Supporting Information

Alkene isomerization/enamide-ene and diene metathesis for the construction of indoles, quinolines, benzofurans and chromenes with a chiral cyclopropane substituent

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Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 500 MHz, with TMS as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 125 MHz. All moisture-sensitive reactions were performed under an Ar atmosphere. Flash column chromatography was performed with silica gel 60 N (spherical, neutral, 40-50 mm, Kanto Chemical Co., Inc.). **A** and **B** were obtained commercially.

General Procedure for the Preparation of α, ω-Dienes derivatives (6).

A solution of aldehyde, aniline, and MS4A in Et_2O (SM 0.2 M) was stirred at rt for 10 h. After addition of Et_2O (SM 0.1 M), to the resulting solution was added BF_3•Et_2O at –40 °C, and the mixture was stirred at same temperature for 30 min. After addition of vinyl magnesium bromide (1.0 M in THF) or vinyl magnesium chloride (1.46 M in THF) at –40 °C, the mixture was heated gradually to 0 °C, and stirred for 15 h. After addition of sat. aq. NH_4Cl, the mixture was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layers were washed with sat. aq. $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by Flash silica gel column chromatography (hexane) to give the α, ω-diene as a pale yellow oil.

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[1-(4-chloro-2-vinylphenylamino)prop-2-en-1-yl]cyclopropane (6g). **6g** (35 mg, 69.3 μmol, 2 steps 69%, dr = 1 : 1) was prepared from (1*R*, 2*R*)-2-(*tert*-butyldiphenylsiltloxy)methyl-1-formyl cyclopropane [Kazuta, Y. Matsuda, A. Shuto, S., *J. Org. Chem.* **2002**, *67*, 1669-1677.] (34 mg, 99.8 μmol), 2-vinyl-4-chloroaniline [Lee, B. S.; Lee, J. H.; Chi, D. Y., *J. Org. Chem.*, **2002**, *67*, 7884-7886.] (16 mg, 102 μmol), MS4A (33 mg), BF_3•Et_2O (60 μL, 0.486 mmol), and vinyl magnesium bromide (1.00 M in THF, 230 μL, 0.230 mmol). $[\alpha]_D^{21}$ -12.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, diastereo mixture) δ 7.68–7.66 (4H, m), 7.44–7.34 (6H, m), 7.22-7.20 (1H, m), 7.04-7.02 (1H, m), 6.73-6.64 (1H, m), 6.48-6.44 (1H, m), 5.81-5.73 (1H, m), 5.63-5.56 (1H, m), 5.31-5.12 (3H, m), 4.00 (1H, brs), 3.80-3.72

(1H, m), 3.41-3.21 (2H, m), 1.11-1.01 (10H, m), 0.98-0.92 (1H, m), 0.54-0.41 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.09, 138.24, 137.87, 135.57, 135.55, 133.73, 133.69, 133.67, 131.67, 131.53, 129.63, 129.62, 128.19, 128.11, 127.66, 127.62, 126.77, 126.67, 125.56, 125.46, 121.96, 121.90, 117.33, 115.64, 115.43, 113.25, 113.20, 66.75, 66.48, 59.60, 59.00, 26.91, 26.86, 22.54, 22.11, 19.48, 19.22, 19.20, 18.57, 7.86, 7.67; LR-MS (FAB) *m/z* 501 (M^+); Anal. Calcd for $C_{31}H_{36}ClNOSi$: C, 74.15; H, 7.23; N, 2.79; found: C, 73.86; H, 7.33; N, 2.97.

***N*-(1-isopropylprop-2-en-1-yl)-2-vinylaniline (6e)**. **6e** (63 mg, 0.313 mmol, 2 steps 43%, volatile) was prepared from isobutylaldehyde (66 μL, 0.723 mmol), 2-vinylaniline [Lee, B. S.; Lee, J. H.; Chi, D. Y., *J. Org. Chem.*, **2002**, *67*, 7884-7886.] (91 mg, 0.764 mmol), MS4A (66 mg), BF_3•Et_2O (570 μL, 4.62 mmol), and vinyl magnesium chloride (1.46 M in THF, 1.49 mL, 2.18 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (1H, d, *J* = 7.3 Hz), 7.12 (1H, dd, *J* = 7.3, 7.1 Hz), 6.78 (1H, dd, *J* = 17.4, 11.0 Hz), 6.67 (1H, dd, *J* = 8.0, 7.1 Hz), 6.59 (1H, d, *J* = 8.0 Hz), 5.74 (1H, ddd, *J* = 16.9, 10.5, 6.0 Hz), 5.61 (1H, dd, *J* = 17.4, 1.1 Hz), 5.33 (1H, dd, *J* = 11.0, 1.1 Hz), 5.20-5.16 (2H, m), 3.91 (1H, brs), 3.70 (1H, dd, *J* = 6.0, 5.0 Hz), 1.94-1.87 (1H, m), 1.00 (3H, d, *J* = 6.9 Hz), 0.98 (3H, d, *J* = 6.9 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 144.66, 137.69, 133.09, 128.70, 127.54, 124.04, 116.78, 116.22, 116.02, 111.62, 61.19, 32.47, 18.70, 18.62; LR-MS (EI) *m/z* 201 (M^+); HR-MS (EI) calcd for $C_{14}H_{19}N$ 201.1518, found 201.1517 (M^+)

***N*-(1-isobutylprop-2-enyl)-2-vinylaniline (6f)**. **6f** (47 mg, 0.218 mmol, 2 steps 42%) was prepared from isovaleraldehyde (55 μL, 0.513 mmol), 2-vinylaniline (64 mg, 0.537 mmol), MS4A (47 mg), BF_3•Et_2O (403 μL, 3.27 mmol), and vinyl magnesium chloride (1.46 M in THF, 1.05 mL, 1.53 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (1H, d, *J* = 7.4 Hz), 7.12 (1H, dd, *J* = 8.0, 7.4 Hz), 6.76 (1H, dd, *J* = 17.2, 10.9 Hz), 6.68 (1H, dd, *J* = 8.0, 7.4 Hz), 6.62 (1H, d, *J* = 8.0 Hz), 5.73 (1H, ddd, *J* = 17.2, 10.3, 6.3 Hz), 5.60 (1H, d, *J* = 17.2 Hz), 5.32 (1H, d, *J* = 10.9 Hz), 5.19 (1H, d, *J* = 17.2 Hz), 5.10 (1H, d, *J* = 10.3 Hz), 3.92-3.89 (1H, m), 3.75 (1H, brs), 1.83-1.75 (1H, m), 1.53-1.42 (2H, m), 0.97 (3H, d, *J* = 6.9 Hz), 0.92 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.52, 140.28, 133.02, 128.73, 127.45, 124.02, 116.90, 116.25, 114.77, 111.65, 54.01, 45.39, 24.77, 22.74, 22.61; LR-MS (EI) *m/z* 215 (M^+); Anal. Calcd for $C_{15}H_{21}N + 0.1H_2O$: C, 82.97; H, 9.84; N, 6.45; found: C, 83.27; H, 9.94; N, 6.39.

***N*-(1-cyclopropylprop-2-en-1-yl)-2-vinylaniline (6h)**. **6h** (103 mg, 0.517 mmol, 2 steps 31%) was prepared from cyclopropanecarboxaldehyde (125 μL, 1.67 mmol), 2-vinylaniline (210 mg, 1.76 mmol), MS4A (125 mg), BF_3•Et_2O (103 μL, 0.834 mmol), and vinyl magnesium chloride (1.46 M in THF, 2.30 mL, 3.36 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (1H, d, *J* = 8.0 Hz), 7.11 (1H, dd, *J* = 8.0, 7.4 Hz), 6.82 (1H, dd, *J* = 17.2, 10.9 Hz), 6.69 (1H, dd, *J* = 8.0, 7.4 Hz), 6.56 (1H, d, *J* = 8.0 Hz), 5.83 (1H, ddd, *J* = 17.2, 10.3, 5.7 Hz), 5.63 (1H, dd, *J* = 17.2, 1.7 Hz) 5.33 (1H, dd, *J* = 10.9, 1.7 Hz), 5.24 (1H, dd, *J* = 17.2 , 1.2 Hz), 5.14 (1H, dd, *J* = 10.3, 1.2 Hz), 4.08 (1H, brs), 3.27 (1H, dd, *J* = 5.7 ,

5.7 Hz), 1.09-1.01 (1H, m), 0.60-0.53 (2H, m), 0.39-0.32 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.65, 138.56, 133.01, 128.64, 127.30, 124.08, 117.11, 116.15, 115.23, 111.95, 60.11, 16.77, 3.27, 2.56, ; LR-MS (EI) *m/z* 199 (M^+); Anal. Calcd for $C_{14}H_{17}N$ + $0.1H_2O$: C, 83.62; H, 8.62; N, 6.97; found: C, 83.65; H, 8.82; N, 6.81.

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[1-(2-vinylphenylamino)prop-2-en-1-yl]cyclopropane (6i). **6i** (122 mg, 0.261 mmol, 2 steps 26%, dr = 1 : 1) was prepared from (1*R*, 2*R*)-2-(*tert*-butyldiphenylsiltloxy)methyl-1-formyl cyclopropane [Kazuta, Y. Matsuda, A. Shuto, S., *J. Org. Chem.* **2002**, *67*, 1669-1677.] (339 mg, 1.00 mmol), 2-vinylaniline (125 mg, 1.05 mmol), MS4A (340 mg), BF_3•Et_2O (1.57 μL, 2.29 mmol), and vinyl magnesium chloride (1.46 M in THF, 1.57 mL, 2.29 mmol). $[\alpha]_D^{22}$ -9.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, diastereomixture); δ 7.68-7.66 (4H, m), 7.42-7.36 (6H, m), 7.26-7.24 (1H, m), 7.12-7.08 (1H, m), 6.77 (1H, ddd, *J* = 16.7, 10.9, 5.0 Hz), 6.71 (1H, m), 6.57-6.54 (1H, m), 5.85-5.77 (1H, m), 5.62-5.56 (1H, m), 5.29-5.11 (3H, m), 4.02 (1H, brs), 3.78-3.71 (1H, m), 3.43-3.28 (2H, m), 1.10-0.96 (11H, m), 0.53-0.49 (1H, m), 0.47-0.42 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$, diastereomixture) δ 144.57, 138.70, 138.39, 135.58, 133.76, 133.73, 132.85, 132.70, 129.60, 128.65, 128.58, 127.65, 127.62, 127.23, 127.12, 124.16, 124.06, 117.16, 117.12, 116.17, 115.37, 115.21, 112.03, 111.97, 66.78, 66.56, 59.42, 58.97, 26.92, 26.87, 22.57, 22.24, 19.41, 19.22, 19.21, 18.67, 7.91, 7.66; LR-MS (ESI) *m/z* 468 [$(M+H)^+$]; HR-MS (ESI) calcd for $C_{31}H_{38}NOSi$ 468.2723, found 468.2716 [$(M+H)^+$]; Anal. Calcd for $C_{31}H_{37}NOSi$: C, 79.61; H, 7.97; N, 2.99; found: C, 79.41; H, 8.13; N, 2.97;

(1*S*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[1-(2-vinylphenylamino)prop-2-en-1-yl]cyclopropane (6j). **6j** (120 mg, 0.255 mmol, 2 steps 14%, dr = 4 : 1) was prepared from (1*S*, 2*R*)-2-(*tert*-butyldiphenylsiltloxy)methyl-1-formyl cyclopropane [Kazuta, Y. Matsuda, A. Shuto, S., *J. Org. Chem.* **2002**, *67*, 1669-1677.] (600 mg, 1.77 mmol), 2-vinylaniline (232 mg, 1.95 mmol), MS4A (600 mg), BF_3•Et_2O (218 μL, 1.77 mmol), and vinyl magnesium chloride (1.46 M in THF, 2.42 mL, 3.53 mmol). $[\alpha]_D^{23}$ -9.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 4:1 diastereo mixture); δ 7.71-7.21 (11H, m), 7.11-7.08 (1H, m), 6.83-6.76 (1H, m), 6.72-6.68 (1H, m), 6.54 (1H x 0.8, d, *J* = 8.2 Hz), 6.48 (1H x 0.2, d, *J* = 8.2 Hz), 6.19-6.11 (1H x 0.2, m), 5.88 (1H x 0.8, ddd, *J* = 16.8, 10.0, 5.9 Hz), 5.62 (1H x 0.2, d, *J* = 17.7 Hz), 5.54 (1H x 0.8, d, *J* = 17.2 Hz), 5.32-5.08 (3H, m), 4.13 (1H, brs), 3.91 (1H x 0.2, dd, *J* = 11.3, 5.9 Hz), 3.72-3.69 (1H x 0.8, m), 3.63-3.58 (1H, m), 3.44-3.41 (1H x 0.2, m), 3.36-3.32 (1H x 0.8, m), 1.13-1.26 (1H, m), 1.17-1.10 (1H, m), 1.08 (9H x 0.2, s), 0.95 (9H x 0.8), 0.81-0.71 (1H, m), 0.28-0.21 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.70, 144.33, 140.03, 139.52, 135.61, 135.55, 135.48, 133.64, 133.61, 133.54, 133.50, 133.00, 132.78, 129.62, 129.47, 129.42, 128.62, 128.45, 127.67, 127.64, 127.56, 127.53, 127.23, 127.07, 124.34, 123.97, 117.37, 117.06, 116.08, 115.72, 114.56, 113.91, 112.55, 112.05, 63.89, 62.92, 56.55, 55.76, 26.97, 26.84, 22.63, 22.63, 19.18, 19.00, 18.80, 18.63, 7.69, 7.61; LR-MS (ESI) *m/z* 468 [$(M+H)^+$]; HR-MS (ESI)

calcd for $C_{31}H_{38}NOSi$ 468.2723, found 468.2721 [$(M+H)^+$]; Anal. Calcd for $C_{31}H_{37}NOSi + 0.1\ H_2O$: C, 79.30; H, 7.99; N, 2.98; found: C, 79.11; H, 8.17; N, 2.91;

General procedure for the prepartion of the *N*-acetylindole derivatives (5B).

Acetylation: A solution of α, ω-diene (**6**), *N*, *N*-diisopropylethylamine (10 eq.), and acetic anhydride (10 eq.) in toluene (SM 0.1M) was refluxed for 24 h. After cooling and addition of sat. aq. $NaHCO_3$, the reaction mixture was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layers were washed with sat. aq. NH_4Cl, brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography to give *N*-acetyl derivative (**3B**) as a yellow oil.

Isomerization and RCM: The mixture of the corresponding **3B** and $Ru(CO)HCl(PPh_3)_3$ (20 mol%) in xylene (SM 0.1 M) was refluxed for 24 h. After cooling, Grubbs' 2nd cat. (20 mol%) was added, and the resulting mixture was stirred at 120 °C for 5 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography to give the *N*–acetylindole derivative (**5B**) as a colorless oil.

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-(5-chloro-*N*-acetylindole-2-yl)cyclopropane (5Bg).

Acetylation: **3Bg** (21 mg, 38.4 μmol, 91%) was prepared from **6g** (21 mg, 42.2 μmol).

Isomerization-RCM: **5Bg** (15 mg, 29.5 μmol, 2 steps 68%) was prepared from **3Bg** (24 mg, 43.3 μmol). After isomerization, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 8 : 1) to give an enamide derivative (**4Bg**). Then RCM was carried out with the enamide in toluene at 120 °C.

: $[\alpha]_D^{21}$ -41.2 (*c* 1.02, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (1H, d, *J* = 8.6 Hz), 7.67 (4H, m), 7.45-7.37 (7H, m), 7.20 (1H, d, *J* = 8.6 Hz), 6.23 (1H, s), 3.93 (1H, dd, *J* = 10.9, 4.0 Hz), 3.69 (1H, dd, *J* = 10.9, 5.7 Hz), 2.76 (3H, s), 1.98-1.96 (1H, m), 1.54-1.51 (1H, m), 1.07 (9H, s), 0.99-0.94 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.50, 142.59, 135.64, 135.58, 135.56, 133.40, 133.35, 130.19, 129.79, 128.76, 127.73, 127.72, 124.26, 119.27, 117.41, 107.84, 64.93, 27.21, 26.83, 23.96, 19.21, 16.63, 11.92; LR-MS (EI) *m/z* 501 (M^+); HR-MS (EI) calcd for $C_{30}H_{32}ClNO_2Si$ 501.1891, found 501.1896 (M^+)

2-Isobutyl-*N*-acetylindole (5Bf).

Acetylation: **3Bf** (80 mg, 0.311 mmol, 71%) was prepared from **6f** (94 mg, 0.436 mmol).

Isomerization-RCM: **5Bf** (4 mg, 17.2 μmol, 2 steps 27%) was prepared from **3Bf** (17 mg, 64.5 μmol). After isomerization reaction, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1) to give an enamide derivative (**4Bf**). Then RCM was carried out with the enamide in toluene at 120 °C.

: ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, d, *J* = 7.7 Hz), 7.50-7.48 (1H, m), 7.26-7.20 (2H, m),

6.38 (1H, s), 2.87 (2H, d, J = 6.8 Hz), 2.76 (3H, s), 2.02-1.96 (1H, m), 0.97 (6H, d, J = 6.8 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36, 141.69, 136.31, 129.85, 123.33, 122.91, 120.19, 114.62, 109.63, 39.45, 27.78, 27.64, 22.51 ; LR-MS (EI) *m/z* 215 (M^+); Anal. Calcd for $C_{14}H_{17}NO$ + 0.1 H_2O: C, 77.46 ; H, 7.99; N, 6.45; found: C, 77.67; H, 8.15; N, 6.11;

2-cycropropyl-*N*-acetylindole (5Bh)

Acetylation: **3Bh** (29 mg, 0.118 mmol, 92%) was prepared from **6h** (26 mg, 0.128 mmol).

Isomerization-RCM: **5Bh** (9 mg, 43.7 μmol, 2 steps 70%) was prepared from **3Bh** (15 mg, 62.2 μmol).

: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (1H, d, J = 8.3 Hz), 7.43 (1H, d, J = 7.7 Hz), 7.29-7.20 (2H, m), 6.35 (1H, s), 2.86 (3H, s), 2.14-2.09 (1H, m), 1.09-1.06 (2H, m), 0.88-0.86 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.70, 142.31, 137.28, 128.98, 124.29, 123.36, 119.86, 116.27, 108.65, 27.24, 11.67, 8.48 ; LR-MS (EI) *m/z* 199 (M^+); HR-MS (EI) calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0997 (M^+);

General procedure for the prepartion of the *N*-formylindole derivatives (5D).

Formylation: A mixture of acetic anhydride (5 eq.) and formic acid (6 eq.) was stirred at 60 °C for 3 h. After cooling, to the resulting mixture was added α, ω-diene (**6**) in THF (SM 0.1 M) at 0 °C. The mixture was heated gradualy to 60 °C and stirred for 15 h. After cooling, toluene was added to the reaction mixture, then the solvent was concentrated in reduced pressure (x2). The residue was purified by silica gel column chromatography to give corresponding *N*-formyl derivative (**3D**) as a yellow oil.

Isomerization and RCM: The mixture of the **3D** and $Ru(CO)HCl(PPh_3)_3$ (20 mol%) in xylene (SM 0.1 M) was refluxed for 24 h. After cooling, Grubbs' 2nd cat. (20 mol%) was added, and the resulting mixture was stirred at 120 °C for 4 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography to give the *N*–formylindole derivative (**5D**) as a colorless oil.

2-isopropyl-*N*-formylindole (5De).

Formylation: **3De** (71 mg, 0.311 mmol, quant.) was prepared from **6e** (63 mg, 0.311 mmol).

Isomerization and RCM: **5De** (3 mg, 16.0 μmol, 2 steps 23%) was prepared from **3De** (16 mg, 69.3 μmol).

: ^{1}H NMR (400 MHz, $CDCl_3$, 55 °C); δ 9.35 (1H, s), 8.25 (1H, brs), 7.47-7.44 (1H, m), 7.29-7.22 (2H, m), 6.39 (1H, s), 3.37-3.30 (1H, m), 1.39-1.38 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C) δ 158.34, 146.56, 135.85, 129.87, 124.38, 124.23, 120.18, 115.01 (br), 105.83, 26.08, 22.62; LR-MS (EI) *m/z* 187 (M^+); Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48; found: C, 76.69; H, 7.16; N, 7.21;

2-isobutyl-*N*-formylindole (5Df).

Formylation: **3Df** (54 mg, 0.220 mmol, 95%) was prepared from **6f** (50 mg, 0.232 mmol).

Isomerization and RCM: **5Df** (17 mg, 82.5 μmol, 2 steps 94%) was prepared from **3Df** (21 mg, 87.9 μmol).

: ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C) δ 9.30 (1H, s), 8.27 (1H, brs), 7.45 (1H, d, J = 6.9 Hz), 7.28-7.23 (2H, m), 6.35 (1H, s), 2.78 (2H, d, J = 7.4 Hz), 2.03-1.98 (1H, m), 1.02 (6H, d, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 158.39, 138.94, 135.64, 129.86, 124.34, 124.27, 120.02, 115.18 (br), 109.40, 36.35, 28.42, 22.49; LR-MS (EI) *m/z* 201 (M^+); HR-MS (EI) calcd for $C_{13}H_{15}NO$ 201.1154, found 201.1152 (M^+);

2-cycropropyl-*N*-formylindole (5Dh)

Formylation: **3Dh** (54 mg, 0.236 mmol, 94%) was prepared from **6h** (50 mg, 0.251 mmol).

Isomerization and RCM: **5Dh** (14 mg, 73.4 μmol, 2 steps 99%) was prepared from **3Dh** (17 mg, 73.9 μmol).

: ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C) δ 9.60 (1H, s), 8.33 (1H, brd, J = 7.4 Hz), 7.42 (1H, d, J = 7.4 Hz), 7.29-7.21 (2H, m), 6.27 (1H, s), 2.03-1.97 (1H, m), 1.05-1.01 (2H, m), 0.84-0.81 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C) δ 159.07, 141.64, 135.51, 129.72, 124.70, 124.33, 120.16, 115.52 (br), 107.32, 107.28, 7.26, 6.73; LR-MS (EI) *m/z* 185 (M^+); HR-MS (EI) calcd for $C_{12}H_{11}NO$ 185.0841, found 185.0843 (M^+); Anal. Calcd for $C_{12}H_{11}NO$ + 0.2 H_2O : C, 76.33; H, 6.09; N, 7.42; found: C, 76.73; H, 6.12; N, 7.04;

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-(*N*-formylindole-2-yl)cyclopropane (5Di)

Formylation: **3Di** (743 mg, 1.50 mmol, 85%) was prepared from **6i** (824 mg, 1.76 mmol).

Isomerization and RCM: **5Di** (24 mg, 52.7 μmol, 2 steps 87%, colorless oil) was prepared from **3Di** (30 mg, 60.5 μmol).

: $[\alpha]_D^{22}$ 3.5 (*c* 0.82, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C) δ 9.68 (1H, s), 8.36 (1H, brd, J = 8.0 Hz), 7.69-7.67 (4H, m), 7.44-7.36 (7H, m), 7.30-7.21 (2H, m), 6.24 (1H, s), 3.99 (1H, dd, J = 10.9, 4.6 Hz), 3.49 (1H, dd, J = 10.9, 6.9 Hz), 1.93-1.90 (1H, m), 1.49-1.43 (1H, m), 1.11 (9H, s), 1.05-1.01 (1H, m), 0.97-0.93 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C) δ 159.55, 140.67, 135.65, 135.47, 133.64, 133.56, 129.83, 129.67, 127.80, 124.74, 124.29, 120.11, 115.70 (br), 107.48, 107.44, 66.09, 26.96, 23.02, 19.26, 12.90, 10.65 ; LR-MS (ESI) *m/z* 476 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{29}H_{31}NNaO_2Si$ 476.2022, found 476.2023 [$(M+Na)^+$]; Anal. Calcd for $C_{29}H_{31}NO_2Si$: C, 76.78; H, 6.89; N, 3.09; found: C, 76.57; H, 7.02; N, 3.00;

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-(5-chloro-*N*-tosylindole-2-yl)cyclopropane (7)

A mixture of **5Bg** (13 mg, 26.7 μmol) and potassium carbonate (18 mg, 0.133 mmol) in THF (80 μL) and MeOH (800 μL) was stirred at rt for 1 h. After addition of sat. aq. NH_4Cl, the solvent was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced

pressure. To a solution of the residue in THF (270 μL) was added NaH (60% in mineral oil, 1 mg, 35.0 μmol) and tosyl chloride (6 mg, 29.4 μmol) and the mixturewas stirred for 3 h. NaH (60% in mineral oil, 1 mg, 35.0 μmol) and tosyl chloride (6 mg, 29.4 μmol) was added to the mixture again and stirred for 5 h. After addition of sat. aq. NH_4Cl, the solvent was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 40 : 1) to give **7** (10 mg, 16.9 μmol, 2 steps 63%) as a pale yellow oil. $[\alpha]_D^{21}$ -87.0 (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (1H, d, *J* = 8.9 Hz), 7.71-7.67 (4H, m), 7.61 (2H, d, *J* = 8.2 Hz), 7.44-7.37 (6H, m), 7.34 (1H, d, *J* = 1.7 Hz), 7.20 (1H, dd, *J* = 8.9, 1.7 Hz), 7.11 (2H, d, *J* = 8.2 Hz), 6.10 (1H, s), 3.86 (1H, dd, *J* = 10.6, 4.6 Hz), 3.72 (1H, dd, *J* = 10.6, 5.4 Hz), 2.39-2.36 (1H, m), 2.32 (3H, s), 1.37-1.33 (1H, m), 1.07 (9H, s), 1.03-0.99 (1H, m), 0.75-0.72 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.77, 144.70, 136.12, 135.55, 135.51, 133.58, 133.53, 130.54, 129.67, 129.62, 128.95, 127.64, 126.27, 123.77, 119.58, 115.43, 105.51, 64.51, 26.80, 24.00, 21.42, 19.21, 13.71, 12.75; LR-MS (ESI) *m/z* 636 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{35}H_{36}ClNNaO_3SSi$ 636.1771, found: 636.1764

(1*R*,2*R*)-1-(5-Chloro-*N*-tosylindole-2-yl)-2-hydroxymethyl cyclopropane (8)

The mixture of **7** (377 mg, 0.614 mmol) and tetrabutylammonium floride (1.0 M in THF, 0.920 mL, 0.920 mmol) in THF (8.8 mL) was stirred at rt for 2 h. After addition of sat. aq. NH_4Cl, the reaction mixture was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1 = 2 : 1) to give **8** (227 mg, 0.605 mmol, 99%) as a pale yellow oil. $[\alpha]_D^{21}$ -97.2 (*c* 1.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (1H, d, *J* = 8.9 Hz), 7.67 (2H, d, *J* = 8.3 Hz), 7.34 (1H, d, *J* = 2.0 Hz), 7.22 (2H, d, *J* = 8.3 Hz), 7.20 (1H, dd, *J* = 8.9, 2.0 Hz), 6.19 (1H, s), 3.92 (1H, dd, *J* = 11.5, 4.3 Hz), 3.35 (1H, dd, *J* = 11.5, 8.6 Hz), 2.76 (1H, brs), 2.34 (3H, s), 2.24-2.20 (1H, m), 1.44-1.37 (1H, m), 1.11-1.07 (1H, m), 0.96-0.92 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.17, 143.84, 135.61, 135.36, 130.50, 129.94, 129.27, 126.32, 124.21, 119.90, 115.43, 106.73, 66.35, 25.36, 21.53, 16.40, 10.58; LR-MS (EI) *m/z* 398 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{19}H_{18}ClNNaO_3S$ 398.0594, found 398.0597 [$(M+Na)^+$]; Anal. Calcd for $C_{19}H_{18}ClNO_3S + 0.6\ H_2O$: C, 59.02; H, 5.00; N, 3.62; found: C, 58.63; H, 4.71;N, 3.49.

(1*R*,2*R*)-2-(4-Chlorobenzylaminomethyl)-1-(5-Chloro-*N*-tosylindole-2-yl) cyclopropane (9)

The mixture of **8** (70 mg, 0.186 mmol) and Dess-Martin periodinane (118 mg, 0.278 mmol) in CH_2Cl_2 (2.3 mL) was stirred at rt for 4 h. After addition of sat. aq. $Na_2S_2O_4$ / $NaHCO_3$ (1 / 1), the reaction mixture was partitioned between CH_2Cl_2 and sat. aq. $Na_2S_2O_4$ / $NaHCO_3$ (1 / 1). The organic layer was

separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. To a mixture of the residue, 4-chlorobenzylamine (113 μL, 0.924 mmol) and MS4A (70 mg) in CH_2Cl_2 (9.3 mL) was added sodium triacetoxyborohydride (47 mg, 0.222 mmol) at rt and the mixture was stirred for 3 h. After addition of sat. aq. $NaHCO_3$, the reaction mixture was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1 = 1 : 2) to give **9** (70 mg, 0.140 mmol, 2 steps 75%) as a pale white oil. $[\alpha]_D^{22}$ -148.2 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (1H, d, *J* = 9.1 Hz), 7.63 (2H, d, *J* = 8.4 Hz), 7.32 (1H, d, *J* = 1.8 Hz), 7.29-7.16 (7H, m), 6.12 (1H, s), 3.81 (1H, d, *J* = 13.5 Hz), 3.77 (1H, d, *J* = 13.5 Hz), 2.73 (1H, dd, *J* = 12.2, 6.1 Hz), 2.63 (1H, dd, *J* = 12.2, 7.0 Hz), 2.48 (1H, brs), 2.32 (3H, s), 2.25-2.20 (1H, m), 1.38-1.30 (1H, m), 0.93-0.84 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.94, 144.50, 138.62, 135.87, 135.39, 132.49, 130.53, 129.78, 129.39, 129.12, 128.42, 126.29, 12 3.96, 119.72, 115.43, 105.75, 52.89, 23.10, 21.50, 15.99, 13.08; LR-MS (ESI) *m/z* 499 $[(M+H)^+]$; HR-MS (ESI) calcd for $C_{26}H_{25}Cl_2N_2O_2S$, found $[(M+H)^+]$; Anal. Calcd for $C_{26}H_{24}Cl_2N_2O_2S$ + 0.1 H_2O: C, 62.08; H, 4.89; N, 5.57; found: C, 61.84; H, 4.89; N, 5.37.

(1*R*,2*R*)-2-(4-Chlorobenzylaminomethyl)-1-(5-Chloroindole-2-yl) cyclopropane (2a)

A mixture of **9** (70 mg, 0.140 mmol) and potassium hydroxide (157 mg, 2.80 mmol) in EtOH (1.4 mL) was refluxed for 3 h. After cooling sat. aq. NH_4Cl and sat. aq. $NaHCO_3$ was added to the reaction mixture, and EtOH was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 1 : 0 – 98 : 2) to give **2a** (47 mg, 0.136 mmol, 97%, free amine) as a pale yellow oil. The free amine (11 mg, 32.7 μmol) was dissolved in 1 M HCl in EtOH (650 μL), and the solution was evaporated. The resulting residue was triturated with Et_2O to give **2a** (13 mg, 32.7 μmol, hydrochloride) as a pale red hydroscopic amorphous solid. $[\alpha]_D^{21}$ -65.8 (*c* 1.00, CH_3OH, hydrochloride); ^{1}H NMR (500 MHz, $CDCl_3$, hydrochloride) δ 10.34 (1H, s), 9.99 (1H, brs), 9.75 (1H, brs), 7.45 (2H, d, *J* = 8.0 Hz), 7.37 (1H, d, *J* = 2.0 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.14 (1H, d, *J* = 8.6 Hz), 6.99 (1H, dd, *J* = 8.6, 2.0 Hz), 5.63 (1H, s), 3.90-3.88 (1H, m), 3.82-3.79 (1H, m), 3.12 (1H, brs), 2.02 (1H, brs), 1.86 (1H, brs), 0.85 (2H, brs), 0.59 (1H, brs); ^{13}C NMR (125 MHz, $CDCl_3$, hydrochloride)

δ 139.43, 136.05, 134.34, 131.65, 129.50, 129.15, 127.75, 124.83, 121.24, 119.31, 111.35, 97.41, 50.0 4, 49.82, 17.56, 16.75, 10.39; LR-MS (ESI) *m/z* 345 $[(M+H-HCl)^+]$; HR-MS (ESI) calcd for $C_{19}H_{19}Cl_2N_2$ 345.0925, found: 345.0917; Anal. Calcd for $C_{19}H_{19}Cl_3N_2$ + 0.4H_2O (hydrochloride): C, 58.67; H, 5.13; N, 7.20; found: C, 58.71; H, 5.18; N, 6.93.

(1*R*,2*R*)-1-(5-Chloro-*N*-tosylindole-2-yl)-2-[(*E*, *Z*)-2-methoxyethenyl] cyclopropane (10)

The mixture of **8** (73 mg, 0.194 mmol) and Dess-Martin periodinane (124 mg, 0.292 mmol) in CH_2Cl_2 (2.4 mL) was stirred at rt for 2 h. After addition of sat. aq. $Na_2S_2O_4$ / $NaHCO_3$ (1 / 1), the reaction mixture was partitioned between CH_2Cl_2 and sat. aq. $Na_2S_2O_4$ / $NaHCO_3$ (1 / 1). The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. To a suspention of (metoxymethyl)triphenylphosphonium chloride (153 mg, 0.446 mmol) in THF (1.0 mL) was added sodium hexamethyldisilazde (1.9 M in THF, 0.200 mL, 0.380 mL) at 0 °C and the mixture was stirred for 40 min. To the resulting mixture was added a solution of the crude aldehyde derivative in THF (1.5 mL) at 0 °C, and the mixture was stirred at the same temperature for 4 h. After addition of sat. aq. NH_4Cl, the solvent was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 15 : 1 = 10 : 1) to give **10** (65 mg, 0.161 mmol, 2 steps 83%, *E* : *Z* = 1 : 0.8) as a pale yellow oil. $[\alpha]_D^{21}$ -30.0 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (1H × 0.55, d, *J* = 8.8 Hz), 8.08 (1H × 0.45, d, *J* = 8.8 Hz), 7.75 (2H × 0.45, d, *J* = 8.2 Hz), 7.68 (2H × 0.55, d, *J* = 8.2 Hz), 7.33-7.31(1H, m), 7.21-7.17 (3H, m), 6.43 (1H × 0.55, d, *J* = 12.6 Hz), 6.11 (1H × 0.45, s), 6.09 (1H × 0.55, s), 6.04 (1H × 0.45, d, *J* = 6.3 Hz), 4.64 (1H × 0.55, dd, *J* = 12.6, 7.5 Hz), 4.15 (1H × 0.45, dd, *J* = 9.3, 6.3 Hz), 3.66 (3H × 0.45, s), 3.55 (3H × 0.55, s), 2.57-2.52 (1H × 0.45, m), 2.46-2.41 (1H × 0.55, m), 2.35 (3H × 0.55, s), 2.35 (3H × 0.45, s), 1.97-1.90 (1H × 0.45, m), 1.46-1.40 (1H × 0.55, m), 1.18-1.13 (1H × 0.45, m), 1.09-1.00 (2H × 0.55, 1H × 0.45, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.05, 147.01, 144.90, 144.70, 144.68, 136.06, 135.79, 135.53, 135.32, 130.76, 130.59, 129.73, 129.08, 129.03, 126.79, 126.60, 123.89, 123.77, 119.62, 115.55, 115.53, 108.22, 105.03, 104.94, 104.06, 59.79, 56.03, 22.56, 21.58, 21.56, 20.09, 18.22, 17.69, 15.88, 15.37 ; LR-MS (ESI) *m/z* 401 [$(M-H)^+$]; HR-MS (ESI) calcd for $C_{21}H_{19}ClNO_3S$ 400.0769, found 400.0782 [$(M-H)^+$]; Anal. Calcd for $C_{21}H_{20}ClNO_3S$ + 0.1 H_2O: C, 62.48; H, 5.03; N, 3.47; found: C, 62.20; H, 5.03; N, 3.32.

(1*R*,2*S*)-2-[2-(4-Chlorobenzylamino)ethyl]-1-(5-Chloro-*N*-tosylindole-2-yl) cyclopropane (11)

A solution of **10** (27 mg, 66.1 μmol) and aq. HCl (12 *N*, 0.11 mL) in THF (1.3 mL) was stirred at 0 °C for 15 min. After addition of sat. aq. $NaHCO_3$, the solvent was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. To a mixture of the residue, 4-chlorobenzylamine (40 μL, 0.327 mmol) and MS4A (30 mg) in CH_2Cl_2 (1.3 mL) was added Sodium triacetoxyborohydride (17 mg, 79.3 μmol) at rt and the mixture was stirred for 12 h. Afte

addition of sat. aq. $NaHCO_3$, the reaction mixture was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1 = 1 : 2) to give **11** (23 mg, 44.8 μmol, 2 steps 68%) as a pale yellow oil. $[\alpha]_D^{21}$ -128.9 (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (1H, d, *J* = 8.8 Hz), 7.63 (2H, d, *J* = 8.4 Hz), 7.32 (1H, d, *J* = 2.0 Hz), 7.29-7.17 (7H, m), 6.08 (1H, s), 3.77 (2H, s), 2.74 (2H, t, *J* = 7.0 Hz), 2.34 (3H, s), 2.23-2.18 (1H, m), 1.89-1.81 (1H, m), 1.51-1.42 (1H, m), 1.14-1.06 (1H, m), 0.84-0.75 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.19, 144.87, 138.71, 136.13, 135.52, 132.58, 130.61, 129.78, 129.43, 129.10, 128.48, 126.36, 123.90, 119.63, 115.53, 105.36, 53.18, 48.65, 33.93, 21.55, 20.80, 16.36, 15.49.; LR-MS (FAB) *m/z* 513 $[(M+H)^+]$; HR-MS (FAB) calcd for $C_{27}H_{27}Cl_2N_2O_2S$ 513.1170; found 513.1178 $[(M+H)^+]$; Anal. Calcd for $C_{27}H_{26}Cl_2N_2O_2S + 0.4\ H_2O$: C, 62.28; H, 5.19; N, 5.38; found: C, 62.03; H, 5.05; N, 5.22.

(1*R*,2*S*)-2-[2-(4-Chlorobenzylamino)ethyl]-1-(5-Chloroindole-2-yl) cyclopropane (2b)

A mixture of **11** (36 mg, 69.7 μmol) and potassium hydroxide (78 mg, 1.39 mmol) in EtOH (600 μL) was stirred at reflux for 3 h. After cooling sat. aq. NH_4Cl and sat. aq. $NaHCO_3$ was added to the mixture, and EtOH was concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 1 : 0 – 98 : 2) to give **2b** (23 mg, 64.0 μmol, 92%, free amine) as a colorless oil. The free amine (17 mg, 47.3 μmol) was dissolved in 1 M HCl in EtOH (950 μL), and the solution was evaporated. The resulting residue was triturated with Et_2O to give **2b** (19 mg, 47.3 μmol, hydrochloride) as a red hydroscopic amorphous solid. $[\alpha]_D^{21}$ -78.0 (*c* 0.99, CH_3OH, hydrochloride); ^1H NMR (500 MHz, $CDCl_3$, 50 °C, hydrochloride) δ 9.33 (1H, brs), 7.46 (2H, d, *J* = 7.8 Hz), 7.39 (1H, d, *J* = 1.8 Hz), 7.26-7.22 (3H, m), 7.02 (1H, dd, *J* = 8.7, 1.8 Hz), 5.95 (1H, s), 4.00 (1H, d, *J* = 13.3 Hz), 3.96 (1H, d, *J* = 13.3 Hz), 2.91 (2H, brs), 1.89 (1H, brs), 1.72 (1H, brs), 1.61 (1H, brs), 1.18 (1H, brs), 0.92 (1H, brs), 0.66 (1H, brs); ^{13}C NMR (125 MHz, $CDCl_3$, CD_3OD, hydrochloride) δ 142.13, 135.70, 134.20, 131.33, 129.42, 129.24, 128.51, 124.53, 120.53, 118.45, 111.32, 96.19, 50.25, 46.42, 29.99, 19.02, 16.22, 13.93; LR-MS (ESI) *m/z* 359 $[(M+H)^+]$; HR-MS (ESI) calcd for $C_{20}H_{21}Cl_2N_2$ 359.1082, found 359.1085 $[(M-HCl+H)^+]$; Anal. Calcd for $C_{20}H_{20}Cl_2N_2 + 0.1H_2O$ (free amine): C, 66.52; H, 5.64; N, 7.76; found: C, 66.80; H, 5.94; N, 7.38.

General procedure for the prepartion of the quinoline derivatives (12).

A mixture of the *N*-formyl derivative (**3D**) and Grubbs' 2nd cat. (10 mol%) in CH_2Cl_2 (SM 0.05 M) was refluxed for 3 h. After cooling, the solvent was concentrated in reduced pressure. A solution of the

residue in EtOH and 4 *N* HCl aq. (SM 0.05 M, EtOH : 4 *N* HCl aq. = 1 : 1) was stirred at 80 °C for 7 h. After cooling and addition of sat. aq. $NaHCO_3$, the reaction mixture was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography to give the quinoline derivative (**12**) as a brown oil.

