Supporting Information

for

α-Aroyloxyaldehydes; scope and limitations as alternatives to α-haloaldehydes for NHC-catalysed redox transformations

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Contents

General Experimental

All reactions involving moisture sensitive reagents were performed under an atmosphere of argon using standard vacuum line techniques and with anhydrous solvents. All glassware was flame dried and allowed to cool under vacuum.

Anhydrous solvents were obtained from a solvent purification system (MBraun, SPS-800). Petrol refers to the fraction of petroleum ether boiling between 40 °C and 60 °C. All *N*-methyl-*O*-aroylhydroxylamine hydrochloride salts were prepared following the procedures outlined by Tomkinson *et al.*[1] α-Ketoester **27** was prepared following the procedure of Zhang *et al.*[2] All other reagents were used directly as supplied without further purification. Ozonolysis was performed using a Fischer Technology Ozone Generator, OZ 500/5.

Flash column chromatography was carried out on silica gel 60 (0.043–0.060 mm) (Merck) in the solvent system stated. Analytical thin layer chromatography was performed on commercially available pre-coated aluminium-backed plates (Merck silica Kieselgel 60 F_{254}). TLCs were visualised either by UV fluorescence (254 nm), or by staining with basic $KMnO_4$ solution.

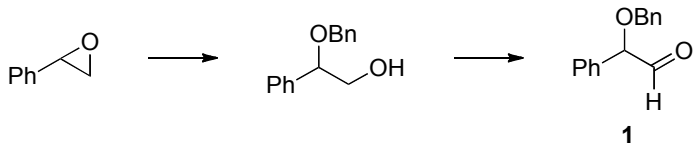
Melting points were recorded on an Electrothermal apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR Spectrometer and analysed either as thin films between NaCl plates (film) or KBr discs (KBr disc) as stated. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}) and only structurally significant peaks are quoted.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz ^{1}H, 75.4 MHz ^{13}C) or a Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometer in the deuterated solvent stated. ^{13}C NMR spectra were recorded with proton decoupling. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to residual

solvent peaks or to $SiMe_4$ as an internal standard ($\delta = 0.00$). Coupling constants, *J*, are quoted in Hz. The abbreviations s, d, dd, dt, td, q and m denote singlet, doublet, doublet of doublets, doublet of triplets, triplet of doublets, quartet and multiplet respectively. The abbreviation Ar is used to denote aromatic.

Mass spectrometric (*m/z*) data was acquired by electrospray ionisation (ESI) or chemical ionisation (CI), either at the University of St Andrews Mass Spectrometry facility ([M+Na] quoted) or at the EPSRC National Mass Spectrometry Service Centre, Swansea ($[M+H]^+$, $[2M+H]^+$, $[M+Na]^+$ or $[2M+Na]^+$ quoted). At the University of St Andrews, low and high resolution ESI MS was carried out on a Micromass LCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, CI MS was carried out on a Micromass Quattro II spectrometer. High resolution ESI was carried out on a Finnigan MAT 900 XLT; a Thermofisher LTQ Orbitrap XL spectrometer was used to obtain high resolution ESI MS for accurate mass determination but also provided fragmentation data for the characterisation of samples. Values are quoted as a ratio of mass to charge in Daltons.

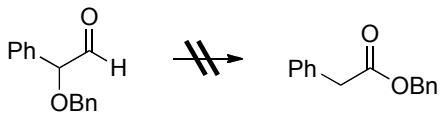
*Preparation of α-benzyloxyaldehyde **1**:*



1

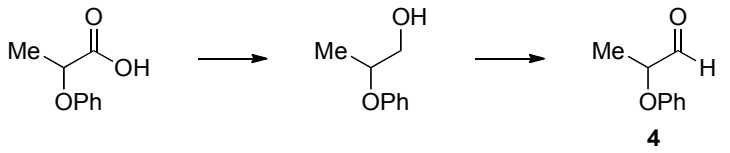
Following the procedure of Schreiner et al.:[3] Styrene oxide (1.14 mL, 10 mmol) was added to a stirred solution of mandelic acid (15.2 mg, 0.10 mmol) and *N*,*N*′-bis-[3,5-bis-(trifluoromethyl)phenyl]-thiourea (50.0 mg, 0.10 mmol) in benzyl alcohol (12.4 mL, 120 mmol) at RT and the mixture stirred for 24 hrs then concentrated *in vacuo*. The mixture was heated at ~70 °C under high vacuum to remove as much benzyl alcohol as possible, then purified by flash column chromatography (silica, 10% EtOAc/petrol) to give 2-(benzyloxy)-2-phenylethanol as a colourless oil (525 mg, 23%). To a stirred solution of 2-(benzyloxy)-2-phenylethanol (456 mg, 2.00 mmol) in CH_2Cl_2 (20 mL) was added Dess-Martin periodinane (1.02, 2.40 mmol) and the mixture stirred at RT for 30 mins (TLC monitoring). Et_2O (20 mL) and sodium thiosulphate (3.5 g, ~11 eq) in sat. aq. $NaHCO_3$ (20 mL) were added and the mixture stirred until both layers became homogenous. The aqueous layer was extracted with Et_2O (3 × 20 mL) then the combined organics were washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried, filtered and concentrated *in vacuo*. Purification by flash column chromatography (silica, petrol → 15% EtOAc/petrol) gave 2-(benzyloxy)-2-phenylacetaldehyde **1** as a colourless oil (237 mg, 52 %) with spectroscopic data in accordance with the literature;[4] δ_H (400MHz, $CDCl_3$) 4.56 (1H, d, *J* 11.8, OC*H*$_A$H$_B$Ph), 4.69 (1H, d, *J* 11.8, OCH$_A$*H*$_B$Ph), 4.81 (1H, d, *J* 1.7, C(2)*H*), 7.27-7.43 (10H, m, *Ph*), 9.64 (1H, d, *J* 1.7, C(1)*H*).

*Procedure for the attempted NHC-mediated redox rearrangement of **1***:



To a flame-dried Schlenk flask under an atmosphere of N_2 was added catalyst **2** (13.7 mg, 0.050 mmol), Cs_2CO_3 (14.7 mg, 0.045 mmol) and toluene or CH_2Cl_2 (2.50 mL) and the mixture stirred at RT for 15 mins. A solution 2-(benzyloxy)-2-phenylacetaldehyde **1** (113 mg, 0.50 mmol) in toluene or CH_2Cl_2 (2.50 mL) was added, the mixture allowed to stir at RT for 16 hrs then concentrated *in vacuo* to give the crude product. ^{1}H NMR analysis showed that in both cases the reaction conversion was <5%.

*Preparation of α-phenoxyaldehyde **4**:*



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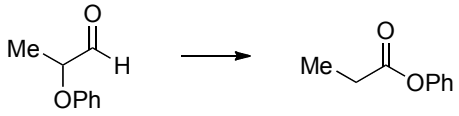
To a stirred solution of 2-phenoxypropionic acid (3.32 g, 20.0 mmol) in Et_2O (50 mL) at 0 °C was added $LiAlH_4$ (2.0M in THF, 18.0 mL, 36.0 mmol) and the mixture stirred at RT for 16 hrs. The reaction was then quenched by the sequential addition of H_2O (1.4 mL), 15% aq. NaOH (1.4 mL) and H_2O (4.2 mL). The resulting mixture was stirred vigorously for 30 mins then filtered through Celite (eluent; MeOH). The filtrate was concentrated *in vacuo*, dissolved in Et_2O then dried, filtered and concentrated *in vacuo* to give a crude product which was purified by flash column chromatography (silica, 10% EtOAc/petrol) to give 2-phenoxypropan-1-ol as a colourless oil (2.80 g, 92%) with spectroscopic data in accordance with the literature;[5] δ_H (300MHz, $CDCl_3$) 1.30 (3H, d, *J* 6.2, C(3)H_3), 3.71-3.80 (2H, m, C(1)H_2), 4.54 (1H, quintet d, *J* 6.2, 3.9, C(2)*H*), 6.95-7.02 (3H, m, *Ph*), 7.29-7.34 (2H, m, *Ph*). To a stirred solution of oxalyl chloride (0.51 mL, 6.00 mmol) in CH_2Cl_2 (40 mL) at −78 °C was added DMSO (0.71 mL, 10.0 mmol) dropwise. After 5 mins, a solution of 2-phenoxypropan-1-ol (761 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) was added dropwise *via* syringe. The solution was stirred at −78 °C for 30 mins then triethylamine (2.79 mL, 20 mmol) was added and the resulting mixture allowed to warm to RT over 30 mins. H_2O (25 mL) was added and the aqueous layer extracted with CH_2Cl_2 (3 × 25 mL). The combined organics were washed with 0.1 M aq. HCl (100 mL), H_2O (100 mL), sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL), then dried, filtered and concentrated *in vacuo* to give 2-phenoxypropanal **4** as a colourless oil (706 mg, 94%) with spectroscopic data in accordance with

the literature;[6] δ_H (300MHz, $CDCl_3$) 1.50 (3H, d, *J* 6.9, C(3)H_3), 4.65 (1H, qd, *J* 6.9, 2.0, C(2)*H*), 6.88-6.92 (2H, m, *Ph*), 6.99 -7.04 (1H, m, *Ph*), 7.27-7.35 (2H, m, *Ph*), 9.74 (1H, d, *J* 2.0, C(1)*H*).

*Procedure for the NHC-mediated redox rearrangement of α-phenoxyaldehyde **4**:*

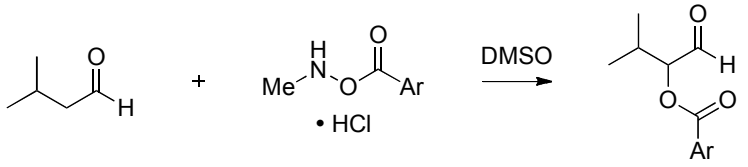


To a flame-dried Schlenk flask under an atmosphere of N_2 was added catalyst **2** (13.7 mg, 0.050 mmol), Cs_2CO_3 (14.7 mg, 0.045 mmol) and toluene (2.50 mL) and the mixture stirred at RT for 15 mins. A solution 2-phenoxypropanal **4** (75 mg, 0.50 mmol) in toluene (2.50 mL) was added, the mixture allowed to stir at RT for 16 hrs, then concentrated *in vacuo* to give the crude product. ^{1}H NMR analysis showed that the reaction conversion was >98% to give phenyl propionate **5** with spectroscopic data in accordance with the literature;[7] δ_H (400MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.6, C(3)H_3), 2.58 (2H, q, *J* 7.6, C(2)H_2), 7.06-7.09 (2H, m, *Ph*), 7.19-7.23 (1H, m, *Ph*), 7.34-7.38 (2H, m, *Ph*).

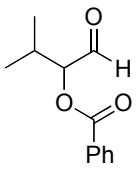
Note - The above reaction also works under identical conditions with CH_2Cl_2 as the solvent.

Preparation of α-aroyloxyaldehydes ***6-9****,* ***12*** *and* ***13***

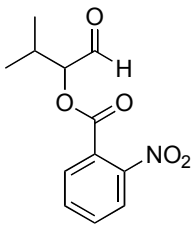
General Procedure A: used for the preparation of ***6–9***



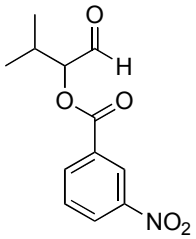
Following the procedure outlined by Tomkinson et al.[1] To a stirred solution of isovaleraldehyde (1.0 eq) in DMSO (0.5 M) at RT was added the requisite *N*-methyl-*O*-acylhydroxylamine hydrochloride salt (1.1–1.2 eq) in one portion, and the mixture stirred at RT for 24–48 hrs. The mixture was then diluted with EtOAc and washed with brine (5×) then dried, filtered and concentrated *in vacuo* to give a crude product which was purified by flash column chromatography using the solvent system stated.



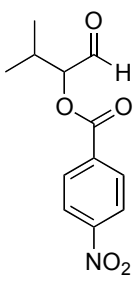
3-Methyl-1-oxobutan-2-yl benzoate 6: Isovaleraldehyde (0.54 mL, 5.00 mmol) and *O*-benzoyl-*N*-methylhydroxylamine hydrochloride (1.13 g, 6.00 mmol) in DMSO (10 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a colourless oil (630 mg, 61%); ν_{max} (film) 2969, 1721 (br), 1602, 1452, 1275, 1112, 711; δ_H (400MHz, $CDCl_3$) 1.12 (3H, d, *J* 6.9, C(3)Me_AMe$_B$), 1.14 (3H, d, *J* 6.9, C(3)Me$_A$$Me_B$), 2.42 (1H, quintet d, *J* 6.9, 4.6, C(3)*H*), 5.08 (1H, dd, *J* 4.6, 0.9, C(2)*H*), 7.47-7.50 (2H, m, *Ph*), 7.59-7.65 (1H, m, *Ph*), 8.10-8.12 (2H, m, *Ph*), 9.66 (1H, d, *J* 0.9, C(1)*H*); δ_C (100MHz, $CDCl_3$) 17.3, 18.9, 29.3, 82.7, 128.4, 129.3, 129.8, 133.5, 166.2, 198.9; *m/z* (NSI) 207 ($[M+H]^+$, 100%); HRMS (NSI) $C_{12}H_{15}O_3$ ($[M+H]^+$ requires 207.1016, found 207.1016 (+0.1 ppm).



3-Methyl-1-oxobutan-2-yl *o*-nitrobenzoate 7: Isovaleraldehyde (0.54 mL, 5.00 mmol) and *N*-methyl-*O*-(*o*-nitrobenzoyl)hydroxylamine hydrochloride (1.28 g, 5.50 mmol) in DMSO (10 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (752 mg, 60%); ν_{max} (film) 2971, 2936, 2879, 1732 (br), 1540, 1352, 1286, 1128, 1075, 736; δ_H (400MHz, $CDCl_3$) 1.01 (3H, d, *J* 6.9, C(3)*Me*$_A$Me$_B$), 1.10 (3H, d, *J* 6.9, C(3)Me$_A$*Me*$_B$), 2.37 (1H, quintet d, *J* 6.9, 4.4, C(3)*H*), 5.11 (1H, dd, *J* 4.4, 0.5, C(2)*H*), 7.66-7.75 (2H, m, *Ar*), 7.86 (1H, dd, *J* 7.4, 1.6, *Ar*), 7.95 (1H, dd, *J* 7.8, 1.4, *Ar*), 9.66 (1H, d, *J* 0.5, C(1)*H*); δ_C (100MHz, $CDCl_3$) 17.0, 19.7, 29.1, 84.0, 124.0, 126.8, 130.3, 132.2, 133.1, 148.1, 165.2, 197.9; *m/z* (NSI) 252 ($[M+H]^+$, 20%), 301 ($[M+MeOH+NH_4]^+$, 100%); HRMS (NSI) $C_{12}H_{14}NO_5$ ($[M+H]^+$ requires 252.0866, found 252.0870 (+1.4 ppm).

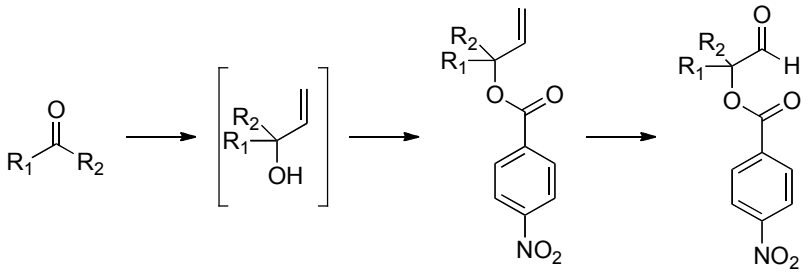


3-Methyl-1-oxobutan-2-yl *m*-nitrobenzoate 8: Isovaleraldehyde (0.27 mL, 2.50 mmol) and *N*-methyl-*O*-(*m*-nitrobenzoyl)hydroxylamine hydrochloride (640 mg, 2.75 mmol) in DMSO (5 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (410 mg, 65%); ν_{max} (film) 2970, 2878, 1731 (br), 1538, 1351, 1267, 1136, 719; δ_H (400MHz, $CDCl_3$) 1.14 (3H, d, *J* 6.9, C(3)*Me*$_A$Me$_B$), 1.17 (3H, d, *J* 6.9, C(3)Me$_A$*Me*$_B$), 2.48 (1H, quintet d, *J* 6.9, 4.6, C(3)*H*), 5.19 (1H, d, *J* 4.6, C(2)*H*), 7.70 (1H, t, *J* 8.0, *Ar*), 8.42 (1H, dt, *J* 7.8, 1.3, *Ar*), 8.47 (1H, ddd, *J* 8.2, 2.3, 1.1, *Ar*), 8.90 (1H, t, *J* 1.9, *Ar*), 9.67 (1H, s, C(1)*H*); δ_C (100MHz, $CDCl_3$) 17.3, 18.9, 29.0, 83.4, 124.7, 127.9, 129.9, 131.3, 135.5, 148.3, 164.0, 197.6; *m/z* (NSI) 252 ($[M+H]^+$, 45%); HRMS (NSI) $C_{12}H_{14}NO_5$ ($[M+H]^+$ requires 252.0866, found 252.0869 (+1.0 ppm).



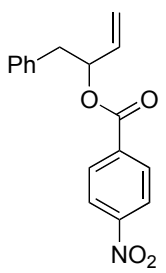
3-Methyl-1-oxobutan-2-yl *p*-nitrobenzoate 9: Isovaleraldehyde (0.27 mL, 2.50 mmol) and *N*-methyl-*O*-(*p*-nitrobenzoyl)hydroxylamine hydrochloride (640 mg, 2.75 mmol) in DMSO (5 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow solid (421 mg, 67%); m.p. 50–52 °C; ν_{max} (KBr) 1728 (br), 1531, 1345, 1280, 1118, 1104, 719; δ_H (400MHz, $CDCl_3$) 1.13 (3H, d, *J* 6.9, C(3)Me_AMe_B), 1.17 (3H, d, *J* 6.9, C(3)Me_AMe_B), 2.47 (1H, quint d, *J* 6.9, 4.5, C(3)*H*), 5.18 (1H, dd, *J* 4.5, 0.5, C(2)*H*), 8.25-8.28 (2H, m, *Ar*), 8.32-8.35 (2H, m, *Ar*), 9.66 (1H, d, *J* 0.5, C(1)*H*); δ_C (100MHz, $CDCl_3$) 17.3, 18.9 , 29.0, 83.4, 123.7, 131.0, 134.7, 150.8, 164.2, 197.3; *m/z* (ASAP) 252 ($[M+H]^+$, 100%); HRMS (ASAP) $C_{12}H_{14}NO_5$ ($[M+H]^+$ requires 252.0866, found 252.0860 (-2.6 ppm).

*General Procedure B: used for the preparation of **12**, **13**, **22** and **24**:*

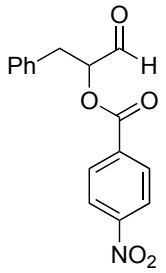


To a stirred solution of the requisite aldehyde or ketone (1.0 eq) in THF (0.5M) at −78 °C was added vinylmagnesium bromide (1.0M in THF, 1.1 eq) dropwise and the resulting solution stirred at −78 °C for 30 mins. 4-nitrobenzoyl chloride (1.2 eq) was then added portionwise over 5 mins and the mixture stirred at RT for 2–18 hrs (until tlc shows complete consumption of the vinyl alcohol). Purification by flash column chromatography afforded the *O*-*p*-nitrobenzoyl vinyl alcohol.

A solution of the requisite *O*-*p*-nitrobenzoyl vinyl alcohol (1.0 eq) in CH_2Cl_2 (0.025M) at –78 °C was subjected to ozonolysis, followed by addition of dimethyl sulfide (2.0 eq). The resulting mixture was concentrated *in vacuo* and the crude product purified by flash column chromatography using the solvent system stated.

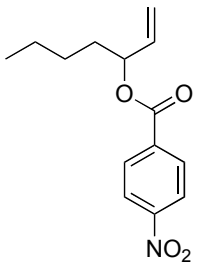


1-phenylbut-3-en-2-yl *p*-nitrobenzoate: Phenylacetaldehyde (0.58 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and *p*-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 10% EtOAc/petrol), the title compound as a yellow oil (1.08 g, 72%); ν_{max} (film) 1725, 1527, 1271, 1116, 1103, 720; δ_H (400MHz, $CDCl_3$) 3.10 (2H, qd, *J*12.7, 6.7, C(1)H_2), 5.25 (1H, dt, *J* 10.5, 1.1, CH=CH_AH$_B$), 5.32 (1H, dt, *J* 17.2, 1.1, CH=CH$_A$$H_B$), 5.71-5.76 (1H, m, C(2)*H*), 5.94 (1H, ddd, *J* 17.2, 10.5, 6.5, C*H*=CH$_2$), 7.22-7.31 (5H, m, *Ph*), 8.15-8.17 (2H, m, *Ar*), 8.26-8.29 (2H, m, *Ar*); δ_C (75MHz, $CDCl_3$) 41.0, 77.0, 118.0, 123.7, 126.9, 128.6, 129.7, 130.8, 135.3, 135.9, 136.5, 150.6, 163.8; *m/z* (ASAP) 315 ($[M+NH_4]^+$, 100%); HRMS (ASAP) $C_{17}H_{19}N_2O_4$ ($[M+NH_4]^+$ requires 315.1339, found 315.1336 (-1.1 ppm).

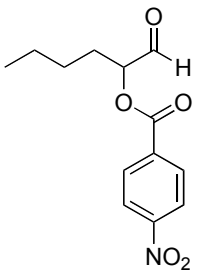


1-oxo-3-phenylpropan-2-yl *p*-nitrobenzoate 12: Ozonolysis of 1-phenylbut-3-en-2-yl *p*-nitrobenzoate (1.35 g, 4.56 mmol) in CH_2Cl_2 (180 mL) at –78 °C, followed by addition of dimethylsulfide (0.67 mL, 9.12 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 30% EtOAc/petrol), the title compound as a white solid (940 mg, 69%); m.p. 64–66 °C; ν_{max} (KBr) 1739, 1721, 1525, 1349, 1293, 1120, 1104; δ_H (400MHz, $CDCl_3$) 3.15 (1H, dd, *J* 14.5, 8.4, C(3)H_AH$_B$), 3.28 (1H, dd, *J* 14.5, 4.9, C(3)H$_A$$H_B$), 5.44 (1H, dd, *J* 8.4, 4.9, C(2)*H*), 7.18-7.27

(5H, m, *Ph*), 8.11 (2H, d, *J* 8.9, *Ar*), 8.22 (2H, d, *J* 8.9, *Ar*), 9.60 (1H, s, C(1)*H*); δ_C (75MHz, $CDCl_3$) 35.2, 79.8, 123.7, 127.4, 128.9, 129.4, 131.0, 134.4, 135.0, 150.9, 164.1, 196.9; *m/z* (NSI) 299 ($[M]^+$, 25%); HRMS (NSI) $C_{16}H_{14}NO_5$ ($[M+H]^+$ requires 300.0869, found 300.0869 (+0.8 ppm).

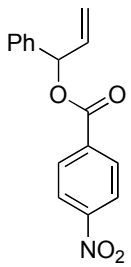


Hept-1-en-3-yl *p*-nitrobenzoate: Valeraldehyde (0.53 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and *p*-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a pale yellow oil (997 mg, 76%); ν_{max} (film) 2958, 2934, 2863, 1725, 1529, 1271, 1115, 1103, 720; δ_H (400MHz, $CDCl_3$) 0.89-0.93 (3H, m, C(6)H_3), 1.33-1.41 (4H, m, C(4)H_2 and C(5)H_2), 1.70-1.86 (2H, m, C(3)H_2), 5.24 (1H, dt, *J* 10.5, 1.1, CH=CH_AH$_B$), 5.34 (1H, dt, *J* 17.2, 1.1, CH=CH$_A$$H_B$), 5.50 (1H, app q, *J* 6.6, C(2)*H*), 5.89 (1H, ddd, *J* 17.2, 10.5, 6.6, C*H*=CH$_2$), 8.20-8.24 (2H, m, *Ar*), 8.27-8.31 (2H, m, *Ar*); δ_C (75MHz, $CDCl_3$) 14.1, 22.6, 27.3, 34.0, 76.8, 117.5, 123.6, 130.8, 136.1, 150.6, 164.1; *m/z* (ASAP) 264 ($[M+H]^+$, 100%); HRMS (ASAP) $C_{14}H_{18}NO_4$ ($[M+H]^+$ requires 264.1230, found 264.1224 (-2.4 ppm).

