



Title	Stereoselective preparation of methylenecyclobutane-fused angular tetracyclic spiroindolines via photosensitized intramolecular [2+2] cycloaddition with allene
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Stereoselective Preparation of Methylenecyclobutane-Fused Angular Tetracyclic Spiroindolines via Photosensitized Intramolecular [2+2] Cycloaddition with Allene

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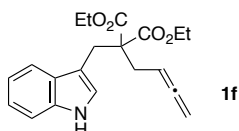
General remarks

NMR spectra were obtained on a JEOL JNM-ECS400 spectrometer. Carbon multiplicity was assigned by a DEPT experiment and described as follows: methyl, CH₃; methylene, CH₂; methine, CH; quaternary, C. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. UV spectra were obtained on a JASCO UV/Vis spectrophotometer Ubest-30. Silica gel column chromatography was performed with Fuji Silysia PSQ60B or FL60D. Preparative thin-layer chromatography (TLC) was carried out with Wako Gel B-5F (FUJIFILM Wako Pure Chemical Corporation). HPLC separation was performed using a JASCO HPLC system comprised of PU-2080 Plus, DG-2080-53, UV-2075 Plus, and CO-2065. Solvents and reagents were used as received unless otherwise noted. Mass spectrometry was carried out at the Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University.

Preparation and physical data of the starting materials

Compound **1f** was the source of malonate-tethered starting materials.

Diethyl 2-(buta-2,3-dienyl)-2-(indol-3-ylmethyl)malonate (**1f**)

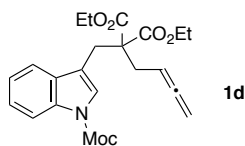


The reported procedure was followed with some modifications.¹ To a flask containing NaH (34.8 mg, 60% oil dispersion, 0.87 mmol, washed with hexane before use) and THF (3 mL) was added diethyl 2-(indol-3-ylmethyl)malonate¹ (230.1 mg, 0.795 mmol) as solid at 0 °C with stirring. After stirring at 0 °C for 30 min, 4-bromobuta-1,2-diene² (ca. 1.0 mmol, crude solution in pentane) was added at 0 °C, and the mixture was stirred for 10 min at 0 °C, then 3 h at rt. The reaction mixture was quenched by addition of saturated NH₄Cl solution and water, followed by extraction with ethyl acetate (15 mL x 3). The combined extracts were washed with brine, and dried with anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (hexane–ethyl acetate, 7:1) gave **1f** as a colorless oil (212.4 mg, 0.622 mmol, 78%).

IR (KBr) 3405, 3058, 2981, 1955, 1724, 1458, 1284, 1243, 1200, 1076, 1012, 855, 742 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, *J*=7.2 Hz, 6H), 2.65 (dt, *J*_d=7.9 Hz, *J*_t=2.6 Hz, 2H), 3.45 (d, *J*=0.3 Hz, 2H), 4.05–4.20 (m, 4H), 4.69 (dt, *J*_d=6.7 Hz, *J*_t=2.6 Hz, 2H), 5.05–5.12 (m, 1H), 7.02 (d, *J*=2.4 Hz, 1H), 7.07–7.11 (m, 1H), 7.14–7.18 (m, 1H), 7.32 (d, *J*=8.0 Hz, 1H), 7.58 (d, *J*=8.0 Hz, 1H), 8.06 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 27.5 (CH₂), 31.8 (CH₂), 58.7 (C), 61.3 (CH₂), 74.7 (CH₂), 84.8 (CH), 109.5 (C), 111.0 (CH), 118.7 (CH), 119.1 (CH), 121.7 (CH), 123.4 (CH), 128.0 (C), 135.7 (C), 171.1 (C), 210.1 (C). HRMS (ESI⁺) *m/z* 364.1515 (M+Na⁺), calcd for C₂₀H₂₃NNaO₄: 364.1519.

The representative substrate **1d** was prepared from **1f** as follows:

Diethyl 2-(buta-2,3-dienyl)-2-(1-methoxycarbonylindol-3-ylmethyl)malonate (**1d**)

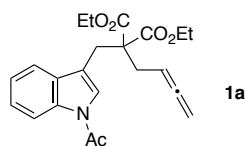


The reported procedure was followed with some modifications.³ To a flask containing NaH (78.8 mg, 60% oil dispersion, 2.0 mmol, washed with hexane before use) and DMF (2 mL) was added a solution of **1f** (0.340 g, 1.0 mmol) in DMF (0.5 mL) followed by 3 washings of the vessel that had contained **1f** with DMF (0.5 mL each) at 0 °C with stirring. After additional stirring at 0 °C for 30 min, methyl chloroformate (160 µL, 2.1 mmol) was added at the temperature, and the mixture was stirred for 10 min at 0 °C, then allowed to warm to rt. After stirring for 2 h, the reaction mixture was quenched by addition of saturated NH₄Cl solution and water, followed by extraction with hexane–ethyl acetate (1:1, 20 mL x 3). The combined extracts were successively washed with water (2 times) and with brine, and dried with anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (hexane–ethyl acetate, 15:1) gave **1d** as a colorless oil (0.405 g, 1.0 mmol, quantitative).

UV (1.2×10^{-4} mol/L, AcOEt) λ 294 (ϵ 6.0×10^3), 284 (ϵ 6.1×10^3) nm. IR (KBr) 2982, 1953, 1755, 1742, 1729, 1456, 1362, 1310, 1256, 1200, 1176, 1092, 866, 766 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.18 (t, $J=7.2$ Hz, 6H), 2.66 (dt, $J_d=7.9$ Hz, $J_t=2.6$ Hz, 2H), 3.36 (d, $J=0.6$ Hz, 2H), 4.01 (s, 3H), 4.04–4.18 (m, 4H), 4.69 (dt, $J_d=6.7$ Hz, $J_t=2.6$ Hz, 2H), 5.00–5.08 (m, 1H), 7.20–7.24 (m, 1H), 7.28–7.32 (m, 1H), 7.43 (s, 1H), 7.50 (d, $J=7.5$ Hz, 1H), 8.12 (br d, $J=8.0$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 27.2 (CH₂), 32.0 (CH₂), 53.7 (CH₃), 58.1 (C), 61.5 (CH₂), 74.9 (CH₂), 84.6 (CH), 115.0 (CH), 115.6 (C), 119.0 (CH), 122.6 (CH), 124.4 (CH), 124.6 (CH), 131.0 (C), 135.0 (C), 151.3 (C), 170.7 (C), 210.2 (C). HRMS (ESI⁺) m/z 422.1569 (M+Na⁺), calcd for C₂₂H₂₅NNaO₆: 422.1574.

Compound **1a–c**, **1e**, and **1g** were prepared by protection of **1f** according to the common methods. The physical data are as follows:

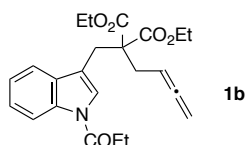
Diethyl 2-(1-acetylindol-3-ylmethyl)-2-(buta-2,3-dienyl)malonate (**1a**)



Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.19 (t, $J=7.1$ Hz, 6H), 2.60 (s, 3H), 2.69 (dt, $J_d=7.9$ Hz, $J_t=2.6$ Hz, 2H), 3.37 (d, $J=0.7$ Hz, 2H), 4.04–4.19 (m, 4H), 4.72 (dt, $J_d=6.7$ Hz, $J_t=2.6$ Hz, 2H), 5.00–5.08 (m, 1H), 7.24–7.35 (m, 3H), 7.49–7.51 (m, 1H), 8.39 (br d, $J=7.6$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃),

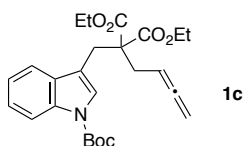
24.0 (CH₃), 27.2 (CH₂), 32.1 (CH₂), 58.0 (C), 61.5 (CH₂), 74.9 (CH₂), 84.6 (CH), 116.5 (CH), 116.7 (C), 118.8 (CH), 123.3 (CH), 124.4 (CH), 125.2 (CH), 131.0 (C), 135.4 (C), 168.3 (C), 170.7 (C), 210.3 (C).

Diethyl 2-(buta-2,3-dienyl)-2-(1-propanoylindol-3-ylmethyl)malonate (1b)



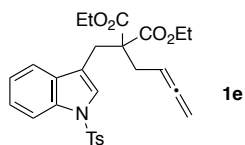
Colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 1.19 (t, *J*=7.2 Hz, 6H), 1.33 (t, *J*=7.3 Hz, 3H), 2.69 (dt, *J*_d=8.0 Hz, *J*_t=2.5 Hz, 2H), 2.91 (q, *J*=7.3 Hz, 2H), 3.37 (s, 2H), 4.01 (s, 3H), 4.04–4.19 (m, 4H), 4.72 (dt, *J*_d=6.7 Hz, *J*_t=2.5 Hz, 2H), 5.00–5.08 (m, 1H), 7.22–7.27 (m, 1H), 7.30–7.34 (m, 2H), 7.50 (d, *J*=7.8 Hz, 1H), 8.42 (br d, *J*=8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 8.7 (CH₃), 13.9 (CH₃), 27.2 (CH₂), 29.2 (CH₂), 32.1 (CH₂), 58.0 (C), 61.5 (CH₂), 74.9 (CH₂), 84.6 (CH), 116.4 (likely an overlap of CH and C), 118.7 (CH), 123.1 (CH), 123.6 (CH), 125.1 (CH), 130.8 (C), 135.4 (C), 170.6 (C), 171.8 (C), 210.2 (C).

Diethyl 2-(buta-2,3-dienyl)-2-(1-*tert*-butoxycarbonylindol-3-ylmethyl)malonate (1c)



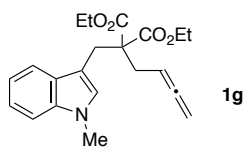
Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.22 (t, *J*=7.2 Hz, 6H), 1.67 (s, 9H), 2.66 (dt, *J*_d=7.9 Hz, *J*_t=2.6 Hz, 2H), 3.37 (d, *J*=0.6 Hz, 2H), 4.01 (s, 3H), 4.07–4.21 (m, 4H), 4.73 (dt, *J*_d=6.7 Hz, *J*_t=2.6 Hz, 2H), 5.01–5.09 (m, 1H), 7.18–7.22 (m, 1H), 7.26–7.30 (m, 1H), 7.42 (br s, 1H), 7.50–7.52 (m, 1H), 8.10 (br d, *J*=5.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 27.0 (CH₂), 28.1 (CH₃), 31.7 (CH₂), 58.2 (C), 61.4 (CH₂), 74.9 (CH₂), 83.5 (C), 84.6 (CH), 114.5 (C), 115.1 (CH), 118.9 (CH), 122.2 (CH), 124.2 (CH), 124.9 (CH), 131.0 (C), 135.0 (C), 149.5 (C), 170.7 (C), 210.2 (C).

Diethyl 2-(buta-2,3-dienyl)-2-(1-toluenesulfonylindol-3-ylmethyl)malonate (1e)



Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.12 (t, *J*=7.2 Hz, 6H), 2.33 (s, 3H), 2.58 (dt, *J*_d=7.9 Hz, *J*_t=2.6 Hz, 2H), 3.33 (d, *J*=0.7 Hz, 2H), 4.01 (s, 3H), 4.01–4.15 (m, 4H), 4.69 (dt, *J*_d=6.7 Hz, *J*_t=2.6 Hz, 2H), 4.97–5.04 (m, 1H), 7.17–7.21 (m, 3H), 7.25–7.29 (m, 1H), 7.40 (s, 1H), 7.44–7.47 (m, 1H), 7.70 (dt, *J*_d=8.5 Hz, *J*_t=1.9 Hz, 2H), 7.93 (dt, *J*_d=8.2 Hz, *J*_t=0.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.8 (CH₃), 21.5 (CH₃), 27.2 (CH₂), 32.0 (CH₂), 58.1 (C), 61.5 (CH₂), 75.0 (CH₂), 84.5 (CH), 113.6 (CH), 117.0 (C), 119.4 (CH), 123.0 (CH), 124.6 (CH), 125.3 (CH), 126.7 (CH), 129.7 (CH), 131.4 (C), 134.7 (C), 135.1 (C), 144.8 (C), 170.6 (C), 210.1 (C).

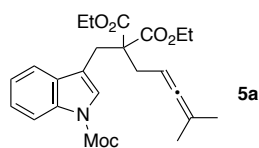
Diethyl 2-(buta-2,3-dienyl)-2-(1-methylindol-3-ylmethyl)malonate (**1g**)



Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 1.22 (t, $J=7.1$ Hz, 6H), 2.65 (dt, $J_d=7.9$ Hz, $J_t=2.6$ Hz, 2H), 3.44 (s, 2H), 3.73 (s, 3H), 4.07–4.21 (m, 4H), 4.70 (dt, $J_d=6.7$ Hz, $J_t=2.6$ Hz, 2H), 5.06–5.14 (m, 1H), 6.86 (s, 1H), 7.06–7.10 (m, 1H), 7.17–7.21 (m, 1H), 7.26 (dt, $J_d=8.1$ Hz, $J_t=0.9$ Hz, 1H), 7.56 (dt, $J_d=7.9$ Hz, $J_t=0.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0 (CH_3), 27.5 (CH_2), 31.8 (CH_2), 32.7 (CH_3), 58.7 (C), 61.2 (CH_2), 74.7 (CH_2), 84.9 (CH), 108.2 (C), 109.1 (CH), 118.7 (CH), 118.9 (CH), 121.4 (CH), 128.1 (CH), 128.6 (C), 136.5 (C), 171.1 (C), 210.1 (C).

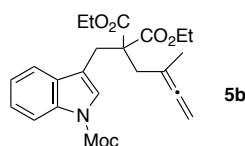
Compound **5a**, **5b** and **13** were prepared by the essentially same procedure as that for **1d** by using the corresponding allenyl moiety.^{4–6} The physical data are as follows:

Diethyl 2-(1-methoxycarbonylindol-3-ylmethyl)-2-(4-methylpenta-2,3-dienyl)malonate (**5a**)



Colorless oil. IR (KBr) 2980, 1969, 1733, 1608, 1456, 1370, 1256, 1199, 1090, 860, 764, 749 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.18 (t, $J=7.2$ Hz, 6H), 2.64 (d, $J=7.5$ Hz, 2H), 3.38 (d, $J=0.7$ Hz, 2H), 4.02 (s, 3H), 4.04–4.16 (m, 4H), 4.85–4.91 (m, 1H), 7.20–7.24 (m, 1H), 7.28–7.32 (m, 1H), 7.45 (s, 1H), 7.51–7.54 (m, 1H), 8.13 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8 (CH_3), 20.5 ($\text{CH}_3 \times 2$), 26.7 (CH_2), 32.3 (CH_2), 53.6 (CH_3), 58.0 (C), 61.3 (CH_2), 83.0 (CH), 95.4 (C), 115.0 (CH), 115.7 (C), 119.0 (CH), 122.5 (CH), 124.5 (CH $\times 2$), 131.0 (C), 135.0 (C), 151.2 (C), 170.7 (C), 204.0 (C). HRMS (ESI⁺) m/z 450.1886 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{24}\text{H}_{29}\text{NNaO}_6$: 450.1887.

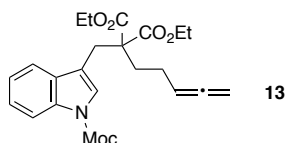
Diethyl 2-(1-methoxycarbonylindol-3-ylmethyl)-2-(2-methylbuta-2,3-dienyl)malonate (**5b**)



Colorless solid. IR (KBr) 2980, 1958, 1737, 1456, 1443, 1381, 1256, 1207, 1091, 860, 764, 748 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.18 (t, $J=7.1$ Hz, 6H), 1.67 (t, $J=3.1$ Hz, 3H), 2.63 (t, $J=2.9$ Hz, 2H), 3.47 (d, $J=0.7$ Hz, 2H), 4.01 (s, 3H), 4.03–4.16 (m, 4H), 4.68–4.72 (m, 2H), 7.20–7.24 (m, 1H), 7.28–7.32 (m, 1H), 7.44 (s, 1H), 7.50–7.52 (m, 1H), 8.13 (br d, $J=5.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8 (CH_3), 20.3 (CH_3), 26.8 (CH_2), 35.2 (CH_2), 53.7 (CH_3), 57.5 (C), 61.4 (CH_2), 75.6 (CH_2), 94.0 (C), 115.0 (CH), 116.0 (C), 119.0 (CH),

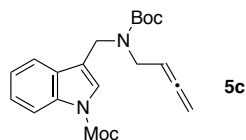
122.6 (CH), 124.3 (CH), 124.5 (CH), 131.1 (C), 135.0 (C), 151.3 (C), 170.8 (C), 207.1 (C). HRMS (ESI⁺) *m/z* 436.1730 (M+Na⁺), calcd for C₂₃H₂₇NNaO₆: 436.1731.

Diethyl 2-(1-methoxycarbonylindol-3-ylmethyl)-2-(2-penta-3,4-dienyl)malonate (13)



Colorless oil. IR (KBr) 2980, 1955, 1734, 1608, 1456, 1443, 1381, 1257, 1192, 1092, 1026, 860, 763, 748 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, *J*=7.1 Hz, 6H), 2.04 (br t, *J*=1.5 Hz, 4H), 3.35 (d, *J*=0.8 Hz, 2H), 4.02 (s, 3H), 4.07–4.20 (m, 4H), 4.67–4.69 (m, 2H), 5.05–5.11 (m, 1H), 7.21–7.25 (m, 1H), 7.29–7.33 (m, 1H), 7.38 (s, 1H), 7.48–7.50 (m, 1H), 8.13 (br d, *J*=6.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 23.3 (CH₂), 27.7 (CH₂), 32.0 (CH₂), 53.7 (CH₃), 57.8 (C), 61.4 (CH₂), 75.7 (CH₂), 89.1 (CH), 115.0 (CH), 115.8 (C), 119.0 (CH), 122.7 (CH), 124.1 (CH), 124.6 (CH), 131.0 (C), 135.0 (C), 151.3 (C), 171.1 (C), 208.4 (C). HRMS (ESI⁺) *m/z* 436.1730 (M+Na⁺), calcd for C₂₃H₂₇NNaO₆: 436.1731.

3-[*N*-(Buta-2,3-dienyl)-*N*-*tert*-butoxycarbonylaminomethyl]-1*H*-indole-1-carboxylic acid methyl ester (5c)

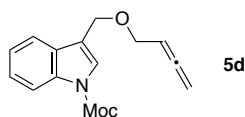


To a flask containing NaH (28.1 mg, 60% oil dispersion, 0.70 mmol, washed with hexane before use) and DMF (0.5 mL) was added a solution of *tert*-butyl 2,3-butadienylcarbamate⁷ (77.6 mg, 0.459 mmol) in DMF (0.5 mL) followed by 3 washings of the vessel that had contained the compound with DMF (0.3–0.4 mL each) at 0 °C with stirring. After additional stirring at 0 °C for 1 h, a solution of 3-bromomethyl-1-methoxycarbonylindole⁸ (182.4 mg, 0.680 mmol) in DMF (1 mL) was added, followed by 3 washings of the vessel that had contained the compound with DMF (0.3–0.4 mL each) at –40 °C, and the mixture was gradually allowed to warm to rt. After stirring overnight, the reaction mixture was quenched by addition of saturated NH₄Cl solution and water, followed by extraction with hexane–ethyl acetate (1:1, 20 mL x 3). The combined extracts were successively washed with water (2 times) and with brine, and dried with anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (hexane–ethyl acetate, 15:1) gave **5c** as a colorless oil (105.3 mg, 0.295 mmol, 64%). Because this product contained a small amount of unidentified impurity, a portion of it was re-purified by preparative TLC before use in the photoreaction.

Colorless oil. IR (KBr) 2976, 1955, 1740, 1692, 1609, 1456, 1413, 1364, 1252, 1170, 1115, 1088, 1019, 876, 851, 761, 749 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, at 55 °C) δ 1.52 (s, 9H), 3.81 (br s, 2H), 4.04 (s, 3H), 4.59

(br s, 2H), 4.71–4.74 (m, 2H), 5.06–5.12 (m, 1H), 7.23–7.27 (m, 1H), 7.32–7.36 (m, 1H), 7.52 (s, 1H), 7.65 (d, $J=7.8$ Hz, 1H), 8.15 (d, $J=8.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 °C) δ 28.5 (CH_3), 40.8 (CH_2), 44.5 (CH_2), 53.6 (CH_3), 76.0 (CH_2), 80.0 (C), 87.0 (CH), 115.2 (CH), 118.4 (C), 119.7 (CH), 123.0 (CH), 124.2 (CH), 124.8 (CH), 129.8 (C), 135.9 (C), 151.4 (C), 155.3 (C), 209.1 (C). HRMS (ESI^+) m/z 379.1624 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{NaO}_4$: 379.1628.

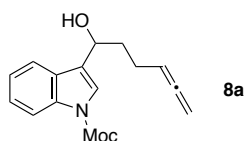
3-(Buta-2,3-dienyloxymethyl)-1*H*-indole-1-carboxylic acid methyl ester (5d)



To a flask containing NaH (25.9 mg, 60% oil dispersion, 0.65 mmol, washed with hexane before use) and DMF (2 mL) was added 2,3-butadien-1-ol⁹ (54.1 mg, 0.772 mmol) at 0 °C with stirring, and stirred for 20 min at the temperature. This solution was added to another flask that had been charged with 3-bromomethyl-1-methoxycarbonylindole⁸ (175.0 mg, 0.653 mmol), tetrabutylammonium iodide (255.9 mg, 0.693 mmol), and DMF (2 mL) at –80 °C. The mixture was gradually allowed to warm to rt. After stirring overnight, the reaction mixture was quenched by addition of saturated NH_4Cl solution and water, followed by extraction with hexane–ethyl acetate (1:1, 20 mL x 3). The combined extracts were successively washed with water (2 times) and with brine, and dried with anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure. Purification of the crude material by silica gel preparative TLC (hexane–ethyl acetate, 4:1) gave **5d** as a colorless oil (18.2 mg, 0.0707 mmol, 9%).

IR (KBr) 2955, 2857, 1955, 1739, 1610, 1572, 1456, 1349, 1255, 1093, 1039, 848, 762, 747 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 4.04 (s, 3H), 4.09 (dt, $J_d=7.0$ Hz, $J_t=2.5$ Hz, 2H), 4.69 (d, $J=0.9$ Hz, 2H), 4.81 (dt, $J_d=6.5$ Hz, $J_t=2.5$ Hz, 2H), 5.25–5.32 (m, 1H), 7.26–7.30 (m, 1H), 7.34–7.38 (m, 1H), 7.60 (br s, 1H), 7.64–7.67 (m, 1H), 8.16 (br d, $J=6.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 53.8 (CH_3), 63.3 (CH_2), 67.6 (CH_2), 75.7 (CH_2), 87.6 (CH), 115.1 (CH), 118.4 (C), 119.7 (CH), 123.0 (CH), 124.2 (CH), 124.8 (CH), 129.6 (C), 135.7 (C), 209.4 (C). The signal corresponding to a quaternary carbon of a methoxycarbonyl group was not observed likely due to broadening. HRMS (ESI^+) m/z 280.0945 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_3$: 280.0944.

3-(1-Hydroxyhexa-4,5-dienyl)-1*H*-indole-1-carboxylic acid methyl ester (8a)

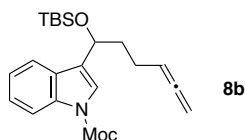


To a solution of methyl 3-formylindole-1-carboxylate¹⁰ (328.0 mg, 1.61 mmol) in THF (8 mL) was added a solution of 3,4-pentadienylmagnesium bromide¹¹ (ca. 0.5 M in THF, 4 mL) at –100 °C with stirring, and then the mixture was stirred for 1 h at –100 °C. The mixture was gradually allowed to warm to –80 °C for 40 min.

The reaction mixture was quenched by addition of saturated NH₄Cl solution and water, followed by extraction with ethyl acetate (20 mL x 3). The combined extracts were washed with brine, and dried with anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (toluene–ethyl acetate, 30:1 to 20:1) gave **8a** as a colorless oil (106.8 mg, 0.394 mmol, 24%) with 44% recovery of unreacted methyl 3-formylindole-1-carboxylate.

Colorless oil. IR (KBr) 3394 (br), 2954, 1955, 1737, 1607, 1569, 1455, 1377, 1308, 1253, 1092, 1070, 1020, 846, 759 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.88 (d, *J*=3.7 Hz, 1H), 2.03–2.09 (m, 2H), 2.14–2.19 (m, 2H), 4.04 (s, 3H), 4.69–4.72 (m, 2H), 5.01–5.05 (m, 1H), 5.14–5.20 (m, 1H), 7.25–7.29 (m, 1H), 7.33–7.38 (m, 1H), 7.56 (s, 1H), 7.69–7.71 (m, 1H), 8.18 (br d, *J*=7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 24.2 (CH₂), 36.0 (CH₂), 53.7 (CH₃), 67.1 (CH), 75.3 (CH₂), 89.3 (CH), 115.1 (CH), 119.9 (CH), 121.8 (CH), 122.8 (CH), 124.6 (CH, likely contains a signal corresponding to an aromatic quaternary carbon), 128.4 (C), 135.7 (C), 151.3 (C), 208.4 (C). HRMS (ESI⁺) *m/z* 294.1104 (M+Na⁺), calcd for C₁₆H₁₇NNaO₃: 294.1102.

3-[1-(*tert*-Butyldimethylsilyloxy)hexa-4,5-dienyl]-1*H*-indole-1-carboxylic acid methyl ester (**8b**)



This compound was prepared by TBS protection of **8a** according to the common method.

Colorless oil. IR (KBr) 2954, 2930, 2856, 1955, 1741, 1455, 1377, 1251, 1092, 837, 764, 746 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ -0.13 (s, 3H), 0.060 (s, 3H), 0.89 (s, 9H), 1.88–2.09 (m, 4H), 4.03 (s, 3H), 4.65–4.69 (m, 2H), 4.97 (dd, *J*=6.5, 5.2 Hz, 1H), 5.8–5.15 (m, 1H), 7.22–7.26 (m, 1H), 7.31–7.35 (m, 1H), 7.46 (s, 1H), 7.67–7.69 (m, 1H), 8.16 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ -5.1 (CH₃), -4.7 (CH₃), 18.2 (C), 24.0 (CH₂), 25.8 (CH₃), 37.9 (CH₂), 53.6 (CH₃), 68.2 (CH), 75.2 (CH₂), 89.6 (CH), 115.1 (CH), 120.5 (CH), 121.7 (CH), 122.6 (CH), 124.5 (CH), 125.6 (C), 128.5 (C), 135.9 (C), 151.5 (C), 208.4 (C). HRMS (ESI⁺) *m/z* 408.1971 (M+Na⁺), calcd for C₂₂H₃₁NNaO₃Si: 408.1965.

General procedure for the photocycloaddition and physical data of the products

The reaction of **1d** is representative.

A small scale reaction for screening (Table 1, Entry 4)

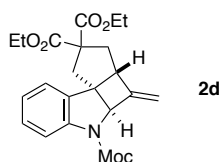
In a Pyrex test tube, **1d** (29.9 mg, 0.0749 mmol) and 3',4'-dimethoxyacetophenone (6.7 mg, 0.037 mmol) were charged. Air present in the tube was replaced with argon by several rapid evacuations/Ar introduction cycles. Ethyl acetate (7.5 mL) that had been degassed by three freeze-thaw cycles was transferred into the tube by a syringe. The solution was externally irradiated by a 100 W high-pressure mercury lamp (UVL-100HA; Riko) for 45 min. After the solution was evaporated, the crude material was purified by silica gel preparative TLC (hexane–ethyl acetate, 15:1 x 1, 10:1 x 2, and finally 5:1 x 2) gave **2d** (colorless oil, 25.1 mg,

0.0628 mmol, 84%) and **3d** (colorless oil, 3.7 mg, 0.0093 mmol, 12%).

A preparative scale reaction (Table 2, Entry 3)

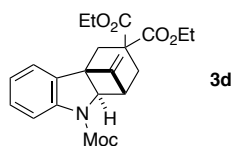
In a Pyrex 50 mL photoreactor (UVL-100HA-50P; Riko), and 3',4'-dimethoxyacetophenone (90.1 mg, 0.500 mmol) was charged, and air present in the vessel was replaced with argon by several rapid evacuations/Ar introduction cycles. A solution of **1d** (400.8 mg, 1.00 mmol) in ethyl acetate (20 mL) that had been degassed by three freeze-thaw cycles was transferred to the vessel through a Teflon cannula. The solution was irradiated by a 100 W high-pressure mercury lamp internally for 30 min. After the solution was evaporated, the crude material was purified by repeated silica gel column chromatography (hexane–ethyl acetate, 7:1 to 3:1, and finally to 2:1) to give a mixture of **2d** and **3d** (389.9 mg, 0.976 mmol, 98%, **2d:3d** = 85:15).

rac-(3*aR*,4*aR*,9*aR*)-1,2,3,3*a*,4,4*a*-Hexahydro-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2,5-tricarboxylic acid 2,2-diethyl 5-methyl ester (**2d**)



IR (KBr) 2981, 1730, 1601, 1483, 1443, 1382, 1292, 1252, 1205, 1191, 1145, 1088, 1063, 904, 863, 753 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 50 $^\circ\text{C}$) δ 1.29 (t, $J=7.1$ Hz, 3H), 1.30 (t, $J=7.1$ Hz, 3H), 2.47 (d, $J=14.3$ Hz, 1H), 2.59 (dd, $J=13.9, 1.9$ Hz, 1H), 2.67 (dd, $J=13.9, 8.3$ Hz, 1H), 2.99 (d, $J=14.3$ Hz, 1H), 3.34–3.38 (m, 1H), 3.84 (s, 3H), 4.17–4.30 (m, 4H), 4.99 (t, $J=1.9$ Hz, 1H), 5.06 (br s, 1H), 5.32 (br s, 1H), 7.00 (dt, $J_d=0.9$ Hz, $J_t=7.5$ Hz, 1H), 7.16 (d, $J=7.5$ Hz, 1H), 7.20–7.24 (m, 1H), 7.87 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 (CH₃), 14.0 (CH₃), 39.5 (CH₂), 41.0 (CH₂), 52.3 (CH₃), 55.4 (C), 56.4 (CH), 61.7 (CH₂), 61.9 (CH₂), 62.9 (C), 67.6 (CH), 113.8 (CH₂), 114.9 (CH), 122.3 (CH), 122.9 (CH), 128.4 (CH), 133.4 (C), 143.9 (C), 149.4 (C), 153.2 (C), 171.3 (C), 171.4 (C). HRMS (ESI⁺) m/z 422.1580 (M+Na⁺), calcd for C₂₂H₂₅NNaO₆: 422.1574.

rac-(1*R*,4*aS*,9*aS*)-1,2,3,4,4*a*,9*a*-Hexahydro-1,4*a*-methano-10-methylene-9*H*-carbazole-3,3,9-tricarboxylic acid 3,3-diethyl 9-methyl ester (**3d**)

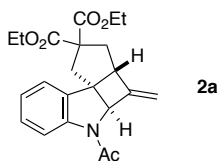


IR (KBr) 2981, 1731, 1605, 1479, 1460, 1443, 1377, 1346, 1255, 1231, 1205, 1074, 888, 863, 763 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 50 $^\circ\text{C}$) δ 1.26 (t, $J=7.1$ Hz, 3H), 1.28 (t, $J=7.1$ Hz, 3H), 2.62 (d, $J=14.1$ Hz, 1H), 2.74 (d, $J=13.6$ Hz, 1H), 3.25 (dd, $J=14.1, 5.7$ Hz, 1H), 3.42 (br d, $J=5.1$ Hz, 1H), 3.55 (d, $J=13.6$ Hz, 1H), 3.84 (s, 3H), 4.02 (s, 1H), 4.19 (q, $J=7.1$ Hz, 4H), 4.55 (s, 1H), 4.86 (s, 1H), 6.97 (dt, $J_d=0.8$ Hz, $J_t=7.5$ Hz, 1H), 7.14 (dd, $J=7.4, 0.8$ Hz, 1H), 7.17–7.21 (m, 1H), 7.76 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0

(CH₃), 14.1 (CH₃), 37.6 (CH₂), 38.1 (CH₂), 47.2 (CH), 52.2 (C), 52.8 (CH₃), 58.9 (C), 62.10 (CH₂), 62.14 (CH₂), 70.4 (CH), 107.0 (CH₂), 115.1 (CH), 121.7 (CH), 122.6 (CH), 128.3 (CH), 132.3 (C), 146.2 (C), 152.9 (C), 154.2 (C), 171.3 (C), 171.9 (C). HRMS (ESI⁺) *m/z* 422.1578 (M+Na⁺), calcd for C₂₂H₂₅NNaO₆: 422.1574.

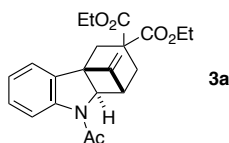
Physical data of the other products were as follows:

***rac*-(3a*R*,4a*R*,9a*R*)-5-Acetyl-2,3,3a,4,4a,5-hexahydro-4-methylene-1*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2-dicarboxylic acid diethyl ester (2a)**



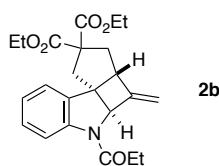
Colorless oil. IR (KBr) 2981, 1731, 1666, 1598, 1479, 1460, 1389, 1285, 1253, 1191, 1085, 756 cm⁻¹. Only the signals of the major rotamer were shown. ¹H NMR (400 MHz, CDCl₃) δ 1.28 (t, *J*=7.1 Hz, 3H), 1.29 (t, *J*=7.1 Hz, 3H), 2.26 (s, 3H), 2.45 (d, *J*=14.3 Hz, 1H), 2.56 (dd, *J*=14.1, 1.7 Hz, 1H), 2.72 (dd, *J*=14.1, 8.7 Hz, 1H), 3.00 (d, *J*=14.3 Hz, 1H), 3.35–3.39 (m, 1H), 4.15–4.31 (m, 4H), 5.07–5.08 (m, 1H), 5.10–5.11 (m, 1H), 5.27–5.28 (m, 1H), 7.05–7.09 (m, 1H), 7.18–7.26 (m, 2H), 8.27 (d, *J*=8.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 14.0 (CH₃), 24.6 (CH₃), 39.6 (CH₂), 41.4 (CH₂), 56.0 (C), 56.8 (CH), 61.8 (CH₂), 62.0 (CH₂), 63.0 (C), 68.6 (CH), 113.7 (CH₂), 117.5 (CH), 122.3 (CH), 124.1 (CH), 128.5 (CH), 133.8 (C), 144.2 (C), 149.7 (C), 169.0 (C), 171.2 (C), 171.5 (C). HRMS (ESI⁺) *m/z* 406.1624 (M+Na⁺), calcd for C₂₂H₂₅NNaO₅: 406.1625.

***rac*-(1*R*,4a*S*,9a*S*)-9-Acetyl-2,3,4,4a,9,9a-hexahydro-1,4a-methano-10-methylene-1*H*-carbazole-3,3-dicarboxylic acid diethyl ester (3a)**



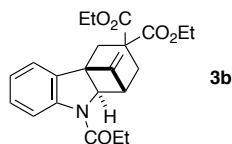
Colorless oil. IR (KBr) 2982, 1732, 1672, 1604, 1475, 1458, 1386, 1258, 1230, 1209, 1179, 1072, 1031, 1017, 890, 864, 757 cm⁻¹. Only the signals of the major rotamer were shown. ¹H NMR (400 MHz, CDCl₃) δ 1.26 (t, *J*=7.1 Hz, 3H), 1.28 (t, *J*=7.1 Hz, 3H), 2.21 (s, 3H), 2.63 (d, *J*=14.0 Hz, 1H), 2.73 (d, *J*=13.7 Hz, 1H), 3.28 (dd, *J*=14.0, 5.3 Hz, 1H), 3.41 (br d, *J*=5.3 Hz, 1H), 3.60 (d, *J*=13.7 Hz, 1H), 4.06 (s, 1H), 4.20 (q, *J*=7.1 Hz, 4H), 4.57 (s, 1H), 4.90 (s, 1H), 7.03 (dt, *J*_d=0.9 Hz, *J*_t=7.5 Hz, 1H), 7.15–7.23 (m, 2H), 8.19 (d, *J*=8.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 14.0 (CH₃), 23.7 (CH₃), 37. (CH₂), 38.1 (CH₂), 47.7 (CH), 52.0 (C), 59.1 (C), 62.1 (CH₂), 62.2 (CH₂), 70.8 (CH), 107.5 (CH₂), 117.2 (CH), 121.4 (CH), 123.5 (CH), 128.4 (CH), 132.2 (C), 146.5 (C), 151.5 (C), 170.0 (C), 171.5 (C), 171.7 (C). HRMS (ESI⁺) *m/z* 406.1626 (M+Na⁺), calcd for C₂₂H₂₅NNaO₅: 406.1625.

***rac*-(3a*R*,4a*R*,9a*R*)-2,3,3a,4,4a,5-Hexahydro-4-methylene-5-propanoyl-1*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2-dicarboxylic acid diethyl ester (2b)**



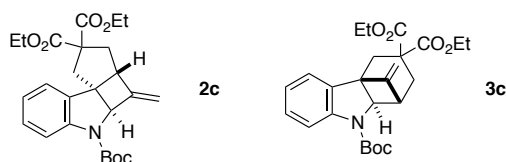
Colorless oil. IR (KBr) 2981, 1731, 1667, 1598, 1479, 1460, 1391, 1253, 1200, 1085, 1056, 906, 859, 755 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 50 $^\circ\text{C}$) δ 1.25 (t, $J=7.3$ Hz, 3H), 1.29 (t, $J=7.2$ Hz, 3H), 1.30 (t, $J=7.1$ Hz, 3H), 2.45–2.53 (br m, 2H, including d ($J=14.4$ Hz, 1H) at 2.49), 2.58 (dd, $J=14.0$, 1.7 Hz, 1H), 2.73 (dd, $J=14.0$, 8.6 Hz, 1H), 2.99 (d, $J=14.4$ Hz, 1H), 3.34–3.38 (m, 1H), 4.18–4.31 (m, 4H), 5.05 (br s, 1H), 5.15 (br s, 1H), 5.26 (br s, 1H), 7.05 (dt, $J_d=0.8$ Hz, $J_t=7.5$ Hz, 1H), 7.19–7.26 (m, 2H), 8.31 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.9 (CH_3), 13.9 (CH_3), 14.0 (CH_3), 29.4 (CH_2), 39.6 (CH_2), 41.4 (CH_2), 56.1 (C), 56.7 (CH), 61.8 (CH_2), 62.0 (CH_2), 63.0 (C), 67.8 (CH), 113.6 (CH_2), 117.5 (CH), 122.3 (CH), 123.9 (CH), 128.5 (CH), 133.7 (C), 144.4 (C), 149.8 (C), 171.2 (C), 171.6 (C), 172.4 (C). HRMS (ESI^+) m/z 398.1963 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_5$: 398.1962.

***rac*-(1*R*,4a*S*,9a*S*)-2,3,4,4a,9a-Hexahydro-10-methylene-1,4a-methano-9-propanoyl-1*H*-carbazole-3,3-dicarboxylic acid diethyl ester (3b)**



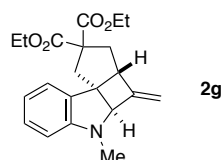
Colorless oil. IR (KBr) 2981, 1733, 1673, 1603, 1475, 1457, 1389, 1282, 1256, 1227, 1177, 1099, 1071, 1052, 1016, 895, 862, 756 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.23 (t, $J=7.3$ Hz, 3H), 1.26 (t, $J=7.1$ Hz, 3H), 1.28 (t, $J=7.1$ Hz, 3H), 2.36–2.49 (m, 2H), 2.63 (dd, $J=14.1$, 0.8 Hz, 1H), 2.73 (d, $J=13.6$ Hz, 1H), 3.27 (dd, $J=14.1$, 5.6 Hz, 1H), 3.41 (br d, $J=5.3$ Hz, 1H), 3.60 (d, $J=13.6$ Hz, 1H), 4.05 (s, 1H), 4.20 (q, $J=7.1$ Hz, 4H), 4.56 (s, 1H), 4.89 (s, 1H), 7.02 (dt, $J_d=1.0$ Hz, $J_t=7.4$ Hz, 1H), 7.15–7.23 (m, 2H), 8.23 (d, $J=7.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.9 (CH_3), 13.9 (CH_3), 14.0 (CH_3), 28.6 (CH_2), 37.8 (CH_2), 38.1 (CH_2), 47.8 (CH), 52.0 (C), 59.1 (C), 62.1 (CH_2), 62.2 (CH_2), 70.3 (CH), 107.3 (CH_2), 117.2 (CH), 121.3 (CH), 123.3 (CH), 128.4 (CH), 132.1 (C), 146.8 (C), 151.5 (C), 171.5 (C), 171.7 (C), 173.6 (C). HRMS (ESI^+) m/z 398.1965 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_5$: 398.1962.