2-isopropylquinoline (12e) [Cho, C. S.; Kim, B. T.; Choi, H. J.; Kimb, T. J.; Shimb, S. C., Tetrahedron **2003**, *59*, 7997–8002.]. **12e** (17 mg, 99.3 μmol, 3 steps 76%) was prepared from **6e** (26 mg, 0.131 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, d, *J* = 8.6 Hz), 8.05 (1H, d, *J* = 8.0 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.68 (1H, dd, *J* = 8.0, 6.9 Hz), 7.48 (1H, dd, *J* = 8.0, 6.9 Hz), 7.34 (1H, d, *J* = 8.6 Hz), 3.30-3.24 (1H, m), 1.40 (6H, d, *J* = 6.9 Hz); LR-MS (EI) *m/z* 171 [M^+];

2-isobutylquinoline (12f)[Lewis, J. C.; Bergman, R. G.; Ellman, J. A., *J. Am. Chem. Soc.* **2007**, *129*, 5332-5333.]. **12f** (15 mg, 81.0 μmol, 3 steps 87%) was prepared from **6f** (20 mg, 92.7 μmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (2H, m), 7.78 (1H, d, *J* = 7.7 Hz), 7.68 (1H, dd, *J* = 7.7, 7.2 Hz), 7.48 (1H, dd, *J* = 7.7, 7.2 Hz), 7.27 (1H, d, *J* = 8.2 Hz), 2.85 (2H, d, *J* = 7.2 Hz), 2.27-2.18 (1H, m), 0.98 (6H, d, *J* = 6.3 Hz); LR-MS (ESI) *m/z* 186 [$(M+H)^+$];

2-Cyclopropylquinoline (12h)[Molander, G. A.; Gormisky, P. E.; *J. Org. Chem.*, **2008**, *73*, 7481–7485.]. **12h** (12 mg, 71.5 μmol, 3 steps 77%) was prepared from **6h** (18 mg, 92.7 μmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (1H, d, *J* = 8.6 Hz), 7.96 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 8.0 Hz), 7.64 (1H, dd, *J* = 8.0, 6.9 Hz), 7.42 (1H, dd, *J* = 8.0, 6.9 Hz), 7.16 (1H, d, *J* = 8.6 Hz), 2.27-2.22 (1H, m), 1.16-1.07 (4H, m); LR-MS (ESI) *m/z* 170 [$(M+H)^+$];

(1*R*,2*R*)-2-Hydroxymethyl-1-(quinol-2-yl)cyclopropane (12i). **12i** (15 mg, 77.3 μmol, 3 steps 67%) was prepared from **6i** (54 mg, 115 mmol). RCM (Step 1) was carried out with Grubbs' 2nd cat. (17 mg, 20 mol%) and benzene (1.0 mL) at 80 °C. $[\alpha]_D^{24}$ -87.0 (*c* 0.20, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, d, *J* = 8.6 Hz), 7.95 (1H, d, *J* = 8.6 Hz), 7.74 (1H, d, *J* = 7.7 Hz), 7.65 (1H, dd, *J* = 8.6, 7.2 Hz), 7.44 (1H, dd, *J* = 7.7, 7.2 Hz), 7.15 (1H, d, *J* = 8.6 Hz), 3.77 (1H, dd, *J* = 11.3, 5.9 Hz), 3.63 (1H, dd, *J* = 11.3, 7.2 Hz), 2.23-2.18 (1H, m), 2.11 (1H, brs), 1.94-1.86 (1H, m), 1.43-1.38 (1H, m), 1.10-1.06 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.97, 147.71, 136.12, 129.47, 128.43, 127.47, 126.71, 125.39, 119.27, 65.99, 26.33, 23.87, 14.53; LR-MS (EI) *m/z* 199 (M^+); HR-MS (EI) calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0999 (M^+);

(1*S*,2*R*)-2-Hydroxymethyl-1-(quinol-2-yl)cyclopropane (12j). **12j** (22 mg, 0.111 mmol, 3 steps 67%) was prepared from **6j** (77 mg, 0.165 mmol). RCM (Step 1) was carried out with Grubbs' 2nd cat. (24 mg, 20 mol%) and benzene (2.8 mL) at 80 °C. $[\alpha]_D^{22}$ 82.0 (*c* 0.10, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, d, *J* = 8.6 Hz), 7.93 (1H, d, *J* = 8.6 Hz), 7.78 (1H, d, *J* = 7.7 Hz), 7.68 (1H, dd, *J* = 8.6, 7.2 Hz), 7.51-7.47 (2H, m), 5.68 (1H, brs), 4.06 (1H, dd, *J* = 12.2, 3.2 Hz), 3.545 (1H, dd, *J* = 12.2, 8.6 Hz), 2.40-2.34 (1H, m), 1.76-1.72 (1H, m), 1.32-1.27 (1H, m), 1.23-1.29 (1H, m); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 161.35, 146.69, 136.48, 129.73, 128.12, 127.42, 126.58, 125.97, 123.45, 61.14, 23.43, 23.33, 11.64; LR-MS (ESI) *m/z* 222 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{13}H_{13}NNaO$ 222.0895, found 222.0889 [$(M+Na)^+$]; Anal. Calcd for $C_{13}H_{13}NO$ + 0.2 H_2O: C, 76.97; H, 6.66; N, 6.90; found: C, 76.57; H, 6.75; N, 6.63;

1-isopropylprop-2-en-1-yl 2-vinylphenyl ether (13a). To a mixture of 4-Methyl-1-penten-3-ol [Hodgson, D. M., Fleming, M. J., Stanway. S. J., *J. Org. Chem.* **2007**, *72*, 4763-4773](100 mg, 0.998 mmol), 2-vinylphenol[Elias, X., Pleixats R., Man, M. W. C., *Tetrahedron*, **2008**, *64*, 6770–6781] (240 mg, 2.00 mmol) and tributylphosphine (375 μL, 1.50 mmol) in THF (10 mL) was added 1,1'-(azocarbonyl)dipiperidine (378 mg, 1.50 mmol) at 0 °C. The resulting mixture was heated to rt, and stirred for 14 h. The solvent was concentrated in reduced pressure. The residue was purified by flash silica gel column chromatography (hexane) to give **13a** (90.8 mg, 0.449 mmol, 45%, volatile) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (1H, dd, *J* = 8.0, 1.7 Hz), 7.17-7.11 (2H, m), 6.90-6.87 (1H, m), 6.84 (1H, d, *J* = 8.6 Hz), 5.83 (1H, ddd, *J* = 17.2, 10.9, 6.3 Hz), 5.73 (1H, dd, *J* = 17.2, 1.7 Hz), 5.26-5.20 (3H, m), 4.41 (1H, dd, *J* = 6.3, 5.7 Hz), 2.06-1.98 (1H, m), 1.04 (3H, d, *J* = 6.9 Hz), 1.01 (3H, d, *J* = 6.9 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 155.53, 136.09, 131.76, 128.48, 127.29, 126.18, 120.39, 117.48, 113.98, 113.86, 83.95, 32.97, 18.32, 18.02; LR-MS (EI) *m/z* 202 (M^+); HR-MS (EI) calcd for $C_{14}H_{18}O$ 202.1358, found 202.1358 (M^+)

Preparation of (1*R*,2*R*)-2--*t*-Butyldiphenylsilyloxymethyl-1-[1-(2-vinyl phenoxy)prop-2-en-1-yl]cyclopropane (13b)

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[1-hydroxyprop-2-en-1-yl]cyclopropane. To a solution of (1*R*, 2*R*)-2-(*tert*-butyldiphenylsiltloxy)methyl-1-formyl cyclopropane [Kazuta, Y. Matsuda, A. Shuto, S., *J. Org. Chem.* **2002**, *67*, 1669-1677.] (600 mg, 1.77 mmol) in THF (16 mL) was added vinyl magnesium chloride (1.46 M in THF, 1.45 mL, 2.12 mmol) at 0 °C and the mixture was stirred for 2 h. After addition of sat. aq. NH_4Cl, the solvent concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 10 : 1) to give diastereomixture of allylalcohol (548 mg, 1.49 mmol, 84%, dr = 1 : 1) as a colorless oil. $[\alpha]_D^{23}$ – 13.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 1 : 1 diastereomixture) δ 7.68-7.65 (4H, m), 7.41-7.34 (6H, m), 5.96-5.85 (1H, m), 5.30-5.21 (1H, m), 5.09-5.06 (1H, m), 3.71-3.66 (1H, m), 3.56-3.51 (1H, m), 3.47-3.43 (1H, m), 2.00 (1H, s), 1.13-0.98 (10H, m), 0.92-0.84 (1H, m), 0.54-0.51 (1H x 0.5, m), 0.47-0.40 (1H + 1H x 0.5, m); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 139.56, 139.31, 135.51, 133.69, 129.56, 129.52, 127.58, 127.53, 114.57, 114.48, 75.86, 75.63, 66.44 , 66.20, 26.82, 26.77, 23.00, 22.74, 19.11, 19.01, 18.09, 7.93, 6.92 ; LR-MS (ESI) *m/z* 389 [(M+Na)$^+$]; HR-MS (ESI) calcd for $C_{23}H_{30}NaO_2Si$ 389.1913, found 389.1907 [(M+Na)$^+$]; Anal. Calcd for $C_{23}H_{30}O_2Si$: C, 75.36; H, 8.25; found: C, 75.21; H, 8.27;

(1*R*,2*R*)-2--*t*-Butyldiphenylsilyloxymethyl-1-[1-(2-vinylphenoxy)prop-2-en-1-yl]cyclopropane (13b) and (1*S*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[3-(2-vinylphenoxy)prop-1-en-1-yl]cyclopropane (13b'). To the mixture of (1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-[1-hydroxyprop-2-en-1-yl]cyclopropane (247 mg, 0.674 mmol), 2-vinylphenol (162 mg, 1.35 mmol) and tributylphosphine (252 μL, 1.01 mmol) in THF (6.7 mL) was added 1,1'-(azocarbonyl)dipiperidine (255 mg, 1.01 mmol) at 0 °C. The resulting mixture was warmed to rt, and stirred for 15 h. The solvent was concentrated in reduced pressure. The residue was purified by flash silica gel column chromatography (hexane) to give a mixture of **13b** and **13b'** (236 mg, 0.503 mmol, 75%, **13b** : **13b'** = 2 : 1, **13b**; dr = 1 : 1) as a colorless oil. $[\alpha]_D^{21}$ -21.4 (*c* 1.01, $CHCl_3$, mixture); ^{1}H NMR (500 MHz, $CDCl_3$, **13b** : **13b'** = 2 : 1, **13b**; dr = 1 : 1 diastereomixture(**13ba**, **13bb**)) δ 7.68-6.82 (45H, m), 5.97-5.85 (2H, m), 5.77-5.69 (4H, m), 5.42-5.36 (1H, m), 5.30-5.16 (7H, m), 4.47 (2H, d, *J* = 4.5 Hz), 4.28-4.25 (1H, m), 4.21-4.18 (1H, m), 3.70-3.47 (6H, m), 1.34-1.30 (1H, m), 1.17-1.04 (32H, m), 0.70-0.65 (1H, m), 0.62-0.48 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$, **13b**, **13b'** mixture) δ 155.86, 155.42, 155.38, 137.58, 137.01, 136.95, 135.57, 133.84, 133.81, 133.78, 131.76, 131.70, 129.57, 129.54, 128.69, 128.45, 128.43, 127.78, 127.76, 127.59, 126.93, 126.39, 126.23, 126.19, 122.63, 120.94, 120.63, 116.41, 116.36, 115.12, 115.10, 114.22, 114.03, 112.3, 82.10, 81.70, 69.04, 66.29, 66.11, 66.05, 26.84, 22.72, 21,10, 20.69, 19.19, 19.02, 18.81, 17.95, 11.4, 8.02, 6.65; LR-MS (ESI) *m/z* 491 [(M+Na)$^+$]; HR-MS (ESI) calcd for $C_{31}H_{36}NaO_2Si$ 491.2382, found 491.2384 [(M+Na)$^+$]; Anal. Calcd for $C_{31}H_{36}O_2Si$: C, 79.44; H, 7.74; found: C, 79.15;

H, 7.86.

Preparation of (1*S*,2*R*)-2-Benzyloxymethyl-1-[1-(2-vinylphenoxy)prop-2-en-1-yl]cyclopropane (13c)

(1*S*,2*R*)- 1,1-dimethoxymethyl-2-Hydroxymethylcyclopropane. A mixture of (1*S*, 2*R*)-2-(*tert*-butyldiphenylsiltloxy)methyl-1-formyl cyclopropane [Kazuta, Y. Matsuda, A. Shuto, S., *J. Org. Chem.* **2002**, *67*, 1669-1677.] (800 mg, 2.36 mmol) and PPTS (59 mg, 0.236 mmol) in MeOH (24 mL) was stirred at 55 °C for 4 h. After cooling and addition of sat. aq. $NaHCO_3$, the reaction mixture was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. To a solution of the residue in THF (24 mL) was added TBAF (1.0 M in THF, 2.40 mL, 2.40 mmol) at rt, and stirred for 2 h. The solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1 – 1 : 2) to give alcohol (322 mg, 2.20 mmol, 2 steps 93%, volatile) as a colorless oil. $[\alpha]_D^{21}$ 34.3 (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (1H, d, *J* = 7.4 Hz), 3.93-3.90 (1H, m), 3.40 (3H, s), 3.39 (3H, s), 3.23 (1H, dd, *J* = 12.0, 9.7 Hz), 2.91 (1H, brs), 1.37-1.29 (2H, m), 0.92-0.87 (1H, m), 0.48-0.45 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.56, 63.22, 53.53, 51.76, 17.15, 17.13, 8.02; LR-MS (ESI) *m/z* 169 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{13}H_{13}NO$ 169.0841, found 169.0835 [$(M+Na)^+$];

(1*S*,2*R*)-2-Benzyloxymethyl-1,1-dimethoxymethylcyclopropane. To a solution of (1*S*,2*R*)-1,1-dimethoxymethyl-2-Hydroxymethylcyclopropane (322 mg, 2.20 mmol) in THF and DMF (15mL, THF : DMF = 1 : 1) was added NaH (60% in mineral oil, 176 mg, 4.40 mmol) at 0 °C, and the mixture was stirred for 30 min. After addition of benzylbromide (0.780 mL, 6.60 mmol), the resulting mixture was heated to rt and stired for 23 h. After addition of sat. aq. NH_4Cl, the reaction mixture was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with sat. aq. $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt = 20 : 1 – 10 : 1) to give benzylether (487 mg, 2.06 mmol, 94%) as a colorless oil. $[\alpha]_D^{20}$ 13.6 (*c* 0.99, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (5H, m), 4.56 (1H, d, *J* = 12.0 Hz), 4.51 (1H, d, *J* = 12.0 Hz), 4.17 (1H, d, *J* = 5.7 Hz), 3.58 (1H, dd, *J* = 10.9, 6.9 Hz), 3.46 (1H, dd, *J* = 10.9, 7.4 Hz), 3.33 (3H, s), 3.32 (3H, s), 1.32-1.22 (2H, m), 0.91-0.86 (1H, m), 0.51-0.48 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.40, 128.30, 127.67, 127.48, 103.47, 72.68, 69.87, 51.99, 17.47, 17.68, 7.63; LR-MS (ESI) *m/z* 259 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{14}H_{20}NaO_3$ 259.1310, found 259.1309 [$(M+Na)^+$]; Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53; found: C, 71.02; H, 8.42;

(1*S*,2*R*)-2-Benzyloxymethyl-1-[1-hydroxyprop-2-en-1-yl]cyclopropane. To a solution of

(1S,2R)-2-Benzyloxymethyl-1,1-dimethoxymethylcyclopropane (313 mg, 1.32 mmol) in Hexane (2.6 mL) was added formic acid (10.5 mL), and stirred at rt for 1 h. After cooling to 0 °C, 2 M NaOH aq. was added, and resulting mixture was partitioned between CH_2Cl_2 and 2 M NaOH aq. . The organic layer was separeted and washed with sat. aq. NH_4Cl, sat. aq. $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated in reduced pressure. To a solution of the residue in THF (13 mL) was added vinyl magnesium chloride (1.46 M in THF, 1.81 mL, 2.64 mmol) at –78 °C and stirred for 1 h. After addition of sat. aq. NH_4Cl, the solvent concentrated in reduced pressure. The residue was partitioned between AcOEt and sat. aq. NH_4Cl. The organic layer was separeted and washed with brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by Flash silica gel column chromatography (hexane : AcOEt = 30 : 1 – 4 : 1) to give allylalcohol **A**(127 mg, 0.582 mmol, 2 steps 44%, major diastereomer) as a colorless oil, and allylalcohol **B** (87 mg, 2 steps 0.399 mmol, 30%, minor diastereomer) as a colorless oil.

major diastereomer, **A**:

: $[\alpha]_D^{20}$ -23.3 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (5H, m, aromatic), 6.02 (1H, ddd, *J* = 17.2, 10.4, 5.4 Hz, OCHC<u>H</u>=CH_2), 5.27 (1H, d, *J* = 17.2 Hz, OCHCH=C<u>Ha</u>Hb), 5.11 (1H, d, *J* = 10.4 Hz, OCHCH=CHa<u>Hb</u>), 4.52 (1H, d, *J* = 11.8 Hz, benzyl-Ha), 4.48 (1H, d, *J* = 11.8 Hz, benzyl-Hb), 3.94 (1H, brs, OC<u>H</u>CH=CH_2), 3.64 (1H, dd, *J* = 10.4, 6.8 Hz, C<u>Ha</u>HbOBn), 3.41 (1H, dd, *J* = 10.4, 8.6 Hz, CHa<u>Hb</u>OBn), 2.11 (1H, brs, OH), 1.37-1.27 (1H, m, H-1), 1.21-1.12 (1H, m, H-2), 0.90-0.84 (1H, m, H-3a), 0.48-0.43 (1H, m, H-3b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.52, 137.96, 128.35, 127.78, 127.64, 113.84, 72.69, 72.23, 70.18, 22.23, 15.81, 8.38; LR-MS (ESI) *m/z* 241 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{14}H_{18}NaO$ 241.1205, found 241.1204 [$(M+Na)^+$]; Anal. Calcd for $C_{14}H_{18}O_2$ + 0.1 H_2O: C, 76.40; H, 8.33; found: C, 76.36; H, 8.34;

minor diastereomer, **B**:

: $[\alpha]_D^{21}$ 98.5 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (5H, m), 6.01 (1H, ddd, *J* = 17.2, 10.4, 6.0 Hz), 5.32 (1H, dd, *J* = 17.2, 1.4 Hz), 5.13 (1H, dd, *J* = 10.4, 1.4 Hz), 4.58 (1H, d, *J* = 11.8 Hz), 4.54 (1H, d, *J* = 11.8 Hz), 3.99 (1H, dd, *J* = 10.4, 5.4 Hz), 3.84 (1H, brs), 3.68 (1H, dd, *J* = 10.4, 5.4 Hz), 3.21 (1H, dd, *J* = 10.9, 10.4 Hz), 1.41-1.31 (1H, m), 1.23-1.15 (1H, m), 0.89-0.83 (1H, m), 0.32-0.28 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.22, 137.23, 128.44, 127.81, 114.11, 73.26, 73.07, 71.08, 23.04, 14.98, 8.77; LR-MS (ESI) *m/z* 241 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{14}H_{18}NaO$ 241.1205, found 241.1205 [$(M+Na)^+$]; Anal. Calcd for $C_{14}H_{18}O_2$ + 0.1 H_2O: C, 76.40; H, 8.33; found: C, 76.59; H, 8.37;

(1*S*,2*R*)-2-Benzyloxymethyl-1-[1-(2-vinylphenoxy)prop-2-en-1-yl]cyclopropane (13c). To a mixture of (1*S*,2*R*)-2-Benzyloxymethyl-1-[1-hydroxyprop-2-en-1-yl]cyclopropane (diastereomer **A**, 200 mg, 0.916 mmol), 2-vinylphenol (170 mg, 1.41 mmol), trimethylphosphine (1.0 M in THF, 1.20 mL, 1.20 mmol) was added 1, 1'-azobis(*N*, *N*-dimethylformamide) (210 mg, 1.22 mmol) at 0 °C and

the mixture was stirred for 30 min. After addition of sat. aq. NH_4Cl, the solvent concentrated in reduced pressure. The residue was partitioned between CH_2Cl_2 and 2 M NaOH aq. . The organic layer was separeted and washed with sat. aq. NH_4Cl, brine, dried over Na_2SO_4, and concentrated in reduced pressure. The residue was purified by Flash silica gel column chromatography (hexane : AcOEt = 1 : 0 – 49 : 1) to give a diastereomixture of **13c** (90 mg, 0.279 mmol, 30%, 2 steps, dr = 1 : 0.3) as a yellow oil. $[\alpha]_D^{21}$ 25.0 (*c* 1.02, $CHCl_3$, diastereomixture);^{1}H NMR (500 MHz, $CDCl_3$, 3:1 diastereomer mixture) δ 7.47-7.07 (8H, m), 6.98-6.85 (1H, m), 6.77-6.69 (1H, m), 6.08 (1H x 0.75, ddd, *J* = 17.2, 10.9, 5.2 Hz), 5.98 (1H x 0.25, ddd, *J* = 17.2, 10.9, 5.7 Hz), 5.74 (1H x 0.75, d, *J* = 17.8 Hz), 5.73 (1H x 0.25, d, *J* = 17.8 Hz), 5.31-5.15 (2H, m), 4.52 (1H x 0.75, d, *J* = 12.0 Hz), 4.43 (1H x 0.75, d, *J* = 12.0 Hz), 4.38 (1H x 0.25, d, *J* = 11.5 Hz), 4.33 (1H x 0.25, d, *J* = 11.5 Hz), 4.28 (1H x 0.75, m), 4.20 (1H x 0.25, m), 3.63 (1H x 0.75, dd, *J* = 10.4, 6.3 Hz), 3.58 (1H x 0.25, dd, *J* = 10.3, 5.7 Hz), 3.43 (1H x 0.75, dd, *J* = 10.4, 8,0 Hz), 3.29 (1H x 0.25, dd, *J* = 10.3, 6.9 Hz), 1.39-1.26 (2H, m), 0.94-0.87 (1H, m), 0.48-0.45 (1H x 0.75, m), 0.41-0.38 (1H x 0.25, m); ^{13}C NMR (100 MHz, CD_3OD) δ 156.74, 156.61, 139.53, 139.46, 139.41, 139.10, 133.32, 133.24, 129.67, 129.64, 129.39, 129.24, 12 9.12, 128.93, 128.90, 128.75, 128.52, 127.24, 127.19, 122.00. 121.85, 116.38, 116.29, 115.85, 115.75, 114.15, 81.21, 80.87, 73.76, 73.71, 71.05, 70.82, 22.27, 22.07, 17.43, 16.50, 8.97, 8.48; LR-MS (ESI) *m/z* 343 $[(M+Na)^+]$; HR-MS (ESI) calcd for $C_{22}H_{24}NaO_2$ 343.1674, found 343.1671 $[(M+Na)^+]$; Anal. Calcd for $C_{22}H_{24}O_2 + 0.1\ H_2O$: C, 82.00; H, 7.71; found: C, 81.93; H, 7.71;

Preparation of the chromene derivatives (14).

2-Isopropyl-2*H*-Chromene (14a)

To a solution of **13a** (30 mg, 0.148 mmol) in toluene (1.5 mL) was added Grubbs' 2nd cat. (25 mg, 20 mol%) at rt, then refluxed for 2 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **14a** (19 mg, 0.111 μmol, 75%, volatile) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.06 (1H, m), 6.95-6.92 (1H, m), 6.83-6.79 (1H, m), 6.77-6.75 (1H, m), 6.42 (1H, dd, *J* = 10.0, 1.4 Hz), 5.69 (1H, dd, *J* = 10.0, 3.2 Hz), 4.63-4,61 (1H, m), 2.04-1.96 (1H, m), 1.01 (3H, d, *J* = 6.8 Hz), 1.00 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.99, 129.03, 126.35, 124.40, 124.23, 121.95, 120.66, 115.60, 79.94, 33.42, 17.76, 17.69; LR-MS (EI) *m/z* 174 (M^+); HR-MS (EI) calcd for $C_{12}H_{14}O$ 174.1045, found 174.1039 (M^+)

(1*R*,2*R*)-2-*t*-Butyldiphenylsilyloxymethyl-1-(2*H*-chromen-2-yl)cyclopropane (14b). To a solution of a mixture of **13b** and **13b'** (37 mg, 79.8 μmol, **13b** : **13b'** = 2 : 1, **13b**; dr = 1 : 1) in toluerne (0.80 mL) was added Grubbs' 2nd cat.(14 mg, 20 mol%) at rt, then refluxed for 4 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **14b** (23 mg, 53.2 μmol, quant., dr = 1 : 1). $[\alpha]_D^{22}$ -27.8 (*c* 0.78,

$CHCl_3$, 1:1 diastereomixture); ^1H NMR (400 MHz, $CDCl_3$, 1:1 diasteromixture) δ 7.67-7.64 (4H, m), 7.42-7.31 (6H, m), 7.11-7.05 (1H, m), 6.98-6.94 (1H, m), 6.86-6.75 (2H, m), 6.41-6.38 (1H, m), 5.76 (1H x 0.5, dd, *J* = 10.0, 3.6 Hz), 5.67 (1H x 0.5, dd, *J* = 10.0, 3.6 Hz), 4.36-4.32 (1H x 0.5, m), 4.26-4.23 (1H x 0.5, m), 3.70 (1H x 0.5, *J* = 10.9, 5.4 Hz), 3.62 (1H x 0.5, *J* = 10.9, 5.9 Hz), 3.52 (1H x 0.5, *J* = 10.9, 6.3 Hz), 3.39 (1H x 0.5, *J* = 10.9, 6.8 Hz), 1.20-1.00 (11H, m), 0.69-0.64 (1H x 0.5, m), 0.54-0.49 (2H x 0.5, m), 0.45-0.40 (1H x 0.5, m); ^{13}C NMR (125 MHz, $CDCl_3$); 153.60, 153.58, 135.62, 135.58, 133.90, 133.87, 133.78, 133.74, 129.59, 129.52, 129.11, 129.10, 127.67, 127.61, 127.57, 126.40, 126.36, 124.93, 124.35, 124.03, 121.85, 121.72, 120.91, 120.77, 115.99, 115.90, 78.60, 77.99, 66.34, 66.32, 26.84 , 21.46, 21.18, 19.22, 18.87, 17.69, 8.29, 6.20; LR-MS (ESI) *m/z* 440 (M^+, 33), 439 [$(M-H)^+$, 100]; HR-MS (ESI) calcd for $C_{29}H_{31}O_2Si$ 439.2089, found 439.2099 [$(M-H)^+$]; Anal. Calcd for $C_{29}H_{32}O_2Si + 0.5\ H_2O$: C, 77.46; H, 7.40; found: C, 77.41; H, 7.30;

(1*R*,2*R*)-2-benzyloxymethyl-1-(2*H*-chromen-2-yl)cyclopropane (14c). To a solution of **13c** (20 mg, 62.4 μmol, dr = 1 : 0.3) in toluene (1.5 mL) was added Grubbs 2nd cat. (25 mg, 20 mol%) at rt and the mixture was refluxed for 7 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **14c** (17 mg, 56.8 μmol, 91%, dr = 1 : 0.6) as a colorless oil.

major diastereomer

^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (5H, m), 7.11-7.07 (1H, m), 6.97-6.96 (1H, m), 6.86-6.83 (1H, m), 6.80-6.79 (1H, m), 6.38 (1H, dd, *J* = 9.7, 1.1 Hz), 5.93 (1H, dd, *J* = 9.7, 3.4 Hz), 4.55 (1H, d, *J* = 12.0 Hz), 4.48 (1H, d, *J* = 12.0 Hz), 4.47-4.40 (1H, m), 3.74 (1H, *J* = 10.3, 5.7 Hz), 3.30 (1H, *J* = 10.3, 8.6 Hz), 1.45-1.33 (2H, m), 0.94-0.90 (1H, m), 0.57-0.54 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$); 153.50, 138.11, 128.99, 128.42, 127.78, 127.69, 126.38, 123.37, 121.98, 120.96, 116.01, 76.21, 72.93, 70.32, 20.62, 15.35, 8.79

minor diastereomer

^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.27 (5H, m), 7.11-7.08 (1H, m), 6.98-6.96 (1H, m), 6.86-6.83 (1H, m), 6.80-6.78 (1H, m), 6.42 (1H, dd, *J* = 9.7, 1.1 Hz), 5.78 (1H, dd, *J* = 9.7, 2.9 Hz), 4.60 (2H, s), 4.41-4.38 (1H, m), 3.85 (1H, *J* = 10.3, 5.7 Hz), 3.50 (1H, *J* = 10.3, 7.4 Hz), 1.49-1.42 (1H, m), 1.40-1.33 (1H, m), 0.94-0.88 (1H, m), 0.37-0.34 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$); 153.50, 138.55, 129.10, 128.36, 127.69, 127.51, 126.43, 125.40, 124.19, 121.83, 120.97, 116.03, 75.89, 72.76, 69.73, 20.41, 15.06, 7.62

: $[\alpha]_D^{21}$ -42.1 (*c* 1.26, $CHCl_3$, 1 : 0.6 diastereomixture) ;LR-MS (ESI) *m/z* 292 (M^+, 22), 291 [$(M-H)^+$, 100]; HR-MS (ESI) calcd for $C_{20}H_{19}O_2$ 291.1380, found 291.1392 [$(M-H)^+$];

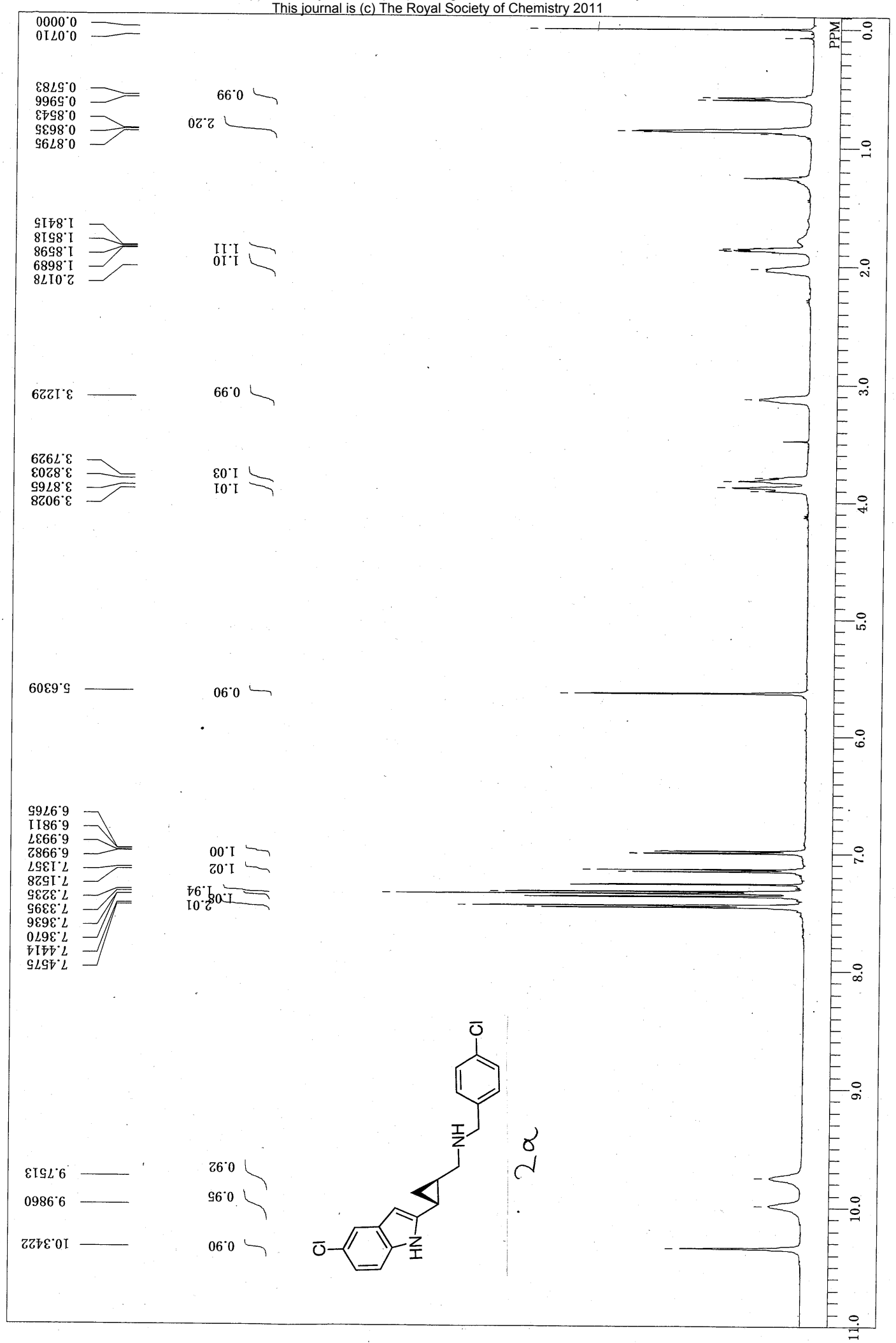
Preparation of the benzofuran derivatives (15).

2-isopropylbenzofurane (15a)[David, M.; Sauleau, J.; Sauleau, A., *Tetrahedron*, **1988**, *44*,

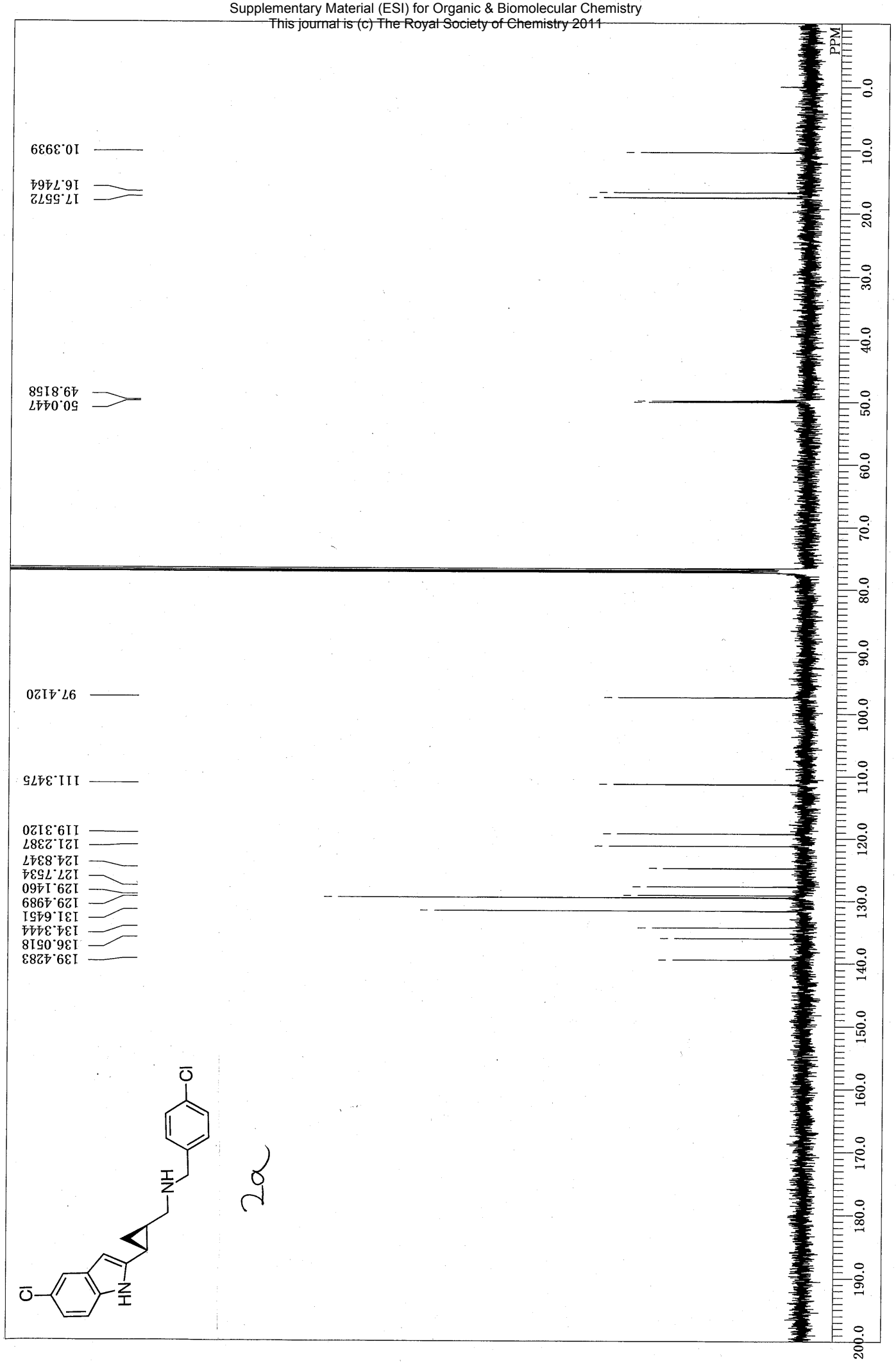
3587-3594.]. To a solution of **13a** (30 mg, 0.148 mmol) in xylene (1.5 mL) was added $Ru(CO)HCl(PPh_3)_3$ (28 mg, 20 mol%) at rt and the mixture was refluxed for 13 h. After cooling, the solvent was concentrated in reduced pressure. To a solution of the residue in toluene (1.5 mL) was added Grubbs' 2nd cat. (25 mg, 20 mol%) and the mixture was heated to 80 °C for 2 h. The solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **15a** (16 mg, 97.3 μmol, 2 steps 66%, volatile) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (1H, m), 7.41 (1H, d, J = 7.7 Hz), 7.22-7.15 (2H, m), 6.36 (1H, s), 3.11-3.04 (1H, m), 1.35 (6H, d, J = 6.8 Hz); LR-MS (EI) *m/z* 160 (M^+)

(1*R*,2*R*)-1-(benzofuran-2-yl)-2-*t*-Butyldiphenylsilyloxymethylcyclopropane (15b). To a solution of a mixture of **13b** and **13b'** (30 mg, 64.0 μmol, **13b** : **13b'** = 2 : 1, **13b**; dr = 1 : 1) in xylene (0.65 mL) was added $Ru(CO)HCl(PPh_3)_3$ (12 mg, 20 mol%) at rt and the mixture was refluxed for 14 h. After cooling, to the mixture Grubbs' 2nd cat. (11 mg, 20 mol%) was added and heated to 80 °C for 2 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **15b** (18 mg, 42.7 μmol, 2 steps quant.) as a colorless oil. $[\alpha]_D^{23}$ -86.1 (*c* 1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.68 (4H, m), 7.45-7.35 (8H, m), 7.19-7.14 (2H, m), 6.32 (1H, s), 3.79 (1H, dd, J = 10.3, 5.2 Hz), 3.69 (1H, dd, J = 10.3, 5.7 Hz), 1.95-1.92 (1H, m), 1.66-1.62 (1H, m), 1.13-1.10 (1H, m), 1.06 (9H, s), 0.98-0.94 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.65, 154.19, 135.62, 135.60, 133.71, 133.65, 129.64, 129.12, 127.66, 122.83, 122.42, 119.85, 110.57, 100.36, 65.28, 26.84, 22.99, 19.26, 14.29, 11.54; LR-MS (ESI) *m/z* 449 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{28}H_{30}NaO_2Si$ 449.1913, found 449.1914 [$(M+Na)^+$]; Anal. Calcd for $C_{28}H_{30}OSi$: C, 78.83; H, 7.09; found: C, 78.53; H, 7.28;

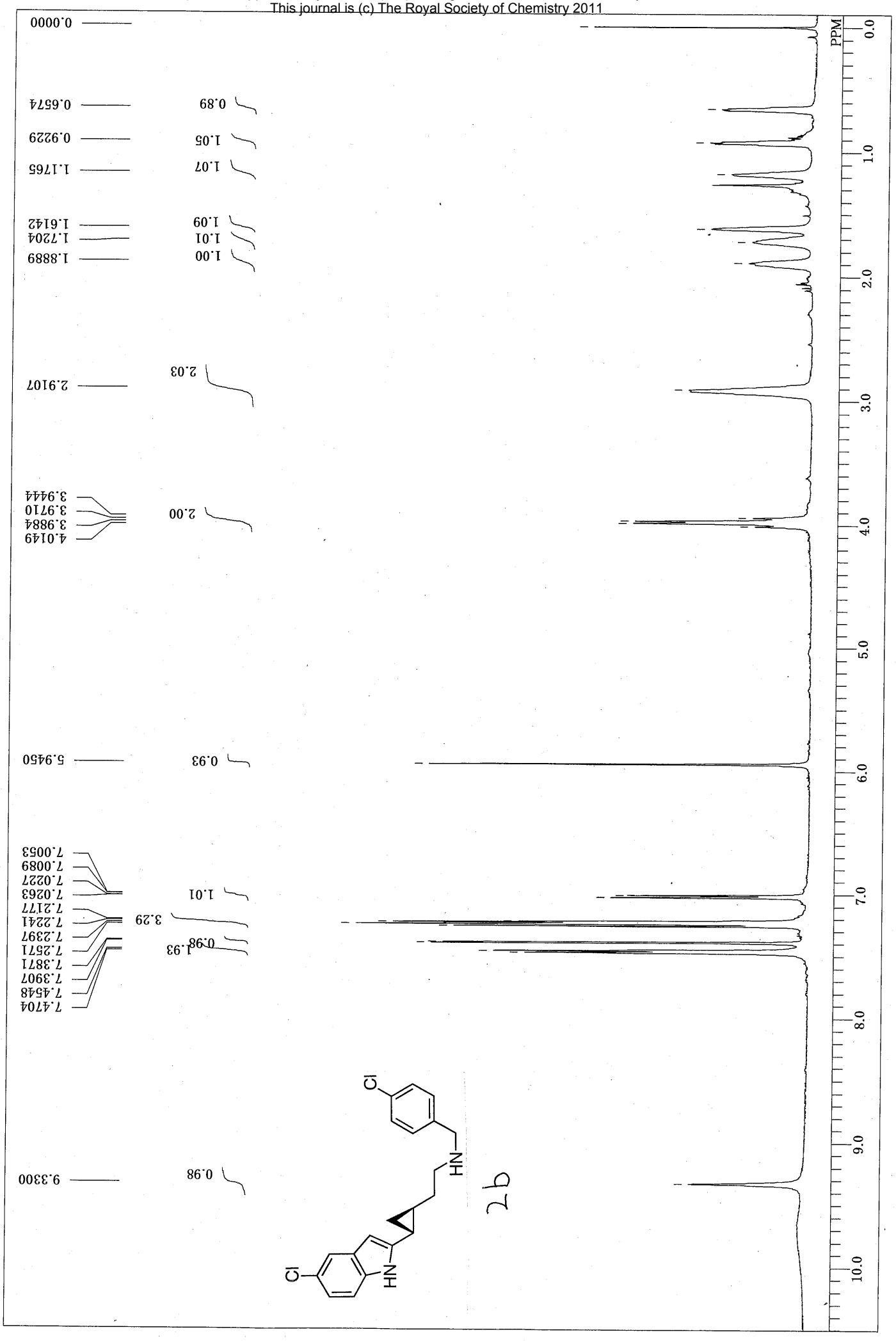
(1*S*,2*R*)-1-(Benzofuran-2-yl)-2-benzyloxymethylcyclopropane (15c). To a solution of **13c** (20 mg, 62.4 μmol, dr = 1 : 0.3) in xylene (0.62 mL) was added $Ru(CO)HCl(PPh_3)_3$ (12 mg, 20 mol%) at rt and the mixture was refluxed for 3 h. After cooling, to the mixture Grubbs' 2nd cat. (11 mg, 20 mol%) was added and the mixture was heated to 80 °C for 3 h. After cooling, the solvent was concentrated in reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **15c** (9 mg, 32.3 μmol, 2steps 52%) as a colorless oil. $[\alpha]_D^{21}$ -5.2 (*c* 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.46 (1H, m), 7.41-7.39 (1H, m), 7.24-7.07 (7H, m), 6.38 (1H, s), 4.41 (1H, d, J = 12.0 Hz), 4.31 (1H, d, J = 12.0 Hz), 3.48 (1H, dd, J = 10.3, 6.3 Hz), 3.32 (1H, dd, J = 10.3, 8.6 Hz), 2.31-2.26 (1H, m), 1.66-1.62 (1H, m), 1.26-1.22 (1H, m), 0.98-0.95 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.06, 154.65, 138.17, 128.79, 128.17, 127.48, 127.36, 123.22, 122.46, 120.17, 110.78, 103.32, 72.74, 69.63, 19.29, 14.09, 9.12; LR-MS (ESI) *m/z* 301 [$(M+Na)^+$]; HR-MS (ESI) calcd for $C_{19}H_{18}O_2Na$ 301.1205, found 301.1199 [$(M+Na)^+$]; Anal. Calcd for $C_{19}H_{18}O_2$ + 0.6 H_2O: C, 78.92; H, 6.69; found: C, 78.83; H, 6.50;



07KT3-91-1 (500,CD3Cl)

