Supporting Information

The Ammonium-Promoted Formylation of Indoles by DMSO and H_2O

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1. Experimental Section

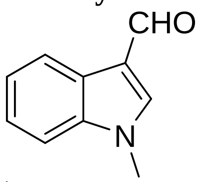
Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a 300 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz), using $CDCl_3$ or DMSO-d^6 as the solvent at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz.

2. Typical procedure

Under N_2, a sealed reaction tube was charged with *N*-methyl indole **1a** (26 mg, 0.2 mmol), ammonium acetate (62 mg, 0.8 mmol) and DMSO/H_2O (1.5 mL/80 μL). The reaction tube was kept stirring at 150 °C. After the completion of the reaction, as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the product.

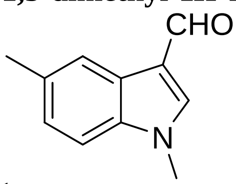
3. Characterization Data for the Products.

1-methyl-1*H*-indole-3-carbaldehyde (2a)[1]



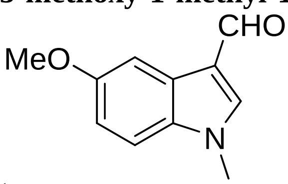
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.93 (s, 1H), 8.31-8.28 (m, 1H), 7.61 (s, 1H), 7.35-7.28 (m, 3H), 3.82 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.4, 139.4, 137.7, 125.1, 123.9, 122.8, 121.9, 117.8, 109.8, 33.6.

1,5-dimethyl-1*H*-indole-3-carbaldehyde (2b) [2]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.89 (s, 1H), 8.10 (s, 1H), 7.56 (s, 1H), 7.21 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 2.48 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.4, 139.4, 136.1, 132.6, 125.4, 125.3, 121.6, 117.4, 109.4, 33.6, 21.3.

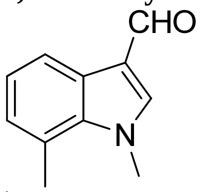
5-methoxy-1-methyl-1*H*-indole-3-carbaldehyde (2c)[3]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.89 (s, 1H), 7.76 (s, 1H), 7.56 (s, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.3, 156.6, 139.4, 132.7, 125.8, 117.6, 114.3, 110.6,

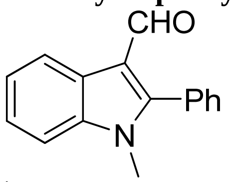
103.2, 55.7, 33.8.

1,7-dimethyl-1*H*-indole-3-carbaldehyde (2d)[2]



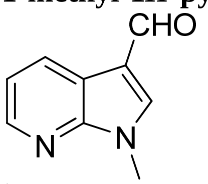
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.86 (s, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.40 (s, 1H), 7.17-7.12 (m, 1H), 6.98 (d, J = 9.0 Hz, 1H), 3.97 (s, 3H), 2.67 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.2, 140.9, 136.3, 126.5, 126.1, 122.9, 121.8, 119.7, 117.2, 37.7, 19.2.

1-methyl-2-phenyl-1*H*-indole-3-carbaldehyde (2e)[2]



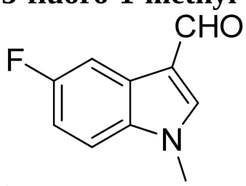
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.74 (s, 1H), 8.46-8.43 (m, 1H), 7.58-7.55 (m, 3H), 7.50-7.47 (m, 2H), 7.41-7.37 (m, 3H), 3.67 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.6, 151.4, 137.3, 130.8, 129.8, 128.6, 128.5, 125.0, 124.0, 123.2, 122.1, 115.6, 109.8, 31.0.

1-methyl-1*H*-pyrrolo[2,3-b]pyridine-3-carbaldehyde (2f)[4]



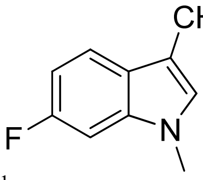
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.93 (s, 1H), 8.51 (d, J = 9.0 Hz, 1H), 8.40 (d, J = 4.5 Hz, 1H), 7.82 (s, 1H), 7.25-7.21 (m, 1H), 3.94 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.4, 148.6, 145.0, 139.0, 130.4, 118.8, 117.5, 116.2, 32.0.

5-fluoro-1-methyl-1*H*-indole-3-carbaldehyde (2g) [2]



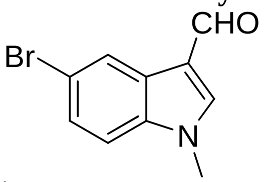
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.85 (s, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.23-7.19 (m, 1H), 7.05-6.98 (m, 1H), 3.80 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.1, 159.7 (d, J_{C-F} = 237.0 Hz), 140.2, 134.2, 125.6 (d, J_{C-F} = 11.2 Hz), 117.6 (d, J_{C-F} = 3.8 Hz), 112.1 (d, J_{C-F} = 26.2 Hz), 110.7 (d, J_{C-F} = 9.8 Hz), 107.2 (d, J_{C-F} = 24.8 Hz), 33.8.

6-fluoro-1-methyl-1*H*-indole-3-carbaldehyde (2h) [2]



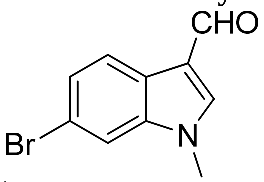
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.92 (s, 1H), 8.22 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz,1H), 7.64 (s, 1H), 7.09-6.99 (m, 2H), 3. 80 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.3, 160.6 (d, $J_{C\text{-}F}$ = 240.0 Hz), 139.7, 138.0 (d, $J_{C\text{-}F}$ = 12.0 Hz), 123.1 (d, $J_{C\text{-}F}$ = 9.8 Hz), 121.4, 118.0, 111.4 (d, $J_{C\text{-}F}$ = 24.0 Hz), 96.6 (d, $J_{C\text{-}F}$= 26.2 Hz), 33.7.

5-bromo-1-methyl-1*H*-indole-3-carbaldehyde (2i)[5]



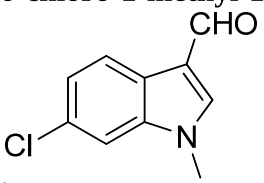
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.81 (s, 1H), 8.33 (s, 1H), 7.54 (s, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 9.0 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.0, 139.8, 136.3, 126.7, 126.3, 124.2, 117.0, 116.3, 111.3, 33.7.

6-bromo-1-methyl-1*H*-indole-3-carbaldehyde(2j) [6]



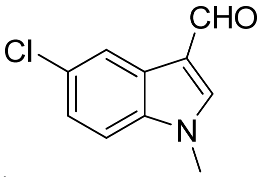
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.89 (s, 1H), 8.10 (d, J = 6.0 Hz, 1H), 7.57 (s, 1H), 7.43 (s, 1H), 7.37 (d, J = 7.5 Hz, 1H), 3.76 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.2, 139.6, 138.4, 125.9, 123.8, 123.1, 117.8, 117.4, 112.9, 33.7.

6-chloro-1-methyl-1*H*-indole-3-carbaldehyde (2k) [2]



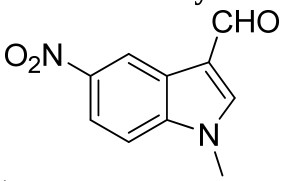
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.88 (s, 1H), 8.16 (d, J = 9.0 Hz, 1H), 7.59 (s, 1H), 7.27 (s, 1H), 7.24 (d, J = 7.5 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.2, 139.7, 138.1, 129.8, 123.4, 123.3, 122.8, 117.8, 110.0, 33.6.

5-chloro-1-methyl-1*H*-indole-3-carbaldehyde (2l)[7]



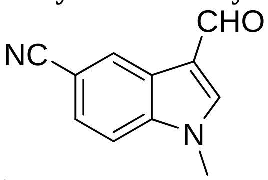
[1]H NMR ($CDCl_3$, 300 MHz): δ 9.89 (s, 1H), 8.25 (s, 1H), 7.63 (s, 1H), 7.28-7.20 (m, 2H), 3.83 (s, 3H).
[13]C NMR ($CDCl_3$, 75 MHz): δ 184.1, 139.9, 136.1, 128.8, 126.0, 124.3, 121.5, 117.4, 110.9, 33.8.

5-nitro-1-methyl-1*H*-indole-3-carbaldehyde (2m) [8]



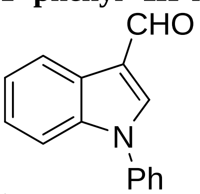
[1]H NMR (DMSO-d^6, 300 MHz): δ 9.97 (s, 1H), 9.89 (s, 1H), 8.53 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 3.96 (s, 3H).
[13]C NMR (DMSO-d^6, 75 MHz): δ 185.0, 144.5, 143.1, 140.5, 123.8, 118.7, 117.9, 117.0, 111.9, 33.9.

5- Cyano -1-methyl-1*H*-indole-3-carbaldehyde (2n) [9]



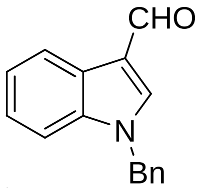
[1]H NMR ($CDCl_3$, 300 MHz): δ 9.98 (s, 1H), 8.61 (s, 1H), 7.81 (s, 1H), 7.54 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 3.93 (s, 3H).
[13]C NMR ($CDCl_3$, 75 MHz): δ 184.2, 140.8, 139.2, 127.4, 127.0, 124.8, 119.7, 118.1, 110.9, 106.1, 34.0.

1- phenyl -1*H*-indole-3-carbaldehyde (2o) [10]



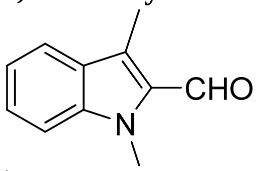
[1]H NMR ($CDCl_3$, 300 MHz): δ 10.08 (s, 1H), 8.41-8.38 (m, 1H), 7.89 (s, 1H), 7.61-7.55 (m, 2H), 7.51-7.45 (m, 4H), 7.39-7.30 (m, 2H).
[13]C NMR ($CDCl_3$, 75 MHz): δ 184.9, 138.2, 137.9, 137.3, 129.9, 128.2, 125.4, 124.7, 124.5, 123.3, 122.1, 119.5, 111.0.

1-benzyl-1*H*-indole-3-carbaldehyde (2p)[11]



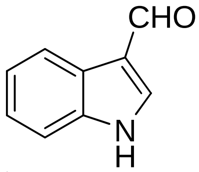
^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.00 (s, 1H), 8.35-8.32 (m, 1H), 7.71 (s, 1H), 7.37-7.29 (m, 6H), 7.18 (d, J = 6.0 Hz, 2H), 5.36 (s, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.6, 138.5, 137.4, 135.2, 129.1, 128.4, 127.2, 125.4, 124.1, 123.0, 122.1, 118.4, 110.3, 50.9.

1,3-dimethyl-1*H*-indole-2-carbaldehyde (2q) [12]



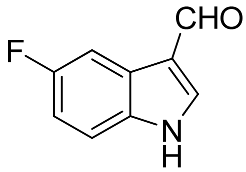
^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.16 (s, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 6.0 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 4.05 (s, 3H), 2.64 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 181.6, 139.7, 131.2, 127.3, 126.8, 126.5, 121.3, 120.0, 110.1, 31.5, 8.5.

1*H*-indole-3-carbaldehyde (2r)[13]



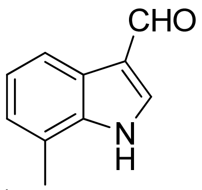
^{1}H NMR (DMSO-d^6, 300 MHz): δ 12.15 (b, 1H), 9.94 (s, 1H), 8.29 (s, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.29-7.19 (m, 2H).
^{13}C NMR (DMSO-d^6, 75 MHz): δ 185.0, 138.5, 137.1, 124.2, 123.5, 122.2, 120.9, 118.2, 112.5.

5-fluoro-1*H*-indole-3-carbaldehyde (2s) [10]



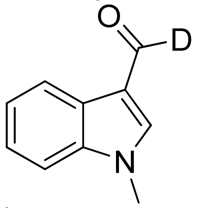
^{1}H NMR (DMSO-d^6, 300MHz): δ 12.25 (b, 1H), 9.92 (s, 1H), 8.35 (s, 3.2 Hz, 1H), 7.76 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.53 (dd, J_1 = 9.0 Hz, J_2= 3.0 Hz, 1H), 7.11 (td, J_1= 9.0 Hz, J = 3.0 Hz, 1H)
^{13}C NMR (DMSO-d^6, 75MHz): δ 185.1, 158.8 (d, J_{C-F} = 234.0Hz), 139.7, 133.7, 124.7 (d, J_{C-F} = 11.2 Hz), 118.1, 113.8 (d, J_{C-F} = 9.8 Hz), 111.6 (d, J_{C-F} = 25.5 Hz), 105.8 (d, J_{C-F} = 24.8Hz)

7-methyl-1*H*-indole-3-carbaldehyde (2t) [10]



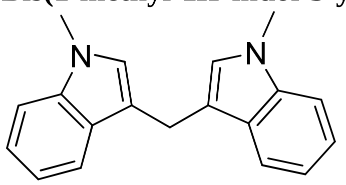
^{1}H NMR (DMSO-d^6, 300 MHz): δ 12.2 (b, 1H), 9.94 (s, 1H), 8.28 (d, *J* = 3.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 2.50 (s, 3H)
^{13}C NMR (DMSO-d^6, 75 MHz): δ 185.1, 138.2, 136.6, 124.1, 124.0, 122.4, 121.8, 118.6, 118.4, 16.7

1-methyl-1*H*-indole-3-carbaldehyde-*d* (d-2a)



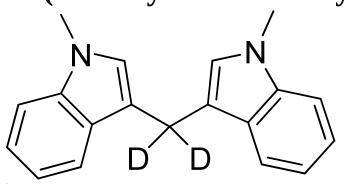
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.94 (s, 0.03H), 8.31-8.28 (m, 1H), 7.62 (s, 1H), 7.35-7.29 (m, 3H), 3.82 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 184.1 (t, *J* = 25.9 Hz), 139.3, 137.8, 125.1, 123.9, 122.8, 121.9, 117.8, 109.8, 33.6.

Bis(1-methyl-1*H*-indol-3-yl)methane (3a)[14]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70 (d, *J* = 9.0 Hz, 2H), 7.37-7.27 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 2H), 6.84 (s, 2H), 4.29 (s, 2H), 3.74 (s, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.1, 127.8, 126.9, 121.3, 119.2, 118.5, 114.2, 109.0, 32.5, 20.9.

Bis(1-methyl-1*H*-indol-3-yl)methane-d_2 (d-3a)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, *J* = 9.0 Hz, 2H), 7.35-7.24 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.83 (s, 0.09H), 4.25 (s, 2H), 3.73 (s, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.1, 127.9, 126.9, 121.3, 119.2, 118.5, 114.2, 109.0, 32.5, 20.3 (quint, *J* = 18.8 Hz).

2. References

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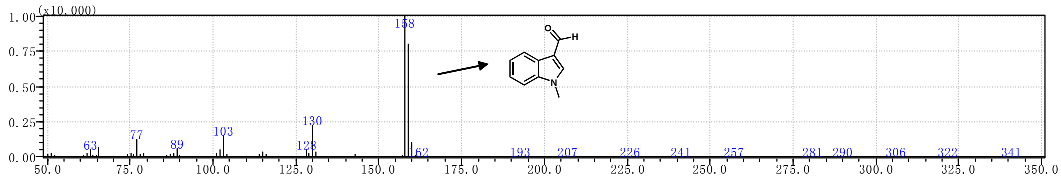
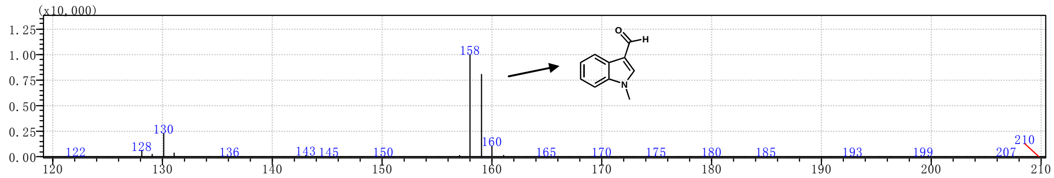
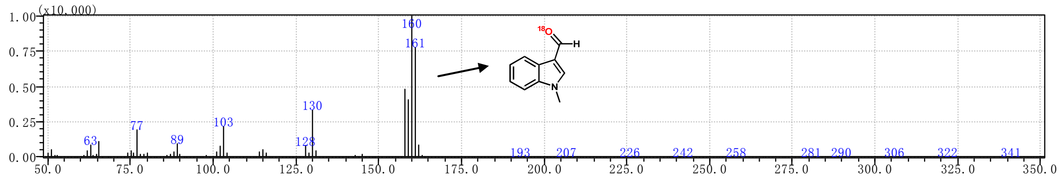
3. Deuterium, ^{18}O Labelling Experiments.

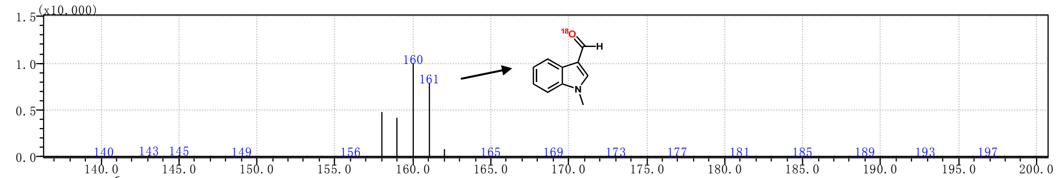
DMSO + D_2O + NH_4OAc



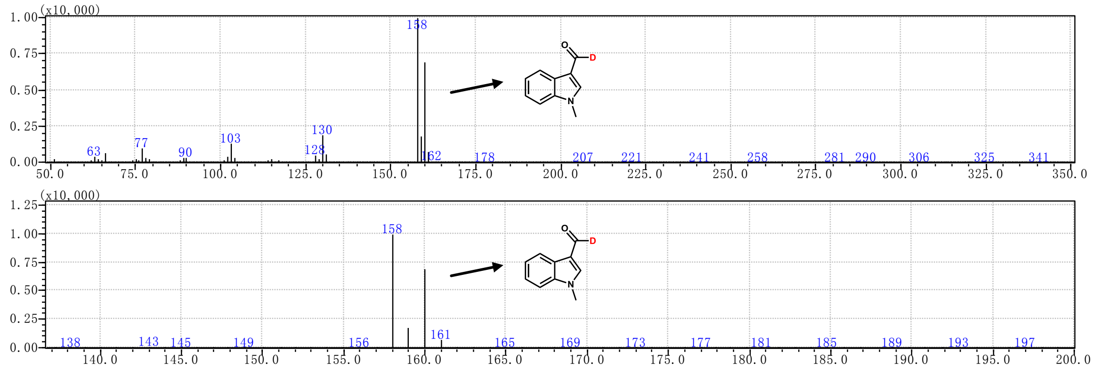


DMSO + $H_2{}^{18}O$ + NH_4OAc

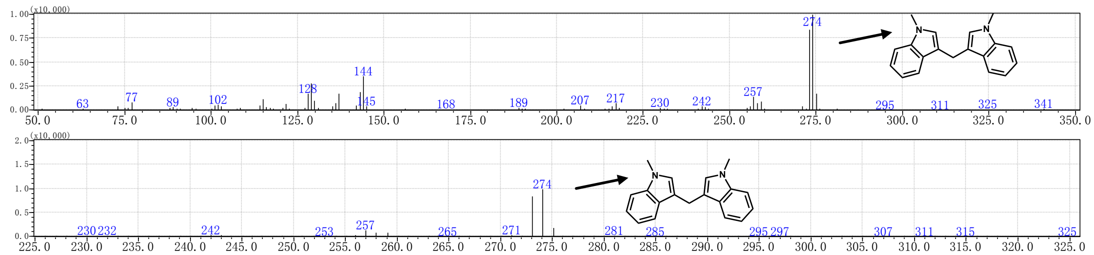




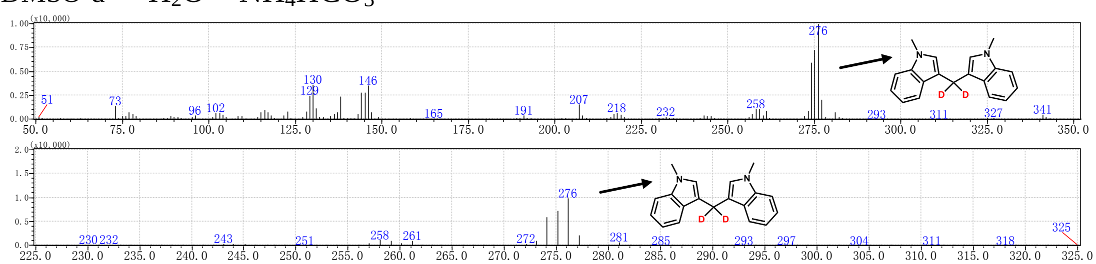
DMSO-d^6 + H_2O + NH_4OAc



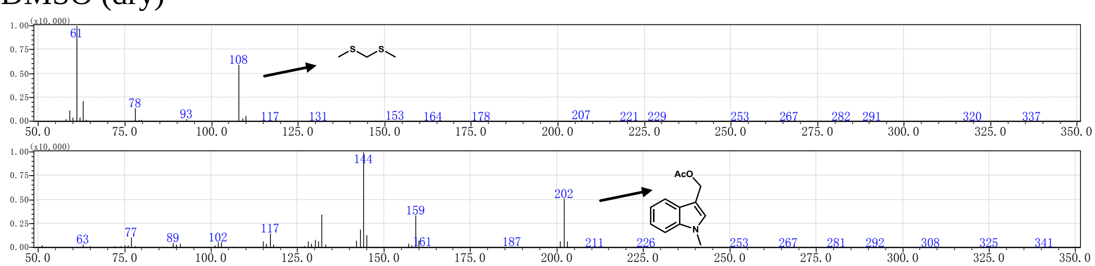
DMSO + D_2O + NH_4HCO_3



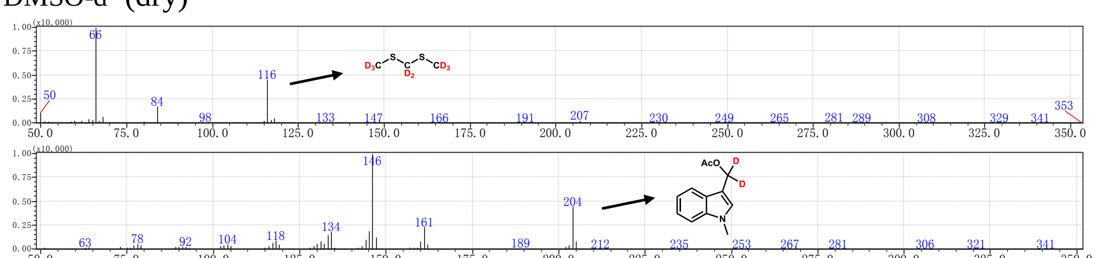
DMSO-d^6 + H_2O + NH_4HCO_3



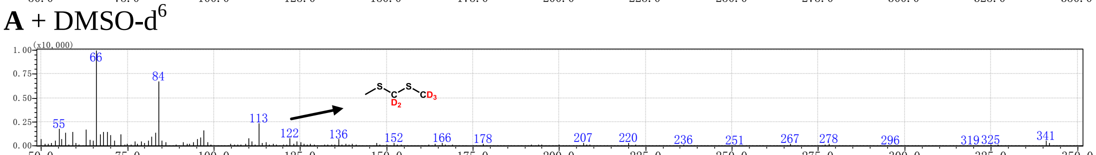
DMSO (dry)



DMSO-d^6 (dry)