***rac*-(3a*R*,4a*R*,9a*R*)-1,2,3,3a,4,4a-Hexahydro-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2,5-tricarboxylic acid 2,2-diethyl 5-*tert*-butyl ester (2c) and *rac*-(1*R*,4a*S*,9a*S*)-1,2,3,4,4a,9a-Hexahydro-1,4a-methano-10-methylene-9*H*-carbazole-3,3,9-tricarboxylic acid 3,3-diethyl 9-*tert*-butyl ester (3c) (an inseparable mixture of parallel (2c)/cross (3c) isomers, 2c:3c = 86:14)**



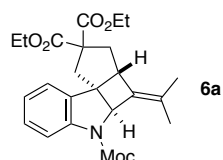
Colorless oil. Only the signals of the major isomer (**2c**) were shown. ^1H NMR (400 MHz, CDCl_3) δ 1.23–1.31 (m, 6H), 1.55 (br s, 9H), 2.44 (d, $J=14.2$ Hz, 1H), 2.57–2.67 (m, 2H), 2.98 (d, $J=14.2$ Hz, 1H), 3.33–3.36 (m, 1H), 4.16–4.28 (m, 4H), 4.96 (br s, 1H), 4.98–4.99 (m, 1H), 5.35 (br s, 1H), 6.95–6.99 (m, 1H), 7.12–7.22 (m, 2H), 7.90 (d, $J=8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 (CH_3), 14.0 (CH_3), 28.5 (CH_3), 39.7 (CH_2), 41.3 (CH_2), 55.3 (C), 56.5 (CH), 61.7 (CH_2), 61.9 (CH_2), 63.1 (C), 67.7 (CH), 80.8 (C), 113.3 (CH_2), 115.0 (CH), 122.3 (CH), 122.5 (CH), 128.4 (CH), 133.3 (C), 144.1 (C), 150.0 (C), 152.0 (C), 171.2 (C), 171.5 (C).

***rac*-(3*aR*,4*aR*,9*aR*)-2,3,3*a*,4,4*a*,5-Hexahydro-5-methyl-4-methylene-1*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2-dicarboxylic acid diethyl ester (**2g**)**



Colorless oil. IR (KBr) 2979, 1731, 1605, 1491, 1367, 1301, 1252, 1191, 1092, 1026, 893, 865, 736 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.27 (t, $J=7.1$ Hz, 6H), 2.38 (d, $J=14.2$ Hz, 1H), 2.53 (dt, $J_d=13.8$ Hz, $J_t=1.3$ Hz, 1H), 2.64 (dd, $J=13.8, 8.2$ Hz, 1H), 2.82 (s, 3H), 2.98 (d, $J=14.2$ Hz, 1H), 3.37–3.40 (m, 1H), 4.10–4.29 (m, 4H), 4.38 (br s, 1H), 4.87 (t, $J=1.8$ Hz, 1H), 5.01–5.02 (m, 1H), 6.33 (d, $J=7.7$ Hz, 1H), 6.59 (dt, $J_d=0.9$ Hz, $J_t=7.3$ Hz, 1H), 6.98 (dd, $J=7.3, 1.0$ Hz, 1H), 7.07 (dt, $J_d=1.3$ Hz, $J_t=7.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 (CH_3), 14.0 (CH_3), 32.5 (CH_3), 39.4 (CH_2), 40.6 (CH_2), 56.1 (C), 56.6 (CH), 61.6 (CH_2), 61.8 (CH_2), 62.8 (C), 73.9 (CH), 105.4 (CH), 110.0 (CH_2), 116.3 (CH), 122.0 (CH), 128.4 (CH), 131.6 (C), 151.5 (C), 153.2 (C), 171.5 (C), 171.7 (C). HRMS (ESI $^+$) m/z 356.1854 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4$: 356.1856.

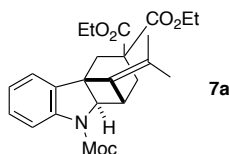
***rac*-(3*aR*,4*aR*,9*aR*)-1,2,3,3*a*,4,4*a*-Hexahydro-4-(1-methylethylidene)-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2,5-tricarboxylic acid 2,2-diethyl 5-methyl ester (**6a**)**



Isomers **6a** and **7a** were separated by HPLC. Conditions: column, COSMOSIL (Nacalai Tesque, Inc., 20 x 250 mm); eluent: $\text{CH}_3\text{CN} : \text{H}_2\text{O} = 80:20$; flow, 5.7 mLmin^{-1} ; column temp, 40 $^\circ\text{C}$; detection, UV 254 nm; **7a**, $t_R = 21.6$ min, **6a**, $t_R = 24.0$ min. Colorless oil. IR (KBr) 2980, 1730, 1712, 1601, 1483, 1442, 1375, 1289, 1252, 1193, 1087, 1061, 859, 752 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.29 (t, $J=7.1$ Hz, 3H), 1.30 (t, $J=7.2$

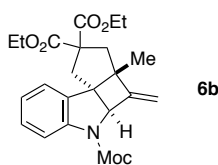
Hz, 3H), 1.53 (s, 3H), 1.74 (s, 3H), 2.46 (d, $J=14.2$ Hz, 1H), 2.57 (dd, $J=13.8, 8.1$ Hz, 1H), 2.63 (dd, $J=13.8, 2.7$ Hz, 1H), 2.97 (d, $J=14.2$ Hz, 1H), 3.28 (br d, $J=7.4$ Hz, 1H), 3.83 (s, 3H), 4.15–4.31 (m, 4H), 5.18 (s, 1H), 7.01 (dt, $J_d=1.0$ Hz, $J_t=7.5$ Hz, 1H), 7.17–7.23 (m, 2H), 7.78 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0 ($\text{CH}_3 \times 2$), 19.4 (CH_3), 19.7 (CH_3), 38.6 (CH_2), 41.1 (CH_2), 52.3 (CH_3), 54.0 (C), 55.1 (CH), 61.5 (CH_2), 61.8 (CH_2), 63.0 (C), 66.9 (CH), 116.0 (CH), 122.2 (CH), 123.1 (CH), 128.0 (CH), 131.5 (C), 134.2 (C), 134.5 (C), 143.8 (C), 153.7 (C), 171.0 (C), 171.6 (C). HRMS (ESI^+) m/z 450.1885 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{24}\text{H}_{29}\text{NNaO}_6$: 450.1887.

***rac*-(1*R*,4*aS*,9*aS*)-1,2,3,4,4*a*,9*a*-Hexahydro-1,4*a*-methano-10-(1-methylethylidene)-9*H*-carbazole-3,3,9-tricarboxylic acid 3,3-diethyl 9-methyl ester (7*a*)**



Colorless oil. IR (KBr) 2980, 2909, 1731, 1604, 1478, 1460, 1443, 1377, 1243, 1220, 1099, 1074, 865, 758 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.22 (s, 3H), 1.25 (t, $J=7.1$ Hz, 3H), 1.29 (t, $J=7.2$ Hz, 3H), 1.42 (s, 3H), 2.51 (d, $J=13.9$ Hz, 1H), 2.61 (d, $J=13.5$ Hz, 1H), 3.26 (ddd, $J=13.9, 5.8, 1.2$ Hz, 1H), 3.38 (br d, $J=5.6$ Hz, 1H), 3.68 (dd, $J=13.5, 1.2$ Hz, 1H), 3.84 (s, 3H), 3.89 (s, 1H), 4.14–4.21 (m, 4H), 6.96 (dt, $J_d=0.9$ Hz, $J_t=7.4$ Hz, 1H), 7.14–7.19 (m, 2H), 7.77 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 14.0 ($\text{CH}_3 \times 2$), 17.4 (CH_3), 19.4 (CH_3), 37.8 (CH_2), 38.0 (CH_2), 43.5 (CH), 52.5 (CH_3), 52.9 (C), 57.1 (C), 61.77 (CH_2), 61.83 (CH_2), 71.2 (CH), 115.0 (CH), 122.2 (CH), 122.8 (CH), 126.5 (C), 127.8 (CH), 132.8 (C), 135.3 (C), 146.2 (C), 154.4 (C), 171.2 (C), 171.9 (C). HRMS (ESI^+) m/z 450.1885 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{24}\text{H}_{29}\text{NNaO}_6$: 450.1887.

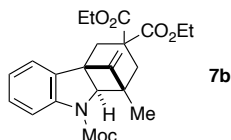
***rac*-(3*aR*,4*aR*,9*aR*)-1,2,3,3*a*,4,4*a*-Hexahydro-3*a*-methyl-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-2,2,5-tricarboxylic acid 2,2-diethyl 5-methyl ester (6*b*)**



Isomers **6b** and **7b** were separated by HPLC. Conditions: column, COSMOSIL (Nacalai Tesque, Inc., 20 x 250 mm); eluent: $\text{CH}_3\text{CN} : \text{H}_2\text{O} = 70:30$; flow, 5.7 mLmin^{-1} ; column temp, 40 $^\circ\text{C}$; detection, UV 254 nm; **7b**, $t_R = 31.4$ min, **6b**, $t_R = 33.3$ min. Colorless oil. IR (KBr) 2980, 1731, 1717, 1601, 1484, 1461, 1443, 1382, 1292, 1251, 1211, 1127, 1071, 909, 858, 758 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 0.87 (s, 3H), 1.28 (t, $J=7.0$ Hz, 3H), 1.29 (t, $J=7.0$ Hz, 3H), 2.33 (d, $J=13.9$ Hz, 1H), 2.50 (d, $J=14.2$ Hz, 1H), 2.75 (d, $J=13.9$ Hz, 1H), 3.01 (d, $J=14.2$ Hz, 1H), 3.83 (s, 3H), 4.16–4.30 (m, 4H), 4.99 (br s, 2H), 5.27 (br s, 1H), 7.00 (dt, $J_d=0.9$ Hz, $J_t=7.4$ Hz, 1H), 7.09 (dd, $J=7.4, 0.9$ Hz, 1H), 7.20–7.24 (m, 1H), 7.89 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9 (CH_3), 14.0 (CH_3), 22.3 (CH_3), 41.0 (CH_2), 46.6 (CH_2), 52.3 (CH_3), 58.5 (C), 58.9 (C),

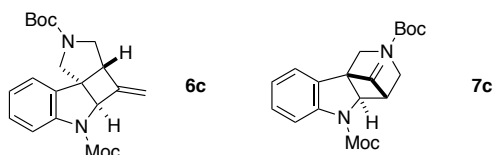
61.2 (C), 61.7 (CH₂), 61.9 (CH₂), 66.3 (CH), 111.5 (CH₂), 114.9 (CH), 122.6 (CH), 123.7 (CH), 128.5 (CH), 130.8 (C), 144.6 (C), 153.3 (C), 154.7 (C), 171.3 (C), 171.5 (C). HRMS (ESI⁺) *m/z* 436.1733 (M+Na⁺), calcd for C₂₃H₂₇NNaO₆: 436.1731.

***rac*-(1*R*,4*aS*,9*aS*)-1,2,3,4,4*a*,9*a*-Hexahydro-1,4*a*-methano-1-methyl-10-methylene-9*H*-carbazole-3,3,9-tricarboxylic acid 3,3-diethyl 9-methyl ester (7b)**



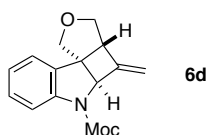
Colorless oil. IR (KBr) 2980, 1732, 1605, 1479, 1460, 1443, 1372, 1350, 1326, 1251, 1208, 1085, 1055, 887, 864, 755 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.17 (s, 3H), 1.25 (t, *J*=7.2 Hz, 3H), 1.27 (t, *J*=7.1 Hz, 3H), 2.62 (d, *J*=13.9 Hz, 1H), 2.70 (d, *J*=13.6 Hz, 1H), 2.96 (d, *J*=13.9 Hz, 1H), 3.51 (dd, *J*=13.6, 0.8 Hz, 1H), 3.82 (s, 3H), 4.07 (s, 1H), 4.15–4.22 (m, 4H), 4.47 (br d, *J*=0.7 Hz, 1H), 4.74 (s, 1H), 6.99 (dt, *J*_d=1.0 Hz, *J*_t=7.4 Hz, 1H), 7.15–7.22 (m, 2H), 7.88 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 14.0 (CH₃), 17.0 (CH₃), 37.3 (CH₂), 45.3 (CH₂), 52.5 (CH₃), 52.8 (C), 53.2 (C), 57.6 (C), 61.9 (CH₂), 62.0 (CH₂), 73.3 (CH), 104.3 (CH₂), 115.0 (CH), 121.7 (CH), 122.5 (CH), 128.1 (CH), 131.8 (C), 146.1 (C), 154.8 (C), 156.9 (C), 171.7 (C), 171.8 (C). HRMS (ESI⁺) *m/z* 436.1730 (M+Na⁺), calcd for C₂₃H₂₇NNaO₆: 436.1731.

***rac*-(3*aR*,4*aR*,9*aR*)-3,3*a*,4,4*a*-Tetrahydro-4-methylene-1*H*-pyrrolo[3',4':2,3]cyclobut[1,2-*b*]indole-2,5-dicarboxylic acid 2-*tert*-butyl 5-methyl ester (6c) and *rac*-(4*R*,4*aS*,9*aS*)-3,4,4*a*,9*b*-Tetrahydro-4,9*b*-methano-10-methylene-1*H*-pyrido[4,3-*b*]indole-2,5-dicarboxylic acid 2-*tert*-butyl 5-methyl ester (7c) (an inseparable mixture of parallel (6c)/cross (7c) isomers, 6c:7c = 93:7)**



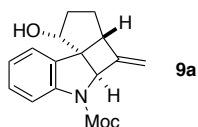
Colorless oil. IR (KBr) 2976, 2864, 1699, 1603, 1485, 1462, 1442, 1383, 1292, 1233, 1173, 1145, 1116, 909, 877, 755 cm⁻¹. Only the signals of the major isomer (6c) were shown. ¹H NMR (400 MHz, CDCl₃, at 55 °C) δ 1.50 (s, 9H), 3.37–3.40 (m, 1H), 3.48 (d, *J*=12.2 Hz, 1H), 3.54 (dd, *J*=11.4, 7.9 Hz, 1H), 3.78 (d, *J*=11.4 Hz, 1H), 3.86 (s, 3H), 4.03 (d, *J*=12.2 Hz, 1H), 5.06–5.07 (br m, 2H), 5.39 (br s, 1H), 7.01 (t, *J*=7.5 Hz, 1H), 7.18 (d, *J*=7.5 Hz, 1H), 7.25 (t, *J*=7.5 Hz, 1H), 7.87 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃, at 55 °C) δ 28.5 (CH₃), 52.46 (CH₃), 52.55 (CH₂), 53.4 (CH₂), 54.4 (C), 55.6 (CH), 68.0 (CH), 79.9 (C), 113.6 (CH₂), 115.5 (CH), 123.1 (CH), 123.2 (CH), 129.0 (CH), 130.8 (C), 144.3 (C), 149.3 (C), 153.4 (C), 154.8 (C). HRMS (ESI⁺) *m/z* 379.1629 (M+Na⁺), calcd for C₂₀H₂₄N₂NaO₄: 379.1628.

***rac*-(3*aR*,4*aR*,9*aR*)-3,3*a*,4,4*a*-Tetrahydro-4-methylene-1*H*-furo[3',4':2,3]cyclobut[1,2-*b*]indole-5-carboxylic acid methyl ester (6d)**



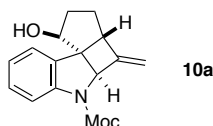
Colorless oil. IR (KBr) 2954, 2849, 1715, 1602, 1485, 1461, 1442, 1383, 1292, 1199, 1148, 1099, 1058, 917, 757 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 3.46–3.49 (m, 1H), 3.82 (d, $J=9.8$ Hz, 1H), 3.87 (s, 3H), 3.90 (dd, $J=9.3, 6.3$ Hz, 1H), 4.07 (d, $J=9.3$ Hz, 1H), 4.19 (d, $J=9.8$ Hz, 1H), 5.04 (br s, 1H), 5.05 (br s, 1H), 5.40 (br s, 1H), 7.01 (t, $J=7.4$ Hz, 1H), 7.16 (dd, $J=7.4, 0.6$ Hz, 1H), 7.23–7.27 (m, 1H), 7.89 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 52.5 (CH_3), 55.9 (C), 57.7 (CH), 67.1 (CH), 73.7 (CH_2), 74.0 (CH_2), 113.3 (CH_2), 115.3 (CH), 123.0 (CH x 2), 128.9 (CH), 129.2 (C), 144.8 (C), 149.1 (C), 153.2 (C). HRMS (ESI $^+$) m/z 280.0947 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_3$: 280.0944.

***rac*-(1*R*,3*aR*,4*aR*,9*aR*)-1,2,3,3*a*,4,4*a*-Hexahydro-1-hydroxy-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-5-carboxylic acid methyl ester (9*a*)**



Isomers **9a** and **11a** were separated by HPLC. Conditions: column, COSMOSIL (Nacalai Tesque, Inc., 20 x 250 mm); eluent: $\text{CH}_3\text{CN} : \text{H}_2\text{O} = 60:40$; flow, 5.7 mLmin^{-1} ; column temp, 40 $^\circ\text{C}$; detection, UV 254 nm; **11a**, $t_{\text{R}} = 16.2$ min, **9a**, $t_{\text{R}} = 18.2$ min. Colorless solid. IR (KBr) 3467 (br), 2952, 2867, 1702, 1601, 1484, 1460, 1444, 1385, 1230, 1199, 1149, 1110, 1090, 1058, 902, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.67 (br s, 1H), 1.68–1.73 (m, 1H), 1.89–2.05 (m, 2H), 2.17–2.23 (m, 1H), 3.18–3.20 (m, 1H), 3.86 (s, 3H), 4.49–4.53 (m, 1H), 5.01 (t, $J=2.0$ Hz, 1H), 5.27 (br s, 1H), 5.39 (br s, 1H), 7.00 (dt, $J_t=7.4$ Hz, $J_d=0.8$ Hz, 1H), 7.15 (dd, $J=7.4, 0.5$ Hz, 1H), 7.21–7.25 (m, 1H), 7.86 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 28.4 (CH_2), 32.5 (CH_2), 52.4 (CH_3), 54.9 (CH), 57.4 (C), 61.6 (CH), 76.1 (CH), 112.5 (CH_2), 115.1 (CH), 122.5 (CH), 122.9 (CH), 128.7 (CH), 131.8 (C), 145.2 (C), 151.3 (C), 153.4 (C). HRMS (ESI $^+$) m/z 294.1110 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{16}\text{H}_{17}\text{NNaO}_3$: 294.1102.

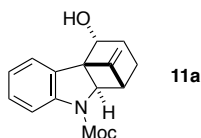
***rac*-(1*R*,3*aS*,4*aS*,9*aS*)-1,2,3,3*a*,4,4*a*-Hexahydro-1-hydroxy-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-5-carboxylic acid methyl ester (10*a*)**



Colorless oil. IR (KBr) 3458 (br), 2953, 1697, 1599, 1484, 1444, 1384, 1309, 1288, 1198, 1154, 1086, 1053, 993, 913, 755 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.73–1.78 (m, 2H), 2.02–2.08 (m, 1H), 2.12–2.21 (m, 1H), 2.27–2.37 (m, 1H), 3.33–3.35 (m, 1H), 3.86 (s, 3H), 4.27 (d, $J=3.0$ Hz, 1H), 4.72 (br s, 1H), 5.03 (t, $J=3.0$ Hz, 1H), 5.35 (br s, 1H), 7.00 (dt, $J_t=7.5$ Hz, $J_d=1.0$ Hz, 1H), 7.22–7.26 (m, 1H), 7.50 (d, $J=7.5$ Hz, 1H),

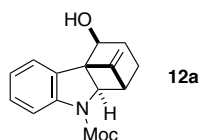
7.90 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 30.7 (CH_2), 35.1 (CH_2), 52.4 (CH_3), 55.5 (CH), 58.1 (C), 65.0 (CH), 77.3 (CH), 113.1 (CH_2), 115.1 (CH), 123.1 (CH), 125.8 (CH), 128.4 (CH), 131.4 (C), 144.7 (C), 151.2 (C), 153.1 (C). HRMS (ESI^+) m/z 294.1102 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{16}\text{H}_{17}\text{NNaO}_3$: 294.1102.

***rac*-(1*R*,4*S*,4*aS*,9*aS*)-1,2,3,4,4*a*,9*a*-Hexahydro-4-hydroxy-1,4*a*-methano-10-methylene-9*H*-carbazole-9-carboxylic acid methyl ester (11a)**



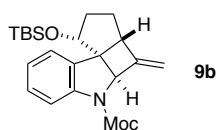
Colorless solid. IR (KBr) 3432 (br), 2954, 2868, 1698, 1604, 1479, 1459, 1444, 1379, 1345, 1207, 1067, 885, 752 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.63 (br s, 1H), 1.72–1.79 (m, 1H), 2.10–2.29 (m, 3H), 3.43 (d, $J=3.5$ Hz, 1H), 3.85 (s, 3H), 4.40 (s, 1H), 4.57 (s, 1H), 4.84–4.86 (m, 2H), 6.99 (t, $J=7.4$ Hz, 1H), 7.14 (d, $J=7.4$ Hz, 1H), 7.19–7.23 (m, 1H), 7.81 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.3 (CH_2), 29.7 (CH_2), 49.2 (CH), 52.7 (CH_3), 64.4 (CH), 66.1 (C), 71.6 (CH), 104.8 (CH_2), 115.2 (CH), 121.3 (CH), 122.5 (CH), 128.4 (CH), 130.2 (C), 147.0 (C), 154.5 (C), 154.7 (C). HRMS (ESI^+) m/z 294.1101 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{16}\text{H}_{17}\text{NNaO}_3$: 294.1102.

***rac*-(1*R*,4*R*,4*aS*,9*aS*)-1,2,3,4,4*a*,9*a*-Hexahydro-4-hydroxy-1,4*a*-methano-10-methylene-9*H*-carbazole-9-carboxylic acid methyl ester (12a)**



Colorless solid. IR (KBr) 3449 (br), 2954, 2866, 1701, 1601, 1478, 1459, 1444, 1377, 1342, 1205, 1152, 1115, 1061, 1016, 886, 765, 756 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 1.62–1.71 (m, 1H), 1.87 (d, $J=8.8$ Hz, 1H), 1.96–2.03 (m, 1H), 2.16–2.33 (m, 2H), 3.43 (br s, 1H), 3.85 (s, 3H), 3.91 (s, 1H), 4.58–4.63 (m, 1H), 4.73 (s, 1H), 4.99 (s, 1H), 6.96 (t, $J=7.4$ Hz, 1H), 7.20 (dt, $J_t=7.8$ Hz, $J_d=1.3$ Hz, 1H), 7.52 (dd, $J=7.4$, 1.2 Hz, 1H), 7.75 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ 28.9 (CH_2), 29.5 (CH_2), 48.7 (CH), 52.6 (CH_3), 64.6 (C), 67.3 (CH), 75.4 (CH), 106.4 (CH_2), 115.0 (CH), 122.7 (CH), 123.7 (CH), 128.1 (CH), 132.3 (C), 146.2 (C), 152.3 (C), 154.3 (C). HRMS (ESI^+) m/z 294.1099 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{16}\text{H}_{17}\text{NNaO}_3$: 294.1102.

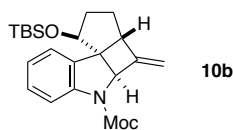
***rac*-(1*R*,3*aR*,4*aR*,9*aR*)-1-(*tert*-Butyldimethylsilyloxy)-1,2,3,3*a*,4,4*a*-hexahydro-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-5-carboxylic acid methyl ester (9b)**



Colorless oil. IR (KBr) 2953, 2857, 1715, 1601, 1484, 1461, 1442, 1312, 1251, 1197, 1125, 1059, 855, 837,

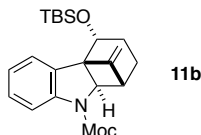
777, 751 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -0.31 (s, 3H), -0.05 (s, 3H), 0.73 (s, 9H), 1.66–1.71 (m, 1H), 1.85–2.21 (m, 3H), 3.12–3.14 (m, 1H), 3.87 (s, 3H), 4.47 (dd, $J=9.5, 6.3$ Hz, 1H), 4.99 (t, $J=2.0$ Hz, 1H), 5.25 (br s, 1H), 5.37 (br s, 1H), 6.96–7.00 (m, 1H), 7.11 (d, $J=6.4$ Hz, 1H), 7.18–7.21 (m, 1H), 7.83 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -5.0 (CH_3), -4.9 (CH_3), 17.9 (C), 25.6 (CH_3), 28.5 (CH_2), 34.1 (CH_2), 52.3 (CH_3), 54.5 (CH), 57.6 (C), 62.3 (CH), 76.7 (CH), 112.1 (CH_2), 115.1 (CH), 122.6 (CH x 2), 128.3 (CH), 133.0 (C), 145.2 (C), 152.0 (C), 153.7 (C). HRMS (ESI $^+$) m/z 408.1962 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{21}\text{H}_{31}\text{NNaO}_3\text{Si}$: 408.1965.

***rac*-(1*R*,3*aS*,4*aS*,9*aS*)-1-(*tert*-Butyldimethylsilyloxy)-1,2,3,3*a*,4,4*a*-hexahydro-4-methylene-5*H*-cyclopenta[2,3]cyclobut[1,2-*b*]indole-5-carboxylic acid methyl ester (**10b**)**



Isomers **10b** and **11b** were separated by HPLC. Conditions: column, COSMOSIL (Nacalai Tesque, Inc., 20 x 250 mm); eluent: CH_3CN ; flow, 5.7 mLmin^{-1} ; column temp, 40 $^\circ\text{C}$; detection, UV 254 nm; **11b**, $t_{\text{R}} = 17.6$ min, **10b**, $t_{\text{R}} = 20.6$ min. Colorless oil. IR (KBr) 2954, 2930, 2857, 1720, 1601, 1483, 1461, 1442, 1382, 1309, 1288, 1256, 1198, 1087, 1055, 1019, 898, 876, 829, 775, 752 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -0.04 (s, 3H), 0.03 (s, 3H), 0.94 (s, 9H), 1.69 (dd, $J=12.3, 6.5$ Hz, 1H), 1.97 (dd, $J=13.3, 6.7$ Hz, 1H), .208 (ddd, $J=13.3, 6.5, 3.5$ Hz, 1H), 2.24–2.34 (m, 1H), 3.28–3.30 (m, 1H), 3.86 (s, 3H), 4.22 (d, $J=3.3$ Hz, 1H), 4.70 (br s, 1H), 5.00 (t, $J=2.0$ Hz, 1H), 5.32 (br s, 1H), 6.94 (t, $J=7.5$ Hz, 1H), 7.20 (d, $J=7.5$ Hz, 1H), 7.52 (d, $J=7.5$ Hz, 1H), 7.85 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -4.8 (CH_3), -4.4 (CH_3), 18.2 (C), 26.0 (CH_3), 30.6 (CH_2), 36.0 (CH_2), 52.3 (CH_3), 56.0 (CH), 58.2 (C), 65.5 (CH), 78.3 (CH), 112.8 (CH_2), 114.8 (CH), 122.5 (CH), 127.4 (CH), 128.1 (CH), 132.0 (C), 144.4 (C), 151.9 (C), 153.3 (C). HRMS (ESI $^+$) m/z 408.1968 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{21}\text{H}_{31}\text{NNaO}_3\text{Si}$: 408.1965.

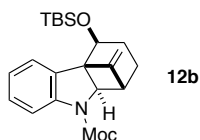
***rac*-(1*R*,4*S*,4*aS*,9*aS*)-4-(*tert*-Butyldimethylsilyloxy)-1,2,3,4,4*a*,9*a*-hexahydro-1,4*a*-methano-10-methylene-9*H*-carbazole-9-carboxylic acid methyl ester (**11b**)**



Colorless oil. IR (KBr) 2954, 2857, 1716, 1605, 1479, 1460, 1442, 1378, 1344, 1254, 1204, 1173, 1084, 839, 775, 763, 751 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -0.09 (s, 3H), 0.08 (s, 3H), 0.76 (s, 9H), 1.62–1.71 (m, 1H), 2.06–2.25 (m, 3H), 3.42 (d, $J=4.0$ Hz, 1H), 3.85 (s, 3H), 4.40 (s, 1H), 4.53 (s, 1H), 4.81 (s, 1H), 4.85 (d, $J=3.8$ Hz, 1H), 6.93 (t, $J=7.3$ Hz, 1H), 7.14 (d, $J=7.3$ Hz, 1H), 7.14–7.18 (m, 1H), 7.75 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , at 55 $^\circ\text{C}$) δ -4.8 (CH_3), -4.4 (CH_3), 18.0 (C), 25.7 (CH_3), 29.5 (CH_2), 29.6 (CH_2), 49.5 (CH), 52.4 (CH_3), 65.0 (CH), 66.7 (C), 72.3 (CH), 104.4 (CH_2), 115.0 (CH), 121.8 (CH), 122.0 (CH),

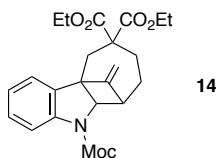
127.8 (CH), 131.7 (C), 146.5 (C), 154.7 (C), 155.3 (C). HRMS (ESI⁺) *m/z* 408.1968 (M+Na⁺), calcd for C₂₁H₃₁NNaO₃Si: 408.1965.

***rac*-(1*R*,4*R*,4*aS*,9*aS*)-4-(*tert*-Butyldimethylsilyloxy)-1,2,3,4,4*a*,9*a*-hexahydro-1,4*a*-methano-10-methylene-9*H*-carbazole-9-carboxylic acid methyl ester (12b)**



Colorless solid. IR (KBr) 2952, 2929, 2858, 1723, 1602, 1476, 1460, 1446, 1377, 1336, 1251, 1213, 1157, 1121, 1060, 877, 837, 772 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, at 55 °C) δ 0.12 (s, 3H), 0.13 (s, 3H), 0.99 (s, 9H), 1.70–1.80 (m, 1H), 1.83–1.91 (m, 1H), 2.08–2.19 (m, 2H), 3.38 (d, *J*=4.6 Hz, 1H), 3.76 (s, 1H), 3.84 (s, 3H), 4.57 (t, *J*=6.8 Hz, 1H), 4.68 (d, *J*=1.1 Hz, 1H), 4.90 (s, 1H), 6.93 (dt, *J*_d=1.0 Hz, *J*_t=7.5 Hz, 1H), 7.15–7.19 (m, 1H), 7.53 (dd, *J*=7.5, 1.4 Hz, 1H), 7.75 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃, at 55 °C) δ -4.3 (CH₃), -3.9 (CH₃), 18.1 (C), 26.0 (CH₃), 28.9 (CH₂), 30.4 (CH₂), 48.5 (CH), 52.5 (CH₃), 64.3 (C), 68.1 (CH), 76.2 (CH), 106.0 (CH₂), 114.8 (CH), 122.3 (CH), 124.5 (CH), 127.8 (CH), 132.8 (C), 146.2 (C), 151.4 (C), 154.3 (C). HRMS (ESI⁺) *m/z* 408.1964 (M+Na⁺), calcd for C₂₁H₃₁NNaO₃Si: 408.1965.

6,7,8,9,10,10*a*-Hexahydro-6,10*a*-methano-11-methylene-cyclohept[*b*]indole-5(5*aH*),9,9-tricarboxylic acid 9,9-diethyl 5-methyl ester (14)

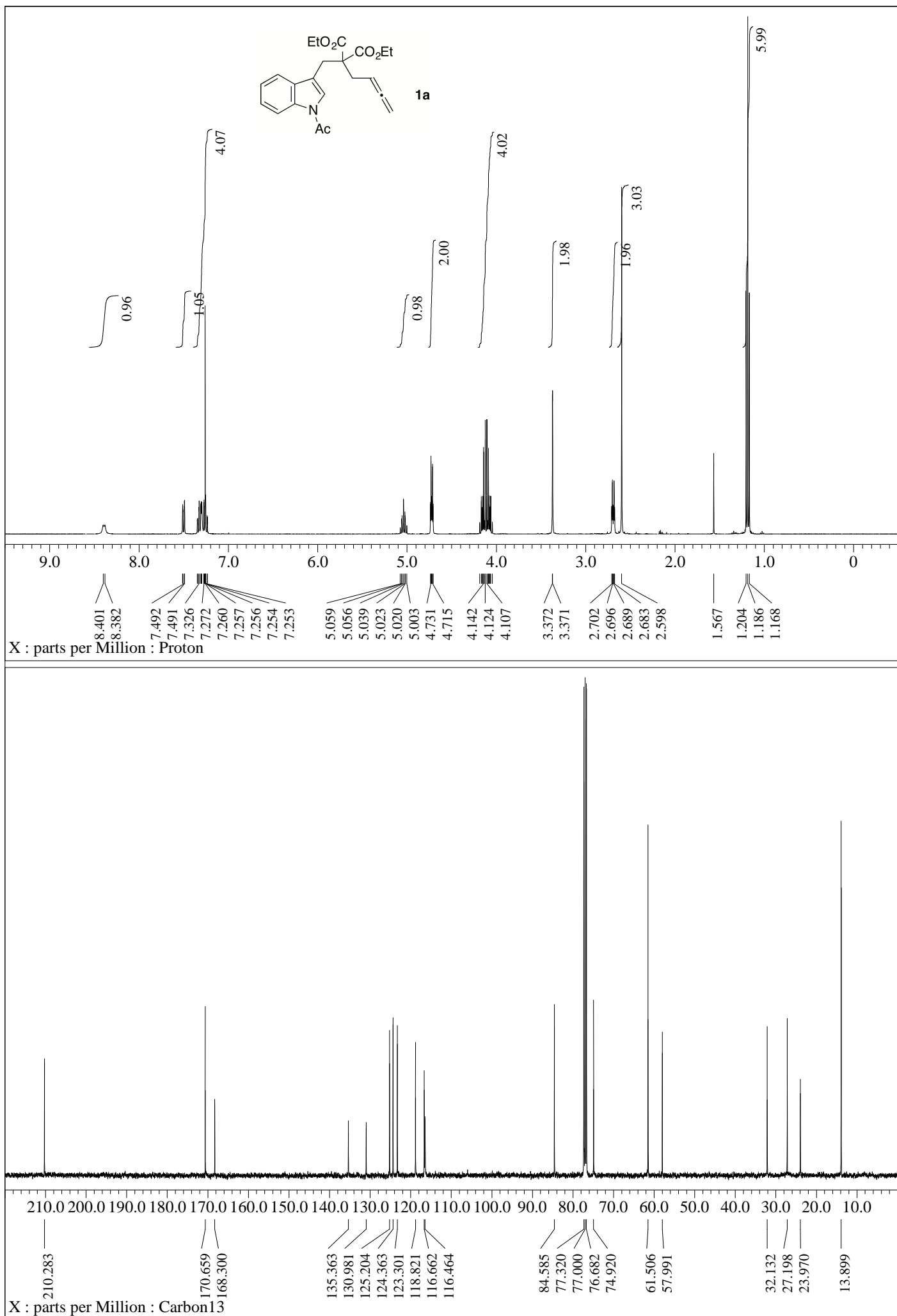


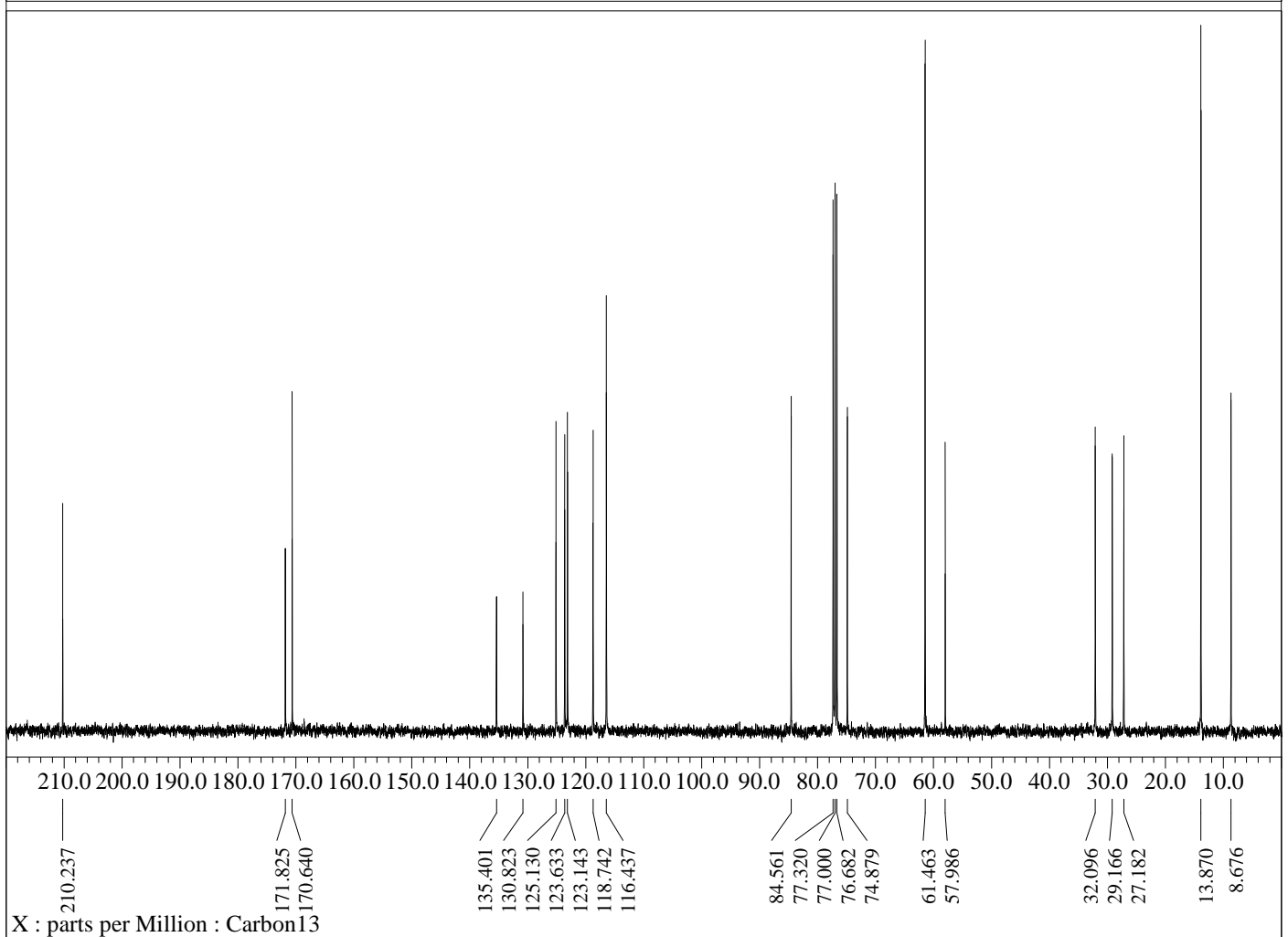
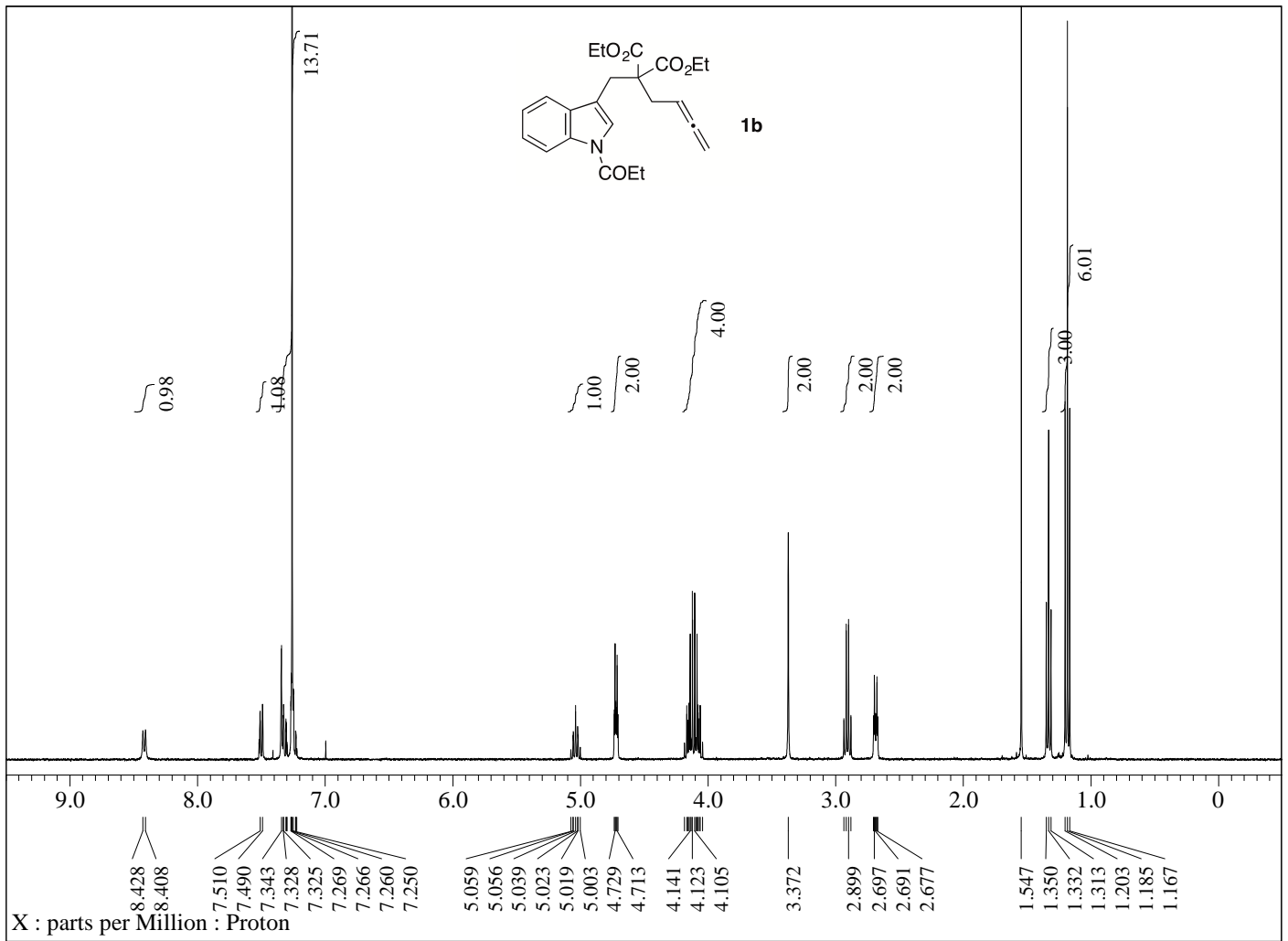
Colorless oil. IR (KBr) 2980, 2955, 1725, 1601, 1480, 1442, 1383, 1331, 1240, 1202, 1131, 1094, 1062, 1025, 887, 863, 760 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, at 55 °C) δ 1.26 (t, *J*=7.1 Hz, 3H), 1.29 (t, *J*=7.1 Hz, 3H), 2.26–2.10 (m, 2H), 2.22–2.29 (m, 1H), 2.46–2.52 (m, 2H), 3.03 (d, *J*=14.0 Hz, 1H), 3.26 (br s, 1H), 3.83 (br s, 3H), 4.05–4.24 (m, 4H), 4.33 (br s, 1H), 4.66 (dd, *J*=1.7, 0.7 Hz, 1H), 4.88 (br s, 1H), 6.98 (dt, *J*_d=1.0 Hz, *J*_t=7.5 Hz, 1H), 7.16–7.20 (m, 2H), 7.78 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃, at 55 °C) δ 13.9 (CH₃ x 2), 26.4 (CH₂), 29.8 (CH₂), 34.5 (CH₂), 49.1 (CH), 52.5 (CH₃), 57.4 (C), 58.7 (C), 61.4 (CH₂), 61.8 (CH₂), 65.7 (CH), 109.7 (CH₂), 114.9 (CH), 121.4 (CH), 122.7 (CH), 128.1 (CH), 135.0 (C), 144.6 (C), 149.4 (C), 153.9 (C x 2, confirmed by HMBC), 171.0 (C), 172.1 (C). HRMS (ESI⁺) *m/z* 436.1726 (M+Na⁺), calcd for C₂₃H₂₇NNaO₆: 436.1731.

