Electronic Supplementary Information

Diastereoselective α-C-H Functionalization of Aliphatic *N*-heterocycles: An Efficient Route to Ring Fused Oxazines

Sujit Mahato, Surajit Haldar, and Chandan K. Jana*
Department of Chemistry, Indian Institute of Technology Guwahati, 781039-Guwahati, Assam, India
E-mail: ckjana@iitg.ernet.in

Experimental Section:

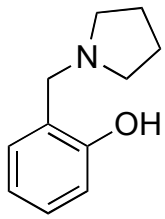
General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. THF and Diethylether (Et_2O) were freshly distilled from Sodium under argon. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus(V)oxide (P_2O_5).Triethylamine (Et_3N) was distilled from CaH_2 and stored under argon. Commercial grade xylene, benzene and toluene were distilled before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^1H, ^{13}C NMR spectroscopy: *Varian Mercury plus 400 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS (δ (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^1H) 7.26 ppm, δ (^{13}C) 77.0 ppm; CD_3OD, (^1H) 3.31 ppm, δ (^{13}C) 49.0 ppm) were used for calibration. Column chromatography: Merck or Spectrochemsilica gel 60-120 under gravity. IR: spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on a Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m/z* (% of basis peak).

X−ray crystallographic data were collected using a Bruker SMART APEX−II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo−Kα radiation (l = 0.71073 Å) at 296(2) K, with increasing w (width of 0.3° per frame) at a scan speed of 3 s/frame. Structures were solved by direct methods using SHELXS−97 and refined with fullmatrix least squares on F^2 using SHELXL−97. Using Olex2[1], structure was solved with

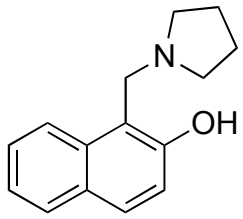
the Superflip[2] structure solution program using Charge Flipping and refined with the olex2.refine[3] refinement package using Gauss–Newton minimisation. All then non–hydrogen atoms were refined anisotropically.

Experimental procedure:

2-((pyrrolidin-1-yl)methyl)phenol (4): Pyrolidine (0.34 mL, 4.09 mmol) was added to a solution of salisaldehyde (0.43 mL, 4.09 mmol) in 2 mL of ethanol and the reaction mixture was stirred at room temperature for 2.5 h. Then $NaBH_4$ (0.15 g, 4.09 mmol) was added and the reaction mixture was stirred for another 16 h at that temperature. The reaction was then quenched with aquoueus 1M HCl (100 μL) solution and the organic solvents were removed under vacuum. Then the mixture was diluted with brine and extracted with ethylacetate (3 X 20 mL). The combined organic layers were dried (Na_2SO_4), concetrated in vaccua and the crude product was subjected to SiO_2-column chromatography (hexane:ethyl acetate, 6:1) to afford **4**[4] as brown oil (0.32 g, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.66 (br. s, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 2H), 2.60 (s, 4H), 1.82 – 1.81 (m, 4H).



1-((pyrrolidin-1-yl)methyl)naphthalen-2-ol (5): Paraformaldehyde (0.16 g, 4.99 mmol) was heated at 70 ^{0}C in benzene (4 mL) for 1 h with stirring. Then mixture was cooled to room temperature and pyrrolidine (0.41 mL, 4.99 mmol), 2-napthol (0.60 g, 4.16 mmol) were added to the mixture. Then the mixture was refluxed for 18 h. Then the reaction mixture was cooled and the product crystalyzed as a brown solid on long standing (4 days) at room temperature. Then the solid was washed with a mixture of hexane & ethyl acetate (15:1, 3 X 15 mL) to get amino alchol **5**[5] as light brown solid (0.82 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.6 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.27 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.29 (s, 2H), 2.74 (br. s, 4H), 1.93 – 1.88 (m, 4H) (-OH proton was not detected).

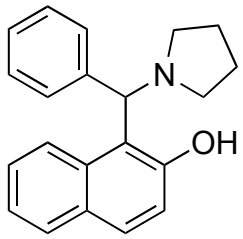


General procedure for the syntheses of Betti base (GP1):

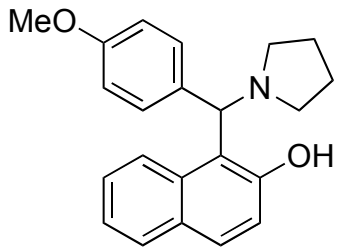
2-naphthol or phenol was added to a solution of seceondary amine and aldehyde in benzene and the mixture was refluxed for 16 h. After the disappreance of the starting material

indicated from TLC, the solvent was removed under reduced pressure and the crude product was subjected to silica gel chromatography or crystalization to afford the amino naphthol/phenol derivatives.

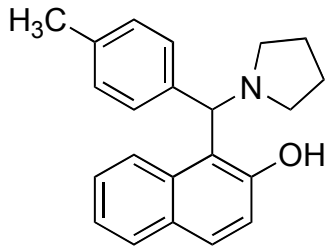
1-(phenyl(pirrolidine-1-yl)methyl)naphthalen-2-ol (7): According to GP1: 2-napthol (1.00 g, 6.94 mmol), benzaldehyde (0.85 mL, 8.33 mmol), pyrrolidine (0.85 mL, 10.41 mmol) in benzene 10 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **7**[6] as light yellow solid (1.26 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.6 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.39 – 7.35 (m, 1H), 7.28 – 7.17 (m, 4H), 7.15 (d, *J* = 9.2 Hz, 1H), 5.13 (s, 1H), 3.29 (br. s, 1H), 2.65 (br. s, 1H), 2.25 (br. s, 1H), 1.85 (br.s, 5H) (-OH proton was not detected).



1-((4-methoxyphenyl)(pyrrolidine-1-yl)methyl)naphthalen-2-ol (9a): According to GP1: 2-napthol (0.20 g, 1.39 mmol), p-methoxy benzaldehyde (0.20 mL, 1.66 mmol), pyrrolidine (0.17 mL, 2.08 mmol) in benzene 2 mL for 20 h, and gave SiO_2 column chromatography (hexane :ethyl acetate, 20:1) **9a**[7] as light orange solid (280 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.22 – 7.19 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.08 (s, 1H), 3.71 (s, 3H), 3.21 (br. s, 1H), 2.66 (br. s, 1H), 2.21 (br.s, 2H), 1.84 (s, 4H) (-OH proton was not detected).



1-((pyrrolidine-1-yl)(*p*-tolyl)methyl)naphthalen-2-ol (9b): According to GP1: 2-napthol (0.40 g, 2.77 mmol), 4-methyl benzaldehyde (0.39 mL, 3.32 mmol) , pyrrolidine (0.27 mL, 3.32 mmol) in benzene 4 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9b**[7] as brownish solid (0.53 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.92 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8 Hz, 2H), 7.35 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.20 (dt, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 9.2 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H) 5.09 (s, 1H), 3.26 – 1.84 (m, 8H), 2.25 (s, 3H).

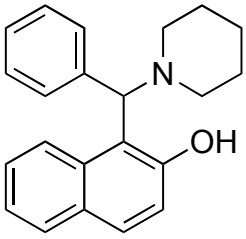


1-((4-chlorophenyl)(pyrrolidine-1-yl)methyl)naphthalen-2-ol (9c): According to GP1: 2-napthol (0.20 g, 1.39 mmol), p-chloro benzaldehyde (0.23 g, 1.66 mmol), pyrrolidine (0.17 mL, 2.08 mmol) in benzene 2 mL for 20 h, and gave SiO_2 column chromatography (hexane:ethyl acetate, 40:1) **9c**[7] as colorless solid (0.44 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.74 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.10 (s, 1H), 3.26 – 1.84 (m, 8H).

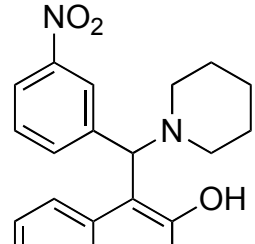
1-((3-nitrophenyl)(pyrrolidin-1-yl)methyl)napthalen-2-ol (9d): According to GP1: 2-napthol (0.40 g, 2.8 mmol), *m*-nitro benzaldehyde (0.50 g , 3.32 mmol), pyrrolidine (0.27 mL, 3.32 mmol) in benzene 4 mL for 20 h, and crystallization gave **9d** as yellow solid (0.40 g, 42%). FTIR (KBr): $\tilde{\nu}$ = 3449, 3086, 2969, 2816, 1621, 1599, 1533, 1468, 1455, 1415, 147, 1313, 1237, 1104, 954, 908, 867, 830, 822, 814, 752, 737, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.49 (s, 1H), 8.46 (s, 1H), 8.08 – 8.06 (m, 1H), 8.00 – 7.98 (m, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.71 (t, *J* = 8.7 Hz, 2H), 7.45 –7.40 (m, 2H), 7.28 – 7.24 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 5.25 (s, 1H), 3.40 – 1.64 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.6, 148.3, 143.5, 134.6, 131.6, 130.2, 130.0, 129.2, 128.7, 126.9, 123.4, 123.0, 122.8, 120.6, 120.1, 115.6, 69.9, 53.6 (br.), 23.5. HRMS (ESI) exact mass calculated for $C_{21}H_{21}N_2O_3$ ($[M + H]^+$): 349.1547, found: 349.1551

1-((pyridine-2-yl)(pyrrolidin-1-yl)methyl)naphthalen-2-ol (9e): According to GP1: 2-napthol (1.00 g, 6.94 mmol), 2-pyridine carboxaldehyde (0.79 mL , 8.33 mmol), pyrrolidine (0.85 mL, 10.41 mmol) in benzene 6 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 15:1) gave **9e** as white solid (1.72 g, 81 %). FTIR (KBr): $\tilde{\nu}$ = 3430, 2971, 2834, 2816, 1622, 1600, 1586, 1519, 1469, 1433, 1353, 1311, 1272, 1146, 1121, 953, 826, 778, 752 719, 629 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.73 (s, 1H), 8.48 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.43 (td, *J* = 7.8, 1.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.21 – 7.16 (m, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.00 – 6.97 (m, 1H), 5.41 (s, 1H), 2.86 – 2.72 (m, 2H), 2.47 – 2.34 (m, 2H), 1.84 – 1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8, 155.7, 148.5, 137.1, 132.2, 129.7, 128.6, 128.9, 126.3, 122.8, 122.7, 122.5, 121.8, 119.9, 115.6, 72.6, 53.1, 23.4. HRMS (ESI) exact mass calculated for $C_{20}H_{21}N_2O$ ($[M + H]^+$): 305.1648, found: 305.1659.

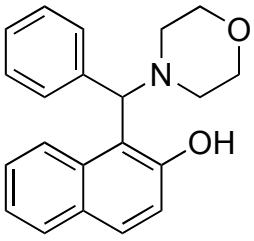
1-(phenyl(piperidine-1-yl)methyl)naphthalen-2-ol (9f): According to GP1: 2-napthol (0.20 g, 1.40 mmol), benzaldehyde (0.14 mL, 1.40 mmol), piperidine (0.14 mL, 1.40 mmol) in benzene 2 mL for 16 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9f**[6] as white solid (0.31 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.6 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.37 – 7.33 (m, 1H), 7.27 – 7.17 (m, 4H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.08 (s, 1H), 3.32 – 1.58 (m, 10H) (-OH proton was not detected).



1-((3-nitrophenyl)(piperidine-1-yl)methyl)naphthalen-2-ol (9g): According to GP1: 2-napthol (0.30 g, 2.08 mmol), m-nitro benzaldehyde (0.38 g, 2.50 mmol), piperidine (0.246 mL, 2.50 mmol) in benzene 3 mL for 16 h, and crystallization gave **9g** as yellow solid (0.75 g, 99%). FTIR (KBr): $\tilde{\nu}$ = 3422, 3091, 2954, 2850, 2807, 1620, 1597, 1533, 1474, 1449, 1343, 1271, 1237, 1155, 1084, 1069, 830, 816, 749, 734, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.60 (s, 1H), 8.40 (s, 1H), 8.07 – 8.04 (m, 1H), 7.98 – 7.89 (m, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.46 – 7.38 (m, 2H), 7.28 – 7.22 (m, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 5.19 (s, 1H), 3.52 – 1.11 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.6, 148.4, 142.1, 135.0, 132.1, 130.1, 129.1, 128.7, 126.9, 123.9, 123.03, 123.0, 122.8, 120.5, 120.2, 115.2, 71.2, 54.6, 52.6, 26.0, 24.0 (restricted inversion of amine leading to 1 carbon more in count). HRMS (ESI) exact mass calculated for $C_{22}H_{23}N_2O_3$ ($[M + H]^+$): 363.1703, found: 363.1685.



1-((morpholino(phenyl)methyl)naphthalen-2-ol (9h): According to GP1: 2-napthol (0.20 g, 1.39 mmol), benzaldehyde (0.17 mL, 1.66 mmol), morpholine (0.14 mL, 1.66 mmol) in benzene 2 mL for 14 h, and crystallization gave **9h**[8] as colorless crystal (0.41 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.12 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.56 – 7.55 (m, 2H), 7.39 – 7.34 (m, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.17 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 5.10 (s, 1H), 3.79 – 3.65 (m, 4H), 3.08 (br. s, 1H), 2.41 – 2.25 (m, 3H).



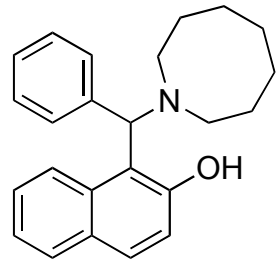
1-(morpholino(3-nitrophynyl)methyl)naphthalen-2-ol (9i): According to GP1: 2-napthol (0.50 g, 3.47 mmol), *m*-nitro benzaldehyde (0.63 mg, 4.16 mmol), morpholine (0.36 mL, 4.16 mmol) in benzene 6 mL for 16 h, and SiO_2 column chromatography (hexane:ethyl acetate, 6:1) gave **9i** as yellow foam (1.08 g, 85%). FTIR (KBr): $\tilde{\nu}$ = 3425, 3070, 2959, 2850, 1621, 1599, 1530, 1466, 1449, 1349, 1272, 1234, 1118, 947, 873, 829, 815, 747, 734, 688 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 12.85 (s, 1H), 8.46 (s, 1H), 8.02 – 8.00 (m, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.67 – 7.65 (m, 2H), 7.341 –7.35 (m, 2H), 7.23 –7.19 (m, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 5.24 (s, 1H), 3.87 – 2.39 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.8, 148.5, 141.0, 135.0, 132.0, 130.5, 130.2, 129.2, 128.9, 127.1, 124.0, 123.3, 123.0, 120.5, 120.0, 114.1, 71.0, 66.7, 52.0 (br.). HRMS (ESI) exact mass calculated for $C_{21}H_{21}N_2O_4$ ($[M + H]^+$): 365.1496, found: 365.1485.

1-((4-methylpiperazin-1-yl)(3-nitrophenyl)methyl)naphthalen-2-ol (9j): According to GP1: 2-napthol (1.00 g, 6.94 mmol), m-nitro benzaldehyde (1.25 g, 8.32 mmol), N-methyl piperizine (0.92 mL, 8.32 mmol) in benzene 8 mL for 16 h, and SiO_2 column chromatography (dichloromethane:methanol, 50:1) gave **9j** as yellow solid (2.58 g, 98%). FTIR (KBr): $\tilde{\nu}$ = 3453, 2939, 2850, 2809, 1623, 1600, 1529, 1465, 1413, 1347, 1291, 1235, 1155, 1137, 1102, 1087, 949, 812, 735, 690, 666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 13.03 (s, 1H), 8.44 (s, 1H), 8.08 – 8.00 (m, 1H), 7.98 – 7.90 (m, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.69 –7.66 (m, 2H), 7.42 – 7.37 (m, 2H), 7.25 – 7.21 (m, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 5.24 (s, 1H), 3.32 – 2.32 (m, 8H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 148.4, 141.6, 135.0, 132.0, 130.3, 130.1, 129.1, 128.8, 127.0, 123.9, 123.2, 122.9, 120.5, 120.0, 114.6, 70.6, 54.9, 53.4, 51.4, 45.7 (restricted inversion of amine leading to 1 carbon more in count). HRMS (ESI) exact mass calculated for $C_{22}H_{24}N_3O_3$ ($[M + H]^+$): 378.1812, found: 378.1813.

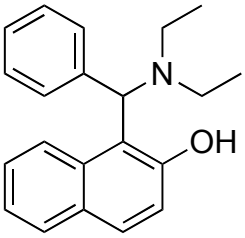
1-((azepan-1-yl)(phenyl)methyl)naphthalen-2-ol (9k): According to GP1: 2-napthol (0.20 g, 1.39 mmol), benzaldehyde (0.17 mL, 1.66 mmol), hexamethyleneimine (0.19 mL, 1.66 mmol) in benzene 2 ml for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9k**[6] as colorless solid (0.16 g, 35%). ^1H NMR (400 MHz, $CDCl_3$) δ =

7.78 (d, J = 8.6 Hz, 1H), 7.58 – 7.51 (m, 4H), 7.28 – 7.25 (m, 1H), 7.15 – 7.10 (m, 3H), 7.07 – 7.03 (m, 2H), 5.19 (s, 1H), 2.67 – 2.42 (m, 4H), 1.72 – 1.40 (m, 8H) (-OH proton was not detected).

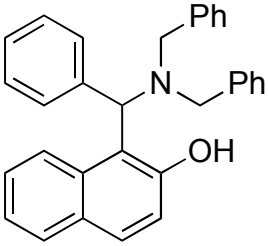
1-((azocan-1-yl)(phenyl)methyl)naphthalen-2-ol (9l): According to GP1: 2-napthol (0.20 g, 1.39 mmol), benzaldehyde (0.17 mL, 1.66 mmol), heptamethyleneimine (0.21 mL, 1.66 mmol) in benzene 2 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9l** as yellow oil (85 mg, 18%). TLC: R_f = 0.5 (hexane:ethyl acetate, 20:1). FTIR (KBr): $\tilde{\nu}$ = 3453, 2923, 2851, 1621, 1600, 1519, 1453, 1415, 1267, 1237, 1157, 1111, 958, 815, 743, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 14.09, (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.64 – 7.61 (m, 4H), 7.36 (t, J = 8.4 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.17 – 7.13 (m, 3H), 5.26 (s, 1H), 2.73 (br. s, 4H), 1.65 – 1.59 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.3, 140.9, 132.2, 129.5, 129.1, 129.1, 128.8, 128.7, 127.9, 126.5, 122.4, 121.0, 120.1, 117.3, 69.8, 53.0, 27.0, 26.8, 25.4. HRMS (ESI) exact mass calculated for $C_{24}H_{28}NO$ ($[M + H]^+$): 346.2165, found: 346.2162.



1-((diethylamino)(phenyl)methyl)naphthalen-2-ol (9m): According to GP1: 2-napthol (0.35 g, 2.43 mmol), benzaldehyde (0.29 mL, 2.91 mmol), diethyl amine (0.30 mL, 2.91 mmol) in benzene 3 mL for 32 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9m**[8] as yellowish solid (0.49 g, 66%). ^1H NMR (400 MHz, $CDCl_3$) δ = 14.31 (s, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.38 – 7.34 (m, 1H), 7.28 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 7.13 (d, J = 8.9 Hz, 1H), 5.44 (s, 1H), 2.78 – 2.70 (m, 4H), 1.04 (br. s, 6H).

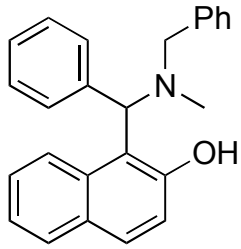


1-((dibenzylamino)(phenyl)methyl)naphthalen-2-ol (9n): According to GP1: 2-napthol (0.20 g, 1.39 mmol), benzaldehyde (0.169 mL, 1.66 mmol), dibenzylamine (0.32 mL, 1.66 mmol) in benzene 2 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9n** as yellow solid (0.25 g, 50%). FTIR (KBr): $\tilde{\nu}$ = 3444, 3060, 3027, 2924, 2851, 1621, 1600, 1584, 1519, 1494, 1467, 452, 1414, 1363, 1266, 1235, 1103, 1082, 1060, 1028, 945, 839, 817, 745, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 13.94 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 8.4 Hz, 1H), 7.53 (s, 2H), 7.40 (t, J = 8.4 Hz, 1H), 7.28 – 7.22 (m, 7H), 7.14 – 7.09 (m, 9H), 5.53 (s, 1H), 3.77 (s, 4H).



^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 139.9, 132.0, 130.0, 129.4, 129.2, 129.1, 128.9, 128.6, 128.1, 127.6, 126.7, 122.7, 121.2, 120.0, 116.1, 67.2, 53.6. (overlap at aromatic region leading less number of carbon in count) HRMS (ESI) exact mass calculated for $C_{31}H_{28}NO$ ($[M + H]^+$): 430.2165, found: 430.2171**.**

1-((*N*-benzyl-*N*-methylamino)(phenyl)methyl)naphthalen-2-ol (9o): According to GP1:

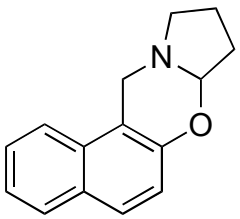


2-napthol (0.20 g, 1.39 mmol), benzaldehyde (0.17 mL, 1.66 mmol), N-methyl benzyl amine (0.32 mL, 1.66 mmol) in benzene 2 mL for 18 h, and SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **9o**[9] as white solid (0.34 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 14.31 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.71 – 7.66 (m, 5H), 7.41 – 7.37 (m, 1H), 7.33 – 7.16 (m, 9H), 5.22 (s, 1H), 3.55 (br. s, 2H), 1.04 (br. s, 3H).

General procedure for the syntheses of Oxazenes (GP2):

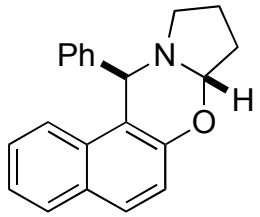
To a solution of Betti base in xylene was added silver oxide and the reaction mixture was refluxed for 24 h. Then the reaction mixture was cooled to room temperature, filtered through a pad of celite and celite cake was washed with ethylacetate. The combined solvents were removed under vacuum and the crude product was subjected to silica gel column chromatography to afford the analytically pure oxazine.

7a,8,9,10-Tetrahydro-11H-7-oxa-10a-aza-cyclopenta[b]phenanthrene (6): According to



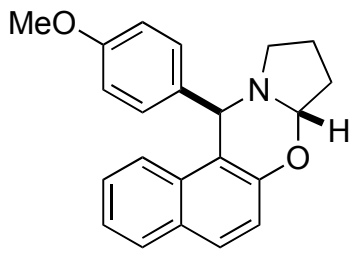
GP2: Betti base **5** (0.25 g, 1.1 mmol), Ag_2O (306 mg, 1.32 mmol) stirred at room temperature for 24 hour in *m*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 10:1) gave **6** as yellow solid (0.16 g, 64 %). FTIR (KBr): $\tilde{\nu}$ = 2979, 2959, 2926, 2838, 1622, 1598, 1513, 1469, 1434, 1397, 1229, 1131, 884, 821, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.54 – 7.50 (m, 1H), 7.42 – 7.38 (m, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 5.25 – 5.08 (m, 1H), 4.64 (d, *J* = 17.1 Hz, 1H), 4.30 (d, *J* = 17.0 Hz, 1H), 3.17 (td, *J* = 8.4, 3.2 Hz, 1H), 3.01 (q, *J* = 8.4 Hz, 1H), 2.28 – 2.19 (m, 2H), 2.16 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.5, 131.7, 129.0, 128.7, 128.0, 126.5, 123.4, 121.2, 119.0, 110.5, 90.2, 50.0, 44.0, 32.1, 21.3. HRMS (ESI) exact mass calculated for $C_{15}H_{16}NO$ ($[M + H]^+$): 226.1226; Found: 226.1221

***rac*-(7aS,11R)-11-Phenyl-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza-cyclopenta**



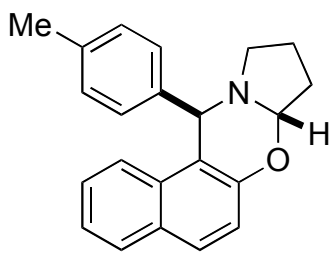
[b]phenanthrene (8): According to GP2: Betti base **7** (0.10 g, 0.33 mmol), Ag_2O (91 mg, 0.39 mmol) reflux for 18 hour in *m*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **8**[6] as brown solid (75 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.7 – 7.74 (m, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.30 – 7.22 (m, 6H), 7.07 (d, *J* = 8.9 Hz, 1H), 5.45 (s, 1H), 5.09 (d, *J* = 3.3 Hz, 1H), 3.36 – 3.31 (m, 1H), 2.92 (q, *J* = 8.3 Hz, 1H), 2.11 – 1.95 (m, 5H).

***rac*-(7aS,11R)-11-(4-Methoxy-phenyl)-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza-**



cyclopenta [b]phenanthrene (10a): According to GP2: Betti base **9a** (0.28 g, 0.84 mmol), Ag_2O (0.23 g, 1.01 mmol) reflux for 18 h in *p*-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40 : 1) gave **10a** as light yellow solid (0.15 g, 55%). FTIR (KBr): $\tilde{\nu}$ = 2956, 2923, 2831, 1653, 1623, 1597, 1511, 1464, 1260,1244, 1234, 1178, 1029, 814, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77–7.73 (m, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.31–7.22 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.40 (s, 1H), 5.09 (d, *J* = 3.4 Hz, 1H), 3.75 (s, 3H), 3.33 – 3.28 (m, 1H), 2.89 (q, *J* = 8.4 Hz, 1H), 2.10 – 1.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.8, 151.8, 135.8, 132.6, 132.3, 129.9, 129.0, 128.6, 126.6, 123.1, 122.8, 118.9, 113.8, 110.7, 86.5, 55.8, 55.3, 50.4, 32.1, 21.1. HRMS (ESI) exact mass calculated for $C_{22}H_{22}NO_2$ ($[M + H]^+$): 332.1645; Found: 332.1660

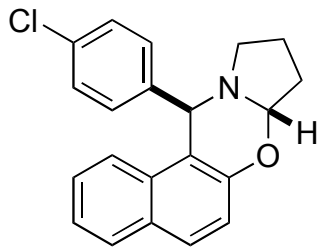
***rac*-(7aS,11R)-11-p-Tolyl-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza-cyclopenta**



[b]phenanthrene (10b): According to GP2: Betti base **9b** (0.20 g, 0.64 mmol), Ag_2O (0.18 g, 0.76 mmol) reflux for 18 h in *p*-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10b** as light yellow solid (0.13 g, 65%). FTIR (KBr): $\tilde{\nu}$ = 2959, 2923, 2836, 1620, 1597, 1510, 1467, 1233, 990, 816, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.69 (m, 2H), 7.27 – 7.25 (m, 2H), 7.14 – 7.12 (m, 2H) 7.07 – 7.05 (m, 4H), 5.41 (s, 1H), 5.09 (d, *J* = 3.2 Hz, 1H), 3.33 – 3.29 (m, 1H), 2.92 – 2.86 (m, 1H), 2.29 (s, 3H), 2.09 – 1.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.8, 140.6, 136.8, 132.6, 129.2, 129.1, 129.0, 128.7, 128.6, 126.5, 123.0, 122.8,

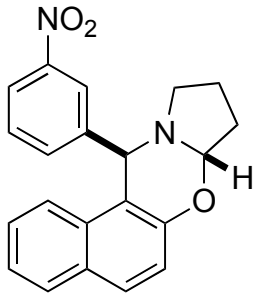
118.9, 110.6, 86.4, 56.1, 50.4, 32.1, 21.2, 21.1. HRMS (ESI) exact mass calculated for $C_{22}H_{22}NO$ ($[M + H]^+$): 316.1696; Found: 316.1680

***rac*-(7aS,11R)-11-(4-Chloro-phenyl)-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza cyclopenta**



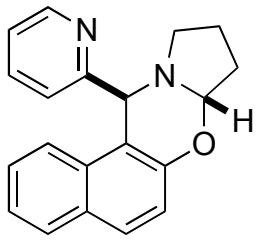
[b]phenanthrene (10c): According to GP2: Betti base **9c** (0.10 g, 0.24 mmol), Ag_2O (82 mg, 0.35 mmol) reflux for 18 hour in *p*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10c** as light yellow solid (70 mg, 70%). FTIR (KBr): $\tilde{\nu}$ = 2961, 2924, 2845, 1654, 1618, 1601, 1261, 1092, 1023, 804 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.75 (m, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 1H), 5.41 (s, 1H), 5.02 (d, *J* = 3.2 Hz, 1H), 3.36 – 3.30 (m, 1H), 2.90 (q, *J* = 8.3 Hz, 1H), 2.17 – 1.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.9, 142.0, 133.1, 132.5, 130.3, 129.3, 129.0, 128.8, 128.6, 126.8, 123.2, 122.6, 119.0, 109.9, 86.4, 55.7, 50.5, 32.2, 21.1. HRMS (ESI) exact mass calculated for $C_{21}H_{19}ClNO$ ($[M + H]^+$): 336.1150; Found: 336.1150.

***rac*-(7aS,11R)-11-(3-Nitro-phenyl)-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza-cyclopenta**



[b]phenanthrene (10d): According to GP2: Betti base **9d** (0.20 g, 0.57 mmol), Ag_2O (0.16 g, 0.69 mmol) reflux for 18 h in *p*-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10d** as brown solid (0.16 g, 82%). FTIR (KBr): $\tilde{\nu}$ = 2694, 2839, 1621, 1596, 1529, 119, 1526, 1464, 1346, 1231, 1069, 890, 816, 808, 678 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 – 7.26 (m, 3H), 7.13 – 7.05 (m, 1H), 5.51 (s, 1H), 4.97 (s, 1H), 3.44 – 3.32 (m, 1H), 3.00 – 2.88 (m, 1H), 2.18 – 1.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 148.7, 145.7, 134.8, 132.3, 129.8, 129.3, 129.1, 128.9, 127.0, 124.0, 123.4, 122.5, 122.2, 119.2, 108.9, 86.3, 55.6, 50.6, 32.2, 21.1. HRMS (ESI) exact mass calculated for $C_{21}H_{19}N_2O_3$ ($[M + H]^+$): 347.1390; Found: 347.1395.

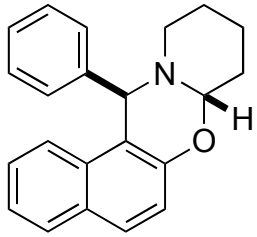
***rac*-(7aS,11S)-11-Pyridin-2-yl-7a,8,9,10-tetrahydro-11H-7-oxa-10a-aza-cyclopenta**



[b]phenanthrene (10e): According to GP2: Betti base **9e** (0.21 g, 0.66 mmol), Ag_2O (0.18 g, 0.79 mmol) reflux for 18 h in *m*-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 10:1) gave **10e** as brown solid (0.13 g, 65%). FTIR (KBr): $\tilde{\nu}$ = 2994, 2961, 2918, 2828,

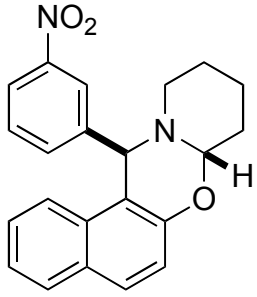
1622, 1598, 1585, 1464, 1434, 1397, 1269, 1240, 1211, 1134, 991, 898, 835, 820, 767, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.72 – 8.70 (m, 1H), 7.75 – 7.71 (m, 2H), 7.50 (td, *J* = 7.7, 1.6 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.29 – 7.24 (m, 2H), 7.17 – 7.14 (m, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.59 (s, 1H), 5.18 (d, *J* = 3.2 Hz, 1H), 3.48 –3.43 (m, 1H), 2.96 (q, *J* = 8.5 Hz, 1H), 2.27 – 1.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 151.9, 150.2, 136.8, 132.4, 129.3, 129.1, 128.7, 126.7, 123.2, 122.8, 122.5, 122.4, 118.9, 109.6, 86.4, 58.9, 50.9, 32.1, 20.8. HRMS (ESI) exact mass calculated for $C_{20}H_{19}N_2O$ ($[M + H]^+$): 303.1492 Found: 303.1494

***rac*-(7aS,12R)-12-Phenyl-8,9,10,11-tetrahydro-7aH,12H-7-oxa-11a-aza-benzo**

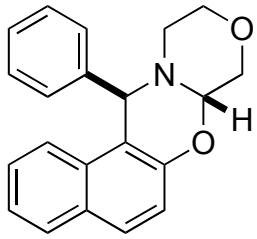


[a]anthracene (10f): According to GP2: Betti base **9f** (0.10 g, 0.31 mmol), Ag_2O (87 mg, 0.38 mmol) reflux for 18 h in *m*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 50:1) gave **10f**[6] as colourlesss solid (0.13 g, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.75 (m, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.29 – 7.20 (m, 7H), 7.12 (d, *J* = 8.9 Hz, 1H), 5.15 (s, 1H), 4.89 (m, 1H), 2.91 – 2.80 (m, 2H), 1.99 – 1.91 (m, 1H), 1.81 – 1.70 (m, 3H), 1.62 – 1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 143.1, 132.4, 129.5, 129.0, 128.6, 128.2, 127.2, 126.5, 123.1, 122.9, 118.8, 111.3, 81.5, 62.9, 48.5, 29.6, 25.5, 18.4 (overlap at aromatic region leading to 1 carbon less in count).

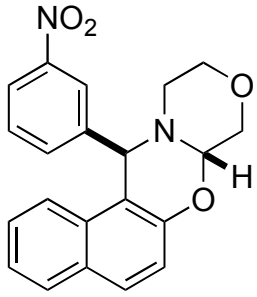
***rac*-(7aS,12R)-12-(3-Nitro-phenyl)-8,9,10,11-tetrahydro-7aH,12H-7-oxa-11a-aza-benzo**



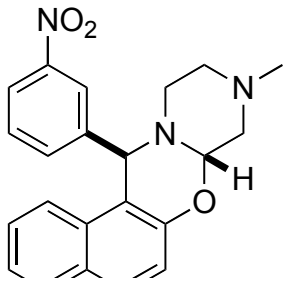
[a]anthracene (10g): According to GP2: Betti base **9g** (0.30 g, 0.82 mmol), Ag_2O (0.23 g, 0.99 mmol) reflux for 18 hour in *m*-xylene 4 mL. SiO_2 column chromatography (hexane:ethyl acetate, 50:1) gave **10g** as yellow solid (0.23 g, 84%). FTIR (KBr): $\tilde{\nu}$ = 2959, 2925, 1619, 1596, 1521, 1529, 1465, 1434, 1403, 1346, 1235, 1205, 11193, 1117, 1102, 1070, 999, 971, 931, 816, 808, 719, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 8.11 – 8.06 (m, 1H), 7.82 – 7.79 (m, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.40 (m, 1H), 7.39 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.14 (d, *J* = 9.0 Hz, 1H), 5.20 (s, 1H), 4.76 (t, *J* = 2.4 Hz, 1H), 2.95 – 2.81 (m, 2H), 2.02 – 1.92 (m, 1H), 1.85 – 1.69 (m, 3H), 1.65 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.5, 148.6, 145.2, 135.5, 132.5, 129.7, 129.1, 129.0, 128.9, 126.9, 124.4, 123.4, 122.4, 122.2, 118.9, 109.7, 81.4, 62.1, 48.5, 29.5, 25.4, 18.2. HRMS (ESI) exact mass calculated for $C_{22}H_{21}N_2O_3$ ($[M + H]^+$): 361.1547; Found: 361.1549.

