Supporting Information for:

Nickel-catalysed cross-coupling reaction of aryl(trialkyl)silanes with aryl chlorides and tosylates

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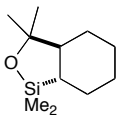
General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a schlenk technique or in a dry box under a nitrogen or argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

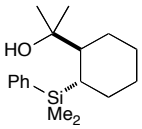
Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400MHz; ^{13}C NMR 101 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Melting points were determined using an OptiMelt MPA100. Infrared spectra (IR) was recorded on a Shimadzu FTIR-8400 spectrometer and is reported in cm^{-1}. Elemental analyses were performed by Elementary Analysis Center of Kyoto University. GC analysis was performed on a Shimadzu GC 2014 equipped with a ENV-1 column (Kanto Chemical, 30 m x 0.25 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

Chemicals. Unless otherwise noted, commercially available liquid chemicals were distilled and degassed before use. Anhydrous DME was purchased from Aldrich. Anhydrous DMF and acetone were purchased from Nacalai Tesque. Anhydrous toluene, THF, and Et_2O were purchased from Kanto Chemical and degassed by purging vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[1] $NiCl_2$•dme and $Ni(PPh_3)_2Cl_2$ were purchased from Strem and used without further purification. $Ni(PPh_2Me)_2Cl_2$ was prepared following the literature procedure.[2] Aryl tosylates were prepared according to the reported protocols.[3] All the spectral data of biaryls shown in Tables 1 and 2 and Eq. 1 agreed perfectly with the those reported previously by ourselves[4] unless otherwise described below. Preparation of **2'** and other organosilanes is described in our previous publications.[4,5]

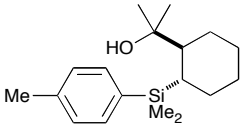


Preparation of 5. To 2-cyclohexen-1-ylpropan-2-ol (7.0 g, 50 mmol) was added $HN(SiMe_2H)_2$ (7.3 g, 55 mmol), and the mixture was stirred at 50 °C overnight. After removal of by-products in *vacuo* (9 Torr, 50 °C) over 15 min, the residue was added dropwise a solution prepared from a 10% solution of *t*-Bu_3P in hexane (0.10 g, 50 μmol) and a 0.01 M solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in hexane (5 mL, 50 μmol), and THF (10 mL) at rt. The resulting mixture was stirred at 70 °C overnight, filtered through a Florisil pad, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to give the title compound as a colorless oil (9.4 g, 95%), R_f 0.31 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92–1.80 (m, 2H), 1.77–1.70 (m, 2H), 1.42–1.02 (m, 5H), 1.26 (s, 3H), 1.02 (s, 3H), 0.79 (td, *J* = 12.5, 3.1 Hz, 1H), 0.19 (s, 3H), 0.07 (s,

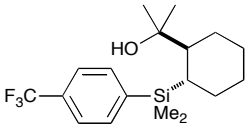
3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 80.6, 53.6, 29.9, 29.6, 29.3, 27.6, 26.8, 26.3, 24.2, –0.2, –2.2; Anal. Calcd for $C_{11}H_{22}OSi$; C, 66.60; H, 11.18. Found: C, 66.45; H, 11.44.



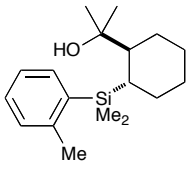
Preparation of 1a. To crude **5** prepared following the above procedure starting with 2-cyclohexen-1-ylpropan-2-ol (2.8 g, 20 mmol) was added a solution of phenylmagnesium bromide in THF (40 mL) prepared from bromobenzene (6.0 g, 38 mmol) and Mg turnings (1.08 g, 45 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight before being quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether for three times, and the combined organic layers were washed with water and then brine, and then dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (4.1 g, 75%) as a colorless oil, R_f 0.28 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.37–7.27 (m, 3H), 1.97–1.88 (m, 1H), 1.76–1.57 (m, 3H), 1.48–0.96 (m, 6H), 1.14 (s, 3H), 0.98 (s, 3H), 0.35 (s, 3H), 0.32 (s, 3H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 133.5, 128.1, 127.6, 74.3, 49.7, 31.2, 29.7, 28.3, 27.4, 26.1, 25.5, 24.1, –0.9, –1.7; Anal. Calcd for $C_{17}H_{28}OSi$; C, 73.85; H, 10.21. Found: C, 73.64; H, 10.07.



Preparation of 1b. To a suspension of Mg (0.26 g, 11 mmol) in THF (2 mL) was added dropwise a solution of 4-bromotoluene (1.7 g, 10 mmol) in THF (10 mL) over 15 min at rt, and the resulting mixture was stirred at rt for 0.5 h. To the solution of the aryl Grignard reagent thus obtained was added **5** (0.99 g, 5.0 mmol) at 0 °C. After being stirred at rt for 36 h, the reaction mixture was quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to give the title compound (1.16 g, 80%) as a colorless oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H), 1.97–1.86 (m, 1H), 1.77–1.54 (m, 3H), 1.43 (td, J = 9.1, 3.4 Hz, 1H), 1.40–1.08 (m, 4H), 1.14 (s, 3H), 1.05–0.96 (m, 1H), 0.98 (s, 3H), 0.93 (s, 1H), 0.32 (s, 3H), 0.30 (s, 3H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.90, 137.87, 133.6, 128.5, 74.3, 49.7, 31.2, 29.7, 28.3, 27.4, 26.1, 25.5, 24.1, 21.5, –0.7, –1.7; Anal. Calcd for $C_{18}H_{30}OSi$; C, 74.42; H, 10.41. Found: C, 74.24; H, 10.62.

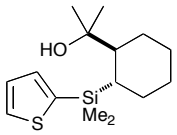


Preparation of 1c. Following the procedure for **1b**, the reaction using a solution of 4-(trifluoromethyl)phenylmagnesium bromide prepared from 1-bromo-4-trifluoromethylbenzene (2.2 g, 10 mmol) with **5** (0.99 g, 5.0 mmol) gave the title compound (1.1 g, 65%) as a colorless oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H), 1.90–1.81 (m, 1H), 1.79–1.59 (m, 3H), 1.42 (td, J = 9.9, 3.3 Hz, 1H), 1.36–0.94 (m, 5H), 1.17 (s, 3H), 0.98 (s, 3H), 0.76 (s, 1H), 0.36 (s, 3H), 0.32 (s, 3H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 133.6, 129.7 (q, J = 31.9 Hz), 124.2 (q, J = 271.2 Hz), 123.8 (q, J = 3.6 Hz), 74.2, 50.3, 31.5, 30.0, 28.7, 27.7, 26.4, 25.7, 23.9, –1.2; Anal. Calcd for $C_{18}H_{27}F_3OSi$; C, 62.76; H, 7.90; Found: C, 62.87; H, 7.81.

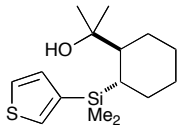


Preparation of 1d. Following the procedure for **1b**, the reaction using a solution of *o*-tolylmagnesium bromide prepared from 2-bromotoluene (1.7 g, 10 mmol) with **5** (0.99 g, 5 mmol) gave the title compounds (1.17 g, 81%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.18–7.10 (m, 2H), 2.48 (s, 3H), 1.92–1.82 (m, 1H), 1.78–1.62 (m, 3H), 1.48 (td, J = 9.5, 2.8 Hz, 1H), 1.38–1.04 (m, 5H), 1.15 (s, 3H), 0.97 (s, 1H), 0.93 (s, 3H), 0.42 (s, 3H), 0.31 (s, 3H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.2, 134.5,

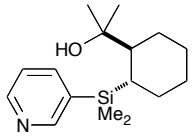
129.8, 128.4, 124.8, 74.0, 49.5, 31.1, 29.9, 28.3, 27.6, 26.3, 25.3, 24.3, 23.4, –0.3, –1.4; Anal. Calcd for $C_{18}H_{30}OSi$; C, 74.42; H, 10.41. Found: C, 74.45; H, 10.35.



Preparation of 1e. To a solution of thiophene (1.26 g, 15 mmol) in Et_2O (10 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexane (9.3 mL, 15 mmol) over 10 min at –78 °C. The resulting mixture was warmed slowly to rt and stirred for 4 h. Magnesium bromide etherate (4.0 g, 15 mmol) was added at –30 °C, and the resulting mixture was stirred at –30 °C for 30 min before treatment with **5** (0.99 g, 5.0 mmol) at the same temperature. The whole was stirred at rt overnight, and then quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether for three times, and the combined organic layers were washed with water and then brine, and dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (0.96 g, 68%) as a colorless oil, R_f 0.23 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.30 (dd, 4.7, 0.8 Hz, 1H), 7.25 (dd, *J* = 3.3, 0.9 Hz, 1H), 7.03 (dd, *J* = 4.7, 3.4 Hz, 1H), 1.96–1.87 (m, 1H), 1.69–1.47 (m, 3H), 1.35 (td, *J* = 10.2, 3.3Hz, 1H), 1.30–1.02 (m, 3H), 0.93 (s, 3H), 0.88–0.78 (m, 4H), 0.87 (s, 3H), 0.66 (s, 1H), 0.55 (s, 3H), 0.53 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 142.4. 134.3, 130.0. 128.1, 73.7, 51.2, 31.6, 30.6, 29.4, 28.2, 27.4, 27.0, 23.8, 2.0, 0.0; Anal. Calcd for $C_{15}H_{26}OSSi$; C, 63.77; H, 9.28; Found: C, 63.61; H, 9.53.

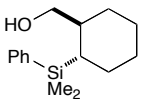


Preparation of 1f. To a solution of 3-bromothiophene (1.61 g, 10 mmol) in Et_2O (10 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexane (6.3 mL, 10 mmol) in over 10 min at –78 °C. The resulting mixture was stirred at 0 °C for 2 h before addition of magnesium bromide etherate (2.6 g, 10 mmol) at –30 °C. The resulting mixture was stirred at –30 °C for additional 30 min, and then treated with **5** (0.99 g, 5.0 mmol) at the same temperature. The resulting mixture was stirred at rt overnight before being quenched with a saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with water and then brine, and dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (1.27 g, 87%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.18 (dd, *J* = 4.8, 1.1 Hz, 1H), 1.92–1.83 (m, 1H), 1.77–1.58 (m, 3H), 1.41 (td, *J* = 9.3, 3.5 Hz, 1H), 1.36–1.07 (m, 4H), 1.16 (s, 3H), 1.04–0.92 (m, 2H), 1.00 (s, 3H), 0.34 (s, 3H), 0.33 (s, 3H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3 131.8, 130.9, 125.3, 74.2, 50.0, 31.3, 29.7, 28.3, 27.4, 26.1, 24.0, –0.5, –0.7; Anal. Calcd for $C_{15}H_{26}OSSi$; C, 63.77; H, 9.28; Found: C, 63.98; H, 9.06.

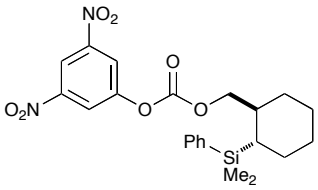


Preparation of 1g. To a solution of 3-bromopyridine (1.6 g, 10 mmol) in Et_2O (10 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexane (6.3 mL, 10 mmol) over 10 min at –78 °C. The resulting mixture was stirred at –78 °C for 2 h before addition of magnesium bromide etherate (2.6 g, 10 mmol) at –30 °C. The resulting mixture was stirred at –30 °C for additional 30 min, and then treated with **5** (0.99 g, 5.0 mmol) at the same temperature. The resulting mixture was stirred at rt overnight before being quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with ethyl acetate for three times. The combined organic layers were washed with water and then brine, and dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (0.87 g, 63%) as a white solid (mp 104.6–105.5 °C), R_f 0.23 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.51 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.75 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.5, 4.8 Hz, 1H), 1.88–1.59 (m, 4H), 1.40 (td, *J* = 9.9, 3.2 Hz, 1H), 1.34–0.91 (m, 5H), 1.16 (s, 3H), 0.97 (s, 3H), 0.89 (s, 1H), 0.35 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 148.5, 141.1, 137.6, 122.8, 73.9, 50.3, 31.5, 29.9, 28.7, 27.7, 26.4, 25.9, 23.9, –1.0, –1.4; Anal. Calcd for $C_{16}H_{27}NOSi$; C, 69.26; H, 9.81; Found: C, 68.98;

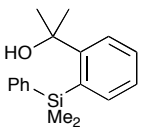
H, 9.59.



Preparation of 1'a. To cyclohexen-1-ylmethanol (1.1 g, 10 mmol) was added $HN(SiMe_2H)_2$ (1.46 g, 11.0 mmol), and the resulting mixture was stirred at rt overnight. After removal of by-products in *vacuo* (9.0 Torr, 50 °C) over 15min, the residue was added dropwise a solution prepared from a 10% solution of *t*-Bu_3P in hexane (20 mg, 20 μmol), a 0.01 M solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in hexane (2 mL, 20 μmol), and THF (5 mL) at rt. The resulting mixture was stirred at 50 °C overnight before being concentrated in *vacuo*. The residue was treated with a solution of phenylmagnesium bromide in THF (5 mL) prepared from bromobenzene (3.2 g, 20 mmol) and Mg turnings (0.50 g, 20 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight before being quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with ethyl acetate for three times, and the combined organic layers were washed with water and then brine, and dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (1.32, 53%) as a colorless oil, R_f 0.27 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.50 (m, 2H), 7.40–7.33 (m, 3H), 3.45 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.31 (dd, *J* = 11.0, 6.3 Hz, 1H), 1.86–1.66 (m, 4H), 1.50–1.37 (m, 1H), 1.36–1.10 (m, 4H), 0.95 (br, 1H), 0.91–0.81 (m, 1H), 0.34 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 133.3, 128.7, 127.8, 67.4, 41.9, 31.2, 28.0, 27.7, 26.7, 26.2, –2.4, –4.2; Anal. Calcd for $C_{15}H_{24}OSi$; C, 72.52; H, 9.74; Found: C, 72.33; H, 9.89.



Preparation of 3,5-dinitrobenzoate of 1'a. To a mixture of **1'a** (0.25 g, 1 mmol) and 3,5-dinitrobenzoyl chloride (0.30 g, 1.3 mmol) in CH_2Cl_2 (3 mL) were added DMAP (12 mg, 0.10 mmol) and Et_3N (0.20 g, 2.0 mmol) at 0 °C sequentially. The resulting mixture was stirred at 0 °C for 3 h before concentration in *vacuo*. The residue was purified by flash chromatography on silica gel to afford the title compound (0.42 g, 95%) as a colorless solid (mp 101.6–102.0 °C), R_f 0.23 (hexane–ethyl acetate = 10:1). Single colorless crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (t, *J* = 2.1 Hz, 1H), 9.00 (d, *J* = 2.2 Hz, 2H), 7.51–7.48 (m, 2H), 7.23–7.20 (m, 3H), 4.35 (dd, *J* = 11.1, 3.2 Hz, 1H), 4.00 (dd, *J* = 11.2, 6.6 Hz, 1H), 1.92–1.70 (m, 5H), 1.39–1.19 (m, 4H), 1.05–0.94 (m, 1H), 0.39 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 148.5, 139.3, 134.0, 133.5, 129.2, 128.8, 127.8, 122.1, 71.2, 38.6, 31.6, 27.7, 27.3, 27.0, 25.8, –2.6, –4.8; Anal. Calcd for $C_{22}H_{26}N_2O_6Si$; C, 59.71; H, 5.92; Found: C, 59.96; H, 5.86.

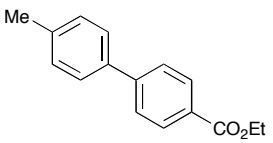


Preparation of 2. A 1.0 M solution of phenylmagnesium bromide in Et_2O (5.5 mL, 5.5 mmol) was added over 15 min to a solution of 1,1,3,3-tetramethyl-2-oxa-1-silaindan[5] (0.96 g, 5.0 mmol) in Et_2O (10 mL) at 0 °C. The mixture was stired at 0 °C for 2 h and then at rt overnight before being quenched with a saturated NH_4Cl aqueous solution at 0 °C. The aqueous layer was extracted with diethyl ether for three times, and the combined organic layers were washed with water and then with brine and dried over anhydrous $MgSO_4$. After concentration in *vacuo*, the residue was purified by flash chromatography on silica gel to afford the title compound (0.72 g, 53%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.49–7.43 (m, 2H), 7.41–7.36 (m, 1H), 7.35–7.23 (m, 5H), 1.46 (s, 6H), 1.39 (s, 1H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 143.3, 137.0, 132.8, 132.6, 129.1, 128.1, 127.8, 125.6, 125.5, 75.2, 33.0, 2.1; Anal. Calcd for $C_{17}H_{22}OSi$; C, 75.50; H, 8.45; Found: C, 75.25; H, 8.45.

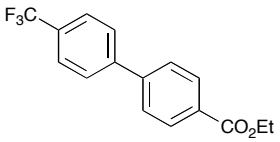
Cross-coupling reactions of 1 with aryl chlorides. *A general procedure*. An oven dried 3 mL-glass vial equipped with a magnetic stir bar was charged with $NiCl_2$•dme (11 mg, 50 μmol), dppf (28 mg, 50 μmol), PCy_3 (14 mg, 50 μmol), Zn powder (6.5 mg, 0.10 mmol), and Cs_2CO_3 (0.65 g, 2.0 mmol), and then sealed tightly with a screw-cap containing a PTFE septum. The vial was evacuated and back filled with argon through a needle. This process was repeated for three times. To the vial was added a solution of **1** (1.3 mmol) and aryl chloride (1.0 mmol) in DMF (0.5 mL) and DME (1.0 mL) via a syringe under a positive flow of argon. The reaction mixture was stirred at rt for a few seconds to create a homogeneous slurry, and then at 60–80 °C until a GC analysis showed complete consumption of the starting materials. After the time specified in Table 1, the mixture was filtered through a Florisil pad, diluted with Et_2O, and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to give the corresponding biaryl in a yield listed in Table 1.

Gram-scale cross-coupling of 1a with ethyl 4-chlorobenzoate (3f). An oven dried 25 mL-Schlenk tube equipped with a magnetic stir bar was charged with $NiCl_2$•dme (0.11g, 0.50 mmol), dppf (0.28 g, 0.50 mmol), PCy_3 (0.14 g, 0.50 mmol), Zn powder (65 mg, 1.0 mmol), and Cs_2CO_3 (6.5 g, 2.0 mmol), and then sealed tightly with a rubber septum. The tube was evacuated and back filled with argon for three times. To this was added a solution of **1a** (3.6 g, 13 mmol) and ethyl 4-chlorobenzoate **3f** (1.84 g, 10 mmol) in DMF (5 mL) and DME (10 mL) via a syringe under a positive flow of argon. The reaction mixture was stirred at rt for a few seconds to create a homogeneous slurry, and then at 75 °C for 30 h. The resulting mixture was filtered through a Florisil pad, diluted with Et_2O, and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in *vacuo*. The crude mixture thus obtained was distilled (5.0 Torr, 120 °C) to give **5** (2.4 g, 93%), and the residue was purified by flash column chromatography on silica gel to give **4af** (1.85 g, 82%) as a colorless solid.

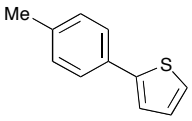
Cross-coupling reaction of 1a with aryl tosylates. *A general procedure*. An oven dried 3 mL-glass vial equipped with a magnetic stir bar was charged with $Ni(PPh_3)_2Cl_2$ (33 mg, 50 μmol), PPh_3 (13 mg, 50 μmol), PCy_3 (42 mg, 0.15 mmol), Zn powder (6.5 mg, 0.10 mmol), and Cs_2CO_3 (0.65 g, 2.0 mmol), and then sealed tightly with a screw-cap containing a PTFE septum. The vial was evacuated and back filled with argon through a needle. This process was repeated for three times. To this was added a solution of **1a** (0.36 g, 1.3 mmol) and aryl tosylates (1.0 mmol) in DMF (0.5 mL) and acetone or DME (1 mL) via a syringe under a positive flow of argon. The reaction mixture was stirred at rt for a few seconds to create a homogeneous slurry, and then at 80 °C until a GC analysis showed complete consumption of the starting materials. After the time specified in Table 2, the mixture was filtered through a Florisil pad, diluted with Et_2O, and washed with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to give the corresponding biaryl in a yield listed in Table 2.



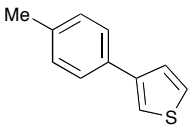
Ethyl 4-tolylbenzoate (4bf).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2 H), 2.40 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 145.3, 137.9, 129.9, 129.5, 128.8, 127.0, 126.6, 60.9, 21.3, 14.5.



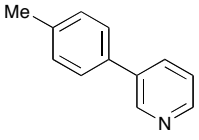
Ethyl 4-[(4-trifluoromethyl)phenyl]benzoate (4cf).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.75–7.70 (m, 4H), 7.66 (d, *J* = 8.6 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 143.8, 143.4, 130.1, 130.0, 129.8, 127.5, 127.1, 125.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 271.4 Hz), 61.2, 14.5.



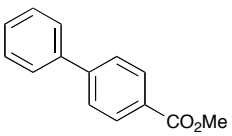
2-(*p*-Tolyl)thiophene (4lb).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.26–7.22 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.05 (dd, *J* = 5.0, 3.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.1, 134.5, 129.4, 127.8, 125.7, 124.1, 122.4, 21.3.



3-(*p*-Tolyl)thiophene (4fb).[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.44–7.37 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 136.7, 132.9, 129.3, 126.7, 126.2, 125.9, 119.5, 21.3.



3-(*p*-Tolyl)pyridine (4qb).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 1.8 Hz, 1H), 8.57 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.88–7.83 (m, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.38–7.32 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 137.9, 136.4, 134.8, 134.0, 129.6, 126.8, 123.4, 21.3.



Methyl 4-phenylbenzoate (4ar).[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.69–7.60 (m, 4H), 7.50–7.36 (m, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.4, 139.8, 129.9, 128.7, 128.75, 128.70, 127.1, 126.9, 52.1.

References

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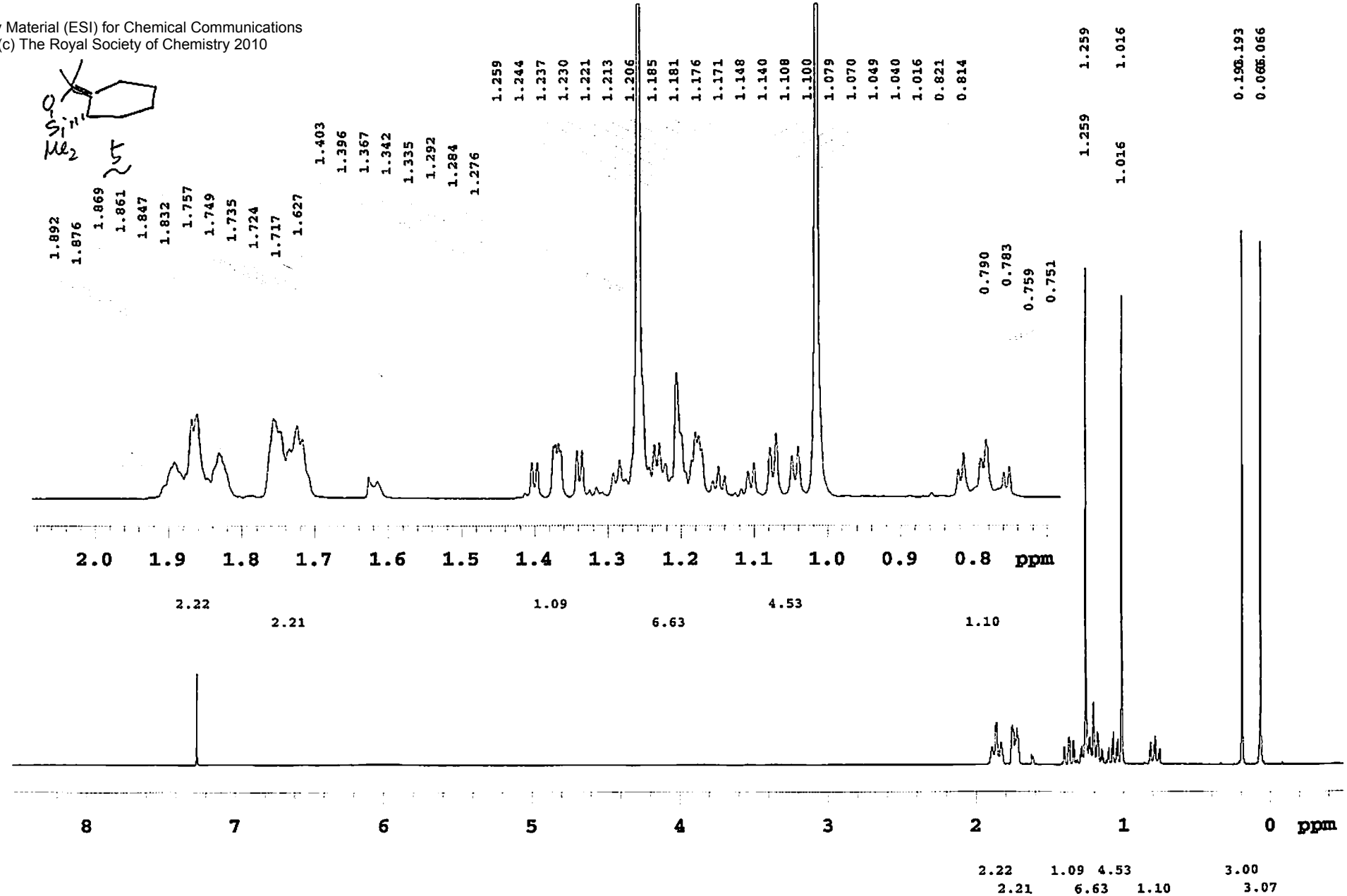
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1.284
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1.213
1.206
1.185
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1.171
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1.079
1.070
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0.783
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2.21
1.09
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4.53
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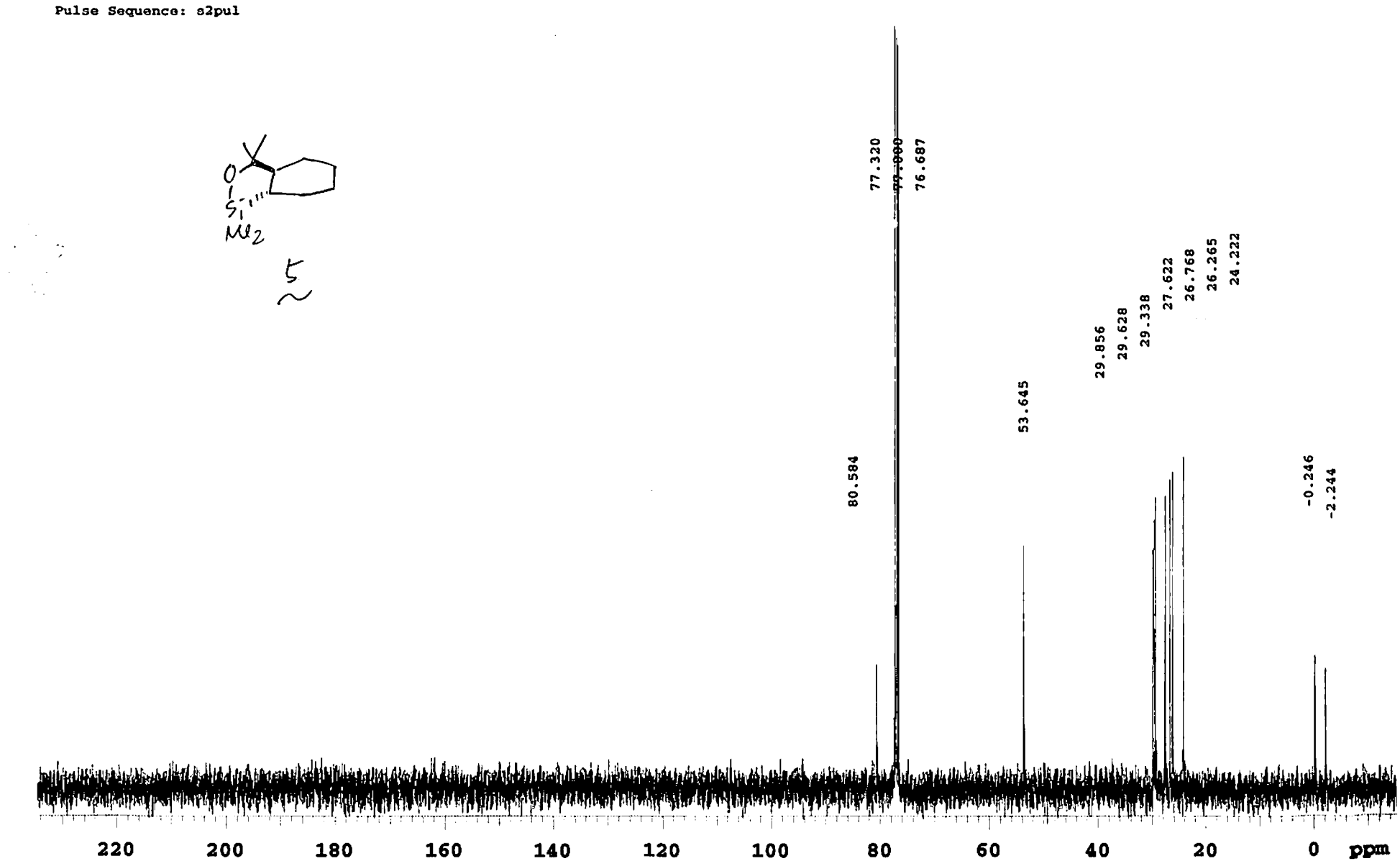
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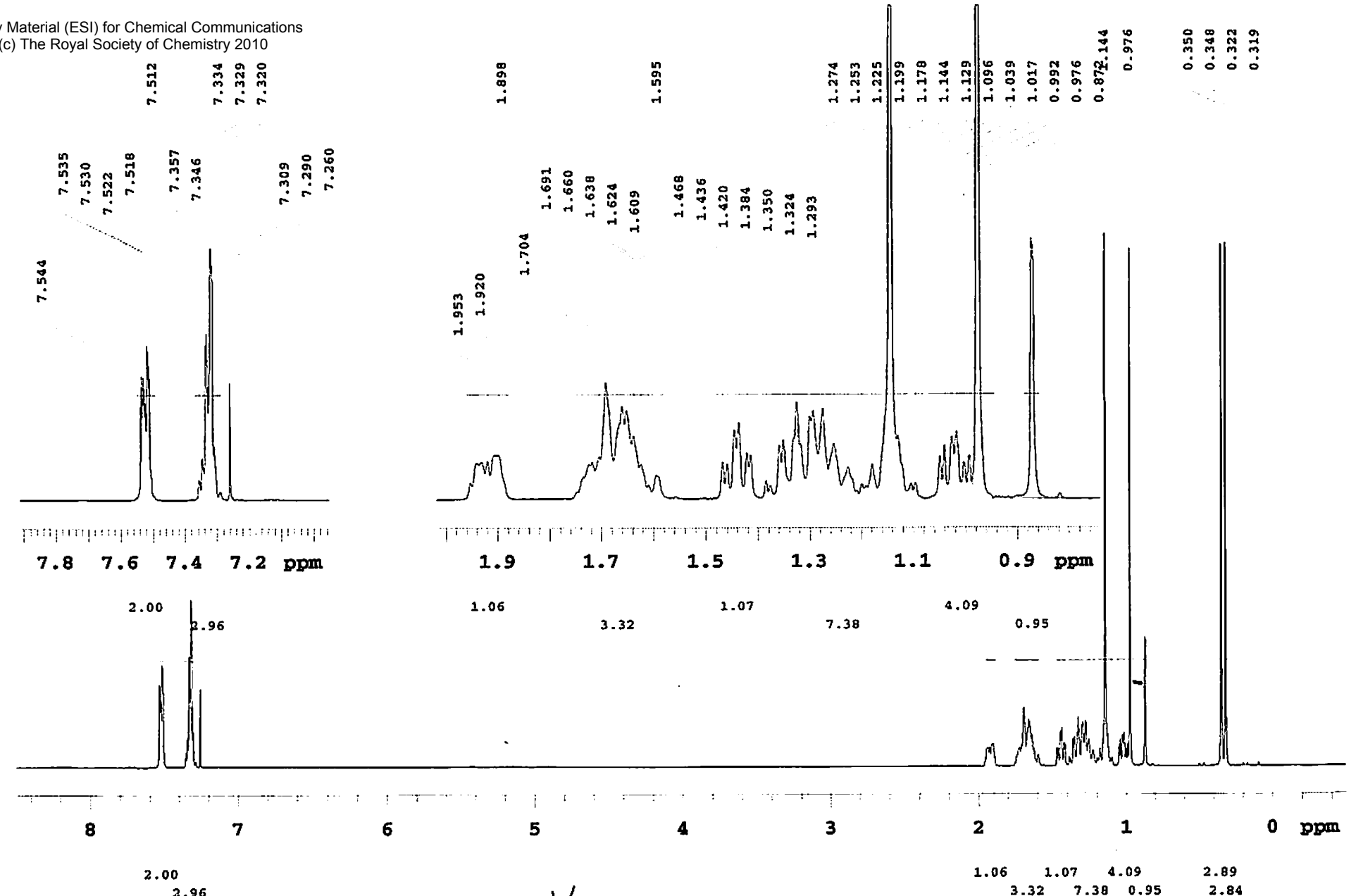
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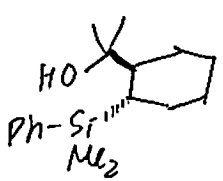
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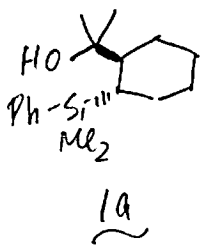

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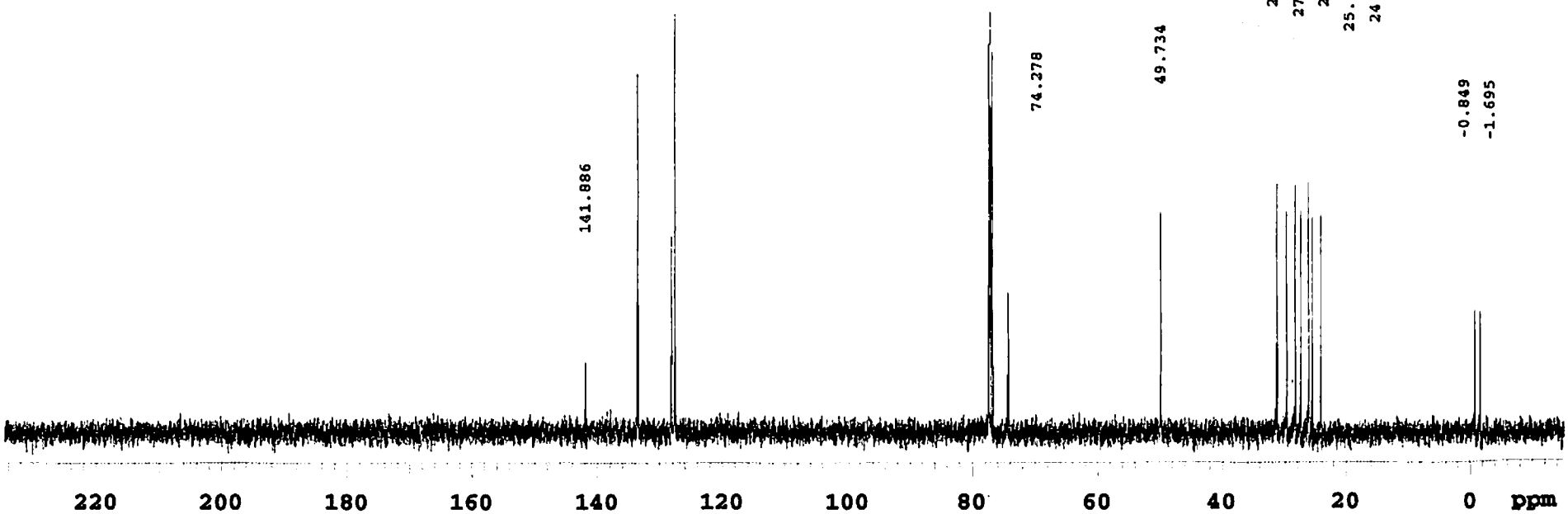

