Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2011

The Design and Synthesis of Novel IBiox N-Heterocyclic Carbene Ligands Derived from Substituted Amino-Indanols.

Jean-Noël Levy,[a] Christopher M. Latham,[b] Loïc Roisin,[a] Nadine Kandziora,[a] Paolo Di Fruscia,[a] Andrew J. P. White,[a] Simon Woodward,[b] Matthew J. Fuchter[a*]

Electronic Supplementary Information

Contents:

Experimental Procedures.....2-21

X-ray data.....22-29

NMR spectra.....30-78

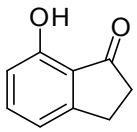
Buried volume calculations.....79-90

[a]*Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom*

[b]*School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, United Kingdom*

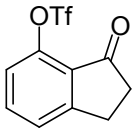
This journal is © The Royal Society of Chemistry 2011

7-Hydroxyindan-1-one (6)[1]



A mixture of 4-chromanone **5** (10.00 g, 67.50 mmol) and anhydrous, powdered $AlCl_3$ (26.00 g, 195.00 mmol) was fused at 250 ˚C for 10 min. After allowing the reaction mixture to cool to ambient temperature, dichloromethane (50 mL) and cold hydrochloric acid (50 mL) were added to the mixture. The resulting black slurry was extracted with dichloromethane (2 L). Removal of the solvent under reduced pressure followed by flash column chromatography (eluent: EtOAc : Petroleum ether 1 : 4) afforded 7-hydroxyindan-1-one (**6**, 7.1 g, 48.00 mmol, 72 %) as yellow solid: m.p. (Petroleum ether / EtOAc) = 48 – 50 ˚C; IR (thin film) 3360, 1678, 1176 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H, O*H*), 7.47 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.94 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.75 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 3.11 (t, *J* = 5.6 Hz, 2H, C*H*$_2$-CH_2CO), 2.72 (t, *J* = 6.0 Hz, 2H, C*H*$_2$CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 157.5, 155.3, 137.6, 117.4, 113.5 (2C), 36.0, 25.9; MS (EI) *m/z* 148 (M); HRMS (EI) *m/z* calc for $C_9H_8O_2$ 148.0524, found: 148.0524.

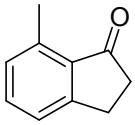
Oxoinden-4-yltrifluoromethanesulfonate



N-phenyltrifluoromethanesulphonimide (2.50 g, 7.00 mmol) was added to a solution of 7-hydroxyindan-1-one **6** (1.00 g, 6.75 mmol) and triethylamine (1.05 mL, 7.50 mmol) in dichloromethane (30 mL). The resulting mixture was stirred 24 h at ambient temperature. The reaction was washed with water (30 mL) and brine (30 mL) and extracted with dichloromethane (2 x 50 mL). The organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (eluent: EtOAc : Petroleum ether 1 : 4) afforded the 3-oxoinden-4-yltrifluoromethanesulfonate (1.85 g, 6.61 mmol, 99 %) as colourless solid: m.p. 42-44 ˚C; IR (thin film) 1727, 1210, 1139, 959 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 7.51 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.17 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 3.20 (t, *J* = 6.0 Hz, 2H, C*H*$_2$-CH_2CO), 2.77 (t, *J* = 6.0 Hz, 2H, C*H*$_2$CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 157.6, 136.0, 127.0, 120.2, 36.6, 25.7; MS (CI) *m/z* 298 (M+NH_4); HRMS (CI) *m/z* calc for $C_{10}H_{11}NO_4F_3S$ 298.0361, found: 298.0359.

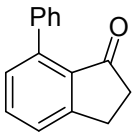
This journal is © The Royal Society of Chemistry 2011

7-7-Methylindan-1-one [2]



To a solution of 3-oxoinden-4-yltrifluoromethanesulfonate (600 mg, 2.14 mmol) in tetrahydrofuran (200 mL) were added sequentially (dppp)$NiCl_2$ (114 mg, 0.21 mmol), dimethylzinc (1.2M solution in toluene, 6.70 mL, 8.00 mmol) at ambient temperature. The mixture was stirred 12 h at ambient temperature. The reaction was quenched with sat. aq. NaH_2PO_4 (50 mL) and extracted with ethyl acetate (2 x 50 mL). The combined organic phase was washed with water (30 mL), brine (30 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (eluent: EtOAc : Petroleum ether 1 : 6) afforded the 7-methylindan-1-one (300 mg, 2.05 mmol, 96 %) as colourless oil: IR (neat)2924, 1703, 1596, 1191, 711, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.28 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.09 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 3.08 (t, *J* = 6.0 Hz, 2H, CH_2-CH_2CO), 2.66 (t, *J* = 6.0 Hz, 2H, CH_2CO), 2.64 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.9, 135.2, 128.9, 128.0, 122.4, 75.5, 35.1, 30.1, 18.3; MS (EI) *m/z* 146 (M); HRMS (EI) *m/z* calc for $C_{10}H_{10}O$ 146.0732, found: 146.0725.

7-7-Phenylindan-1-one [3]

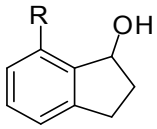


To 3-oxoinden-4-yltrifluoromethanesulfonate (1.00 g, 3.14 mmol), phenylboronic acid (488 mg, 4.00 mmol) and $Pd(PPh_3)_4$ (410 mg, 0.31 mmol) were placed in a round-bottom flask, fitted with a condenser, under nitrogen. Tetrahydrofuran (100 mL, degassed with argon) and aqueous sodium carbonate (1.0 M, 30 mL) were added *via* a septum. The mixture was heated under reflux overnight then poured onto aqueous hydrochloric acid (1 M, 50 mL). The aqueous phase was extracted with dichloromethane (2 x 100 mL), the extracts washed with water (3 x 100 mL), dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (eluent: EtOAc : Petroleum ether 1 : 6) afforded the 7-phenylindan-1-one (640 mg, 3.08 mmol, 98 %) as white powder: m.p. (EtOAc / Petroleum ether) = 78 – 79 ˚C; IR (neat) 1701, 1587, 1466, 1231, 759, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.0 Hz, 1H, Ar-

This journal is © The Royal Society of Chemistry 2011

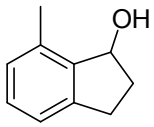
H), 7.38-7.46 (m, 6H, Ar-*H*), 7.25-7.27 (m, 1H, Ar-*H*), 3.16 (t, *J* = 5.6 Hz, 2H, C*H*$_2$-CH$_2$CO), 2.69 (t, *J* = 6.0 Hz, 2H, C*H*$_2$CO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 156.4, 141.5, 138.0, 133.9, 133.1, 129.5, 129.3 (2C), 127.8 (2C), 125.7, 36.9, 25.4, MS (EI) *m/z* 208 (M); HRMS (EI) *m/z* calc for $C_{15}H_{12}O$ 208.0888, found: 208.0877.

General procedure A for the formation of indanol:



Sodium borohydride (3 equiv.) was added to a solution of indanone (1 equiv.) in methanol at 0 ˚C. The mixture was then allowed to warm to ambient temperature and was stirred 1 h. The mixture was washed with water, extracted with dichloromethane and dried over anhydrous $MgSO_4$.

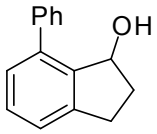
7-Methylindan-1-ol [4]



Following general procedure A with sodium borohydride (227 mg, 6.00 mmol) and 7-methylindan-1-one (300 mg, 2.00 mmol) afforded the 7-methylindan-1-ol (270 mg, 1.82 mmol, 91 %) as pale yellow solid: IR (neat) 3268, 2924, 1599, 1464, 1181, 1045, 960, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 7.09 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.02 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.32-5.31 (m, 1H, C*H*-OH), 3.19-3.11 (m, 1H, C*H*$_2$-CH$_2$CHOH), 2.86-2.79 (m, 1H, C*H*$_2$-CH$_2$CHOH), 2.43 (s, 3H, CH_3), 2.43-2.33 (m, 1H, C*H*$_2$-CHOH), 2.08-2.03 (m, 1H, C*H*$_2$-CHOH), 1.60 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.9, 135.2, 128.9, 128.0, 122.4, 75.5, 35.1, 30.1, 18.3; MS (EI) *m/z* 148 (M); HRMS (EI) *m/z* calc for $C_{10}H_{12}O$ 148.0888, found: 148.0883.

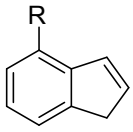
This journal is © The Royal Society of Chemistry 2011

7-Phenylindan-1-ol



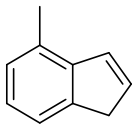
Following general procedure A with sodium borohydride (160 mg, 4.30 mmol) and 7-phenylindan-1-one (300 mg, 1.44 mmol) afforded the 7-phenylindan-1-ol (300 mg, 1.43 mmol, 98 %) as white solid: m.p. ($CHCl_3$) = 60 – 61 ˚C; IR (neat) 3236, 1592, 1468, 955, 755, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H, Ar-*H*), 7.47-7.43 (m, 2H, Ar-*H*), 7.39-7.32 (m, 2H, Ar-*H*), 7.29-7.21 (m, 2H, Ar-*H*), 5.41 (dd, *J* = 6.4, 3.2 Hz, 1H, C*H*-OH), 3.25-3.17 (m, 1H, CH_2-CH_2CHOH), 2.93-2.85 (m, 1H, CH_2-CH_2CHOH), 2.41-2.32 (m, 1H, CH_2-CHOH), 2.11-2.03 (m, 1H, CH_2-CHOH), 1.65 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.3, 140.4, 139.1, 128.9, 128.6 (2C), 127.6, 127.4, 124.1, 75.1, 35.0, 30.0; MS (EI) *m/z* 210 (M); HRMS (EI) *m/z* calc for $C_{15}H_{14}O$ 210.1045, found: 210.1035.

General procedure B for the formation of indene:



PPTS (2 equiv.) was added to a solution of indan-1-ol (1 equiv.) in dichloromethane. The reaction was refluxed. After consumption of the starting material, the reaction was cooled to ambient temperature and a concentrated solution of $CuSO_4$ was added. Extraction with dichloromethane and evaporation of the solvent afforded the corresponding indene.

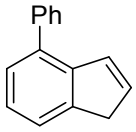
4-Methyl-1H-indene



This journal is © The Royal Society of Chemistry 2011

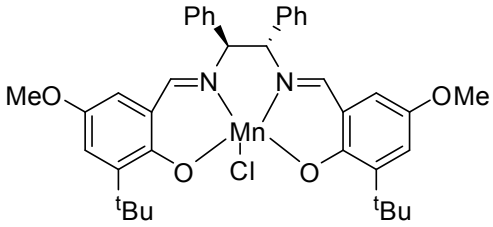
Following general procedure B with 4-methylindan-1-ol (1.00 g, 6.76 mmol) and PPTS (3.40 g, 13.46 mmol) afforded indene as pale yellow oil. The crude product was used in the next step without further purification: IR (thin film) 2924, 1599, 1476, 1047, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 7.15-7.09 (m, 2H, Ar-*H*), 7.03-7.00 (m, 1H, C*H*-Ar), 6.57-6.55 (m, 1H, C*H*-CH-Ar), 3.43-3.41 (m, 2H, CH_2-CH), 2.47 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.5, 133.5, 130.2, 127.2, 124.6, 121.1, 39.3, 18.6; MS (EI) *m/z* 130 (M); HRMS (EI) *m/z* calc for $C_{10}H_{10}$ 130.0783, found: 130.0779.

4-Phenyl-1H-indene



Amberlyst 15 was gradually added to 4-phenylindan-1-ol (500 mg, 2.38 mmol) in hexane (10 mL). The solution was stirred for 1 h at 0 °C and 2 h at ambient temperature and then filtrated. The solvent was evaporated and indene was obtained as pale yellow solid. The crude product was used in the next step without further purification: IR (thin film) 3059, 1594, 1464, 763, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 7.15-7.09 (m, 2H, Ar-*H*), 7.03-7.00 (m, 1H, C*H*-Ar), 6.60-6.59 (m, 1H, C*H*-CH-Ar), 3.50-3.49 (m, 2H, CH_2-CH); MS (EI) *m/z* 192 (M); HRMS (EI) *m/z* calc for $C_{15}H_{12}$ 192.0939, found: 192.0932.

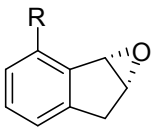
Catalyst 11 [5]



Following literature procedure. NMR of the precursor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.52 (s, 2H), 8.29 (s, 2H), 7.12-7.21 (m, 10H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 1.5 Hz, 2H), 4.67 (s, 2H), 2.17 (s, 6H), 1.42 (s, 18H).

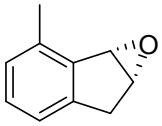
This journal is © The Royal Society of Chemistry 2011

General procedure C for the conversion of indene to epoxide:



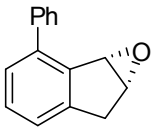
A solution of indene (1 equiv.), NMO (5 equiv.), and catalyst **11** (0.07 eq.) in dry dichloromethane was cooled to -78 °C for 15 min before the addition of solid *m*-CPBA (2 to 2.5 equiv.). After stirring for 2 to 3 h at -78 °C, 3N NaOH and water were added to the solution followed by celite©. After filtration, the organic phase was separated, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was evaporated to provide the epoxide.

(1S,2R)-Epoxy-7'-methylindane



Following general procedure C with 4-methylindene (6.76 mmol), NMO (4.30 g, 36.40 mmol), catalyst **11** (310 mg, 0.44 mmol) and solid *m*-CPBA (2.32 g, 13.42 mmol) gave epoxide as brown oil. The crude product was used in the next step without further purification: IR (thin film) 2917, 1721, 1598, 1477, 831, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-6.94 (m, 3H, Ar-*H*), 4.35 (m, 1H, C*H*-CH-CH_2), 4.10 (t, *J* = 2.9 Hz, 1H, CH-C*H*-CH_2), 3.21 (d, *J* = 18.1 Hz, 1H, C$H_{trans}H_{cis}$), 2.98 (dd, *J* = 18.1, 2.9 Hz, 1H, $CH_{trans}H_{cis}$), 2.48 (s, 3H, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.6, 135.1, 128.5, 127.5, 123.4, 57.6, 57.3, 34.7, 18.3; MS (EI) *m/z* 146 (M); HRMS (EI) *m/z* calc for $C_{10}H_{10}O$ 146.0732, found: 146.0729.

(1S,2R)-Epoxy-7'-phenylindane

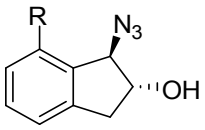


Following general procedure C with 4-phenylindene (2.38 mmol), NMO (1.51 g, 12.80 mmol), catalyst **11** (109.4 mg, 0.16 mmol) and solid *m*-CPBA (821 mg, 4.75 mmol) gave epoxide as brown oil. The crude product was used in the next step without further purification: Chiral HPLC: major (Rt = 7.37 min) : minor (Rt = 10.56

This journal is © The Royal Society of Chemistry 2011

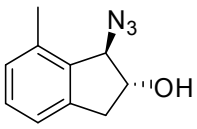
min) 94 : 6; IR (thin film) 2917, 1714, 1469, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2, 2H, Ar-*H*), 7.48 (t, *J* = 7.3, 2H, Ar-*H*), 7.41-7.22 (m, 4H, Ar-*H*), 4.31 (dd, *J* = 2.8, 1Hz, 1H, C*H*-CH-CH_2), 4.13 (t, *J* = 3 Hz, 1H, CH-C*H*-CH_2), 3.31 (d, *J* = 18 Hz, 1H, C$H_{trans}H_{cis}$), 3.06 (dd, *J* = 18; 3.1 Hz, 1H, $CH_{trans}H_{cis}$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.3, 140.0, 139.5, 128.8 (2C), 128.6 (2C), 127.3, 126.6, 124.9, 124.1, 59.0, 58.3, 34.8; MS (EI) *m/z* 208 (M); HRMS (EI) *m/z* calc for $C_{15}H_{12}O$ 208.0888, found: 208.0884.

General procedure D for the conversion of epoxide to azide:



Epoxide (1 equiv.), NH_4Cl (2 equiv.), and NaN_3 (2 equiv.) were dissolved in 80 % v/v aqueous ethanol. After stirring for 2 h at reflux, the mixture was cooled to ambient temperature and water was added. The aqueous phase was extracted with ethyl acetate and the organic phase was washed with brine and dried over anhydrous $MgSO_4$. The solvent was evaporated followed by flash chromatography to give the corresponding azide.

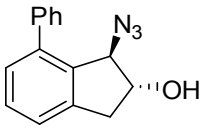
(1R,2R)-1-Azido-7-methyl-2,3-dihydro-1H-inden-2-ol



Following general procedure D with methylindane (6.76 mmol), NH_4Cl (680 mg, 12.40 mmol), NaN_3 (812 mg, 12.40 mmol). Flash column chromatography on silica gel (eluent: EtOAc : Petroleum ether 1 : 6) afforded azide (702 mg, 3.71 mmol, 55 % over 3 steps, 94 % e.e.) as yellow oil: $[\alpha]_D$ = +16 ˚ (c 0.1, DCM); Chiral HPLC: major (Rt = 3.81 min) : minor (Rt = 5.69 min) 97 : 3; IR (thin film) 3378, 2920, 2096, 1600, 770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8, 1H, Ar-*H*), 7.12-7.07 (m, 2H, Ar-*H*), 4.67 (br, 1H, C*H*-N_3), 4.56-4.54 (m, 1H, C*H*-OH), 3.37 (dd, *J* = 16.6, 5.9 Hz, 1H, C$H_{trans}H_{cis}$), 2.84 (dd, *J* = 16.6, 2.4 Hz, 1H, $CH_{trans}H_{cis}$), 2.41 (s, 3H, CH_3);

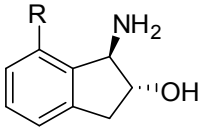
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 136.1, 129.7, 128.8, 122.9, 77.8, 71.5, 60.4, 40.1, 21.0, 18.7, 14.2; MS (EI) *m/z* 189 (M); HRMS (EI) *m/z* calc for $C_{10}H_{11}N_3O$ 189.0902, found: 189.0902.

(1R,2R)-1-Azido-7-phenyl-2,3-dihydro-1H-inden-2-ol



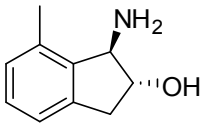
Following general procedure D with phenylindane (2.38 mmol), NH_4Cl (213 mg, 3.92 mmol), NaN_3 (255 mg, 3.92 mmol). Flash column chromatography on silica gel (eluent: EtOAc : Petroleum ether 1 : 6) afforded azide (350mg, 1.39 mmol, 58% over 3 steps) as yellow oil: $[\alpha]_D$ = +32.7 ° (c 1.15, DCM); IR (thin film) 3351, 2920, 2097, 1592, 1468, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.38 (m, 6H, Ar-*H*), 7.31-7.27 (m, 2H, Ar-*H*), 4.79 (br, 1H, C*H*-N_3), 4.52-4.53 (m, 1H, C*H*-OH), 3.43 (dd, *J* = 16.6, 4.9 Hz, 1H, C$H_{trans}H_{cis}$), 2.93 (dd, *J* = 16.6, 2.4 Hz, 1H, $CH_{trans}H_{cis}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.9, 139.8, 135.5, 129.8, 128.6 (2C), 128.5 (3C), 127.5, 124.6, 77.9, 71.2, 39.9; MS (EI) *m/z* 251 (M); HRMS (EI) *m/z* calc for $C_{15}H_{13}N_3O$ 251.1059, found: 251.1059.

General procedure E for the reduction of the azide:



Azide derivatives were dissolved in methanol and Pd/C added (10% w). The mixture was stirred 20 min under hydrogen atmosphere. Then the mixture was filtrated through celite© and solvent evaporated to give the corresponding amino-indanol.

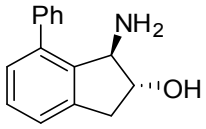
(1R,2R)-1-Amino-7-methyl-2,3-dihydro-1H-inden-2-ol



This journal is © The Royal Society of Chemistry 2011

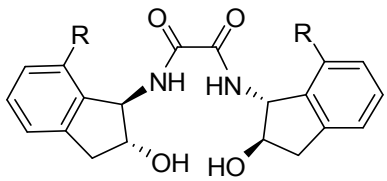
Following general procedure E with azide (670 mg, 3.54 mmol), Pd/C (67 mg) afforded amino-indanol as pale yellow oil. The crude product was used in the next step without further purification: IR (thin film) 3351, 2916, 1597, 1465, 1042, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 7.08-7.07 (m, 1H, Ar-*H*), 7.01 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 4.24-4.22 (m, 2H, C*H*-OH, C*H*-NH_2), 3.38 (dd, *J* = 16.6, 5.8 Hz, 1H, C$H_{trans}H_{cis}$), 2.77 (dd, *J* = 16.6, 2.4 Hz, 1H, $CH_{trans}H_{cis}$), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.4, 134.9, 128.6, 128.4, 122.9, 80.6, 64.1, 39.3, 18.5; MS (ESI) *m/z* 147 (M-NH_2); HRMS (ESI) *m/z* calc for $C_{10}H_{11}O$ 147.0810, found: 147.0813.

(1R,2R)-1-Amino-7-phenyl-2,3-dihydro-1H-inden-2-ol



Following general procedure E with azide (340 mg, 1.35 mmol), Pd/C (34 mg) afforded amino-indanol as dark oil (96 % e.e.). The crude product was used in the next step without further purification: Chiral HPLC: major (Rt = 31.11 min) : minor (Rt = 36.46 min) 98 : 2; IR (thin film) 2259, 1590, 1467, 1074, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.43 (m, 4H, Ar-*H*), 7.39-7.35 (m, 1H, Ar-*H*), 7.32-7.29 (m, 1H, Ar-*H*), 7.18 (dd, *J* = 15.1, 7.3 Hz, 2H, Ar-*H*), 4.43 (d, *J* = 4.4 Hz, 1H, C*H*-NH_2), 4.20-4.15 (m, 1H, C*H*-OH), 3.29 (dd, *J* = 16.1, 6.8 Hz, 1H, C$H_{trans}H_{cis}$), 2.89 (dd, *J* = 15.6, 6.8 Hz, 1H, $CH_{trans}H_{cis}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.5, 140.2, 139.0, 128.8 (2C), 128.6, 128.5 (2C), 128.2, 127.5, 124.3, 80.7, 63.9, 38.3; MS (ESI) *m/z* 250 (M+H_2+Na); HRMS (ESI) *m/z* calc for $C_{15}H_{17}NONa$ 250.1208, found: 250.1213.

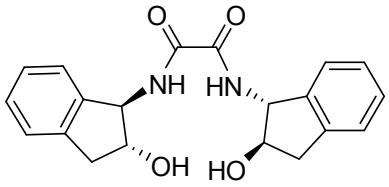
General procedure F for the formation of oxalamide:



Amino-indanol (2 equiv.) was dissolved in tetrahydrofuran. Diethyl oxalate (1 equiv.) and acetic acid (0.1 equiv.) were added and the reaction was refluxed for 16 h. The solvent was evaporated to afford the corresponding product.

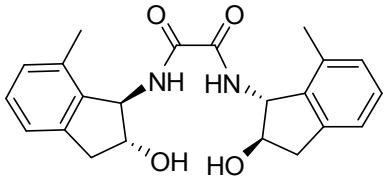
This journal is © The Royal Society of Chemistry 2011

N1,N2-bis((1R,2R)-2-Hydroxy-2,3-dihydro-1H-inden-1-yl)oxalamide



Following general procedure F with (1R, 2R)-(-)-*trans*-1-amino-2-indanol (1.00 g, 6.70 mmol), tetrahydrofuran (20 mL), diethyl oxalate (0.44 mL, 3.35 mmol) and acetic acid (0.040 mL, 0.70 mmol) afforded the desired product as white solid: ^{1}H NMR (400 MHz, *d*-DMSO) δ 9.10 (d, *J* = 8.8 Hz, 2H), 7.21-7.16 (m, 6H, Ar-*H*), 7.10-7.05 (m, 2H, Ar-*H*), 5.09 (t, *J* = 7.8 Hz, 2H, C*H*-NH), 4.53-4.48 (m, 2H, C*H*-OH), 3.16 (dd, *J* = 15.1, 7.3 Hz, 2H, CH_2), 2.72 (dd, *J* = 15.1, 7.8 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, *d*-DMSO) δ 160.5, 141.1, 139.7, 127.6, 126.5, 124.6, 123.5, 76.8, 61.3, 25.0; MS (ESI) *m/z* 353 (M+H); HRMS (ESI) *m/z* calc for $C_{20}H_{21}N_2O_4$ 353.1501, found: 353.1497.

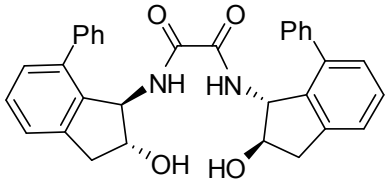
N1,N2-bis((1R,2R)-2-Hydroxy-7-methyl-2,3-dihydro-1H-inden-1-yl)oxalamide



Following general procedure F with *trans*-amino-indanol (2.50 mmol), diethyl oxalate (0.16 mL, 1.75 mmol) and acetic acid (0.016 mL, 0.30 mmol) afforded the desired product as white solid: m.p. (CH_2Cl_2) = 276 – 278 ˚C; IR (neat) = 3262, 1653, 1505, 1070, 765 cm^{-1}; ^{1}H NMR (400 MHz, *d*-DMSO) δ 9.93 (d, *J* = 9.8 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.03 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 6.96 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 5.24 (br, 2H, O*H*), 5.15 (dd, *J* = 9.3, 3.9 Hz, 2H, C*H*-NH), 4.34-4.30 (m, 2H, C*H*-OH), 3.30 (dd, *J* = 16.1, 6.8 Hz, 2H, CH_{trans}H$_{cis}$), 2.64 (dd, *J* = 16.1, 4.9 Hz, 2H, CH$_{trans}$$H_{cis}$), 2.10 (s, 6H, C$H_3$); ^{13}C NMR (100 MHz, *d*-DMSO) δ 159.5, 141.8, 139.0, 134.3, 127.9, 122.2, 76.8, 61.1, 25.0, 17.7; Anal. Calc for $C_{22}H_{24}N_2O_4$: C, 69.46; H, 6.36; N, 7.36; Found: C, 69.50; H, 6.43; N, 7.37.

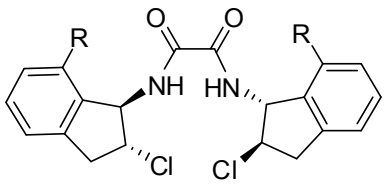
This journal is © The Royal Society of Chemistry 2011

N1,N2-bis((1R,2R)-2-Hydroxy-7-phenyl-2,3-dihydro-1H-inden-1-yl)oxalamide



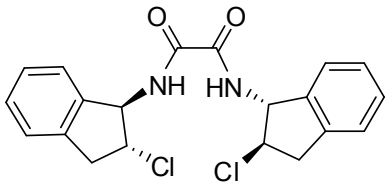
Following general procedure F with *trans*-amino-indanol (3.00 mmol), diethyl oxalate (0.20 mL, 1.50 mmol) and acetic acid (0.020 mL, 0.35 mmol) afforded the desired product as white solid: ^{1}H NMR (400 MHz, *d*-DMSO) δ 7.42-7.32 (m, 12H, Ar-*H*), 7.22 (t, *J* = 6.8 Hz, 4H, Ar-*H*), 7.10 (d, *J* = 5.8 Hz, 2H, Ar-*H*), 5.20 (t, *J* = 5.4 Hz, 2H, C*H*-NH), 4.38-4.33 (m, 2H, C*H*-OH), 3.32 (dd, *J* = 15.6, 7.3 Hz, 2H, CH_{trans}H$_{cis}$), 2.97 (dd, *J* = 16.1, 6.4 Hz, 2H, CH$_{trans}$$H_{cis}$); ^{13}C NMR (100 MHz, *d*-DMSO) δ 159.4, 141.7, 139.2, 138.8, 135.0, 129.4, 128.7 (4C), 128.3 (4C), 127.8, 124.4, 80.0, 63.8, 38.6.

General procedure G for the chlorination of the oxalamide:



The alcohol (1 equiv.) was partially dissolved in toluene. Thionyl chloride (5 equiv.) was added and the reaction was refluxed for 16 h. All the volatile were removed under reduce pressure to afford the corresponding product.

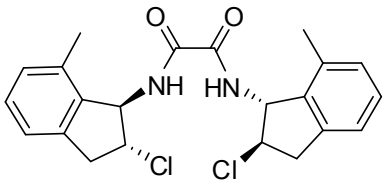
N1,N2-bis((1R,2R)-2-Chloro-2,3-dihydro-1H-inden-1-yl)oxalamide



Following general procedure G with alcohol (3.35 mmol) and thionyl chloride (1.24 mL, 17.0 mmol) afforded the desired product as white solid: ^{1}H NMR (400 MHz, *d*-DMSO) δ 9.47 (d, *J* = 9.3 Hz, 2H), 7.29-7.28 (m, 6H,

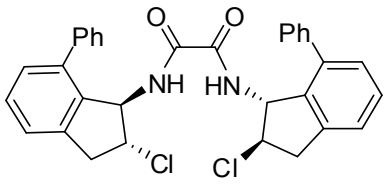
Ar-*H*), 7.19-7.16 (m, 2H, Ar-*H*), 5.44 (t, *J* = 8.8 Hz, 2H, C*H*-NH), 4.77 (q, *J* = 7.8 Hz, 2H, C*H*-Cl), 3.55 (dd, *J* = 15.1, 7.3 Hz, 2H, CH_{trans}H$_{cis}$), 3.12 (dd, *J* = 15.1, 7.8 Hz, 2H, CH$_{trans}$$H_{cis}$); ^{13}C NMR (100 MHz, *d*-DMSO) δ 160.2, 157.3, 140.0, 139.1, 128.2, 127.2, 124.4, 123.3, 62.1, 61.1.

N1,N2-bis((1R,2R)-2-Chloro-7-methyl-2,3-dihydro-1H-inden-1-yl)oxalamide



Following general procedure G with alcohol (1.70 mmol) and thionyl chloride (0.62 mL, 8.50 mmol) afforded the desired product as white solid: ^{1}H NMR (400 MHz, *d*-DMSO) δ 9.36-9.30 (m, 2H), 7.22-7.19 (m, 2H, Ar-*H*), 7.12-7.10 (m, 2H, Ar-*H*), 7.06-7.04 (m, 2H, Ar-*H*), 5.48-5.42 (m, 2H, C*H*-NH), 4.65 (br, 2H, C*H*-Cl), 3.75-3.69 (m, 2H, CH_{trans}H$_{cis}$), 3.05-3.00 (m, 2H, CH$_{trans}$$H_{cis}$), 2.12 (s, 6H, C$H_3$).

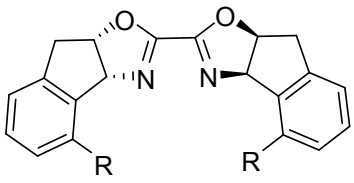
N1,N2-bis((1R,2R)-2-Chloro-7-phenyl-2,3-dihydro-1H-inden-1-yl)oxalamide



Following general procedure G with alcohol (0.47 mmol) and thionyl chloride (0.17 mL, 2.35 mmol) afforded the desired product as white solid: ^{1}H NMR (400 MHz, *d*-DMSO) δ 7.40 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.32-7.15 (m, 16H, Ar-*H*), 7.03 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 5.42 (dd, *J* = 7.8, 3.9 Hz, 2H, C*H*-NH), 4.41-4.38 (m, 2H, C*H*-Cl), 3.59 (dd, *J* = 16.6, 6.3 Hz, 2H, CH_{trans}H$_{cis}$), 3.21 (dd, *J* = 16.6, 4.4 Hz, 2H, CH$_{trans}$$H_{cis}$).

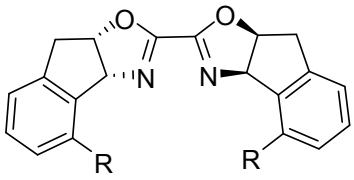
This journal is © The Royal Society of Chemistry 2011

General procedure H for the formation of the oxazole:



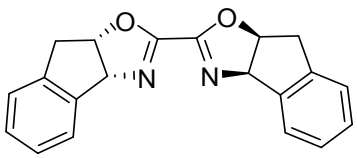
The chloride (1 equiv.) was dissolved in tetrahydrofuran and a solution of NaOH (3.75 equiv.) in ethanol was added. The mixture was refluxed for 3 h and the solvent was evaporated under reduce pressure. Flash chromatography afforded the corresponding oxazole compound.

General procedure I for the formation of the oxazole:



The alcohol (1 equiv.) was partially dissolved in dichloromethane and cooled to 0 ˚C. Then a solution of deoxofluor (50 % in tetrahydrofuran, 1.2 equiv.) was added. The mixture was warmed to ambient temperature for 1 h and the solvent was evaporated under reduce pressure. Flash chromatography afforded the corresponding oxazole compound.

(3aR,3'aS,8aS,8'aS)-8,8a,8',8'a-Tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole

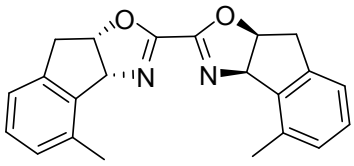


Following general procedure H with chloride (3.35 mmol) and NaOH (500 mg, 12.5 mmol) afforded oxazole (900 mg, 2.85 mmol, 85 % over 3 steps) as light brown solid: m.p. (CH_2Cl_2) = 178 – 182 ˚C; $[\alpha]_D$ = +254.8 ˚ (c 0.39, DCM); IR (neat) = 2923, 1612, 1121, 981, 747 cm^{-1}; ^1H NMR (400 MHz, *d*-DMSO) δ 7.50-7.48 (m, 2H, Ar-*H*), 7.24-7.21 (m, 6H, Ar-*H*), 5.72 (d, *J* = 8.0 Hz, 2H, C*H*-N), 5.49-5.45 (m, 2H, C*H*-O), 3.43 (dd, *J* = 18.0, 6.4 Hz,

This journal is © The Royal Society of Chemistry 2011

2H, , CH_{trans}H$_{cis}$), 3.35 (dd, *J* = 17.6, 1.9 Hz, 2H, CH$_{trans}$$H_{cis}$); ^{13}C NMR (100 MHz, *d*-DMSO) δ 155.1, 140.4, 139.5, 128.8, 127.5, 125.7, 125.3, 84.5, 77.2, 77.1, 39.4; MS (ESI) *m/z* 317 (M+H); HRMS (ESI) *m/z* calc for $C_{20}H_{17}N_2O_2$ 317.1290, found: 317.1292.

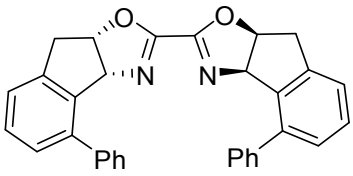
(3aR,3'aR,8aS,8'aS)-4,4'-Dimethyl-8,8a,8',8'a-tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole



Following general procedure H with chloride (1.75 mmol) and NaOH (256 mg, 6.40 mmol) afforded oxazole (350 mg, 1.02 mmol, 58 % over 4 steps).

Following general procedure I with alcohol (280 mg, 0.73 mmol) and deoxofluor (0.39mL, 0.87 mmol) afforded oxazole (235 mg, 0.68 mmol, 94%) as light brown solid: m.p. (CH_2Cl_2) = 179 – 181 ˚C; $[\alpha]_D$ = +291.0 ˚ (c 0.10, MeOH); IR (neat) = 3258, 1652, 1511, 1110, 764 cm^{-1}; ^{1}H NMR (400 MHz, *d*-DMSO) δ 7.15 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.04-7.01 (m, 4H, Ar-*H*), 5.75 (d, *J* = 8.3 Hz, 2H, C*H*-N), 5.48-5.44 (m, 2H, C*H*-O), 3.44-3.32 (m, 4H, CH_2), 2.38 (s, 6H, CH_3); ^{13}C NMR (100 MHz, *d*-DMSO) δ 155.0, 139.6, 139.1, 136.0, 129.0, 128.4, 122.4, 83.9, 76.8, 39.6, 19.0; MS (ESI) *m/z* 345 (M+H); HRMS (ESI) *m/z* calc for $C_{22}H_{21}N_2O_2$ 345.1603, found: 345.1601.

