Electronic Supplementary Information (ESI)

For

Iron-Catalysed Oxidative Amidation of Alcohols with Amines

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Experimental Procedures

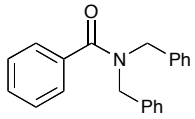
General Information.

All reagents and solvents were as obtained by commercial source. All the reactions were carried out under N_2 atmosphere using standard techniques. Column chromatography was generally performed on silica gel (pore size 60 A°, 40-63 mm particle size) and reactions were monitored by thin-layer chromatography (TLC) analysis was performed with Merck Kieselgel 60 F254 plates and visualized using UV light at 254 nm and KMnO4 staining. 1H NMR and 13C NMR spectra were measured on a Bruker Avance III 400 spectrometer (400 MHz or 100 MHz, respectively) with CDCl3 as solvent and recordered in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet; br, broad. The coupling constants, J, are reported in Hertz (Hz). The IR spectra were recorded on a Jasco FTIR-480 Plus Fourier Transform spectrometer. Melting points were determined in open capillary tubes and are uncorrected. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

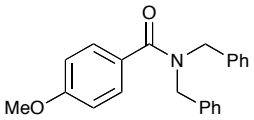
General procedures for amides 4a-q: An amine (0.32 mmol) was added to a solution of *N*-chlorosuccinimide (0.352 mmol) in 10 mL of acetonitrile under N_2 atmosphere and at room temperature. The reaction was monitored by TLC until disappearance of the amine (1-2 hours), then were added an alcohol (1.6 mmol), TBHP (1.6 mmol, 0.22 mL of a 70 wt% in water) and $FeCl_3{\cdot}6H_2O$ (0.045 mmol) under N_2 atmosphere.

The resulting reaction mixture was heated in an oil bath at 85°C (the reaction was monitored by TLC until disappearance of *N*-chloroamine). Then the reaction mixture was quenched with 20 mL of a saturated solution of Na_2SO_3 (for removal of excess TBHP) and extracted three times with 40 mL of diethyl ether. The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to provide the desired amides 4a-q.

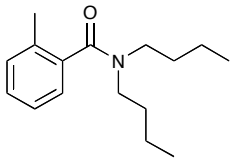
Compound characterizations



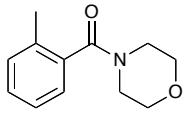
***N,N*-dibenzylbenzamide (4a).**[1] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 4.2/0.8), R_f = 0.44, to afford a white solid in 96% yield (m.p. 113-115°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (s, 2H), 4.70 (s, 2H), 7.13-7.15 (m, 2H), 7.24 -7.39 (m, 11H), 7.48-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 51.4, 126.7, 127.0, 127.5, 128.4, 128.5, 128.7, 129.6, 136.2, 172.2; IR (neat) ν = 3058, 3028, 2924, 1633, 1494, 1452, 1423, 1362, 1265, 1143, 1076, 1027, 991, 736, 700.



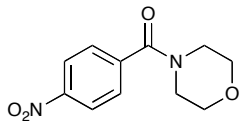
***N,N*-dibenzyl-4-methoxybenzamide (4b).**[12] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 3.8/1.2), R_f = 0.38, to afford a white solid in 74% yield (m.p. 119-121°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.48 (br s, 2H), 4.67 br (s, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.2-7.38 (m, 10H), 7.48 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.1, 55.2, 60.3, 113.8, 126.9, 127.5, 128.2, 128.5, 128.7, 136.9, 160.2, 172.2; IR (neat) ν = 3062, 2924, 2853, 1629, 1513, 1494, 1421, 1363, 1265, 1176, 1030, 993, 738, 701.



***N,N*-dibutyl-2-methylbenzamide (4c).** Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 4/1), R_f = 0.51, to afford a pale yellow oil in 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, J = 7.2 Hz, 2H), 0.98 (t, J = 7.4 Hz, 2H), 1.1 (q, J = 7.4 Hz, 2H), 1.37-1.47 (m, 4H), 1.6-1.7 (m, 2H), 2.28 (s, 3H), 3.04 (t, J = 7.4 Hz, 2H), 3.3 (br s, 2H), 3.65 (br s, 2H), 7.12-7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 14.1, 19.1, 19.9, 20.6, 29.8, 30.8, 44.2, 48.2, 125.8, 125.9, 128.6, 130.4, 134.1, 137.4, 171.4; IR (neat) ν = 2958, 2931, 2869, 1633, 1463, 1423, 1376, 1301, 1261, 746. HRMS (EI) ([M^+]) Calcd. For $C_{16}H_{25}NO$: 247.1936, Found: 247.1933.

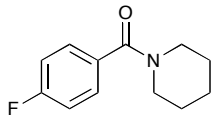


morpholino(*o*-tolyl)methanone (4d).[2] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 2.5/2.5), R_f = 0.31, to afford a yellow oil in 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3,24 (br d, J = 4,5 Hz, 2H), 3.57 (br t, J = 4.5 Hz, 2H), 3.76-3.84 (br m, 4H), 7.14-7.3 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 41.9, 47.3, 66.9, 67.0, 125.8, 126.0, 129.1, 130.5, 134.2, 135.6, 170.1; IR (neat) ν = 3054, 2983, 2923, 2859, 1633, 1431, 1265, 1157, 704.

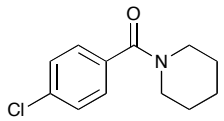


morpholino(4-nitrophenyl)methanone (4e).[2] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 2.5/2.5), R_f = 0.23, to afford a white solid in 77% yield (m.p. 98-101°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41-3.82 (br m, 8H), 7.61 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz,

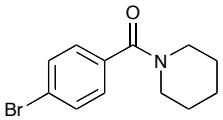
$CDCl_3$) δ 42.6, 48.0, 66.8, 124.0, 128.2, 141.4, 148.5, 168.1; IR (neat) ν = 2922, 2856, 1637, 1523, 1435, 1352, 1279, 1113, 1012, 895, 839, 735.



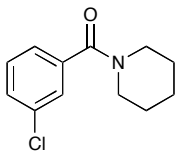
(4-fluorophenyl)(piperidin-1-yl)methanone (4f).[3] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 3/2), R_f = 0.2, to afford a pale yellow oil in 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (br s, 2H), 1.71 (br s,4H), 3.37 (br s, 2H), 3.71 (br s, 2H), 7.08-7.12 (m, 2H), 7.39-7.43 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 25.7, 26.6, 43.2, 48.9, 115.3, 115.6, 129.0, 129.1, 132.4, 132.5, 161.9, 164.4, 169.4; IR (neat) ν = 2942, 1628, 1442, 1265, 1157, 1004, 847, 739.



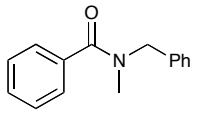
(4-chlorophenyl)(piperidin-1-yl)methanone (4g).[3] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 3/2), R_f = 0.2, to afford a white solid in 69% yield (m.p. 59-61°C);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (br, s, 2H), 1.70 (br s, 4H), 3.35 (br s, 2H), 3.71 (br s, 2H), 7.34-7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.6, 26.6, 43.2, 48.9, 128.4, 128.7, 134.8, 135.4, 169.2; IR (neat) ν = 2937, 1629, 1440, 1277, 1090, 1003, 737.



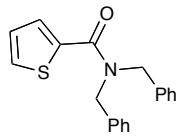
(4-bromophenyl)(piperidin-1-yl)methanone (4h).[4] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 3/2), R_f = 0.23, to afford a white solid in 80% yield (m.p. 75-78°C);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (br s, 2H), 1.70 (br s, 4H), 3.26 (br s, 2H), 3.71 (br s, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.6, 26.5, 43.3, 48.8, 123.6, 128.6, 131.6, 135.3, 169.3; IR (neat) ν = 2933, 2854, 1631,1441, 1277, 1111, 1068, 1001, 833, 733.



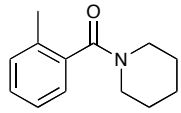
(3-chlorophenyl)(piperidin-1-yl)methanone (4i).[5] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 3.8/1.2), R_f = 0.45, to afford a yellow oil in 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (br s, 4H),1.71 (br s, 4H), 3.35 (br s, 2H), 3.72 (br s, 2H), 7.27-7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.6, 26.6, 43.2, 48.8, 124.9, 127.0, 129.5, 129.8, 134.5, 138.2, 168.7; IR (neat) n = 2931, 2856, 1631, 1566, 1439, 1280, 800, 739.



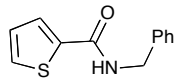
***N*-benzyl-*N*-methylbenzamide (4j).**[4] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 3.5/1.5), R_f=0.26,to afford a pale yellow oil in 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (br s, 1.5H), 3.06 (br s, 1.5H), 4.54 (br s, 1H), 4.79 (br s, 1H), 7.20-7.47 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.2, 37.1, 50.8, 55.2, 126.8, 127.0, 127.6, 127.9, 128.2, 128.4, 128.8, 129.6, 136.3, 136.6, 137.1, 170.8, 171.6; IR (neat) ν = 2921, 1631, 1450, 1400, 1265, 1070, 1026, 698.



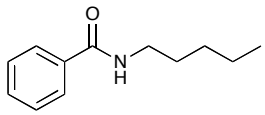
***N*,*N*-dibenzylthiophene-2-carboxamide (4k).**[1] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 3/2), R_f = 0.58, to afford a white solid in 98% yield (m.p. 47-50°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (s, 4H), 6.98 (dd, J = 3.7 Hz, J = 5.1Hz, 1H), 7.30-7.42 (m, 11H), 7.47 (dd, J = 1.2 Hz, J = 5.1Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.1, 126.9, 127.6, 128.6, 128.8, 129.3, 136.6, 137.7, 165.1. IR (neat) ν = 3062, 3004, 2978, 2954, 2914, 1611, 1583, 1519, 1494, 1453, 1422, 1364, 1347, 1306, 1250, 1078, 889.



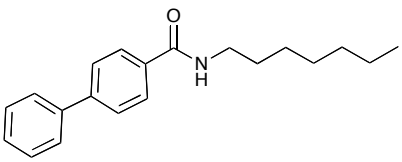
piperidin-1-yl(*o*-tolyl)methanone (4l).[6] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 3.5/1.5), R_f = 0.38, to afford a pale yellow oil in 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 2H), 1.66 (s, 4H), 2.31 (s, 3H), 3.17 (d, J = 4.1 Hz, 2H), 3.71 (br s, 1H), 3.79 (br s, 1H), 7.21 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 24.5, 25.7, 26.5, 42.3, 47.8, 125.6, 125.8, 128.5, 130.2, 134.0, 136.7, 169.8; IR (neat) ν = 3049, 2938, 2857, 1627, 1444, 1350, 1288, 1271, 1240, 1129, 1097, 1027, 1000, 733, 700, 665.



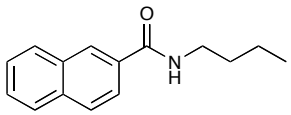
***N*-benzylthiophene-2-carboxamide (4m).**[7] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 2.5/2.5), R_f =0.35, to afford a pale yellow oil in 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (d, J = 5.7Hz, 2H), 6.35 (br s, 1H), 7.09 (dd, , J = 3.7 Hz, J = 5.1Hz, 1H), 7.31-7.35 (m, 1H), 7.37-7.38 (m, 4H), 7.50 (dd, , J = 1.2 Hz, J = 5.1Hz, 1H), 7.53 (dd, , J = 1.1 Hz, J = 2.5Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.0, 127.6, 127.7, 127.9, 128.1, 128.8, 130.0, 138.0, 138.7, 161.8; IR (neat) ν = 2922, 1629, 1545, 1421, 1265, 737.



***N*-pentylbenzamide (4n).**[8] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 2.5/2.5), R_f =0.51,to afford a pale yellow oil in 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.1Hz, 3H), 1.38 (m, 4H), 1.64 (t, J = 7.3Hz, 2H), 3.47 (q, J = 7.2 Hz, 2H), 6.19 (br s, 1H), 7.42-7.53 (m, 3H), 7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.4, 29.1, 29.4, 40.1, 126.8, 128.5, 131.3, 134.9, 167.5; IR (neat) ν = 3064, 2956, 2929, 2860, 1639, 1576, 1545, 1491, 1464, 1375, 1309, 1209, 1153, 1074, 1028, 928, 877, 804, 698.

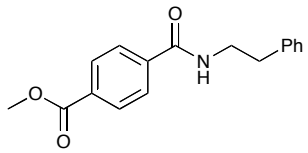


***N*-heptylbiphenyl-4-carboxamide (4o).** Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-AcOEt = 4/1), R_f =0.39,to afford a pale yellow oil in 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 6.9 Hz, 3H), 1.28-1.42 (m, 8H), 1.63-1.70 (m, 2H), 3.50 (q, J = 6.9 Hz, 2H), 6.18 (br s, 1H), 7.41 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7Hz, 2H), 7.62-7.69 (m, 4H), 7.85 (d, J = 8.5Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.0, 29.0, 29.7, 31.8, 40.1, 127.1, 127.2, 127.3, 127.9, 128.9, 133.5, 140.1, 144.1, 167.2; ; IR (neat) ν = 3041, 2922, 2852, 1630, 1537, 1469, 1265, 850, 740; HRMS (EI) ([M^+]) Calcd. For $C_{20}H_{25}NO$: 295.1936, Found: 295.1938.



***N*-butylnaphthalene-2-carboxamide (4p).**[9] Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 3/2), R_f = 0.25, to afford a white solid in 81% yield (m.p. 98-101°C);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J = 7.3 Hz, 3H), 1.44-1.53 (m, 2H), 1.64-1.71 (m, 2H), 3.57 (q, J =8.4 Hz, 2H), 6.00 (br s, 1H),

7.45-7.49 (m, 1H), 7.52-7.61 (m, 3H), 7.88-7.94 (m, 2H), 8.31 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 20.2, 31.8, 39.8, 124.7, 125.4, 126.4, 127.1, 128.3, 130.1, 133.7, 134.9, 169.5. IR (neat) ν = 3051, 2927, 1637, 1539, 1460, 1304, 1257, 1151, 1020, 779, 734.



methyl 4-(phenethylcarbamoyl)benzoate (4q). Prepared according to the general procedure. The product was purified by flash chromatography on silica gel (v/v petroleum ether-Et_2O = 2/3), R_f =0.34, to afford a white solid in 98% yield (m.p. 141-145°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (t, , J = 6.8 Hz, 2H), 3.76 (q, , J = 6.2 Hz, 2H), 3.95 (s, 3H), 6.23 (br s, 1H), 7.25-7.38 (m, 5H), 7.76 (d, J = 8.3 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.6, 41.2, 52.4, 126.7, 126.9, 128.7, 128.8, 129.8, 132.7, 138.5, 138.7, 166.3, 166.6. IR (neat) ν = 3327, 2923, 1720, 1635, 1543, 1439, 1280, 1196, 1157, 1113, 870, 821, 739, 698; HRMS (EI) ([M^+]) Calcd. For $C_{17}H_{17}NO_3$: 283.1208, Found: 283.1211.

