Polymer grafted layered double hydroxides (LDHs-g-POEGMA): a highly efficient reusable solid catalyst for the synthesis of chromene incorporated dihydroquinoline derivatives under solvent-free conditions

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Content

1. Experimental

i). Anchoring of BTPT onto LDHs surface (LDHs-BTPT)

The mixture of 0.7g of LDHs and 20 mL of dry toluene was stirred at 100 °C. Then, 0.724 g (2 mmol) of BTPT in 10 mL dry toluene was injected into the flask under N_2. The reaction was conducted for 24 h. The crude product was filtered off and washed with DCM for three times to remove all unreacted BTPT. The final product was dried under vacuum overnight.

ii). Preparation of LDHs-*g*-POEGMA by RAFT polymerization

2 g of PEGMA, 0.3 g of LDHs-BTPT, 20 mg of AIBN, and 4 mL of dry toluene were placed in a round bottom flask. The polymerization reaction was performed at 80 °C for 24 h under N_2. The mixture was precipitated in diethyl ether and washed three times with methanol. The product was dried under vacuum at 40 °C overnight (yield, 60%).

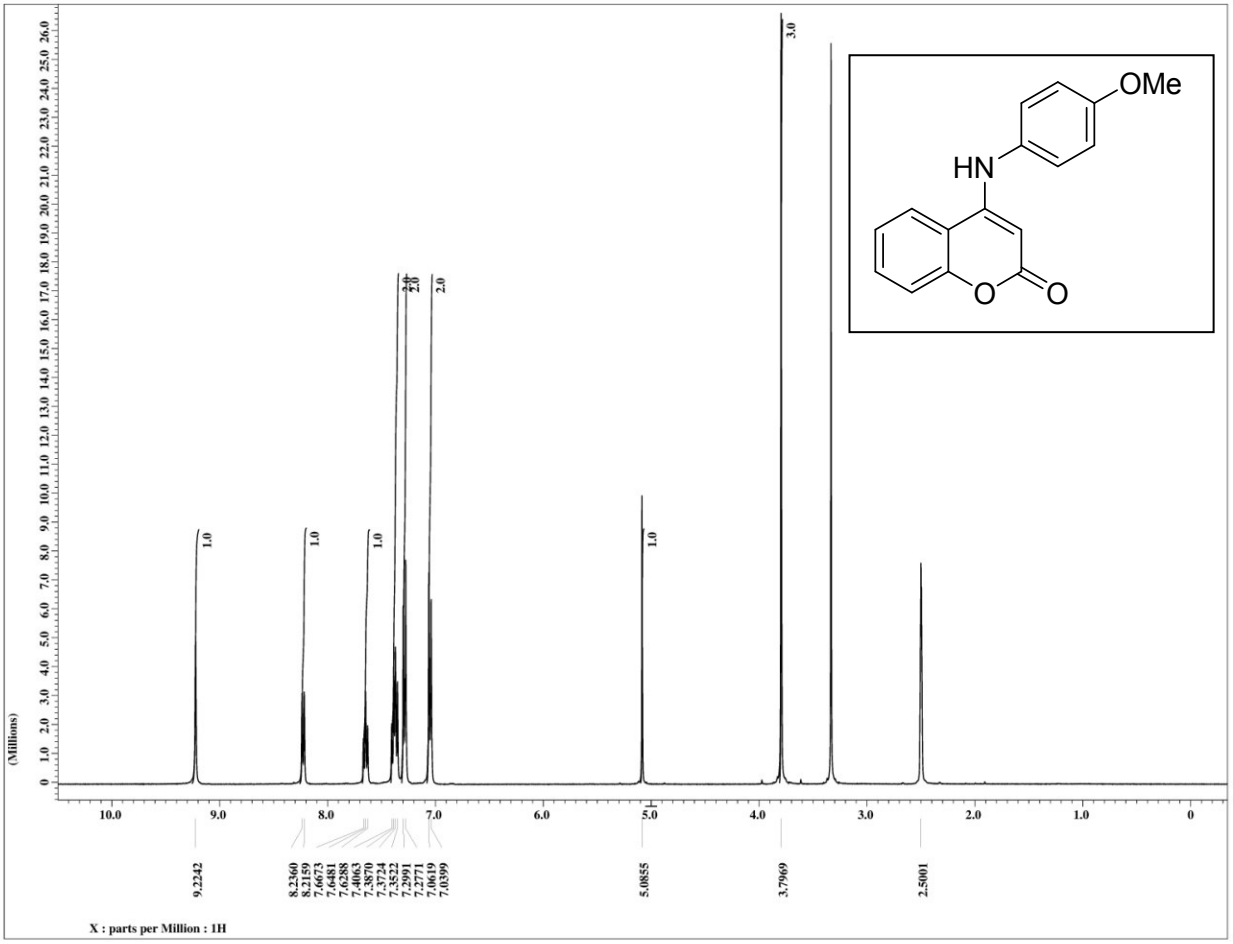
iii). Preparation of 9-methoxy-7-o-tolyl-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (4a)

LDHs-*g*-POEGMA (5 mg) was added to a mixture of 4-hydroxy-2*H*-chromen-2-one1 (**1**, 1 mmol), 4-methoxybenzenamine (**2a** 1 mmol), and 2-methylbenzaldehyde (**3a**, 1 mmol), was stirred at 60 °C under solvent-free conditions for 10 min (Table 2, **entry 4a**). After the completion of the reaction (confirmed by TLC), and cooled to RT, then EA (15 mL) was added and the reaction mixture was filtered. The solid catalyst was washed with acetone (2 × 10 mL) and dried under vacuum before reuse. Pure **4a** was afforded by evaporation of the solvent followed by recrystallization from ethanol.

2. Physical and spectral data of intermediates, enamine (A) and imines (B).

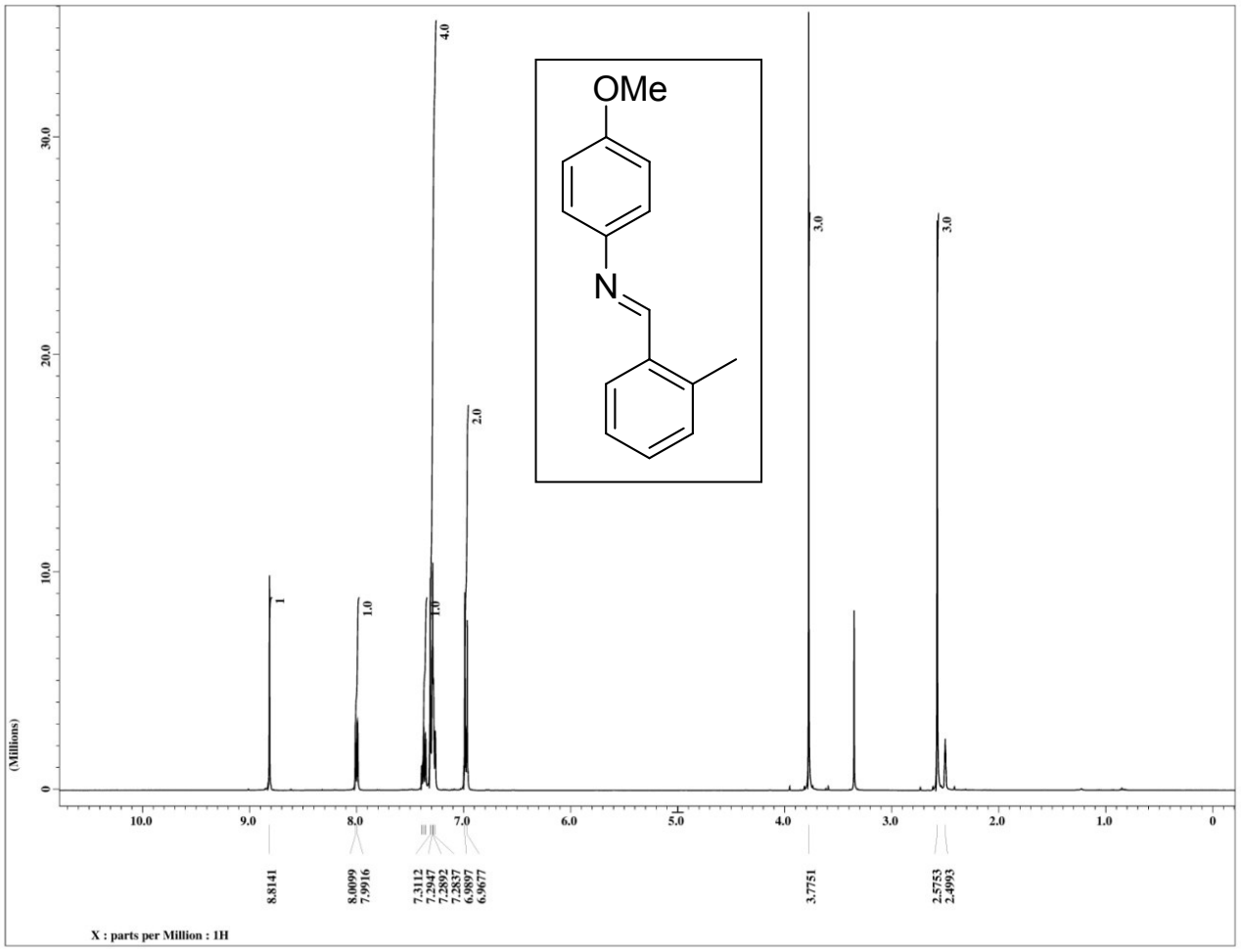
i). 4-(4-Methoxyphenylamino)-2*H*-chromen-2-one (**A**)

Yield 95%; white solid; mp 240-243 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.22 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.40-7.35 (m, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 5.08 (s, 1H), 3.79 (s, 3H).



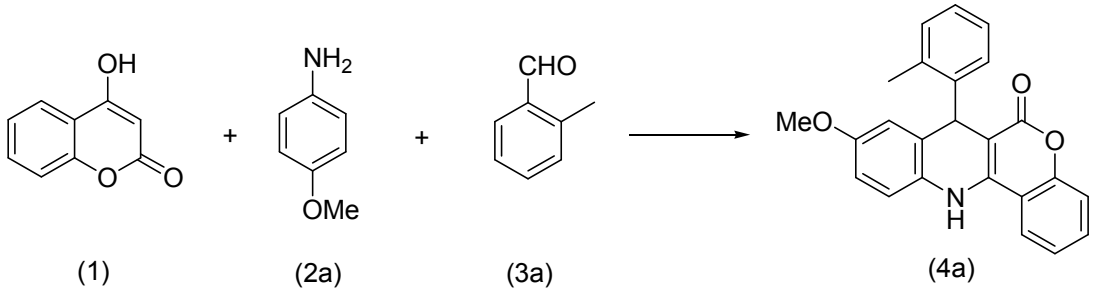
ii). (*E*)-4-Methoxy-*N*-(2-methylbenzylidene)aniline (**B**).

Yield 85%; white solid; mp 58-60 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.81 (s, 1H), 8.00 (d, J = 7.3 Hz, 1H), 7.39-7.35 (m, 1H), 7.31-7.26 (m, 4H), 6.97 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.57 (s, 3H).



3. Calculation of green chemistry metrics

Green chemistry calculations for **LDHs-*g*-POEGMA** catalyzed 9-methoxy-7-o-tolyl-7H-chromeno[4,3-b]quinolin-6(12H)-one (**4a**):



(1) (2a) (3a) (4a)

E-factor = [0.162 g (4-hydroxy-2H-chromen-2-one **1**) + 0.123 g (4-methoxybenzenamine 2a) + 0.120 g (2-methylbenzaldehyde 3a) – 0.351 g (product **4a**)]/ 0.351 g

E-factor = **0.15**

Process mass intensity (PMI) = E-factor + 1

= 0.15 + 1

PMI = **1.15**

Atom economy (AE) = MW of product ÷ ∑(MW of stoichiometric reactants) × 100

= 369-.14 (4) ÷ [162.03 (**1**) + 123.07 (**2a**) + 120.06 (**3a**)] × 100

AE = 91.11%

Reaction mass efficiency (RME) = mass of product /∑(mass of stoichiometic reactants) × 100

= 0.351 g (**4a**)/ [0.16203 (**1**) + 0.12307 (**2a**) + 0.12006 (**3**)] × 100

= [0.351/ 0.40516] × 100

RME = 86.63%

4. Physical and spectral data of titled compounds (4a-z, 4a´-d´)

9-Methoxy-7-*o*-tolyl-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4a**): Yield 95%; Light yellow solid; mp 274-276 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.80 (s, 1H), 8.30 (dd, *J* = 1.1, 8.2 Hz, 1H), 7.63-7.59 (m, 1H), 7.46-7.42 (m, 1H), 7.35-7.28 (m, 2H), 7.09-7.04 (m, 2H), 76.98-6.96 (m, 2H), 6.79 (dd, *J* = 2.0, 9.3 Hz, 1H), 6.50 (d, *J* = 6.9 Hz, 1H), 5.43 (s, 1H), 3.63 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 155.6, 152.1, 147.2, 143.8, 133.7, 131.6, 129.9, 128.8, 128.7, 126.5, 126.3, 125.9, 123.6, 122.6, 117.5, 116.8, 95.9, 55.1, 37.1, 19.7; HRMS (ESI, m/z): calcd for $C_{24}H_{19}NO_3$ (M+H$^+$) 369.1365, found: 369.1361.

7-(3-Chlorophenyl)-9-fluoro-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4b**): Yield 92%; White solid; mp 326-328 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.99 (s, 1H), 8.30 (d, *J* = 7.3 Hz, 1H), 7.64-7.60 (m, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.40-7.35 (m, 3H), 7.25-7.13 (m, 4H), 7.10-7.05 (m, 1H), 5.30 (s, 1H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 158.5 (d, *J* = 238.2 Hz), 152.2, 149.1, 143.9, 133.0, 131.9, 130.4, 126.9, 126.4, 125.8, 125.4, 125.3, 123.7, 122.7, 118.0, 117.9, 116.9, 115.6, 115.4, 114.8, 114.6, 113.2, 94.6, 40.6 ; HRMS (ESI, m/z): calcd for $C_{22}H_{13}ClFNO_2$ (M+H$^+$) 377.0619, found: 377.0612.

7-(4-Chlorophenyl)-8,10-dimethoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4c**): Yield 94%; Light yellow solid; mp 279-281 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.84 (s, 1H), 8.29 (d, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 6.9 Hz, 1H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26-7.18 (m, 4H), 6.62 (d, *J* = 1.8 Hz, 1H), 6.24 (d, *J* = 1.8 Hz, 1H), 5.23 (s, 1H), 3.77 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 159.7, 157.5, 152.1, 145.5, 143.6, 137.2, 131.7, 130.5, 129.2, 127.8, 123.7, 122.6, 116.8, 113.3, 104.6, 91.7, 94.1, 93.3, 55.5, 55.1, 34.7 ; HRMS (ESI, m/z): calcd for $C_{24}H_{18}ClNO_4$ (M+H$^+$) 419.0924, found: 419.0928.

7-(2-Chlorophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4d**): Yield 93%; Light yellow solid; mp 278-280 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.88 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 6.9 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.40-7.36 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.19-7.12 (m, 2H), 6.83 (dd, *J* = 2.1, 8.0 Hz, 1H), 6.75 (d, *J* = 6.9 Hz, 1H), 5.15 (s, 1H), 3.64 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.2,

155.6, 152.3, 145.2, 144.1, 131.8, 130.1, 129.3, 127.9, 127.8, 124.9, 123.7, 117.7, 116.1, 113.4, 113.2, 94.2, 55.1, 38.0; HRMS (ESI, m/z): calcd for $C_{23}H_{16}ClNO_3$ ($M+H^+$) 389.0819, found: 389.0811.

9-Fluoro-7-*o*-tolyl-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4e**): Yield 95%; White solid; mp 287-289 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.87 (s, 1H), 8.29 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 6.9 Hz, 1H), 7.43 (t, J = 6.9 Hz, 1H), 7.37-7.31 (m, 2H), 7.10-6.97 (m, 5H), 6.74 (dd, J = 2.1, 8.2 Hz, 1H), 5.41 (s, 1H), 2.62 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 158.3 (d, J = 236.2 Hz), 146.9, 143.4, 133.8, 131.8, 129.9, 128.8, 126.8, 126.5, 126.1, 123.6, 122.6, 118.0, 117.9, 116.8, 115.1, 114.9, 114.4, 114.2, 113.2, 96.3, 37.0, 19.6; HRMS (ESI, m/z): calcd for $C_{23}H_{16}FNO_2$ ($M+H^+$) 357.1165, found: 357.1160.

7-(3-Chlorophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4f**): Yield 91%; Light yellow solid; mp 265-267 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1H), 8.32 (d, J = 7.3 Hz, 1H), 7.63 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.39-7.22 (m, 4H), 7.15 (s, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 5.74 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ: 160.2, 155.6, 152.3, 145.2, 144.1, 131.8, 130.1, 129.3, 127.9, 127.8, 124.9, 123.7, 117.7, 116.1, 113.4, 113.2, 94.2, 55.1, 38.0; HRMS (ESI, m/z): calcd for $C_{23}H_{16}ClNO_3$ ($M+H^+$) 389.0819, found: 389.0824.

7-(3-Fluorophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4g**) Yield 91%; Light yellow solid; mp 255-257 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.89 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.37-7.24 (m, 3H), 7.07 (t, J = 7.3 Hz, 2H), 6.97-6.92 (m, 1H), 6.85-6.82 (m, 2H), 5.28 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 155.9, 152.2, 150.0, 143.7, 131.8, 130.2, 128.9, 124.8, 123.7, 123.1, 122.7, 117.5, 116.9, 114.1, 113.5, 113.4, 112.9, 94.2, 55.2, 40.9; HRMS (ESI, m/z): calcd for $C_{23}H_{16}FNO_3$ ($M+H^+$) 373.1114, found: 373.1120.

9-Methoxy-7-(2-nitrophenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4h**): Yield 93%; Yellow solid; mp 263-265 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.98 (s, 1H), 8.32 (d, J = 7.6 Hz, 1H), 8.11-8.10 (m, 1H), 8.00-7.97 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.36-7.33 (m, 2H), 6.87-6.84 (m, 2H),

5.43 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 156.0, 152.2, 149.2, 147.7, 143.8, 134.0, 131.9, 129.9, 128.9, 124.3, 123.7, 122.8, 121.6, 121.4, 117.7, 116.9, 114.2, 113.8, 113.3, 94.0, 55.2, 40.8; HRMS (ESI, m/z): calcd for $C_{23}H_{16}N_2O_5$ ($M+H^+$) 400.1059, found: 400.1053.

7-(2-Bromophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4i**): Yield 90%; Light yellow solid; mp 302-304 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.43-7.39 (m, 3H), 7.35-7.30 (m, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.84-6.79 (m, 2H), 5.24 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 155.9, 152.2, 146.6, 143.6, 131.6, 131.1, 129.3, 128.9, 124.9, 123.6, 122.7, 119.3, 117.5, 116.8, 114.0, 113.4, 94.3, 55.2, 40.7; HRMS (ESI, m/z): calcd for $C_{23}H_{16}BrNO_3$ ($M+H^+$) 434.2820, found: 434.2825.

9-Fluoro-7-(4-isopropylphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4j**): Yield 96%; White solid; mp 322-324 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.95 (s, 1H), 8.30 (d, J = 7.3 Hz, 1H), 7.66-7.61 (m, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.38-7.35 (m, 2H), 7.16-7.03 (m, 6H), 5.22 (s, 1H), 2.78-2.71 (m, 1H), 1.09 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 158.5 (d, J = 238.2 Hz), 152.2, 146.4, 144.3, 143.7, 131.8, 126.9, 126.3, 123.7, 122.7, 117.8, 116.9, 115.6, 115.3, 114.5, 114.2, 113.3, 95.4, 40.9, 32.9, 23.7 ; HRMS (ESI, m/z): calcd for $C_{25}H_{20}FNO_2$ ($M+H^+$) 385.1478, found: 385.1472

9-Fluoro-7-(3,4,5-trimethoxyphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4k**): Yield 95%; White solid; mp 328-330 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.95 (s, 1H), 8.30 (dd, J = 1.0, 8.0 Hz, 1H), 7.65-7.61 (m, 1H), 7.46-7.42 (m, 1H), 7.38-7.35 (m, 2H), 7.20 (d, J = 8.2 Hz, 1H), 7.09-7.04 (m, 1H), 6.55 (s, 2H), 5.22 (s, 1H), 3.65 (s, 6H), 3.56 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4 158.0 (d, J = 240.2 Hz), 152.8, 152.2, 143.7, 142.7, 136.2, 131.9, 131.8, 126.1, 123.7, 122.7, 117.8, 117.6, 116.8, 115.3, 114.5, 114.3, 113.3, 104.5, 95.1, 59.8. 55.8, 41.1; HRMS (ESI, m/z): calcd for $C_{25}H_{20}FNO_5$ ($M+H^+$) 433.1326, found: 433.1319.

7-(4-Chlorophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4l**):

Yield 93%; Light yellow solid; mp 274-276 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.85 (s, 1H), 8.29 (d, J = 7.7 Hz, 1H), 7.64-7.57 (m, 2H), 7.43-7.39 (m, 2H), 7.34-7.29 (m, 2H), 7.26 (br s, 2H), 6.83-6.78 (m, 2H), 5.24 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 155.9 152.2, 146.2, 143.6, 137.7, 130.8, 130.0, 128.9, 128.3, 124.9, 123.6, 122.7, 117.5, 116.8, 114.0, 113.4, 94.4, 55.2, 40.6; HRMS (ESI, m/z): calcd for $C_{23}H_{16}ClNO_3$ (M+H$^+$) 389.0819, found: 389.0810.

7-(4-Ethoxyphenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4m**): Yield 96%; Light yellow solid; mp 265-267 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.81 (s, 1H), 8.29 (dd, J = 1.0, 8.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.44-7.40 (m, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.82-6.78 (m, 2H), 6.74 (d, J = 8.1 Hz, 2H), 5.16 (s, 1H), 3.91-3.87 (q, 2H), 3.66 (s, 3H), 1.23 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 156.9, 155.8, 152.1, 143.3, 139.5, 131.5, 129.0, 128.0, 125.8, 123.6, 122.6, 117.2, 116.8, 114.1, 114.0, 113.5, 113.1, 95.1, 62.8, 55.1, 40.3, 14.5; HRMS (ESI, m/z): calcd for $C_{25}H_{21}NO_4$ (M+H$^+$) 399.1471, found: 399.1465.

9-Methoxy-7-(4-methoxyphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4n**): Yield 95%; Light yellow solid; mp 279-281 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.82 (s, 1H), 8.29 (d, J = 7.3 Hz, 1H), 7.61 (t, J = 6.9 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 7.7 Hz, 2H), 6.83-6.75 (m, 4H), 5.16 (s, 1H), 3.66 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 155.8, 155.7, 152.2, 143.2, 138.0, 131.5, 129.0, 128.0, 123.6, 122.7, 117.2, 116.8, 115.0, 113.7, 95.3, 55.2, 54.9, 40.3; HRMS (ESI, m/z): calcd for $C_{24}H_{19}NO_4$ (M+H$^+$) 385.1314, found: 385.1311.

7-(4-Chlorophenyl)-9-fluoro-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4o**): Yield 94%; White solid; mp 273-275 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.98 (s, 1H), 8.31 (d, J = 7.7 Hz, 1H), 7.84-7.82 (m, 1H), 7.69-7.63 (m, 1H), 7.54-7.46 (m, 2H), 7.40-7.35 (m, 2H), 7.28 (br s, 2H), 7.14-7.05 (m, 2H), 5.30 (s, 1H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 15.3 (d, J = 236.2 Hz), 146.9, 143.4, 133.8, 131.8, 129.9, 128.8, 126.8, 126.5, 126.1, 123.6, 122.6, 118.0, 117.9, 116.8, 115.1, 114.9, 114.4, 114.2, 113.2, 94.6, 41.2; HRMS (ESI, m/z): calcd for $C_{22}H_{13}ClFNO_2$ (M+H$^+$) 377.0619, found: 377.0612.

9-Fluoro-7-(4-nitrophenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12H)-one (**4p**): Yield 92%; White solid; mp 280-282 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.05 (s, 1H), 8.30 (d, J = 7.3 Hz, 1H), 8.11 (d, J = 8.2 Hz, 2H), 7.67-7.63 (m, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.48-7.36 (m, 3H), 7.15-7.07 (m, 2H), 5.46 (s, 1H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.3, 158.3 (d, J = 240.2 Hz), 153.8, 152.3, 146.1, 144.0, 132.0, 131.9, 128.4, 123.7, 122.8, 118.2, 118.1, 116.9, 115.5, 115.1, 114.8, 113.1, 94.2, 40.8; HRMS (ESI, m/z): calcd for $C_{22}H_{13}FN_2O_4$ ($M+H^+$) 388.0859, found: 388.0853.

9-Methoxy-7-(3,4,5-trimethoxyphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4q**): Yield 96%; Light yellow solid; mp 278-280 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1H), 8.30 (d, J = 7.3 Hz, 1H), 7.65-7.60 (m, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 6.9 Hz, 1H), 6.83 (dd, J = 2.1, 8.2 Hz, 1H), 6.54 (s, 2H), 5.19 (s, 1H), 3.68 (s, 3H), 3.63 (s, 6H), 3.56 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 155.8, 152.7, 152.2, 143.6, 143.0, 136.1, 131.6, 128.9, 125.3, 123.6, 122.6, 117.3, 116.8, 114.1, 104.5, 94.6, 59.8, 55.7, 55.2, 41.3; HRMS (ESI, m/z): calcd for $C_{26}H_{23}NO_6$ ($M+H^+$) 445.1525, found: 445.1518.

7-(*o*-Tolyl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[g]quinolin-6(7*H*)-one (**4r**): Yield 94%; White solid; mp 271-273 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.72 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 6.9 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.18 (s, 1H), 7.18-7.03 (m, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 5.38 (s, 1H), 2.78 (t, J = 7.3 Hz, 2H), 2.74-2.68 (m, 2H), 2.62 (s, 3H), 1.93-1.86 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 152.3, 147.8, 142.9, 139.3, 133.6, 130.1, 128.8, 125.6, 124.3, 123.1, 122.5, 116.8, 113.4,112.3, 97.0, 36.9, 32.1, 31.7, 25.1, 19.7; HRMS (ESI, m/z): calcd for $C_{26}H_{21}NO_2$ ($M+H^+$) 379.1572, found: 379.1565.

7-(4-Methoxyphenyl)-9-nitro-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4s**): Yield 92%; Yellow solid; mp 246-248 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.93 (s, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.69-7.60 (m, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.47-7.31 (m, 3H), 6.85-6.82 (m, 1H), 5.42 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 156.0, 154.4, 152.3, 151.7, 147.2, 146.0, 143.9, 136.3, 131.9, 129.6, 128.4, 123.7,

123.4, 117.9, 116.8, 114.2, 93.7, 55.2, 41.1; HRMS (ESI, m/z): calcd for $C_{23}H_{16}N_2O_5$ ($M+H^+$) 400.1059, found: 400.1053.

4-(7,12-Dihydro-9-methoxy-6-oxo-6*H*-chromeno[4,3-*b*]quinolin-7-yl)benzonitrile (**4t**): Yield 93%; Light yellow solid; mp 301-303 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.92 (s, 1H), 8.31 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.61 (t, J = 6.9 Hz, 1H), 7.47-7.41 (m, 3H), 7.33 (t, J = 7.4 Hz, 2H), 6.85-6.81 (m, 2H), 5.35 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 155.9, 152.4, 152.2, 143.9, 132.4, 131.8, 128.9, 128.2, 124.2, 123.7, 122.8, 118.8, 117.6, 116.9, 114.2, 113.7, 113.3, 109.1, 93.8, 55.2, 41.3; HRMS (ESI, m/z): calcd for $C_{24}H_{16}N_2O_3$ ($M+H^+$) 380.1161, found: 380.1155.

7-(3-Bromophenyl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[g]quinolin-6(7*H*)-one (**4u**): Yield 92%; Light yellow solid; mp 281-283 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.82 (s, 1H), 8.32 (dd, J = 1.0, 8.0 Hz, 1H), 7.65-7.61 (m, 1H), 7.46-7.42 (m, 2H), 7.37-7.35 (m, 1H), 7.31-7.28 (m, 1H), 7.22-7.16 (m, 3H), 7.05 (s, 1H), 5.21 (s, 1H), 2.81 (t, J = 7.3 Hz, 2H), 2.76-2.68 (m, 2H), 1.99-1.92 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 152.5, 150.3, 143.9, 143.5, 139.8, 134.2, 132.0, 129.9, 129.1, 126.3, 124.8, 122.9, 121.6, 116.9, 113.4, 112.2, 95.2, 41.2, 32.1, 31.7, 25.1; HRMS (ESI, m/z): calcd for $C_{25}H_{18}BrNO_2$ ($M+H^+$) 444.3199, found: 444.3192.

7-(3-Methoxyphenyl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[*g*]quinolin-6(7*H*)-one (**4v**): Yield 94%; White solid; mp 263-265 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.79 (s, 1H), 8.32 (dd, J = 1.1, 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.46-7.43 (m, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.07 (s, 1H), 6.79 (s, 1H), 6.75 (d, J = 6.9 Hz, 1H), 6.68 (dd, J = 2.1, 8.2 Hz, 1H), 5.14 (s, 1H), 3.65 (s, 3H), 2.81(t, J = 7.3 Hz, 2H), 2.77-2.68 (m, 2H), 1.98-1.93 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.6, 159.3, 152.9, 149.5, 143.9, 139.3, 133.7, 131.9, 129.3, 124.7, 123.7, 122.8, 122.2, 119.6, 116.8, 113.5, 113.4, 112.0, 110.6, 95.6, 54.9, 41.2, 32.1, 31.8, 25.3; HRMS (ESI, m/z): calcd for $C_{26}H_{21}NO_3$ ($M+H^+$) 395.1521, found: 395.1515.

7-(3-Bromophenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4w**): Yield 92%; Light yellow solid; mp 260-262 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 8.30 (d,

J = 7.3 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.36 (d, *J* = 6.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23-7.18 (m, 2H), 6.85 (s, 2H), 5.26 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 155.9, 152.2, 149.8, 143.7, 137.7, 131.8, 130.7, 129.7, 129.1, 126.2, 124.7, 123.7, 122.7, 117.5, 116.9, 114.2, 113.5, 94.2, 55.2, 40.8; HRMS (ESI, m/z): calcd for $C_{23}H_{16}BrNO_3$ ($M+H^+$) 434.2820, found: 434.2814.

9-Methoxy-7-(4-nitrophenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4x**): Yield 92%; Yellow solid; mp 266-268 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.94 (s, 1H), 8.23 (br s, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.63-7.34 (m, 6H), 6.83 (br s, 2H), 5.42 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ: 160.2, 155.6, 152.3, 145.2, 144.1, 131.8, 130.1, 129.3, 127.9, 127.8, 124.9, 123.7, 122.8, 117.7, 116.9, 113.4, 113.2, 94.2, 55.1, 38.2; HRMS (ESI, m/z): calcd for $C_{23}H_{16}N_2O_5$ ($M+H^+$) 400.1059, found: 400.1051.

7-(3,4,5-Trimethoxyphenyl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[*g*]quinolin-6(7*H*)-one (**4y**): Yield 96%; White solid; mp 330-332 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.80 (s, 1H), 8.31 (d, *J* = 7.3 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.20 (s, 1H), 7.12 (s, 1H), 6.52 (s, 2H), 5.13 (s, 1H), 3.63 (s, 6H), 3.55 (s, 3H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.00-1.93 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 152.7, 151.1, 143.6, 143.0, 139.2, 136.2, 133.7, 131.6, 124.6, 123.7, 122.7, 116.8, 113.5, 112.0, 104.5, 96.1, 59.8, 55.7, 41.4, 32.0, 31.7, 25.1; HRMS (ESI, m/z): calcd for $C_{28}H_{25}NO_5$ ($M+H^+$) 455.1733, found: 455.1727.

7-(4-Chlorophenyl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[g]quinolin-6(7*H*)-one (**4z**): Yield 92%; White solid; mp 241-243 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.81 (s, 1H), 8.33 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.46-7.43 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.26-7.23 (m, 5H), 7.03 (s, 1H), 5.21 (s, 1H), 2.85-2.79 (m, 2H), 2.73-2.66 (m, 2H), 1.98-1.94 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 152.2, 146.7, 143.2, 139.4, 133.6, 131.7, 128.9, 128.2, 124.7, 123.7, 122.7, 121.8, 116.8, 112.1, 95.5, 40.6, 32.1, 31.6, 25.1; HRMS (ESI, m/z): calcd for $C_{25}H_{18}ClNO_2$ ($M+H^+$) 399.1026, found: 399.1031.