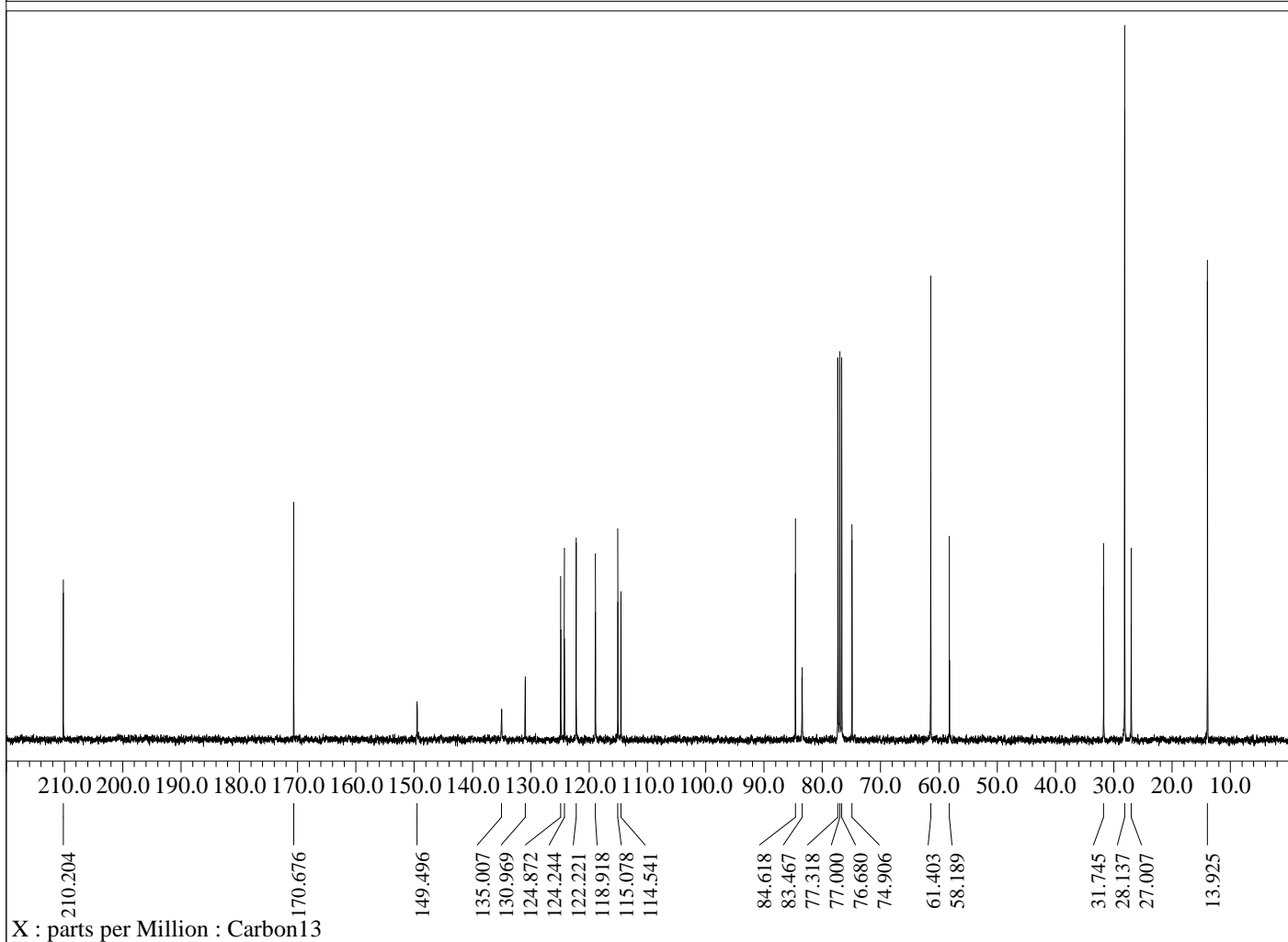
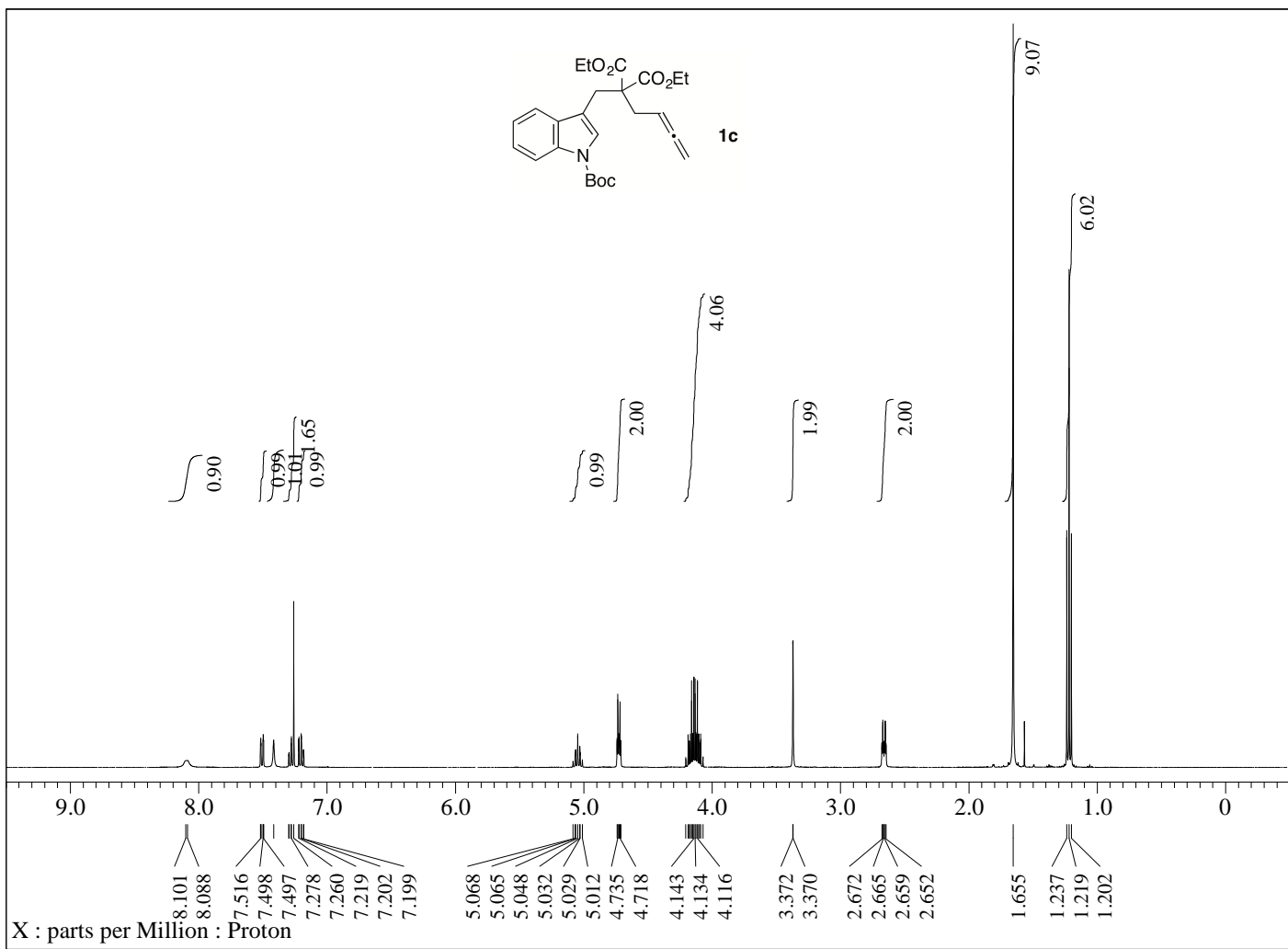
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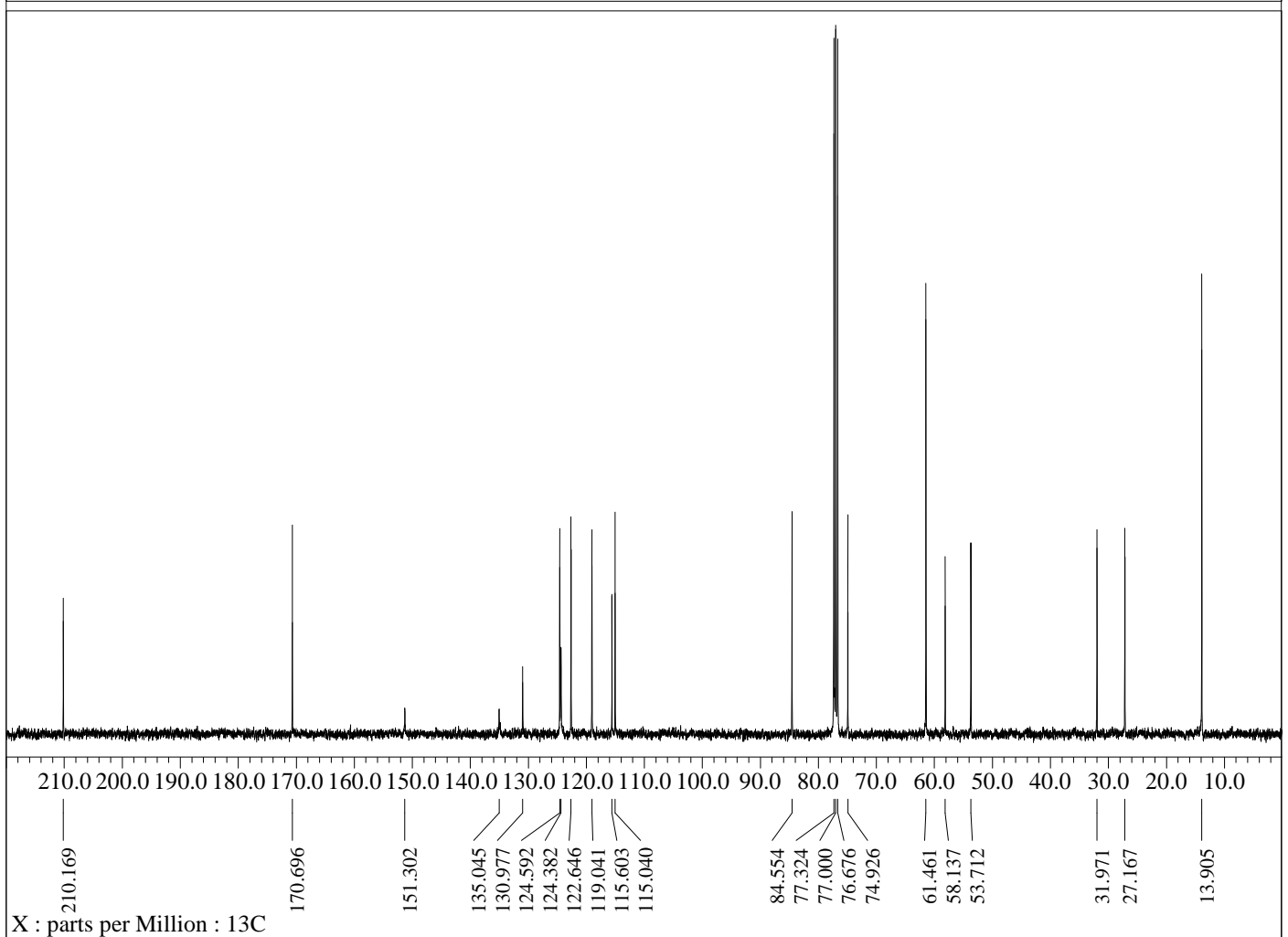
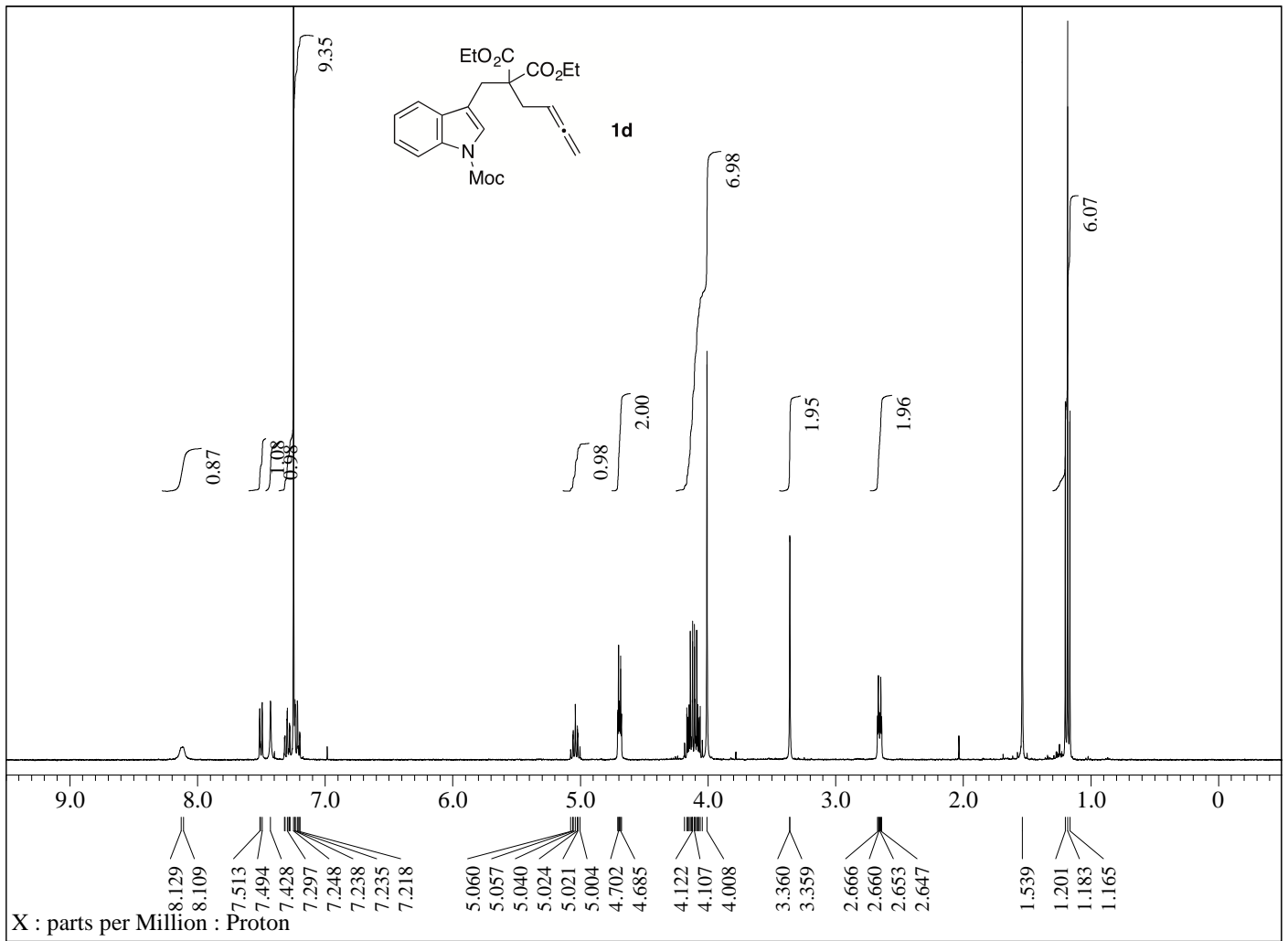
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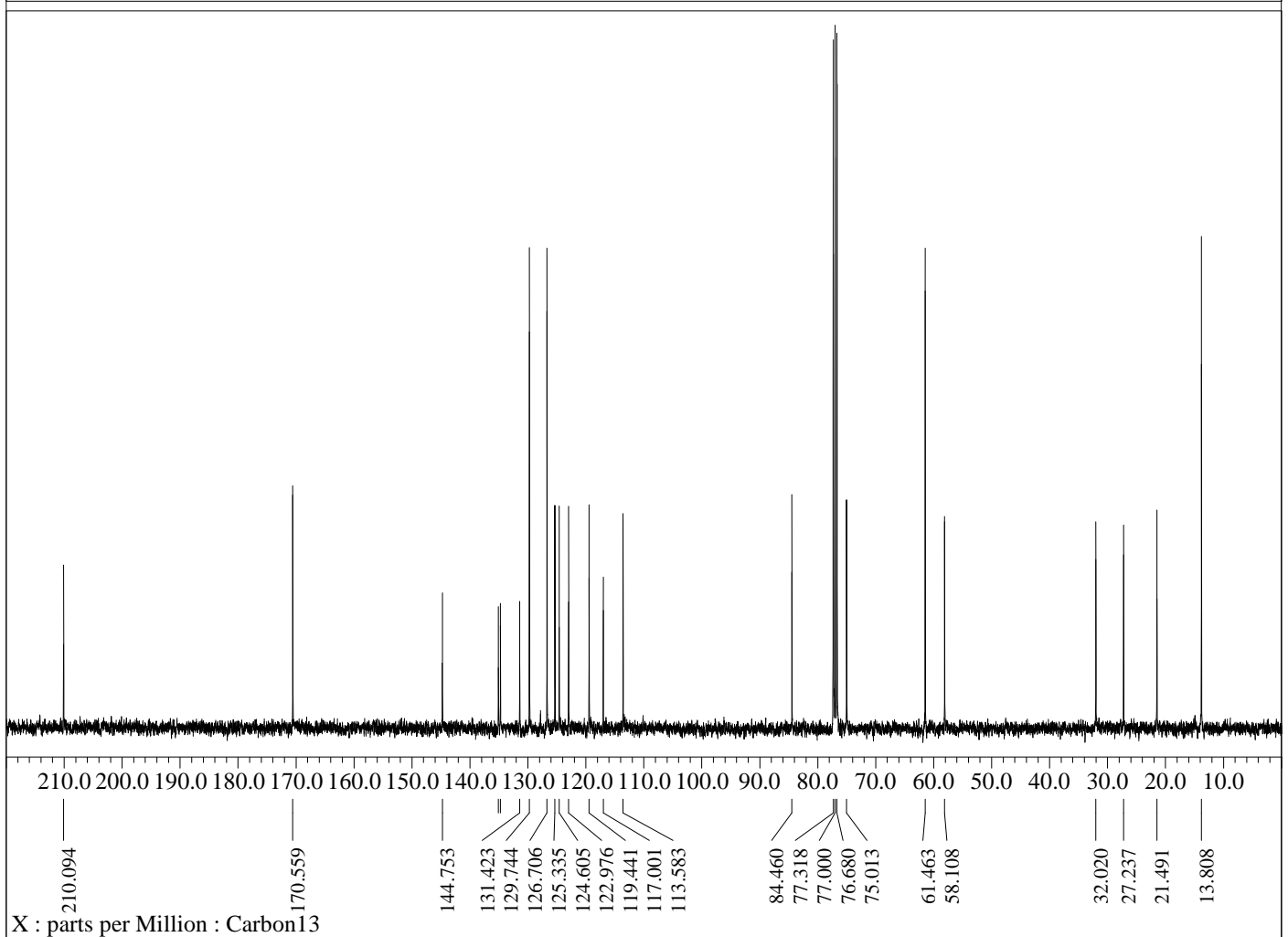
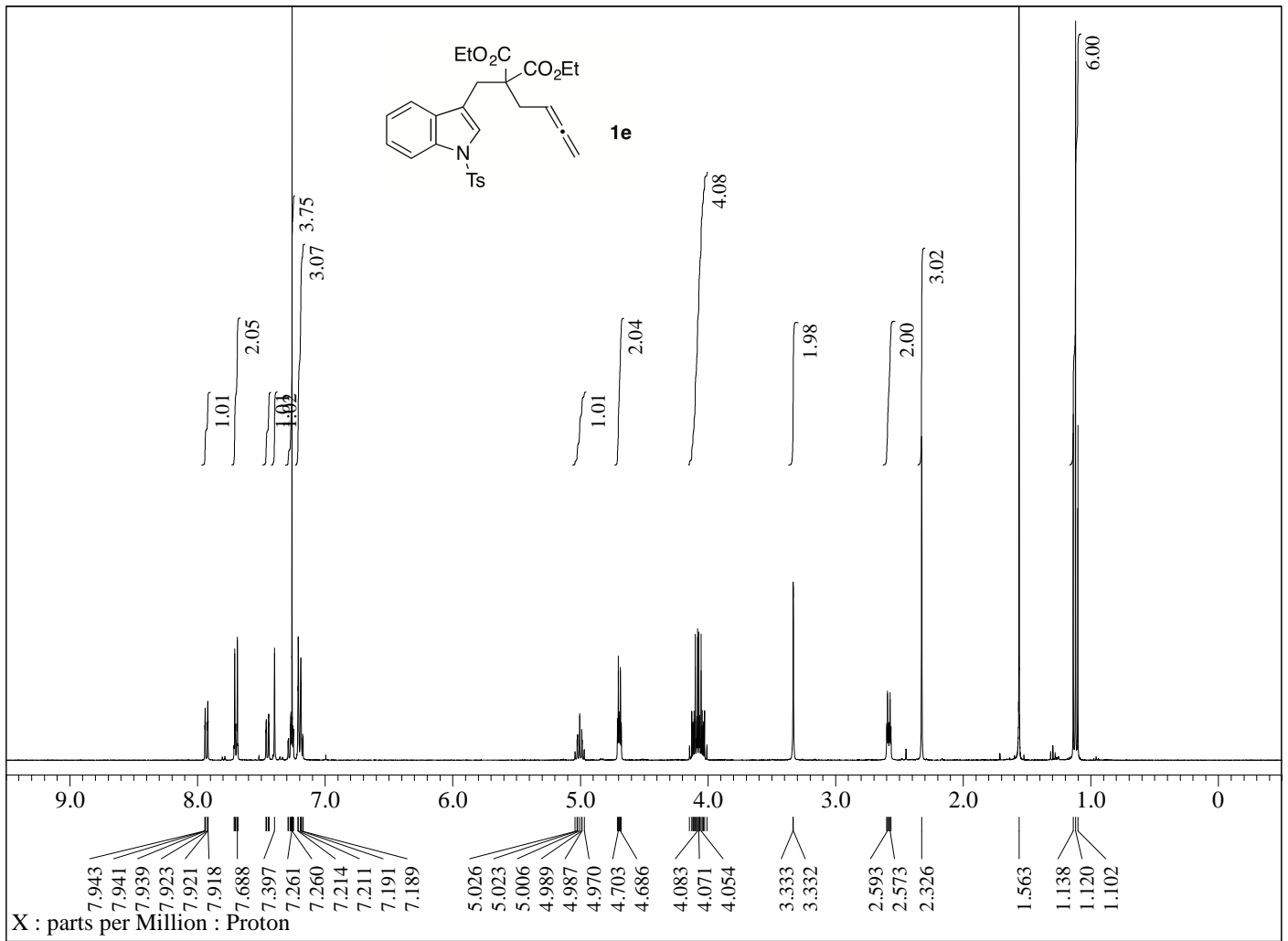
¹H and ¹³C NMR charts of the starting materials

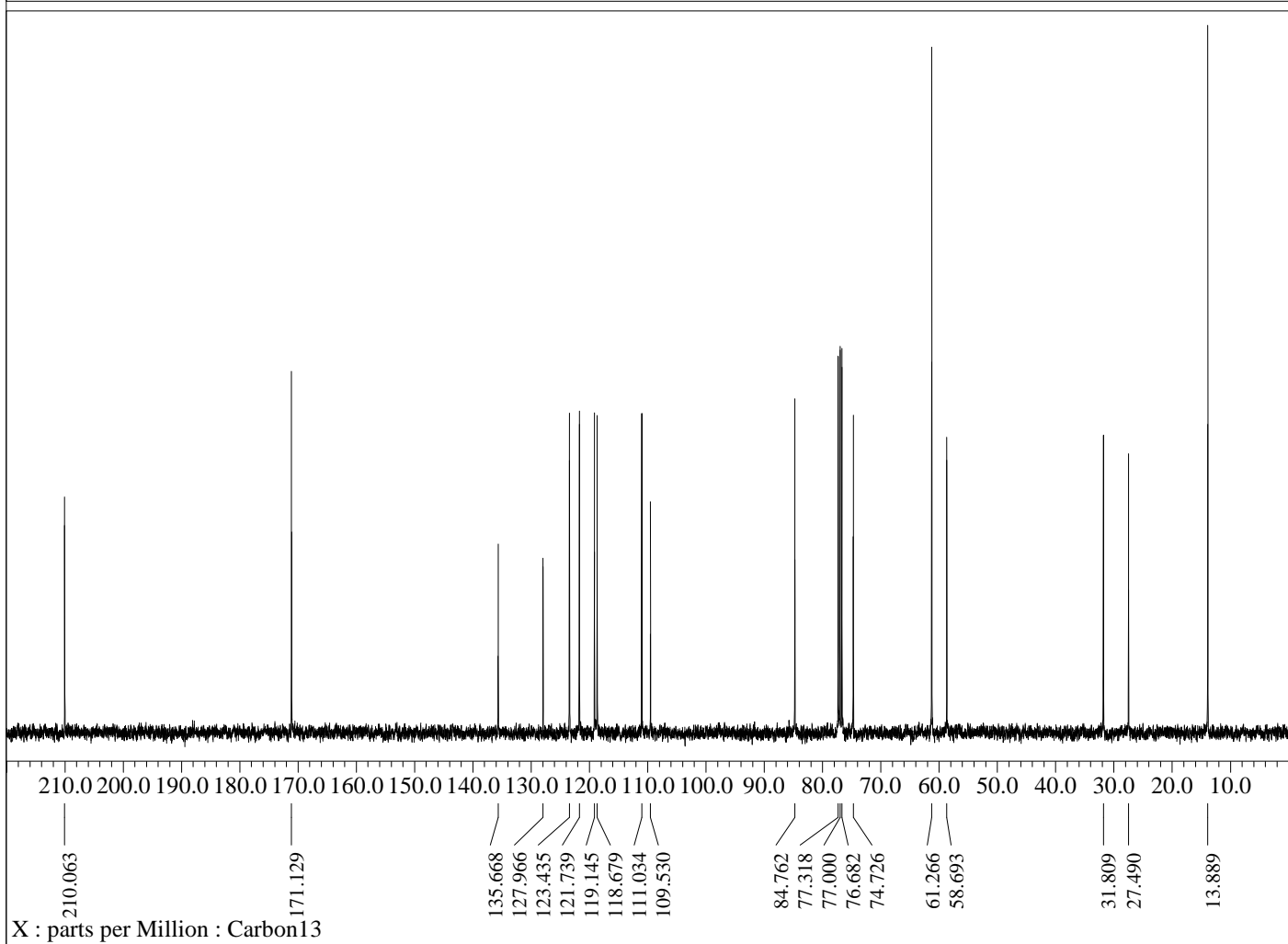
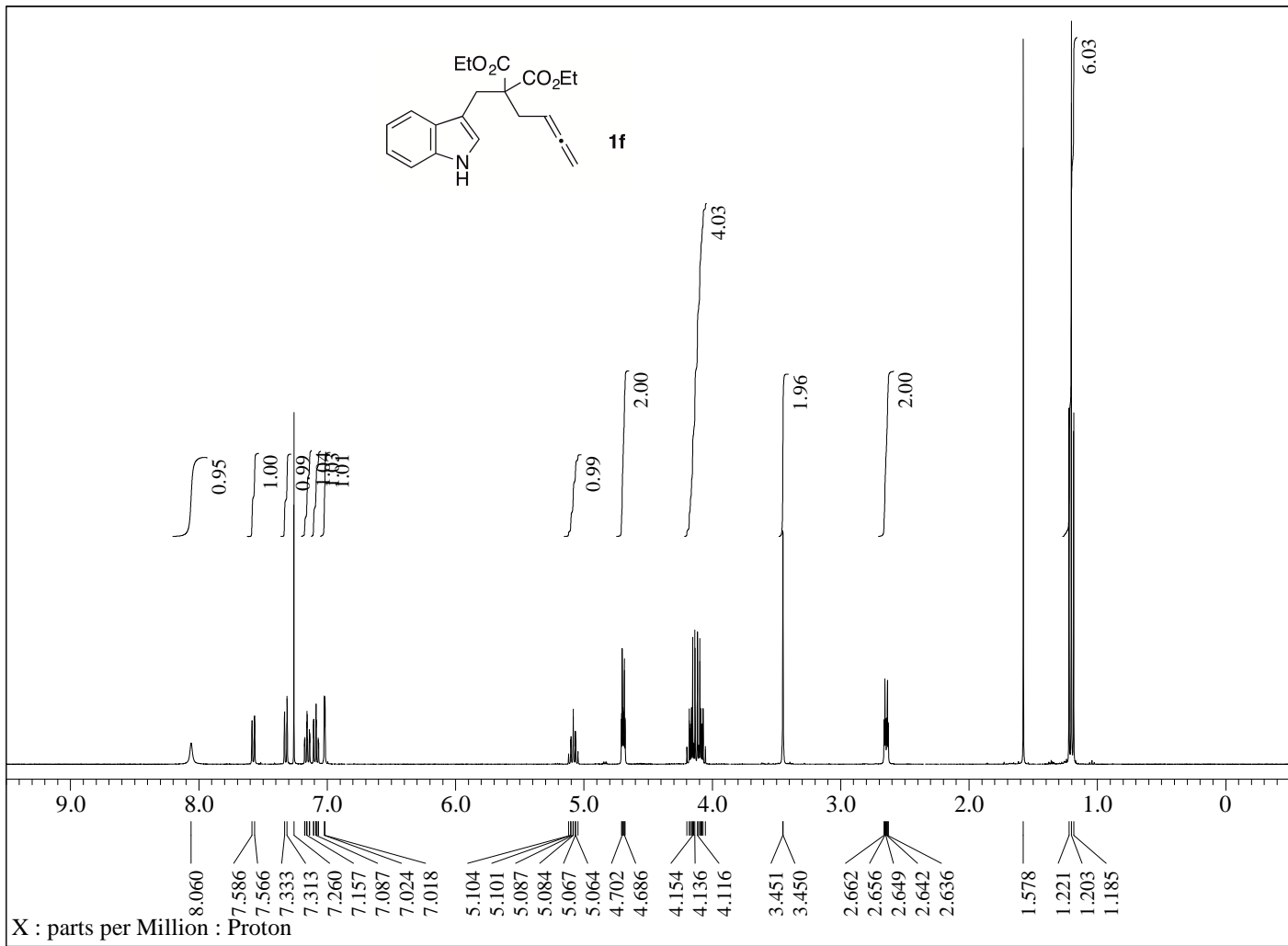


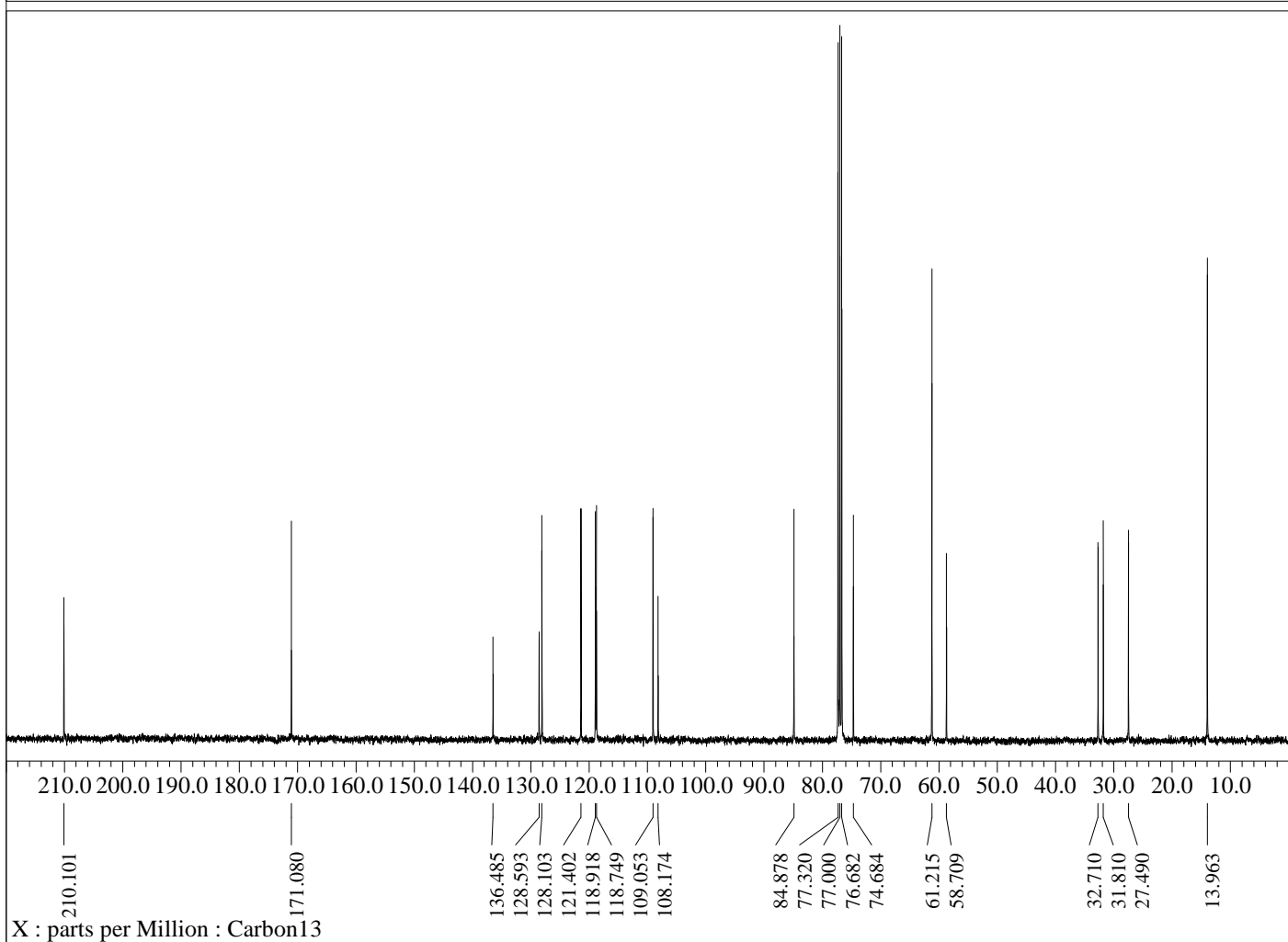
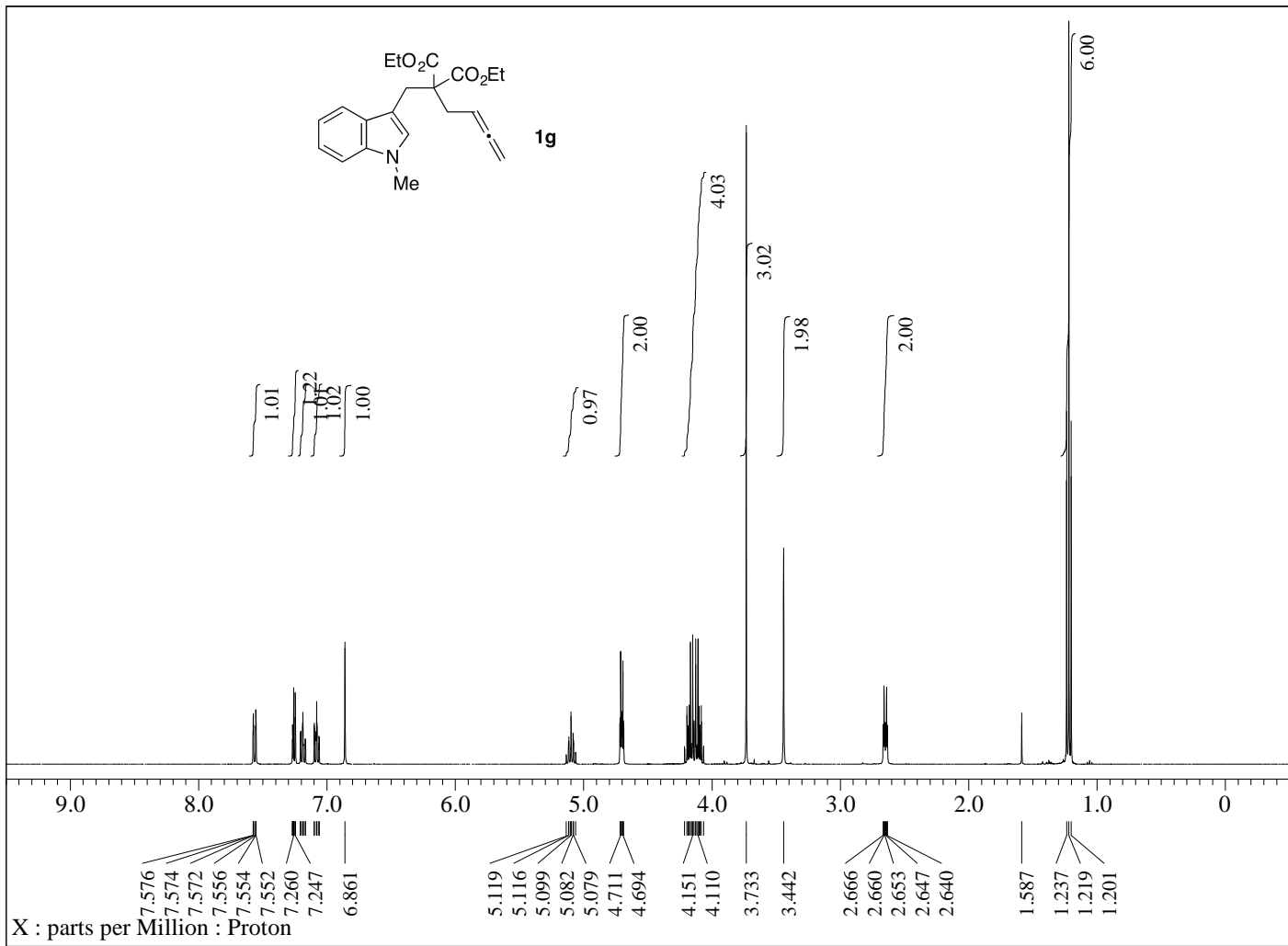