References

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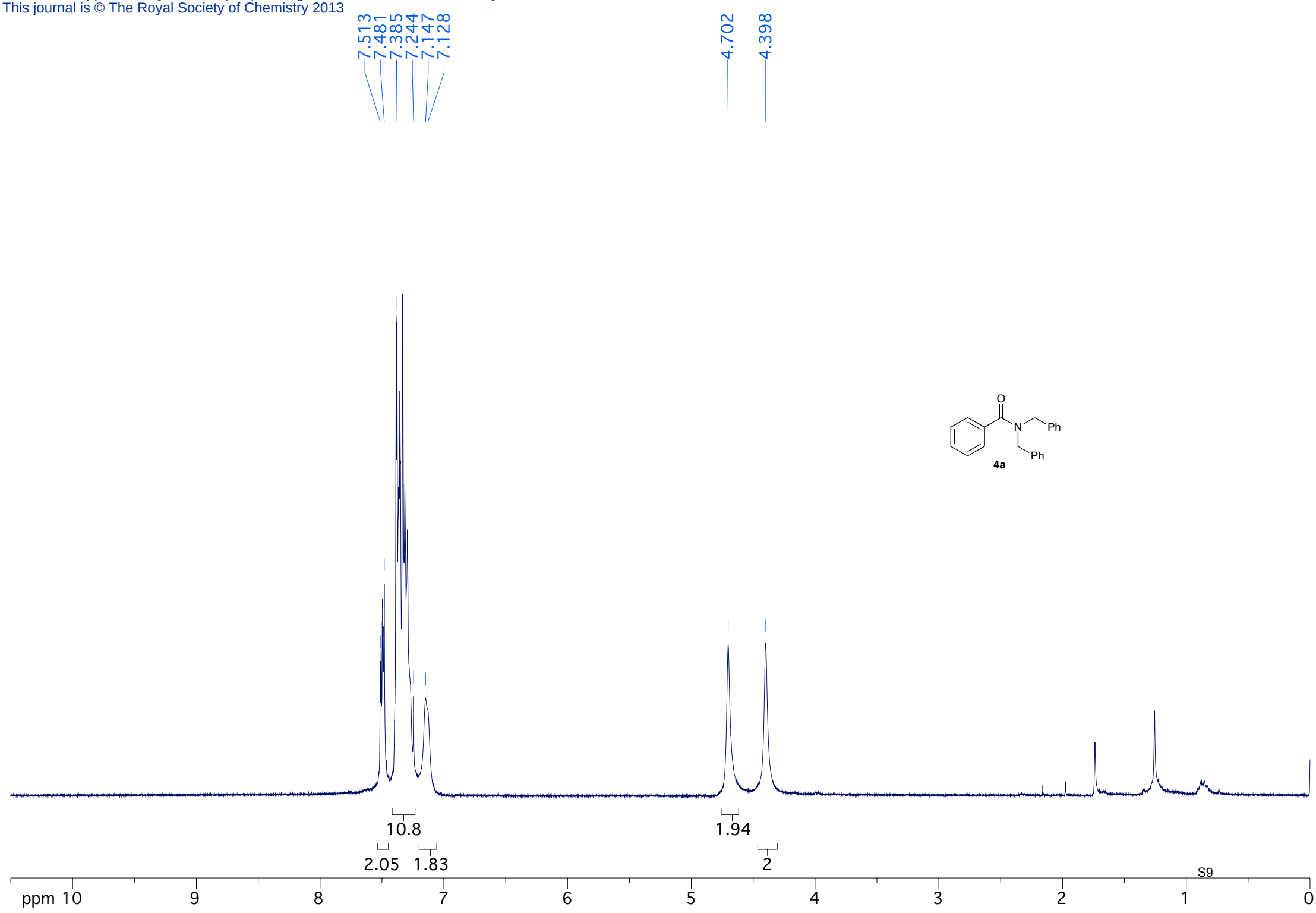