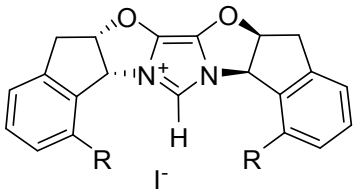
(3aR,3'aR,8aS,8'aS)-4,4'-Diphenyl-8,8a,8',8'a-tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole



Following general procedure H with chloride (0.40 mmol) and NaOH (60 mg, 1.50 mmol) afforded oxazole as light brown solid (80 mg, 0.17 mmol, 42 % over 4 steps): m.p. (CH_2Cl_2) = 182 – 184 ˚C; $[\alpha]_D$ = +680.0 ˚ (c 1.02, DCM); IR (neat) = 3055, 1641, 1108, 757, 700 cm^{-1}; ^{1}H NMR (400 MHz, *d*-DMSO) δ 7.78 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.46 (t, *J* = 6.8 Hz, 4H, Ar-*H*), 7.38-7.32 (m, 4H, Ar-*H*), 7.27 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.20 (d, *J* = 6.8 Hz, 2H,

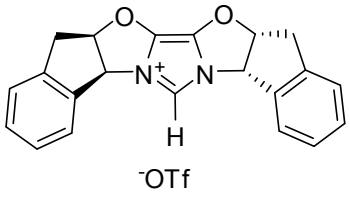
Ar-*H*), 5.68 (d, *J* = 8.3 Hz, 2H, C*H*-N), 5.47 (dt, *J* = 7.8, 2.9 Hz, 2H, C*H*-O), 3.48 (dd, *J* = 17.1, 7.3 Hz, 2H, , $CH_{trans}H_{cis}$), 3.36 (dd, *J* = 18.1, 2.9 Hz, 2H, $CH_{trans}H_{cis}$); ^{13}C NMR (100 MHz, *d*-DMSO) δ 154.2, 140.8, 140.5, 140.2, 137.8, 129.3 (6C), 128.5, 128.3 (4C), 127.3, 124.0, 83.2, 76.8 40.3; MS (ESI) *m/z* 469 (M+H); HRMS (ESI) *m/z* calc for $C_{32}H_{25}N_2O_2$ 469.1916, found: 469.1906.

General procedure J for the formation of the imidazolium salt:



Chloromethyl ethylether (1.1 equiv.) and silver triflate (1.1 equiv.) were added to a solution of oxazole (1 equiv.) in dichloromethane. The mixture was stirred 2 h at ambient temperature in the dark. The supernatant was collected and the solvent evaporated. The crude was dissolved in acetone and NaI (10 equiv.) was added. After 2 h at ambient temperature, the solvent was evaporated and a column chromatography afforded the desired imidazolium salt.

Imidazolium salt (15a)

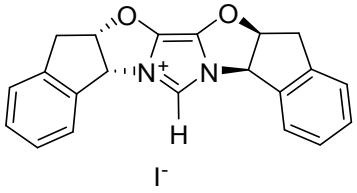


Chloromethyl pivalate (0.13 mL, 0.96 mmol) was added to a mixture of silver triflate (246 mg, 0.84 mmol) in degassed and dry over molecular sielves CH_2Cl_2 (3 mL). The mixture was stirred 1h at ambient temperature in the dark. Then 2 mL of the mixture was transferred to a solution of diimine (60 mg, 0.19 mmol) in degassed and dry CH_2Cl_2 (1 mL). The mixture reacted in microwave at 90 °C for 30 min. Another 1 mL of the solution was transferred to the solution and the mixture reacted 30 more minutes at 90 °C. Removal of the solvent under reduced pressure followed by flash column chromatography on silica gel afforded the imidazolium salt **15a** (20 mg, 22%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H, N-C*H*-N), 7.84 (d, *J* = 7.8 Hz, 2H,

This journal is © The Royal Society of Chemistry 2011

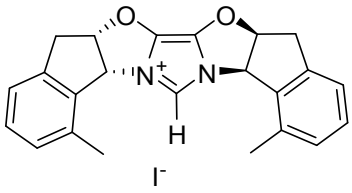
Ar-*H*), 7.40-7.28 (m, 6H, Ar-*H*), 6.32 (d, *J* = 6.3 Hz, 2H, C*H*-N), 6.10-6.07 (m, 2H, C*H*-O), 3.56-3.45 (m, 4H, CH_2); ^{13}C NMR (400 MHz, *d*-DMSO) δ 139.6, 134.8, 130.8, 129.0, 126.1, 125.2, 124.8, 114.4, 95.1, 66.9, 38.3; MS (ESI+) *m/z* 329 (M+); HRMS (ESI+) *m/z* calc for $C_{21}H_{17}N_2O_2$ 329.1290, found: 329.1280; MS (ESI-) *m/z* 149 (M-); HRMS (ESI-) *m/z* calc for CF_3O_3S 148.9520, found: 148.9527.

Imidazolium salt (15b)



Following general procedure J with oxazole (220 mg, 0.69 mmol), chloromethyl ethylether (0.076 mL, 0.70 mmol), silver triflate (245 mg, 0.70 mmol) and NaI (1 g, 7.00 mmol) afforded imidazolium salt **15b** (190 mg, 0.42 mmol, 61%) as pale yellow oil: m.p. (CH_2Cl_2) = 112 – 114 ˚C; $[\alpha]_D$ = -76.4 ˚ (c 0.67, DCM); IR (neat) = 2924, 2854, 1707, 1519, 1170, 755, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H, N-C*H*-N), 8.07-8.04 (m, 2H, Ar-*H*), 7.44 77.41 (m, 4H, Ar-*H*), 7.32-7.30 (m, 2H, Ar-*H*), 6.45 (d, *J* = 6.3 Hz, 2H, C*H*-N), 6.13-6.09 (m, 2H, C*H*-O), 3.54-3.52 (m, 4H, CH_2); ^{13}C NMR (100 MHz, *d*-DMSO) δ 139.6, 134.6, 130.8, 129.1, 126.8, 125.2, 124.8, 115.6, 95.2, 66.8, 38.3; MS (ESI+) *m/z* 329 (M+); HRMS (ESI+) *m/z* calc for $C_{21}H_{17}N_2O_2$ 329.1290, found: 329.1280.

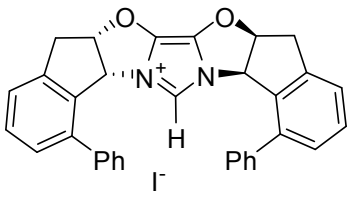
Methyl Imidazolium salt (16b)



Following general procedure J with oxazole (20 mg, 0.06 mmol), chloromethyl ethylether (0.007 mL, 0.06 mmol), silver triflate (22 mg, 0.06 mmol) and NaI (100 mg, 0.70 mmol) afforded imidazolium salt **16b** as a white solid (16 mg, 0.03 mmol, 55 %): m.p. (CH_2Cl_2/Et_2O) = 146 – 148 ˚C; $[\alpha]_D$ = -105.0 ˚ (c 0.20, DCM); IR

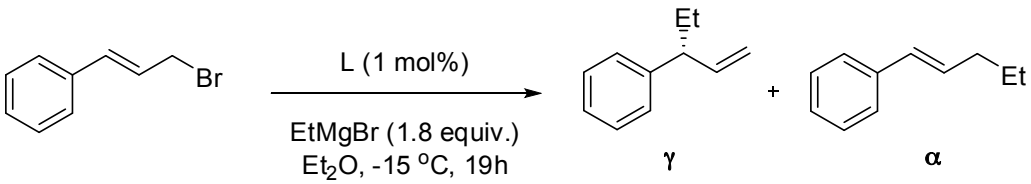
(neat) = 2926, 1730, 1514, 1164, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H, N-C*H*-N), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.14 (d, *J* = 7.3 Hz, 4H, Ar-*H*), 6.80 (d, *J* = 6.8 Hz, 2H, C*H*-N), 6.11 (dt, *J* = 5.4, 2.4 Hz, 2H, C*H*-O), 3.50-3.42 (m, 4H, CH_2), 2.81 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ140.4, 136.7, 132.7, 131.3, 130.1, 125.6 (1C), 123.0, 115.4, 95.4, 67.8, 37.8, 21.0; MS (ESI+) *m/z* 357 (M+); HRMS (ESI+) *m/z* calc for $C_{23}H_{21}N_2O_2$ 357.1603, found: 357.1602; Anal. Calc for $C_{23}H_{21}IN_2O_2$: C, 57.04; H, 4.37; N, 5.78; Found: C, 57.08; H, 4.47; N, 5.69.

Phenyl Imidazolium salt (17b)



Following general procedure J with oxazole (76 mg, 0.16 mmol), chloromethyl ethylether (0.015 mL, 0.16 mmol), silver triflate (52 mg, 0.16 mmol) and NaI (200 mg, 1.40 mmol) afforded imidazolium salt **17b** as pale yellow solid (43 mg, 0.07 mmol, 41 %): m.p. (CH_2Cl_2/Et_2O) = 130 – 134 ˚C; $[\alpha]_D$ = -17.8 ˚ (c 0.32, DCM); IR (neat) = 2970, 1507, 1160, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 8H, Ar-*H*), 7.45-7.39 (m, 6H, Ar-*H*), 7.30 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H, C*H*-N), 6.84 (d, *J* = 5.9 Hz, 2H, C*H*-O), 6.21-6.18 (m, 2H), 4.71 (s, 1H, N-C*H*-N), 3.58-3.46 (m, 4H, CH_2); ^{13}C NMR (100 MHz, *d*-DMSO) δ 141.6, 140.1, 138.2, 131.4, 131.2, 129.9 (4C), 129.8, 129.1, 128.3 (4C), 125.6 (1C), 124.9, 112.1, 95.9, 68.1, 37.4.

General procedure for the allylic alkylation:

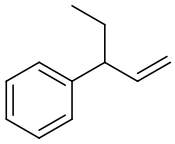


Imidazolium salt (1%) and cinnamyl bromide (0.5 mmol) were dissolved in Et_2O. The solution was cooled to -15˚C and ethyl magnesium bromide (1.8 eq) was added slowly over four minutes. The mixture was stirred 19h at -15˚C and quenched at -15˚C with acidified ammonium chloride saturated solution (NH4Cl Dissolved in ~0.5 M HCl) and the product extracted with ether, dried with $MgSO_4$. Removal of solvent under vacuum gives the crude product as a mixture of **γ** and **α** (colourless oil). Enantiomeric excess was determined by Gas chromatography (GC). Conversion was determined by ^{1}H NMR ratio analysis.

Chiral GC Method :

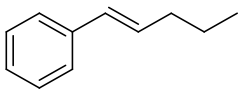
Column: Chiracil-Dex-CB; Oven temperature program: 50 °C (2.0 mins), 20 °C/min to 90 °C, 90 °C (15.0 mins), 20 °C/min to 110 °C, 110 °C (10.0 mins), 20 °C/min to 180 °C, 180 °C (1.5 mins); total time: 35.0 mins. Flow: 1.0 ml/min, helium.

Pent-1-en-3-ylbenzene (**19γ**)[6]



19γ: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34-7.39 (m, 2 H, Ar), 7.24-7.29 (m, 3 H, Ar), 5.98-6.07 (m, 1 H, C*H* =CH_2), 5.10-5.14 (m, 1 H, $CH_{2\beta}$), 5.09 (s, 1 H, $CH_{2\alpha}$), 3.21 (q, *J* = 7.2 Hz, 1 H, ArC*H*), 1.76-1.87 (m, 2 H, MeCH_2), 0.95 (t, *J* = 8.8 Hz, 3 H, Me);

(E)-pent-1-en-1-ylbenzene(**19α**) [6]

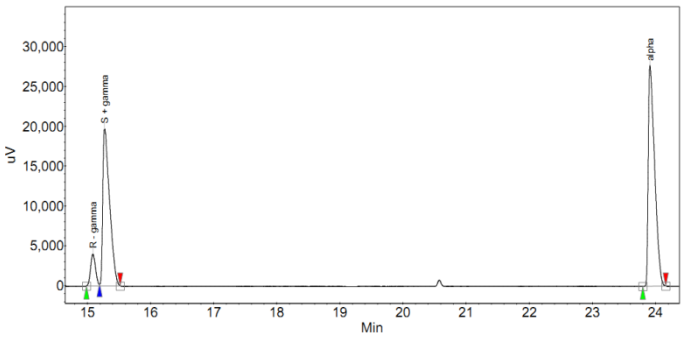


19α: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.32-7.43 (m, 3 H, Ar), 7.22-7.28 (m, 2 H, Ar), 6.45 (d, *J* = 15.8 Hz, 1 H, ArC(*H*)=C), 6.29 (dt, *J* = 15.8, 6.8 Hz, 1 H, C=C*H*CH_2), 2.25 (qd, *J* = 7.2, 0.8 Hz, 2 H, $CH_2CH_2CH_3$), 3.12 (sextet, *J* = 7.2 Hz, 2 H, $CH_2CH_2CH_3$), 1.02 (t, *J* = 7.2 Hz, 3 H, Me);

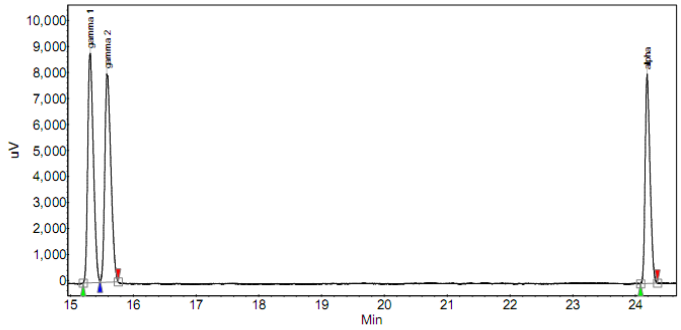
GC; (**19γ**, *R*-(-)): 15.1 min. (**19γ**, *S* (**+**)): 15.3 min. (**19α**): 23.9 min.

Using Imidazolium Salt **15b:**

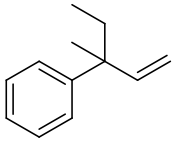
This journal is © The Royal Society of Chemistry 2011



Using SIMes:

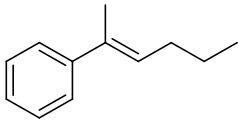


(3-Methylpent-1-en-3-yl)benzene(20γ) [6]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.42 (m, 4 H, Ar), 7.22-7.26 (m, 1 H, Ar), 6.10 (dd, *J* = 17.6, 10.8 Hz, 1 H, C*H*=CH_2), 5.18 (d, *J* = 10.8 Hz, 1 H, C-C$H_{2\beta}$), 5.11 (d, *J* = 17.2 Hz, 1 H, C=C$H_{2\alpha}$), 1.78-1.96 (m, 2 H, CH_3CH_2), 1.424 (s, 3 H, Me), 0.84 (t, *J* = 7.6 Hz, 3 H, CH_2*Me*);

(E)-hex-2-en-2-ylbenzene(20α) [6]

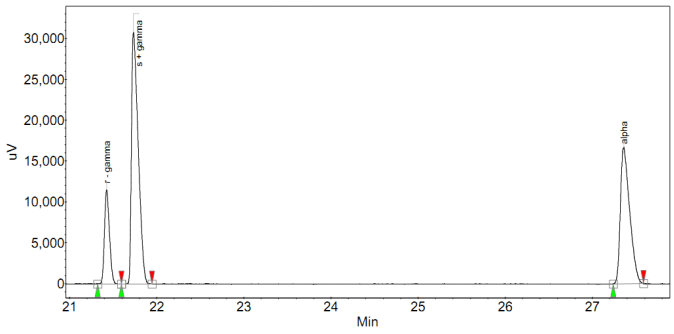


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15-7.60 (m, 5H, Ar), 5.82-5.86 (m, 1H, C=C*H*), 2.21-2.28 (m, 2H, $CH_2CH_2CH_3$), 2.09 (s, 3H, C=C*Me*), 1.50-1.58 (m, 2H, $CH_2CH_2CH_3$), 1.02 (t, *J* = 7.6 Hz, 3H, CH_2CH_3);

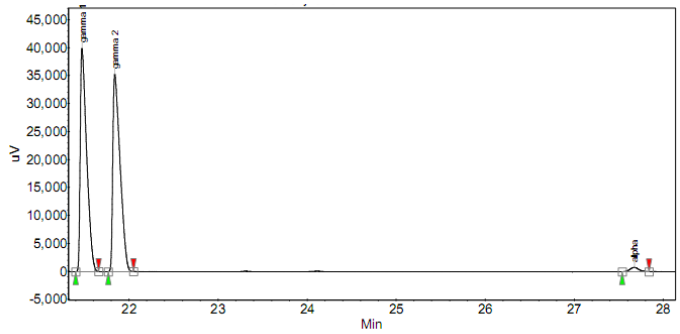
GC; (**20γ**, *R*-(-)): 21.4 min. (**20γ**, *S* (**+**)): 21.8 min. (**20α**): 27.4 min.

This journal is © The Royal Society of Chemistry 2011

Using Imidazolium Salt **15b:**



Using SIMes:



References:

(1) L. Minuti, A. Taticchi, A. Marrocchi, D. Lanari, A. Broggi, E. Gacs-Baitz, *Tetrahedron: Asymmetry* 2003, **14**, 481.
(2) R. S. Senaiar, J. A. Teske, D. D. Young, A. Deiters, *J. Org. Chem.* 2007, **72**, 7801.
(3) A. Watzke, R. Wilson, S. J. O'Malley, R. G. Bergman, J. A. Ellman, *Synlett* 2007, **15**, 2383.
(4) J. A. Elvidge, R. G. Foster, *J. Chem. Soc.* 1963, 590.
(5) M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Güler, T. Ishida, E. N. Jacobsen, *J. Am. Chem. Soc.* 1998, **120**, 948.
(6) O. Jackowski, A. Alexakis, *Angew. Chem. Int. Ed.* 2010, **49**, 3346.

This journal is © The Royal Society of Chemistry 2011

The X-ray crystal structure of *ent*-15a (prepared in an analogous fashion to above).

Crystal data for **15a**: $(C_{21}H_{17}N_2O_2)(CF_3SO_3)$, M = 478.44, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.02411(5), b = 10.34453(6), c = 20.23764(11) Å, V = 2098.535(19) Å^3, Z = 4, D_c = 1.514 g cm^{-3}, μ(Cu-Kα) = 1.967 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 4146 independent measured reflections (R_{int} = 0.0230), F^2 refinement, R_1(obs) = 0.0270, wR_2(all) = 0.0709, 4004 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 298 parameters. The absolute structure of **15a** was determined by a combination of R-factor tests [R_1^+ = 0.0270, R_1^- = 0.0428] and by use of the Flack parameter [x^+ = 0.000(12), x^- = 1.003(12)]. CCDC 842971.

The X-ray crystal structure of 16b

Crystal data for **16b**: $(C_{23}H_{21}N_2O_2)(I)\cdot{}^4/_3C_7H_{16}$, M = 617.92, hexagonal, $P6_1$ (no. 169), a = 21.382(2), c = 10.7536(10) Å, V = 4257.7(8) Å^3, Z = 6, D_c = 1.446 g cm^{-3}, μ(Cu-Kα) = 9.102 mm^{-1}, T = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3982 independent measured reflections (R_{int} = 0.0675), F^2 refinement, R_1(obs) = 0.0916, wR_2(all) = 0.3676, 1503 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 146°], 243 parameters. The absolute structure of **16b** was determined by a combination of R-factor tests [R_1^+ = 0.0916, R_1^- = 0.1144] and by use of the Flack parameter [x^+ = 0.08(3), x^- = 0.92(3)]. CCDC 842972.

The crystals of **16b** were found to be of very poor quality and suffered from clear twinning issues. Additionally, having a needle morphology, only a comparatively small volume of material could be bathed in the X-ray beam (the crystal studied had dimensions of *ca*. 0.25 mm × 0.04 mm × 0.03 mm). Consequently, despite a *ca*. 107 hour data collection time for an experiment using Cu-Kα radiation and that was designed to collect only trigonal data to a resolution of only 0.84 Å, the overall intensity of the data set was still low, the mean I/σ being *ca*. 5.4. (An earlier crystal had been tried using Mo-Kα radiation to address absorption issues caused by the presence of an iodine atom, but the scattering was incredibly weak with an estimated data collection time of over 400 hours.) As a result of the weak scattering, the ratio of observed to unique reflections is low (*ca*. 0.38) and the final R-factors are relatively high (this is most easily seen in the wR_2(all) value of 0.3676). This latter issue is also a consequence of the included solvent being found to be highly disordered. This was handled using the SQUEEZE routine of PLATON[X1] which suggested a total of 450 electrons per unit cell, equivalent to 75 electrons per asymmetric unit. During synthesis and crystallisation the solvents used were acetone, toluene, heptane and tetrahydrofuran. From ΔF maps prior to the use of

This journal is © The Royal Society of Chemistry 2011

SQUEEZE, the electron density in the disordered solvent areas had most resembled heptane [C_7H_{16}, 58 electrons]. $^4/_3$ heptane molecules equates to 77.3, so this was used as the solvent present. The atom list for the asymmetric unit is thus low by $C_{9.33}H_{21.33}$ (and that for the unit cell by $C_{56}H_{128}$) compared to what is actually presumed to be present.

Despite all these issues however, there is little doubt as to the identity of the species present.

The X-ray crystal structure of 17a

Crystal data for **17a**: $(C_{33}H_{25}N_2O_2)(CF_3SO_3)$, M = 630.62, monoclinic, $P2_1$ (no. 4), a = 8.31659(11), b = 20.0565(2), c = 17.4123(2) Å, β = 95.0536(12)°, V = 2893.11(6) Å^3, Z = 4 [two independent cation:anion pairs], D_c = 1.448 g cm^{-3}, μ(Cu-Kα) = 1.577 mm^{-1}, T = 173 K, colourless tablets, Oxford Diffraction Xcalibur PX Ultra diffractometer; 8580 independent measured reflections (R_{int} = 0.0303), F^2 refinement, R_1(obs) = 0.0388, wR_2(all) = 0.1013, 7605 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 845 parameters. The absolute structure of **17a** was determined by a combination of R-factor tests [R_1^+ = 0.0388, R_1^- = 0.0471] and by use of the Flack parameter [x^+ = 0.054(15), x^- = 0.946(15)]. CCDC 842973.

The structure of **17a** was found to contain two crystallographically independent cations in the asymmetric unit (**17a-A** and **17a-B**). For both of these cations the C-2 proton is encapsulated by the phenyl substituents such that there are a pair of C–H···π interactions. For molecule **17a-A** the H···centroid separations are *ca*. 2.59 and 2.80 Å with the H···π vectors inclined by *ca*. 89 and 80° to the ring plane respectively, whilst for molecule **17a-B** the H···centroid separations are *ca*. 2.66 and 3.02 Å with the H···π vectors inclined by *ca*. 72 and 83° to the ring plane respectively. Note that one of the phenyl rings in molecule **17a-B** was found to be disordered, and two orientations were identified (see below); the geometries given here use the major occupancy orientation.

The C(32B)-based phenyl ring in molecule **17a-B** was found to be disordered. Two orientations were identified of *ca*. 68 and 32% occupancy, both orientations were treated as idealised hexagons with a side length of 1.39 Å, the thermal parameters of adjacent atoms were restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically. The S(50)-based triflate anion was found to be disordered. Two orientations were identified of *ca*. 70 and 30% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically.

This journal is © The Royal Society of Chemistry 2011

References

X1 A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.

Figures

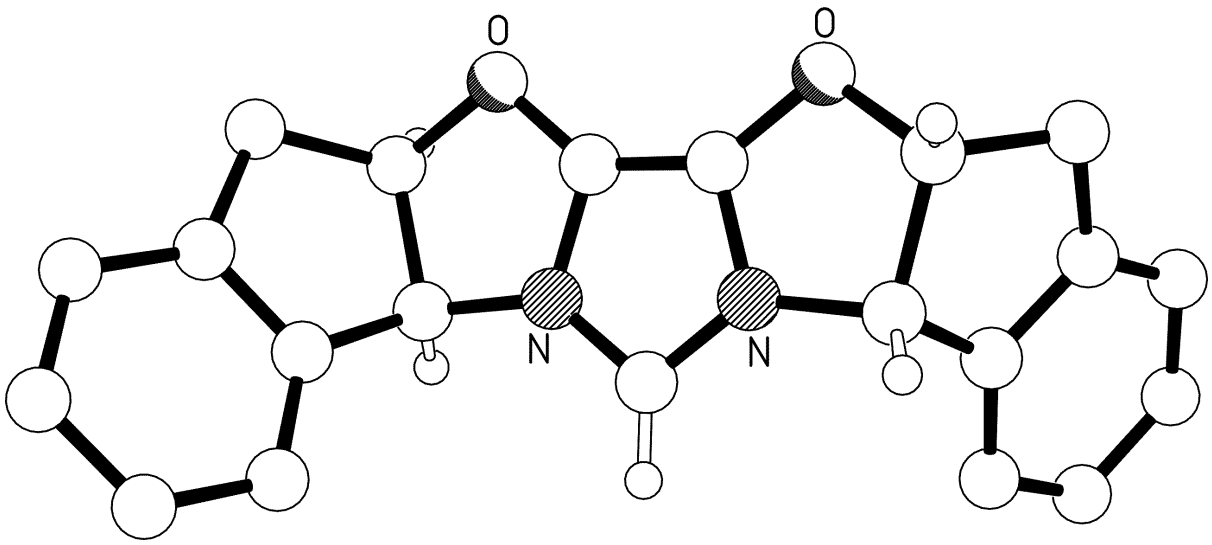


Fig. S1 The molecular structure of the cation present in the crystals of ***ent*-15a**.

This journal is © The Royal Society of Chemistry 2011

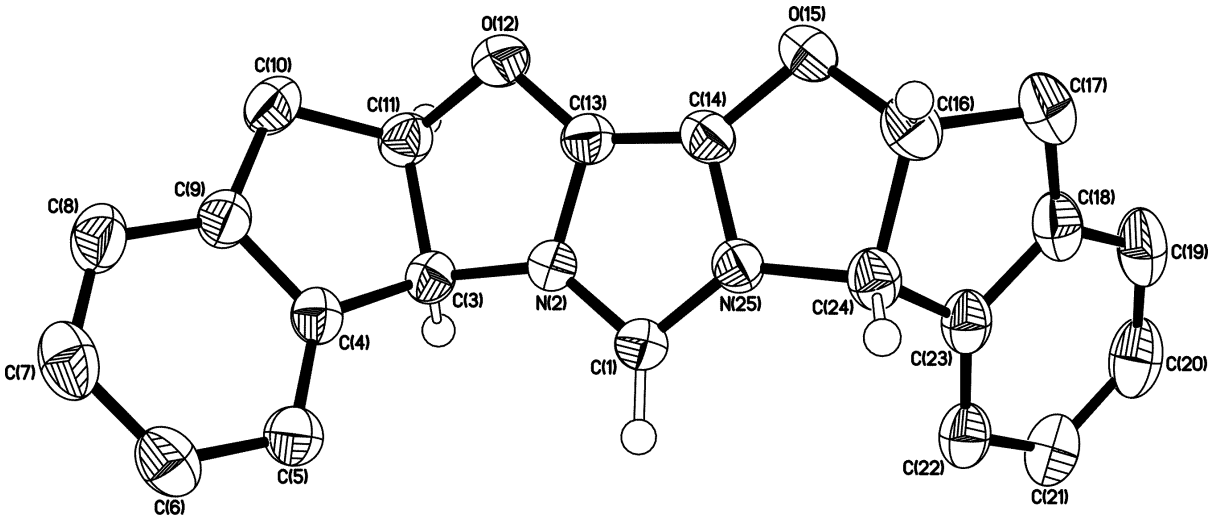


Fig. S2 The molecular structure of the cation present in the crystals of ***ent*-15a** (50% probability ellipsoids)

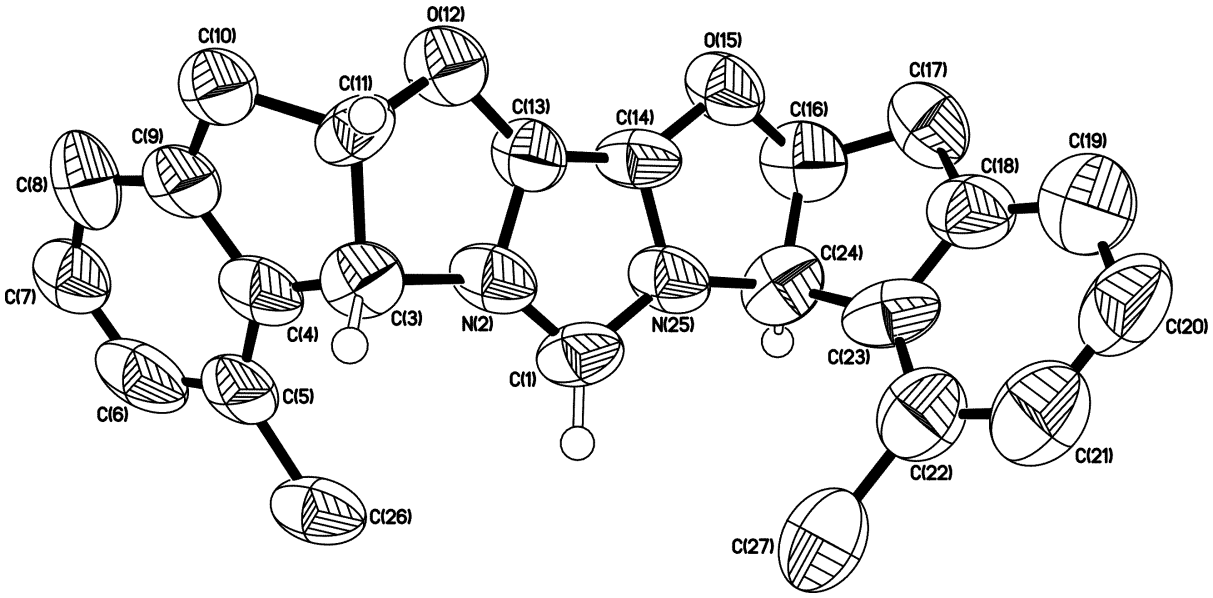


Fig. S3 The molecular structure of the cation present in the crystals of **16b** (20% probability ellipsoids).

This journal is © The Royal Society of Chemistry 2011

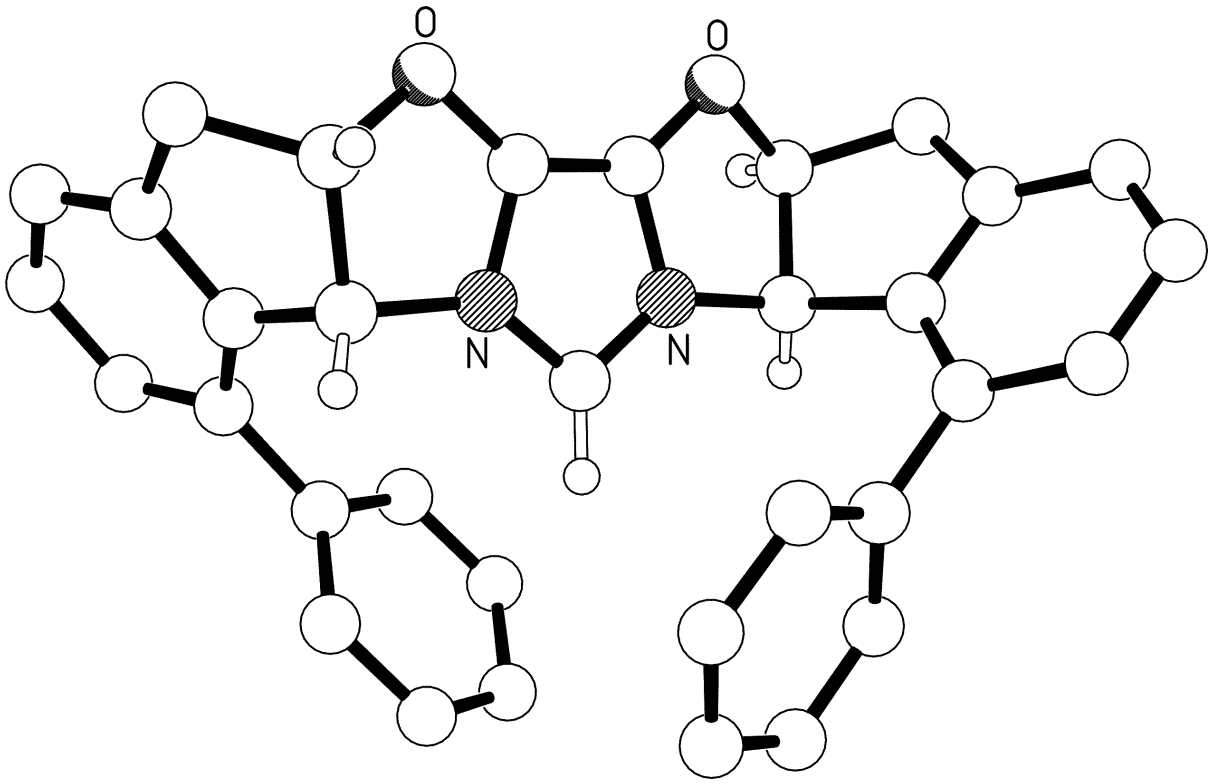


Fig. S4 The molecular structure of one (**17a-A**) of the two independent cations present in the crystals of **17a**.

This journal is © The Royal Society of Chemistry 2011

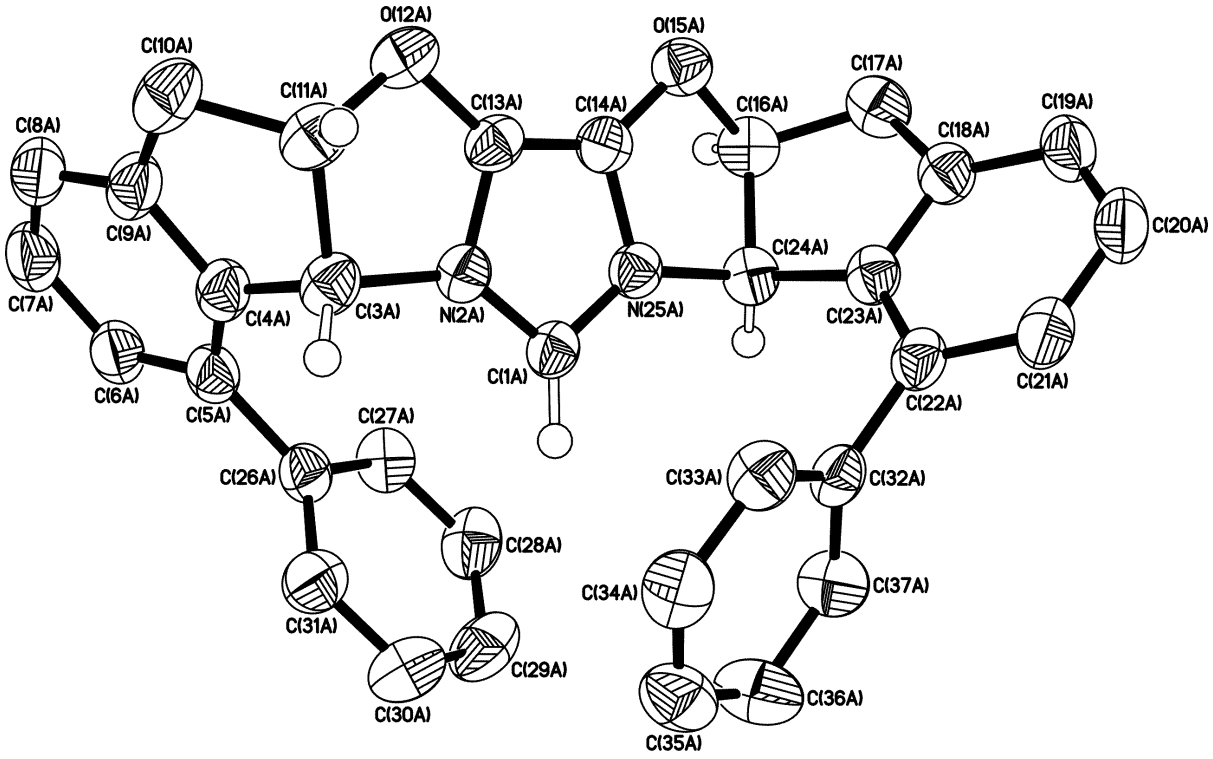


Fig. S5 The molecular structure of one (**17a-A**) of the two independent cations present in the crystals of **17a** (50% probability ellipsoids).