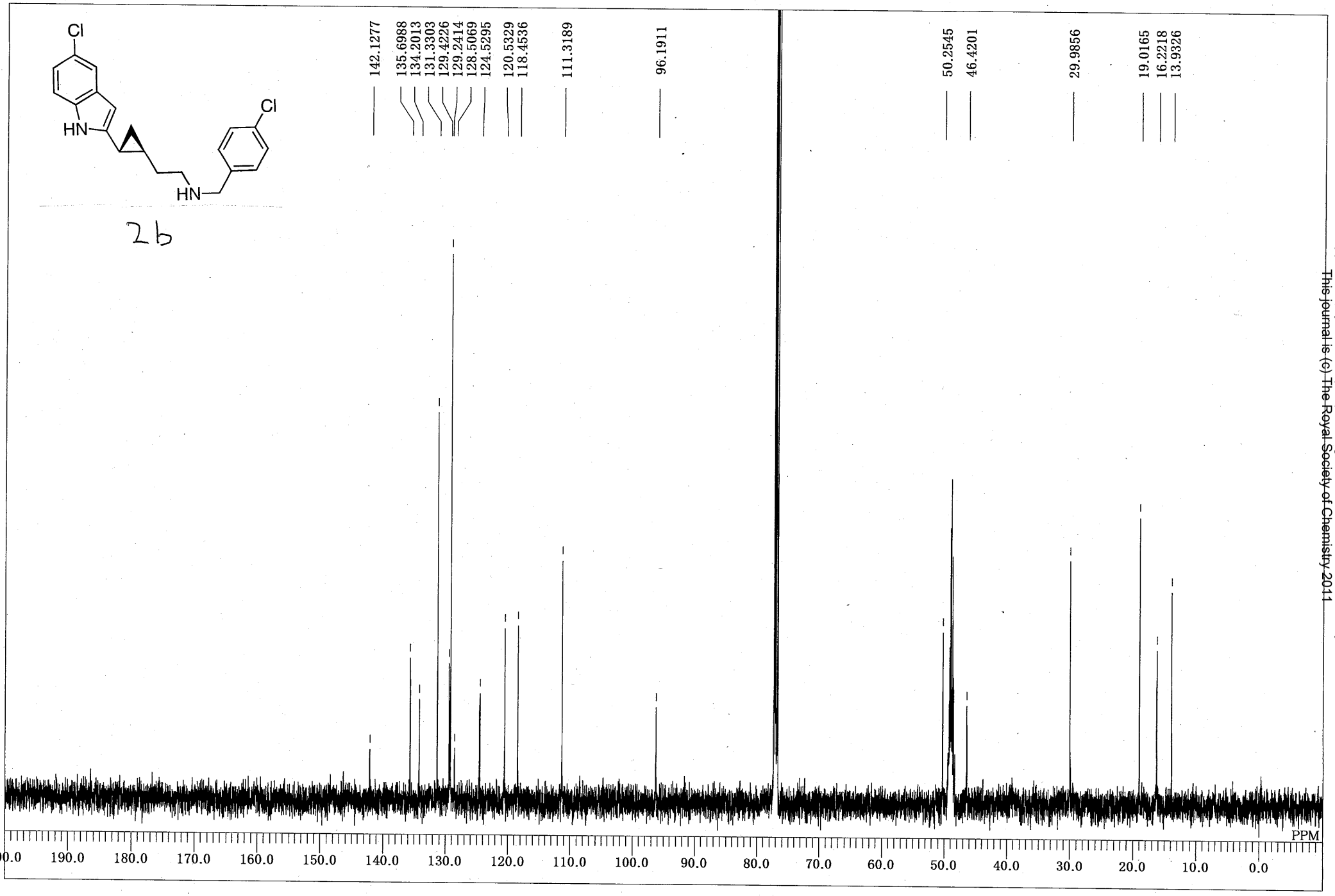


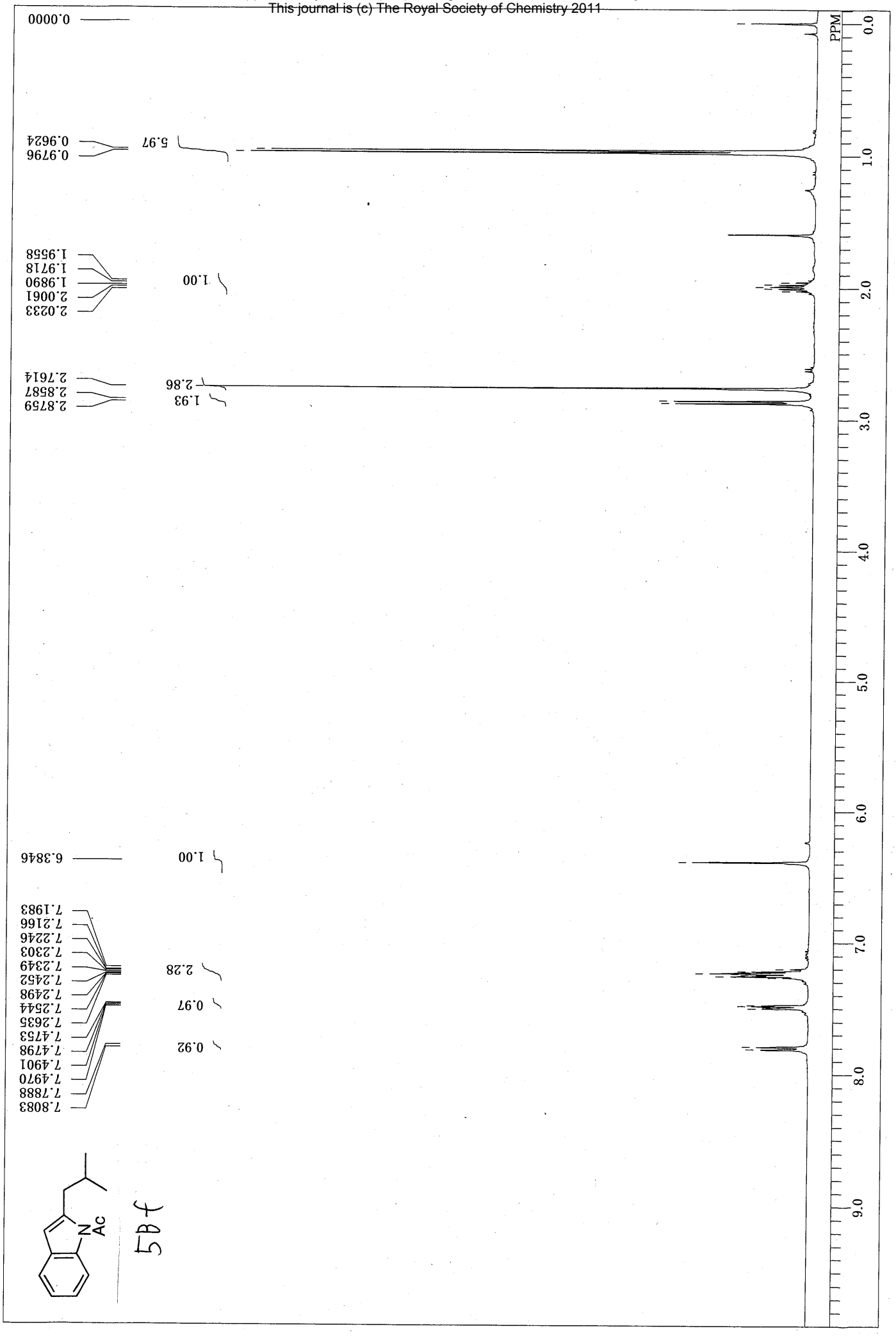
07KT3-91-1C (500,CDCl3)



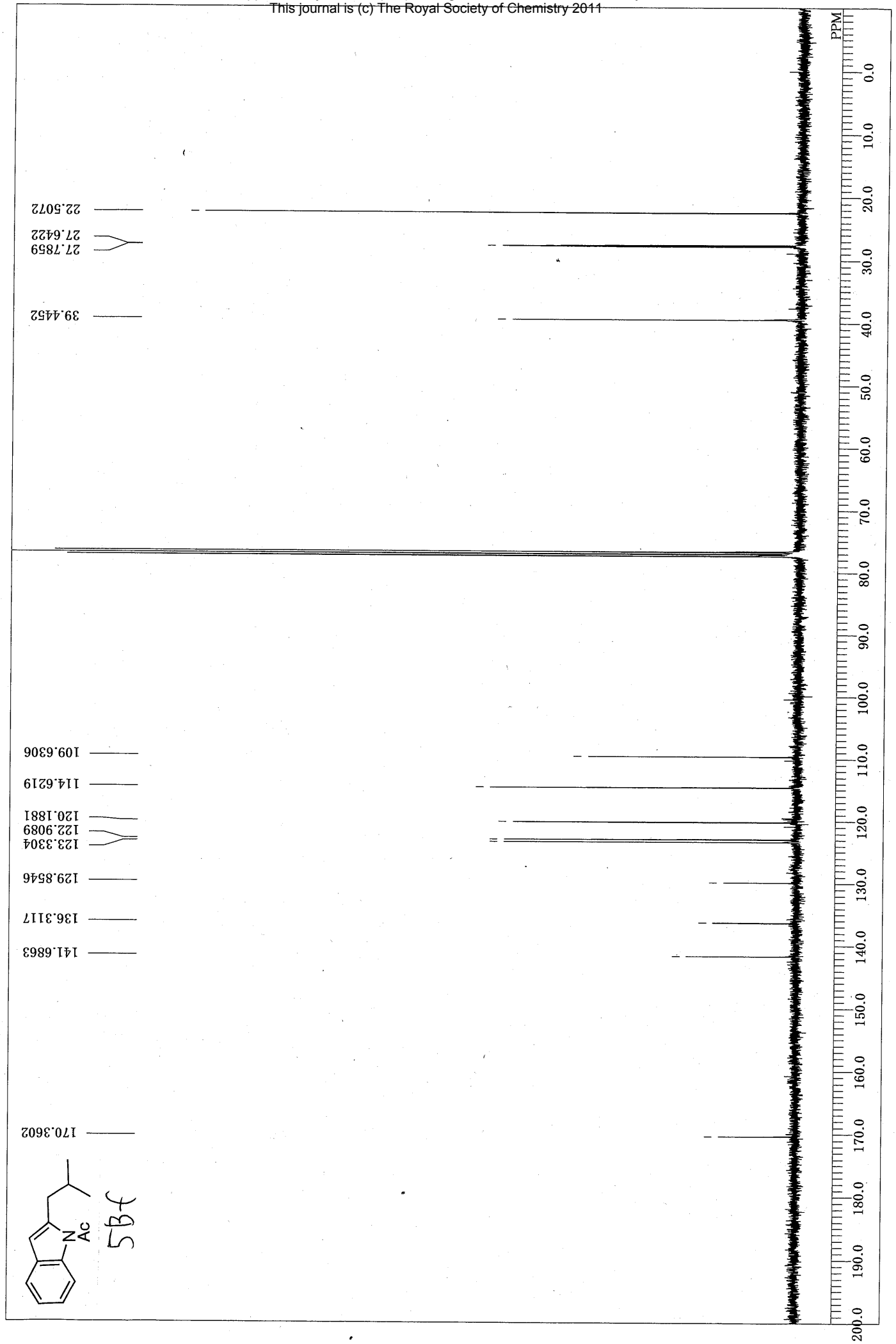
07KT4-6-1 CDCl3 (500,CDCl3,t50)

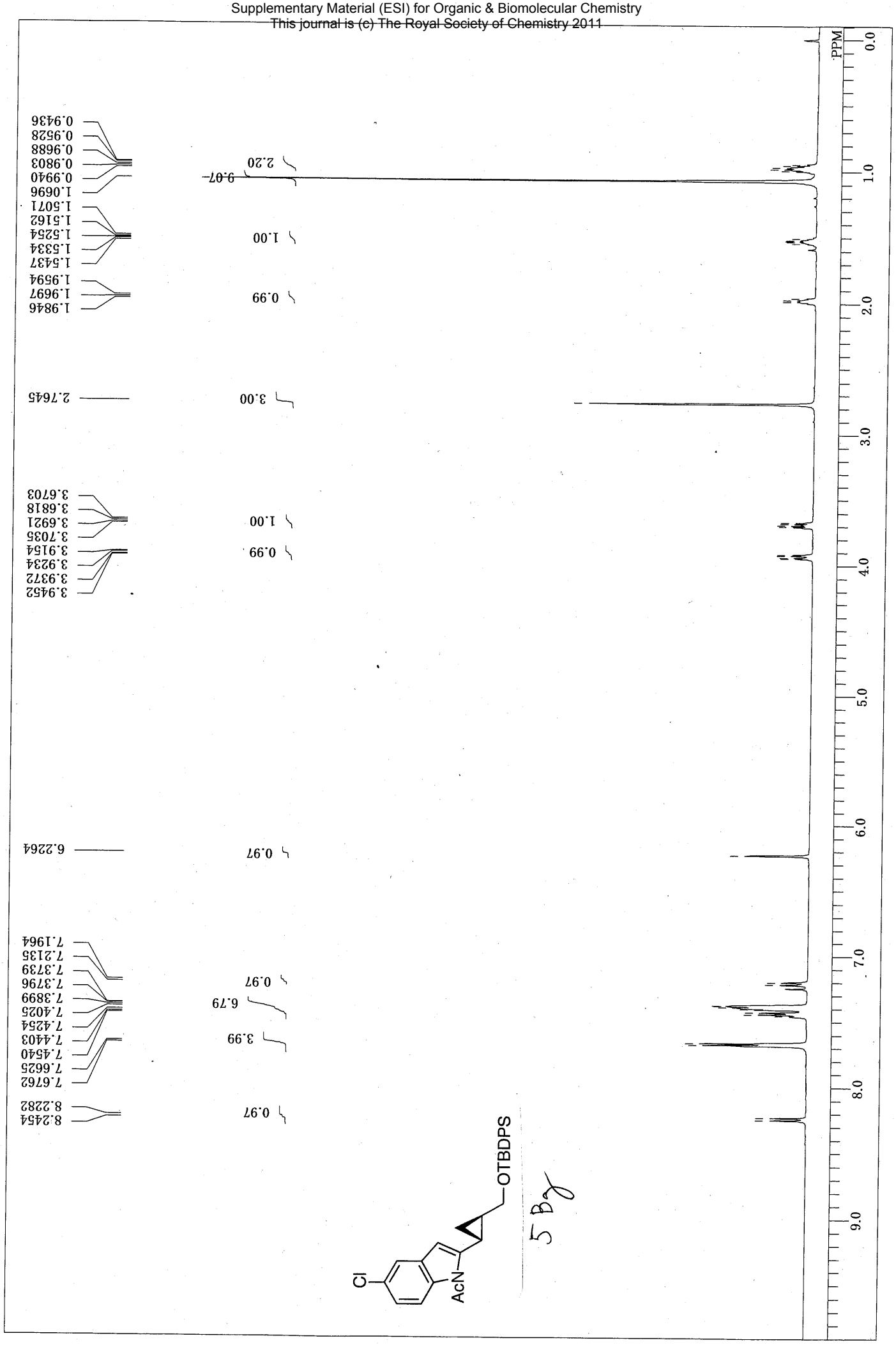
07KT4-6-1 C(500,CDCl3CD3OD)





07KT5-54-1(400,CDCl3)





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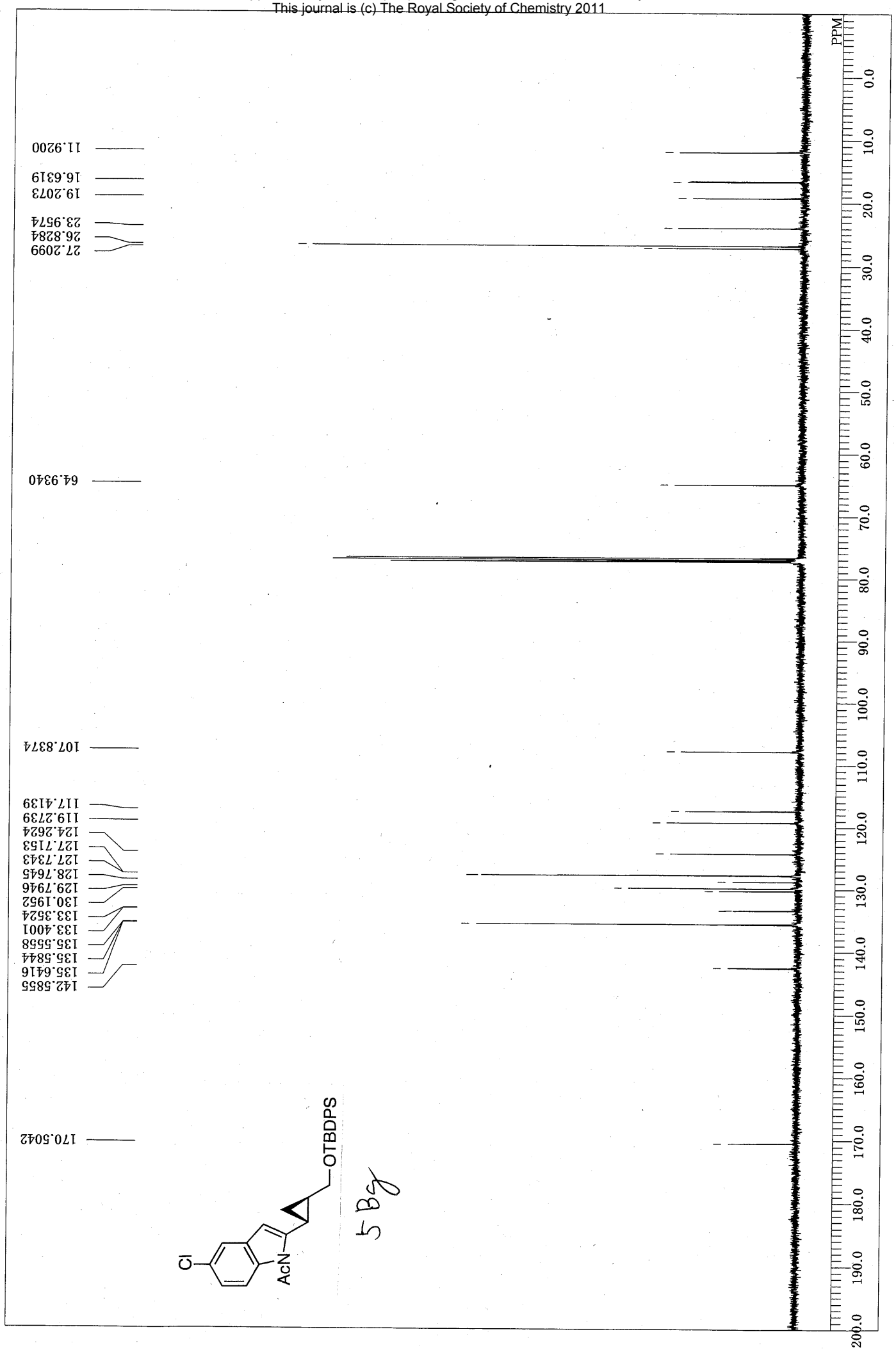

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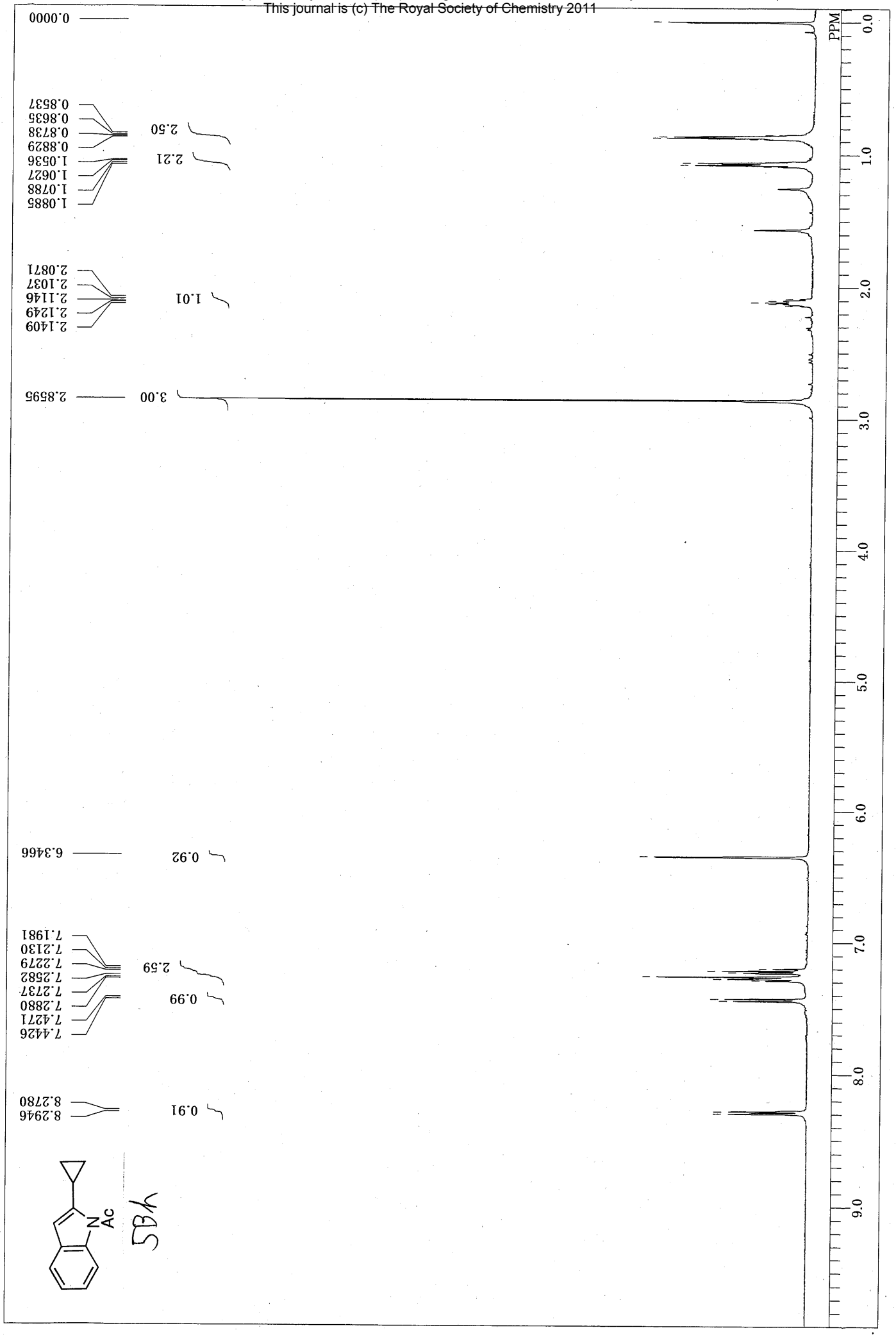
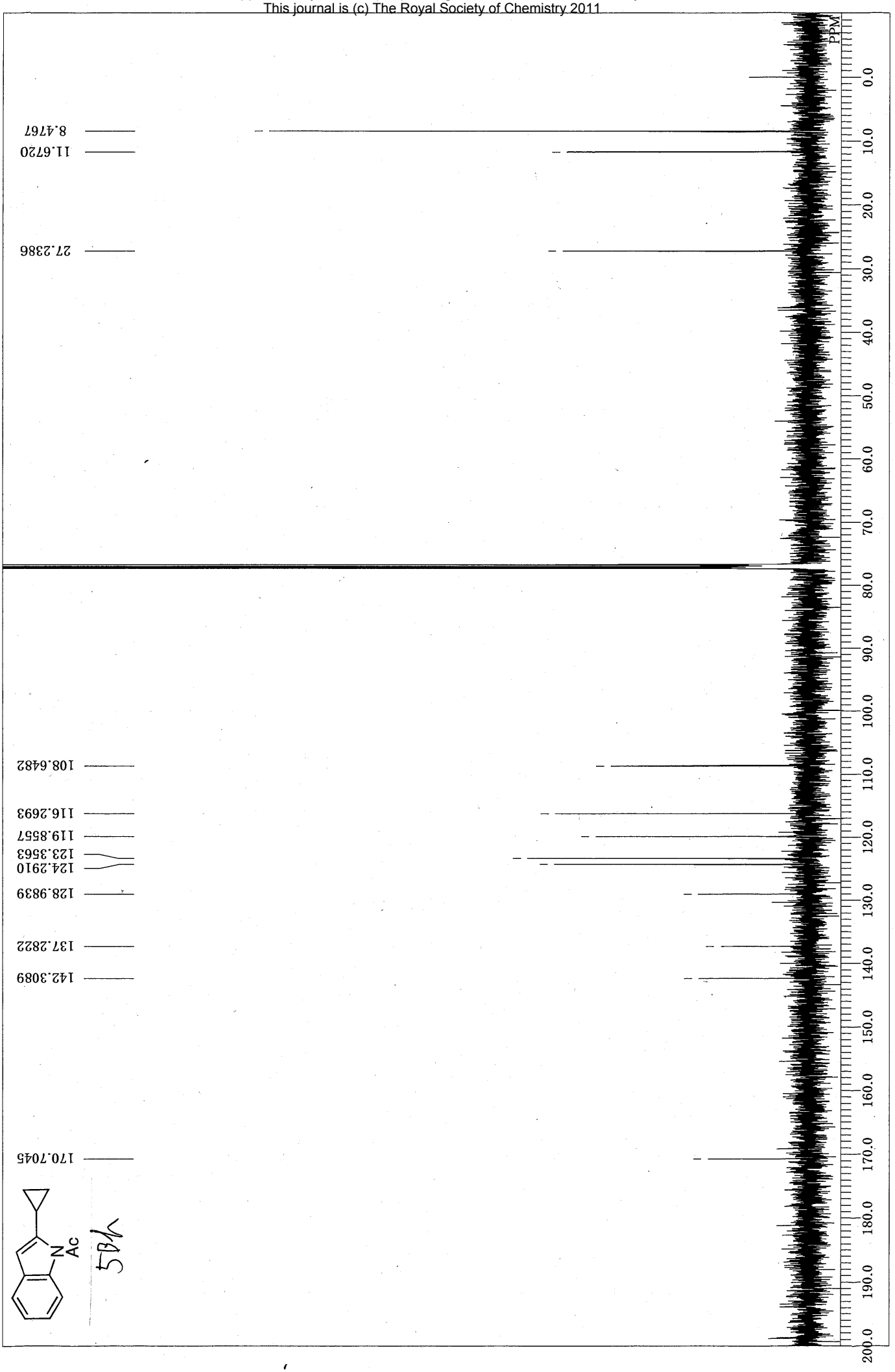


07KT3-86-1(500,CDCl3)



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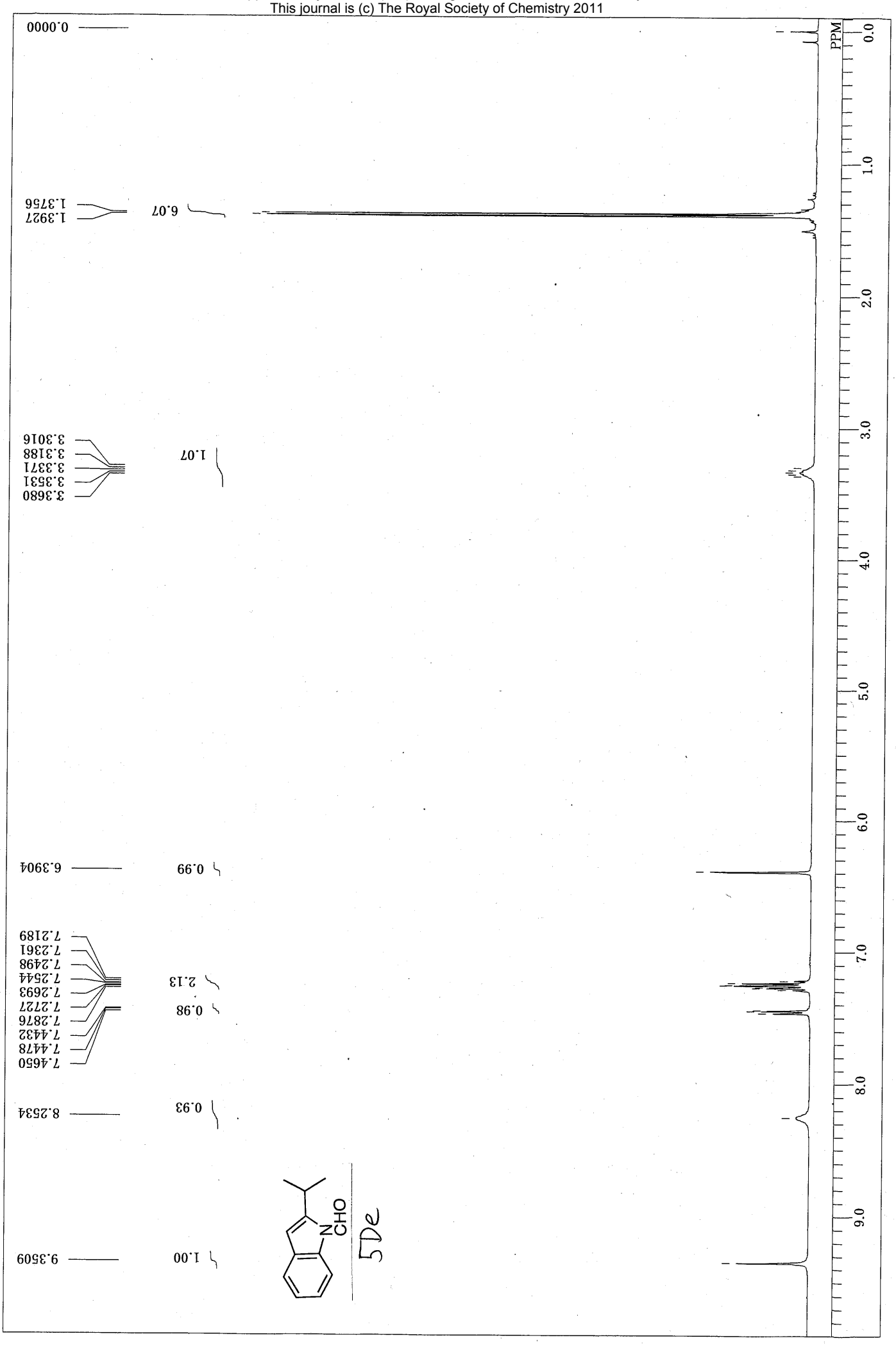
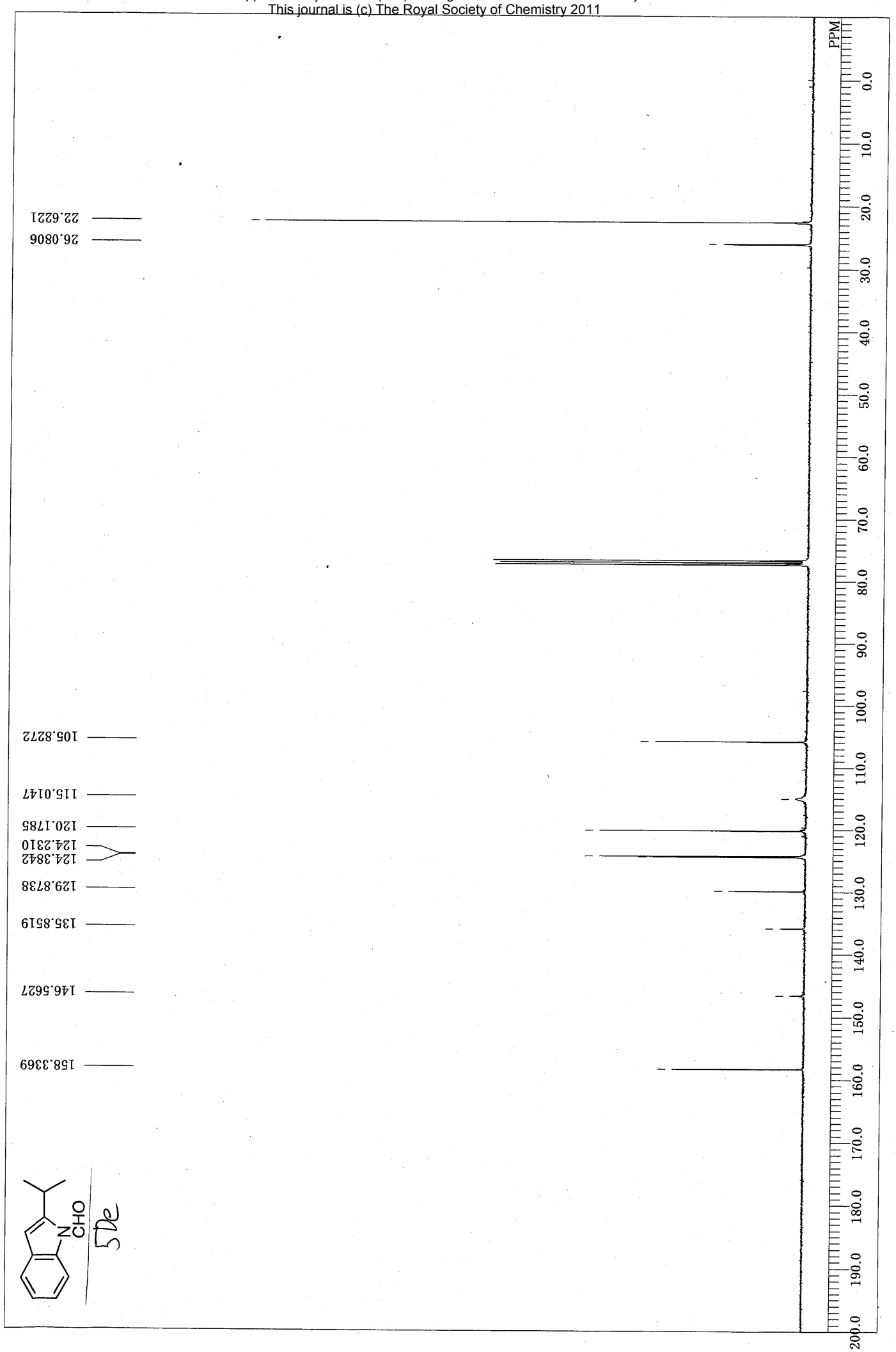


07KT5-55-2(400,CDCl3,t55)



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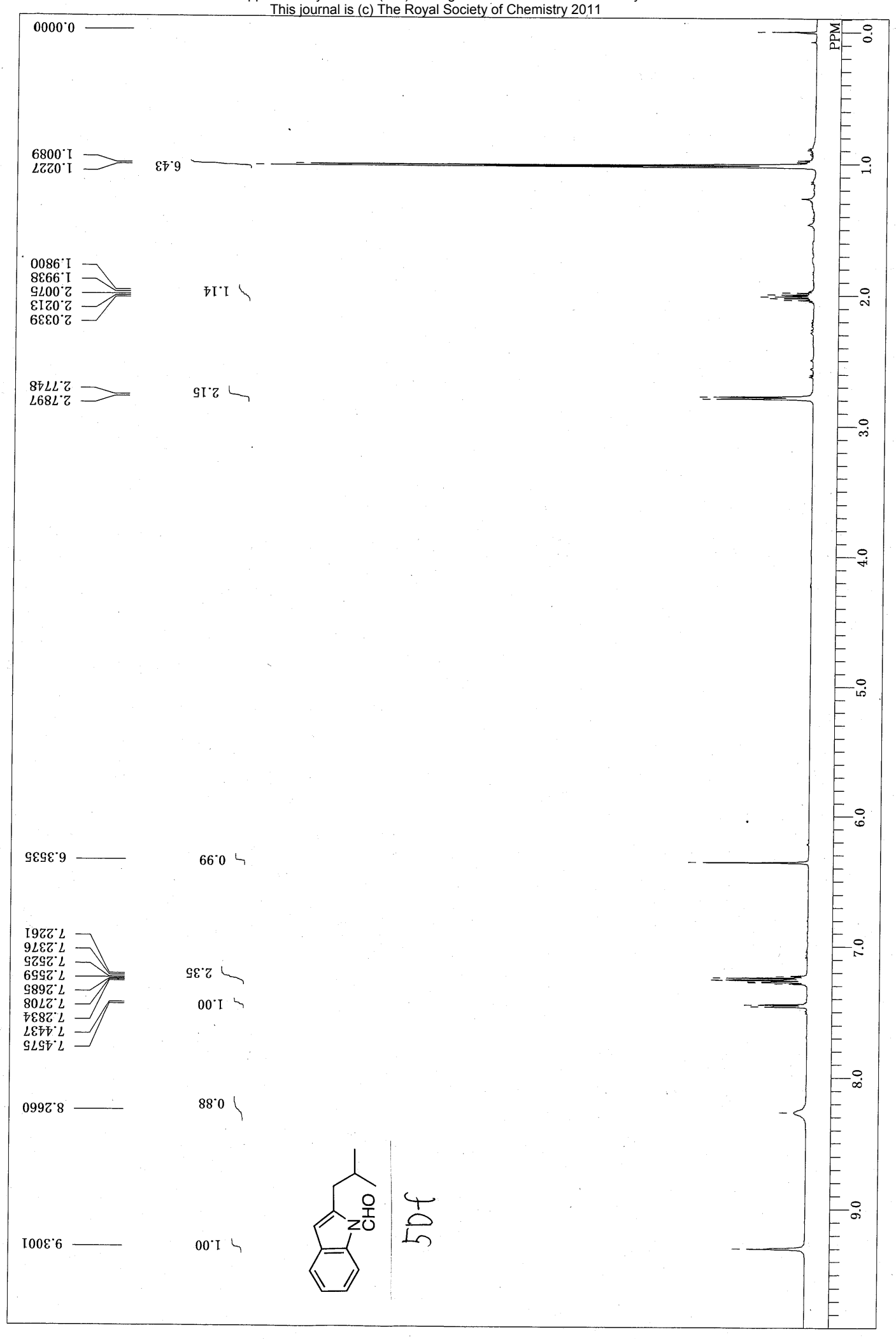
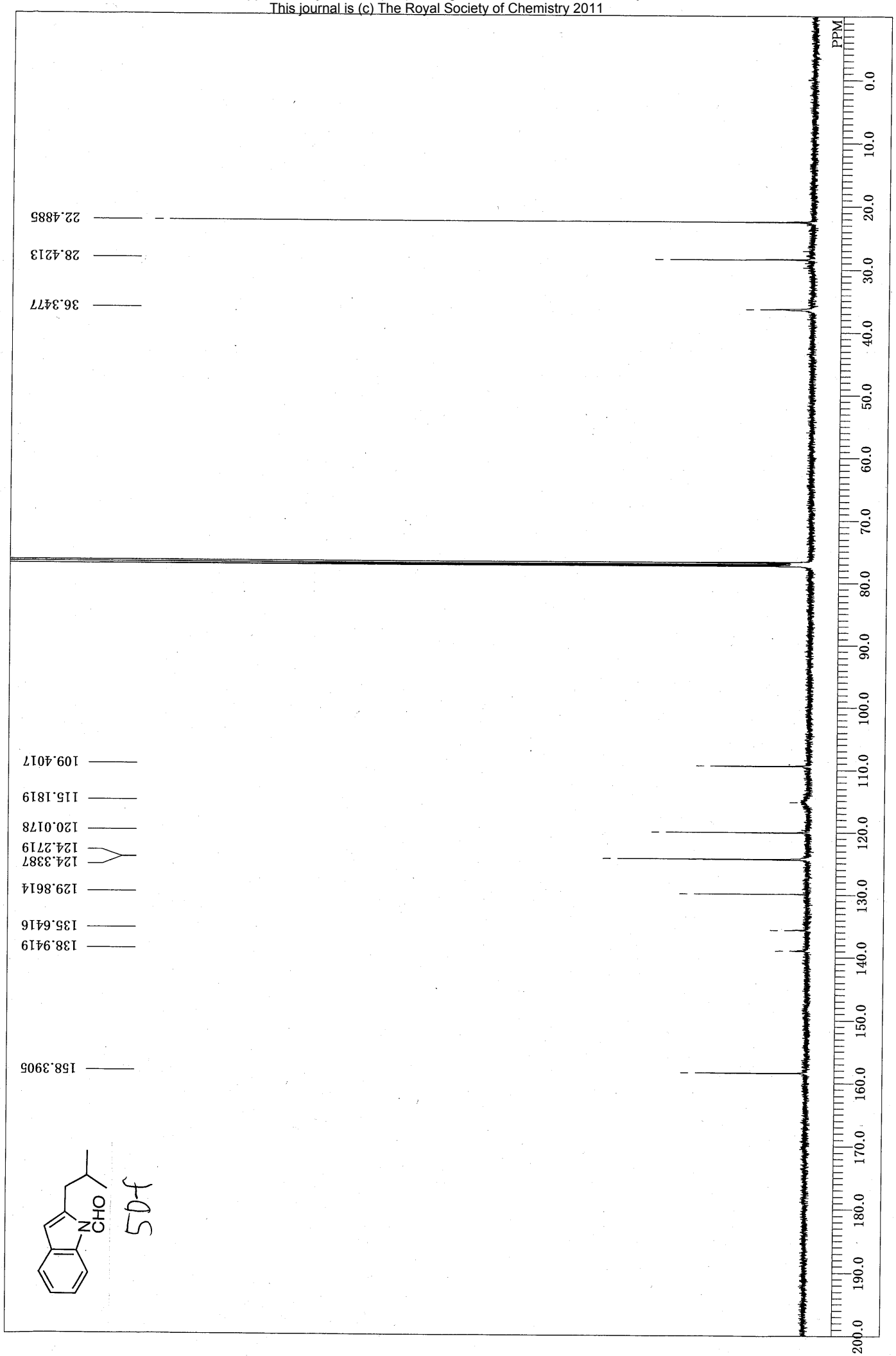
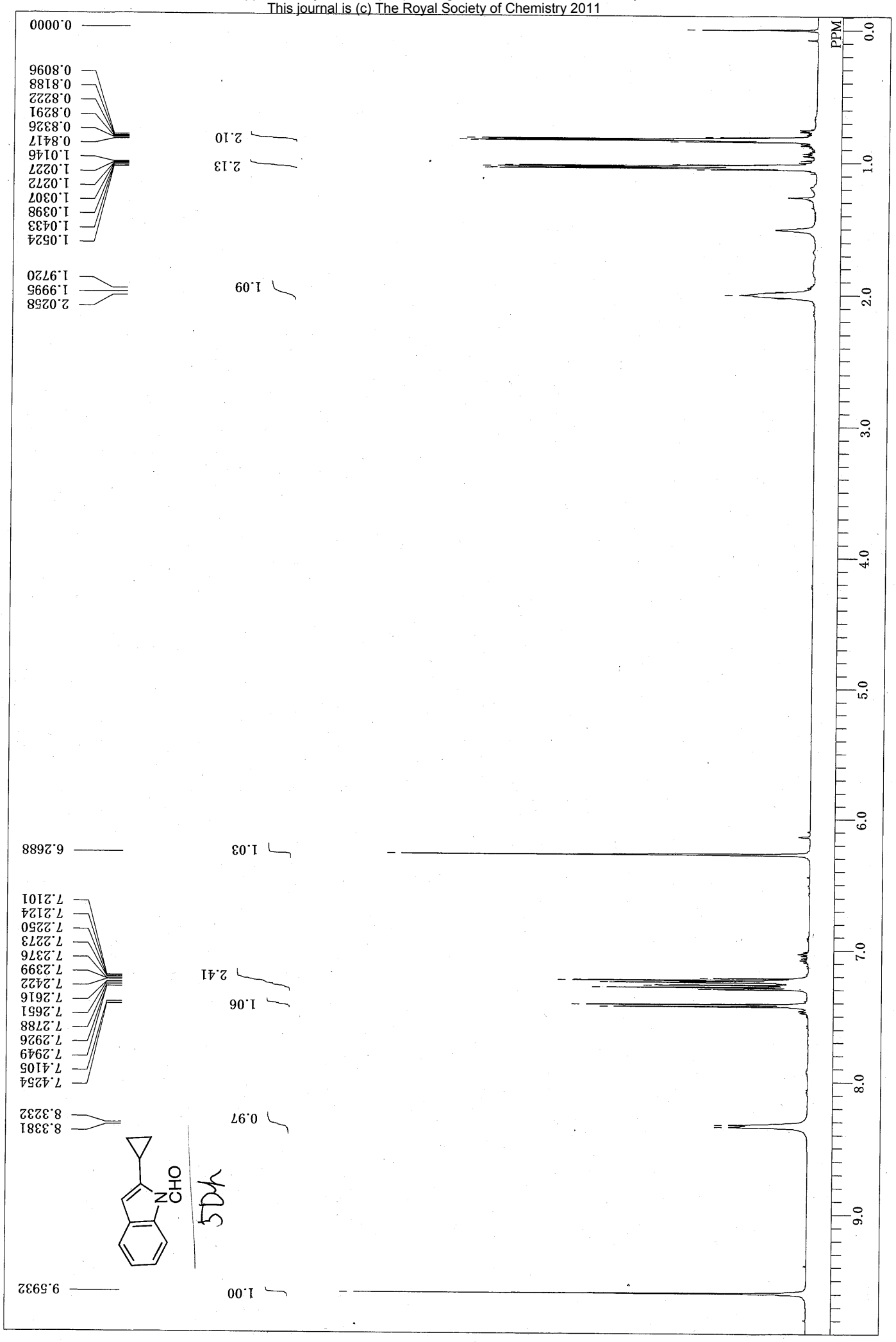


