# Iron(II)-catalyzed aminobromination of allyl *N*-tosyloxycarbamates

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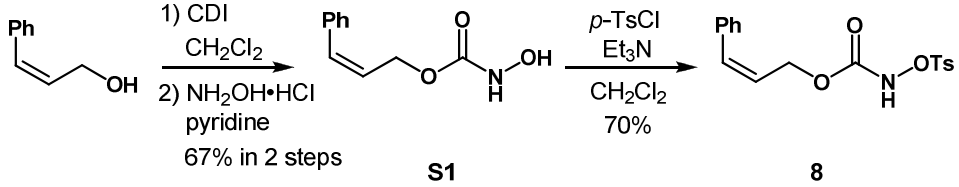
**Supplementary Information**

**General.** Melting points are uncorrected. All reagents were used as received from commercial suppliers unless otherwise stated. $^{1}$H NMR spectra (500, 400 or 300 MHz) and $^{13}$C NMR spectra (125, 100 or 75 MHz) were measured in the specified solvents. Chemical shifts are reported in ppm relative to the internal solvent signal [chloroform-*d*: 7.26 ppm ($^{1}$H NMR), 77.0 ppm ($^{13}$C NMR)]. FT-IR spectra were recorded for samples loaded as neat films on NaCl plates. Mass spectra were obtained according to the specified technique. Analytical thin layer chromatography (TLC) was performed using Kieselgel 60 $F_{254}$, and compounds were visualized with UV light, anisaldehyde solution or phosphomolybdic acid in EtOH.

***Scheme 1.*** Preparation of *N*-tosyloxy carbamate **8**



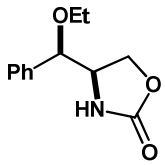

**Preparation of (*Z*)-3-Phenylallyl hydroxycarbamate (S1)**: To a stirred solution of (*Z*)-cinnamyl alcohol (624 mg, 4.7 mmol) in $CH_2Cl_2$ (8 mL) at room temperature was added CDI (829 mg, 5.1 mmol). After 1 h, the mixture was poured into a separation funnel where it was partitioned between sat. $NH_4Cl$ and $CH_2Cl_2$. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was used for the next reaction without purification. The residue was dissolved in pyridine (10 mL), and hydroxylamine hydrochloride (969 mg, 14.0 mmol) was added to the mixture. After being stirred for 30 min at room temperature, the mixture was extracted with $Et_2O$ and washed with 10% $H_2SO_4$. The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 1:2) to give *N*-hydroxy carbamate **S1** (606 mg, 67% in 2 steps) as a colorless solid. ***N*-hydroxy carbamate S1**: Colorless solids of mp 35-36 $^{o}$C; IR (neat) ν 3291, 1717 cm$^{-1}$; $^{1}$H NMR (300 MHz $CDCl_3$) δ 7.41-7.15 (m, 5H), 6.69 (d, 1H, *J* = 11.7 Hz), 6.14 (brs, 1H), 5.81 (dt, 1H, *J* = 11.7, 6.9 Hz), 4.94 (dd, 2H, *J* = 6.9, 1.7 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.1, 135.8, 133.5, 128.7, 128.4, 127.6, 125.2, 63.1; MS *m/z*: 216 $[M+Na]^+$, 55 (100%); HRMS (FAB) calcd for $C_{10}H_{11}NO_3Na$ $[M+Na]^+$: 216.0637, found: 216.0626.

**Preparation of (*Z*)-3-phenylallyl hydroxycarbamate (8)**: To a stirred solution of *N*-hydroxy carbamate **S1** (548 mg, 2.8 mmol) in $Et_2O$ (8 mL) at room temperature were added *p*-TsCl (541 mg, 2.8 mmol) and $Et_3N$ (356 μL, 2.6 mmol). After 3 h, the mixture was filtered through a pad of celite, and the filter cake was washed with $Et_2O$. The filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 1:3) to give *N*-tosyloxy carbamate **8** (688 mg, 70%) as a colorless solid. ***N*-tosyloxy carbamate 8:** Colorless fine needles of mp 119-120 $^{o}$C (EtOAc/*n*-hexane); IR (neat) ν 3281, 1742, 1381, 1192, 1090 cm$^{-1}$; $^{1}$H NMR (300 MHz $CDCl_3$) δ 7.93-7.84 (m, 3H), 7.39-7.24 (m, 5H), 7.16-7.10 (m, 2H), 6.65 (d, 1H, *J* = 11.7 Hz), 5.59 (dt, 1H, *J* = 11.7, 6.5 Hz), 4.76 (dd, 1H, *J* = 6.9, 1.7 Hz), 2.41 (s, 3H); $^{13}$C NMR (100

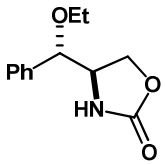
MHz, $CDCl_3$) δ 155.3, 146.1, 135.5, 133.7, 130.1, 129.7, 129.5, 128.6, 128.4, 127.7, 124.3, 63.7, 21.7; MS *m/z*: 348 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_{17}H_{18}SNO_5$ $[M+H]^+$: 348.0906, found: 348.0888.

***NOTE:*** All other substrates **1**, **9**, **10**, **11**, and **12** are known. They were prepared by the established methods,[1,3] and their spectroscopic and analytical data were identical with those reported in the literatures.

**Table 1, entry 1:** To a stirred solution of *N*-tosyloxy carbamate **1** (102 mg, 0.30 mmol) in EtOH (5 mL) at room temperature were added *n*-$Bu_4NBr$ (114 mg, 0.35 mmol) and $FeBr_2$ (6.5 mg, 0.030 mmol). After sonicating for 3 min, the mixture was stirred at room temperature for a further 17 h. The mixture was transferred to a separatory funnel where it was partitioned between $H_2O$ and EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/*n*-hexane 2:5 to 1:1) to give unreacted *N*-tosyloxy carbamate **1** (47.8 mg, 47%) as a colorless solid, carbamate **7** (8.4 mg, 16%) as a colorless solid, and a mixture of bromide **4a**, **4b**, oxazolidinone derivative **5a**, and **5b** (25.3 mg) as a colorless solid. The yields and the ratio of the products were determined by $^1H$ NMR analysis to be **4a**/**4b** (15.6 mg, 21%, dr = 1.5:1) and **5a**/**5b** (9.7 mg, 15%). The spectroscopic and analytical data of compounds **4a**/**4b** and **7** were identical with those obtained by the typical procedure described in the paper.




**5a**



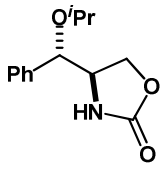

**5b**

**(*RS*)-4-[(*RS*)-Ethoxy(phenyl)methyl]oxazolidin-2-one (5a)**: Colorless solids of mp 97-98 $^oC$; IR (neat) ν 3283, 1759, $cm^{-1}$; $^1H$ NMR (400 MHz $CD_3OD$) δ 7.40-7.19 (m, 5H), 4.19 (m, 1H), 4.10-3.94 (m, 3H), 3.39-3.23 (m, 2H), 1.10 (dt, 3H, *J* = 6.9, 1.4 Hz); $^{13}C$ NMR (100 MHz, $CD_3OD$) δ 162.2, 138.8, 129.8, 129.7, 128.6, 84.8, 67.6, 65.4, 58.7, 15.5; MS *m/z*: 222 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, found: 222.1146.

**(*RS*)-4-[(*SR*)-Ethoxy(phenyl)methyl]oxazolidin-2-one (5b)**: Colorless solids of mp 113-114 $^oC$; IR (neat) ν 3279, 1751, $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) δ 7.43-7.29 (m, 5H), 4.67 (brs, 1H), 4.53 (dd, 1H, *J* = 9.2, 8.2 Hz), 4.44 (dd, 1H, *J* = 9.2, 4.6 Hz), 3.89 (ddt, 1H, *J* = 8.2, 4.6, 0.9 Hz), 3.49-3.29 (m, 2H), 1.17 (t, 3H, *J* = 6.9 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.8, 137.7, 129.0, 128.9, 127.2, 83.2, 68.4, 64.5, 57.0, 15.1; MS *m/z*: 222 $[M+H]^+$, 222 (100%); HRMS (FAB) calcd for $C_{12}H_{16}NO_3[M+H]^+$: 222.1130, found: 222.1128.

**Table 1, entry 2:** *N*-Tosyloxy carbamate **1** (102 mg, 0.3 mmol) in *i*-PrOH (5 mL) was treated with $FeBr_2$ (6.2 mg, 0.029 mmol) and *n*-$Bu_4NBr$ (113 mg, 0.35 mmol) for 14 h. The above-mentioned work-up and subsequent purification of the crude material by silica gel column chromatography

(EtOAc/*n*-hexane 2:5 to 1:1) gave unreacted *N*-tosyloxy carbamate **1** (6.6 mg, 6%) as a colorless solid, carbamate **7** (7.4 mg, 14%) as a colorless solid, and a mixture of bromide **4a**, **4b**, and oxazolidinone derivative **6** (57.5 mg) as a colorless solid. The yields and the ratio of the products were determined by $^1$H NMR analysis to be **4a**/**4b** (51.6 mg, 69%, dr = 3.3:1) and **6** (5.9 mg, 9%).




**6**

**(*RS*)-4-[(*SR*)-Isopropoxy(phenyl)methyl]oxazolidin-2-one (6)**: Colorless solids of mp 116-118 $^o$C; IR (neat) ν 3279, 1751 cm$^{-1}$; $^1$H NMR (400 MHz $CDCl_3$) δ 7.42-7.30 (m, 5H), 4.77 (brs, 1H), 4.50 (t, 1H, *J* = 8.7 Hz), 4.40 (dd, 1H, *J* = 9.2, 4.6 Hz), 4.26 (d, 1H, *J* = 8.2 Hz), 3.85 (dt, 1H, *J* = 7.8, 4.6 Hz), 3.52 (septet, 1H, *J* = 6.0 Hz), 1.15 (d, 3H, *J* = 6.0 Hz), 1.06 (d, 3H, *J* = 6.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.9, 138.4, 128.9, 128.8, 127.2, 80.5, 69.4, 68.4, 57.1, 23.3, 20.9; MS *m/z*: 236 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$: 236.1287, found: 236.1286.

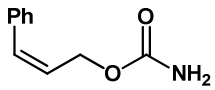
**Table 1, entry 3:** The details are already provided in the paper.

**Table 1, entry 4:** *N*-Tosyloxy carbamate **1** (42.9 mg, 0.12 mmol) in *t*-BuOH (15 mL) was treated with $FeBr_2$ (30 mg, 0.14 mmol) for 1 h. The above-mentioned work-up and subsequent purification by silica gel column chromatography (EtOAc/*n*-hexane 2:5 to 1:1) gave carbamate **7** (4.7 mg, 21%) as a colorless solid and a mixture of bromides **4a** and **4b** (19.5 mg, 61%, dr = 1.1:1 determined by $^1$H NMR analysis) as a colorless solid.

**Table 1, entry 5:** *N*-Tosyloxy carbamate **1** (20.9 mg, 0.060 mmol) in *t*-BuOH (2 mL) was treated with *n*-$Bu_4NBr$ (19.4 mg, 0.060 mmol) for 17 h. The above-mentioned work-up and subsequent purification by silica gel column chromatography (EtOAc/*n*-hexane 1:3 to 2:5) gave unreacted carbamate **1** (3.4 mg, 16%) as a colorless solid and carbamate **7** (3.4 mg, 32%) as a colorless solid.

**Table 1, entry 6:** Azidoformate **2** (105.1 mg, 0.52 mmol) in *t*-BuOH (8 mL) was treated with $FeBr_2$ (11.4 mg, 0.052 mmol) and *n*-$Bu_4NBr$ (200 mg, 0.62 mmol) for 22 h. The above-mentioned work-up and subsequent purification by silica gel column chromatography (EtOAc/*n*-hexane 1:10 to 1:1) gave azidoformate **2** (72.0 mg, 69%) as a colorless solid, carbamate **7** (1.8 mg, 2%) as a colorless solid, and a mixture of bromide **4a** and **4b** (25.6 mg, 19%, dr = 5:1 determined by $^1$H NMR analysis).

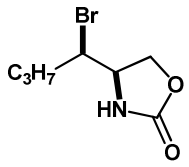
**Table 2, entry1:** *N*-Tosyloxy carbamate **8** (108 mg, 0.31 mmol) in *t*-BuOH (5 mL) was treated with $FeBr_2$ (13.6 mg, 0.062 mmol) and *n*-$Bu_4NBr$ (120 mg, 0.37 mmol) for 1 h. The above-mentioned work-up and subsequent purification of the crude material by silica gel column chromatography (EtOAc/*n*-hexane 1:2) gave carbamate **S2** (4.1 mg, 7%) as a colorless solid and a mixture of bromide **4a** and **4b** (70.2 mg, 88%, dr = 1:1.5 determined by $^1$H NMR analysis).



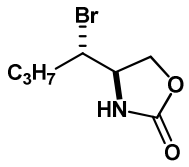

**S2**

**(*Z*)-3-Phenylallyl carbamate (S2)**: Colorless solids of mp 68-70 °C; IR (neat) ν 3480, 3345, 1715, 1385, 1321 $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) δ 7.42-7.17 (m, 5H), 6.66 (d, 1H, *J* = 11.9 Hz), 5.82 (dt, 1H, *J* = 11.9, 6.4 Hz), 4.85 (dd, 2H, *J* = 6.4, 1.4 Hz), 4.67 (brs, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 156.6, 136.0, 132.7, 128.7, 128.4, 127.5, 126.1, 62.1; MS *m/z*: 177 ($M^+$), 115 (100%); HRMS (EI) calcd for $C_{10}H_{11}NO_2$ ($M^+$): 177.0790, found: 177.0815.

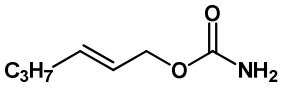
**Table 2, entry 2:** *N*-Tosyloxy carbamate **9**[3] (112 mg, 0.36 mmol) in *t*-BuOH (6 mL) was treated with $FeBr_2$ (7.9 mg, 0.036 mmol) and *n*-$Bu_4NBr$ (138 mg, 0.43 mmol) for 5 h. The above-mentioned work-up and subsequent purification of the crude material by silica gel column chromatography (EtOAc/*n*-hexane 4:5 to 1:0) gave carbamate **S3** (2.0 mg, 4%) as a colorless solid and a mixture of bromide **13a** and **13b** (68.4 mg, 87%, dr = 1:1.5 determined by $^1H$ NMR analysis).




**13a**




**13b**




**S3**

**(*RS*)-4-[(*RS*)-1-Bromobutyl]oxazolidin-2-one (13a):** Colorless cubic crystals of mp 97-98 °C (EtOAc/*n*-hexane); IR (neat) ν 3264, 1748, $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) δ 5.59 (brs, 1H), 4.51 (t, 1H, *J* = 9.2 Hz), 4.23 (dd, 1H, *J* = 9.2, 5.5 Hz), 4.09 (m, 1H), 3.94 (m, 1H), 1.78-1.63 (m, 3H), 1.46 (m, 1H), 0.96 (t, 3H, *J* = 7.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.0, 67.8, 57.5, 57.3, 35.4, 20.6, 13.3; MS *m/z*: 222 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_7H_{13}{}^{79}BrNO_2$ $[M+H]^+$: 222.0130, found: 222.0135.

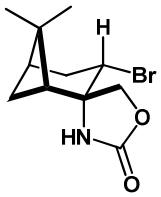
**(*RS*)-4-[(*SR*)-1-Bromobutyl]oxazolidin-2-one (13b):** Colorless needles of mp 58-60 °C (EtOAc/*n*-hexane); IR (neat) ν 3258, 1751 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) δ 6.03 (brs, 1H), 4.53 (t, 1H, *J* = 9.2 Hz), 4.30 (dd, 1H, *J* = 9.2, 4.9 Hz), 4.08 (m, 1H), 3.92 (ddd, 1H, *J* = 9.8, 7.3, 3.1 Hz), 1.85-1.61 (m, 3H), 1.47 (m, 1H), 0.96 (t, 3H, *J* = 7.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.0, 69.2, 57.7, 57.3, 36.0, 20.2, 13.2; MS *m/z*: 222 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_7H_{13}{}^{79}BrNO_2$ $[M+H]^+$: 222.0130, found: 222.0134.

**(*E*)-Hex-2-en-1-yl carbamate (S3)**: Colorless solids of mp 47-48 °C; IR (neat) ν 3435, 3335, 1683, $cm^{-1}$; $^1H$ NMR (400 MHz $CDCl_3$) δ 5.77 (dt, 1H, *J* = 15.1, 6.9 Hz) 5.57 (dt, 1H, *J* = 15.1, 6.4 Hz) 4.67 (brs, 2H), 4.50 (d, 1H, *J* = 6.4 Hz), 2.03 (q, 2H, *J* = 7.3 Hz), 1.41 (sextet, 2H, *J* = 7.3 Hz), 0.90 (t, 3H, *J* = 7.3 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 156.7, 136.2, 124.2, 65.9, 34.3, 22.0, 13.6; MS *m/z*: 143 ($M^+$) 67 (100%); HRMS (EI) calcd for $C_7H_{13}NO_2$ ($M^+$): 143.0946, found: 143.0952.

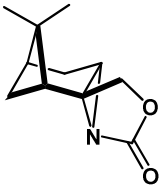
**Table 2, entry 3:** *N*-Tosyloxy carbamate **10**[1] (100 mg, 0.32 mmol) in *t*-BuOH (5 mL) was treated with $FeBr_2$ (14.1 mg, 0.064 mmol) and *n*-$Bu_4NBr$ (124 mg, 0.39 mmol) for 1 h. The above-mentioned

work-up and subsequent purification of the crude material by silica gel column chromatography (EtOAc/*n*-hexane 2:3) gave a mixture of bromide **13a** and **13b** (61.8 mg, 87%, dr = 1:1.9 determined by $^1$H NMR analysis). The spectroscopic and analytical data of compounds **13a**/**13b** were identical with those obtained above.

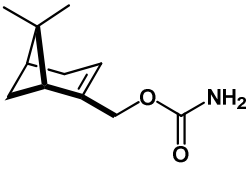
**Table 2, entry 4:** *N*-Tosyloxy carbamate **11**[1] (110 mg, 0.30 mmol) in *t*-BuOH (5 mL) was treated with $FeBr_2$ (13.3 mg, 0.060 mmol) and *n*-$Bu_4NBr$ (117 mg, 0.36 mmol) for 3 h. The above-mentioned work-up and subsequent purification of the crude material by silica gel column chromatography (EtOAc/*n*-hexane 1:5 to 1:0) gave azirizine **16** (2.2 mg, 4%) as a colorless solid, carbamate **S4** (3.5 mg, 6%) as a colorless solid, and bromide **14** (70.6 mg, 85%) as a colorless solid. The spectroscopic data of azirizine **16** were identical with those reported.[1]



**14**



**16**

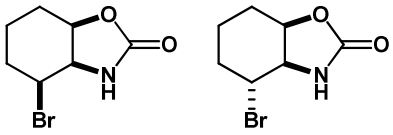


**S4**

**(1*R*,2*S*,3*S*,5*R*)-3-Bromo-6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,4'-oxazolidin]-2'-one (14)**: Colorless cubic crystals of mp 156-157 $^o$C (EtOAc/*n*-hexane);$[\alpha]_D^{25}$ +25.3 (*c* 1.01, $CHCl_3$); IR (neat) ν 3237, 1751 cm$^{-1}$; $^1$H NMR (300 MHz $CDCl_3$) δ 6.52 (brs, 1H), 4.60 (dd, 1H, *J* = 10.0, 7.6 Hz), 4.21 (d, 1H, *J* = 16.2 Hz), 4.18 (d, 1H, *J* = 16.2 Hz), 2.73 (m, 1H), 2.53-2.34 (m, 3H), 2.04 (m, 1H), 1.30 (s, 3H), 1.22 (d, 1H, *J* = 11.0 Hz), 1.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.6, 76.8, 65.2, 53.8, 52.4, 41.7, 39.8, 38.2, 29.6, 27.2, 23.6; MS *m/z*: 274 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_{11}H_{17}{}^{79}Br\,NO_2$ $[M+H]^+$: 274.0443, found: 274.0421.

**[(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]methyl carbamate (S4)**: Colorless needles of mp 62-63 $^o$C (EtOAc/*n*-hexane); $[\alpha]_D^{25}$ -42.5(*c* 1.71, $CHCl_3$); IR (neat) ν 3464, 3347, 1715, 1329 cm$^{-1}$; $^1$H NMR (400 MHz $CDCl_3$) δ 5.56 (m, 1H), 4.61 (brs, 2H), 4.49-4.38 (m, 2H), 2.40 (dt, 1H, *J* = 8.7, 5.5 Hz), 2.36-2.20 (m, 2H), 2.16-2.07 (m, 2H), 1.60 (d, 1H, *J* = 3.2 Hz), 1.29 (s, 3H), 1.18 (d, 1H, 8.2 Hz), 0.83 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.1, 143.2, 121.1, 67.6, 43.3, 40.6, 38.0, 31.4, 31.2, 26.1, 21.0; MS *m/z*: 218 $[M+Na]^+$, 23 (100%); HRMS (FAB) calcd for $C_{11}H_{17}NO_2Na$ $[M+Na]^+$: 218.1157, found: 218.1154.

**Table 2, entry 5:** *N*-Tosyloxy carbamate **12**[3] (101 mg, 0.32 mmol) in *t*-BuOH (5 mL) was treated with $FeBr_2$ (14.3 mg, 0.065 mmol) and *n*-$Bu_4NBr$ (126 mg, 0.39 mmol) for 4 h. The above-mentioned work-up and subsequent purification of the crude material by silica gel column chromatography (EtOAc/*n*-hexane 2:3 to 2:1) gave bromide bromide **15a** (53.2 mg, 75%) as a colorless solid and **15b** (14.0 mg, 20%) as a colorless solid.