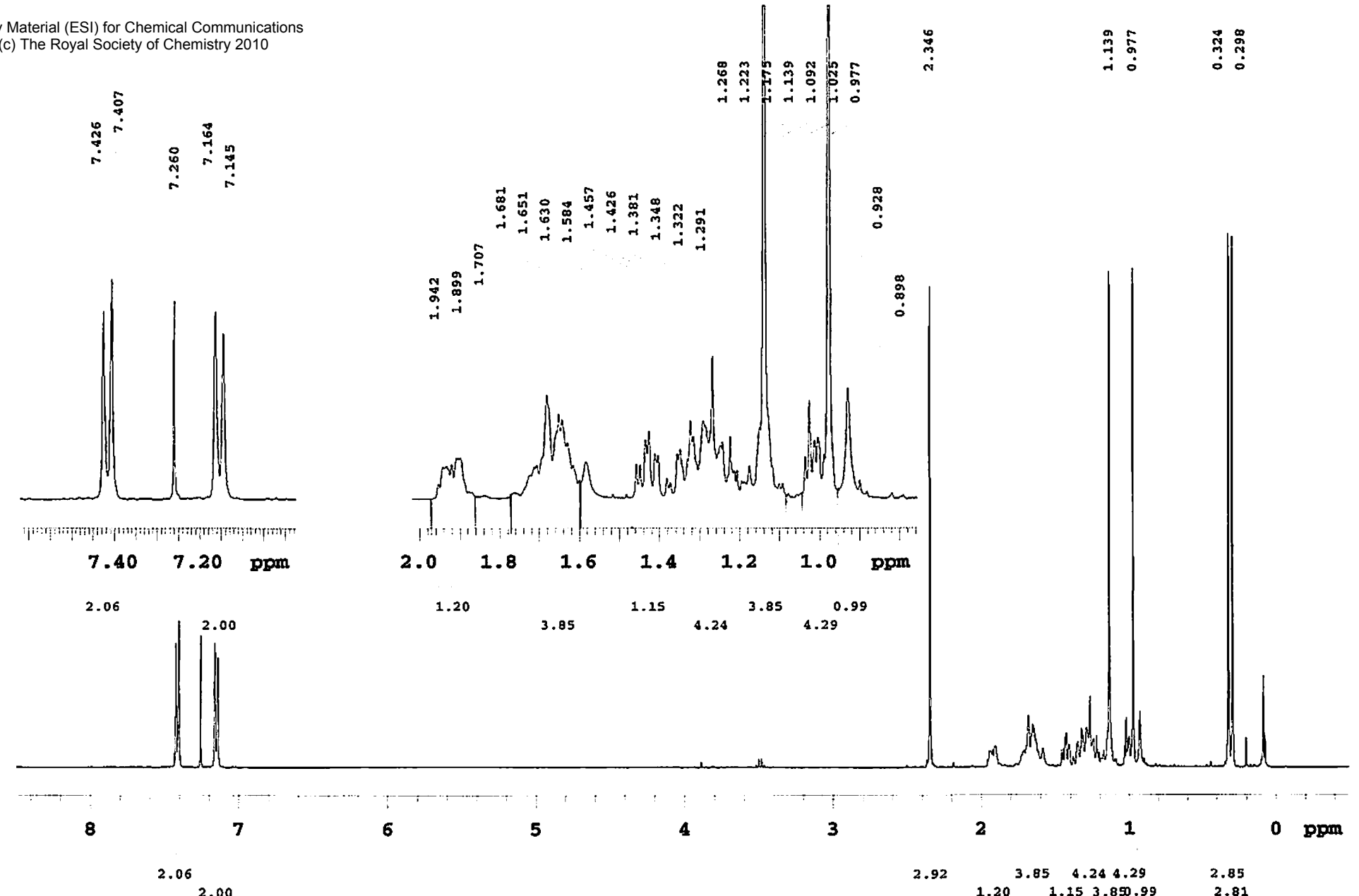
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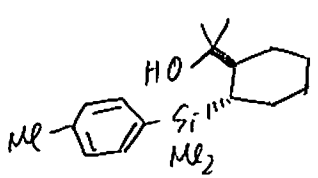
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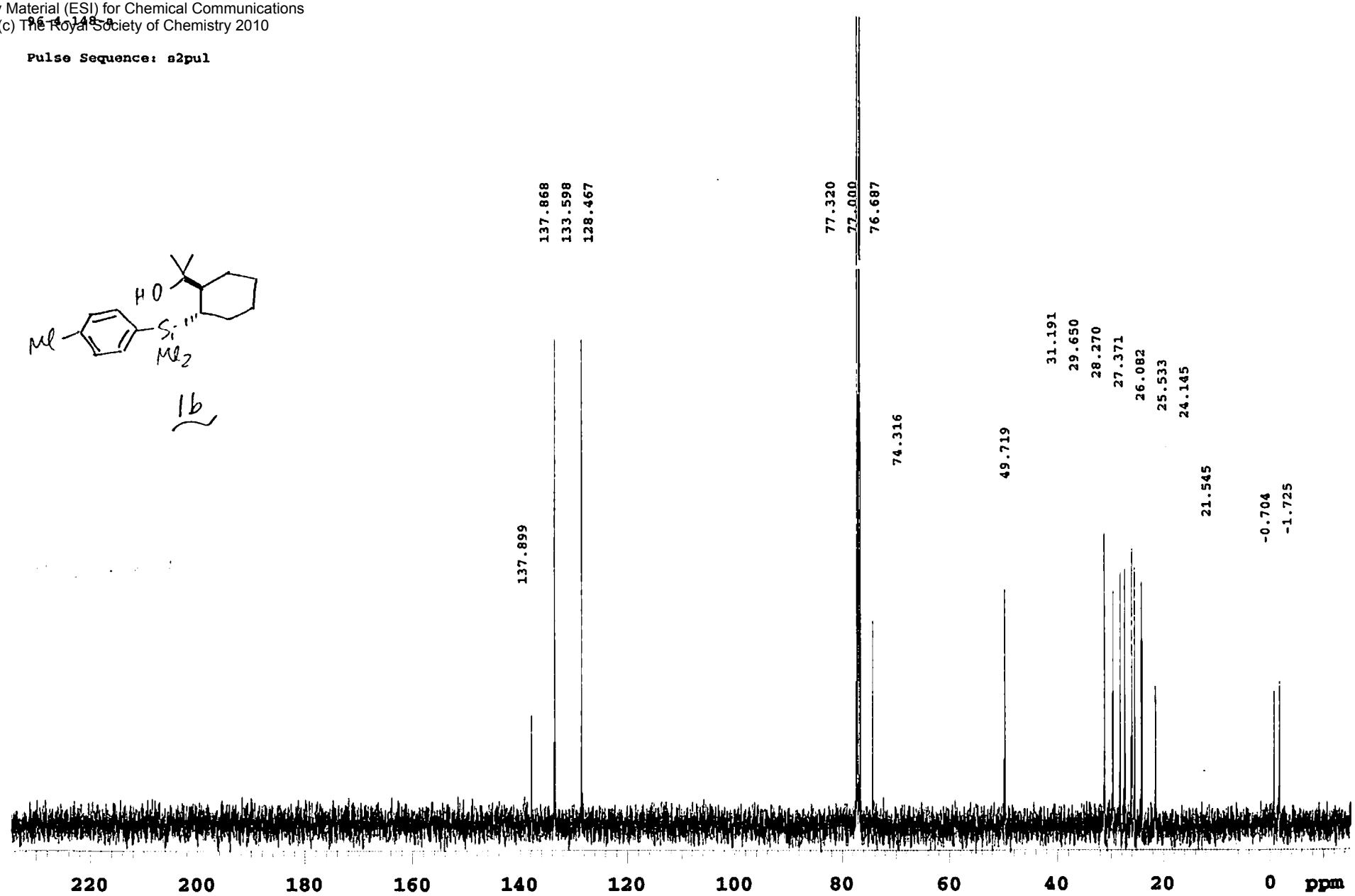

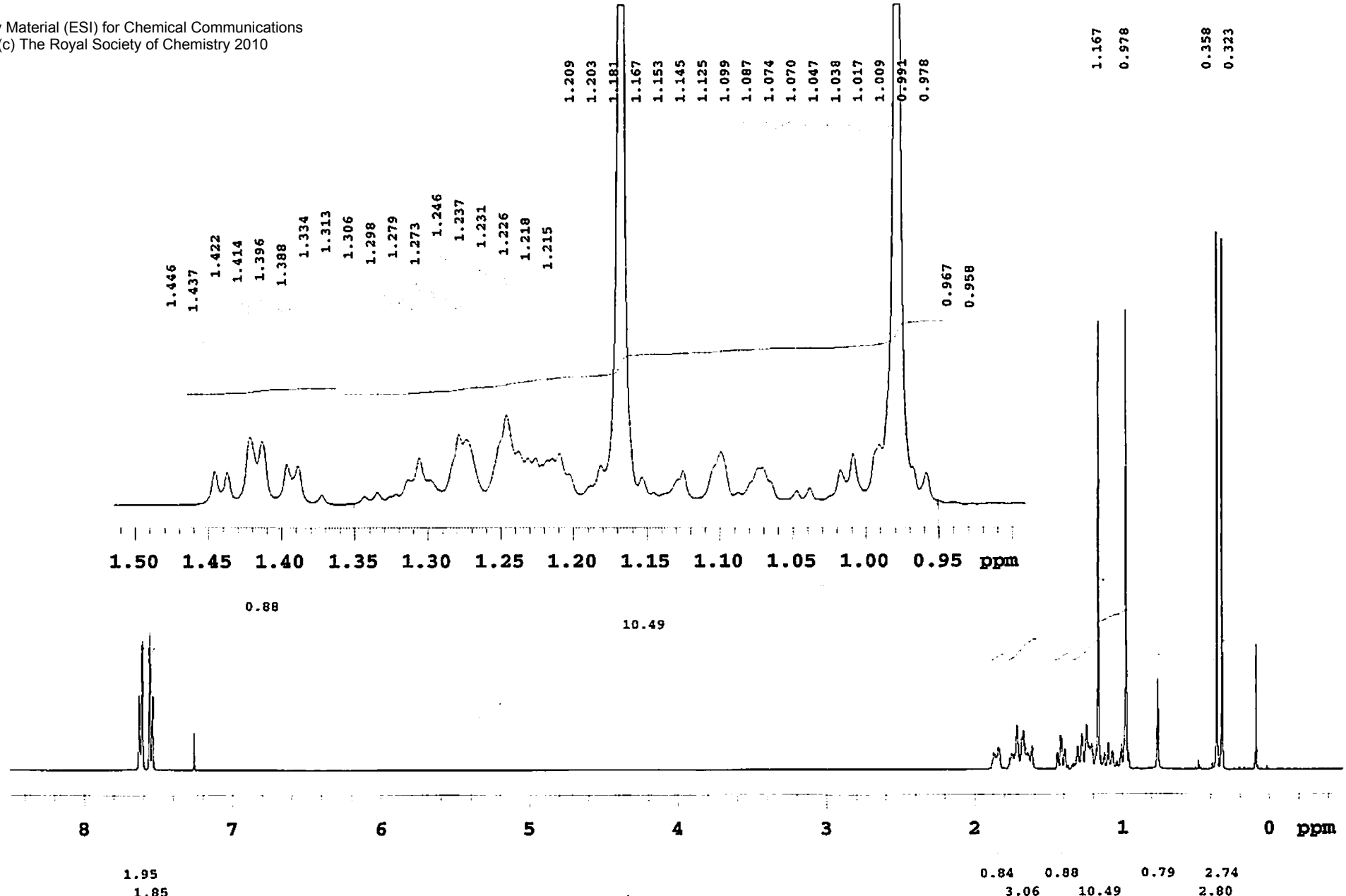
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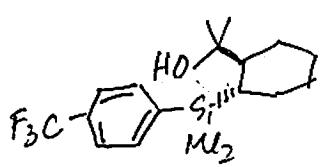
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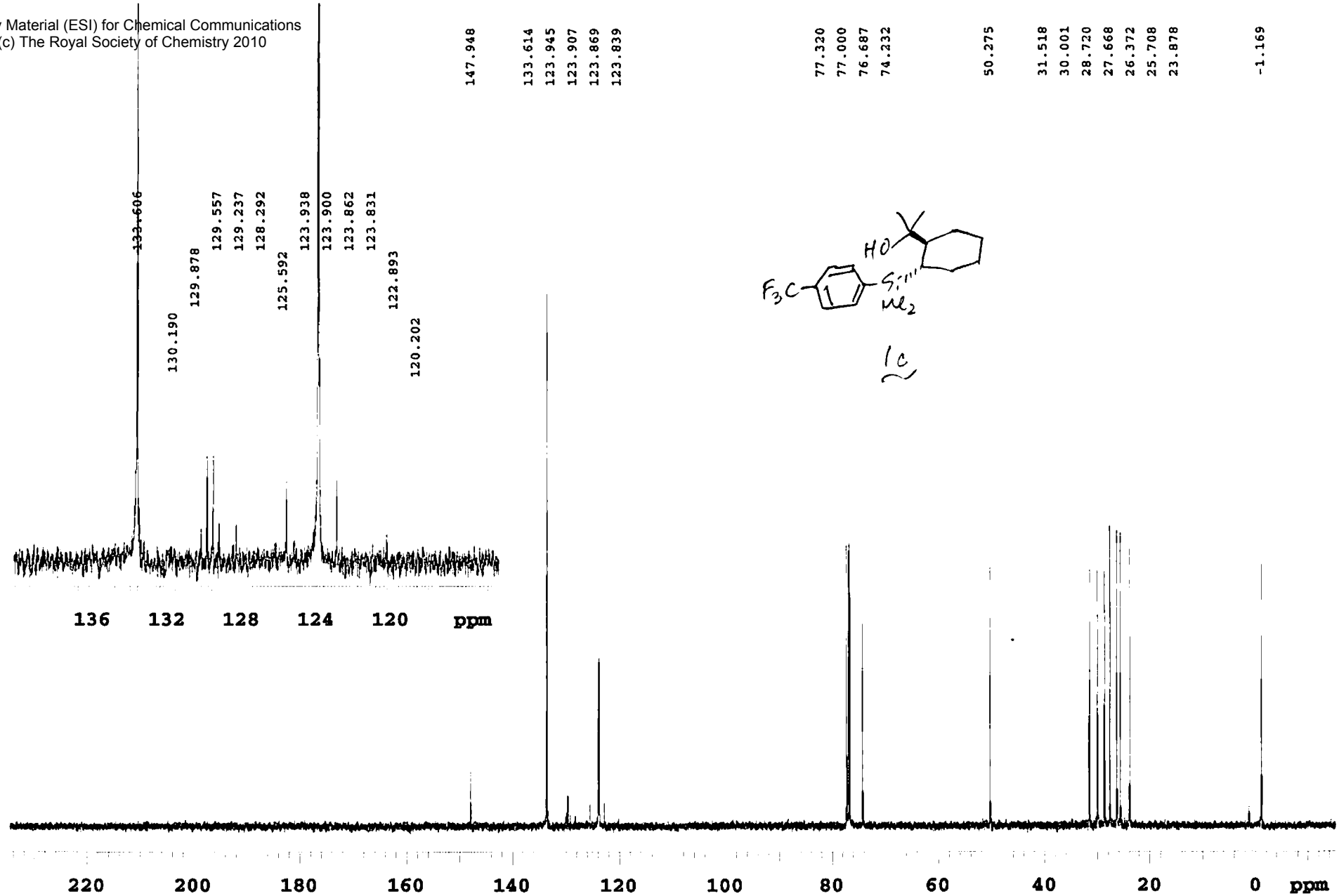
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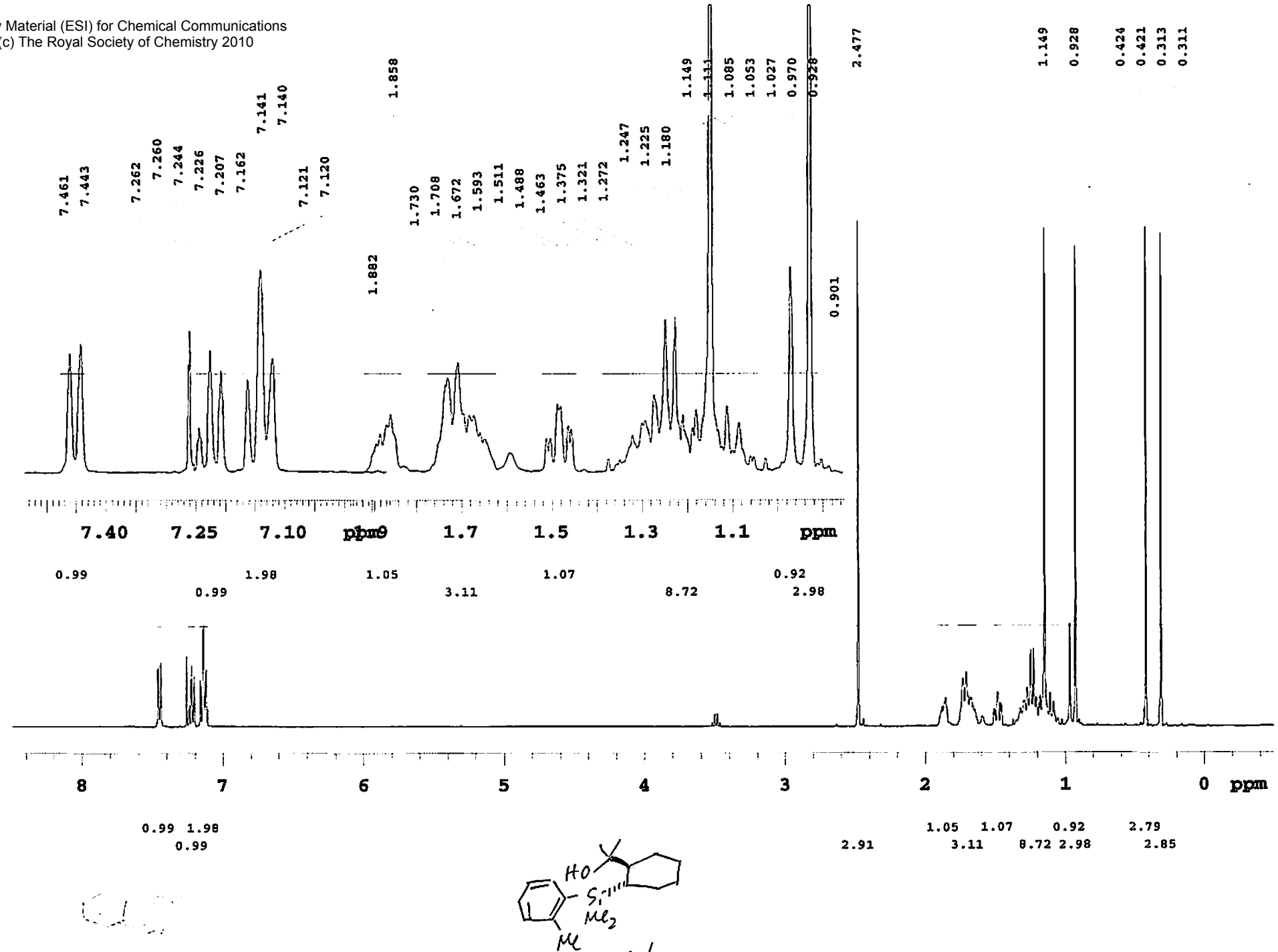
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2.98
8
7
6
5
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0.99 1.98
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Me

96-4-148-B

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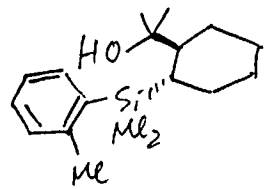
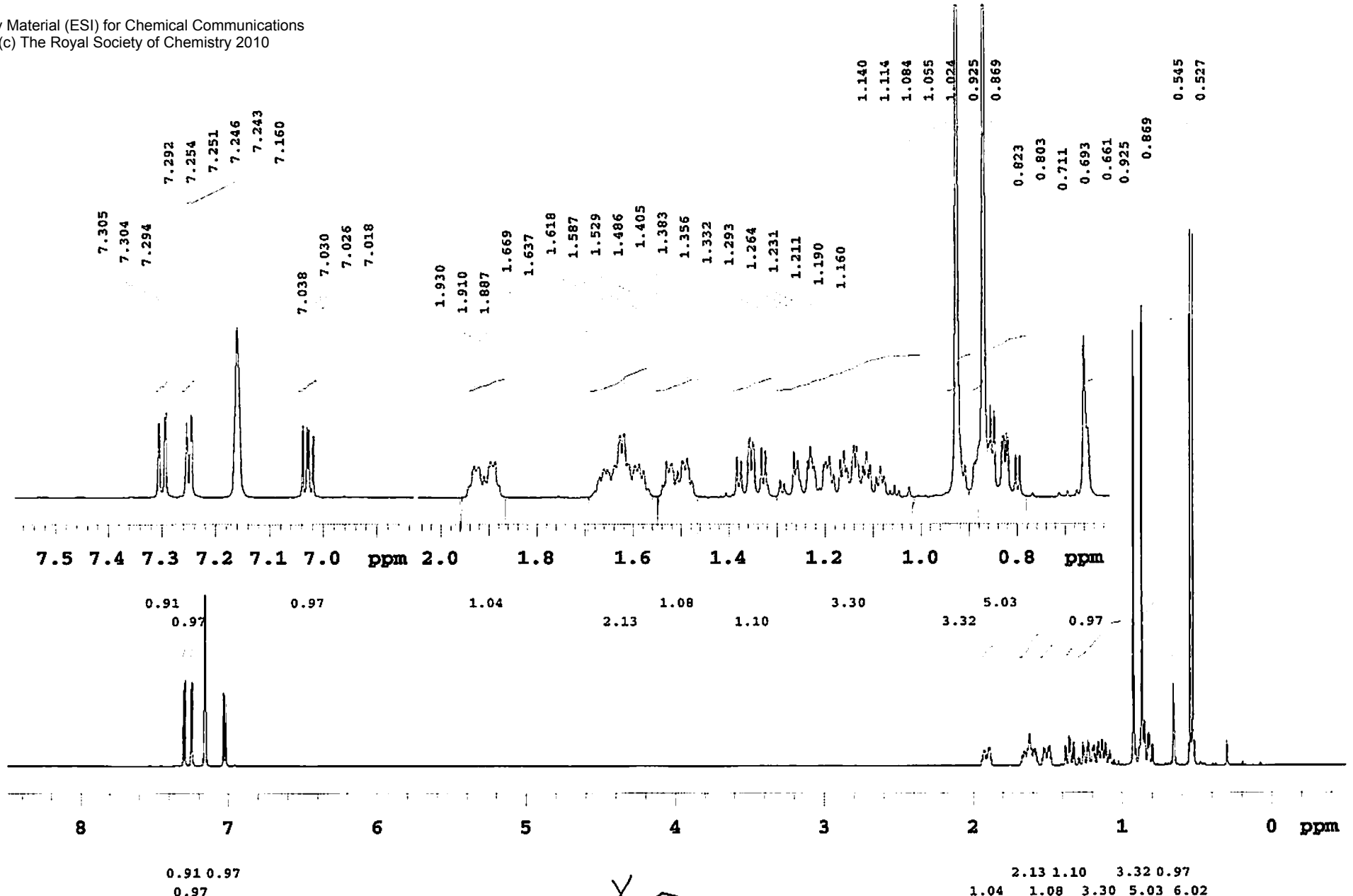
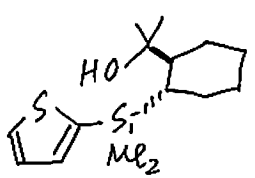
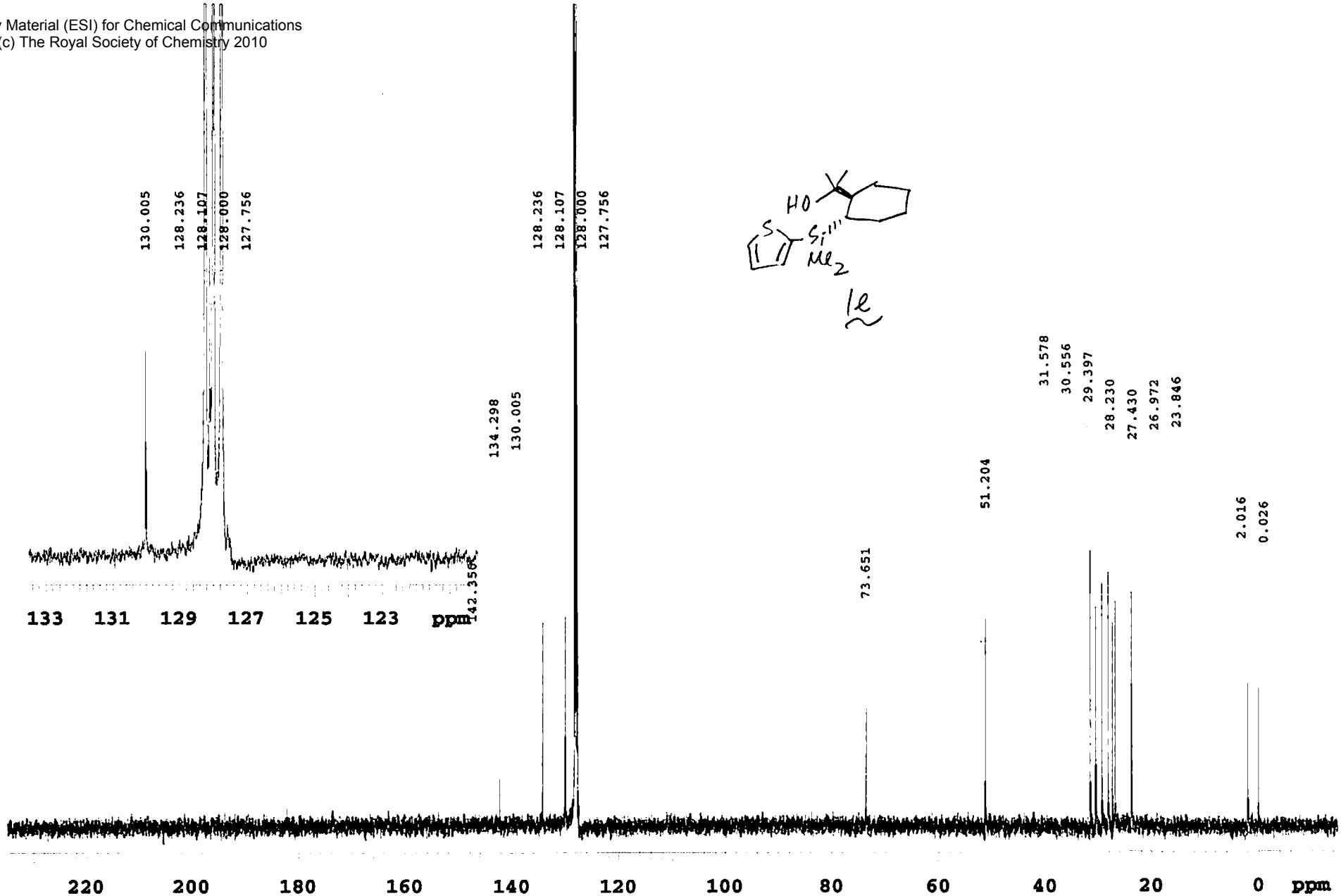
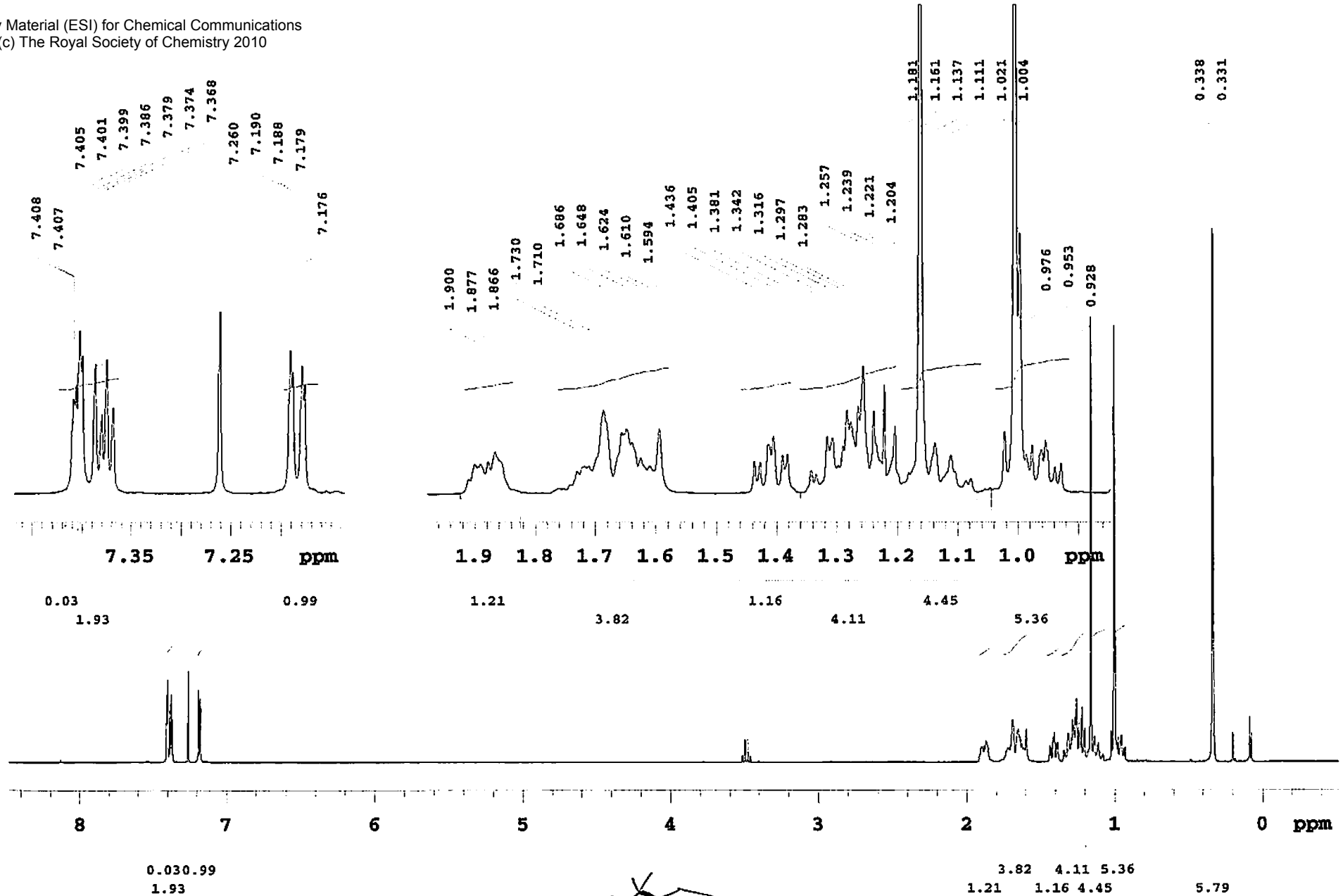


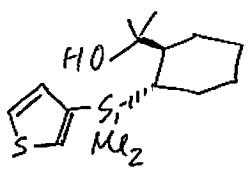
1d



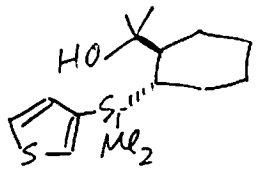



130.005
128.236
128.107
128.000
127.756
134.298
130.005
128.236
128.107
128.000
127.756
73.651
51.204
31.578
30.556
29.397
28.230
27.430
26.972
23.846
2.016
0.026
42.350
133 131 129 127 125 123 ppm
220 200 180 160 140 120 100 80 60 40 20 0 ppm
HO
Si
Me2
S
12

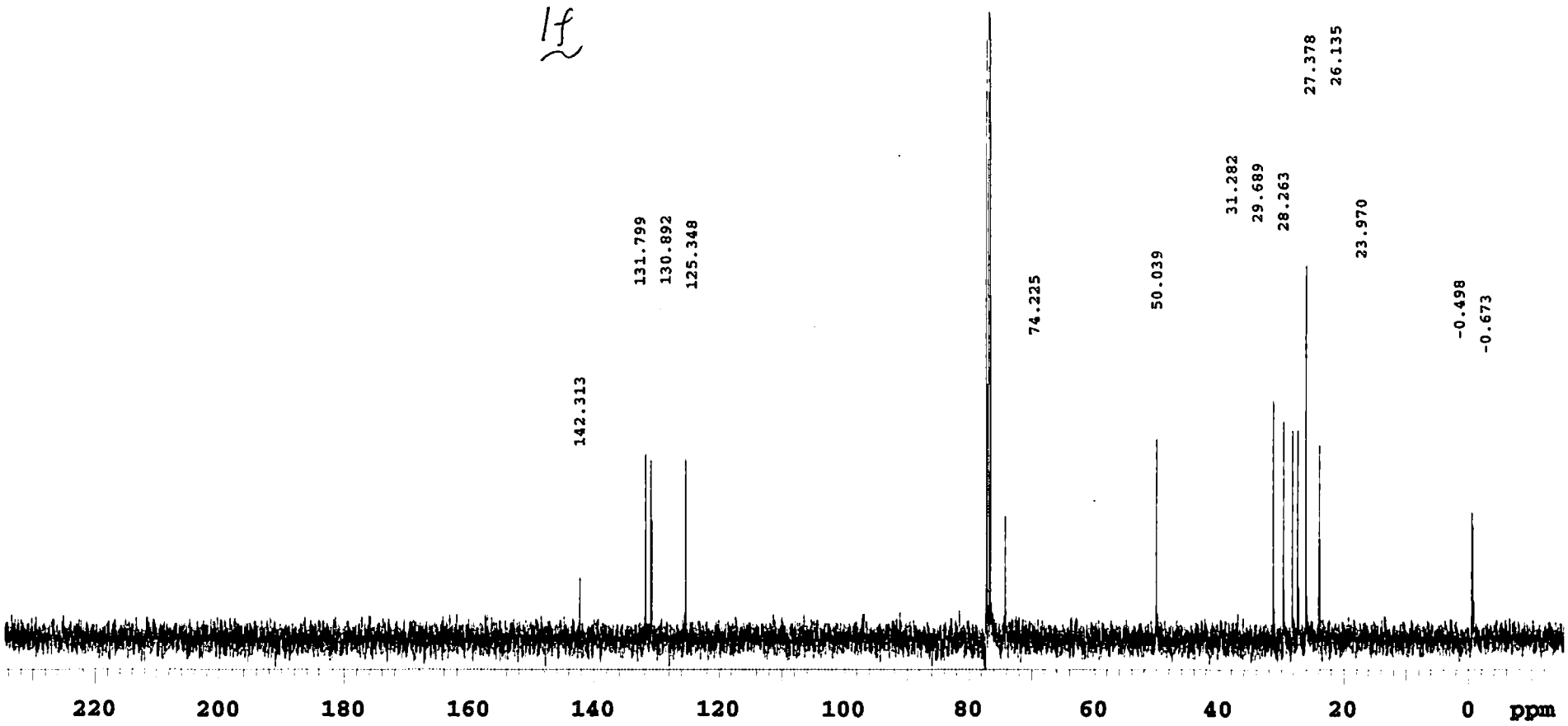

7.408
7.407
7.405
7.401
7.399
7.386
7.379
7.374
7.368
7.260
7.190
7.188
7.179
7.176
1.900
1.877
1.866
1.730
1.710
1.686
1.648
1.624
1.610
1.594
1.436
1.405
1.381
1.342
1.316
1.297
1.283
1.257
1.239
1.221
1.204
1.181
1.161
1.137
1.111
1.021
1.004
0.976
0.953
0.928
0.338
0.331
7.35 7.25 ppm
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 ppm
0.03
1.93
0.99
1.21
3.82
1.16
4.11
4.45
5.36
8 7 6 5 4 3 2 1 0 ppm
0.030.99
1.93
3.82 4.11 5.36
1.21 1.16 4.45
5.79