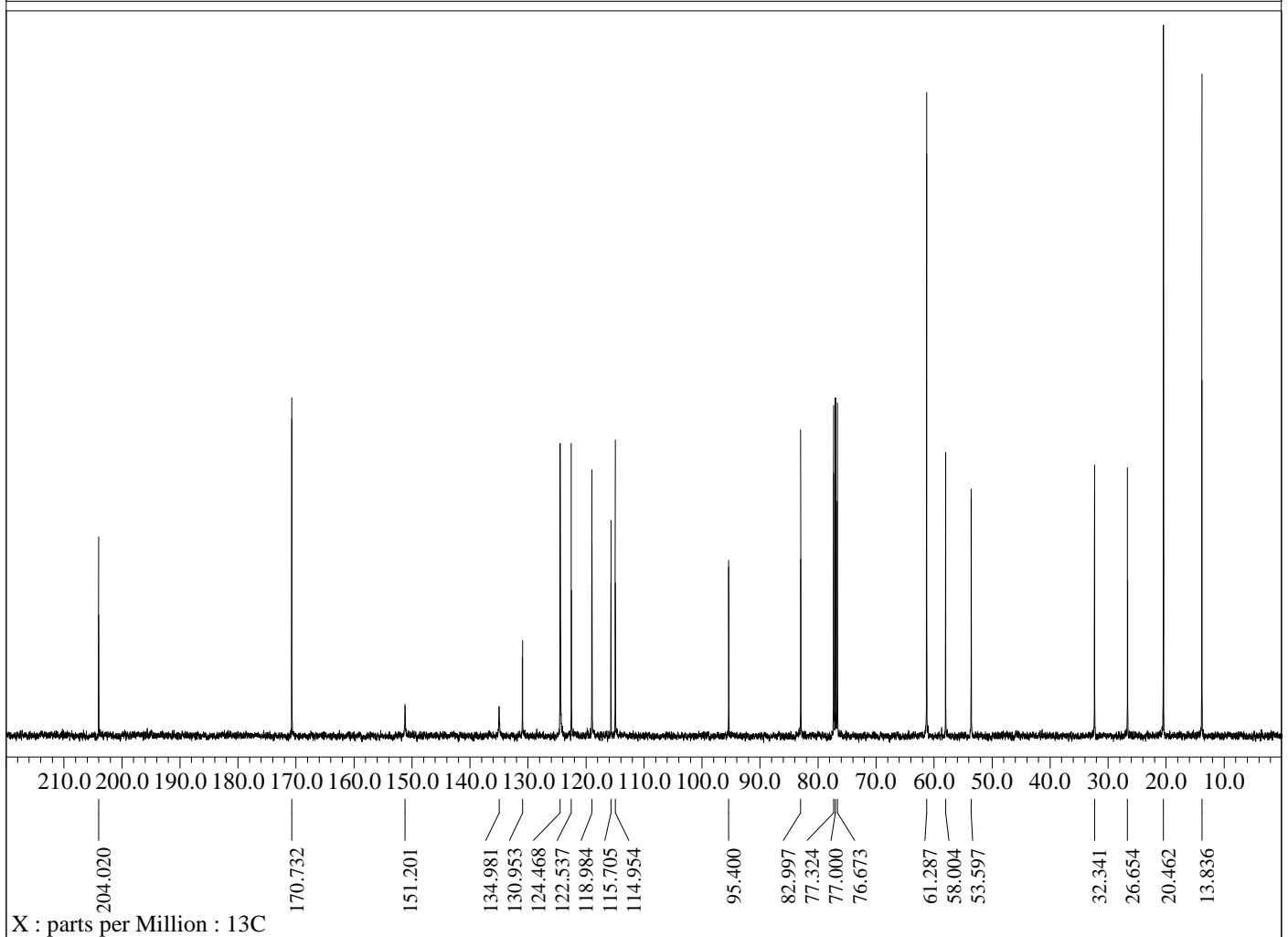
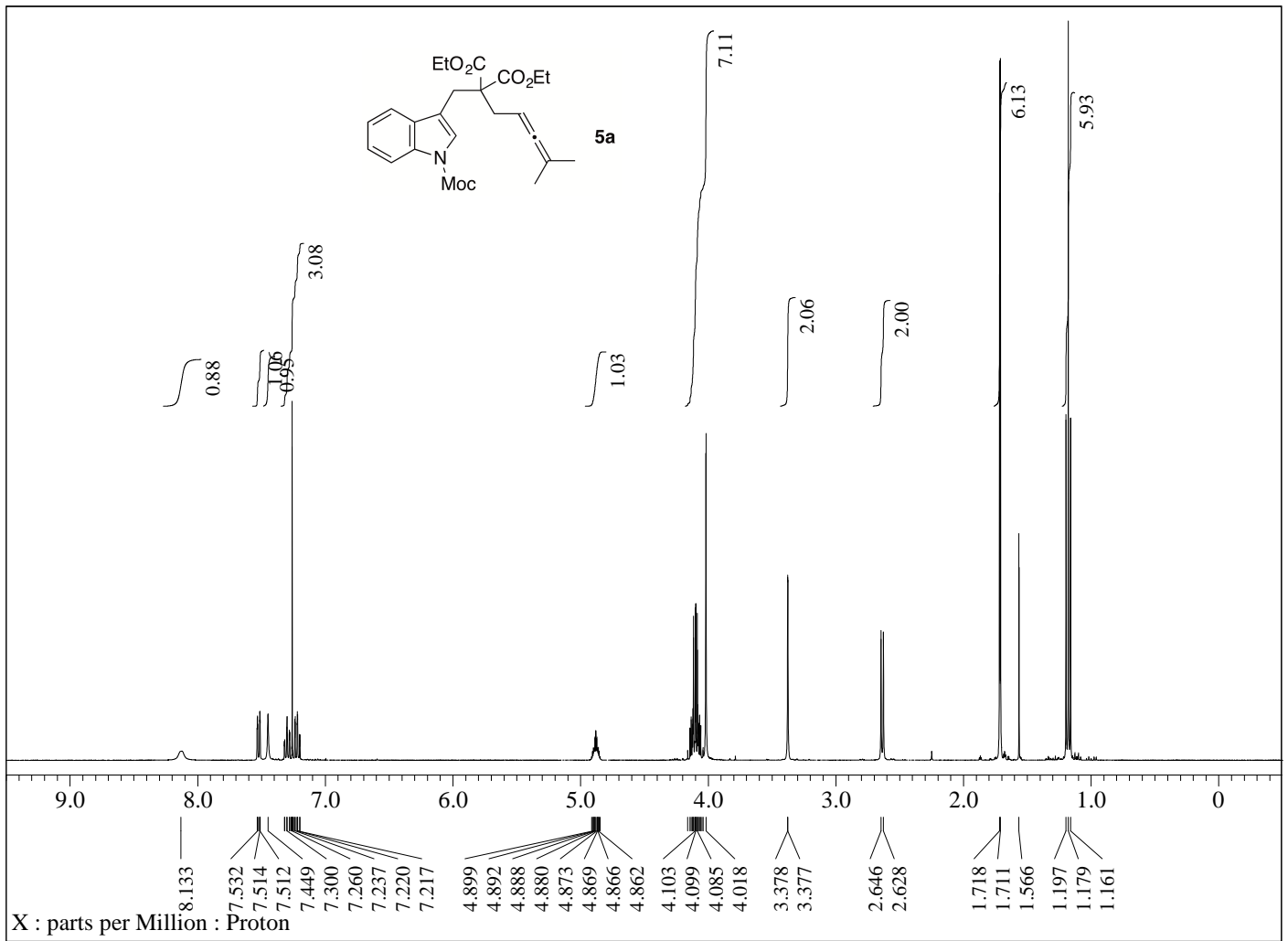


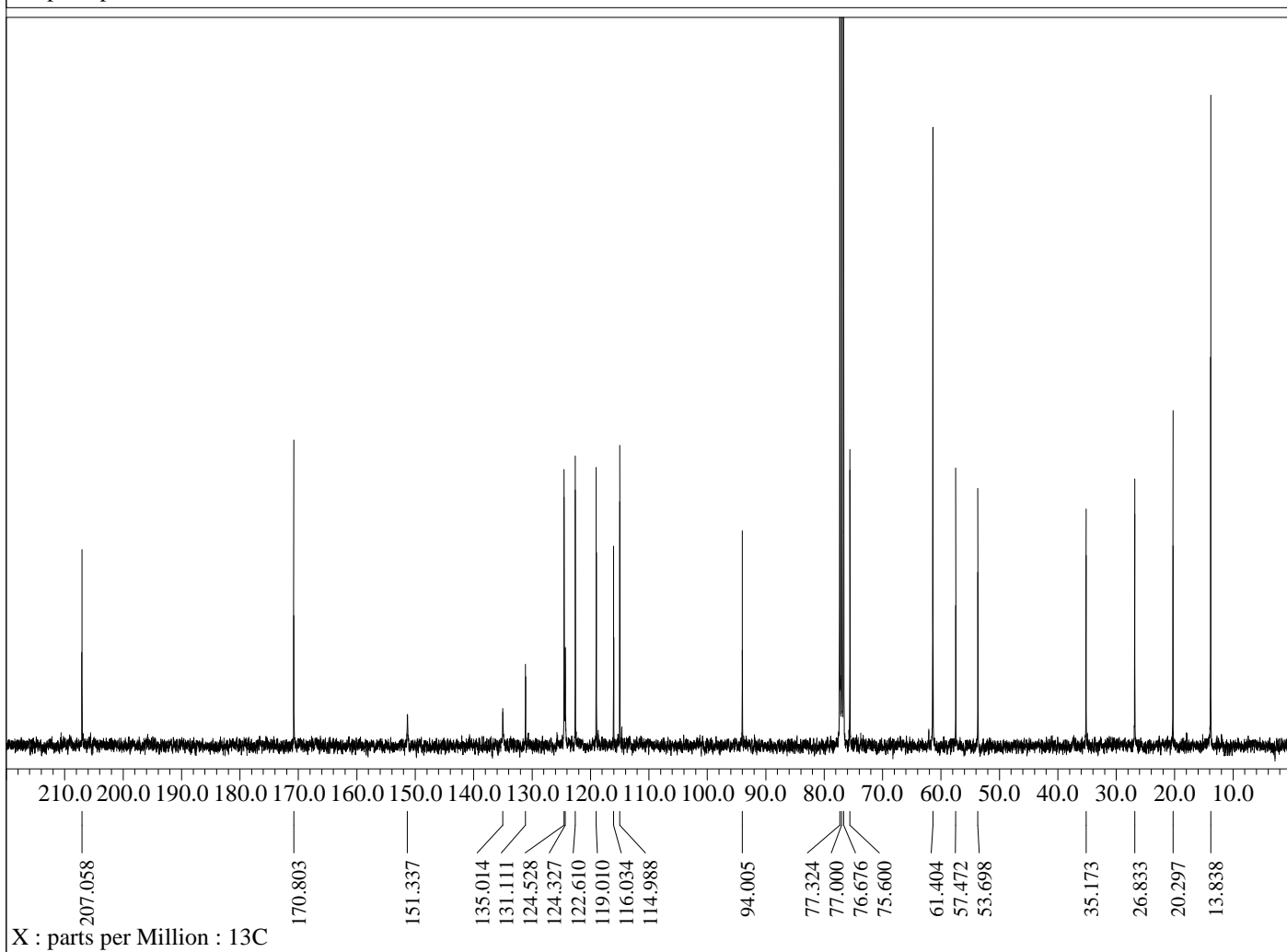
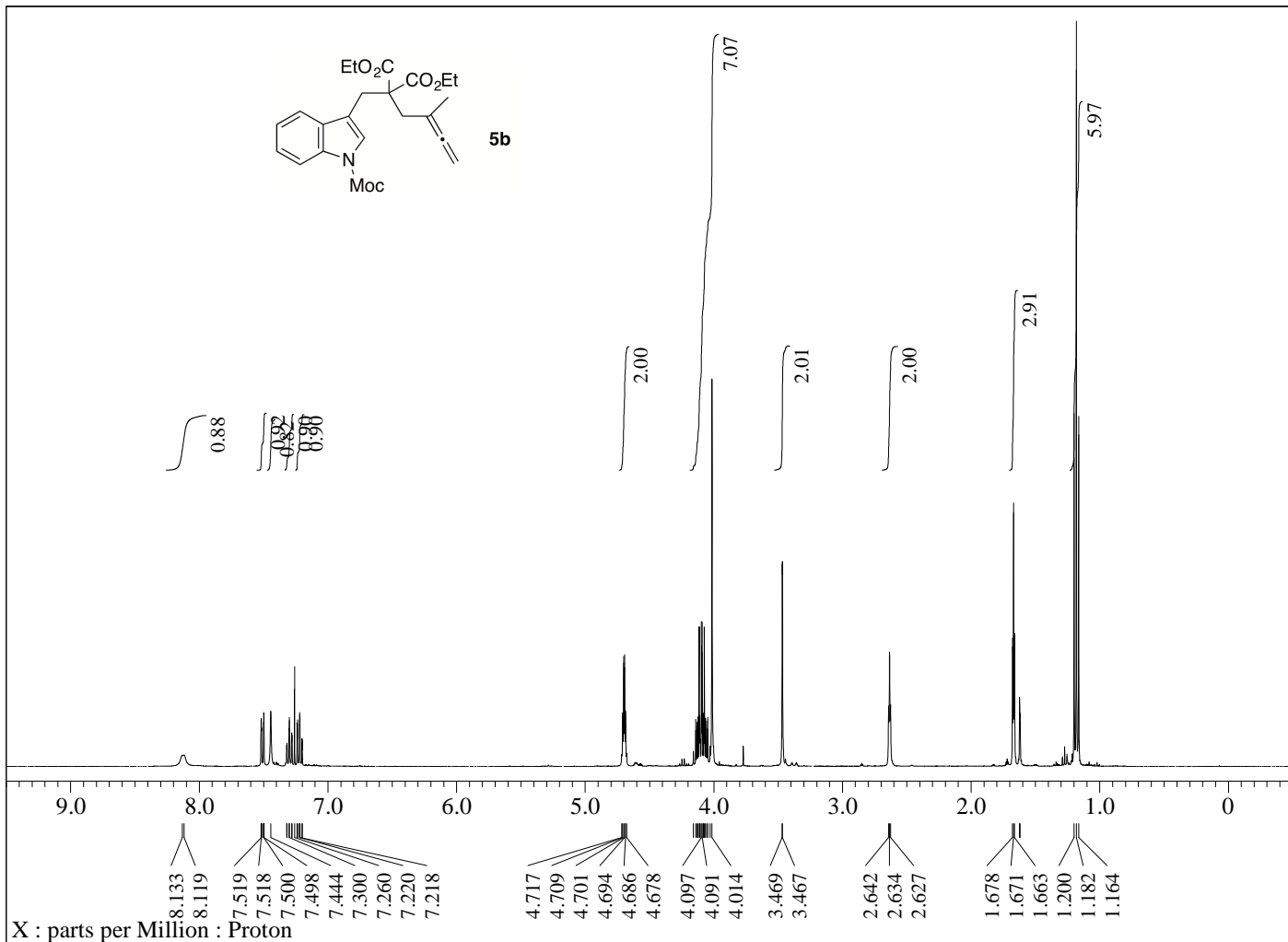
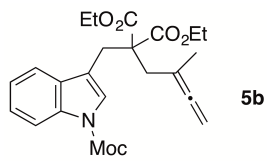


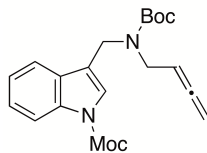




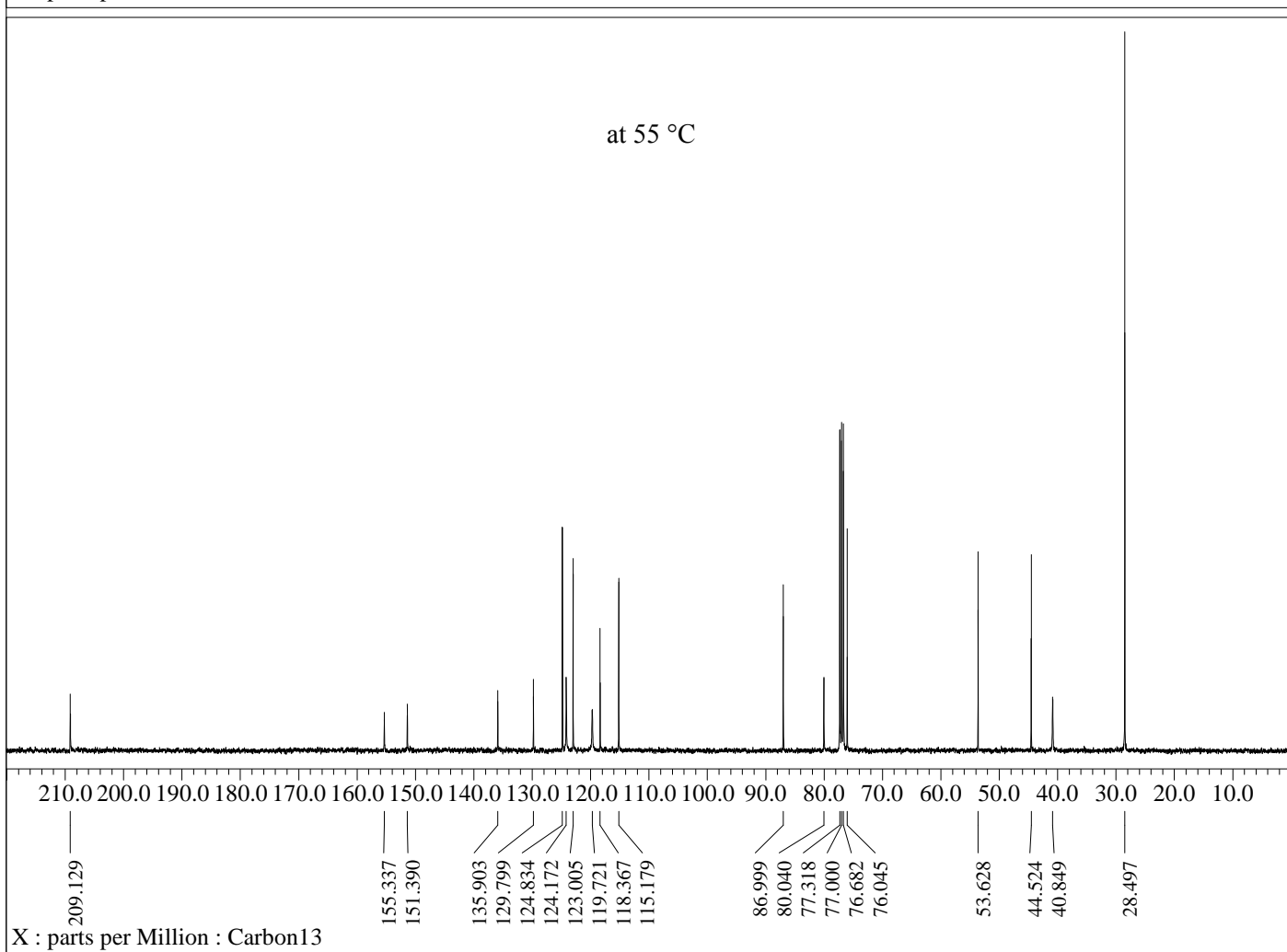
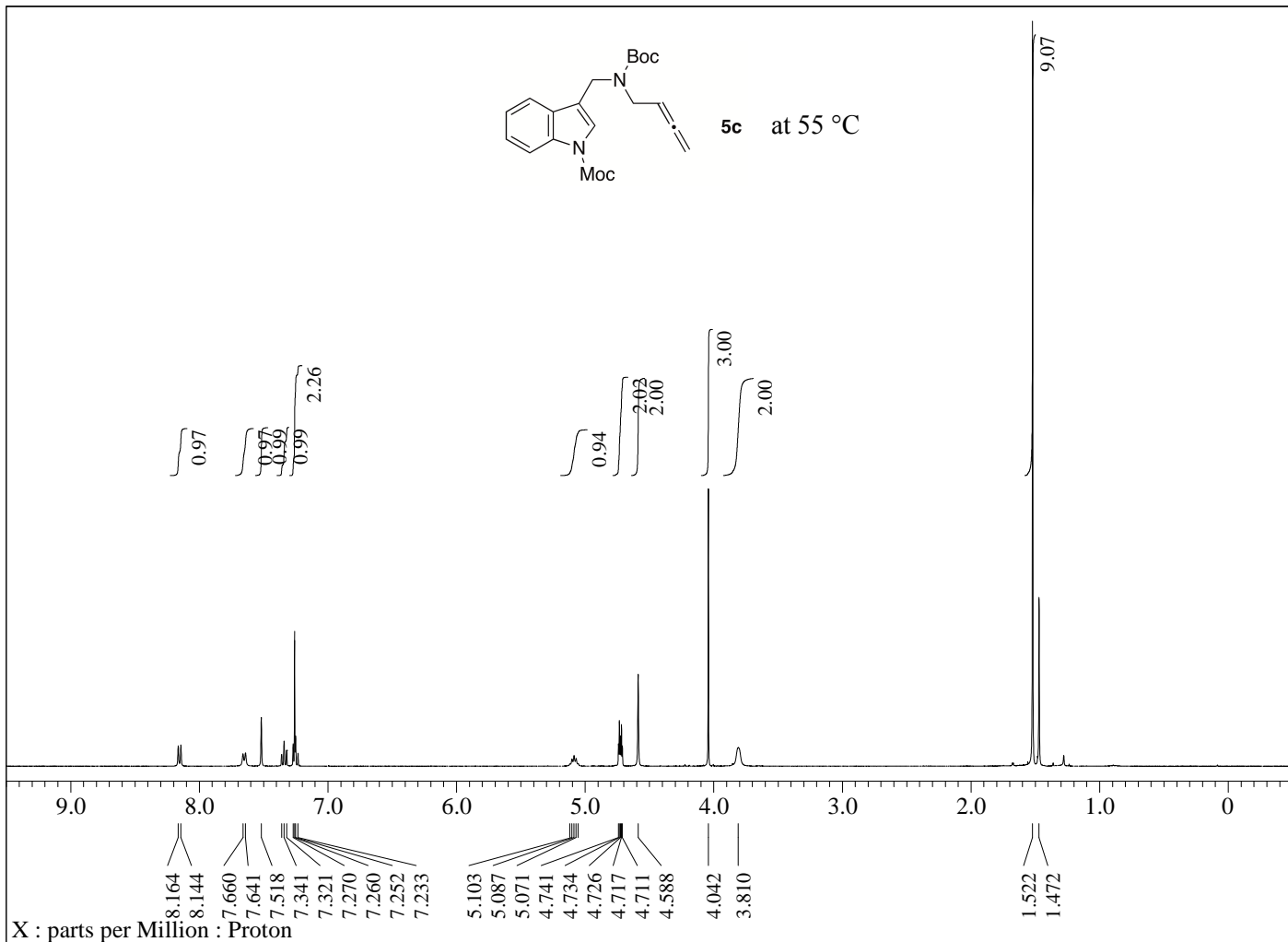


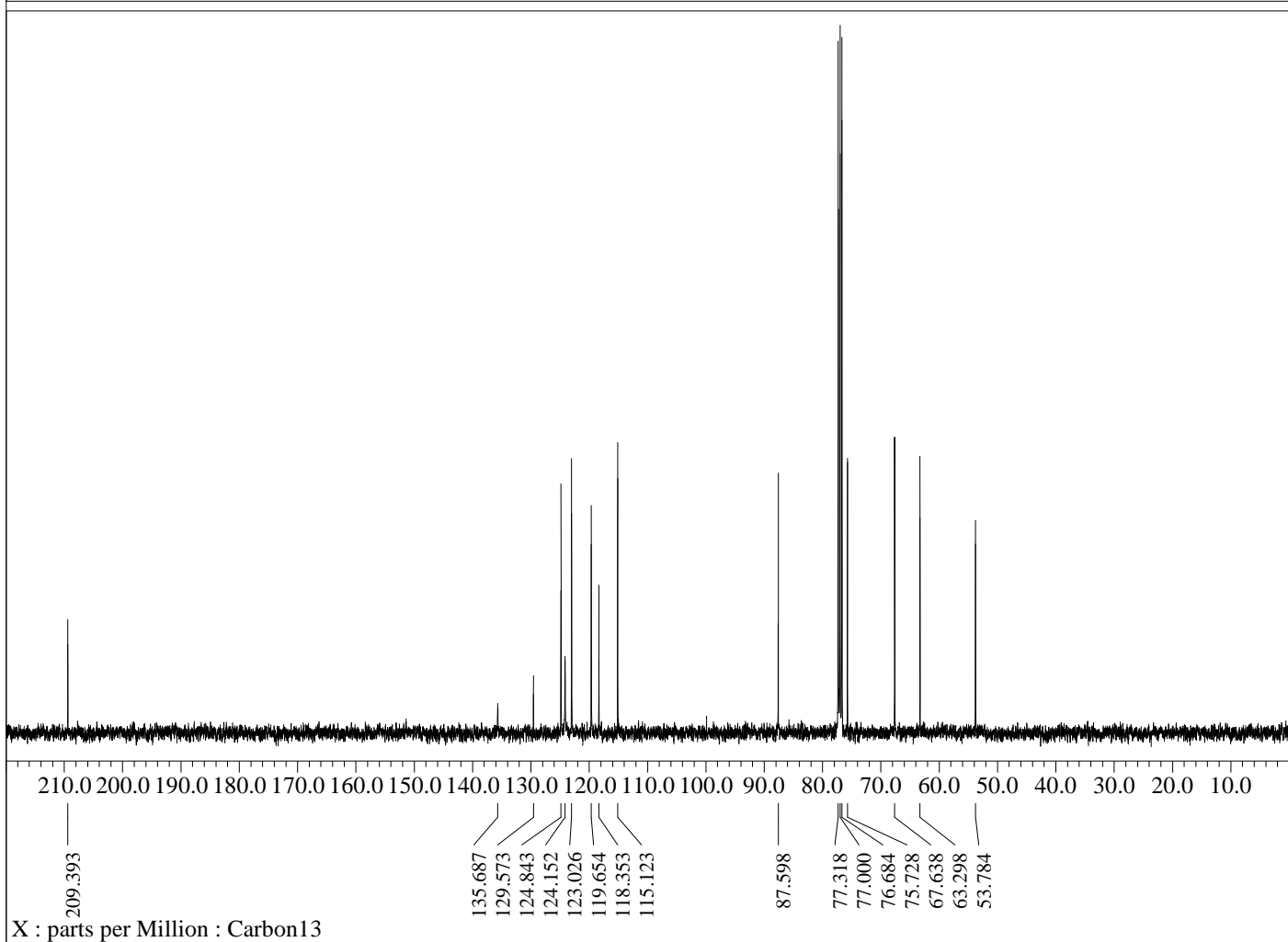
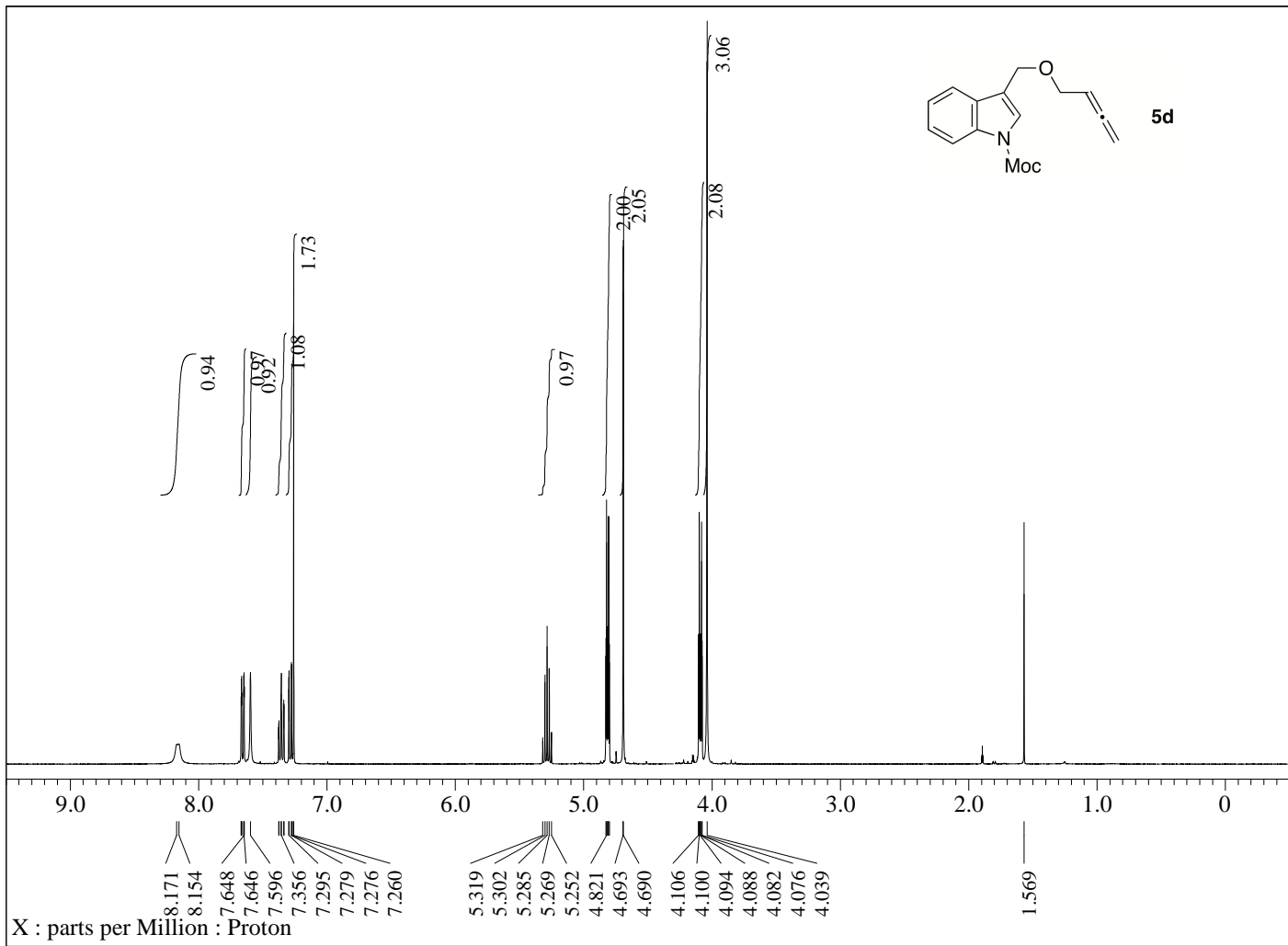


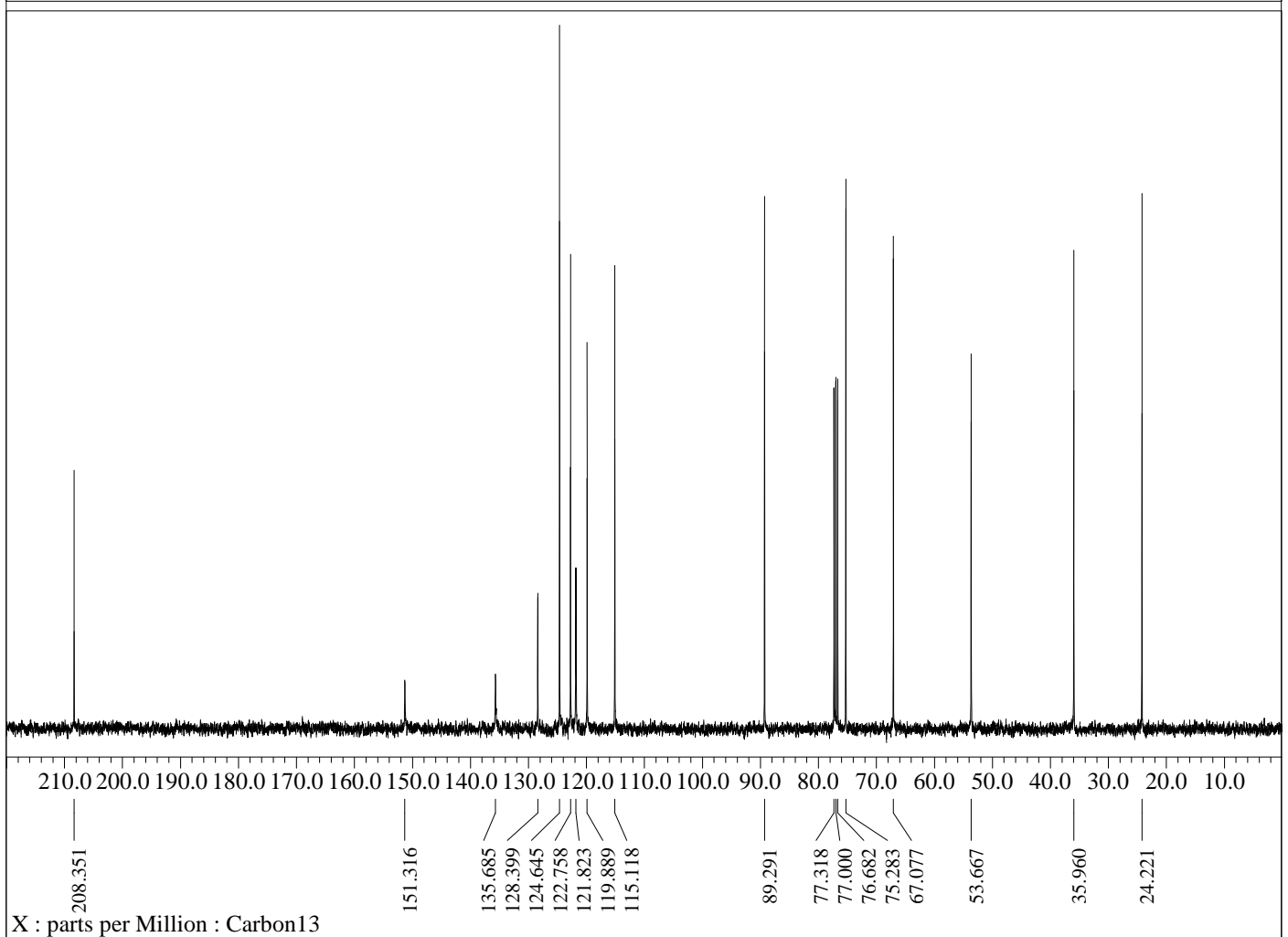
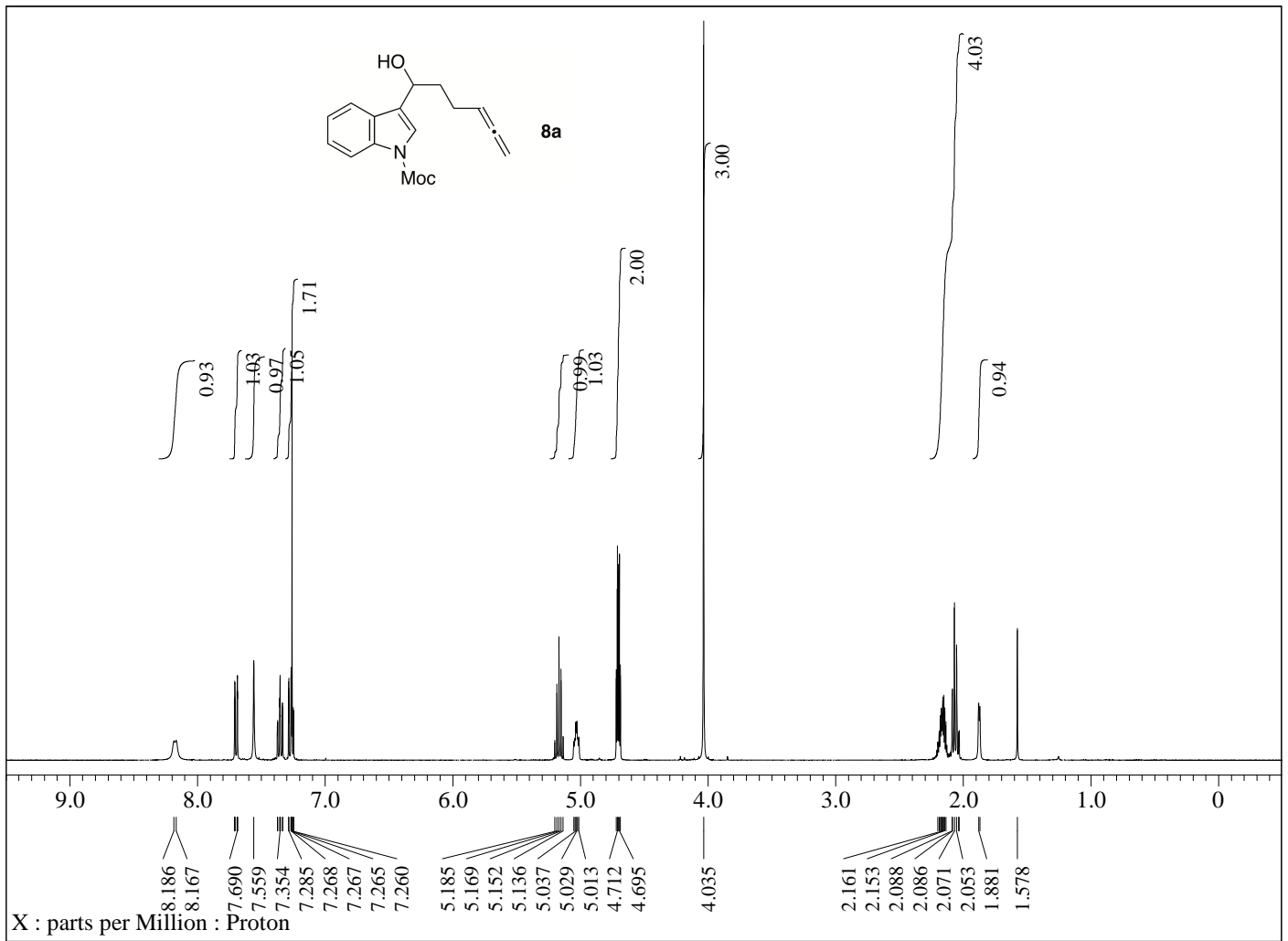


