Supplementary Information.

Experimental preparations and spectroscopic and analytical data for the new compounds.

Three-component reaction involving isocyanide, phosphine and ketenimine functionalities

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All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen prior to use.

Compound **3a**: To a solution of $(PPh_2)_2C{=}C{=}NPh$ (**1a**) (0.04 g, 0.08 mmol) in THF (10 mL) CN*t*Bu (90 μL, 0.80 mmol) and H_2O (4 μL, 0.22 mmol) were added. The mixture was stirred for 12 h at room temperature. The solution was then concentrated to 2 mL and hexane (15 mL) added to yield a white solid, which was filtered and washed with hexane (2 x 5 mL). Crystals of **3a** suitable for X-ray analysis were obtained by crystallization from dichloromethane/hexane. Yield: 0.04 g (86%). Anal. Calcd for $C_{37}H_{36}N_2OP_2$: C, 75.74; H, 6.19; N, 4.78. Found: C, 75.92; H, 6.06; N, 4.78. ^{1}H NMR (300 MHz, CD_2Cl_2, 25ºC): δ = 1.02 (s, 9H, CH_3), 4.02 (d, ^3J(P,H) = 8 Hz , 2H, CH_2), 6.66 (d, ^3J(H,H) = 7 Hz, 2H, H_{orto} NPh), 6.86 (t, ^3J(H,H) = 7 Hz, 1H, H_{para} NPh), 7.28 (t, ^3J(H,H) = 7 Hz, 2H, H_{meta} NPh), 7.3-8.1 ppm (20H, Ph); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25ºC): δ = 29.6 (s, CH_3), 52.0 (t, ^2J(P,C) = ^3J(P,C) = 10 Hz, CH_2), 56.6 (s, $C(CH_3)_3$), 122,8 (s, C_{orto} NPh), 128-138 (Ph), 154.8 (s, C_{ipso} NPh), 163.7 ppm (dd, ^2J(P,C) = 18 Hz, ^2J(P,C) = 4 Hz *C*=NPh); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 25ºC): δ = 27.4 (d, ^2J(P,P) = 52 Hz, $Ph_2P{=}O$), 57.1 ppm (d, ^2J(P,P) = 52 Hz, $Ph_2P{=}C$).

Compound **3b**: This was prepared similarly to **3a** starting from $(PPh_2)_2C{=}C{=}NXylyl$ (**1b**) (0.04 g, 0.08 mmol) and CN*t*Bu (90 μL, 0.80 mmol). Yield: 0.032 g (65%). Anal. Calcd for $C_{39}H_{40}N_2OP_2$: C, 76.20; H, 6.56; N, 4.56. Found: C, 76.35; H, 6.68; N, 4.32. ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ = 0.97 (s, 9H, CH_3 (*t*Bu)), 1.90 (s, 6H, CH_3 (Xylyl)), 3.58 (d, ^3J(P,H) = 8 Hz , 2H, CH_2), 6.7-8.1 (23H, aromatics); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25ºC): δ = 18.8 (s, CH_3 (Xylyl), 29.5 (s, CH_3 (*t*Bu), 52.7 (t, ^2J(P,C)

= ^{3}J(P,C) = 10 Hz, CH_2), 56.0 (s, $C(CH_3)_3$), 121.2 (C_{orto} NXylyl), 127-138 (aromatics), 152.5 (s, C_{ipso} NXylyl), 162.2 ppm (br, *C*=NXylyl); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2, 25ºC): δ = 29.3 (d, ^{2}J(P,P) = 52 Hz, Ph_2P=O), 58.5 ppm (d, ^{2}J(P,P) = 52 Hz, Ph_2P=C).

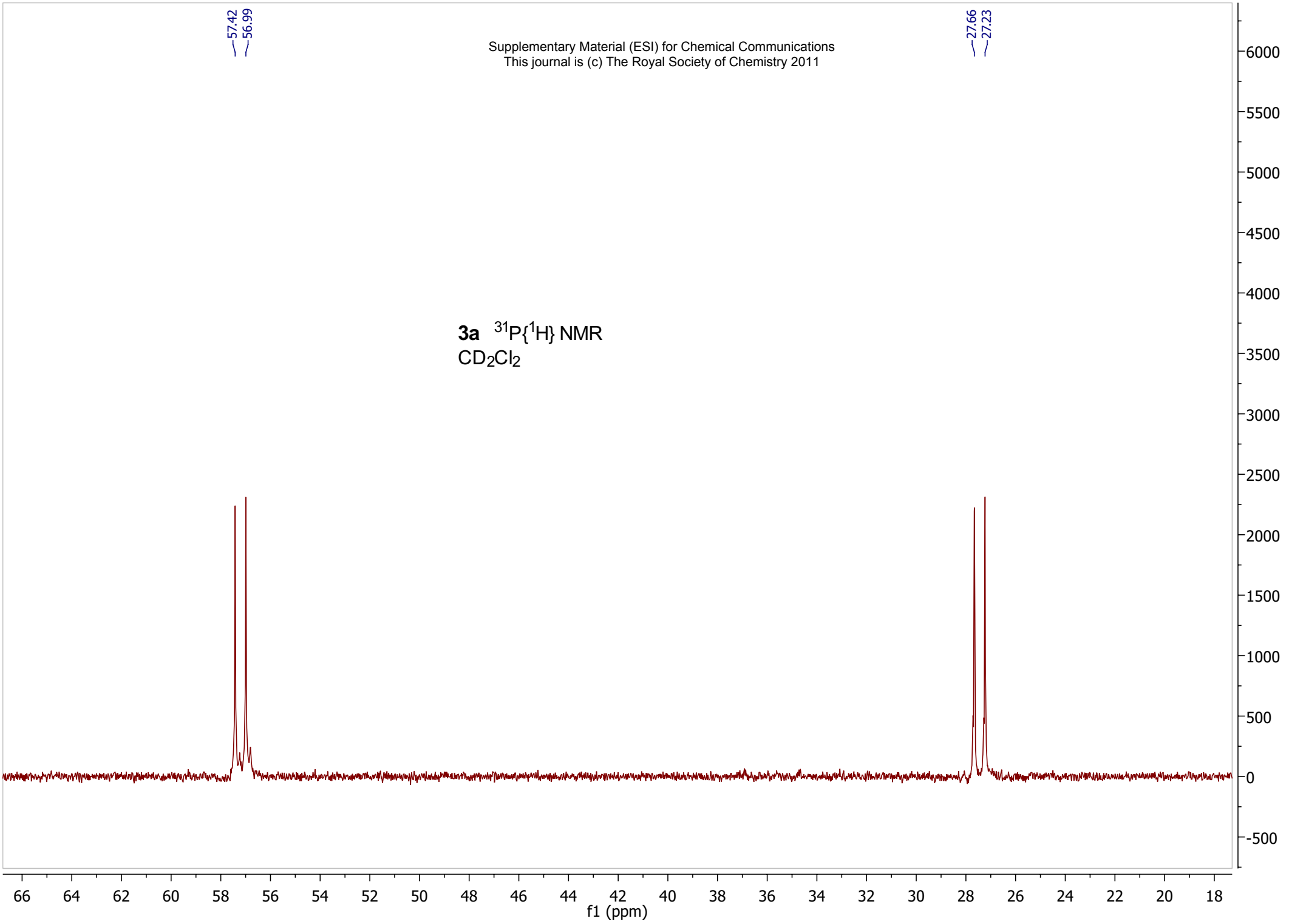
Compound **3c**: To a solution of $(PPh_2)_2C$=C=NPh (**1a**) (0.05 g, 0.10 mmol) in THF (10 mL) benzylisocyanide (126 μL, 1.0 mmol) and H_2O (5 μL, 0.26 mmol) were added. The mixture was stirred for 18 h at room temperature and then the solvent evaporated to dryness under vacuum. The resulting oil was washed with hexane (3 x 5 mL). The remaining residue was then disolved in 10 ml of diethyl ether and hexane (5 mL) added to the solution. Concentration of the solution to 1 mL gave a pale yellow precipitate, which was filtered and dried under vacuum. Yield: 0.031 g (50%). Anal. Calcd for $C_{40}H_{34}N_2OP_2$: C, 77.41; H, 5.52; N, 4.51. Found: C, 77.02; H, 5.73; N, 4.28. ^{1}H NMR (300 MHz, CD_2Cl_2, 25ºC): δ = 3.81 (d, ^{3}J(P,H) = 8 Hz , 2H, CH_2), 4.09 (d, ^{3}J(P,H) = 7 Hz , 2H, CH_2), 6.63 (d, ^{3}J(H,H) = 7 Hz, 2H, H_{orto} NPh), 6.78 (t, ^{3}J(H,H) = 7 Hz, 1H, H_{para} NPh), 6.7-8.0 ppm (27H, Ph); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2, 25ºC): δ = 27.4 (d, ^{2}J(P,P) = 49 Hz, Ph_2P=O), 62.2 ppm (d, ^{2}J(P,P) = 49 Hz, Ph_2P=C).

