

SUPPORTING INFORMATION

Experimental

NMR spectra were obtained on a Bruker AV 300 spectrometer (^1H NMR at 300 MHz, ^{13}C NMR at 75 MHz) in CDCl_3 using TMS as an internal standard. Chemical shifts (δ) were given in ppm and coupling constants (J) in Hz. HRMS data were obtained on a Micromass GCT Mass Spectrometer or Bruker Solarix XR FTMS. TLC was performed with precoated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on 100-200 mesh silica gel. Reagents and solvents are commercial grade and were used as supplied. Substrates are commercially available and were purchased from Innochem.

General procedures for dichlorination of olefin acids using Ph_2SO and $(\text{COCl})_2$

To a solution of oxalyl chloride (0.51 mL, 6.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) cooled at -78°C was added dropwise a solution of diphenyl sulfoxide (1.21 g, 6.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) under the atmosphere of nitrogen. After 10 min, a solution of alkenoic acid (5 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added. The mixture was then allowed to warm up to room temperature and stirred for 1 h. The mixture was carefully basified with saturated NaHCO_3 (aq.) at 0°C . The aqueous layer was separated and extracted with CH_2Cl_2 (3×20 mL). The aqueous layer was acidified with 2 M HCl solution, and extracted with CH_2Cl_2 (3×20 mL). The combined extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuum to afford the corresponding dichloro acids (**2**, **5**, **8**, **11**).

anti-3,4-Dichloropentanoic acid (**2**)

Colorless oil, 598 mg, 70% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.32 (ddd, $J = 9.3, 7.5, 3.3$ Hz, 1 H), 4.19 (dq, $J = 7.5, 6.6$ Hz, 1 H), 3.23 (dd, $J = 16.8, 3.3$ Hz, 1 H), 2.87 (dd, $J = 16.8, 9.3$ Hz, 1 H), 1.68 (d, $J = 6.6$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 176.21, 60.78, 59.33, 40.71, 22.51. All measured values were identical to those in the literature.^[1]

4,5-Dichloropentanoic acid (**5**)

Colorless oil, 420 mg, 49% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.20-4.10 (m, 1 H), 3.80 (dd, $J = 11.4, 4.2$ Hz, 1 H), 3.66 (dd, $J = 11.4, 7.5$ Hz, 1 H), 2.74-2.53 (m, 2 H), 2.46-2.34 (m, 1 H), 2.05-1.91 (m, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 178.88, 59.66, 47.88, 30.36, 29.93. All measured values were identical to those in the literature.^[2]

5,6-Dichlorohexanoic acid (**8**)

Colorless oil, 805 mg, 87% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.11-3.99 (m, 1 H), 3.78 (dd, $J = 11.4, 5.1$ Hz, 1 H), 3.65 (dd, $J = 11.4, 7.8$ Hz, 1 H), 2.43 (t, $J = 6.9$ Hz, 2 H), 2.15-1.87 (m, 2 H), 1.86-1.67 (m, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ 179.64, 60.41, 47.90, 34.09, 33.18, 20.94. All measured values were identical to those in the literature.^[3]

trans-3,4-Dichlorocyclopentanecarboxylic acid (**11**)

White solid, 778 mg, 85% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 4.43-4.40 (m, 1 H, H-C-3 or H-C-4), 4.37-4.32 (m, 1 H, H-C-4 or H-C-3), 3.39-3.24 (m, 1 H, H-C-1), 2.92-2.76 (m, 2 H, H-C-2 and H-C-5), 2.48-2.28 (m, 2 H, H'-C-2 and H'-C-5). ^{13}C NMR (CDCl_3 , 75 MHz) δ 180.60 (COOH), 65.39, 64.17 (C-3 and C-4), 40.21 (C-1), 36.49, 36.39 (C-2 and C-5). HRMS (ESI), m/z $[\text{M} - \text{H}]^-$ calcd for $\text{C}_6\text{H}_7\text{Cl}_2\text{O}_2$: 180.9828; found: 180.9826.

(E)-2,3-Dichloropropyl but-2-enoate (16)

Colorless oil, 788 mg, 80% yield. ^1H NMR (300 MHz, CDCl_3) δ 7.04 (dq, $J = 15.6, 6.9$ Hz, 1 H), 5.88 (dq, $J = 15.6, 1.5$ Hz, 1 H), 4.47 (dd, $J = 12.0, 5.1$ Hz, 1 H), 4.42 (dd, $J = 12.0, 5.1$ Hz, 1 H), 4.31-4.23 (m, 1 H), 3.79 (d, $J = 6.0$ Hz, 2 H), 1.91 (dd, $J = 6.9, 1.8$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 165.79, 146.41, 121.86, 64.11, 57.04, 44.88, 18.24. All measured values were identical to those in the literature.^[4]

General Procedure for dichlorination of olefins or olefins with hydroxy or carbonyl group using Ph_2SO and $(\text{COCl})_2$.

To a solution of oxalyl chloride (0.51 mL, 6.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) cooled at -78°C was added dropwise a solution of diphenyl sulfoxide (1.21 g, 6.0 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) under the atmosphere of nitrogen. After 10 min, a solution of substrate (5 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added. The mixture was then allowed to warm up to the temperature and stirred until TLC showed the reaction completed. Distilled water (30 mL) was added dropwise at 0°C . After stirring for 10 min, the organic layer was separated and successively washed with brine. The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuum. For **16**, **34**, **35**, and **37**, the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1 for **16**, and 10:1 for **34**, **35** and **37**). For **17**, **19**, **21**, **24**, **26**, **28** and **32**, the corresponding dichloroalkanes and the byproduct diphenyl sulfide cannot be separated by chromatography due to the similar polarity. The problem can be solved by oxidizing diphenyl sulfide to diphenyl sulfoxide to differentiate the polarity. The residue was dissolved in CH_3CN (20 mL), then aqueous 30% H_2O_2 (1.5 mL, 15 mmol, 3.0 equiv) and TMSCl (0.96 mL, 7.5 mmol, 1.5 equiv) were added. The mixture was stirred at room temperature for 30 min. After disappearance of diphenyl sulfide, the reaction mixture was quenched by adding water (20 mL), extracted with CH_2Cl_2 (3 x 20 mL), and the extract washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuum. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) afforded the corresponding dichloroalkanes.

trans-1,2-Dichlorocyclohexane (18)

Colorless oil, 631 mg, 83% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.08-3.94 (m, 2 H), 2.40-2.26 (m, 2 H), 1.84-1.65 (m, 4 H), 1.50-1.34 (m, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ 63.30, 33.58, 23.20. All measured values were identical to those in the literature.^[5]

1,2-Dichlorodecane (20)

Colorless oil, 966 mg, 92% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.03 (dddd, $J = 9.0, 7.5, 5.1, 3.9$ Hz, 1 H), 3.76 (dd, $J = 11.1, 5.1$ Hz, 1 H), 3.65 (dd, $J = 11.1, 7.5$ Hz, 1 H), 1.99 (dddd, $J = 13.8, 9.9, 5.4, 3.9$ Hz, 1 H), 1.78-1.64 (m, 1 H), 1.61-1.48 (m, 1 H), 1.48-1.38 (m, 1 H), 1.36-1.24 (m, 10 H), 0.88 (t, $J = 6.9$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 61.41, 48.41, 35.21, 31.97, 29.51, 29.33, 29.13, 25.96, 22.80, 14.24. All measured values were identical to those in the literature.^[6]

1-(2,3-Dichloropropyl)benzene (22) and 1-(1,3-dichloropropan-2-yl)benzene (23)

1-Allylbenzene (**21**) gave a mixture of two isomers (**22** and **23**) with a ratio of 1:0.25. Colorless oil, 895 mg, 93% yield.

1-(2,3-Dichloropropyl)benzene (**22**): ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.14 (m, 5 H), 4.23-4.14 (m, 1 H), 3.66 (dd, $J = 11.4, 4.8$ Hz, 1 H), 3.58 (dd, $J = 11.4, 6.9$ Hz, 1 H), 3.23 (dd, $J = 14.1,$

5.7 Hz, 1 H), 2.99 (dd, $J = 14.1, 7.2$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 136.44, 129.69, 128.72, 127.34, 61.11, 47.60, 41.17. All measured values were identical to those in the literature.^[7]

1-(1,3-Dichloropropan-2-yl)benzene (**23**): ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.14 (m, 5 H), 3.85 (dd, $J = 11.1, 6.9$ Hz, 2 H), 3.78 (dd, $J = 11.1, 6.0$ Hz, 2 H), 3.27 (quin., $J = 6.3$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 138.94, 128.91, 128.03, 127.96, 49.51, 46.02. All measured values were identical to those in the literature.^[8]

1-(1,2-Dichloroethyl)benzene (**25**)

Colorless oil, 621 mg, 71% yield. ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.36 (m, 5 H), 5.01 (dd, $J = 7.8, 6.6$ Hz, 1 H), 4.01 (dd, $J = 11.4, 6.6$ Hz, 1 H), 3.94 (dd, $J = 11.4, 7.8$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 138.14, 129.29, 128.95, 127.53, 61.89, 48.48. All measured values were identical to those in the literature.^[5]

2-(1,2-Dichloroethyl)naphthalene (**27**)

White solid, 821 mg, 73% yield. ^1H NMR (300 MHz, CDCl_3) δ 7.92-7.83 (m, 4 H), 7.57-7.51 (m, 3 H), 5.18 (dd, $J = 8.1, 6.6$ Hz, 1 H), 4.10 (dd, $J = 11.4, 6.6$ Hz, 1 H), 4.04 (dd, $J = 11.4, 8.1$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 135.29, 133.66, 133.09, 129.12, 128.31, 127.92, 127.41, 126.99, 126.82, 124.30, 62.18, 48.30. All measured values were identical to those in the literature.^[5]

anti-1,2-Dichloro-1-phenylpropane (**29**) and *syn*-1,2-dichloro-1-phenylpropane (**30**)

(*Z*)-1-(Prop-1-enyl)benzene (**28**) gave a mixture of two dichloro-isomers (**29** and **30**) with a ratio of 1:0.4 (705 mg, 75% yield) and one monochloro-isomer (**31**) (61 mg, 8% yield). (*E*)-1-(Prop-1-enyl)benzene (**32**) gave a mixture of two dichloro-isomers (**29** and **30**) with a ratio of 1:0.23 (colorless oil, 770 mg, 82% yield) and one monochloro-isomer (**31**) (colorless oil, 83 mg, 11% yield).

anti-1,2-Dichloro-1-phenylpropane (**29**): ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.22 (m, 5 H), 4.83 (d, $J = 7.8$ Hz, 1 H), 4.30 (dq, $J = 7.8, 6.3$ Hz, 1 H), 1.62 (d, $J = 6.3$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 138.77, 128.90, 128.64, 127.87, 67.55, 60.32, 22.28. All measured values were identical to those in the literature.^[5]

syn-1,2-Dichloro-1-phenylpropane (**30**): ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.26 (m, 5 H), 4.92 (d, $J = 6.0$ Hz, 1 H), 4.38-4.27 (m, 1 H), 1.38 (d, $J = 6.6$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.50, 128.98, 128.55, 128.22, 67.57, 61.35, 21.82. All measured values were identical to those in the literature.^[5]

(*E*)-1-Phenyl-2-chloro-1-propene (**31**): ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.24 (m, 2 H, H-phenyl), 7.20-7.12 (m, 3 H, H-phenyl), 6.63 (s, 1 H, H-CHPh), 2.20 (d, $J = 1.2$ Hz, 3 H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz) δ 136.06 (C1-phenyl), 133.04 (C-Cl), 128.62, 128.55 (C-*o*-phenyl and C-*m*-phenyl), 128.22 (C-CHCCl), 127.24 (C-*p*-phenyl), 22.64 (CH_3). HRMS (EI), m/z [$\text{M}]^+$ calcd for $\text{C}_9\text{H}_9\text{Cl}$: 152.0393; found: 152.0395.

anti-1,2-Dichlorohexan-3-ol (**34**) and *syn*-1,2-dichlorohexan-3-ol (**35**)

1,2-Dichlorohexan-3-ol was obtained as a mixture of two isomers (**34** + **35**) with a ratio of 1:2.2. Colorless oil, 727 mg, 85% yield.

anti-1,2-Dichlorohexan-3-ol (**34**): ^1H NMR (CDCl_3 , 300 MHz) δ 4.10 (dt, $J = 5.7, 5.7$ Hz, 1 H, H-C-2), 3.98-3.92 (m, 1 H, H-C-3), 3.87 (dd, $J = 13.8, 5.7$ Hz, 1 H, H-C-1), 3.83 (dd, $J = 13.8, 5.7$

Hz, 1 H, H'-C-1), 1.95 (s, 1 H, -OH), 1.70-1.49 (m, 3 H, H-C-4 and H-C-5), 1.47-1.32 (m, 1 H, H'-C-5), 0.97 (t, $J = 7.2$ Hz, 3 H, C-6). ^{13}C NMR (CDCl_3 , 75 MHz) δ 72.42 (C-3), 65.55 (C-2), 45.59 (C-1), 34.77 (C-4), 18.93 (C-5), 14.02 (C-6). HRMS (ESI), m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{NaO}$: 193.0157; found: 193.0157.

syn-1,2-Dichlorohexan-3-ol (**35**): ^1H NMR (CDCl_3 , 300 MHz) δ 4.07-4.01 (m, 2 H, H-C-2 and H-C-3), 3.92 (dd, $J = 10.8, 8.4$ Hz, 1 H, H-C-1), 3.75 (dd, $J = 10.8, 5.1$ Hz, 1 H, H'-C-1), 1.73-1.60 (m, 2 H, -OH and H-C-4), 1.59-1.34 (m, 3 H, H'-C-4 and H-C-5), 0.96 (t, $J = 7.2$ Hz, 3 H, H-C-6). ^{13}C NMR (CDCl_3 , 75 MHz) δ 69.51 (C-3), 65.67 (C-2), 44.72 (C-1), 37.15 (C-4), 18.94 (C-5), 14.01 (C-6). HRMS (EI), m/z $[\text{M} - \text{H}]^+$ calcd for $\text{C}_6\text{H}_{11}\text{Cl}_2\text{O}$: 169.0182; found: 169.0181.

***anti*-2,3-Dichloro-1-hexanol (37)**

Colorless oil, 761 mg, 89% yield. ^1H NMR (300 MHz, CDCl_3) δ 0.96 (t, $J = 7.5$ Hz, 3 H), 1.40-1.54 (m, 1 H), 1.56-1.70 (m, 1H), 1.70-1.84 (m, 1H), 1.90-2.10 (m, 2H), 4.00-4.17 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 66.46, 64.52, 61.53, 36.98, 18.95, 13.40. All measured values were identical to those in the literature^[9]

***anti*-3,4-Dichloro-1-hexanol (39)**

Light yellow oil, 795 mg, 93% yield. ^1H NMR (300 MHz, CDCl_3) δ 1.01 (t, $J = 7.1$ Hz, 3 H), 1.70-2.04 (m, 3 H), 2.23 (dddd, $J = 14.7, 8.1, 6.9, 2.7$ Hz, 1 H), 2.49 (s, 1 H), 3.78 (m, 2 H), 3.93 (ddd, $J = 9.3, 6.3, 3.3$ Hz, 1 H), 4.16 (ddd, $J = 10.5, 6.3, 2.7$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 67.92, 62.02, 59.20, 37.03, 28.11, 10.60. All measured values were identical to those in the literature.^[10]

***syn*-3,4-Dichloro-1-hexanol (41)**

Colorless oil, 778 mg, 91% yield. ^1H NMR (300 MHz, CDCl_3) δ 1.00 (t, $J = 7.5$ Hz, 3 H), 1.60 (s, 1 H), 1.72-2.15 (m, 4 H), 3.78 (dd, $J = 7.2, 4.5$ Hz, 2 H), 3.92 (ddd, $J = 9.3, 4.2, 2.7$ Hz, 1 H), 4.29 (ddd, $J = 9.9, 3.6, 2.7$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ 67.46, 61.63, 59.36, 37.49, 28.19, 11.38. All measured values were identical to those in the literature.^[10]

(1*R,3*S**,4*S**)-3,4-Dichlorocyclohexylmethanol (43)**

Colorless oil, 823 mg, 90% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 4.40 (m, 1 H, H-C-2), 4.34 (q, $J = 3.0$ Hz, 1 H, H-C-1), 3.53 (d, $J = 5.7$ Hz, 2 H, H-C- CH_2OH), 2.35 (dddd, $J = 15.3, 12.3, 4.2, 3.0$ Hz, 1 H, H'-C-6), 2.00-2.14 (m, 2 H, H'-C-3 and H-C-4), 1.84-1.98 (m, 2 H, H-C-3 and H-C-6), 1.50-1.70 (m, 2 H, H-C-5), 1.45 (br, 1 H, OH). ^{13}C NMR (CDCl_3 , 75 MHz) δ 66.93 (C- CH_2OH), 59.81 (C-1), 59.74 (C-2), 33.33 (C-4), 30.63 (C-3), 27.16 (C-6), 22.33 (C-5). HRMS (EI), m/z $[\text{M} - \text{H}_2\text{O}]^+$ calcd for $\text{C}_7\text{H}_{10}\text{Cl}_2$: 164.0154; found: 164.0152.

1-Mesyloxy-3,4-dichlorobutane (45)

Colorless oil, 994 mg, 90% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 4.41 (m, 2 H, H-C-1), 4.23 (m, 1 H, H-C-3), 3.82 (dd, $J = 11.7, 5.1$ Hz, 1 H, H-C-4), 3.70 (dd, $J = 11.7, 6.9$ Hz, 1 H, H'-C-4), 3.03 (s, 3 H, CH_3 (MsO)), 2.48 (m, 1 H, H-C-2), 2.05 (1 H, H'-C-2). ^{13}C NMR (CDCl_3 , 75 MHz) δ 66.10 (C-1), 56.46 (C-3), 47.96 (C-4), 37.25 (CH_3 (MsO)), 34.53 (C-2). HRMS (ESI), m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_5\text{H}_{10}\text{Cl}_2\text{NaO}_3\text{S}$: 242.9620; found: 242.9621.

5,6-Dichloro-2-hexanone (47)

Light yellow oil, 835 mg, 87% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 4.12 (dddd, $J = 9.9, 7.2, 5.1, 3.0$ Hz, 1 H, H-C-5), 3.78 (dd, $J = 11.4, 5.1$ Hz, 1 H, H'-C-6), 3.66 (dd, $J = 11.4, 7.2$ Hz, 1 H, H-C-

6), 2.61-2.80 (m, 2 H, H-C-3), 2.30-2.42 (m, 1 H, H'-C-4), 2.19 (s, 3 H, H-C-1), 1.83-1.97 (m, 1 H, H-C-4). ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.04 (C-2), 60.30 (C-5), 48.20 (C-6), 39.58 (C-3), 29.99 (C-1), 29.01 (C-4). HRMS (ESI), m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_6\text{H}_{10}\text{Cl}_2\text{NaO}$: 191.0001; found: 191.0005.