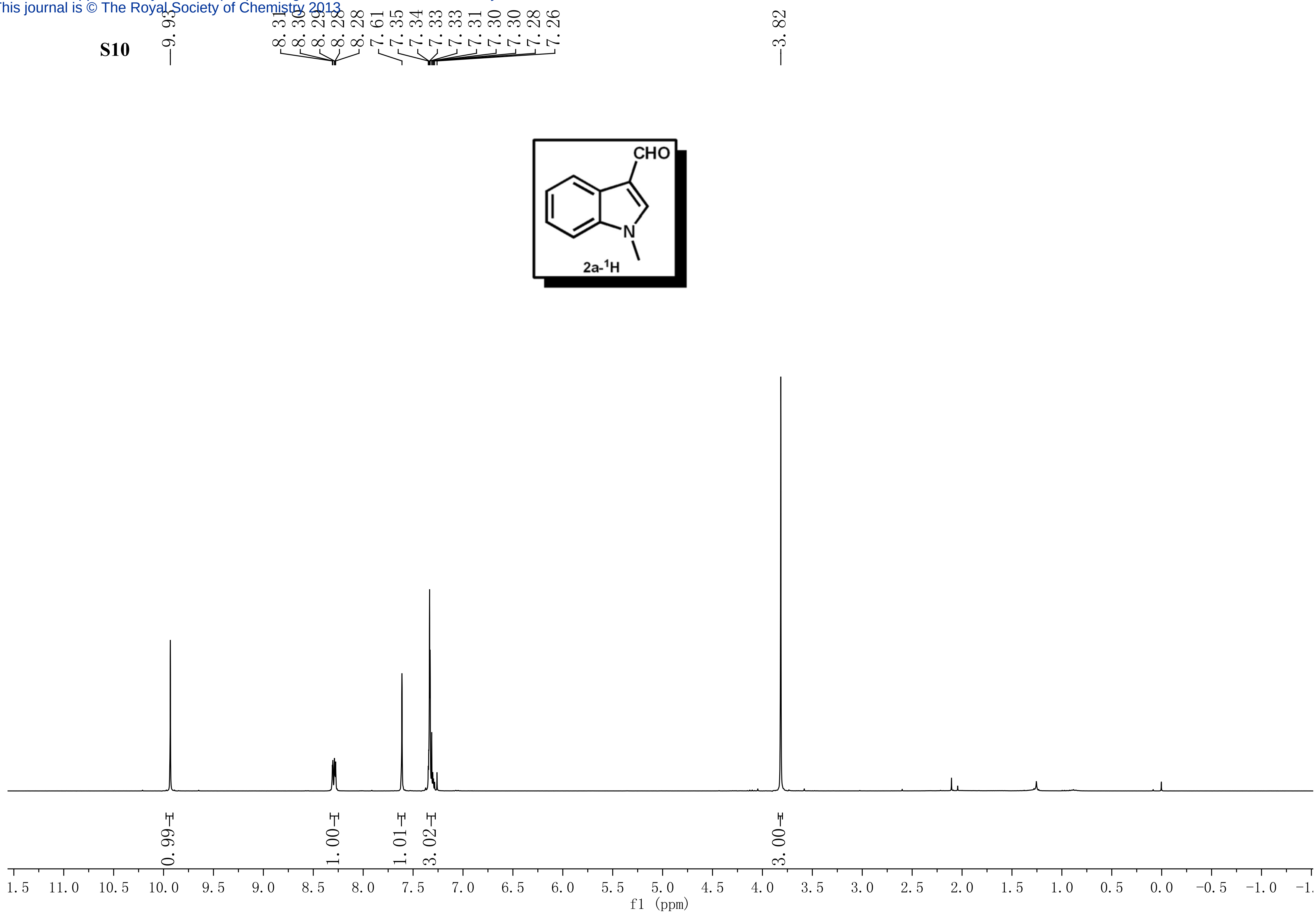


A + DMSO-d^6

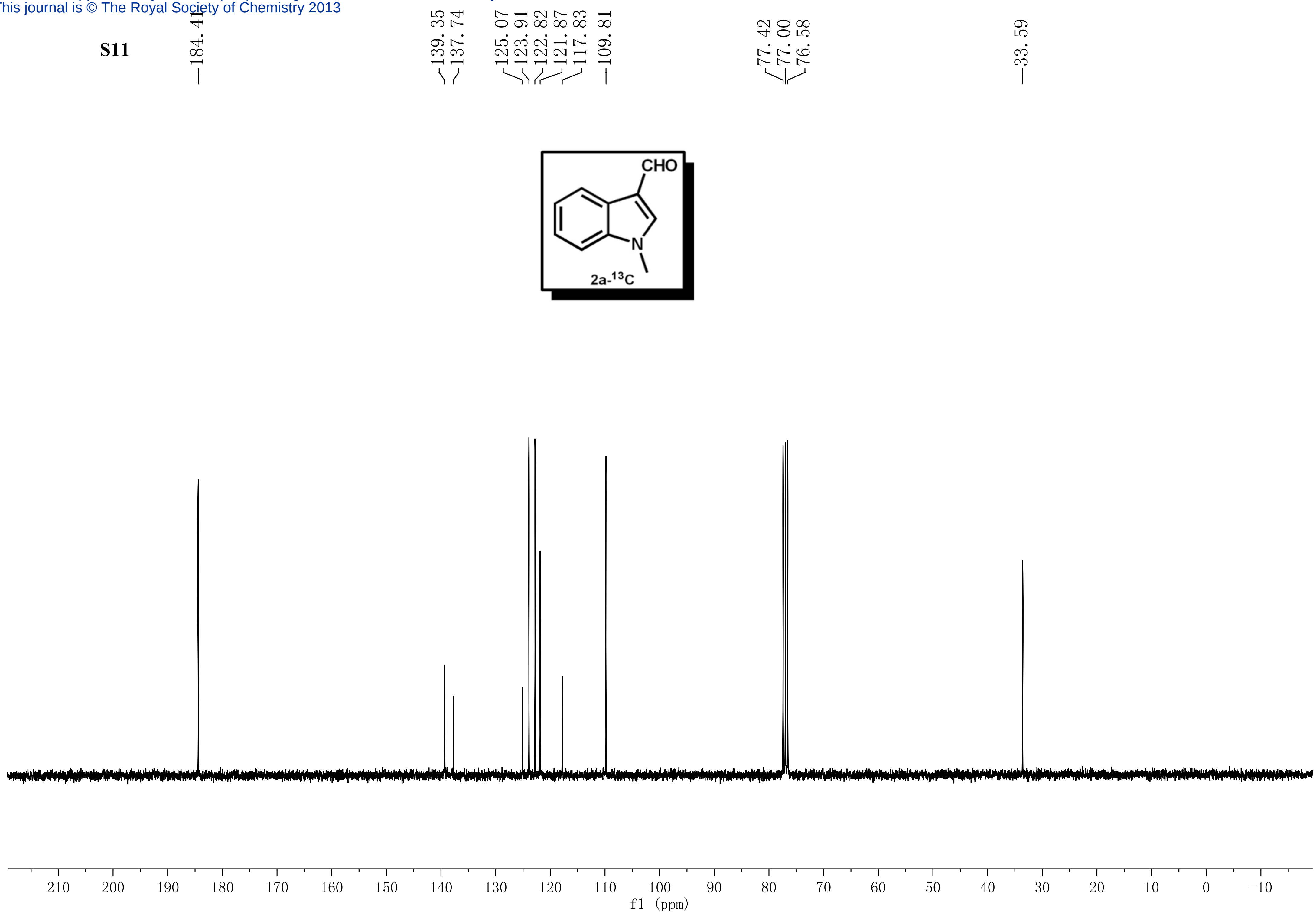


Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

S10

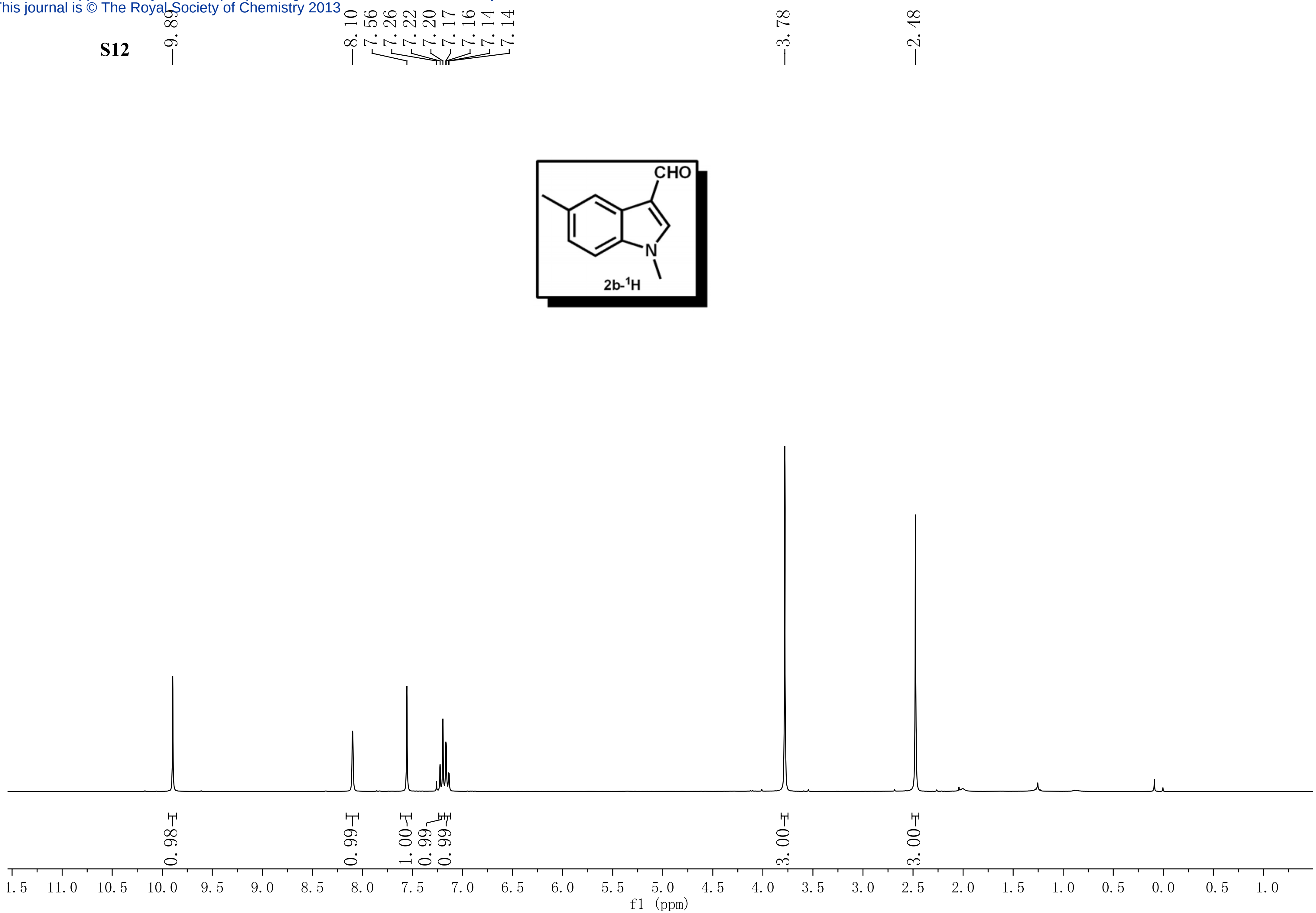


S11

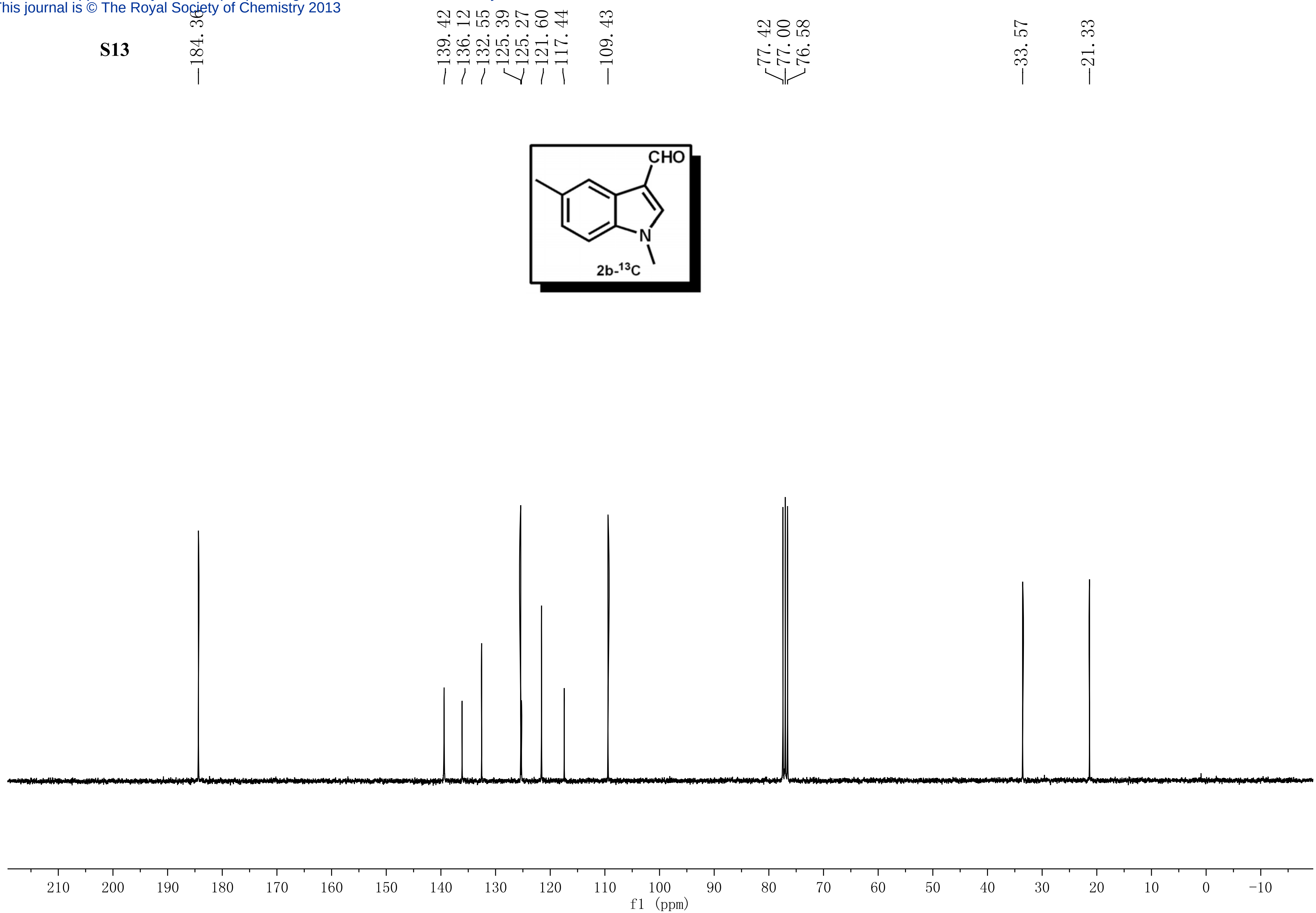

184.41
139.35
137.74
125.07
123.91
122.82
121.87
117.83
109.81
77.42
77.00
76.58
33.59
CHO
N
2a-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

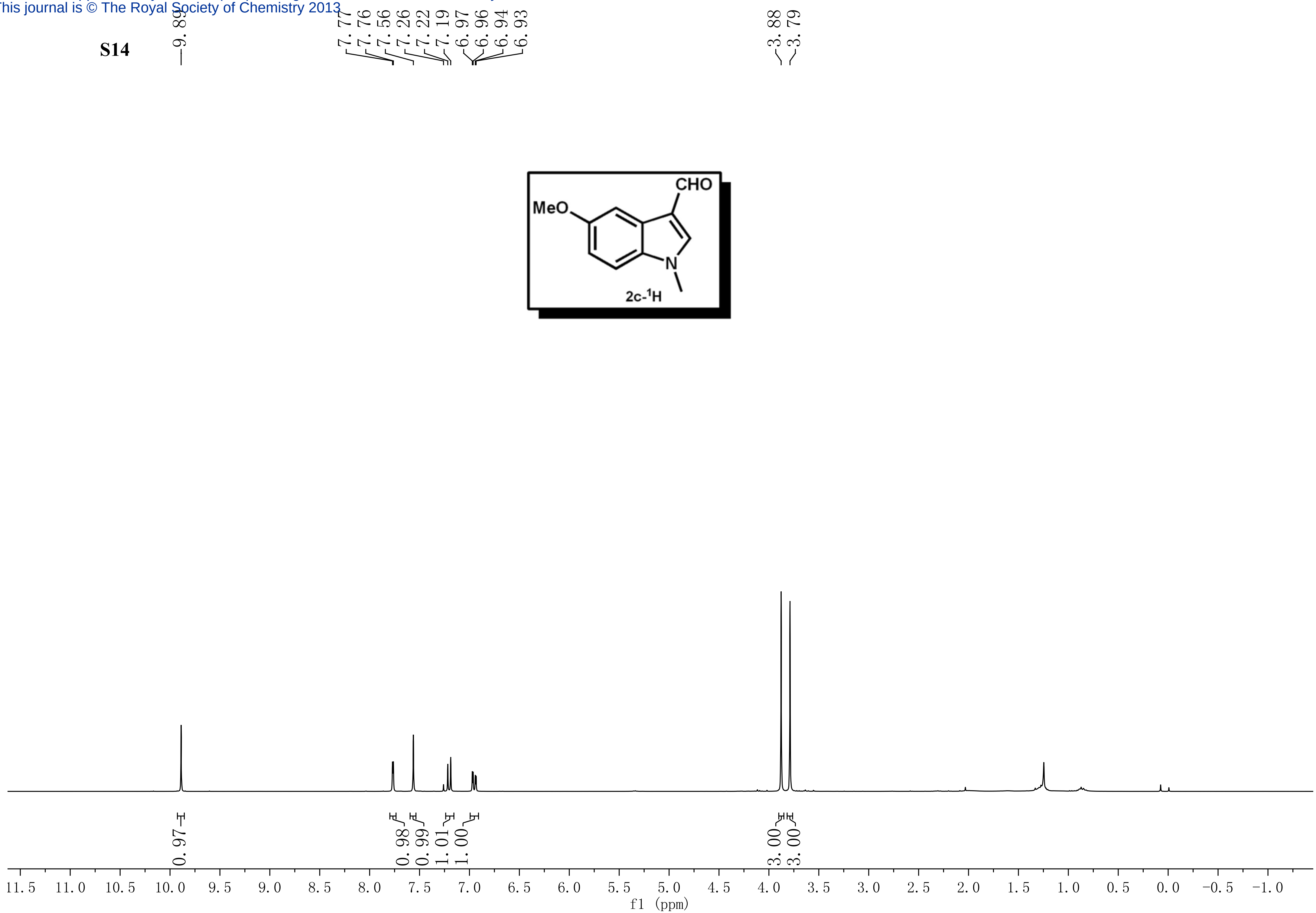
S12

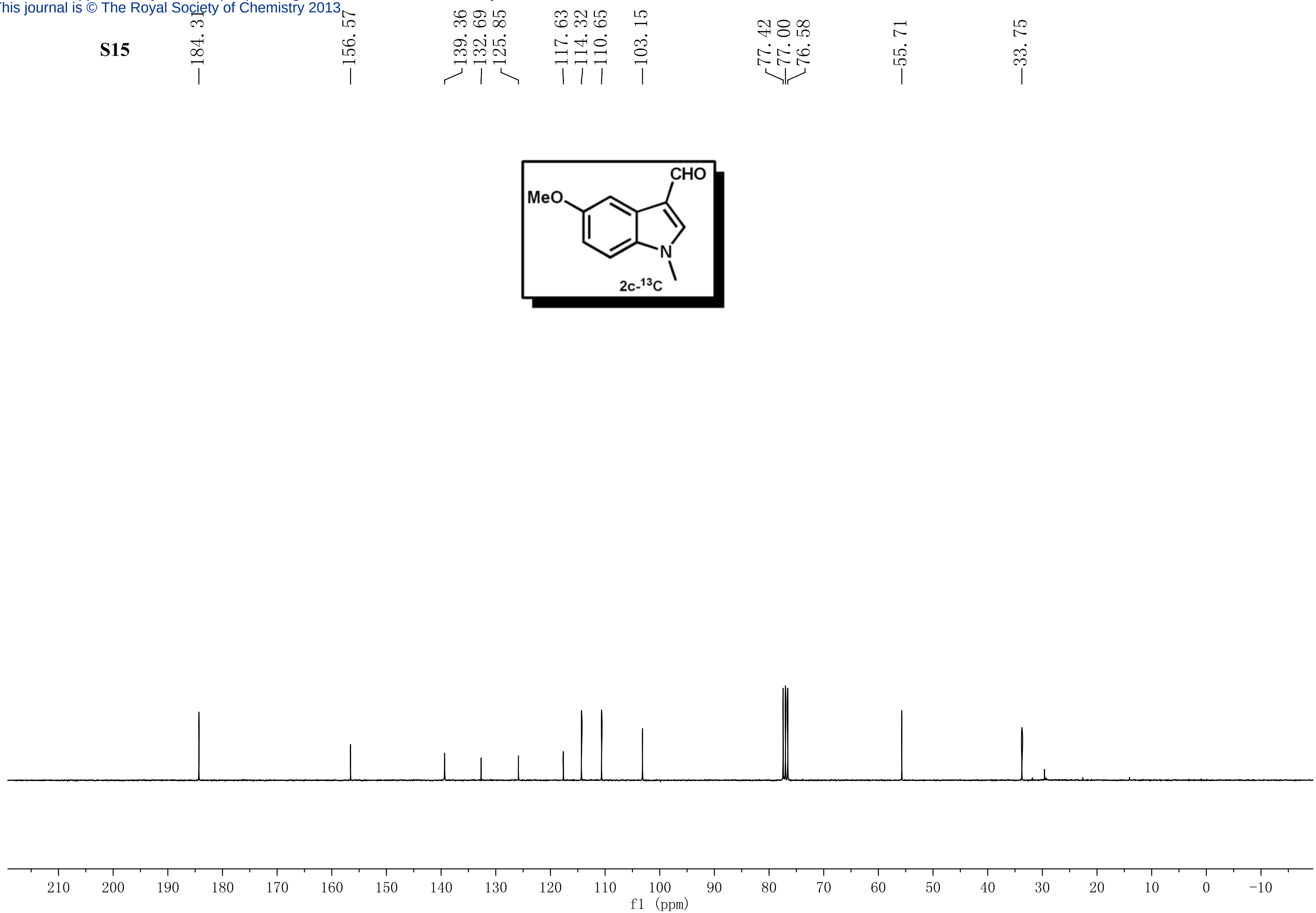


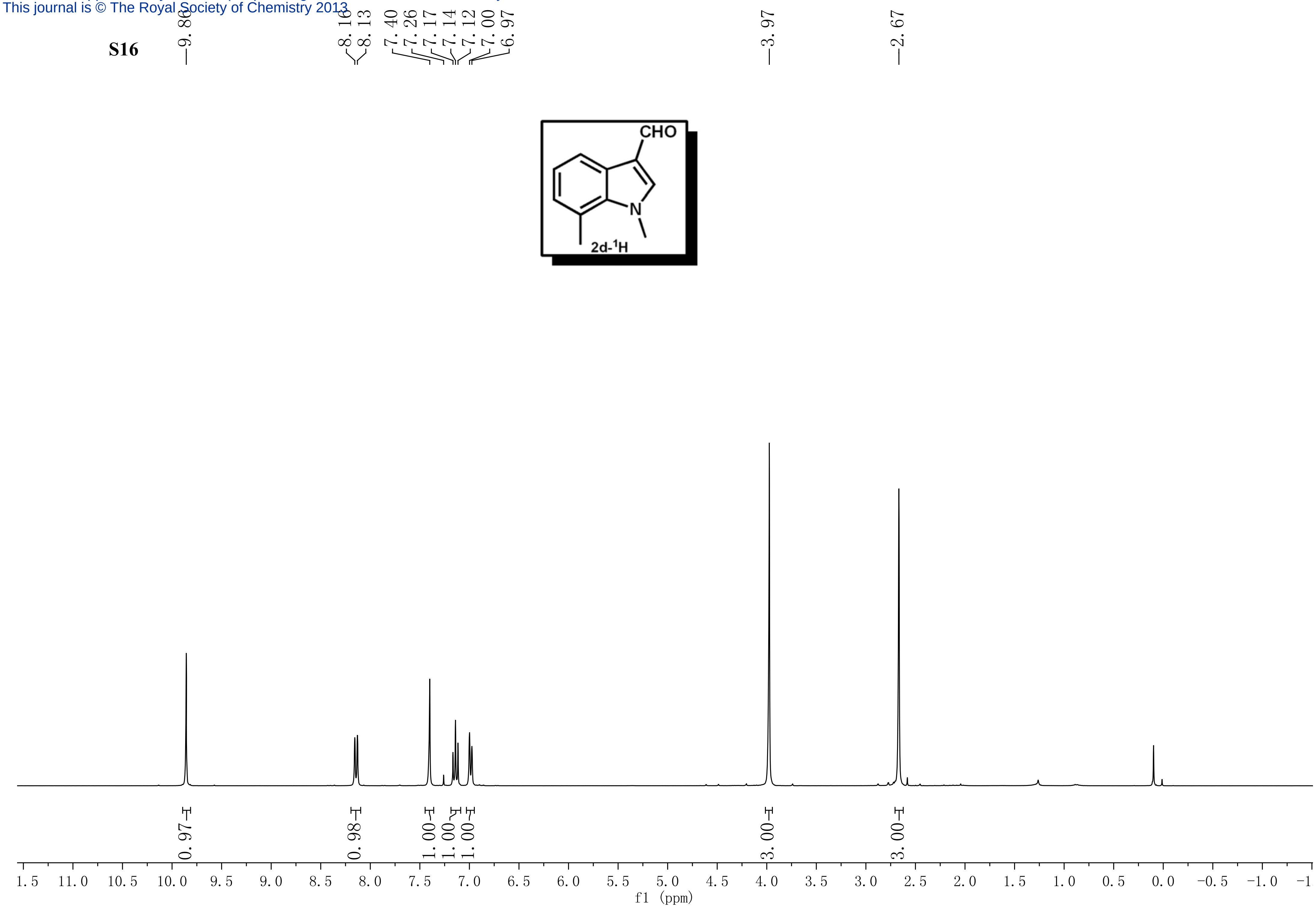
S13


184.36
139.42
136.12
132.55
125.39
125.27
121.60
117.44
109.43
77.42
77.00
76.58
33.57
21.33
CHO
N
2b-^{13}C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