***rac*-(7aS,12R)-12-Phenyl-7a,8,10,11-tetrahydro-12H-7,9-dioxa-11a-aza-benzo[a]anthracene (10h):** 

According to GP2: Betti base **9h** (0.25 g, 0.79 mmol), Ag_2O (0.22 g, 0.95 mmol) reflux for 18 h in *m*-xylene 4 mL. Neutral alumina column chromatography (hexane:ethyl acetate, 40:1) gave **10h** as white solid (0.11 g, 45%) along with recovered starting material (66 mg, 26%). FTIR (KBr): $\tilde{\nu}$ = 3070, 2918, 2863, 1621, 1597, 1465, 1232, 1134, 1126, 1024, 972, 878, 861, 748, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.71 (m, 2H), 7.40 – 7.18 (m, 9H), 5.19 (s, 1H), 4.69 (s, 1H), 4.04 (d, *J* = 12.1 Hz, 1H), 3.95 (dd, *J* = 11.1, 3.1 Hz, 1H), 3.85 (td, *J* = 11.3, 2.5 Hz, 1H), 3.60 (dd, *J* = 12.1, 1.3 Hz, 1H), 3.17 (td, *J* = 11.4, 3.5 Hz, 1H), 2.74 (d, *J* = 11.3 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 151.9, 142.1, 132.3, 129.9, 129.8, 129.7, 128.8, 128.8, 127.6, 126.8, 123.5, 122.8, 119.0, 110.5, 79.8, 68.0, 66.0, 62.1, 46.6. HRMS (ESI) exact mass calculated for $C_{21}H_{20}NO_2$ ($[M + H]^+$): 318.1489; Found: 318.1492

***rac*-(7aS,12R)-12-(3-Nitro-phenyl)-7a,8,10,11-tetrahydro-12H-7,9-dioxa-11a-aza-benzo [a]anthracene (10i):** 

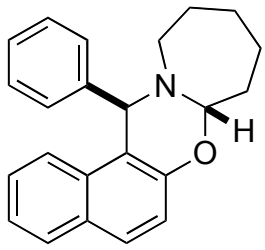
According to GP2: Betti base **9i** (0.20 g, 0.55 mmol), Ag_2O (0.15 g, 0.66 mmol) reflux for 24 h in *m*-xylene 2 mL. Neutral alumina column chromatography (hexane:ethyl acetate, 10:1) gave **10i** as yellow solid (0.11 g, 55%). FTIR (KBr): $\tilde{\nu}$ = 2975, 2904, 2850, 1624, 1599, 1530, 1519, 1470, 1438, 1348, 1324, 1276, 1259, 1238, 1216, 1166, 1133, 1094, 1057, 977, 943, 879, 858, 814, 750, 738, 715, 686, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H) , 8.11 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.793 (m, 2H), 7.42 – 7.37 (m, 2H), 7.33 – 7.21 (m, 4H), 5.25 (s, 1H), 4.57 (s, 1H), 4.06 (d, *J* = 12.8 Hz, 1H), 3.98 (d, *J* = 10.0 Hz, 1H), 3.88 (t, *J* = 11.6 Hz, 1H), 3.61 (d, *J* = 12.4 Hz, 1H), 3.21 (dt, *J* = 3.2, *J* = 11.2 Hz, 1H), 2.80 (d, *J* =11.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 152.0, 148.7, 144.3, 135.5, 132.2, 130.1, 129.3, 129.1, 127.1, 124.4, 123.7, 122.8, 122.1, 119.1, 109,1, 79.4, 68.5, 66.7, 61.6, 47.6. (overlap at 129 leading to 1 carbon less in count). HRMS (ESI) exact mass calculated for $C_{21}H_{19}N_2O_4$ ($[M + H]^+$): 363.1339; Found: 363.1339.

***rac*-(7aS,12R)-9-Methyl-12-(3-nitro-phenyl)-8,9,10,11-tetrahydro-7aH,12H-7-oxa-9,11a-diaza-benzo [a]anthracene (10j):** 

According to GP2: Betti base **9j** (66 mg, 0.17 mmol), Ag_2O (55 mg, 0.19 mmol) heated under 100

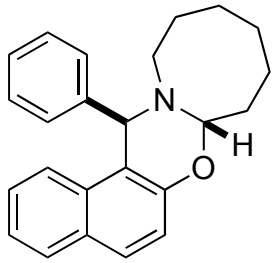
^{0}C for 24 h in *m*-xylene 2 mL. SiO_2 column chromatography (methanol: dichloromethane, 1:100) gave **10j** as yellow solid (38 mg, 58%). FTIR (KBr): $\tilde{\nu}$ = 2929, 1623, 1529, 1237, 1212, 1159, 1078, 814 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 8.13 – 8.08 (m, 1H), 7.82 – 7.78 (m, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 2H), 5.28 (s, 1H), 4.70 (m, 1H), 3.25 – 3.19 (m, 1H), 3.14 – 3.12 (m, 1H), 2.95 – 2.89 (m, 2H), 2.48 – 2.42 (m, 1H), 2.36 (s, 3H), 2.20 (dd, *J* = 12.0, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.3, 148.6, 144.8, 135.4, 132.1, 129.7, 129.2, 129.1, 128.9, 126.9, 124.3, 123.5, 122.6, 122.2, 119.4, 109.3, 79.9, 61.2, 57.5, 54.6, 47.9, 46.1. HRMS (ESI) exact mass calculated for $C_{22}H_{22}N_3O_3$ ([M + H]$^+$): 376.1656; Found: 376.1672.

***rac*-(7aS,13R)-13-Phenyl-7a,8,9,10,11,12-hexahydro-13H-7-oxa-12a-aza-cyclohepta**

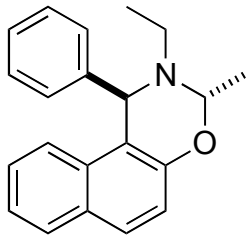


[b]phenanthrene (10k): According to GP2: Betti base **9k** (0.50 g, 1.51 mmol), Ag_2O (0.42 g, 1.81 mmol) reflux for 24 h in *m*-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10K**[6] as colorless solid (0.39 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.62 (m, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.25 – 7.05 (m, 8H), 7.00 (d, *J* = 8.9 Hz, 1H), 5.18 (s, 1H), 4.76 (t, *J* = 7.1 Hz, 1H), 3.20 – 3.04 (m, 1H), 2.62 – 2.49 (m, 1H), 2.12 – 2.05 (m, 1H), 1.81 – 1.50 (m, 5H), 1.42 – 1.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 143.1, 132.5, 129.2, 128.9, 128.4, 127.9, 127.0, 126.4, 122.8, 122.6, 118.9, 112.6, 85.2, 64.6, 49.7, 33.9, 30.5, 30.2, 21.8 (overlap at aromatic region leading to 1 carbon less in count). HRMS (ESI) exact mass calculated for $C_{23}H_{24}NO$ ([M + H]$^+$): 330.1852; Found: 330.1853.

***rac*-Oxazene 10l:** According to GP2: Betti base **9l** (74 mg, 0.21 mmol), Ag_2O (69 mg, 0.26 mmol) reflux for 24 h in *m*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10l** as light yellow solid (53 mg, 72%). FTIR (KBr): $\tilde{\nu}$ = 2963, 2923, 1621, 1596, 1468, 1446, 1404, 1261, 1095, 1920, 1020, 800 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 – 7.65 (m, 1H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.26 – 7.12 (m, 8H), 7.01 (d, *J* = 8.9 Hz, 1H), 5.20 (s, 1H), 4.62 – 4.58 (m, 1H), 3.20 – 3.13 (m, 1H), 2.54 – 2.43 (m, 1H), 1.97 – 1.72 (m, 5H), 1.55 – 1.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.7, 143.1, 133.0, 129.6, 129.0, 128.6, 128.2, 127.2, 126.6, 123.1, 122.9, 119.2, 112.6, 86.0, 63.7, 47.0, 30.2, 29.9, 26.4, 25.5, 23.9 (overlap at aromatic region leading to 1 carbon less in count). HRMS (ESI) exact mass calculated for $C_{24}H_{26}NO$ ([M + H]$^+$): 344.2009; Found: 344.2009.

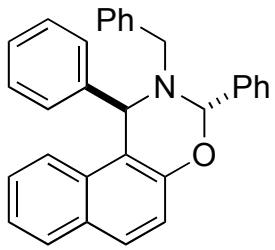


***rac*-(1R,3S)-2-Ethyl-3-methyl-1-phenyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine**



(10m): According to GP2: Betti base **9m** (0.15 g, 0.49 mmol), Ag_2O (0.14 g, 0.59 mmol) stirred in room temperature in *m*-xylene 2 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10m** as brown solid (0.11 g, 73%). FTIR (KBr): $\tilde{\nu}$ = 2964, 2925, 2848, 1651, 1623, 1599, 1513, 1499, 1466, 1449, 1411, 1261, 1236, 1171, 1093, 1051, 1030, 849, 808, 755, 735, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.79 – 7.74 (m, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.27 (m, 8H), 7.09 (d, *J* = 8.9 Hz, 1H), 5.40 (s, 1H), 4.95 (q, *J* = 6.0 Hz, 1H), 3.15 – 3.06 (m, 1H), 2.52 – 2.43 (m, 1H), 1.43 (d, *J* = 6.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 143.4, 133.1, 129.6, 129.1, 128.7, 128.2, 127.2, 126.6, 123.7, 122.9, 118.8, 111.8, 82.6, 59.2, 39.3, 18.8, 15.1 (overlap at aromatic region leading to 1 carbon less in count). HRMS (ESI) exact mass calculated for $C_{21}H_{22}NO$ ($[M + H]^+$): 304.1696; Found: 304.1693.

***rac*-(1R,3S)-2-Benzyl-1,3-diphenyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (10n):**

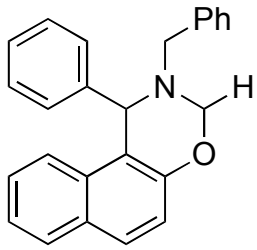


According to GP2: Betti base **9n** (1.10 g, 2.56 mmol), Ag_2O (0.71 mg, 3.07 mmol) reflux 20 h in *m*-xylene 10 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave **10n**[10] as light yellow solid (1.04 g, 95%). FTIR (KBr): $\tilde{\nu}$ = 3022, 2917, 2898, 2881, 2837, 1623, 1597, 1515, 1493, 1466, 1448, 1433, 1396, 1337, 1037, 1233, 1124, 1102, 1066, 1027, 990, 974, 941, 923, 814, 750, 736, 695, cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.81 (m, 1H), 7.70 – 7.68 (m, 1H), 7.43 – 7.20 (m, 19H), 5.99 (s, 1H), 5.39 (s, 1H), 3.90 (d, *J* = 13.9 Hz, 1H), 3.38 (d, *J* = 13.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 143.2, 139.5, 138.2, 133.4, 129.5, 129.4, 129.3, 128.7, 128.5, 128.4, 128.3, 128.1, 127.4, 126.8, 126.6, 123.6, 123.2, 119.0, 112.2, 85.7, 58.1, 49.8 (overlap at aromatic region leading to 2 carbon less in count). HRMS (ESI) exact mass calculated for $C_{31}H_{26}NO$ ($[M + H]^+$): 428.2009; Found: 428.2010.

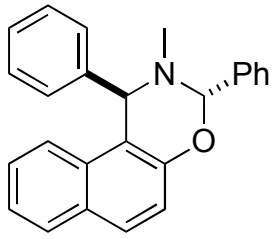
2-Benzyl-1-phenyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (10o) and *rac*-(1R,3S)-2-Methyl-1,3-diphenyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (10p): According to

GP2: Betti base **9o** (0.26 g, 0.73 mmol), Ag_2O (0.20 g, 0.87 mmol) reflux 16 h in m-xylene 3 mL. SiO_2 column chromatography (hexane:ethyl acetate, 40:1) gave diasterioisomeric mixture of **10o** & **10p** as colorless solid (0.19 g, 76%). The isomeric ratio (**10o** : **10p**, 1: 2.6) was determined from 1H-NMR of the crude product. Diasteriosiomers were further purified for analytical purpose.

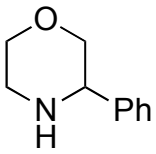
10o: FTIR (KBr): $\tilde{\nu}$ = 3025, 2997, 2983, 2918, 2852, 16222, 1599, 1511, 1492, 1468, 1451, 1435, 1402, 1253, 1242, 1226, 1210, 1179, 1141, 1062, 978, 954, 920, 903, 815, 755, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.80 – 7.74 (m, 2H), 7.47– 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.19 (m, 7H), 7.18 – 7.11 (m, 3H), 5.26 (s, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 4.71 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.12 (d, *J* = 13.3 Hz, 1H), 3.94 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 143.0, 138.7, 133.0, 129.5, 129.4, 129.3, 129.2, 128.7, 128.6, 128.3, 127.7, 127.4, 126.7, 123.4, 122.8, 118.8, 111.8, 77.9, 57.9, 57.0. HRMS (ESI) exact mass calculated for $C_{25}H_{22}NO$ ($[M + H]^+$): 352.1696; Found: 352.1698.



10p: FTIR (KBr): $\tilde{\nu}$ = 3060, 3027, 2885, 2798, 1625, 1597, 1512, 1396, 1333, 1232, 1128, , 989, 942, 923, 810, 751, 705, 670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.78 (m, 2H), 7.54 – 7.52(m, 2H), 7.45 – 7.20 (m, 12H), 5.77 (s, 1H), 5.40 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 152.4, 143.2, 138.1, 133.2, 129.6, 129.3, 128.7, 128.3, 128.2, 128.0, 127.5, 126.7, 126.6, 123.5, 123.1, 119.0, 112.1, 85.4, 63.2, 35.0 (overlap at aromatic region leading to 1 carbon less in count). HRMS (ESI) exact mass calculated for $C_{25}H_{22}NO$ ($[M + H]^+$): 352.1696; Found: 352.1694.



3-Phenylmorpholine (16): Phenylmagnesiumbromide (1 M in THF, 1.89 mL, 1.89 mmol) was added dropwise to a powdered oxazine **10h** (0.20 g, 0.63 mmol) at 0 ^0C under argon atmosphere. Then the mixture was stirred at room temperature for 18 h. Then the reaction was quenched by adding saturated aquoues solution of NH_4Cl. The mixture was extracted (3 X 20 mL) with EtOAc. The combined organic layer were dried (Na_2SO_4) and concentrated in vaccuo. The crude product was solidified over long (3 days) standing and solid was washed with ice cold hexane: ethyl acetate 3:1 (5 X 2 mL) to afford the desired amino naphthol (0.21 g, 85%) as white solid. HRMS (ESI) exact mass calculated for $C_{27}H_{26}NO_2$ ($[M + H]^+$): 396.1958; Found: 396.1968. Amino naphthol (48 mg, 0.12 mmol) was added to a aqueous solution of NaOH (6 M, 0.12

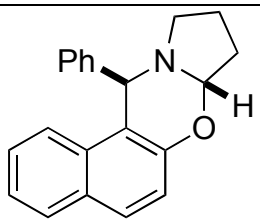


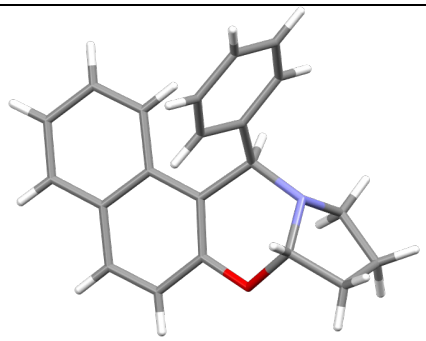
mL) in THF (0.26 mL) and methanol (0.26 mL). Then the temperature was allowed to increase to 80 ^{0}C and the mixture was stirred for 10 h at that temperature. After the disappearance of the starting material indicated from TLC, the reaction mixture was cooled to room temperature, extracted with diethyl ether (3 X 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuum and the crude product was subjected to neutral alumina column chromatography (DCM:MeOH, 500:1) to afford **16** (12 mg, 61%) as colorless oil. FTIR (KBr): $\tilde{\nu}$ = 3283, 2973, 2850, 1603, 1493, 1455, 1442, 1340, 1316, 1300, 1107, 1075, 908, 880, 885, 756, 700, 647, 525 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.28 (m, 5H), 3.94 – 3.81 (m, 3H), 3.66 (td, *J* = 11.3, 2.7 Hz, 1H), 3.40 (dd, *J* = 11.0, 10.2 Hz, 1H), 3.13 (td, *J* = 11.6, 3.3 Hz, 1H), 3.02 – 2.97 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.7, 128.7, 127.9, 127.3, 73.8, 67.4, 60.7, 46.8. HRMS (ESI) exact mass calculated for $C_{10}H_{14}NO$ ($[M + H]^+$): 164.1070; Found: 164.1075.

Procedure for one pot synthesis of oxazines 10d: 2-naphthol (0.20 g, 1.38 mmol) was added to a solution of pyrrolidine (0.11 mL, 1.38 mmol) and 3-nitrobenzadehyde (0.21 g, 1.38 mmol) in xylene and the mixture was stirred under 100 ^{0}C for 24 h. Then the reaction mixture was cooled to room temperature. Silver oxide (0.48 g, 2.07 mmol) was added, the mixture was heated to reflux and stirred for another 24 h at that temperature. Then the reaction mixture was cooled, filtered through a pad of celite and the celite cake was washed with ethylacetate (3 X 10 mL). The combined solvents were removed under vacuum and the crude product was subjected to SiO_2 column chromatography (hexane:EtOAc, 15:1) to afford the oxazine **10d** as yellow solid (0.27 g, 57%). The analytical data is the same as described before.

One pot synthesis of oxazines 10g: One pot functionalization of piperidine followed the same procedure as described for **10d.** 2-napthol (0.20 g, 1.38 mmol), piperidine (0.14 mL, 1.38 mmol), 3-nitrobenzaldehyde (0.21 g, 1.38 mmol), Ag_2O (0.48 g, 2.07 mmol) in 2 mL xylene and SiO_2 column chromatography (hexane: EtOAc, 15:1) gave **10g** as solid (0.24 g, 48%). The analytical data is the same as described before.

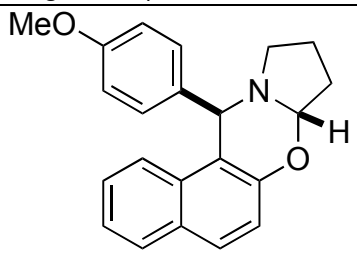
Crystal Structures:

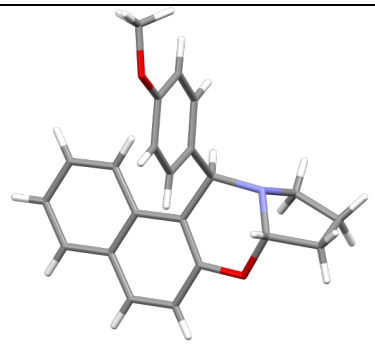




Crystal data and structure refinement for **8**[6]

Empirical formula	$C_{21}H_{19}NO$
Formula weight	301.37
Crystal habit, colour	needle / yellowish
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P2(1)/c'*
Unit cell dimensions	a = 9.7033(6)Å
	b = 6.1115(4)Å
	c = 26.7428(16)Å
	α = 90.00°, γ = 90.00°, β = 97.569(3))°
Volume, V($Å^3$)	1572.08(17)
Z	4
Calculated density, $Mg{\cdot}m^{-3}$	1.273
Absorption coefficient, μ(mm^{-1})	0.078
F(000)	640
θrange for data collection	1.54° to 28.34°
Limiting indices	$-12 \le h \le 12$, $-8 \le k \le 7$, $-35 \le l \le 35$
Reflection collected / unique	23369 / 2056 [*R*(int) = 0.1541]
Completeness to θ	99.6% (θ = 28.34°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	2056 / 0 / 208
Goodness–of–fit on F^2	1.067
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0524, *wR*2 = 0.1054
R indices (all data)	*R*1 = 0.0950, *wR*2 = 0.1129
Largest diff. peak and hole	0.186and –0.217e·$Å^{-3}$

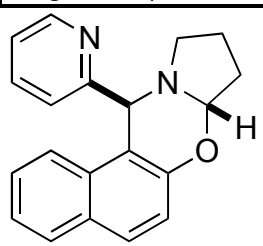


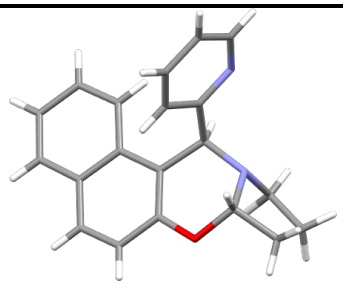


Crystal data and structure refinement for **10a** (CCDC 952462)

Empirical formula	$C_{22}H_{21}NO_2$
Formula weight	331.40
Crystal habit, colour	columer / colorless

Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	triclinic
Space group	*'p-1'*
Unit cell dimensions	*a* = 6.5142(6)Å
	b = 8.4766(7)Å
	c = 32.727(3)Å
	α = 89.968(6)°, γ = 72.066(6)°, β = 89.725(6)°
Volume, *V*($Å^3$)	1719.3(3)
Z	4
Calculated density, $Mg·m^{-3}$	1.280
Absorption coefficient, μ(mm^{-1})	0.082
F(000)	704
θ range for data collection	0.62° to 19.90°
Limiting indices	$-6 \le h \le 6, -7 \le k \le 8, -31 \le l \le 30$
Reflection collected / unique	14886 / 2306 [*R*(int) = 0.1751]
Completeness to θ	98.5% (θ = 19.9°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	2306 / 0 / 453
Goodness–of–fit on F^2	1.149
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0728, *wR*2 = 0.2107
R indices (all data)	*R*1 = 0.0901, *wR*2 = 0.2190
Largest diff. peak and hole	0.243 and $-0.262 e·Å^{-3}$

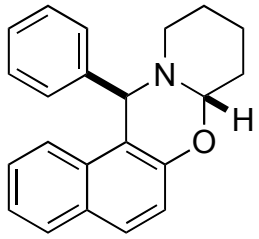


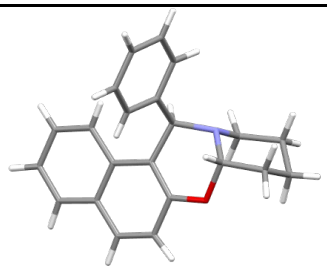


Crystal data and structure refinement for **10e** (CCDC 952463)

Empirical formula	$C_{20} H_{18} N_2 O$
Formula weight	302.36
Crystal habit, colour	needle / colorless
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P* 21/c'
Unit cell dimensions	*a* = 10.5276(5)Å
	b = 8.3530(4)Å
	c = 18.0400(8)Å
	α = 90.00°, γ = 90.00°, β = 101.988(3)°
Volume, *V*($Å^3$)	1551.79(13)
Z	4
Calculated density, $Mg·m^{-3}$	1.294
Absorption coefficient, μ(mm^{-1})	0.081
F(000)	640
θ range for data collection	1.98° to 28.23°
Limiting indices	$-13 \le h \le 13, -8 \le k \le 11, -16 \le l \le 22$
Reflection collected / unique	15036 / 1693 [*R*(int) = 0.0368]

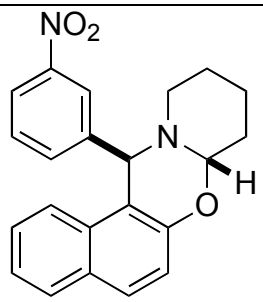
Completeness to θ	90.0% (θ = 28.23°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	1693 / 0 / 208
Goodness–of–fit on F^2	0.975
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0529, *wR*2 = 0.1046
R indices (all data)	*R*1 = 0.1305, *wR*2 = 0.1285
Largest diff. peak and hole	0. 133and –0.174e·Å^{-3}

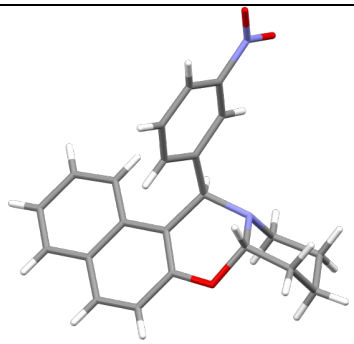




Crystal data and structure refinement for **10f**[6]

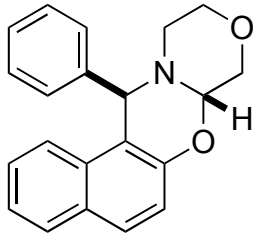
Empirical formula	C_{22} H_{21} N O
Formula weight	315.40
Crystal habit, colour	needle / colorless
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P21/n'*
Unit cell dimensions	*a* = 10.2330(6)Å
	b = 10.1943(6)Å
	c = 16.2308(9)Å
	α = 90.00°, γ = 90.00°, β = 97.754(5)°
Volume, *V*(Å^3)	1677.69(17)
Z	4
Calculated density, Mg·m^{-3}	1.249
Absorption coefficient, μ(mm^{-1})	0.076
F(000)	672
θ range for data collection	2.99° to 25.00°
Limiting indices	$-12 \le h \le 12$, $-12 \le k \le 11$, $-19 \le l \le 18$
Reflection collected / unique	5971 / 1961 [*R*(int) = 0.0366]
Completeness to θ	99.8% (θ = 25.00°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	1961 / 0 / 217
Goodness–of–fit on F^2	1.099
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0525, *wR*2 = 0.1267
R indices (all data)	*R*1 = 0.0814, *wR*2 = 0.1503
Largest diff. peak and hole	0.144and –0.186e·Å^{-3}

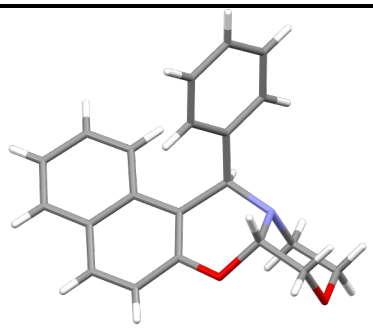




Crystal data and structure refinement for **10g** (CCDC 952465)

Empirical formula	$C_{22}\ H_{20}\ N_2\ O_3$
Formula weight	360.40
Crystal habit, colour	needle / yellow
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	orthorhombic
Space group	*'Pca2(1)'*
Unit cell dimensions	*a* = 8.8679(18)Å
	b = 15.764(3)Å
	c = 13.088(3)Å
	α = 90.00°, γ = 90.00°, β = 90.00°
Volume, *V*($Å^3$)	1829.7(7)
Z	4
Calculated density, $Mg{\cdot}m^{-3}$	1.308
Absorption coefficient, μ(mm^{-1})	0.088
F(000)	760
θ range for data collection	2.58° to 27.59°
Limiting indices	$-11 \le h \le 11, -20 \le k \le 20, -16 \le l \le 16$
Reflection collected / unique	19032 / 2632 [*R*(int) = 0.0680]
Completeness to θ	98.6% (θ = 27.59°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	2632 / 0 / 244
Goodness–of–fit on F^2	1.011
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0456, *wR*2 = 0.0855
R indices (all data)	*R*1 = 0.0825, *wR*2 = 0.1078
Largest diff. peak and hole	0. 282and –0.280·$Å^{-3}$

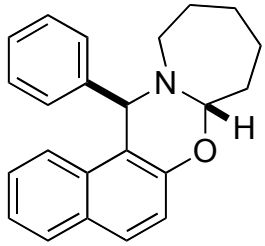


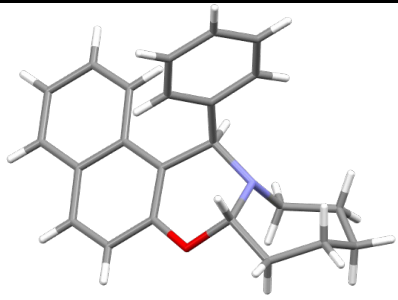


Crystal data and structure refinement for **10h** (CCDC 952460)

Empirical formula	$C_{21}\ H_{19}\ N\ O_2$

Formula weight	317.37
Crystal habit, colour	needle / colorless
Crystal size, mm^3	
Temperature, *T*	293(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P 21/n'*
Unit cell dimensions	*a* = 16.6693(12)Å
	b = 6.1313(3)Å
	c = 17.7664(17)Å
	α = 90.00°, γ = 90.00°, β = 115.984(11)°
Volume, *V*($Å^3$)	1632.3(2)
Z	4
Calculated density, $Mg·m^{-3}$	1.291
Absorption coefficient, μ(mm^{-1})	0.083
F(000)	672
θ range for data collection	3.45° to 25.00°
Limiting indices	$-18 \le h \le 19$, $-6 \le k \le 7$, $-21 \le l \le 10$
Reflection collected / unique	5126 / 1946 [*R*(int) = 0.0485]
Completeness to θ	97% (θ = 25.00°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	1946 / 0 / 217
Goodness–of–fit on F^2	1.091
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0550, *wR*2 = 0.1233
R indices (all data)	*R*1 = 0.0817, *wR*2 = 0.1407
Largest diff. peak and hole	0. 216and –0.211e·$Å^3$

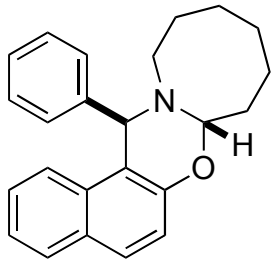


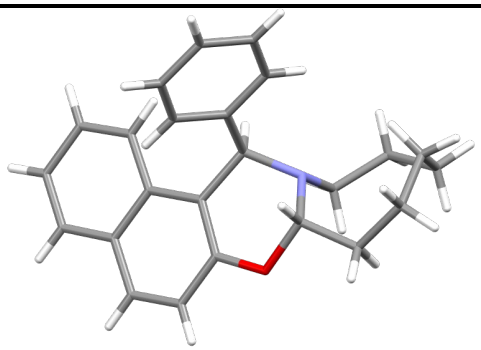


Crystal data and structure refinement for **10k**[6]

Empirical formula	C_{23} H_{23} N O
Formula weight	329.42
Crystal habit, colour	needle / yellowish
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P2(1)/n'*
Unit cell dimensions	*a* = 13.6779(8)Å
	b = 15.7357(9)Å
	c = 17.4244(11)Å
	α = 90.00°, γ = 90.00°, β = 106.959(4)
Volume, *V*($Å^3$)	3587.2(4)
Z	8
Calculated density, $Mg·m^{-3}$	1.220
Absorption coefficient, μ(mm^{-1})	0.074
F(000)	1408
θ range for data collection	1.68° to 21.74°

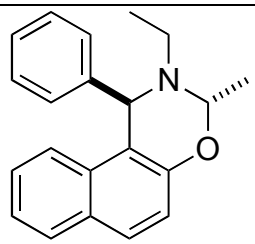
Limiting indices	$-14 \le h \le 14, -16 \le k \le 16, -18 \le l \le 18$
Reflection collected / unique	27568 / 2665 [R(int) = 0.1065]
Completeness to θ	98.4% (θ = 21.74°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	2665 / 0 / 451
Goodness–of–fit on F^2	1.022
Final R indices [I>2sigma(I)]	$R1$ = 0.0598, $wR2$ = 0.1531
R indices (all data)	$R1$ = 0.1037, $wR2$ = 0.1890
Largest diff. peak and hole	0.738and –0.670e·Å^{-3}

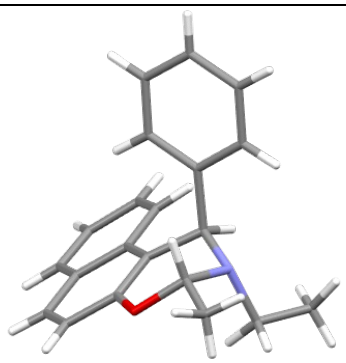




Crystal data and structure refinement for **10l** (CCDC 952458)

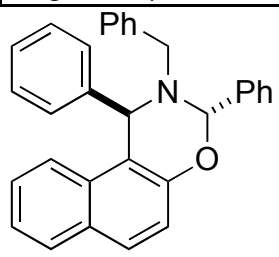
Empirical formula	C_{24} H_{25} N O
Formula weight	343.45
Crystal habit, colour	needle / yellowish
Crystal size, mm^3	
Temperature, T	293(2) K
Wavelength, λ(Å)	0.71073
Crystal system	orthorhombic
Space group	*'Pbca'*
Unit cell dimensions	a = 15.2770(6)Å
	b = 12.2434(5)Å
	c = 20.3925(10)Å
	α = 90.00°, γ = 90.00°, β = 90.00°
Volume, V(Å^3)	3814.3(3)
Z	8
Calculated density, Mg·m^{-3}	1.196
Absorption coefficient, μ(mm^{-1})	0.072
F(000)	1472
θ range for data collection	3.14° to 28.78°
Limiting indices	$-19 \le h \le 20, -11 \le k \le 16, -25 \le l \le 19$
Reflection collected / unique	10757 / 2091 [R(int) = 0.0506]
Completeness to θ	88.2% (θ = 28.78°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	2091 / 0 / 235
Goodness–of–fit on F^2	0.908
Final R indices [I>2sigma(I)]	$R1$ = 0.0708, $wR2$ = 0.2398
R indices (all data)	$R1$ = 0.1561, $wR2$ = 0.3194
Largest diff. peak and hole	0. 143and –0.172e·Å^{-3}

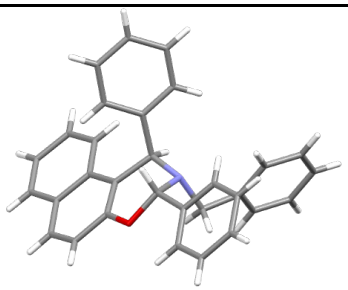




Crystal data and structure refinement for **10m** (CCDC 952464)

Empirical formula	$C_{21}H_{21}NO$
Formula weight	303.39
Crystal habit, colour	needle / yellowish
Crystal size, mm^3	
Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P 1 21/c 1'*
Unit cell dimensions	*a* = 8.4433(3)Å
	b = 11.6711(4)Å
	c = 17.1926(6)Å
	α = 90.00°, γ = 90.00°, β = 94.061(2)°
Volume, *V*($Å^3$)	1689.95(10)
Z	4
Calculated density, $Mg{\cdot}m^{-3}$	1.192
Absorption coefficient, μ(mm^{-1})	0.073
F(000)	648
θ range for data collection	2.11° to 25.00°
Limiting indices	$-10 \le h \le 10, -13 \le k \le 13, -20 \le l \le 20$
Reflection collected / unique	19899 / 1258 [*R*(int) = 0.1741]
Completeness to θ	99.9% (θ = 25.00°)
Max. and min. transmission	
Refinement method	'SHELXL–97 (Sheldrick, 1997)'
Data / restraints / parameters	1258 / 0 / 210
Goodness–of–fit on F^2	0.89
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0479, *wR*2 = 0.0644
R indices (all data)	*R*1 = 0.1216, *wR*2 = 0.0732
Largest diff. peak and hole	0.125and –0.148e·$Å^3$





Crystal data and structure refinement for **10n**[10]

Empirical formula	$C_{31}H_{25}NO$
Formula weight	427.52
Crystal habit, colour	needle / colorless
Crystal size, mm^3	

Temperature, *T*	296(2) K
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*'P2(1)/n'*
Unit cell dimensions	*a* = 9.06410(10)Å
	b = 23.4826(4)Å
	c = 10.6362(2)Å
	α = 90.00°, γ = 90.00°, β = 97.5920(10)
Volume, *V*(Å^3)	2244.06(6
Z	4
Calculated density, Mg·m^{-3}	1.265
Absorption coefficient, μ(mm^{-1})	0.076
F(000)	904
θ range for data collection	1.73° to 38.46°
Limiting indices	−15 ≤ *h* ≤ 14, −40 ≤ *k* ≤ 41, −18≤ *l* ≤ 17
Reflection collected / unique	52477 / 6098 [*R*(int) = 0.0447]
Completeness to θ	94.1% (θ = 38.46°)
Max. and min. transmission	
Refinement method	'SHELXL−97 (Sheldrick, 1997)'
Data / restraints / parameters	1258 / 0 / 298
Goodness−of−fit on F^2	1.043
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0597, *wR*2 = 0.1552
R indices (all data)	*R*1 = 0.1251, *wR*2 = 0.1830
Largest diff. peak and hole	0. 336and −0.189e·Å^{-3}

References:

[1]Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K. Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* **2007**, *40*, 786-790.