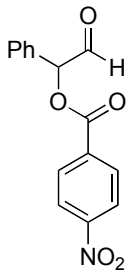


1-oxohexan-2-yl *p*-nitrobenzoate 13: Ozonolysis of hept-1-en-3-yl *p*-nitrobenzoate (790 mg, 3.0 mmol) in CH_2Cl_2 (120 mL) at −78 °C, followed by addition of dimethylsulfide (0.44 mL, 6.0 mmol) gave, after purification by flash

column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (640 mg, 80%); ν_{max} (film) 2959, 2933, 2864, 1731 (br), 1608, 1530, 1350, 1271, 1004, 874, 844, 720; δ_H (400MHz, $CDCl_3$) 0.95 (3H, t, *J* 7.2, C(6)H_3), 1.36-1.54 (4H, m, C(4)H_2 and C(5)H_2), 1.88-2.07 (2H, m, C(3)H_2), 5.31 (1H, dd, *J* 8.3, 4.7, C(2)*H*), 8.26-8.28 (2H, m, *Ar*), 8.31-8.34 (2H, m, *Ar*), 9.64 (1H, d, *J* 0.4, C(1)*H*); δ_C (75MHz, $CDCl_3$) 13.8, 22.4, 27.2, 28.4, 79.6, 123.7, 131.0, 134.6, 150.8, 164.3, 197.2; *m/z* (NSI) 265 ($[M]^+$, 45%); HRMS (NSI) $C_{13}H_{16}NO_5$ ($[M+H]^+$ requires 266.1023, found 266.1026 (+1.1 ppm).

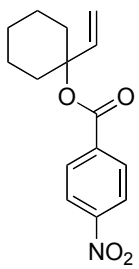


1-phenylallyl *p*-nitrobenzoate: Benzaldehyde (0.51 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and *p*-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a pale yellow solid (1.10 g, 78%); m.p. 38–39 °C; ν_{max} (KBr) 3120, 1719, 1526, 1348, 1270, 1119 1104, 716; δ_H (400MHz, $CDCl_3$) 5.35 (1H, dt, *J* 10.5, 1.2, CH=C$H_A$$H_B$), 5.41 (1H, dt, *J* 17.1, 1.2, CH=C$H_A$$H_B$), 6.15 (1H, ddd, *J* 17.1, 10.5, 6.2, C*H*=CH_2), 6.53 (1H, d, *J* 6.0, C(1)*H*), 7.33-7.47 (5H, m, *Ph*), 8.24-8.31 (4H, m, *Ar*); δ_C (75MHz, $CDCl_3$) 78.0, 117.9, 123.7, 127.3, 128.7, 128.9, 135.8, 138.4, 150.7, 163.8; *m/z* (ASAP) 264 ($[M]^+$, 55%); HRMS (ASAP) $C_{16}H_{13}NO_4$ ($[M]^+$ requires 283.0839, found 283.0838 (-0.4 ppm).

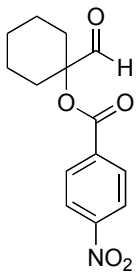


2-oxo-1-phenylethyl *p*-nitrobenzoate 22: Ozonolysis of 1-phenylallyl *p*-nitrobenzoate (567 mg, 2.0 mmol) in CH_2Cl_2 (80 mL) at −78 °C, followed by addition of dimethylsulfide (0.29 mL, 4.00 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a white solid (479 mg, 84%); m.p. 108–110 °C; ν_{max} (KBr) 1747, 1719, 1530,

1342, 1270, 1123, 1104, 720, 700; δ_H (400MHz, $CDCl_3$) 6.34 (1H, s, C(1)*H*), 7.48-7.50 (5H, m, *Ph*), 8.29-8.34 (4H, m, *Ar*), 9.67 (1H, s, C(2)*H*); δ_C (75MHz, $CDCl_3$) 81.6, 123.8, 128.3, 129.6, 130.6, 131.2, 134.6, 151.0, 163.8, 193.0; *m/z* (NSI) 285 ($[M]^+$, 10%); HRMS (NSI) $C_{13}H_{16}NO_5$ ($[M+H]^+$ requires 286.0710, found 286.0712 (+0.7 ppm).



1-vinylcyclohexyl *p*-nitrobenzoate: Cyclohexanone (0.50 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and *p*-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as an off-white solid (720 mg, 52%); m.p. 75–77 °C; ν_{max} (KBr) 2938, 1719, 1524, 1271, 1103, 717; δ_H (400MHz, $CDCl_3$) 1.25-1.32 (1H, m, CH_2), 1.48-1.67 (7H, m, CH_2), 2.31 (2H, br d, *J* 12.7, CH_2), 5.13-5.21 (2H, m, CH=CH_2), 6.13 (1H, dd, *J* 17.6, 11.0, C*H*=CH_2), 8.12 (2H, d, *J* 8.9, *Ar*), 8.20 (2H, d, *J* 8.9); δ_C (100MHz, $CDCl_3$) 22.1, 25.4, 34.9, 84.1, 114.6, 123.6, 130.6, 137.1, 141.2, 150.4, 163.2; *m/z* (ASAP) 276 ($[M+H]^+$, 20%); HRMS (ASAP) $C_{15}H_{18}NO_4$ ($[M+H]^+$ requires 276.1230, found 276.1227 (-1.2 ppm).

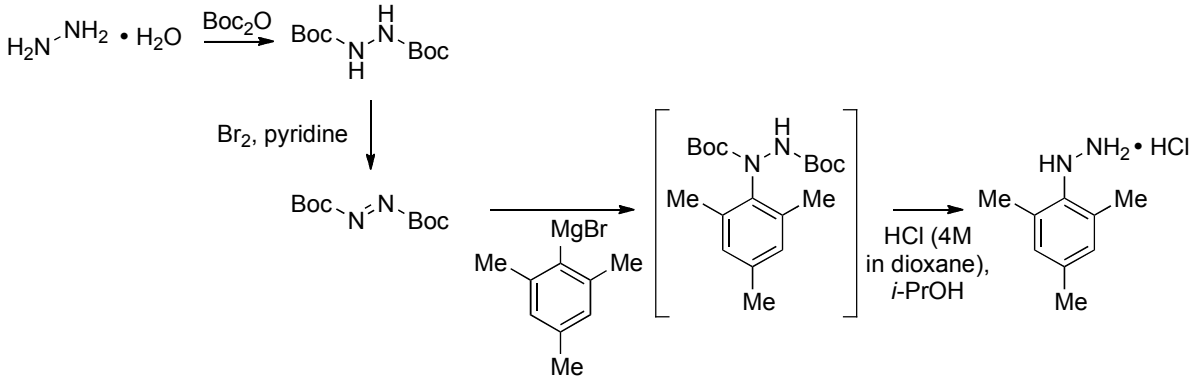


1-formylcyclohexyl *p*-nitrobenzoate 24: Ozonolysis of 1-vinylcyclohexyl *p*-nitrobenzoate (720 mg, 2.62 mmol) in CH_2Cl_2 (105 mL) at –78 °C, followed by addition of dimethylsulfide (0.39 mL, 5.24 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a white solid (510 mg, 70%); m.p. 92–94 °C; ν_{max} (KBr) 2938, 1738, 1710, 1529, 1306, 1119, 1103, 718; δ_H (300MHz, $CDCl_3$) 1.32-1.44 (1H, m, CH_2), 1.60-1.84 (7H, m, CH_2), 2.14-2.19 (2H, m, CH_2), 8.23-8.28 (2H, m, *Ar*), 8.31-8.34 (2H, m, *Ar*), 9.62 (1H, s, C*H*O); δ_C (75MHz, $CDCl_3$) 21.1, 24.8, 29.4, 85.8, 123.7, 131.0, 134.9, 150.9, 163.8, 198.0; *m/z* (ASAP)

278 ([M+H]$^+$, 100%); HRMS (ASAP) $C_{14}H_{16}NO_5$ ([M+H]$^+$ requires 278.1023, found 278.1020 (-1.1 ppm).

*Preparation of catalyst **10***:

(a) Preparation of mesitylhydrazine hydrochloride:



To a stirred solution of di-*tert*-butyl dicarbonate (48.0 g, 220 mmol) in MeOH (50 mL), cooled to −10 °C, was added a solution of hydrazine monohydrate (4.86 mL, 200 mmol) in MeOH (50 mL) dropwise over ~30 mins *via* a pressure-equalised dropping funnel. The resulting mixture was allowed to stir at RT for 3 hrs then concentrated *in vacuo*. The resulting solid was triturated with hexane (250 mL) to give di-tert-butyl hydrazine-1,2-dicarboxylate as a white solid (19.4 g, 84%) with spectroscopic data in accordance with the literature;[8] m.p. 121−122 °C {lit.[8] m.p. 122 °C}; δ_H (300MHz, $CDCl_3$) 1.46 (18H, s, 2 × C*Me*$_3$), 6.26 (2H, br s, 2 × N*H*). [*Note* – Concentration of the mother liquor and repetition of the process generally affords a second crop of equal purity]

Following the procedure of Mäeorg et al.;[9] To a stirred solution of di-*tert*-butyl hydrazine-1,2-dicarboxylate (11.6 g, 50 mmol) and pyridine (8.29 mL, 102 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added a solution of Br_2 (2.82 mL, 55 mmol) in CH_2Cl_2 (20 mL) dropwise over ~15 mins *via*

a pressure-equalised dropping funnel. The resulting solution was stirred at 0 °C for 30 mins then diluted with CH_2Cl_2 (50 mL) and washed with 1M aq. HCl (100 mL), sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL). The organic layer was dried, filtered and concentrated *in vacuo* to give the crude product which was triturated with cold hexane (100 mL) to give di-*tert*-butyl azodicarboxylate as a pale yellow solid (10.0 g, 87%) with spectroscopic data in accordance with the literature; m.p. 85–87 °C {lit.[10] m.p. 90–92 °C}; δ_H (300MHz, $CDCl_3$) 1.63 (18H, s, 2 × C*Me*$_3$). [*Note* – Concentration of the mother liquor and repetition of the process generally affords a second crop of equal purity].

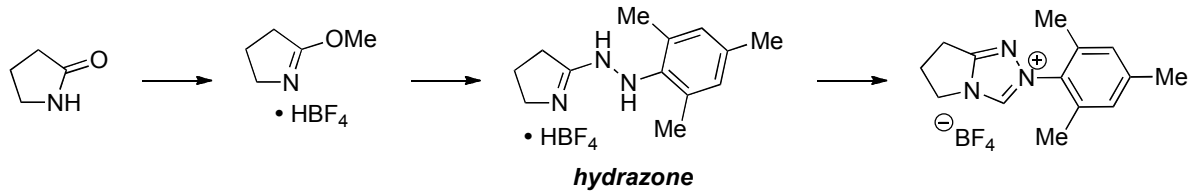
Following the procedure of Demers and Klauber;[11] To a stirred solution of di-*tert*-butyl azodicarboxylate (11.3 g, 49 mmol) in THF (200 mL) at –78 °C was added 2-mesitylmagnesium bromide (1.0 M in Et_2O, 49 mL, 49 mmol) and the resulting solution stirred at –78 °C for 30 mins then quenched with acetic acid (2.9 mL, 50 mmol). The mixture was allowed to warm to RT then H_2O (100 mL) was added and the mixture extracted with Et_2O (3 × 100 mL). The combined organics were washed with brine (100 mL), dried, filtered and concentrated *in vacuo* to give the crude product, which was used directly in the next step.

The crude product was dissolved in *i*-PrOH (125 mL) and HCl (4M in dioxane, 125 mL, 500 mmol) was added. The mixture was heated at reflux for 30 mins then cooled to 0 °C and diluted with Et_2O (125 mL). The precipitate was collected by filtration, then washed with Et_2O (3×) and dried under vacuum for several hours to give mesitylhydrazine hydrochloride as an off-white solid (6.51 g, 71%) with spectroscopic data in accordance with the literature;[12] m.p. 192–194 °C {lit.[12] m.p. 195–197 °C (dec)}; δ_H (300MHz, D_2O) 2.27 (3H, s, C(4)*Me*), 2.36 (6H, s, C(2,6)*Me*), 7.04 (2H, s, C(3,5)*H*).

(b) Procedure for obtaining free based mesitylhydrazine

To a mixture of 1 M aq. NaOH (50 mL) and Et_2O (50 mL) cooled to −10 °C was added mesitylhydrazine hydrochloride (1.87 g, 10 mmol) and the mixture stirred at −10 °C until almost all the solid has dissolved (typically ~15 mins). The layers were separated and the aqueous layer extracted with Et_2O (2 × 25 mL). The combined organics were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give mesitylhydrazine as a pale yellow solid (1.22 g, 81%) which was used immediately without further purification; δ_H (300MHz, $CDCl_3$) 2.17 (6H, s, C(2,6)*Me*), 2.24 (3H, s, C(4)*Me*), 6.81 (2H, s, C(3,5)*H*); [In our hands, mesitylhydrazine was stable for a period of a few hours under an inert atmosphere but readily decomposed upon exposure to air].

(c) Preparation of the triazolium salt **10**



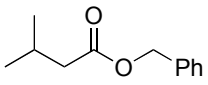
hydrazone

Following the general procedure of Rovis et al.:[13] To a stirred solution of pyrrolidin-2-one (0.52 mL, 6.8 mmol) in anhydrous CH_2Cl_2 (25 mL) was added trimethyloxonium tetrafluoroborate (1.03 g, 6.96 mmol) and the mixture stirred at RT for 18 hrs. Mesitylhydrazine (1.06 g, 6.96 mmol) was then added and the resulting orange solution stirred for a further 18 hours at RT. The mixture was then concentrated *in vacuo* and EtOAc (25 mL) was added. The solid was collected by filtration, washed with EtOAc (3 × 10 mL), then dried under vacuum for several hours to give the hydrazone as an off-white solid (1.06 g, 51%). To the hydrazone was added chlorobenzene (7 mL) and triethylorthoformate (2.89 mL, 17.4 mmol) and the mixture then heated at 120 °C for 72 hours. The mixture was concentrated in vacuo then EtOAc (15 mL) was added and the solid

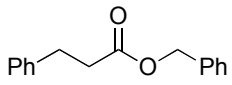
collected by filtration, washed with EtOAc (3 × 10 mL) , then dried under vacuum for several hours to give 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium tetrafluoroborate **10** as a an off-white solid (860 mg, 79%) with spectroscopic data in accordance with the literature;[14] m.p. 174–176 °C; δ_H (400MHz, $CDCl_3$) 2.07 (6H, s, 2 × *o*-Ar*Me*), 2.36 (3H, s, *p*-Ar*Me*), 2.90 (2H, quintet, *J* 7.6, CH_2), 3.25 (2H, t, *J* 7.8, CH_2), 4.70 (2H, t, *J* 7.4, CH_2), 6.99 (2H, s, 2 × *m*-Ar*H*), 9.52 (1H, s, NC*H*N).

Procedure for the NHC-mediated redox esterification of α-aroyloxyaldehydes:

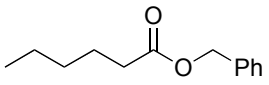
To a flame-dried Schlenk flask under an atmosphere of N_2 was added the appropriate α-aroyloxy aldehyde (1.0 eq), the requisite alcohol (2.0 eq), catalyst **10** (0.20 eq) and THF (0.1M) followed by triethylamine (1.5 eq). The resulting mixture was stirred at RT for 16 hrs then concentrated *in vacuo* to give a crude product, which was purified as described.



Benzyl 3-methylbutanoate 11: **9** (126 mg, 0.50 mmol), benzyl alcohol (0.10 mL, 1.00 mmol), catalyst **10** (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (71 mg, 74%) with spectroscopic data in accordance with the literature;[15] δ_H (400MHz, $CDCl_3$) 0.96 (6H, d, *J* 6.6, C(3)Me_2), 2.08-2.18 (1H, m, C(3)*H*), 2.25 (2H, d, *J* 7.0, C(2)H_2), 5.12 (2H, s, OCH_2Ph), 7.31-7.39 (5H, m, *Ph*).

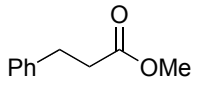


Benzyl 3-phenylpropanoate 14: 12 (75 mg, 0.25 mmol), benzyl alcohol (52 μL, 0.50 mmol), catalyst **10** (15.8 mg, 0.050 mmol) and triethylamine (52 μL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (40 mg, 67%) with spectroscopic data in accordance with the literature;[14] δ_H (400MHz, $CDCl_3$) 2.68 (2H, dd, *J* 8.4, 7.2, C(2)H_2), 2.96 (2H, t, *J* 7.8, C(3)H_2), 5.10 (2H, s, OCH_2Ph), 7.16-7.36 (10H, m, 2 × *Ph*).

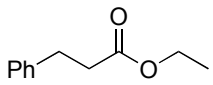


Benzyl hexanoate 15: 13 (133 mg, 0.50 mmol), benzyl alcohol (0.10 mL, 1.00 mmol), catalyst **10** (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (73 mg, 71%) with

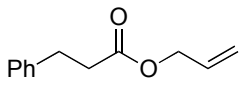
spectroscopic data in accordance with the literature;[16] δ_H (300MHz, $CDCl_3$) 0.89 (3H, t, *J* 6.9, C(6)H_3), 1.27-1.34 (4H, m, C(4)H_2 and C(5)H_2), 1.60-1.70 (2H, m, C(3)H_2), 2.36 (2H, t, *J* 7.6, C(2)H_2), 5.12 (2H, s, OCH_2Ph), 7.30-7.38 (5H, m, *Ph*).



Methyl 3-phenylpropanoate 16: 12 (116 mg, 0.39 mmol), methanol (32 μL, 0.78 mmol), catalyst **10** (24.4 mg, 0.078 mmol) and triethylamine (81 μL, 0.58 mmol) in THF (3.9 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (42 mg, 66%) with spectroscopic data in accordance with the literature;[14] δ_H (400MHz, $CDCl_3$) 2.64 (2H, dd, *J* 8.5, 7.2, C(2)H_2), 2.96 (2H, t, *J* 7.9, C(3)H_2), 3.68 (3H, s, O*Me*), 7.19-7.23 (3H, m, *Ph*).

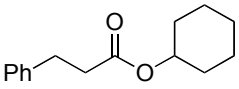


Ethyl 3-phenylpropanoate 17: 12 (150 mg, 0.50 mmol), ethanol (58 μL, 1.00 mmol), catalyst **10** (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (52 mg, 58%) with spectroscopic data in accordance with the literature;[14] δ_H (300MHz, $CDCl_3$) 1.23 (3H, t, *J* 7.1, OCH_2CH_3), 2.62 (2H, dd, *J* 8.5, 7.1, C(2)H_2), 2.95 (2H, t, *J* 7.8, C(3)H_2), 4.12 (2H, q, *J* 7.1, OC$H_2$$CH_3$), 7.17-7.31 (5H, m, *Ph*).

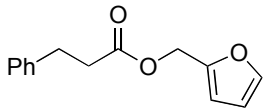


Allyl 3-phenylpropanoate 18: 12 (75 mg, 0.25 mmol), allyl alcohol (34 μL, 0.50 mmol), catalyst **10** (15.8 mg, 0.050 mmol) and triethylamine (52 μL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (45 mg, 95%) with spectroscopic data in accordance with the literature;[17] δ_H (400MHz, $CDCl_3$) 2.68 (2H, dd, *J* 8.5, 7.2, C(2)H_2), 2.98 (2H, t, *J* 7.8, C(3)H_2), 4.59 (2H, dt, *J* 5.7, 1.4, OC$H_2$$CH=CH_2$), 5.23 (1H, dq, *J*

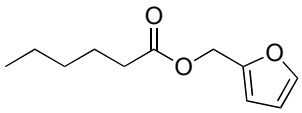
10.4, 1.3, $OCH_2CH=CH_AH_B$), 5.29 (1H, dq, *J* 17.2, 1.5, $OCH_2CH=CH_AH_B$), 5.90 (1H, ddt, *J* 17.2, 10.4, 5.7, $OCH_2CH=CH_2$), 7.19-7.23 (3H, m, *Ph*), 7.28-7.32 (2H, m, *Ph*).



Cyclohexyl 3-phenylpropionate 19: 12 (75 mg, 0.25 mmol), cyclohexanol (53 μL, 0.50 mmol), catalyst **10** (15.8 mg, 0.05 mmol) and triethylamine (52 μL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (13 mg, 22%) with spectroscopic data in accordance with the literature;[18] δ_H (400MHz, $CDCl_3$) 1.13-1.76 (10H, m, 5 × CH_2), 2.52-2.56 (2H, m, C(2)H_2), 2.88 (2H, t, *J* 7.8, C(3)H_2), 4.68 (1H, td, *J* 8.8, 4.1, OC*H*), 7.18-7.23 (3H, m, *Ph*), 7.27-7.31 (2H, m, *Ph*).



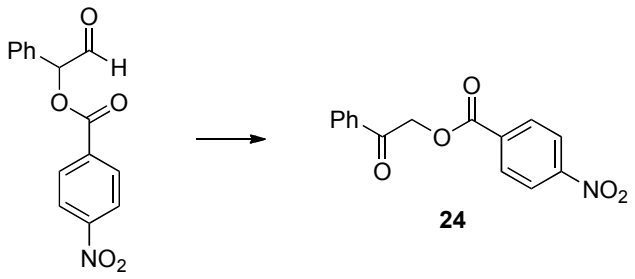
Furan-2-ylmethyl 3-phenylpropanoate 20: 12 (39 mg, 0.13 mmol), furfuryl alcohol (22 μL, 0.26 mmol), catalyst **10** (8.2 mg, 0.026 mmol) and triethylamine (27 μL, 0.195 mmol) in THF (1.3 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (23 mg, 77%) with spectroscopic data in accordance with the literature;[19] δ_H (300MHz, $CDCl_3$) 2.68 (2H, dd, *J* 8.4, 7.1, C(2)H_2), 2.97 (2H, t, *J* 7.8, C(3)H_2), 5.08 (2H, s, OCH_2Ar), 6.37-6.41 (2H, m, *Ar*), 7.18-7.24 (3H, m, *Ph*), 7.26-7.32 (2H, m, *Ph*), 7.44 (1H, dd, *J* 1.8, 0.9, *Ar*).



Furan-2-ylmethyl hexanoate 21: 13 (66 mg, 0.25 mmol), furfuryl alcohol (43 μL, 0.50 mmol), catalyst **10** (15.8 mg, 0.050 mmol) and triethylamine (52 mL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (31 mg, 63%); ν_{max} (film2959, 2933, 2873, 1740, 1243, 1229. 1164, 743; δ_H (300MHz, $CDCl_3$) 0.88 (3H, t, *J* 6.9, C(6)H_3), 1.26-1.31 (4H, m, C(4)H_2 and C(5)H_2), 1.58-1.67 (2H, m, C(3)H_2), 2.32

(2H, t, *J* 7.6, C(2)H_2), 5.06 (2H, s, OCH_2Ar), 6.35 (1H, dd, *J* 3.1, 1.8, *Ar*), 6.39 (1H, d, *J* 3.1, *Ar*), 7.41 (1H, dd, *J* 1.8, 0.7, *Ar*); δ_C (100MHz, $CDCl_3$) 14.0, 22.4, 24.7, 31.4, 34.2, 58.0, 110.6, 110.7, 143.3, 149.8, 173.6; *m/z* (ASAP) 214 ($[M+NH_4]^+$, 45%); HRMS (ASAP) $C_{11}H_{20}NO_3$ ($[M+NH_4]^+$ requires 214.1438, found 214.1432 (-2.7 ppm).

*Procedure for the base-mediated rearrangement of **22**:*



22 **24**

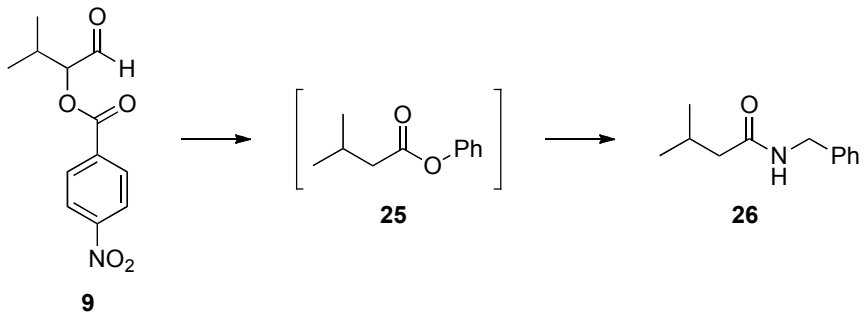
(a) under NHC-mediated redox esterification conditions:

To a flame-dried Schlenk flask under an atmosphere of N_2 was added **22** (71 mg, 0.25 mmol), benzyl alcohol (52 μL, 0.50 mmol), catalyst **10** (15.8 mg, 0.050 mmol), THF (2.5 mL) and triethylamine (52 μL, 0.375 mmol). The resulting mixture was stirred at RT for 16 hrs then concentrated *in vacuo* to give a crude product. ^{1}H NMR analysis showed that 2-oxo-2-phenylethyl 4-nitrobenzoate **23** was the major product of the reaction.

(b) with triethylamine only:

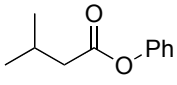
To a stirred solution of **22** (71 mg, 0.25 mmol) in THF (2.5 mL) at RT was added triethylamine (52 μL, 0.375 mmol, 1.5 eq) and the mixture stirred at RT for 3 hrs then concentrated *in vacuo* to give 2-oxo-2-phenylethyl 4-nitrobenzoate **24** as a white solid (71 mg, quant.) with spectroscopic data in accordance with the literature;[20] m.p. 120–121 °C;{lit.[21] m.p. 124–125 °C}; δ_H (400MHz, $CDCl_3$) 5.65 (2H, s, CH_2), 7.51-7.56 (2H, m, *Ph*), 7.63-7.68 (1H, m, *Ph*), 7.96-7.98 (2H, m, *Ph*), 8.33 (4H, app s, *Ar*).