10,11-Dichloro-1-undecanal (49)

Light yellow oil, 1111 mg, 93% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 9.71 (t, $J = 2.1$ Hz, 1 H, H-C-1), 3.99 (dddd, $J = 9.0, 7.2, 5.1, 3.9$ Hz, 1 H, H-C-10), 3.71 (dd, $J = 11.4, 5.1$ Hz, 1 H, H-C-11), 3.61 (dd, $J = 11.4, 7.2$ Hz, 1 H, H-C-11), 2.38 (td, $J = 7.2, 2.1$ Hz, 2 H, H-C-2), 1.91 (m, 1 H, H'-C-9), 1.67 (m, 1 H, H-C-9), 1.20-1.62 (m, 12 H, H-C-3~8). ^{13}C NMR (CDCl_3 , 75 MHz) δ 202.62 (C-1), 61.09 (C-10), 48.15 (C-11), 43.71 (C-2), 34.87 (C-9), 29.05, 29.00, 28.93, 28.72 (C-4~7), 25.62 (C-8), 21.87 (C-3). HRMS (ESI), m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{20}\text{Cl}_2\text{NaO}$: 261.0783; found: 261.0776.

anti-2,3-Dichloro-1,3-diphenylpropan-1-one (51)

White solid, 767 mg, 55% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 8.10 (m, 2 H), 7.67 (m, 1 H), 7.60-7.50 (m, 4 H), 7.48-7.40 (m, 3 H), 5.52 (d, $J = 10.5$ Hz, 1 H), 5.48 (d, $J = 10.5$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.31, 137.04, 134.65, 134.27, 129.34, 128.98, 128.77, 128.31, 60.03, 56.96. All measured values were identical to those in the literature.^[11]

(Z)-2-Chloro-1,3-diphenylprop-2-en-1-one (52)

Light yellow oil, 327 mg, 27% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.88-7.76 (m, 4 H), 7.57 (m, 1 H), 7.53-7.40 (m, 6 H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.33, 139.83, 136.86, 132.90, 132.58, 130.72, 130.50, 130.44, 129.58, 128.66, 128.51. All measured values were identical to those in the literature.^[12]

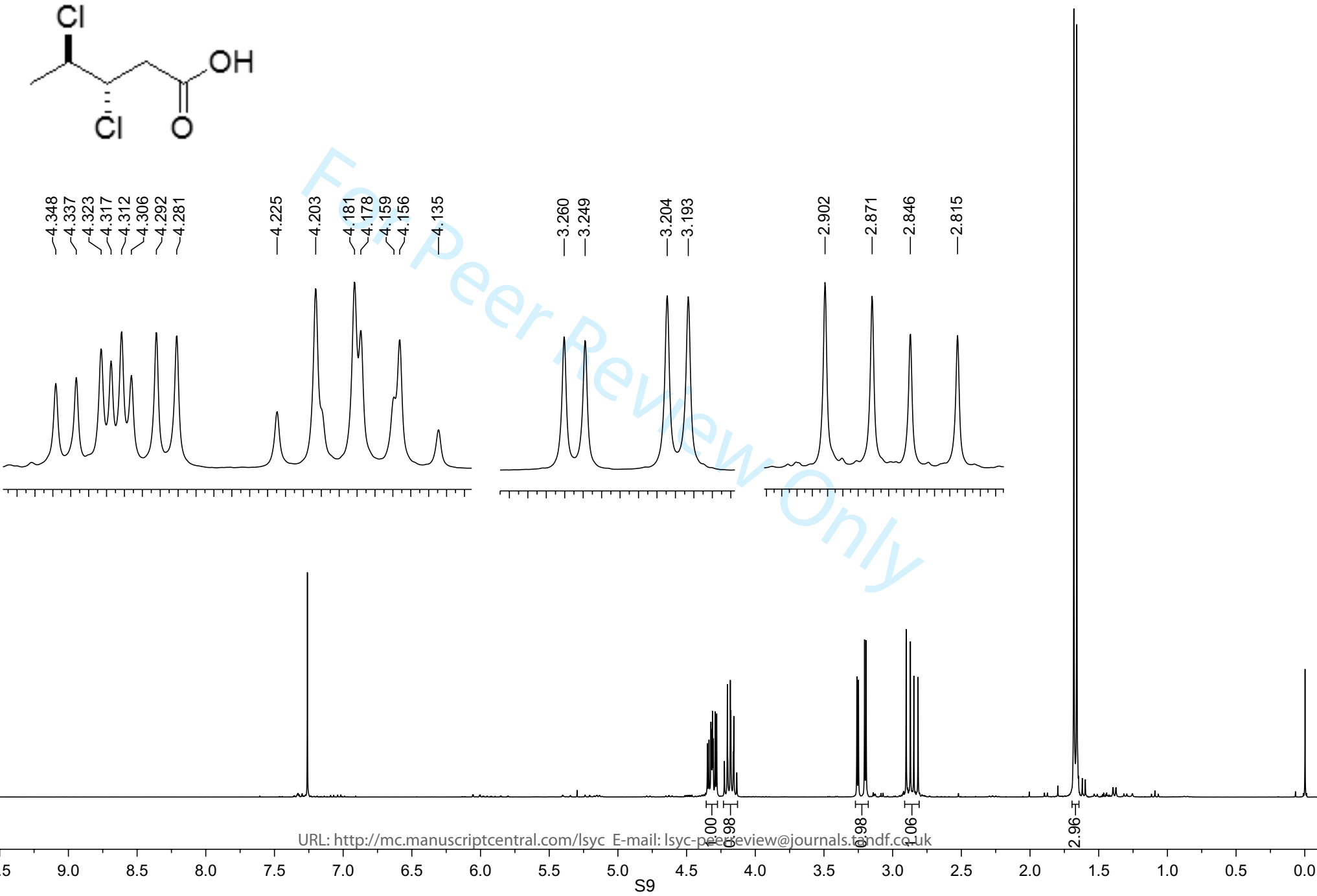
anti-2,3-Dichloro-1-phenyl-3-p-methoxyphenylpropan-1-one (54)

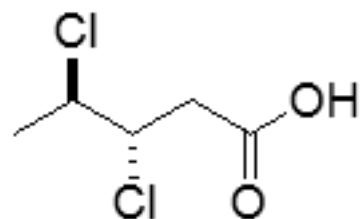
White solid, 1250 mg, 81% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (m, 2 H), 7.66 (m, 1 H), 7.55 (m, 2 H), 7.45 (d, $J = 8.7$ Hz, 2 H), 6.96 (d, $J = 8.7$ Hz, 2 H), 5.50 (d, $J = 10.5$ Hz, 1 H), 5.46 (d, $J = 10.5$ Hz, 1 H), 3.84 (s, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.43, 160.22, 134.70, 134.21, 129.54, 129.04, 128.95, 114.13, 60.07, 57.12, 55.31. All measured values were identical to those in the literature.^[11]

References

- [1] Ding, R.; Lan, L.; Li, S.; Liu, Y.; Yang, S.; Tian, H.; Sun, B. A novel method for the chlorolactonization of alkenoic acids using diphenyl sulfoxide/oxalyl chloride. *Synthesis*, **2018**, 50, 2555-2566.
- [2] Sakai, K.; Sugimoto, K.; Shigeizumi, S.; Kondo, K. A new selective dichlorination of C-C double bonds. *Tetrahedron Lett.*, **1994**, 35, 737-740.
- [3] Fadel, A.; Salauen, J.; Conia, J. M. Small ring compounds—XLI : cyclobutene cycloadditions; synthesis and reactivity in the bicyclo[2.2.0]hexan-2-one series. *Tetrahedron*, **1983**, 39, 1567-1573.
- [4] Markó, I. E.; Richardson, P. F. Controlling the reactivity of permanganate anion. Novel, stereospecific, dichlorination of olefins. *Tetrahedron Lett.*, **1991**, 32, 1831-1834.
- [5] Swamy, P.; Reddy, M. M.; Kumar, M. A.; Naresh, M.; Narender, N. Vicinal dichlorination of olefins using NH_4Cl and Oxone®. *Synthesis*, **2014**, 46, 251-257.
- [6] Heath, E.; Brown, W. A.; Jensen, S. R.; Bratty, M. P. Biodegradation of chlorinated alkanes and their commercial

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3 mixtures by *Pseudomonas* sp. strain 273. *J. Ind. Microbiol. Biotechnol.*, **2006**, 33, 197-207.
- 4 [7] Denton, R. M.; Tang, X.; Przeslak, A. Catalysis of phosphorus(V)-mediated transformations: dichlorination
5 reactions of epoxides under Appel conditions. *Org. Lett.*, **2010**, 12, 4678-4681.
- 6 [8] Fain, D.; Dubois, J.-E. Aryl-assisted halogen exchange and rearrangements of 2-bromo-1-chloro-3-arylpropanes
7 and 1-bromo-3-chloro-2-arylpropanes. Evidence for a competitive bromine-assisted pathway in the case of 1,2-
8 dibromo-3-arylpropanes. *J. Org. Chem.*, **1987**, 52, 260-267.
- 9 [9] Schlama, T.; Gabriel, K.; Gouverneur, V.; Mioskowski, C. Tetraethylammonium trichloride : a versatile reagent
10 for chlorinations and oxidations. *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 2342-2344.
- 11 [10] Ren, J.; Tong, R. Convenient in situ generation of various dechlorinating agents from oxone and chloride:
12 diastereoselective dichlorination of allylic and homoallylic alcohol derivatives. *Org. Biomol. Chem.*, **2013**, 11, 4312-
13 4315.
- 14 [11] Liu, X.; Wang, L.; Zou, J. Mn(III)-Mediated Chlorination of Conjugated Ketones. *Chin. J. Chem.*, **2011**, 29,
15 2097-2100.
- 16 [12] Chehal, N. K.; Budzelaar, P. H. M.; Hultin, P. G. E-Z isomerization in Suzuki cross-couplings of haloenones:
17 ligand effects and evidence for a separate catalytic cycle. *Org. Biomol. Chem.*, **2018**, 16, 1134-1143.
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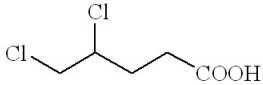
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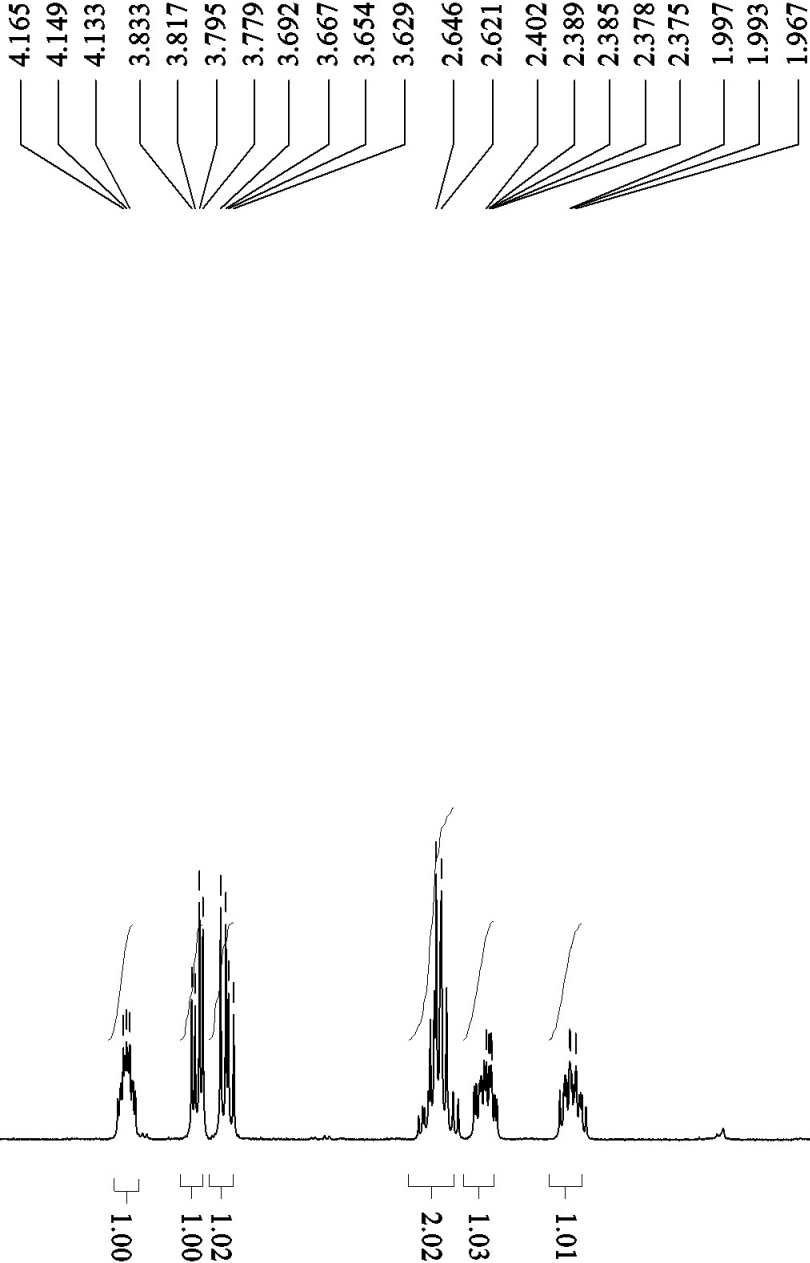
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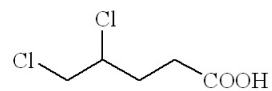


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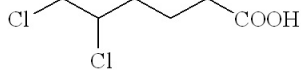
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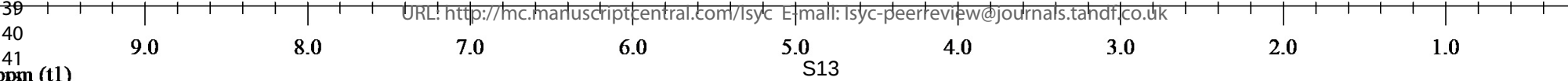
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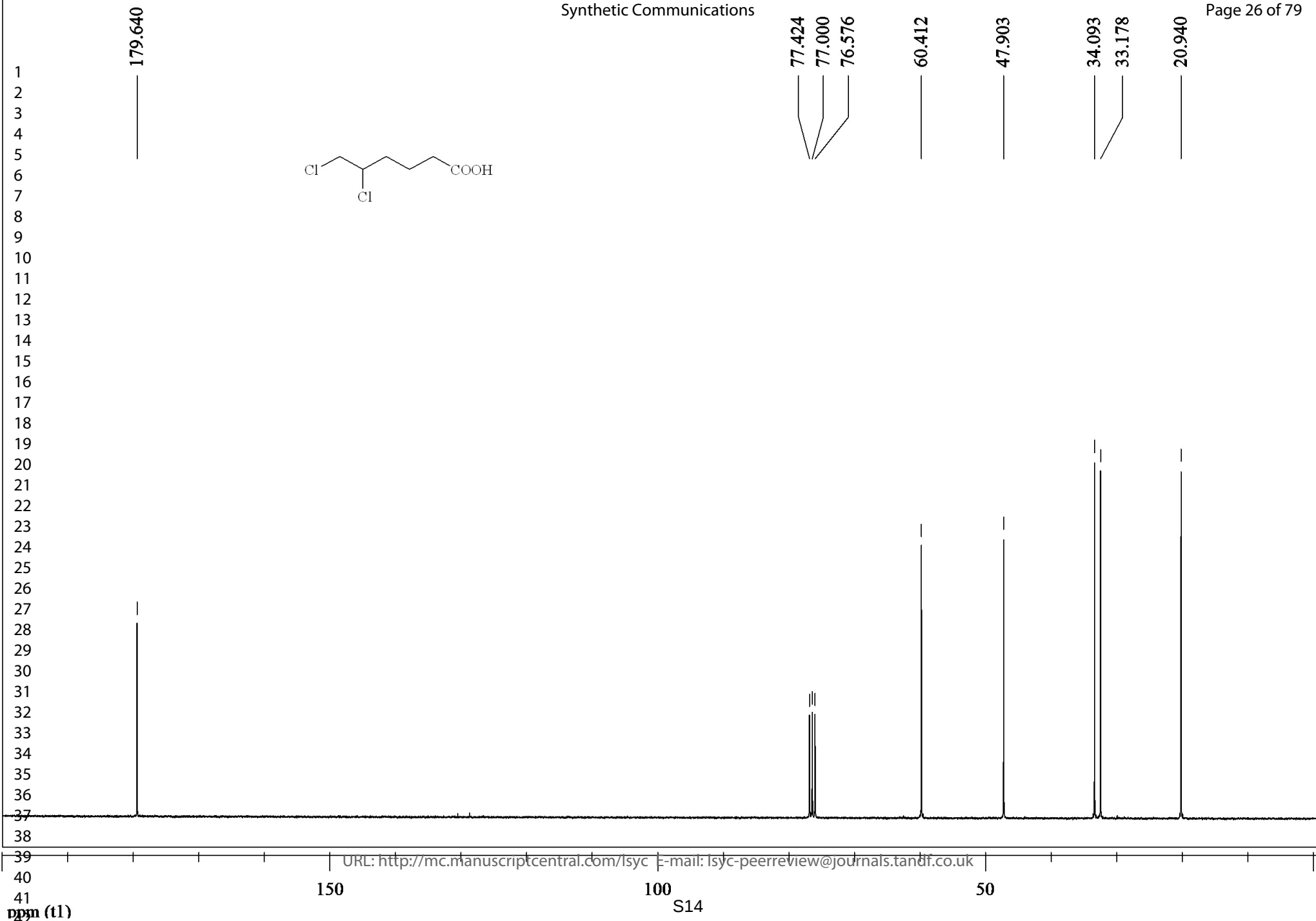


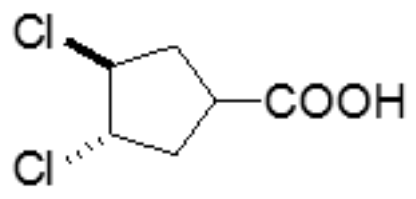
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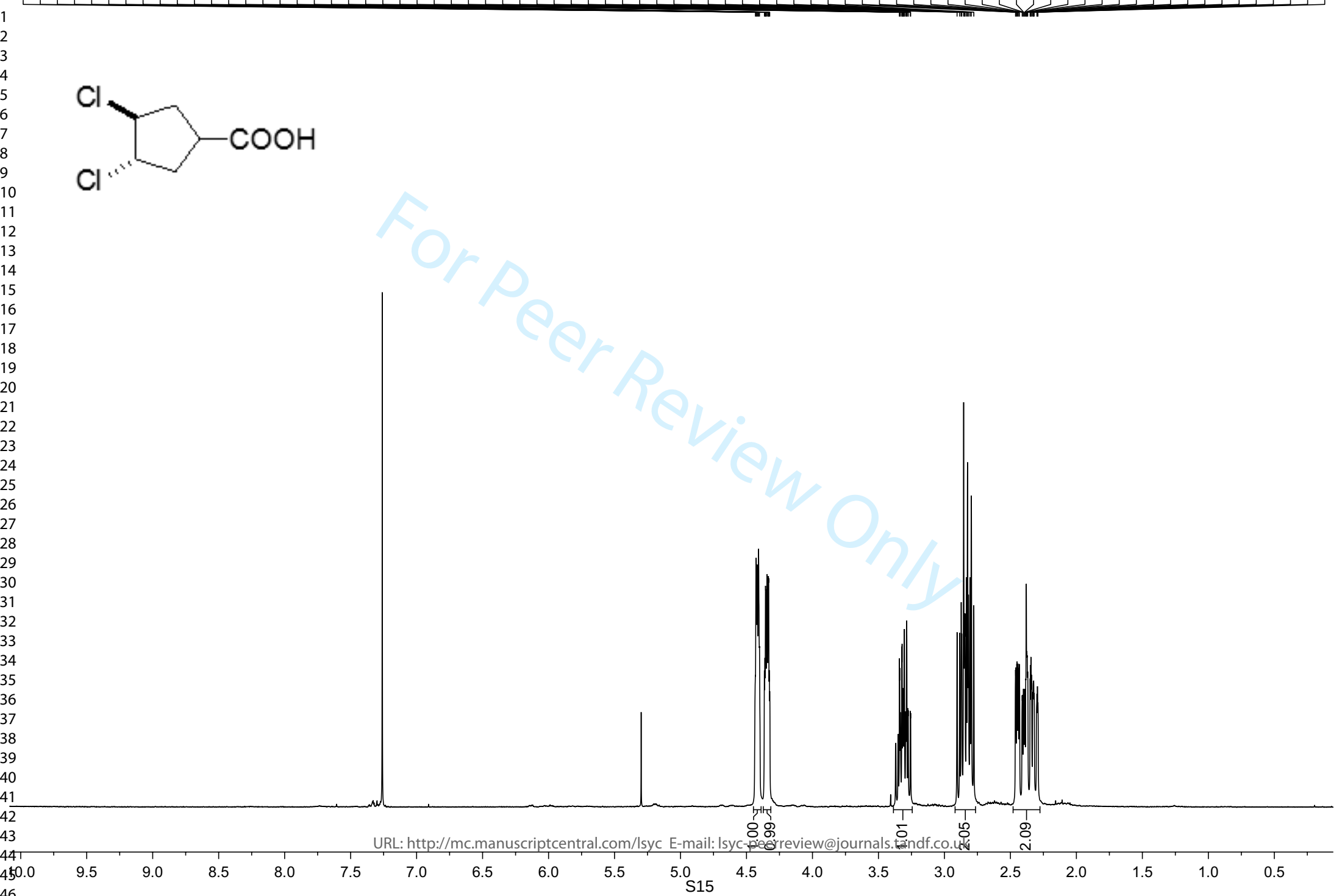
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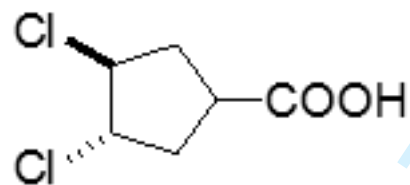