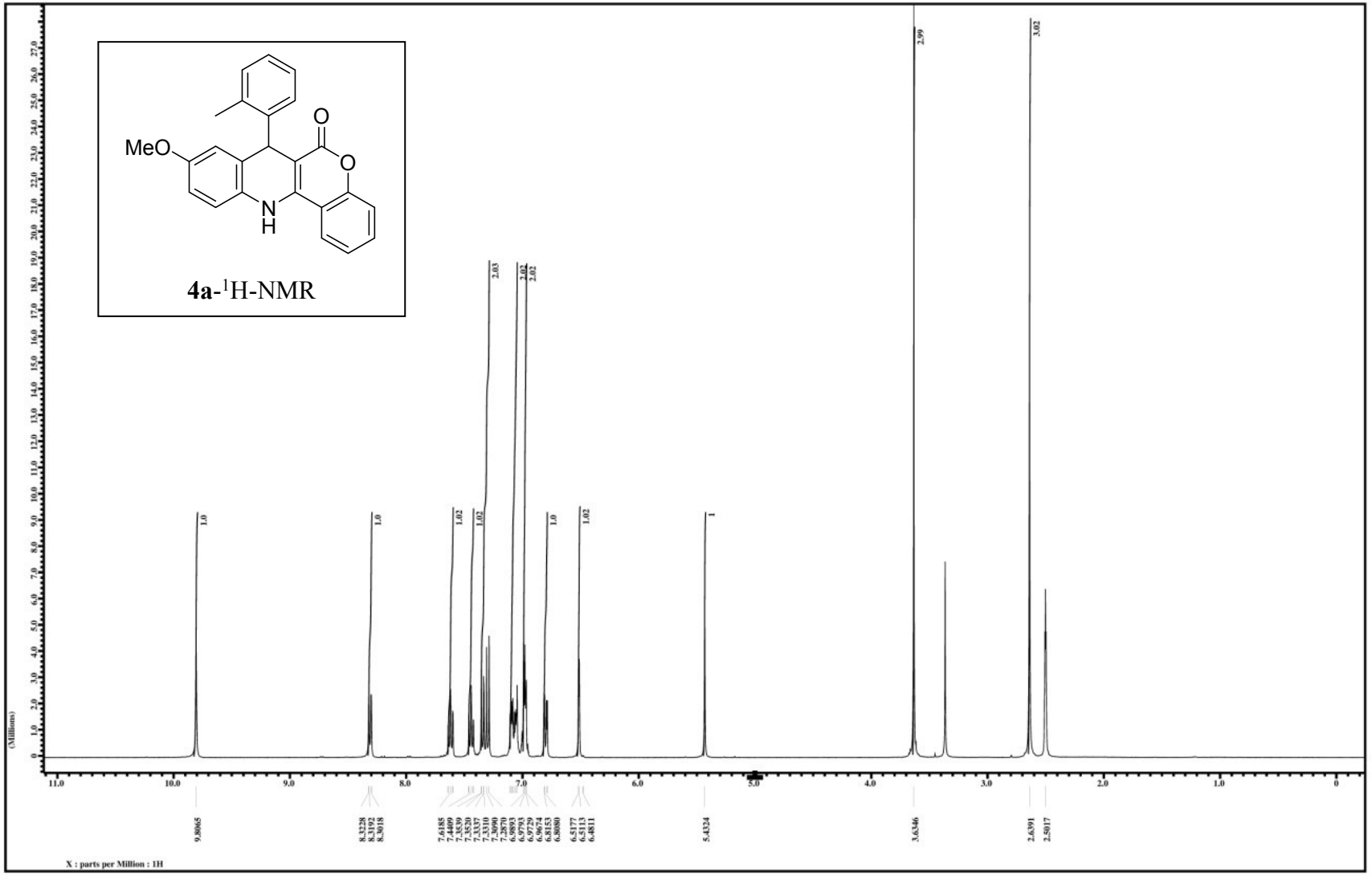
7-(Thiophen-2-yl)-9,10,11,13-tetrahydrochromeno[4,3-*b*]cyclopenta[*g*]quinolin-6(7*H*)-one (**4a´**): Yield 90%; White solid; mp 280-282 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.89 (s,

1H), 8.30 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.66-7.61 (m, 1H), 7.45-7.41 (m, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.20-7.16 (m, 3H), 6.83-6.79 (m, 2H), 5.49 (s, 1H), 2.85-2.75 (m, 4H), 2.00-1.94 (m, 2H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.4, 152.2, 151.5, 143.5, 139.5, 133.7, 131.8, 126.6, 124.7, 124.1, 123.8, 123.1, 122.0, 116.9, 113.6, 112.0, 95.5, 36.1, 32.1, 31.7, 25.2; HRMS (ESI, m/z): calcd for $C_{23}H_{17}NO_2S$ ($M+H^+$) 371.098, found: 371.091.

7-(4-Hydroxyphenyl)-9-methoxy-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4b´**): Yield 92%; Yellow solid; mp 295-297 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.77 (s, 1H), 9.18 (s, 1H), 8.28 (d, *J* = 7.3Hz, 1H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 6.9 Hz, 1H),7.01 (d, *J* = 8.0 Hz, 2H), 6.80-6.77 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 155.8, 152.2, 143.3, 138.1, 131.6, 129.0, 128.1, 127.9, 126.1, 117.3, 115.0, 114.0, 113.6, 113.0, 95.3, 55.2, 40.2; HRMS (ESI, m/z): calcd for $C_{23}H_{17}NO_4$ ($M+H^+$) 371.1158, found: 371.1153.

7-(4-Ethoxyphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4c´**): Yield 95%; White solid; mp 258-260 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.88 (s, 1H), 8.34 (d, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.39-7.33 (m, 2H), 7.21-7.16 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 2H), 5.17 (s, 1H), 3.90-3.87 (q, 2H), 1.24 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:167.4, 159.6, 157.4, 148.6, 137.2, 136.3, 132.1, 131.6, 129.2, 128.1, 126.0, 123.7, 122.7, 121.6, 119.5, 117.7, 114.4, 96.2, 62.8, 40.1, 14.6; HRMS (ESI, m/z): calcd for $C_{24}H_{19}NO_3$ ($M+H^+$) 369.1365, found: 369.1359.

7-(3,4,5-Trimethoxyphenyl)-7*H*-chromeno[4,3-*b*]quinolin-6(12*H*)-one (**4d´**): Yield 96%; White solid; mp 337-339 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 8.42 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.47-7.43 (m, 1H), 7.40-7.34 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.03-6.99 (m, 1H), 6.52 (s, 2H), 5.21 (s, 1H), 3.63 (s, 6H), 3.56 (s, 3H); ^{13}C NMR (100. MHz, DMSO-d_6) δ:160.5, 152.7, 152.3, 143.8, 143.3, 136.0, 135.4, 131.9, 129.5, 127.4, 124.1, 123.8, 123.7, 122.9, 116.8, 116.3, 113.4, 104.4, 96.1, 59.9, 55.8, 41.6; HRMS (ESI, m/z): calcd for $C_{25}H_{21}NO_5$ ($M+H^+$) 415.1419, found: 415.1413.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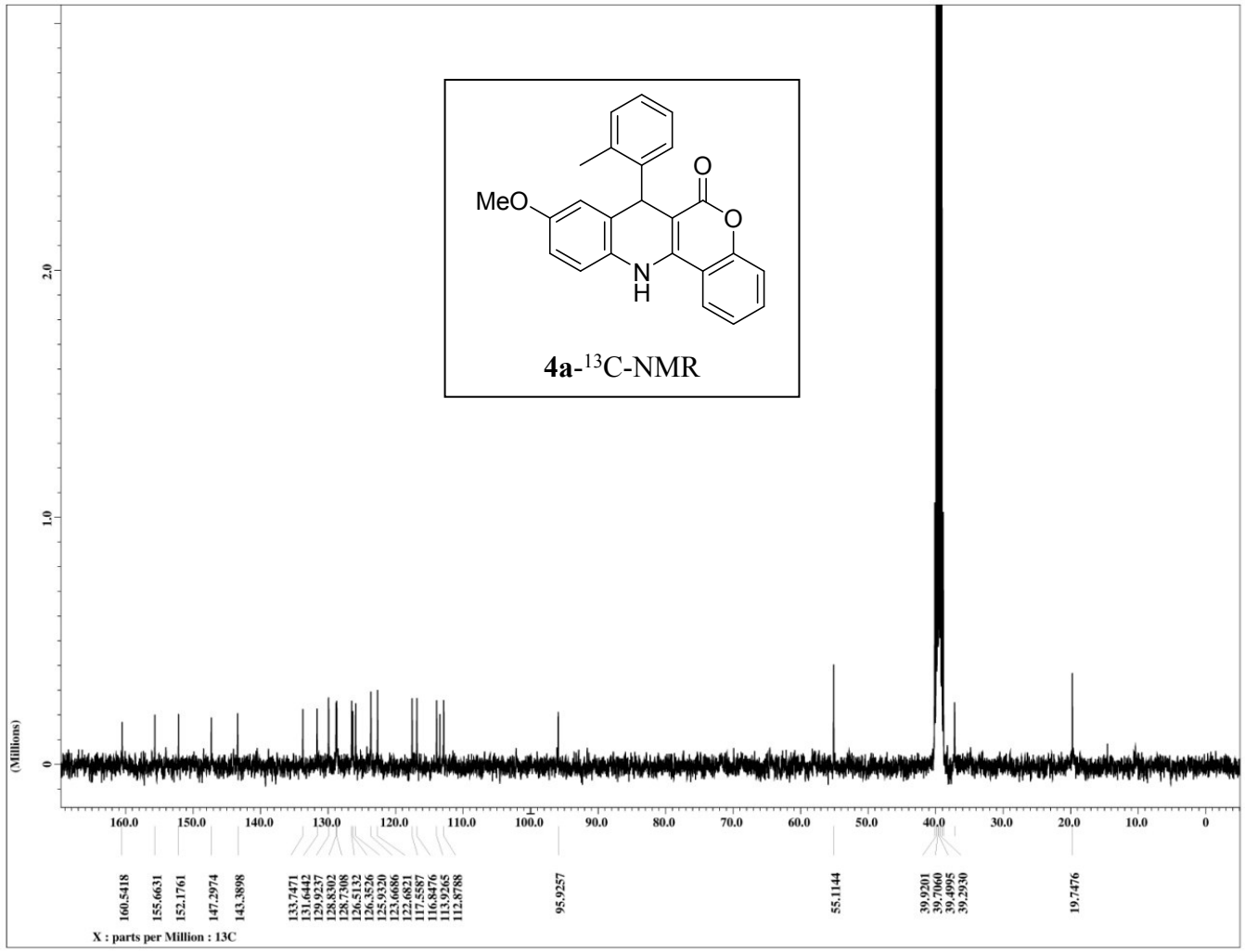
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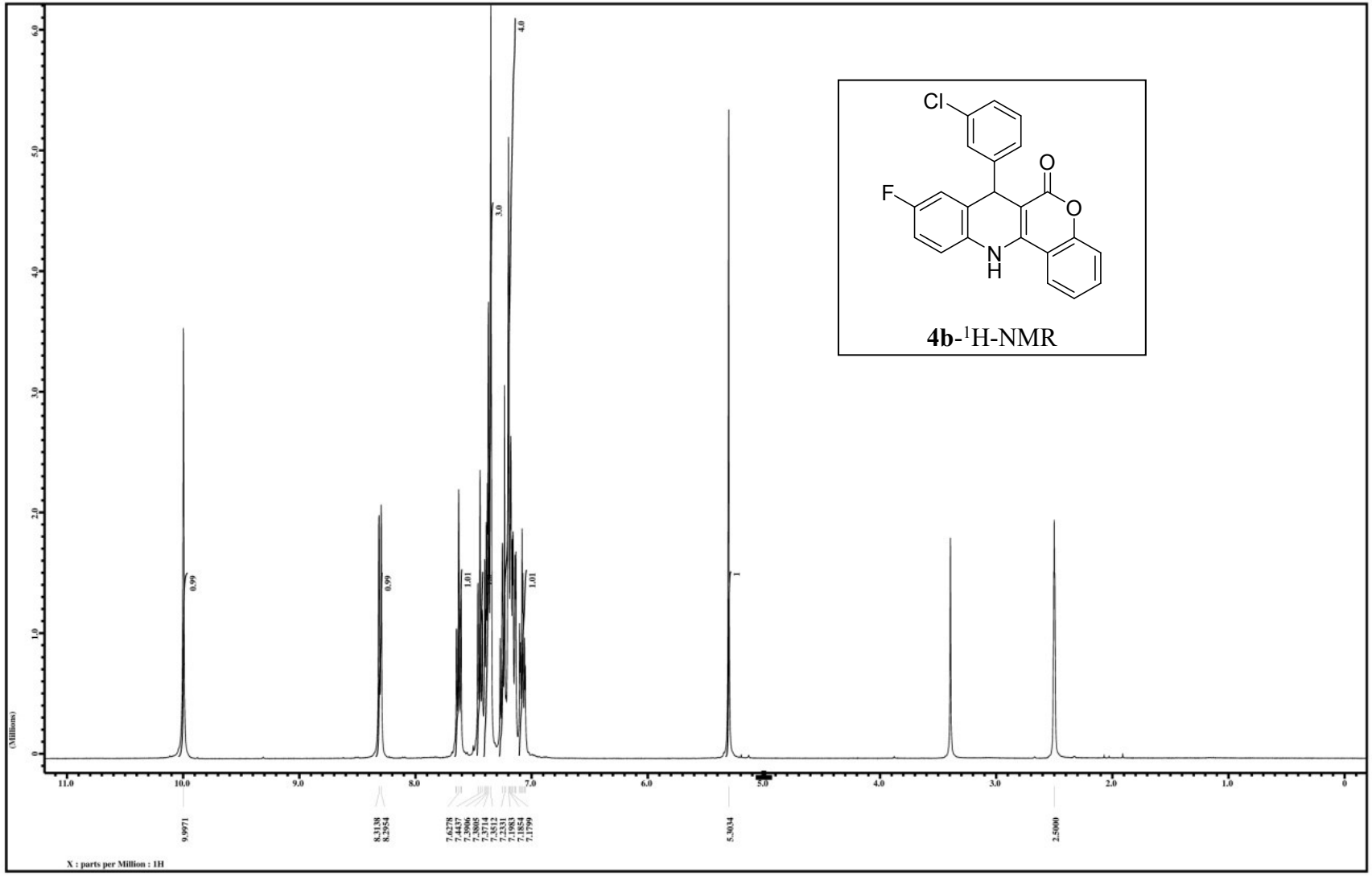
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(Millions)
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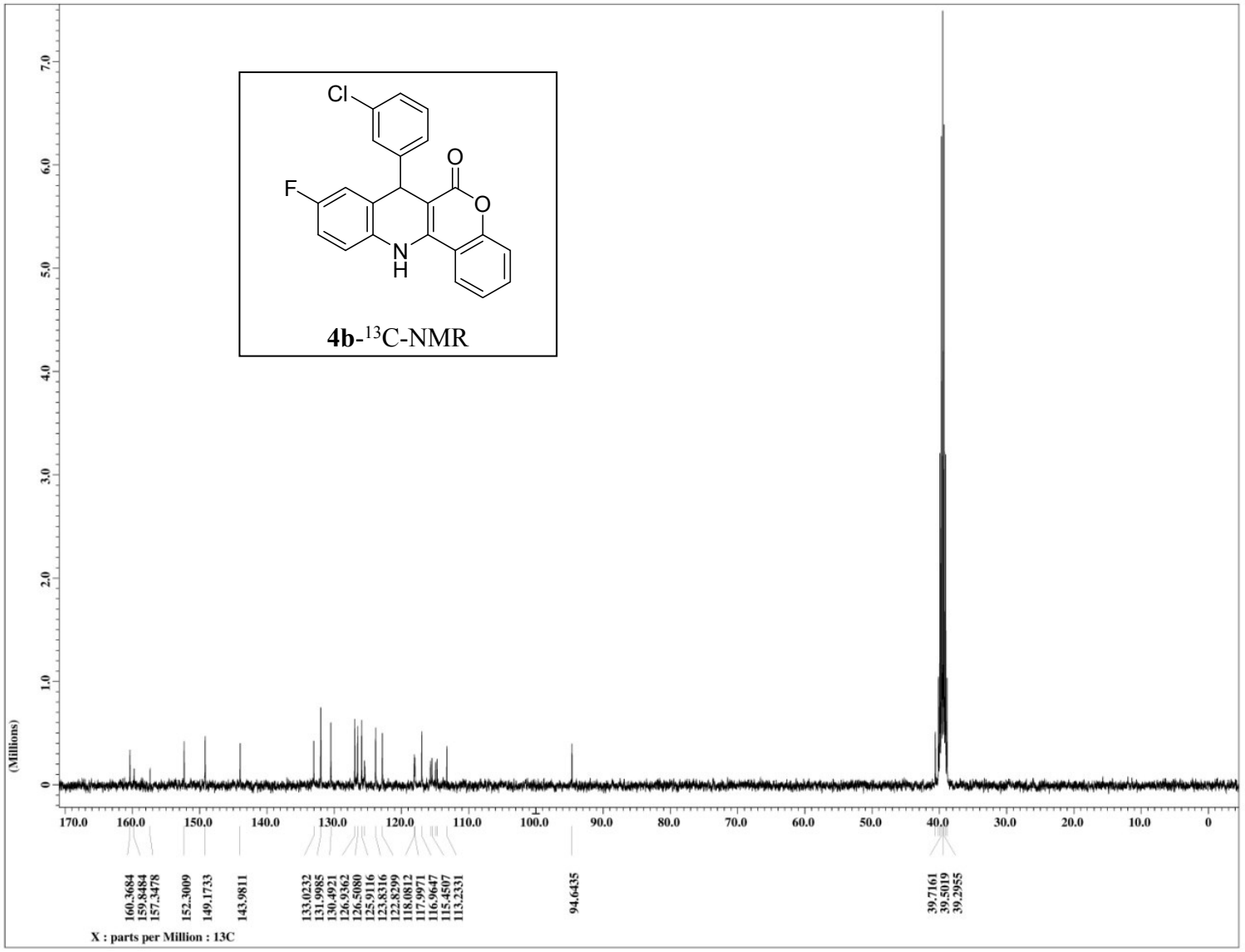
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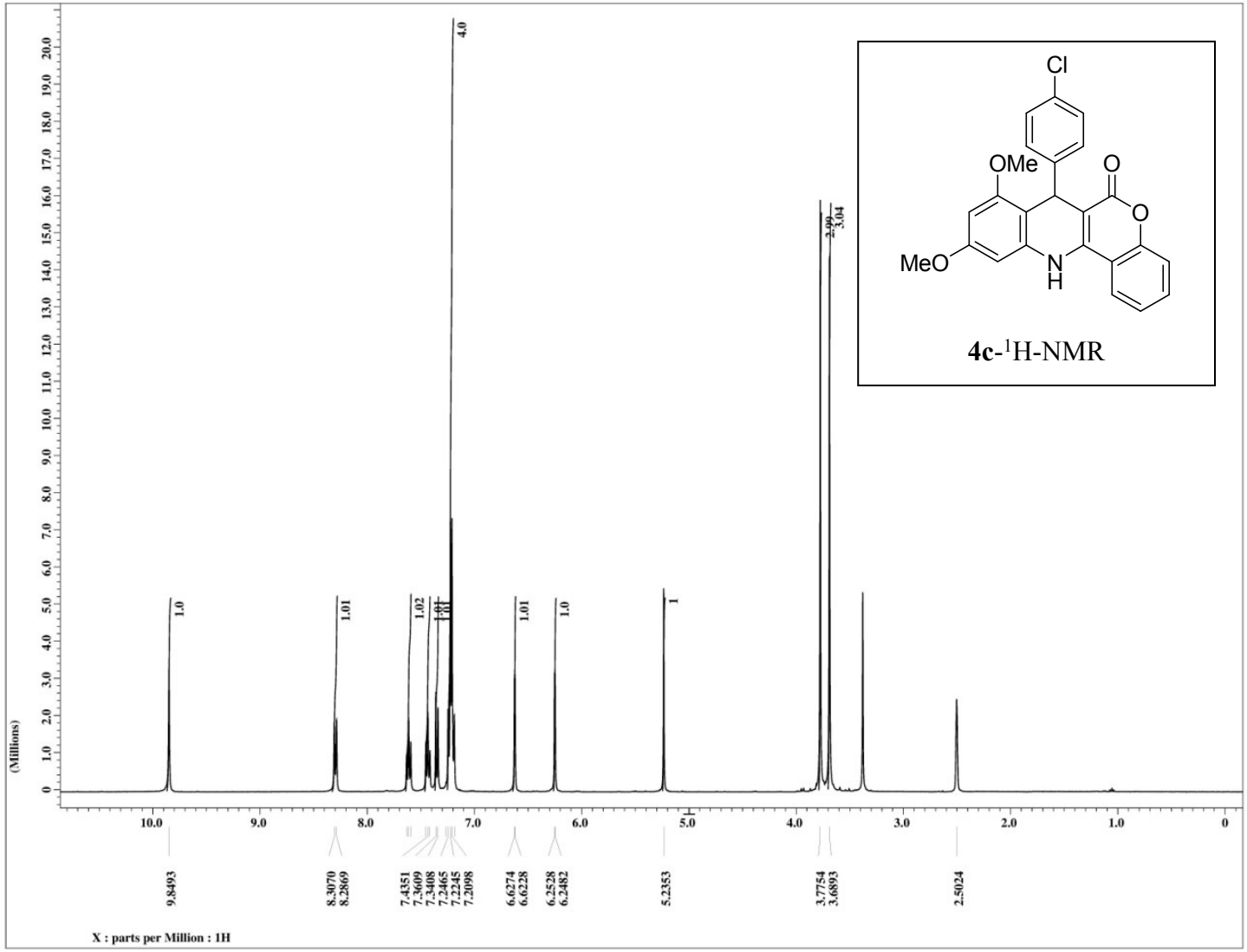
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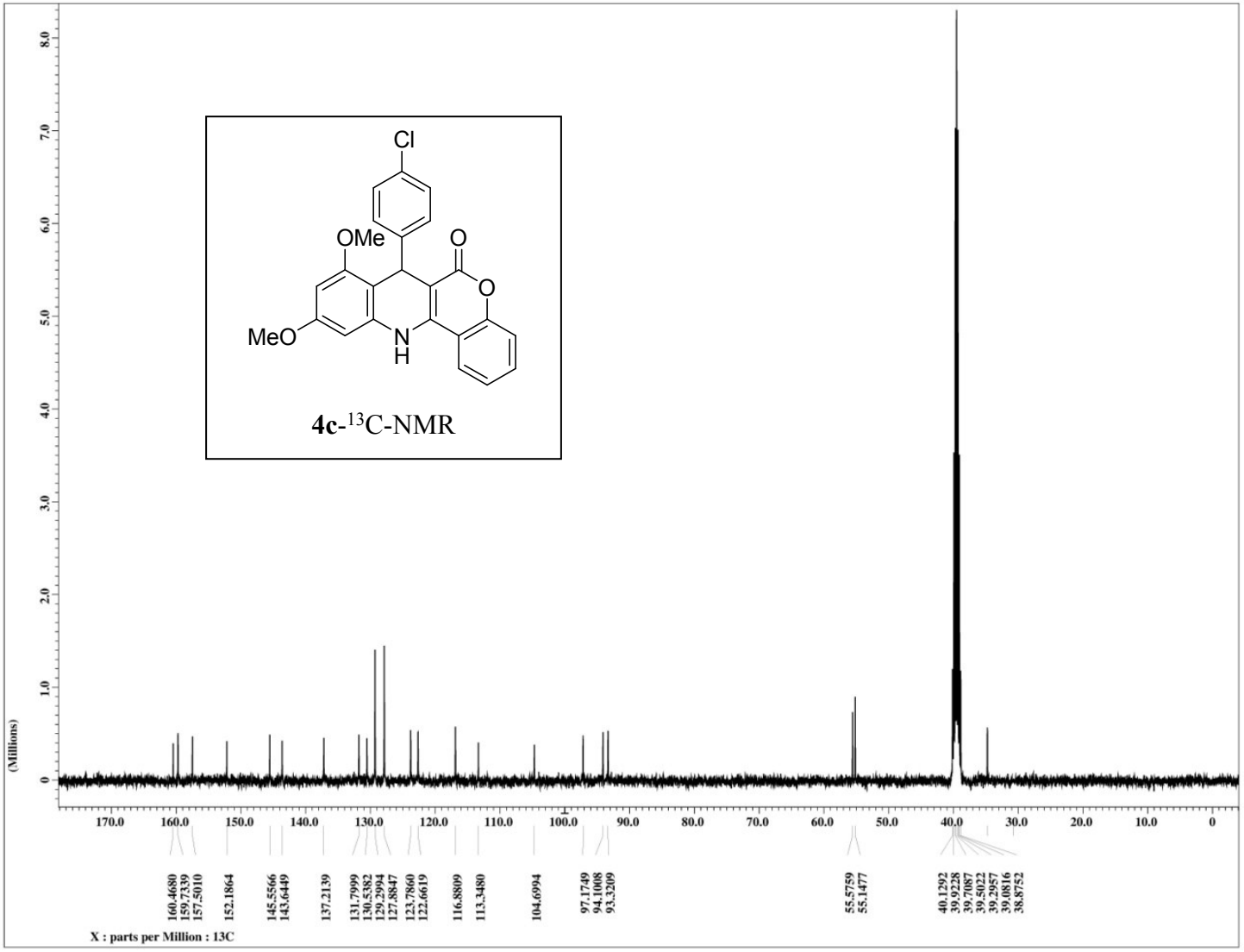
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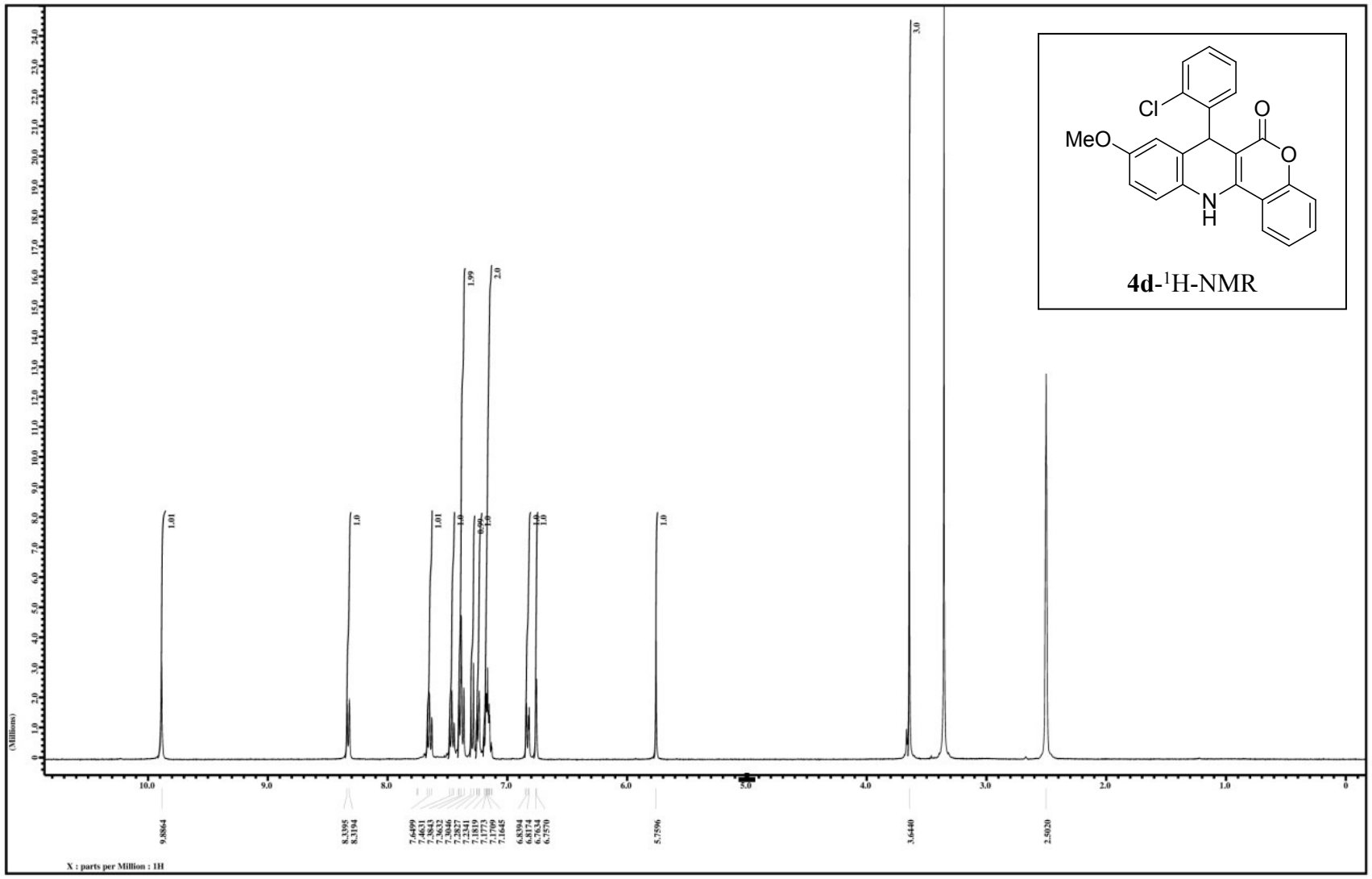
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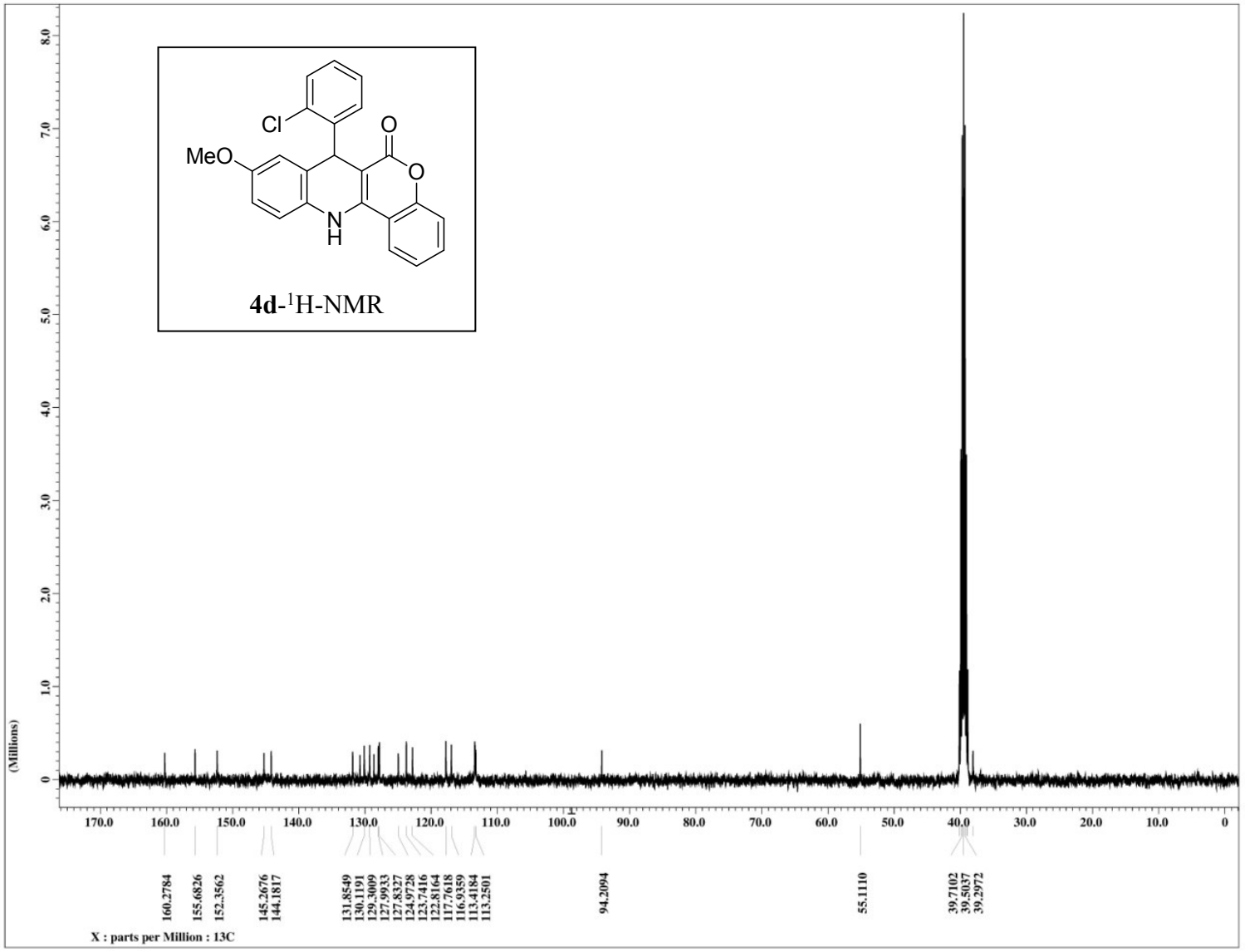
4d-1H-NMR
X : parts per Million : 1H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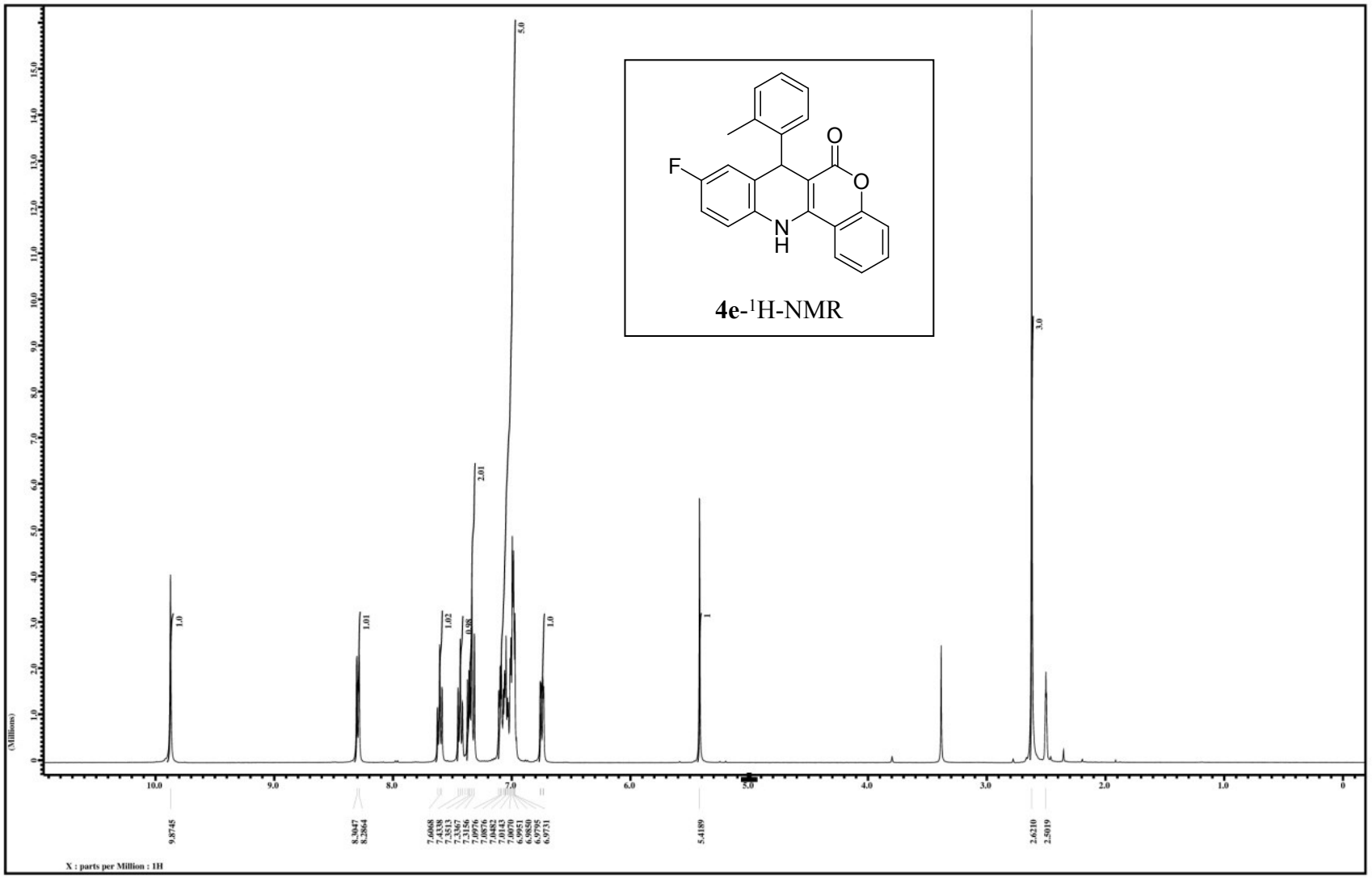
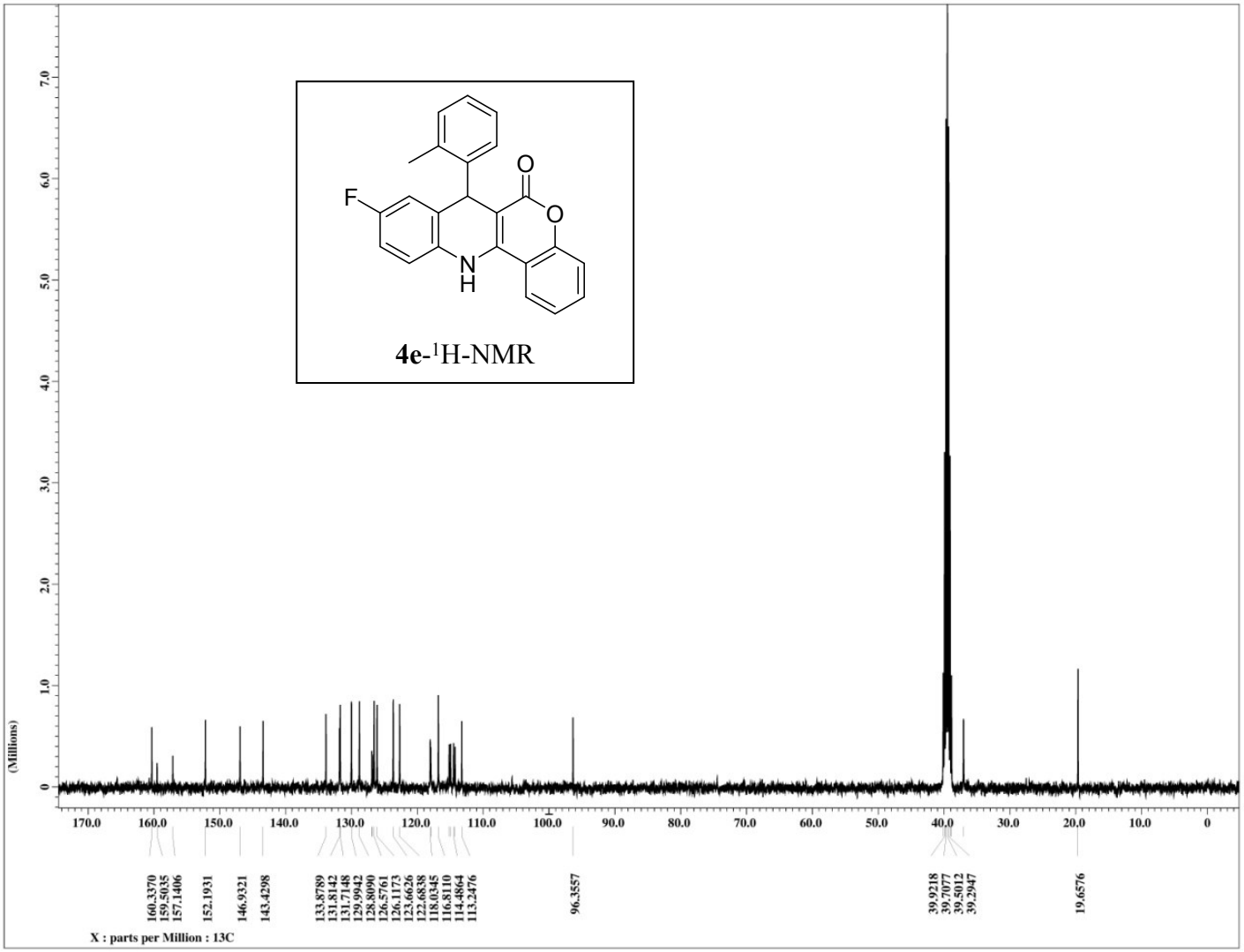
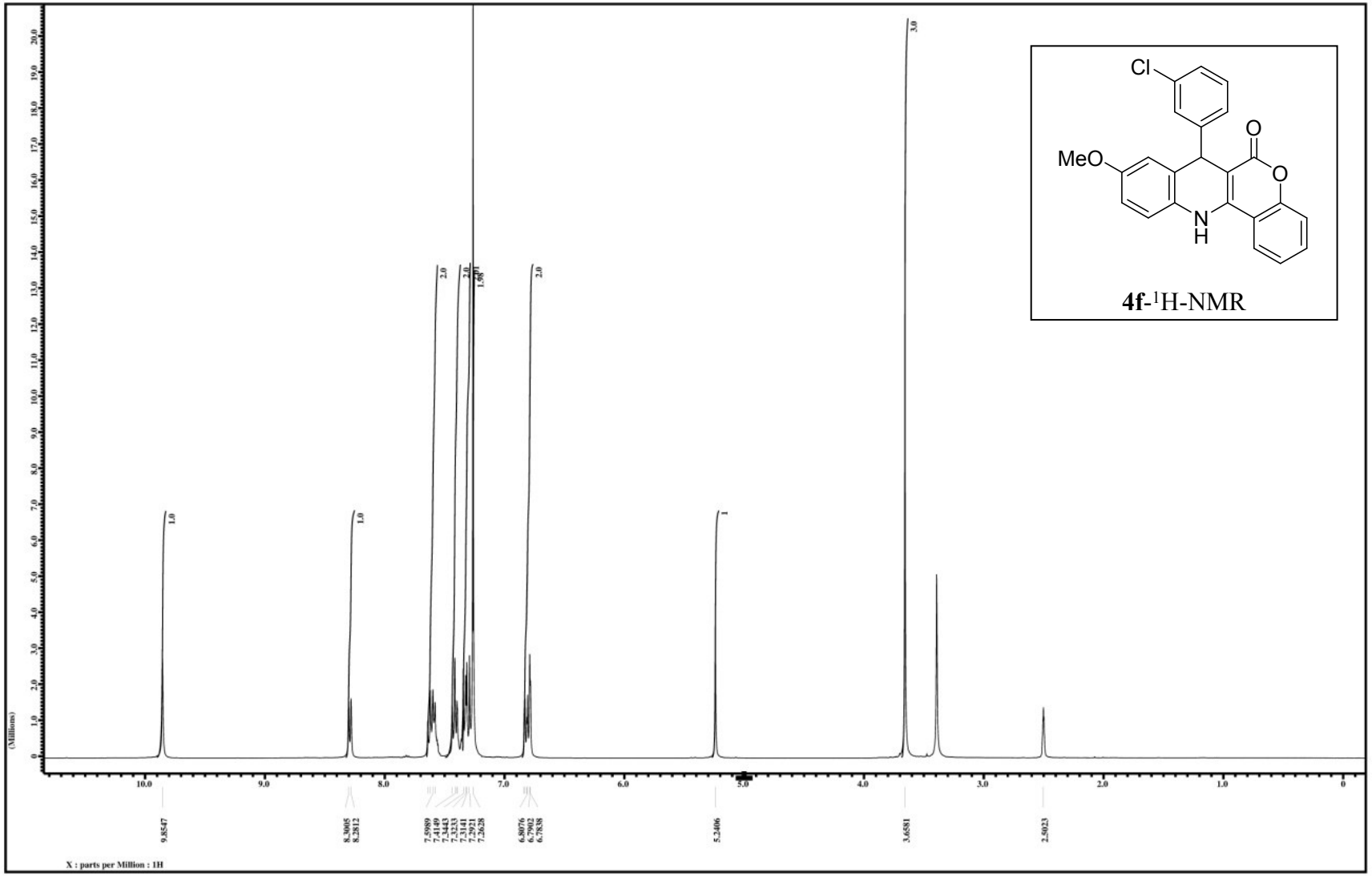
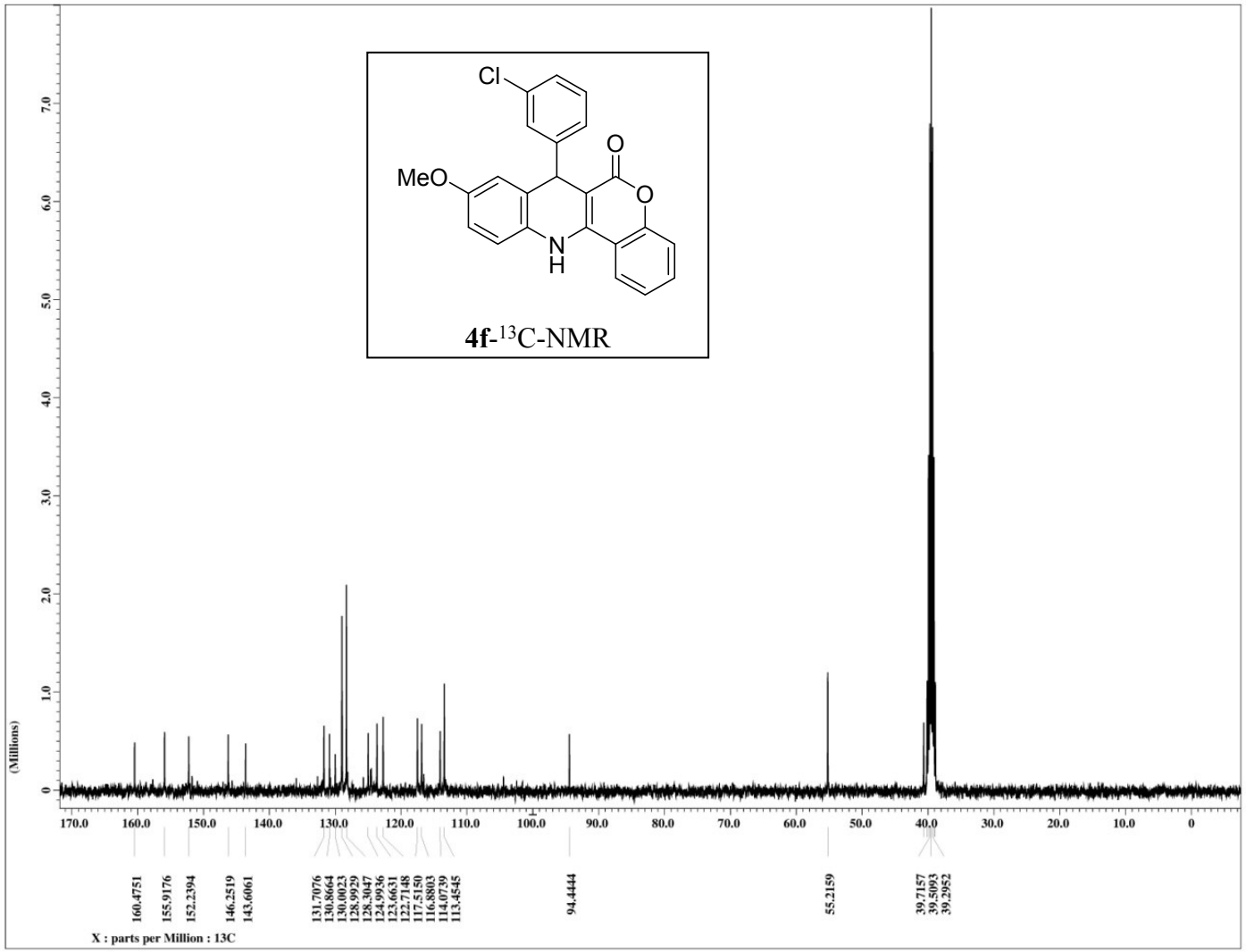
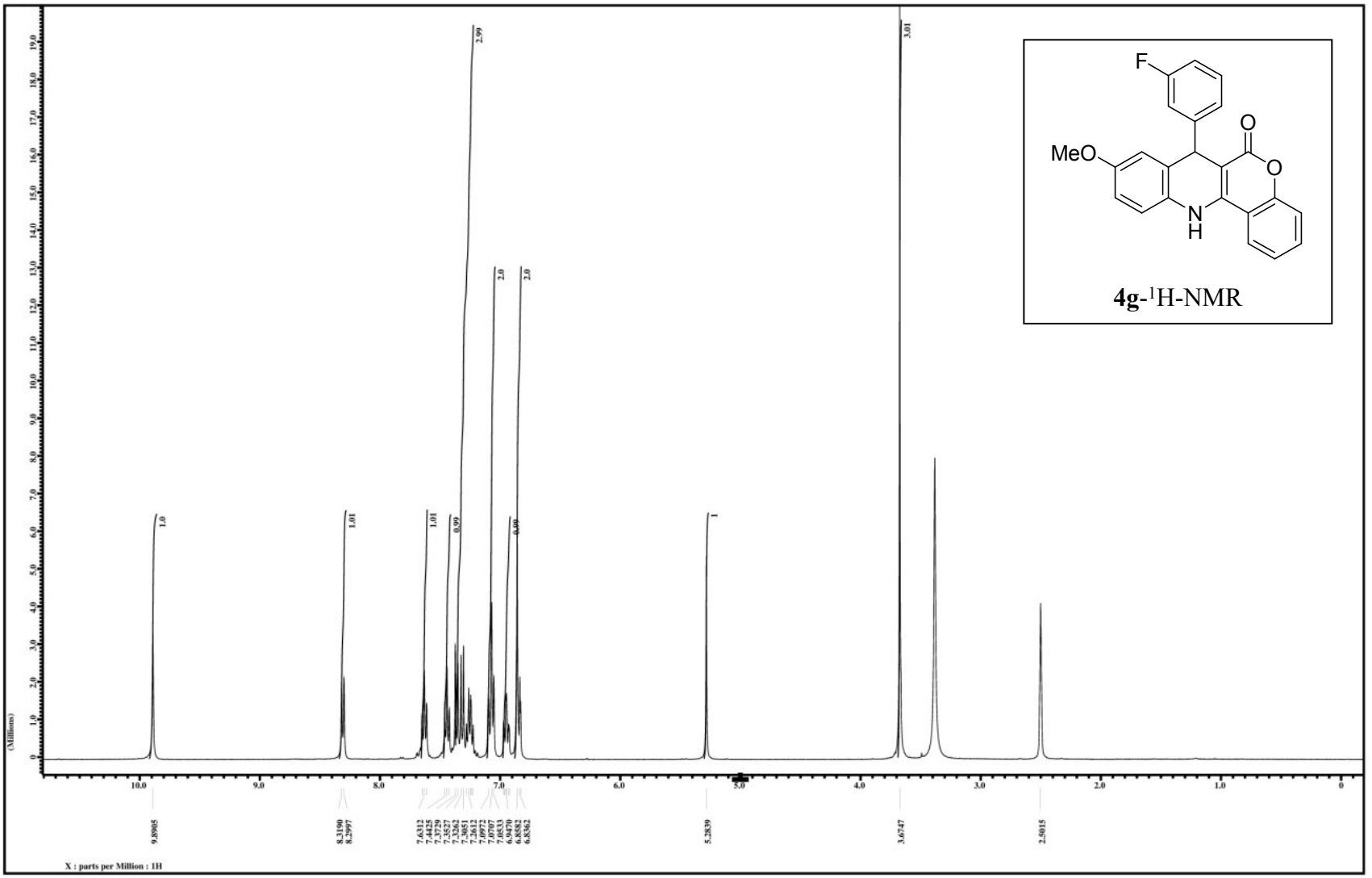
39.5037
39.2972
X : parts per Million : 13C