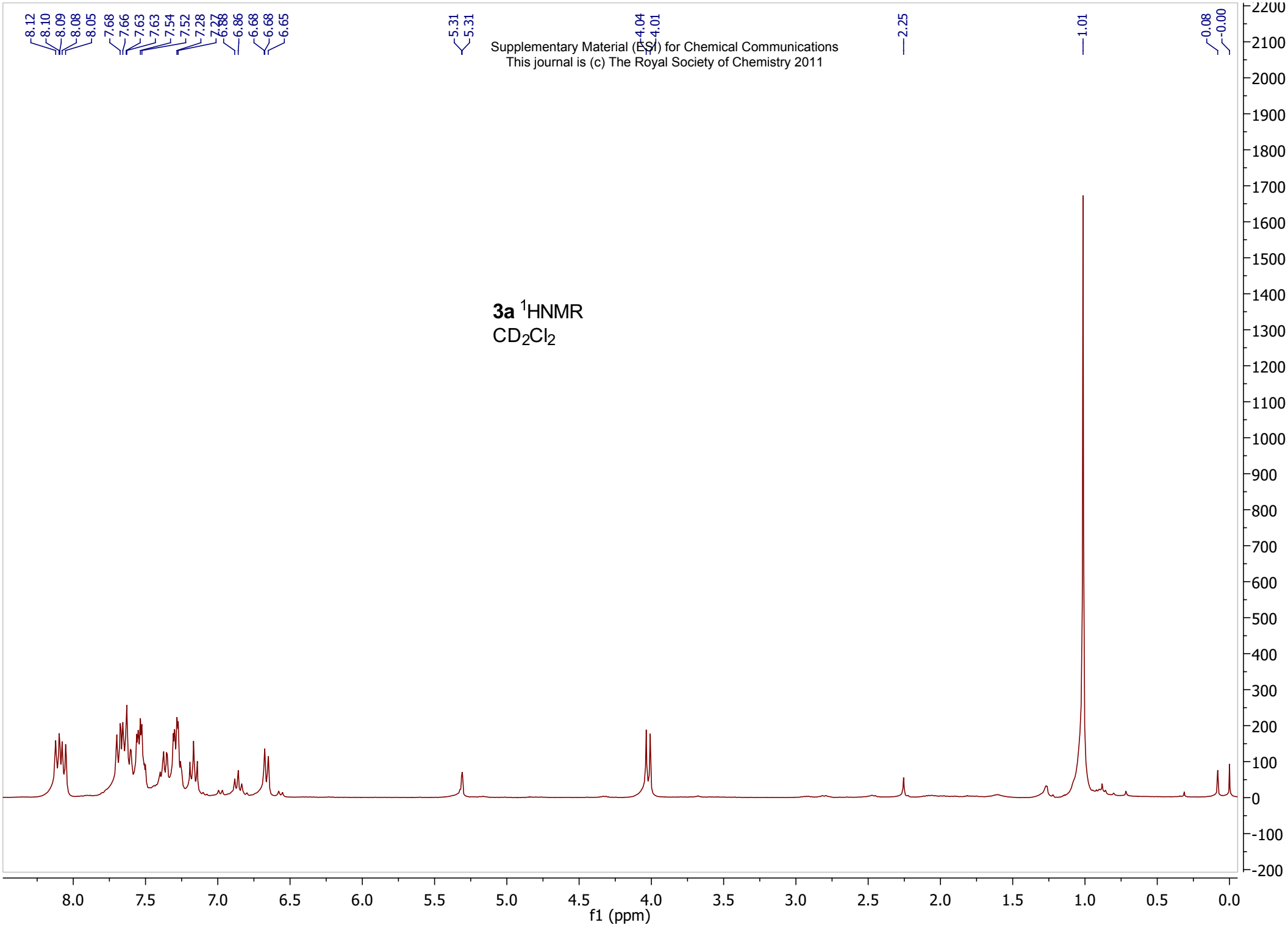
Compound **3d**: This was prepared similarly to **3a** starting from $(PPh_2)_2C$=C=NXylyl (**1b**) (0.06 g, 0.12 mmol) and CNXylyl (92 mg, 0.70 mmol), but with a longer reaction time (36 h). Yield: 0.06 g (75%). Anal. Calcd for $C_{43}H_{40}N_2OP_2$: C, 77.93; H, 6.08; N, 4.23. Found: C, 77.85; H, 6.14; N, 4.12. ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ = 1.71 (s, 6H, CH_3 (Xylyl)), 2.10 (s, 6H, CH_3 (Xylyl)), 3.86 (d, ^{3}J(P,H) = 7 Hz , 2H, CH_2), 6.7-8.1 ppm (26H, aromatics); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25ºC): δ = 18.4 (s, CH_3 (Xylyl)), 18.8 (s, CH_3 (Xylyl)), 50.7 (t, ^{1}J(P,C) = 110 Hz, P_2C), 58.9 (t, ^{2}J(P,C) = ^{3}J(P,C) = 11 Hz, CH_2), 121-138 (aromatic), 151.7 (s, C_{ipso} NXylyl), 163.0 ppm (d, ^{2}J(P,C) = 13 Hz, *C*=NXylyl); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2, 25ºC): δ = 26.1 (d, ^{2}J(P,P) = 46 Hz, Ph_2P=O), 60.4 ppm (d, ^{2}J(P,P) = 46 Hz, Ph_2P=C).

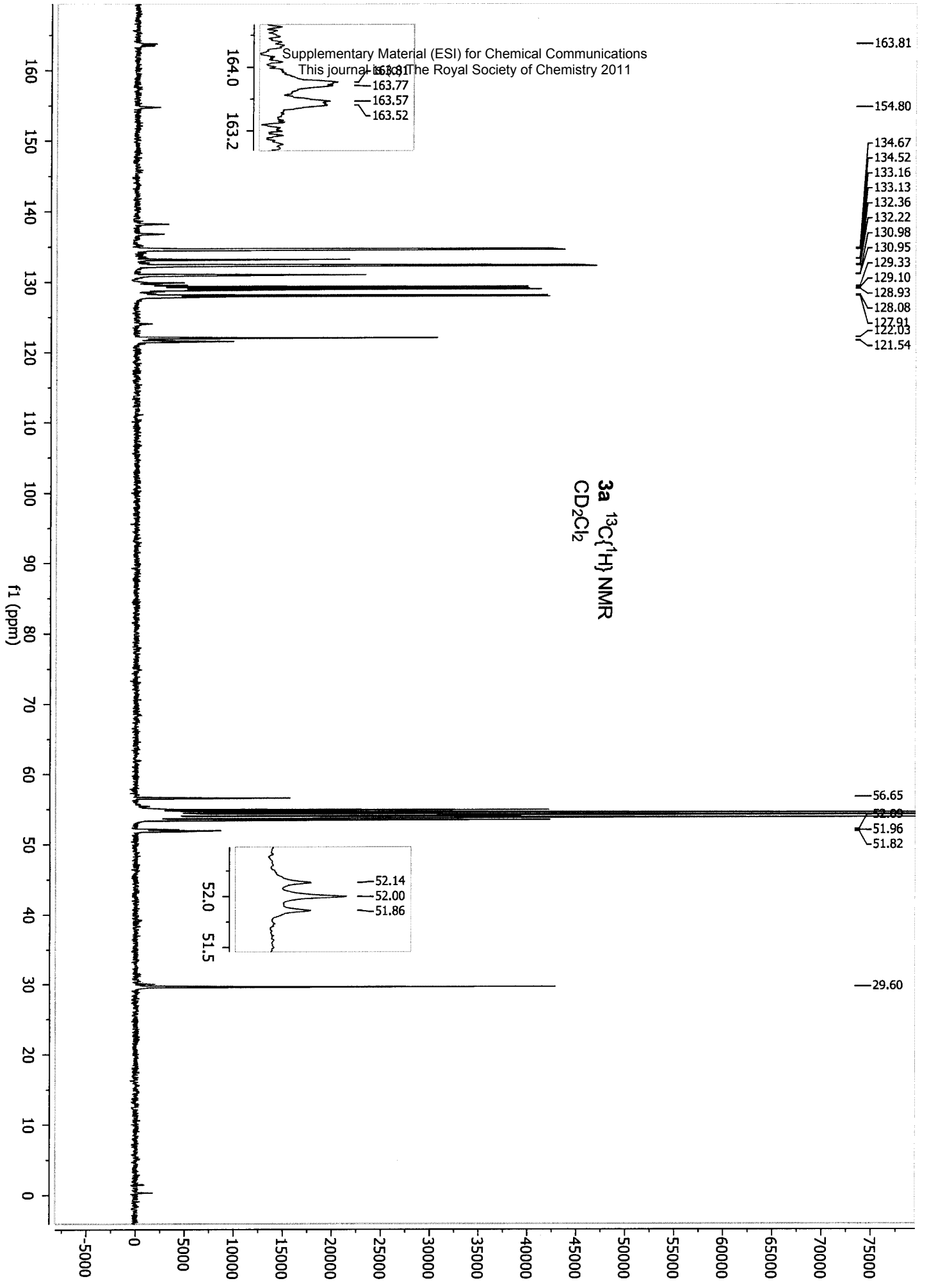
Compound **4a**: A mixture of $(PPh_2)_2C$=C=NPh (**1a**) (0.04 g, 0.08 mmol), CN*t*Bu (400 μL, 3.54 mmol) and ethanol (100 μL, 1.71 mmol) was stirred for 3 h at room temperature. Then hexane (10 mL) was added and the resulting solution evaporated to dryness, causing the formation of a pale yellow solid. Yield: 0.041 g (81%). Compound 4a resulted to be highly soluble in hexane and moisture sensitive, and slowly evolves to 3a, which precluded fine purification (the elemental analysis is not very accurate as shown below) and growing of crystals for X-ray analysis. Anal. Calcd for $C_{43}H_{40}N_2OP_2$:

