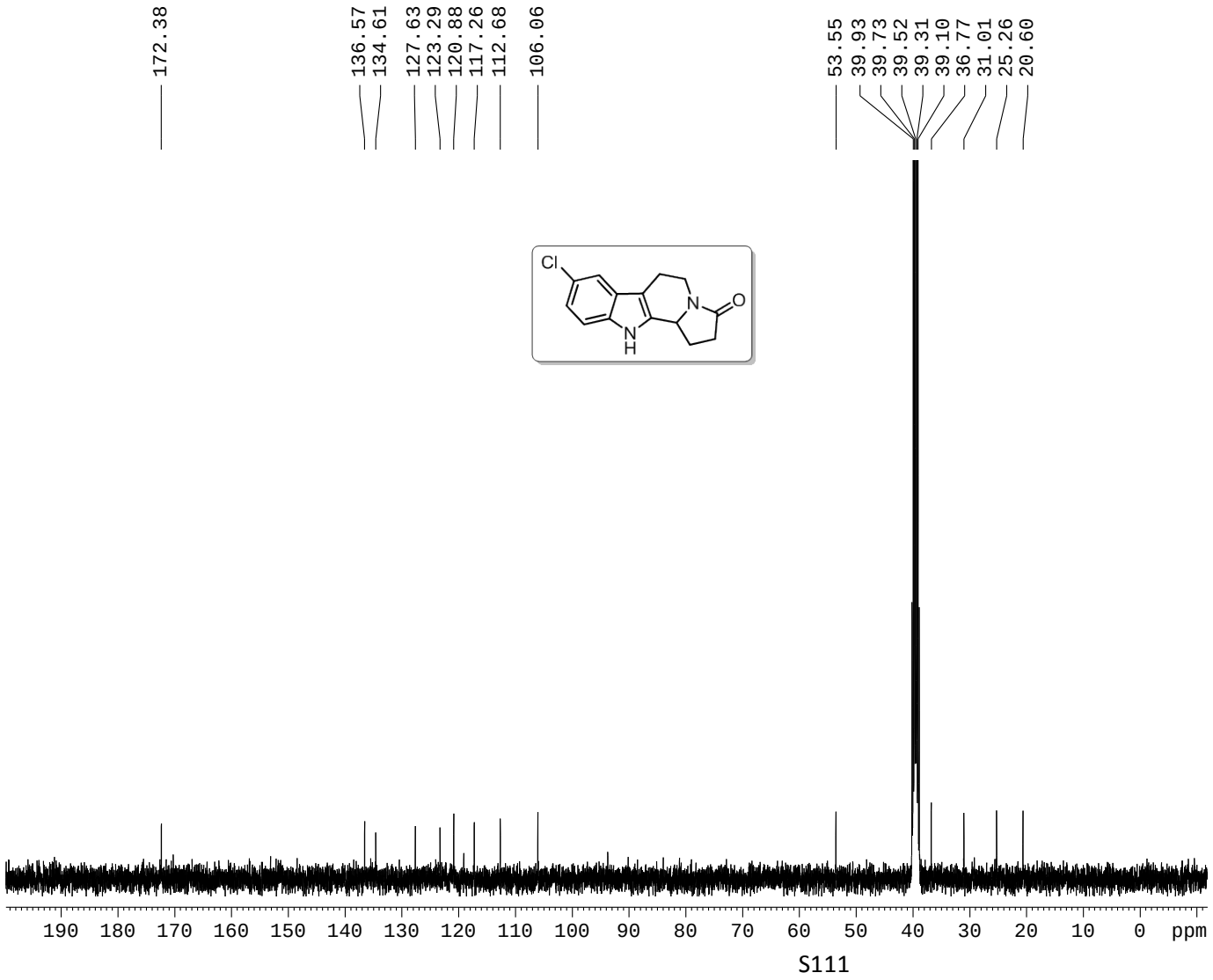
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



This journal is © The Royal Society of Chemistry 2012

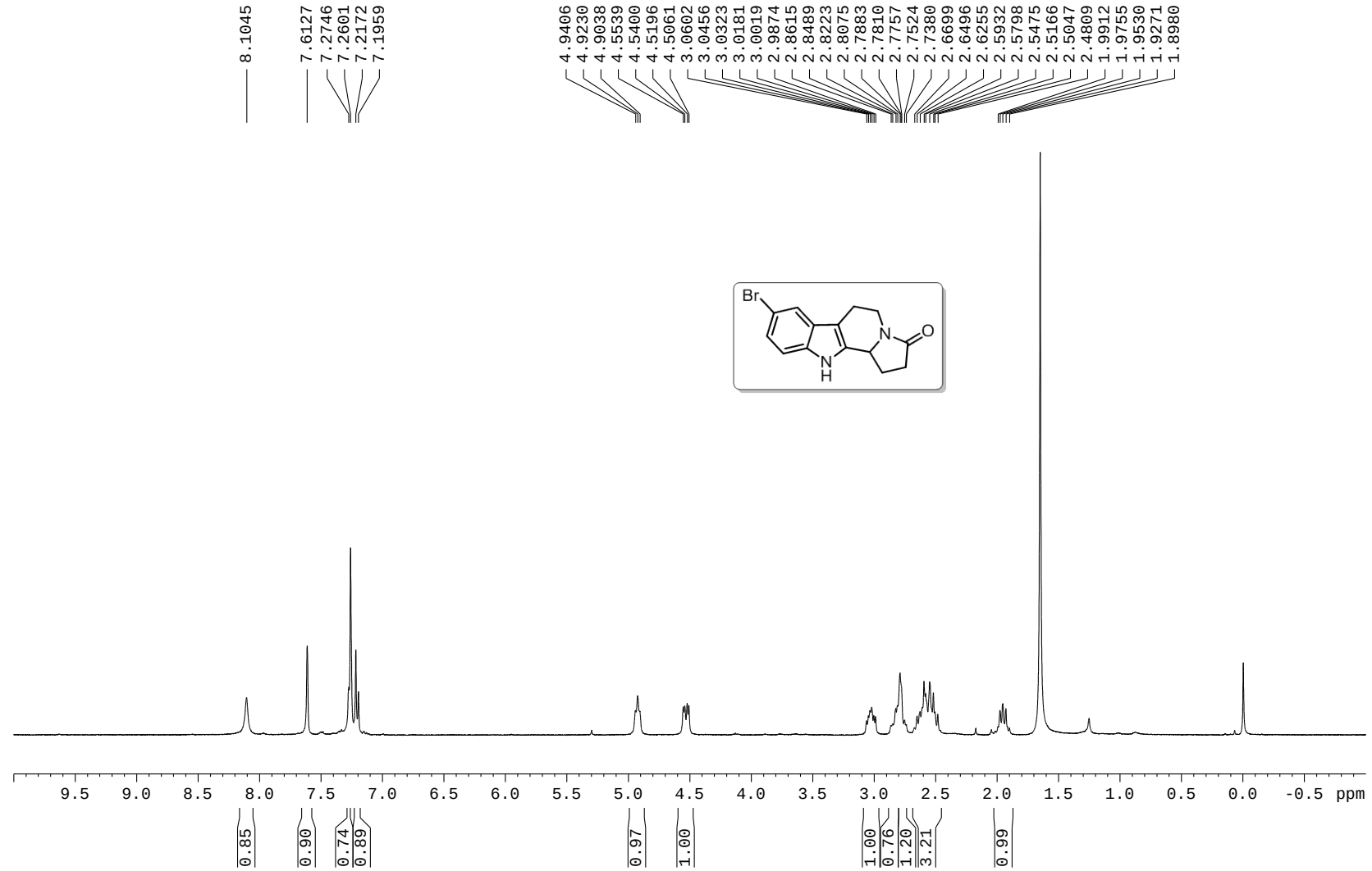
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME       SMR-I-196-2A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20110330
Time              14.53
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                295.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6132885 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