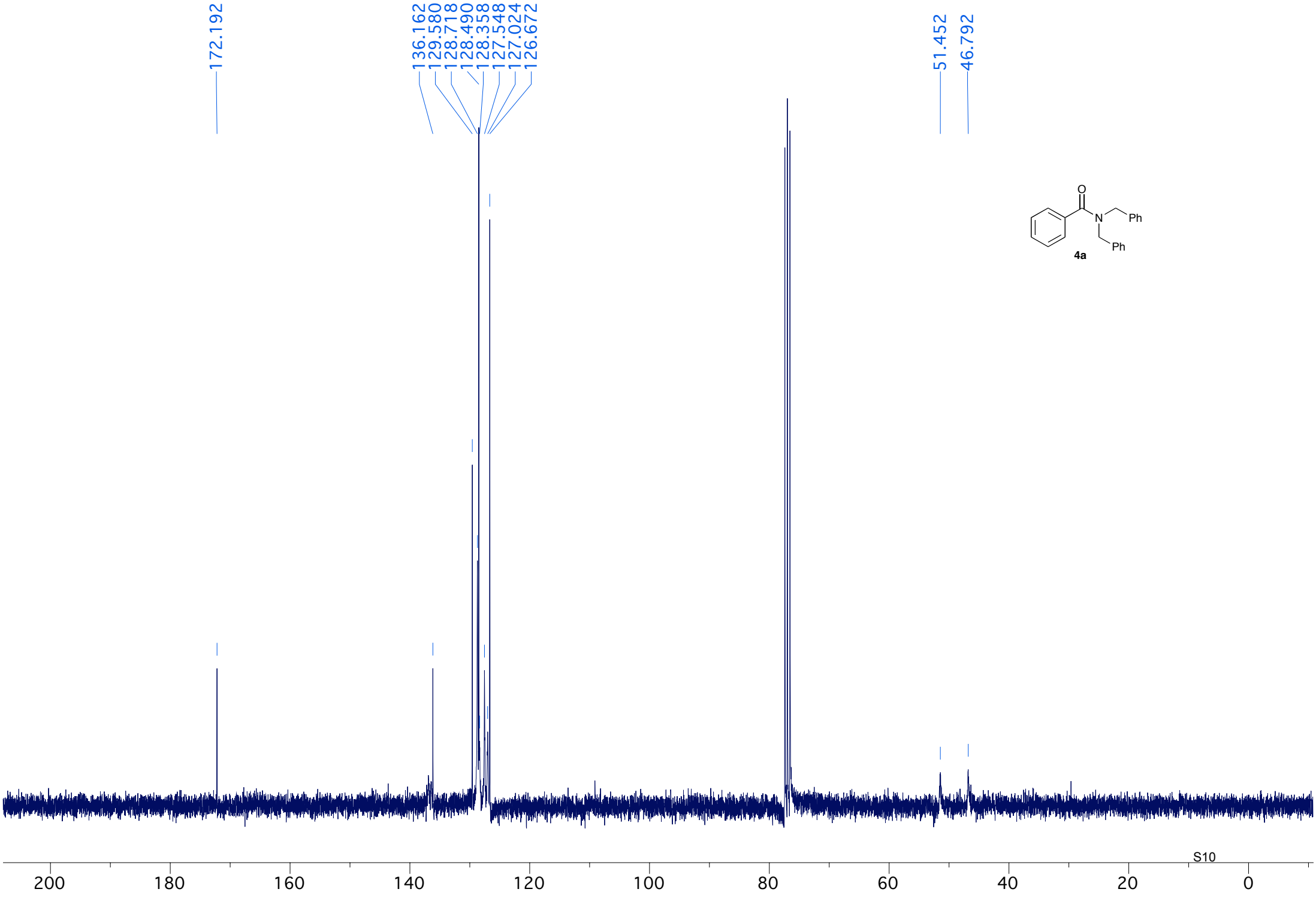

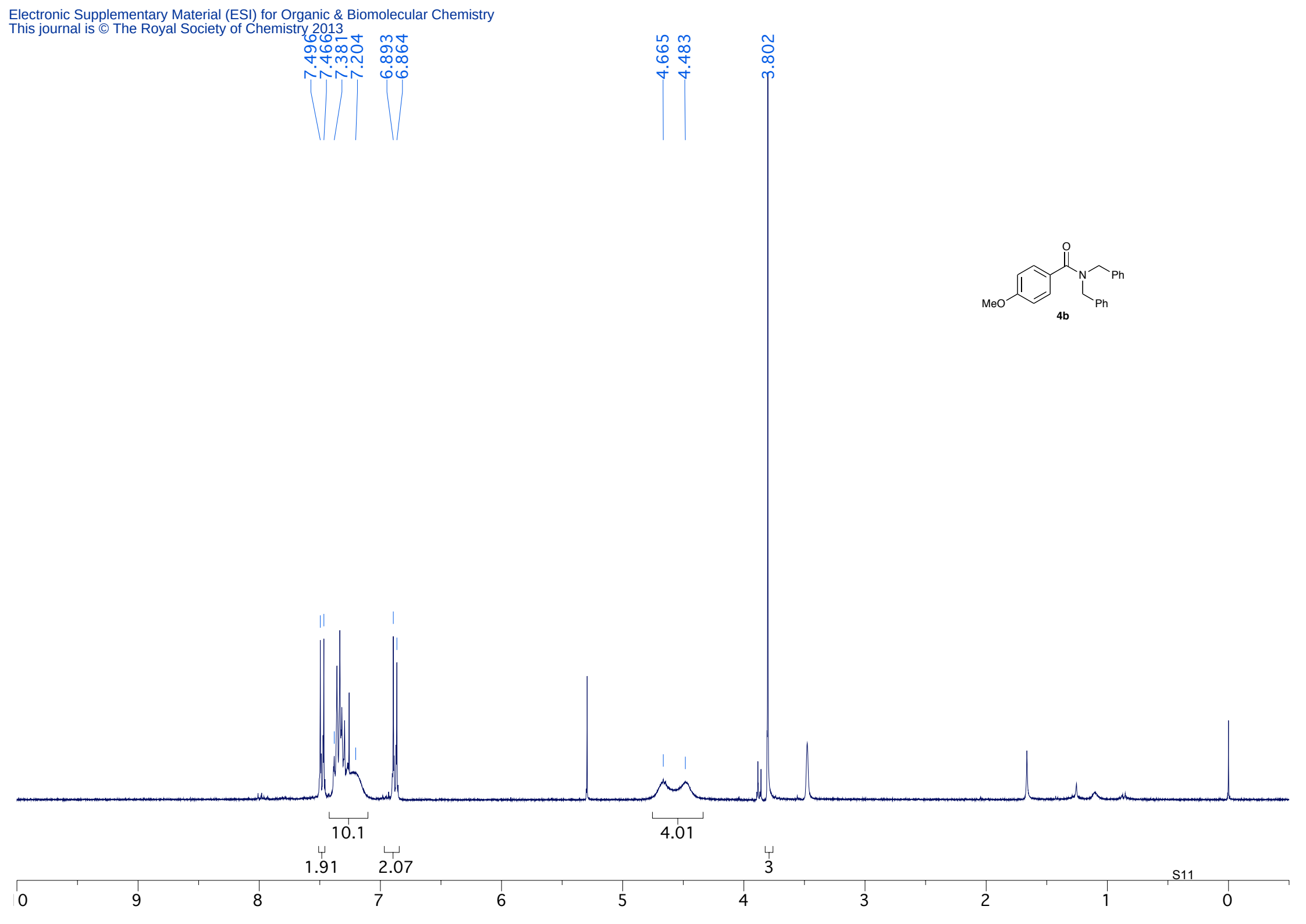

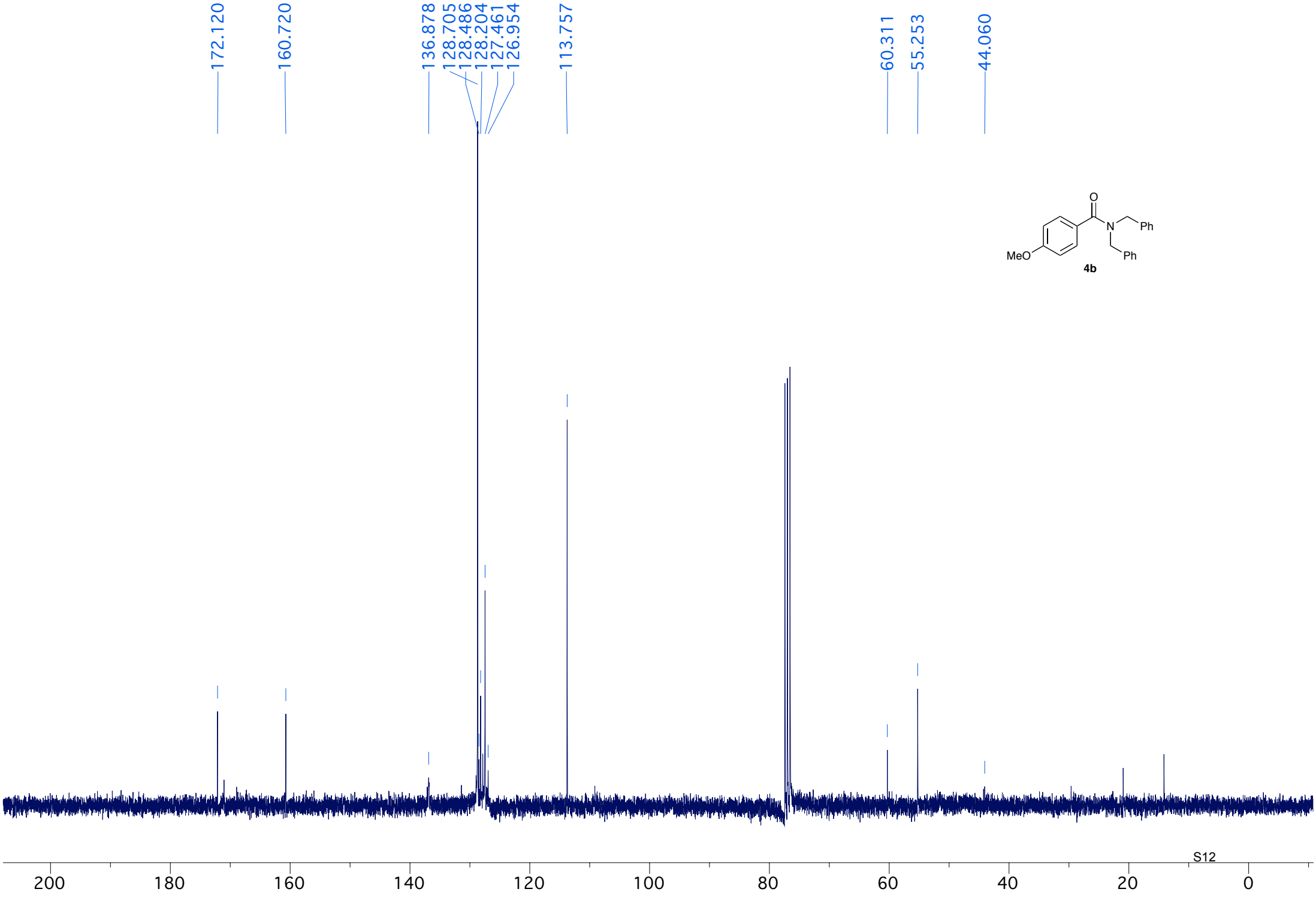

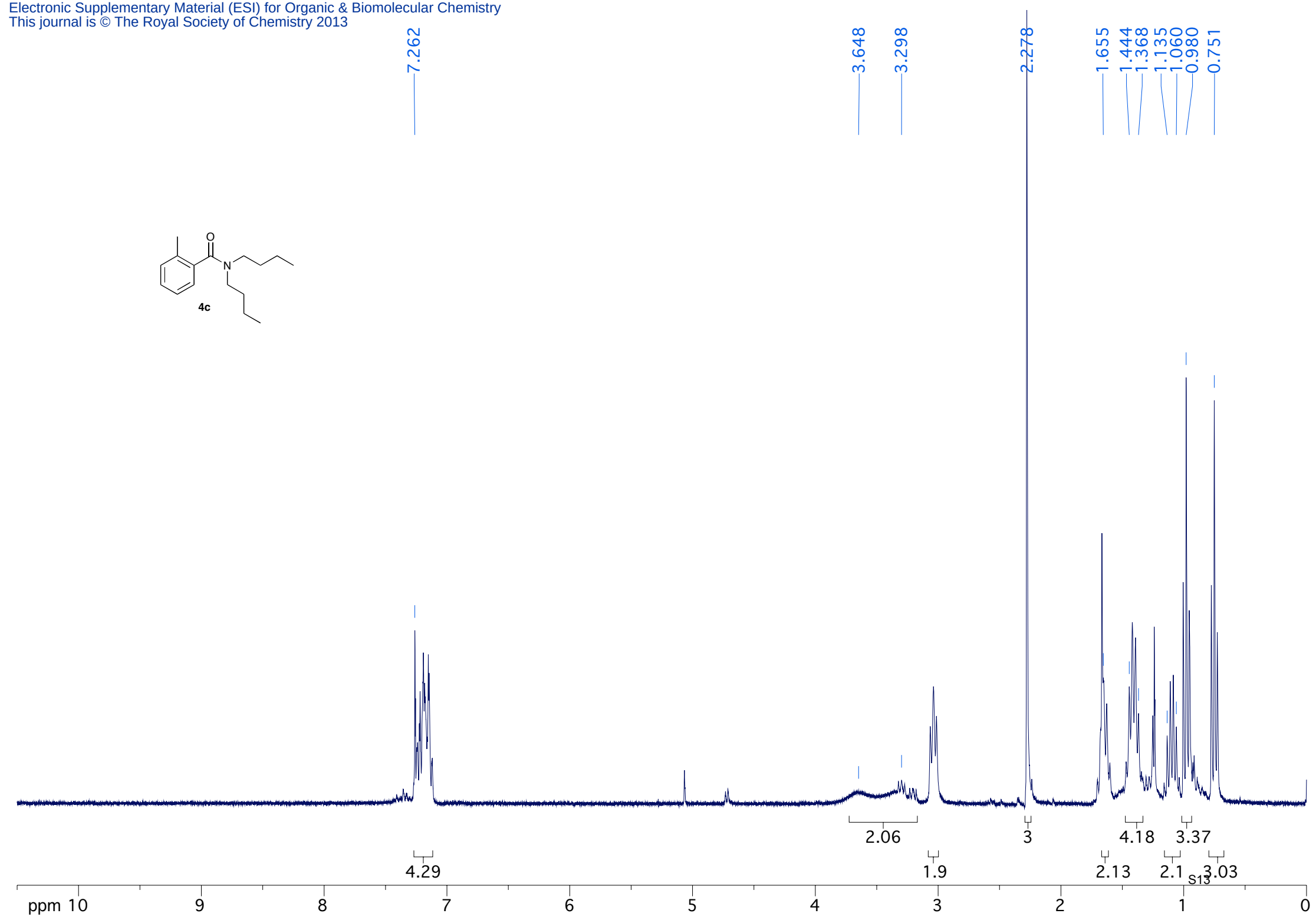

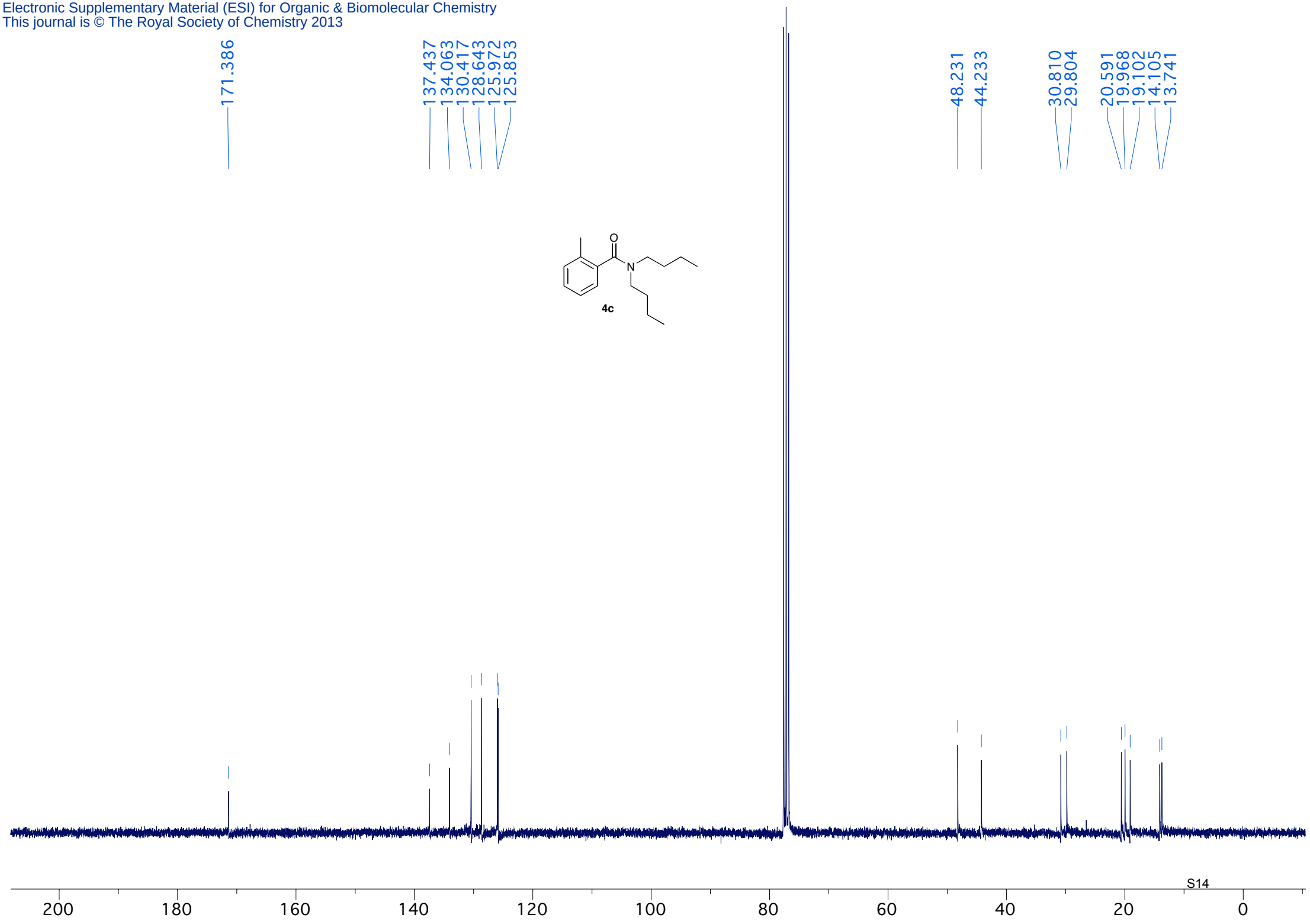