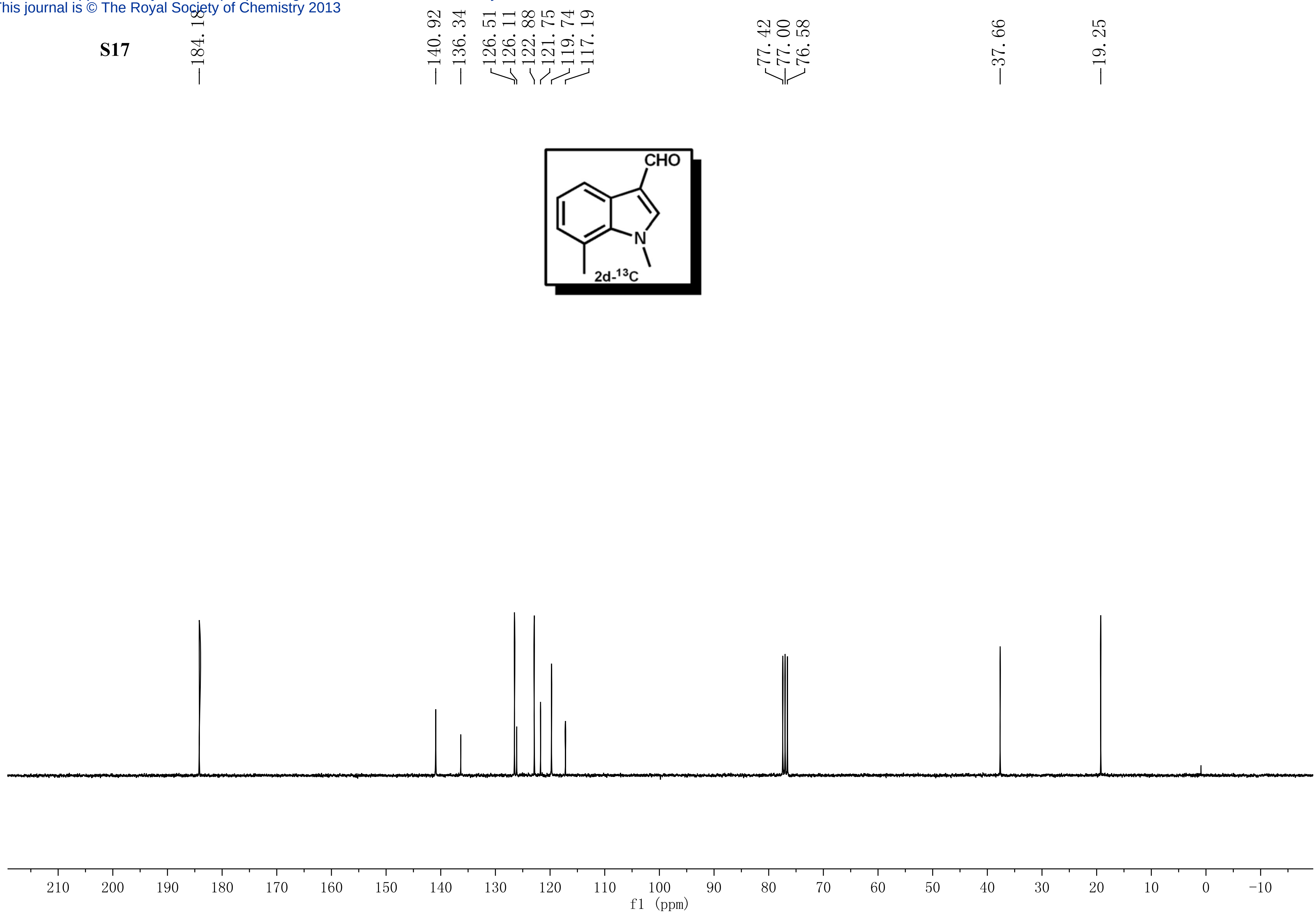
S14

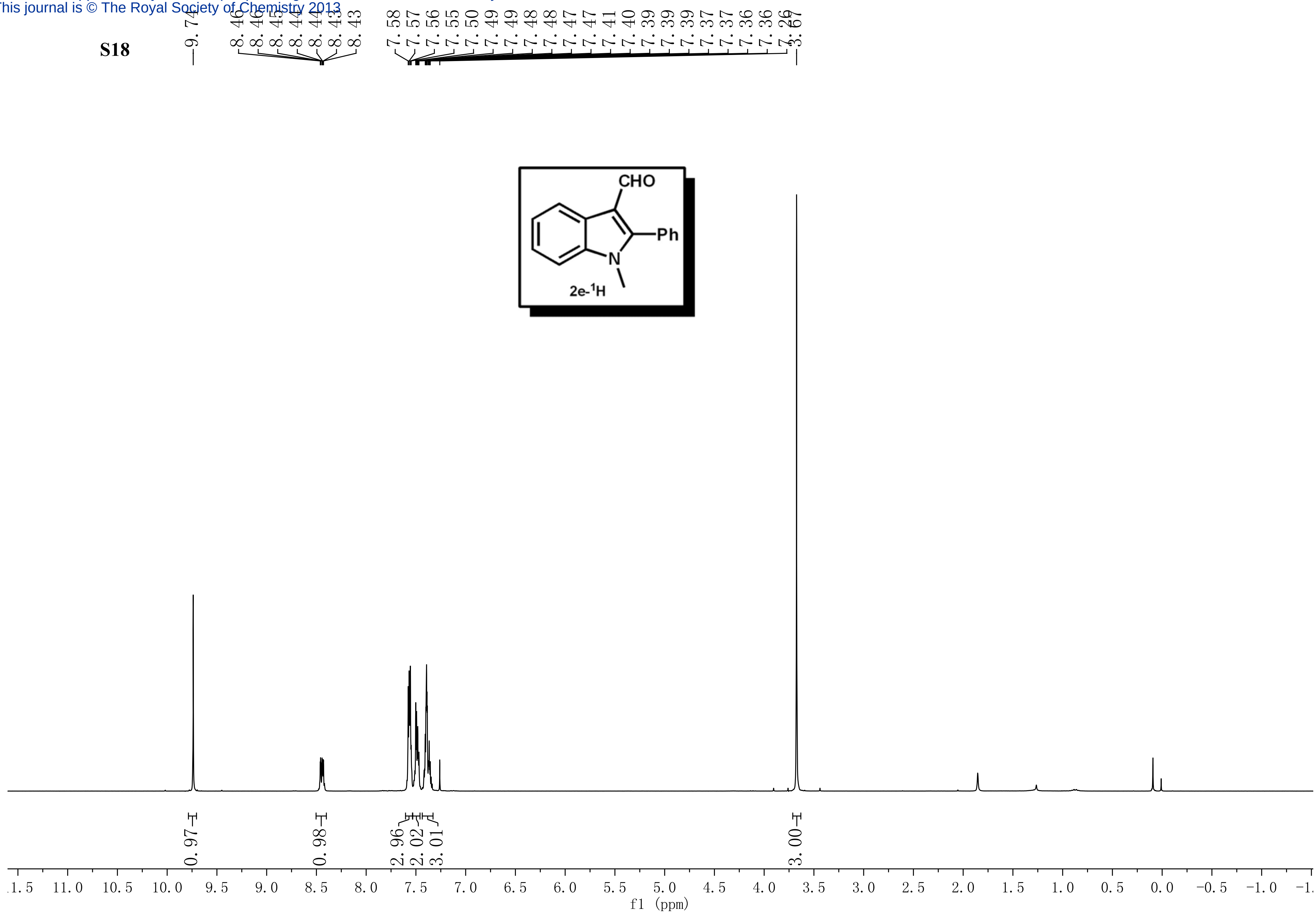

9.89
7.77
7.76
7.56
7.26
7.22
7.19
6.97
6.96
6.94
6.93
3.88
3.79
CHO
MeO
N
2c-1H
0.97
0.98
0.99
1.01
1.00
3.00
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


184.31
156.57
139.36
132.69
125.85
117.63
114.32
110.65
103.15
77.42
77.00
76.58
55.71
33.75
CHO
MeO
N
2c-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

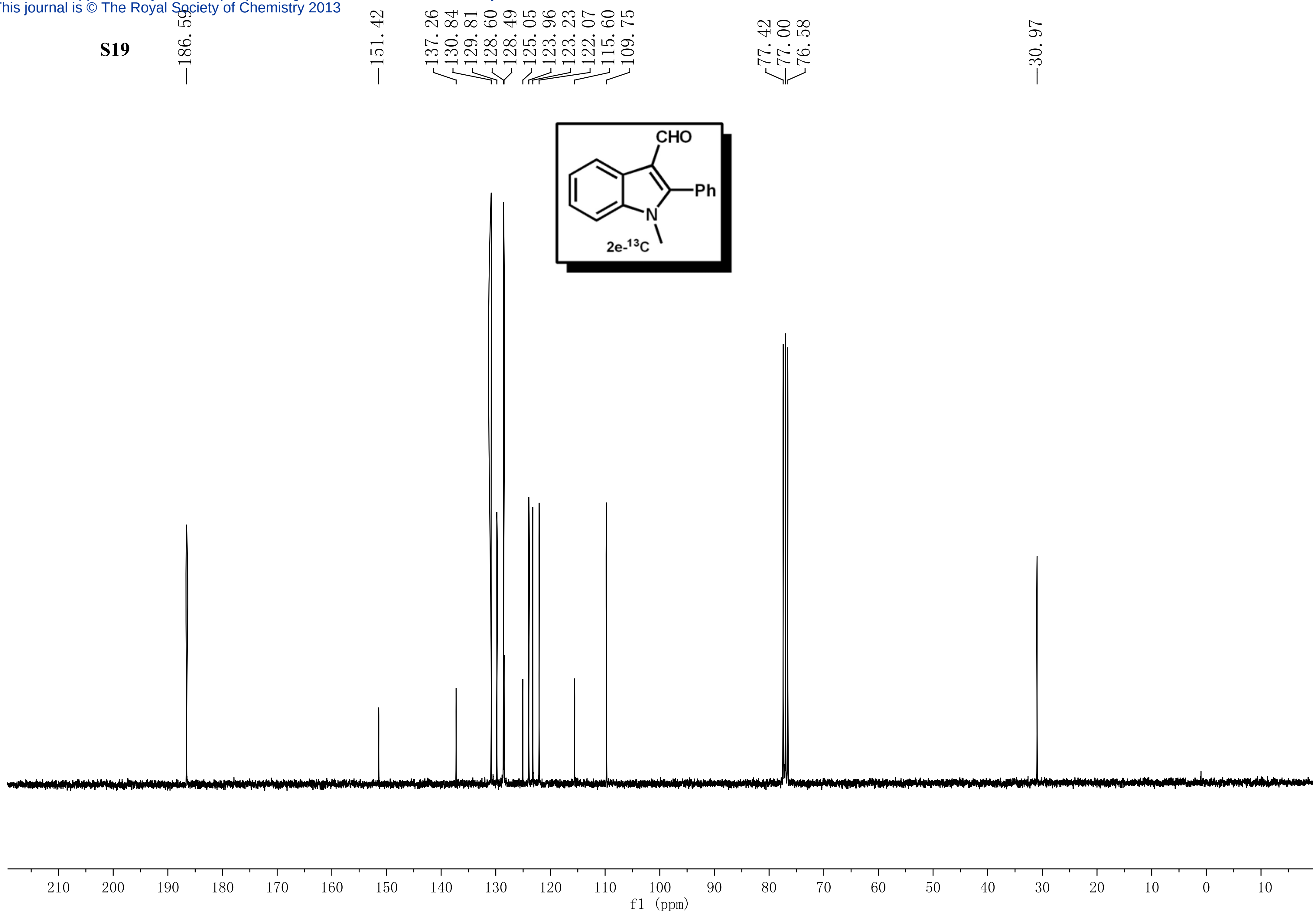

S16
9.86
8.16
8.13
7.40
7.26
7.17
7.14
7.12
7.00
6.97
3.97
2.67
CHO
N
2d-¹H
0.97
0.98
1.00
1.00
1.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

S17


184.18
140.92
136.34
126.51
126.11
122.88
121.75
119.74
117.19
77.42
77.00
76.58
37.66
19.25
CHO
N
2d-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

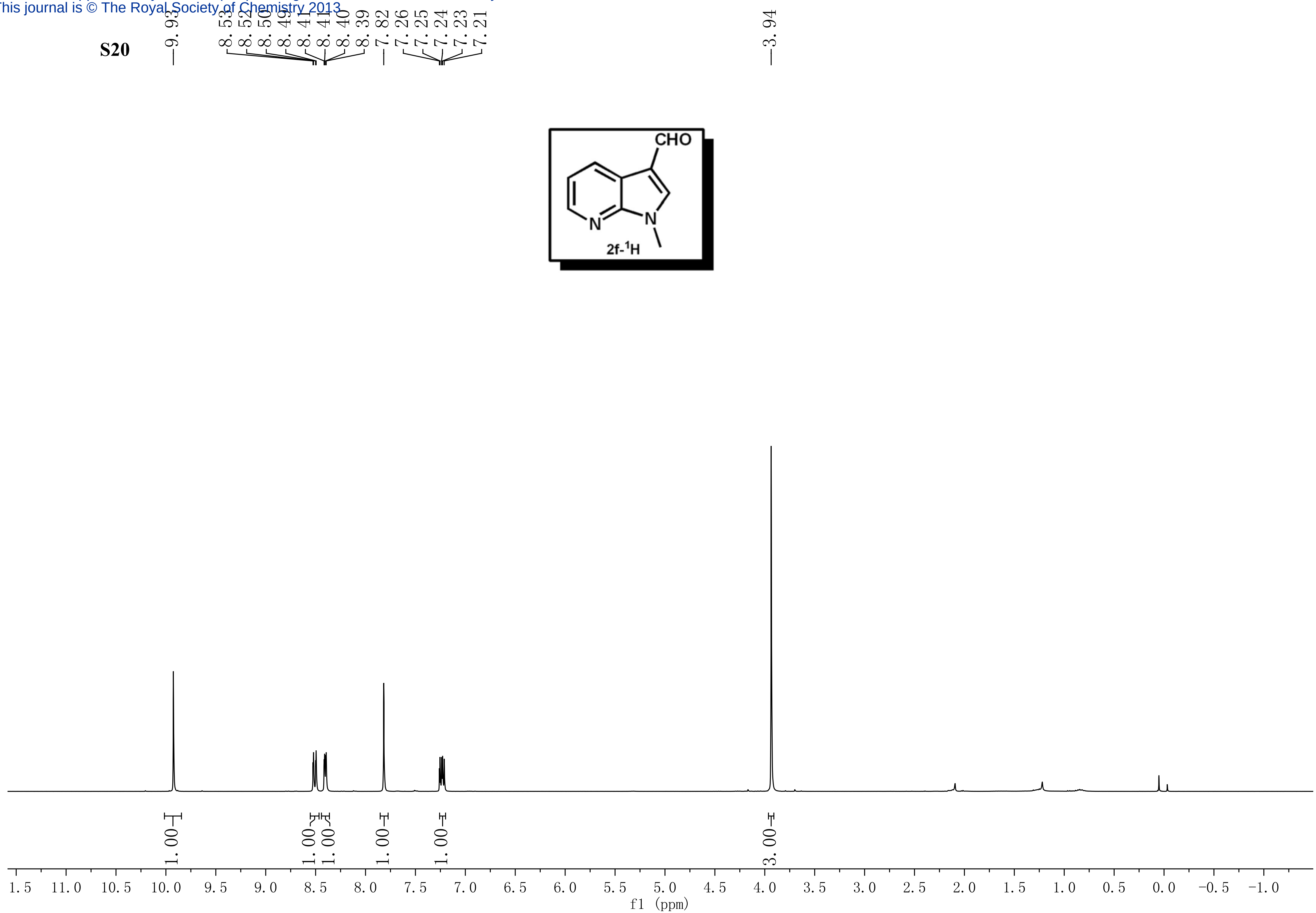

9.74
8.46
8.46
8.45
8.44
8.44
8.43
8.43
7.58
7.57
7.56
7.55
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.41
7.40
7.39
7.39
7.39
7.37
7.37
7.36
7.36
7.26
3.67
CHO
Ph
N
2e-1H
0.97
0.98
2.96
2.02
3.01
3.00
f1 (ppm)

S19

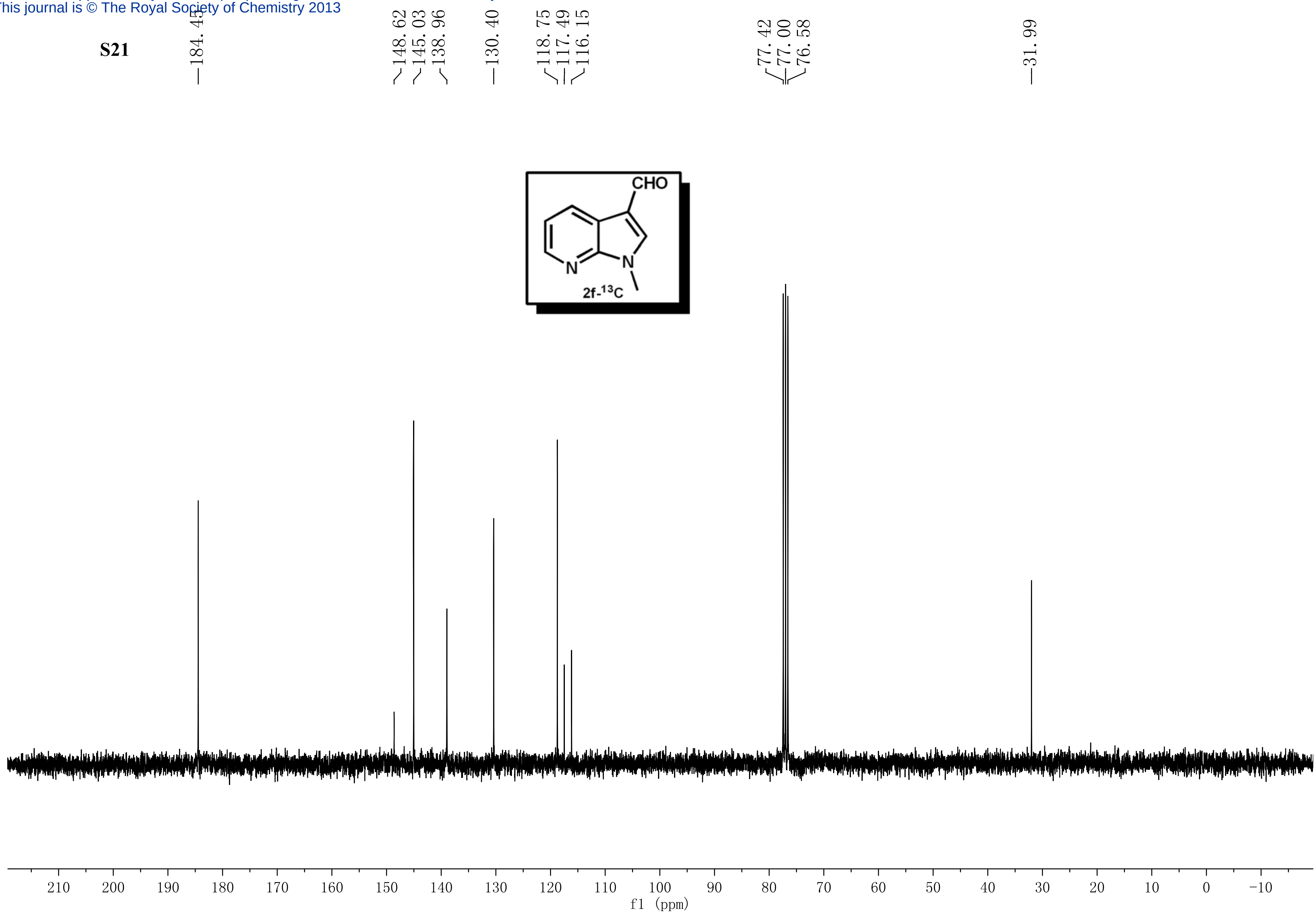

186.59
151.42
137.26
130.84
129.81
128.60
128.49
125.05
123.96
123.23
122.07
115.60
109.75
77.42
77.00
76.58
30.97
CHO
Ph
N
2e-^{13}C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

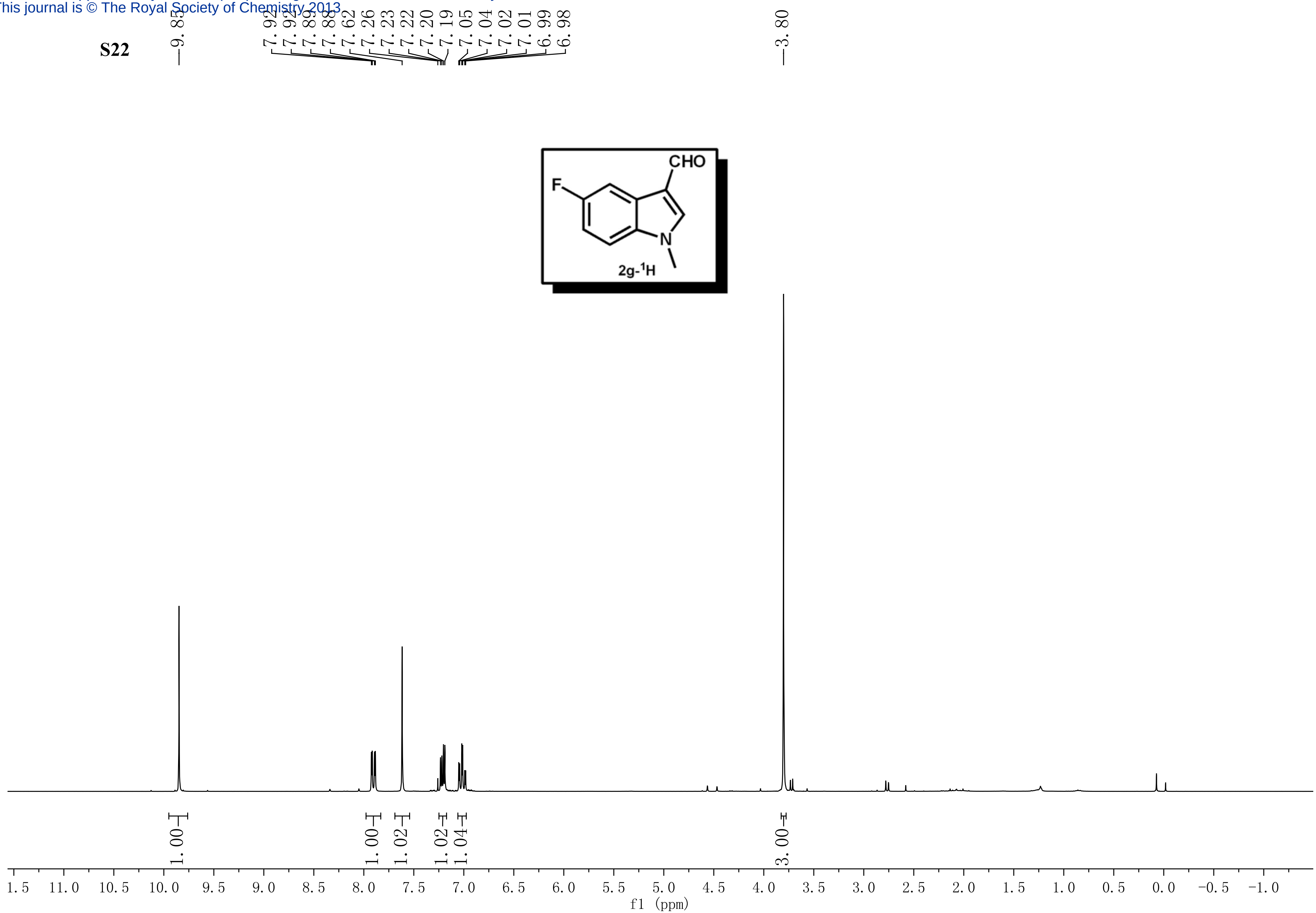
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