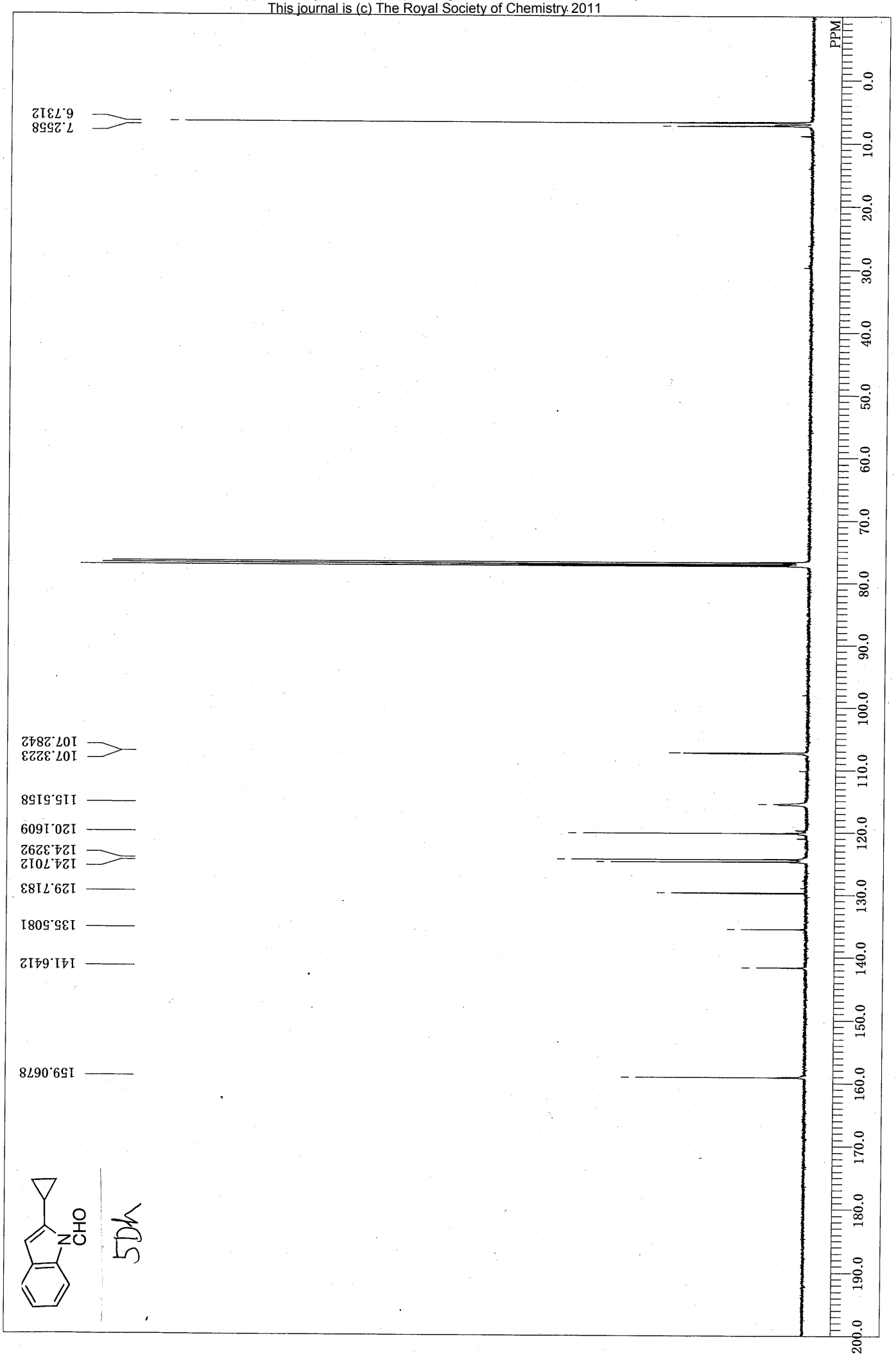
07KT4-17-1(500,CDCl3,t60)



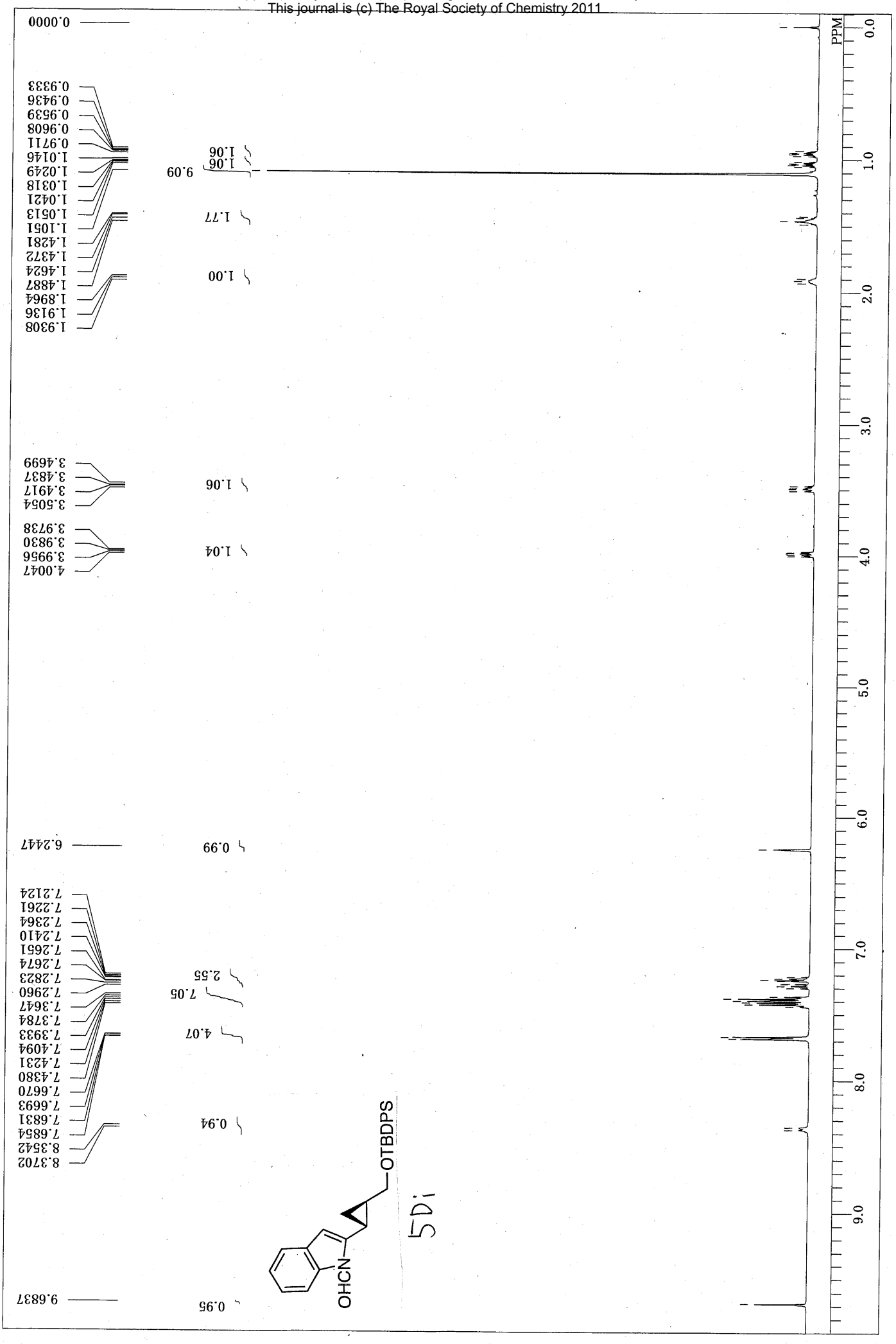
07KT4-17-1C(500,CDCl3,t50)



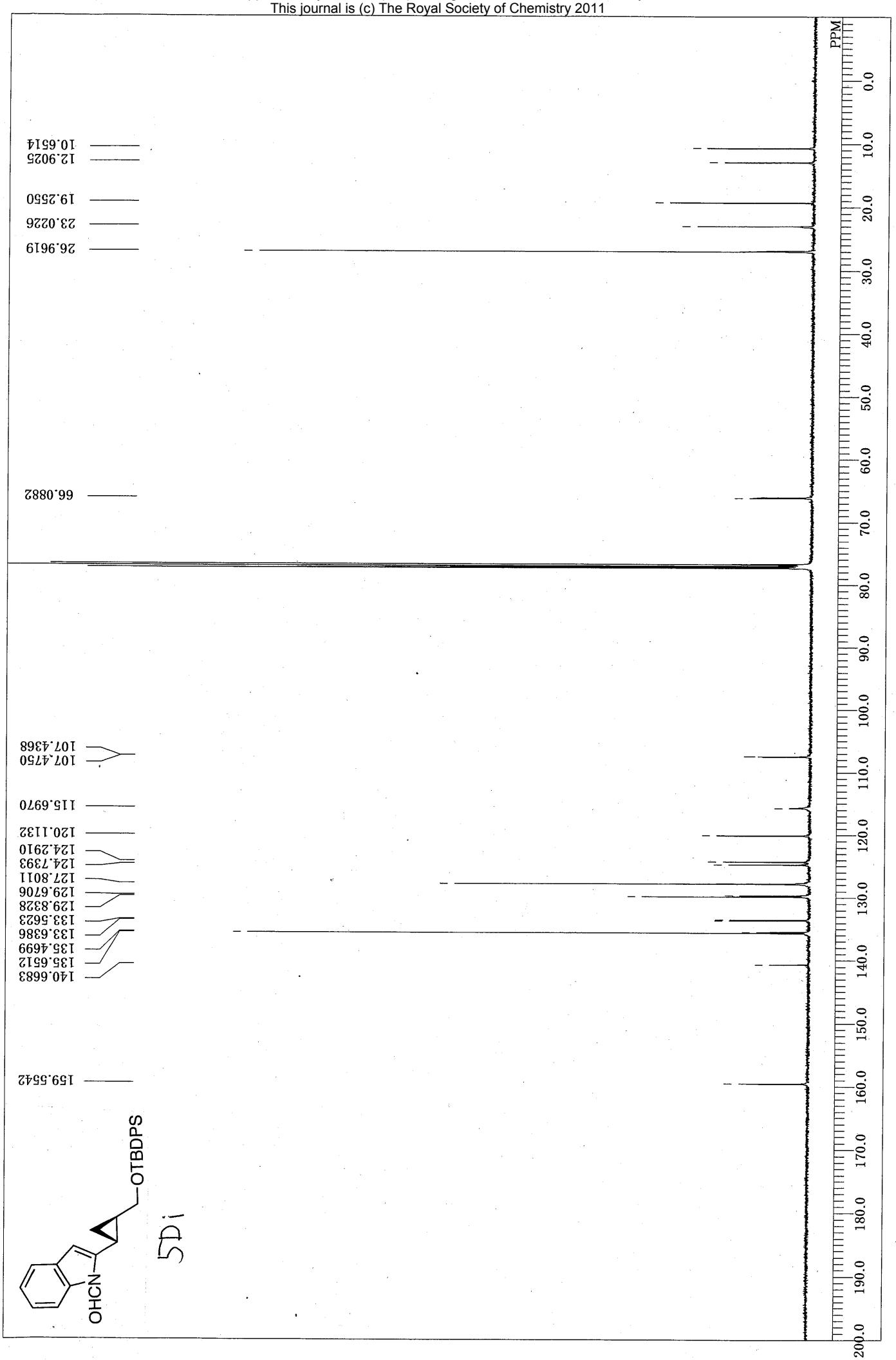
07KT5-56-1(500,CDCl3,t55)



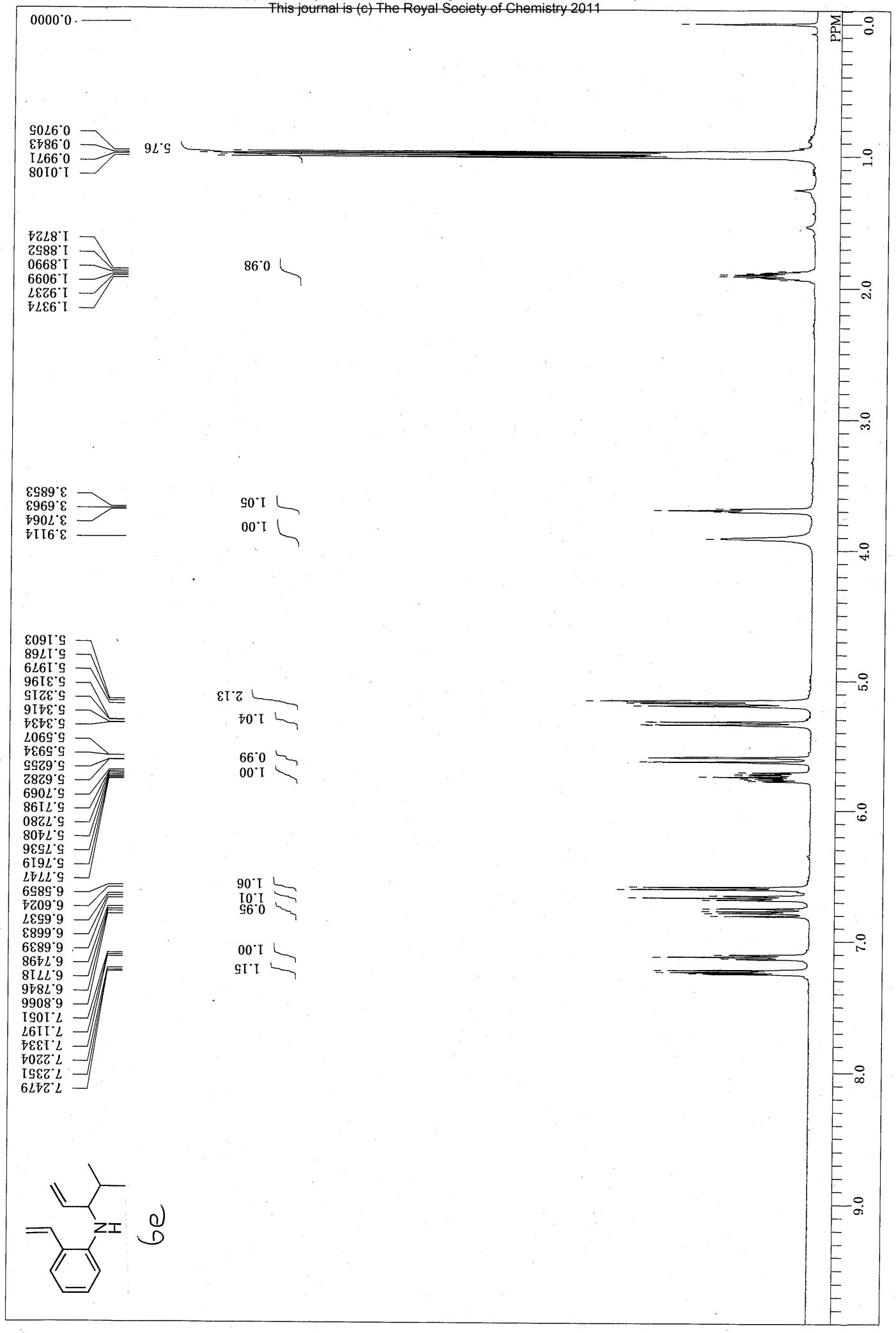
07KT5-56-1C(500,CDCl3,t55)

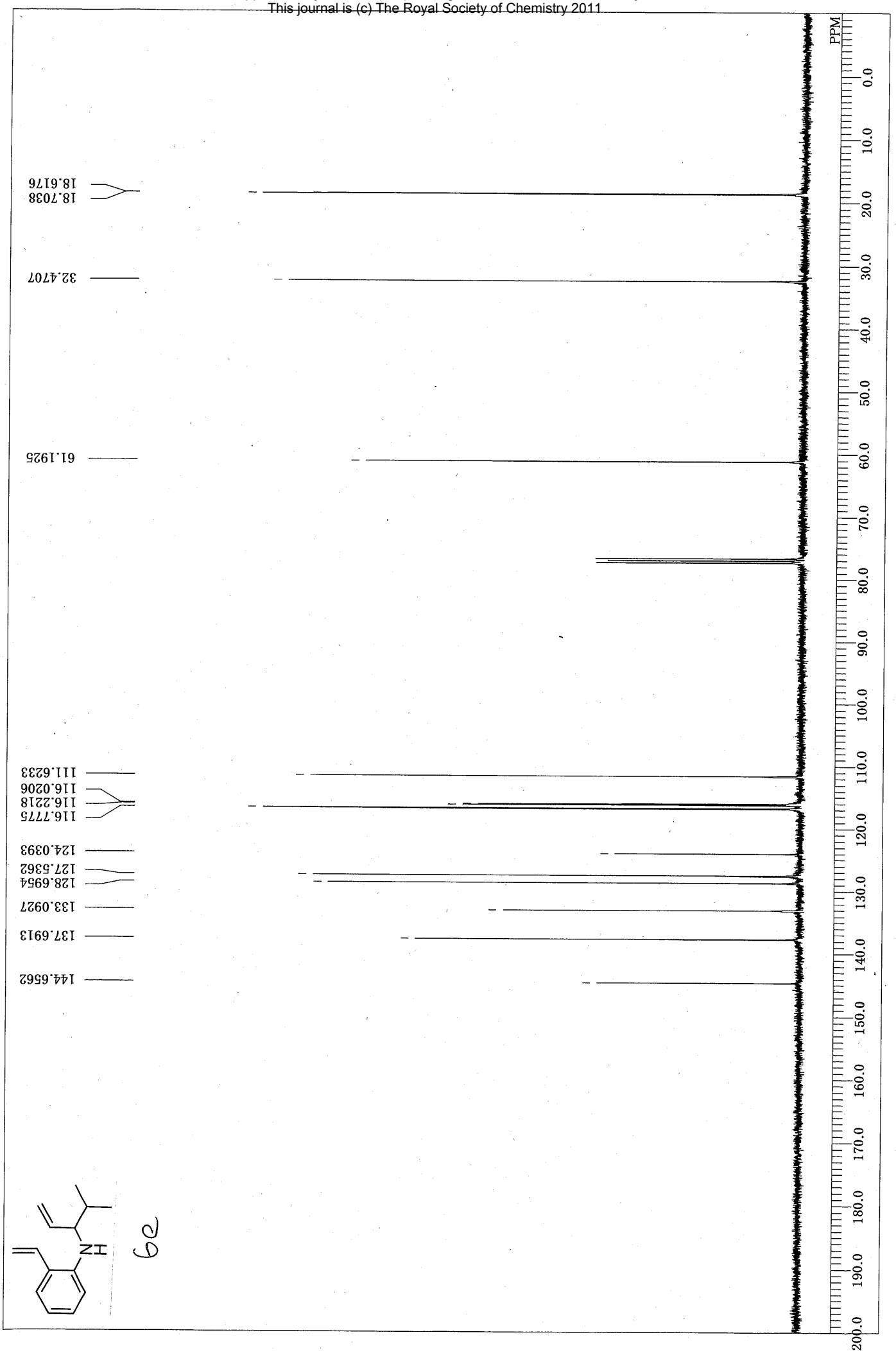


07KT5-92-1a(500,CDCl3,t55)

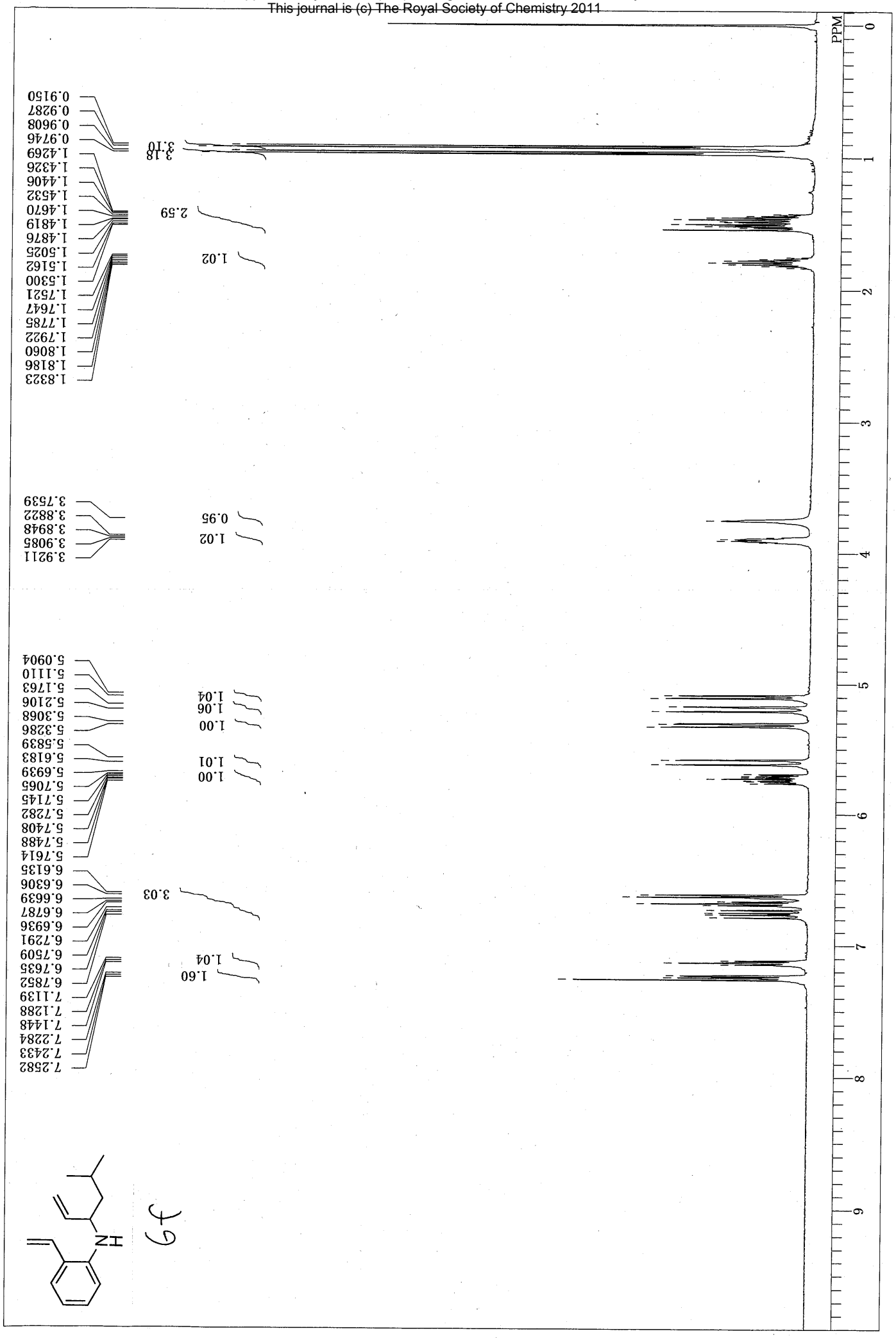


07KT5-92-1a C(500,CDCl3,t55)



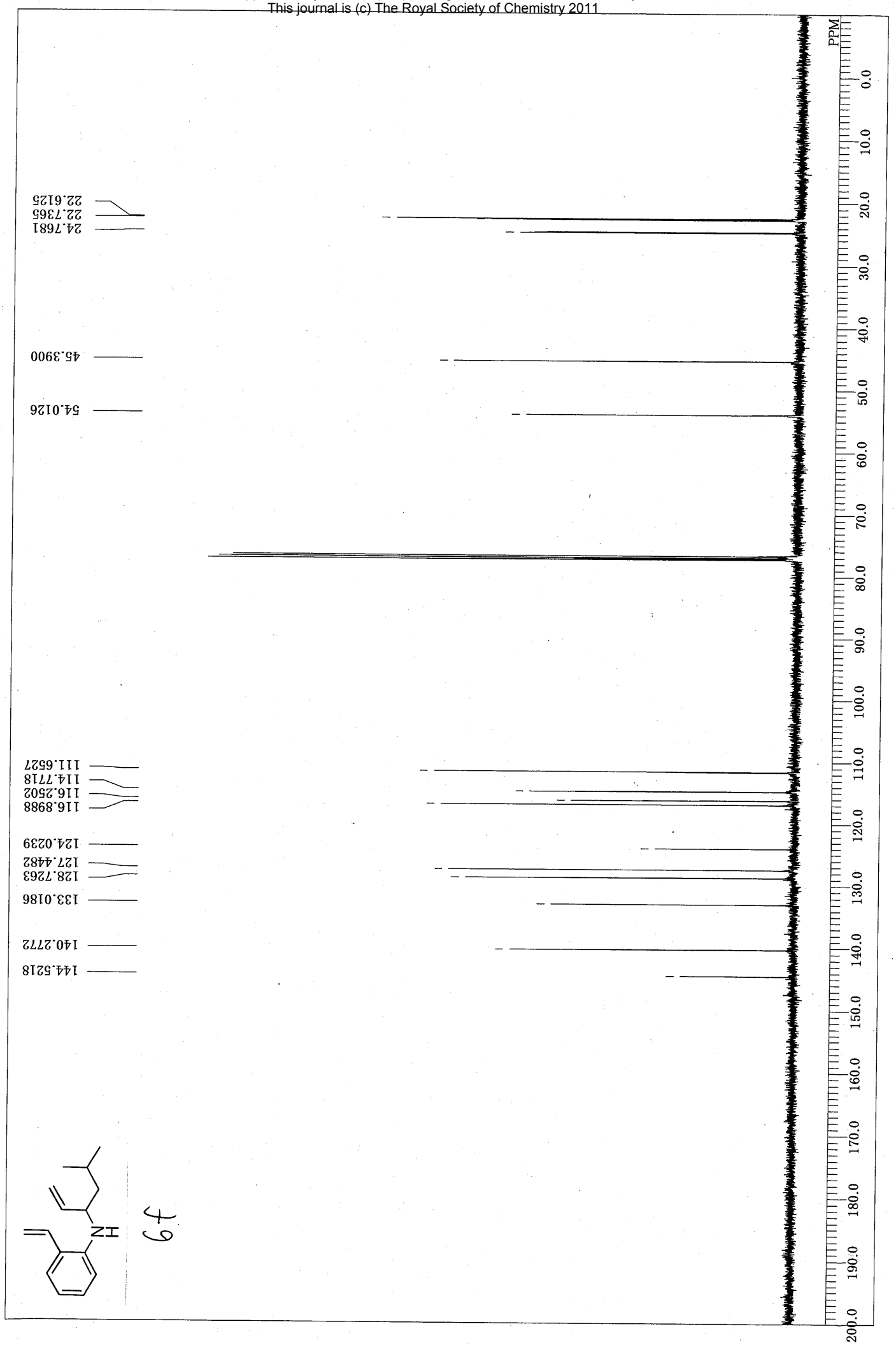


07KT3-93-2C(400,CDCl3)



07KT4-3-2(500,CDCl3)

9f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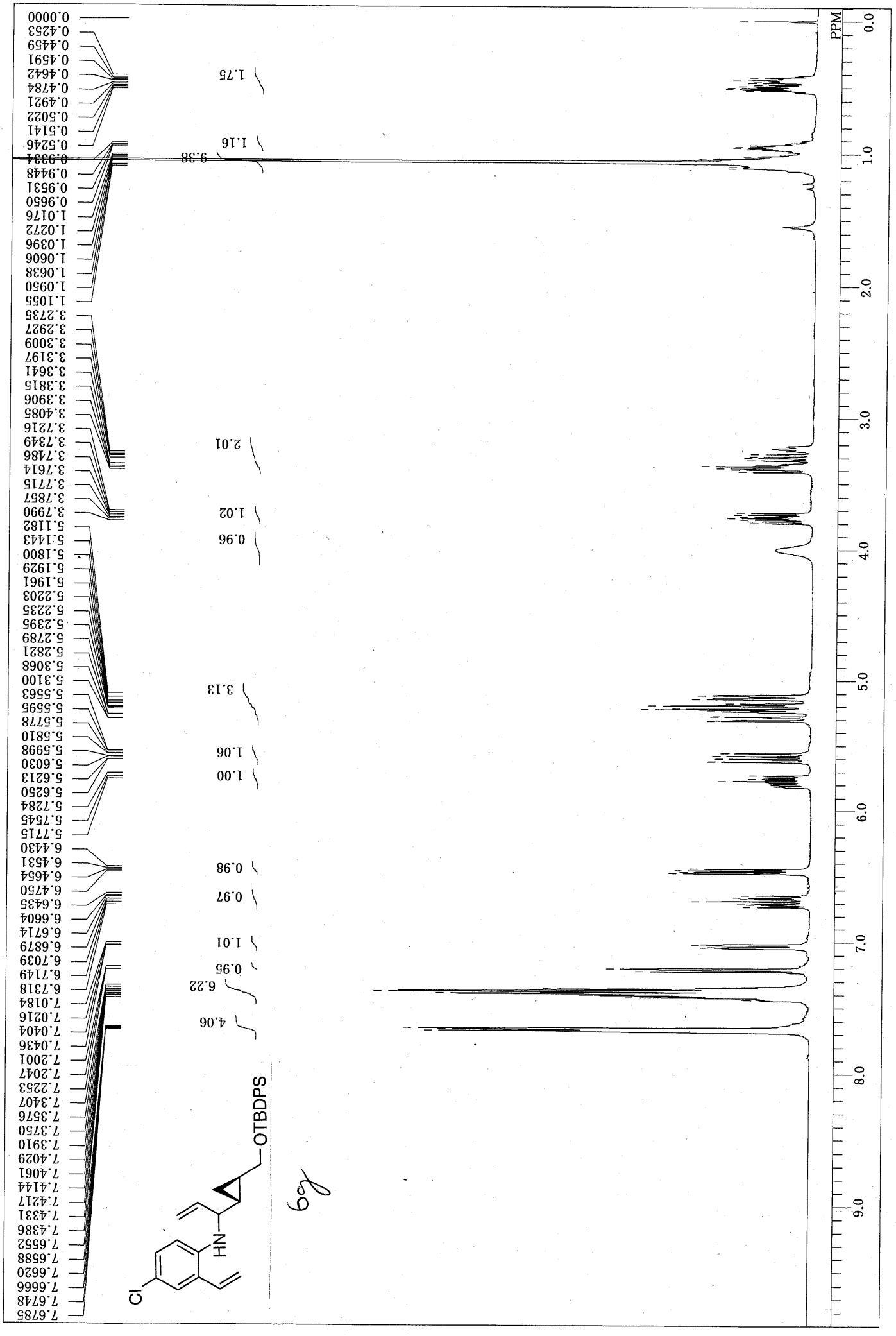
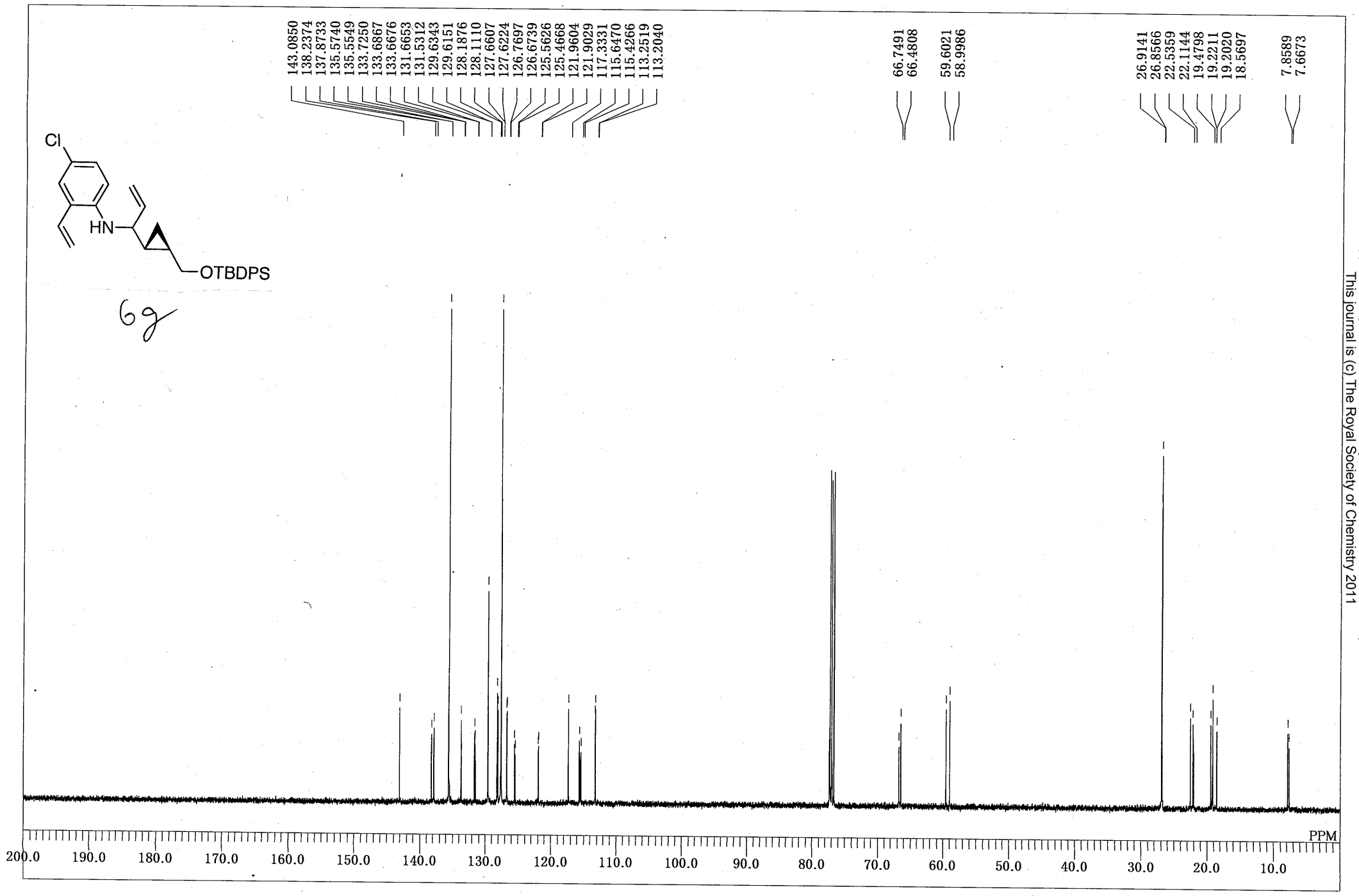
22.7365
24.7681
45.3900
54.0126
111.6527
114.7718
116.2502
116.8988
124.0239
127.4482
128.7263
133.0186
140.2772
144.5218
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0

H
N

6f


07KT2-74-2(400,CDCl3)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
1.75
1.16
9.38
2.01
1.02
0.96
3.13
1.06
1.00
0.98
0.97
1.01
0.95
6.22
4.06
OTBDPS
HN
Cl
69

07KT2-74-2C(400,CDCl3)



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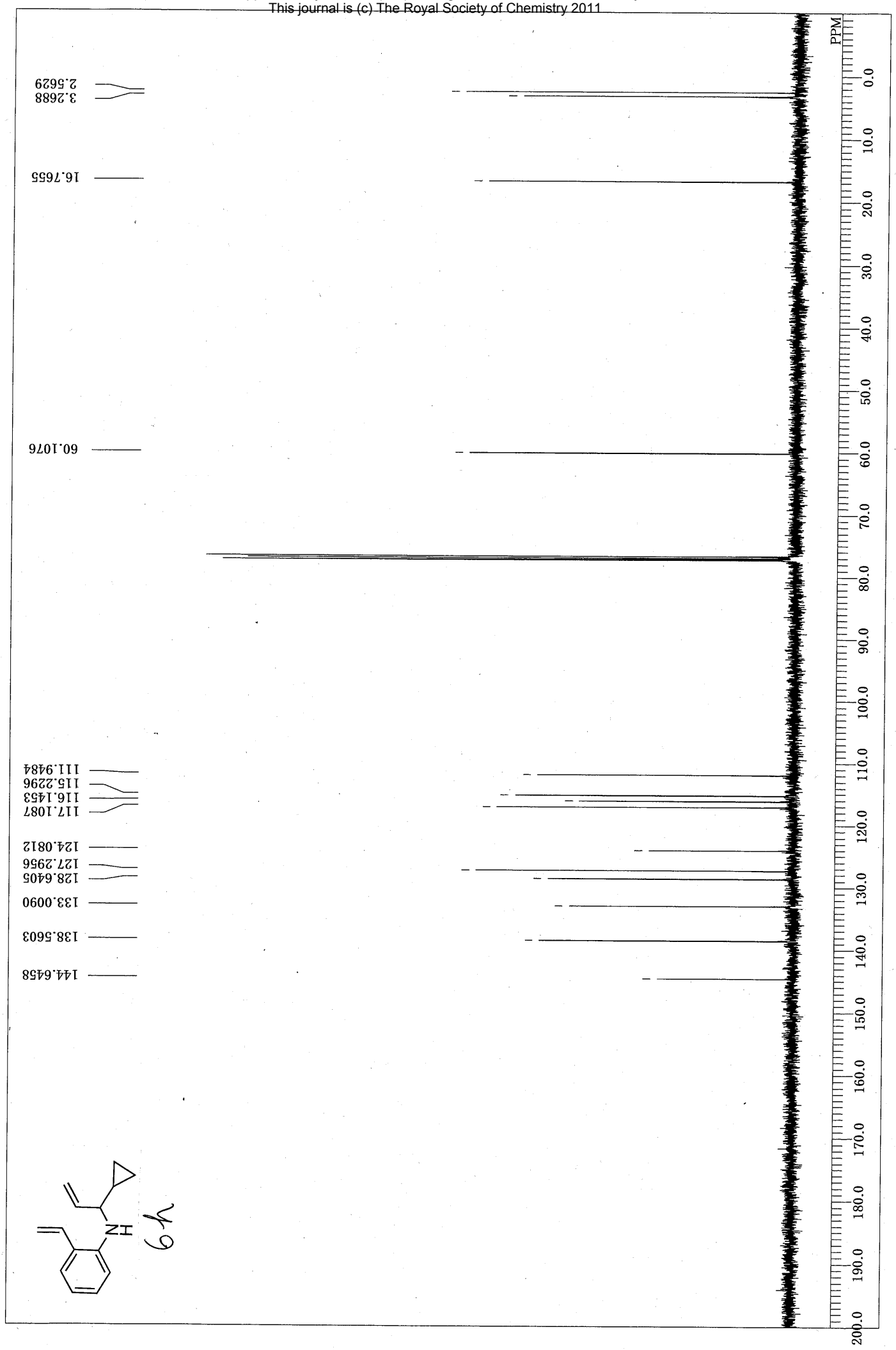

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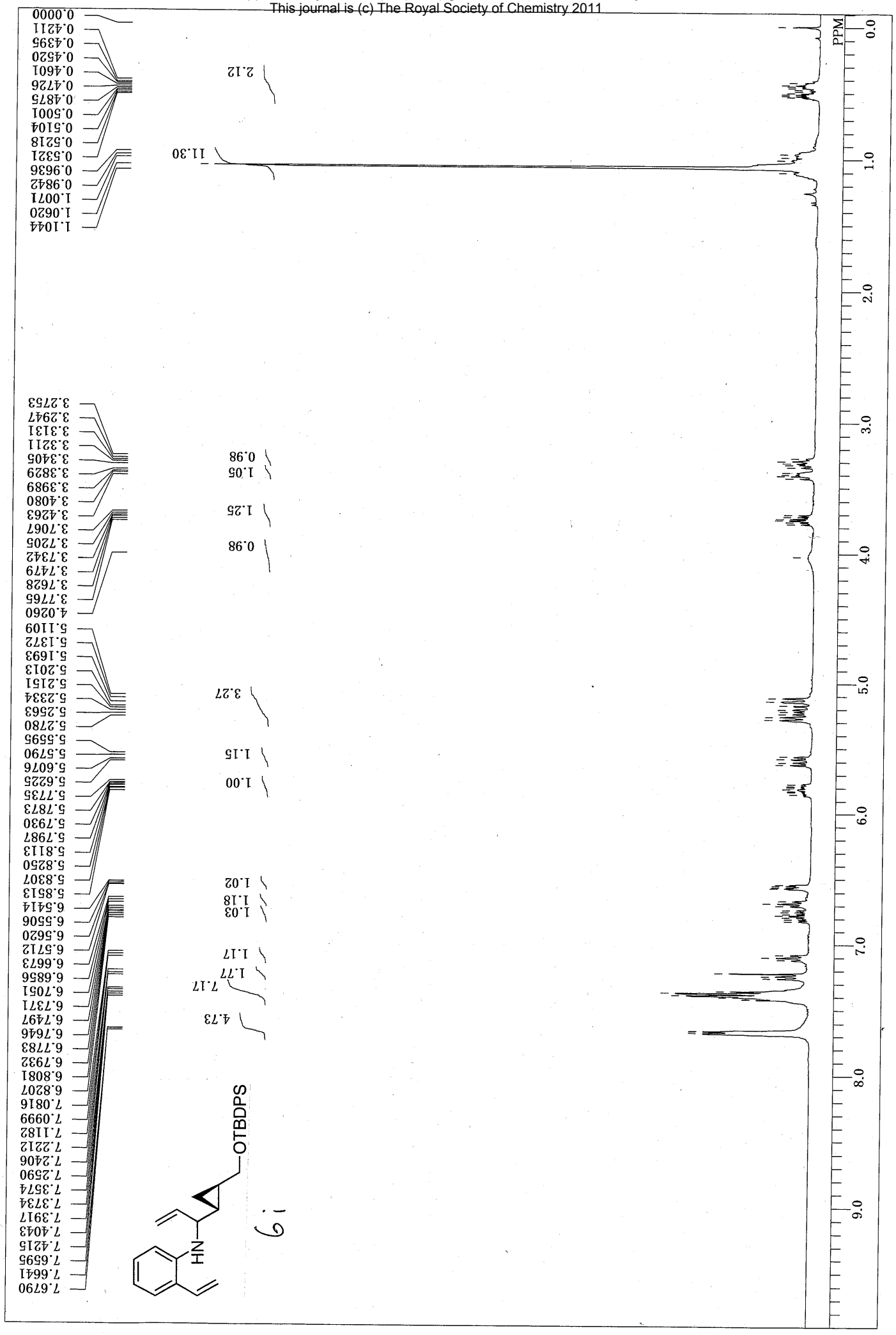
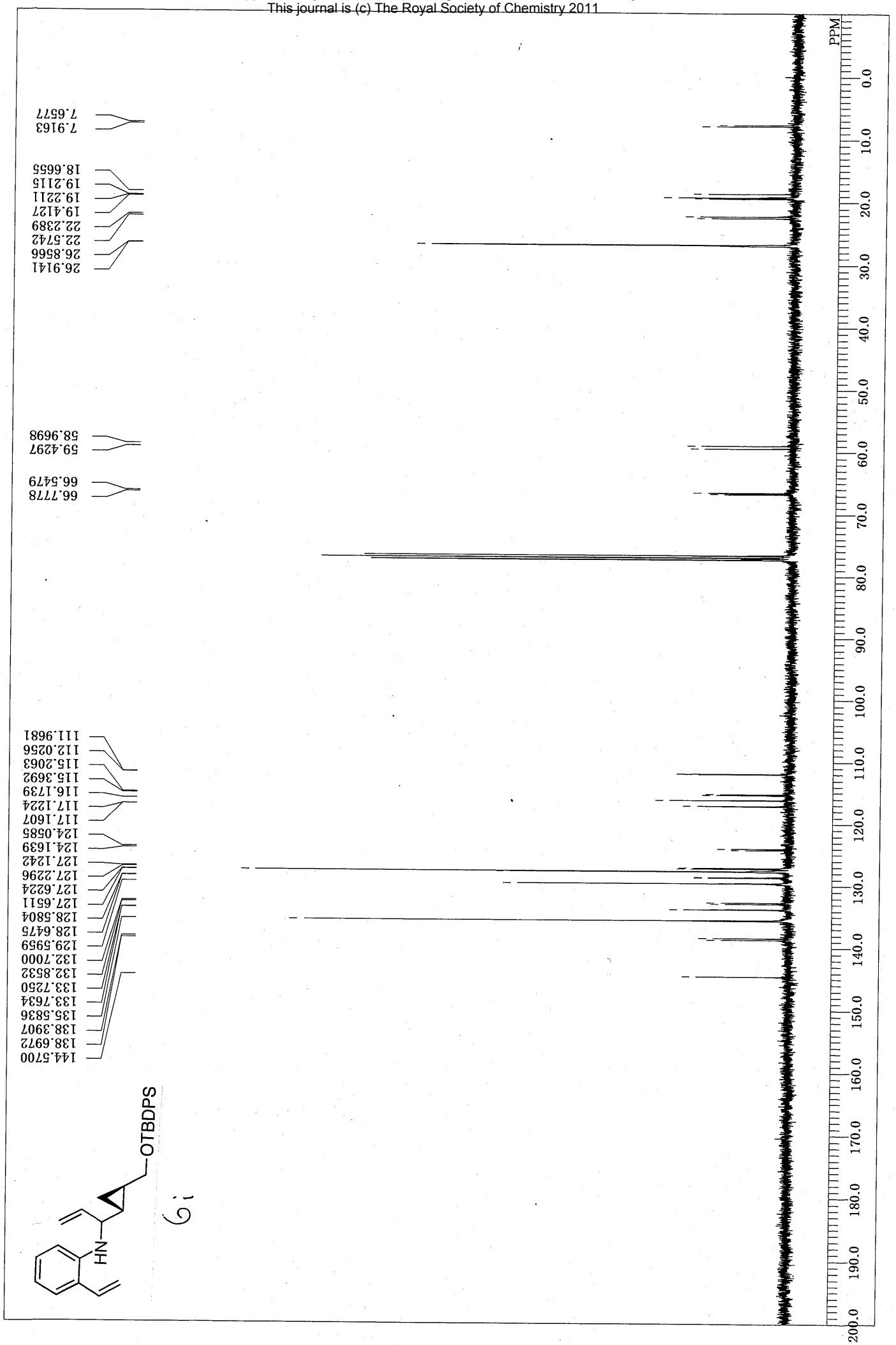


