Supporting Information

Asymmetric Dearomatization of 1-Aminonaphthalene Derivatives by Gold-Catalyzed Intramolecular Double C–C Bond Formation

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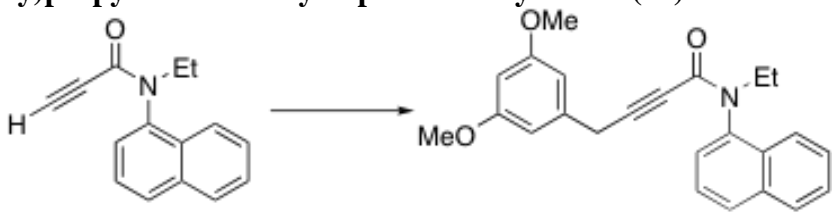
I. General

Infrared spectra (IR) analyses were carried out on a JASCO FT/IR-6200. ^{1}H and ^{13}C NMR data were collected on a JEOL AL-300 (300 MHz) and a JEOL JNM-ECA500 (500 MHz) at ambient temperature. HRMS data were obtained on a Bruker micrOTOF Focus II. Anhydrous $(CH_2Cl)_2$ (No. 28,450-5) and CH_3CN (No. 27,100-4) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. *N*-Benzylalkynylamido **4**[1] was already reported. All reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of *N*-Aryl Alkynylamides

3-(3,5-Dimethoxy)propynoic acid ethylnaphthalen-1-ylamide (1a)



A **1a**

To a stirred solution of dicyclohexylcarbodiimide (DCC, 2.27 g, 11.0 mmol) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added *N*-ethyl-1-naphtylamine (1.71 g, 10.0 mmol). After cooling to 0 ºC, propiolic acid (0.770 g, 11.0 mmol) was added dropwise to the reaction mixture and the mixture was stirring at room temperature for overnight. Urea was removed by filtration through a paper and a short pad of silica gel

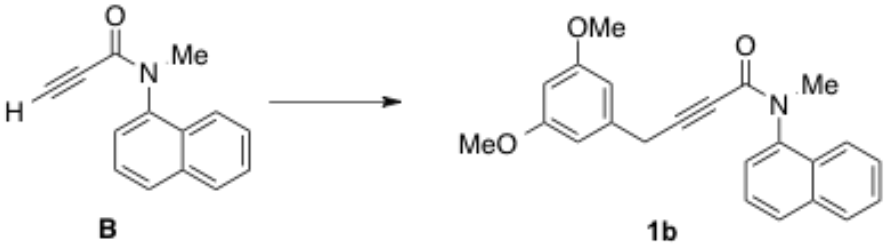
(hecane/EtOAc = 3:1). The residue was then submitted to column chromatography on silica gel (hexane/EtOAc = 3:1) to give propiolamide **A** (1.29 g, 7.5 mmol) as a pale yellow solid in 75% yield from *N*-ethyl-1-naphthylamine.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96–7.91 (m, 2H), 7.89–7.81 (m, 0.9H), 7.74–7.71 (m, 0.1H), 7.62–7.49 (m, 3H), 7.41 (dd, J = 7.1, 0.9 Hz, 0.9H), 7.34 (dd, J = 7.1, 0.9 Hz, 0.1H), 4.29 (dq, J = 13.9, 7.1 Hz, 1H), 3.90 (dq, J = 13.9, 7.1 Hz, 0.1H), 3.41 (dq, J = 13.9, 7.1 Hz, 0.9H), 3.25 (s, 0.1H), 2.53 (s, 0.9H), 1.26 (t, J = 7.1 Hz, 0.3H), 1.19 (t, J = 7.1 Hz, 2.7H).

Propiolamide **A** (135 mg, 0.600 mmol) was added to a mixture of 3.5-dimethoxybenzyl bromide (60.0 mg, 0.300 mmol), copper(I) iodide (57.1 mg, 0.300 mmol), potassium carbonate (41.5 mg, 0.300 mmol), and tetrabutylammonium iodide (72.7 mg, 0.300 mmol) in dry acetonitrile (4 mL). The resulting slurry was stirred at 40 ºC for 4 d. The reaction mixture was then diluted with saturated aqueous ammonium chloride and extracted twice with diethyl ether. The combined organic layers were dried over Na_2SO_4 and passed through a filter to remove the drying agent. The filtrate was concentrated and purified on silica gel column chromatography (hexane/EtOAc/CH_2Cl_2 = 3:1:3) to afford **1a** in 57% yield from **A**.

Orange sticky oil; IR (KBr) 2970, 2936, 2232, 1634, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88–7.82 (m, 3H), 7.56–7.34 (m, 4H), 6.57 (d, J = 2.2 Hz, 0.2H), 6.40 (t, J = 2.2 Hz, 0.1H), 6.21 (t, J = 2.2 Hz, 0.9H), 5.87 (d, J = 2.2 Hz, 1.8H), 4.29 (dq, J = 13.9, 6.9 Hz, 1H), 3.81 (s, 0.6H), 3.65 (s, 5.4H), 3.50 (dq, J = 13.9, 6.9 Hz, 1H), 3.25 (d, J = 18.7 Hz, 1H), 3.18 (d, J = 18.7 Hz, 1H) 1.24 (t, J = 6.9 Hz, 0.3H), 1.17 (t, J = 6.9 Hz, 2.7H); ^{13}C NMR (CDCl , 125 MHz) δ 160.6, 154.6, 137.5, 136.5, 134.4, 130.8, 128.9, 128.4, 127.2, 127.0, 126.3, 125.2, 122.6, 105.7, 98.6, 89.9, 76.8, 55.1, 43.4, 25.1, 13.1; HRMS (ESI) calcd for $C_{24}H_{23}O_3NNa$ $[M+Na]^+$ 396.1570, found 396.1584.

4-(3,5-Dimethoxyphenyl)-*N*-methyl-*N*-(naphthalen-1-yl)but-2-ynamide (1b)



B **1b**

N-1-Naphthalenylpropiolamide (0.586 g, 3.00 mmol) and iodomethane (0.28 mL, 4.5 mmol) was added to K_2CO_3 (0.456 g, 3.30 mmol) in CH_3CN (30 mL) at room temperature, and the mixture was stirred for overnight. The reaction was quenched with water and extracted with Et_2O. The organic layer was dried over Na_2SO_4, concentrated, and purified on silica gel column chromatography (hexane/EtOAc = 3:1) to afford propiolamide **B** as a pale yellow solid in 55% yield from *N*-1-naphthylenyl propiolamide.

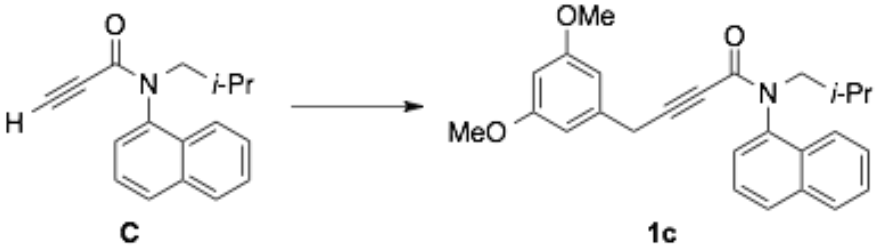
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96–7.90 (m, 2H), 7.83–7.79 (m, 1H), 7.61–7.54 (m, 2H), 7.51 (d, J = 8.2 Hz, 1H) 7.45 (dd, J = 7.1, 1.3 Hz, 1H), 3.67 (s, 0.3H), 3.43 (s, 2.7H), 3.31 (s, 0.1H), 2.56 (s, 0.9H).

The title compound **1b** was prepared from propiolamide **B** and 3,5-dimethoxybenzyl bromide in 47% yield by the procedure used for **1a**.

Orange oil; IR (neat) 2937, 2838, 2232, 1640, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90–7.79 (m, 3H), 7.58–7.48 (m, 2H), 7.47–7.39 (m, 1.9H), 7.37–7.35 (m, 0.1H), 6.57 (d, J = 2.2 Hz, 0.2H), 6.39 (t, J = 2.2 Hz, 0.1H), 6.21 (t, J = 2.2 Hz, 0.9H), 5.88 (d, J = 2.2 Hz, 1.8H), 3.82 (s, 0.6H), 3.65 (s, 5.4H), 3.42 (s, 2.7H), 3.32 (s, 0.3H), 3.27 (d, J = 19.1 Hz, 1H), 3.19 (d, J = 19.1 Hz, 1H), 2.17 (s, 0.1H), 1.66 (s, 0.9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.6, 155.0, 139.2, 136.4,

134.4, 130.3, 128.9, 128.5, 127.1, 126.4, 126.1, 125.4, 122.3, 105.6, 98.6, 90.3, 76.5, 55.1, 36.5, 25.1; HRMS (ESI) calcd for $C_{23}H_{21}O_3NNa$ $[M+Na]^+$ 382.1414, found 382.1406.

4-(3,5-Dimethoxyphenyl)-*N*-isobutyl-*N*-(naphtylen-1-yl)but-2-ynamide (1c)



C **1c**

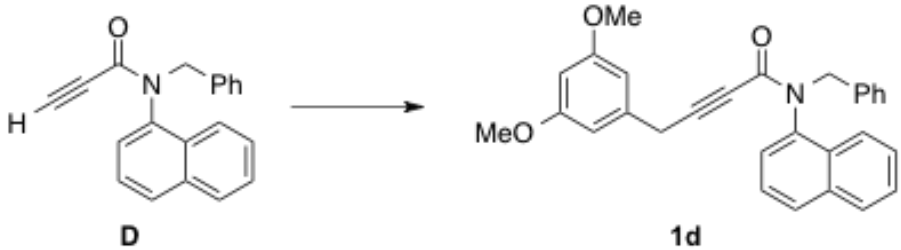
N-Isobutyl-*N*-(naphthalen-1-yl)propiolamide **C** was prepared from *N*-isobutylnaphthylamine with propiolic acid as a pale yellow solid in 65% yield by the procedure for propiolamide **A**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95–7.88 (m, 1.8H), 7.86–7.80 (m, 1H), 7.74–7.72 (m, 0.2H), 7.61–7.43 (m, 3.8H), 7.36–7.32 (m, 0.2H), 4.25 (dd, J = 13.3, 9.3 Hz, 0.9H), 4.12 (dd, J = 13.3, 9.3 Hz, 0.1 H), 3.65 (dd, J = 13.3, 5.3 Hz, 0.1H), 3.16 (dd, J = 13.3, 5.3 Hz, 0.9H), 2.56 (s, 0.9H), 2.05 (s, 0.1H), 1.94–1.80 (m, 1H), 1.08 (d, J = 6.8 Hz, 0.3H), 1.04 (d, J = 6.8 Hz, 2.7H), 0.93 (d, J = 6.8 Hz, 0.3H), 0.90 (d, J = 6.8 Hz, 2.7H).

The title compound **1d** was prepared from propiolamide **C** and 3,5-dimethoxybenzyl bromide in 63% yield from **C** by the procedure used for **1a**.

Orange sticky oil; IR (KBr) 2960, 2229, 1644, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90–7.79 (m, 2.8H), 7.74–7.73 (m, 0.1H), 7.55–7.47 (m, 2.2H), 7.44–7.39 (m, 1.8H), 7.33 (dd, J = 7.5, 1.2 Hz, 0.1H), 6.56 (d, J = 2.3 Hz, 0.2H), 6.39 (t, J = 2.3 Hz, 0.1H), 6.21 (t, J = 2.3 Hz, 0.9H), 5.86 (d, J = 2.3 Hz, 1.8H), 4.24 (dd, J = 13.3, 9.2 Hz, 0.9H), 4.08 (dd, J = 13.3, 9.2 Hz, 0.1H), 3.80 (s, 0.6H), 3.65 (s, 5.4H), 3.56 (dd, J = 13.3, 5.6 Hz, 0.1H), 3.24 (d, J = 19.0 Hz, 1H), 3.19 (d, J = 19.0 Hz, 1H), 3.14 (dd, J = 13.3, 5.6 Hz, 0.9H), 1.89–1.76 (m, 1H), 1.02 (d, J = 6.7 Hz, 2.7H), 1.01 (d, J = 6.7 Hz, 0.3H), 0.88 (d, J = 6.7 Hz, 2.7H), 0.86 (d, J = 6.7 Hz, 0.3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.6, 155.3, 138.0, 136.6, 134.5, 130.5, 128.9, 128.5, 127.3, 127.0, 126.2, 125.1, 122.5, 105.7, 98.6, 90.4, 76.8, 55.2, 55.1, 27.5, 25.1, 20.3, 20.1; HRMS (ESI) calcd for $C_{26}H_{27}O_3NNa$ $[M+Na]^+$ 424.1883, found 424.1901.

***N*-Benzyl-4-(3,5-dimethoxyphenyl)-*N*-(naphthalen-1-yl)but-2-ynamide (1d)**



D **1d**

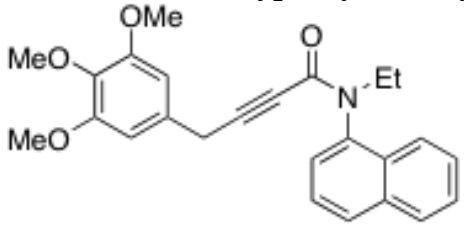
N-Benzyl-*N*-(naphthalen-1-yl)propiolamide **D** was obtained as a pale yellow solid in 81% yield from *N*-1-naphthalenylpropiolamide with benzyl iodide by the procedure for **B**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93–7.89 (m, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.81–7.77 (m, 0.9 H), 7.68–7.67 (m, 0.1H), 7.57–7.53 (m, 1.8H), 7.51–7.49 (m, 0.2H), 7.37–7.32 (m, 1H), 7.28–7.17 (m, 5H), 7.00 (dd, J = 7.5, 1.2 Hz, 0.9H), 6.92 (dd, J = 7.5, 1.2 Hz, 0.1H), 5.68 (d, J = 14.3 Hz, 0.1H), 5.66 (d, J = 14.3 Hz, 0.9H), 4.72 (d, J = 14.3 Hz, 0.1H), 4.35 (d, J = 14.3 Hz, 0.9H), 3.35 (s, 0.1H), 2.54 (s, 0.9H).

The title compound **1d** was prepared from propiolamide **D** and 3,5-dimethoxybenzyl bromide in 21% yield from **D** by the procedure used for **1a**.

Orange sticky oil; IR (KBr) 2937, 2837, 2242, 1638, 1596 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.87–7.83 (m, 1H), 7.79–7.77 (m, 2H), 7.53–7.48 (m, 2H), 7.30–7.17 (m, 6H), 6.98 (d, J = 7.5 Hz, 0.9H), 6.93 (d, J = 7.5 Hz, 0.1H), 6.54 (d, J = 2.3 Hz, 0.2H), 6.37 (t, J = 2.3 Hz, 0.1H), 6.20 (t, J = 2.3 Hz, 0.9H), 5.84 (d, J = 2.3 Hz, 1.8H), 5.68 (d, J = 14.3 Hz, 0.9H), 5.67 (d, J = 14.3 Hz, 0.1H), 4.66 (d, J = 14.3 Hz, 0.1H), 4.31 (d, J = 14.3 Hz, 0.9H), 3.74 (s, 0.6H), 3.64 (s, 5.4H), 3.22 (d, J = 18.9 Hz, 1H), 3.17 (d, J = 18.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.6, 137.2, 136.8, 136.4, 134.4, 130.5, 129.3, 129.0, 128.5, 128.4, 127.7, 127.6 127.1, 126.3, 125.1, 122.4, 105.7, 98.6, 90.7, 76.5, 55.2, 51.9, 29.7, 25.2; HRMS (ESI) calcd for $C_{29}H_{25}O_3NNa$ $[M+Na]^+$ 458.1727, found 458.1746.

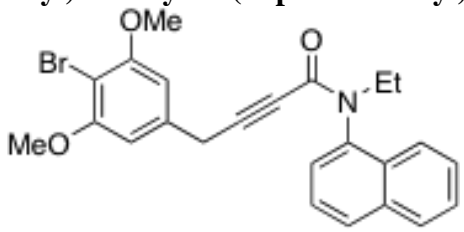
_N_-Ethyl-_N_-(naphthalen-1-yl)-4-(3,4,5-trimethoxyphenyl)but-2-ynamide (1e)



The title compound **1e** was prepared from propiolamide **A** and 3,4,5-trimethoxybenzyl chloride in 94% yield from **A** by the procedure used for **1a**.

Orange sticky oil; IR (KBr) 2937, 2233, 1638, 1593 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88–7.80 (m, 3H), 7.54–7.48 (m, 2H), 7.41–7.38 (m, 1H), 7.34 (dd, J = 6.9, 1.2 Hz, 1H), 6.62 (s, 0.2H), 5 96 (s, 1.8H), 4.27 (dq, J = 14.3, 7.5 Hz, 1H), 3.89 (s, 0.6H), 3.85 (s, 0.3H), 3.77 (s, 2.7H), 3.64 (s, 5.4H), 3.49 (dq, J = 14.3, 7.5 Hz, 1H), 3.22 (d, J = 18.9 Hz, 1H), 3.18 (d, J = 18.9 Hz, 1H), 1.23 (t, J = 7.5 Hz, 0.3H), 1.15 (t, J = 7.5 Hz, 2.7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.6, 153.0, 137.5, 136.6, 134.4, 130.8, 130.0, 128.8, 128.4, 127.1, 127.0, 126.4, 125.1, 122.6, 104.6, 90.1, 76.8, 60.8, 56.0, 43.4, 25.3, 13.1; HRMS (ESI) calcd for $C_{25}H_{25}O_4NNa$ $[M+Na]^+$ 426.1676, found 426.1686.

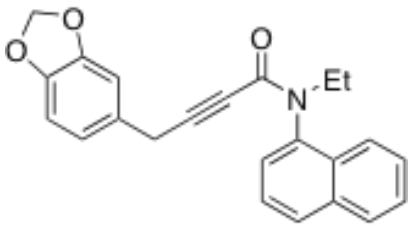
4-(4-Bromo-3,5-dimethoxyphenyl)-_N_-ethyl-_N_-(naphthalen-1-yl)but-2-ynamide (1f)



The title compound **1f** was prepared from amide **A** and 4-bromo-3,5-dimethoxybenzyl bromide in 24% yield from **A** by the procedure used for **1a**.

Yellow solid; Mp 113.0–113.6 °C; IR (KBr) 2974, 2936, 2240, 1638, 1591 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88–7.71 (m, 3H), 7.51–7.45 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.31 (dd, J = 7.5, 1.2 Hz, 1H), 6.63 (s, 0.2H), 5.91 (s, 1.8H), 4.24 (dq, J = 14.3, 7.5 Hz, 1H), 3.92 (s, 0.6H), 3.65 (s, 5.4H), 3.51 (dq, J = 14.3, 7.5 Hz, 1H), 3.19 (s, 2H), 1.22 (t, J = 7.5 Hz, 0.3H), 1.15 (t, J = 7.5 Hz, 2.7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.7, 154.4, 137.4, 135.1, 134.3, 130.7, 128.8, 128.4, 126.9, 126.3, 125.0, 122.5, 104.2, 99.0, 89.4, 77.2, 56.2, 43.4, 25.3, 13.0; HRMS (ESI) calcd for $C_{24}H_{22}O_3BrNNa$ $[M+Na]^+$ 474.0675, found 474.0692.

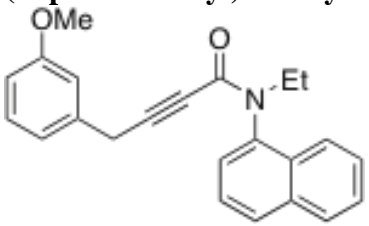
4-(Benzo[d][1,3]dioxol-5-yl)-_N_-ethyl-_N_-(naphthalen-1-yl)but-2-ynamide (1g)



The title compound **1g** was prepared from propiolamide **A** and 3,4-methylenedioxybenzyl bromide in 94% yield by the procedure used for **1a**.

Orange sticky oil; IR (KBr) 2977, 2893, 2239, 1634, 1595 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.93–7.85 (m, 3H), 7.57–7.39 (m, 3H), 7.40 (dd, J = 7.4, 1.2 Hz, 1H), 6.41 (d, J = 8.1 Hz, 1H), 5.97–5.94 (m, 1H), 5.87 (s, 2H), 5.79 (d, J = 8.0 Hz, 1H), 4.26 (dq, J = 14.0, 7.0 Hz, 1H), 3.80 (s, 0.2H), 3.57 (dq, J = 14.0, 7.0 Hz, 1H), 3.22 (s, 1.8H), 1.23 (t, J = 7.0 Hz, 0.3H), 1.19 (t, J = 7.0 Hz, 2.7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.6, 147.3, 146.0, 137.6, 134.4, 131.0, 128.9, 128.4, 127.8, 127.1, 127.1, 126.4, 125.3, 122.6, 120.1, 107.9, 107.8, 100.8, 90.0, 76.9, 43.4, 24.4, 13.1; HRMS (ESI) calcd for $C_{23}H_{19}O_3NNa$ $[M+Na]^+$ 380.1260, found 380.1257.

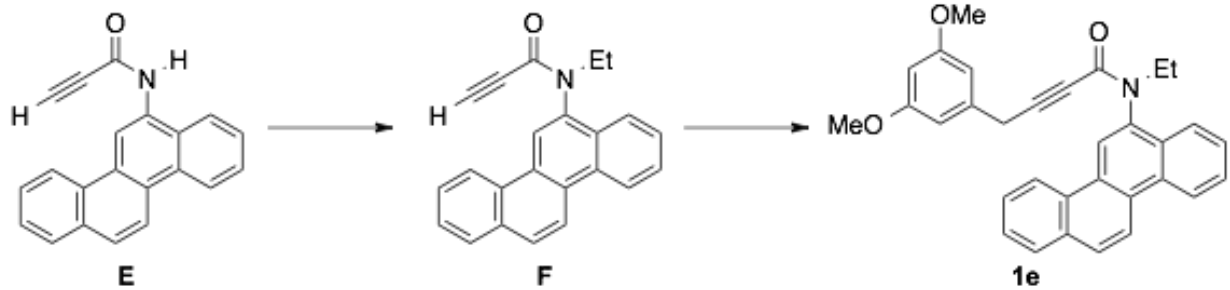
4-(3-Methoxyphenyl)-*N*-ethyl-*N*-(naphthalen-1-yl)but-2-ynamide (1h)



The title compound **1h** was prepared from amide **A** and 3-methoxybenzyl bromide in 27% yield from **A** by the procedure used for **1a**.

Orange oil; IR (neat) 2935, 2235, 1634, 1598 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.92–7.83 (m, 3H), 7.57–7.49 (m, 2H), 7.46–7.44 (m, 0.9H), 7.40–7.38 (m, 0.9H), 7.34–7.25 (m, 0.2H), 6.87 (t, J = 8.3 Hz, 1H), 6.62 (dd, J = 8.3, 2.3 Hz, 1H), 6.27 (s, 1H), 5.87 (d, J = 7.5 Hz, 1H), 4.27 (dq, J = 14.3, 6.9 Hz, 1H), 3.83 (s, 0.3H), 3.66 (s, 2.7H), 3.54 (dq, J = 14.3, 6.9 Hz, 1H), 3.29 (d J = 19.5 Hz, 1H), 3.25 (d, J = 19.5 Hz, 1H), 1.23 (t, J = 6.9 Hz, 0.3H), 1.18 (t, J = 6.9 Hz, 2.7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.3, 154.6, 137.5, 135.6, 134.4, 130.9, 129.2, 128.9, 128.3, 127.2, 127.1, 126.4, 125.3, 122.6, 119.4, 113.0, 111.9, 90.0, 76.9, 55.0, 43.4, 24.8, 13.0; HRMS (ESI) calcd for $C_{23}H_{21}O_2NNa$ $[M+Na]^+$ 366.1465, found 366.1453.

***N*-(Chrysen-6-yl)-4-(3,5-dimethoxyphenyl)-*N*-ethylbut-2-ynamide (1i)**



E **F** **1e**

To a stirred solution of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 0.545 g, 2.40 mmol) and PPh_3 (0.630 g, 2.40 mmol) in CH_2Cl_2 (20 mL) was added 6-aminochrysene (0.500 g, 2.00 mmol). After cooling to 0 ºC, propiolic acid (0.140 g, 2.00 mmol) was added dropwise to this mixture and the resulting mixture was stirred at room temperature for overnight. The reaction was quenched with 0.4 N HCl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, concentrated,

and purified on silica gel column chromatography (hexane/EtOAc/toluene = 3:1:2) to afford **E** as a pale yellow solid in 50% yield from 6-aminochrysene.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.3 (s, 1H), 8.87–8.84 (m, 1H), 8.77–8.73 (m, 1H), 8.70–8.65 (m, 1H), 8.05–7.97 (m, 3H), 7.78–7.61 (m, 4H), 3.08 (s, 0.9H), 2.36 (s. 0.1H).

N-(Chrysen-6-yl)-*N*-ethylpropiolamide **F** was prepared from propiolamide **E** and iodoethane as a pale yellow solid in 49% yield by the procedure for **B**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.88–8.85 (m, 0.9H), 0.82–8.79 (m, 0.1H), 8.76–8.72 (m, 1.8H), 8.65 (s, 1H), 8.60–8.58 (m, 0.2H), 8.11–7.98 (m, 3H), 7.82–7.61 (m, 4H), 4.43 (dq, J = 13.9, 7.1 Hz, 1H), 3.61 (dq, J = 13.9, 7.1 H, 0.9H), 3.48 (dq, J = 13.9, 7.1 H, 0.1H), 2.45 (s, 0.9H), 2.36 (s, 0.1H), 1.36 (t, J = 7.1 Hz, 0.3H), 1.29 (t, J = 7.1 Hz, 2.7H).

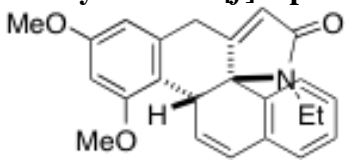
The title compound **1i** was prepared from propiolamide **F** and 3,5-dimethoxybenzyl bromide in 25% yield by the procedure used for **1a**.

Orange sticky oil; IR (KBr) 2965, 2934, 2236, 1637, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.82 (d, J = 8.0 Hz, 0.1H), 8.79 (d, J = 8.0 Hz, 0.9H), 8.69 (d, J = 9.2 Hz, 1H), 8.65 (d, J = 8.6 Hz, 1H), 8.59 (s, 0.9H), 8.57 (s, 0.1H), 8.05 (d, J = 9.2 Hz, 1H), 8.04–7.97 (m, 2H), 7.75–7.63 (m, 4H), 6.60 (d, J = 2.3 Hz, 0.2H), 6.41 (t, J = 2.3 Hz, 0.1H), 6.93 (t, J = 2.3 Hz, 0.9H), 5.68 (t, J = 2.3 Hz, 1.8H), 4.43 (m, 1H), 3.97 (dq, J = 14.3, 6.9 Hz, 0.1H), 3.83 (s, 0.6H), 3.60 (dq, J = 14.3, 6.9 Hz, 1H), 3.35 (s, 5.4H), 3.1 (s, 2H), 1.33 (t, J = 6.9 Hz, 0.3H), 1.25 (t, J = 6.9 Hz, 2.7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.3, 154.8, 136.6, 136.4, 132.2, 131.6, 130.3, 129.6, 128.6, 128.4, 128.2, 127.6, 127.2, 127.0, 126.7, 123.7, 123.4, 123.0, 122.7, 120.9, 105.2, 98.7, 90.5, 76.9, 54.8, 43.5, 25.2, 13.2; HRMS (ESI) calcd for $C_{32}H_{27}O_3NNa$ $[M+Na]^+$ 496.1883, found 496.1866.

III. Gold-Catalyzed Dearomatization via Intramolecular Double C-C Bond Formation

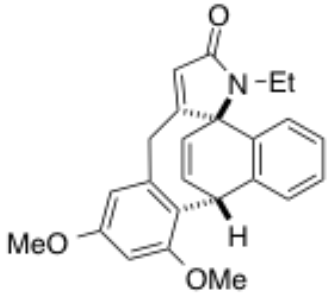
Representative procedure: (*R*)-Xyl-BINAP-$(AuCl)_2$ (12.0 mg, 0.010 mmol) and $AgSbF_6$ (6.9 mg, 0.020 mmol) were dissolved in $(CH_2Cl)_2$ (1.0 mL), which was added to a solution of **1a** (74.7 mg, 0.200 mmol) in $(CH_2Cl)_2$ (1.0 mL) at 0 ºC. The mixture was stirred at 0 ºC for 72 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc = 1:1), which furnished (+)-**2a** (50.2 mg, 0.134 mmol, 67% yield, 87% ee) and (+)-**3a** (17.4 mg, 0.0466 mol, 23% yield, 44% ee).

(+)-5-Ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2a]



Colorless solid; Mp 209.7–211.0 °C; $[\alpha]^{25}_D$ +742° (*c* 2.28, $CHCl_3$, 87% ee); IR (KBr) 2968, 2932, 1675, 1607, 1583 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (td, J = 7.5, 1.2 Hz, 1H), 7.27 (td, J = 7.5, 1.2 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.90 (dd, J = 10.3, 5.7 Hz, 1H), 6.46 (d, J = 10.3 Hz, 1H), 6.29 (d, J = 2.3 Hz, 1H), 6.13 (d, J = 2.3 Hz, 1H), 6.10 (s, 1H), 3.92 (d, J = 5.7 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.63 (s, 2H), 3.34 (dq, J = 14.3, 7.2 Hz, 1H), 3.11 (dq, J = 14.3, 7.2 Hz, 1H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.7, 161.1, 159.2, 158.0, 135.4, 133.5, 130.3, 129.5, 128.9, 128.5, 126.8, 126.1, 124.9, 120.3, 118.1, 103.9, 97.5, 66.6, 55.3, 55.2, 44.7, 35.5, 31.4, 14.4; HRMS (ESI) calcd for $C_{24}H_{23}O_3NNa$ $[M+Na]^+$ 396.1570, found 396.1554; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 13.2 min (major isomer) and 25.9 min (minor isomer).

(+)-1-Ethyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one [(+)-**3a**]



Colorless solid; Mp 70.5–72.0 °C; $[\alpha]^{25}_{D}$ +85° (*c* 0.315, $CHCl_3$, 44% ee); IR (KBr) 2936, 2838, 1692, 1602, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.38 (m, 1H), 7.28–7.23 (m, 2H), 7.14–7.11 (m, 1H), 6.46 (dd, *J* = 9.0, 6.2 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 5.78 (d, *J* = 1.7 Hz, 1H), 5.74 (d, *J* = 9.0 Hz, 1H), 5.58 (d, *J* = 6.2 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 3.57 (dq, *J* = 14.3, 7.3 Hz, 1H), 3.53 (d, *J* = 16.2 Hz, 1H), 3.44 (dq, *J* = 14.3, 7.3 Hz, 1H), 3.16 (dd, *J* = 16.2, 1.7 Hz, 1H), 1.35 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.9, 156.7, 151.7, 150.6, 131.4, 130.4, 128.9, 128.1, 122.2, 121.2, 120.5, 120.3, 118.3, 115.4, 113.9, 102.8, 90.5, 66.5, 49.4, 48.5, 32.1, 31.4, 30.0, 7.8; HRMS (ESI) calcd for $C_{24}H_{23}O_3NNa$ $[M+Na]^+$ 396.1570, found 396.1567; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 10.7 min (minor isomer) and 17.2 min (major isomer).

The structure of this unexpected eight-membered dearomatization product was determined by the X-ray crystallographic analysis of (±)-**3a** (Figure S-1).

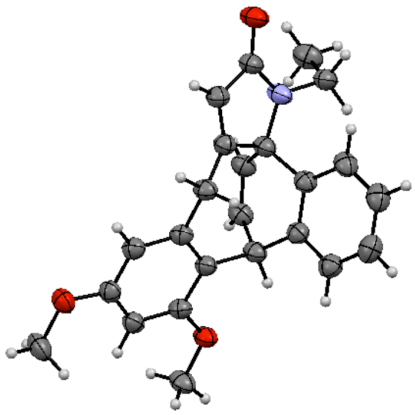
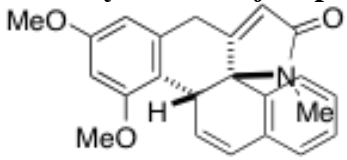


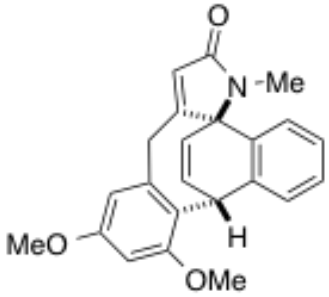
Figure S-1. ORTEP diagram of (±)-**3a** with ellipsoids at 30% probability.

(+)-10,12-Dimethoxy-5-methyl-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-**2b**]



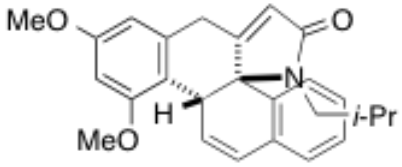
Colorless solid; Mp 173.1–175.0 °C; $[\alpha]^{25}_{D}$ +719° (*c* 1.84, $CHCl_3$, 87% ee); IR (KBr) 2957, 2935, 1685, 1602, 1587 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.25 (t, *J* = 7.5 Hz, 1H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.08 (d. *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 9.7, 5.9 Hz, 1H), 6.45 (d, *J* = 9.7 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.14 (d, *J* = 2.3 Hz,1H), 6.1 (s, 1H), 3.83 (d, *J* = 5.9 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.65 (s, 2H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 161.3, 159.3, 158.1, 135.7, 133.5, 129.6, 129.2, 128.9, 128.5, 126.8, 126.1, 124.8, 120.3, 118.0, 103.9, 97.5, 66.5, 55.3, 55.2, 44.1, 31.5, 25.4; HRMS (ESI) calcd for $C_{22}H_{21}O_3NNa$ $[M+Na]^+$ 382.1414, found 382.1401; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 14.0 min (major isomer) and 30.5 min (minor isomer).

(–)-6,8-Dimethoxy-1-methyl-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]-pyrrol-2(1*H*)-one [(–)-**3b**]



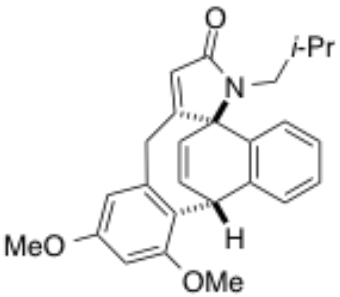
Yellow solid; Mp 224.5 °C (decomposition); $[\alpha]^{25}_{D}$ –59° (*c* 0.38, $CHCl_3$, 48% ee); IR (KBr) 2964, 2938, 1694, 1597, 1568 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.32–7.30 (m, 1H), 7.24–7.21 (m, 2H), 7.00–6.98 (m, 1H), 6.50 (d, *J* = 2.3 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 1H), 6.11 (dd, *J* = 9.2, 6.3 Hz, 1H), 6.04 (t, *J* = 2.3 Hz, 1H), 5.96 (d, *J* = 9.2 Hz, 1H), 5.67 (d, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 3.72 (s, 3H), 3.49–3.38 (m, 2H), 2.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.8, 157.9, 157.4, 144.2, 137.0, 136.0, 134.6, 128.0, 127.7, 127.2, 126.9, 126.5, 124.2, 120.5, 112.1, 98.6, 67.8, 56.4, 55.2, 38.5, 36.0, 26.3; HRMS (ESI) calcd for $C_{23}H_{21}O_3NNa$ $[M+Na]^+$ 382.1414, found 382.1420; CHIRALPAK AD-H, hexane/2-PrOH = 10:1, 1.0 mL/min, retention times: 14.5 min (major isomer) and 15.8 min (minor isomer).

(+)-5-Isobutyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-**2c**]



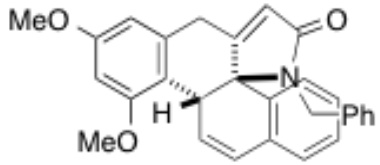
Yellow solid; Mp 71.0–72.5 °C; $[\alpha]^{25}_{D}$ +445° (*c* 2.22, $CHCl_3$, 66% ee); IR (KBr) 2958, 1686, 1605, 1586 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.23 (td, *J* = 7.5, 1.3 Hz, 1H), 7.17 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.88 (dd, *J* = 10.0, 5.9 Hz, 1H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.13–6.11 (m, 2H), 3.90 (d, *J* = 5.9, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.62 (s, 2H), 3.08 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.87 (dd, *J* = 13.8, 7.6 Hz, 1H), 1.53–1.45 (m, 1H), 0.73 (d, *J* = 6.9 Hz, 3H), 0.67 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 161.1, 159.3, 158.0, 135.4, 133.5, 130.6, 129.6, 128.9, 128.4, 126.7, 126.2, 124.7, 120.3, 118.2, 103.9, 97.5, 66.8, 55.3, 55.2, 48.3, 44.5, 31.5, 28.1, 20.4, 20.1; HRMS (ESI) calcd for $C_{26}H_{27}O_3NNa$ $[M+Na]^+$ 424.1883, found 424.1885; CHIRALCEL OD-H, hexane/2-PrOH = 10:1, 1.0 mL/min, retention times: 11.4 min (minor isomer) and 31.1 min (major isomer).

(+)-1-Isobutyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]-pyrrol-2(1*H*)-one [(+)-**3c**]



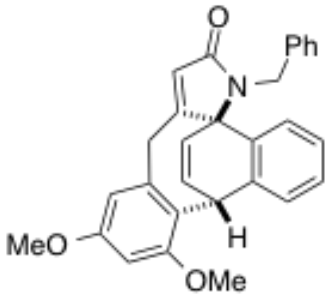
Yellow solid; Mp 73.5–75.0 °C; $[\alpha]^{25}_{D}$ +69° (*c* 1.45, $CHCl_3$, 44% ee); IR (KBr) 2958, 1691, 1602, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41–7.37 (m, 1H), 7.26–7.21 (m, 2H), 7.06–7.01 (m, 1H), 6.47–6.42 (m, 2H), 6.22 (d, *J* = 2.4 Hz, 1H), 5.85–5.82 (m, 2H), 5.61 (d, *J* = 6.2 Hz, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 3.66 (d, *J* = 16.3 Hz, 1H), 3.48 (dd, *J* = 13.9, 8.4 Hz, 1H), 3.23 (d, *J* = 16.3 Hz, 1H), 3.10 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.20–2.05 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.1, 164.0, 158.4, 157.3, 138.0, 137.2, 135.6, 133.5, 128.4, 128.2, 127.1, 124.9, 122.5, 120.5, 109.5, 97.4, 73.0, 56.1, 55.2, 44.2, 49.1, 38.6, 38.2, 28.1, 20.7, 20.4; HRMS (ESI) calcd for $C_{26}H_{27}O_3NNa$ $[M+Na]^+$ 424.1883, found 424.1886; CHIRALPAK AD-H, hexane/2-PrOH = 10:1, 1.0 mL/min, retention times: 14.6 min (major isomer) and 17.9 min (minor isomer).

(+)-5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-**2d**]



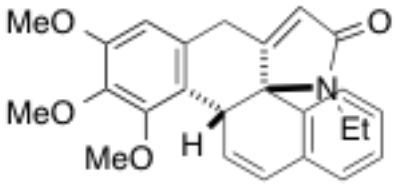
Yellow solid; Mp 173.0 °C (decomposition); $[\alpha]^{25}_{D}$ +78° (*c* 0.86, $CHCl_3$, 52% ee); IR (KBr) 2939, 2836, 1698, 1604, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.39–7.13 (m, 8H), 6.89–6.87 (m, 1H), 6.41 (s, 1H), 6.33–6.30 (m, 1H), 6.20 (s, 1H), 5.88 (s, 1H), 5.57–5.49 (m, 2H), 4.98–4.94 (m, 1H), 4.40–4.36 (m, 1H), 3.90 (s, 3H), 3.73 (s, 3H), 3.61 (d, *J* = 16.4 Hz, 1H), 3.44 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.5, 164.4, 158.4, 157.3, 138.3, 137.8, 137.1, 135.5, 133.8, 128.8, 128.5, 128.3, 127.8, 127.7, 127.2, 127.1, 124.8, 122.4, 120.3, 109.4, 97.3, 73.3, 56.1, 55.2, 44.9, 38.7, 38.2; HRMS (ESI) calcd for $C_{29}H_{25}O_3NNa$ $[M+Na]^+$ 458.1727, found 458.1721; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 13.4 min (major isomer) and 15.3 min (minor isomer).

(+)-1-Benzyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one [(+)-**3d**]



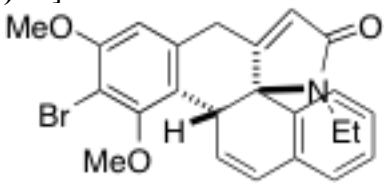
Colorless solid; Mp 172.5–173.4 ºC; $[\alpha]^{25}_{D}$ +51° (*c* 0.085, $CHCl_3$, 41% ee); IR (KBr) 2934, 2835, 1698, 1604, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.39–7.38 (m, 1H), 7.34–7.33 (m, 2H), 7.27–7.20 (m, 4H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 6.87 (dd, *J* = 6.9, 1.2 Hz, 1H), 6.40 (d, *J* = 2.5 Hz, 1H), 6.31 (dd, *J* = 9.2, 6.3 Hz, 1H), 6.20 (d, *J* = 2.5 Hz, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 5.56 (d, *J* = 6.3 Hz, 1H), 5.49 (d, *J* = 9.1 Hz, 1H), 4.95 (d, *J* = 15.3 Hz, 1H), 4.38 (d, *J* = 15.3 Hz, 1H), 3.90 (s, 3H), 3.73 (s, 3H), 3.60 (d, *J* = 16.3 Hz, 1H), 3.22 (dd, *J* = 16.3, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.6, 164.4, 158.4, 157.4, 138.3, 137.8, 137.1, 135.5, 133.8, 128.8, 128.5, 128.3, 127.8, 127.7, 127.2, 127.1, 124.8, 122.4, 120.3, 109.4, 97.4, 73.3, 56.1, 55.2, 44.9, 38.7, 38.2; HRMS (ESI) calcd for $C_{29}H_{25}O_3NNa$ $[M+Na]^+$ 458.1727, found 458.1731; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 19.2 min (major isomer) and 34.5 min (minor isomer).

(+)-5-Ethyl-10,11,12-trimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-**2e**]



Colorless solid; Mp 230.5–231.8 °C; $[\alpha]^{25}_{D}$ +466° (*c* 3.57, $CHCl_3$, 62% ee); IR (KBr) 2972, 2941, 1680, 1655, 1596 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.88 (dd, *J* = 9.7, 6.3 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H), 6.27 (s, 1H), 6.12 (s, 1H), 3.90 (s, 3H), 3.83 (d, *J* = 5.7 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.65 (d, *J* = 17.8 Hz, 1H), 3.62 (d, *J* = 17.8 Hz, 1H), 3.35 (dq, *J* = 14.3, 7.5 Hz, 1H), 3.10 (dq, *J* = 14.3, 7.5 Hz, 1H), 0.861 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 160.5, 152.4, 151.7, 141.0, 133.5, 130.3, 129.8, 128.9, 128.7, 128.5, 126.8, 126.1, 125.1, 122.8, 120.7, 106.5, 66.3, 60.6, 60.5, 55.7, 45.0, 35.5, 30.9, 14.4; HRMS (ESI) calcd for $C_{25}H_{25}O_4NNa$ $[M+Na]^+$ 426.1676, found 426.1680; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 8.7 min (major isomer) and 10.8 min (minor isomer).

(4b*S*,12b*R*)-(+)-11-bromo-5-ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(4b*S*,12b*R*)-(+)-2f]



Colorless solid; Mp 269.6 °C (decomposition); $[\alpha]^{25}_{D}$ +468° (*c* 2.25, $CHCl_3$, 45% ee); IR (KBr) 2969, 2939, 1681, 1659, 1585 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 7.20 (td, *J* = 7.5, 1.2 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 9.7, 5.7 Hz, 1H), 6.52 (d, *J* = 9.7 Hz, 1H), 6.33 (s, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 3.85 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.70 (d, *J* = 17.7 Hz, 1H), 3.65 (d, *J* = 17.7 Hz, 1H) 3.37 (dq, *J* = 14.3, 7.4 Hz, 1H), 3.13 (dq, *J* = 14.3, 7.4 Hz, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 159.8, 156.3, 155.7, 134.4, 133.4, 130.0, 129.2, 128.9, 128.7, 127.0, 126.1, 125.6, 124.1, 121.2, 107.2, 106.2, 66.3, 60.2, 56.3, 45.2, 35.7, 31.1, 14.5; HRMS (ESI) calcd for $C_{24}H_{22}BrO_3NNa$ $[M+Na]^+$ 474.0675, found 474.0686; CHIRALPAK AD-H, hexane/2-PrOH = 20:1, 1.0 mL/min, retention times: 38.7 min (minor isomer) and 43.5 min (major isomer).

The relative and absolute configurations of (+)-**2f** was determined by the X-ray crystallographic analysis (Figure S-2).

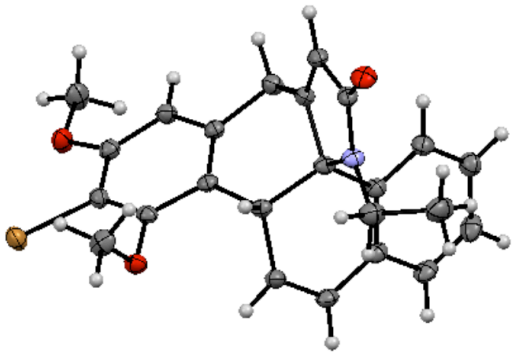
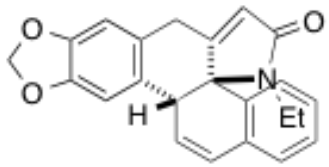


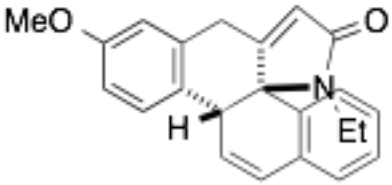
Figure S-2. ORTEP diagram of (+)-**2f** with ellipsoids at 30% probability.

(+)-5-Ethyl-8,13b-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2g]



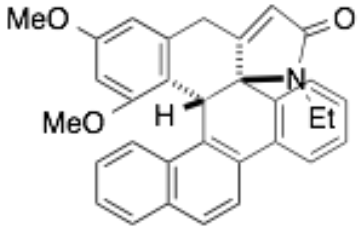
Orange solid; Mp 107.5–107.8 °C; $[\alpha]^{25}_{D}$ +308° (*c* 2.66, $CHCl_3$, 51% ee); IR (KBr) 2981, 2882, 2234, 1650, 1505 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13–7.10 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 6.69–6.68 (m, 2H), 6.41–6.40 (m, 1H), 6.20 (d, *J* = 1.7 Hz, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.81 (d, *J* = 1.4 Hz, 1H), 3.79 (d, *J* = 18.3, 1H), 3.66 (d, *J* = 18.3 Hz, 1H), 3.59–3.54 (m, 1H), 3.37 (dq, *J* = 14.1, 7.0 Hz, 1H), 3.00 (dq, *J* = 14.1, 7.0 Hz, 1H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 159.2, 146.7, 146.7, 133.4, 130.3, 129.5, 129.12, 129.06, 129.0, 127.4, 127.2, 126.1, 125.8, 121.9, 107.4, 107.2, 101.1, 66.1, 45.5, 35.5, 30.6, 14.5; HRMS (ESI) calcd for $C_{23}H_{19}O_3NNa$ $[M+Na]^+$ 380.1257, found 380.1247; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times:13.7 min (major isomer) and 27.0 min (minor isomer).

(+)-5-Ethyl-10-methoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2h]



Colorless solid; Mp 243.2–244.8 °C; $[\alpha]^{25}_{D}$ +238° (*c* 2.24 $CHCl_3$, 60% ee); IR (KBr) 2981, 2925, 1686, 1653, 1607 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.25–7.16 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 9.7, 6.3 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.67 (d, *J* = 9.7 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 6.22 (d, *J* = 2.1 Hz, 1H), 3.89 (d, *J* = 18.3 Hz, 1H), 3.75 (d, *J* = 18.3 Hz, 1H), 3.69 (s, 3H), 3.61 (d, *J* = 6.3 Hz, 1H), 3.39 (dq, *J* = 14.3, 6.9 Hz, 1H), 3.02 (dq, *J* = 14.3, 6.9 Hz, 1H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 159.2, 158.2, 133.9, 133.6, 130.3, 129.9, 129.02, 128.97, 128.5, 127.2, 127.1, 126.2, 122.1, 113.2, 112.4, 66.3, 55.1, 45.2, 35.4, 30.8, 14.5; HRMS (ESI) calcd for $C_{23}H_{21}O_2NNa$ $[M+Na]^+$ 366.1465, found 366.1447; CHIRALPAK AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 10.3 min (major isomer) and 26.5 min (minor isomer).

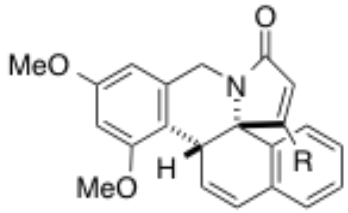
(+)-5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]chryseno[5,6-*h*]indol-6(5*H*)-one [(+)-**2i**]



Colorless solid; Mp 254.5–255.0 °C; $[\alpha]^{25}_{D}$ +101° (*c* 0.59 $CHCl_3$, 40% ee); IR (KBr) 2952, 2933, 1678, 1606, 1578 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.22 (d, *J* = 8.6 Hz, 1H), 7.86–7.85 (m, 3H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.53–7.46 (m, 2H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.28 (d, *J* = 2.3 Hz, 1H), 6.12 (d, *J* = 2.3, 1H), 5.93 (d, *J* = 2.3 Hz, 1H), 4.99 (s, 1H), 4.05 (d, *J* = 20.1 Hz, 1H), 3.94 (d, *J* = 20.1, 1.2 Hz, 1H), 3.64 (s, 3H), 2.64 (dq, *J* = 14.3, 6.9 Hz, 1H), 2.55 (s, 3H), 2.33 (dq, *J* = 14.3, 6.9 Hz, 1H), 0.15 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.0, 160.1, 159.3, 159.2, 136.5, 135.9, 134.5, 132.4, 131.8, 129.4, 129.3, 128.4, 128.2, 128.0, 126.9, 125.9, 125.4, 125.1, 124.0, 122.6, 121.8, 117.4, 104.4, 98.4, 68.6, 55.0, 54.5, 44.6, 36.5, 31.5, 13.9; HRMS (ESI) calcd for $C_{32}H_{27}O_3NNa$ $[M+Na]^+$ 496.1883, found

406.1885; CHIRALPAK IA, hexane/$CHCl_3$ = 1:1, 0.4 mL/min, retention times: 13.3 min (minor isomer) and 16.8 min (major isomer).

(–)-11,13-Dimethoxy-5-(2-methoxyphenyl)-9,13b-dihydro-7*H*-benzo[*c*]pyrrolo[2,1-*e*]-phenanthridin-7-one [(–)-5][1]

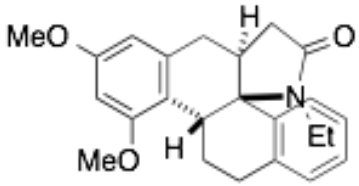


(R = 2-$MeOC_6H_4$)

Colorless solid; $[\alpha]^{25}_D$ –145.7 ° (*c* 3.90, $CHCl_3$, 29% ee); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25–7.21 (m, 1H), 7.18–7.16 (m, 2H), 7.13–7.10 (m, 1H), 6.93–6.90 (m, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.68 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.53 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.35 (s, 1H), 6.28–6.24 (m, 3H), 6.02 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 16.5 Hz, 1H), 4.38 (d, *J* = 5.5 Hz, 1H), 4.03 (d, *J* = 16.5 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.1, 163.1, 158.9, 158.0, 157.5, 135.6, 133.6, 130.6, 129.8, 129.4, 129.2, 128.4, 128.1, 126.6, 125.2, 124.1, 123.1, 121.5, 119.7, 116.4, 110.5, 101.8, 97.8, 68.3, 55.24, 55.20, 39.4, 37.7; CHIRALCEL AD-H, hexane/2-PrOH = 5:1, 1.0 mL/min, retention times: 16.0 min (major isomer) and 21.0 min (minor isomer).

IV. Hydrogenation of 2a

5-Ethyl-10,12-dimethoxy-7,7a,8,12b,13,14-hexahydrobenzo[*f*]naphtha-[2,1-*h*]indol-6(5*H*)-one (6)



To a solution of **2a** (30.0 mg, 0.080 mmol) in MeOH (1 mL) was added 5% Pd/C (60.0 mg) in MeOH (1.0 mL). H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 16 h, the reaction mixture was filtered, concentrated, and purified by preparative TLC (hexane/EtOAc = 1:1), which furnished **6** (28.4 mg, 0.075 mmol, 95% yield).

Colorless solid; Mp 159.3 °C (decomposition); IR (KBr) 2936, 1677, 1594 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.18 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.15–7.12 (m, 2H), 6.34 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.69 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.23 (dd, *J* = 15.1, 5.8 Hz, 1H), 3.11 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.06–2.94 (m, 2H), 2.85 (dd, *J* = 17.1, 10.8 Hz, 1H), 2.89–2.82 (m, 1H), 2.55 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.43 (dd, *J* = 15.2, 1.5 Hz, 1H), 2.11 (dd, *J* = 17.1, 5.8 Hz, 1H), 1.99 (td, *J* = 12.9, 4.7 Hz, 1H), 1.84–1.77 (m, 2H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.7, 159.2, 157.4, 141.8, 137.8, 136.4, 128.7, 127.7, 127.0, 127.0, 120.2, 105.6, 96.9, 69.8, 55.3, 55.2, 41.3, 37.7, 36.6, 35.7, 33.5, 29.9, 26.4, 13.0; HRMS (ESI) calcd for $C_{24}H_{27}O_3NNa$ $[M+Na]^+$ 400.1883, found 400.1870.

The relative configuration of **6** was determined by the X-ray crystallographic analysis (Figure S-3).

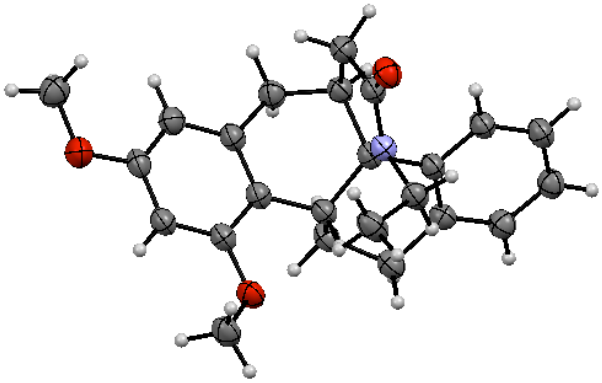


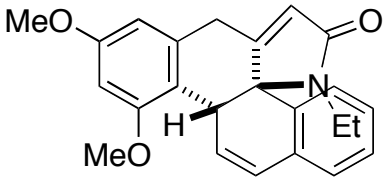
Figure S-3. ORTEP diagram of **6** with ellipsoids at 30% probability.

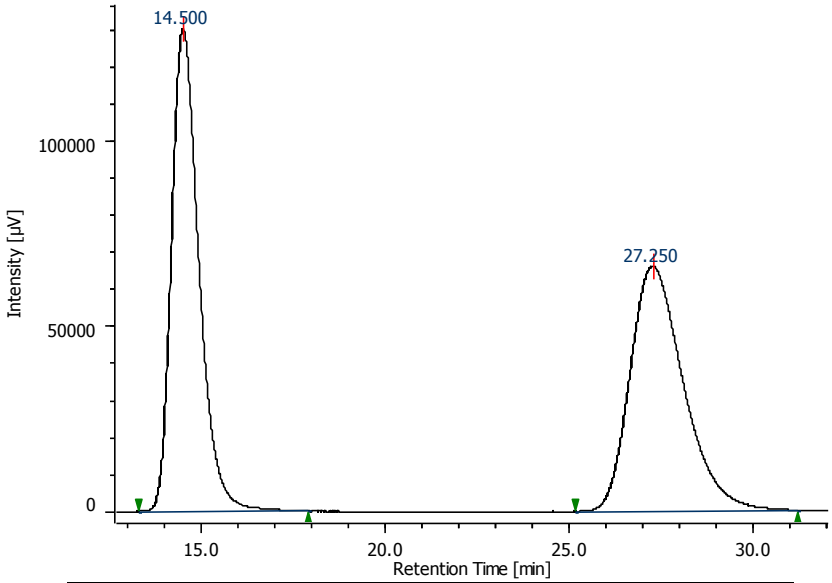
V. References

(1) Shibuya, T.; Noguchi, K.; Tanaka, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 6219.

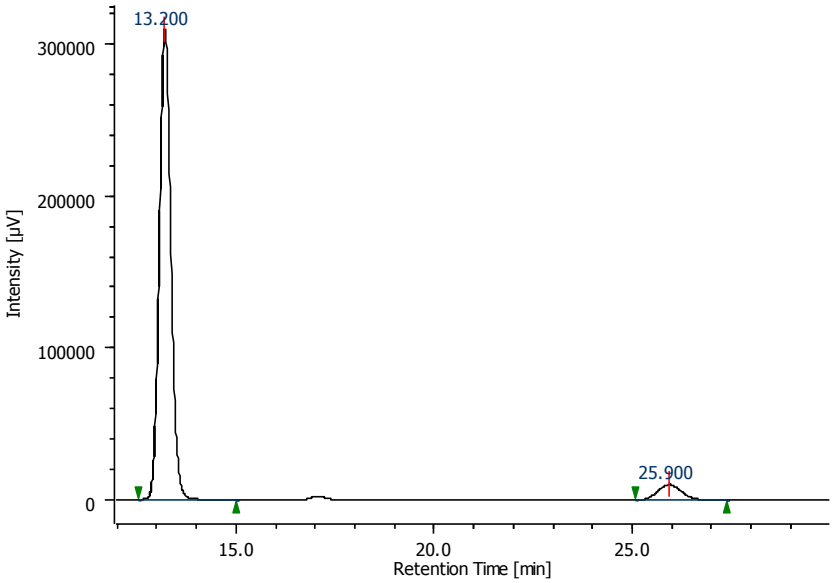
VI. Chiral HPLC Charts

(+)-5-Ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2a]



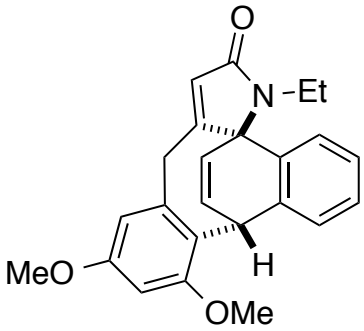


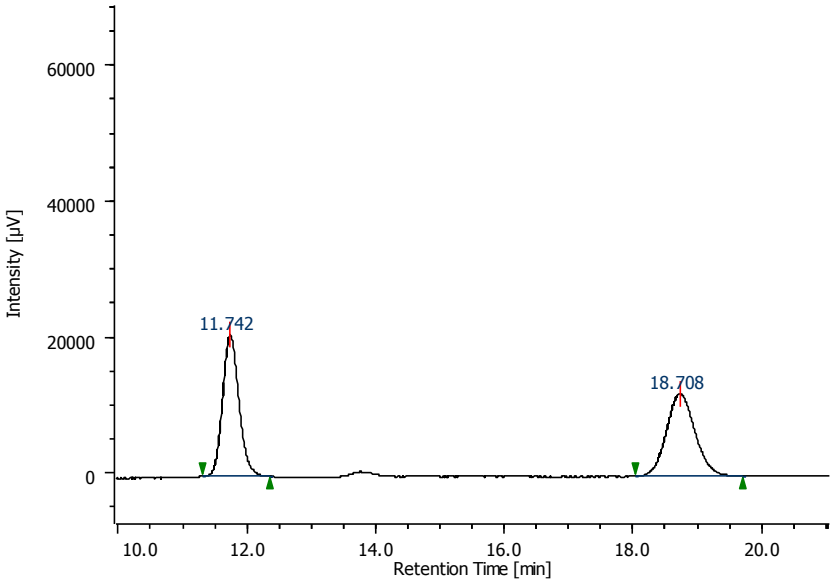
Peak No.	Retention Time (min)	Area (%)
1	14.500	50.123
2	27.250	49.877



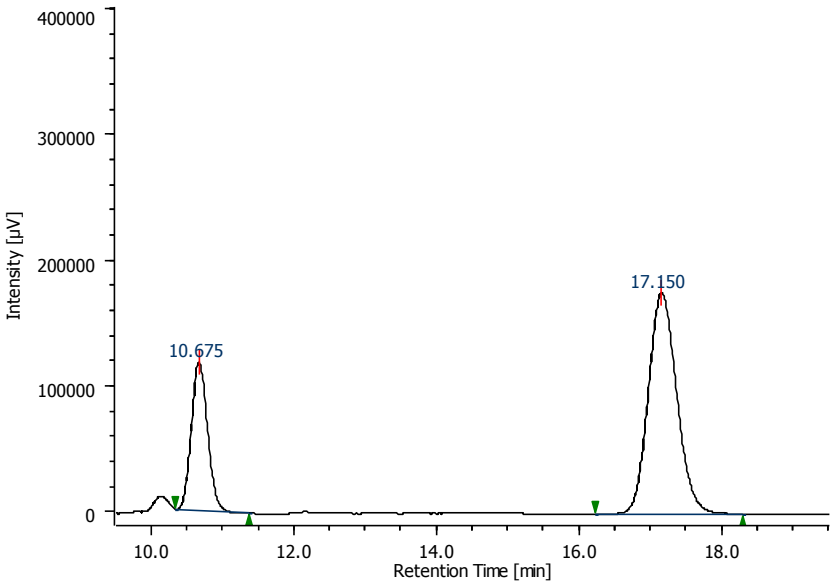
Peak No.	Retention Time (min)	Area (%)
1	13.200	93.397
2	25.892	6.603

(+)-1-Ethyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one [(+)-**3a**]



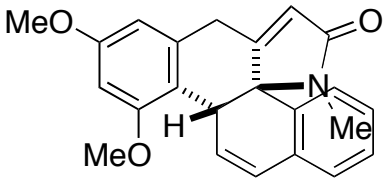


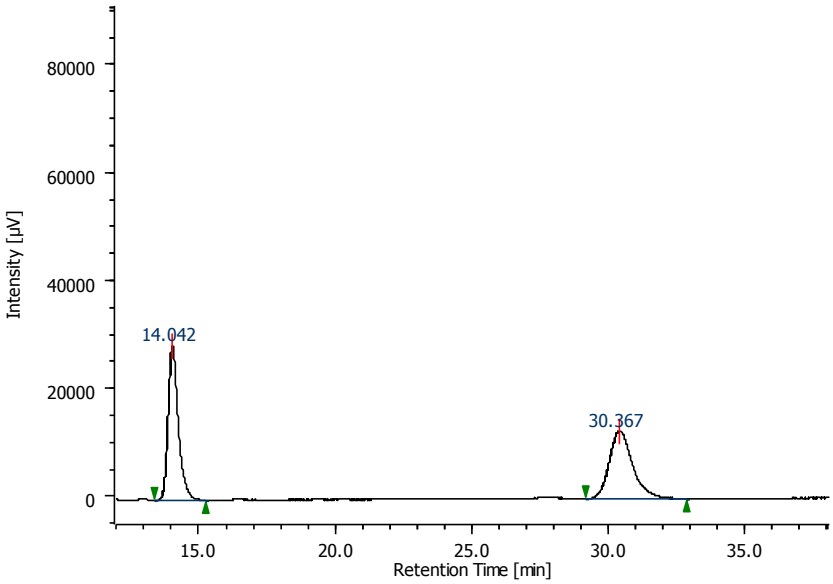
Peak No.	Retention Time (min)	Area (%)
1	11.742	49.428
2	18.708	50.572



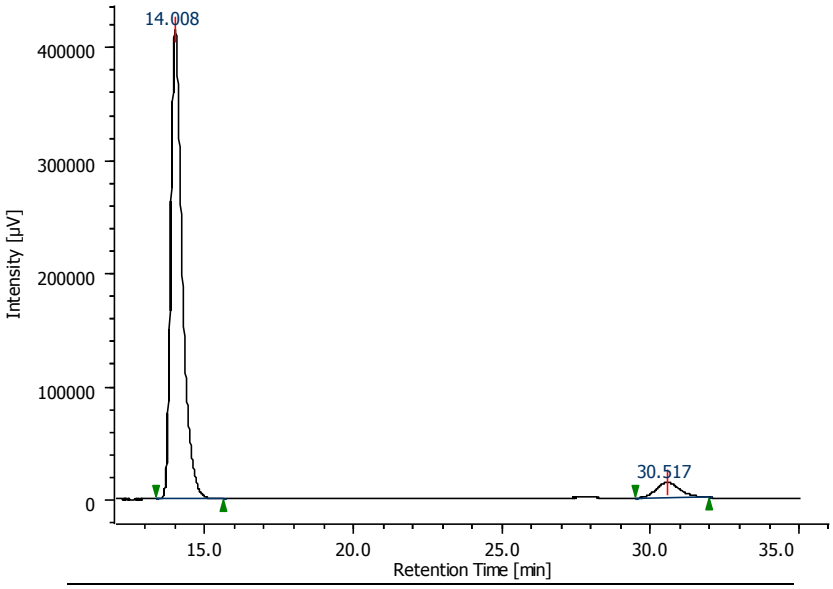
Peak No.	Retention Time (min)	Area (%)
1	10.675	27.778
2	17.150	72.222

(+)-10,12-Dimethoxy-5-methyl-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2b]



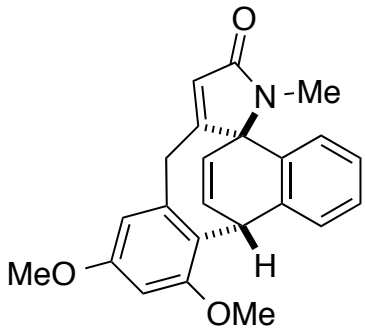


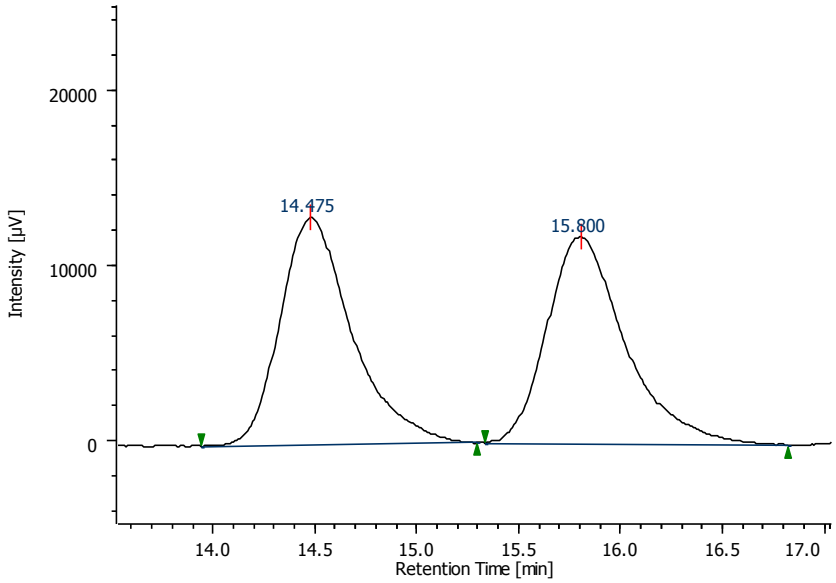
Peak No.	Retention Time (min)	Area (%)
1	14.042	50.149
2	30.367	49.851



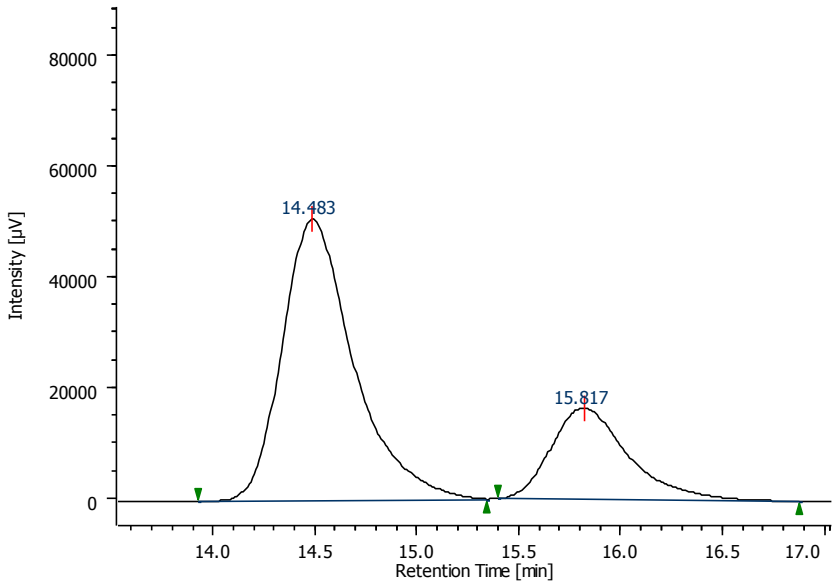
Peak No.	Retention Time (min)	Area (%)
1	14.008	93.597
2	30.517	6.403

(–)-6,8-Dimethoxy-1-methyl-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]-pyrrol-2(1*H*)-one [(–)-**3b**]



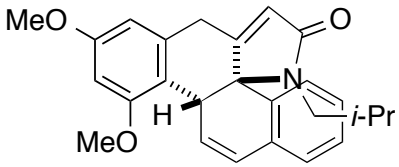


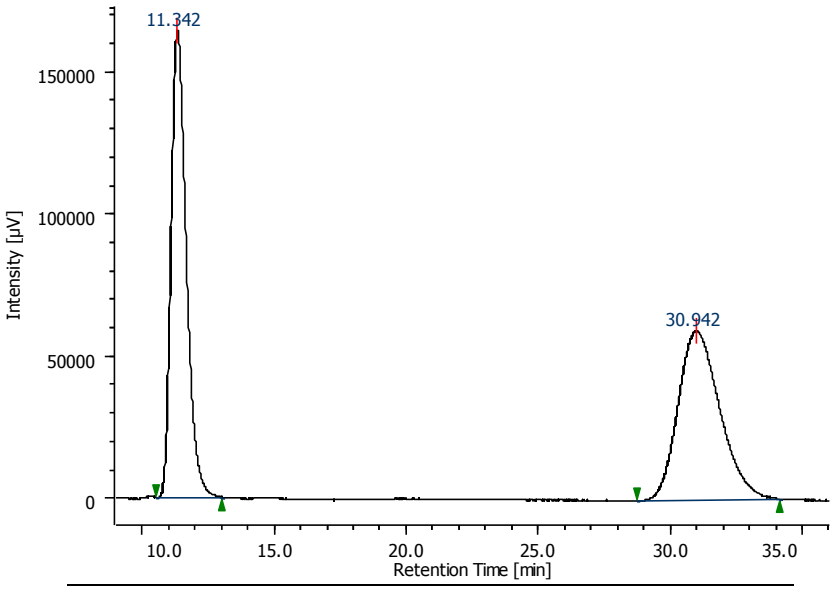
Peak No.	Retention Time (min)	Area (%)
1	14.475	50.451
2	15.792	49.549



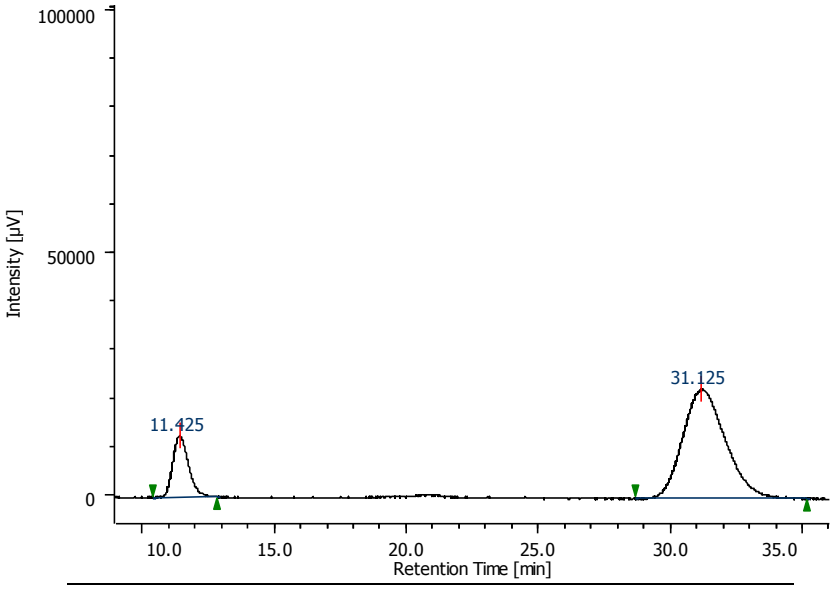
Peak No.	Retention Time (min)	Area (%)
1	14.492	73.943
2	15.800	26.057

(+)-5-Isobutyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2c**]**



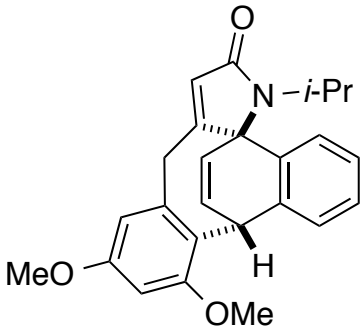


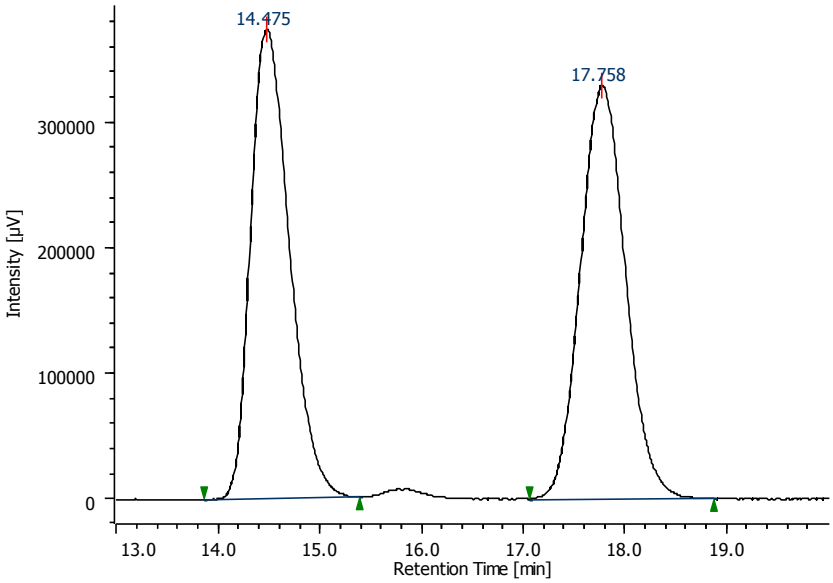
Peak No.	Retention Time (min)	Area (%)
1	11.342	50.134
2	30.942	49.866



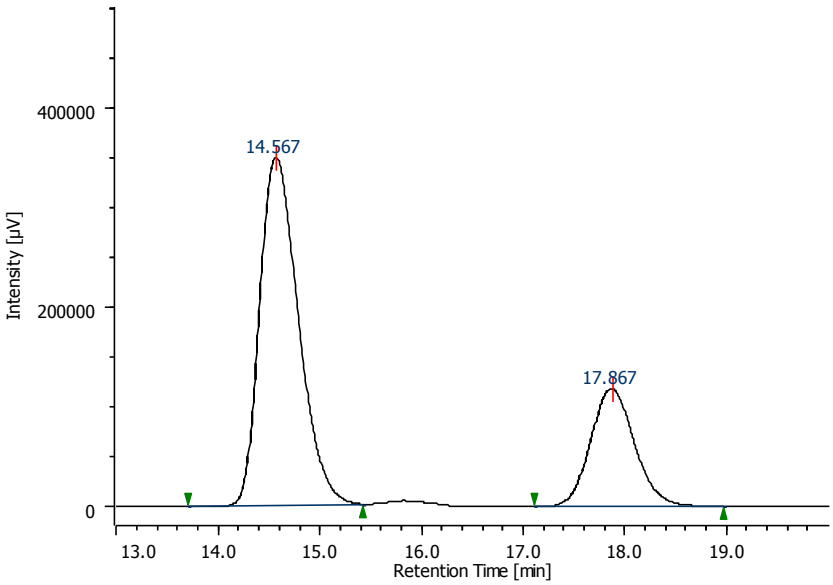
Peak No.	Retention Time (min)	Area (%)
1	11.425	17.037
2	31.125	82.963

(+)-1-Isobutyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]-pyrrol-2(1*H*)-one [(+)-**3c**]



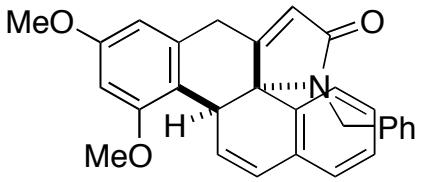


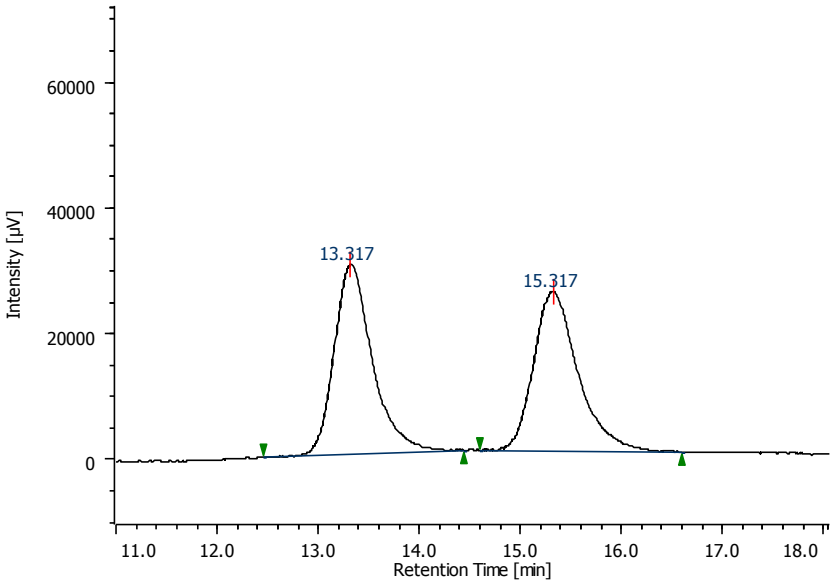
Peak No.	Retention Time (min)	Area (%)
1	14.475	49.333
2	17.758	50.667



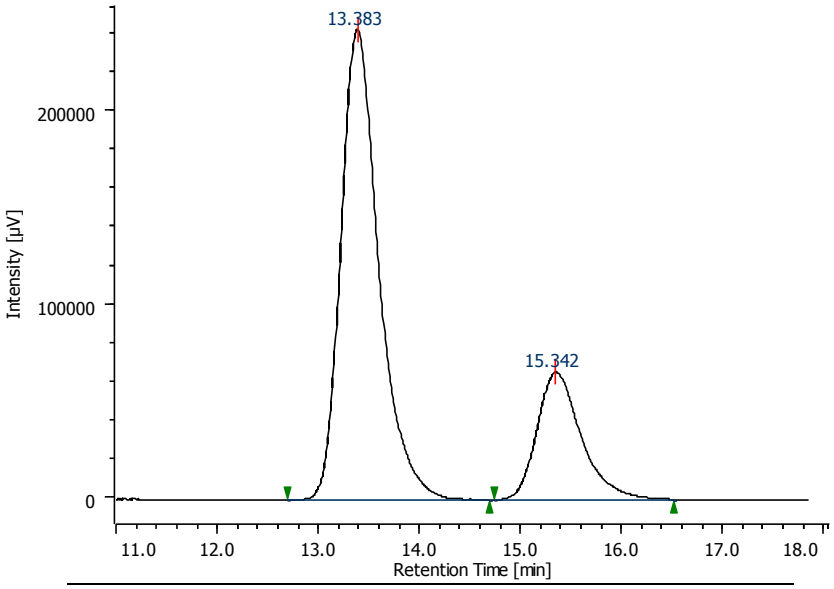
Peak No.	Retention Time (min)	Area (%)
1	14.567	72.216
2	17.867	27.784

(+)-5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-**2d**]



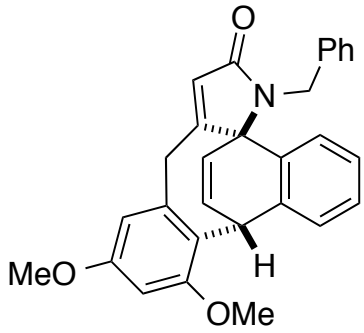


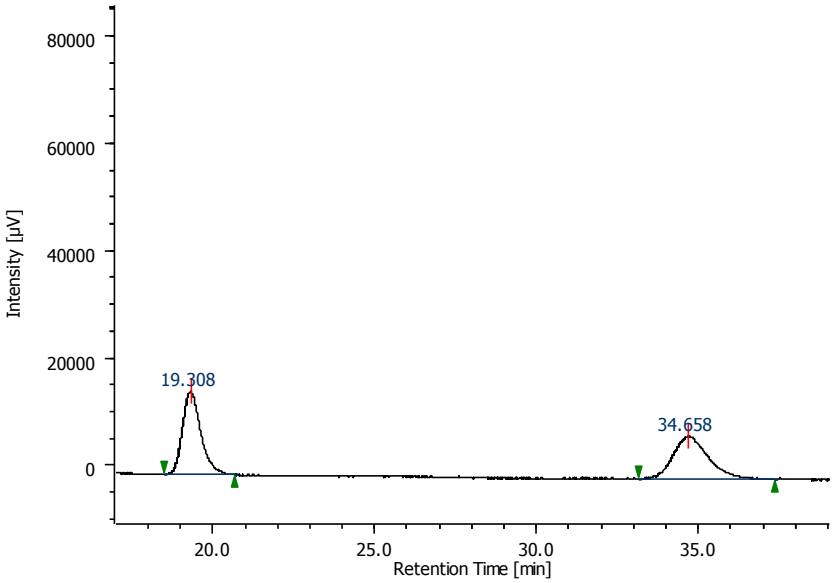
Peak No.	Retention Time (min)	Area (%)
1	13.317	50.492
2	15.317	49.508



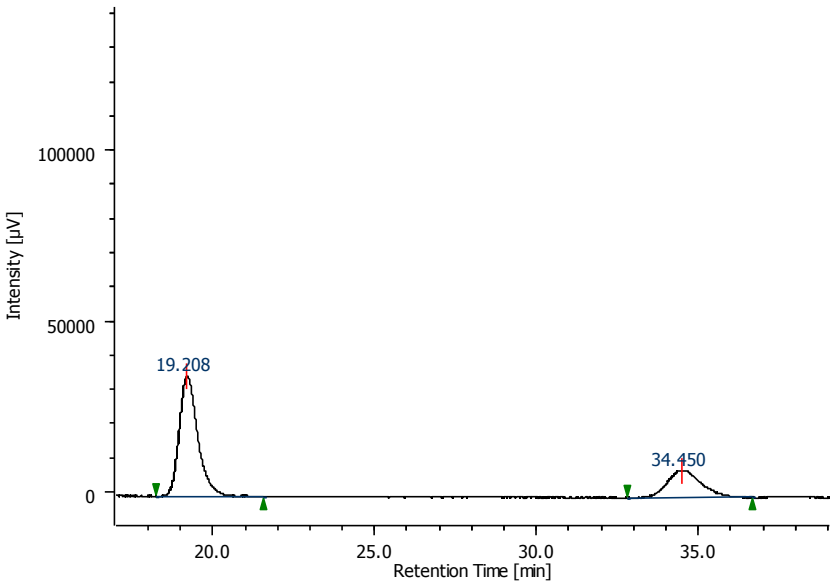
Peak No.	Retention Time (min)	Area (%)
1	13.383	76.059
2	15.342	23.941

(+)-1-Benzyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one [(+)-3d]



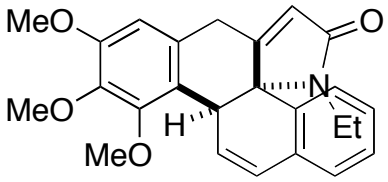


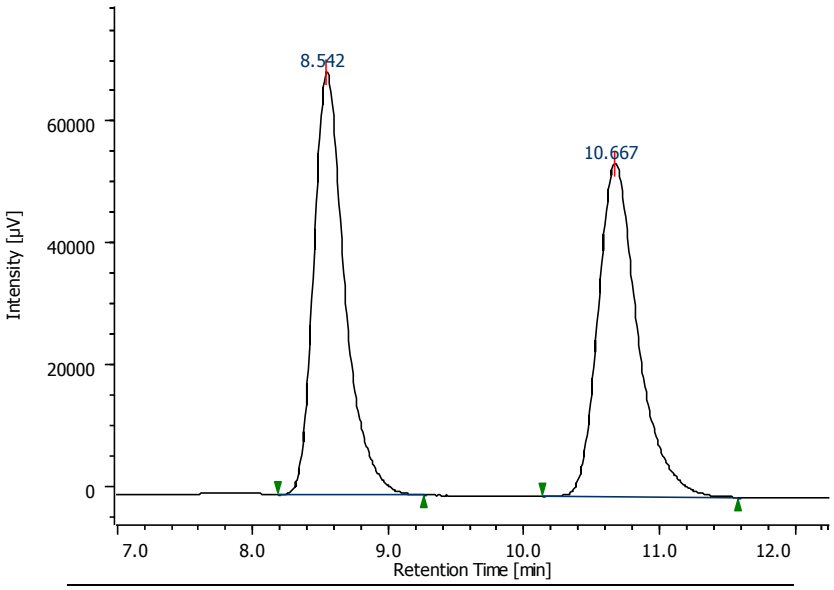
Peak No.	Retention Time (min)	Area (%)
1	19.308	51.747
2	34.658	48.253



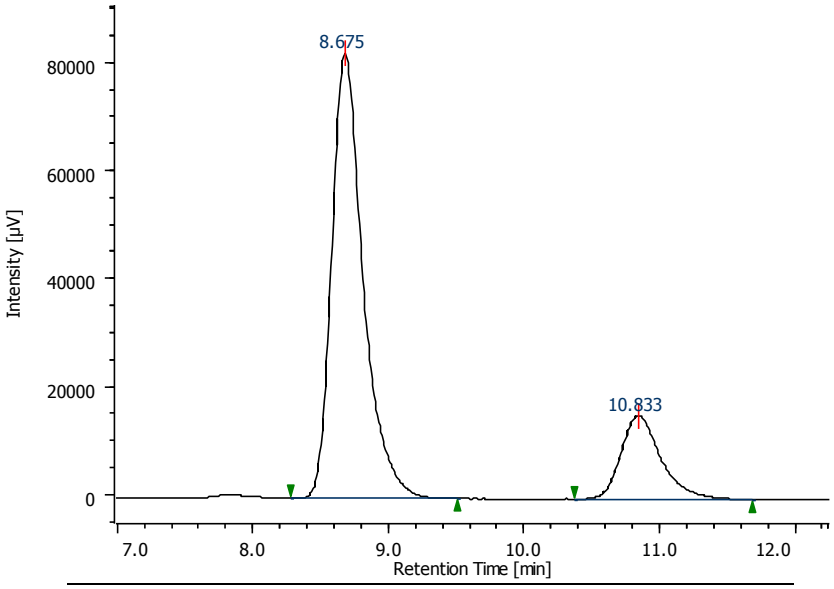
Peak No.	Retention Time (min)	Area (%)
1	19.208	70.496
2	34.450	29.504

(+)-5-Ethyl-10,11,12-trimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2e**]**



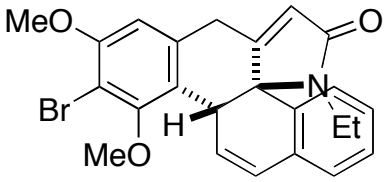


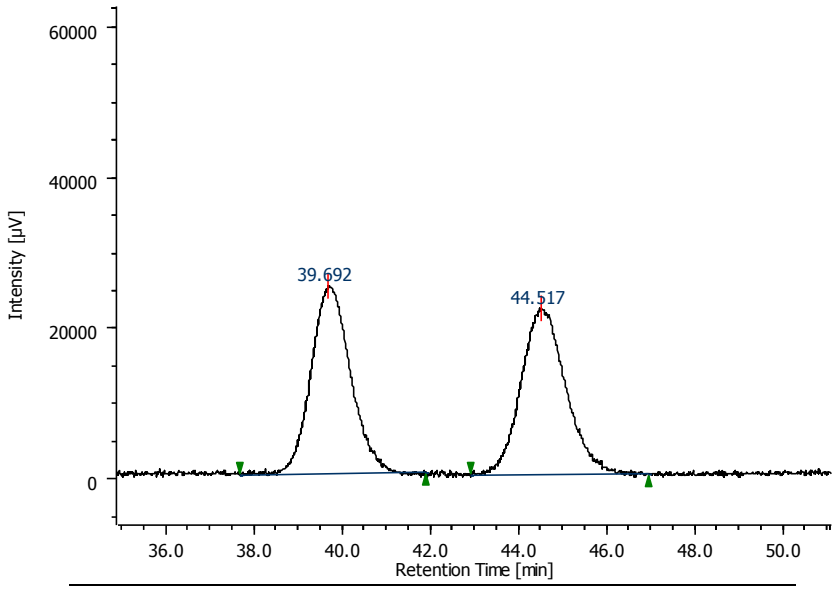
Peak No.	Retention Time (min)	Area (%)
1	8.542	49.948
2	10.667	50.052



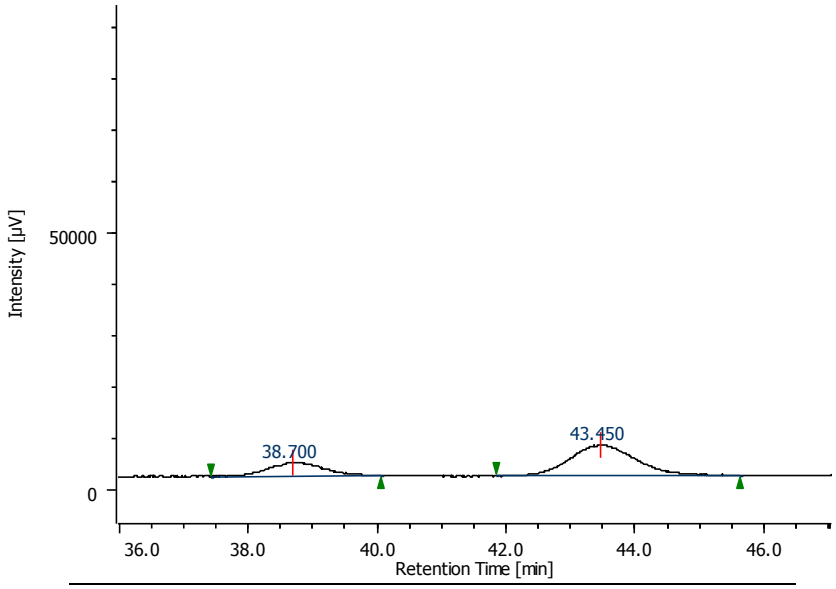
Peak No.	Retention Time (min)	Area (%)
1	8.675	80.810
2	10.833	19.190

(4b*S*,12b*R*)-(+)-11-bromo-5-ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(4b*S*,12b*R*)-(+)-2f]



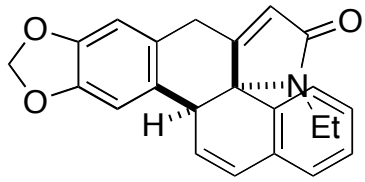


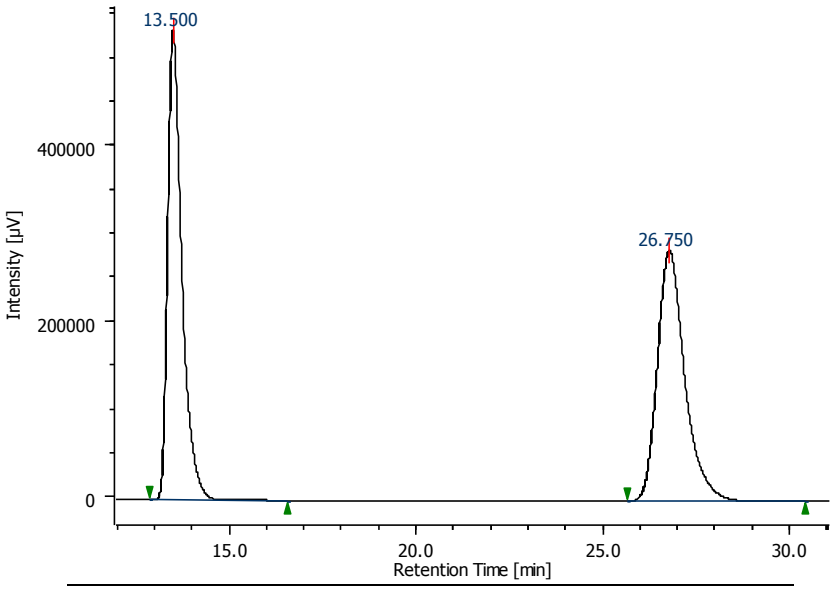
Peak No.	Retention Time (min)	Area (%)
1	39.692	49.860
2	44.517	50.140



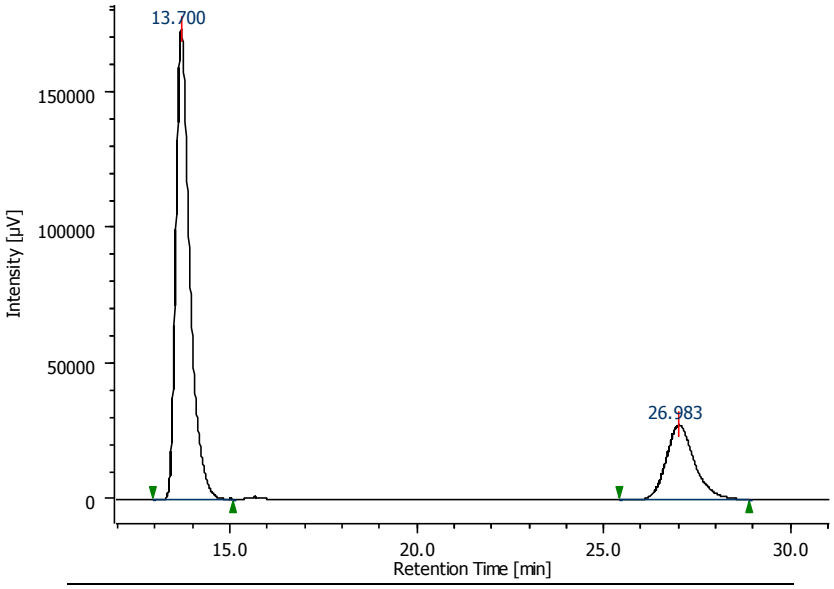
Peak No.	Retention Time (min)	Area (%)
1	38.700	27.516
2	43.450	72.484

(+)-5-Ethyl-8,13b-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2g]



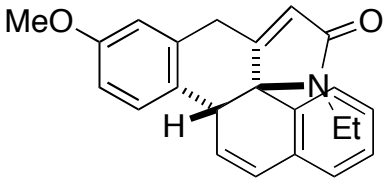


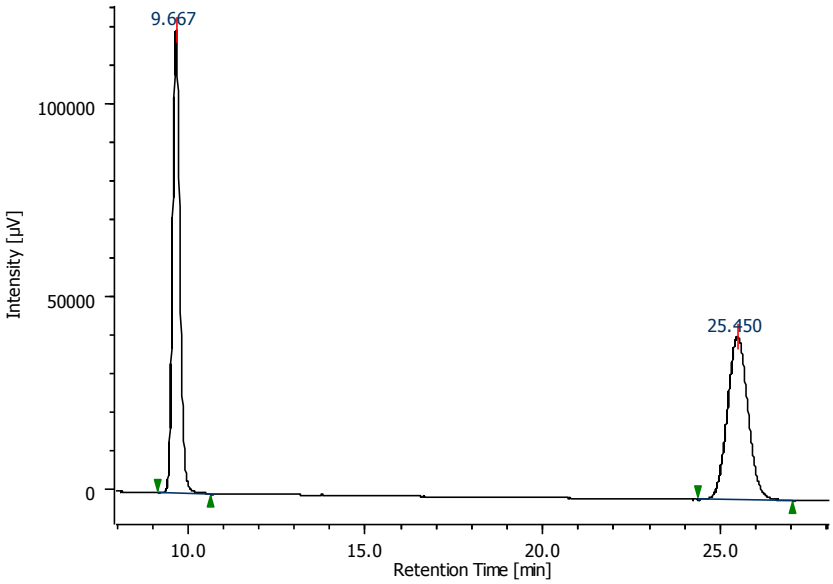
Peak No.	Retention Time (min)	Area (%)
1	13.500	49.500
2	26.750	50.500



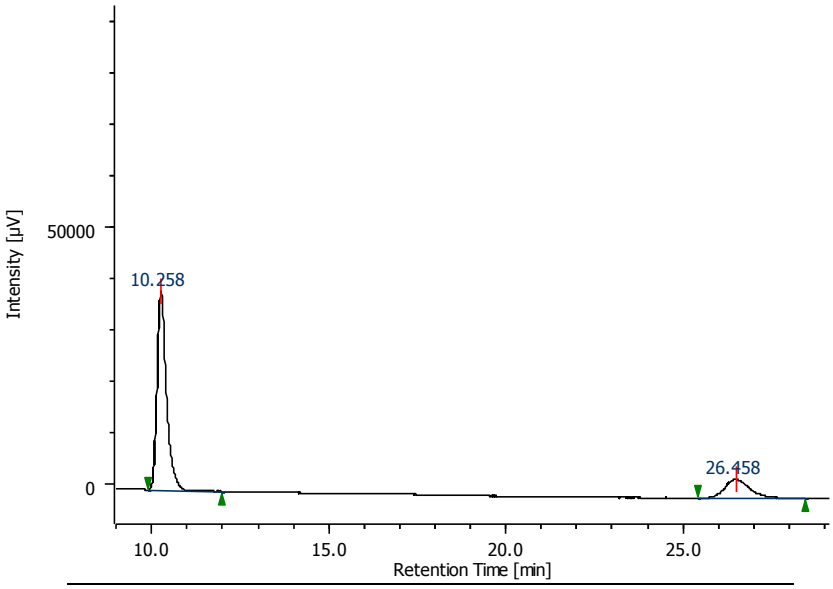
Peak No.	Retention Time (min)	Area (%)
1	13.700	75.275
2	26.983	24.725

(+)-5-Ethyl-10-methoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(+)-2h]



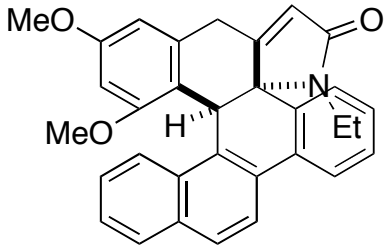


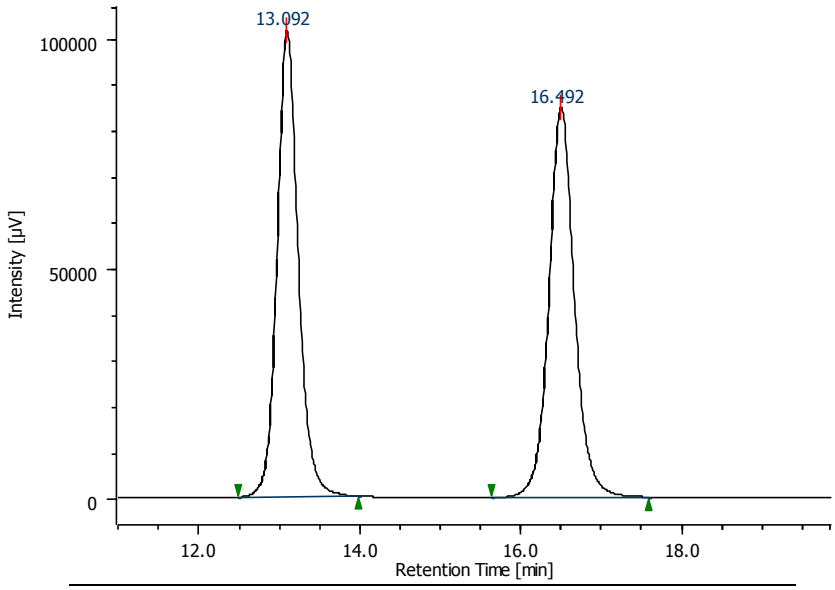
Peak No.	Retention Time (min)	Area (%)
1	9.667	49.824
2	25.450	50.176



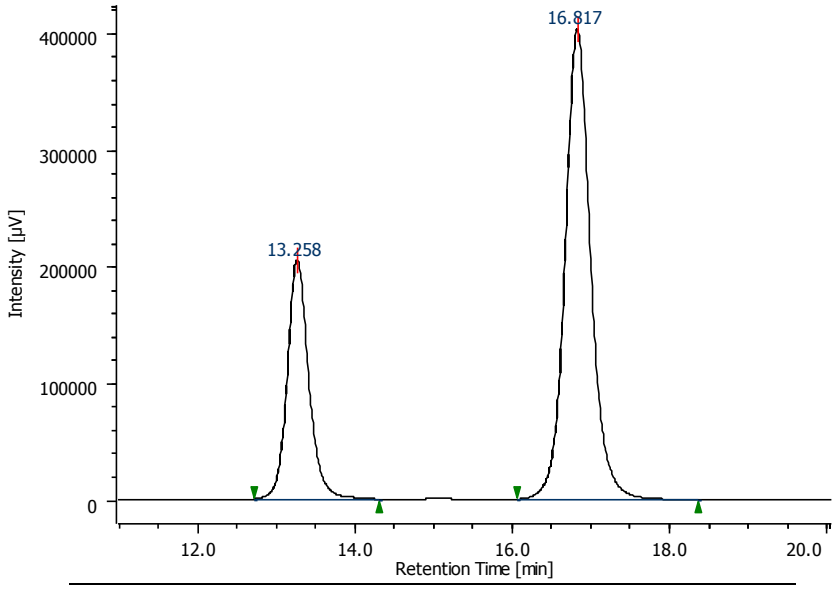
Peak No.	Retention Time (min)	Area (%)
1	10.258	79.843
2	26.458	20.157

(+)-5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]chryseno[5,6-*h*]indol-6(5*H*)-one [(+)-2i**]**



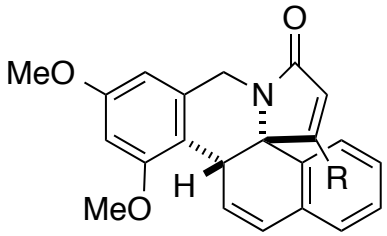


Peak No.	Retention Time (min)	Area (%)
1	13.092	49.747
2	16.492	50.253

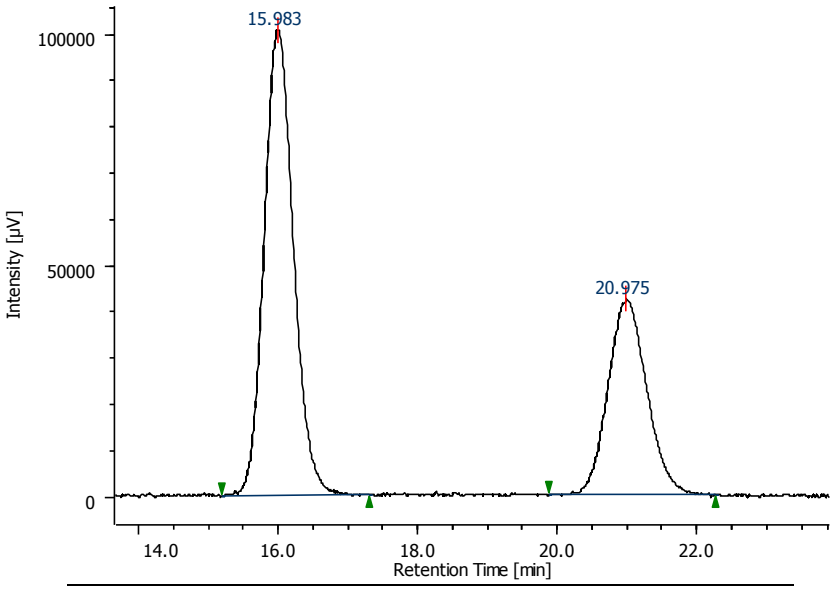


Peak No.	Retention Time (min)	Area (%)
1	13.258	29.872
2	16.817	70.128

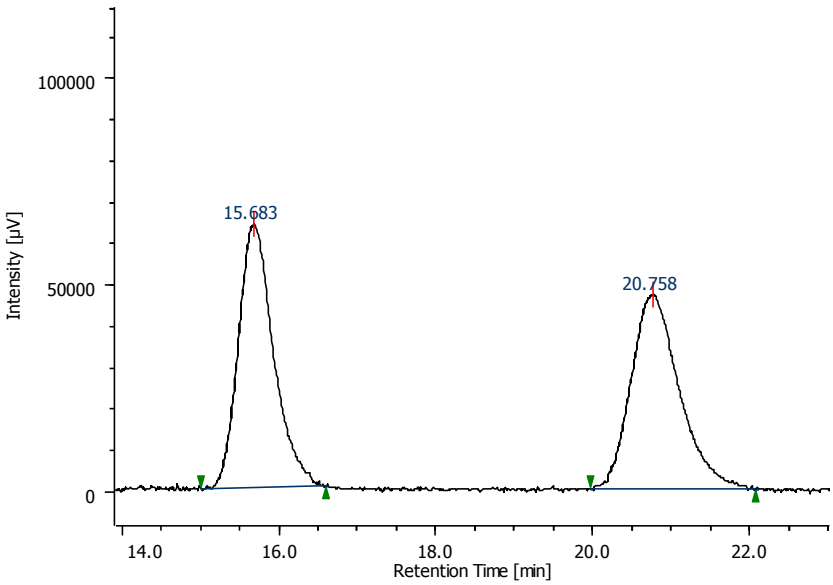
(–)-11,13-Dimethoxy-5-(2-methoxyphenyl)-9,13b-dihydro-7*H*-benzo[*c*]pyrrolo[2,1-*e*]-phenanthridin-7-one [(–)-5]



(R = 2-MeOC$_6$H$_4$)



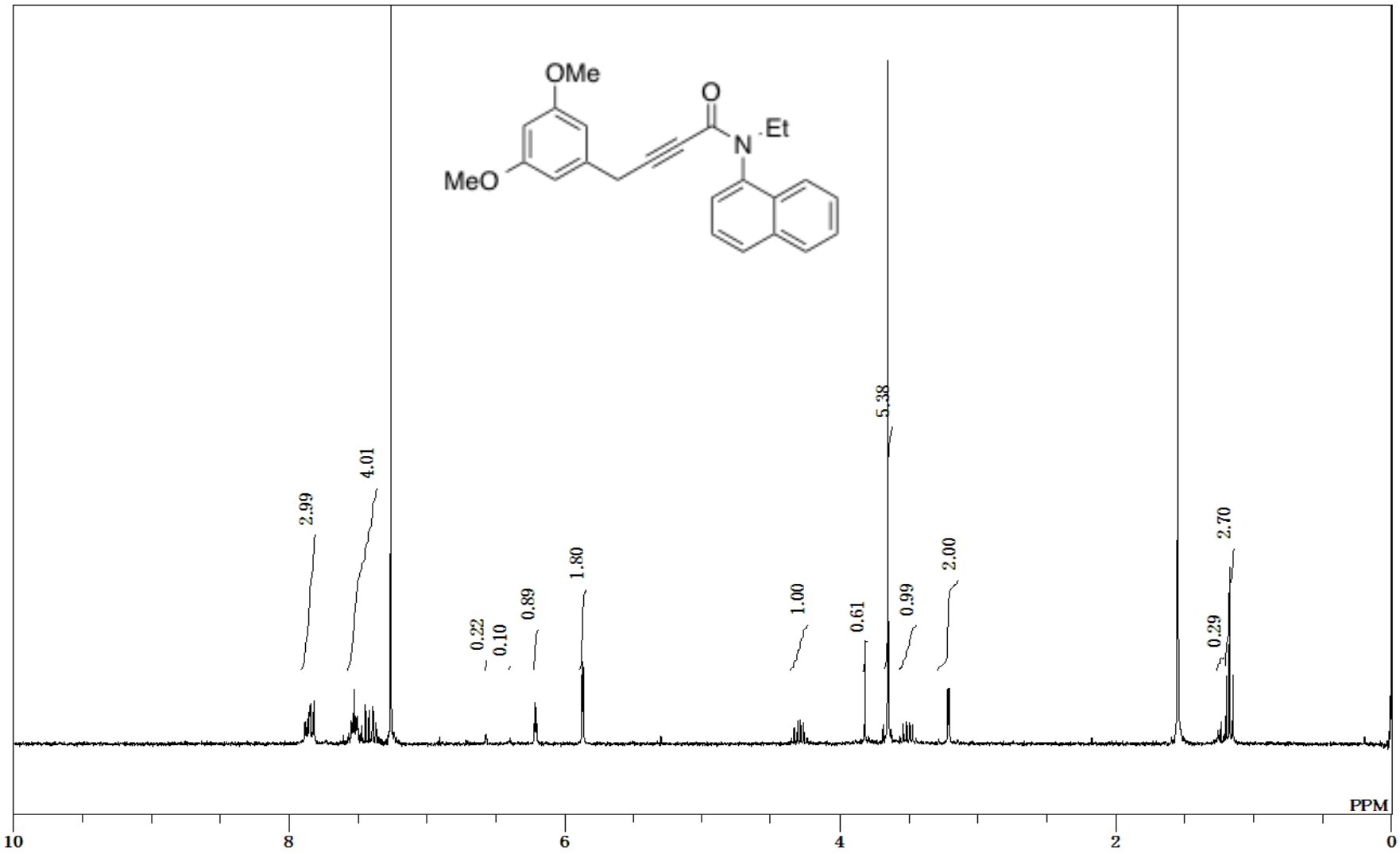
Peak No.	Retention Time (min)	Area (%)
1	15.683	49.684
2	20.758	50.316

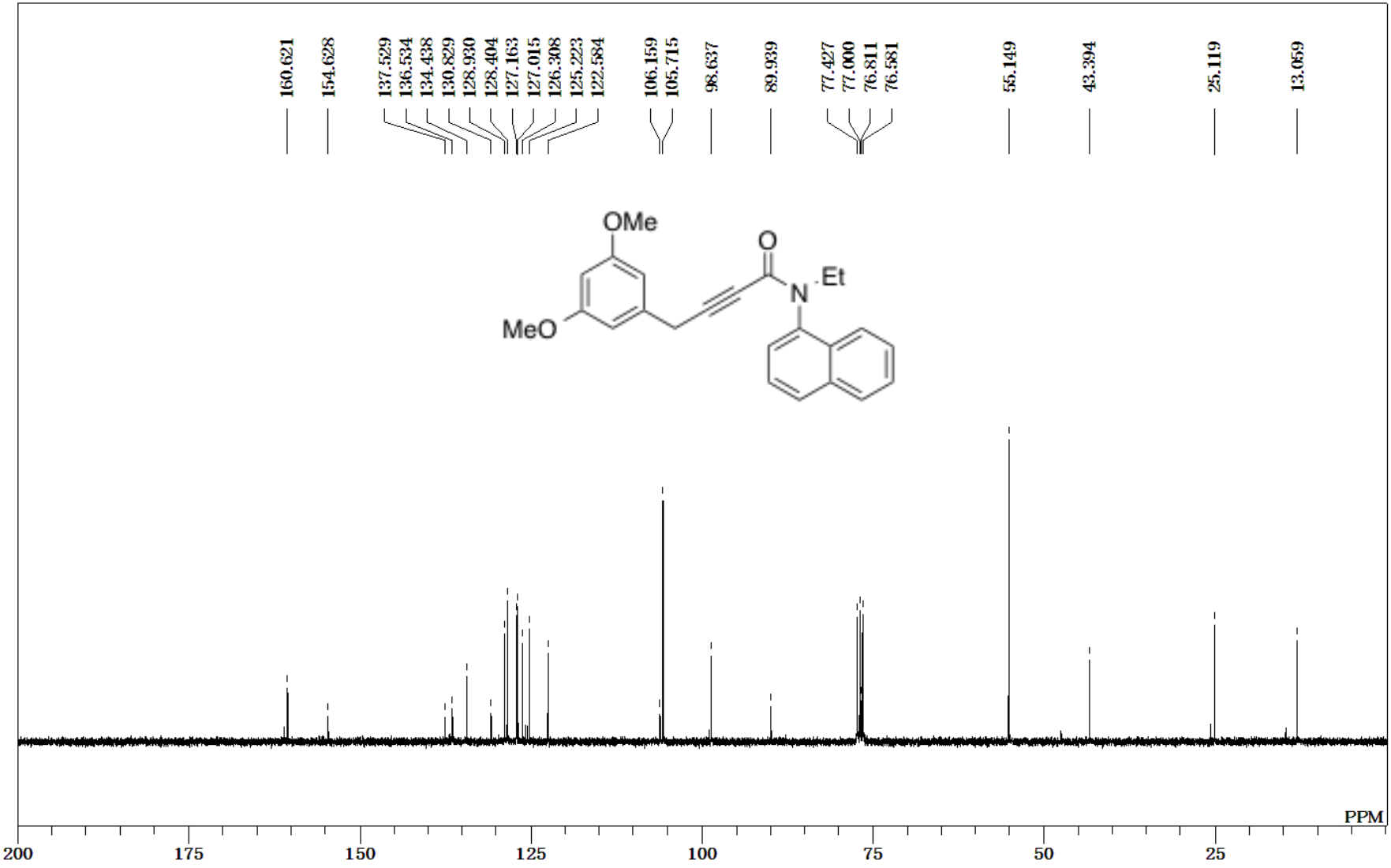


Peak No.	Retention Time (min)	Area (%)
1	15.983	64.267
2	20.975	35.733

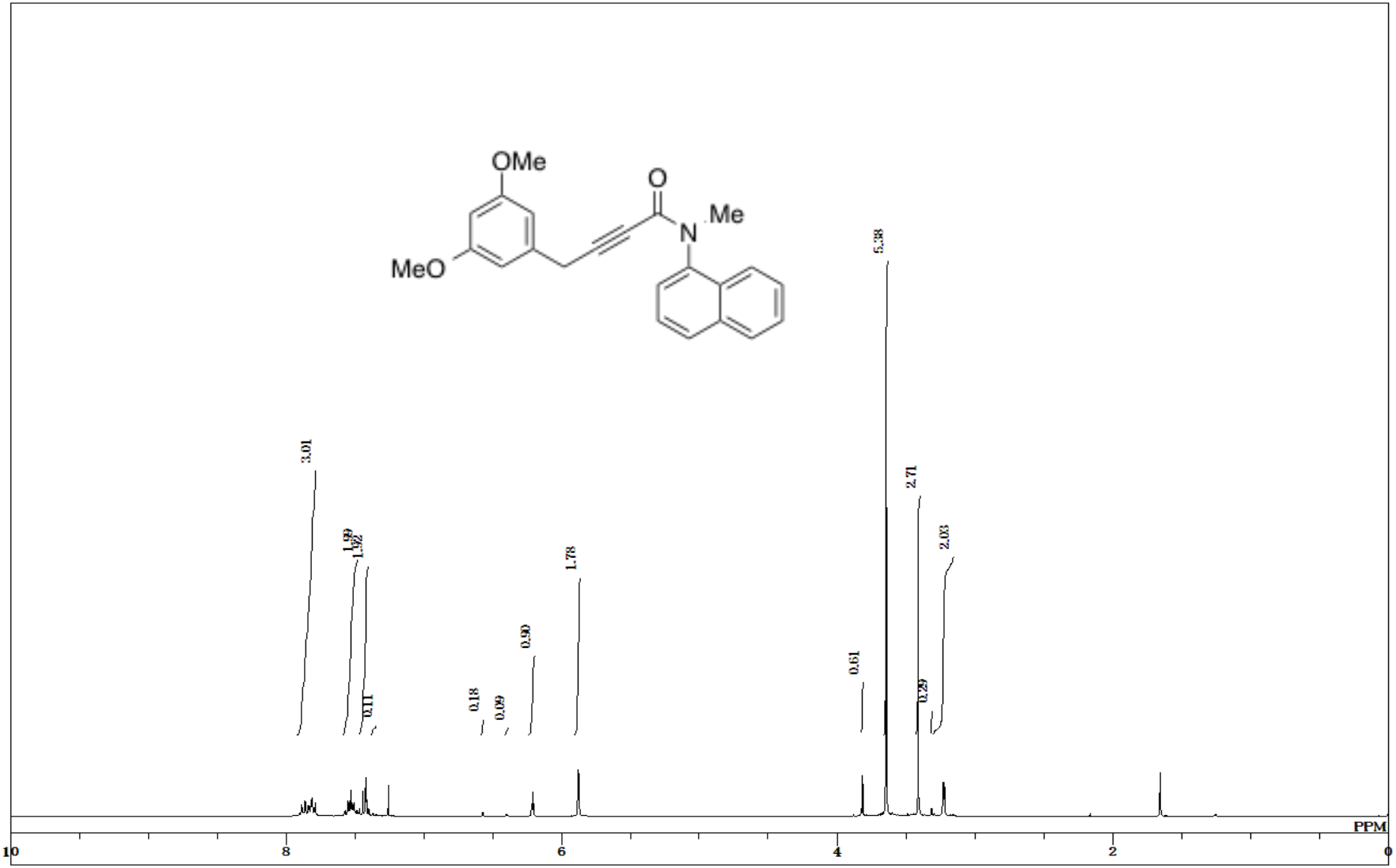
VII. ^{1}H and ^{13}C NMR Spectra

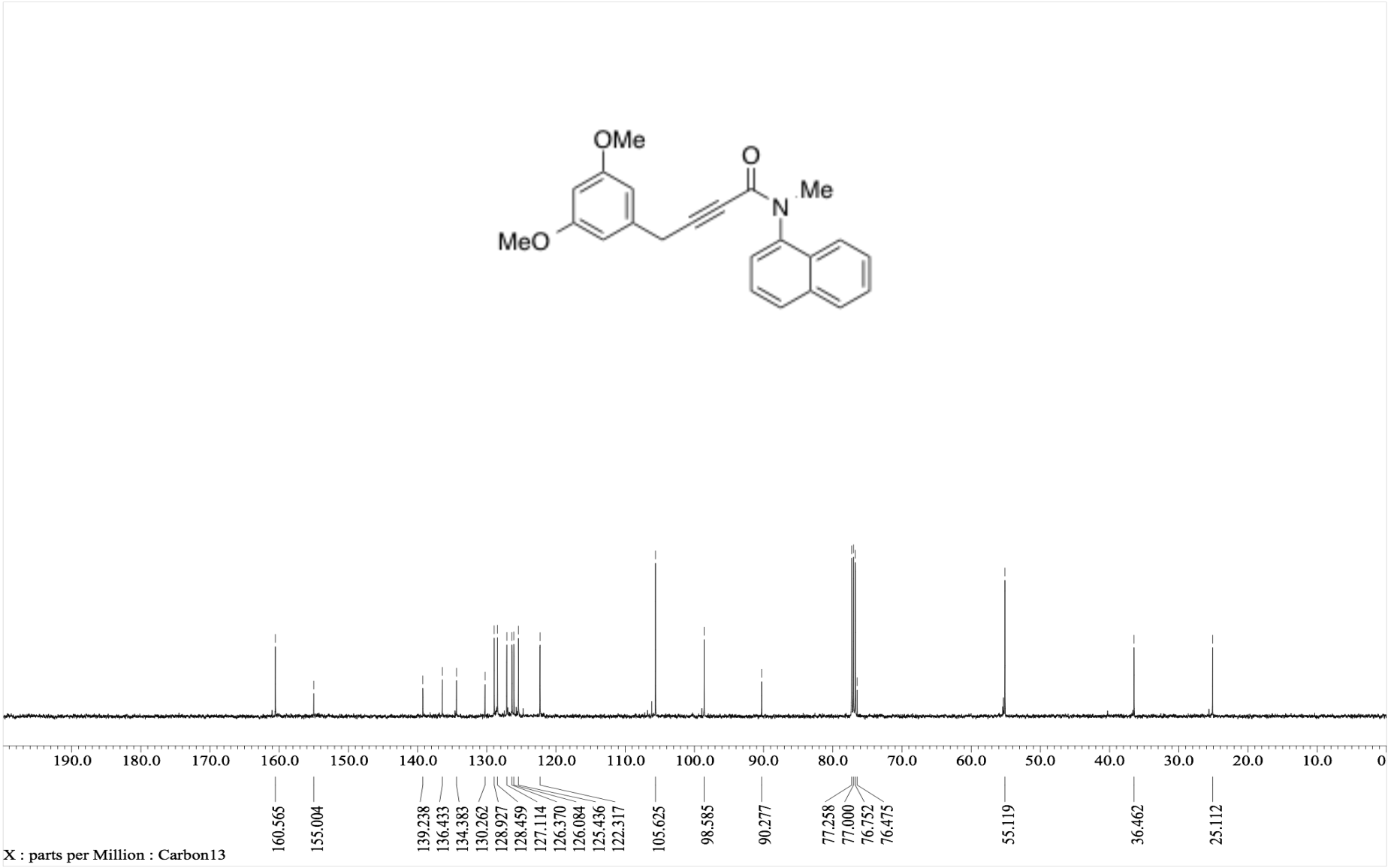
3-(3,5-Dimethoxy)propynoic acid ethylnaphthalen-1-ylamide (1a)



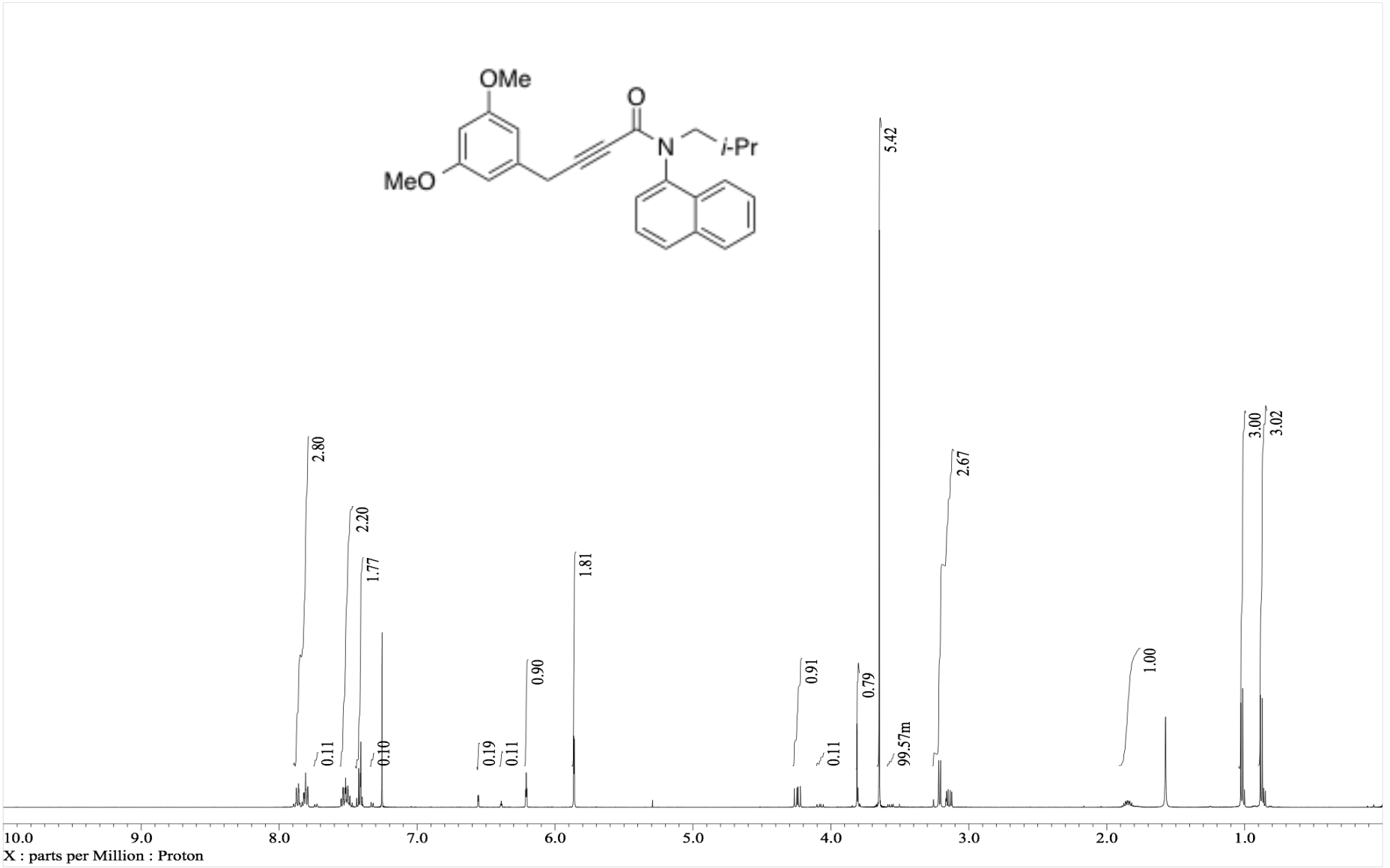

160.621
154.628
137.529
136.534
134.438
130.829
128.930
128.404
127.163
127.015
126.308
125.223
122.584
106.159
105.715
98.637
89.939
77.427
77.000
76.811
76.581
55.149
43.394
25.119
13.059
OMe
MeO
O
N
Et
PPM
200
175
150
125
100
75
50
25

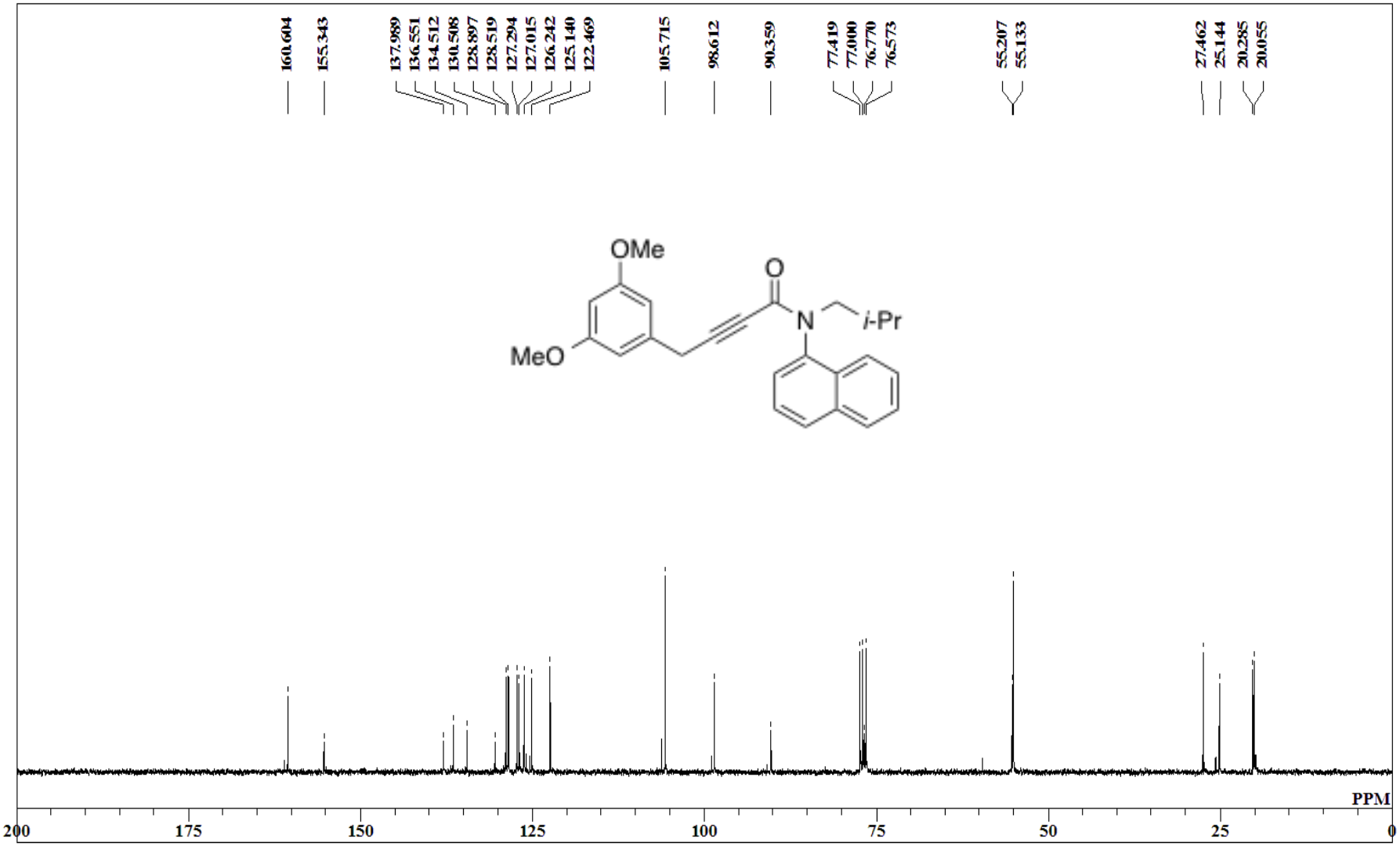
4-(3,5-Dimethoxyphenyl)-*N*-methyl-*N*-(naphthalen-1-yl)but-2-ynamide (1b)



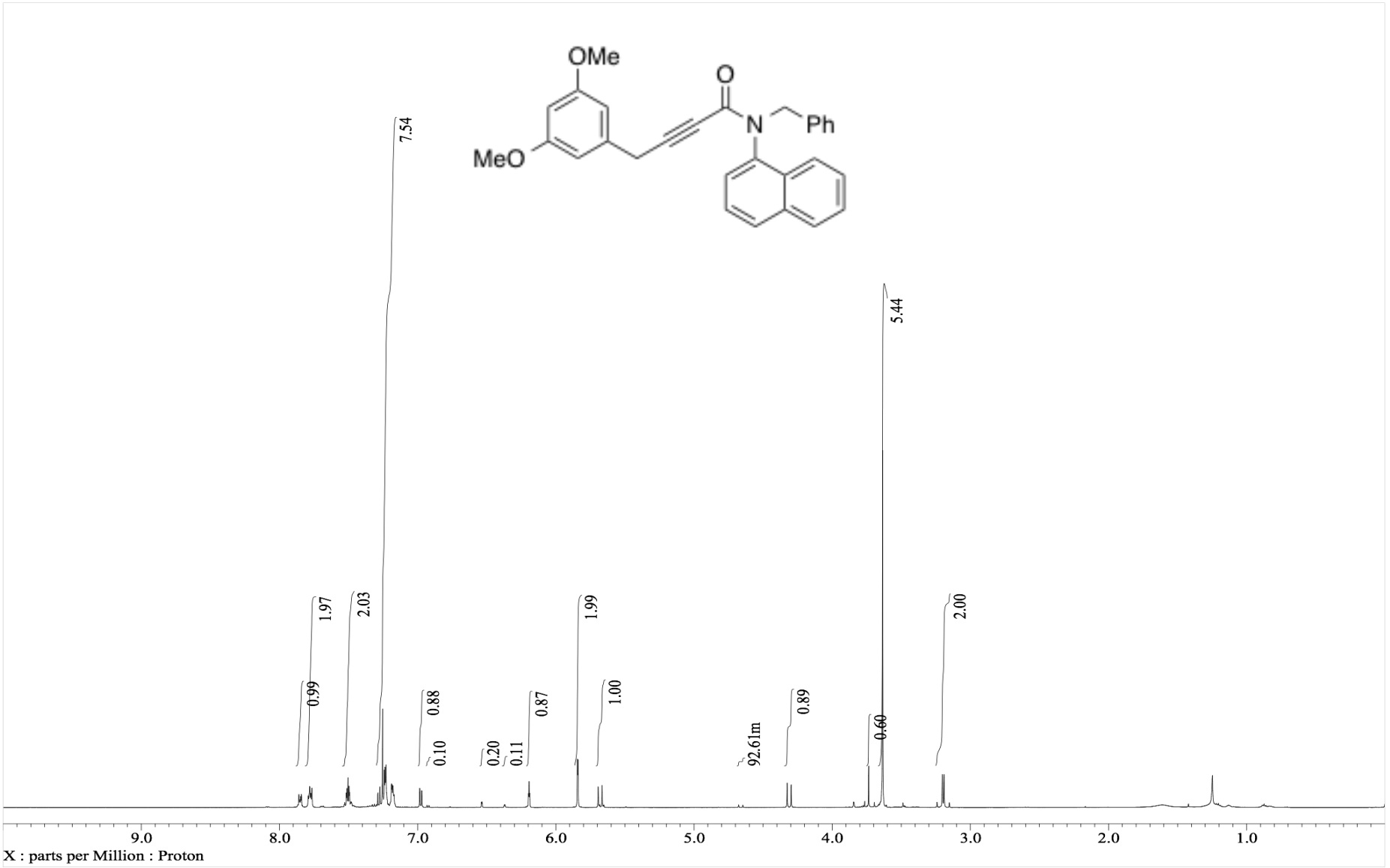

OMe
O
Me
N
MeO
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.565
155.004
139.238
136.433
134.383
130.262
128.927
128.459
127.114
126.370
126.084
125.436
122.317
105.625
98.585
90.277
77.258
77.000
76.752
76.475
55.119
36.462
25.112
X : parts per Million : Carbon13

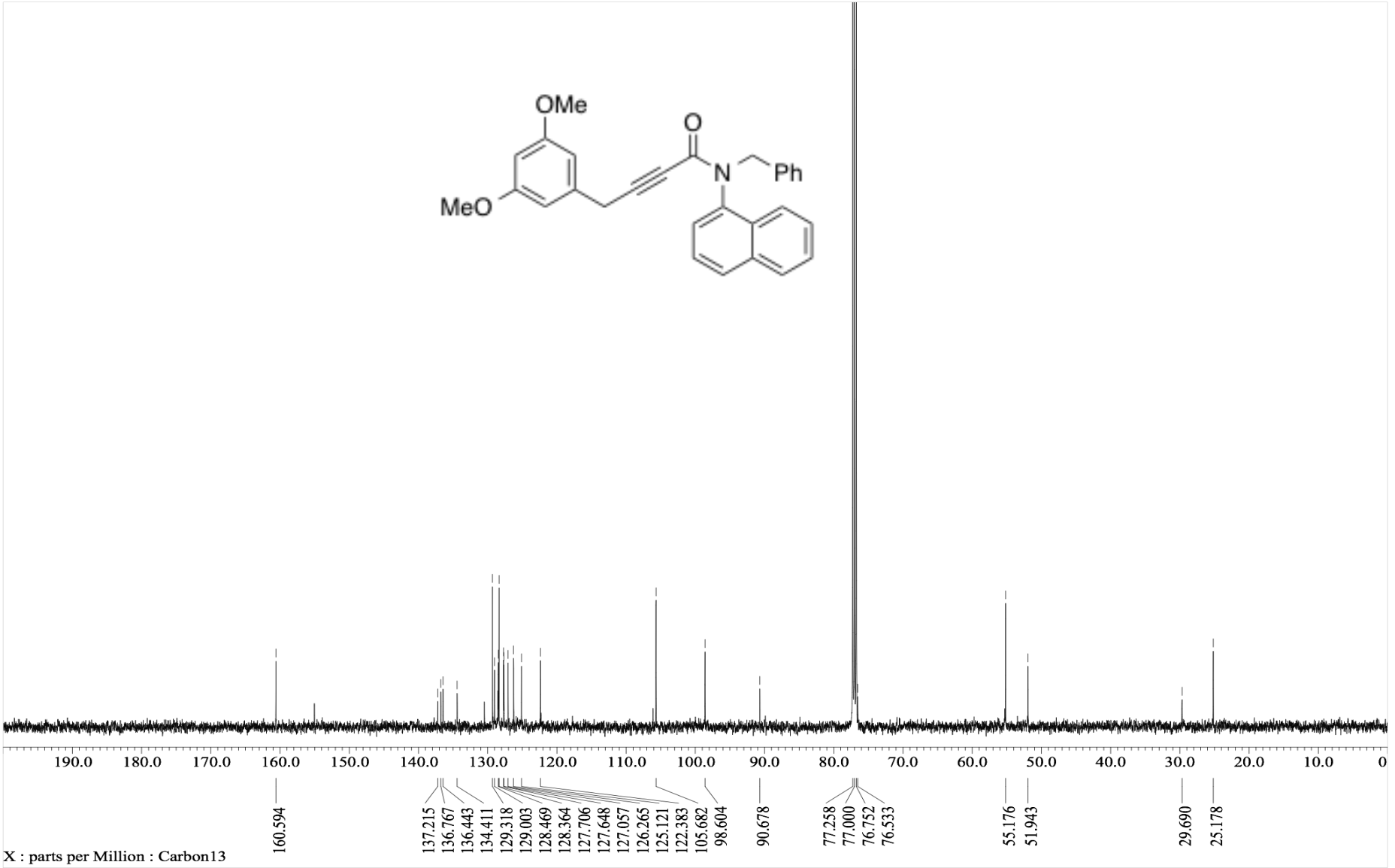
4-(3,5-Dimethoxyphenyl)-*N*-isobutyl-*N*-(naphtylen-1-yl)but-2-ynamide (1c)



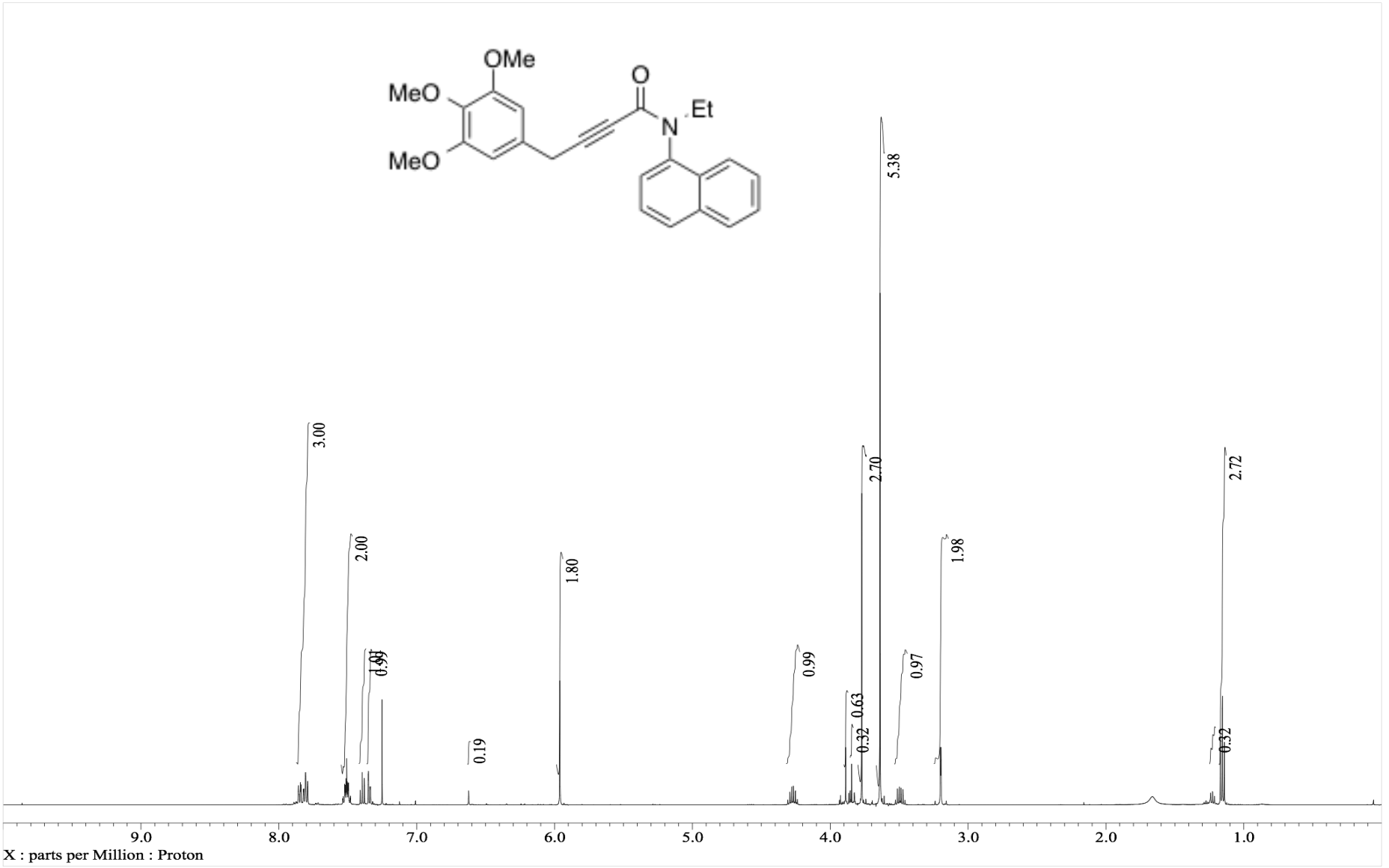

160.604
155.343
137.989
136.551
134.512
130.508
128.897
128.519
127.294
127.015
126.242
125.140
122.469
105.715
98.612
90.359
77.419
77.000
76.770
76.573
55.207
55.133
27.462
25.144
20.285
20.055
OMe
MeO
O
N
i-Pr
PPM
200
175
150
125
100
75
50
25
0

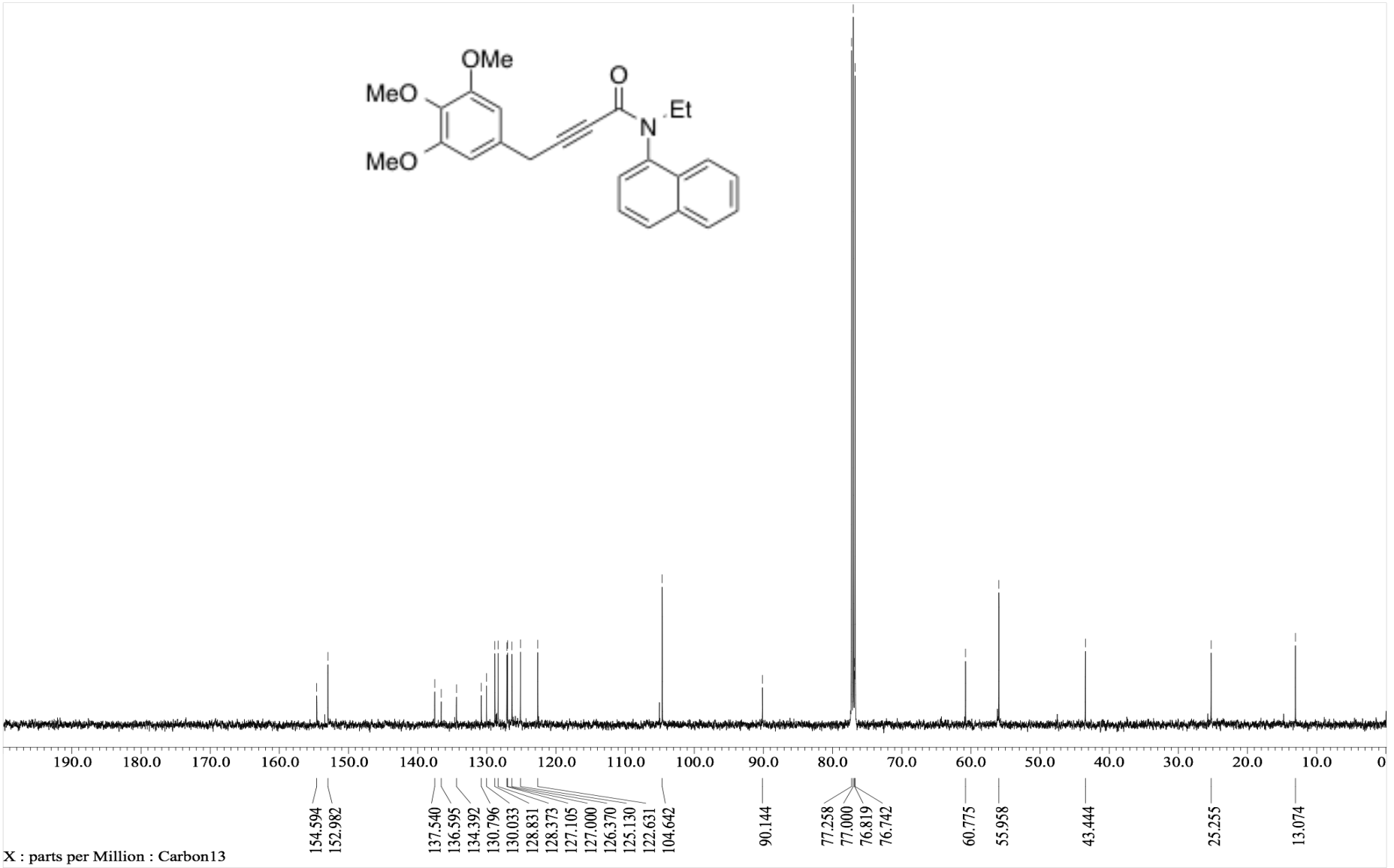
_N_-Benzyl-4-(3,5-dimethoxyphenyl)-_N_-(naphthalen-1-yl)but-2-ynamide (1d)



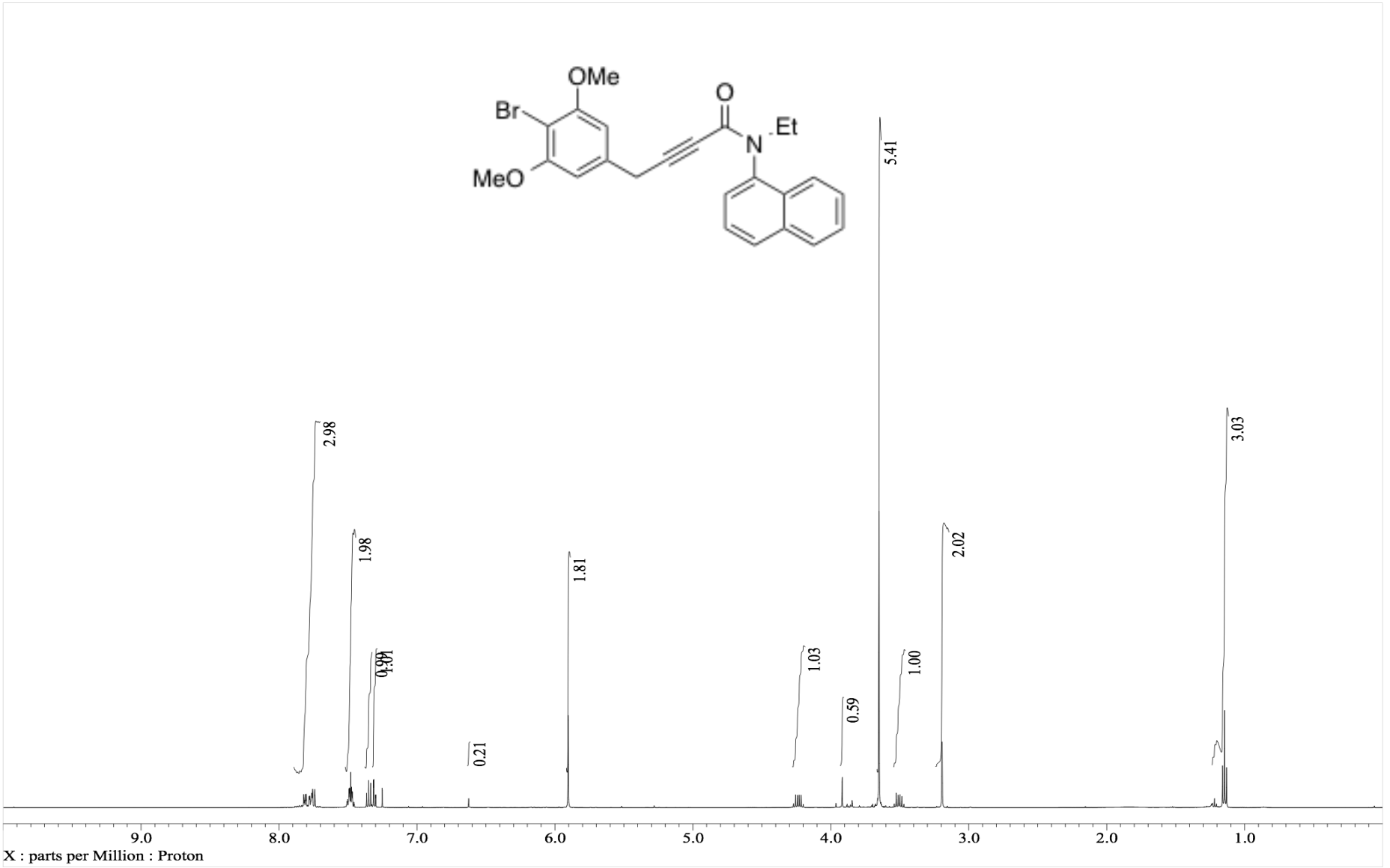

OMe
O
N
Ph
MeO
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.594
137.215
136.767
136.443
134.411
129.318
129.003
128.469
128.364
127.706
127.648
127.057
126.265
125.121
122.383
105.682
98.604
90.678
77.258
77.000
76.752
76.533
55.176
51.943
29.690
25.178
X : parts per Million : Carbon13

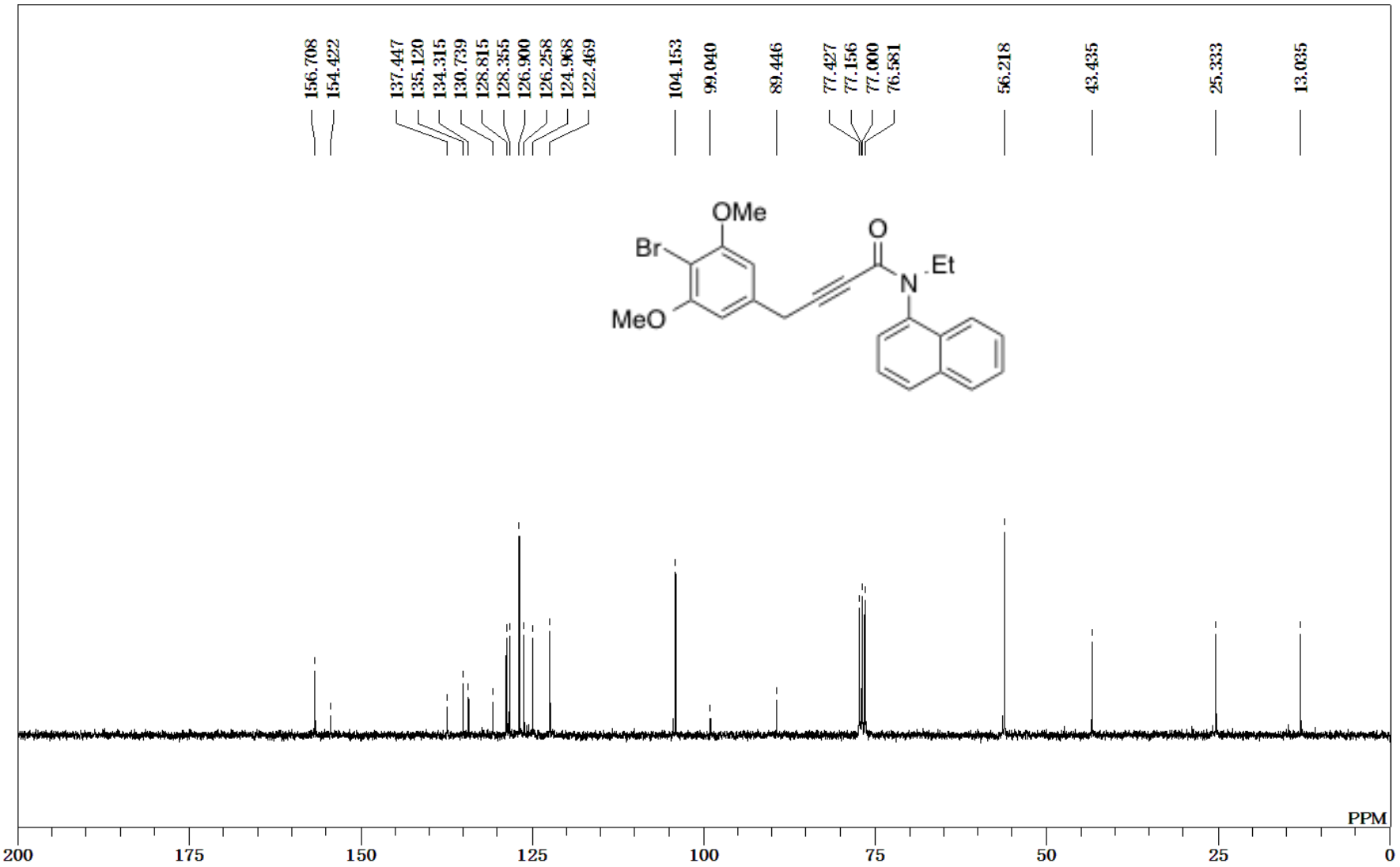
_N_-Ethyl-_N_-(naphthalen-1-yl)-4-(3,4,5-trimethoxyphenyl)but-2-ynamide (1e)



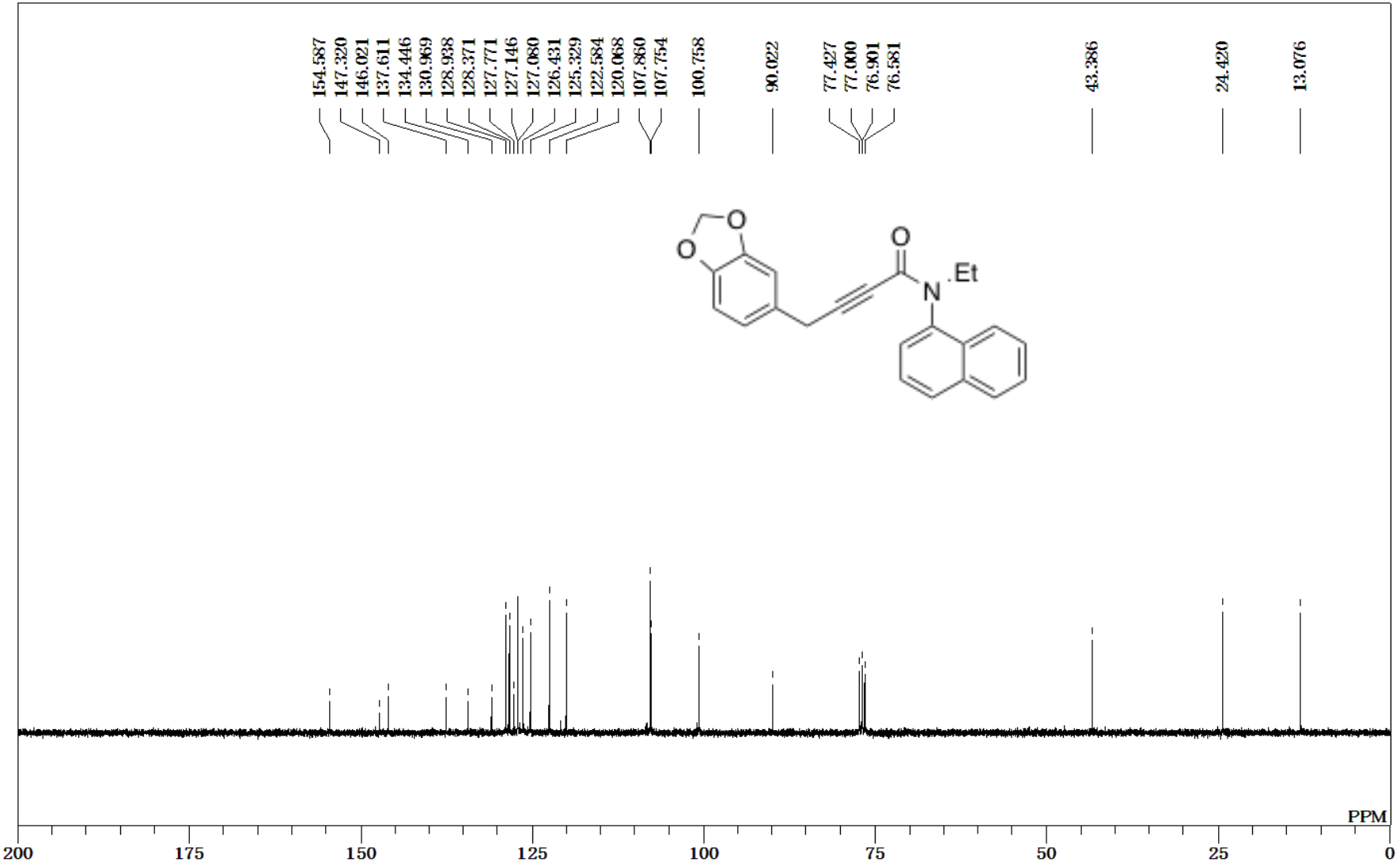

OMe
MeO
MeO
O
N
Et
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.594
152.982
137.540
136.595
134.392
130.796
130.033
128.831
128.373
127.105
127.000
126.370
125.130
122.631
104.642
90.144
77.258
77.000
76.819
76.742
60.775
55.958
43.444
25.255
13.074
X : parts per Million : Carbon13

4-(4-Bromo-3,5-dimethoxyphenyl)-*N*-ethyl-*N*-(naphthalen-1-yl)but-2-ynamide (1f)

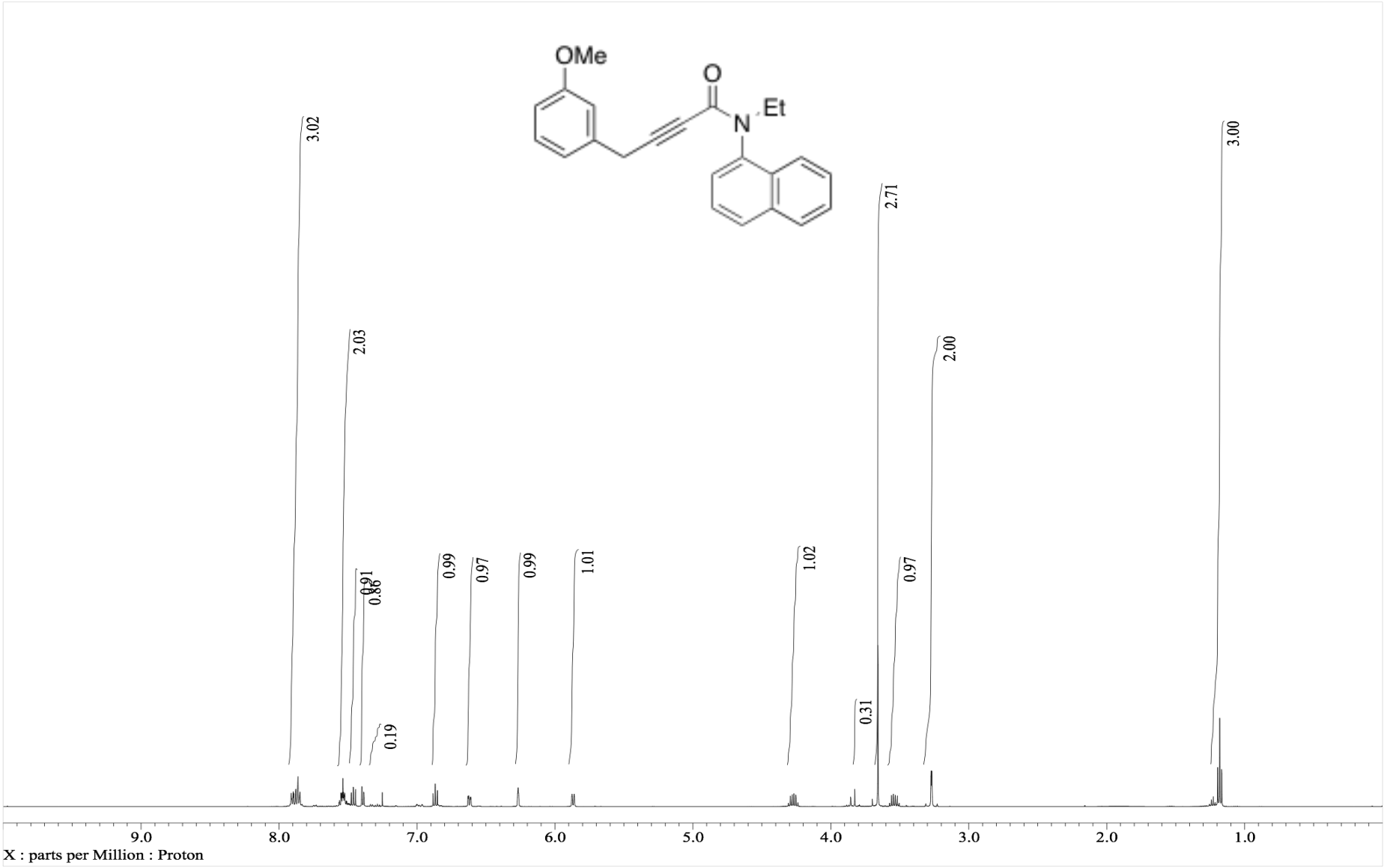


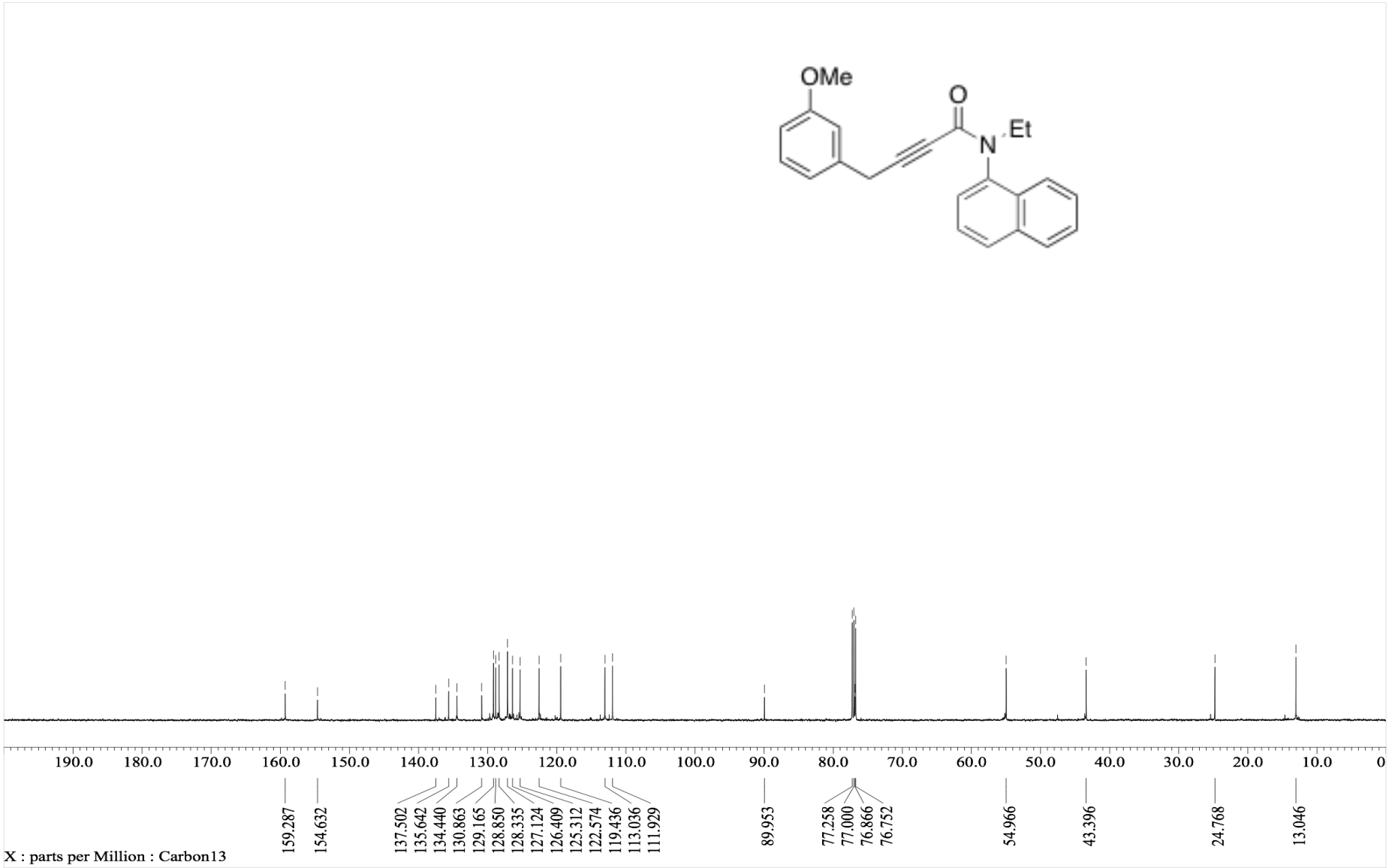

156.708
154.422
137.447
135.120
134.315
130.739
128.815
128.355
126.900
126.258
124.968
122.469
104.153
99.040
89.446
77.427
77.156
77.000
76.581
56.218
43.435
25.333
13.035
OMe
Br
MeO
O
N
Et
PPM
200
175
150
125
100
75
50
25
0

4-(Benzo[d][1,3]dioxol-5-yl)-*N*-ethyl-*N*-(naphthalen-1-yl)but-2-ynamide (1g)

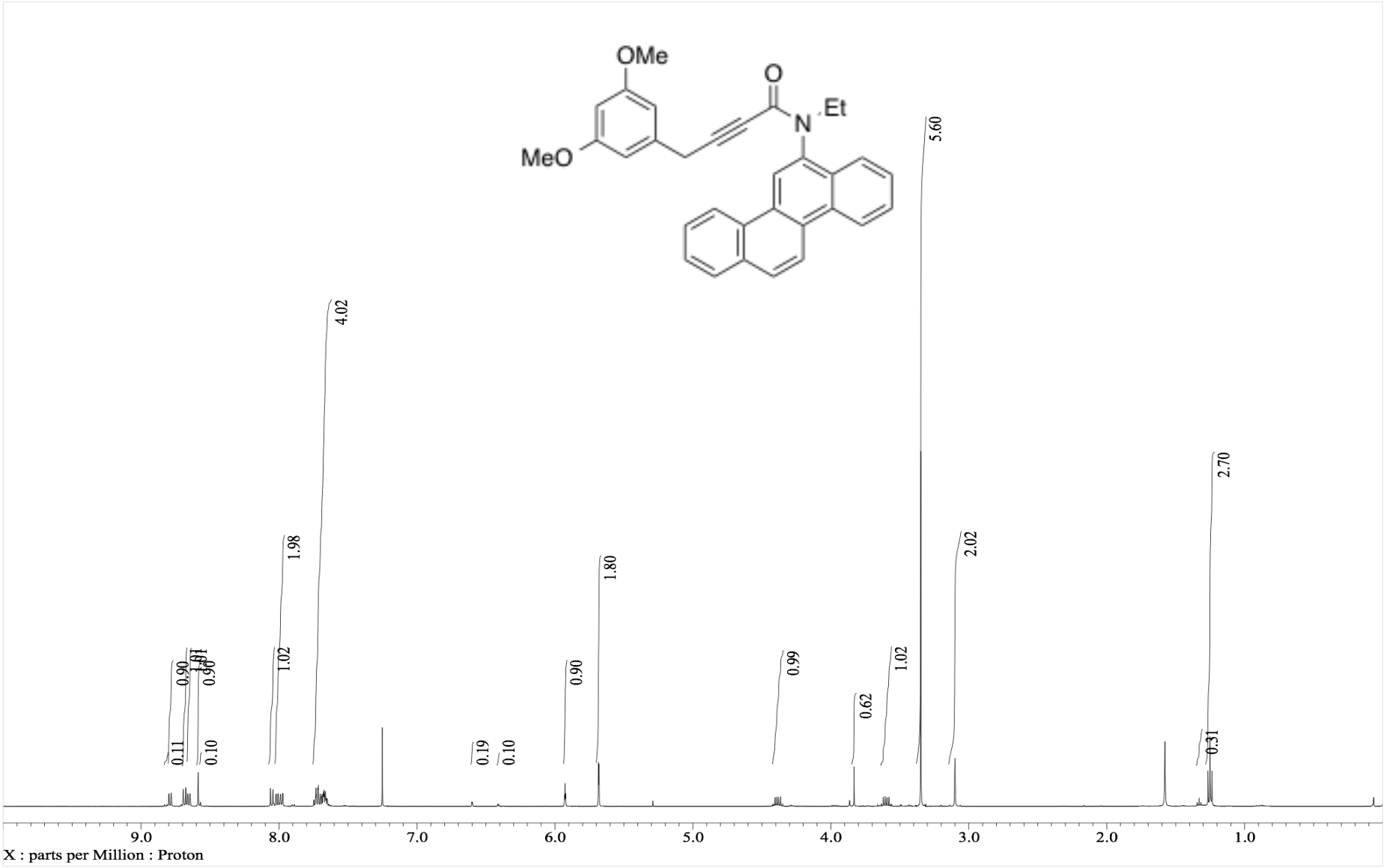

154.587
147.320
146.021
137.611
134.446
130.969
128.938
128.371
127.771
127.146
127.080
126.431
125.329
122.584
120.068
107.860
107.754
100.758
90.022
77.427
77.000
76.901
76.581
43.386
24.420
13.076
O
O
O
N
Et
PPM
200
175
150
125
100
75
50
25
0

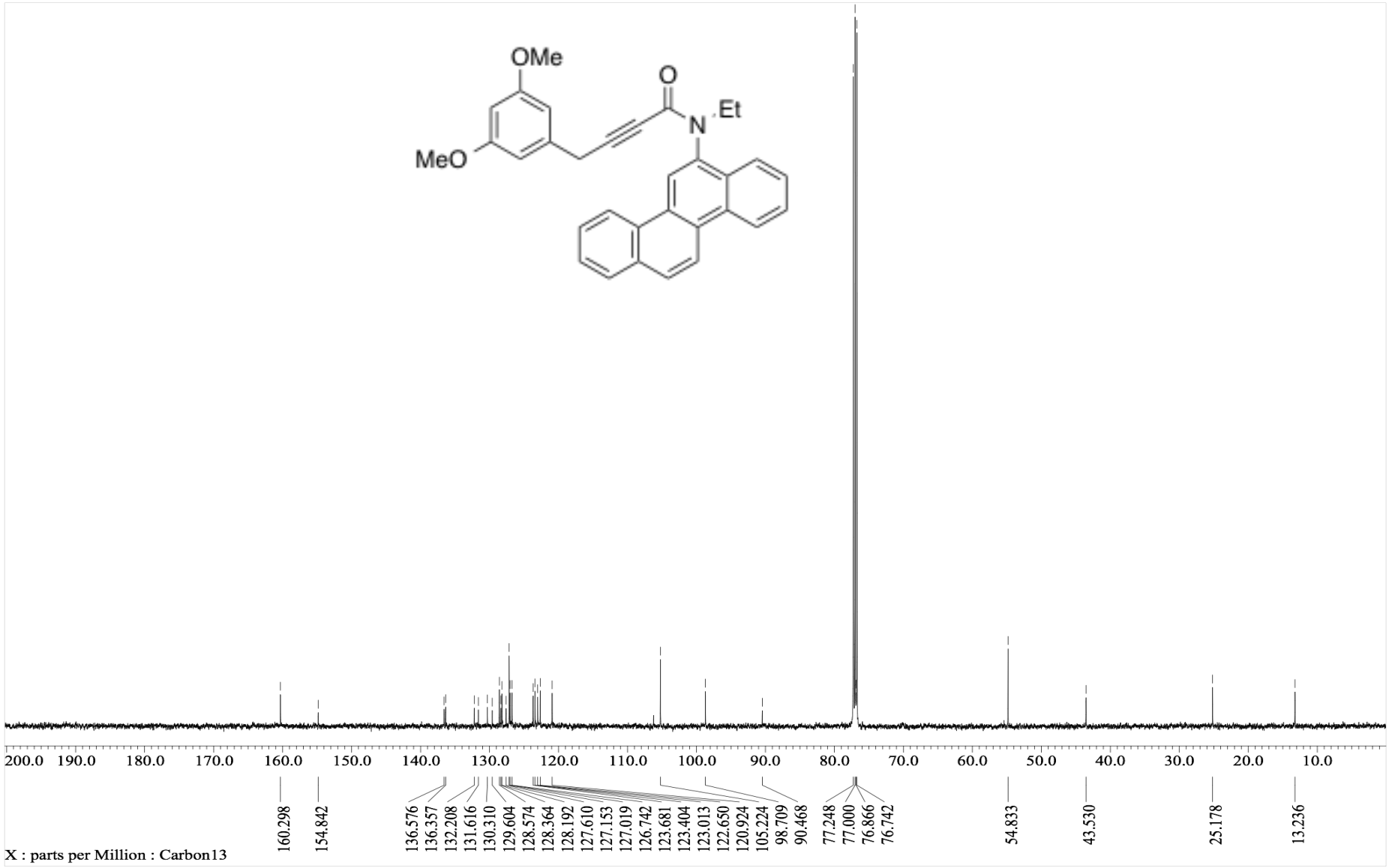
4-(3-Methoxyphenyl)-*N*-ethyl-*N*-(naphthalen-1-yl)but-2-ynamide (1h)



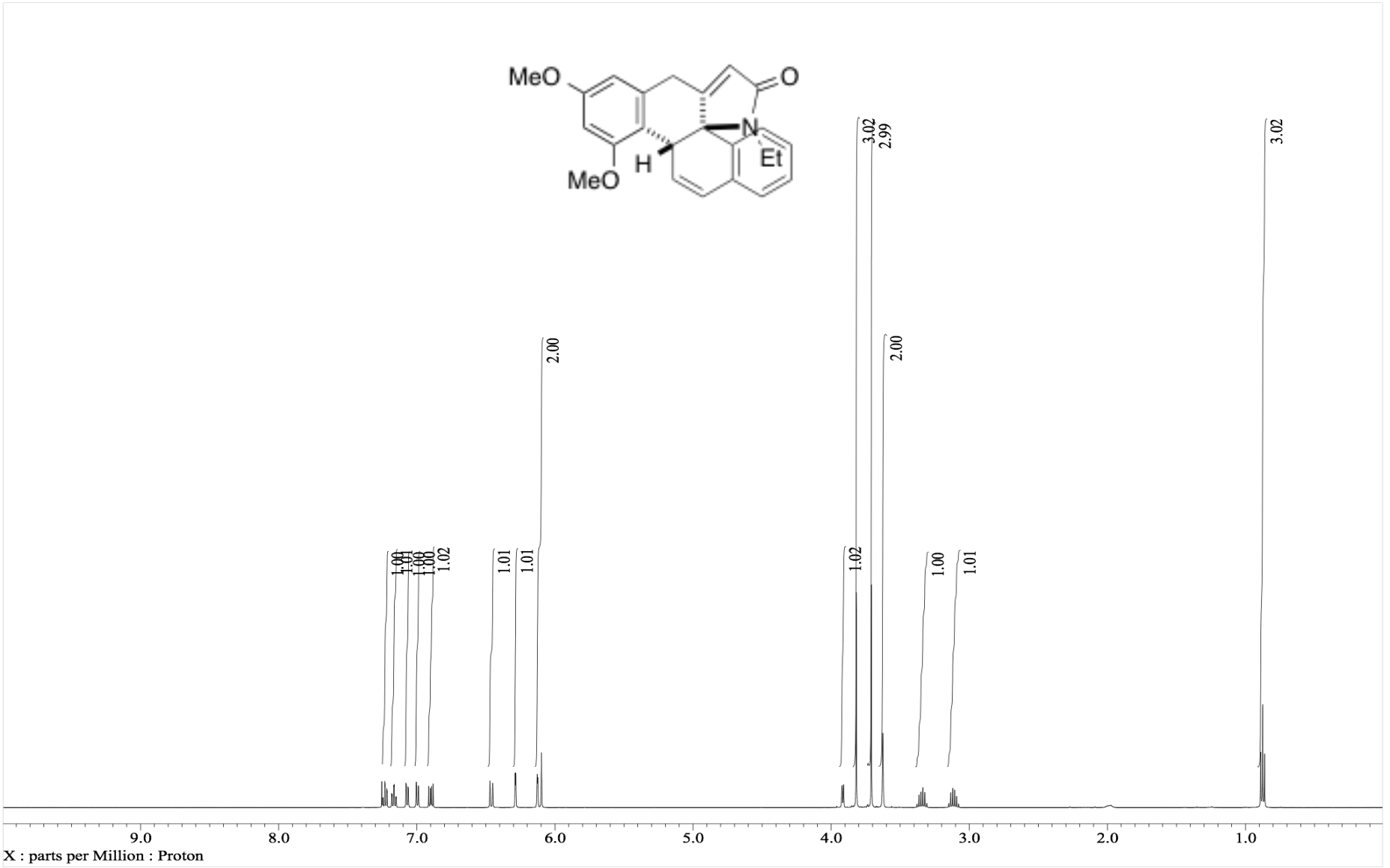

OMe
O
N
Et
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.287
154.632
137.502
135.642
134.440
130.863
129.165
128.850
128.335
127.124
126.409
125.312
122.574
119.436
113.036
111.929
89.953
77.258
77.000
76.866
76.752
54.966
43.396
24.768
13.046
X : parts per Million : Carbon13

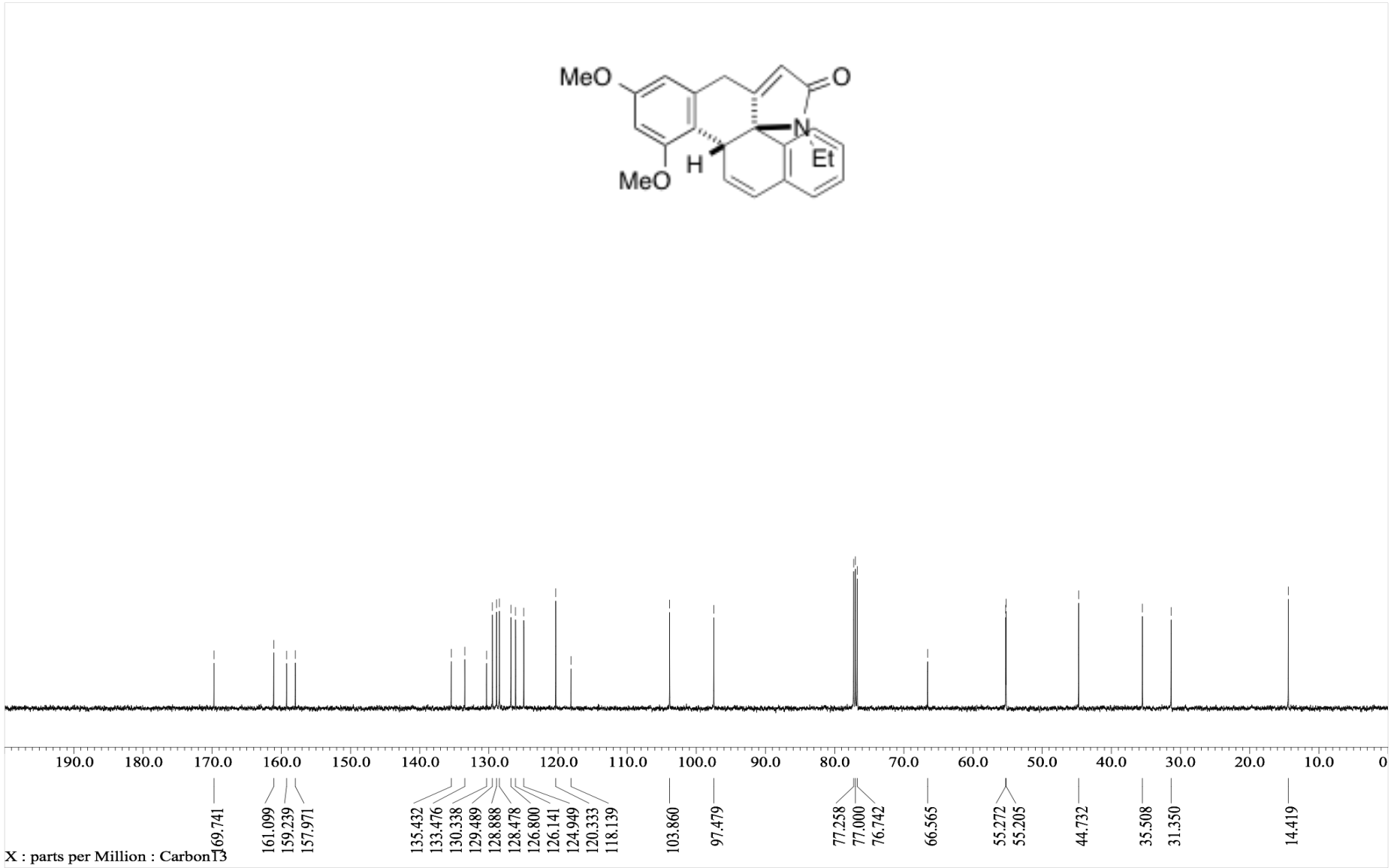
_N_-(Chrysen-6-yl)-4-(3,5-dimethoxyphenyl)-_N_-ethylbut-2-ynamide (1i)



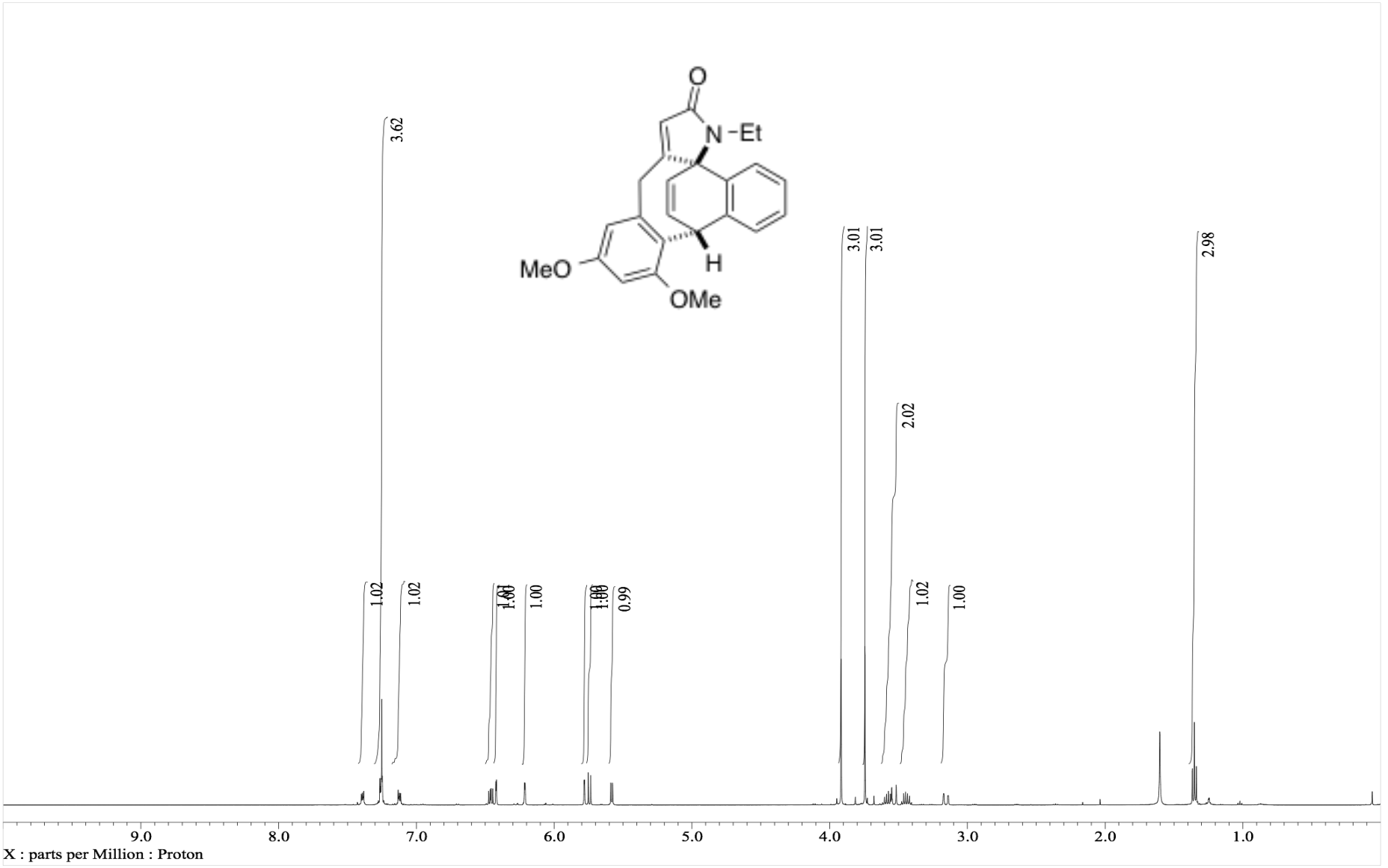

OMe
O
N
Et
MeO
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
160.298
154.842
136.576
136.357
132.208
131.616
130.310
129.604
128.574
128.364
128.192
127.610
127.153
127.019
126.742
123.681
123.404
123.013
122.650
120.924
105.224
98.709
90.468
77.248
77.000
76.866
76.742
54.833
43.530
25.178
13.236
X : parts per Million : Carbon13

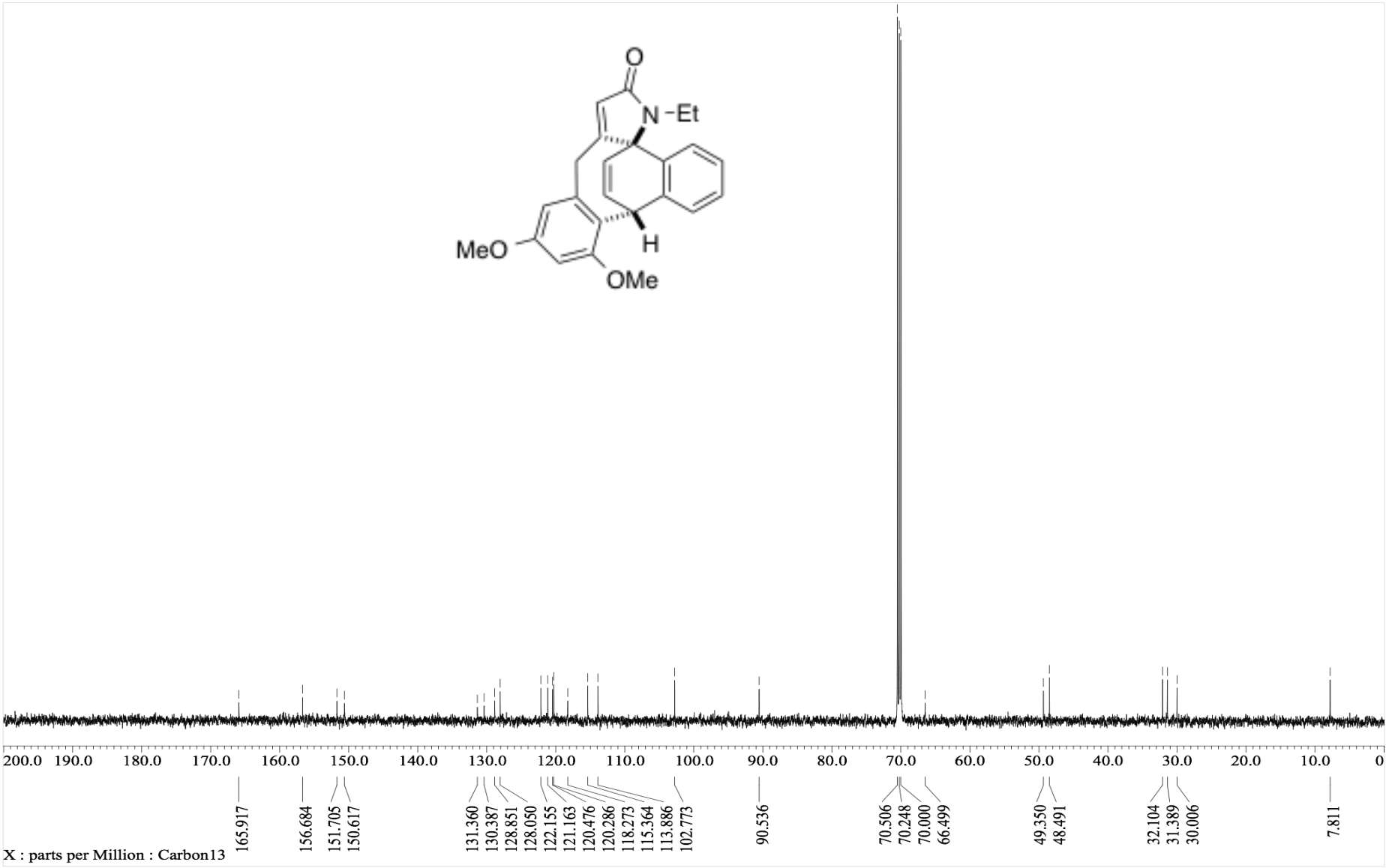
5-Ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2a)



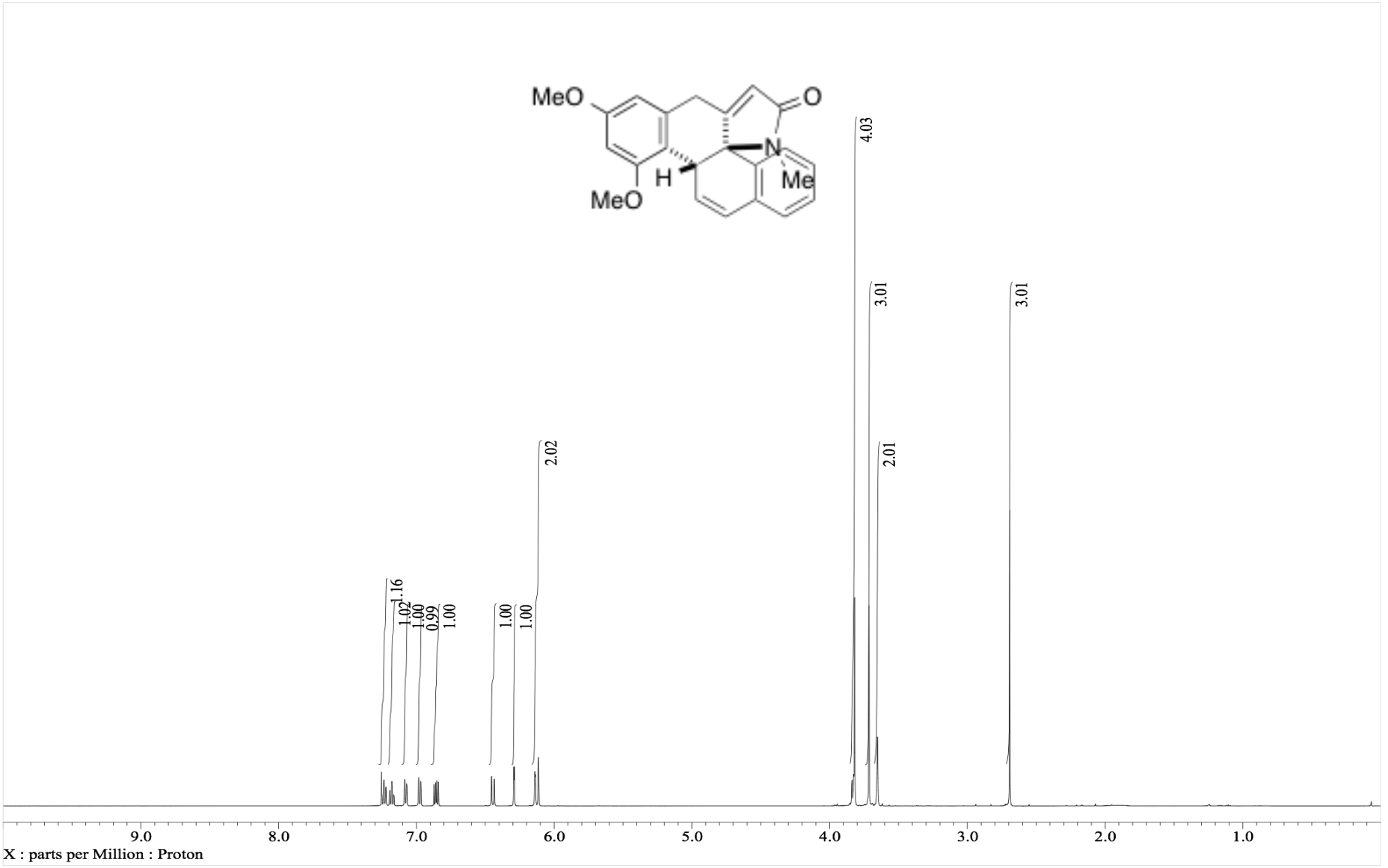

MeO
O
N
Et
H
MeO
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.741
161.099
159.239
157.971
135.432
133.476
130.338
129.489
128.888
128.478
126.800
126.141
124.949
120.333
118.139
103.860
97.479
77.258
77.000
76.742
66.565
55.272
55.205
44.732
35.508
31.350
14.419
X : parts per Million : Carbon13

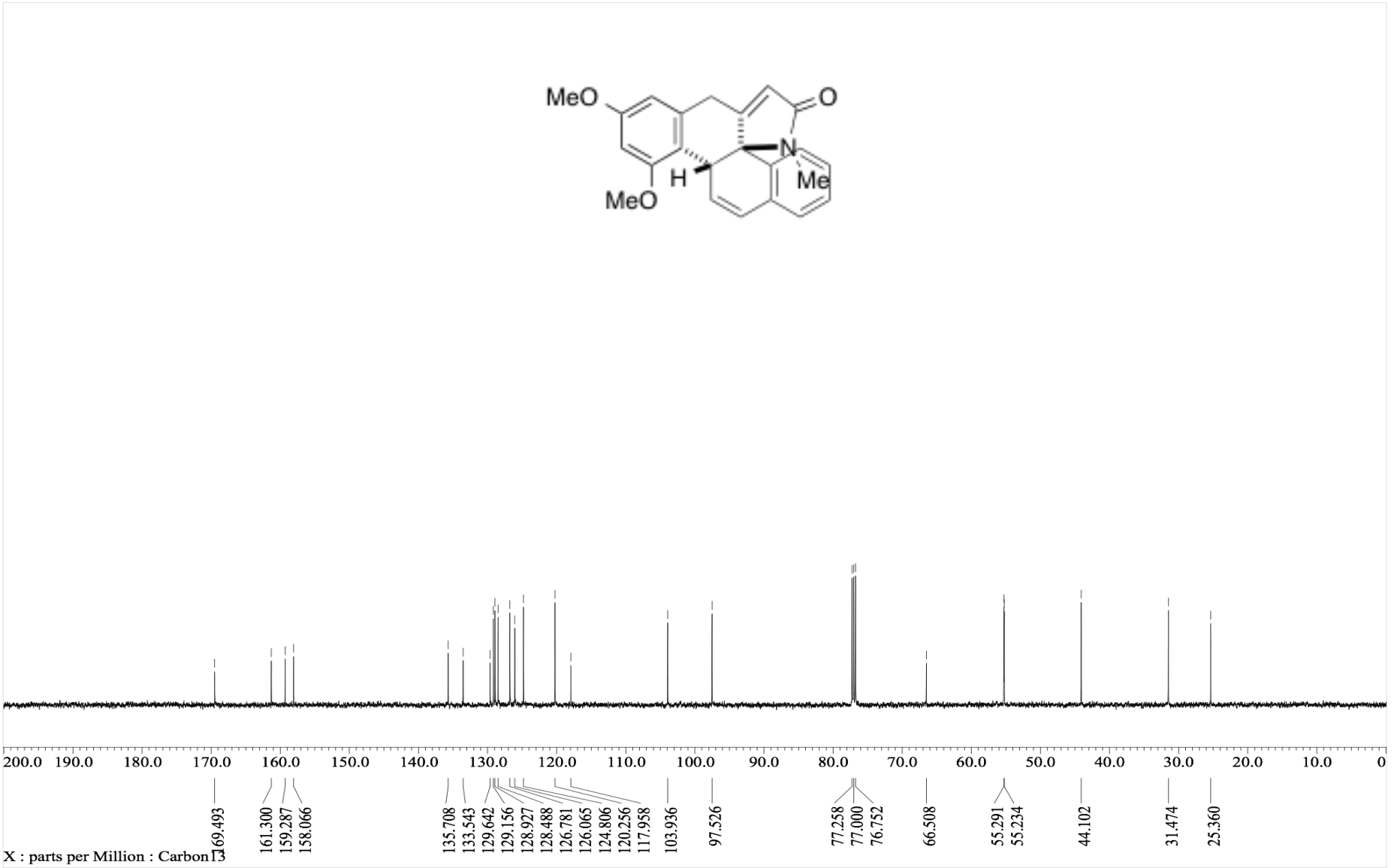
1-Ethyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one (3a)



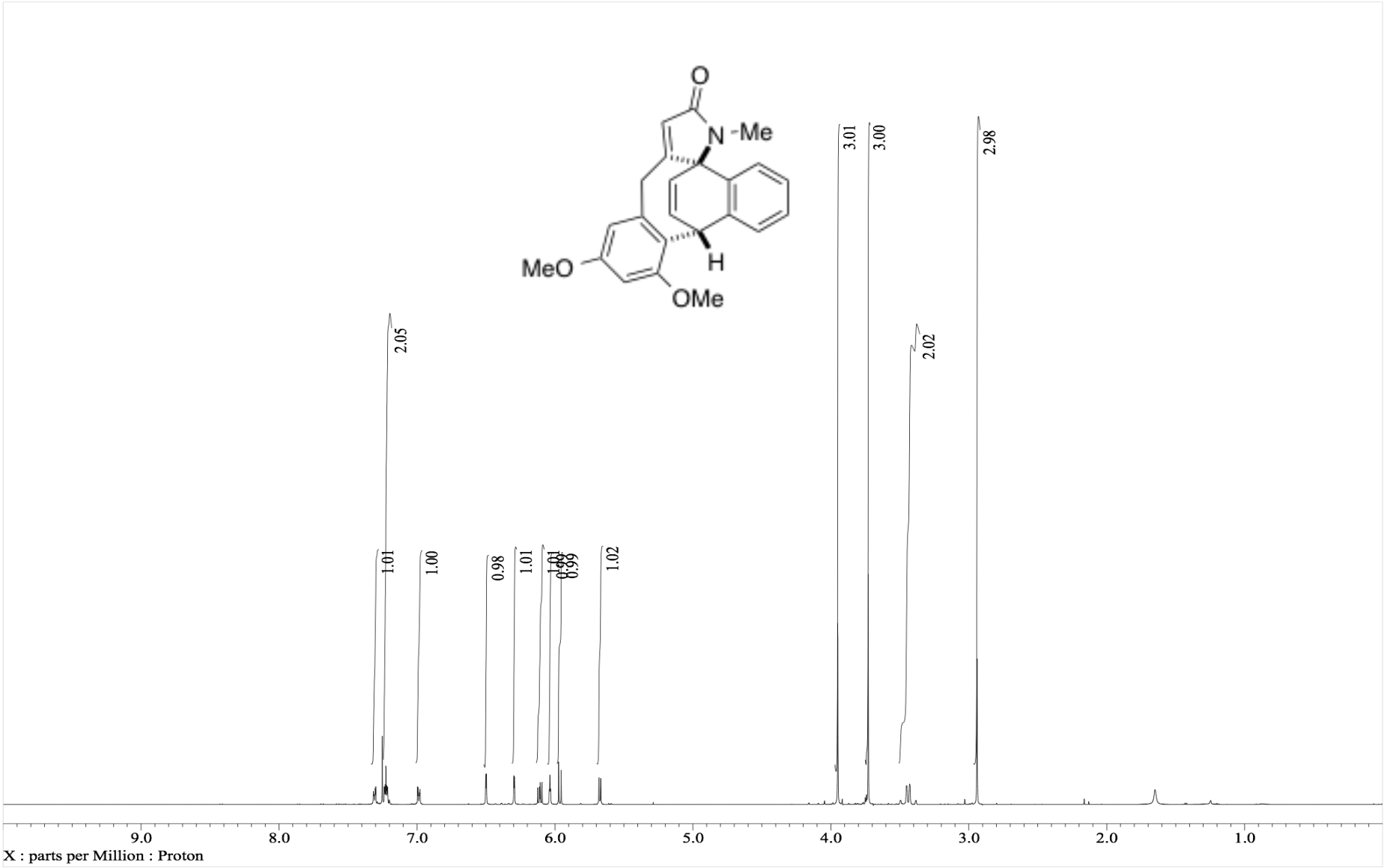

O
N
Et
MeO
OMe
H
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.917
156.684
151.705
150.617
131.360
130.387
128.851
128.050
122.155
121.163
120.476
120.286
118.273
115.364
113.886
102.773
90.536
70.506
70.248
70.000
66.499
49.350
48.491
32.104
31.389
30.006
7.811
X : parts per Million : Carbon13

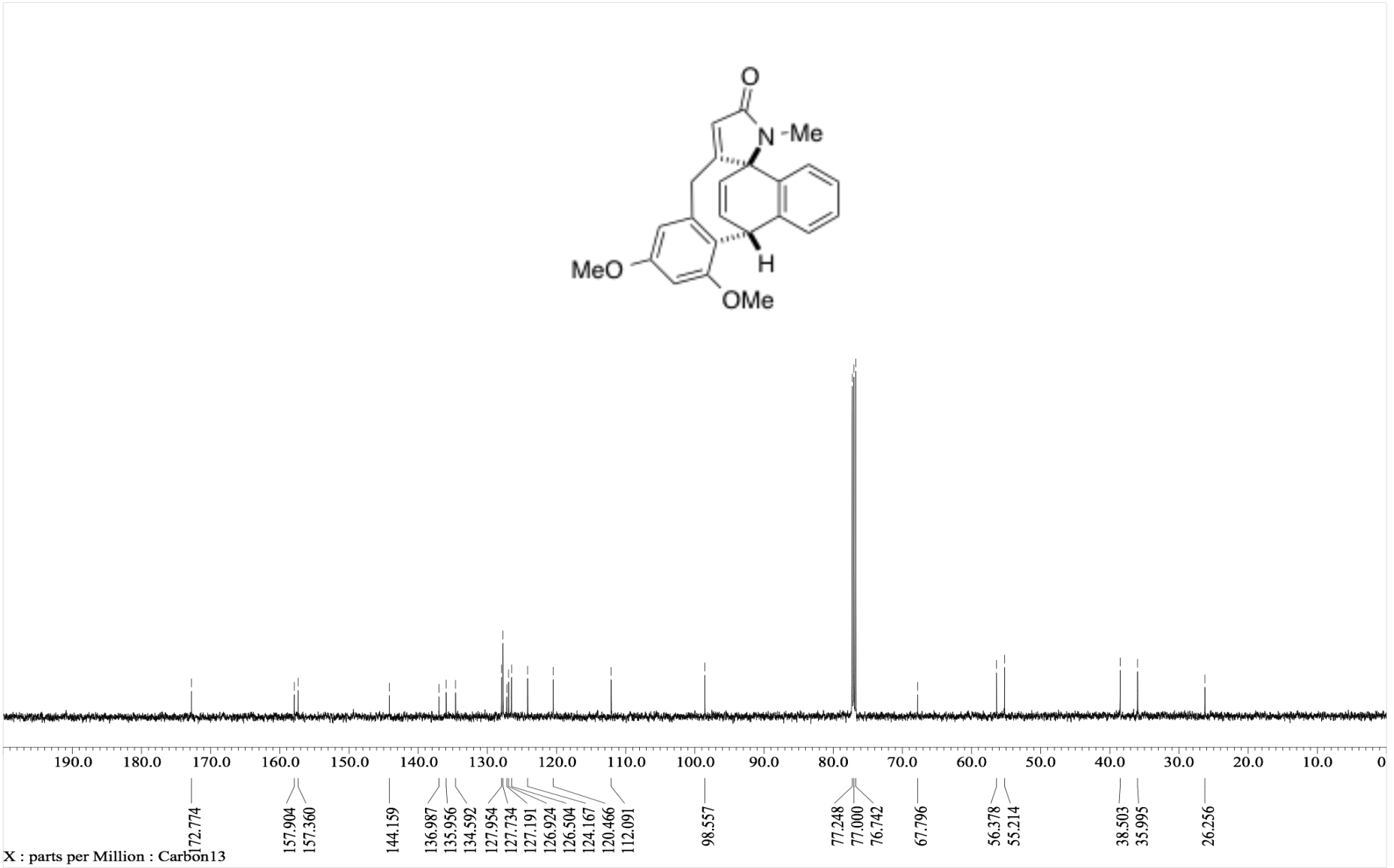
10,12-Dimethoxy-5-methyl-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2b)



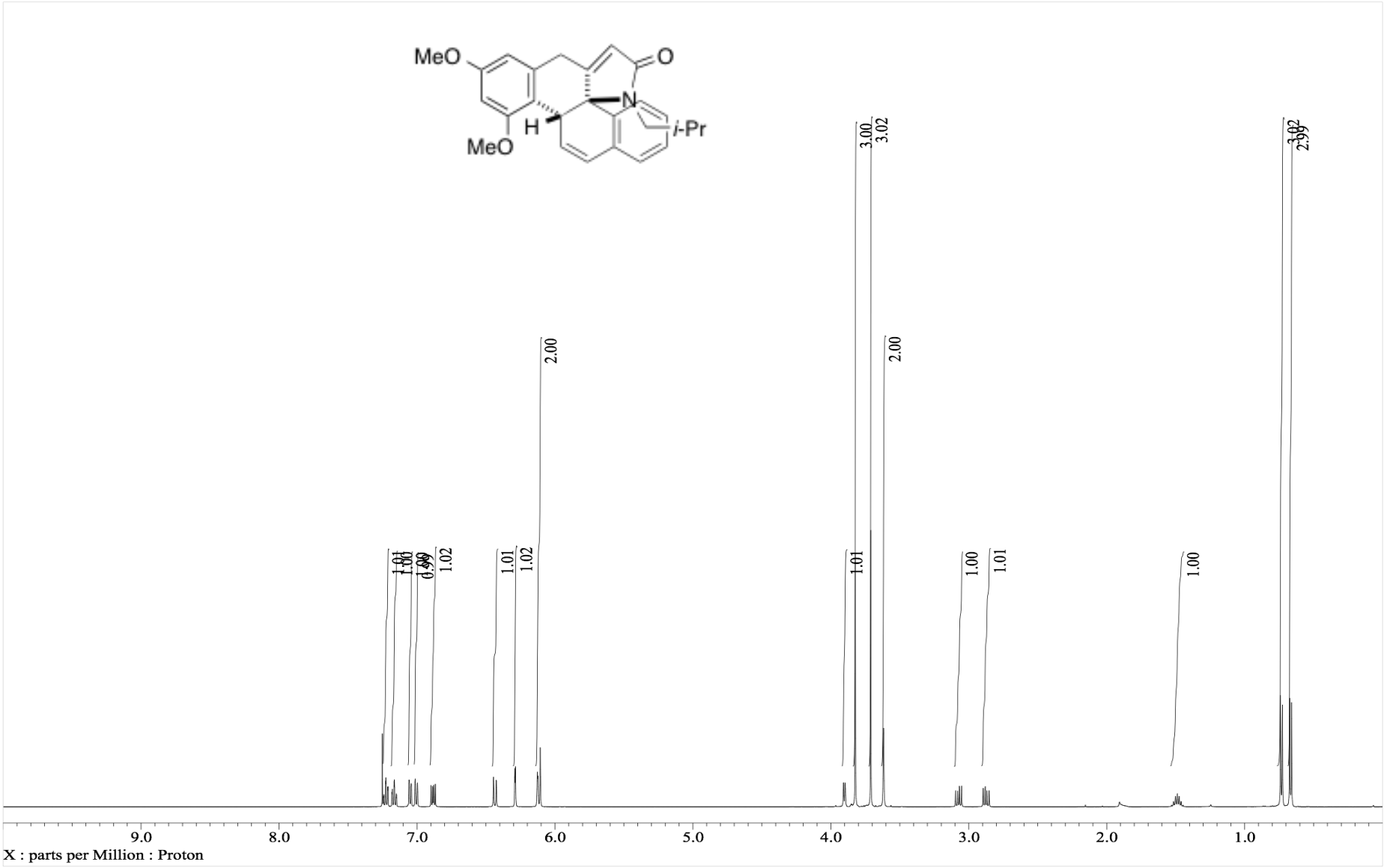

MeO
O
N
H
Me
MeO
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
169.493
161.300
159.287
158.066
135.708
133.543
129.642
129.156
128.927
128.488
126.781
126.065
124.806
120.256
117.958
103.936
97.526
77.258
77.000
76.752
66.508
55.291
55.234
44.102
31.474
25.360
X : parts per Million : Carbon13

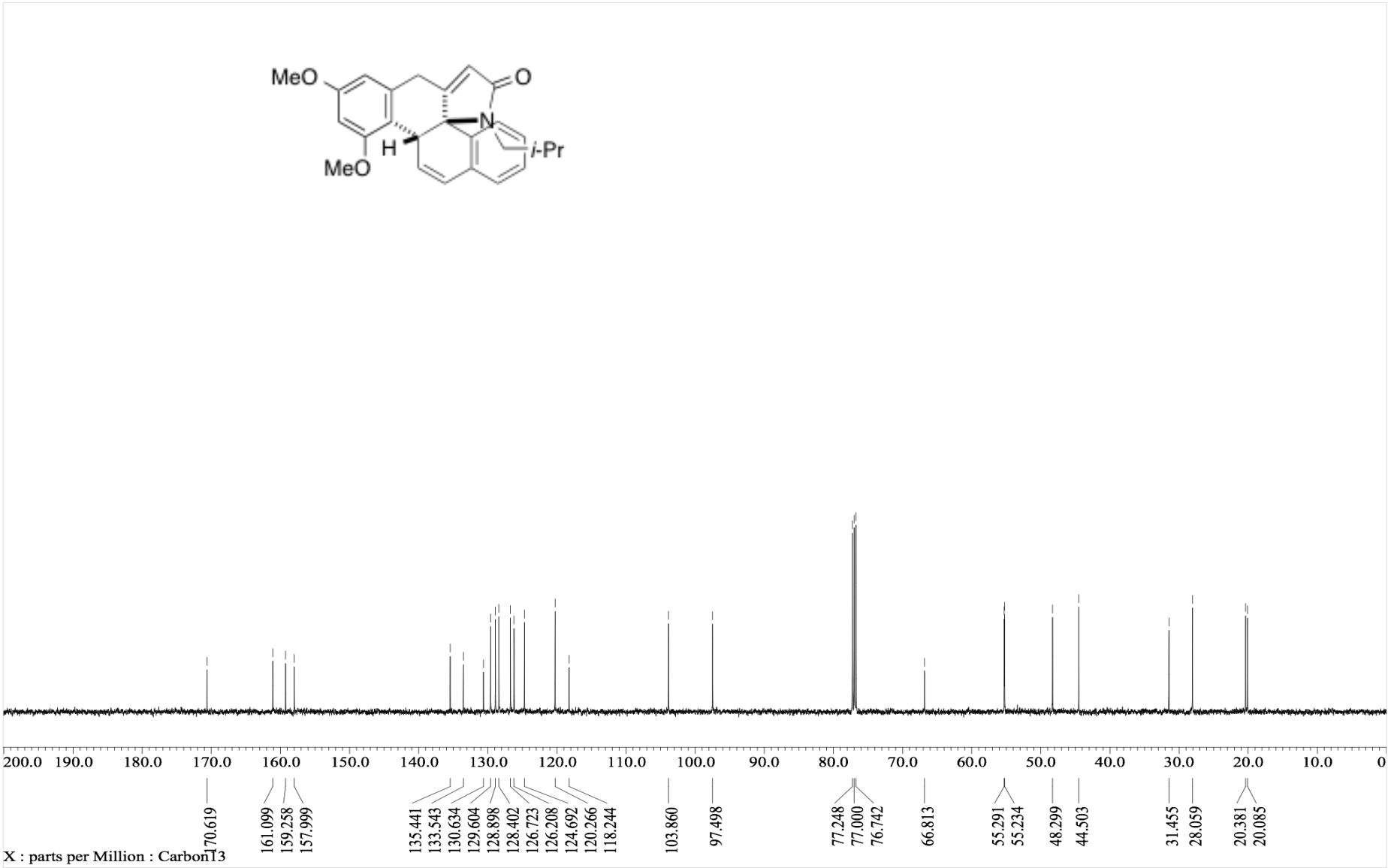
6,8-Dimethoxy-1-methyl-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one (3b)



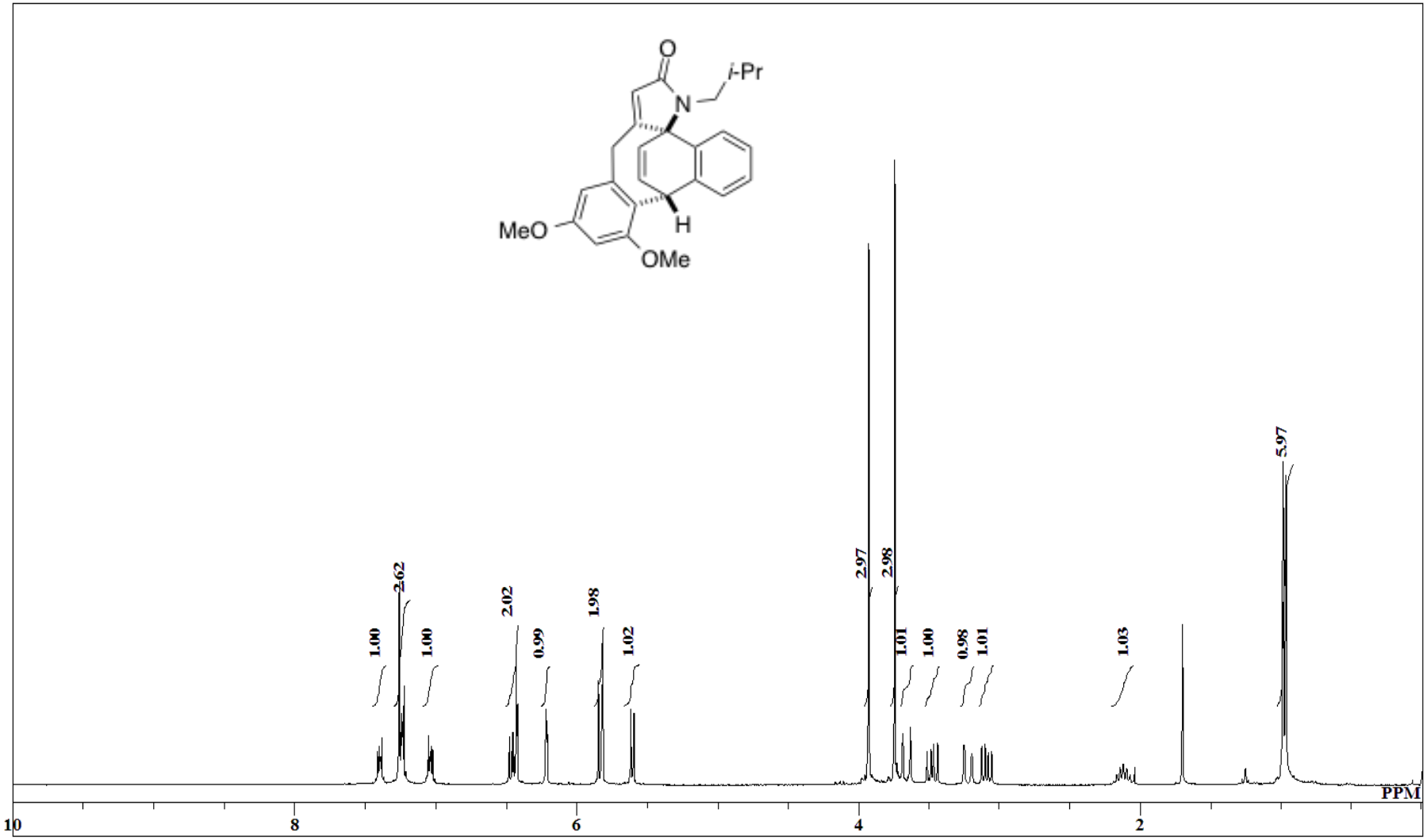

O
N
Me
MeO
H
OMe
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.774
157.904
157.360
144.159
136.987
135.956
134.592
127.954
127.734
127.191
126.924
126.504
124.167
120.466
112.091
98.557
77.248
77.000
76.742
67.796
56.378
55.214
38.503
35.995
26.256
X : parts per Million : Carbon13

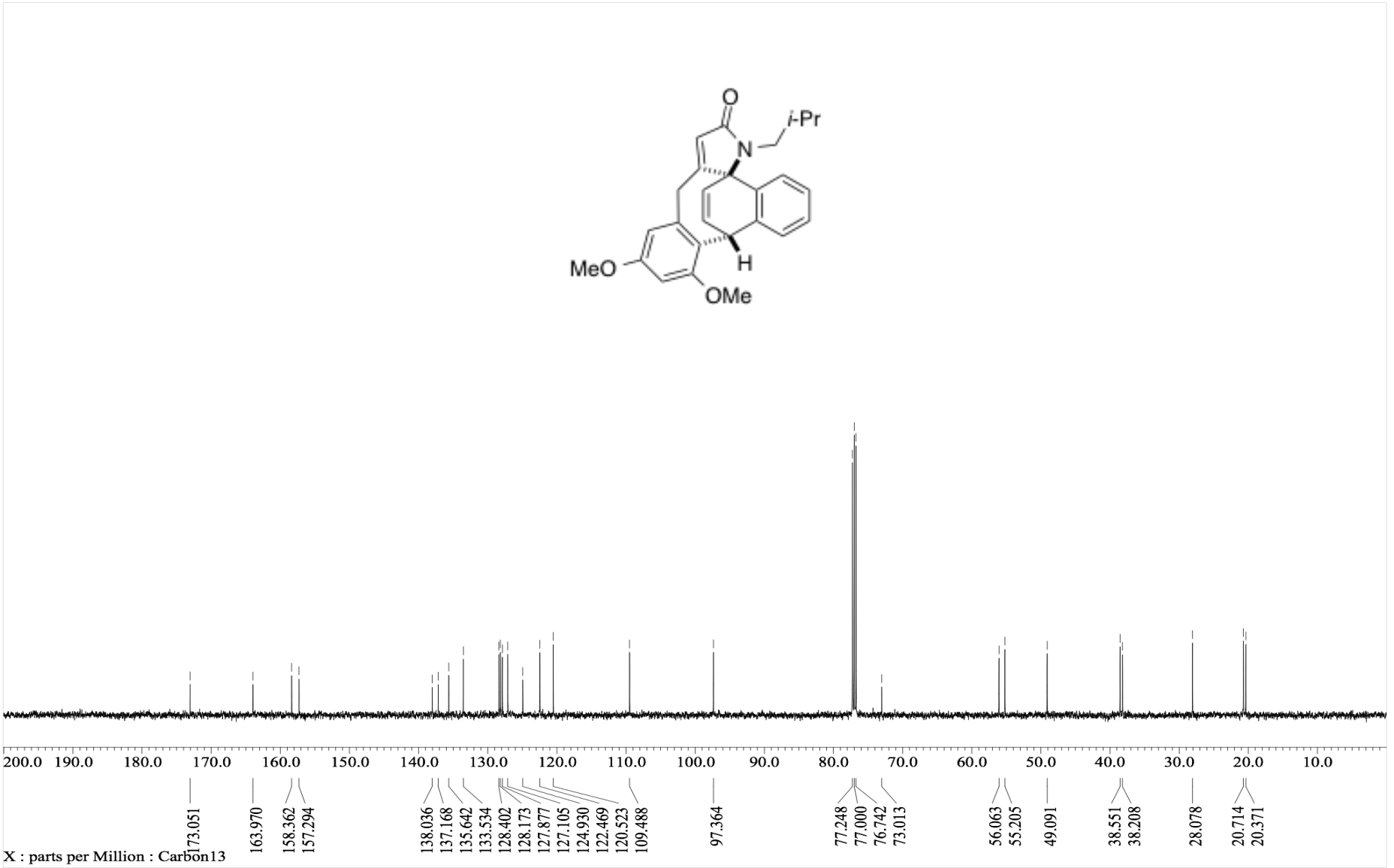
5-Isobutyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2c)



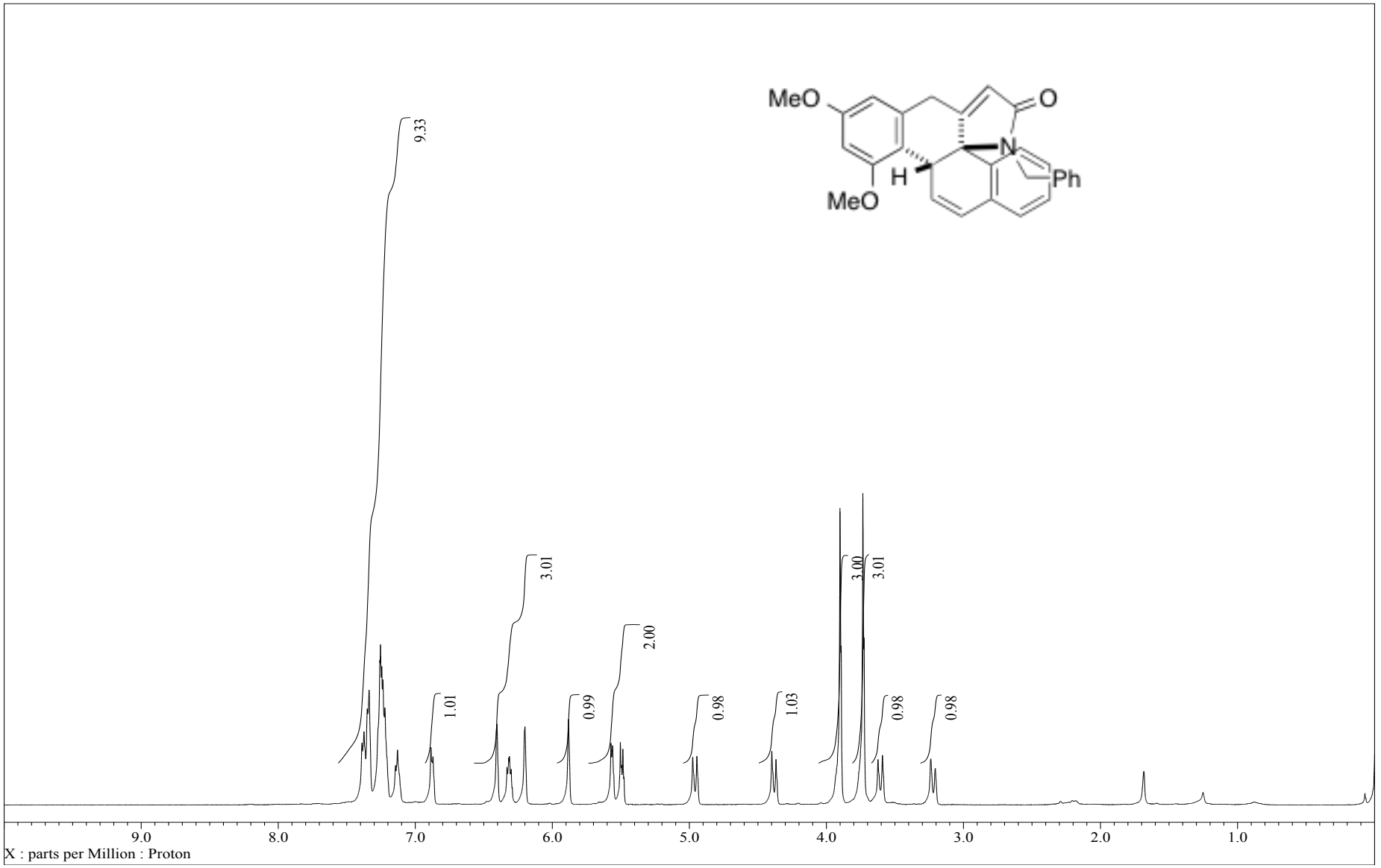

MeO
O
N
H
i-Pr
MeO
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.619
161.099
159.258
157.999
135.441
133.543
130.634
129.604
128.898
128.402
126.723
126.208
124.692
120.266
118.244
103.860
97.498
77.248
77.000
76.742
66.813
55.291
55.234
48.299
44.503
31.455
28.059
20.381
20.085
X : parts per Million : Carbon13

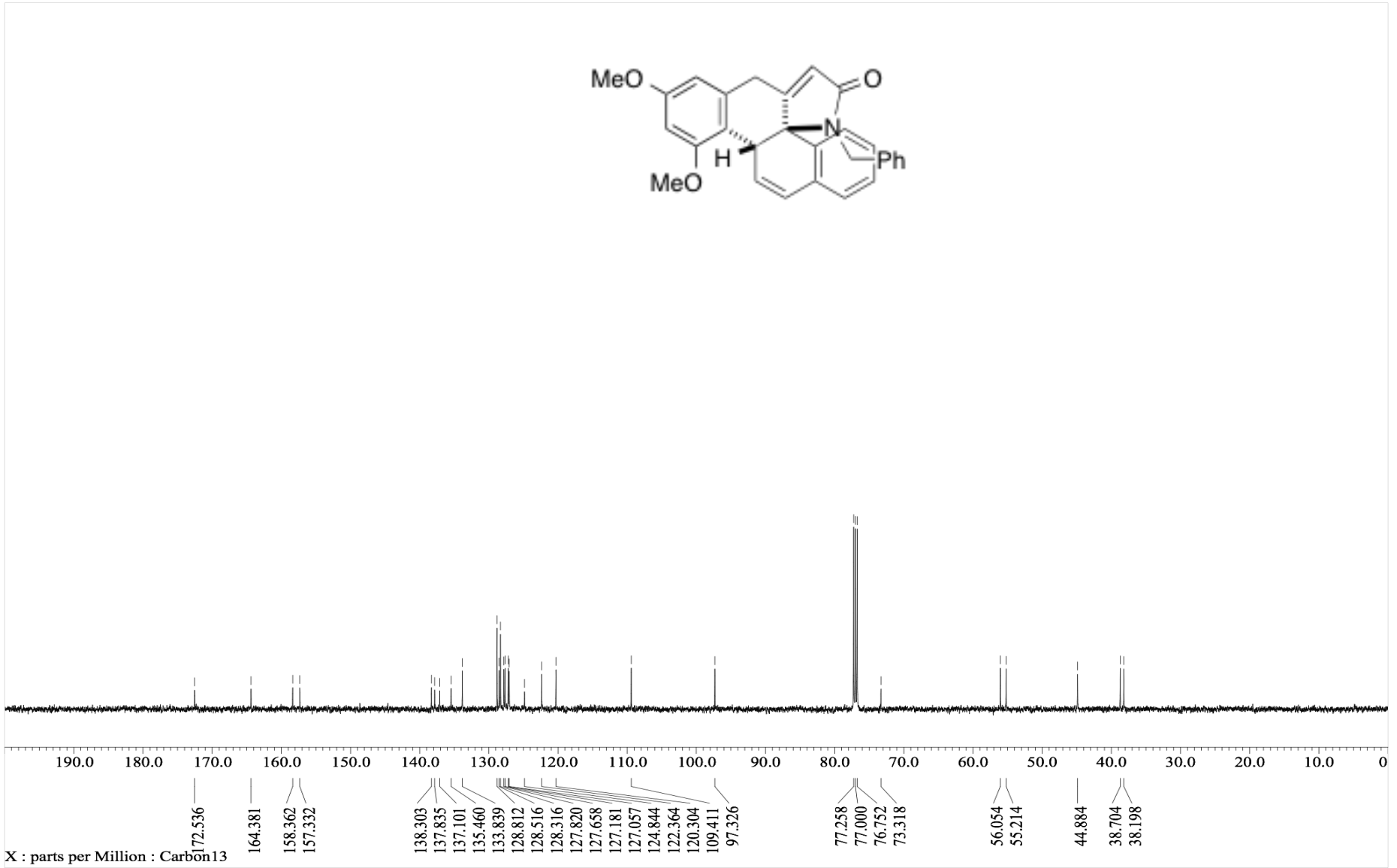
1-Isobutyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenz[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one (3c)



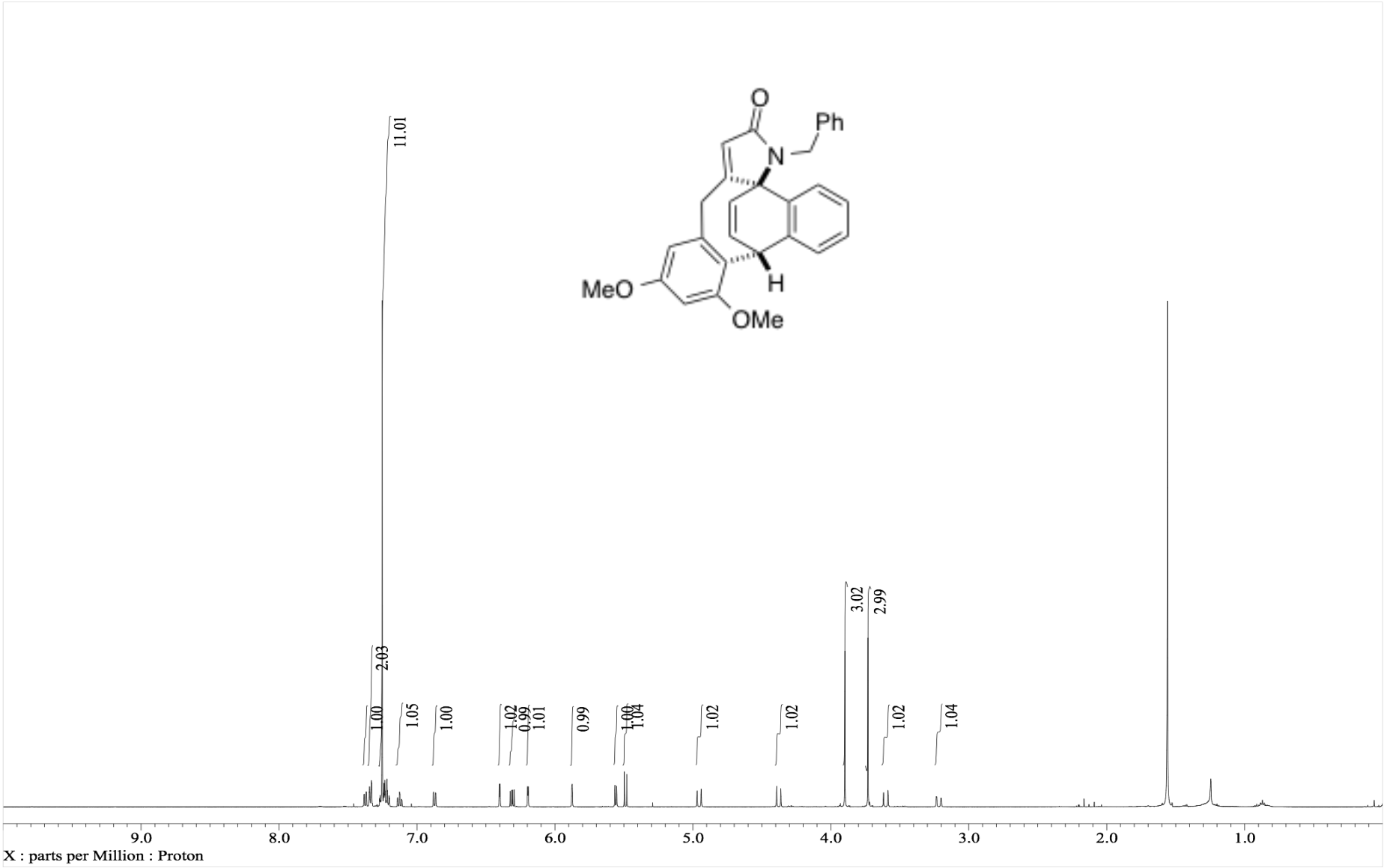

O
i-Pr
N
MeO
H
OMe
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
173.051
163.970
158.362
157.294
138.036
137.168
135.642
133.534
128.402
128.173
127.877
127.105
124.930
122.469
120.523
109.488
97.364
77.248
77.000
76.742
73.013
56.063
55.205
49.091
38.551
38.208
28.078
20.714
20.371
X : parts per Million : Carbon13

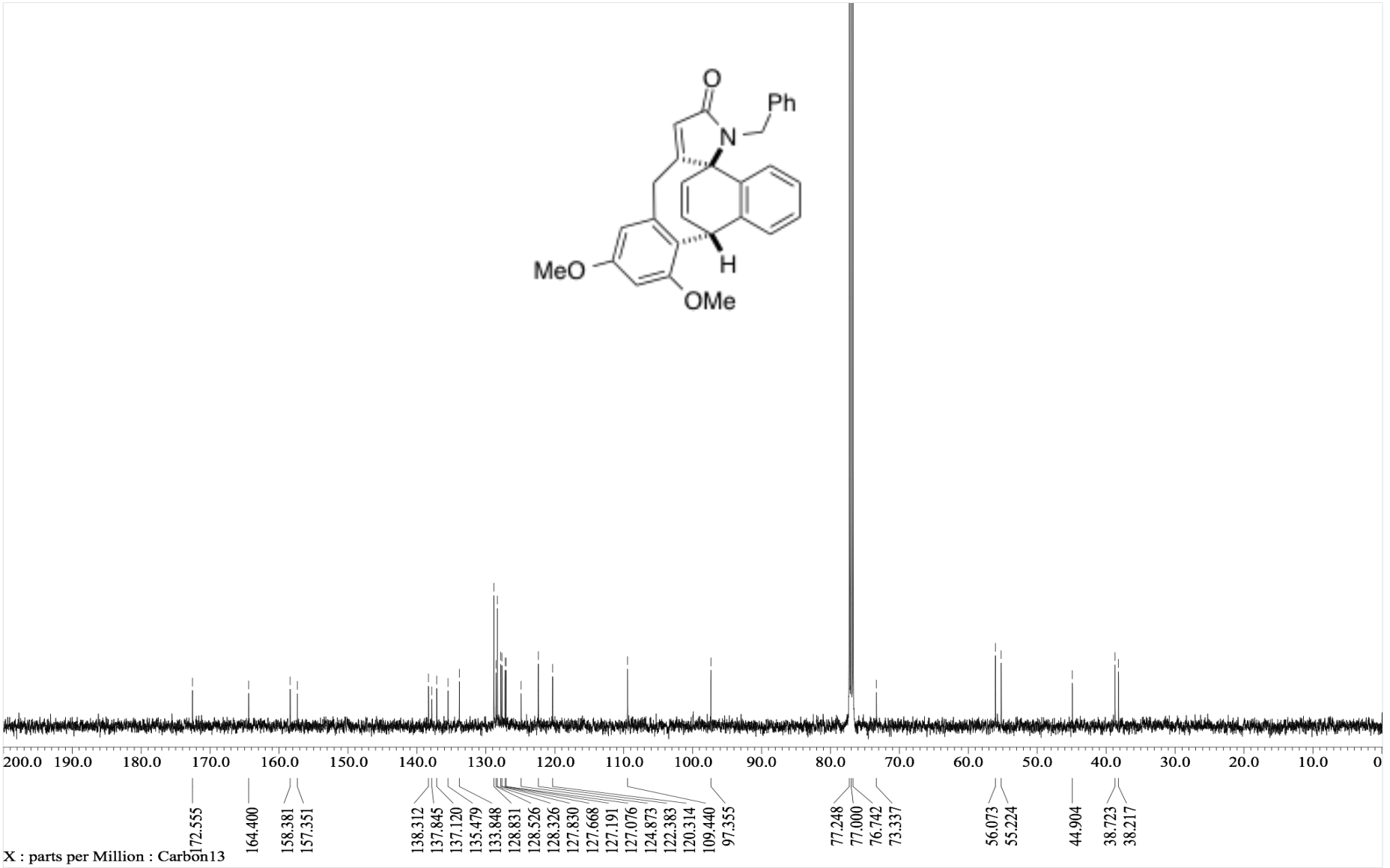
5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2d)



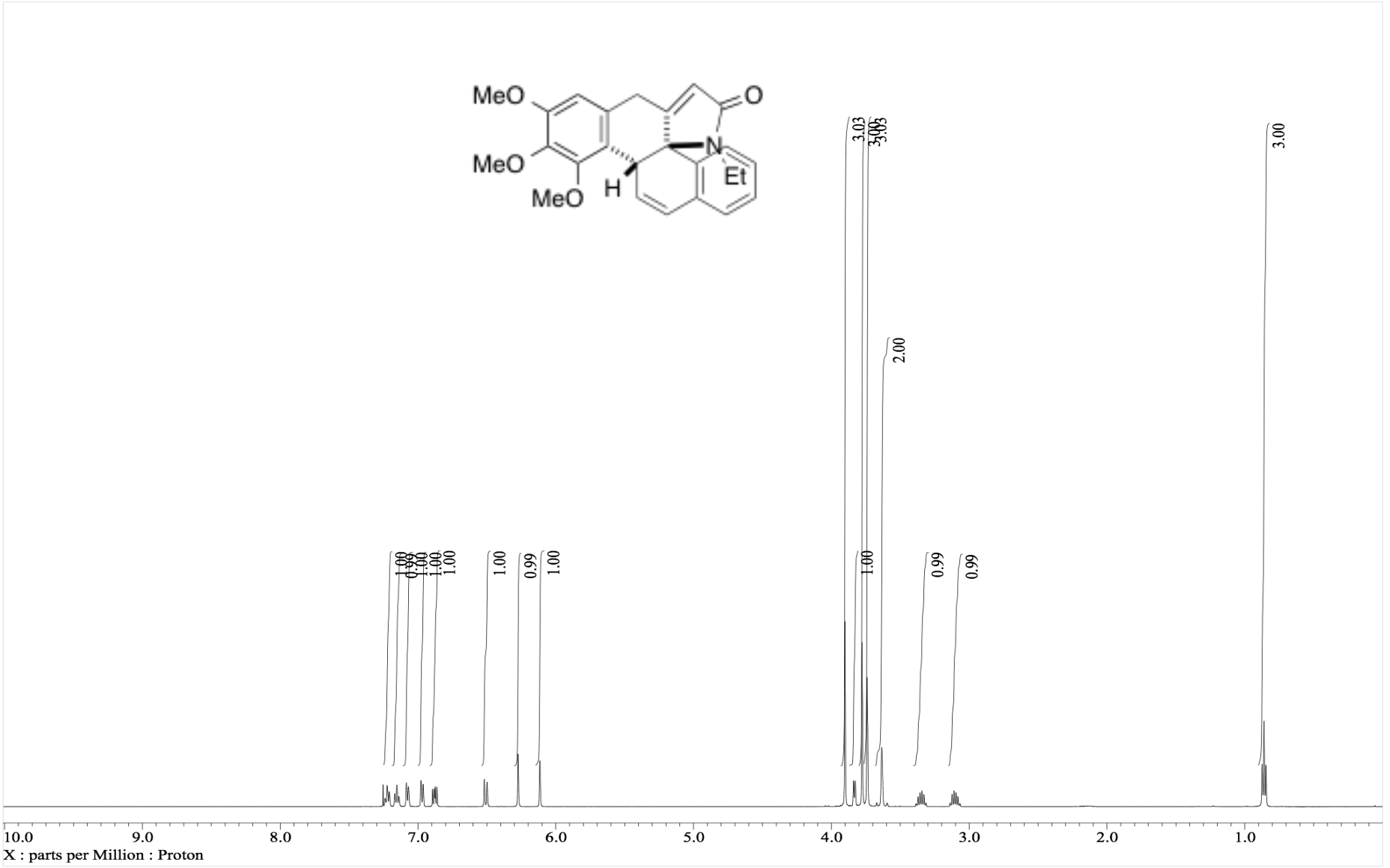

MeO
O
N
H
Ph
MeO
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.536
164.381
158.362
157.332
138.303
137.835
137.101
135.460
133.839
128.812
128.516
128.316
127.820
127.658
127.181
127.057
124.844
122.364
120.304
109.411
97.326
77.258
77.000
76.752
73.318
56.054
55.214
44.884
38.704
38.198
X : parts per Million : Carbon13

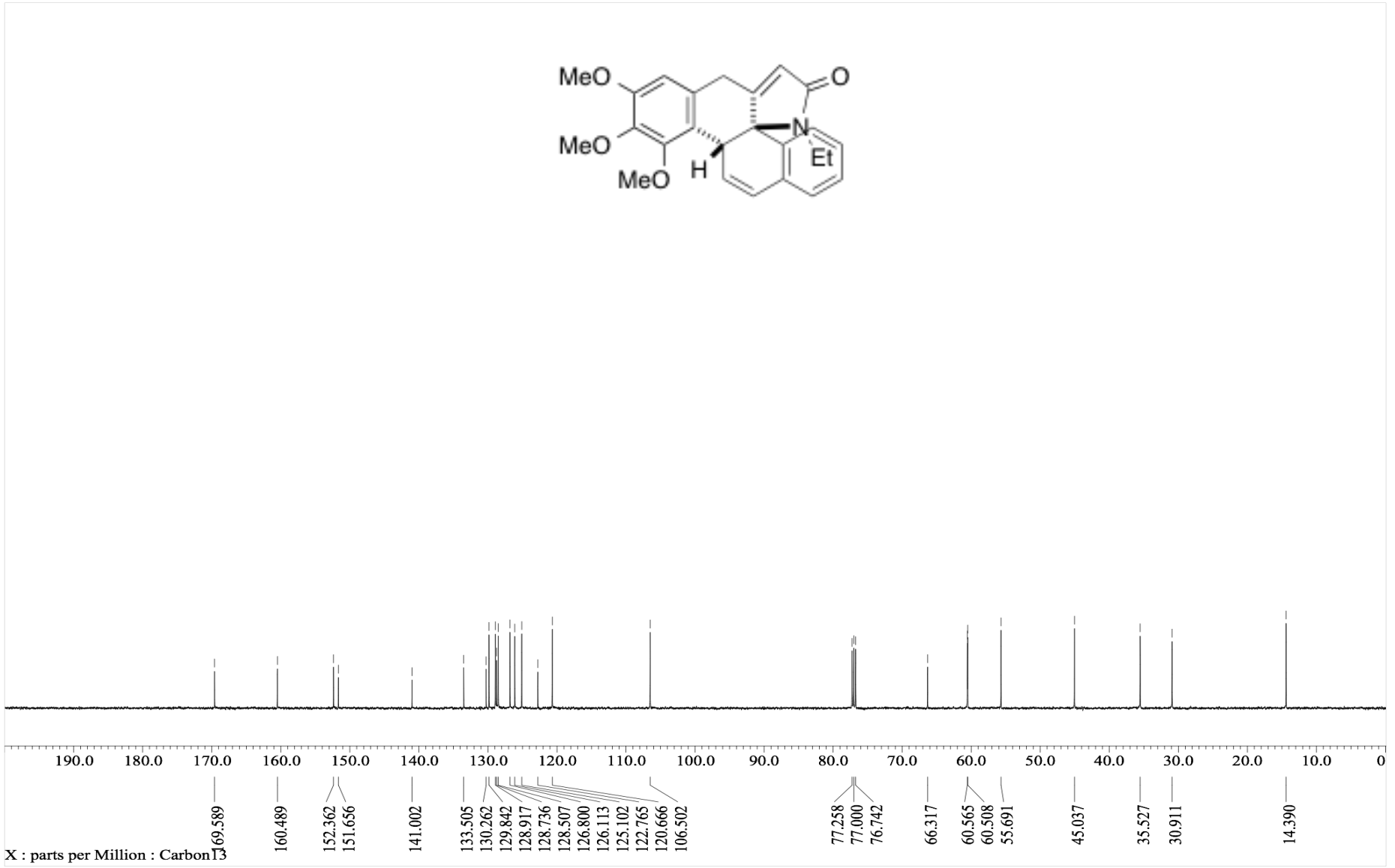
1-Benzyl-6,8-dimethoxy-4,9-dihydro-9,13b-ethenodibenzo[4,5:7,8]cycloocta[1,2-*b*]pyrrol-2(1*H*)-one (3d)



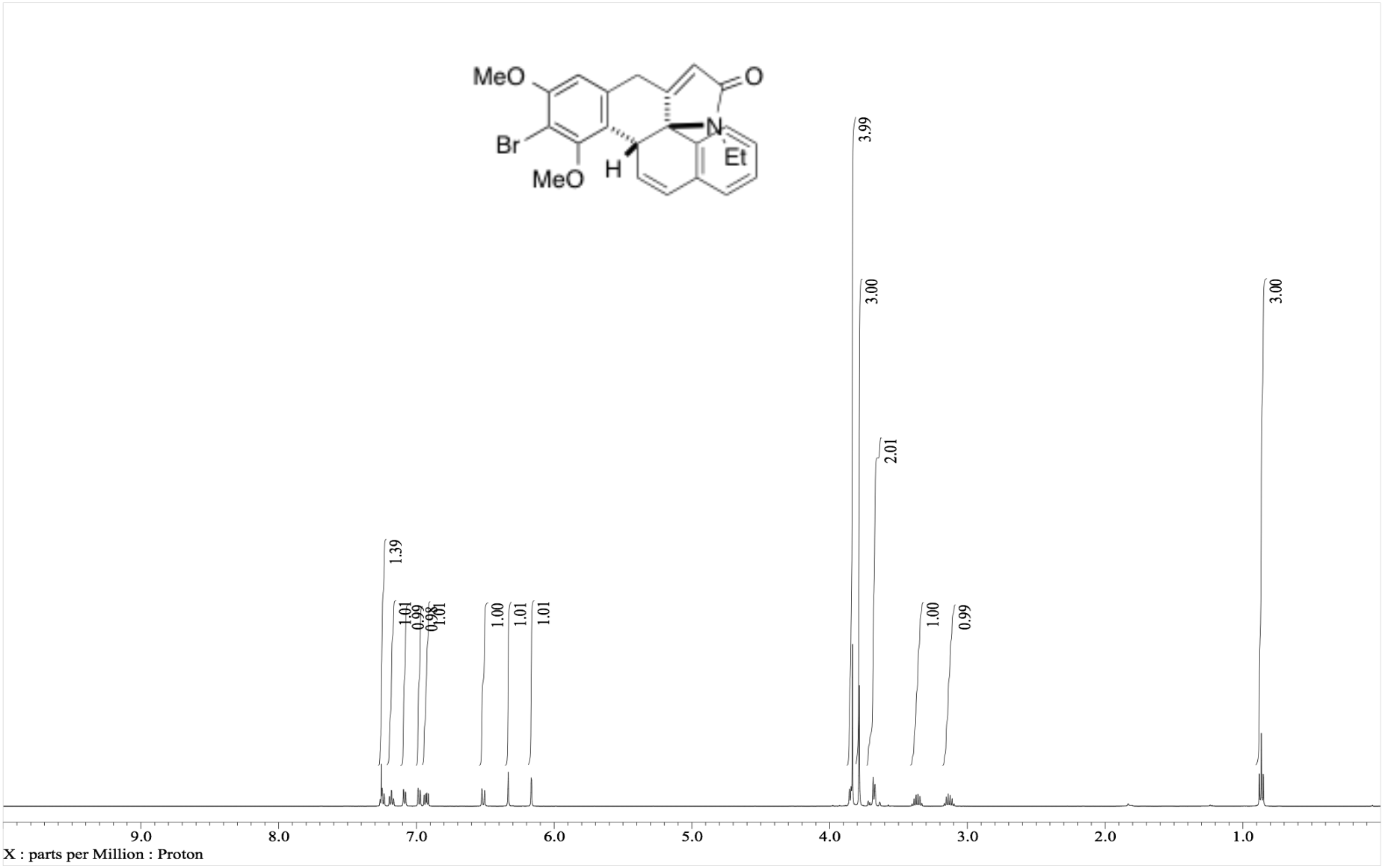

O
Ph
N
MeO
H
OMe
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.555
164.400
158.381
157.351
138.312
137.845
137.120
135.479
133.848
128.831
128.526
128.326
127.830
127.668
127.191
127.076
124.873
122.383
120.314
109.440
97.355
77.248
77.000
76.742
73.337
56.073
55.224
44.904
38.723
38.217
X : parts per Million : Carbon13

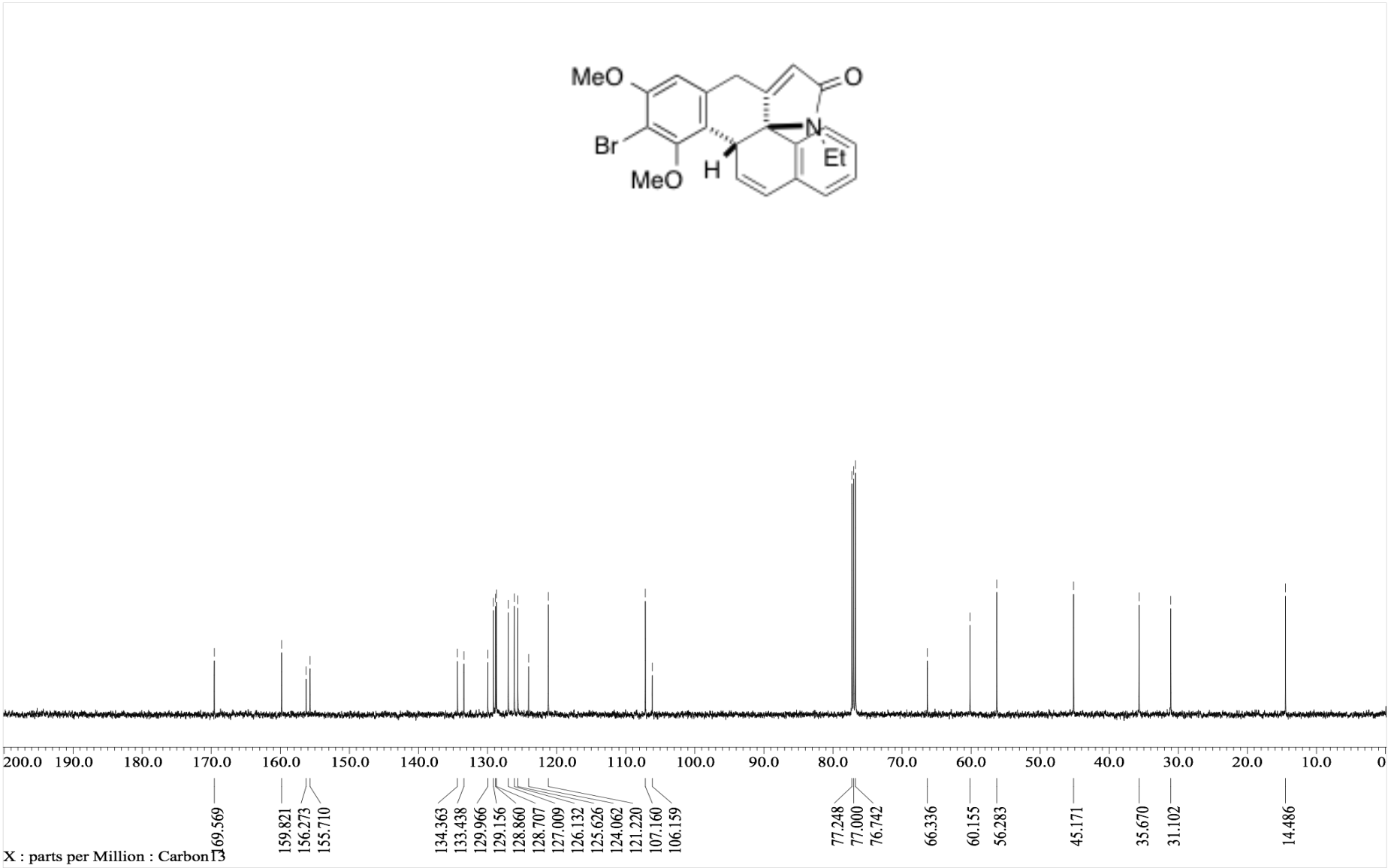
5-Ethyl-10,11,12-trimethoxy-8,12b-dihydrobenzo[f]naphtho[2,1-h]indol-6(5H)-one (2e)



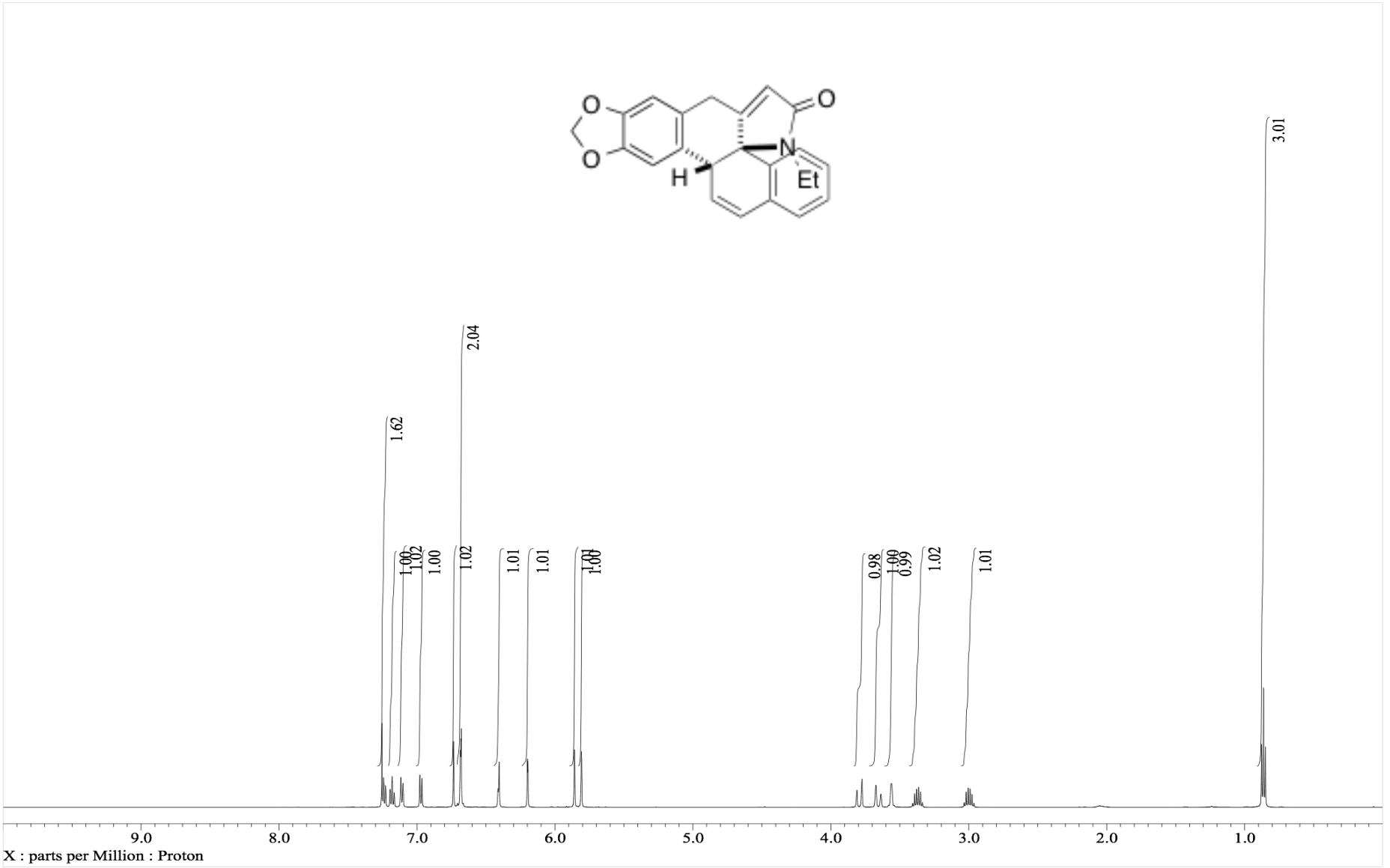

MeO
MeO
MeO
H
N
Et
O
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.589
160.489
152.362
151.656
141.002
133.505
130.262
129.842
128.917
128.736
128.507
126.800
126.113
125.102
122.765
120.666
106.502
77.258
77.000
76.742
66.317
60.565
60.508
55.691
45.037
35.527
30.911
14.390
X : parts per Million : Carbon13

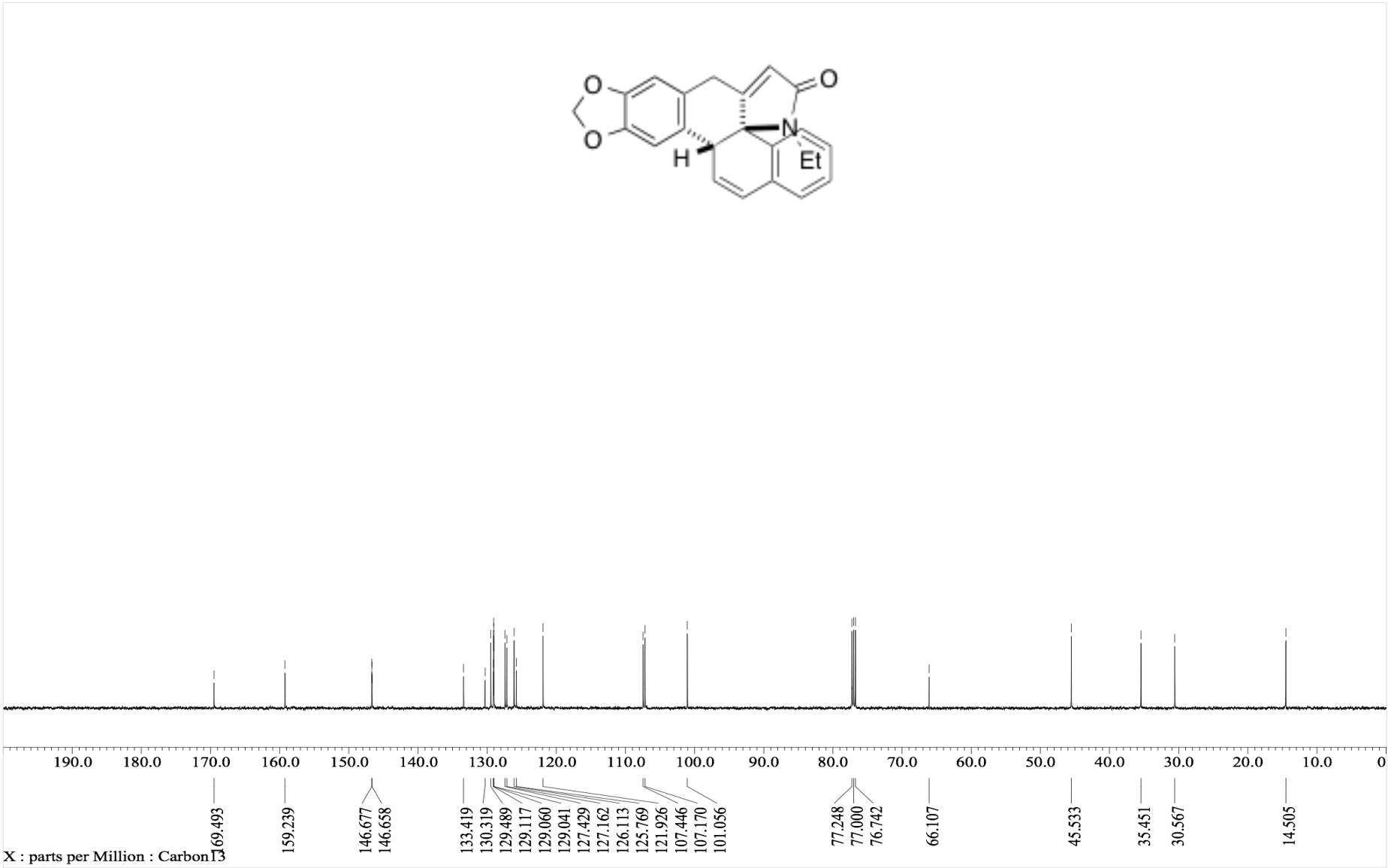
(4b*S*,12b*R*)-(+)-11-bromo-5-ethyl-10,12-dimethoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one [(4b*S*,12b*R*)-(+)-2f]



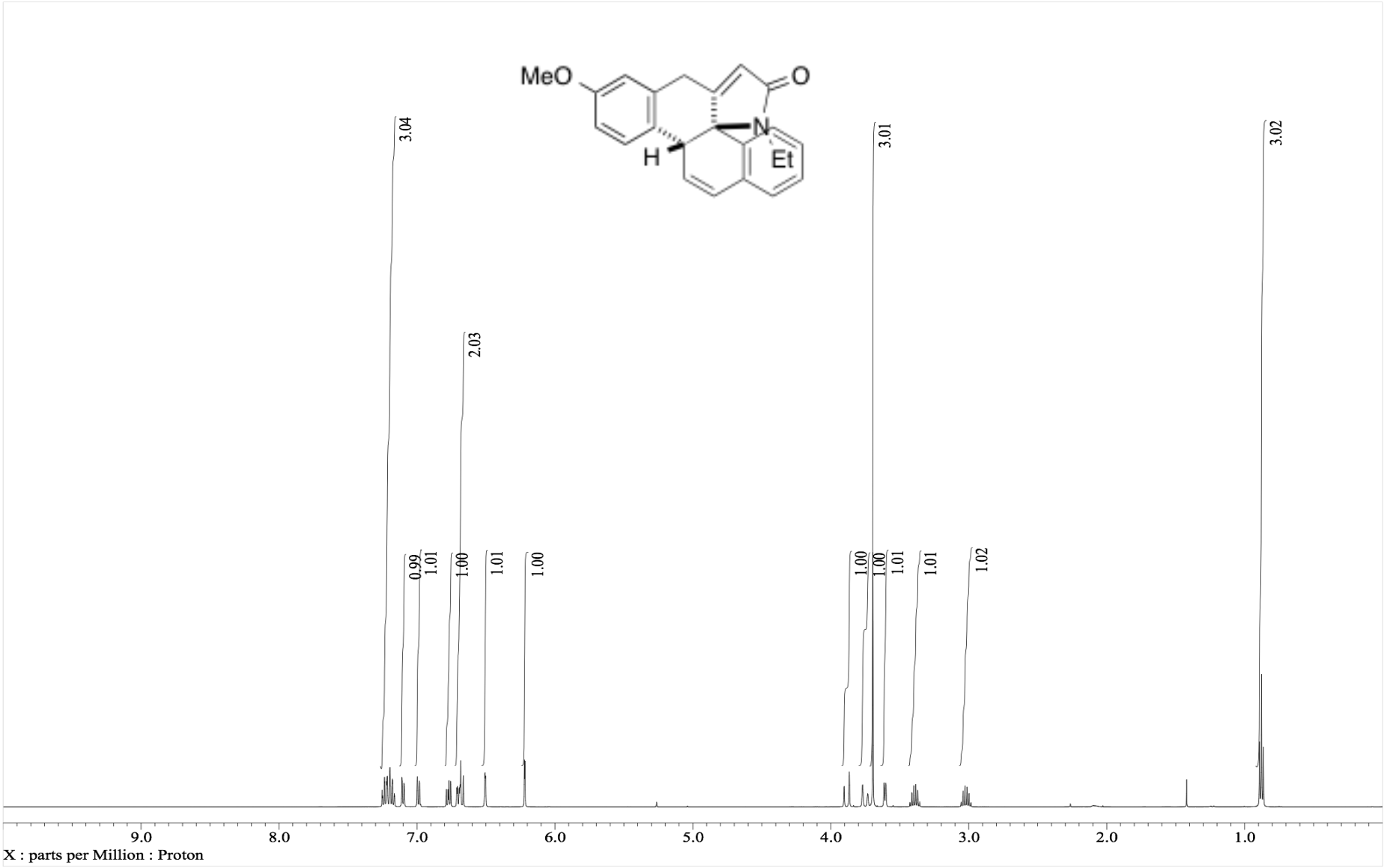

MeO
O
Br
N
Et
H
MeO
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
169.569
159.821
156.273
155.710
134.363
133.438
129.966
129.156
128.860
128.707
127.009
126.132
125.626
124.062
121.220
107.160
106.159
77.248
77.000
76.742
66.336
60.155
56.283
45.171
35.670
31.102
14.486
X : parts per Million : Carbon13

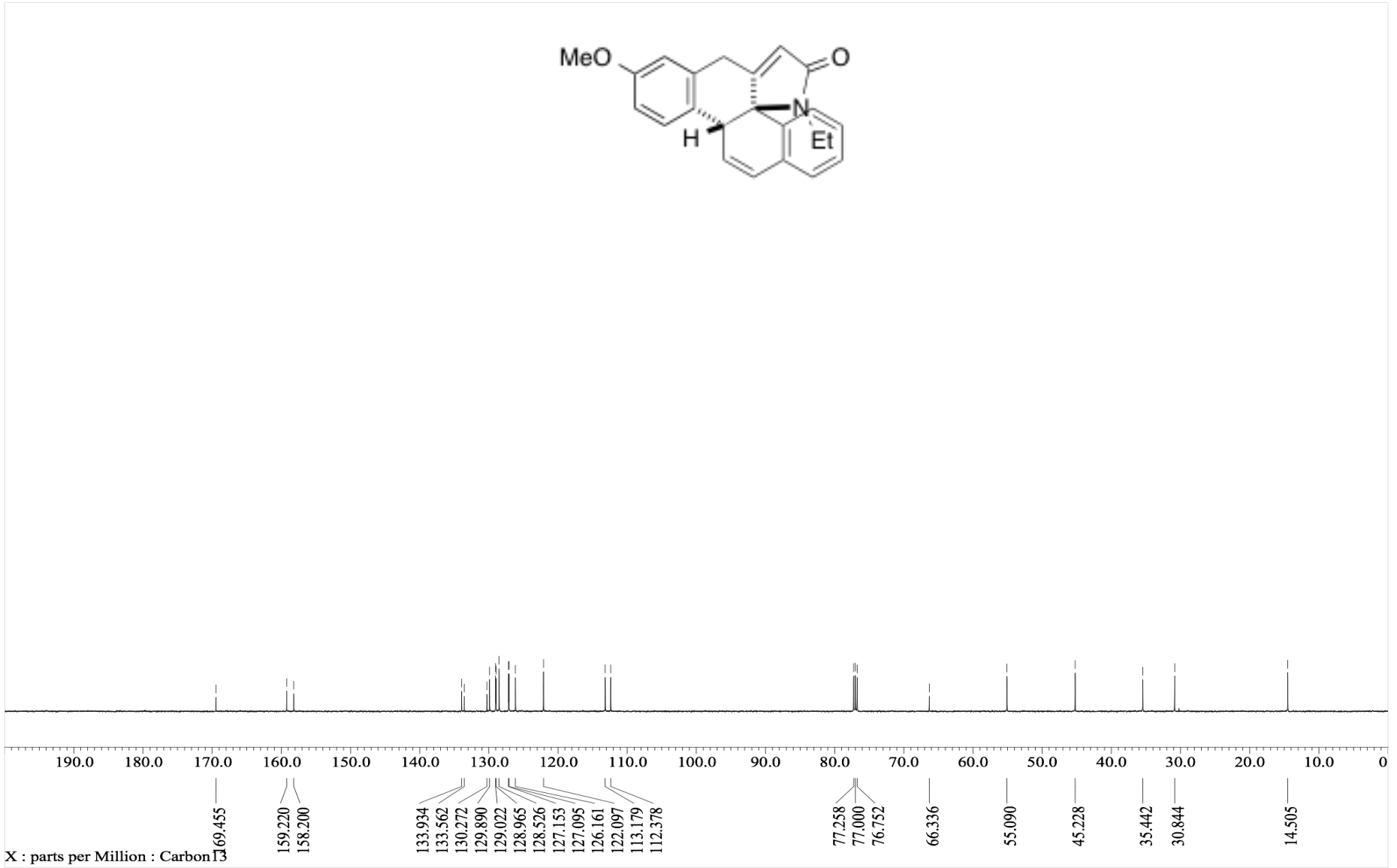
5-Ethyl-8,13b-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2g)



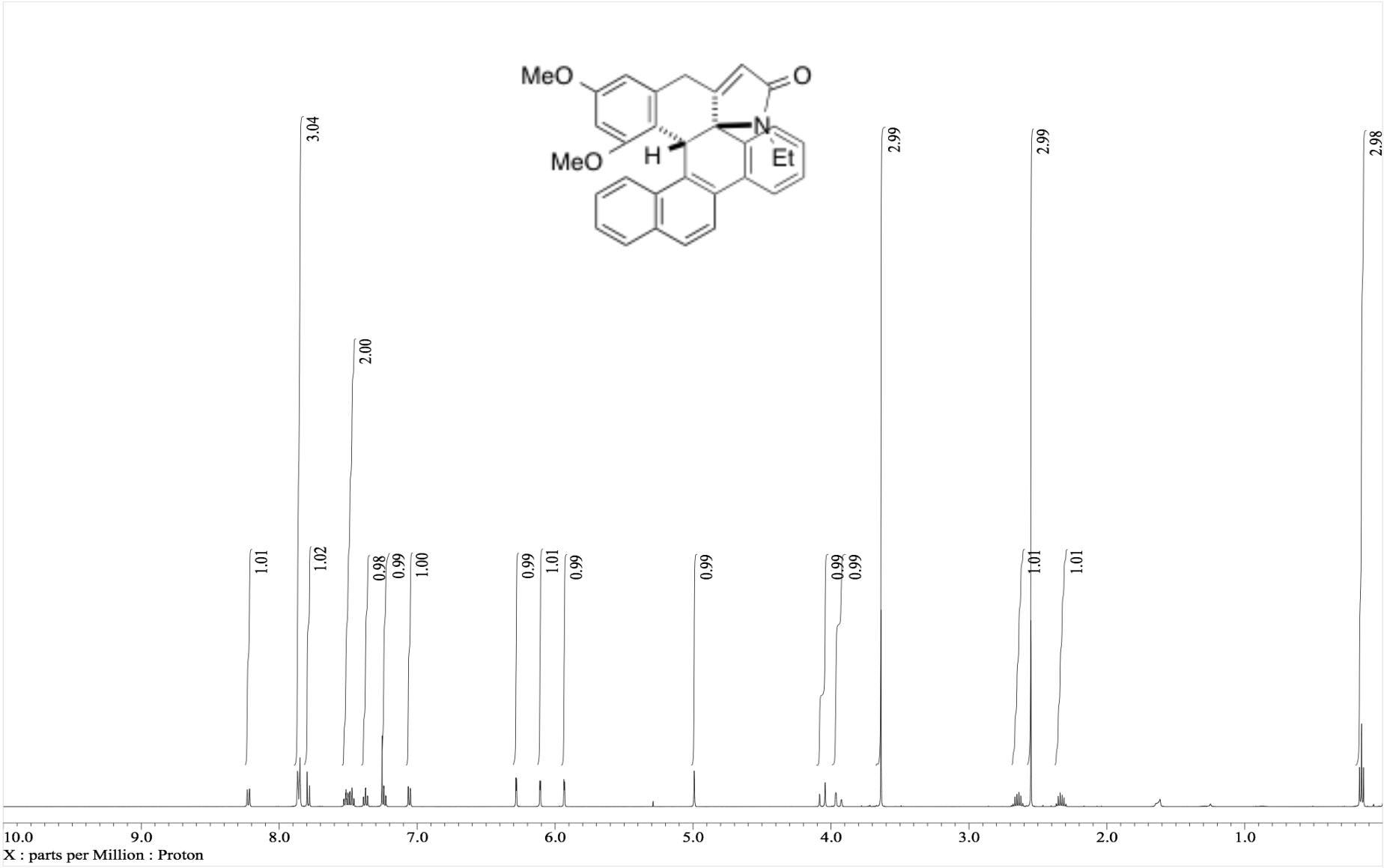

O
O
O
N
H
Et
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.493
159.239
146.677
146.658
133.419
130.319
129.489
129.117
129.060
129.041
127.429
127.162
126.113
125.769
121.926
107.446
107.170
101.056
77.248
77.000
76.742
66.107
45.533
35.451
30.567
14.505
X : parts per Million : Carbon13

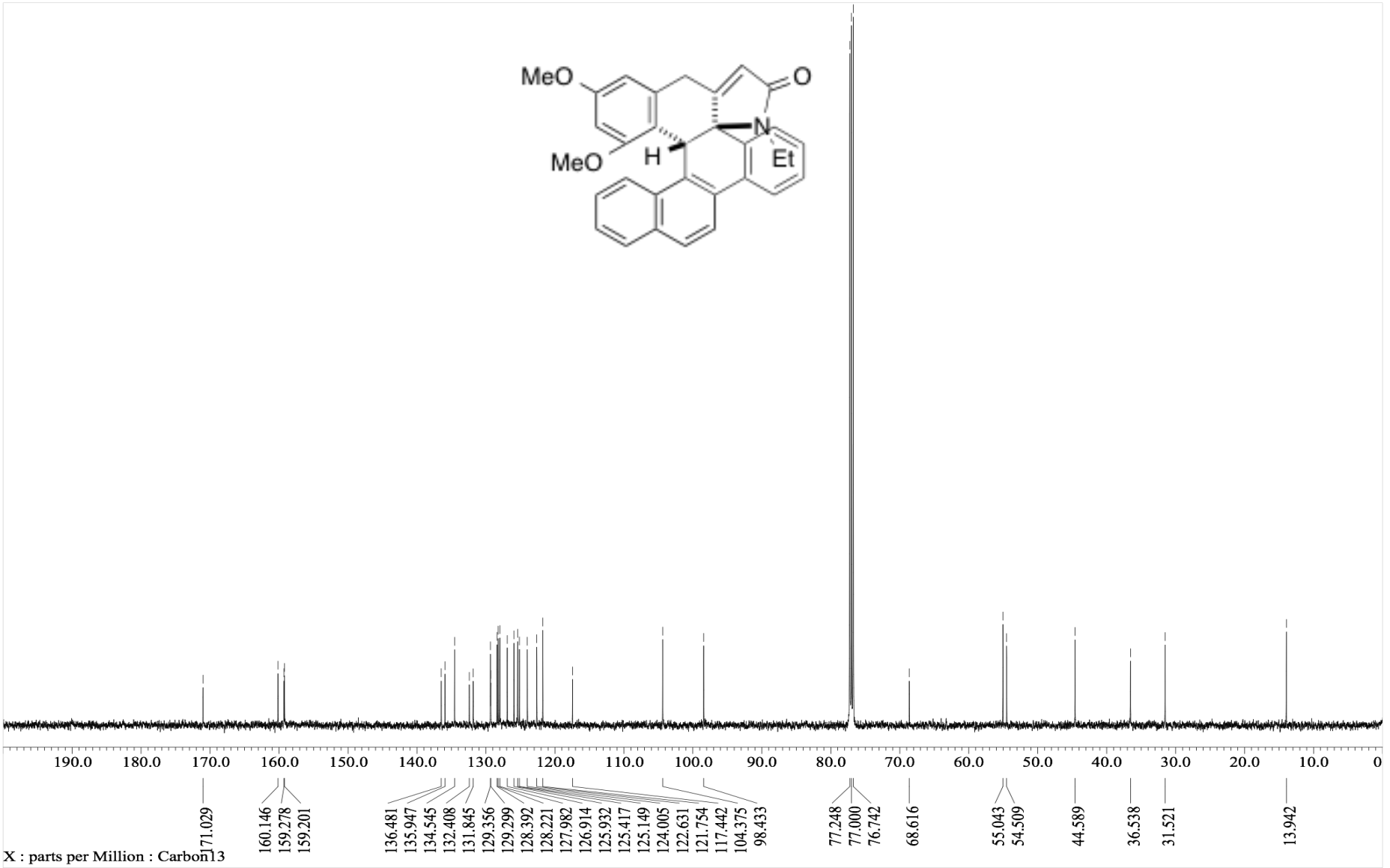
5-Ethyl-10-methoxy-8,12b-dihydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (2h)



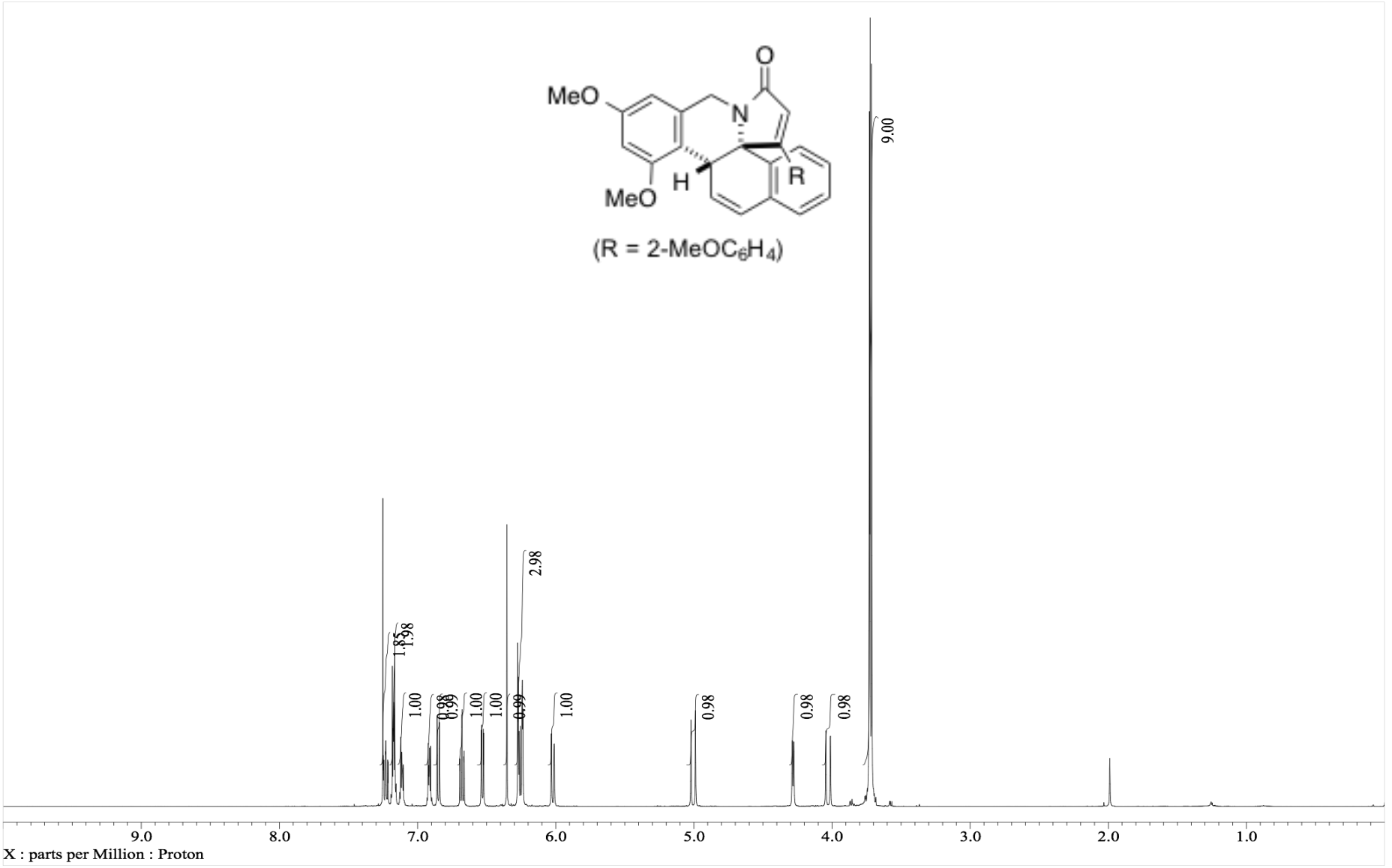

MeO
O
N
H
Et
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.455
159.220
158.200
133.934
133.562
130.272
129.890
129.022
128.965
128.526
127.153
127.095
126.161
122.097
113.179
112.378
77.258
77.000
76.752
66.336
55.090
45.228
35.442
30.844
14.505
X : parts per Million : Carbon13

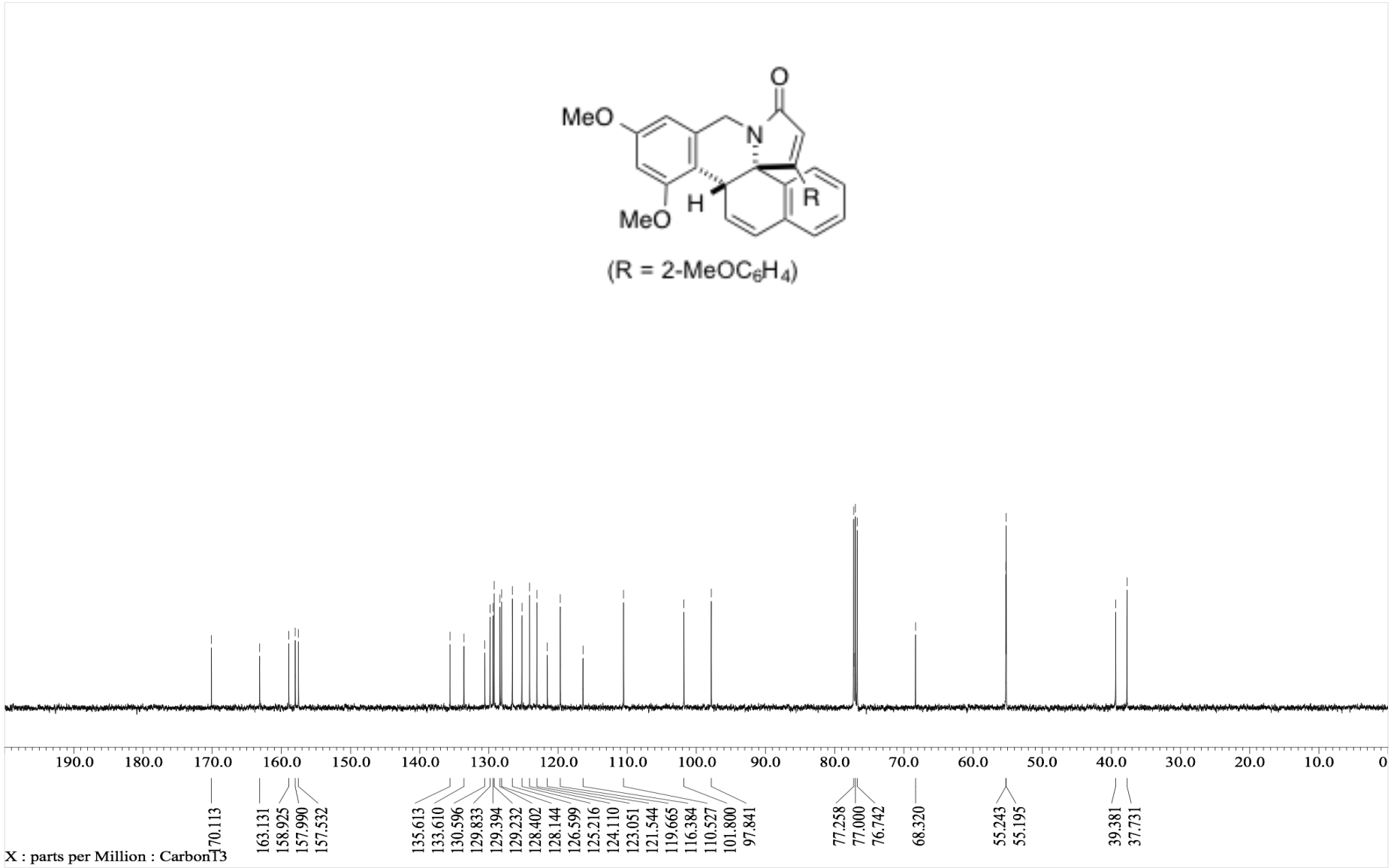
5-Benzyl-10,12-dimethoxy-8,12b-dihydrobenzo[f]chryseno[5,6-h]indol-6(5H)-one (2i)



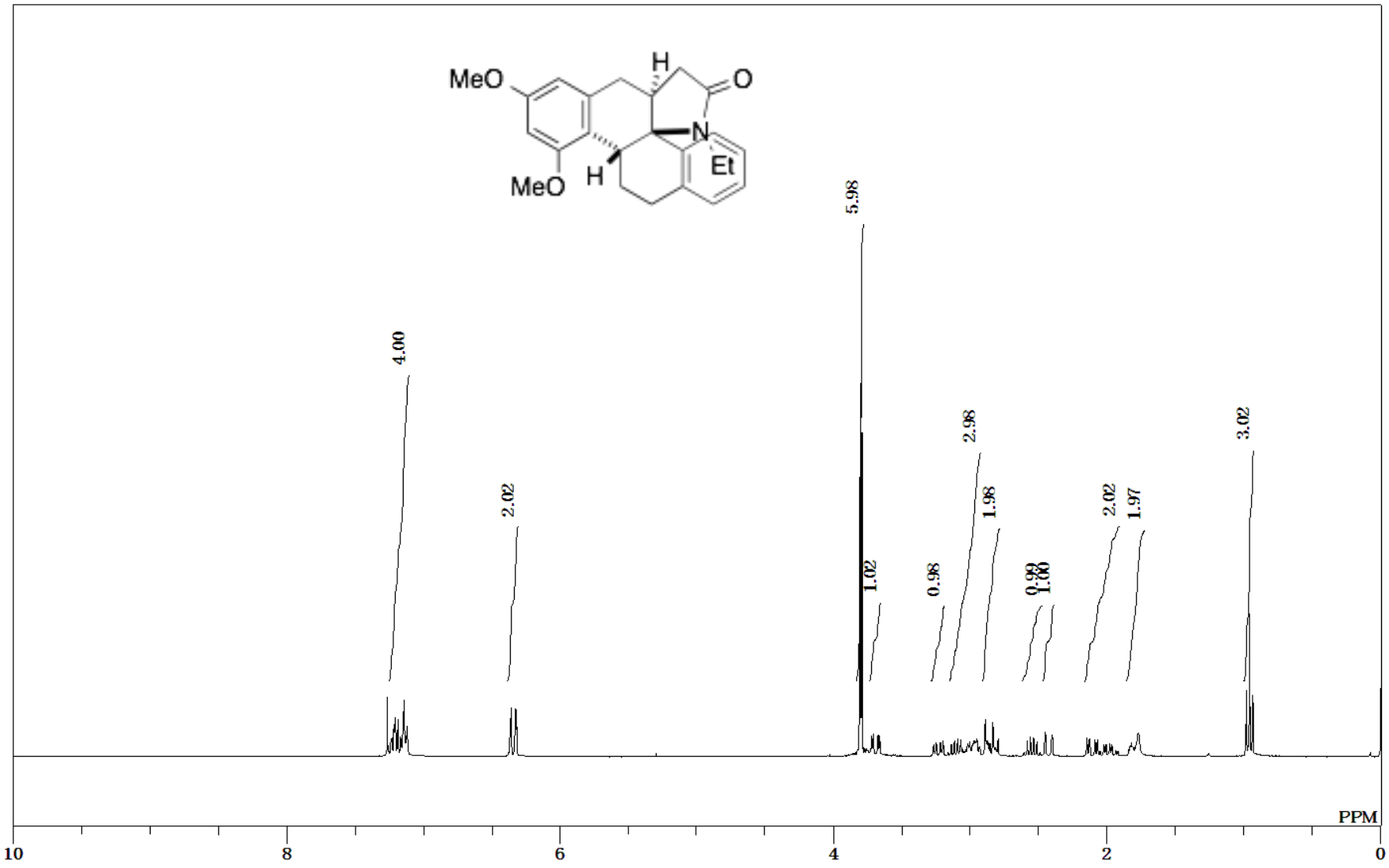

MeO
O
N
H
MeO
Et
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.029
160.146
159.278
159.201
136.481
135.947
134.545
132.408
131.845
129.356
129.299
128.392
128.221
127.982
126.914
125.932
125.417
125.149
124.005
122.631
121.754
117.442
104.375
98.433
77.248
77.000
76.742
68.616
55.043
54.509
44.589
36.538
31.521
13.942
X : parts per Million : Carbon13

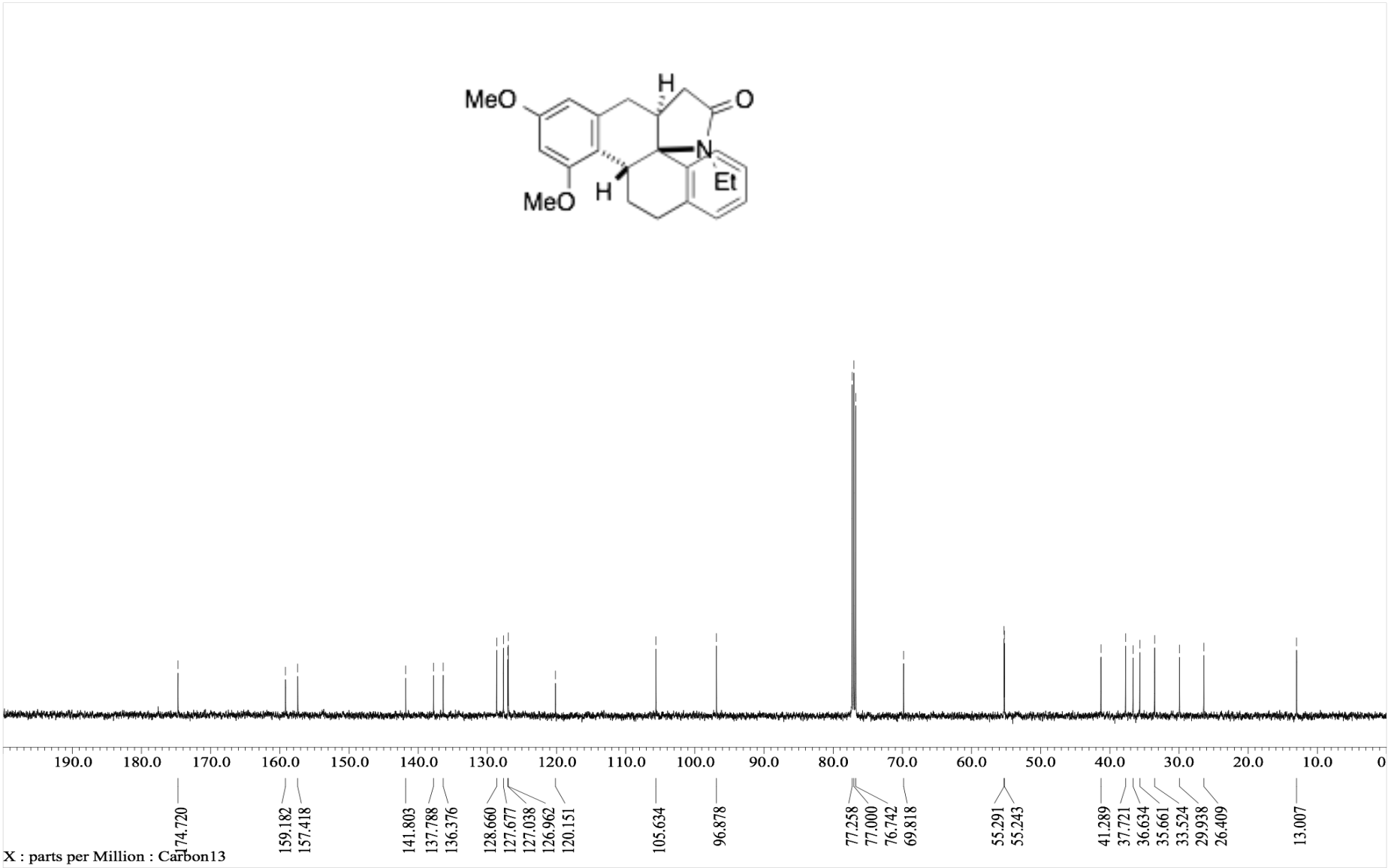
11,13-Dimethoxy-5-(2-methoxyphenyl)-9,13b-dihydro-7*H*-benzo[*c*]pyrrolo[2,1-*e*]phenanthridin-7-one (5)




MeO
O
N
H
R
MeO
(R = 2-MeOC6H4)
190.0
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
170.113
163.131
158.925
157.990
157.532
135.613
133.610
130.596
129.833
129.394
129.232
128.402
128.144
126.599
125.216
124.110
123.051
121.544
119.665
116.384
110.527
101.800
97.841
77.258
77.000
76.742
68.320
55.243
55.195
39.381
37.731
X : parts per Million : Carbon13

5-Ethyl-10,12-dimethoxy-7,7a,8,12b,13,14-hexahydrobenzo[*f*]naphtho[2,1-*h*]indol-6(5*H*)-one (6)




MeO
H
O
N
Et
MeO
H
190.0
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
174.720
159.182
157.418
141.803
137.788
136.376
128.660
127.677
127.038
126.962
120.151
105.634
96.878
77.258
77.000
76.742
69.818
55.291
55.243
41.289
37.721
36.634
35.661
33.524
29.938
26.409
13.007
X : parts per Million : Carbon13