Ru(II)–Catalyzed Intermolecular *Ortho*–C–H Amidation of Aromatic Ketones with Sulfonyl Azides

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Electronic Supplementary Information

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General Experimental

All the reactions were performed in an oven-dried Schlenk flask under an argon atmosphere. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel procured from Merck (100-200 Mesh) eluting with hexanes and ethyl acetate mixture. Flash column chromatography was performed using silica gel procured from Acme's (230-400 Mesh) eluting with hexanes and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 (Merck) plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber or an aqueous alkaline $KMnO_4$ solution followed by heating.

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded on a Bruker Avance 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) spectrometer, Bruker Avance 500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz) spectrometer having solvent resonance as internal standard (^{1}H NMR, $CHCl_3$ at 7.26

ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in (Hz), and integration. Data for ^{13}C NMR, ^{19}F NMR were reported in terms of chemical shift (ppm). GC analysis was performed on a Shimadzu GCMS QP2010 equipped with ZB-1 column (30 m x 0.25 mm, pressure = 20.0 kPa, detector = EI, 300 ^{o}C) with helium gas as carrier. IR spectra were recorded on JASCO FT/IR-5300 spectrometer and reported in cm^{-1}. LC-MS spectra were obtained with a Shimadzu 2010A (EI-positive/ negative mode) with ionization voltage of 70ev; data was reported in the form of m/z (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using THERMO FINNIGAN FLASH EA 1112 analyzer. Melting points were determined on electro-thermal melting point apparatus and are uncorrected. X-ray data was collected at 298K on a Bruker-Nonius SMART APEX CCD single crystal diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å).

Materials: Unless otherwise noted, all the reagents were obtained commercially and used without purification. 1,2-Dichloroethane (DCE) are distilled over $CaCl_2$. Aryl ketones, $[RuCl_2(p\text{-cymene})]_2$, $Cu(OAc)_2.H_2O$ and $AgSbF_6$ were purchased from Sigma Aldrich Ltd. and used as received. Analytical and spectral data of all those known compounds are exactly matching with the reported values.

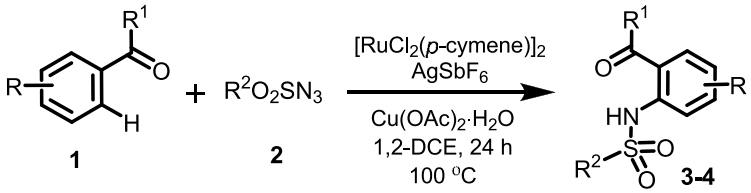
Experimental Procedures:

Synthesis of Azides: [S1]

The azides are prepared following the known procedure.

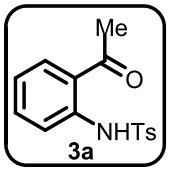
To a solution of sodium azide (1.99 g, 30 mmol) in water (10 mL) was added a solution of *p*-toluenesulfonyl chloride (3.85 g, 20 mmol) in acetone (20 mL) dropwise at 0 °C. The reaction was warmed up to room temperature and stirred for over night, the acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (20 mL) for three times. The combined organic layers were washed with water and saturated Na_2CO_3 solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product is subsequently used without further purification.

Ortho-C-H Amidation of Ketones with Sulfonyl Azides; General procedure (GP-1):



Aryl ketones (**1**; 1.0 mmol), sulfonyl azides (**2**; 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (50 mol%) and $AgSbF_6$ (20 mol%) were taken in an oven-dried Schlenk flask under an argon atmosphere. 1,2-Dichloroethane (DCE) (2.0 mL) was added to this mixture. The resulting solution was stirred at 100 °C for 24 h. The crude reaction mixture was diluted with dichloromethane and passed through a small pad of Celite. After evaporation of the solvent, the crude reaction mixture was purified using column chromatography on silica gel.

N-(2-Acetylphenyl)-4-methylbenzenesulfonamide (3a):[S2]



Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 °C for 24 h. Finally, the

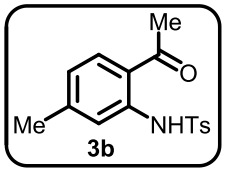
crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (6:1) to afford **3a** (209 mg) in 72% yield as colorless solid.

mp = 150–151 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.79 (dd, J = 8.0, 1.2 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 8.0 Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 143.8, 139.8, 136.3, 134.8, 131.9, 129.5, 127.1, 122.5, 122.1, 118.8, 28.0, 21.4.

***N*-(2-Acetyl-5-methylphenyl)-4-methylbenzenesulfonamide (3b):**



3b

Following the general procedure (GP-1); 4'-methylacetophenone (**1b**; 134 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3b** (255 mg) in 84% yield as colorless solid.

mp = 133–134 ^{o}C

R_f = 0.36 (4:1 hexane/EtOAc); [Silica, UV and I_2]

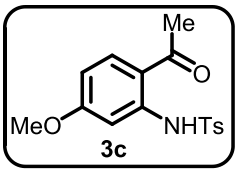
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (s, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 146.4, 143.8, 140.2, 136.6, 131.9, 129.6, 127.3, 123.5, 119.9, 119.3, 28.0, 22.1, 21.6.

IR (KBr) ν_{max} 2926, 1649, 1567, 1161, 657, 536 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{17}NO_3SNa$, 326.0827; found, 326.0831.

***N*-(2-Acetyl-5-methoxyphenyl)-4-methylbenzenesulfonamide (3c):**



3c

Following the general procedure (GP-1); 4'-methoxyacetophenone (**1c**; 150 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3c** (299 mg) in 94% yield as colorless solid.

mp = 139–140 ^oC

R_f = 0.29 (4:1 hexane/EtOAc); [Silica, UV and I_2]

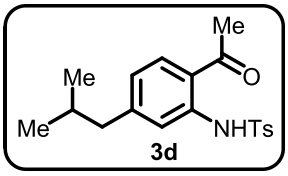
^1H NMR (400 MHz, $CDCl_3$) δ 11.92 (s, 1H), 7.85 –7.66 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 2.0 Hz, 1H), 6.51 (dd, J = 9.2, 2.4 Hz, 1H), 3.79 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 164.3, 143.9, 142.5, 136.3, 134.0, 129.6, 127.2, 115.3, 108.8, 102.6, 55.5, 27.7, 21.4.

IR (KBr) ν_{max} 2947, 1632, 1265, 1161, 887, 663, 548 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{17}NO_4SNa$, 342.0776; found, 342.0777.

***N*-(2-Acetyl-5-*iso*-butylphenyl)-4-methylbenzenesulfonamide (3d):**



3d

Following the general procedure (GP-1); 1-(4-isobutylphenyl)ethanone (**1d**; 120 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3d** (286 mg) in 83% yield as brown color solid.

mp = 91–92 ^oC

R_f = 0.50 (4:1 hexane/EtOAc); [Silica, UV and I_2]

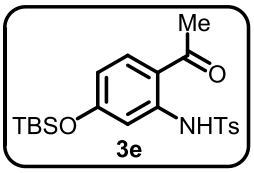
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.69 (t, J = 8.4 Hz, 3H), 7.46 (bd, J = 1.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.82 (dd, J = 8.0, 1.6 Hz, 1H), 2.52 (s, 3H), 2.44 (d, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.89–1.75 (m, 1H), 0.82 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 149.9, 143.7, 139.9, 136.3, 131.8, 129.5, 127.2, 123.5, 120.0, 119.3, 45.4, 29.9, 27.9, 22.1, 21.4.

IR (KBr) ν_{max} 2964, 1643, 1429, 1160, 651 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{19}H_{23}NO_3SNa$, 368.1296; found, 368.1297.

_N_-(2-Acetyl-5-(tert-butyldimethylsilyloxy)phenyl)-4-methylbenzenesulfonamide (3e):



Following the general procedure (GP-1); 1-(4-(*tert*-butyldimethylsilyloxy)phenyl)ethanone (**1e**; 250 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (15:1) to afford **3e** (304 mg) in 73% yield as brown color semi-solid.

R_f = 0.28 (15:1 hexane/EtOAc); [Silica, UV and I_2]

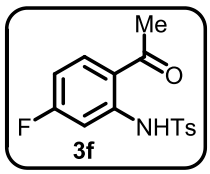
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.08 (bd, J = 2.0 Hz, 1H), 6.46 (dd, J = 8.0, 1.2 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H), 0.94 (s, 9H), 0.91 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 161.3, 143.8, 142.3, 136.4, 134.0, 129.5, 127.1, 115.9, 114.5, 109.0, 27.7, 25.4, 21.4, 18.1, –4.6.

IR (Neat) ν_{max} 2964, 1632, 1599, 1342, 1255, 1161, 915, 641 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{21}H_{30}NO_4SSi$, 420.1665; found, 420.1664.

_N_-(2-Acetyl-5-fluorophenyl)-4-methylbenzenesulfonamide (3f):



Following the general procedure (GP-1); 4'-fluoroacetophenone (**1f**; 138 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3f** (197 mg) in 64% yield as colorless solid.

mp = 150–151 ^oC

R_f = 0.30 (4:1 hexane/EtOAc); [Silica, UV and I_2]

^1H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 1H), 7.84 (bt, J = 4.0 Hz, 1H), 7.77 (bd, J = 1.6 Hz, 2H), 7.42 (d, J = 8.8 Hz, 1H), 7.27 (bd, J = 6.0 Hz, 2H), 6.74 (bt, J = 6.0 Hz, 1H), 2.57 (s, 3H), 2.39 (s, 3H).

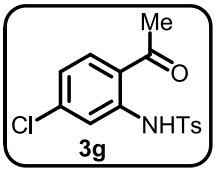
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 165.97 (d, J = 205.9 Hz), 144.2, 142.84 (d, J = 9.4 Hz), 136.2, 134.55 (d, J = 8.4 Hz), 129.8, 127.2, 118.3, 109.65 (d, J = 17.8 Hz), 105.46 (d, J = 21.6 Hz), 28.1, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –99.27 (quin)

IR (KBr) ν_{max} 3090, 1659, 1593, 1429, 1171, 892, 662 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{15}H_{14}FNO_3SNa$, 330.0576; found, 330.0570.

***N*-(2-Acetyl-5-chlorophenyl)-4-methylbenzenesulfonamide (3g):**[S3]



3g

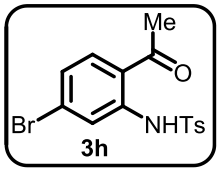
Following the general procedure (GP-1); 4'-chloroacetophenone (**1g**; 155 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3g** (262 mg) in 81% yield as colorless solid.

mp = 162–163 ^oC

^1H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.76 (dd, J = 8.4, 2.0 Hz, 2H), 7.73 (d, J = 4.0 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.00 (dd, J = 8.8, 2.0 Hz, 1H), 2.55 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 144.2, 141.2, 141.1, 136.1, 133.0, 129.8, 127.2, 122.6, 120.1, 118.4, 28.1, 21.5.

_N_-(2-Acetyl-5-bromophenyl)-4-methylbenzenesulfonamide (3h):



Following the general procedure (GP-1); 4'-bromoacetophenone (**1h**; 198 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 0.5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3h** (257 mg) in 70% yield as light brown color solid.

mp = 171–172 ^{o}C

R_f = 0.47 (4:1 hexane/EtOAc); [Silica, UV and I_2]

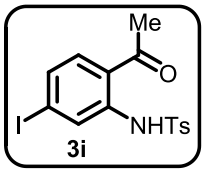
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.85 (s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.8 Hz, 1H), 2.54 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 144.2, 140.9, 136.0, 133.0, 129.7, 127.1, 125.6, 121.4, 120.4, 28.1, 21.5.

IR (KBr) ν_{max} 3063, 1649, 1561, 1161, 926, 657, 569 cm^{-1}

HRMS–ESI (*m/z*): $[M+H]^+$ Calcd for $C_{15}H_{15}BrNO_3S$, 367.9956; found, 367.9954.

_N_-(2-Acetyl-5-iodophenyl)-4-methylbenzenesulfonamide (3i):



Following the general procedure (GP-1); 4'-iodoacetophenone (**1i**; 246 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3i** (269 mg) in 65% yield as colorless solid.

mp = 167–168 ^{o}C

R_f = 0.38 (4:1 hexane/EtOAc); [Silica, UV and I_2]

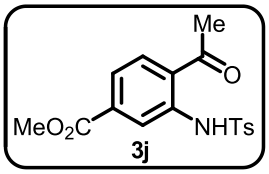
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 8.08 (bd, J = 0.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.49–7.37 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.53 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 144.2, 140.6, 136.2, 132.6, 131.7, 129.8, 127.7, 127.3, 121.0, 102.7, 28.0, 21.5.

IR (KBr) ν_{max} 2925, 1659, 1588, 1484, 1160, 930, 662 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{15}H_{15}INO_3S$, 415.9817; found, 415.9819.

Methyl 4-acetyl-3-(4-methylphenylsulfonamido)benzoate (3j):



3j

Following the general procedure (GP-1); methyl 4-acetylbenzoate (**1j**; 178 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3j** (201 mg) in 58% yield as colorless solid.

mp = 152–153 ^{o}C

R_f = 0.25 (4:1 hexane/EtOAc); [Silica, UV and I_2]

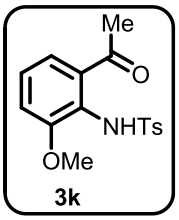
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.31 (bd, J = 0.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.68 (dd, J = 8.4, 1.6 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 2.59 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 165.4, 144.1, 140.0, 136.2, 135.3, 131.8, 129.7, 127.4, 124.7, 123.1, 119.9, 52.7, 28.4, 21.5.

IR (KBr) ν_{max} 2953, 1720, 1649, 1419, 1156, 926, 663, 536 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{17}H_{18}NO_5S$, 348.0906; found, 348.0907.

***N*-(2-Acetyl-6-methoxyphenyl)-4-methylbenzenesulfonamide (3k):**



Following the general procedure (GP-1); 3'-methoxyacetophenone (**1k**; 150 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3k** (27 mg) in 8% yield as ash color solid and **3k′** (68 mg) in 21% yield as colorless solid.

mp = 175–176 ^oC

R_f = 0.13 (4:1 hexane/EtOAc); [Silica, UV and I_2]

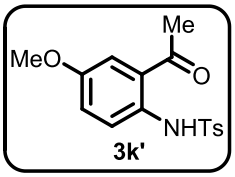
^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (bd, J = 1.6 Hz, 1H), 7.80 (d, J = 1.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H), 7.19 (bd, J = 2.0 Hz, 1H), 3.90 (s, 3H), 2.62 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 147.2, 145.2, 143.6, 139.6, 129.8, 127.0, 125.8, 124.8, 115.7, 109.4, 56.1, 28.0, 21.5.

IR (KBr) ν_{max} 3430, 3314, 2932, 1654, 1604, 1144, 668, 585 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{16}H_{18}NO_4S$, 320.0957; found, 320.0955.

***N*-(2-Acetyl-4-methoxyphenyl)-4-methylbenzenesulfonamide (3k′):**[S3]

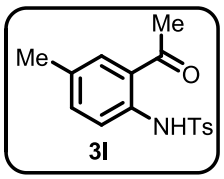


mp = 119–120 ^oC

^1H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.63 (d, J = 9.2 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 2.8 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.02 (dd, J = 9.2, 3.2 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 155.2, 143.6, 136.0, 132.3, 129.4, 127.1, 124.7, 122.5, 119.8, 116.5, 55.6, 28.0, 21.4.

***N*-(2-Acetyl-4-methylphenyl)-4-methylbenzenesulfonamide (3l):**



Following the general procedure (GP-1); 3'-methylacetophenone (**1l**; 134 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3l** (90 mg) in 30% yield as colorless solid.

mp = 134–135 ^oC

R_f = 0.44 (4:1 hexane/EtOAc); [Silica, UV and I_2]

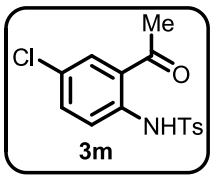
^1H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.56 (s, 1H), 7.30–7.24 (m, 1H), 7.20 (d, J = 8.4 Hz, 2H), 2.52 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 143.7, 137.4, 136.5, 135.6, 132.3, 132.0, 129.5, 127.2, 122.6, 119.5, 28.1, 21.5, 20.6.

IR (KBr) ν_{max} 3057, 1660, 1484, 1095, 646 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{17}NO_3SNa$, 326.0827; found, 326.0828.

***N*-(2-Acetyl-4-chlorophenyl)-4-methylbenzenesulfonamide (3m):**



Following the general procedure (GP-1); 3'-chloroacetophenone (**1m**; 154 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (6:1) to afford **3m** (81 mg) in 25% yield as brown color solid.

mp = 135–136 ^oC

R_f = 0.48 (6:1 hexane/EtOAc); [Silica, UV and I_2]

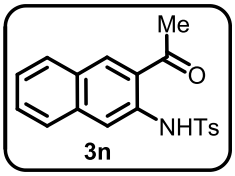
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.73 (d, J = 2.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.39 (dd, J = 8.8, 2.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 2.54 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 144.1, 138.4, 136.1, 134.6, 131.3, 129.7, 127.8, 127.2, 123.2, 120.6, 28.1, 21.5.

IR (KBr) ν_{max} 3073, 2931, 1649, 1588, 1249, 926, 657 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{15}H_{15}ClNO_3S$, 324.0461; found, 324.0464.

_N_-(3-Acetylnaphthalen-2-yl)-4-methylbenzenesulfonamide (3n):



3n

Following the general procedure (GP-1); 2-acetonaphthone (**1n**; 170 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (3:1) to afford **3n** (299 mg) in 88% yield as pale yellow solid.

mp = 154–155 ^{o}C

R_f = 0.48 (3:1 hexane/EtOAc); [Silica, UV and I_2]

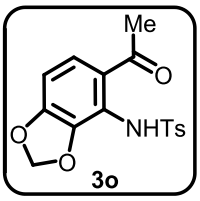
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 8.32 (s, 1H), 8.00 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.71 (bt, J = 7.6 Hz, 3H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 143.6, 136.2, 135.8, 134.8, 134.4, 129.8, 129.4, 129.0, 128.4, 127.1, 127.0, 125.8, 123.1, 116.9, 28.0, 21.3.

IR (KBr) ν_{max} 3095, 2926, 1649, 1506, 1160, 897, 673, 541 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{19}H_{17}NO_3SNa$, 362.0827; found, 362.0827.

_N_-(6-Acetylbenzo[_d_][1,3]dioxol-5-yl)-4-methylbenzenesulfonamide (3o):



Following the general procedure (GP-1); 3',4'-(methylenedioxy)acetophenone (**1o**; 164 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (3:1) to afford **3o** (95 mg) in 28% yield as pale yellow solid.

mp = 107–108 ^oC

R_f = 0.47 (3:1 hexane/EtOAc); [Silica, UV and I_2]

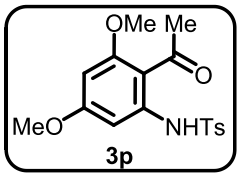
^1H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 8.4 Hz, 1H), 6.05 (s, 2H), 2.39 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 153.0, 143.6, 142.2, 136.4, 129.1, 127.5, 127.0, 123.2, 121.7, 104.8, 102.4, 27.8, 21.5.

IR (KBr) ν_{max} 2915, 1644, 1463, 1320, 1156, 909, 663, 542 cm^{-1}

HRMS–ESI (_m/z_): $[M+H]^+$ Calcd for $C_{16}H_{16}NO_5S$, 334.0749; found, 334.0752.

_N_-(2-Acetyl-3,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (3p):



Following the general procedure (GP-1); 2',4'-dimethoxyacetophenone (**1p**; 180 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3p** (137 mg) in 39% yield as pale yellow solid.

mp = 144–145 ^oC

R_f = 0.27 (4:1 hexane/EtOAc); [Silica, UV and I_2]

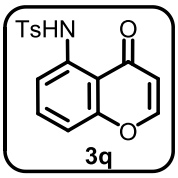
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.80 (bd, J = 2.4 Hz, 1H), 6.10 (bd, J = 2.0 Hz, 1H), 3.80 (s, 6H), 2.38 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 164.1, 162.6, 143.7, 142.5, 136.3, 129.5, 127.2, 109.3, 96.3, 94.0, 55.5, 33.5, 21.4.

IR (KBr) ν_{max} 3260, 2931, 1605, 1277, 1161, 674, 548 cm^{-1}

HRMS–ESI (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{20}NO_5S$, 350.1062; found, 350.1062.

4-Methyl-*N*-(4-oxo-4*H*-chromen-5-yl)benzenesulfonamide (3q):



Following the general procedure (GP-1); chromone (**1q**; 146 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (3:1) to afford **3q** (200 mg) in 63% yield as colorless solid.

mp = 176–177 ^{o}C

R_f = 0.37 (3:1 hexane/EtOAc); [Silica, UV and I_2]

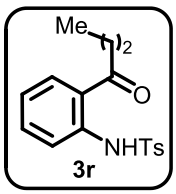
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 5.6 Hz, 1H), 7.54–7.47 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.02 (dd, J = 7.2, 6.4 Hz, 1H), 6.26 (d, J = 6.0 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 157.3, 155.2, 144.0, 140.1, 136.5, 134.7, 129.7, 127.4, 112.9, 112.5, 112.4, 111.6, 21.6.

IR (KBr) ν_{max} 2915, 1633, 1484, 1150, 1008, 657, 542 cm^{-1}

HRMS–ESI (*m/z*): $[M+Na]^+$ Calcd for $C_{16}H_{13}NO_4SNa$, 338.0463; found, 338.0467.

***N*-(2-Butyrylphenyl)-4-methylbenzenesulfonamide (3r):**



Following the general procedure (GP-1); butyrophenone (**1r**; 148 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3r** (270 mg) in 85% yield as colorless solid.

mp = 112–113 ^oC

R_f = 0.51 (4:1 hexane/EtOAc); [Silica, UV and I_2]

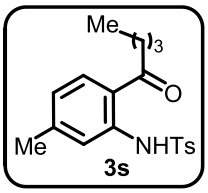
^1H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 7.80 (dd, J = 8.0, 1.2 Hz, 1H), 7.73–7.65 (m, 3H), 7.43 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.8 Hz, 1H), 2.85 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 1.72–1.59 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 143.8, 139.8, 136.5, 134.5, 130.9, 129.5, 127.1, 122.7, 122.4, 119.5, 41.4, 21.4, 17.8, 13.6.

IR (KBr) ν_{max} 2964, 2876, 1649, 1501, 1161, 931, 569 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{17}H_{19}NO_3SNa$, 340.0983; found, 340.0988.

4-Methyl-*N*-(5-methyl-2-pentanoylphenyl)benzenesulfonamide (3s):



3s

Following the general procedure (GP-1); 4'-methylvalerophenone (**1s**; 176 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (15:1) to afford **3s** (253 mg) in 73% yield as pale yellow semi-solid.

R_f = 0.37 (15:1 hexane/EtOAc); [Silica, UV and I_2]

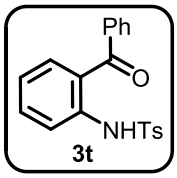
^1H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 7.67 (d, J = 8.0 Hz, 3H), 7.48 (s, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 2.81 (t, J = 7.4 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.62–1.49 (m, 2H), 1.38–1.23 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 145.8, 143.6, 139.8, 136.4, 131.0, 129.4, 127.0, 123.7, 119.9, 119.7, 39.1, 26.5, 22.1, 21.8, 21.3, 13.8.

IR (Neat) ν_{max} 2953, 1649, 1566, 1155, 662, 569 cm^{-1}

HRMS–ESI (*m/z*): $[M+H]^+$ Calcd for $C_{19}H_{24}NO_3S$, 346.1477; found, 346.1482.

_N_-(2-Benzoylphenyl)-4-methylbenzenesulfonamide (3t):[S2]



3t

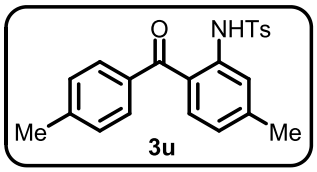
Following the general procedure (GP-1); benzophenone (**1t**; 182 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 °C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (9:1) to afford **3t** (236 mg) in 67% yield as colorless solid.

mp = 125–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63–7.46 (m, 4H), 7.44–7.29 (m, 5H), 7.10 (td, J = 7.7, 0.8 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 143.7, 138.7, 137.3, 135.6, 133.7, 133.0, 132.6, 129.7, 129.5, 128.0, 127.1, 126.2, 123.5, 123.1, 21.3.

4-Methyl-_N_-(5-methyl-2-(4-methylbenzoyl)phenyl)benzenesulfonamide (3u):



3u

Following the general procedure (GP-1); 4,4'-dimethylbenzophenone (**1u**; 210 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 °C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (6:1) to afford **3u** (265 mg) in 70% yield as colorless solid.

mp = 161–162 °C

R_f = 0.61 (6:1 hexane/EtOAc); [Silica, UV and I_2]

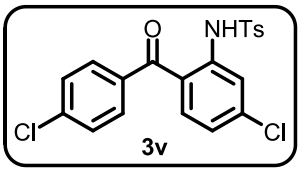
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.59 (s, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.30–7.23 (m, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 144.8, 143.5, 143.3, 138.9, 135.8, 135.0, 133.0, 129.9, 129.4, 128.6, 127.1, 124.3, 123.9, 123.4, 21.9, 21.6, 21.3.

IR (KBr) ν_{max} 3249, 2920, 1648, 1604, 1374, 1171, 541 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{22}H_{22}NO_3S$, 380.1320; found, 380.1319.

_N_-(5-Chloro-2-(4-chlorobenzoyl)phenyl)-4-methylbenzenesulfonamide (3v):



3v

Following the general procedure (GP-1); 4,4'-dichlorobenzophenone (**1v**; 251 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (16:1) to afford **3v** (210 mg) in 50% yield as colorless solid.

mp = 111–112 ^{o}C

R_f = 0.37 (16:1 hexane/EtOAc); [Silica, UV and I_2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.80 (bd, J = 2.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.44–7.29 (m, 5H), 7.11 (d, J = 8.4 Hz, 2H), 7.07 (dd, J = 8.4, 1.6 Hz, 1H), 2.28 (s, 3H).

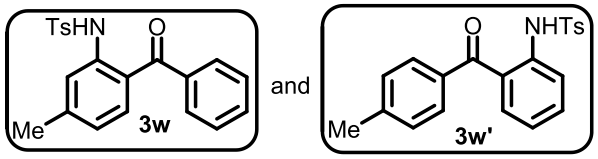
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 144.1, 140.3, 139.4, 135.6, 133.8, 131.0, 129.7, 128.6, 127.2, 123.5, 123.4, 122.3, 21.4.

IR (KBr) ν_{max} 3243, 1649, 1588, 1166, 952 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{20}H_{16}Cl_2NO_3S$, 420.0228; found, 420.0223.

_N_-(2-Benzoyl-5-methylphenyl)-4-methylbenzenesulfonamide (3w):

4-Methyl-_N_-(2-(4-methylbenzoyl)phenyl)benzenesulfonamide (3w'):



Following the general procedure (GP-1); 4-methylbenzophenone (**1w**; 196 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (15:1) to afford inseparable mixture **3w** and **3w′** (64:36; 251 mg) in 69% yield as yellow thik liquid.

R_f = 0.32 (15:1 hexane/EtOAc); [Silica, UV and I_2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 9.88 (s, 0.56H), 7.77 (d, J = 8.4 Hz, 0.64H), 7.64–7.47 (m, 6H), 7.42–7.32 (m, 5H), 7.29–7.24 (m, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 2.42 (s, 1.8H), 2.39 (s, 3H), 2.23 (s, 3H), 2.20 (s, 1.7H).

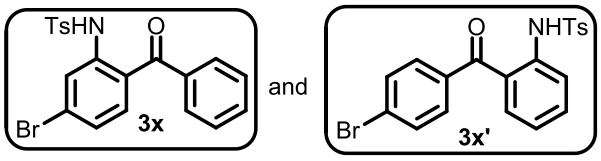
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 197.9, 145.1, 143.6, 139.1, 138.5, 137.7, 135.7, 135.6, 134.6, 133.4, 133.3, 132.7, 132.3, 130.0, 129.6, 129.4, 128.7, 127.9, 127.1, 126.8, 124.3, 123.5, 123.4, 123.3, 123.2, 21.9, 21.6, 21.3.

IR (KBr) ν_{max} 3243, 2915, 1627, 1386, 1265, 1156, 1095, 909, 701 cm^{-1}

HRMS–ESI (m/z): $[M+H]^+$ Calcd for $C_{21}H_{20}NO_3S$, 366.1164; found, 366.1164.

_N_-(2-Benzoyl-5-bromophenyl)-4-methylbenzenesulfonamide (3x):

_N_-(2-(4-Bromobenzoyl)phenyl)-4-methylbenzenesulfonamide (3x'):



Following the general procedure (GP-1); 4-bromobenzophenone (**1x**; 261 mg, 1.0 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg,

50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (15:1) to afford inseparable mixture **3x** and **3x′** (64:36; 291 mg) in 68% yield as yellow thik liquid.

R_f = 0.32 (15:1 hexane/EtOAc); [Silica, UV and I_2]

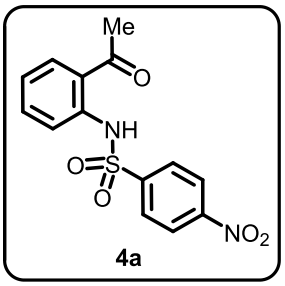
^1H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 9.83 (s, 0.56H), 7.97 (bd, J = 1.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.0 Hz, 3H), 7.57–7.50 (m, 3H), 7.45–7.31 (m, 5H), 7.29–7.19 (m, 3H), 7.08 (d, J = 8.0 Hz, 3H), 7.08 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 197.1, 144.0, 143.8, 140.2, 138.7, 137.2, 136.1, 135.6, 135.5, 134.2, 133.9, 132.8, 132.5, 131.3, 131.2, 129.7, 129.6, 129.5, 128.5, 128.2, 127.9, 127.8, 127.1, 126.4, 126.0, 125.2, 124.2, 123.6, 123.4, 21.4.

IR (KBr) ν_{max} 3249, 2931, 1632, 1589, 1484, 1380, 1167, 1090, 942, 663 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{16}BrNO_3SNa$, 451.9932; found, 451.9935.

***N*-(2-Acetylphenyl)-4-nitrobenzenesulfonamide (4a):**



4a

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), 4-nitrobenzenesulfonyl azide (**2b**; 342 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **4a** (196 mg) in 61% yield as colorless solid.

mp = 149–150 ^oC

R_f = 0.33 (4:1 hexane/EtOAc); [Silica, UV and I_2]

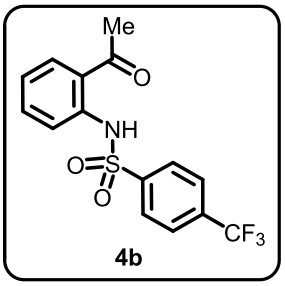
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.61 (d, J = 8.8 Hz, 2H), 8.37 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 2.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 150.2, 145.2, 139.2, 135.3, 132.3, 128.5, 124.3, 123.6, 122.4, 119.2, 28.2.

IR (KBr) ν_{max} 3106, 1643, 1539, 1353, 1161, 931, 608 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{14}H_{12}N_2O_5SNa$, 343.0365; found, 343.0364.

_N_-(2-Acetylphenyl)-4-(trifluoromethyl)benzenesulfonamide (4b):



4b

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), 4-(trifluoromethyl)benzenesulfonyl azide (**2c**; 376 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **4b** (334 mg) in 97% yield as colorless solid.

mp = 133–134 ^{o}C

R_f = 0.48 (4:1 hexane/EtOAc); [Silica, UV and I_2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.73–7.67 (m, 3H), 7.49 (td, J = 7.9, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 1.2 Hz, 1H), 2.57 (s, 3H).

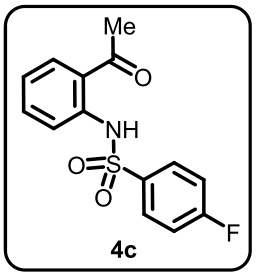
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 143.0, 139.3, 135.1, 134.52 (q, J = 33.3 Hz), 132.1, 127.7, 126.2, 126.1, 123.3, 122.83 (q, J = 91.9 Hz), 119.1, 28.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.21

IR (KBr) ν_{max} 3057, 1638, 1578, 1408, 1320, 1161, 1139, 608 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{15}H_{12}F_3NO_3SNa$, 366.0388; found, 366.0388.

_N_-(2-Acetylphenyl)-4-fluorobenzenesulfonamide (4c):



4c

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), 4-fluorobenzenesulfonyl azide (**2d**; 302 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **4c** (278 mg) in 95% yield as colorless solid.

mp = 158–159 ^oC

R_f = 0.39 (4:1 hexane/EtOAc); [Silica, UV and I_2]

^1H NMR (400 MHz, $CDCl_3$) δ 11.50 (s, 1H), 7.90–7.84 (m, 2H), 7.82 (dd, J = 8.2, 1.4 Hz, 1H), 7.69 (dd, J = 8.2, 0.6 Hz, 1H), 7.48 (td, J = 7.9, 1.3 Hz, 1H), 7.15–7.06 (m, 3H), 2.57 (s, 3H).

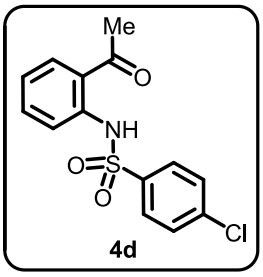
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 165.17 (d, J = 256 Hz), 139.7, 135.5, 135.0, 132.0, 129.95 (d, J = 9.09 Hz), 123.0, 122.4, 119.2, 116.27 (d, J = 22.2 Hz), 28.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –104.48.

IR (KBr) ν_{max} 3101, 1649, 1490, 1172, 931, 558 cm^{-1}

HRMS–ESI (_m/z_): $[M+Na]^+$ Calcd for $C_{14}H_{12}FNO_3SNa$, 316.0420; found, 316.0416.

_N_-(2-Acetylphenyl)-4-chlorobenzenesulfonamide (4d):



4d

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), 4-chlorobenzenesulfonyl azide (**2e**; 326 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%),

$Cu(OAc)_2 \cdot H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **4d** (224 mg) in 72% yield as colorless solid.

mp = 135–136 ^oC

R_f = 0.46 (4:1 hexane/EtOAc); [Silica, UV and I_2]

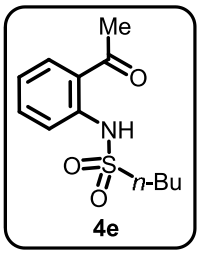
^1H NMR (400 MHz, $CDCl_3$) δ 11.54 (s, 1H), 7.82 (dd, J = 7.8, 1.4 Hz, 1H), 7.79–7.73 (m, 2H), 7.67 (bd, J =8.0 Hz, 1H), 7.46 (td, J = 8.4, 1.2 Hz, 1H), 7.38 (dt, J = 8.8, 2.0 Hz, 2H), 7.09 (td, J = 8.0, 1.0 Hz, 1H), 2.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 139.5, 139.4, 137.8, 135.0, 132.0, 129.2, 128.6, 123.0, 122.2, 119.0, 28.1.