07KT5-69-1(400,CDCl3)


07KT5-69-1C(400,CDCl3)
7.9163
7.6577
18.6655
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19.2211
19.4127
22.2389
22.5742
26.8566
26.9141
58.9698
59.4297
66.5479
66.7778
111.9681
112.0256
115.2063
115.3692
116.1739
117.1224
117.1607
124.0585
124.1639
127.1242
127.2296
127.6224
127.6511
128.5804
128.6475
129.5959
132.7000
132.8532
133.7250
133.7634
135.5836
138.3907
138.6972
144.5700
OTBDPS
NH
6i
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
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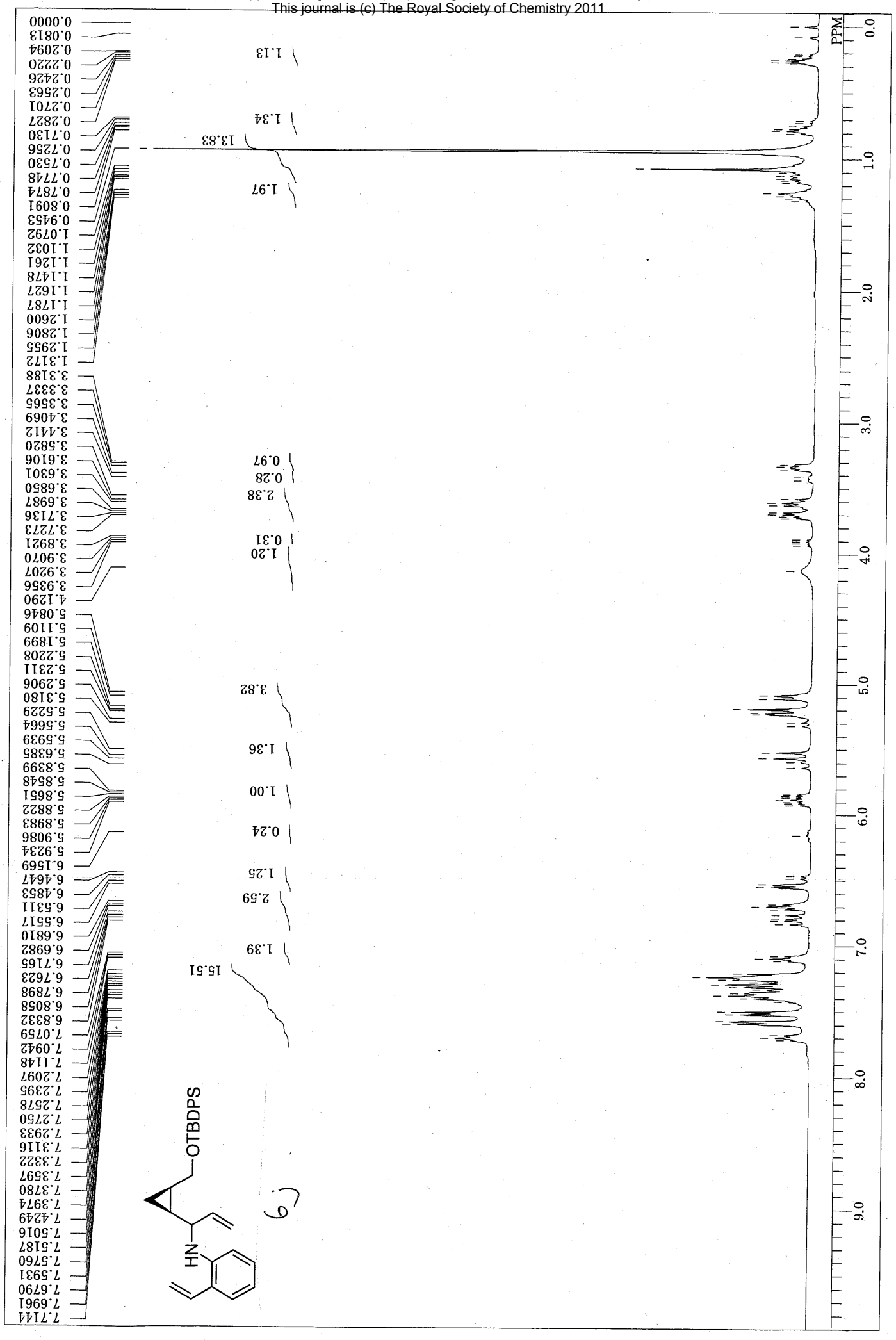
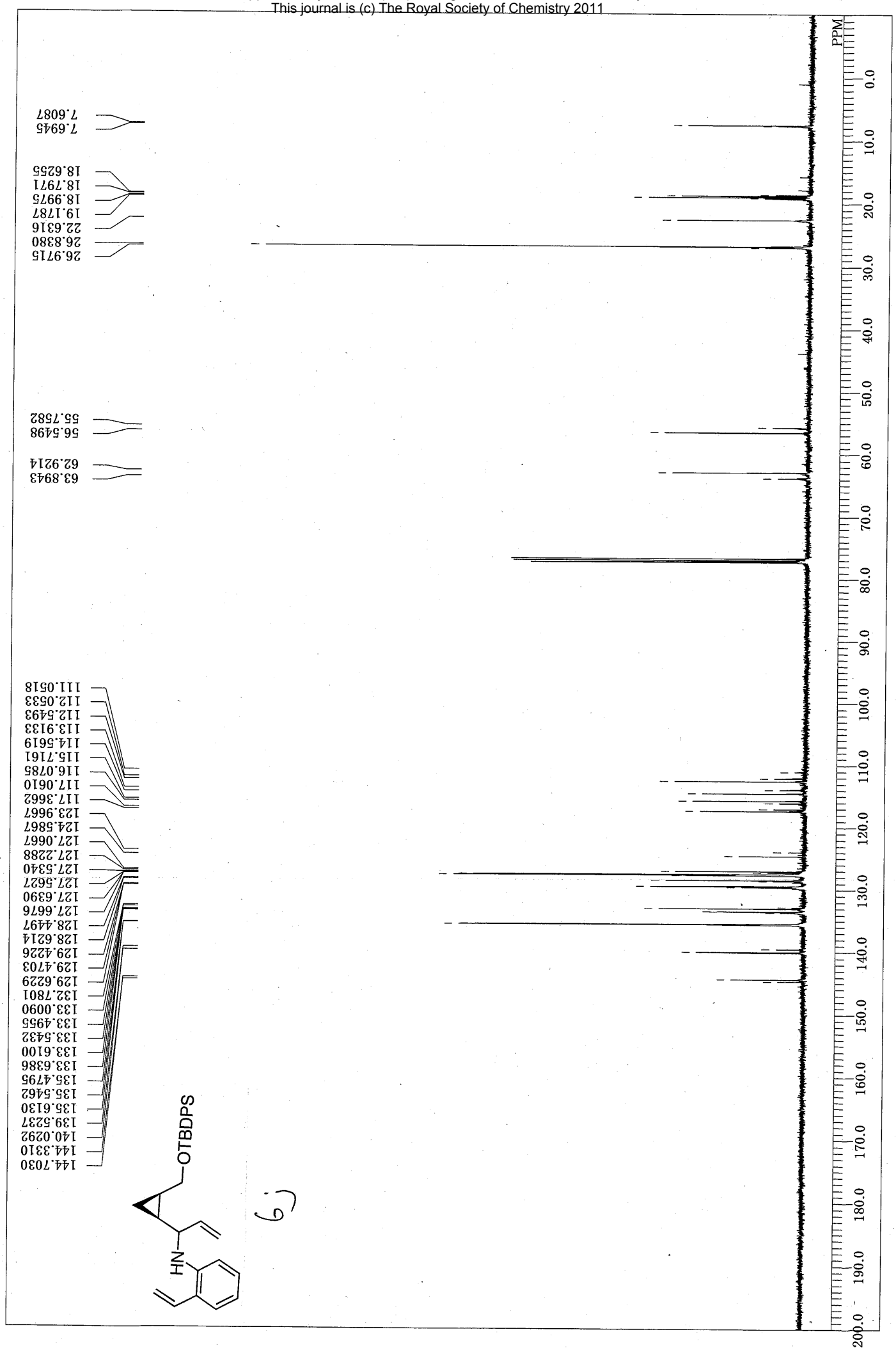
140.0
150.0
160.0
170.0
180.0
190.0
200.0




07KT5-88-1C(500,CDCl3)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
7.6087
7.6945
18.6255
18.7971
18.9975
19.1787
22.6316
26.8380
26.9715
55.7582
56.5498
62.9214
63.8943
111.0518
112.0533
112.5493
113.9133
114.5619
115.7161
116.0785
117.0610
117.3662
123.9667
124.5867
127.0667
127.2288
127.5340
127.5627
127.6390
127.6676
128.4497
128.6214
129.4226
129.4703
129.6229
132.7801
133.0090
133.4955
133.5432
133.6100
133.6386
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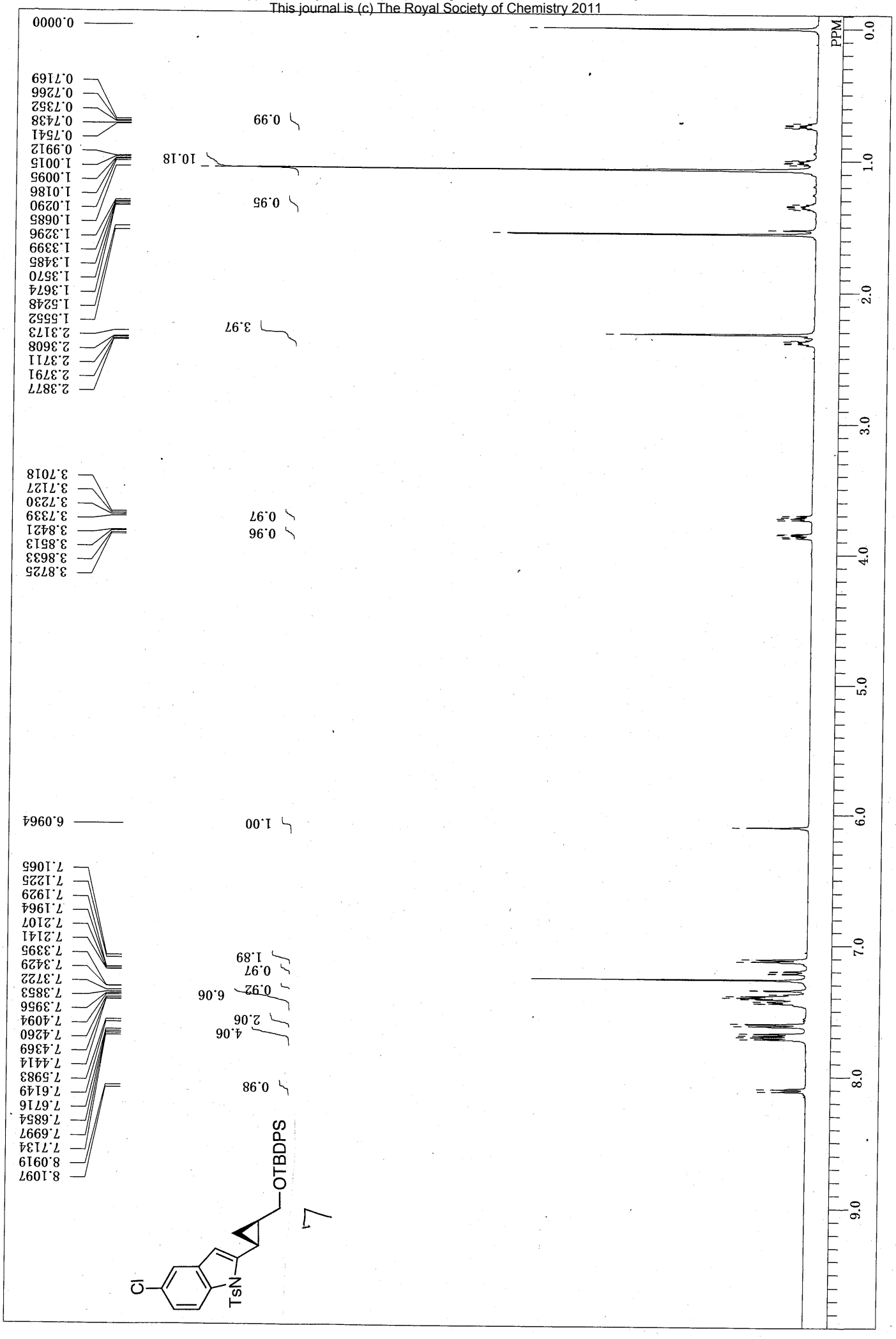
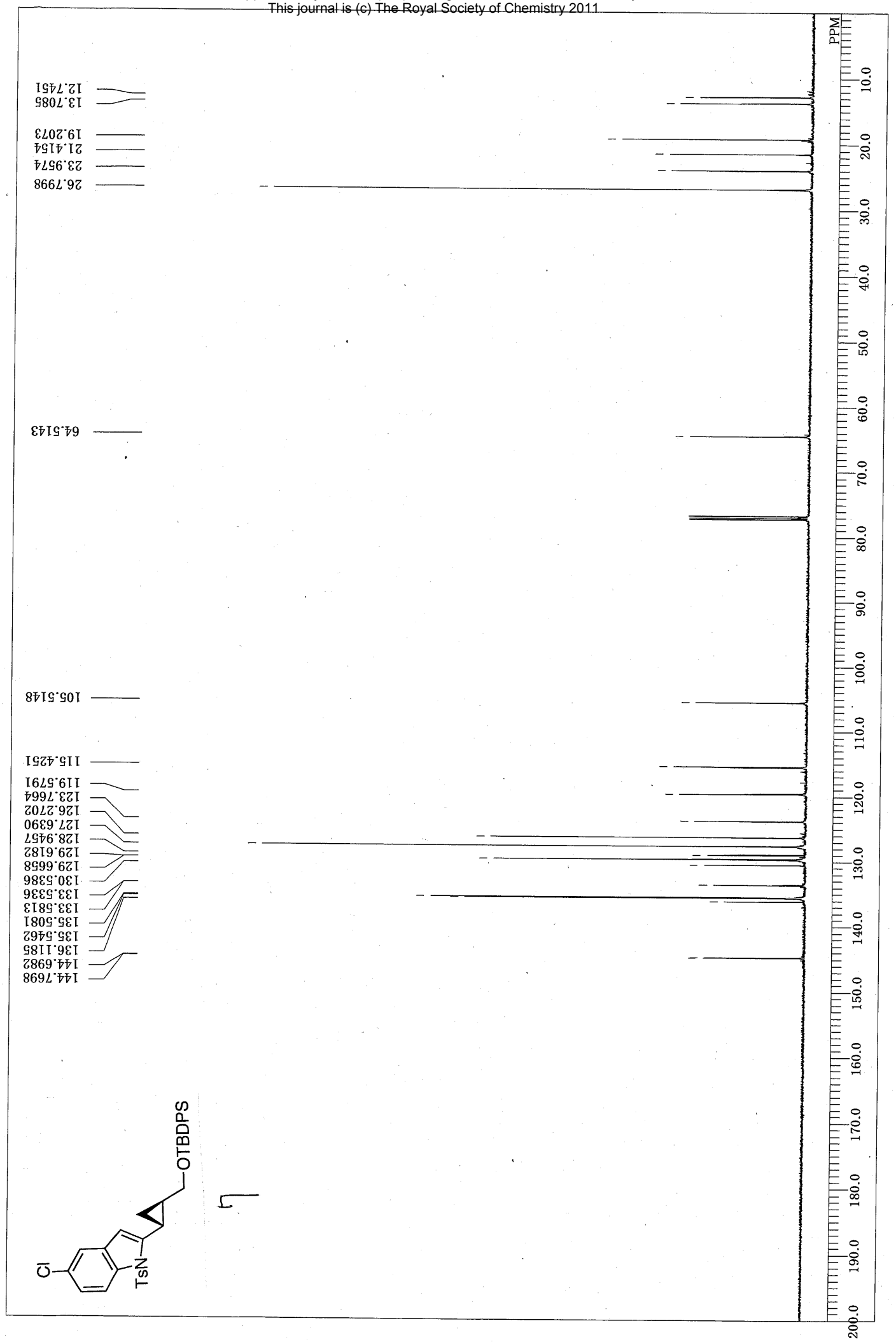
135.5462
135.6130
139.5237
140.0292
144.3310
144.7030
OTBDPS
NH
(j)

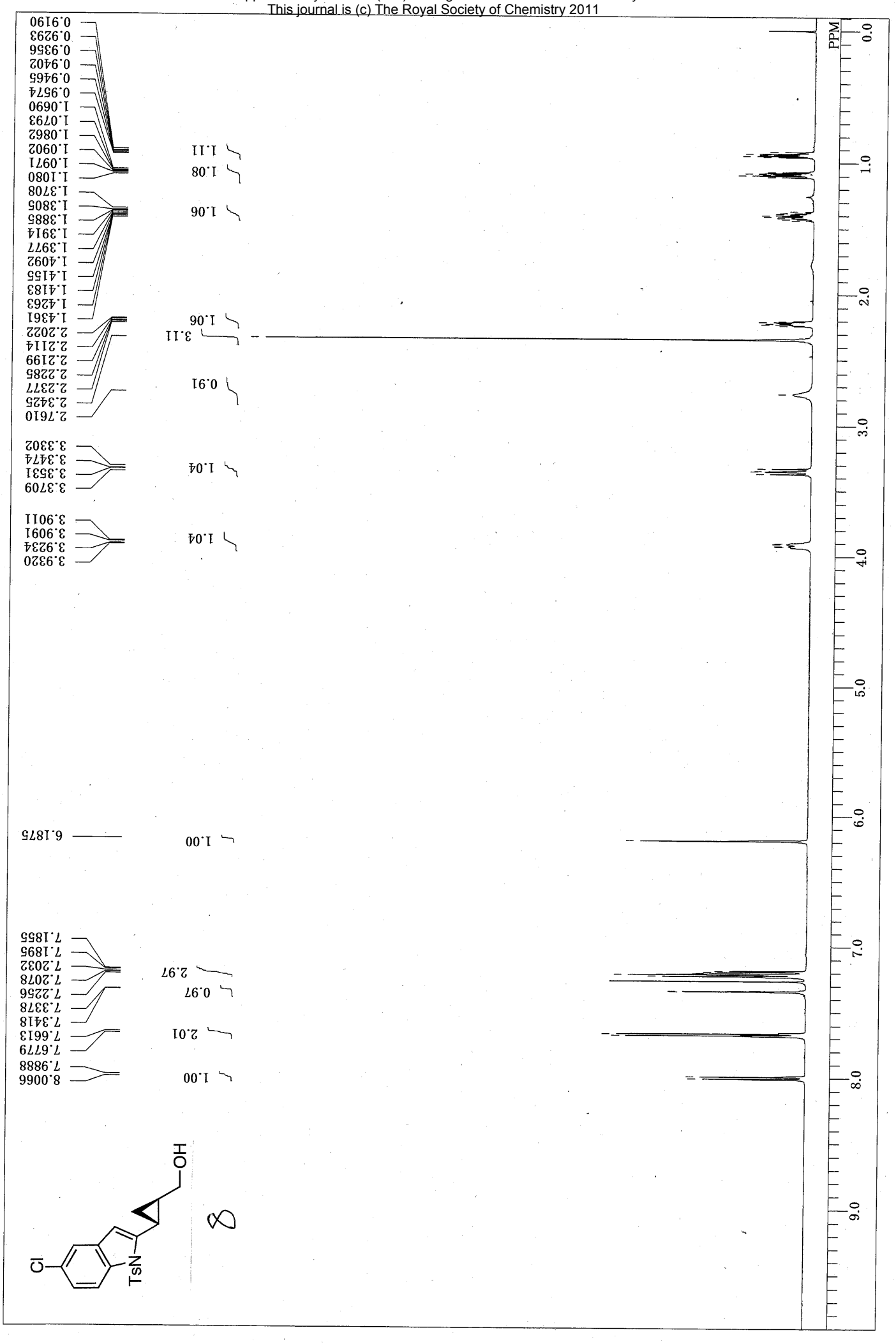


07KT3-20-1(500,CDCl3)

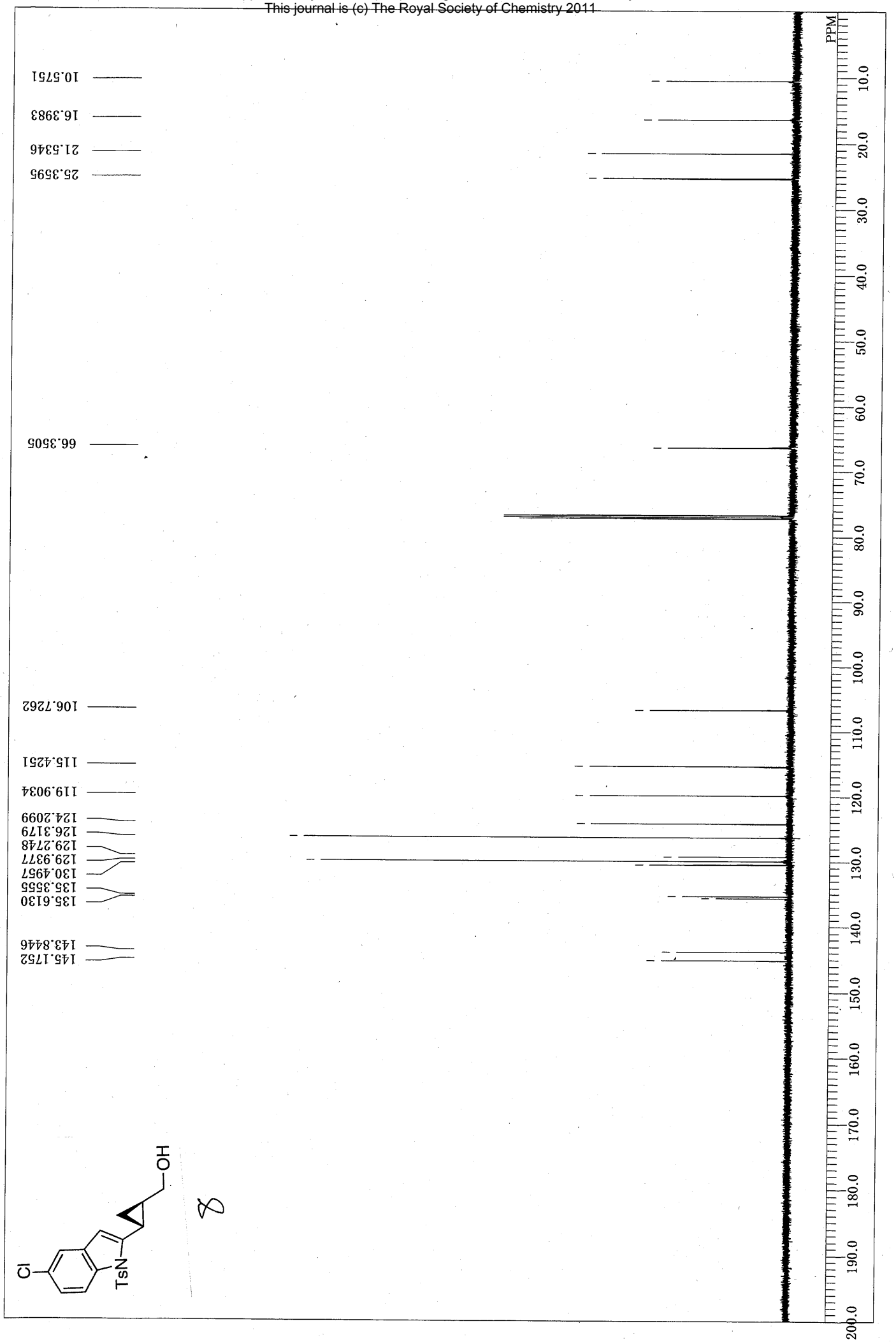


4

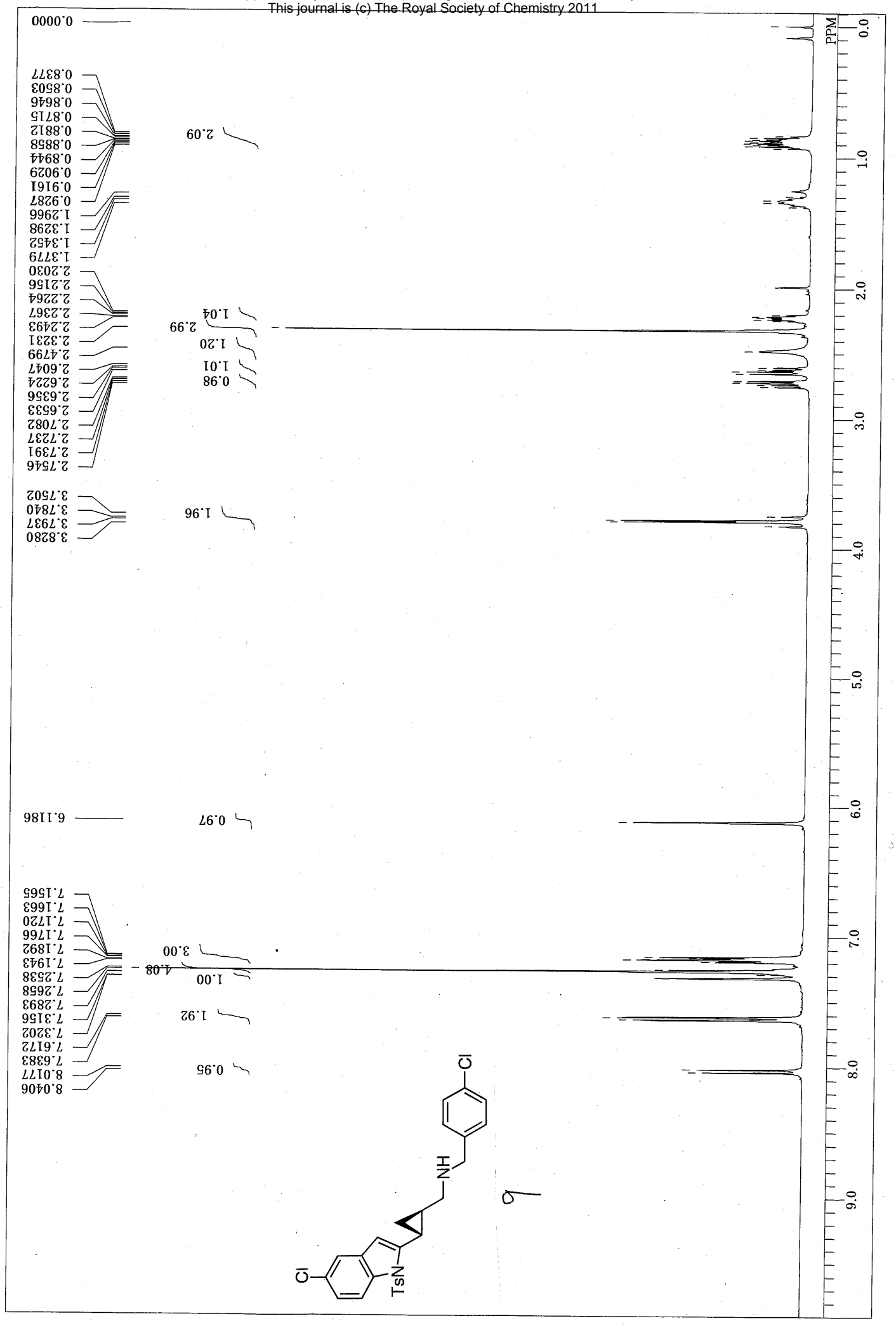
07KT3-20-1 C(500,CDCl3)



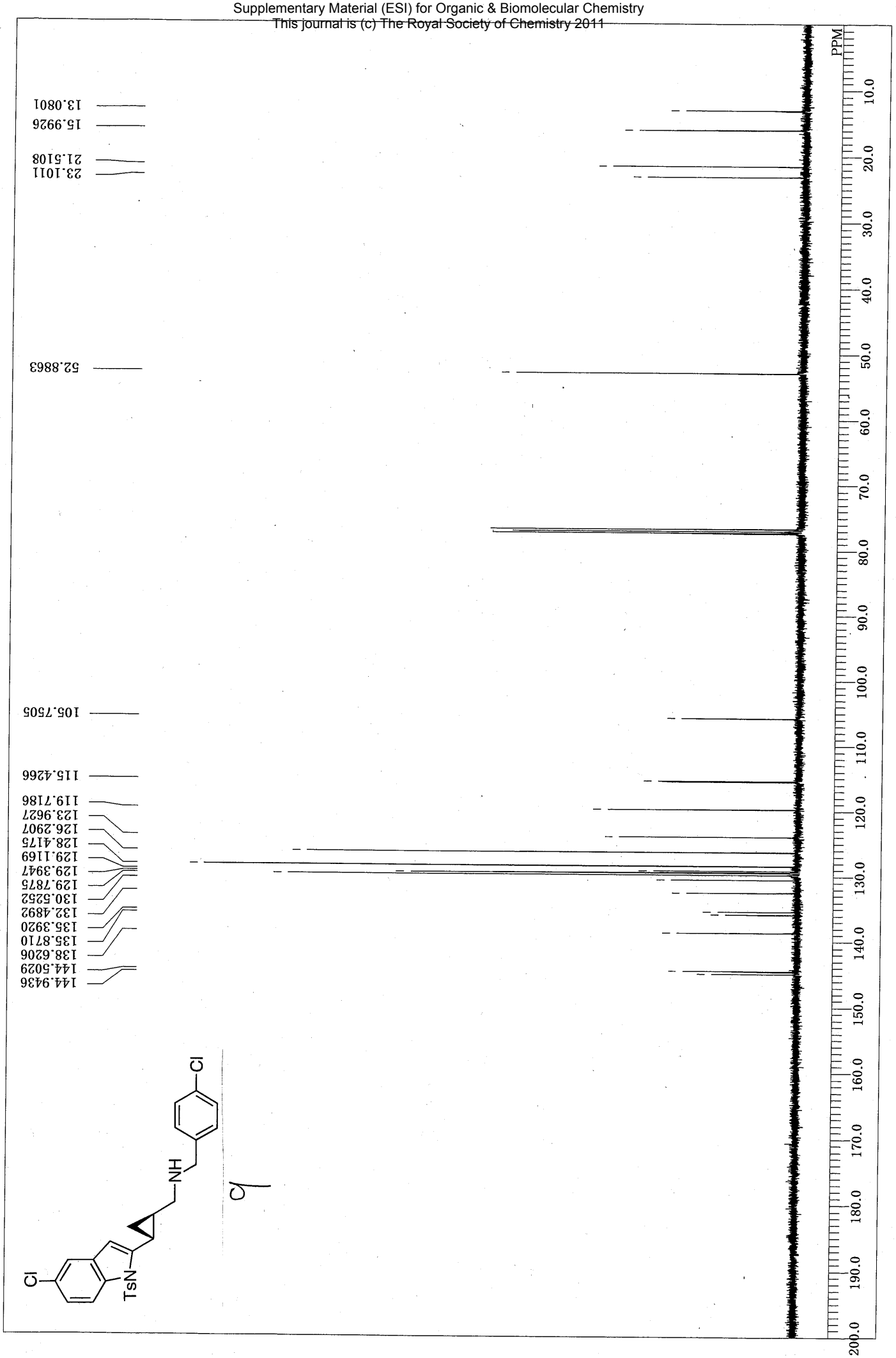
07KT3-23-1(500,CDCl3)



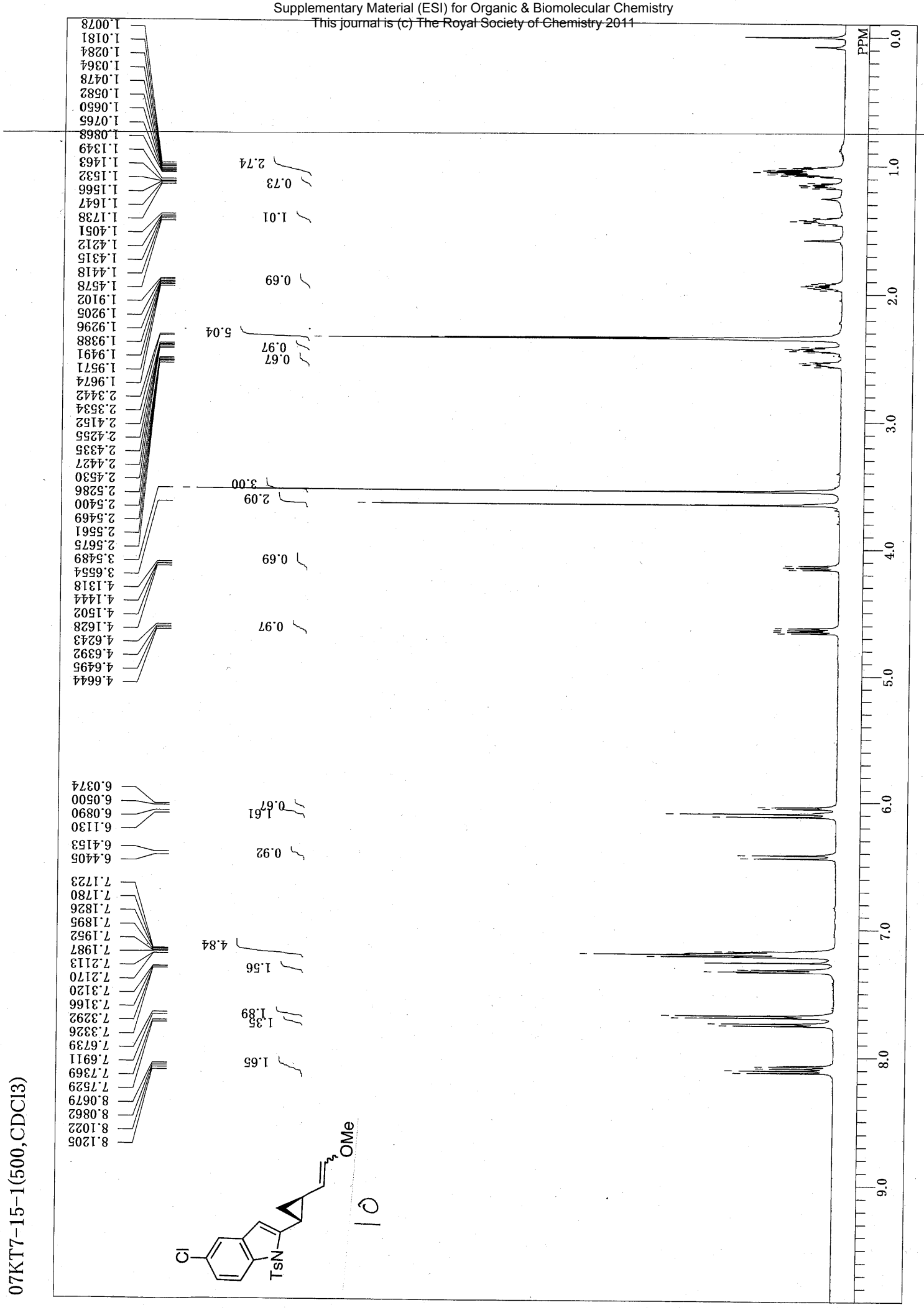
07KT3-23-1C(500,CDCl3)

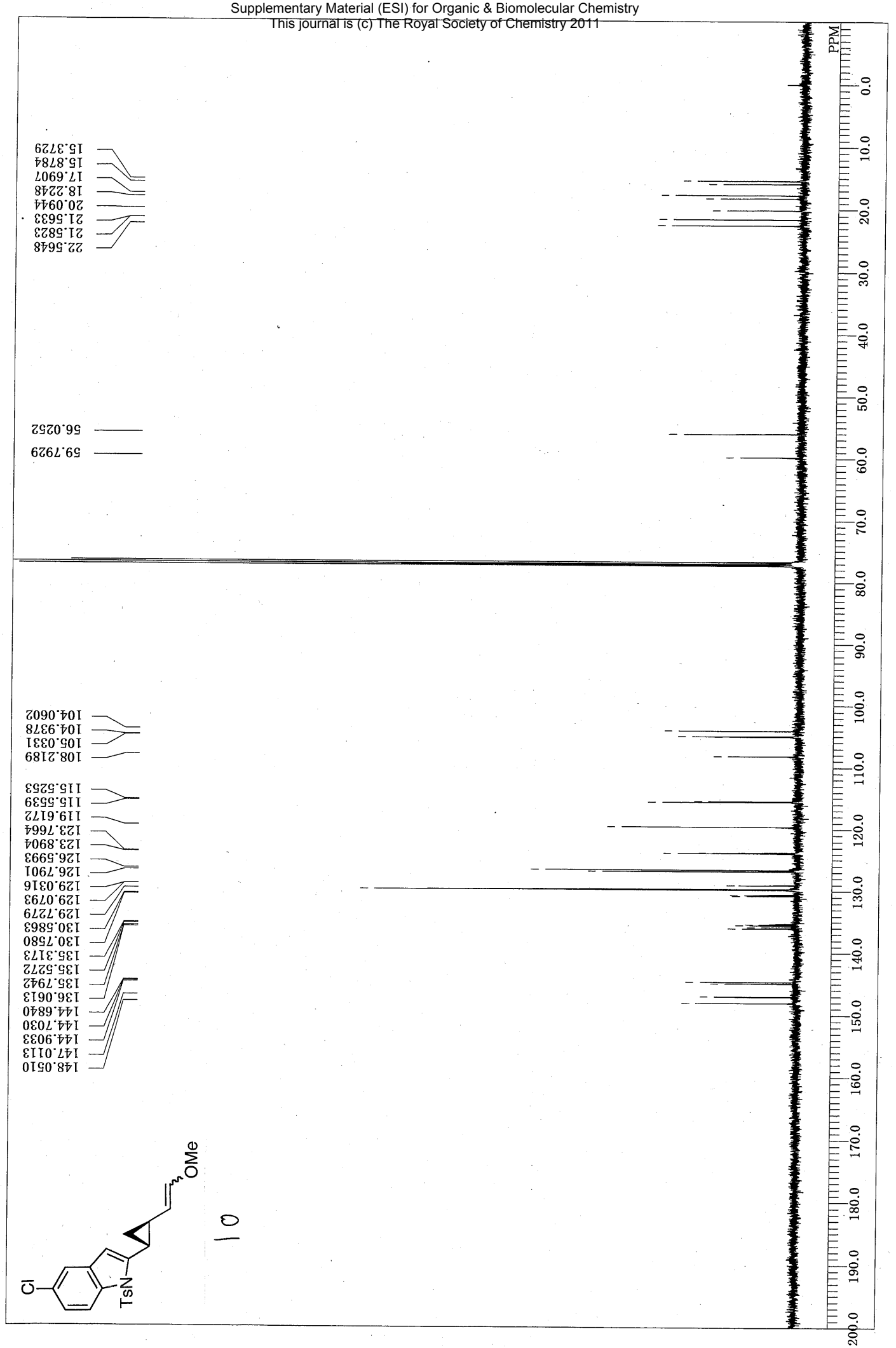


07KT3-25-1(400,CDCl3)

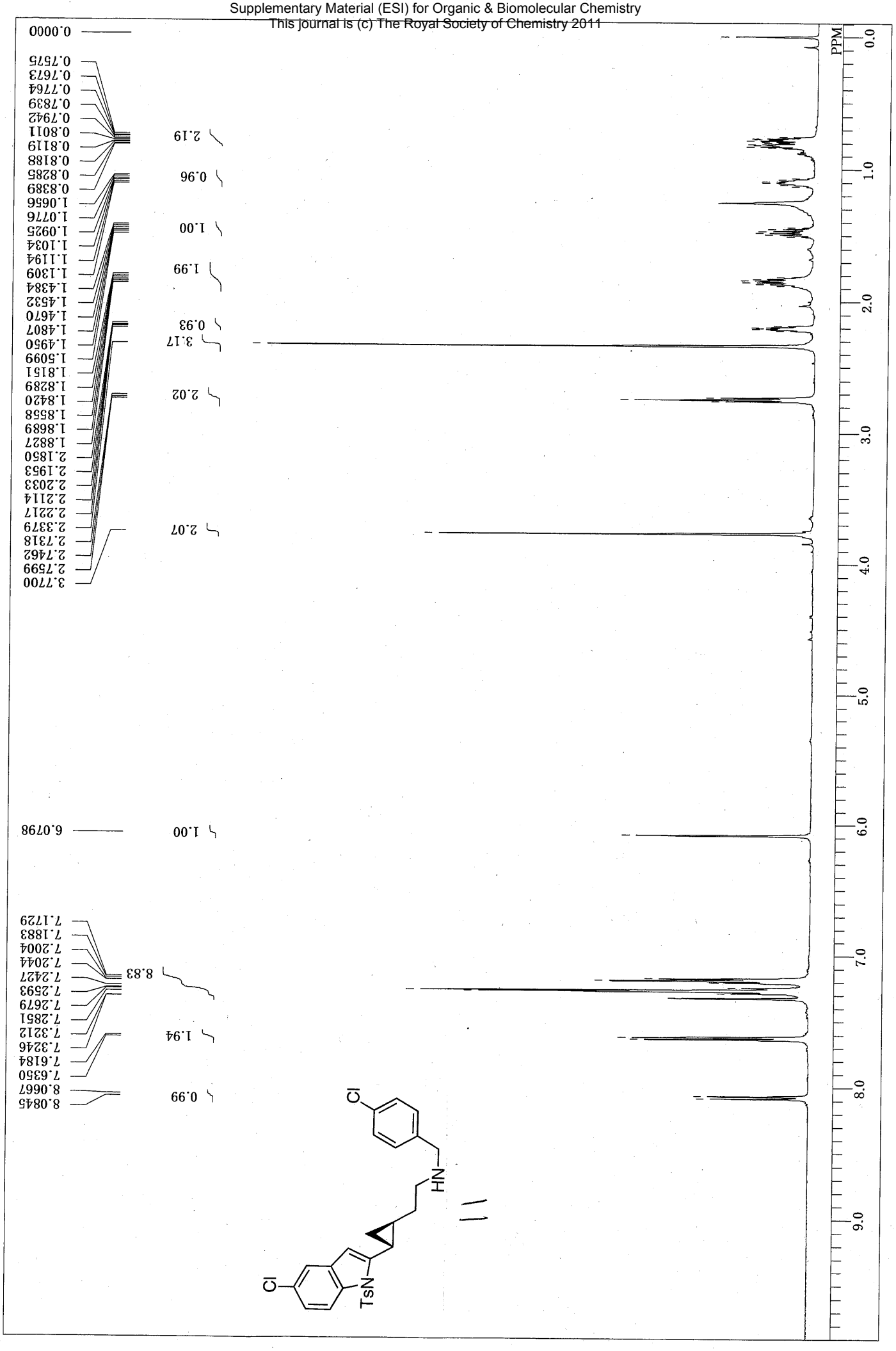


07KT3-25-1C(400,CDCl3)