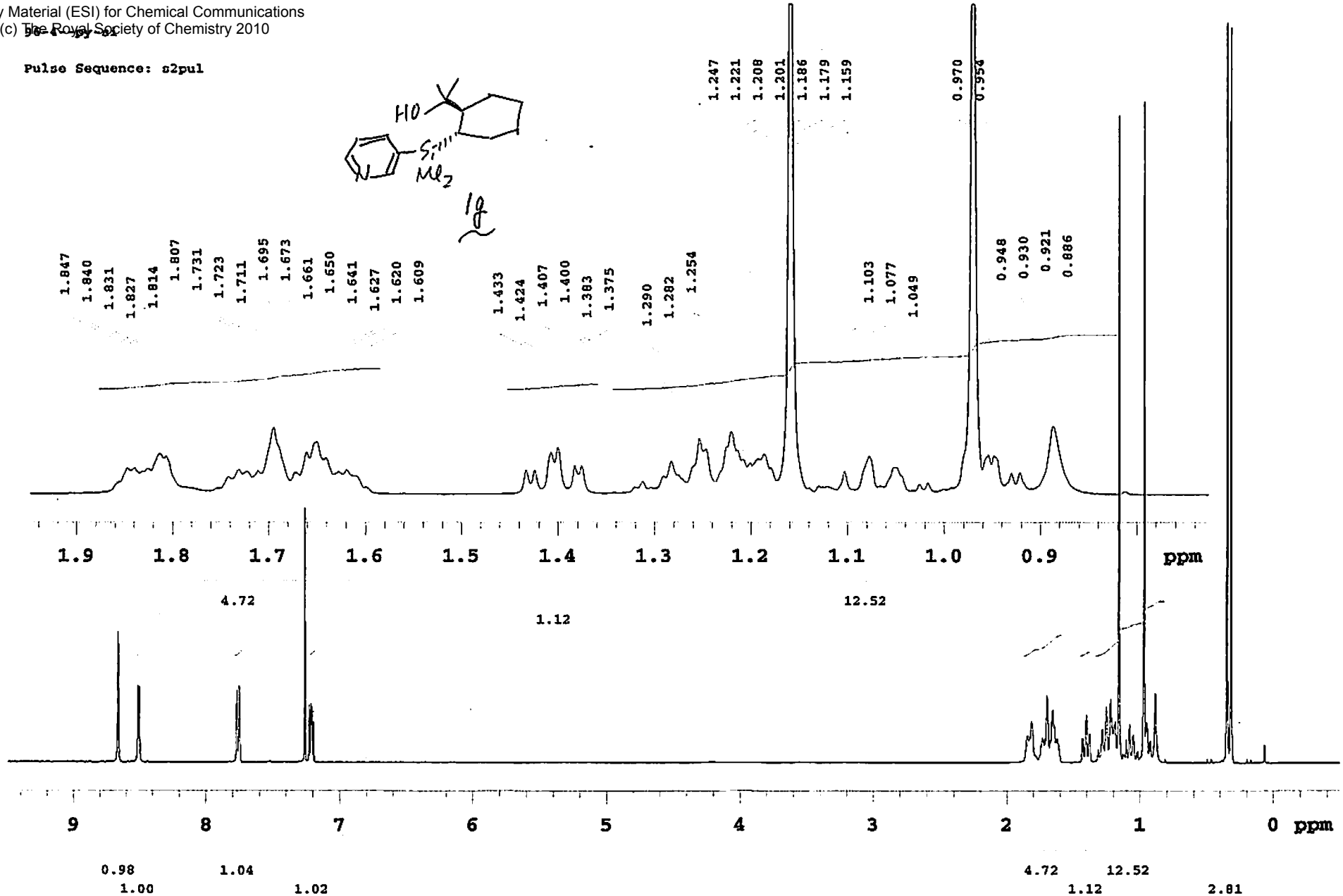

HO
Si
Me2
S

Pulse Sequence: s2pul

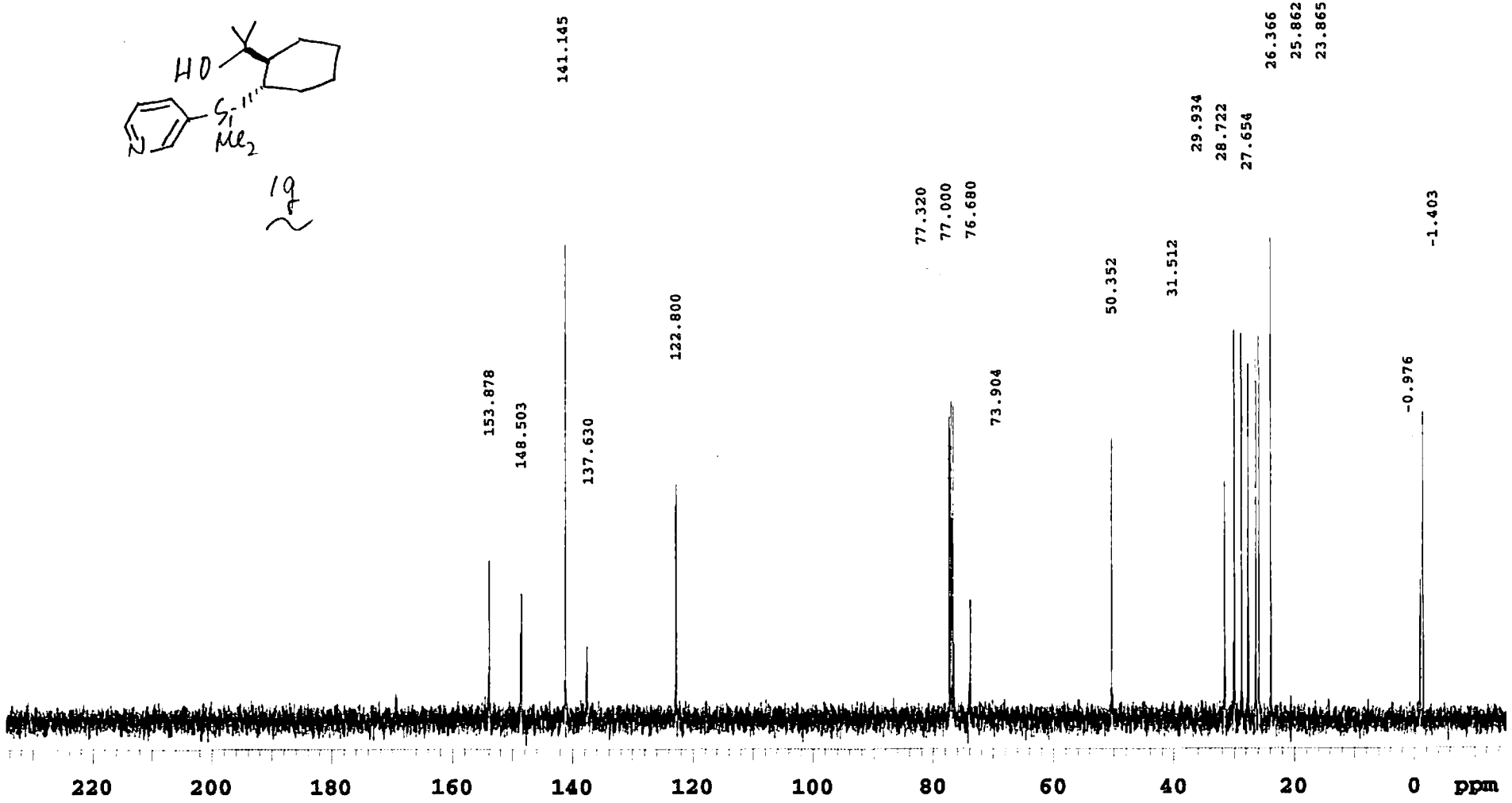


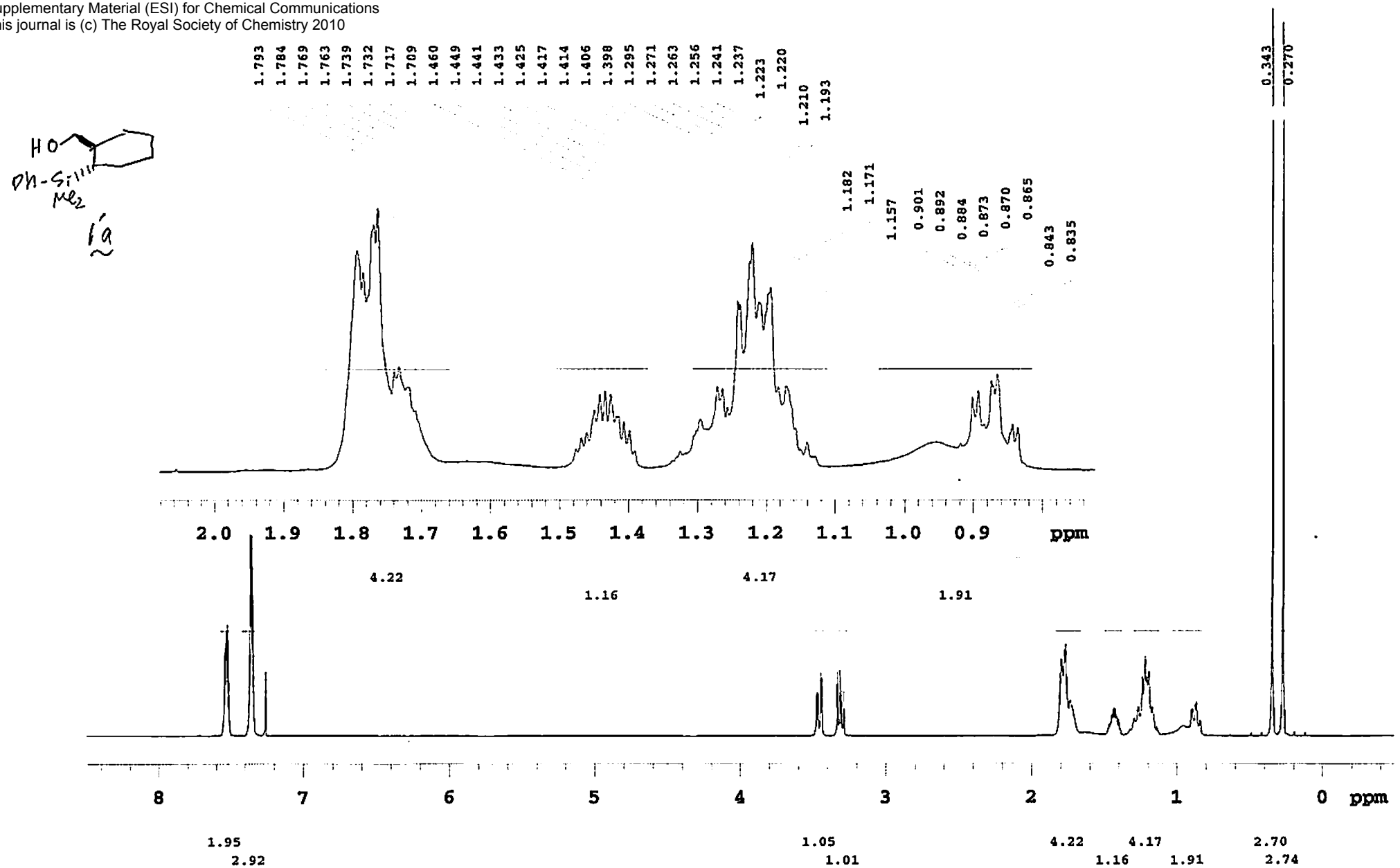
1f

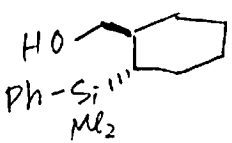




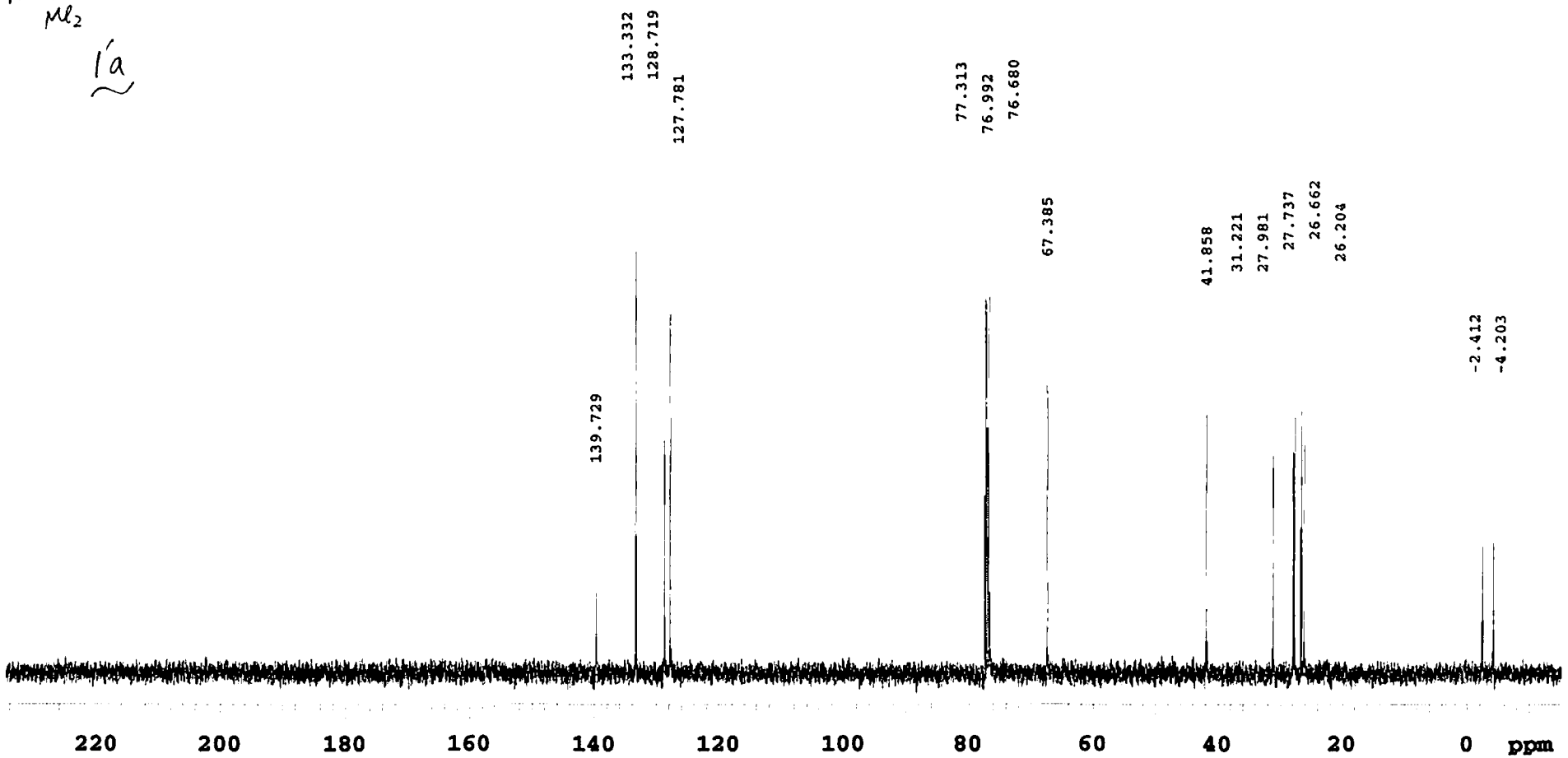
Pulse Sequence: s2pul

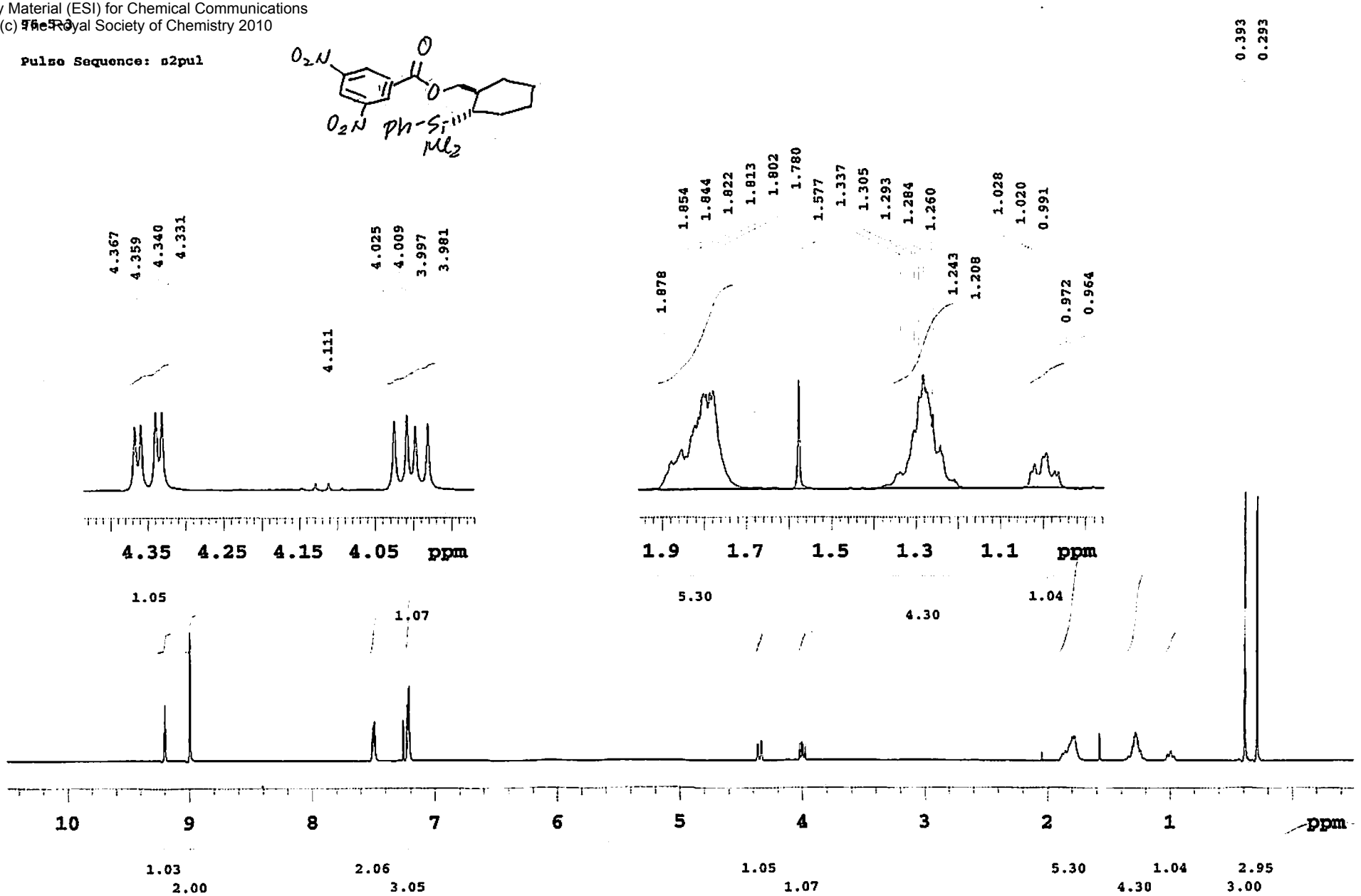



HO
Ph-Si
Me2
1a
1.793
1.784
1.769
1.763
1.739
1.732
1.717
1.709
1.460
1.449
1.441
1.433
1.425
1.417
1.414
1.406
1.398
1.295
1.271
1.263
1.256
1.241
1.237
1.223
1.220
1.210
1.193
1.182
1.171
1.157
0.901
0.892
0.884
0.873
0.870
0.865
0.843
0.835
0.343
0.270
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm
4.22
1.16
4.17
1.91
8 7 6 5 4 3 2 1 0 ppm
1.95
2.92
1.05
1.01
4.22
1.16
4.17
1.91
2.70
2.74

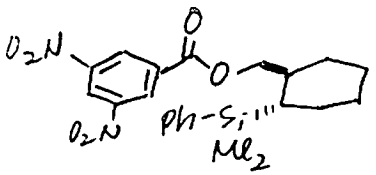

HO
Ph-Si
Me2

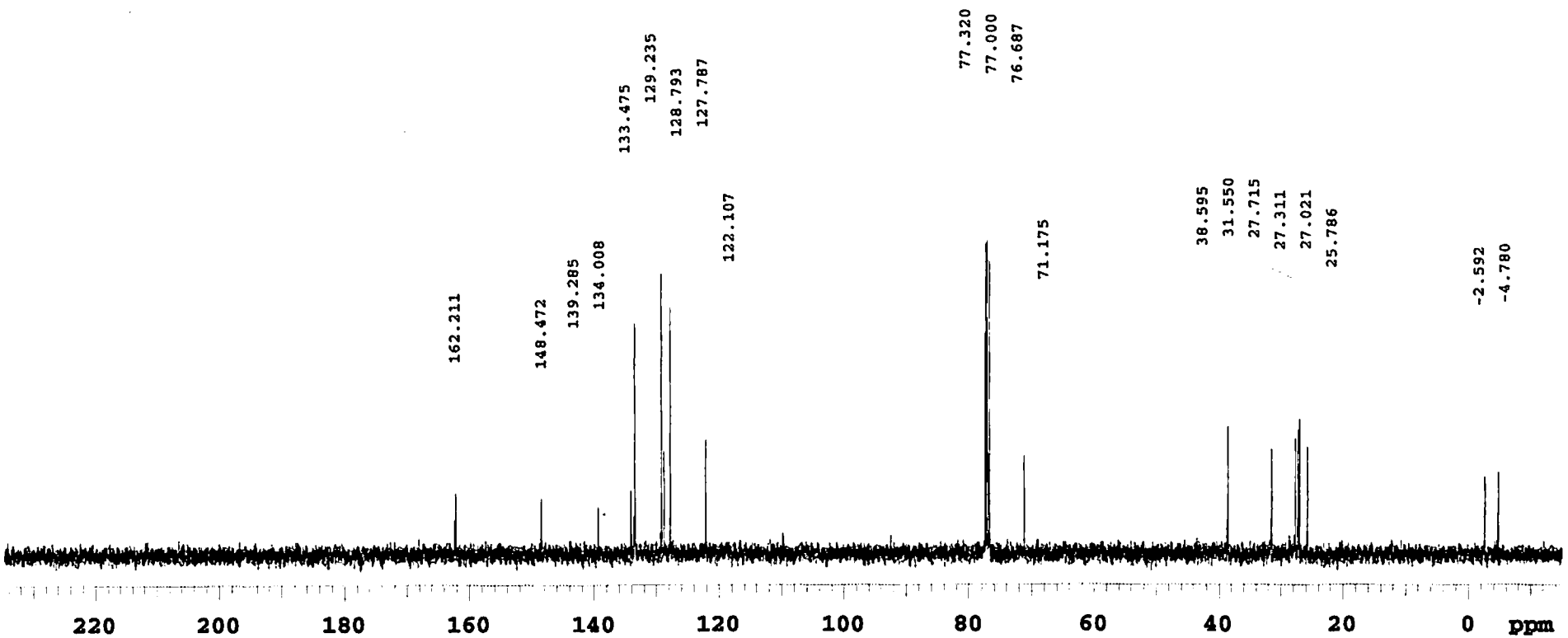
1'a

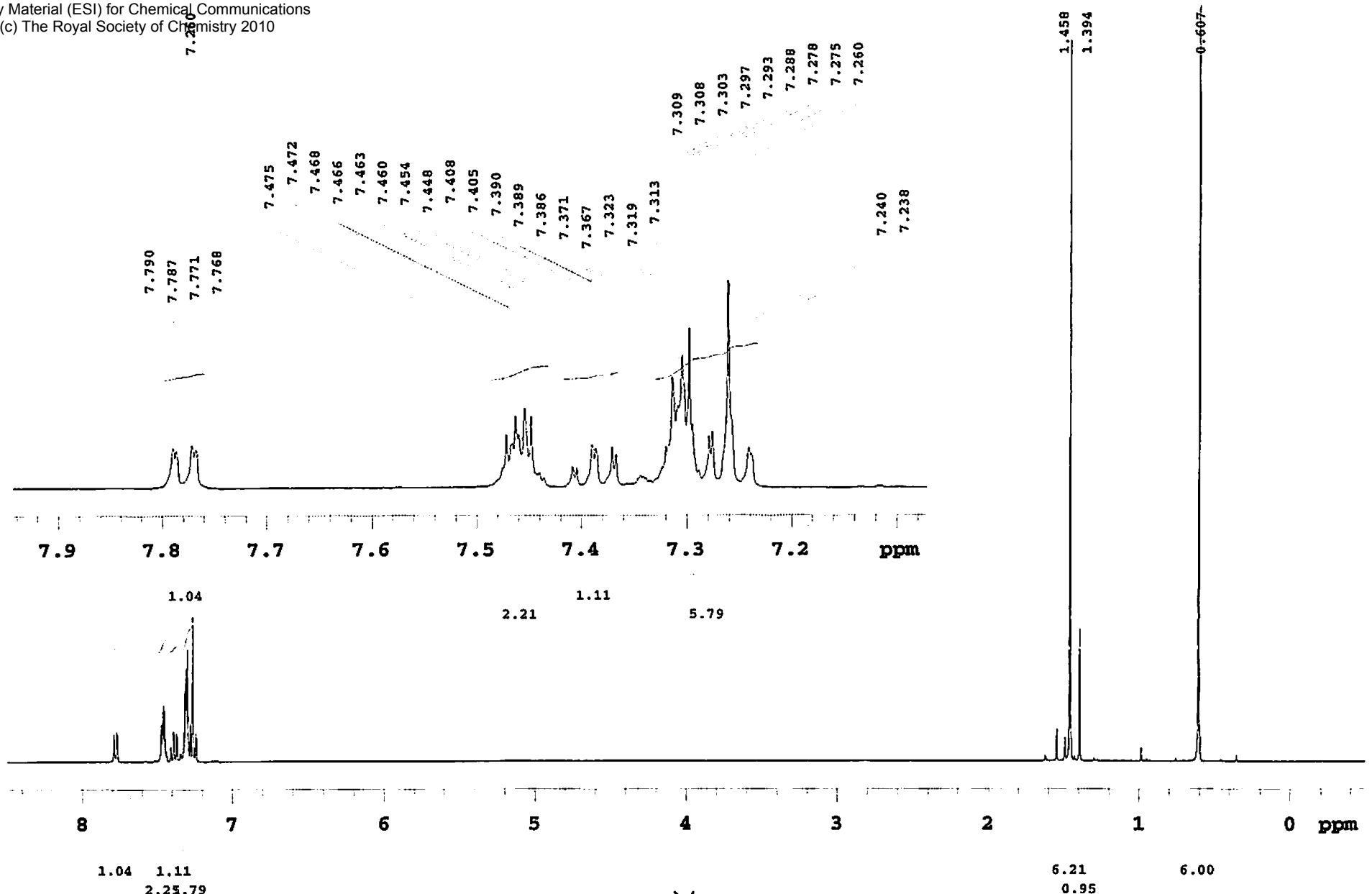

133.332
128.719
127.781
77.313
76.992
76.680
67.385
41.858
31.221
27.981
27.737
26.662
26.204
-2.412
-4.203
139.729
220
200
180
160
140
120
100
80
60
40
20
0
ppm

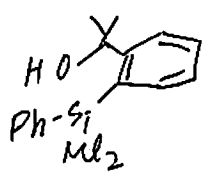

Pulse Sequence: s2pul
4.367
4.359
4.340
4.331
4.111
4.025
4.009
3.997
3.981
4.35 4.25 4.15 4.05 ppm
1.854
1.844
1.822
1.813
1.802
1.780
1.577
1.337
1.305
1.293
1.284
1.260
1.878
1.243
1.208
1.028
1.020
0.991
0.972
0.964
1.9 1.7 1.5 1.3 1.1 ppm
0.393
0.293
1.05
1.07
5.30
4.30
1.04
10 9 8 7 6 5 4 3 2 1 ppm
1.03
2.00
2.06
3.05
1.05
1.07
5.30
4.30
1.04
2.95
3.00