[3] olex2.refine (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011).

[4] N. Assimomytis, Y. Sariyannis, , G. Stavropoulos, P. G. Tsoungas, G. Varvounis *Synlett*, **2009**, *17*, 2777-2782

[5] J. P. Huang, T. C. Stanley, A. Jha *Tetrahedron Letters*, **2009**, *50,* 51-54.

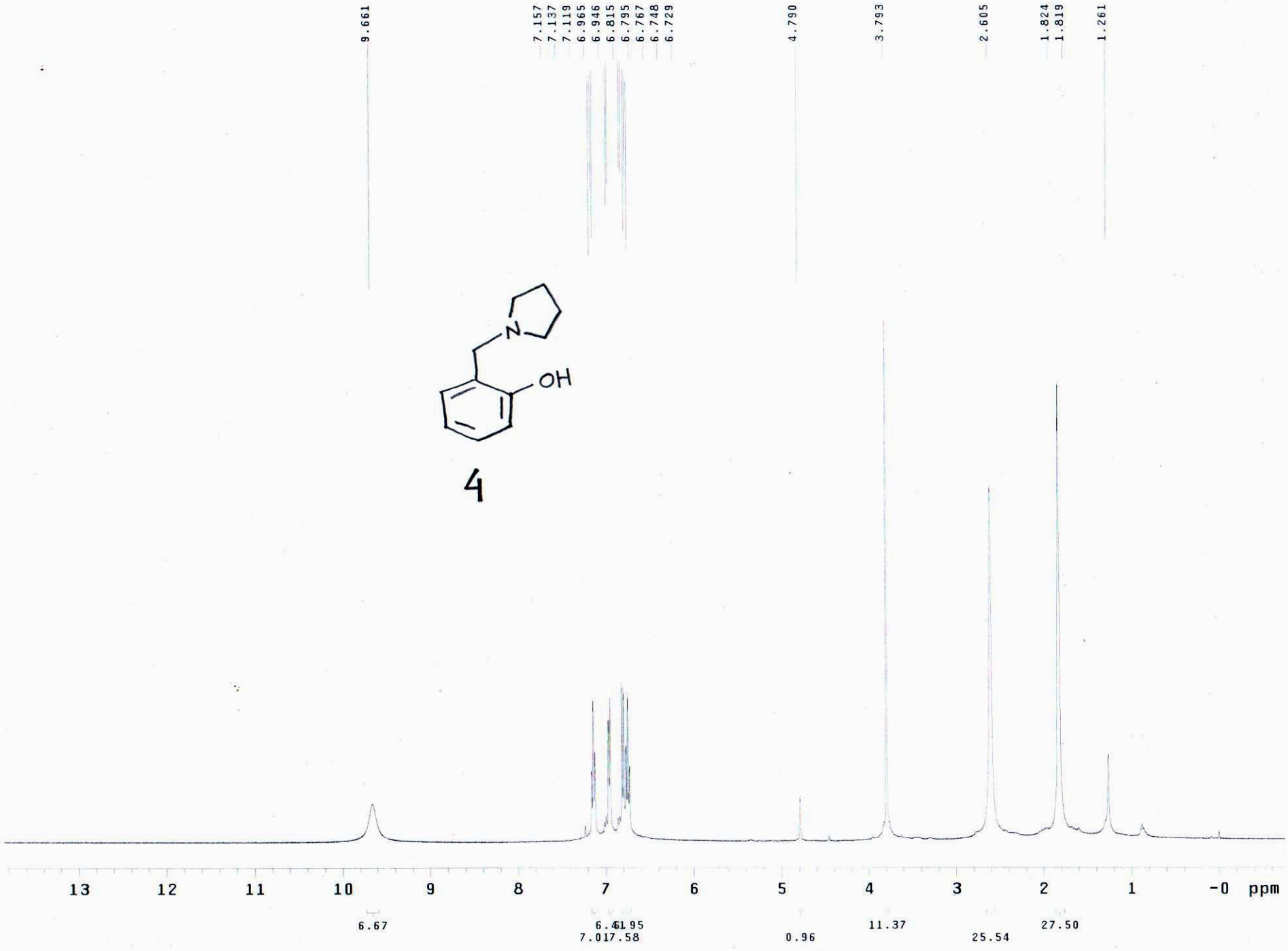
[6] J. Lu, X. Xu, S. Wang, C. Wang, Y. Hu, H. Hu *J. Chem. Soc., Perkin Trans. 1*, **2002**, *24*, 2900-2903**.**

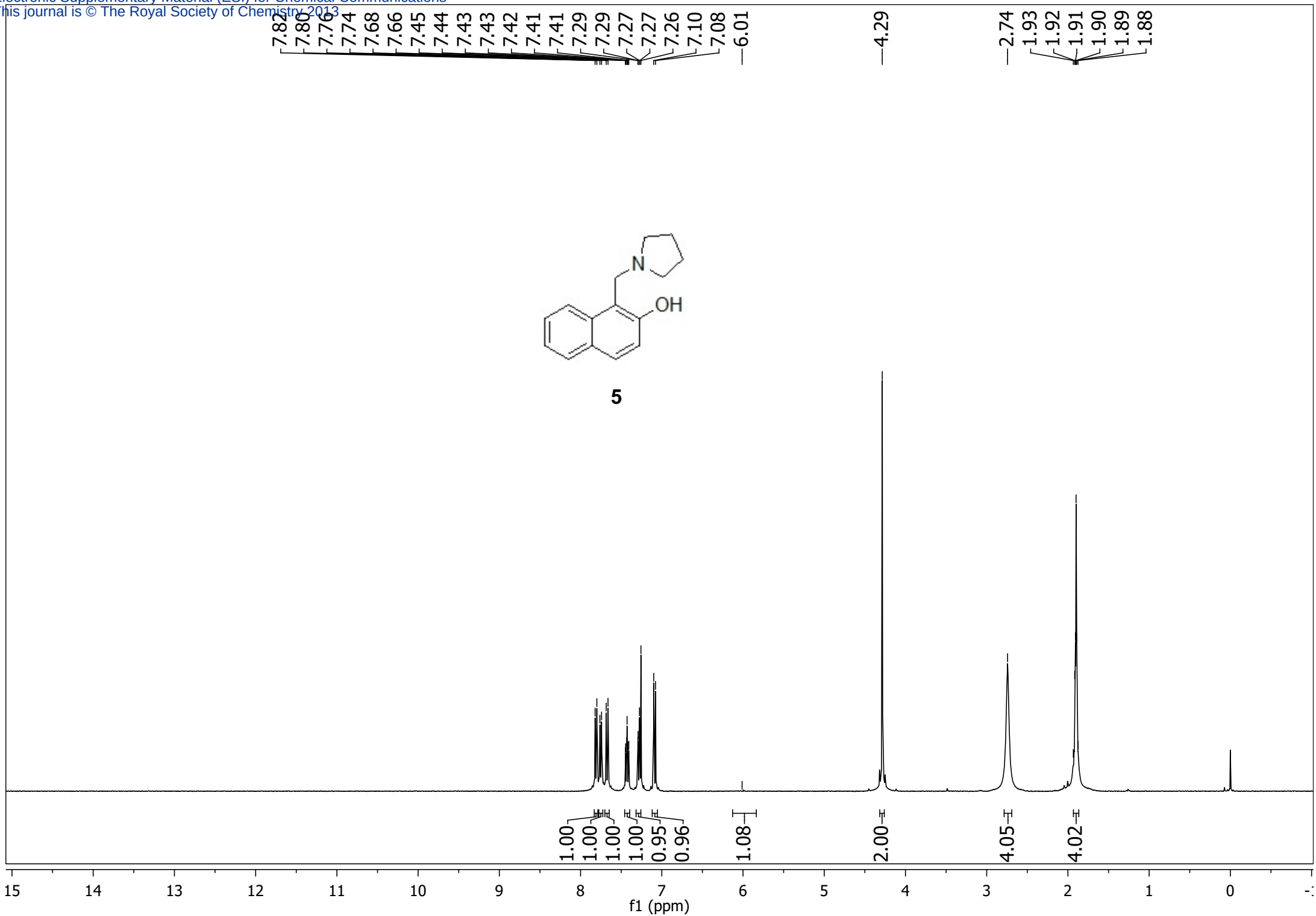
[7] B. Karmakar, J. Banerji *Tetrahedron Letters,* **2011,** *52,* 4957-4960

[8] S. S. Ganesan, N. Rajendran, S. I. Sundarakumar, A. Ganesan, B. Pemiah *Synthesis* **2013**, *45*, 1564-1568.

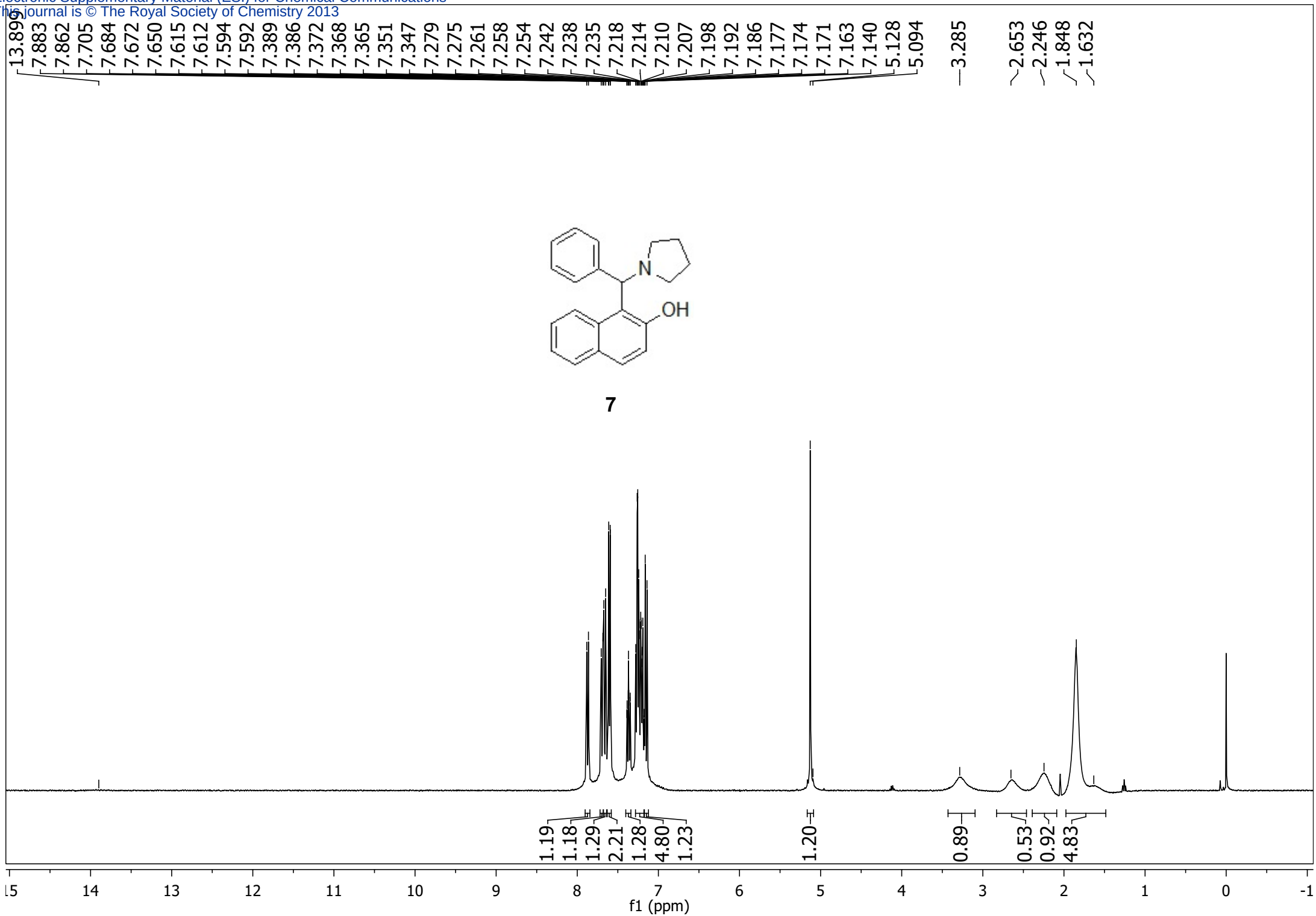
[9] Y. Dong, J. Sun, X. Wang, X. Xu, L. Cao, Y. Hu *Tetrahedron: Asymmetry*, **2004**, *15*, 1667-1672 .

[10] Y. Zhang, Y. H. Li *Acta Cryst*. **2009**, *E65*, o1796.





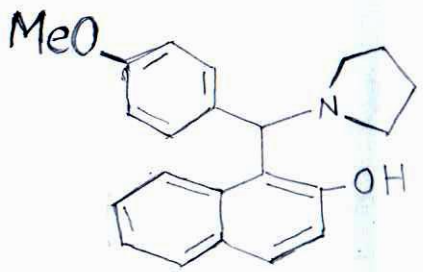
5



SH-1-022-B

exp1 s2pul

SAMPLE		SPECIAL	
date	Dec 4 2012	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	19.700
at	1.996	alfa	20.000
np	39952	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-84.9
tpwr	57	wp	6682.0
pw	9.850	rfl	2609.8
DECOUPLER		rfp	0
dn	C13	rp	129.3
dof	0	lp	-131.4
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	50	sc	0
dmf	15900	vs	146
		th	10
		nm	cdc ph

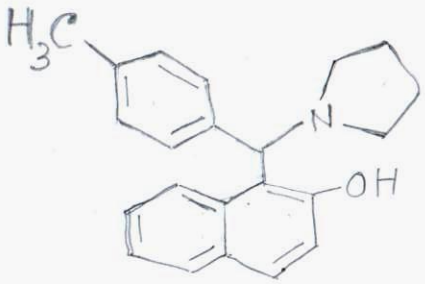


9a

SH-1-026

exp1 s2pul

SAMPLE		SPECIAL	
date	Dec 7 2012	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	19.700
at	1.996	alfa	20.000
np	39952	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-359.3
tpwr	57	wp	6787.1
pw	9.850	rfl	2608.3
DECOUPLER		rfp	0
dn	C13	rp	123.1
dof	0	lp	-125.4
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	50	sc	0
dmf	15900	vs	163
		th	14
		nm	cdc ph

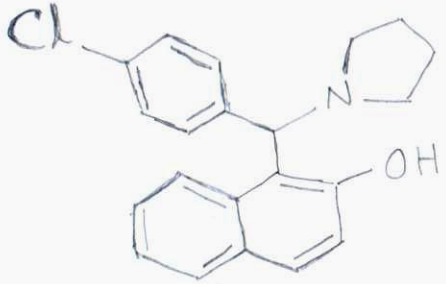


9b

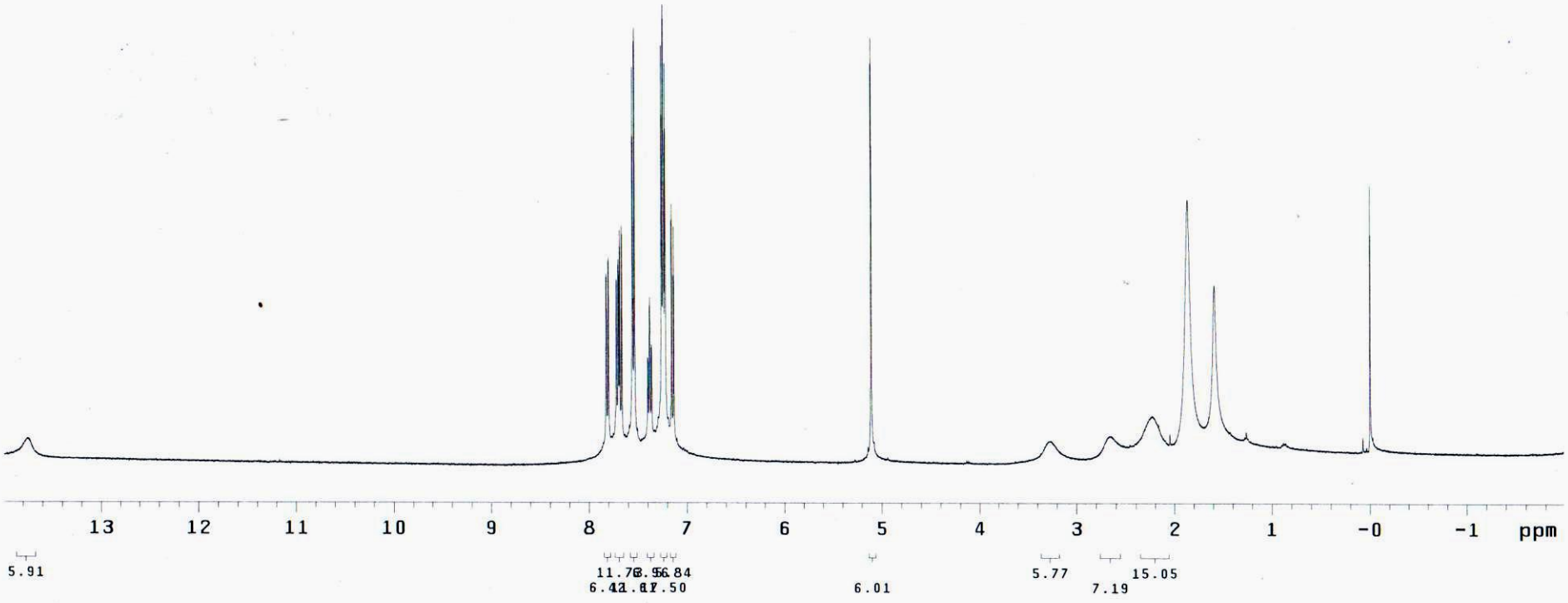
SH-1-021

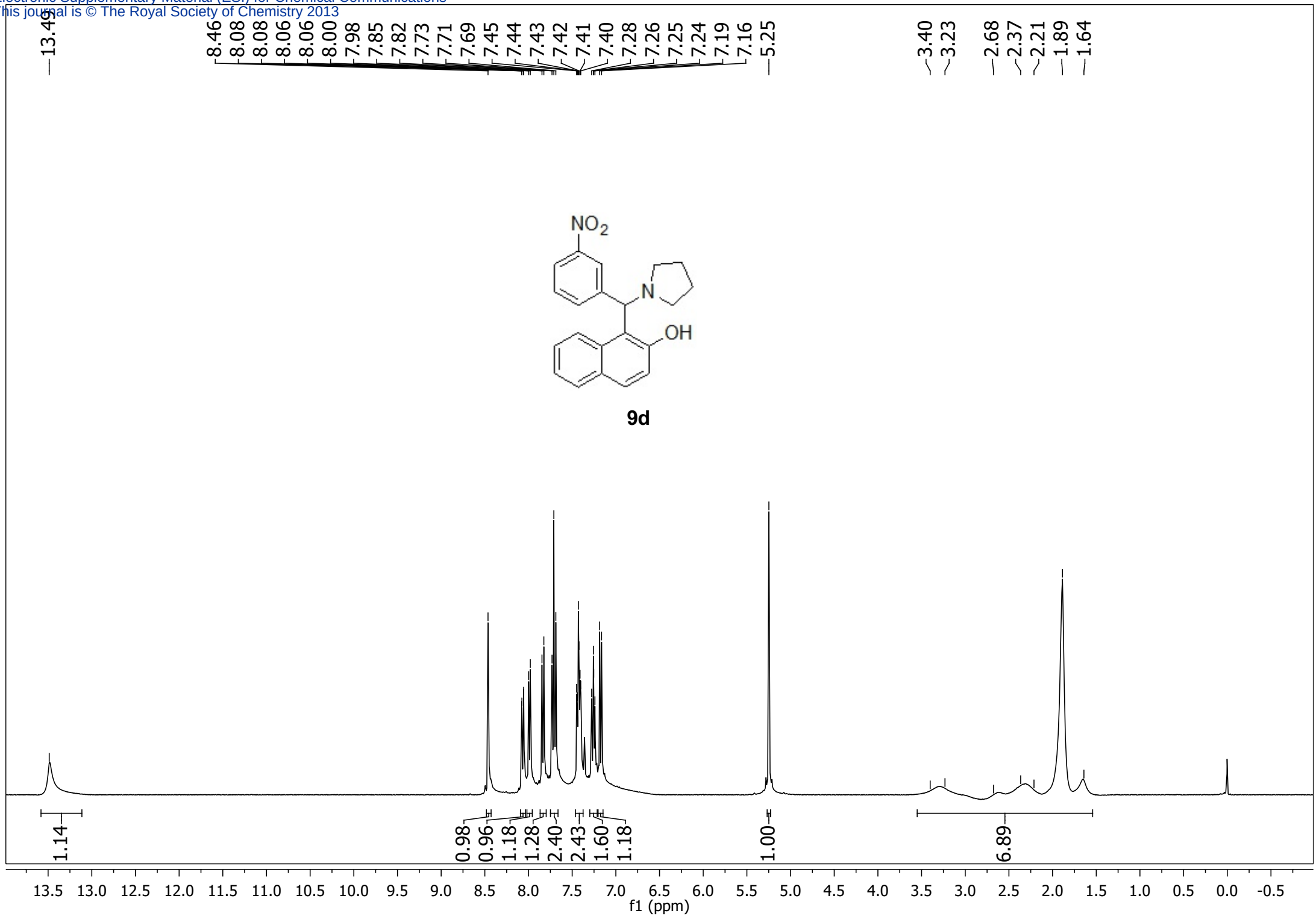
exp1 s2pul

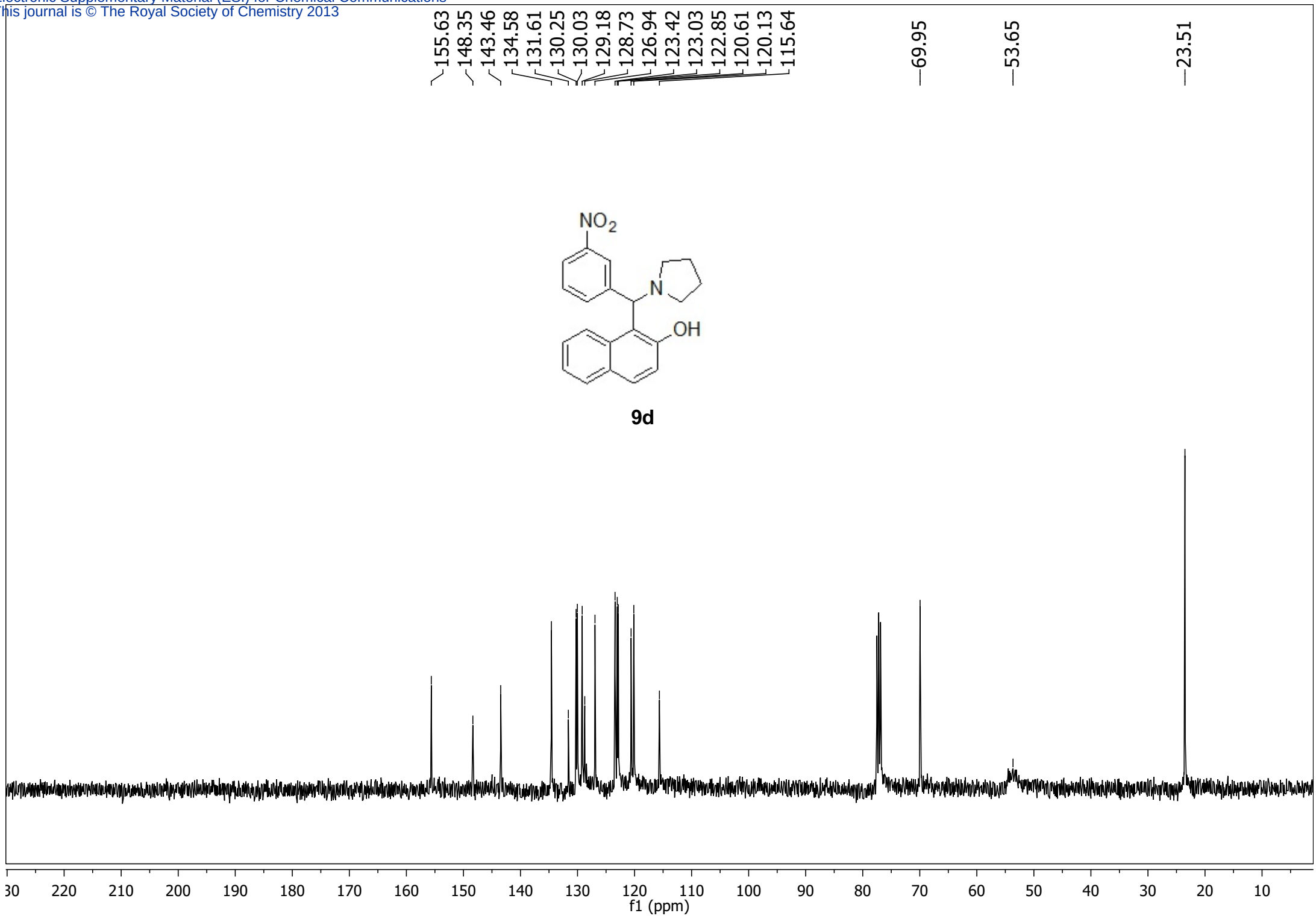
SAMPLE		SPECIAL	
date	Dec 1 2012	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	6389.8	pw90	19.700
at	1.998	alfa	20.000
np	25528	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-795.8
tpwr	57	wp	6389.8
pw	9.850	rfl	795.8
DECOUPLER		rfp	0
dn	C13	rp	76.8
dof	0	lp	-55.8
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	50	sc	0
dmf	15900	vs	74
		th	20
		nm	cdc ph