C, 76.20; H, 6.56; N, 4.56. Found: C, 75.61; H, 6.08; N, 4.97. ^{1}H NMR (300 MHz, CD_2Cl_2, 25ºC): δ = 0.62 (s, 9H, CH_3 (*t*Bu)), 1.56 (t, ^{3}J(H,H) = 7 Hz, 3H, OCH_2CH_3), 4.65 (quintet, ^{3}J(P,H) = ^{3}J(H,H) = 7 Hz , 2H, OCH_2CH_3), 6.22 (d, ^{3}J(H,H) = 7 Hz, 2H, H_{orto} NPh), 6.74 (t, ^{3}J(H,H) = 7 Hz, 1H, H_{para} NPh), 6.97 (t, ^{3}J(H,H) = 7 Hz, 2H, H_{meta} NPh), 7.2-7.9 ppm (21H, Ph and C=CH); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25ºC): δ = 17.3 (d, ^{3}J(P,C) = 7 Hz, OCH_2CH_3), 28.9 (s, CH_3 (*t*Bu)), 52.8 (d, ^{1}J(P,C) = 18 Hz, P_2C), 58.2 (s, $C(CH_3)_3$), 65.7 (d, ^{2}J(P,C) = 6 Hz, OCH_2CH_3), 122-141 (Ph), 152.2 (s, C_{ipso} NPh), 156.5 (d, ^{2}J(P,C) = 12 Hz, C=*C*H), 169.2 ppm (dd, ^{2}J(P,C) = 8 Hz, ^{2}J(P,C) = 2 Hz, *C*-NPh); ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 25ºC): δ = -14.5 (d, ^{2}J(P,P) = 181 Hz, Ph_2P-O), 57.8 ppm (d, ^{2}J(P,P) = 181 Hz, Ph_2P=C).

Compound **5a**: To a solution of compound **4a** (0.04 g, 0.06 mmol) in dichloromethane (10 mL) HBF_4 (54% in diethyl ether, 8 μL, 0.06 mmol) was added. The reaction mixture was stirred for 5 min at room temperature. Then the solution was concentrated to 1 mL and hexane (5 mL) added to obtain a pale yellow solid, which was filtered and dry under vacuum. Yield: 0.04 g (89%). Anal. Calcd for $C_{39}H_{41}N_2BF_4OP_2$: C, 66.68; H, 5.88; N, 3.99. Found: C, 66.25; H, 5.54; N, 3.61. ^{1}H NMR (300 MHz, CD_2Cl_2, 25ºC): δ = 0.86 (s, 9H, CH_3 (*t*Bu)), 1.56 (t, ^{3}J(H,H) = 7 Hz, 3H, OCH_2CH_3), 2.87 (s, 2H, CH_2), 4.76 (quintet, ^{3}J(P,H) = ^{3}J(H,H) = 7 Hz , 2H, OCH_2CH_3), 6.02 (d, ^{3}J(H,H) = 8 Hz, 2H, H_{orto} NPh), 6.78 (t, ^{3}J(H,H) = 7 Hz, 1H, H_{para} NPh), 6.99 (t, ^{3}J(H,H) = 8 Hz, 2H, H_{meta} NPh), 7.2-7.9 ppm (20H, Ph); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25ºC): δ = 16.6 (d, ^{3}J(P,C) = 6 Hz, OCH_2CH_3, 28.7 (s, CH_3 (*t*Bu)), 44.2 (d, ^{2}J(P,C) = 8 Hz, CH_2), 50.6 (s, $C(CH_3)_3$), 65.5 (d, ^{2}J(P,C) = 6 Hz, OCH_2CH_3), 121.9 (s, C_{orto} NPh), 128-134 (Ph), 151.2 (s, C_{ipso} NPh), 172.1 ppm (d, ^{2}J(P,C) = 8 Hz, *C*=NPh); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 25ºC): δ = 21.4 (d, ^{2}J(P,P) = 54 Hz, Ph_2P-O), 50.6 ppm (d, ^{2}J(P,P) = 54 Hz, Ph_2P=C).


57.42
56.99
27.66
27.23
3a $^{31}P\{^{1}H\}$ NMR
CD_2Cl_2
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
f1 (ppm)