S20

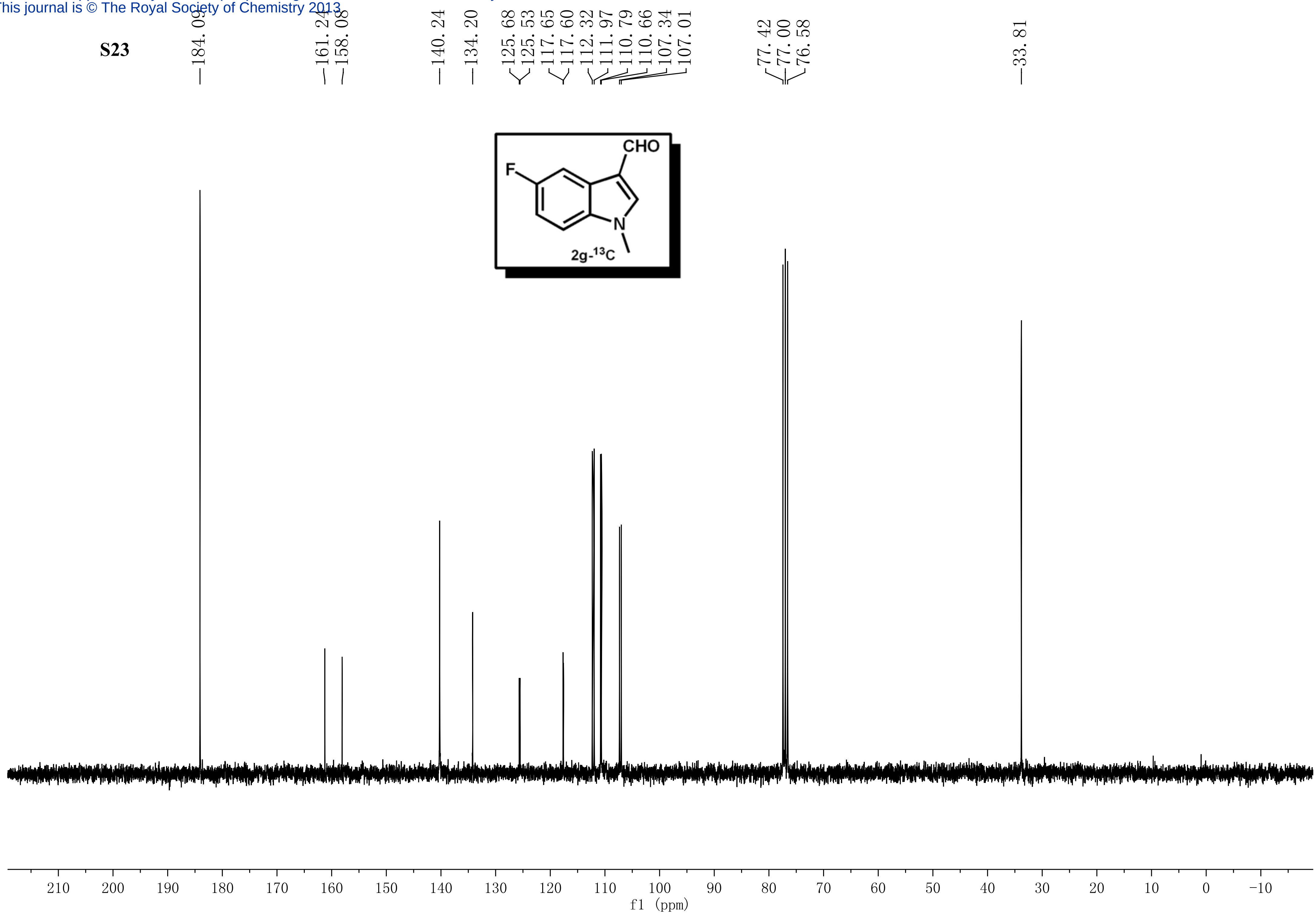


S21

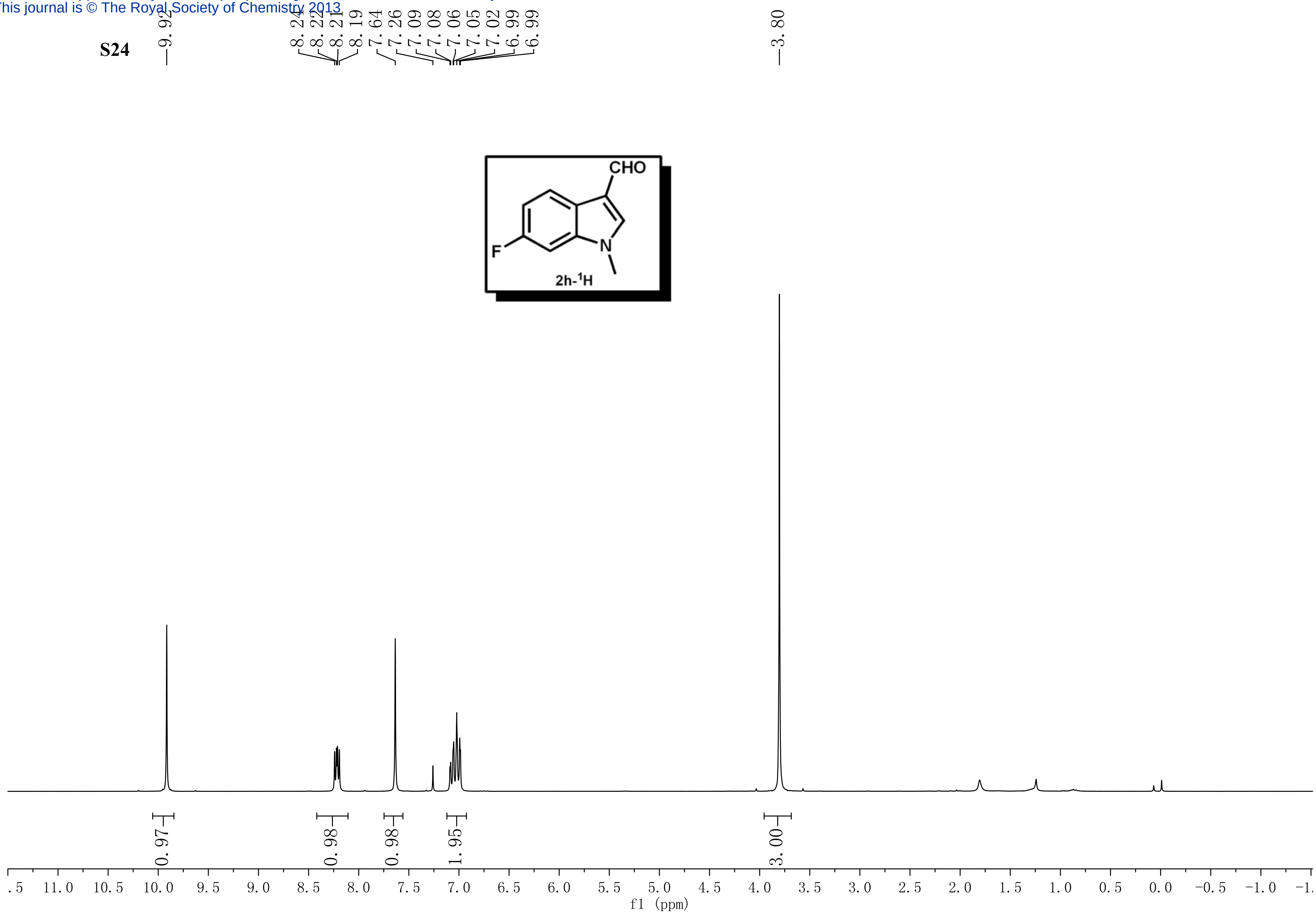

184.45
148.62
145.03
138.96
130.40
118.75
117.49
116.15
77.42
77.00
76.58
31.99
CHO
N
N
2f-13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.85
7.92
7.92
7.89
7.88
7.62
7.26
7.23
7.22
7.20
7.19
7.05
7.04
7.02
7.01
6.99
6.98
3.80
CHO
F
N
2g-1H
1.00
1.00
1.02
1.02
1.04
3.00
f1 (ppm)

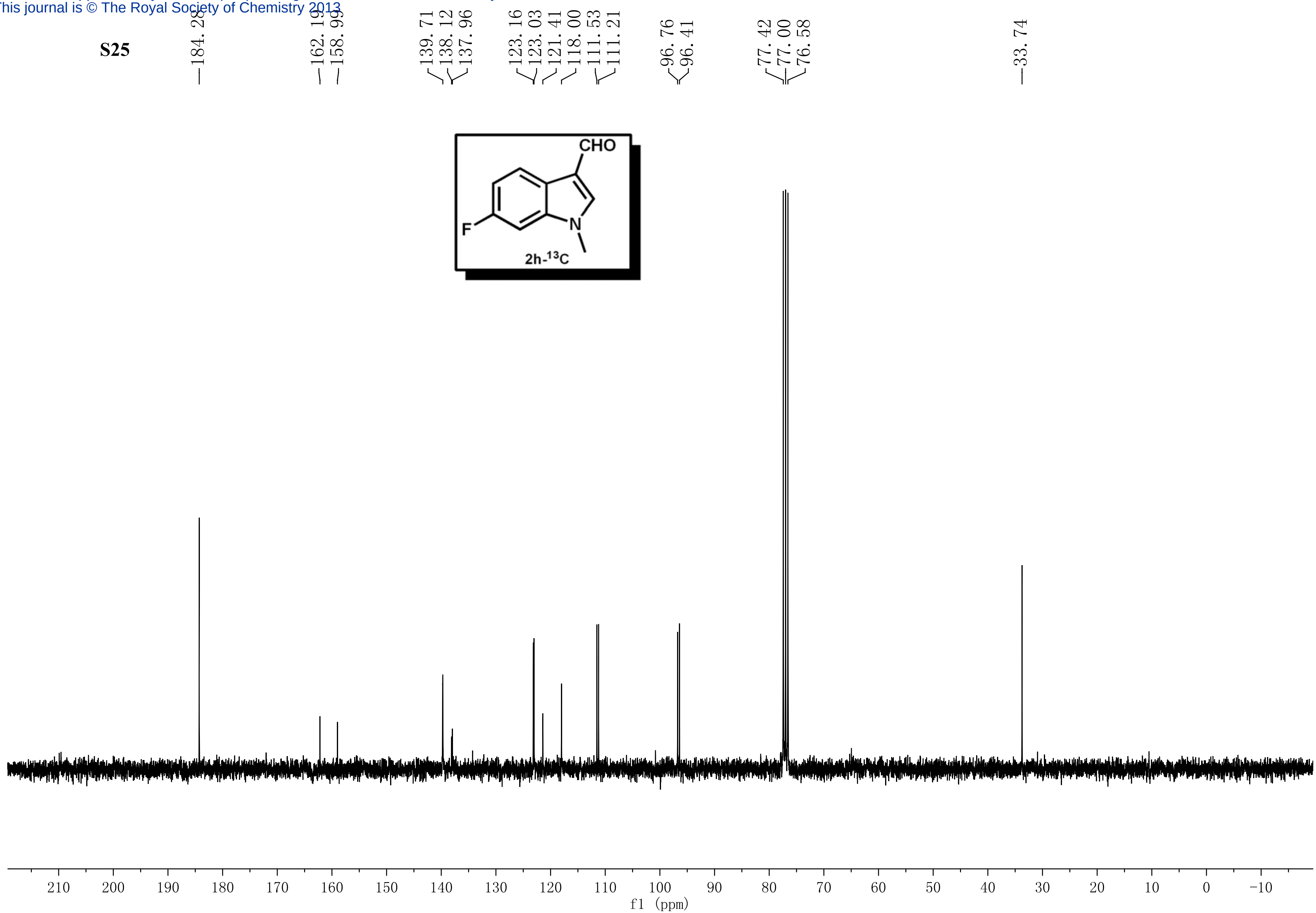
S23


184.09
161.24
158.08
140.24
134.20
125.68
125.53
117.65
117.60
112.32
111.97
110.79
110.66
107.34
107.01
77.42
77.00
76.58
33.81
CHO
F
N
2g-^{13}C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

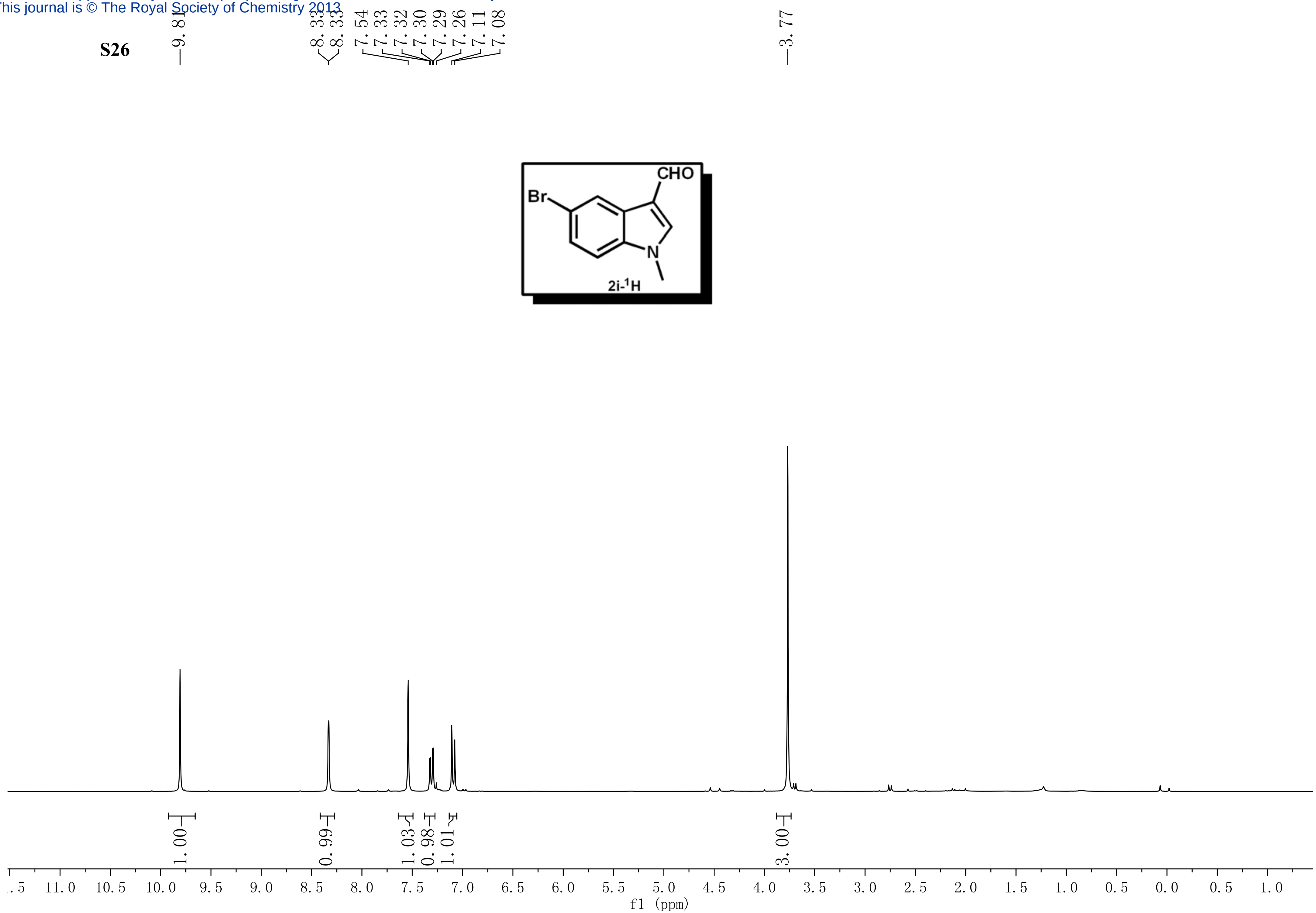
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



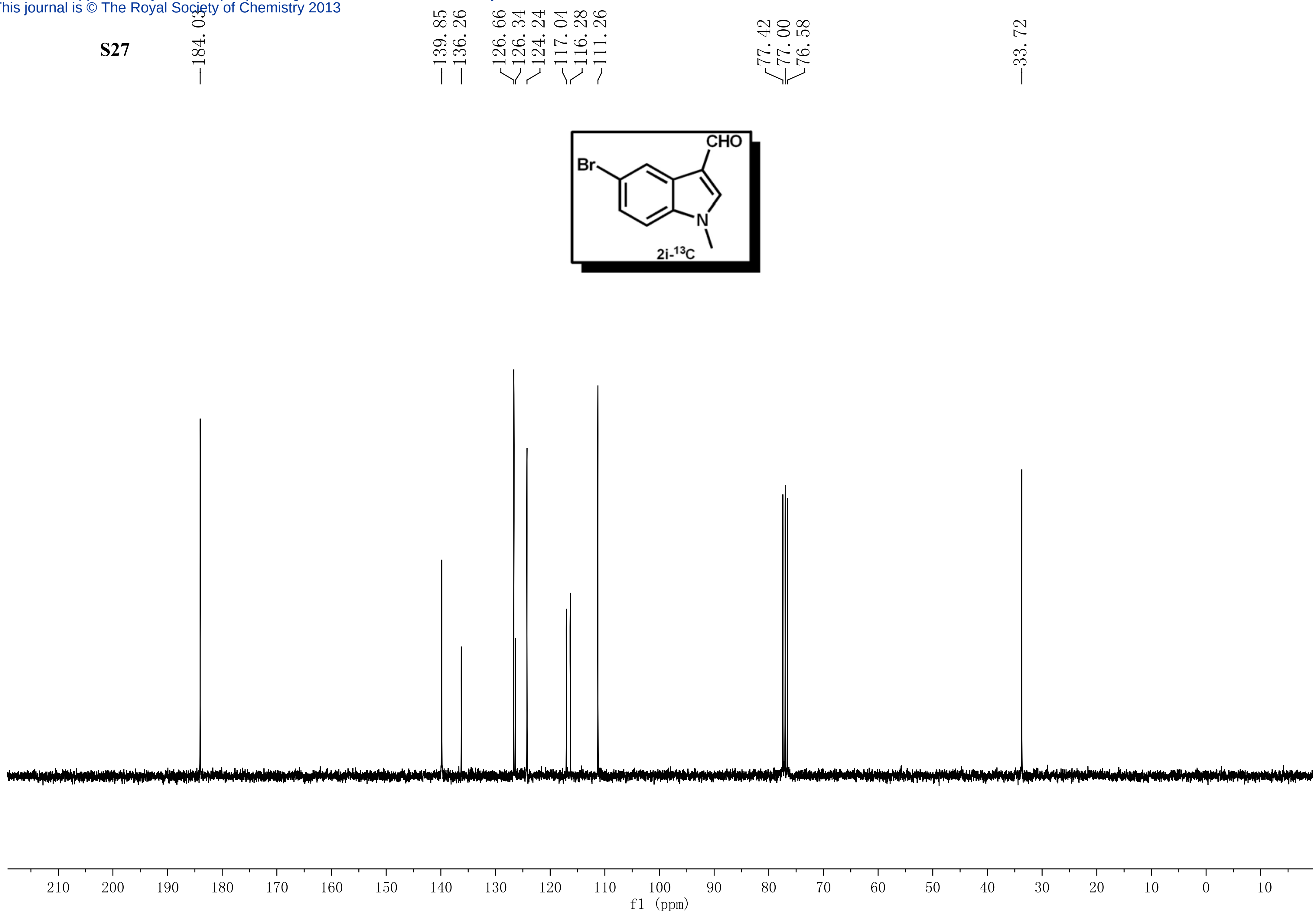
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

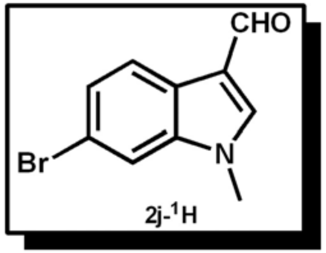


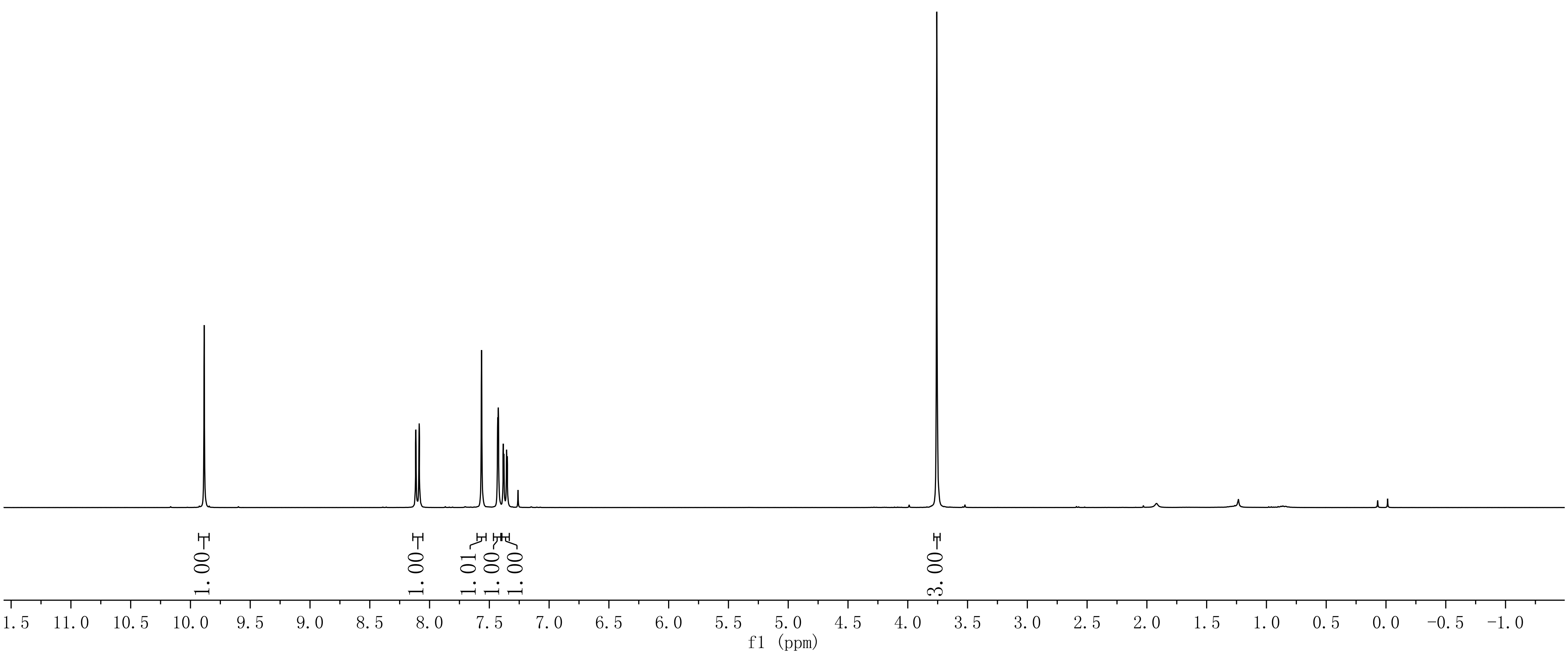
S26


9.81
8.33
8.33
7.54
7.33
7.32
7.30
7.29
7.26
7.11
7.08
3.77
CHO
Br
N
2i-1H
1.00
0.99
1.03
0.98
1.01
3.00
.5 11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)