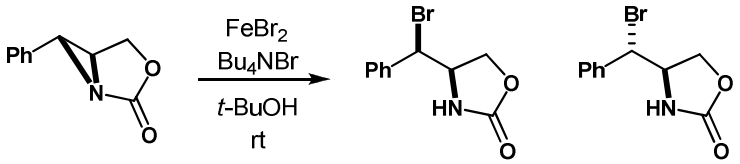
**15a** **15b**

**(3a*RS*,4*SR*,7a*RS*)-4-Bromohexahydrobenzo[d]oxazol-2(3*H*)-one (15a)**: Colorless needles of mp 164-165 °C (EtOAc/*n*-hexane); IR (neat) ν 3204, 1764 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) δ 5.21 (brs, 1H), 4.70 (dt, 1H, *J* = 7.3, 5.5 Hz), 4.29 (dd, 2H, *J* = 7.3, 4.3 Hz), 4.14 (ddd, 1H, *J* = 12.2, 4.3, 4.3 Hz), 2.15-1.94 (m, 3H), 1.92-1.83 (m, 1H), 1.78-1.69 (m, 1H), 1.48-1.37 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 158.4, 75.5, 56.5, 48.6, 28.8, 25.2, 19.7; MS *m/z*: 220 ($M^+$), 154 (100%); HRMS (FAB) calcd for $C_7H_{11}{}^{79}BrNO_2$ $[M+H]^+$: 219.9973, found: 219.9990.

**(3a*RS*,4*RS*,7a*RS*)-4-Bromohexahydrobenzo[d]oxazol-2(3*H*)-one (15b)**: Colorless cubic crystals of mp 128-129 °C (EtOAc/*n*-hexane); IR (neat) ν 3275, 1755 $cm^{-1}$; $^1H$ NMR (500 MHz $CDCl_3$) δ 5.57 (brs, 1H), 4.66 (m, 1H), 3.86 (ddd, 1H, *J* = 12.2, 8.5, 3.7 Hz), 3.78 (dd, 1H, *J* = 8.5, 6.1 Hz), 2.31-2.22 (m, 2H), 1.79-1.56 (m, 4H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 159.1, 76.9, 60.8, 53.7, 32.5, 25.8, 20.6; MS *m/z*: 220 $[M+H]^+$, 154 (100%); HRMS (FAB) calcd for $C_7H_{11}{}^{79}BrNO_2$ $[M+H]^+$: 219.9973, found: 219.9975.

**Preparation of authentic bromides by nucleophilic bromination of azirizines 17-19:**

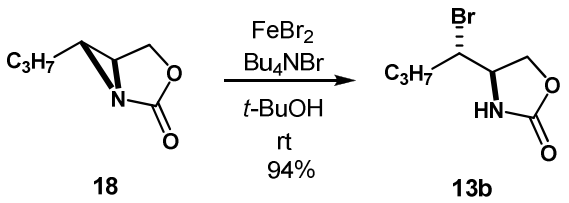
***Scheme 2.*** Bromination of aziridine **17**




**17** **4a** (5%) **4b** (78%)

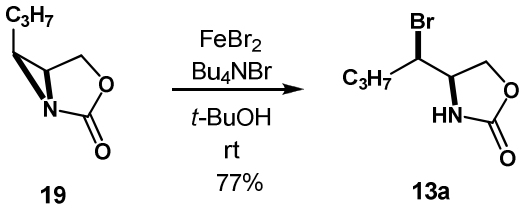
**(*RS*)-4-[(*RS*)-Bromo(phenyl)methyl]oxazolidin-2-one (4a),**
**(*RS*)-4-[(*SR*)-Bromo(phenyl)methyl]oxazolidin-2-one (4b):** To a stirred solution of azirizine **17**[1] (13.3 mg, 0.0759 mmol) in *t*-BuOH (11 mL) at room temperature were added *n*-$Bu_4NBr$ (48.9 mg, 0.152 mmol) and $FeBr_2$ (16.7 mg, 0.0759 mmol). The mixture was stirred at room temperature for further 30 min. The mixture was transferred to a separation funnel where it was partitioned between $H_2O$ and EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 1:1) to give inseparable mixture of bromides **4a** and **4b** (16.1 mg, 83%, dr = 1:16 determined by $^1H$ NMR analysis) as a colorless solid.

***Scheme 3.*** Bromination of aziridine **18**




**(*RS*)-4-[(*SR*)-1-Bromobutyl]oxazolidin-2-one (13b):** To a stirred solution of azirizine **18** [1] (17.7 mg, 0.125 mmol) in *t*-BuOH (15 mL) at room temperature were added *n*-$Bu_4NBr$ (80.6 mg, 0.250 mmol) and $FeBr_2$ (27.6 mg, 0.125 mmol). The mixture was stirred at room temperature for further 30 min. The mixture was transferred to a separation funnel where it was partitioned between $H_2O$ and EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 1:1) to give bromide **13b** (26.0 mg, 94%) as a colorless solid.

***Scheme 4.*** Bromination of aziridine **19**

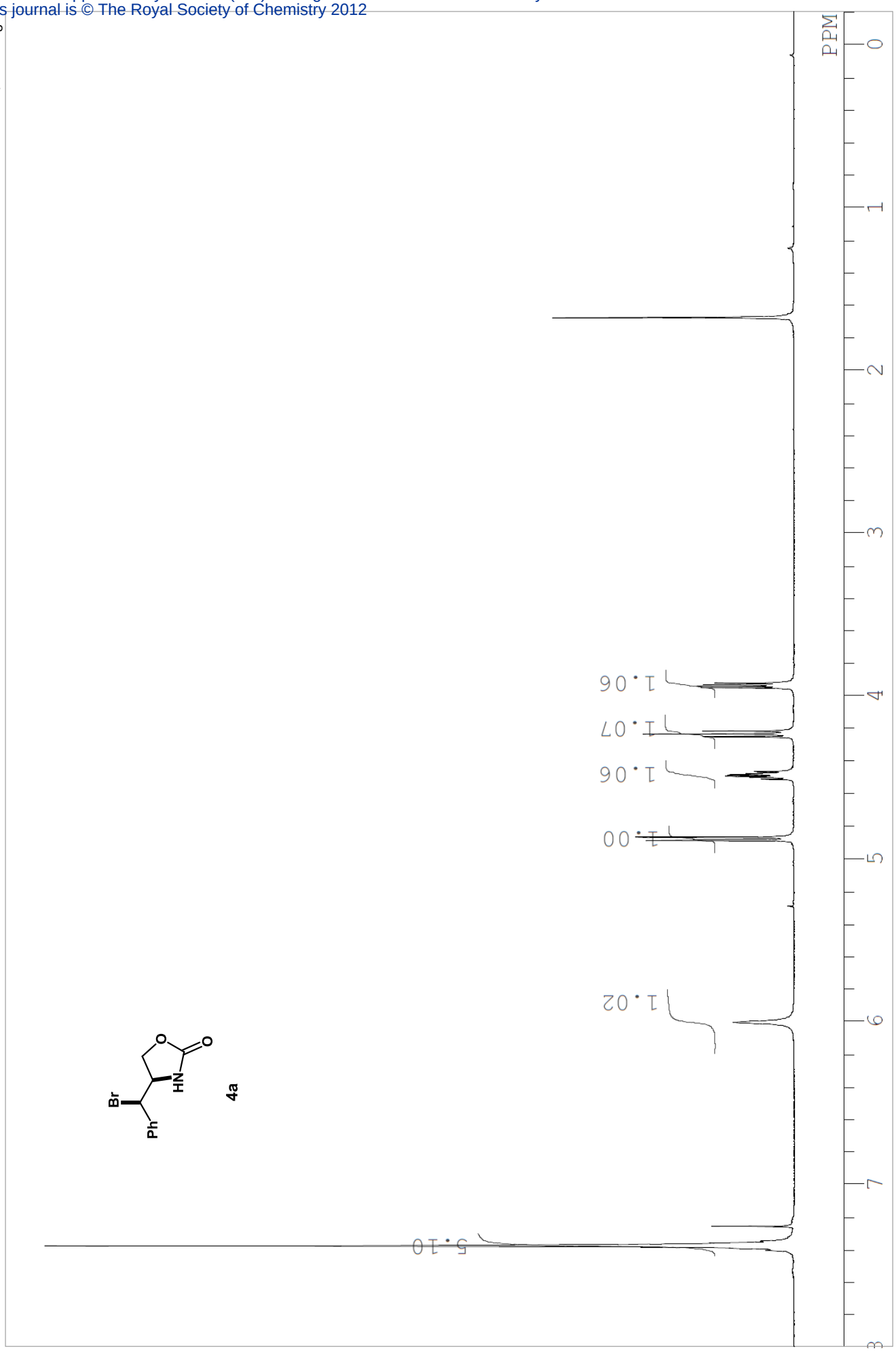


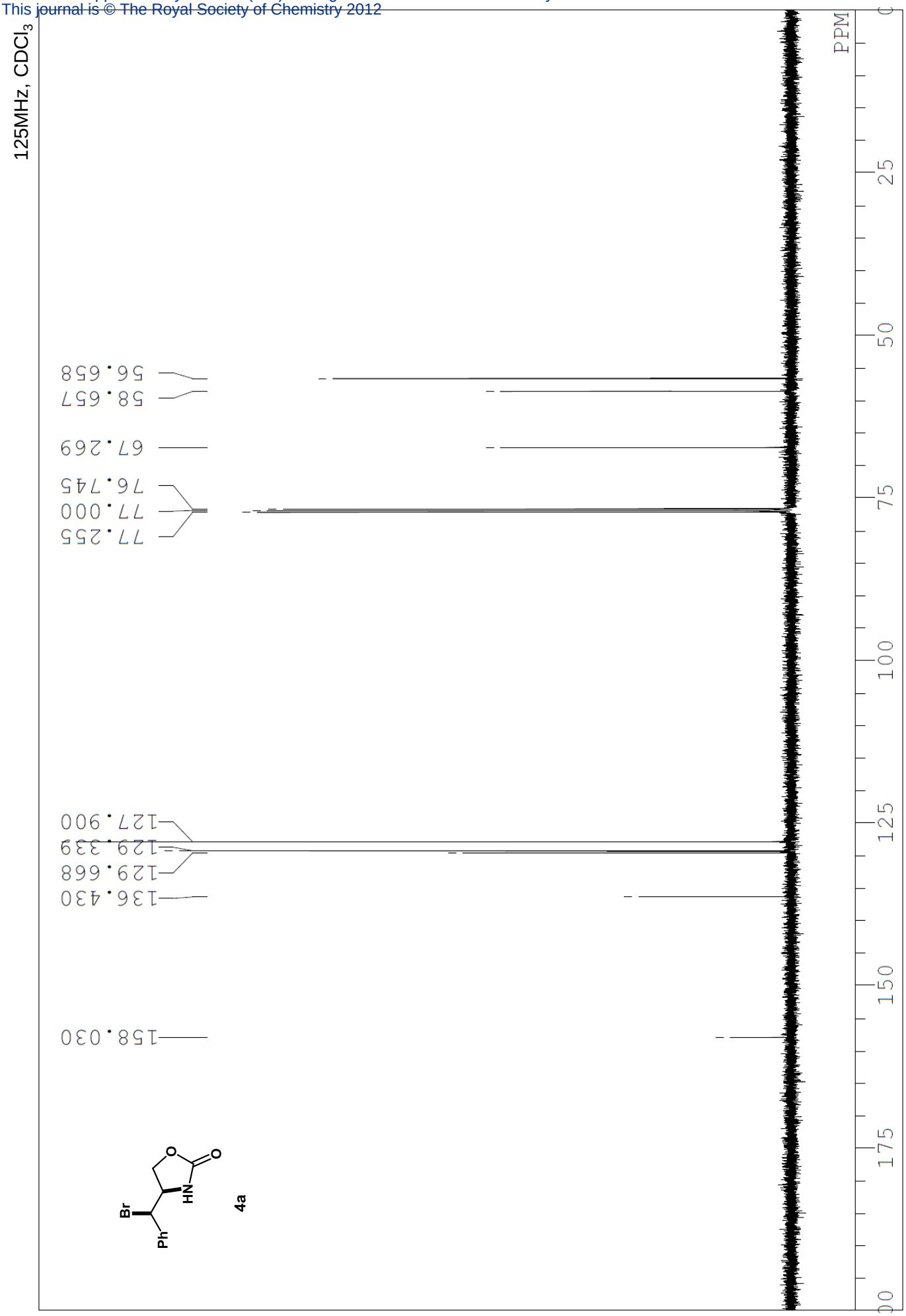

**(*RS*)-4-[(*RS*)-1-Bromobutyl]oxazolidin-2-one (13a):** To a stirred solution of azirizine **19** [1] (14.4 mg, 0.102 mmol) in *t*-BuOH (11 mL) at room temperature were added *n*-$Bu_4NBr$ (65.8 mg, 0.204 mmol) and $FeBr_2$ (22.0 mg, 0.102 mmol). The mixture was stirred at room temperature for further 1 h. The mixture was transferred to a separation funnel where it was partitioned between $H_2O$ and EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 1:1) to give bromide **13a** (17.4 mg, 77%) as a colorless solid.

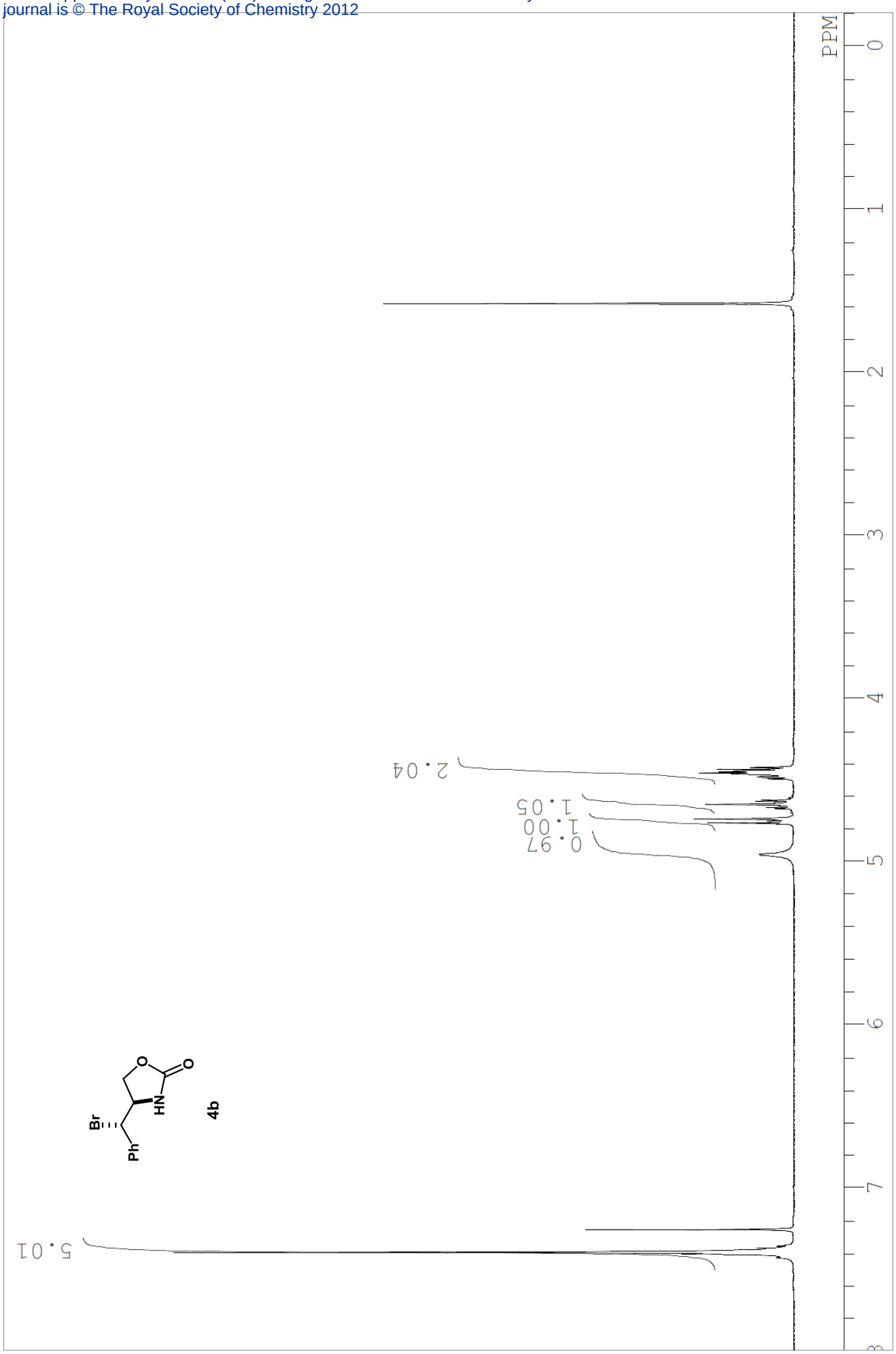
**Reference**

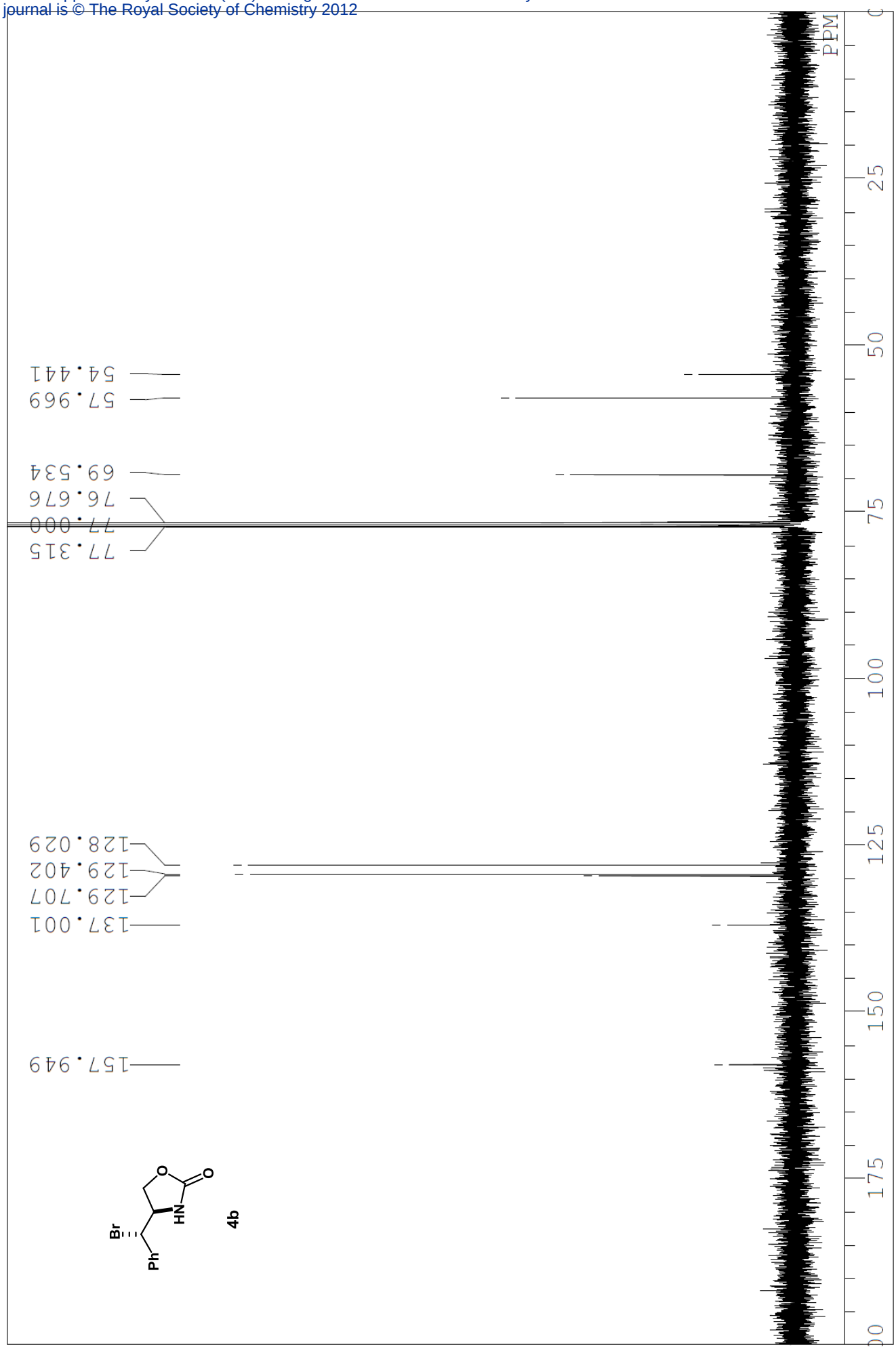
1. (a) Lebel, H.; Huard, K.; Lectard, S. *J. Am. Chem. Soc.* **2005**, *127*, 14198. (b) Lebel, H.; Lectard, S.; Parmentier, M. *Org. Lett.* **2007**, *9*, 4797-4800.
2. Jung, Y. H.; Kim, J. D. *Arch. Pharm. Res.* **2001**, *24*, 371-376.
3. Liu, R.; Herron, S. R.; Fleming, S. A. *J. Org. Chem*. **2007**. *72*, 5587-5591.