3a $^{13}C\{^{1}H\}$ NMR
CD_2Cl_2
f1 (ppm)
163.81
154.80
134.67
134.52
133.16
133.13
132.36
132.22
130.98
130.95
129.33
129.10
128.93
128.08
127.91
122.03
121.54
56.65
52.69
51.96
51.82
29.60
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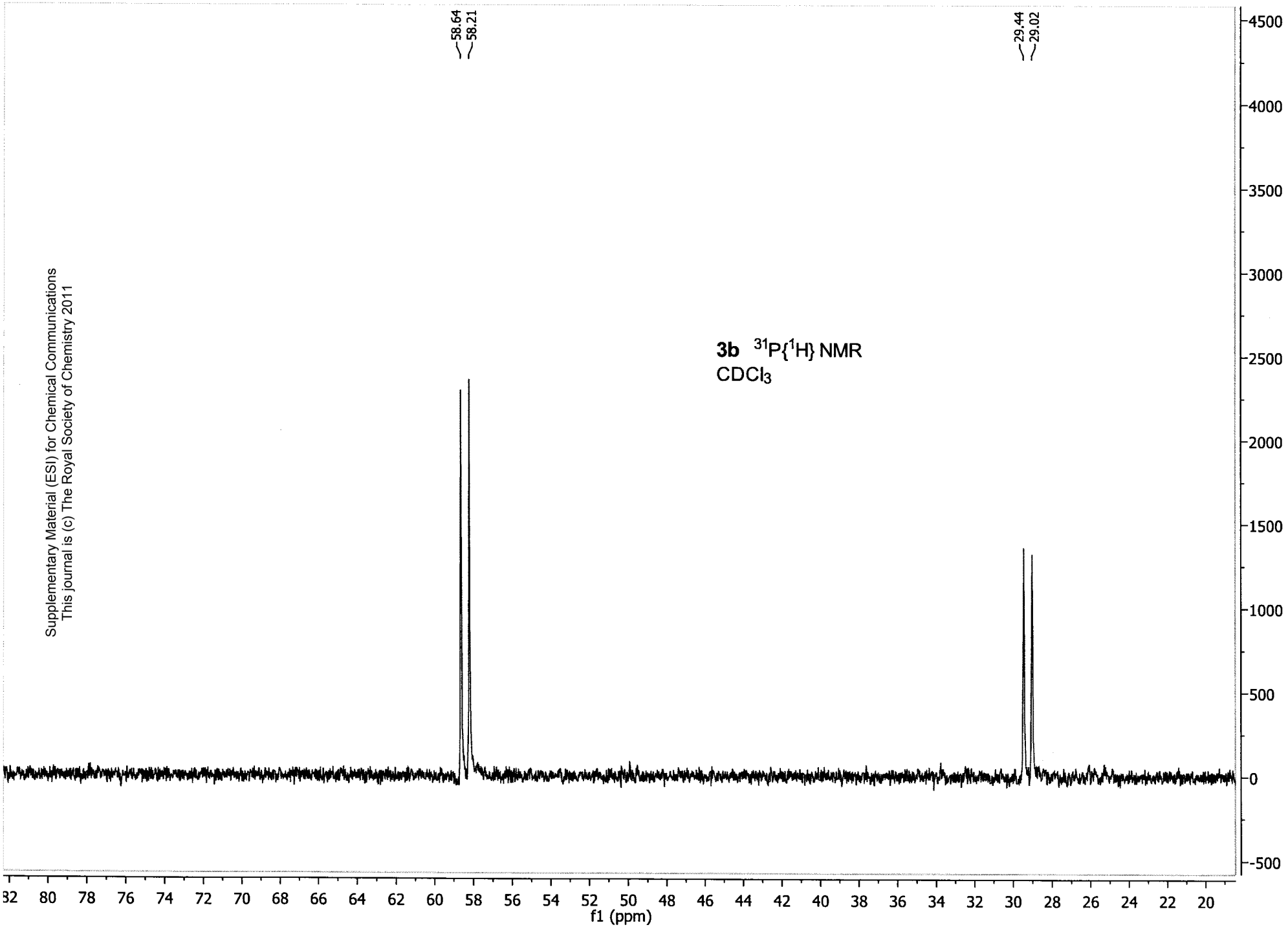