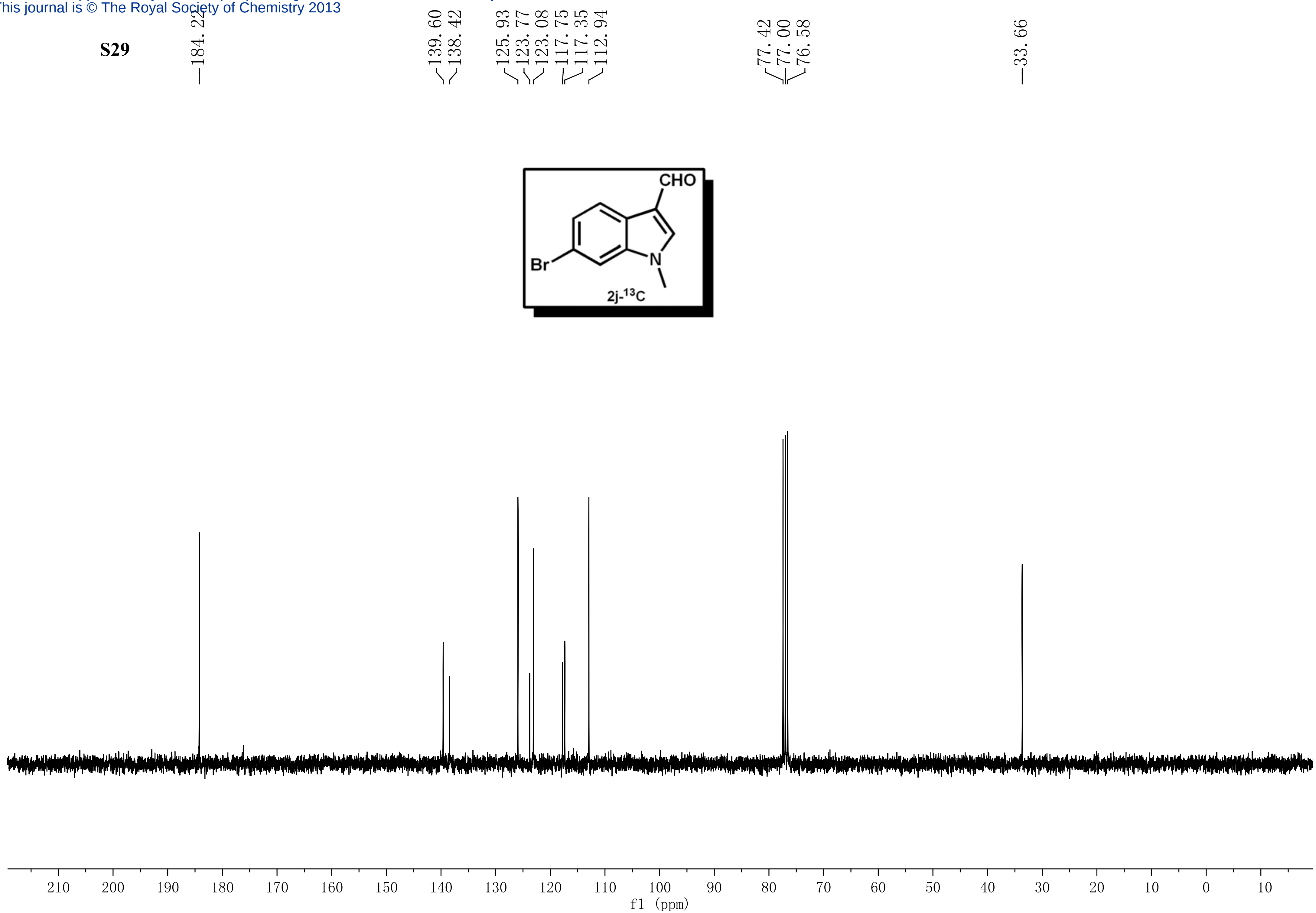
S27

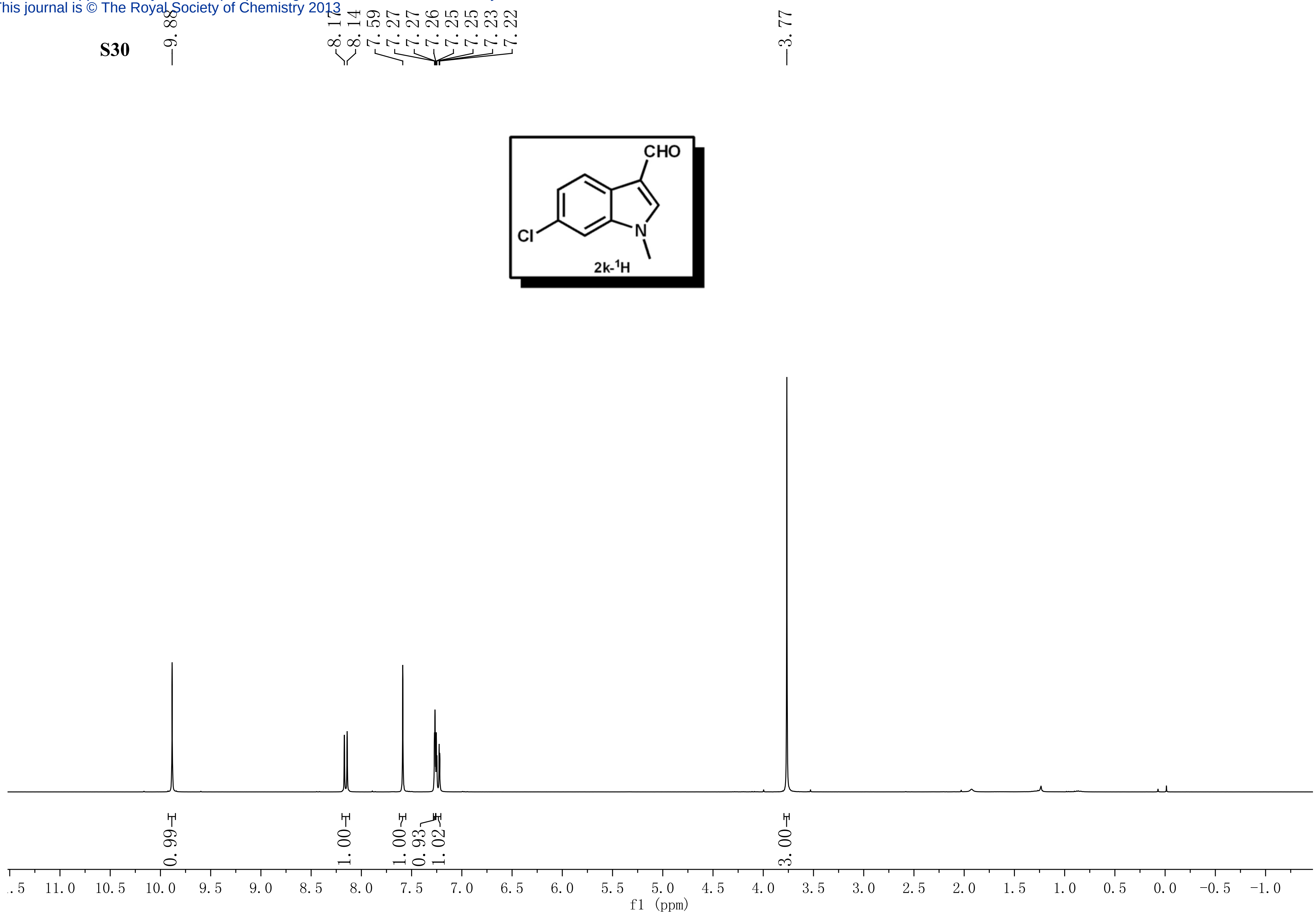

184.03
139.85
136.26
126.66
126.34
124.24
117.04
116.28
111.26
77.42
77.00
76.58
33.72
CHO
Br
N
2i-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

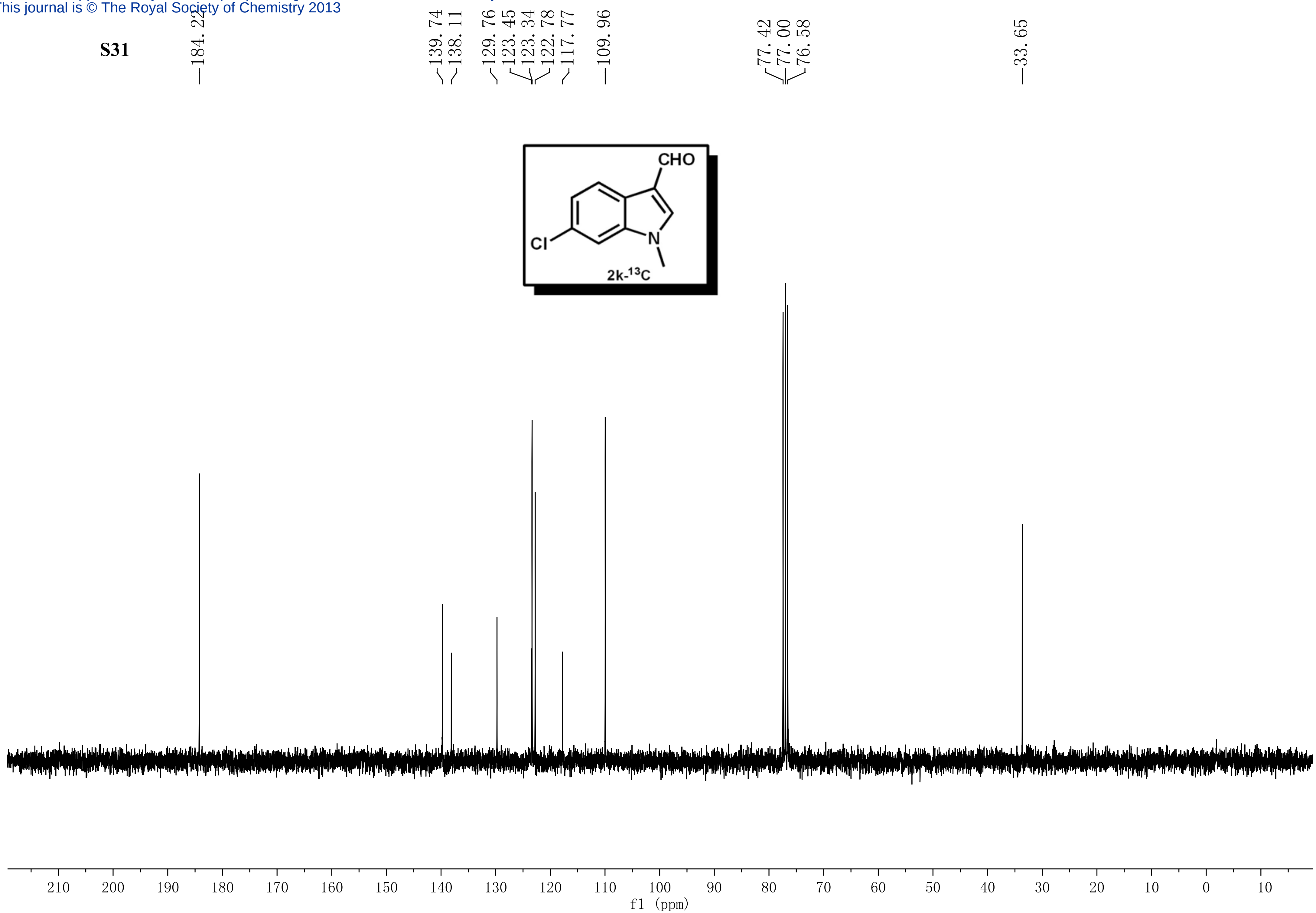

CHO
Br
N
2j-¹H


9.89
8.11
8.09
7.57
7.43
7.43
7.38
7.38
7.36
7.35
7.26
3.76
1.00
1.00
1.01
1.00
1.00
3.00
1.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

S29

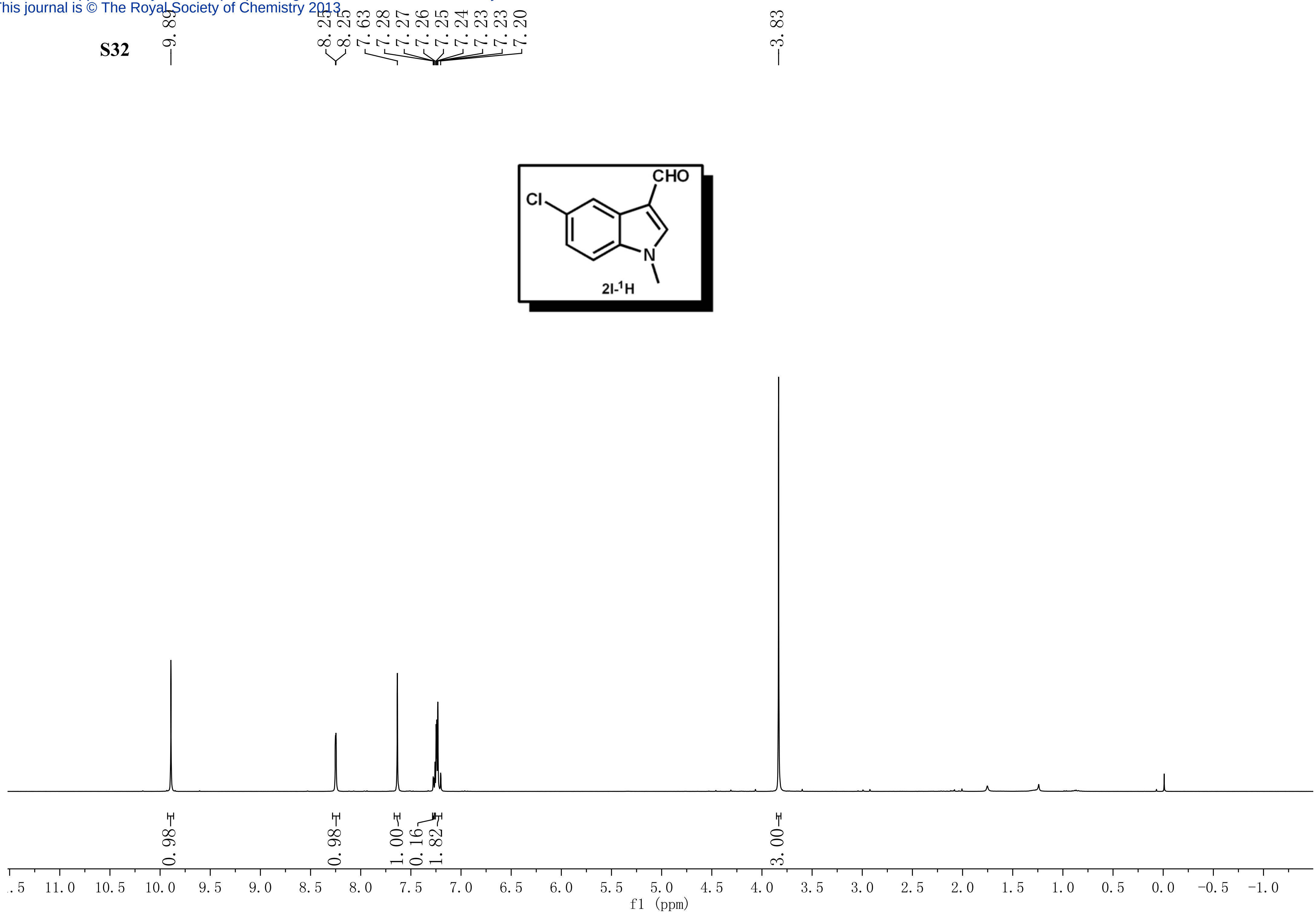

184.22
139.60
138.42
125.93
123.77
123.08
117.75
117.35
112.94
77.42
77.00
76.58
33.66
CHO
Br
N
2j-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


9.88
8.17
8.14
7.59
7.27
7.27
7.26
7.25
7.25
7.23
7.22
3.77
CHO
Cl
N
2k-1H
0.99
1.00
1.00
0.93
1.02
3.00
.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

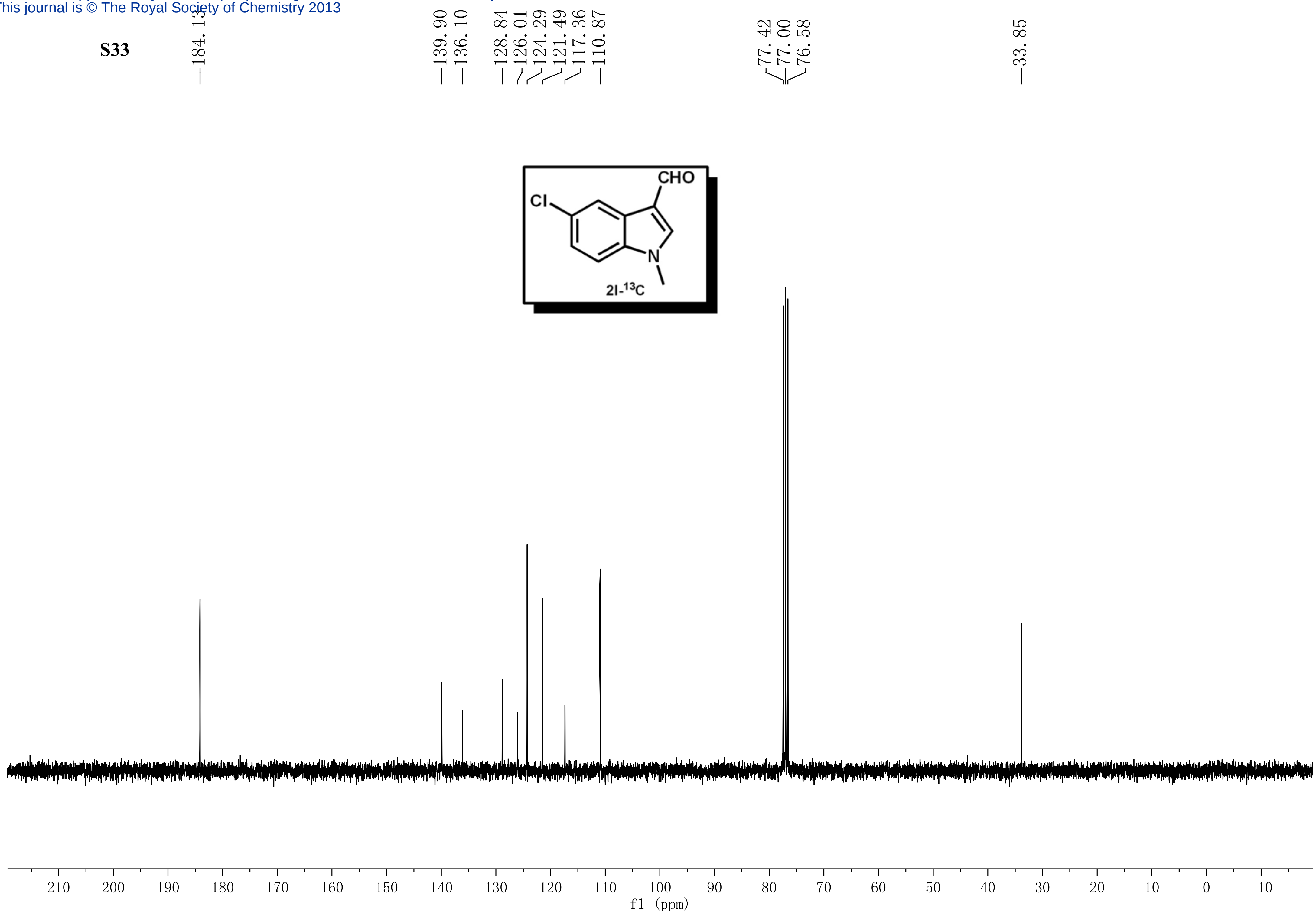


184.22
139.74
138.11
129.76
123.45
123.34
122.78
117.77
109.96
77.42
77.00
76.58
33.65
CHO
Cl
N
2k-13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

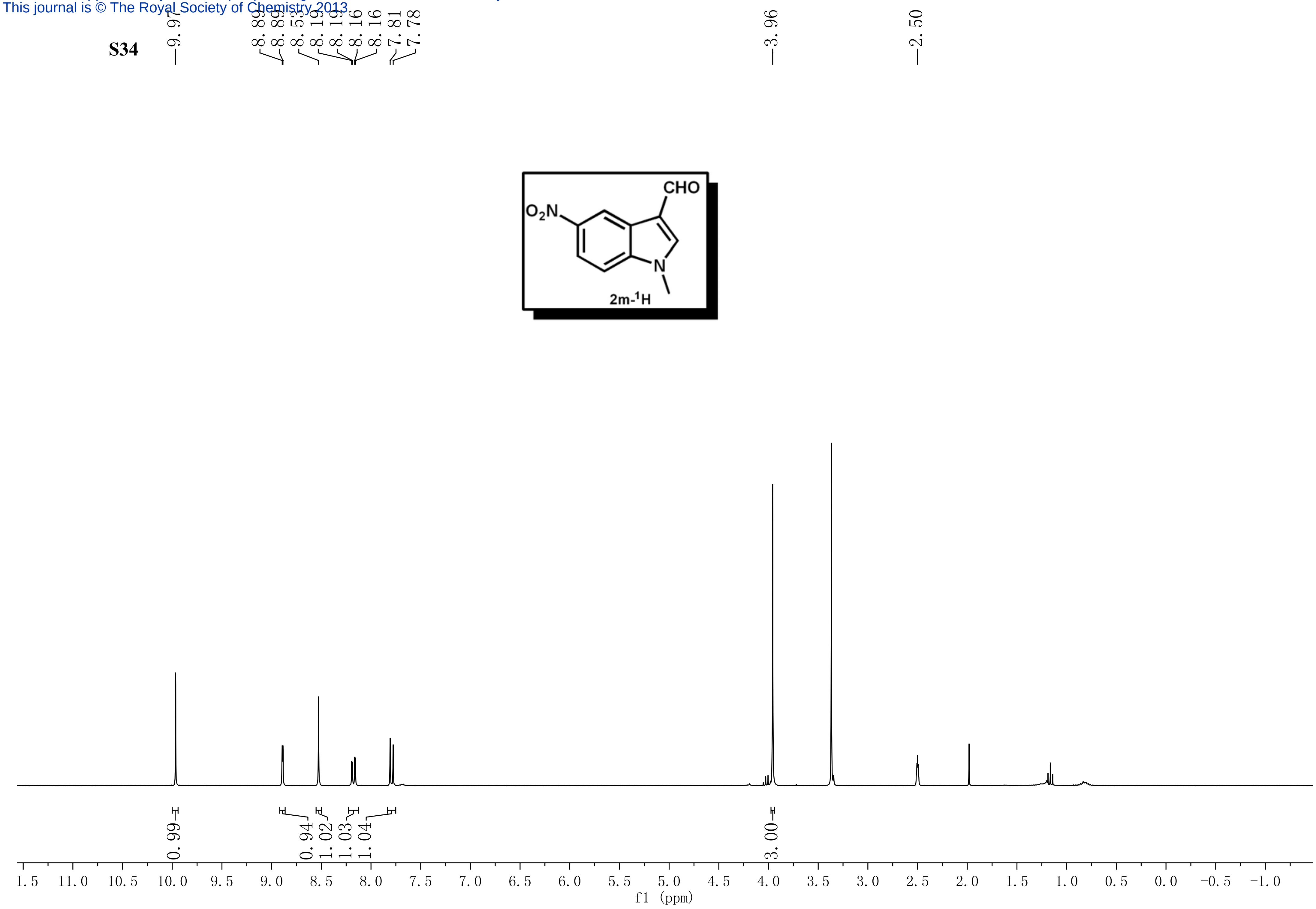
S32


9.89
8.25
8.25
7.63
7.28
7.27
7.26
7.25
7.24
7.23
7.23
7.20
3.83
CHO
Cl
N
2l-1H
0.98
0.98
1.00
0.16
1.82
3.00
.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

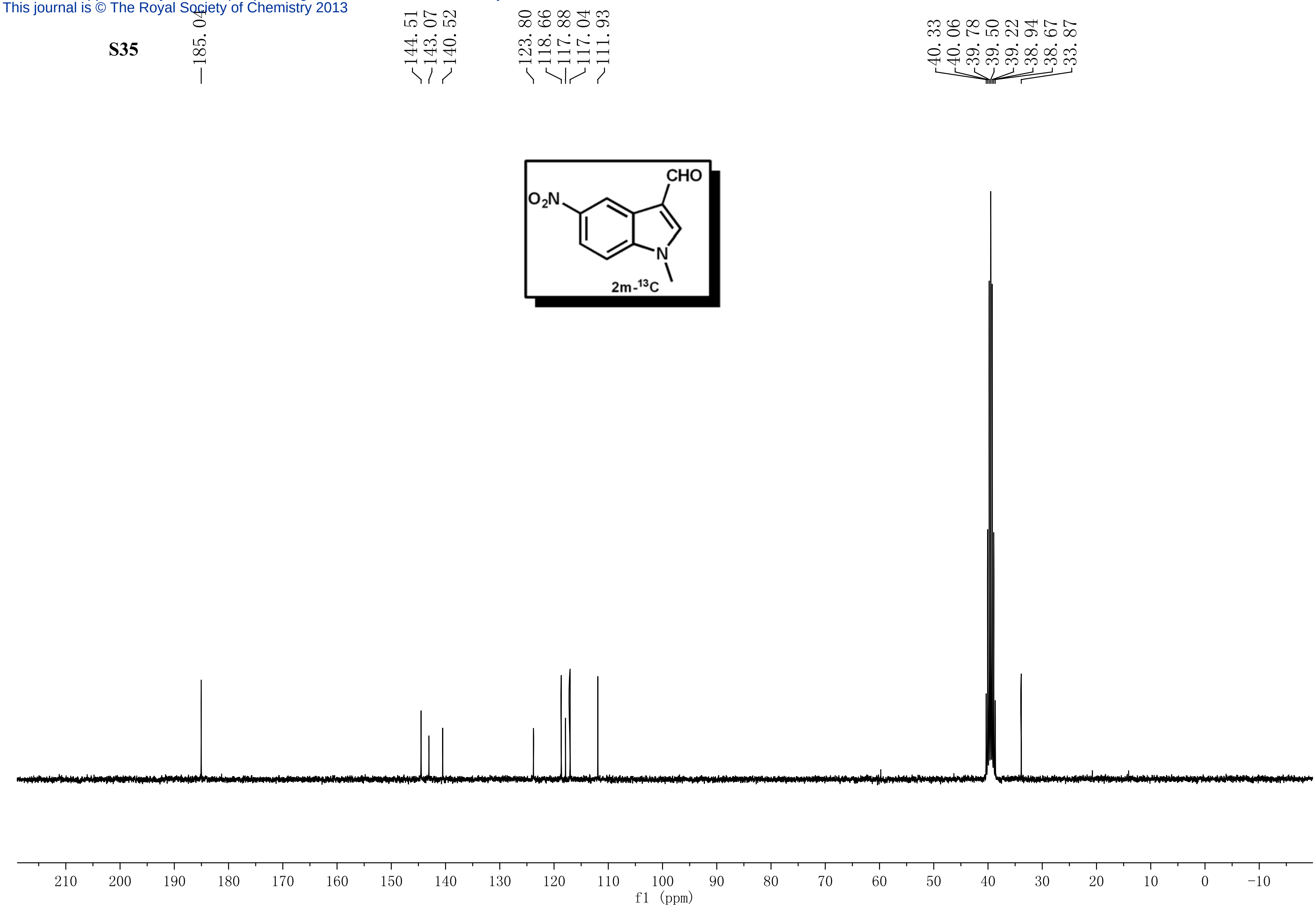
S33


184.13
139.90
136.10
128.84
126.01
124.29
121.49
117.36
110.87
77.42
77.00
76.58
33.85
CHO
Cl
N
2l-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