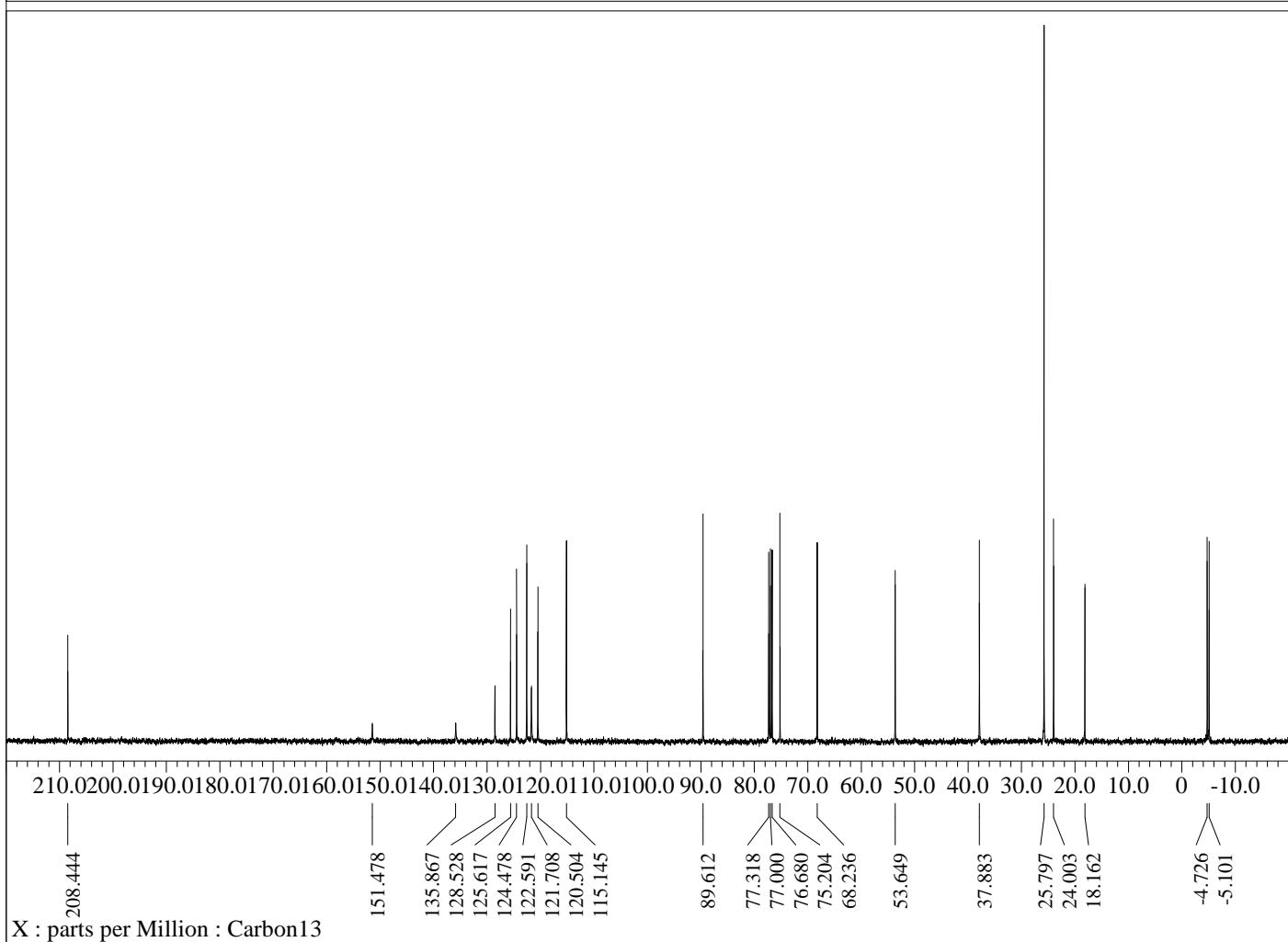
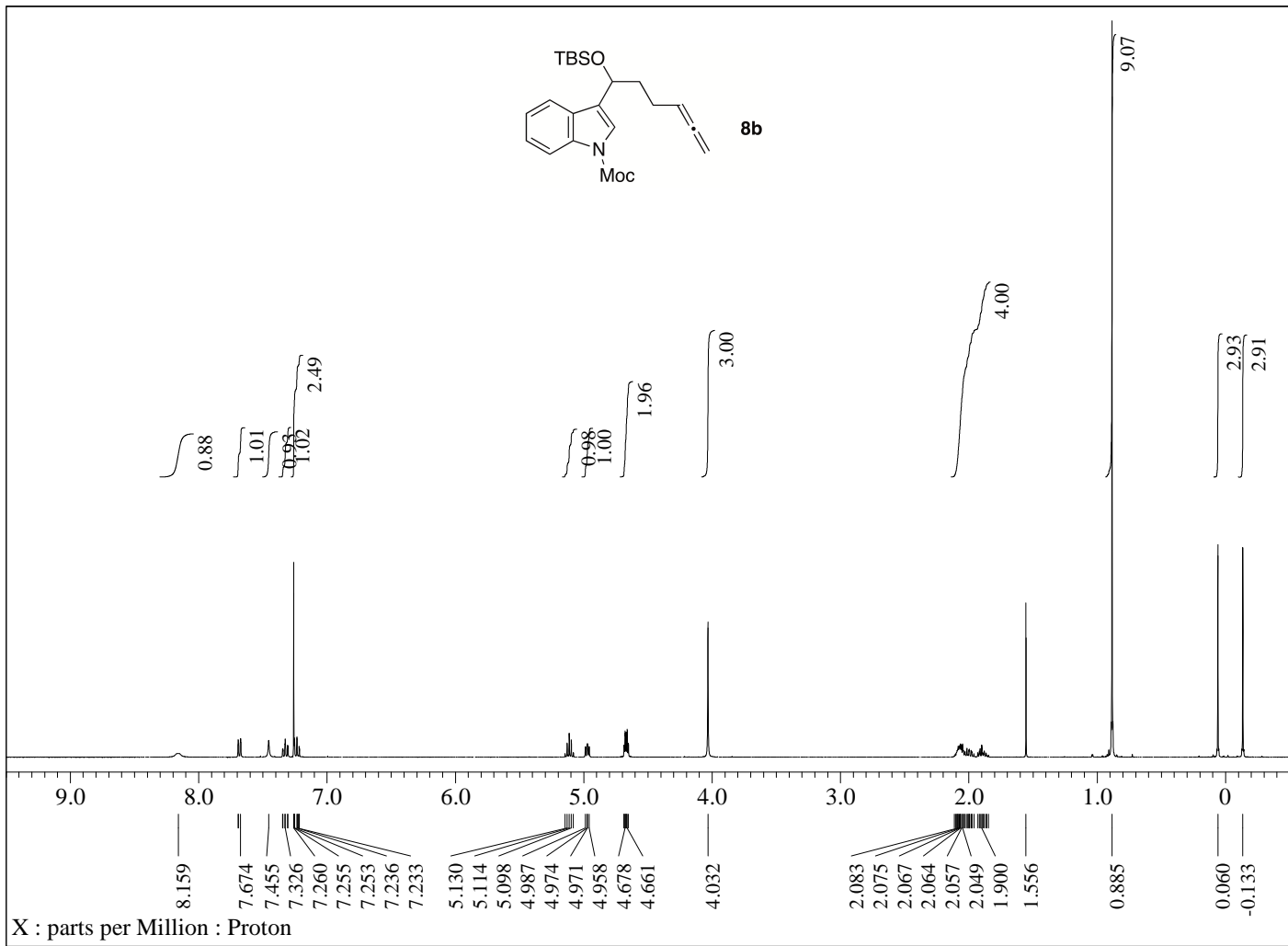


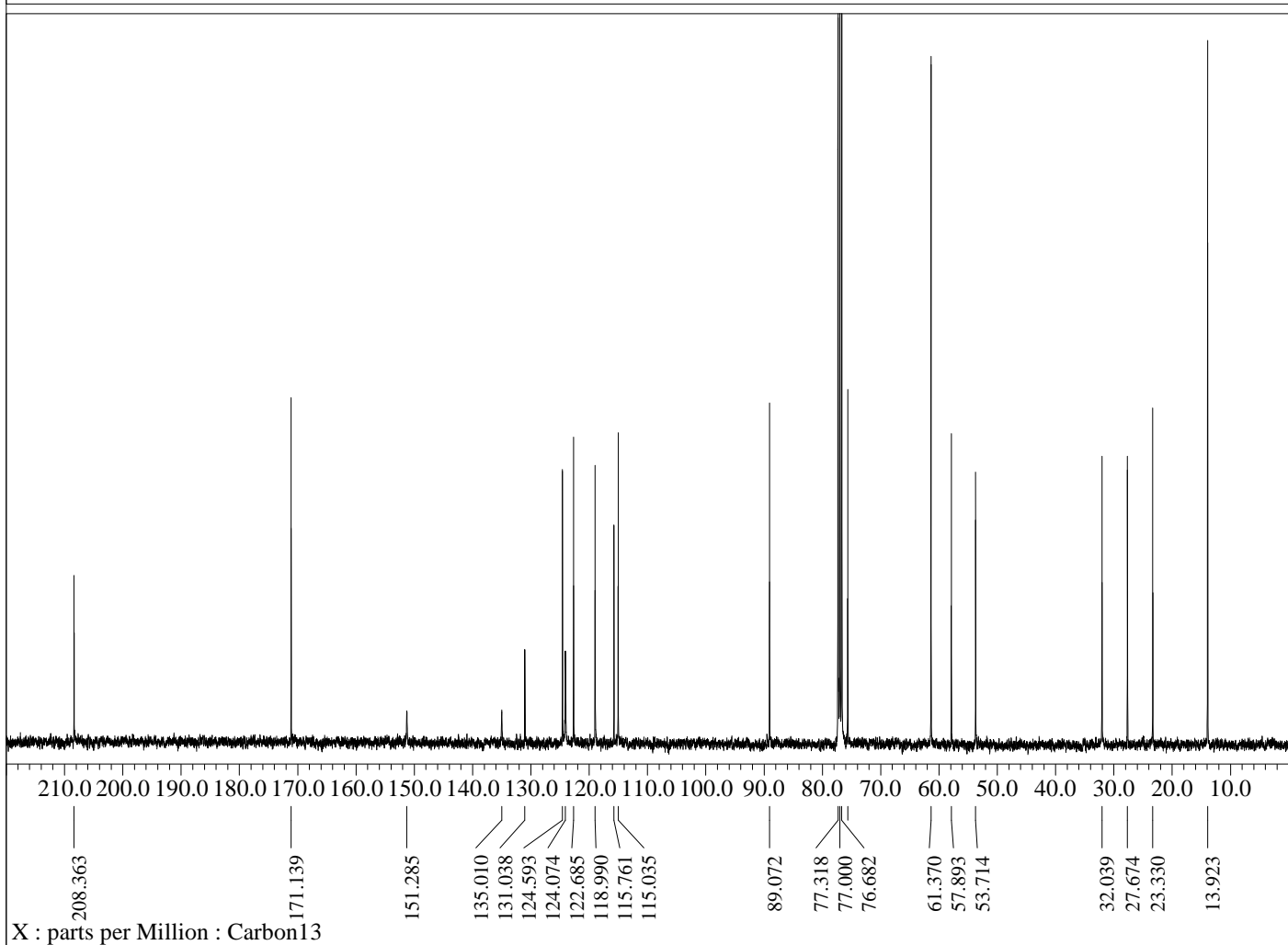
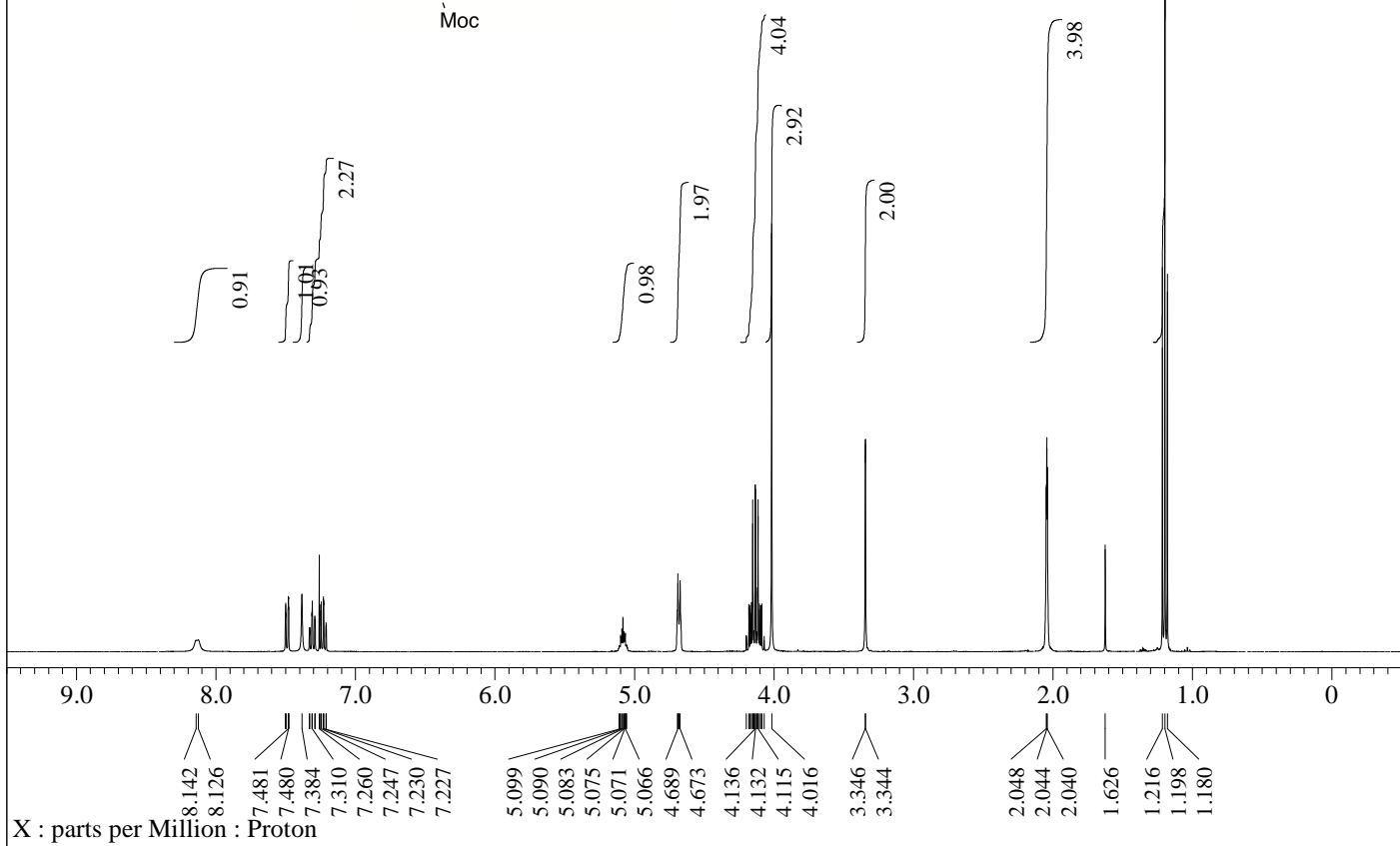
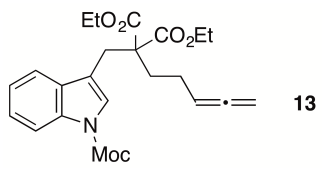
5c at 55 °C



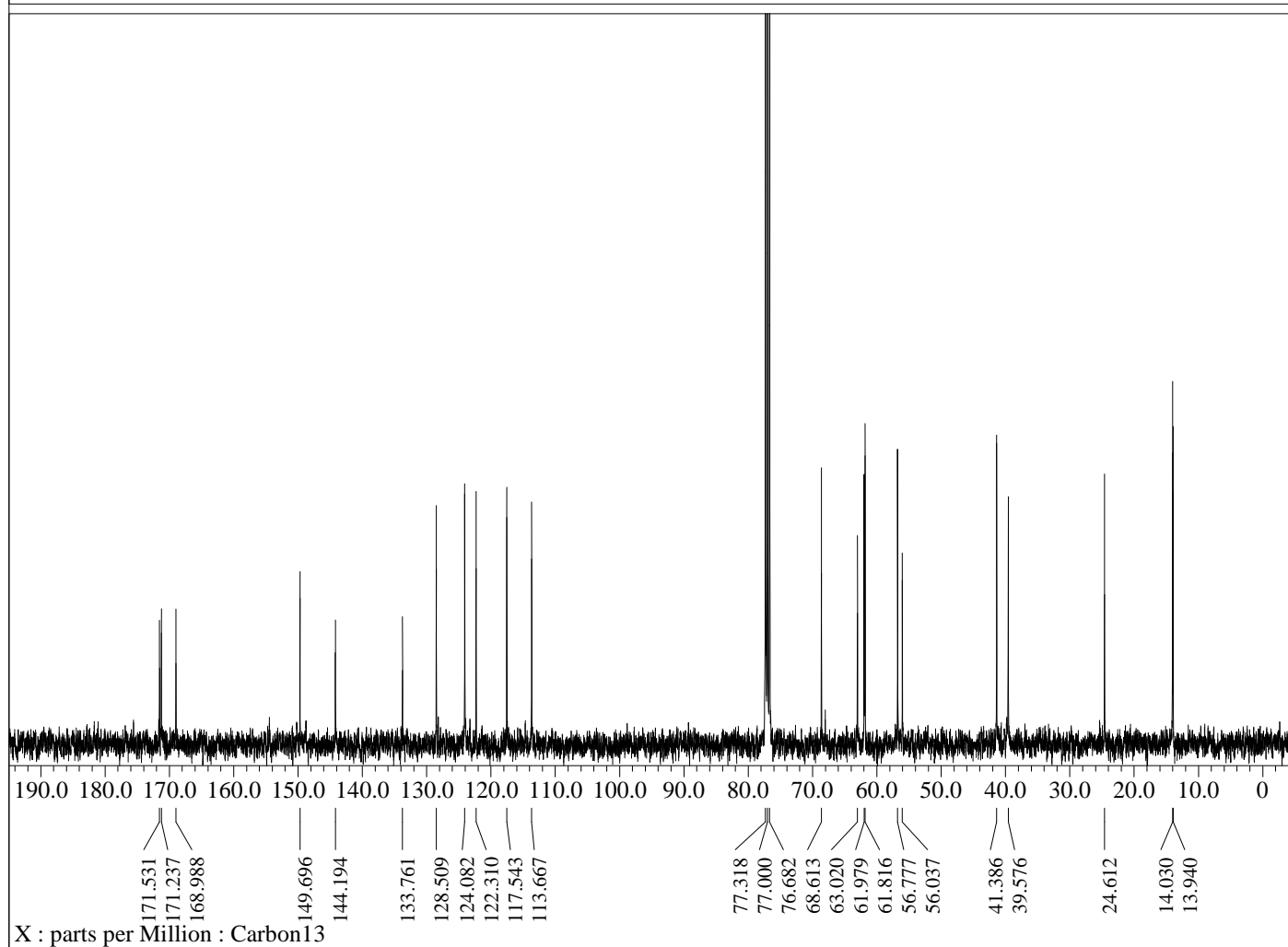
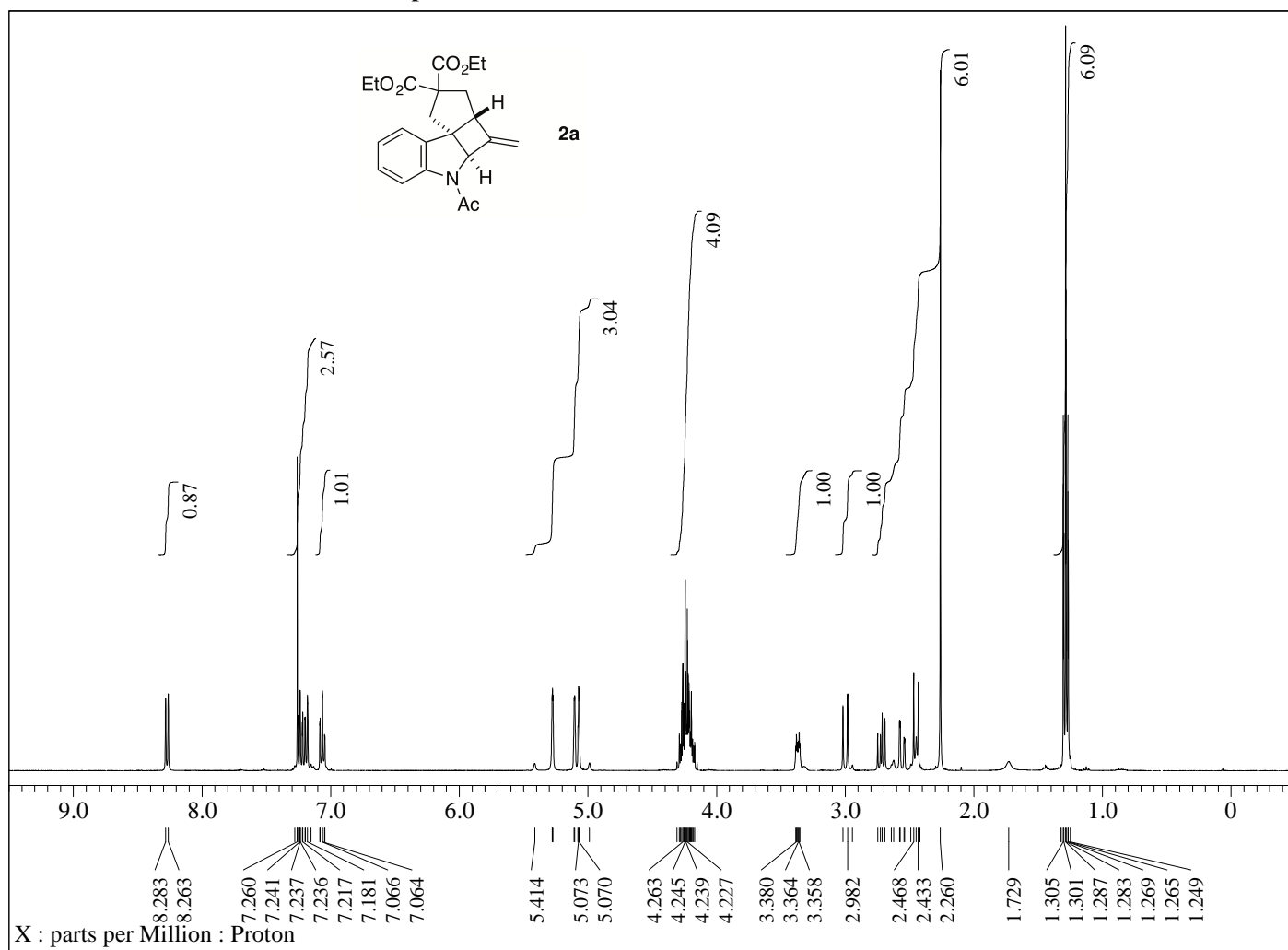


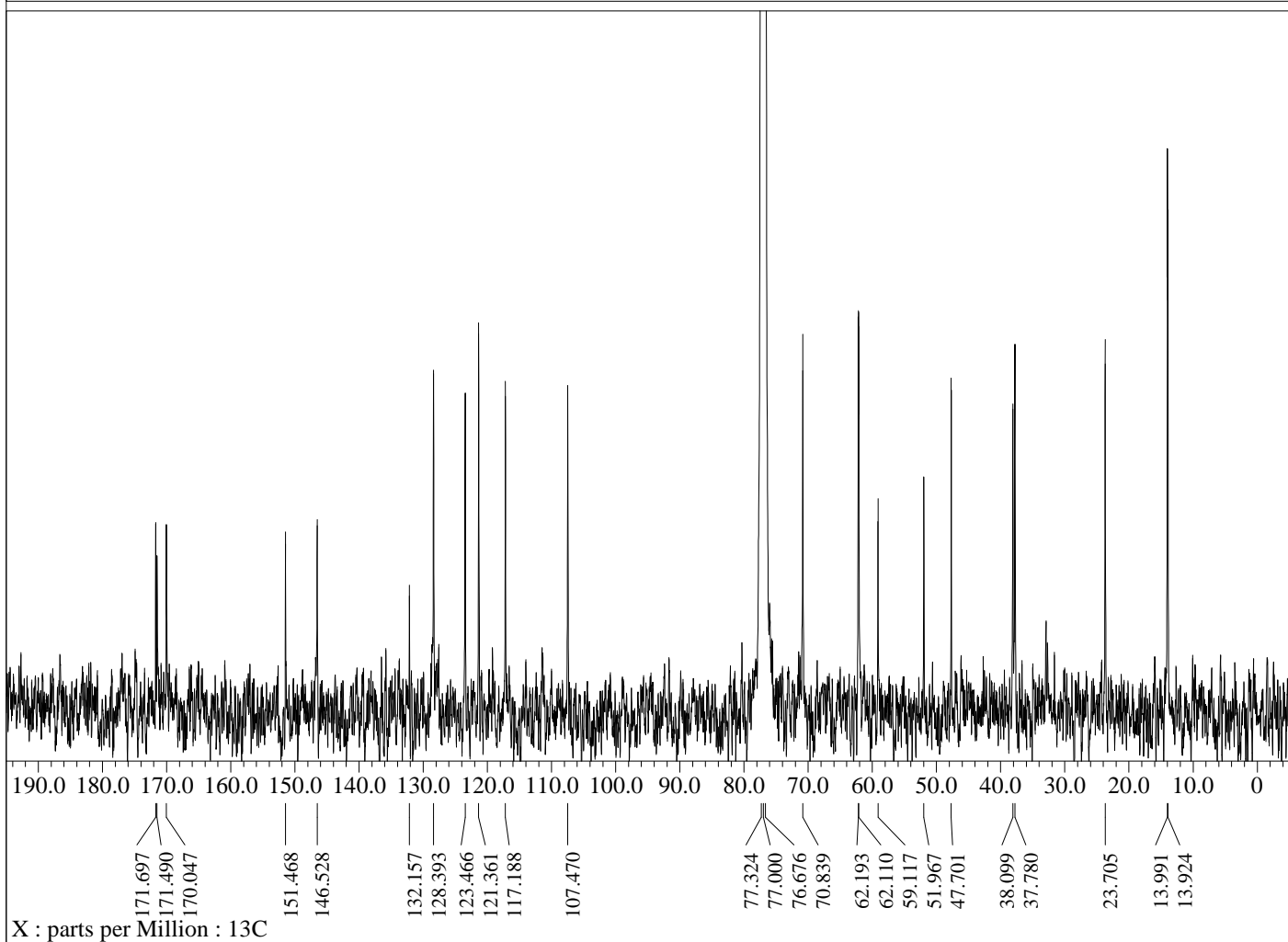
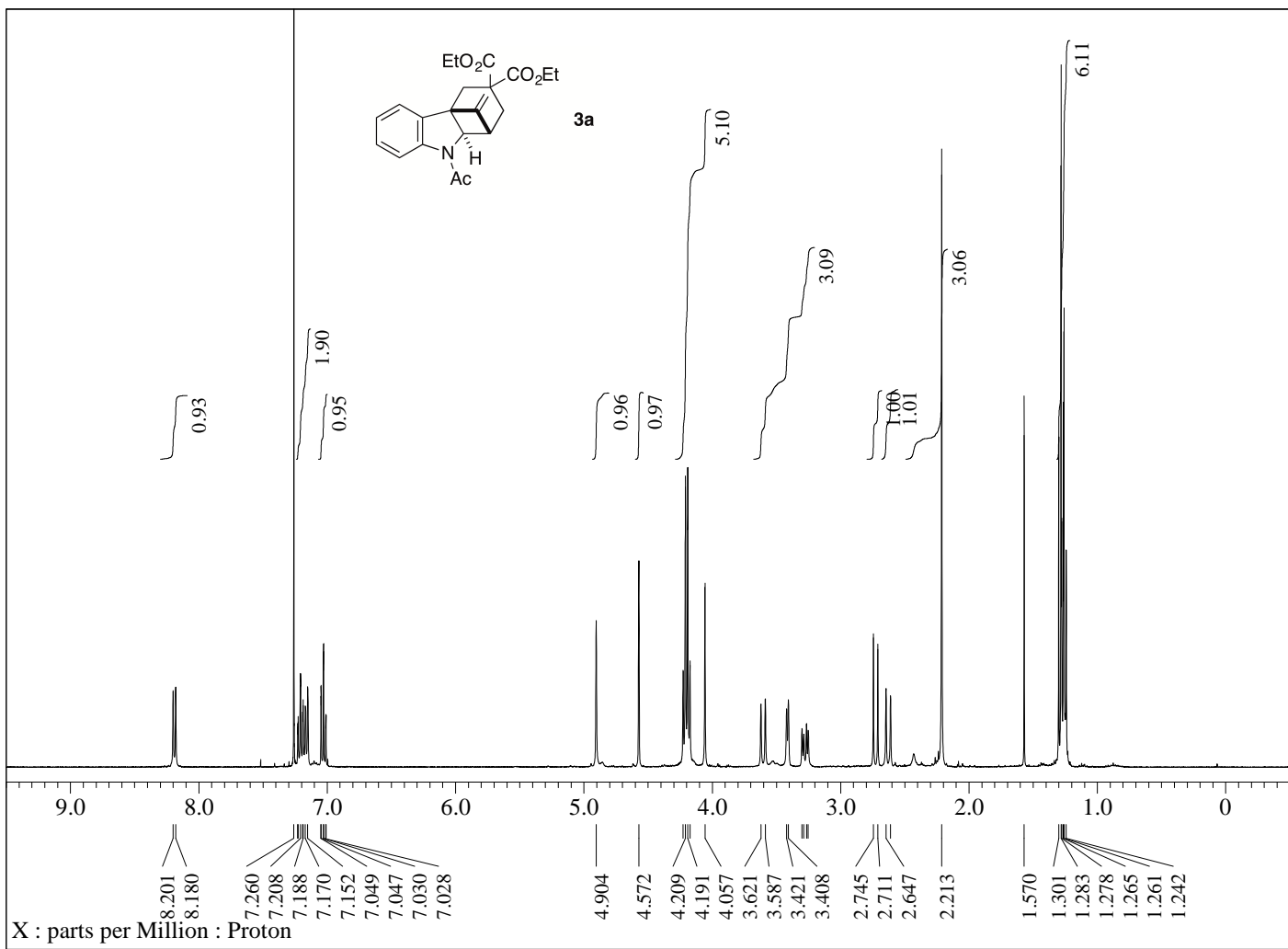


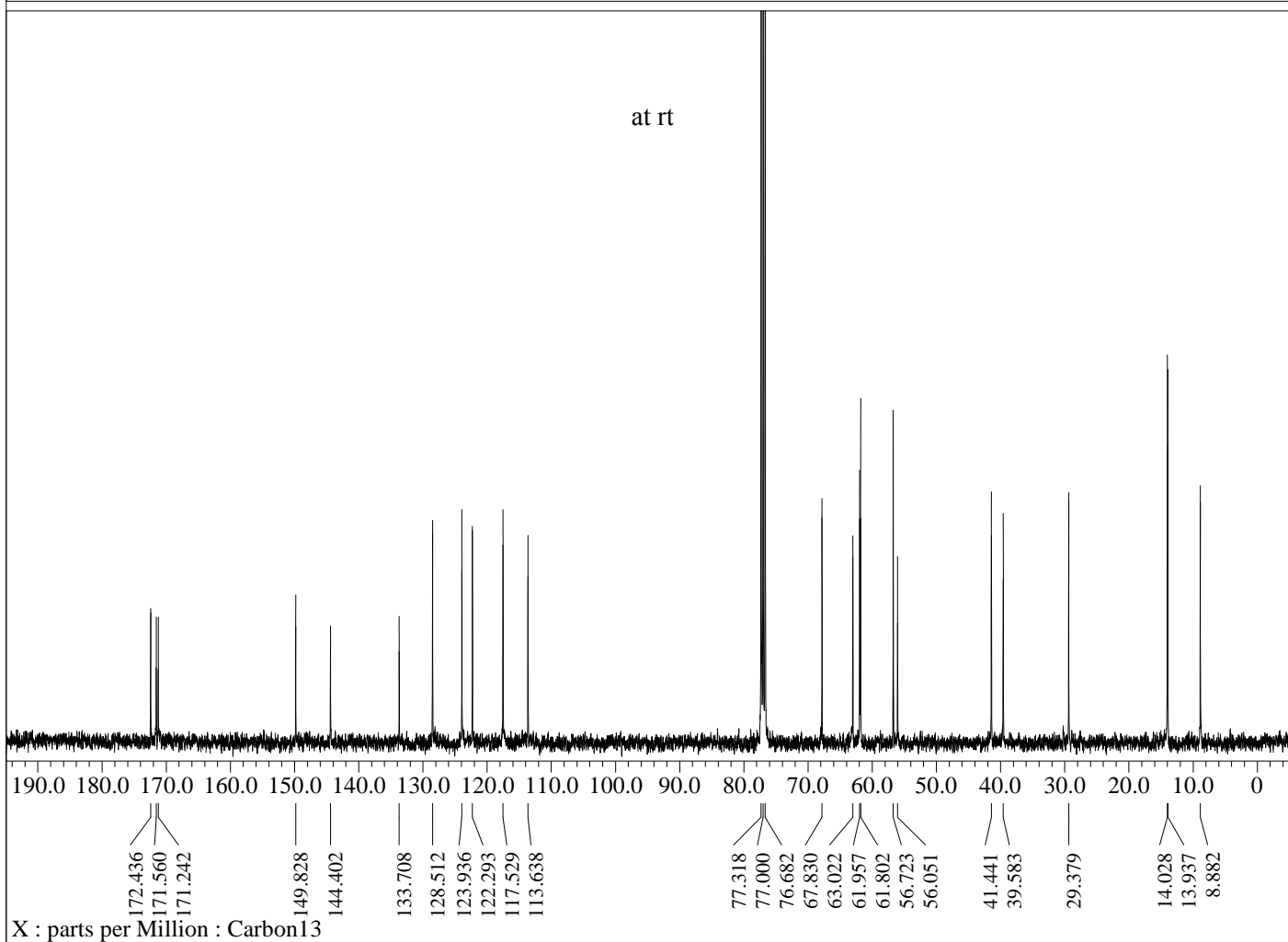
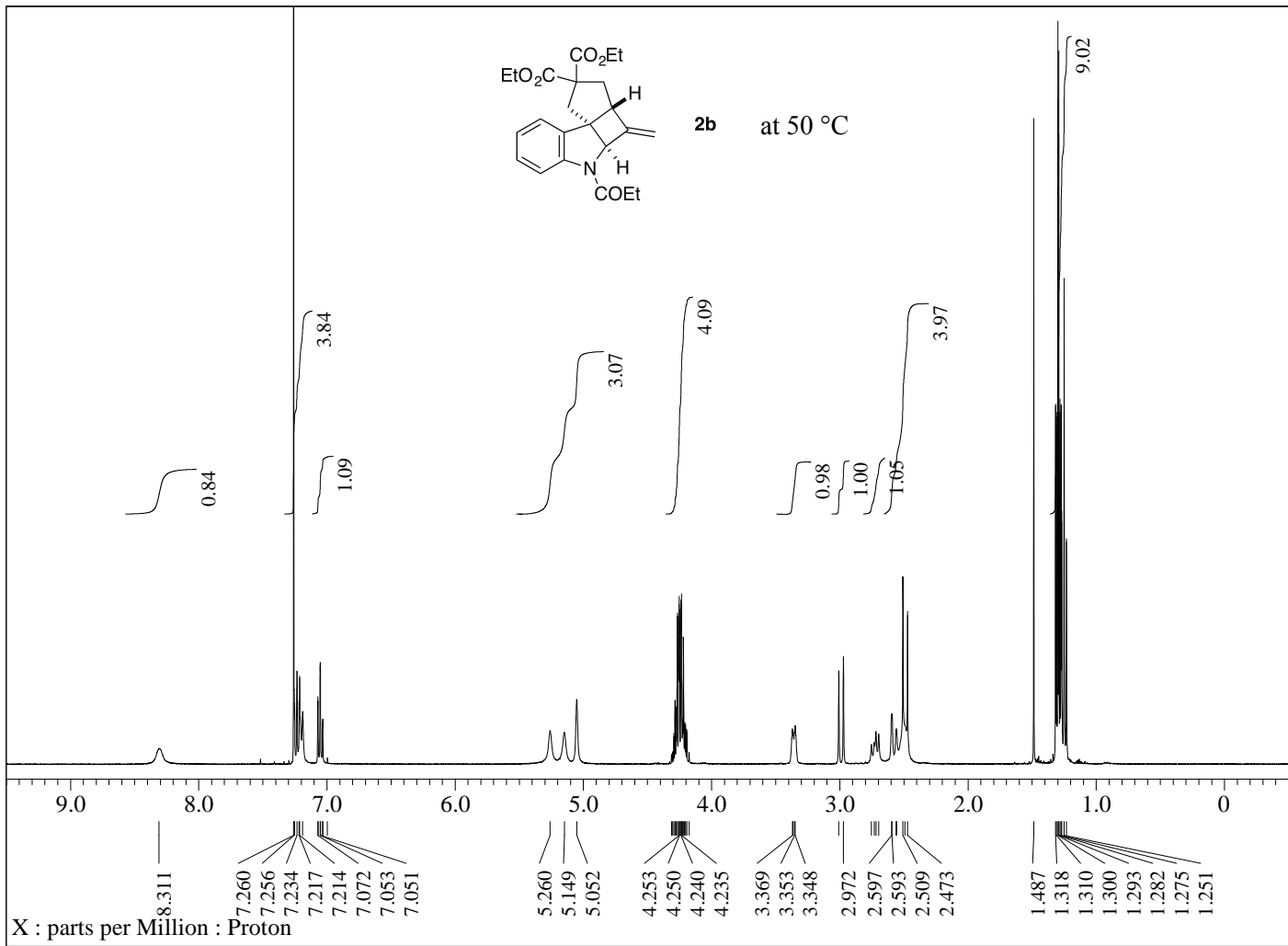