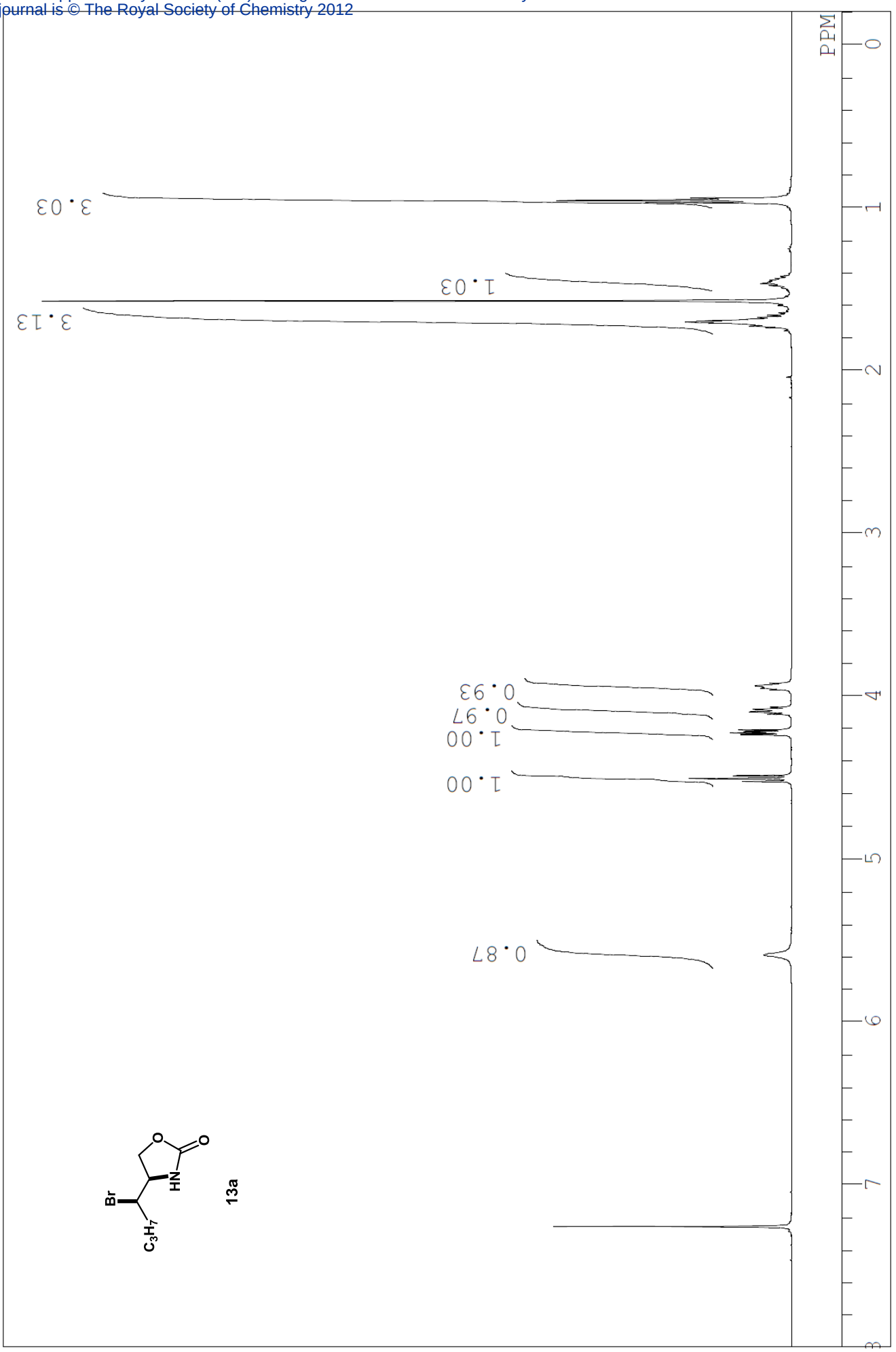
500MHz, $CDCl_3$

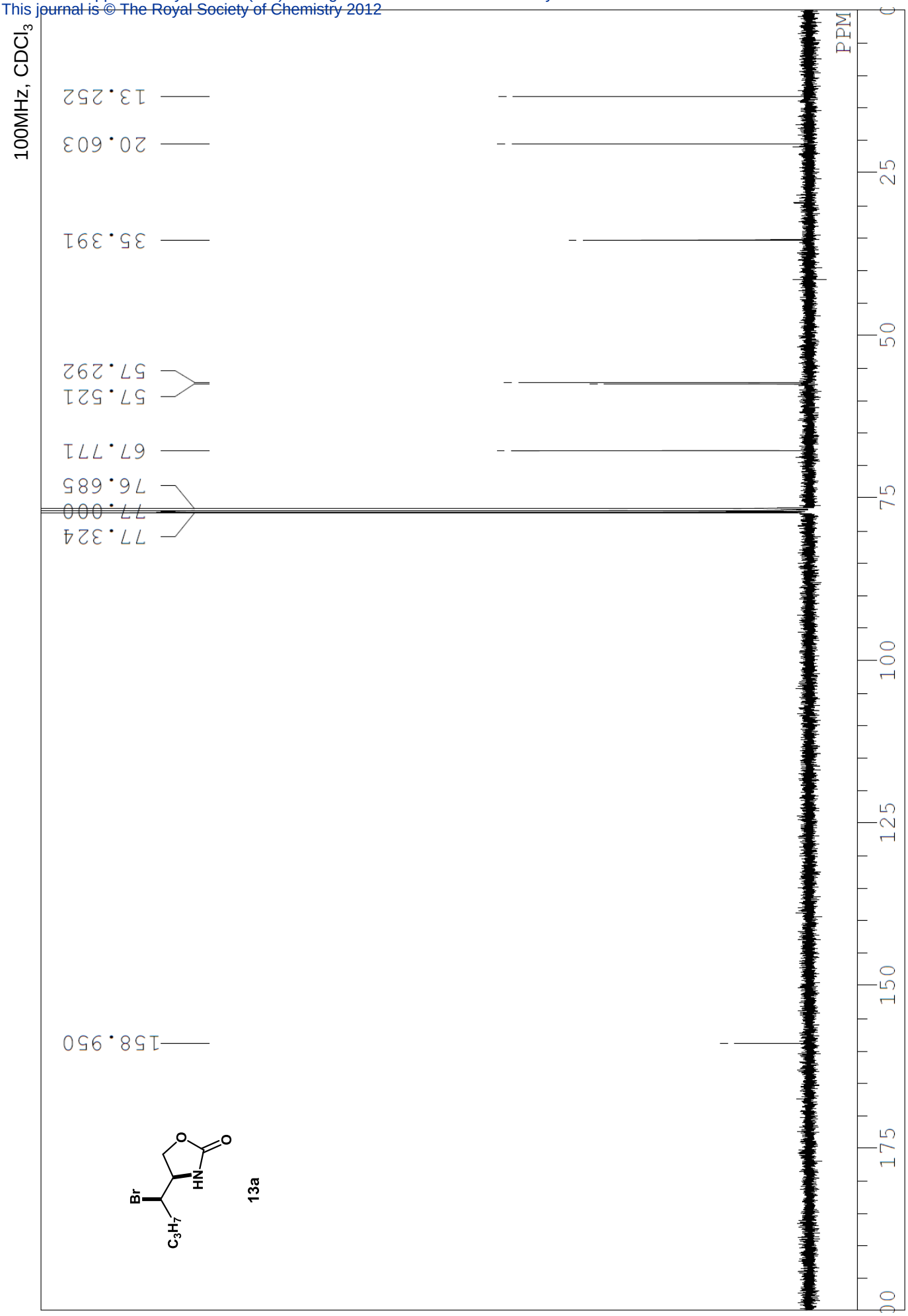




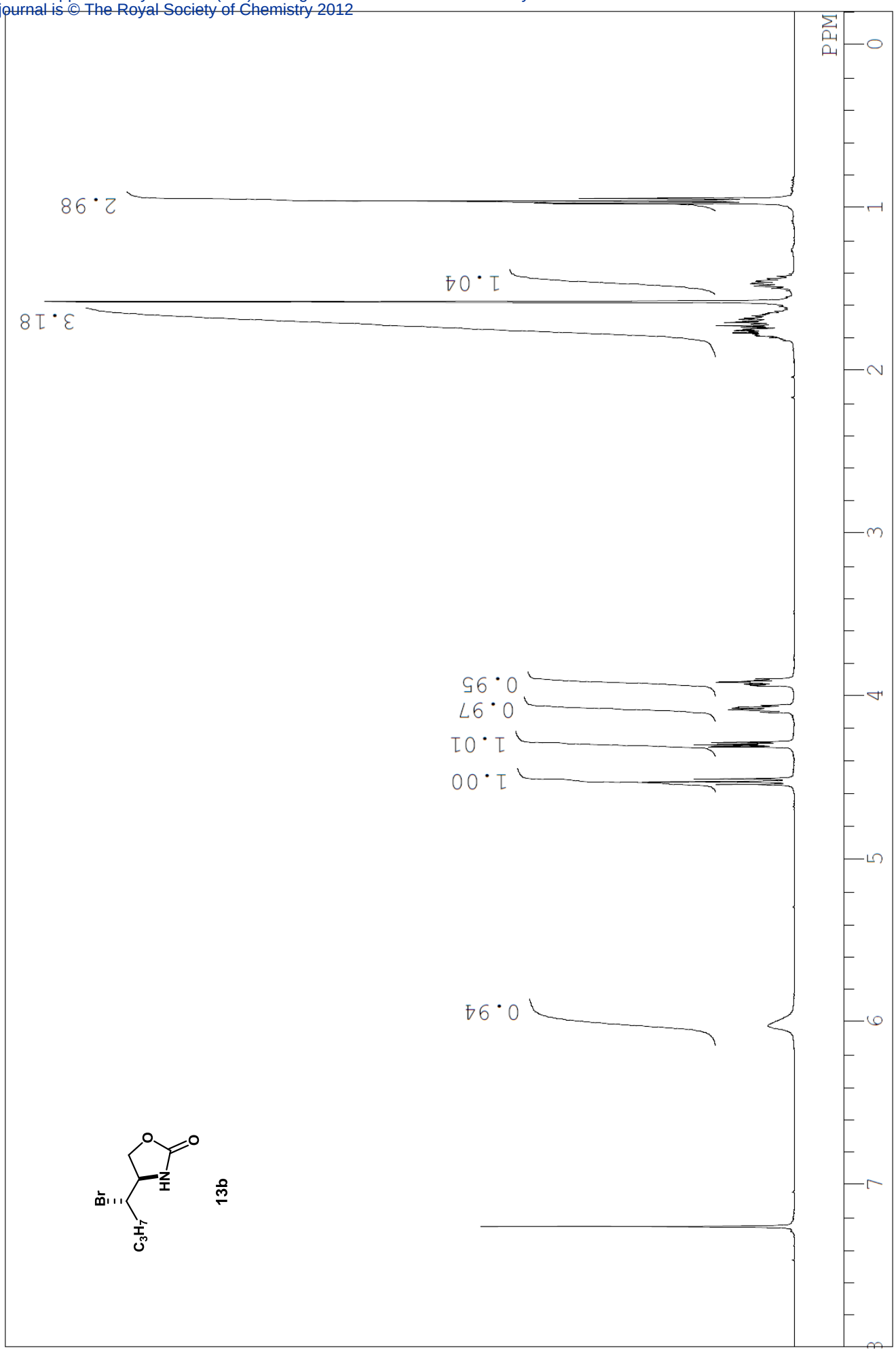


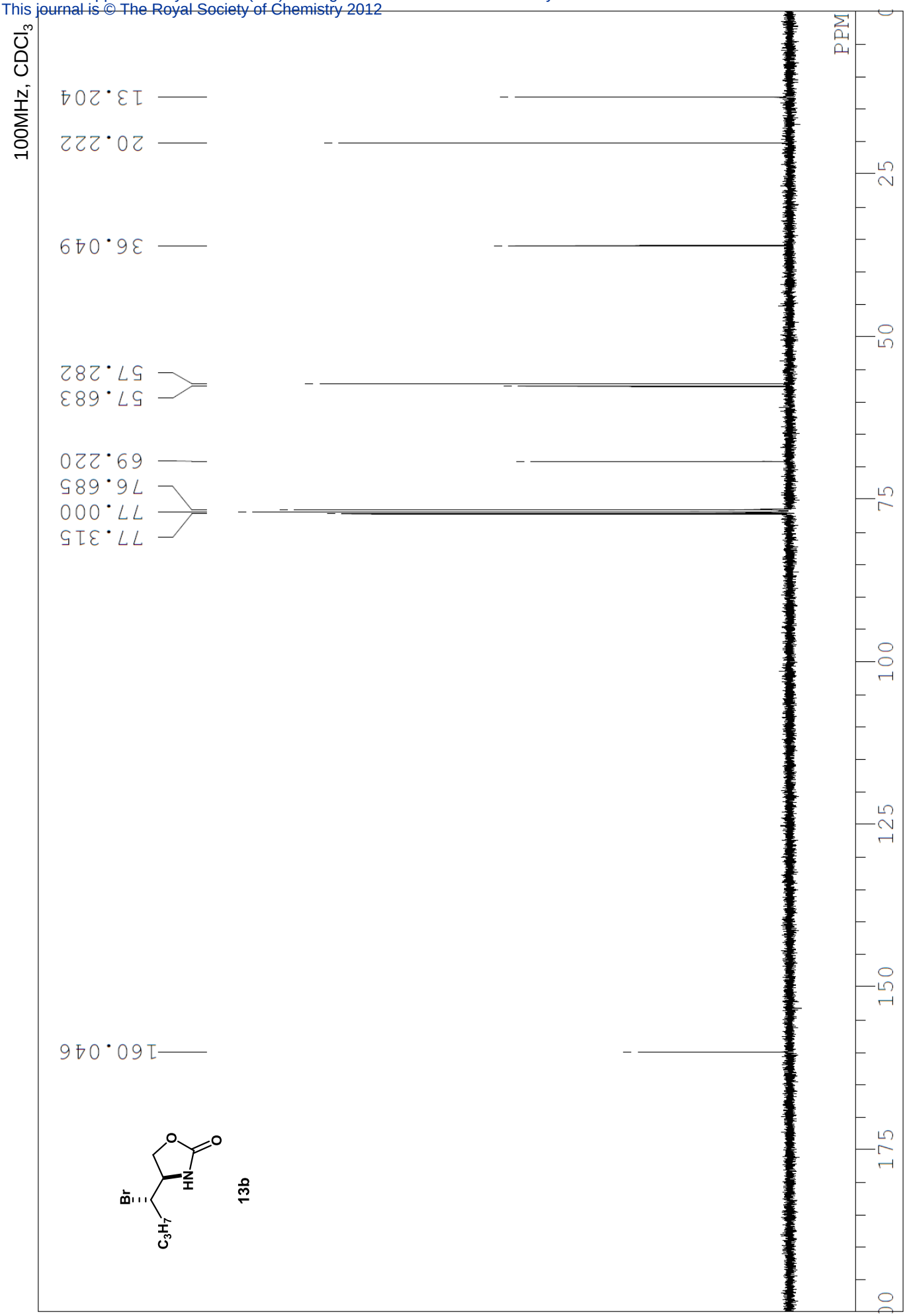


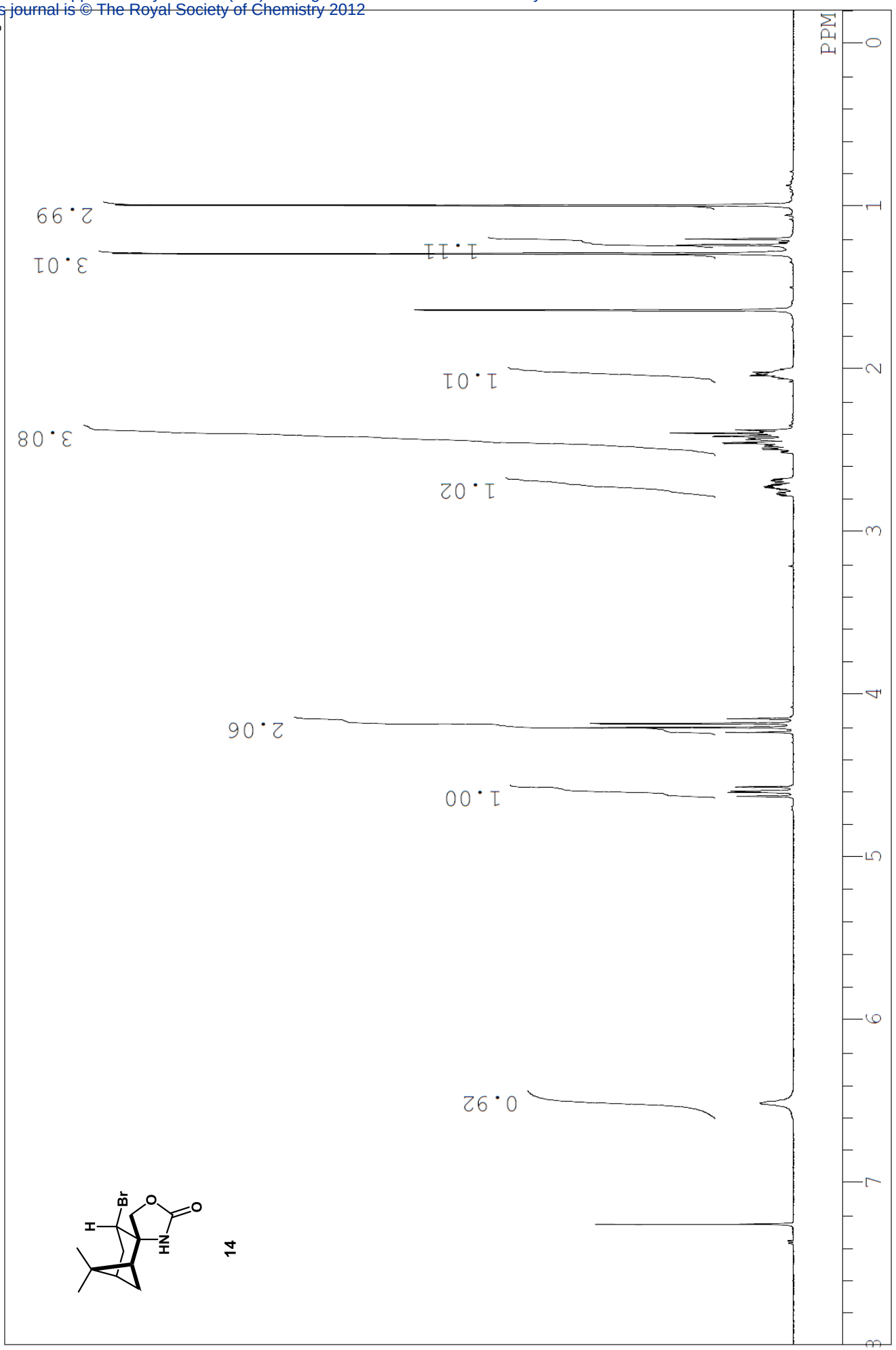


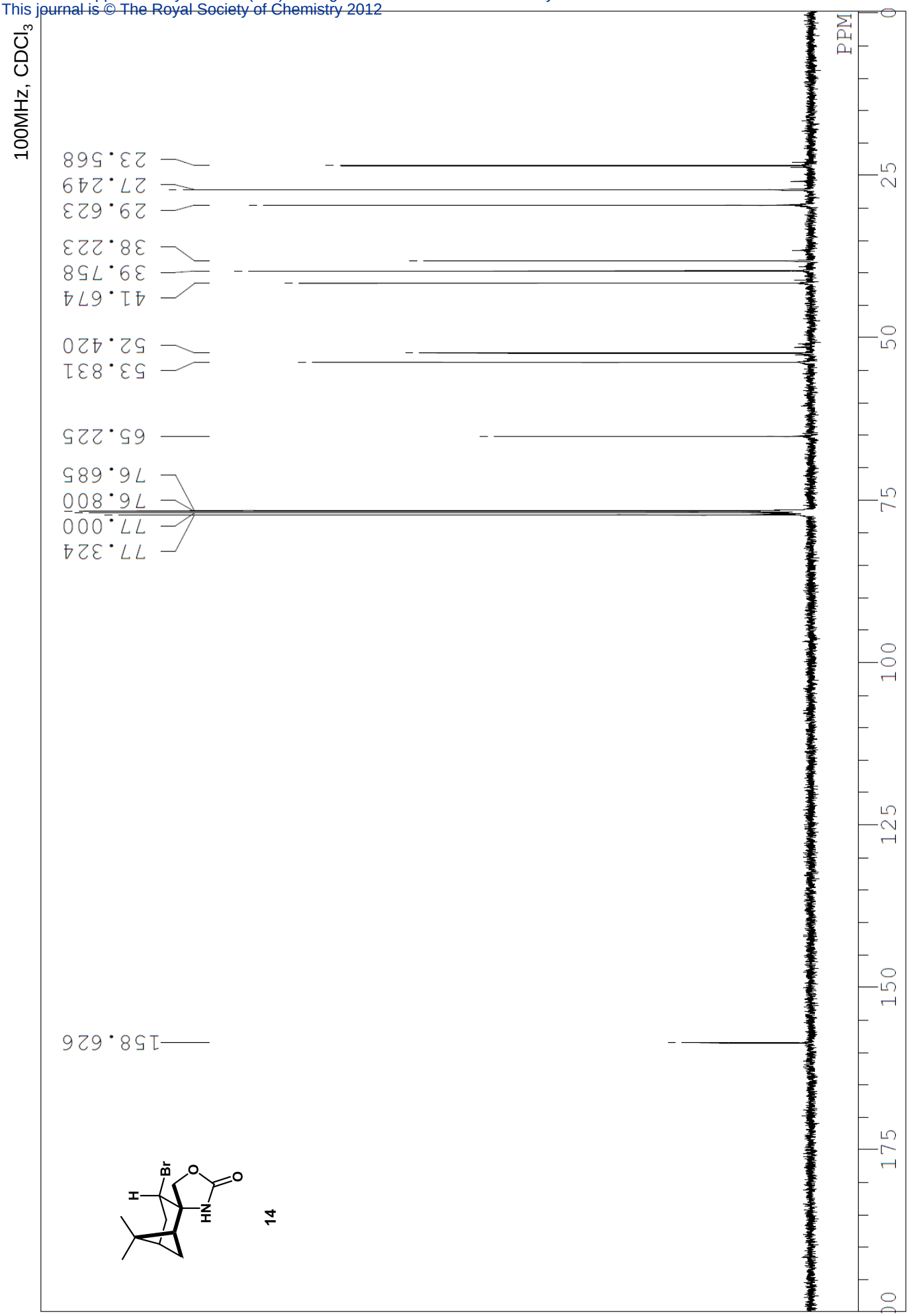


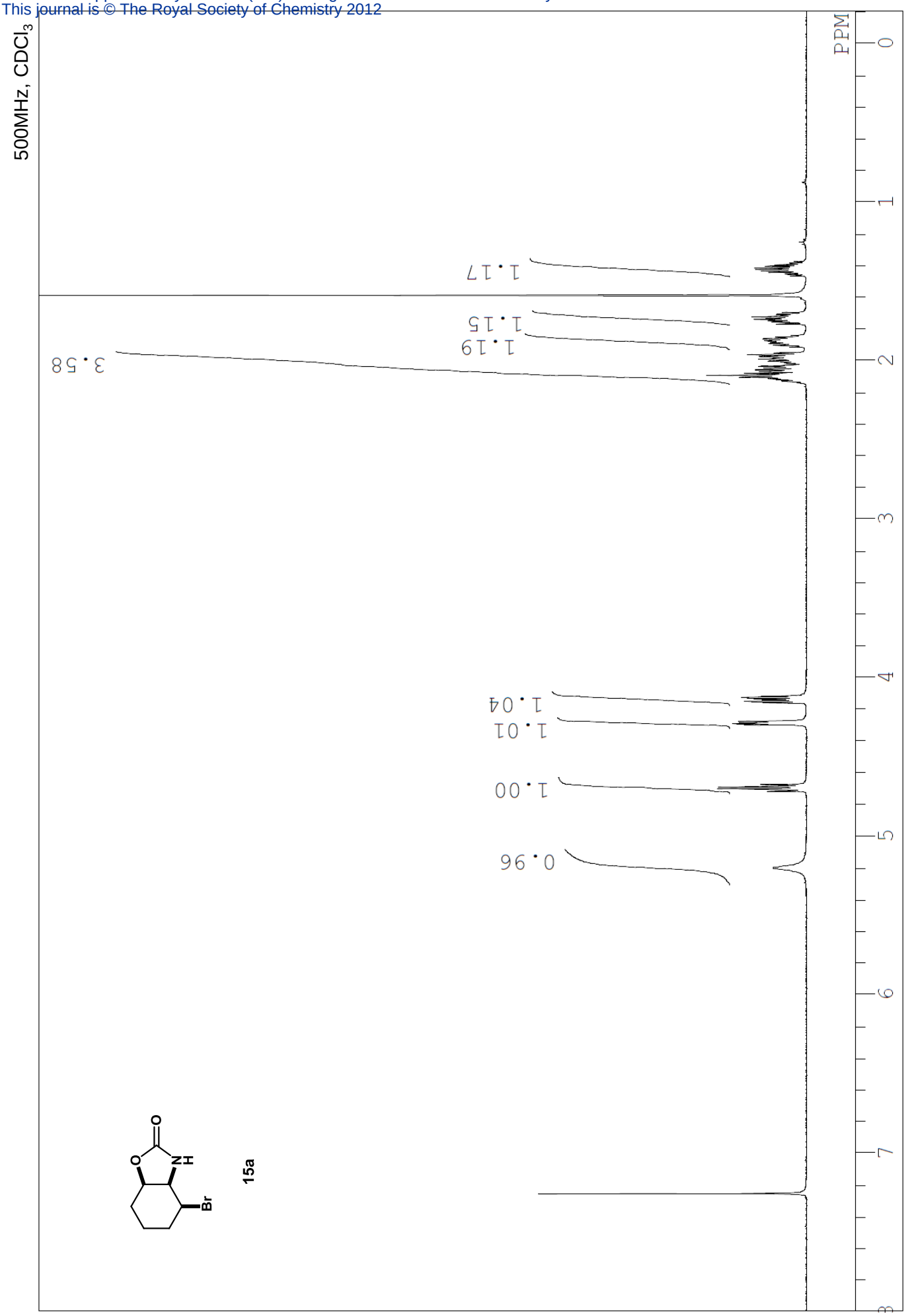