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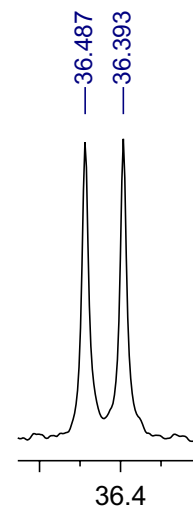


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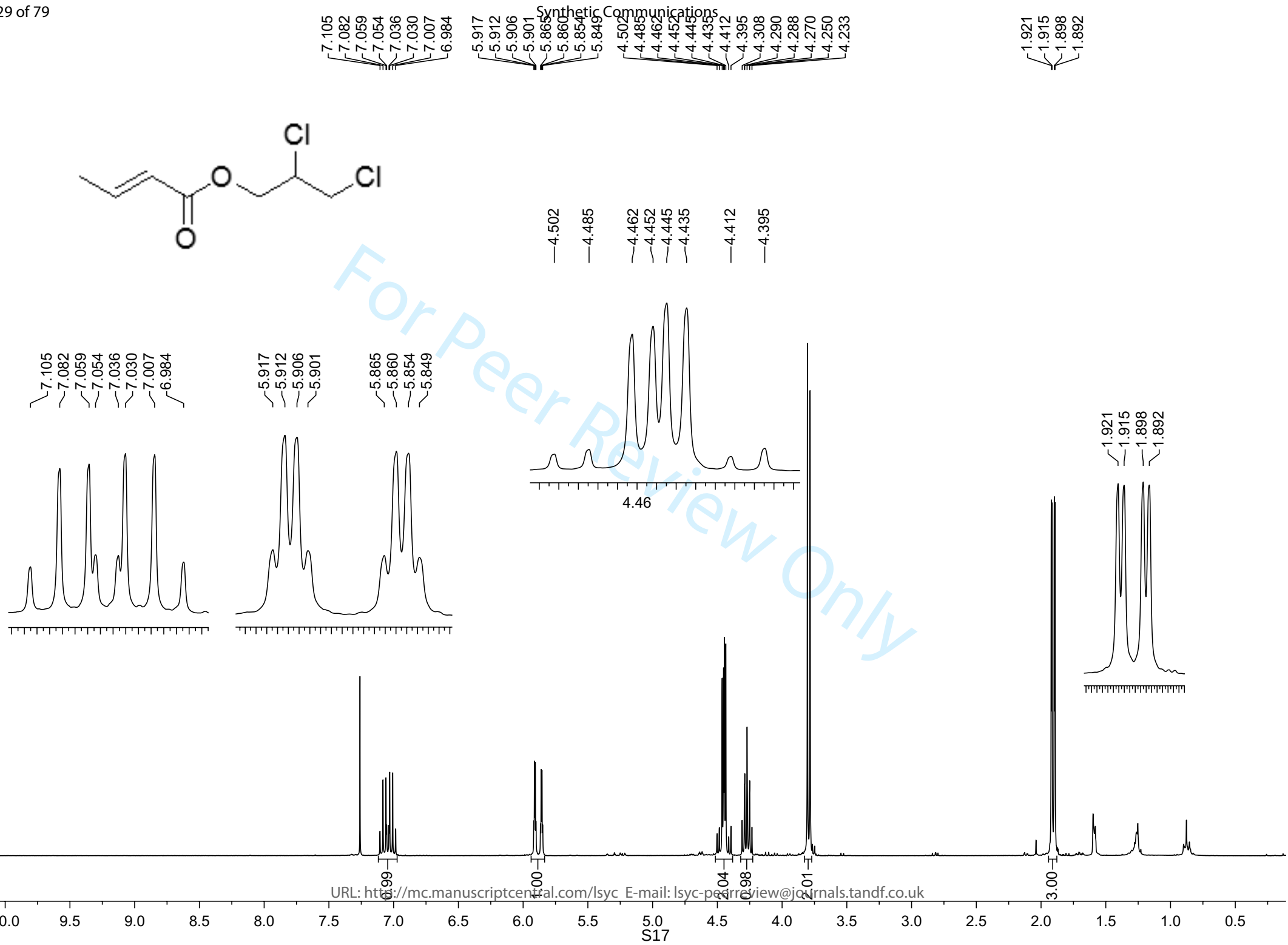
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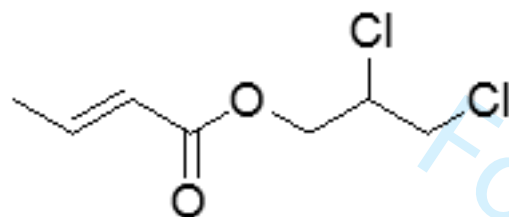
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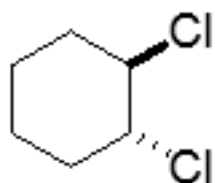
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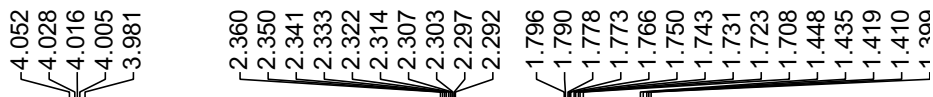
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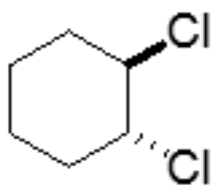
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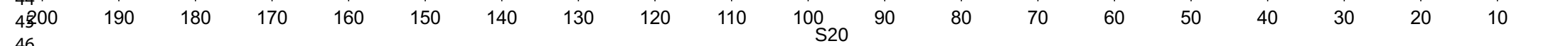


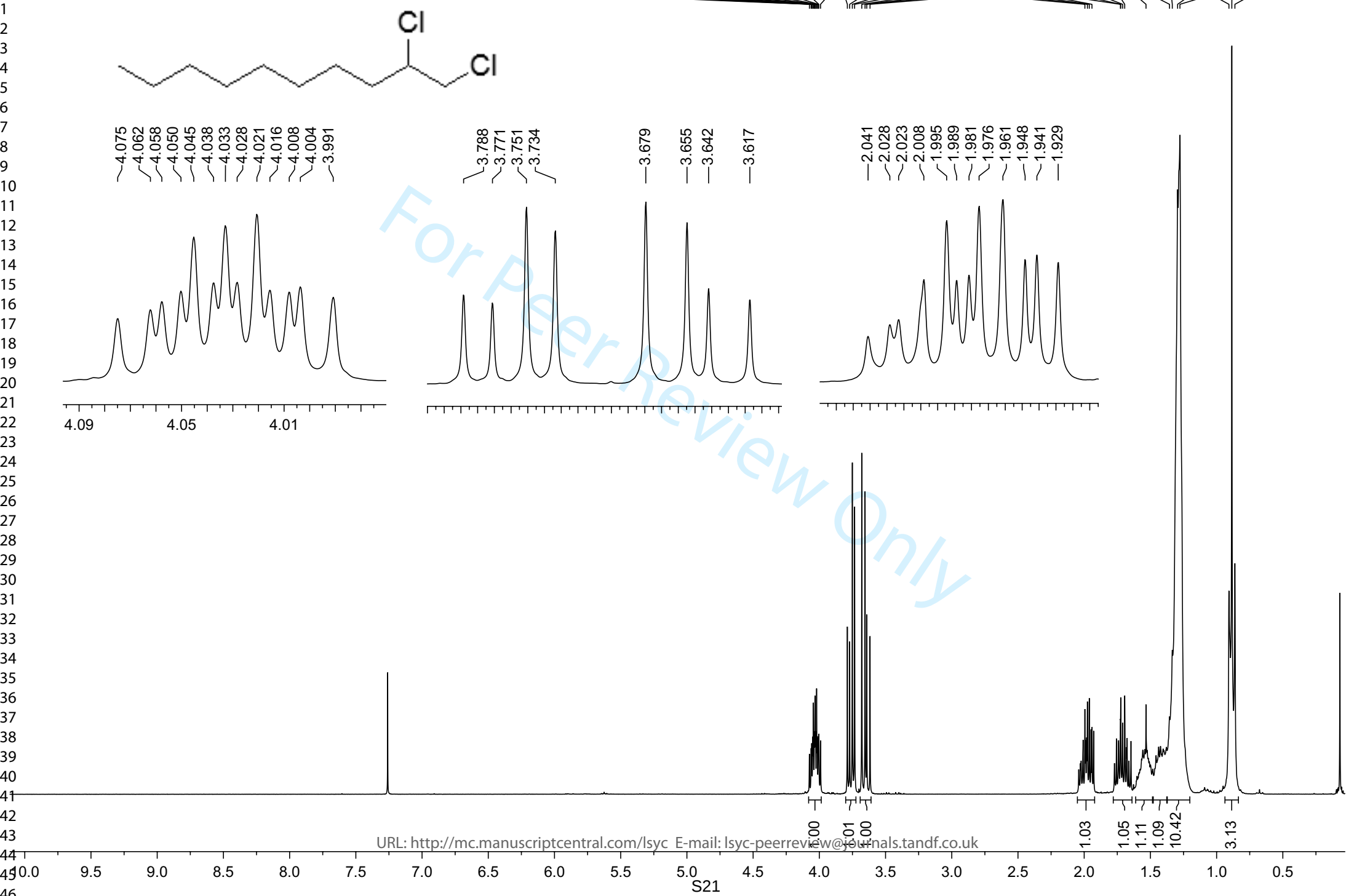
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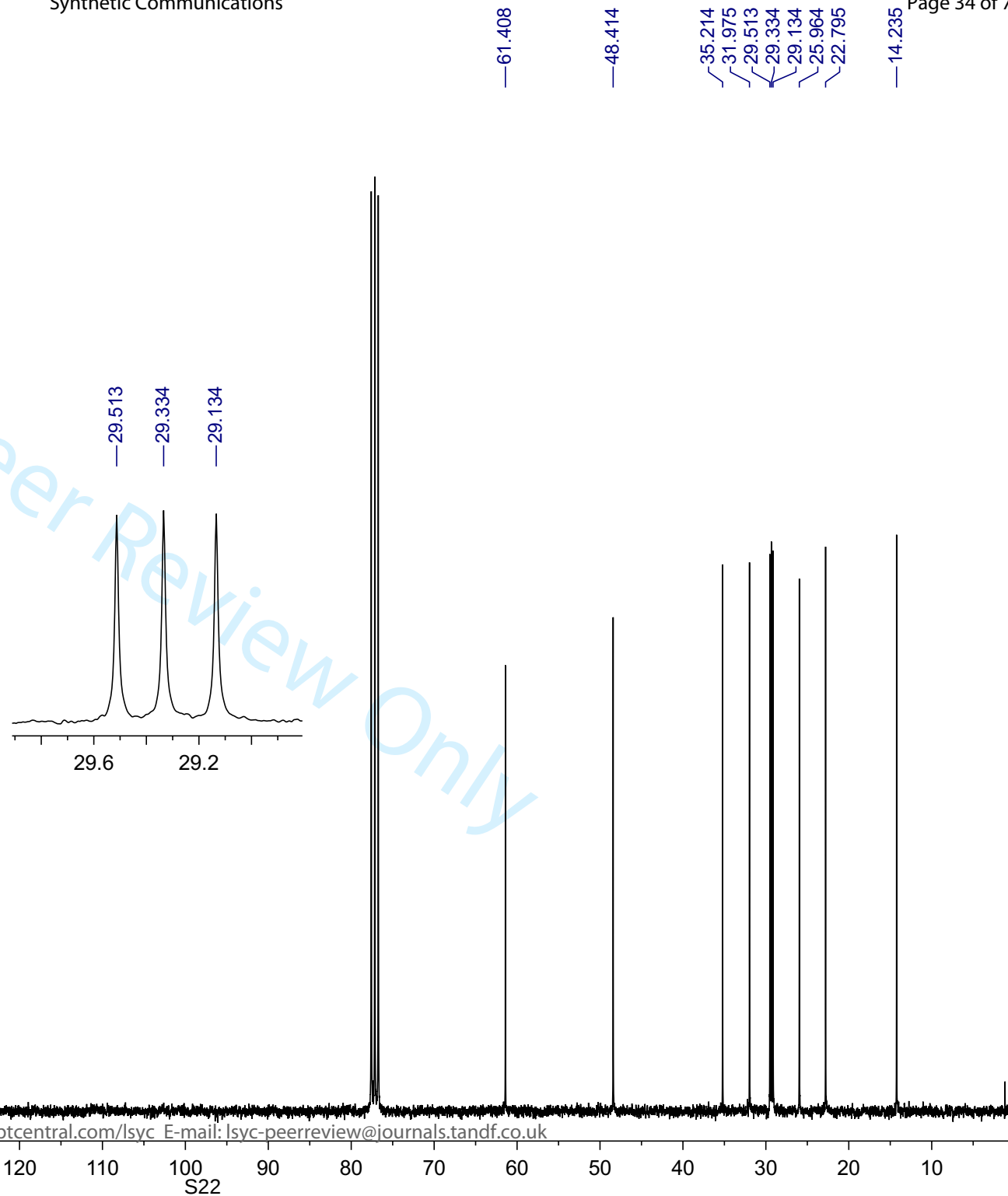
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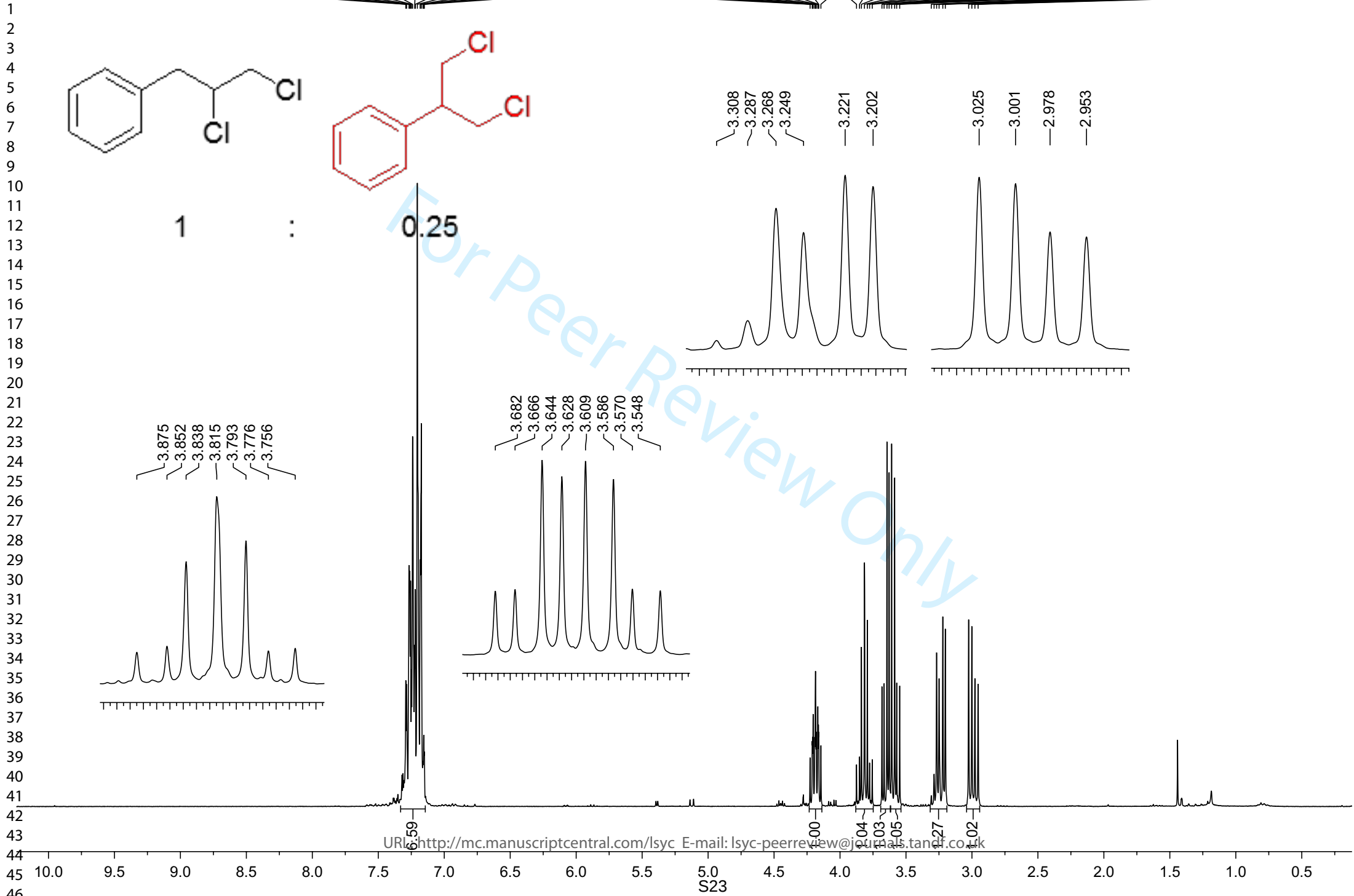
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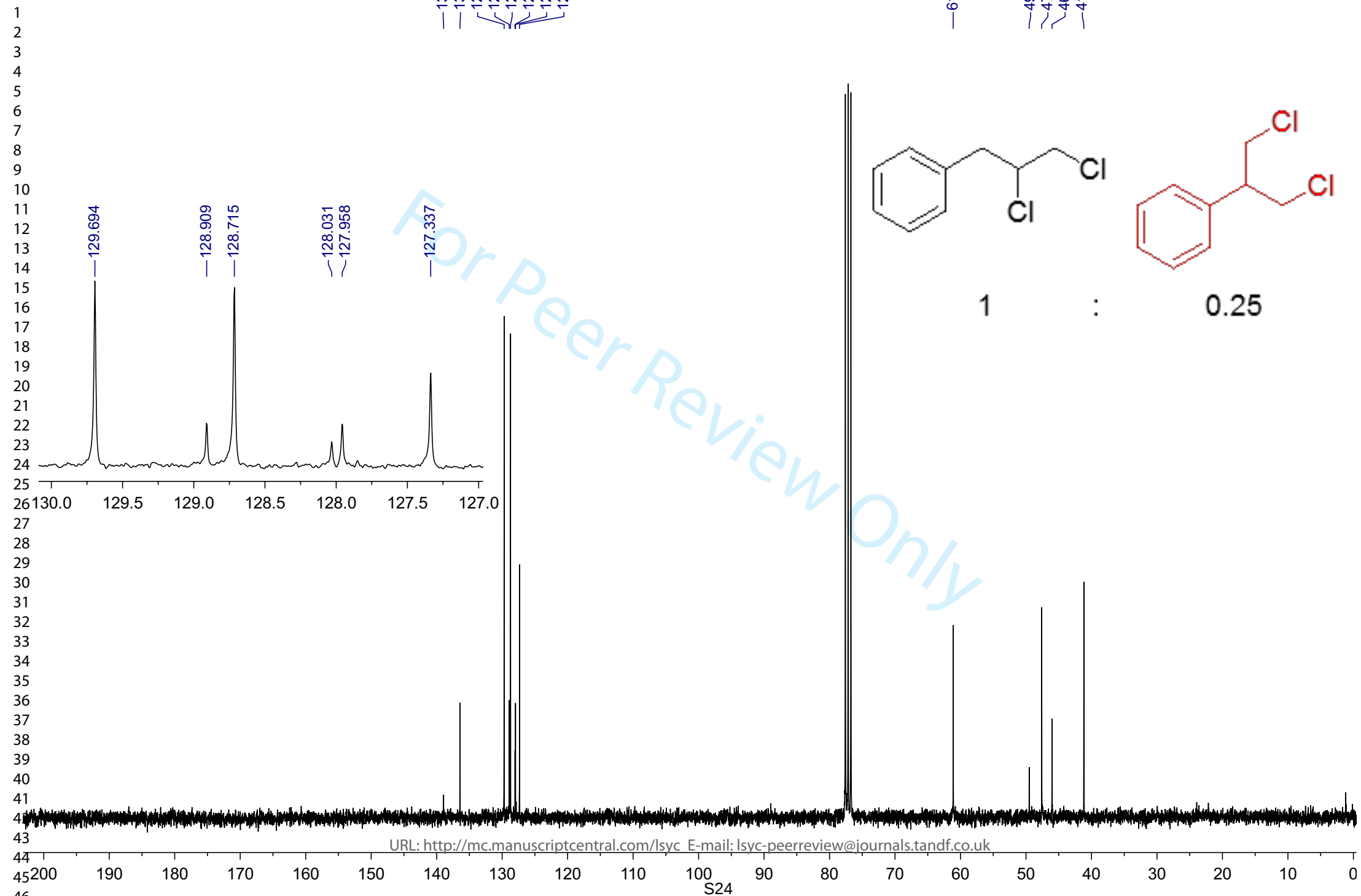
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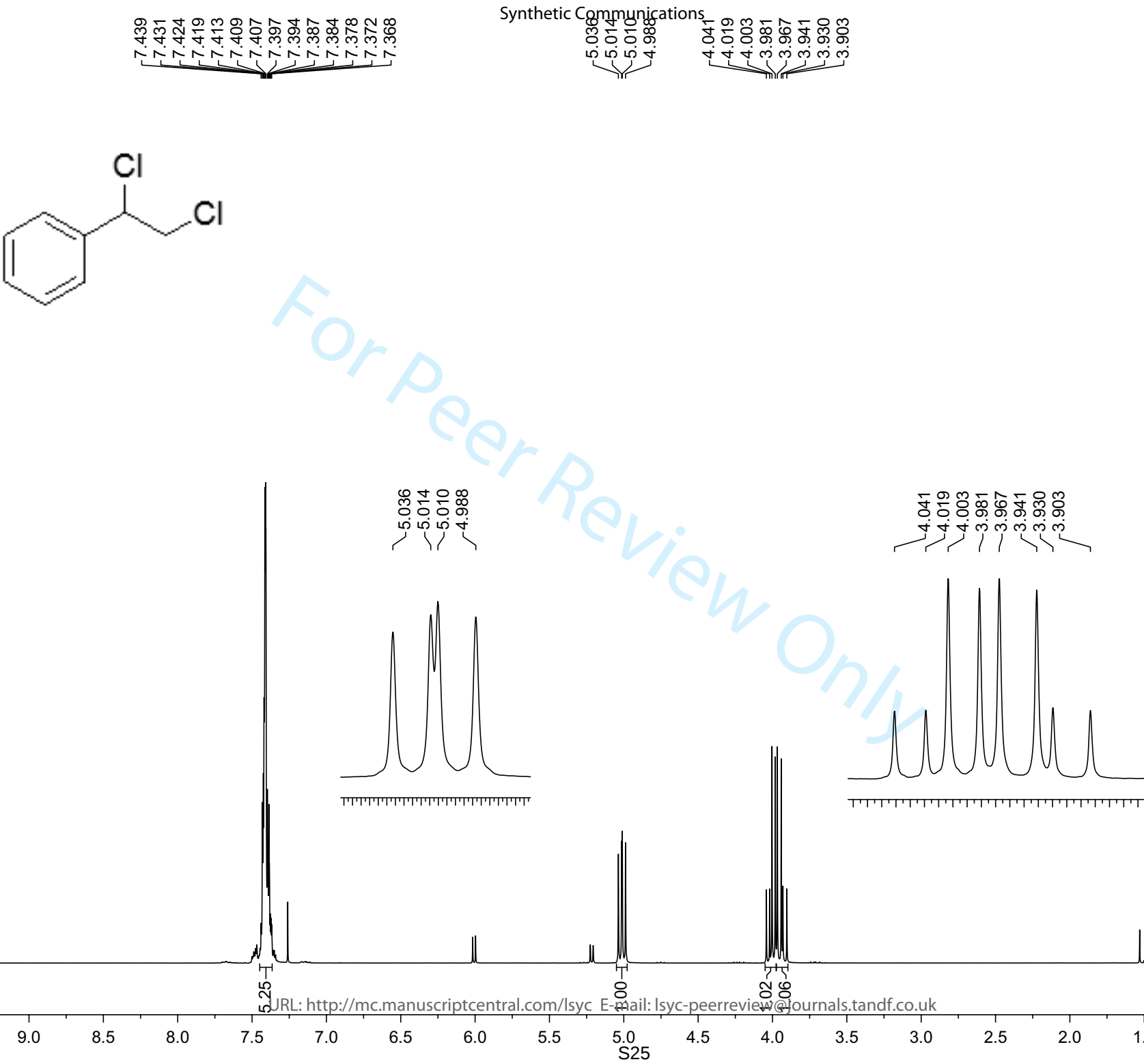