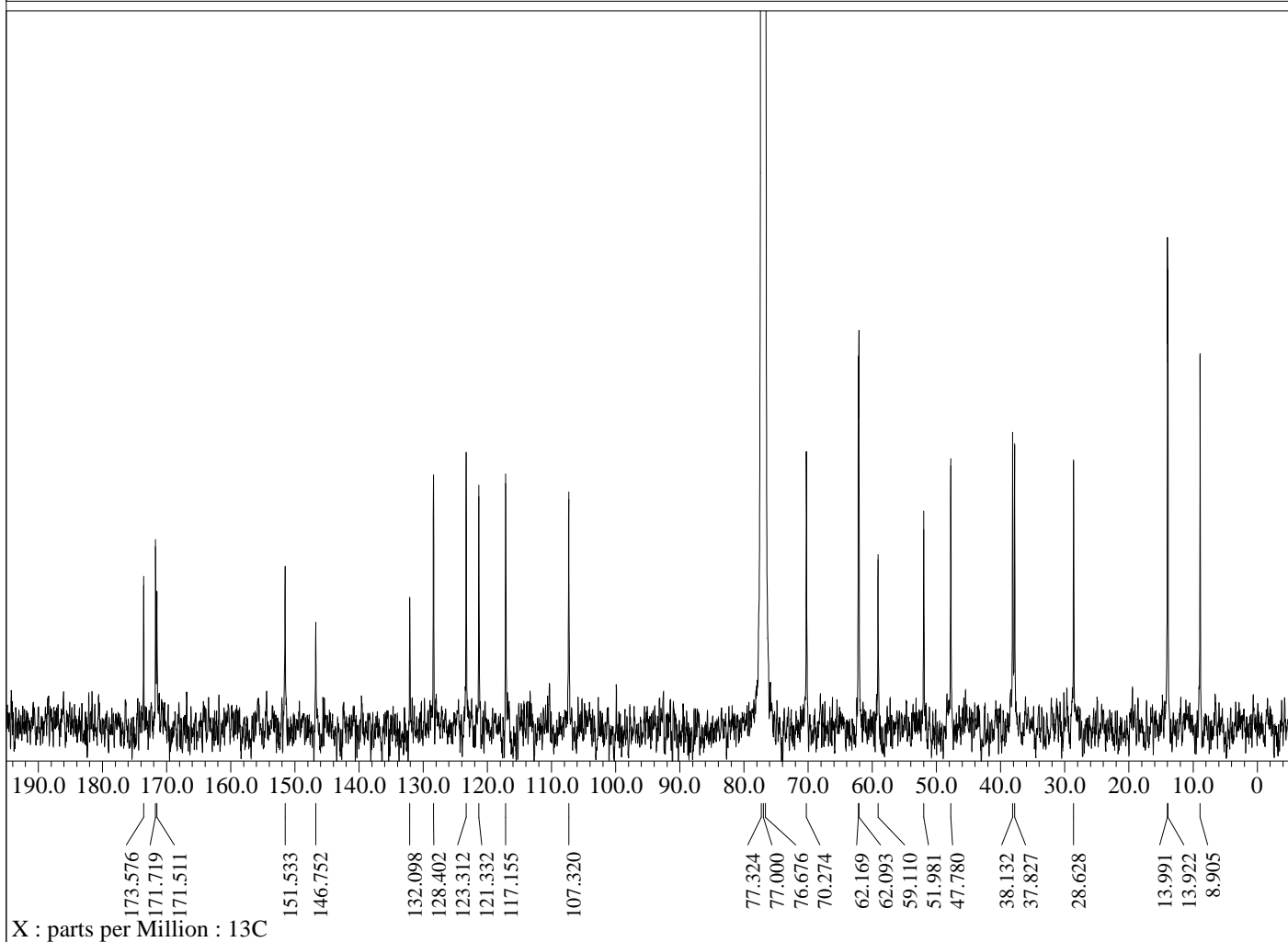
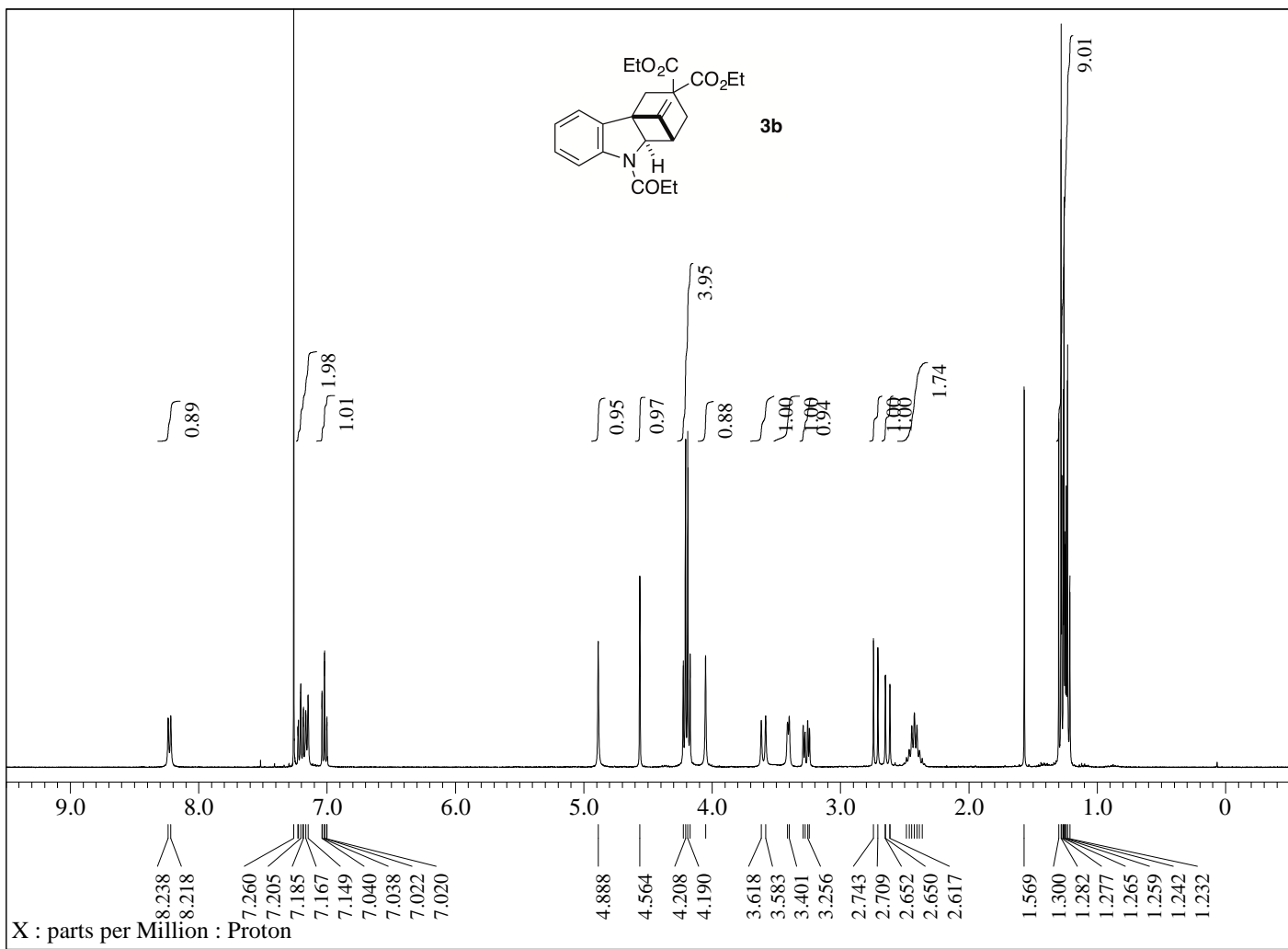


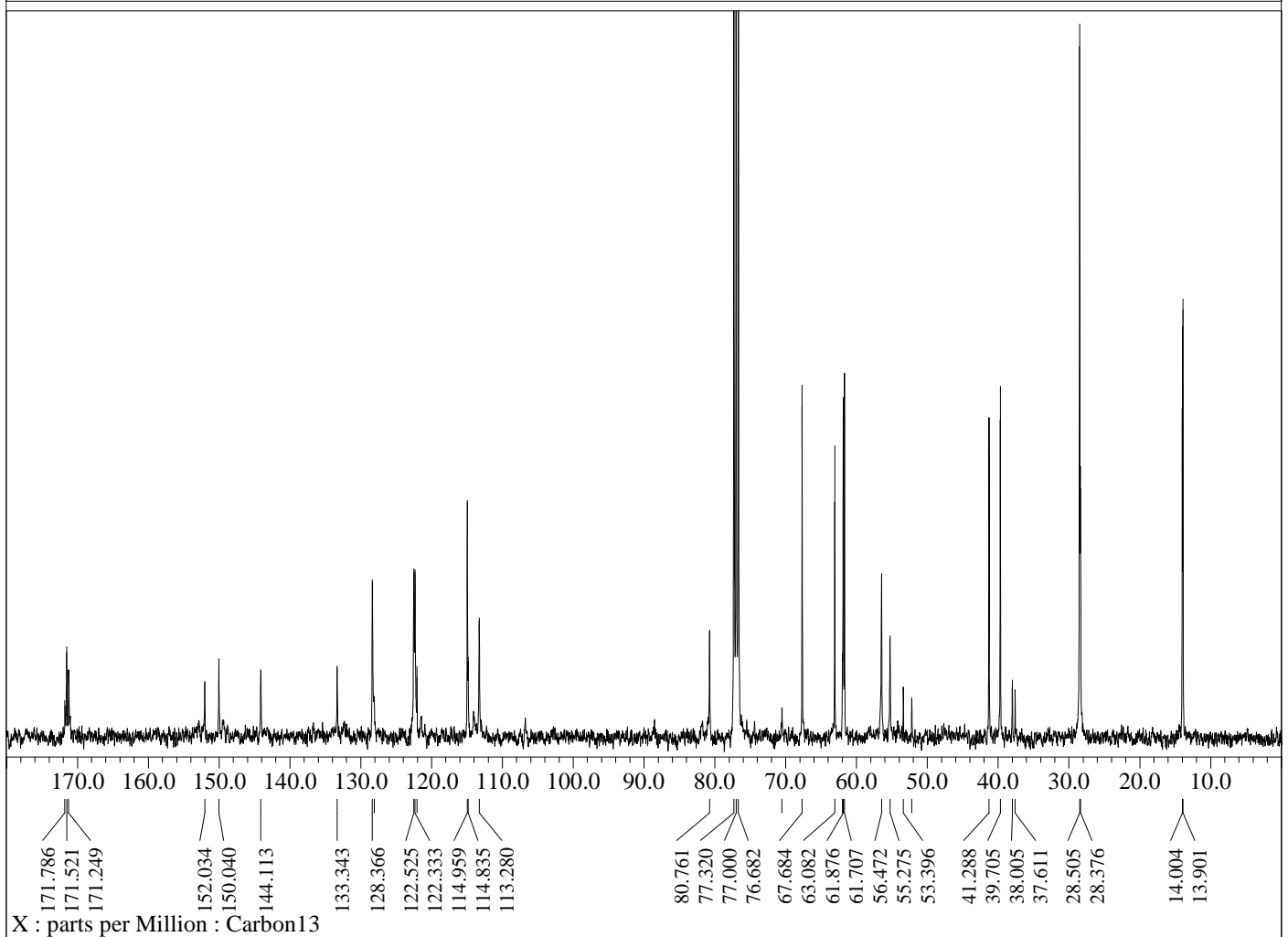
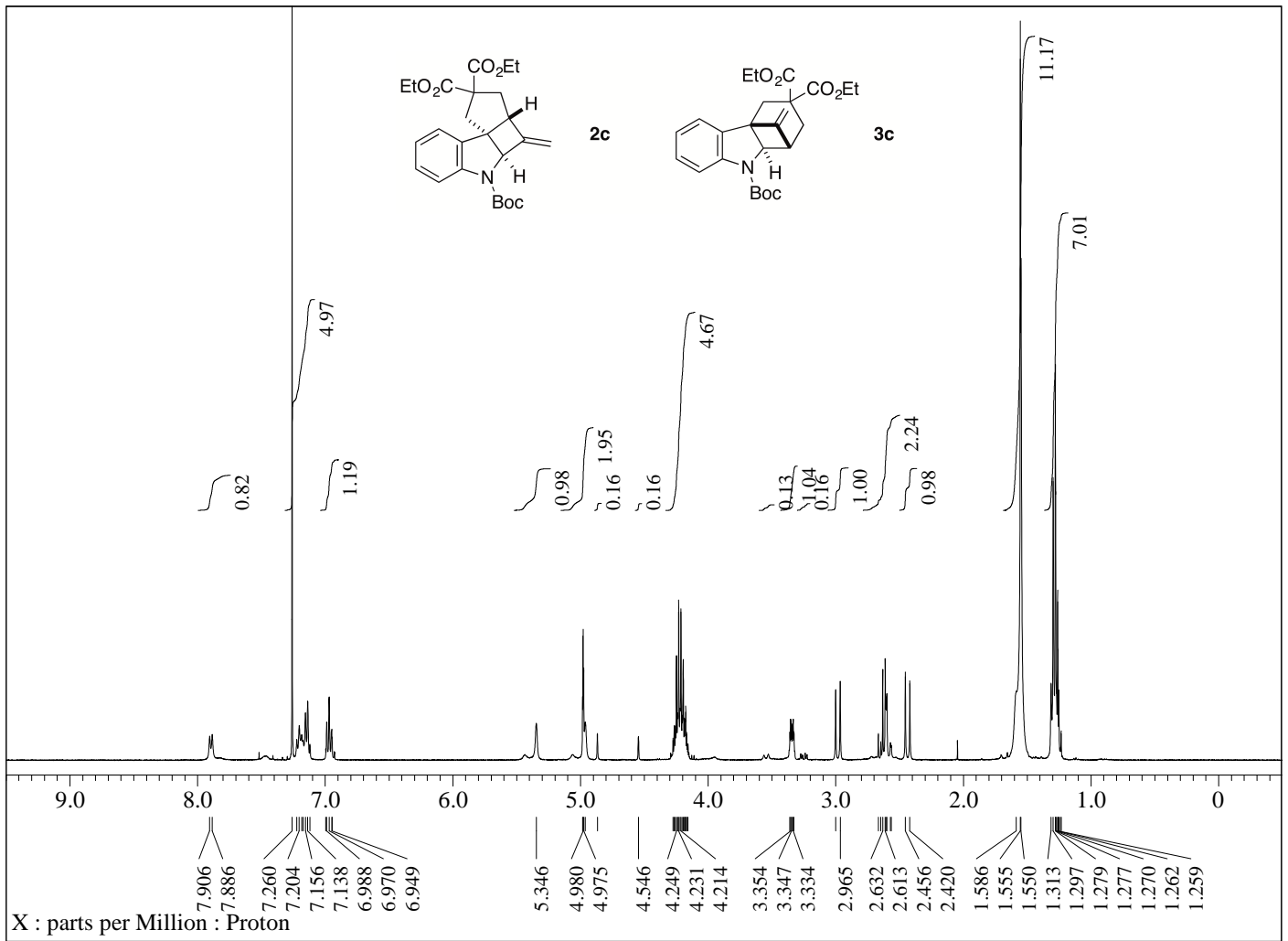
¹H and ¹³C NMR charts of the products

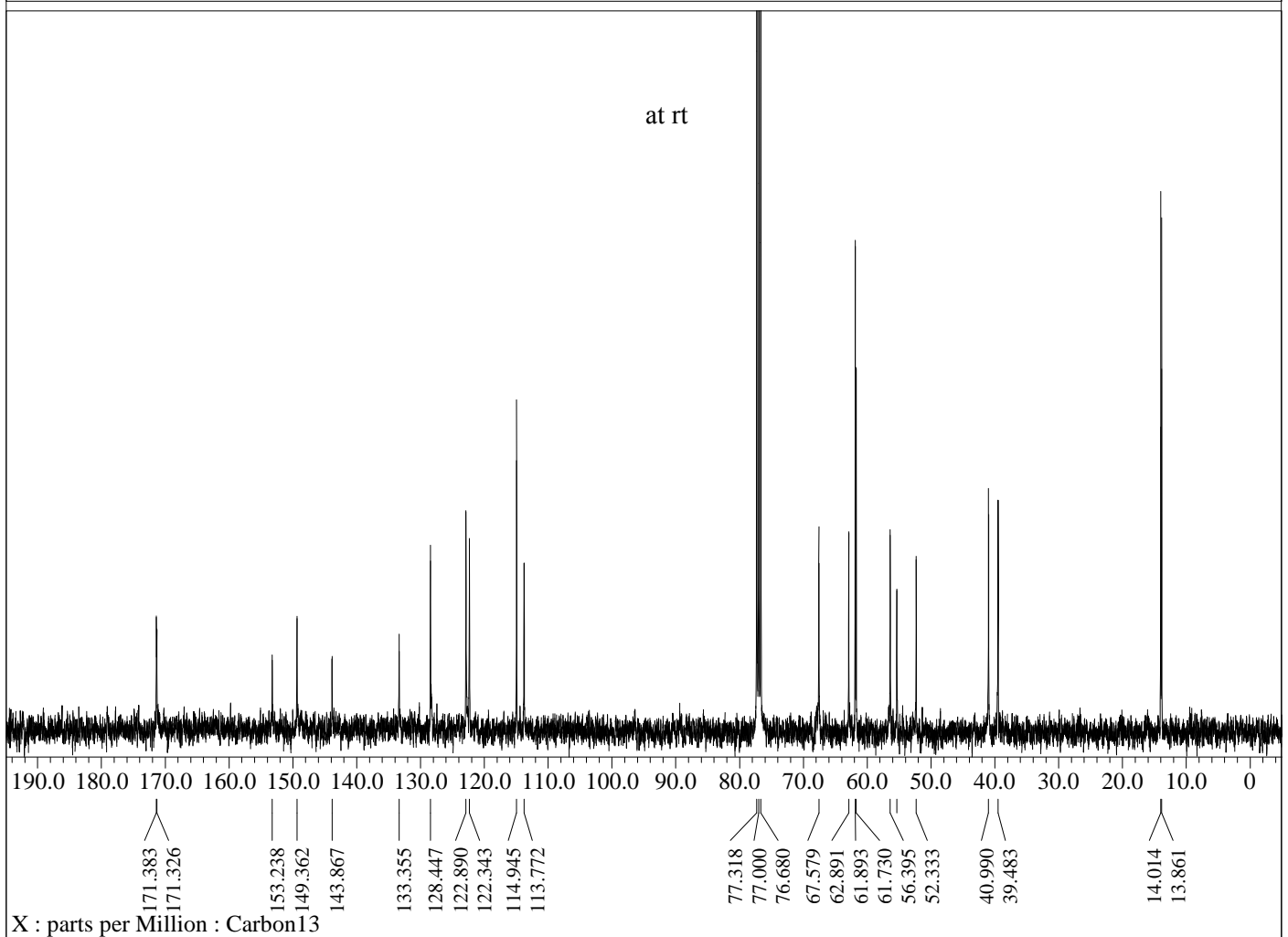
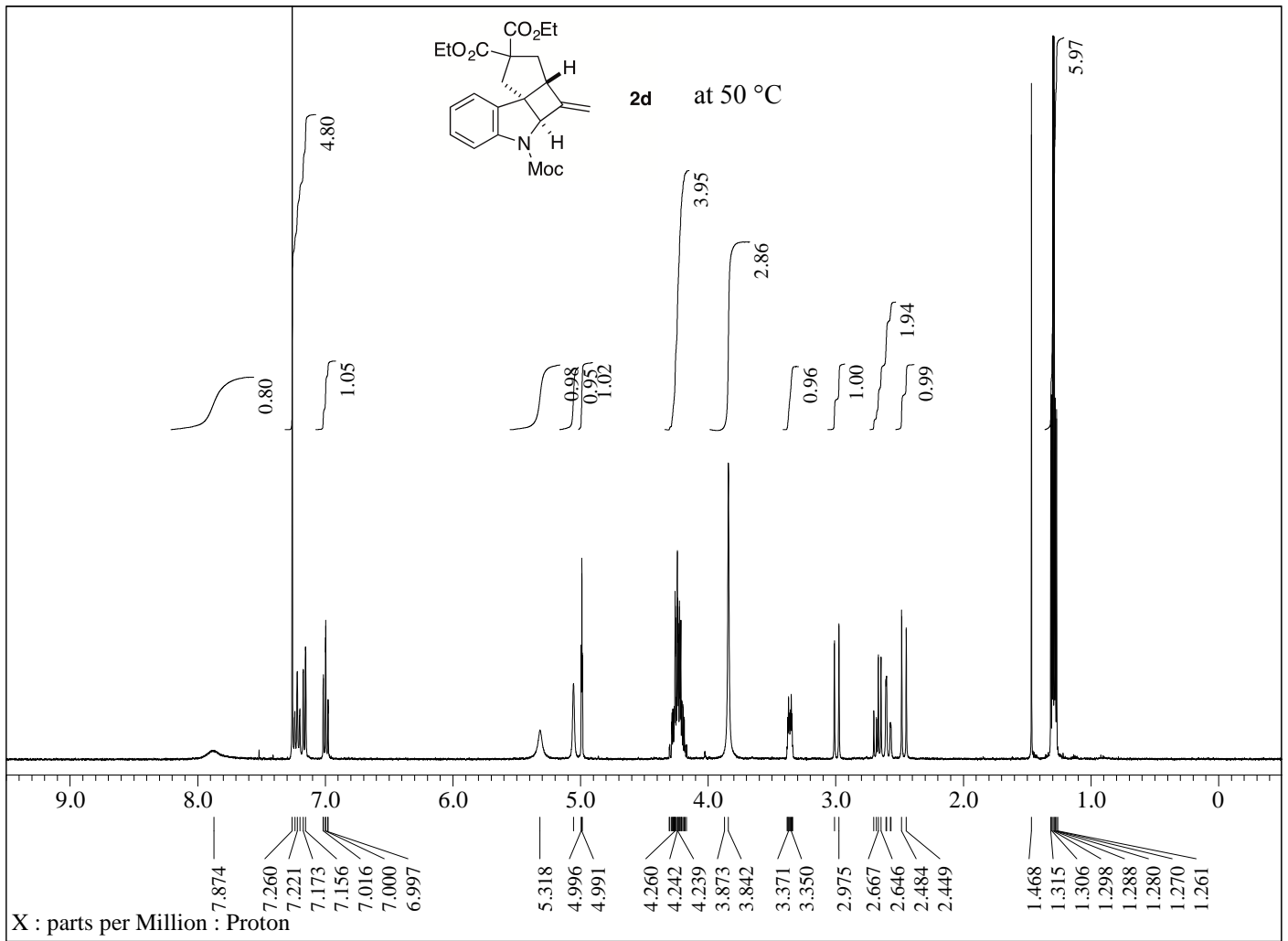


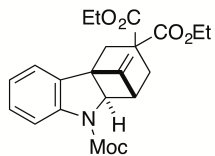




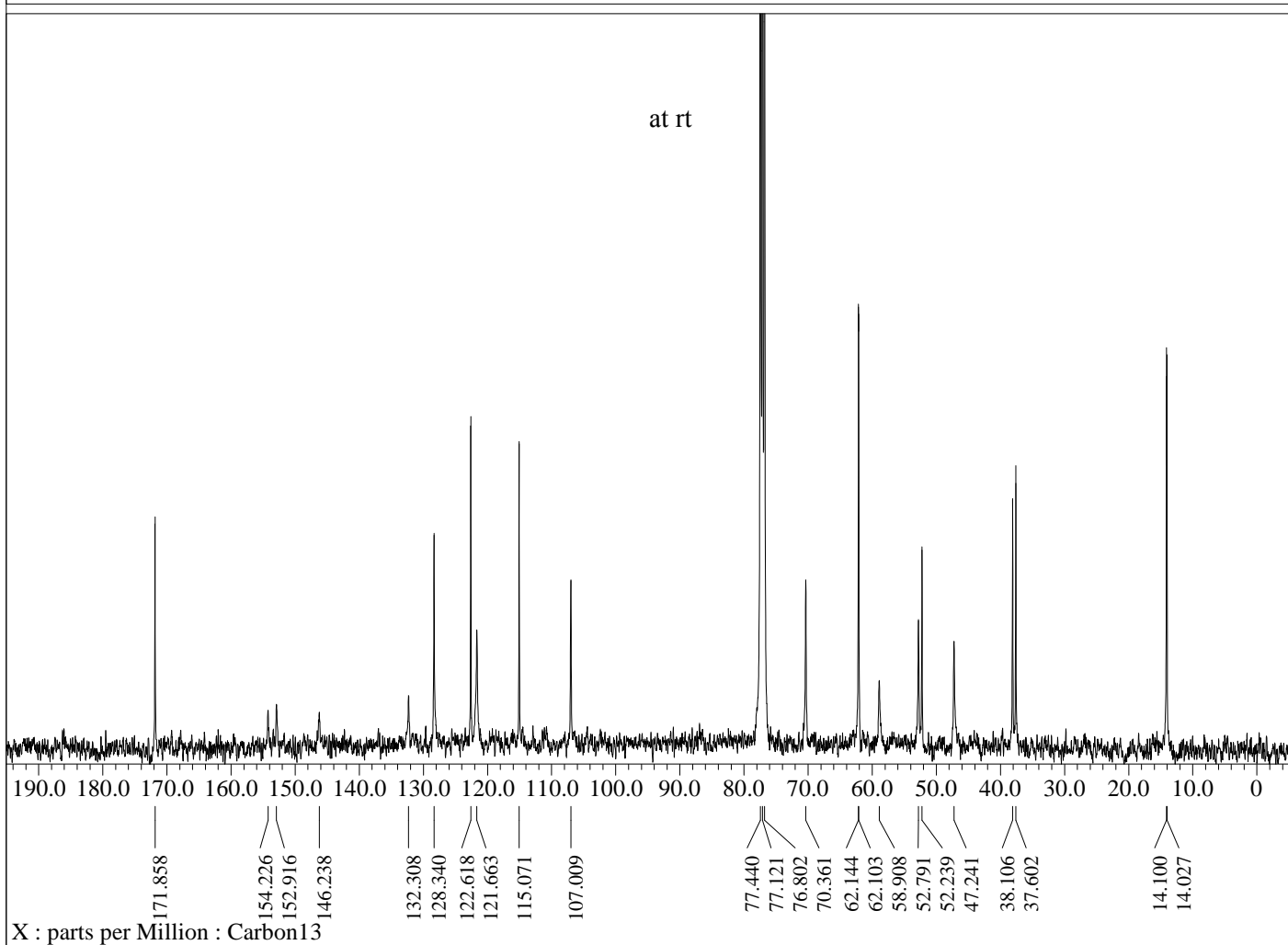
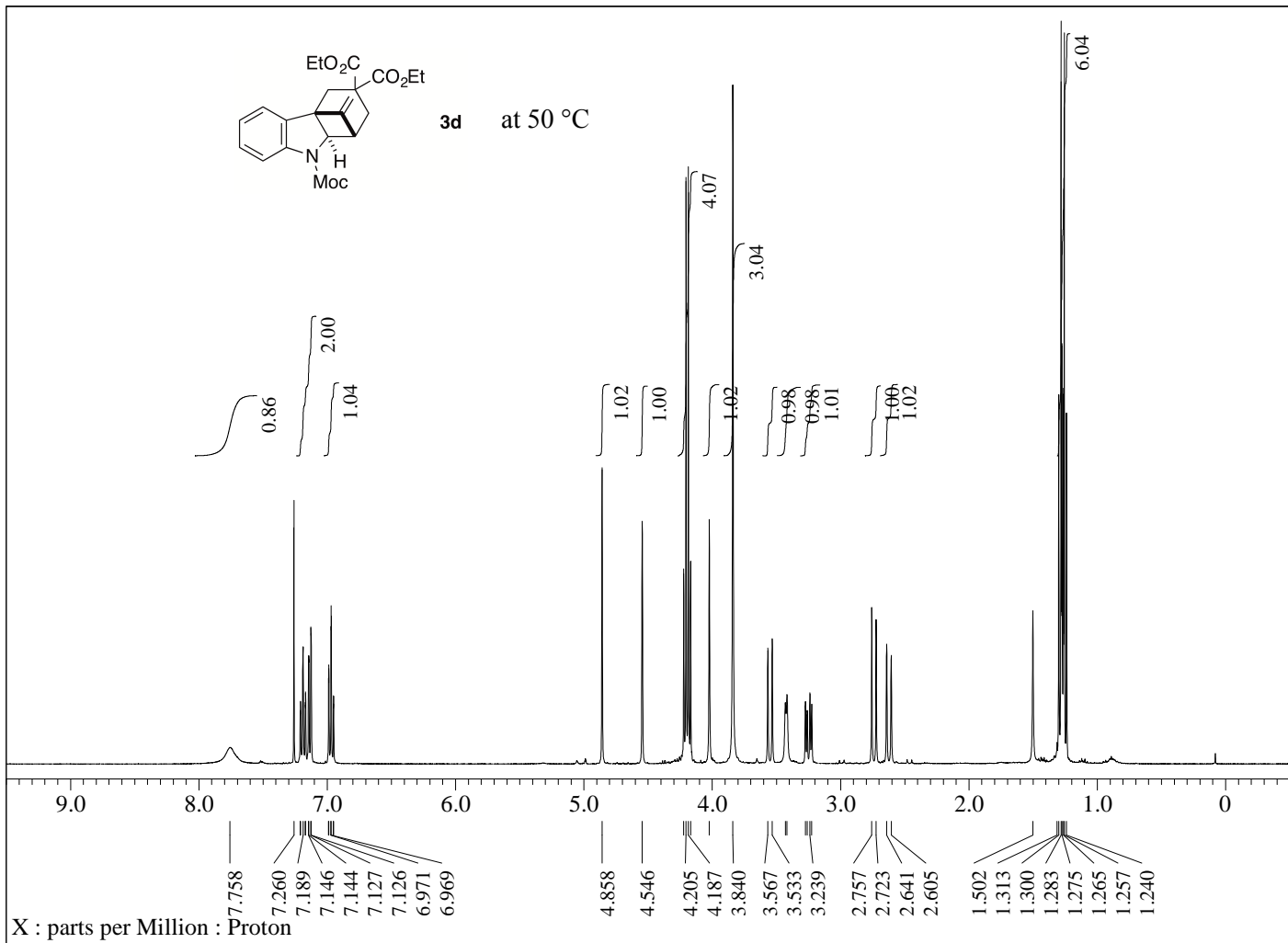


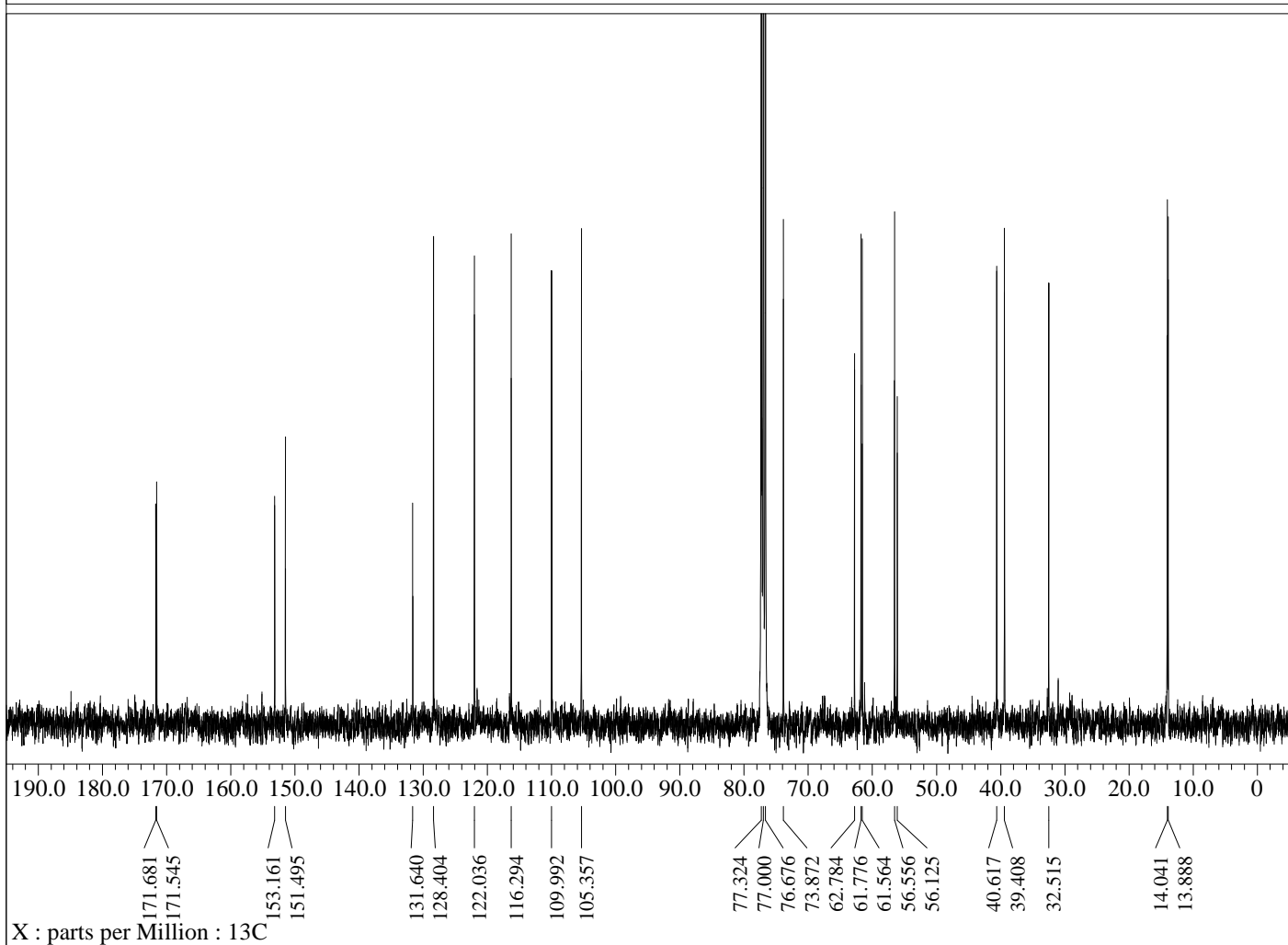
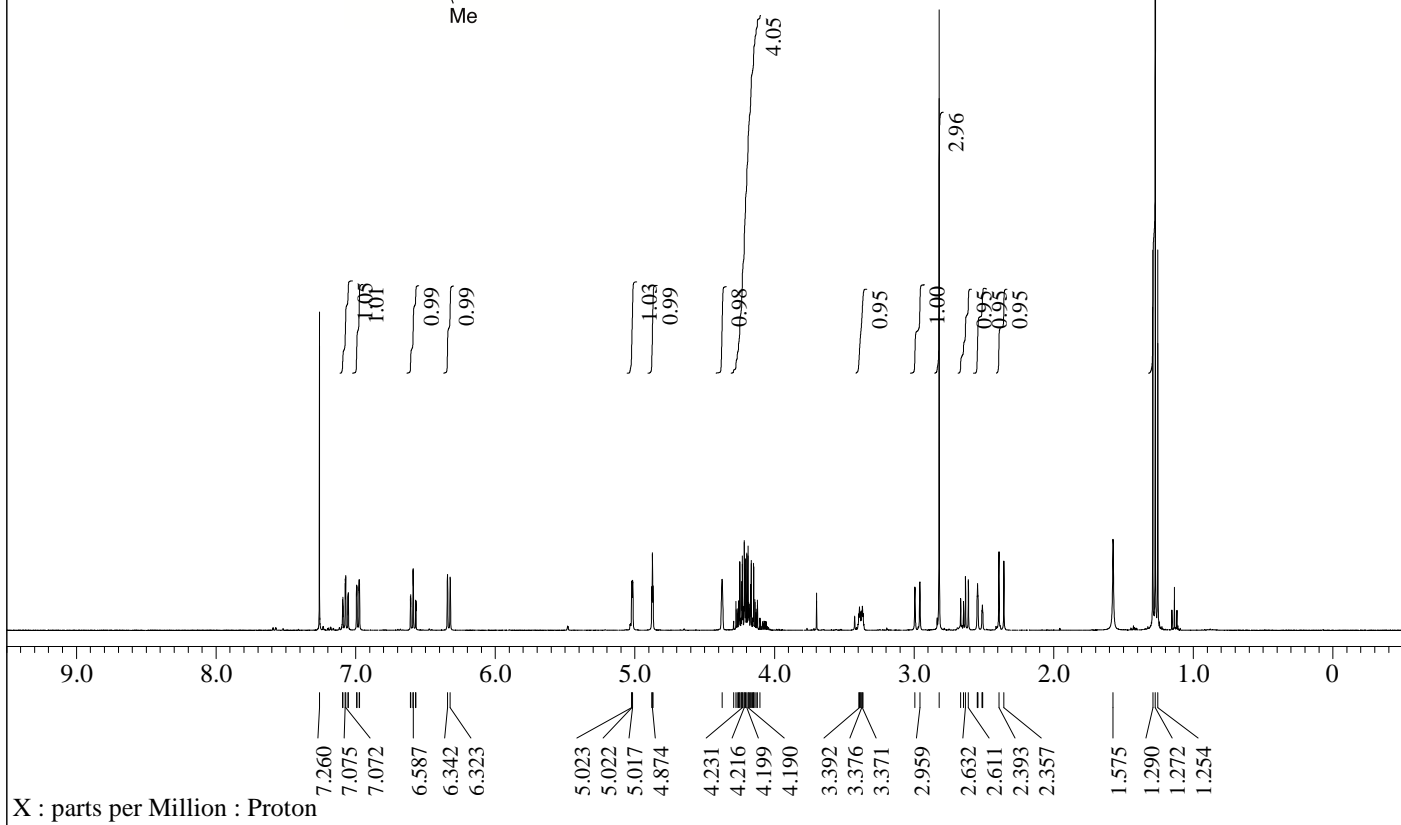
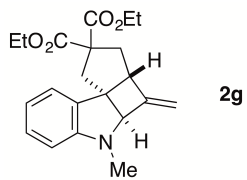


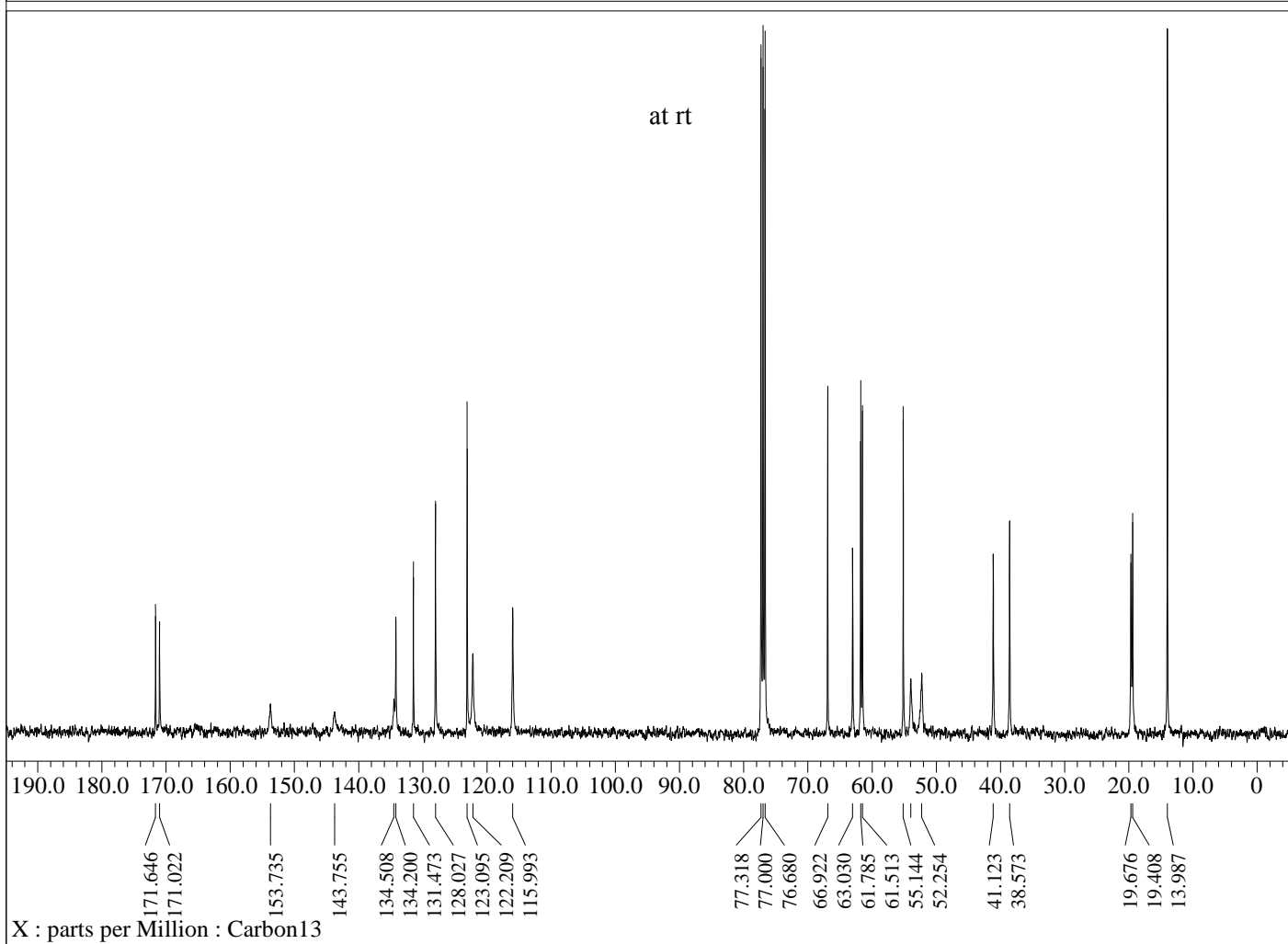
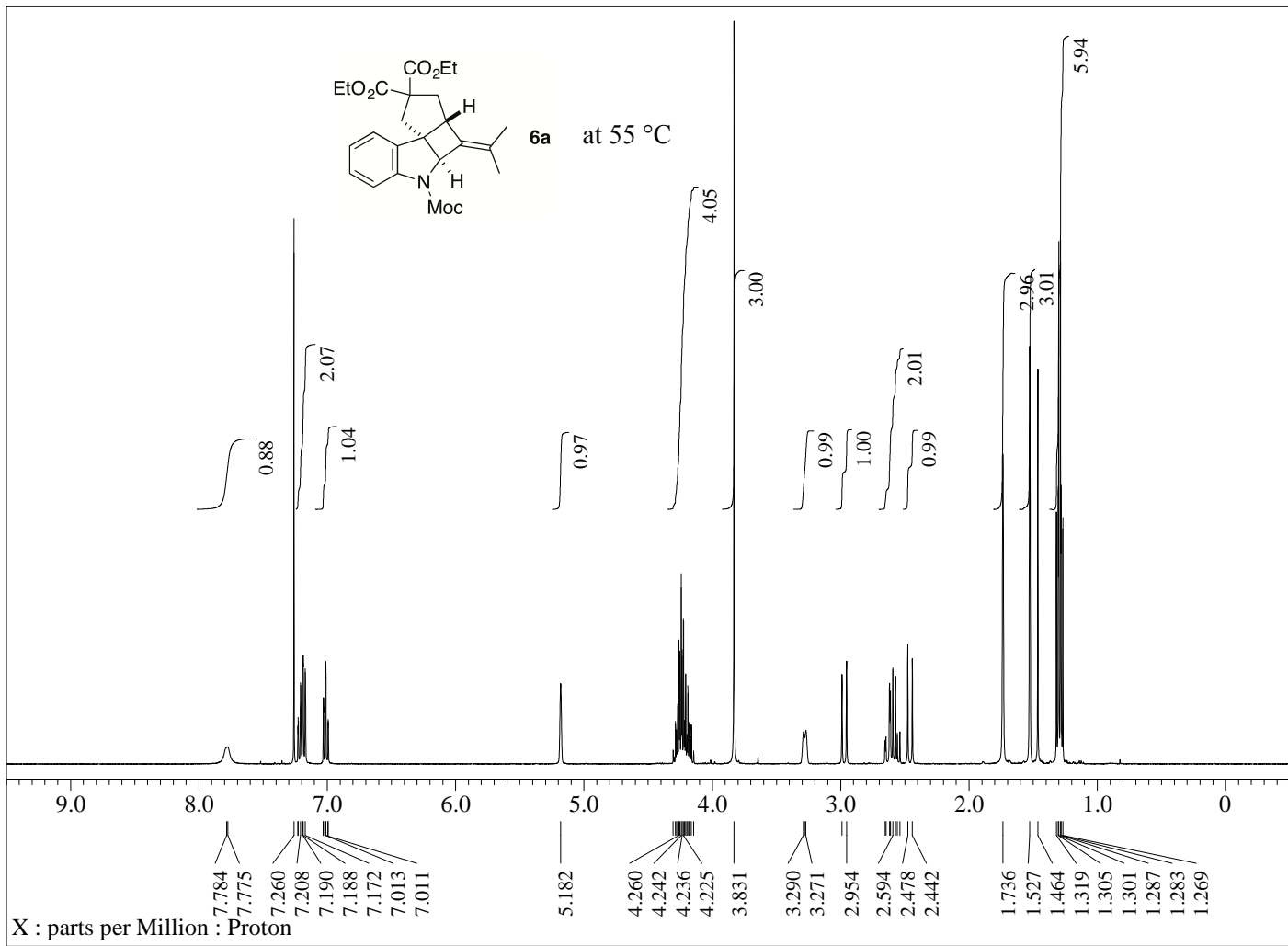