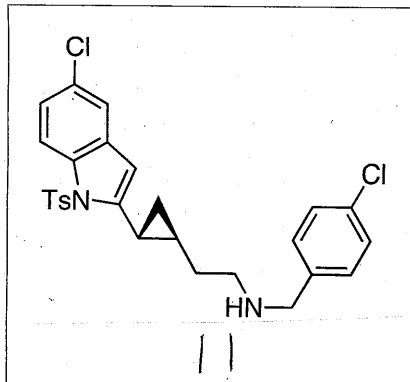


07KT7-15-1C(500,CDCl3)



07KT3-28-1(500,CDCl3)

07KT3-28-1C(500,CDCl3)



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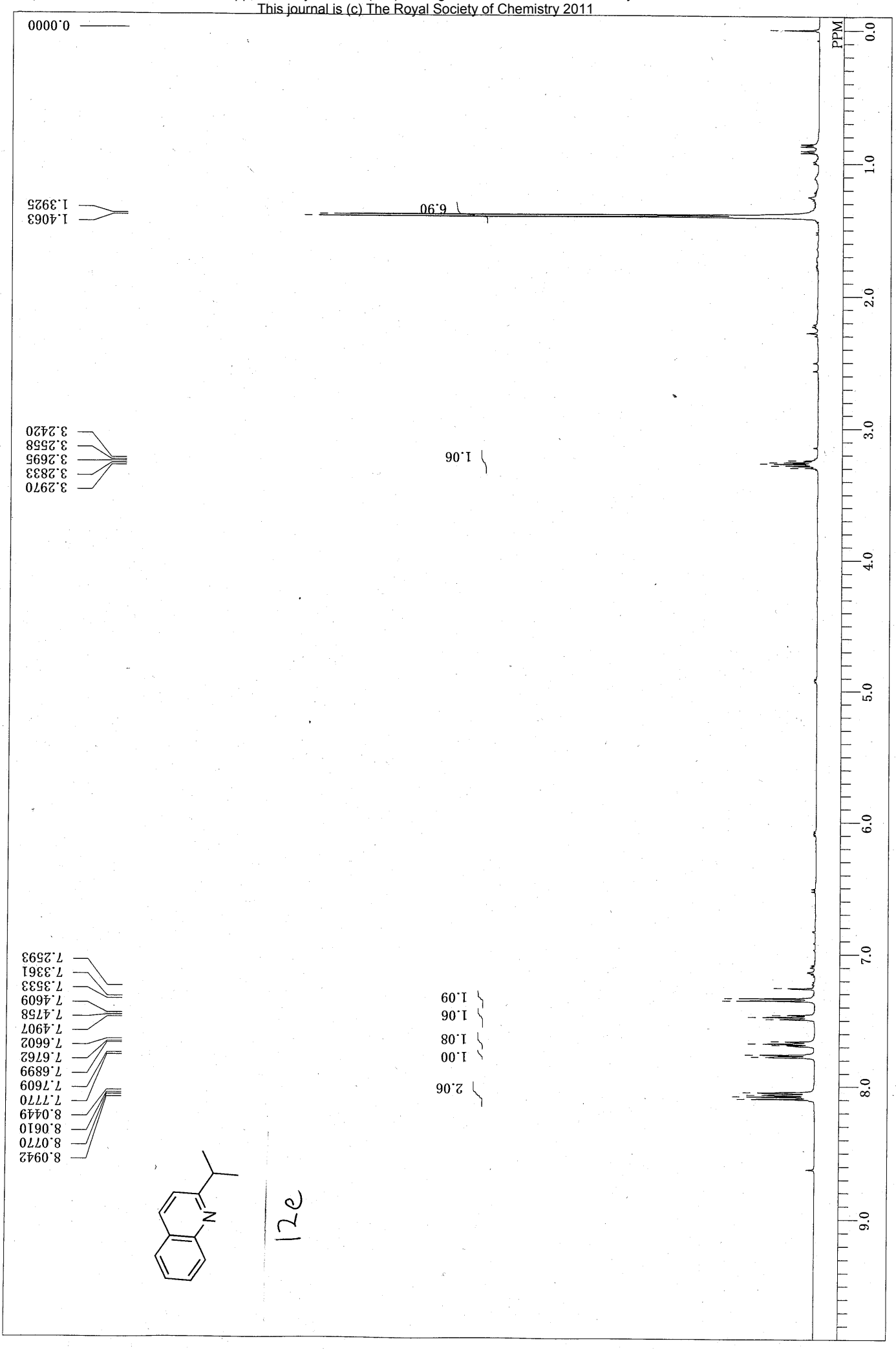
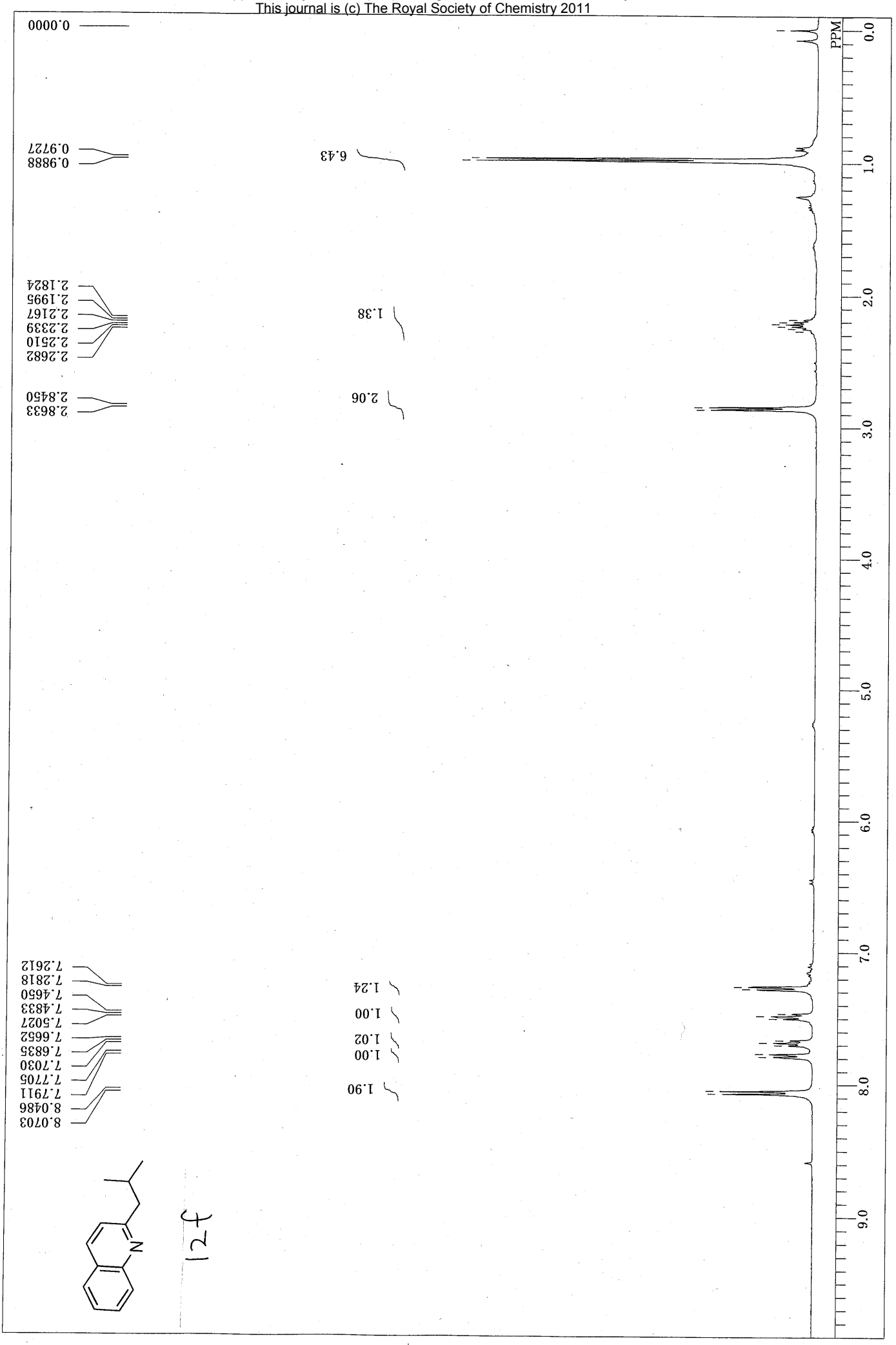
144.8747
138.7130
136.1281
135.5176
132.5798
130.6054
129.7755
129.4226
129.0983
128.4783
126.3608
123.8999
119.6268
115.5253
105.3574
53.1828
48.6521
33.9345
21.5537
20.8002
16.3649
15.4873

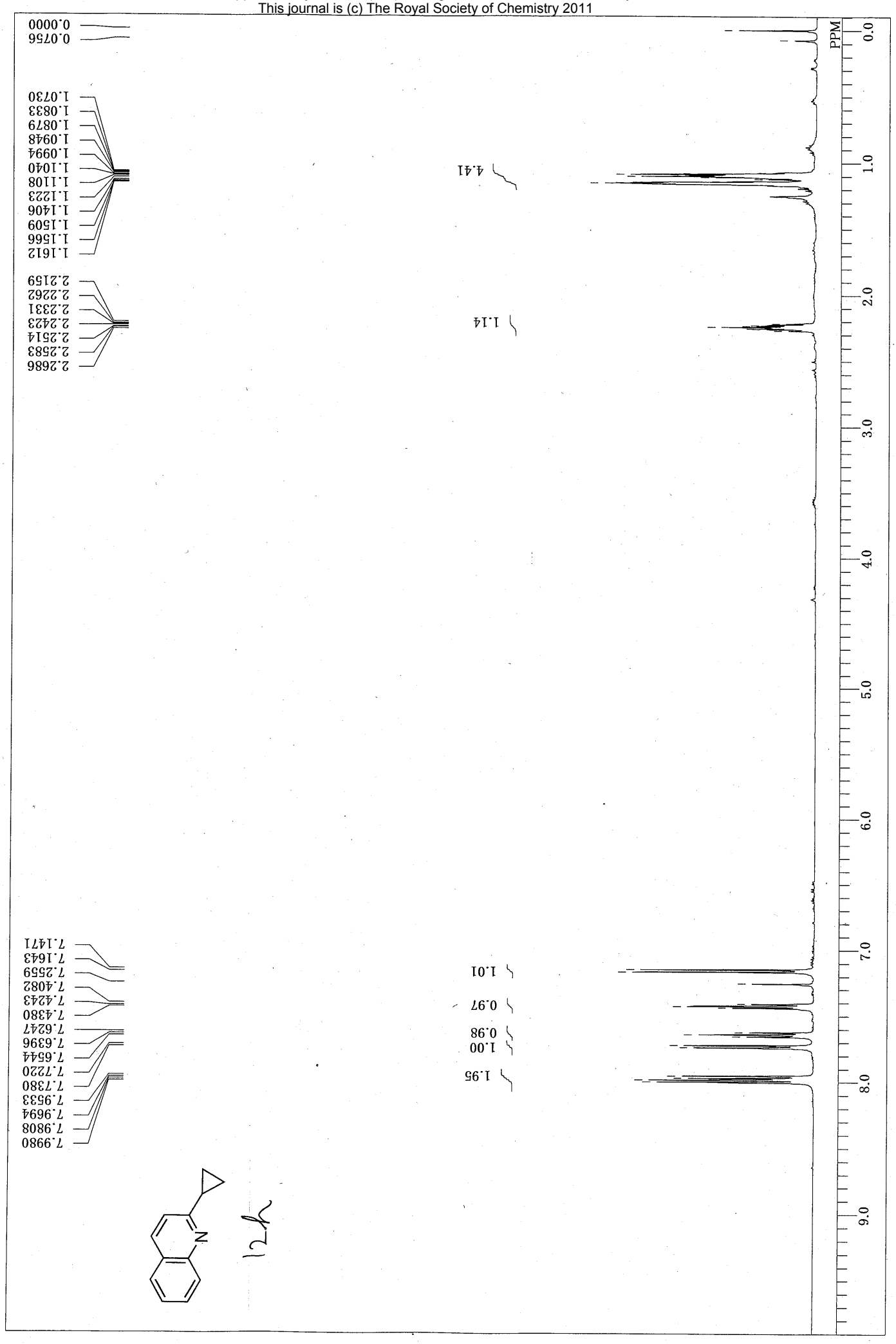
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0



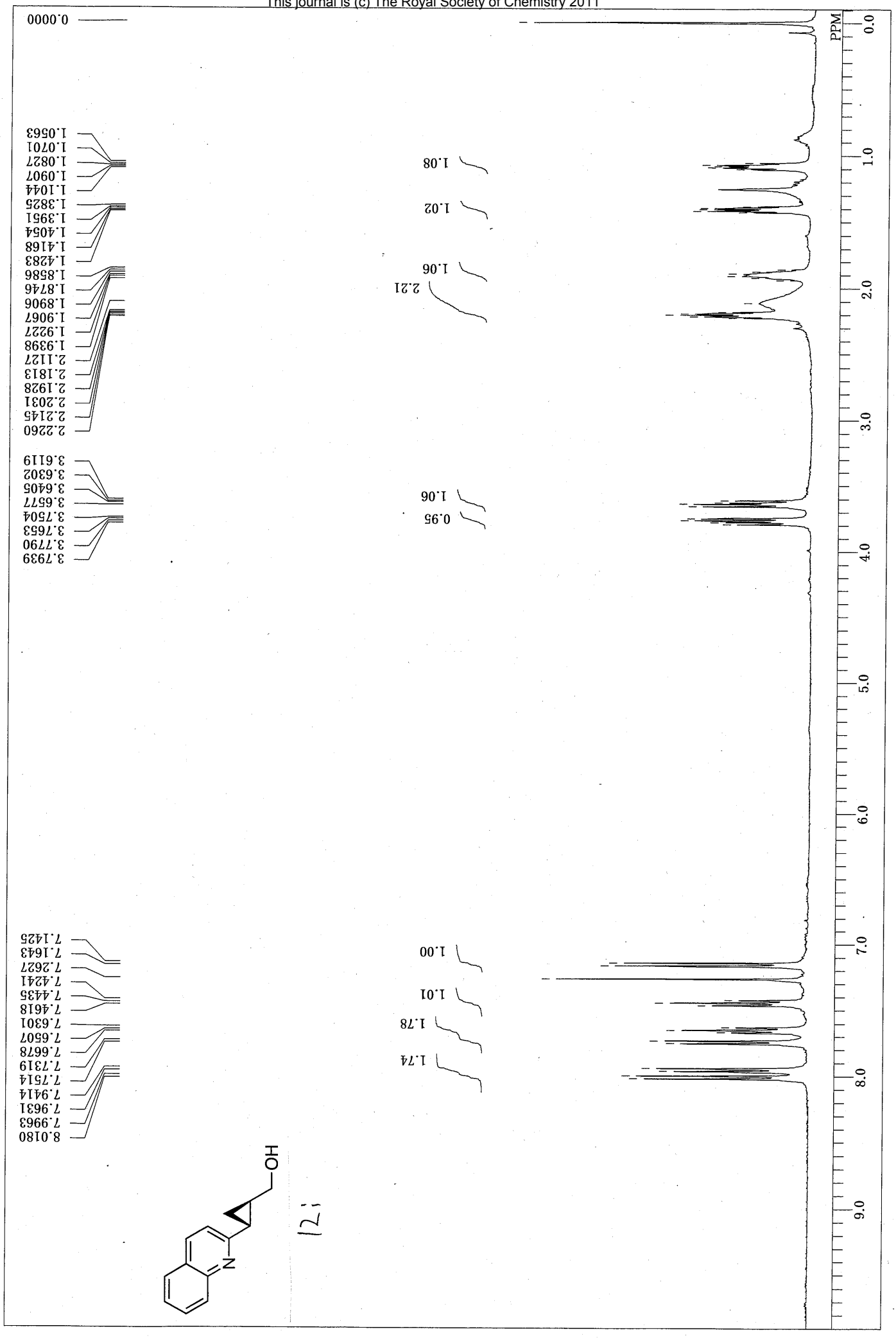
07KT4-82-1(500,CDCl3)



07KT4-80-1(400,CDCl3)

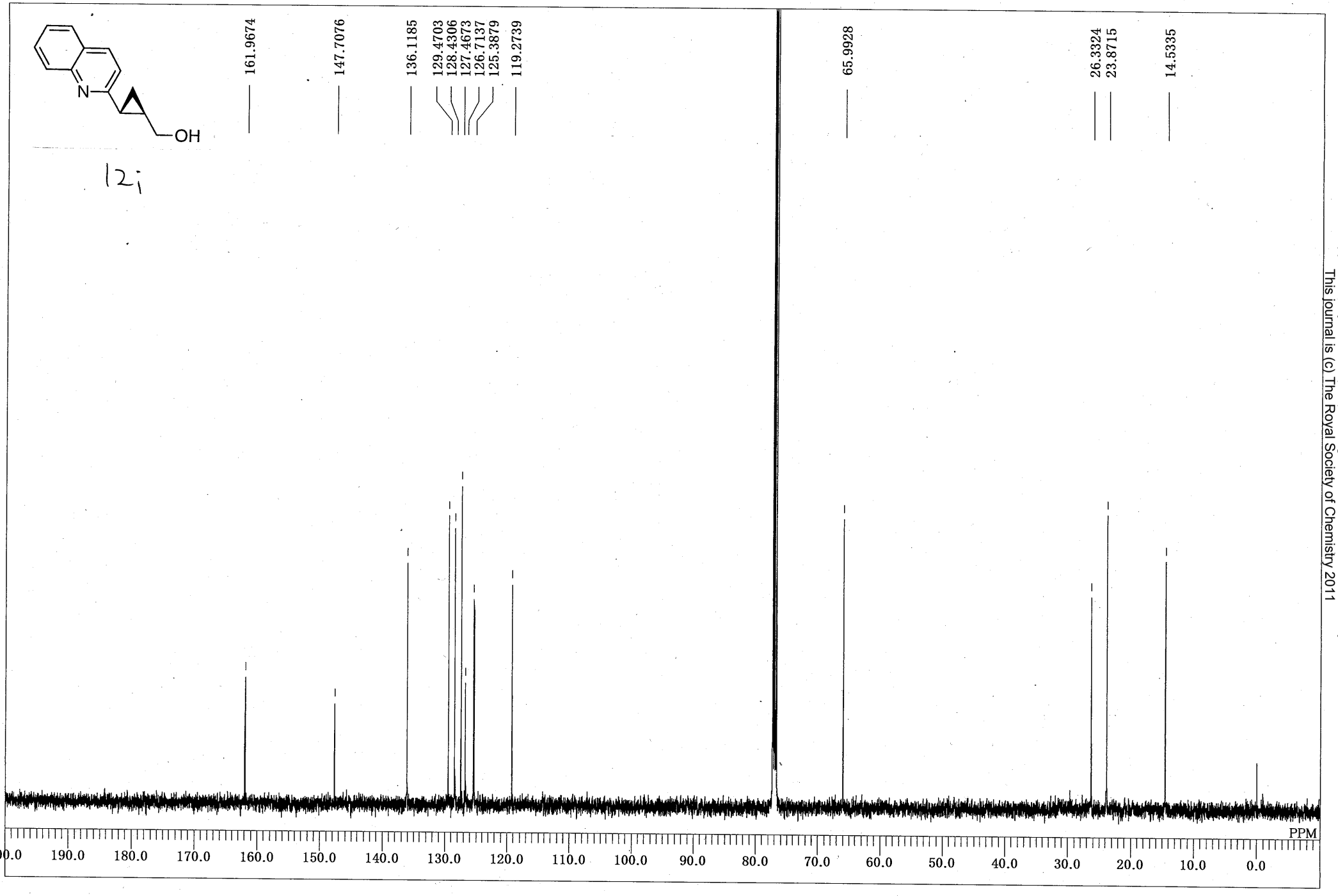


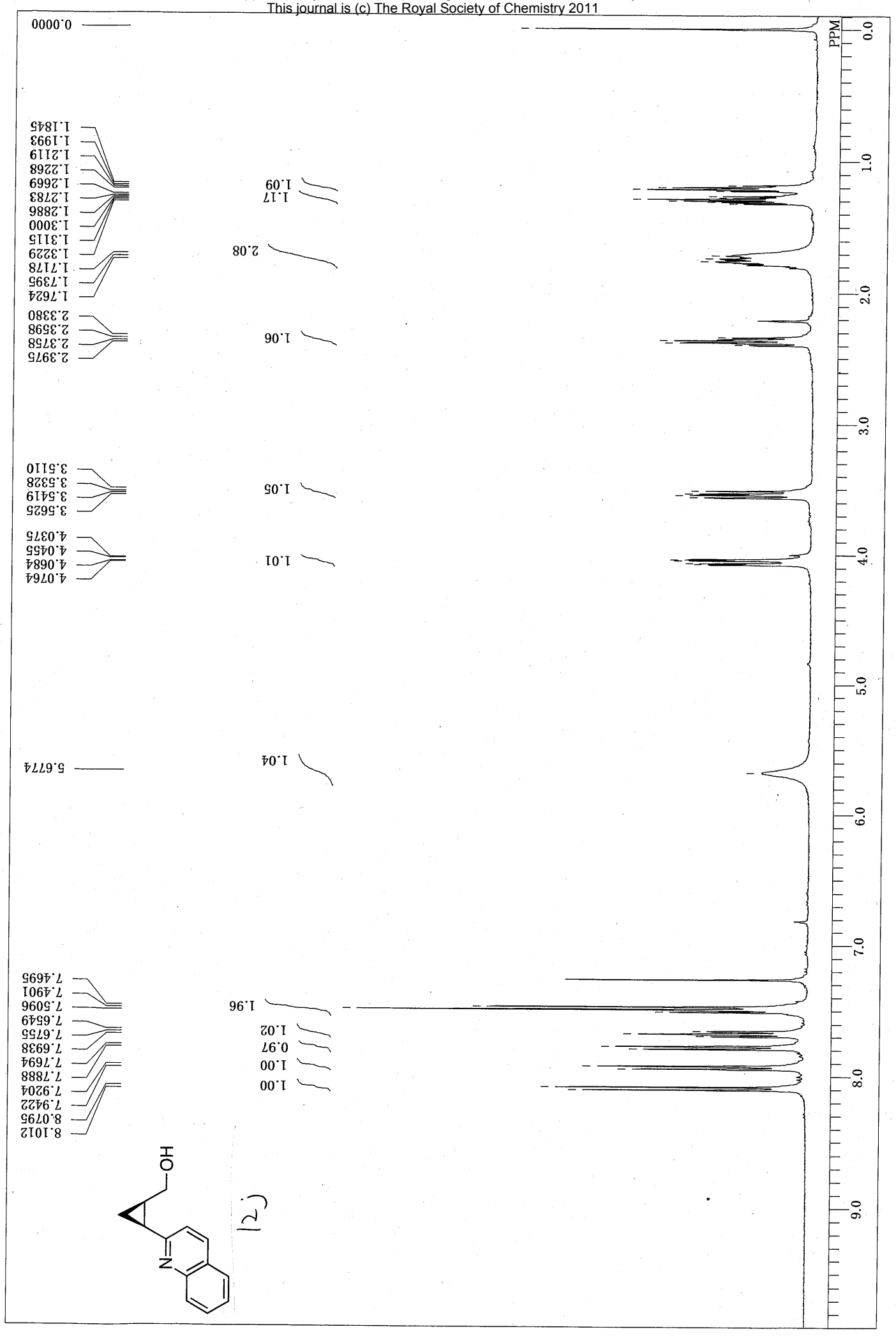
07KT4-83-1(500,CDCl3)



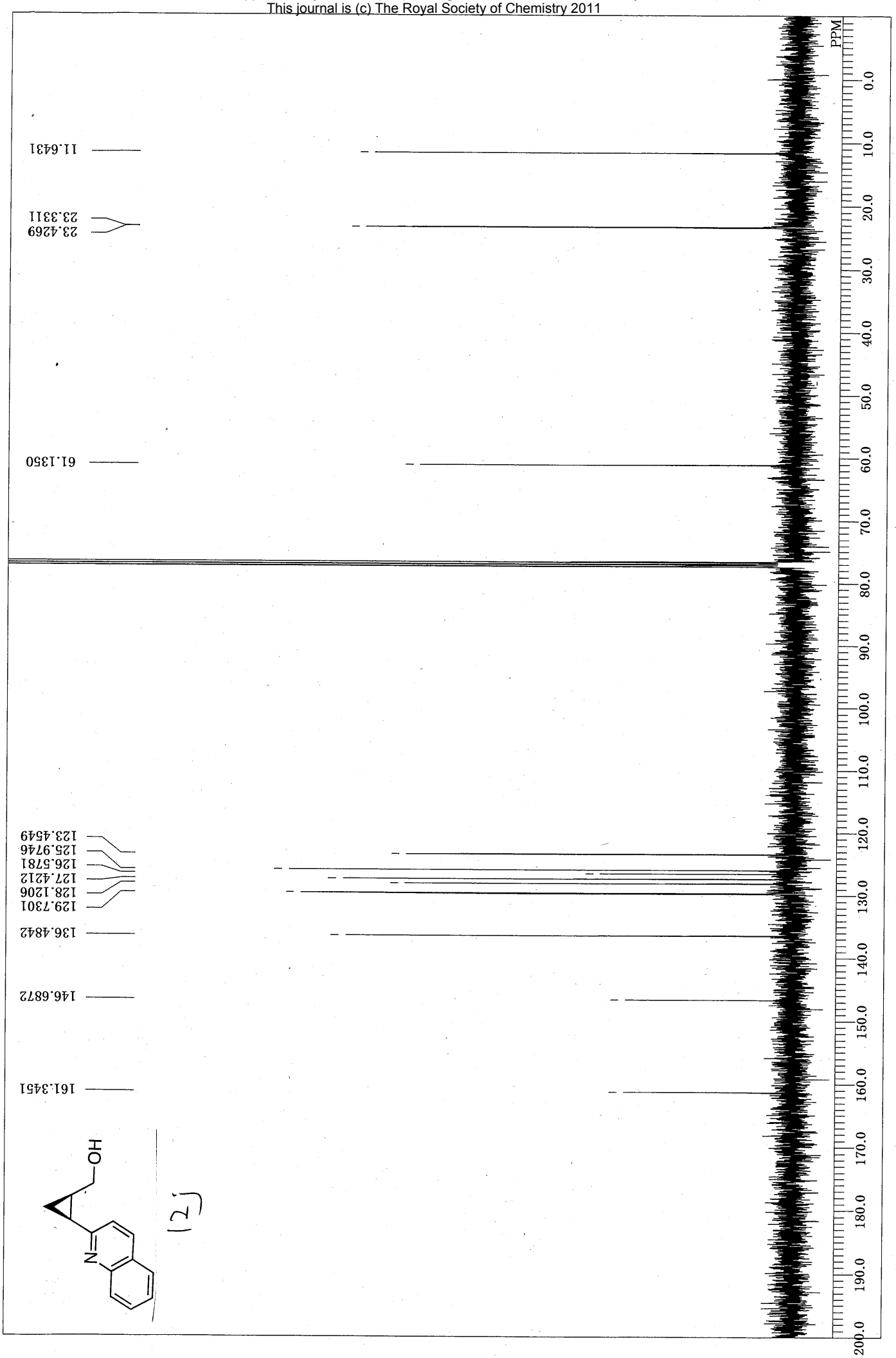
07KT5-44-1a(400,CDCl3)

07KT5-44-1a C(500,CDCl3)

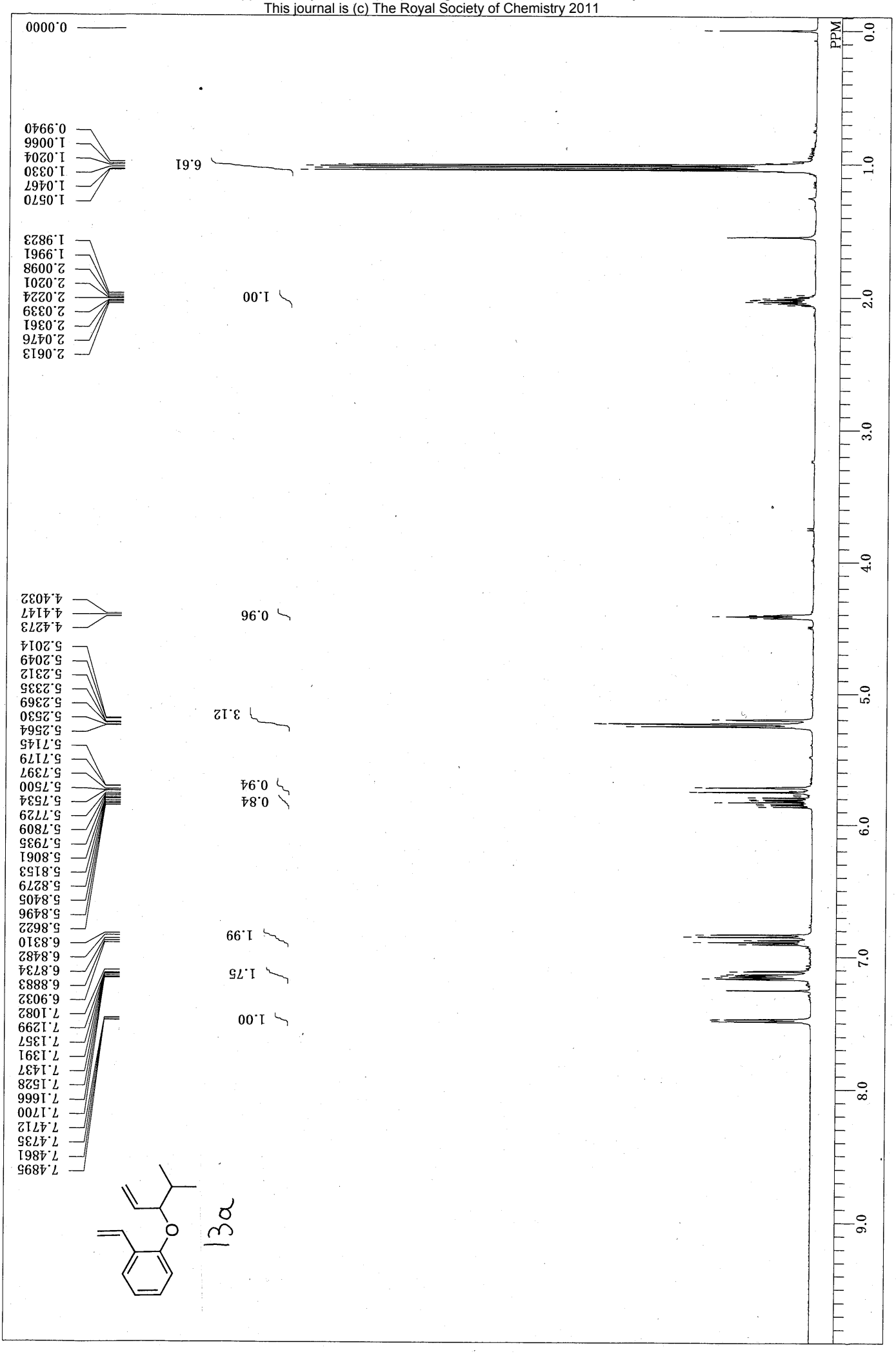


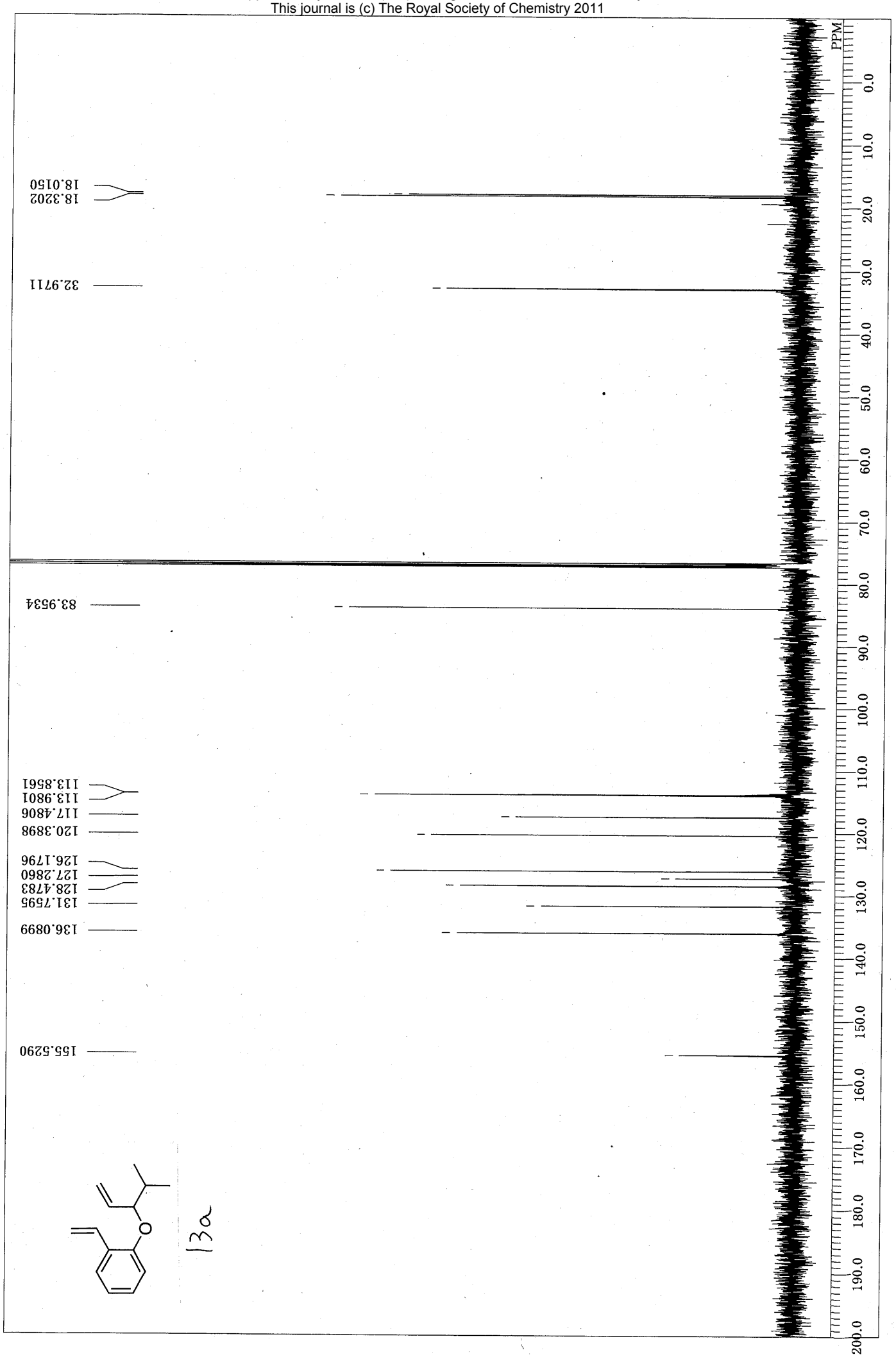


07KT5-95-2(400,CDCl3)

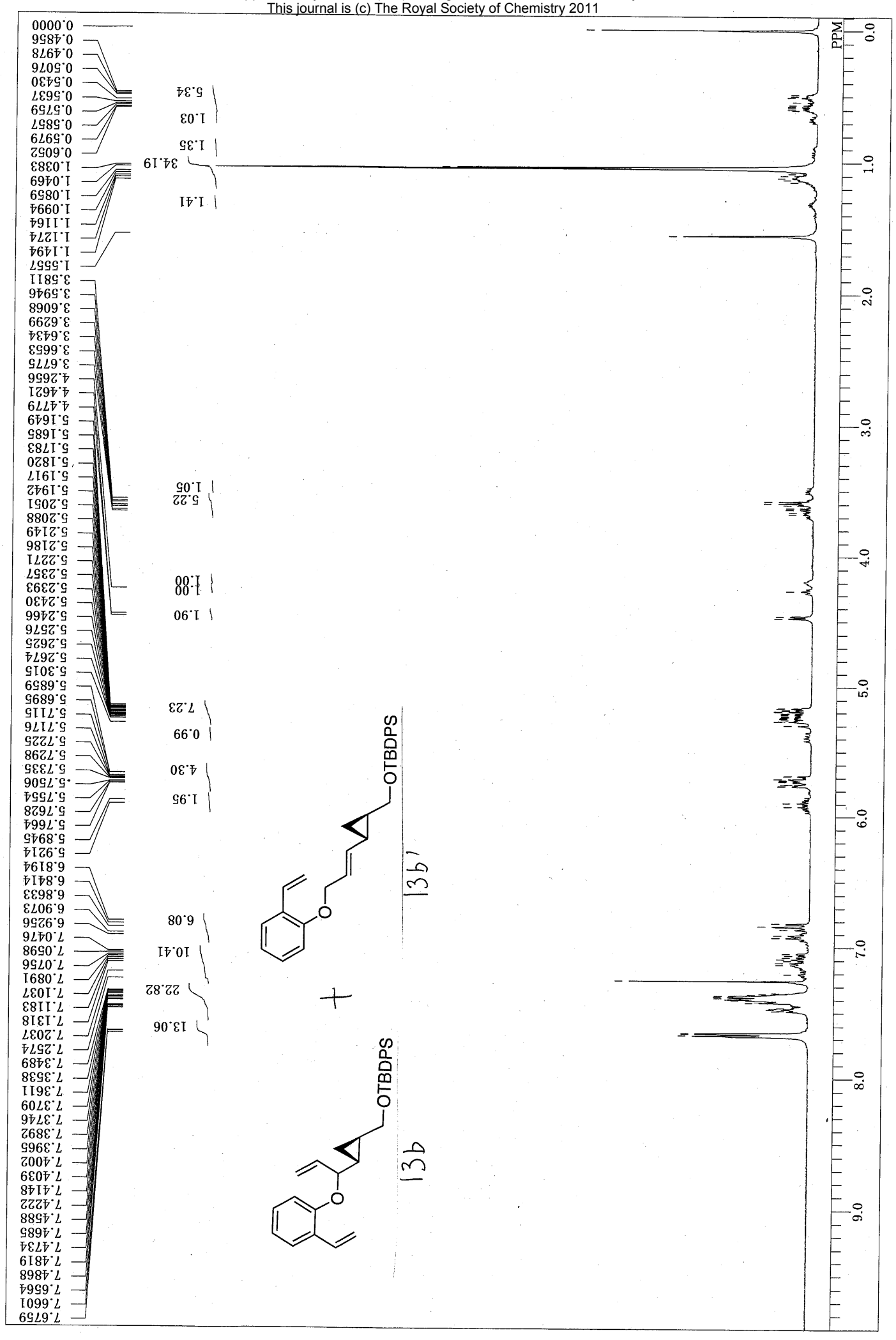


07KT5-95-1C(400,CDCl3)

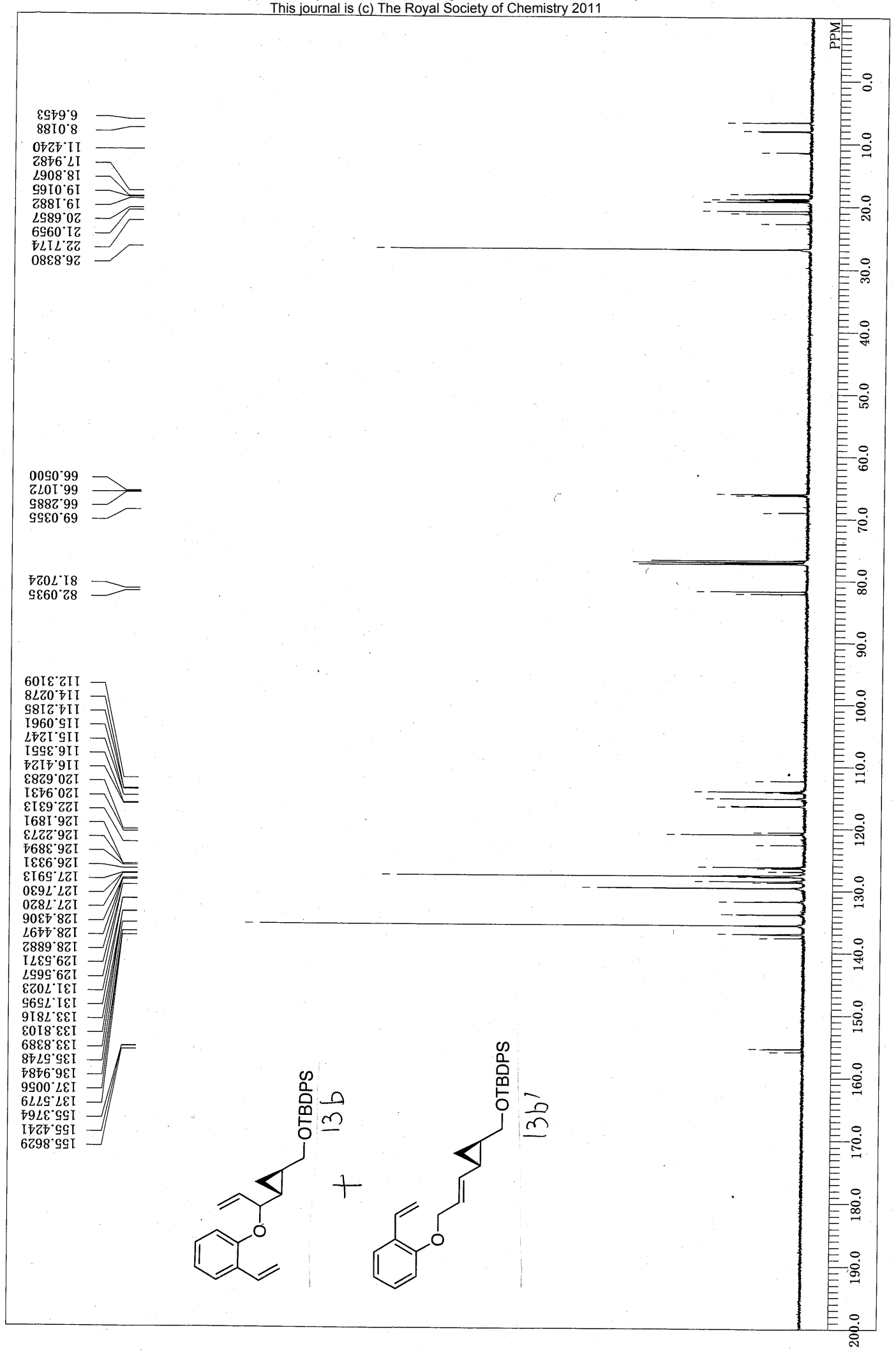

0.0000
0.9940
1.0066
1.0204
1.0330
1.0467
1.0570
1.9823
1.9961
2.0098
2.0201
2.0224
2.0339
2.0361
2.0476
2.0613
4.4032
4.4147
4.4273
5.2014
5.2049
5.2312
5.2335
5.2369
5.2530
5.2564
5.7145
5.7179
5.7397
5.7500
5.7534
5.7729
5.7809
5.7935
5.8061
5.8153
5.8279
5.8405
5.8496
5.8622
6.8310
6.8482
6.8734
6.8883
6.9032
7.1082
7.1299
7.1357
7.1391
7.1437
7.1528
7.1666
7.1700
7.4712
7.4735
7.4861
7.4895
6.61
1.00
0.96
3.12
0.94
0.84
1.99
1.75
1.00
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
13a
07KT4-100-1(500,CDCl3)