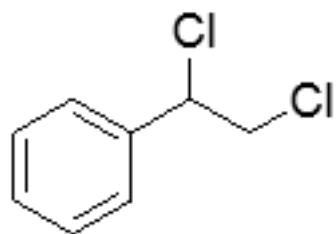






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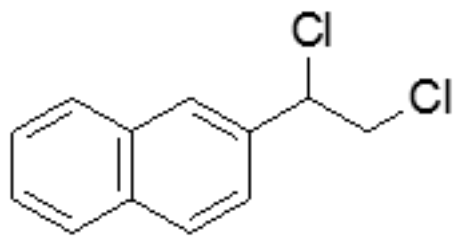
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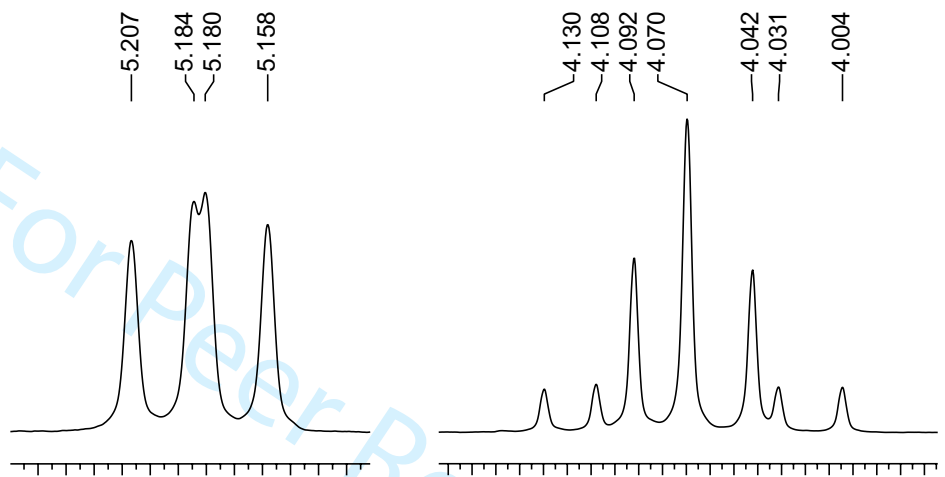
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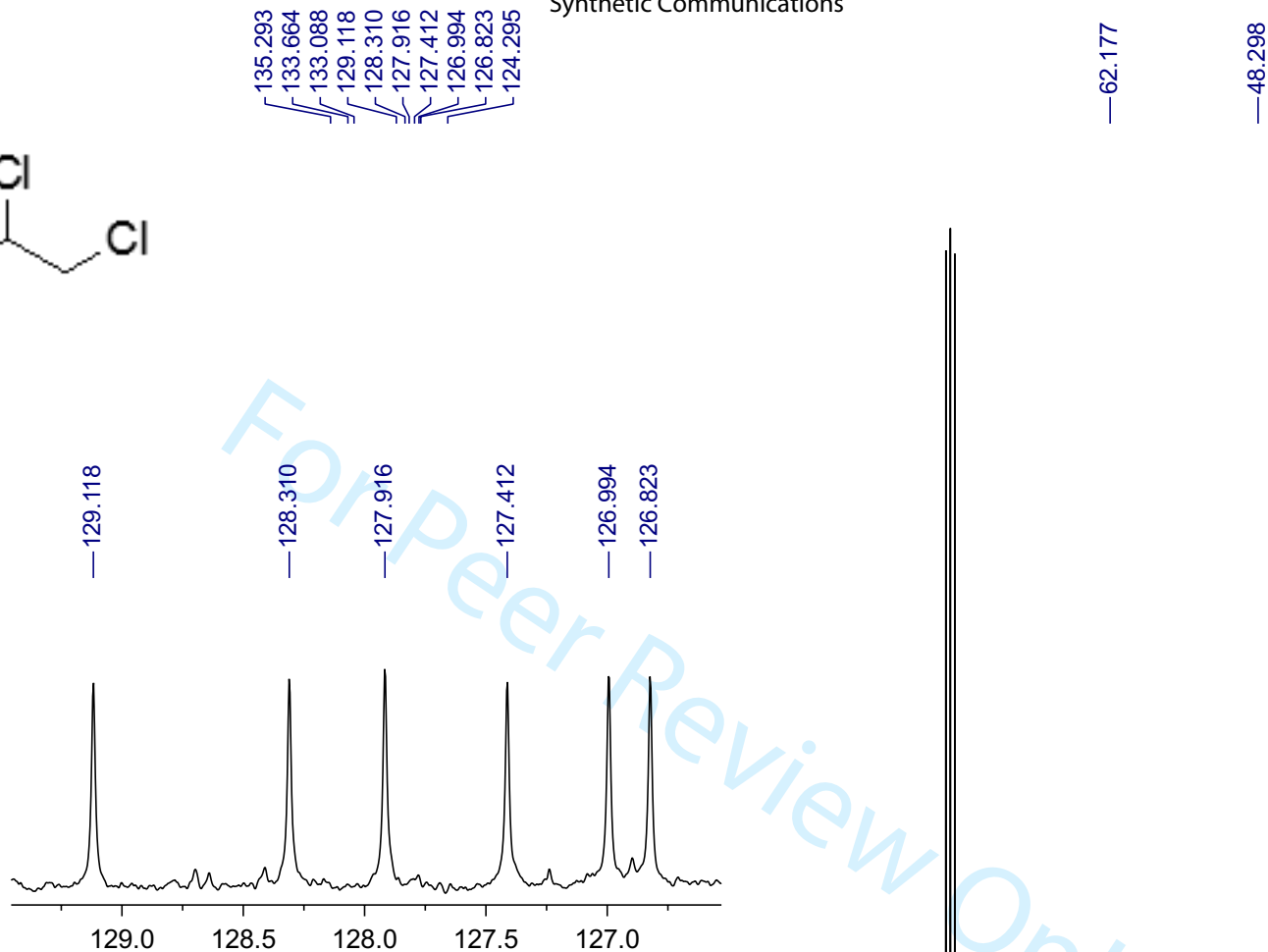
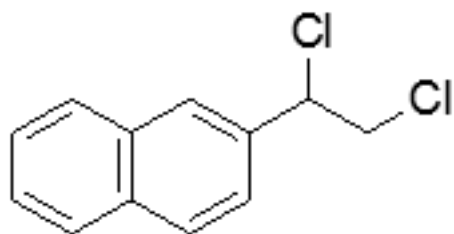


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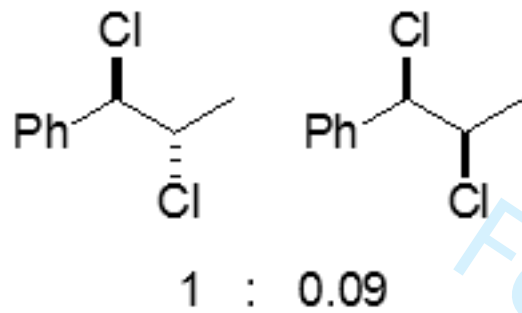
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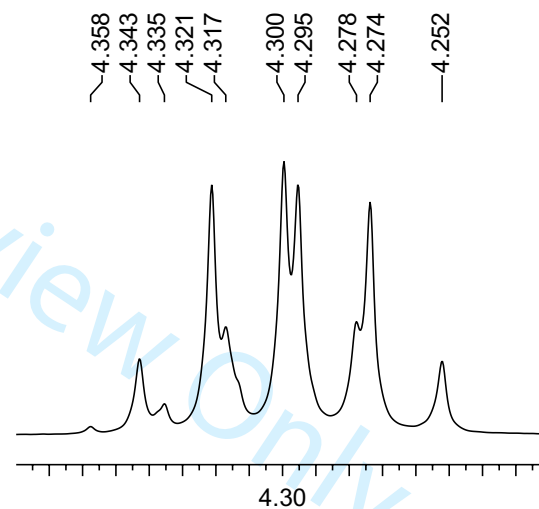


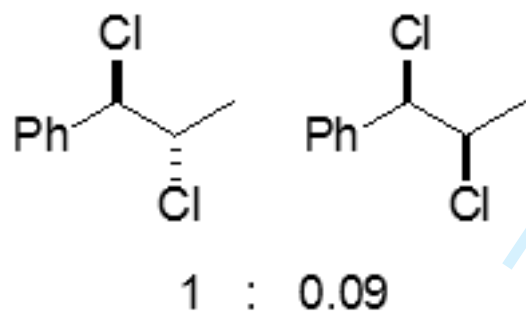
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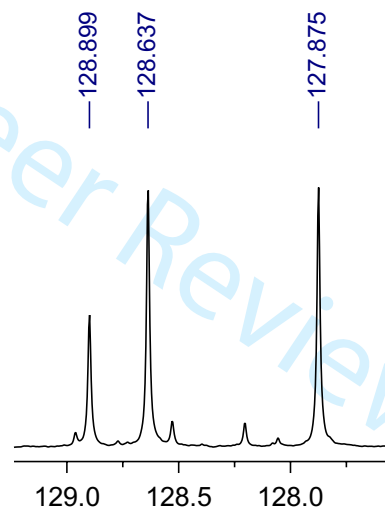


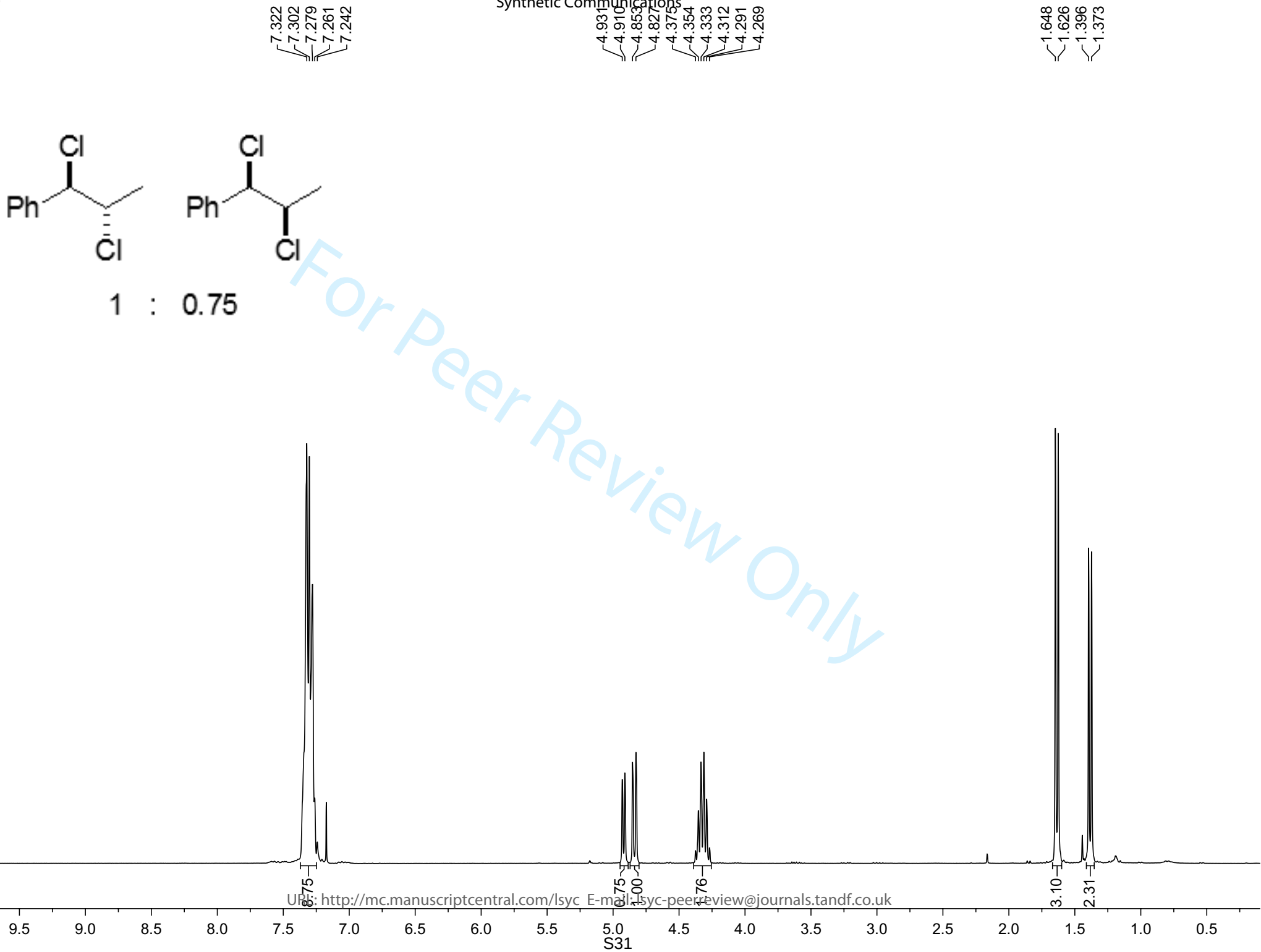


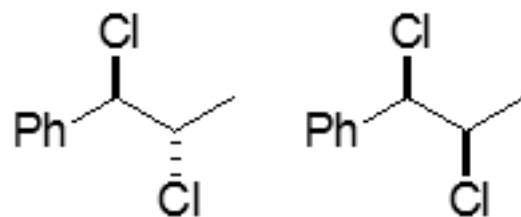
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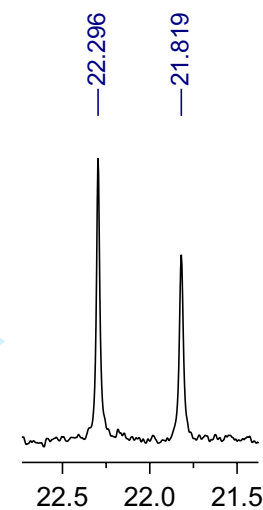
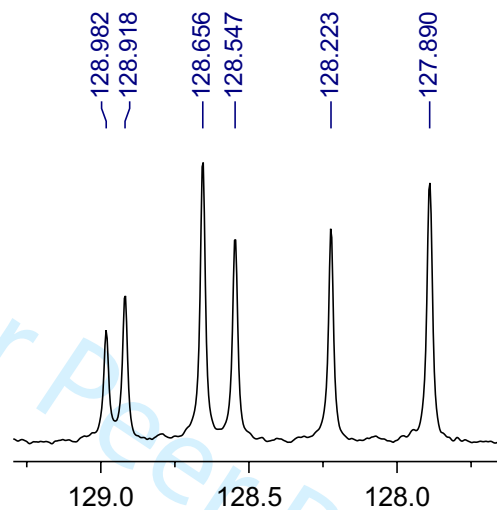