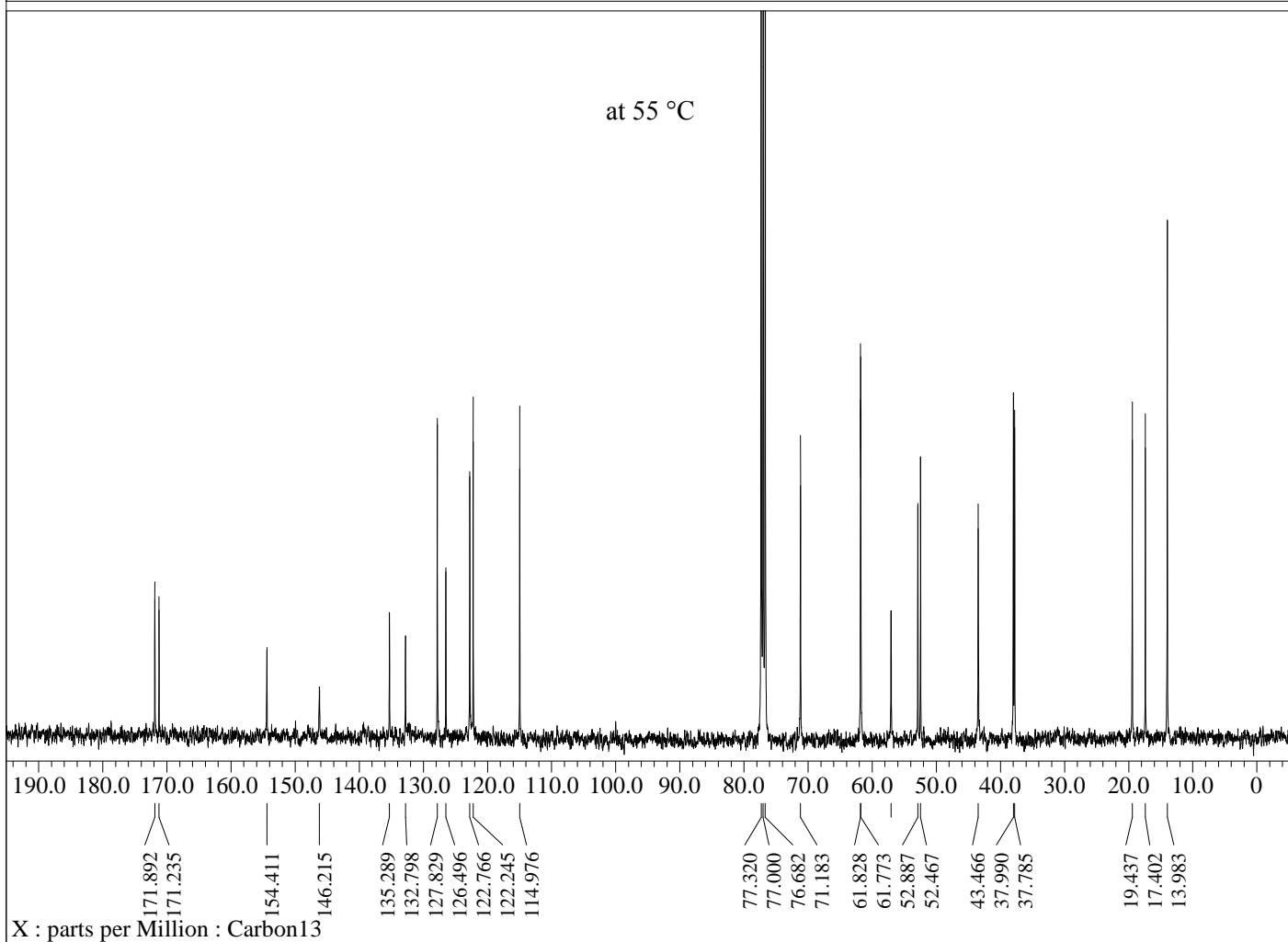
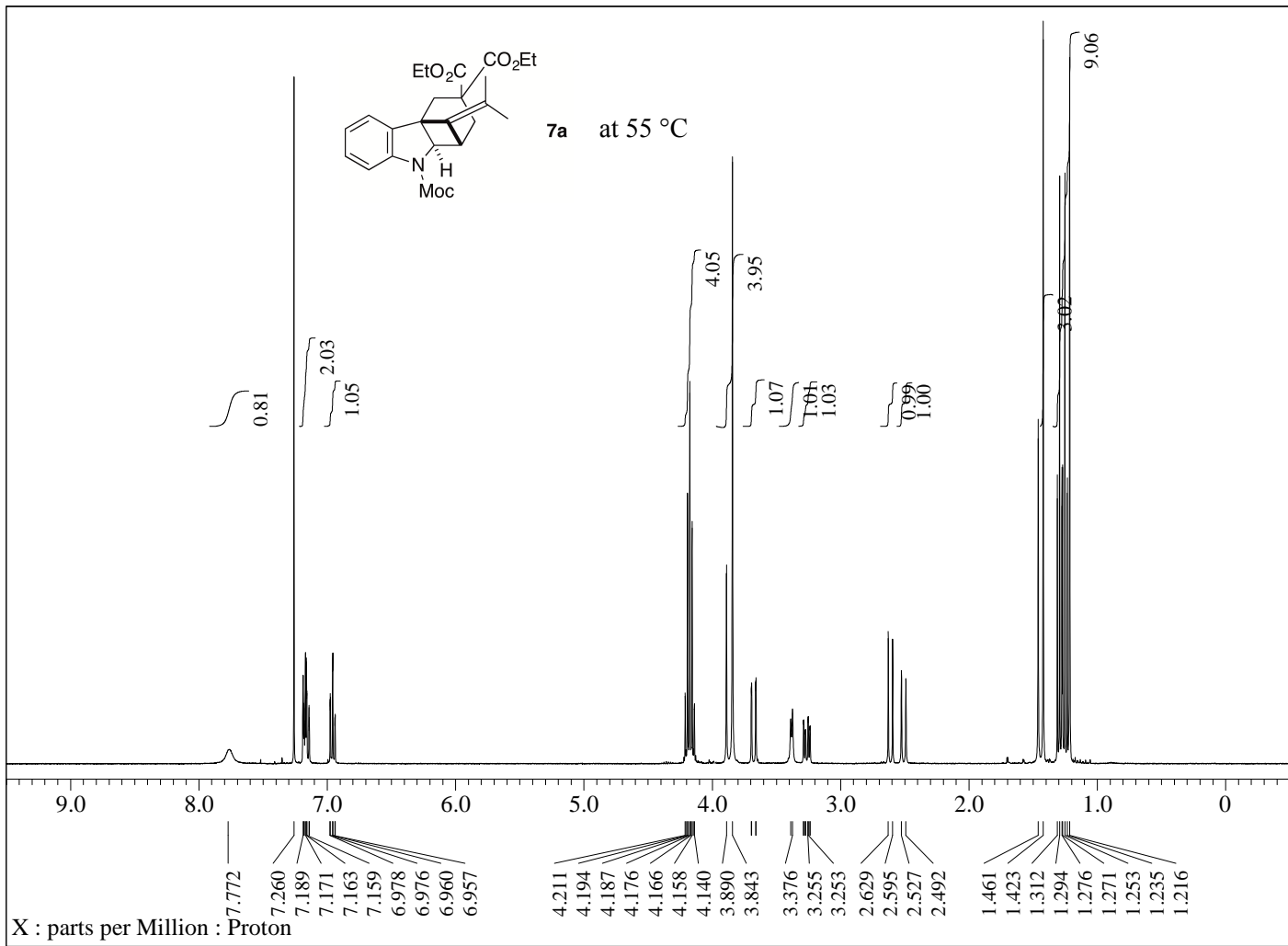


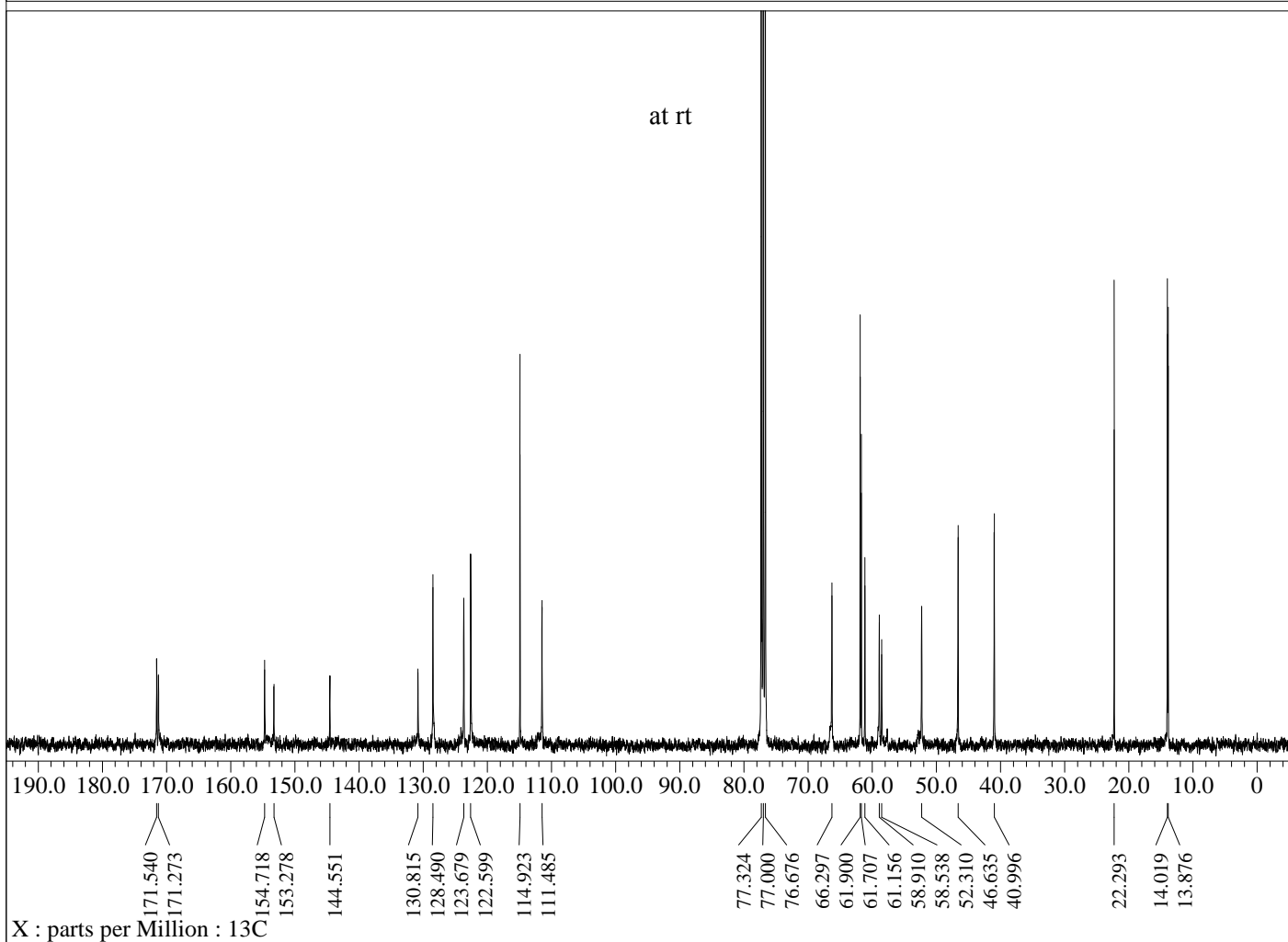
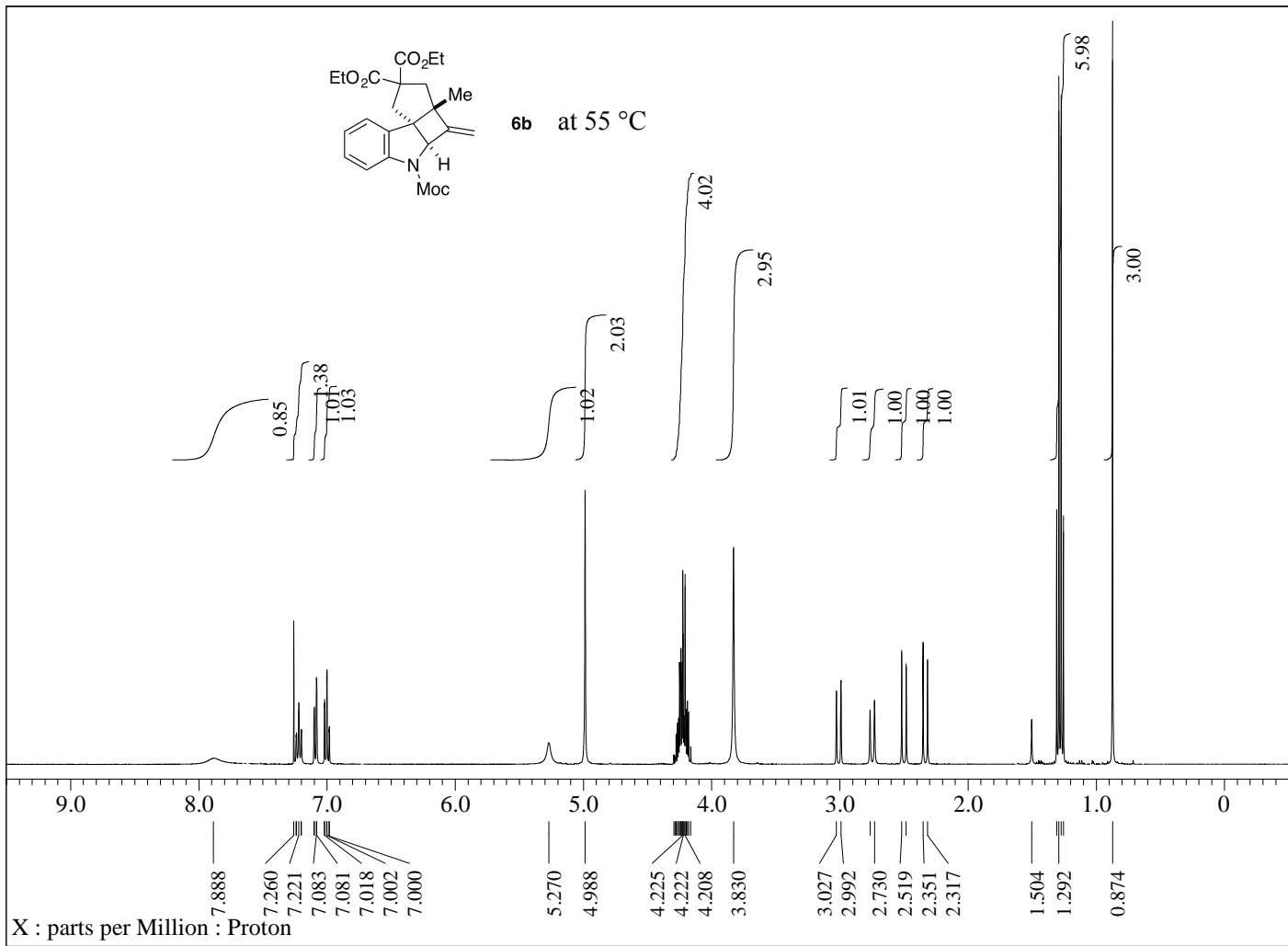
3d at 50 °C

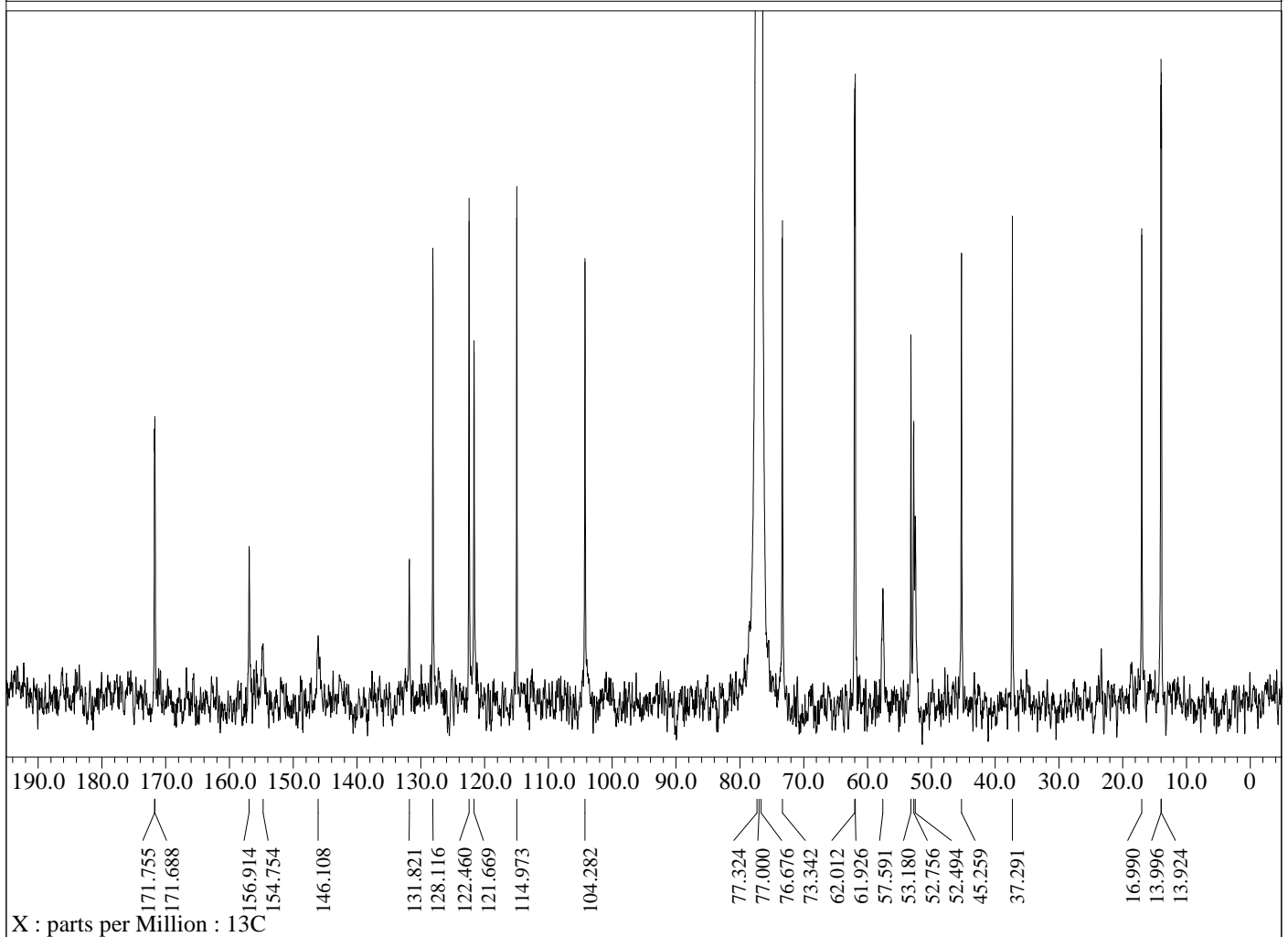
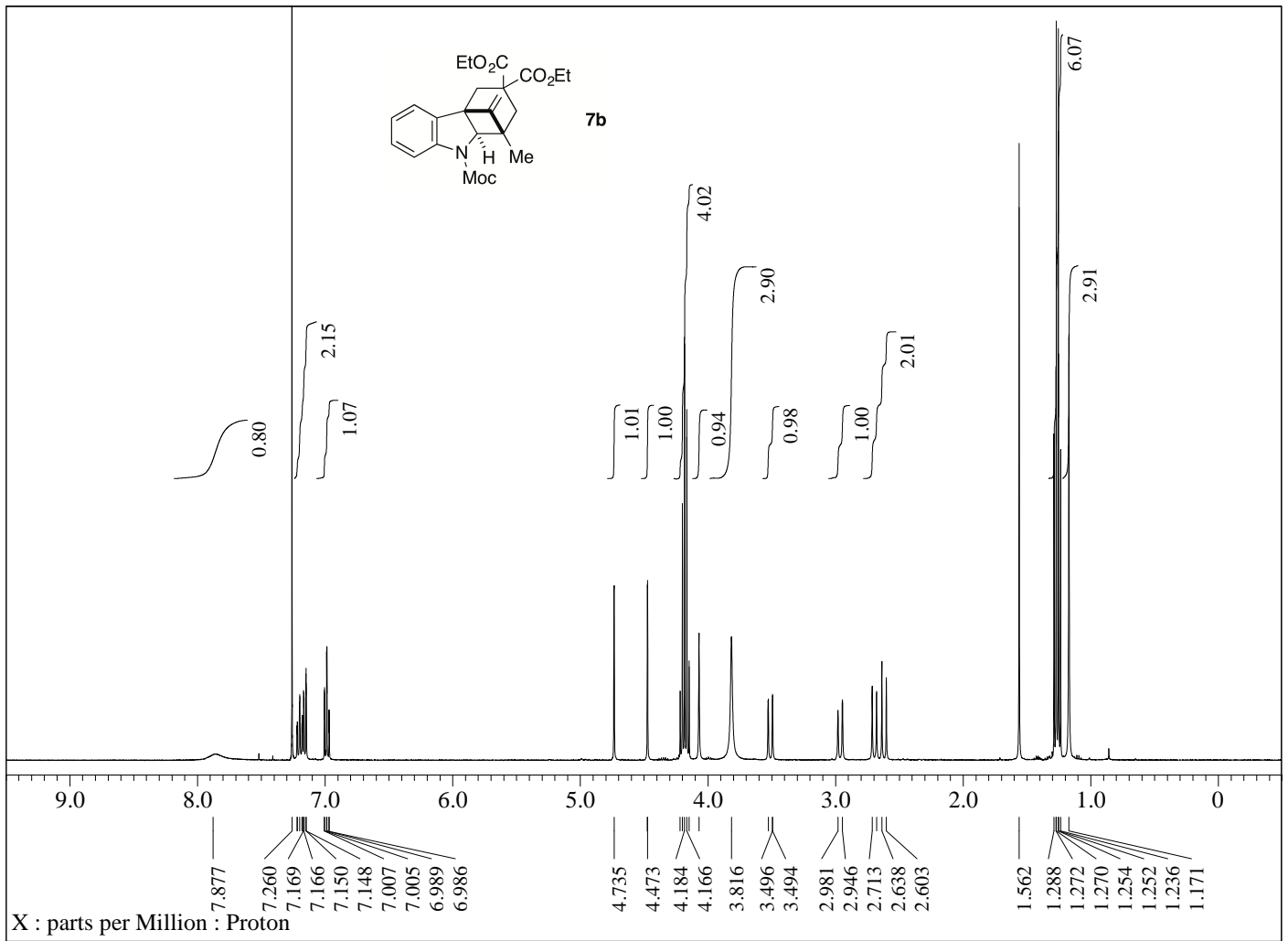


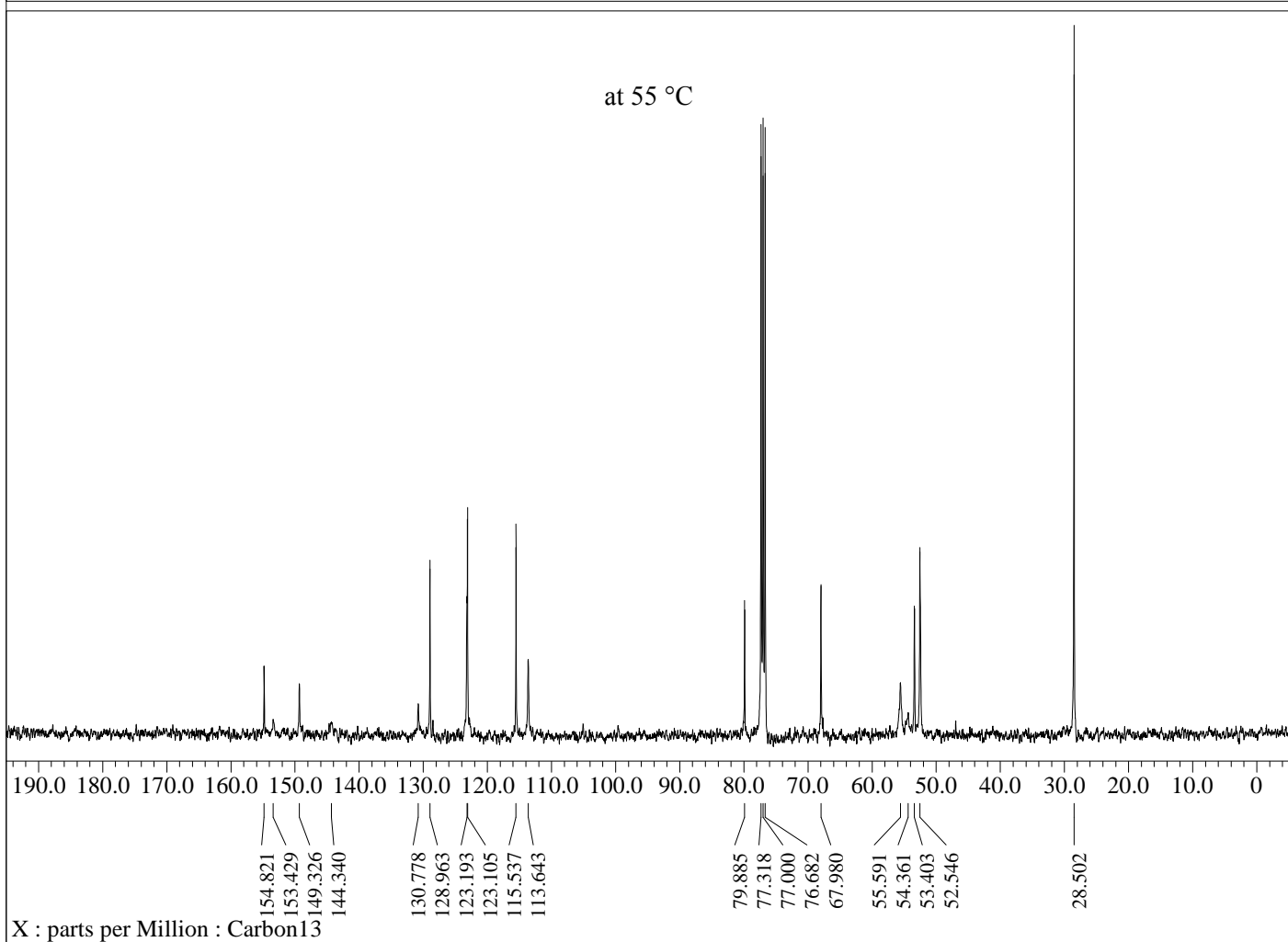
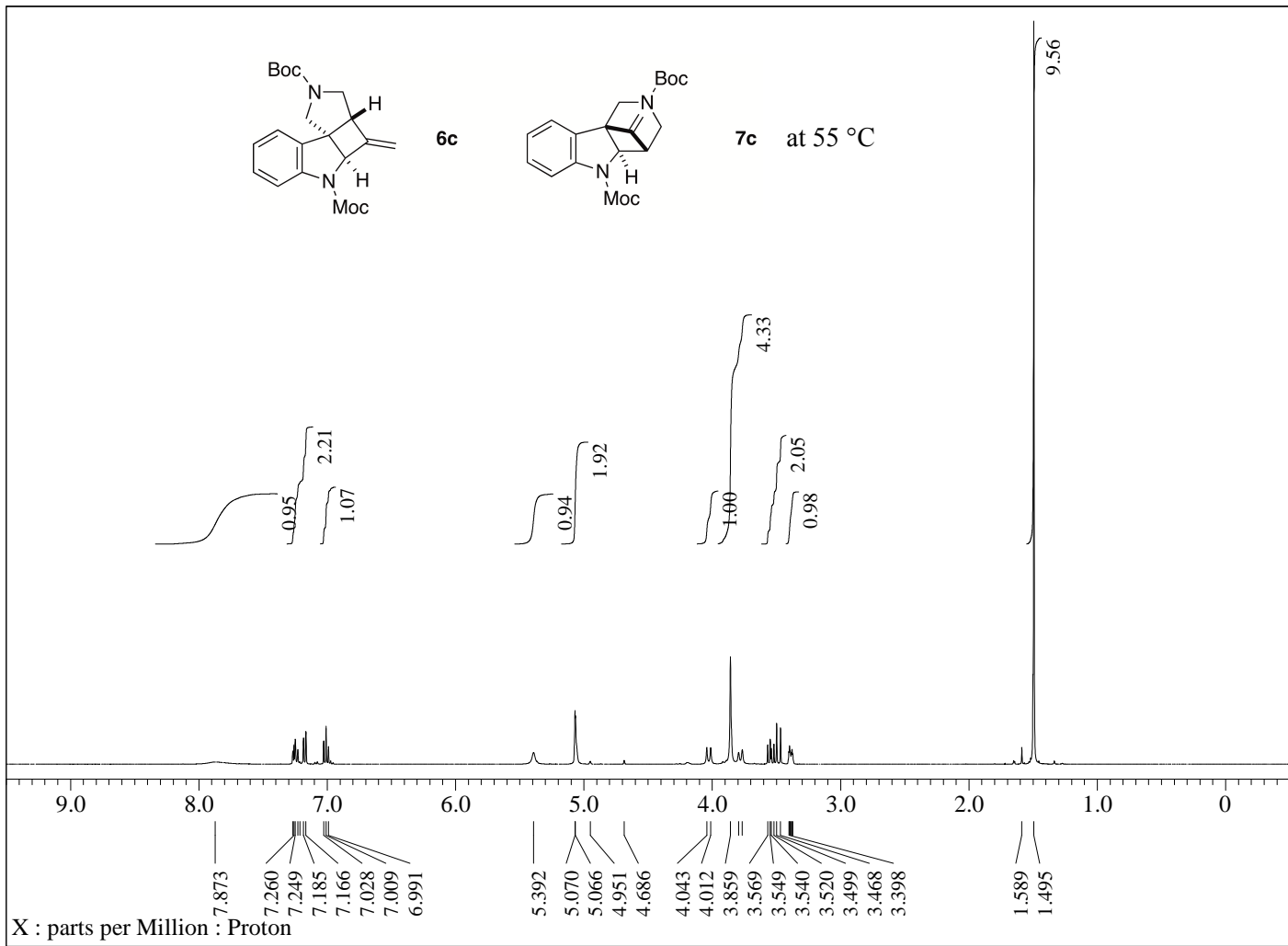


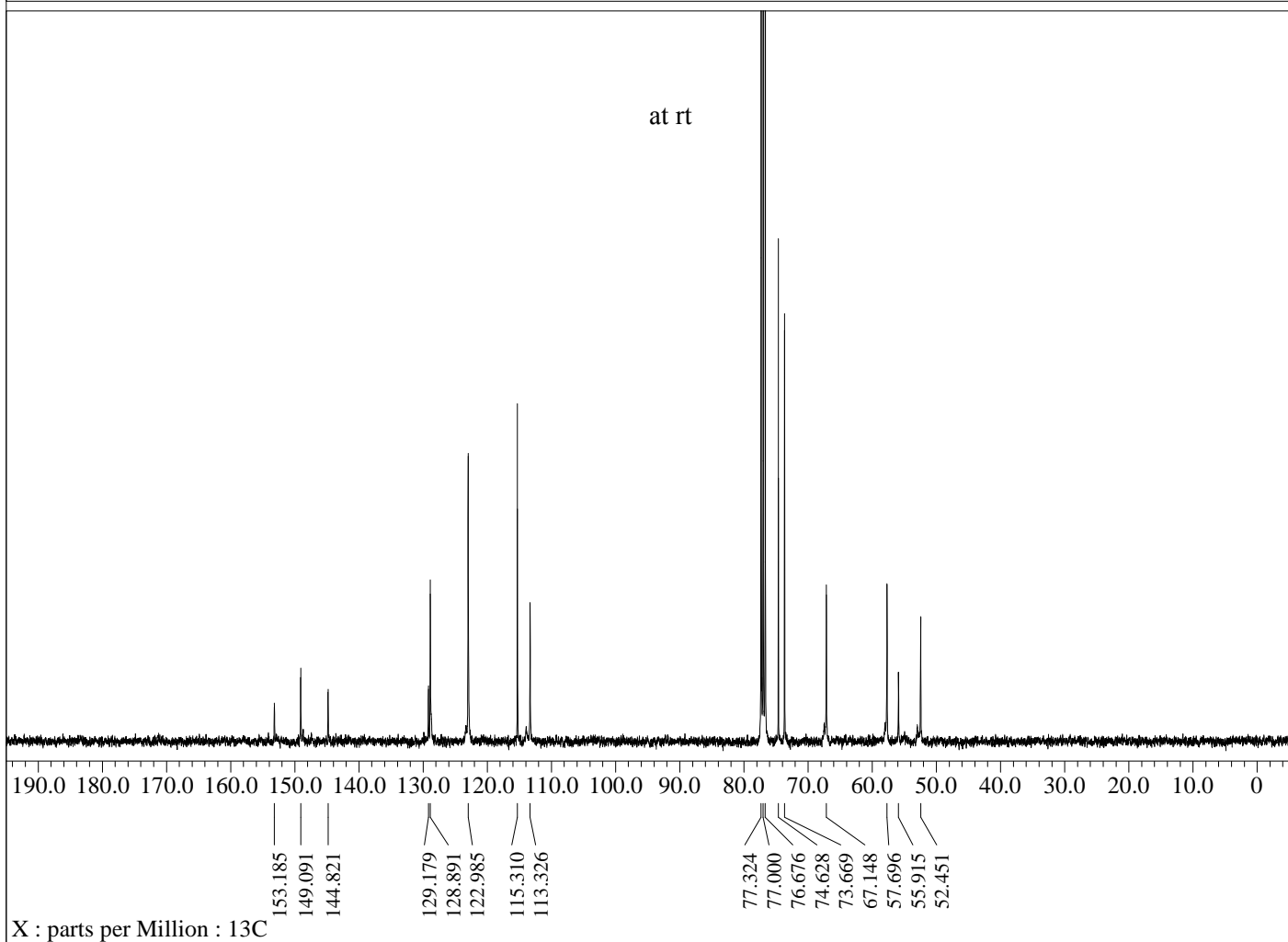
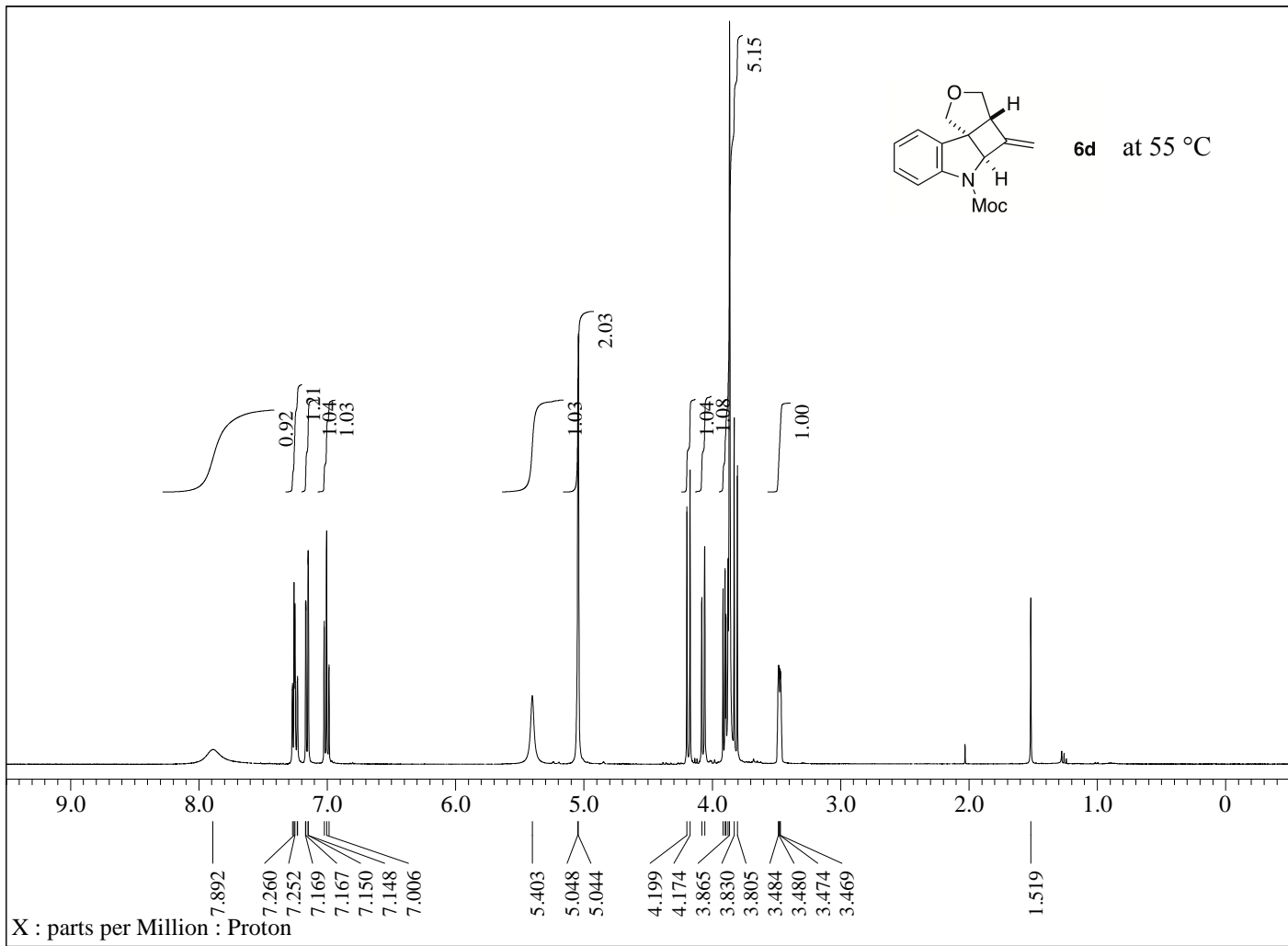