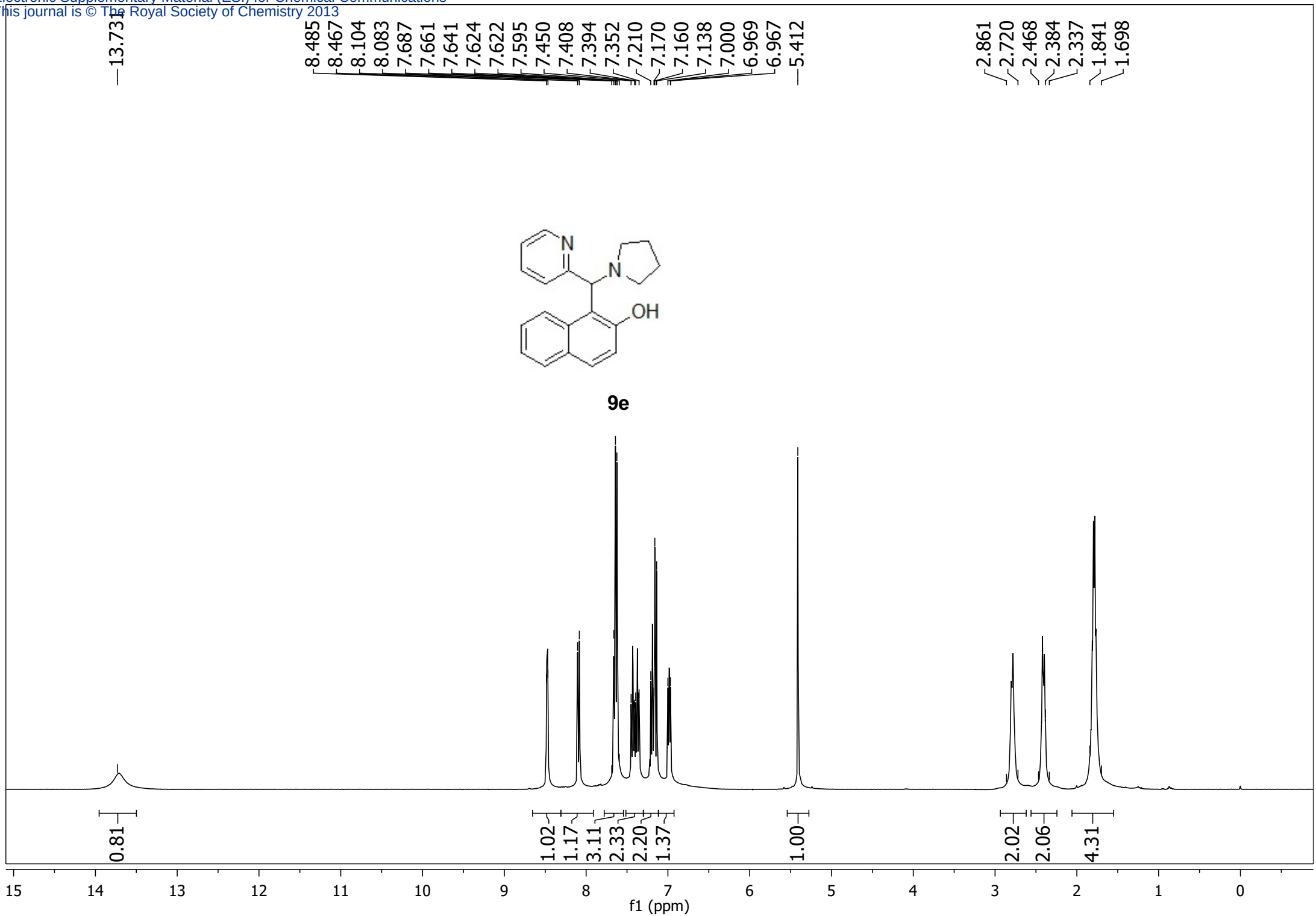


9c

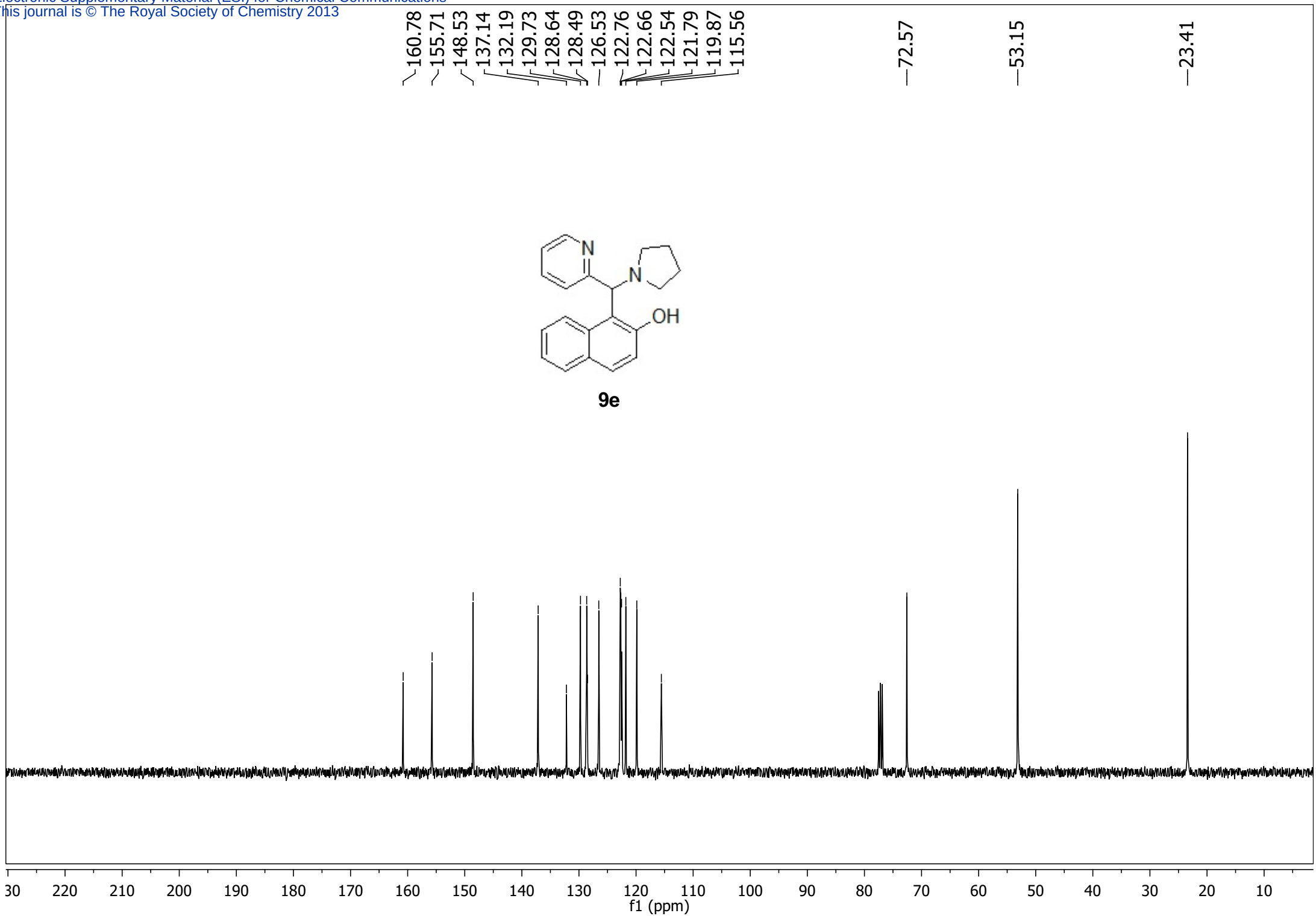


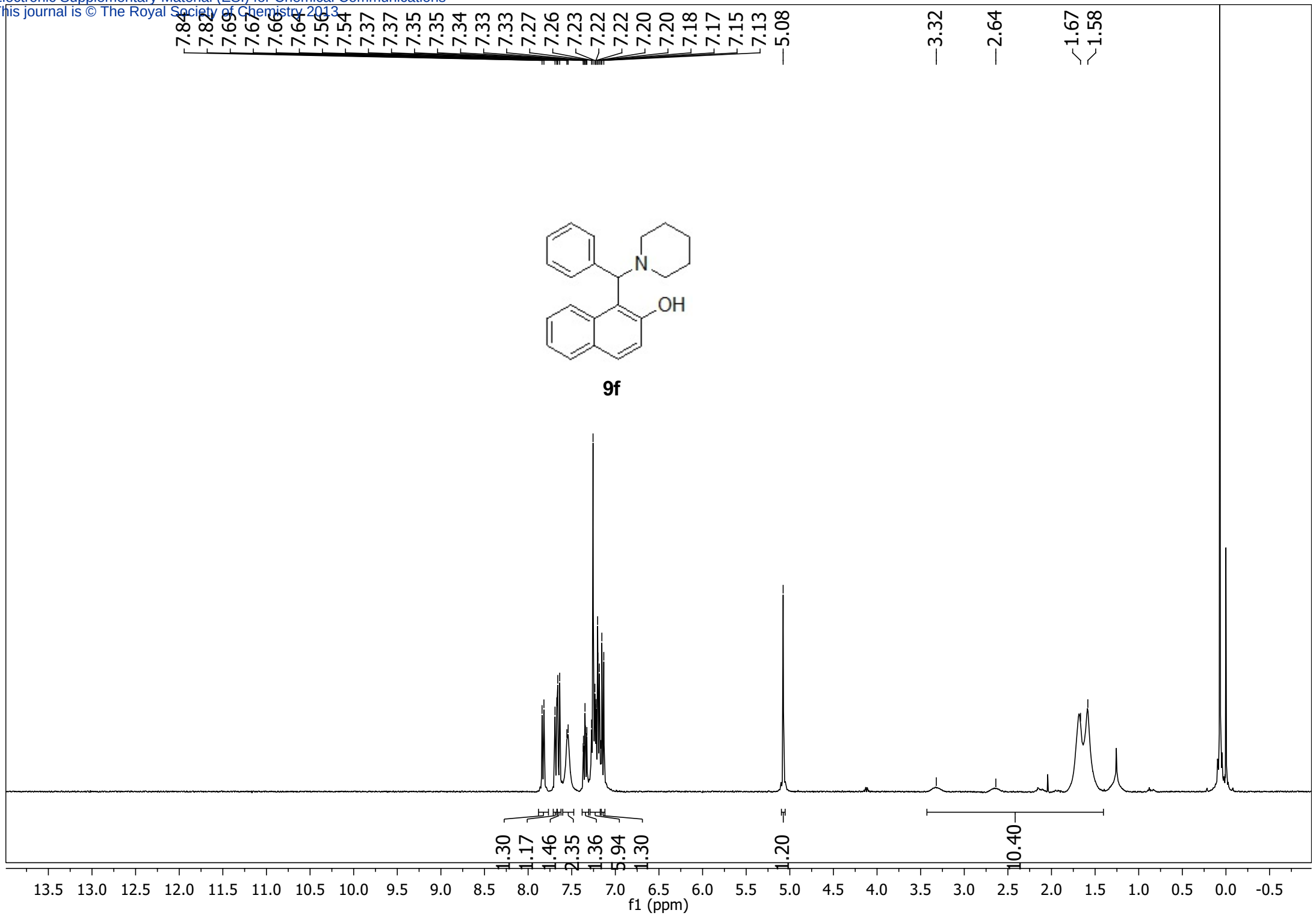




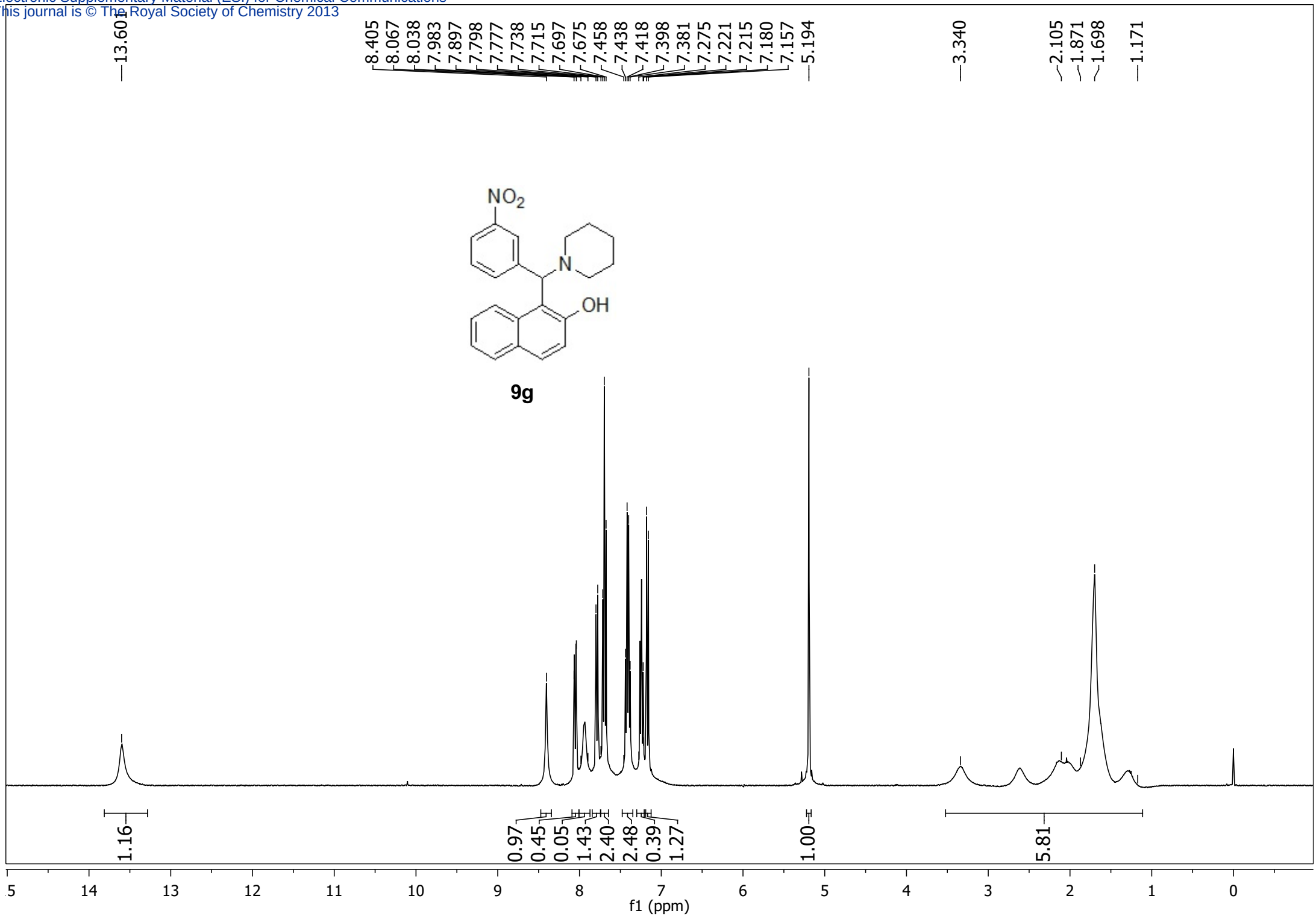


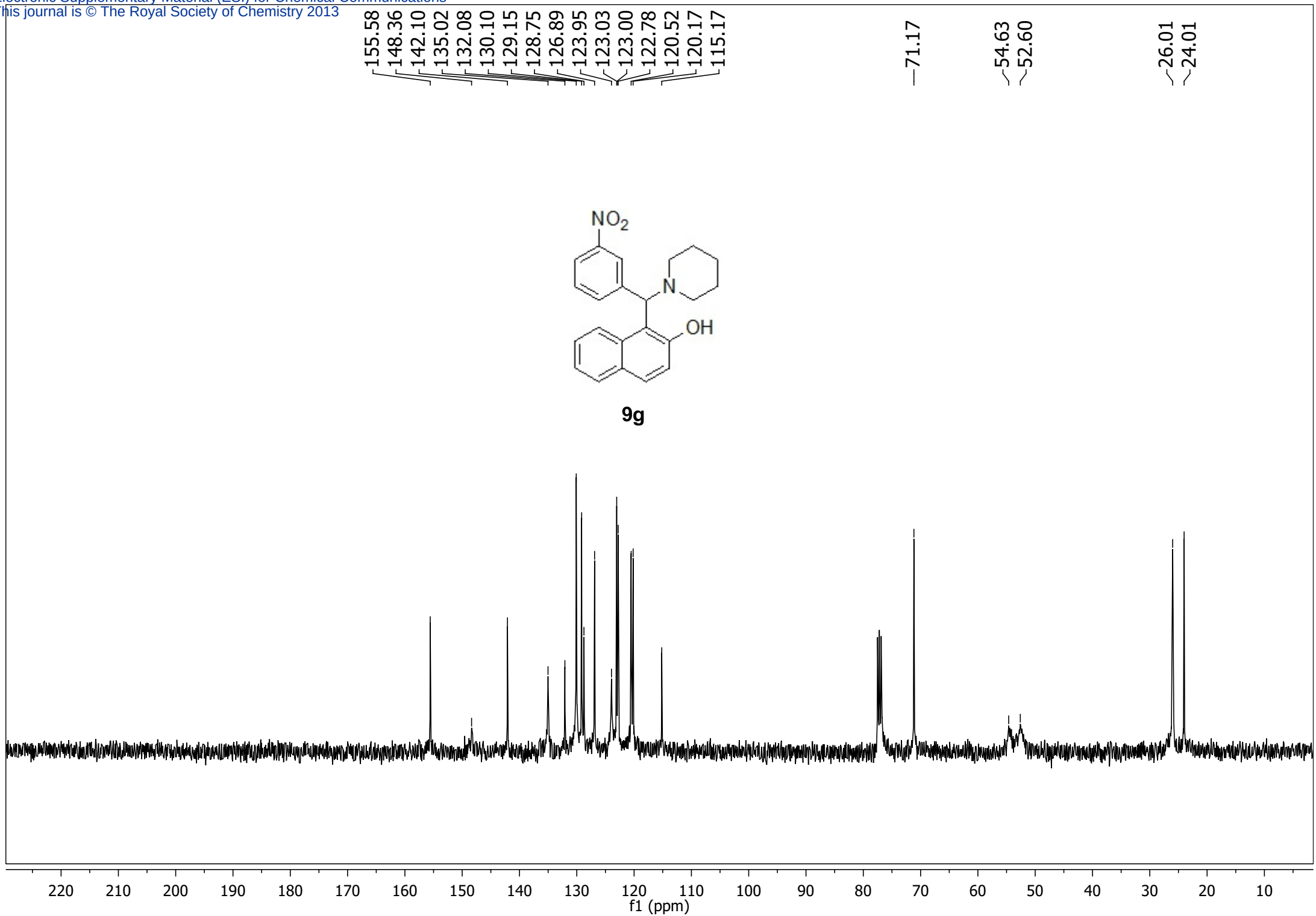
9e

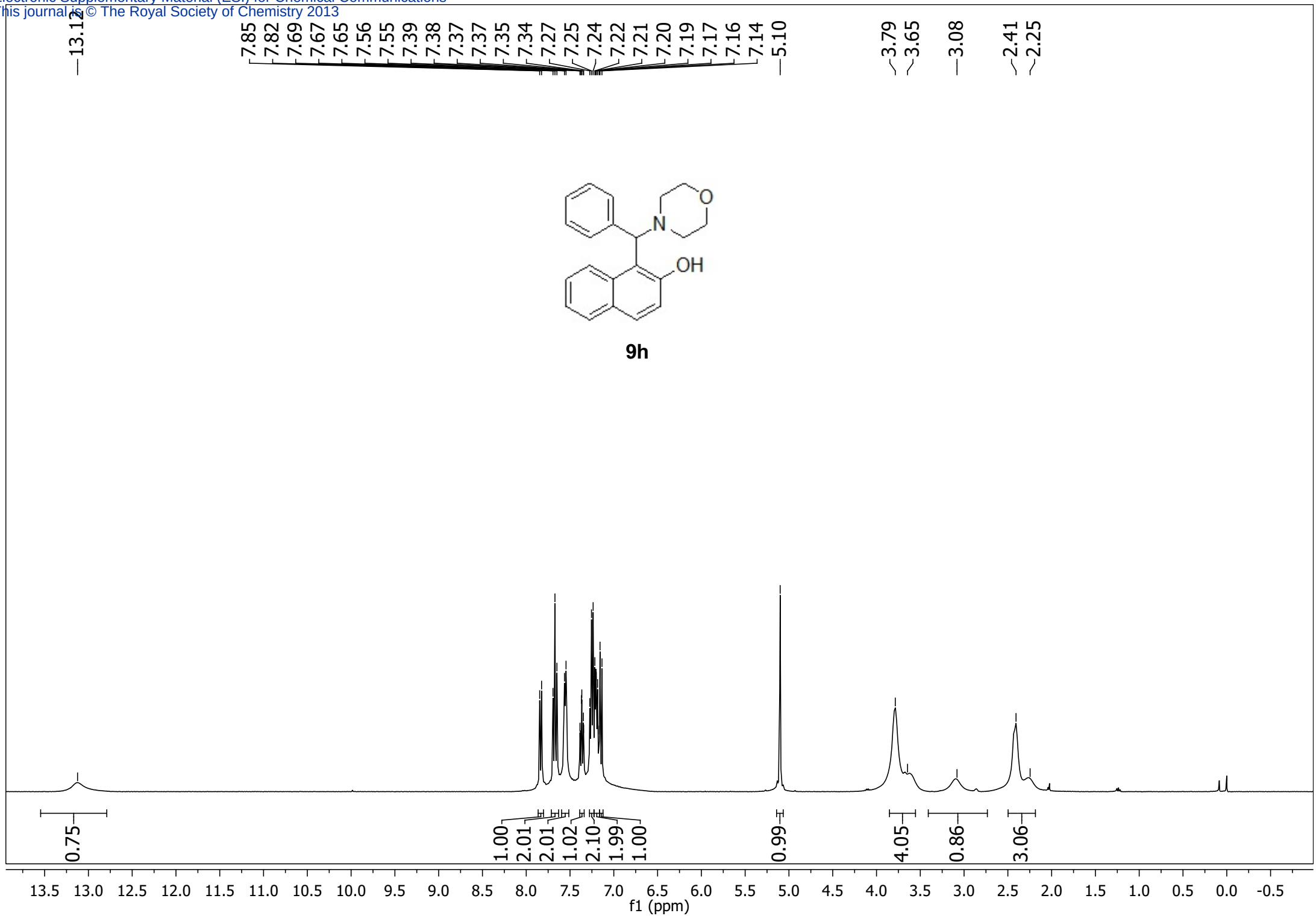




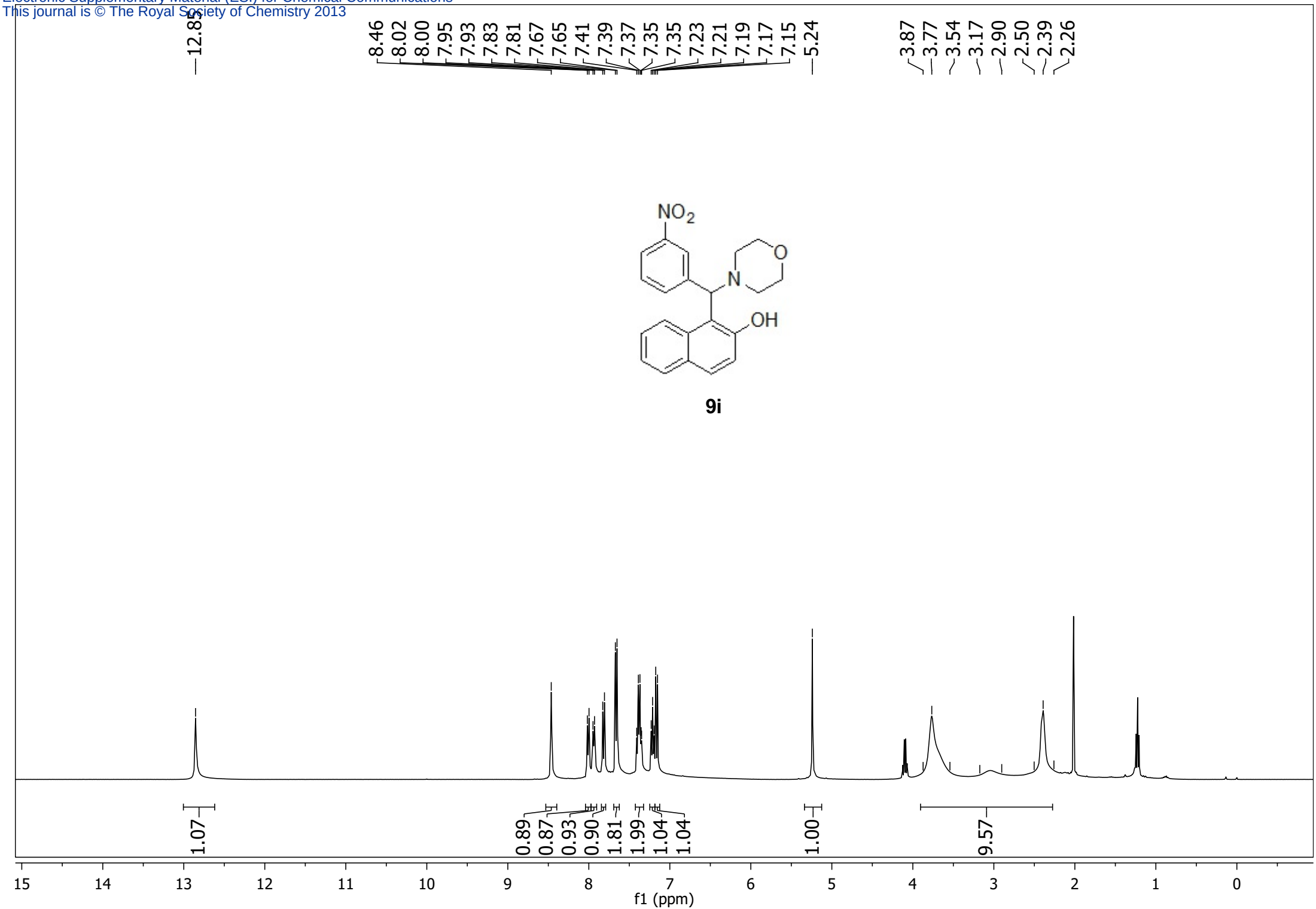
9f







9h



9i

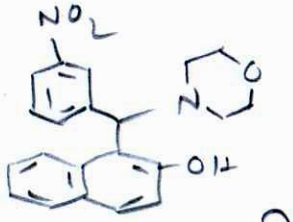
CKJ-1-181B-13C

expl s2pul

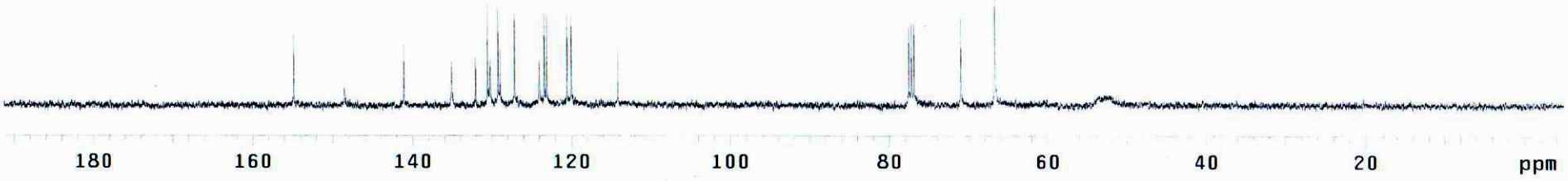
SAMPLE		SPECIAL	
date	May 31 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25125.6	pw90	9.400
at	1.199	alfa	20.000
np	60270	FLAGS	
fb	13800	il	n
bs	4	in	n
d1	1.000	dp	y
nt	3000	hs	nn
ct	372	PROCESSING	
TRANSMITTER		lb	2.00
tn	C13	fn	65536
sfrq	100.554	DISPLAY	
tof	1536.3	sp	-503.5
tpwr	61	wp	19736.6
pw	4.700	rfl	9287.4
DECOUPLER		rfp	7764.9
dn	H1	rp	-63.7
dof	0	lp	-324.9
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	42	sc	0
dmf	8500	vs	26
		th	2
		nm	no ph

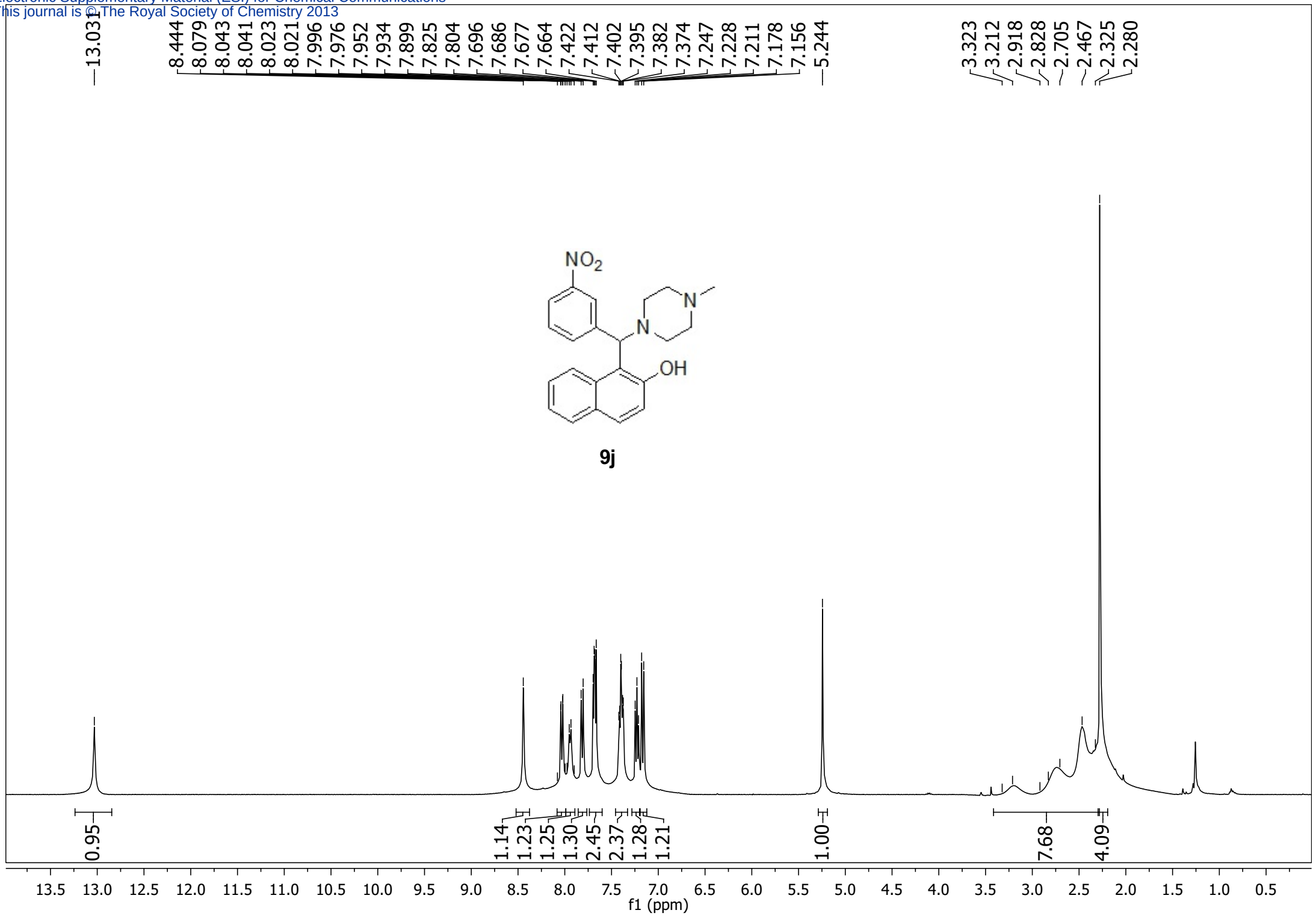
154.876 148.500 141.072 135.070 132.058 130.547 130.242 129.228 128.946 127.138 124.019 123.386 123.096 120.518 120.008 114.143

77.550 77.230 76.910 71.068 66.751

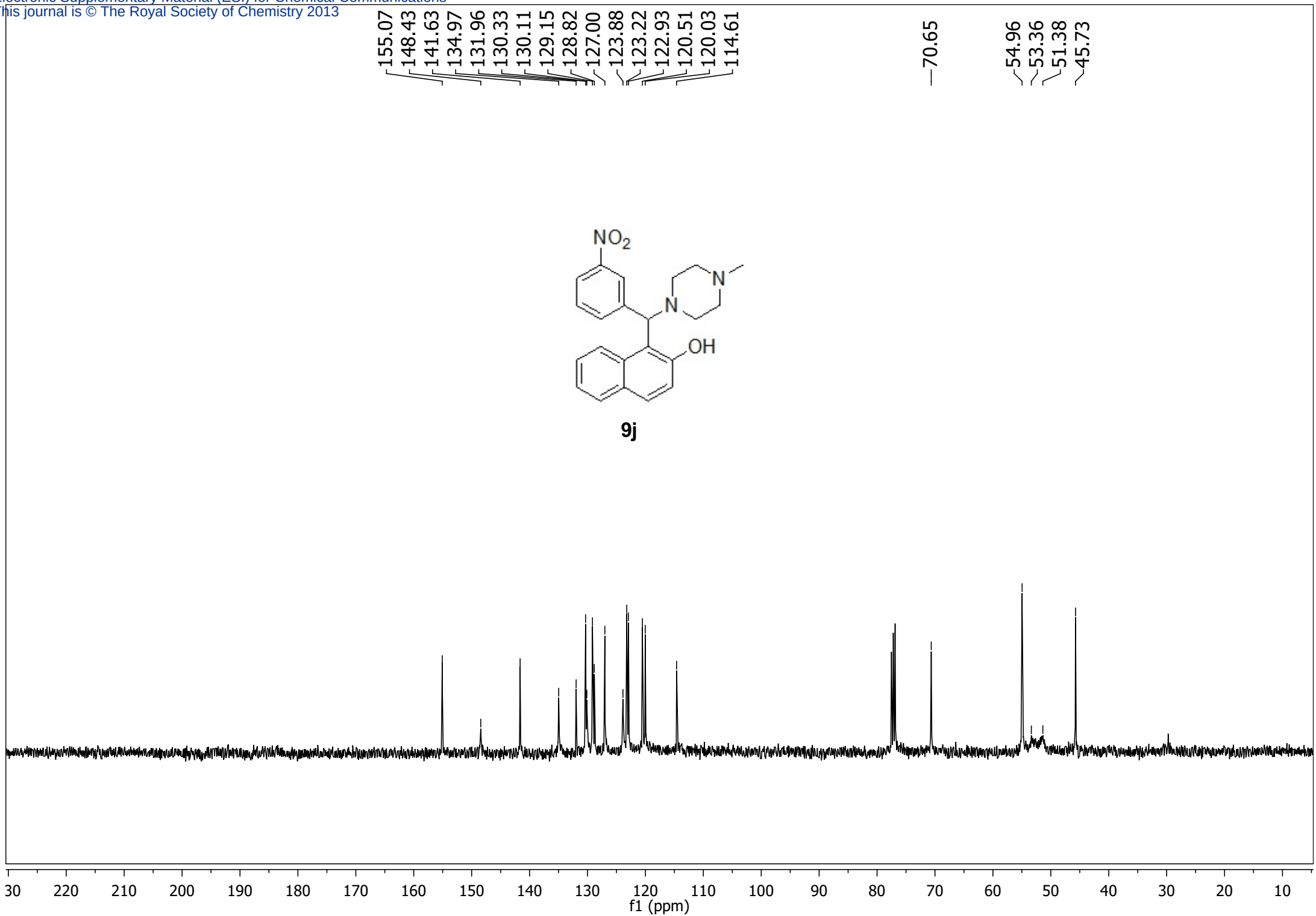


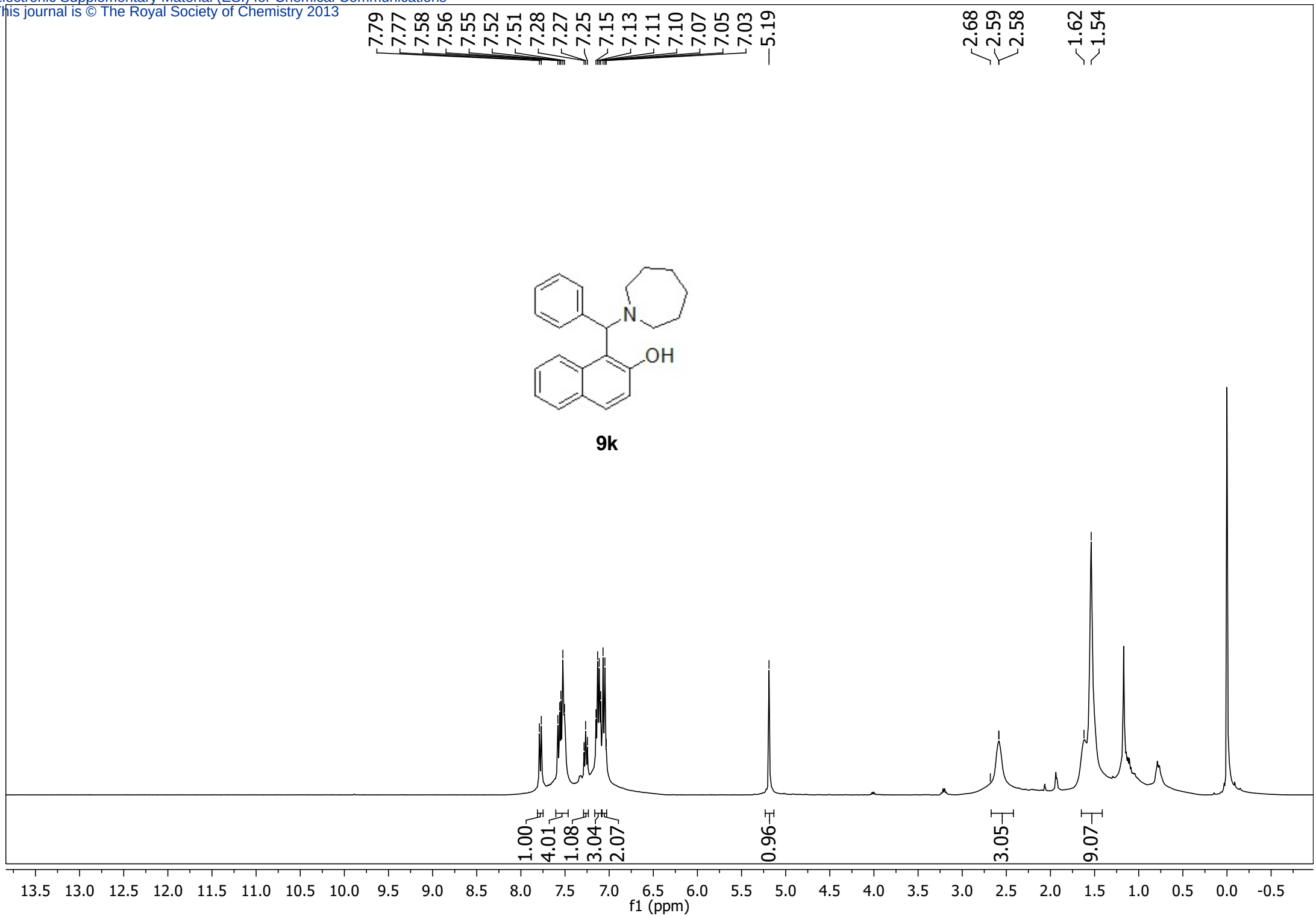
9i





9j





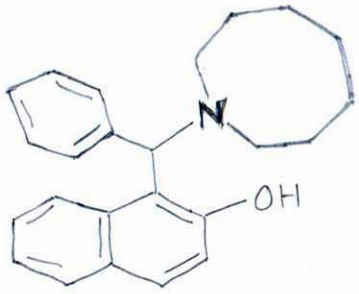
9k

CKJ-1-275 14.098

expl s2pul

SAMPLE		SPECIAL	
date	Jul 16 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	15.100
at	1.996	alfa	20.000
np	39952	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-205.0
tpwr	59	wp	6524.1
pw	7.550	rfl	2625.1
DECOUPLER		rfp	0
dn	C13	rp	-162.8
dof	0	lp	-157.3
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	44	sc	0
dmf	17100	vs	96
		th	3
		nm	cdc ph

9.989 7.921 7.900 7.858 7.840 7.836 7.674 7.654 7.645 7.636 7.613 7.587 7.569 7.507 7.488 7.467 7.386 7.368 7.347 7.241 7.222 7.211 7.202 7.193 7.173 7.160 7.154 7.142 7.132 6.985 6.706 5.265 5.228 4.113 4.096 2.779 2.685 2.347 2.305 2.024 1.653 1.597 1.419 1.256 1.238 1.219 1.155 1.132 1.116 1.021 0.970 0.953 0.893 0.879 0.871 0.861 0.856 0.840 0.792 0.083 0.000