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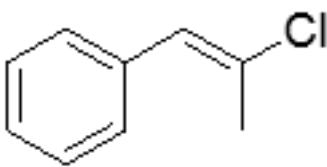
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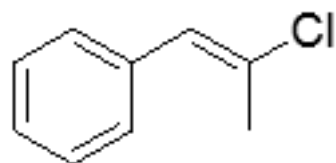
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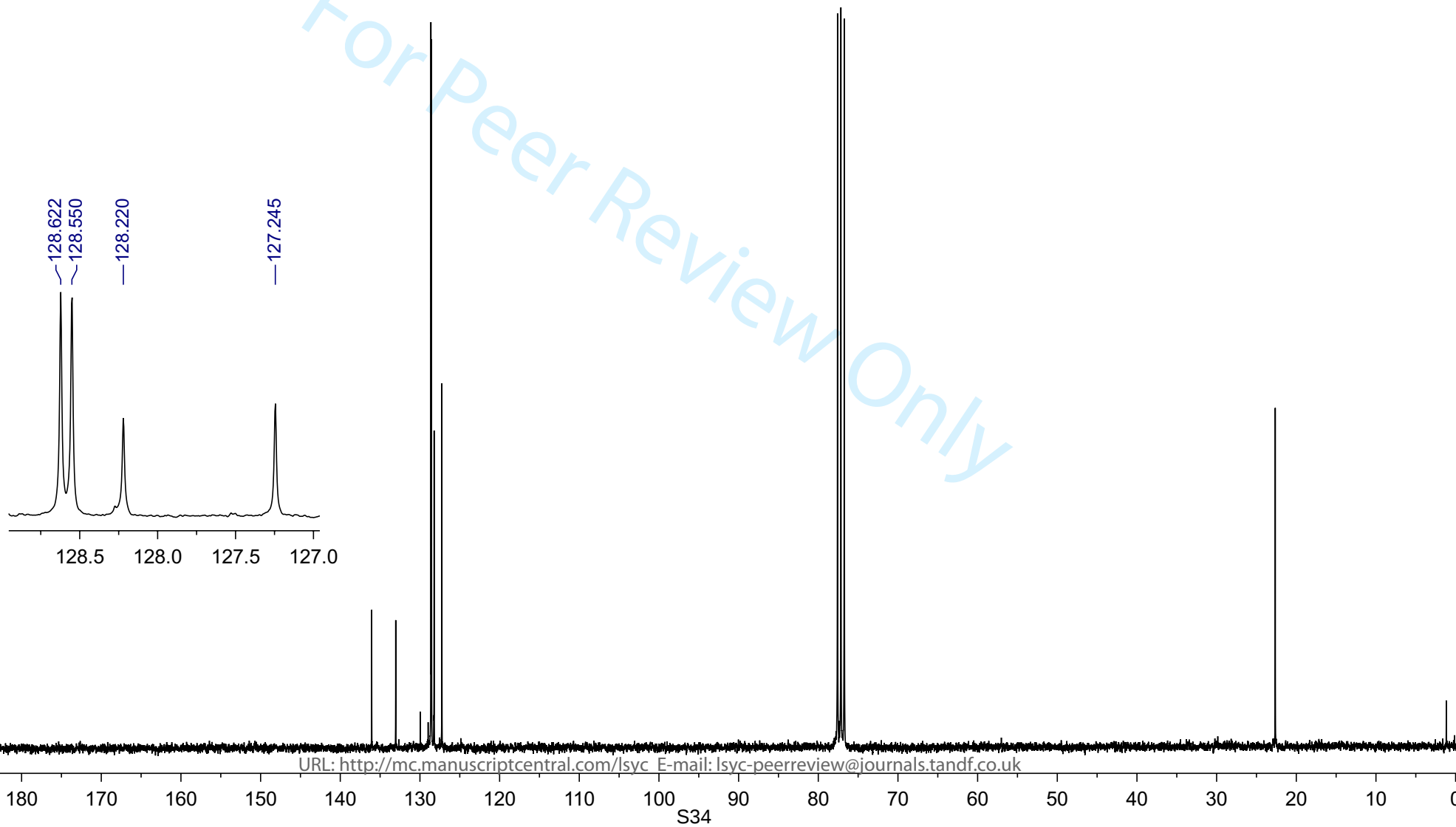


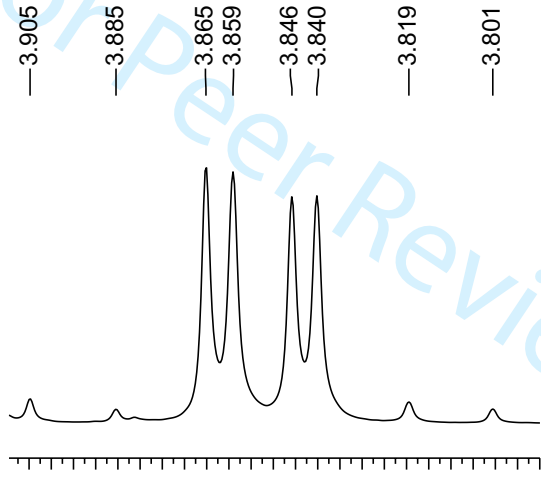
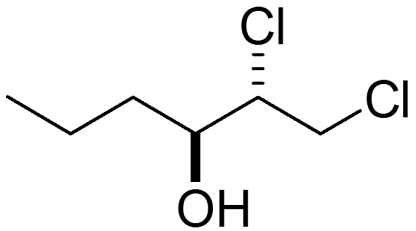
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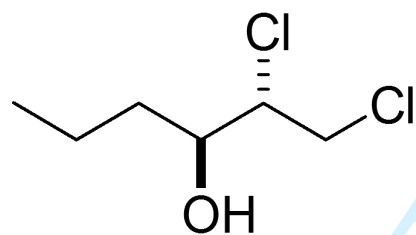
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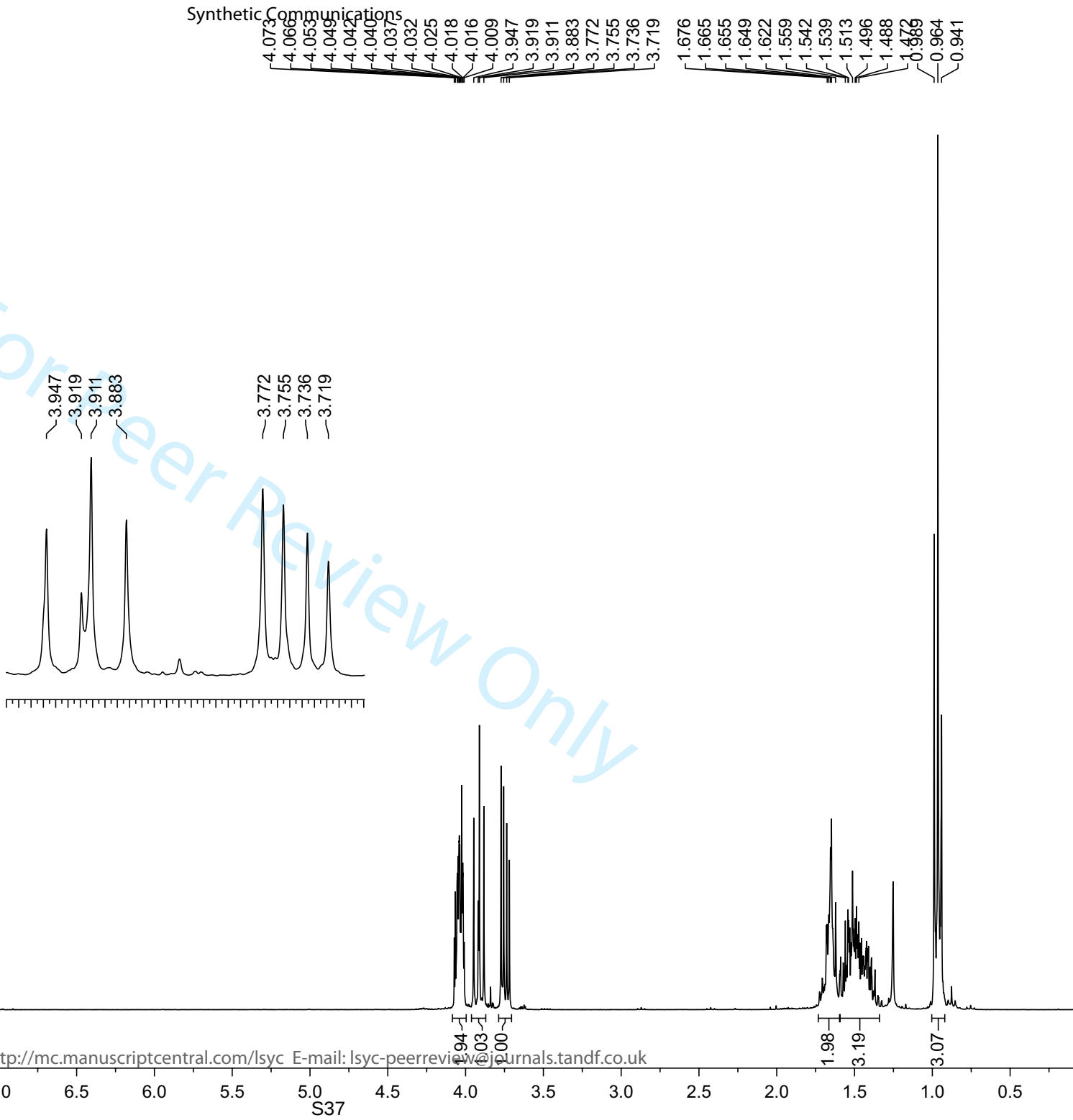
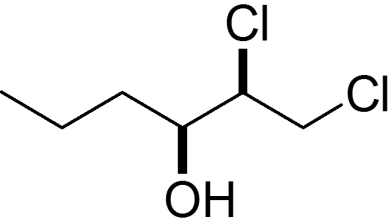
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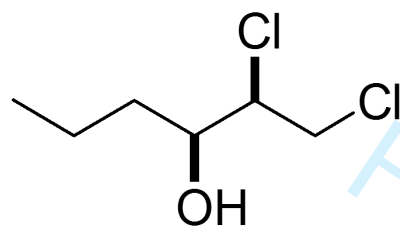
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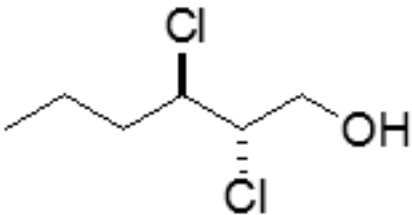
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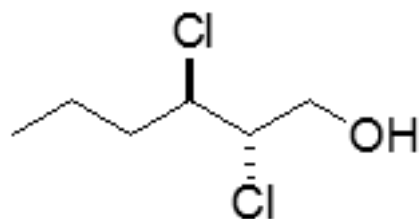
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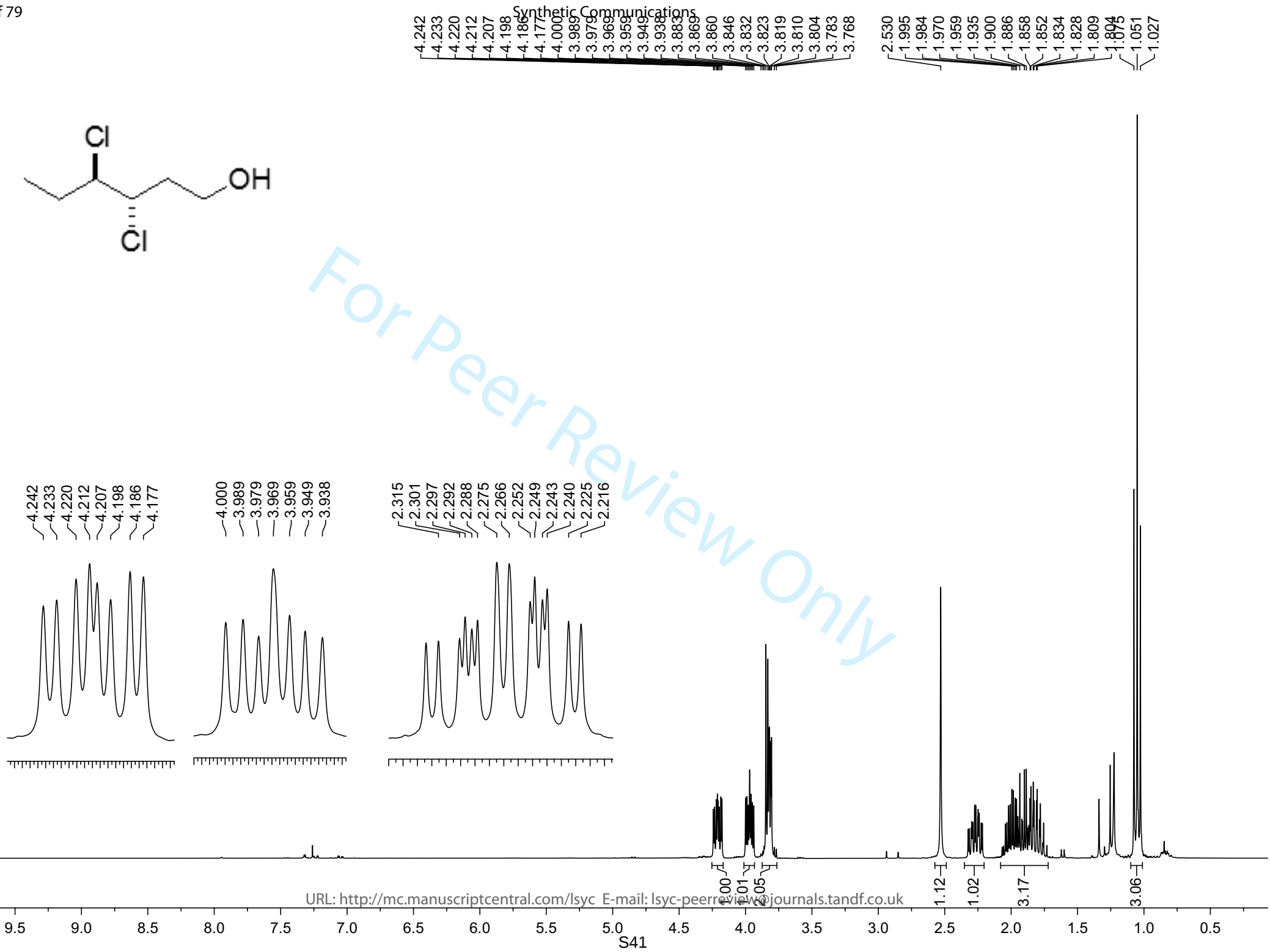
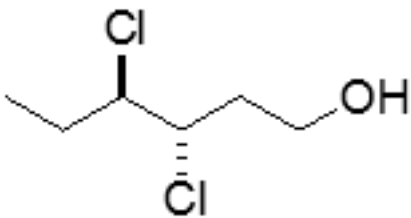
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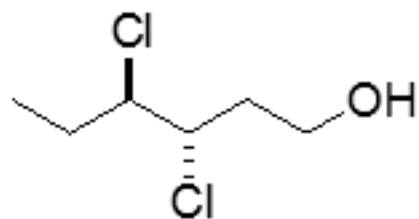
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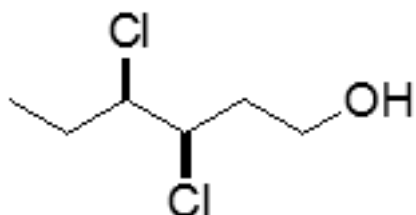
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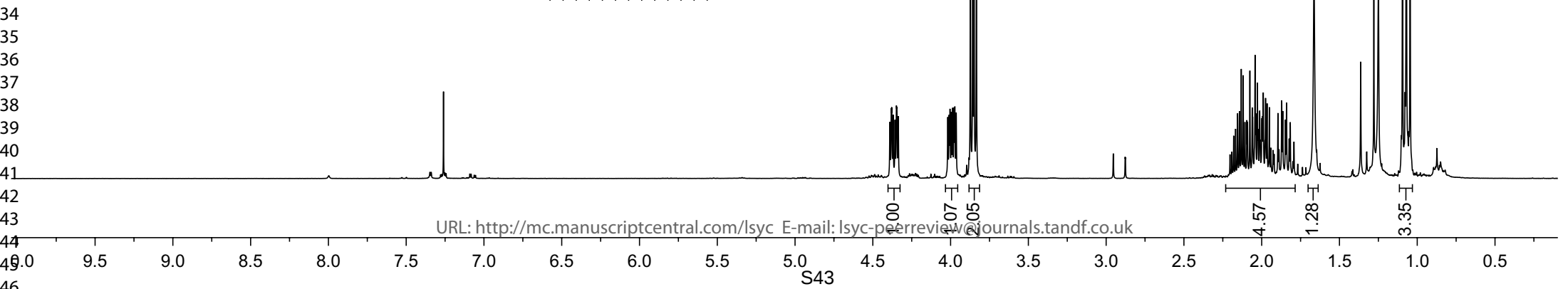
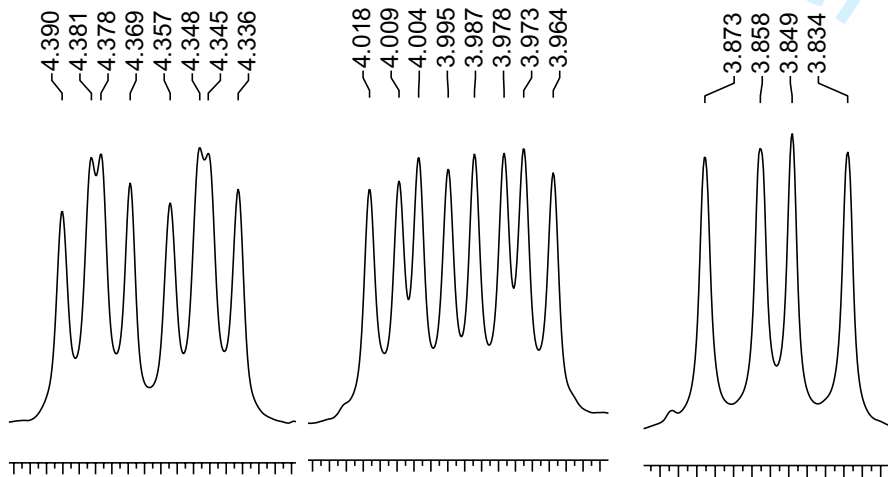


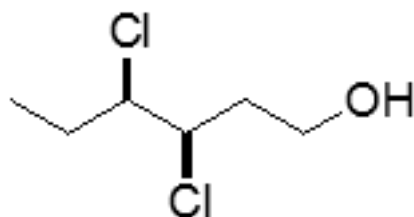
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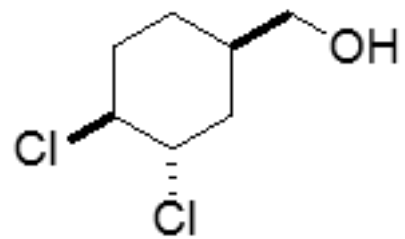
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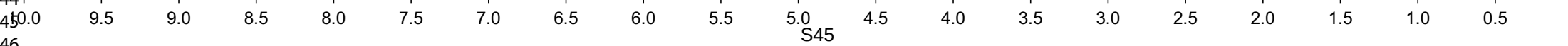
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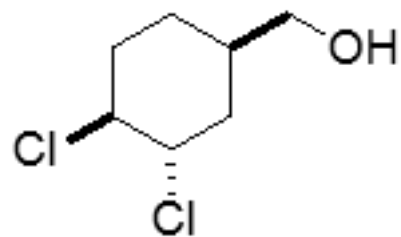