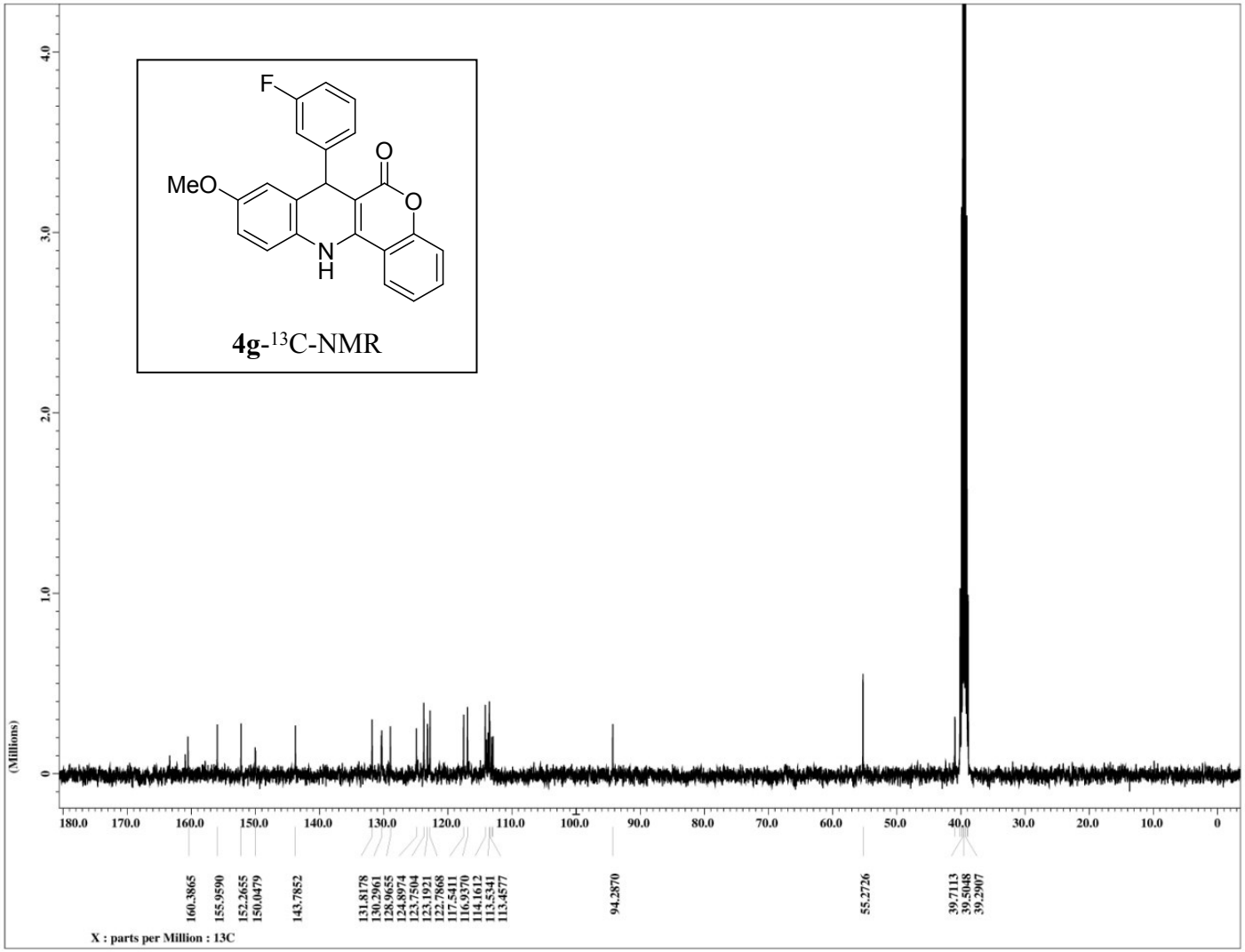

F
O
O
N
H
4e-1H-NMR
X : parts per Million : 1H

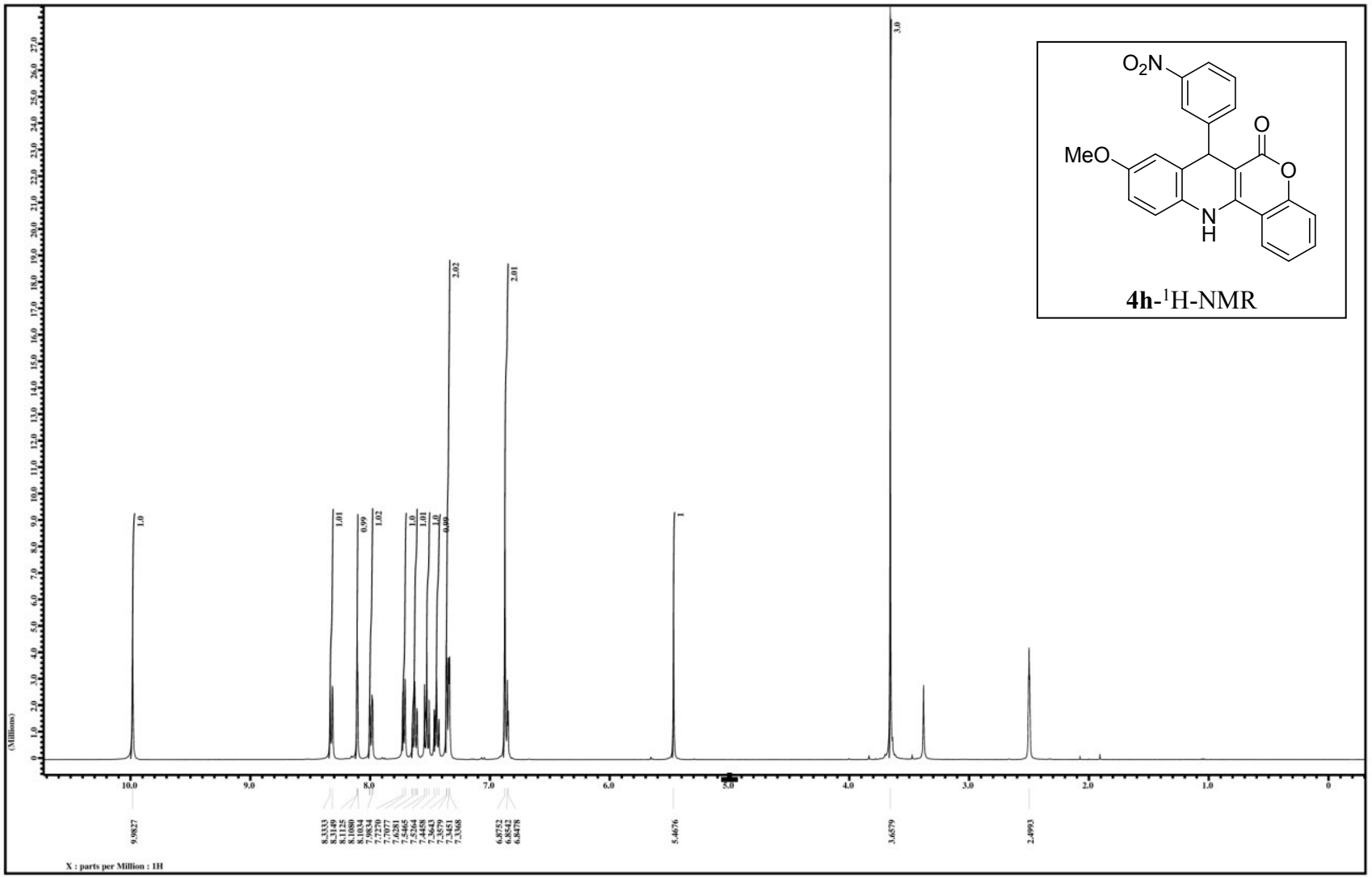

F
O
O
N
H
4e-1H-NMR
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.3370
159.5035
157.1406
152.1931
146.9321
143.4298
133.8789
131.8142
131.7148
129.9942
128.8090
126.5761
126.1173
123.6626
122.6838
118.0345
116.8110
114.4864
113.2476
96.3557
39.9218
39.7077
39.5012
39.2947
19.6576
X : parts per Million : 13C

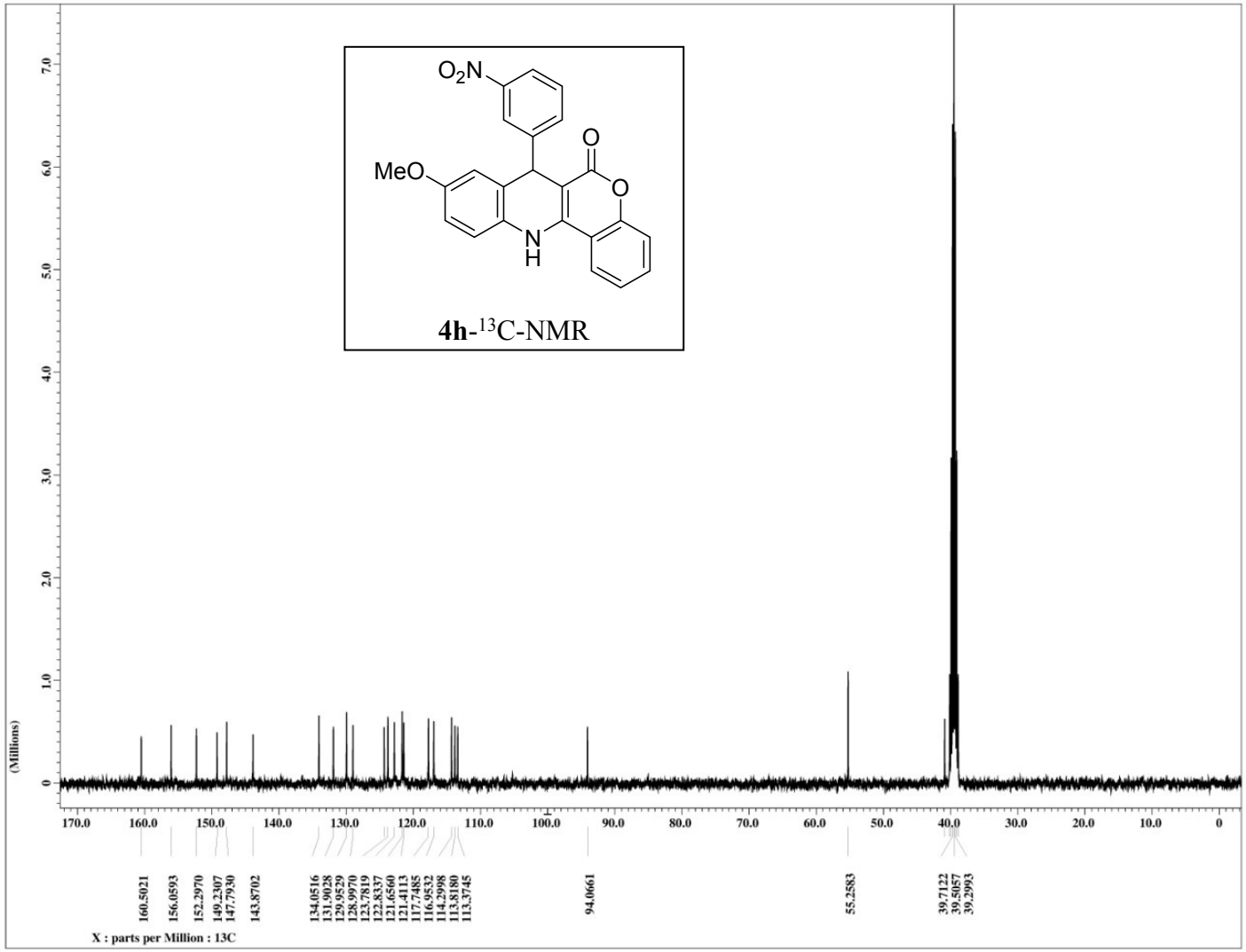

Cl
MeO
O
O
N
H
4f-1H-NMR
X : parts per Million : 1H

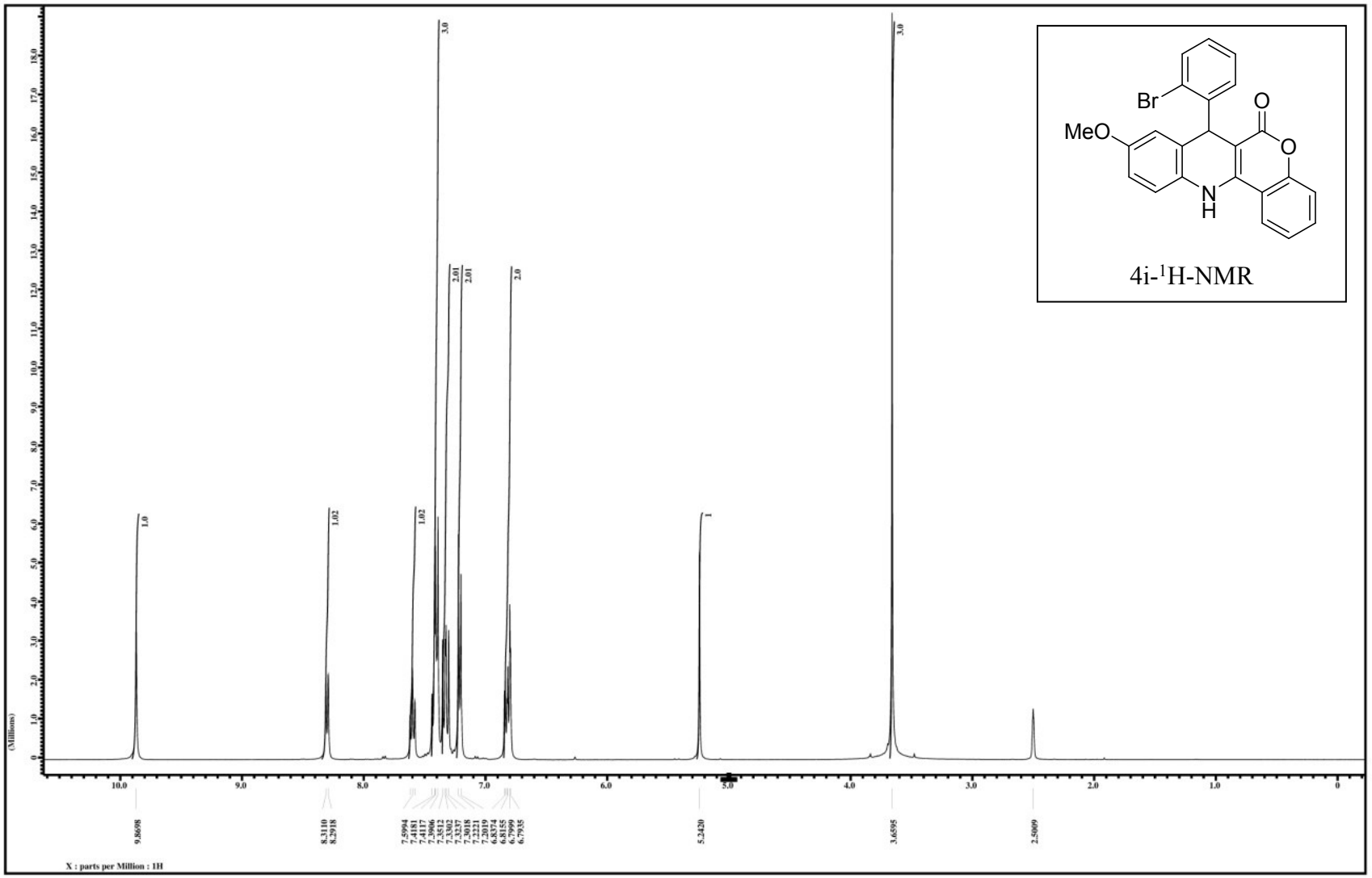

Cl
O
MeO
O
N
H
4f-13C-NMR
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4751
155.9176
152.2394
146.2519
143.6061
131.7076
130.8664
130.0023
128.9929
128.3047
124.9936
123.6631
122.7148
117.5150
116.8803
114.0739
113.4545
94.4444
55.2159
39.7157
39.5093
39.2952
X : parts per Million : 13C

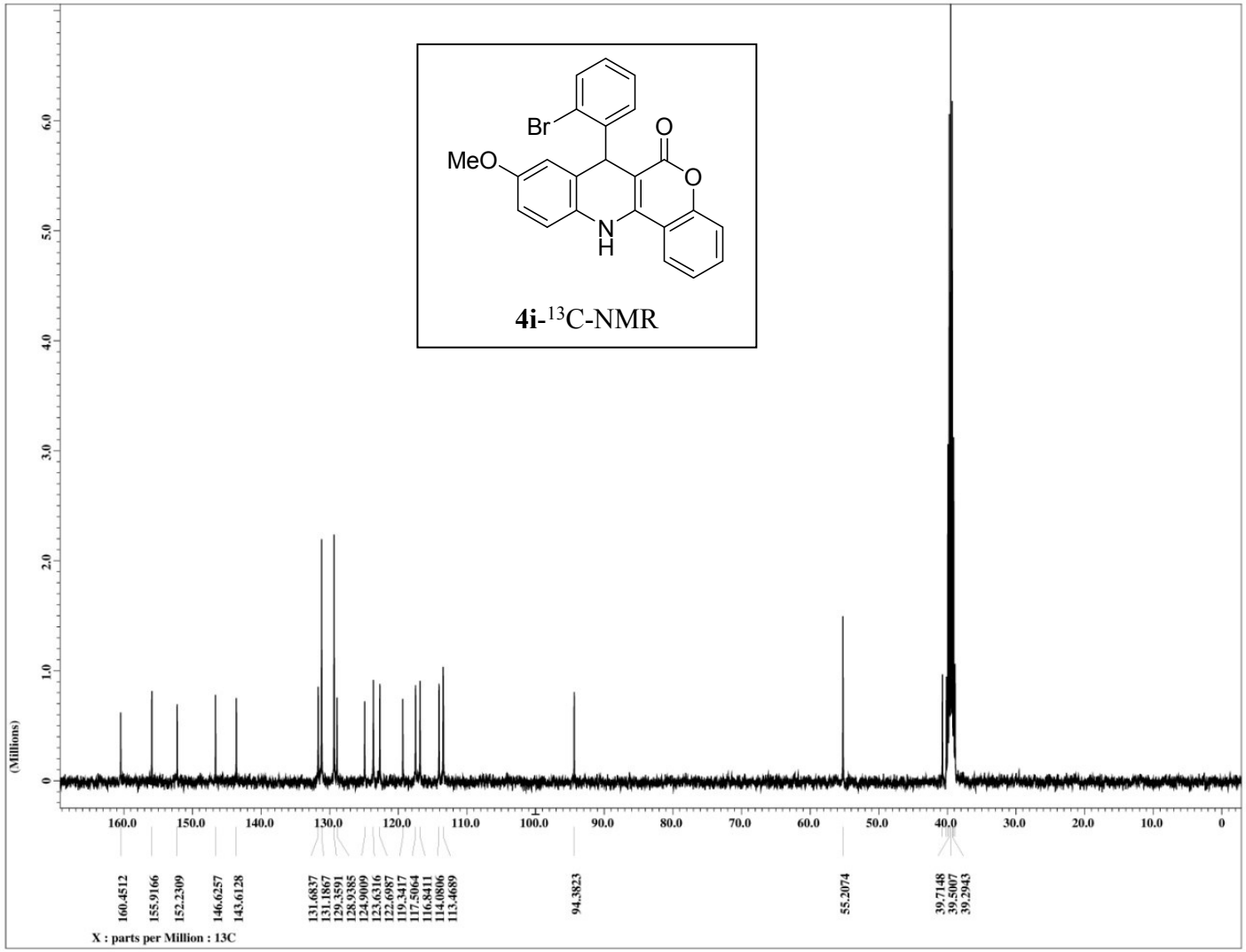

F
O
MeO
O
N
H
4g-1H-NMR
X : parts per Million : 1H

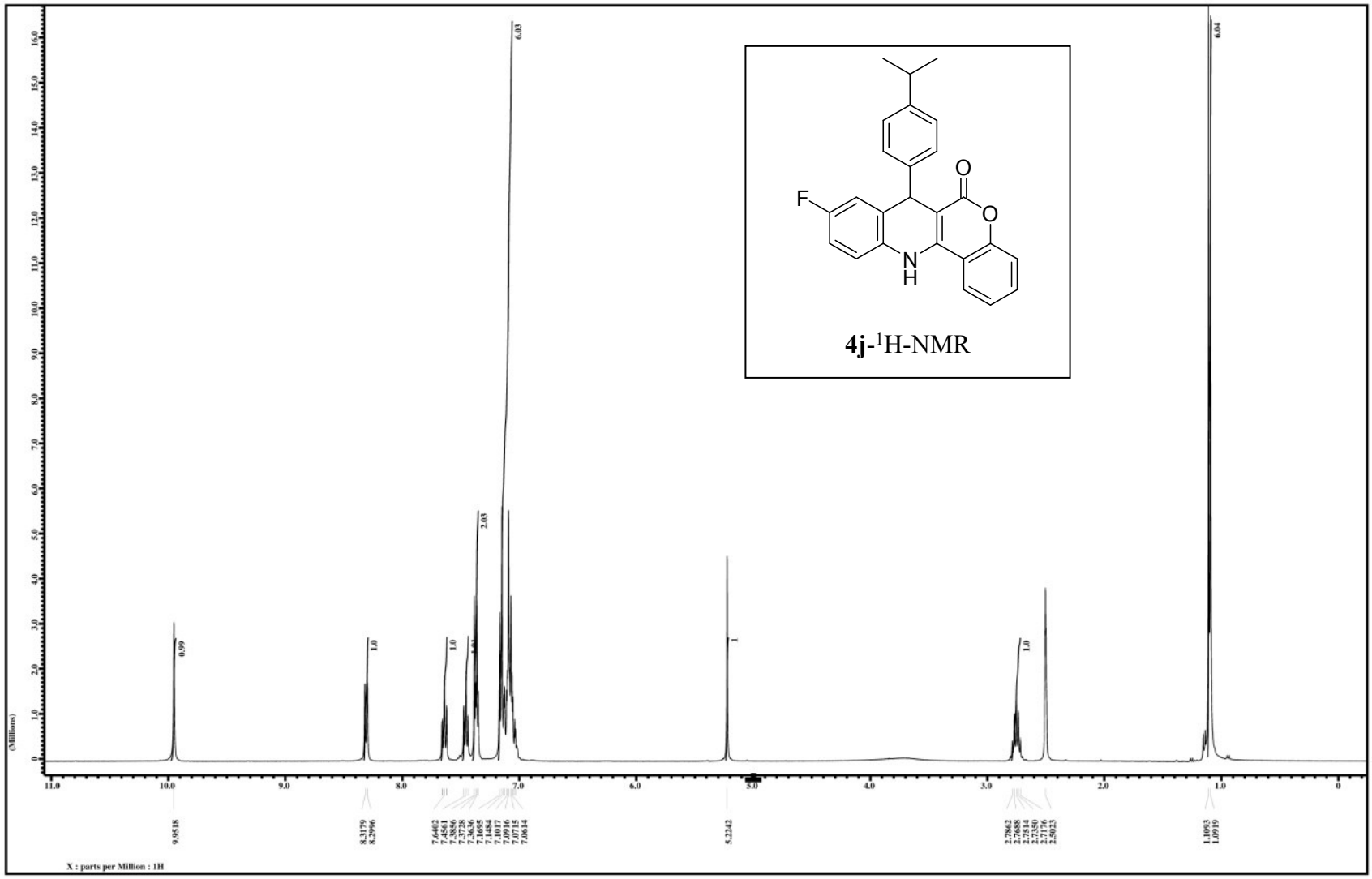

F
MeO
O
O
N
H
4g-13C-NMR
(Millions)
4.0
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.3865
155.9590
152.2655
150.0479
143.7852
131.8178
130.2961
128.9655
124.8974
123.7504
123.1921
122.7868
117.5411
116.9370
114.1612
113.5341
113.4577
94.2870
55.2726
39.7113
39.5048
39.2907
X : parts per Million : 13C

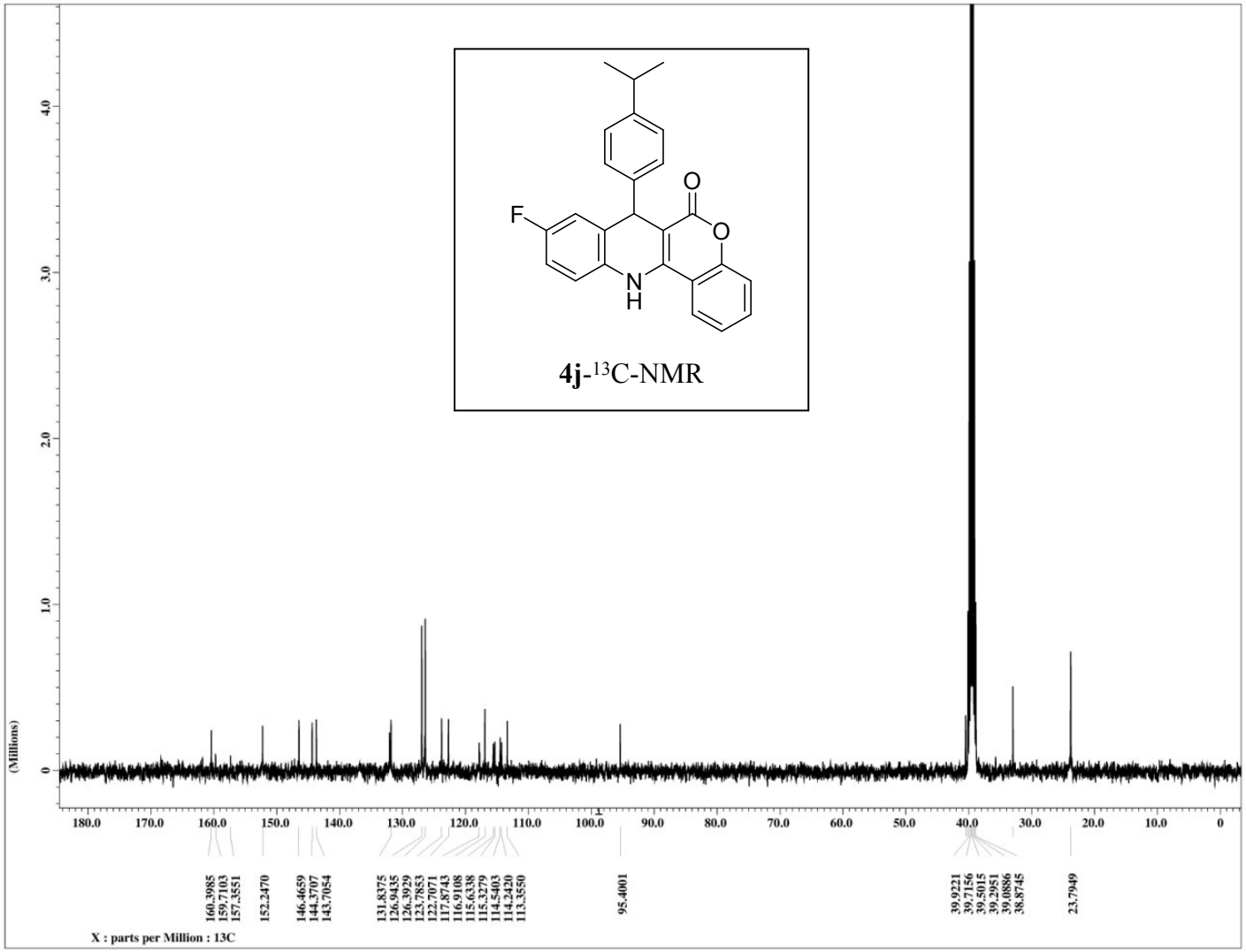

O_2N
MeO
O
O
N
H
4h-^{1}H-NMR
X : parts per Million : 1H

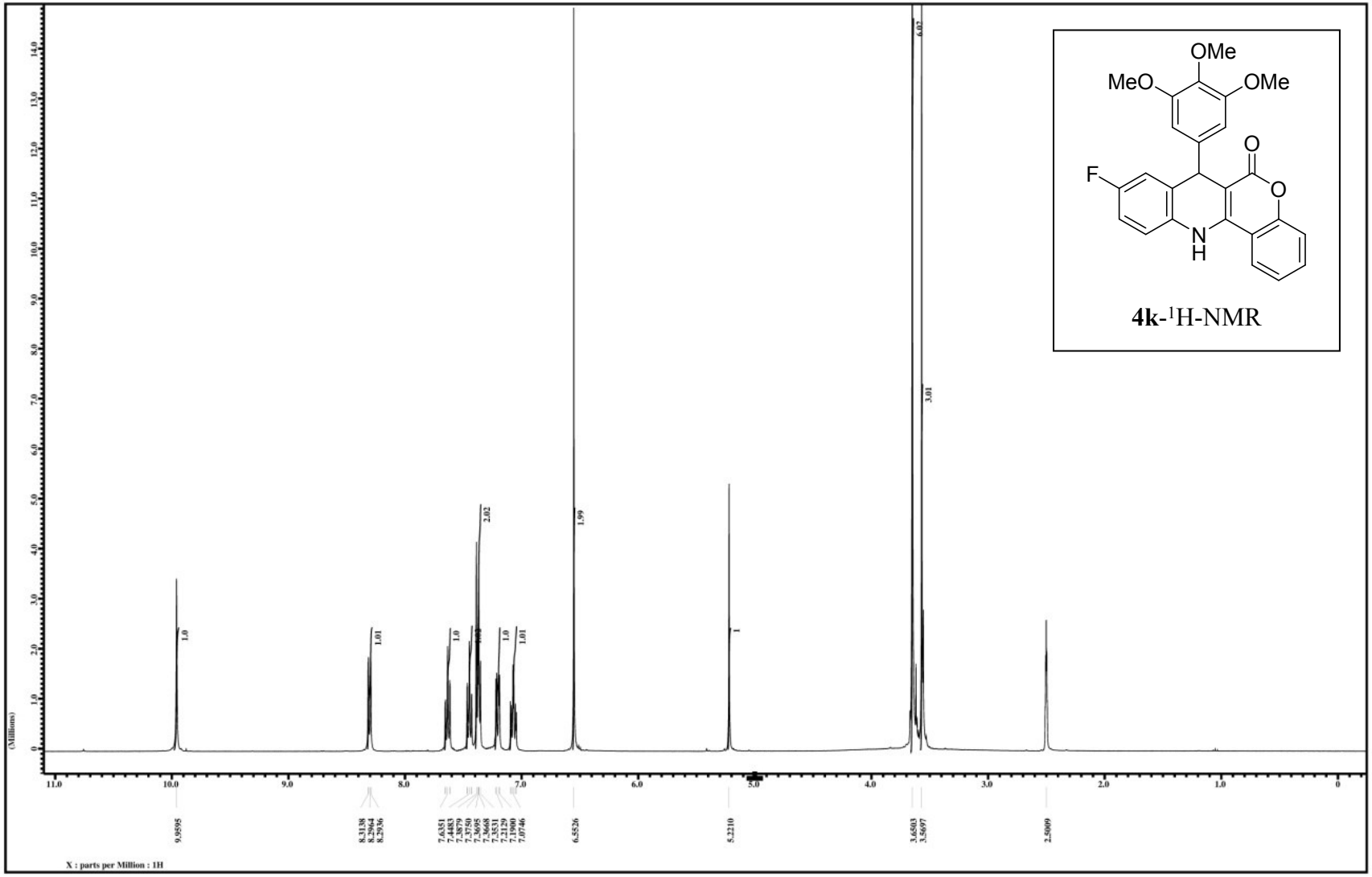

O2N
MeO
O
O
N
H
4h-13C-NMR
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5021
156.0593
152.2970
149.2307
147.7930
143.8702
134.0516
131.9028
129.9529
128.9970
123.7819
122.8337
121.6560
121.4113
117.7485
116.9532
114.2998
113.8180
113.3745
94.0661
55.2583
39.7122
39.5057
39.2993
X : parts per Million : 13C

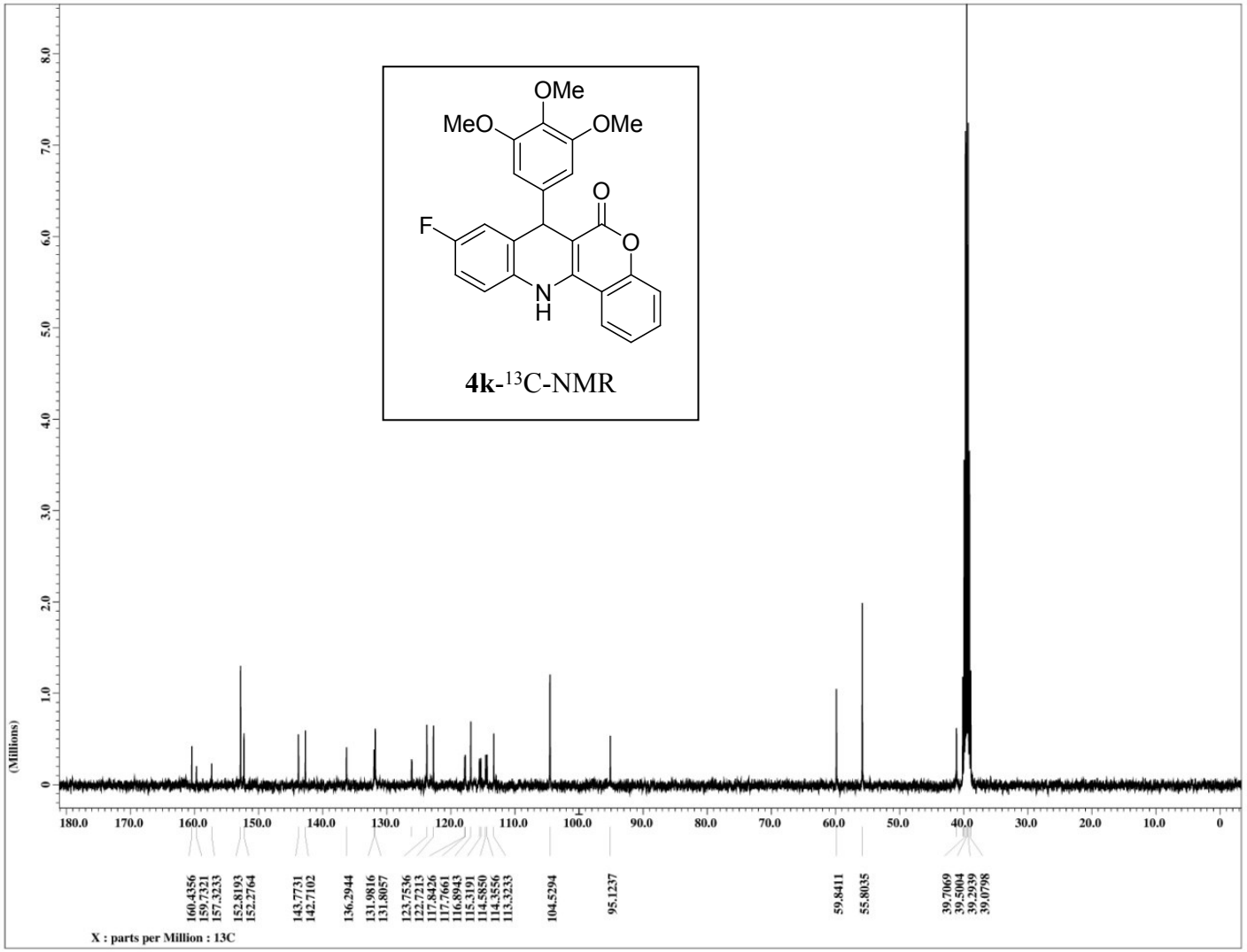

Br
O
MeO
O
N
H
4i-1H-NMR
X : parts per Million : 1H

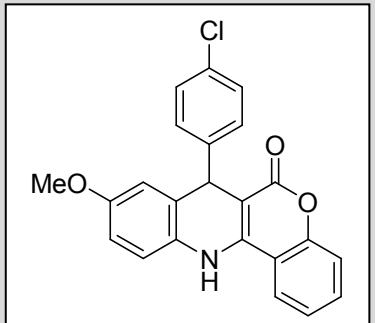

Br
O
MeO
O
N
H
4i-13C-NMR
(Millions)
6.0
5.0
4.0
3.0
2.0
1.0
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4512
155.9166
152.2309
146.6257
143.6128
131.6837
131.1867
129.3591
128.9385
124.9009
123.6316
122.6987
119.3417
117.5064
116.8411
114.0806
113.4689
94.3823
55.2074
39.7148
39.5607
39.2943
X : parts per Million : 13C


F
O
O
N
H
4j-1H-NMR
X : parts per Million : 1H

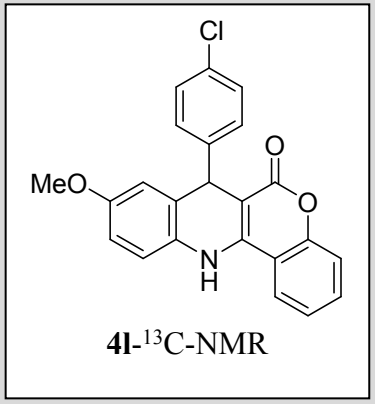

F
O
O
N
H
4j-13C-NMR
(Millions)
4.0
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.3985
159.7103
157.3551
152.2470
146.4659
144.3707
143.7054
131.8375
126.9435
126.3929
123.7853
122.7071
117.8743
116.9108
115.6338
115.3279
114.5403
114.2420
113.3550
95.4001
39.9221
39.7156
39.5015
39.2951
39.0886
38.8745
23.7949
X : parts per Million : 13C


OMe
MeO
OMe
O
F
O
N
H
4k-1H-NMR
X : parts per Million : 1H

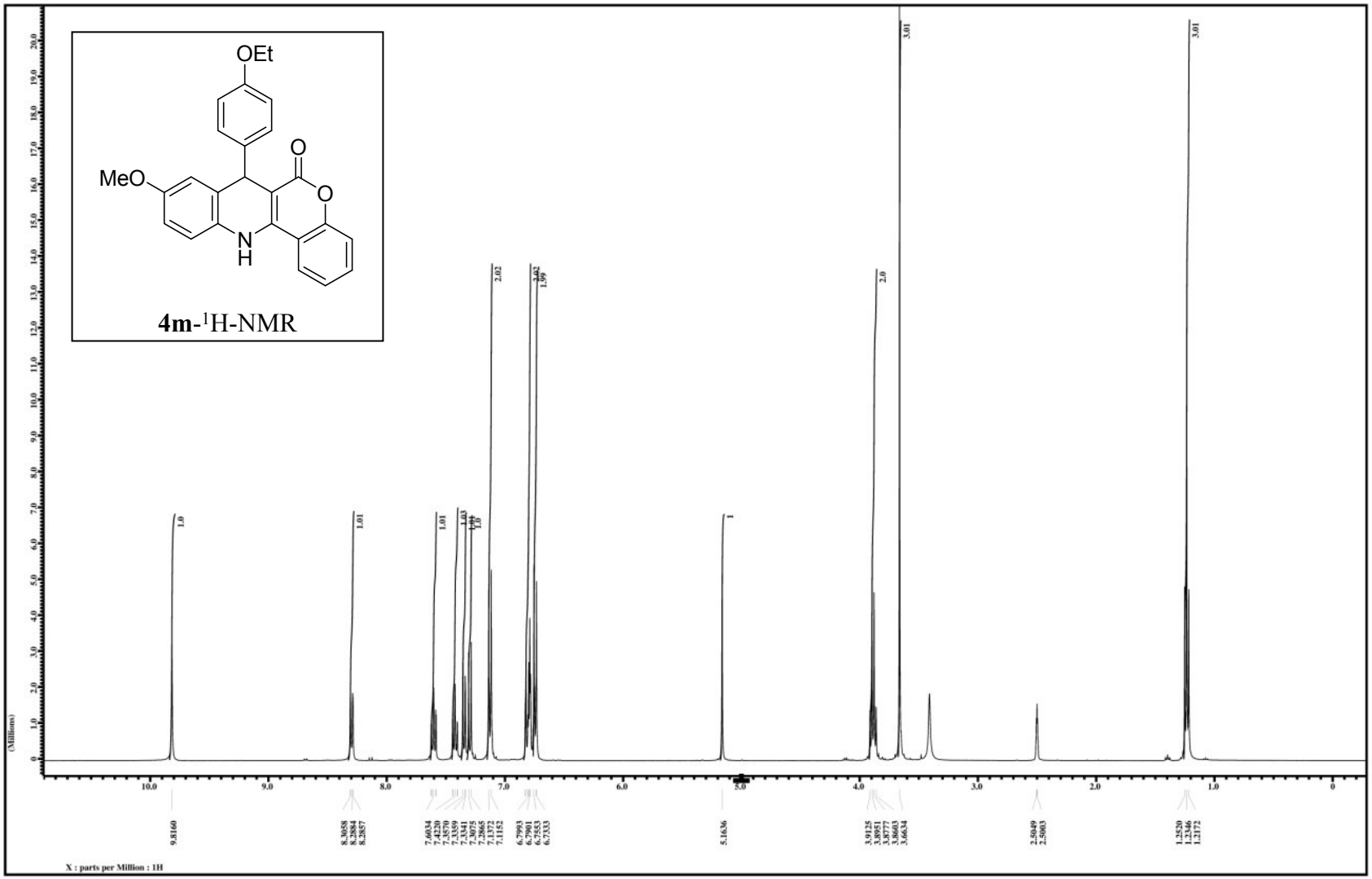

OMe
MeO
OMe
O
F
O
N
H
4k-13C-NMR
(Millions)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4356
159.7321
157.3233
152.8193
152.2764
143.7731
142.7102
136.2944
131.9816
131.8057
123.7536
122.7213
117.8426
117.7661
116.8943
115.3191
114.5850
114.3556
113.3233
104.5294
95.1237
59.8411
55.8035
39.7069
39.5004
39.2939
39.0798
X : parts per Million : 13C

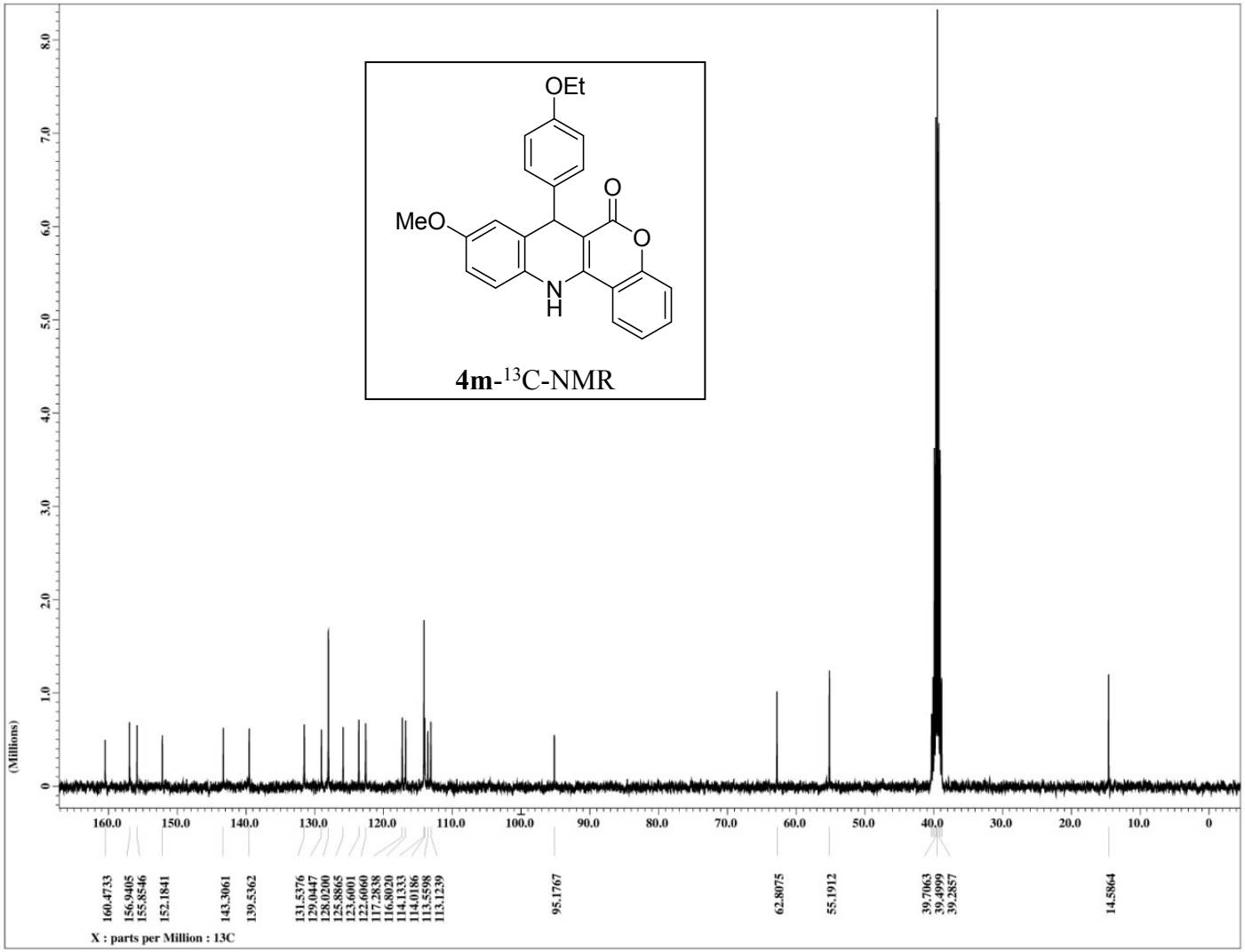


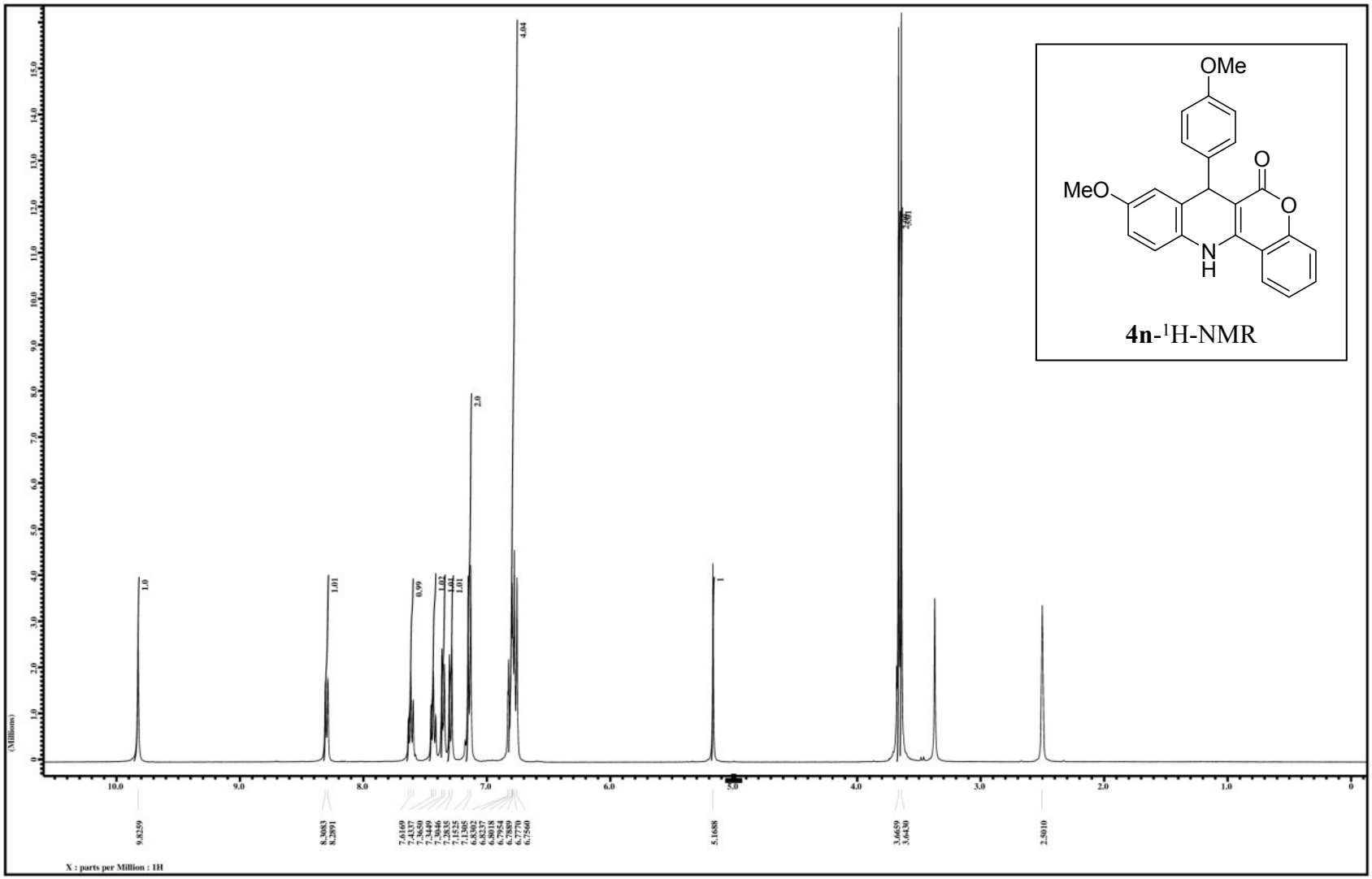
4l-^{1}H-NMR

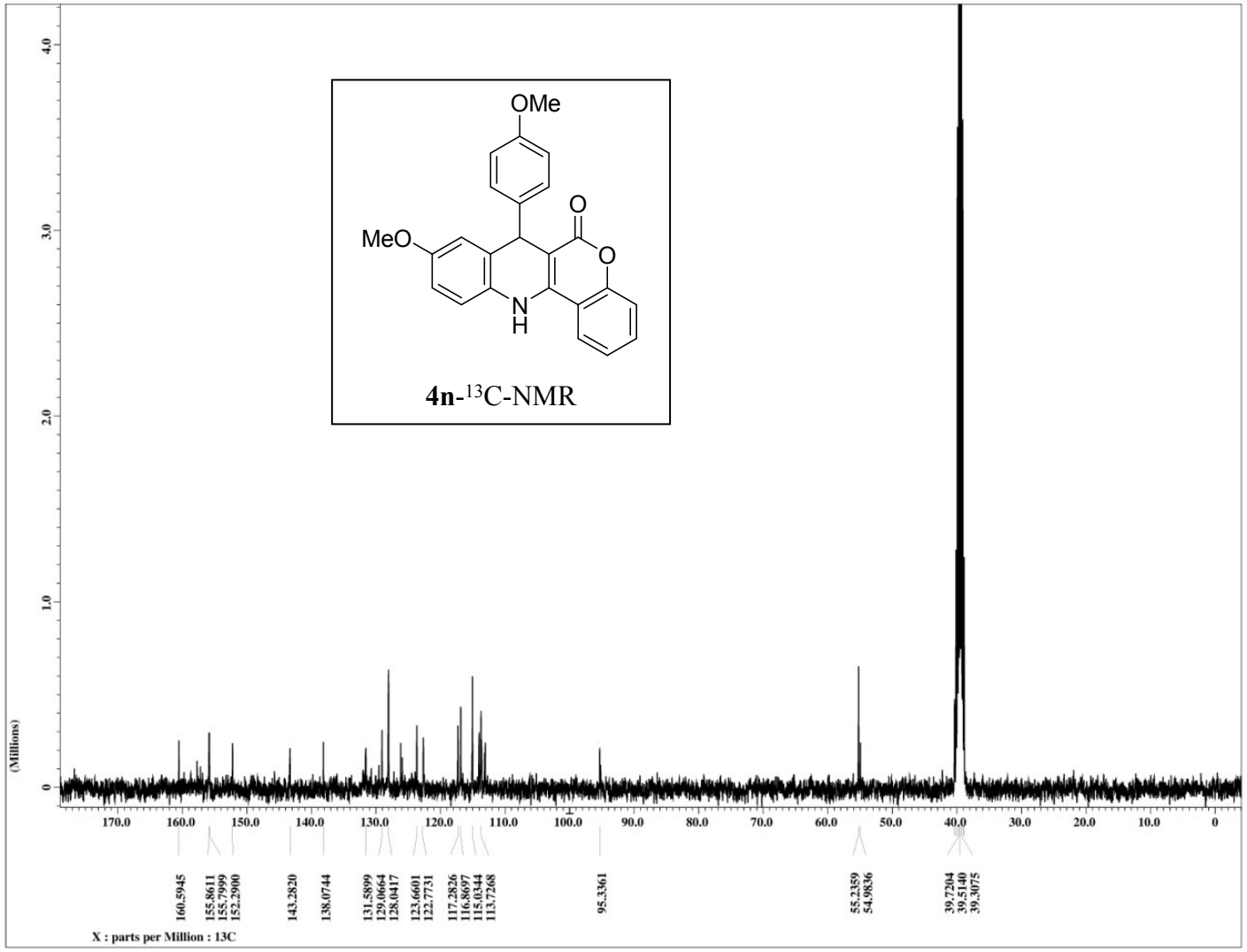


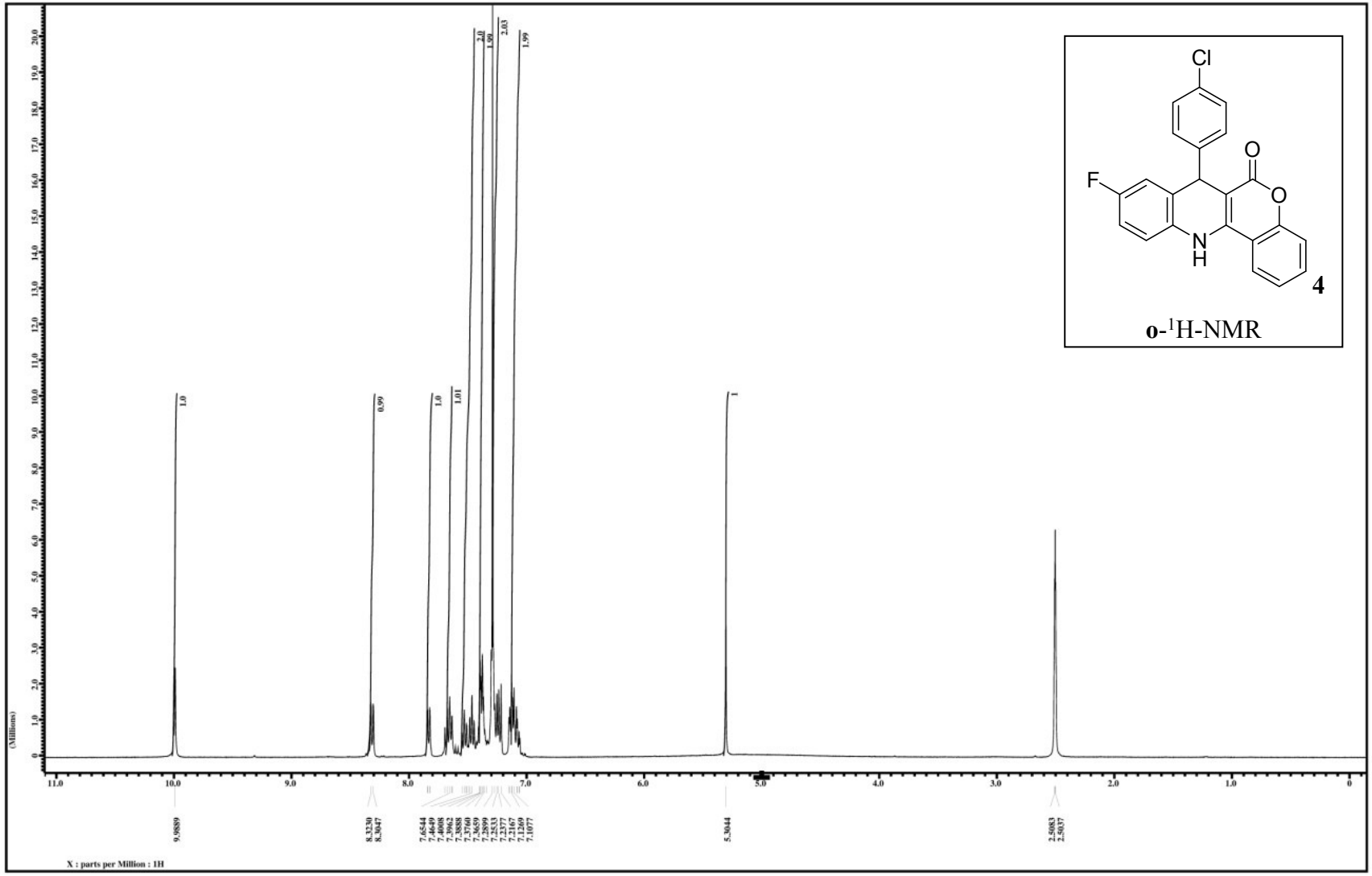
4l-^{13}C-NMR

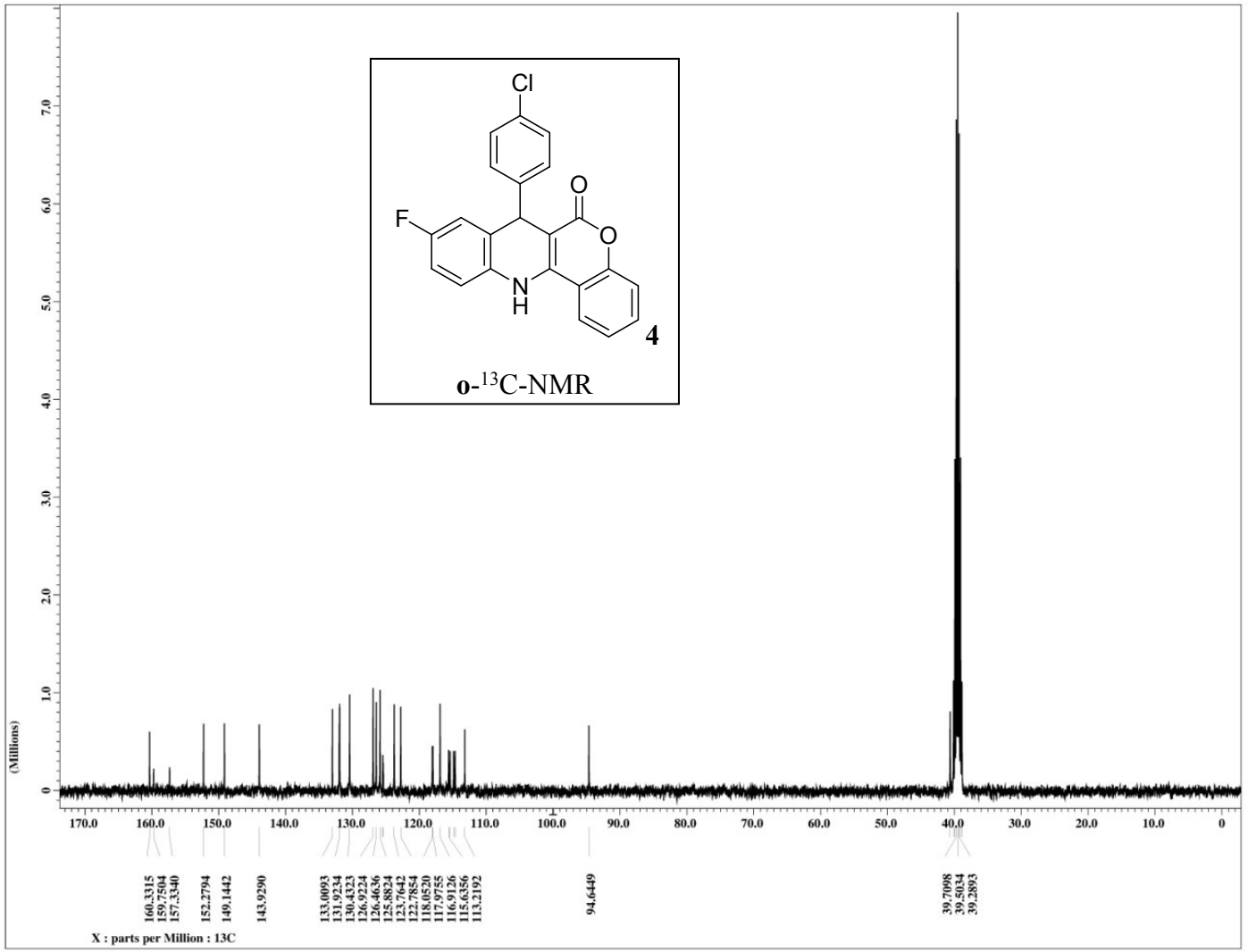

OEt
MeO
O
O
N
H
4m-1H-NMR
X : parts per Million : 1H

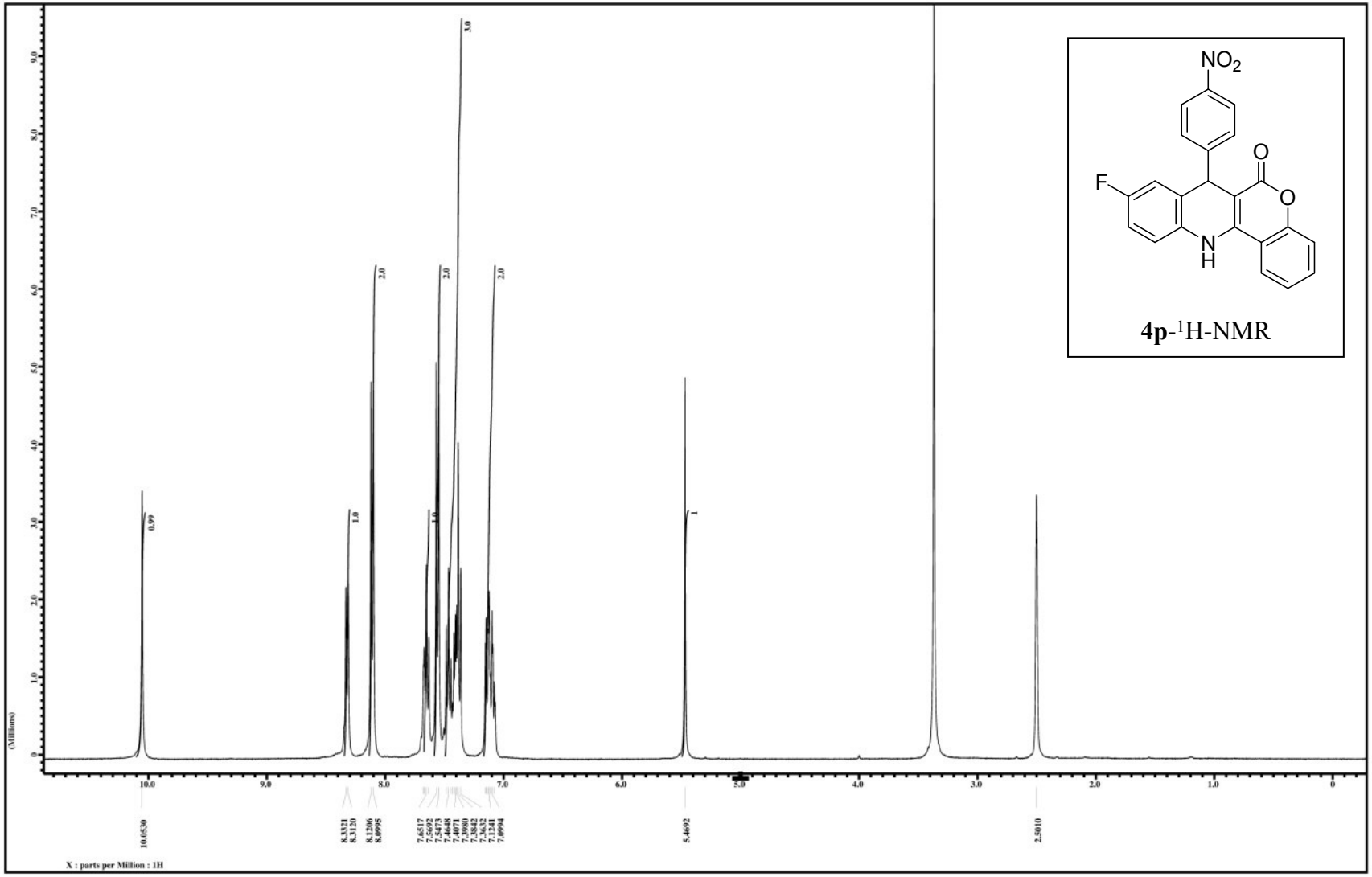

OEt
O
MeO
O
N
H
4m-13C-NMR
(Millions)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4733
156.9405
155.8546
152.1841
143.3061
139.5362
131.5376
129.0447
128.0200
125.8865
123.6001
122.6060
117.2838
116.8020
114.1333
114.0186
113.5598
113.1239
95.1767
62.8075
55.1912
39.7063
39.4999
39.2857
14.5864
X : parts per Million : 13C

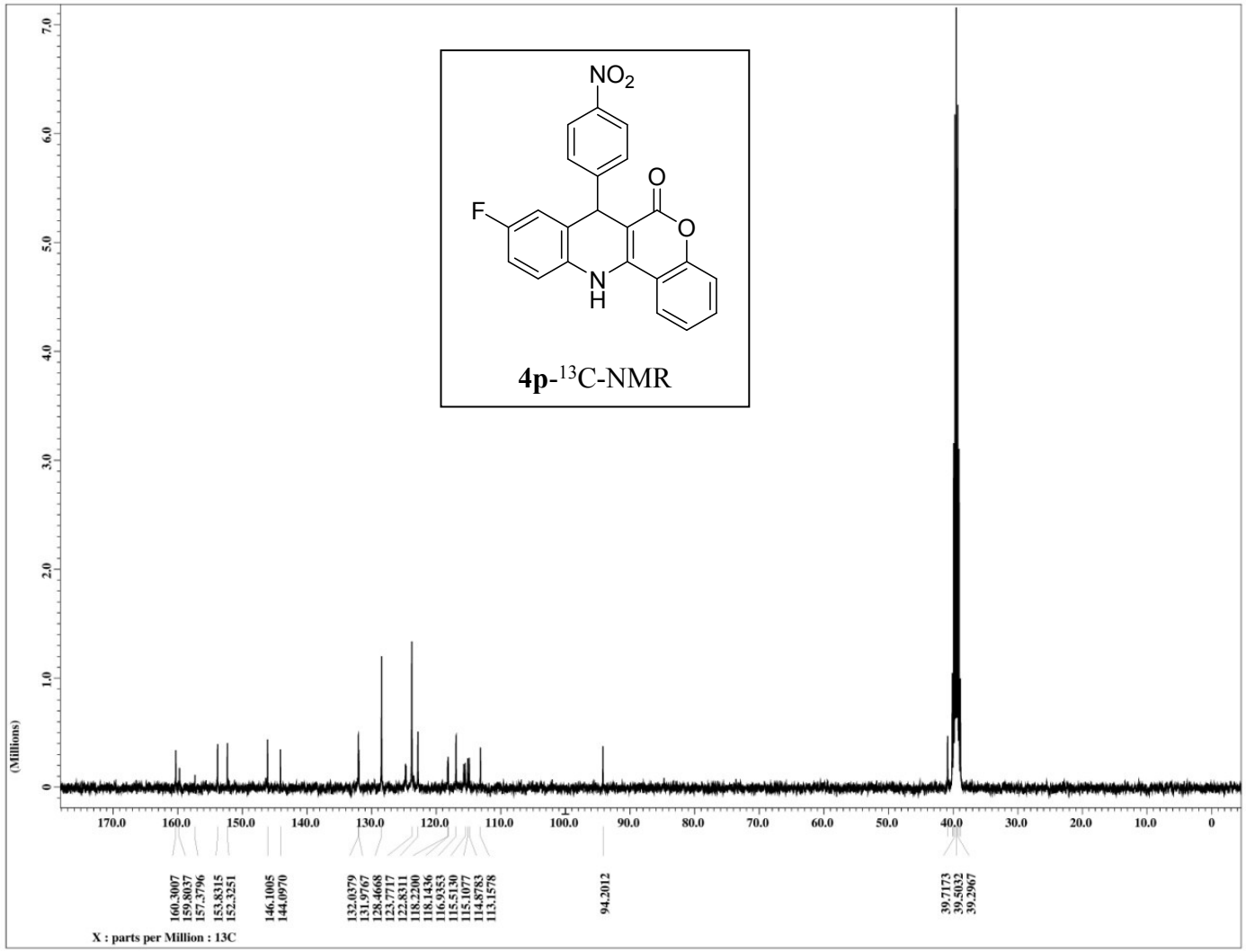

OMe
MeO
O
O
N
H
4n-1H-NMR
(Millions)
X : parts per Million : 1H

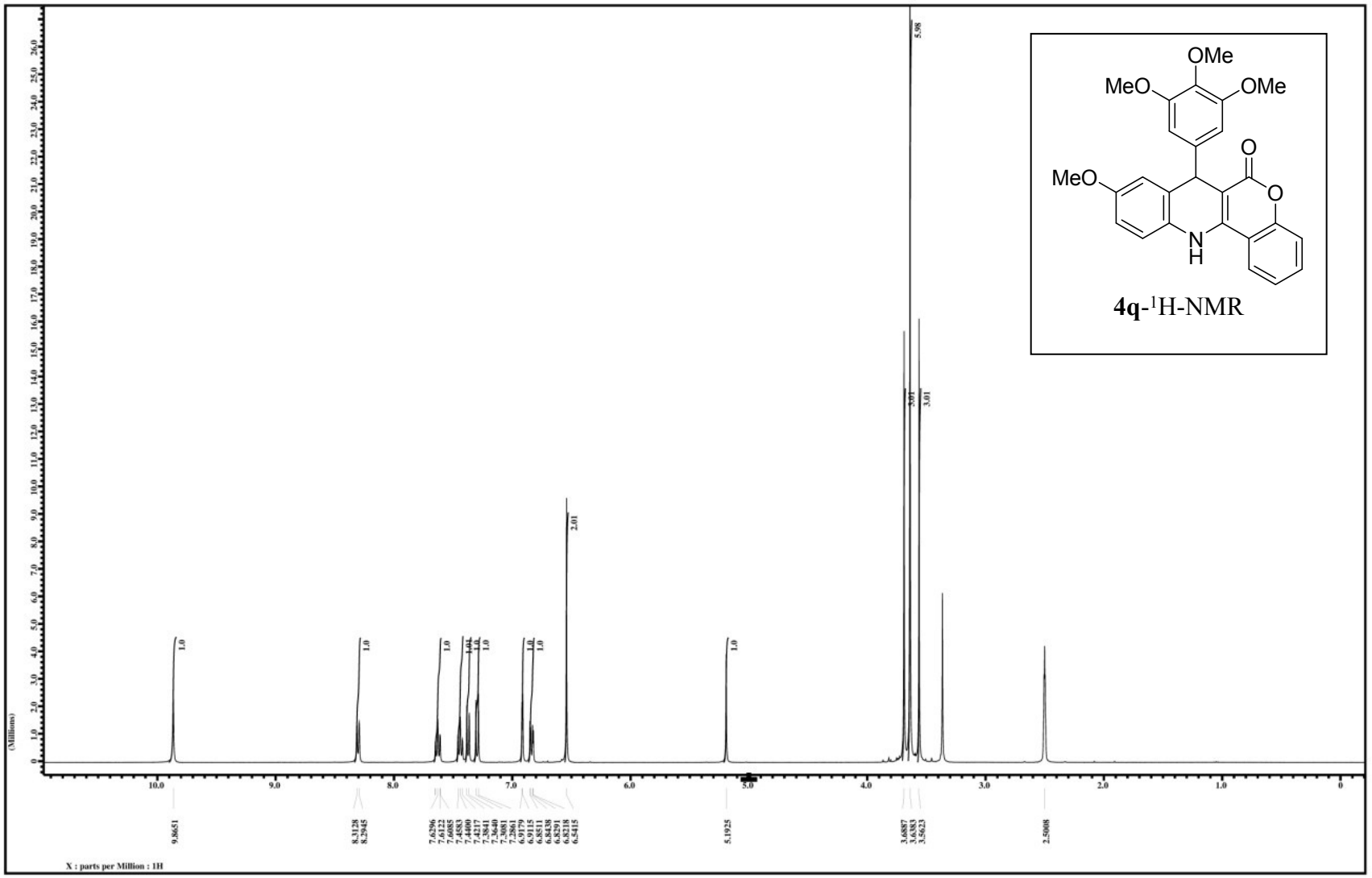

OMe
MeO
O
O
N
H
4n-13C-NMR
(Millions)
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5945
155.8611
155.7999
152.2900
143.2820
138.0744
131.5899
129.0664
128.0417
123.6601
122.7731
117.2826
116.8697
115.0344
113.7268
95.3361
55.2359
54.9836
39.7204
39.5140
39.3075
X : parts per Million : 13C

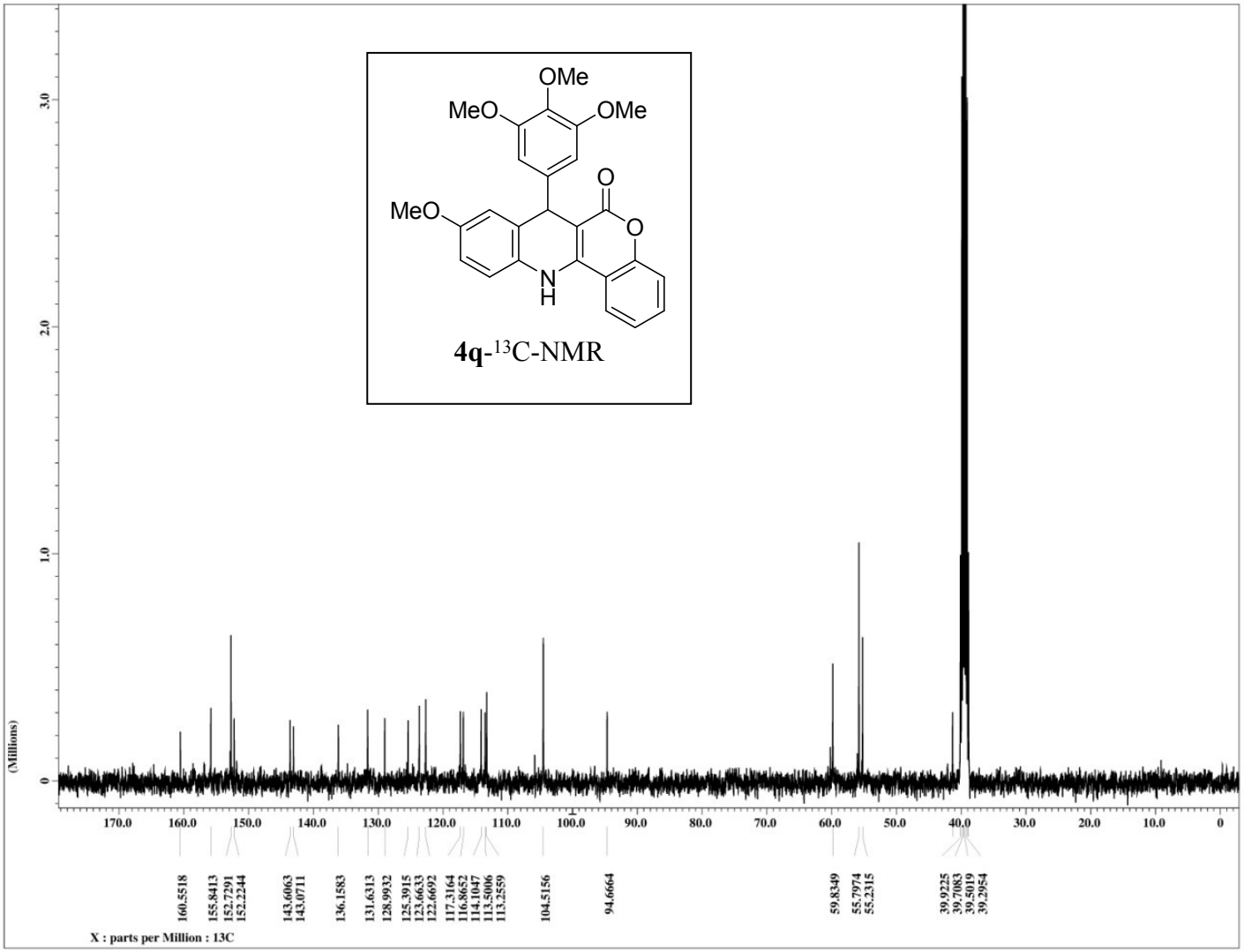

Cl
O
F
O
N
H
4
o-1H-NMR
X : parts per Million : 1H

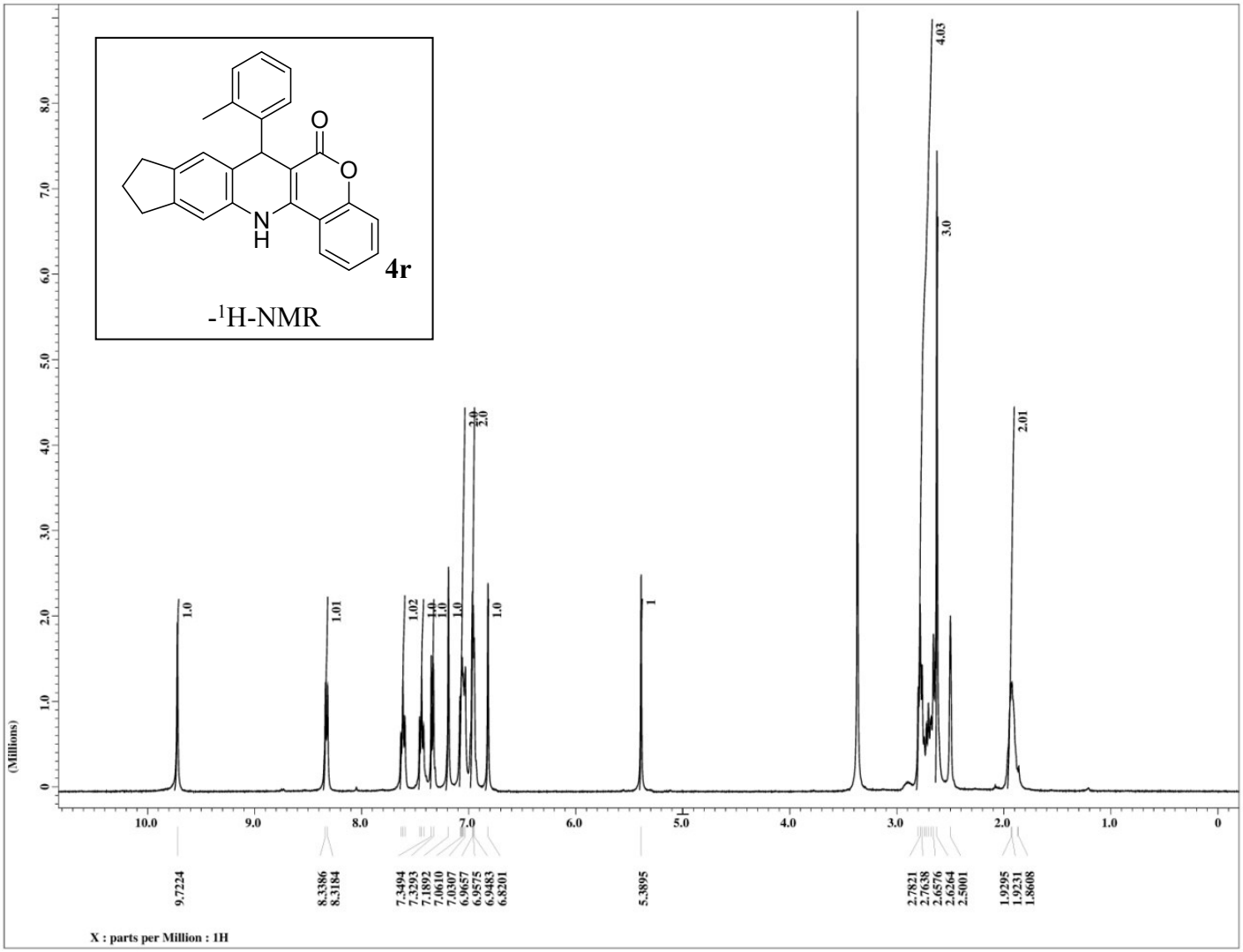

Cl
O
F
O
N
H
4
o-13C-NMR
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.3315
159.7504
157.3340
152.2794
149.1442
143.9290
133.0093
131.9234
130.4323
126.9224
126.4636
125.8824
123.7642
122.7854
118.0520
117.9755
116.9126
115.6356
113.2192
94.6449
39.7098
39.5034
39.2893
X : parts per Million : 13C

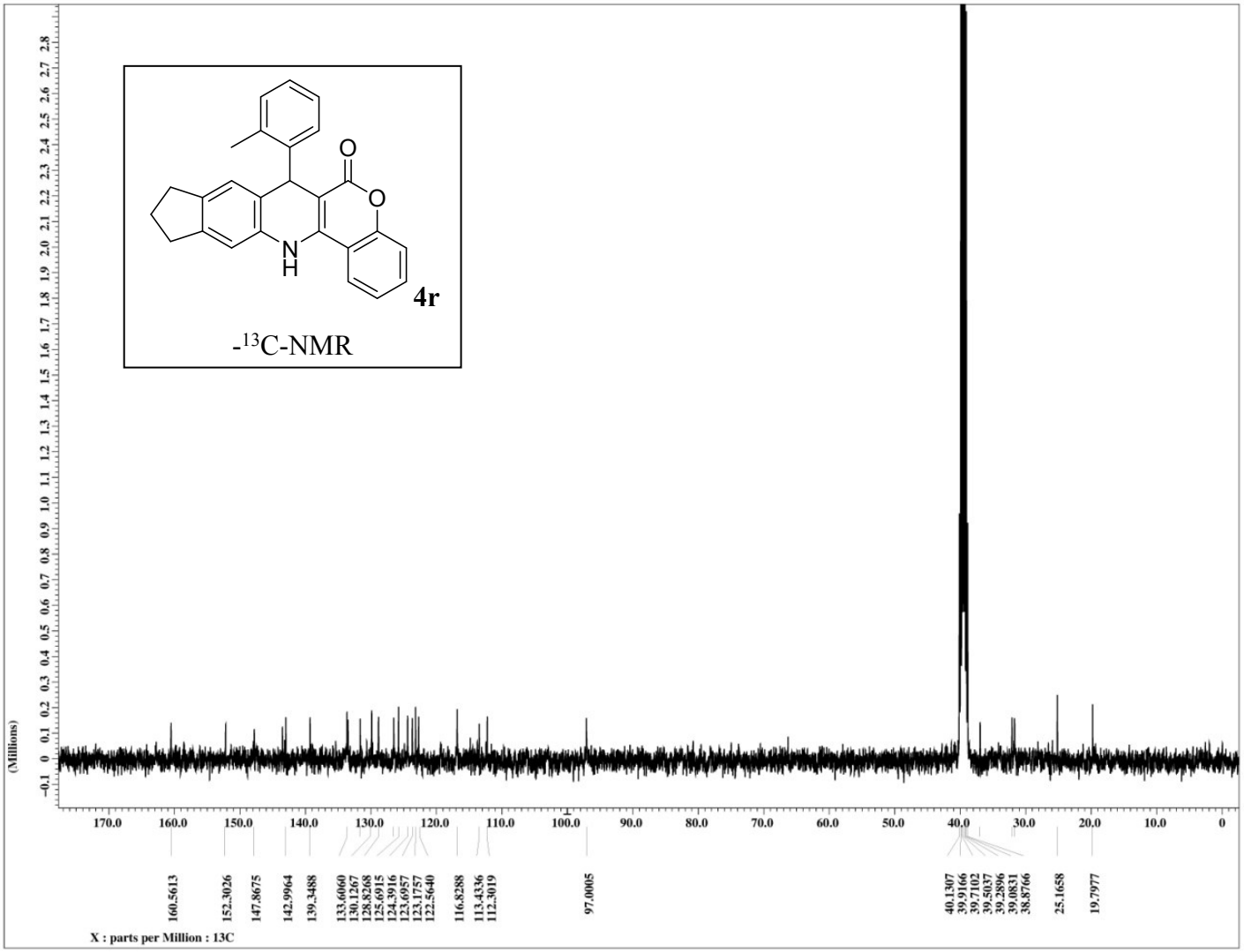

NO2
O
F
O
N
H
4p-1H-NMR
(Millions)
X : parts per Million : 1H

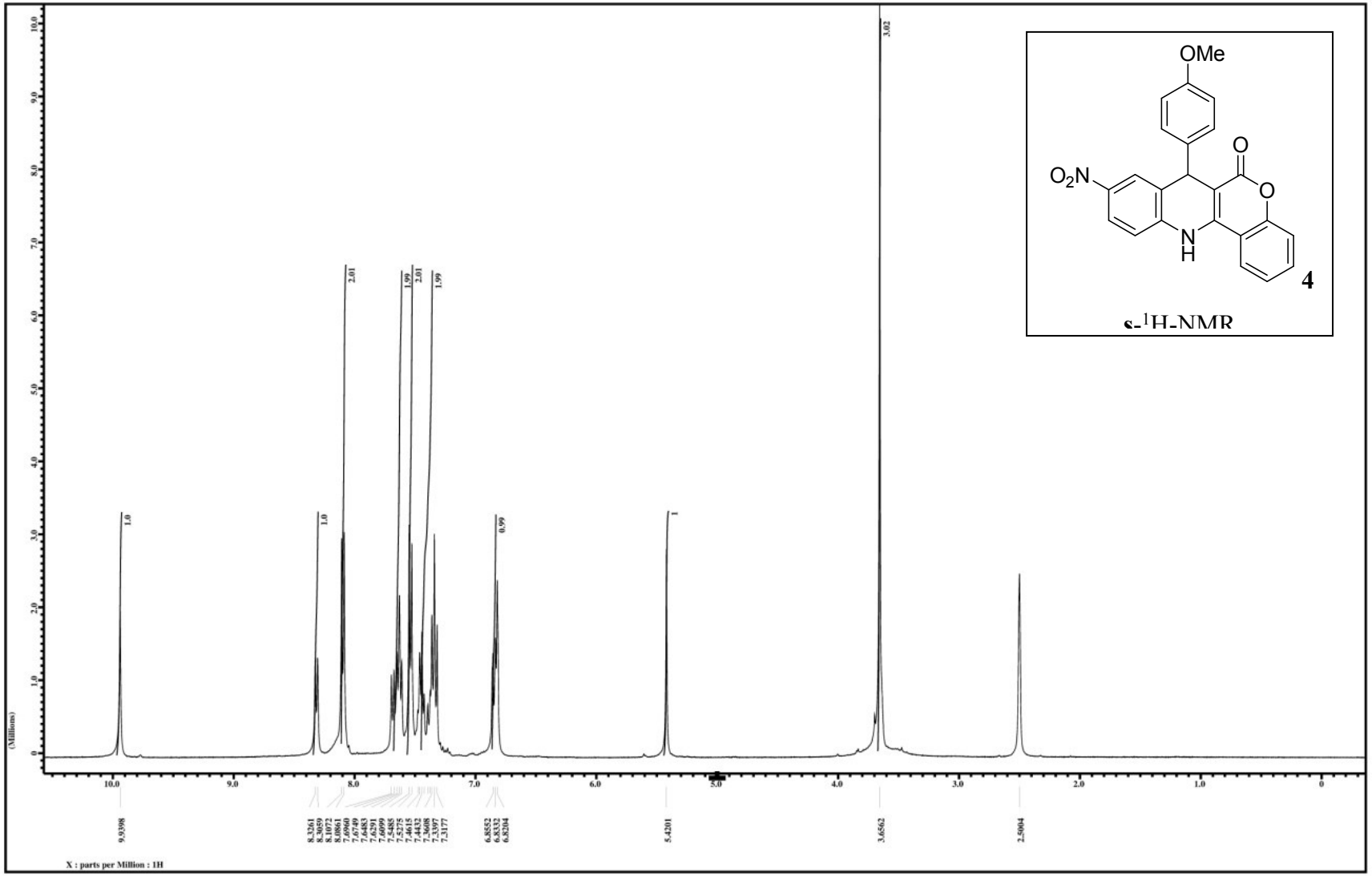

NO2
O
F
O
N
H
4p-13C-NMR
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.3007
159.8037
157.3796
153.8315
152.3251
146.1005
144.0970
132.0379
131.9767
128.4668
123.7717
123.5711
122.8531
118.2200
118.1436
116.9353
115.5130
115.1077
114.8783
113.1578
94.2012
39.7173
39.5032
39.2967
X : parts per Million : 13C

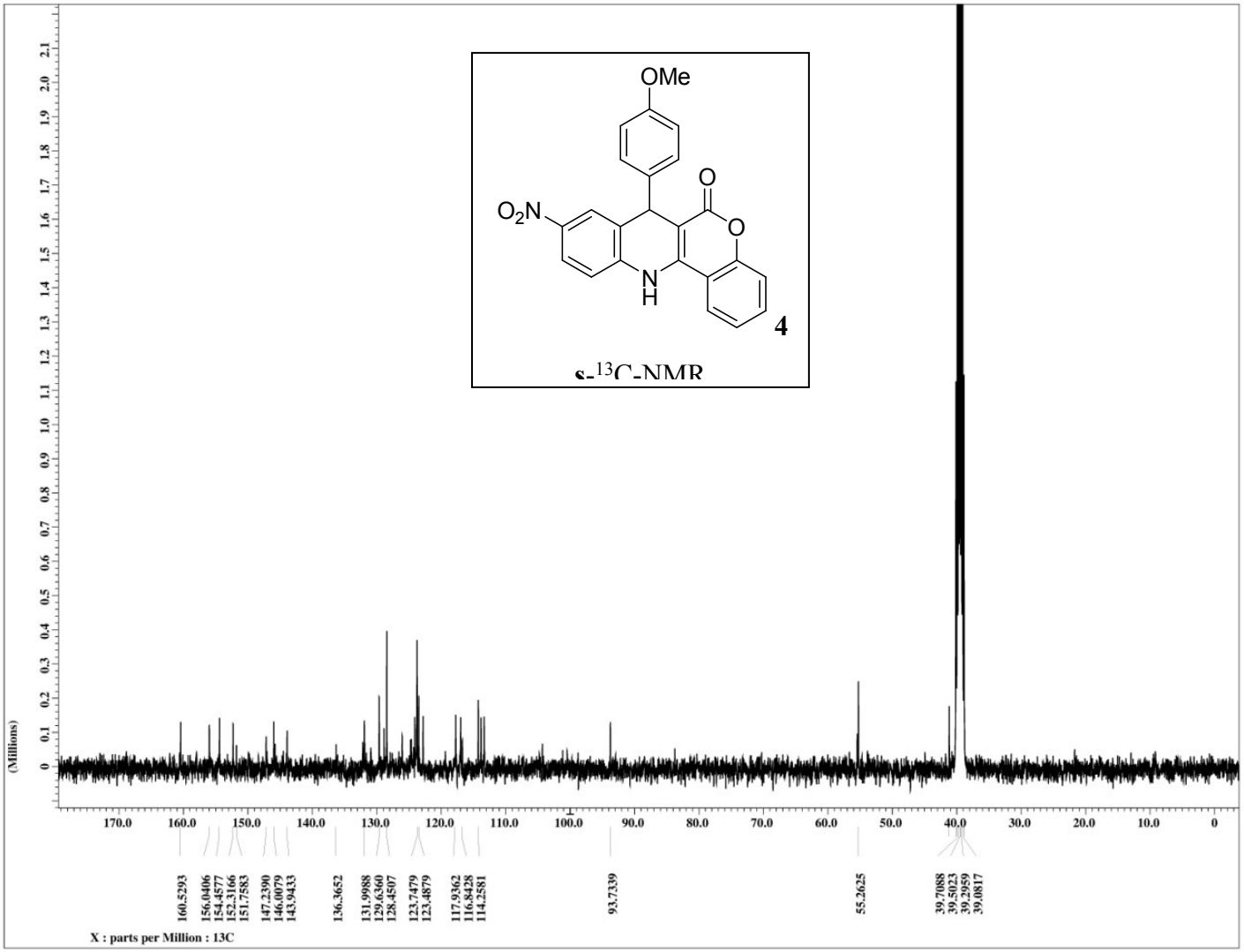

OMe
MeO
OMe
O
MeO
O
N
H
4q-1H-NMR
X : parts per Million : 1H

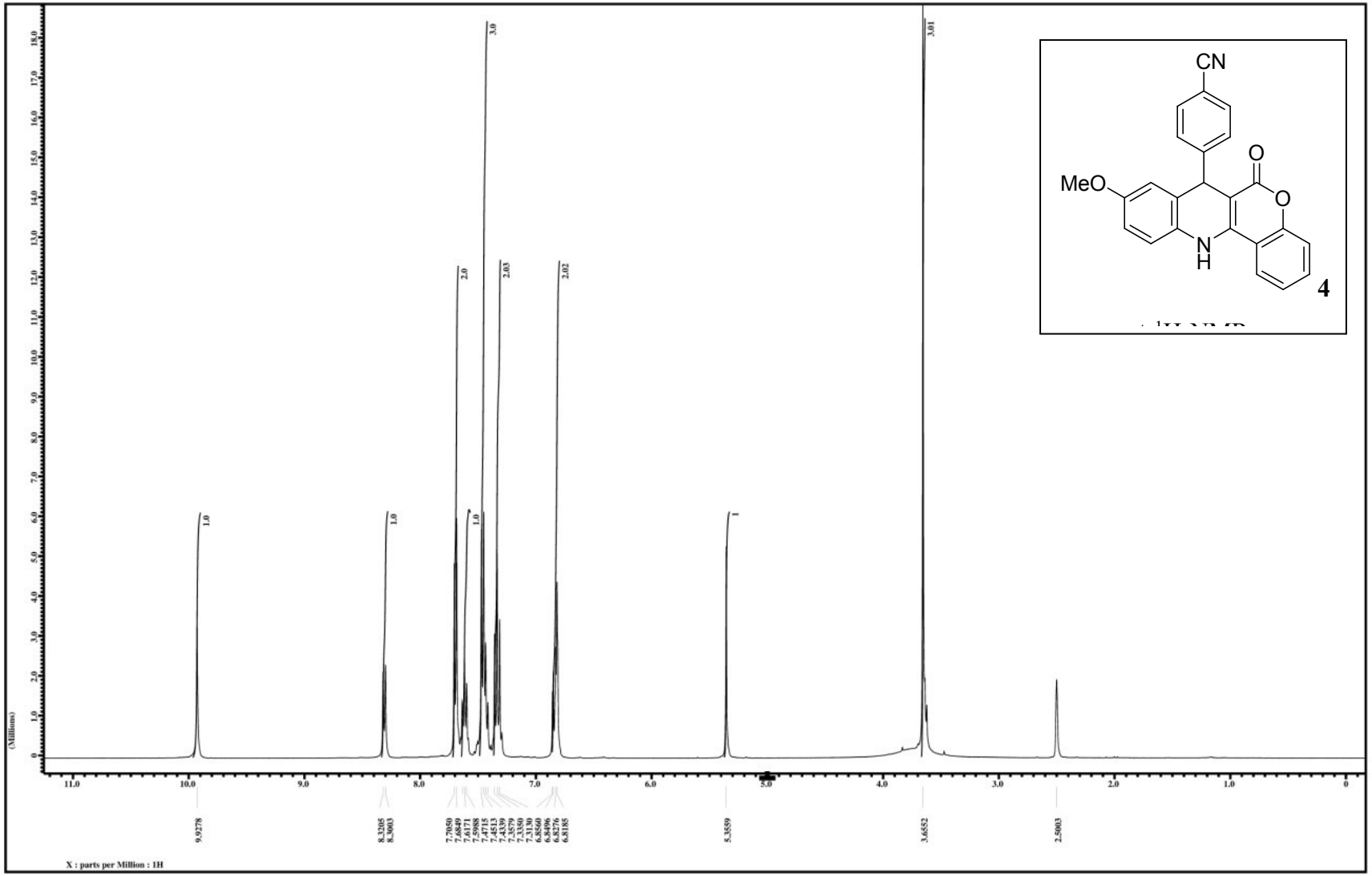

OMe
MeO
OMe
O
MeO
O
N
H
4q-13C-NMR
(Millions)
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5518
155.8413
152.7291
152.2244
143.6063
143.0711
136.1583
131.6313
128.9932
125.3915
123.6633
122.6692
117.3164
116.8652
114.1047
113.5006
113.2559
104.5156
94.6664
59.8349
55.7974
55.2315
39.9225
39.7083
39.5019
39.2954
X : parts per Million : 13C

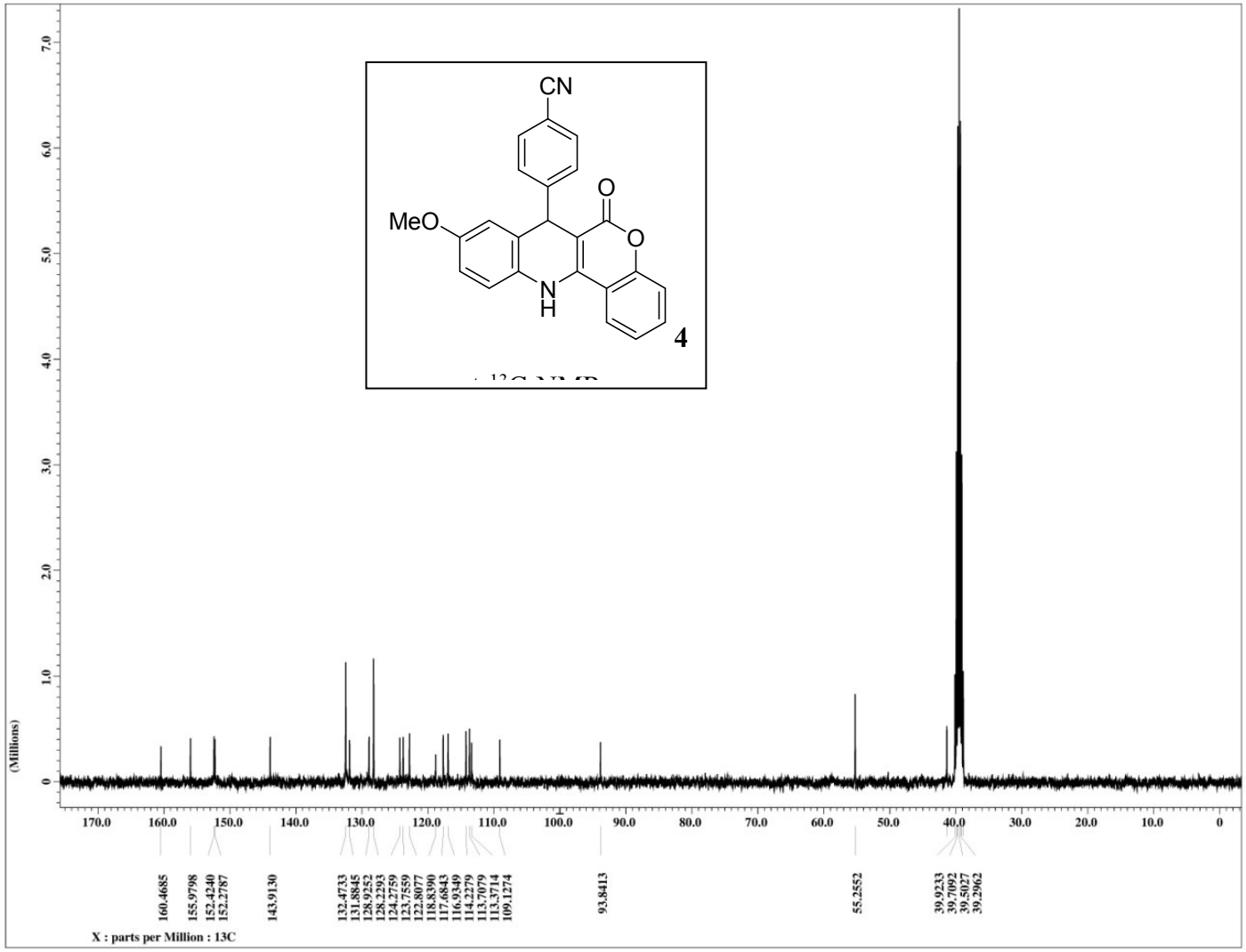

4r
-1H-NMR
(Millions)
X : parts per Million : 1H

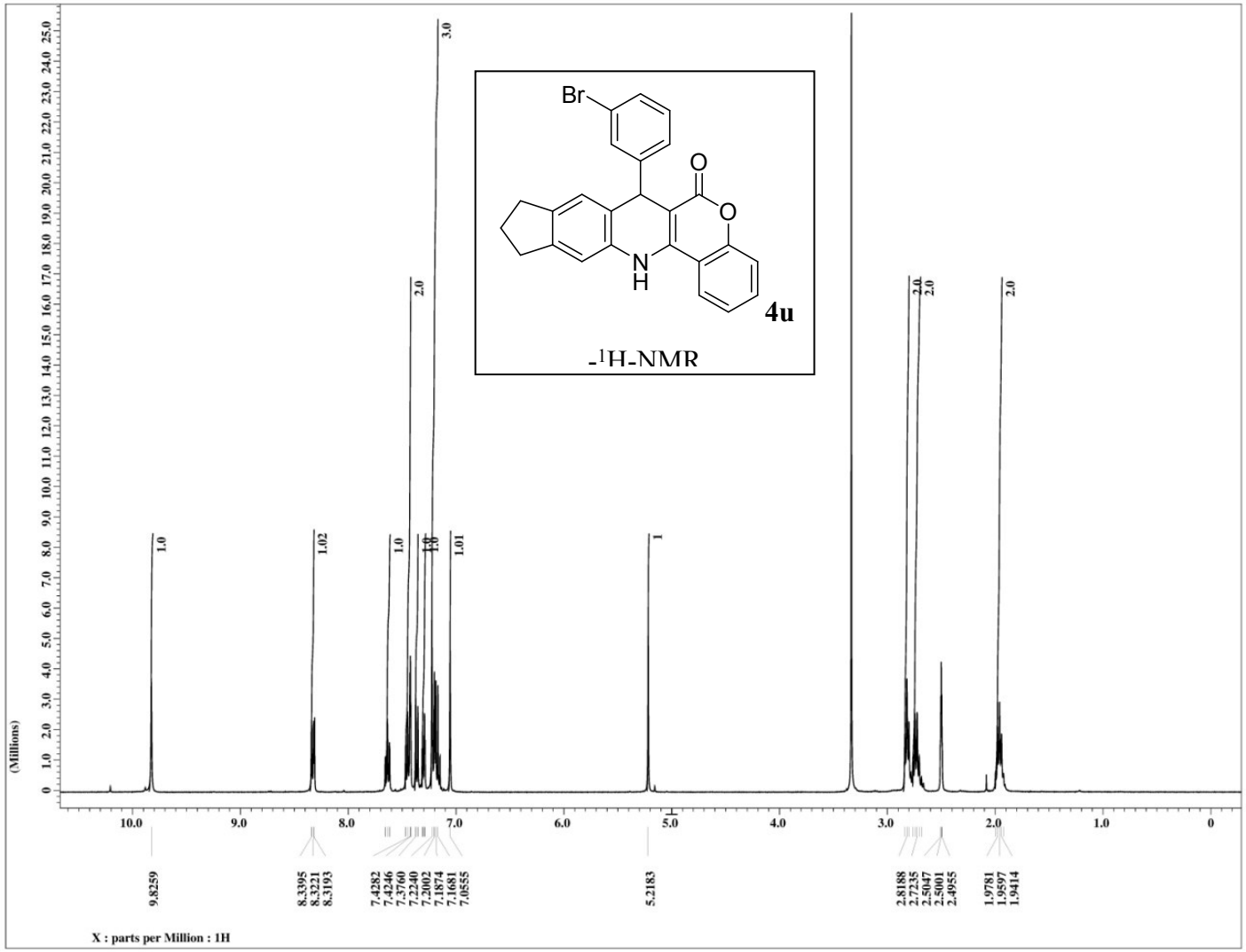

4r
-13C-NMR
(Millions)
X : parts per Million : 13C
160.5613
152.3026
147.8675
142.9964
139.3488
133.6060
130.1267
128.8268
125.6915
124.3916
123.6957
123.1757
122.5640
116.8288
113.4336
112.3019
97.0005
40.1307
39.9166
39.7102
39.5037
39.2896
39.0831
38.8766
25.1658
19.7977

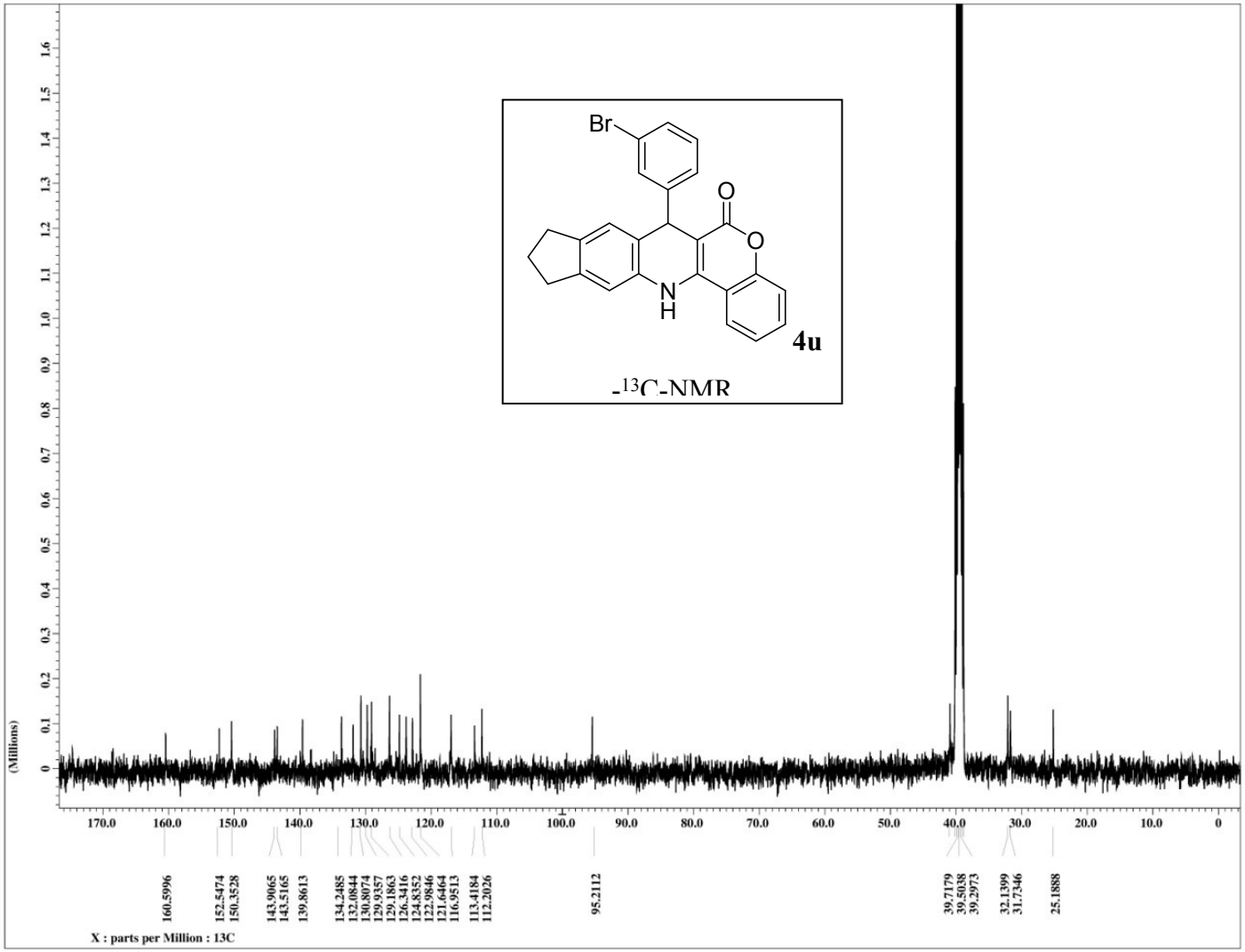

OMe
O
O_2N
O
N
H
4
s-^{1}H-NMR
(Millions)
X : parts per Million : 1H

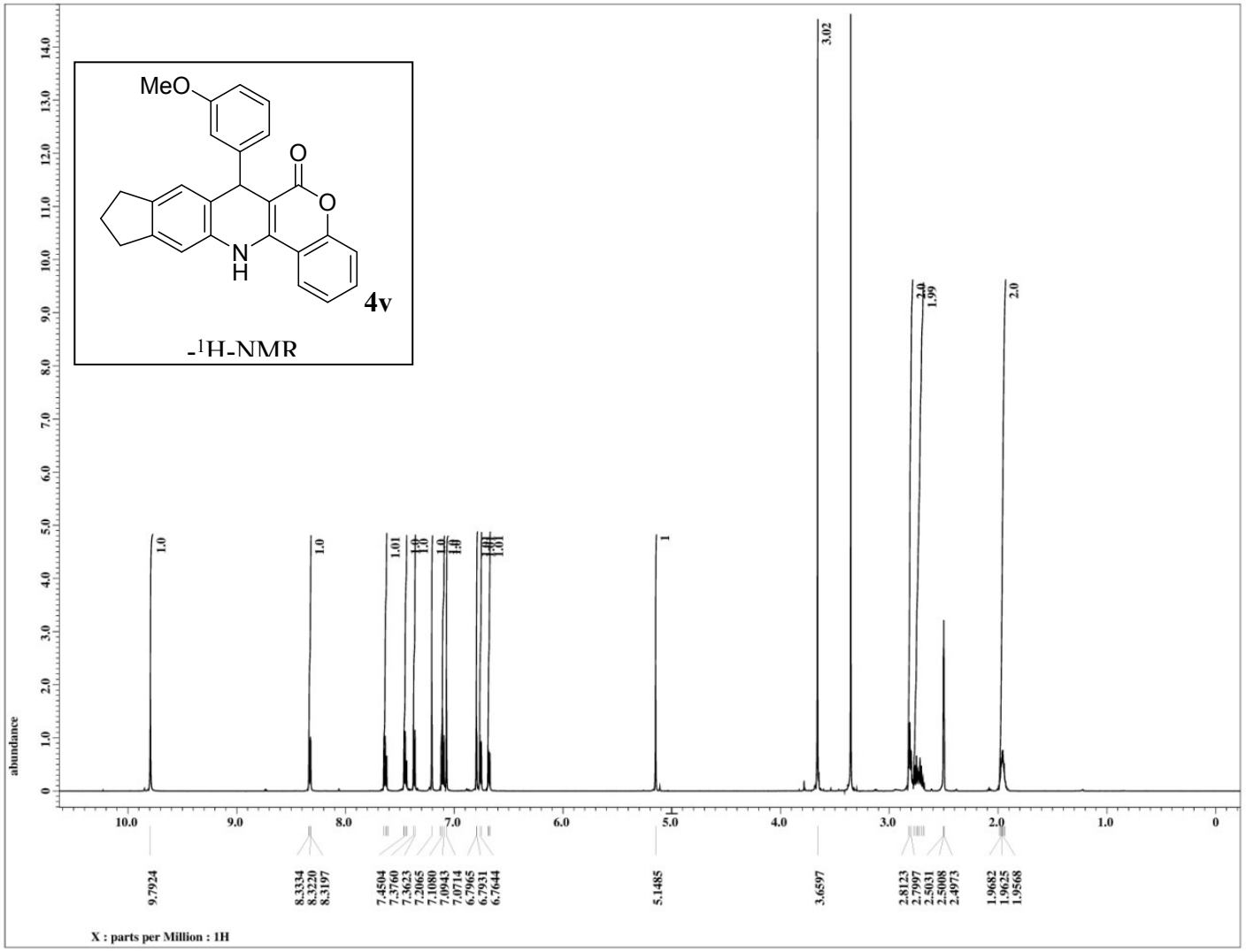

OMe
O
O_2N
O
N
H
4
s-^{13}C-NMR
(Millions)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5293
156.0406
154.4577
152.3166
151.7583
147.2390
146.0079
143.9433
136.3652
131.9988
129.6360
128.4507
123.7479
123.4879
117.9362
116.8428
114.2581
93.7339
55.2625
39.7088
39.5023
39.2959
39.0817
X : parts per Million : 13C

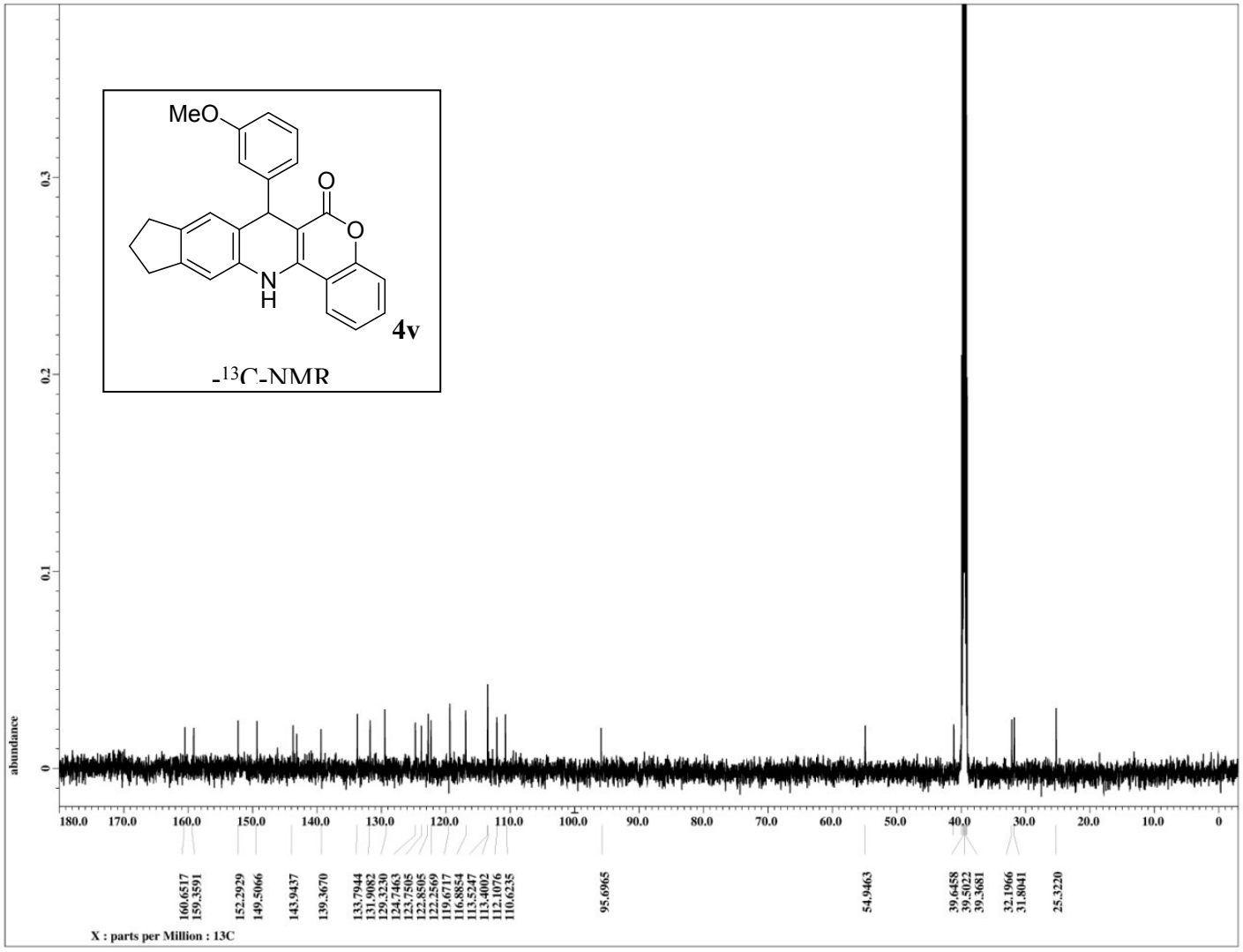

CN
O
MeO
O
N
H
4
X : parts per Million : 1H

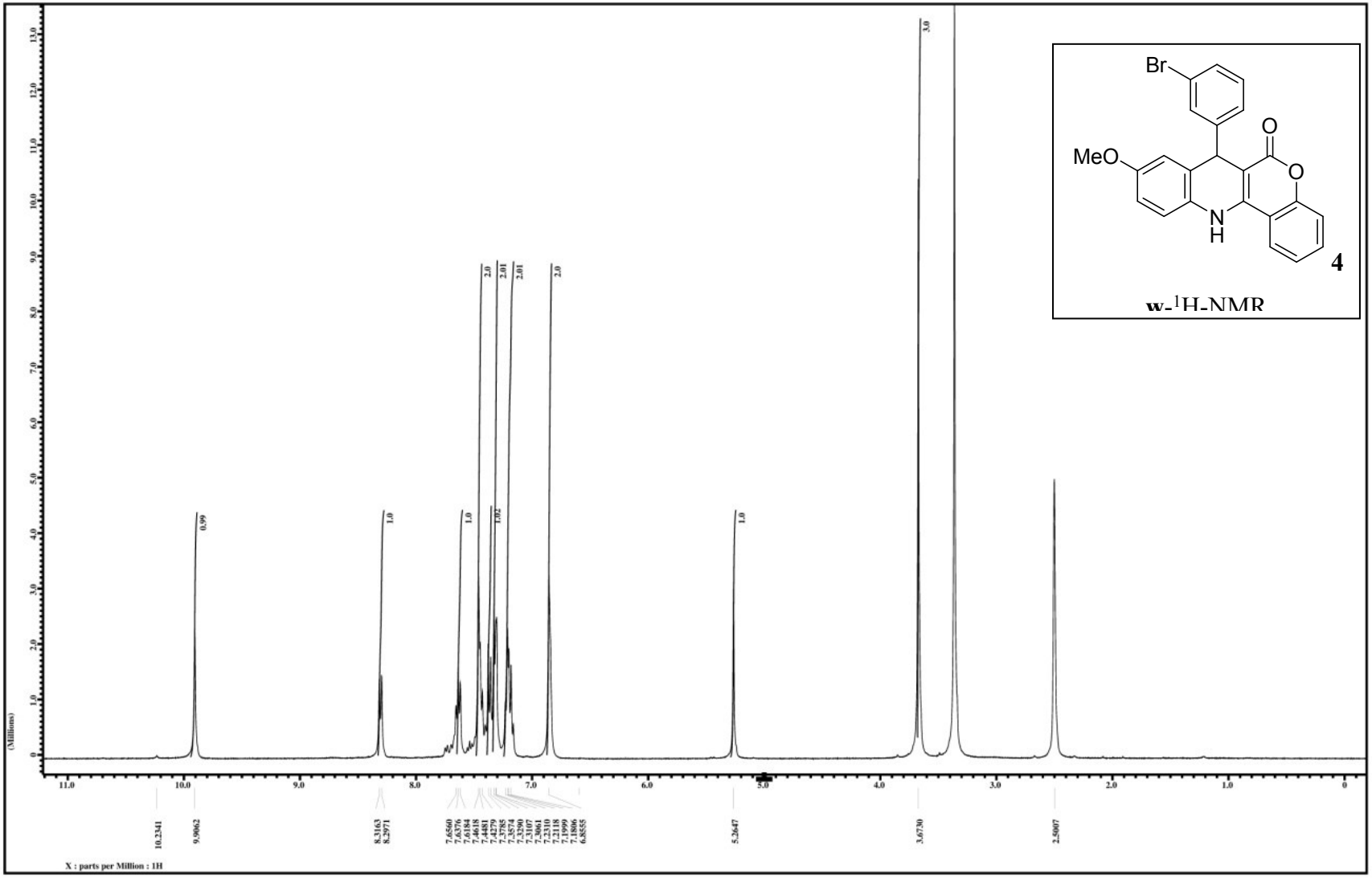

CN
O
MeO
O
N
H
4
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4685
155.9798
152.4240
152.2787
143.9130
132.4733
131.8845
128.9252
128.2293
124.2759
123.7559
122.8077
118.8390
117.6843
116.9349
114.2279
113.7079
113.3714
109.1274
93.8413
55.2552
39.9233
39.7092
39.5027
39.2962
X : parts per Million : 13C

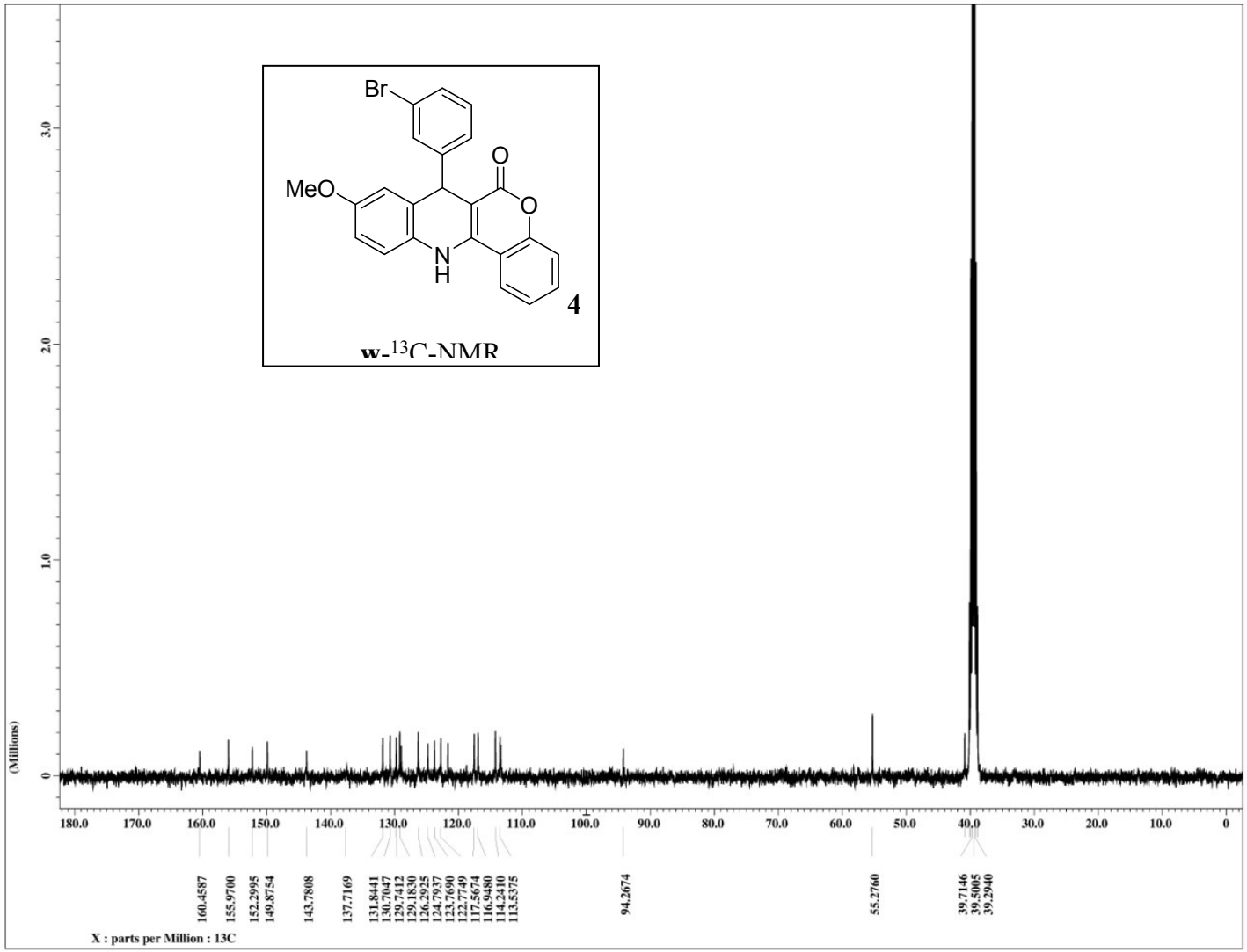

Br
O
O
N
H
4u
-1H-NMR
(Millions)
X : parts per Million : 1H

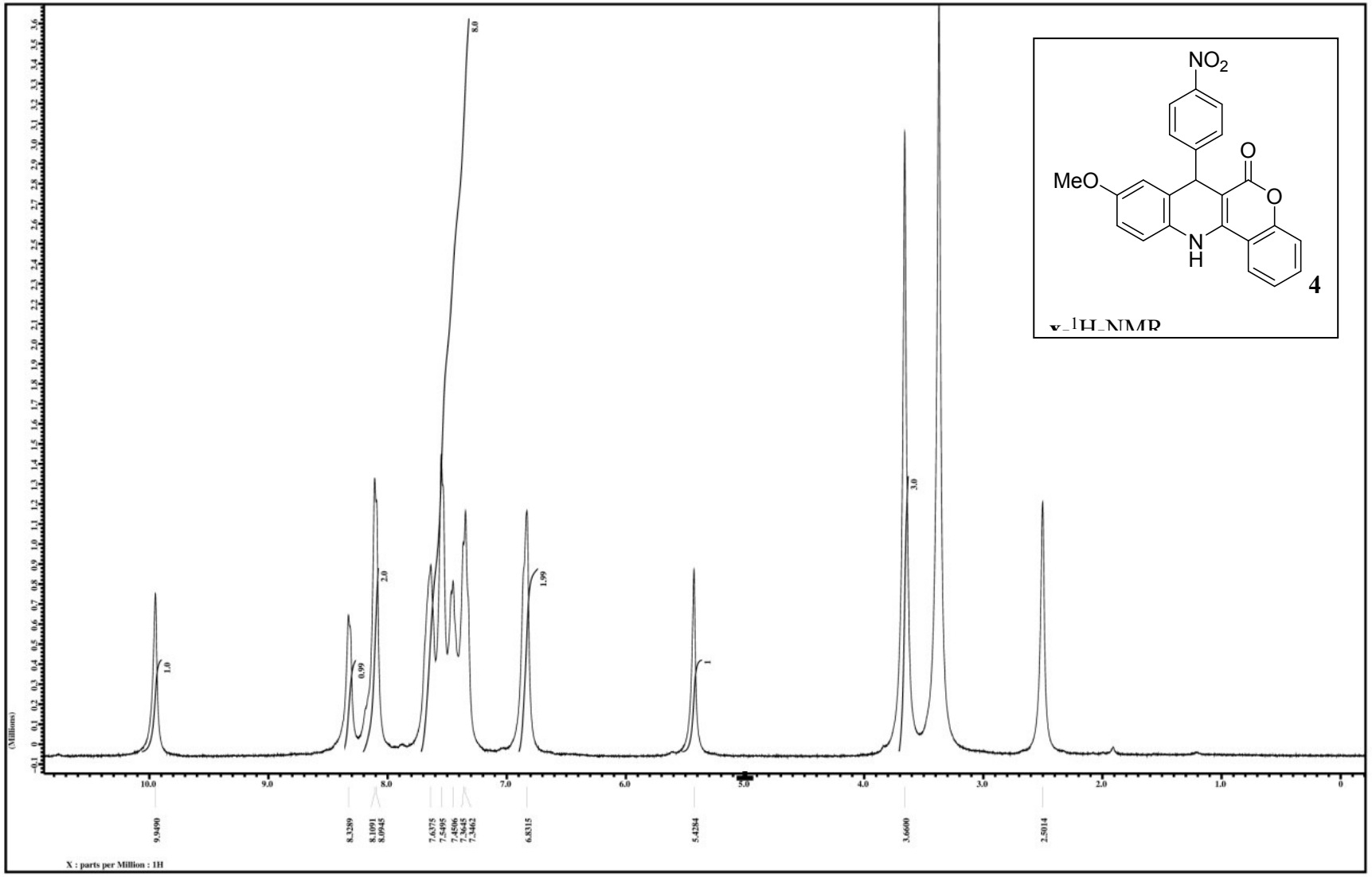

Br
O
O
N
H
4u
-13C-NMR
(Millions)
160.5996
152.5474
150.3528
143.9065
143.5165
139.8613
134.2485
132.0844
130.8074
129.9357
129.1863
126.3416
124.8352
123.9846
121.6464
116.9513
113.4184
112.2026
95.2112
39.7179
39.5038
39.2973
32.1399
31.7346
25.1888
X : parts per Million : 13C

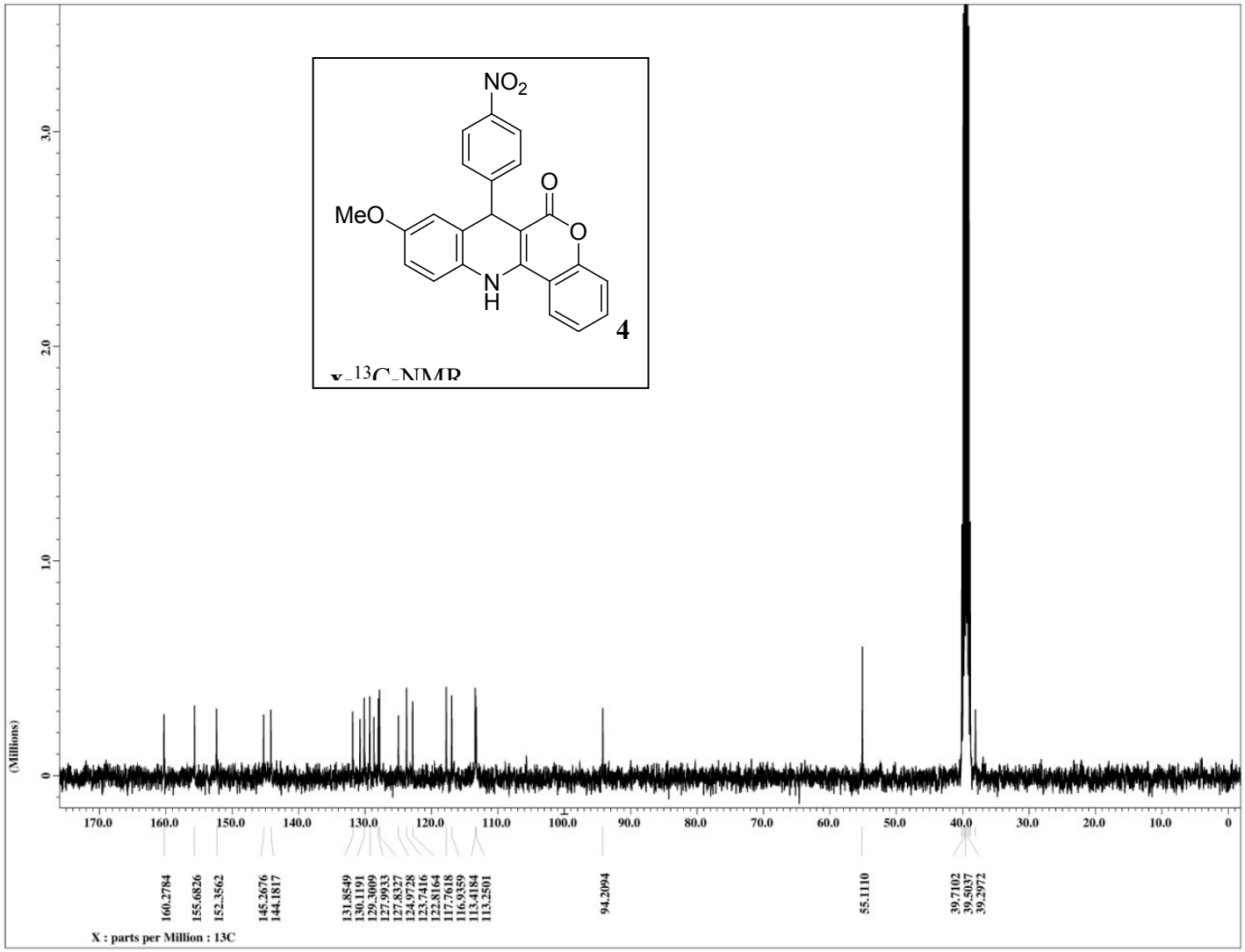

MeO
O
O
N
H
4v
-1H-NMR
abundance
X : parts per Million : 1H

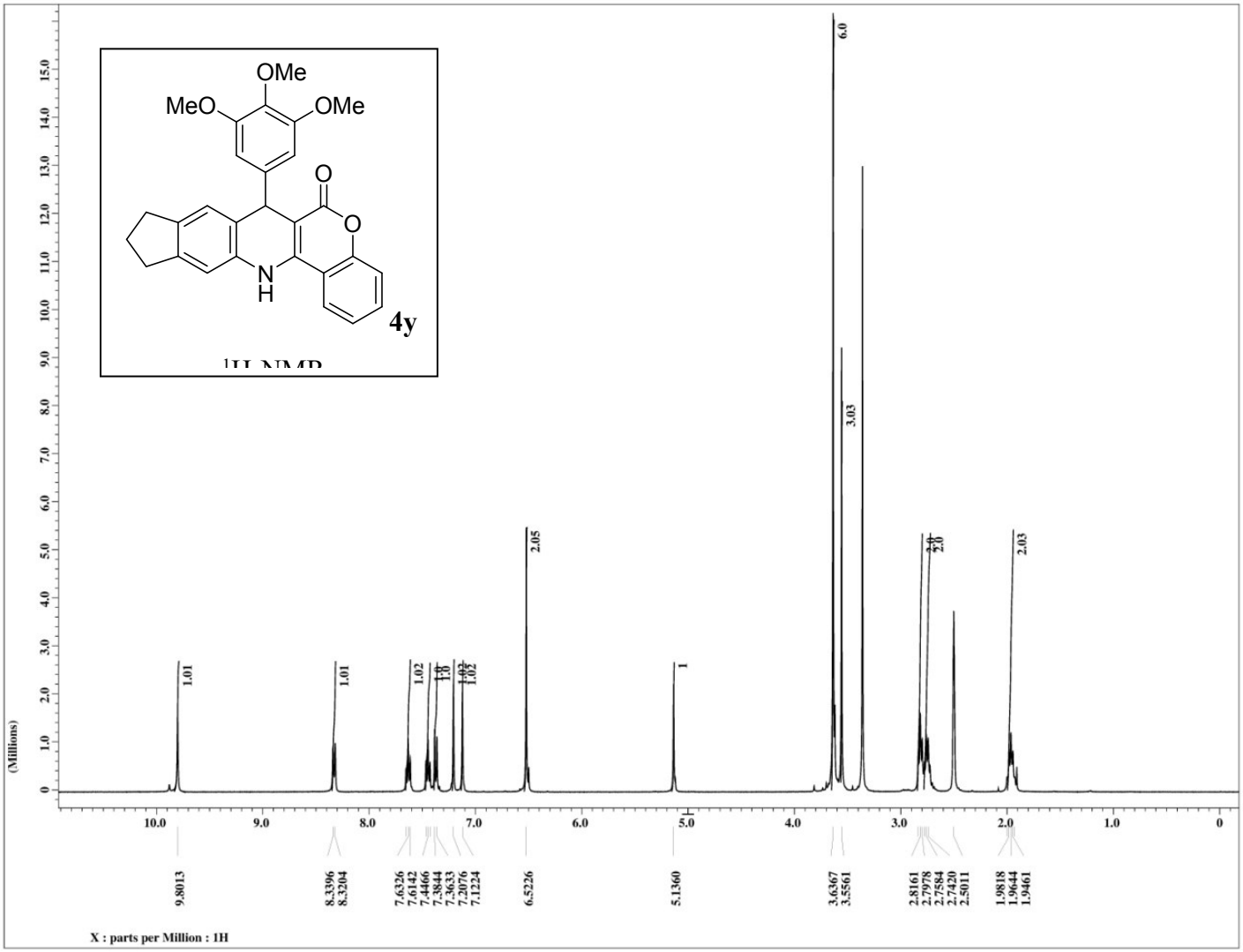

MeO
O
O
N
H
4v
-13C-NMR
abundance
0.3
0.2
0.1
0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
160.6517
159.3591
152.2929
149.5066
143.9437
139.3670
133.7944
131.9082
129.3230
124.7463
123.7505
122.8505
122.2569
119.6717
116.8854
113.5247
113.4002
112.1076
110.6235
95.6965
54.9463
39.6458
39.5022
39.3681
32.1966
31.8041
25.3220
X : parts per Million : 13C

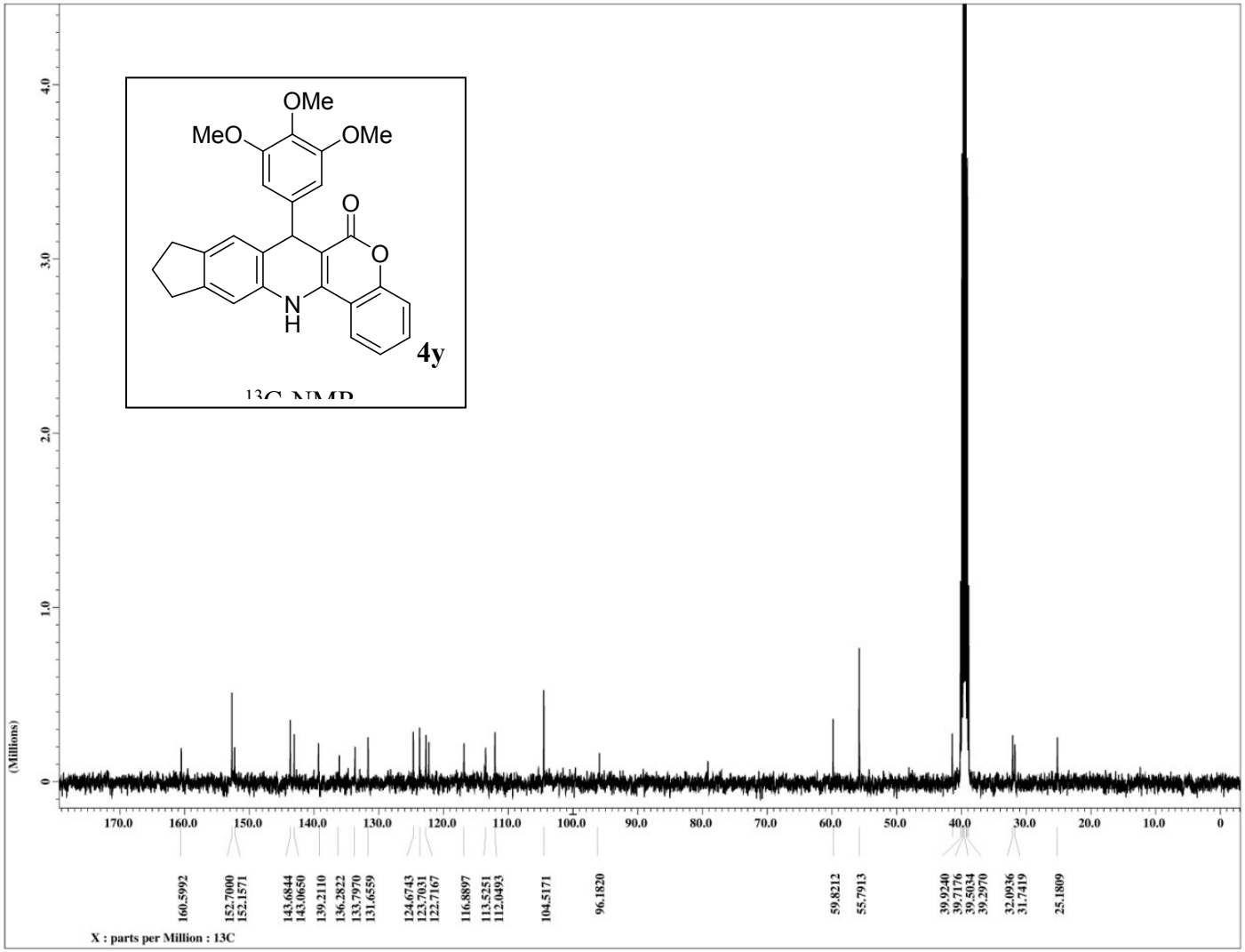

Br
O
MeO
O
N
H
4
w-1H-NMR
(Millions)
X : parts per Million : 1H

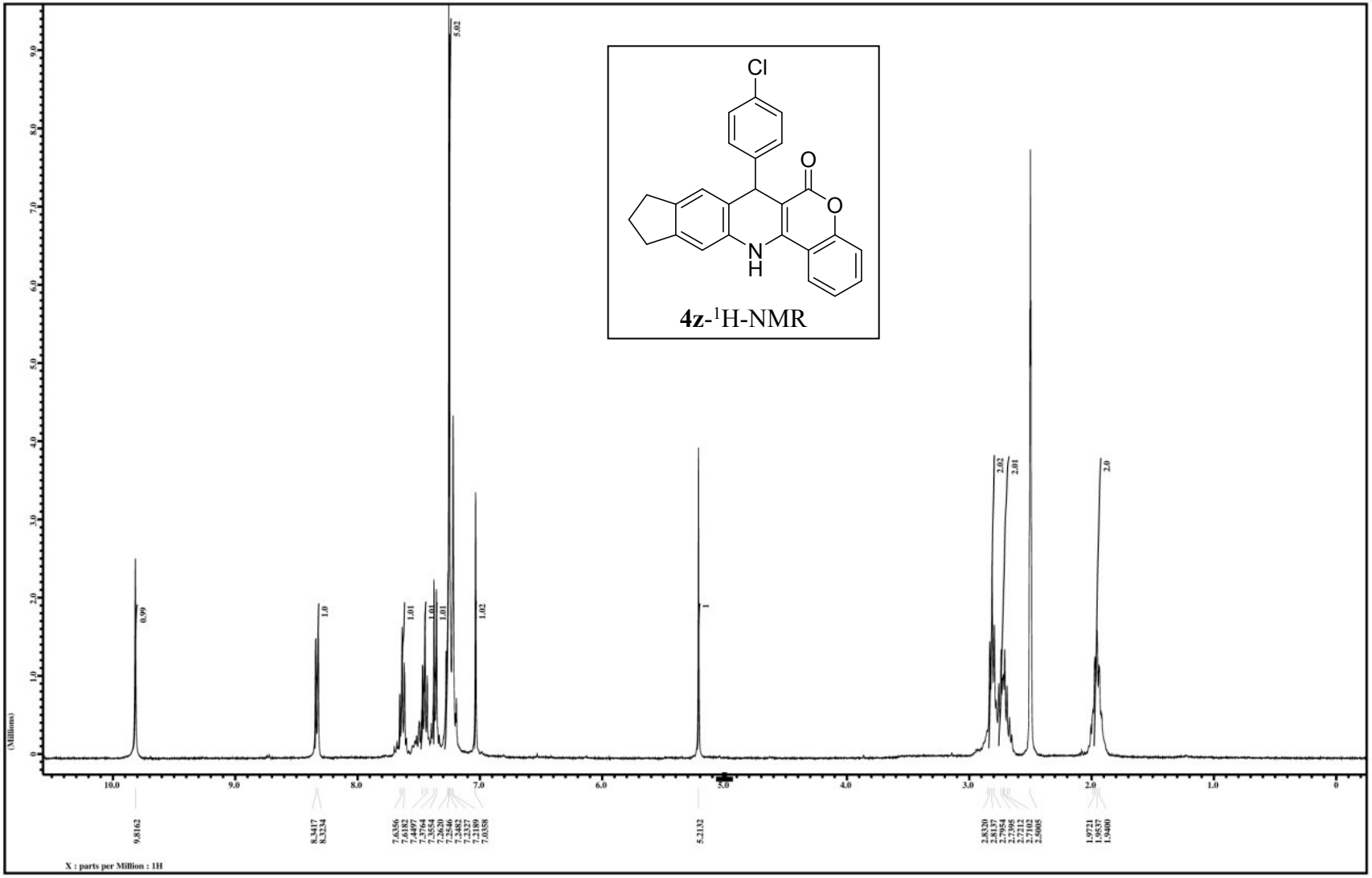

Br
O
MeO
O
N
H
4
w-13C-NMR
(Millions)
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4587
155.9700
152.2995
149.8754
143.7808
137.7169
131.8441
130.7047
129.7412
129.1830
126.2925
124.7937
123.7690
122.7749
117.5674
116.9480
114.2410
113.5375
94.2674
55.2760
39.7146
39.5005
39.2940
X : parts per Million : 13C

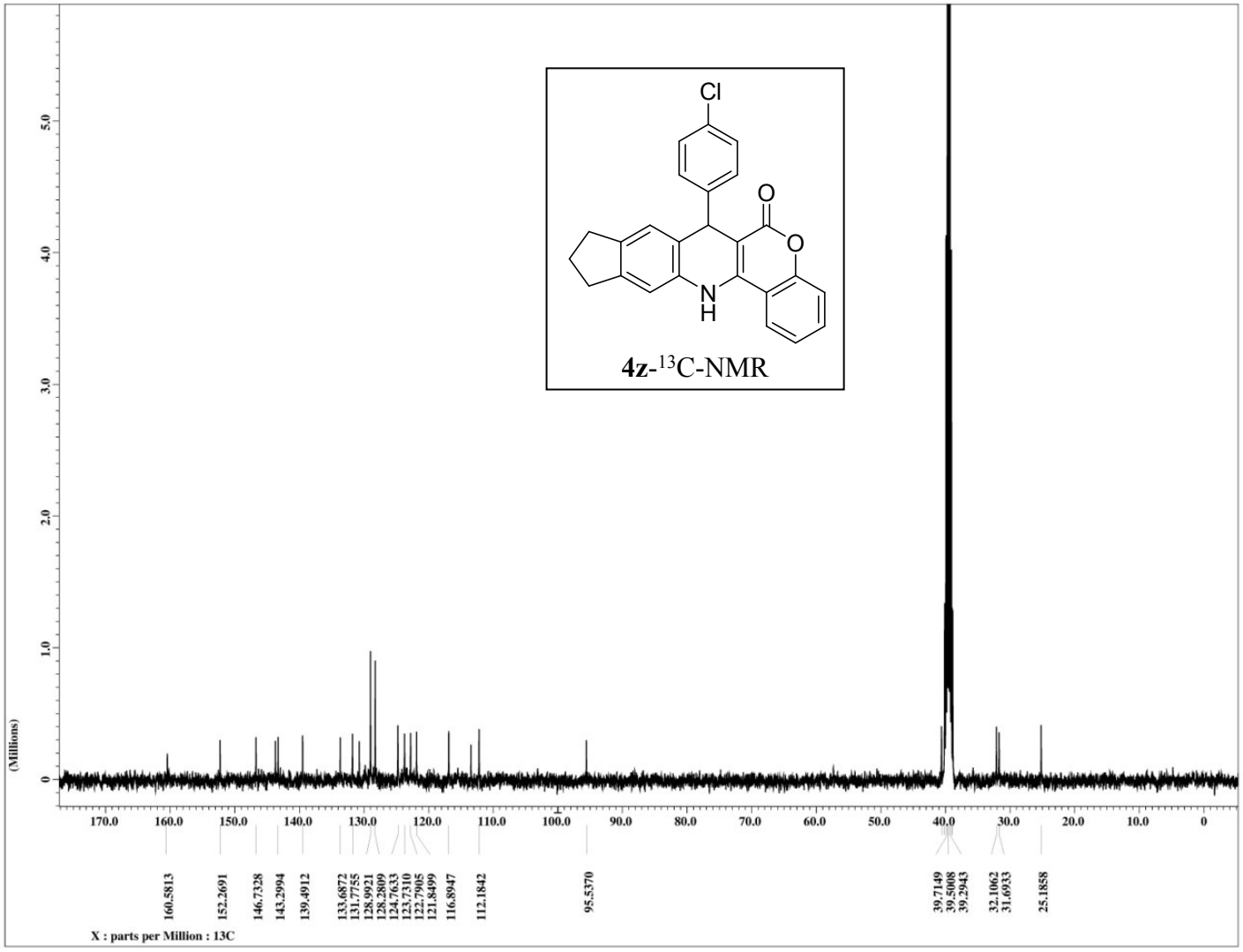

NO2
O
MeO
O
N
H
4
x_1H_NMR
(Millions)
8.0
3.0
2.0
1.99
1.0
0.99
1
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.9490
8.3289
8.1091
8.0945
7.6375
7.5495
7.4506
7.3445
7.3462
6.8315
5.4284
3.6600
2.5014
X : parts per Million : 1H

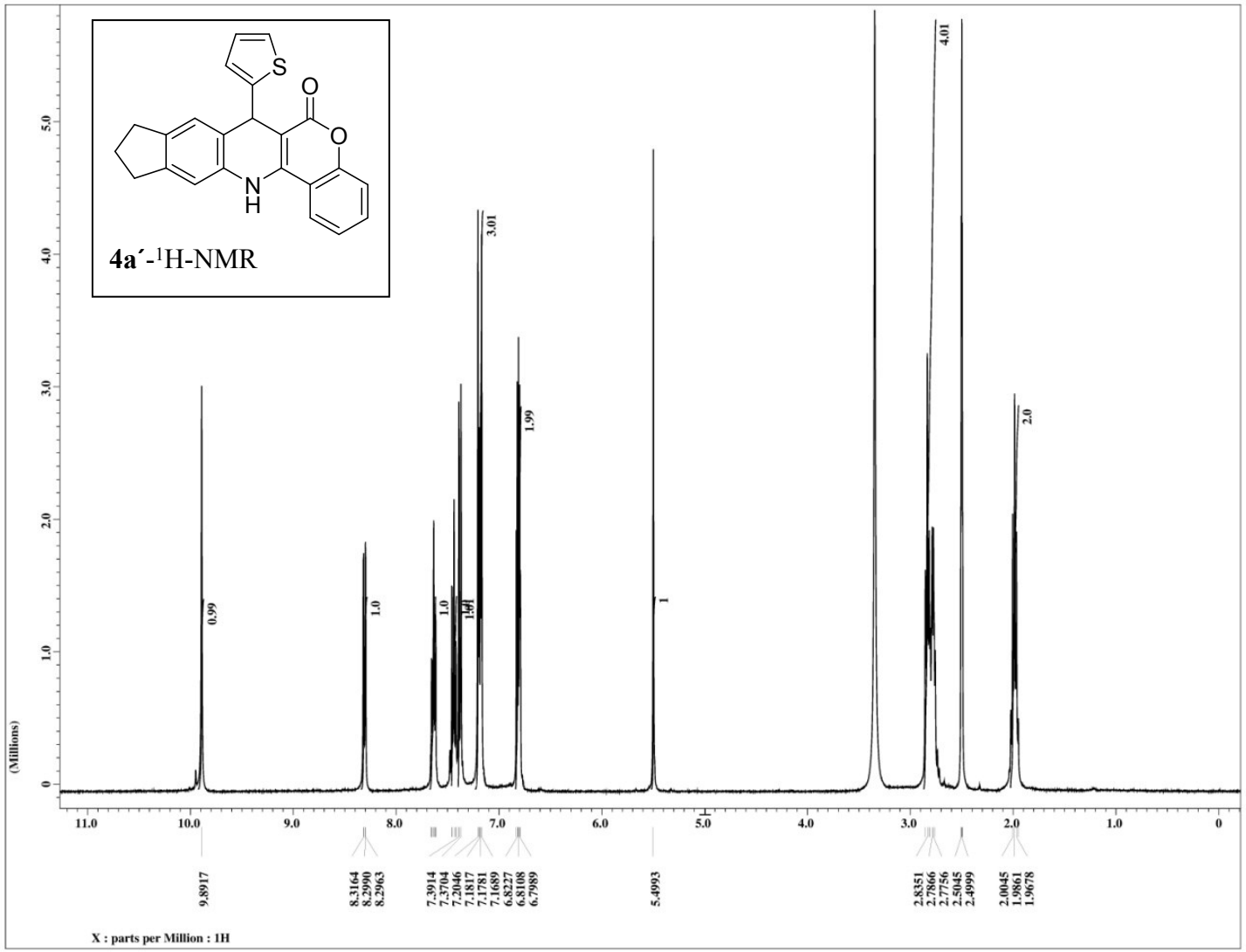

NO2
O
MeO
O
N
H
4
x-13C-NMR
(Millions)
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.2784
155.6826
152.3562
145.2676
144.1817
131.8549
130.1191
129.3069
127.9933
127.8327
124.9728
123.7416
122.8164
117.7618
116.9359
113.4184
113.2501
94.2094
55.1110
39.7102
39.5037
39.2972
X : parts per Million : 13C

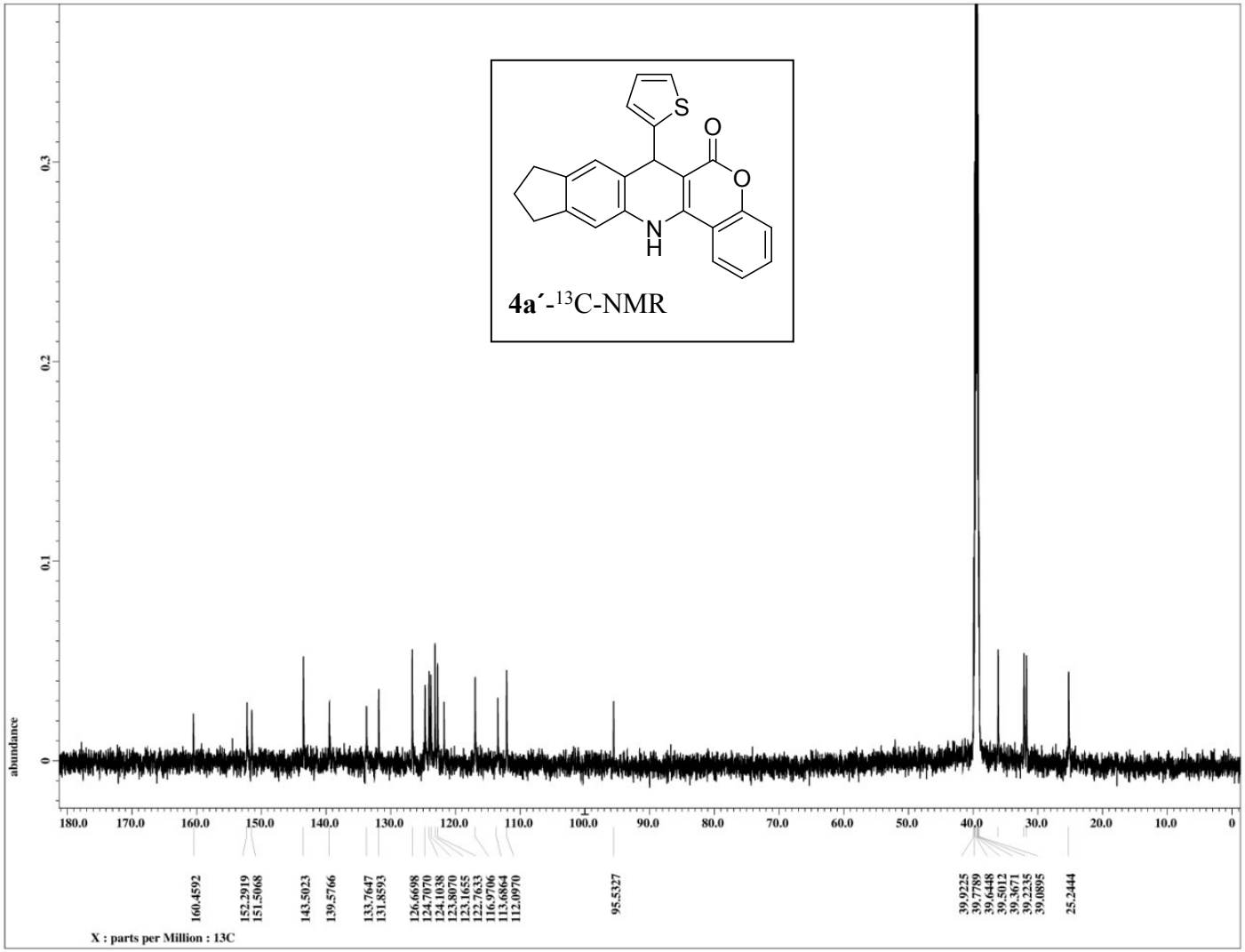

OMe
MeO
OMe
O
O
N
H
4y
1H NMR
(Millions)
X : parts per Million : 1H

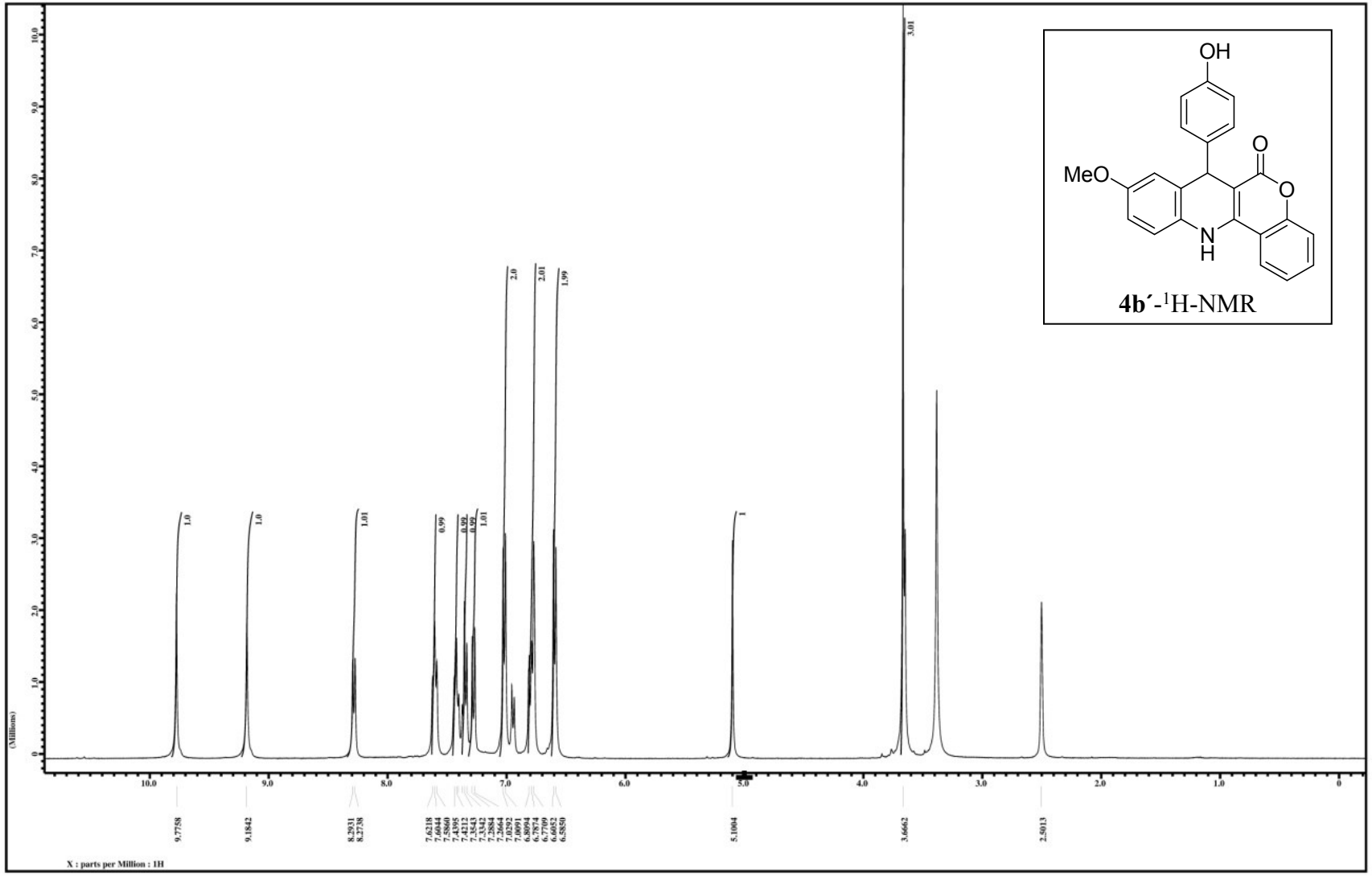

OMe
MeO
OMe
O
O
N
H
4y
13C NMR
(Millions)
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5992
152.7000
152.1571
143.6844
143.0650
139.2110
136.2822
133.7970
131.6559
124.6743
123.7031
122.7167
116.8897
113.5251
112.0493
104.5171
96.1820
59.8212
55.7913
39.9240
39.7176
39.5034
39.2970
32.0936
31.7419
25.1809
X : parts per Million : 13C

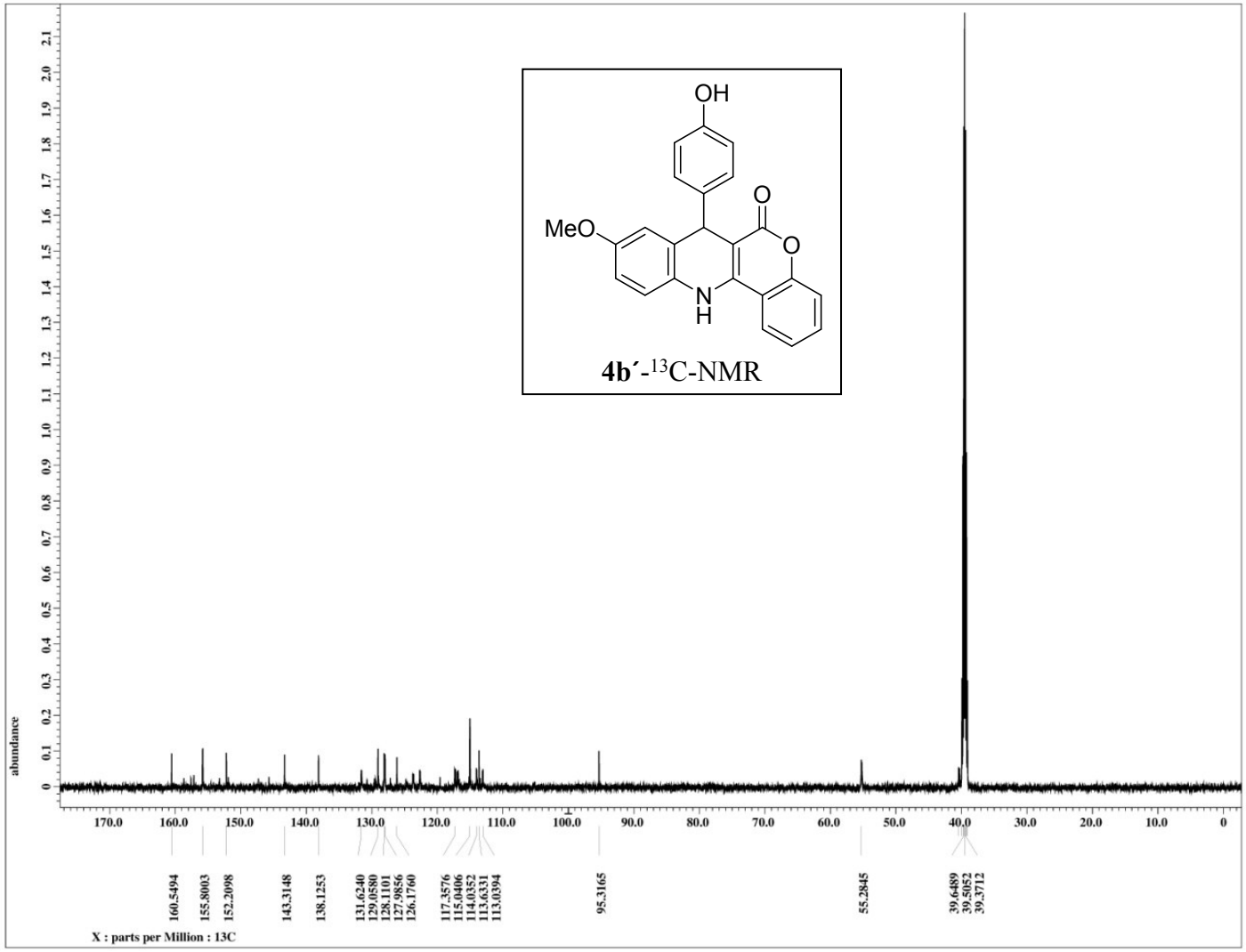

Cl
O
O
N
H
4z-1H-NMR
X : parts per Million : 1H

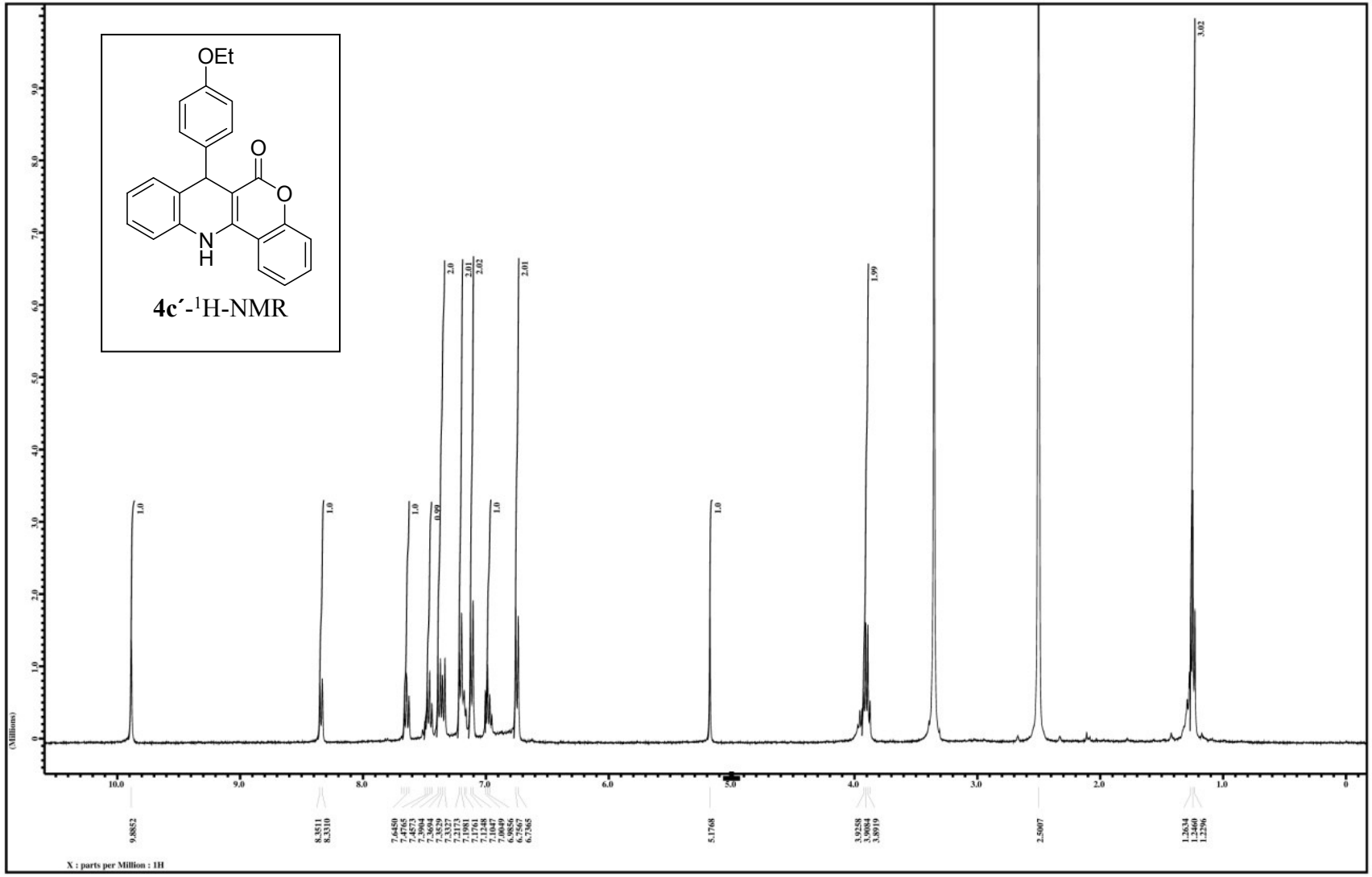

Cl
O
O
N
H
4z-13C-NMR
(Millions)
5.0
4.0
3.0
2.0
1.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.5813
152.2691
146.7328
143.2994
139.4912
133.6872
131.7755
128.9921
128.2809
124.7633
123.7310
122.7905
121.8499
116.8947
112.1842
95.5370
39.7149
39.5008
39.2943
32.1062
31.6933
25.1858
X : parts per Million : 13C

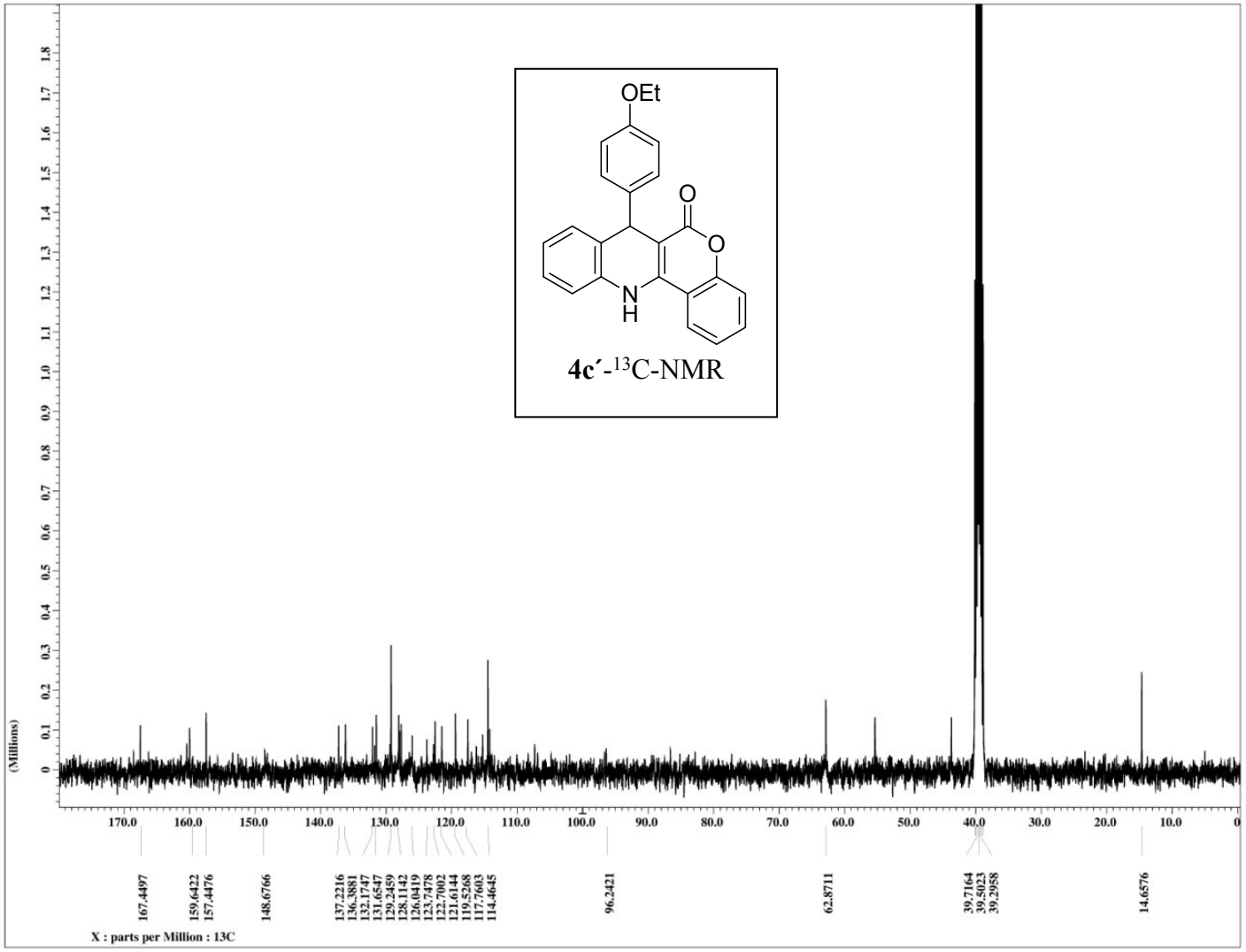

4a´-1H-NMR
(Millions)
X : parts per Million : 1H

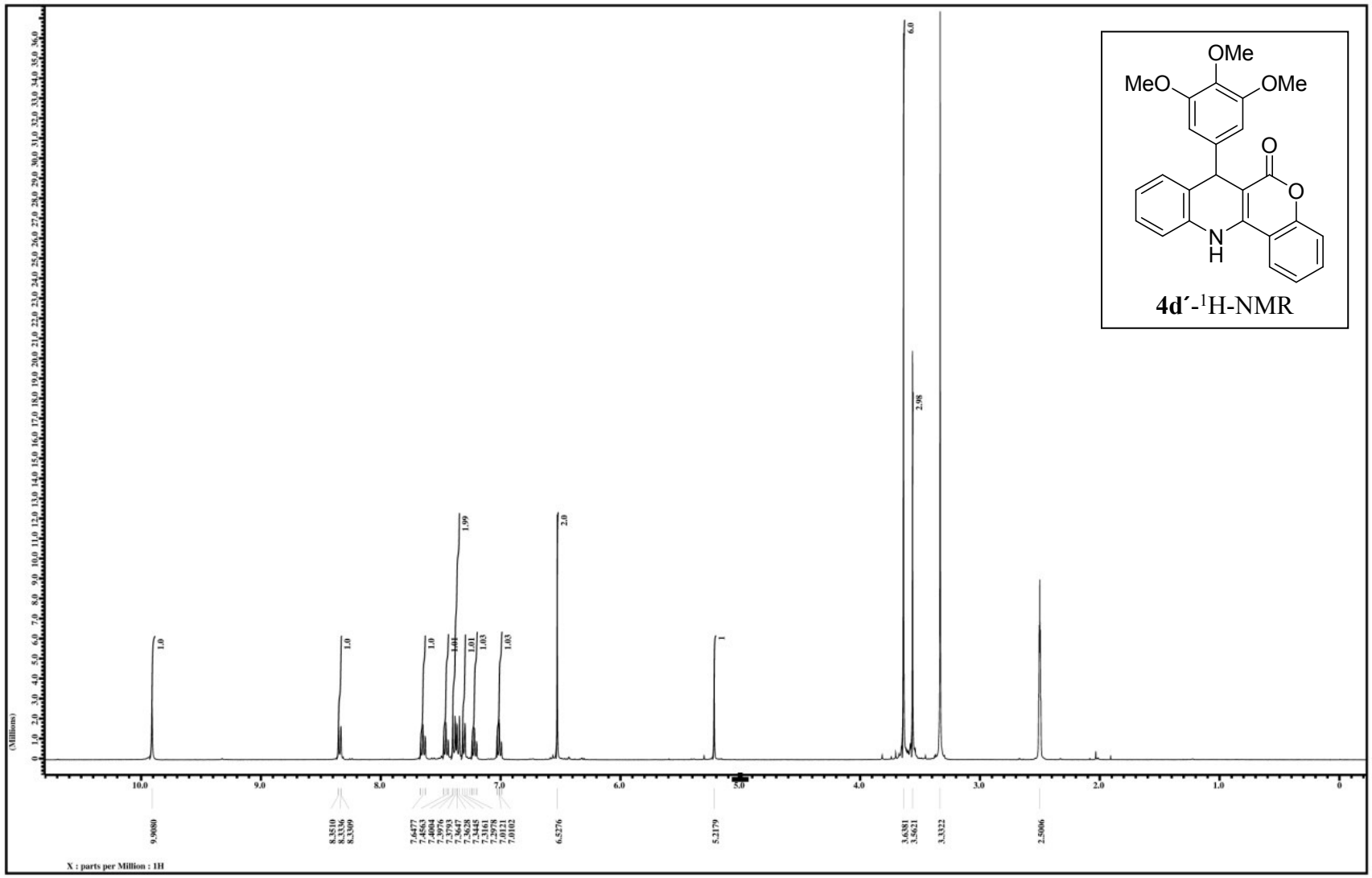

S
O
O
N
H
4a´-13C-NMR
abundance
0.3
0.2
0.1
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.4592
152.2919
151.5068
143.5023
139.5766
133.7647
131.8593
126.6698
124.7070
124.1038
123.8070
123.1655
122.7633
116.9706
113.6864
112.0970
95.5327
39.9235
39.7789
39.6448
39.5012
39.3671
39.2235
39.0895
25.2444
X : parts per Million : 13C

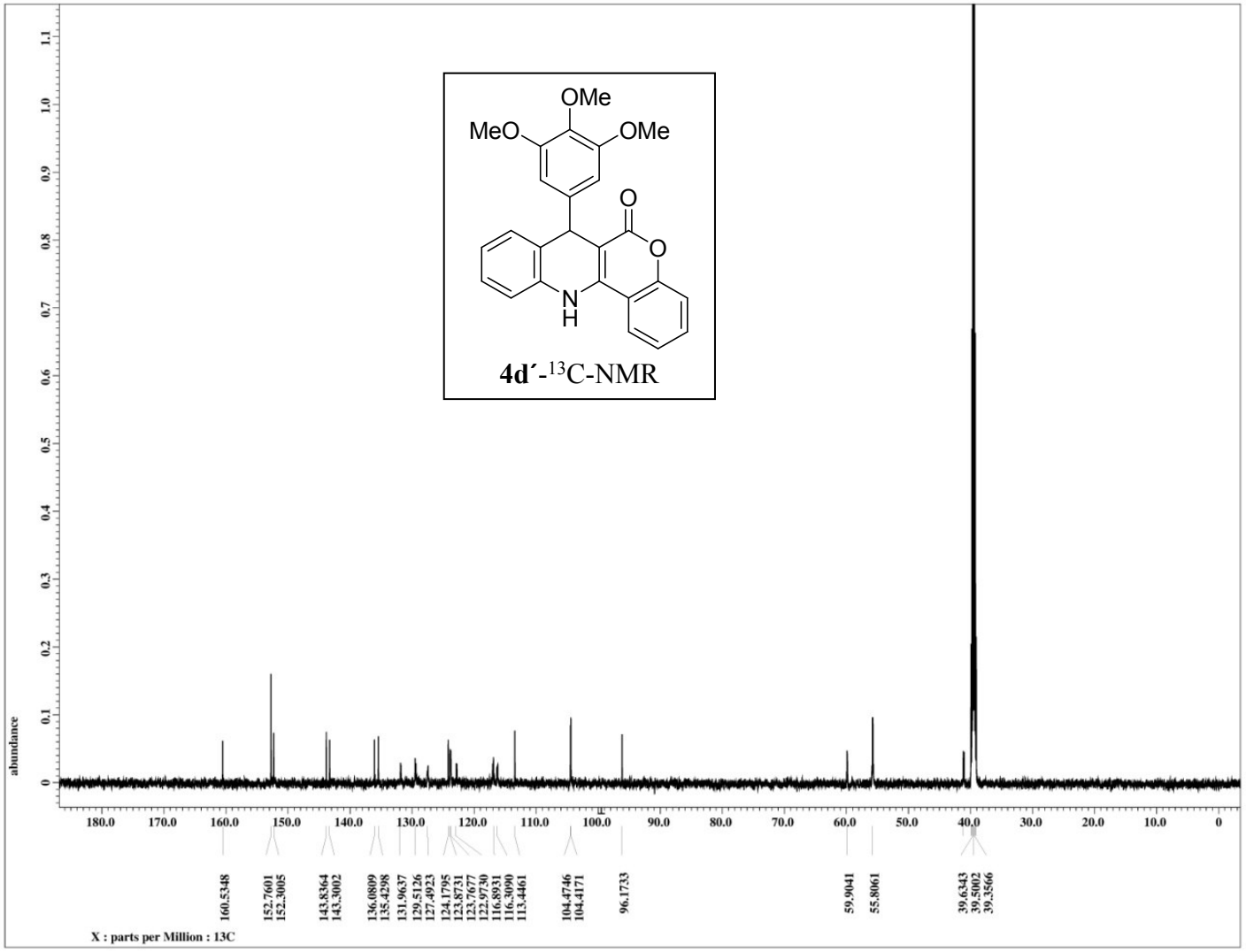

OH
MeO
O
O
N
H
4b´-1H-NMR
X : parts per Million : 1H


OH
O
MeO
O
N
H
4b´-13C-NMR
abundance
160.5494
155.8003
152.2098
143.3148
138.1253
131.6240
129.0580
128.1101
127.9856
126.1760
117.3576
115.0406
114.0352
113.6331
113.0394
95.3165
55.2845
39.6489
39.5052
39.3712
X : parts per Million : 13C


OEt
O
O
N
H
4c´-1H-NMR
X : parts per Million : 1H


OEt
O
O
N
H
4c´-13C-NMR
(Millions)
X : parts per Million : 13C
167.4497
159.6422
157.4476
148.6766
137.2216
136.3881
132.1747
131.6547
129.2459
128.1142
126.0419
123.7478
122.7002
121.6144
119.5268
117.7603
114.4645
96.2421
62.8711
39.7164
39.5023
39.2958
14.6576


OMe
MeO
OMe
O
O
N
H
4d´-1H-NMR
X : parts per Million : 1H


OMe
MeO
OMe
O
O
N
H
4d´-13C-NMR
abundance
X : parts per Million : 13C
160.5348
152.7601
152.3005
143.8364
143.3002
136.0809
135.4298
131.9637
129.5126
127.4923
124.1795
123.8731
123.7677
122.9730
116.8931
116.3090
113.4461
104.4746
104.4171
96.1733
59.9041
55.8061
39.6343
39.5002
39.3566