IR (KBr) ν_{max} 3090, 2926, 1649, 1495, 1249, 1167, 920, 756, 558 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{14}H_{12}ClNO_3SNa$, 332.0124; found, 332.0125.

***N*-(2-Acetylphenyl)butane-1-sulfonamide (4e):**



4e

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), butane-1-sulfonyl azide (**2f**; 244 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2 \cdot H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (16:1) to afford **4e** (143 mg) in 56% yield as pale yellow oil.

R_f = 0.19 (16:1 hexane/EtOAc); [Silica, UV and I_2]

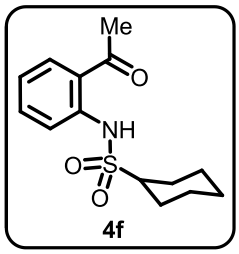
^1H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.72 (dd, J = 8.0, 1.2 Hz, 1H), 7.51 (td, J = 8.0, 1.2 Hz, 1H), 7.11 (td, J = 8.4, 1.2 Hz, 1H), 3.20–3.03 (m, 2H), 2.64 (s, 3H), 1.81–1.63 (m, 2H), 1.42–1.31 (m, 2H), 0.84 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 140.6, 135.4, 132.5, 122.4, 121.4, 117.6, 51.9, 28.3, 25.3, 21.3, 13.5.

IR (Neat) ν_{max} 3095, 2964, 1654, 1601, 1577, 1248, 1150, 930, 749, 629 cm^{-1}

HRMS–ESI (*m/z*): $[M+Na]^+$ Calcd for $C_{12}H_{17}NO_3SNa$, 278.0827; found, 278.0827.

_N_-(2-Acetylphenyl)cyclohexanesulfonamide (4f):



Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), cyclohexanesulfonyl azide (**2g**; 284 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (16:1) to afford **4f** (124 mg) in 44% yield as brown color semi-solid.

R_f = 0.19 (16:1 hexane/EtOAc); [Silica, UV and I_2]

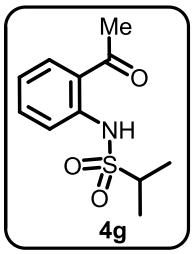
^1H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.50 (td, J = 8.8, 1.6 Hz, 1H), 7.09 (td, J = 8.0, 1.0 Hz, 1H), 3.10–2.99 (m, 1H), 2.64 (s, 3H), 2.10–2.05 (m, 2H), 1.86–1.80 (m, 2H), 1.65–1.48 (m, 3H), 1.24–1.10 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 141.2, 135.3, 132.4, 122.1, 121.1, 117.7, 61.0, 28.3, 26.2, 25.04, 24.98.

IR (Neat) ν_{max} 3068, 2931, 2854, 1649, 1489, 1249, 925, 766, 634 cm^{-1}

HRMS–ESI (*m/z*): $[M+H]^+$ Calcd for $C_{14}H_{20}NO_3S$, 282.1164; found, 282.1164.

_N_-(2-Acetylphenyl)propane-2-sulfonamide (4g):



Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), propane-2-sulfonyl azide (**2h**; 223 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$

(100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (16:1) to afford **4g** (110 mg) in 46% yield as pink color oil.

R_f = 0.19 (16:1 hexane/EtOAc); [Silica, UV and I_2]

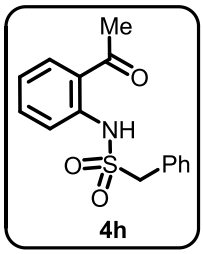
^1H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 7.92 (bd, J = 7.2 Hz, 1H), 7.81 (bd, J = 8.4 Hz, 1H), 7.51 (bt, J = 7.0 Hz, 1H), 7.11 (bt, J = 7.4 Hz, 1H), 3.33 (bt, J = 6.8 Hz, 1H), 2.66 (s, 3H), 1.36 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 141.0, 135.2, 132.3, 122.1, 121.2, 117.8, 53.0, 28.2, 16.3.

IR (Neat) ν_{max} 3112, 2980, 1649, 1489, 1330, 1249, 1144, 925, 761 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{11}H_{15}NO_3SNa$, 264.0671; found, 264.0673.

_N_-(2-Acetylphenyl)-1-phenylmethanesulfonamide (4h):



4h

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), phenylmethanesulfonyl azide (**2i**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (9:1) to afford **4h** (146 mg) in 50% yield as brown color solid.

mp = 119–120 ^oC

R_f = 0.44 (9:1 hexane/EtOAc); [Silica, UV and I_2]

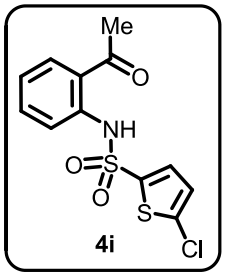
^1H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.35–7.23 (m, 3H), 7.21–7.09 (m, 3H), 4.40 (s, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 140.7, 135.1, 132.1, 130.5, 128.8, 128.6, 128.0, 122.4, 121.4, 117.8, 58.4, 28.1.

IR (KBr) ν_{max} 3041, 2936, 1654, 1495, 1254, 1134, 936, 601 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{15}H_{15}NO_3SNa$, 312.0671; found, 312.0671.

***N*-(2-Acetylphenyl)-5-chlorothiophene-2-sulfonamide (4i):**



4i

Following the general procedure (GP-1); acetophenone (**1a**; 120 mg, 1.0 mmol), 5-chlorothiophene-2-sulfonyl azide (**2j**; 335 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^oC for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (6:1) to afford **4i** (200 mg) in 63% yield as light brown color solid.

mp = 107–108 ^oC

R_f = 0.28 (6:1 hexane/EtOAc); [Silica, UV and I_2]

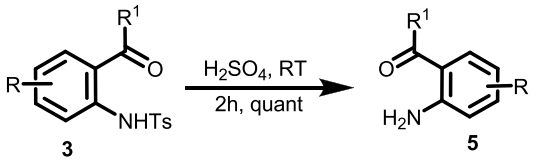
^1H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.53 (bt, J = 7.6 Hz, 1H), 7.39 (d, J = 4.0 Hz, 1H), 7.16 (bt, J = 7.6 Hz, 1H), 6.83 (d, J = 4.0 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 139.3, 138.0, 137.8, 135.2, 132.24, 132.19, 126.7, 123.4, 122.4, 119.1, 28.2.

IR (KBr) ν_{max} 3101, 1649, 1578, 1249, 1161, 920, 602 cm^{-1}

HRMS–ESI (m/z): $[M+Na]^+$ Calcd for $C_{12}H_{10}ClNO_3S_2Na$, 337.9688; found, 337.9689.

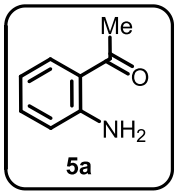
General Procedure for deprotection of tosylgroup (GP-2): [S4]



3 **5**

The *ortho*-amidated aromatic ketone (1.0 mmol) was added to the cold conc H_2SO_4 (6 mL) at 0 ^oC. The mixture was stirred at RT for 2 h. Upon completion, the reaction mixture was quenched with $NaHCO_3$ solution and the resulting mixture was extracted with EtOAc (2 × 10 mL). The organic layers were dried over Na_2SO_4, and concentrated in vacuum to give *ortho*-amino aromatic ketones.

2′-Aminoacetophenone (5a):

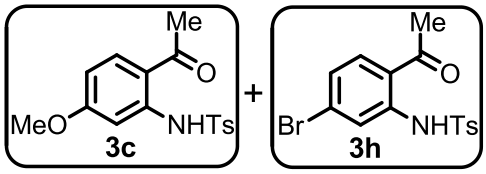


Following the general procedure (GP-2); *N*-(2-acetylphenyl)-4-methylbenzenesulfonamide acetophenone (**3a**; 100 mg, 0.35 mmol) was added to cold conc H_2SO_4 (1.0 mL). The mixture was stirred at RT for 2 h. After usal work-up, the organic layer was dried over Na_2SO_4, and concentrated in vacuum to give 2-amino acetophenone (**5a**) in quantitative yield as light brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.4, 1.2Hz, 1H), 7.26 (dt, J = 8.0, 0.8 Hz, 1H), 6.72–6.58 (m, 2H), 6.50–6.07 (bs, 1H), 2.57 (s, 3H).

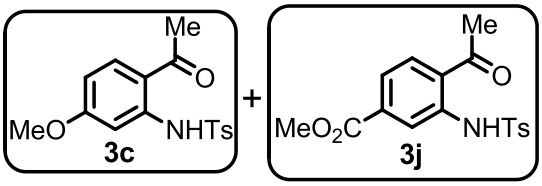
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 150.2, 134.3, 132.0, 118.1, 117.1, 115.6, 27.8.

Competative Experiment (A):



Following the general procedure (GP-1); 4'-methoxyacetophenone (**1c**; 75 mg, 0.5 mmol), 4'-bromoacetophenone (**1h**; 99 mg, 0.5 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%) in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford the products **3c**/**3h** (**3c**, 37% and **3h**, 25% yield) in 1.5/1.0 ratio.

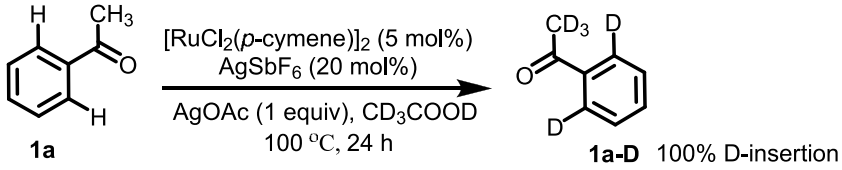
Competative Experiment (B):



Following the general procedure (GP-1); 4'-methoxyacetophenone (**1c**; 75 mg, 0.5 mmol), methyl 4-acetylbenzoate (**1j**; 89 mg, 0.5 mmol), tosyl azide (**2a**; 296 mg, 1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (31 mg, 5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (100 mg, 50 mol%) and $AgSbF_6$ (69 mg, 20 mol%)

in 1,2-DCE (2.0 mL) was heated at 100 ^{o}C for 3 h. Finally, the crude mixture was filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under the reduced pressure. On the basis of the integration of the N-H signal in ^{1}H NMR spectra, the ratio of products **3c**/**3j** was determined 2.5:1.

Deuteration Experiments:



Deuterium experiment was carried out in a 10 mL Schlenk tube with high pressure valve and side arm. The tube was charged with acetophenone (**1a,** 30 mg, 0.25 mmol), $[RuCl_2(p\text{-cymene})]_2$ (8.0 mg, 5 mol%), AgOAc (42.0 mg, 0.25mmol). Subsequently, $AgSbF_6$ (17 mg, 20 mol %) was introduced to the flask in a glovebox. CD_3CO_2D (0.5 mL) was added to the mixture and the resulting mixture was stirred at 100 ^{o}C for 24 h. The reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with dichloromethane (3 × 10 mL). The solvents were evaporated under the reduced pressure. The ^{1}H NMR showed the 100% deuterium insertion on the *ortho*-C–H bonds of **1a**.

This preliminary deuterium scrambling data suggests the reversible cyclo-ruthenation step in the Ru(II)-catalyzed *o*-C–H bond functionalization of acetophenone.

References:

S1. J. Waser, B. Gaspar, S. K. Richardson, E. M. Carreira, *J. Am. Chem. Soc.,* 2006, **128**, 11693.
S2. Y. Hari, T. Kanie, T. Miyagi and T. Aoyama, *Synthesis*, 2006, **8**, 1249.
S3. C. Theeraladanon, M. Arisawa, A. Nishida and M. Nakagawa, *Tetrahedron*, 2004, **60**, 3017.
S4. B. Xiao, T.-J. Gong, J. Xu, Z.-J. Liu and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 1466.

X-ray crystallography: Single crystal X-ray data for the compounds **4a** was collected at on a Bruker SMART APEX CCD area detector system [λ(Mo-Kα) = 0.71073 Å] at 298K **(4a)** respectively, graphite monochromator with a ω scan width of 0.3°, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software[1] was used for the intensity data acquisition and the SAINTPLUS Software[1] was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,[1] an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97,[2] and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

X-ray crystal structure and data for 4a:

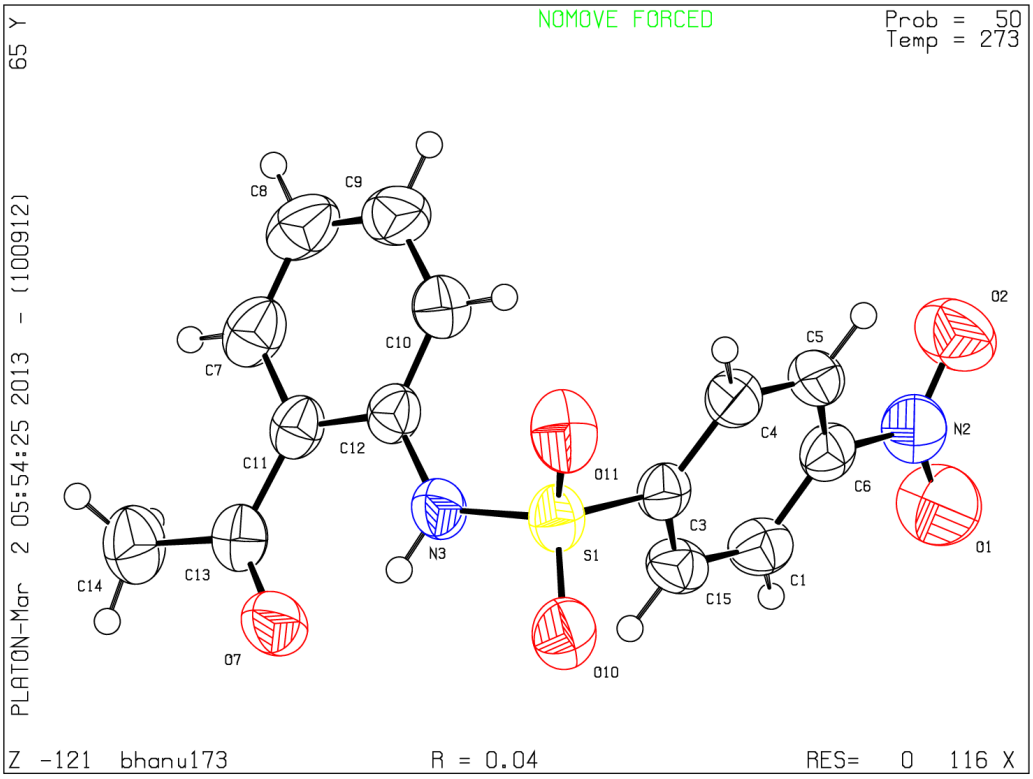


Figure 1. Thermal ellipsoidal plot of compound **4a** with atom labeling Scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

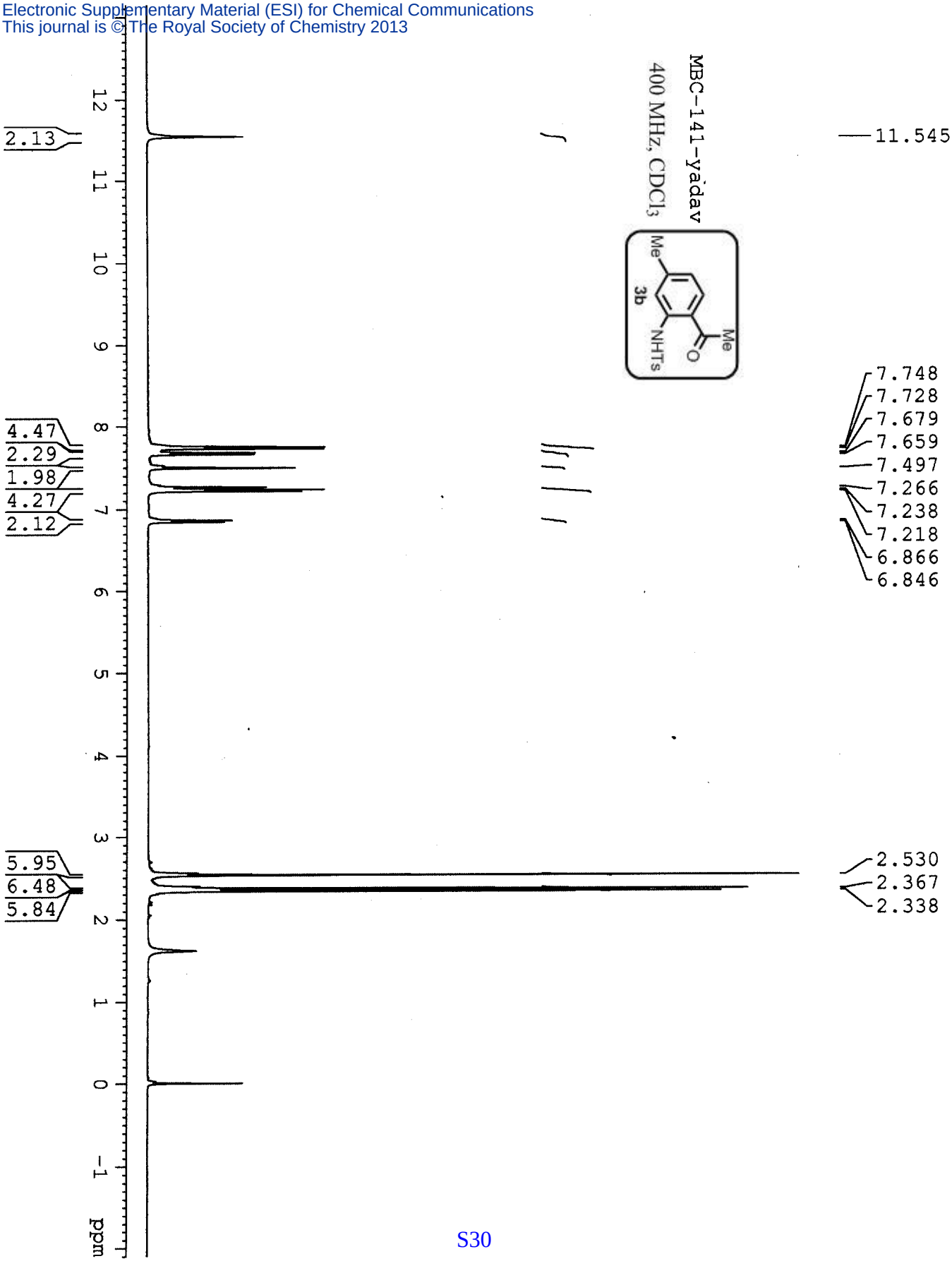
Table 1. crystal data for 4a.

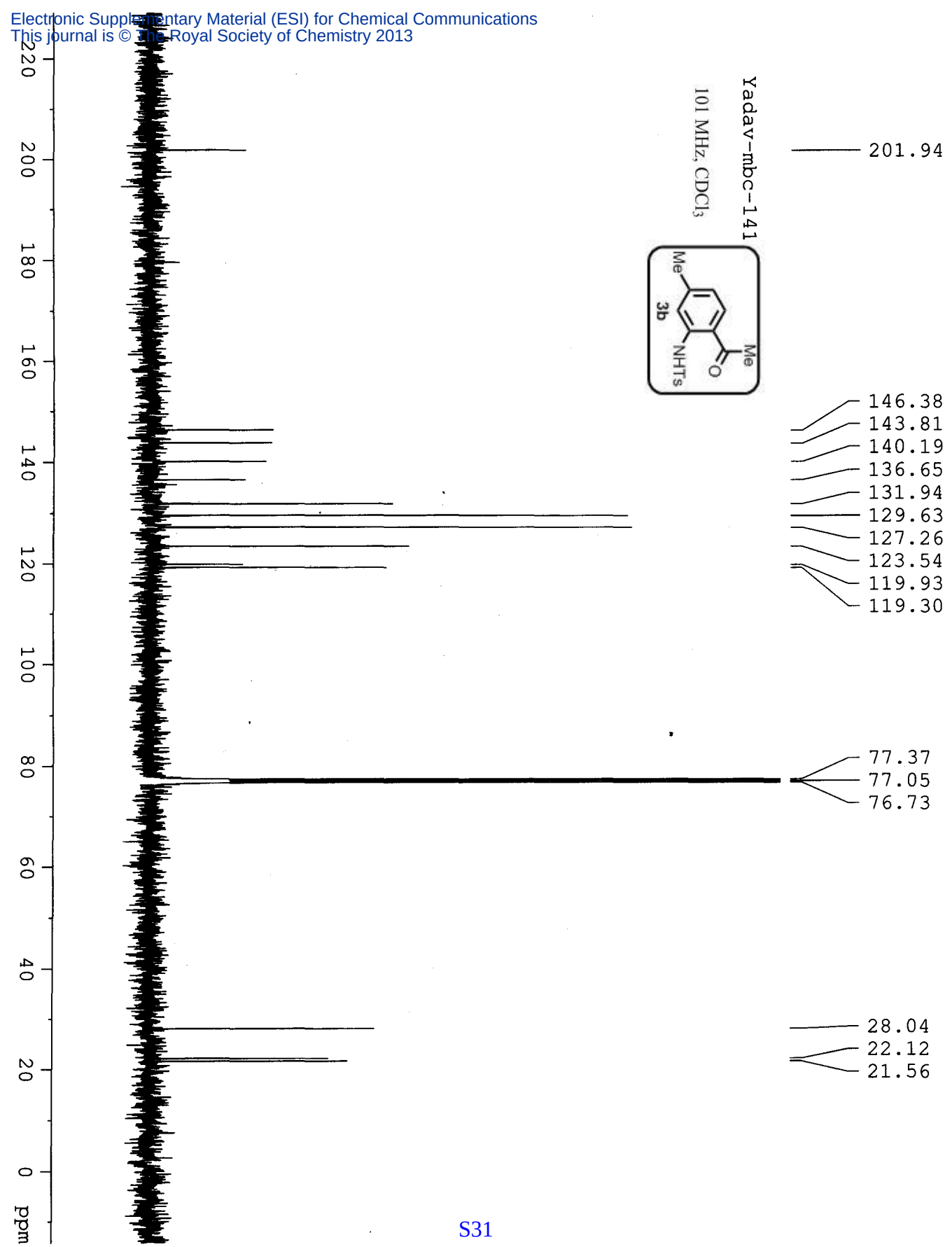
Compound	**4a**
formula	$C_{14}H_{12}N_2O_5S$
M_w	320.33
Crystal system	Triclinic
Space group	P_1^-
T [K]	293(2)
a [Å]	7.7099(16)
b [Å]	8.2501(17)
c [Å]	11.659(2)
α [°]	99.961(3)
β [°]	101.130(3)
γ [°]	92.491(3)
Z	2
V [Å^3]	714.4(2)
D_{calc} [g cm^{-3}]	1.489
μ [mm^{-1}]	0.253
total reflns	2777
unique reflns	2750
Observed reflns	2750
R_1 [$I > 2\sigma(I)$]	0.0424
wR_2 [all]	0.1146
GOF	1.053
Diffractometer	SHELXL-97

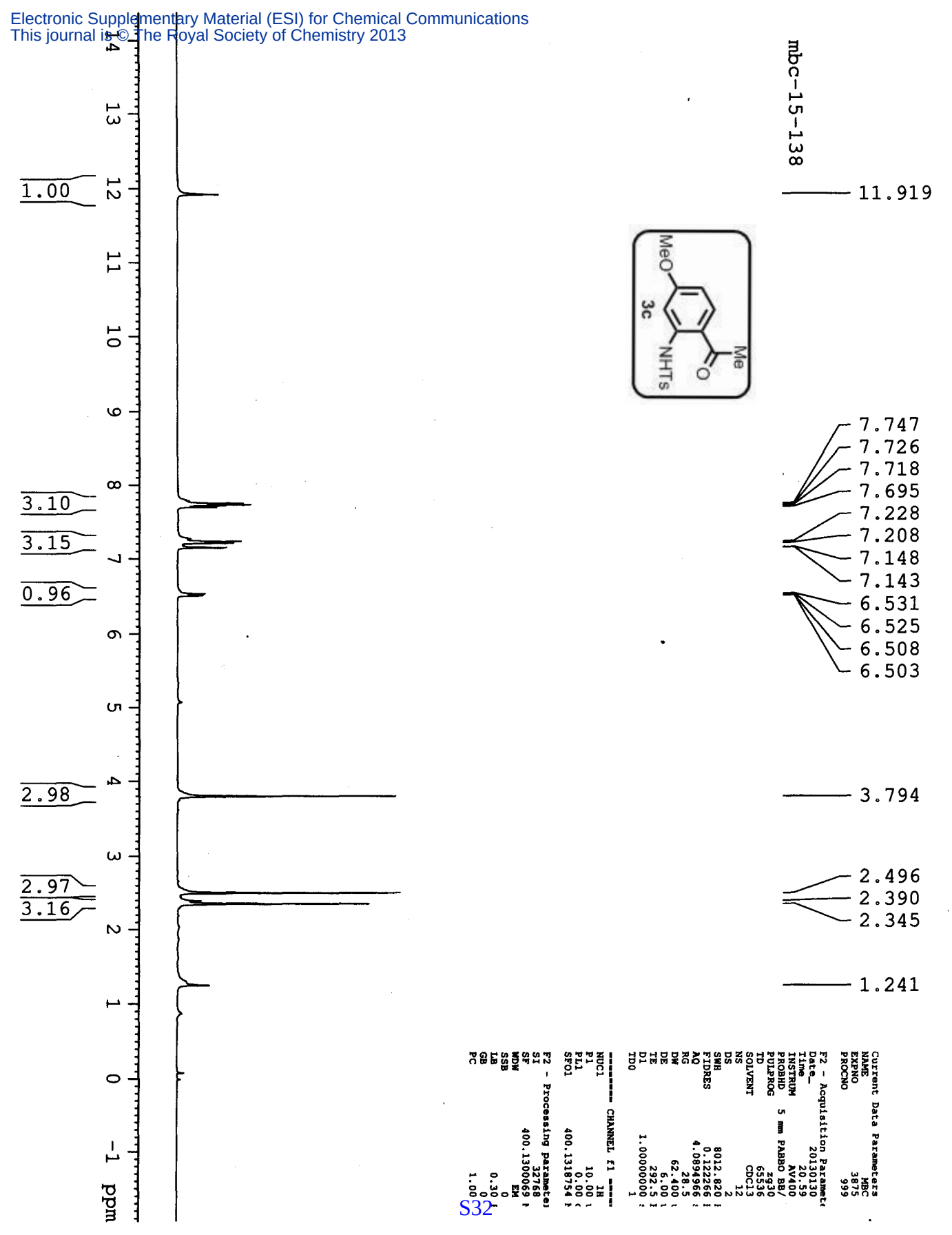
References:

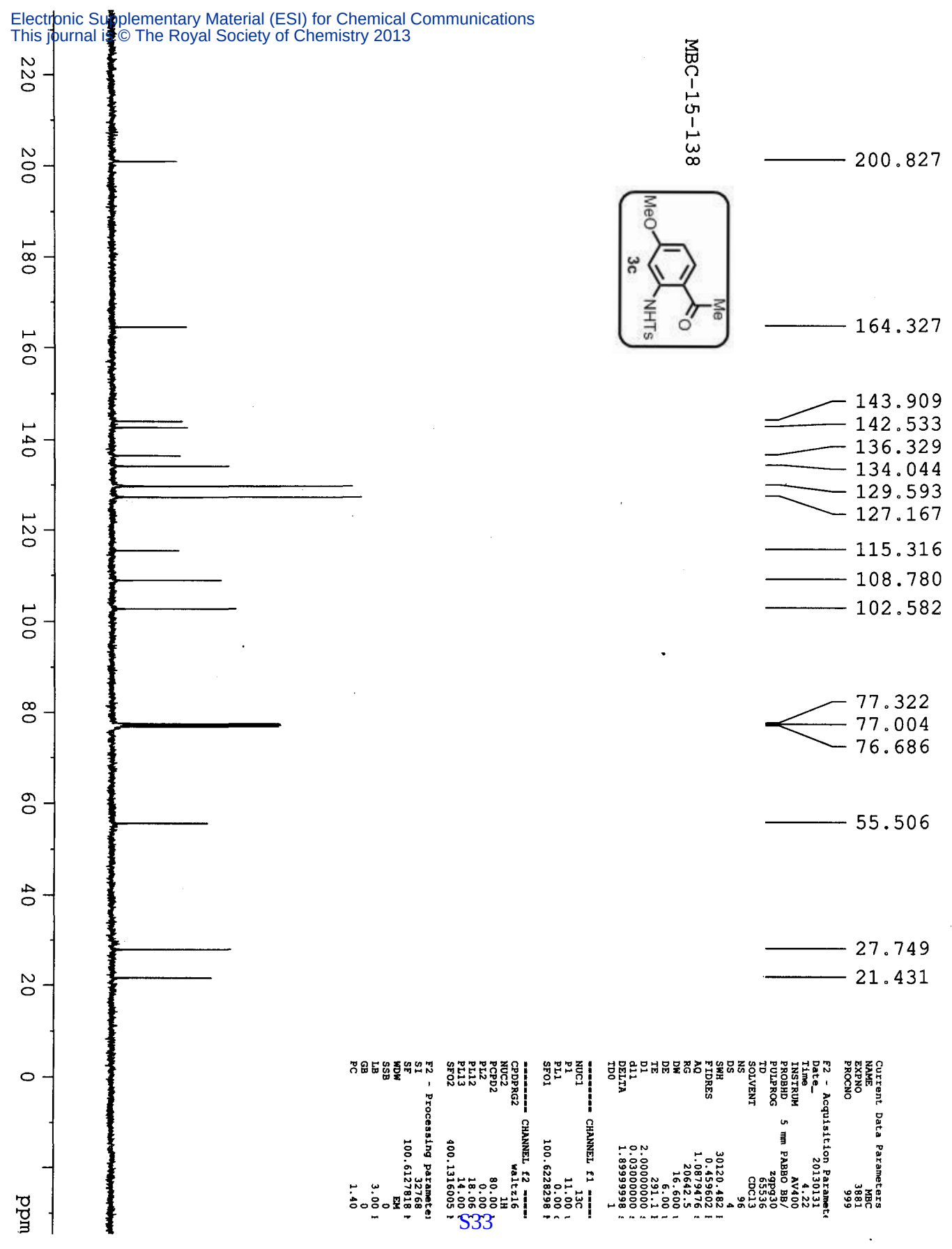
1. Bruker SMART V5.630 and SAINT-PLUS V6.45, Bruker-Nonius Analytical X-ray Systems Inc.:Madison, Wisconsin, USA 2003. SADABS, Empirical absorption correction program, Bruker AXS Inc., Madison, Wisconsin, USA 1997.

2. Sheldrick G M, *Acta Crystallogr* 64A (2008) 112.





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O
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136.329
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77.004
76.686
55.506
27.749
21.431
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40
20
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ppm
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EXPNO 3881
PROCNO 999
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FIDRES 0.459602 Hz
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RG 20642.5
DW 16.600 usec
DE 6.00 usec
TE 291.1 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
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P1 11.00 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
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PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.06 dB
PL13 14.00 dB
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SF 100.6127818 MHz
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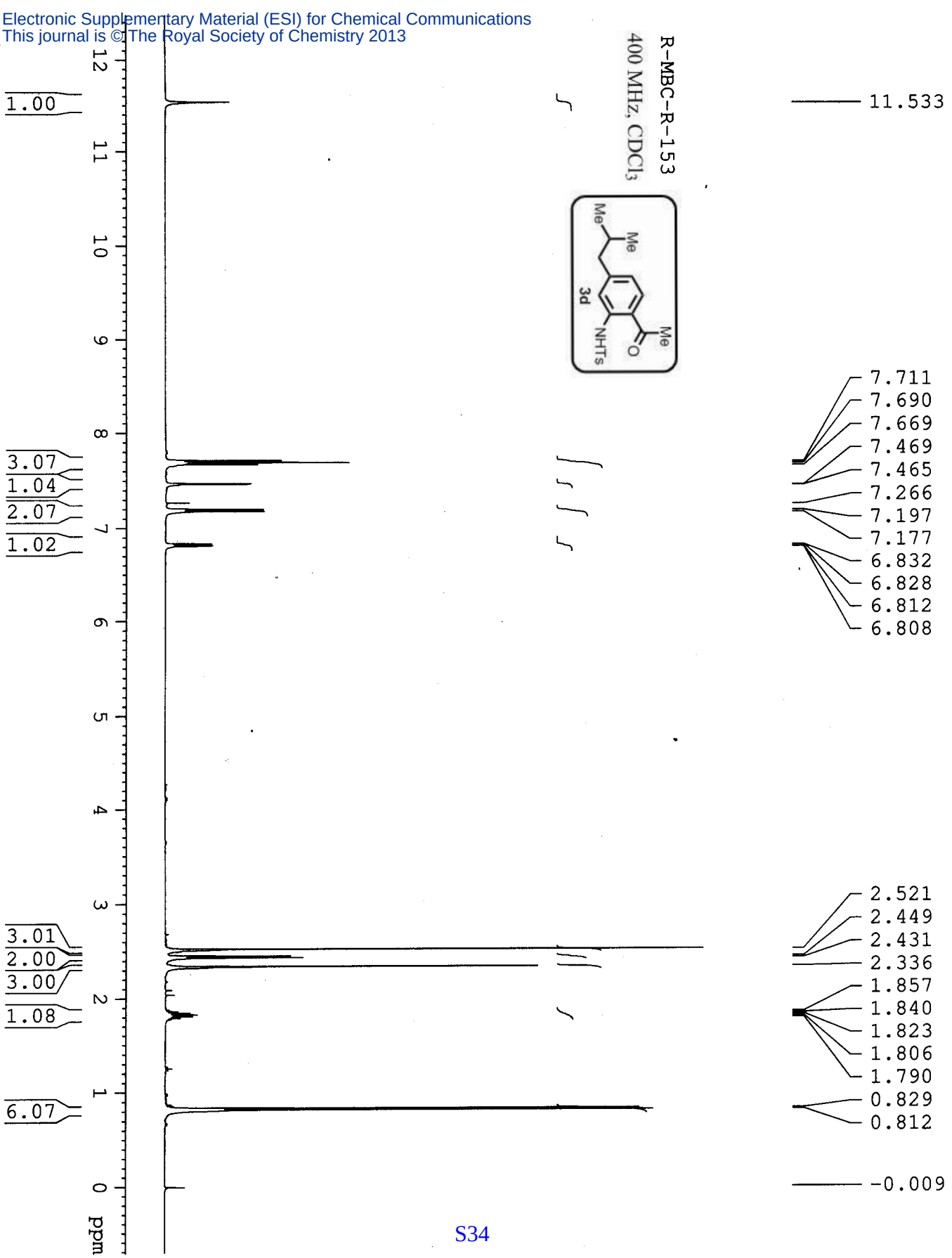
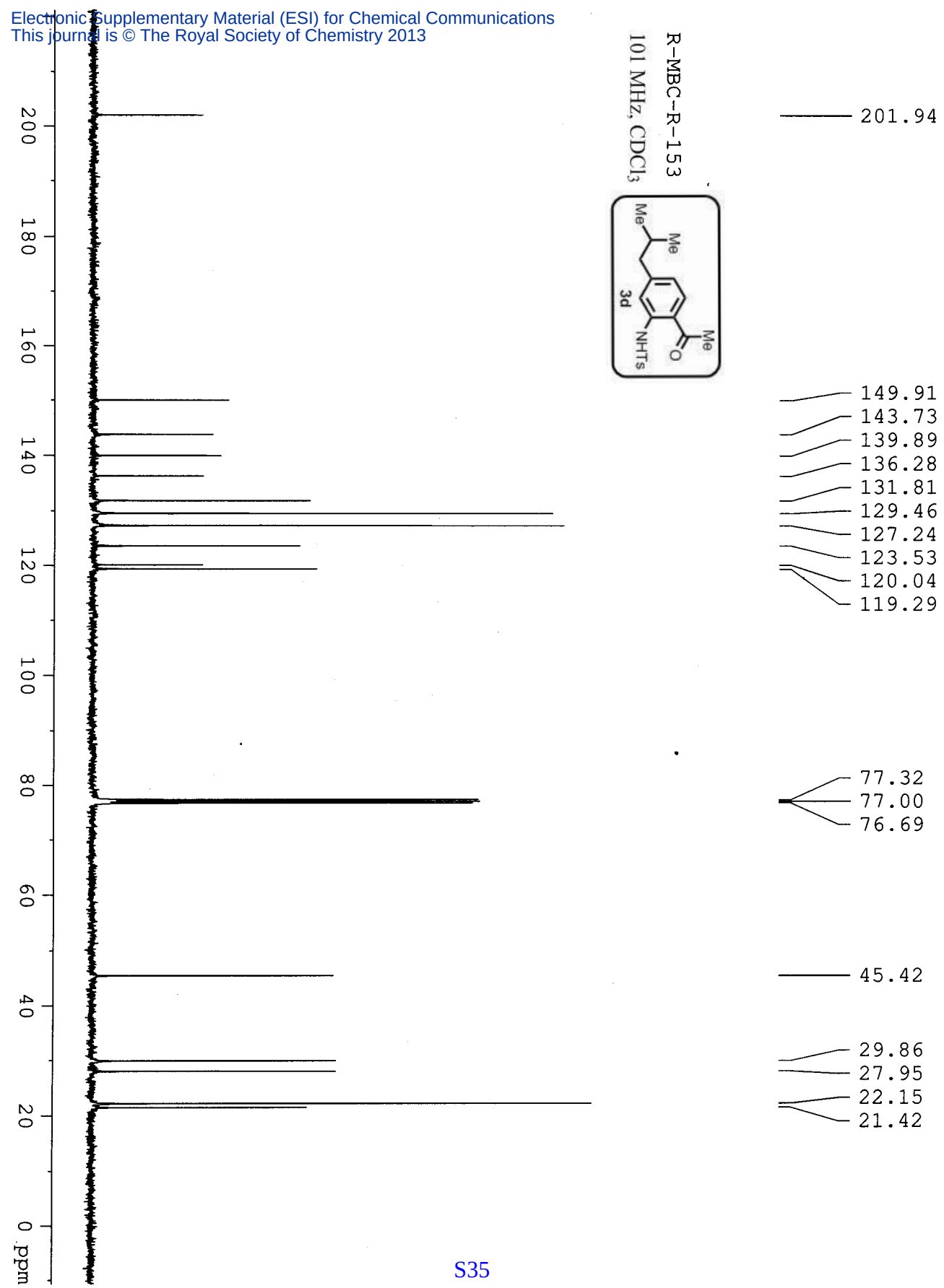
PC 1.40

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3d
NHTs
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O
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143.73
139.89
136.28
131.81
129.46
127.24
123.53
120.04
119.29
77.32
77.00
76.69
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29.86
27.95
22.15
21.42
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140
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60
40
20
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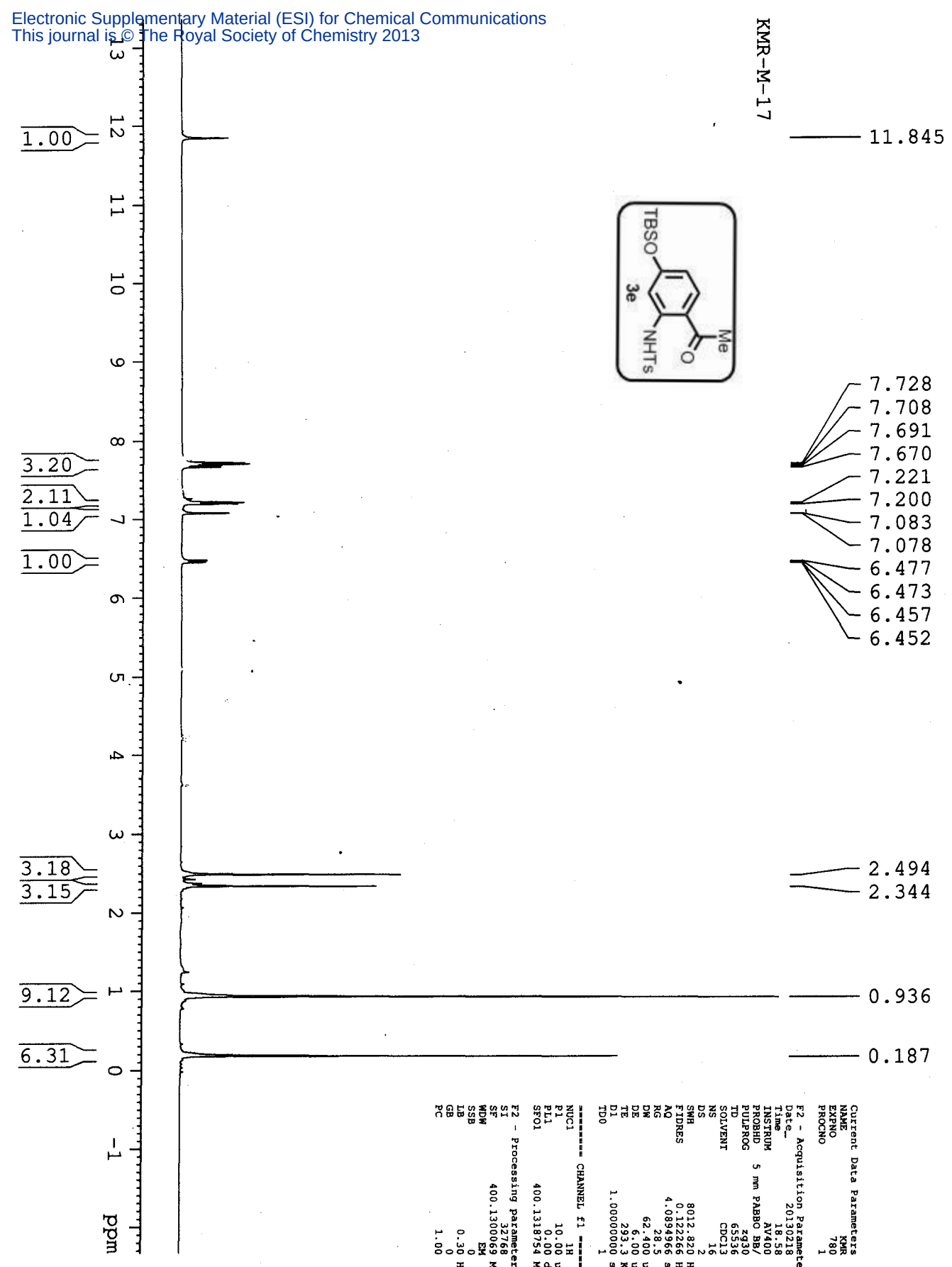
ppm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TBSO
3e
NHTs
Me
O
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7.728
7.708
7.691
7.670
7.221
7.200
7.083
7.078
6.477
6.473
6.457
6.452
2.494
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0.187
1.00
3.20
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6.31
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PULPROG zg30
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SOLVENT CDCl3
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FIDRES 0.122266 Hz
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RG 28.5
DW 62.400 use
DE 6.00 use
TE 293.3 K
D1 1.00000000 sec
TD0 1
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WDW EM
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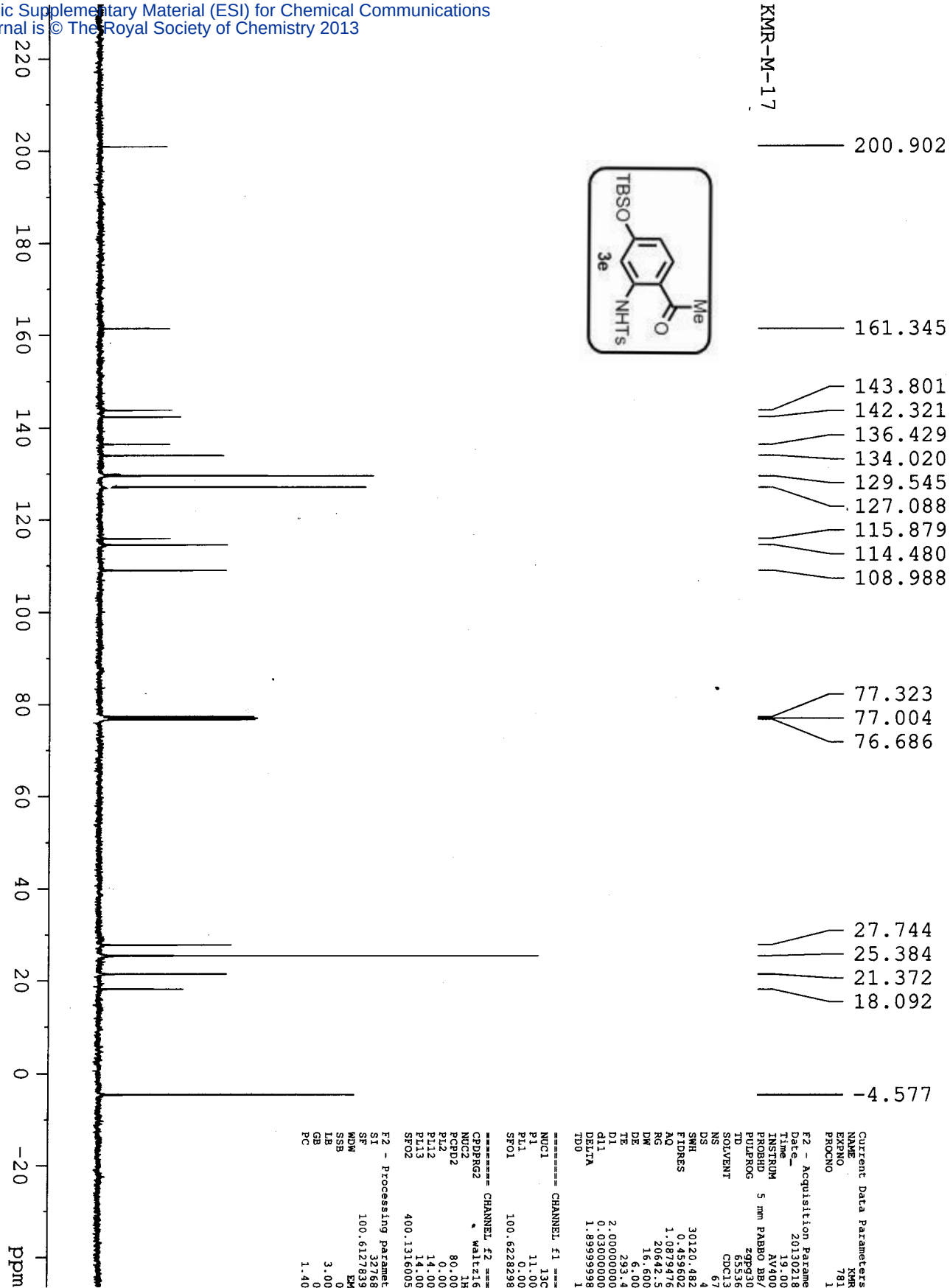
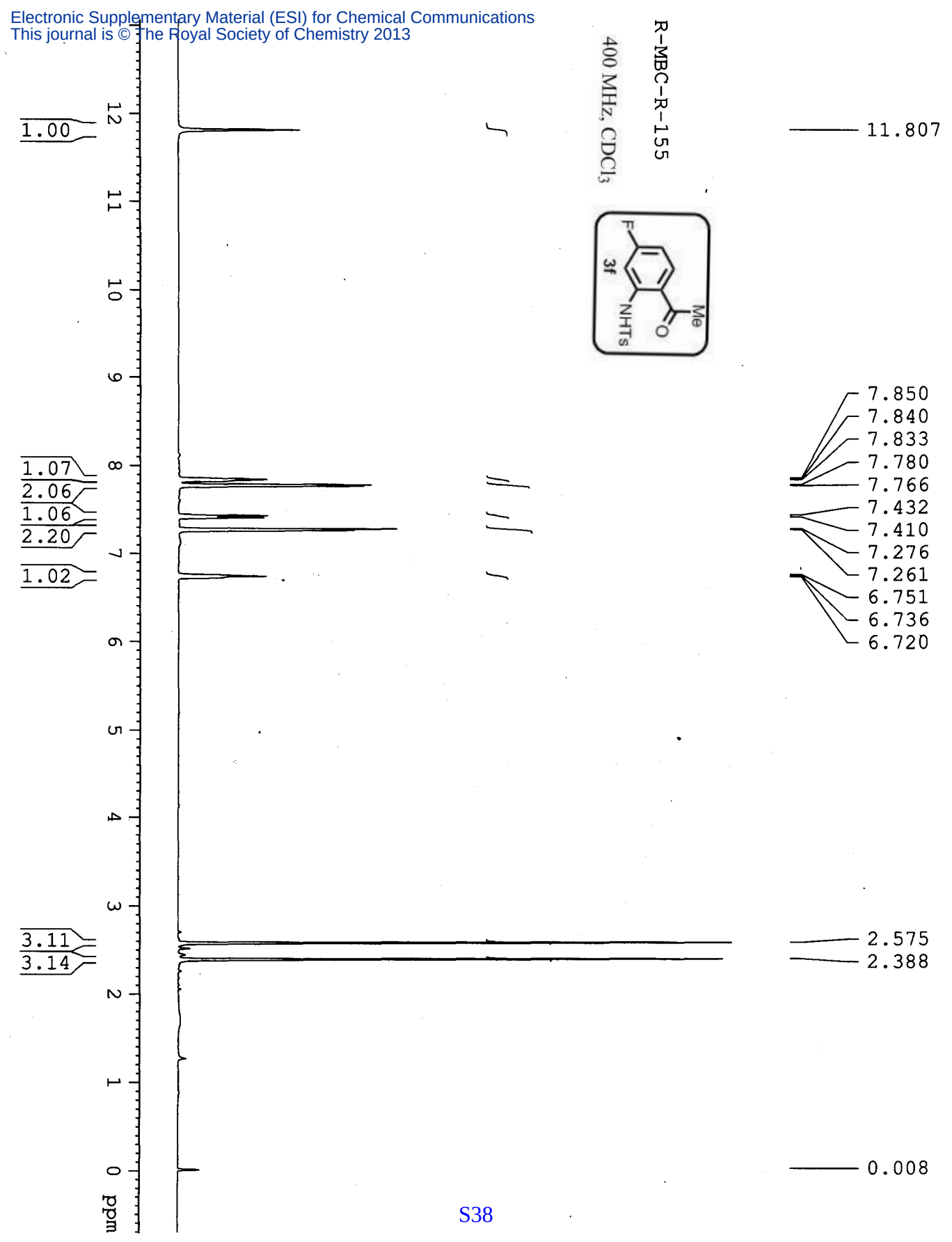
PC 1.00

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NHTs
Me
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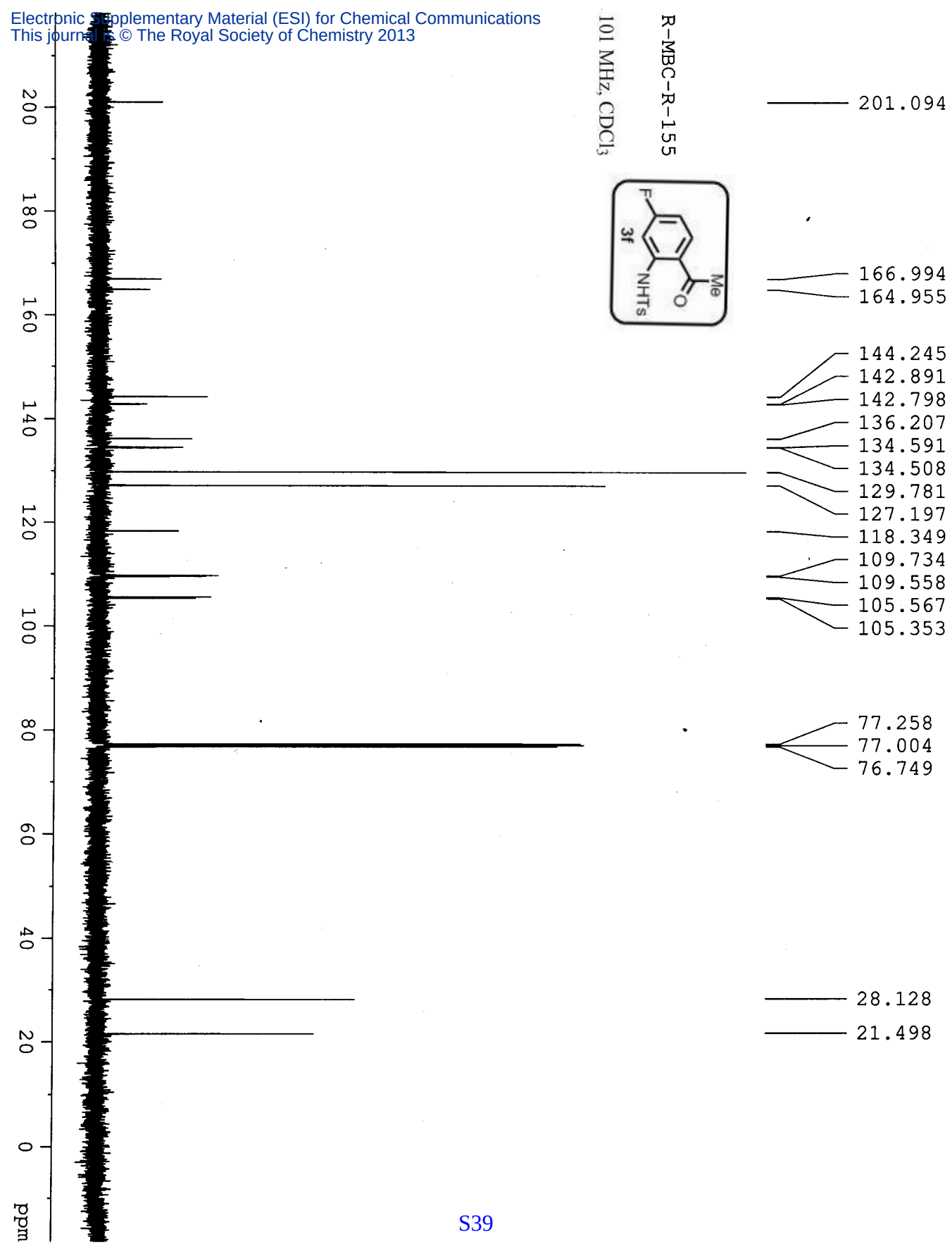
1.07
2.06
1.06
2.20
1.02
3.11
3.14
11.807
7.850
7.840
7.833
7.780
7.766
7.432
7.410
7.276
7.261
6.751
6.736
6.720
2.575
2.388
0.008
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


101 MHz, CDCl3
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NHTs
Me
O
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142.798
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134.591
134.508
129.781
127.197
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109.734
109.558
105.567
105.353
77.258
77.004
76.749
28.128
21.498
200
180
160
140
120
100
80
60
40
20
0
ppm

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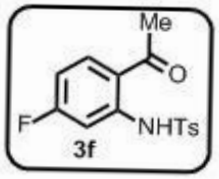
R-MBC-R-155

376 MHz, $CDCl_3$



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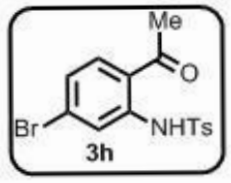
MBC-15-159



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7.627
7.256
7.236
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7.163
7.146
7.144
7.142

2.539
2.365

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RG	28.5
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TE	292.5 K
D1	1.00000000 sec
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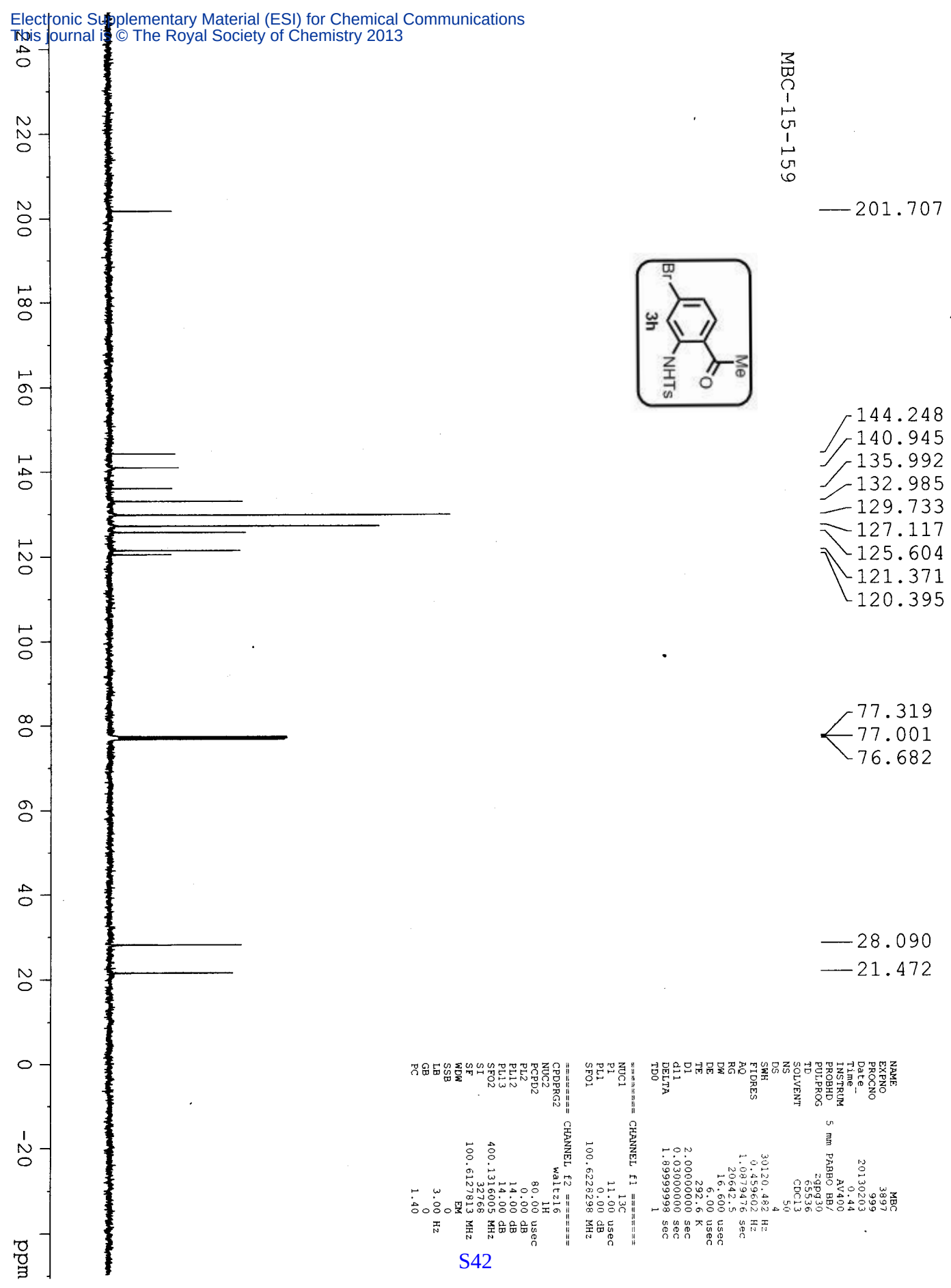


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d11                           0.03000000 sec
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TD0                                   1

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PL1                                0.00 dB
SFO1                     100.6228298 MHz

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PCPD2                             80.00 usec
PL2                                0.00 dB
PL12                              14.00 dB
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SF                       100.6127813 MHz
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GB                                    0
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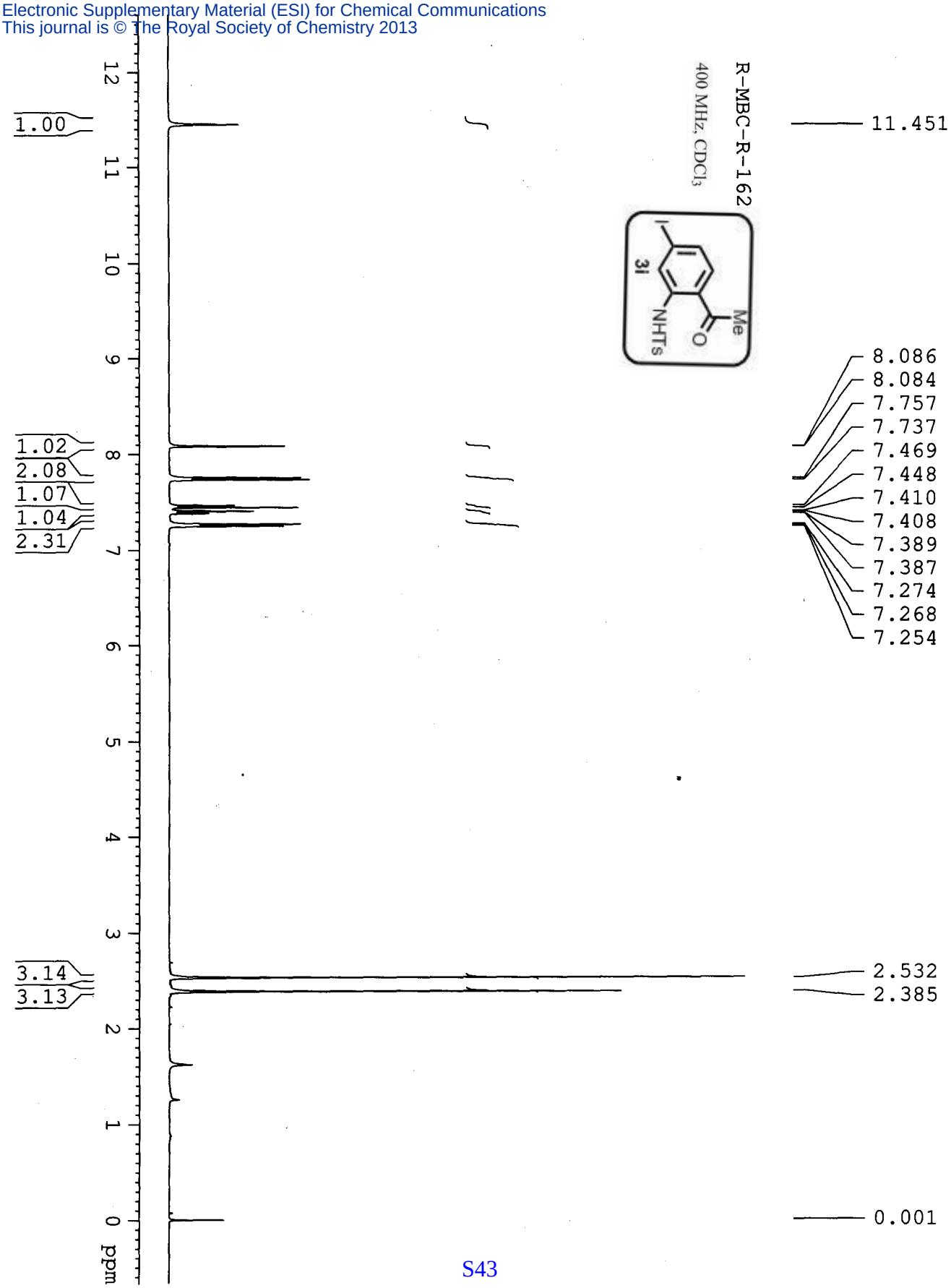
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7.410
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7.268
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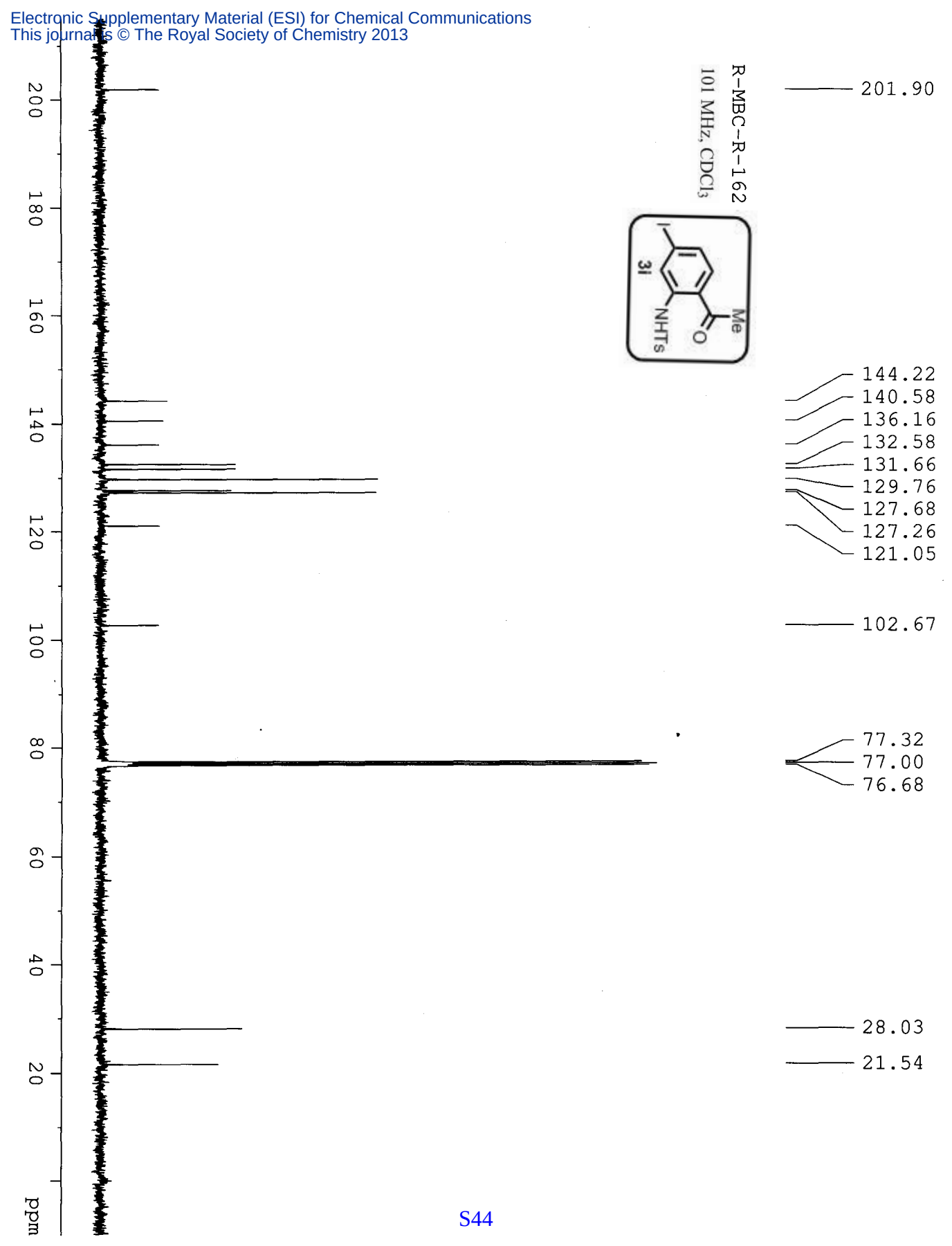

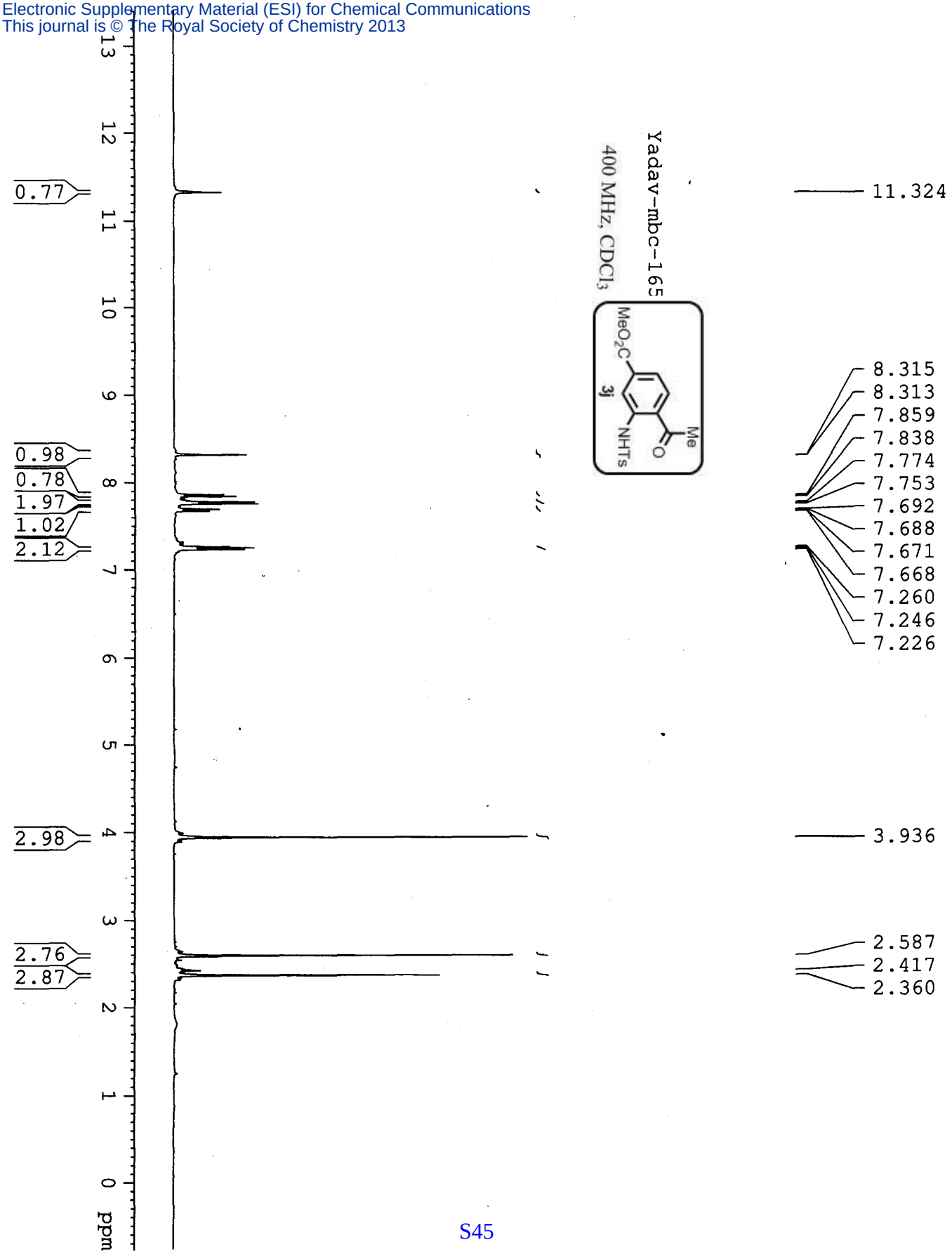

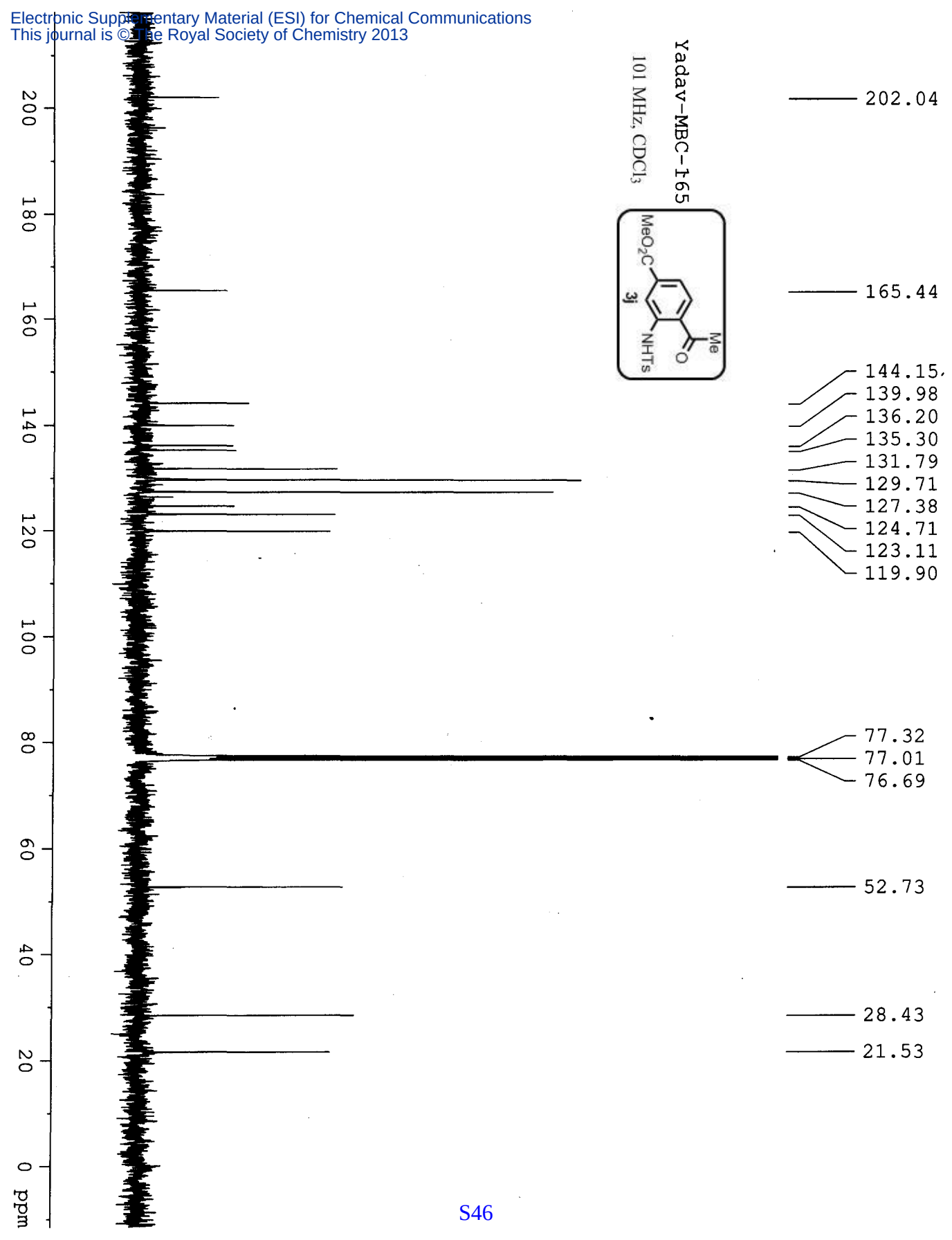
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135.30
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129.71
127.38
124.71
123.11
119.90
77.32
77.01
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200
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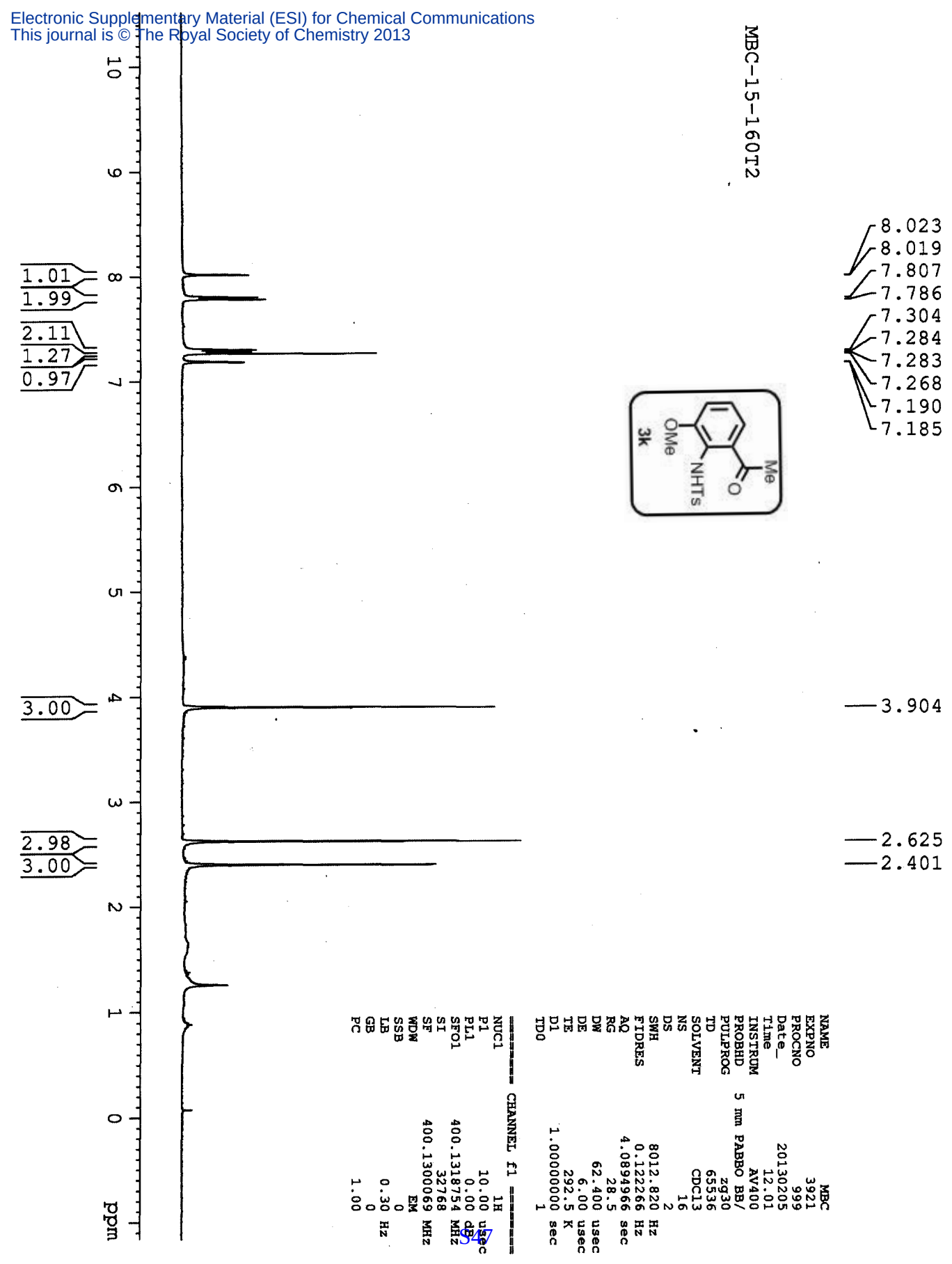
160
140
120
100
80
60
40
20
0
ppm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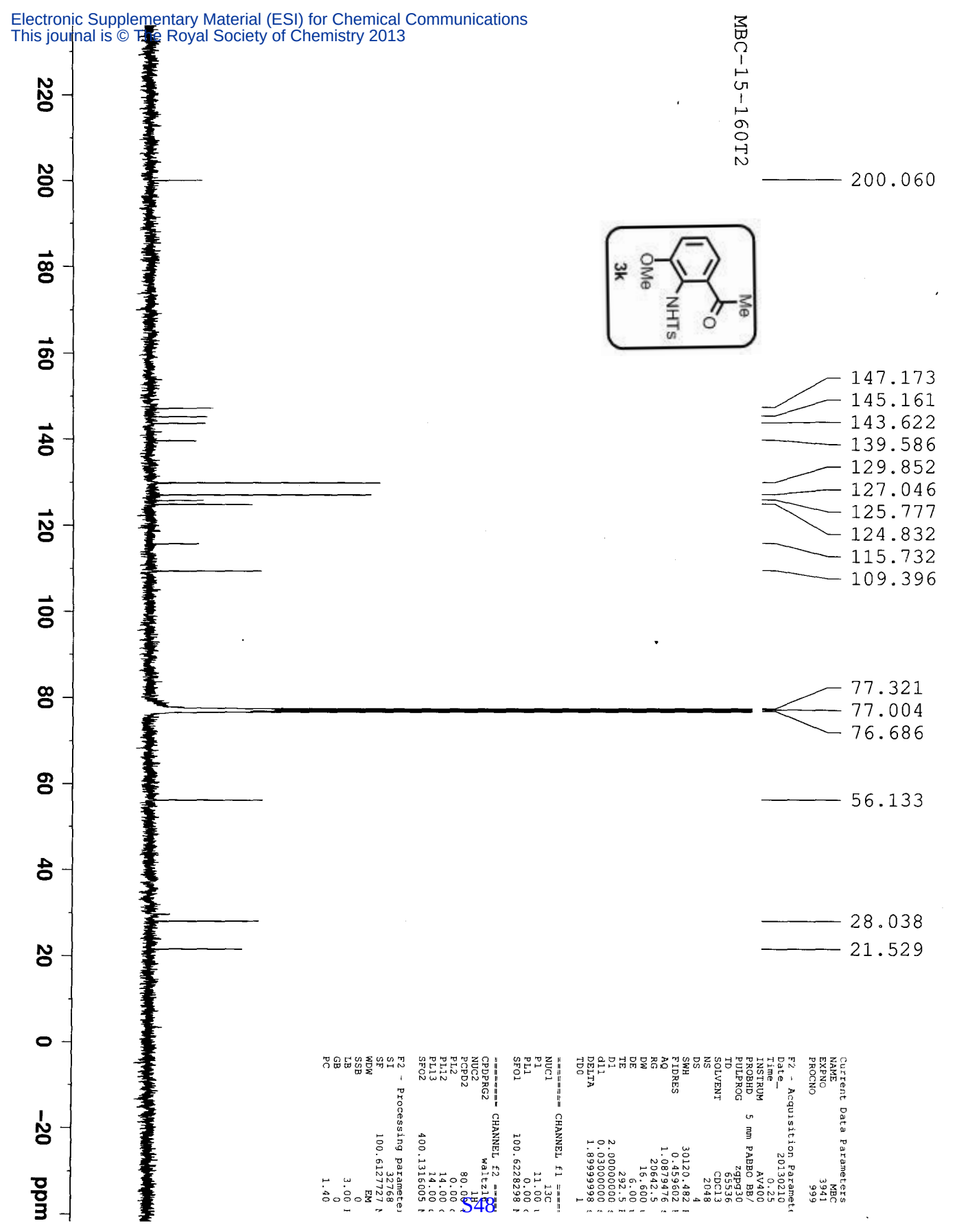
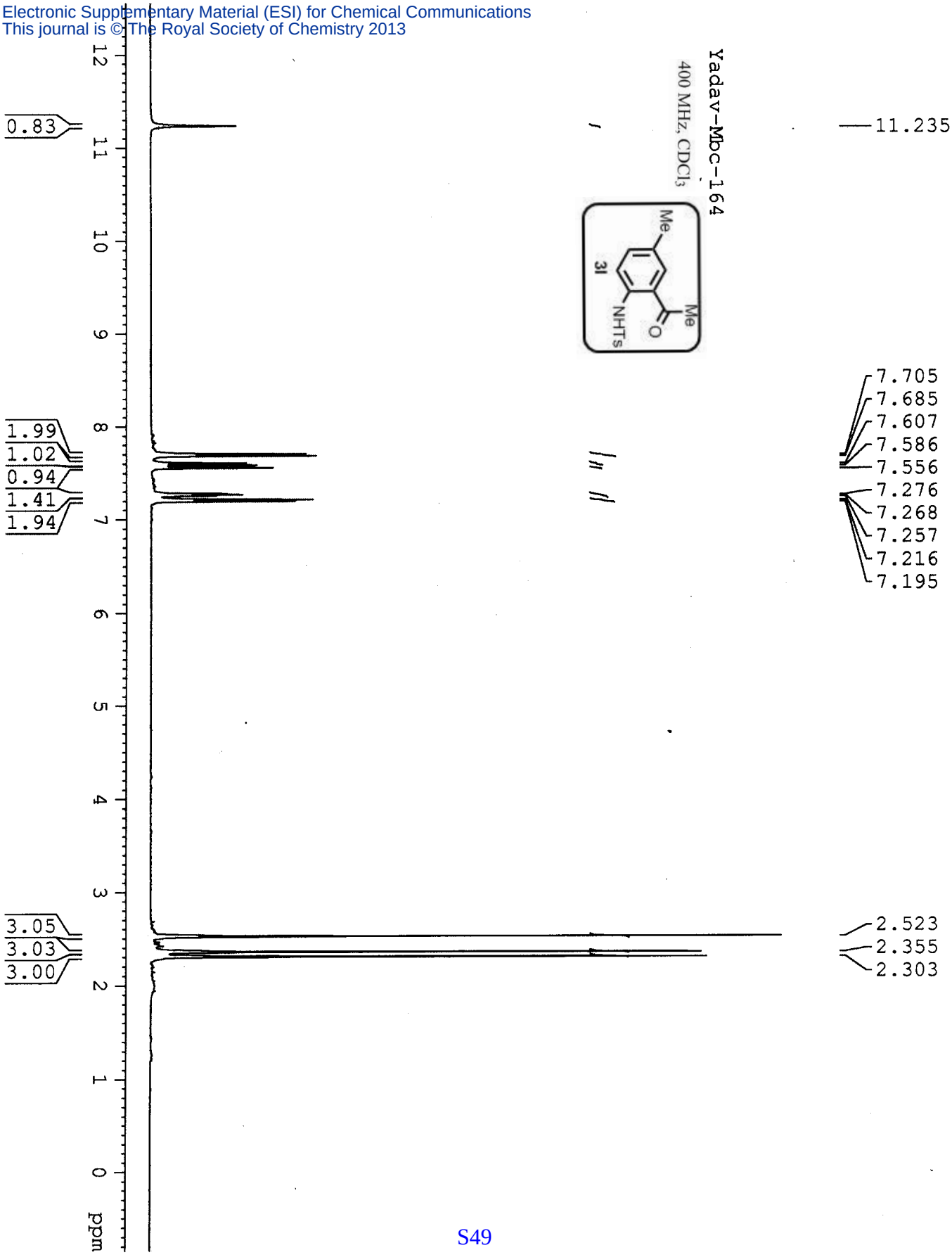
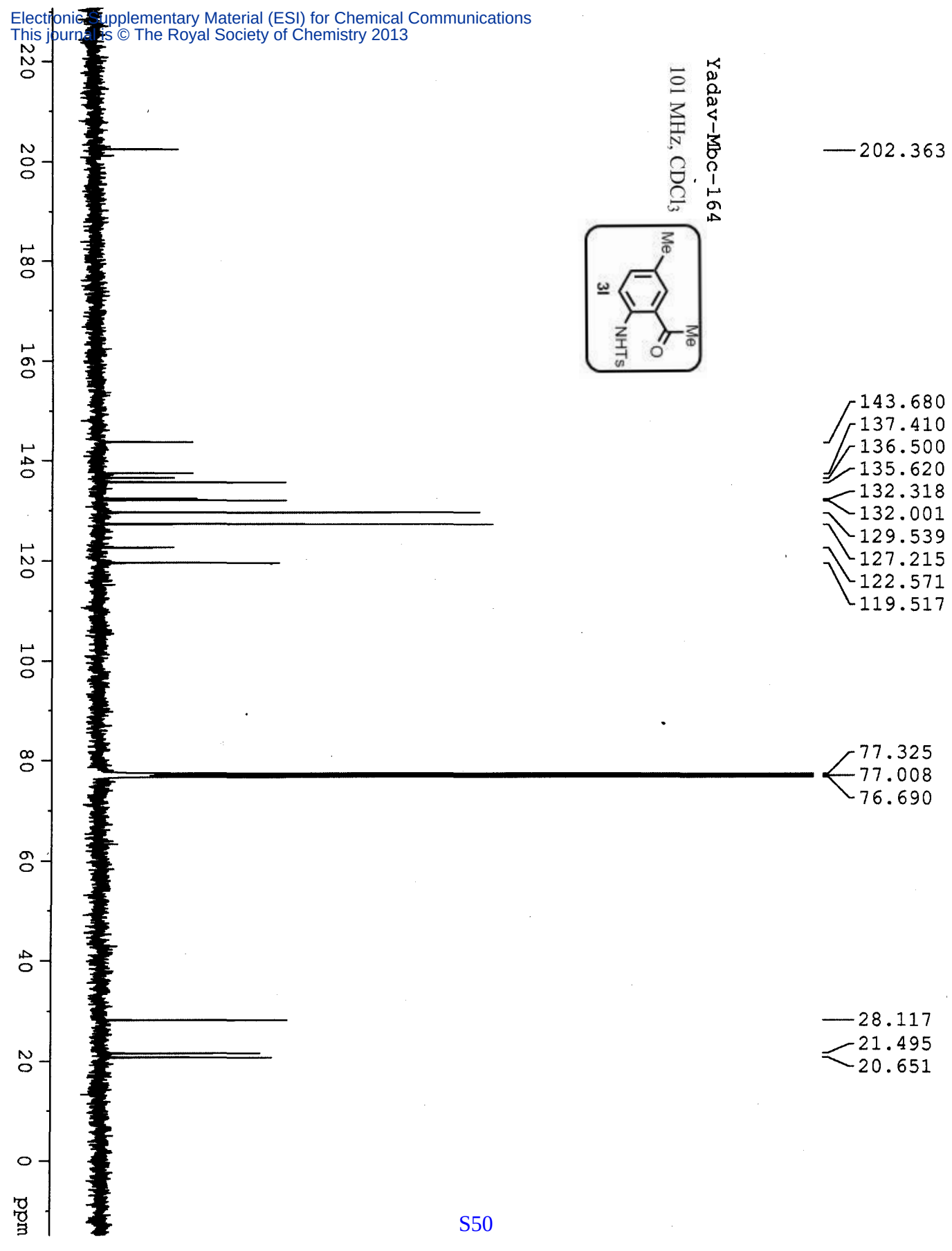
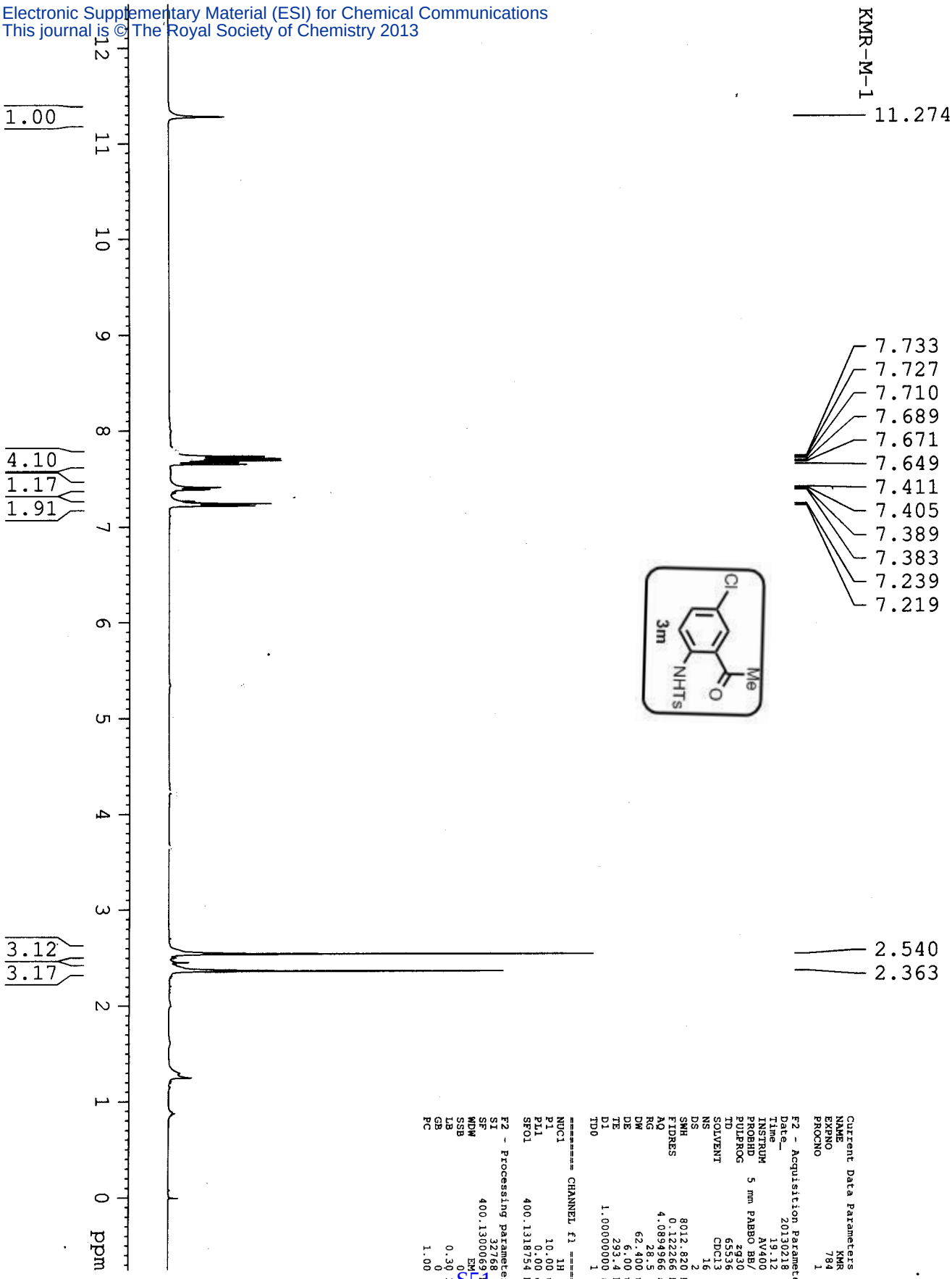
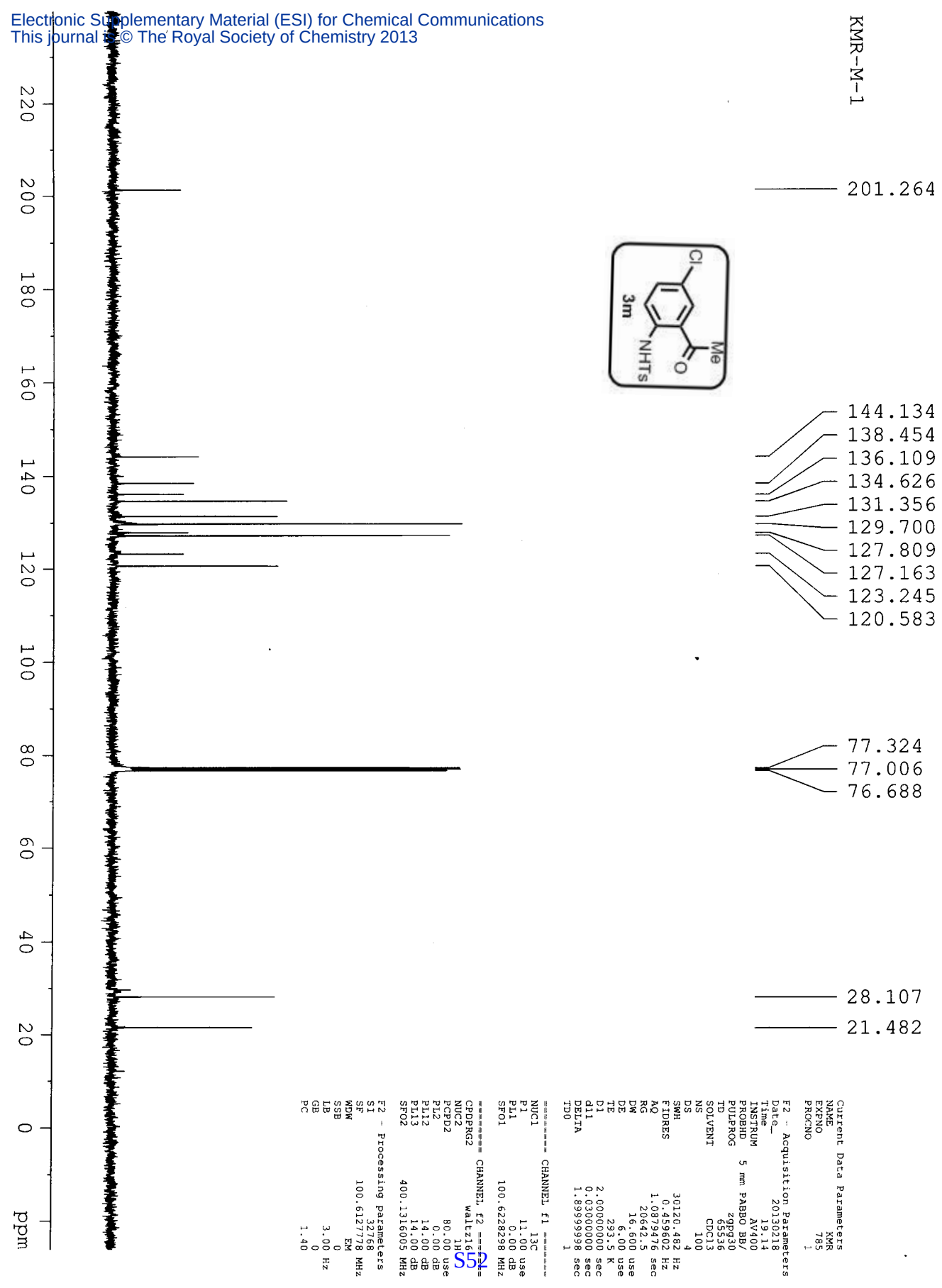
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
SFO1 400.1318754 MHz
SI 32768
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

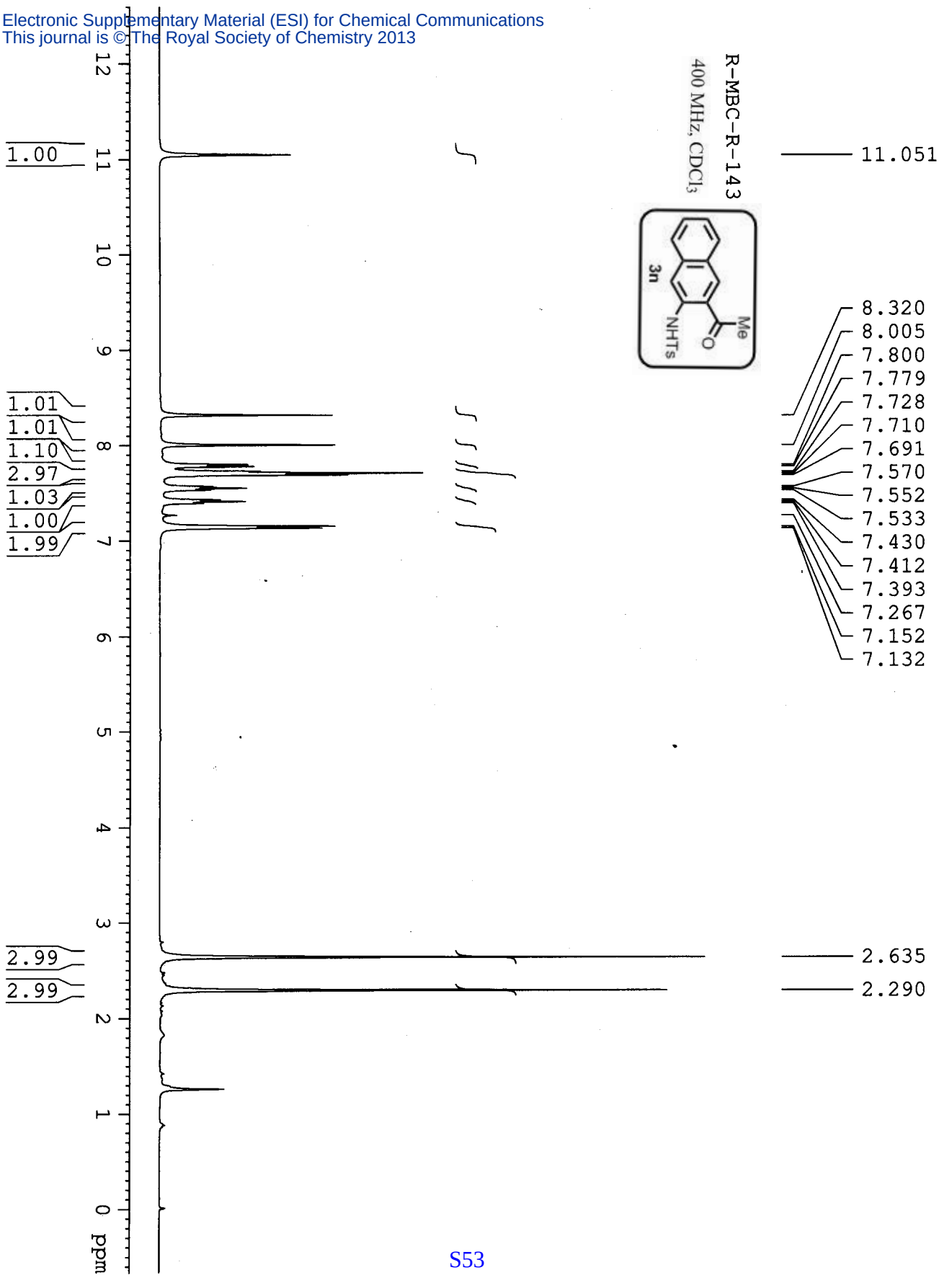

MBC-15-160T2
200.060
147.173
145.161
143.622
139.586
129.852
127.046
125.777
124.832
115.732
109.396
77.321
77.004
76.686
56.133
28.038
21.529
Me
O
NHTs
OMe
3k
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
Current Data Parameters
NAME MBC
EXPNO 3941
PROCNO 999
F2 - Acquisition Parameters
Date_ 20130210
Time_ 0.25
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 30120.482 H
FIDRES 0.459602 H
AQ 1.0879476 s
RG 20642.5
DW 16.600 u
DE 6.00 u
TE 292.5 K
D1 2.00000000 s
D11 0.03000000 s
DELTA 1.89999998 s
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 u
PL1 0.00 d
SFO1 100.6228298 M
======== CHANNEL f2 ========
CPDPRG2 waltz1
NUC2 1H
PCPD2 80.00 u
PL2 0.00 d
PL12 14.00 d
PL13 14.00 d
SFO2 400.1316005 M
F2 - Processing parameters
SI 32768
SF 100.6127727 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40

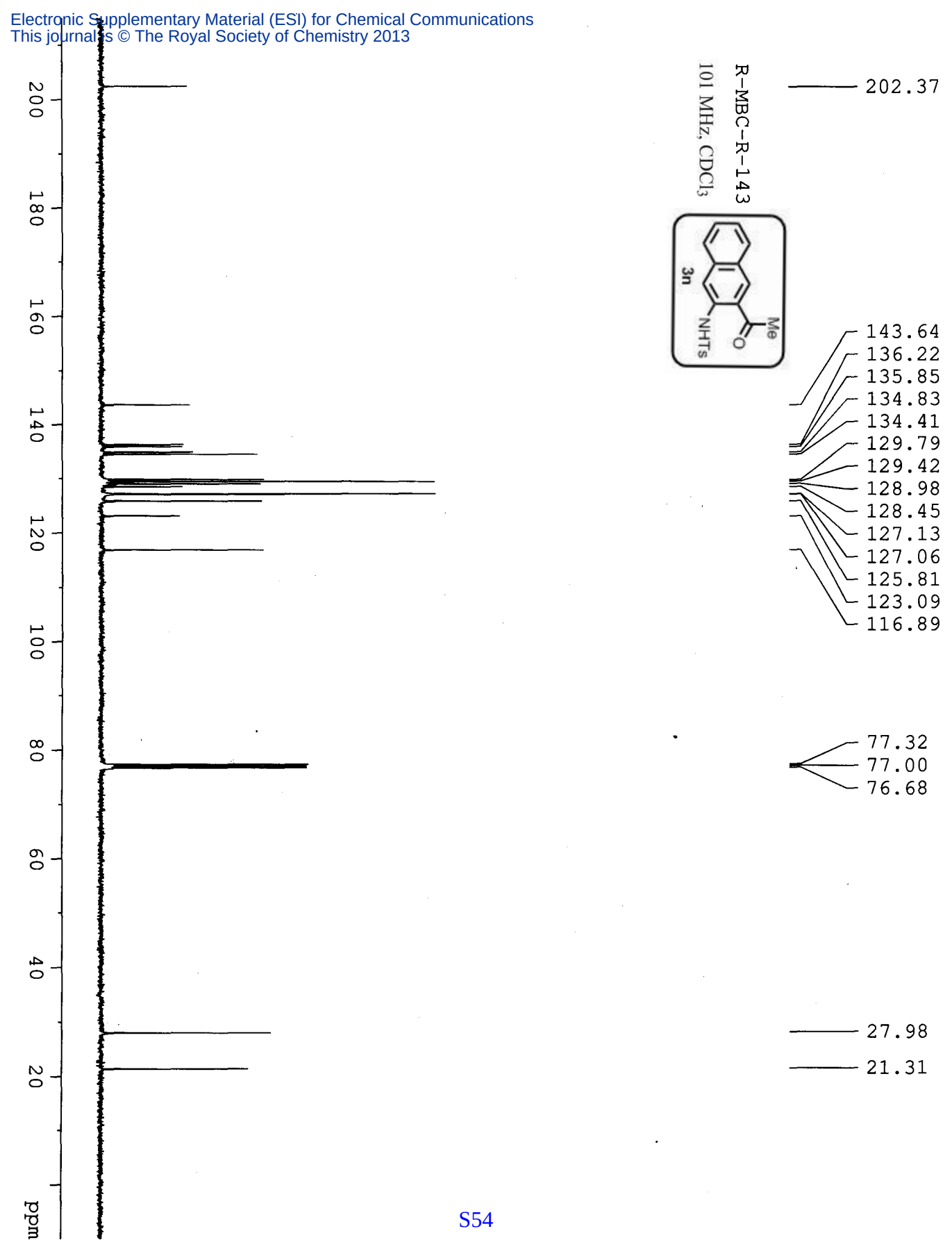

Yadav-Mbc-164
400 MHz, CDCl3
Me
Me
NHTs
O
0.83
1.99
1.02
0.94
1.41
1.94
3.05
3.03
3.00
11.235
7.705
7.685
7.607
7.586
7.556
7.276
7.268
7.257
7.216
7.195
2.523
2.355
2.303
ppm

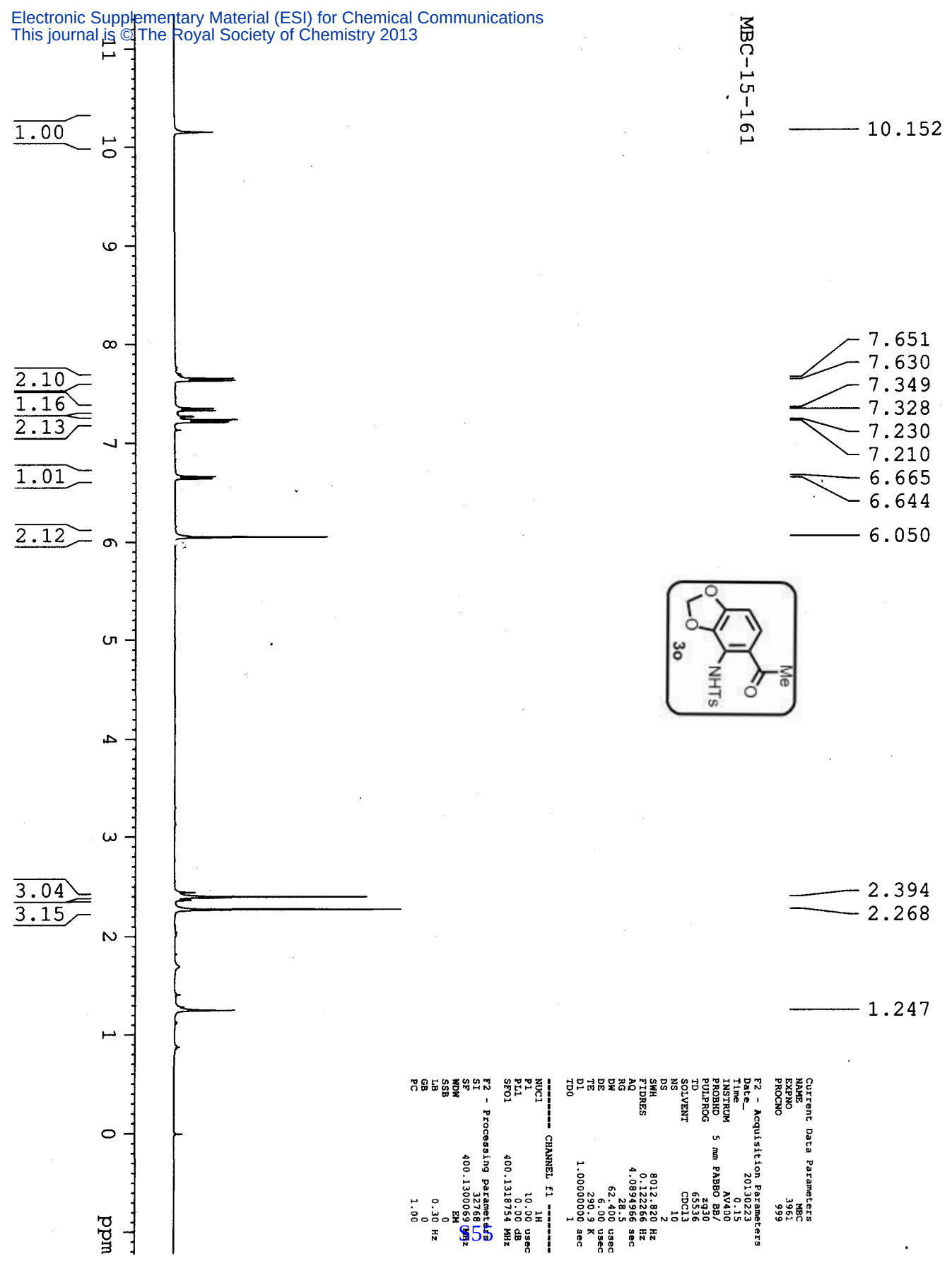


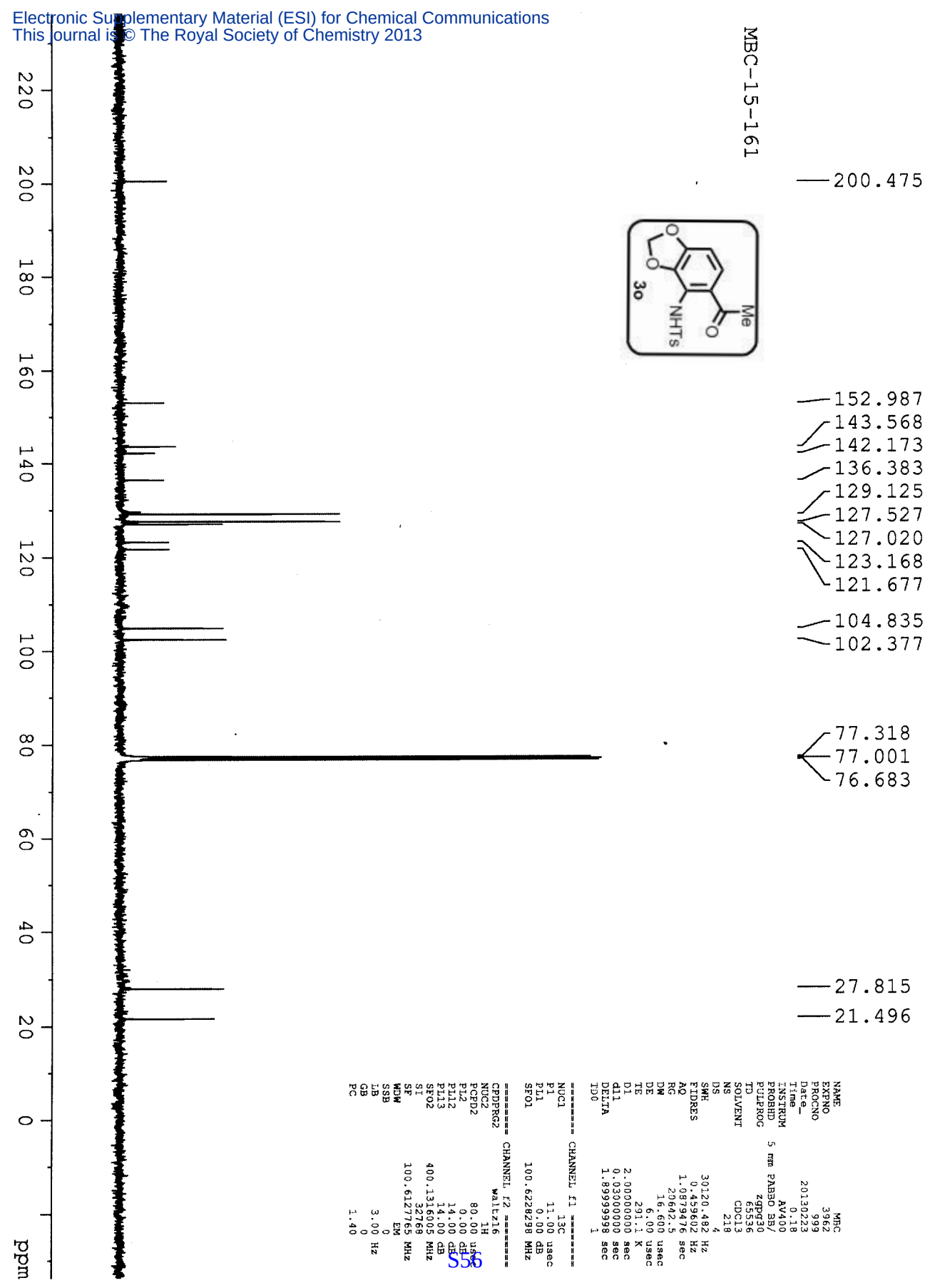

KMR-M-1
11.274
7.733
7.727
7.710
7.689
7.671
7.649
7.411
7.405
7.389
7.383
7.239
7.219
2.540
2.363
1.00
4.10
1.17
1.91
3.12
3.17
Cl
3m
NHTs
Me
O
ppm
Current Data Parameters
NAME KMR
EXPNO 784
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130218
Time 19.12
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 28.5
DW 62.400 use
DE 6.00 use
TE 293.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 use
PL1 0.00 dB
SFO1 400.1318754 MHz
F2 - Processing parameters
SI 32768
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

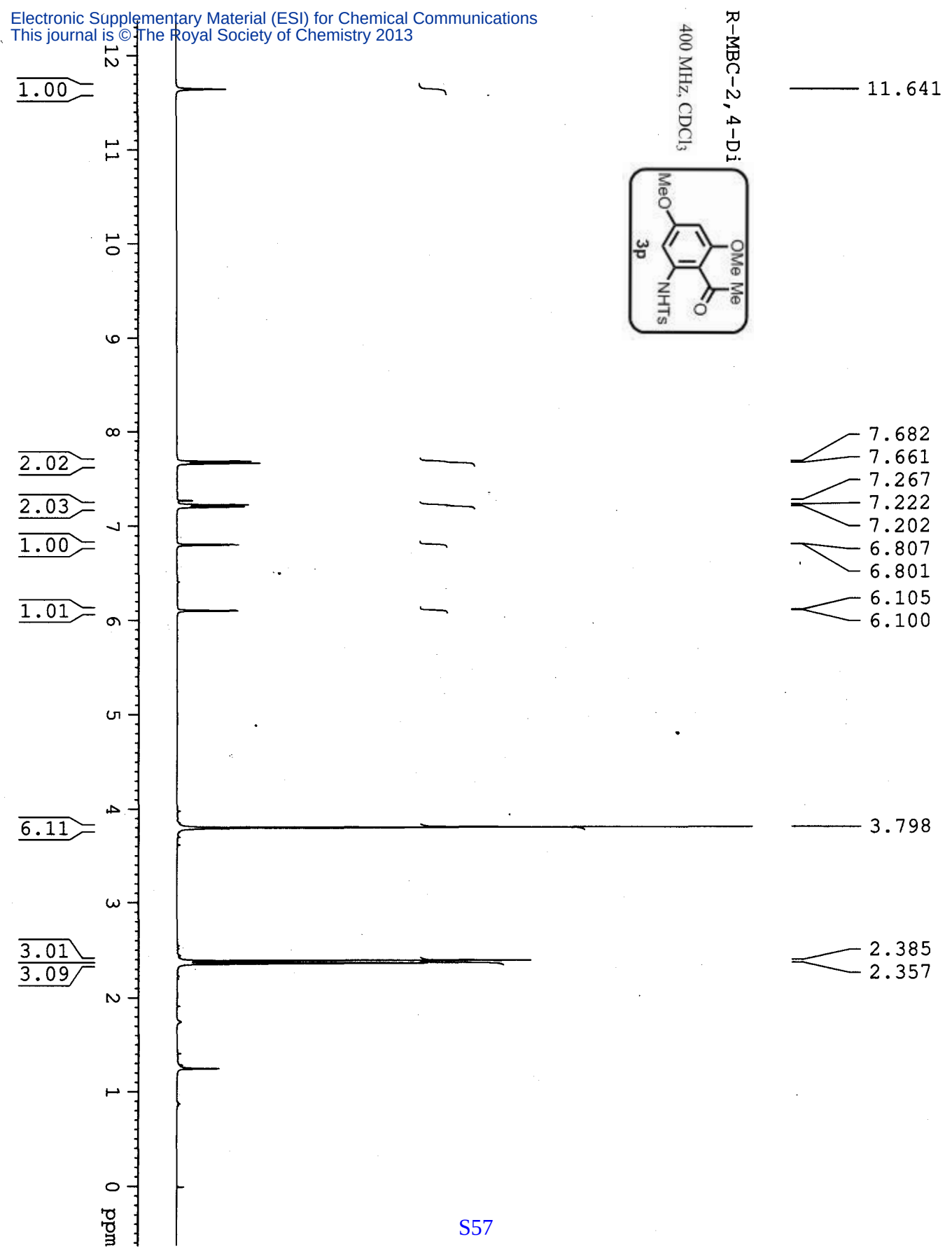

KMR-M-1
201.264
144.134
138.454
136.109
134.626
131.356
129.700
127.809
127.163
123.245
120.583
77.324
77.006
76.688
28.107
21.482
Cl
Me
O
NHTs
3m
220
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME KMR
EXPNO 785
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130218
Time 19.14
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 20642.5
DW 16.600 use
DE 6.00 use
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 use
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127778 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

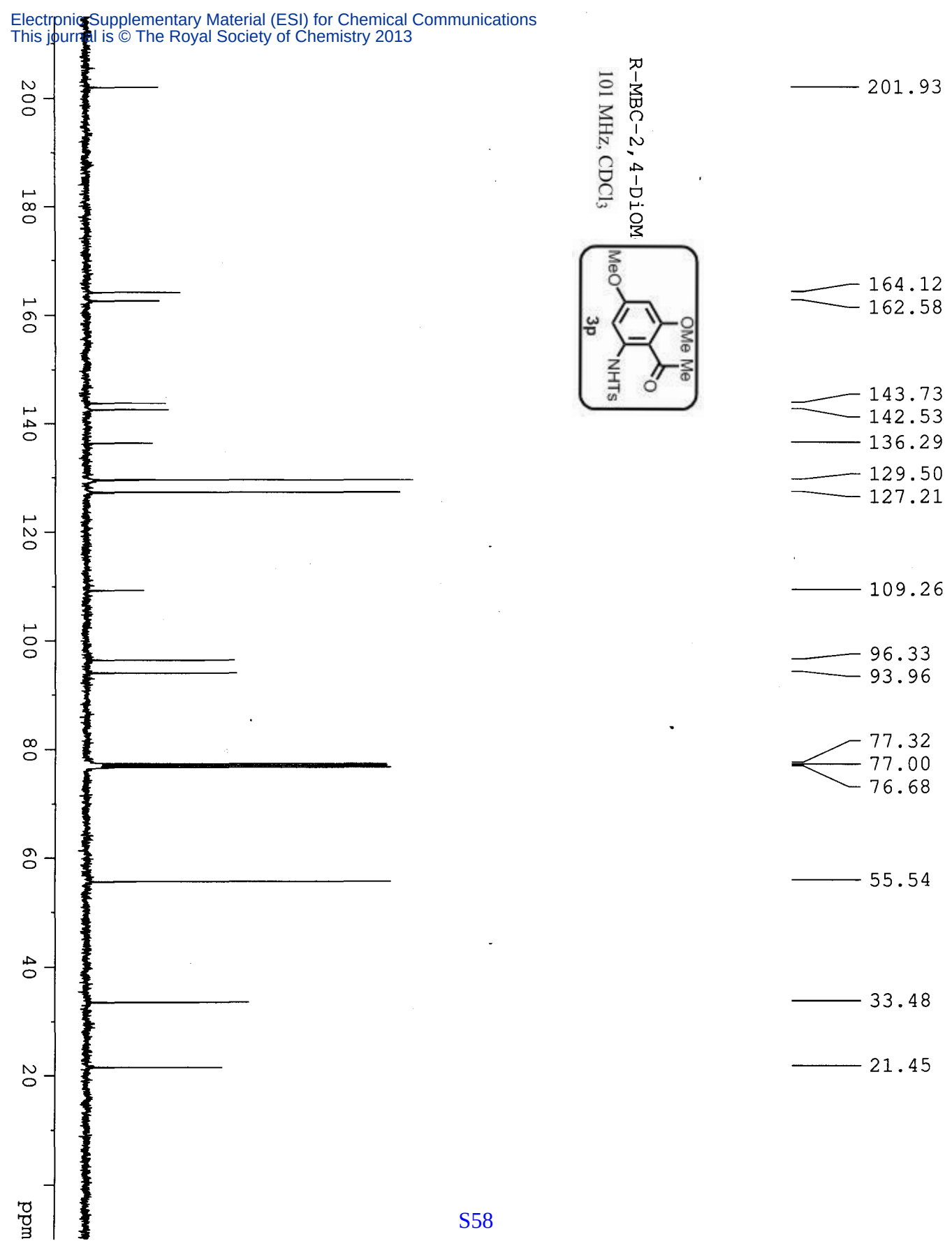

R-MBC-R-143
400 MHz, CDCl3
3n
NHTs
Me
O
11.051
8.320
8.005
7.800
7.779
7.728
7.710
7.691
7.570
7.552
7.533
7.430
7.412
7.393
7.267
7.152
7.132
2.635
2.290
1.00
1.01
1.01
1.10
2.97
1.03
1.00
1.99
2.99
2.99
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

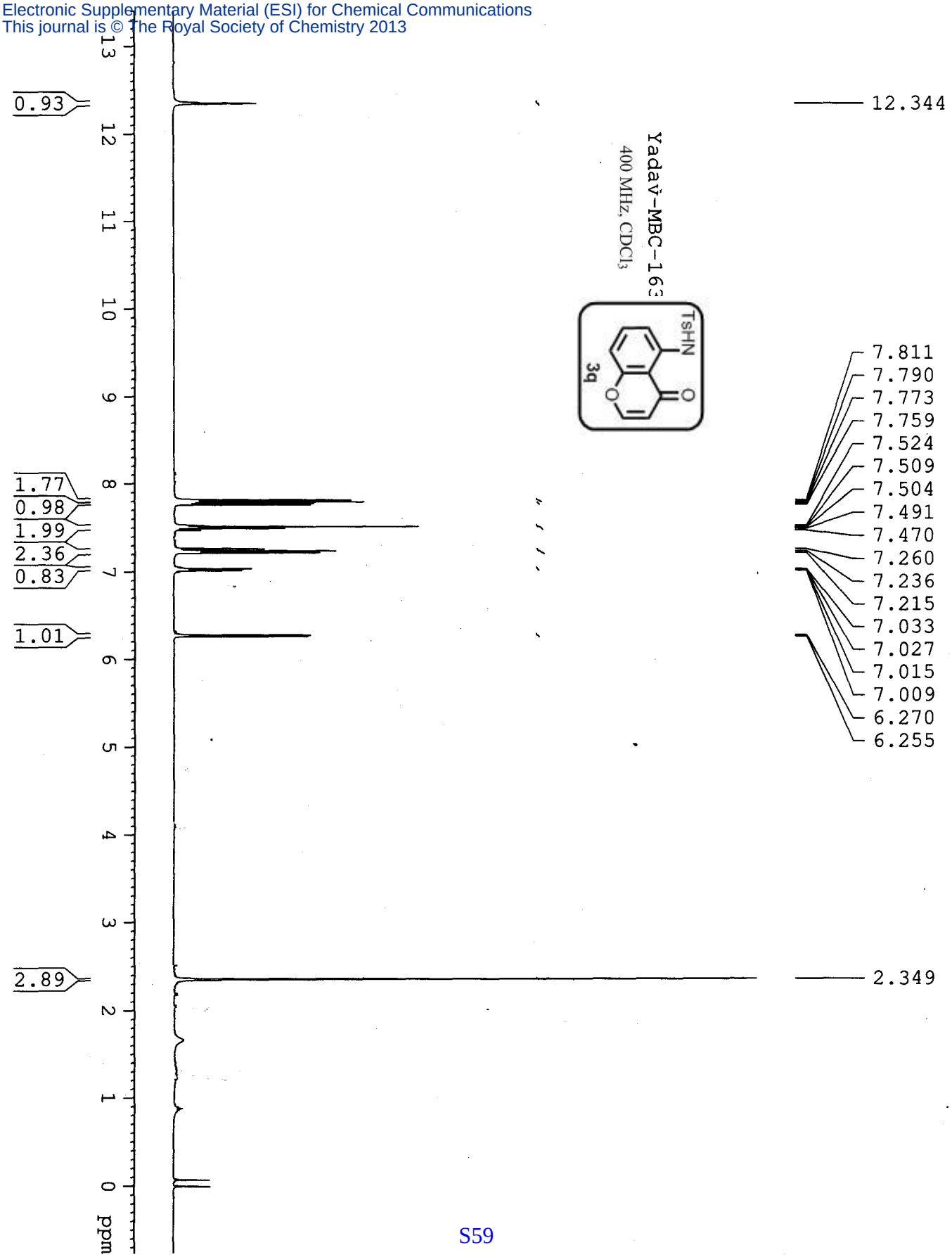

R-MBC-R-143
101 MHz, CDCl3
3n
NHTs
Me
O
202.37
143.64
136.22
135.85
134.83
134.41
129.79
129.42
128.98
128.45
127.13
127.06
125.81
123.09
116.89
77.32
77.00
76.68
27.98
21.31
200
180
160
140
120
100
80
60
40
20
ppm

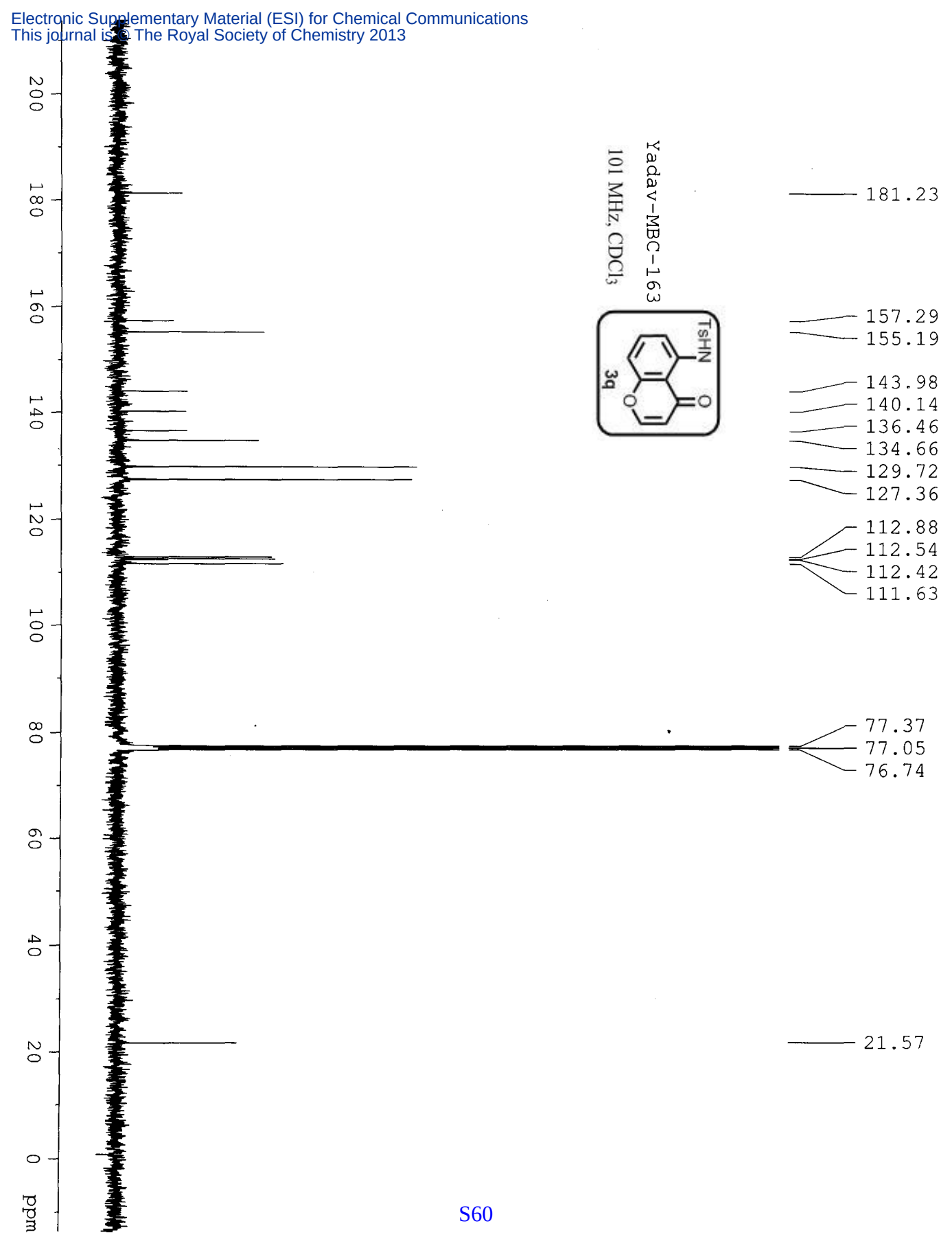


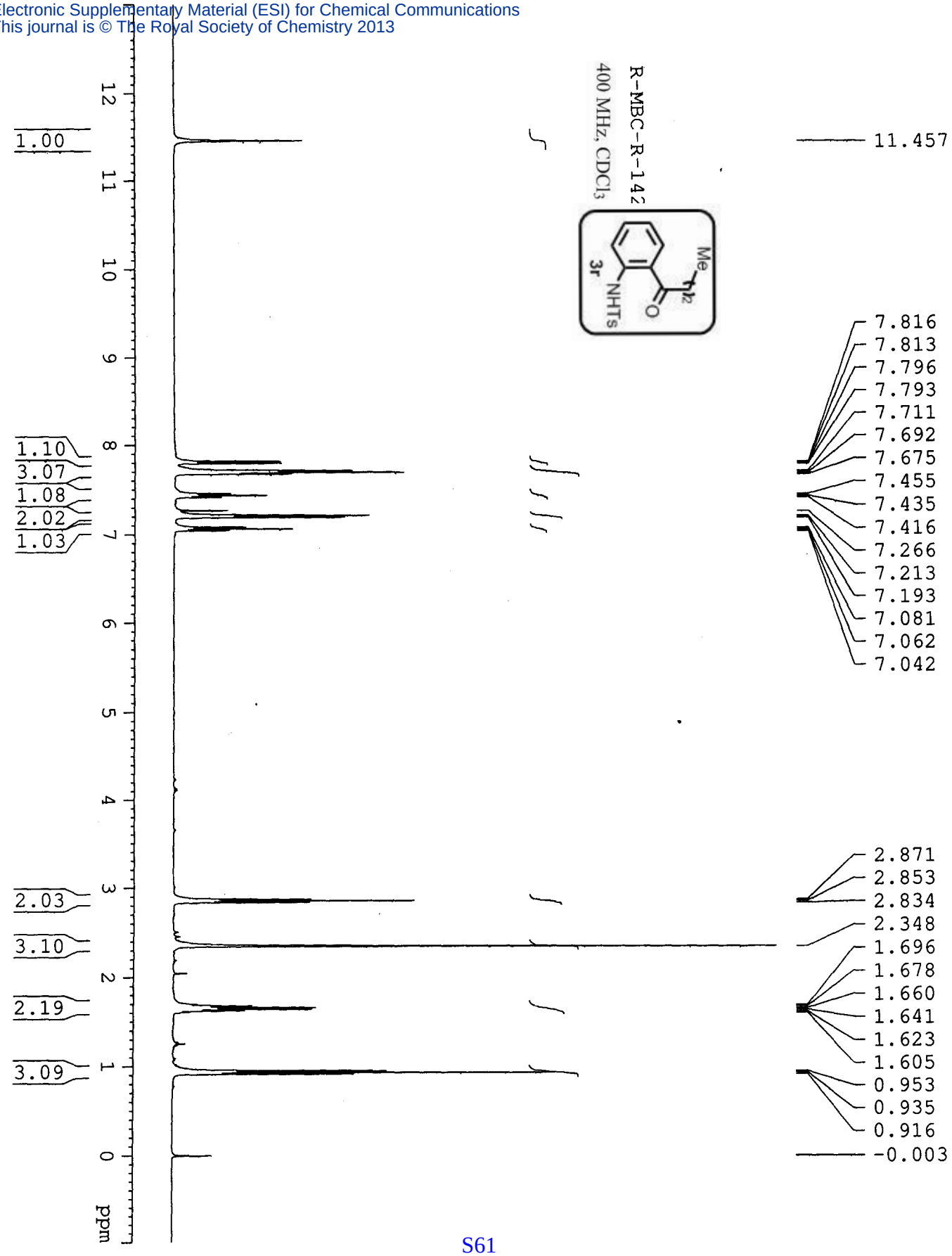

MBC-15-161
200.475
152.987
143.568
142.173
136.383
129.125
127.527
127.020
123.168
121.677
104.835
102.377
77.318
77.001
76.683
27.815
21.496
3o
NHTs
Me
O
O
O
O
ppm
220
200
180
160
140
120
100
80
60
40
20
0
NAME MBC
EXPNO 3962
PROCNO 999
Date_ 20130223
Time 0.18
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 218
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 20642.5
DW 16.600 usec
DE 6.00 usec
TE 291.1 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127765 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

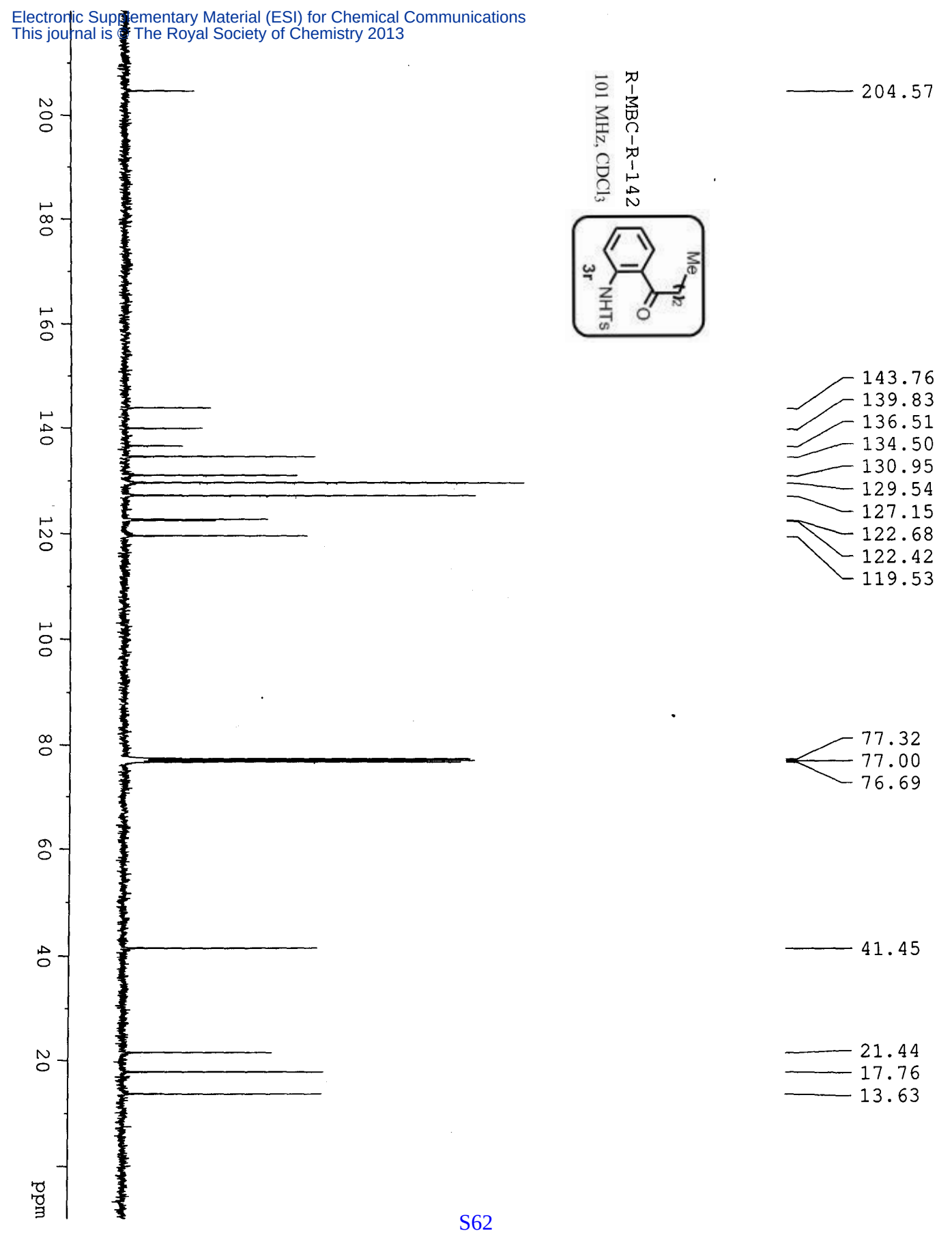


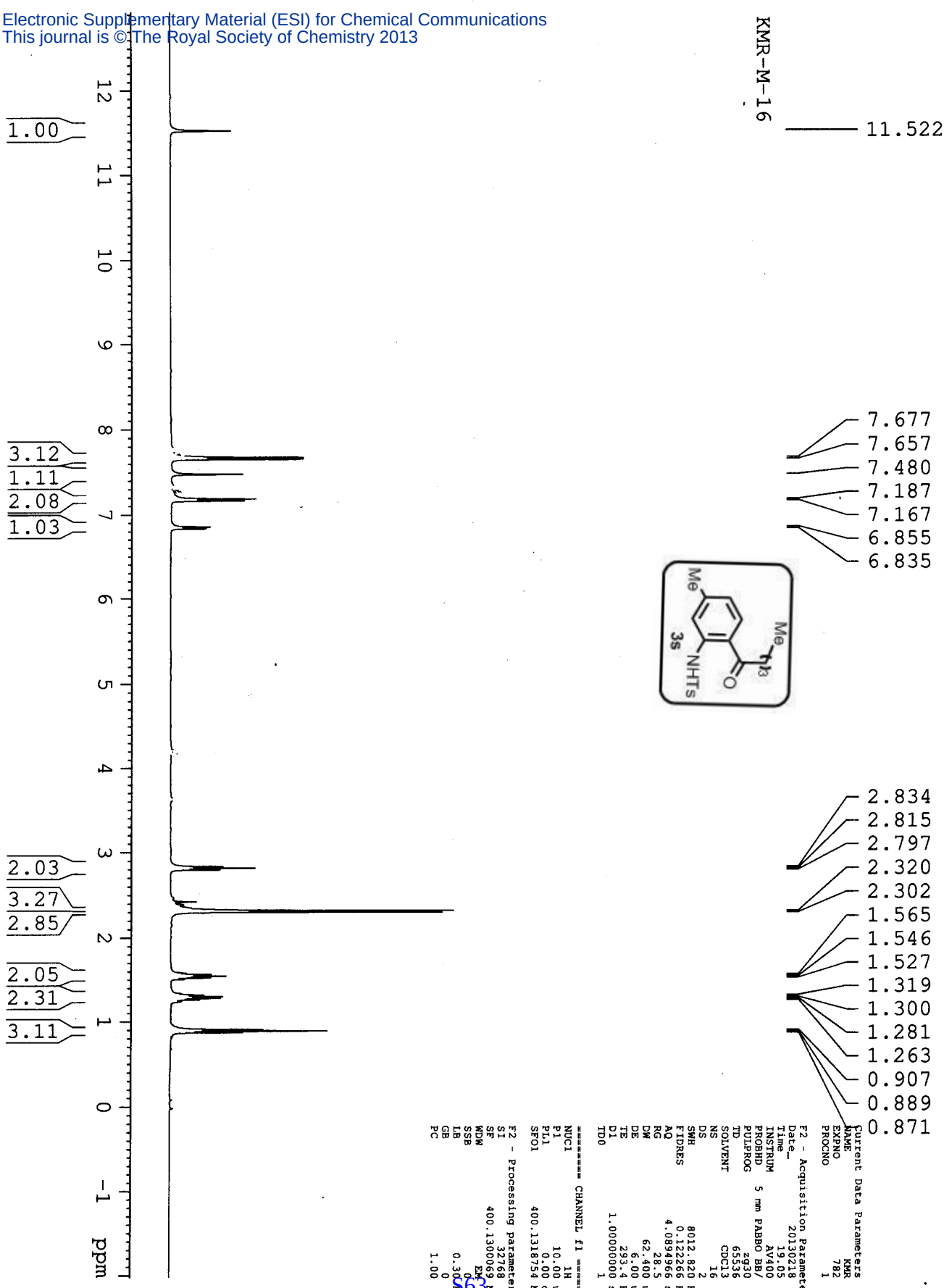

R-MBC-2,4-DiOM
101 MHz, CDCl3
MeO
OMe Me
NHTs
O
3p
201.93
164.12
162.58
143.73
142.53
136.29
129.50
127.21
109.26
96.33
93.96
77.32
77.00
76.68
55.54
33.48
21.45
200
180
160
140
120
100
80
60
40
20
ppm



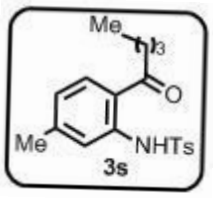

Yadav-MBC-163
101 MHz, CDCl3
TsHN
O
O
3q
181.23
157.29
155.19
143.98
140.14
136.46
134.66
129.72
127.36
112.88
112.54
112.42
111.63
77.37
77.05
76.74
21.57
200
180
160
140
120
100
80
60
40
20
0
ppm


R-MBC-R-142
400 MHz, CDCl3
3r
NHTs
Me
Ph
O
11.457
7.816
7.813
7.796
7.793
7.711
7.692
7.675
7.455
7.435
7.416
7.266
7.213
7.193
7.081
7.062
7.042
2.871
2.853
2.834
2.348
1.696
1.678
1.660
1.641
1.623
1.605
0.953
0.935
0.916
-0.003
1.00
1.10
3.07
1.08
2.02
1.03
2.03
3.10
2.19
3.09
ppm


R-MBC-R-142
101 MHz, CDCl3
3r
NHTs
O
Me
204.57
143.76
139.83
136.51
134.50
130.95
129.54
127.15
122.68
122.42
119.53
77.32
77.00
76.69
41.45
21.44
17.76
13.63
200
180
160
140
120
100
80
60
40
20
ppm


KMR-M-16
11.522
7.677
7.657
7.480
7.187
7.167
6.855
6.835
2.834
2.815
2.797
2.320
2.302
1.565
1.546
1.527
1.319
1.300
1.281
1.263
0.907
0.889
0.871
1.00
3.12
1.11
2.08
1.03
2.03
3.27
2.85
2.05
2.31
3.11
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
Me
Me
NHTs
3s
Current Data Parameters
NAME KMR
EXPNO 782
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130218
Time 19.05
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 28.5
DW 62.400 use
DE 6.00 use
TE 293.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 use
PL1 0.00 dB
SFO1 400.1318754 MHz
F2 - Processing parameters
SI 32768
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

KMR-M-16



204.325

145.762
143.612
139.806
136.408
130.967
129.406
126.985
123.665
119.942
119.731

77.326
77.008
76.689

39.061
26.497
22.121
21.837
21.318
13.759

Current Data Parameters
NAME KMR
EXPNO 783
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130218
Time 19.07
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 54
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 20642.5
DW 16.600 use
DE 6.00 use
TE 293.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

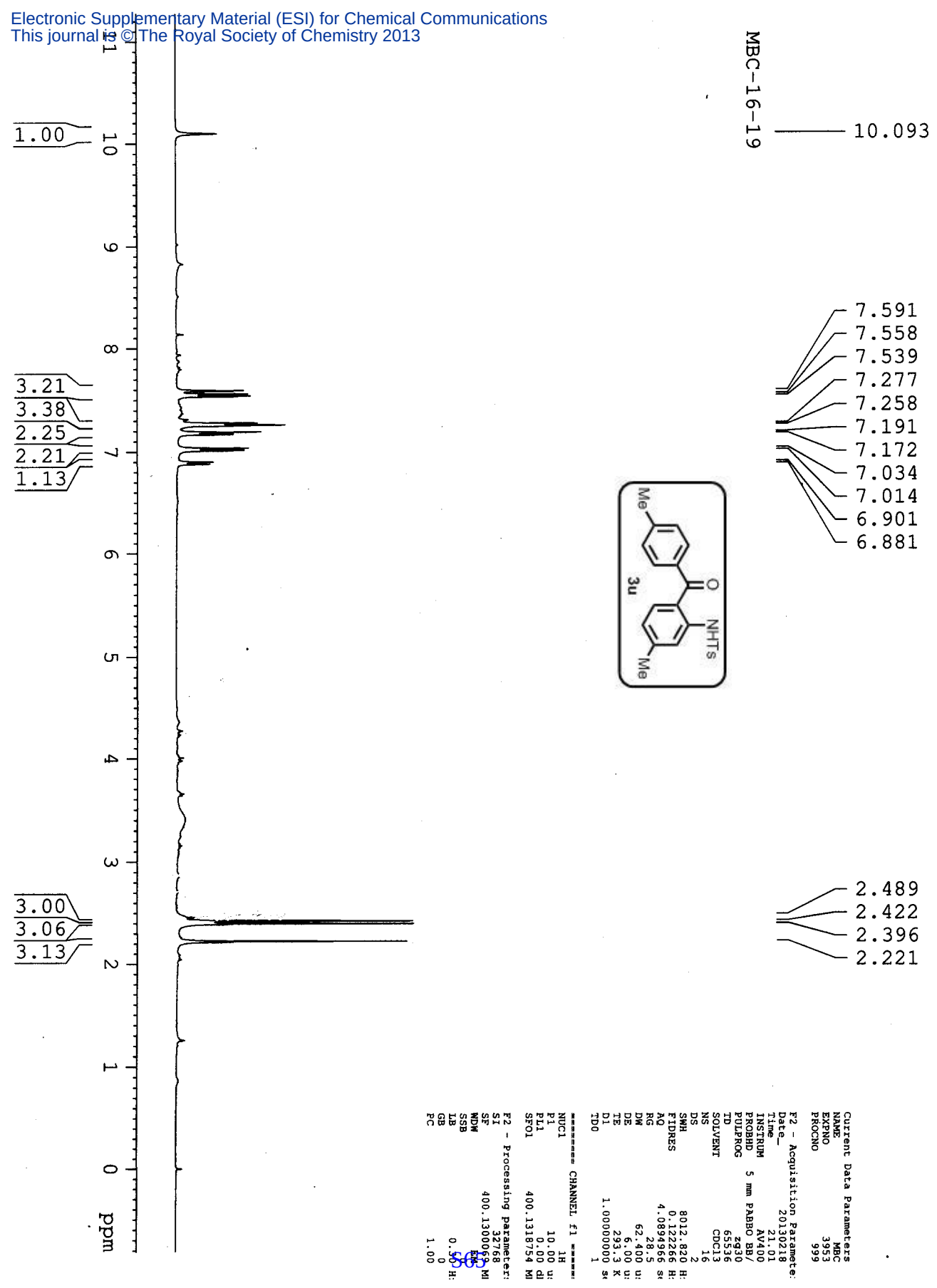
======== CHANNEL f1 =======
NUC1 13C
P1 11.00 use
PL1 0.00 dB
SFO1 100.6228298 MHz

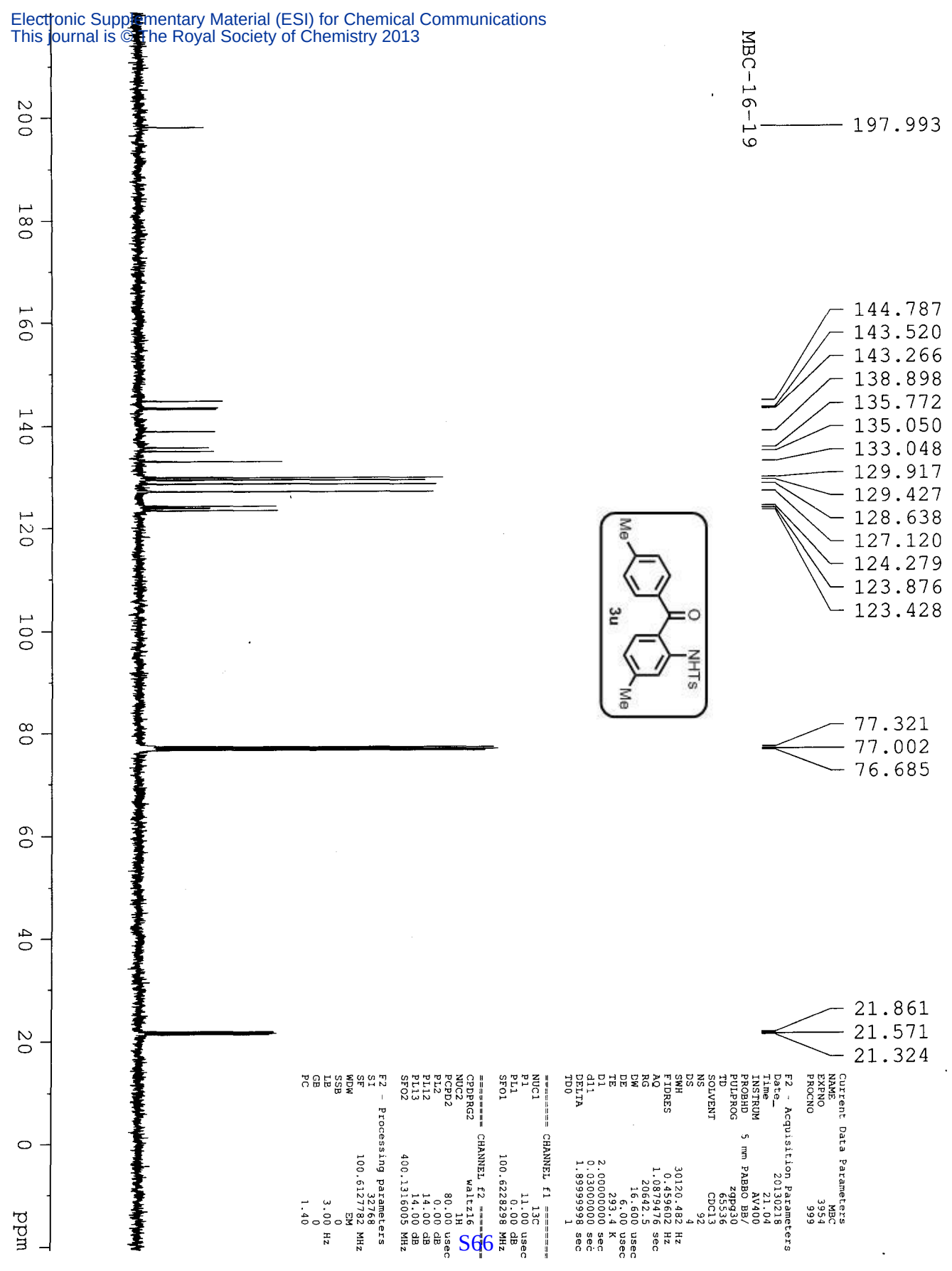
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127871 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

S64

220 200 180 160 140 120 100 80 60 40 20 0 -20 ppm



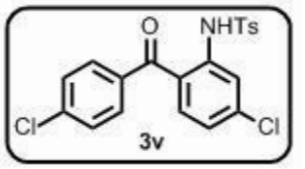

MBC-16-19
197.993
144.787
143.520
143.266
138.898
135.772
135.050
133.048
129.917
129.427
128.638
127.120
124.279
123.876
123.428
77.321
77.002
76.685
21.861
21.571
21.324
Me
O
NHTs
3u
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

MBC-16-18

10.081

7.799 7.794 7.616 7.595 7.408 7.387 7.359 7.338 7.323 7.302 7.118 7.097 7.080 7.076 7.059 7.055

2.281

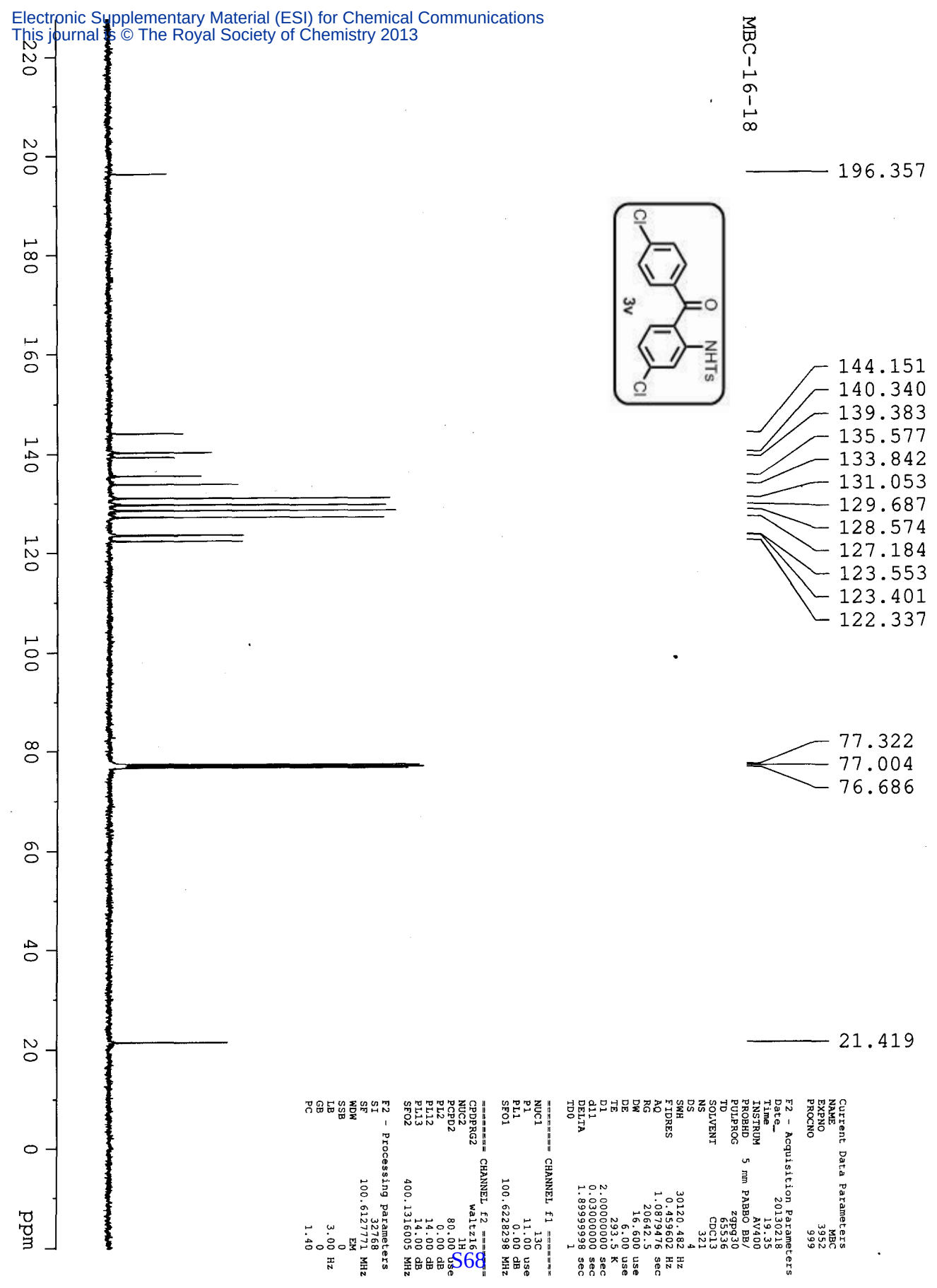


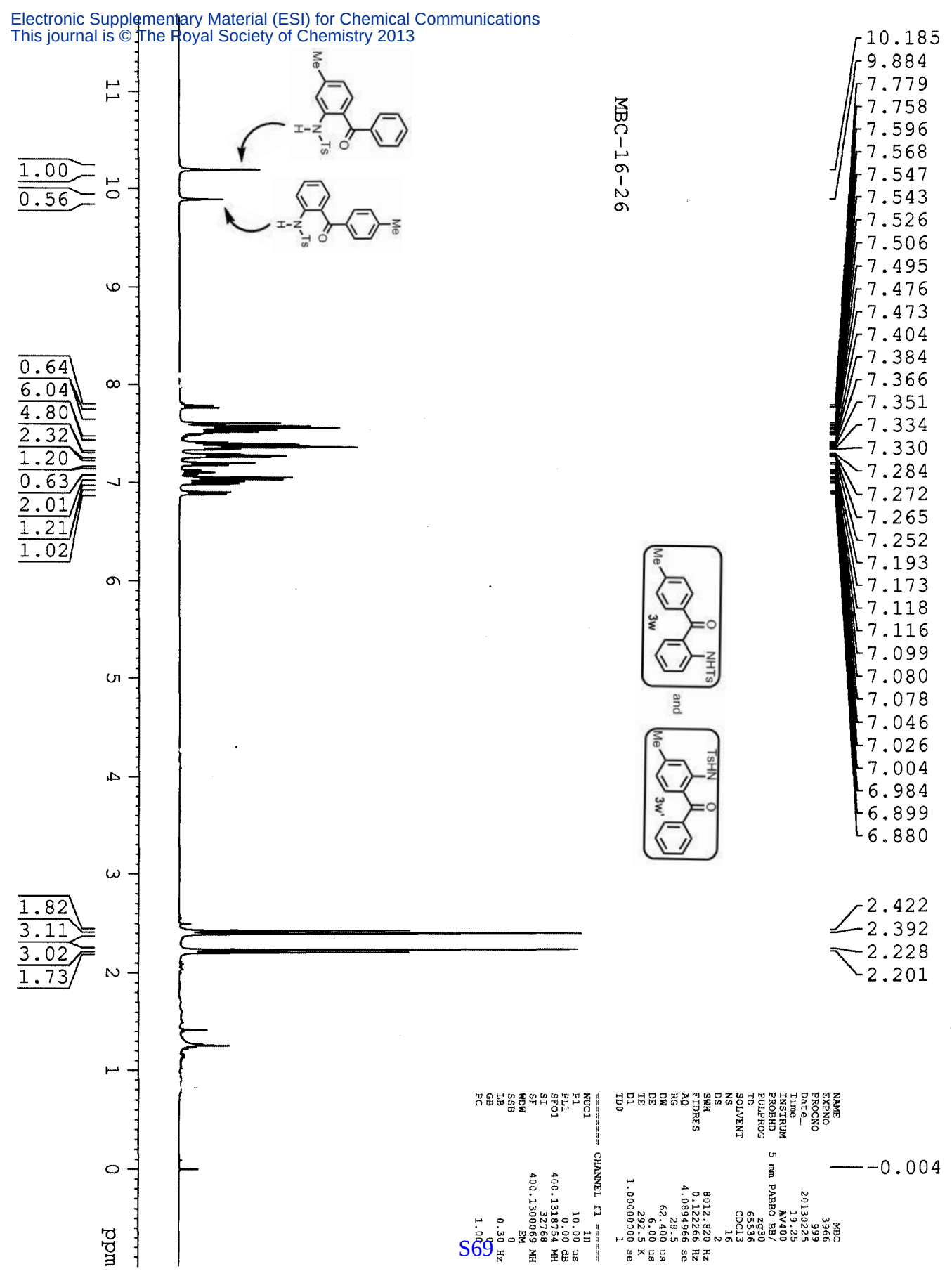
3v

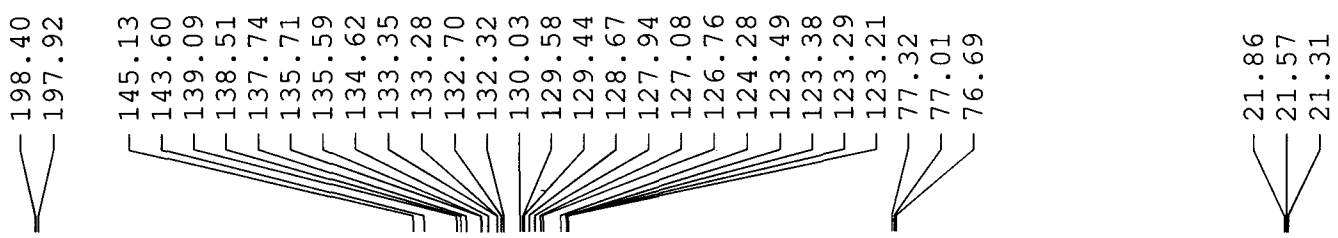
```
Current Data Parameters
NAME                  MBC
EXPNO                3951
PROCNO                999

F2 - Acquisition Parameter
Date_             20130218
Time                 19.32
INSTRUM              AV400
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       5
DS                       2
SWH               8012.820 H
FIDRES               0.122266 H
AQ                4.0894966 s
RG                    28.5
DW                   62.400 u
DE                    6.00 u
TE                   293.3 K
D1             1.00000000 s
TD0                      1

======== CHANNEL f1 ======
NUC1                    1H
P1                   10.00 u
PL1                   0.00 d
SFO1          400.1318754 M

F2 - Processing parameter
SI                   32768
SF            400.1300069 M
WDW                     EM
SSB                      0
LB                    0.1  H
GB                       0
PC                    1.00
```


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

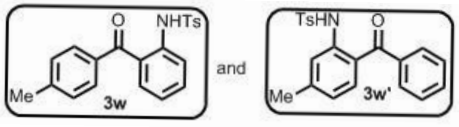
1.00 1.09 2.06 5.28 3.11 3.09


MBC-16-18
196.357
144.151
140.340
139.383
135.577
133.842
131.053
129.687
128.574
127.184
123.553
123.401
122.337
77.322
77.004
76.686
21.419
Cl
O
NHTs
3v
Cl
220
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME MBC
EXPNO 3952
PROCNO 999
F2 - Acquisition Parameters
Date_ 20130218
Time 19.35
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 321
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.08794760 sec
RG 20642.5
DW 16.600 use
DE 6.00 use
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 use
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127771 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

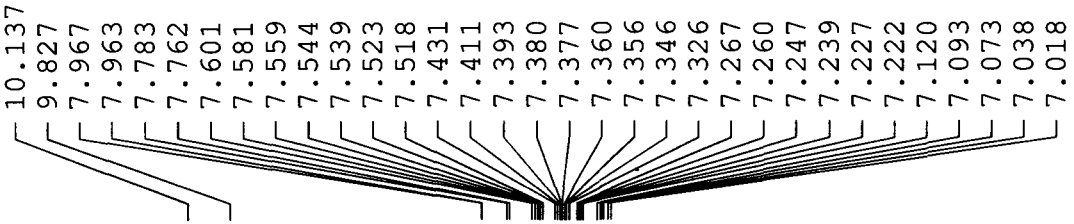

MBC-16-26
10.185
9.884
7.779
7.758
7.596
7.568
7.547
7.543
7.526
7.506
7.495
7.476
7.473
7.404
7.384
7.366
7.351
7.334
7.330
7.284
7.272
7.265
7.252
7.193
7.173
7.118
7.116
7.099
7.080
7.078
7.046
7.026
7.004
6.984
6.899
6.880
2.422
2.392
2.228
2.201
-0.004
1.00
0.56
0.64
6.04
4.80
2.32
1.20
0.63
2.01
1.21
1.02
1.82
3.11
3.02
1.73
Me
NHTs
3w
and
TsHN
3w'
ppm
NAME MBC
EXPNO 3966
PROCNO 999
Date_ 20130225
Time 19.25
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 se
RG 28.5
DW 62.400 us
DE 6.00 us
TE 292.5 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 us
PL1 0.00 dB
SFO1 400.1318754 MH
SI 32768
SF 400.1300069 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



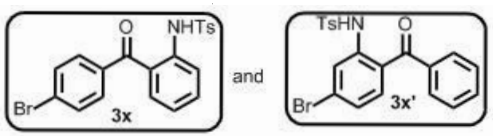
MBC-16-26




```
Current Data Parameters
NAME                  MBC
EXPNO                3967
PROCNO                999

F2 - Acquisition Parameters
Date_             20130225
Time                19.27
INSTRUM             AV400
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   156
DS                     4
SWH           30120.482 Hz
FIDRES         0.459602 Hz
AQ            1.0879476 sec
RG              20642.5
DW               16.600 usec
DE                6.00 usec
TE               292.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               11.00 usec
PL1               0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             14.00 dB
PL13             14.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127820 MHz
WDW                EM
SSB                 0
LB               3.00 Hz
GB                  0
PC                1.40
```



MBC-16-25



Current Data Parameters

NAME	MBC
EXPNO	3964
PROCNO	999

F2 - Acquisition Parameters

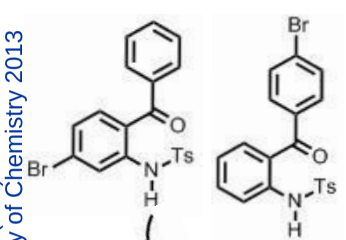
Date_	20130223
Time	23.26
INSTRUM	AV400
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	28.5
DW	62.400 usec
DE	6.00 usec
TE	294.3 K
D1	1.00000000 sec
TD0	1

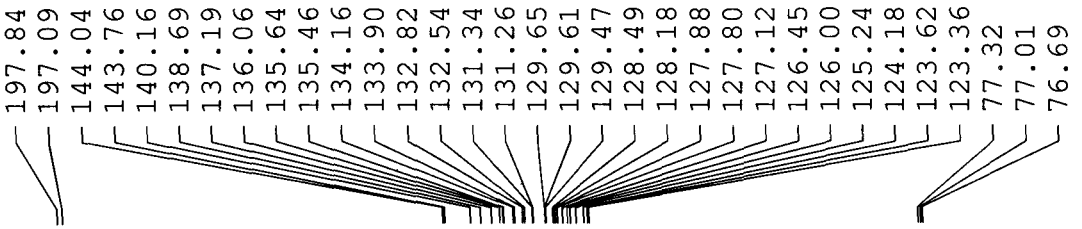
======== CHANNEL f1 ========

NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	400.1318754 MHz

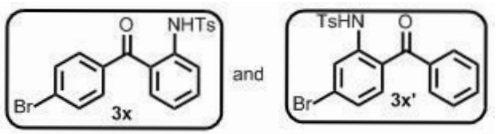
F2 - Processing parameters

SI	32768
SF	400.1300069 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





MBC-16-25



Current Data Parameters

NAME	MBC
EXPNO	3965
PROCNO	999

F2 - Acquisition Parameters

Date_	20130223
Time	23.28
INSTRUM	AV400
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	112
DS	4
SWH	30120.482 Hz
FIDRES	0.459602 Hz
AQ	1.0879476 sec
RG	20642.5
DW	16.600 usec
DE	6.00 usec
TE	294.5 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	11.00 usec
PL1	0.00 dB
SFO1	100.6228298 MHz

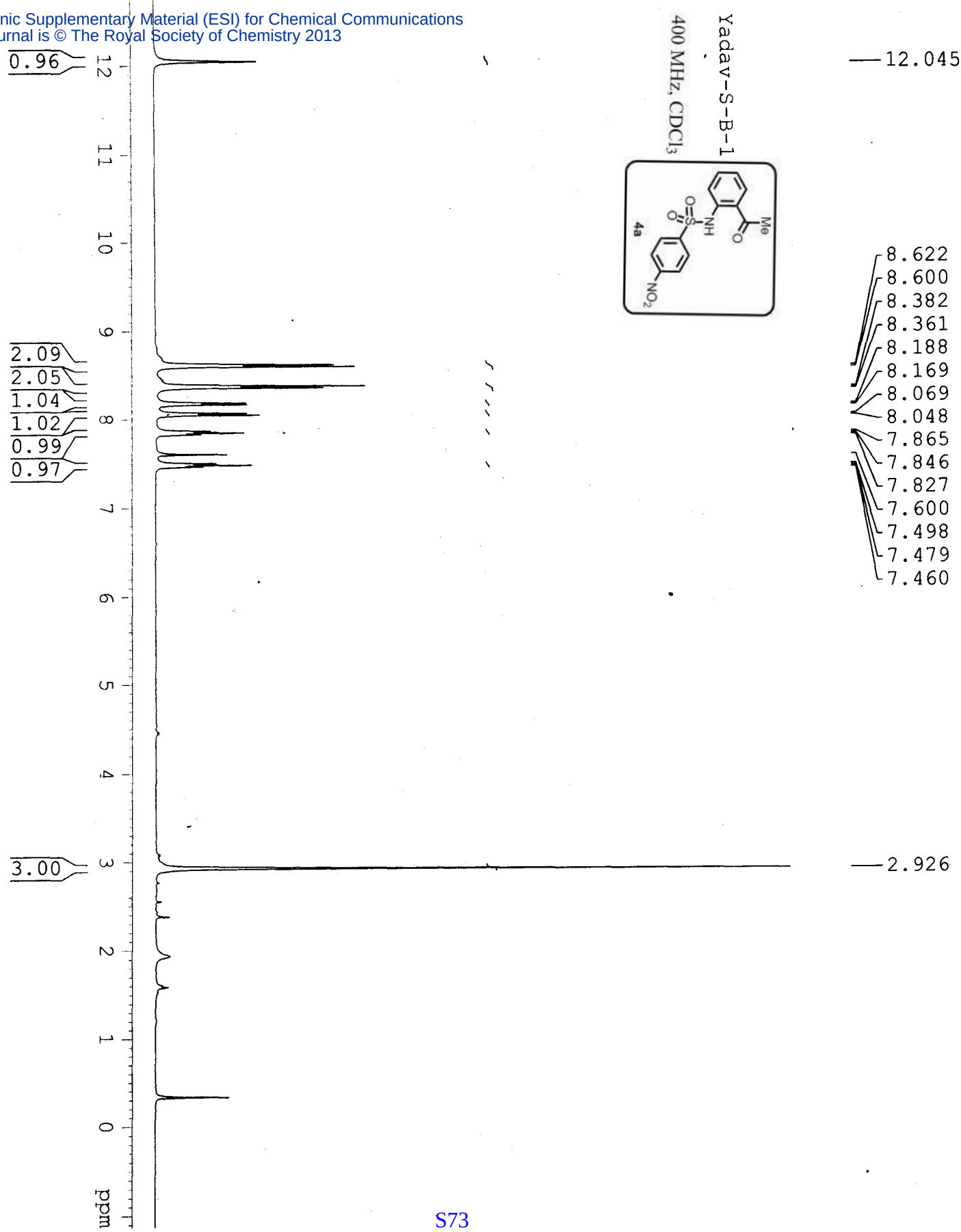
======== CHANNEL f2 ========

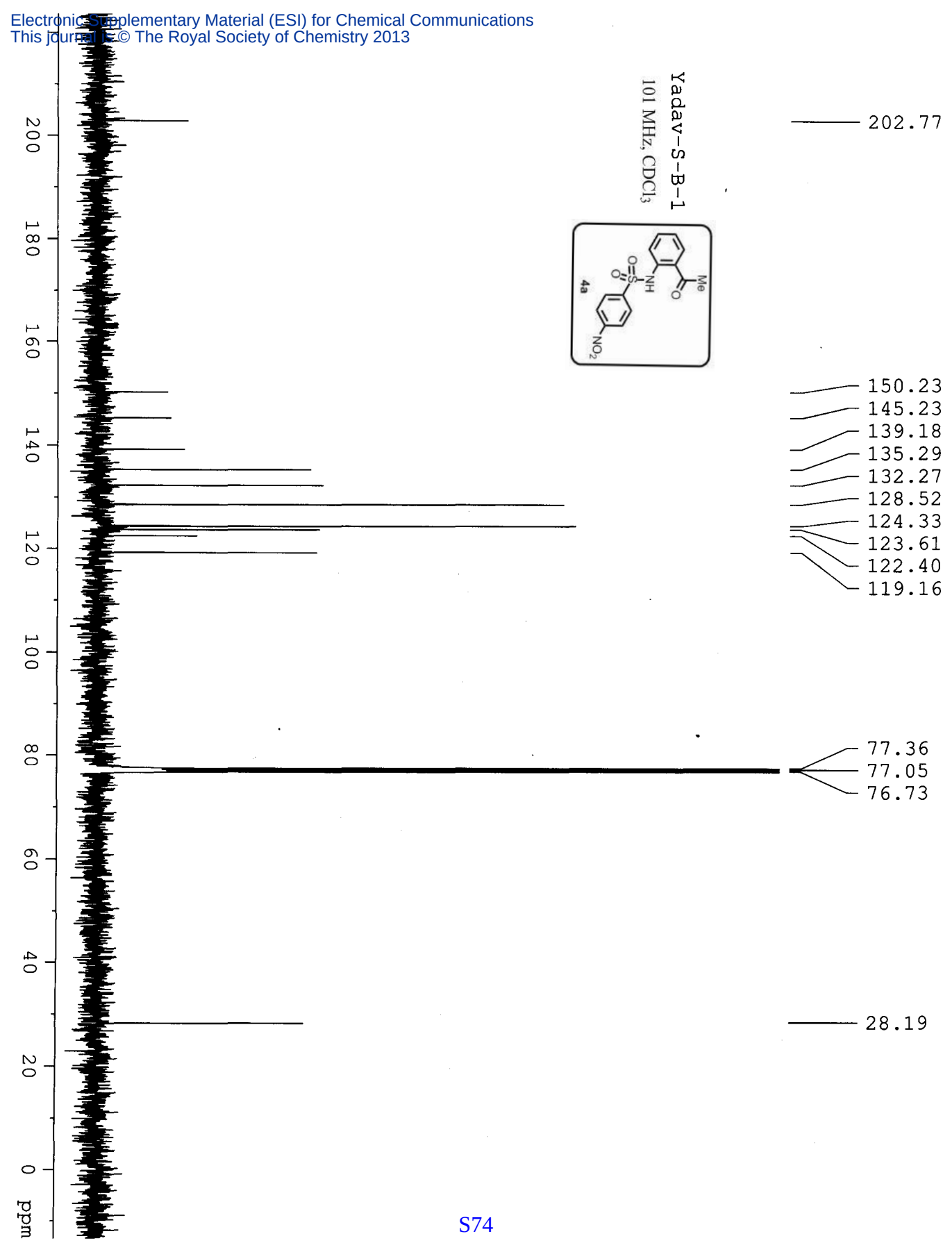
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	14.00 dB
PL13	14.00 dB
SFO2	400.1316005 MHz

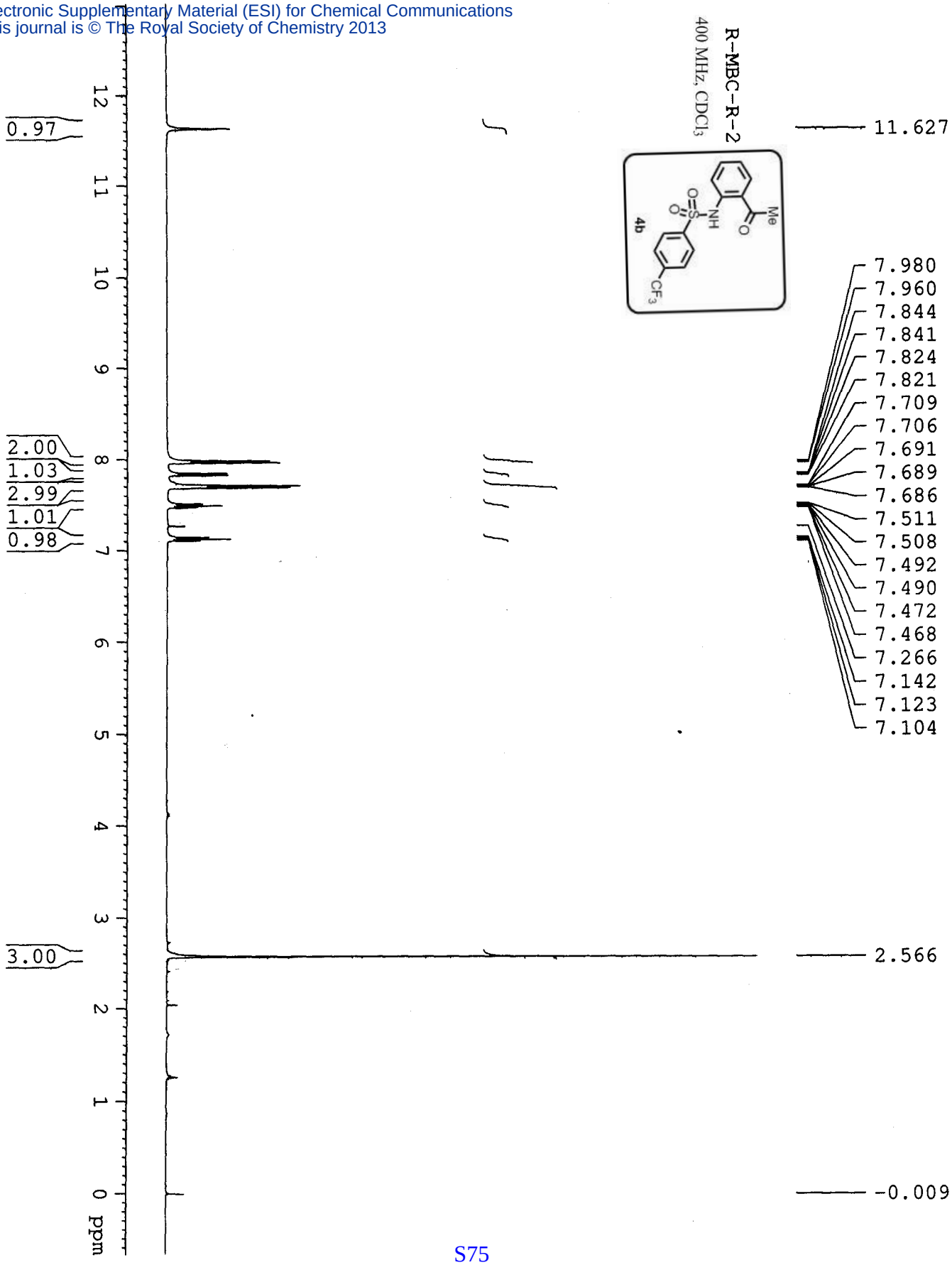
F2 - Processing parameters

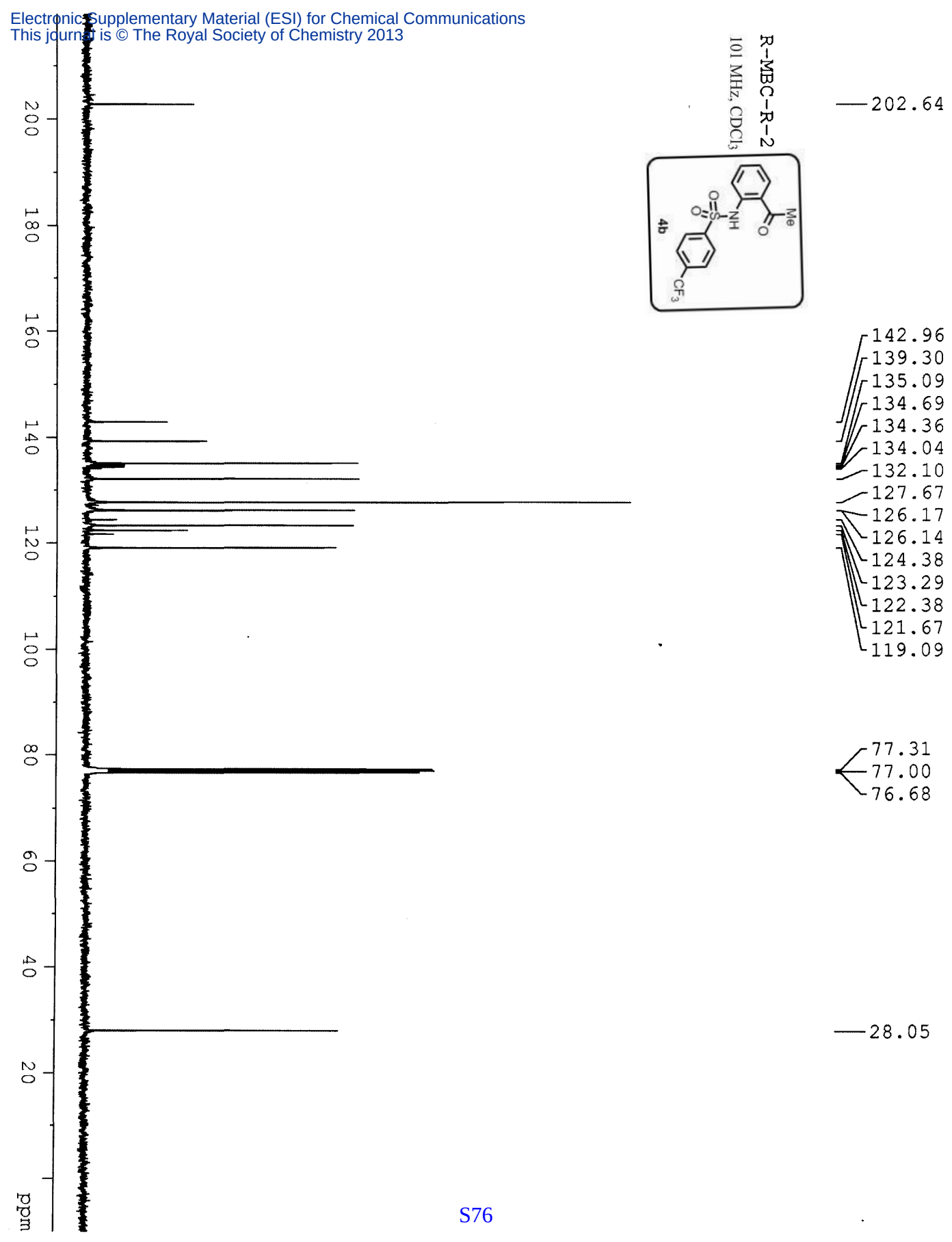
SI	32768
SF	100.6127809 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

200 180 160 140 120 100 80 60 40 20 0 ppm

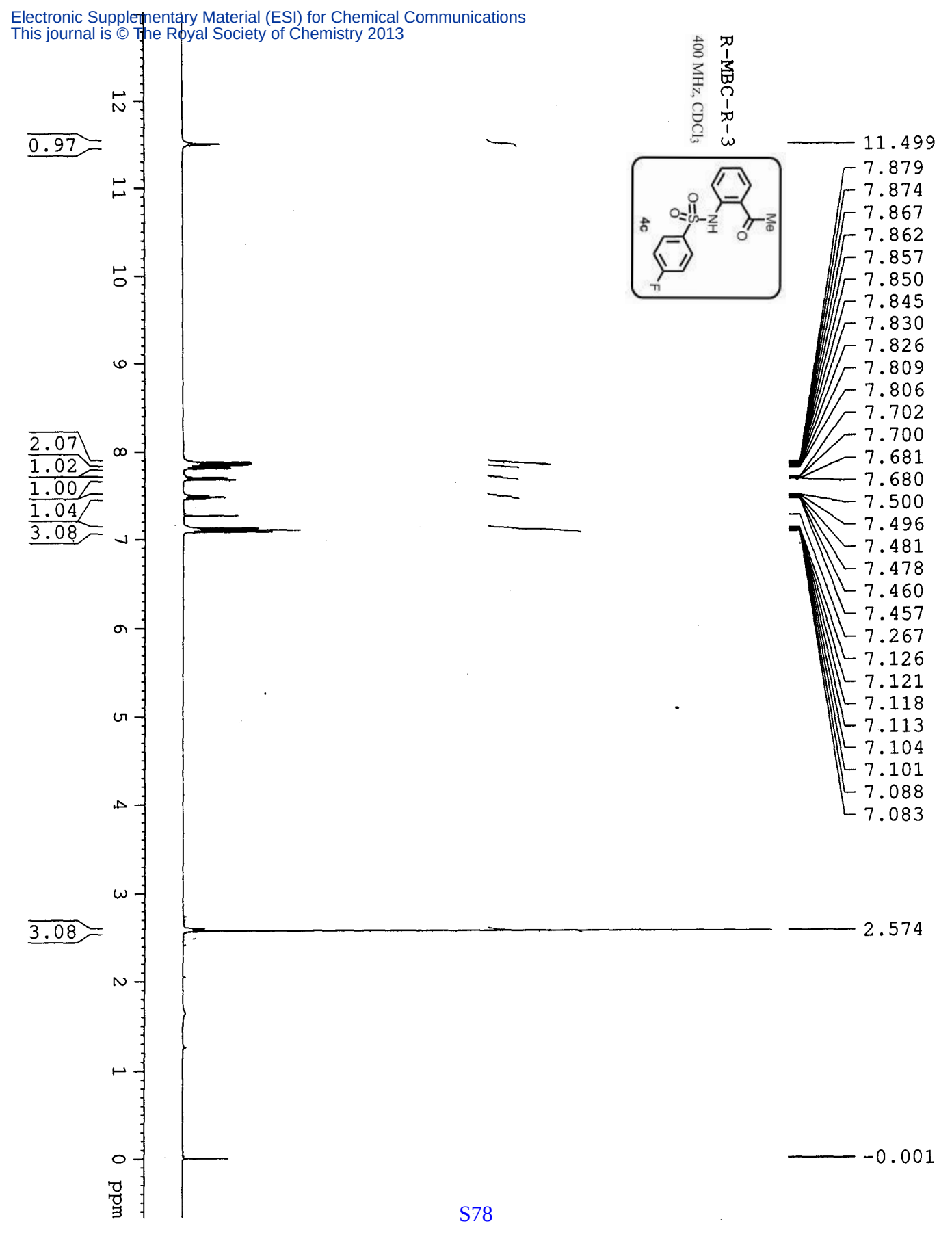

Yadav-S-B-1
400 MHz, CDCl3
4a
NH
Me
O
NO2
12.045
8.622
8.600
8.382
8.361
8.188
8.169
8.069
8.048
7.865
7.846
7.827
7.600
7.498
7.479
7.460
2.926
0.96
2.09
2.05
1.04
1.02
0.99
0.97
3.00
ppm

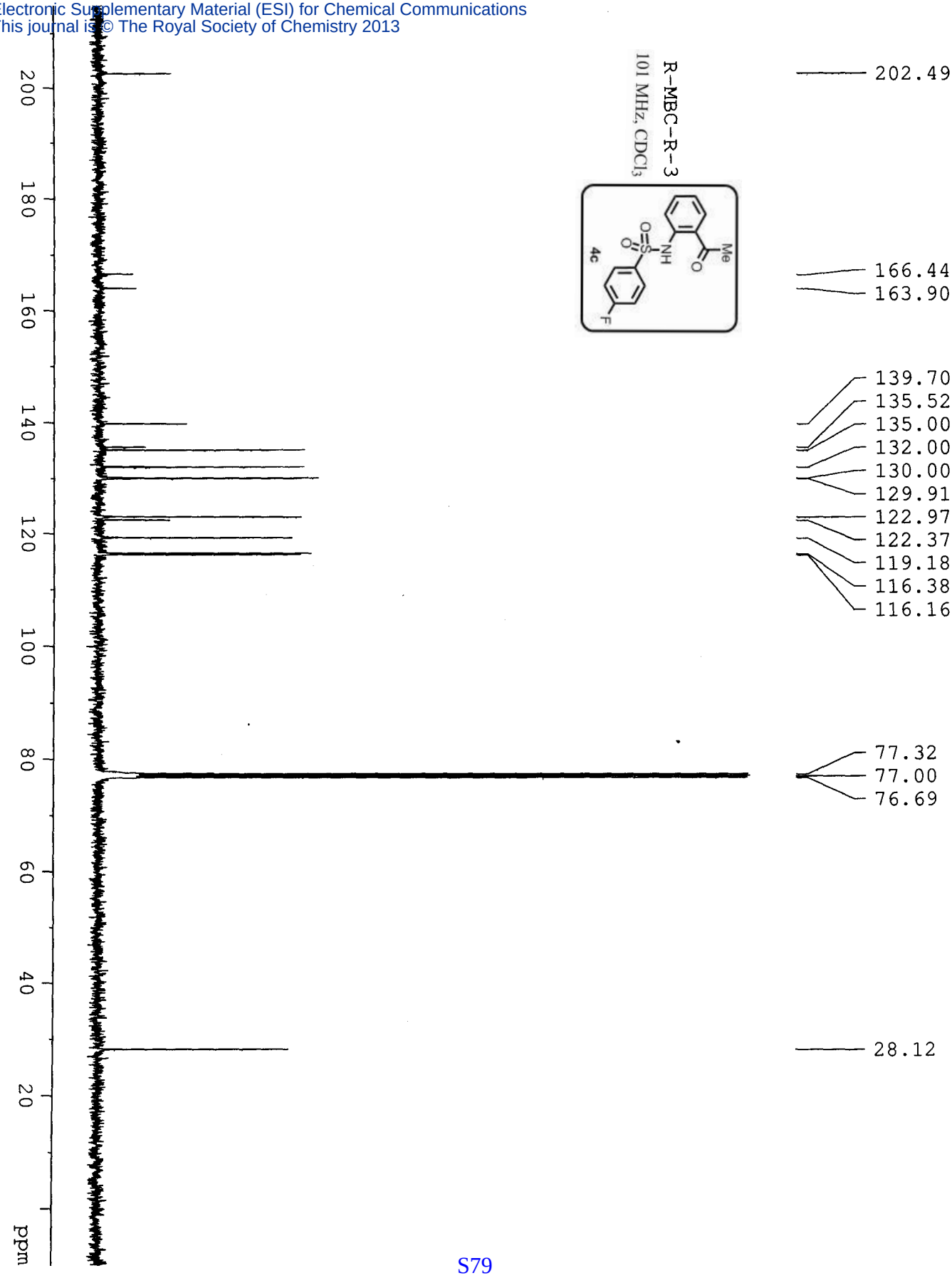

Yadav-S-B-1
101 MHz, CDCl3
4a
202.77
150.23
145.23
139.18
135.29
132.27
128.52
124.33
123.61
122.40
119.16
77.36
77.05
76.73
28.19
200
180
160
140
120
100
80
60
40
20
0
ppm

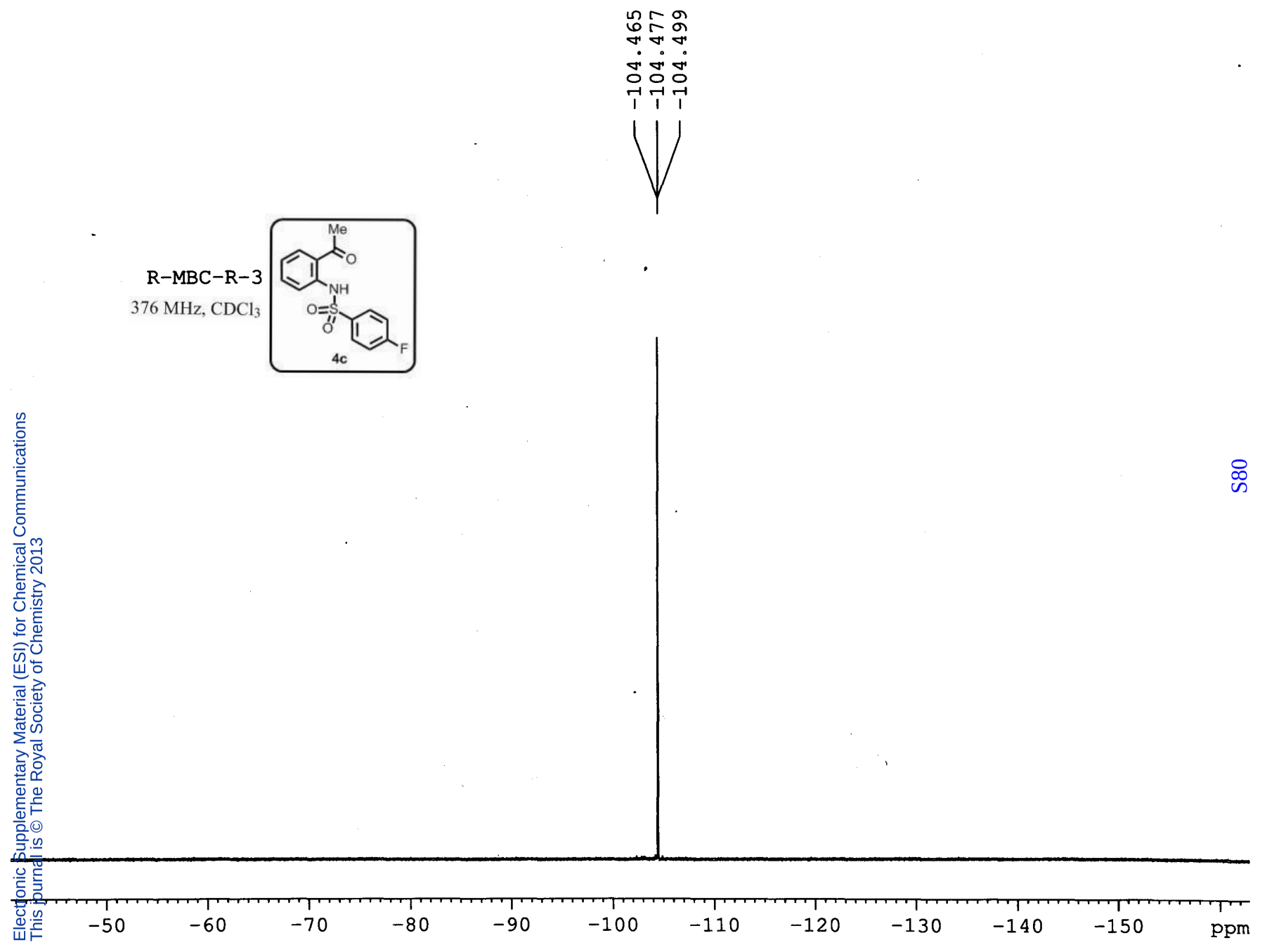

R-MBC-R-2
400 MHz, CDCl3
4b
Me
NH
CF3
11.627
7.980
7.960
7.844
7.841
7.824
7.821
7.709
7.706
7.691
7.689
7.686
7.511
7.508
7.492
7.490
7.472
7.468
7.266
7.142
7.123
7.104
2.566
-0.009
0.97
2.00
1.03
2.99
1.01
0.98
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

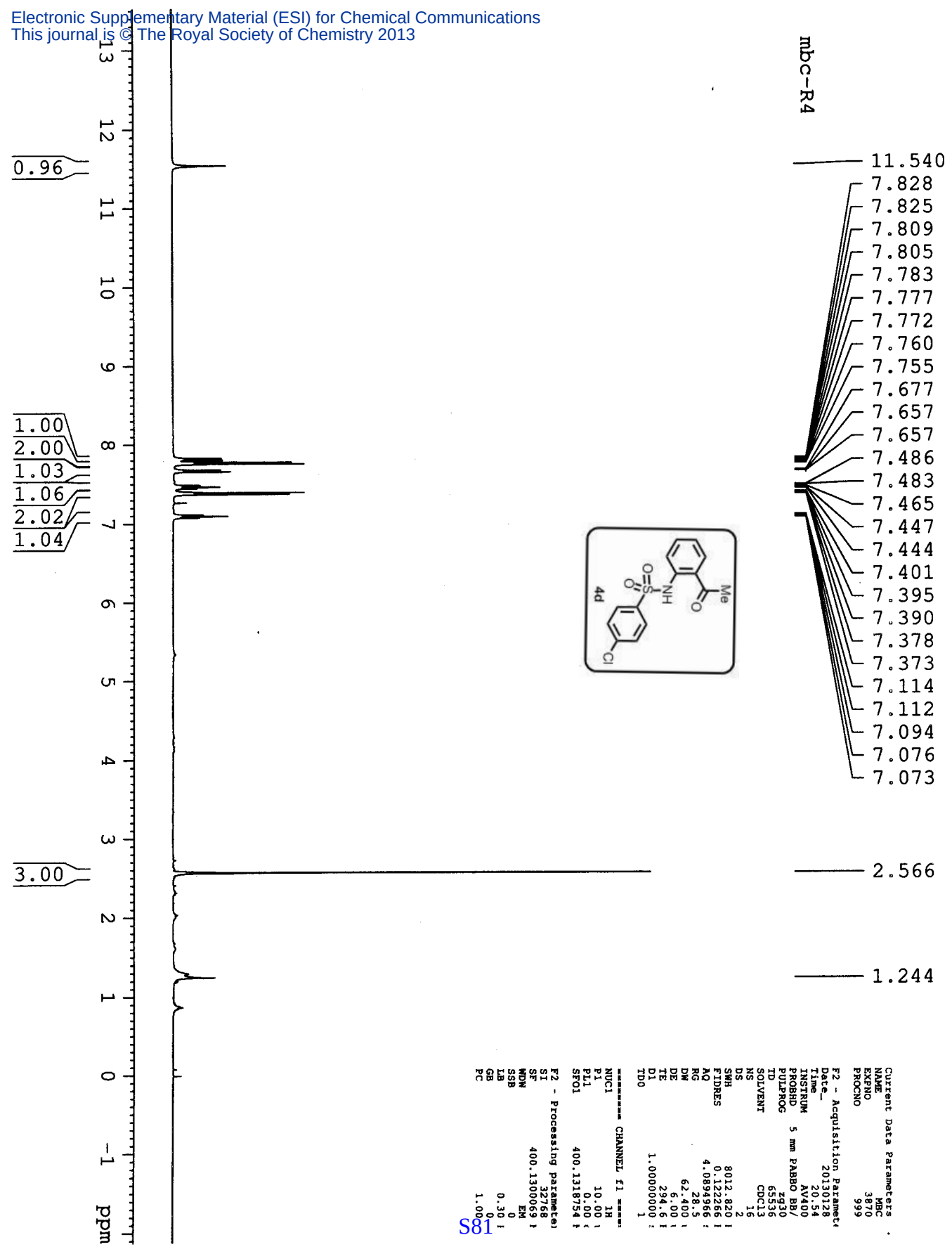

R-MBC-R-2
101 MHz, CDCl3
4b
NH
Me
CF3
202.64
142.96
139.30
135.09
134.69
134.36
134.04
132.10
127.67
126.17
126.14
124.38
123.29
122.38
121.67
119.09
77.31
77.00
76.68
28.05
200
180
160
140
120
100
80
60
40
20
ppm

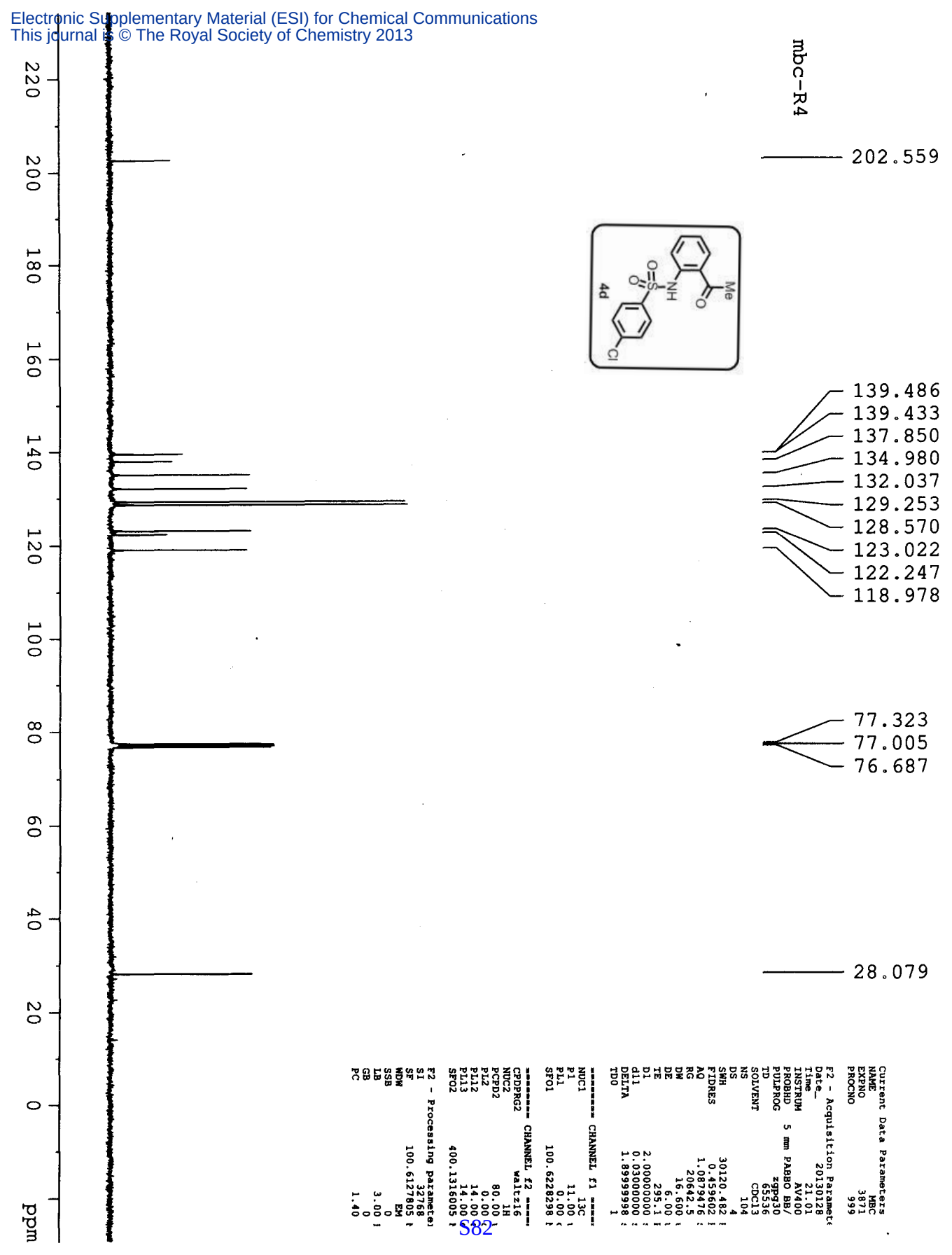
R-MBC-R-2
376 MHz, CDCl3
4b
Me
O
NH
O=S=O
CF3
-63.208
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
ppm