Pulse Sequence: s2pul

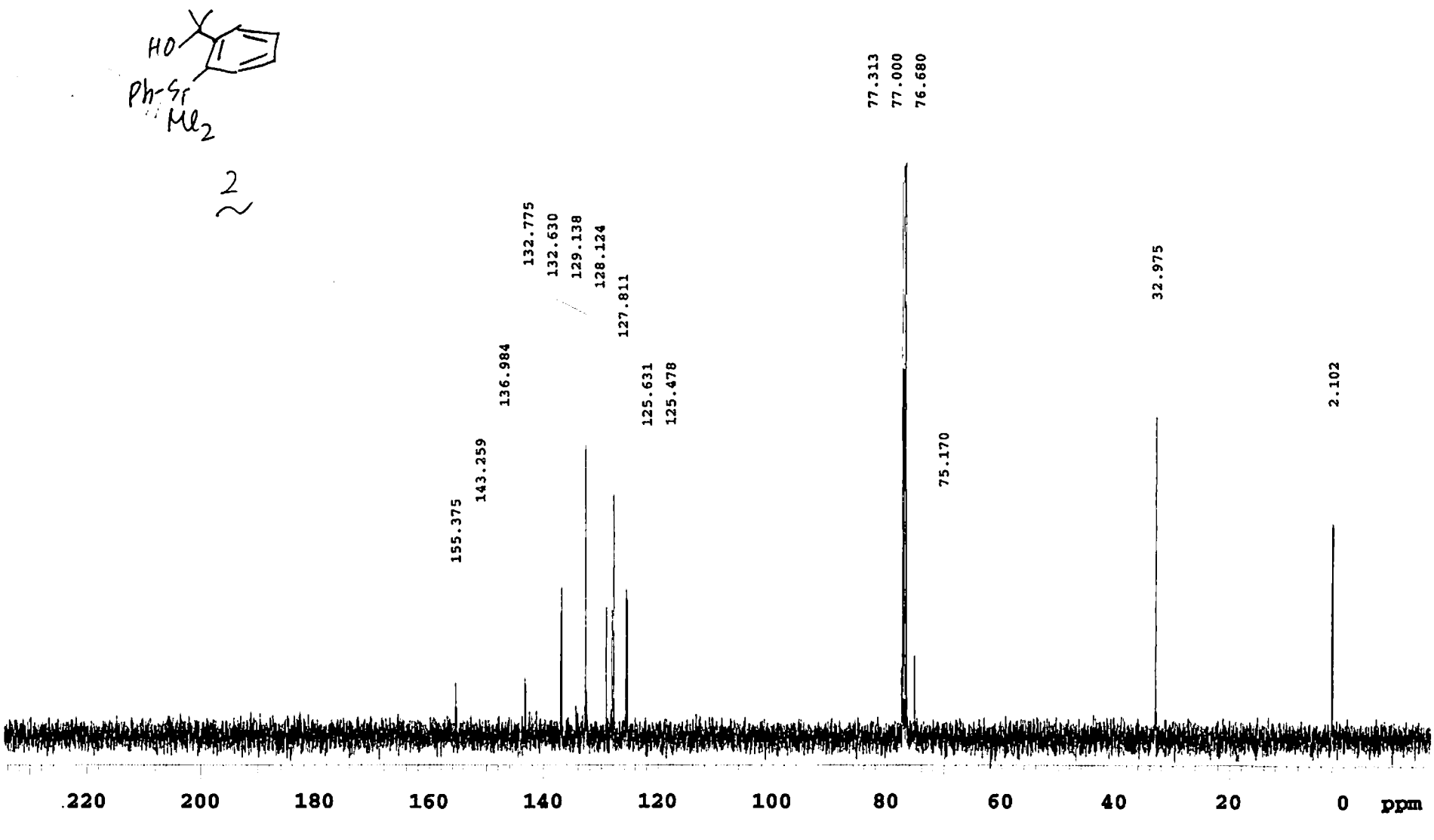


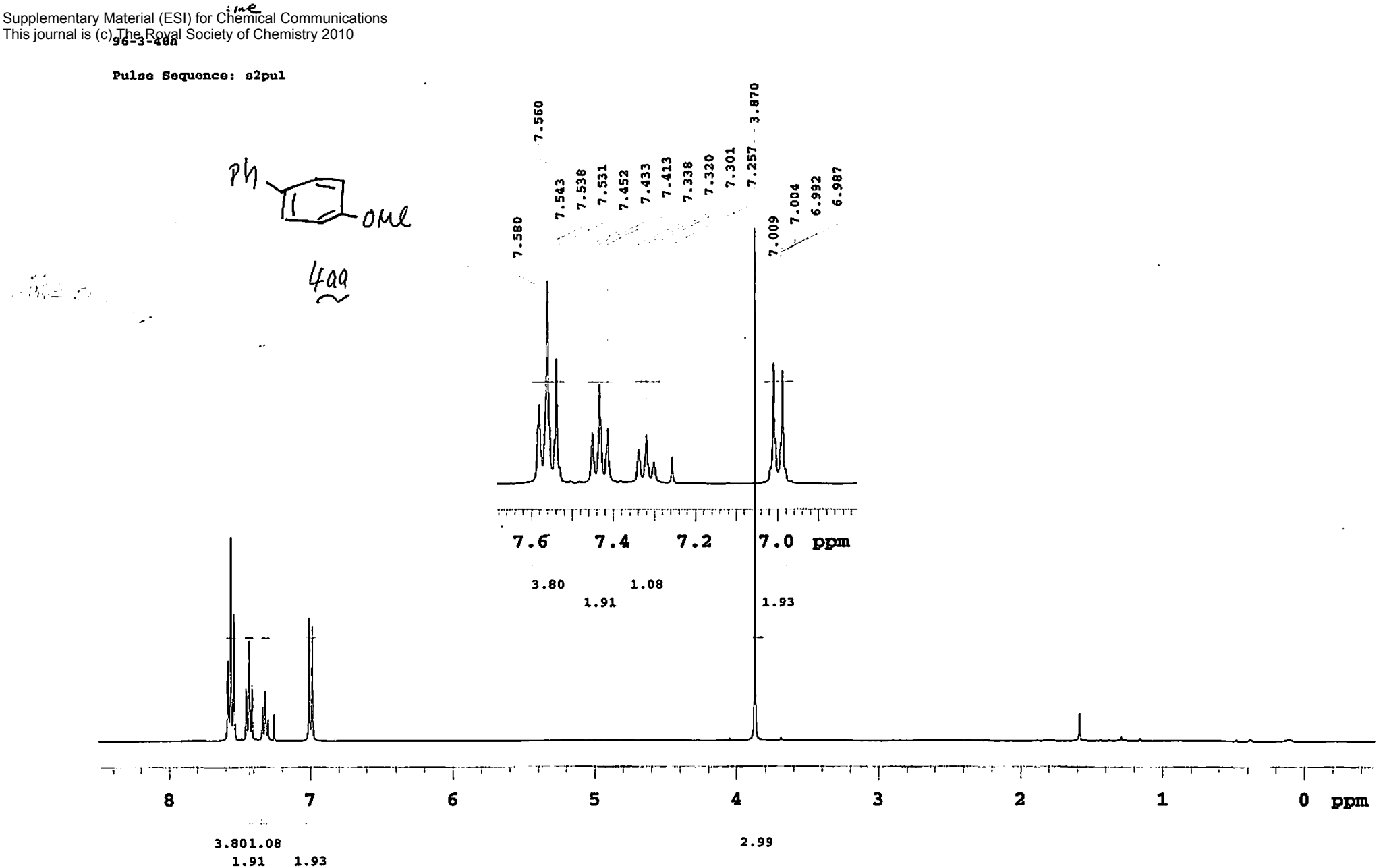






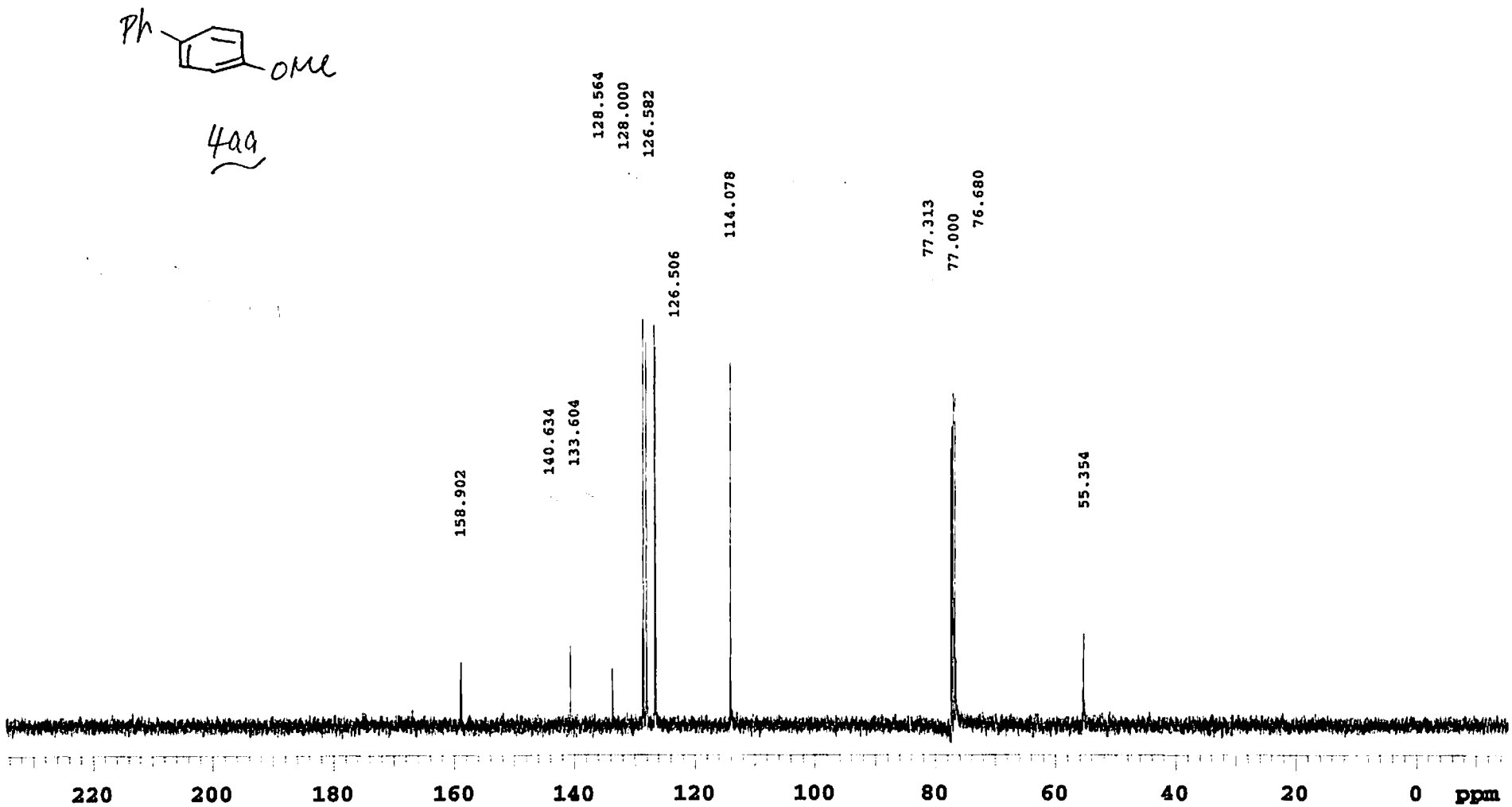
Pulse Sequence: s2pul

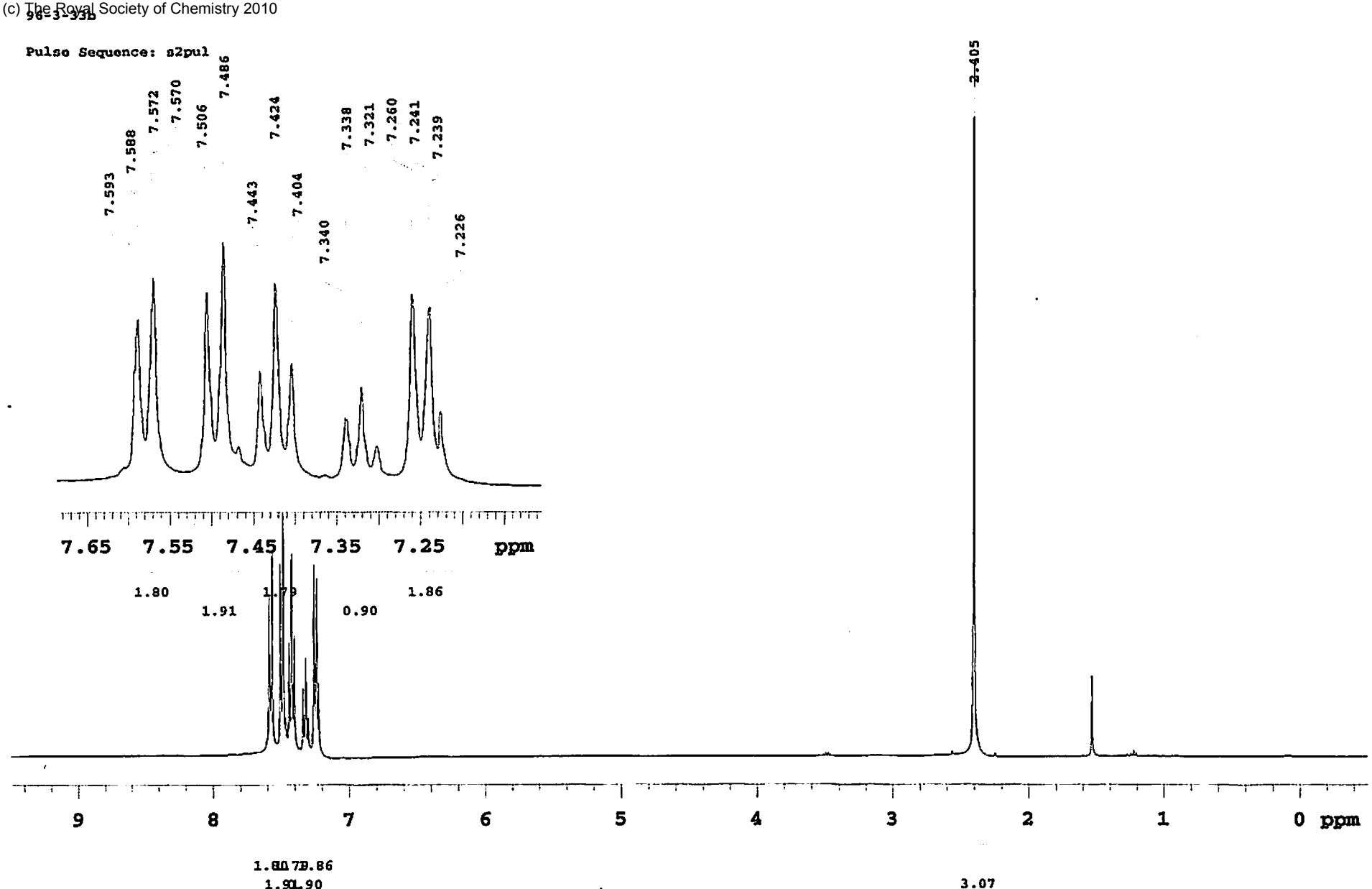


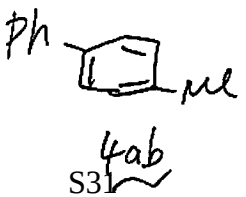

96-3-40a
Pulse Sequence: s2pul
Ph
OMe
4aa
7.560
7.543
7.538
7.531
7.452
7.433
7.413
7.338
7.320
7.301
7.257
3.870
7.580
7.009
7.004
6.992
6.987
7.6
7.4
7.2
7.0 ppm
3.80
1.08
1.91
1.93
8
7
6
5
4
3
2
1
0 ppm
3.80
1.08
1.91
1.93
2.99

96-3-40a

Pulse Sequence: s2pul



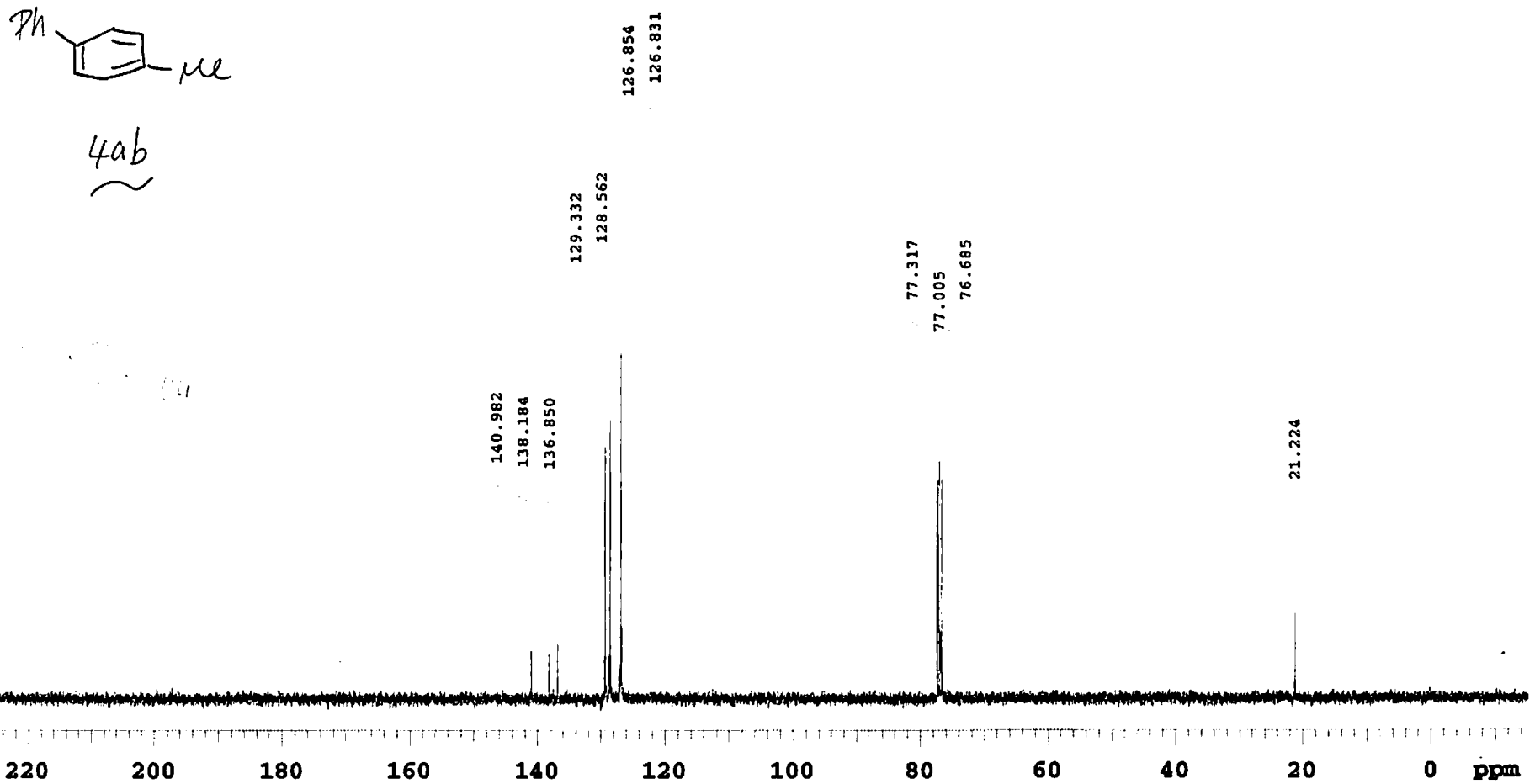

96-3-33b
Pulse Sequence: s2pul
7.593
7.588
7.572
7.570
7.506
7.486
7.443
7.424
7.404
7.340
7.338
7.321
7.260
7.241
7.239
7.226
2.405
7.65
7.55
7.45
7.35
7.25
ppm
1.80
1.91
1.79
0.90
1.86
9
8
7
6
5
4
3
2
1
0 ppm
1.80 1.79 1.86
1.91 0.90
3.07

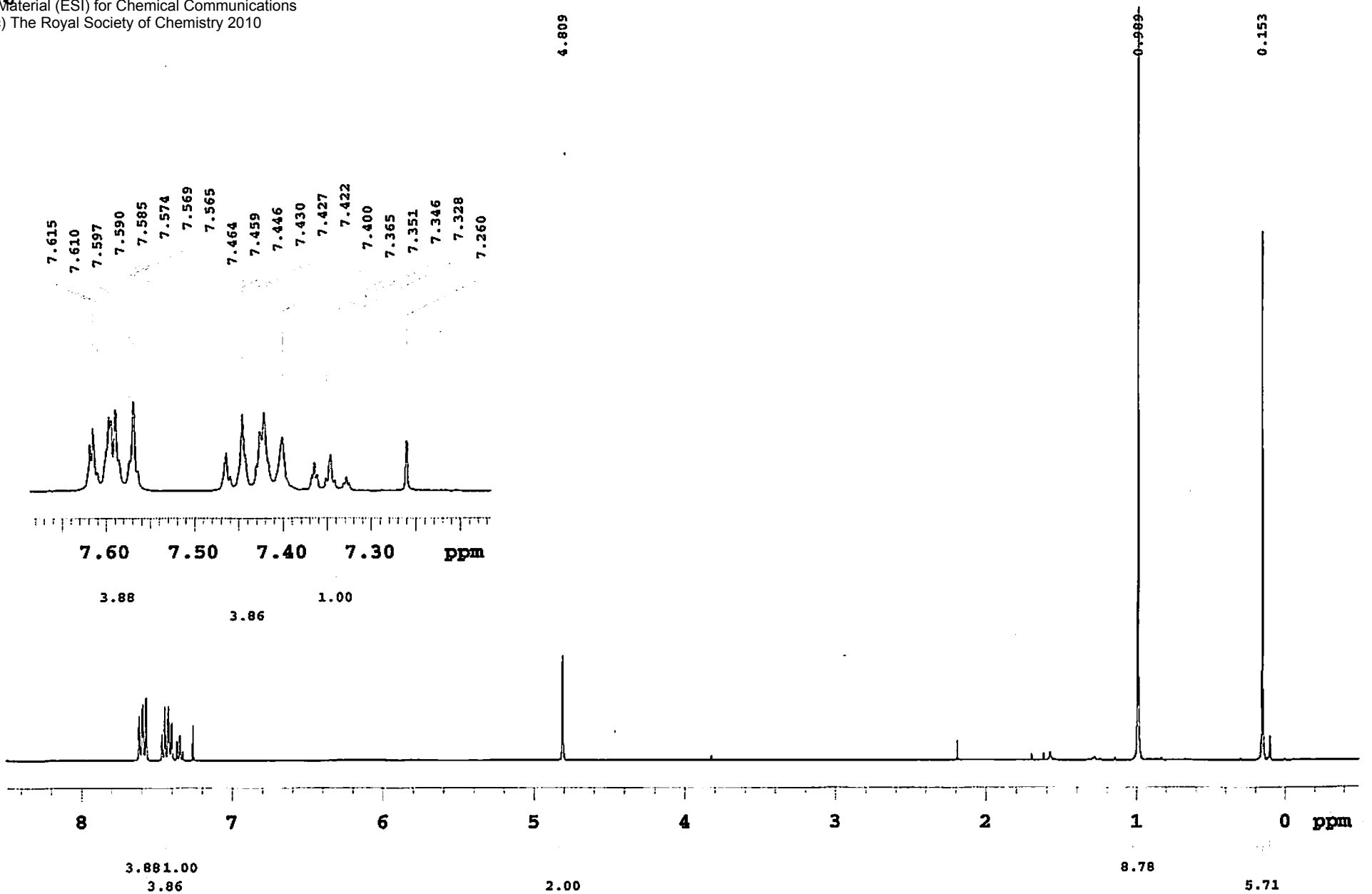

Ph
Me

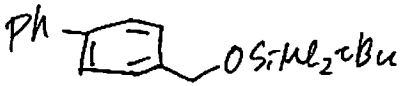
4ab

96-3-339

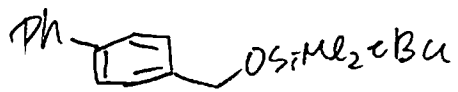
Pulse Sequence: s2pul



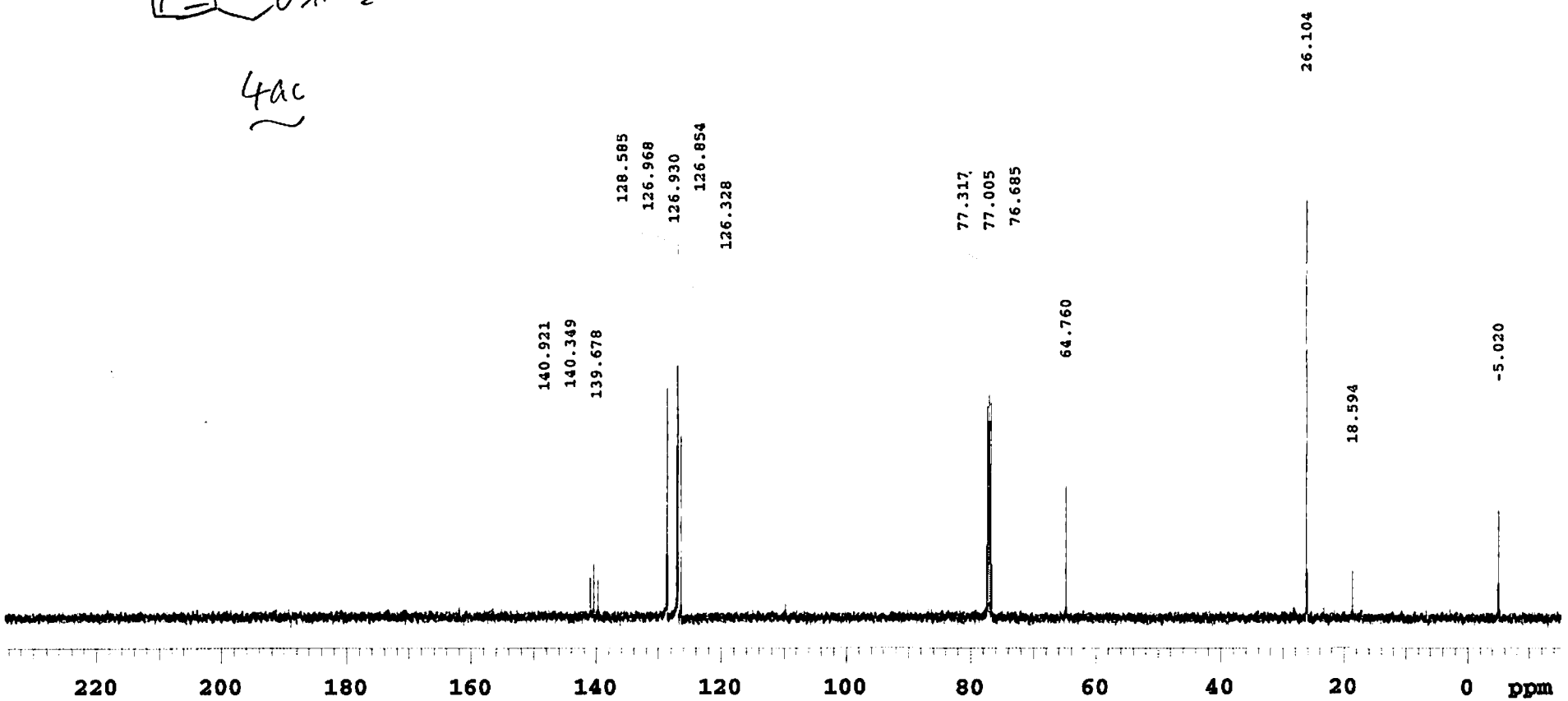


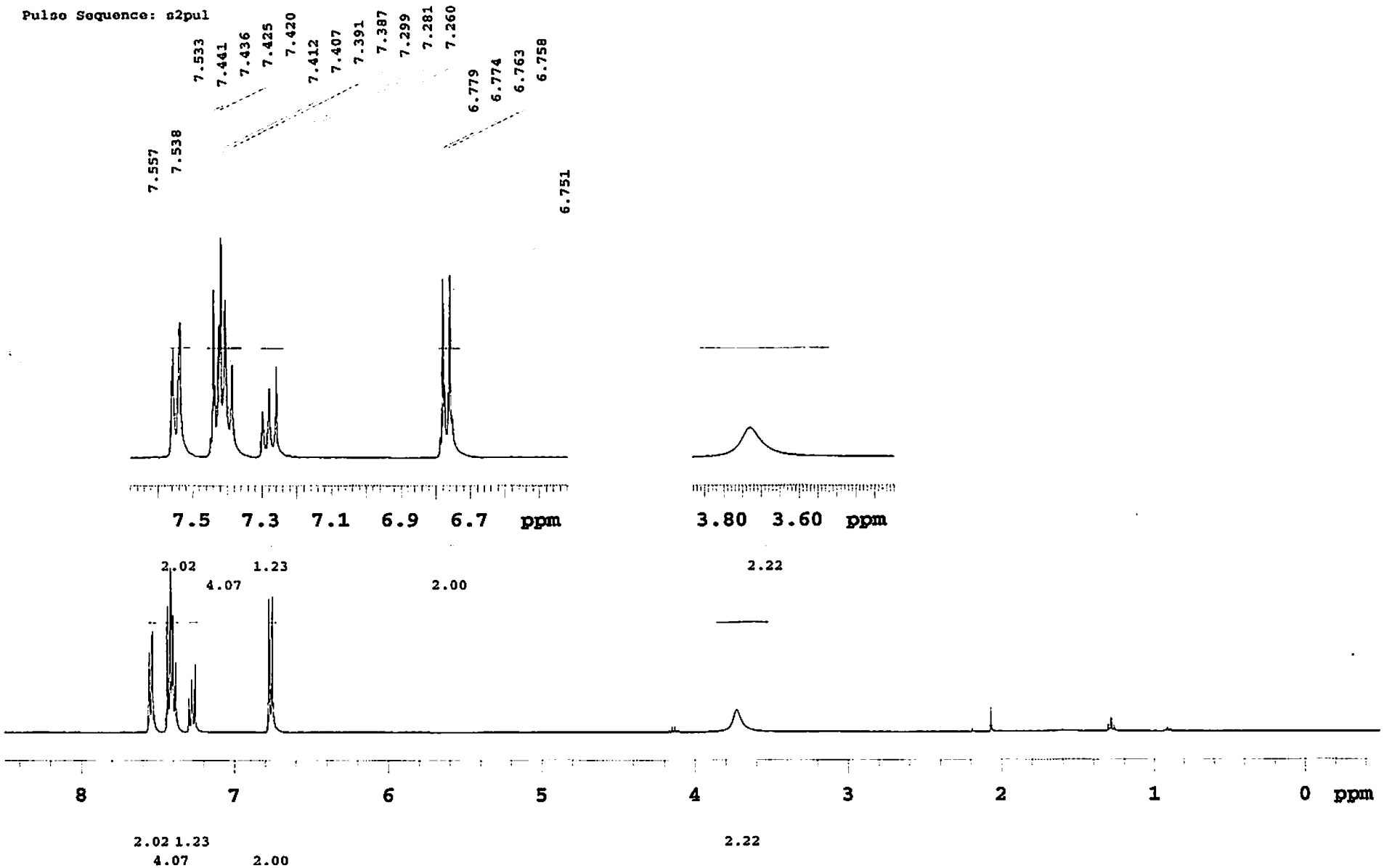


4ac


Ph
OSiMe2tBu

4ac

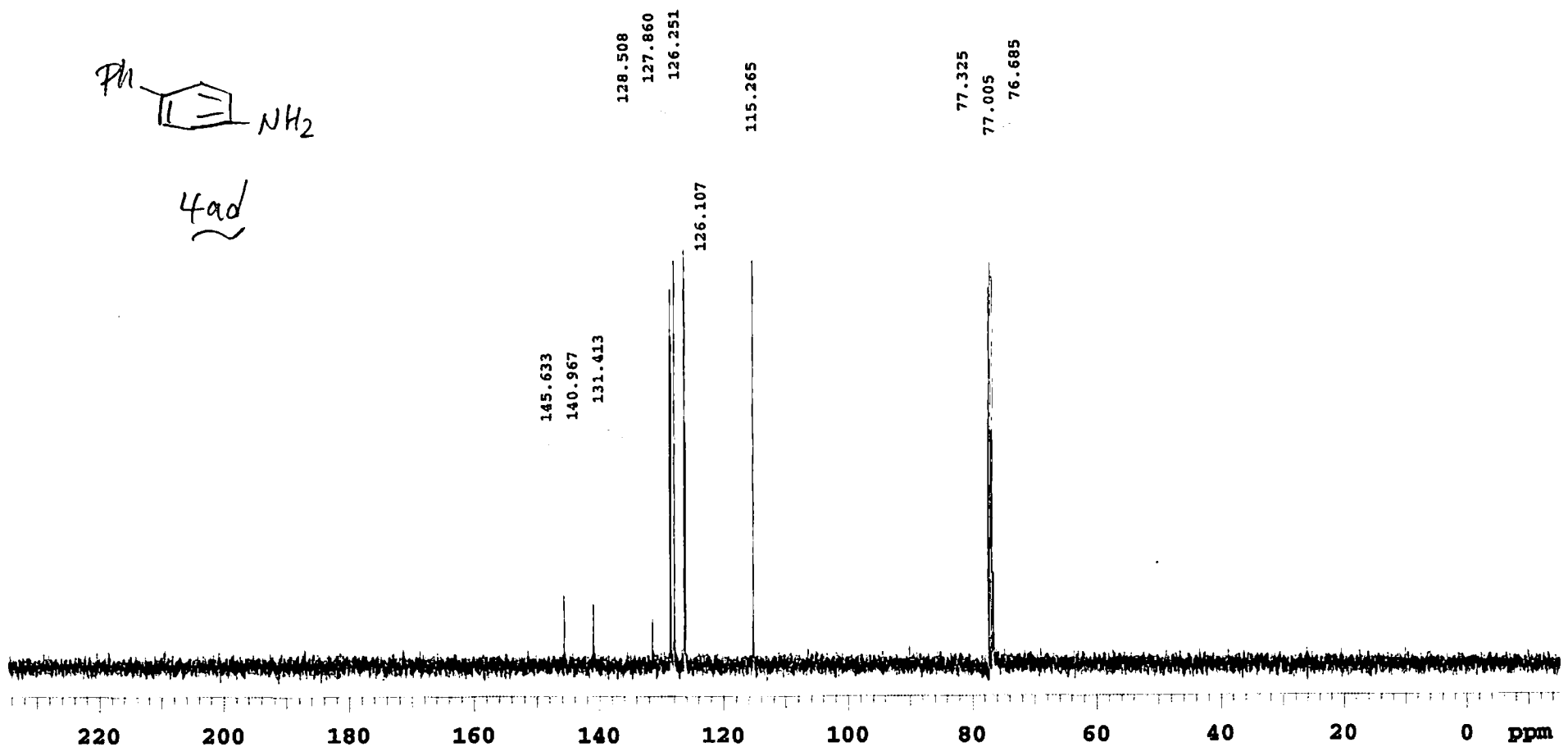

140.921
140.349
139.678
128.585
126.968
126.930
126.854
126.328
77.317
77.005
76.685
64.760
26.104
18.594
-5.020
220
200
180
160
140
120
100
80
60
40
20
0
ppm


963-188E
Pulse Sequence: s2pul
7.557
7.538
7.533
7.441
7.436
7.425
7.420
7.412
7.407
7.391
7.387
7.299
7.281
7.260
6.779
6.774
6.763
6.758
6.751
7.5 7.3 7.1 6.9 6.7 ppm
3.80 3.60 ppm
2.02
4.07
1.23
2.00
2.22
8 7 6 5 4 3 2 1 0 ppm
2.02 1.23
4.07 2.00
2.22

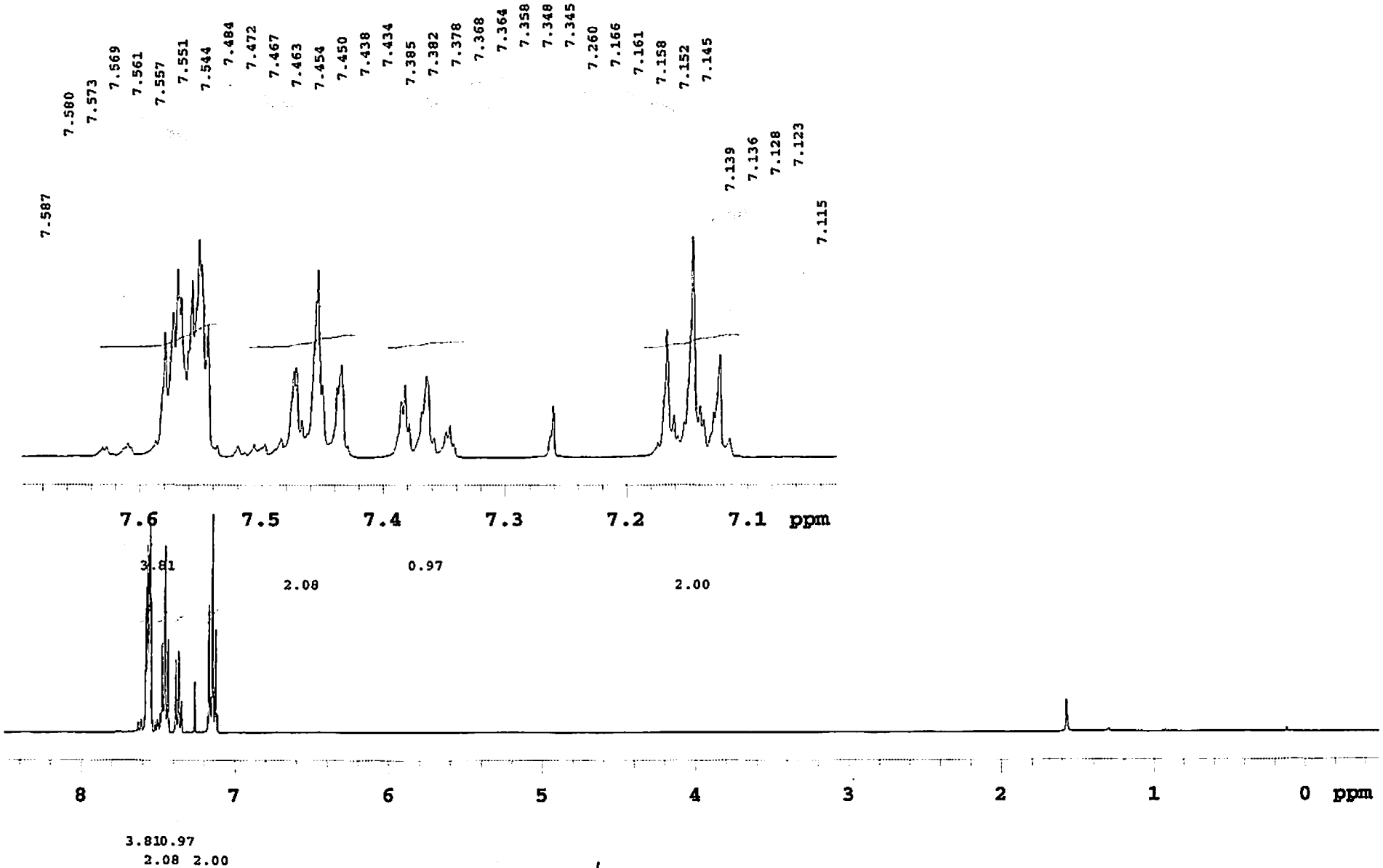

Ph
NH2

96-3-188c

Pulse Sequence: s2pul

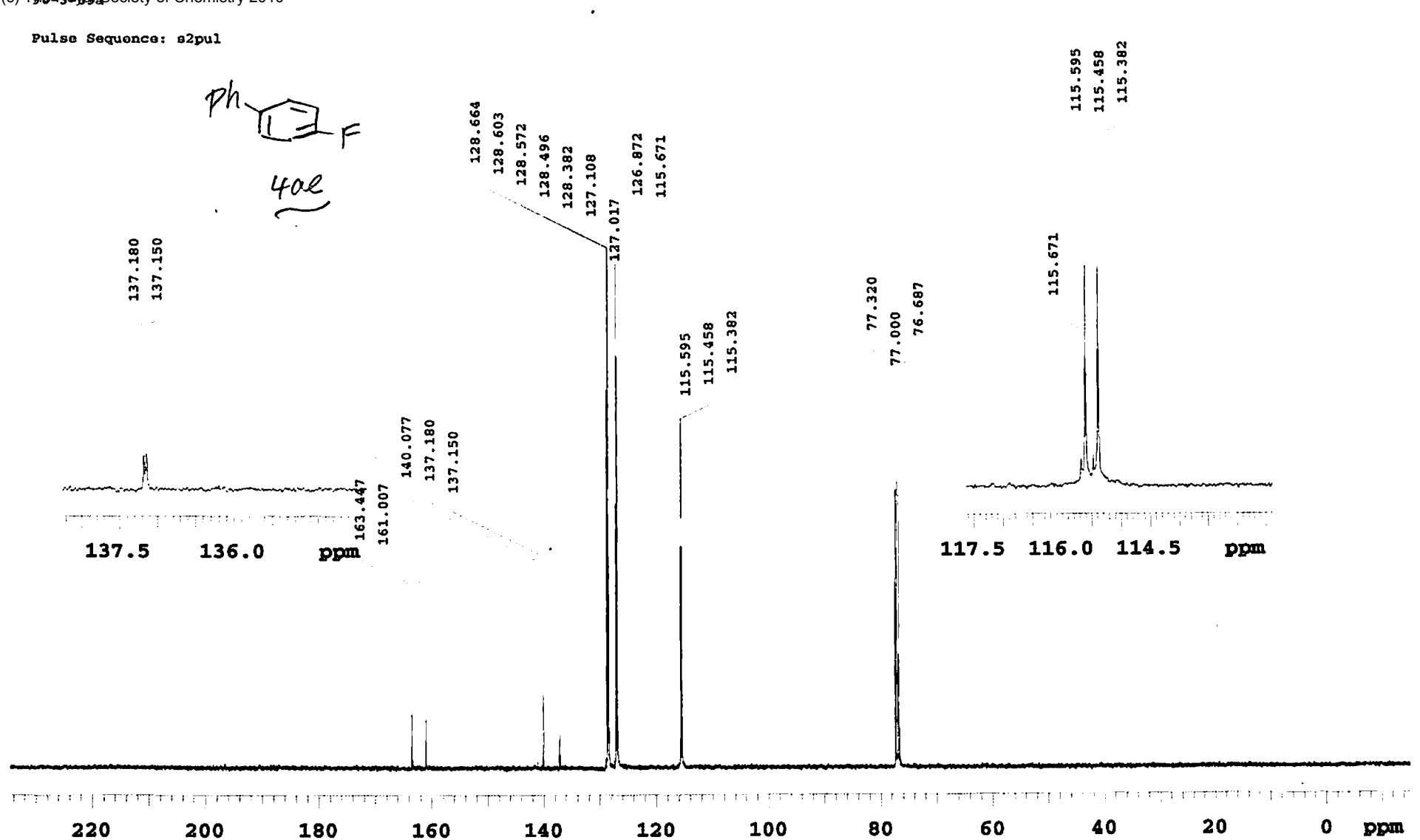


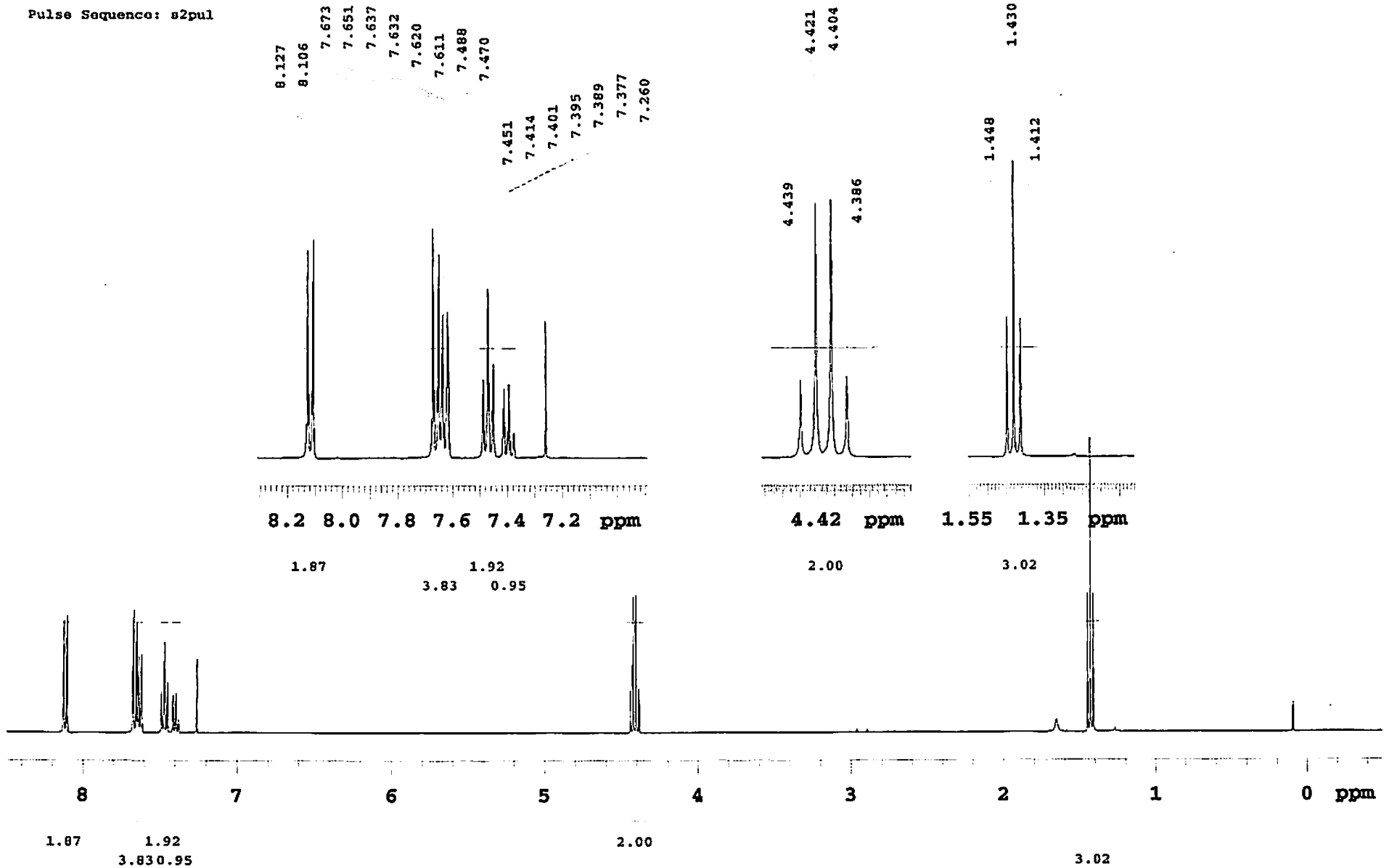
Supplementary Material (ESI) for Chemical Communications



Ph  F

4ae


96-3-89a
Pulse Sequence: s2pul
Ph
F
40e
128.664
128.603
128.572
128.496
128.382
127.108
127.017
126.872
115.671
115.595
115.458
115.382
77.320
77.000
76.687
137.180
137.150
140.077
137.180
137.150
163.447
161.007
137.5
136.0
ppm
115.671
115.595
115.458
115.382
117.5
116.0
114.5
ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm

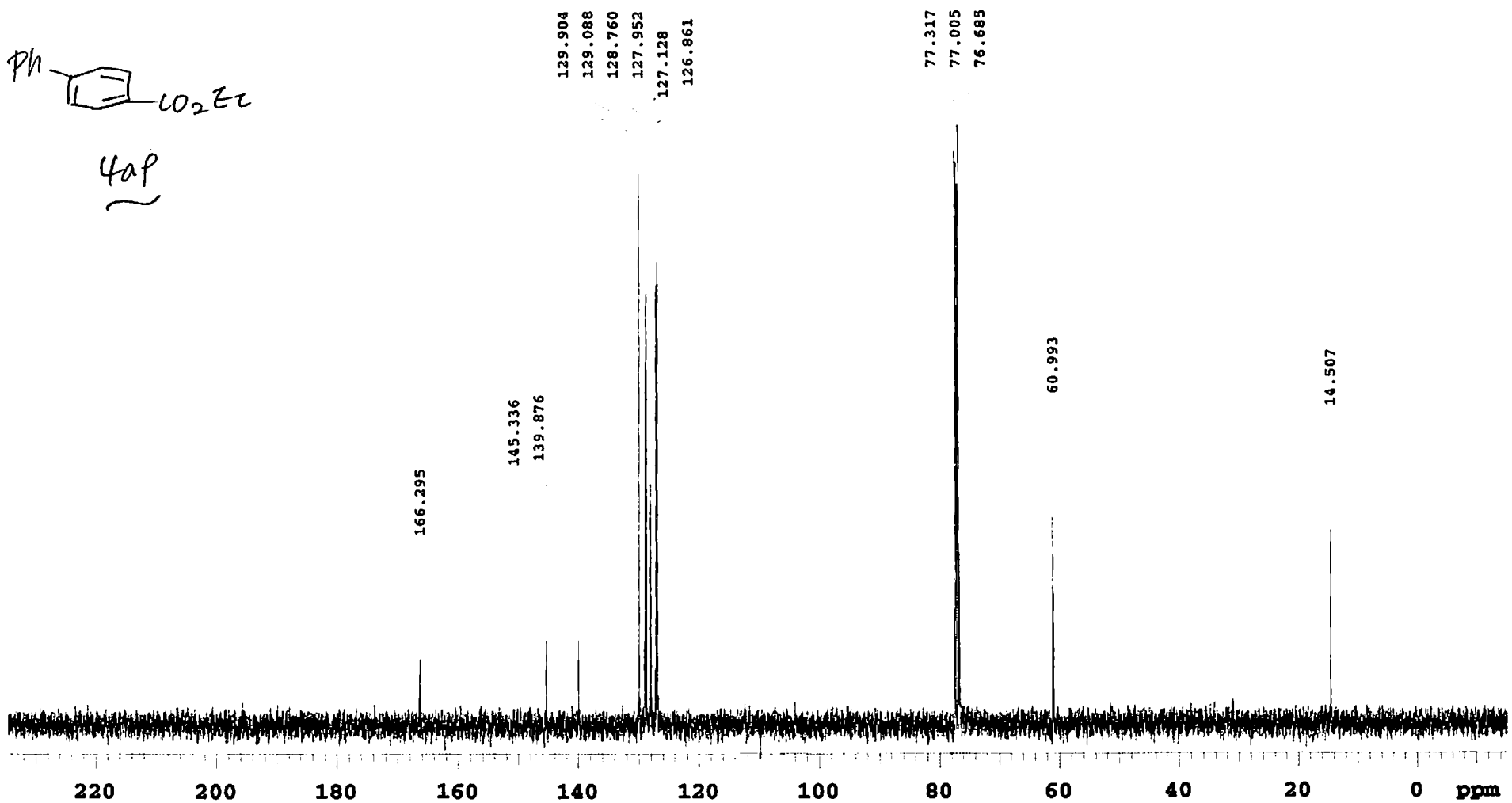

Pulse Sequence: s2pul
8.127
8.106
7.673
7.651
7.637
7.632
7.620
7.611
7.488
7.470
7.451
7.414
7.401
7.395
7.389
7.377
7.260
4.421
4.404
4.439
4.386
1.430
1.448
1.412
8.2 8.0 7.8 7.6 7.4 7.2 ppm
4.42 ppm
1.55 1.35 ppm
1.87
1.92
3.83
0.95
2.00
3.02
8 7 6 5 4 3 2 1 0 ppm


Ph
CO2Et

4af

96-3-338

Pulse Sequence: s2pul



Supplementary Material (ESI) for Chemical Communications
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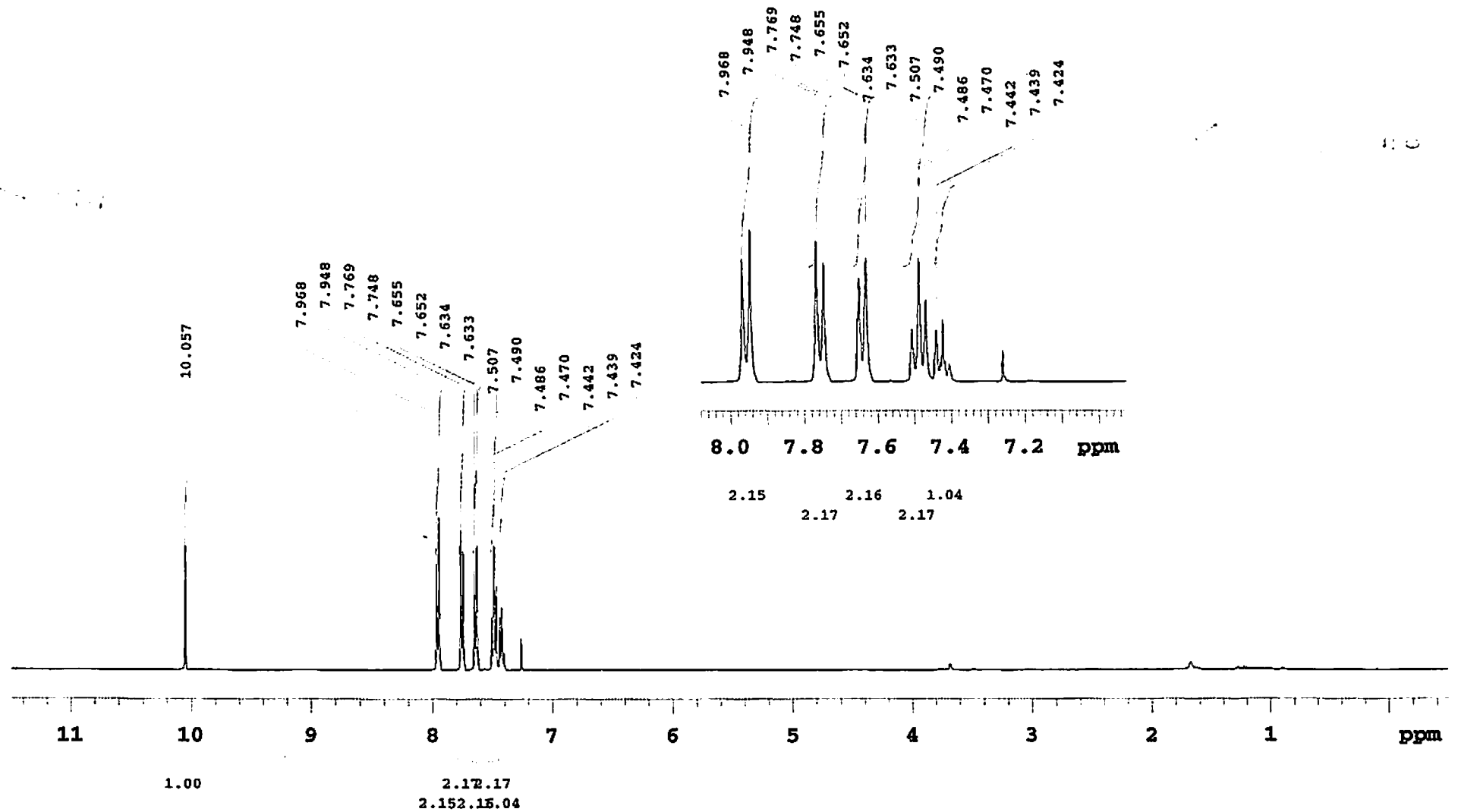
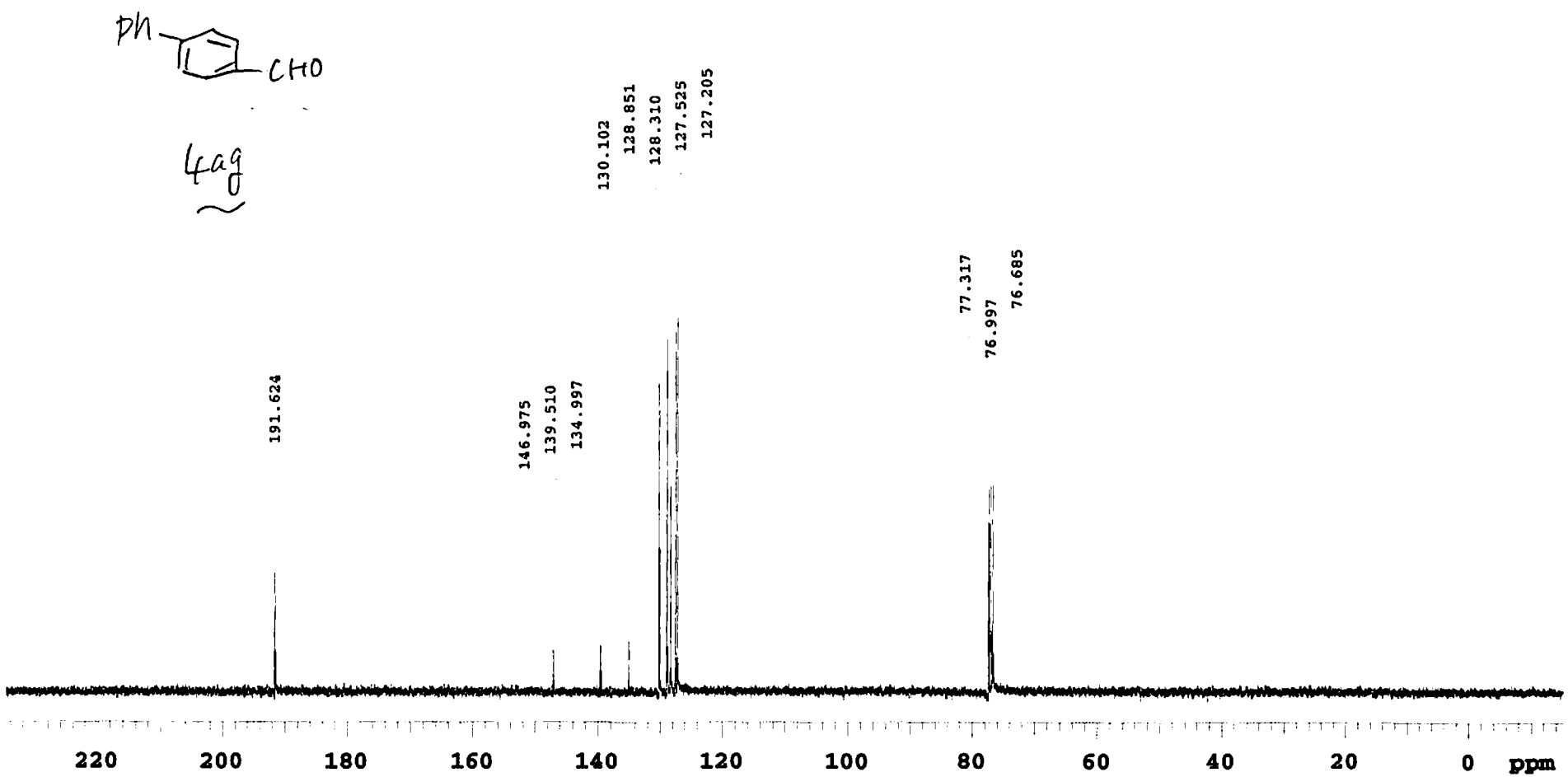
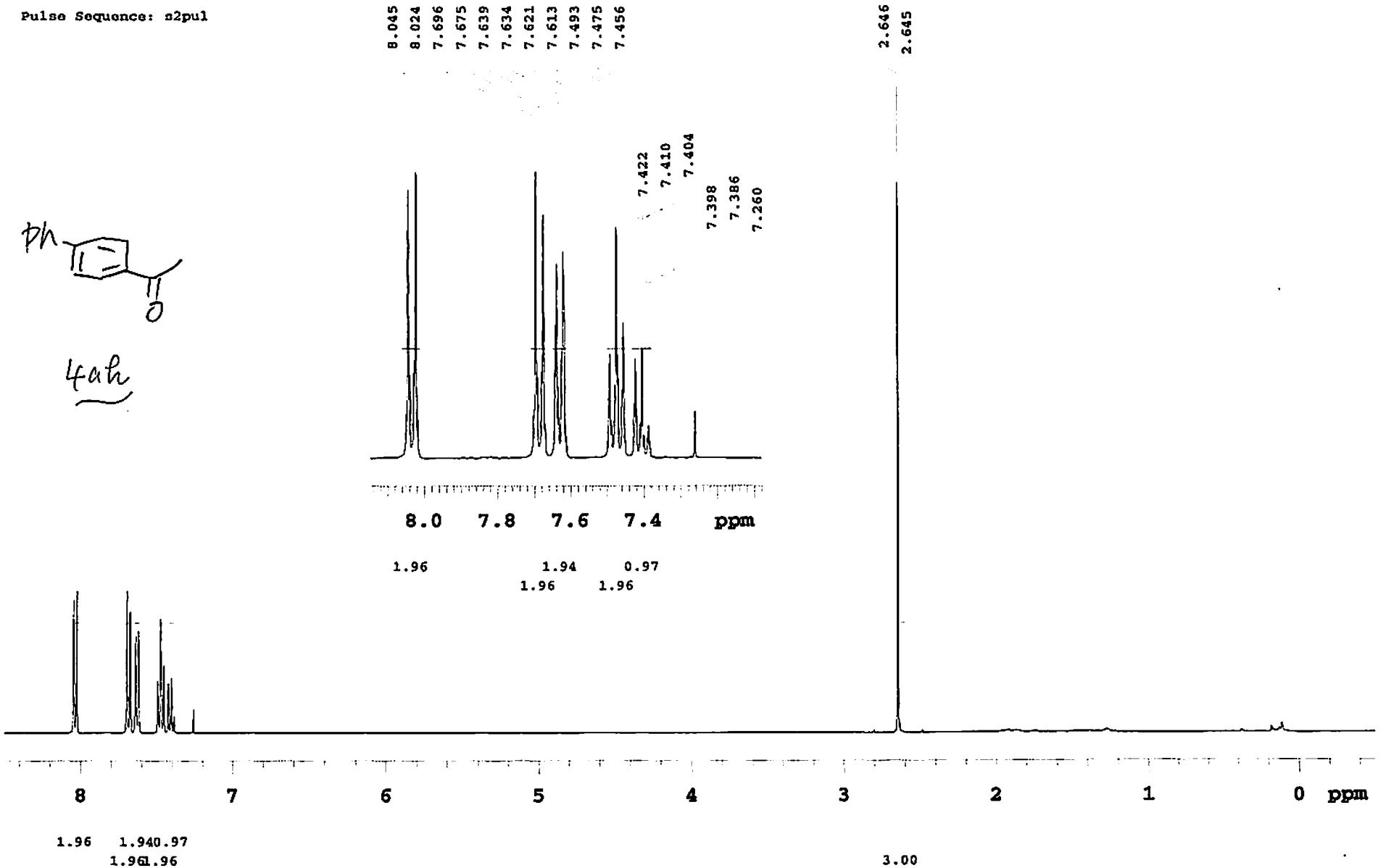
Pulse Sequence: s2pul



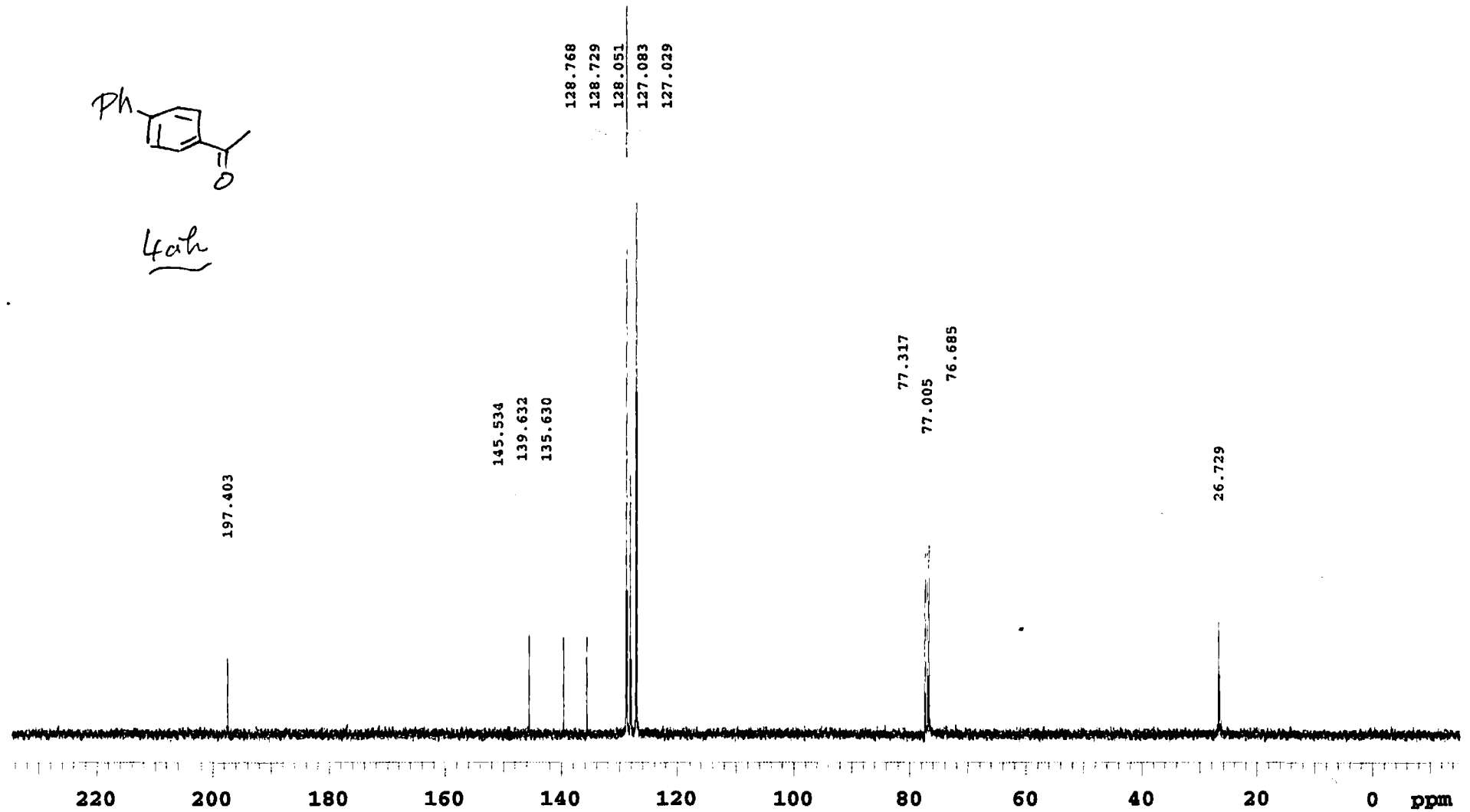
4ag

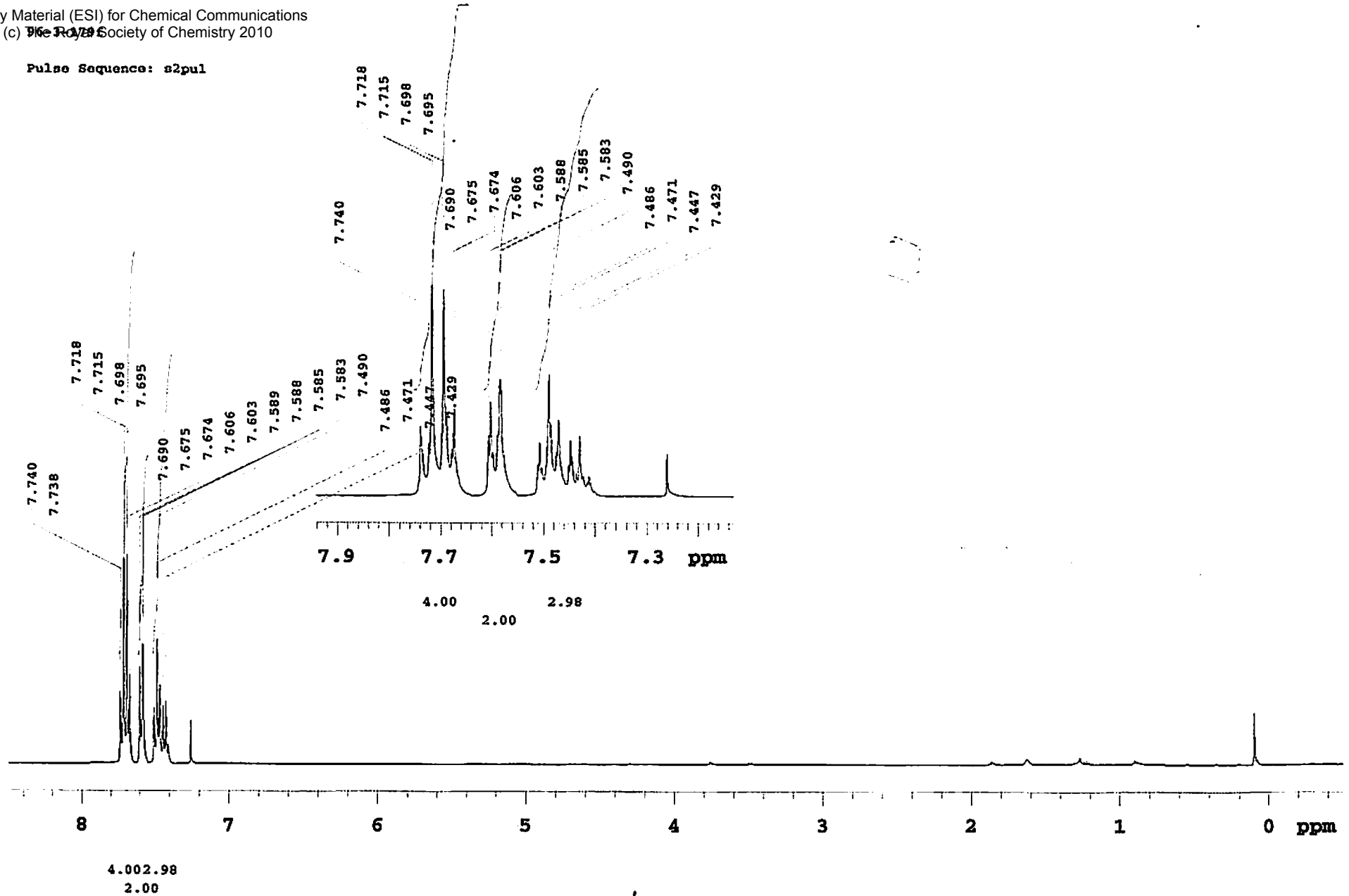

ph
CHO
4ag
191.624
146.975
139.510
134.997
130.102
128.851
128.310
127.525
127.205
77.317
76.997
76.685
220
200
180
160
140
120
100
80
60
40
20
0
ppm

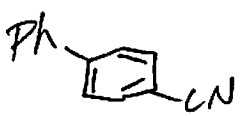

96-3-32e
Pulse Sequence: s2pul
8.045
8.024
7.696
7.675
7.639
7.634
7.621
7.613
7.493
7.475
7.456
7.422
7.410
7.404
7.398
7.386
7.260
2.646
2.645
Ph
4ah
8.0
7.8
7.6
7.4
ppm
1.96
1.94
0.97
1.96
1.96
8
7
6
5
4
3
2
1
0
ppm
1.96
1.94
0.97
1.96
1.96
3.00

96-3-32c

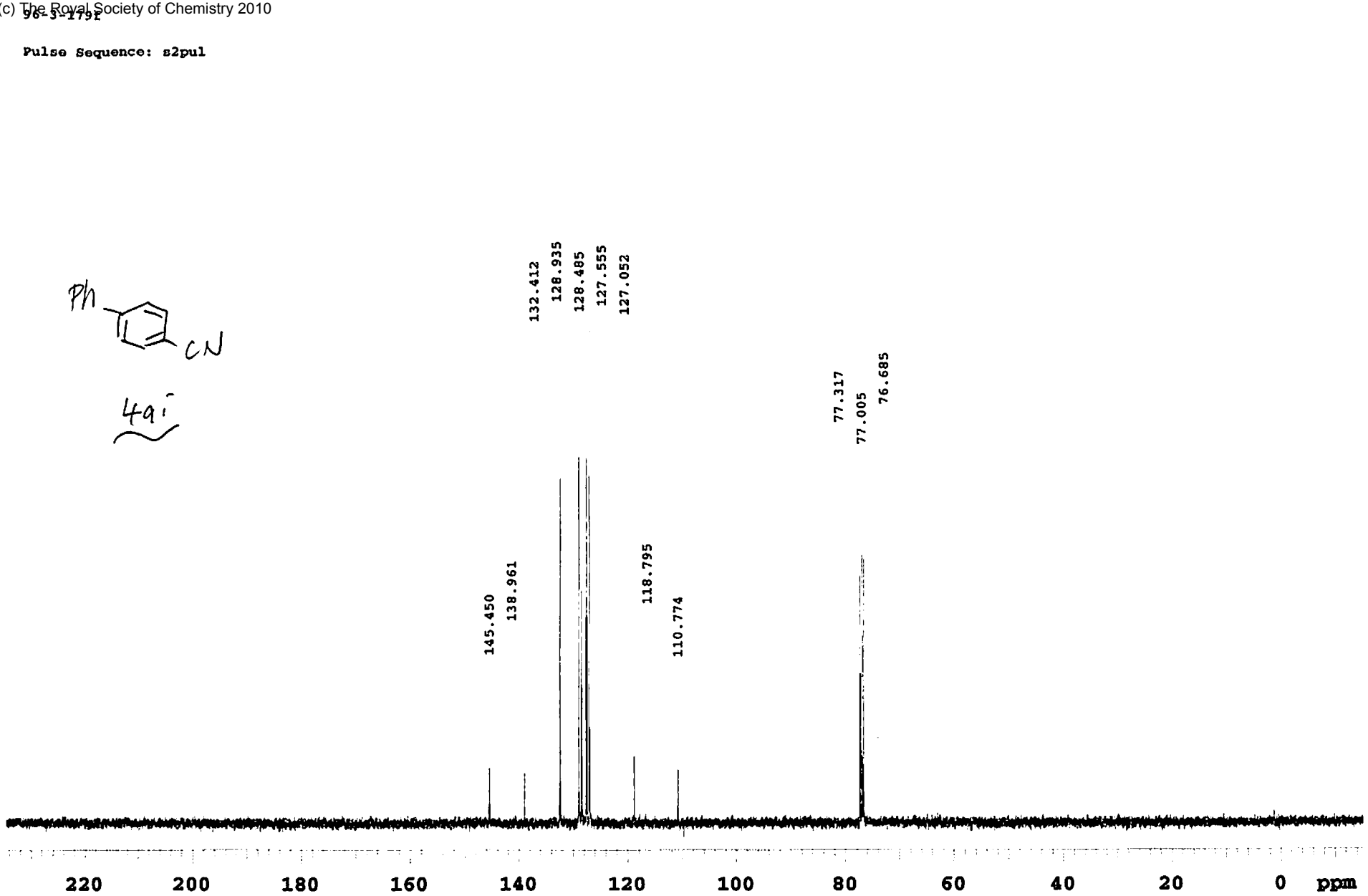
Pulse Sequence: s2pul



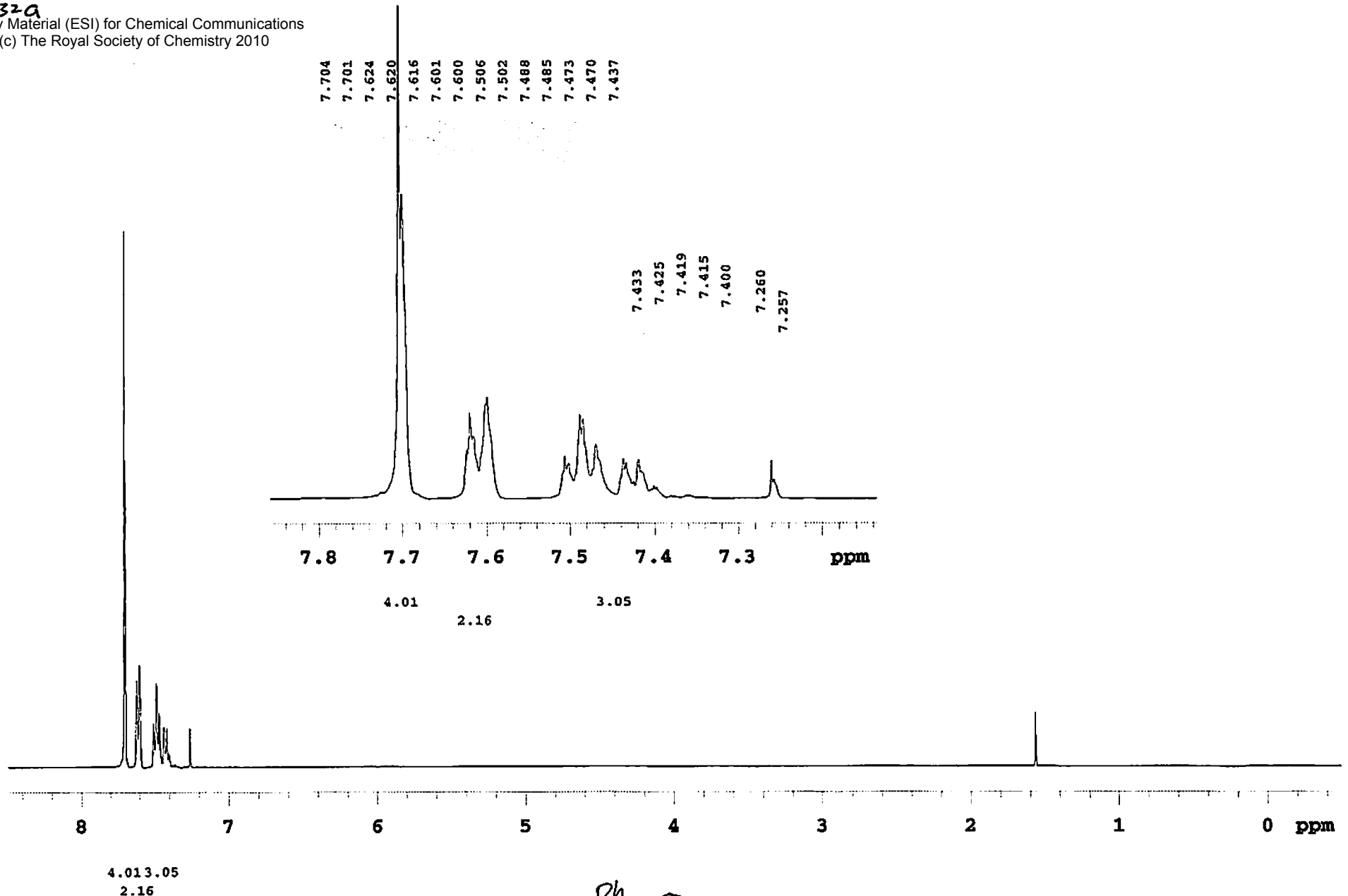

Pulse Sequence: s2pul
7.740
7.738
7.718
7.715
7.698
7.695
7.690
7.675
7.674
7.606
7.603
7.589
7.588
7.585
7.583
7.490
7.486
7.471
7.447
7.429
8
7
6
5
4
3
2
1
0
ppm
4.002.98
2.00
7.9
7.7
7.5
7.3
ppm
4.00
2.98
2.00

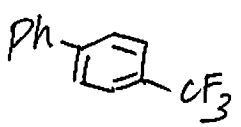

Ph
CN

4ai

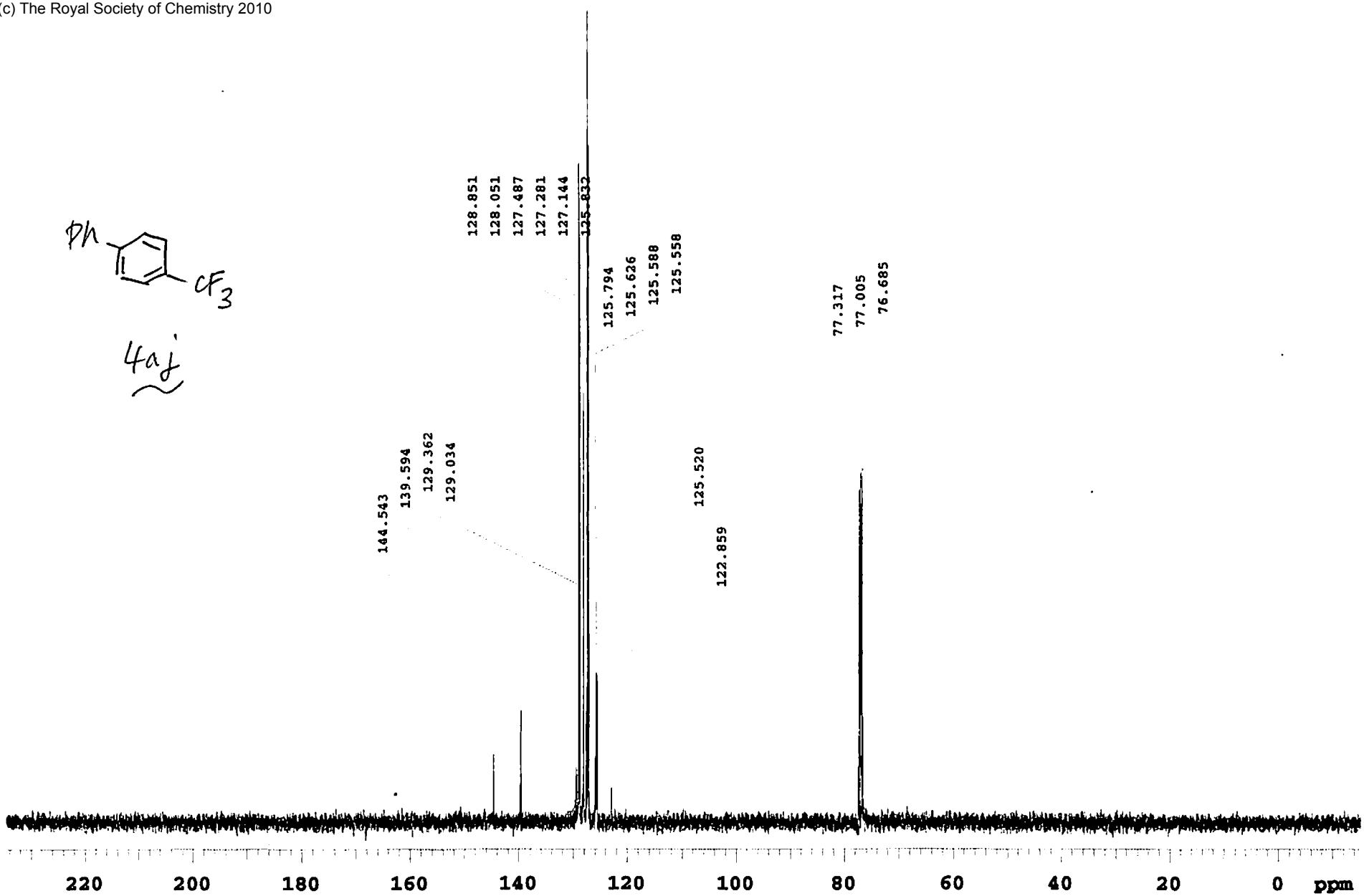

96-3-179I
Pulse Sequence: s2pul
Ph
CN
4qi
132.412
128.935
128.485
127.555
127.052
77.317
77.005
76.685
145.450
138.961
118.795
110.774
220
200
180
160
140
120
100
80
60
40
20
0
ppm

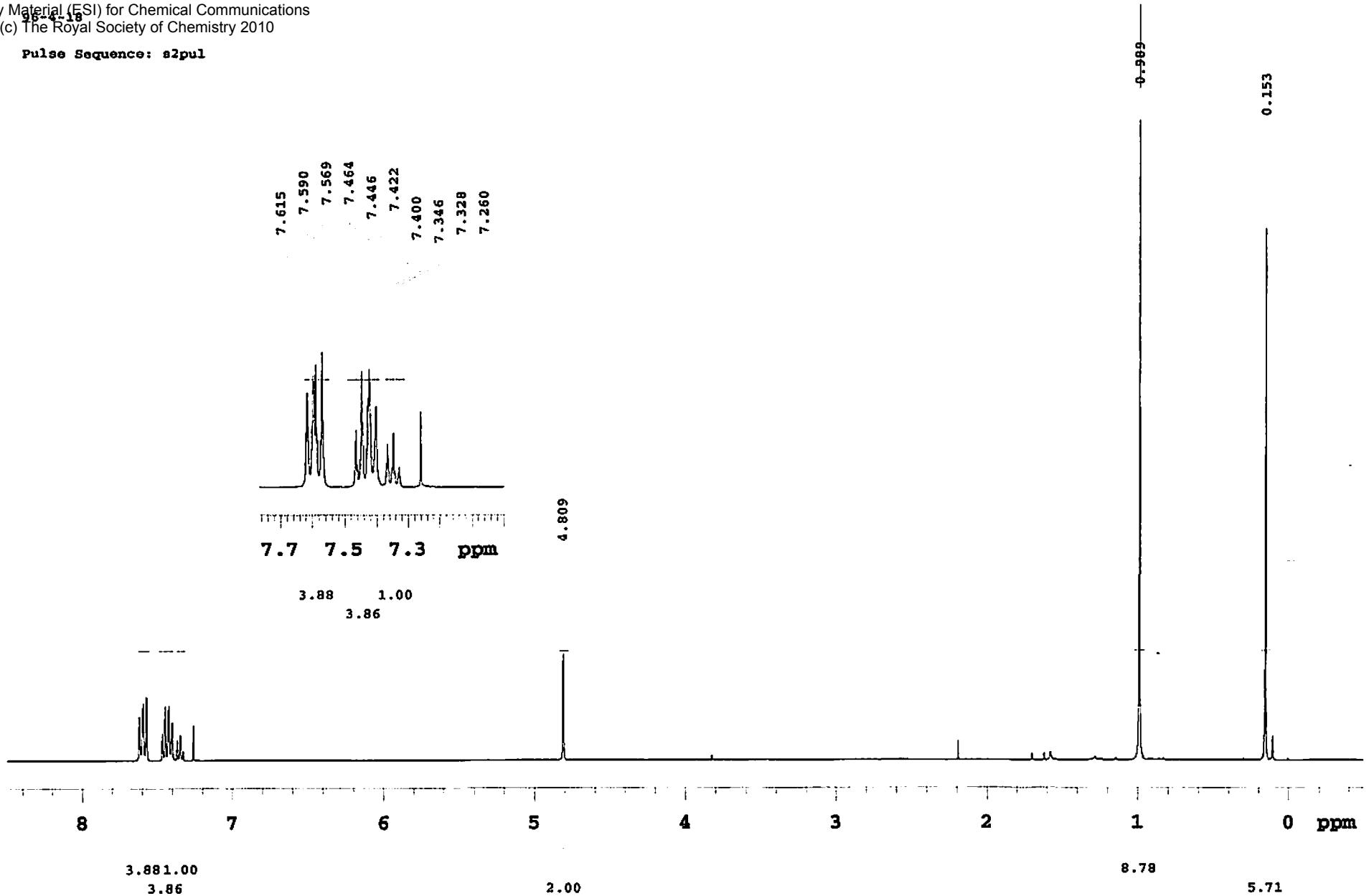
Supplementary Material (ESI) for Chemical Communications

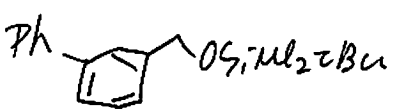




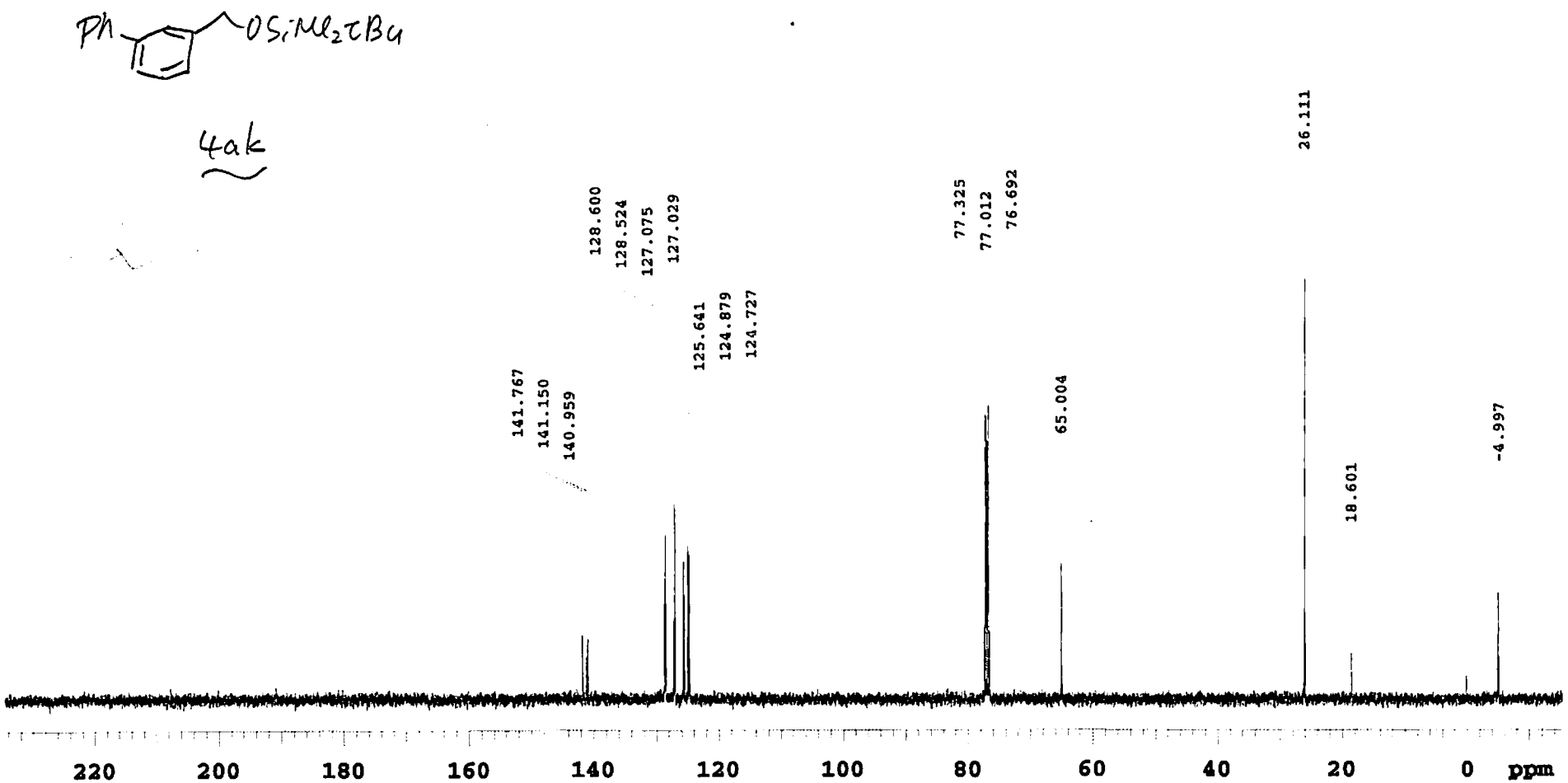
4aj

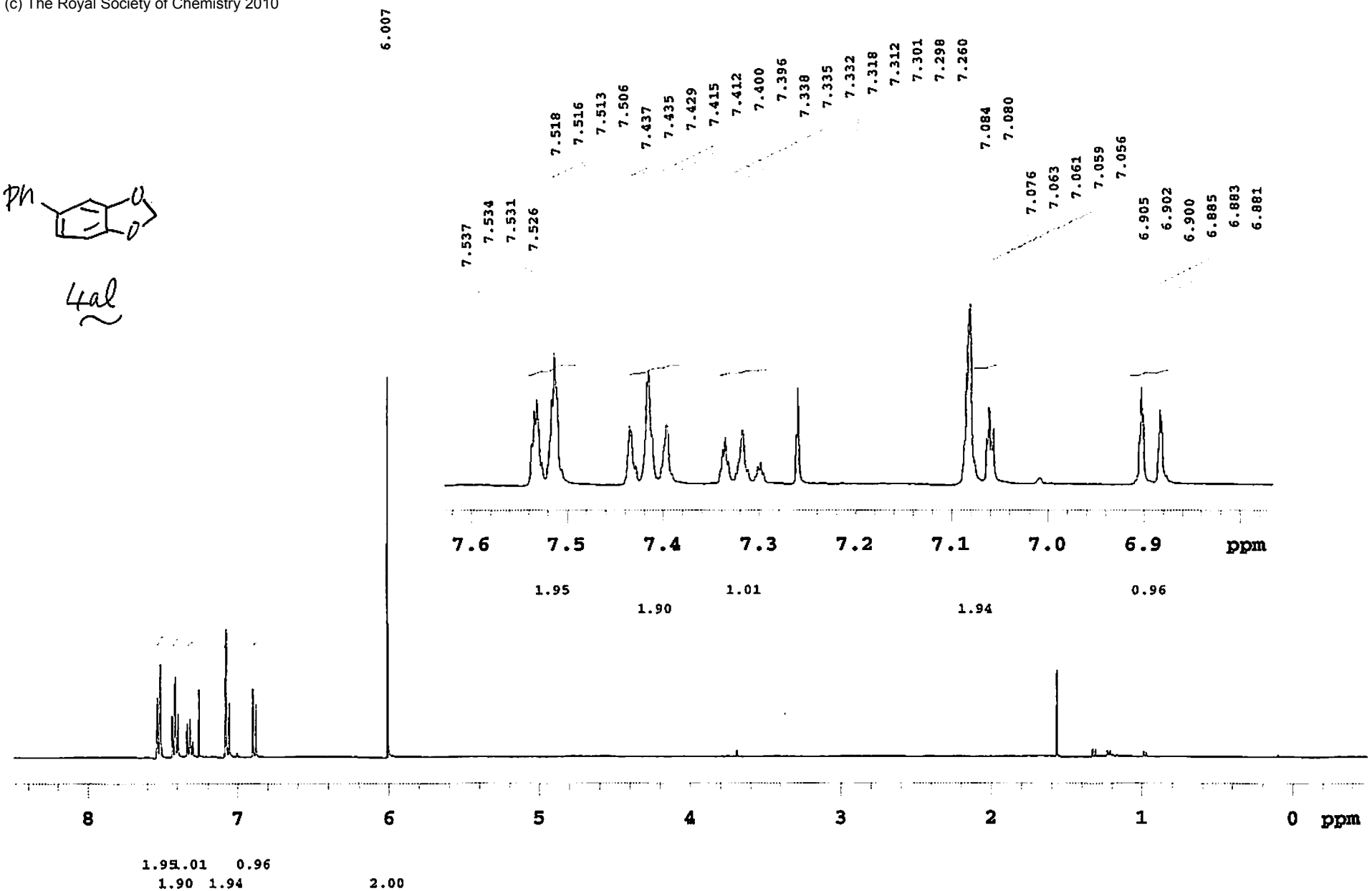

Ph
CF3
4aj
128.851
128.051
127.487
127.281
127.144
125.832
125.794
125.626
125.588
125.558
77.317
77.005
76.685
144.543
139.594
129.362
129.034
125.520
122.859
220
200
180
160
140
120
100
80
60
40
20
0
ppm


96-4-1a
Pulse Sequence: s2pul
7.615
7.590
7.569
7.464
7.446
7.422
7.400
7.346
7.328
7.260
7.7 7.5 7.3 ppm
3.88 1.00
3.86
4.809
0.989
0.153
8 7 6 5 4 3 2 1 0 ppm
3.88 1.00
3.86
2.00
8.78
5.71


Ph
OSiMe2tBu

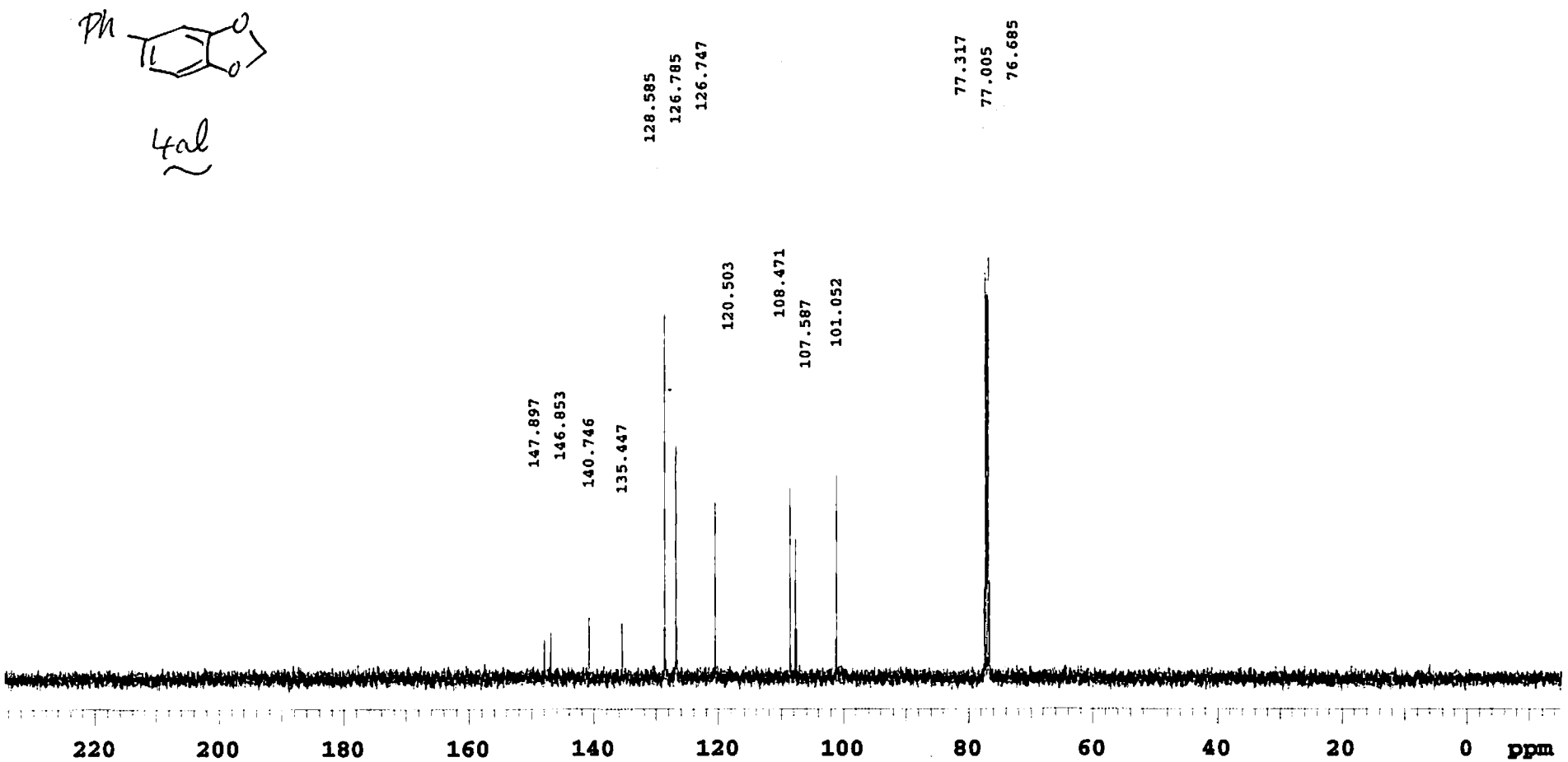
4ak

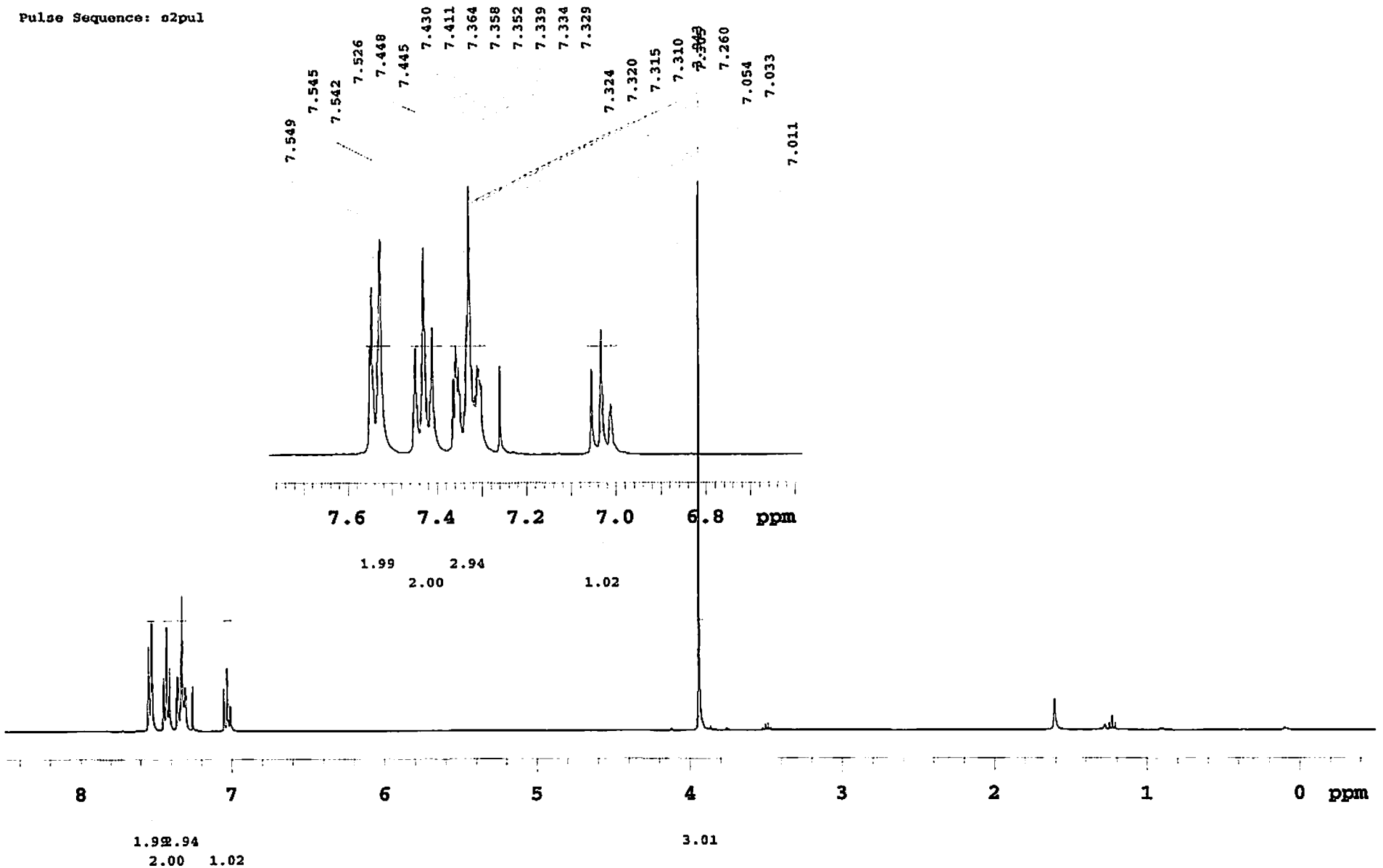

Ph
OSiMe2tBu
4ak
141.767
141.150
140.959
128.600
128.524
127.075
127.029
125.641
124.879
124.727
77.325
77.012
76.692
65.004
26.111
18.601
-4.997
220
200
180
160
140
120
100
80
60
40
20
0
ppm

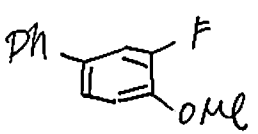

Ph
O
O
4al
6.007
7.537
7.534
7.531
7.526
7.518
7.516
7.513
7.506
7.437
7.435
7.429
7.415
7.412
7.400
7.396
7.338
7.335
7.332
7.318
7.312
7.301
7.298
7.260
7.084
7.080
7.076
7.063
7.061
7.059
7.056
6.905
6.902
6.900
6.885
6.883
6.881
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
1.95
1.90
1.01
1.94
0.96
8
7
6
5
4
3
2
1
0
ppm
1.95
1.90
1.01
1.94
0.96
2.00

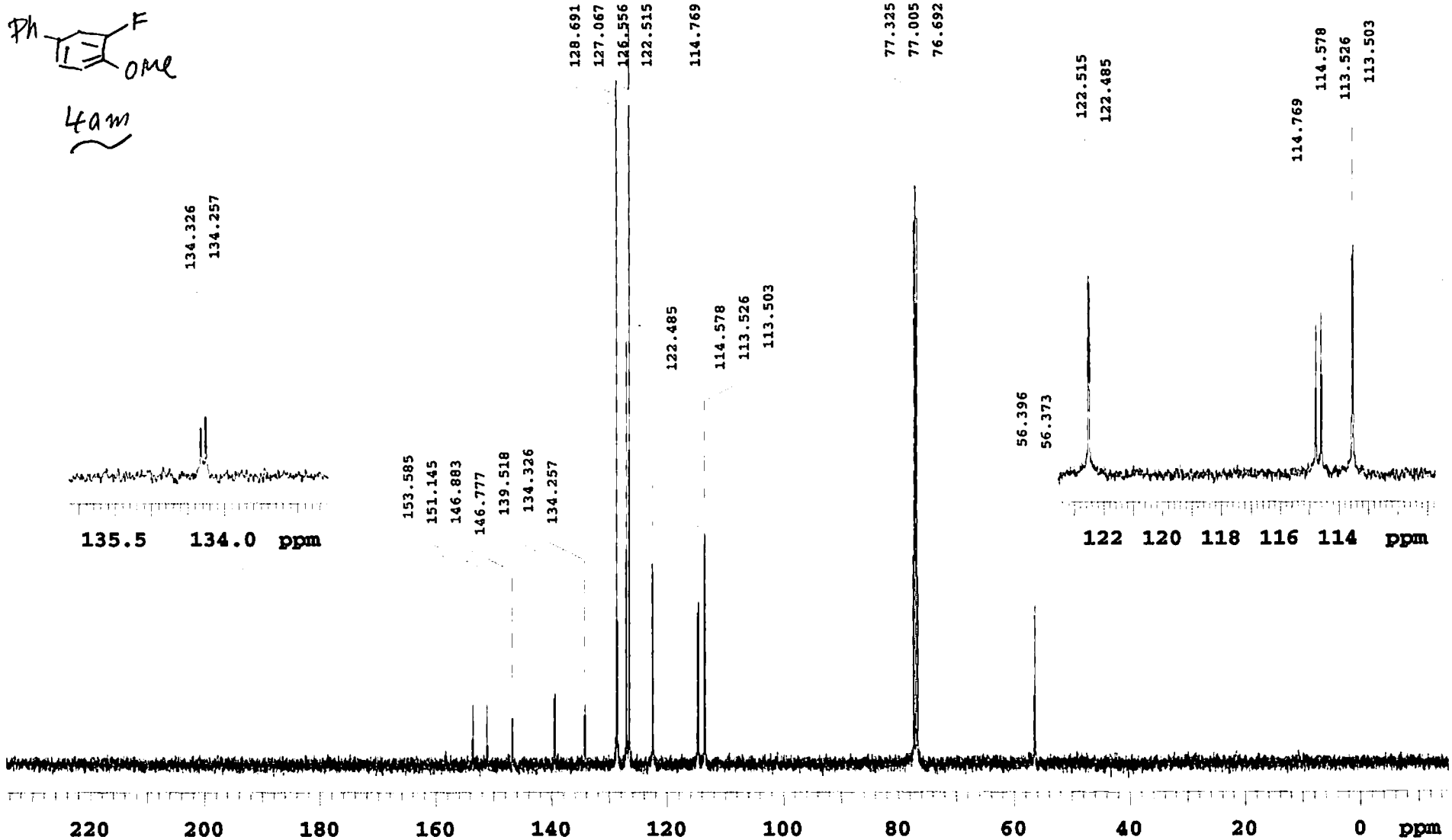
13C OBSERVE

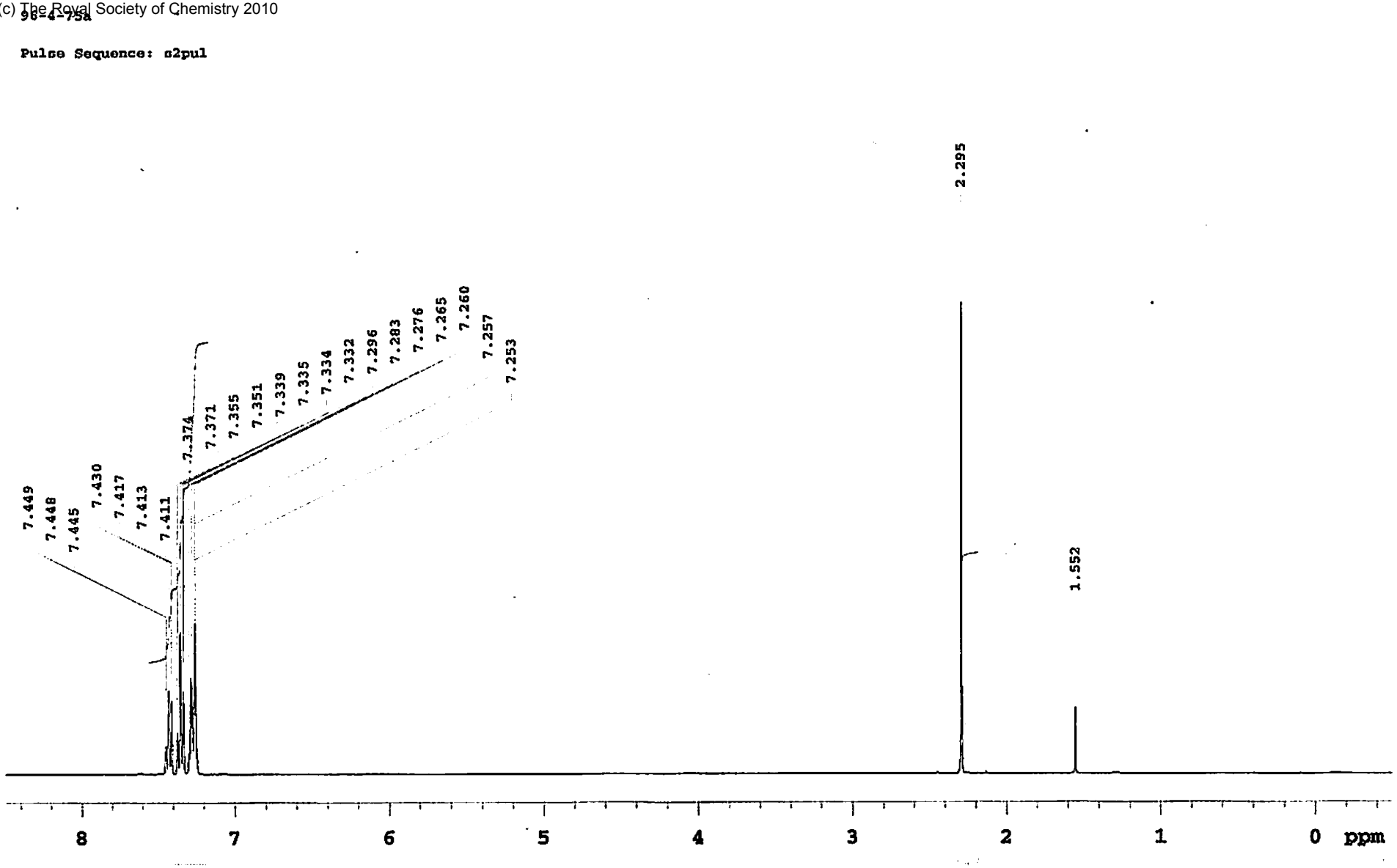
Pulse Sequence: s2pul



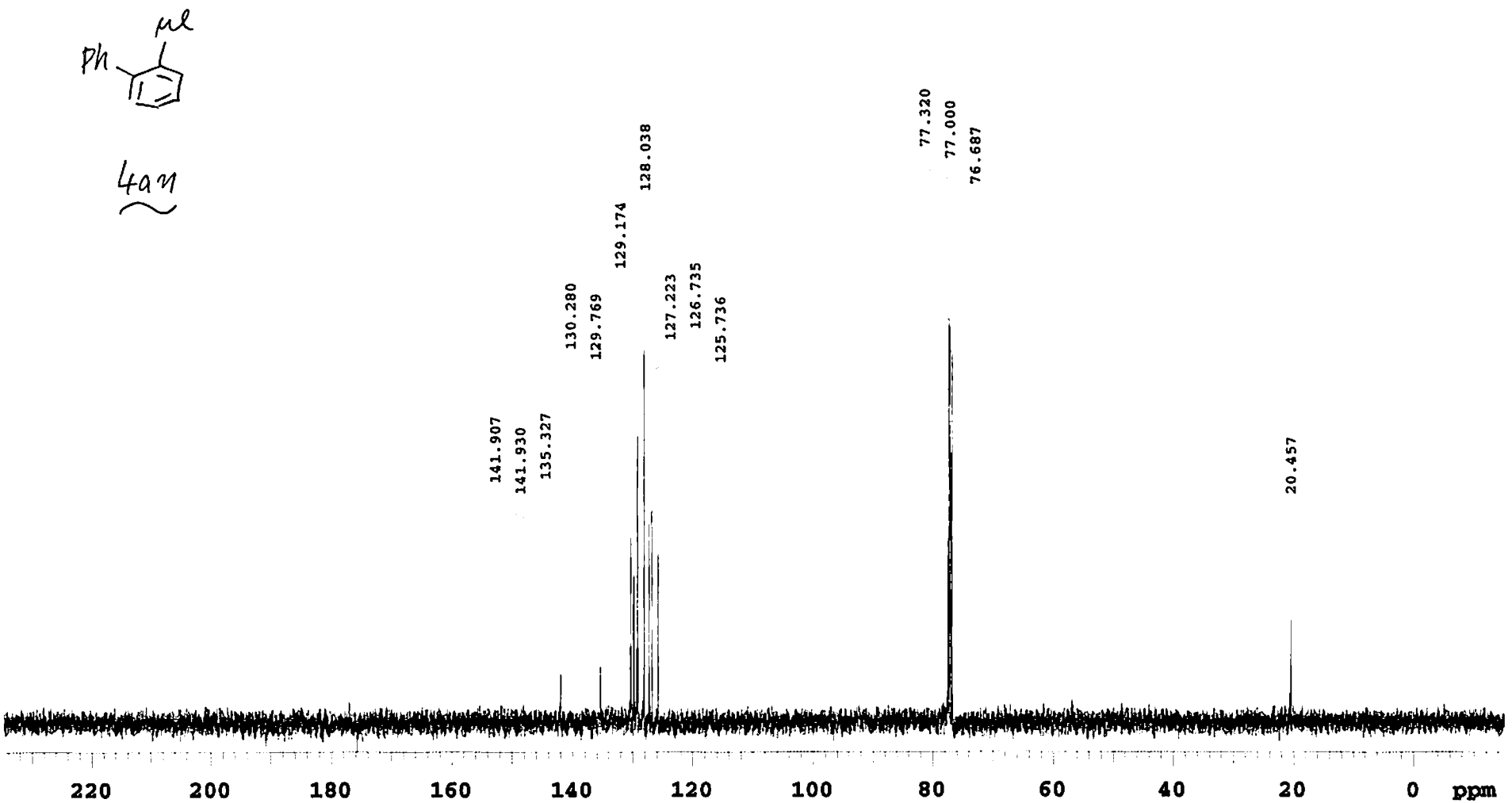

Pulse Sequence: s2pul
7.549
7.545
7.542
7.526
7.448
7.445
7.430
7.411
7.364
7.358
7.352
7.339
7.334
7.329
7.324
7.320
7.315
7.310
7.260
7.054
7.033
7.011
7.6
7.4
7.2
7.0
6.8
ppm
1.99
2.94
2.00
1.02
8
7
6
5
4
3
2
1
0
ppm
1.92
2.94
2.00
1.02
3.01


Ph
F
OMe

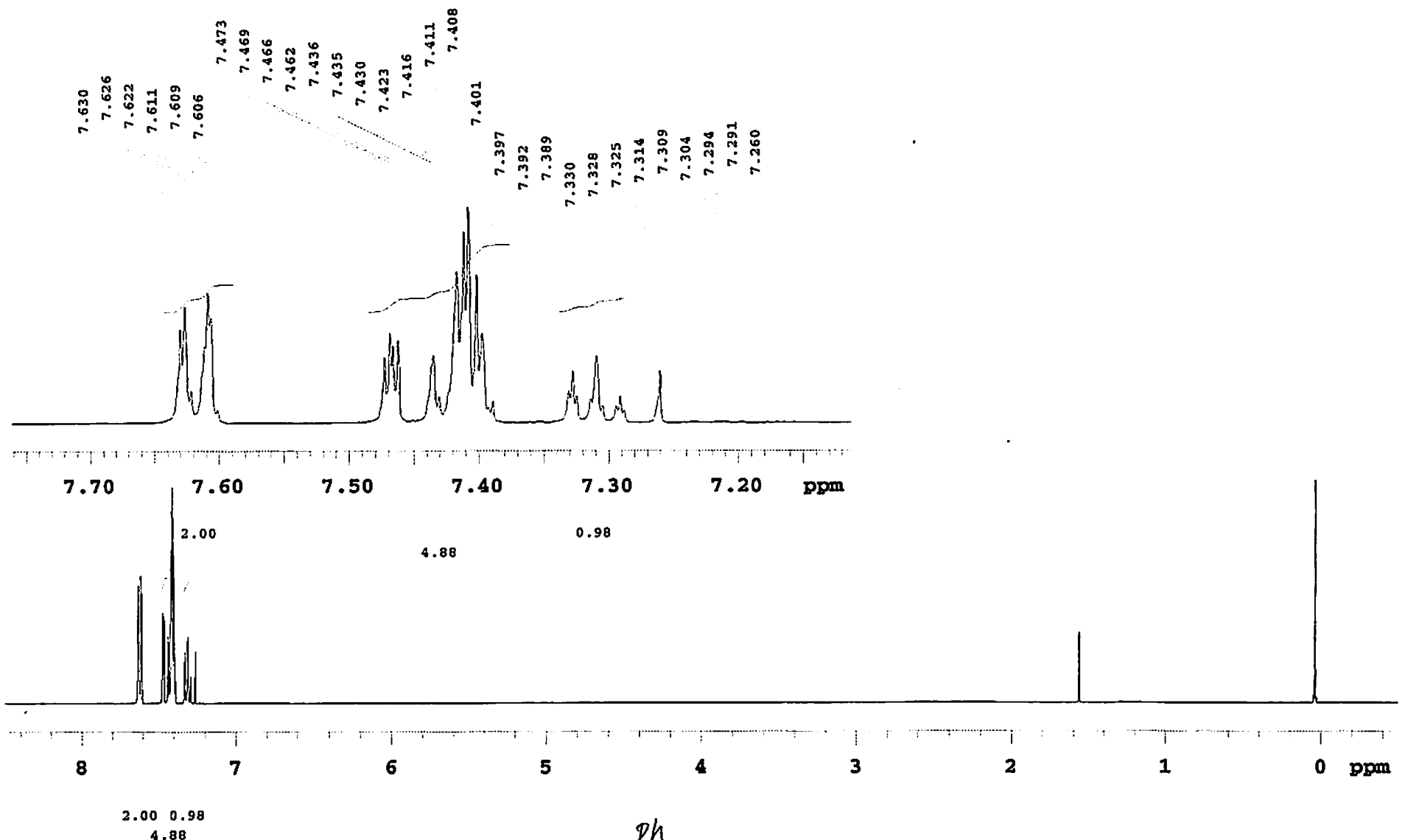

Ph
F
OMe
4am
128.691
127.067
126.556
122.515
114.769
77.325
77.005
76.692
122.515
122.485
114.769
114.578
113.526
113.503
134.326
134.257
122.485
114.578
113.526
113.503
56.396
56.373
153.585
151.145
146.883
146.777
139.518
134.326
134.257
135.5 134.0 ppm
122 120 118 116 114 ppm
220 200 180 160 140 120 100 80 60 40 20 0 ppm

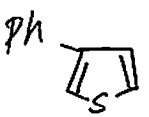

96-4-75a
Pulse Sequence: s2pul
7.449
7.448
7.445
7.430
7.417
7.413
7.411
7.374
7.371
7.355
7.351
7.339
7.335
7.334
7.332
7.296
7.283
7.276
7.265
7.260
7.257
7.253
2.295
1.552
8
7
6
5
4
3
2
1
0
ppm
8.84
3.00
Ph
Me

4am

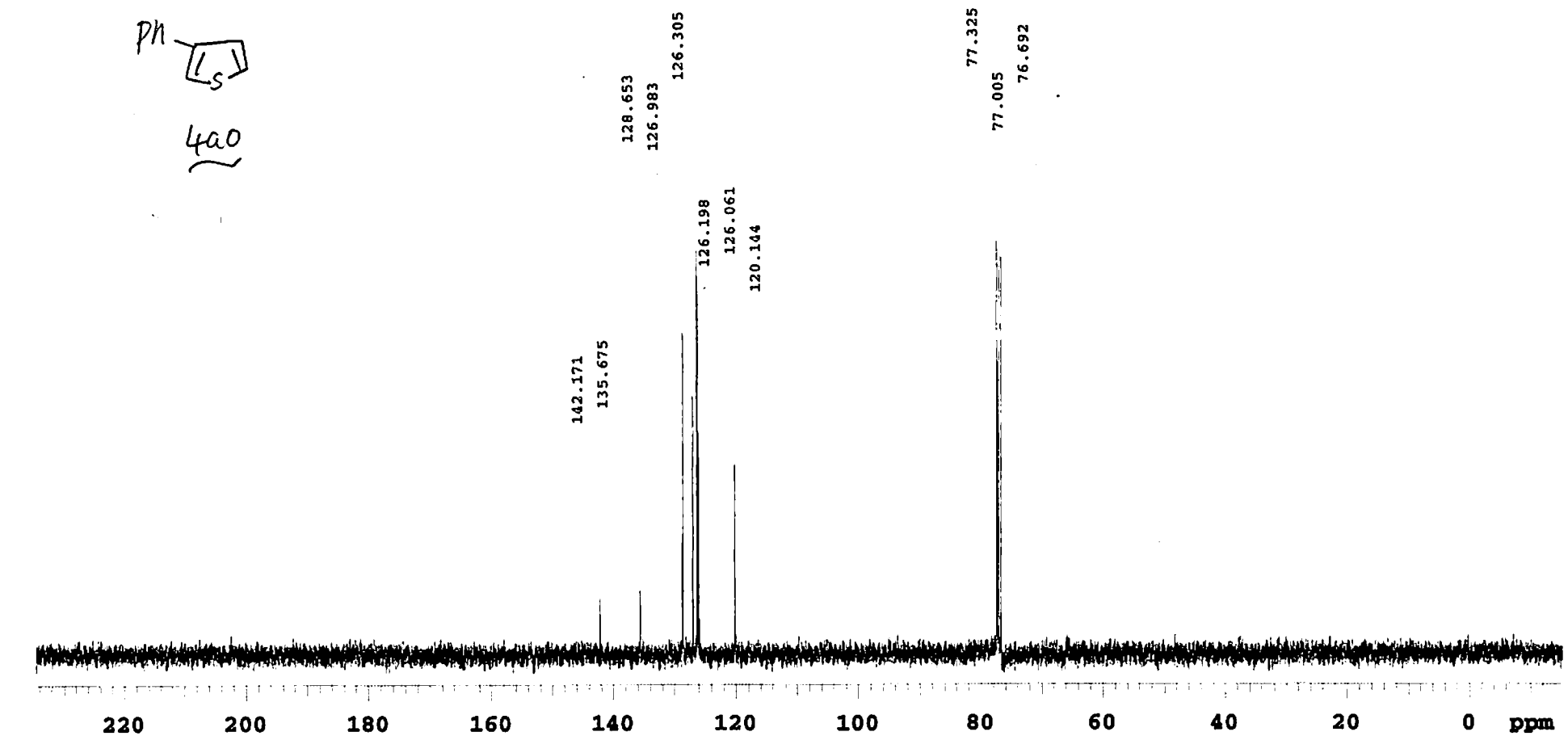

Me
Ph
4am
141.907
141.930
135.327
130.280
129.769
129.174
128.038
127.223
126.735
125.736
77.320
77.000
76.687
20.457
220
200
180
160
140
120
100
80
60
40
20
0
ppm

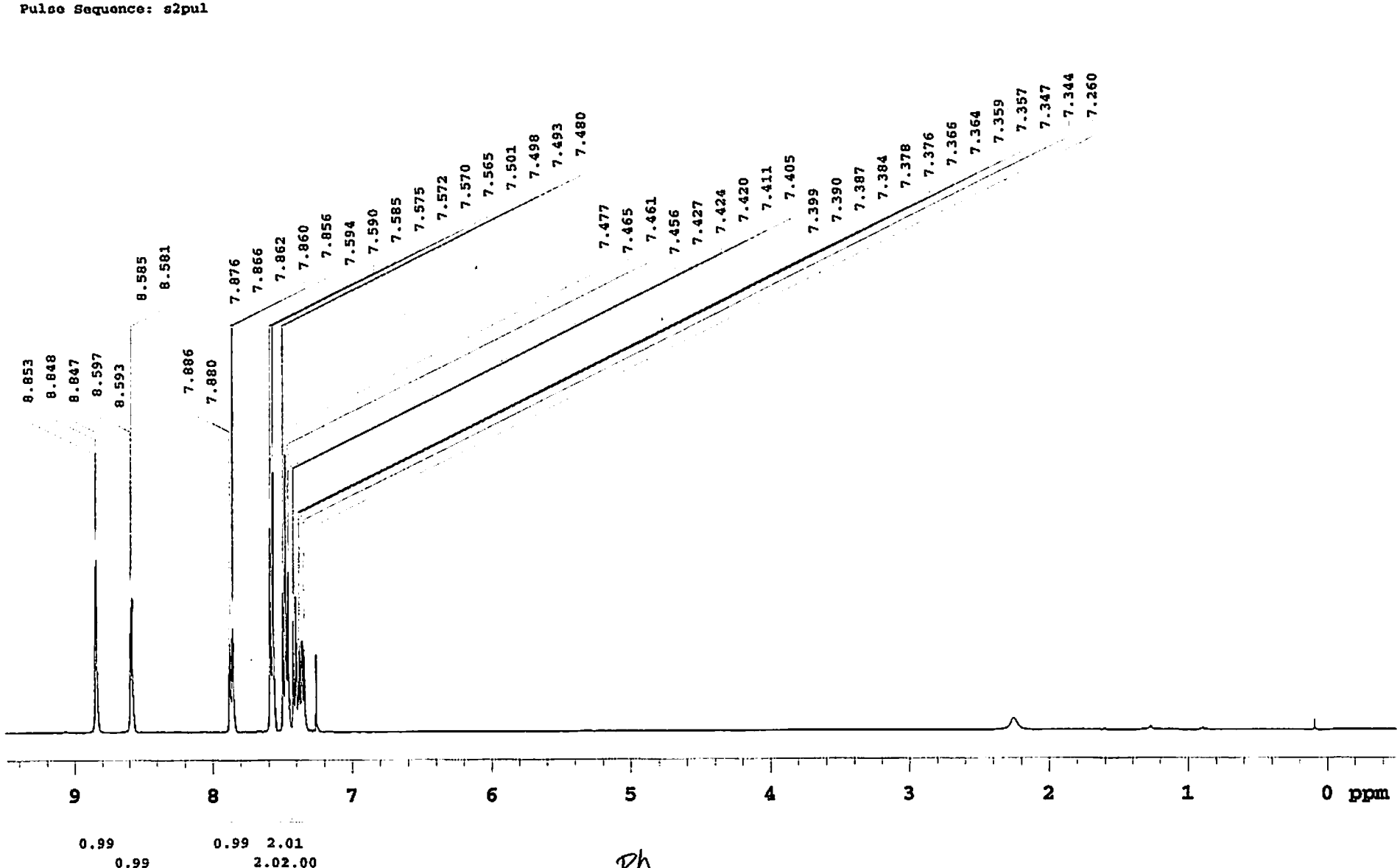
Supplementary Material (ESI) for Chemical Communications





4ao


Ph
Ls
4a0
142.171
135.675
128.653
126.983
126.305
126.198
126.061
120.144
77.325
77.005
76.692
220
200
180
160
140
120
100
80
60
40
20
0
ppm

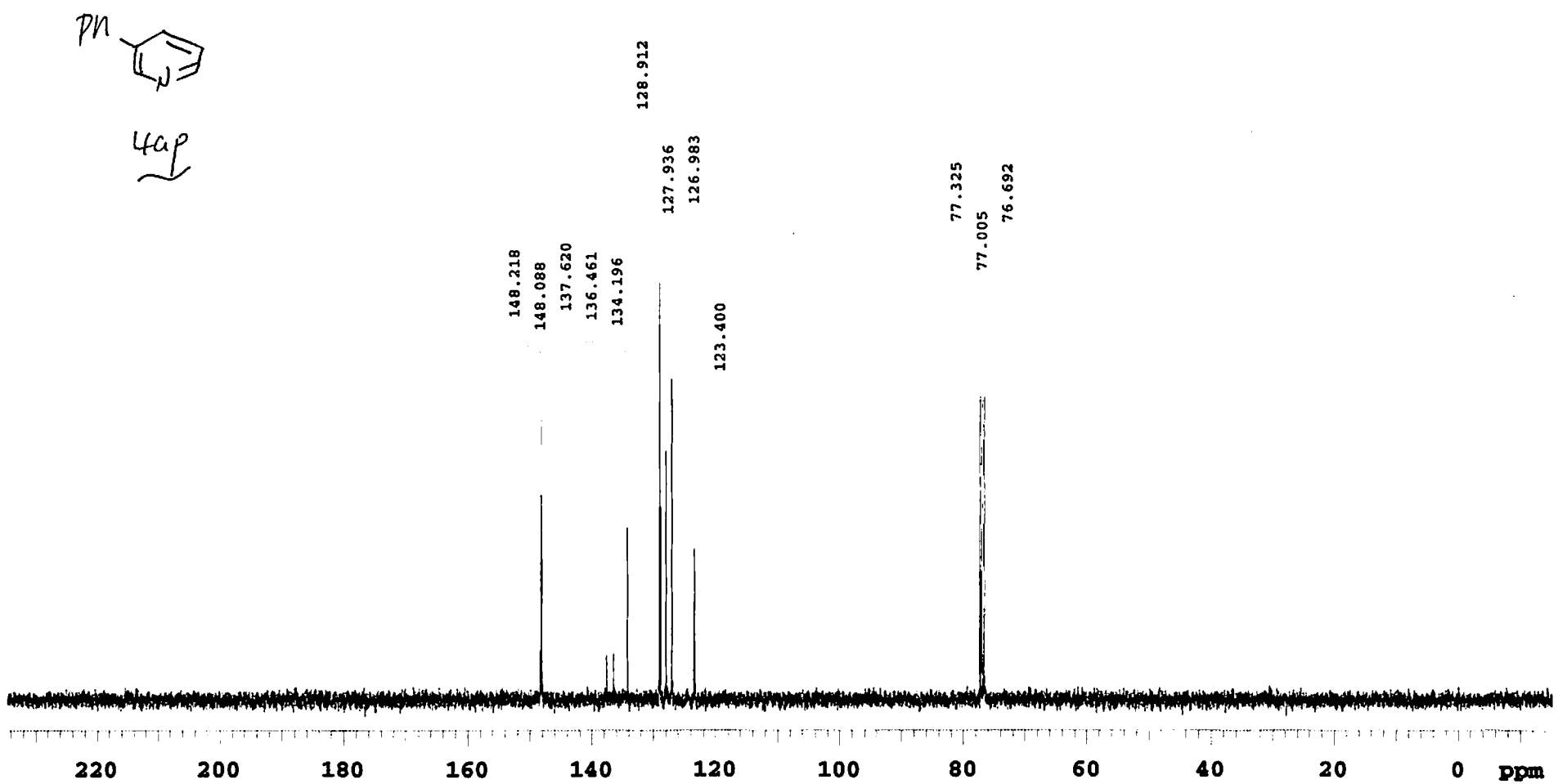

Pulse Sequence: s2pul
8.853
8.848
8.847
8.597
8.593
8.585
8.581
7.886
7.880
7.876
7.866
7.862
7.860
7.856
7.594
7.590
7.585
7.575
7.572
7.570
7.565
7.501
7.498
7.493
7.480
7.477
7.465
7.461
7.456
7.427
7.424
7.420
7.411
7.405
7.399
7.390
7.387
7.384
7.378
7.376
7.366
7.364
7.359
7.357
7.347
7.344
7.260
9
8
7
6
5
4
3
2
1
0 ppm
0.99
0.99
0.99
2.01
2.02.00


Ph
N

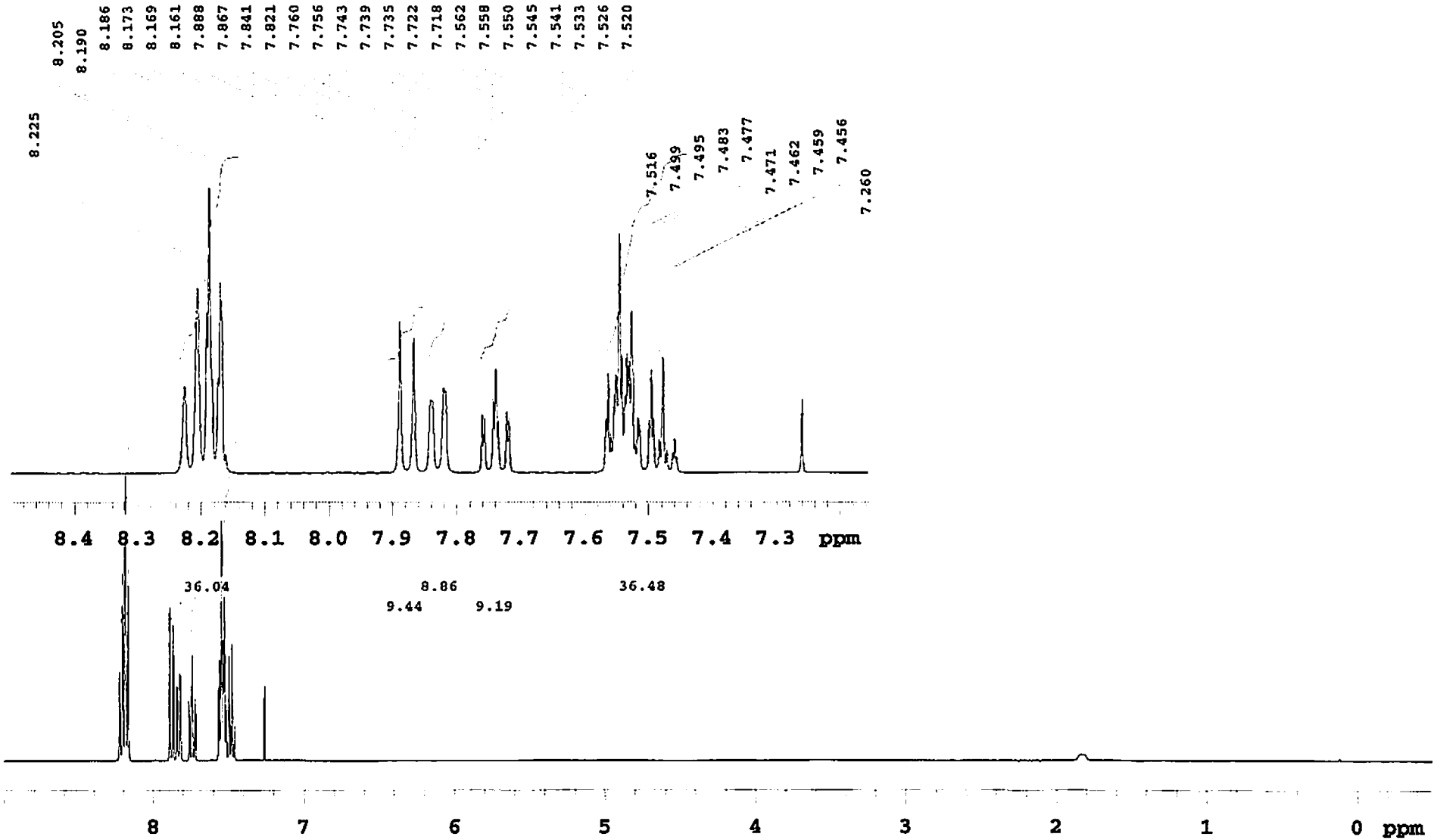
4aP

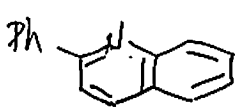
96-3-161b

Pulse Sequence: s2pul

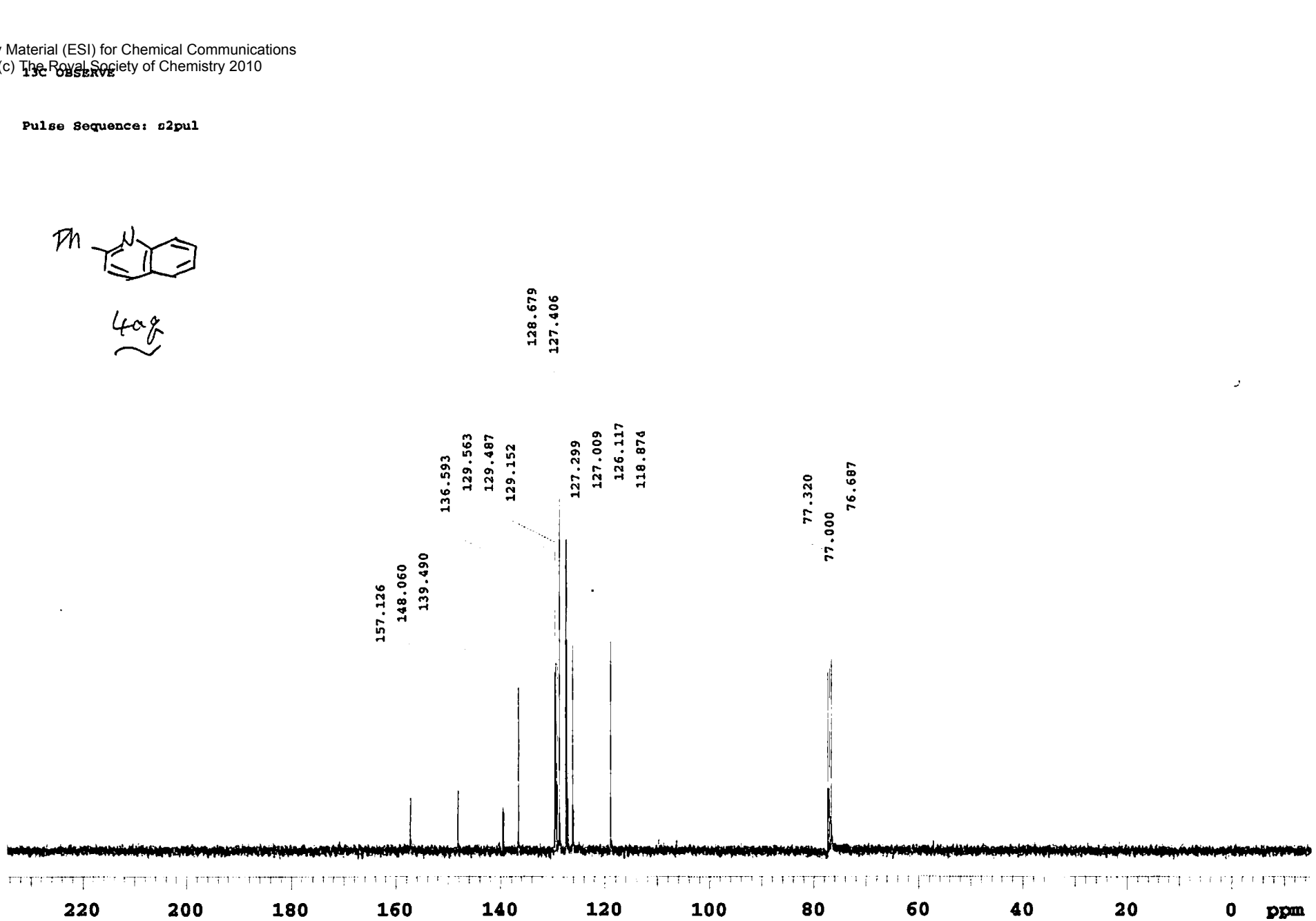


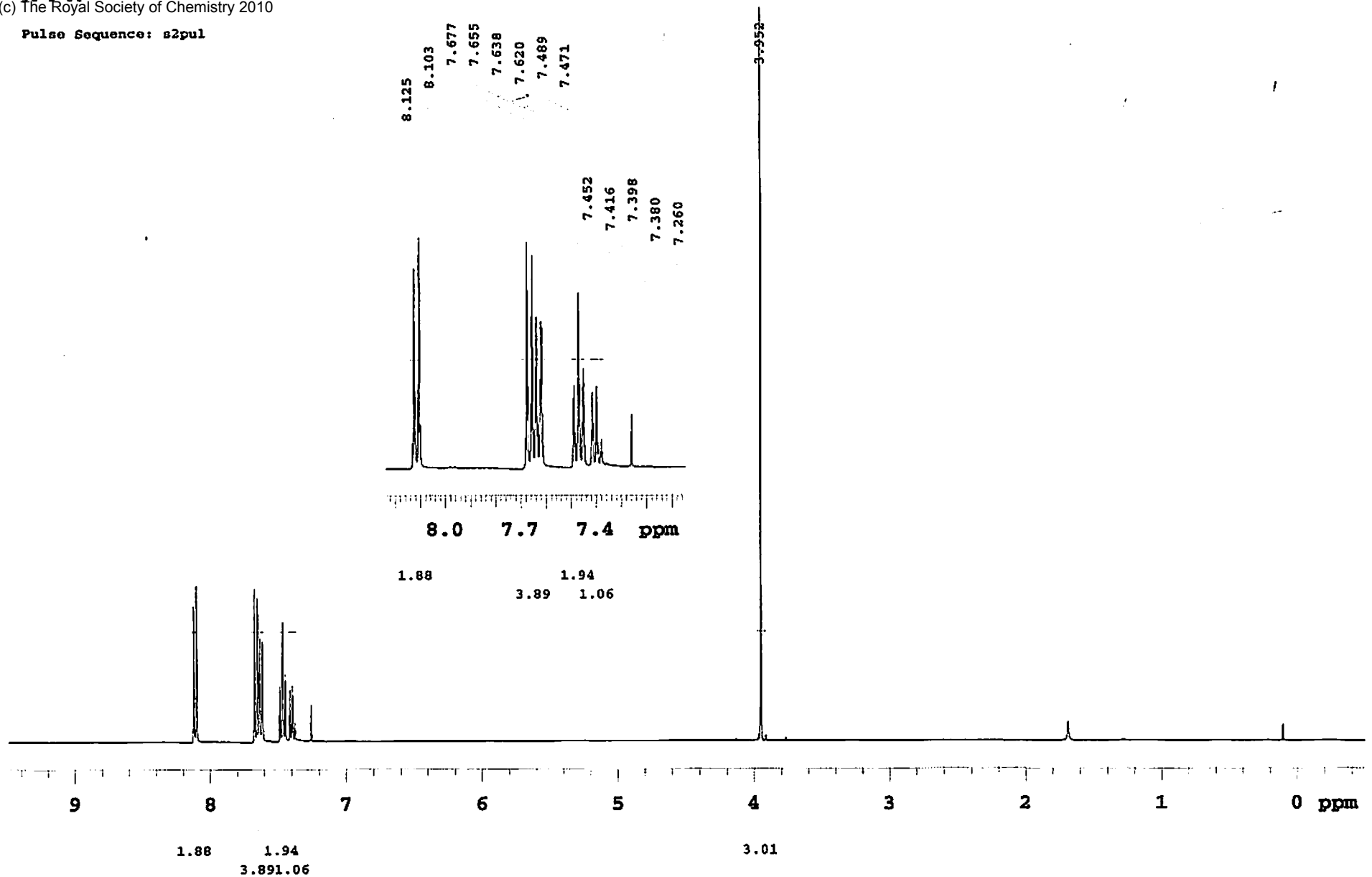
96-4-67

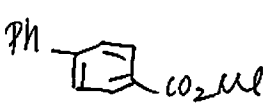




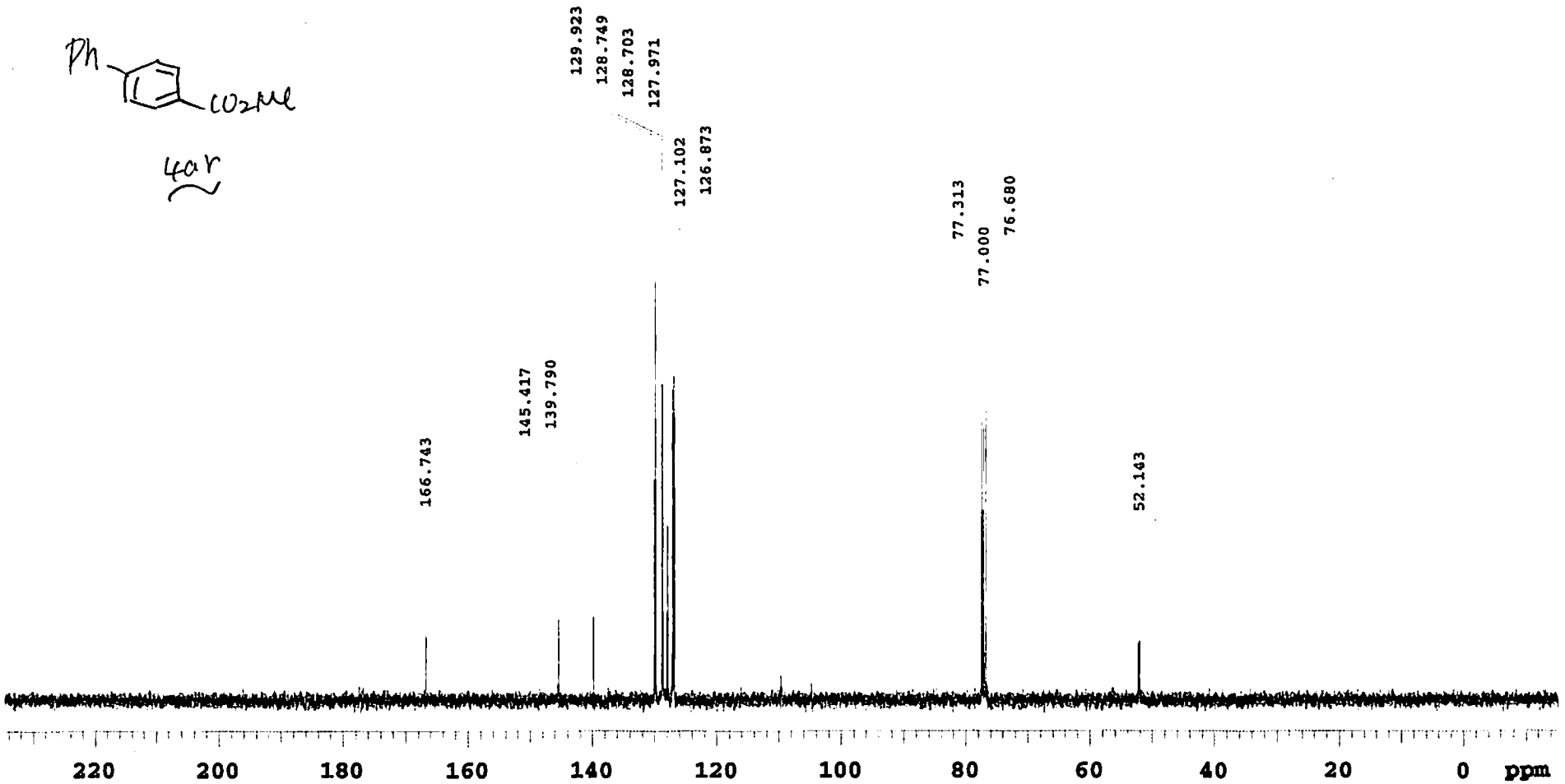
4aq

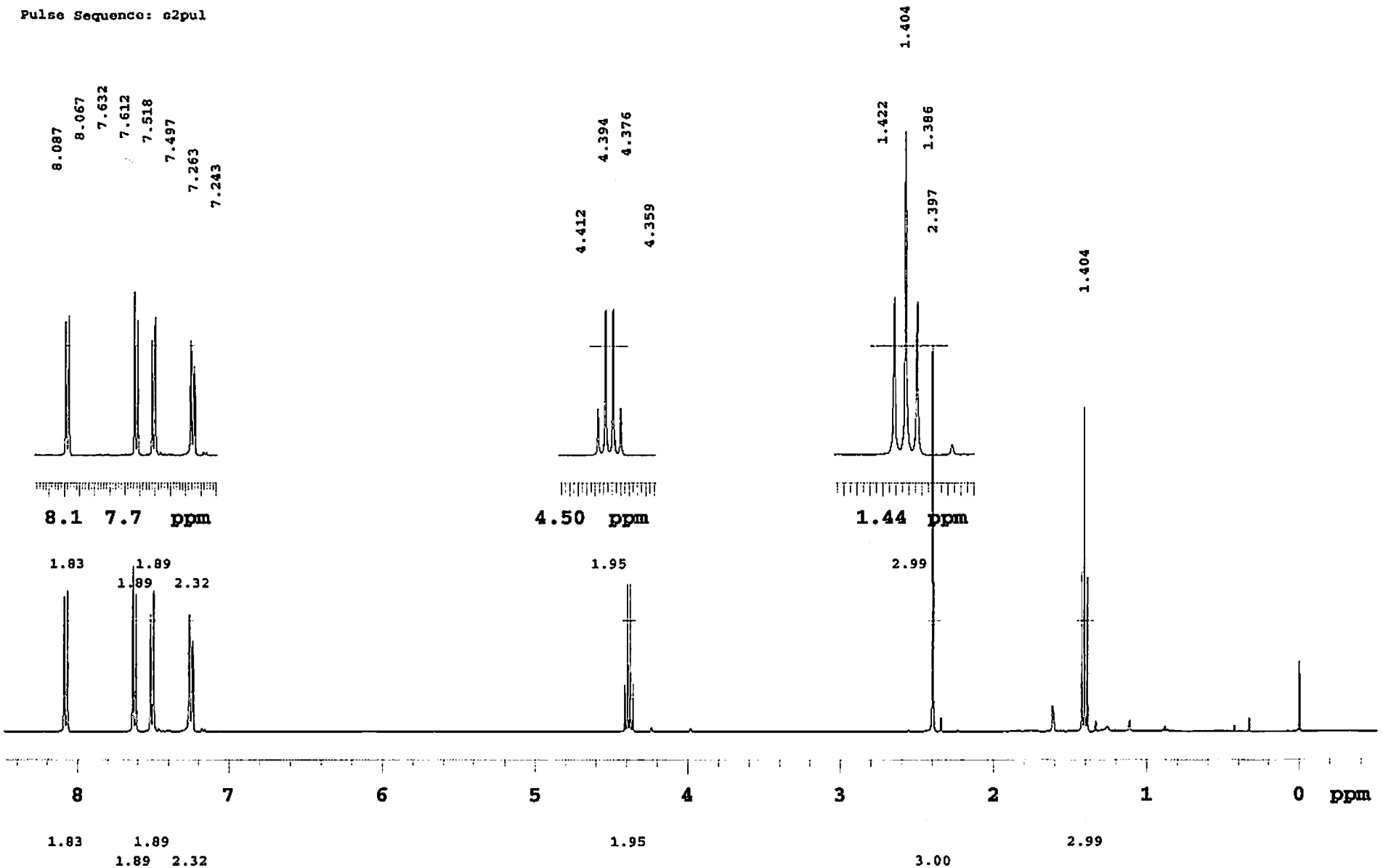

13C OBSERVE
Pulse Sequence: s2pul
Ph
N
4ag
128.679
127.406
136.593
129.563
129.487
129.152
127.299
127.009
126.117
118.874
157.126
148.060
139.490
77.320
77.000
76.687
220
200
180
160
140
120
100
80
60
40
20
0
ppm


26-3-64
Pulse Sequence: s2pul
8.125
8.103
7.677
7.655
7.638
7.620
7.489
7.471
7.452
7.416
7.398
7.380
7.260
3.952
8.0
7.7
7.4
ppm
1.88
1.94
3.89
1.06
9
8
7
6
5
4
3
2
1
0
ppm
1.88
1.94
3.891.06
3.01


Ph
CO2Me

4ar


Pulse Sequence: s2pul
Ph
CO2Me
40r
129.923
128.749
128.703
127.971
127.102
126.873
77.313
77.000
76.680
166.743
145.417
139.790
52.143
220
200
180
160
140
120
100
80
60
40
20
0
ppm

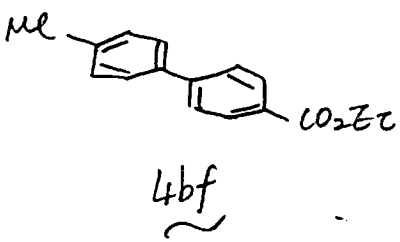

96-1-119
Pulse Sequence: s2pul
8.087
8.067
7.632
7.612
7.518
7.497
7.263
7.243
4.412
4.394
4.376
4.359
1.422
1.404
1.386
2.397
8.1 7.7 ppm
4.50 ppm
1.44 ppm
1.83
1.89
1.89
2.32
1.95
2.99
8 7 6 5 4 3 2 1 0 ppm
1.83
1.89
1.89
2.32
1.95
3.00
2.99


Me
CO2Et

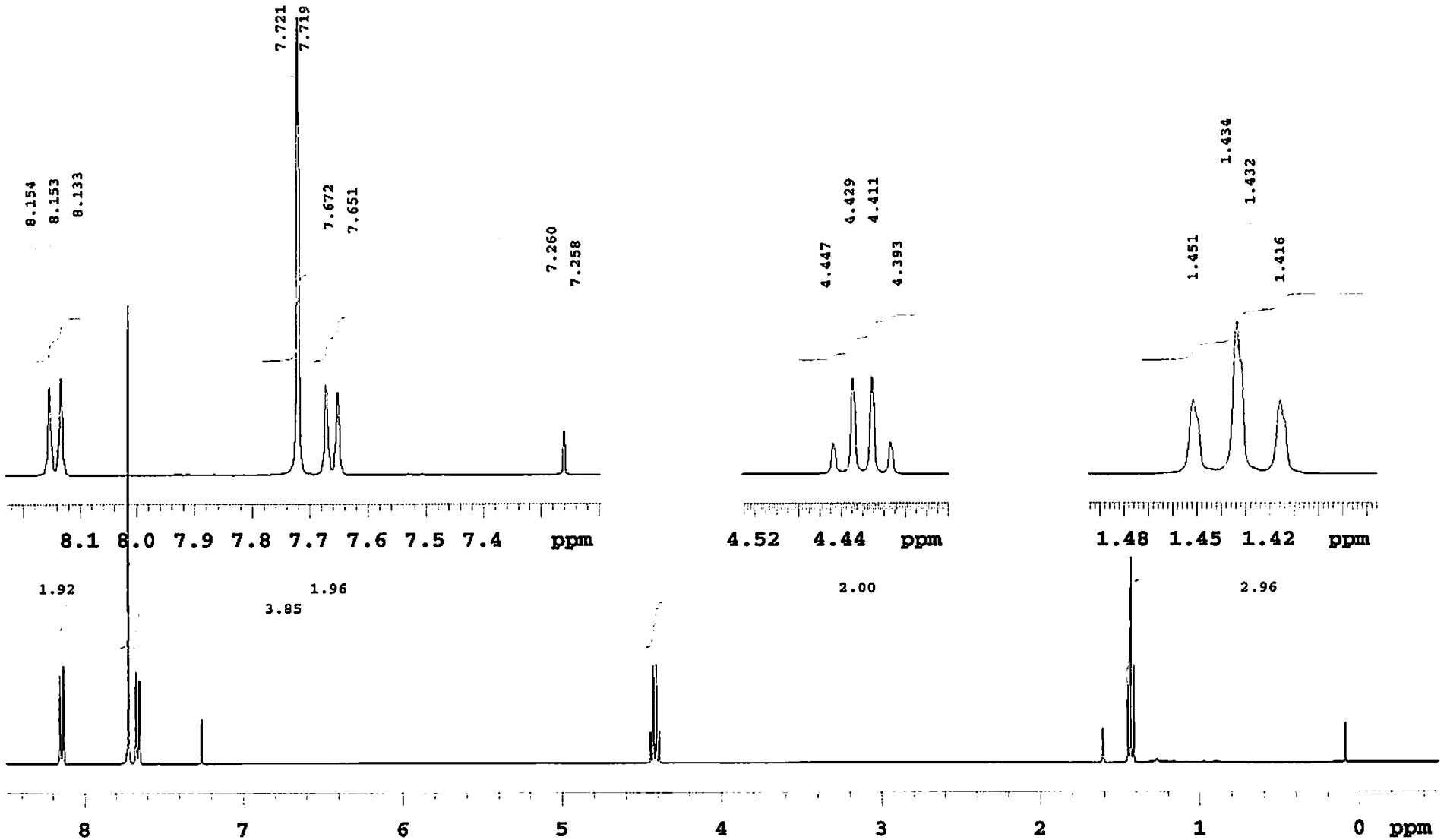
4bf

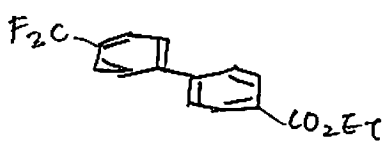
96-3-119

Pulse Sequence: s2pul

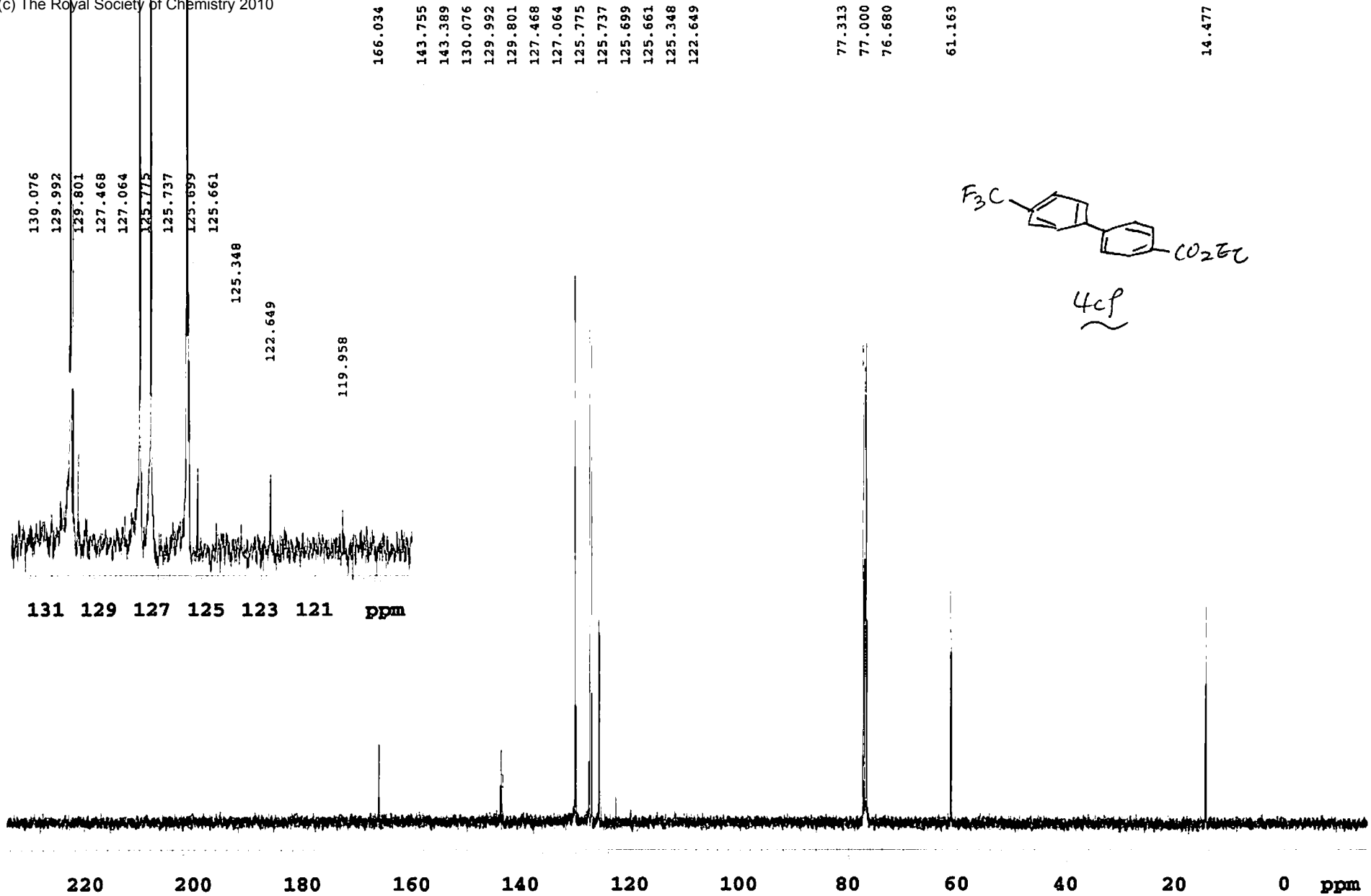


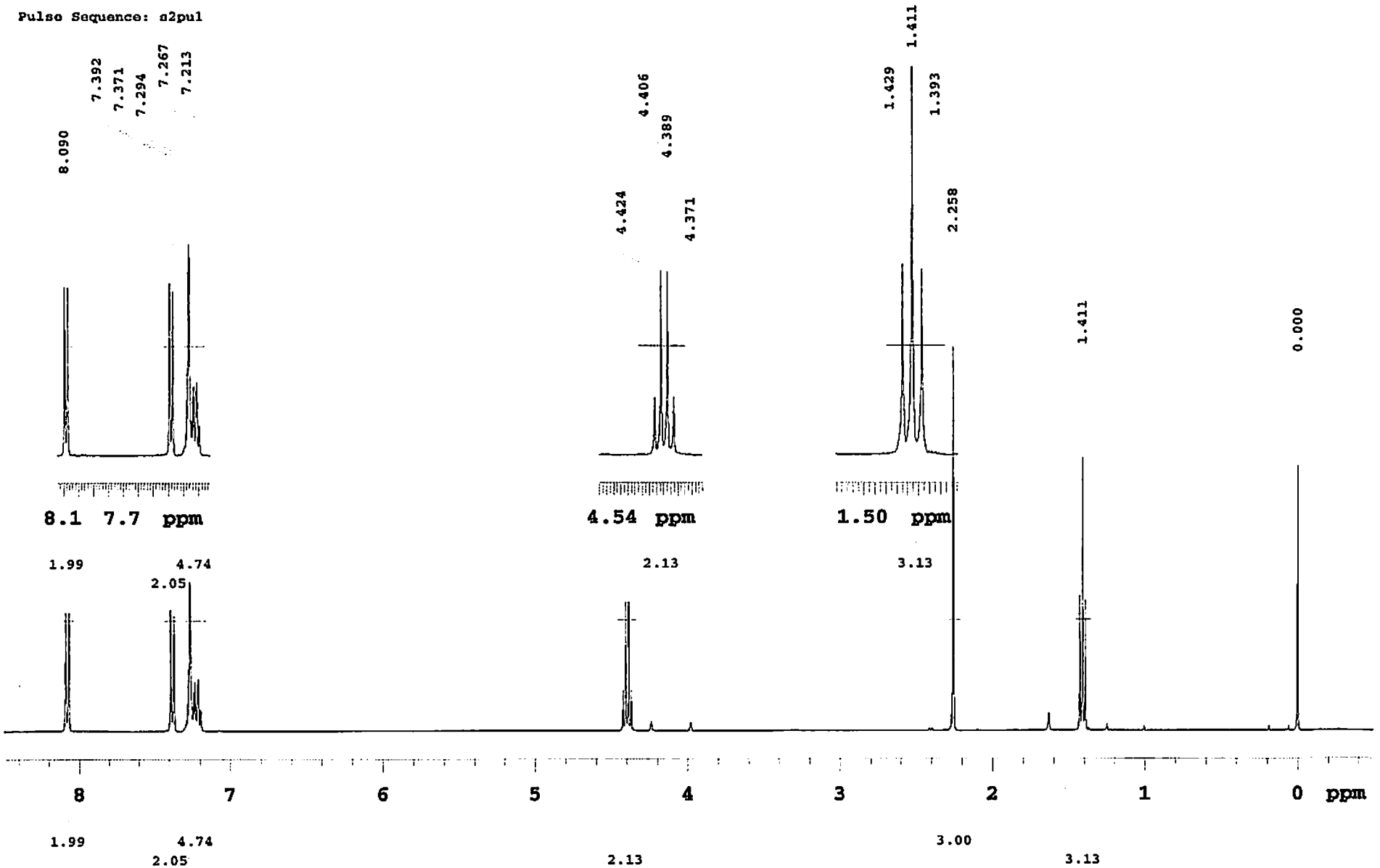
4bf

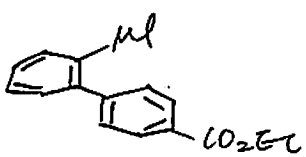




4cf

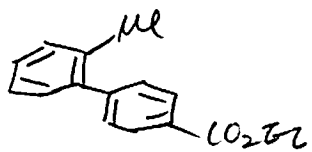

166.034
143.755
143.389
130.076
129.992
129.801
127.468
127.064
125.775
125.737
125.699
125.661
125.348
122.649
77.313
77.000
76.680
61.163
14.477
130.076
129.992
129.801
127.468
127.064
125.775
125.737
125.699
125.661
125.348
122.649
119.958
131 129 127 125 123 121 ppm
F3C
CO2Et
4cf
220 200 180 160 140 120 100 80 60 40 20 0 ppm


Pulse Sequence: s2pul
8.090
7.392
7.371
7.294
7.267
7.213
4.424
4.406
4.389
4.371
1.429
1.411
1.393
2.258
1.411
0.000
8.1 7.7 ppm
4.54 ppm
1.50 ppm
1.99
4.74
2.05
2.13
3.13
8
7
6
5
4
3
2
1
0 ppm
1.99
4.74
2.05
2.13
3.00
3.13

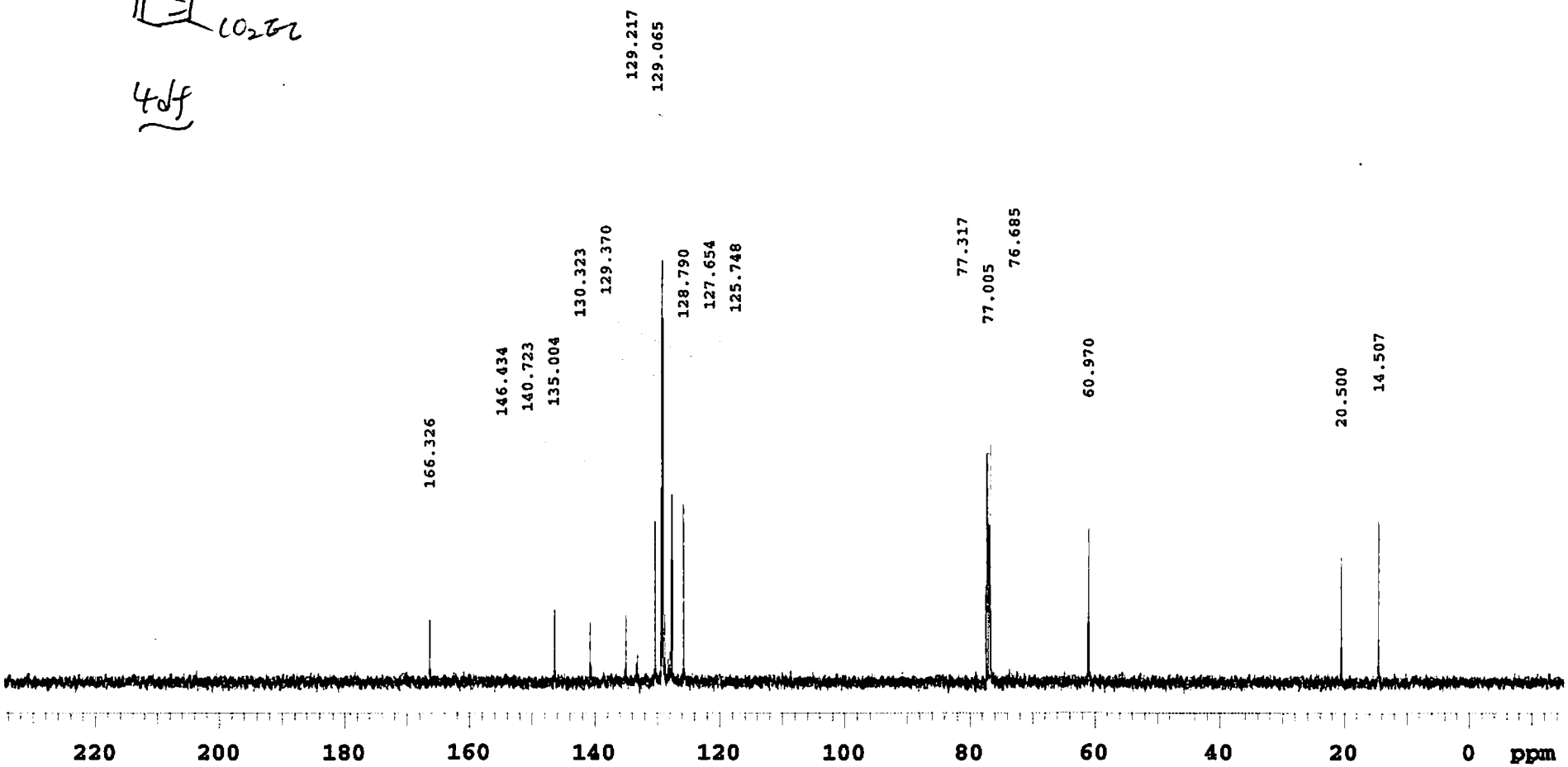

Me
CO2Et

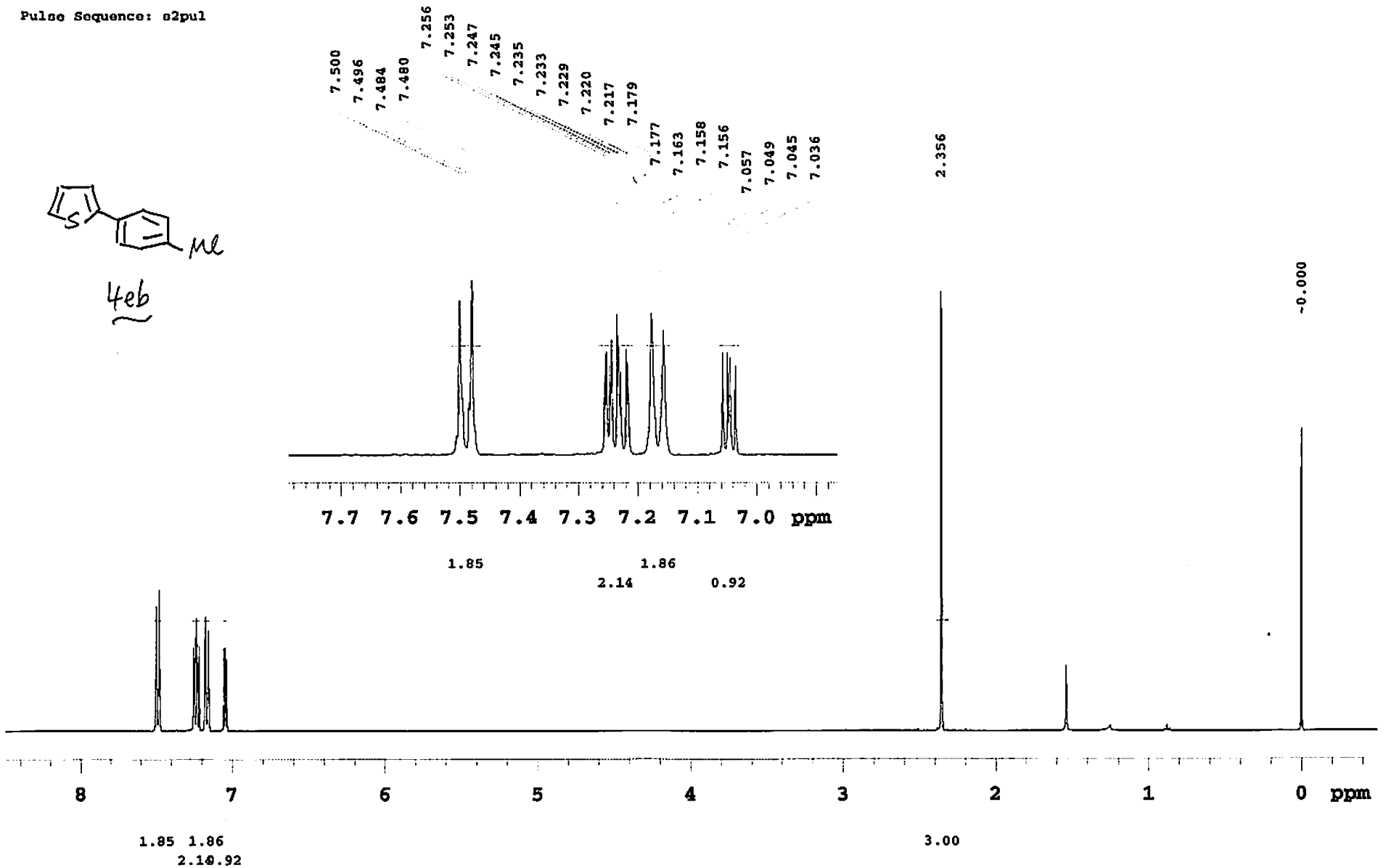
96-3-101

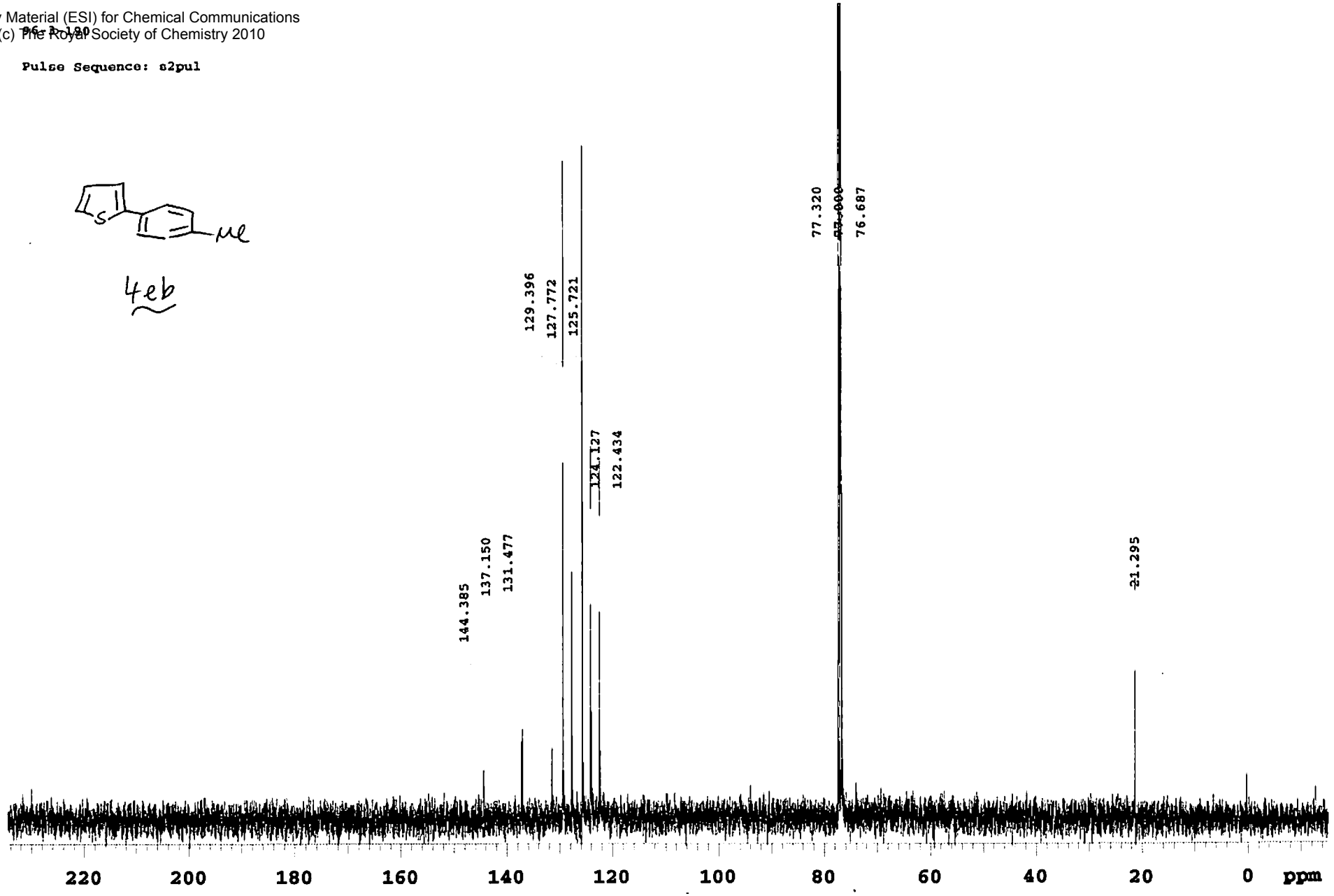
Pulse Sequence: s2pul



4df




96-1-190
Pulse Sequence: s2pul
7.500
7.496
7.484
7.480
7.256
7.253
7.247
7.245
7.235
7.233
7.229
7.220
7.217
7.179
7.177
7.163
7.158
7.156
7.057
7.049
7.045
7.036
2.356
-0.000
Me
4eb
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
1.85
1.86
2.14
0.92
8 7 6 5 4 3 2 1 0 ppm
1.85 1.86
2.14 0.92
3.00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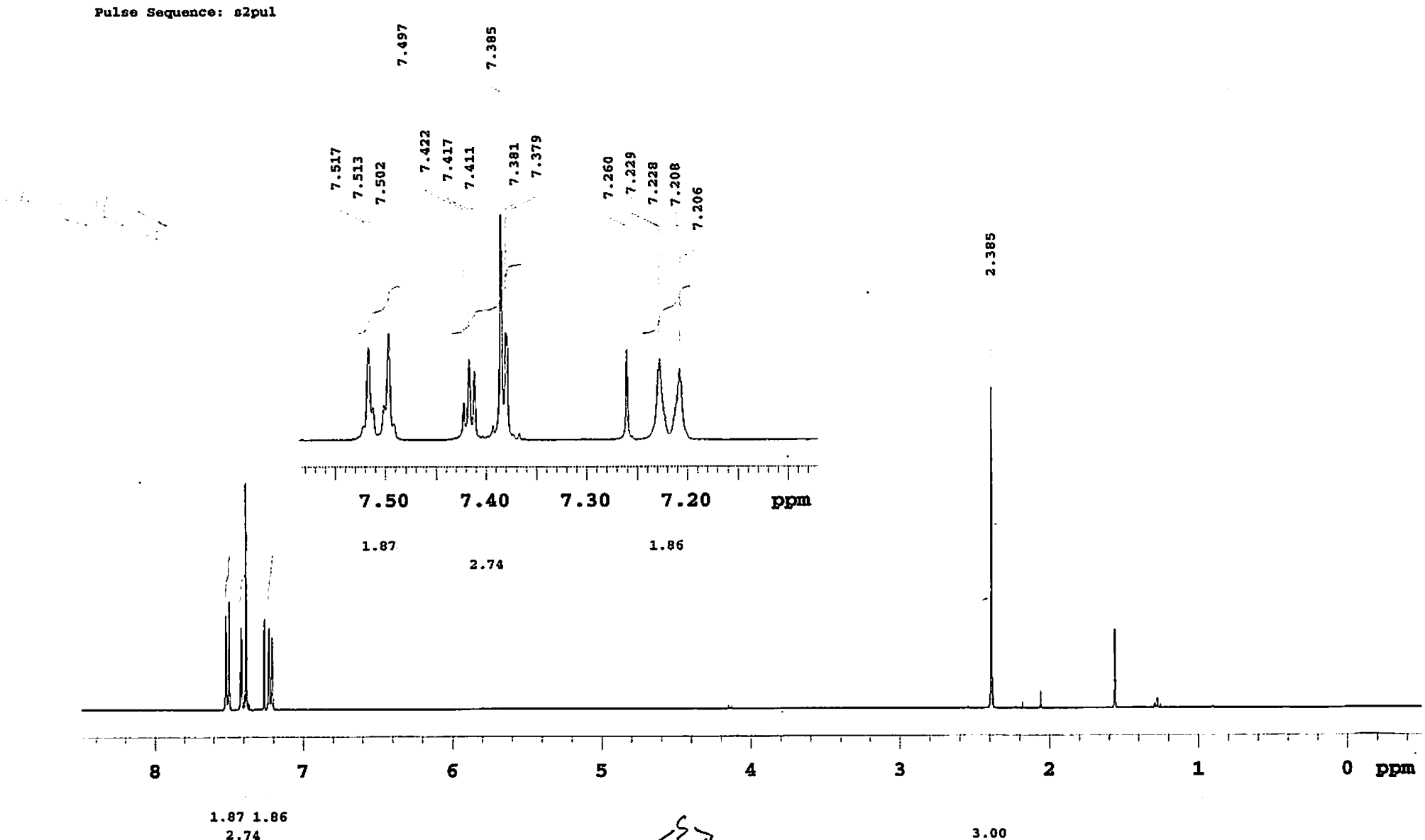
Me
4eb
144.385
137.150
131.477
129.396
127.772
125.721
124.127
122.434
77.320
77.000
76.687
21.295
220
200
180
160
140
120
100
80
60
40
20
0
ppm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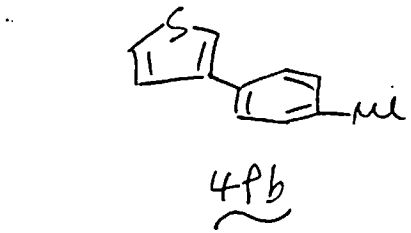
7.497
7.385
7.517
7.513
7.502
7.422
7.417
7.411
7.381
7.379
7.260
7.229
7.228
7.208
7.206
2.385
7.50
7.40
7.30
7.20
ppm
1.87
2.74
1.86
8
7
6
5
4
3
2
1
0
ppm
1.87 1.86
2.74
3.00
Me

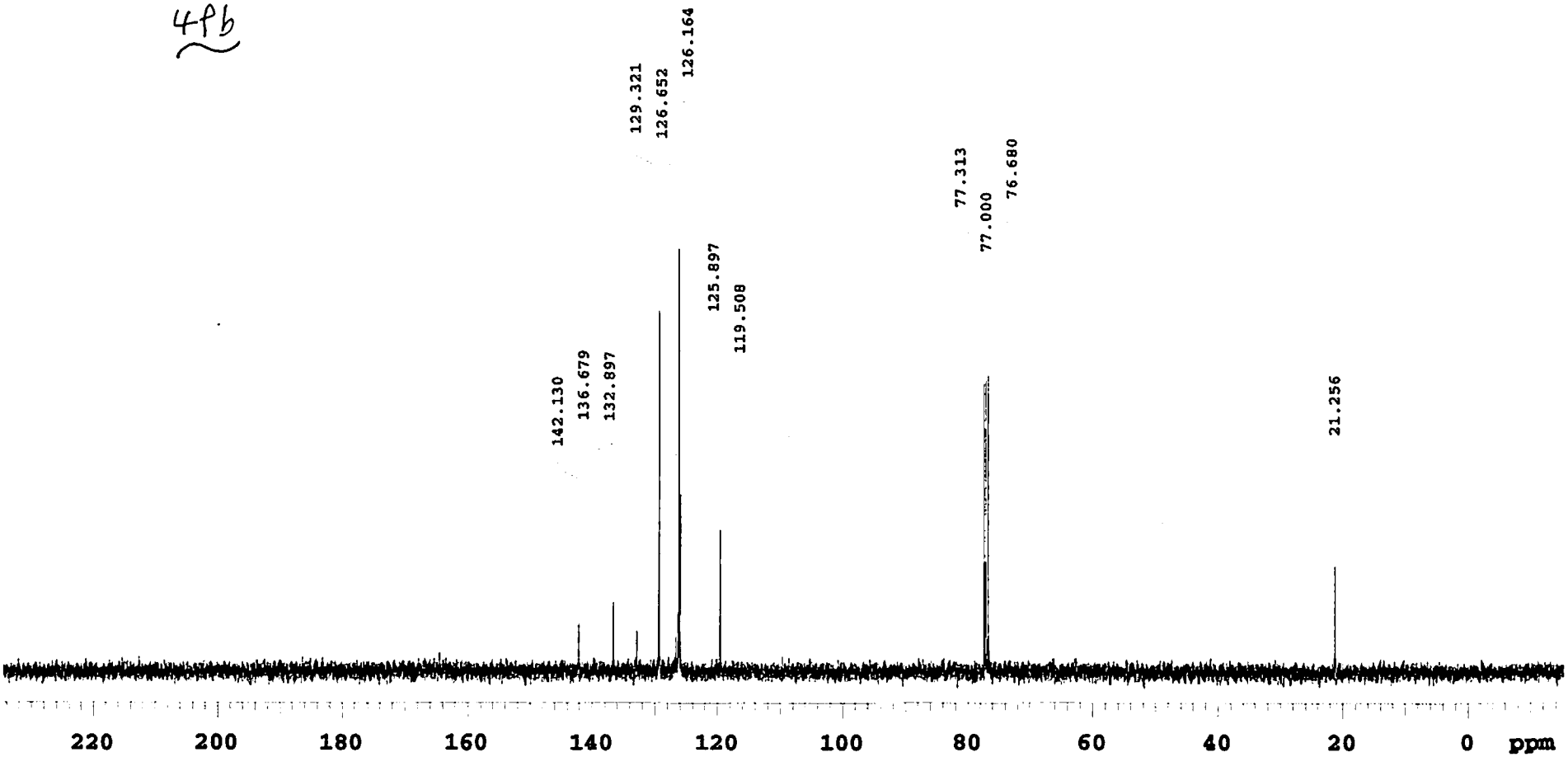
4pb

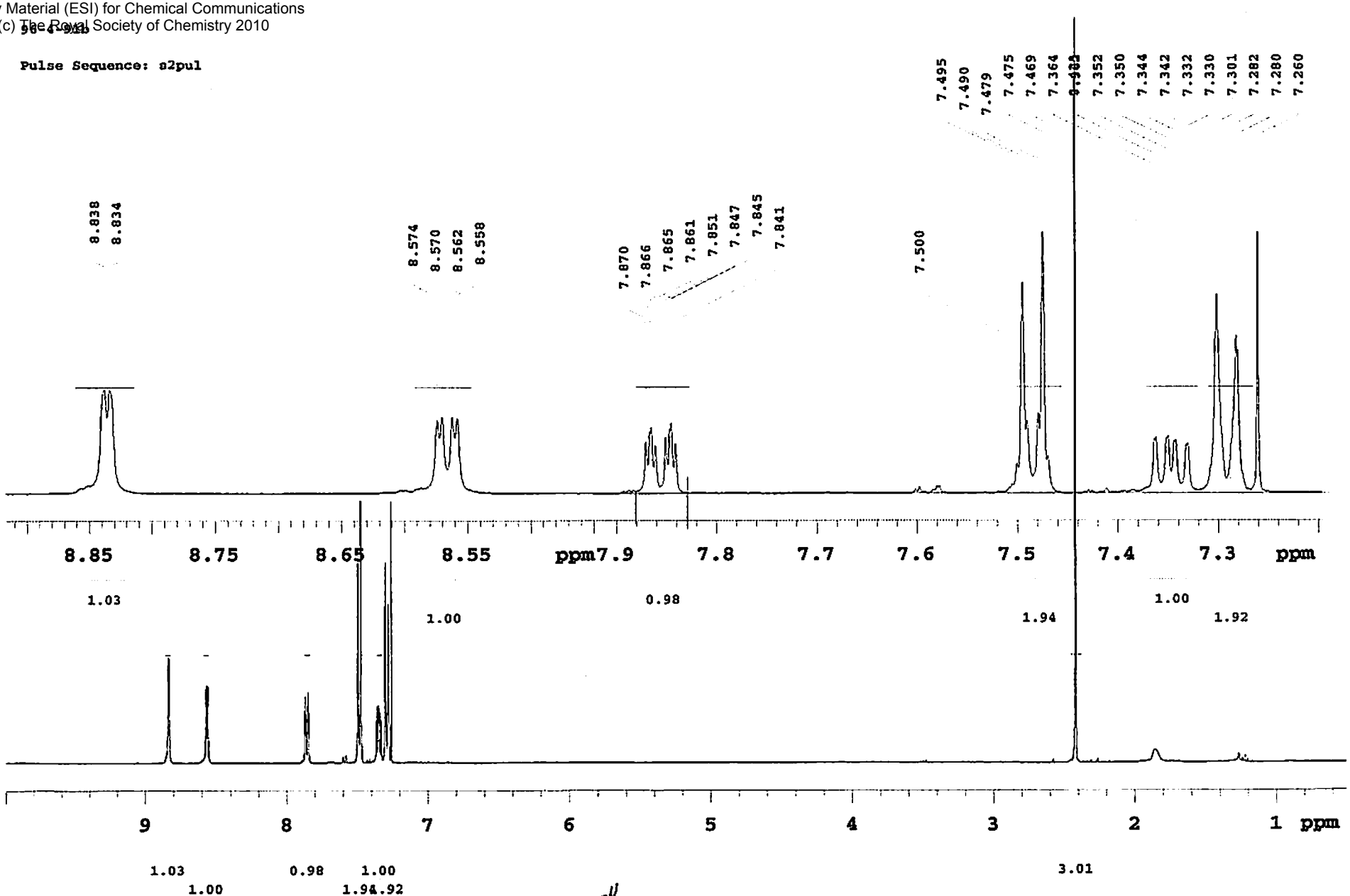
98-4-569c

Pulse Sequence: s2pul



4fb

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8.838
8.834
8.574
8.570
8.562
8.558
7.870
7.866
7.865
7.861
7.851
7.847
7.845
7.841
7.500
7.495
7.490
7.479
7.475
7.469
7.364
7.352
7.350
7.344
7.342
7.332
7.330
7.301
7.282
7.280
7.260
8.85
8.75
8.65
8.55
ppm7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
1.03
1.00
0.98
1.94
1.00
1.92
9
8
7
6
5
4
3
2
1
ppm
1.03
1.00
0.98
1.00
1.94.92
3.01

4gb

Pulse Sequence: s2pul