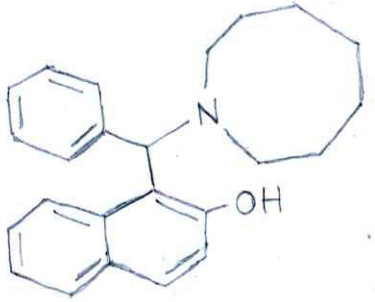
91

CKJ-1-275-13C

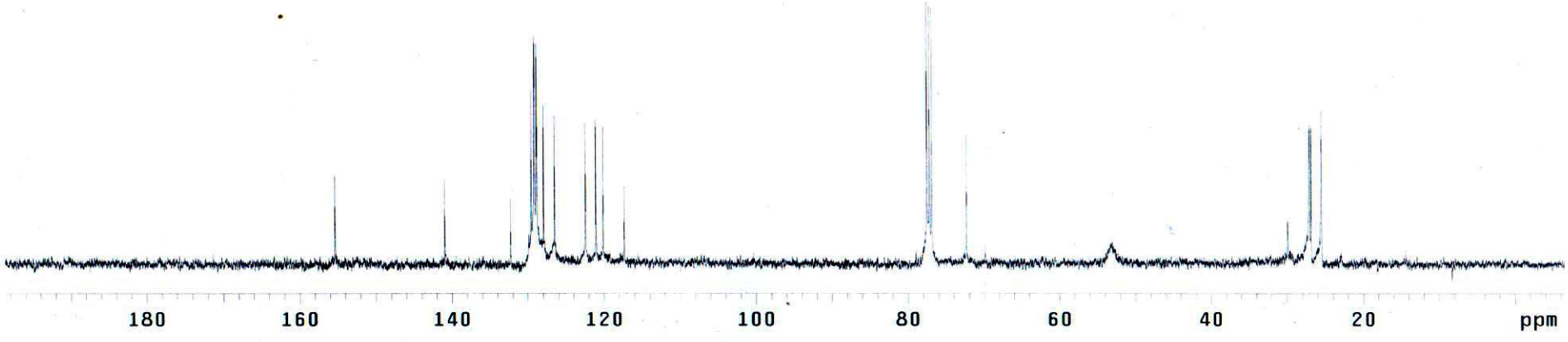
exp1 s2pul

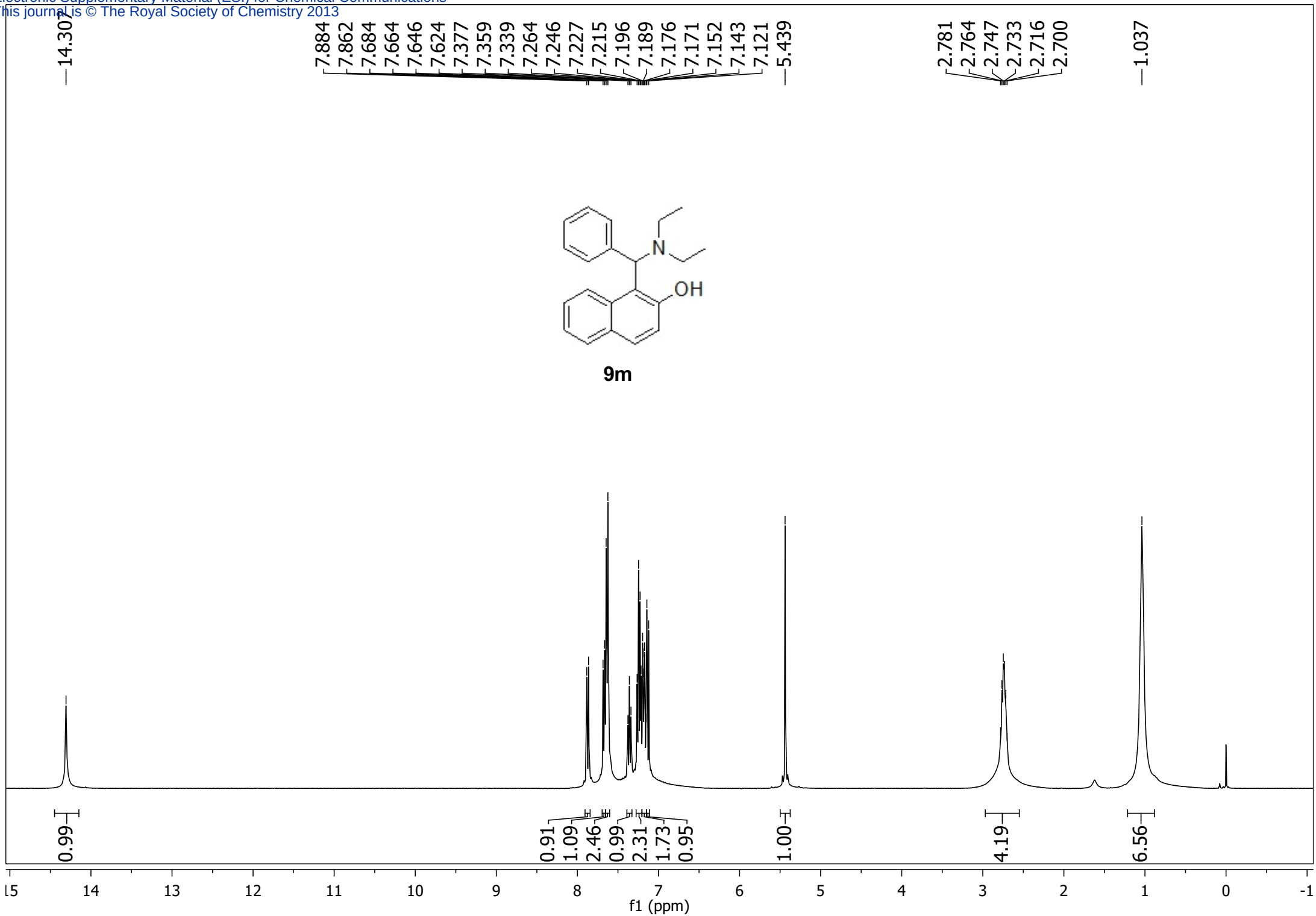
SAMPLE		SPECIAL	
date	Jul 17 2013	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
mercury/CKJ-1-275-~		hst	0.008
	13C	pw90	9.400
ACQUISITION		alfa	20.000
sw	25125.6	FLAGS	
at	1.199	il	n
np	60270	in	n
fb	13800	dp	y
bs	8	hs	nn
d1	1.000	PROCESSING	
nt	10000	lb	2.00
ct	3528	fn	65536
TRANSMITTER		DISPLAY	
tn	C13	sp	-653.8
sfrq	100.554	wp	20629.1
tof	1536.3	rfl	9277.5
tpwr	61	rfp	7764.9
pw	4.700	rp	-41.8
DECOUPLER		lp	-368.2
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	42
dpwr	42	th	2
dmf	8500	nm no	ph

155.349
140.973
132.286
129.541
129.152
129.114
128.839
128.778
127.924
126.513
122.448
121.045
120.122
117.315
78.961
77.543
77.230
76.910
72.357
69.855
53.046
29.892
27.070
26.834
25.499



91



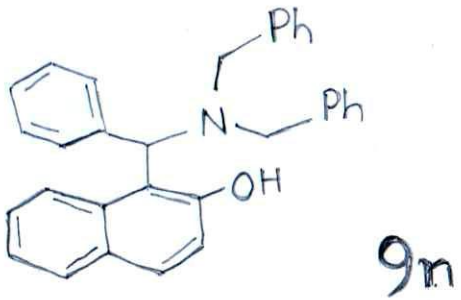


9m

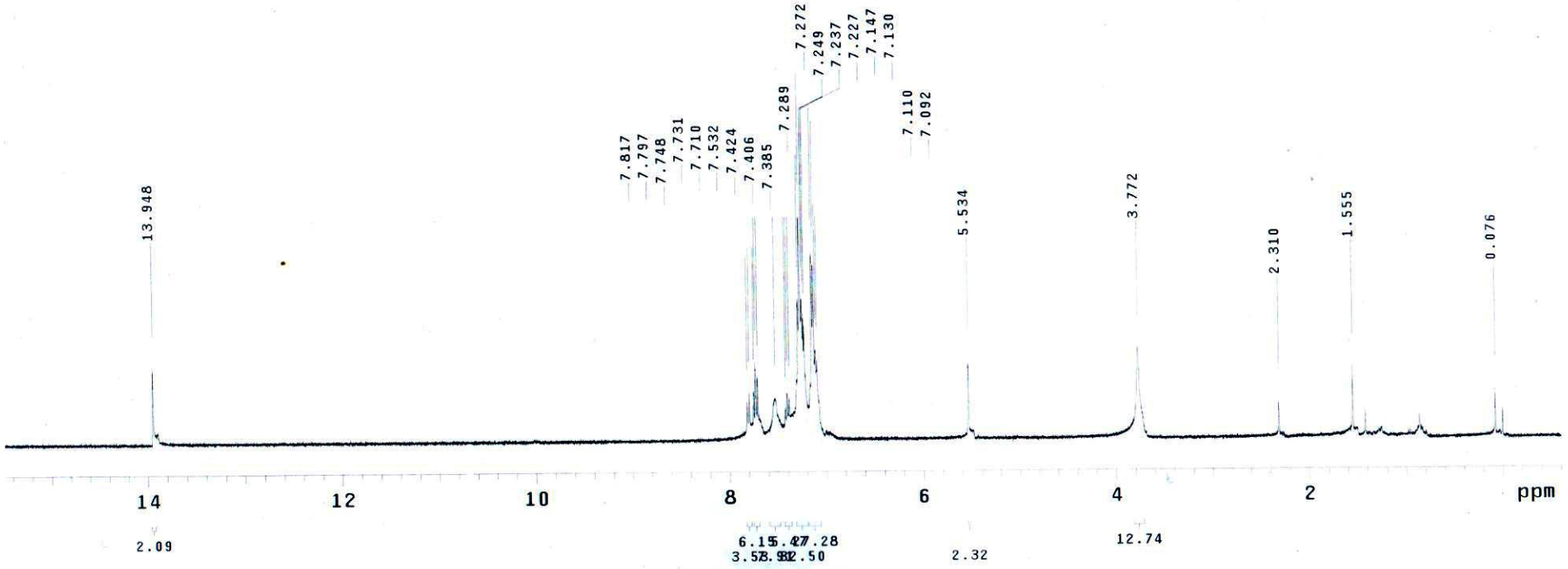
CKJ-1-284

exp1 std1h

SAMPLE		SPECIAL	
date	Jul 18 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	15.100
at	1.993	alfa	20.000
np	39900	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	399.853	sp	-241.9
tof	0	wp	6432.1
tpwr	59	rfl	2977.6
pw	7.000	rfp	0
DECOUPLER		rp	-109.1
dn	C13	lp	-202.2
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	44	vs	36
dmf	17100	th	5
		nm	cdc ph



9n

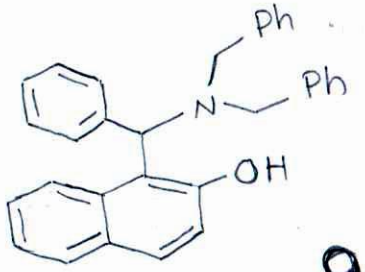


CKJ-1-284-13C

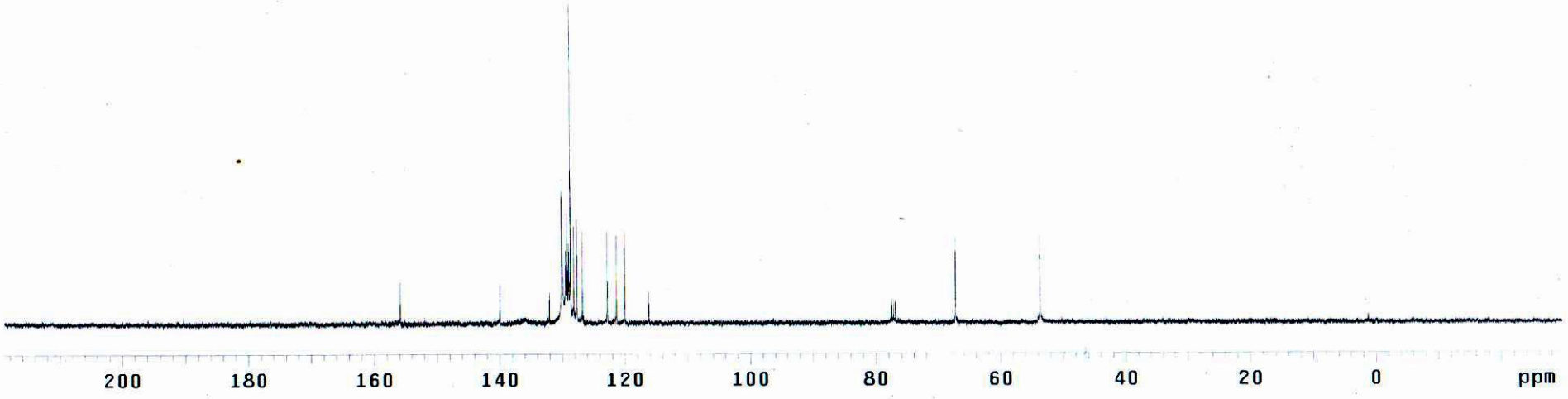
exp1 std13c

SAMPLE		SPECIAL	
date	Jul 18 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25000.0	pw90	9.400
at	1.199	alfa	20.000
np	59968	FLAGS	
fb	13800	il	n
bs	10	in	n
d1	0	dp	y
nt	10000	hs	nn
ct	470	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.552	DISPLAY	
tof	0	sp	-2992.1
tpwr	61	wp	25000.0
pw	8.667	rfl	10757.0
DECOUPLER		rfp	7764.9
dn	H1	rp	-53.9
dof	0	lp	-314.7
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	42	sc	0
dmf	8500	vs	51
		th	3
		nm	no ph

155.854 139.918 132.057 130.030 129.431 129.218 129.127 128.953 128.627 128.164 127.648 126.729 122.761 121.296 120.006 116.144 77.541 77.222 76.904 67.266 53.675



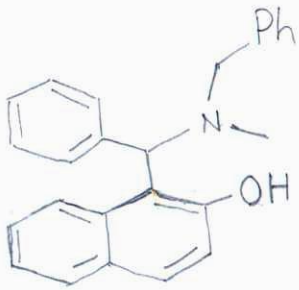
9n



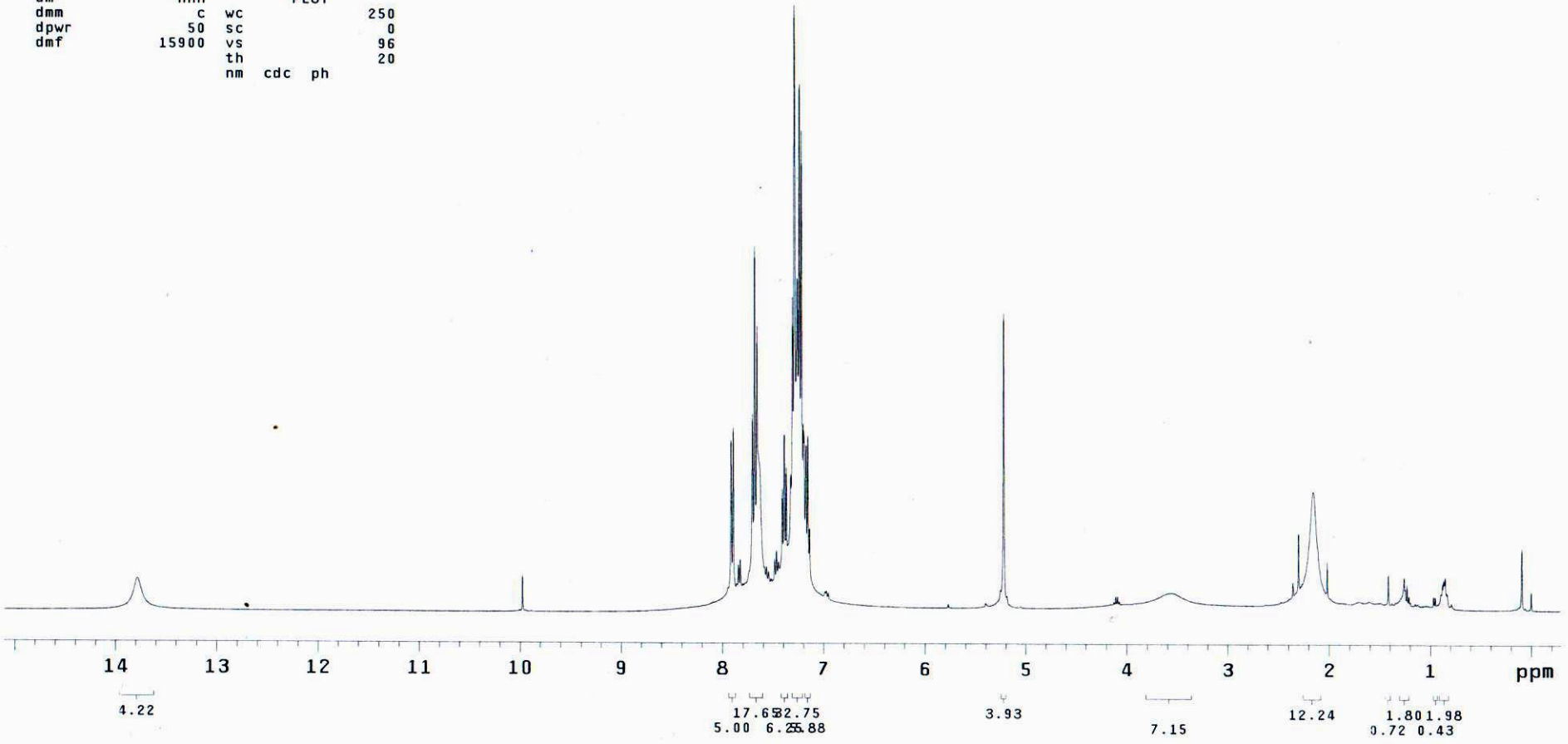
CKJ-1-111

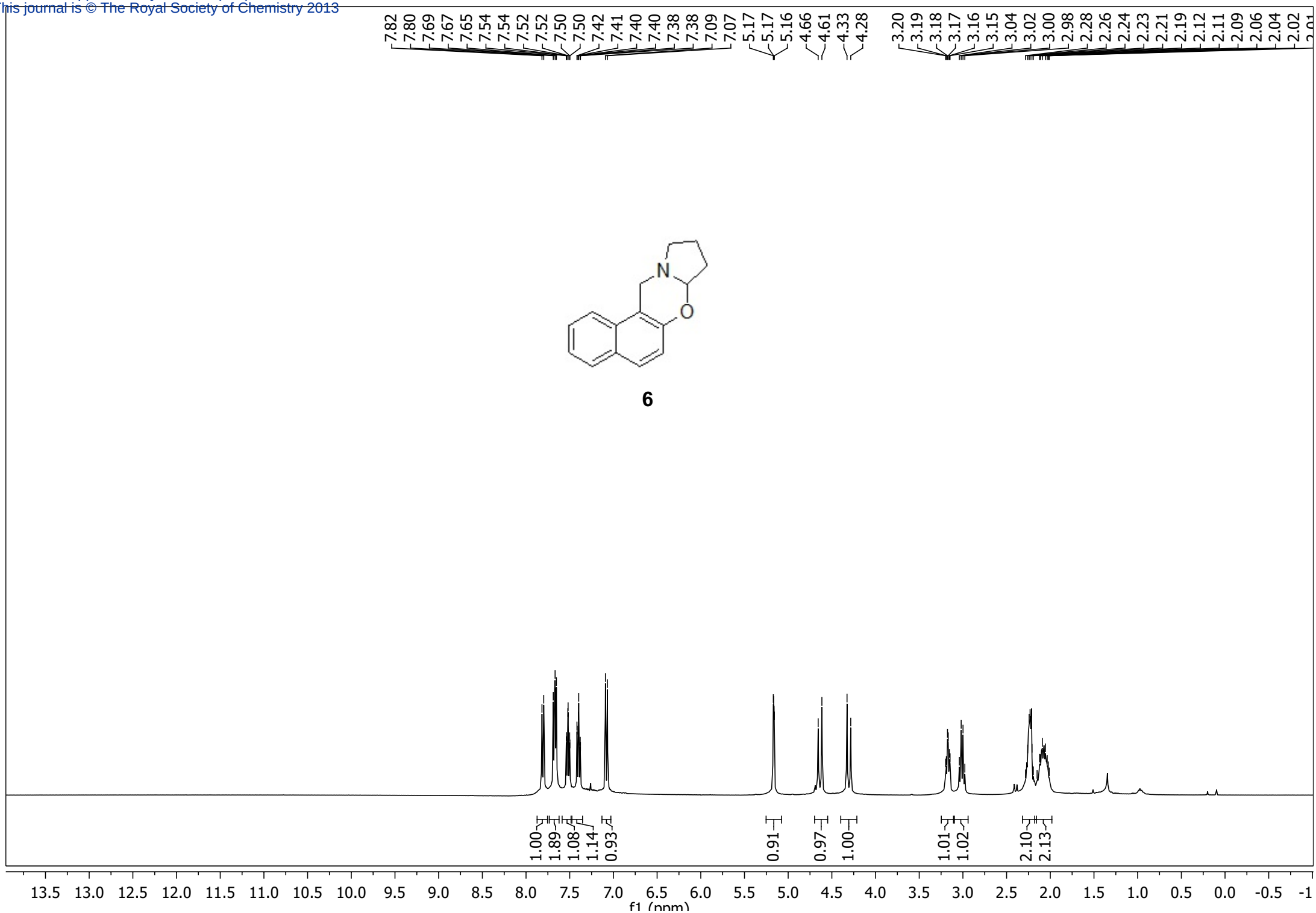
exp1 s2pul

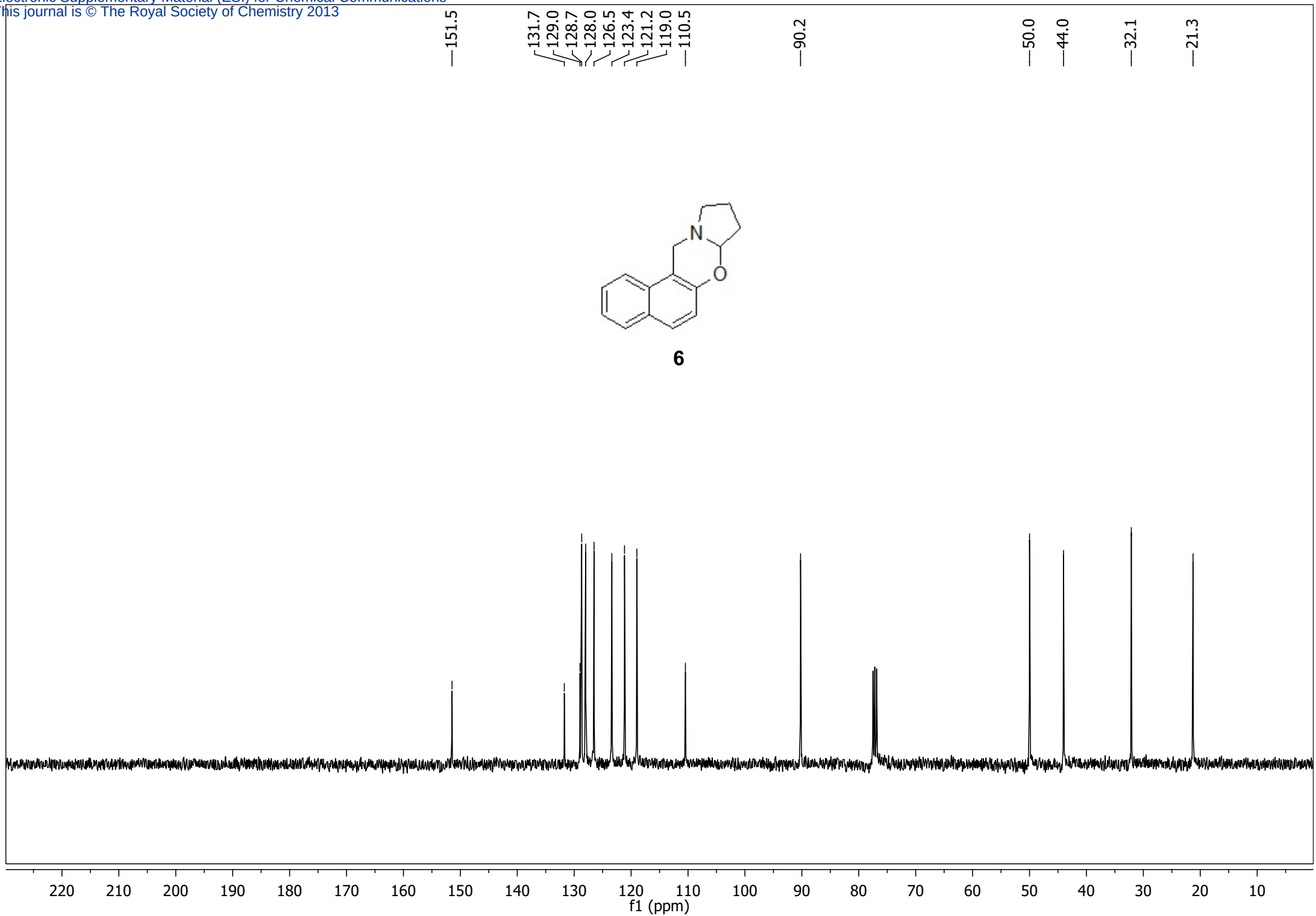
SAMPLE		SPECIAL	
date	Dec 1 2012	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	19.700
at	1.996	alfa	20.000
np	39952	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-116.7
tpwr	57	wp	6155.9
pw	9.850	rfl	2636.1
DECOUPLER		rfp	0
dn	C13	rp	137.6
dof	0	lp	-158.0
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	50	sc	0
dmf	15900	vs	96
		th	20
		nm	cdc ph

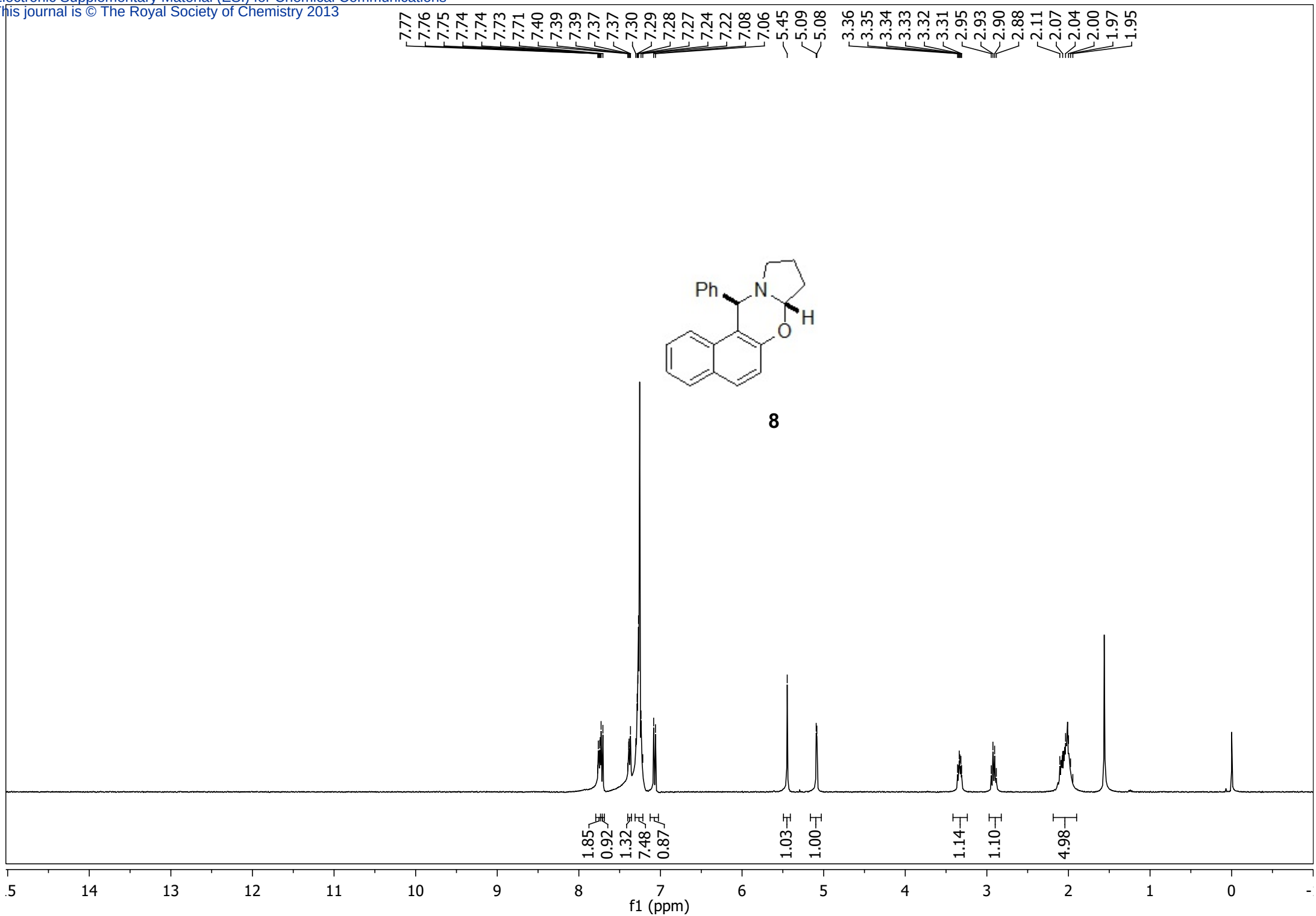


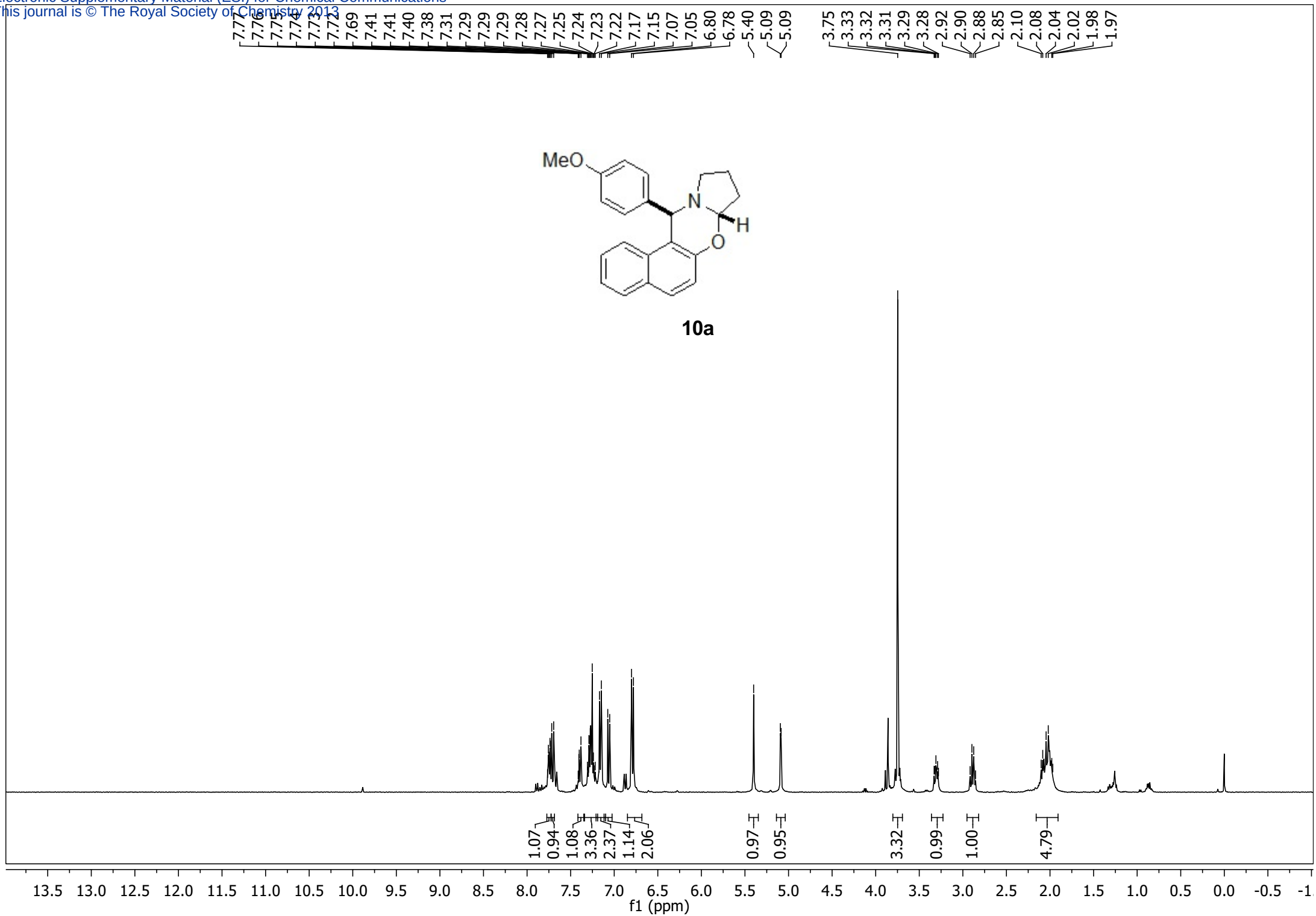
90

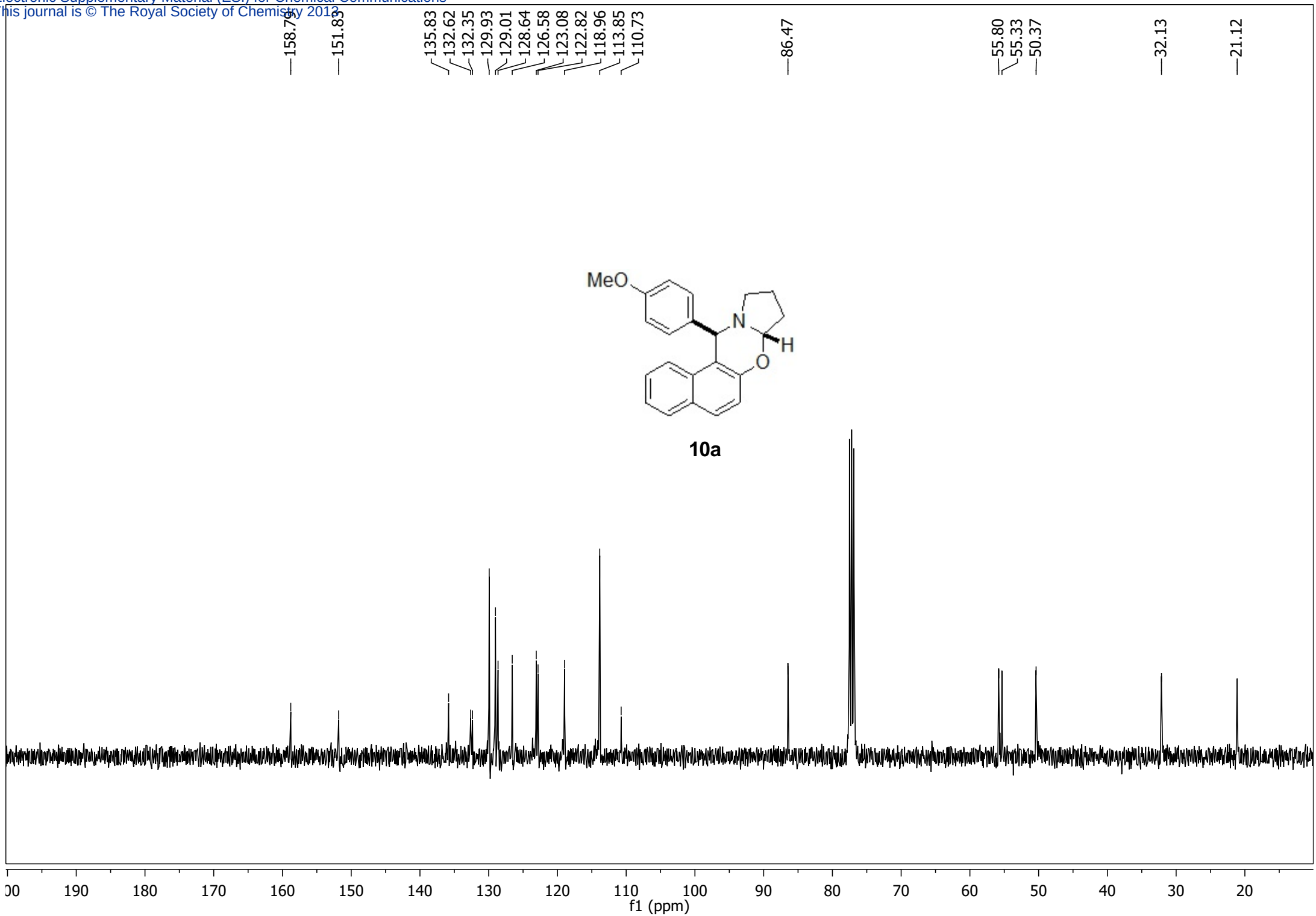










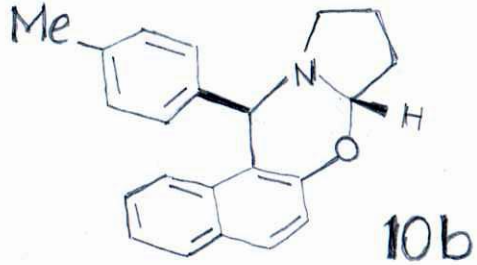


CKJ-SH-1-037-2nd

exp1 s2pul

SAMPLE		SPECIAL	
date	Jul 17 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	15.100
at	1.996	alfa	20.000
np	39952	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-336.3
tpwr	59	wp	5695.6
pw	7.550	rfl	2611.9
DECOUPLER		rfp	0
dn	C13	rp	-143.8
dof	0	lp	-205.1
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	44	sc	0
dmf	17100	vs	91
		th	4
		nm	cdc ph