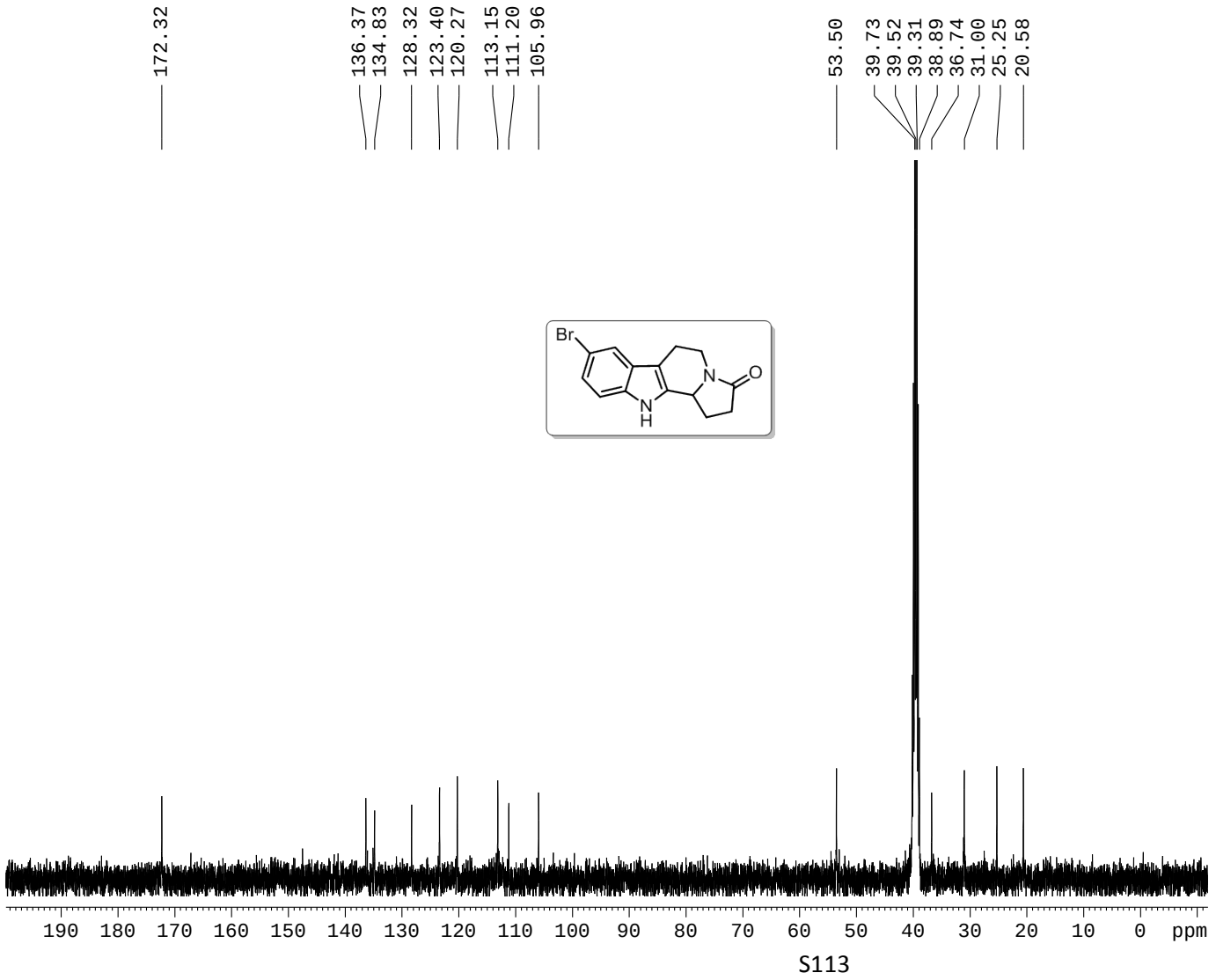
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



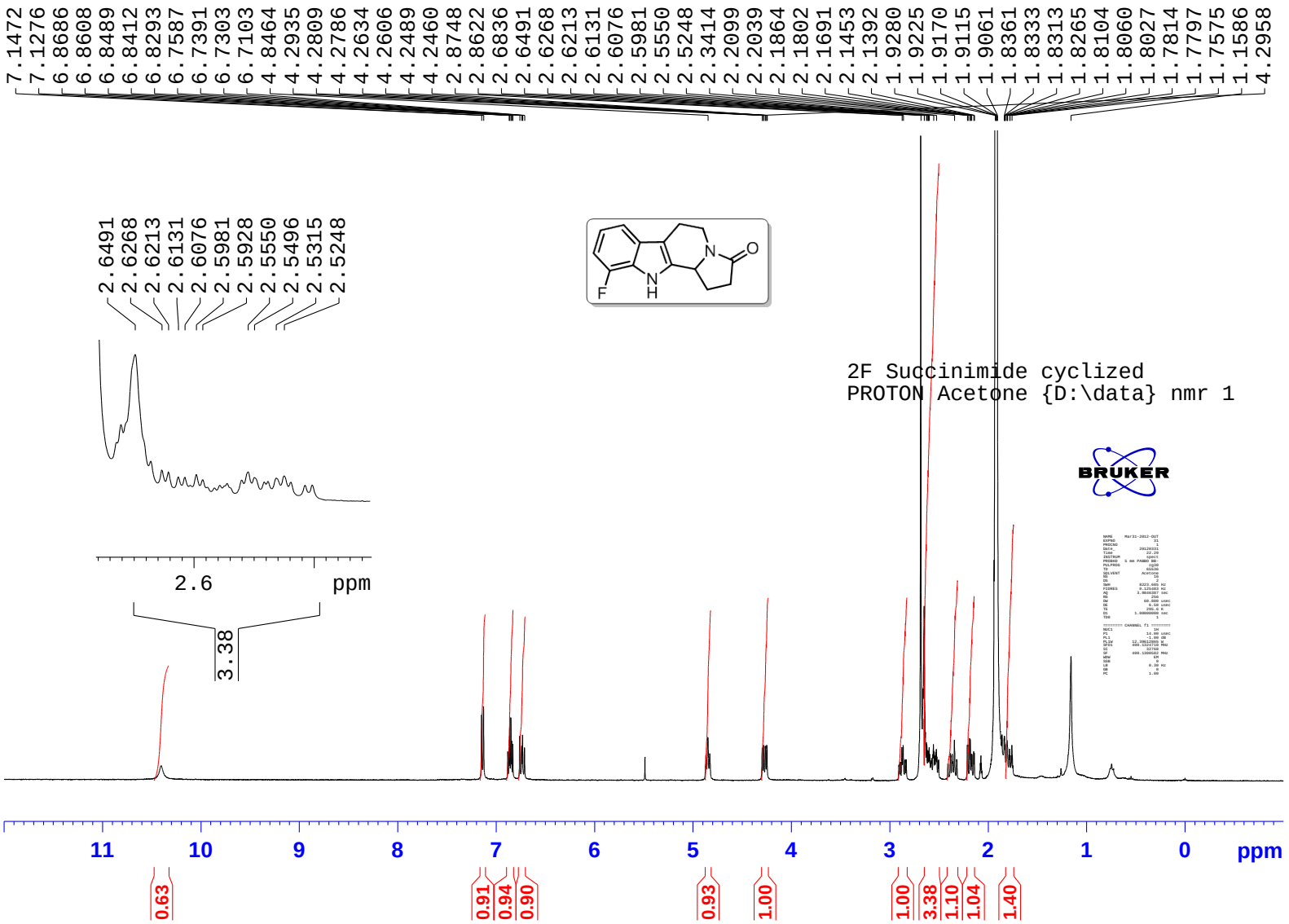
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1