*Procedure for the NHC-mediated redox amination of **9** to give **26***:



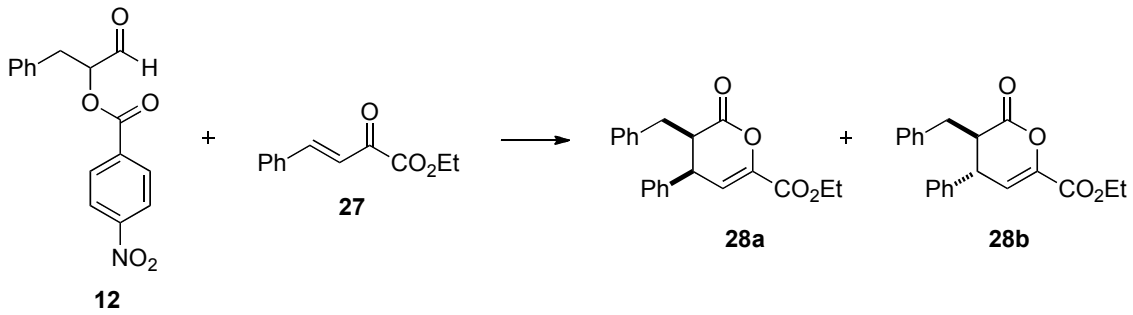
To a flame-dried Schlenk flask under an atmosphere of N_2 was added **9** (63 mg, 0.25 mmol), phenol (47 mg, 0.50 mmol), catalyst **10** (15.8 mg, 0.050 mmol), THF (2.5 mL) and triethylamine (52 μL, 0.375 mmol). The resulting mixture was stirred at RT for 16 hrs then benzylamine (68 μL, 0.625 mmol, 2.5 eq) and DMAP (6 mg, 0.05 mmol) were added and the mixture stirred at RT for a further 48 hrs then concentrated *in vacuo*. Purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol) gave *N*-benzyl-3-methylbutanamide **26** as a colourless oil (30 mg, 63%) with spectroscopic data in accordance with the literature;[22] δ_H (400MHz, $CDCl_3$) 0.89 (6H, d, *J* 6.4, C(3)Me_2), 1.99-2.01 (2H, m, C(2)H_2), 2.03-2.13 (1H, m, C(3)*H*), 4.37 (2H, d, *J* 5.7, NCH_2Ph), 5.76 (1H, br s, N*H*), 7.18-7.21 (3H, m, *Ph*), 7.24-7.28 (2H, m, *Ph*).

N.B. It was also possible to isolate the intermediate phenyl ester in moderate yield:

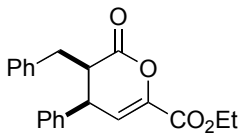


Phenyl 3-methylbutanoate 25: Concentration *in vacuo* after the first step, and purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), gave the title compound as a colourless oil (18 mg, 40%) with spectroscopic data in accordance with the literature;[23] δ_H (400MHz, $CDCl_3$) 0.99 (6H, d, *J* 6.7, C(3)Me_2), 2.12-2.23 (1H, m, C(3)*H*), 2.36 (2H, d, *J* 7.2, C(2)H_2), 7.00 (2H, dd, *J* 8.6, 1.1, *o*-Ph), 7.12-7.18 (1H, m, *p*-Ph), 7.28-7.33 (2H, m, *m*-Ph).

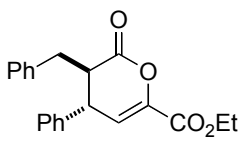
Procedure for the formal [4+2] cycloaddition reaction:



To a stirred solution of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate **27** (20.4 mg, 0.10 mmol), **12** (47 mg, 0.157 mmol) and catalyst **10** (9.9 mg, 0.031 mmol) in THF (1.5 mL) at RT was added triethylamine (21 μL, 0.15 mmol) and the mixture stirred at RT for 16 hrs then concentrated *in vacuo*. Purification by flash column chromatography (silica, 10% EtOAc/petrol) gave an inseparable 69:31 diastereoisomeric mixture of dihydropyranones **28a** and **28b** as a colourless oil (18 mg, 54% combined yield);[24]



(3*RS*,4*RS*)-Ethyl 3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate 28a *(major diastereoisomer)*: δ_H (400MHz, $CDCl_3$) 1.35 (3H, t, *J* 7.1, OCH_2CH_3), 2.42 (1H, dd, *J* 15.8, 10.6, CH_AH_BPh), 3.26-3.31 (2H, m, CH_AH_BPh and C(3)*H*), 3.64 (1H, t, *J* 6.8, C(2)*H*), 4.32 (2H, q, *J* 7.1, OCH_2CH_3), 6.67 (1H, d, *J* 6.8, C(5)*H*), 7.02-7.09 (4H, m, *Ph*), 7.25-7.36 (6H, m, *Ph*); δ_C (75MHz, $CDCl_3$) 14.3, 32.2, 40.7, 44.9, 62.1, 118.6, 126.8, 127.5, 128.5, 128.7, 129.0, 129.3, 135.9, 138.2, 142.6, 160.6, 168.7.



(3*RS*,4*SR*)-Ethyl 3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate 28b *(minor diastereoisomer)*: δ_H (400MHz, $CDCl_3$) 1.37 (3H, t, *J* 7.1, OCH_2CH_3), 2.92 (1H, dt, *J* 12.6, 6.2, C(3)*H*), 3.05-3.14 (2H, m,

C*H*$_2$Ph), 3.60-3.65 (1H, m, C(2)*H*), 4.35 (2H, obsc q, OC*H*$_2$CH$_3$), 6.52 (1H, d, *J* 5.0, C(5)*H*), 7.02-7.09 (2H, m, *Ph*), 7.16 (2H, m, *Ph*), 7.25-7.36 (6H, m, *Ph*); δ_C (75MHz, $CDCl_3$) 14.3, 35.7, 41.5, 47.8, 62.2, 116.4, 127.2, 128.1, 128.4, 128.8, 129.3, 129.4, 135.6, 137.4, 142.6, 160.6, 168.2.

m/z (NSI) 278 ($[M+NH_4]^+$, 100%); HRMS (NSI) $C_{21}H_{24}NO_4$ ($[M+NH_4]^+$ requires 354.1700, found 354.1704 (+1.2 ppm).

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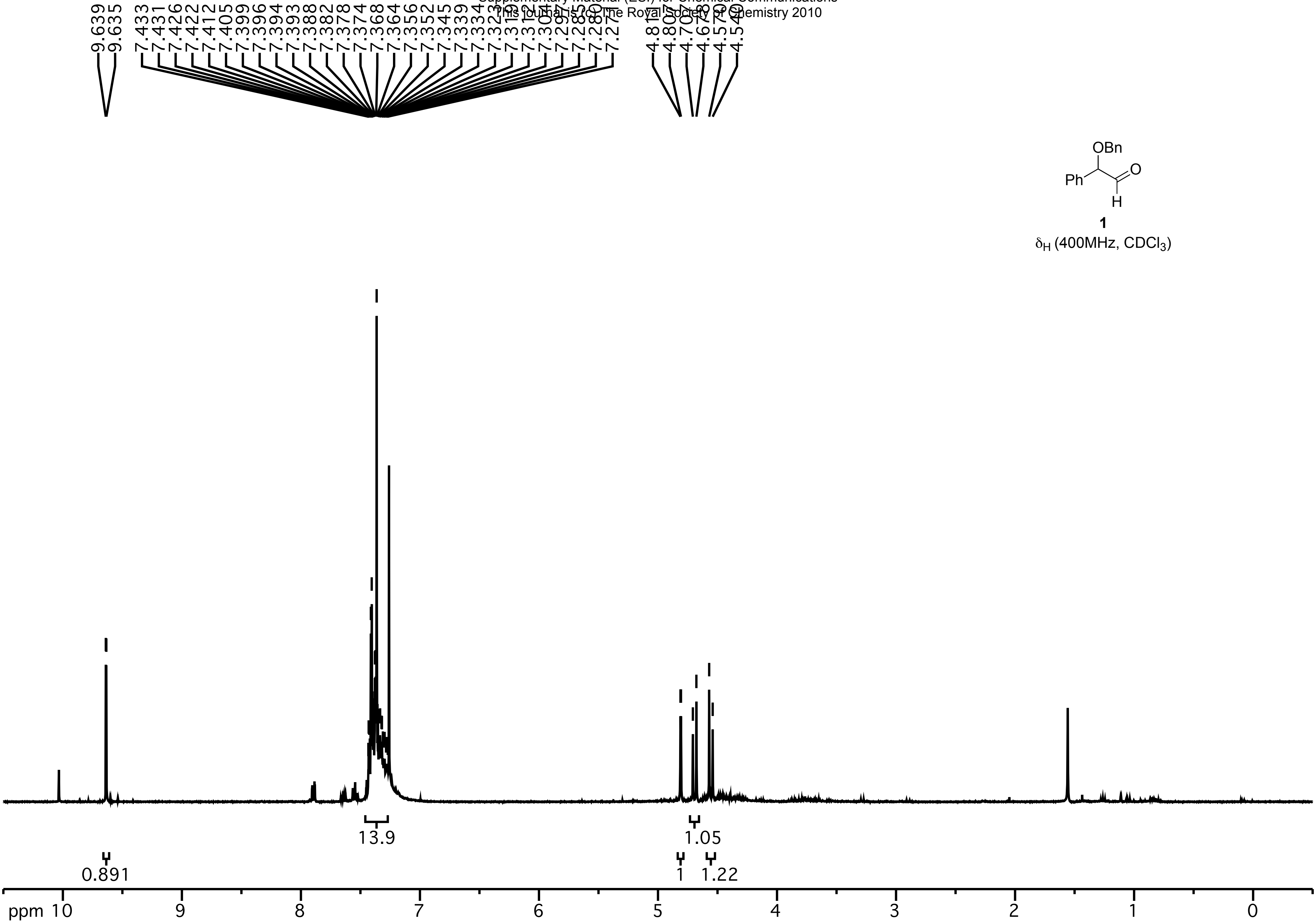
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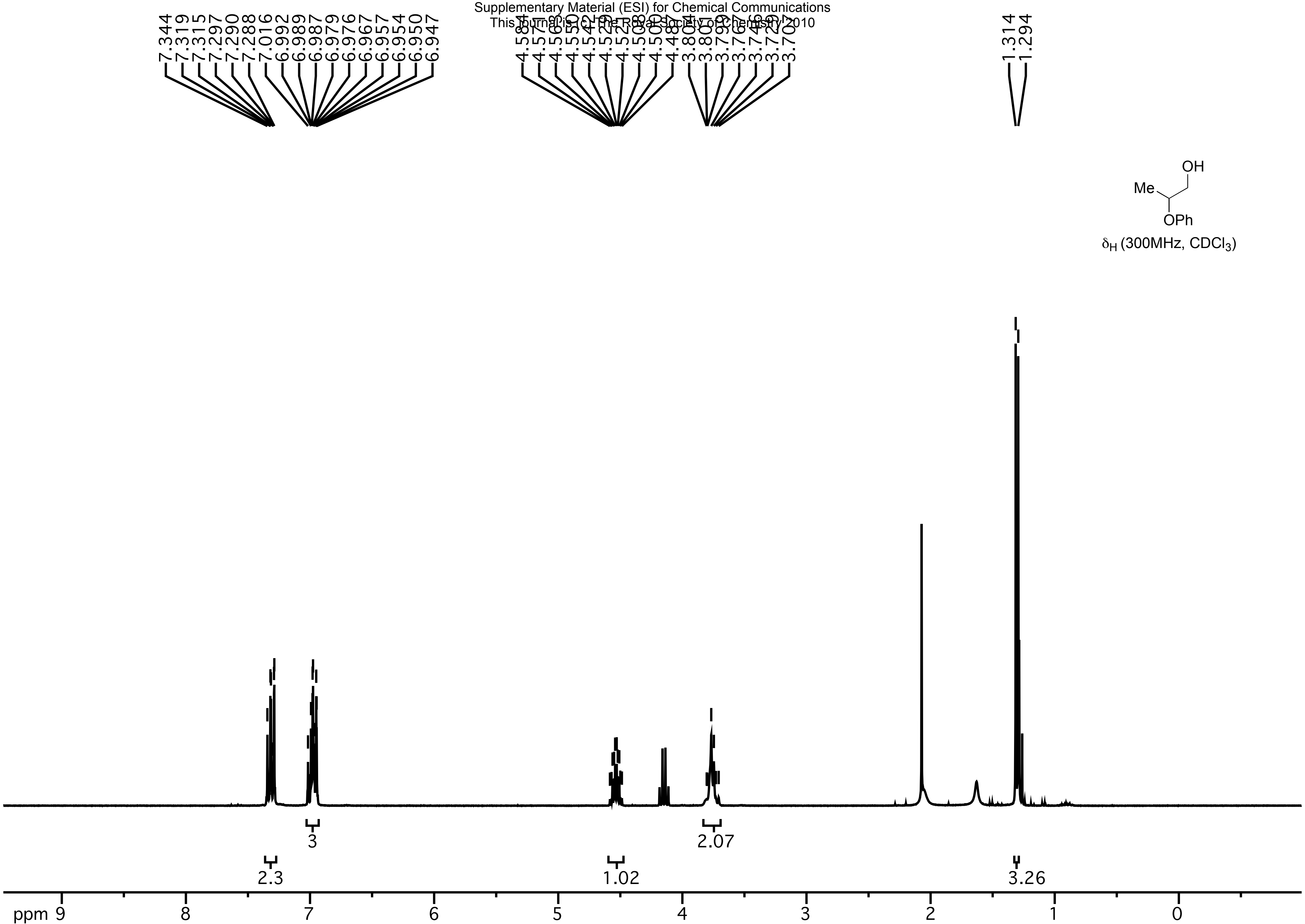