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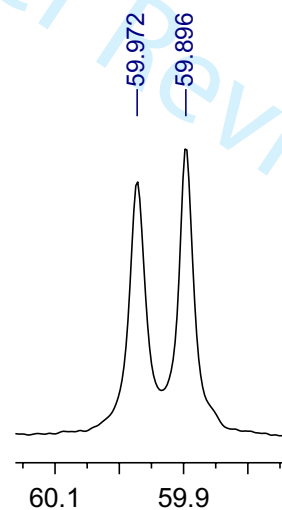
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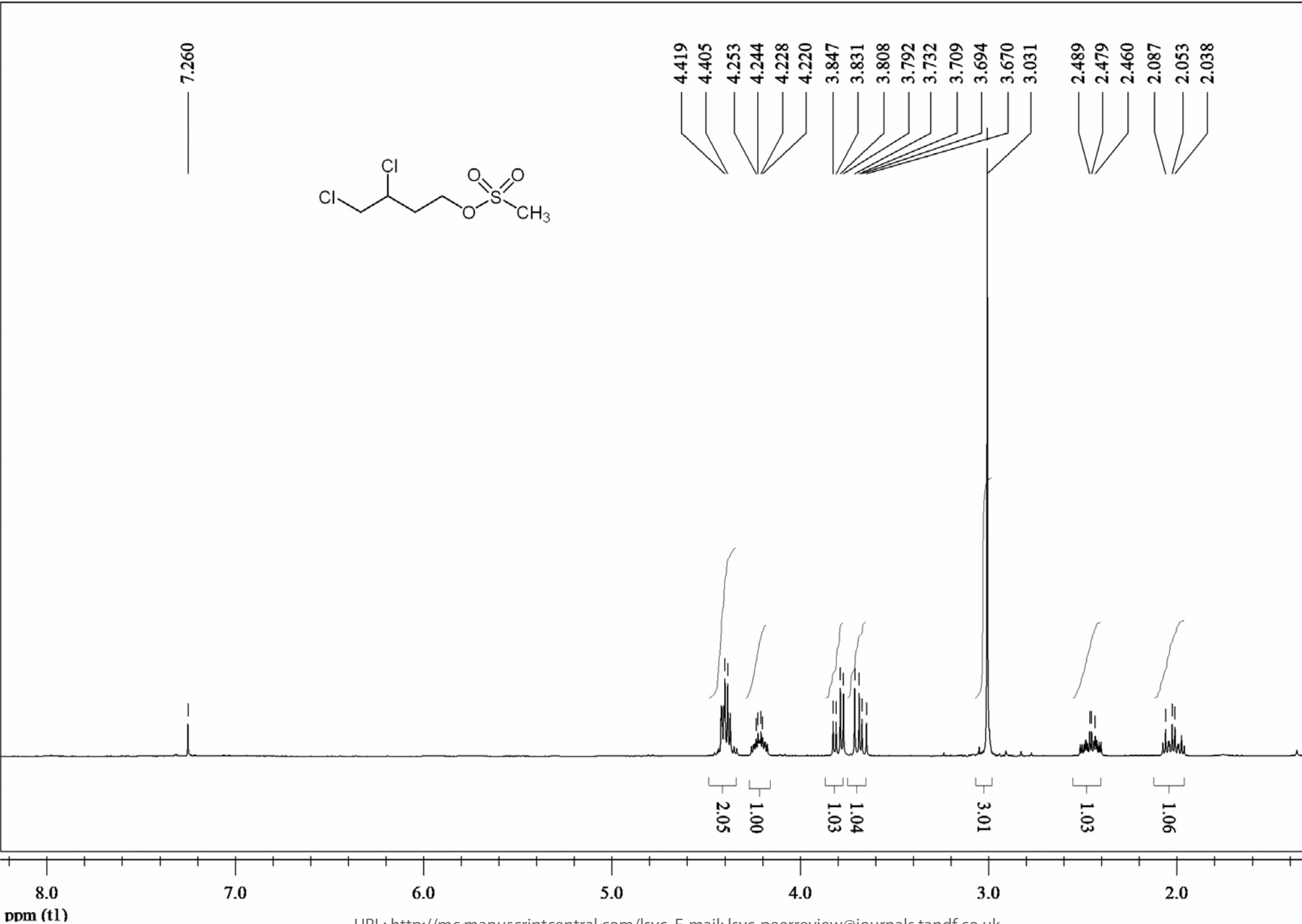
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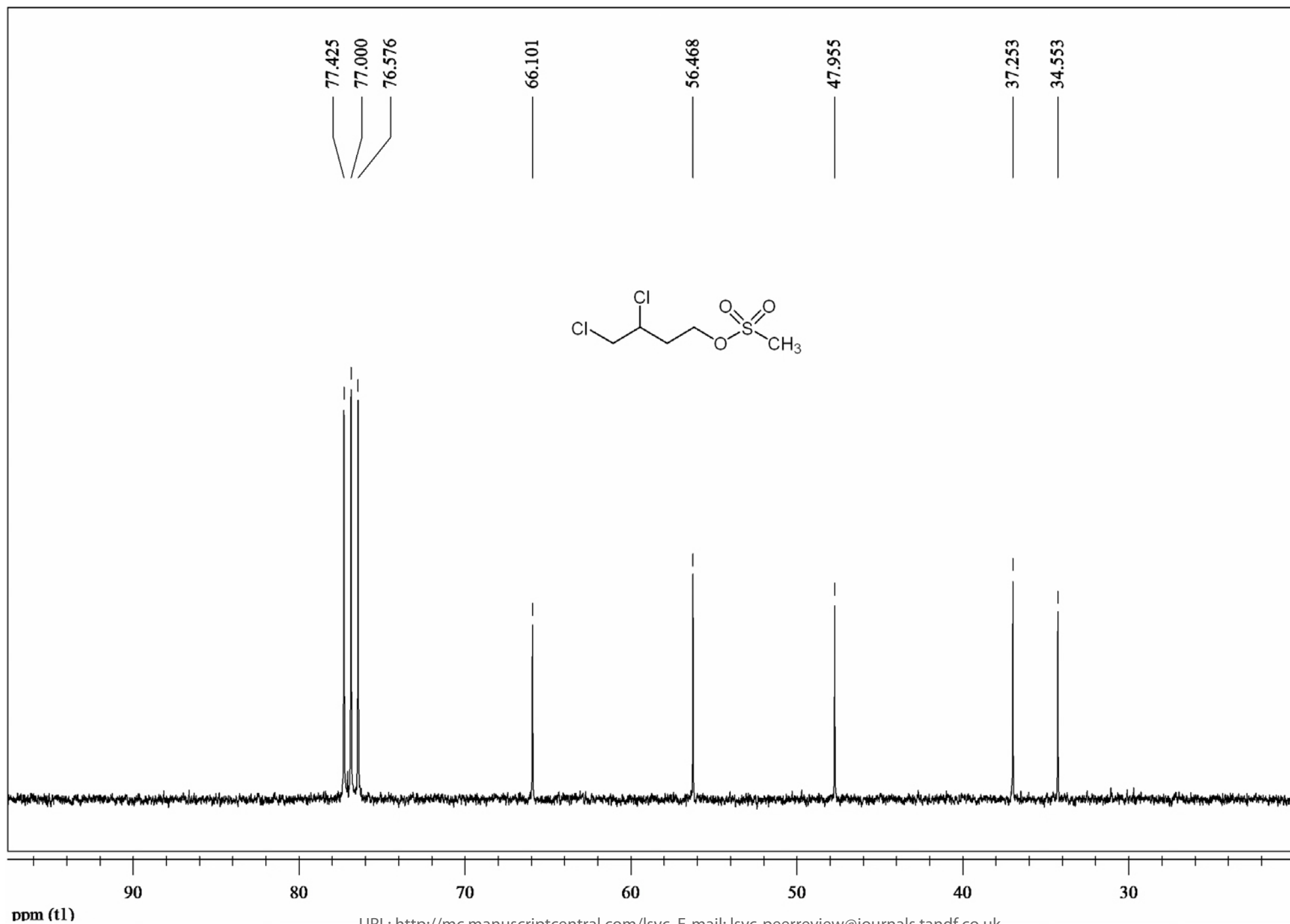
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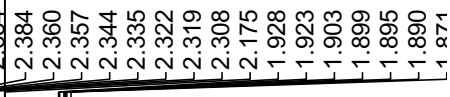
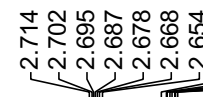
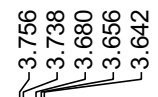
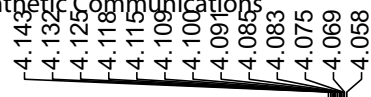
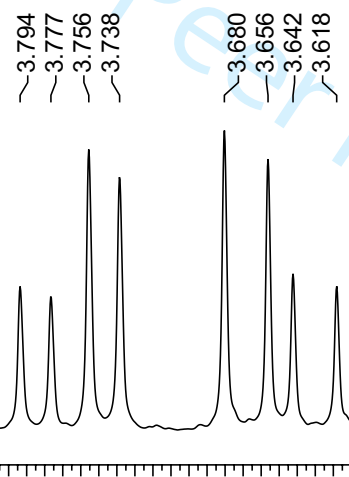
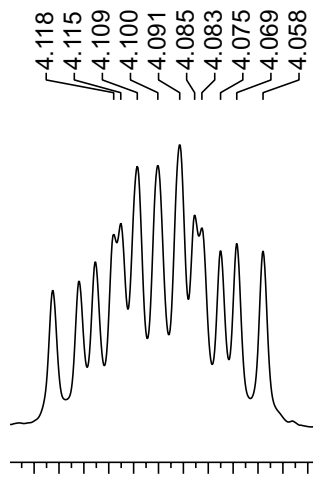
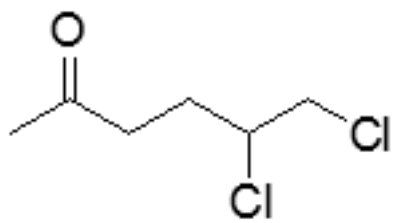
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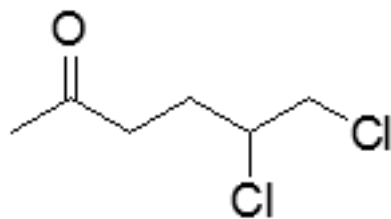


URL: <http://mc.manuscriptcentral.com/lsyc> E-mail: lsyc-peerreview@journals.tandf.co.uk



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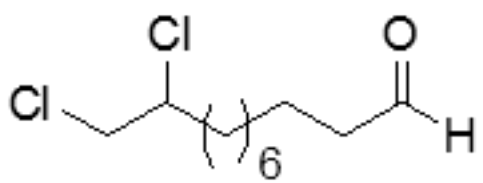
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URL: <http://mc.manuscriptcentral.com/lsc> E-mail: lsc-peerreview@journals.tandf.co.uk

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S50



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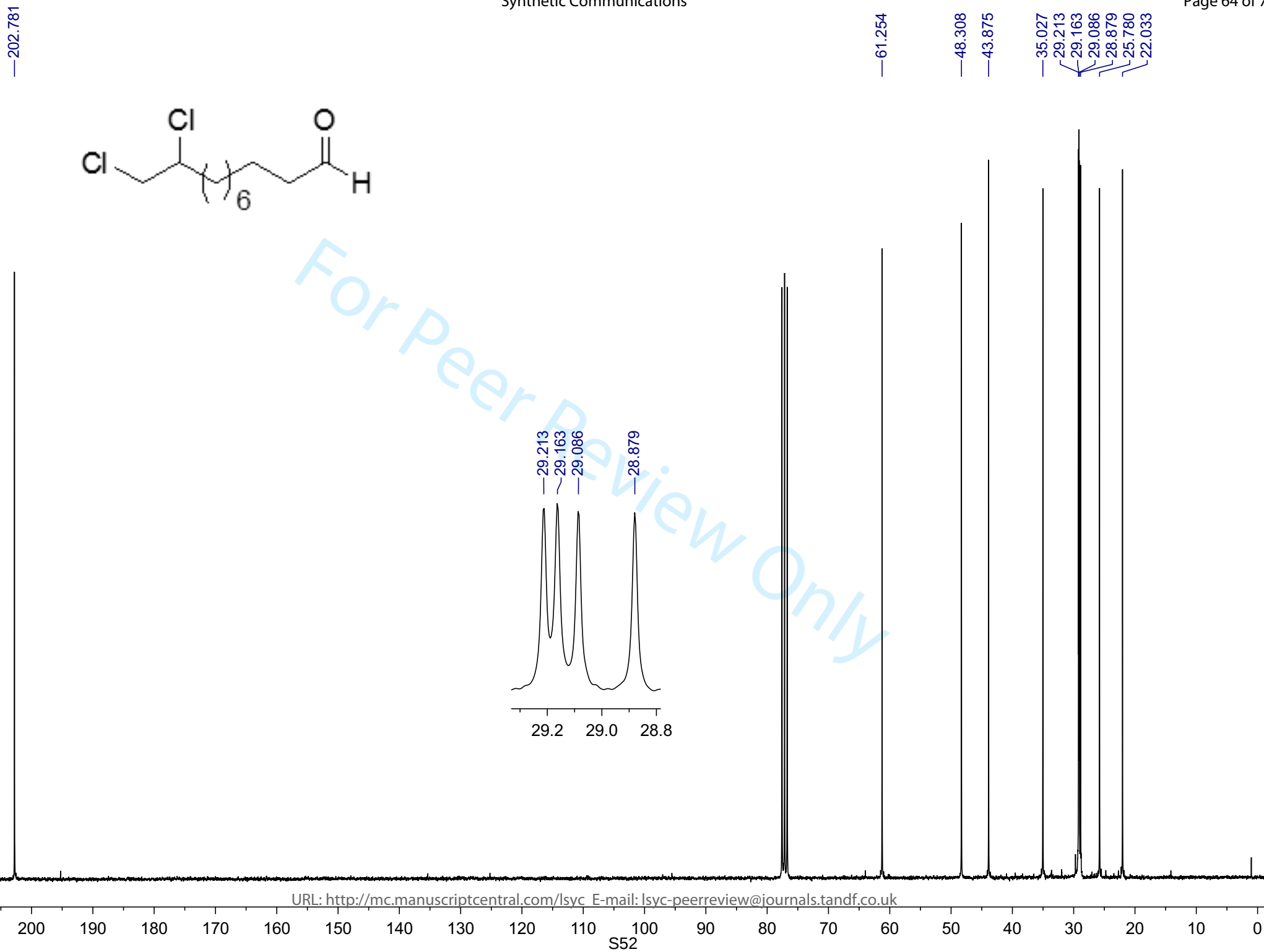
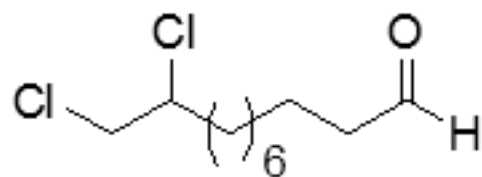
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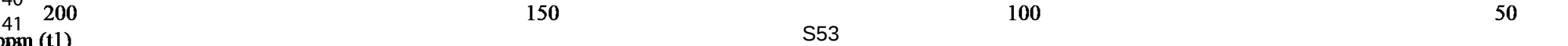
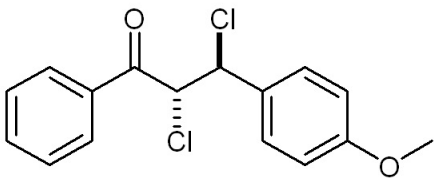
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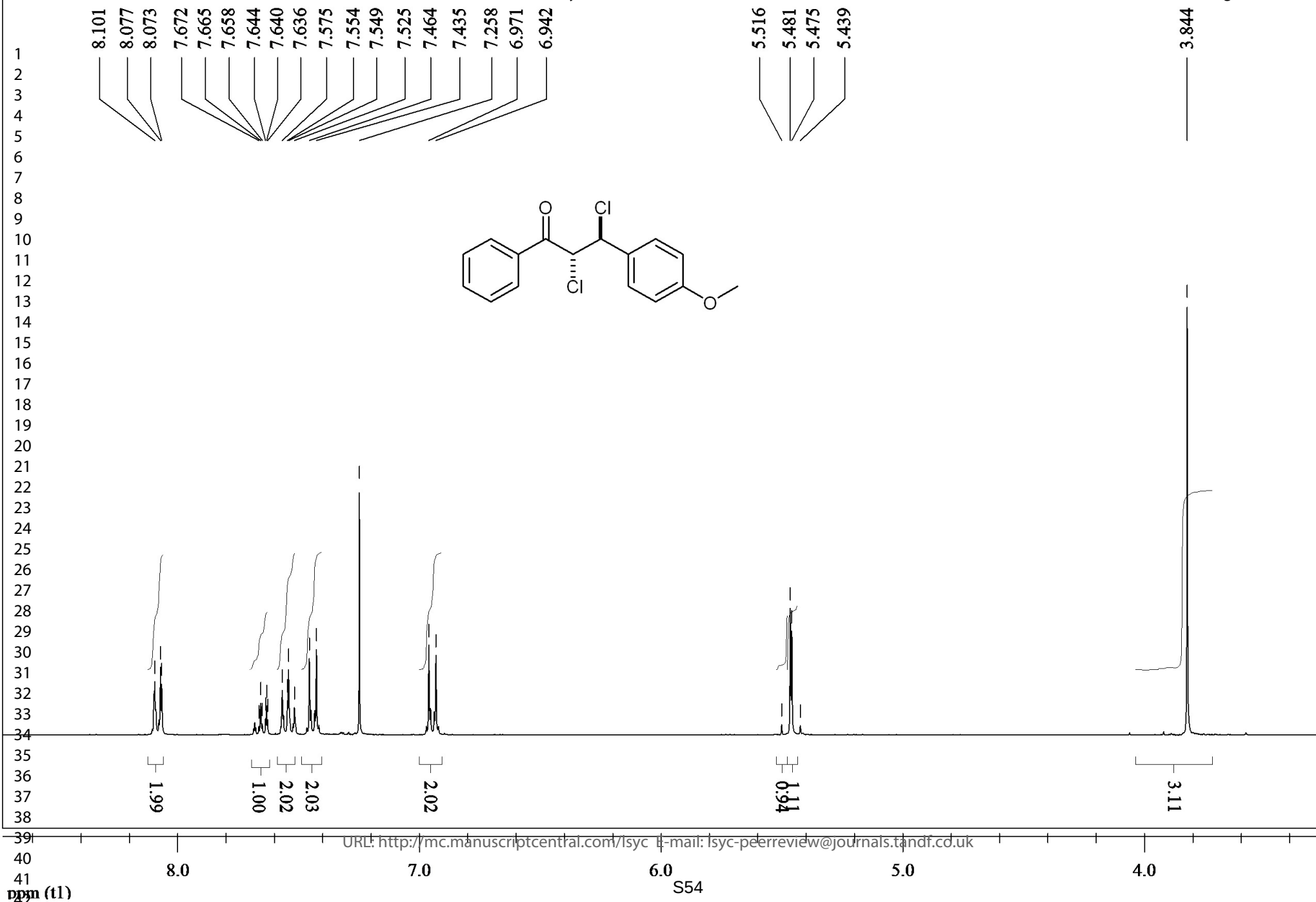
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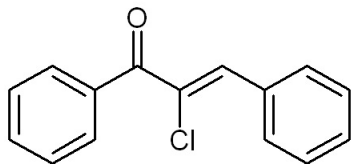
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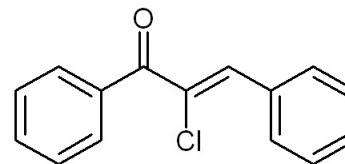
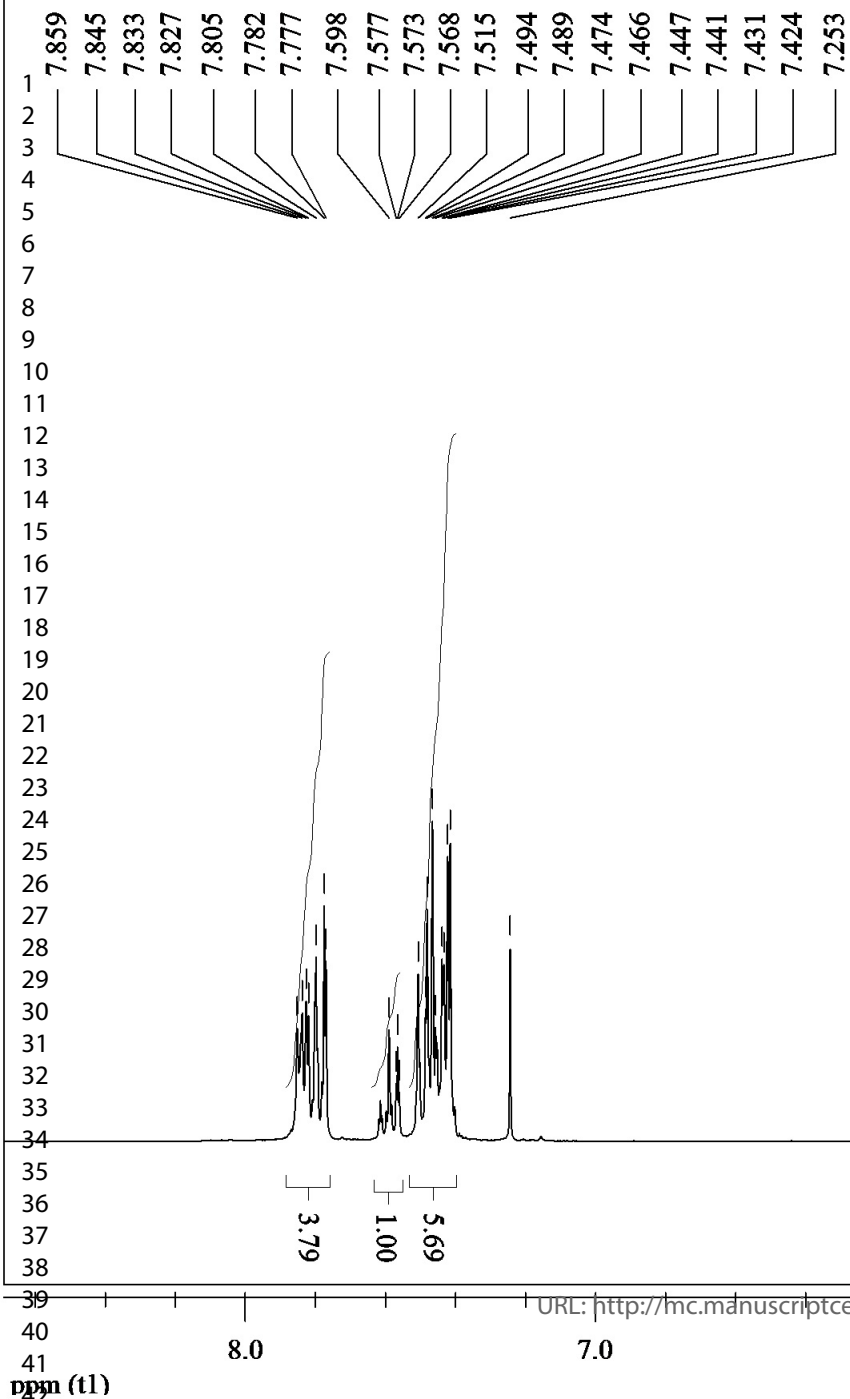
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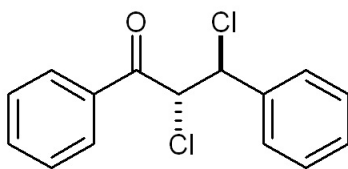
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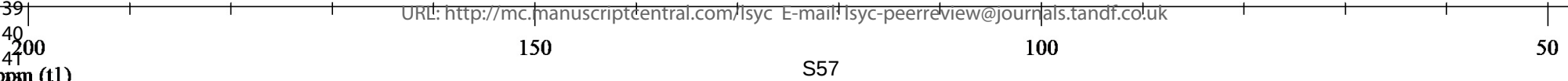