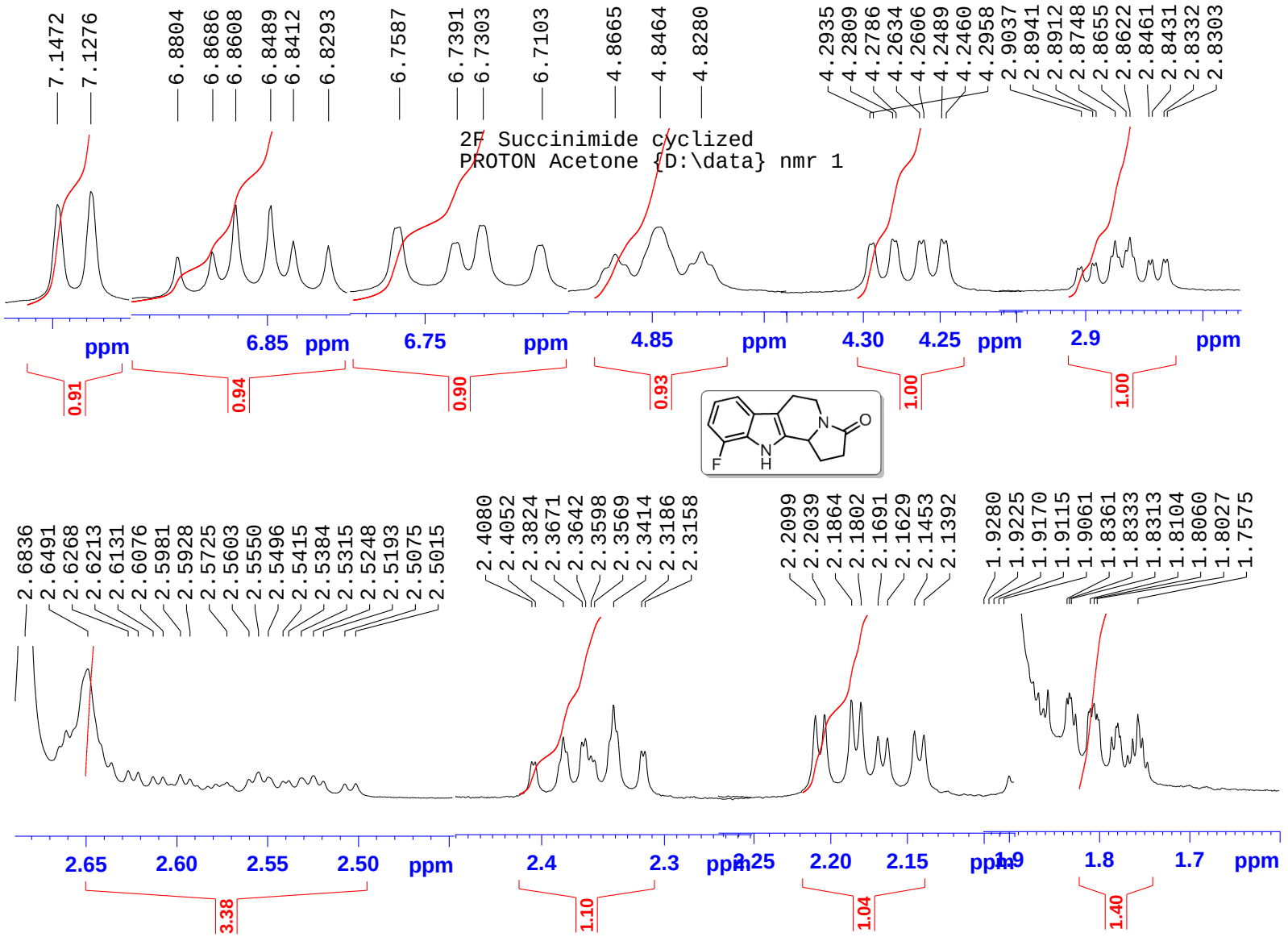



```
Current Data Parameters
NAME        SMR-I-189-2
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20110321
Time              17.11
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  123
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  912
DW               20.800 usec
DE                6.00 usec
TE                294.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6132883 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012

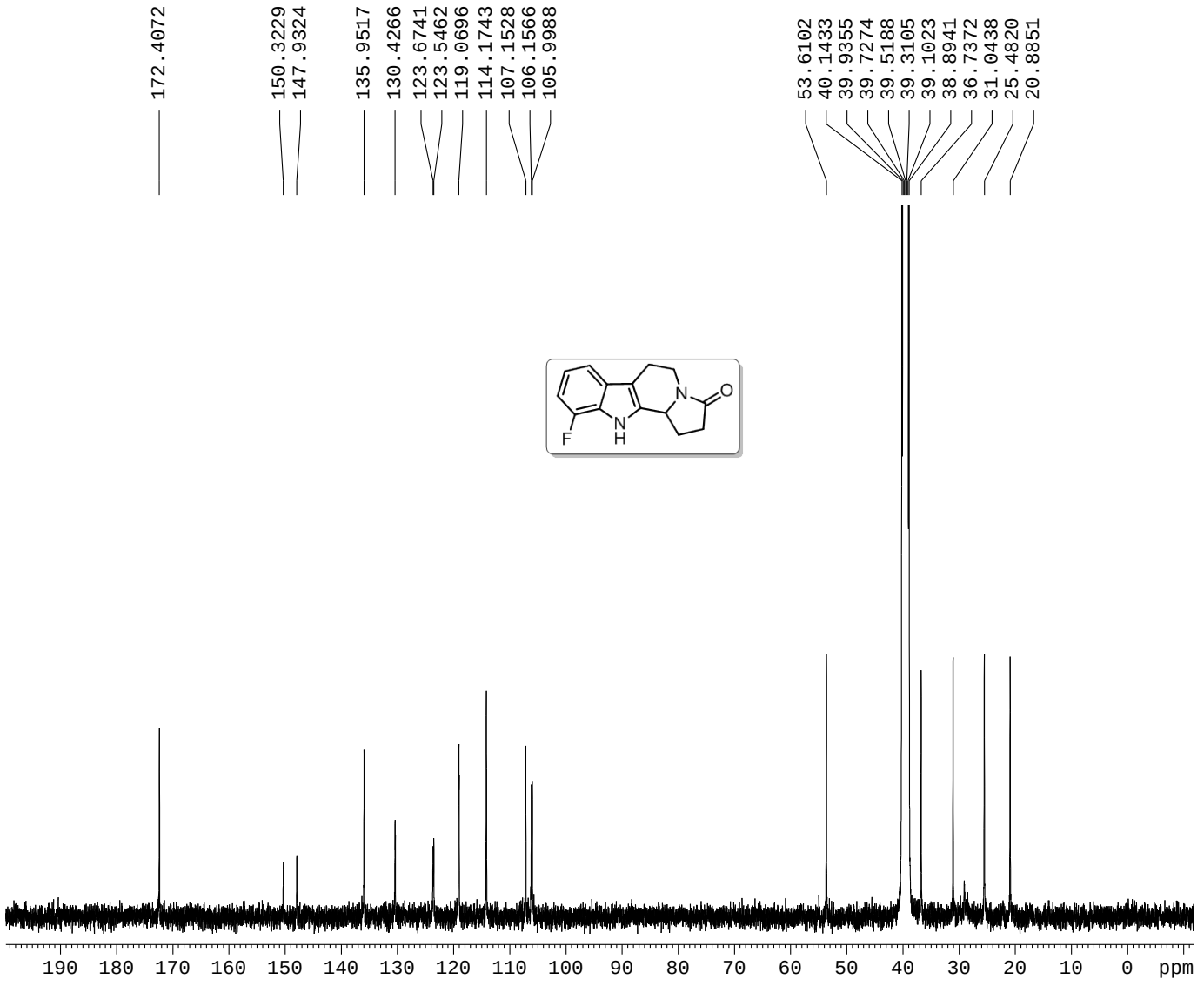


This journal is © The Royal Society of Chemistry 2012



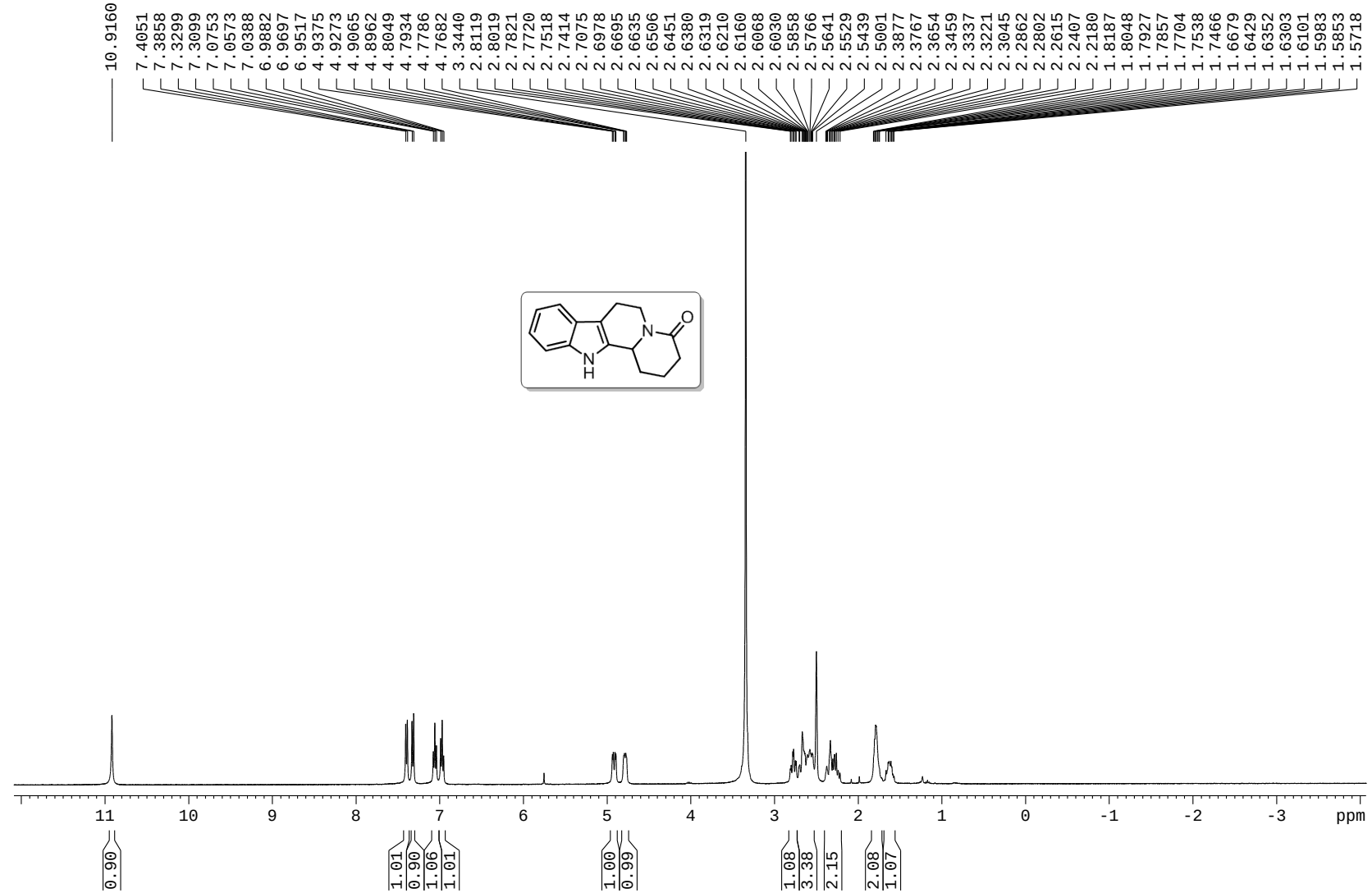
This journal is © The Royal Society of Chemistry 2012

C13CPD DMSO {D:\CRR} KOPAL 1



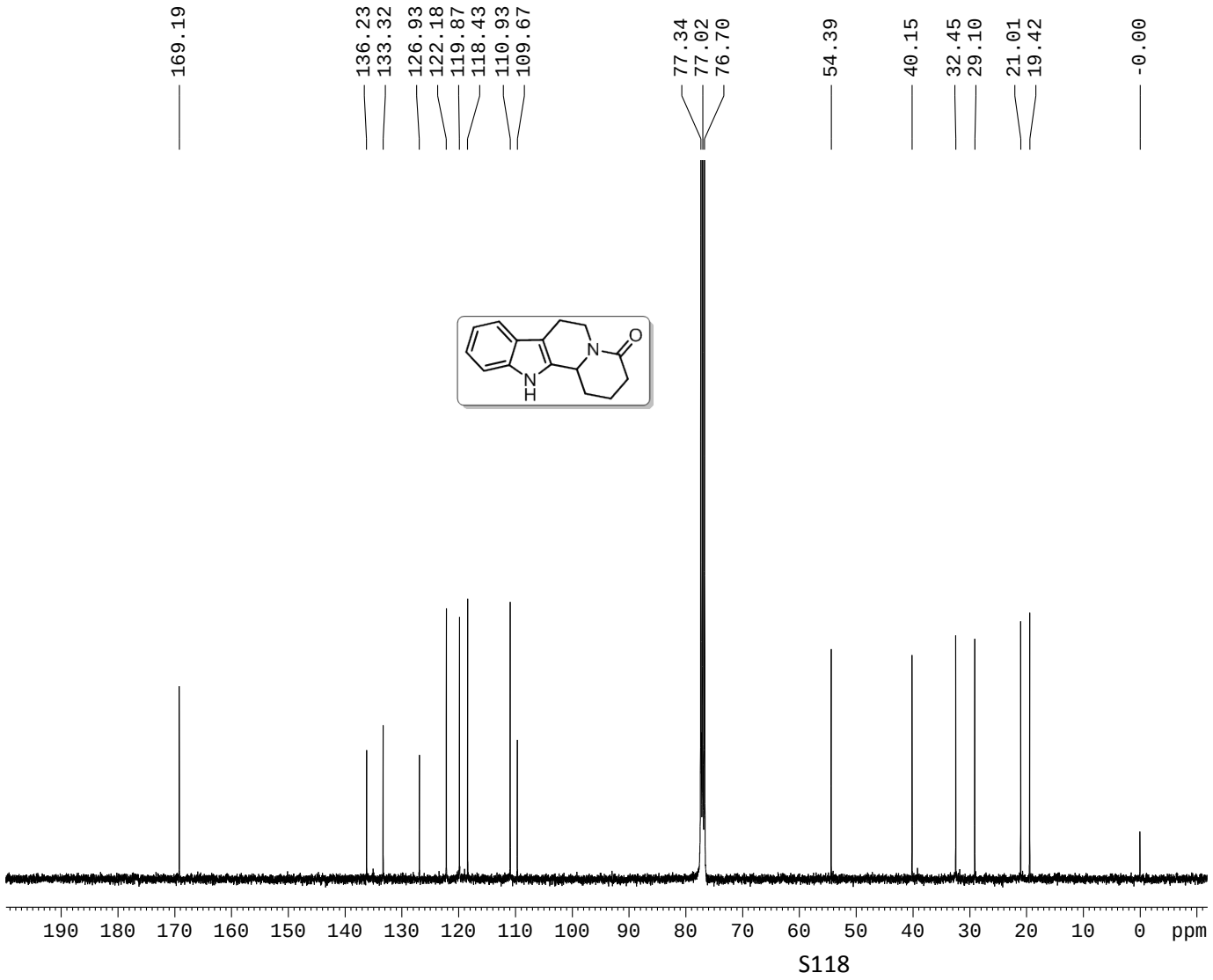