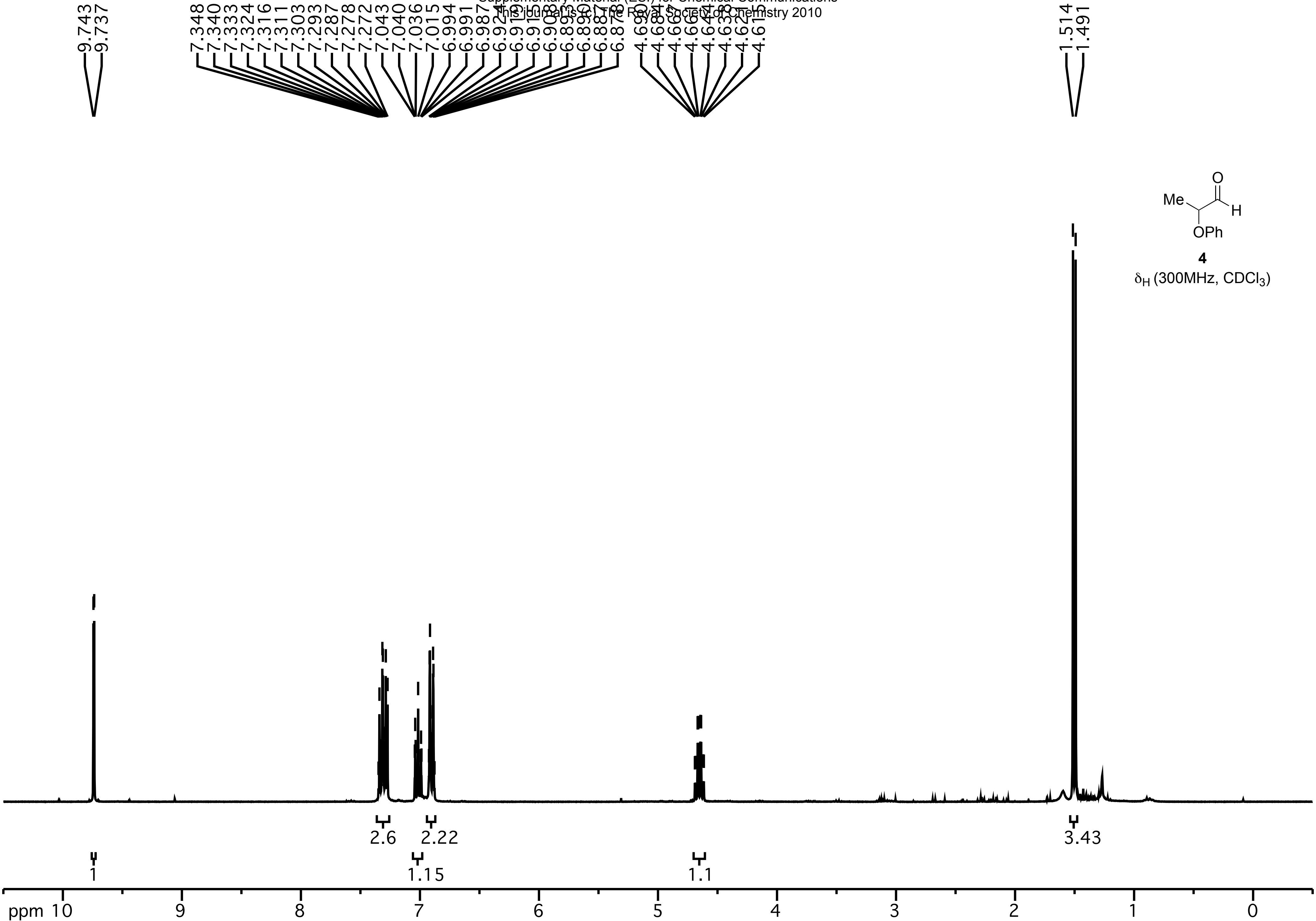

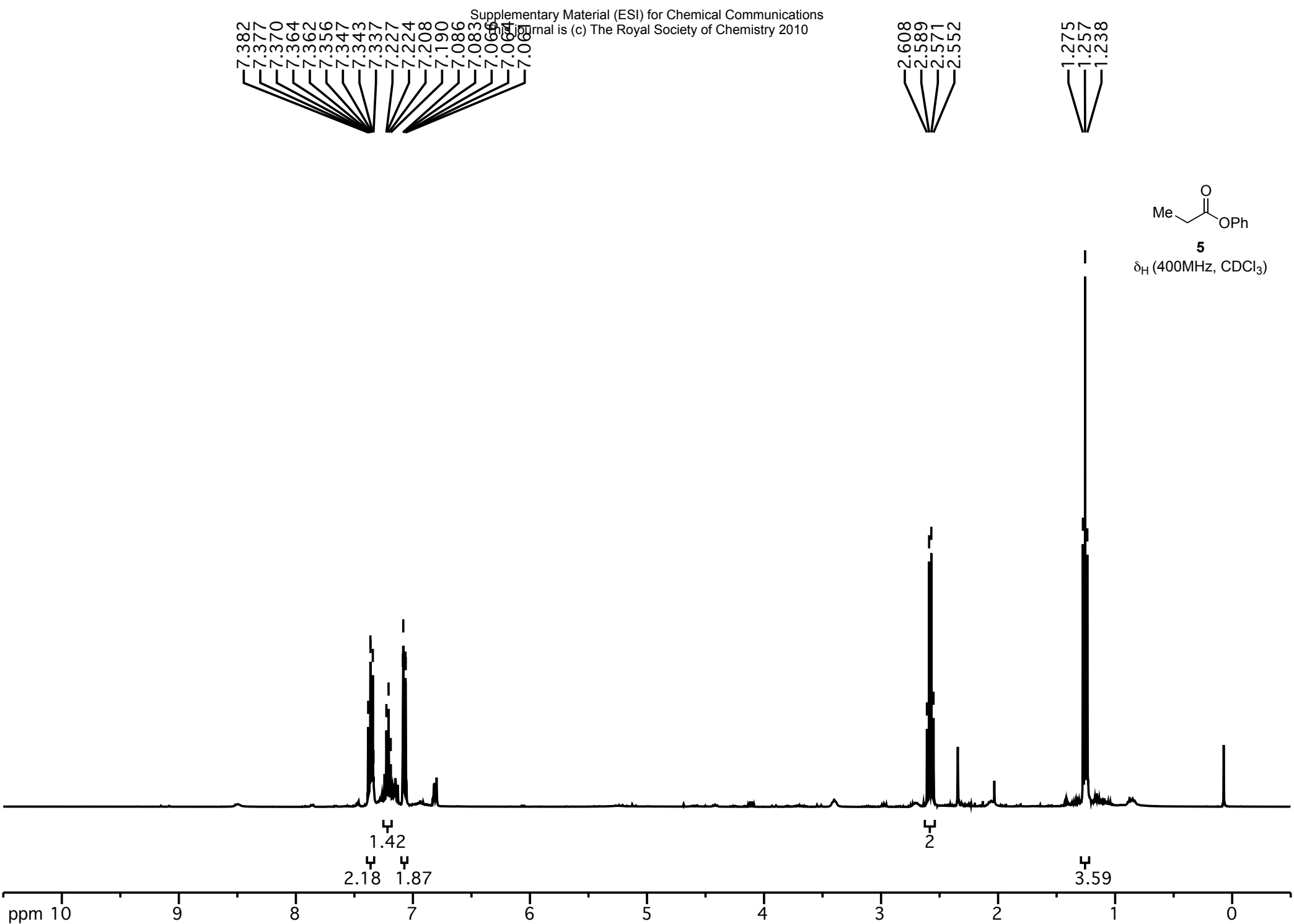
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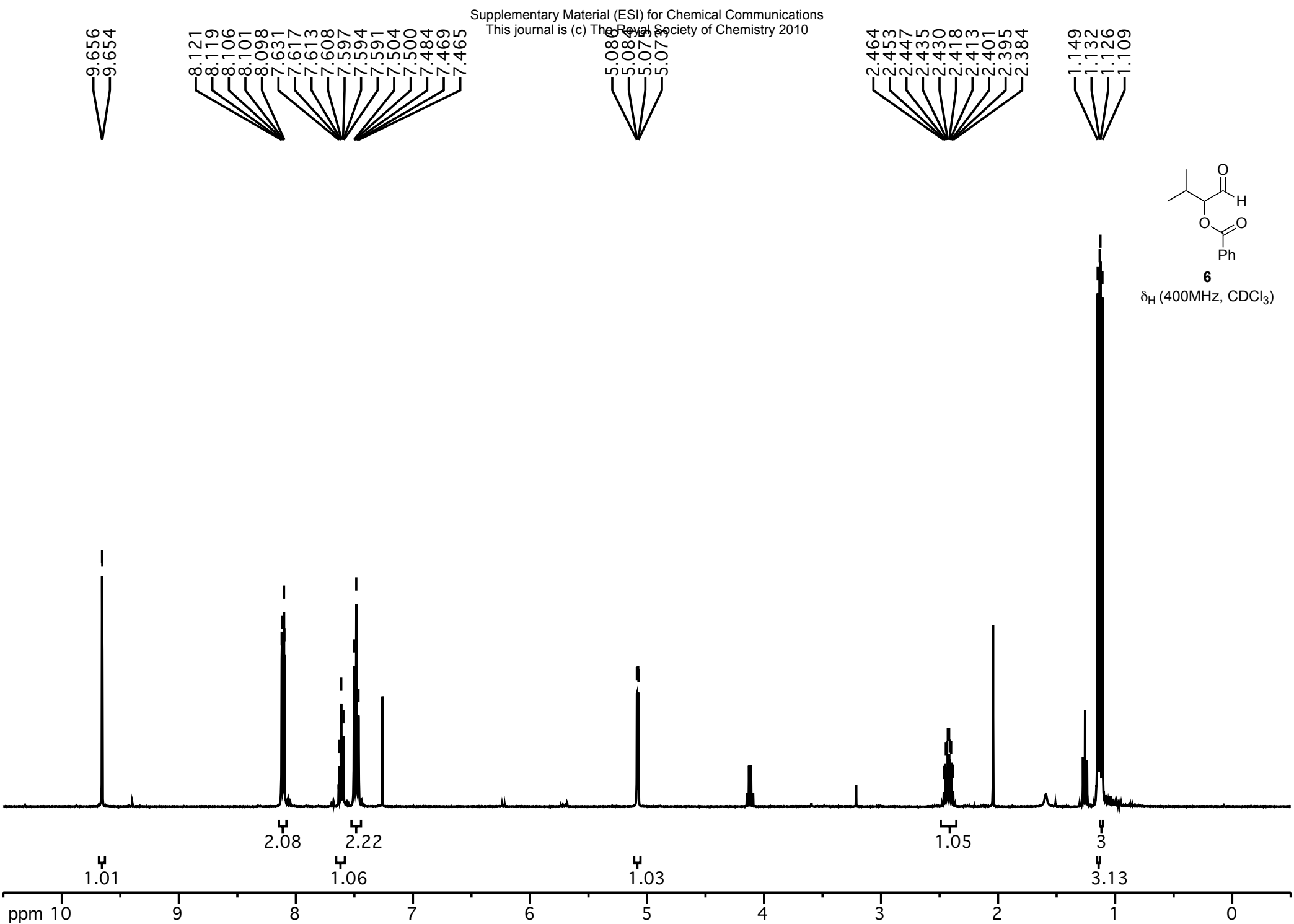
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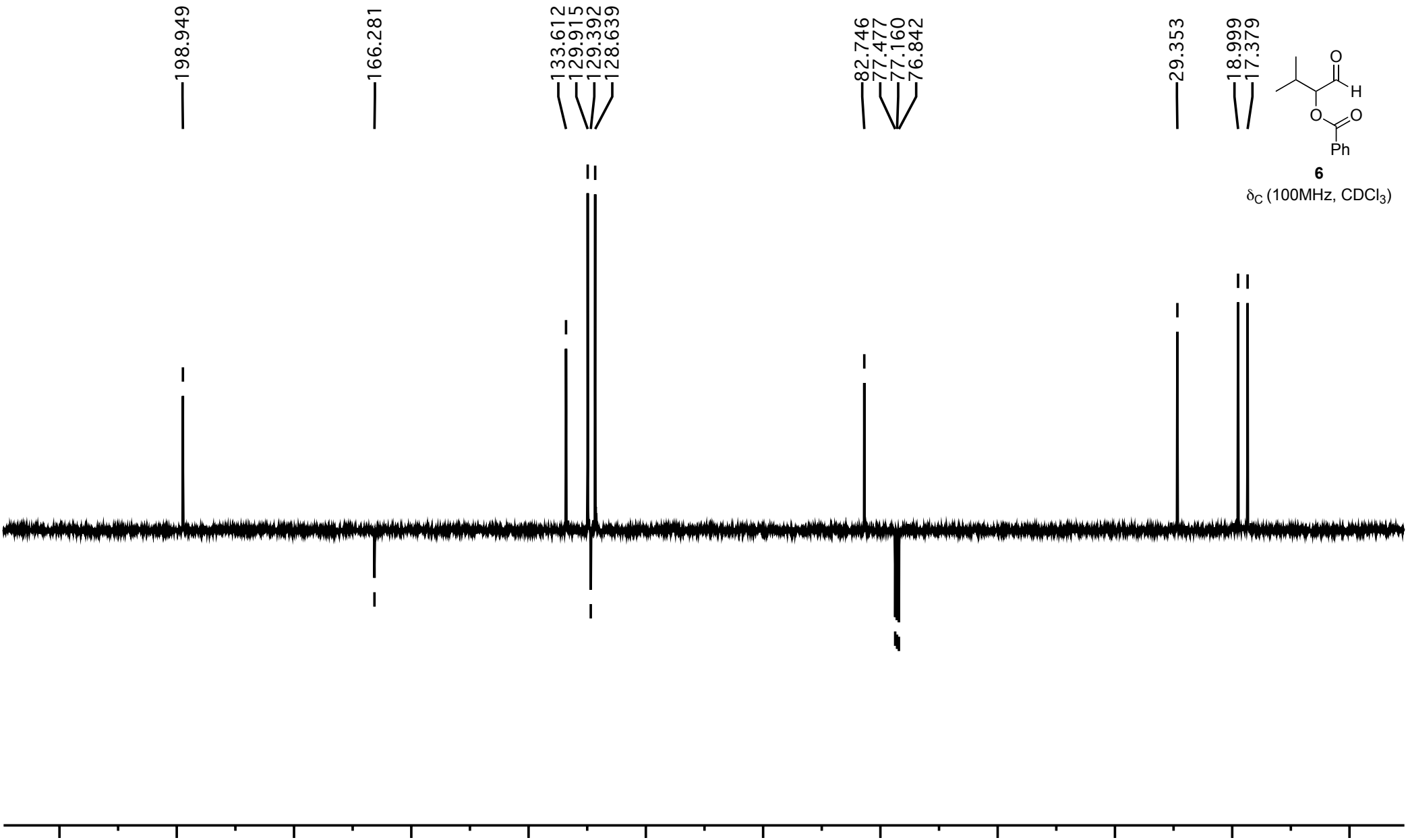
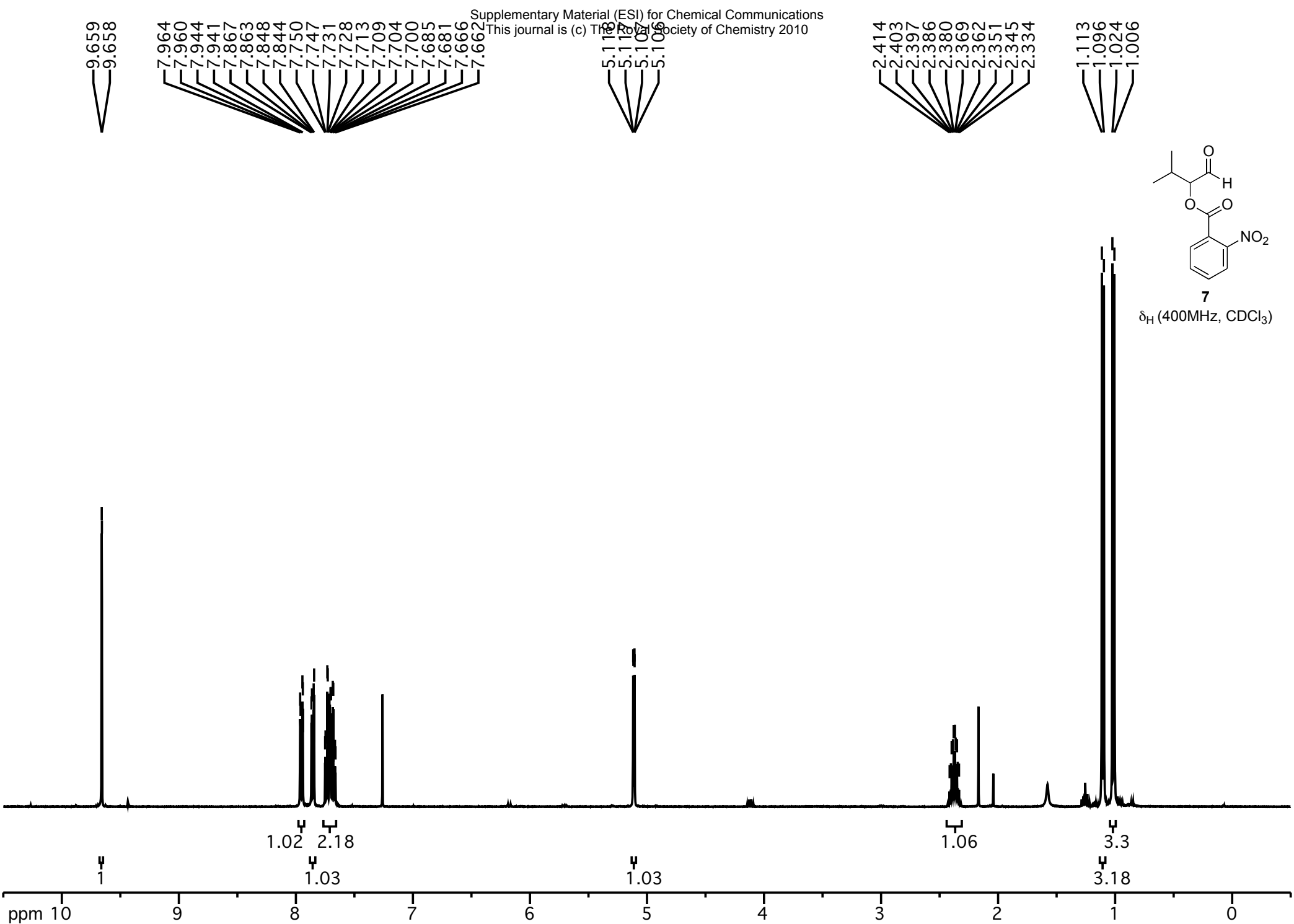
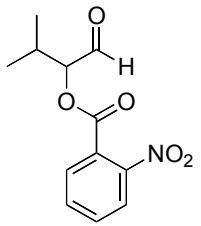


6

δ_C (100MHz, $CDCl_3$)





7

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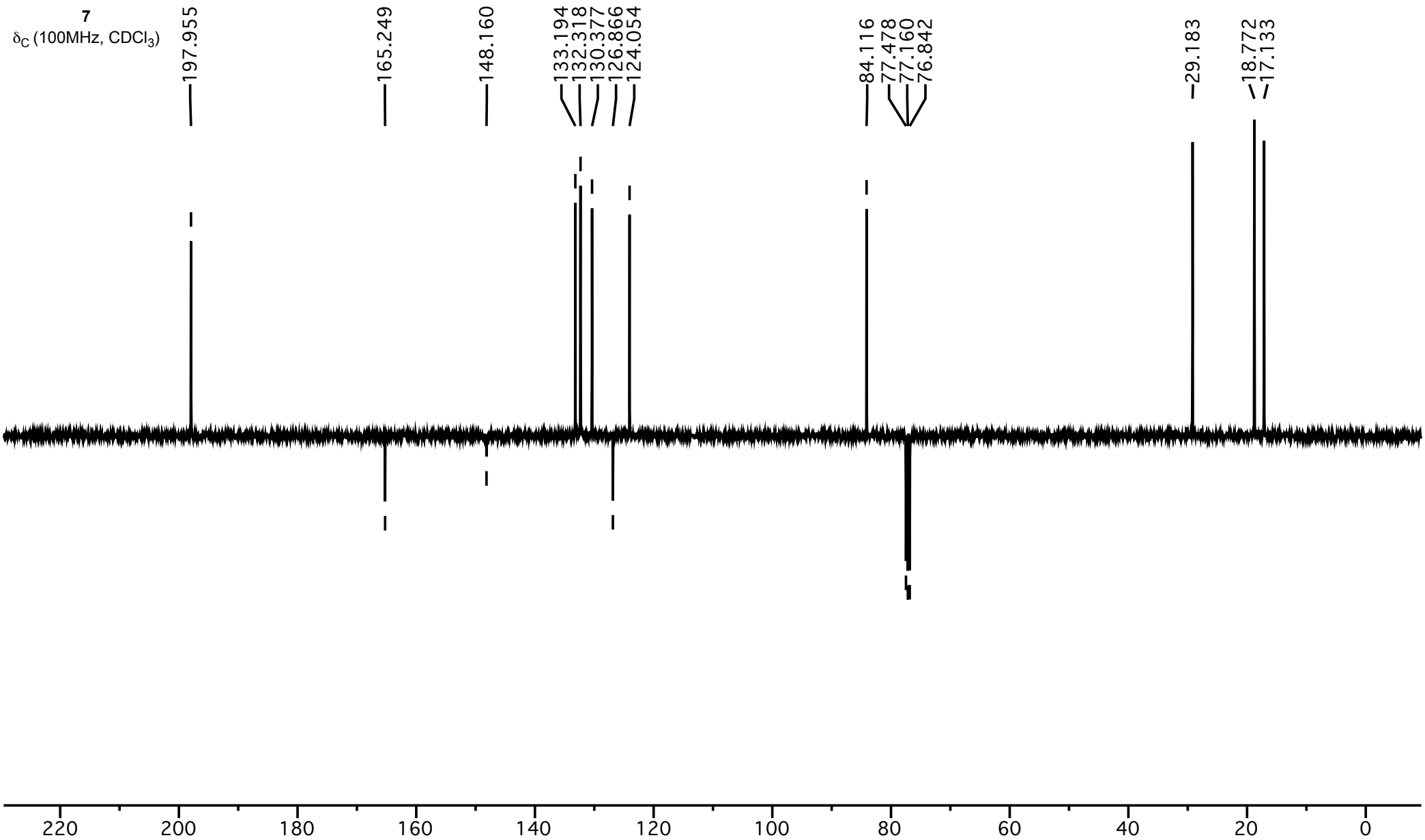

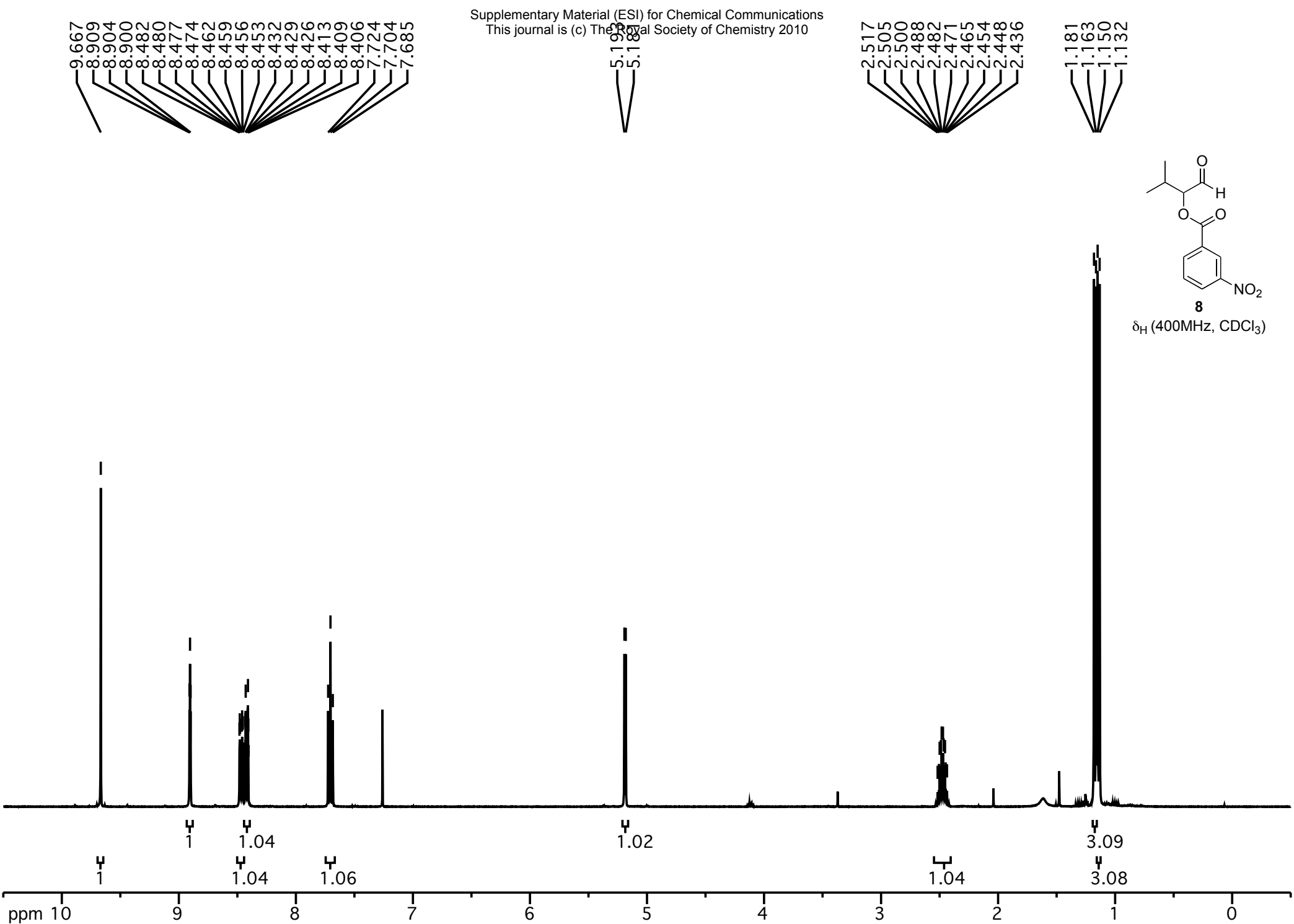
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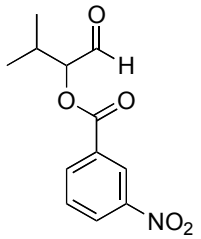
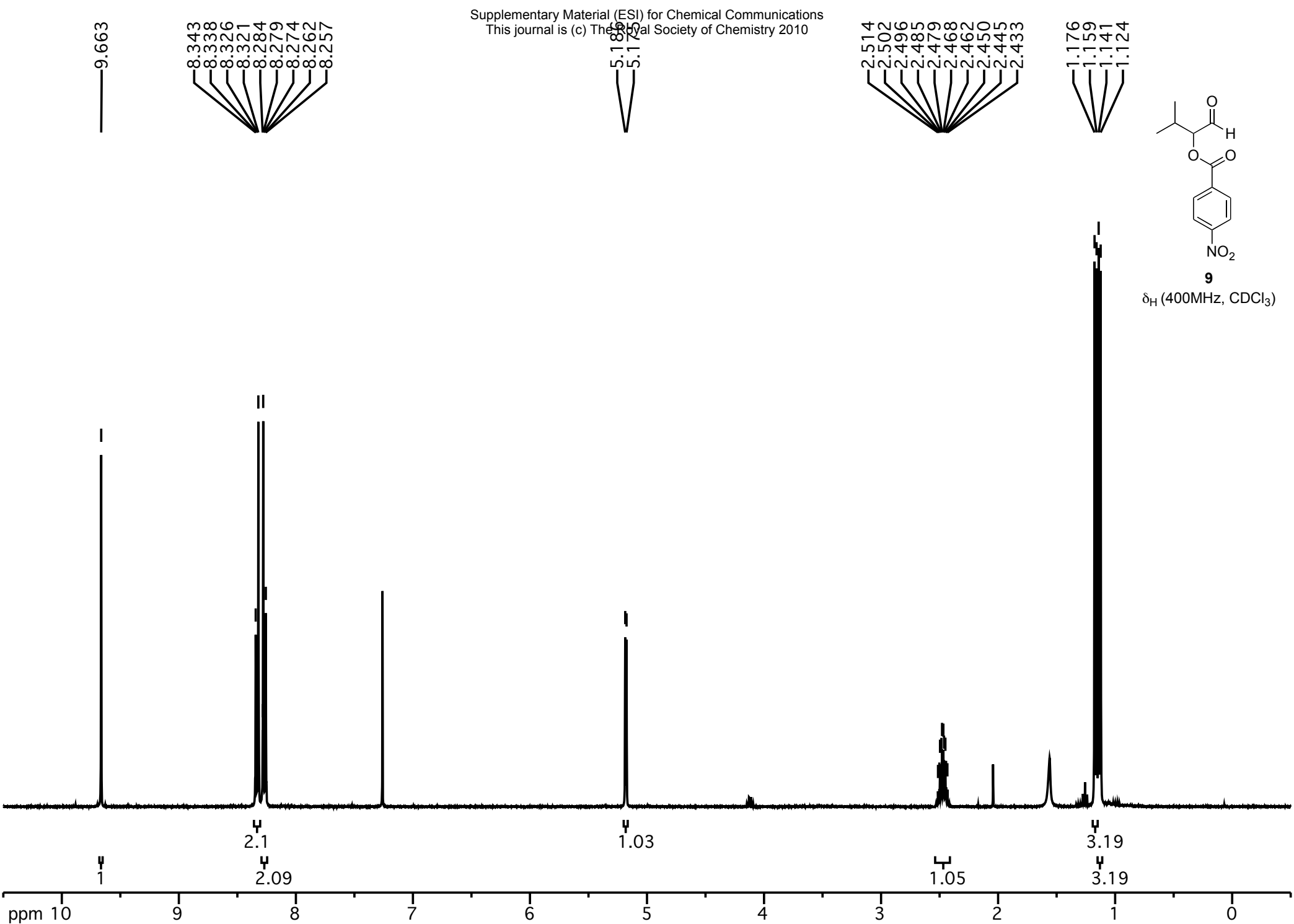
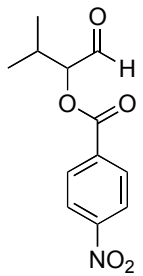


8

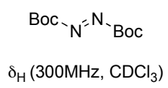
δ_C (100MHz, $CDCl_3$)



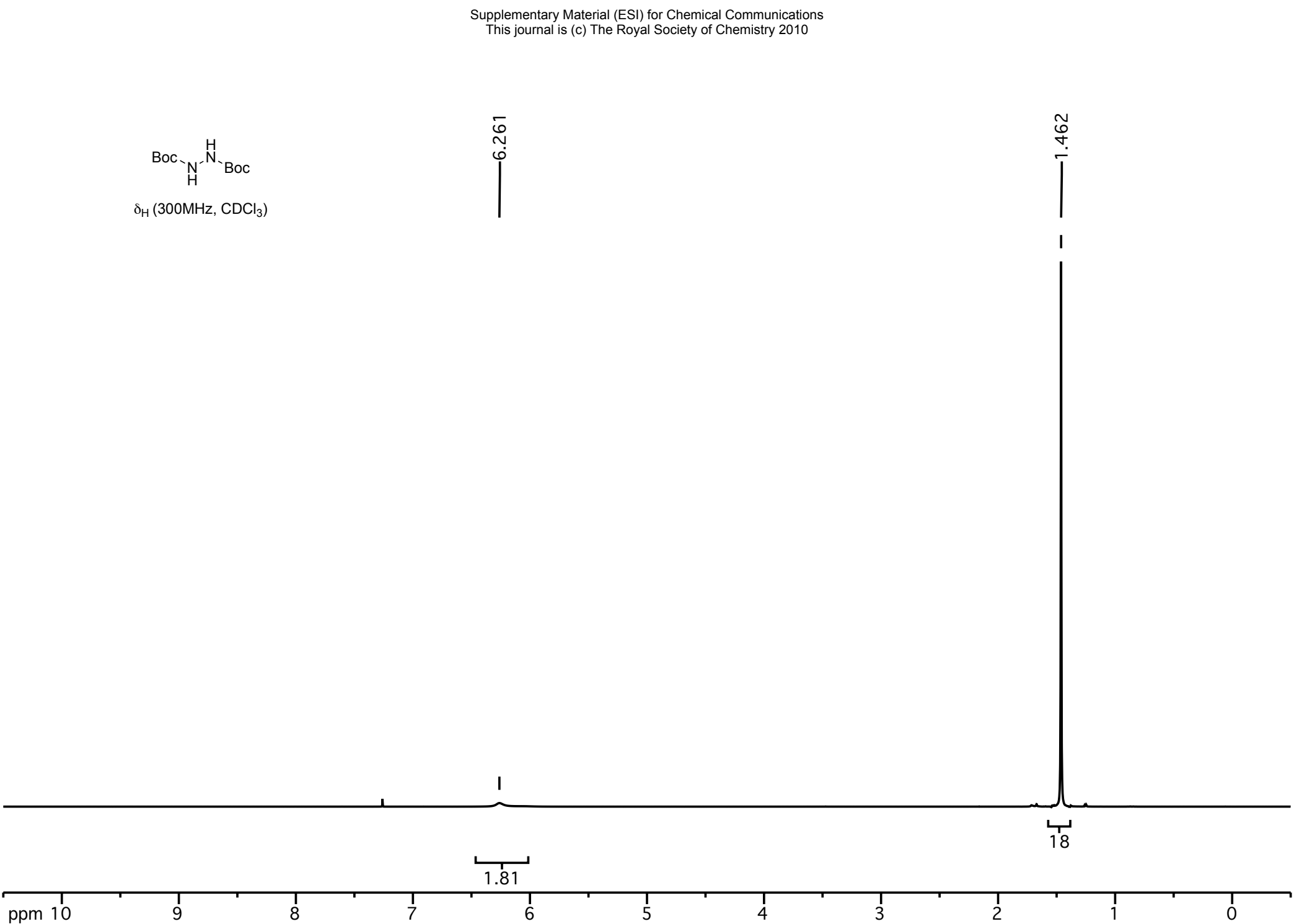


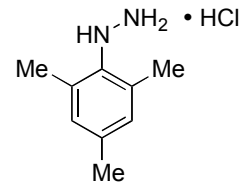
9

δ_C (100MHz, $CDCl_3$)

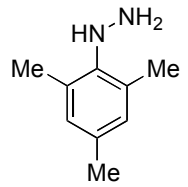


δ_H (300MHz, $CDCl_3$)