13a

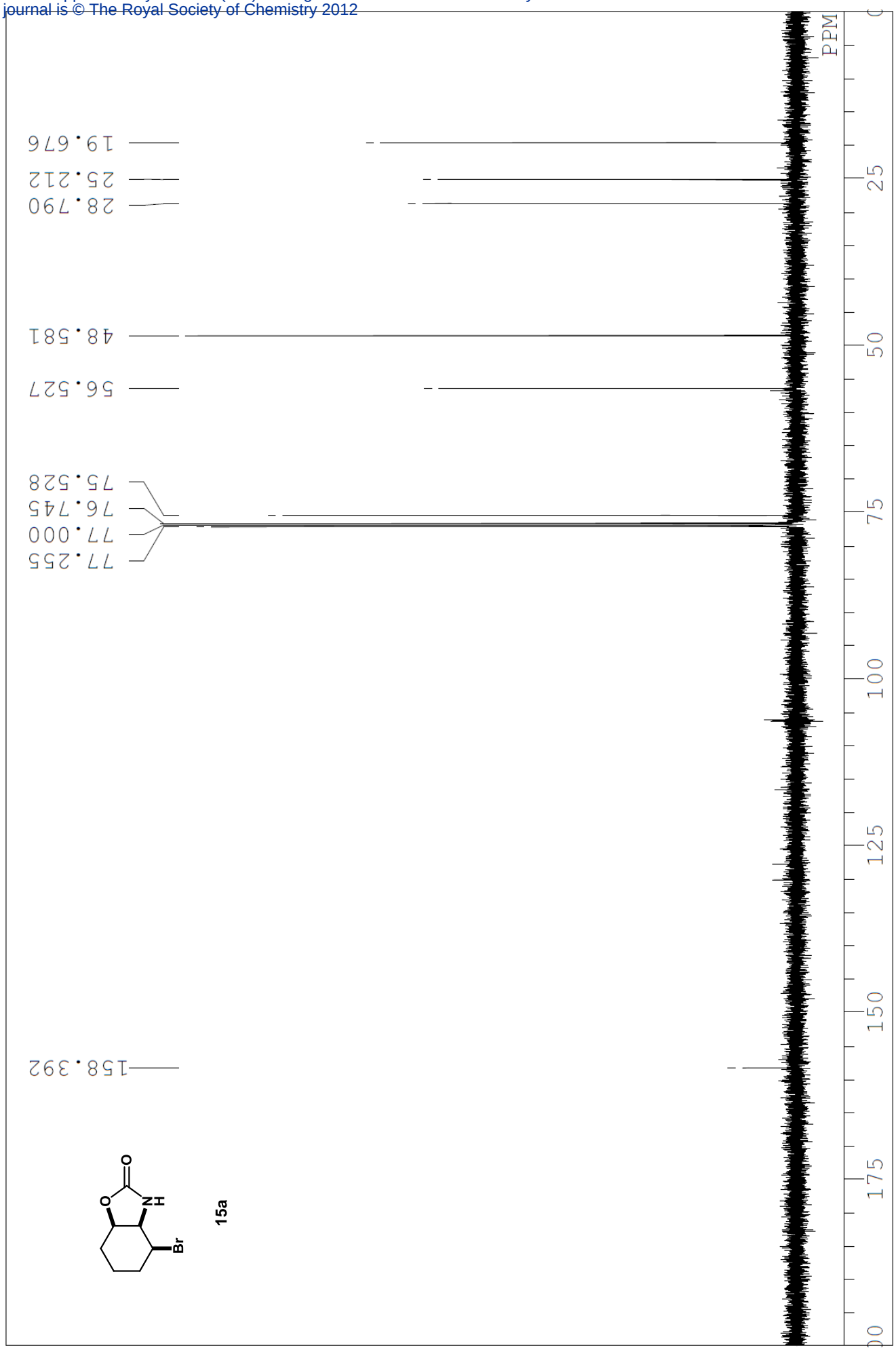


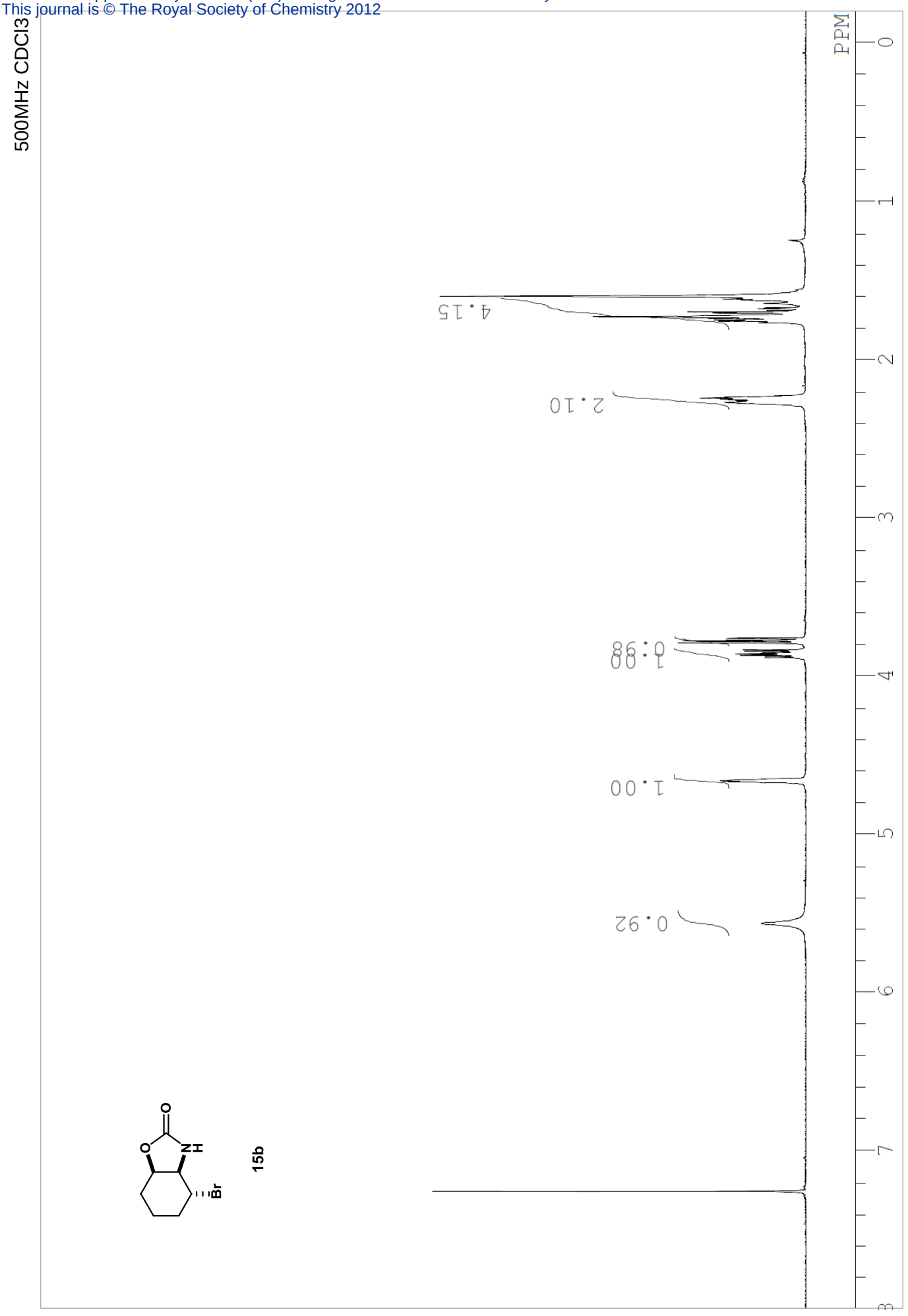


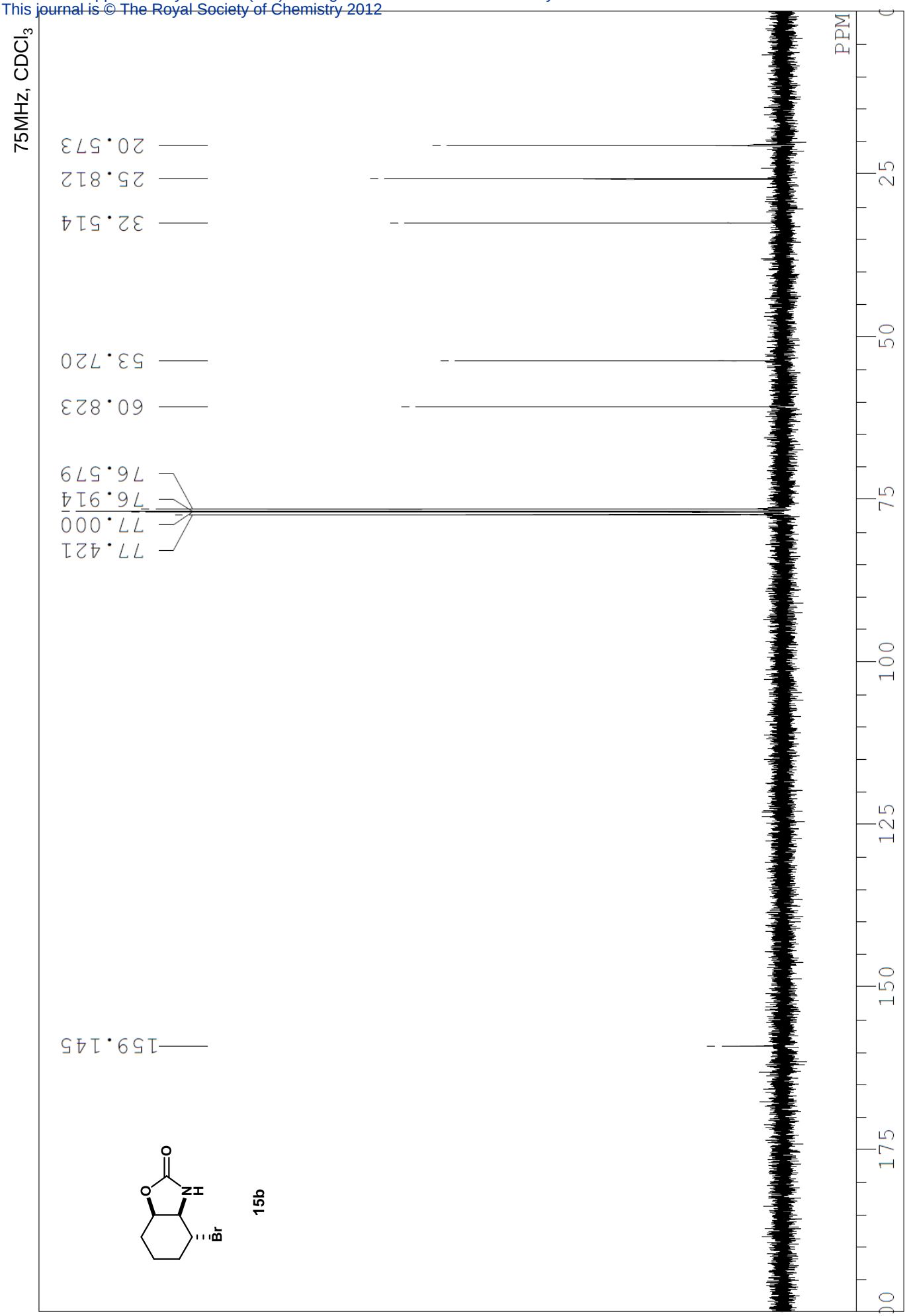


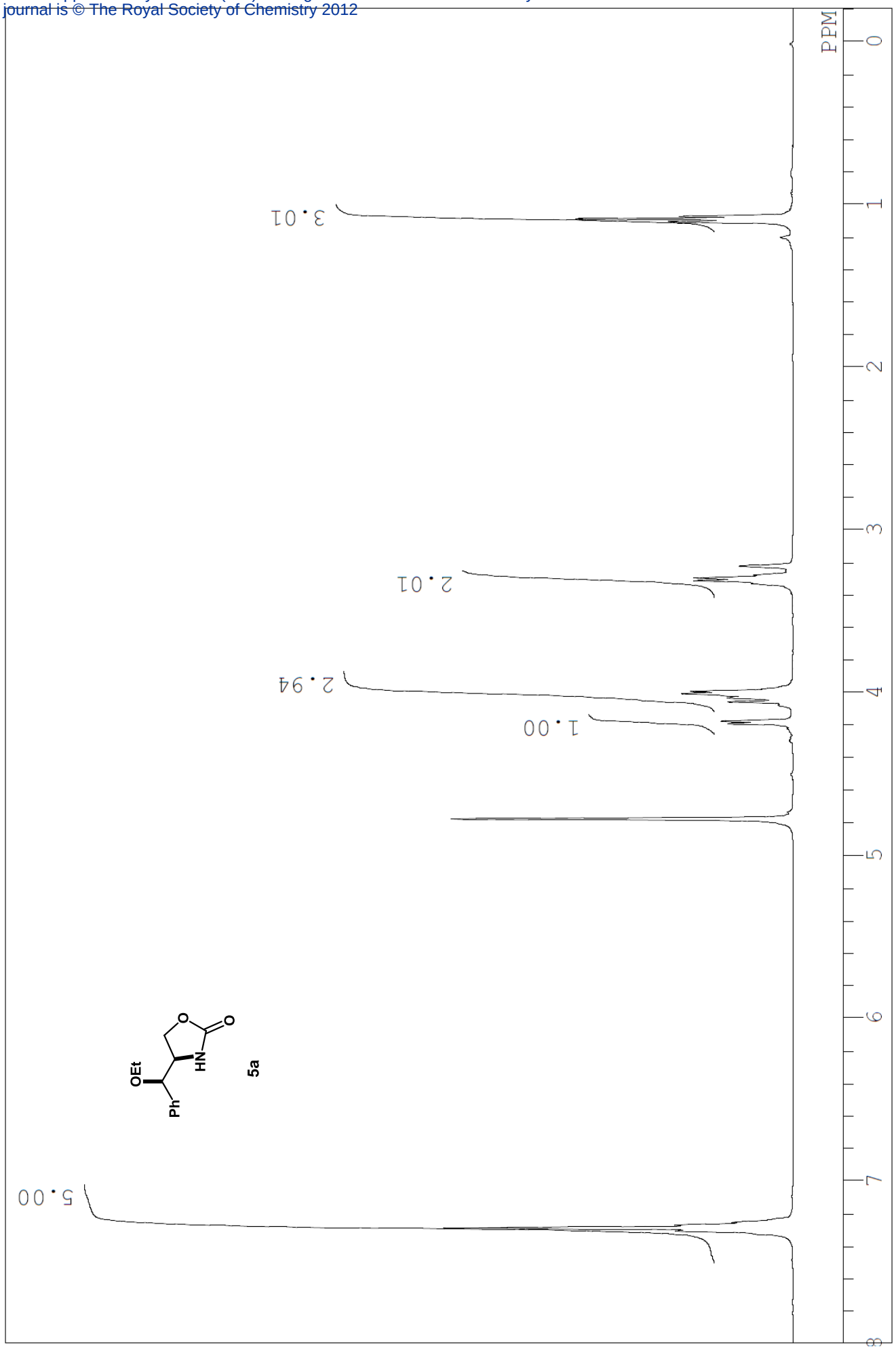


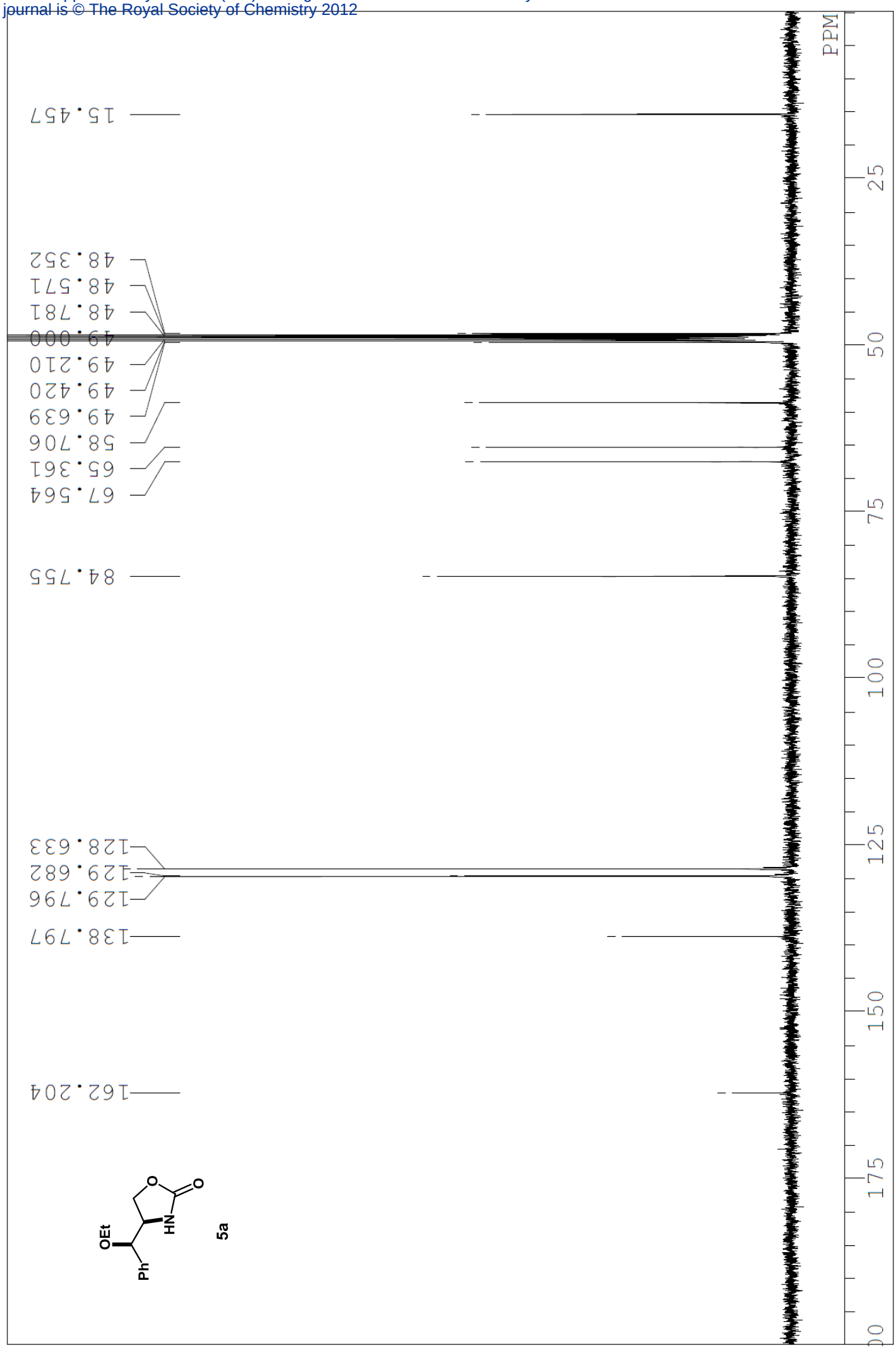


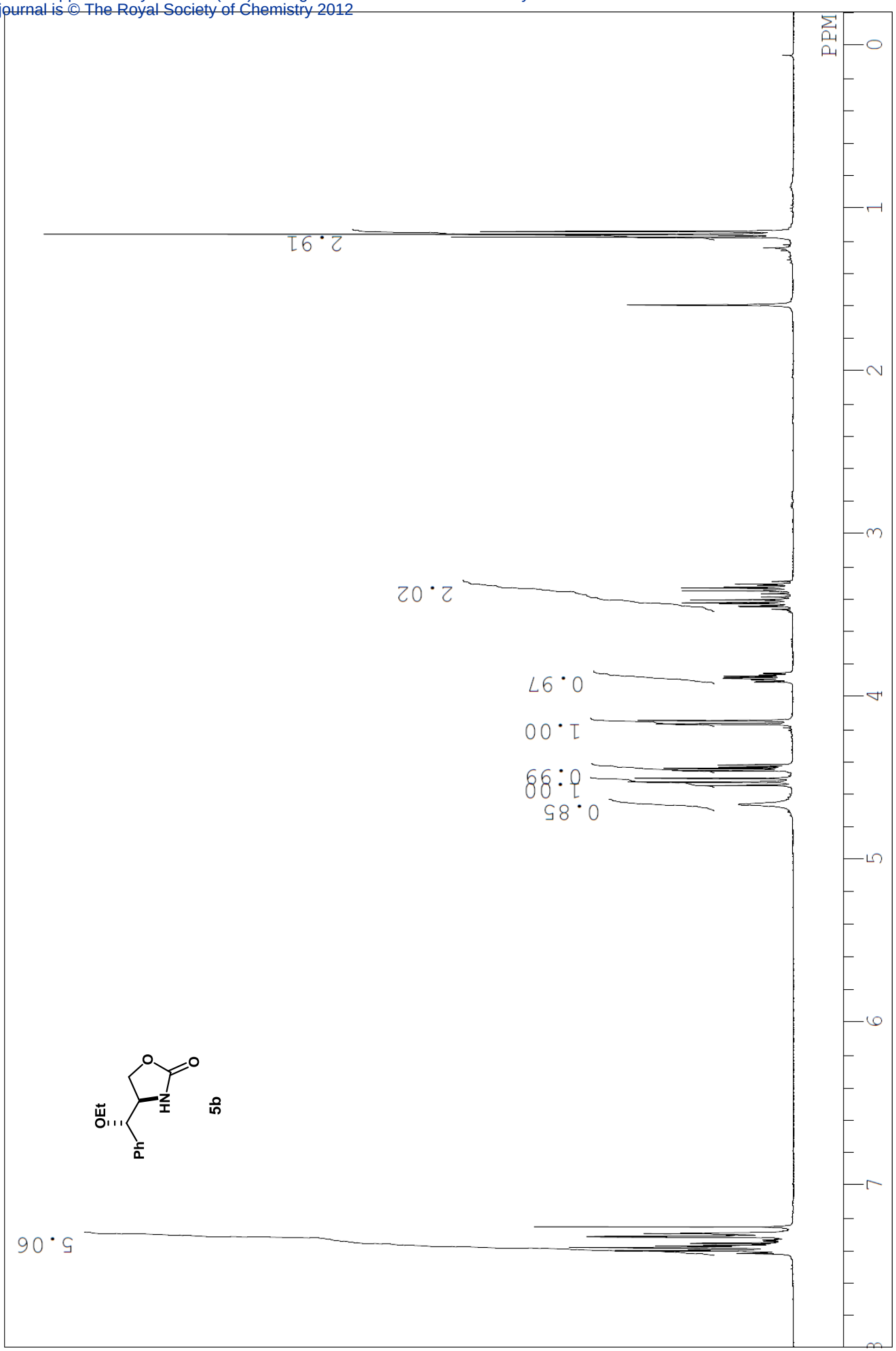