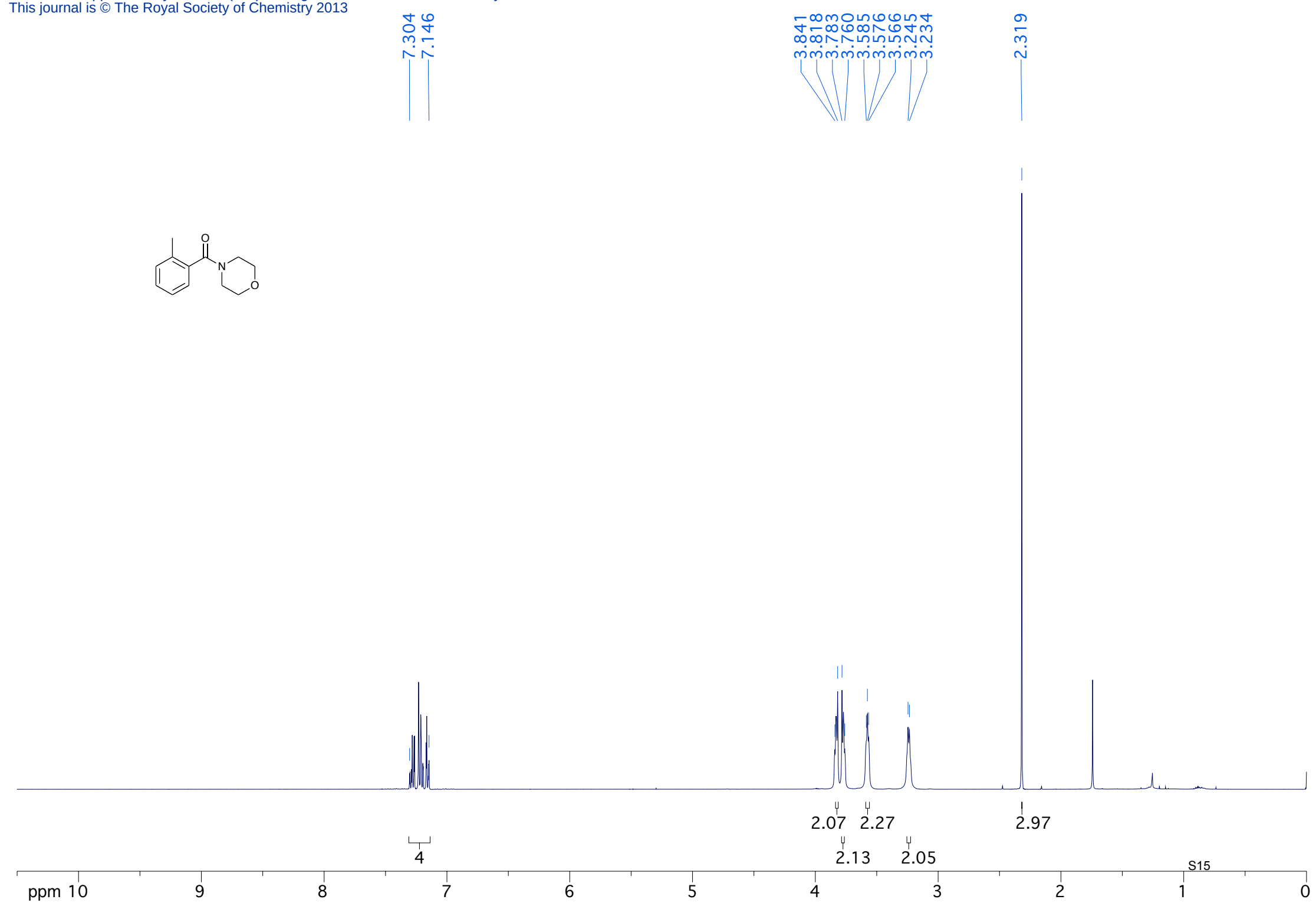

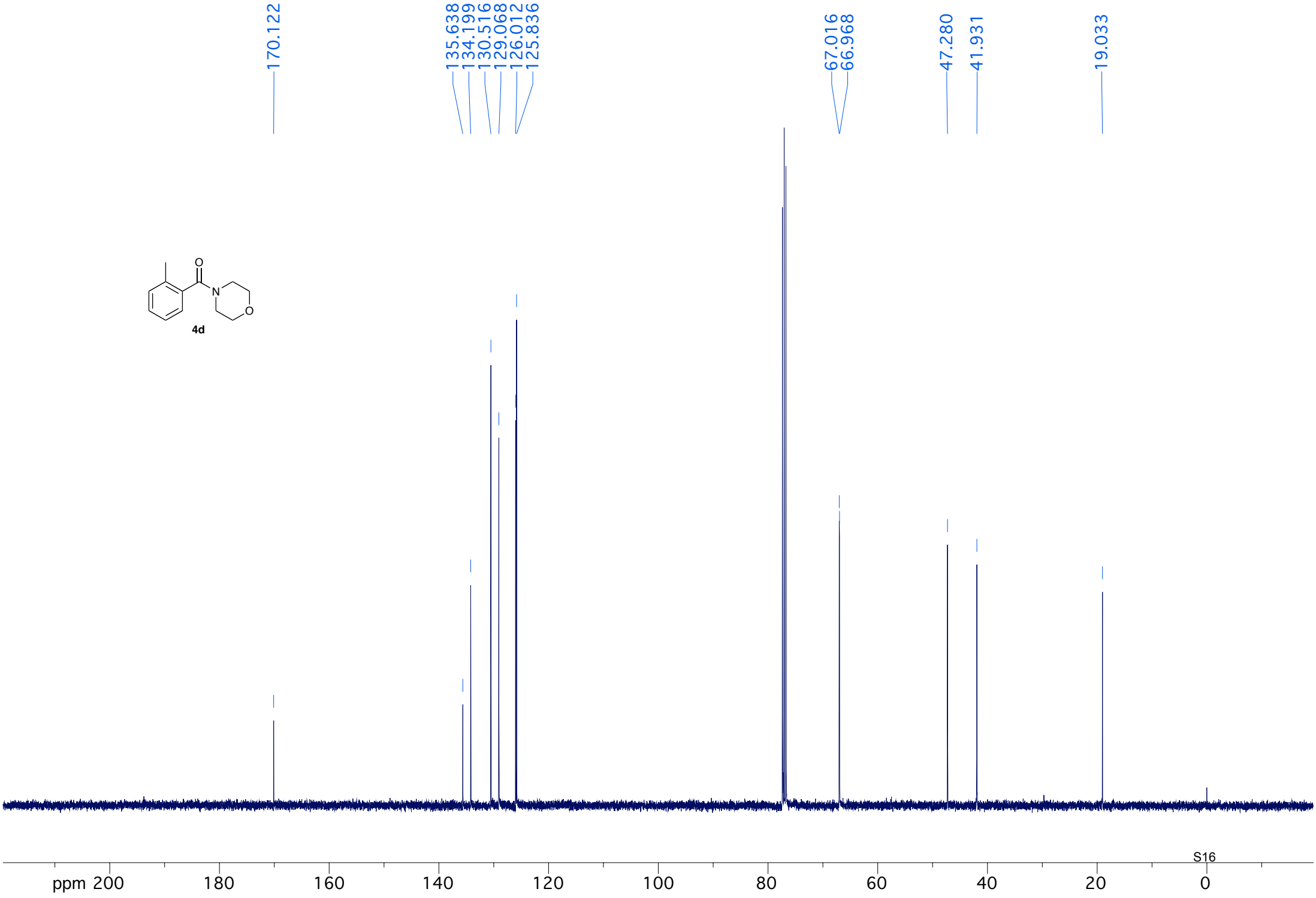

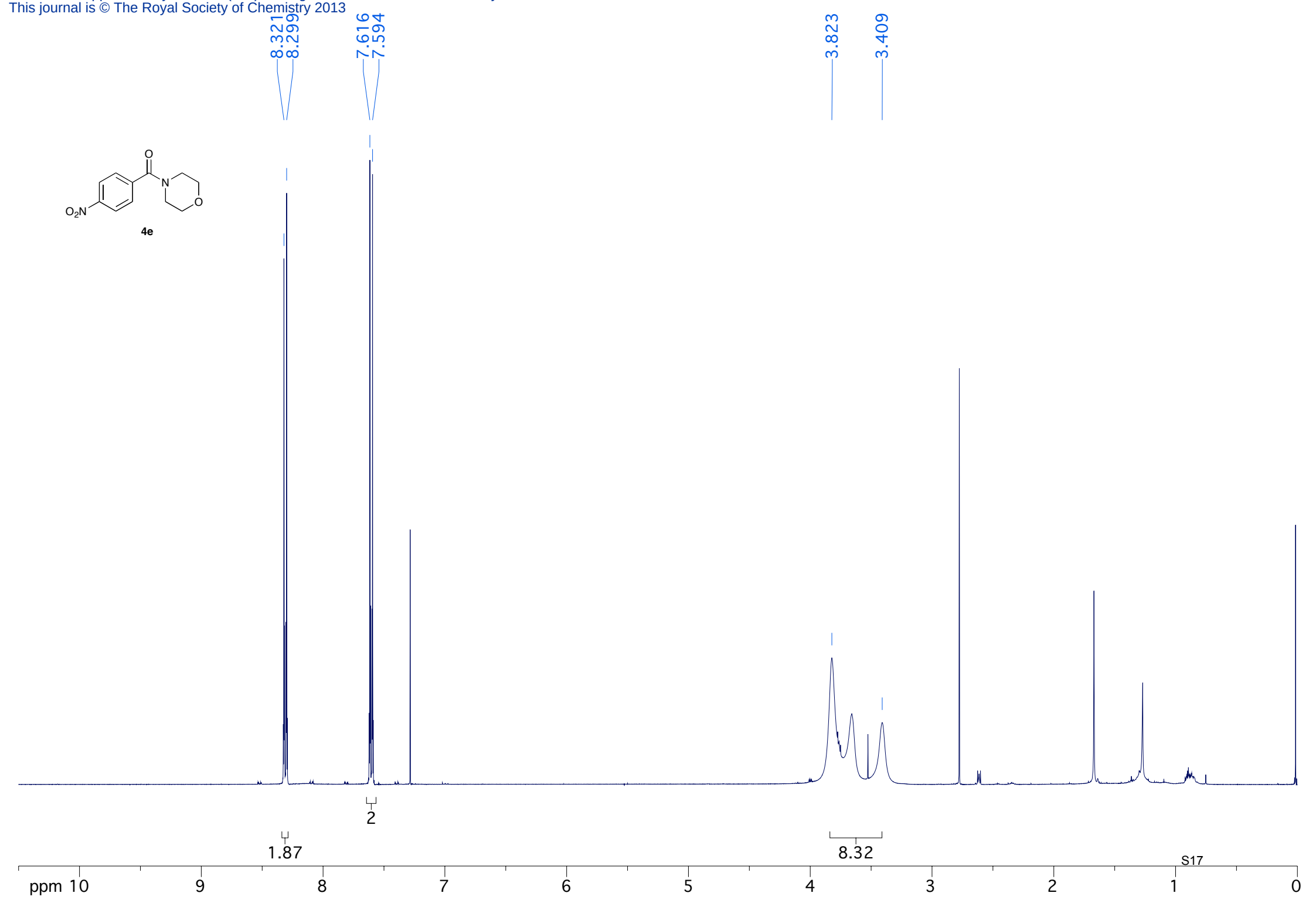

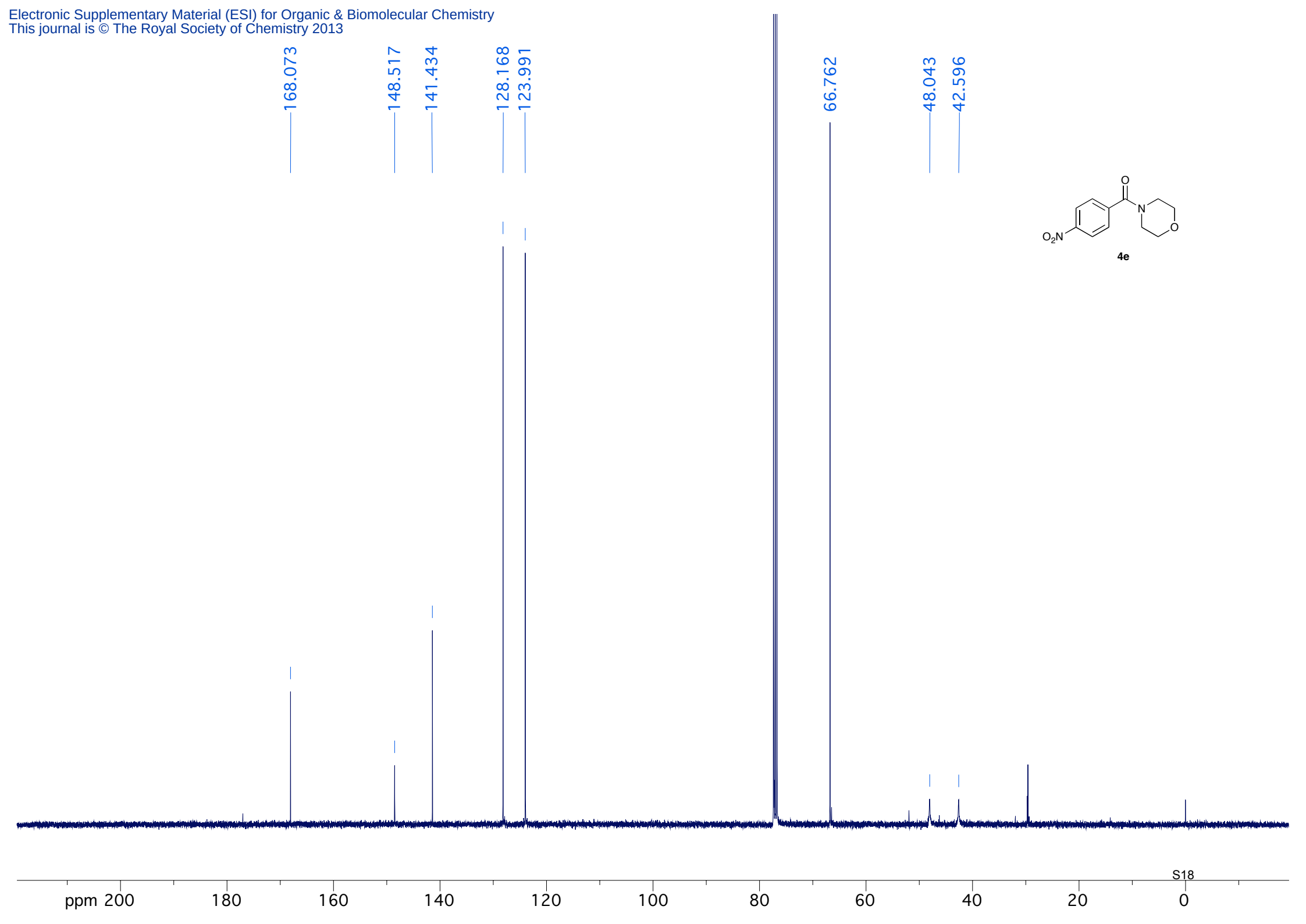

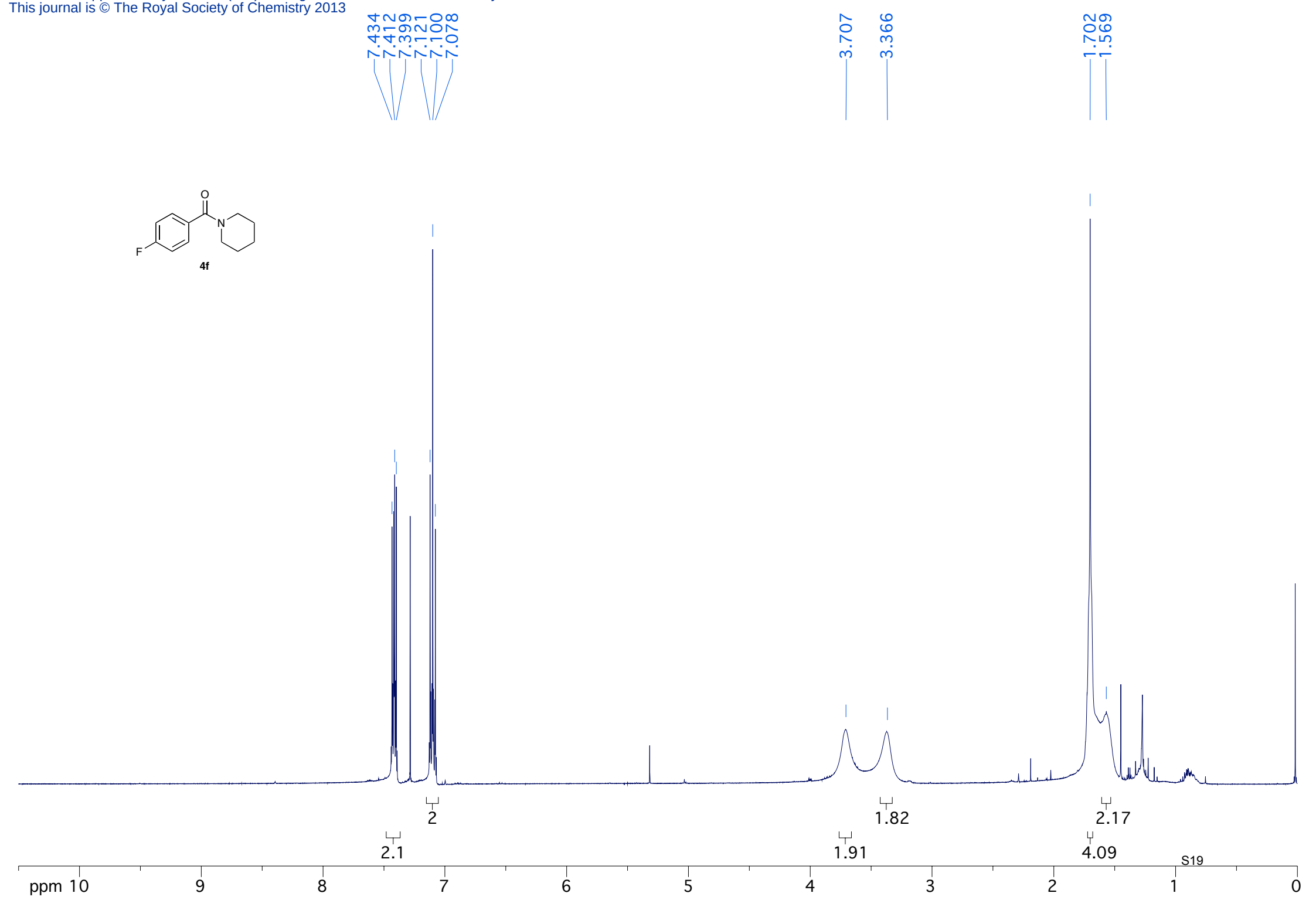