```
Current Data Parameters
NAME        CRR-SMR-2FS
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120124
Time              10.13
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                17942
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 50.8
DW                20.800 usec
DE                 6.00 usec
TE                291.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6128073 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

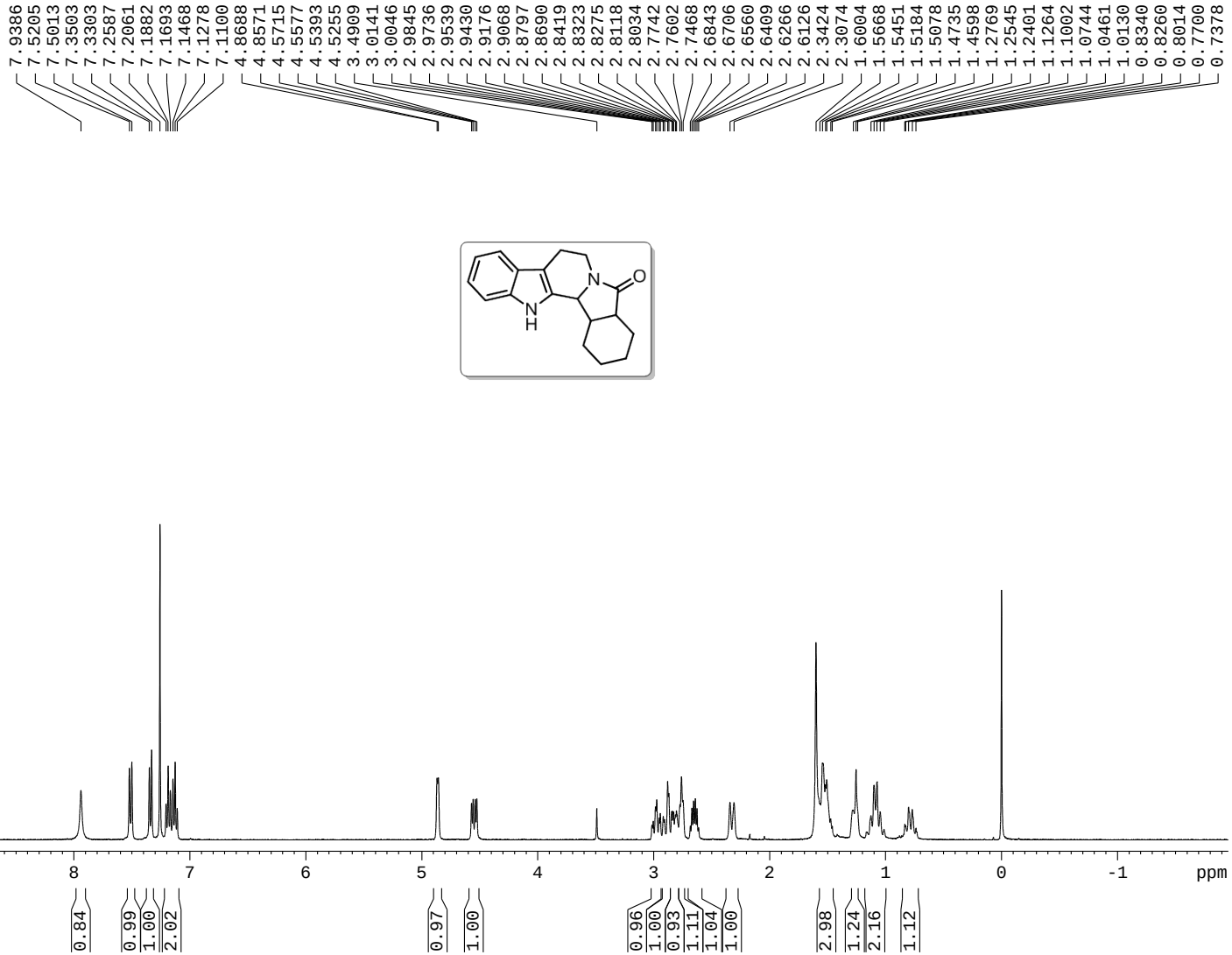
C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME          SMR-CON-D
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120221
Time              21.37
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                13497
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 50.8
DW               20.800 usec
DE                6.00 usec
TE                298.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL12              15.60 dB
PL13              15.60 dB
PL2               -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127673 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