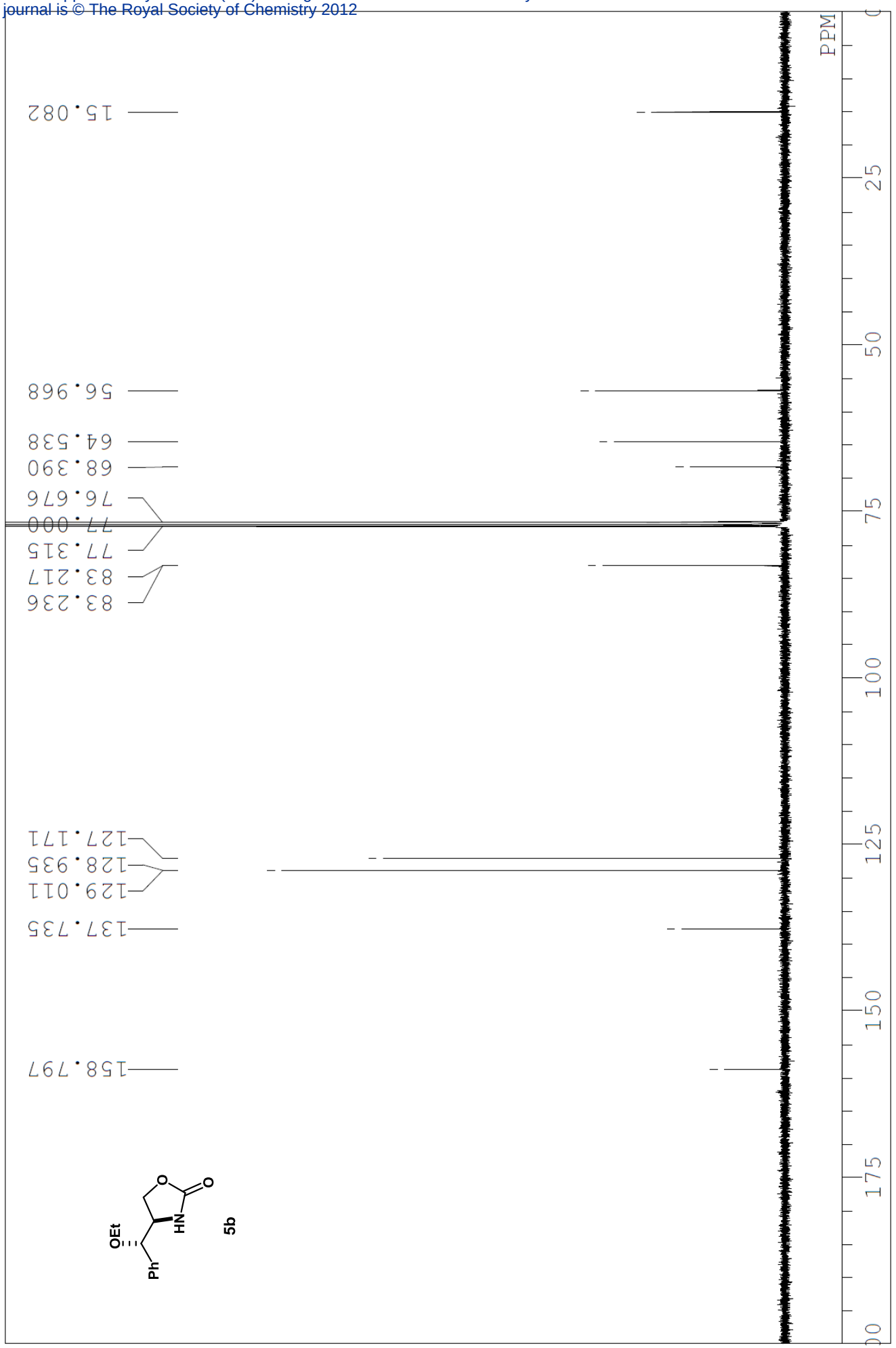








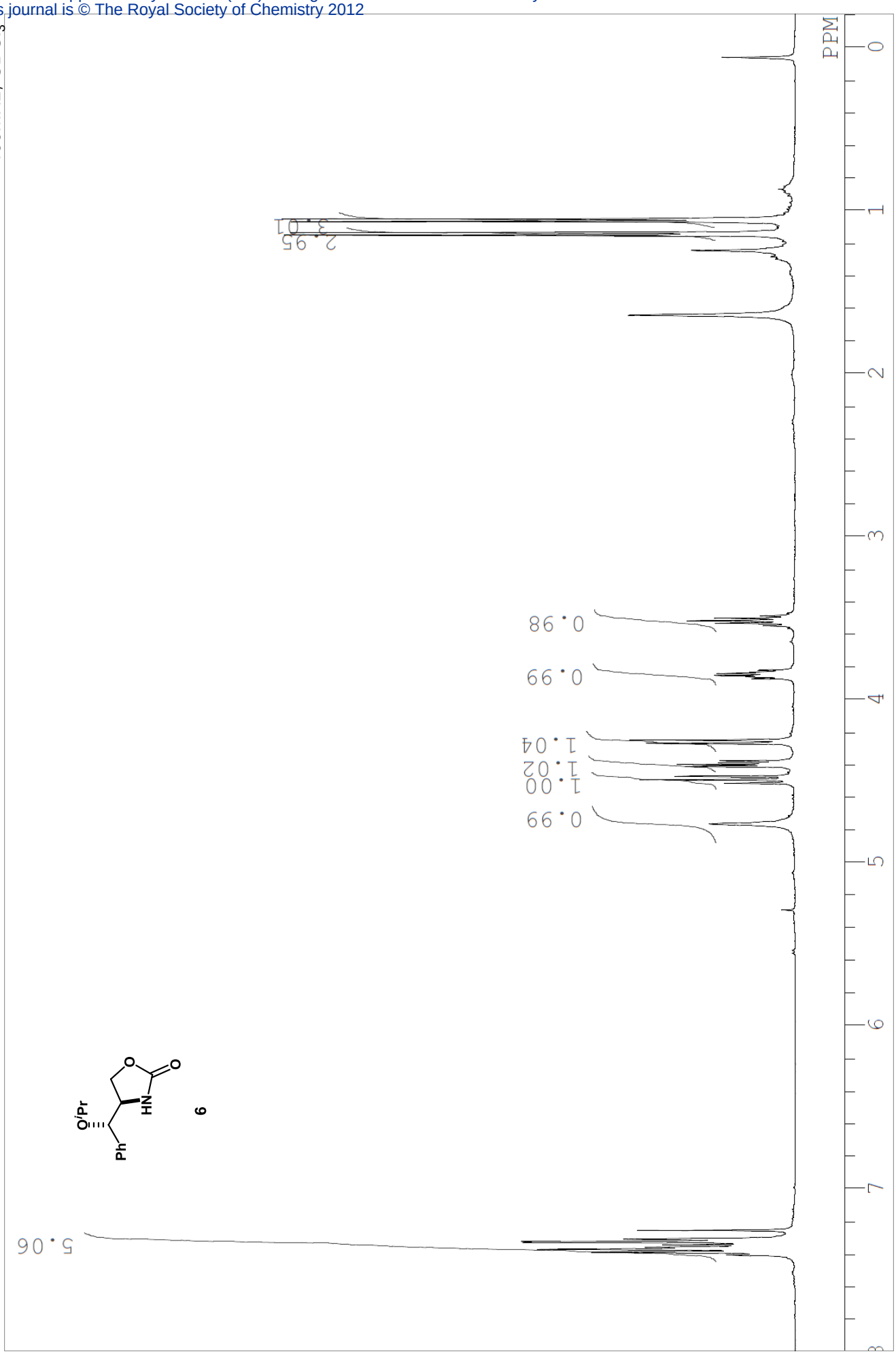
100MHz, $CDCl_3$

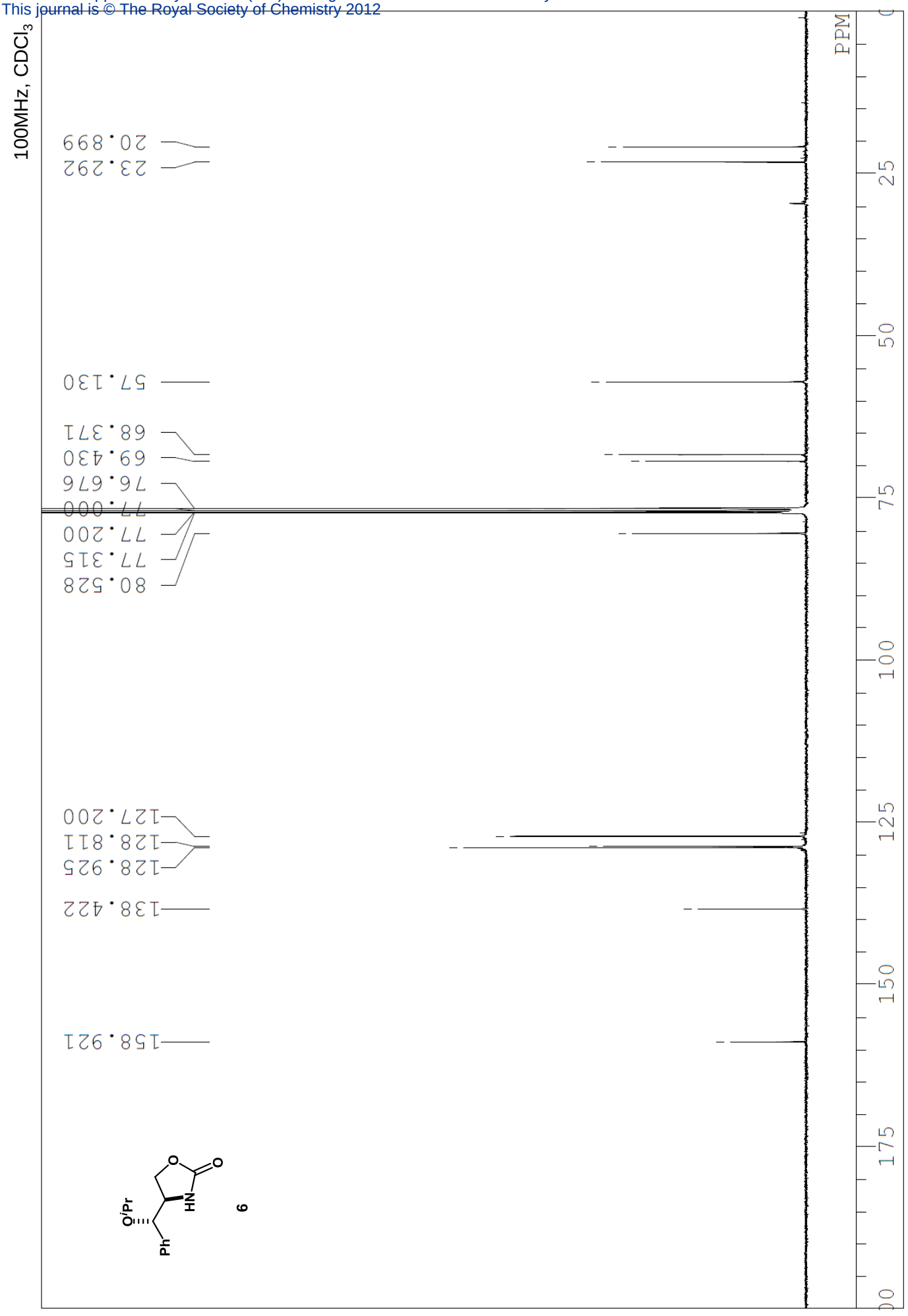


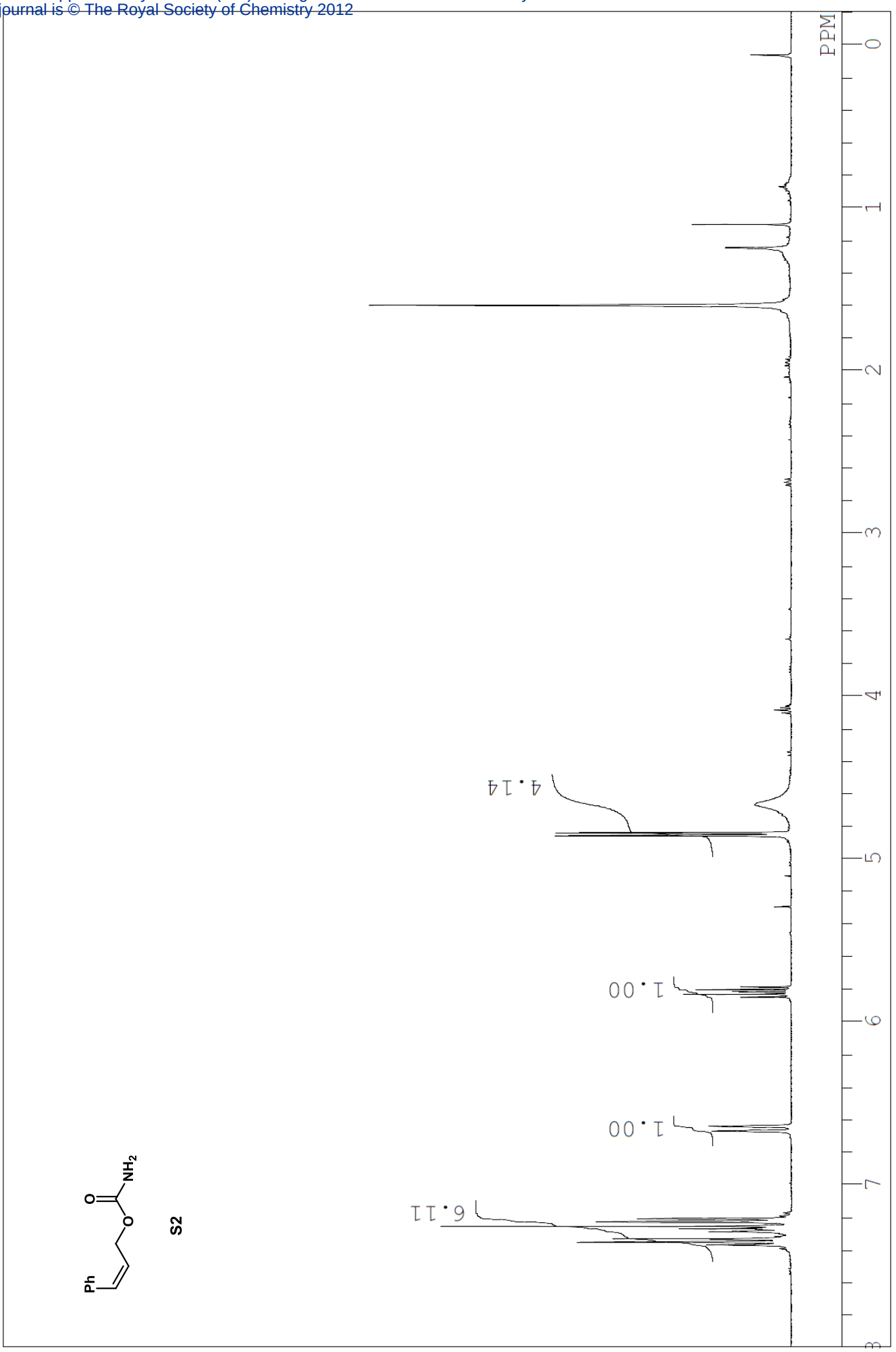


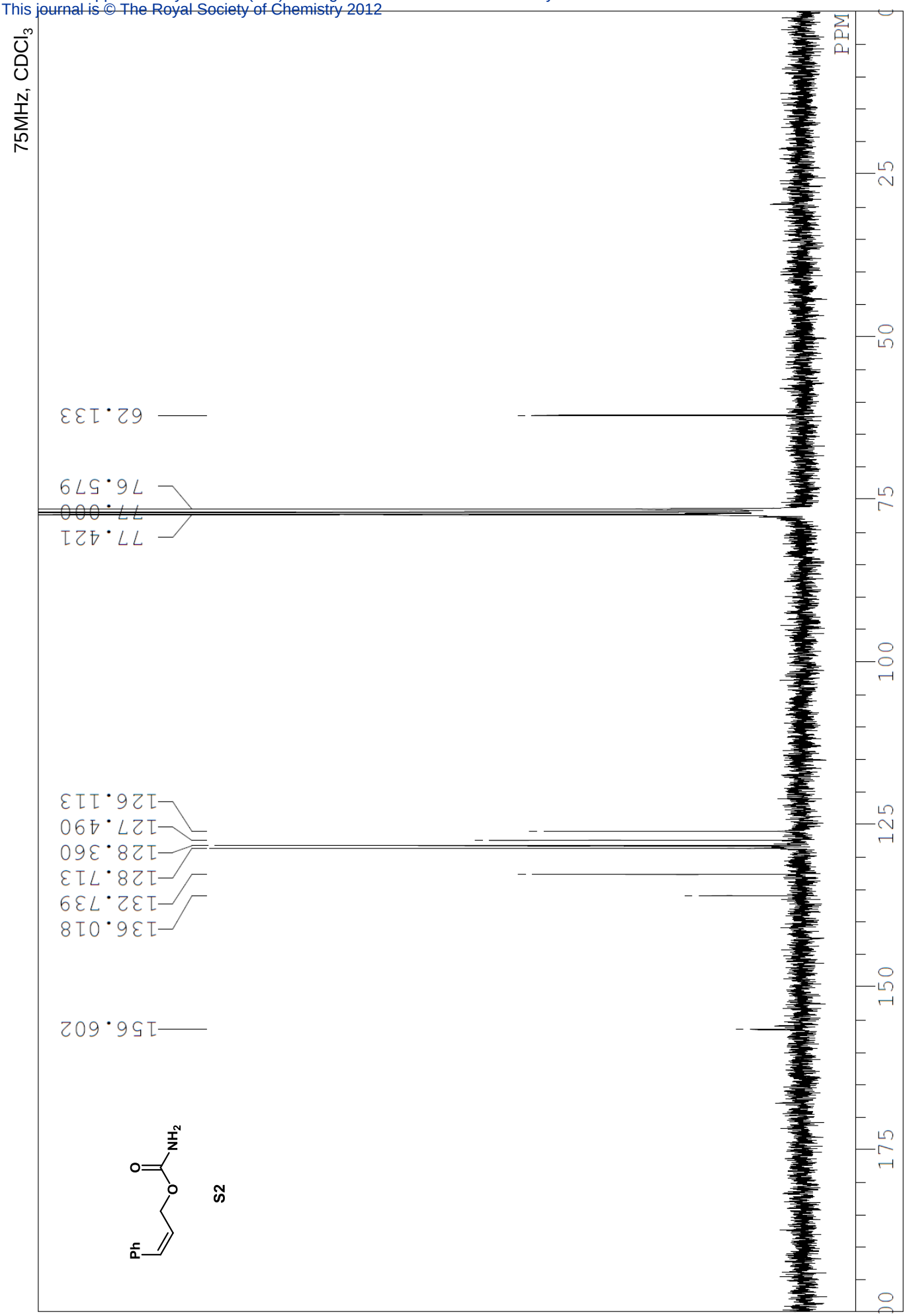


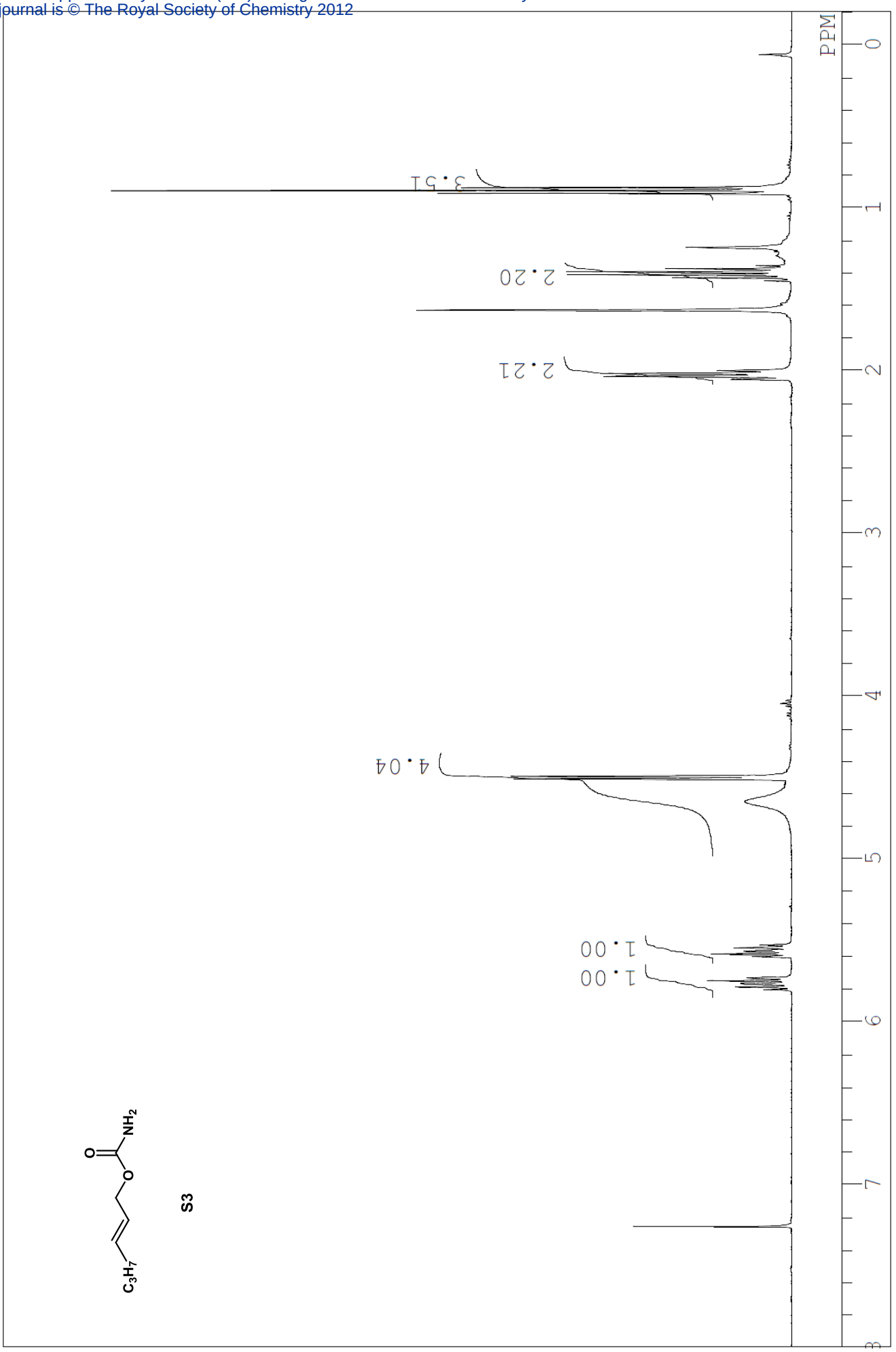
5b



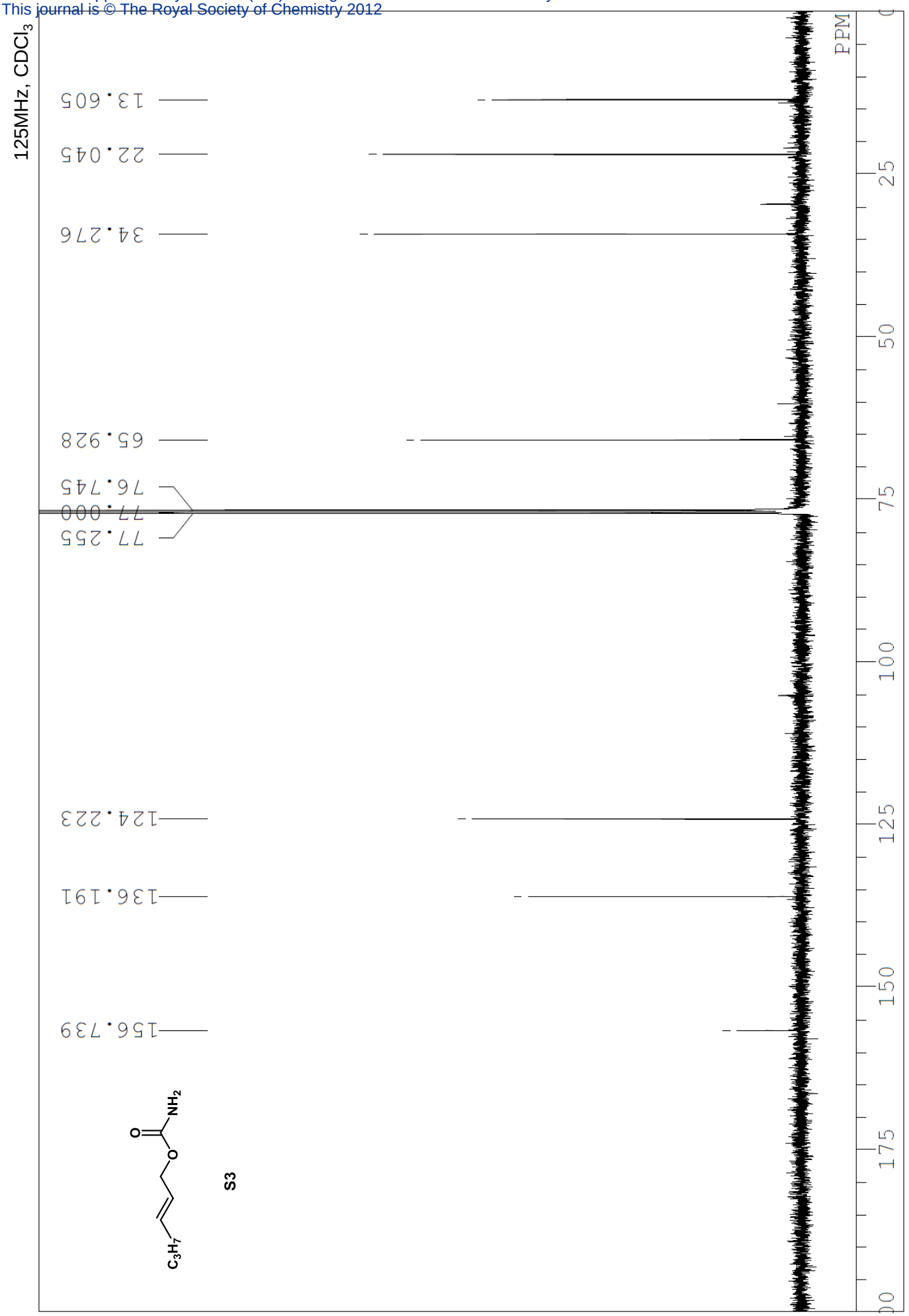