S34

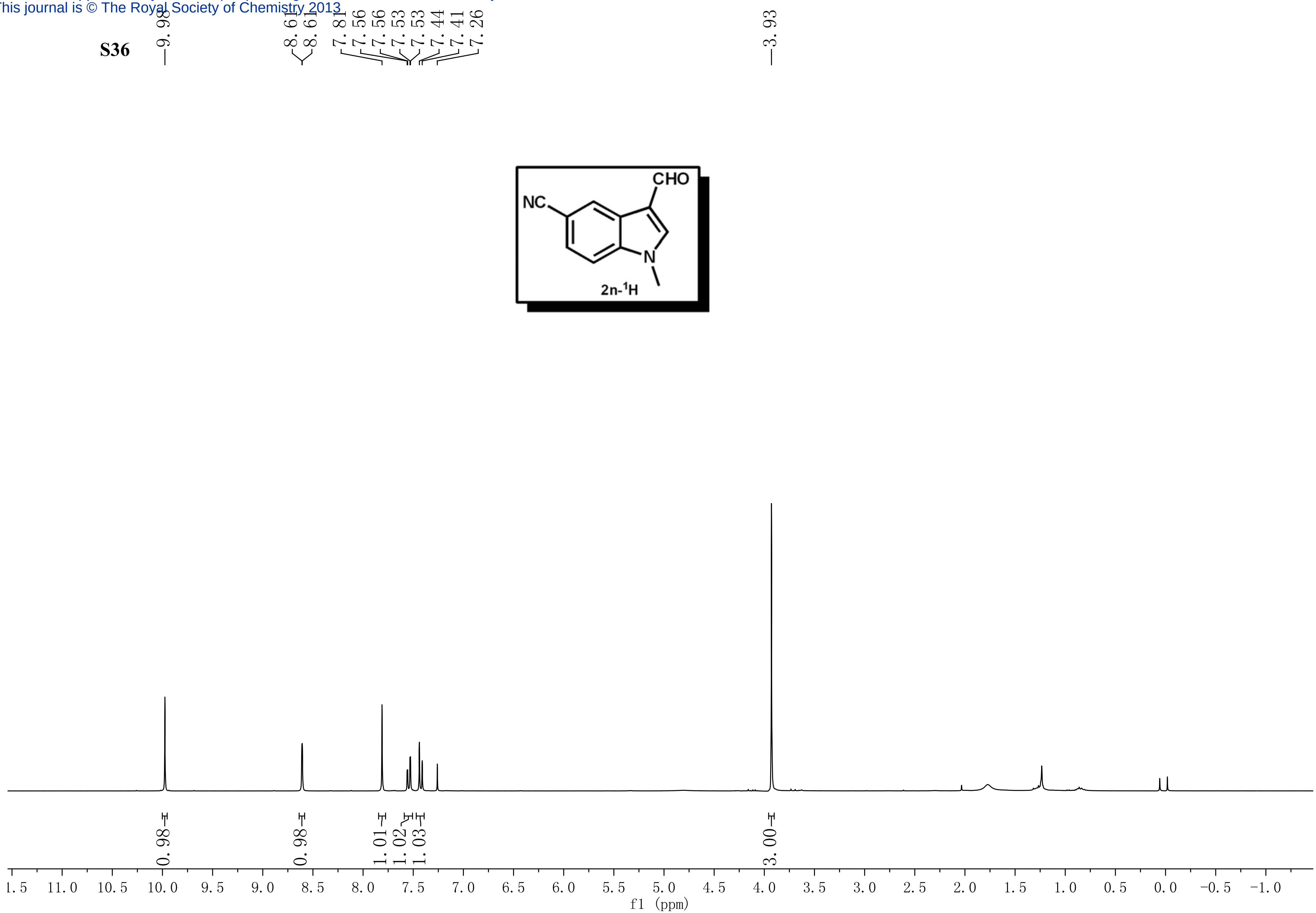

9.97
8.89
8.89
8.53
8.19
8.19
8.16
8.16
7.81
7.78
3.96
2.50
CHO
O2N
N
2m-1H
0.99
0.94
1.02
1.03
1.04
3.00
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

S35

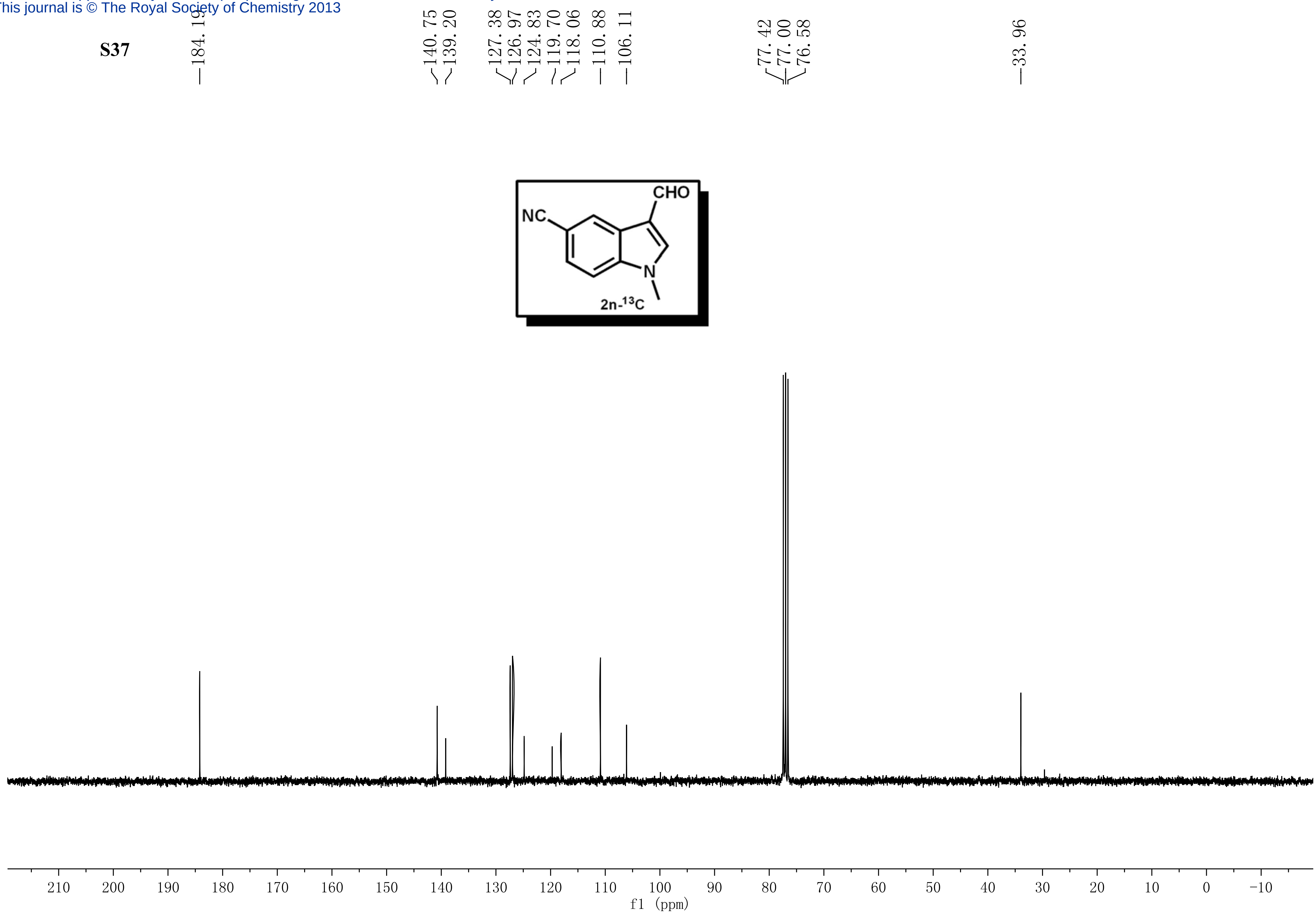


185.04
144.51
143.07
140.52
123.80
118.66
117.88
117.04
111.93
40.33
40.06
39.78
39.50
39.22
38.94
38.67
33.87
CHO
O_2N
N
2m-^{13}C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

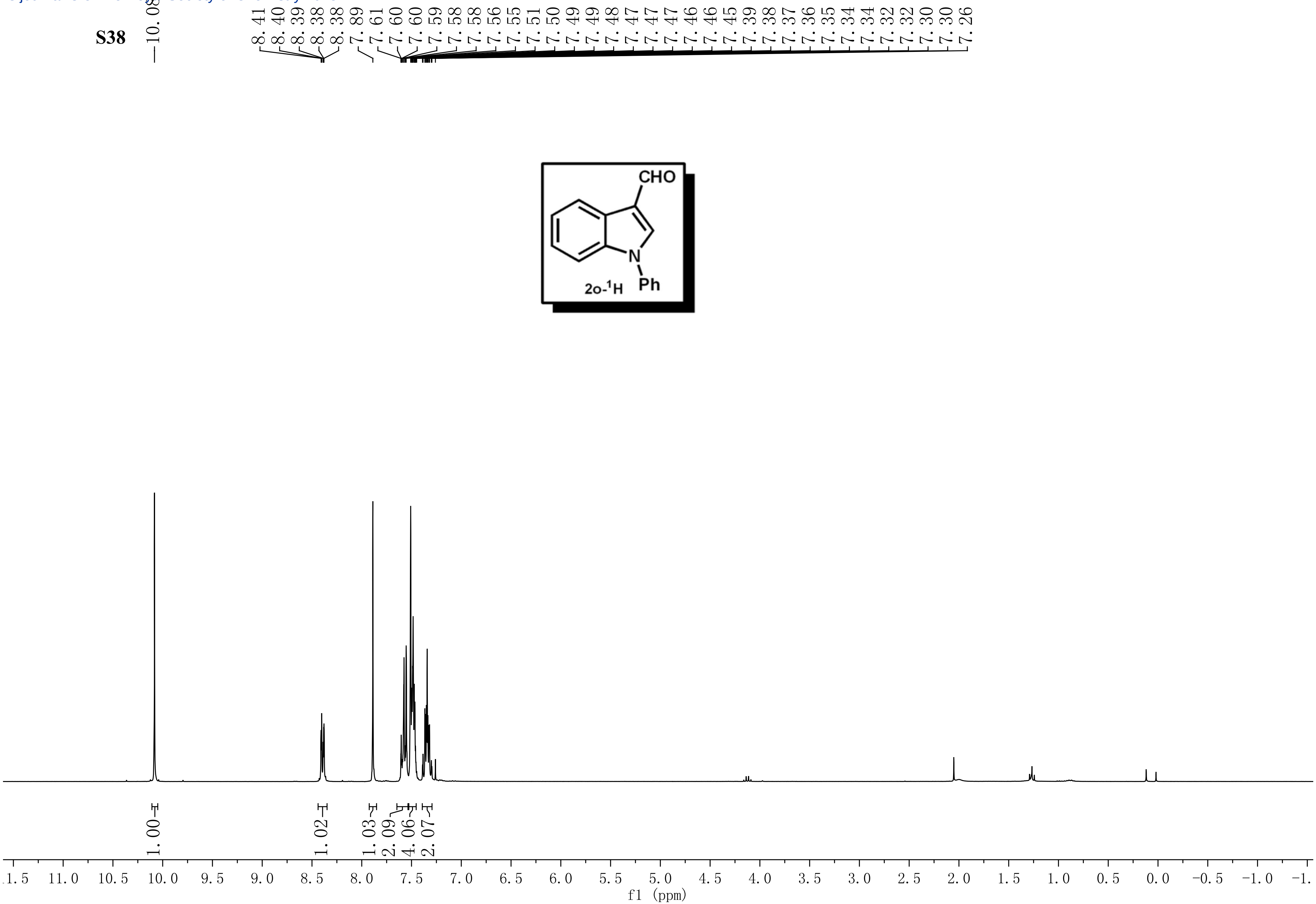
S36


9.98
8.61
8.61
7.81
7.56
7.56
7.53
7.53
7.44
7.41
7.26
3.93
CHO
NC
N
2n-1H
0.98
0.98
1.01
1.02
1.03
3.00
1.5 11.0 10.5 10.0 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 −0.5 −1.0
f1 (ppm)

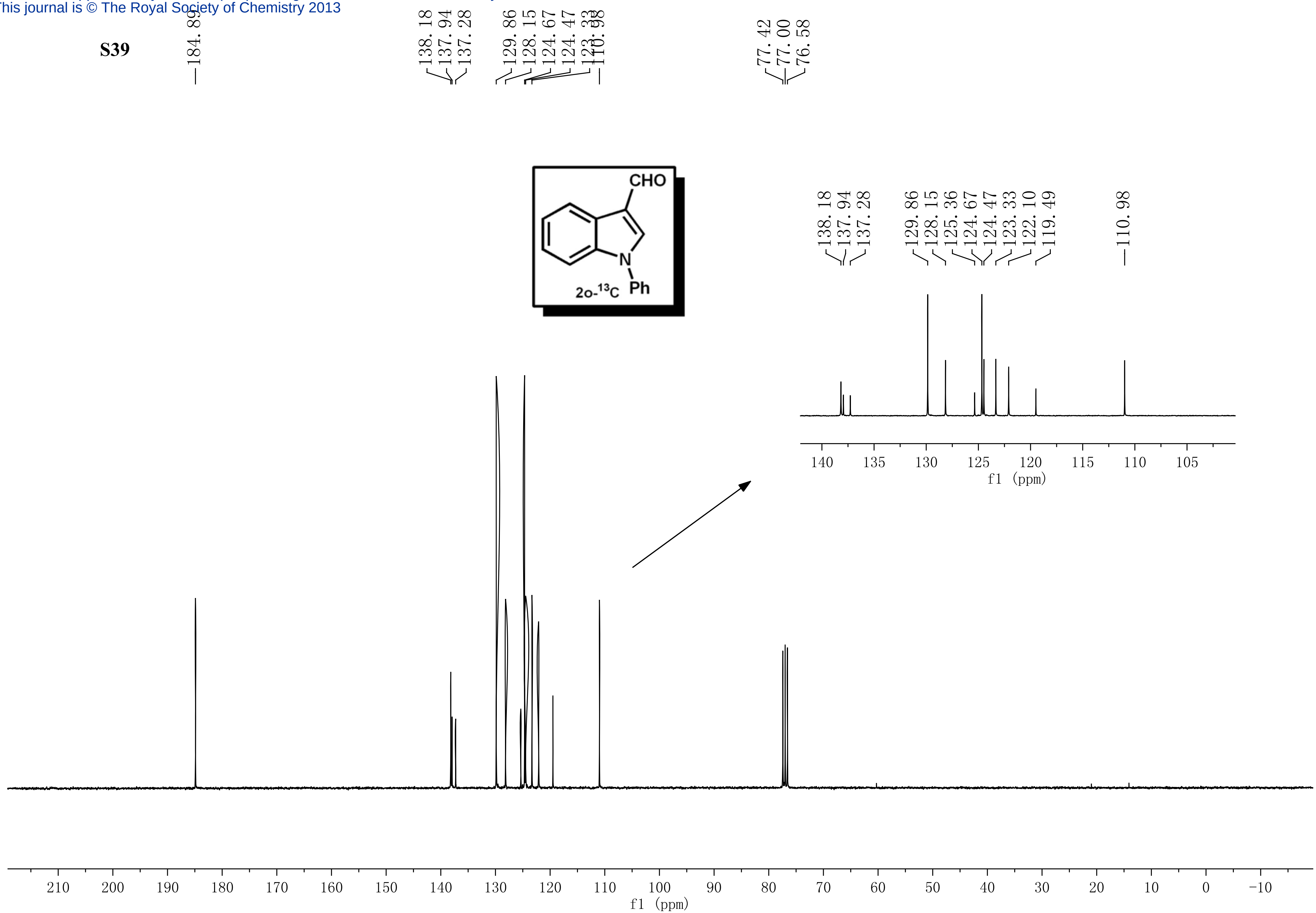
S37


184.19
140.75
139.20
127.38
126.97
124.83
119.70
118.06
110.88
106.11
77.42
77.00
76.58
33.96
CHO
NC
N
2n-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

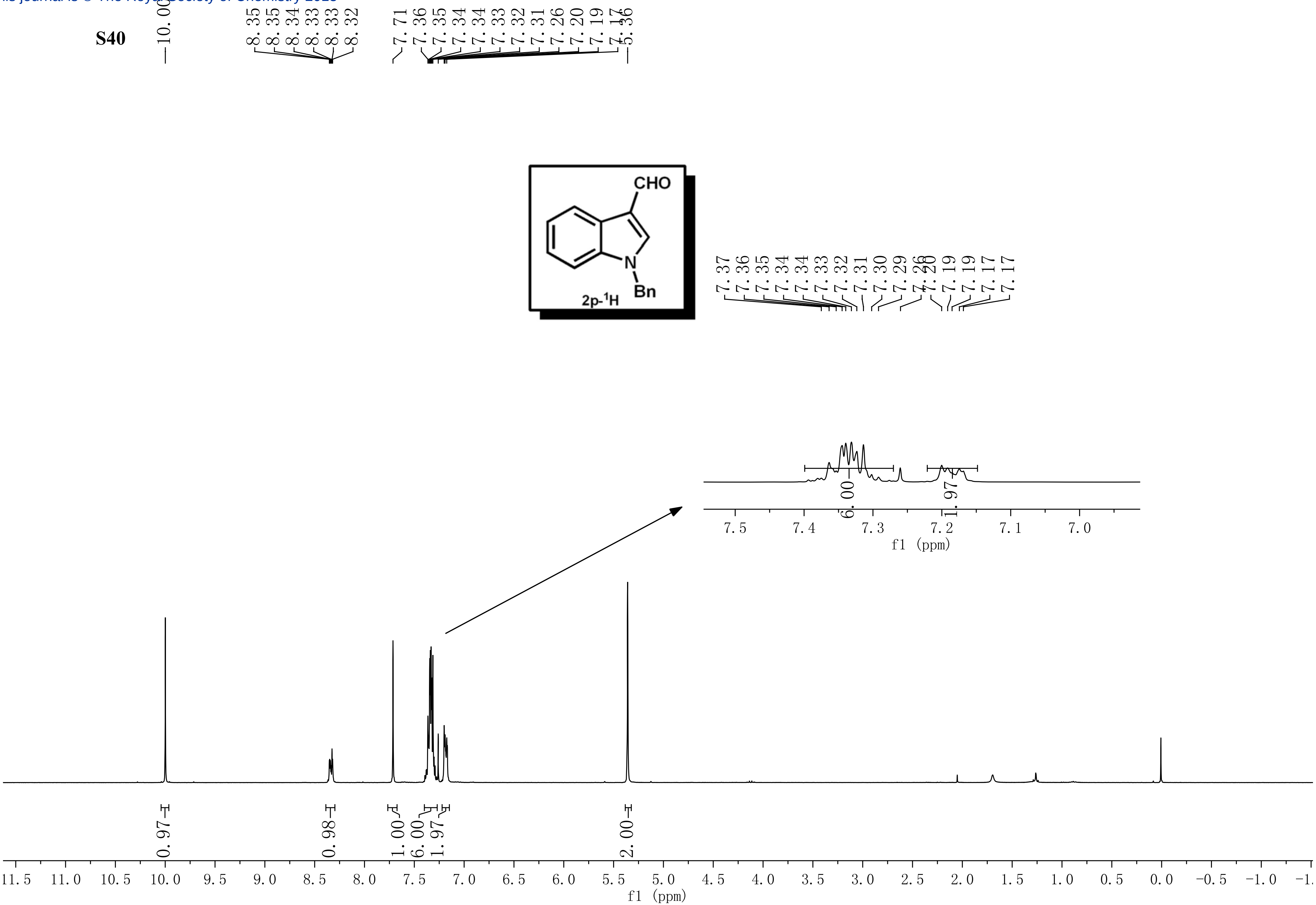
S38


10.08
8.41
8.40
8.39
8.38
8.38
7.89
7.61
7.60
7.60
7.59
7.58
7.58
7.56
7.55
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.30
7.30
7.26
CHO
N
Ph
2o-1H
1.00
1.02
1.03
2.09
4.06
2.07
f1 (ppm)

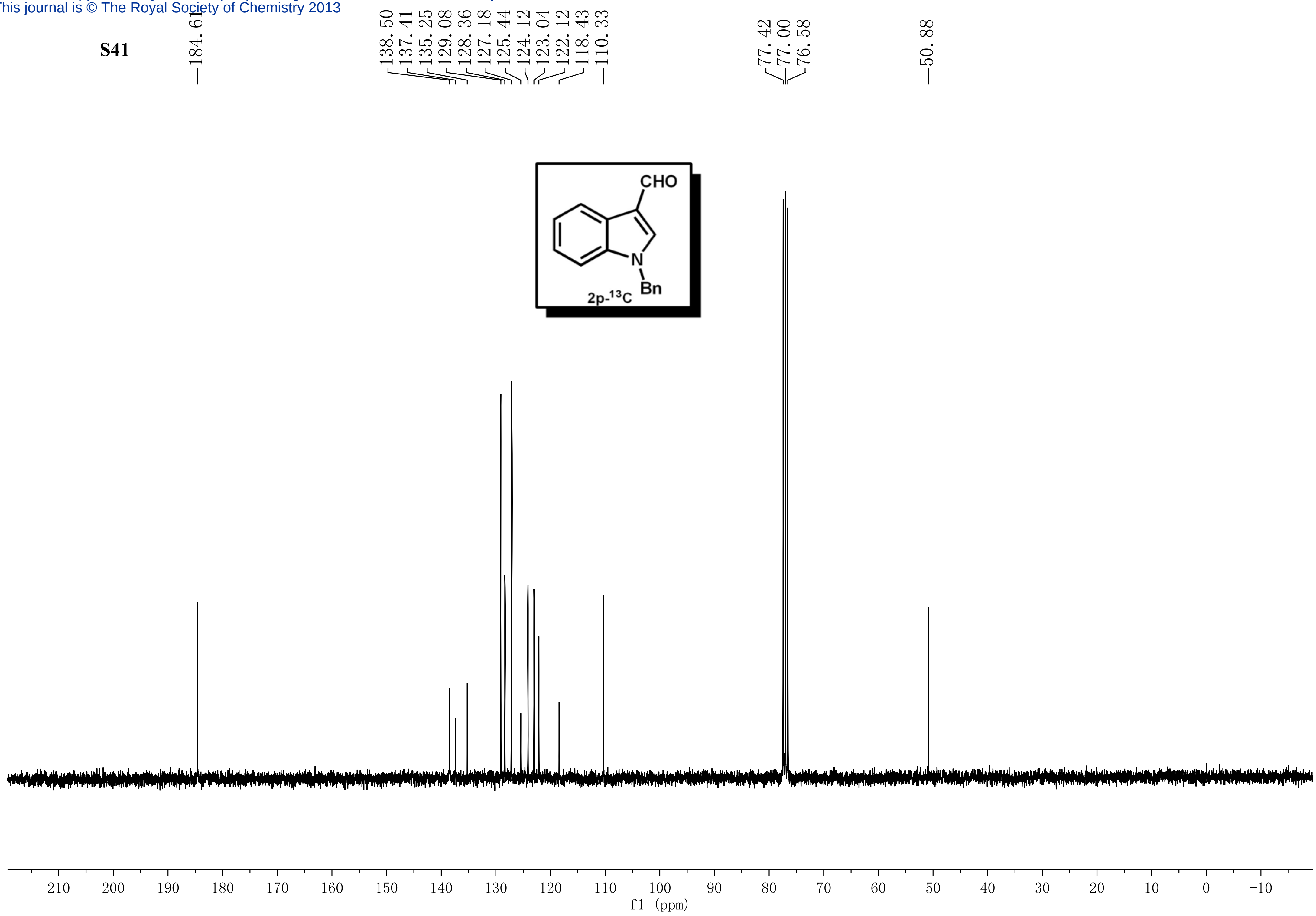
S39


184.89
138.18
137.94
137.28
129.86
128.15
124.67
124.47
123.33
110.98
77.42
77.00
76.58
CHO
N
Ph
2o-^{13}C
138.18
137.94
137.28
129.86
128.15
125.36
124.67
124.47
123.33
122.10
119.49
110.98
140 135 130 125 120 115 110 105
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