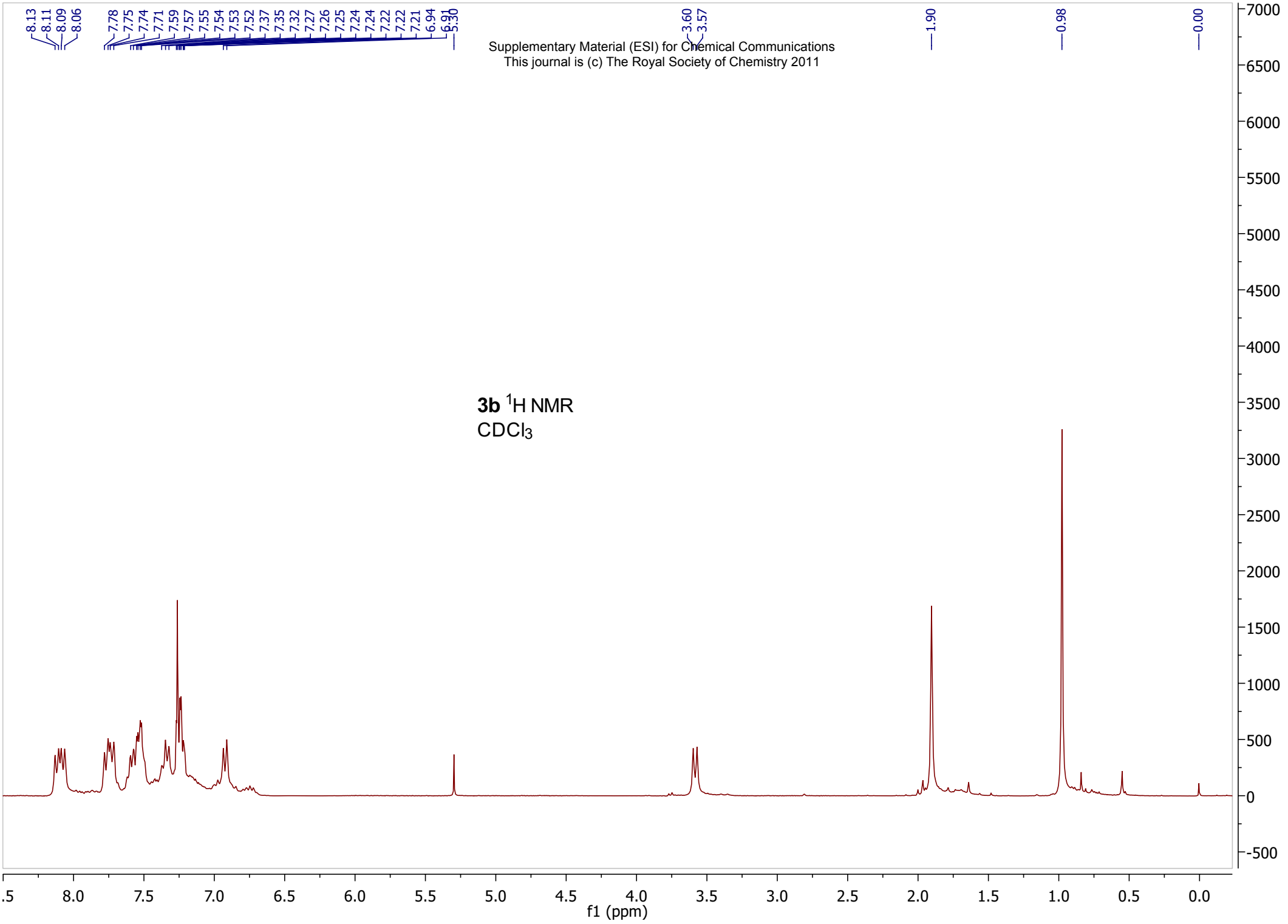
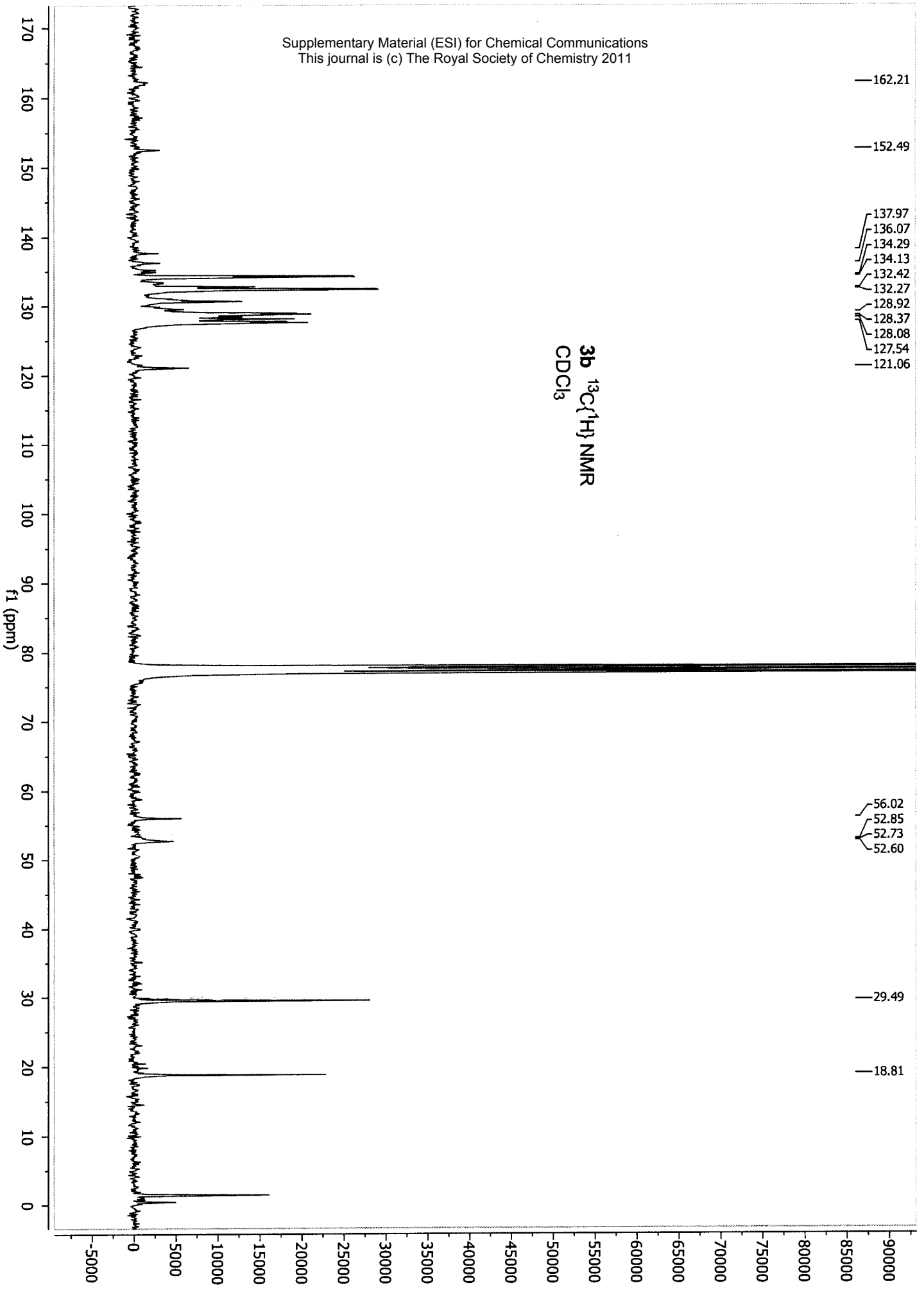
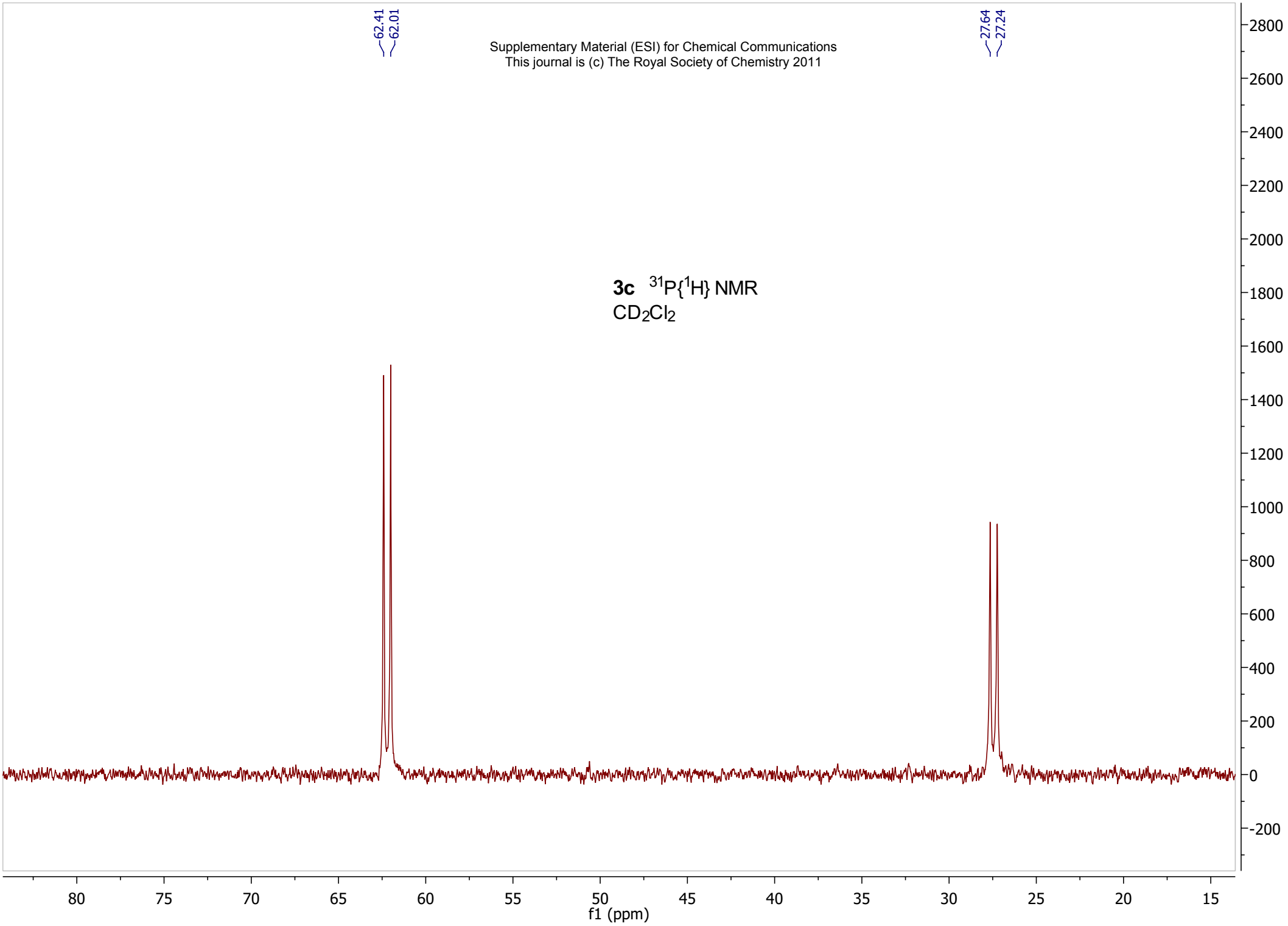
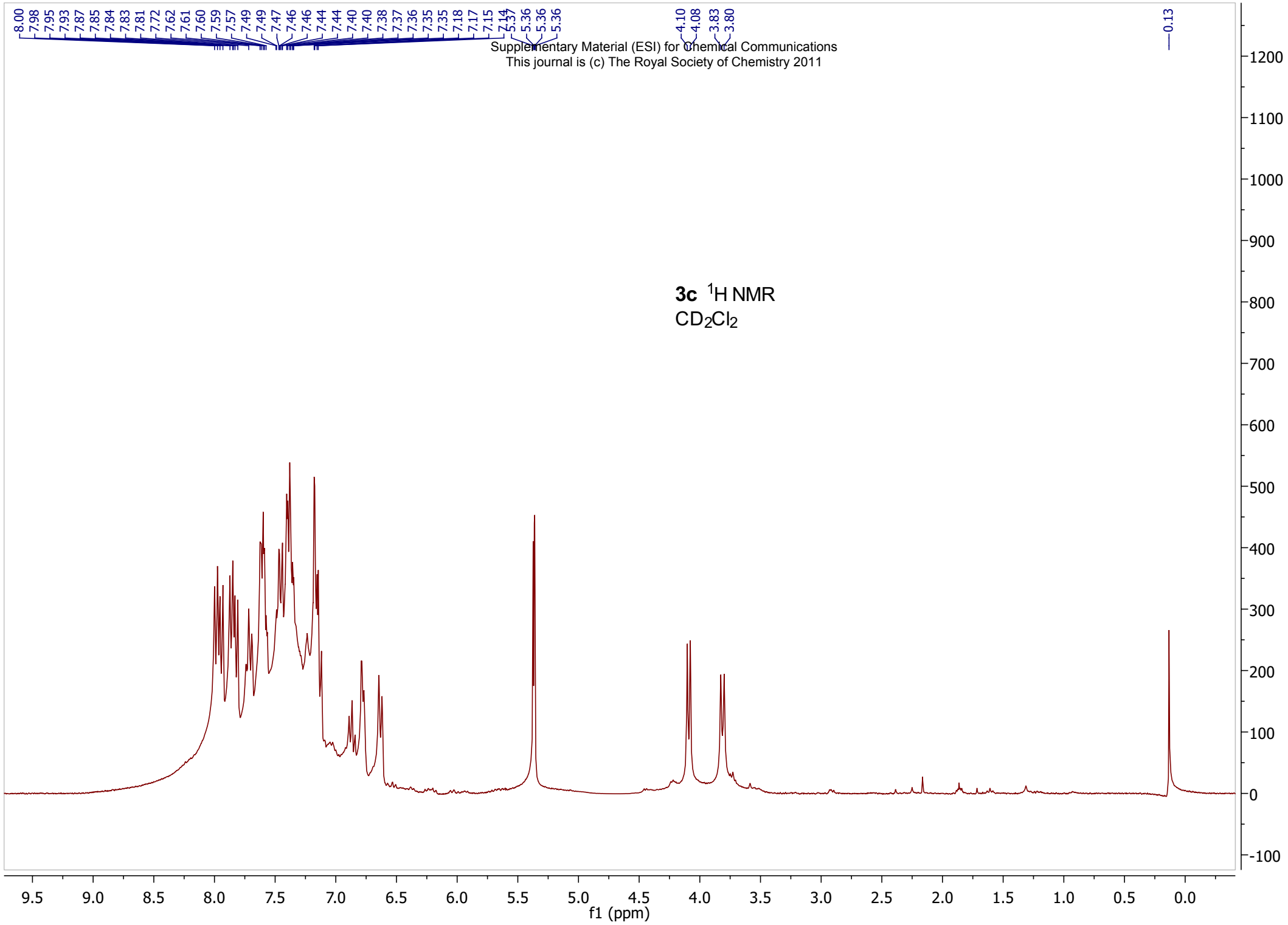
163.2
163.81
163.77
163.57
163.52
52.0
51.5
52.14
52.00
51.86