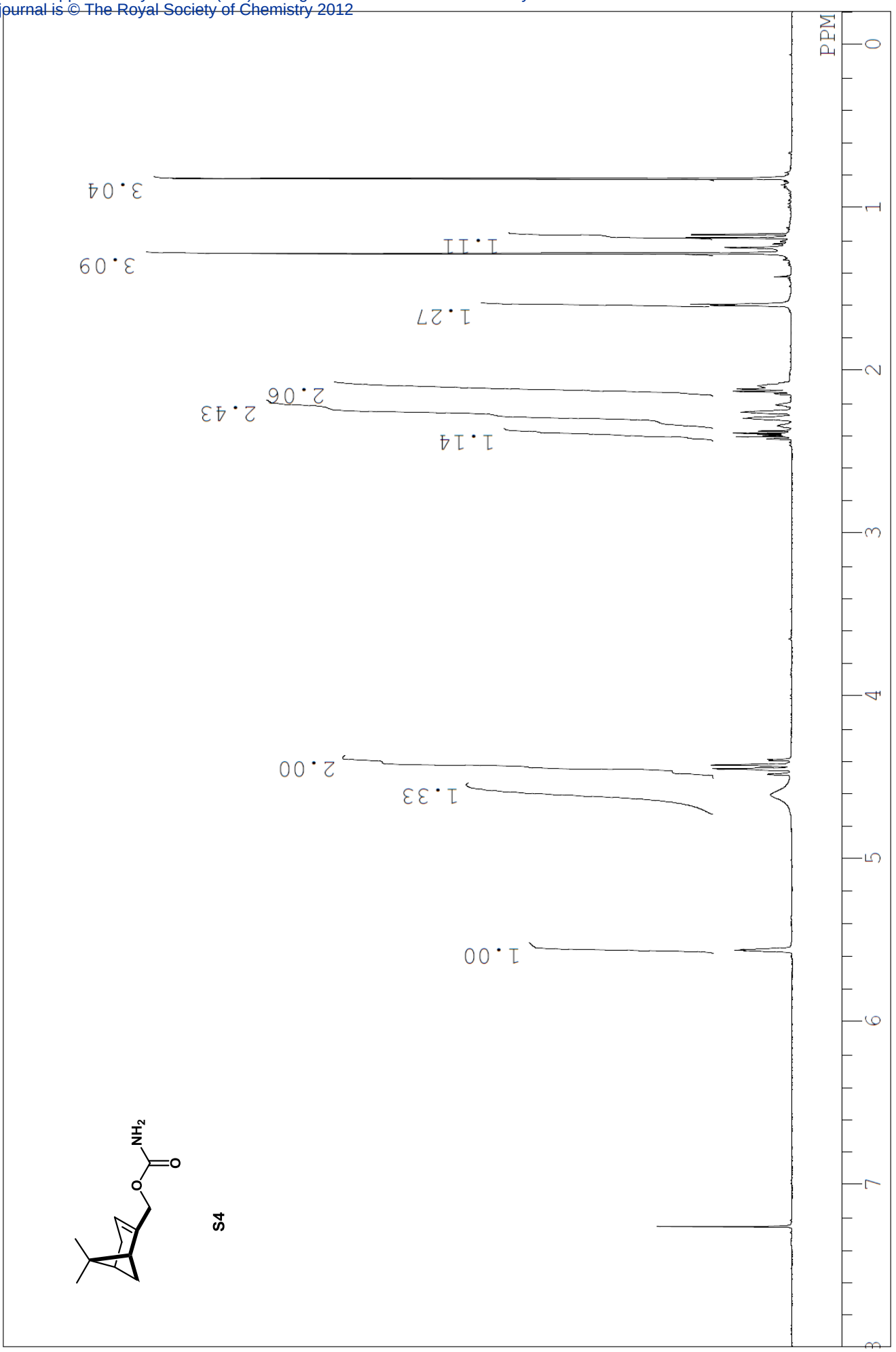


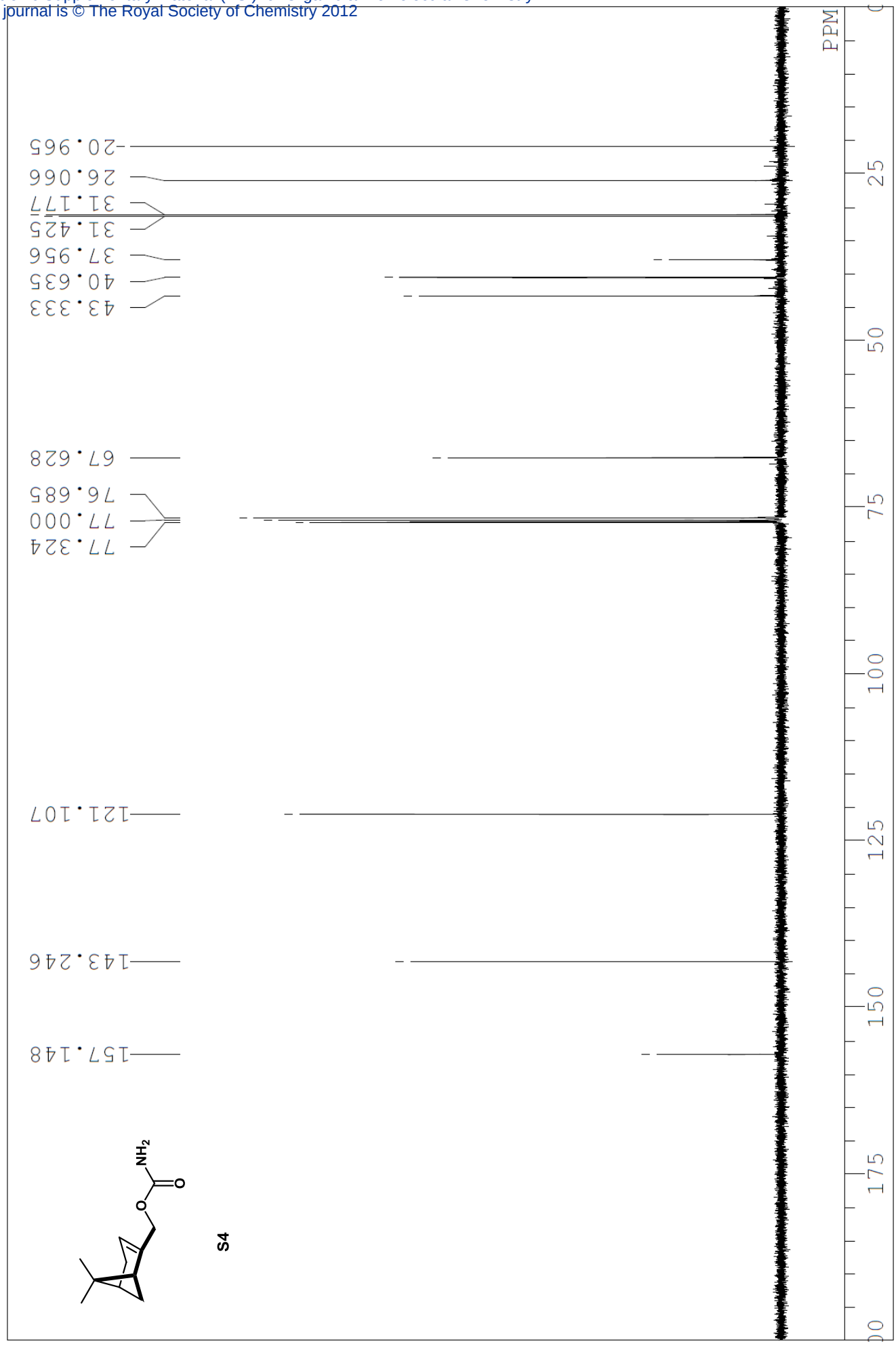

75MHz, CDCl3
PPM
62.133
76.579
77.000
77.421
126.113
127.490
128.360
128.713
132.739
136.018
156.602
NH2
O
O
Ph
S2

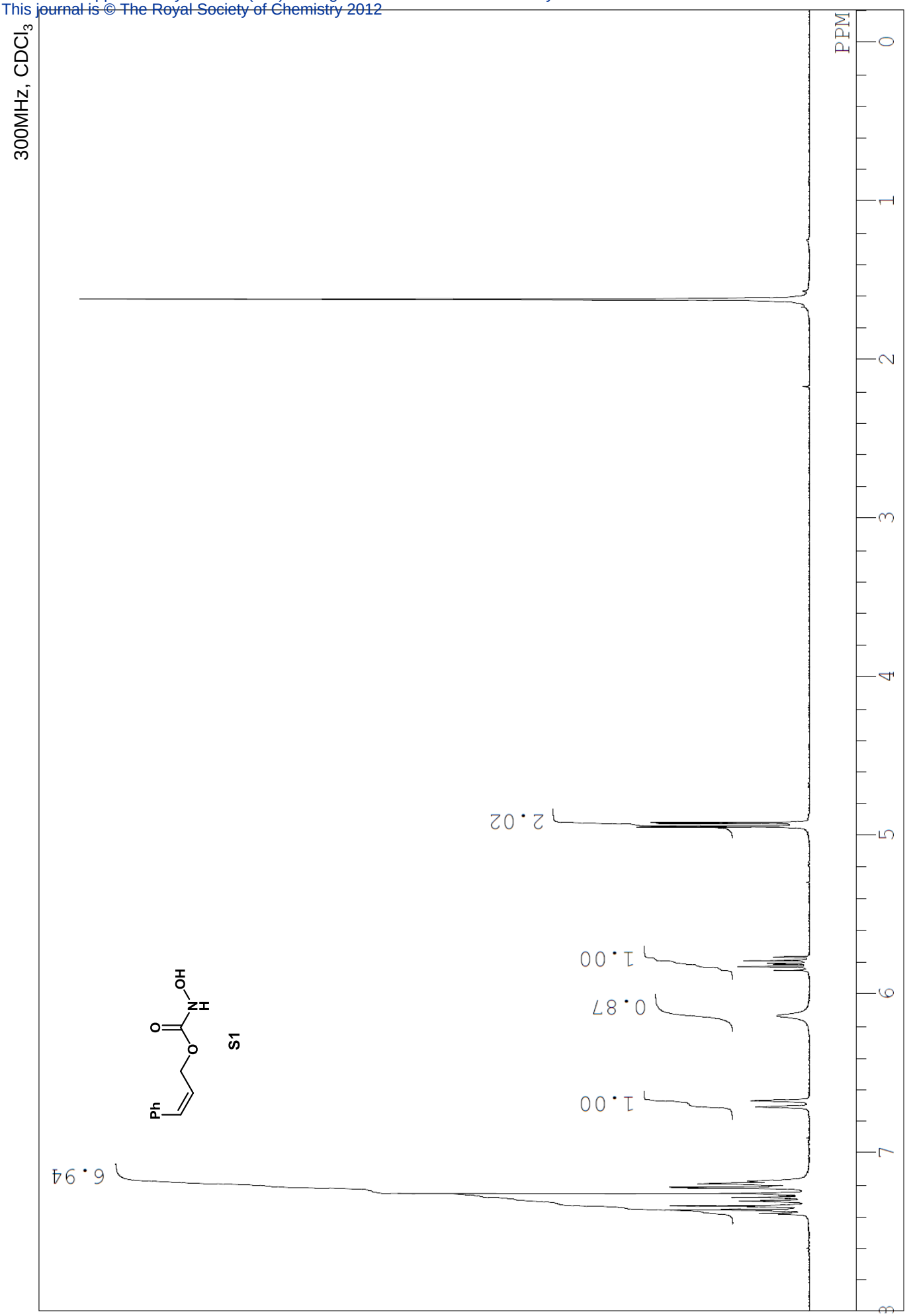


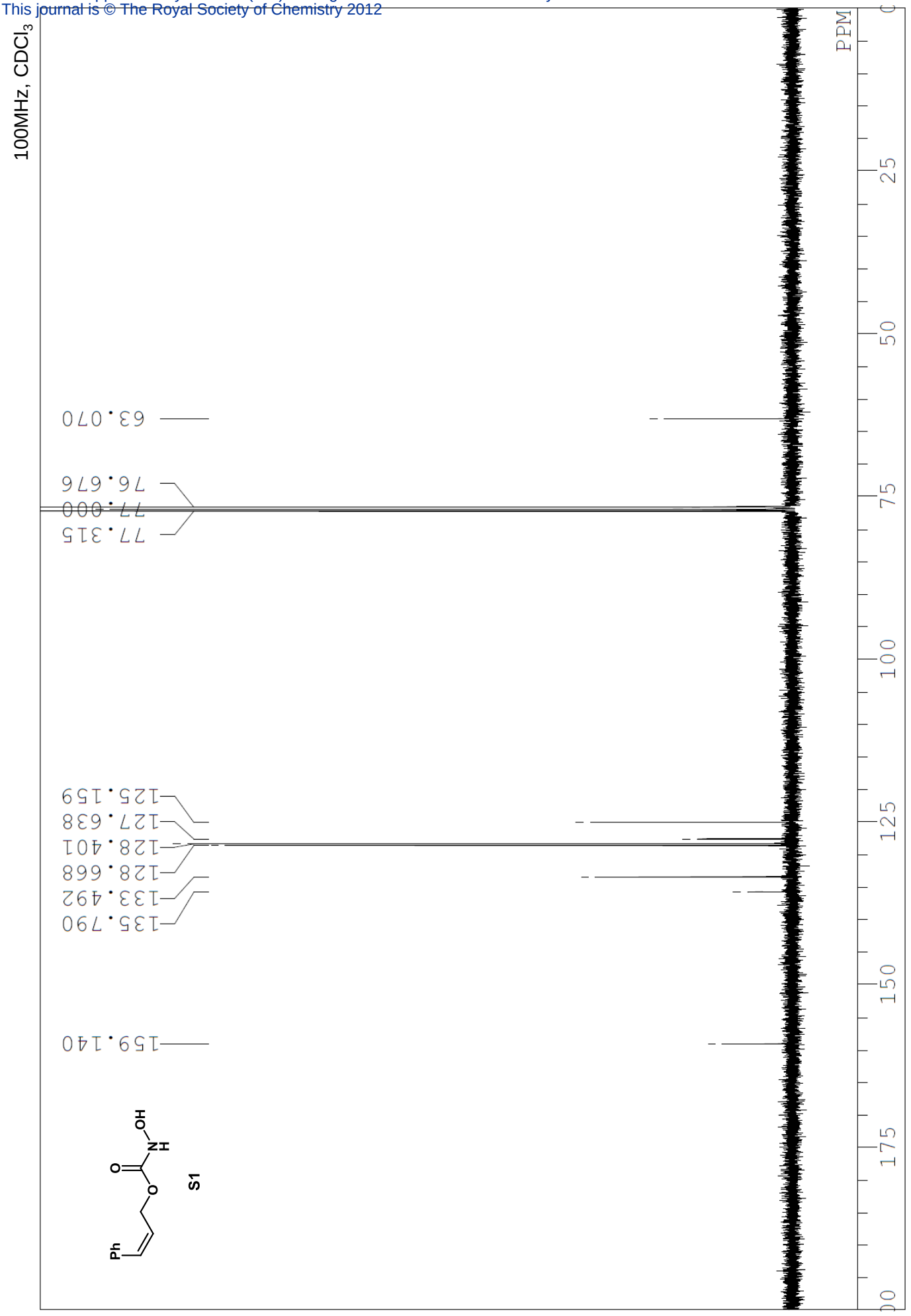