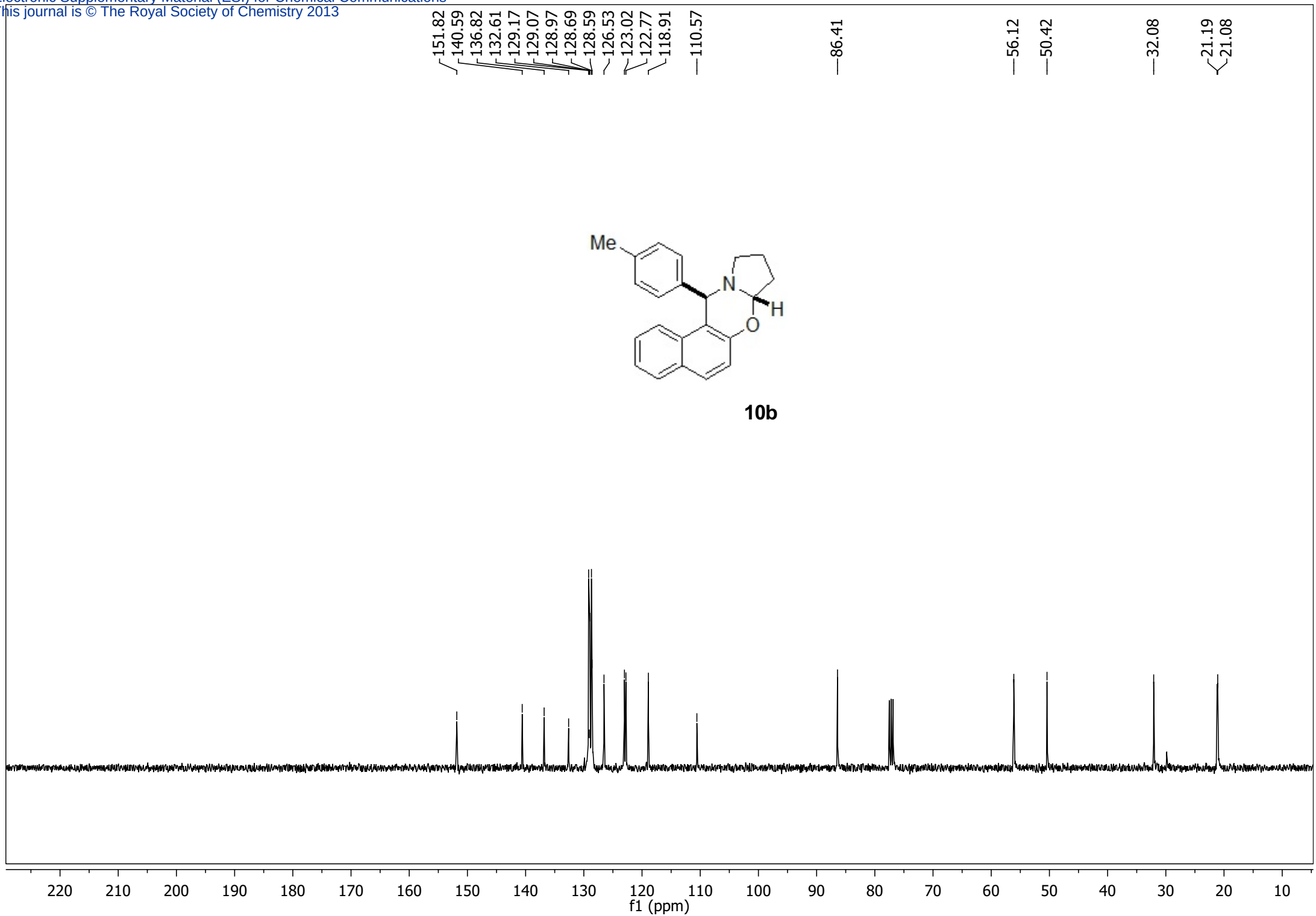
7.751 7.743 7.733 7.728 7.715 7.693 7.394 7.376 7.292 7.279 7.275 7.267 7.261 7.254 7.248 7.244 7.231 7.215 7.180 7.142 7.122 7.076 7.053 5.410 5.095 5.087 3.337 3.316 3.308 3.297 2.927 2.906 2.886 2.864 2.407 2.390 2.317 2.293 2.261 2.095 2.078 2.065 2.048 2.035 2.025 2.010 1.999 1.986 1.943 1.282 1.255 0.073 0.000



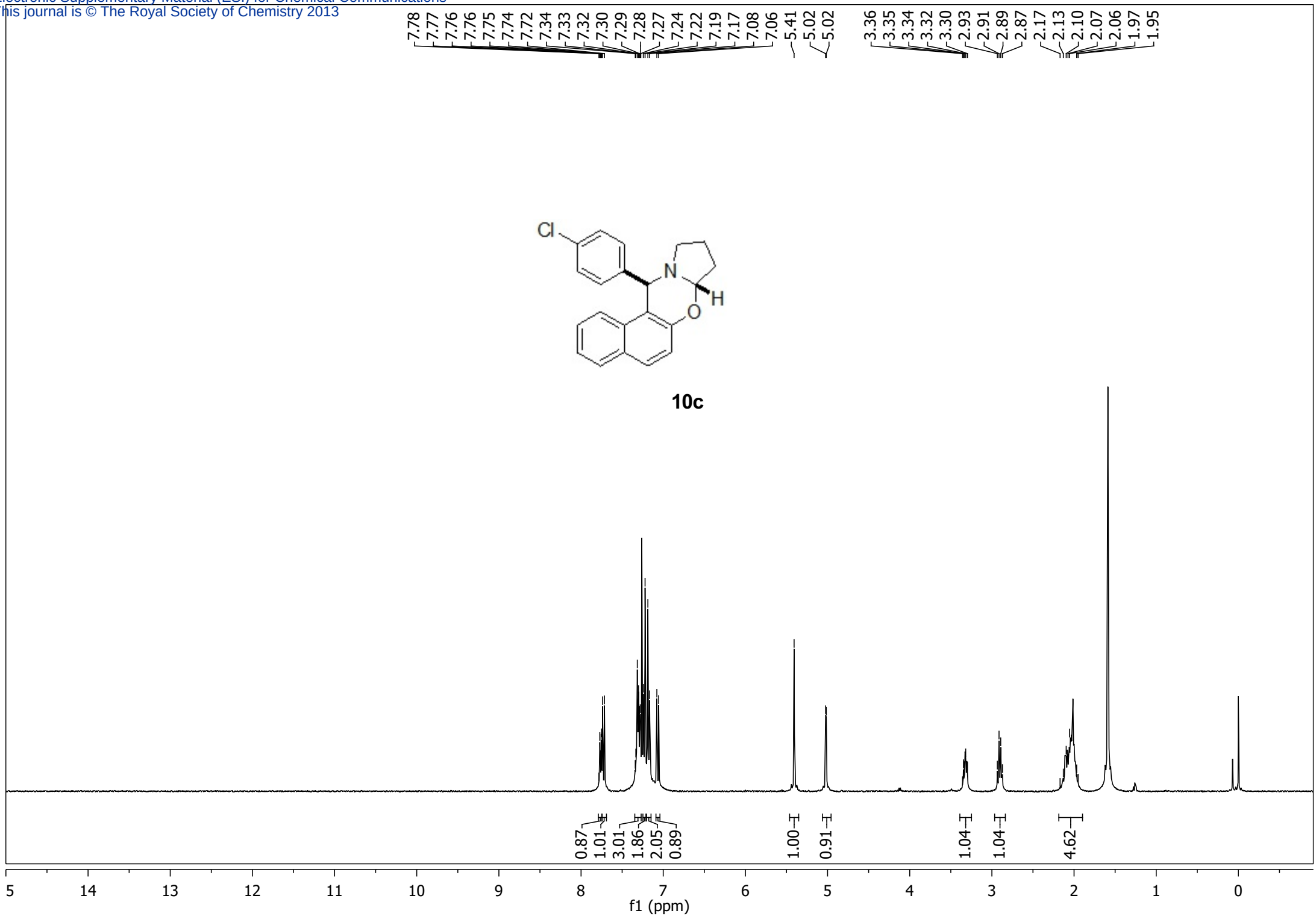
10b

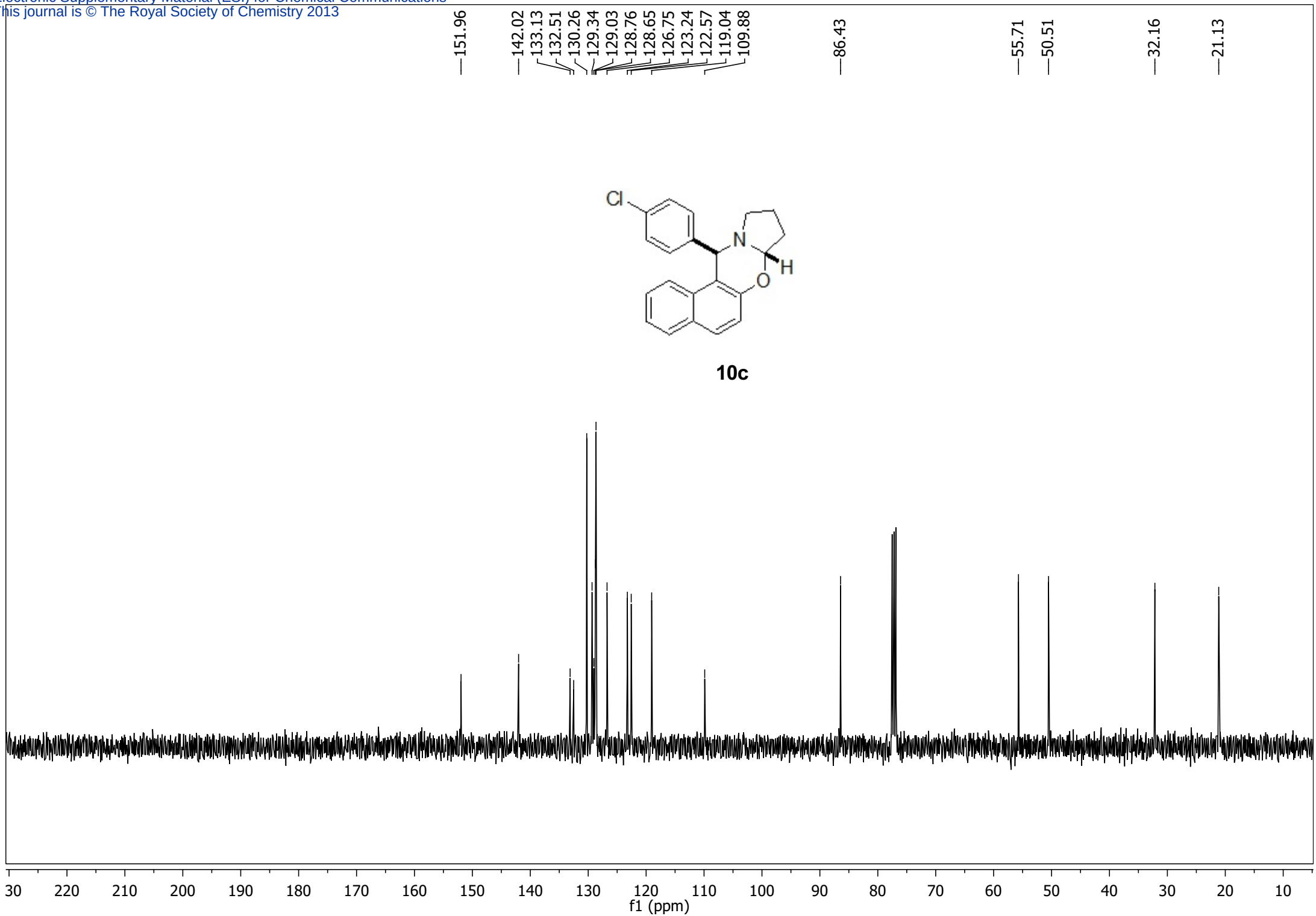
13 12 11 10 9 8 7 6 5 4 3 2 1 -0 ppm

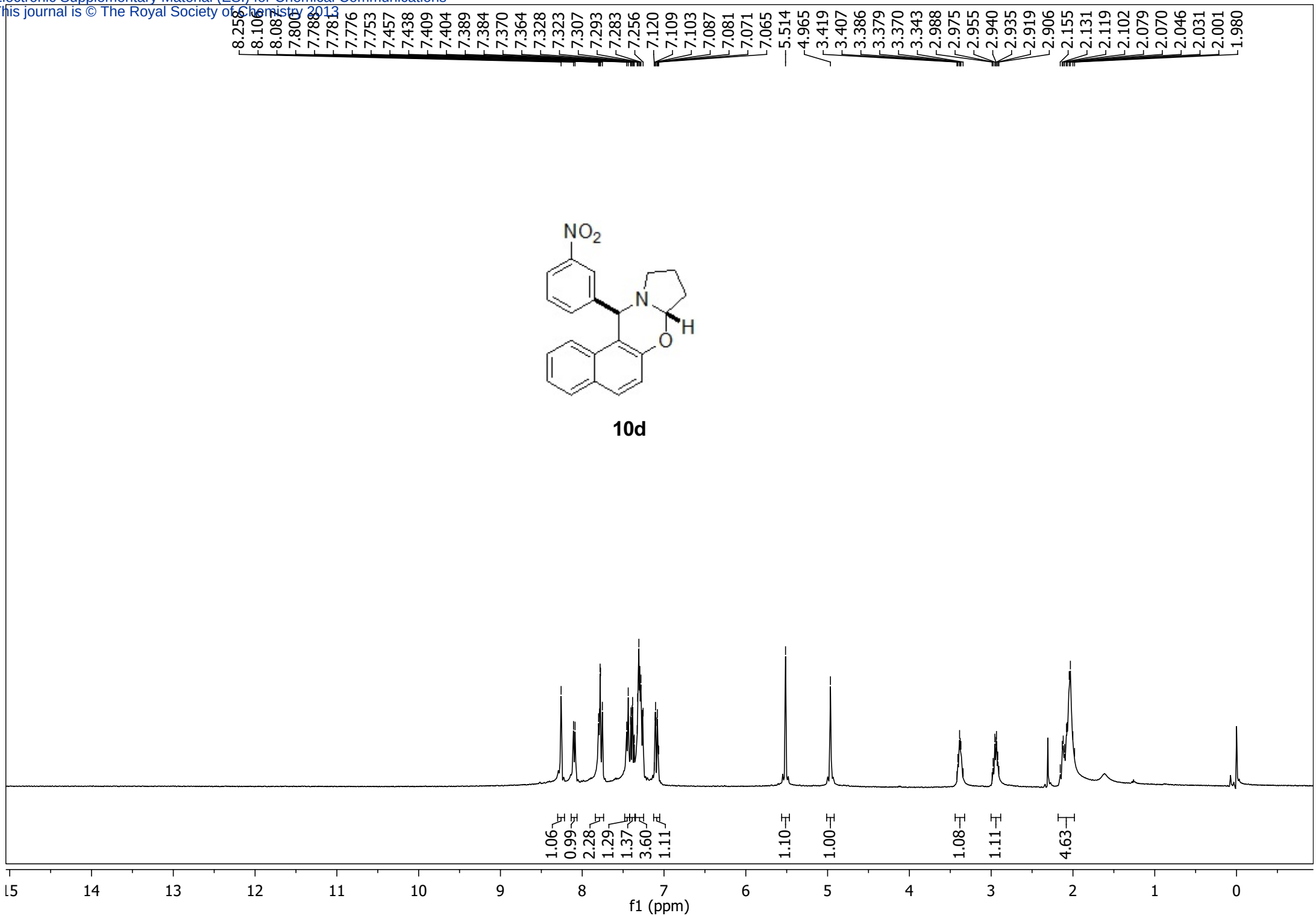
8.62 13.11 7.95 4.19 10.39 3.42 3.38 5.54 4.35 21.61 10.39