3b $^{13}C\{^{1}H\}$ NMR
$CDCl_3$
162.21
152.49
137.97
136.07
134.29
134.13
132.42
132.27
128.92
128.37
128.08
127.54
121.06
56.02
52.85
52.73
52.60
29.49
18.81
f1 (ppm)


62.41
62.01
27.64
27.24
3c $^{31}P\{^{1}H\}$ NMR
CD_2Cl_2
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


8.00
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7.87
7.85
7.84
7.83
7.81
7.72
7.62
7.61
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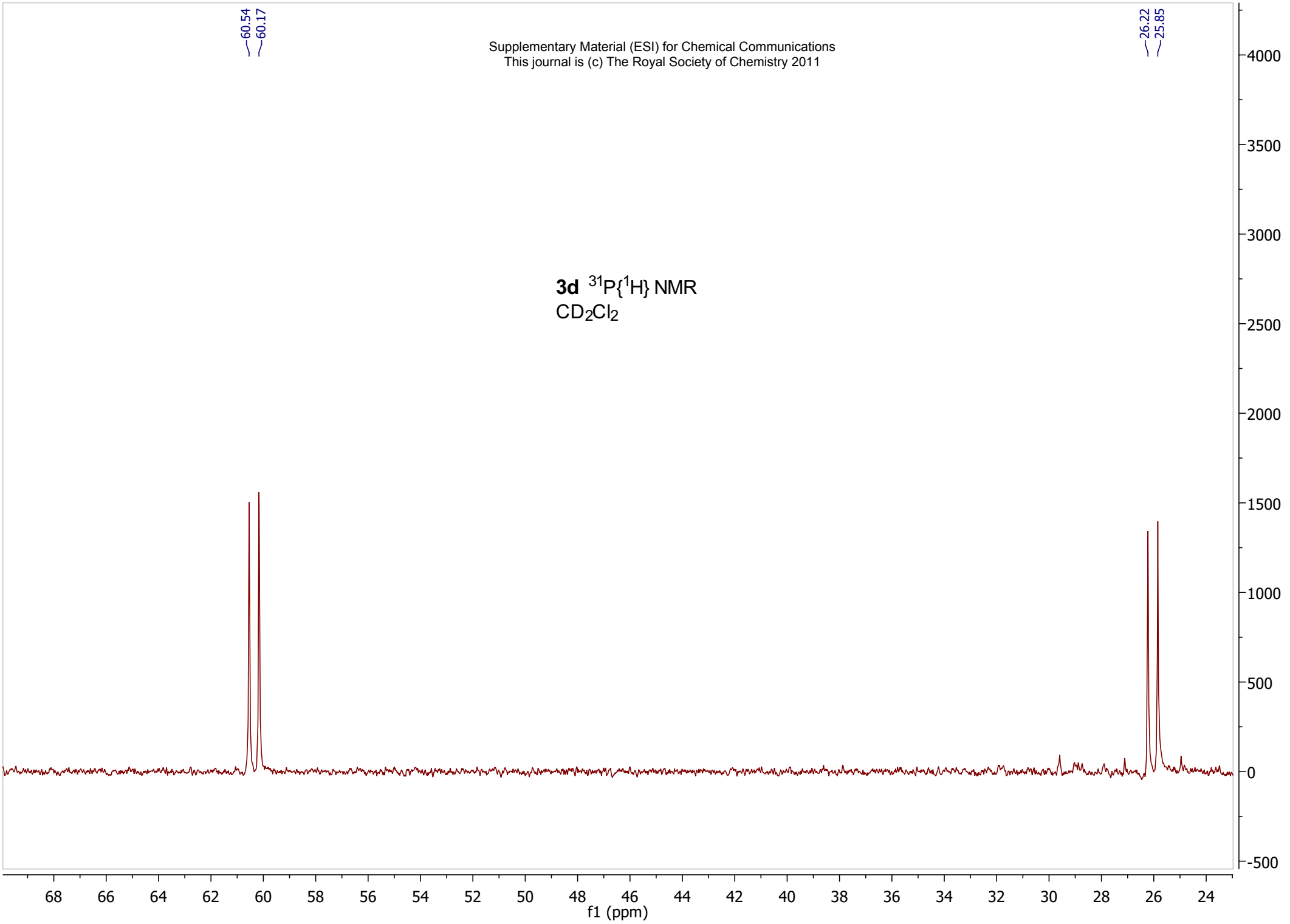
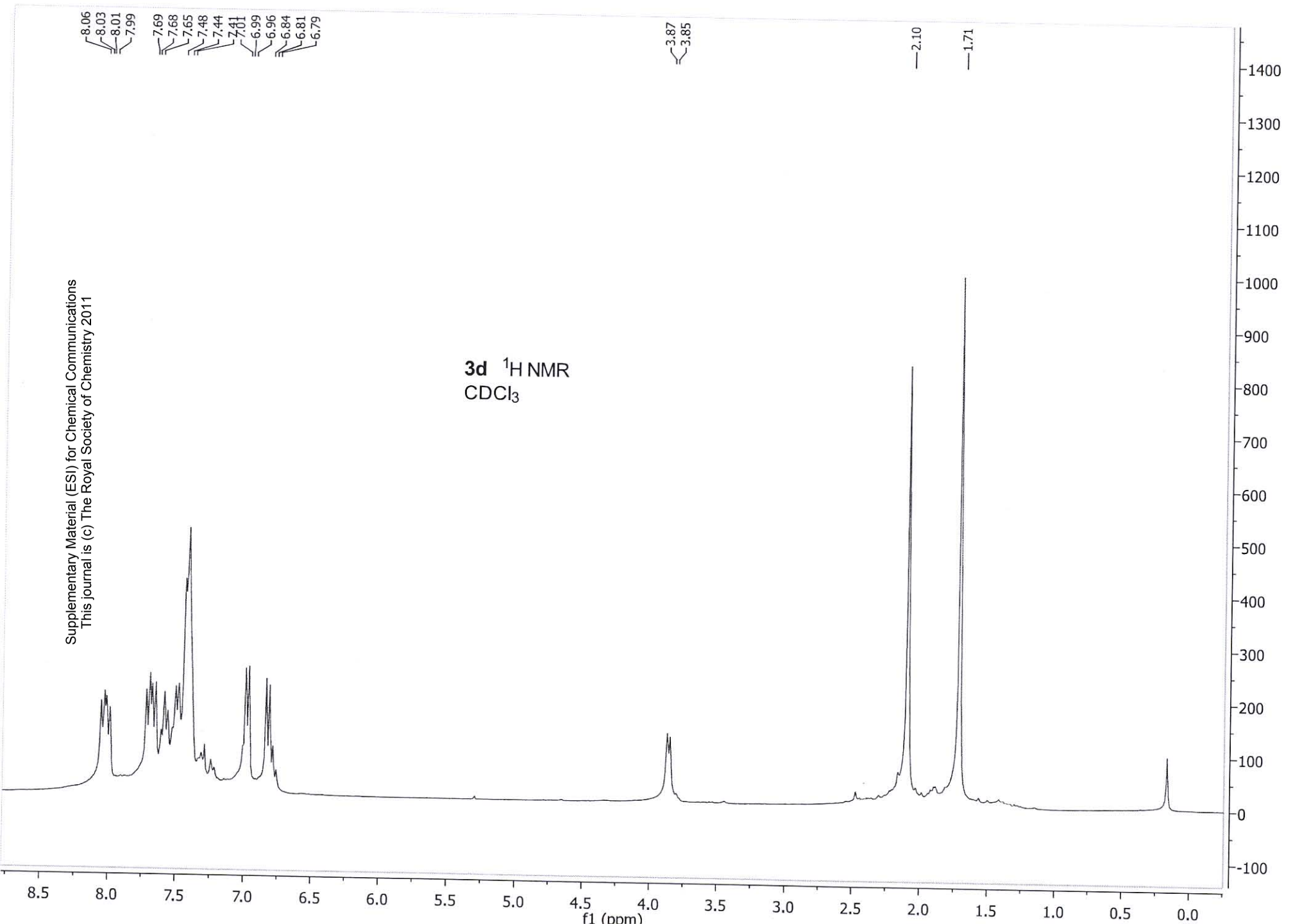
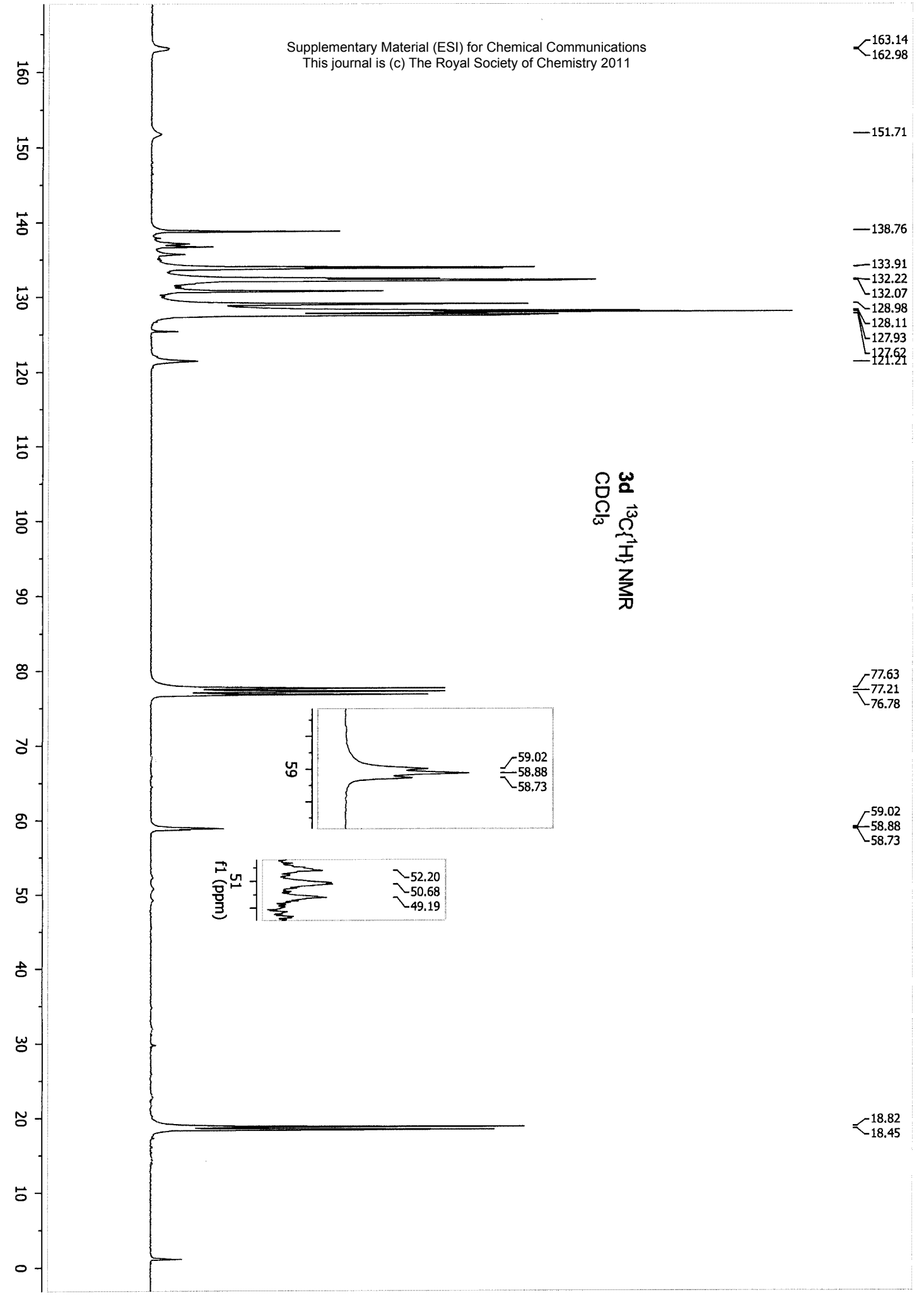
7.59
7.57
7.49
7.49
7.47
7.46
7.46
7.44
7.44
7.40
7.40
7.38
7.37
7.36
7.35
7.35
7.18
7.17
7.15
7.14
5.37
5.36
5.36
5.36
4.10
4.08
3.83
3.80
0.13
3c 1H NMR
CD2Cl2
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


60.54
60.17
26.22
25.85
3d $^{31}P\{^{1}H\}$ NMR
CD_2Cl_2
4000
3500
3000
2500
2000
1500
1000
500
0
-500
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
f1 (ppm)