S3

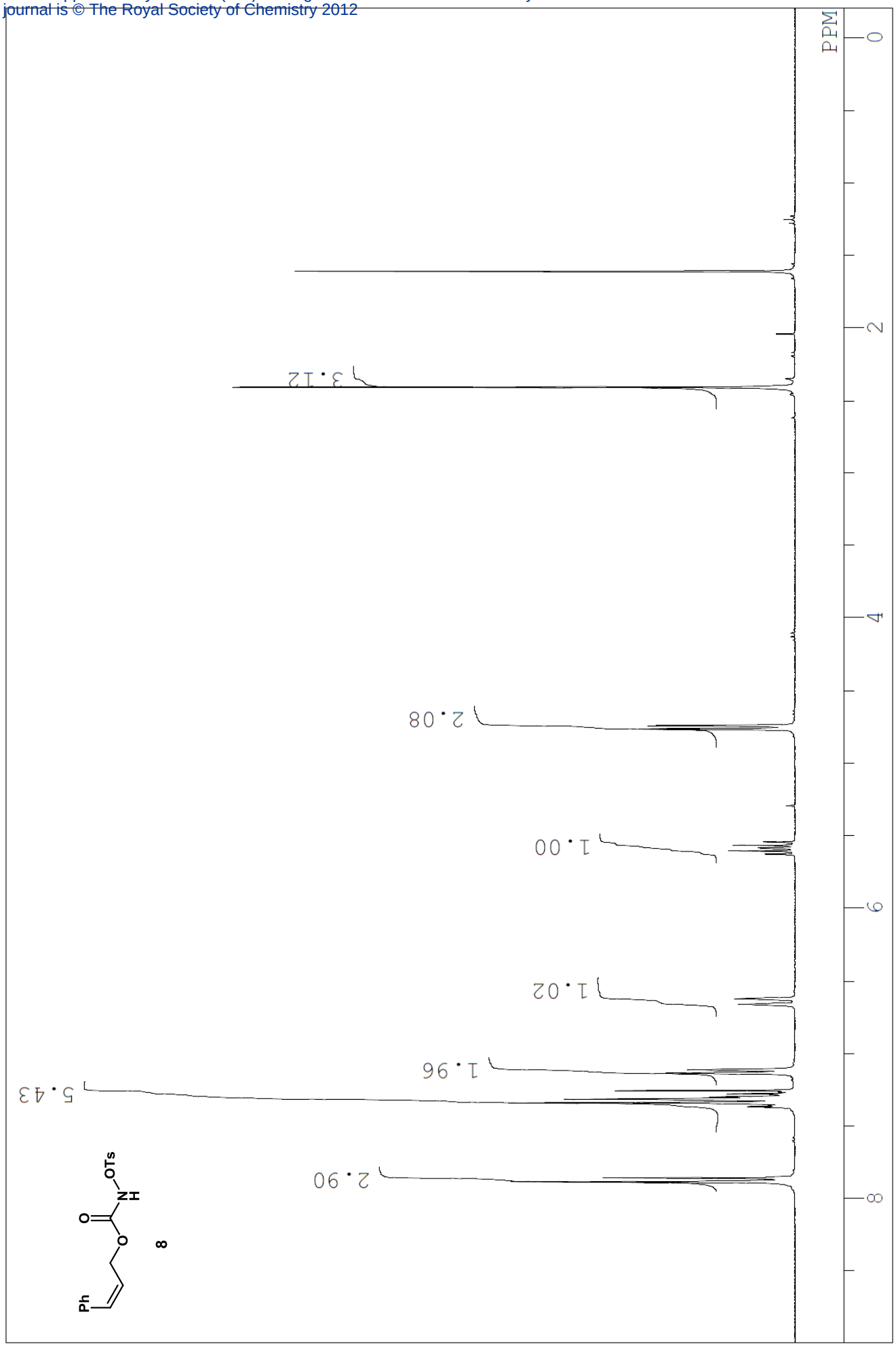







300MHz, CDCl3
PPM
0
1
2
3
4
5
6
7
8
2.02
1.00
0.87
1.00
6.94
S1
OH
N
H
O
O
Ph





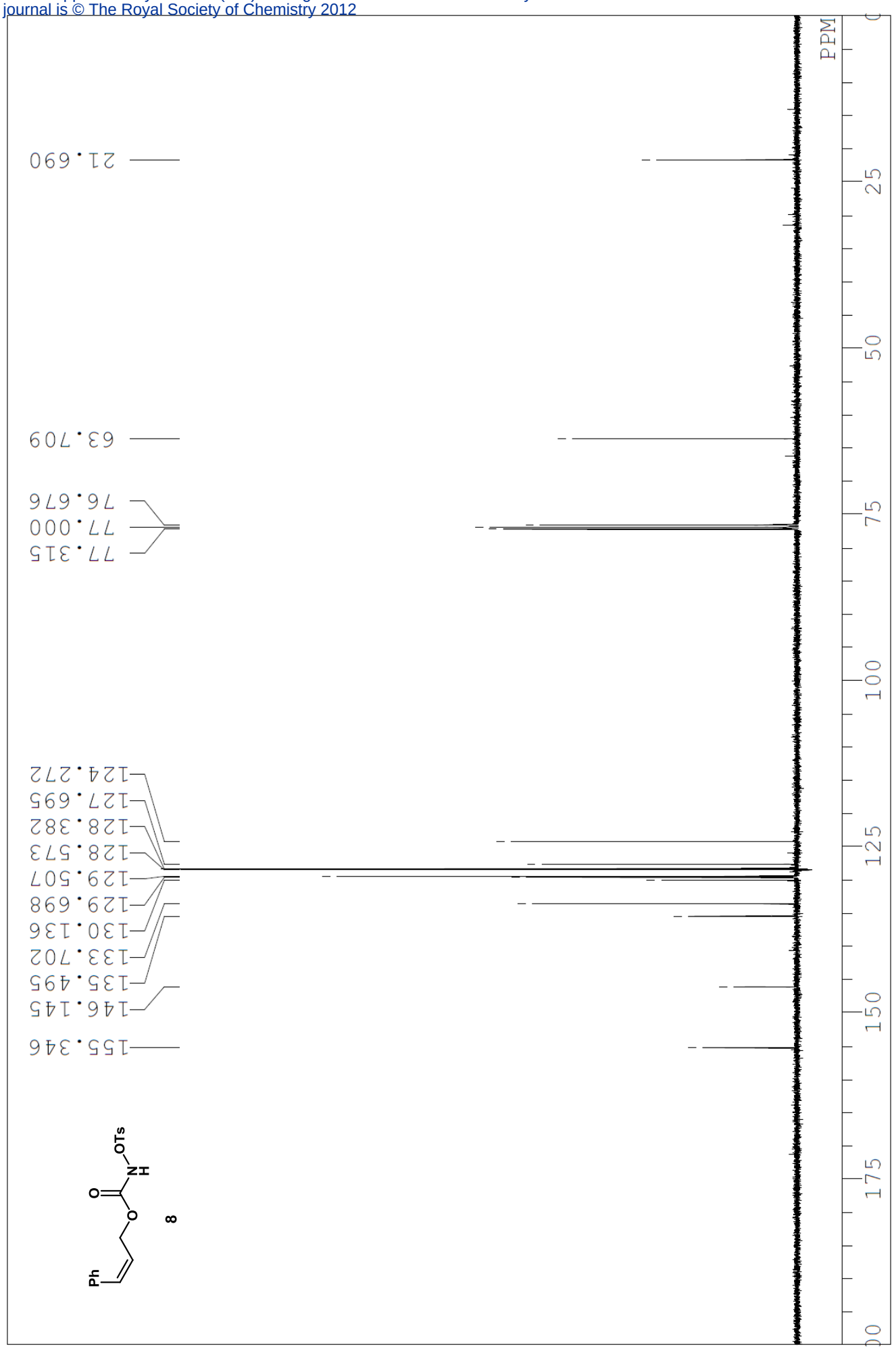
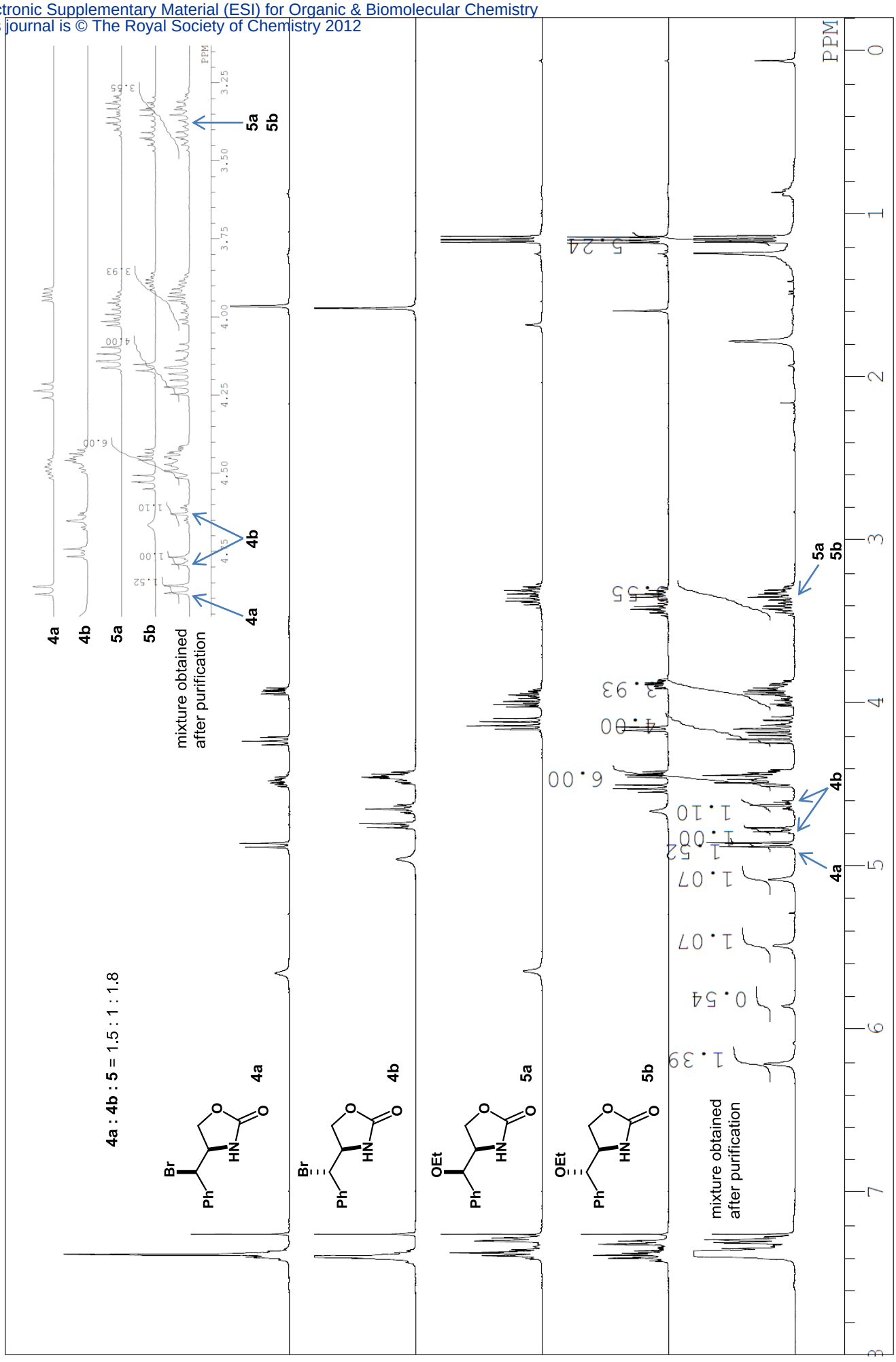
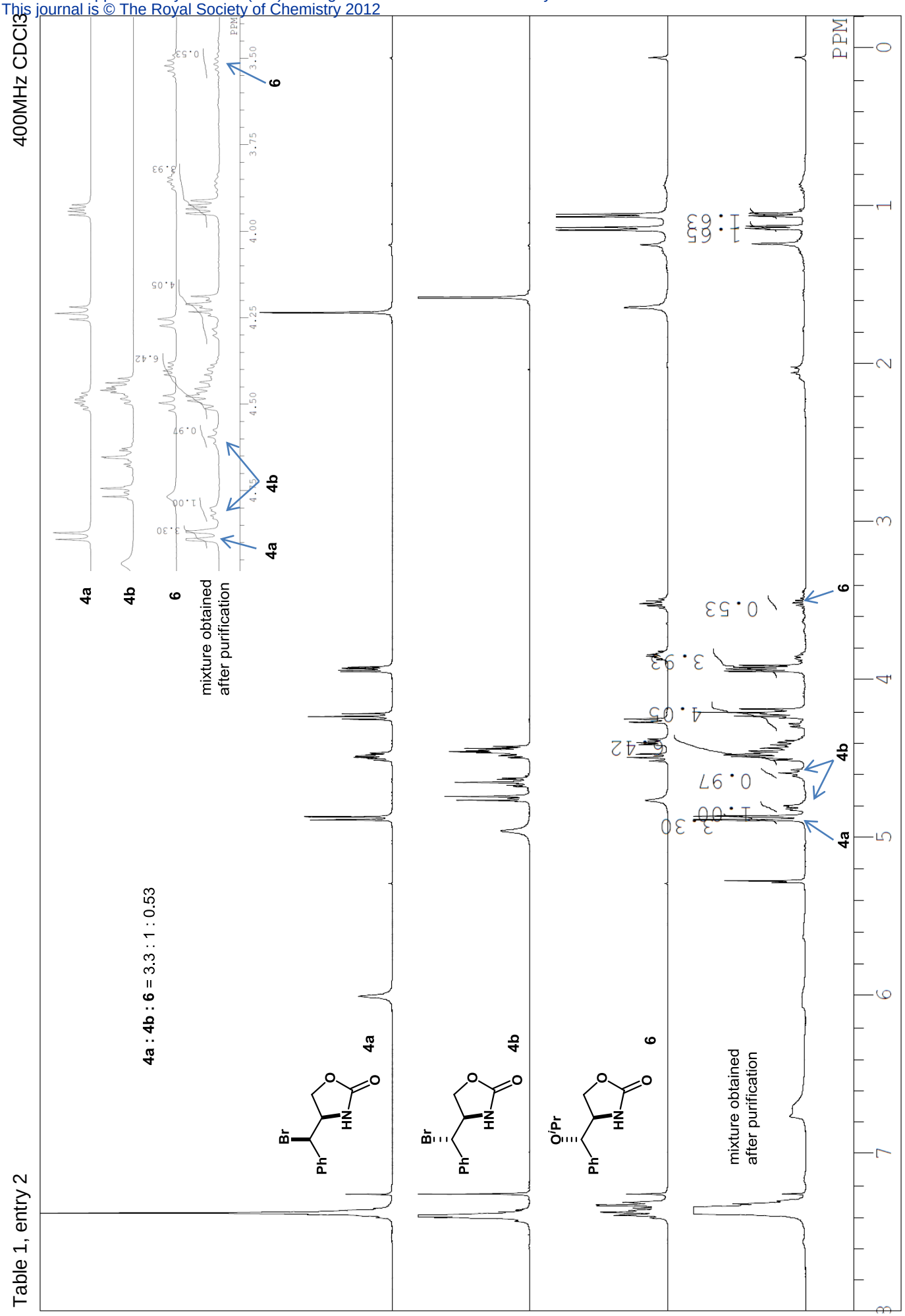
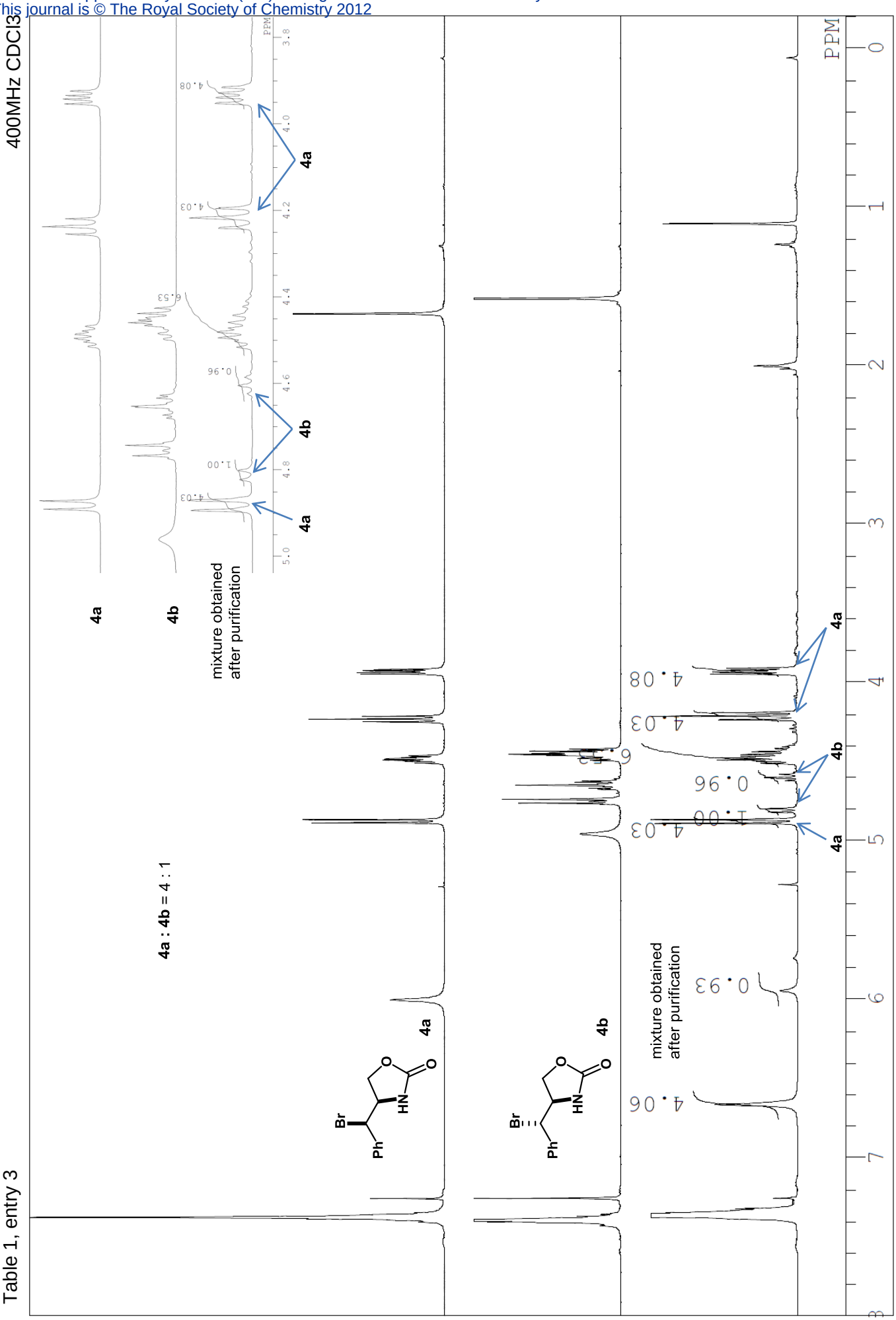