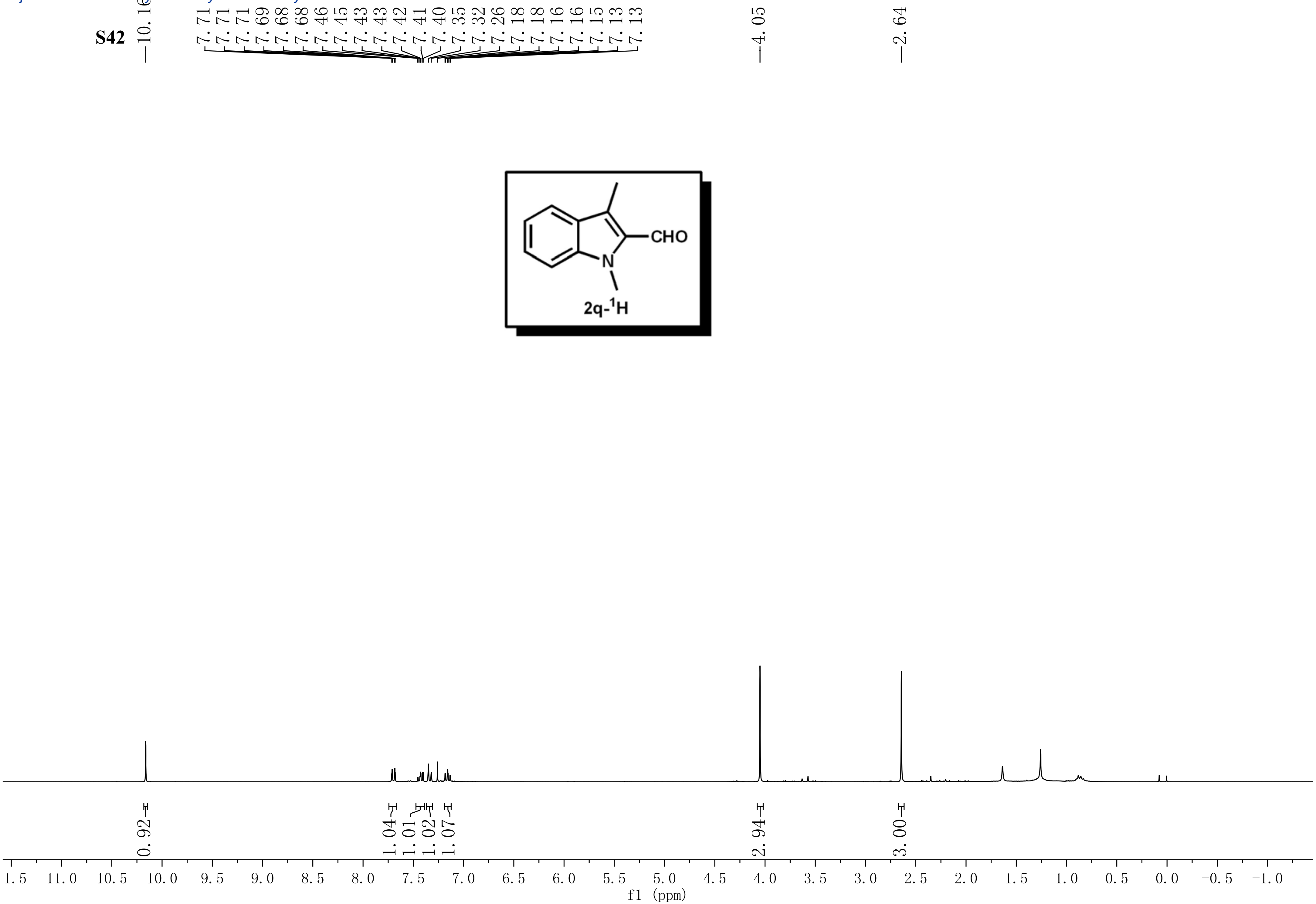
S40



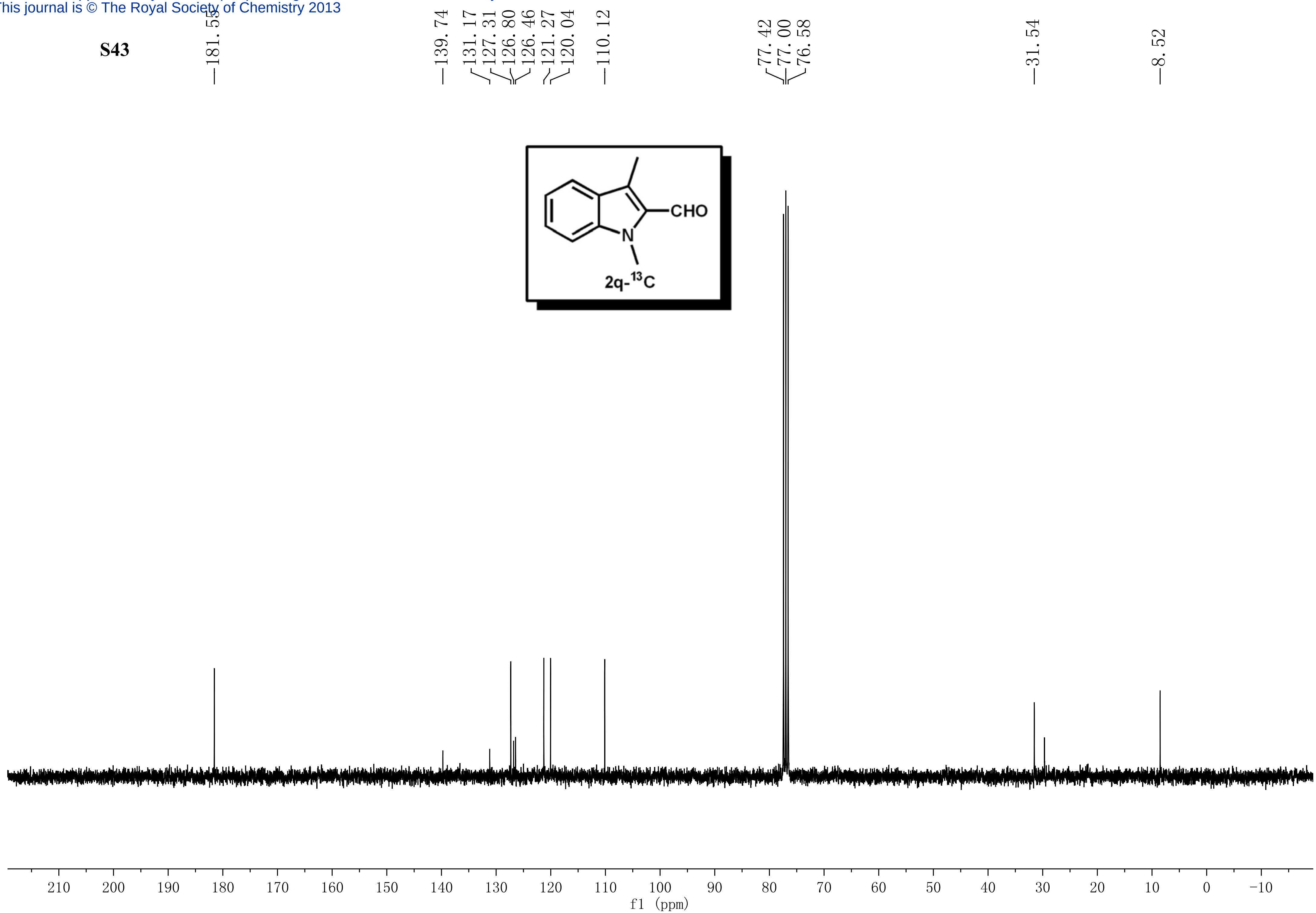
10.00
8.35
8.35
8.34
8.33
8.33
8.32
7.71
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.26
7.20
7.19
7.17
5.36
CHO
N
Bn
2p-1H
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.26
7.20
7.19
7.19
7.17
7.17
6.00
1.97
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
0.97
0.98
1.00
6.00
1.97
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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
-0.5
-1.0
f1 (ppm)

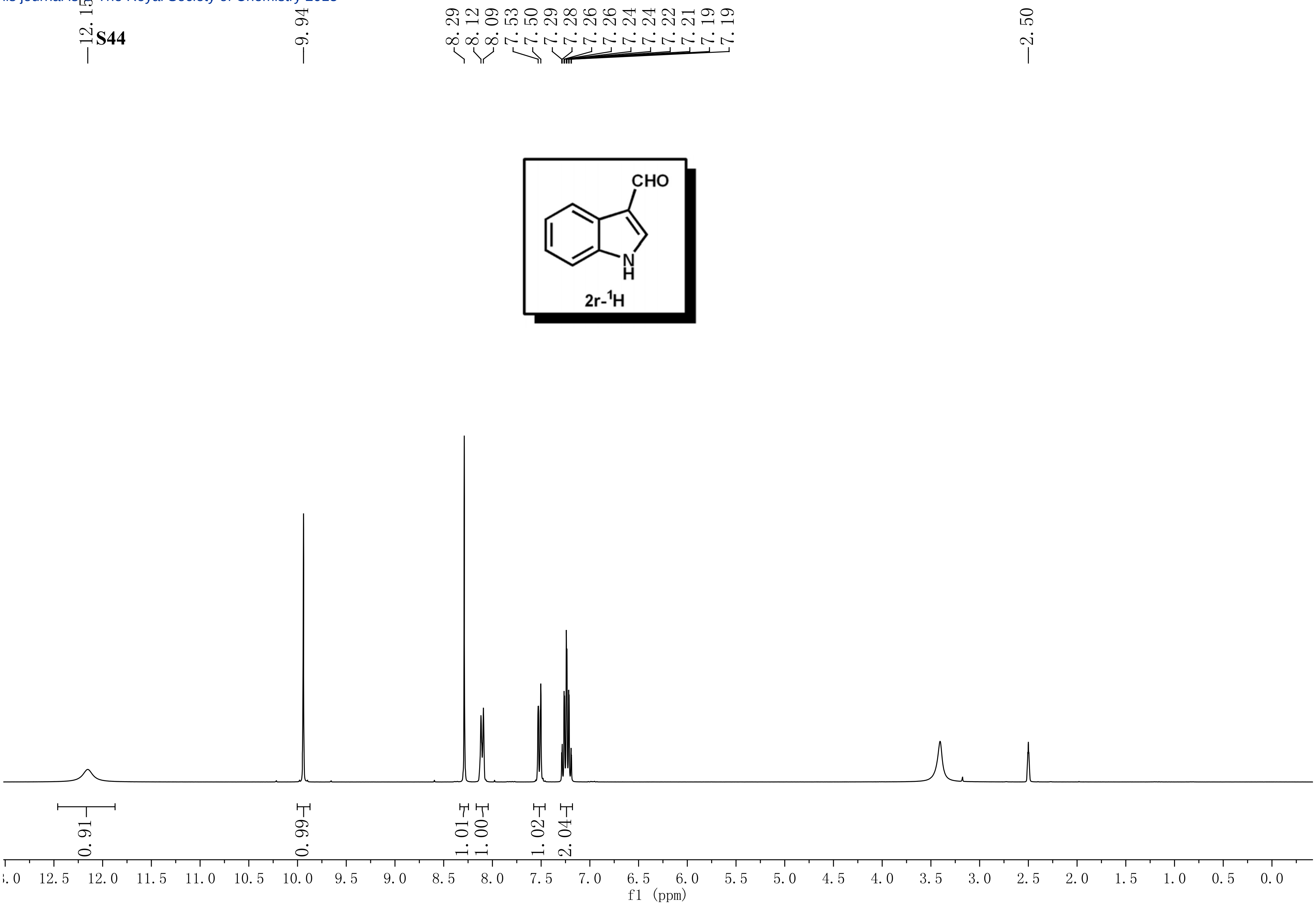

184.61
138.50
137.41
135.25
129.08
128.36
127.18
125.44
124.12
123.04
122.12
118.43
110.33
77.42
77.00
76.58
50.88
CHO
N
Bn
2p-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

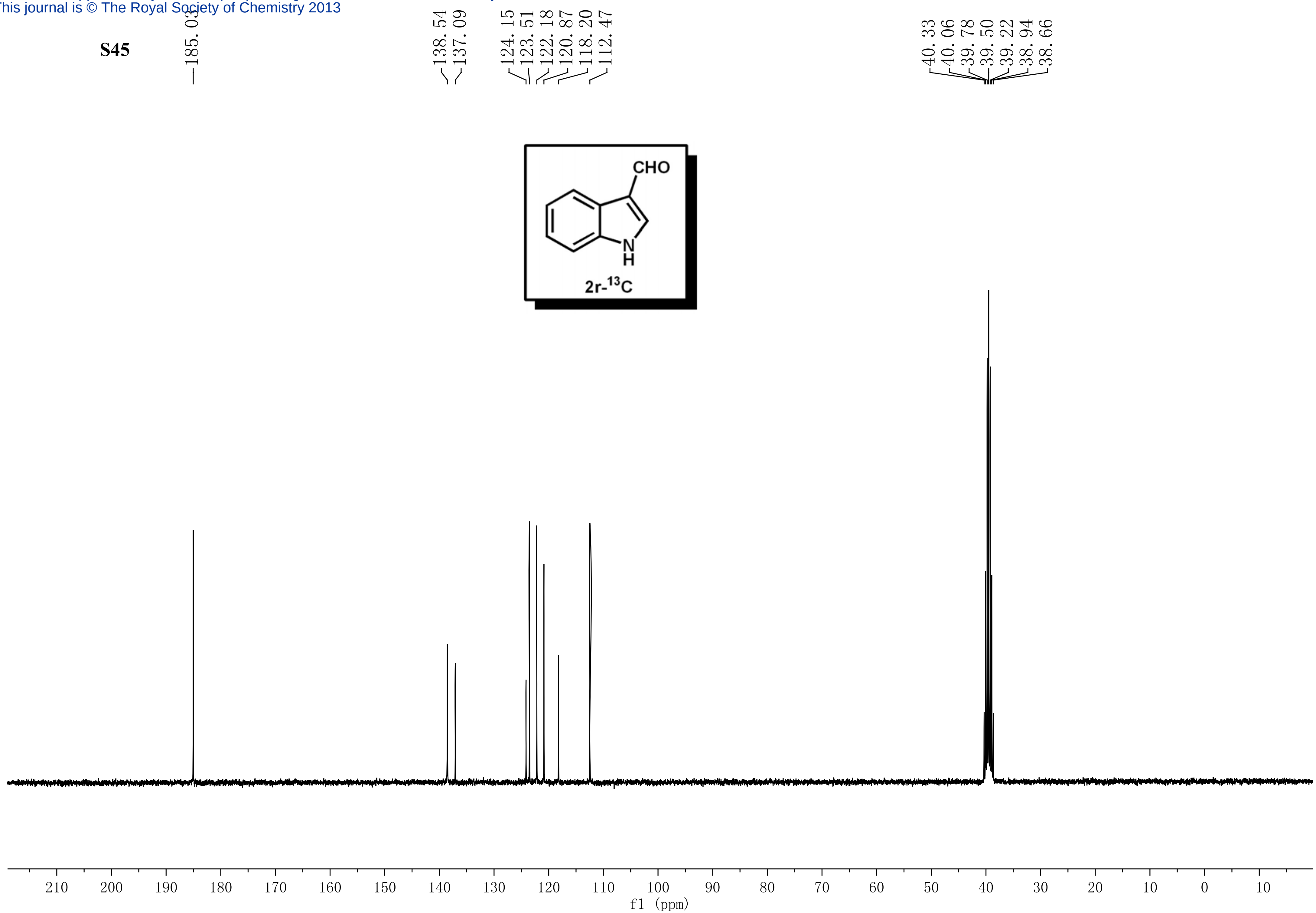
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



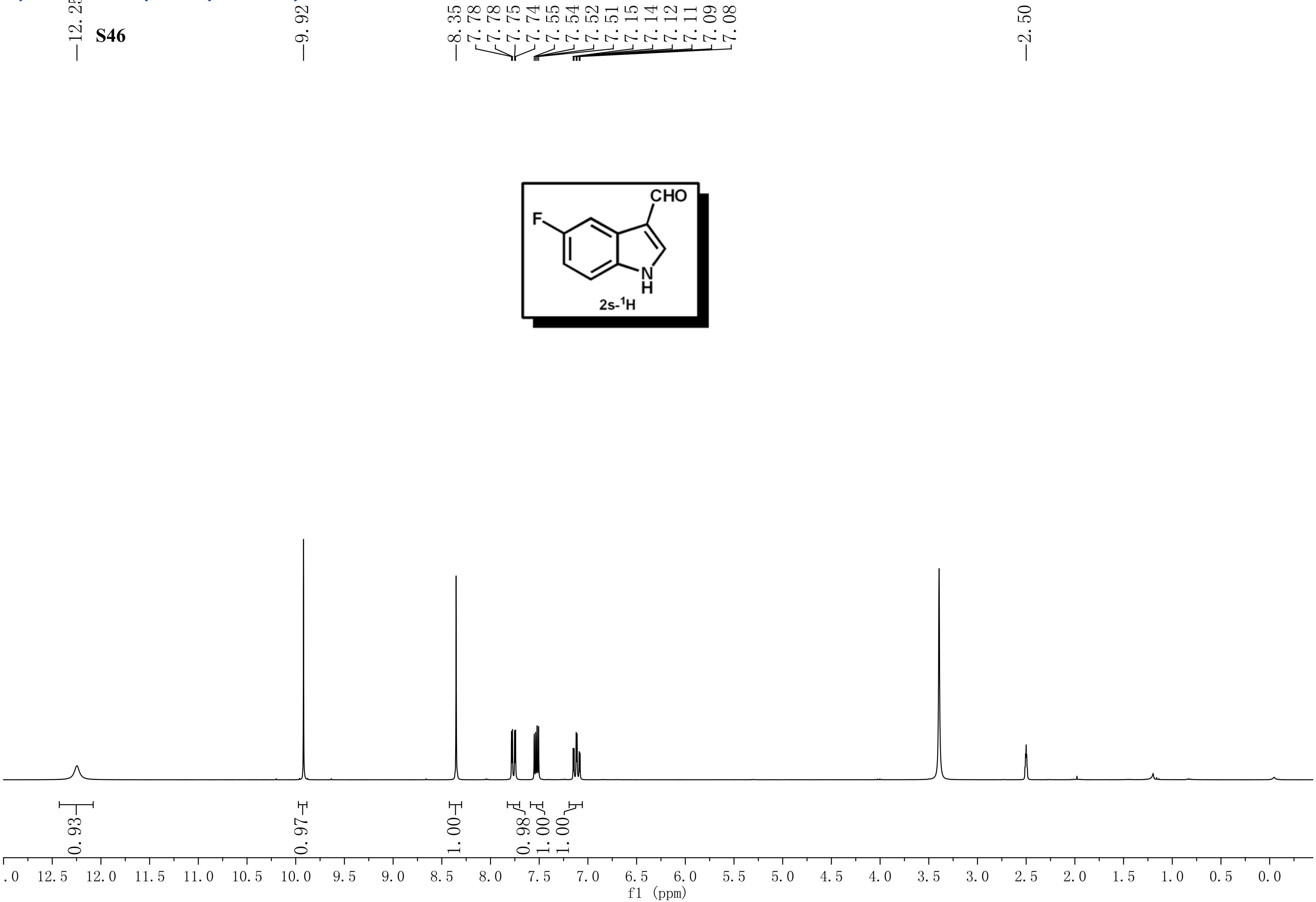
S43

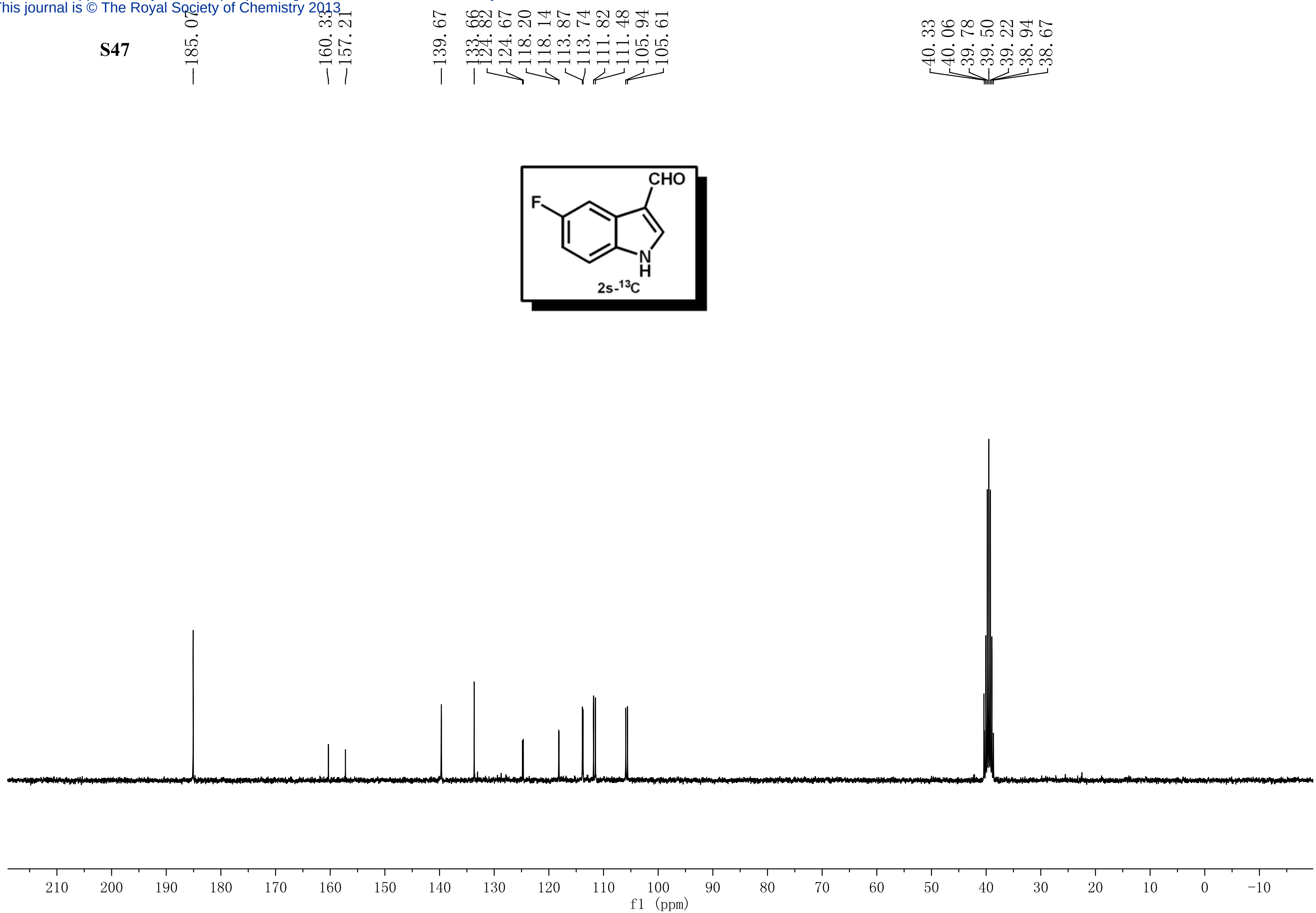

181.53
139.74
131.17
127.31
126.80
126.46
121.27
120.04
110.12
77.42
77.00
76.58
31.54
8.52
CHO
N
2q-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


12.15
9.94
8.29
8.12
8.09
7.53
7.50
7.29
7.28
7.26
7.26
7.24
7.24
7.22
7.21
7.19
7.19
2.50
CHO
N
H
2r-1H
0.91
0.99
1.01
1.00
1.02
2.04
12.5
12.0
11.5
11.0
10.5
10.0
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)

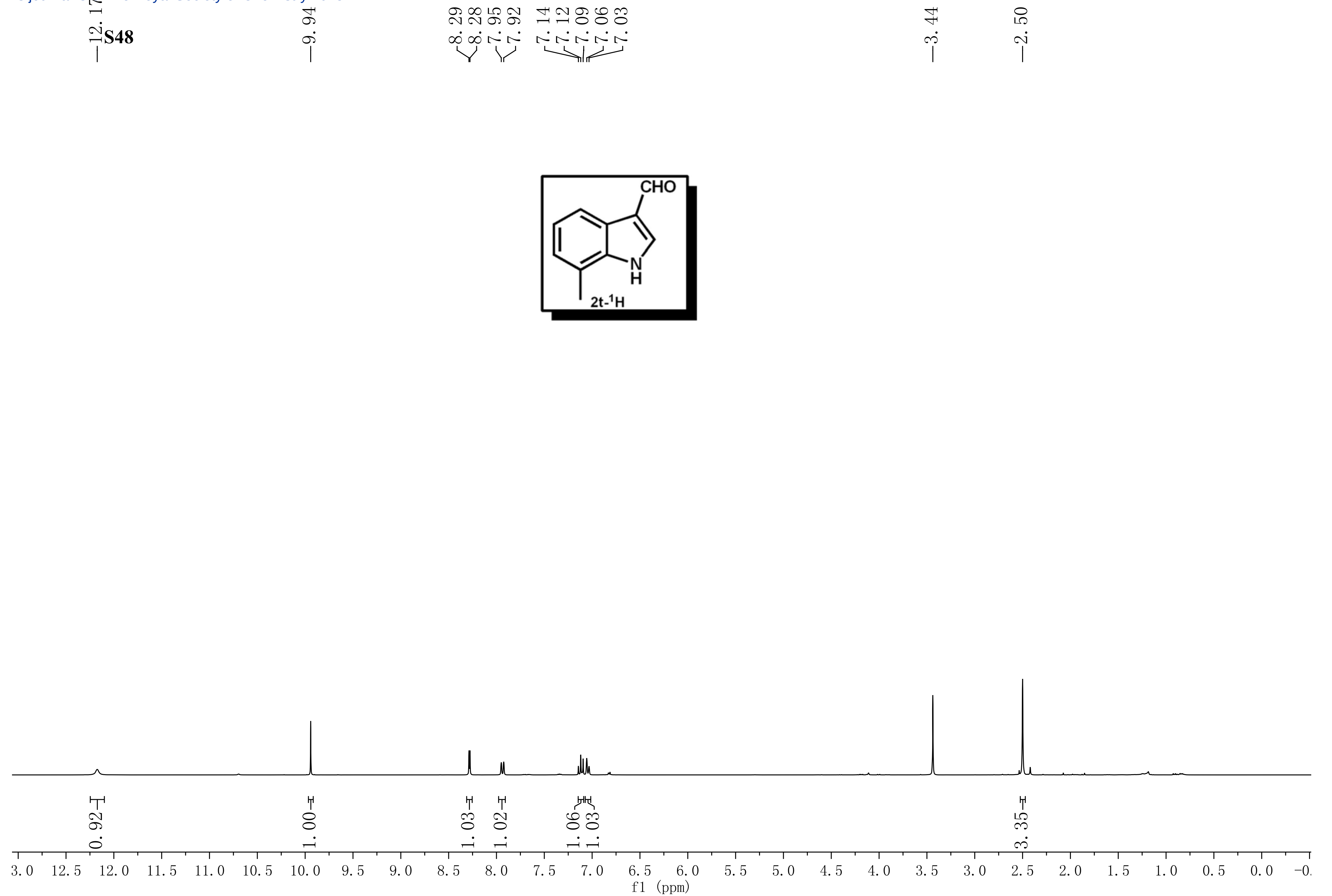

185.03
138.54
137.09
124.15
123.51
122.18
120.87
118.20
112.47
40.33
40.06
39.78
39.50
39.22
38.94
38.66
CHO
N
H
2r-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S46