3d $^{13}C\{^1H\}$ NMR
$CDCl_3$
163.14
162.98
151.71
138.76
133.91
132.22
132.07
128.98
128.11
127.93
127.62
121.21
77.63
77.21
76.78
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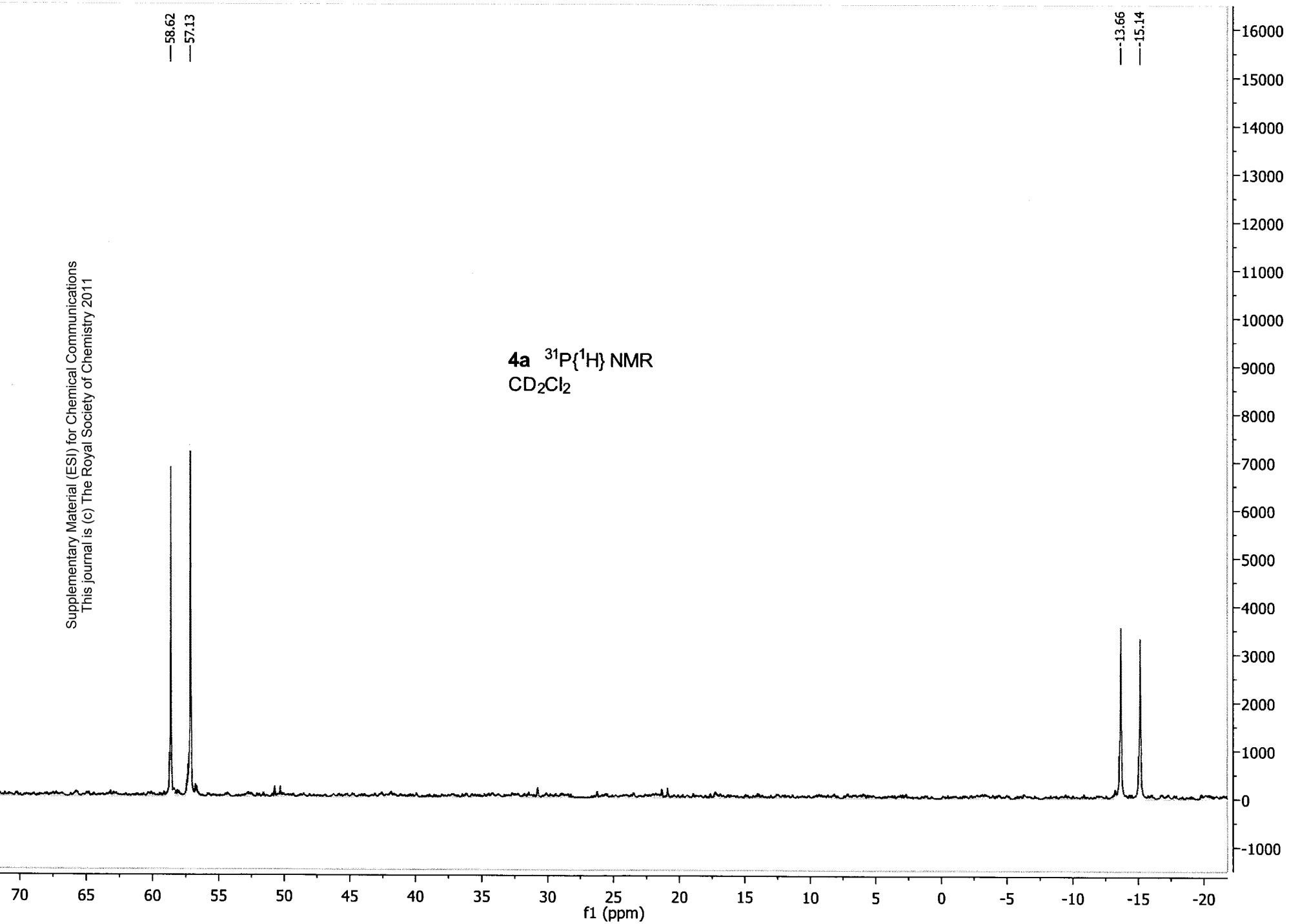
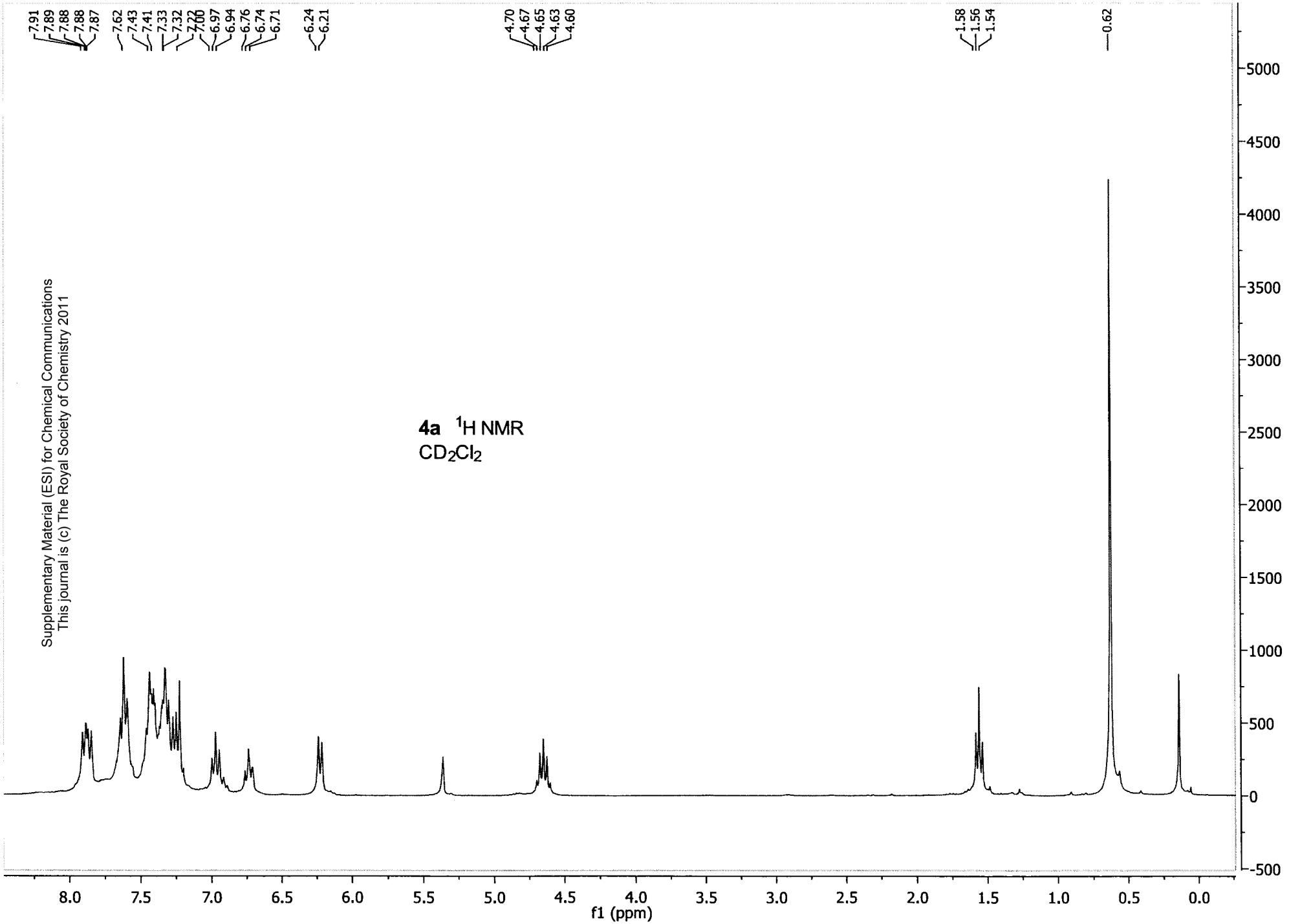
52.20
50.68
49.19
18.82
18.45
59
51
f1 (ppm)

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7.43
7.41
7.33
7.32
7.22
7.00
6.97
6.94
6.76
6.74
6.71
6.24
6.21
4.70
4.67
4.65
4.63
4.60
1.58
1.56
1.54
0.62
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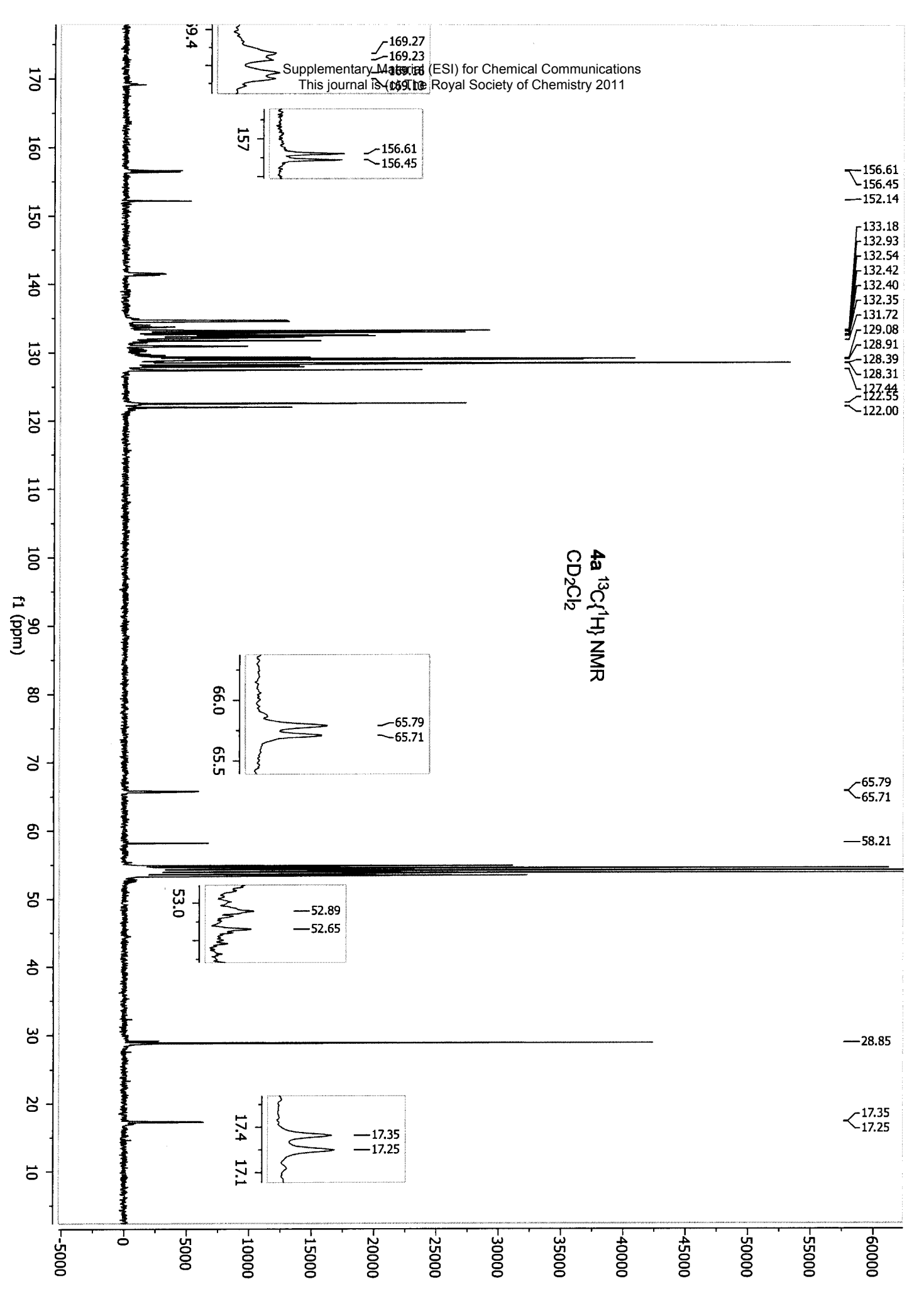
4a ^{1}H NMR
CD_2Cl_2
f1 (ppm)