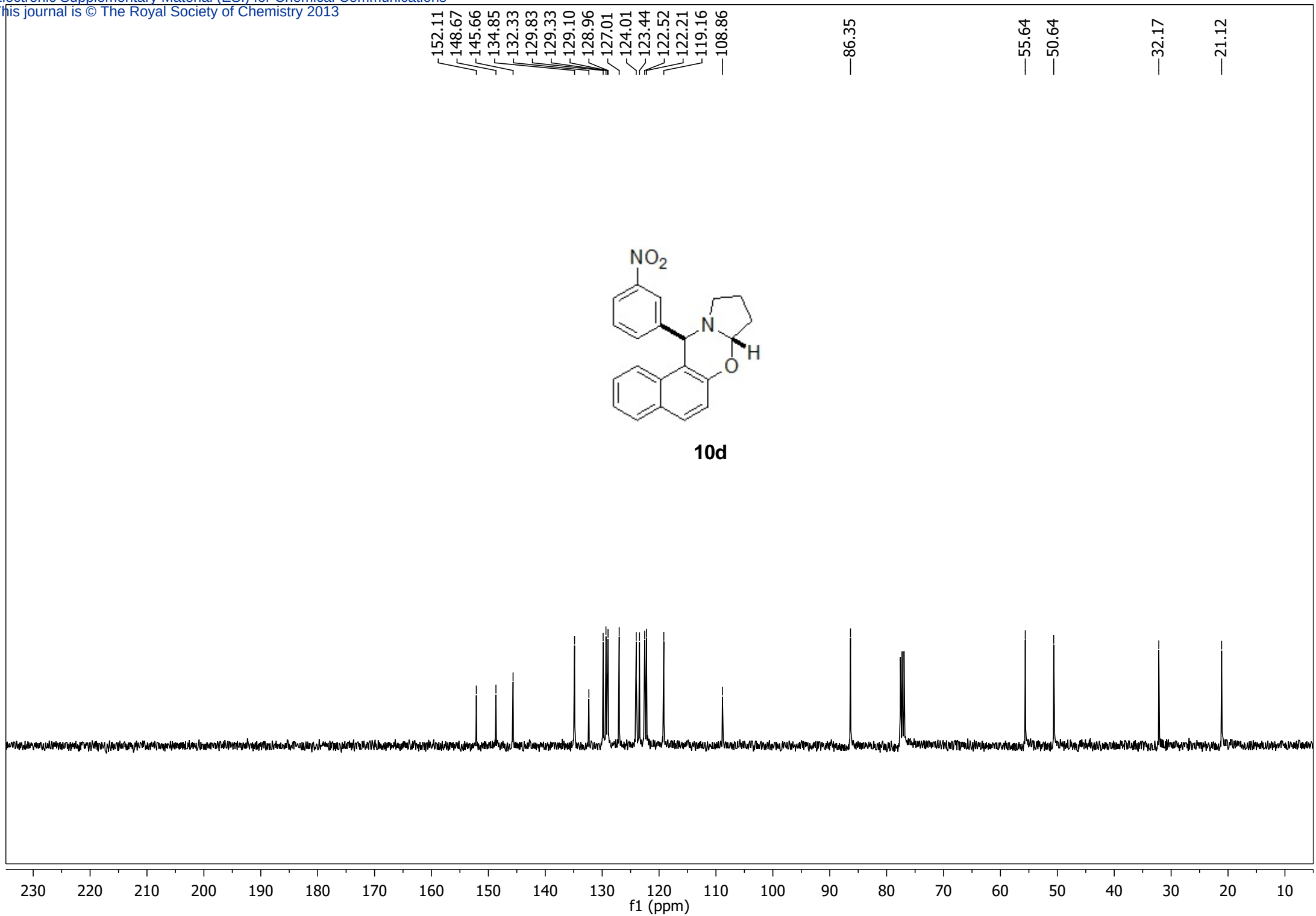
10b



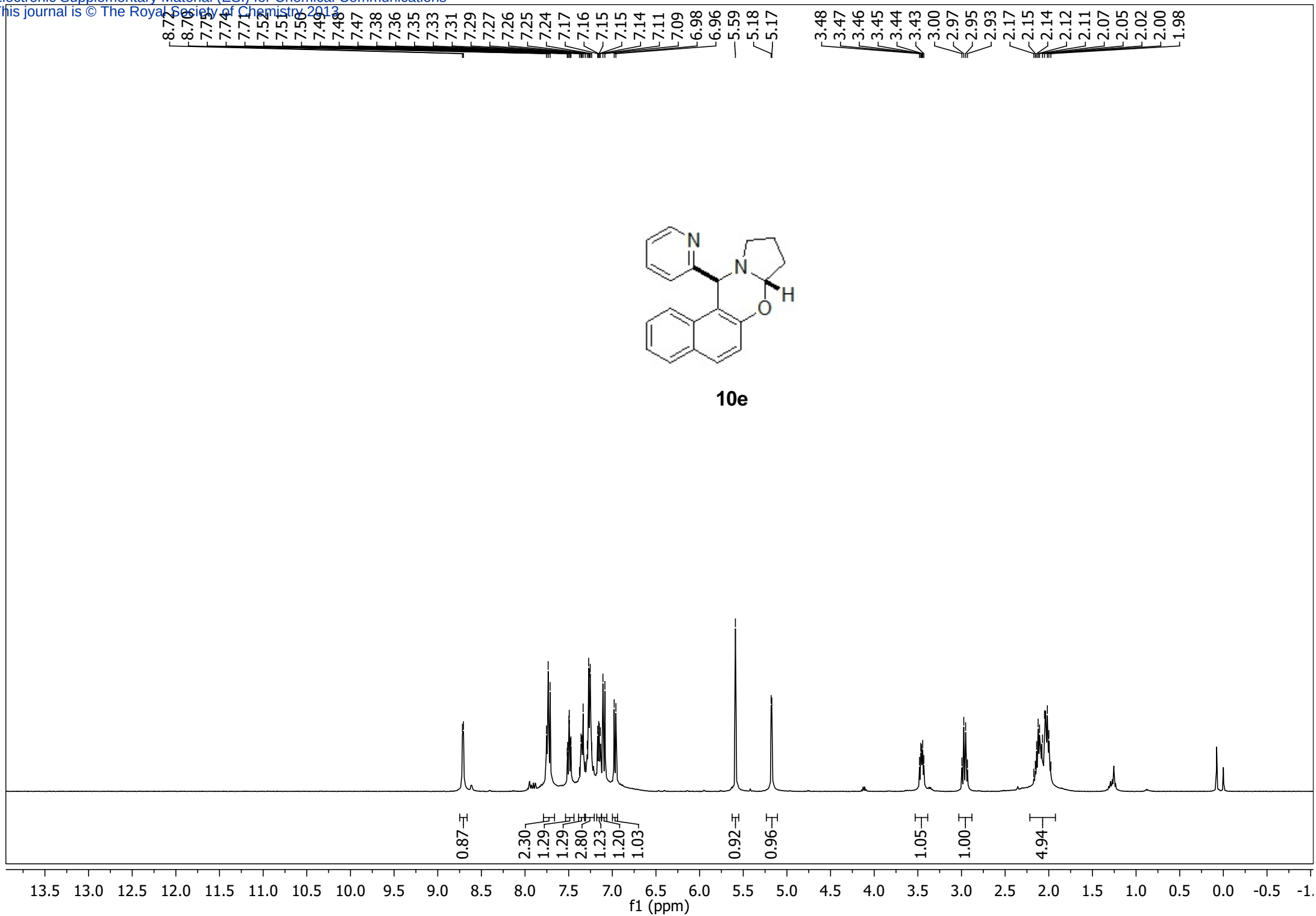


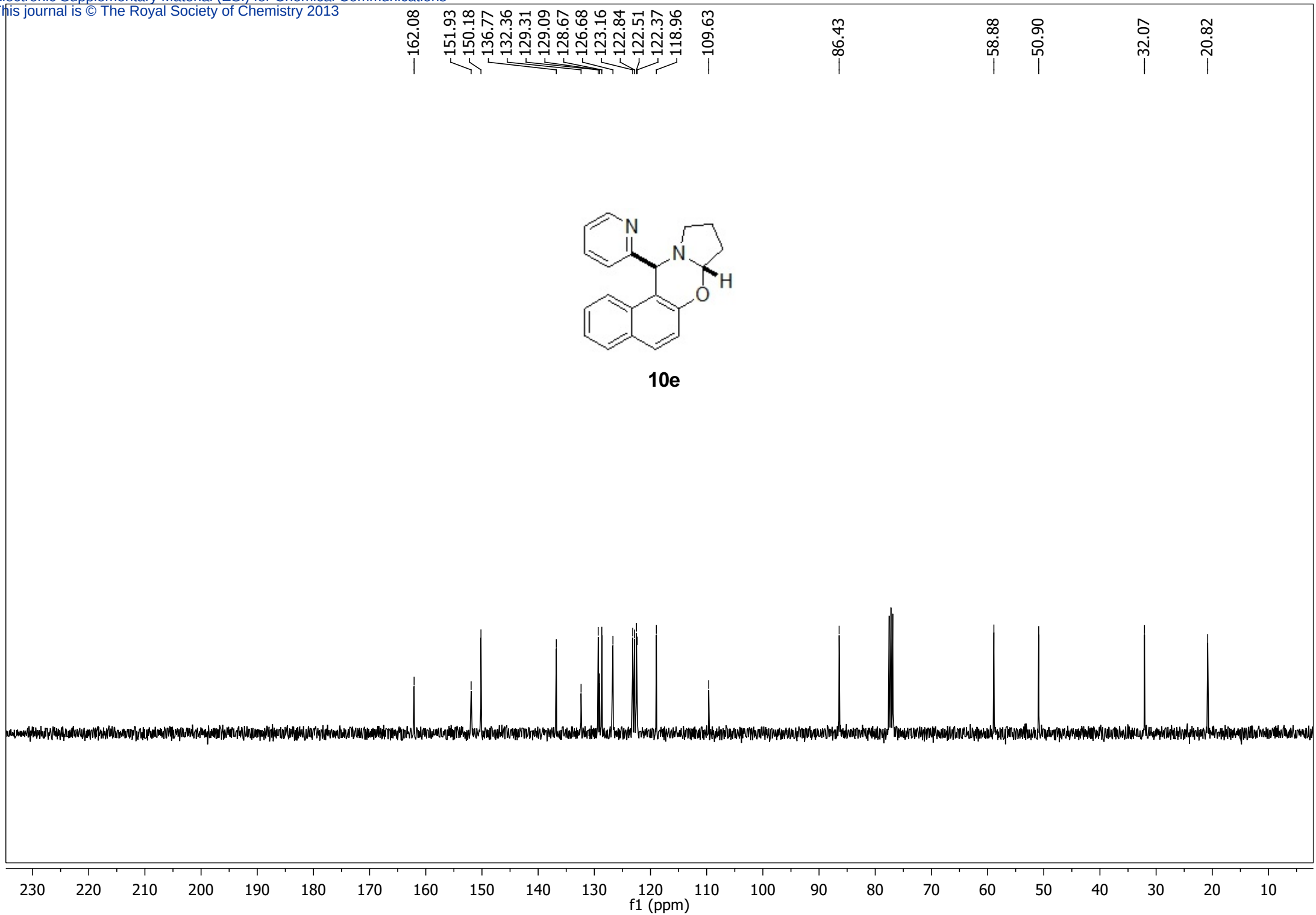


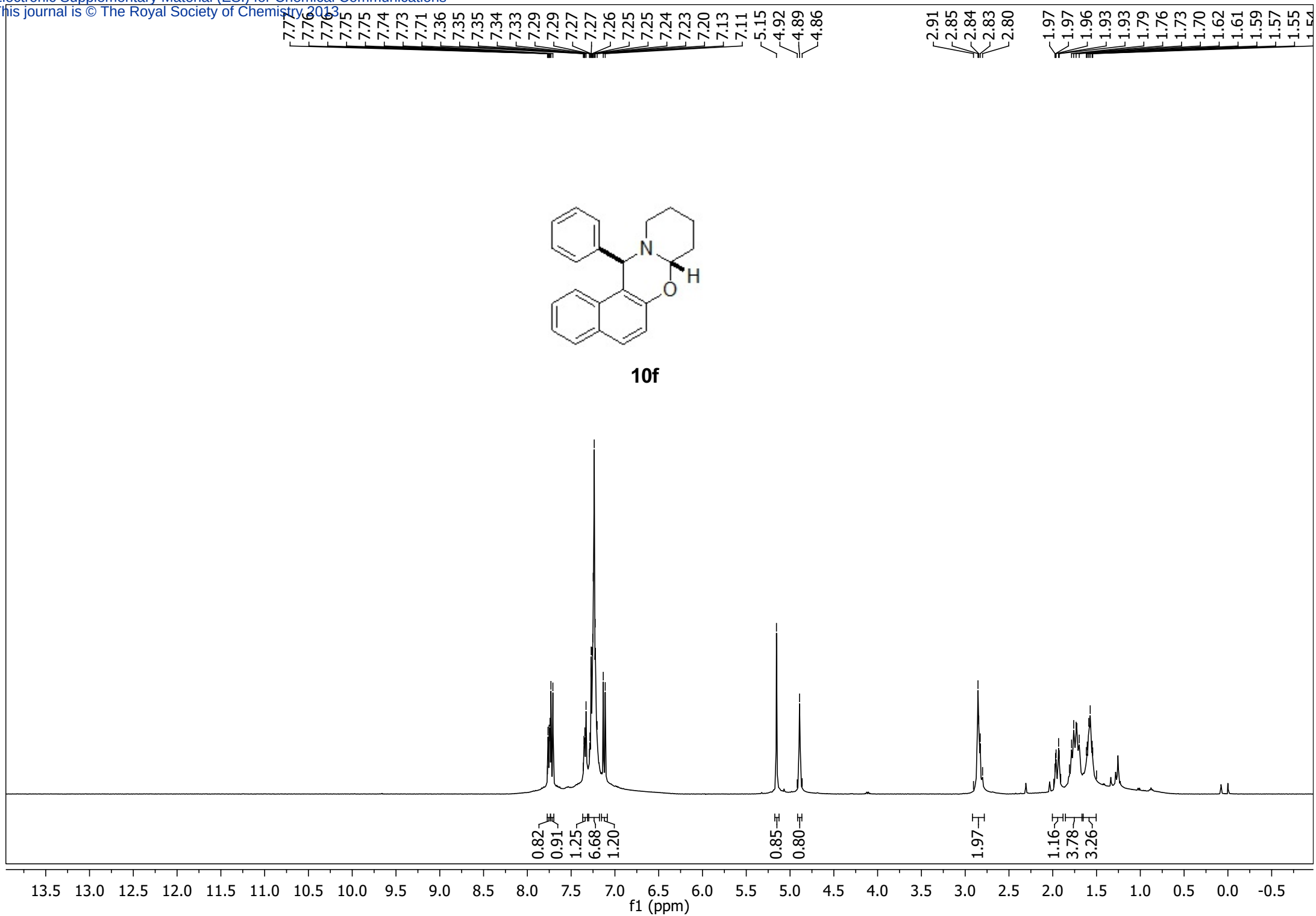
10d



10d



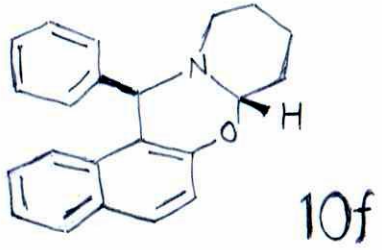




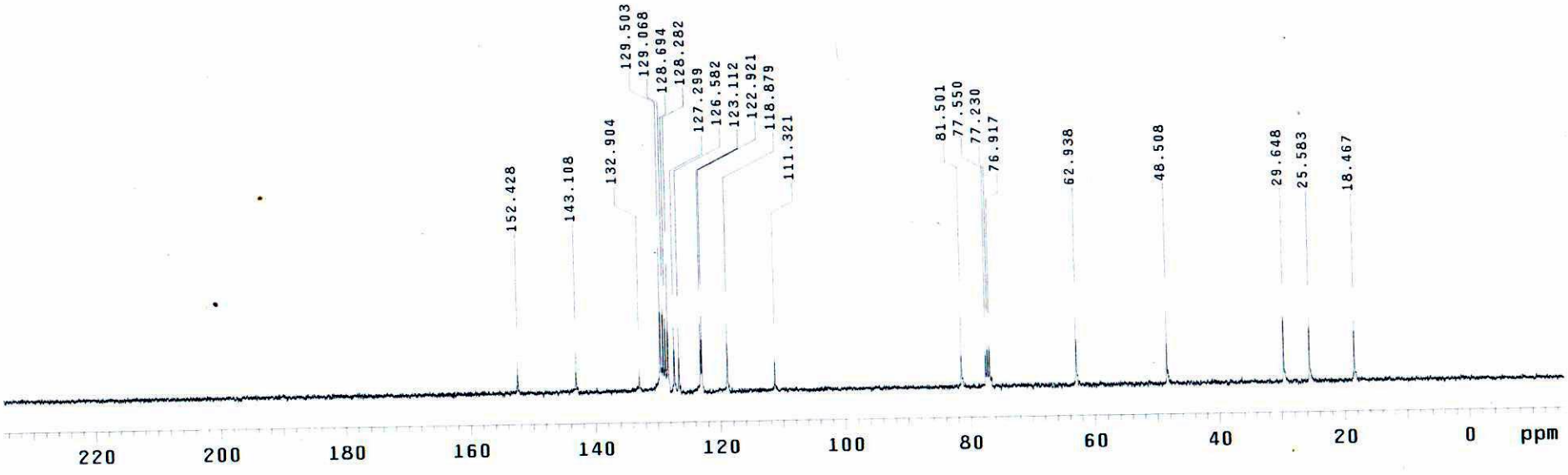
CKJ-1-222-13C

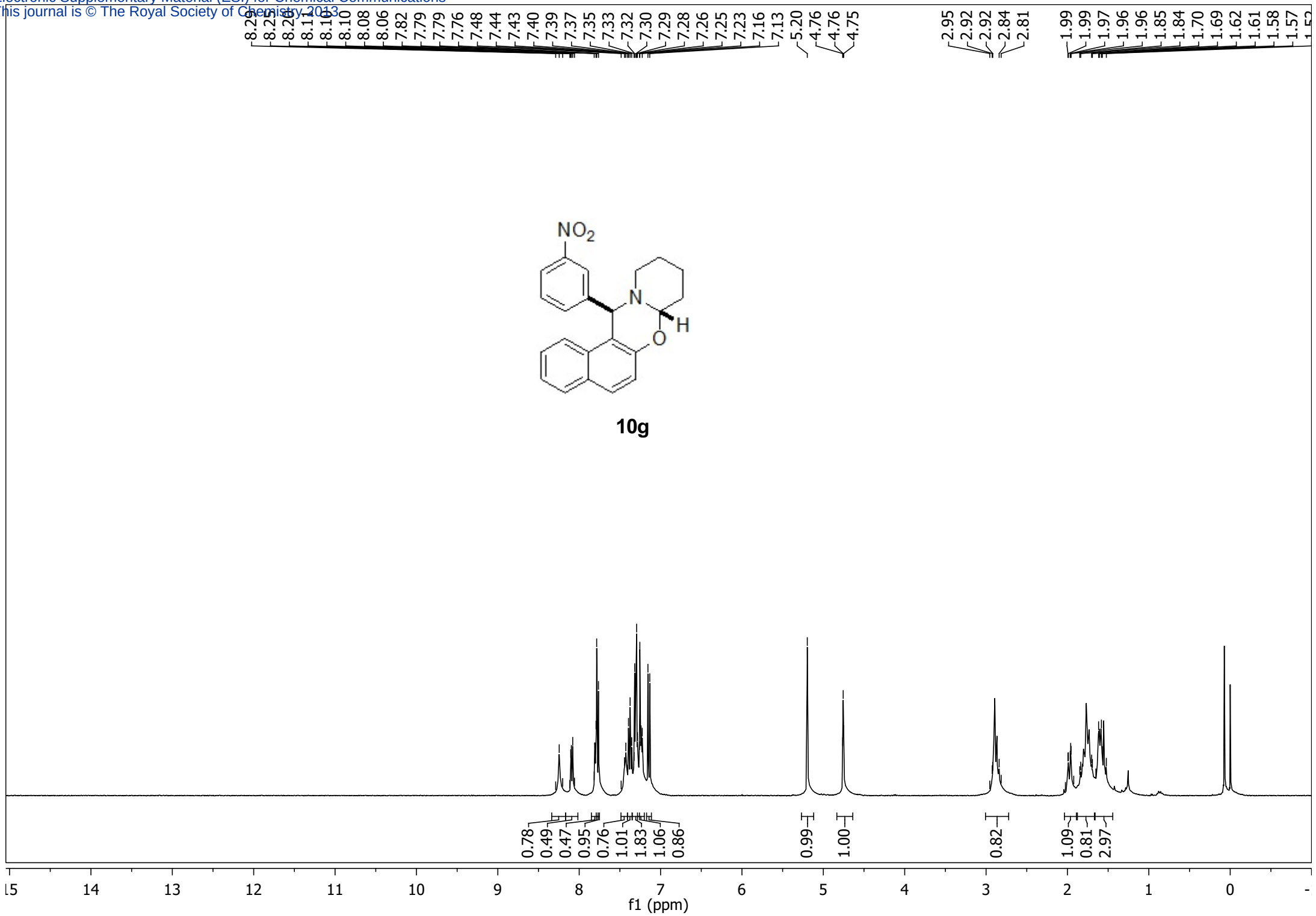
exp1 s2pul

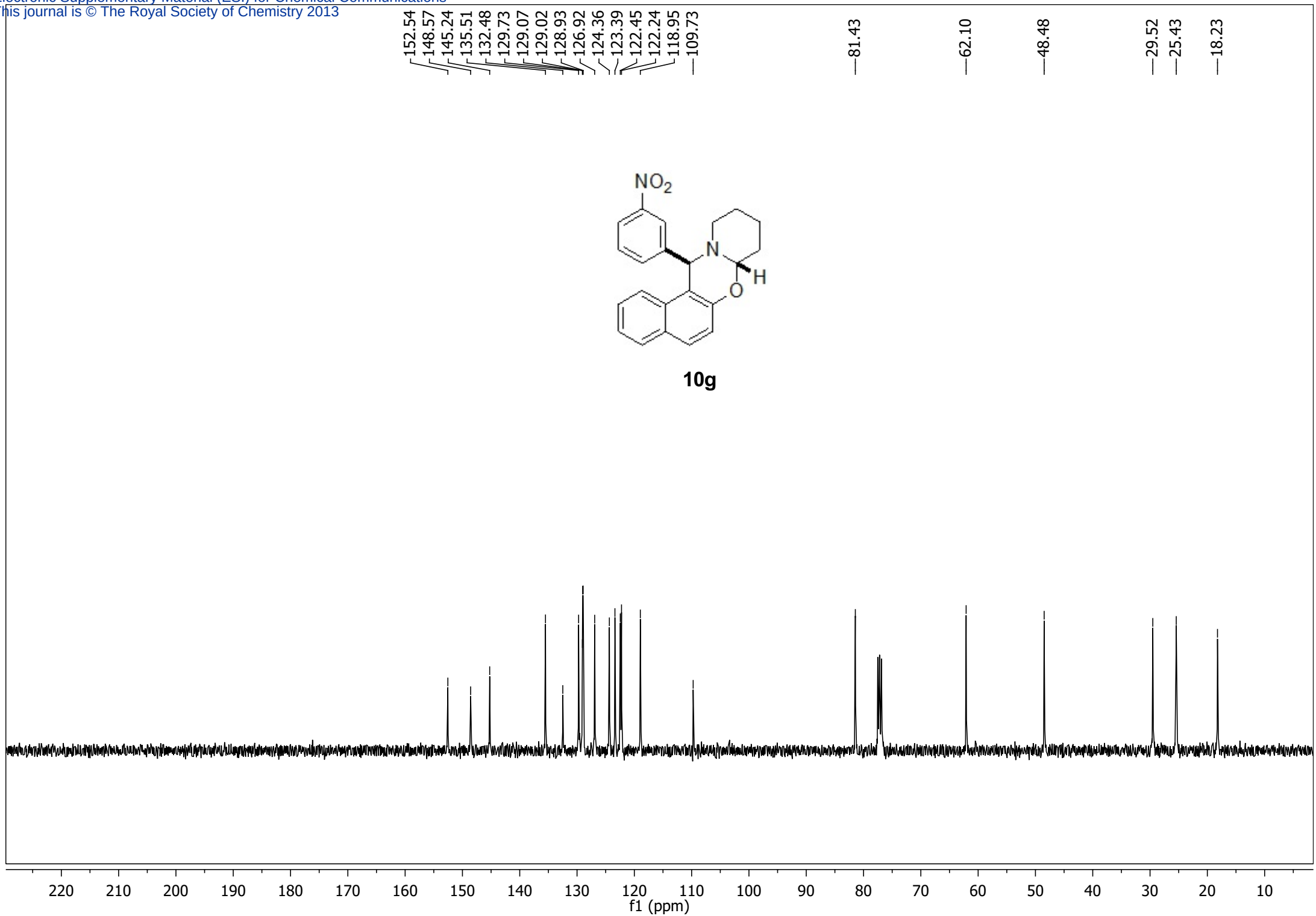
SAMPLE		SPECIAL	
date	May 9 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25125.6	pw90	9.400
at	1.199	alfa	20.000
np	60270	**FLAGS**	
fb	13800	il	n
bs	8	in	n
d1	1.000	dp	y
nt	3000	hs	nn
ct	456	**PROCESSING**	
TRANSMITTER		lb	2.00
tn	C13	fn	65536
sfrq	100.554	**DISPLAY**	
tof	1536.3	sp	-1522.5
tpwr	61	wp	25125.6
pw	4.700	rfl	9287.4
DECOUPLER		rfp	7764.9
dn	H1	rp	-71.7
dof	0	lp	-258.5
dm	yyy	**PLOT**	
dmm	w	wc	250
dpwr	42	sc	0
dmf	8500	vs	23
		th	4
		nm	no ph

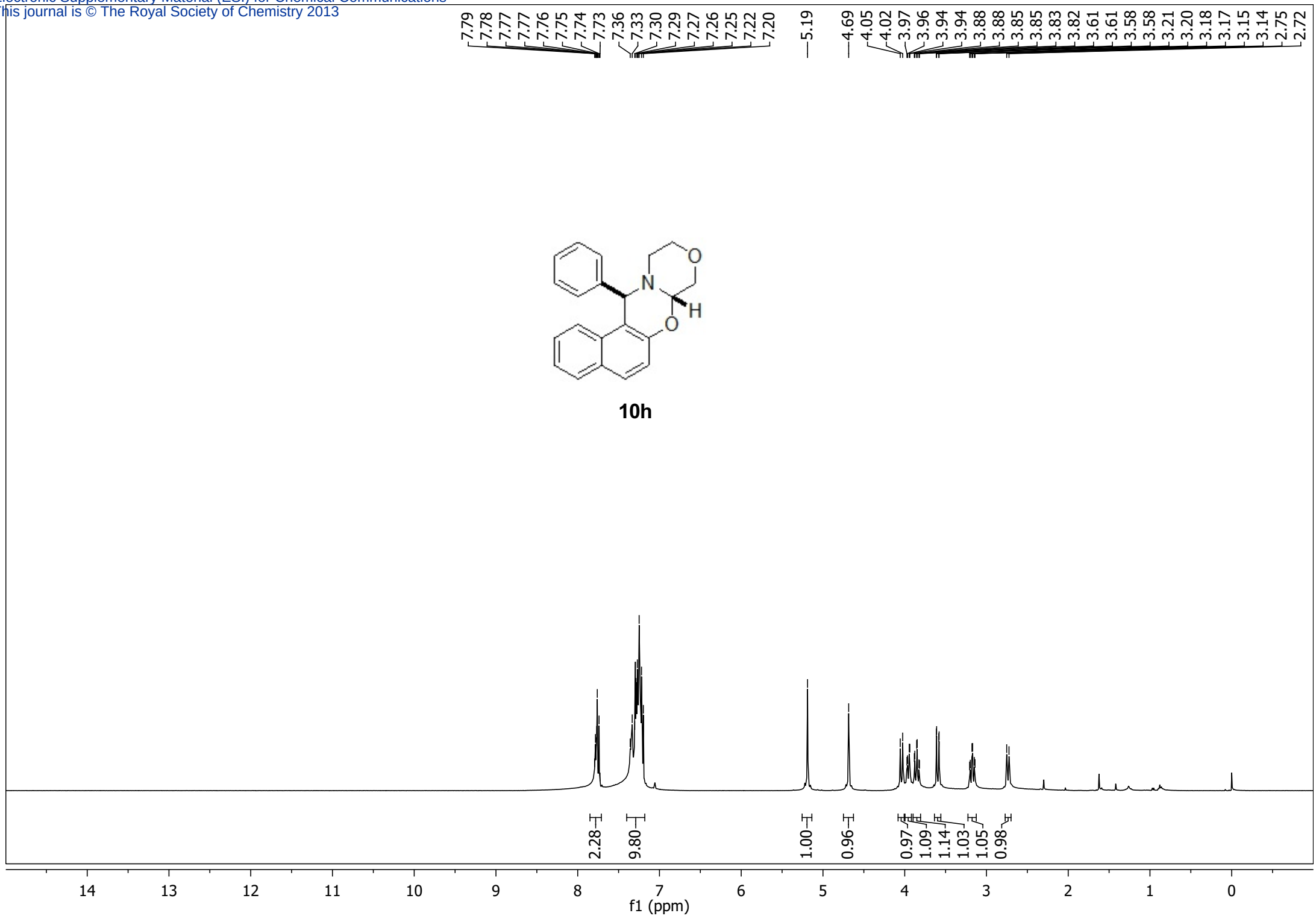


10f







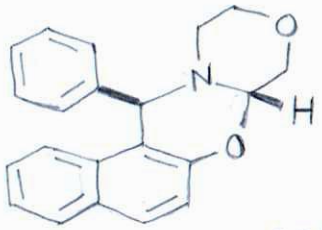


10h

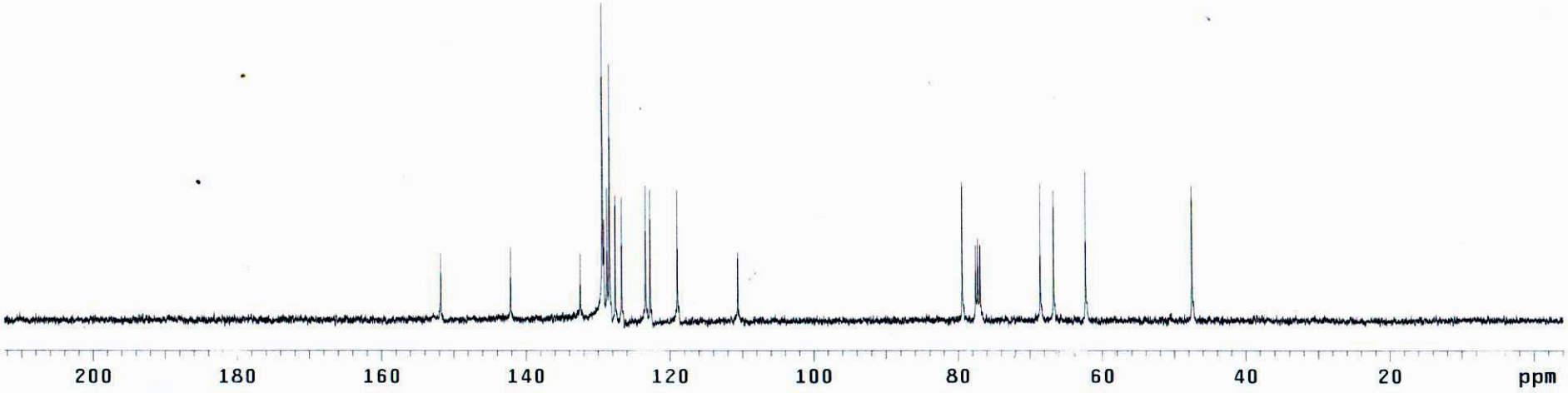
CKJ-1-215B

exp1 s2pul

SAMPLE		SPECIAL	
date	Apr 18 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25125.6	pw90	9.400
at	1.199	alfa	20.000
np	60270	FLAGS	
fb	13800	il	n
bs	4	in	n
d1	1.000	dp	y
nt	3000	hs	nn
ct	352	PROCESSING	
TRANSMITTER		lb	2.00
tn	C13	fn	65536
sfrq	100.554	DISPLAY	
tof	1536.3	sp	-406.1
tpwr	61	wp	21757.9
pw	4.700	rfl	9292.8
DECOUPLER		rfp	7764.9
dn	H1	rp	-51.0
dof	0	lp	-281.2
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	42	sc	0
dmf	8500	vs	50
		th	5
		nm	no ph



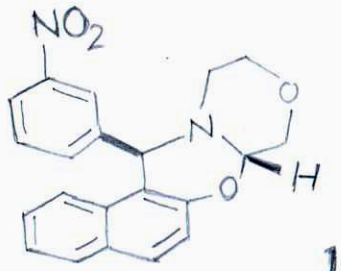
10h



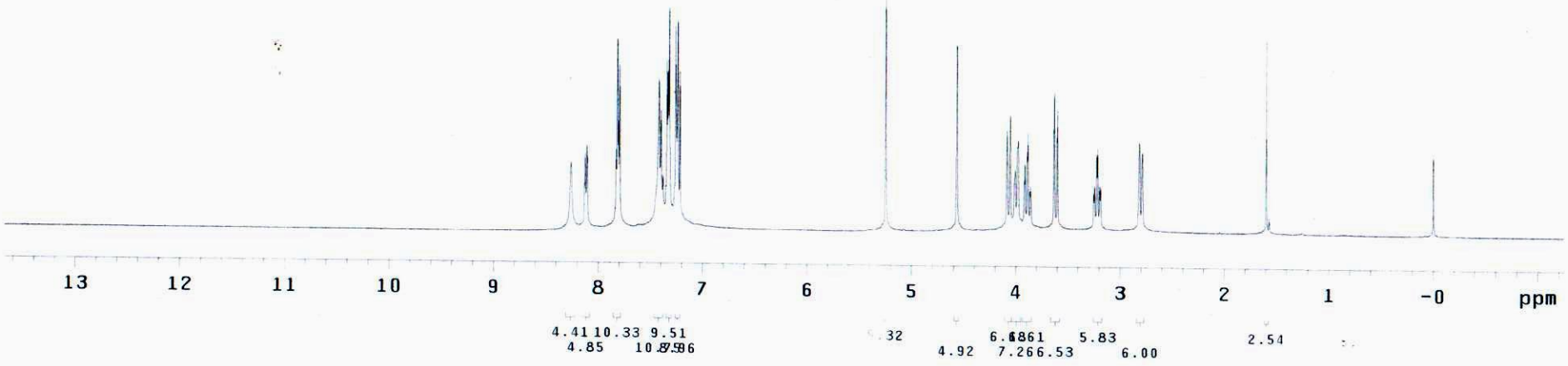
SH-1-083-B

exp1 s2pul

SAMPLE		SPECIAL	
date	Mar 20 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	14.100
at	1.994	alfa	20.000
np	39912	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.10
tn	H1	fn	65536
sfrq	399.853	DISPLAY	
tof	362.8	sp	-501.3
tpwr	62	wp	5971.7
pw	7.050	rfl	2605.8
DECOUPLER		rfp	0
dn	C13	rp	93.9
dof	0	lp	-146.4
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	50	sc	0
dmf	15900	vs	37
		th	3
		nm	cdc ph



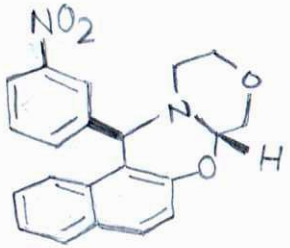
10i



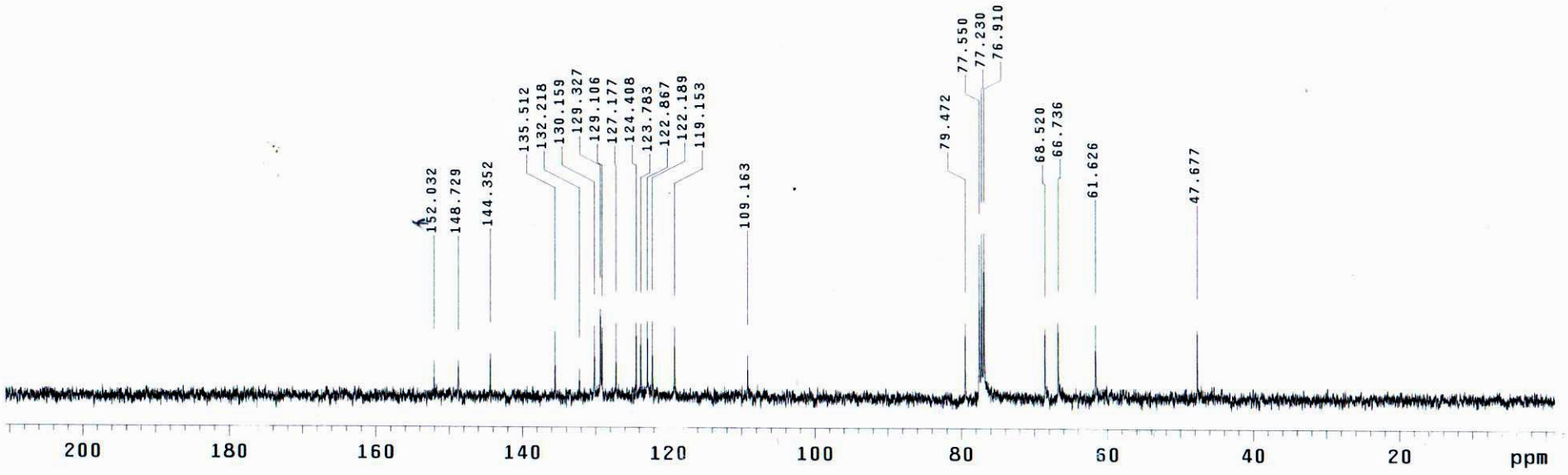
CKJ-SH-1-083B 13C

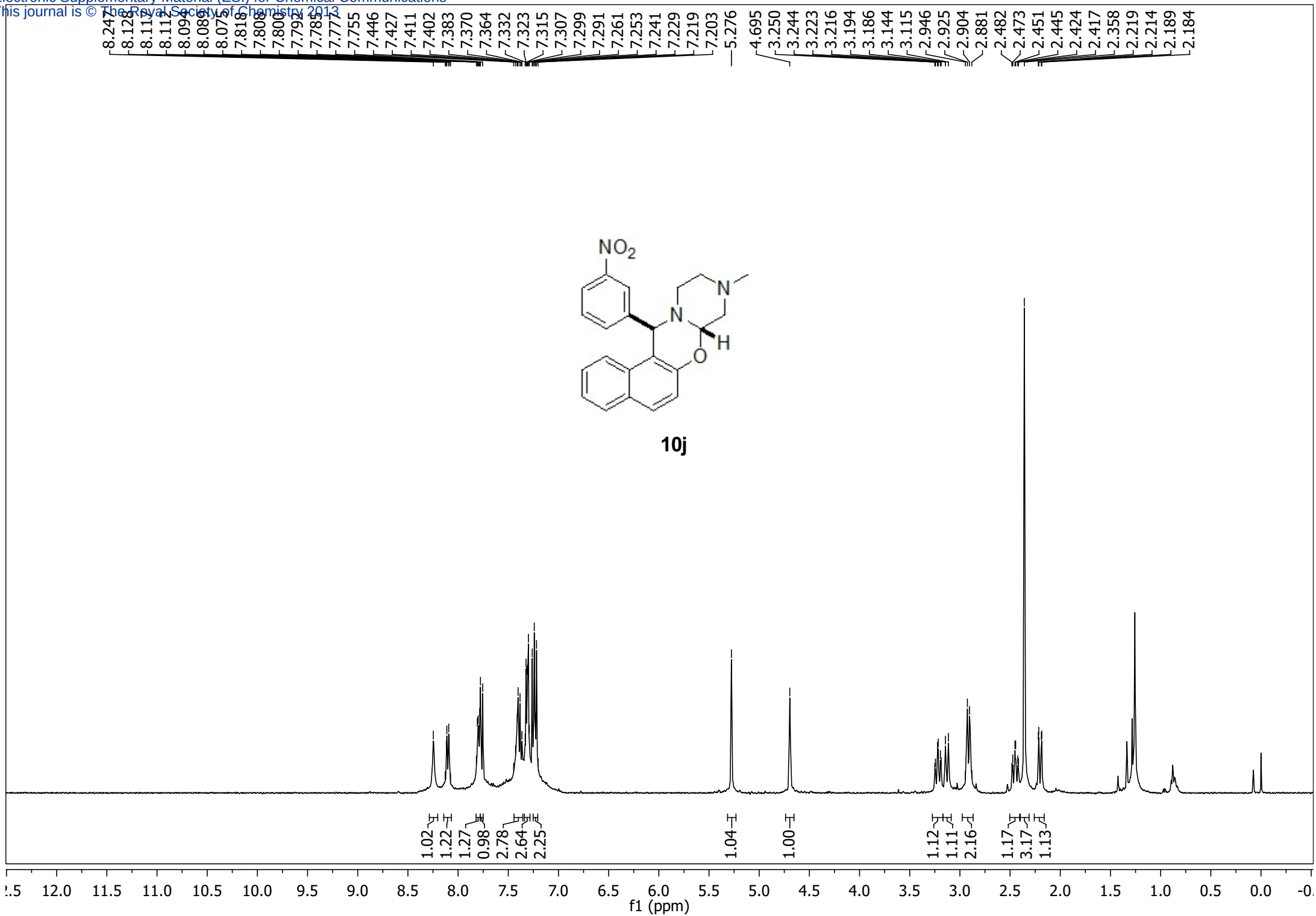
exp1 s2pul

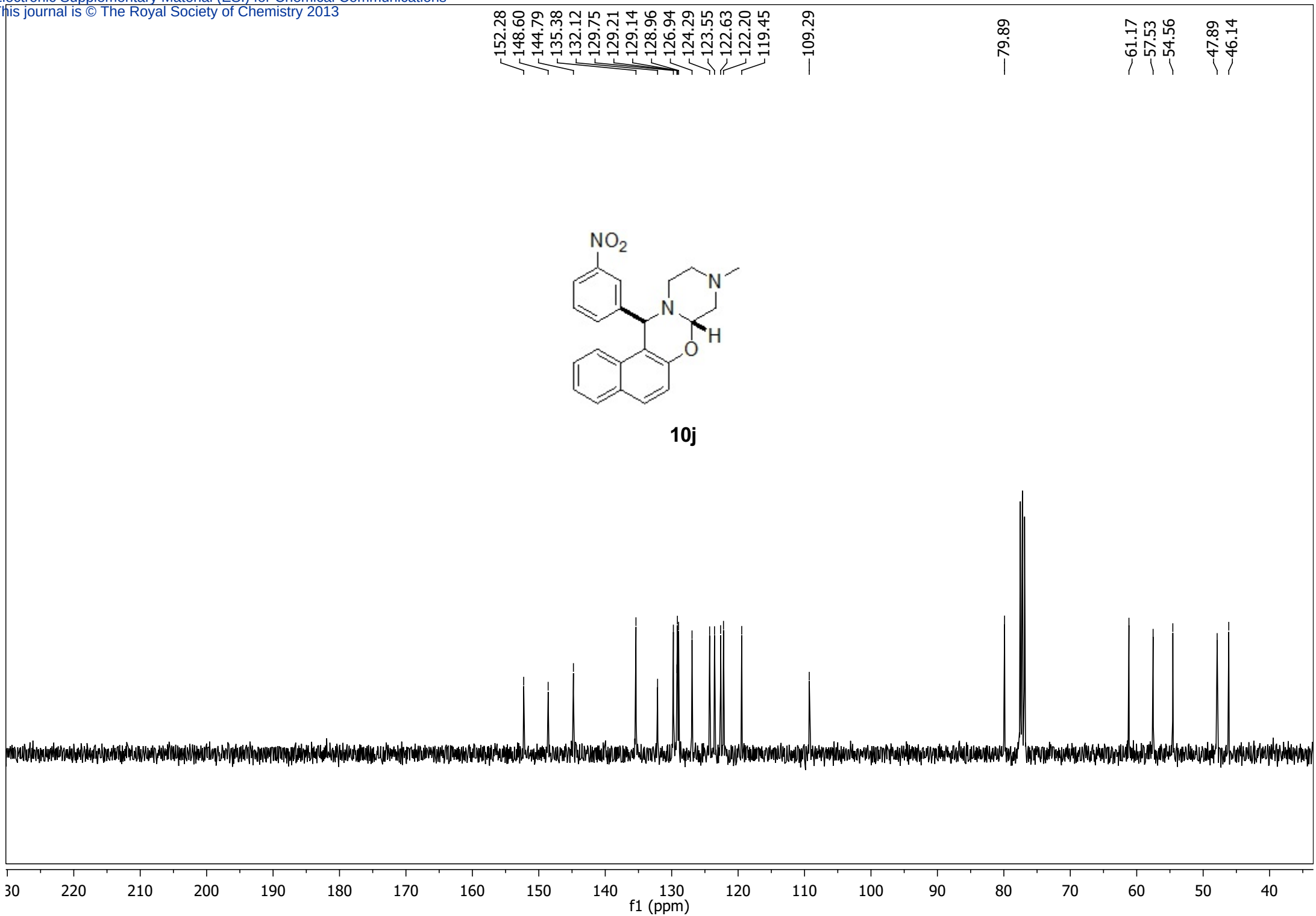
SAMPLE		SPECIAL	
date	Apr 18 2013	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25125.6	pw90	9.400
at	1.199	alfa	20.000
np	60270	FLAGS	
fb	13800	il	n
bs	4	in	n
d1	1.000	dp	y
nt	2000	hs	nn
ct	404	PROCESSING	
TRANSMITTER		lb	2.00
tn	C13	fn	65536
sfrq	100.554	DISPLAY	
tof	1536.3	sp	-123.9
tpwr	61	wp	21295.5
pw	4.700	rfl	9275.2
DECOUPLER		rfp	7764.9
dn	H1	rp	-88.6
dof	0	lp	-271.4
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	42	sc	0
dmf	8500	vs	26
		th	3
		nm	no ph