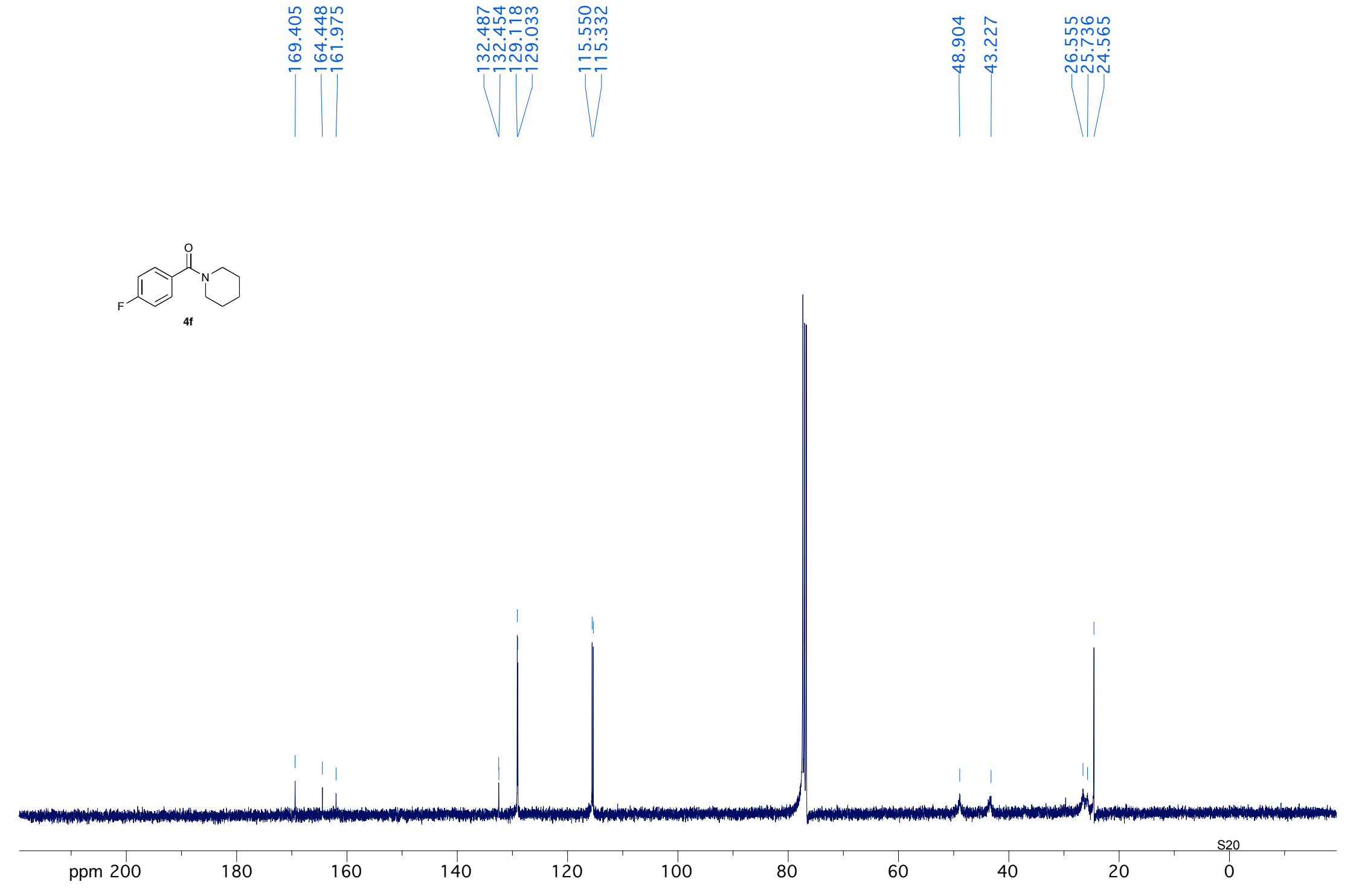

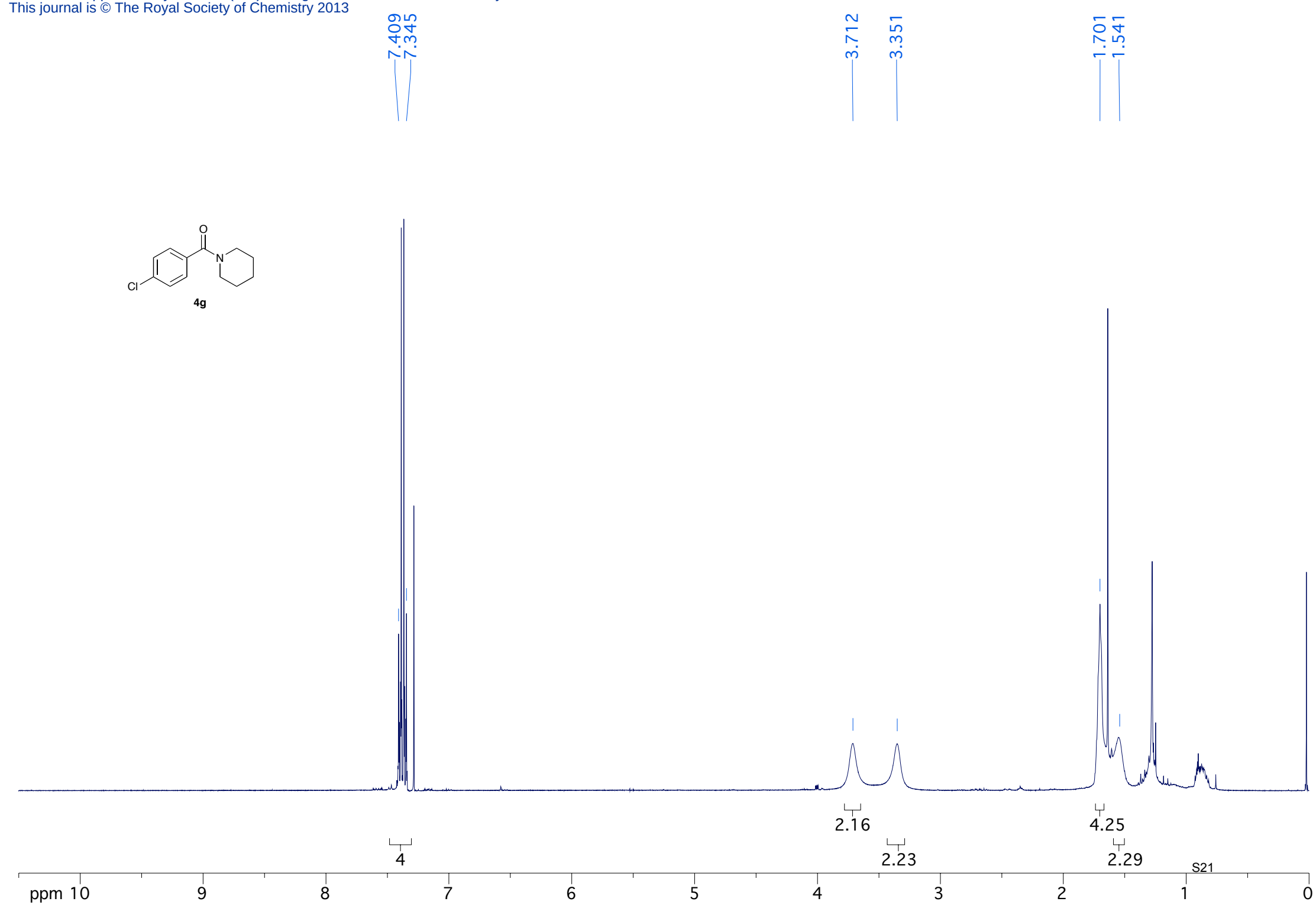

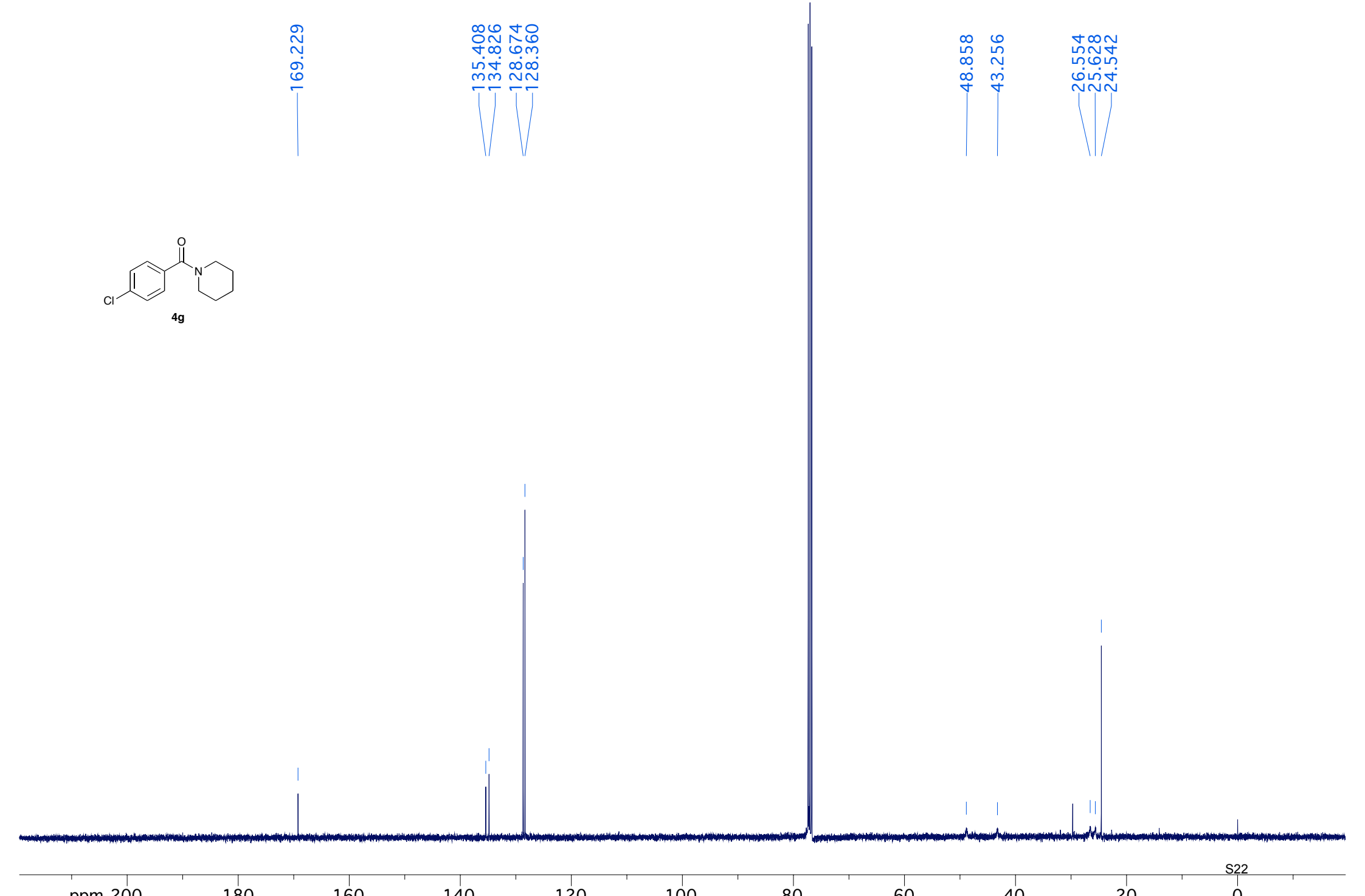

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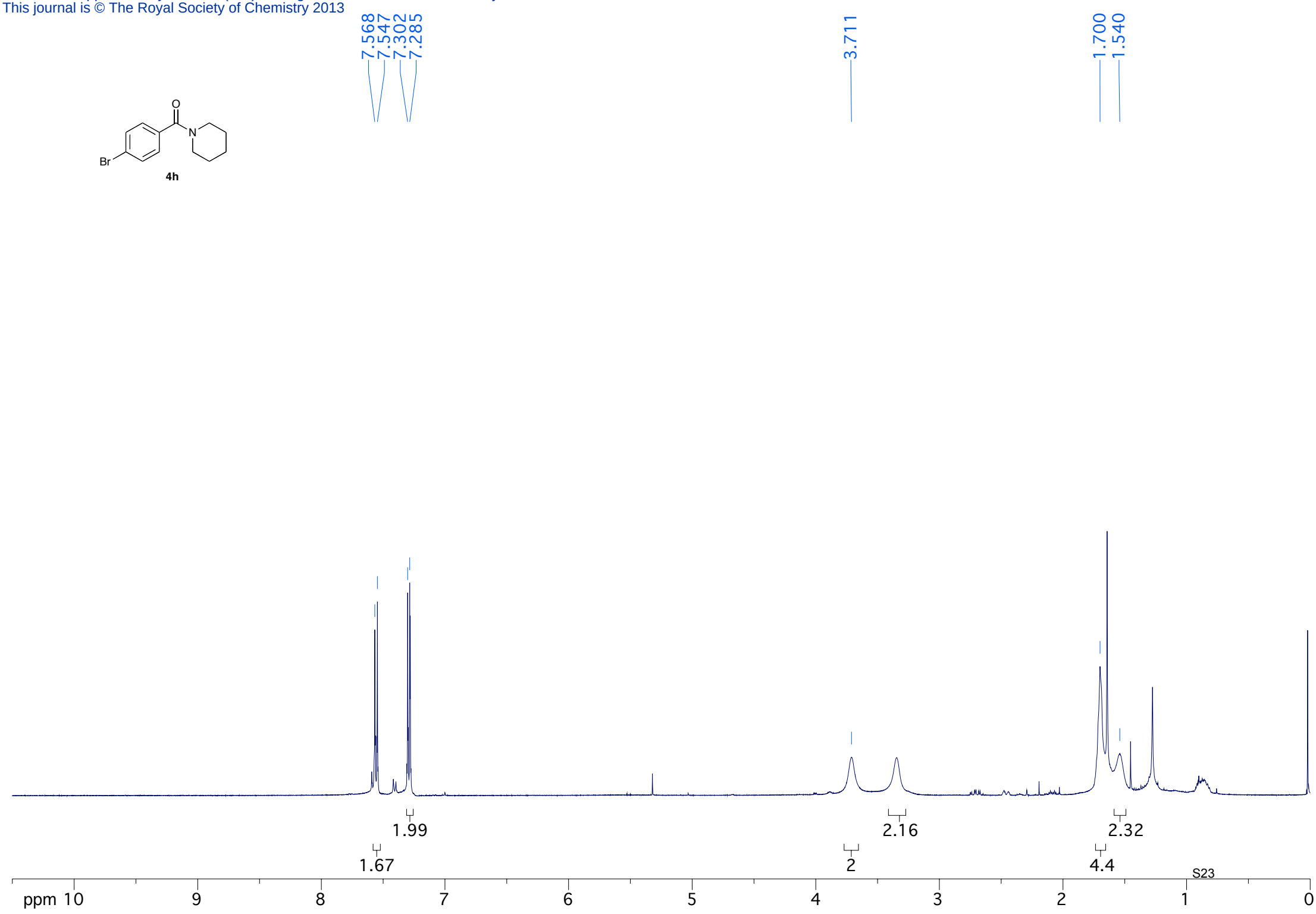