4a $^{13}C\{^{1}H\}$ NMR
CD_2Cl_2
f1 (ppm)
169.27
169.23
157
156.61
156.45
152.14
133.18
132.93
132.54
132.42
132.40
132.35
131.72
129.08
128.91
128.39
128.31
127.44
122.55
122.00
66.0
65.5
65.79
65.71
58.21
53.0
52.89
52.65
28.85
17.4
17.1
17.35
17.25

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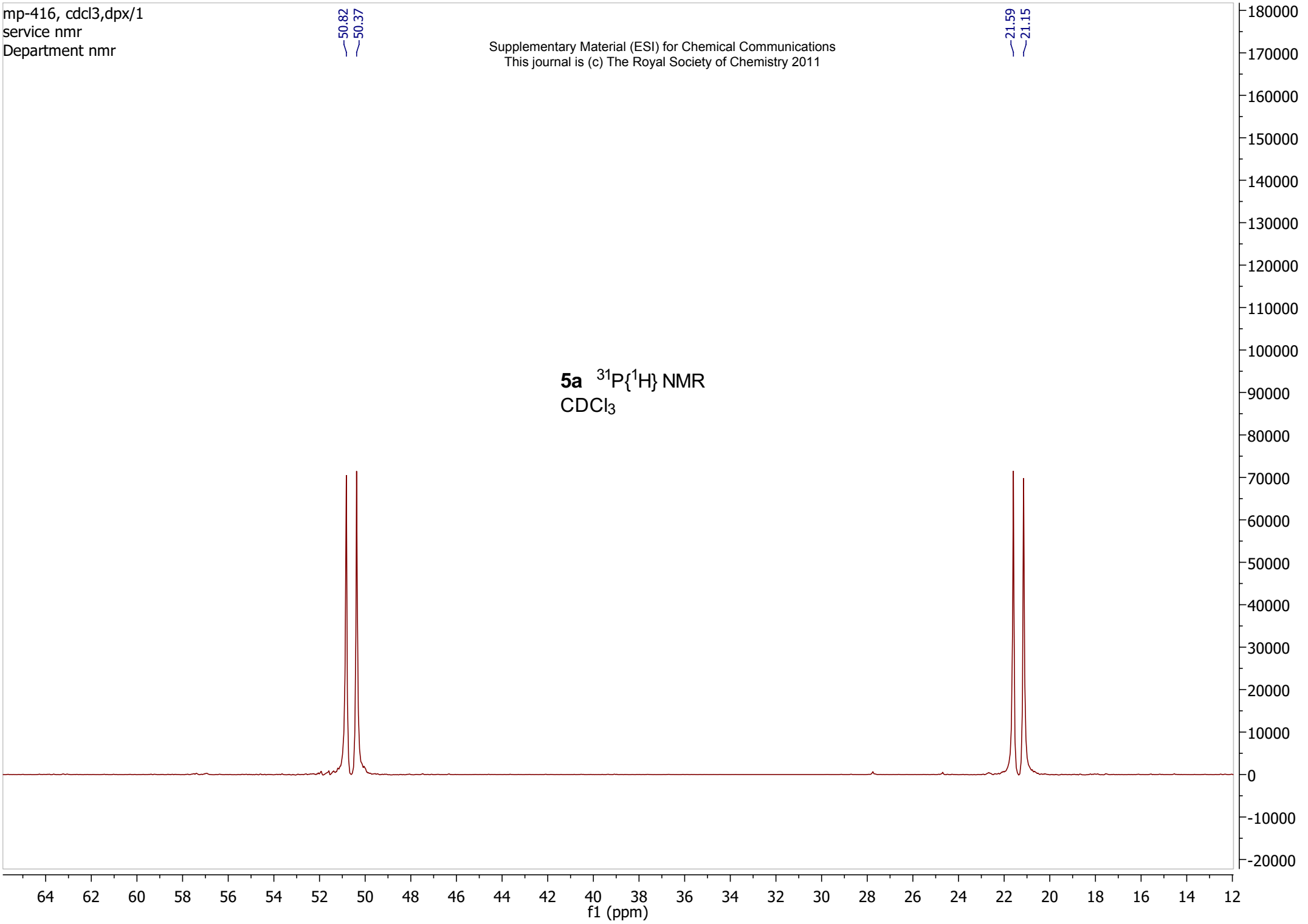

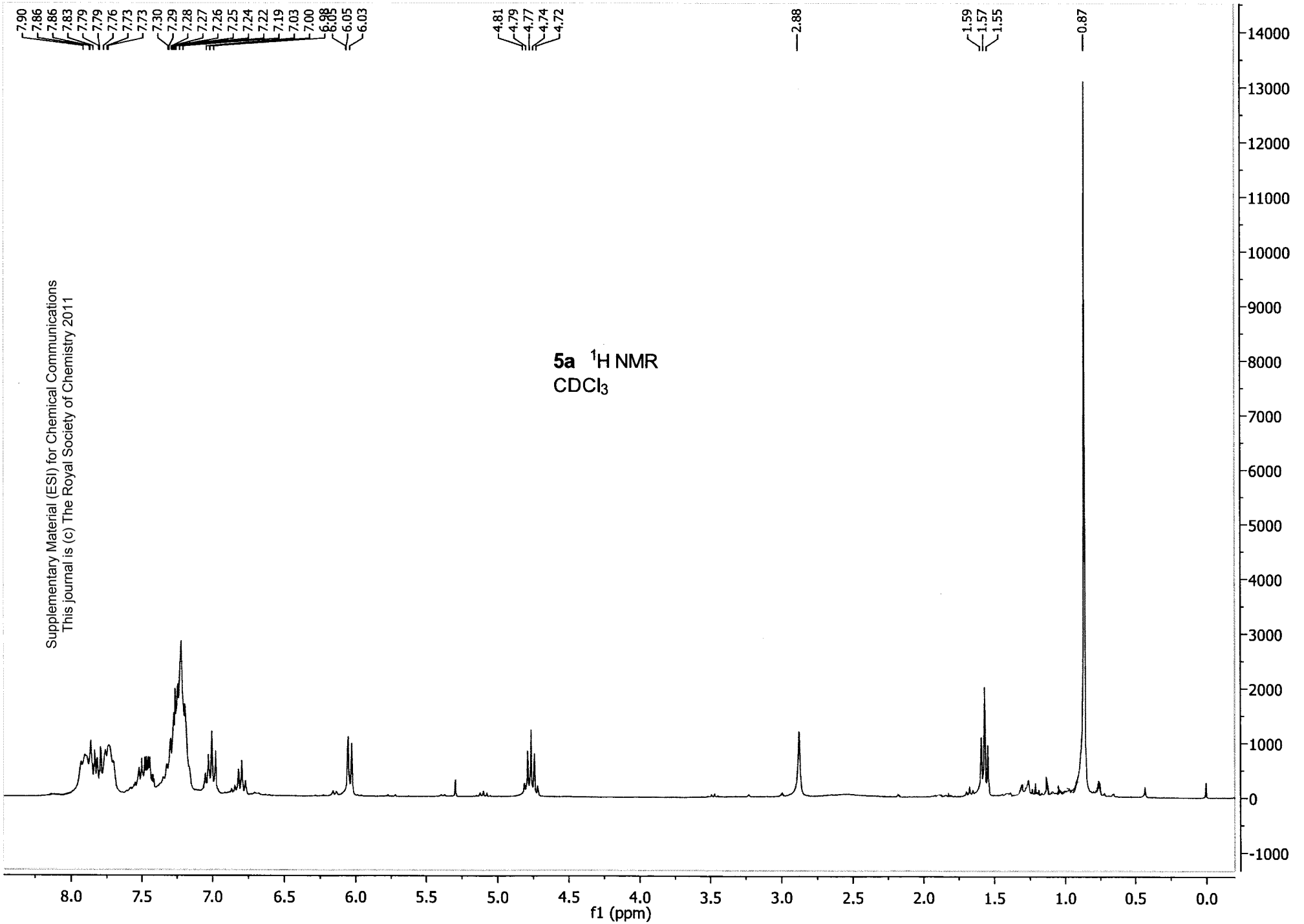
7.90
7.86
7.86
7.83
7.79
7.79
7.76
7.73
7.73
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.22
7.19
7.03
7.00
6.88
6.85
6.05
6.03
4.81
4.79
4.77
4.74
4.72
2.88
1.59
1.57
1.55
0.87
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5a ^{1}H NMR
$CDCl_3$
f1 (ppm)