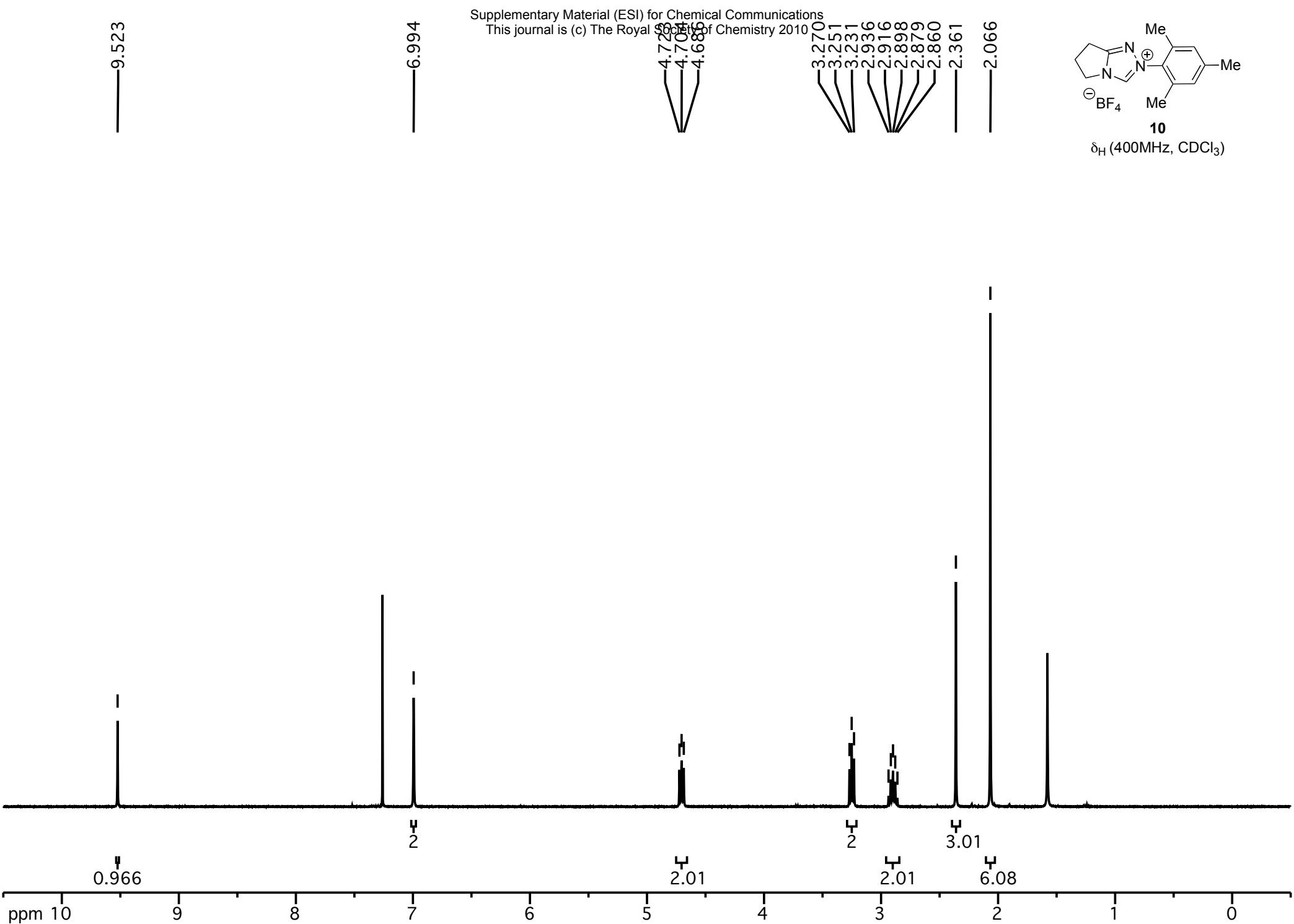

Boc
N
H
N
H
Boc
δH (300MHz, CDCl3)
6.261
1.462
1.81
18
ppm 10
9
8
7
6
5
4
3
2
1
0

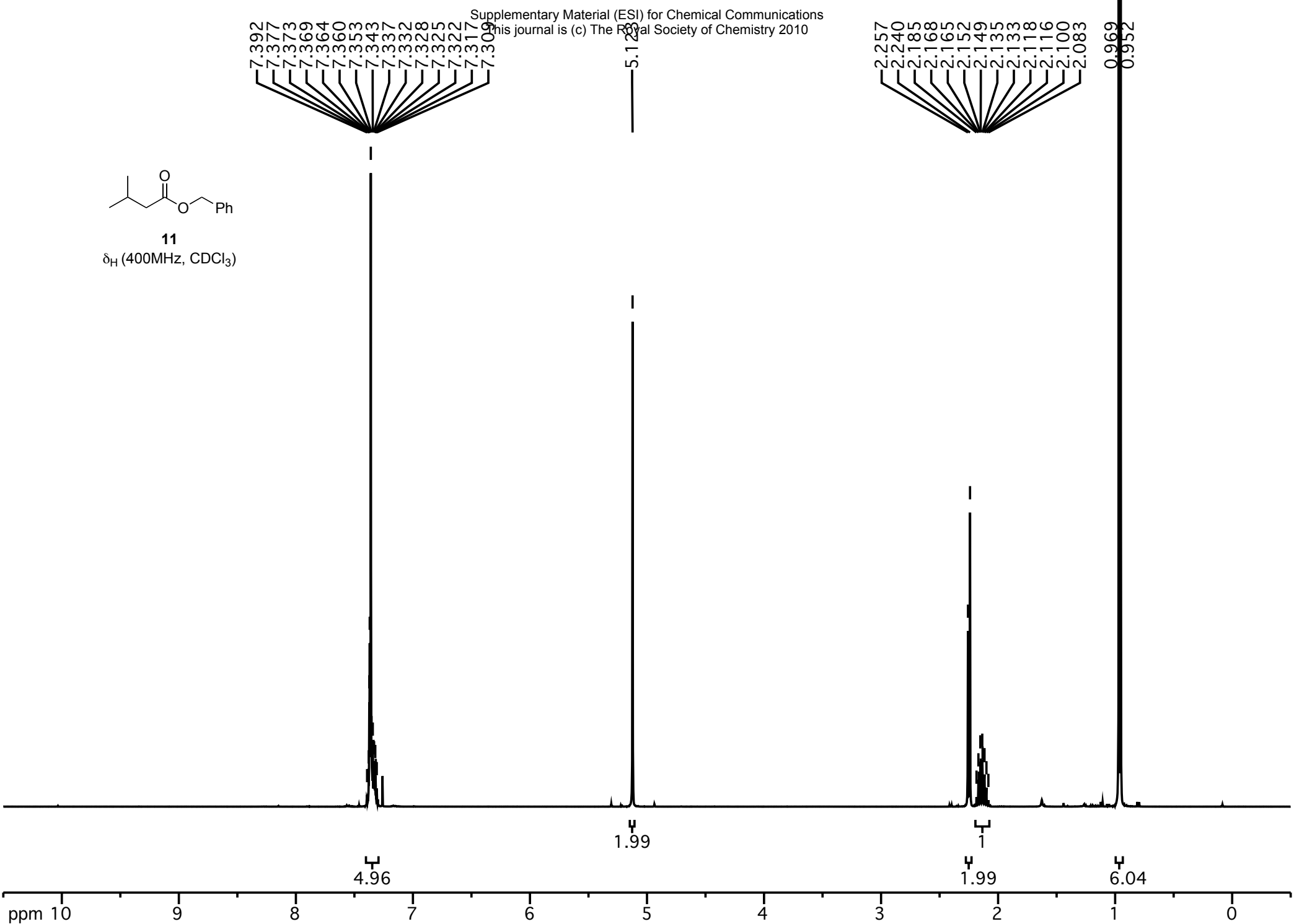


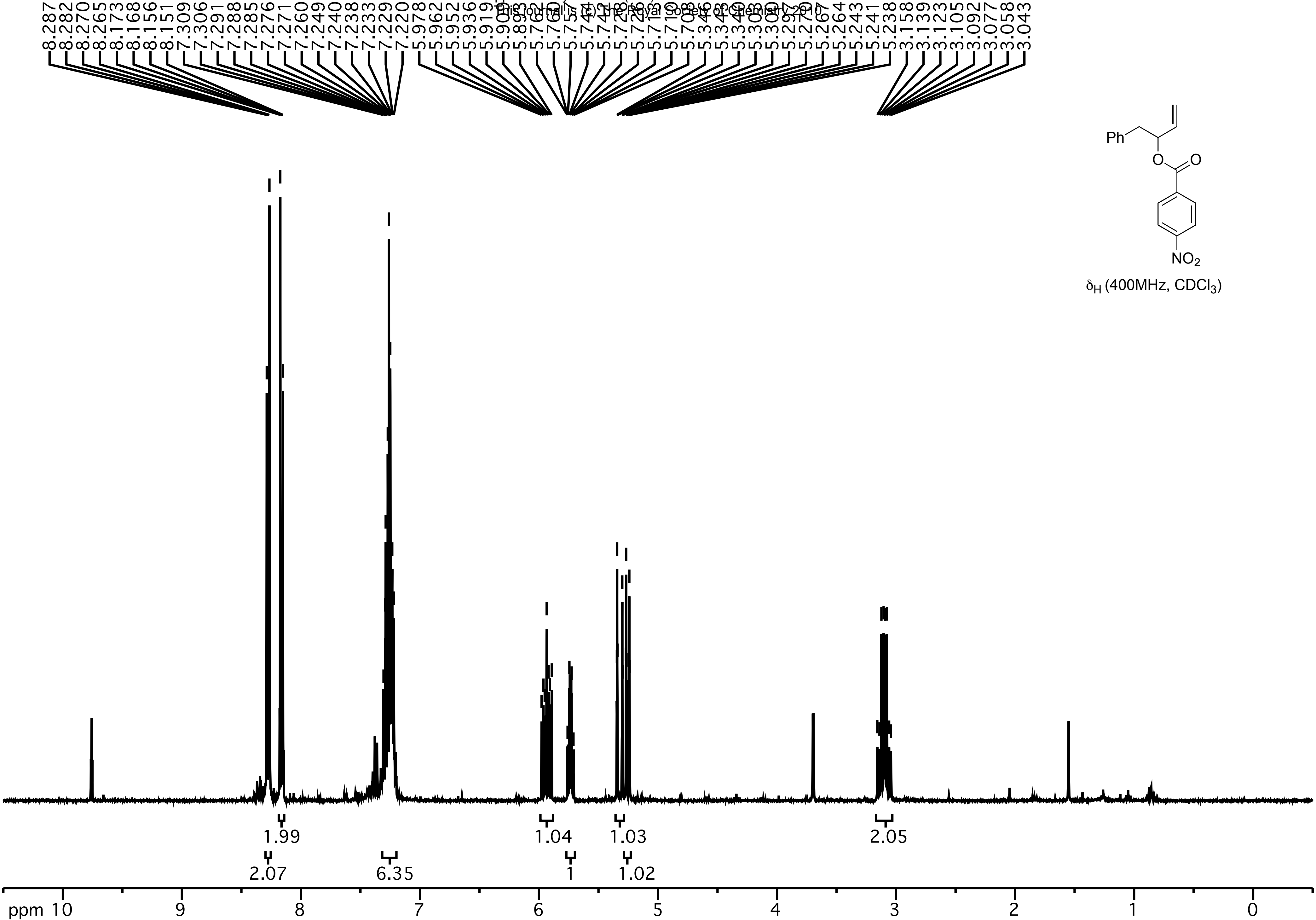
δ_H (300MHz, D_2O)

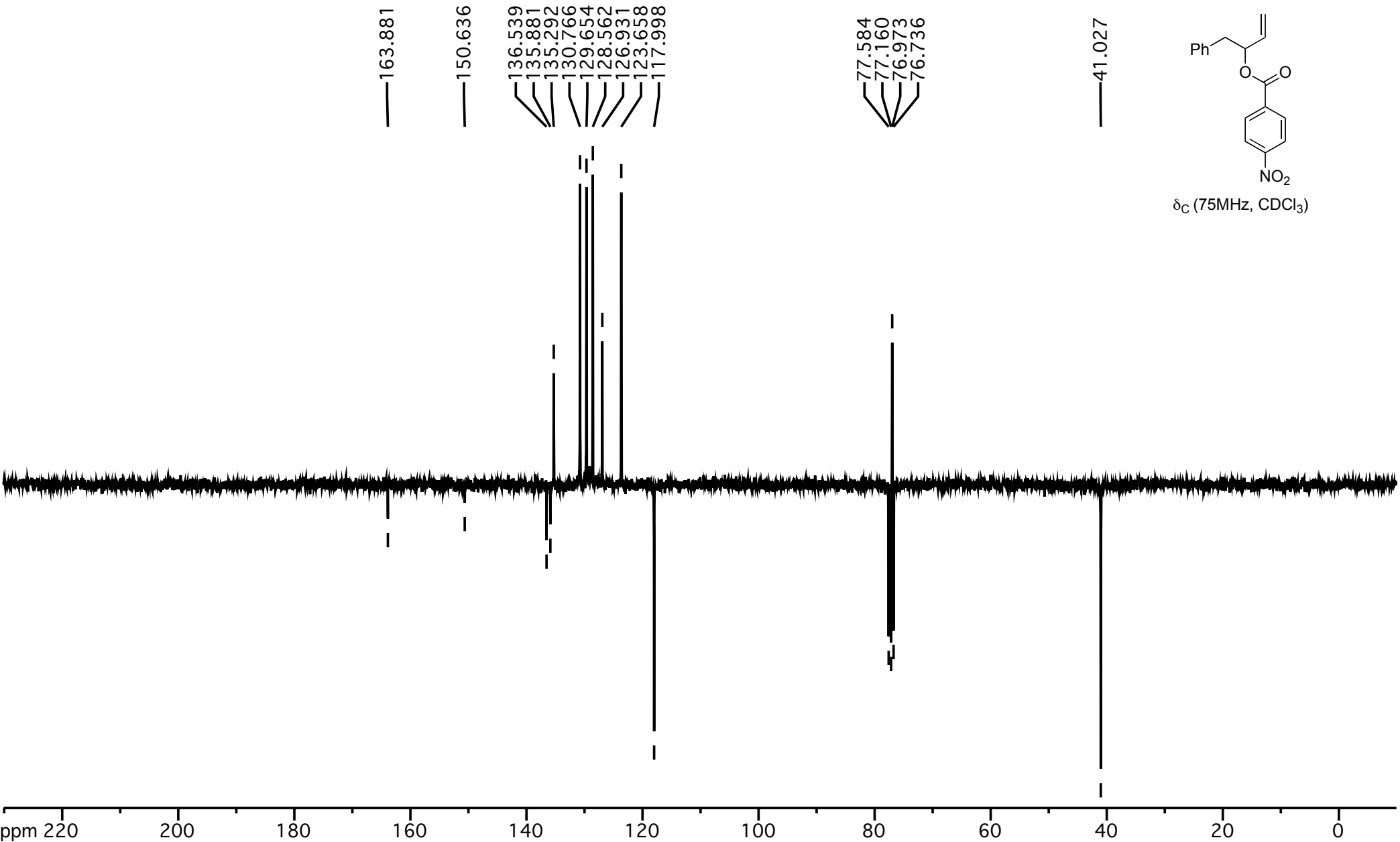


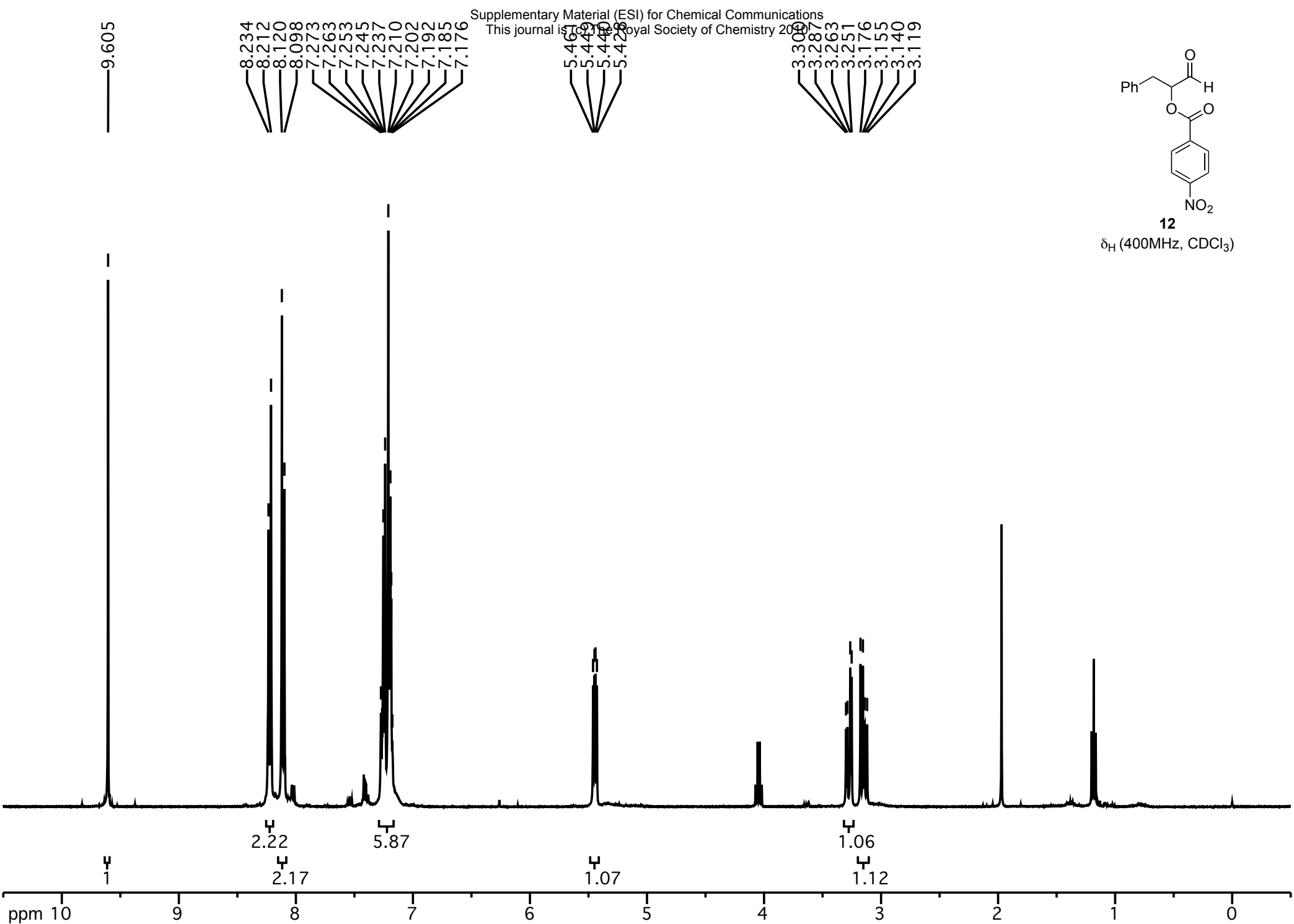
δ_H (300MHz, $CDCl_3$)


9.523
6.994
4.722
4.704
4.686
3.270
3.251
3.231
2.936
2.916
2.898
2.879
2.860
2.361
2.066
Me
Me
Me
N
N
BF4
10
δH (400MHz, CDCl3)
0.966
2
2.01
2
2.01
3.01
6.08
ppm 10
9
8
7
6
5
4
3
2
1
0



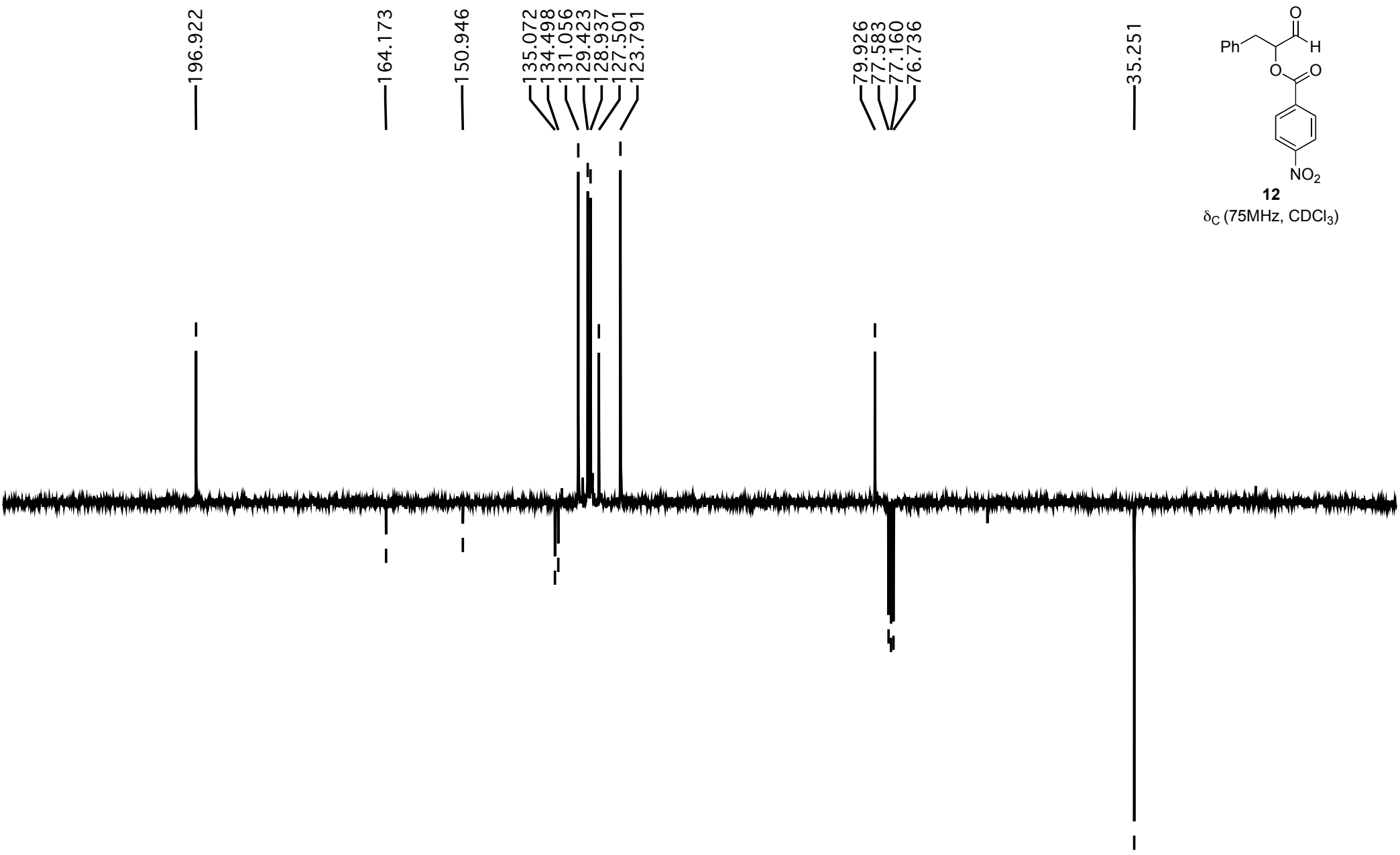

8.287
8.282
8.270
8.265
8.173
8.168
8.156
8.151
7.309
7.306
7.291
7.288
7.285
7.276
7.271
7.260
7.249
7.240
7.238
7.233
7.229
7.220
5.978
5.962
5.952
5.936
5.919
3.158
3.139
3.123
3.105
3.092
3.077
3.058
3.043
Ph
O
O
NO2
δH (400MHz, CDCl3)
1.99
1.04
1.03
2.05
2.07
6.35
1
1.02
ppm 10
9
8
7
6
5
4
3
2
1
0

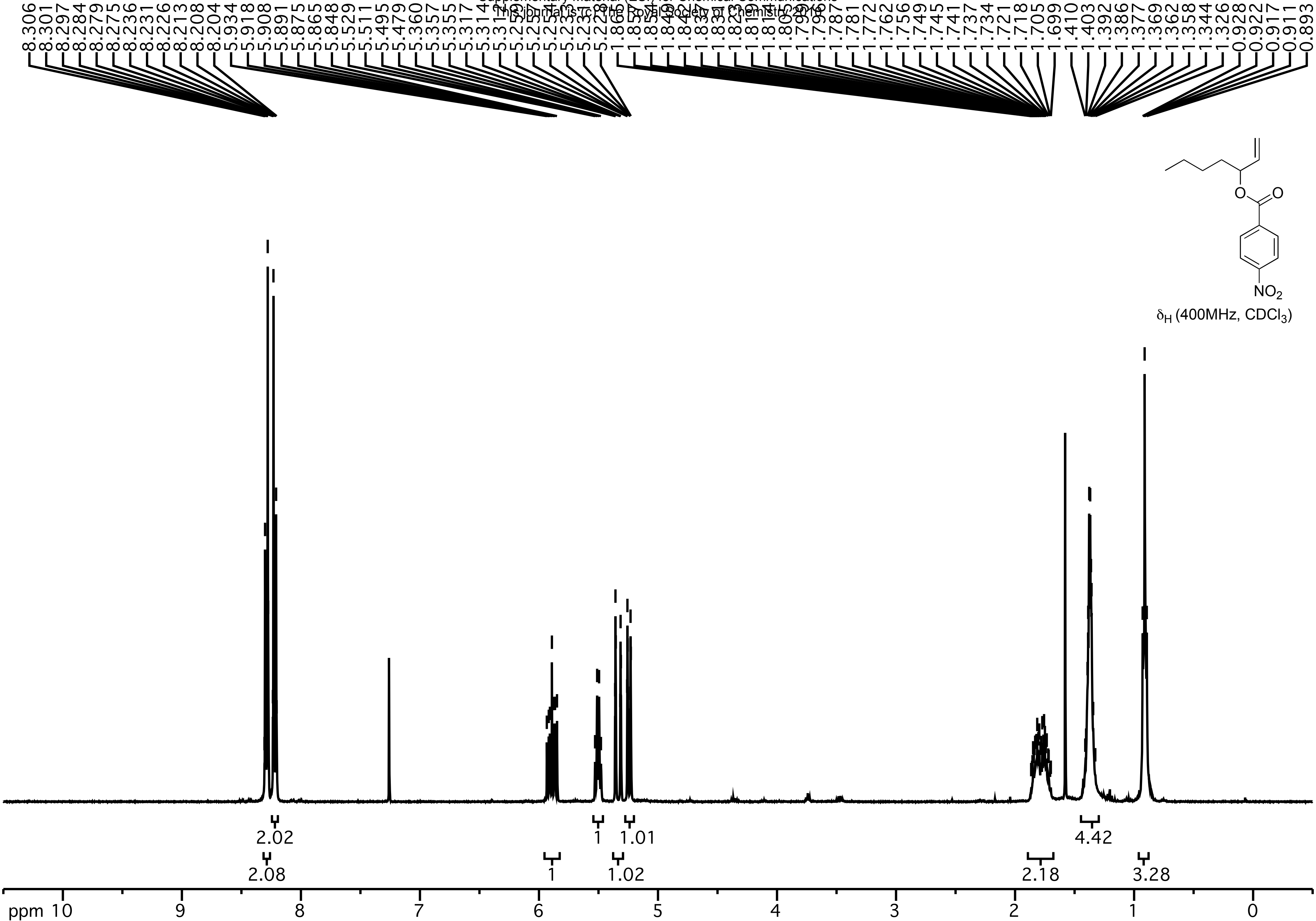

163.881
150.636
136.539
135.881
135.292
130.766
129.654
128.562
126.931
123.658
117.998
77.584
77.160
76.973
76.736
41.027
Ph
O
O
NO2
δC (75MHz, CDCl3)
ppm 220
200
180
160
140
120
100
80
60
40
20
0