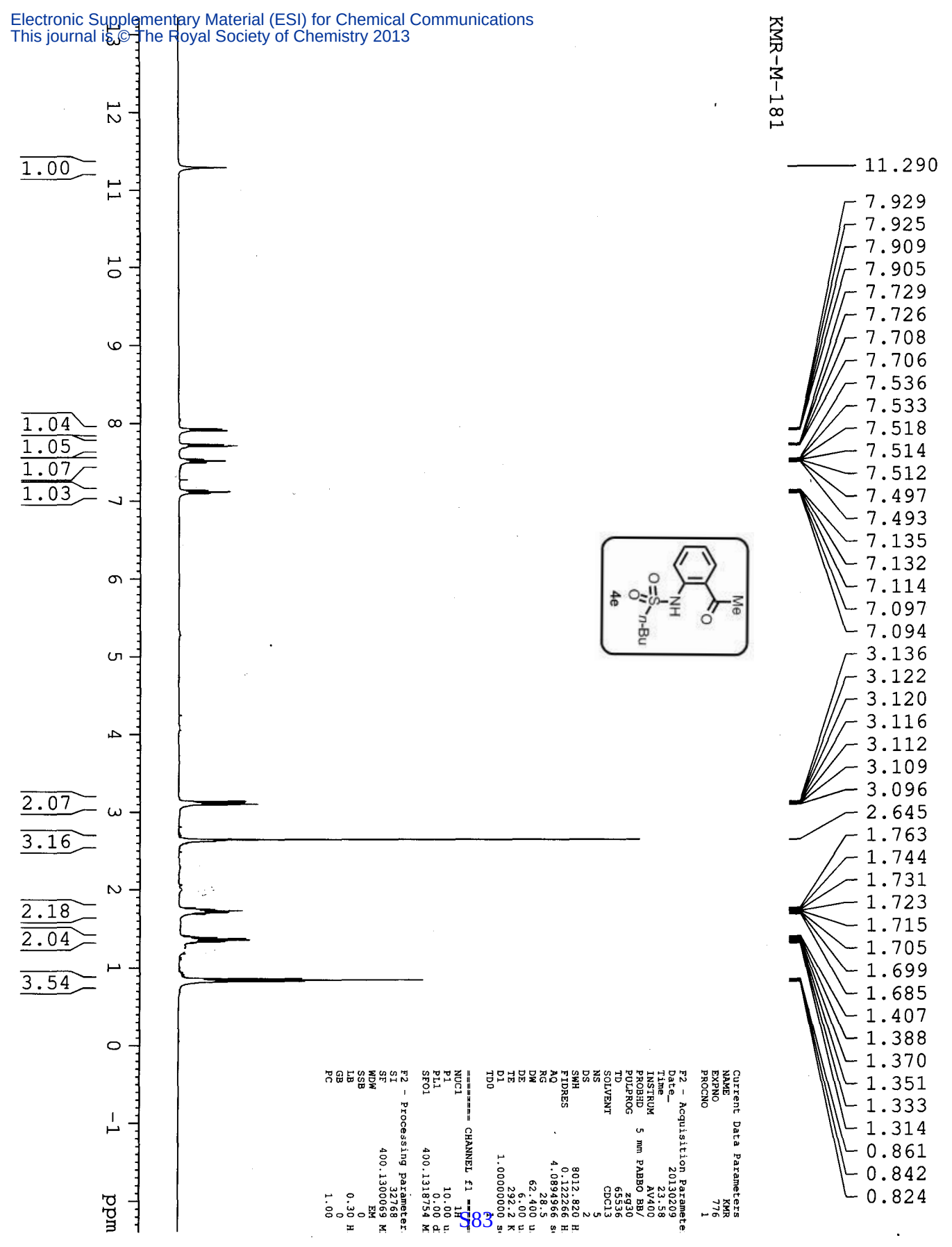


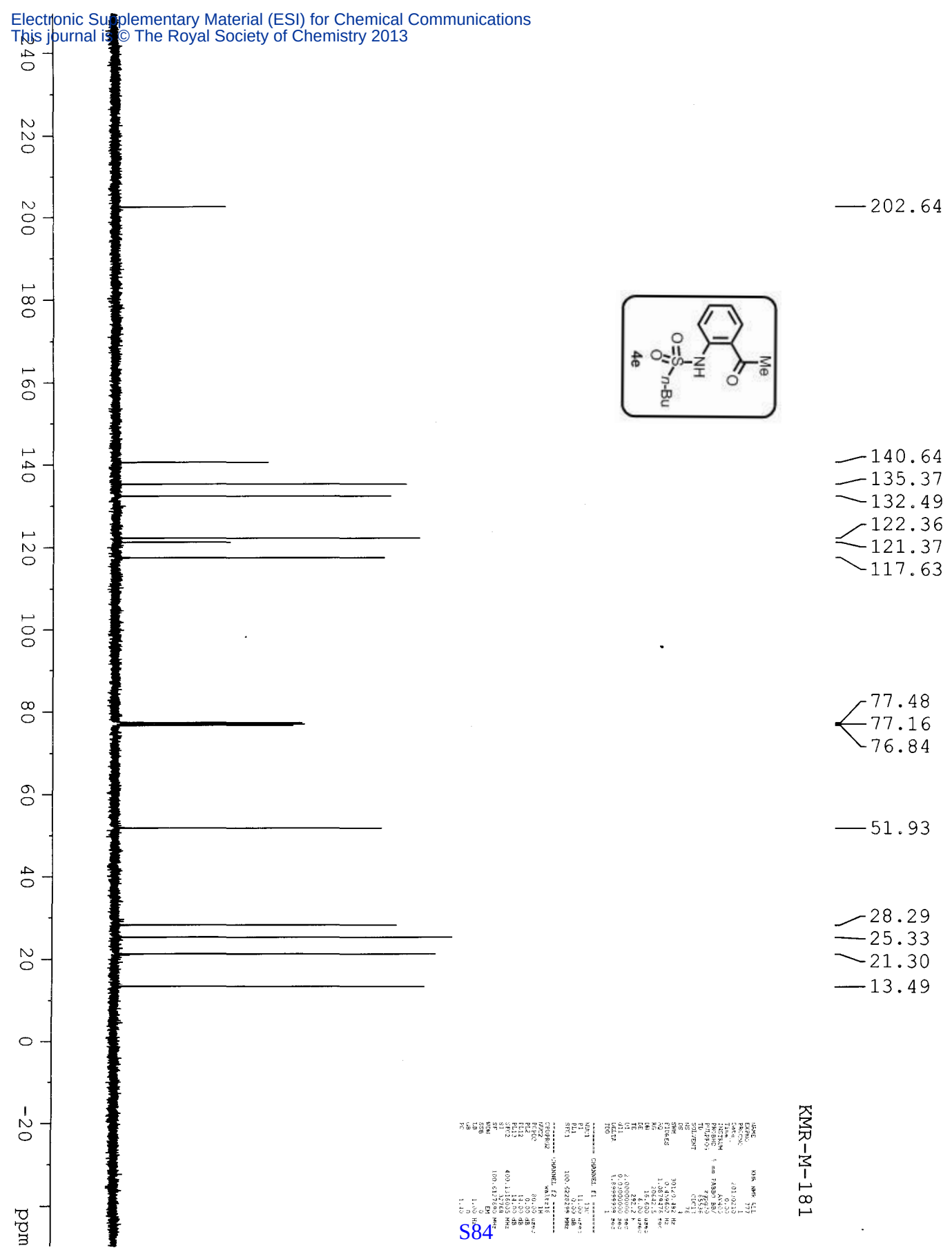


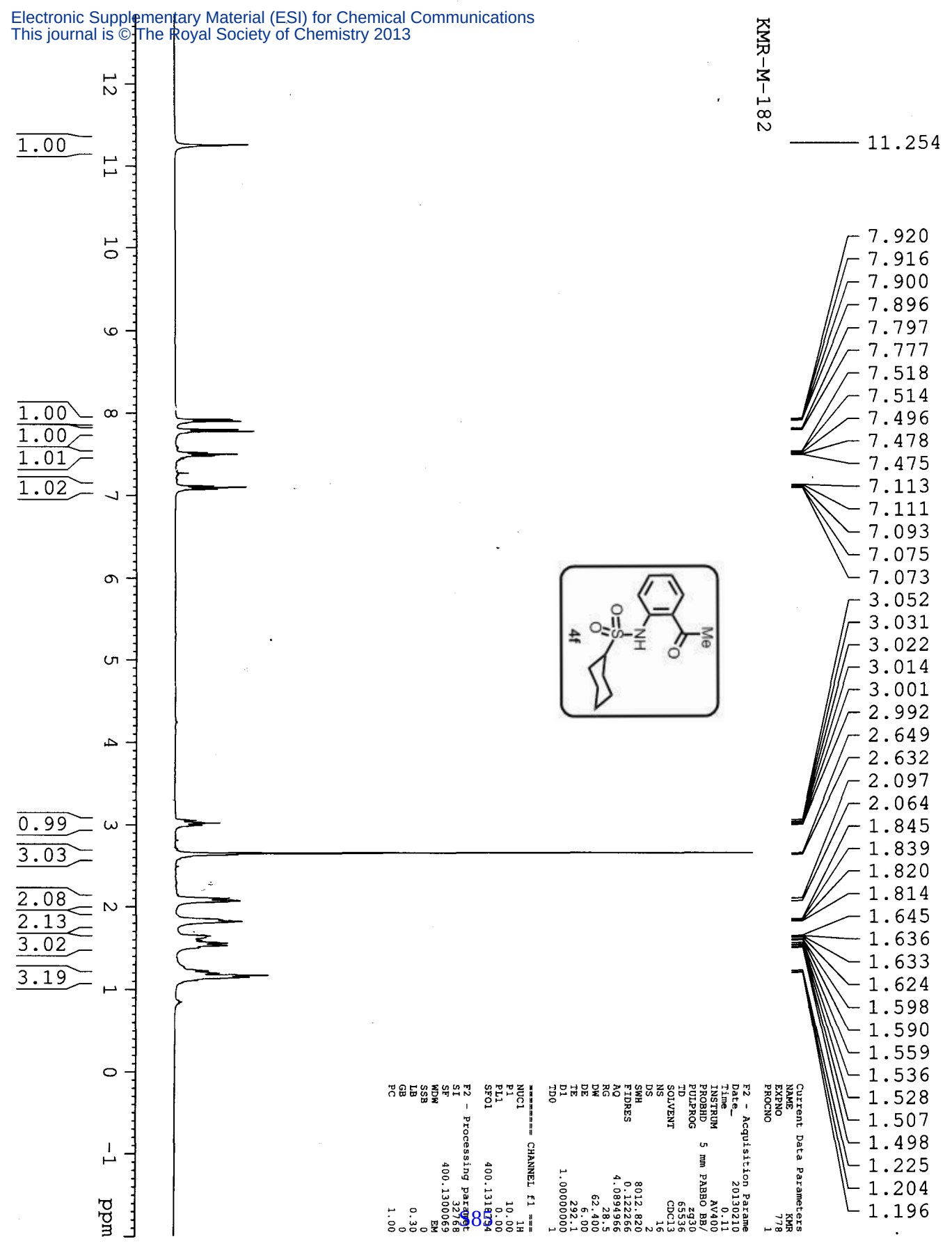


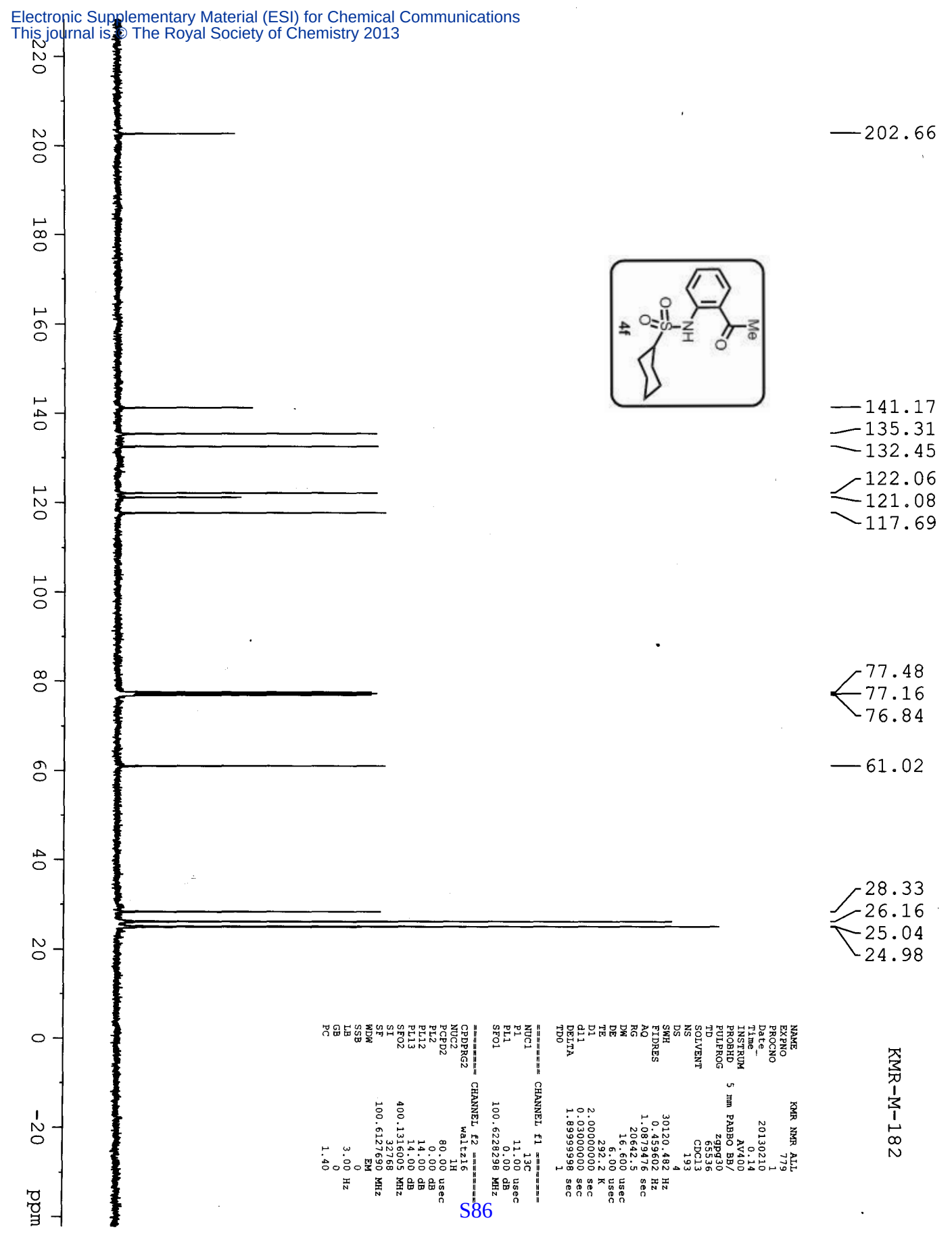


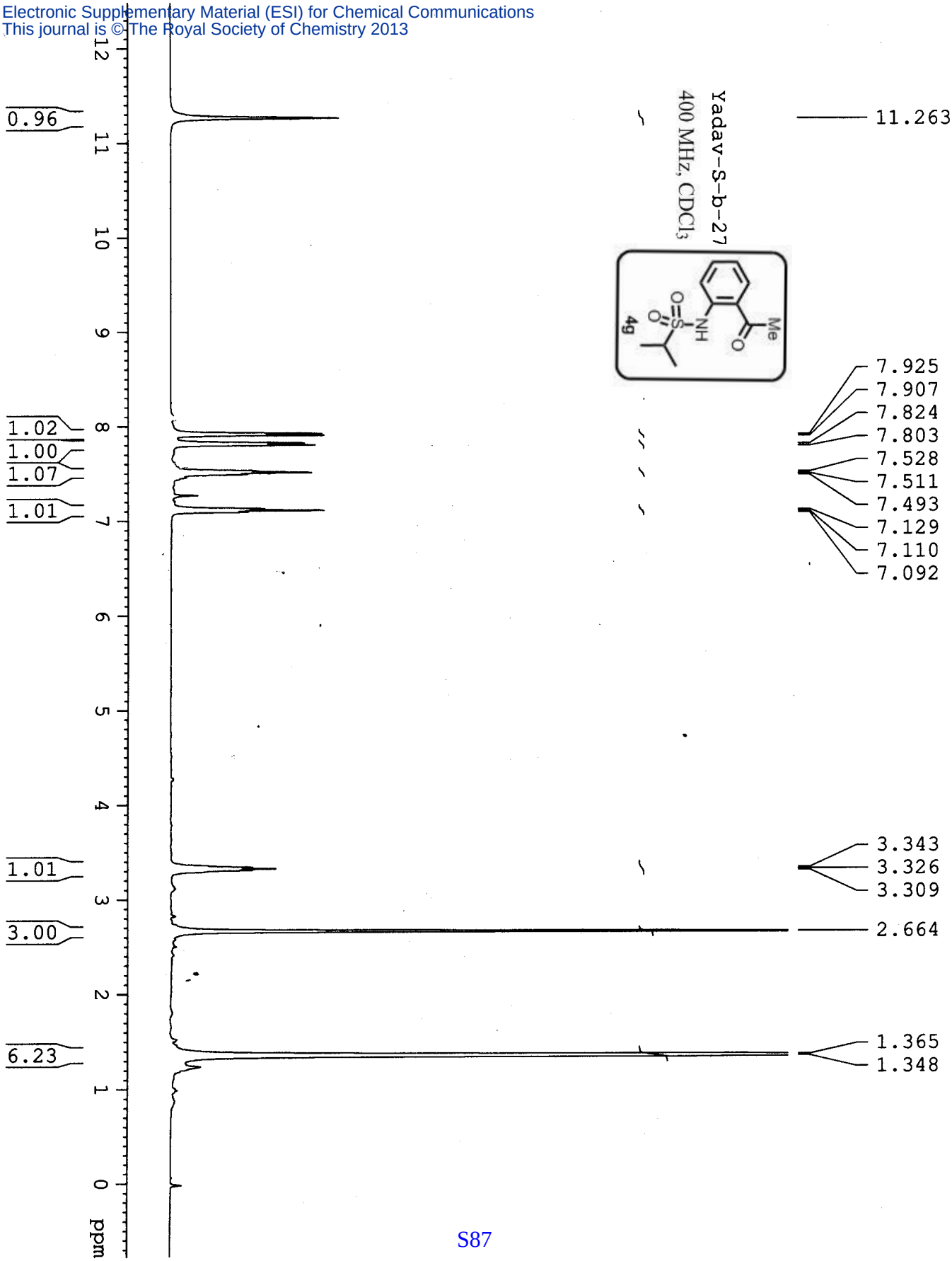

mbc-R4
202.559
139.486
139.433
137.850
134.980
132.037
129.253
128.570
123.022
122.247
118.978
77.323
77.005
76.687
28.079
4d
Me
NH
O=S=O
Cl
ppm
220
200
180
160
140
120
100
80
60
40
20
0

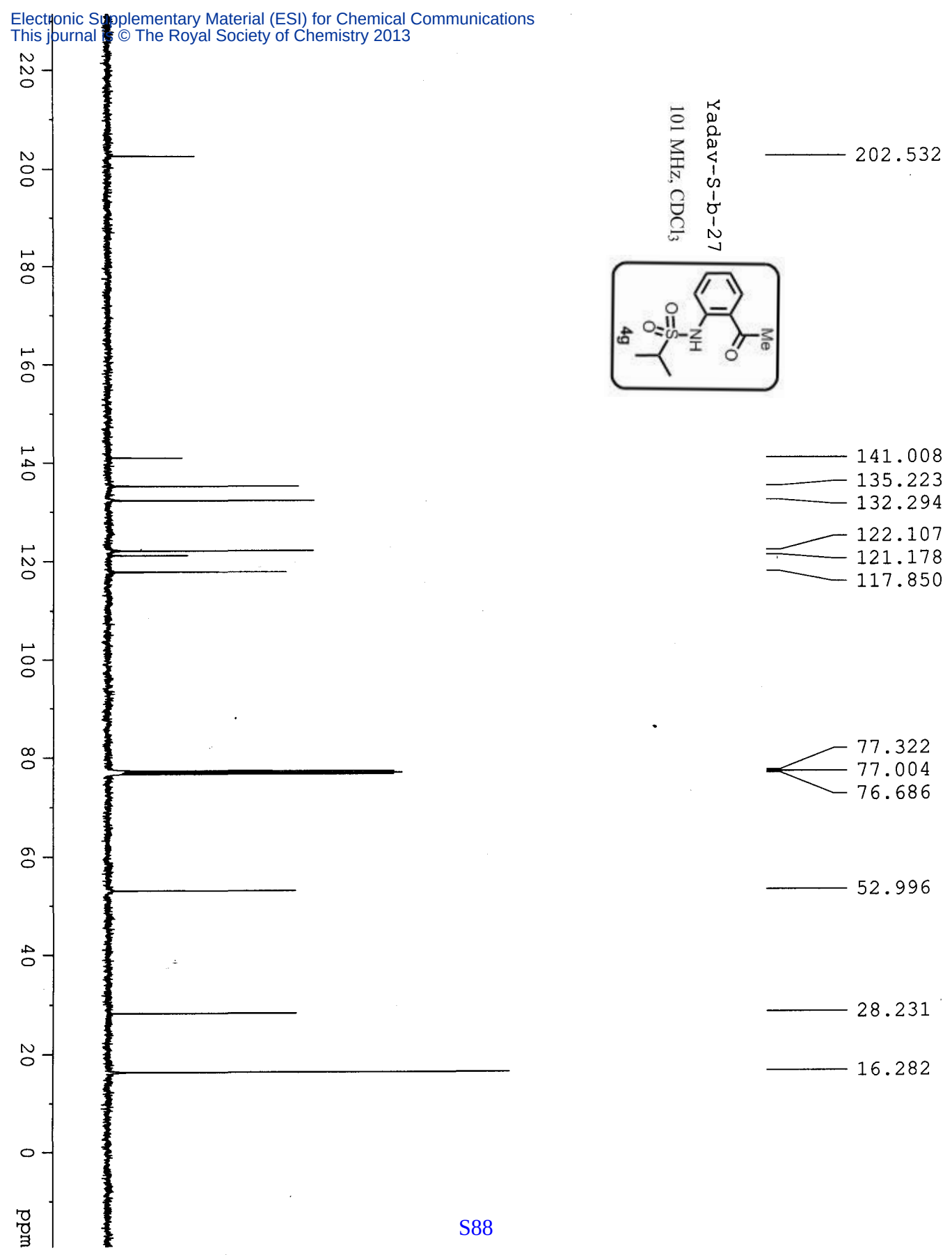

KMR-M-181
11.290
7.929
7.925
7.909
7.905
7.729
7.726
7.708
7.706
7.536
7.533
7.518
7.514
7.512
7.497
7.493
7.135
7.132
7.114
7.097
7.094
3.136
3.122
3.120
3.116
3.112
3.109
3.096
2.645
1.763
1.744
1.731
1.723
1.715
1.705
1.699
1.685
1.407
1.388
1.370
1.351
1.333
1.314
0.861
0.842
0.824
1.00
1.04
1.05
1.07
1.03
2.07
3.16
2.18
2.04
3.54
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
Me
NH
O
S
O
n-Bu
4e
Current Data Parameters
NAME KMR
EXPNO 776
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130209
Time 23.58
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 28.5
DW 62.400 usec
DE 6.00 usec
TE 292.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
SFO1 400.1318754 MHz
F2 - Processing parameters
SI 32768
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

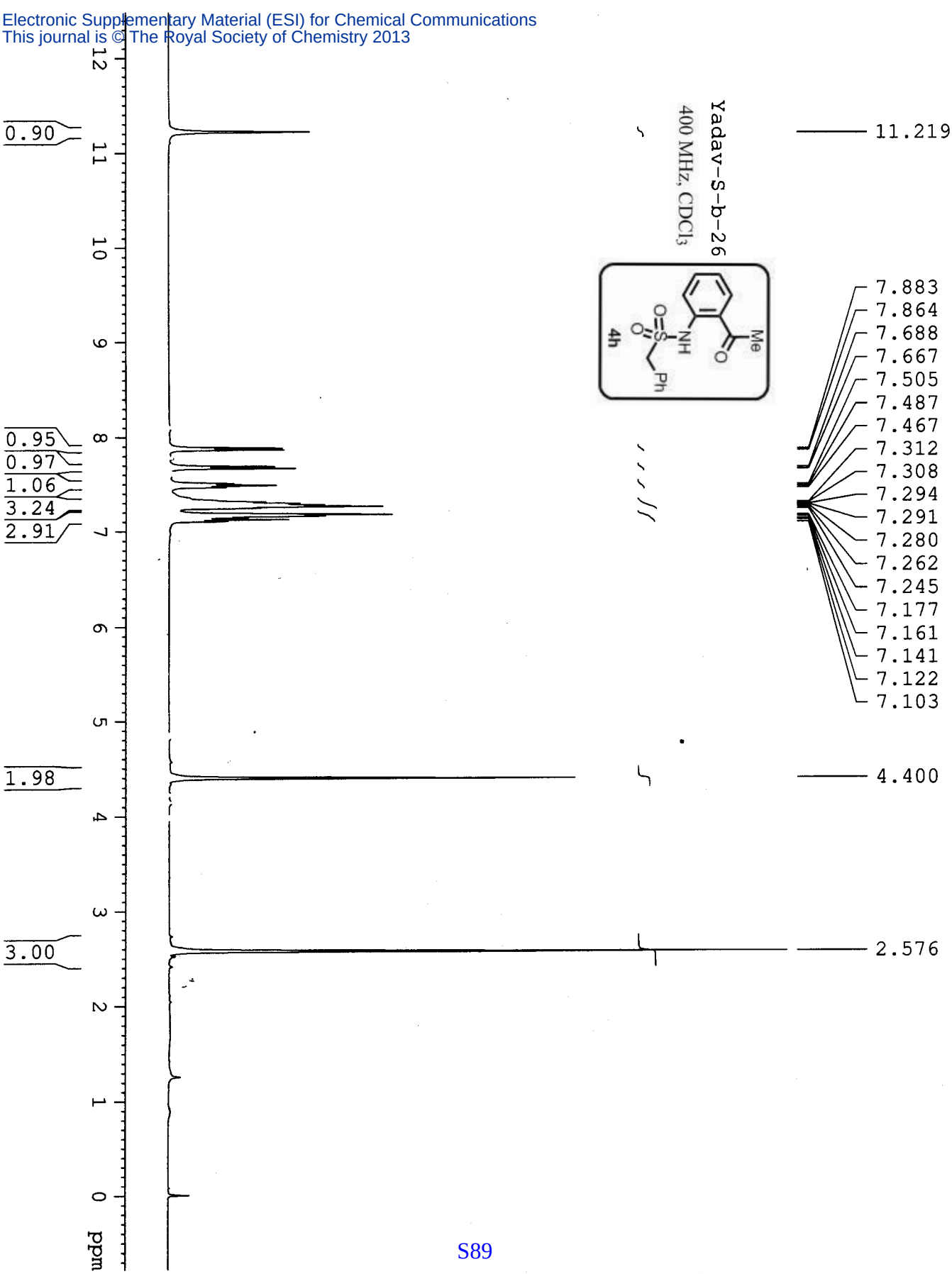

240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
202.64
140.64
135.37
132.49
122.36
121.37
117.63
77.48
77.16
76.84
51.93
28.29
25.33
21.30
13.49
Me
NH
O
O
S
n-Bu
4e
KMR-M-181

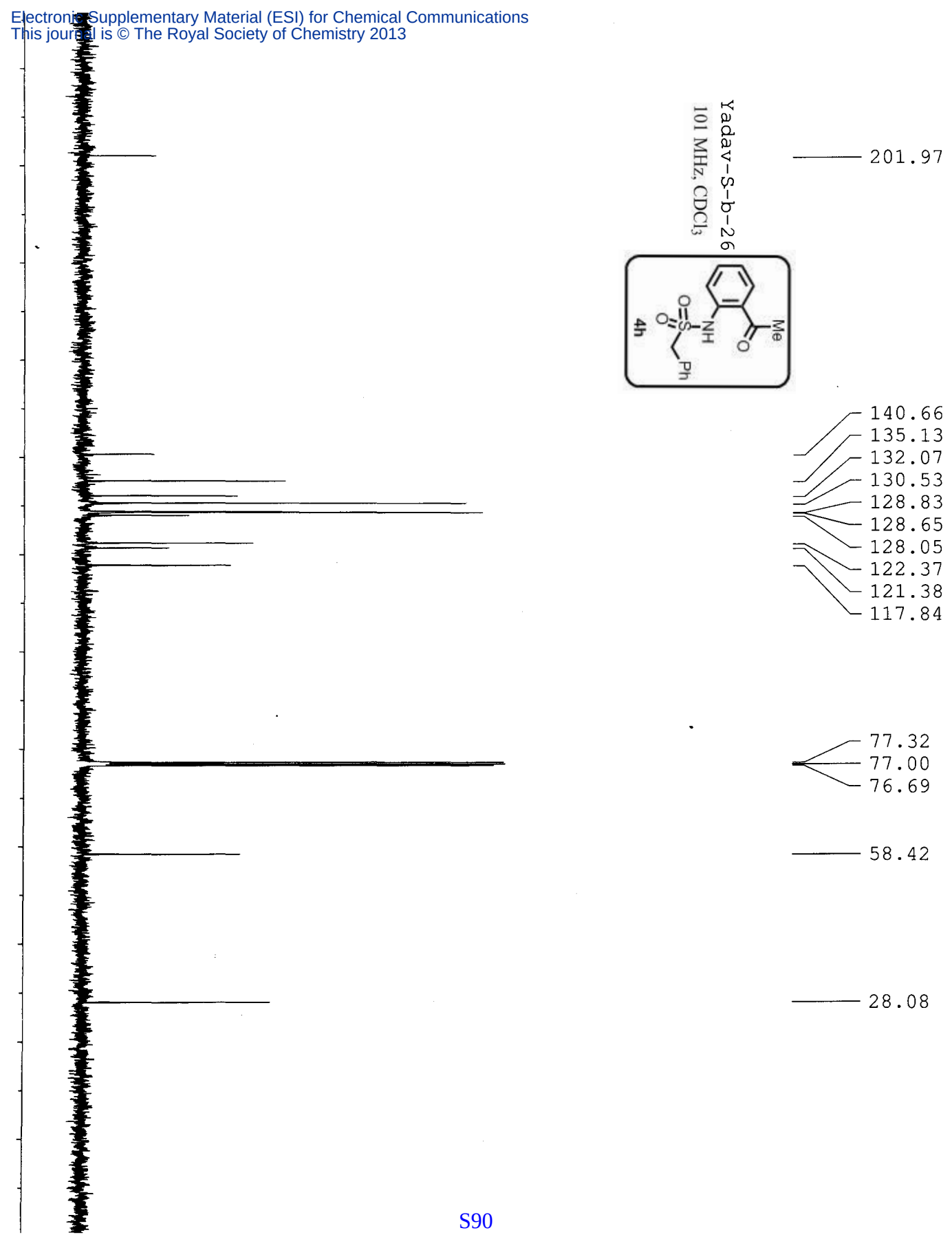


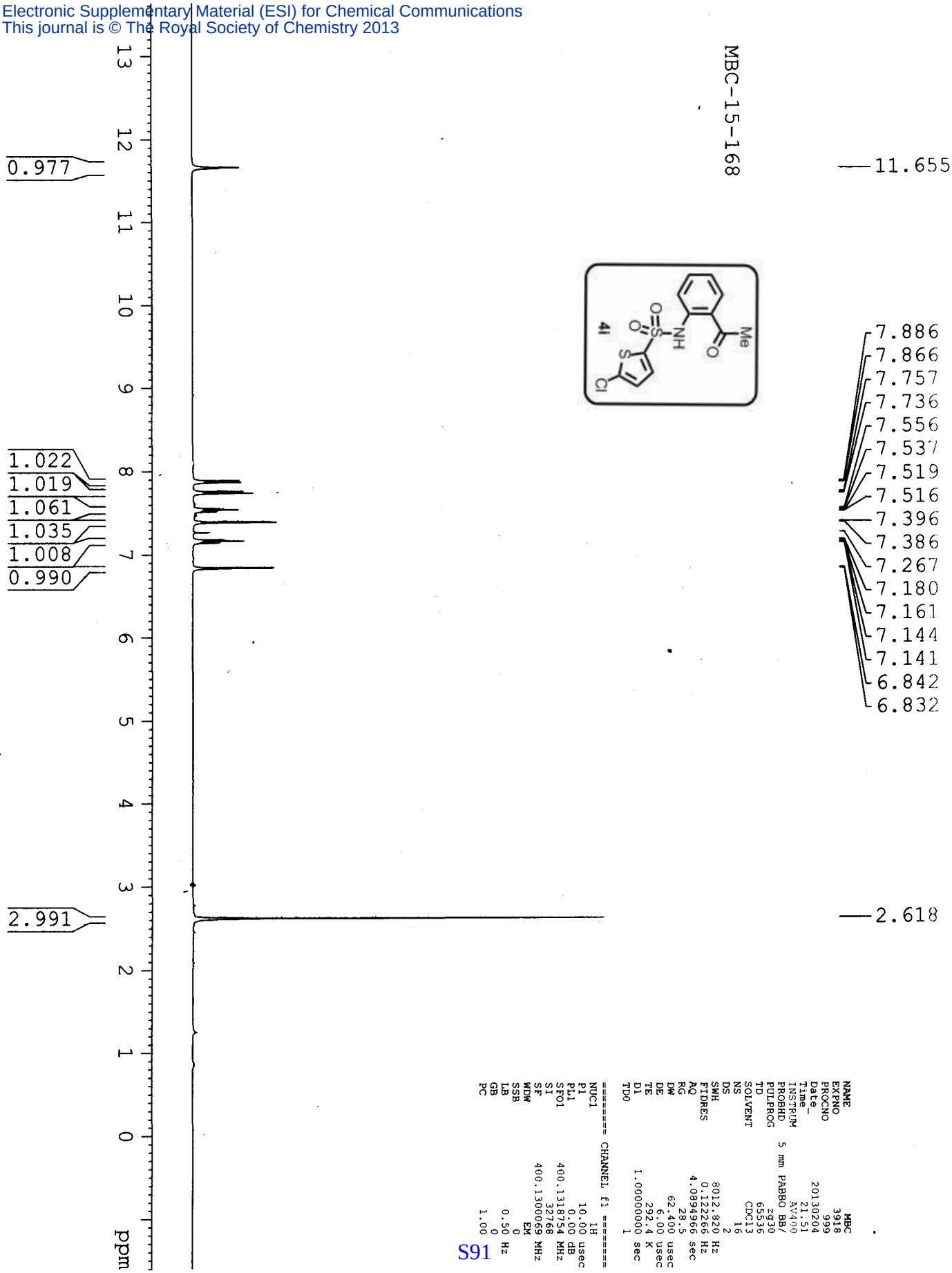

202.66
141.17
135.31
132.45
122.06
121.08
117.69
77.48
77.16
76.84
61.02
28.33
26.16
25.04
24.98
Me
NH
O
O=S
O
4f
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
KMR-M-182
NAME KMR NMR ALL
EXPNO 779
PROCNO 1
Date_ 20130210
Time_ 0.14
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 193
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 20642.5
DW 16.600 usec
DE 6.00 usec
TE 292.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

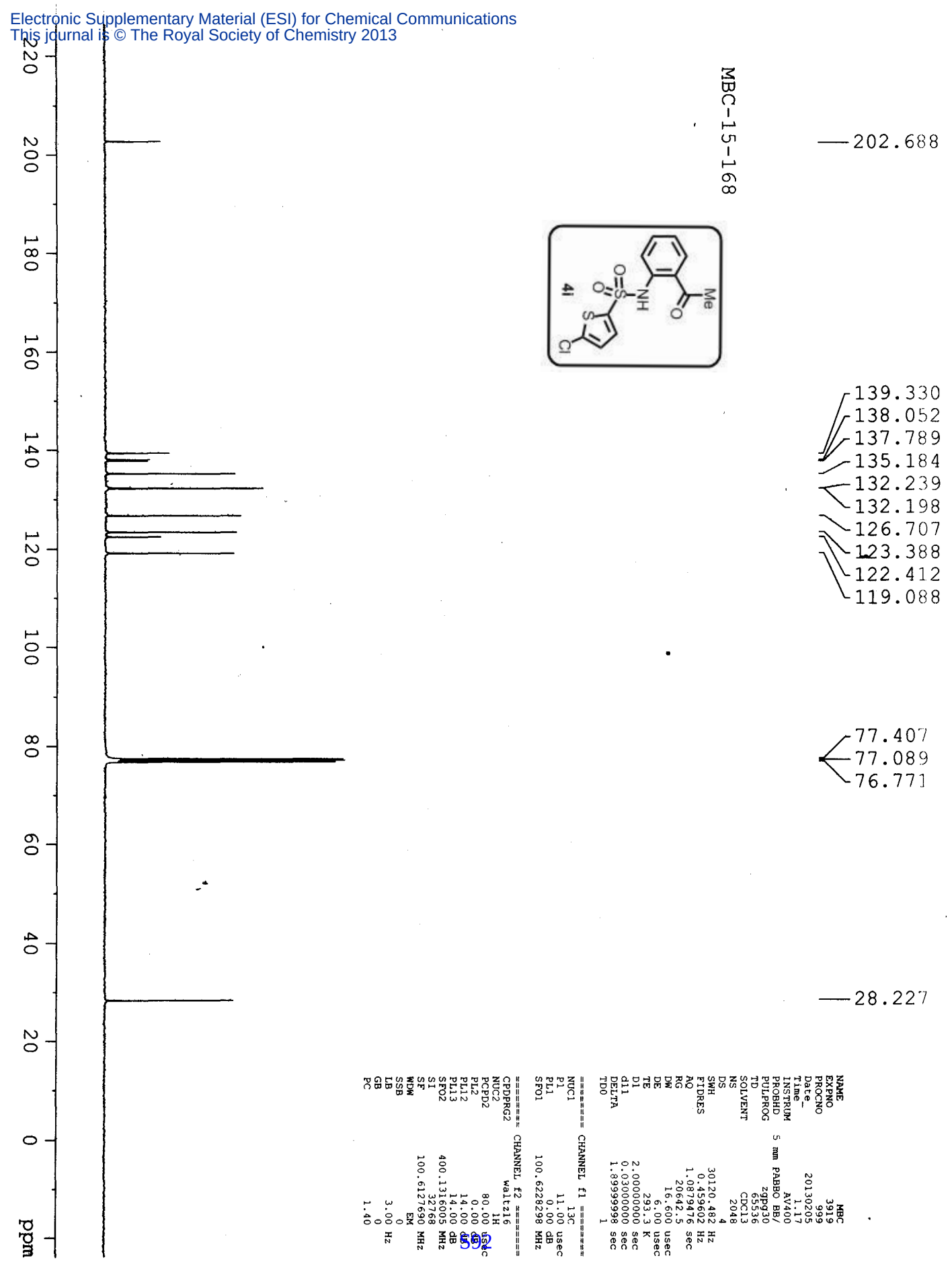

Yadav-S-b-27
400 MHz, CDCl3
4g
NH
Me
11.263
7.925
7.907
7.824
7.803
7.528
7.511
7.493
7.129
7.110
7.092
3.343
3.326
3.309
2.664
1.365
1.348
0.96
1.02
1.00
1.07
1.01
1.01
3.00
6.23
ppm


Yadav-S-b-27
101 MHz, CDCl3
4g
NH
Me
202.532
141.008
135.223
132.294
122.107
121.178
117.850
77.322
77.004
76.686
52.996
28.231
16.282
220
200
180
160
140
120
100
80
60
40
20
0
ppm




Yadav-S-b-26
101 MHz, CDCl3
4h
NH
Me
Ph
201.97
140.66
135.13
132.07
130.53
128.83
128.65
128.05
122.37
121.38
117.84
77.32
77.00
76.69
58.42
28.08


MBC-15-168
4i
Me
NH
O
S
Cl
11.655
7.886
7.866
7.757
7.736
7.556
7.537
7.519
7.516
7.396
7.386
7.267
7.180
7.161
7.144
7.141
6.842
6.832
2.618
0.977
1.022
1.019
1.061
1.035
1.008
0.990
2.991
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm
NAME MBC
EXPNO 3918
PROCNO 999
Date_ 20130204
Time_ 21.51
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 28.5
DW 62.400 usec
DE 6.00 usec
TE 292.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
SFO1 400.1318754 MHz
SI 32768
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00


MBC-15-168
4i
Me
NH
O
S
O
S
Cl
202.688
139.330
138.052
137.789
135.184
132.239
132.198
126.707
123.388
122.412
119.088
77.407
77.089
76.771
28.227
220
200
180
160
140
120
100
80
60
40
20
0
ppm
NAME MBC
EXPNO 3919
PROCNO 999
Date_ 20130205
Time 1.17
INSTRUM AV400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 30120.482 Hz
FIDRES 0.459602 Hz
AQ 1.08719476 sec
RG 20642.5
DW 16.600 usec
DE 6.00 usec
TE 293.3 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

MBC-16-125