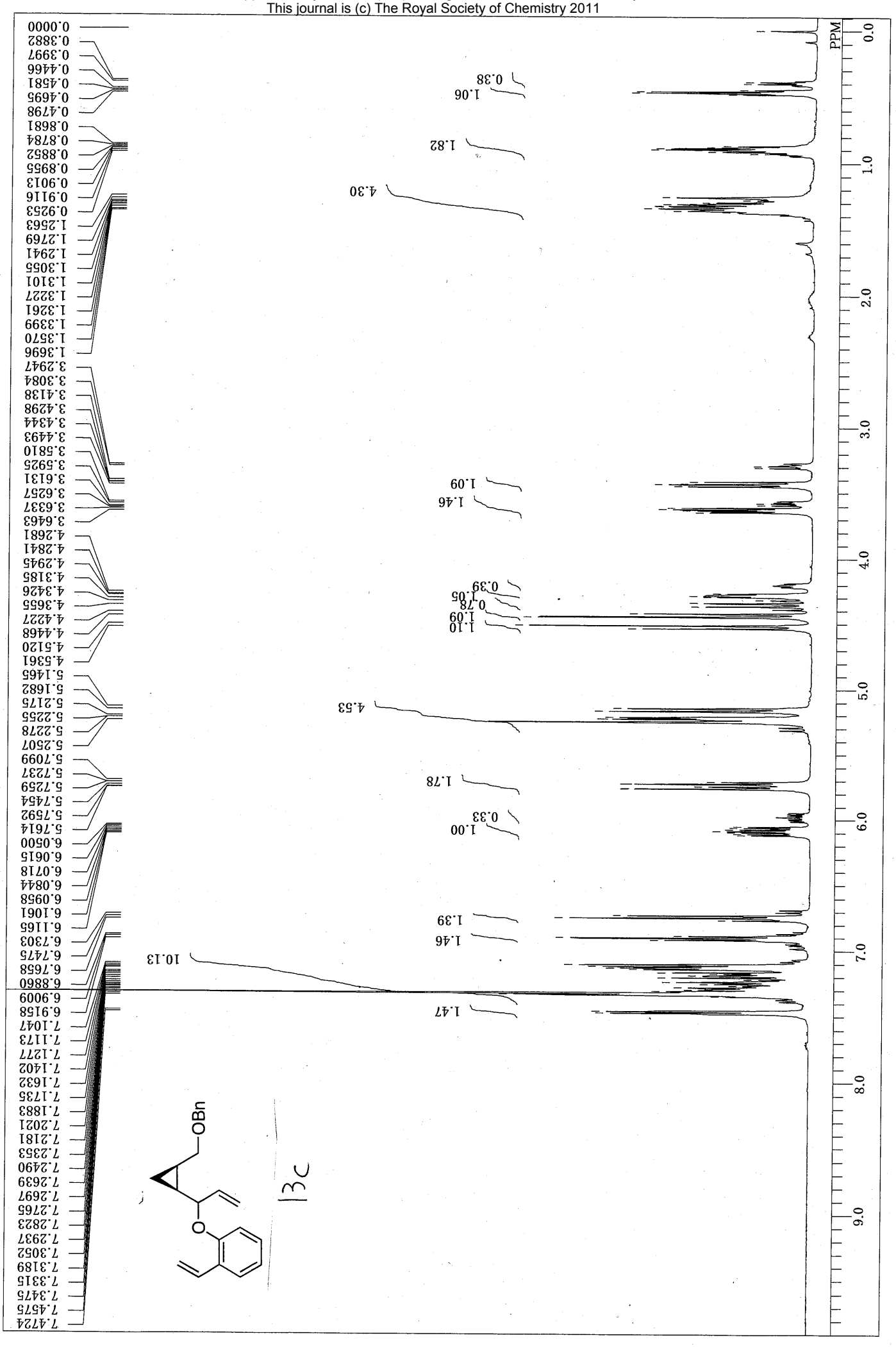
07KT4-100-1C(500,CDCl3)

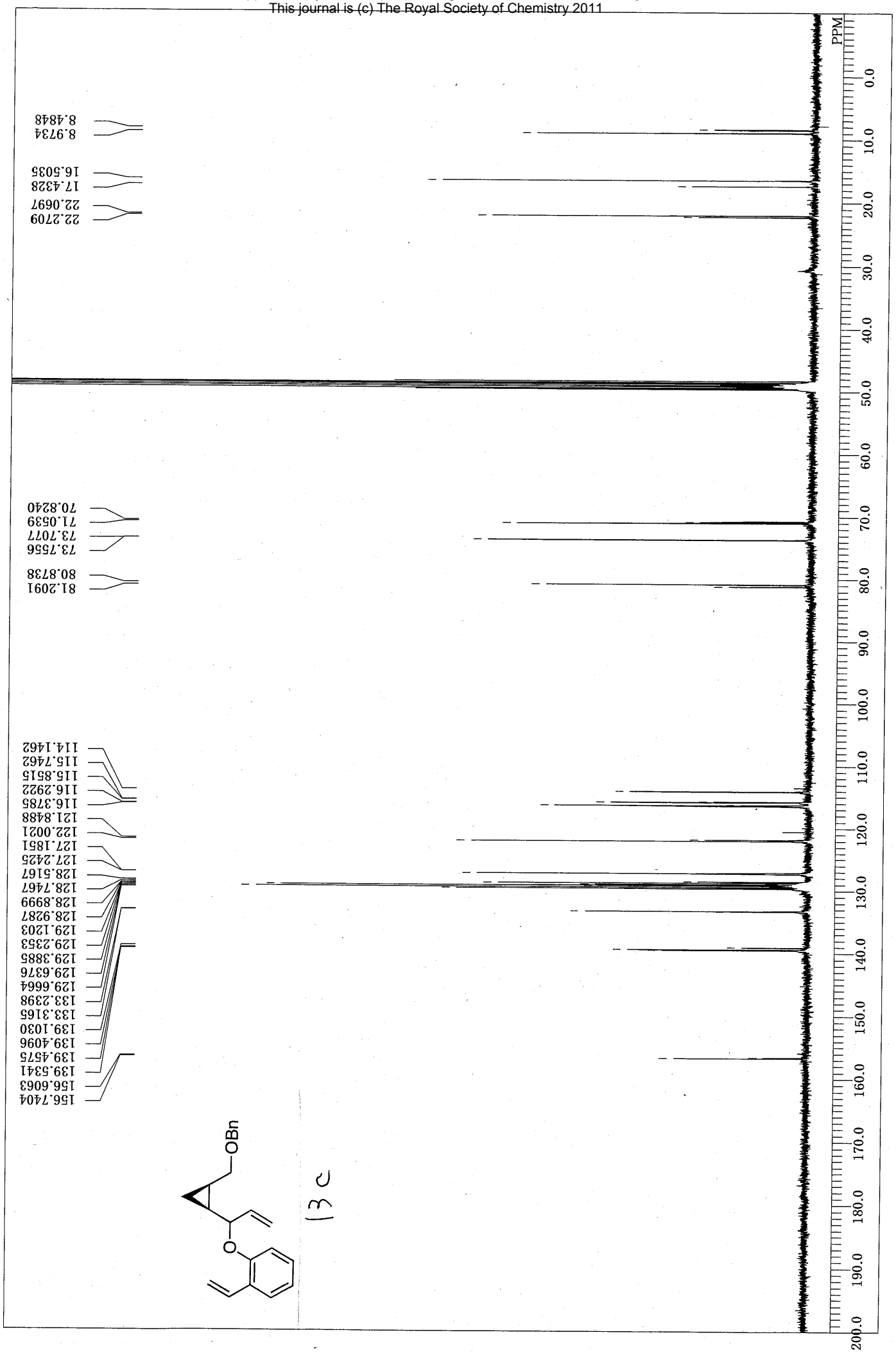


07KT5-78-2(400MHz,CDCl3)

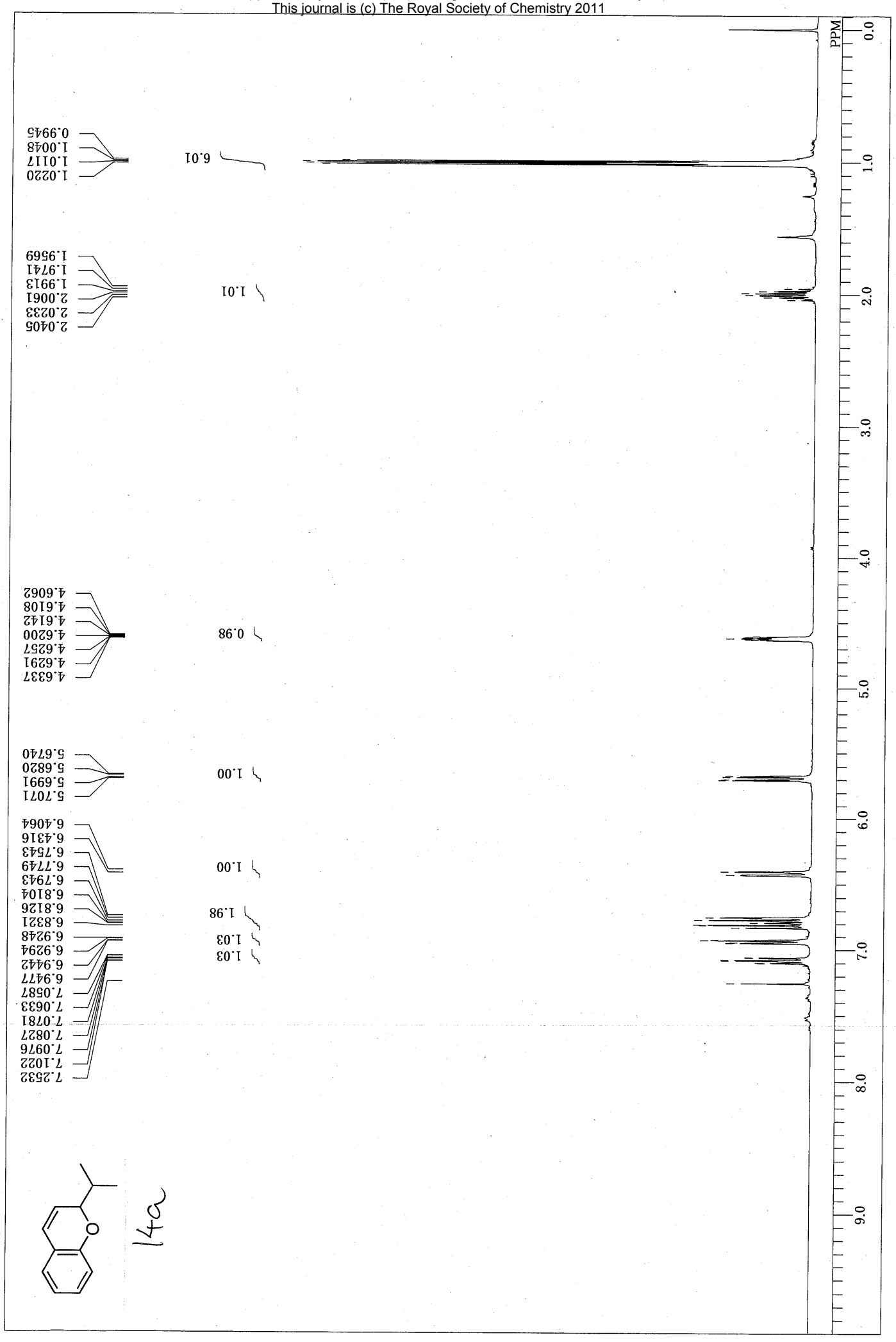


07KT5-78-1C(500,CDCl3)

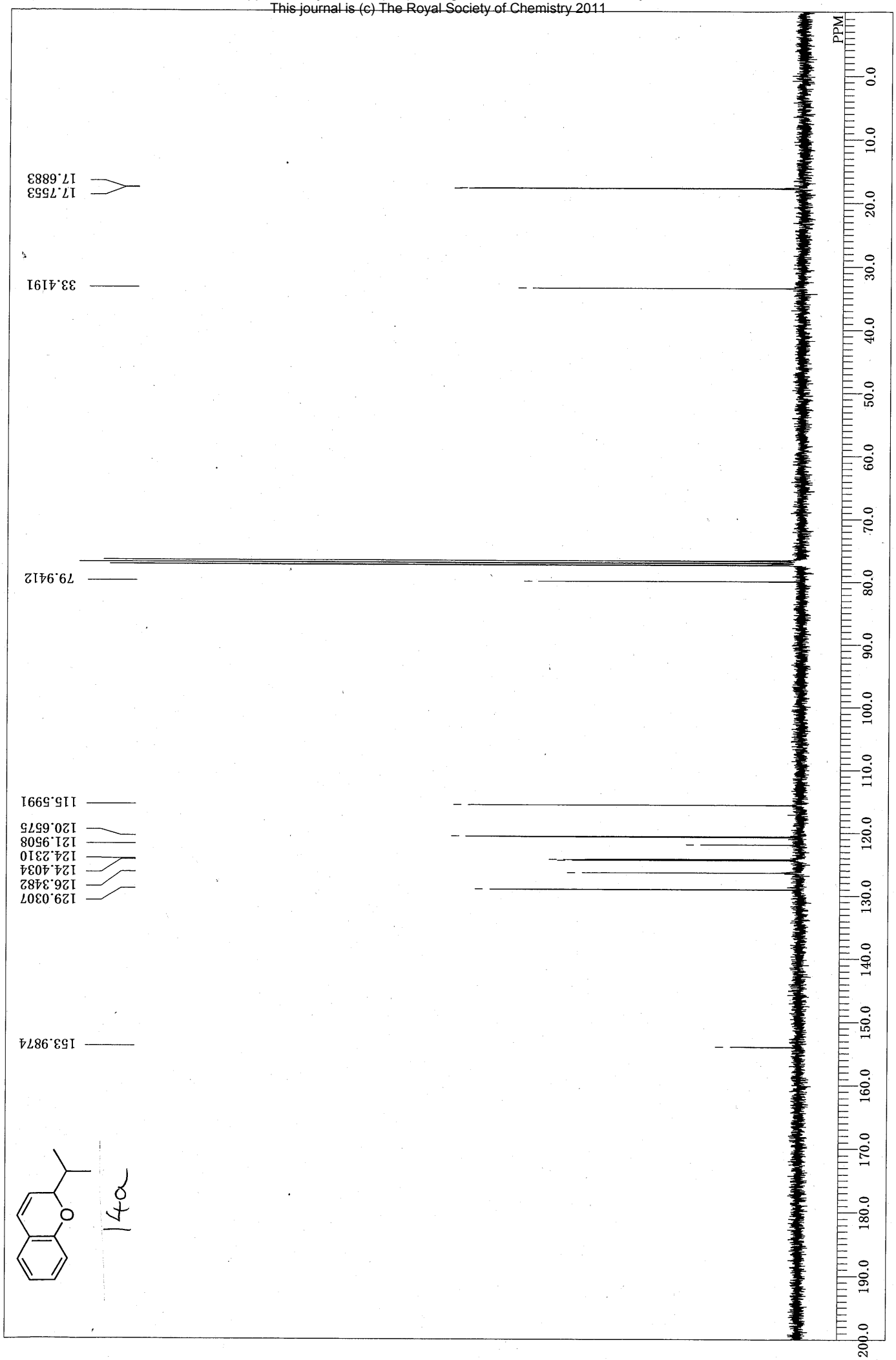

07KT7-13-1(500,CDCl3)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.13
4.53
4.30
1.82
1.78
1.47
1.46
1.39
1.10
1.09
1.06
1.05
1.00
0.78
0.39
0.38
0.33
OBn
O
13c



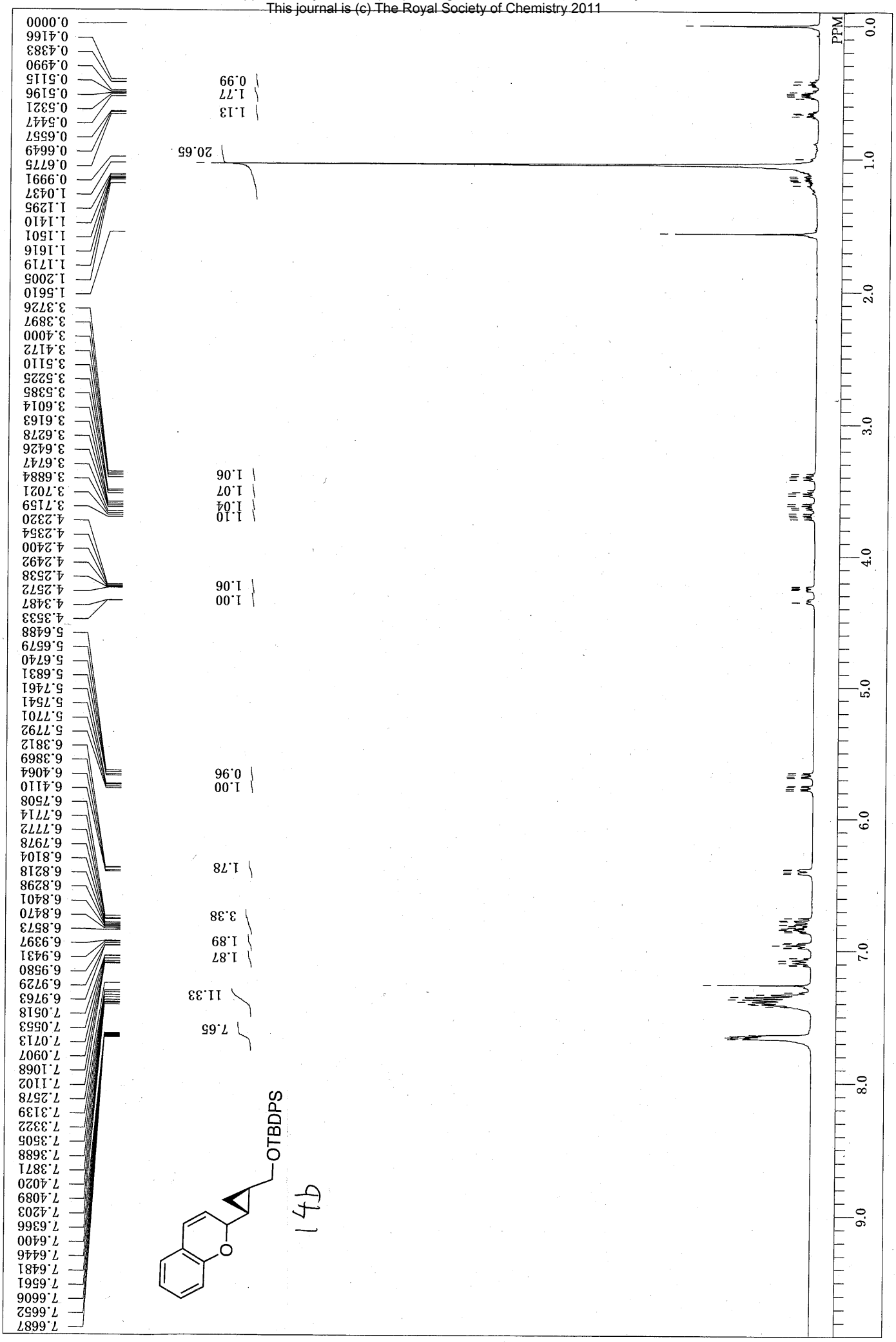
07KT7-13-1C (400,CD3OD)

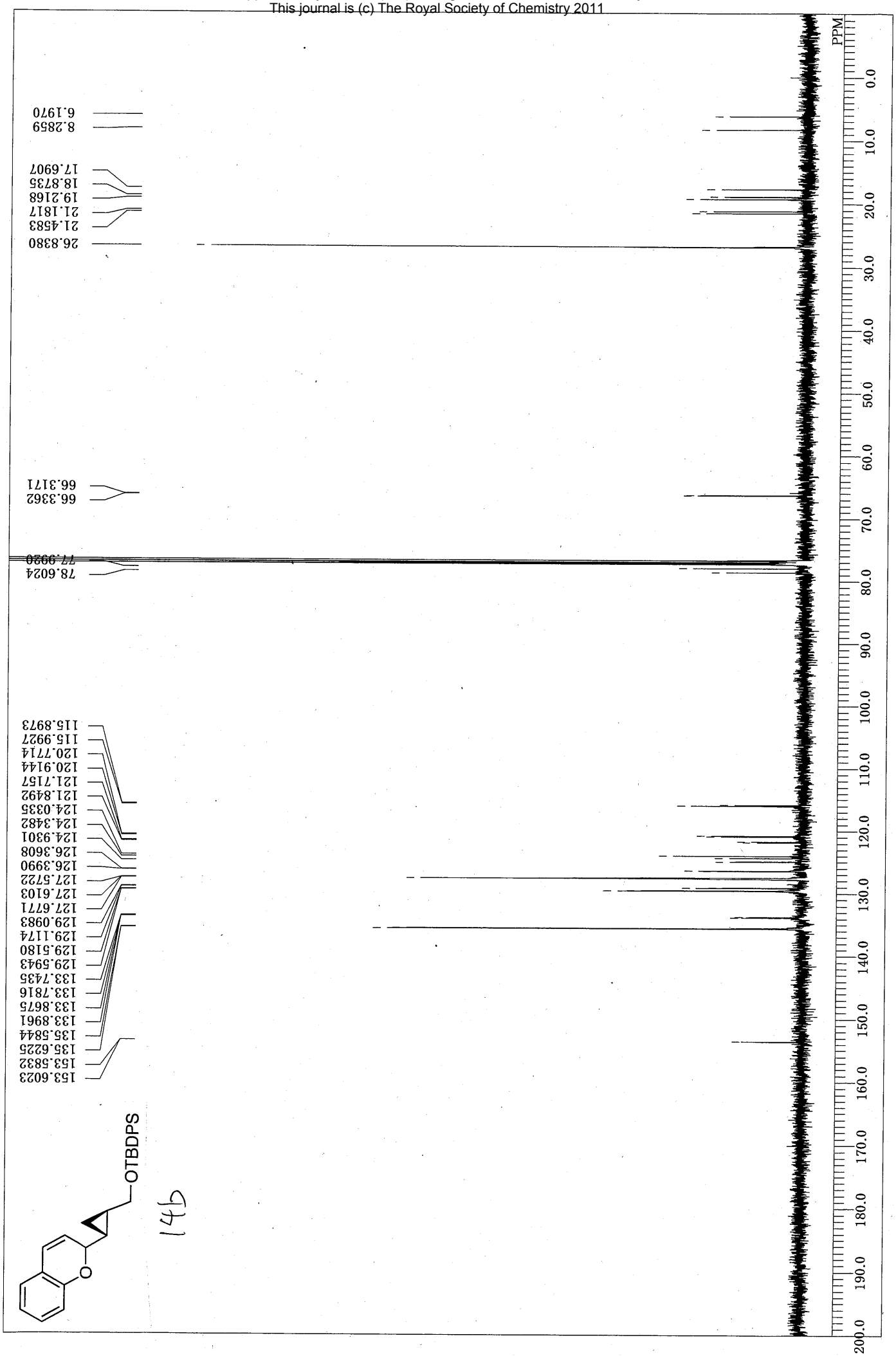


07KT5-84-2(400,CDCl3)

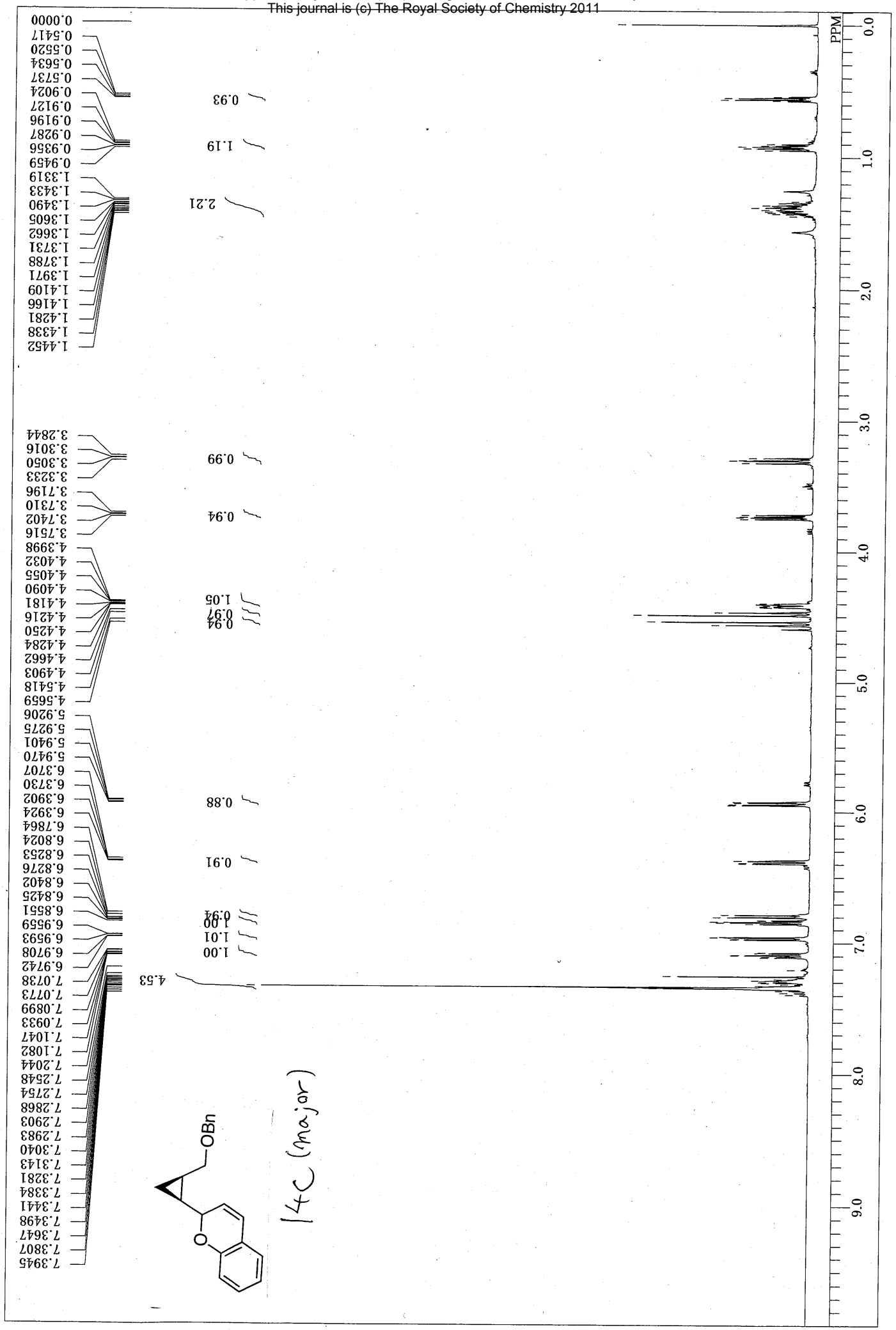


07KT5-84-2C(400,CDCl3)

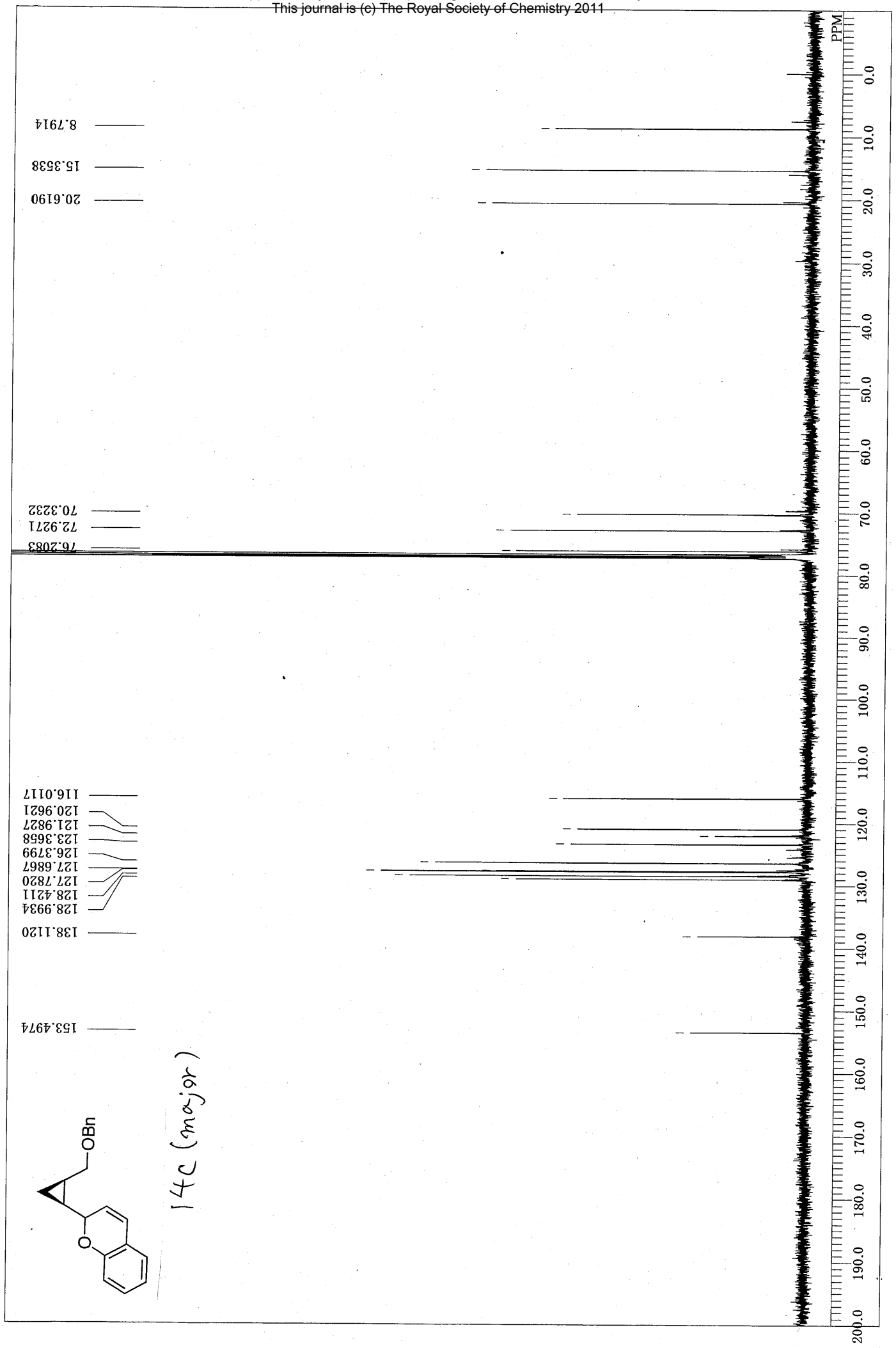

07KT5-82-2(400,CDCl3)
OTBDPS
q71
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
0.99
1.77
1.13
20.65
1.06
1.07
1.04
1.10
1.06
1.00
0.96
1.00
1.78
3.38
1.89
1.87
11.33
7.65



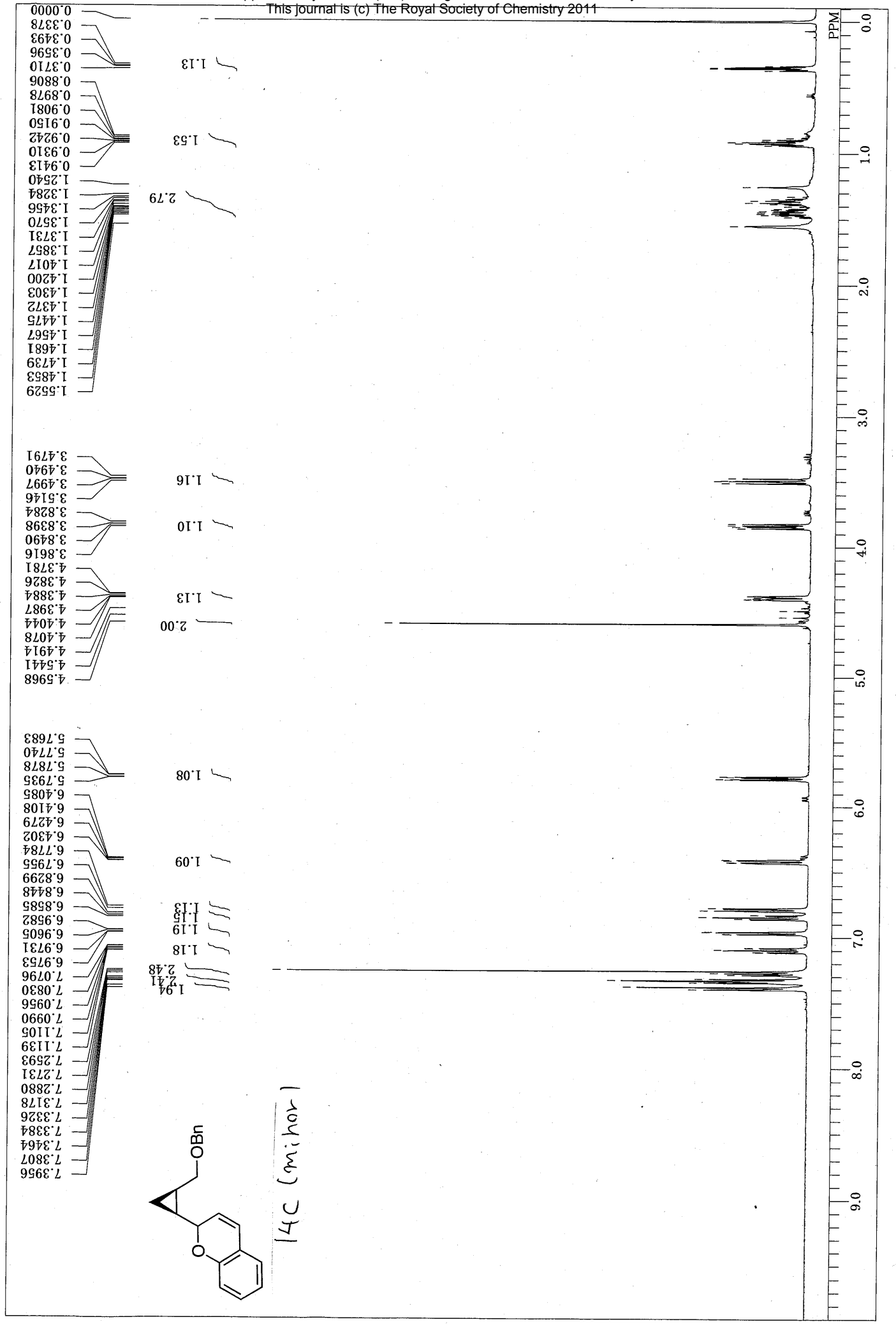
07KT5-82-1C(500,CDCl3)



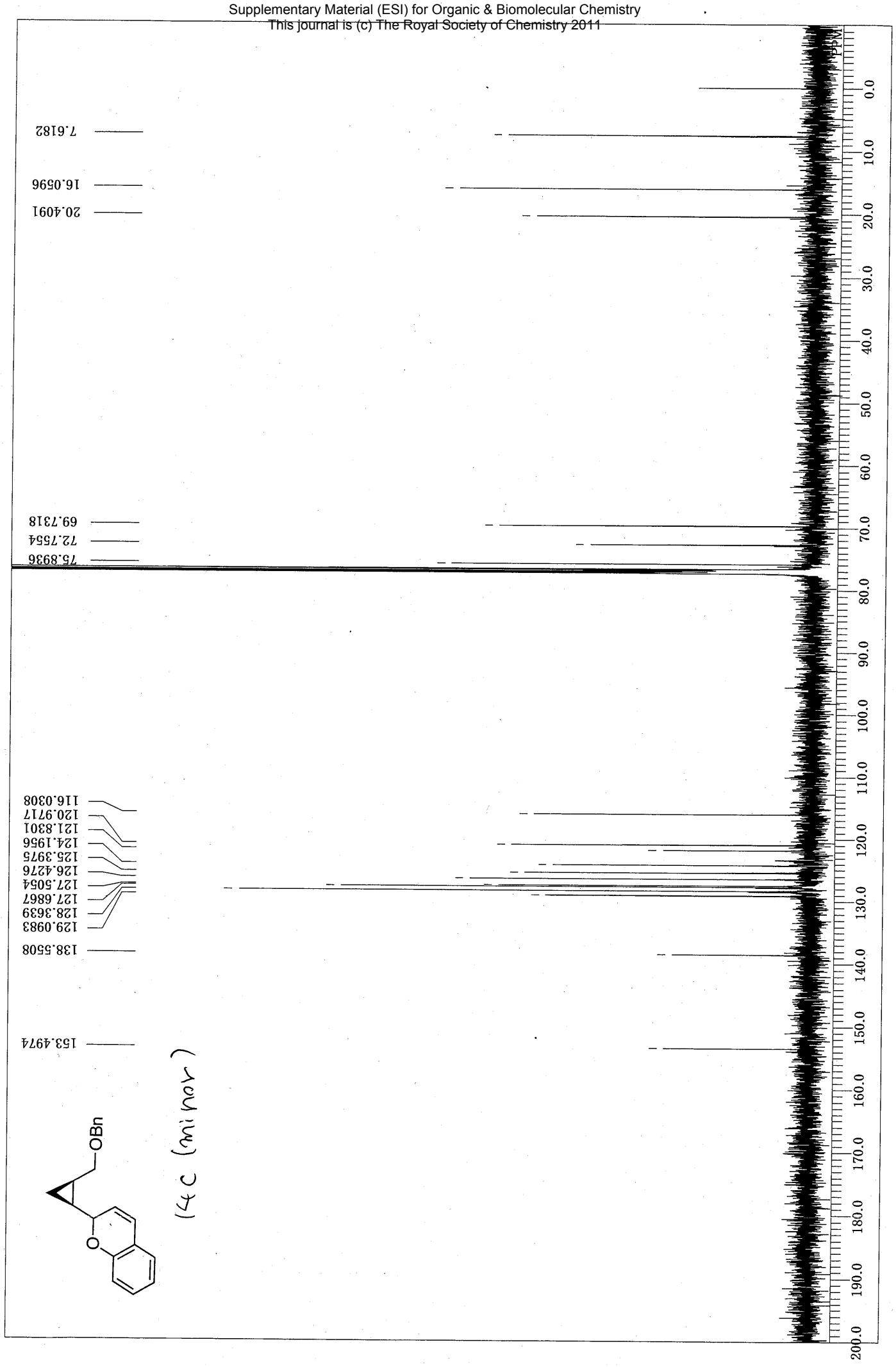
07KT7-18-1(500,CDCl3)

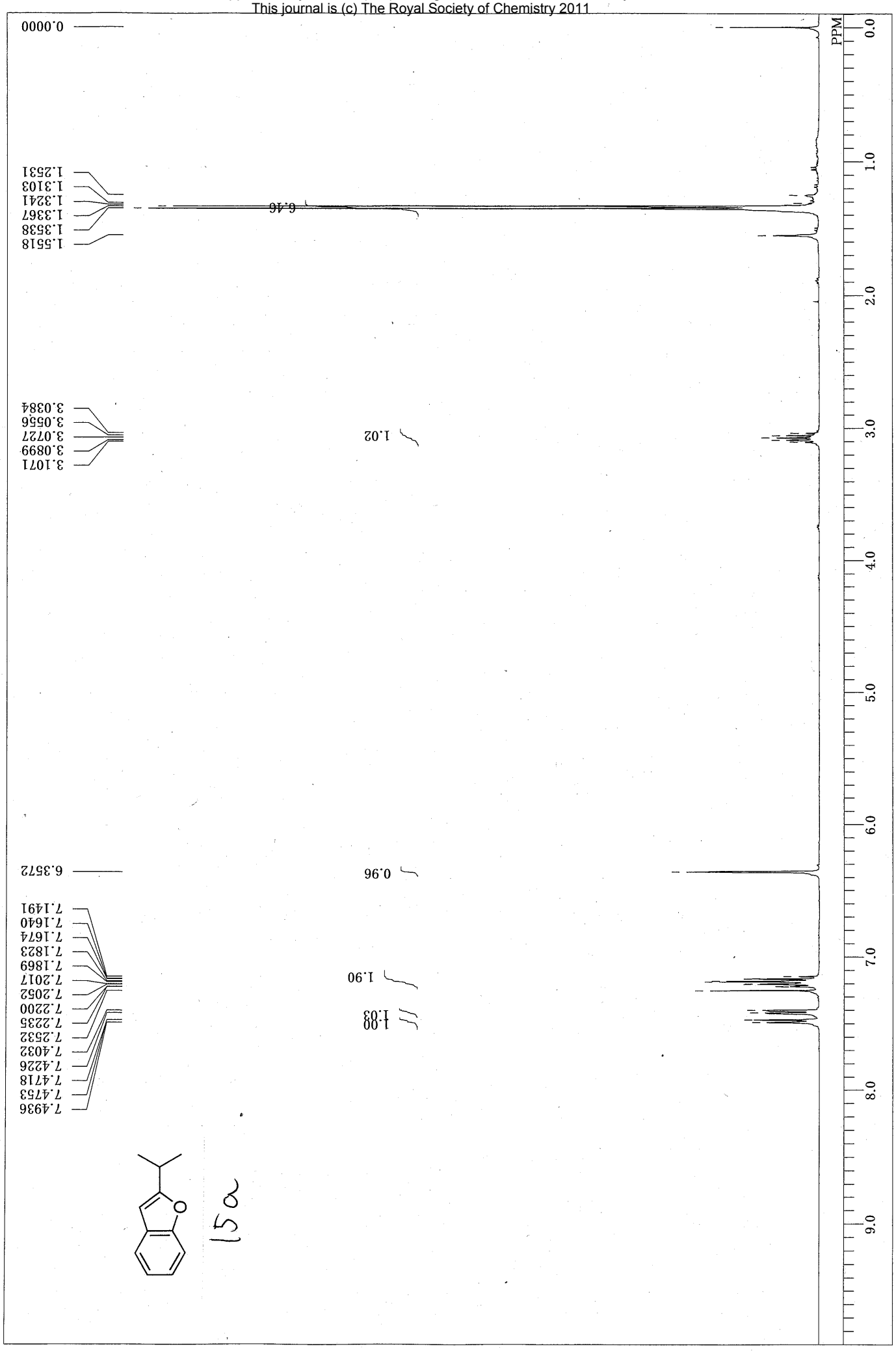


07KT7-18-1C(500,CDCl3)



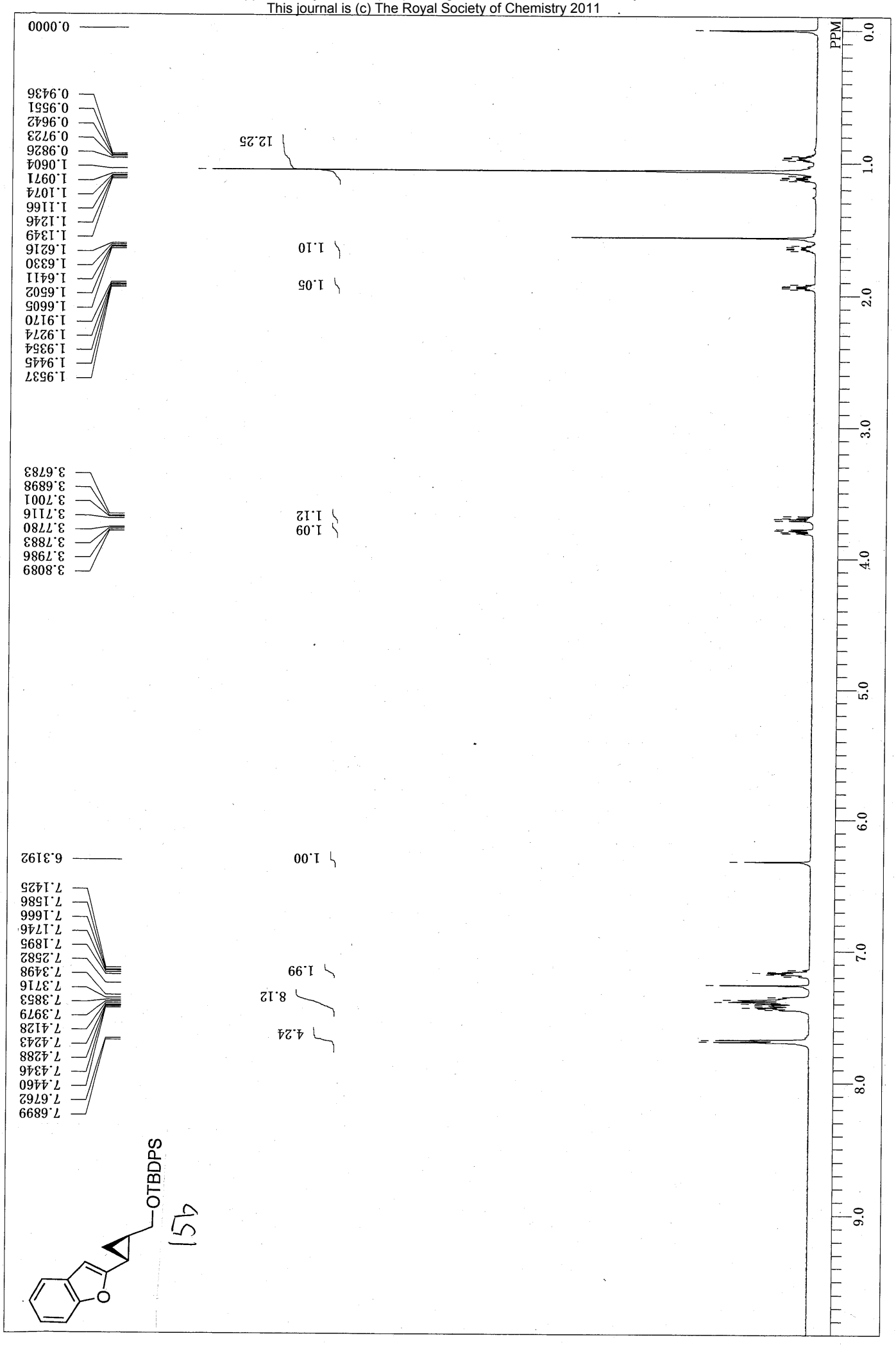
07KT7-18-2a(500,CDCl3)