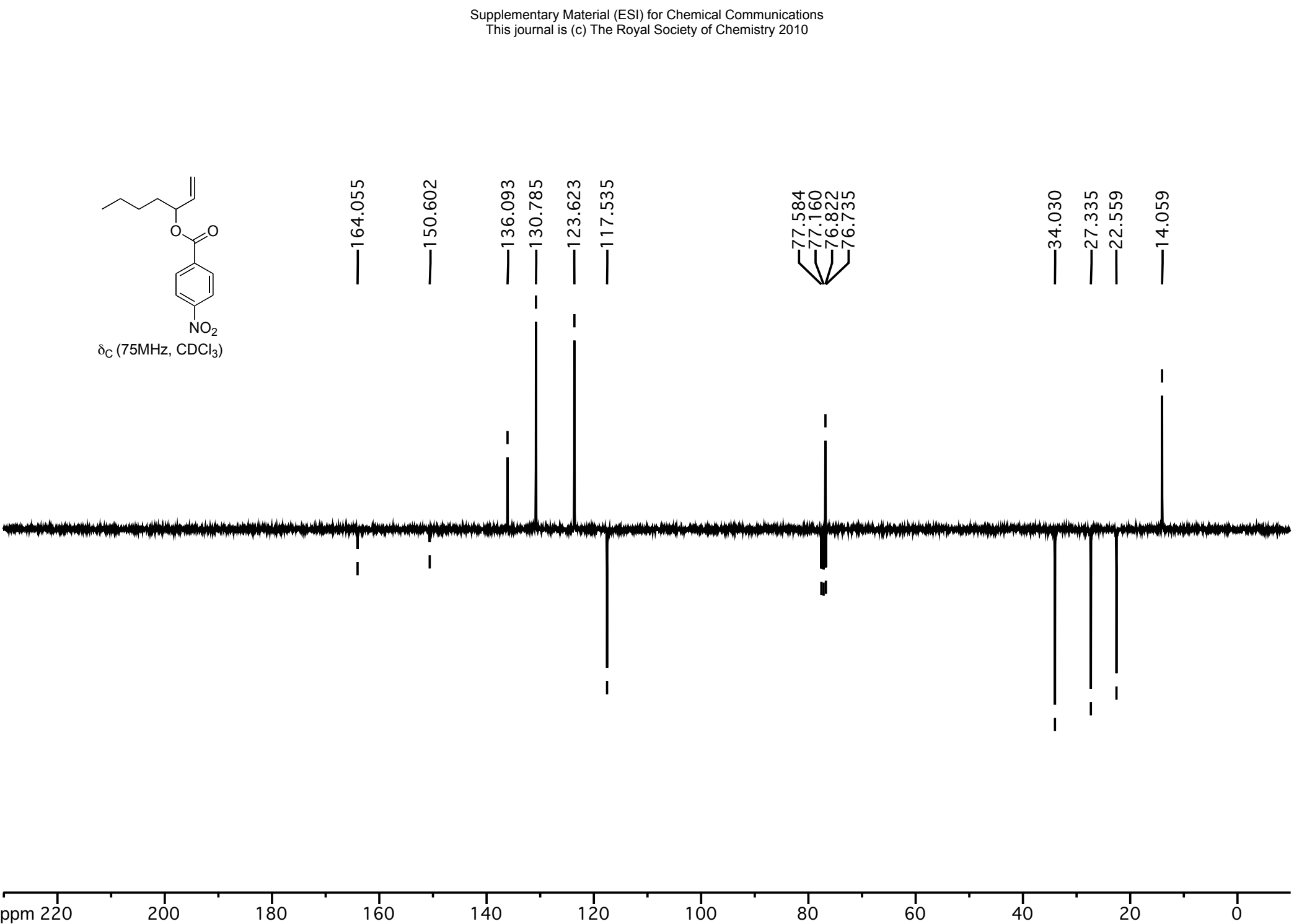


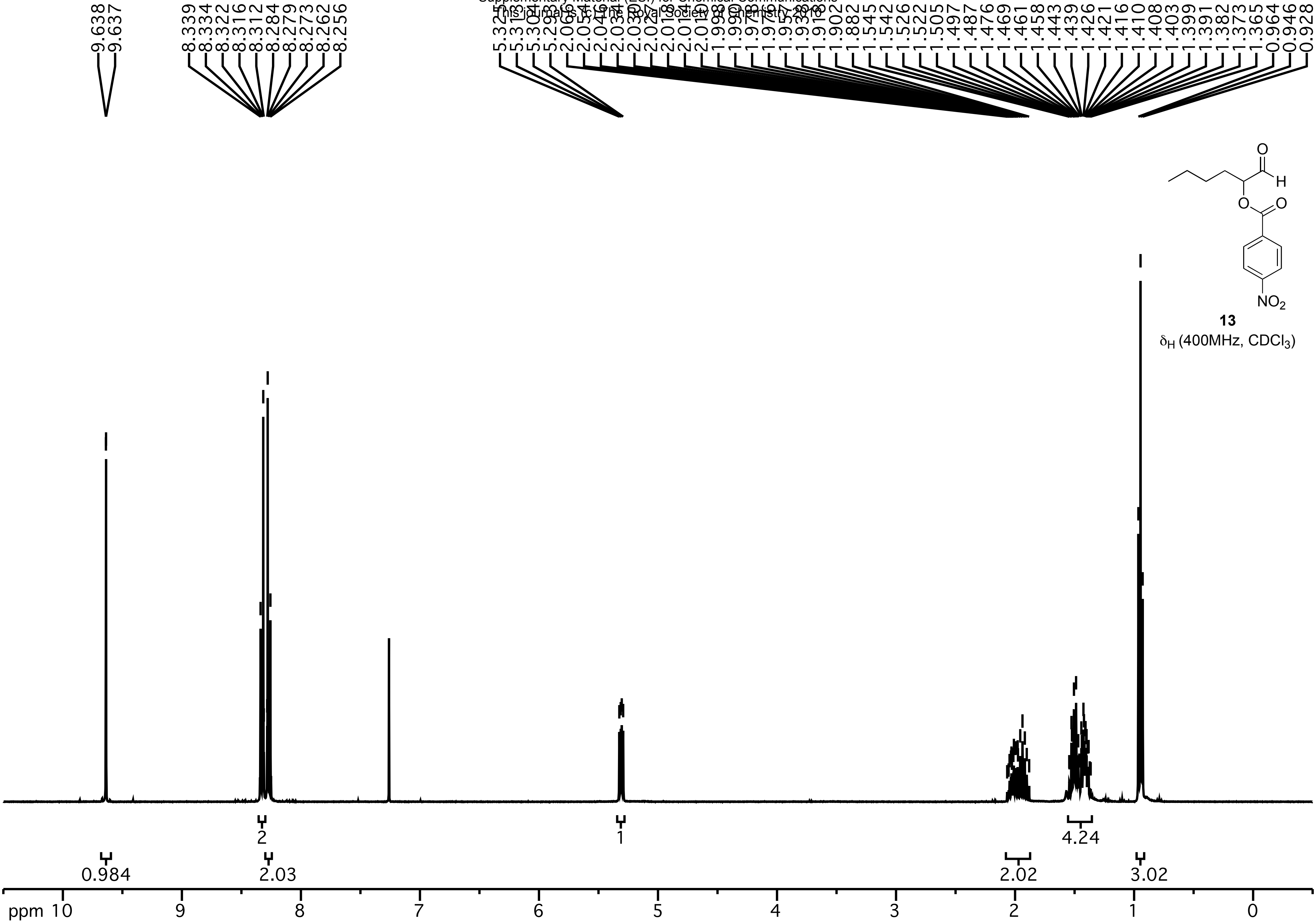
12

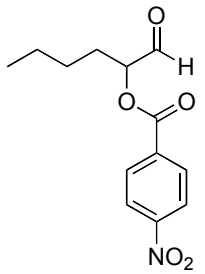
δ_H (400MHz, $CDCl_3$)


196.922
164.173
150.946
135.072
134.498
131.056
129.423
128.937
127.501
123.791
79.926
77.583
77.160
76.736
35.251
Ph
O
H
O
O
NO2
12
δC (75MHz, CDCl3)
ppm 220
200
180
160
140
120
100
80
60
40
20
0



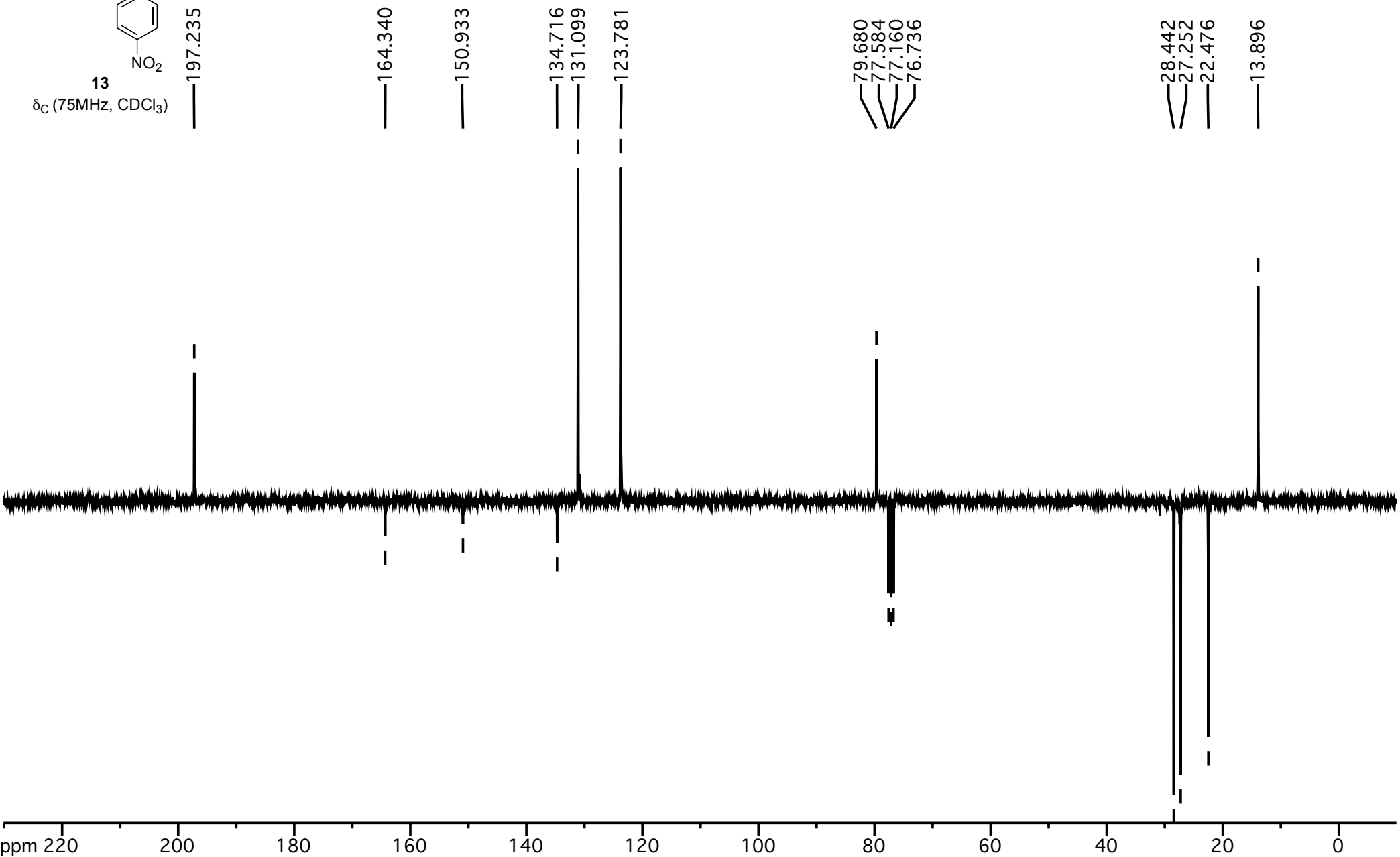

O
O
NO2
δC (75MHz, CDCl3)
164.055
150.602
136.093
130.785
123.623
117.535
77.584
77.160
76.822
76.735
34.030
27.335
22.559
14.059
ppm 220
200
180
160
140
120
100
80
60
40
20
0

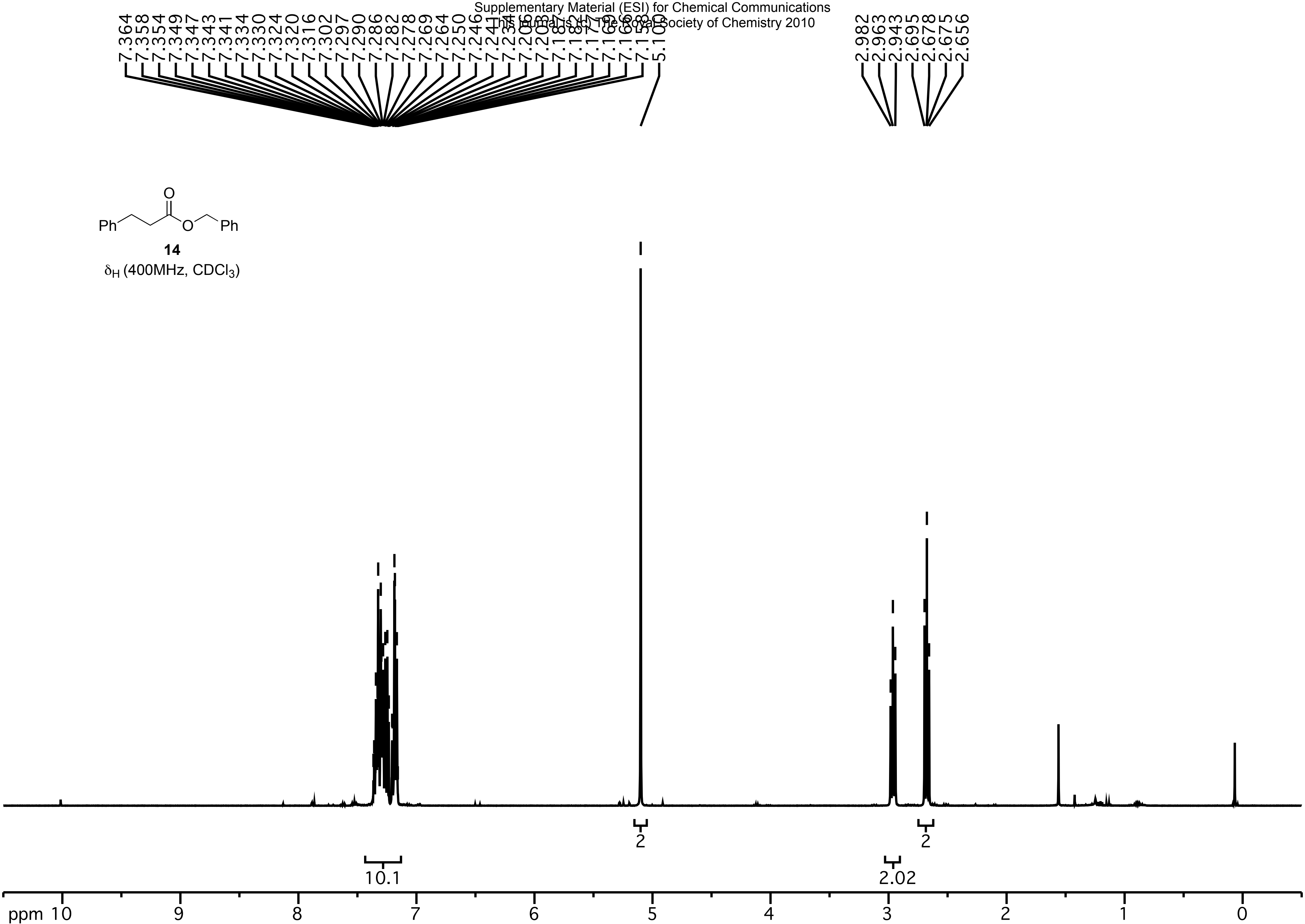


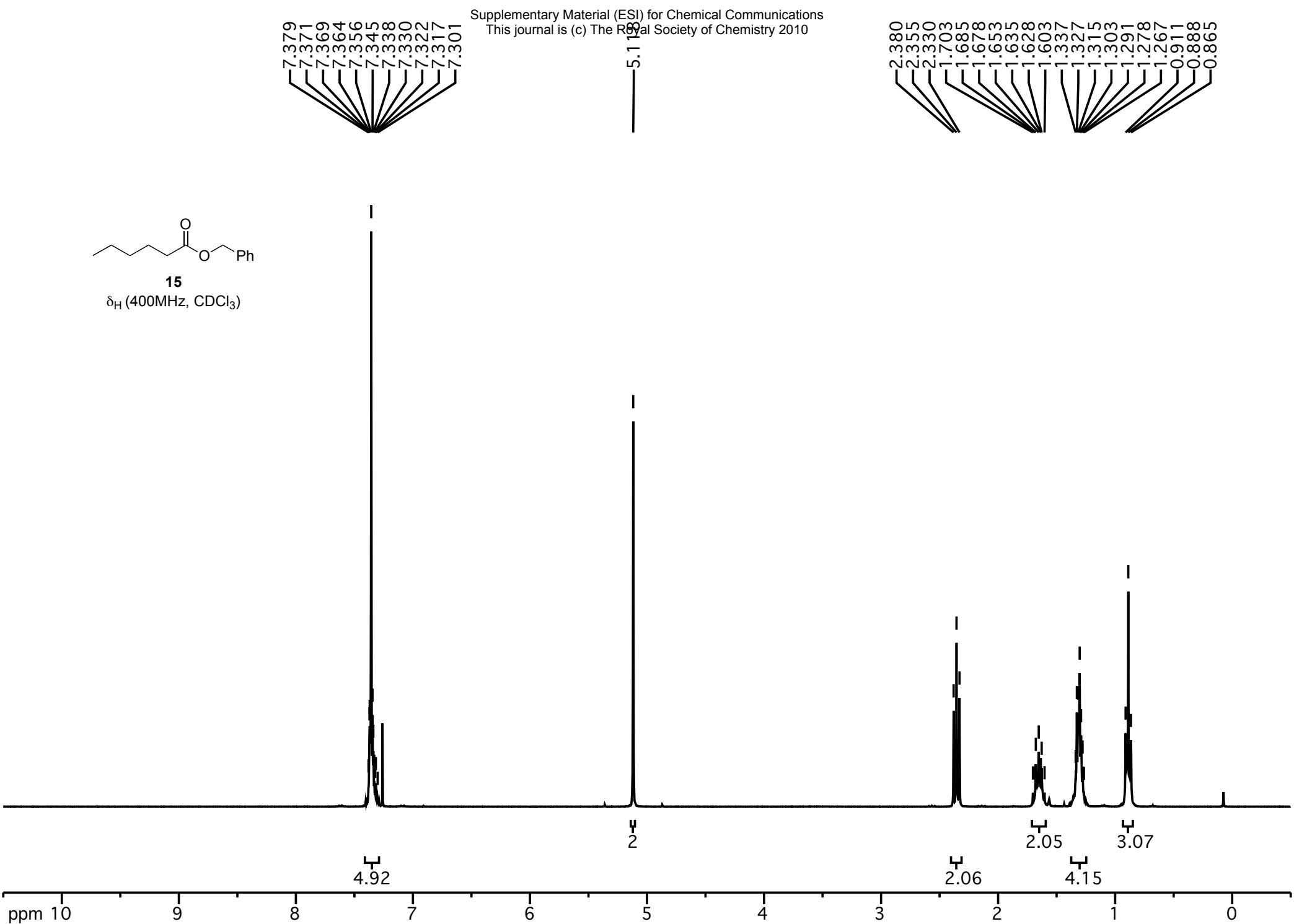


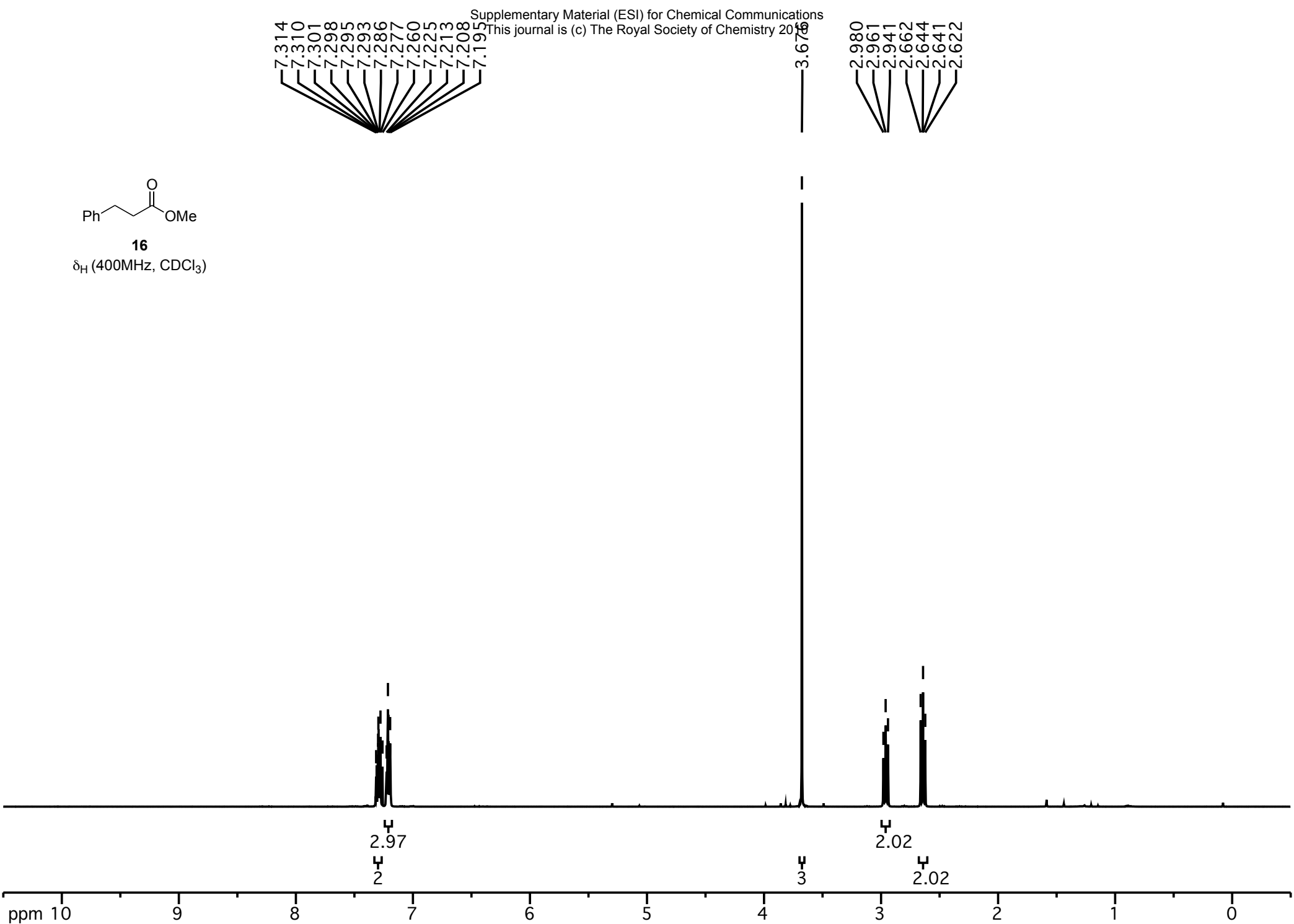
13

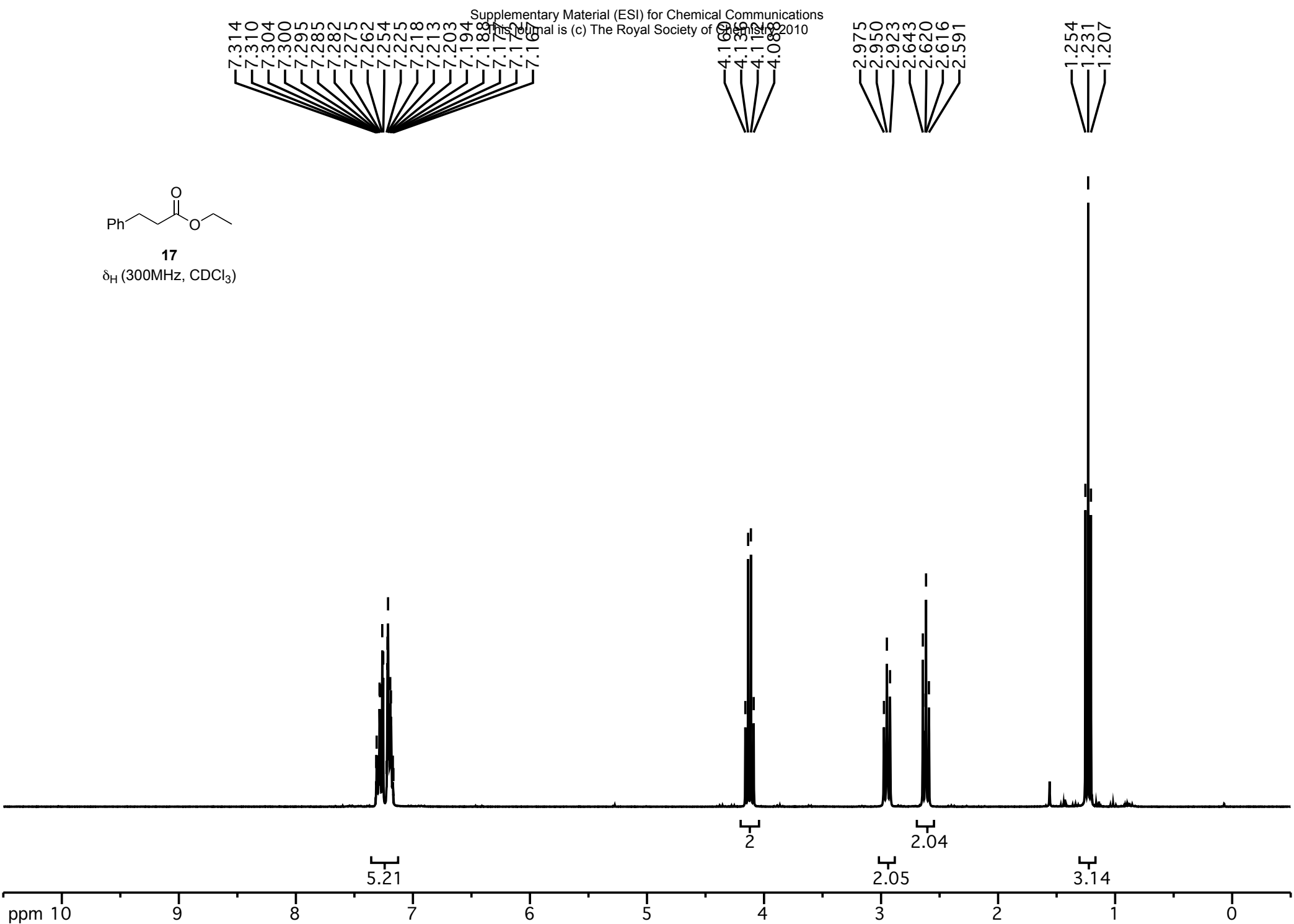
δ_C (75MHz, $CDCl_3$)

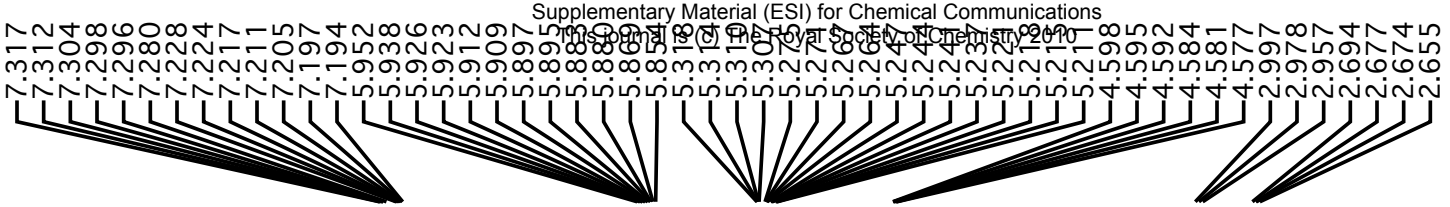


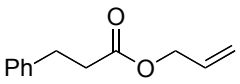



7.379
7.371
7.369
7.364
7.356
7.345
7.338
7.330
7.322
7.317
7.301
5.119
2.380
2.355
2.330
1.703
1.685
1.678
1.653
1.635
1.628
1.603
1.337
1.327
1.315
1.303
1.291
1.278
1.267
0.911
0.888
0.865
O
O
Ph
15
δH (400MHz, CDCl3)
4.92
2
2.05
3.07
2.06
4.15
ppm 10
9
8
7
6
5
4
3
2
1
0


7.314
7.310
7.301
7.298
7.295
7.293
7.286
7.277
7.260
7.225
7.213
7.208
7.195
3.676
2.980
2.961
2.941
2.662
2.644
2.641
2.622
O
Ph
OMe
16
δH (400MHz, CDCl3)
2.97
2.02
2
3
2.02
ppm 10
9
8
7
6
5
4
3
2
1
0

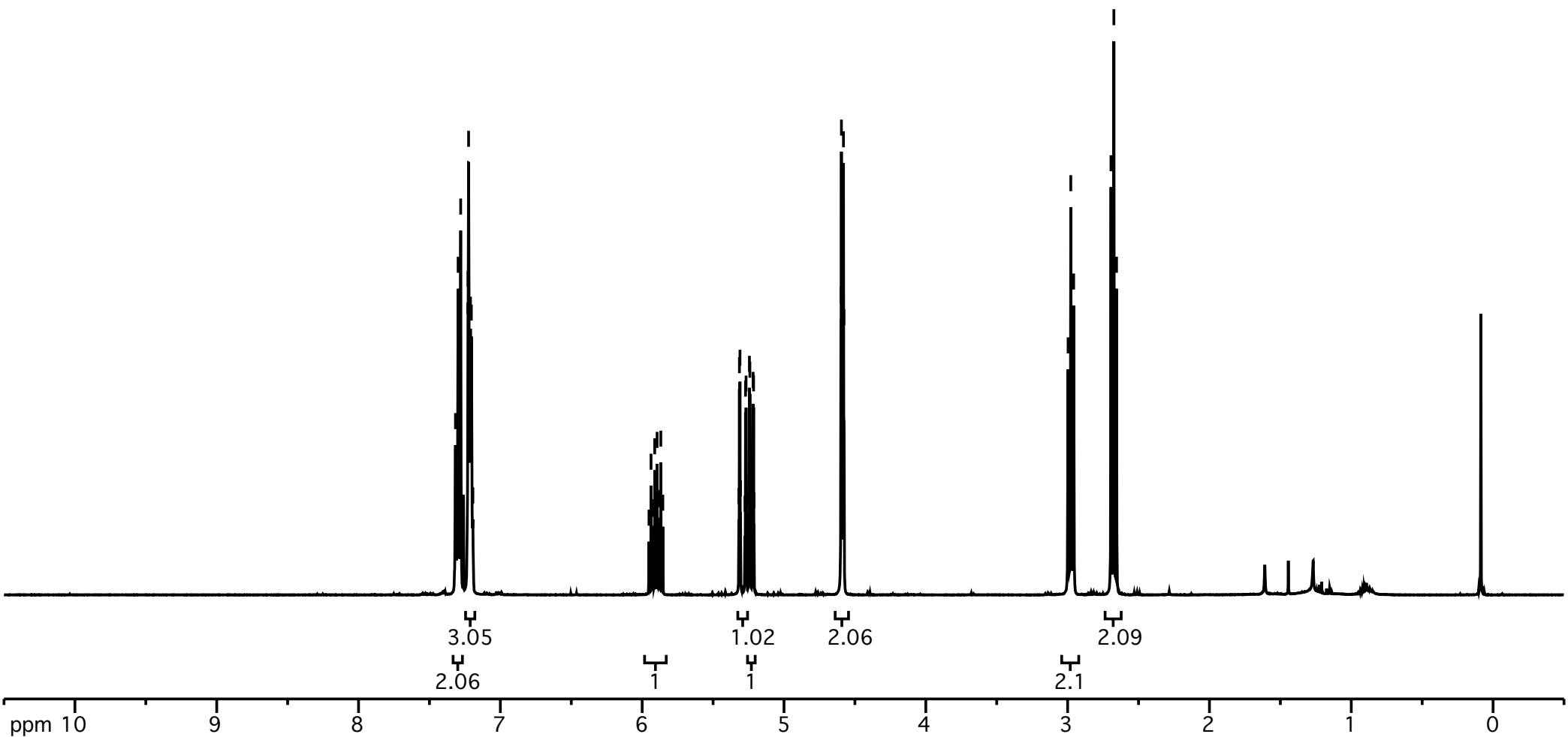


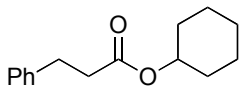




18

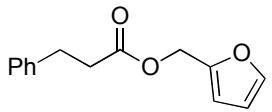
δ_H (400MHz, $CDCl_3$)





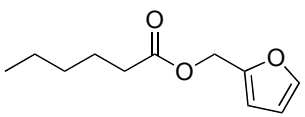
19

δ_H (400MHz, $CDCl_3$)



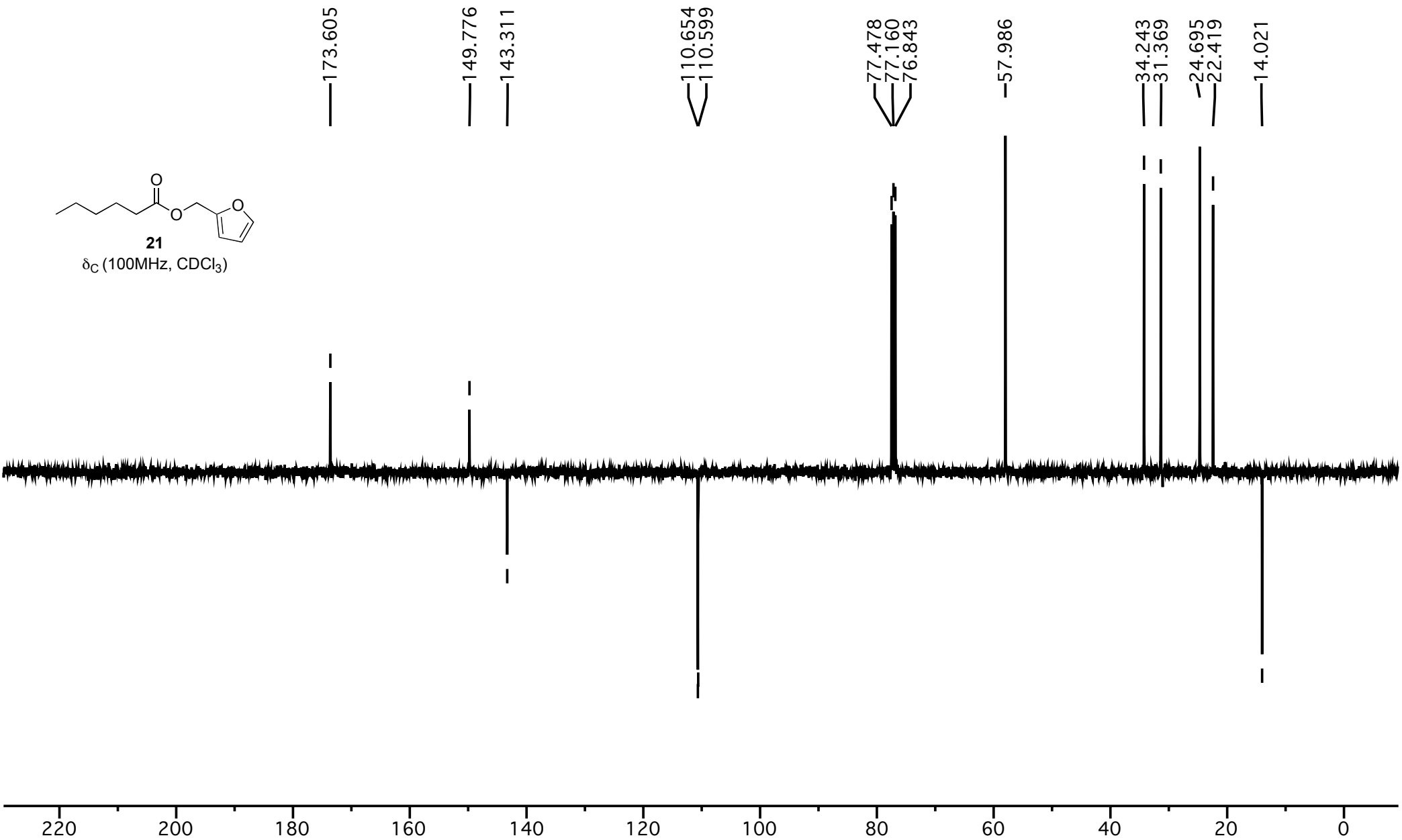
20

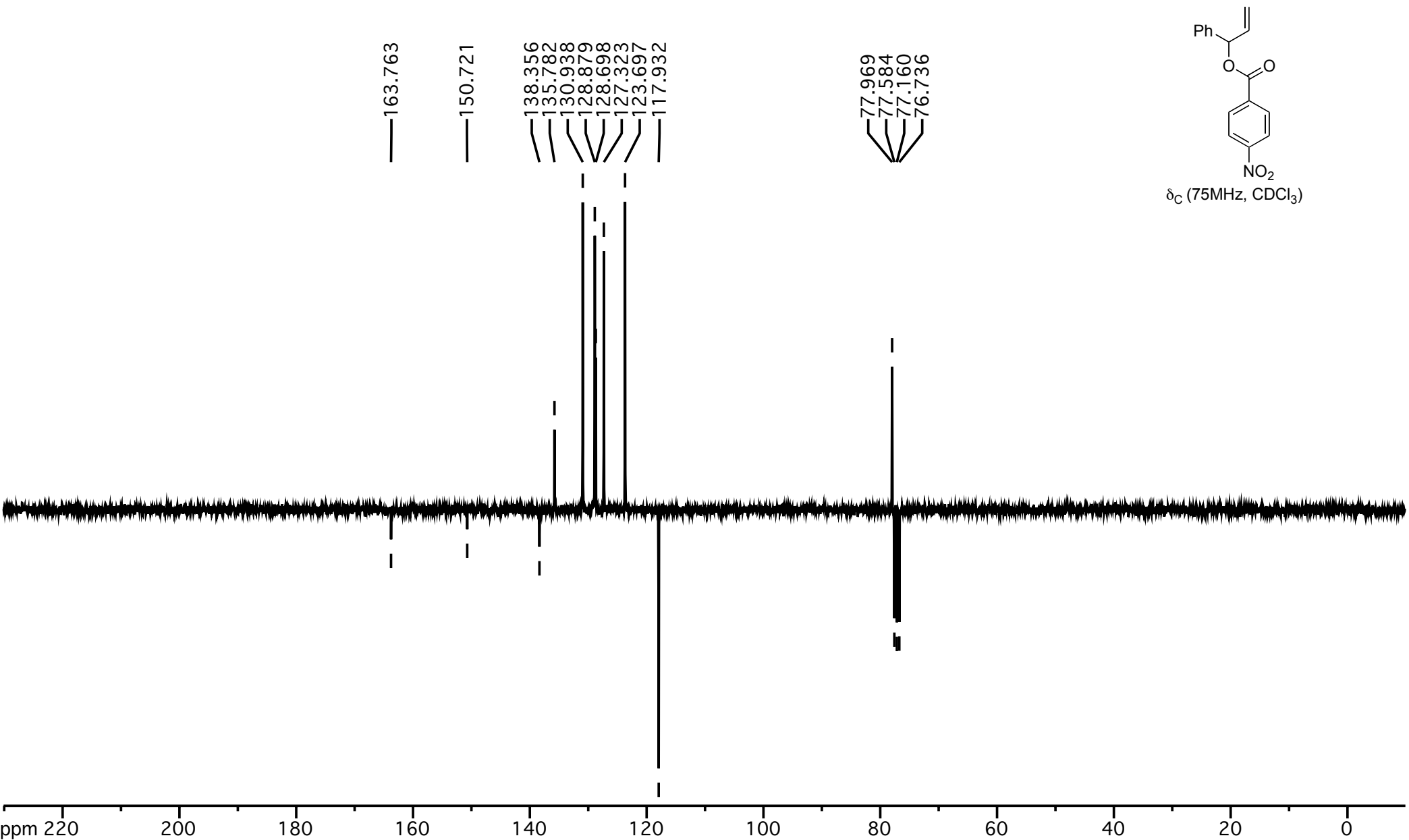
δ_H (300MHz, $CDCl_3$)

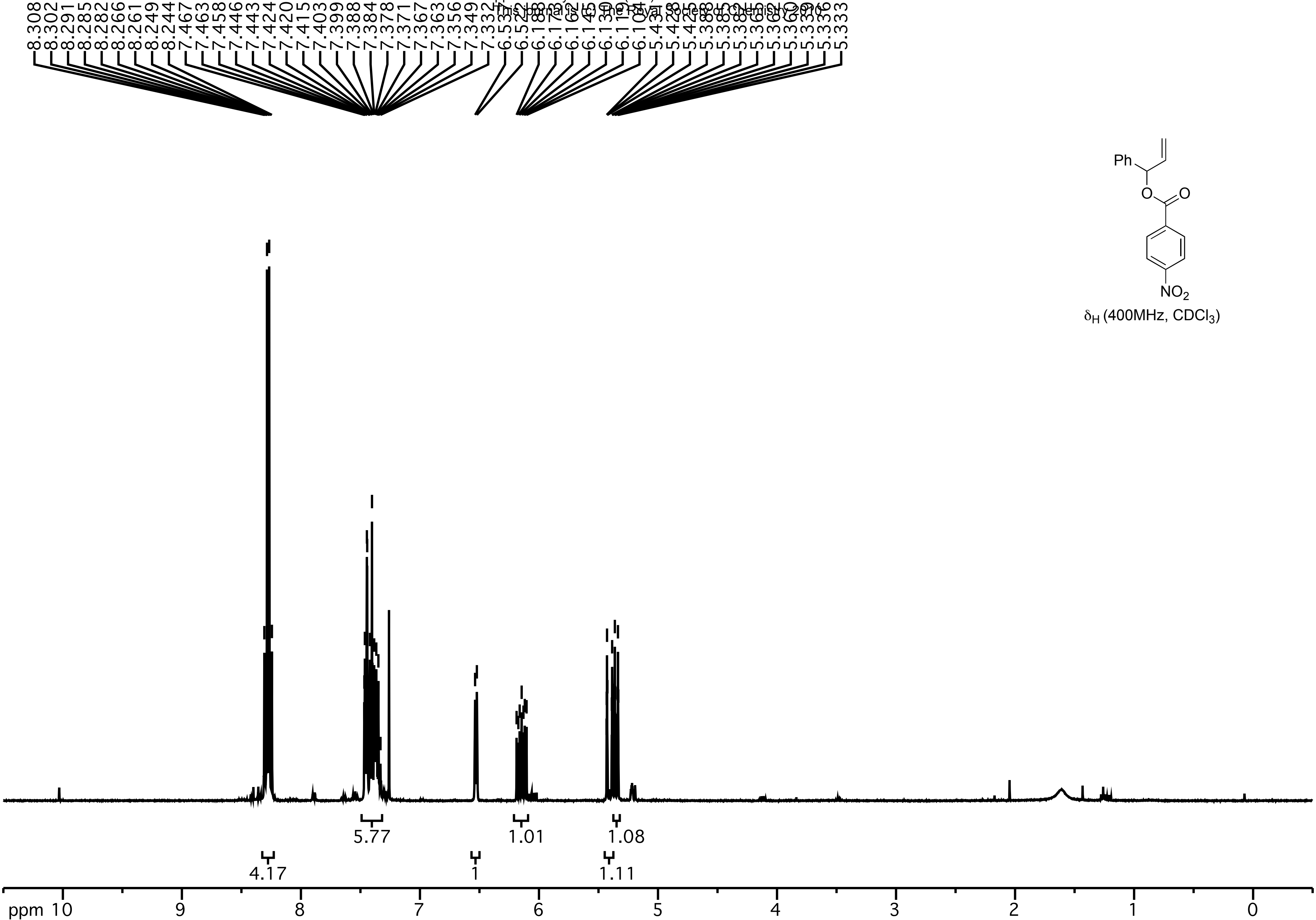


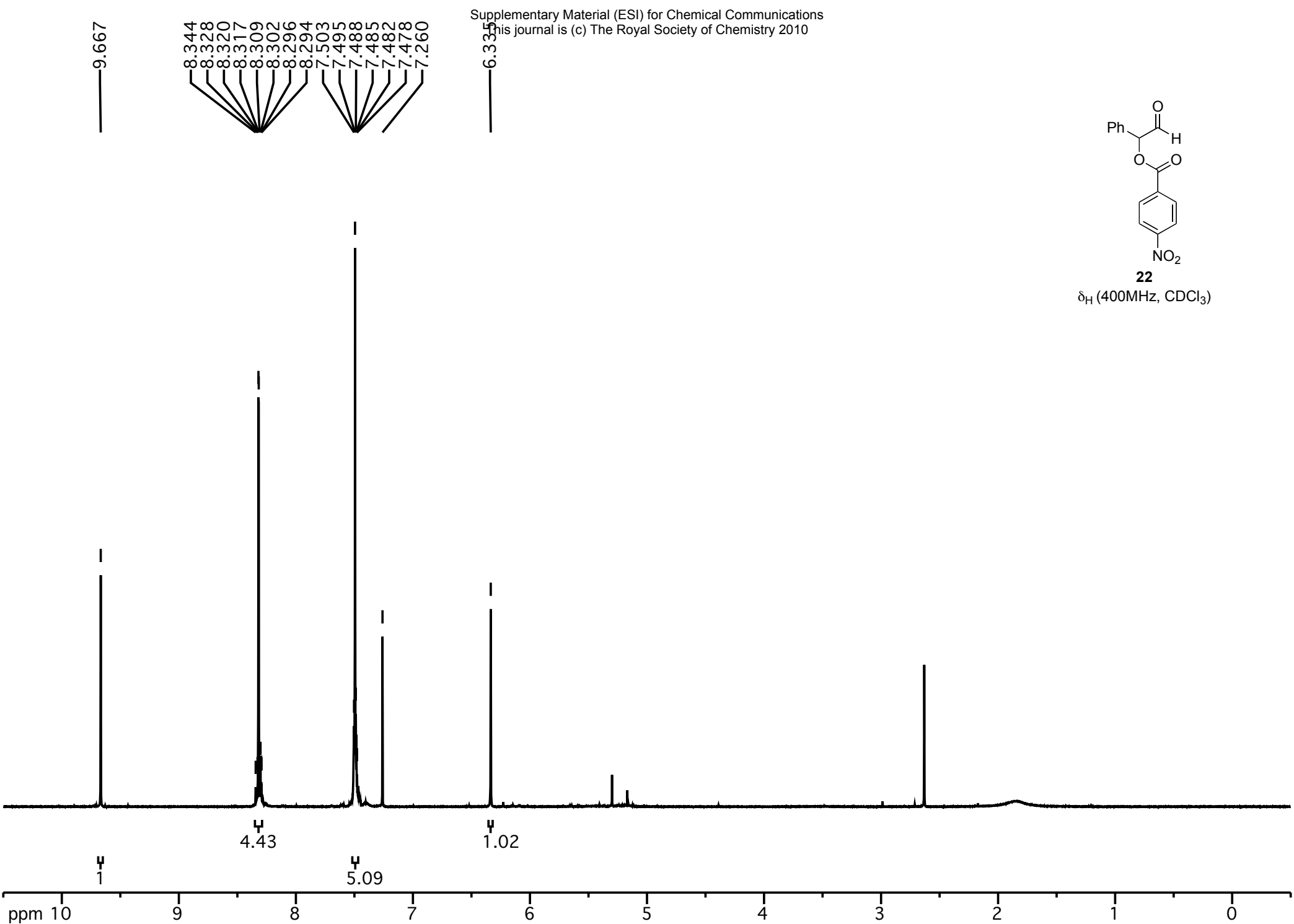
21

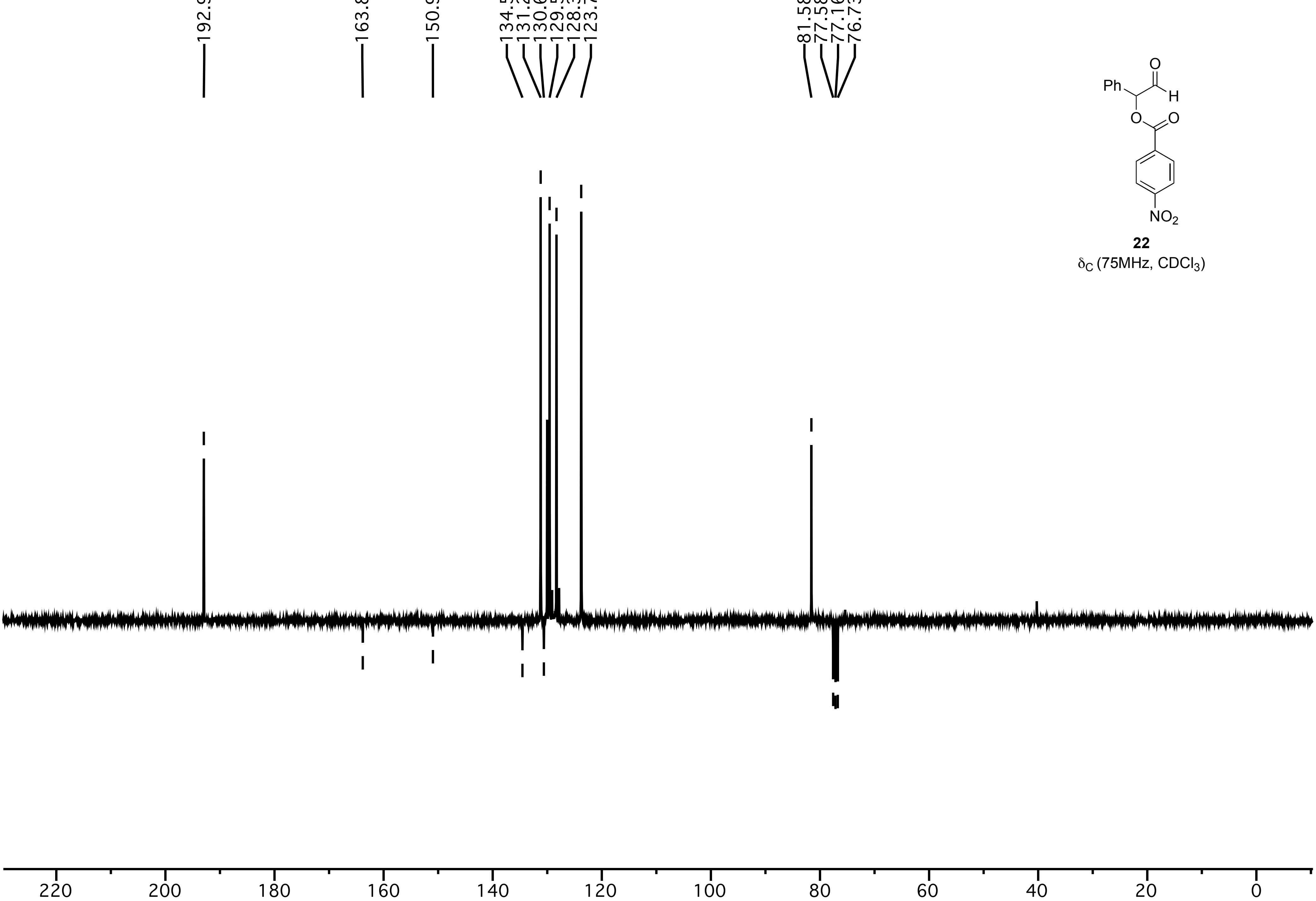
δ_H (300MHz, $CDCl_3$)


173.605
149.776
143.311
110.654
110.599
77.478
77.160
76.843
57.986
34.243
31.369
24.695
22.419
14.021
O
O
O
21
δC (100MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0


163.763
150.721
138.356
135.782
130.938
128.879
128.698
127.323
123.697
117.932
77.969
77.584
77.160
76.736
Ph
O
O
NO2
δC (75MHz, CDCl3)
ppm 220
200
180
160
140
120
100
80
60
40
20
0

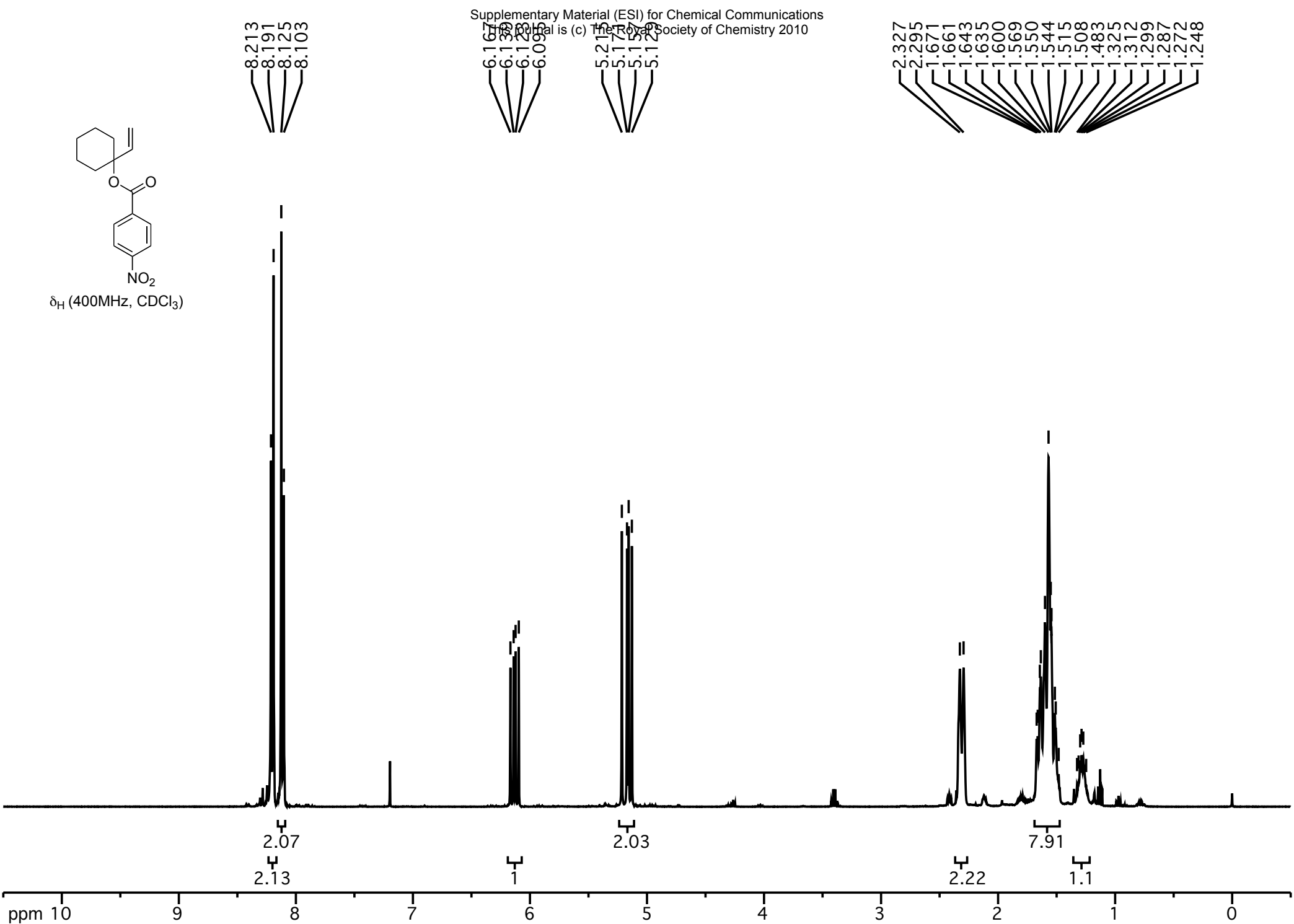

8.308
8.302
8.291
8.285
8.282
8.266
8.261
8.249
8.244
7.467
7.463
7.458
7.446
7.443
7.424
7.420
7.415
7.403
7.399
7.388
7.384
7.378
7.371
7.367
7.363
7.356
7.349
7.332
Ph
O
O
NO_2
δ_H (400MHz, $CDCl_3$)
5.77
1.01
1.08
4.17
1
1.11
ppm 10
9
8
7
6
5
4
3
2
1
0

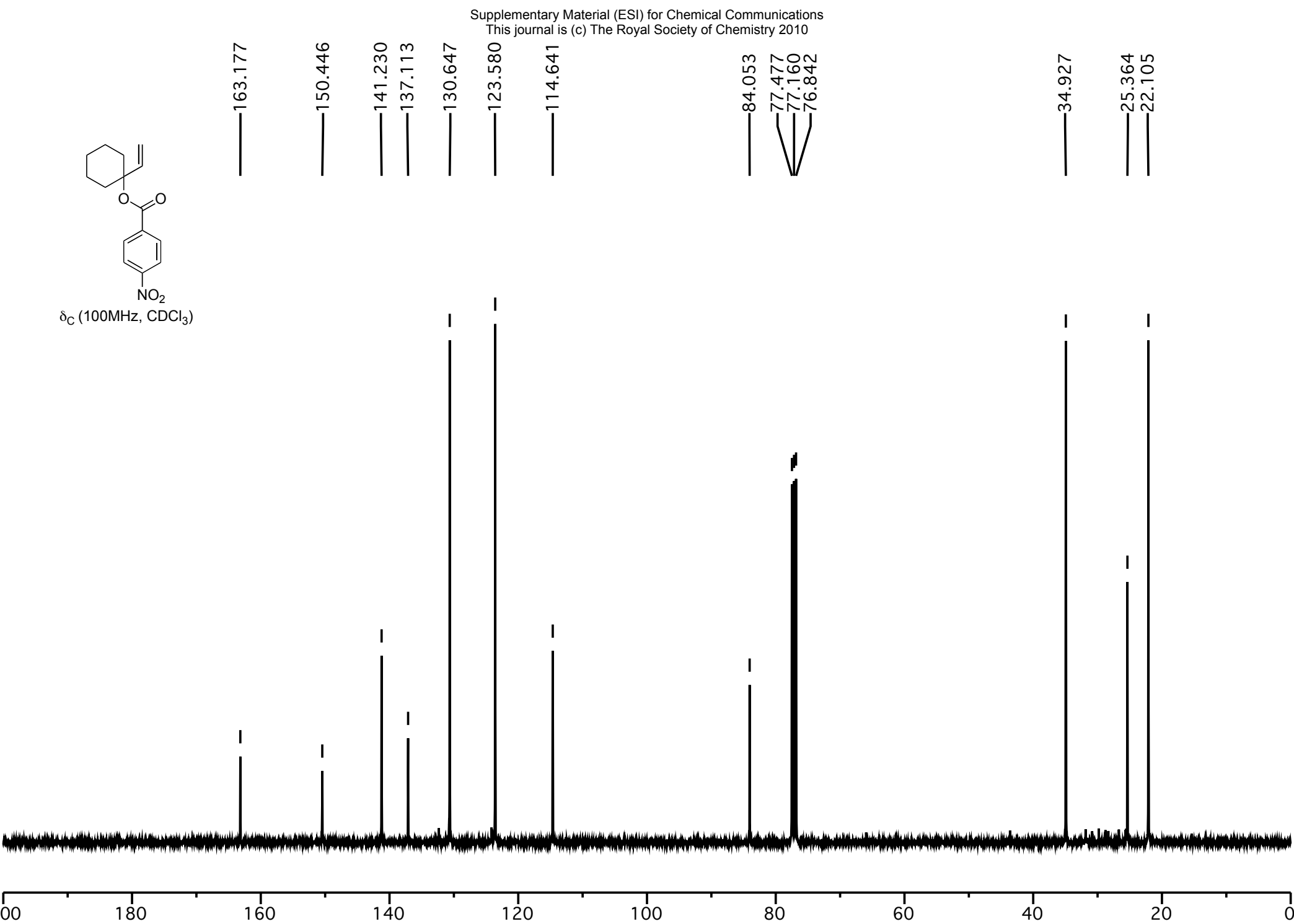


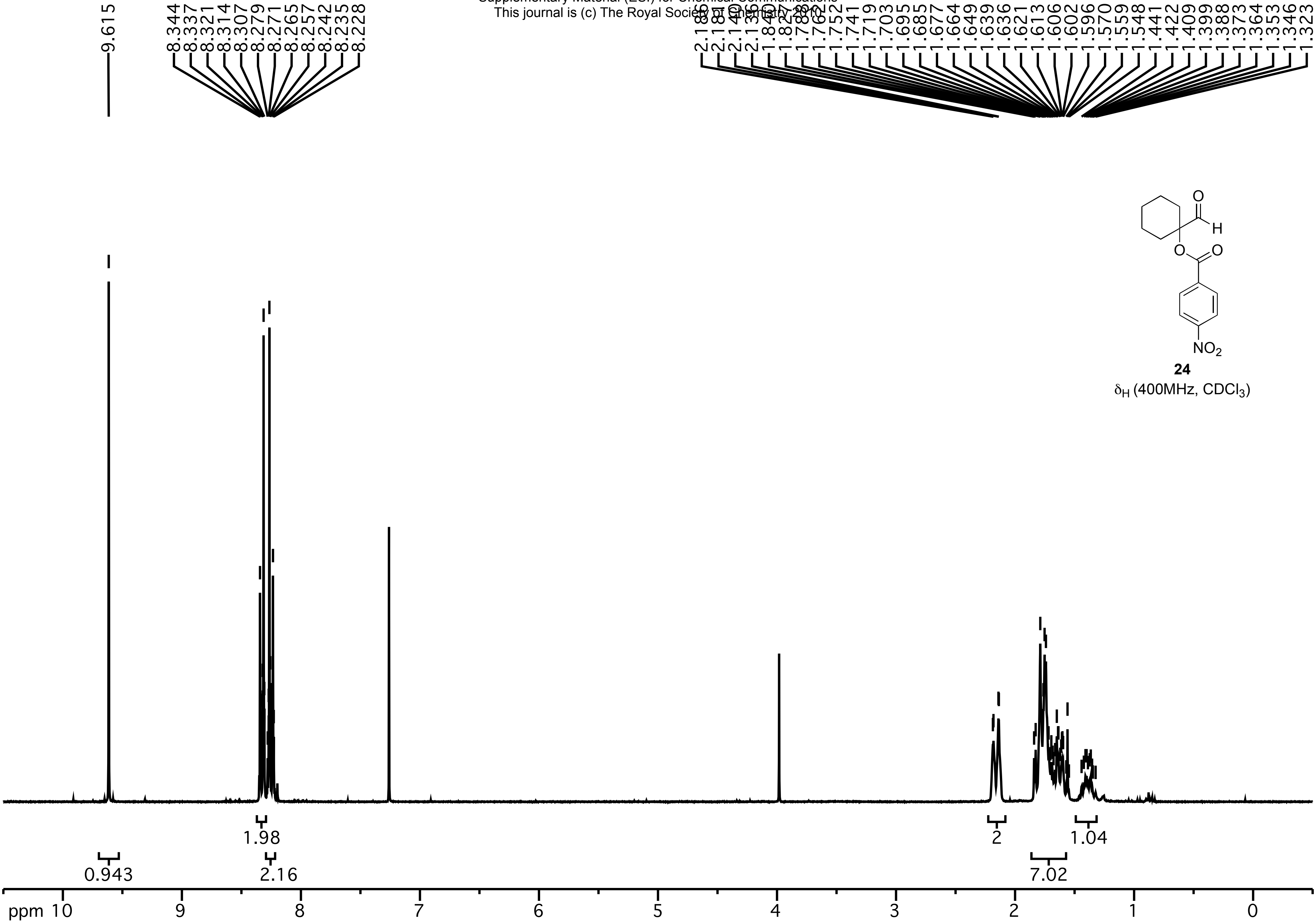


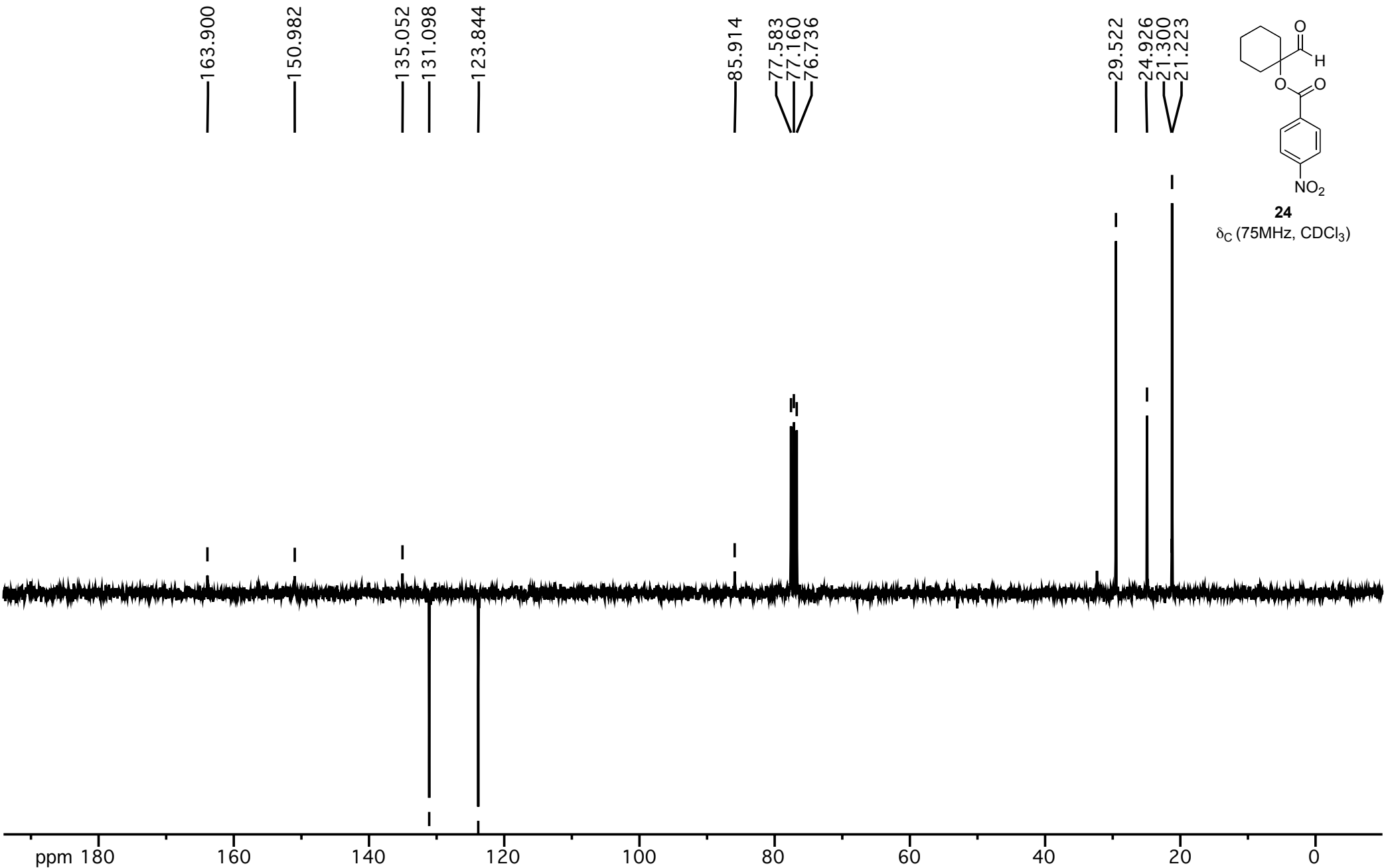
22

δ_C (75MHz, $CDCl_3$)



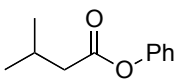

163.177
150.446
141.230
137.113
130.647
123.580
114.641
84.053
77.477
77.160
76.842
34.927
25.364
22.105
O
O
NO2
δC (100MHz, CDCl3)
00
180
160
140
120
100
80
60
40
20
0


9.615
8.344 8.337 8.321 8.314 8.307 8.279 8.271 8.265 8.257 8.242 8.235 8.228
1.741 1.719 1.703 1.695 1.685 1.677 1.664 1.649 1.639 1.636 1.621 1.613 1.606 1.602 1.596 1.570 1.559 1.548 1.441 1.422 1.409 1.399 1.388 1.373 1.364 1.353 1.346 1.323
O
H
O
O
NO2
24
δH (400MHz, CDCl3)
1.98
0.943
2.16
2
1.04
7.02
ppm 10 9 8 7 6 5 4 3 2 1 0



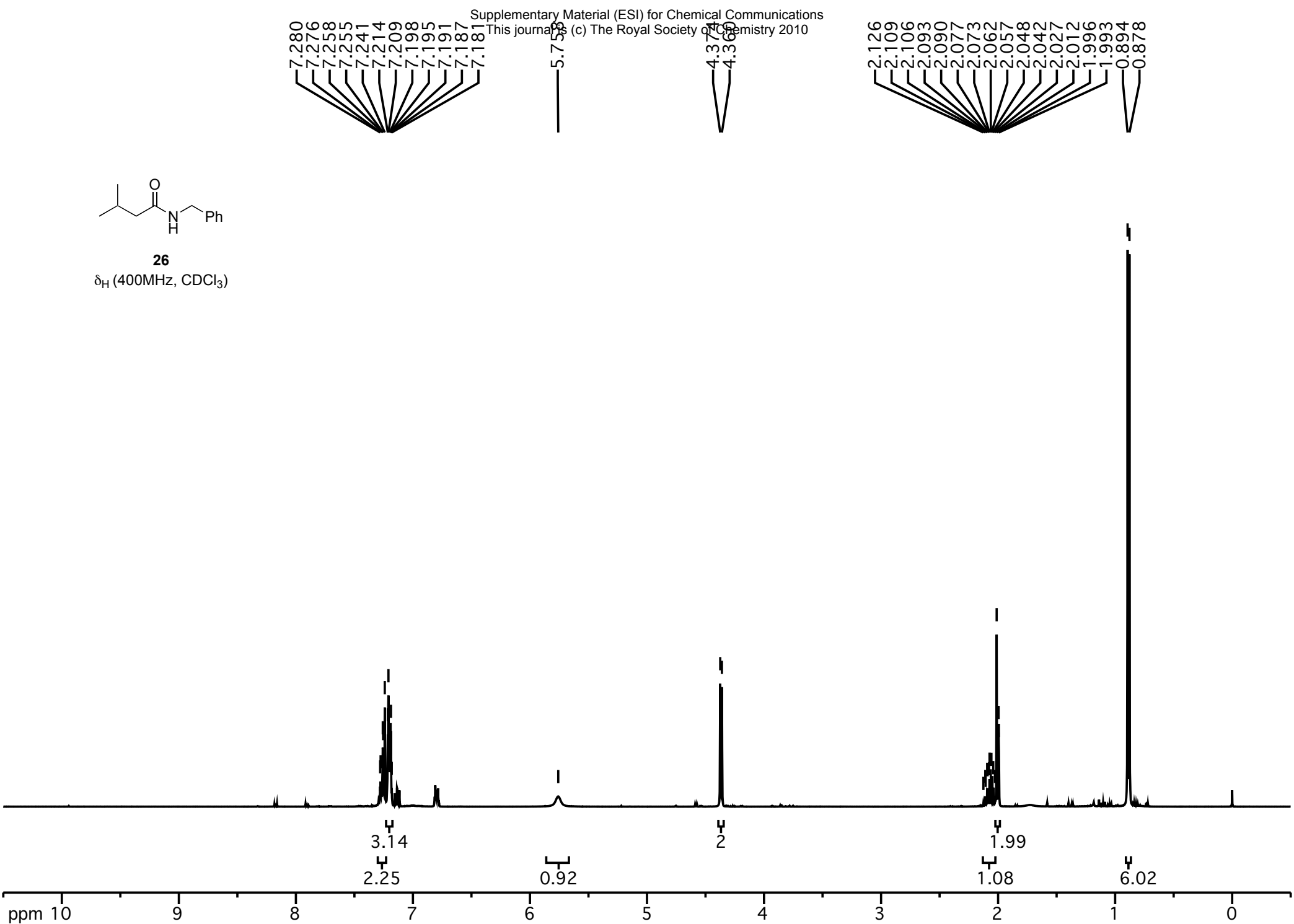
24

δ_C (75MHz, $CDCl_3$)



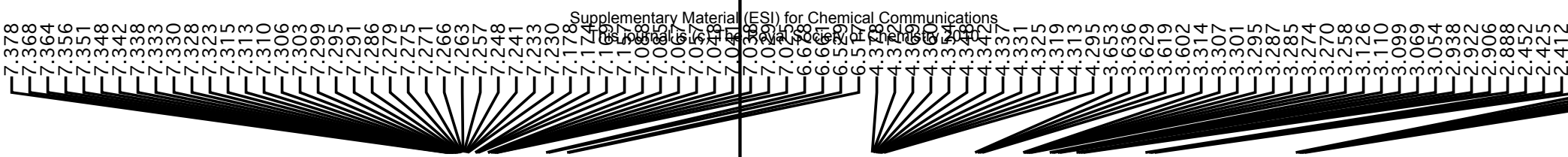
25

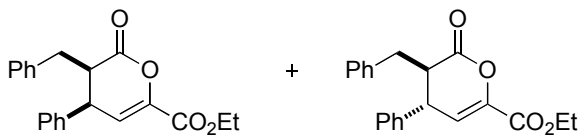
δ_H (400MHz, $CDCl_3$)



26

δ_H (400MHz, $CDCl_3$)





28a **28b**

δ_H (400MHz, $CDCl_3$)