Table 1, entry 1

400MHz CDCl3







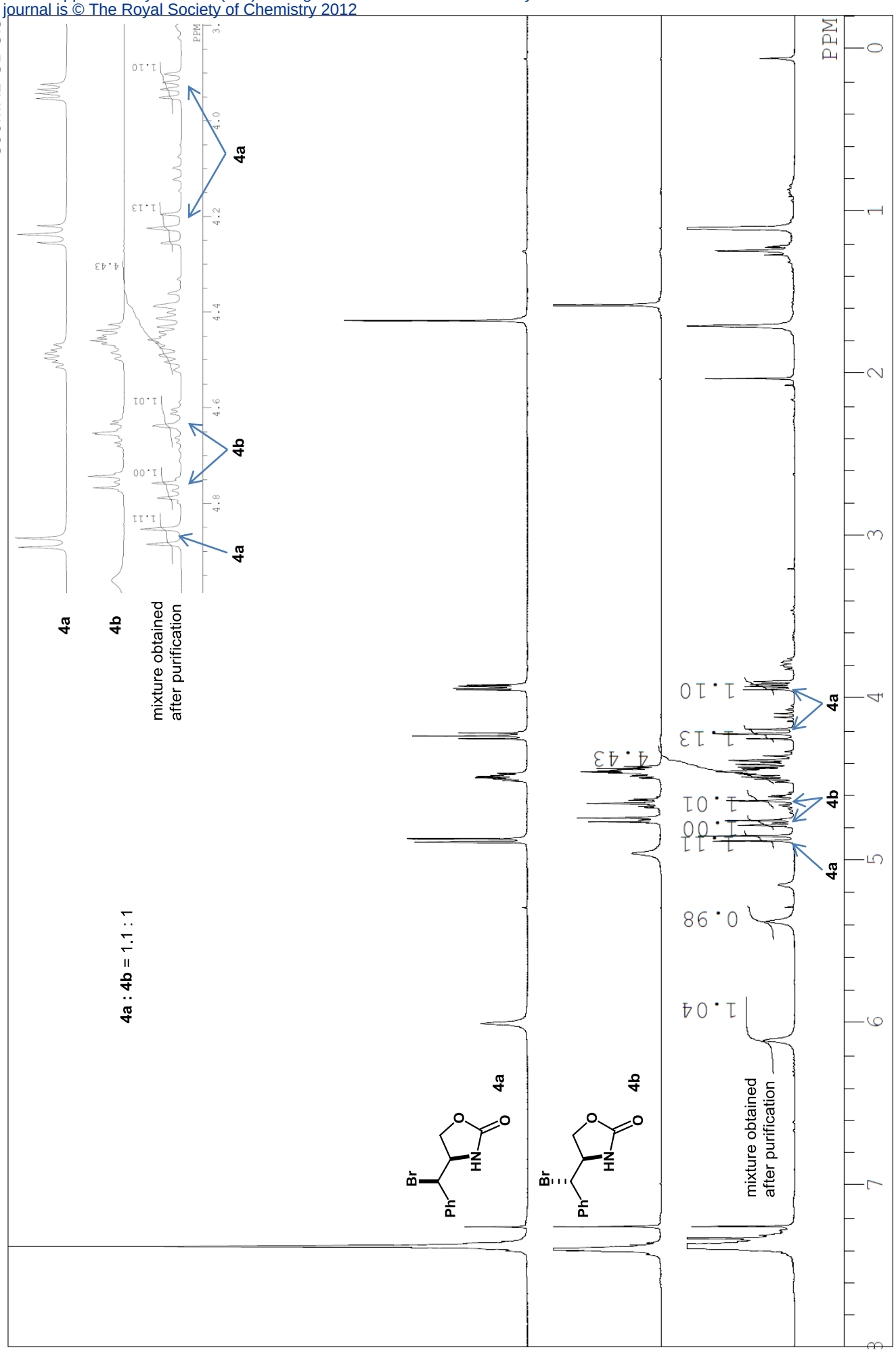
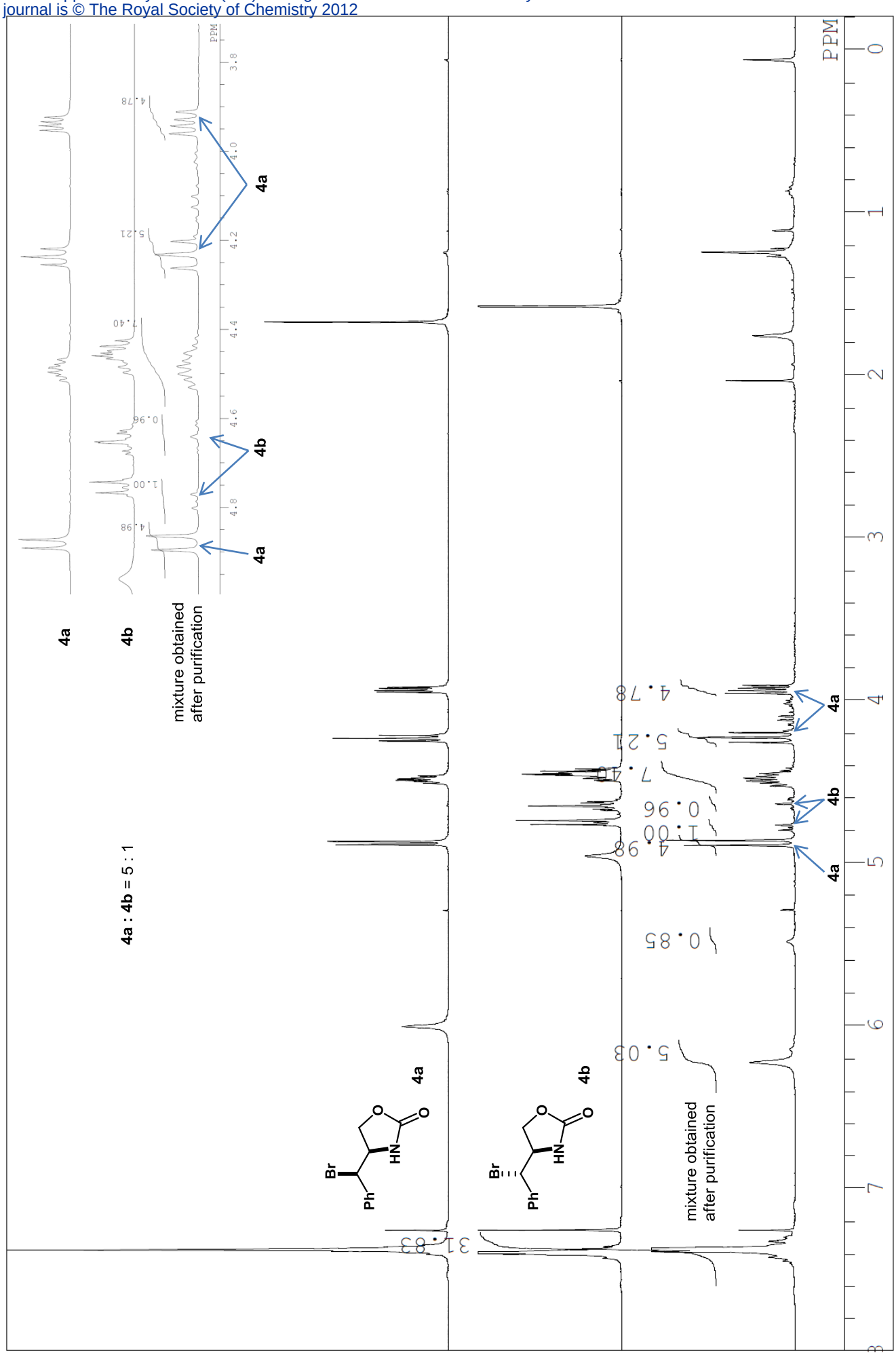



Table 1, entry 4



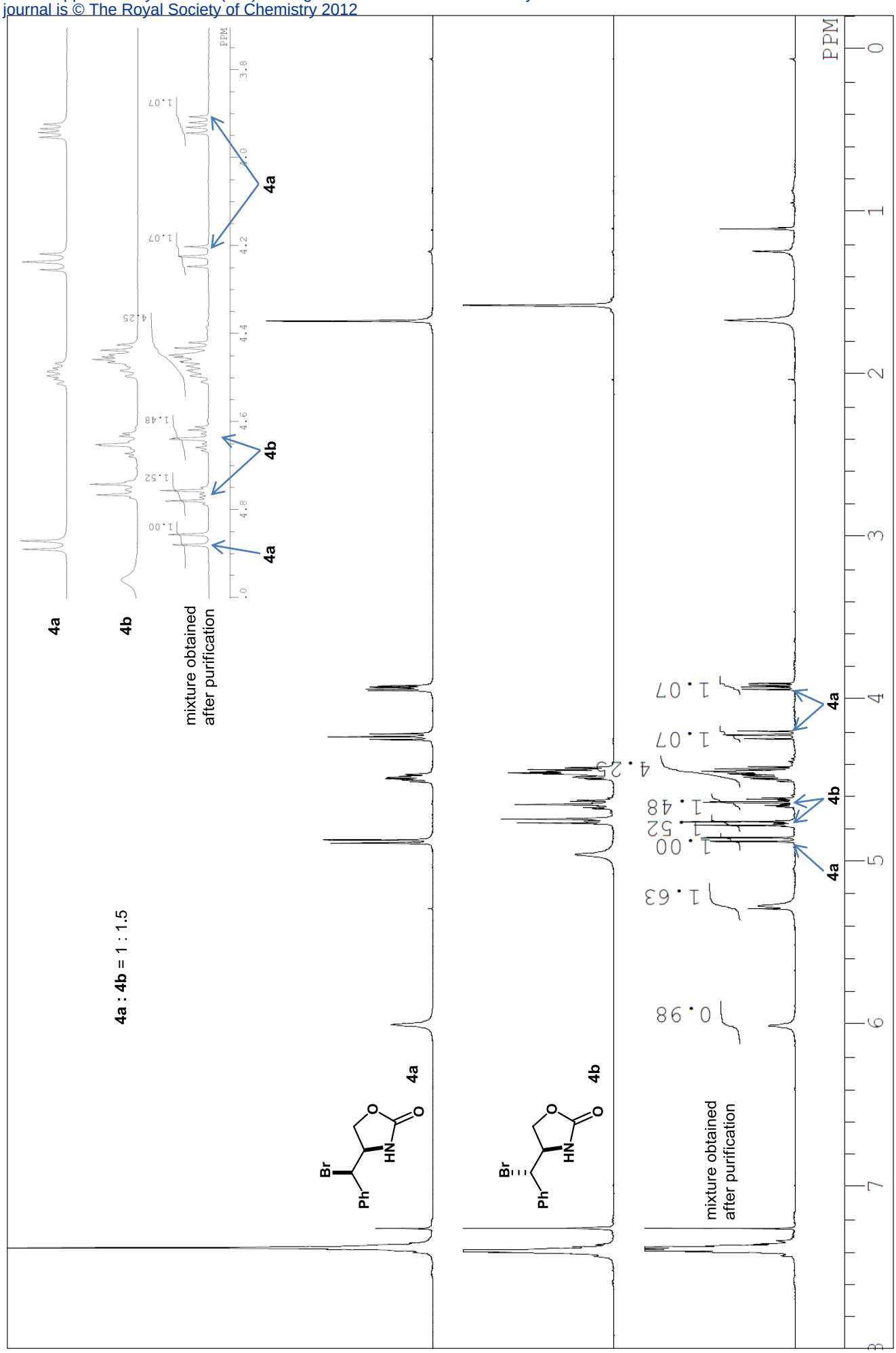
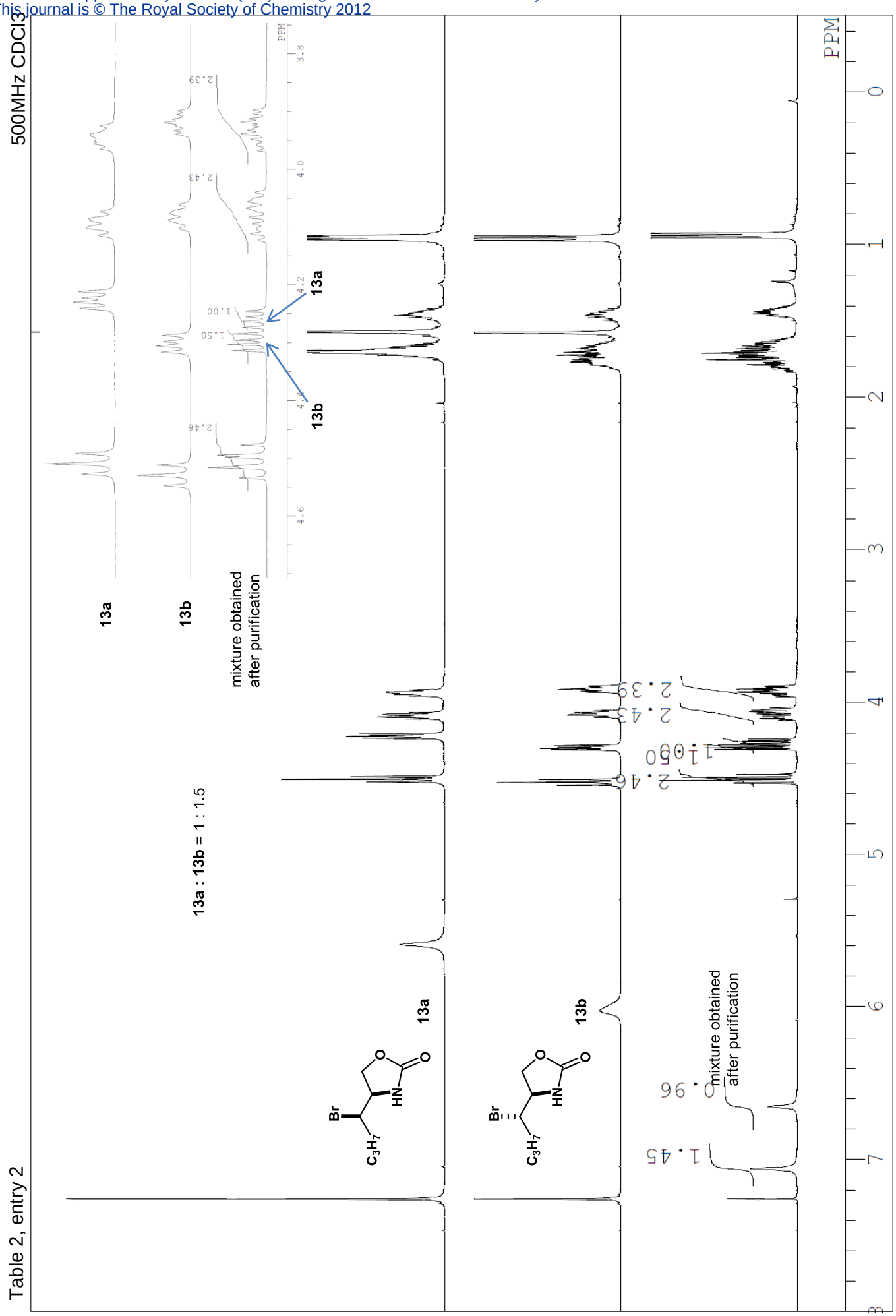
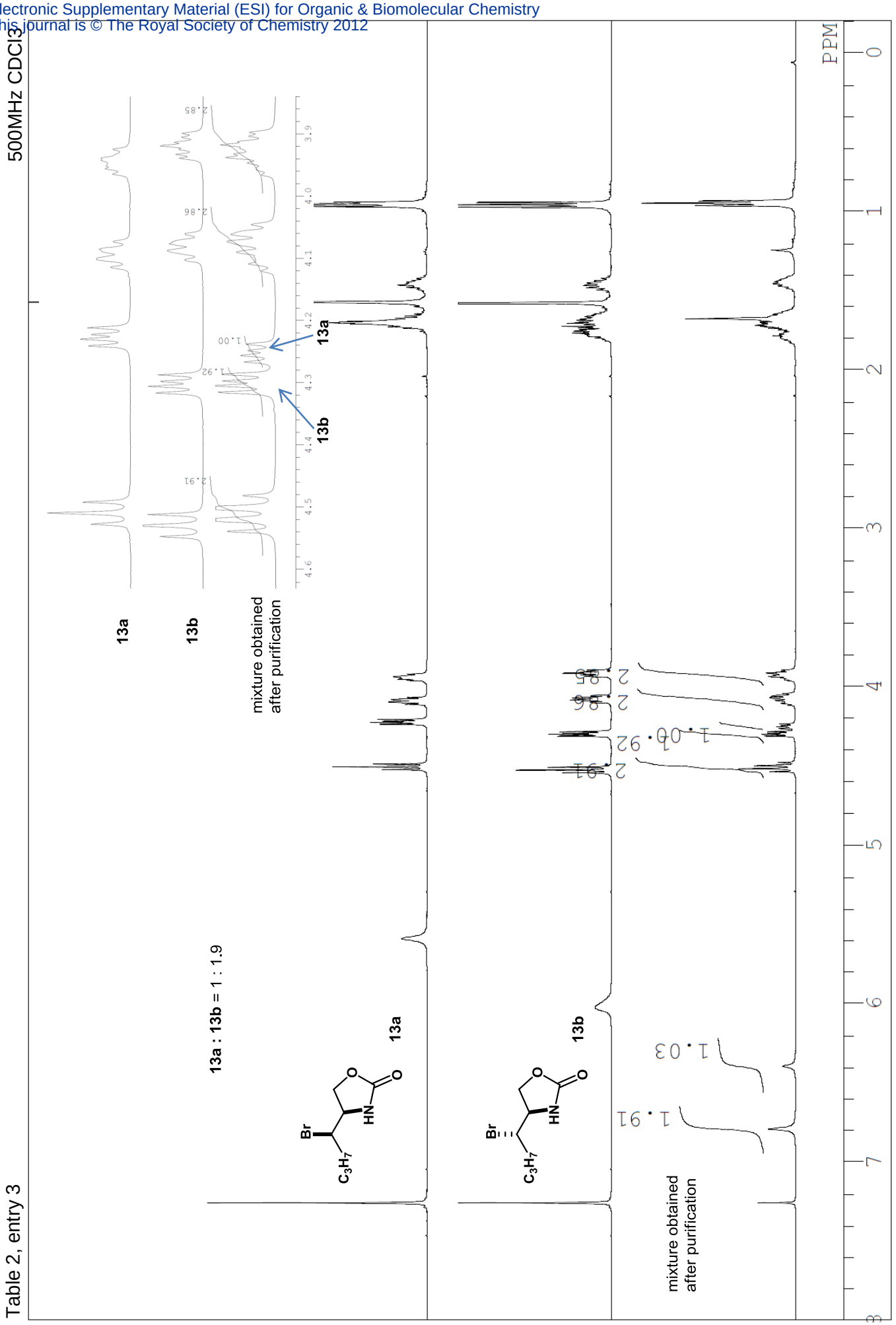
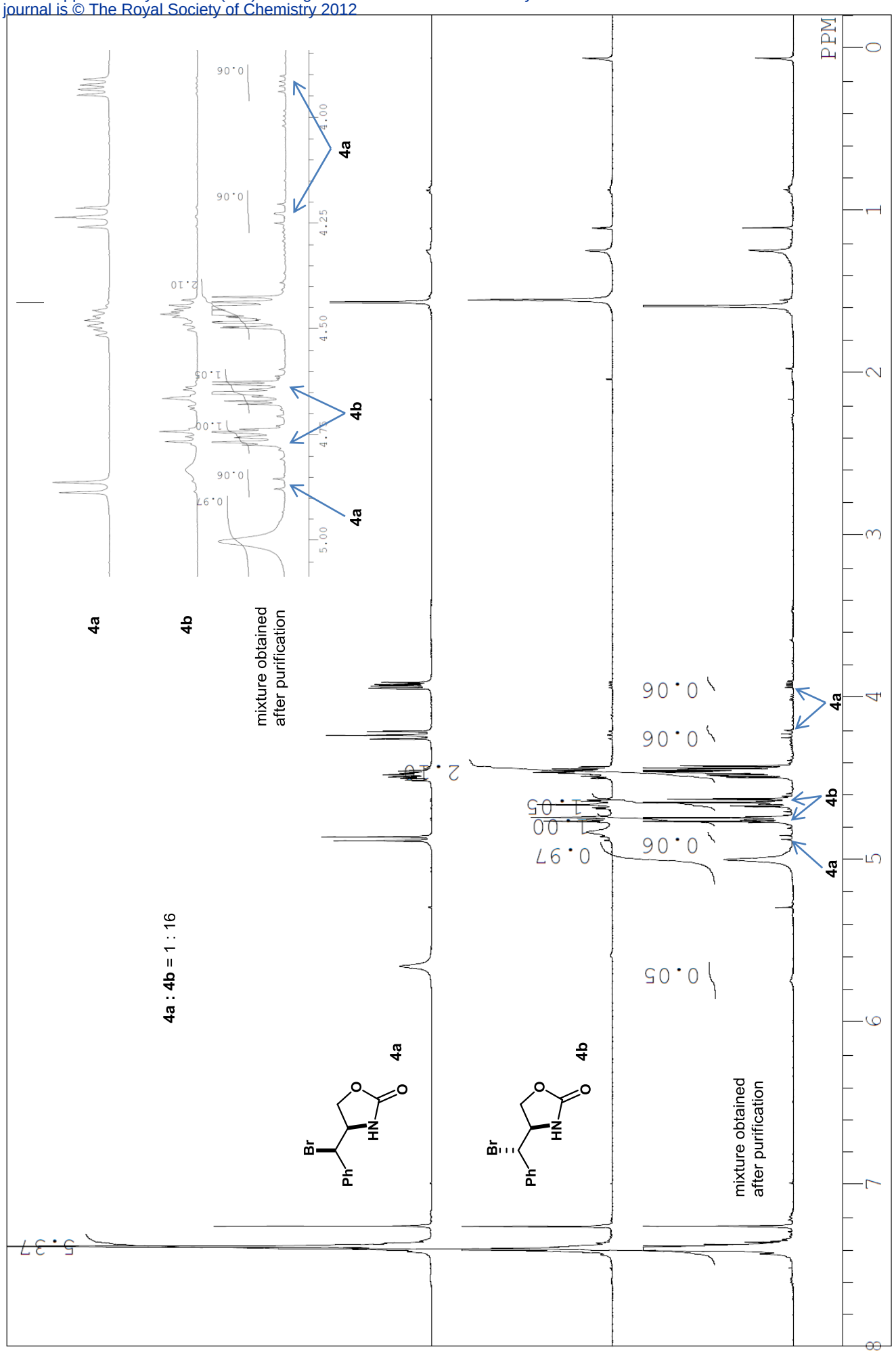



Table 2, entry 1






400MHz CDCl3
Bromination of aziridine 17
4a : 4b = 1 : 16
4a
4b
mixture obtained after purification
Br
Ph
HN
O
PPM
0
1
2
3
4
5
6
7
8