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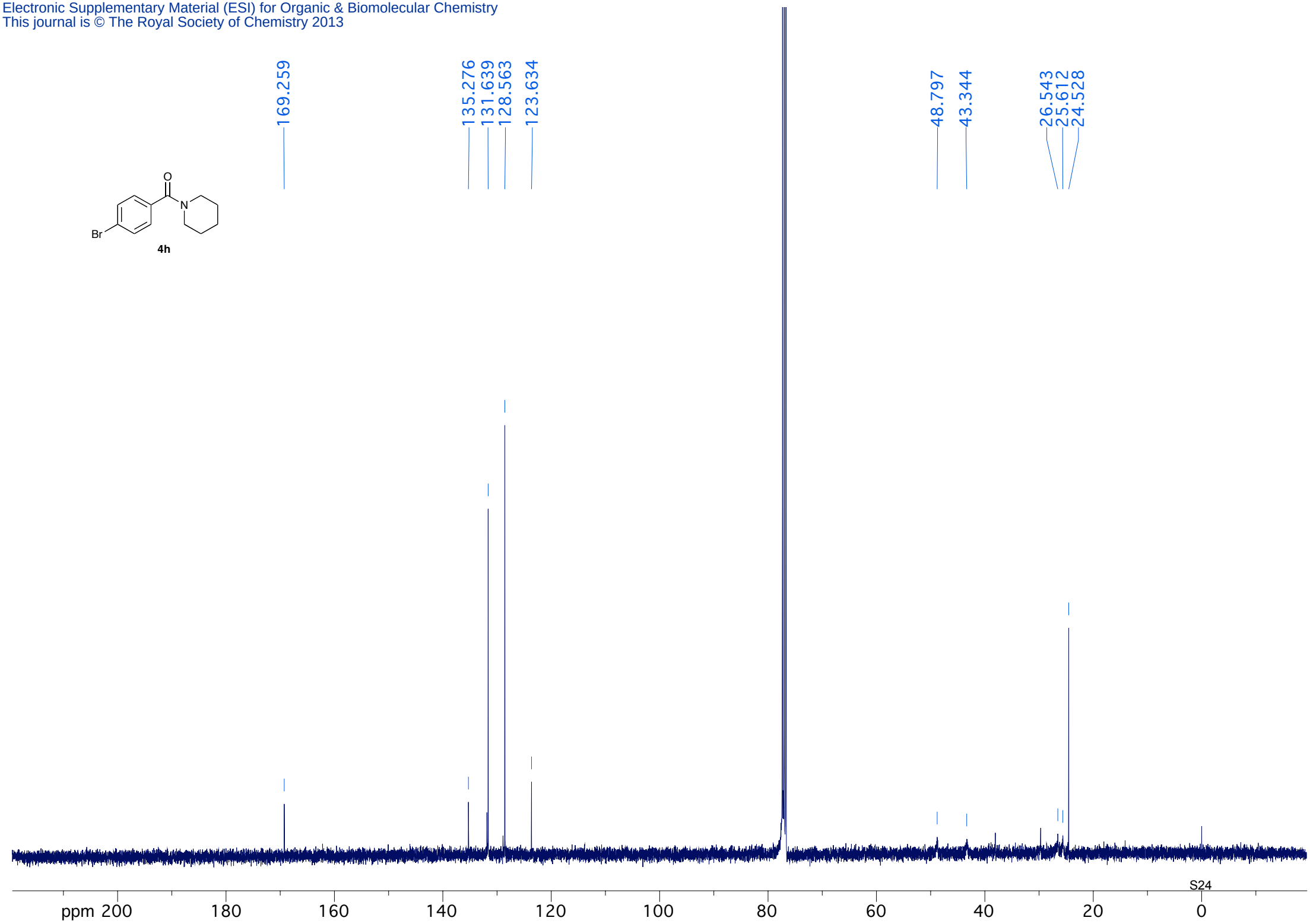

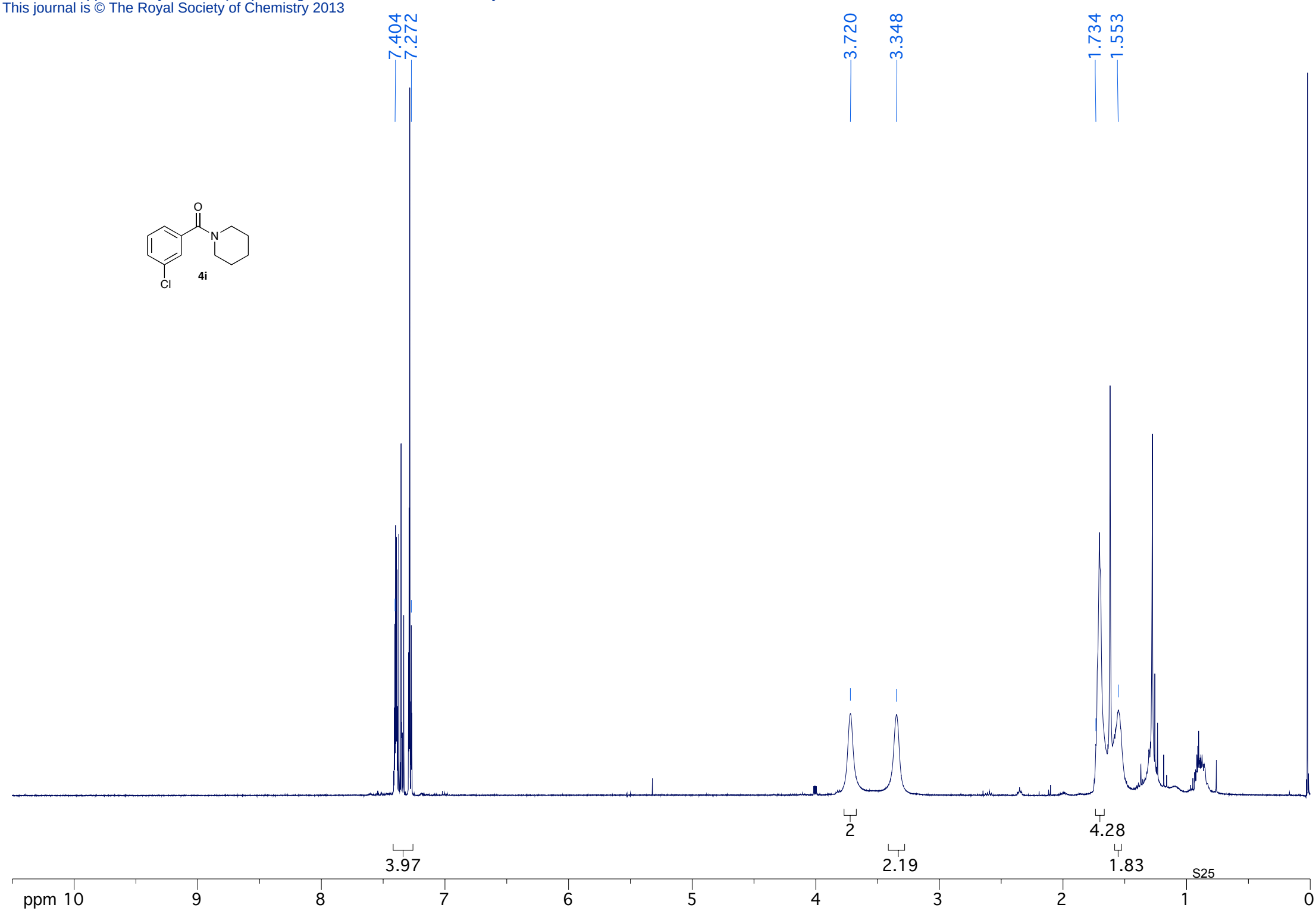

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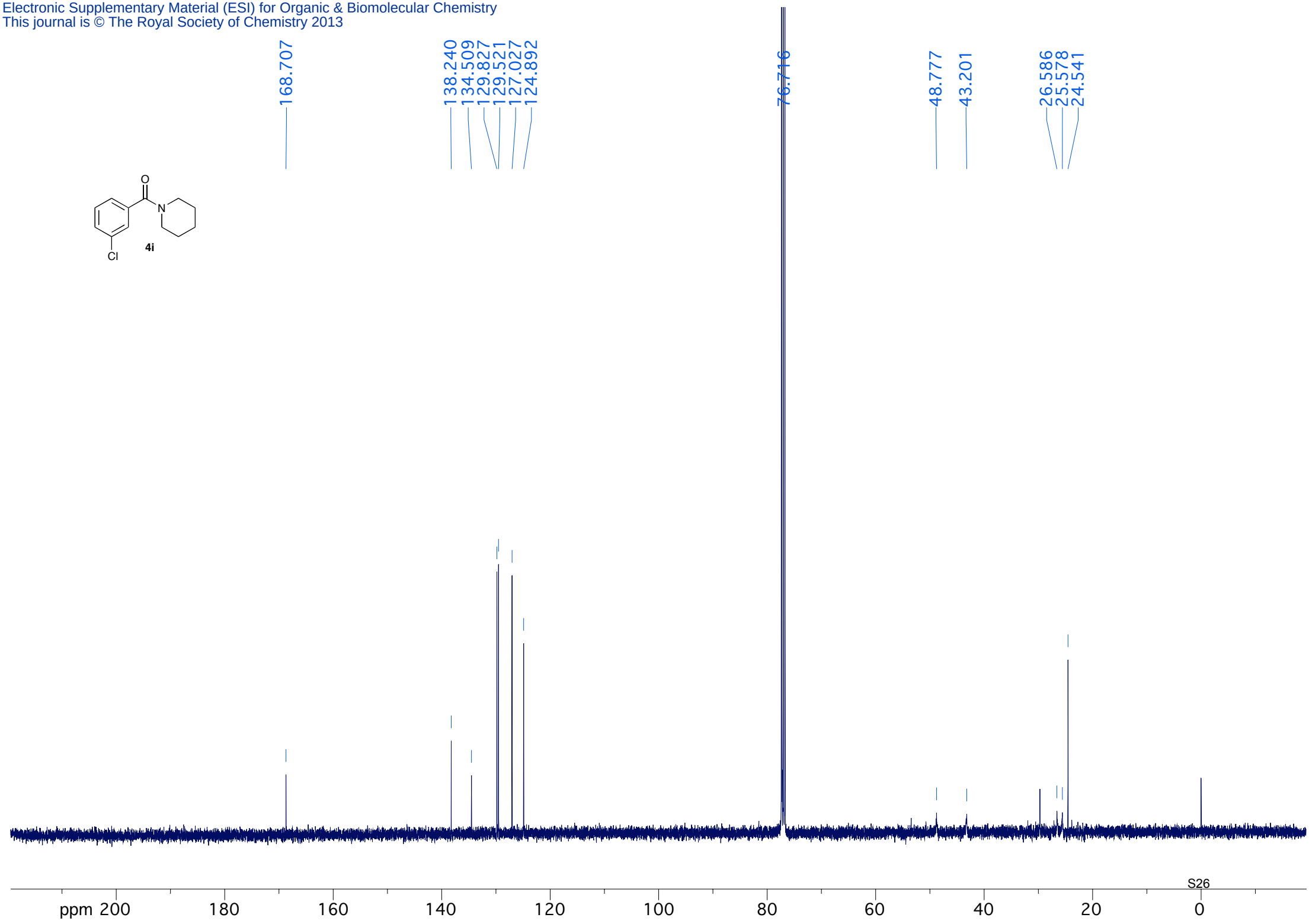

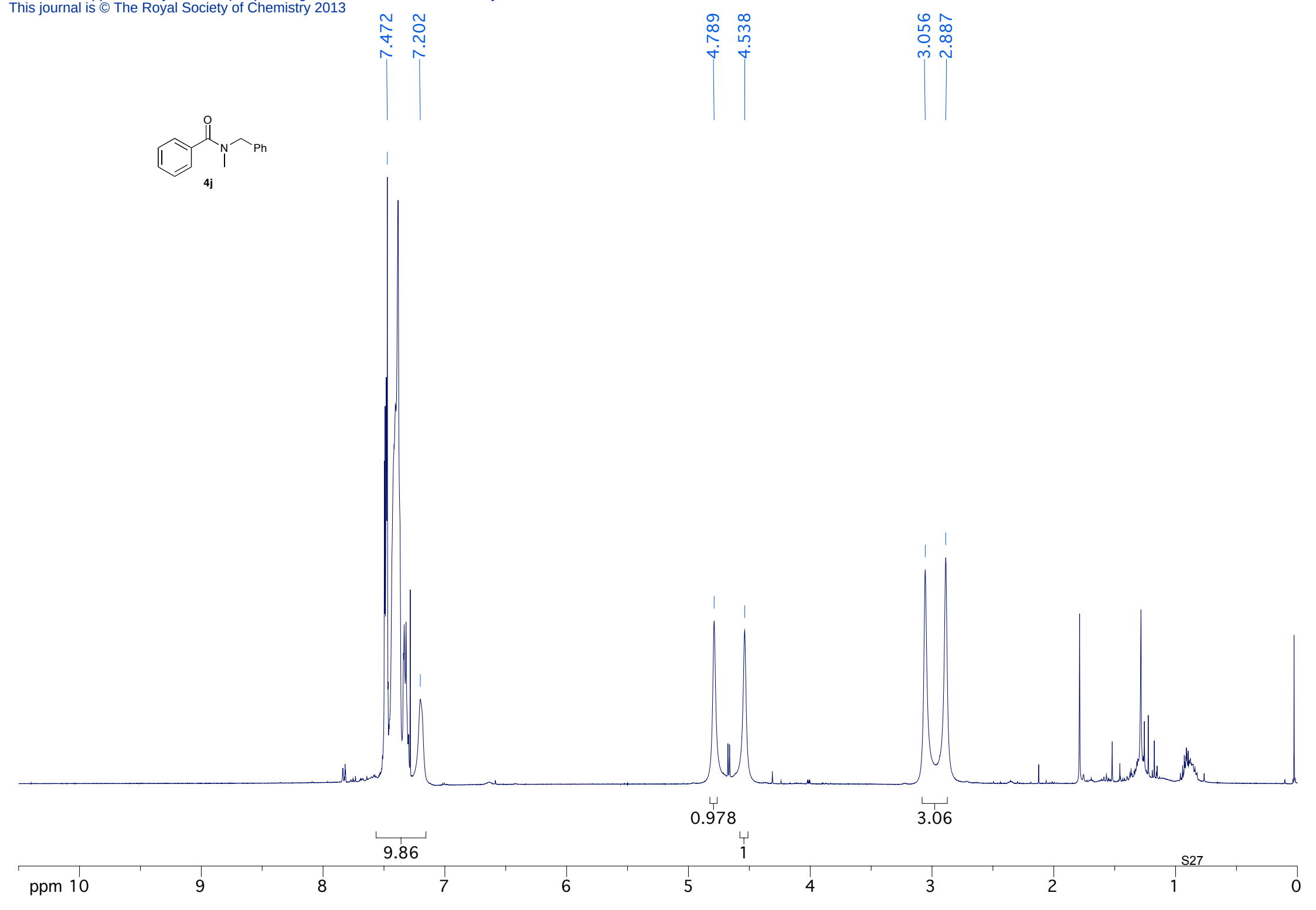

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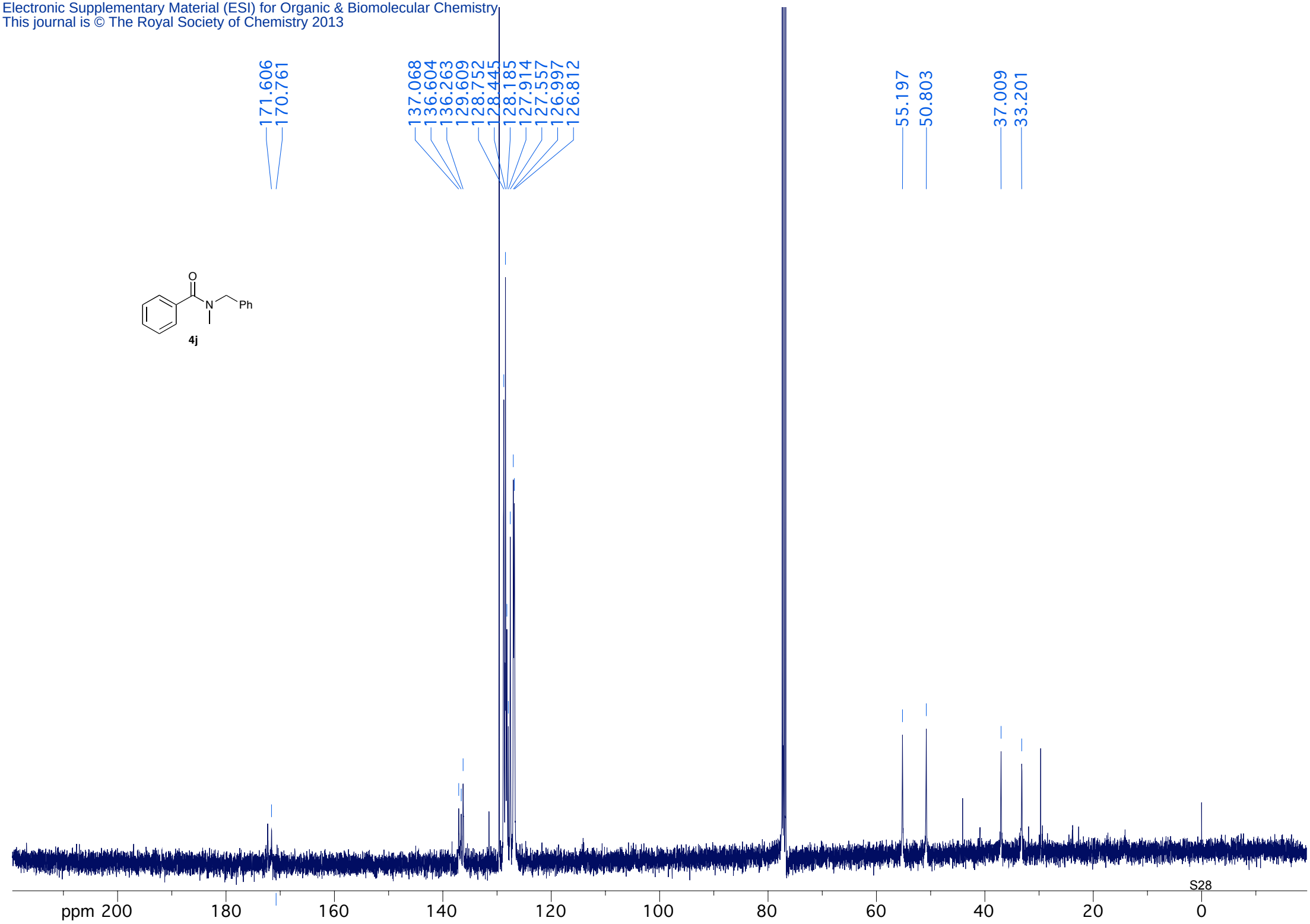

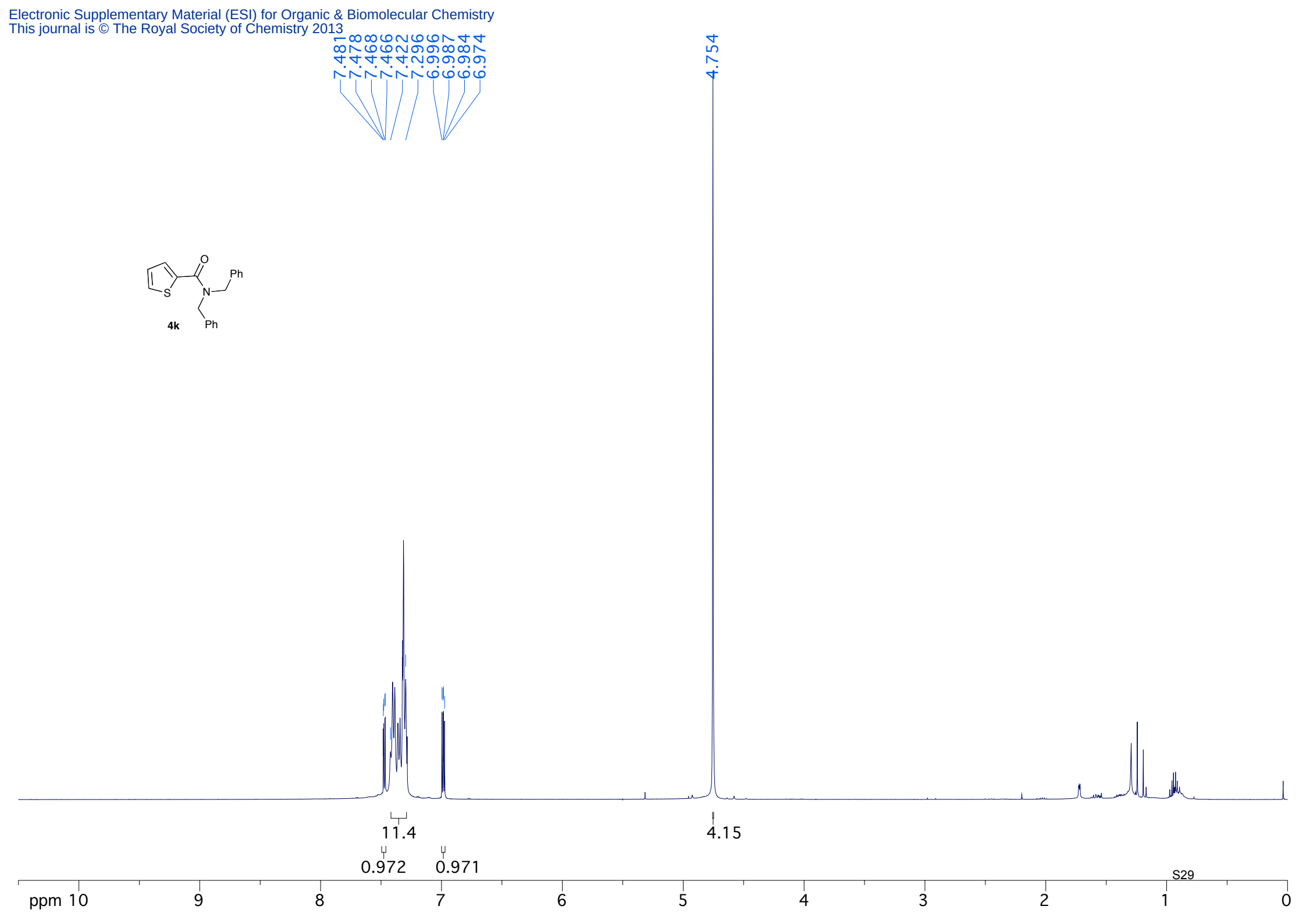

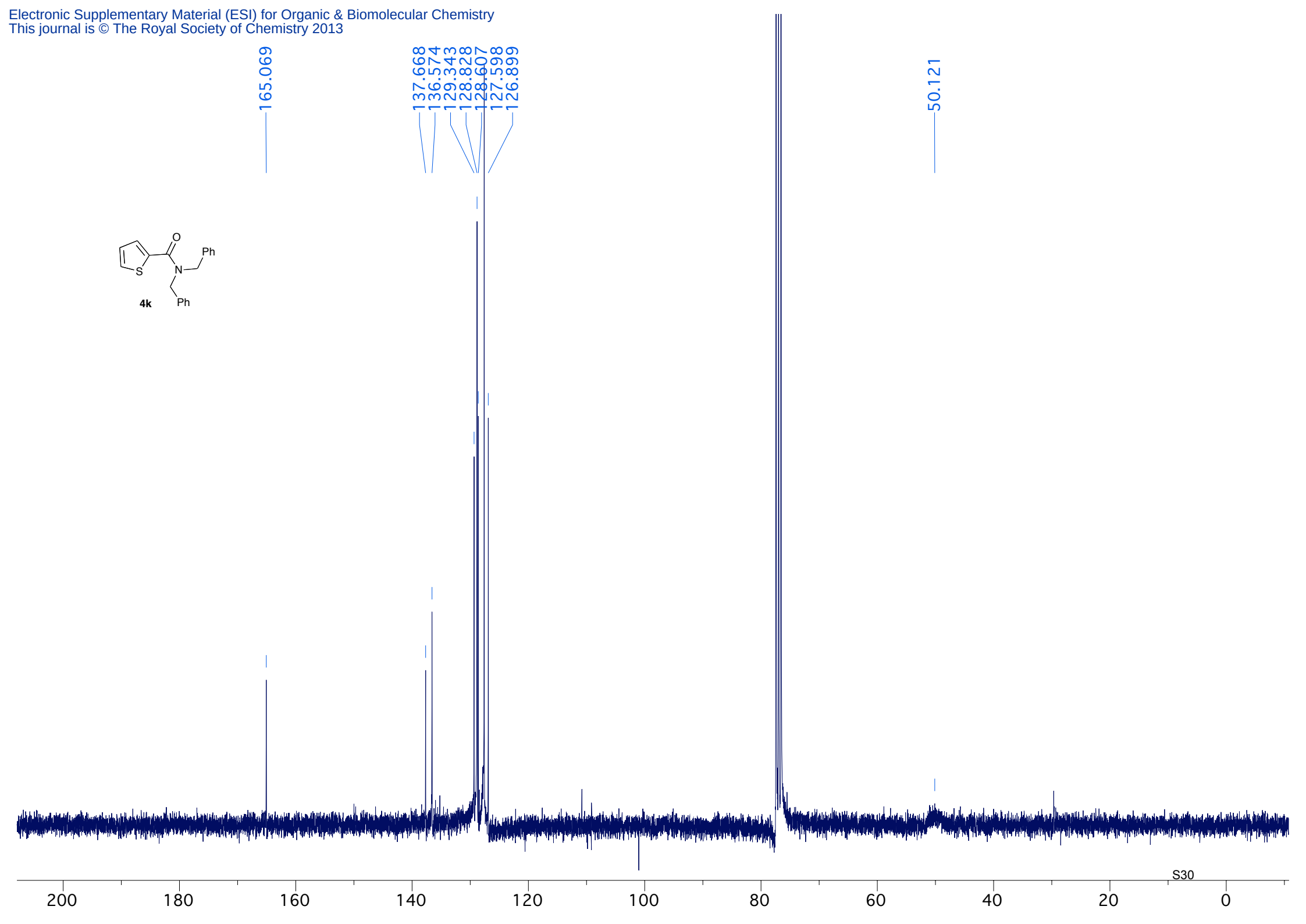

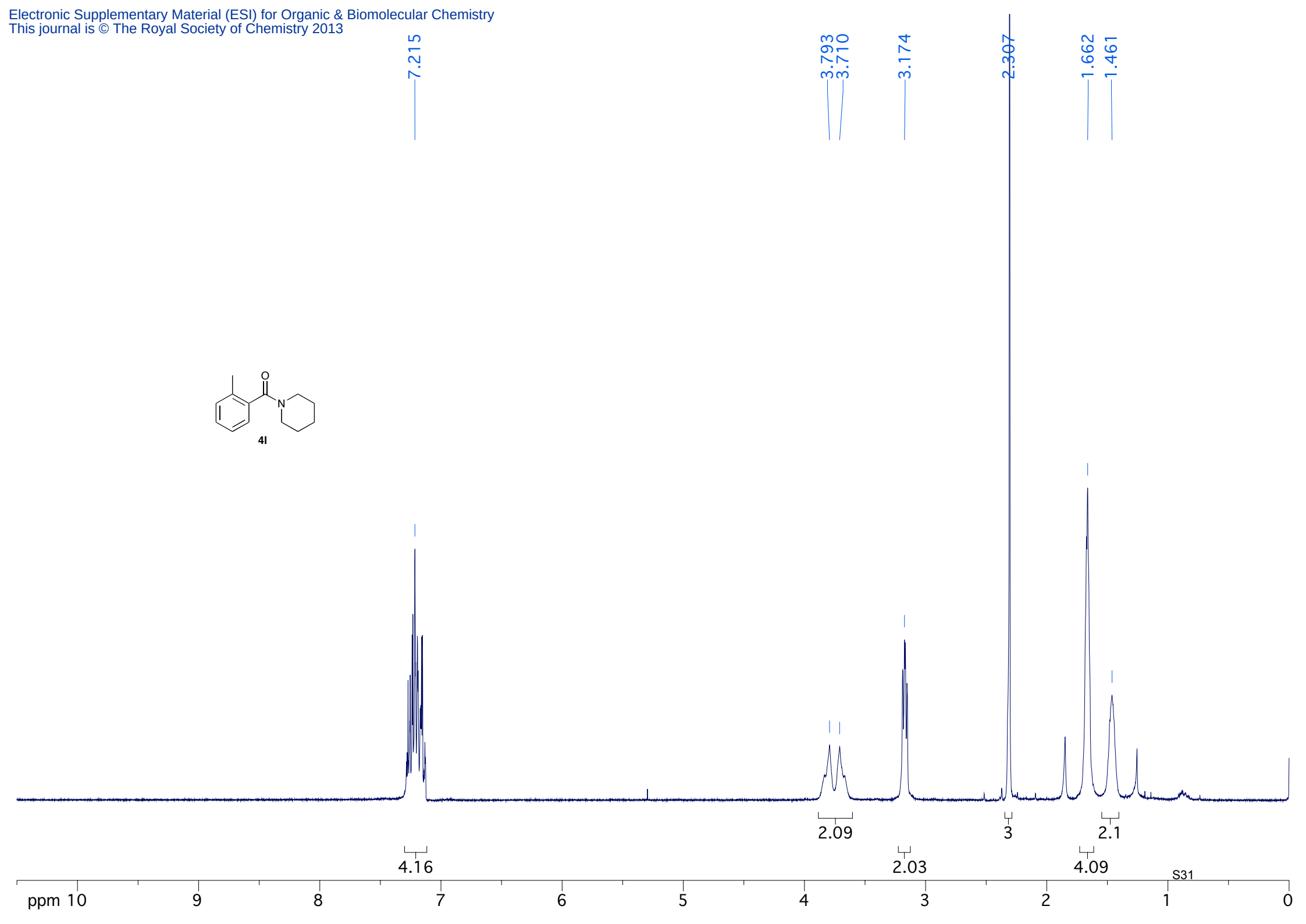

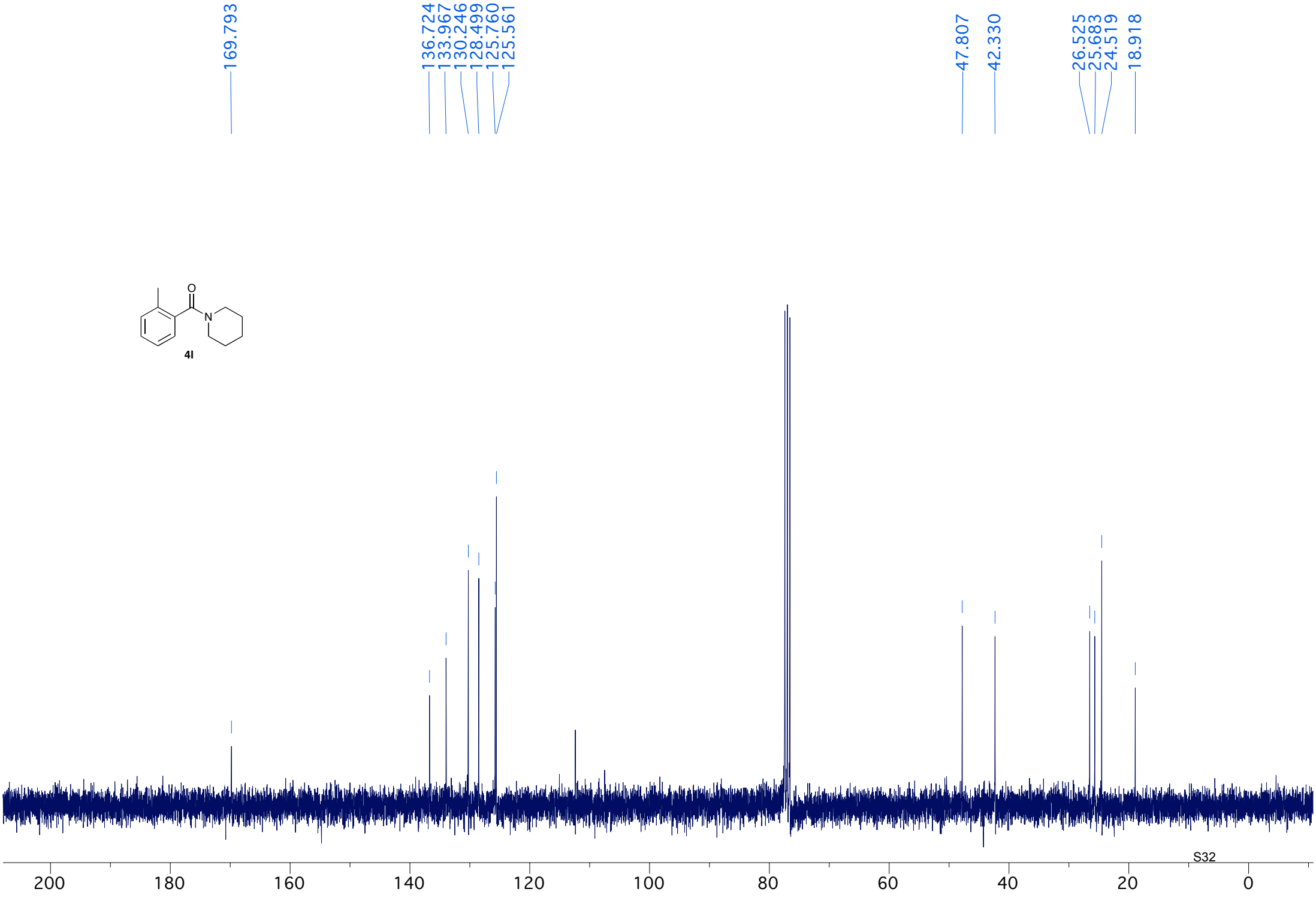

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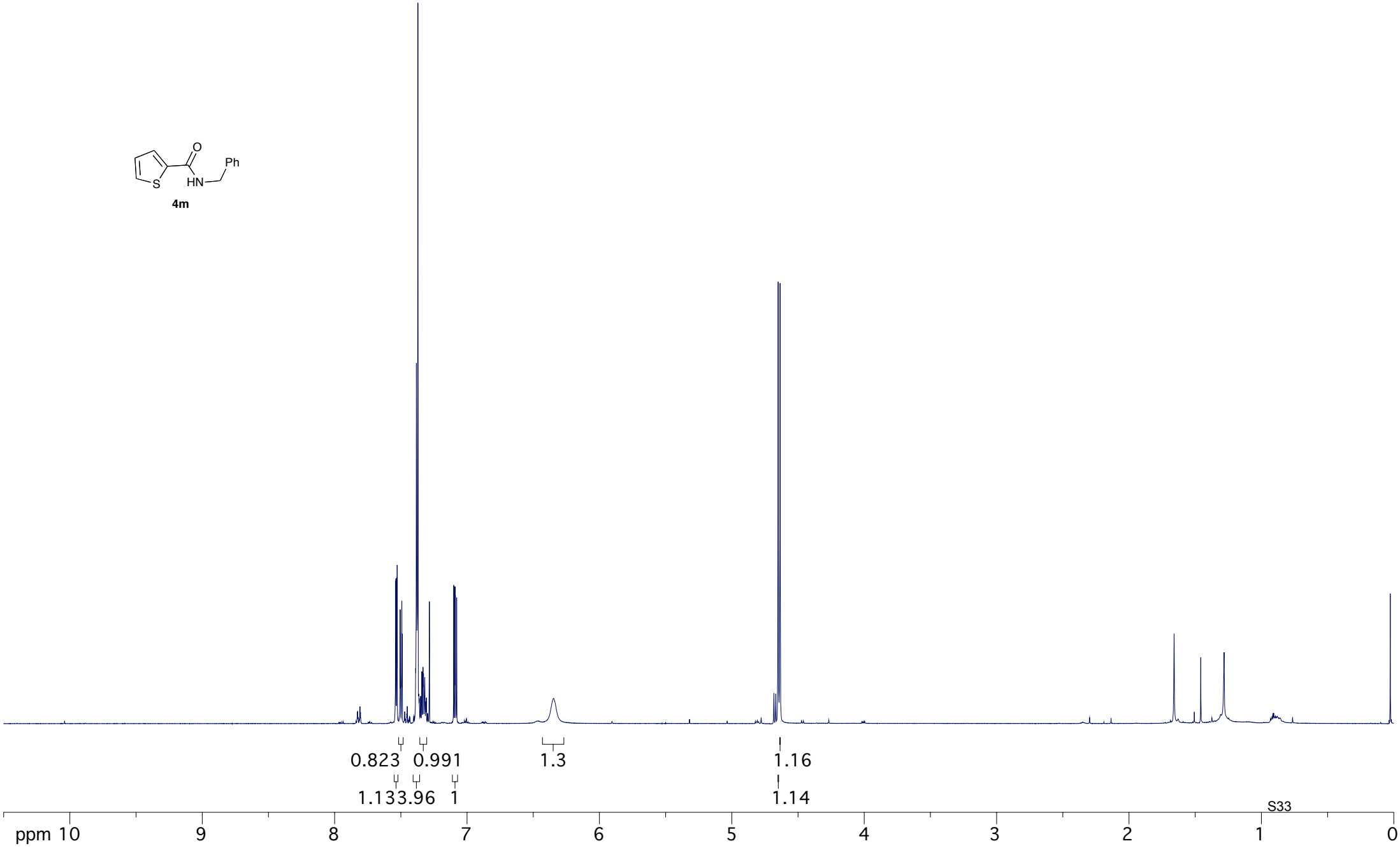

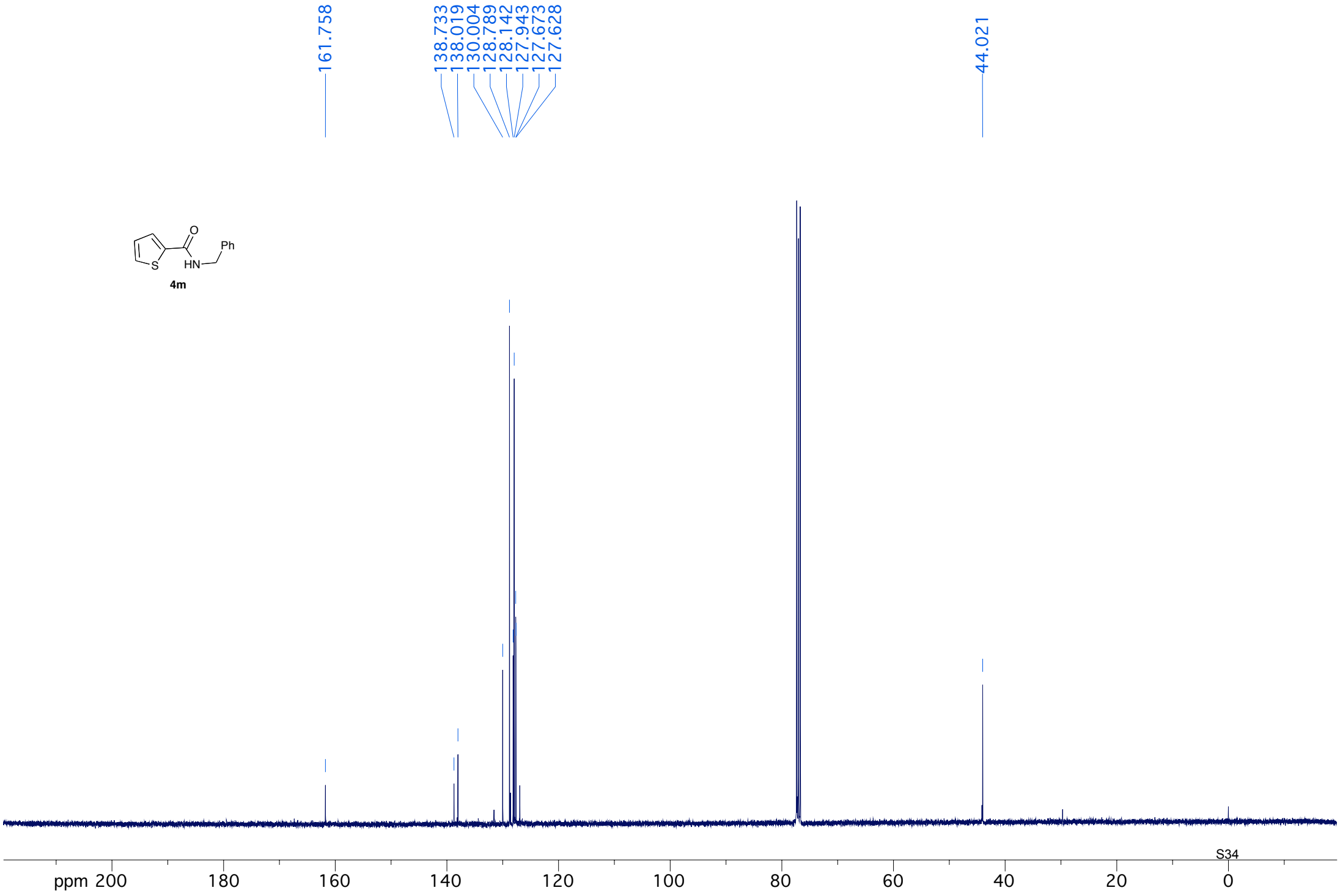

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