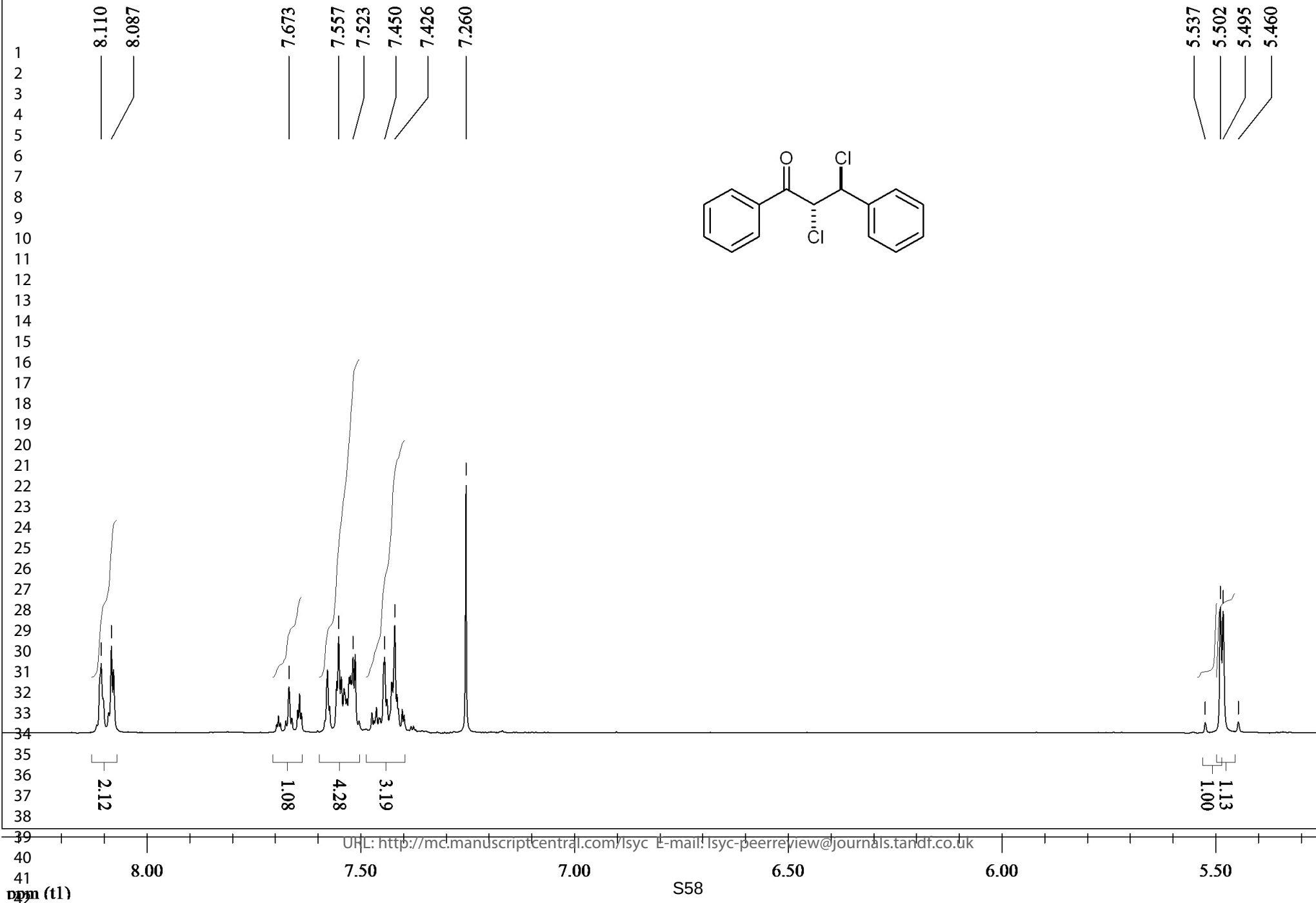
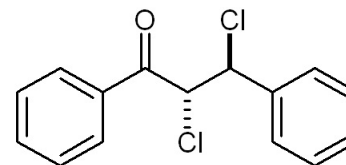
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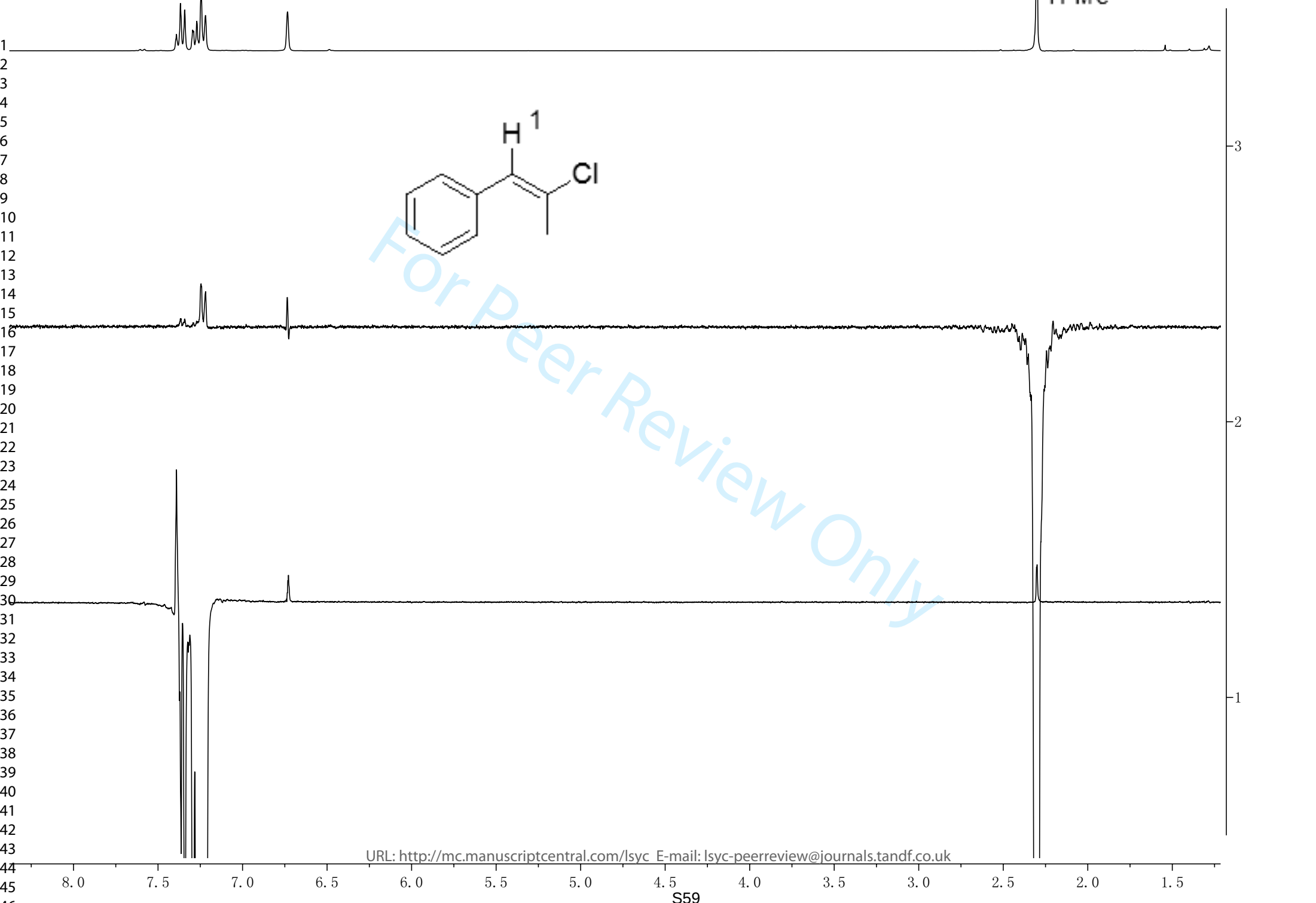
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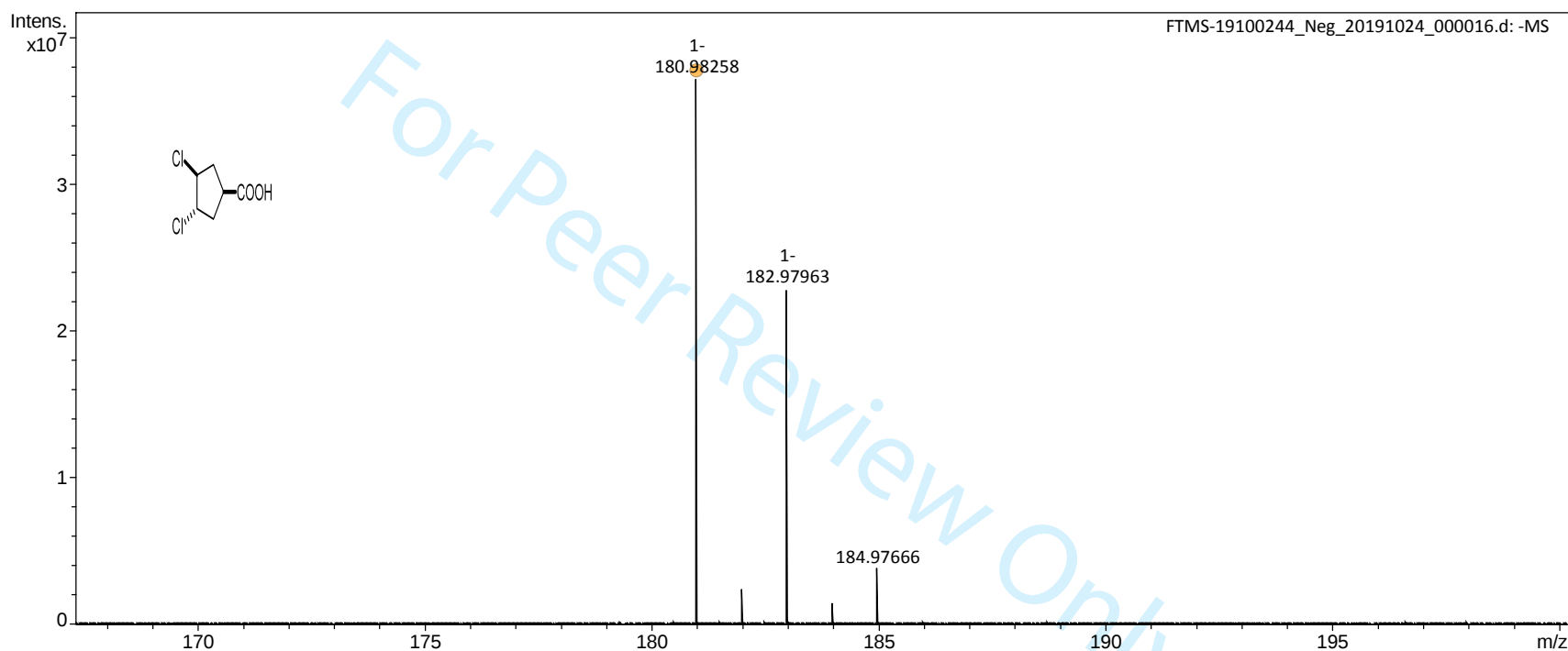


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name FTMS-19100244_Neg_20191024_000016.d
Sample v-1
Comment

Acquisition Date 10/24/2019 4:33:12 PM
Instrument Bruker Solarix XR FTMS
Operator Peking University

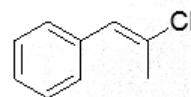
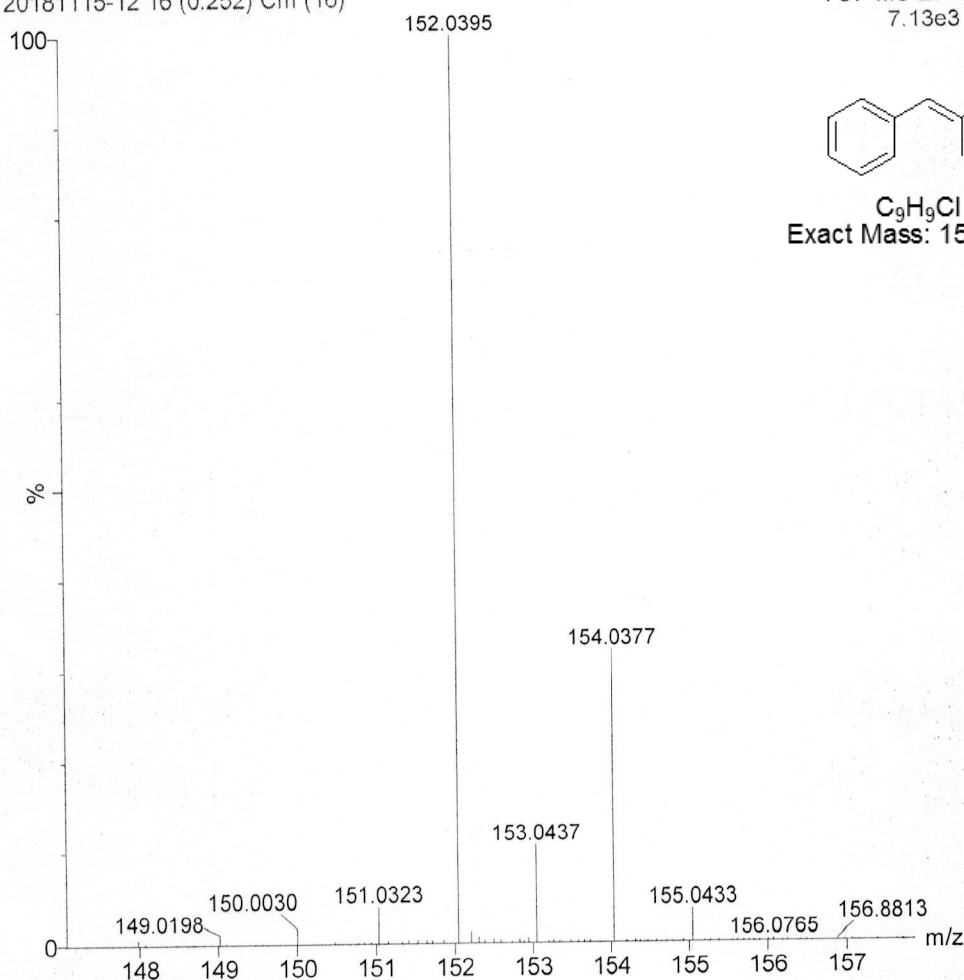


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
180.982583	1	C ₆ H ₇ ClO ₂	100.00	180.982858	1.5	1.7	10.0	8.0	even	ok

A-1

A-1

20181115-12 16 (0.252) Cm (16)