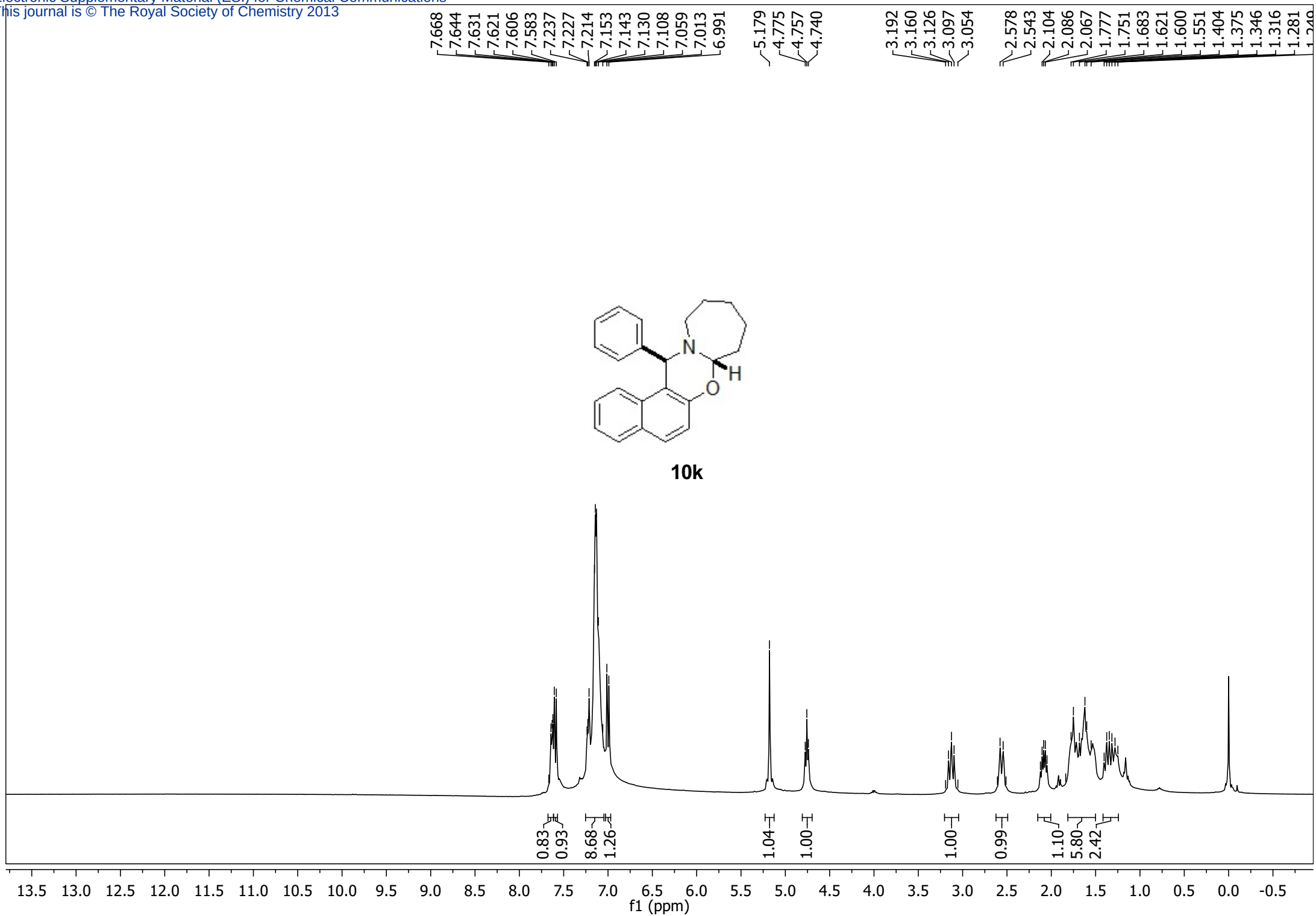


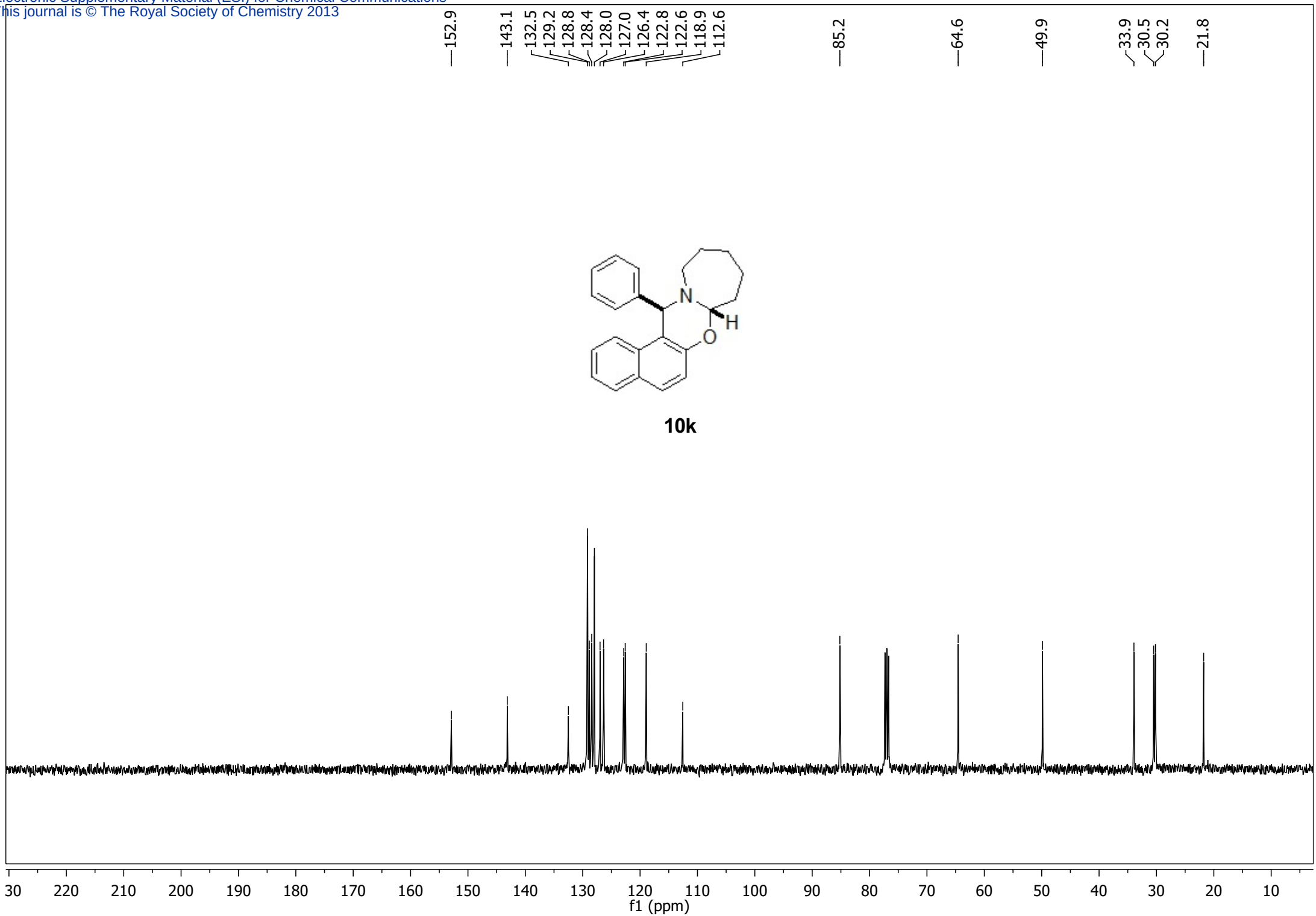
10i

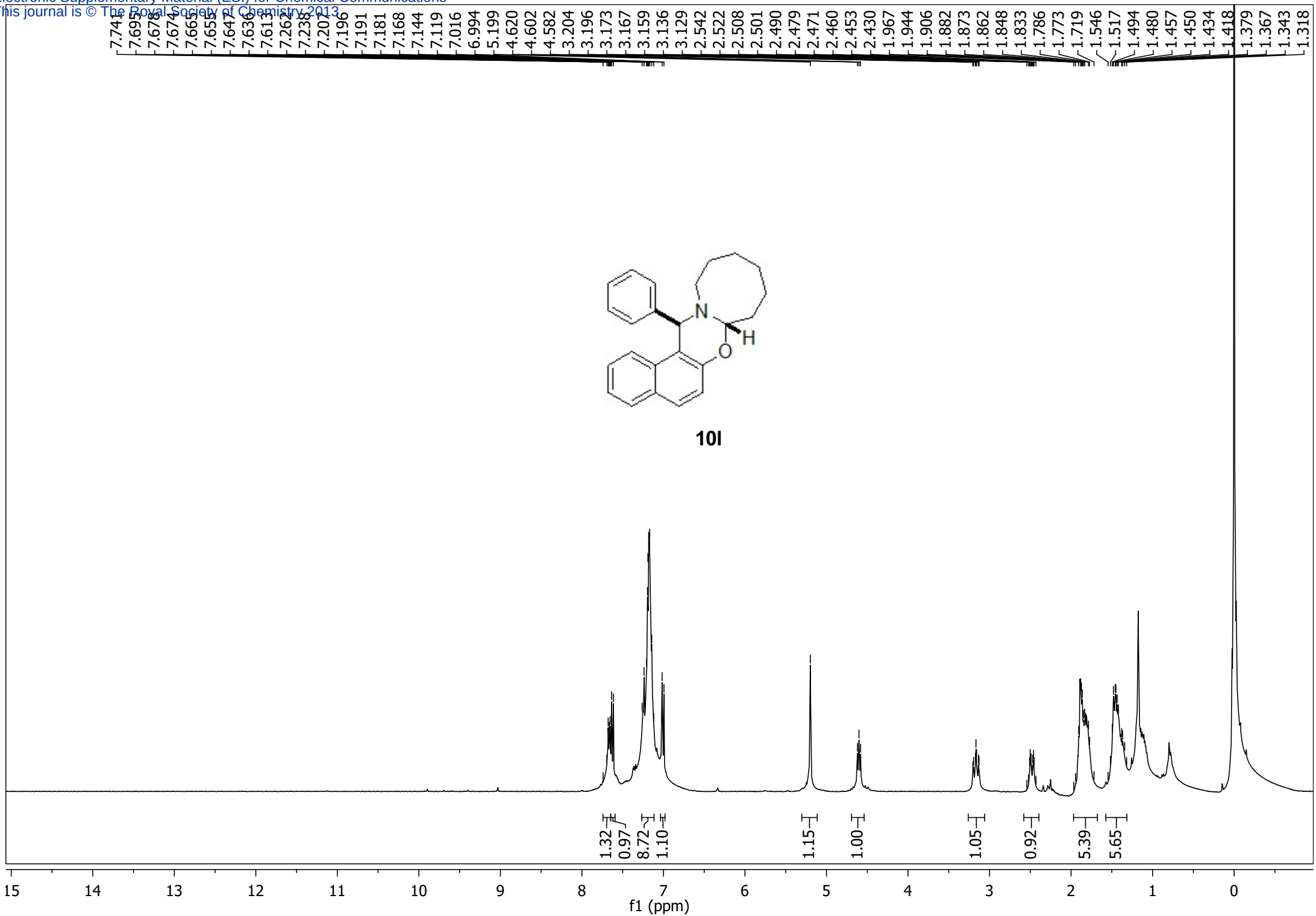




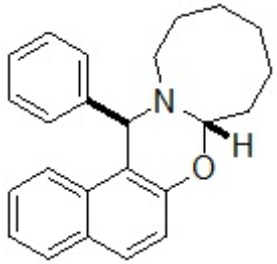




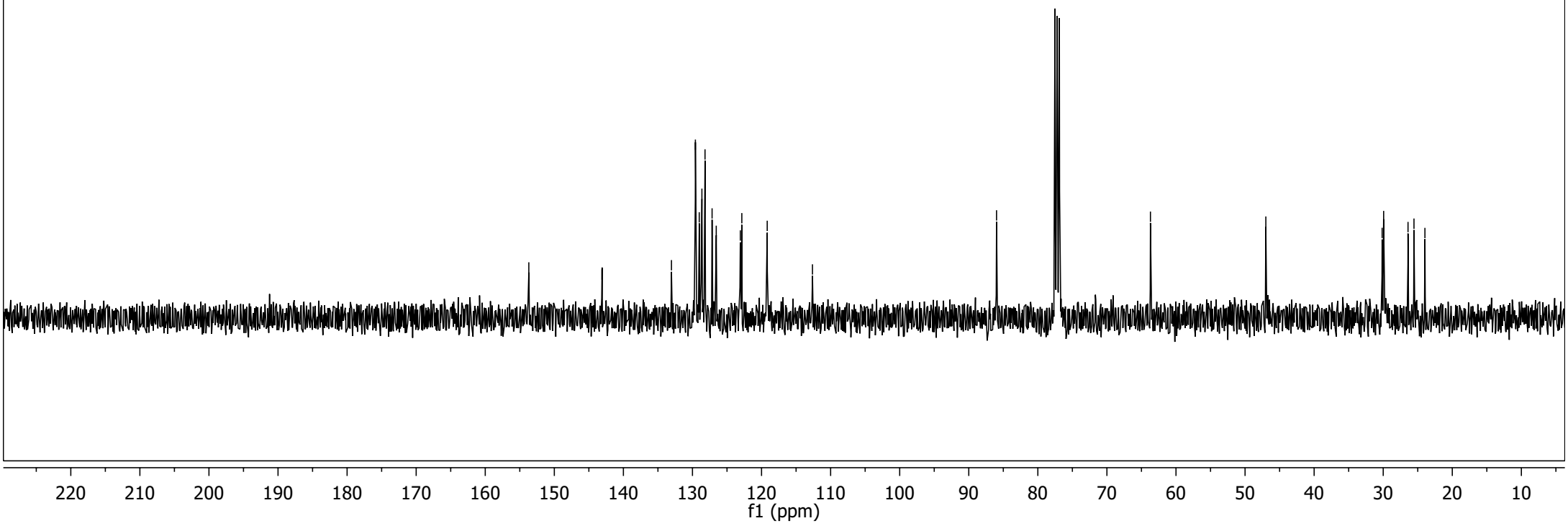


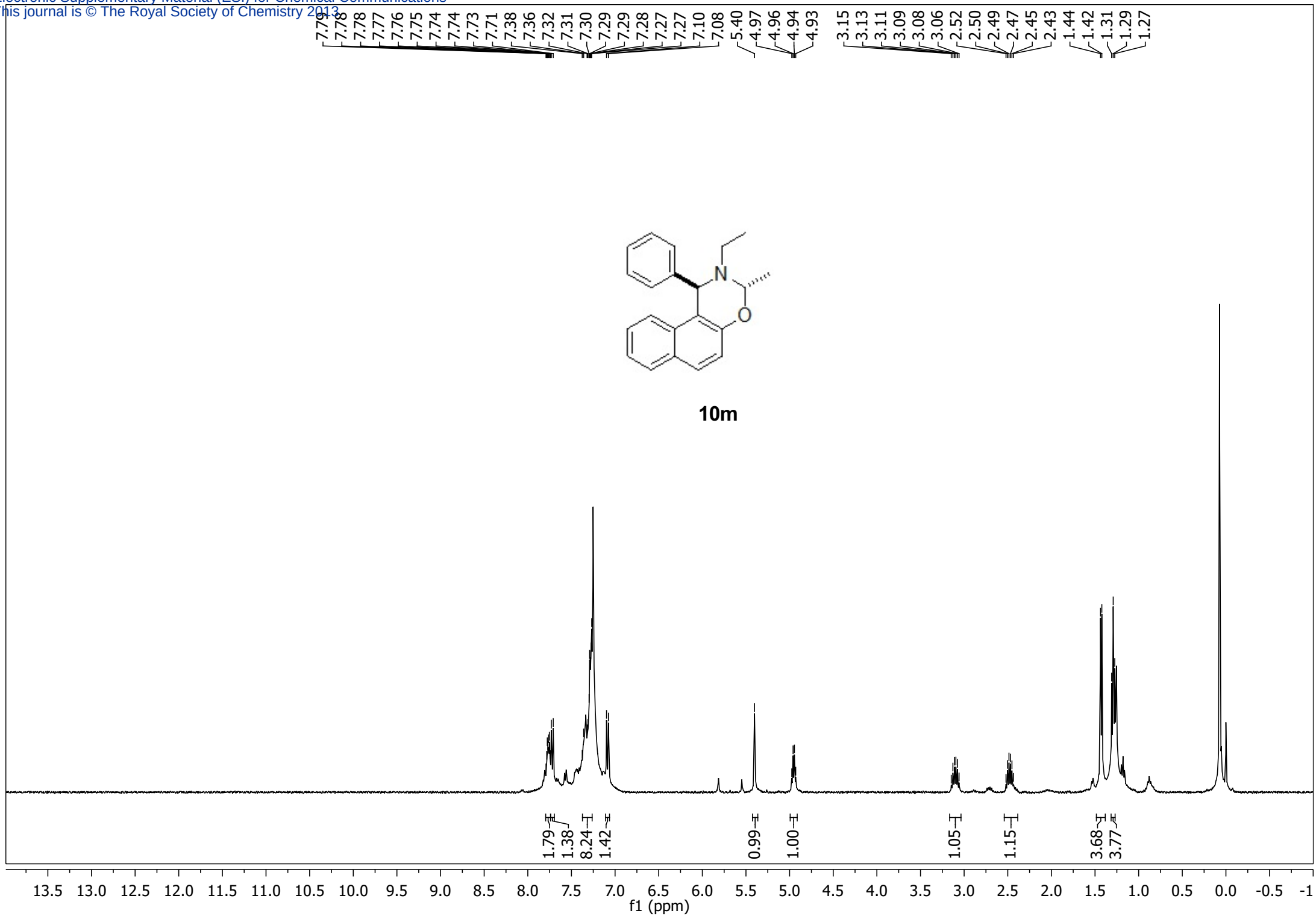


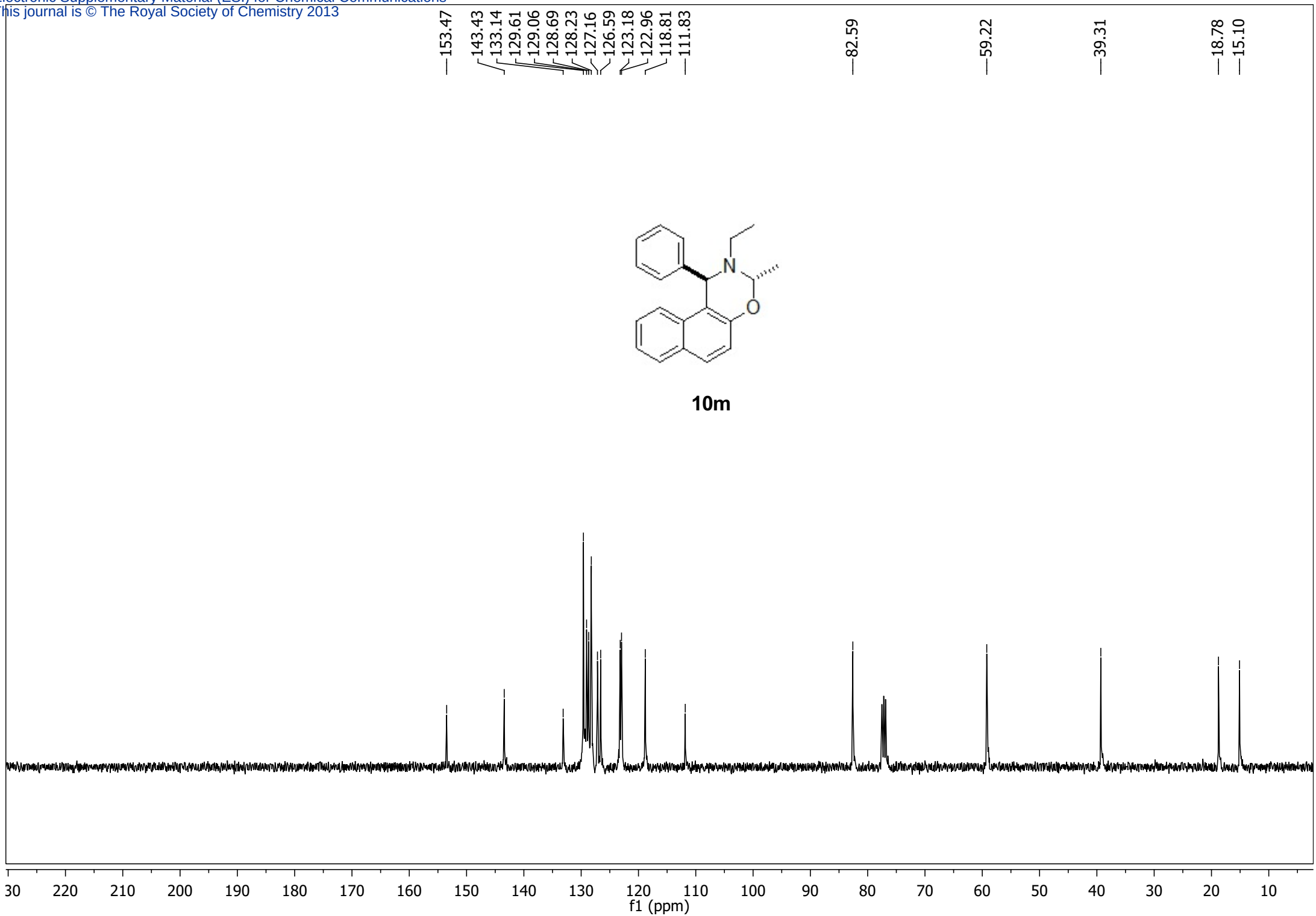
153.69
143.10
133.04
129.58
129.02
128.63
128.18
127.16
126.56
123.07
122.86
119.18
112.63
85.98
63.70
46.99
30.16
29.94
26.41
25.55
23.96

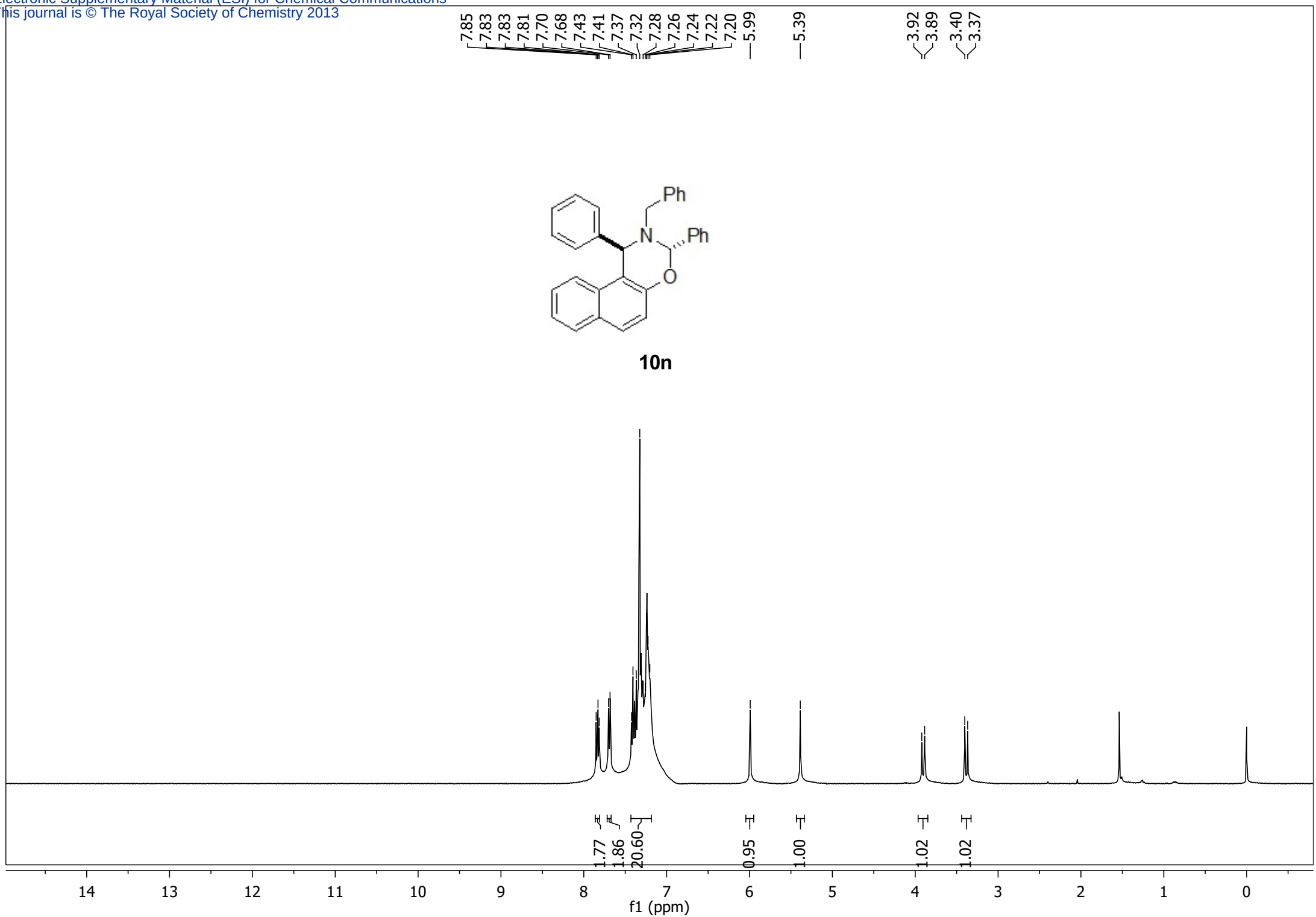


10l

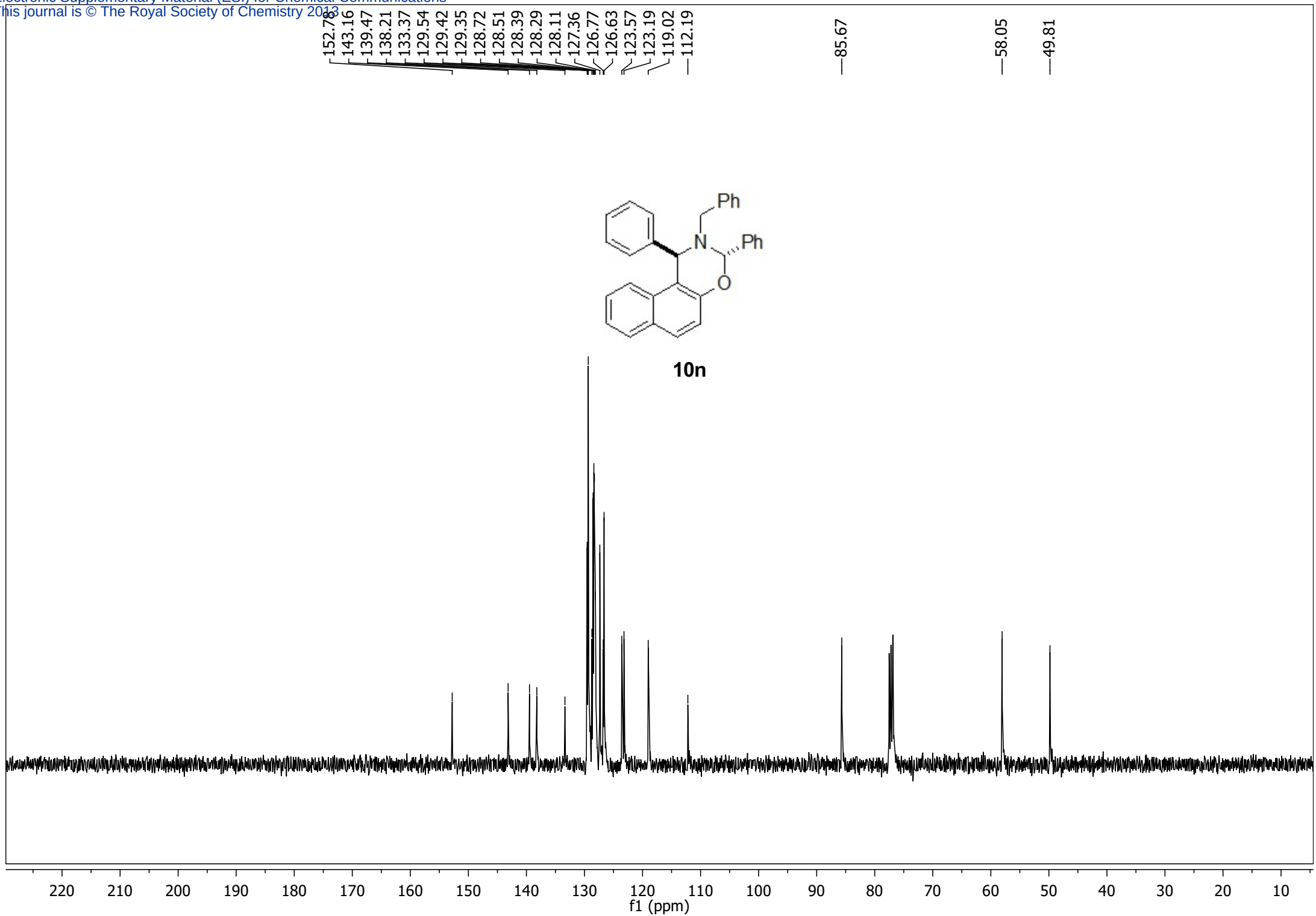


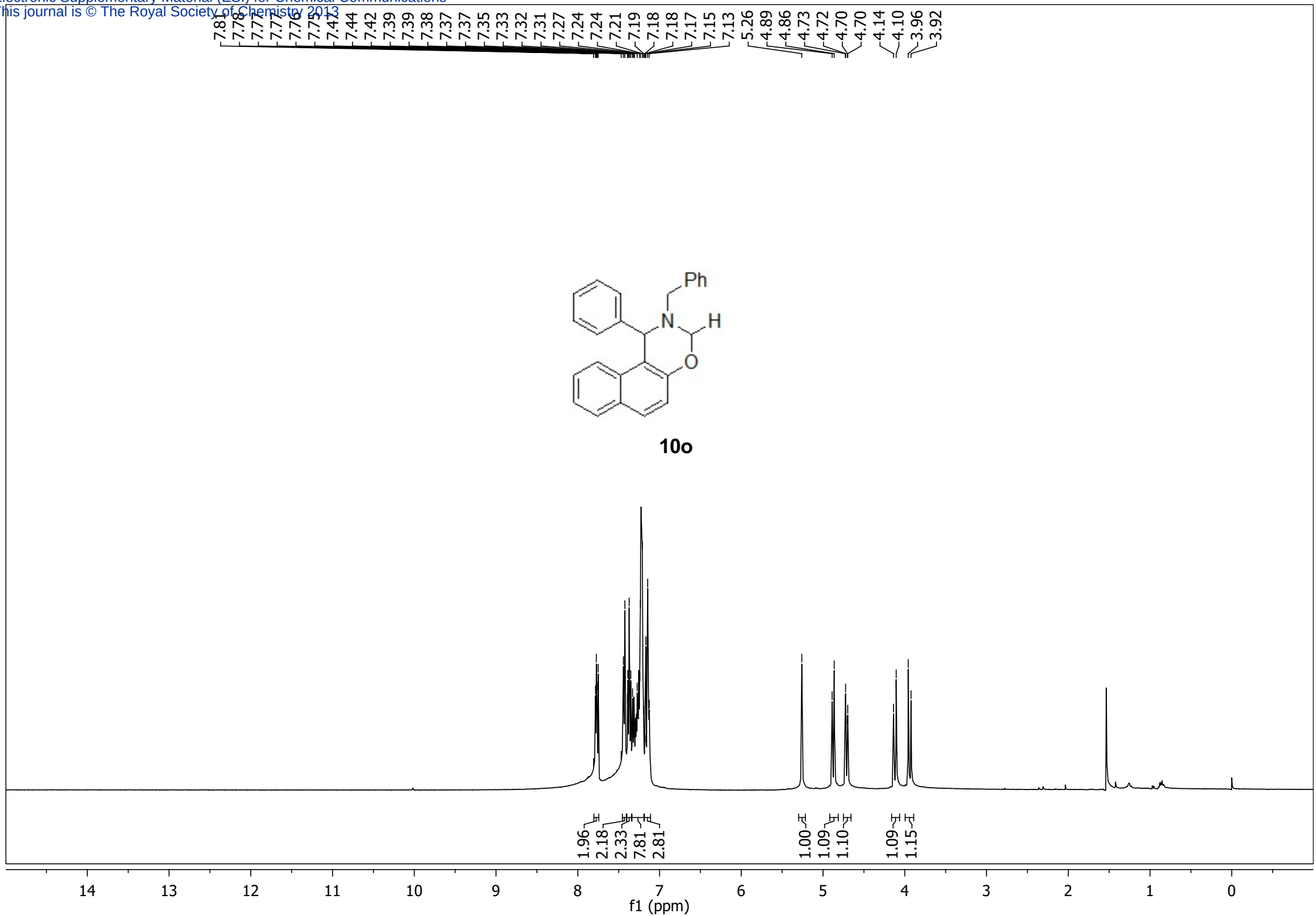


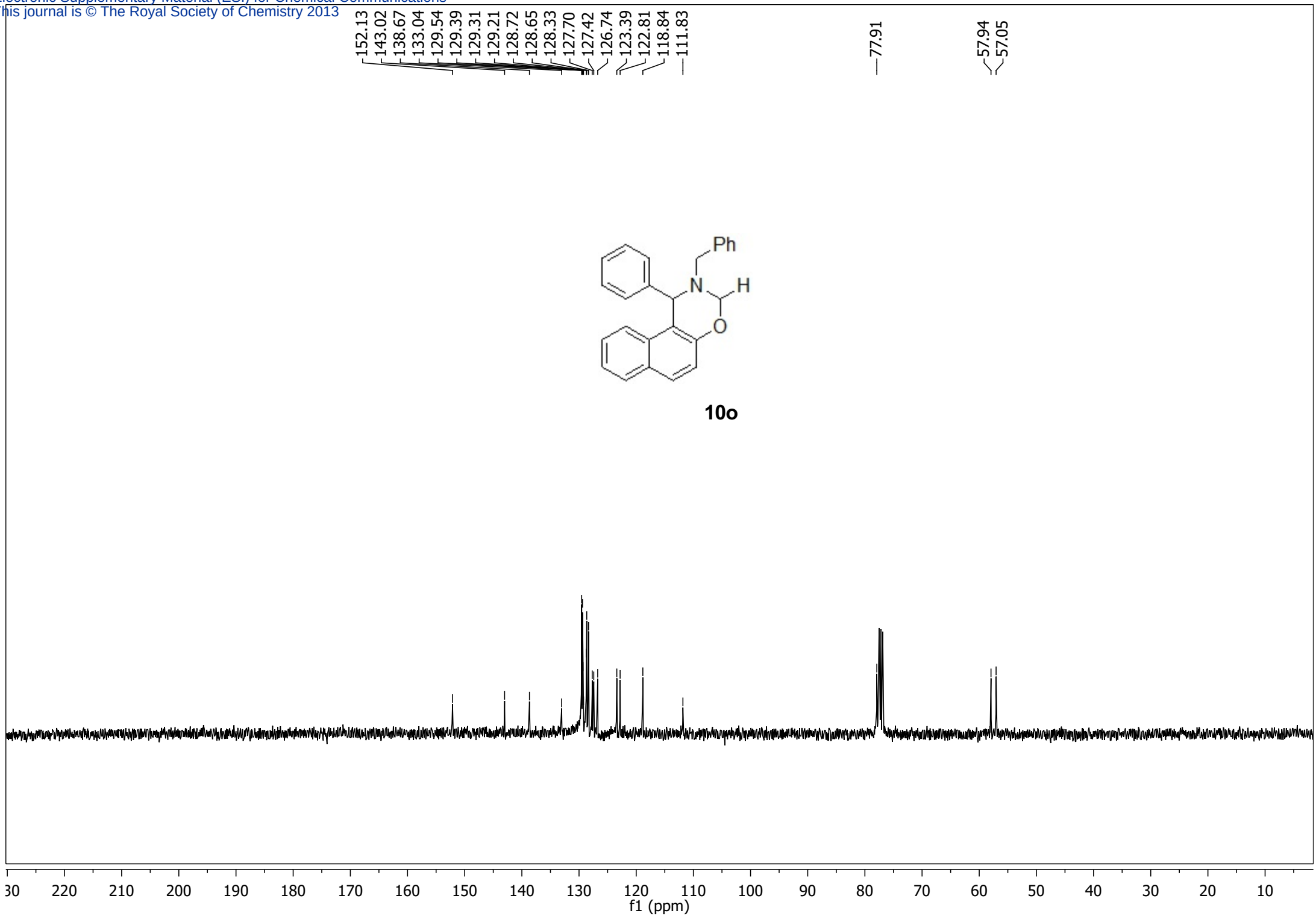


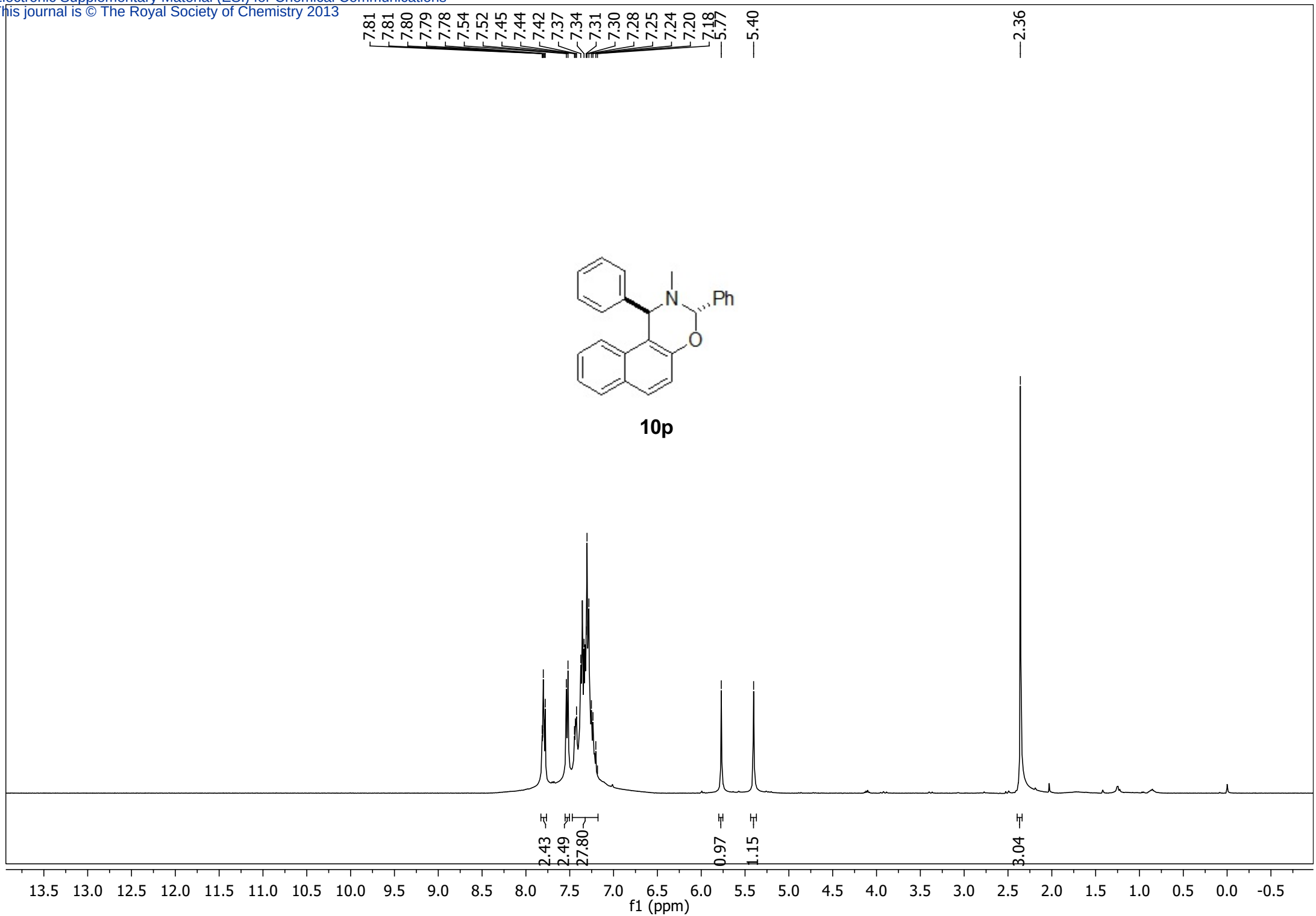


10n





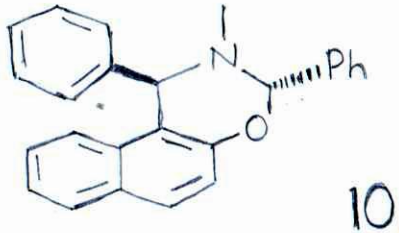




-KJ-1-184A-13C

```
expl  s2pul

      SAMPLE              SPECIAL
date    Apr 12 2013   temp        not used
solvent       CDCl3   gain        not used
file            exp   spin        not used
   ACQUISITION        hst            0.008
sw           25125.6   pw90           9.400
at             1.199   alfa          20.000
np             60270        FLAGS
fb             13800   il                 n
bs                 4   in                 n
d1             1.000   dp                 y
nt              5000   hs                nn
ct               988        PROCESSING
   TRANSMITTER         lb              2.00
tn                C13   fn             65536
sfrq          100.554        DISPLAY
tof            1536.3   sp           -1517.9
tpwr               61   wp           25125.6
pw              4.700   rfl           9282.8
     DECOUPLER         rfp           7764.9
dn                 H1   rp             -77.9
dof                 0   lp            -271.4
dm                yyy         PLOT
dmm                 w   wc               250
dpwr               42   sc                 0
dmf              8500   vs                38
                        th                 5
                        nm  no  ph
```



10p