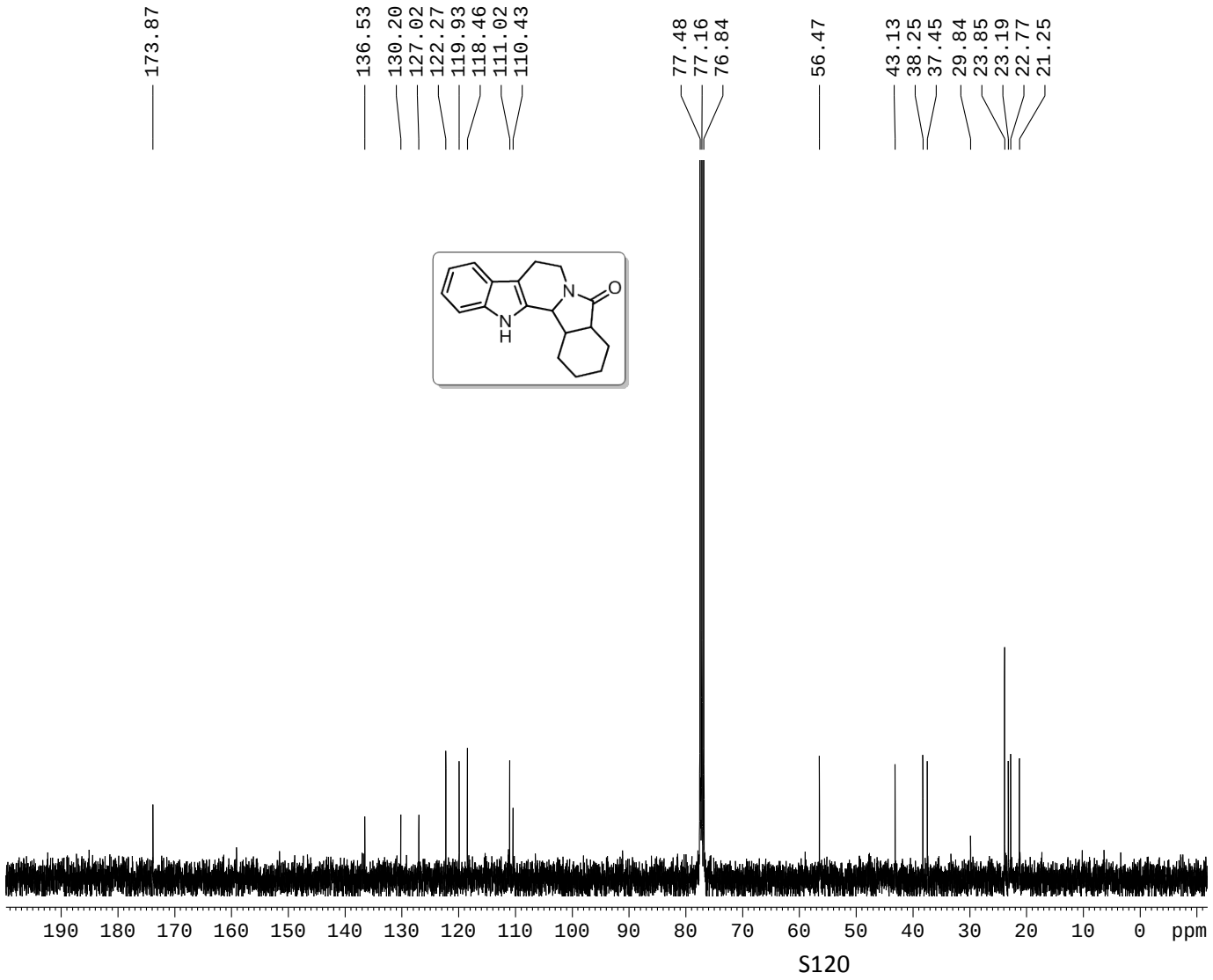
This journal is © The Royal Society of Chemistry 2012

PROTON CDCl3 {D:\CRR} KOPAL 1



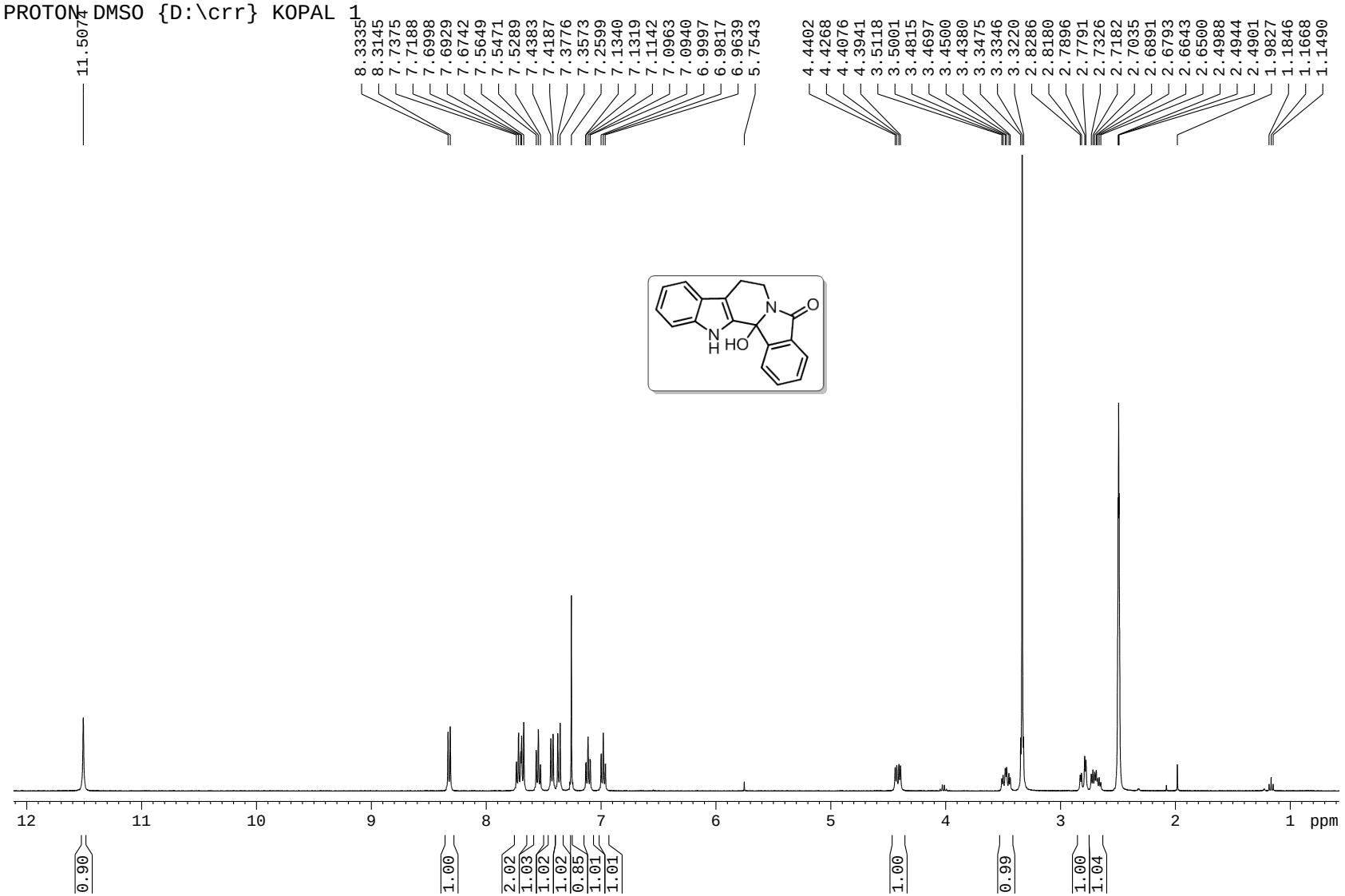
Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



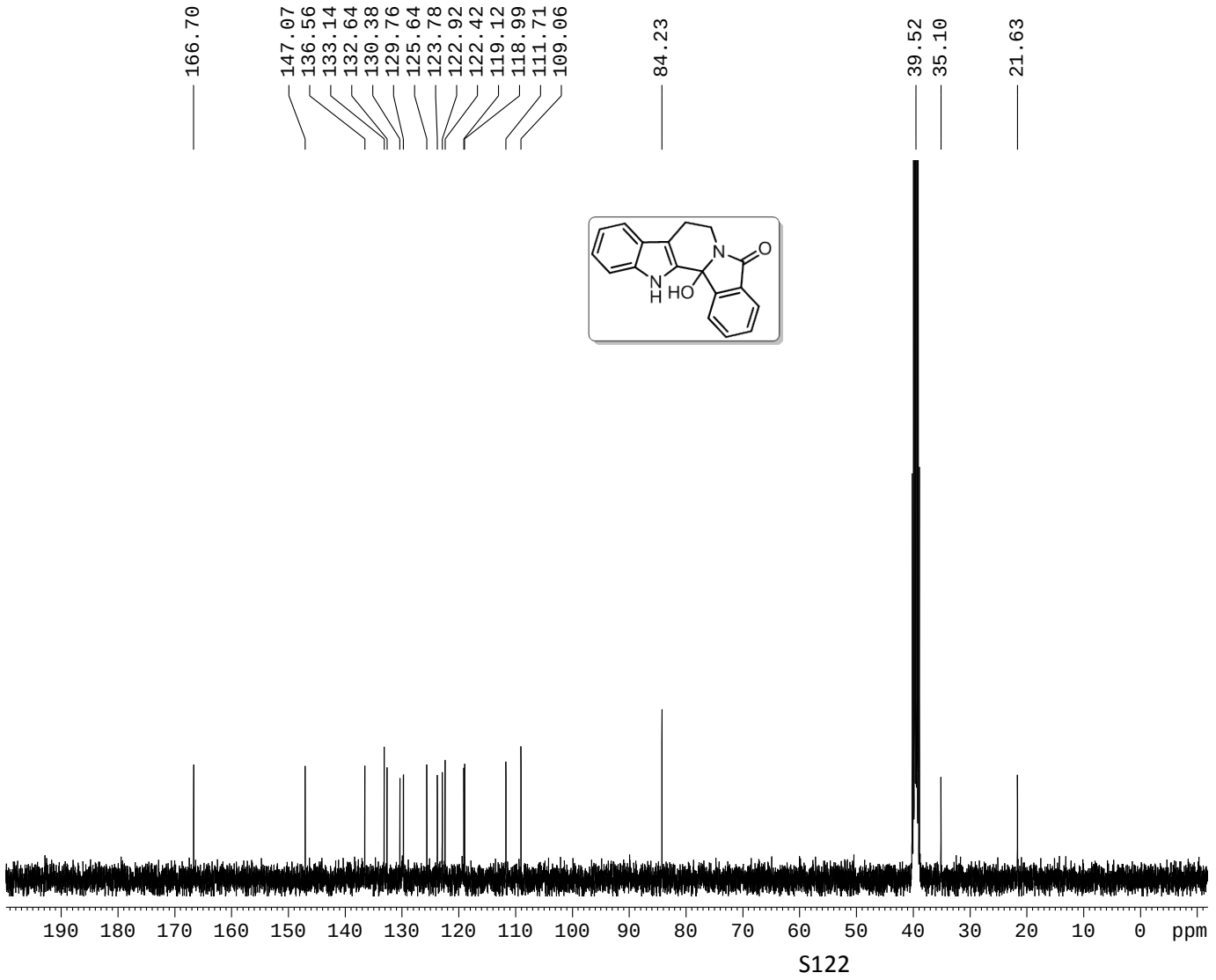

```
Current Data Parameters
NAME            SMR-HEX
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110809
Time              14.22
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  346
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1150
DW               20.800 usec
DE                6.00 usec
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL12             15.60 dB
PL13             15.60 dB
PL2              -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127532 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

This journal is © The Royal Society of Chemistry 2012



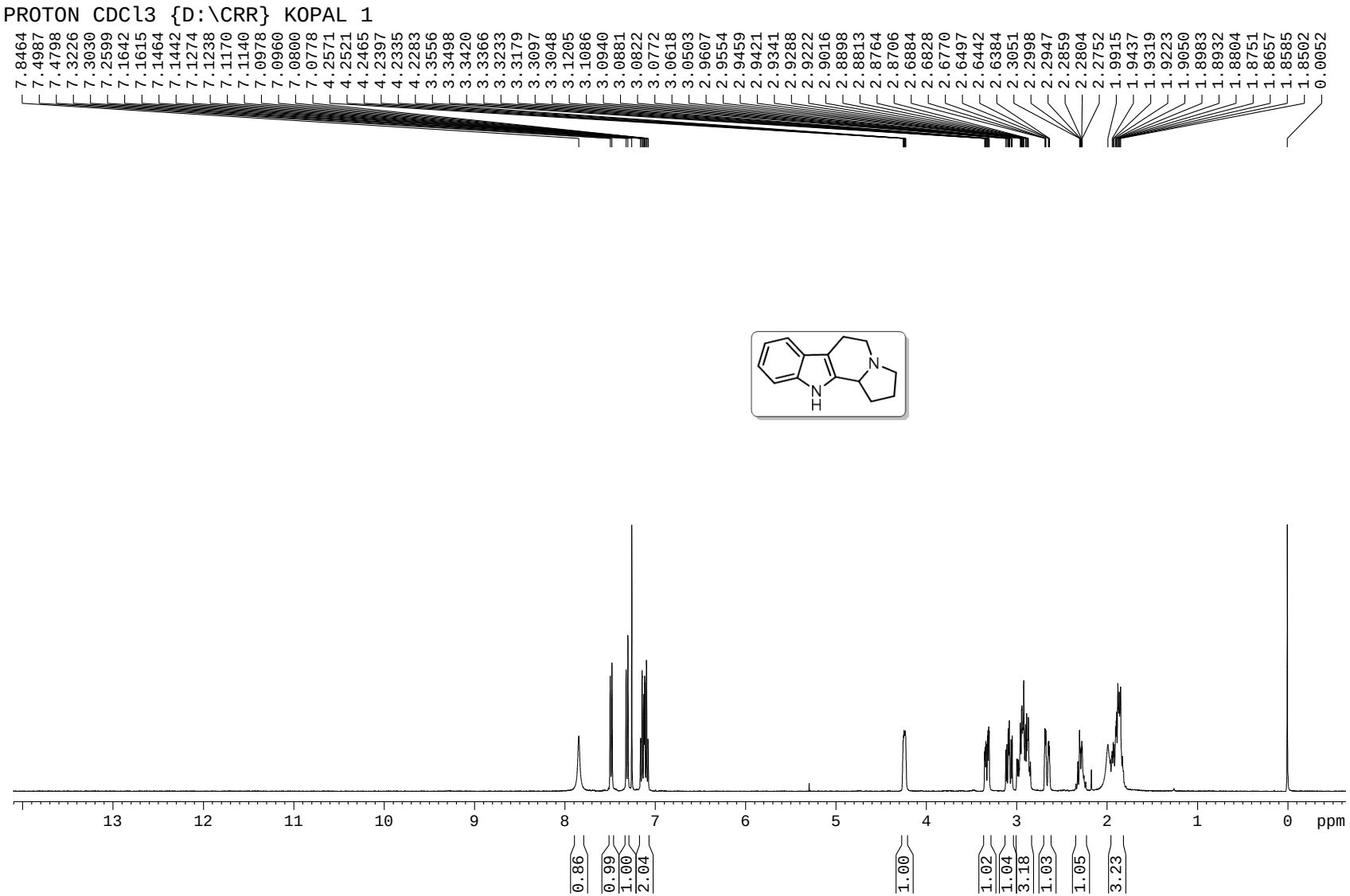
This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1

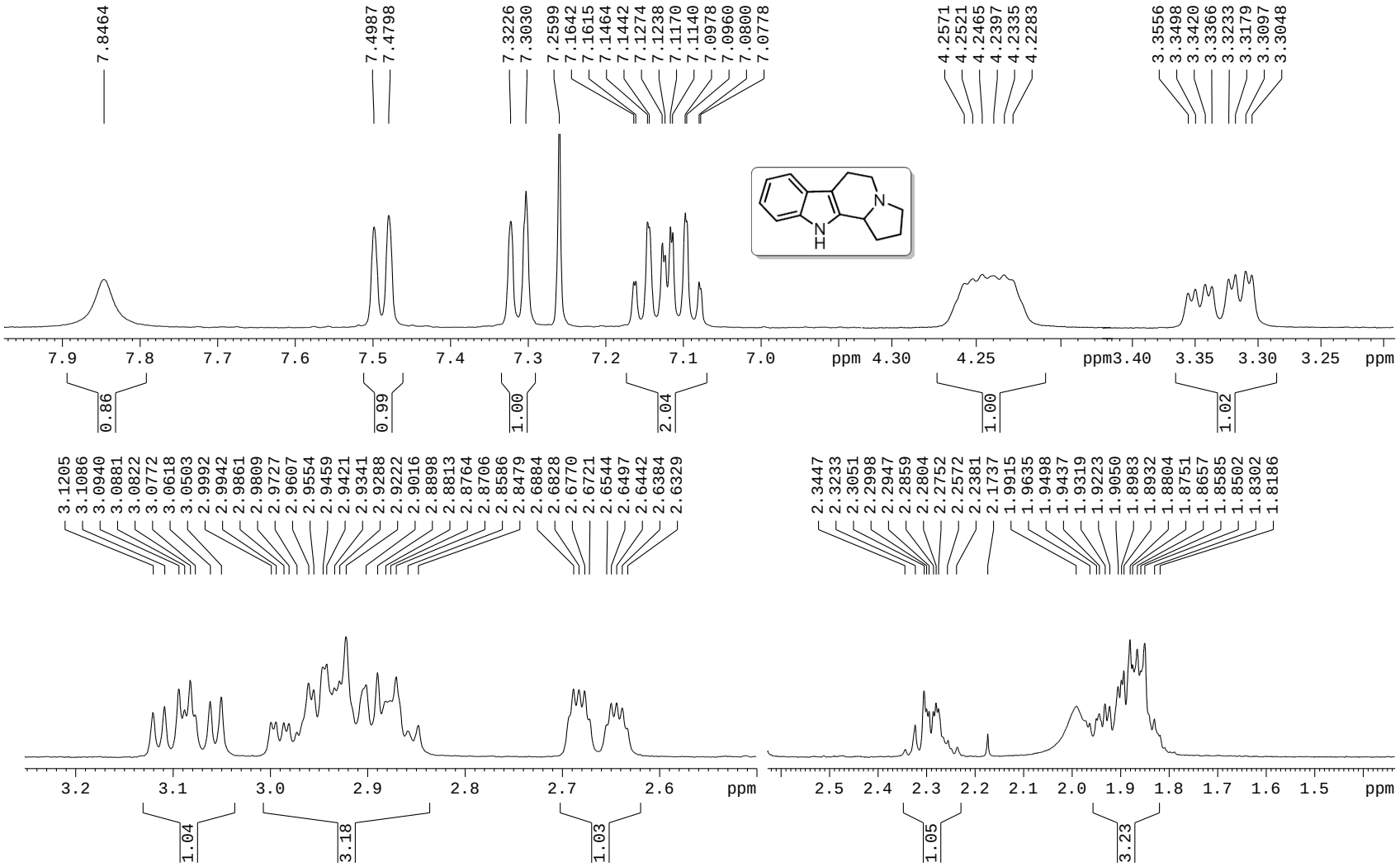



```
Current Data Parameters
NAME        SMR-I-108-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100819
Time              16.15
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  812
DW               20.800 usec
DE                6.00 usec
TE                296.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6132729 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

This journal is © The Royal Society of Chemistry 2012

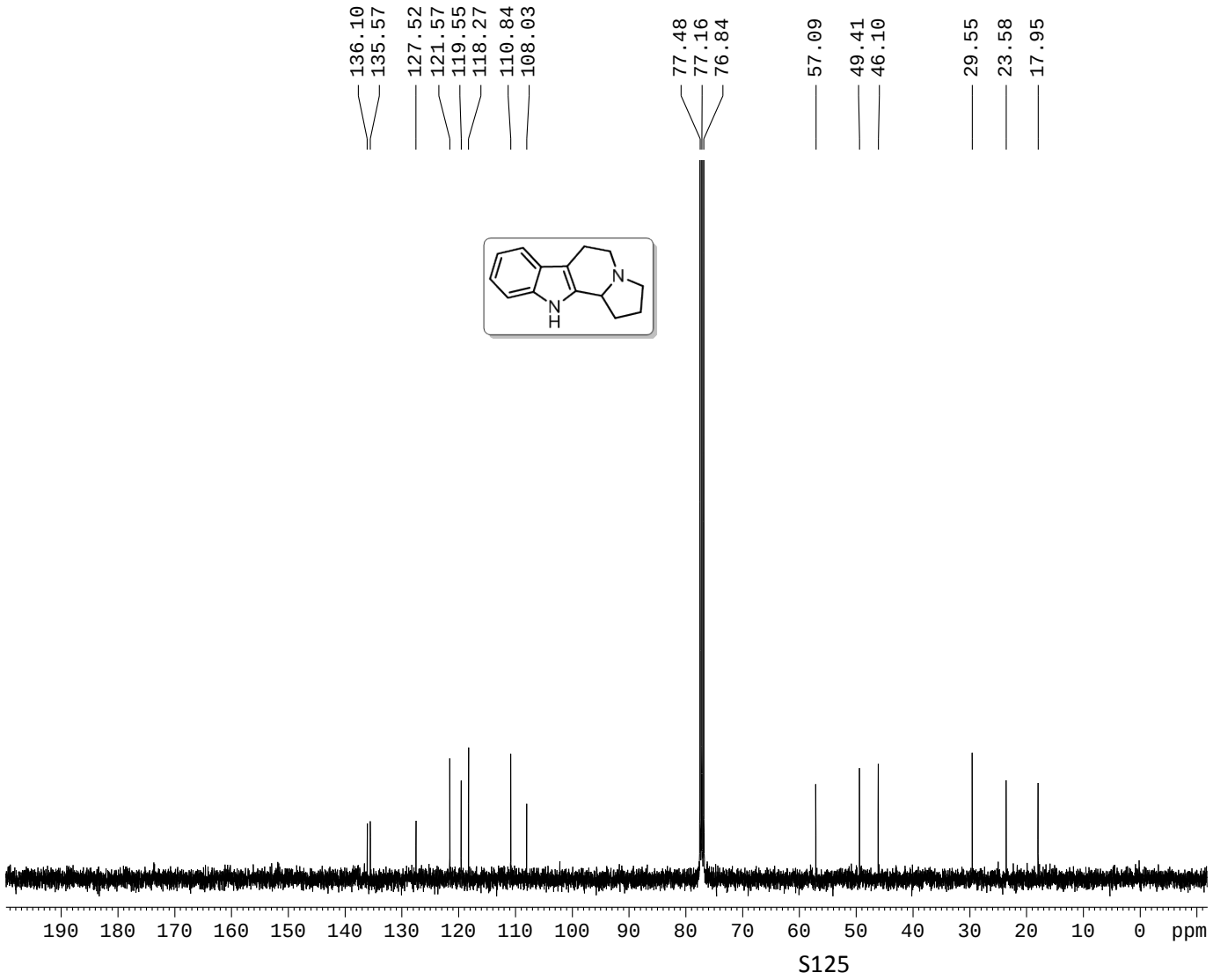


This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1



Current Data Parameters
NAME SMR-AL
EXPNO 2
PROCNO 1

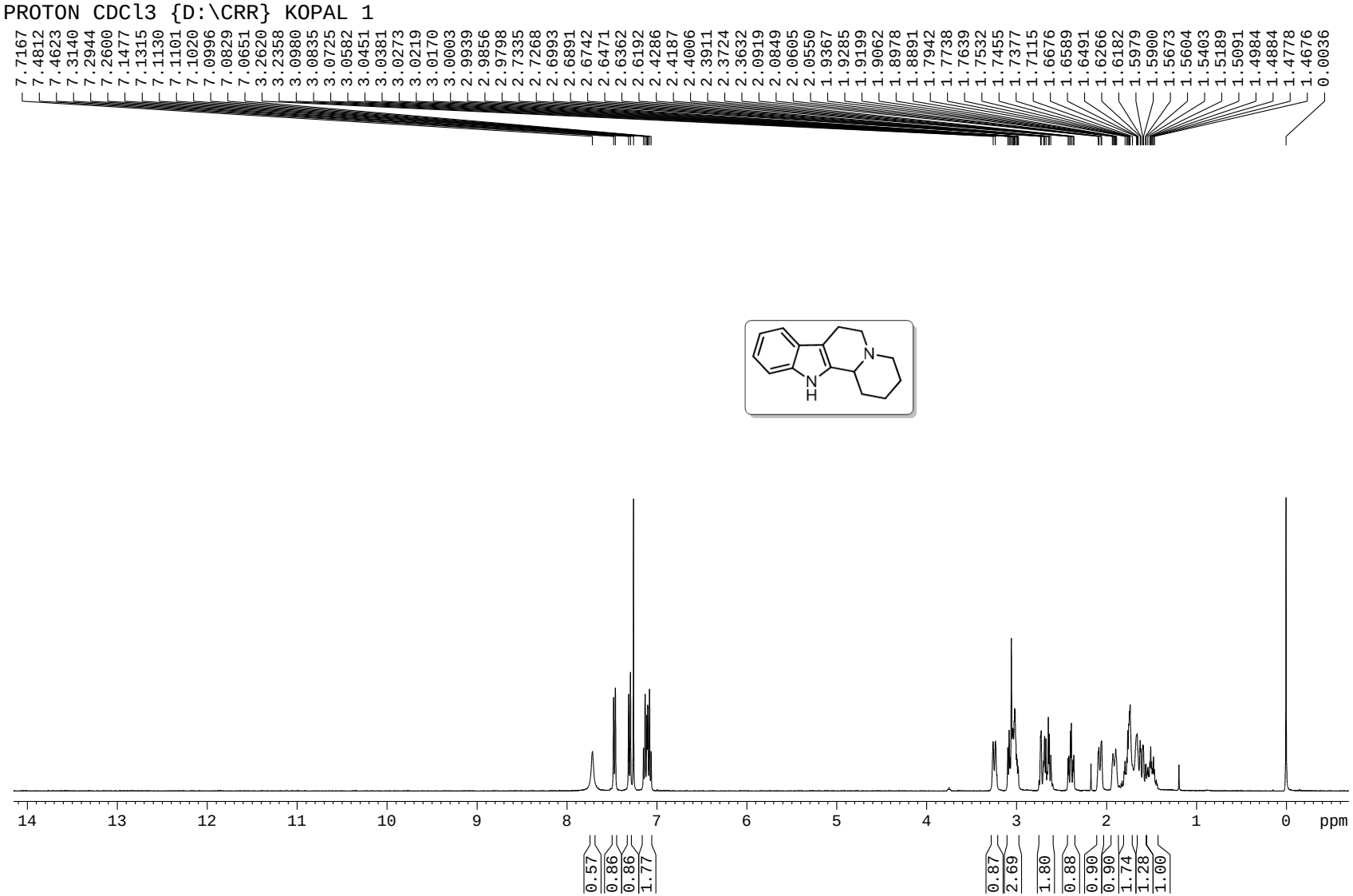
F2 - Acquisition Parameters
Date_ 20111125
Time 12.10
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 295.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.60 dB
SFO1 100.6228298 MHz

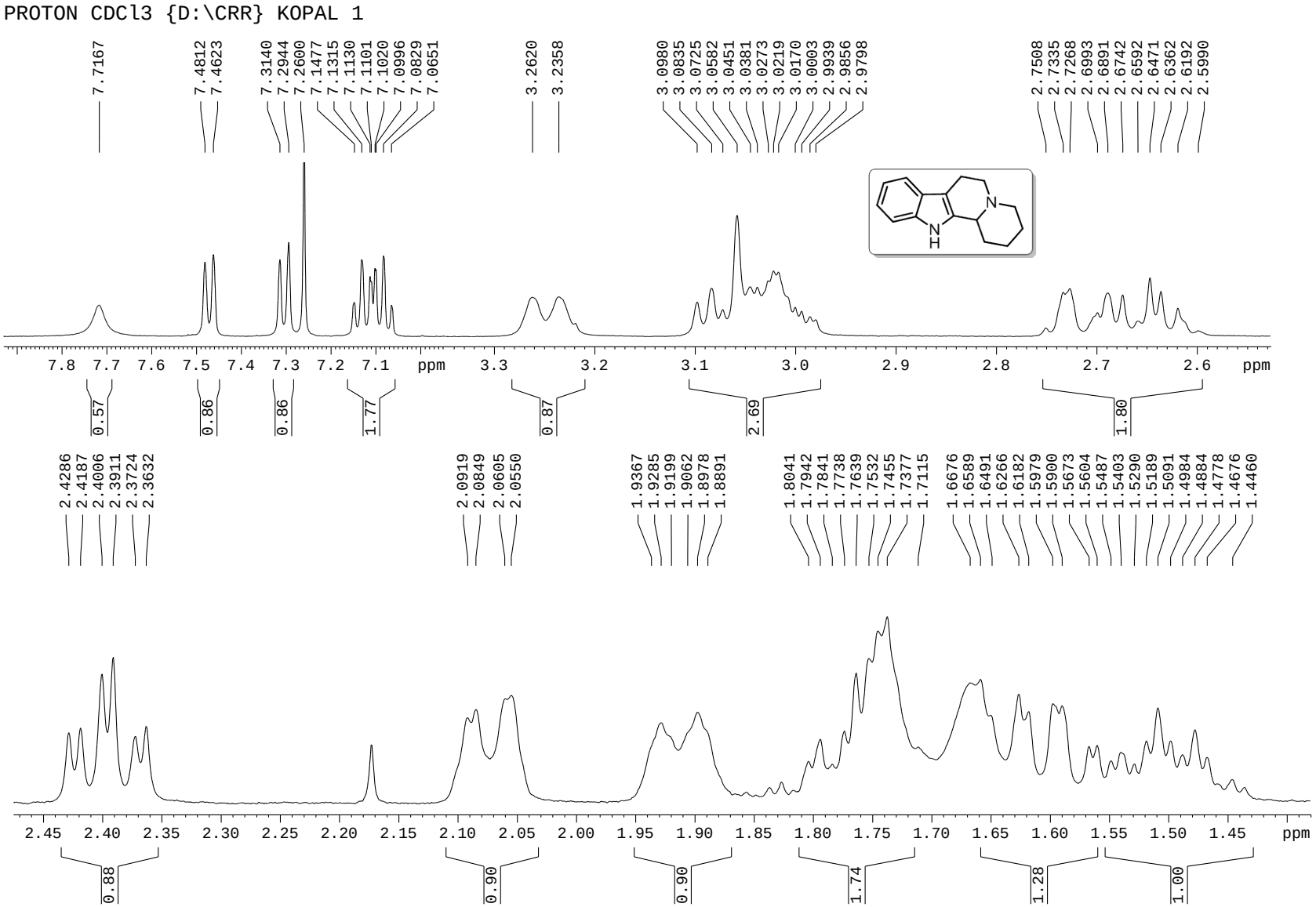
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 15.60 dB
PL13 15.60 dB
PL2 -0.90 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127541 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

This journal is © The Royal Society of Chemistry 2012

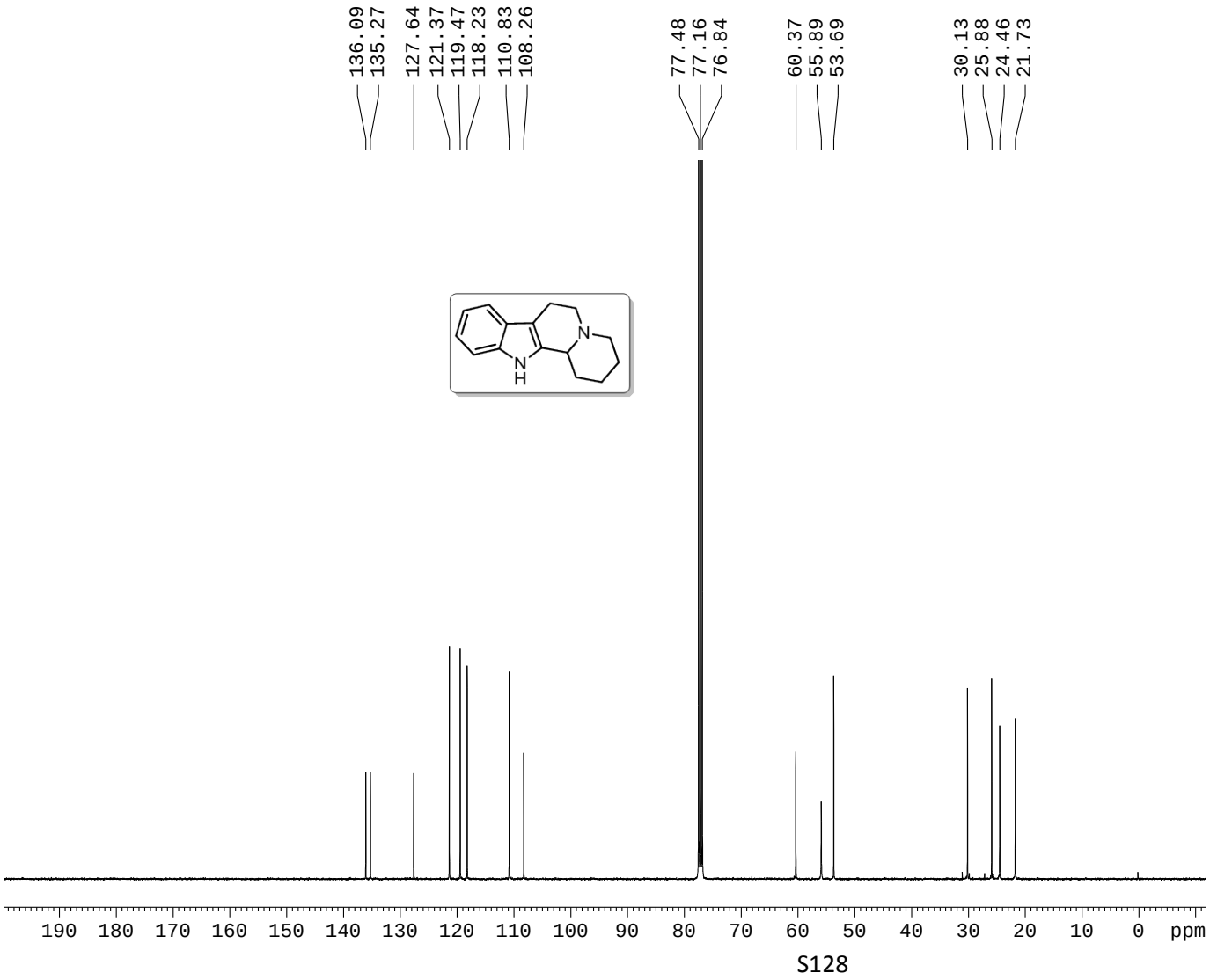


This journal is © The Royal Society of Chemistry 2012



This journal is © The Royal Society of Chemistry 2012

C13CPD CDCl3 {D:\CRR} KOPAL 1




```
Current Data Parameters
NAME            SMR-DES
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120201
Time               9.32
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                17000
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1150
DW               20.800 usec
DE                6.00 usec
TE                296.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -0.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12               15.60 dB
PL13               15.60 dB
PL2                -0.90 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127566 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```