CHO
F
N
H
2s-1H
12.25
9.92
8.35
7.78
7.78
7.75
7.74
7.55
7.54
7.52
7.51
7.15
7.14
7.12
7.11
7.09
7.08
2.50
0.93
0.97
1.00
0.98
1.00
1.00
f1 (ppm)


185.07
160.33
157.21
139.67
133.66
124.82
124.67
118.20
118.14
113.87
113.74
111.82
111.48
105.94
105.61
40.33
40.06
39.78
39.50
39.22
38.94
38.67
CHO
F
N
H
2s-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



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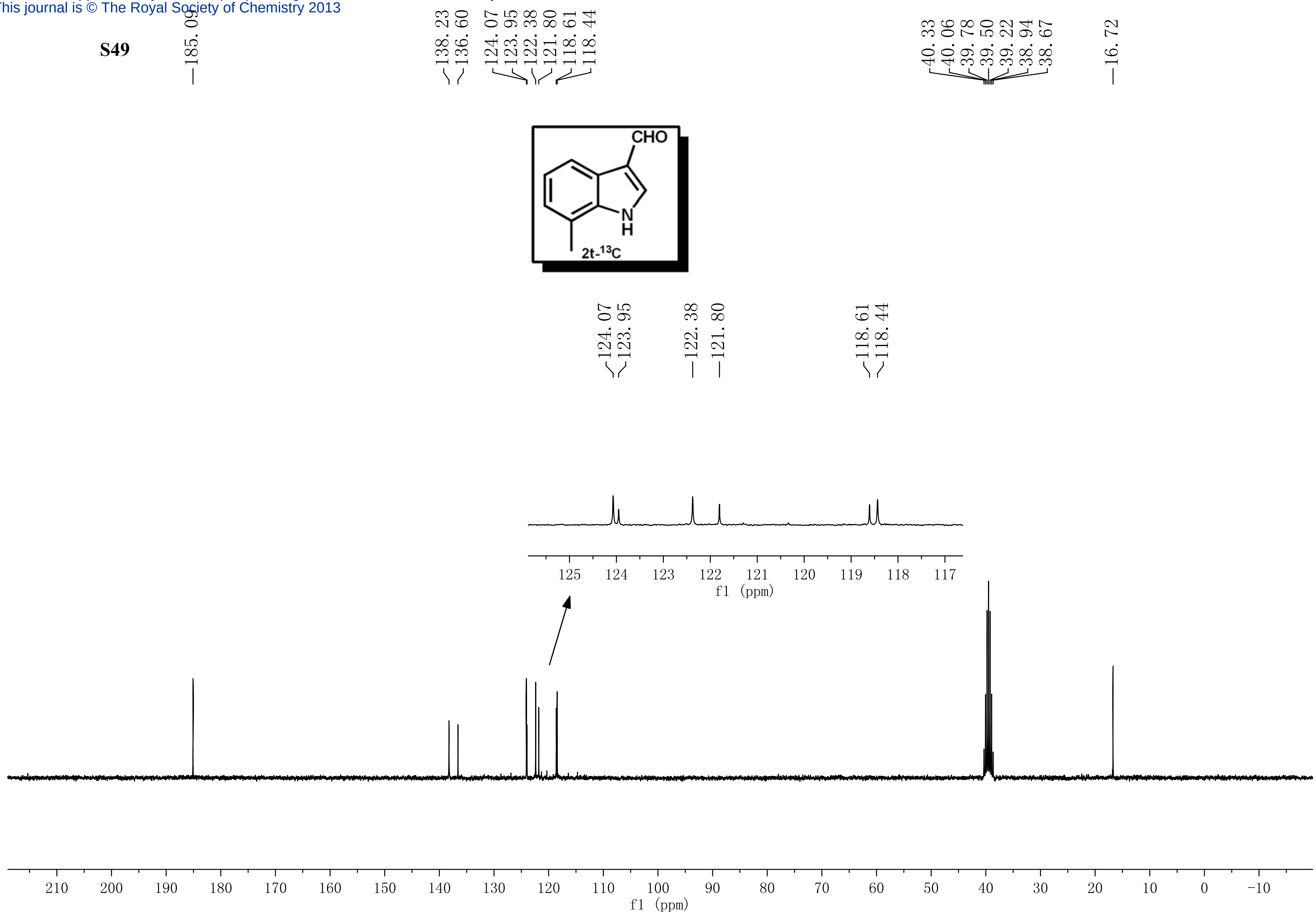
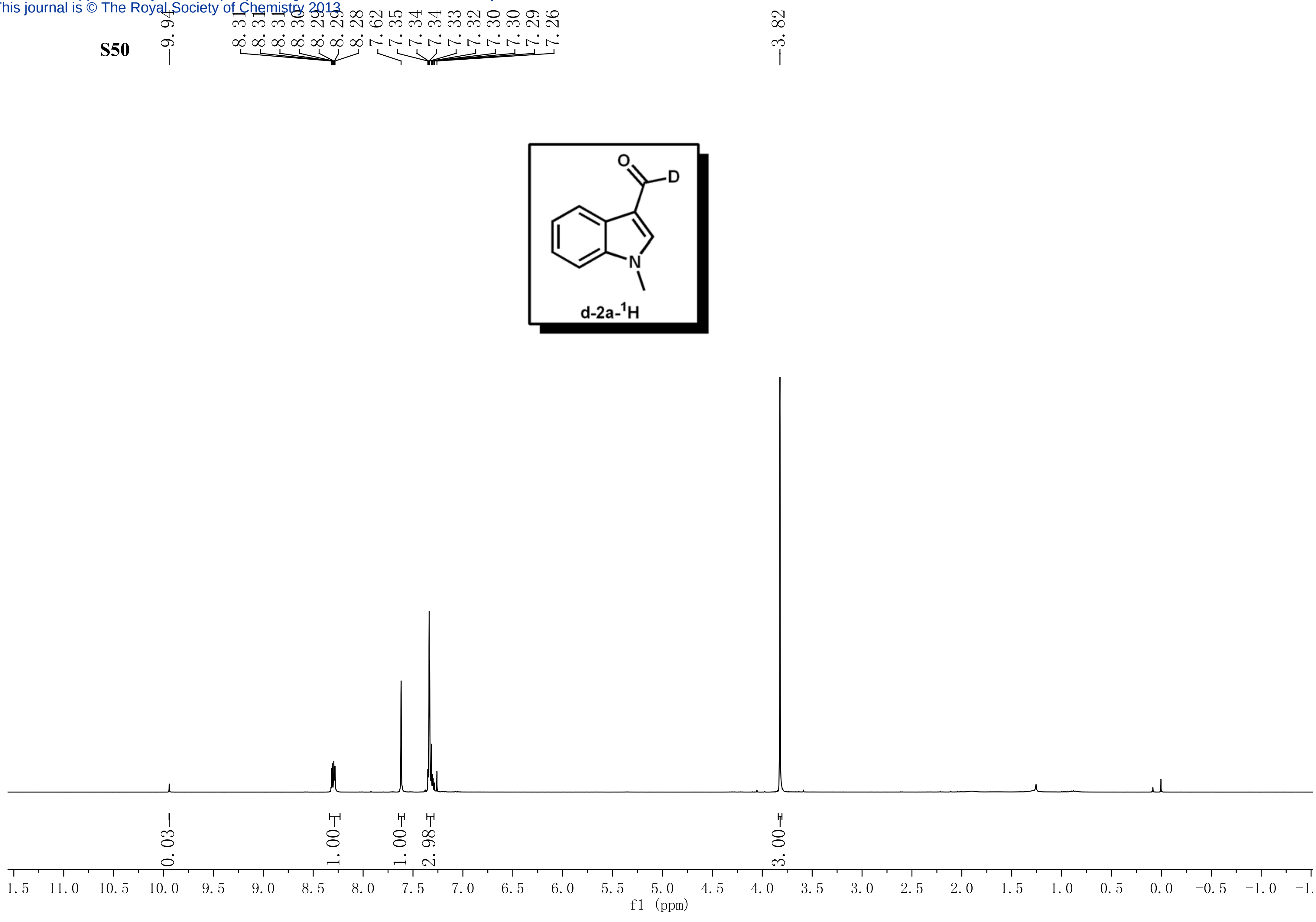
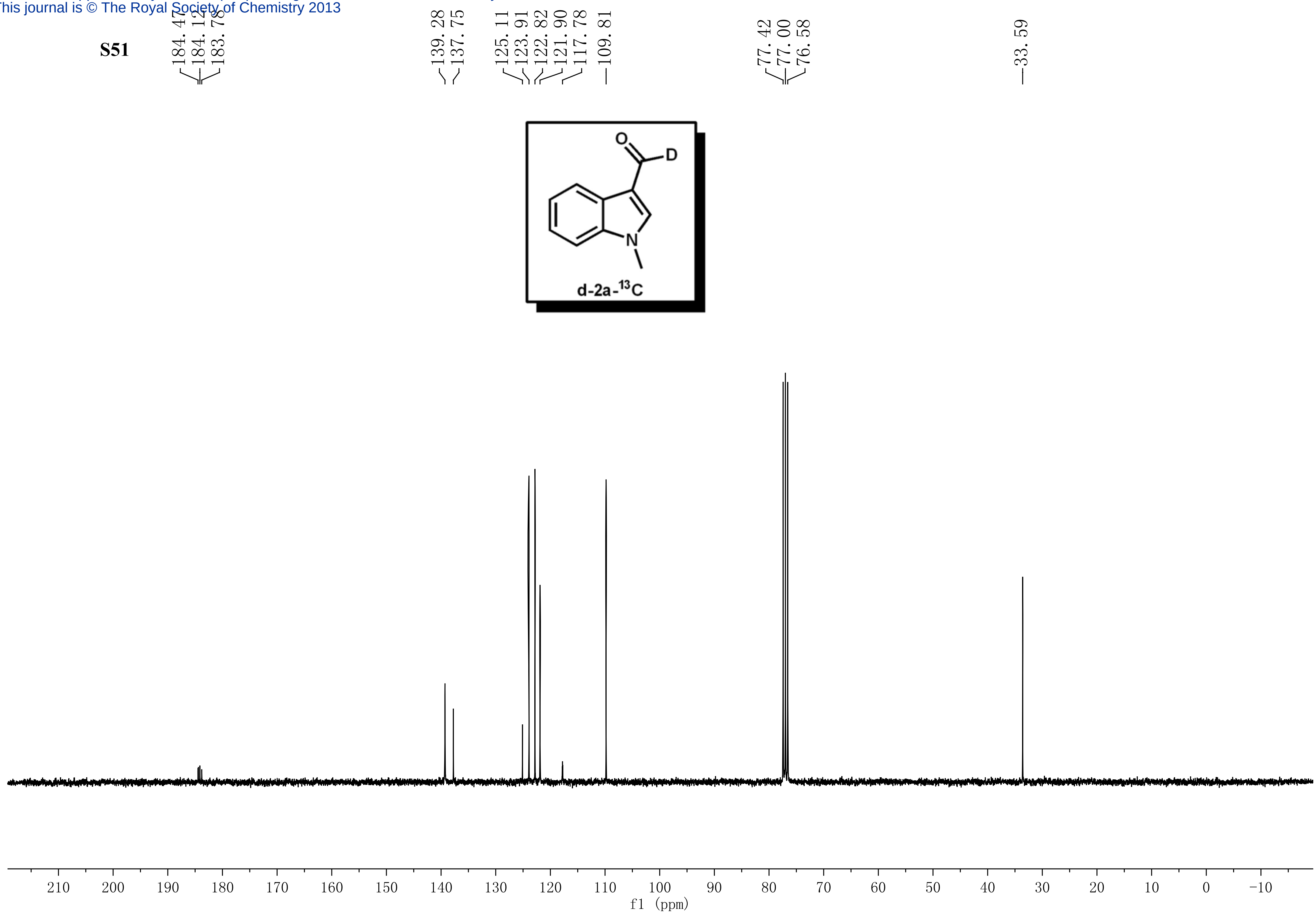
S49

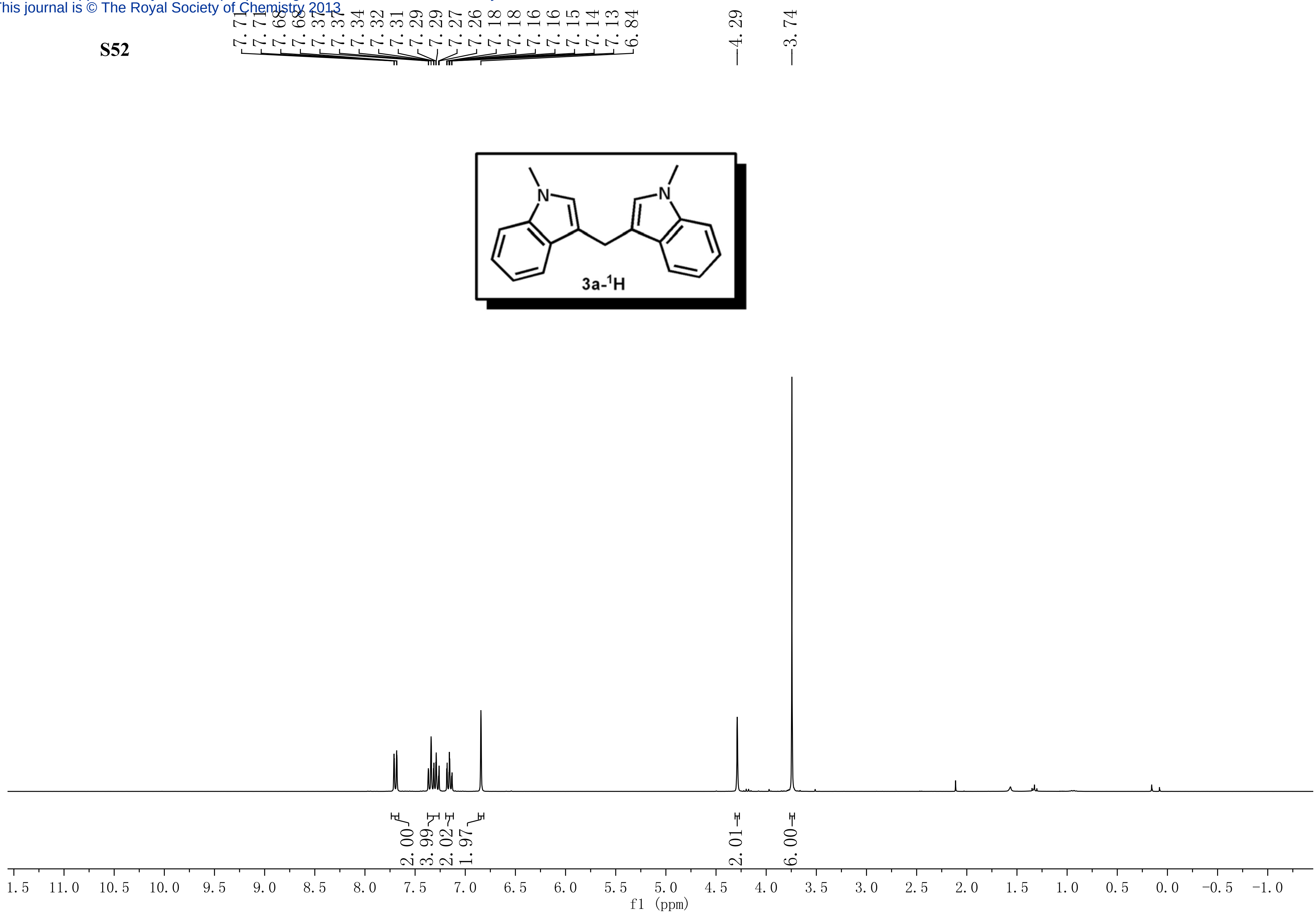


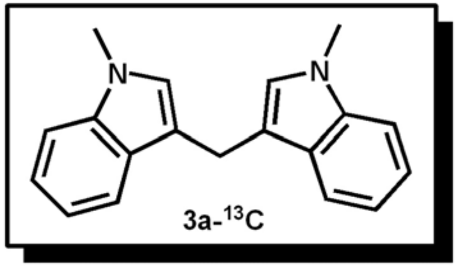
S50


9.94
8.31
8.31
8.31
8.30
8.29
8.29
8.28
7.62
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.29
7.26
3.82
O
D
N
d-2a-1H
0.03
1.00
1.00
2.98
3.00
f1 (ppm)

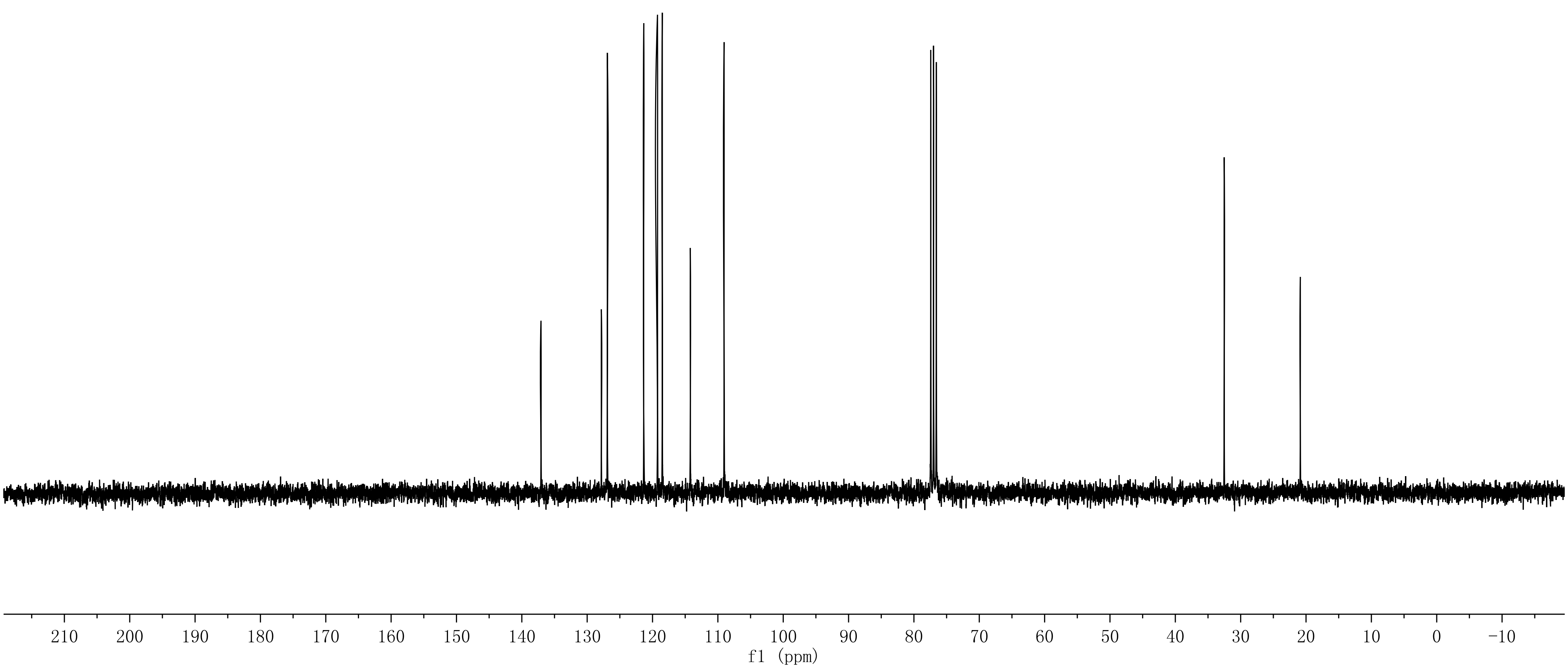
S51


184.47
184.12
183.78
139.28
137.75
125.11
123.91
122.82
121.90
117.78
109.81
77.42
77.00
76.58
33.59
O
D
N
d-2a-13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

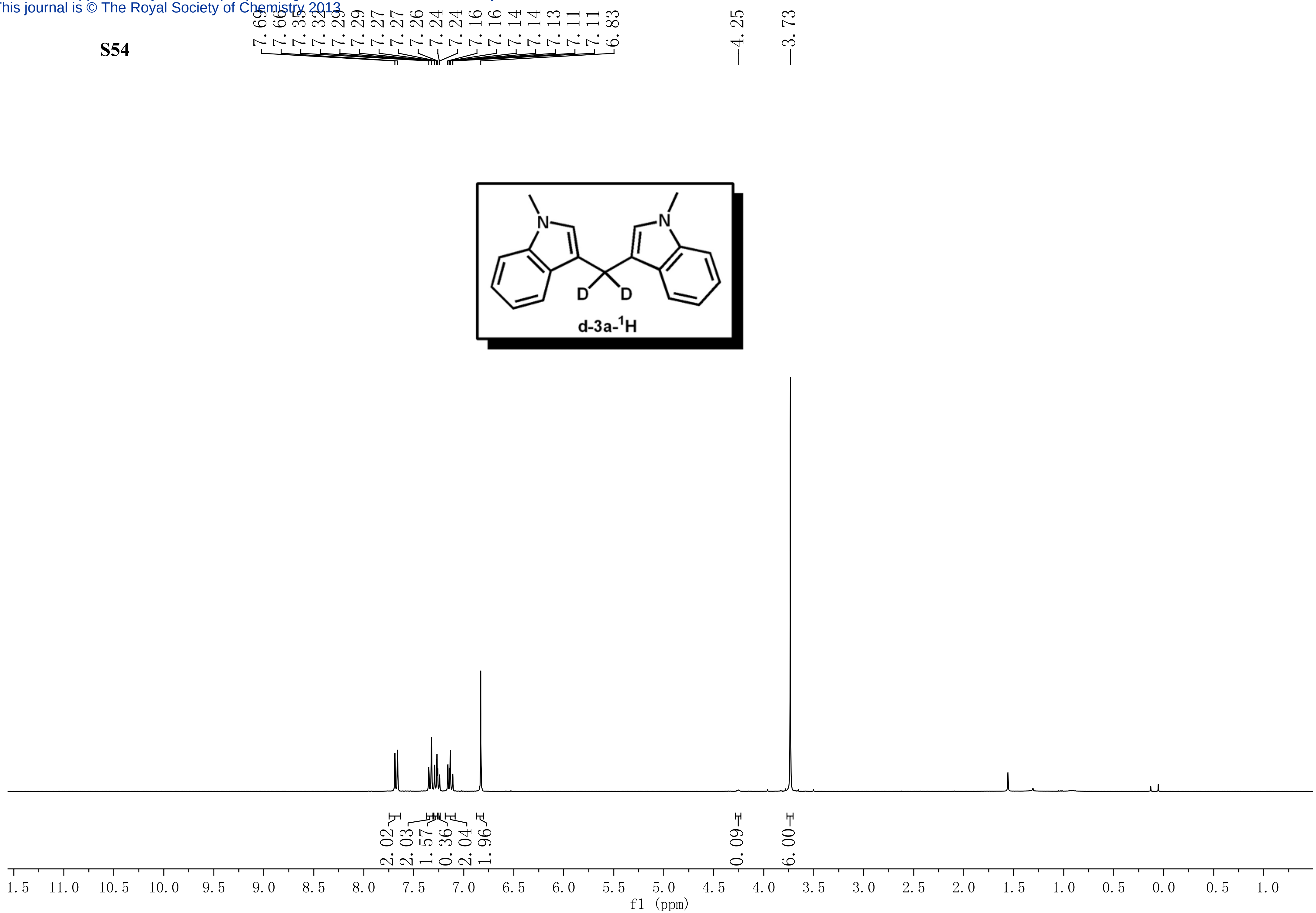

7.71
7.71
7.68
7.68
7.37
7.37
7.34
7.32
7.31
7.29
7.29
7.27
7.26
7.18
7.18
7.16
7.16
7.15
7.14
7.13
6.84
4.29
3.74
3a-1H
2.00
3.99
2.02
1.97
2.01
6.00
f1 (ppm)



3a-^{13}C


137.06
127.83
126.92
121.34
119.24
118.51
114.22
109.05
77.42
77.00
76.58
32.52
20.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

S54


7.69
7.66
7.35
7.32
7.29
7.29
7.27
7.27
7.26
7.24
7.24
7.16
7.16
7.14
7.14
7.13
7.11
7.11
6.83
4.25
3.73
d-3a-^{1}H
2.02
2.03
1.57
0.36
2.04
1.96
0.09
6.00
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry