Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Silver-catalyzed furoquinolines synthesis: From nitrogen effects to the use of silver imidazolate polymer as a new and robust silver catalyst

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General methods:

General procedure for the AgOTf-catalyzed cyclization/acetalization tandem reaction.

Silver triflate (5 mol%) was added in one portion to a solution of 2-alkynyl-3-carbaldehyde quinoline (0.1 mmol) in *N*,*N*-diethylaminoethanol (2 mL, 0.05M) under argon. The mixture was stirred at r.t. until completion of the reaction (TLC monitoring) and filtered through celite. The celite pad was abundantly washed with dichloromethane (20 mL) and the filtrate was washed with sat. aq. solution of $NaHCO_3$ (×3) and brine. The organic layer was then dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (*c*-Hexane / EtOAc (1%Et_3N); 9 : 1 to 0 : 1) afforded the desired furoquinoline.

General procedure for the Ag_2O-catalyzed cyclization/acetalization tandem reaction.

Silver(I) oxide (5 mol%) was added in one portion to a solution of 2-alkynyl-3-carbaldehyde quinoline (0.1 mmol) in *N*,*N*-diethylaminoethanol (2 mL, 0.05M) under argon. The mixture was stirred at r.t. until completion of the reaction (TLC monitoring) and filtered through celite. The celite pad was abundantly washed with dichloromethane (20 mL) and the filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (×3) and brine to afford the desired compound.

Representative procedure for the $[Ag(Im)]_n$-catalyzed cyclization/acetalization tandem reaction, compound (12). A *N*,*N*-diethylaminoethanol solution (1 mL) containing $[Ag(Im)]_n$ (1.7 mg, 9.7 μmol, 5 mol%) and PPh_3 (2.6 mg, 9.7 μmol, 5 mol%) is vigorously stirred during 30 min at r.t. and the 2-phenylalkynyl-3-carbaldehyde quinoline[1] (47.0 mg, 0.2 mmol) is added in one portion. After 30 min (TLC monitoring) the reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure. Flash chromatography on basic alumina (*c*-Hexane / EtOAc ; 8 : 2 to 0 : 1) afforded the desired furoquinoline **12** (68 mg, 100%) as a yellow oil.

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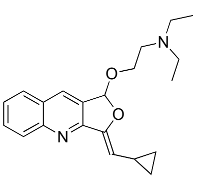
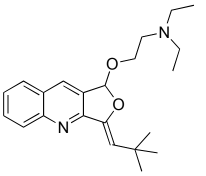
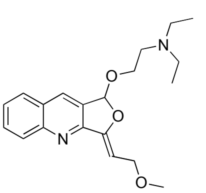
[1] The detailed experimental procedure for the quinolines starting materials and compounds **1**-**6** can be found in :
- A. Patin, P. Belmont *Synthesis* 2005, (14), 2400-2406.
- T. Godet, C. Vaxelaire, C. Michel, A. Milet and P. Belmont, *Chem.--Eur. J.*, 2007, *13*, 5632- 5641.



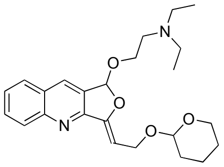
(7) Yellow oil. ∂_H (300 MHz; $CDCl_3$) 0.59-0.64 (2H, m, C$H_{2(cyclopropyl)}$), 0.88-0.95 (2H, m, $CH_{2(cyclopropyl)}$), 1.04 (6H, t, *J* 7.2, N(CH_2-CH_3)$_2$), 1.89-2.01 (1H, m, C$H_{(cyclopropyl)}$), 2.61 (4H, q, *J* 7.2, N(CH_2-CH_3)$_2$), 2.79 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 3.79-3.93 (2H, m, O-CH_2-CH_2-N), 5.33 (1H, d, *J* 10.2, C=C*H*-CH), 6.62 (1H, s, C*H*-O), 7.50 (1H, ddd, *J* 1.2 and 6.9 and 8.1, H_{Ar}), 7.71 (1H, ddd, *J* 1.5 and 6.9 and 8.4, H_{Ar}), 7.82 (1H, dd, *J* 1.2 and 8.1, H_{Ar}), 8.06 (1H, d, *J* 8.4, H_{Ar}) and 8.16 (1H, s, H_{Ar}); ∂_C (75 MHz; $CDCl_3$) 7.8, 8.0, 8.8, 11.8, 47.7, 52.4, 66.1, 103.4, 107.4, 126.4, 127.6, 128.6, 129.0, 129.3, 130.5, 131.6, 149.9, 150.4 and 153.9; ν_{max}/cm^{-1} 2966 and 2926 (C-H), 1623 (C=C), 1308 (C=N), 1065 (C-O) and 1027 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{21}H_{27}N_2O_2]^+$: 339.2067; found: 339.2068



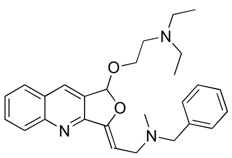
(8) Yellow oil. ∂_H (300 MHz; $CDCl_3$) 1.05 (6H, t, *J* 7.2, N(CH_2-CH_3)$_2$), 1.31 (9H, s, C(CH_3)$_3$), 2.62 (4H, q, *J* 7.2, N(CH_2-CH_3)$_2$), 2.79 (2H, t, *J* 7.3, O-CH_2-CH_2-N), 3.84 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 5.83 (1H, s, C*H*-*t*-Bu), 6.59 (1H, s, C*H*-O), 7.51 (1H, ddd, *J* 1.2 and 6.9 and 8.1, H_{Ar}), 7.72 (1H, ddd, *J* 1.2 and 6.9 and 8.4, H_{Ar}), 7.83 (1H, d, *J* 8.1, H_{Ar}), 8.10 (1H, d, *J* 8.7, H_{Ar}) and 8.17 (1H, s, H_{Ar}); ∂_C (75 MHz, $CDCl_3$) 11.8, 30.5, 31.9, 47.7, 52.4, 65.8, 103.5, 112.0, 126.5, 127.7, 128.6, 129.4, 130.5, 131.5, 148.8, 149.9 and 155.1; ν_{max}/cm^{-1} 2960 (C-H), 1625 and 1504 (C=C), 1069 (C-O) and 1023 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{22}H_{31}N_2O_2]^+$: 355.2380 found: 355.2382



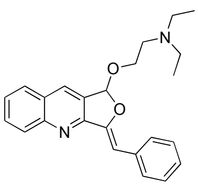
(9) Yellow oil. ∂_H (300 MHz; $CDCl_3$) 1.02 (6H, t, *J* 7.1, N(CH_2-CH_3)$_2$), 2.58 (4H, q, *J* 7.1, N(CH_2-CH_3)$_2$), 2.74 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 3.41 (3H, s, OCH_3), 3.76-3.80 (2H, m, O-CH_2-CH_2-N), 4.27-4.41 (2H, m, CH_2-OCH_3), 5.93 (1H, t, *J* 7.3, C*H*-CH_2-OCH_3), 6.60 (1H, s, C*H*-O), 7.54 (1H, ddd, *J* 1.0 and 7.0 and 8.2, H_{Ar}), 7.75 (1H, ddd, *J* 1.5 and 7.0 and 8.5, H_{Ar}), 7.85 (1H, d, *J* 8.2, H_{Ar}), 8.13 (1H, d, *J* 8.5, H_{Ar}) and 8.19 (1H, s, H_{Ar}); ∂_C (75 MHz, $CDCl_3$) 11.6, 47.7, 52.3, 57.9, 62.3, 66.3, 97.4, 104.1, 127.0, 127.9, 128.6, 129.3, 129.7, 130.7, 131.6, 150.0, 153.0 and 153.5; ν_{max}/cm^{-1} 2968, 2926, 2874 and 2817 (C-H), 1624 and 1505 (C=C), 1115 and 1074 (C-O and C-N) ; HRMS (CI): *m/z* calcd for $[C_{20}H_{27}N_2O_3]^+$: 343.2022; found: 343.2022



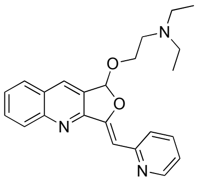
(10) Orange oil. ∂_H (300 MHz; $CDCl_3$) 1.05 (6H, t, *J* 7.2, N(CH_2-CH_3)$_2$), 1.50-1.88 (6H, m, 3 x C$H_{2(THP)}$), 2.62 (4H, q, *J* 7.2, N(CH_2-CH_3)$_2$), 2.78 (2H, br s, O-CH_2-CH_2-N), 3.52-3.58 (1H, m, $H_{5b(THP)}$), 3.85-3.99 (3H, m, $H_{5a(THP)}$ and O-CH_2-CH_2-N), 4.43-4.62 (2H, m, =CH-CH_2-O), 4.79 (1H, dd, *J* 3.0 and 6.3, $H_{1(THP)}$), 5.96 (1H, t, *J* 7.5, =C*H*-CH_2O), 6.60 (1H, s, C*H*-O), 7.54 (1H, ddd, *J* 1.5 and 6.9 and 8.1, H_{Ar}), 7.74 (1H, ddd, *J* 1.2 and 6.9 and 8.4, H_{Ar}), 7.85 (1H, d, *J* 8.1, H_{Ar}), 8.12 (1H, d, *J* 8.4, H_{Ar}) and 8.20 (1H, s, H_{Ar}); ∂_C (75 MHz; $CDCl_3$) 11.6, 19.5, 25.7, 30.8, 47.7, 52.3, 61.1, 62.2, 66.3, 97.8, 104.1, 127.0, 127.9, 128.6, 129.4, 129.7, 130.6, 131.6, 150.0, 152.6 and 153.6; ν_{max}/cm^{-1} 2937 and 2871 (C-H), 1623 and 1505 (C=C), 1312 (C=N), 1114 and 1075 (C-O) and 1021 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{24}H_{33}N_2O_4]^+$: 413.2435; found: 413.2445



(11) Yellow oil. ∂_H (400 MHz; $CDCl_3$) 1.02 (6H, t, *J* 7.2, N(CH_2-CH_3)$_2$), 2.31 (3H, s, NCH_3), 2.57 (4H, q, *J* 7.2, N(CH_2-CH_3)$_2$), 2.74 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 3.48 (2H, dd, *J* 2.8 and 7.4, =CH-CH_2N), 3.61 (1H, d, *J* 13.2, NCH$_a$$H_b$Ph), 3.66 (1H, d, *J* 13.2, NCH_aH$_b$Ph), 3.75-3.86 (2H, m, O-CH_2-CH_2-N), 5.99 (1H, t, *J* 7.4, =C*H*-CH_2N), 6.59 (1H, s, C*H*-O), 7.24 (1H, d, *J* 7.1, H_{Ar}), 7.31 (2H, dd, *J* 7.1 and 7.2, H_{Ar}), 7.38 (2H, d, *J* 7.2, H_{Ar}), 7.53 (1H, ddd, *J* 1.1 and 6.9 and 8.1, H_{Ar}), 7.74 (1H, ddd, *J* 1.4 and 6.9 and 8.6, H_{Ar}), 7.84 (1H, d, *J* 8.1, H_{Ar}), 8.14 (1H, d, *J* 8.6, H_{Ar}) and 8.18 (1H, s, H_{Ar}); ∂_C (100 MHz; $CDCl_3$) 11.9, 42.2, 47.7, 52.2, 52.4, 61.6, 66.3, 98.1, 103.7, 126.8, 127.0, 127.8, 128.3, 128.6, 129.2, 129.4, 129.6, 130.6, 131.6, 139.4, 150.0, 152.7 and 153.7; ν_{max}/cm^{-1} 2967, 2931 and 2788 (C-H), 1625 and 1505 (C=C), 1310 (C=N), 1122 (C-O) and 1073 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{27}H_{34}N_3O_2]^+$: 432.2646; found: 432.2642

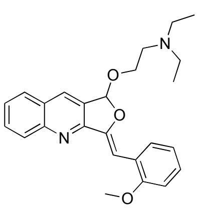


(12) yellow oil. ∂_H (300 MHz; ($CDCl_3$) 1.03 (6H, t, *J* 7.1, N(CH_2-CH_3)$_2$), 2.60 (4H, q, *J* 7.1, N(CH_2-CH_3)$_2$), 2.79 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 3.85-4.02 (2H, m, O-CH_2-CH_2-N), 6.72 (1H, s, =C*H*-Ph), 6.75 (1H, s, C*H*-O), 7.24 (1H, ddd, *J* 1.1 and 7.3 and 7.3, H_{Ar}), 7.39 (2H, dd, *J* 7.3 and 7.9, H_{Ar}), 7.51 (1H, ddd, *J* 1.1 and 6.9 and 8.2, H_{Ar}), 7.73 (1H, ddd, *J* 1.4 and 6.9 and 8.5, H_{Ar}), 7.82 (1H, dd, *J* 1.1 and 8.2, H_{Ar}), 7.89 (2H, dd, *J* 1.3 and 7.9, H_{Ar}), 8.15 (1H, d, *J* 8.5, H_{Ar}) and 8.18 (1H, s, H_{Ar}); ∂_C (125 MHz; $(CD_3)_2CO$) 12.2, 48.3, 53.2, 68.0, 100.9, 106.2, 127.5, 127.6, 128.7, 129.3, 129.7, 129.9, 130.0, 130.1, 131.4, 132.6, 136.3, 150.7, 151.9 and 155.1; ν_{max}/cm^{-1} 2965 and 2834 (C-H), 1620 and 1489 (C=C),1234 (C=N), 1110 (C-O) and 1026 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{23}H_{26}N_3O_2]^+$: 375.2073; found : 375.2073

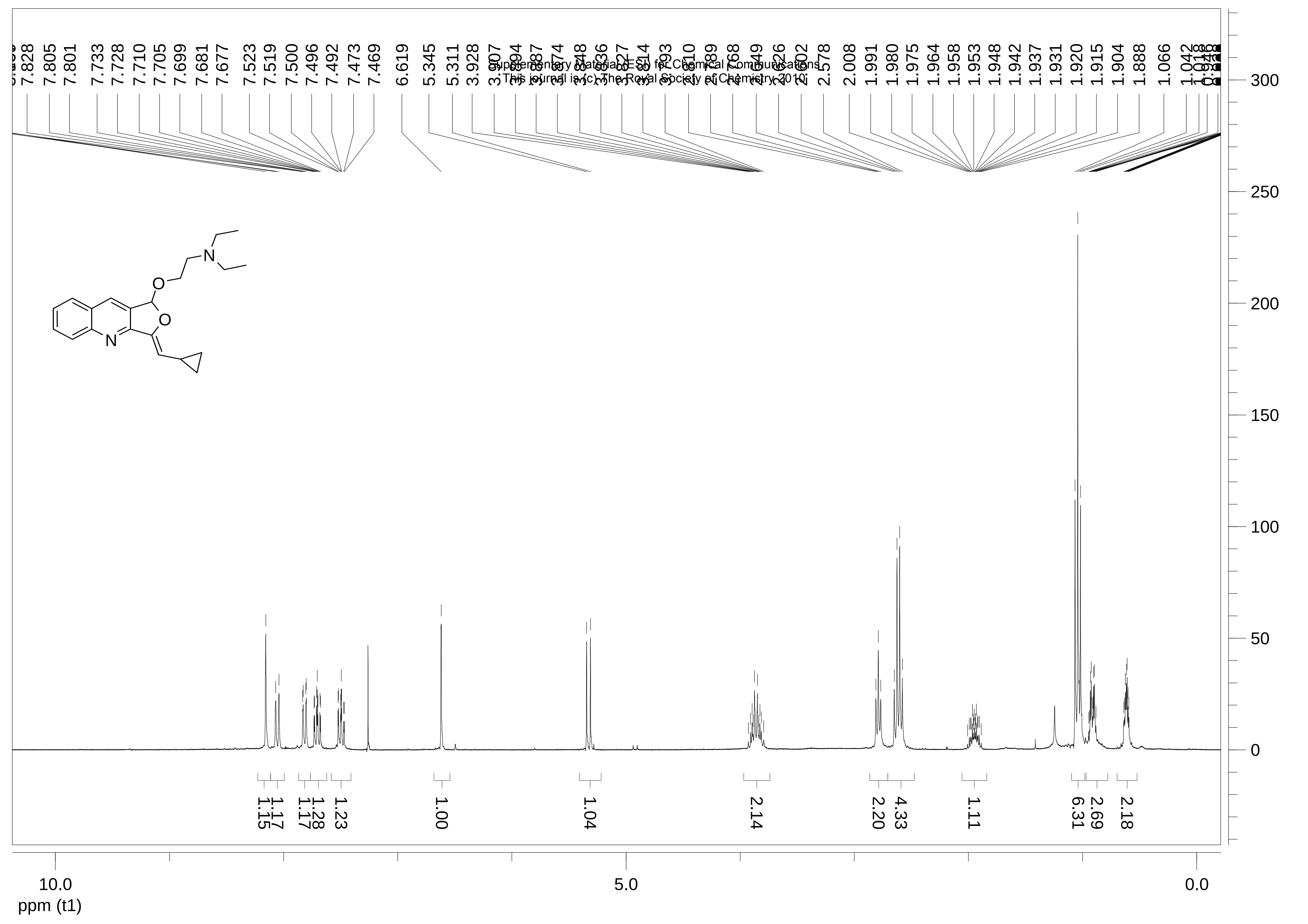


(13) Yellow oil. ∂_H (300 MHz; $CDCl_3$) 1.00 (6H, t, *J* 7.2, $N(CH_2\text{-}CH_3)_2$), 2.57 (4H, q, *J* 7.2, $N(CH_2\text{-}CH_3)_2$), 2.76 (2H, t, *J* 6.3, O-CH_2-CH_2-N), 3.83-3.96 (2H, m, O-CH_2-CH_2-N), 6.78 (1H, s, C*H*-O), 6.97 (1H, s, =C*H*-C_5H_5N), 7.07 (1H, ddd, *J* 1.0 and 4.9 and 7.4, H_{Ar}), 7.53 (1H, ddd, *J* 1.0 and 7.0 and 8.0, H_{Ar}), 7.66 (1H, ddd, *J* 1.8 and 7.4 and 7.4, H_{Ar}), 7.74 (1H, ddd, *J* 1.4 and 7.0 and 8.4, H_{Ar}), 7.83 (1H, dd, *J* 1.0 and 8.0, H_{Ar}), 8.14 (1H, d, *J* 7.4, H_{Ar}), 8.16 (1H, d, *J* 8.4, H_{Ar}), 8.21 (1H, s, H_{Ar}) and 8.61 (1H, d, *J* 4.9, H_{Ar}); ∂_C (75 MHz; $CDCl_3$) 11.7, 47.6, 52.4, 66.7, 101.7, 105.4, 121.0, 124.2, 127.2, 127.9, 128.6, 128.7, 129.9, 130.8, 131.5, 136.1, 149.6, 150.2, 153.3, 154.2 and 154.8; ν_{max}/cm^{-1} 2967 and 2808 C-H), 1582 and 1465 (C=C), 1341 (C=N), 1099 and 1070 (C-O and C-N)

HRMS (ESI+): *m/z* calcd for $[C_{23}H_{25}N_3O_2Na]^+$: 398.1844; found: 398.1845.



(14) Yellow oil. ∂_H (300 MHz; $CDCl_3$) 1.03 (6H, t, *J* 7.1, $N(CH_2\text{-}CH_3)_2$), 2.58 (4H, q, *J* 7.1, $N(CH_2\text{-}CH_3)_2$), 2.78 (2H, t, *J* 6.4, O-CH_2-CH_2-N), 3.81-3.98 (2H, m, O-CH_2-CH_2-N), 3.98 (3H, s, O-CH_3) 6.75 (1H, s, C*H*-O), 6.91 (1H, dd, *J* 0.8 and 8.2, H_{Ar}), 7.02 (1H, ddd, *J* 0.8 and 7.6 and 7.8, H_{Ar}), 7.23 (1H, ddd, *J* 1.7 and 7.6 and 8.2, H_{Ar}), 7.25 (1H, s, =C*H*-(2-MeO-Ph)), 7.52 (1H, ddd, *J* 1.1 and 6.9 and 8.1, H_{Ar}), 7.74 (1H, ddd, *J* 1.4 and 6.9 and 8.4, H_{Ar}), 7.84 (1H, dd, *J* 1.4 and 8.1, H_{Ar}), 8.18 (1H, d, *J* 8.4, H_{Ar}), 8.19 (1H, s, H_{Ar}) and 8.35 (1H, dd, *J* 1.7 and 7.8, H_{Ar}); ∂_C (75 MHz; $CDCl_3$) 11.4, 47.5, 52.2, 55.6, 66.1, 94.8, 104.7, 110.4, 120.6, 124.2, 126.6, 127.7, 128.1, 128.6, 128.7, 129.6, 130.0, 130.6, 131.5, 150.2, 150.7, 154.9 and 157.0; ν_{max}/cm^{-1} 2965, 2932 and 2834 (C-H), 1620 and 1489 (C=C), 1234 (C=N), 1110 (C-O) and 1055 (C-N); HRMS (ESI+): *m/z* calcd for $[C_{25}H_{29}N_2O_3]^+$: 405.2173; found: 405.2172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6.619
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5.311
3.928
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1.980
1.975
1.964
1.958
1.953
1.948
1.942
1.937
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1.042
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O
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N
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2.20
4.33
1.11
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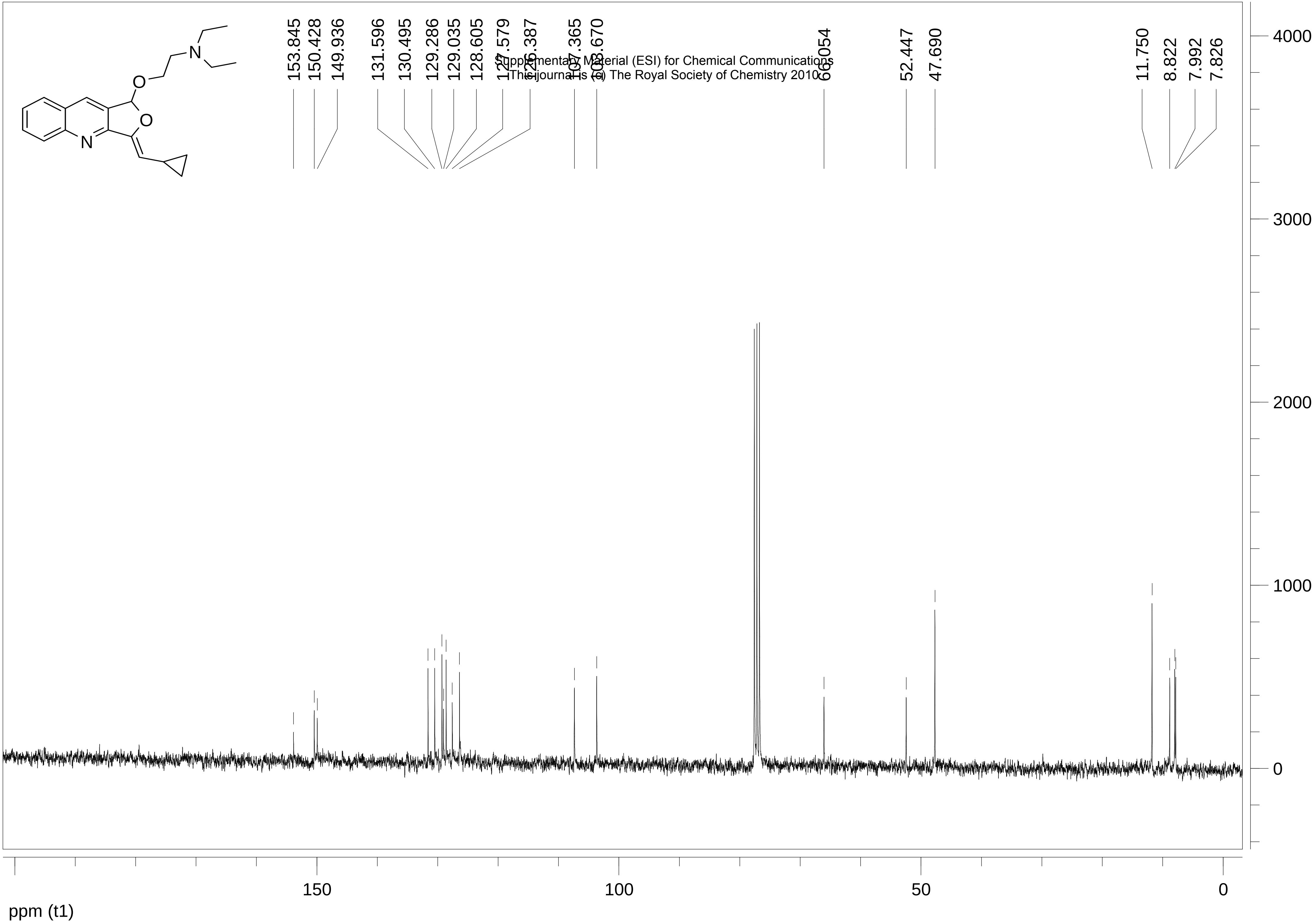
0.0
ppm (t1)



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66.054
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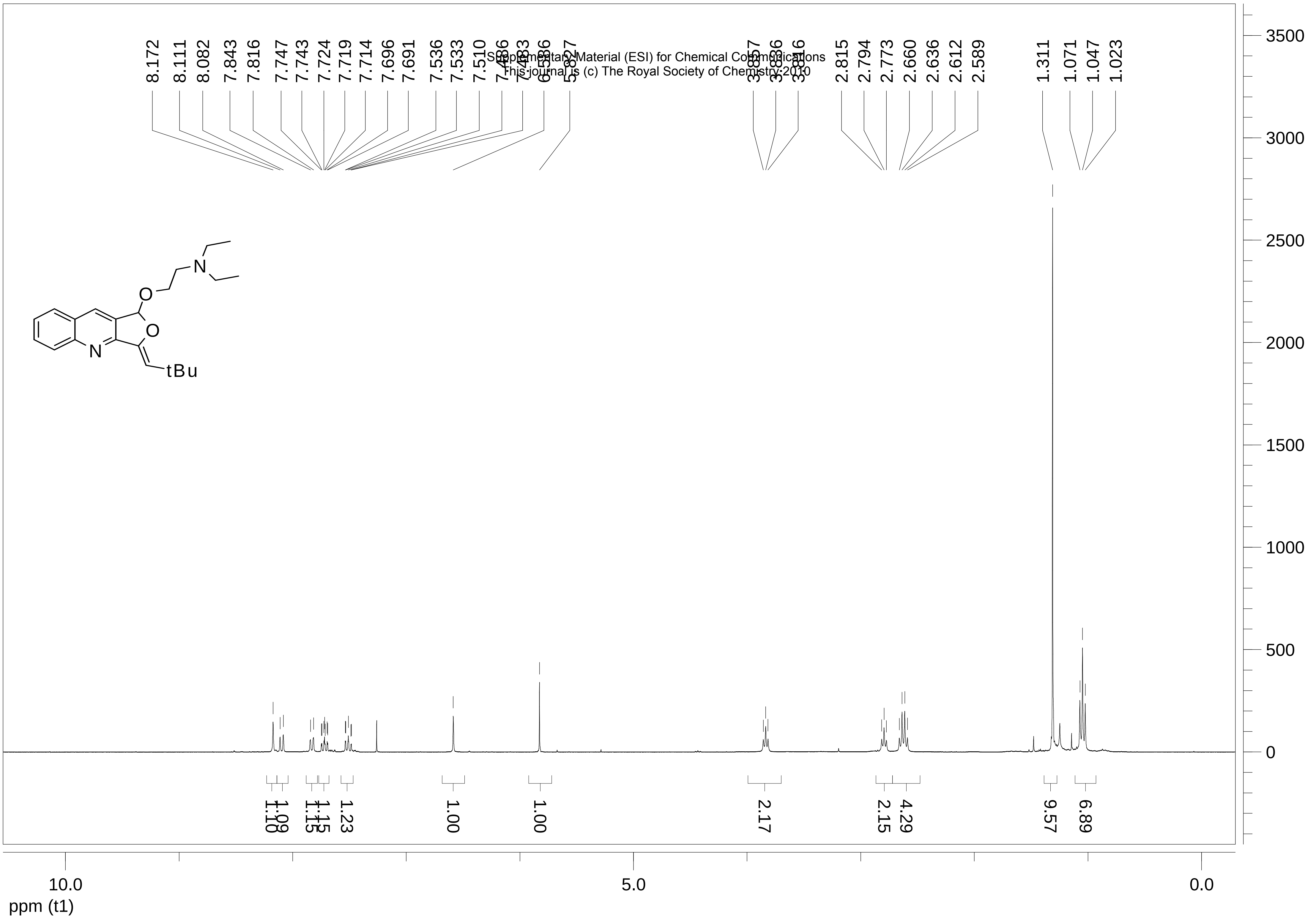
ppm (t1)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2.794
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2.636
2.612
2.589
1.311
1.071
1.047
1.023
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O
O
N
tBu
1.10
1.09
1.15
1.23
1.00
1.00
2.17
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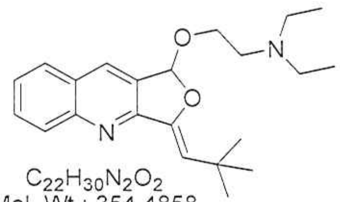
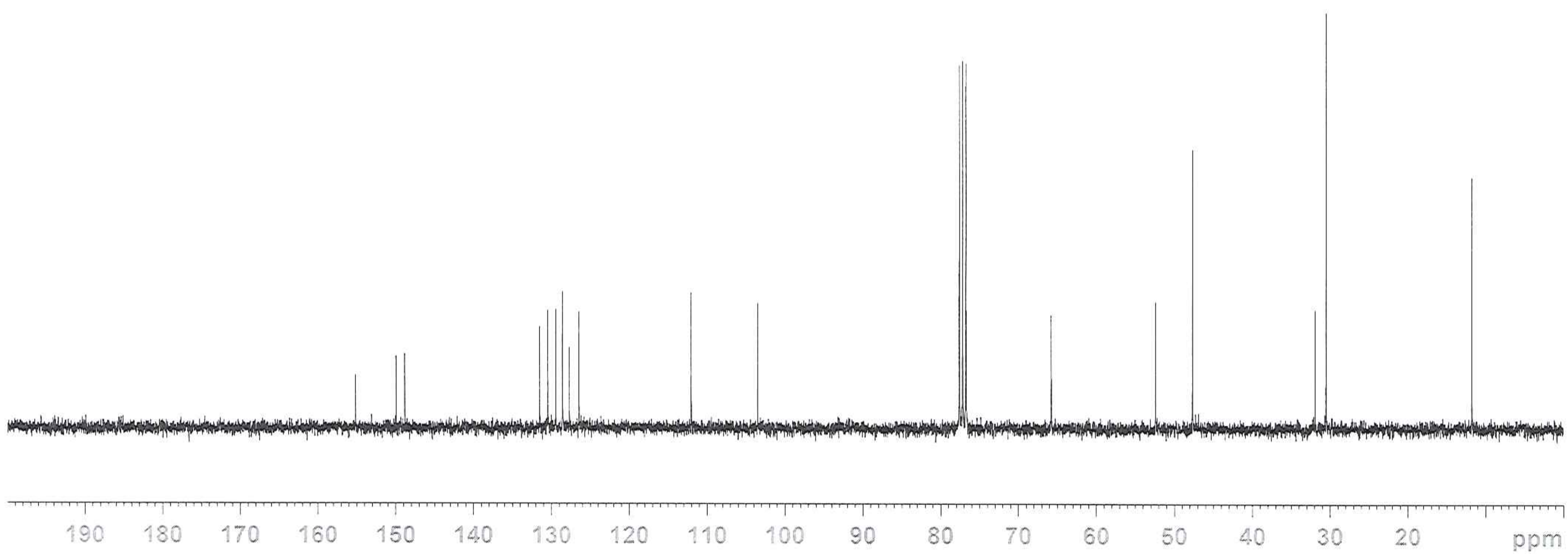
ppm (t1)

13C NMR - CDCl3 - 75MHz

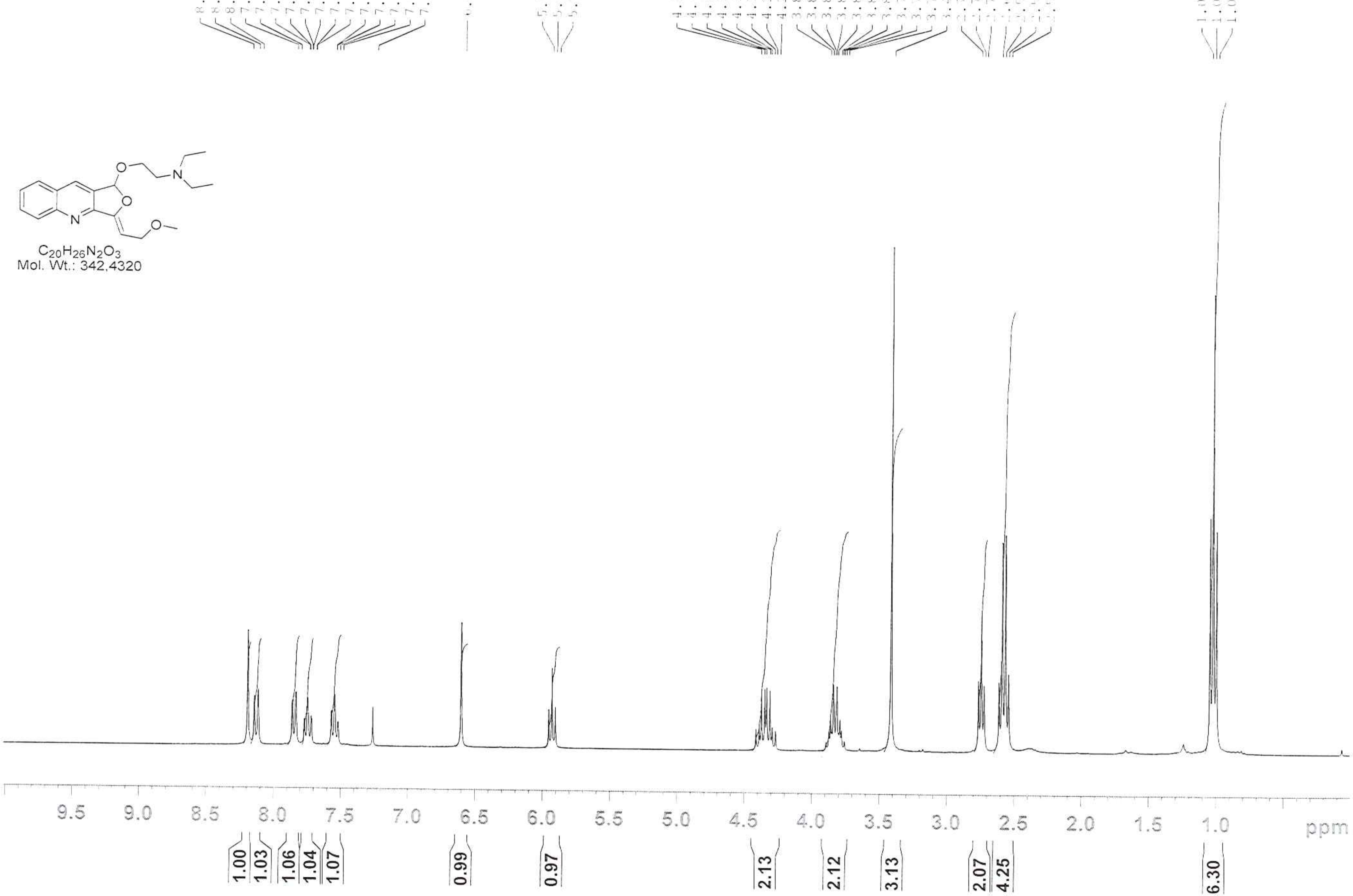


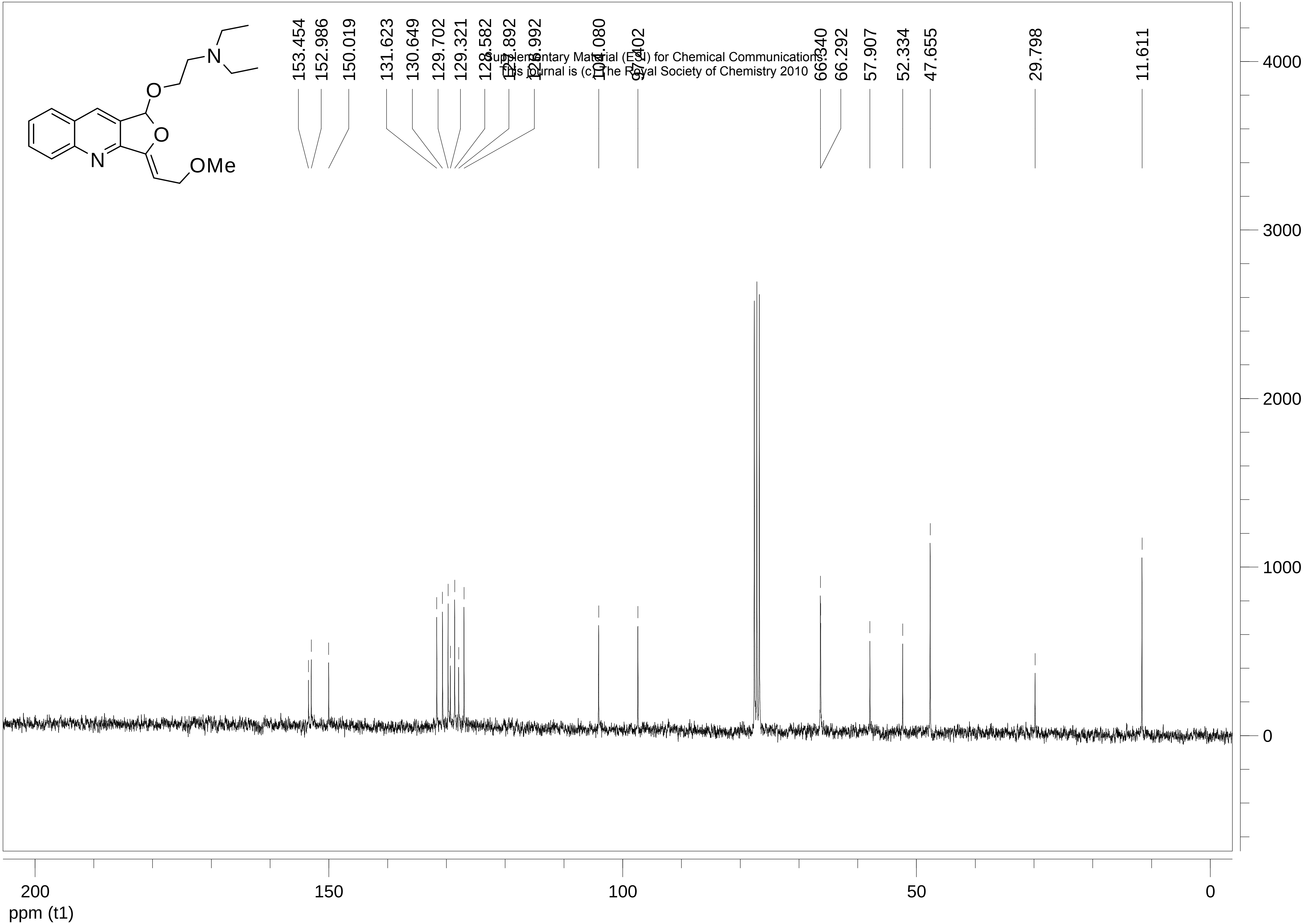
$C_{22}H_{30}N_2O_2$
Mol. Wt.: 354,4858



1H - CDCl3 - 300MHz

$C_{20}H_{26}N_2O_3$
Mol. Wt.: 342,4320

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66.292
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2000
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0
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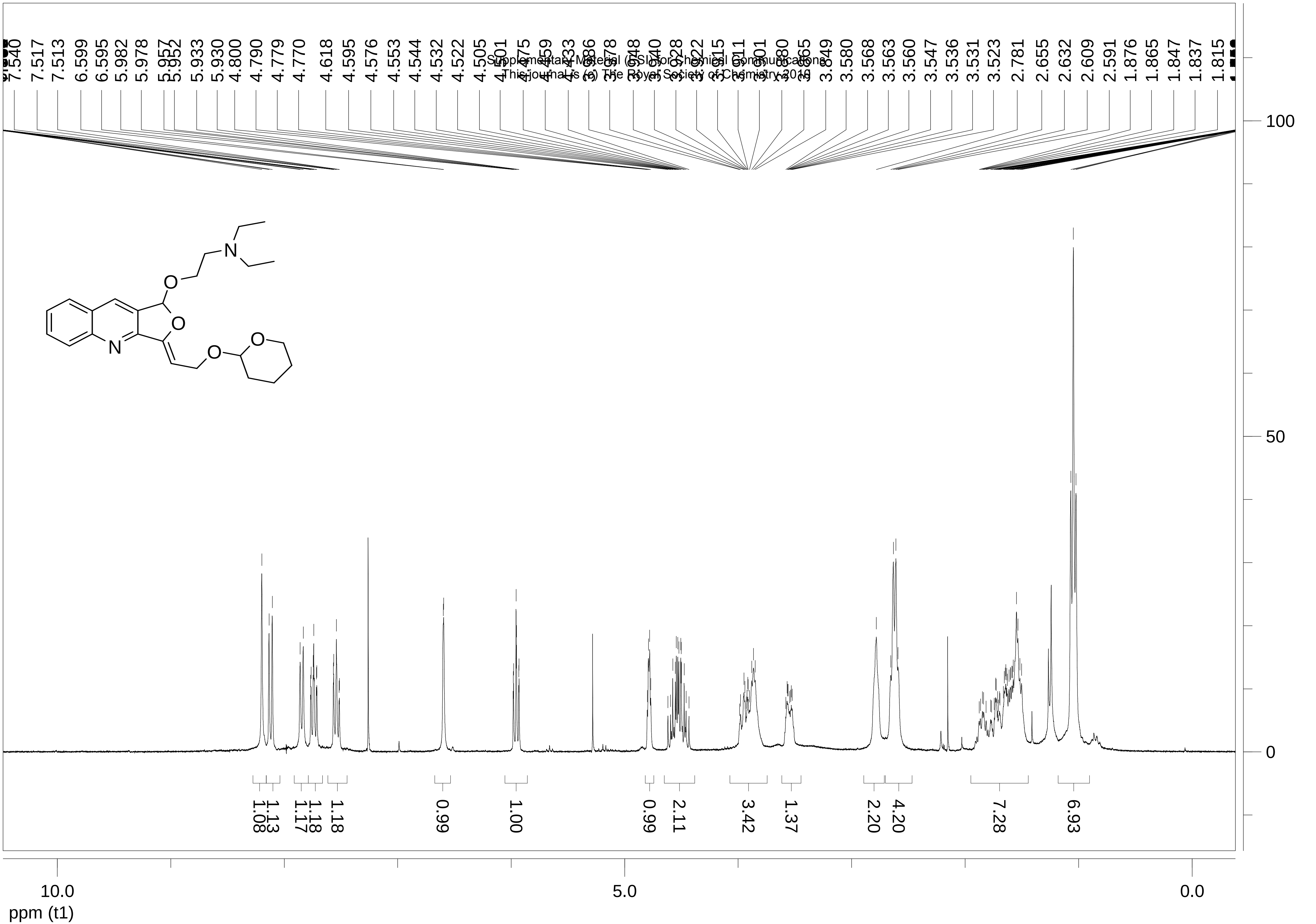
50
0
ppm (t1)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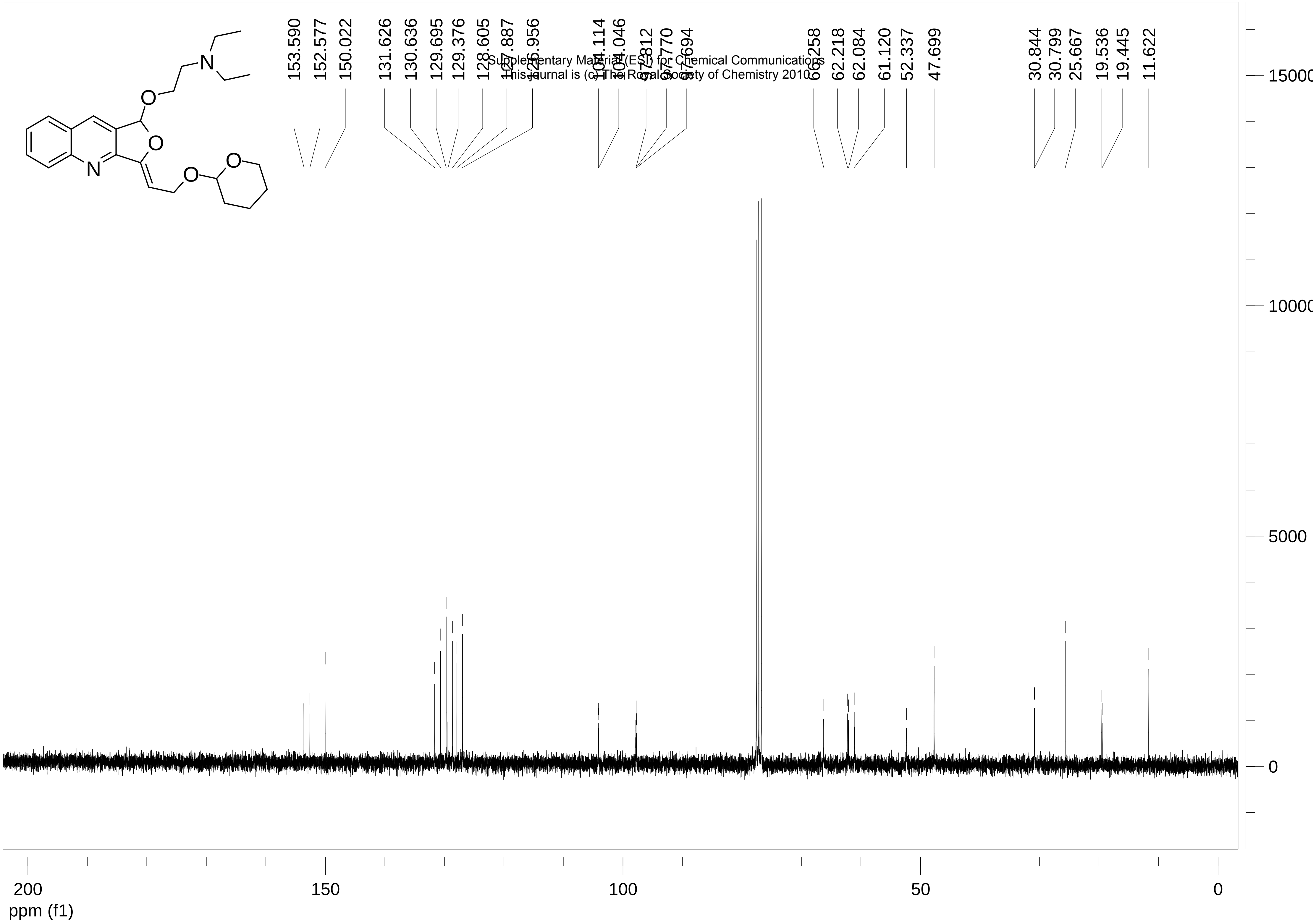
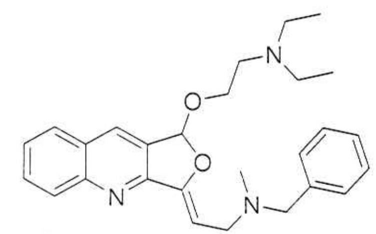
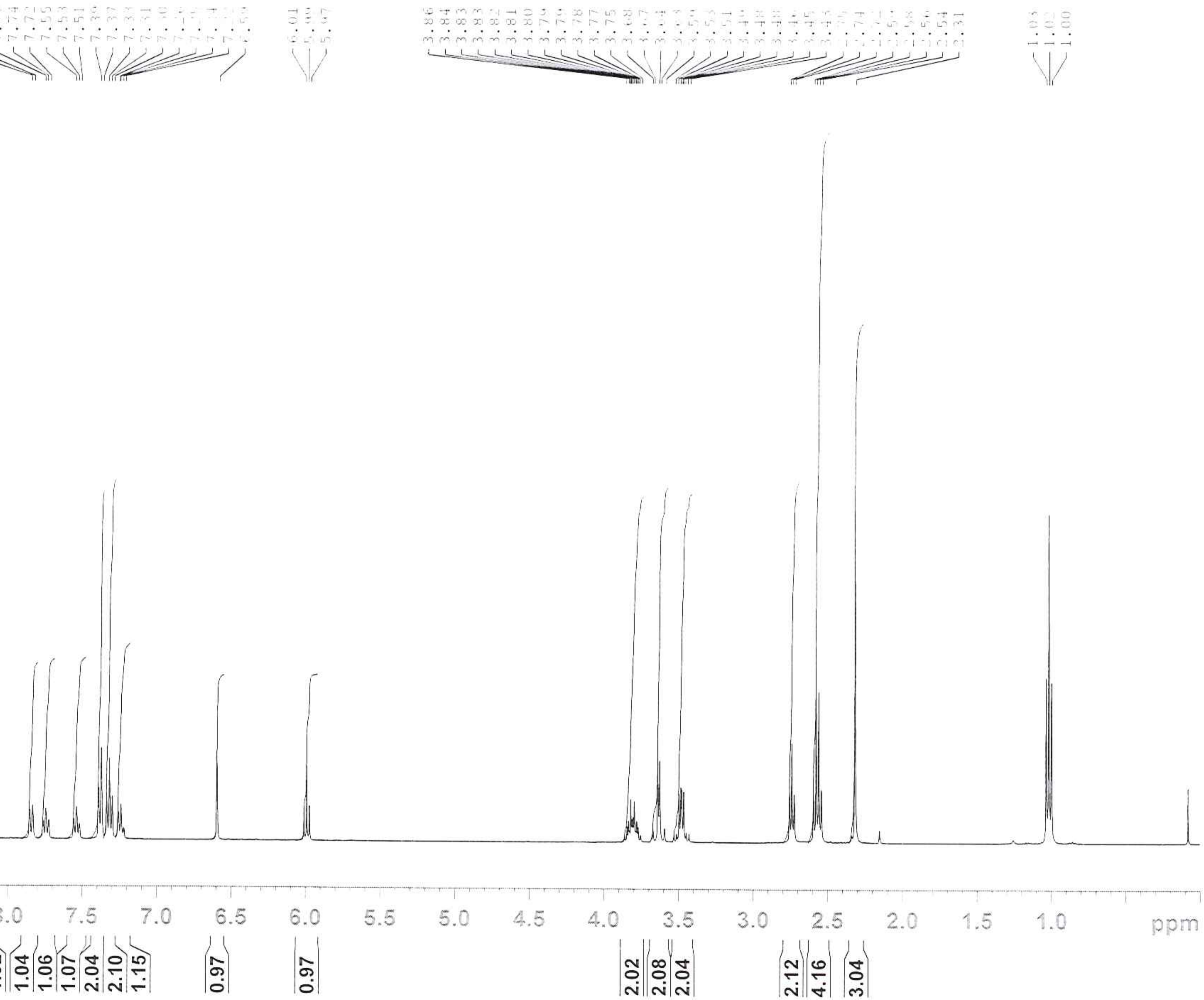
4.779
4.770
4.618
4.595
4.576
4.553
4.544
4.532
4.522
4.505
3.580
3.568
3.563
3.560
3.547
3.536
3.531
3.523
2.781
2.655
2.632
2.609
2.591
1.876
1.865
1.847
1.837
1.815
100
50
0
N
O
O
O
O
N
1.08
1.13
1.17
1.18
1.18
0.99
1.00
0.99
2.11
3.42
1.37
2.20
4.20
7.28
6.93
10.0
5.0
0.0
ppm (t1)


153.590
152.577
150.022
131.626
130.636
129.695
129.376
128.605
127.887
126.956
104.114
104.046
62.218
62.084
61.120
52.337
47.699
30.844
30.799
25.667
19.536
19.445
11.622
15000
10000
5000
0
200
150
100
50
0
ppm (f1)
N
O

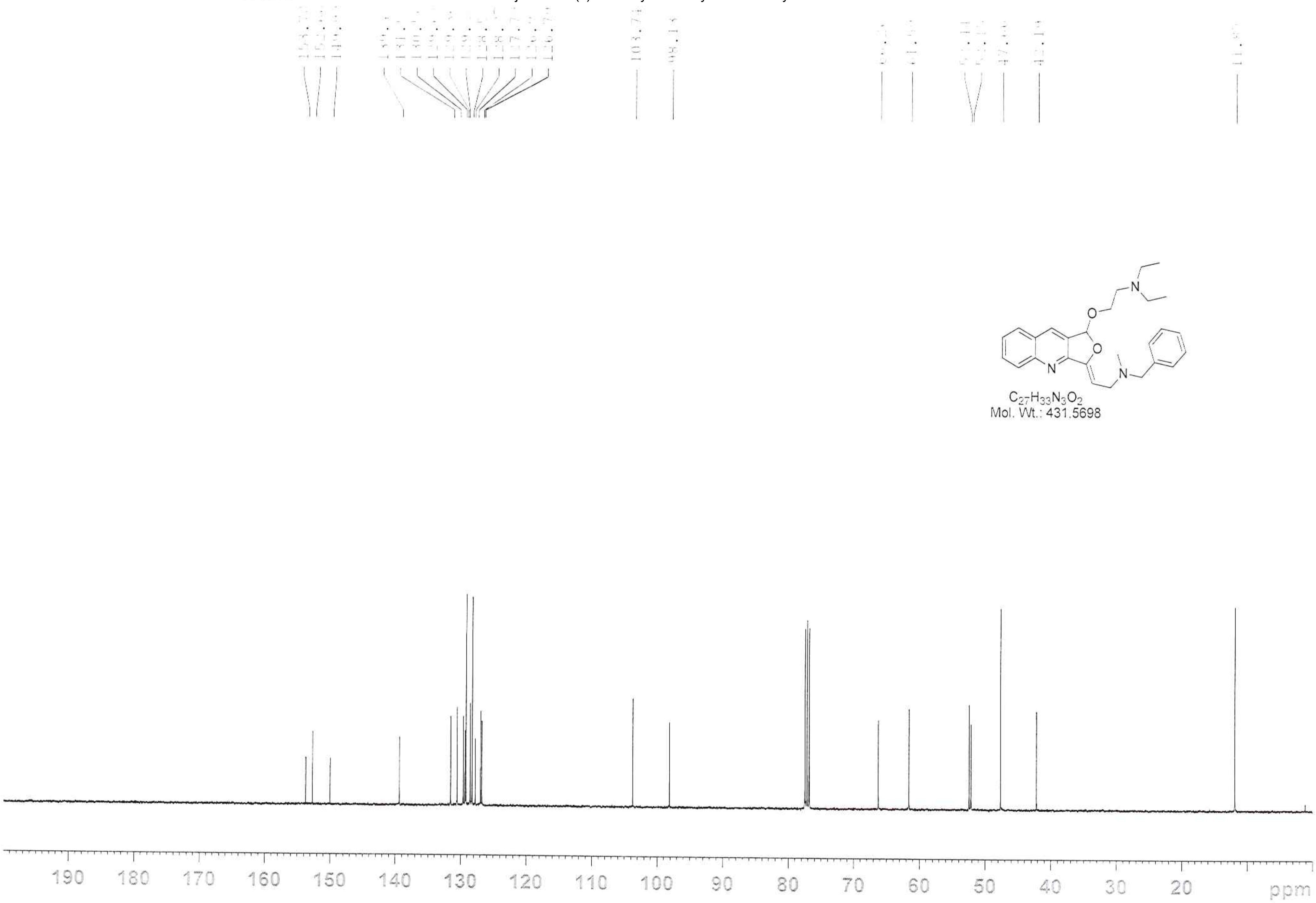
1H - CDCl3 - 400MHz



$C_{27}H_{33}N_3O_2$
Mol. Wt.: 431,5698



13C NMR - CDCl3 - 100MHz



Supplementary Material (ESI) for Chemical Communications
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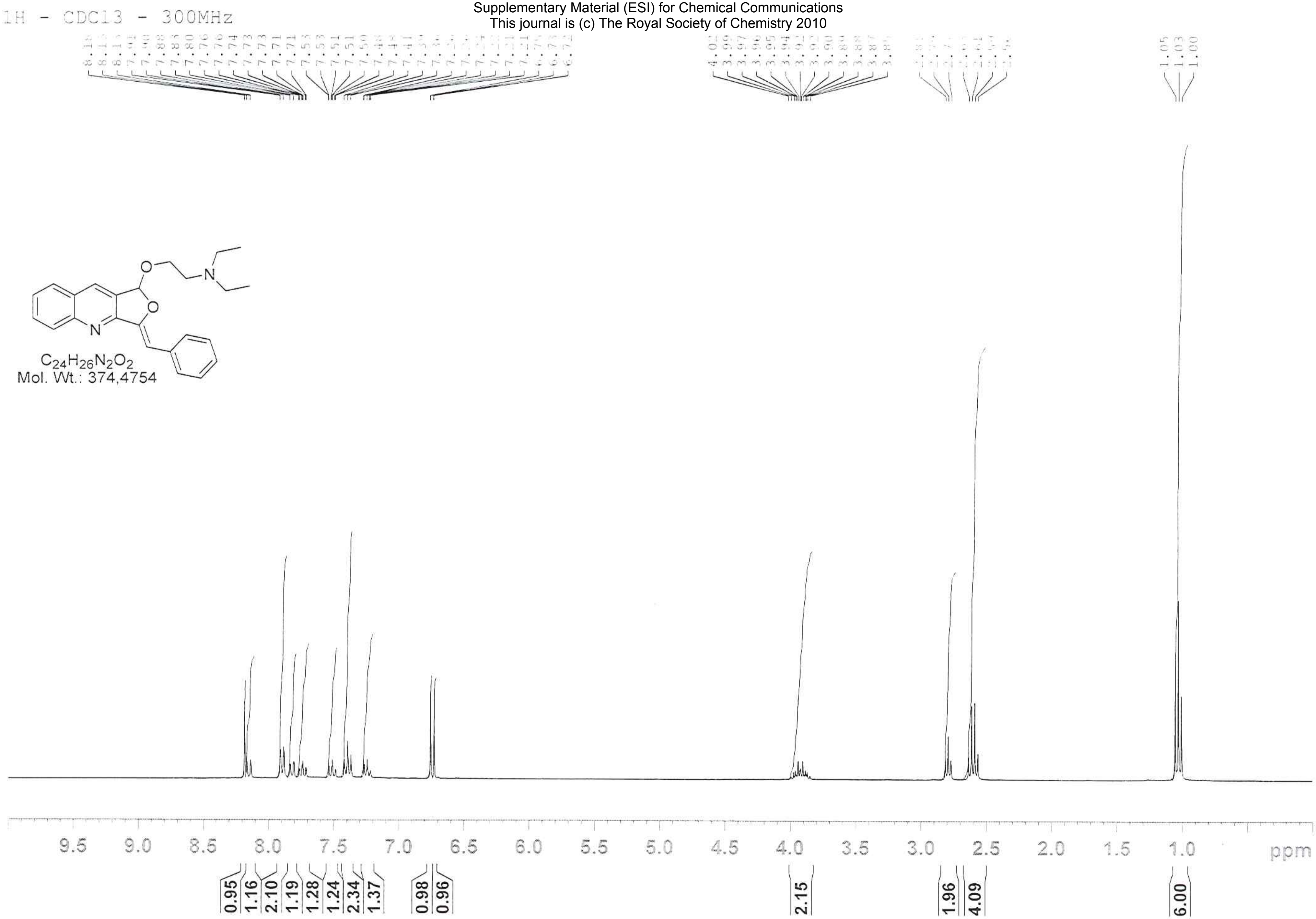
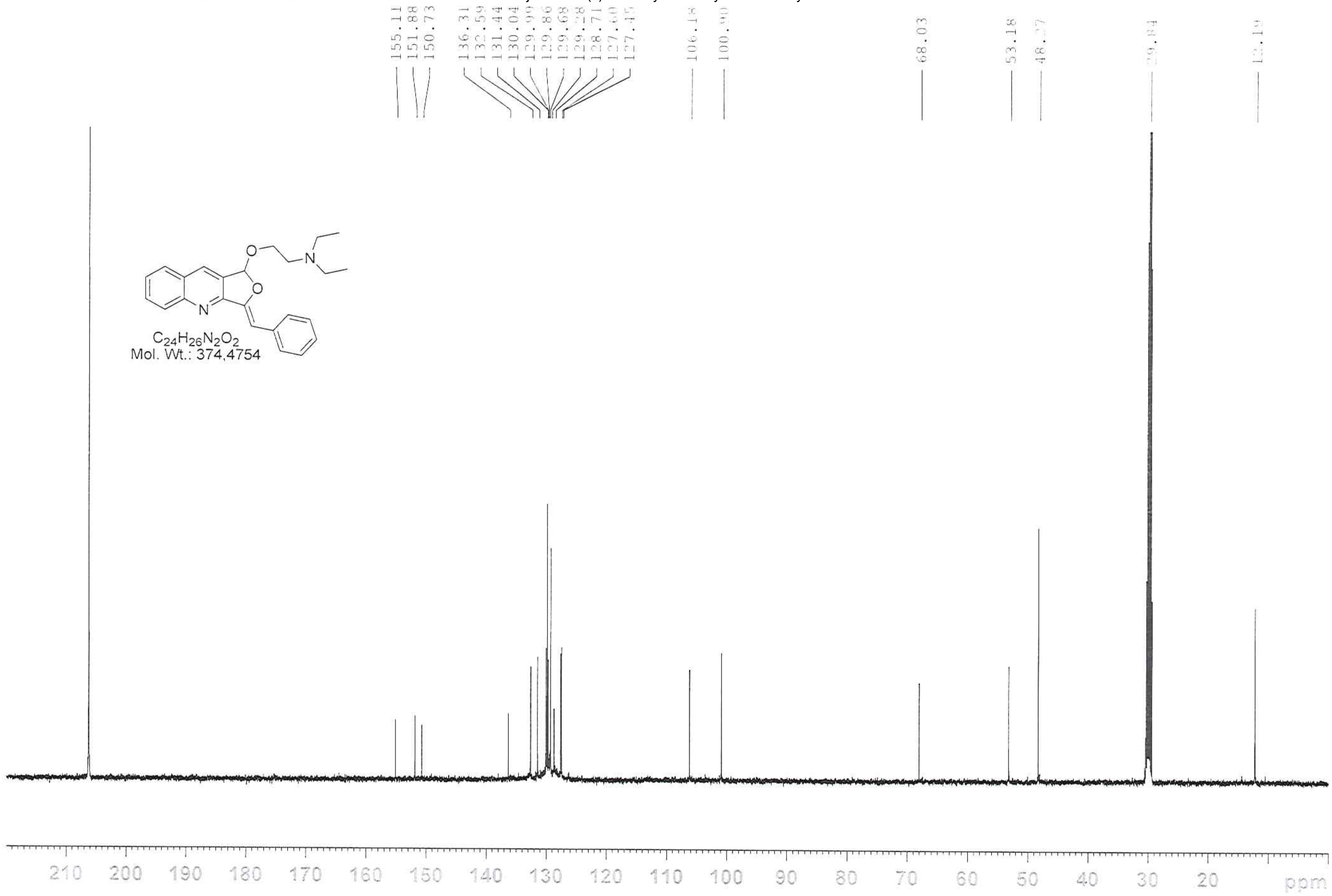
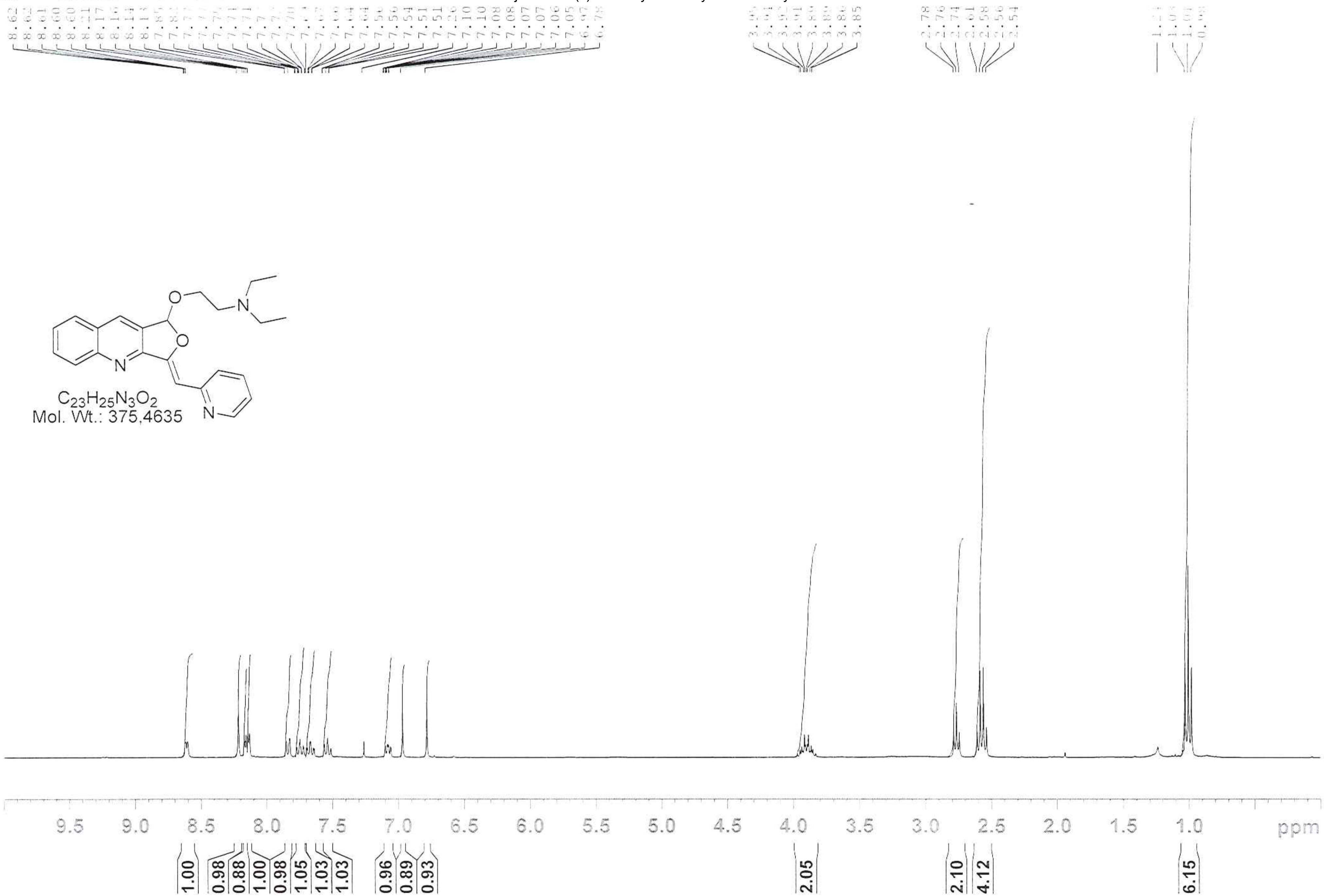


13C NMR - CO(CD3)2 - 125MHz

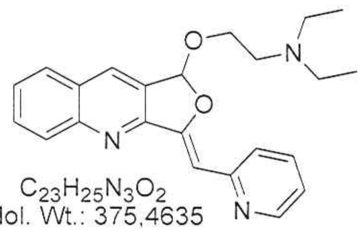


1H - CDCl3 - 300MHz

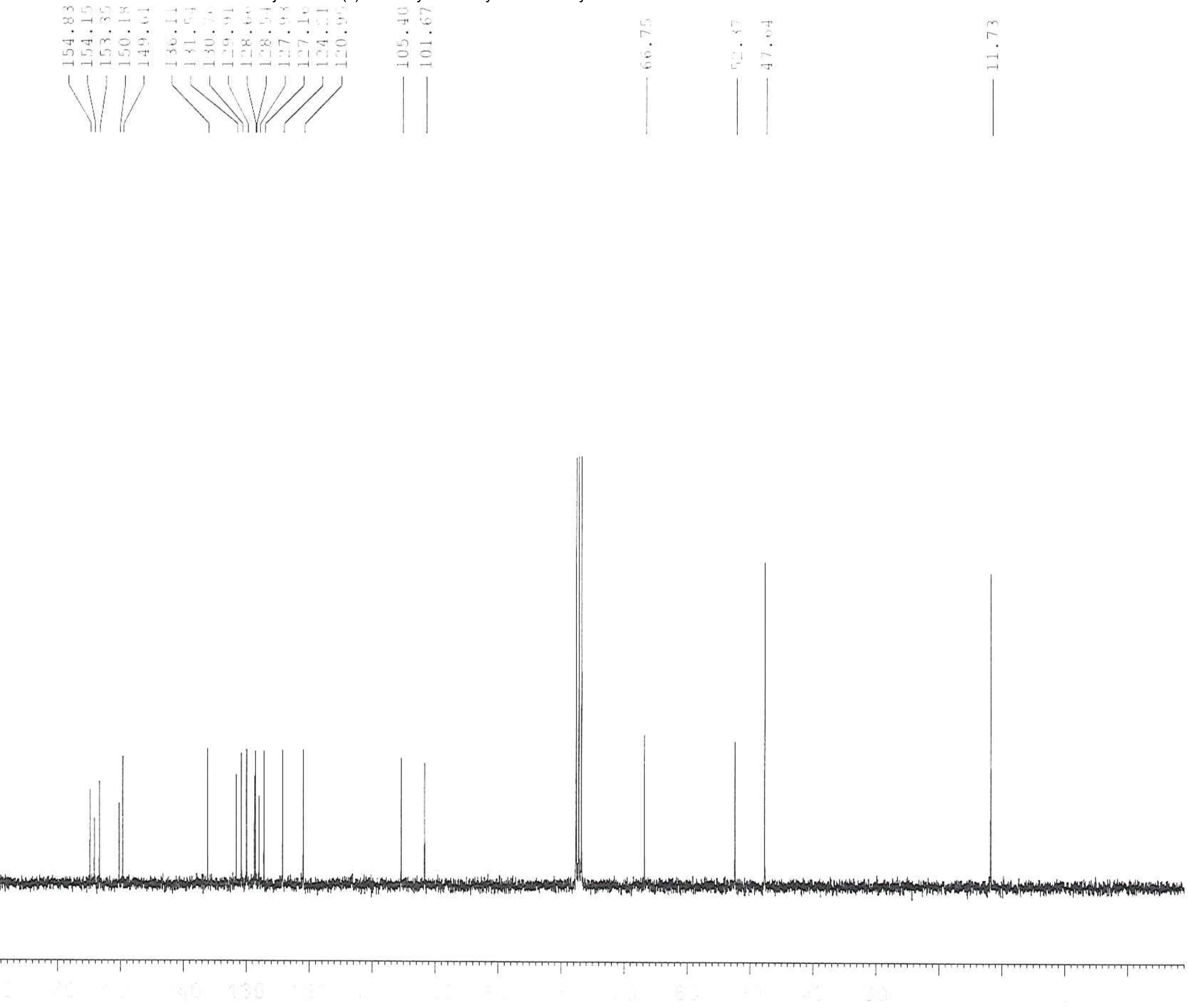


$C_{23}H_{25}N_3O_2$
Mol. Wt.: 375,4635

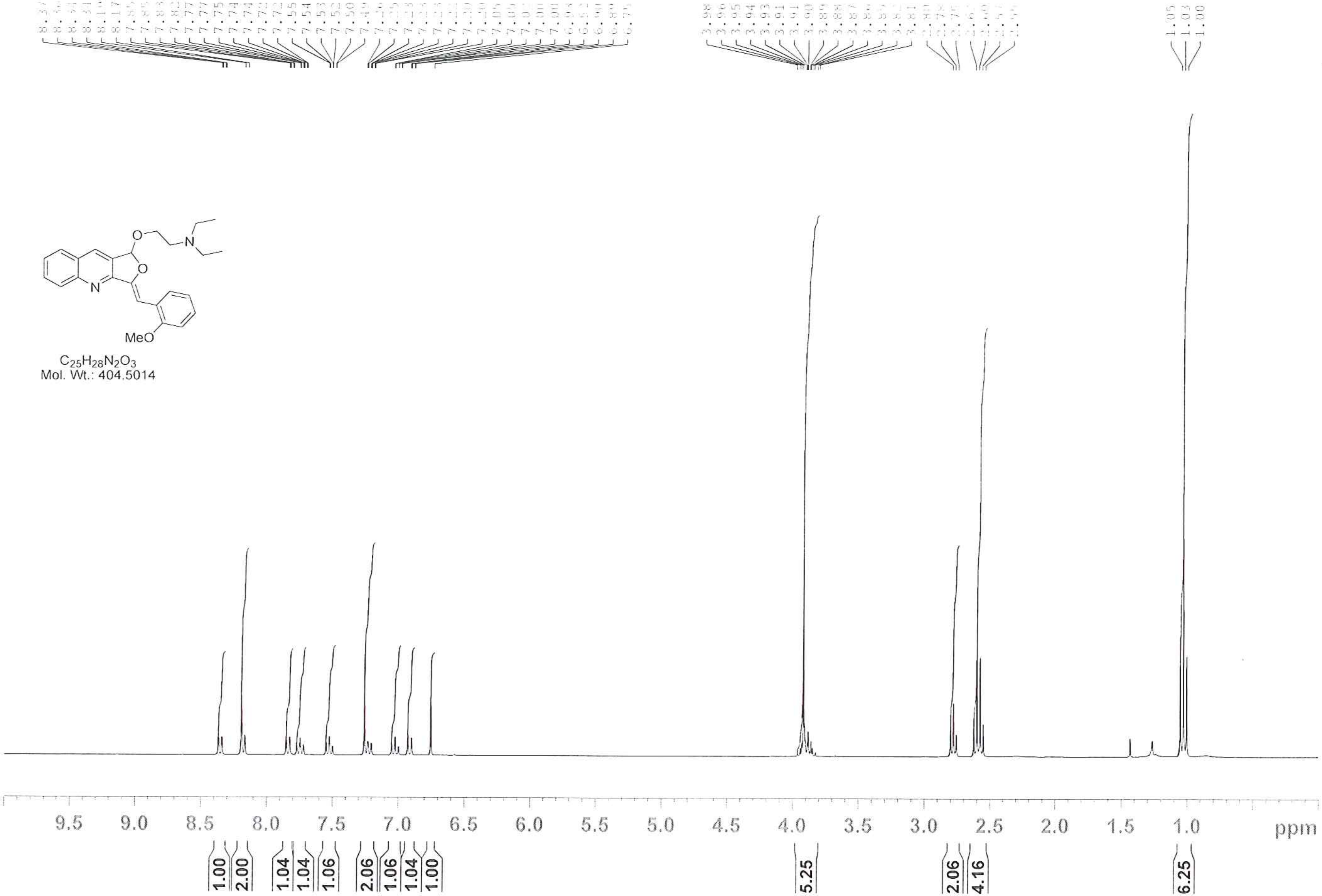
13C NMR - CDCl3 - 75MHz



$C_{23}H_{25}N_3O_2$
Mol. Wt.: 375,4635

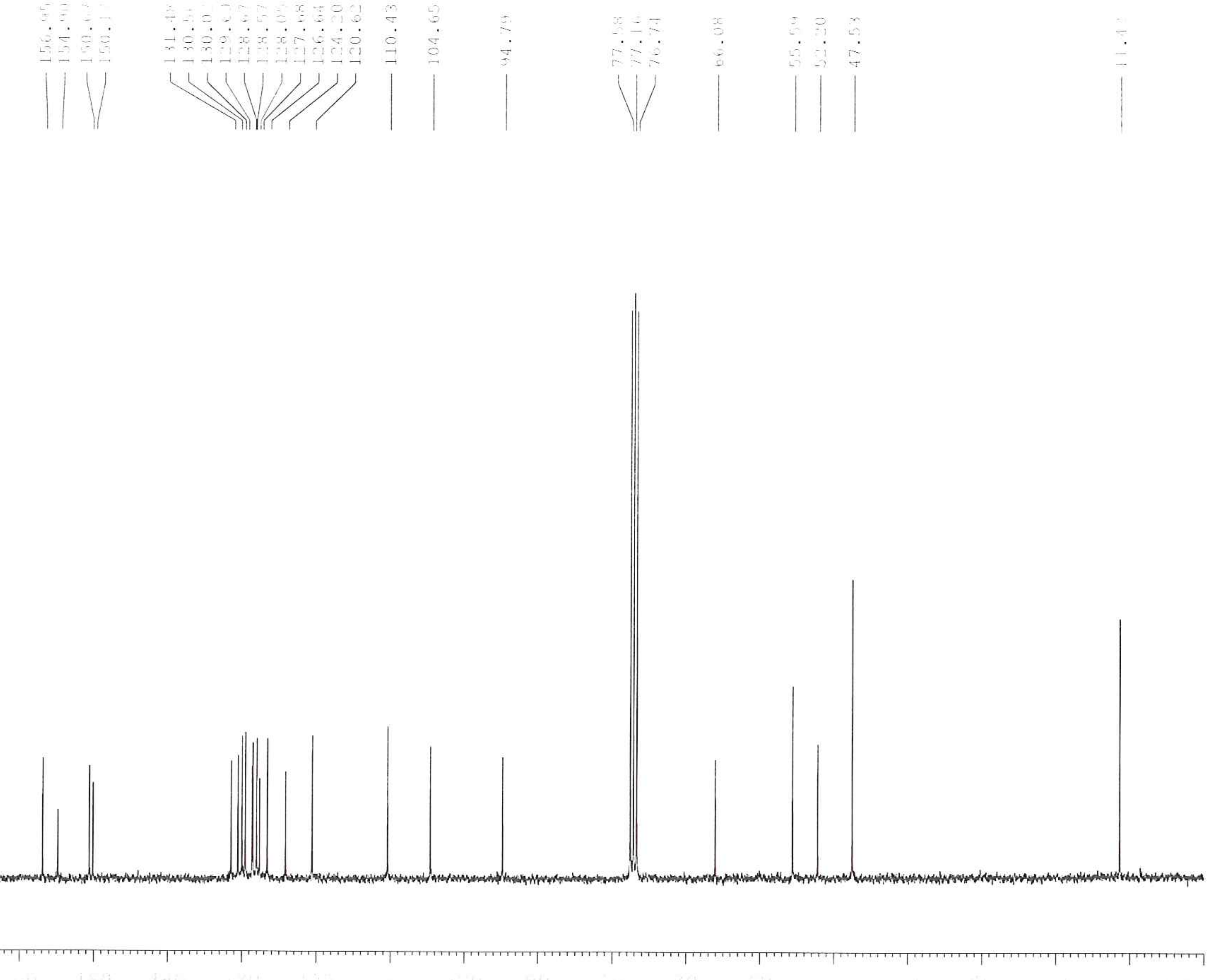


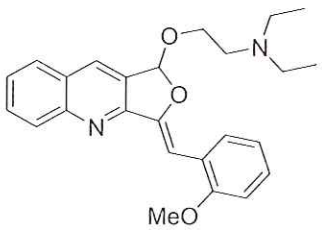
1H - CDCl3 - 300MHz



$C_{25}H_{28}N_2O_3$
Mol. Wt.: 404.5014

13C NMR - CDCl3 - 75MHz





$C_{25}H_{28}N_2O_3$
Mol. Wt.: 404,5014