This journal is © The Royal Society of Chemistry 2011

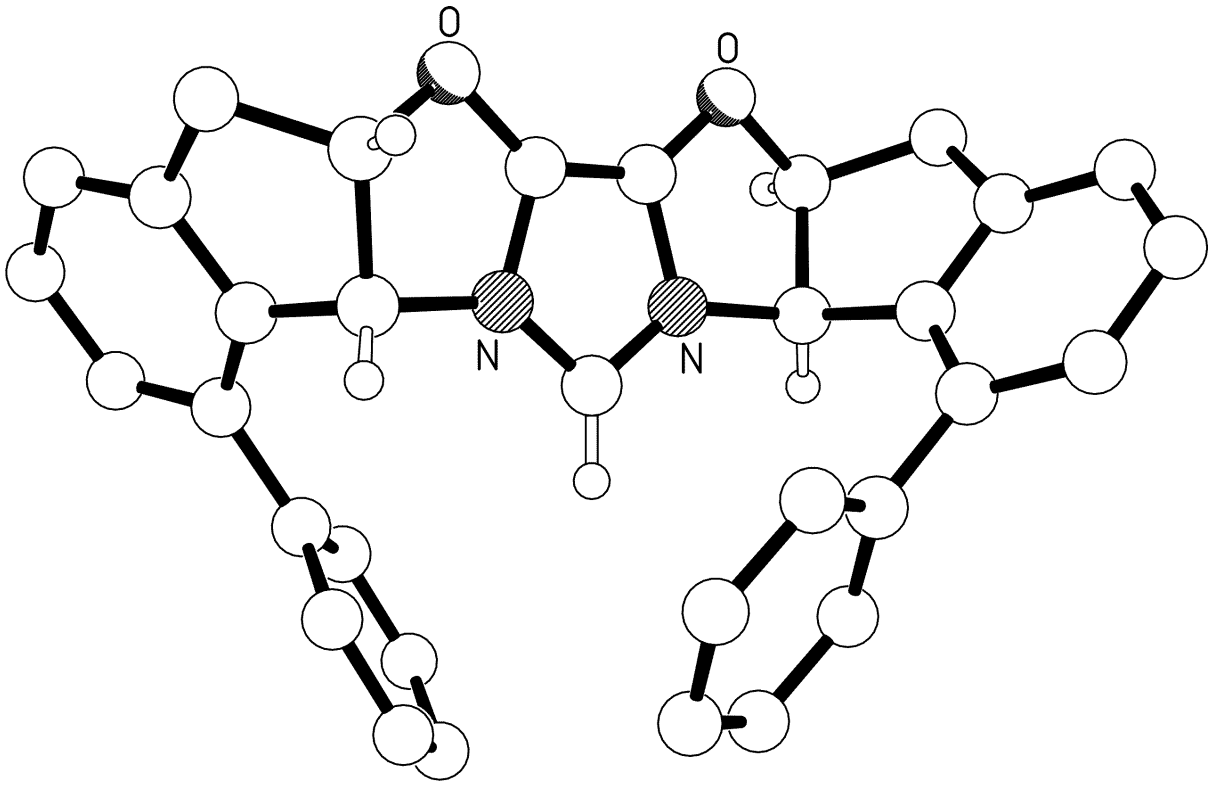


Fig. S6 The molecular structure of one (**17a-B**) of the two independent cations present in the crystals of **17a**.

This journal is © The Royal Society of Chemistry 2011

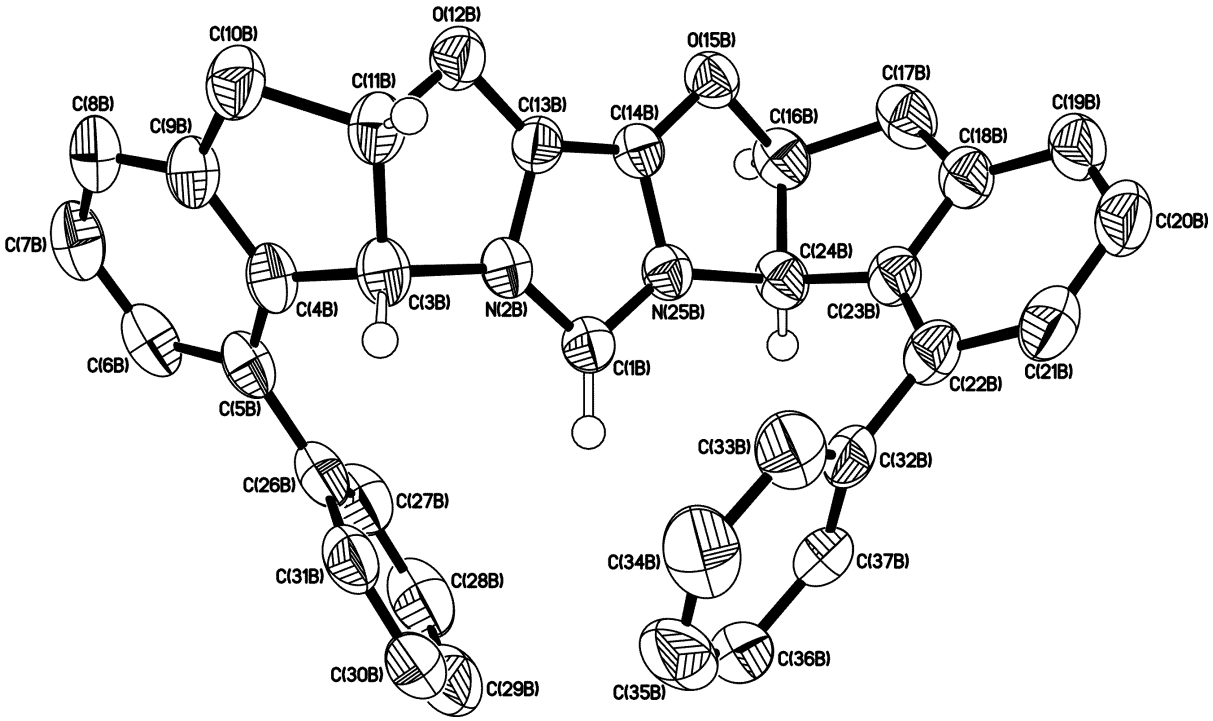
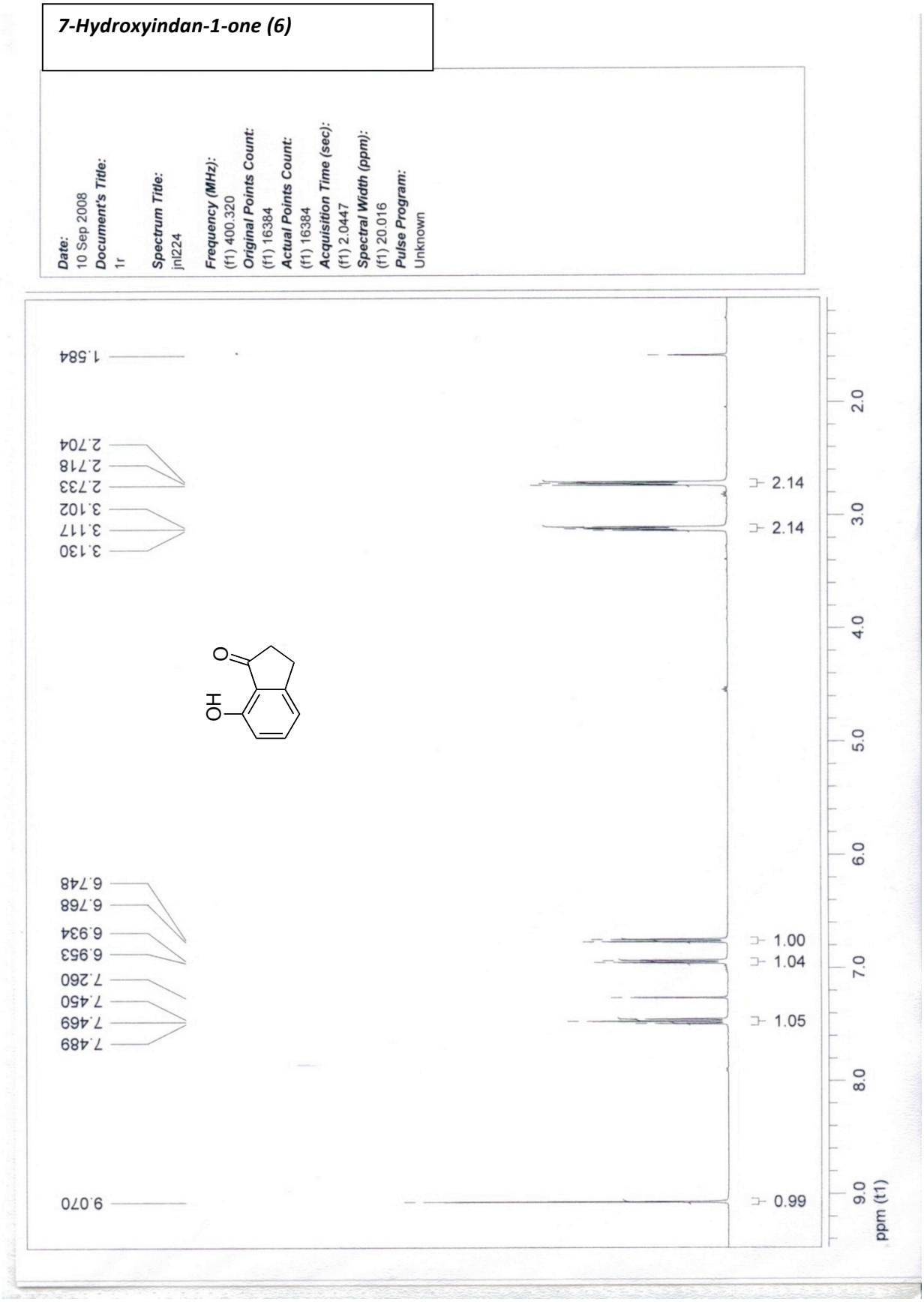


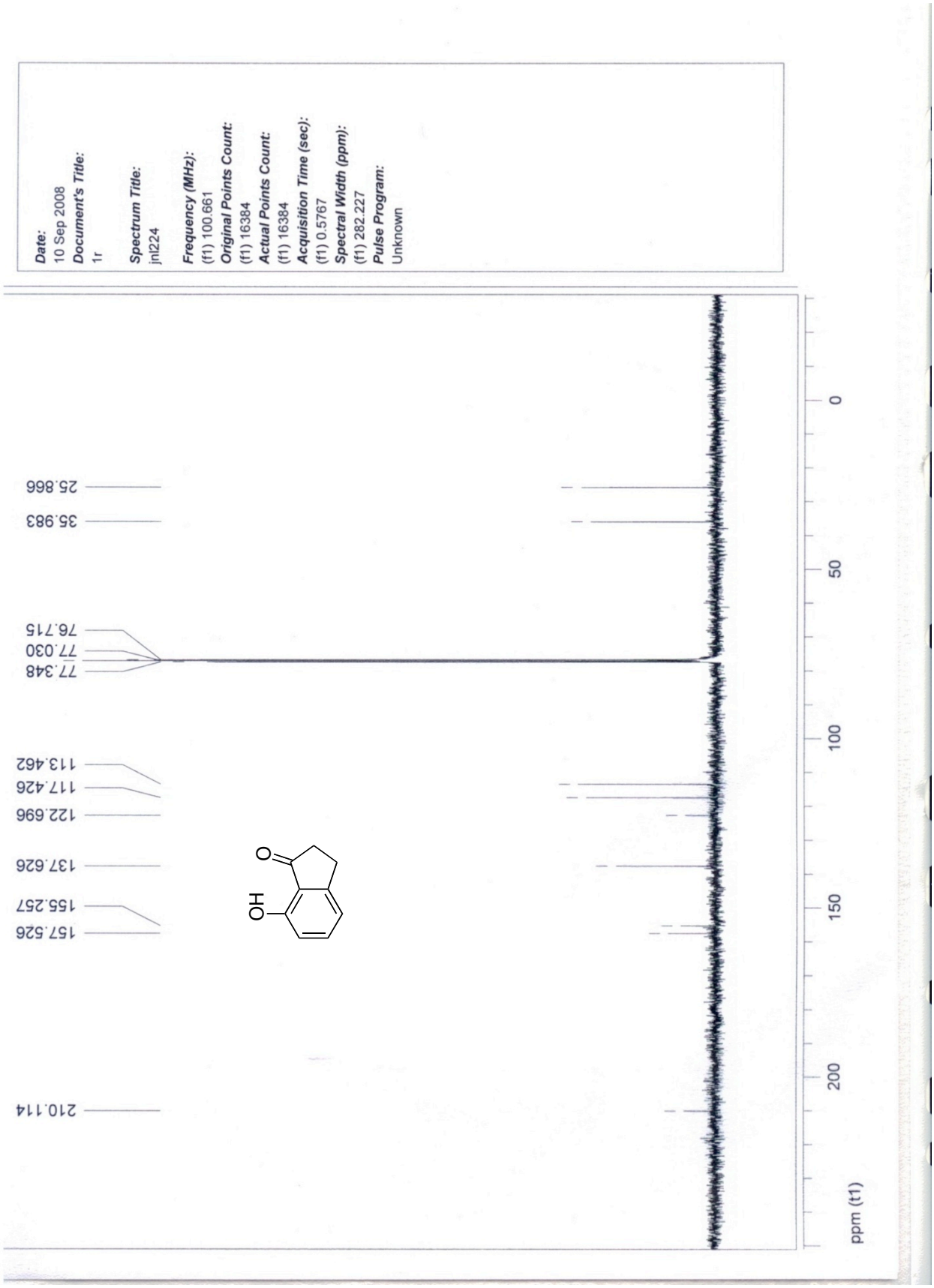
Fig. S7 The molecular structure of one (**17a-B**) of the two independent cations present in the crystals of **17a** (50% probability ellipsoids).

This journal is © The Royal Society of Chemistry 2011

7-Hydroxyindan-1-one (6)

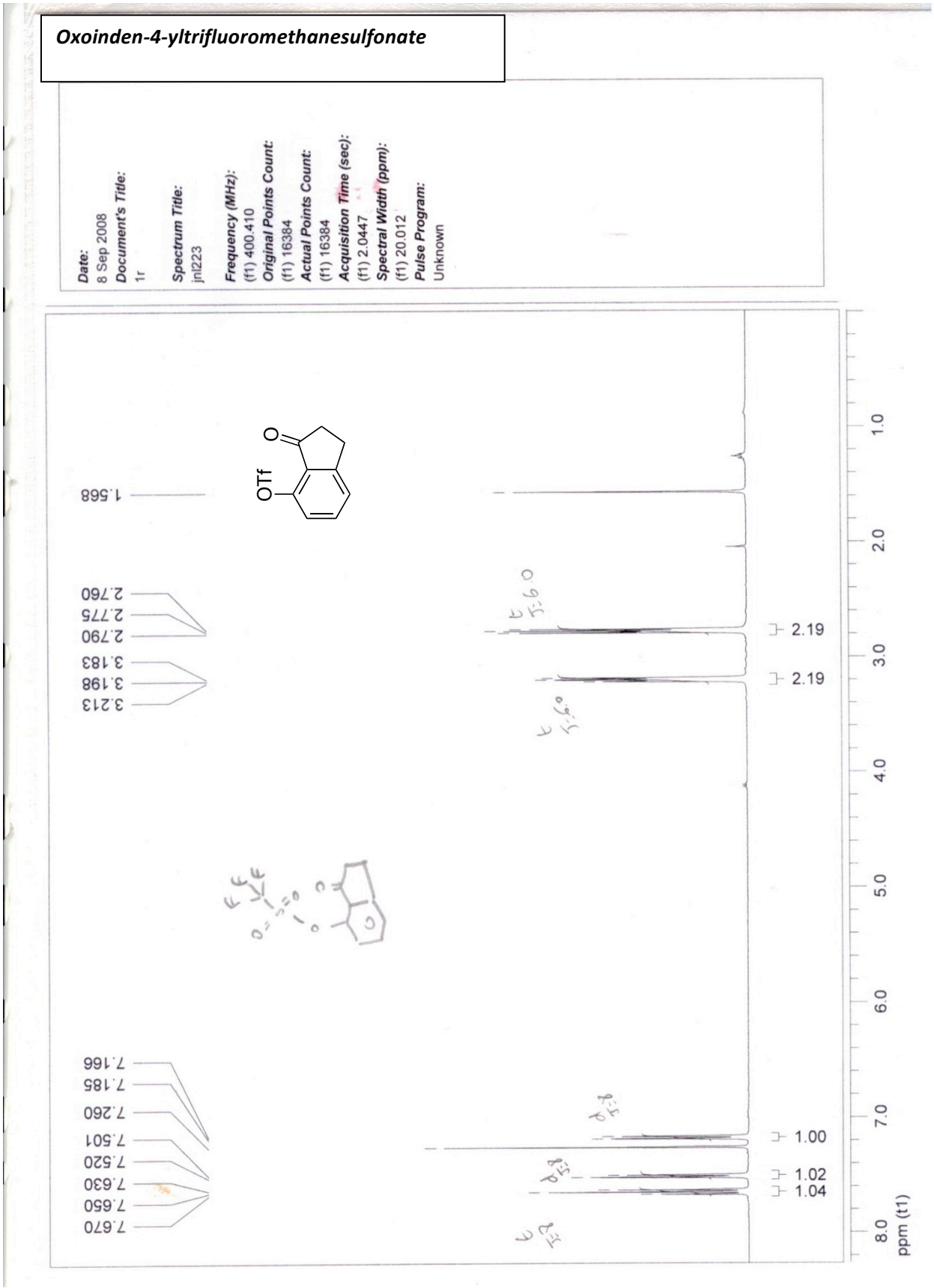


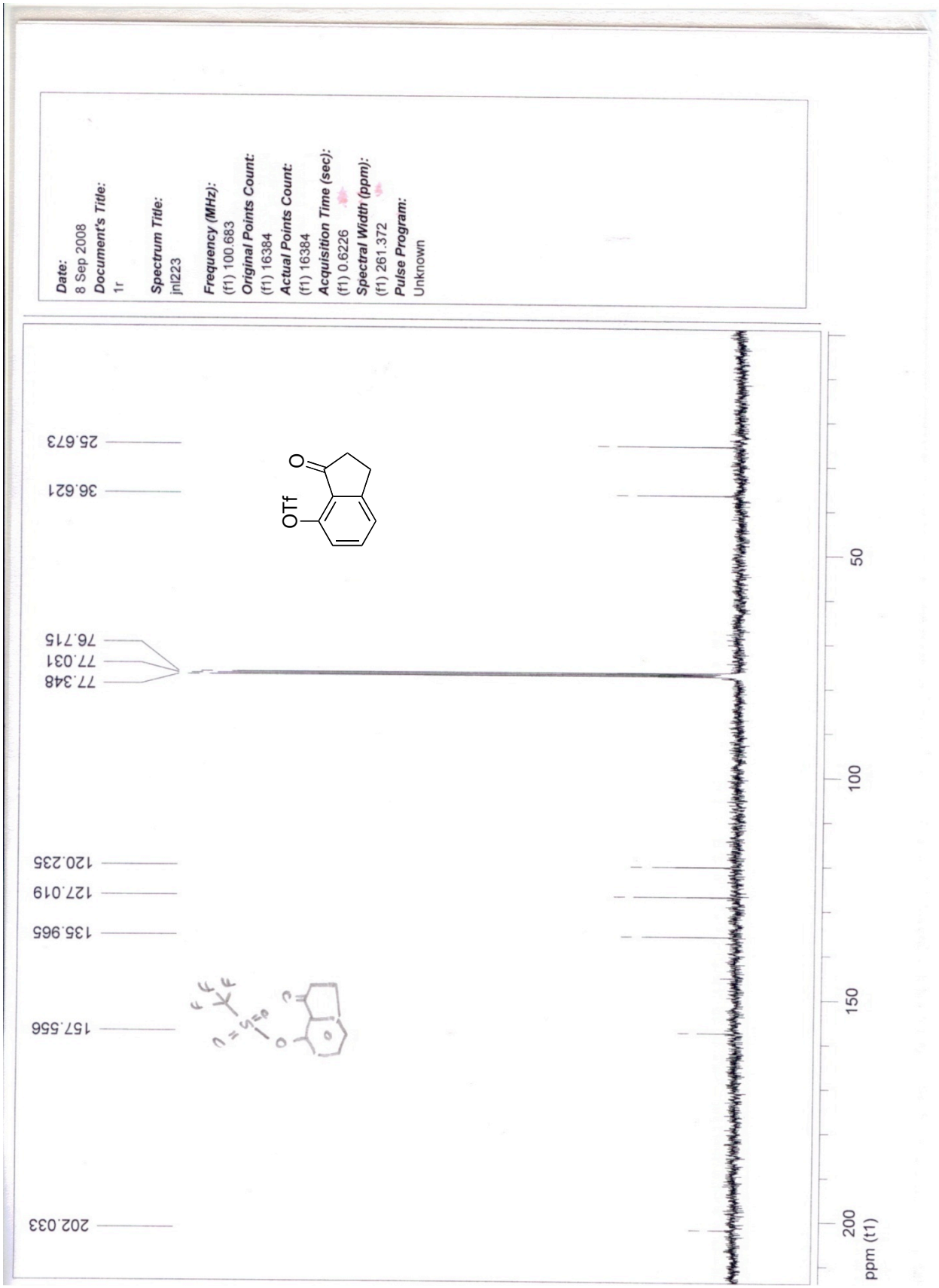
This journal is © The Royal Society of Chemistry 2011



This journal is © The Royal Society of Chemistry 2011

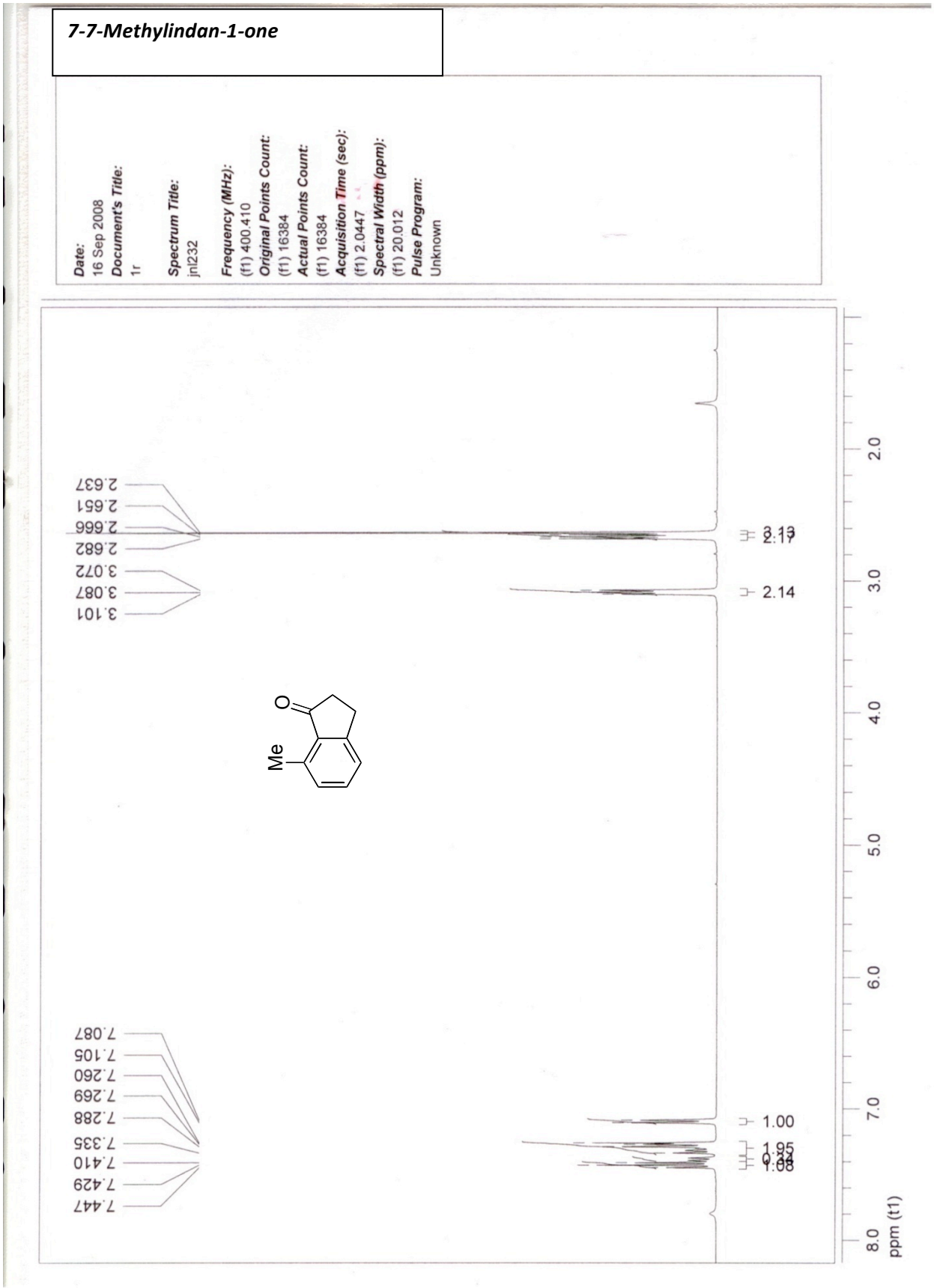
Oxoinden-4-yltrifluoromethanesulfonate



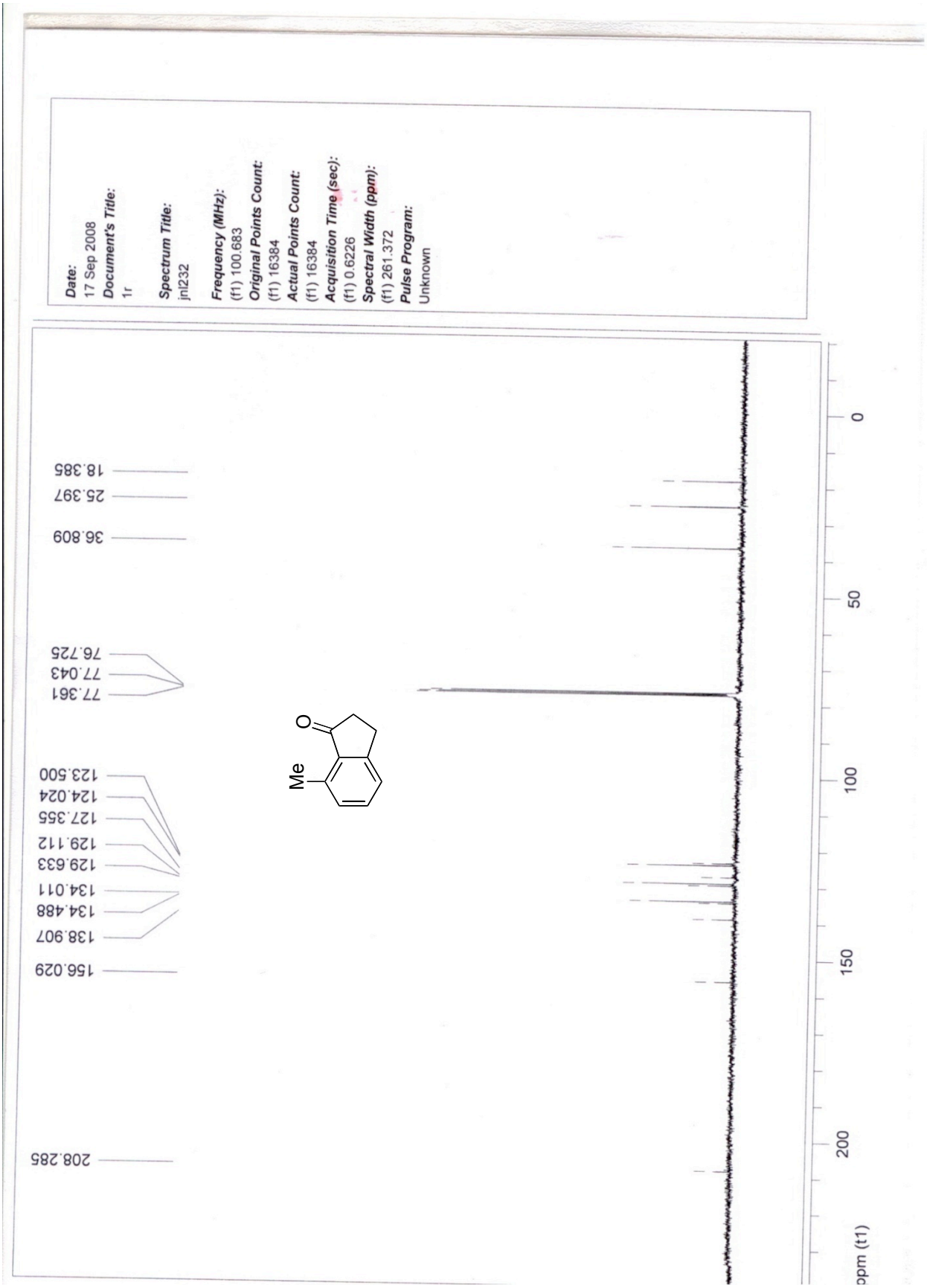

Date:
8 Sep 2008
Document's Title:
1r
Spectrum Title:
jnl223
Frequency (MHz):
(f1) 100.683
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 16384
Acquisition Time (sec):
(f1) 0.6226
Spectral Width (ppm):
(f1) 261.372
Pulse Program:
Unknown
25.673
36.621
76.715
77.031
77.348
120.235
127.019
135.965
157.556
202.033
OTf
O
50
100
150
200
ppm (t1)

This journal is © The Royal Society of Chemistry 2011

7-7-Methylindan-1-one

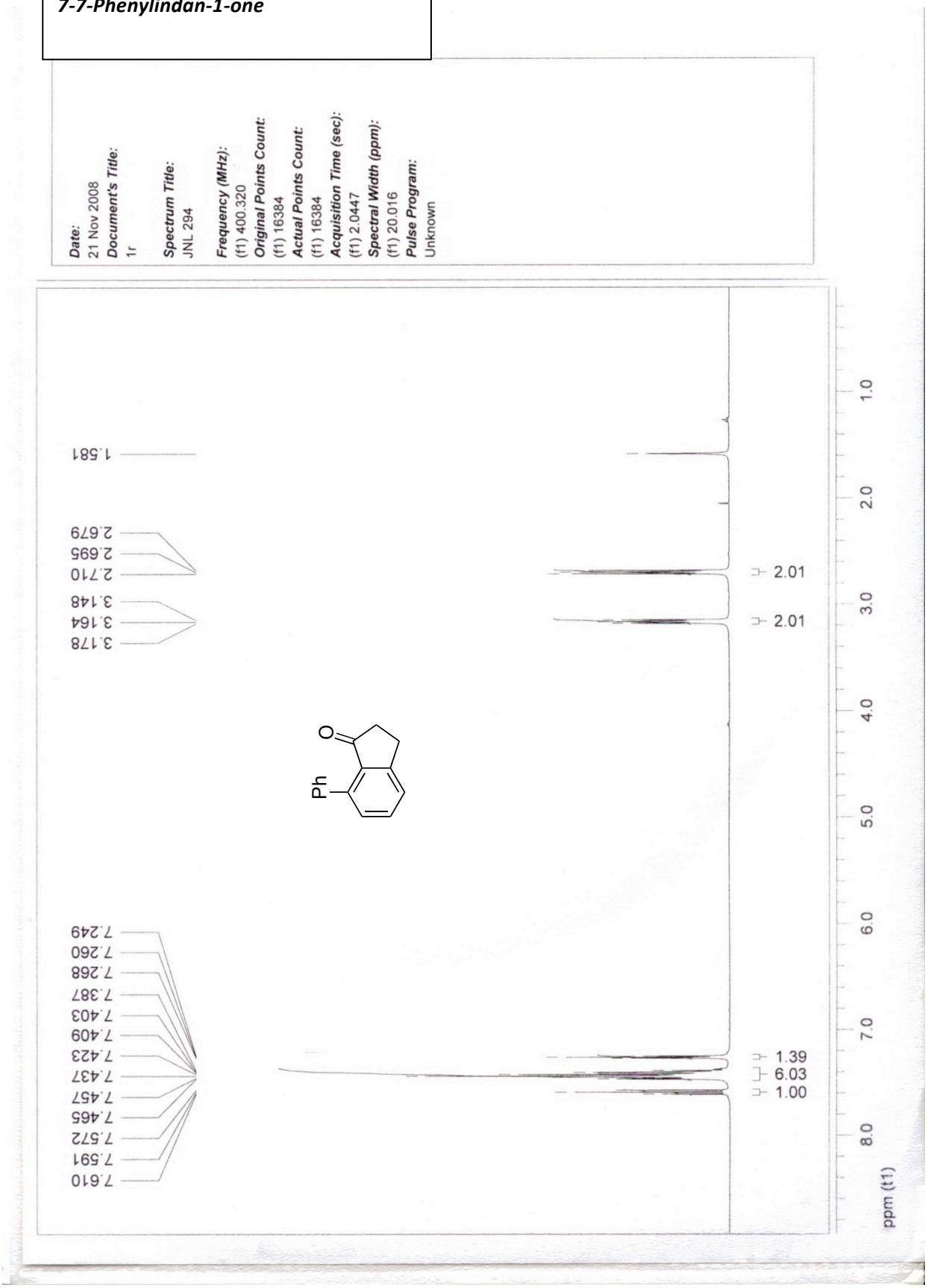


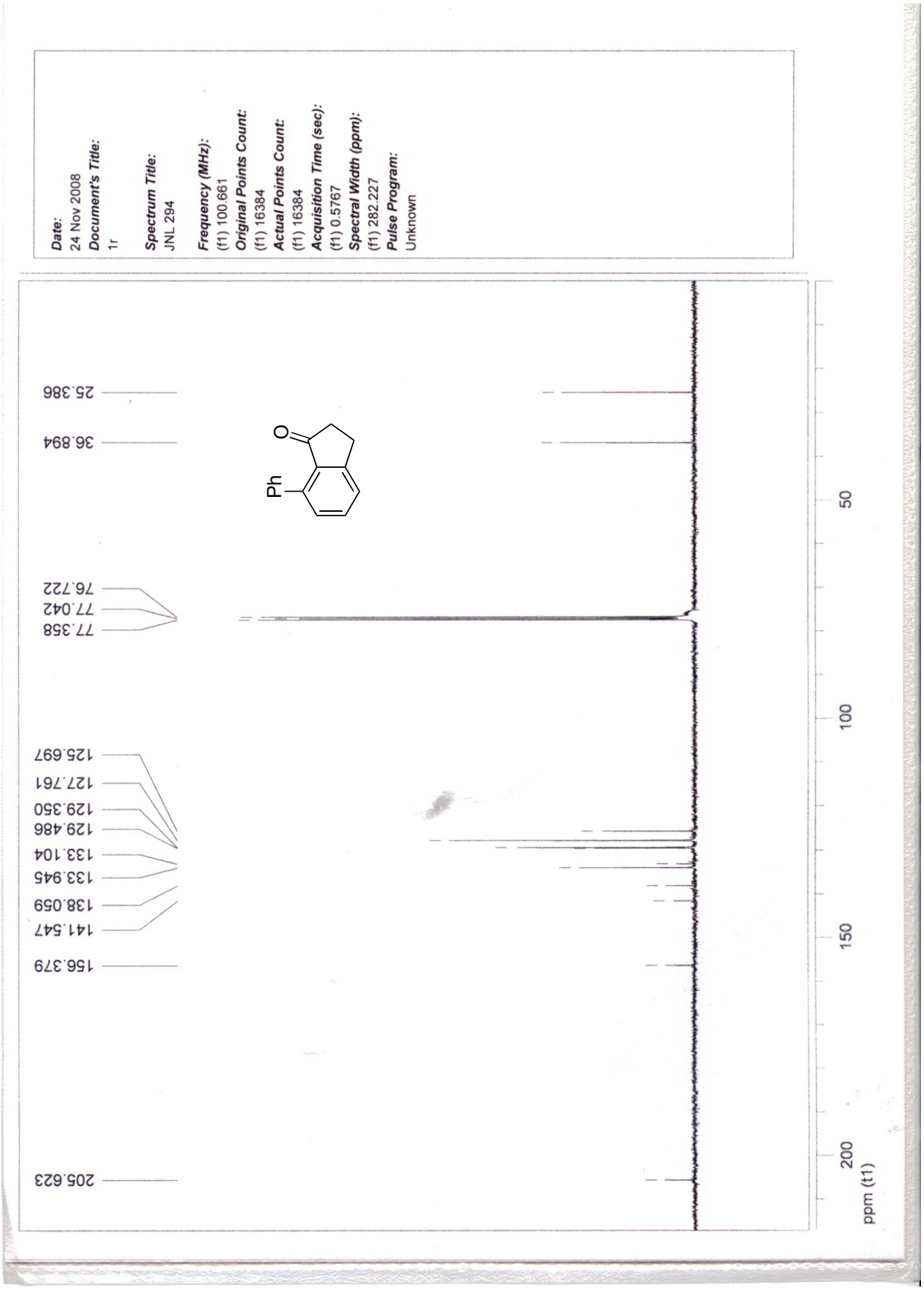
This journal is © The Royal Society of Chemistry 2011



This journal is © The Royal Society of Chemistry 2011

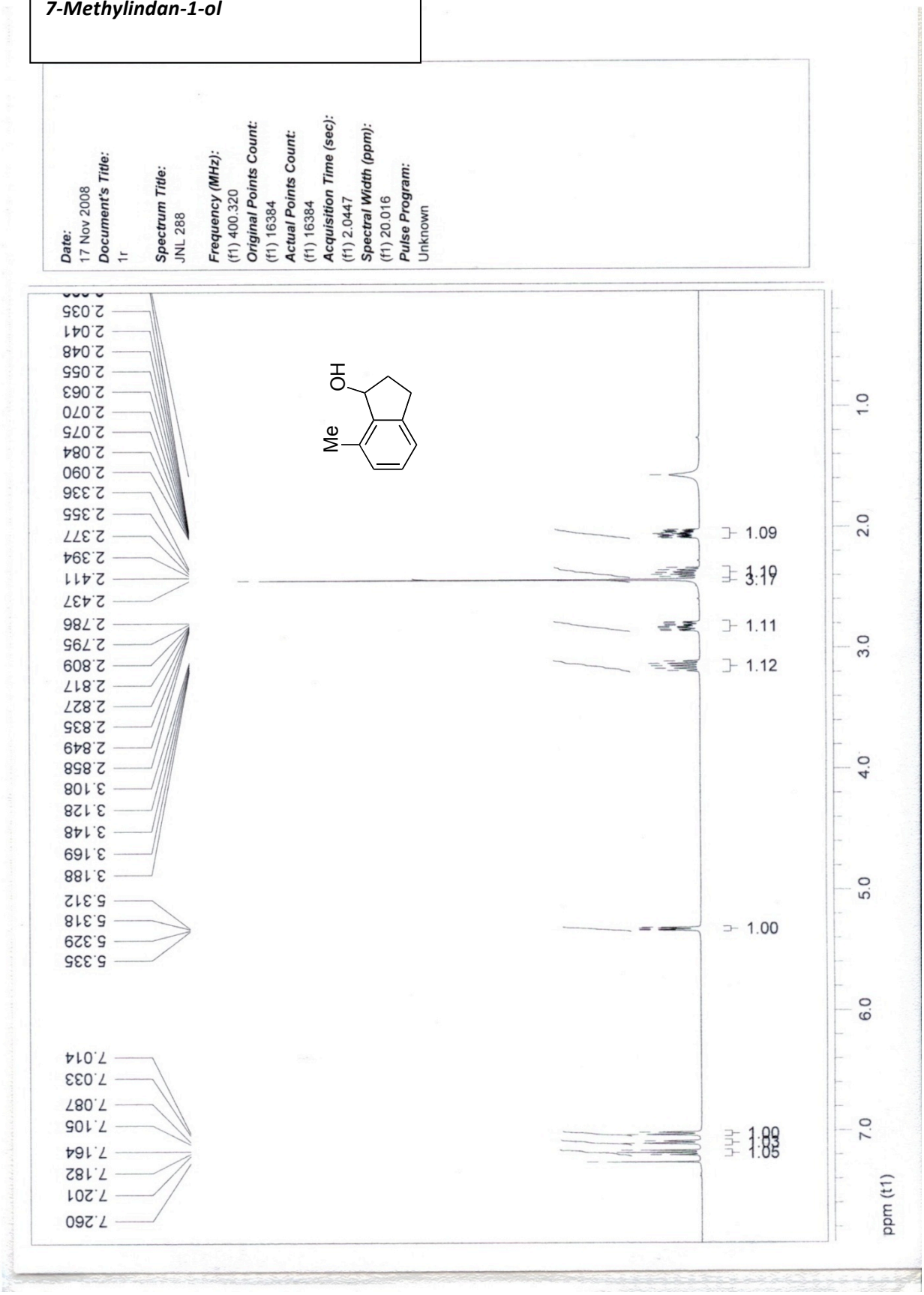
7-7-Phenylindan-1-one



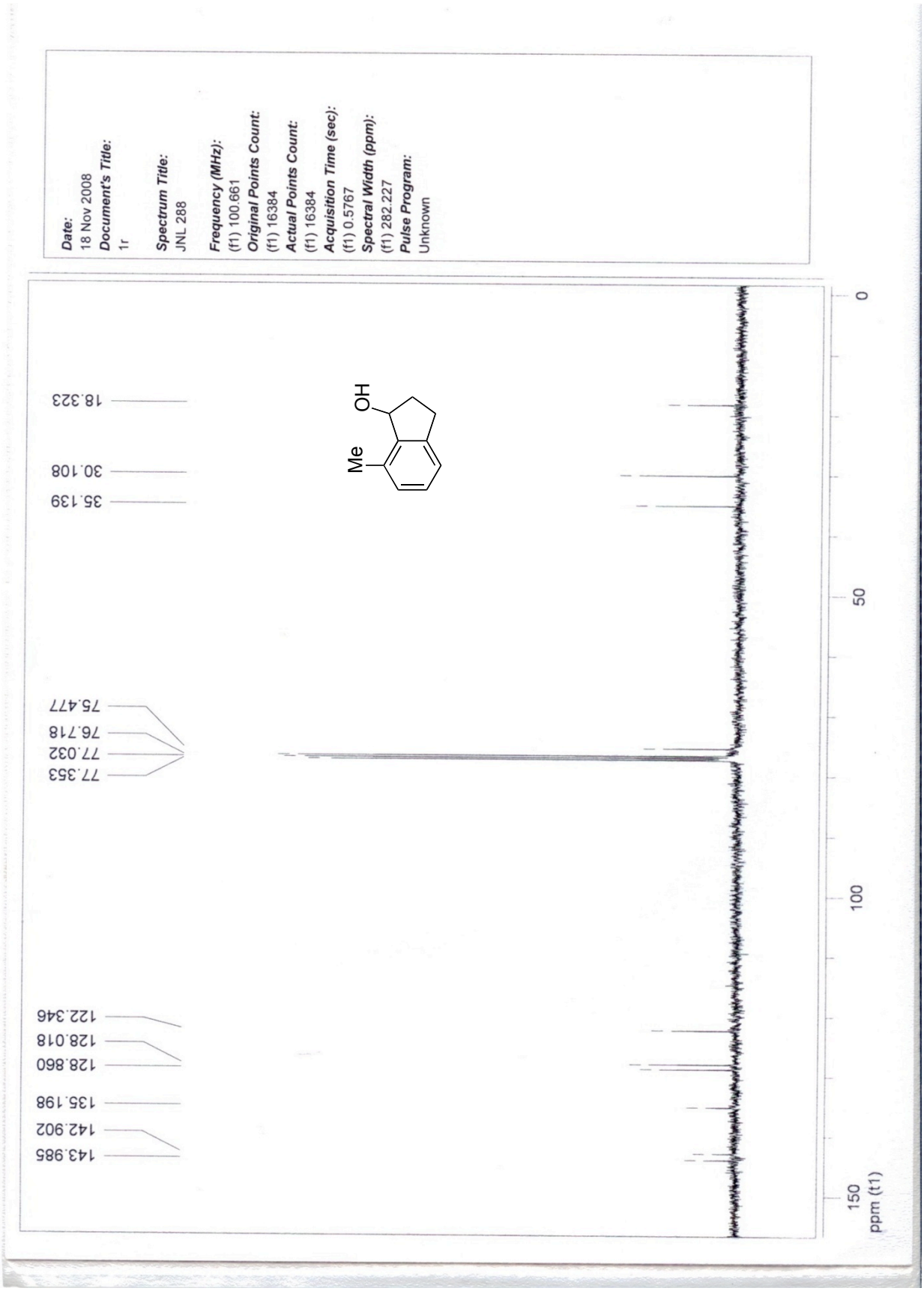

Date:
24 Nov 2008
Document's Title:
1r
Spectrum Title:
JNL 294
Frequency (MHz):
(f1) 100.661
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 16384
Acquisition Time (sec):
(f1) 0.5767
Spectral Width (ppm):
(f1) 282.227
Pulse Program:
Unknown
O
Ph
25.386
36.894
76.722
77.042
77.358
125.697
127.761
129.350
129.486
133.104
133.945
138.059
141.547
156.379
205.623
50
100
150
200
ppm (t1)

This journal is © The Royal Society of Chemistry 2011

7-Methylindan-1-ol

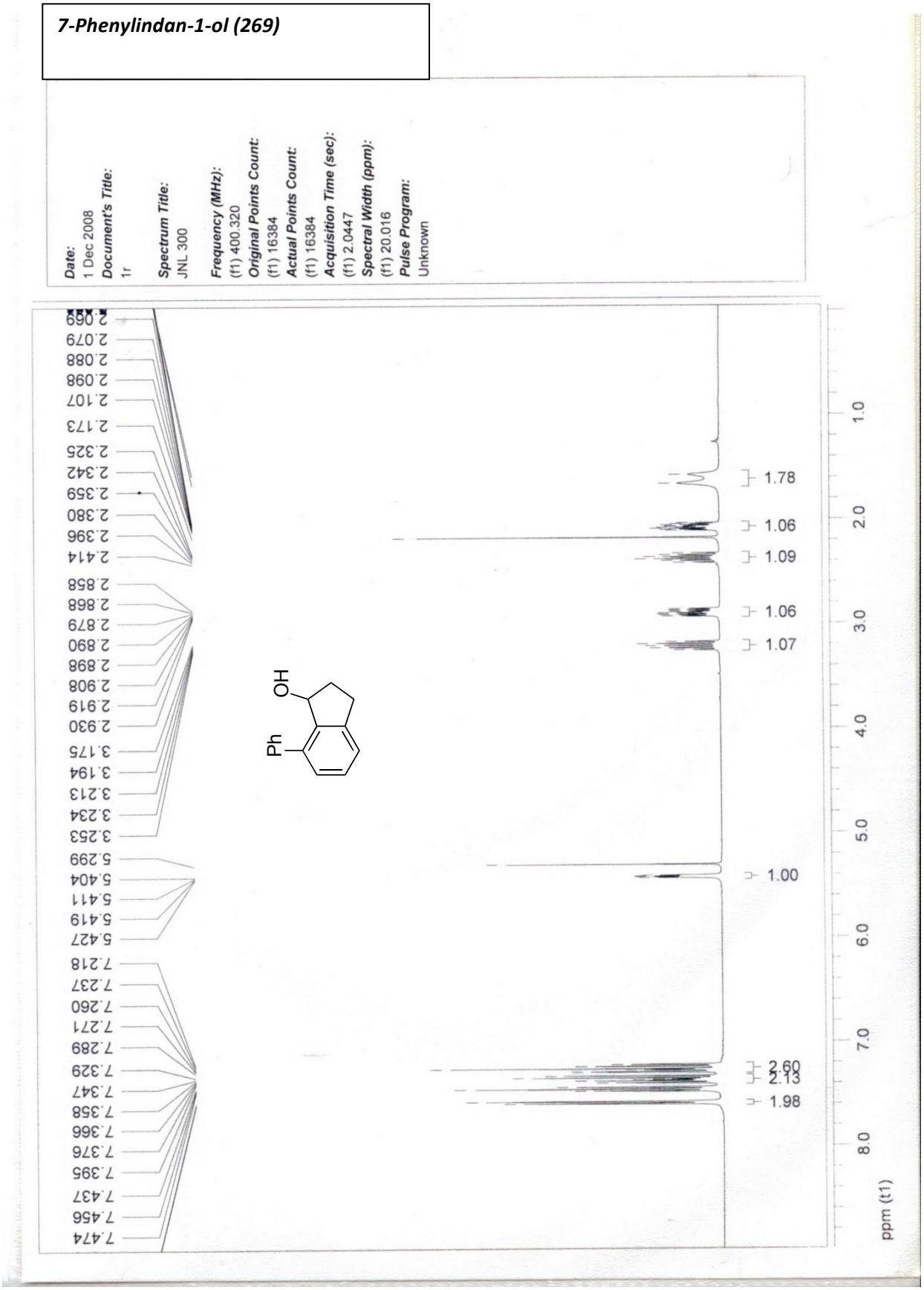


This journal is © The Royal Society of Chemistry 2011

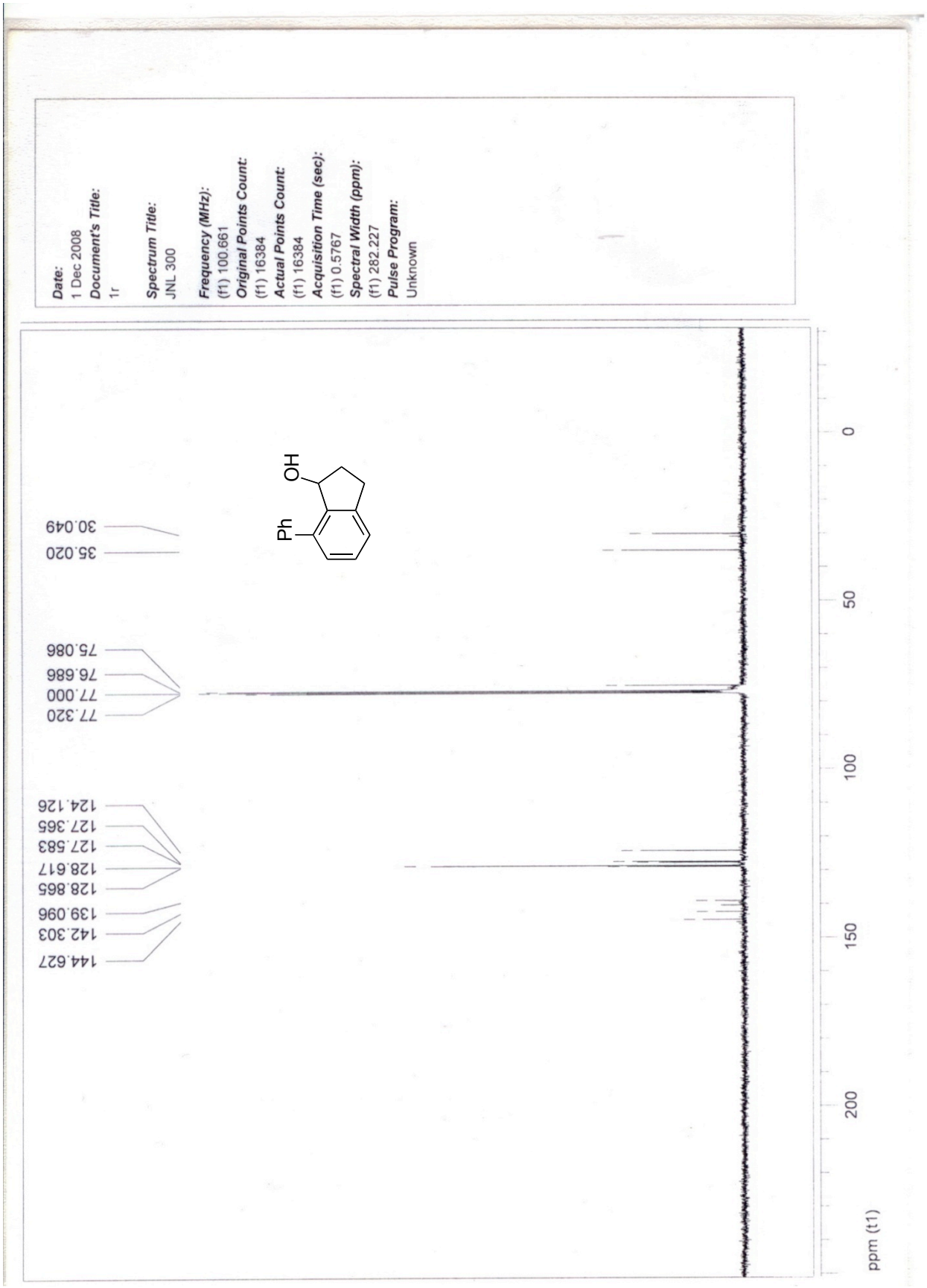


This journal is © The Royal Society of Chemistry 2011

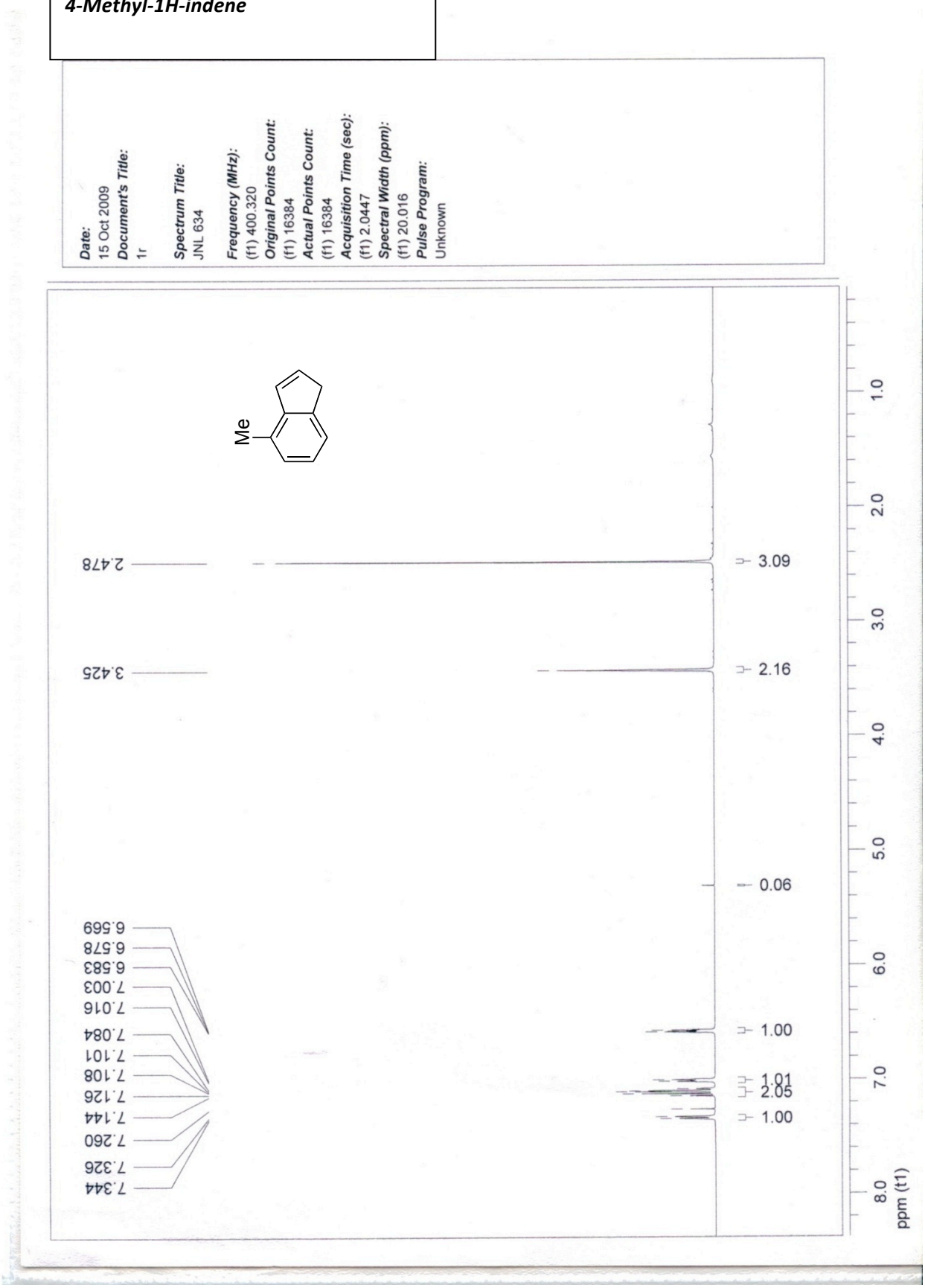
7-Phenylindan-1-ol (269)



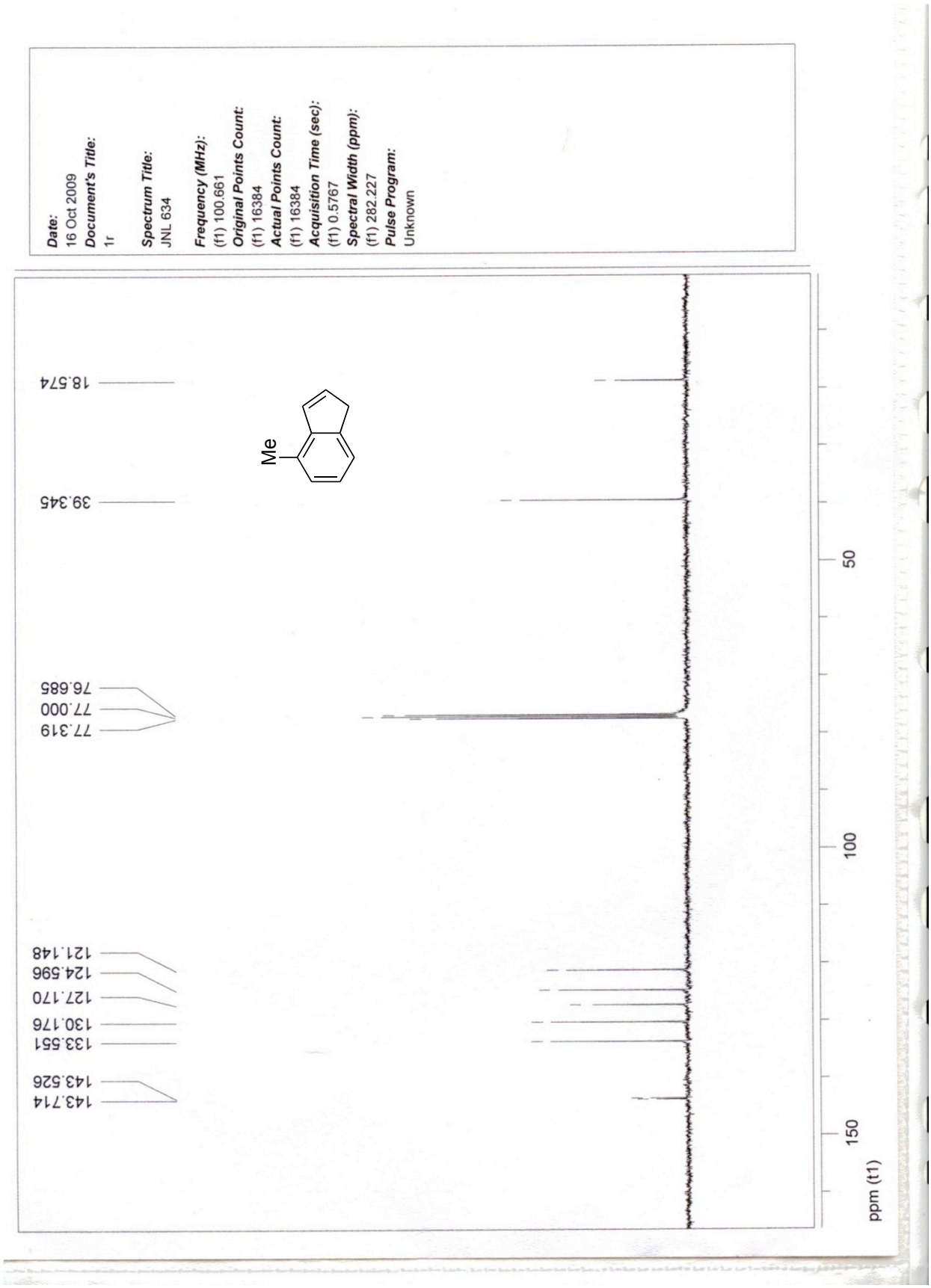
This journal is © The Royal Society of Chemistry 2011



4-Methyl-1H-indene

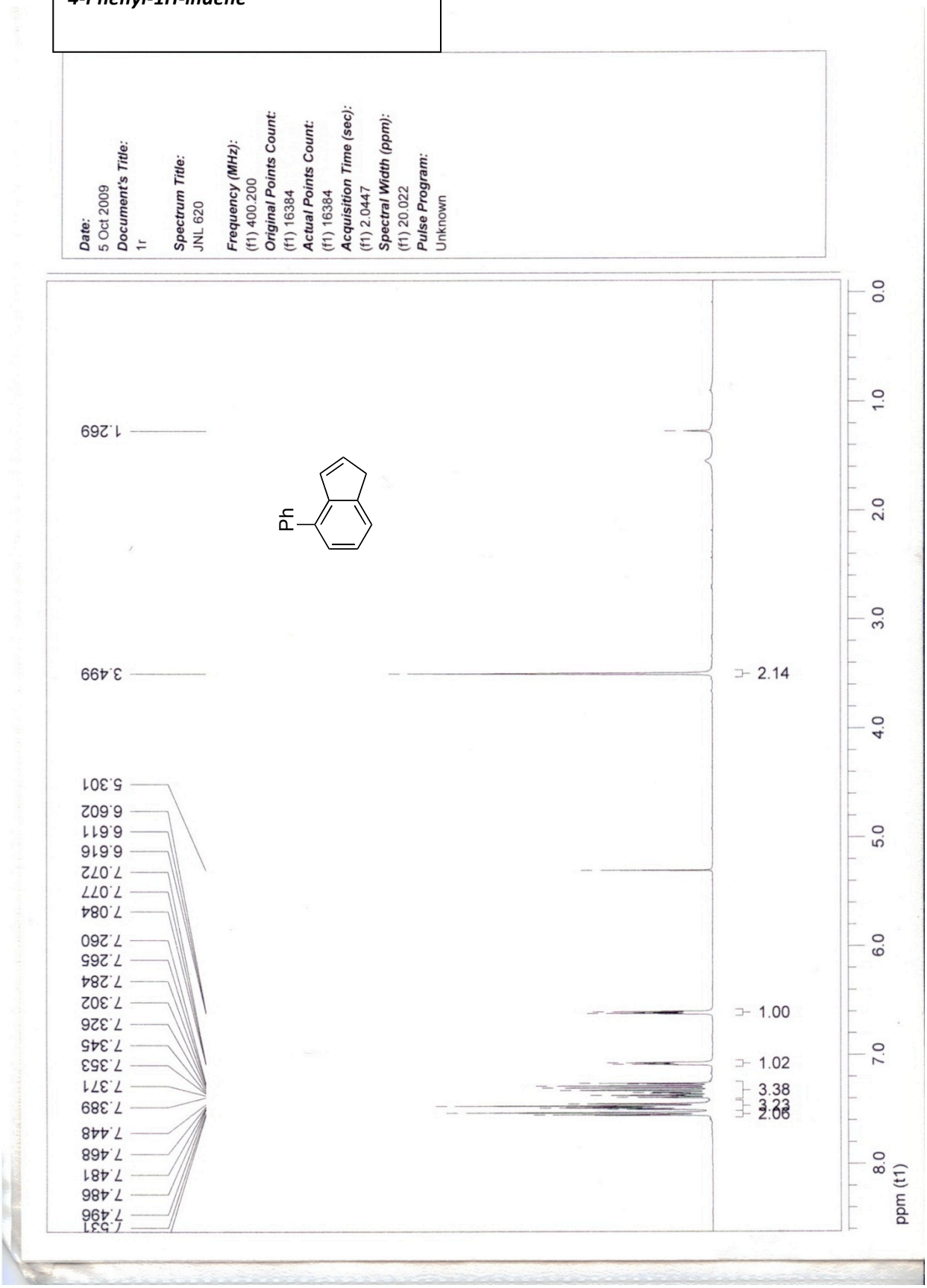


This journal is © The Royal Society of Chemistry 2011

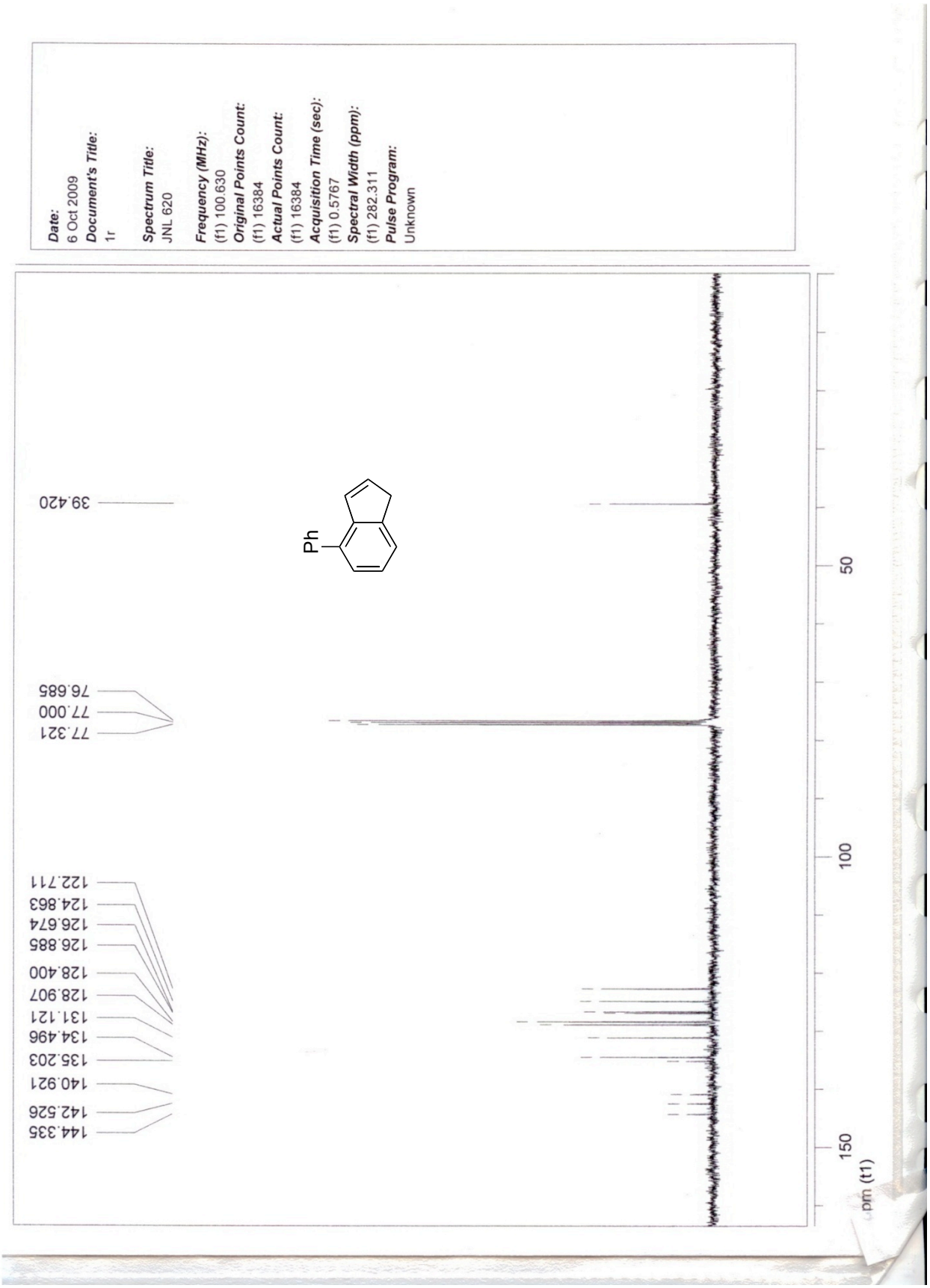


This journal is © The Royal Society of Chemistry 2011

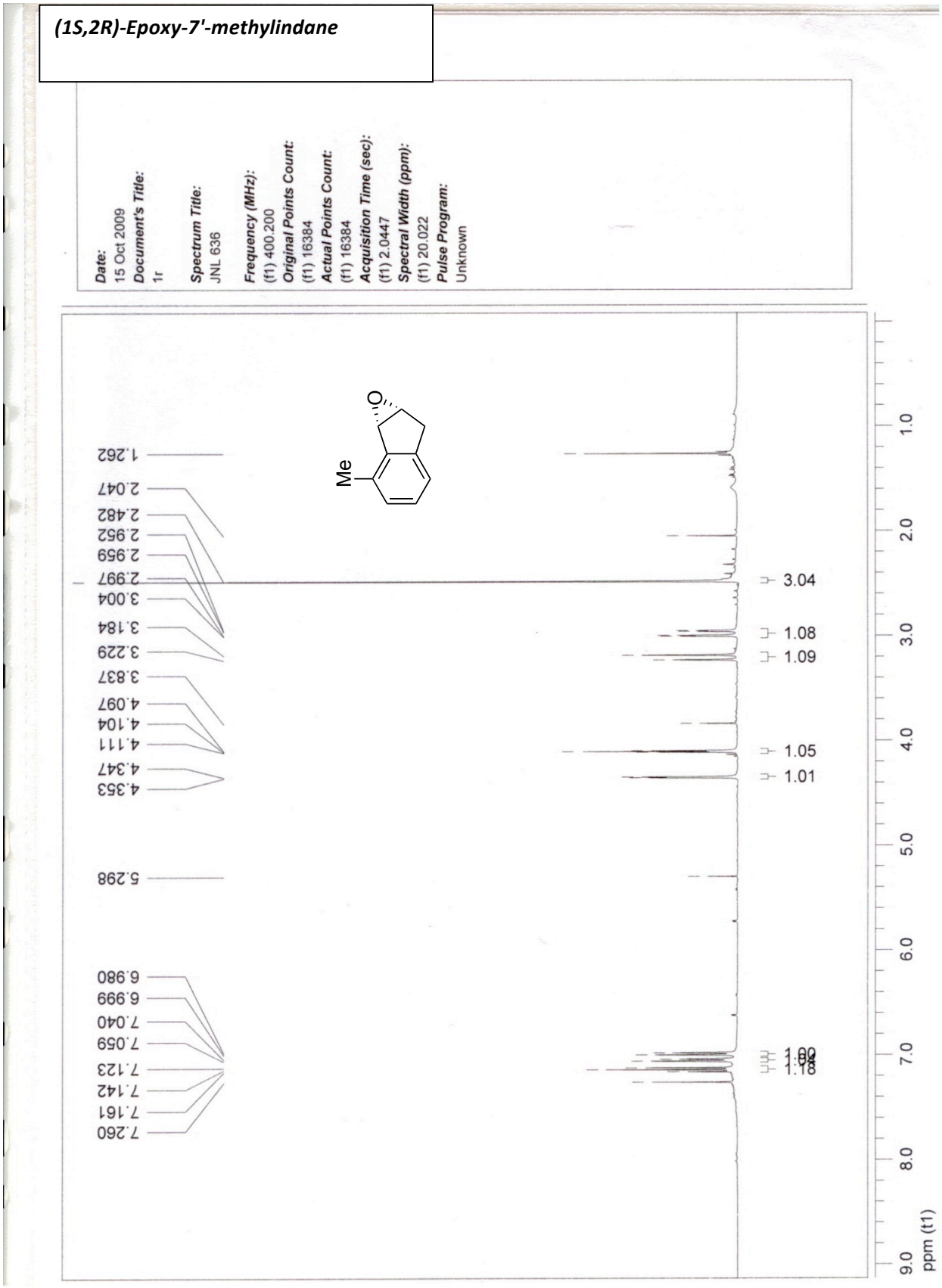
4-Phenyl-1H-indene



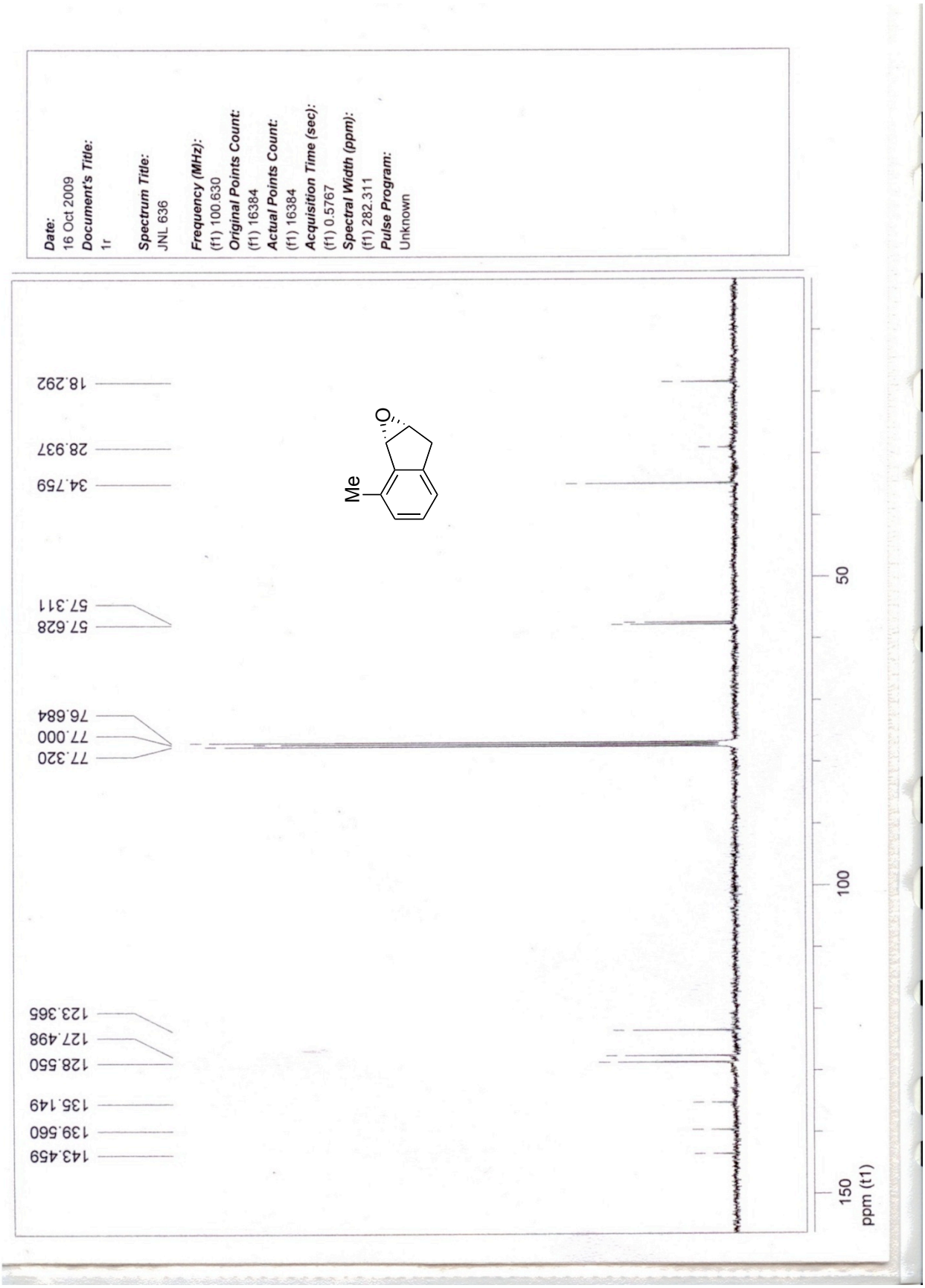
This journal is © The Royal Society of Chemistry 2011



(1S,2R)-Epoxy-7'-methylindane

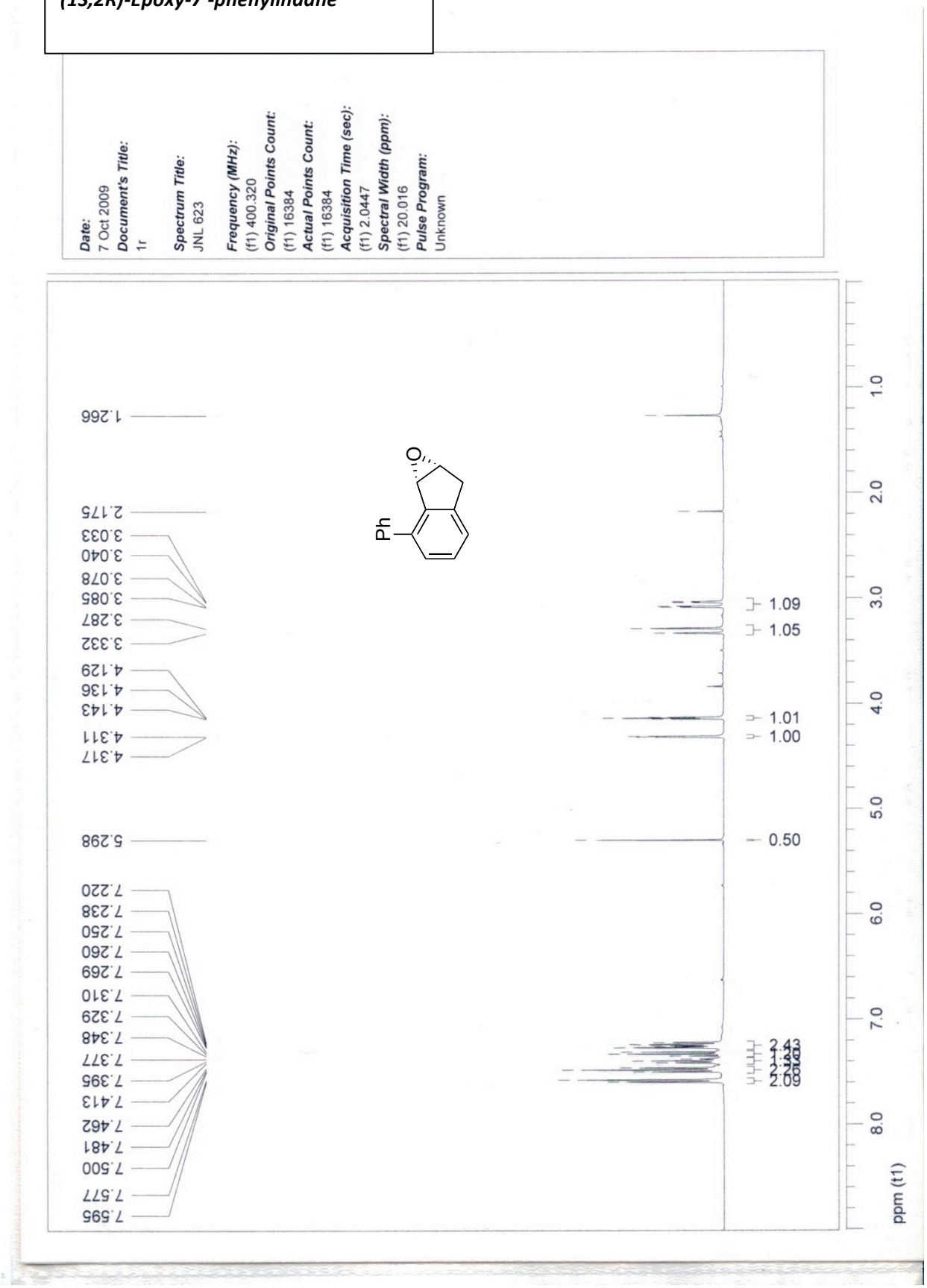


This journal is © The Royal Society of Chemistry 2011

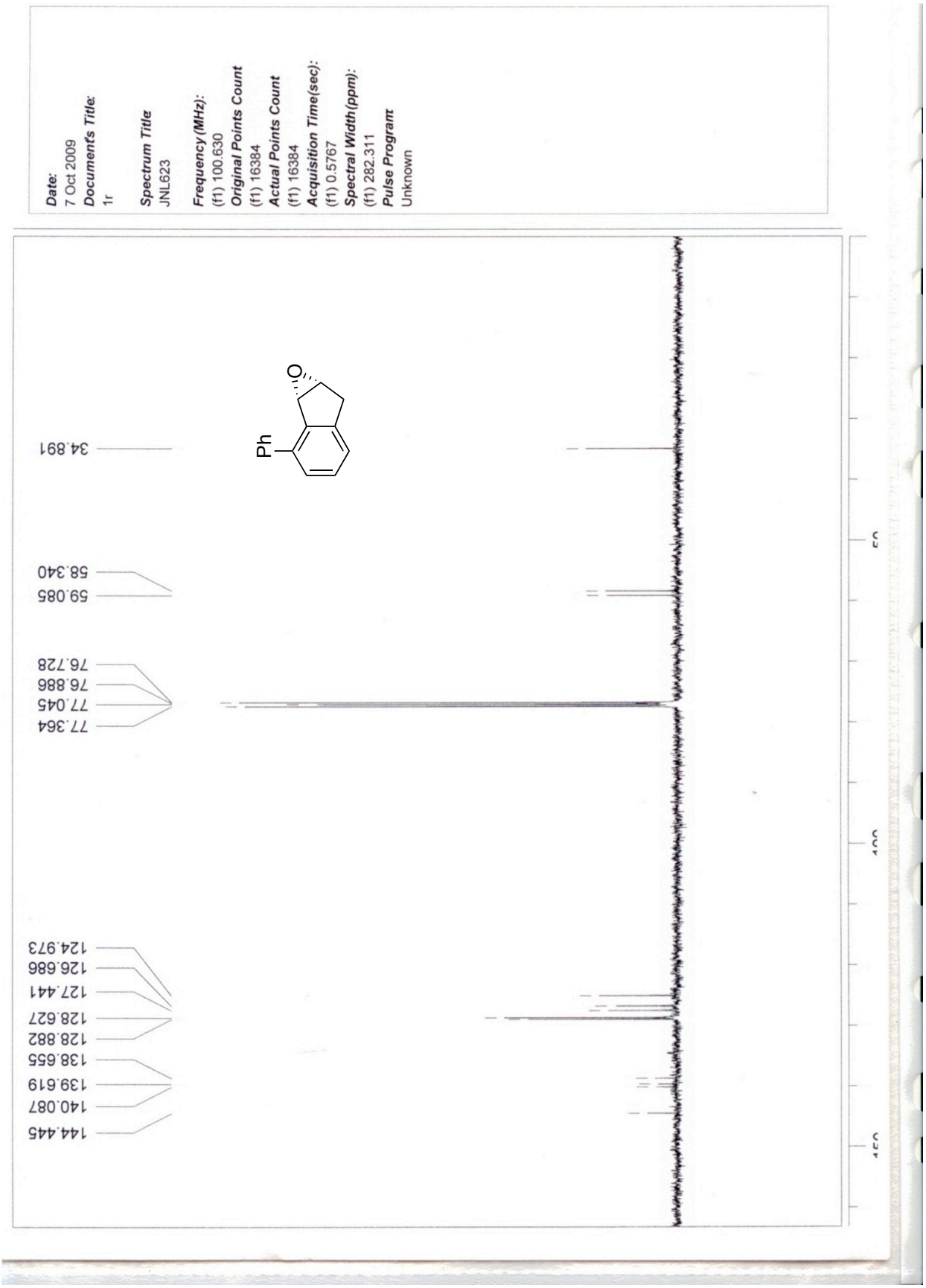


This journal is © The Royal Society of Chemistry 2011

(1S,2R)-Epoxy-7'-phenylindane

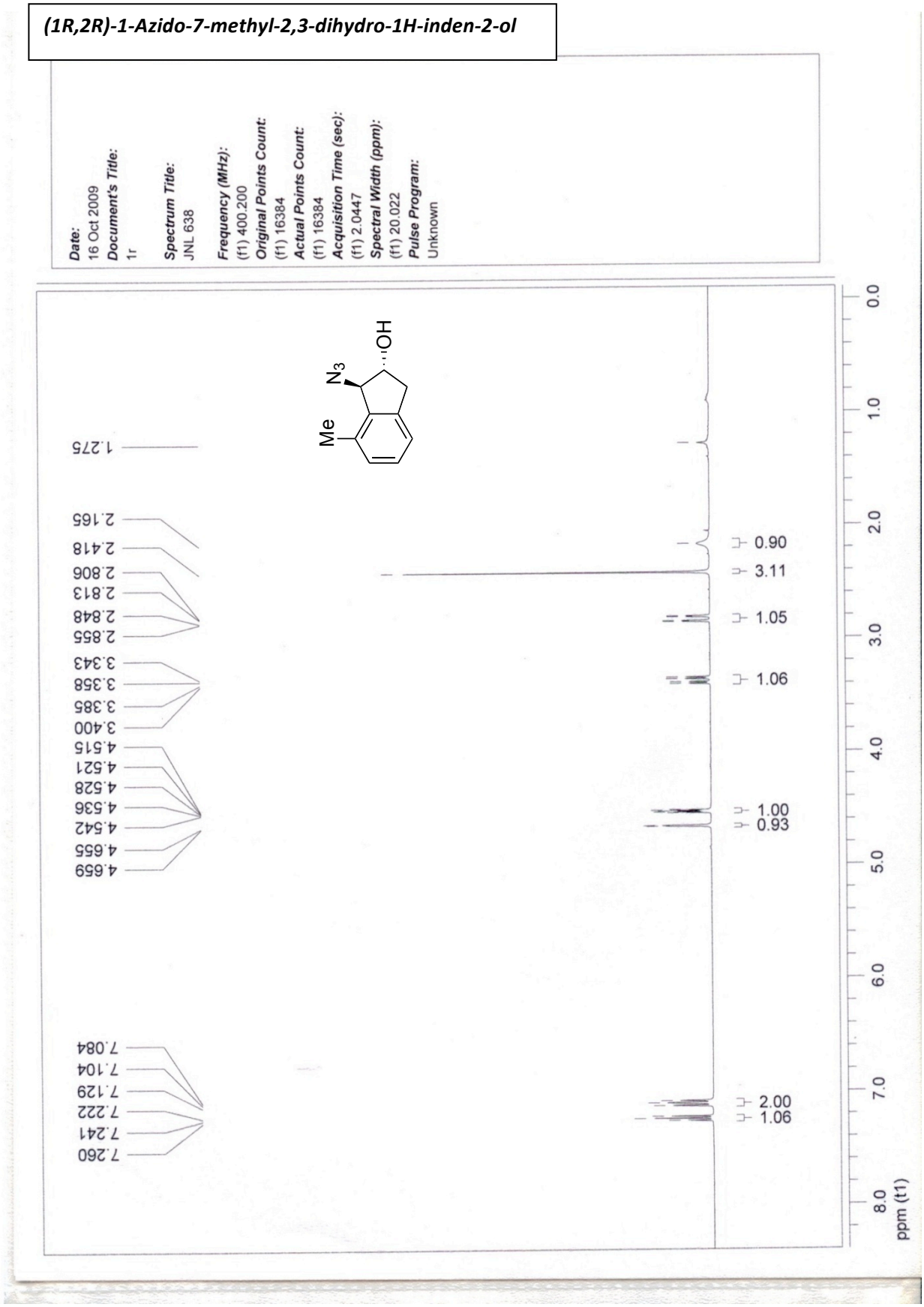


This journal is © The Royal Society of Chemistry 2011

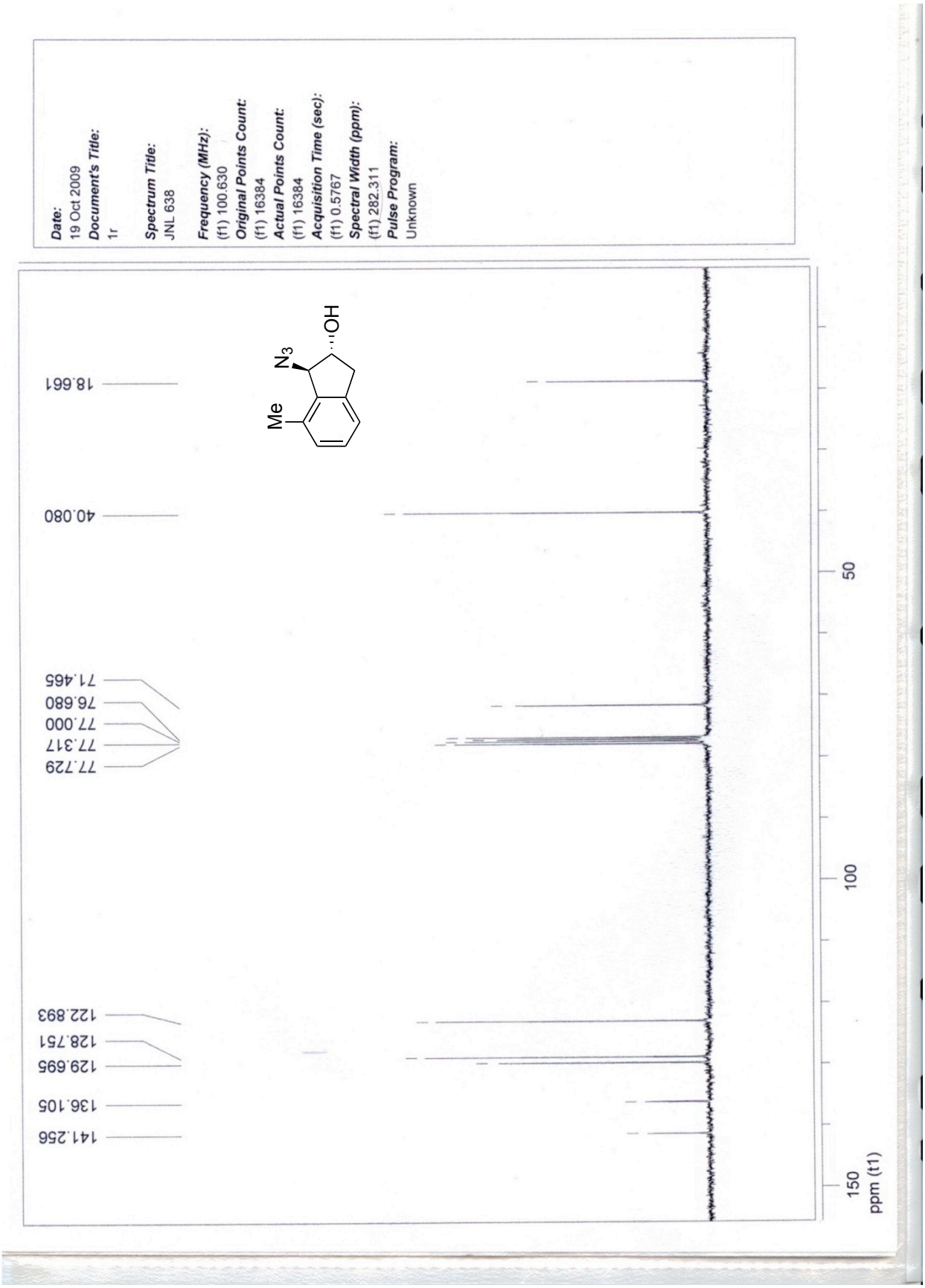


This journal is © The Royal Society of Chemistry 2011

(1R,2R)-1-Azido-7-methyl-2,3-dihydro-1H-inden-2-ol

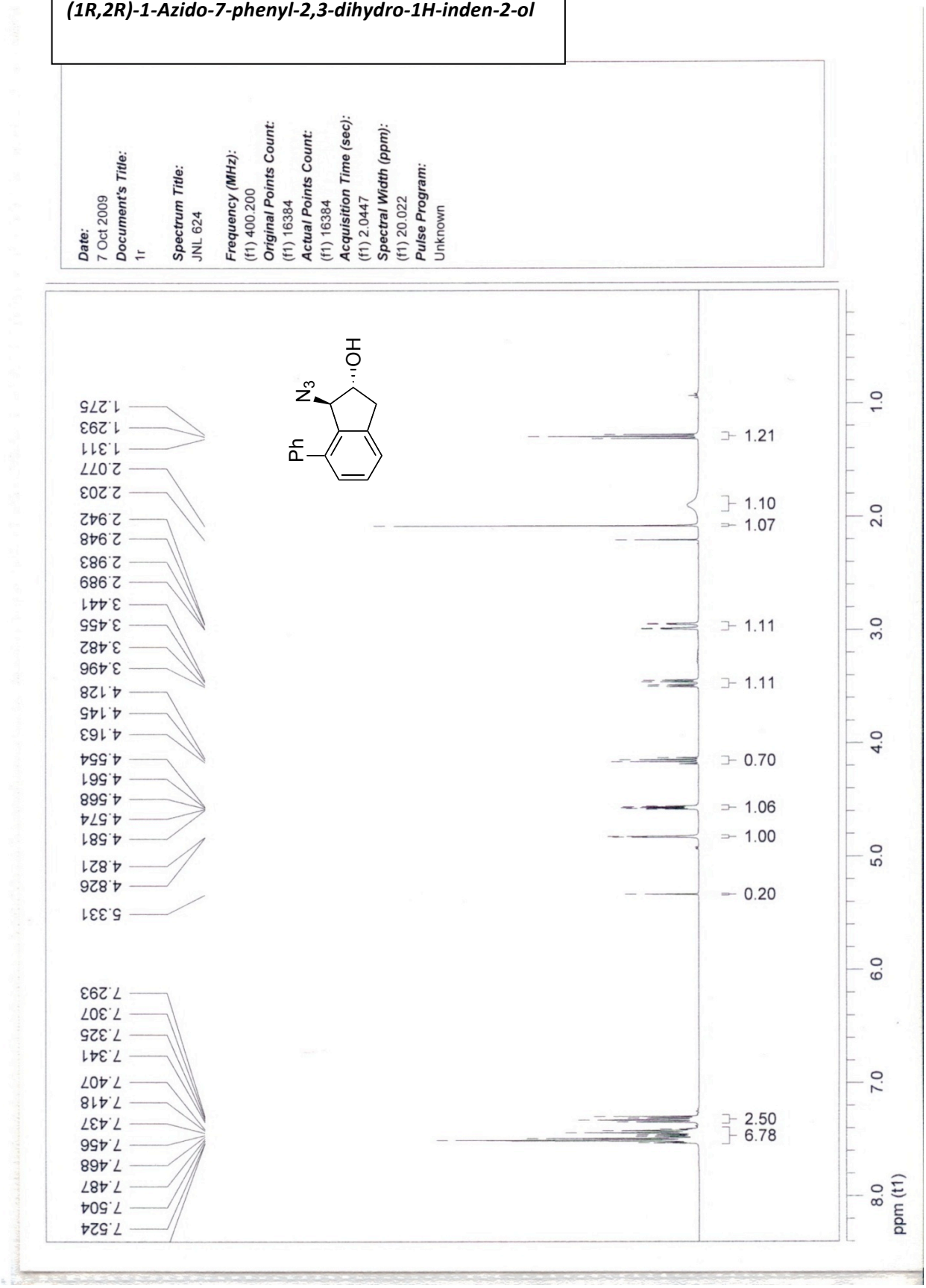


This journal is © The Royal Society of Chemistry 2011

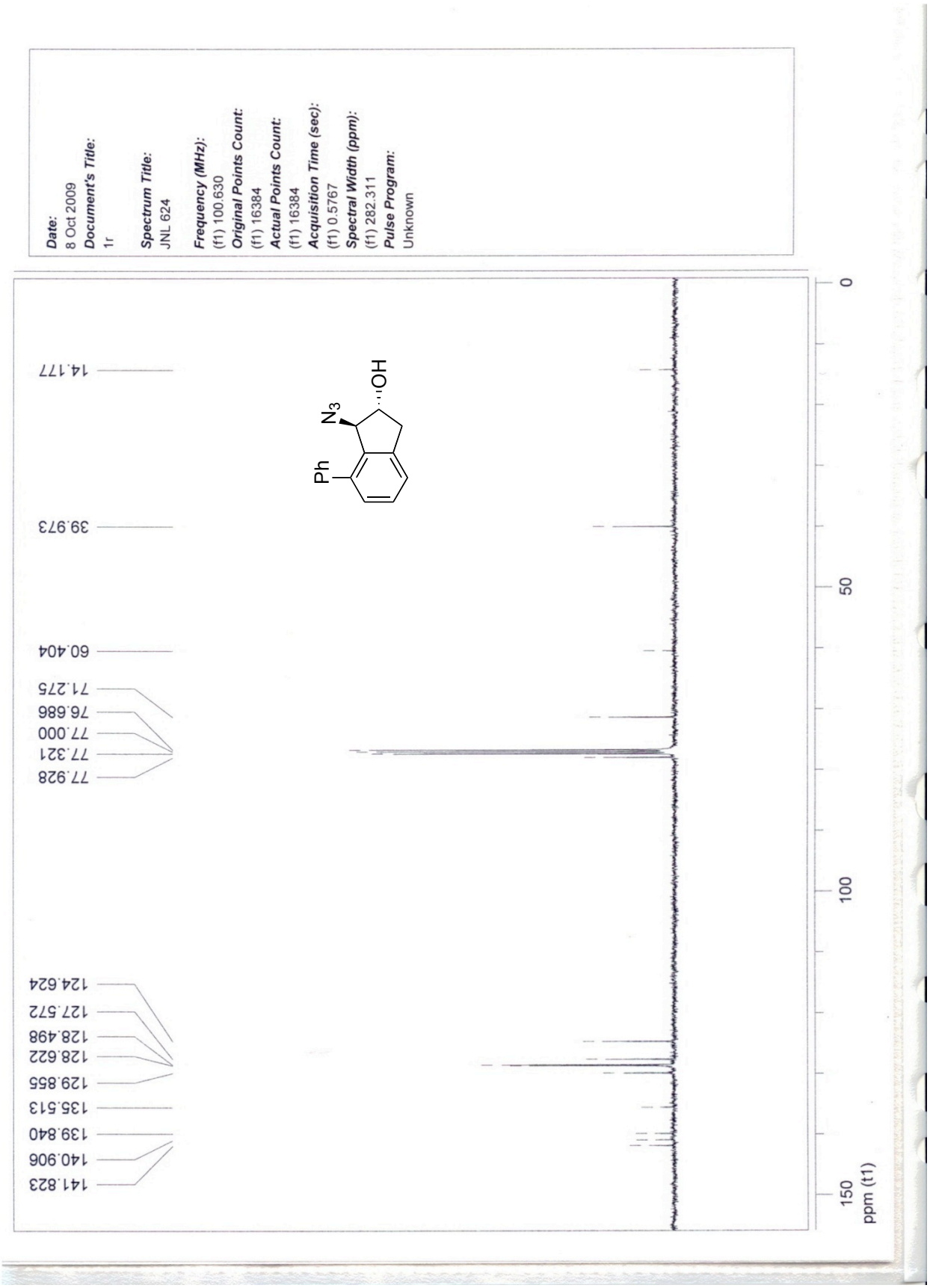


This journal is © The Royal Society of Chemistry 2011

(1R,2R)-1-Azido-7-phenyl-2,3-dihydro-1H-inden-2-ol

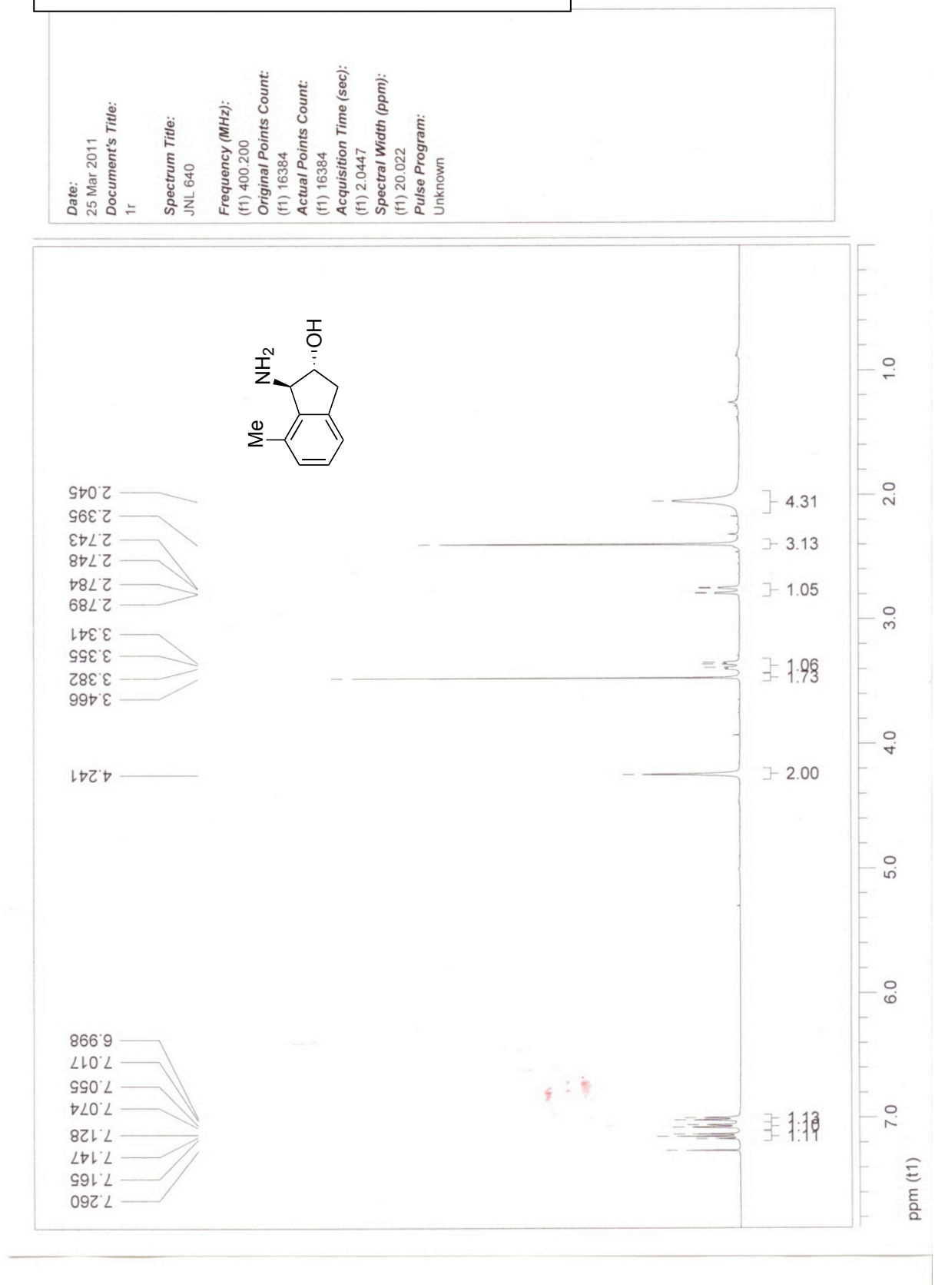


This journal is © The Royal Society of Chemistry 2011

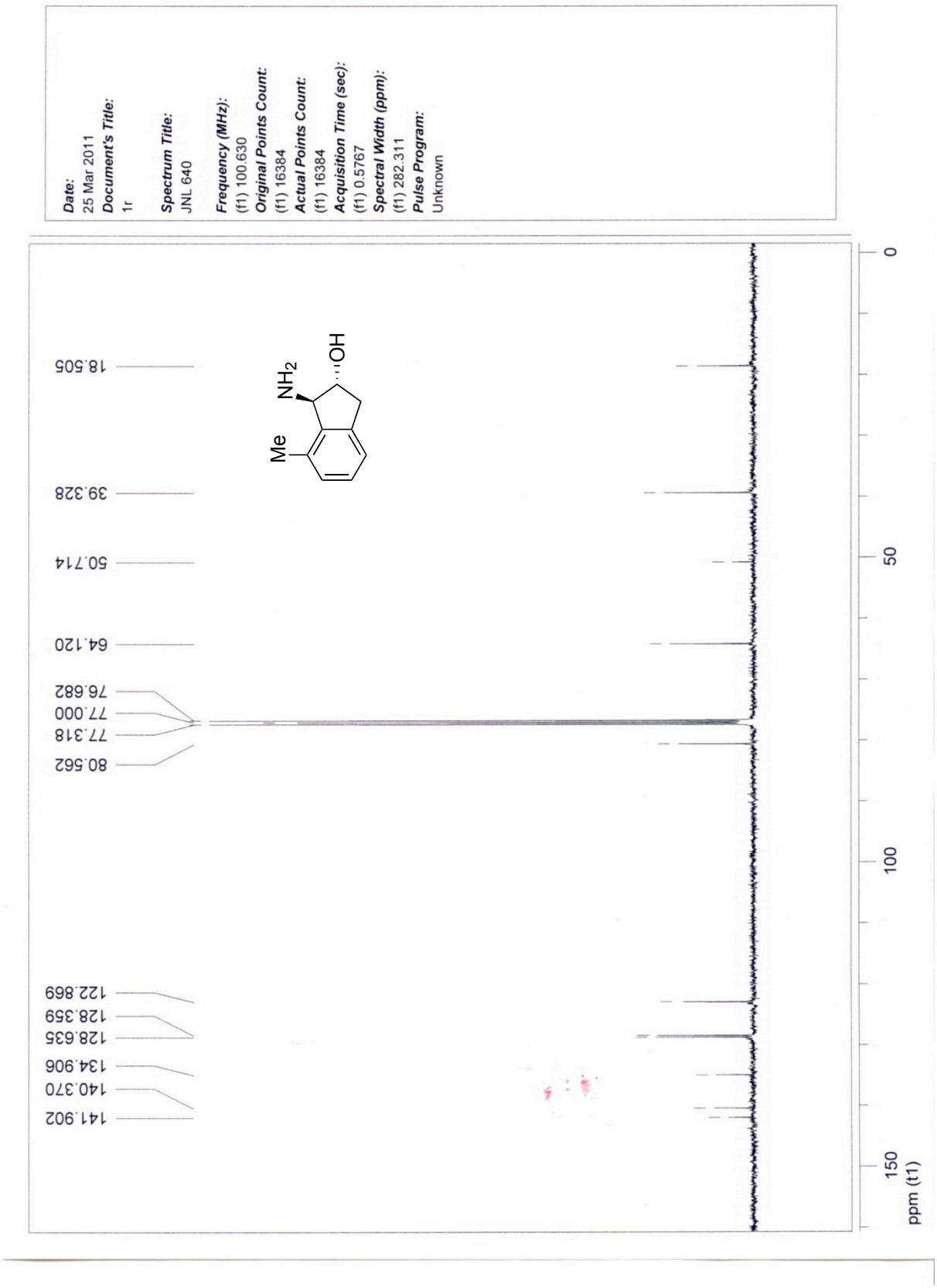


This journal is © The Royal Society of Chemistry 2011

(1R,2R)-1-Amino-7-methyl-2,3-dihydro-1H-inden-2-ol

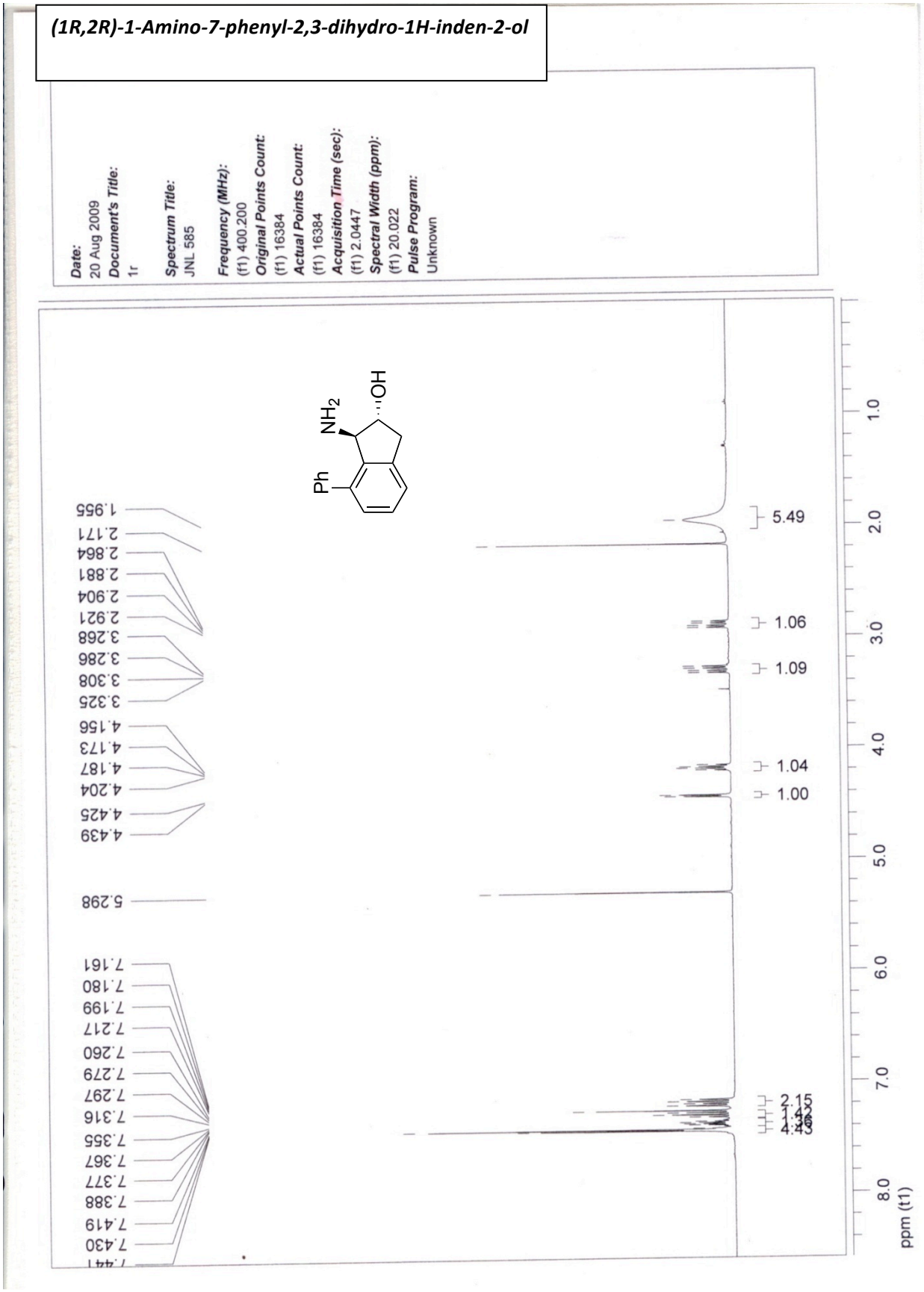


This journal is © The Royal Society of Chemistry 2011



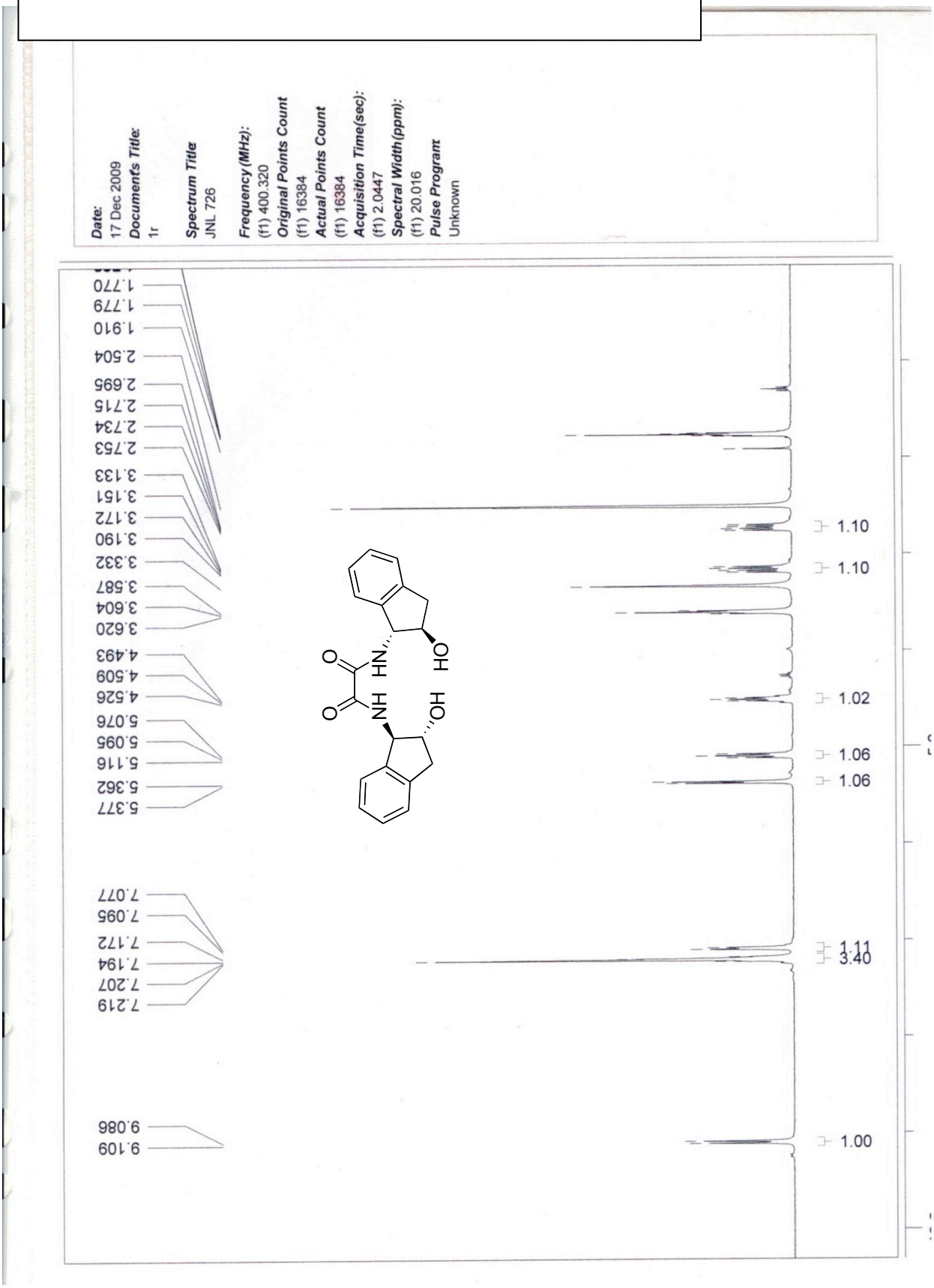
This journal is © The Royal Society of Chemistry 2011

(1R,2R)-1-Amino-7-phenyl-2,3-dihydro-1H-inden-2-ol

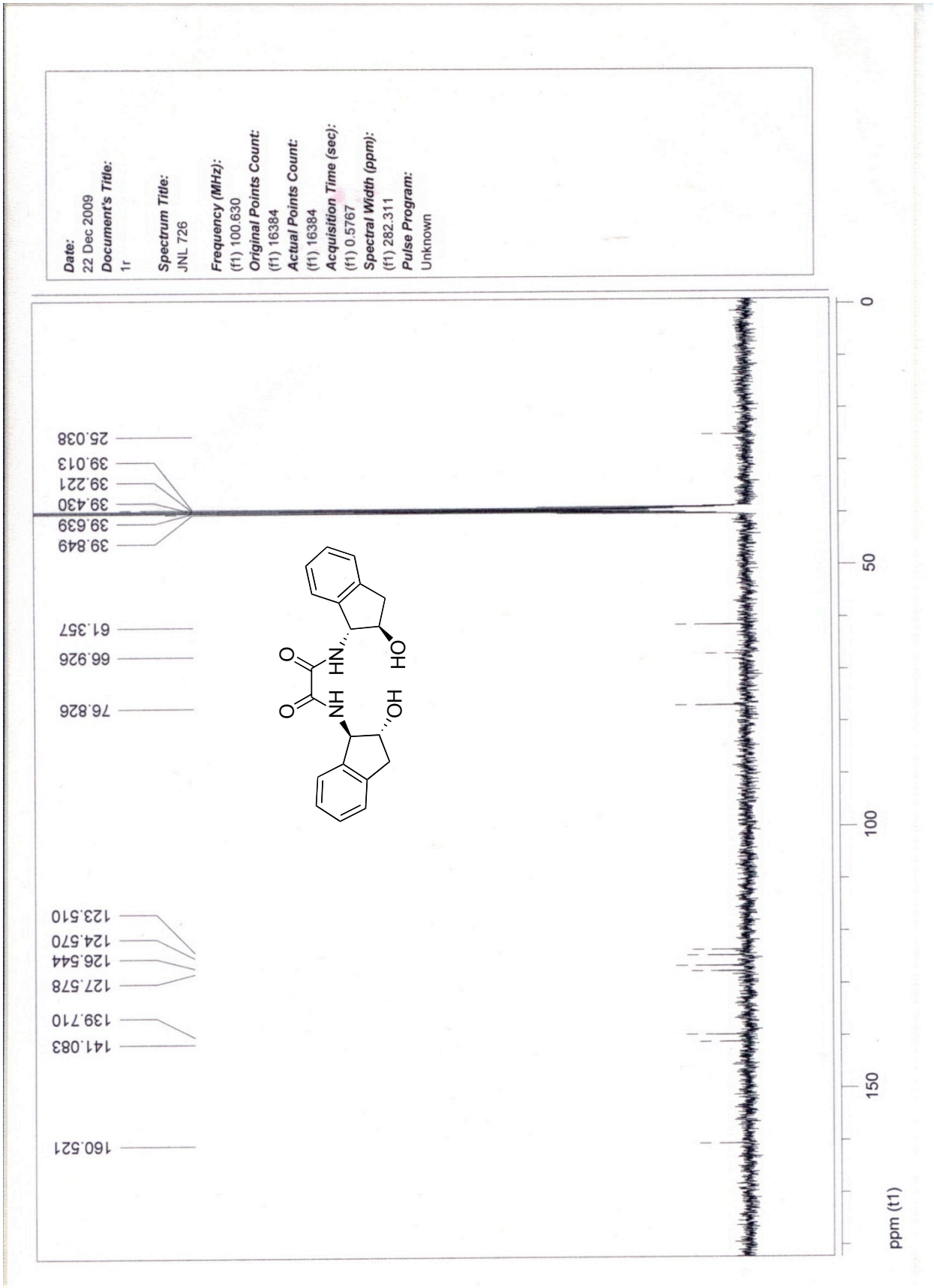


This journal is © The Royal Society of Chemistry 2011

N1,N2-bis((1R,2R)-2-Hydroxy-2,3-dihydro-1H-inden-1-yl)oxalamide

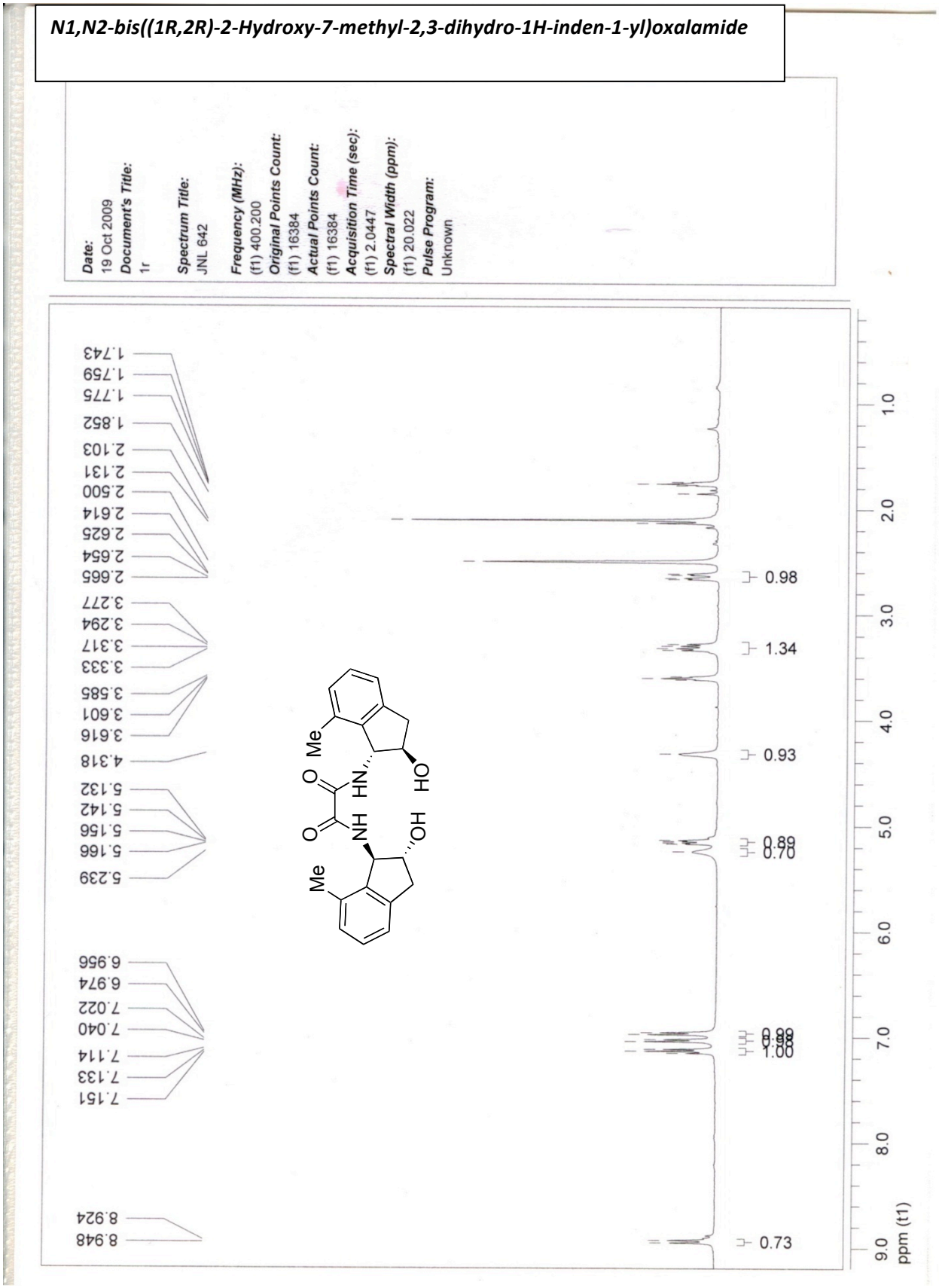


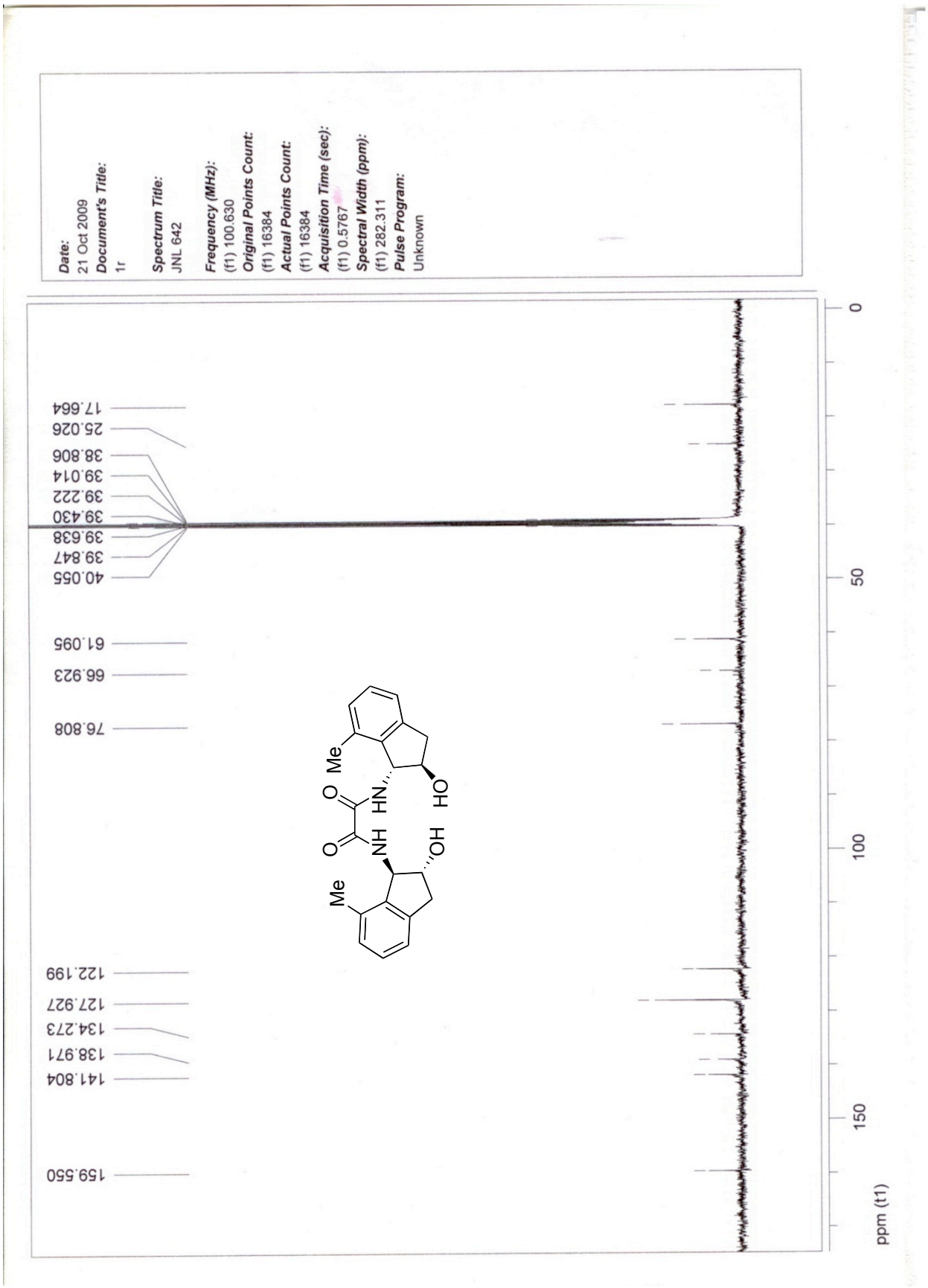
This journal is © The Royal Society of Chemistry 2011



This journal is © The Royal Society of Chemistry 2011

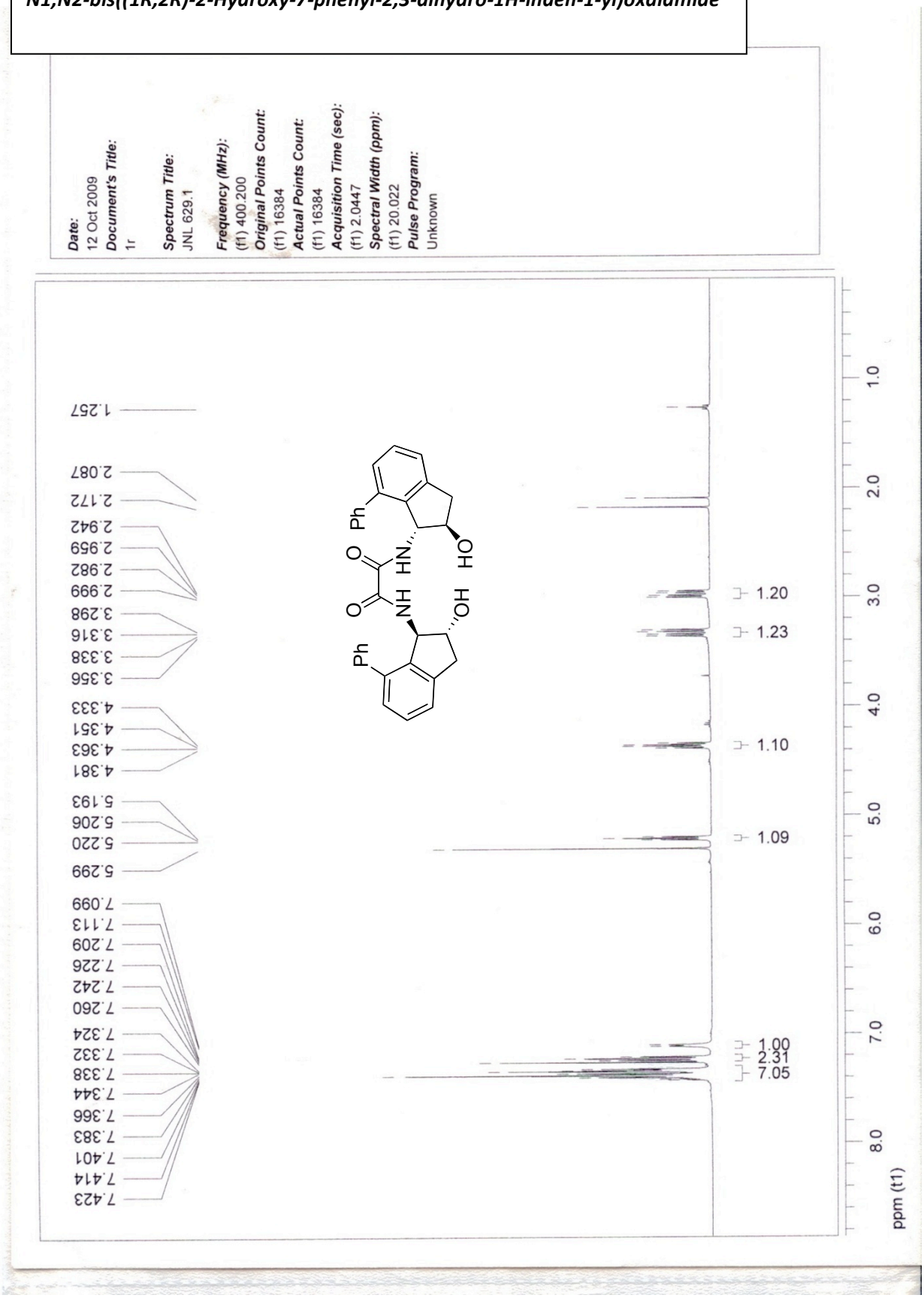
N1,N2-bis((1R,2R)-2-Hydroxy-7-methyl-2,3-dihydro-1H-inden-1-yl)oxalamide



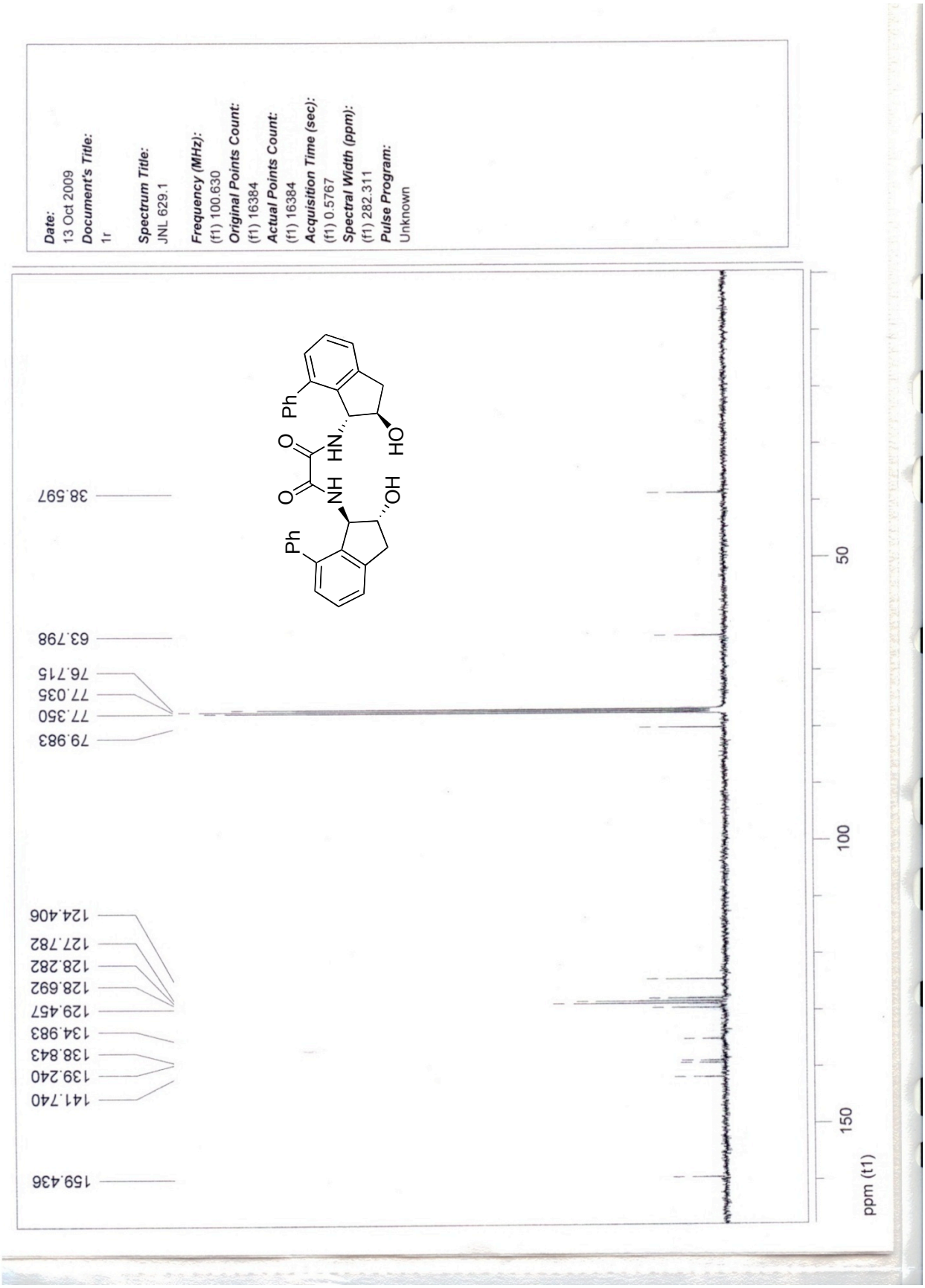

Date:
21 Oct 2009
Document's Title:
1r
Spectrum Title:
JNL 642
Frequency (MHz):
(f1) 100.630
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 16384
Acquisition Time (sec):
(f1) 0.5767
Spectral Width (ppm):
(f1) 282.311
Pulse Program:
Unknown
17.664
25.026
38.806
39.014
39.222
39.430
39.638
39.847
40.055
61.095
66.923
76.808
122.199
127.927
134.273
138.971
141.804
159.550
Me
O
HN
HO
NH
O
OH
Me
0
50
100
150
ppm (t1)

This journal is © The Royal Society of Chemistry 2011

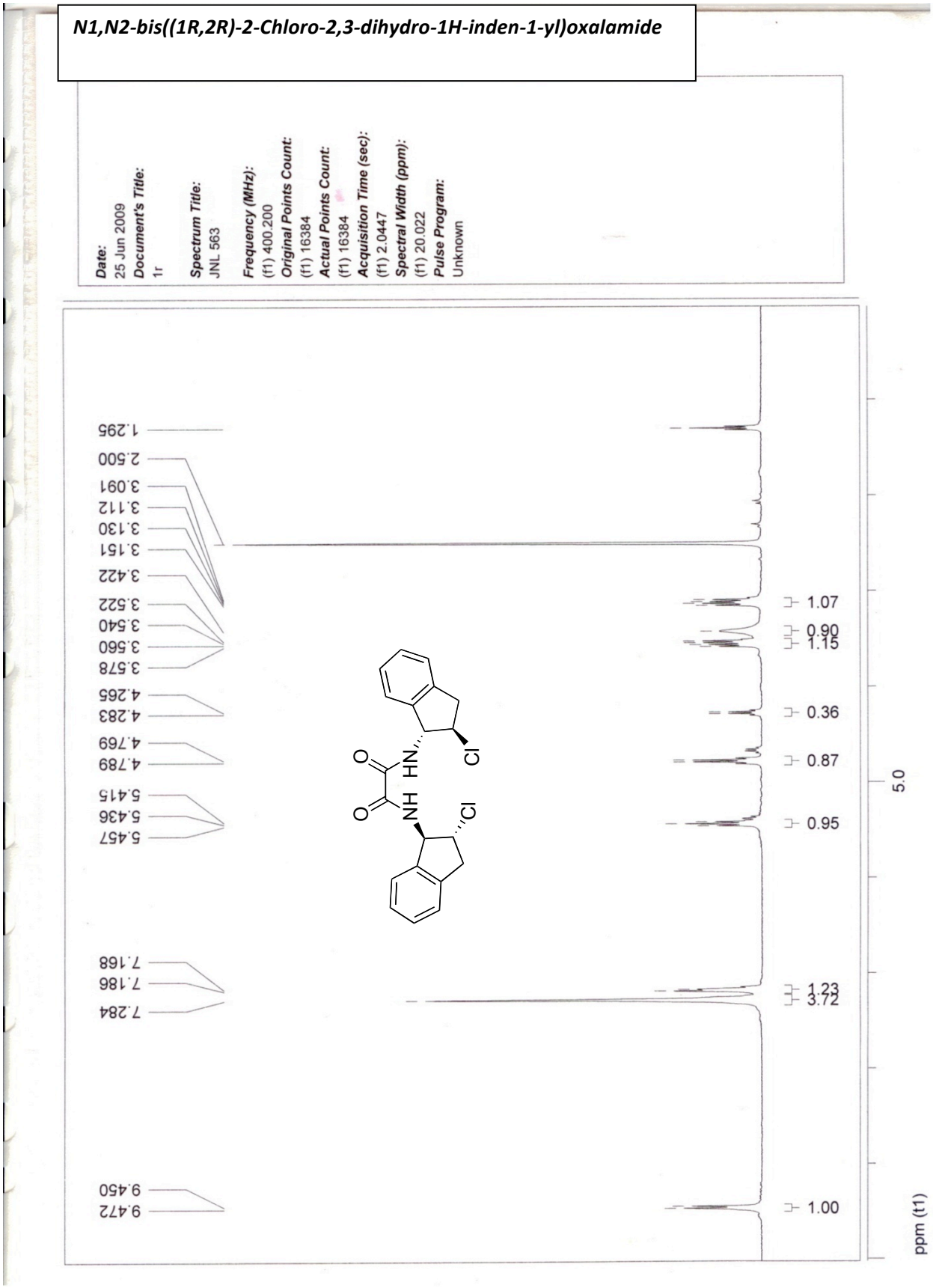
N1,N2-bis((1R,2R)-2-Hydroxy-7-phenyl-2,3-dihydro-1H-inden-1-yl)oxalamide



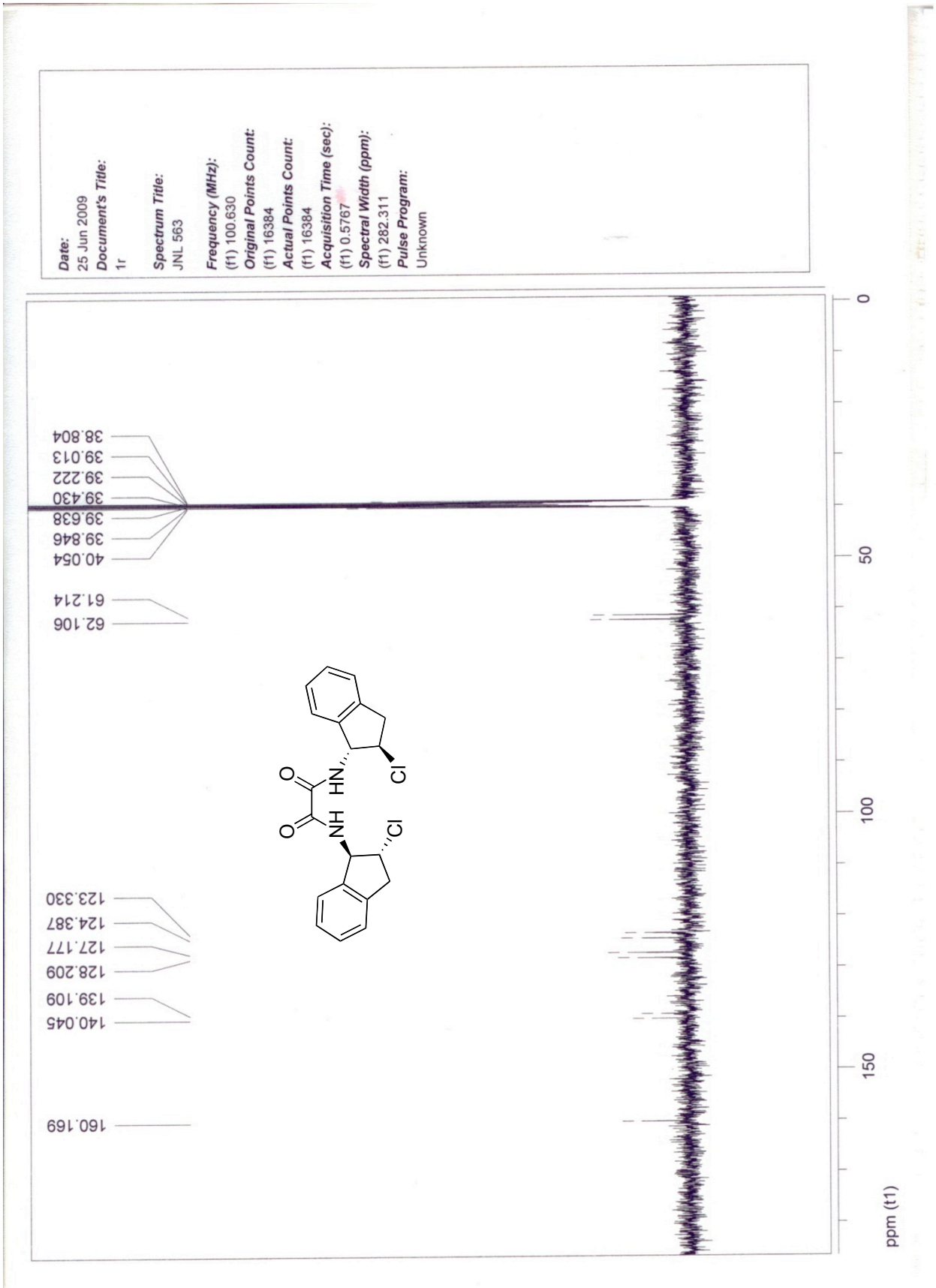
This journal is © The Royal Society of Chemistry 2011



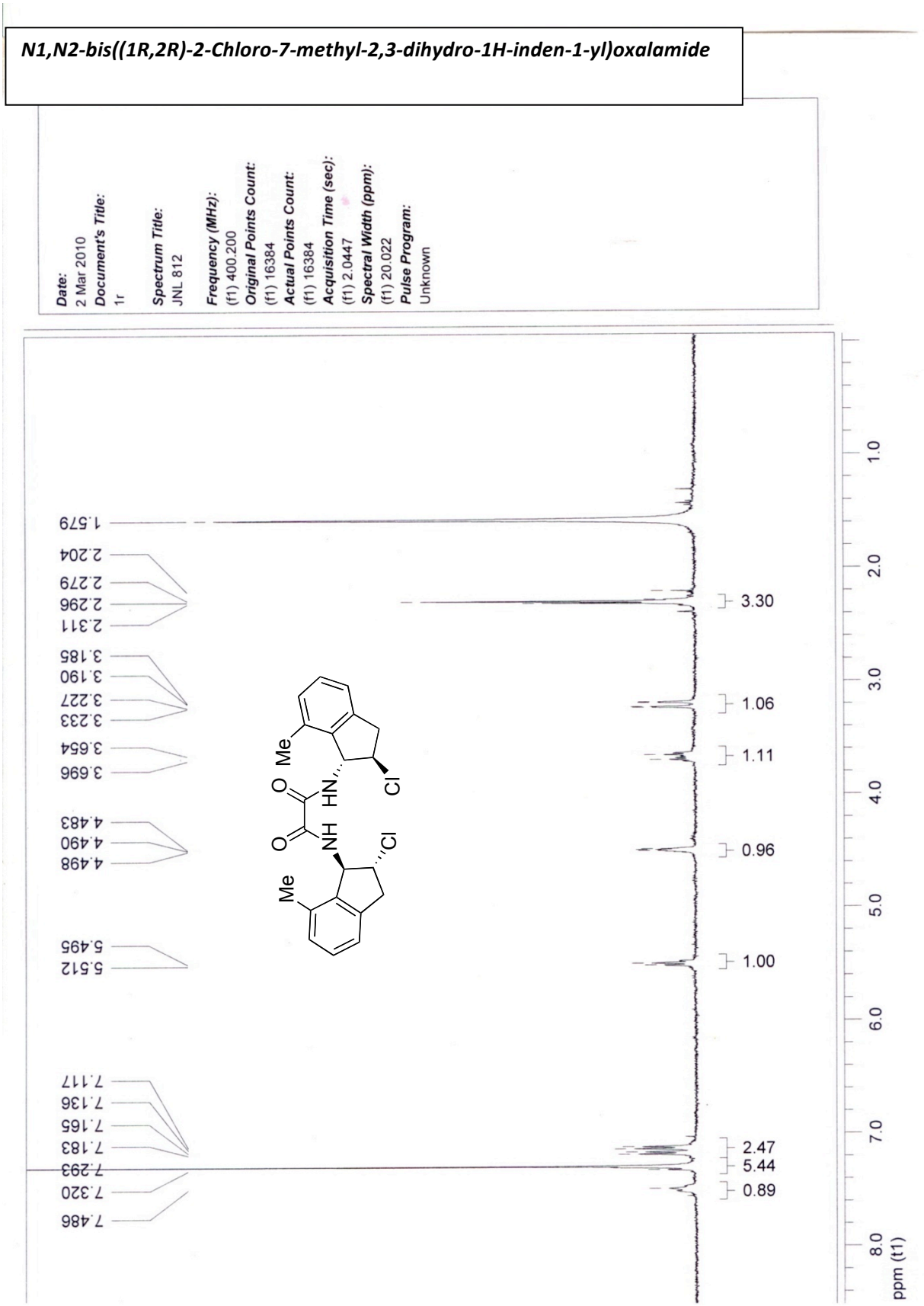
N1,N2-bis((1R,2R)-2-Chloro-2,3-dihydro-1H-inden-1-yl)oxalamide



This journal is © The Royal Society of Chemistry 2011

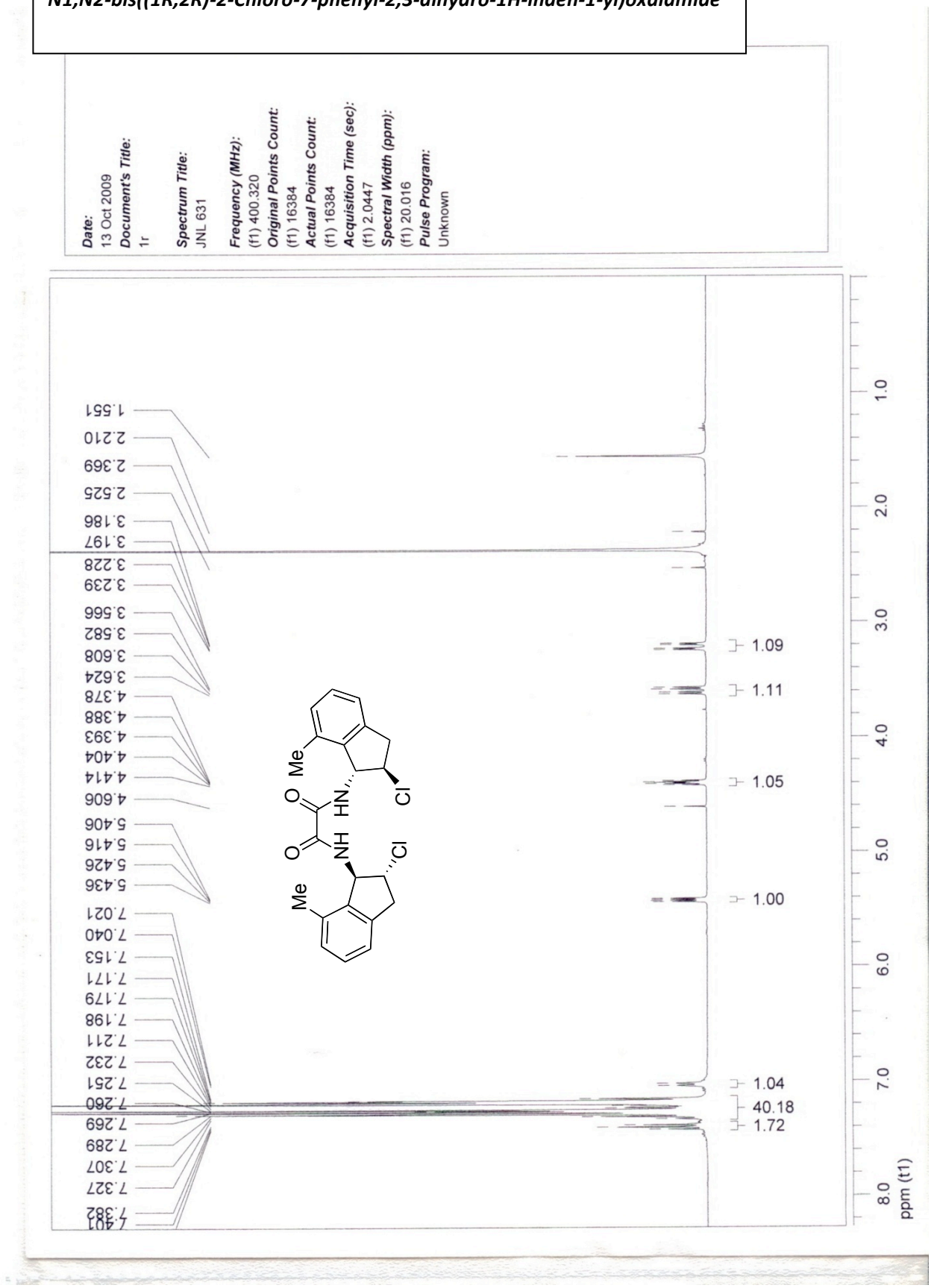


N1,N2-bis((1R,2R)-2-Chloro-7-methyl-2,3-dihydro-1H-inden-1-yl)oxalamide



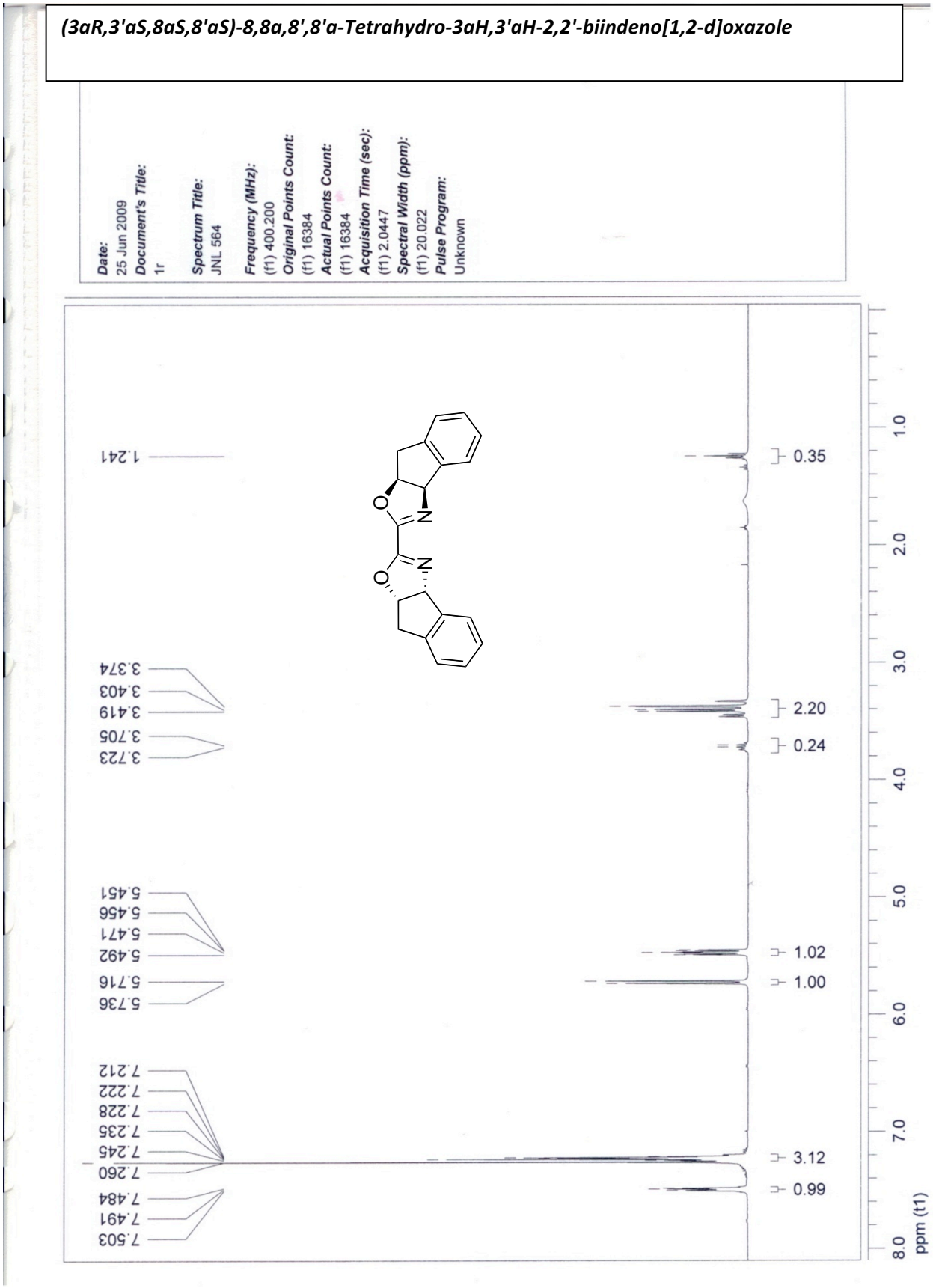
This journal is © The Royal Society of Chemistry 2011

N1,N2-bis((1R,2R)-2-Chloro-7-phenyl-2,3-dihydro-1H-inden-1-yl)oxalamide

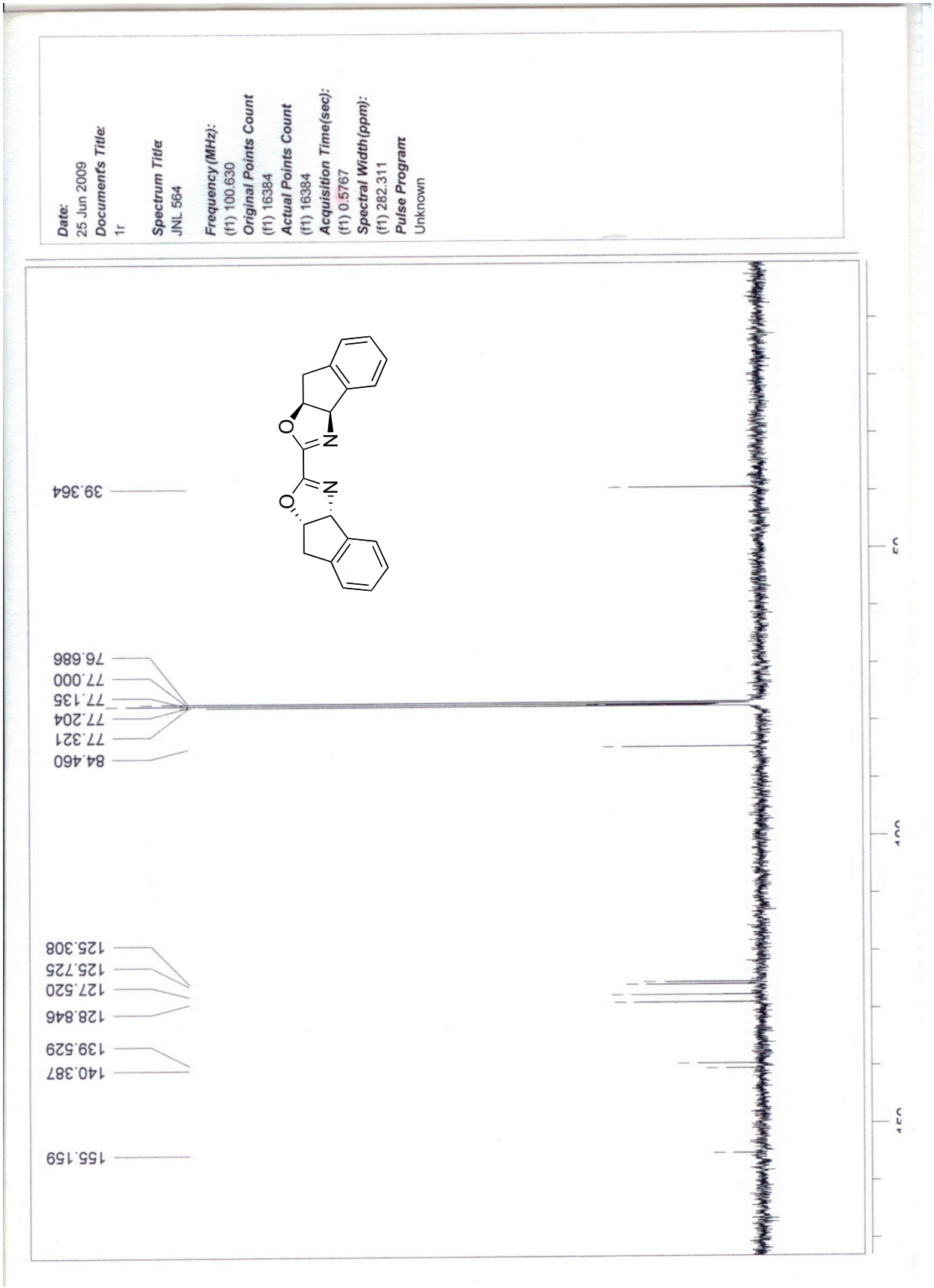


This journal is © The Royal Society of Chemistry 2011

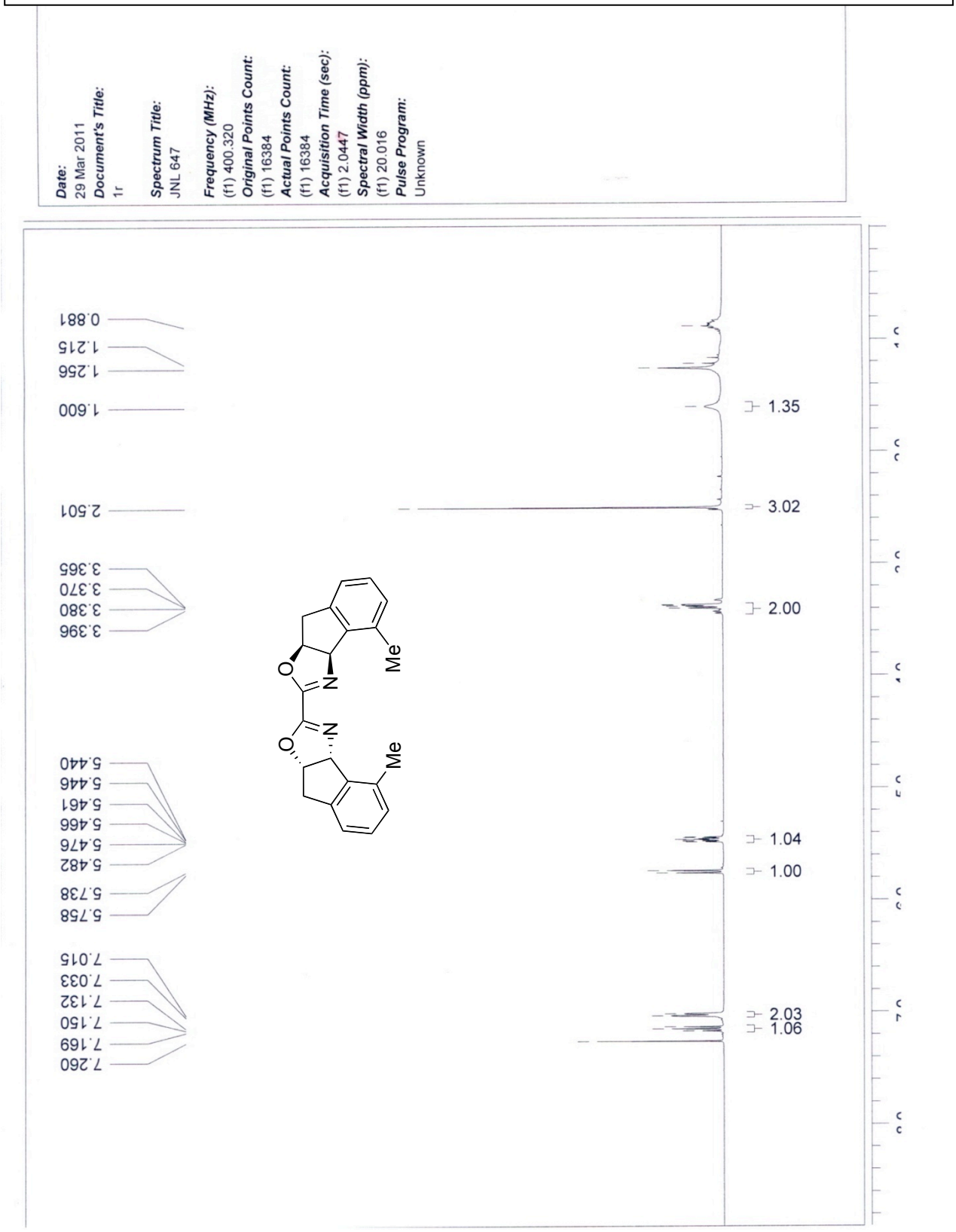
(3aR,3'aS,8aS,8'aS)-8,8a,8',8'a-Tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole



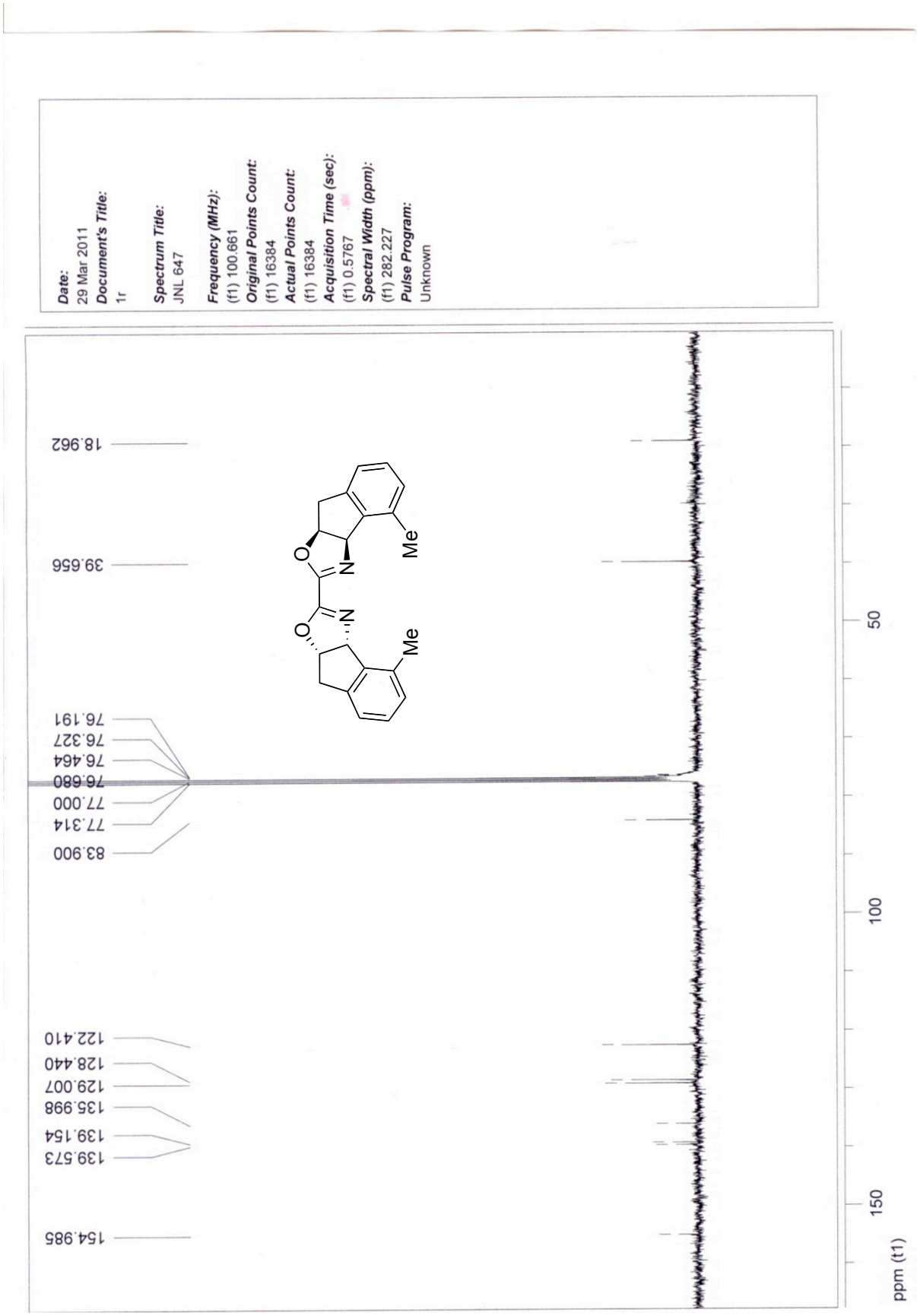
This journal is © The Royal Society of Chemistry 2011



(3aR,3'aR,8aS,8'aS)-4,4'-Dimethyl-8,8a,8',8'a-tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole

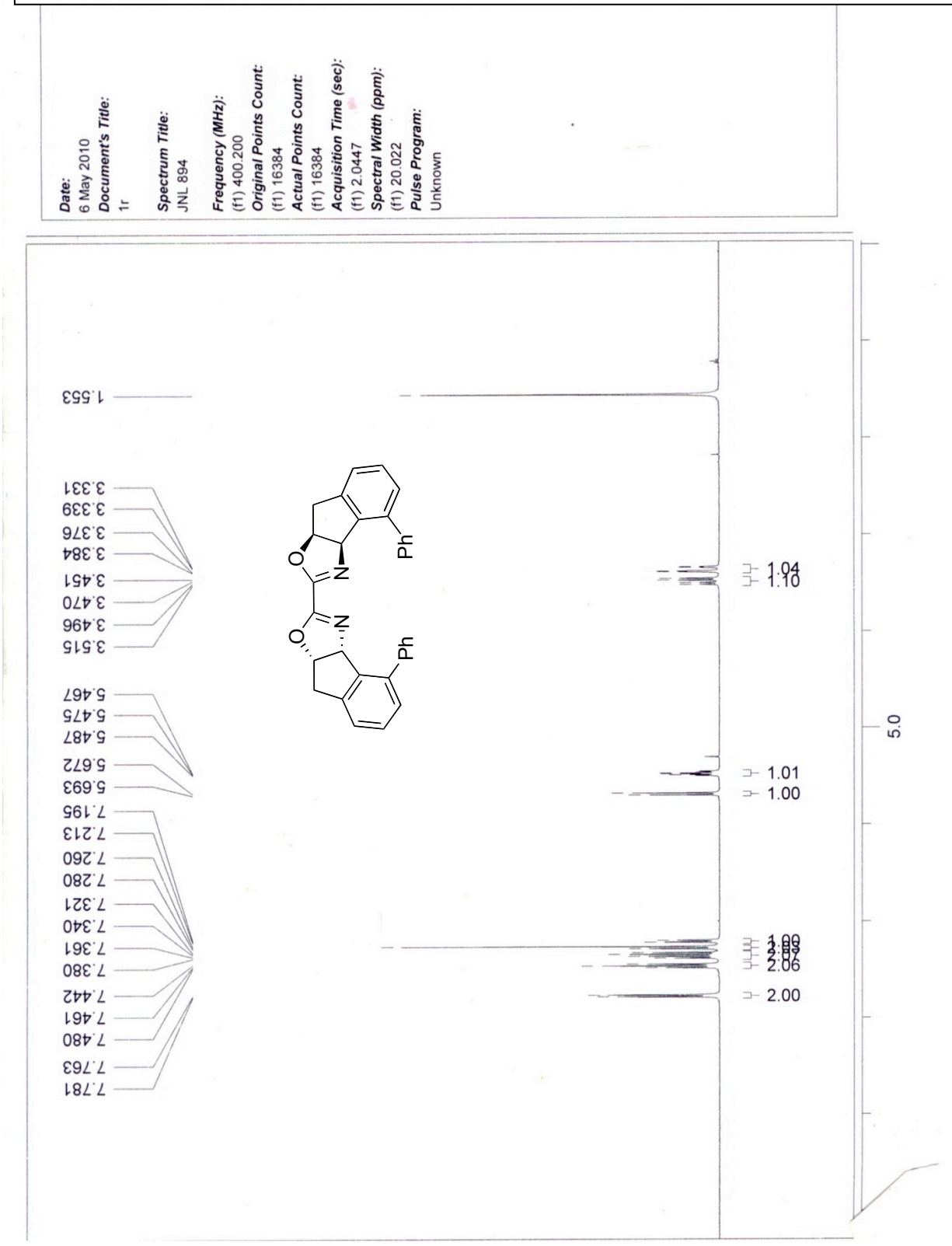


This journal is © The Royal Society of Chemistry 2011

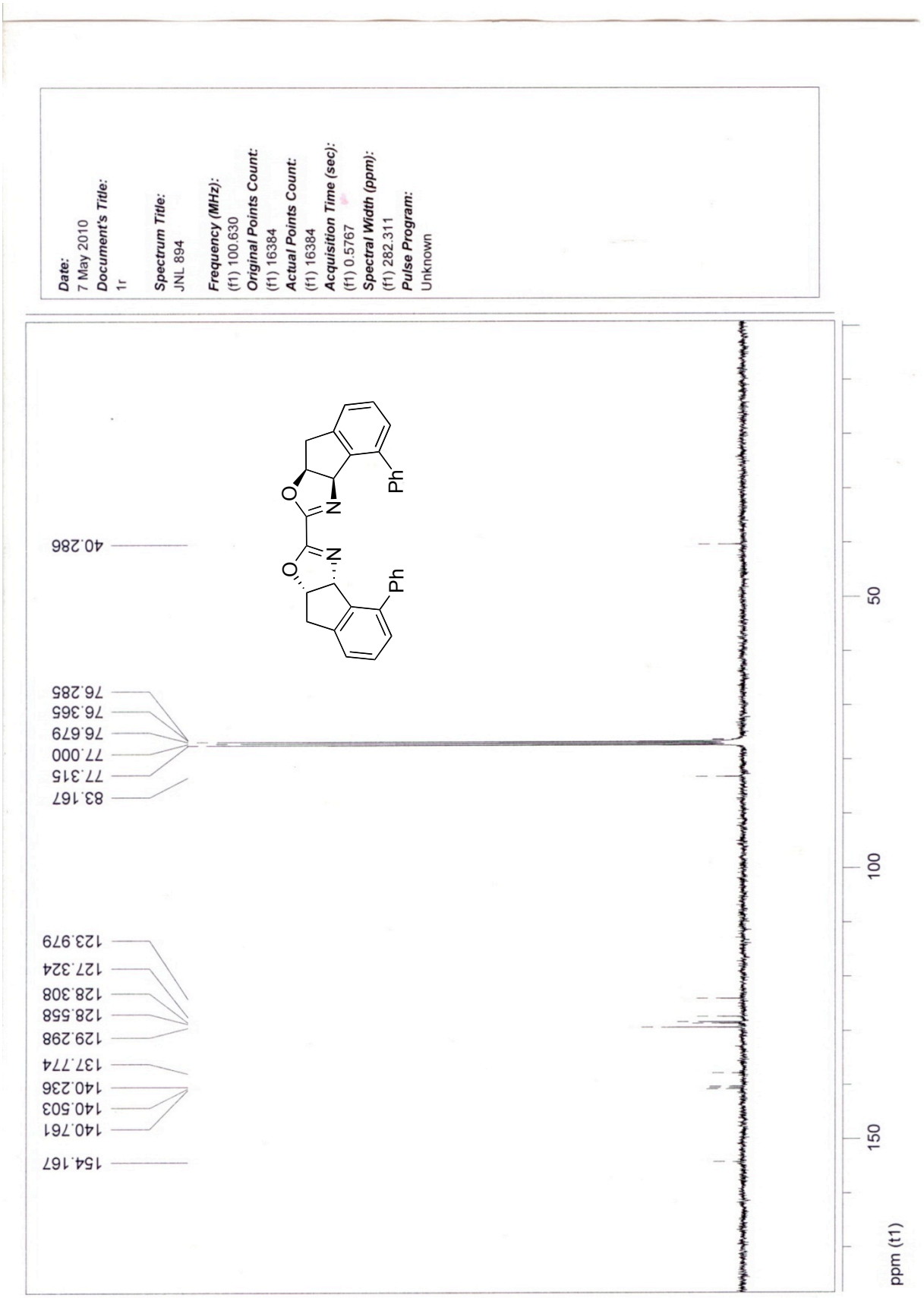


This journal is © The Royal Society of Chemistry 2011

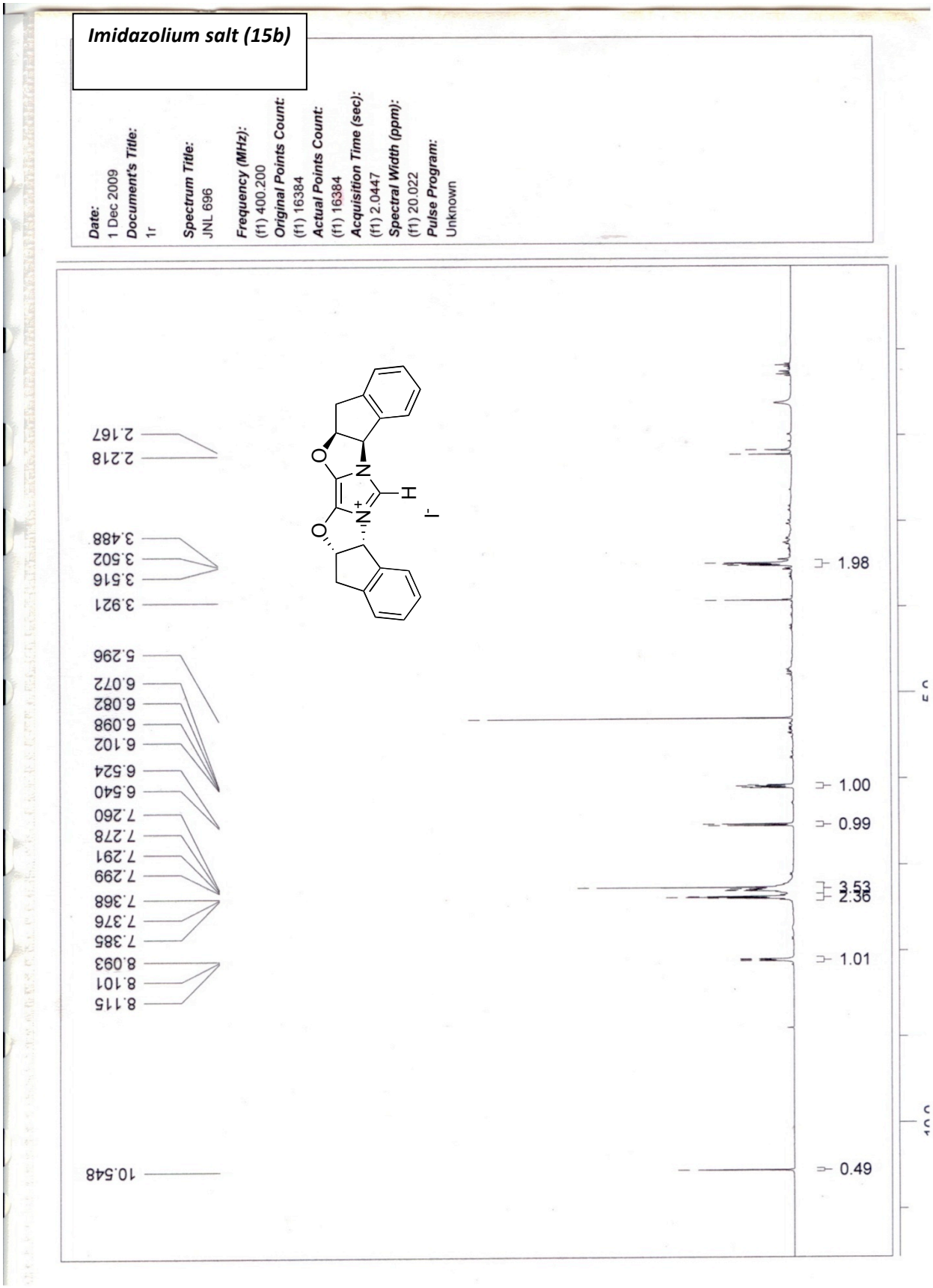
(3aR,3'aR,8aS,8'aS)-4,4'-Diphenyl-8,8a,8',8'a-tetrahydro-3aH,3'aH-2,2'-biindeno[1,2-d]oxazole



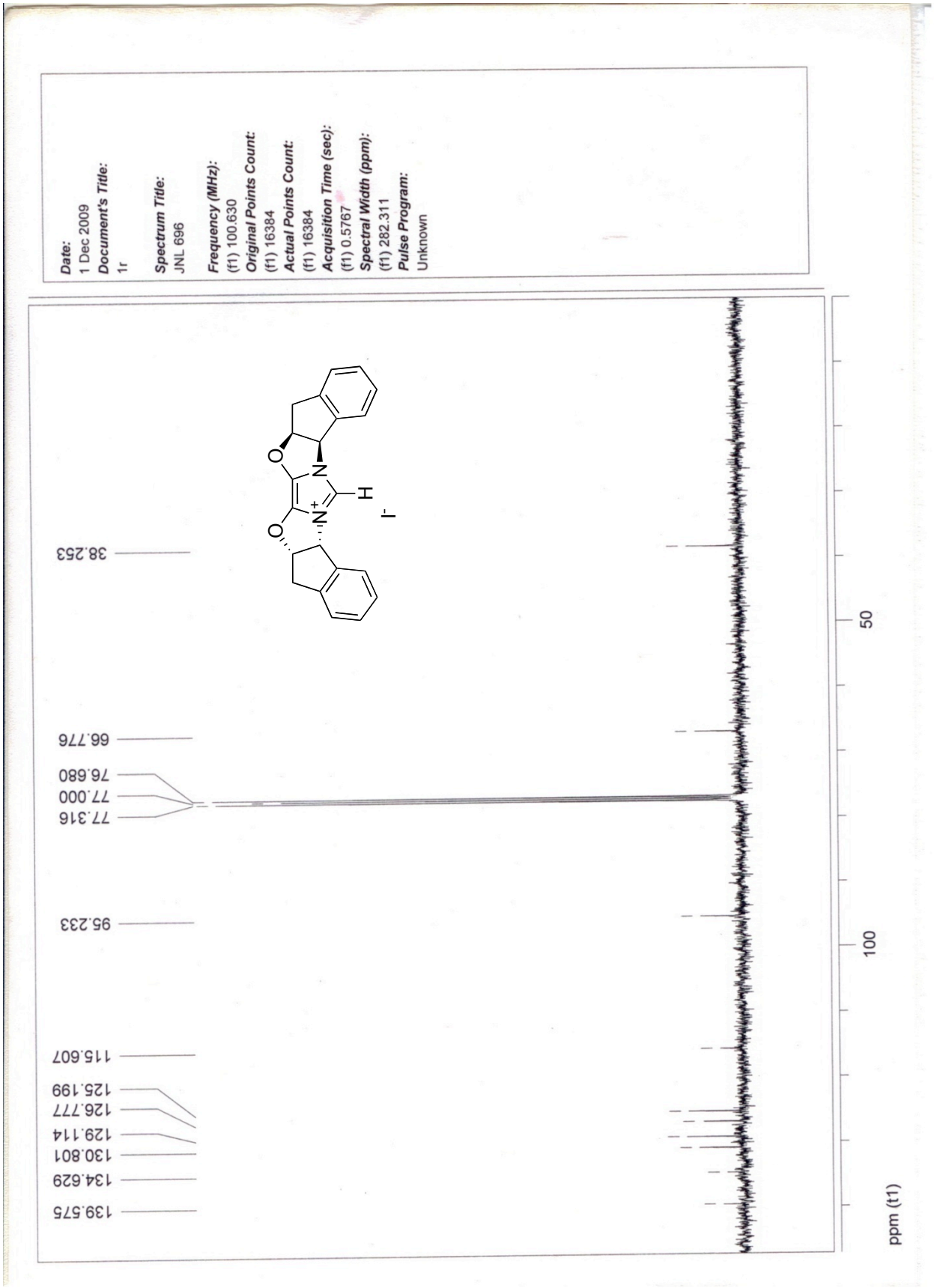
This journal is © The Royal Society of Chemistry 2011



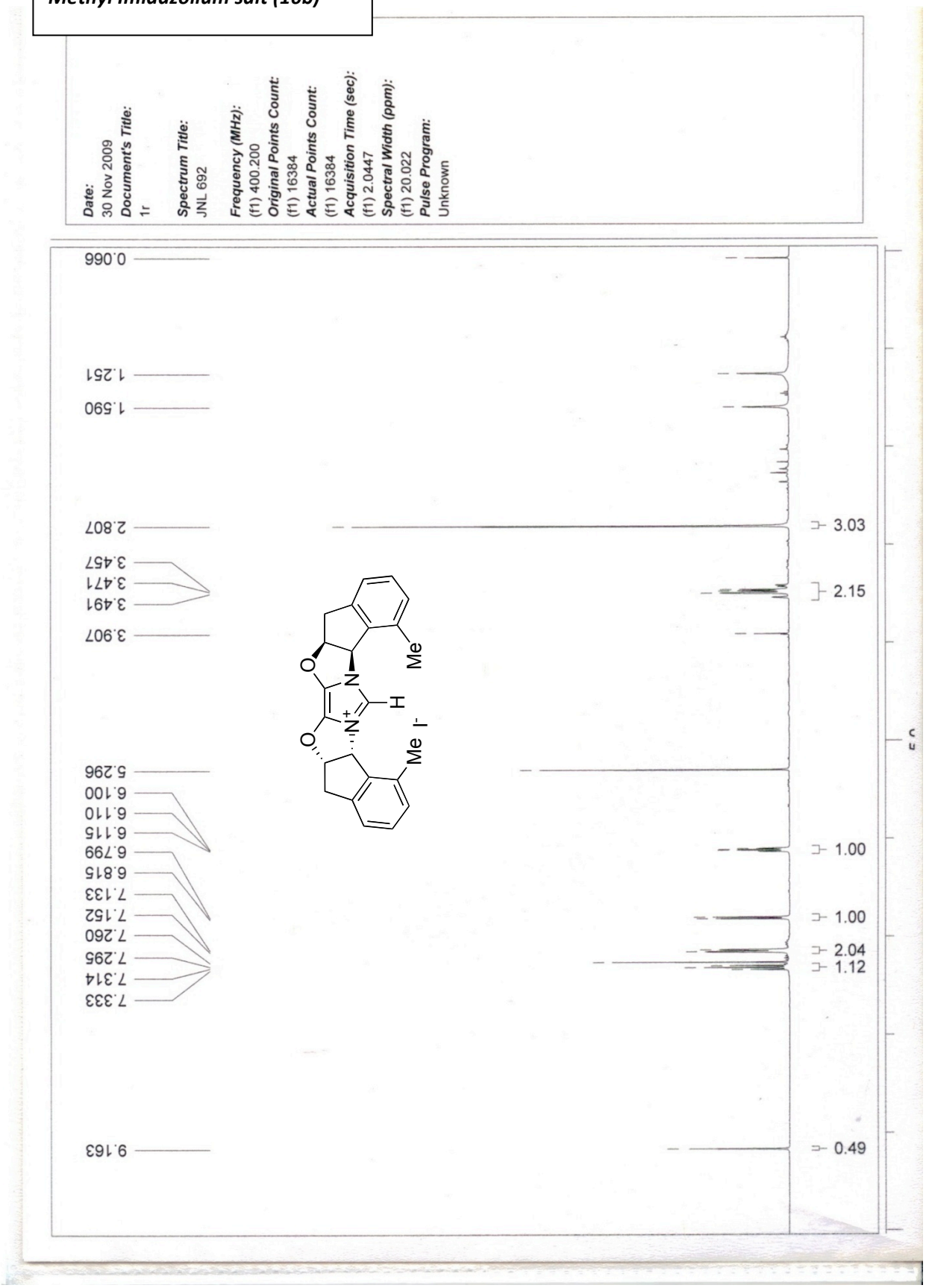
This journal is © The Royal Society of Chemistry 2011



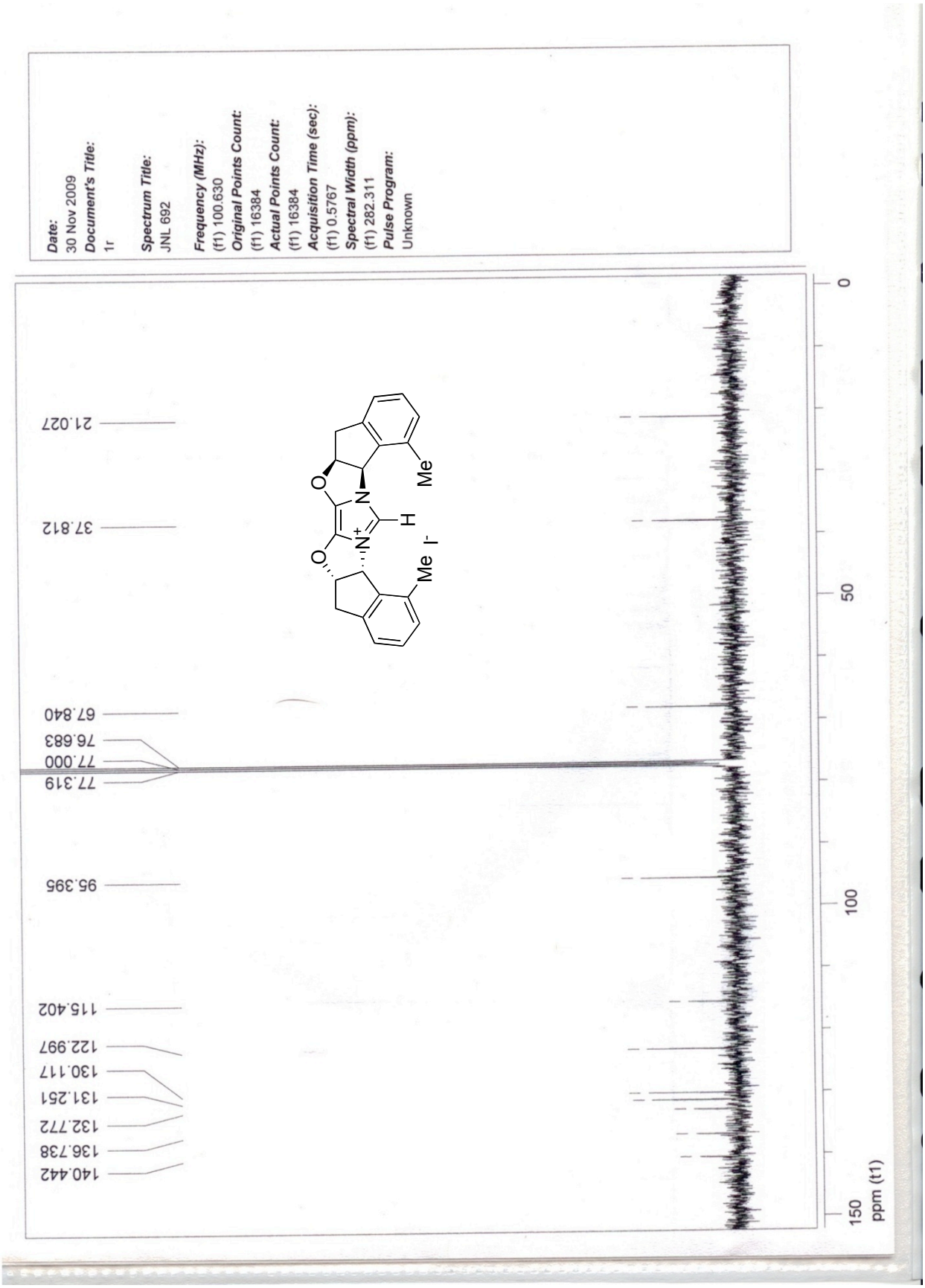
This journal is © The Royal Society of Chemistry 2011



Methyl Imidazolium salt (16b)

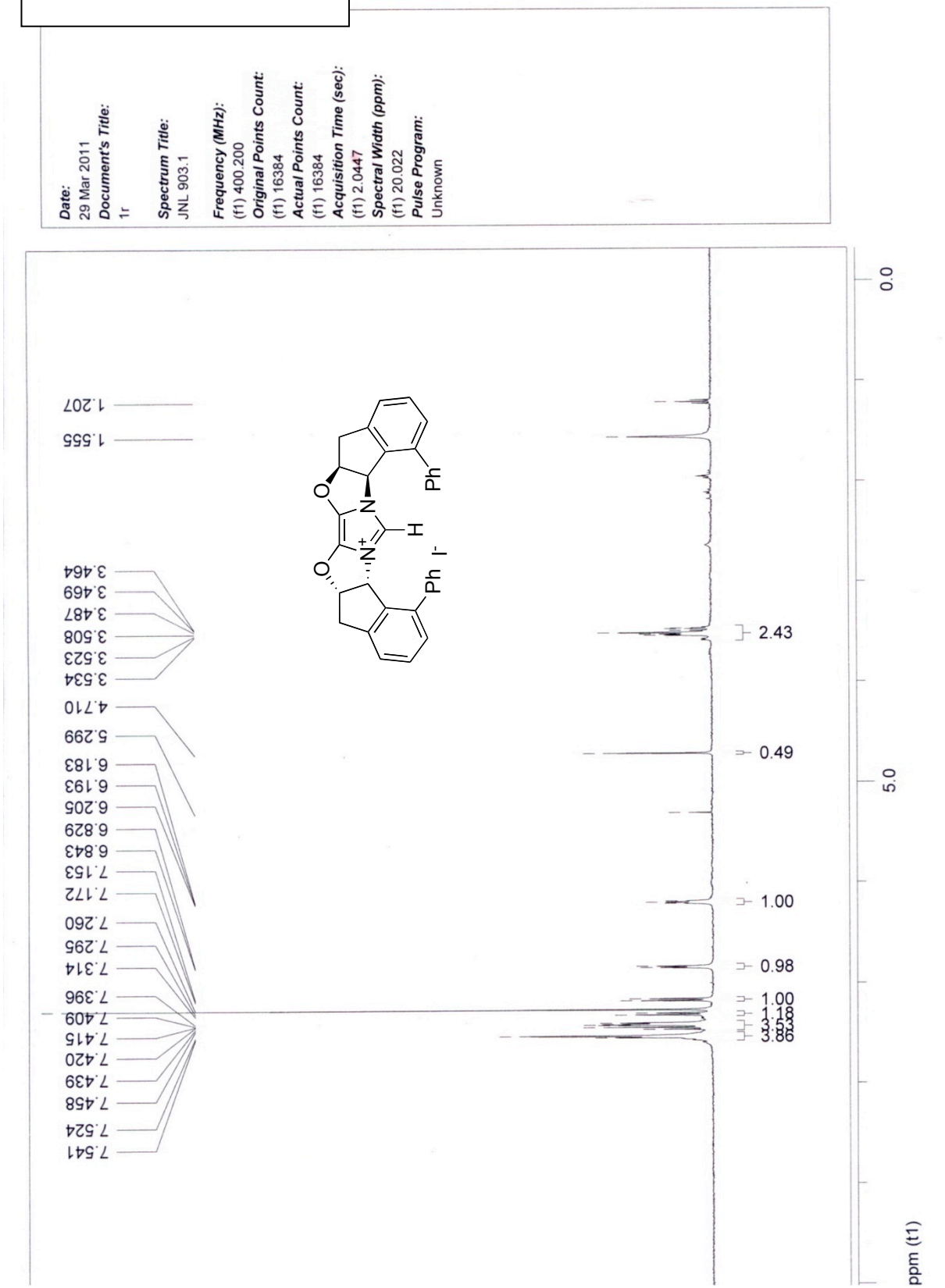


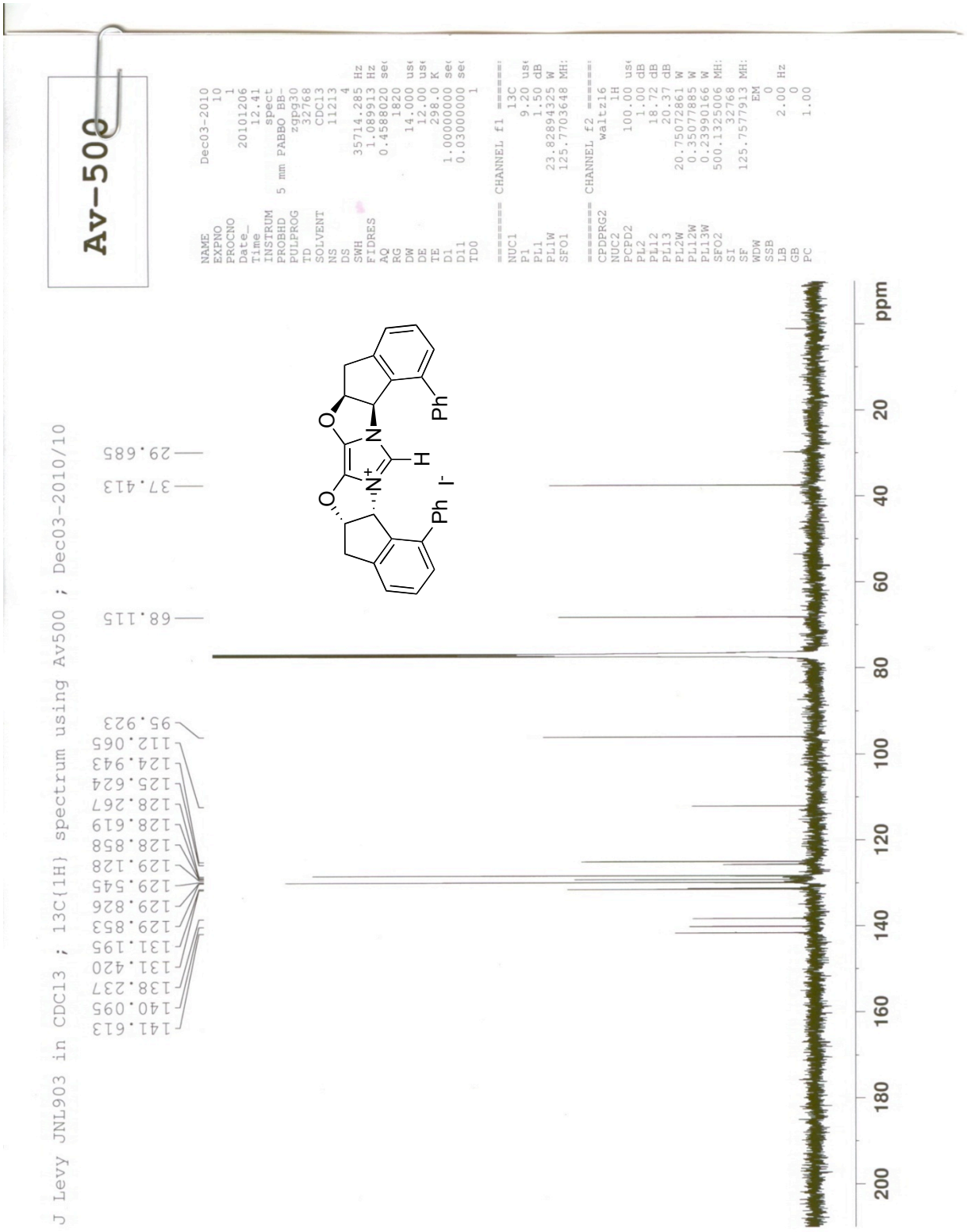
This journal is © The Royal Society of Chemistry 2011



This journal is © The Royal Society of Chemistry 2011

Phenyl Imidazolium salt (17b)




Av-500
J Levy JNL903 in CDCl3 ; 13C{1H} spectrum using Av500 ; Dec03-2010/10
NAME Dec03-2010
EXPNO 10
PROCNO 1
Date_ 20101206
Time 12.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 11213
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.45880200 sec
RG 1820
DW 14.000 usec
DE 12.00 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.20 usec
PL1 1.50 dB
PL1W 23.82894325 W
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.00 dB
PL12 18.72 dB
PL13 20.37 dB
PL2W 20.75072861 W
PL12W 0.35077885 W
PL13W 0.23990166 W
SFO2 500.1325006 MHz
SI 32768
SF 125.7577913 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00
Ph
H
N
O
Ph
I-
29.685
37.413
68.115
95.923
112.065
124.943
125.624
128.267
128.619
128.858
129.128
129.545
129.826
129.853
131.195
131.420
138.237
140.095
141.613
200
180
160
140
120
100
80
60
40
20
ppm

This journal is © The Royal Society of Chemistry 2011

Calculation of the Buried Volume of the imidazolium salts

The buried volume (%V_{Bur}; the fraction of the space buried by the NHC ligand of a sphere around the metal) of the IBiox-ligands was calculated by using the web application Samb*V*ca developed by Cavallo et al. for the calculation of the buried volume of any type of ligands.[179] As an input file for this computer program, only the coordinates of the ligand must be supplied. This program positions the putative metal atom at 2.10 Å from the coordinating atom of the ligand; a value of 3.5 Å is taken for the radius of the sphere around this metal atom. For our calculations of the buried volumes, we took the coordinates from the crystal structure analyses of the imidazolium salts from which the proton at C2 and the anion were deleted.

This journal is © The Royal Society of Chemistry 2011

Imidazolium salt 15a:

```
              ------------------------------------------------------
              |                                                    |
              |                  S A M B V C A                     |
              |                                                    |
              |              Buried Volume in Salerno              |
              |                                                    |
              |   http://www.molnac.unisa.it/OM-tools/SambVca      |
              |                                                    |
              |    L. Cavallo et al. email: lcavallo@unisa.it      |
              |                                                    |
              ------------------------------------------------------
```

Molecule from input :

```
  Molecule from input :

Imidazolium salt

     Number of atoms             :   41
     Atom that is coordinated    :    1
     Atoms that define the axis  :    2
     ID of these atoms           :    2  25

     Radius of sphere (Angs)     :    3.500
     Distance from sphere (Angs) :    2.100
     Mesh step (Angs)            :    0.050
     H atoms omitted in the V_bur calculation
```

Cartesian coordinates from input :

```
  Cartesian coordinates from input :
C       -5.02950    4.01916   10.99390
N       -4.12402    3.90589   11.96935
C       -3.01044    3.01988   12.31197
H       -2.32960    2.98129   11.57998
C       -3.40138    1.64943   12.77744
C       -4.01486    0.64829   12.04281
H       -4.29633    0.80894   11.14892
C       -4.21093   -0.58860   12.63031
H       -4.61911   -1.28893   12.13449
C       -3.81347   -0.81143   13.94313
H       -3.95451   -1.66340   14.33837
C       -3.21443    0.19530   14.68038
H       -2.94208    0.03931   15.57691
C       -3.01575    1.44130   14.08924
C       -2.37471    2.67303   14.68261
H       -2.86689    2.97095   15.48787
H       -1.43345    2.49303   14.93133
C       -2.44909    3.72724   13.58533
H       -1.54471    4.11402   13.40541
O       -3.41160    4.79045   13.93220
C       -4.27719    4.89596   12.91344
C       -5.30205    5.66880   12.48076
O       -5.96745    6.80225   12.78412
```

This journal is © The Royal Society of Chemistry 2011

C	-7.14769	6.85801	11.89508
H	-7.98420	6.60912	12.38341
C	-7.26587	8.23383	11.25132
H	-6.79935	8.91802	11.79450
H	-8.21576	8.49596	11.15296
C	-6.60950	8.07877	9.90349
C	-6.24903	9.05105	8.97276
H	-6.35428	9.97316	9.17372
C	-5.73499	8.65237	7.74980
H	-5.48018	9.31215	7.11555
C	-5.58443	7.31089	7.43005
H	-5.25263	7.06014	6.57521
C	-5.91894	6.33530	8.35794
H	-5.80797	5.41433	8.15577
C	-6.41894	6.73584	9.58819
C	-6.84867	5.86369	10.73465
H	-7.63837	5.29329	10.50738
N	-5.75023	5.09158	11.31507

Atoms and radius in the parameter file

Atoms and radius in the parameter file

H	1.29
C2	1.99
C3	1.99
C	1.99
N2	1.81
N3	1.81
N	1.81
O	1.78
F	1.72
Si	2.45
P	2.11
S	2.10
Cl	2.05
Br	2.16

Coordinates scaled to put the metal at the origin

Coordinates scaled to put the metal at the origin

C	-1.07833	1.30327	1.24447
N	-0.17285	1.19000	2.21992
C	0.94073	0.30399	2.56254
H	1.62157	0.26540	1.83055
C	0.54979	-1.06646	3.02801
C	-0.06369	-2.06760	2.29338
H	-0.34516	-1.90695	1.39949
C	-0.25976	-3.30449	2.88088
H	-0.66794	-4.00482	2.38506
C	0.13770	-3.52732	4.19370
H	-0.00334	-4.37929	4.58894
C	0.73674	-2.52059	4.93095
H	1.00909	-2.67658	5.82748
C	0.93542	-1.27459	4.33981
C	1.57646	-0.04286	4.93318
H	1.08428	0.25506	5.73844

```
H       2.51772  -0.22286   5.18190
C       1.50208   1.01135   3.83590
H       2.40646   1.39813   3.65598
O       0.53957   2.07456   4.18277
C      -0.32602   2.18007   3.16401
C      -1.35088   2.95291   2.73133
O      -2.01628   4.08636   3.03469
C      -3.19652   4.14212   2.14565
H      -4.03303   3.89323   2.63398
C      -3.31470   5.51794   1.50189
H      -2.84818   6.20213   2.04507
H      -4.26459   5.78007   1.40353
C      -2.65833   5.36288   0.15406
C      -2.29786   6.33516  -0.77667
H      -2.40311   7.25727  -0.57571
C      -1.78382   5.93648  -1.99963
H      -1.52901   6.59626  -2.63388
C      -1.63326   4.59500  -2.31938
H      -1.30146   4.34425  -3.17422
C      -1.96777   3.61941  -1.39149
H      -1.85680   2.69844  -1.59366
C      -2.46777   4.01995  -0.16124
C      -2.89750   3.14780   0.98522
H      -3.68720   2.57740   0.75795
N      -1.79906   2.37569   1.56564
XX      0.00000   0.00000   0.00000
```

Results : Volumes in Angs^3

```
  Results : Volumes in Angs^3

       N of voxels examined :         1436277
       Volume of voxel      :       0.125E-03

    V Free   V Buried  V Total   V Exact
   114.308    65.226   179.535   179.594

  %V_Free    %V_Bur  % Tot/Ex
  63.669     36.331    99.967
```

The %V_Bur of your molecule is: 36.3

This journal is © The Royal Society of Chemistry 2011

Imidazolium salt 16b :

```
              ------------------------------------------------------
              |                                                    |
              |                  S A M B V C A                     |
              |                                                    |
              |              Buried Volume in Salerno              |
              |                                                    |
              |   http://www.molnac.unisa.it/OM-tools/SambVca      |
              |                                                    |
              |    L. Cavallo et al. email: lcavallo@unisa.it      |
              |                                                    |
              ------------------------------------------------------
```

Molecule from input :

```
  Molecule from input :

Imidazolium salt

     Number of atoms             :   47
     Atom that is coordinated    :    1
     Atoms that define the axis  :    2
     ID of these atoms           :    2  25

     Radius of sphere (Angs)     :    3.500
     Distance from sphere (Angs) :    2.100
     Mesh step (Angs)            :    0.050
     H atoms omitted in the V_bur calculation
```

Cartesian coordinates from input :

```
  Cartesian coordinates from input :
C       -6.21895    7.07178    2.49914
N       -7.10203    6.19776    2.97445
C       -8.02253    5.99962    4.07669
H       -7.56923    6.09591    4.96171
C       -9.29475    6.74032    4.03368
C       -9.49254    8.13838    4.07884
C      -10.82250    8.58650    4.08637
H      -10.96255    9.51792    4.21003
C      -11.93436    7.80877    3.91646
H      -12.79606    8.20134    3.85301
C      -11.77934    6.48107    3.84764
H      -12.53947    5.91629    3.76268
C      -10.45259    5.90518    3.90356
C       -9.94263    4.47379    4.00141
H      -10.15003    4.09974    4.89504
H      -10.38203    3.90901    3.31749
C       -8.41061    4.48305    3.77559
H       -7.91989    3.82569    4.34768
O       -8.20427    4.29232    2.41741
C       -7.32975    5.22560    2.03781
C       -6.56748    5.50521    0.97213
O       -6.19116    5.02746   -0.19356
```

This journal is © The Royal Society of Chemistry 2011

C	-5.39789	6.00888	-0.88180
H	-5.96451	6.50144	-1.54207
C	-4.27105	5.39781	-1.55927
H	-4.44959	4.45528	-1.79693
H	-4.00378	5.90518	-2.36257
C	-3.23617	5.51632	-0.43982
C	-2.01525	4.85710	-0.36562
H	-1.78754	4.20714	-1.02267
C	-1.12576	5.14968	0.65597
H	-0.29186	4.69785	0.70759
C	-1.45718	6.10147	1.61304
H	-0.85100	6.29960	2.31848
C	-2.68023	6.76069	1.54529
C	-3.56759	6.46811	0.51725
C	-4.97238	6.91994	0.19356
H	-5.01729	7.88284	-0.07420
N	-5.85118	6.60514	1.29473
C	-8.30691	9.17350	4.21541
H	-8.66612	10.05122	4.46167
H	-7.68148	8.86796	4.89934
H	-7.83971	9.24572	3.35190
C	-3.08863	7.94580	2.63463
H	-4.06044	7.94765	2.76260
H	-2.64602	7.77173	3.48847
H	-2.80318	8.81796	2.28837

Atoms and radius in the parameter file

Atoms and radius in the parameter file

H	1.29
C2	1.99
C3	1.99
C	1.99
N2	1.81
N3	1.81
N	1.81
O	1.78
F	1.72
Si	2.45
P	2.11
S	2.10
Cl	2.05
Br	2.16

Coordinates scaled to put the metal at the origin

Coordinates scaled to put the metal at the origin

C	0.49430	-1.18281	-1.66332
N	-0.38878	-2.05683	-1.18801
C	-1.30928	-2.25497	-0.08577
H	-0.85598	-2.15868	0.79925
C	-2.58150	-1.51427	-0.12878
C	-2.77929	-0.11621	-0.08362
C	-4.10925	0.33191	-0.07609
H	-4.24930	1.26333	0.04757

```
C       -5.22111  -0.44582  -0.24600
H       -6.08281  -0.05325  -0.30945
C       -5.06609  -1.77352  -0.31482
H       -5.82622  -2.33830  -0.39978
C       -3.73934  -2.34941  -0.25890
C       -3.22938  -3.78080  -0.16105
H       -3.43678  -4.15485   0.73258
H       -3.66878  -4.34558  -0.84497
C       -1.69736  -3.77154  -0.38687
H       -1.20664  -4.42890   0.18522
O       -1.49102  -3.96227  -1.74505
C       -0.61650  -3.02899  -2.12465
C        0.14577  -2.74938  -3.19033
O        0.52209  -3.22713  -4.35602
C        1.31536  -2.24571  -5.04426
H        0.74874  -1.75315  -5.70453
C        2.44220  -2.85678  -5.72173
H        2.26366  -3.79931  -5.95939
H        2.70947  -2.34941  -6.52503
C        3.47708  -2.73827  -4.60228
C        4.69800  -3.39749  -4.52808
H        4.92571  -4.04745  -5.18513
C        5.58749  -3.10491  -3.50649
H        6.42139  -3.55674  -3.45487
C        5.25607  -2.15312  -2.54942
H        5.86225  -1.95499  -1.84398
C        4.03302  -1.49390  -2.61717
C        3.14566  -1.78648  -3.64521
C        1.74087  -1.33465  -3.96890
H        1.69596  -0.37175  -4.23666
N        0.86207  -1.64945  -2.86773
C       -1.59366   0.91891   0.05295
H       -1.95287   1.79663   0.29921
H       -0.96823   0.61337   0.73688
H       -1.12646   0.99113  -0.81056
C        3.62462  -0.30879  -1.52783
H        2.65281  -0.30694  -1.39986
H        4.06723  -0.48286  -0.67399
H        3.91007   0.56337  -1.87409
XX       0.00000   0.00000   0.00000
```

Results : Volumes in Angs^3

```
  Results : Volumes in Angs^3

       N of voxels examined :         1436277
       Volume of voxel      :       0.125E-03

    V Free   V Buried  V Total   V Exact
    89.578    89.957   179.535   179.594

  %V_Free    %V_Bur  % Tot/Ex
  49.895     50.105    99.967
```

The %V_Bur of your molecule is: 50.1

This journal is © The Royal Society of Chemistry 2011

Imidazolium salt 17b :

SambVca @ MoLNaC
Results page

```
-----------------------------------------------------
|                                                   |
|                  S A M B V C A                    |
|                                                   |
|              Buried Volume in Salerno             |
|                                                   |
|   http://www.molnac.unisa.it/OM-tools/SambVca     |
|                                                   |
|    L. Cavallo et al. email: lcavallo@unisa.it     |
|                                                   |
-----------------------------------------------------
```

Molecule from input :

```
  Molecule from input :


     Number of atoms             :   61
     Atom that is coordinated    :    1
     Atoms that define the axis  :    2
     ID of these atoms           :    2  25

     Radius of sphere (Angs)     :    3.500
     Distance from sphere (Angs) :    2.100
     Mesh step (Angs)            :    0.050
     H atoms omitted in the V_bur calculation
```

Cartesian coordinates from input :

```
  Cartesian coordinates from input :
C       -3.01937  13.82675   8.34623
N       -3.65629  12.76576   7.85867
C       -3.68812  11.29442   8.02535
H       -2.77812  10.88466   8.09300
```

This journal is © The Royal Society of Chemistry 2011

C	-4.63846	10.83592	9.12847
C	-4.63576	11.15262	10.48499
C	-5.69547	10.64799	11.24486
H	-5.73751	10.85859	12.17072
C	-6.68389	9.85135	10.69469
H	-7.38543	9.52283	11.24451
C	-6.65940	9.53125	9.35412
H	-7.34434	8.99333	8.97237
C	-5.62049	10.00619	8.57535
C	-5.38930	9.78155	7.09880
H	-6.23608	9.84774	6.58922
H	-4.97917	8.89506	6.93091
C	-4.44283	10.89890	6.73249
H	-3.81851	10.63797	5.99603
O	-5.24876	12.09066	6.38386
C	-4.61276	13.13279	6.93628
C	-4.59018	14.48801	6.89067
O	-5.20531	15.51430	6.29211
C	-4.73254	16.73655	6.96421
H	-5.37875	17.06808	7.65071
C	-4.42884	17.77567	5.91261
H	-4.50744	18.69065	6.28395
H	-5.04030	17.68783	5.13921
C	-3.00603	17.47242	5.51576
C	-2.33089	17.82401	4.36651
H	-2.76199	18.35170	3.70481
C	-1.03436	17.41024	4.17814
H	-0.56226	17.66376	3.39434
C	-0.41549	16.62002	5.13869
H	0.48015	16.33802	4.99698
C	-1.06911	16.23373	6.29627
C	-2.38025	16.66294	6.47925
C	-3.36812	16.33802	7.58116
H	-3.16993	16.81136	8.43989
N	-3.58586	14.88172	7.75217
C	-3.58004	11.97413	11.12848
C	-3.91065	13.03472	11.97923
H	-4.82418	13.25333	12.12562
C	-2.91915	13.77099	12.61127
H	-3.15825	14.49283	13.18017
C	-1.59190	13.46192	12.42221
H	-0.91854	13.96735	12.86103
C	-1.24092	12.41918	11.59487
H	-0.32497	12.20237	11.46652
C	-2.22652	11.68391	10.94497
H	-1.97575	10.97291	10.36688
C	-0.41127	15.26500	7.20842
C	-0.13306	13.97737	6.77134
H	-0.32630	13.72667	5.87462
C	0.42895	13.05076	7.64377

This journal is © The Royal Society of Chemistry 2011

```
H        0.61864   12.17028    7.34371
C        0.71207   13.41579    8.95502
H        1.09583   12.78401    9.55168
C        0.43386   14.70543    9.39211
H        0.62709   14.95413   10.28883
C       -0.12732   15.63003    8.51967
H       -0.31785   16.51252    8.81974
```

Atoms and radius in the parameter file

```
  Atoms and radius in the parameter file
H     1.29
C2    1.99
C3    1.99
C     1.99
N2    1.81
N3    1.81
N     1.81
O     1.78
F     1.72
Si    2.45
P     2.11
S     2.10
Cl    2.05
Br    2.16
```

Coordinates scaled to put the metal at the origin

```
  Coordinates scaled to put the metal at the origin

C       -0.93641    1.32149   -1.33671
N       -1.57333    0.26050   -1.82427
C       -1.60516   -1.21084   -1.65759
H       -0.69516   -1.62060   -1.58994
C       -2.55550   -1.66934   -0.55447
C       -2.55280   -1.35264    0.80205
C       -3.61251   -1.85727    1.56192
H       -3.65455   -1.64667    2.48778
C       -4.60093   -2.65391    1.01175
H       -5.30247   -2.98243    1.56157
C       -4.57644   -2.97401   -0.32882
H       -5.26138   -3.51193   -0.71057
```

This journal is © The Royal Society of Chemistry 2011

C	-3.53753	-2.49907	-1.10759
C	-3.30634	-2.72371	-2.58414
H	-4.15312	-2.65752	-3.09372
H	-2.89621	-3.61020	-2.75203
C	-2.35987	-1.60636	-2.95045
H	-1.73555	-1.86729	-3.68691
O	-3.16580	-0.41460	-3.29908
C	-2.52980	0.62753	-2.74666
C	-2.50722	1.98275	-2.79227
O	-3.12235	3.00904	-3.39083
C	-2.64958	4.23129	-2.71873
H	-3.29579	4.56282	-2.03223
C	-2.34588	5.27041	-3.77033
H	-2.42448	6.18539	-3.39899
H	-2.95734	5.18257	-4.54373
C	-0.92307	4.96716	-4.16718
C	-0.24793	5.31875	-5.31643
H	-0.67903	5.84644	-5.97813
C	1.04860	4.90498	-5.50480
H	1.52070	5.15850	-6.28860
C	1.66747	4.11476	-4.54425
H	2.56311	3.83276	-4.68596
C	1.01385	3.72847	-3.38667
C	-0.29729	4.15768	-3.20369
C	-1.28516	3.83276	-2.10178
H	-1.08697	4.30610	-1.24305
N	-1.50290	2.37646	-1.93077
C	-1.49708	-0.53113	1.44554
C	-1.82769	0.52946	2.29629
H	-2.74122	0.74807	2.44268
C	-0.83619	1.26573	2.92833
H	-1.07529	1.98757	3.49723
C	0.49106	0.95666	2.73927
H	1.16442	1.46209	3.17809
C	0.84204	-0.08608	1.91193
H	1.75799	-0.30289	1.78358
C	-0.14356	-0.82135	1.26203
H	0.10721	-1.53235	0.68394
C	1.67169	2.75974	-2.47452
C	1.94990	1.47211	-2.91160
H	1.75666	1.22141	-3.80832
C	2.51191	0.54550	-2.03917
H	2.70160	-0.33498	-2.33923
C	2.79503	0.91053	-0.72792
H	3.17879	0.27875	-0.13126
C	2.51682	2.20017	-0.29083
H	2.71005	2.44887	0.60589
C	1.95564	3.12477	-1.16327
H	1.76511	4.00726	-0.86320
XX	0.00000	0.00000	0.00000

This journal is © The Royal Society of Chemistry 2011

Results : Volumes in Angs^3

```
 Results : Volumes in Angs^3

      N of voxels examined :         1436277
      Volume of voxel      :       0.125E-03

   V Free   V Buried  V Total   V Exact
   34.989   144.546   179.535   179.594

 %V_Free    %V_Bur  % Tot/Ex
 19.489     80.511    99.967
```

The %V_Bur of your molecule is: 80.5