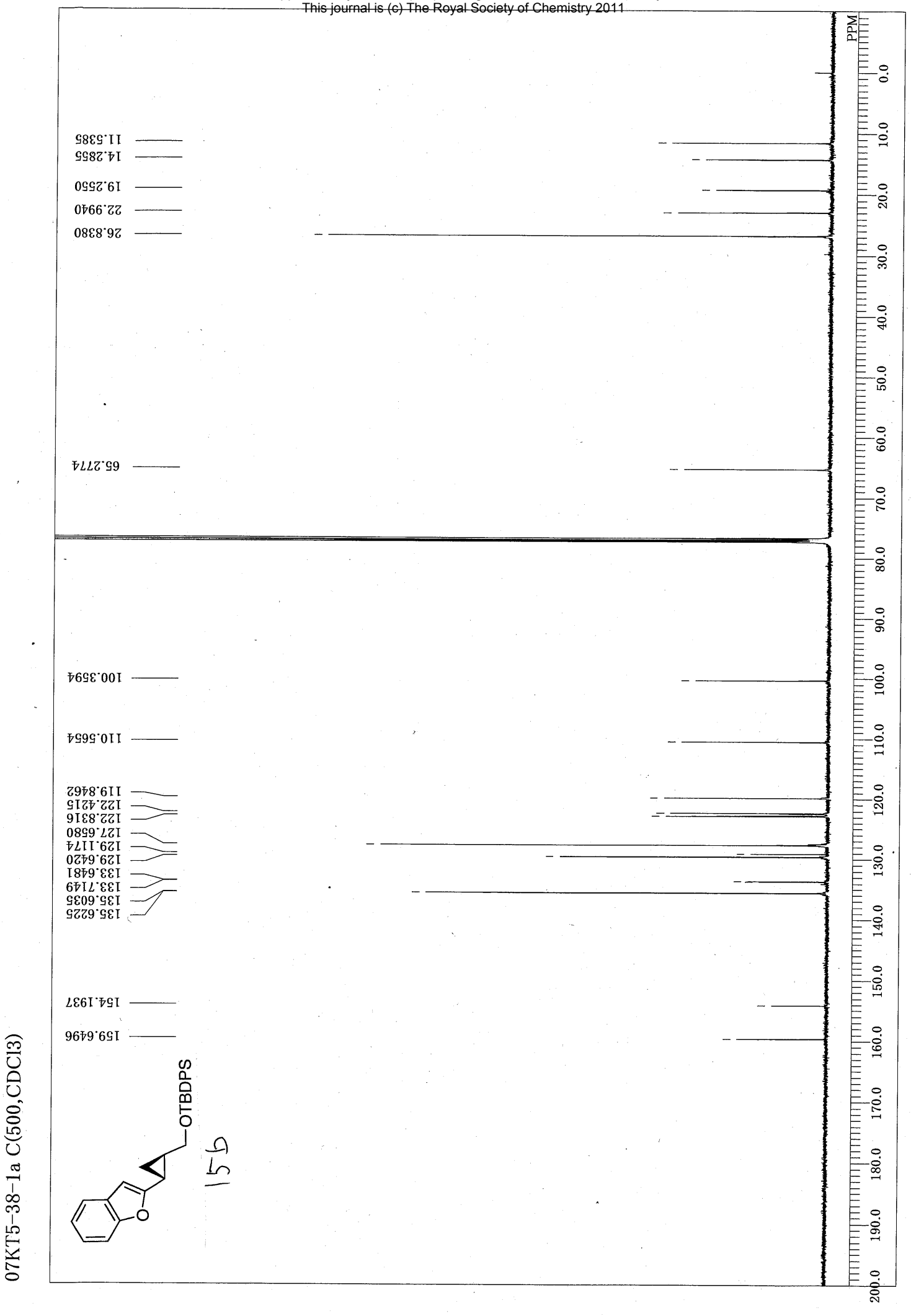


15a

07KT5-19-2(500,CDCl3)_



07KT5-38-1a(500,CDCl3)


07KT5-38-1a C(500,CDCl3)
11.5385
14.2855
19.2550
22.9940
26.8380
65.2774
100.3594
110.5654
119.8462
122.4215
122.8316
127.6580
129.1174
129.6420
133.6481
133.7149
135.6035
135.6225
154.1937
159.6496
OTBDPS
15g
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
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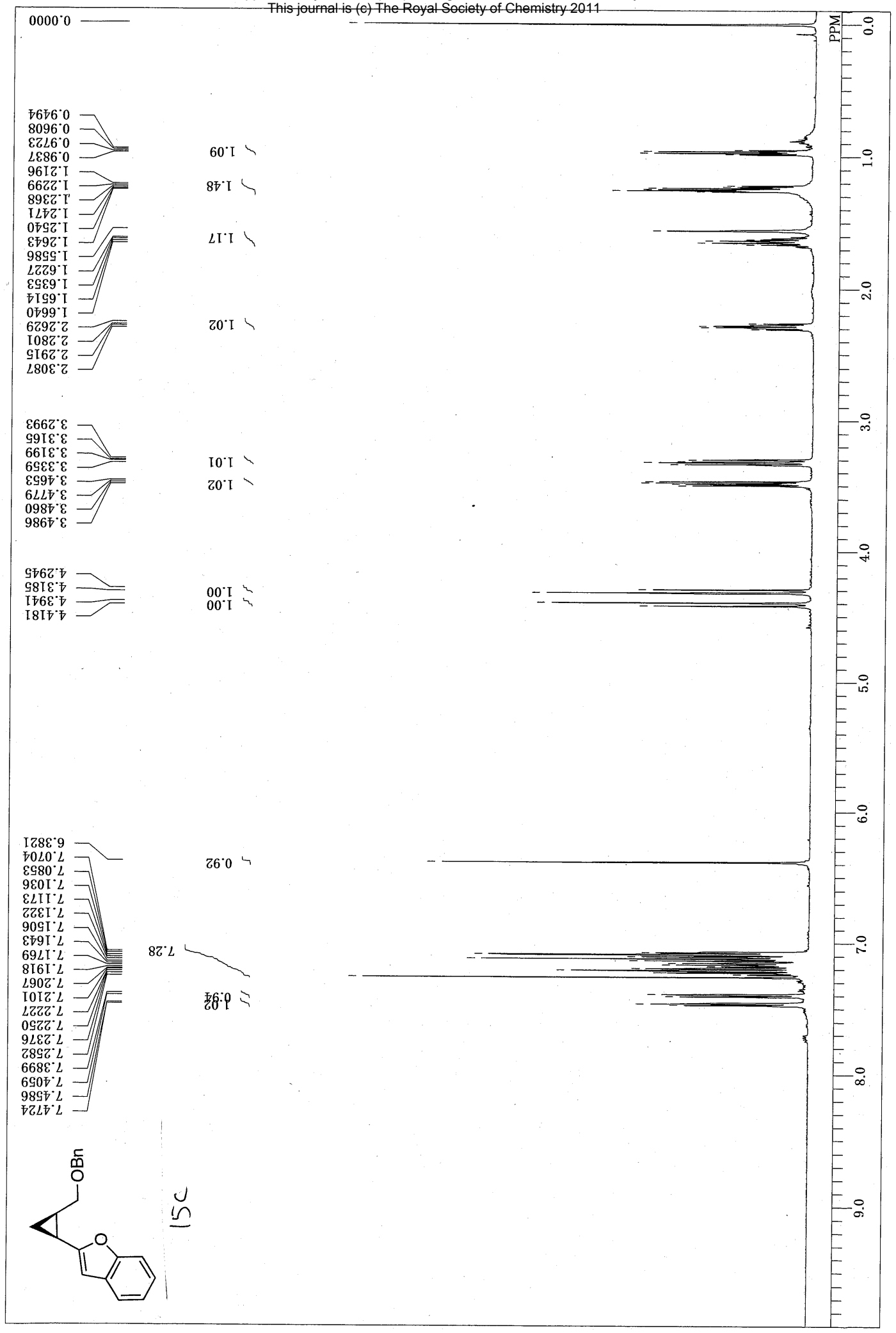
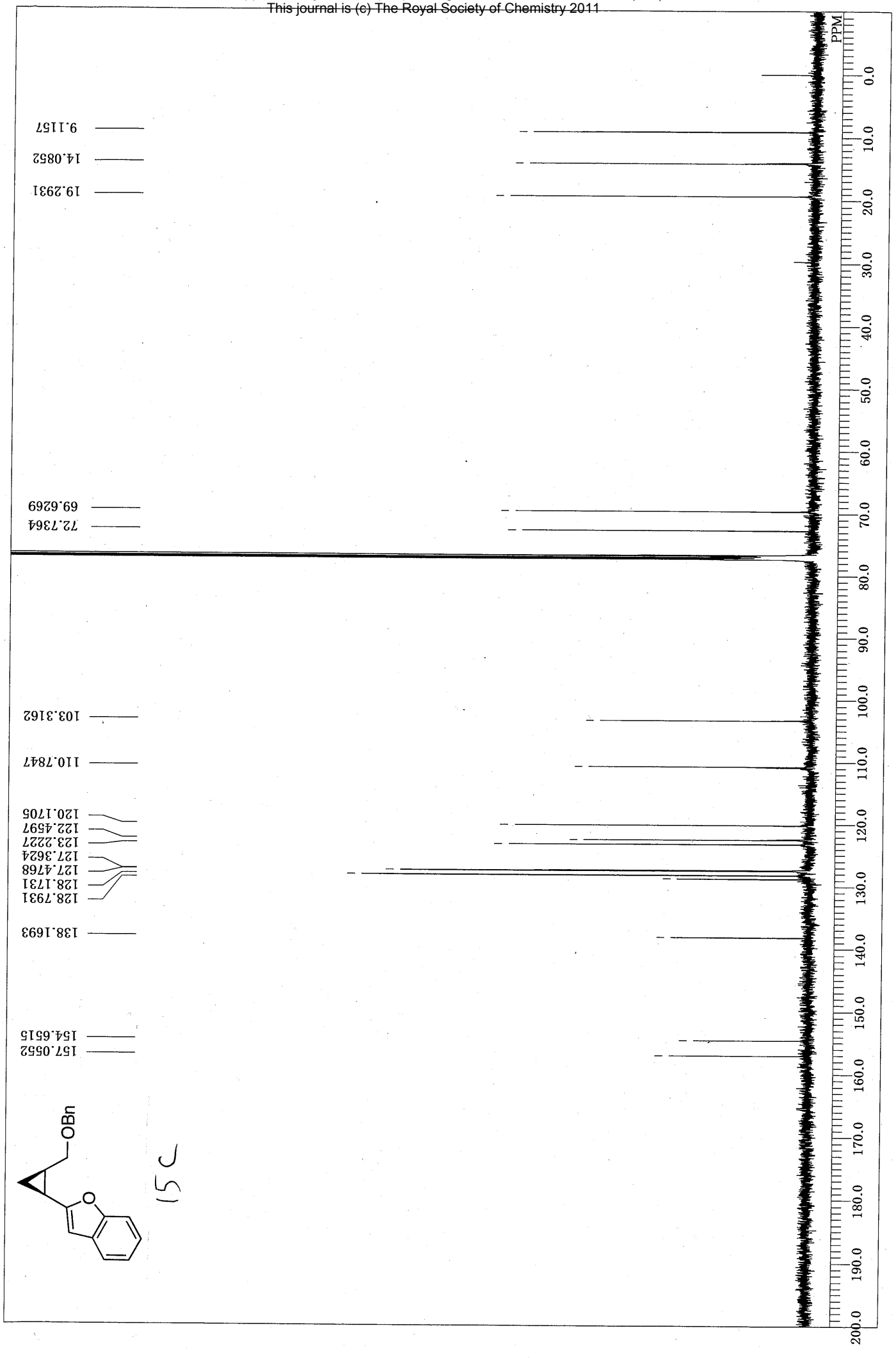
150.0
160.0
170.0
180.0
190.0
200.0



07KT7-17-1a (500, CDCl3)


07KT7-17-1aC(500,CDCl3)
9.1157
14.0852
19.2931
69.6269
72.7364
103.3162
110.7847
120.1705
122.4597
123.2227
127.3624
127.4768
128.1731
128.7931
138.1693
154.6515
157.0552
OBn
O
15C
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
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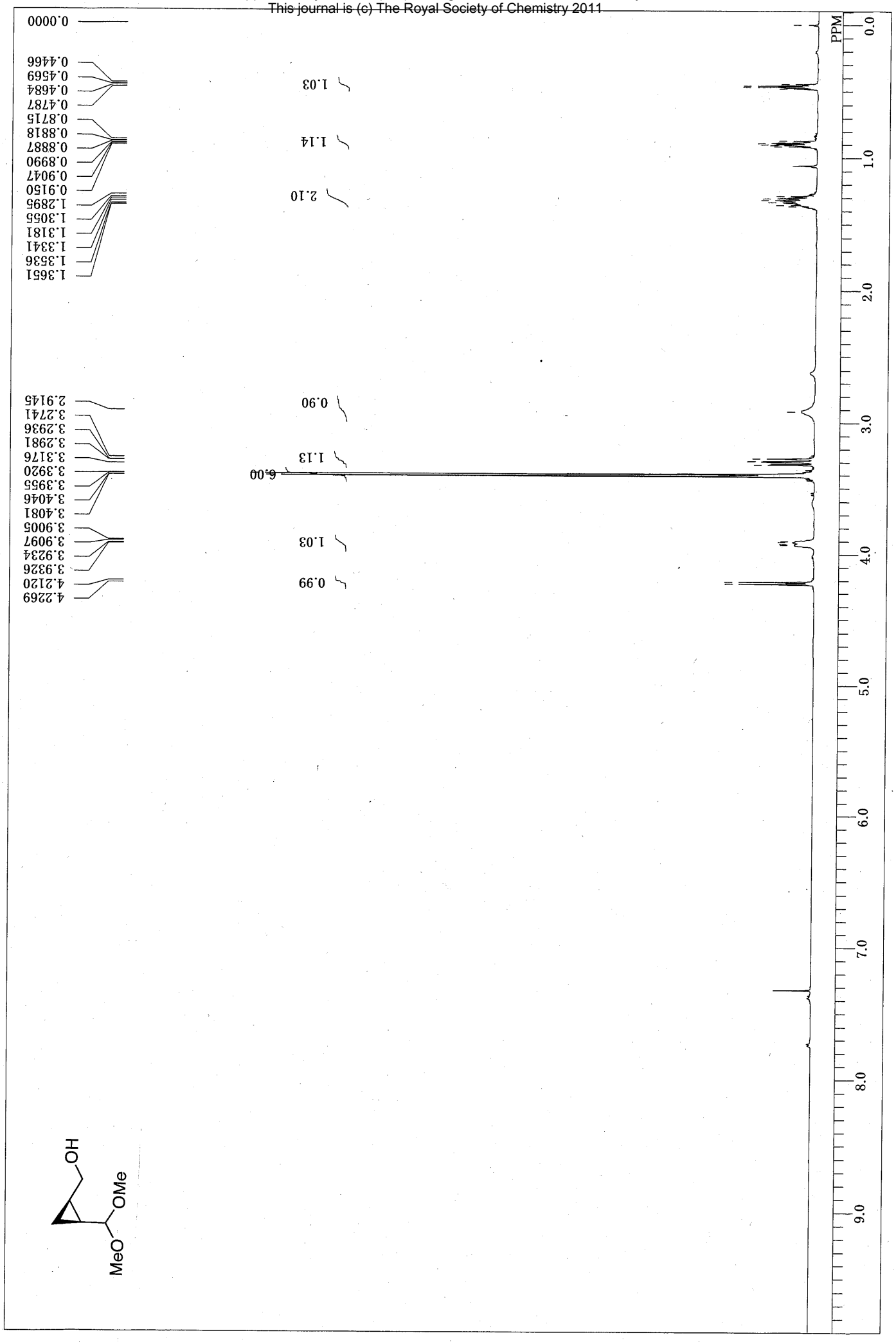
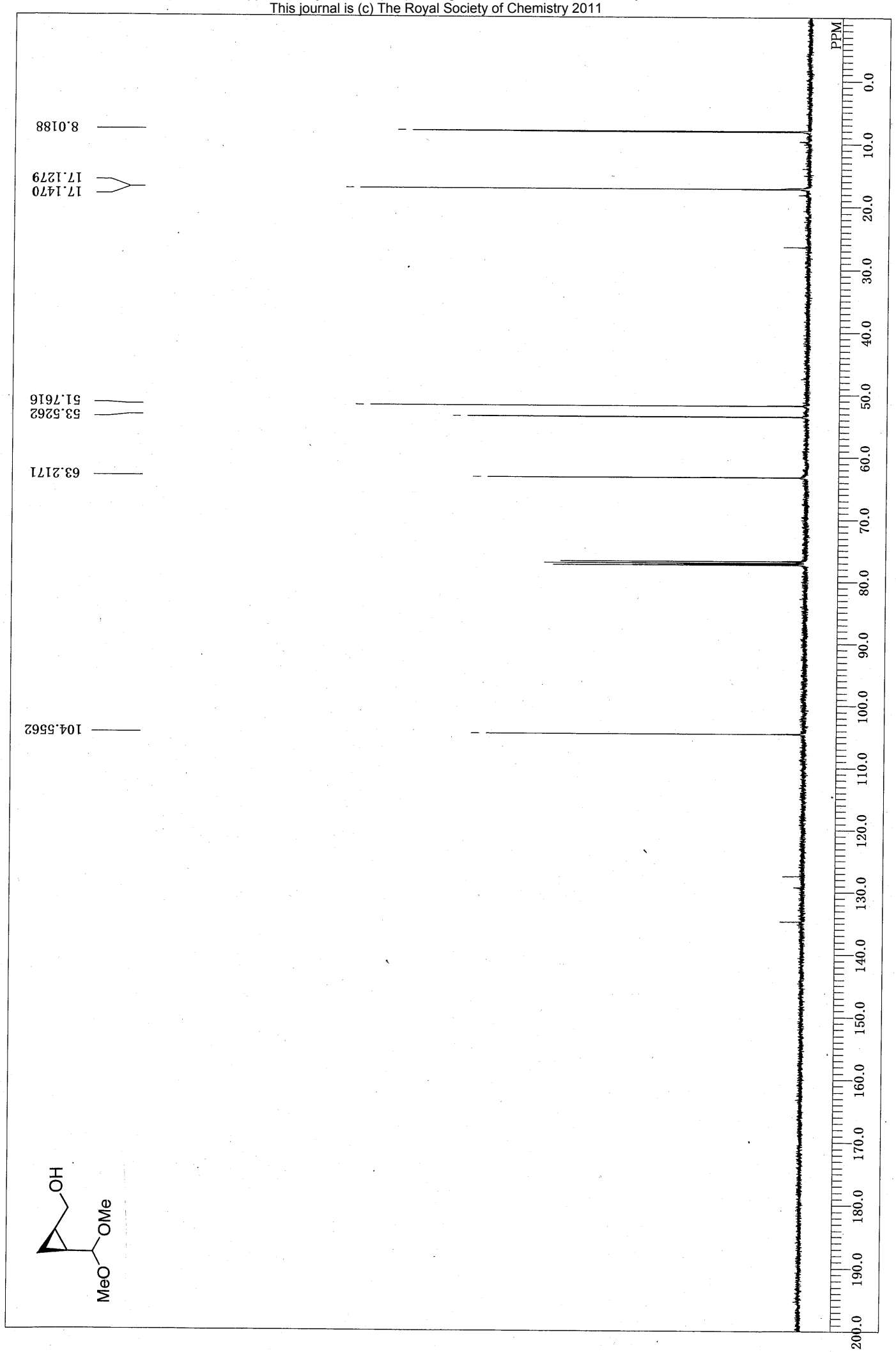
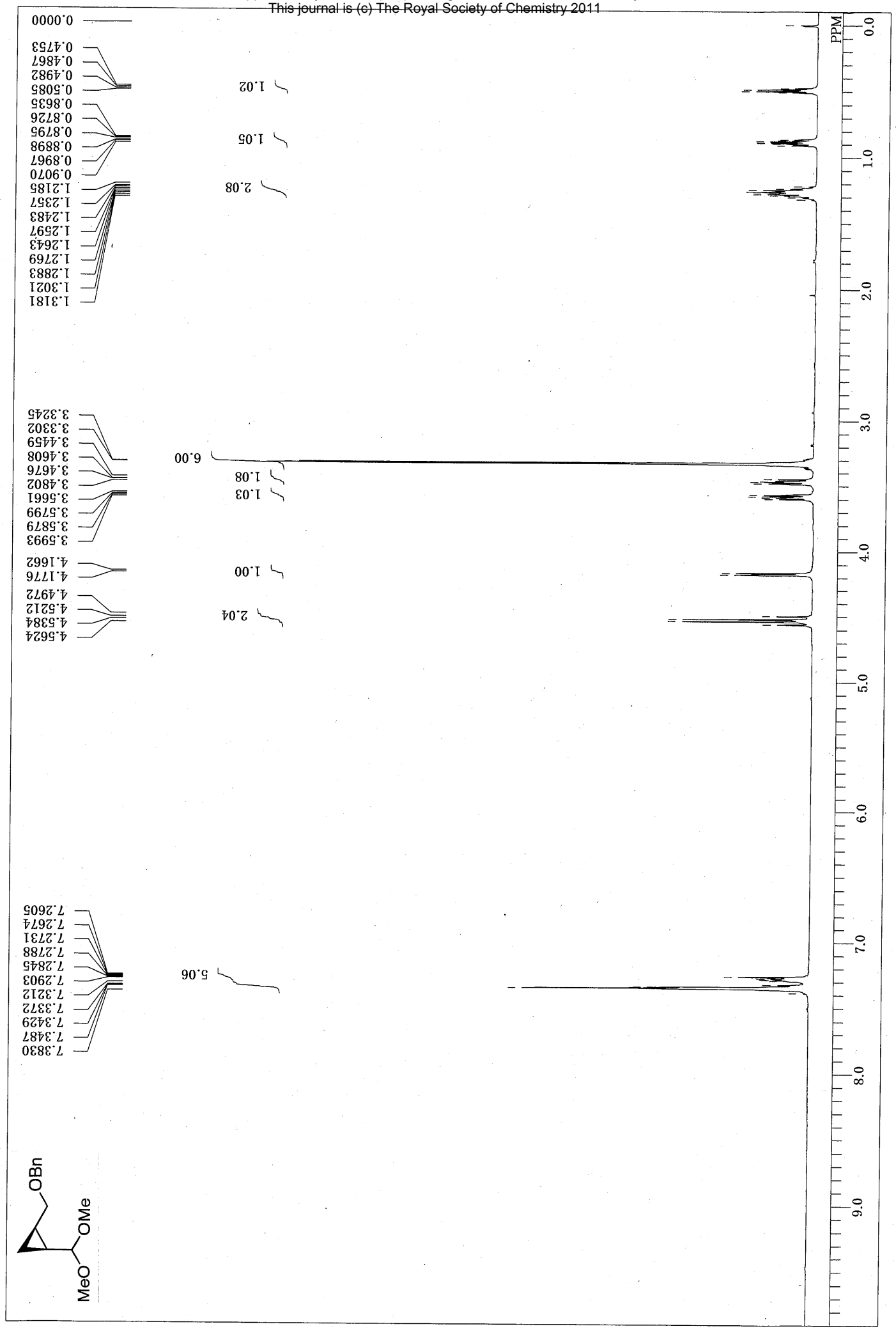
150.0
160.0
170.0
180.0
190.0
200.0



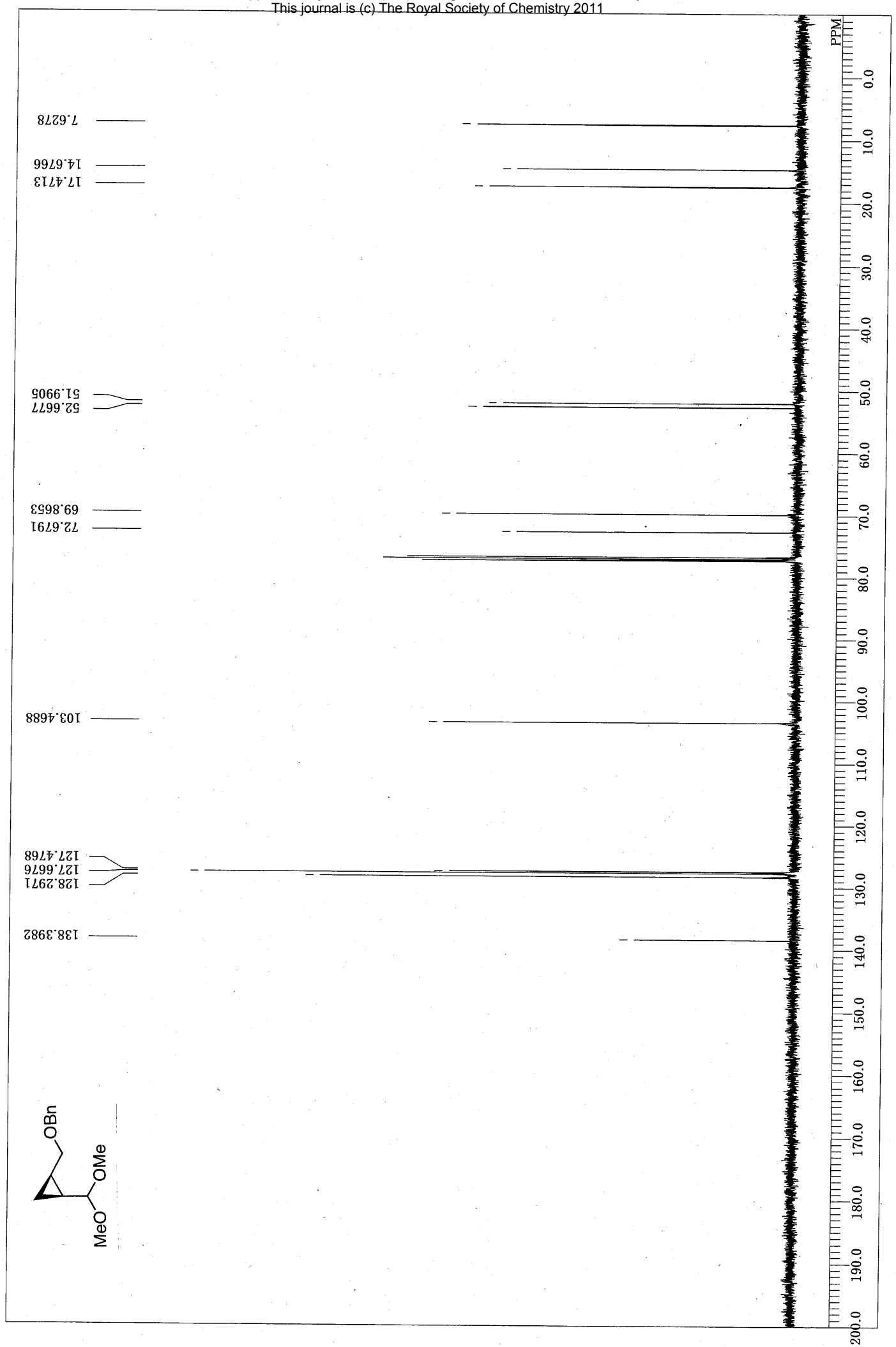
07KT6-99-1(500,CDCl3)



07KT6-99-1C(500,CDCl3)



07KT6-100-1(500,CDCl3)


07KT6-100-1C(500,CDCl3)
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
7.6278
14.6766
17.4713
51.9905
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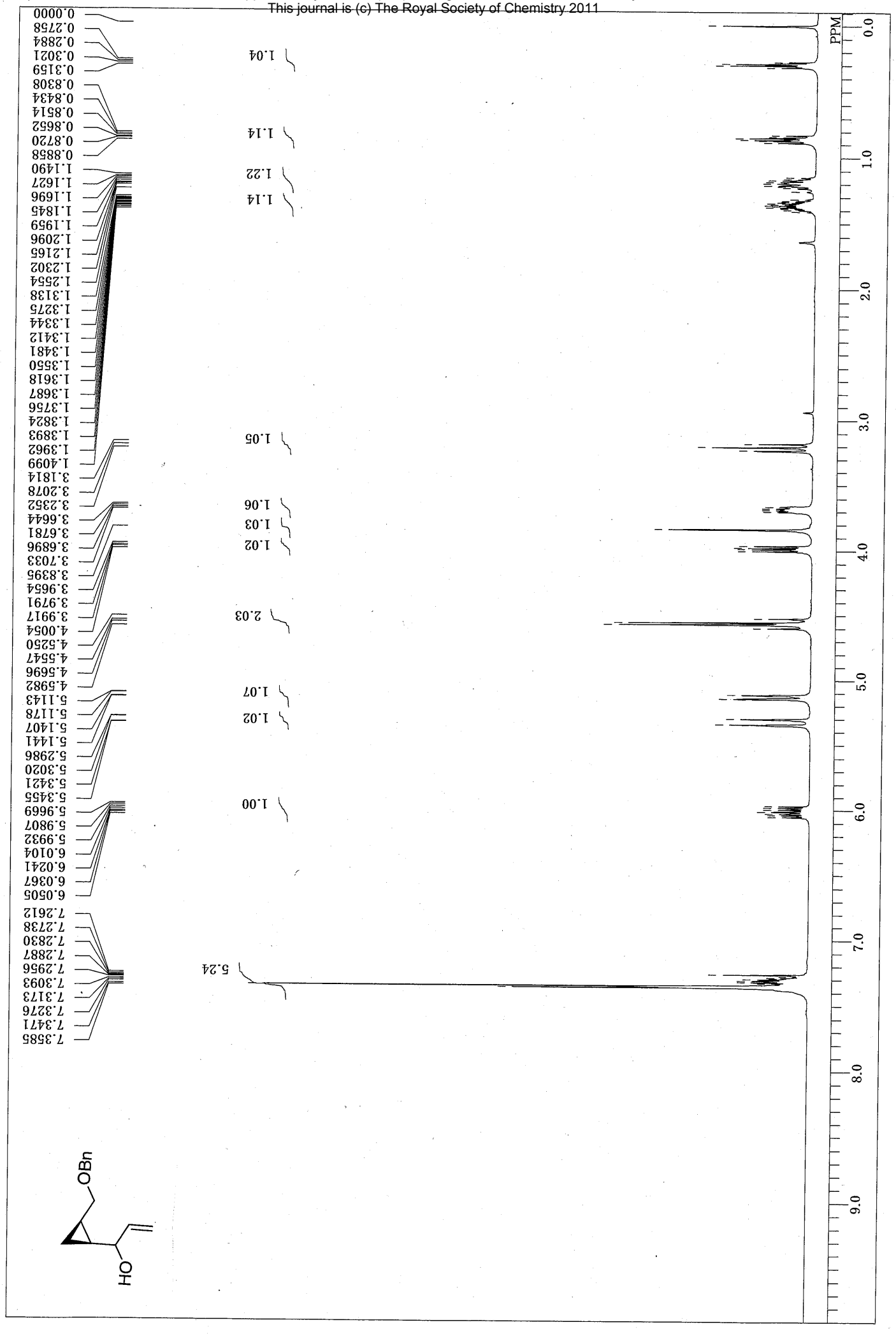
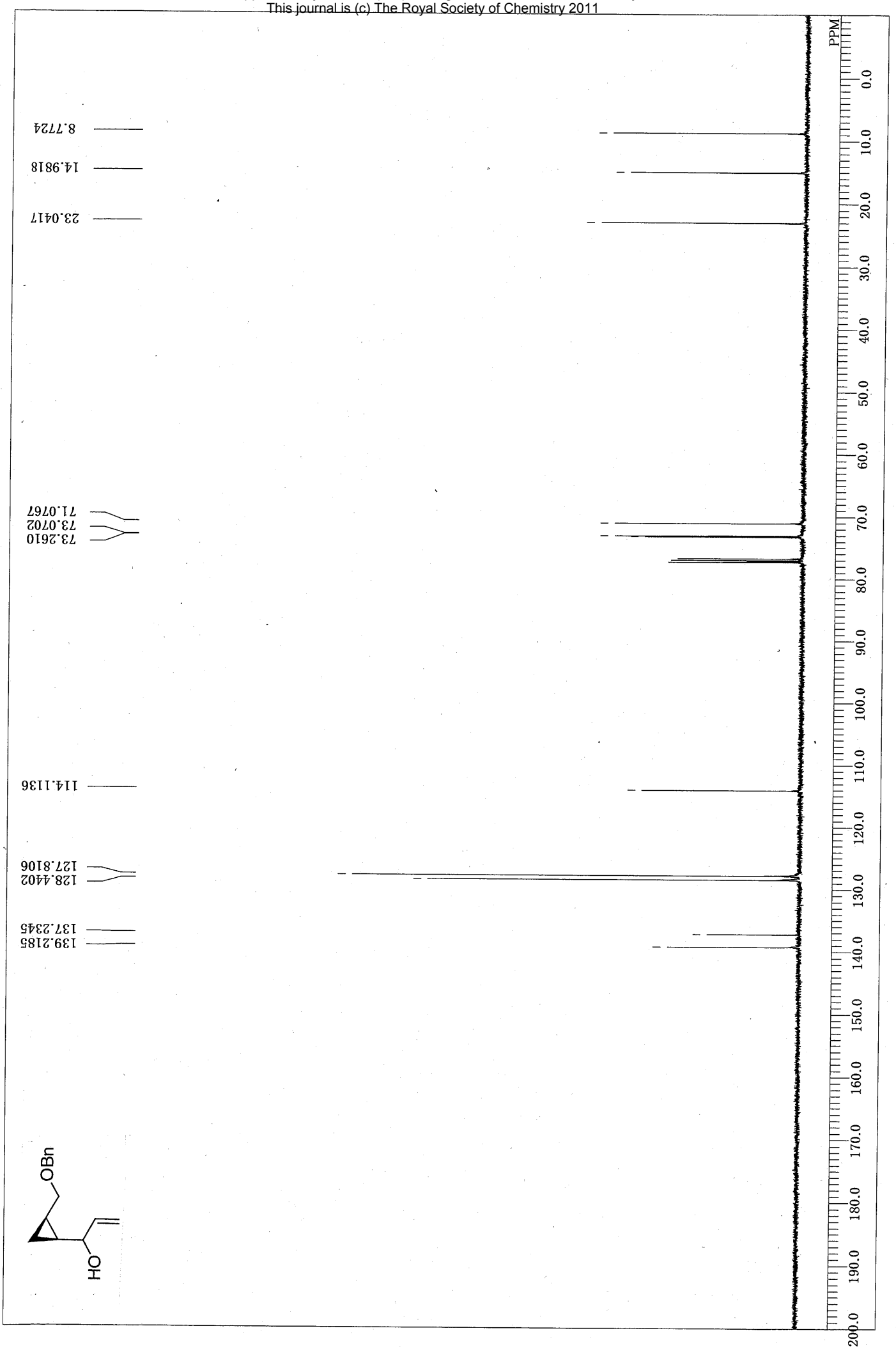
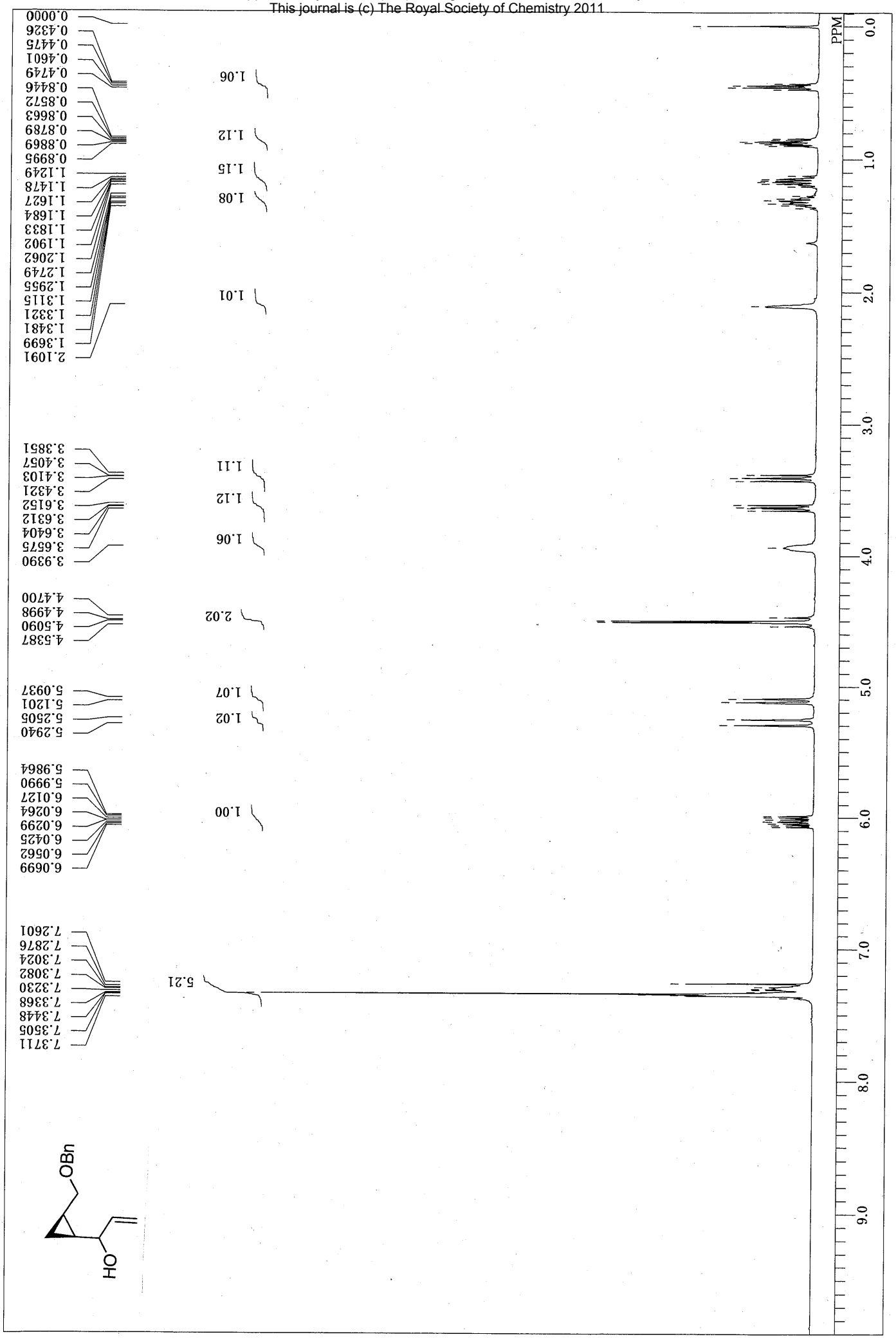
69.8653
72.6791
103.4688
127.4768
127.6676
128.2971
138.3982
OBn
OMe
MeO



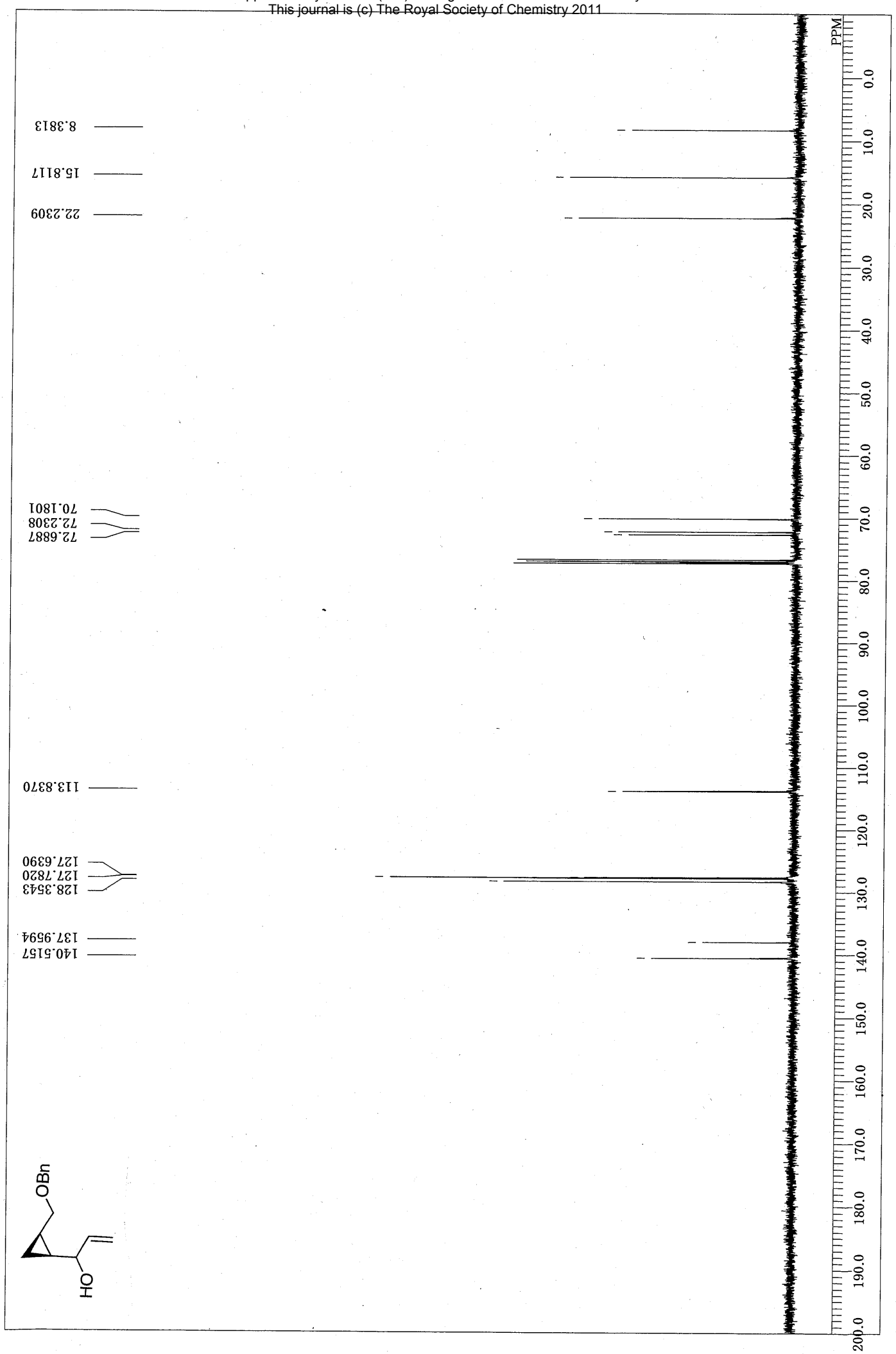
07KT6-90-1(400,CDCl3)



07KT6-90-1C(500,CDCl3)



07KT6-90-2(400,CDCl3)



07KT6-90-2C(500,CDCl3)