TOF MS EI+
7.13e3 C_9H_9Cl
Exact Mass: 152.0393

Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

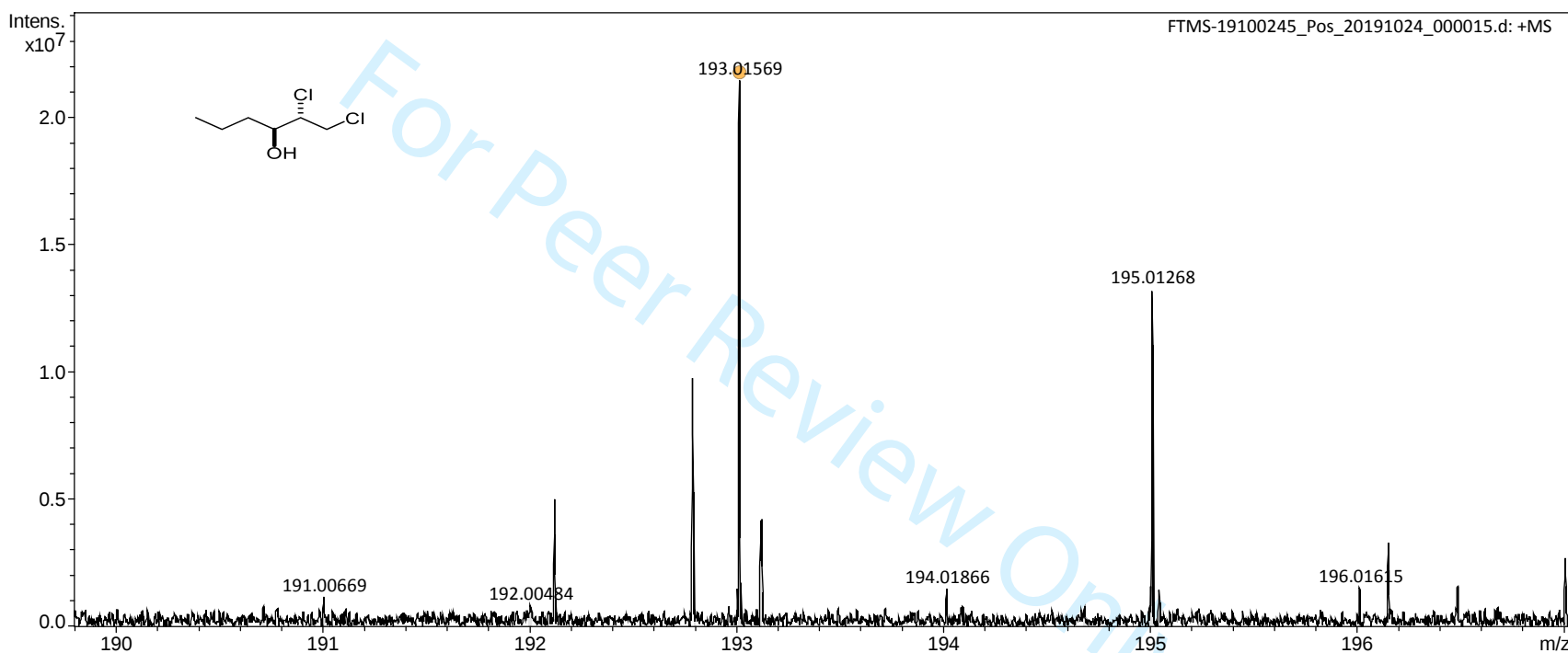
Minimum:	30.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
152.0395	100.00	152.0393	0.2	1.5	5.0	1	C9 H9 Cl

Peking University Mass Spectrometry Sample Analysis Report

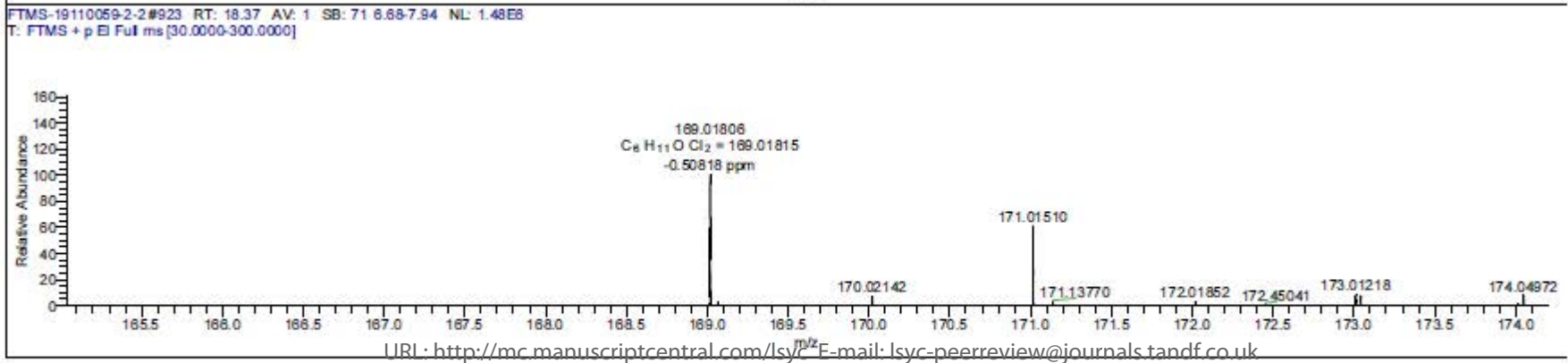
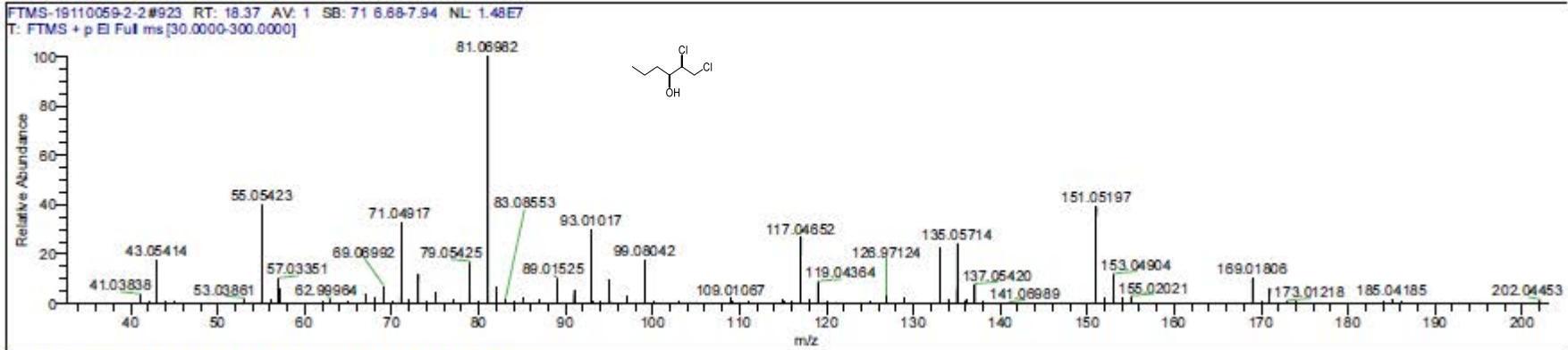
Analysis Info

Analysis Name FTMS-19100245_Pos_20191024_000015.d
Sample W-P2
Comment

Acquisition Date 10/24/2019 3:53:19 PM
Instrument Bruker Solarix XR FTMS
Operator Peking University

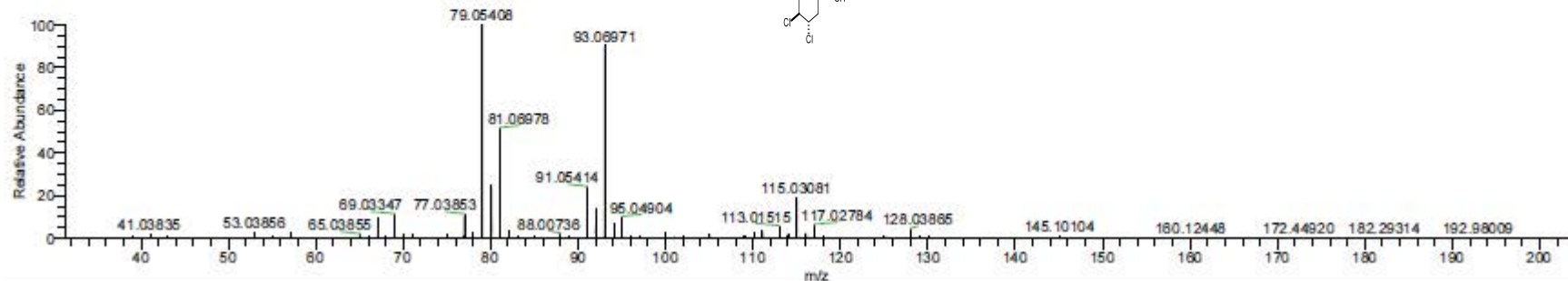


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
193.015685	1	C ₆ H ₁₂ Cl ₂ NaO	100.00	193.015741	0.3	0.6	19.4	6.0	even	ok

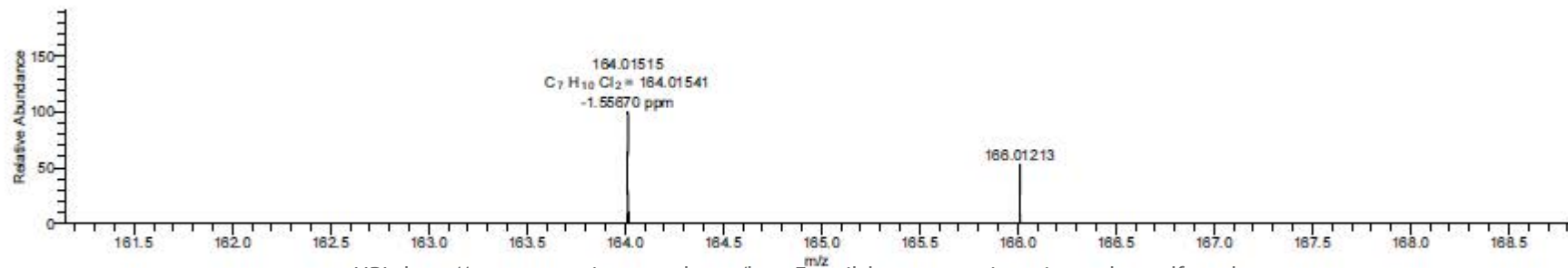


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T: FTMS + p EI Full ms [30.0000-300.0000]



FTMS-19110059-1 #525 RT: 12.92 AV: 1 NL: 1.21E4
T: FTMS + p EI Full ms [30.0000-300.0000]



URL: <http://mc.manuscriptcentral.com/lsyc> E-mail: lsyc-peerreview@journals.tandf.co.uk

Peking University Mass Spectrometry Sample Analysis Report

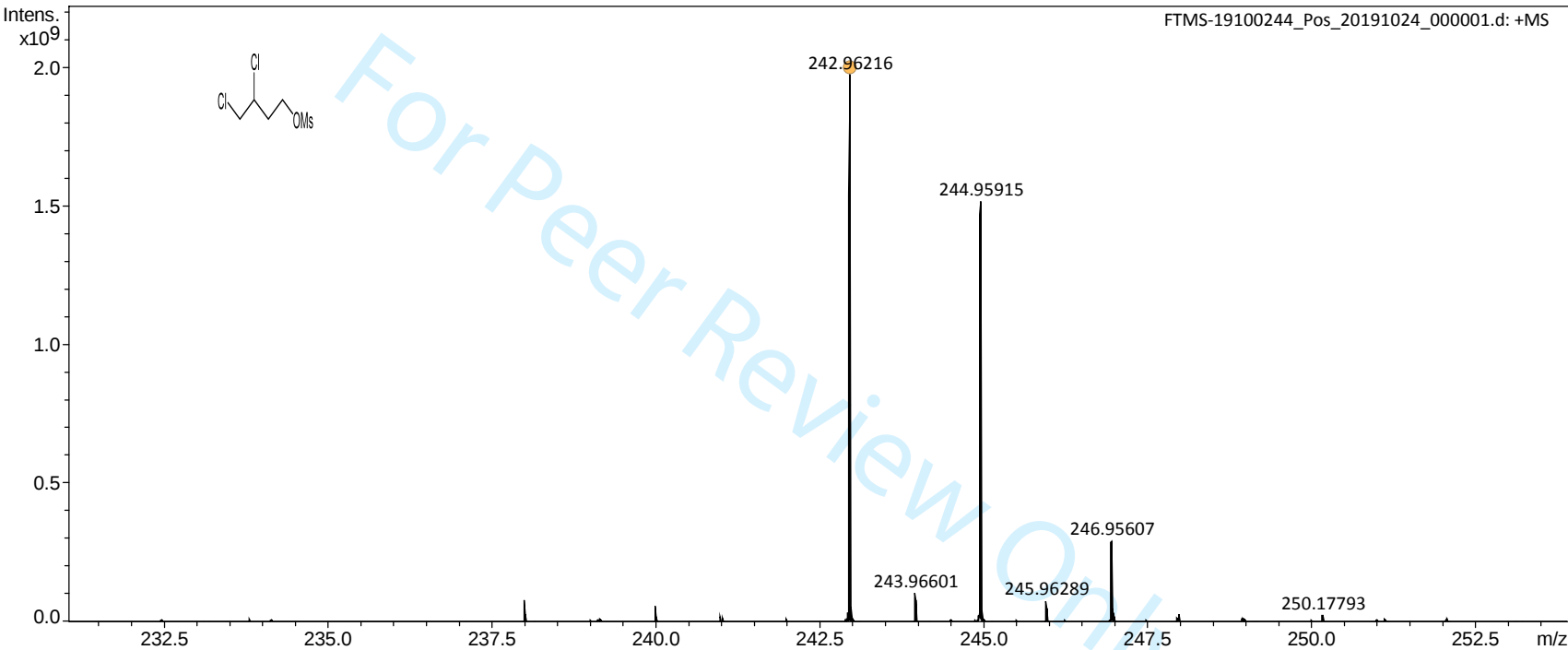
Analysis Info

Analysis Name
Sample
Comment

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Y-P

Acquisition Date
Instrument
Operator

10/24/2019 4:01:59 PM
Bruker Solarix XR FTMS
Peking University



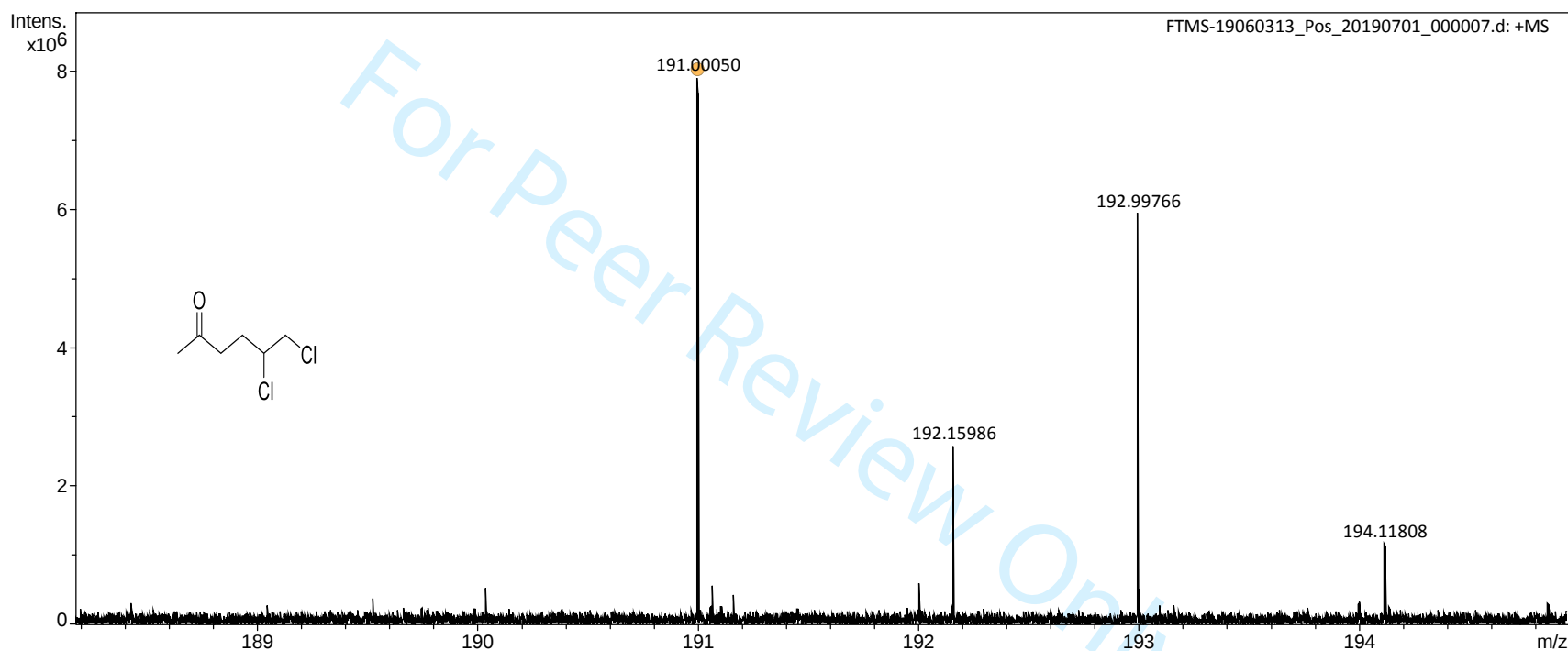
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242.962158	1	C5H10Cl2NaO3S	100.00	242.961991	-0.7	-1.8	35.4	8.0	even		ok

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name FTMS-19060313_Pos_20190701_000007.d
Sample O-1
Comment

Acquisition Date 7/1/2019 3:44:52 PM
Instrument Bruker Solarix XR FTMS
Operator Peking University



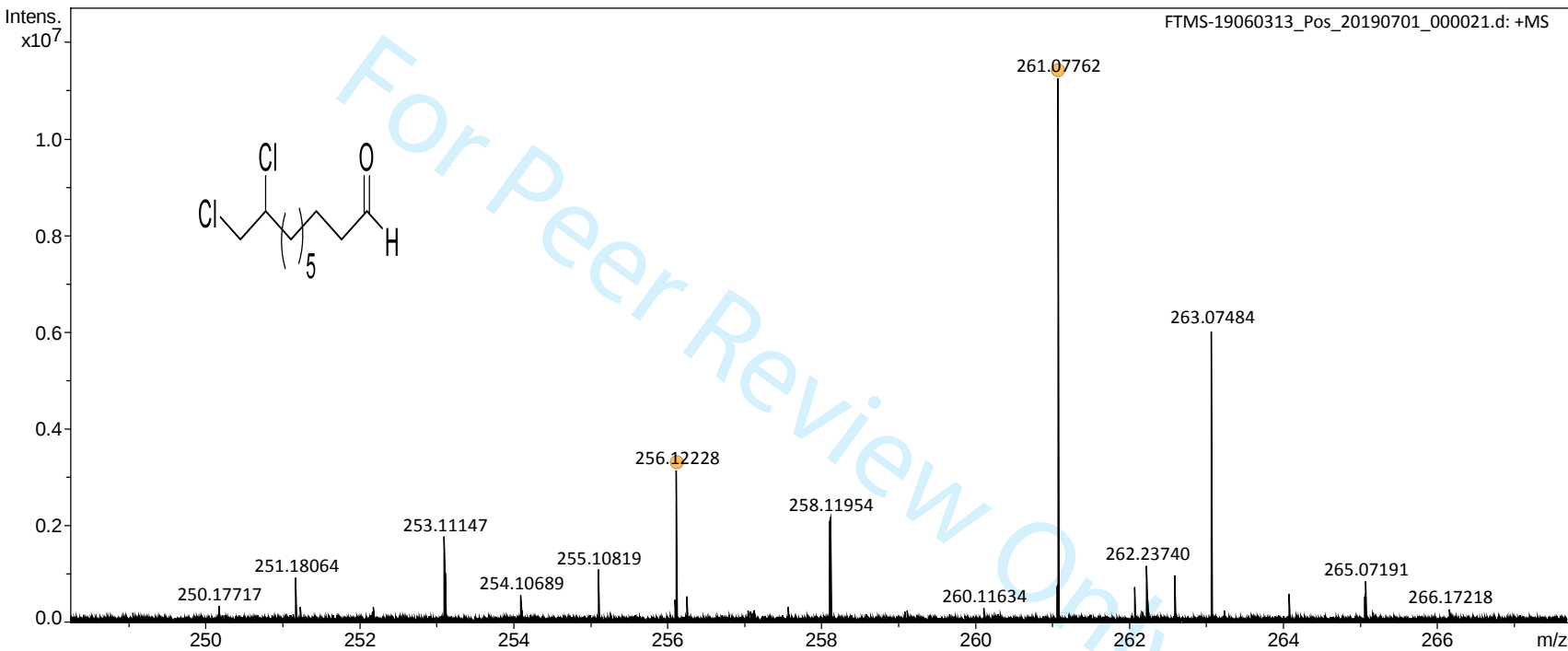
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name FTMS-19060313_Pos_20190701_000021.d
Sample K-1
Comment

Acquisition Date 7/1/2019 4:30:07 PM
Instrument Bruker Solarix XR FTMS
Operator Peking University



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
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261.077619	1	C11H20Cl2NaO	100.00	261.078341	2.8	1.6	45.3	7.0	even	ok