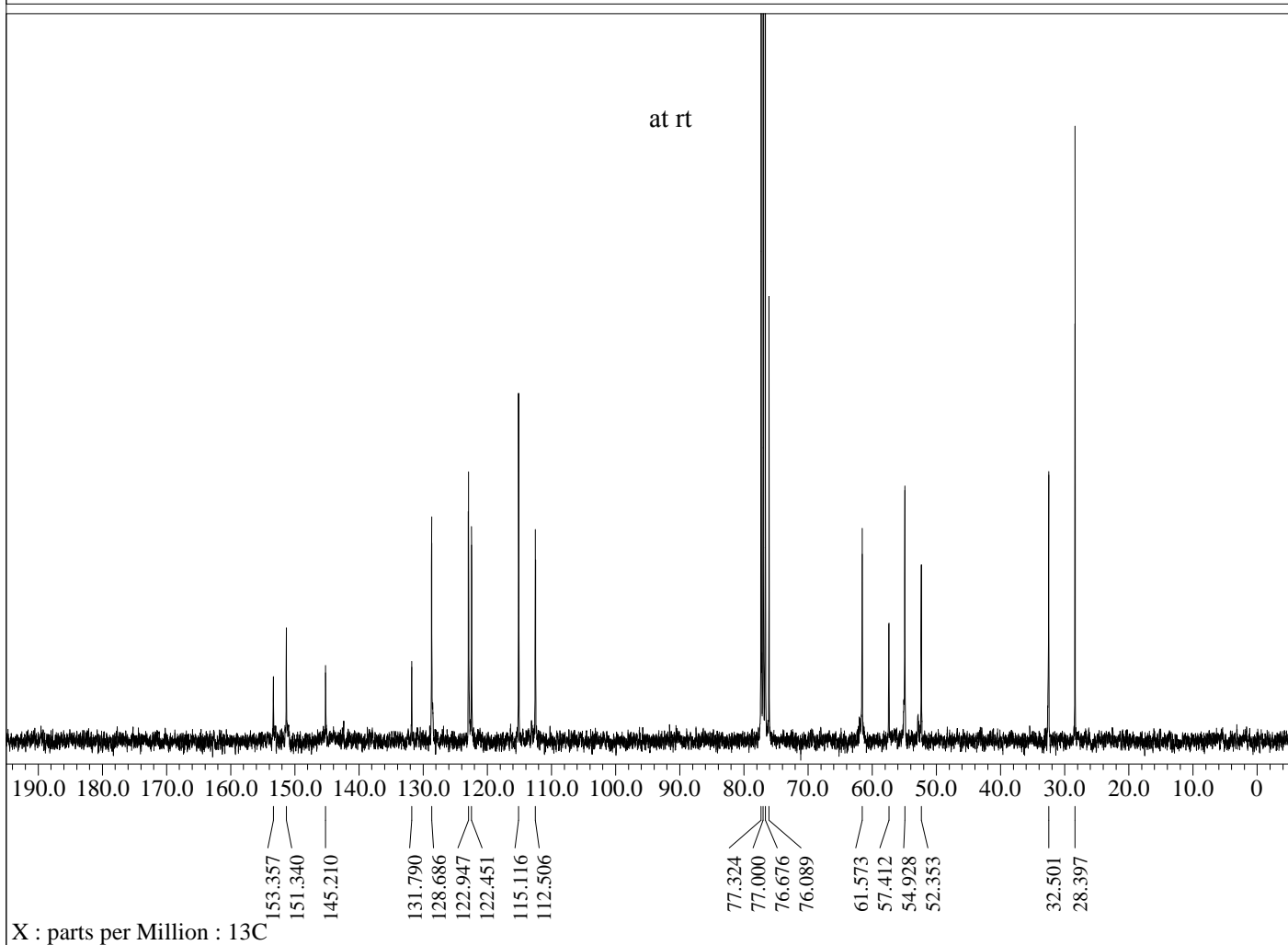
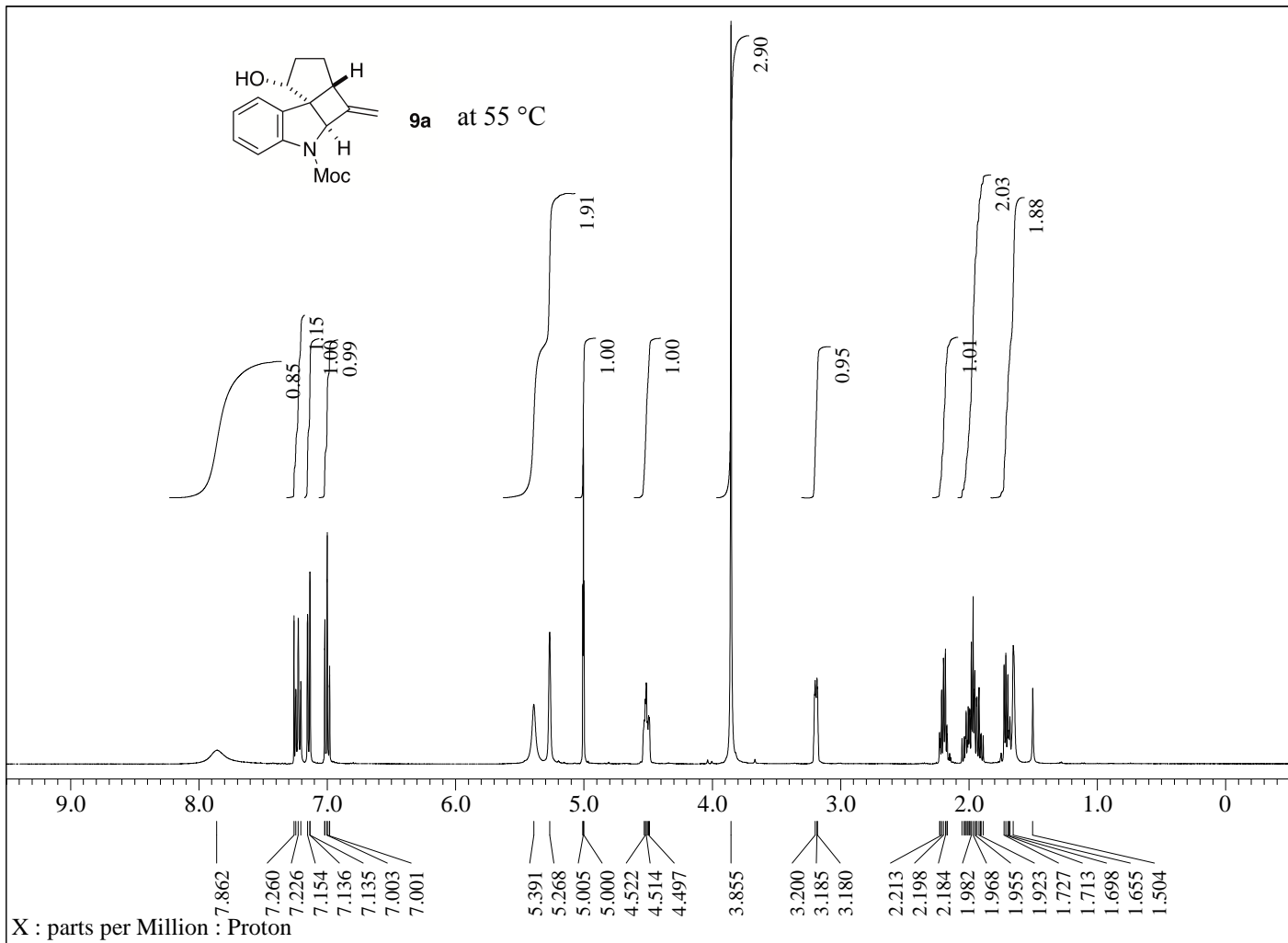


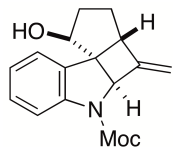




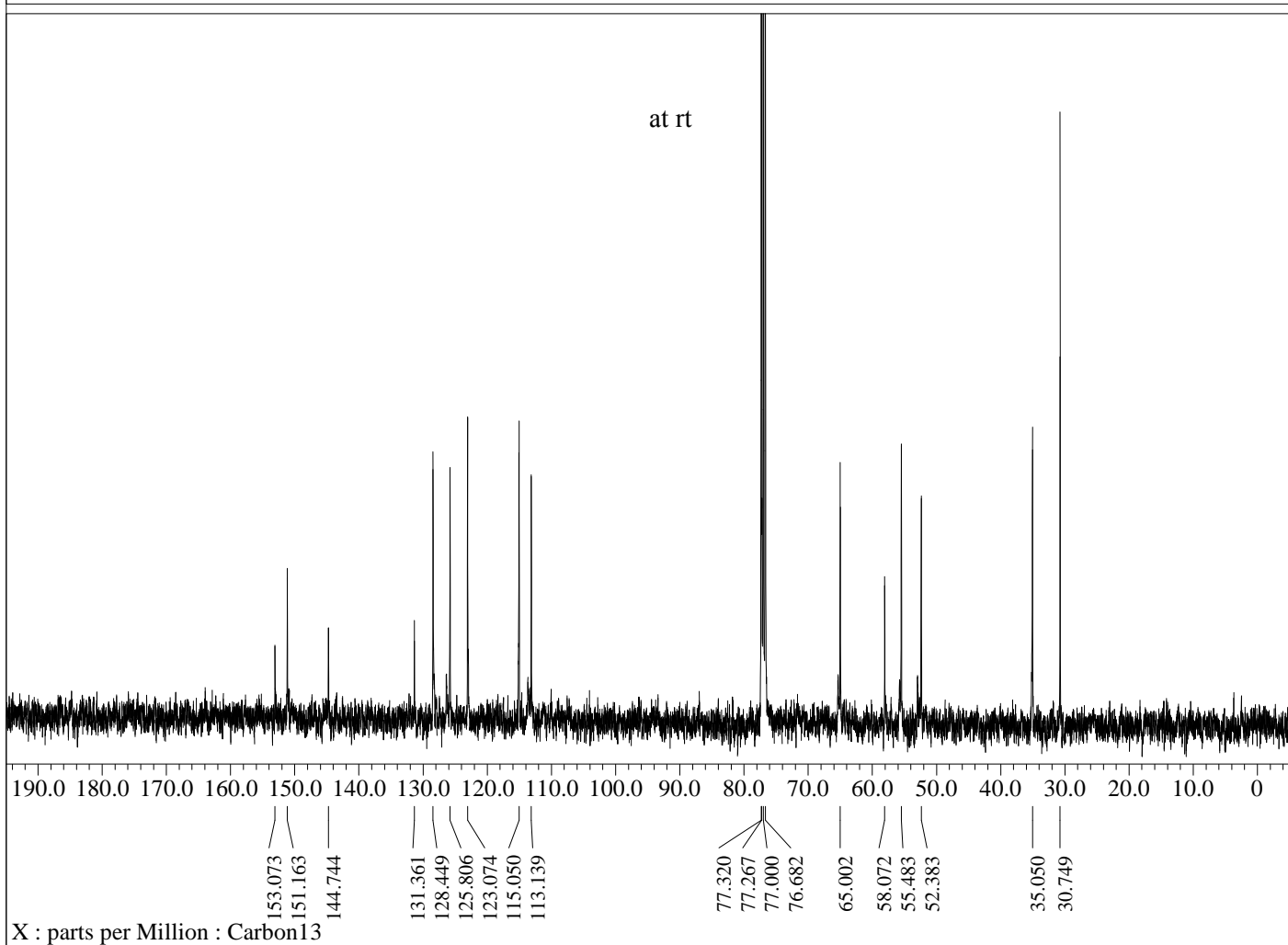
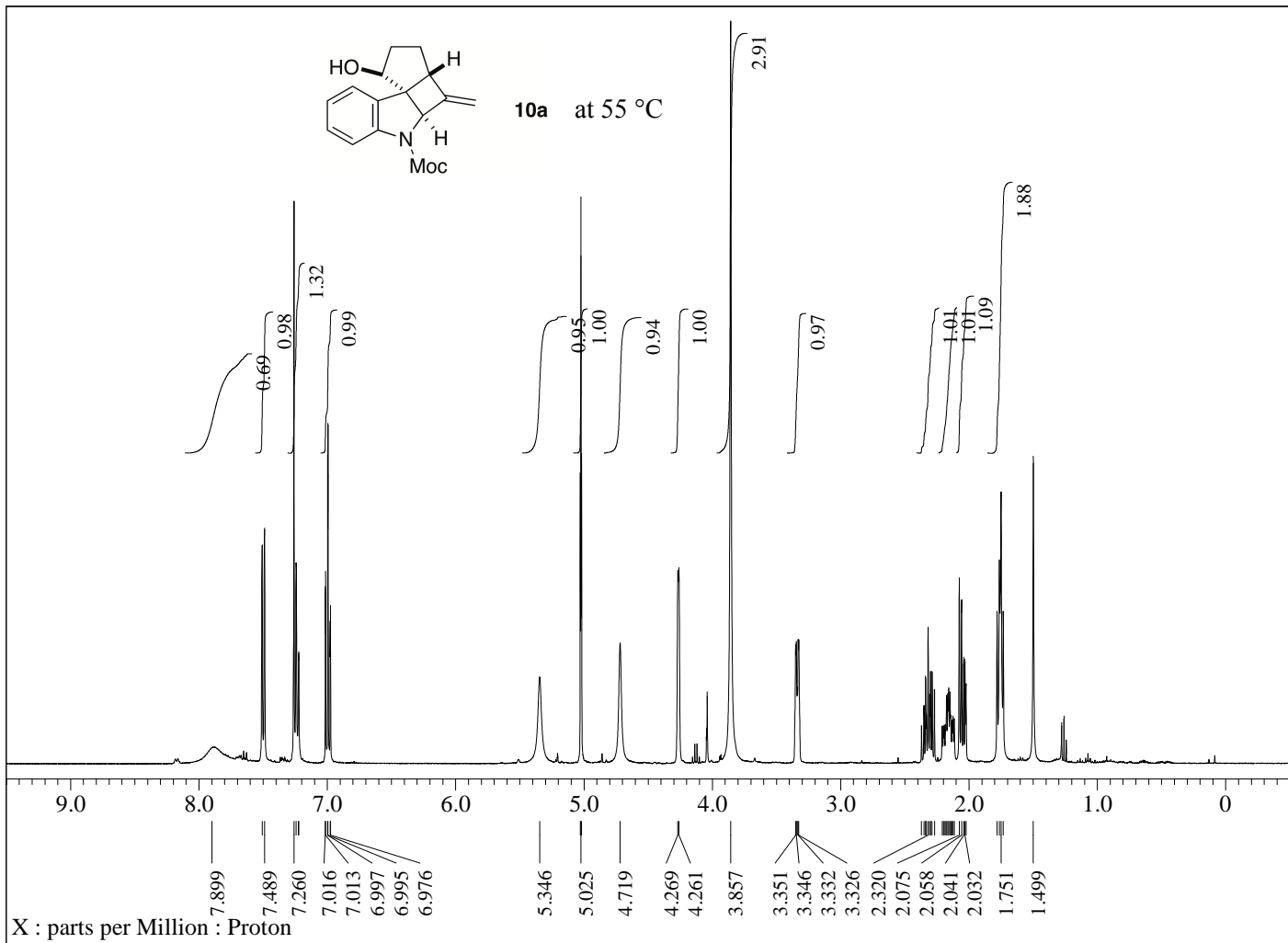


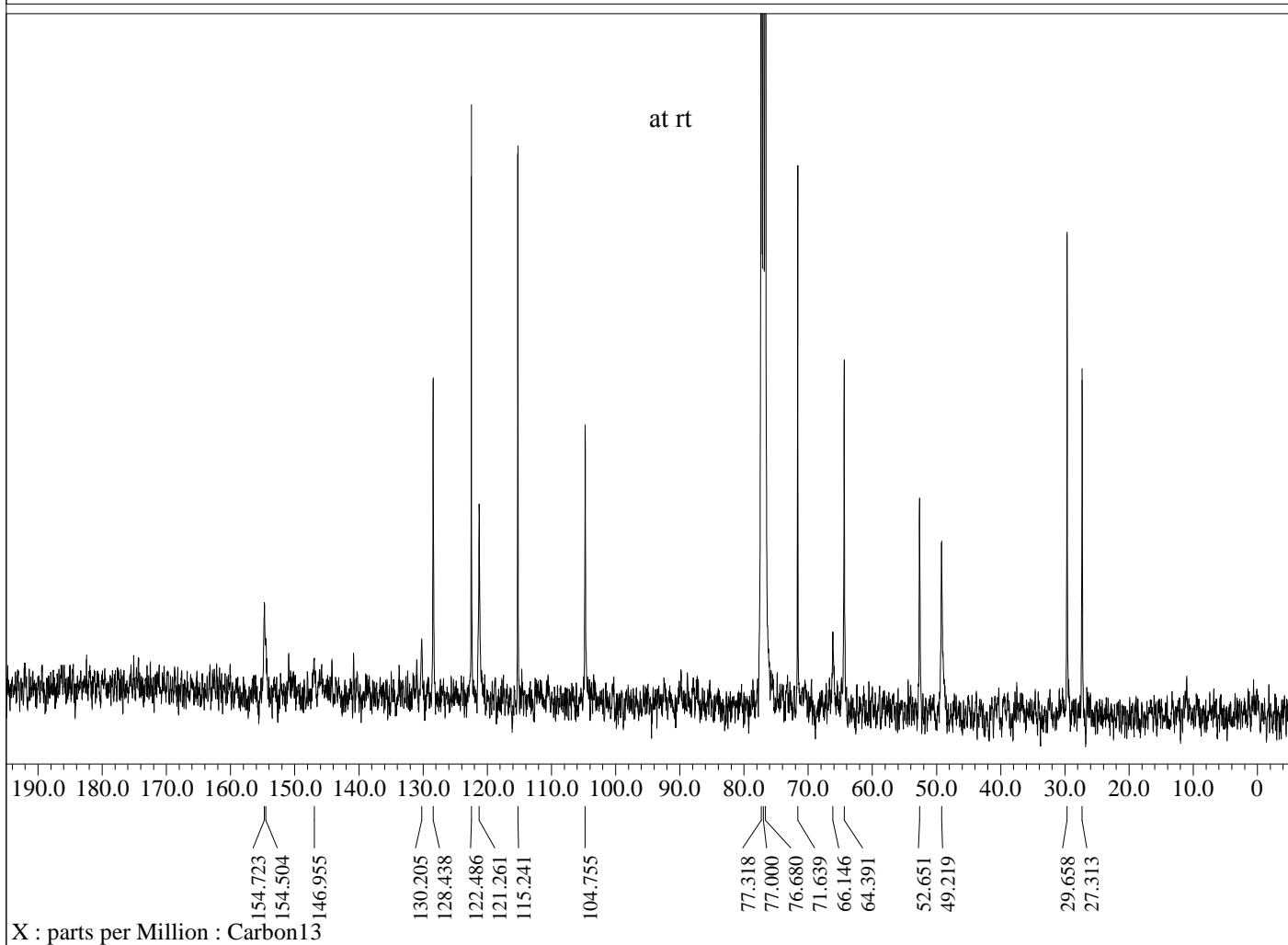
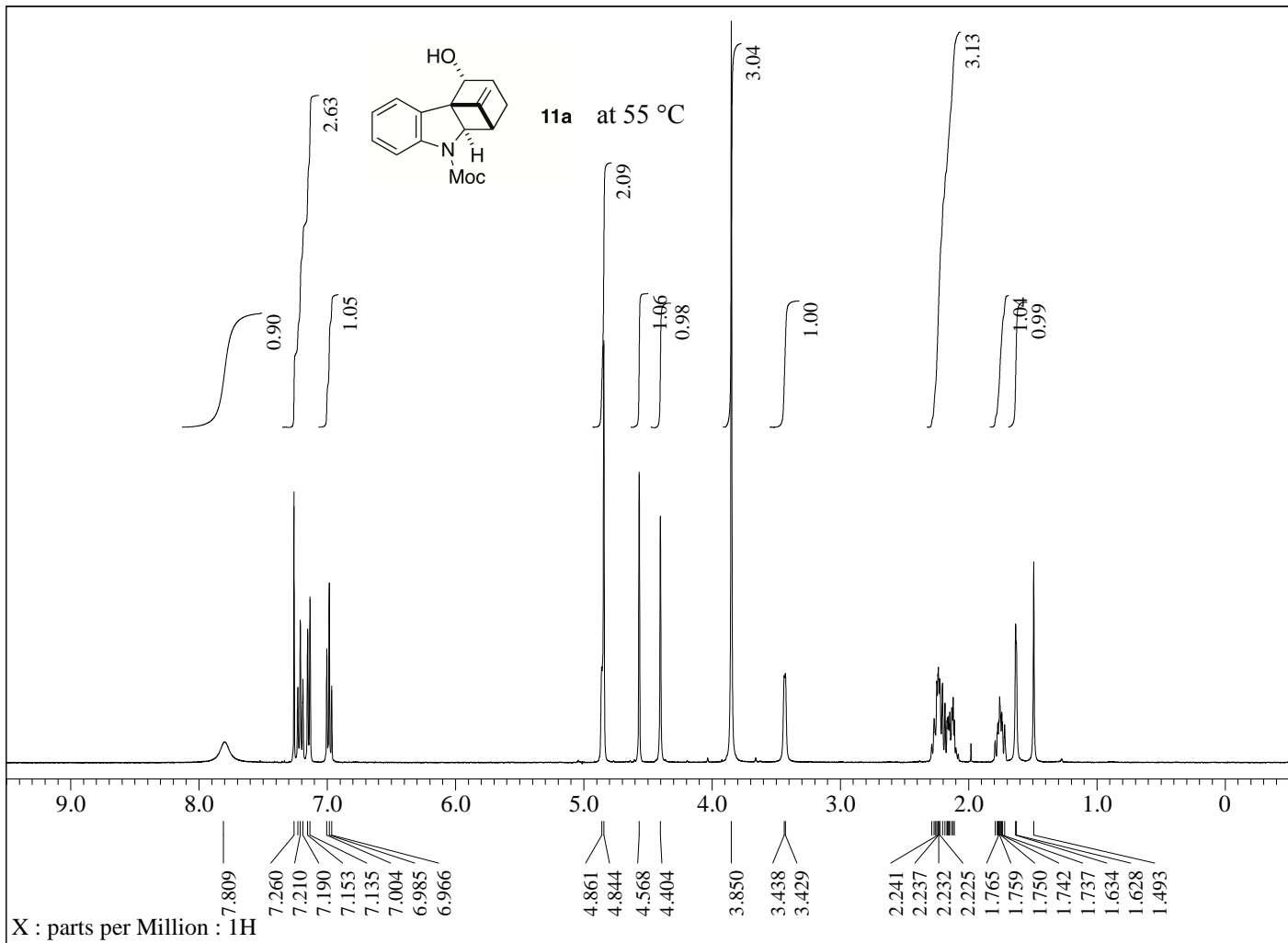


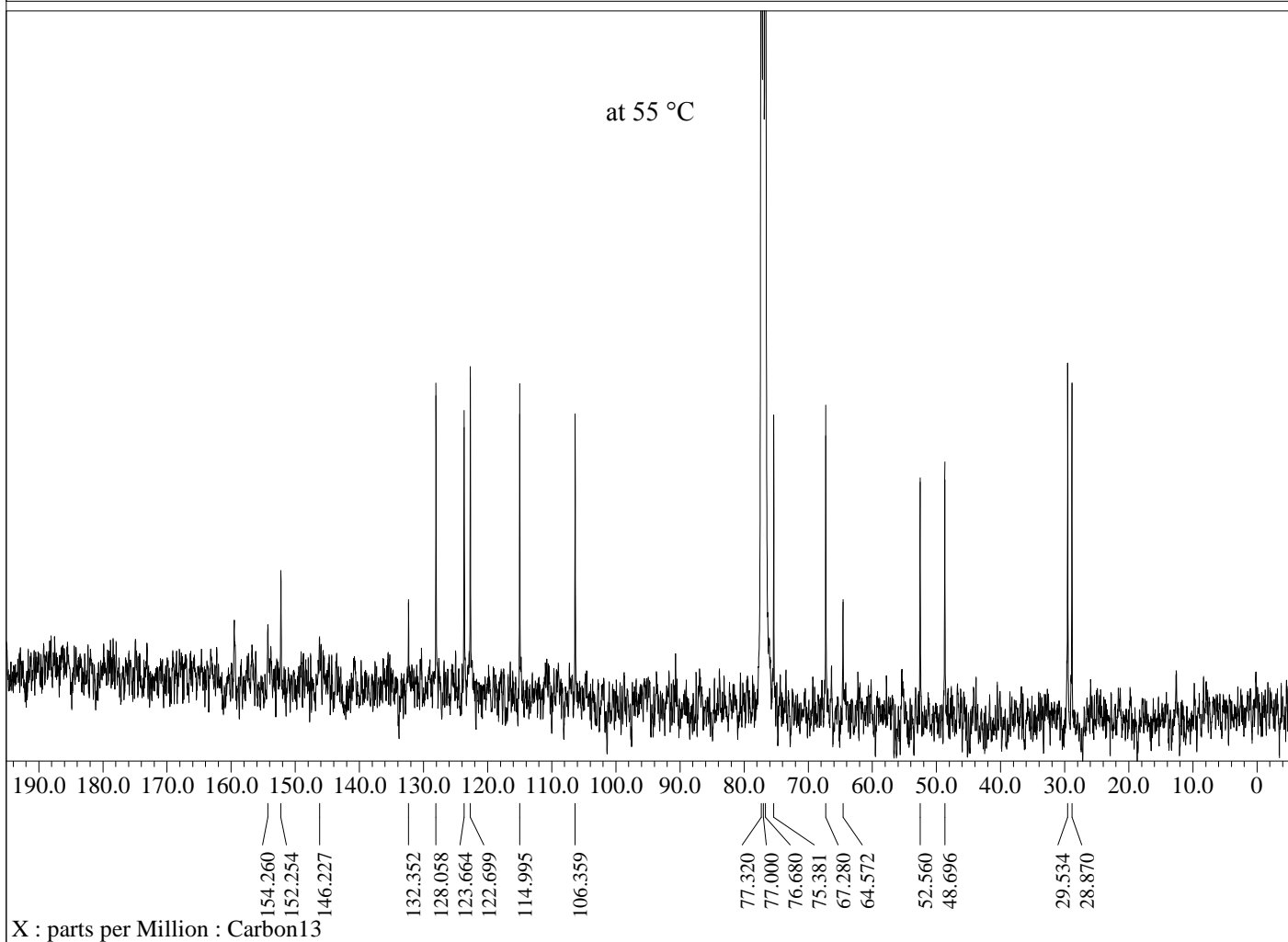
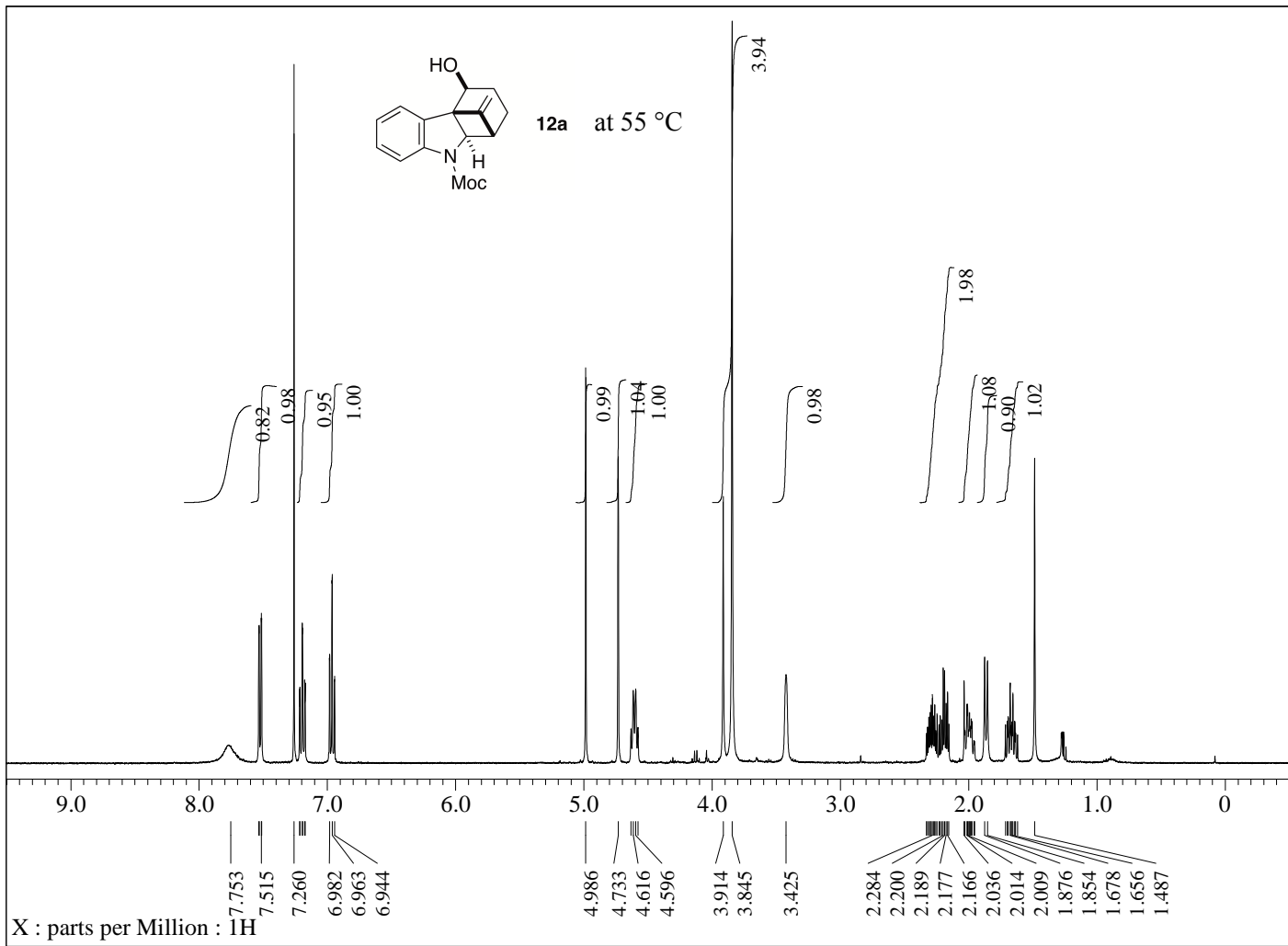


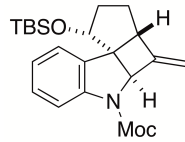


10a at 55 °C

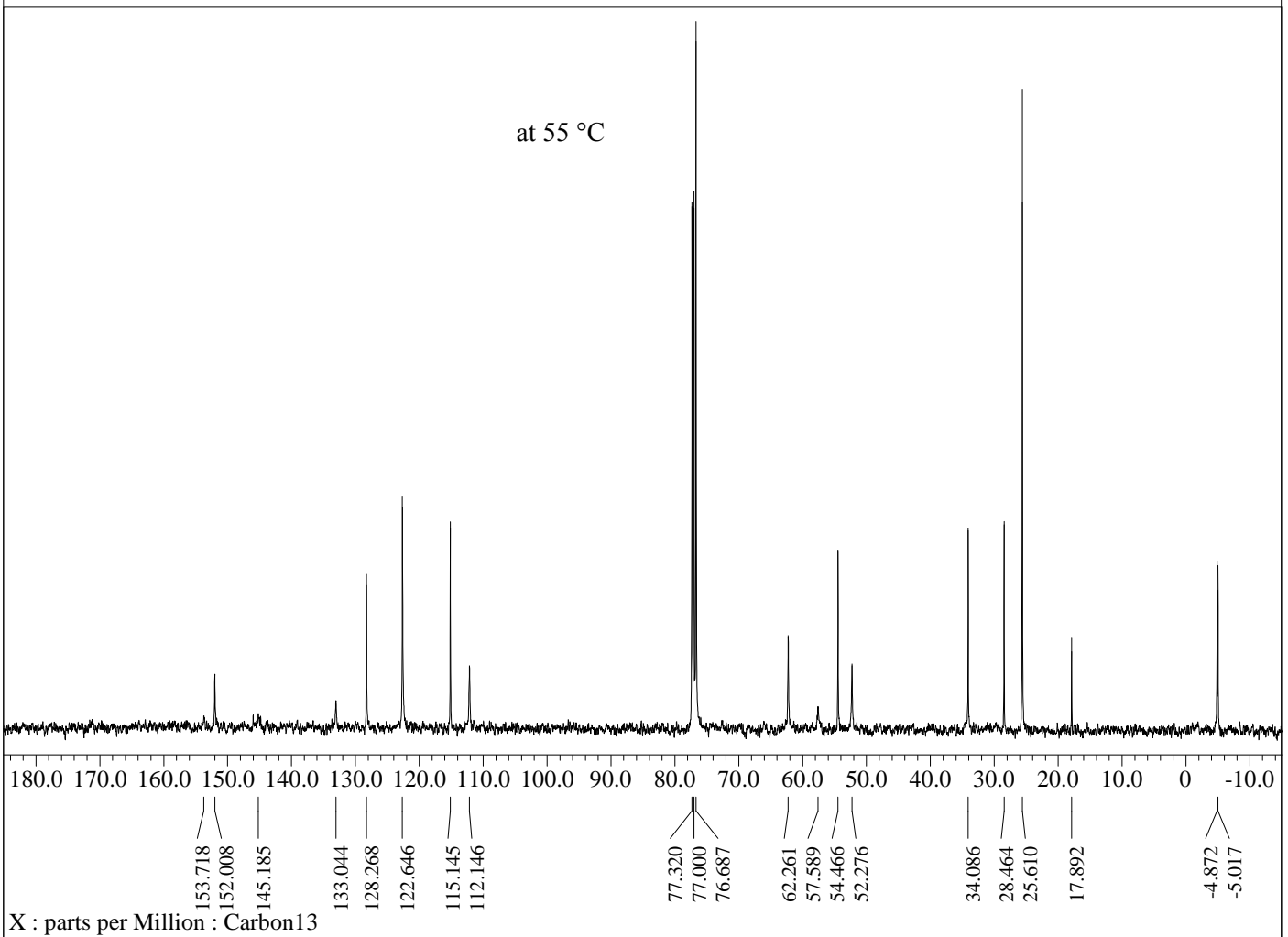
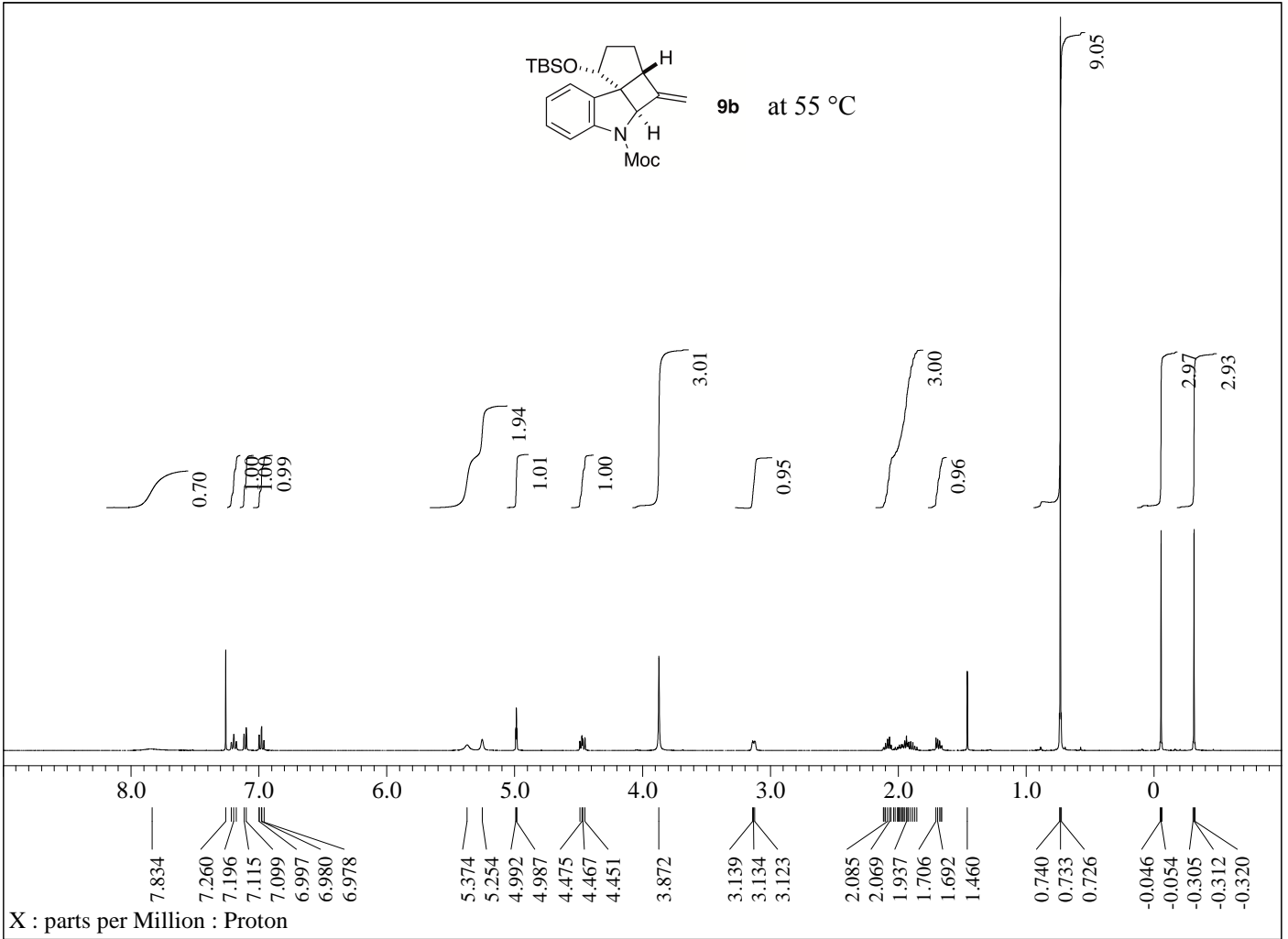


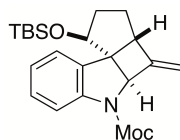




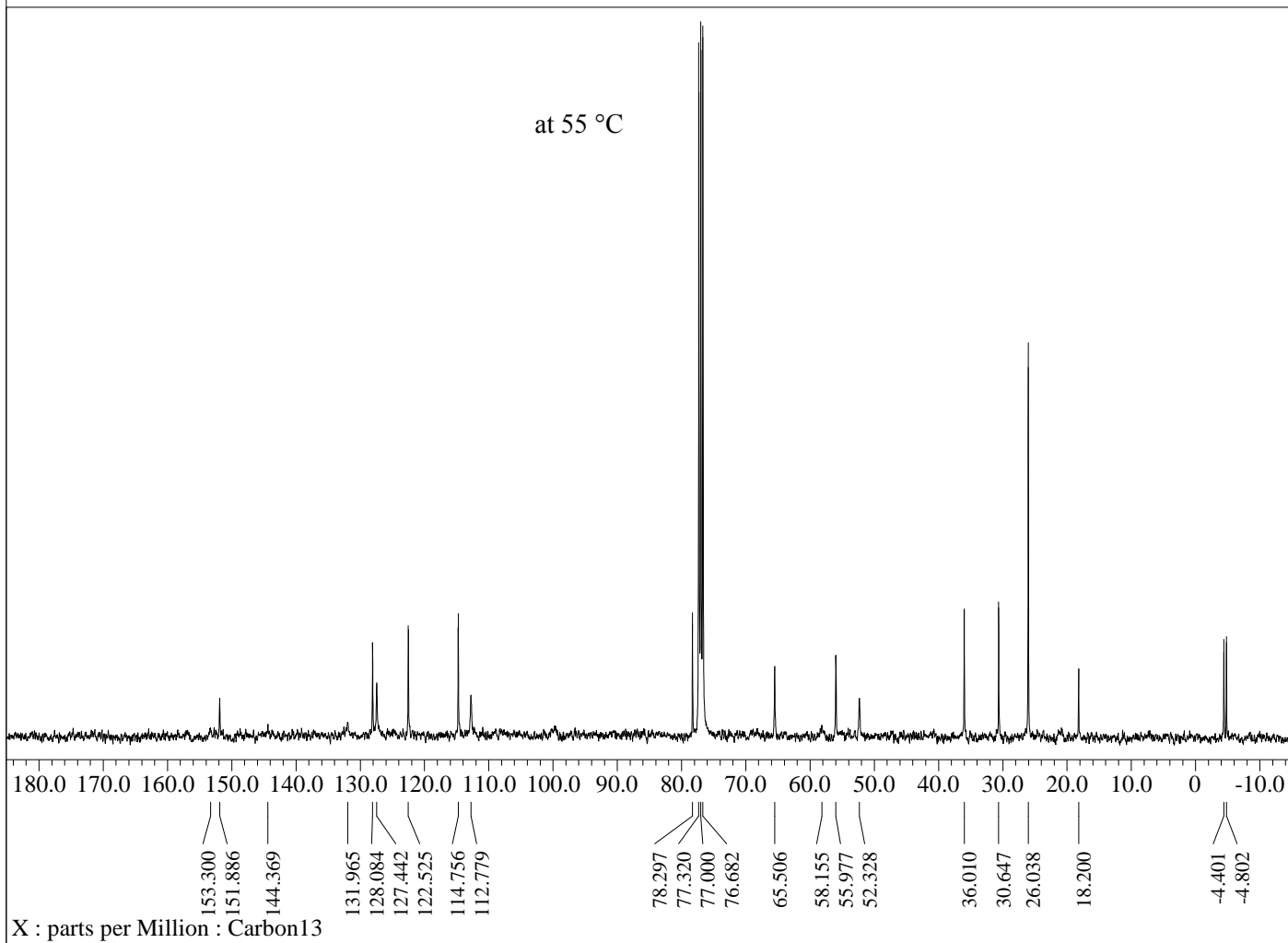
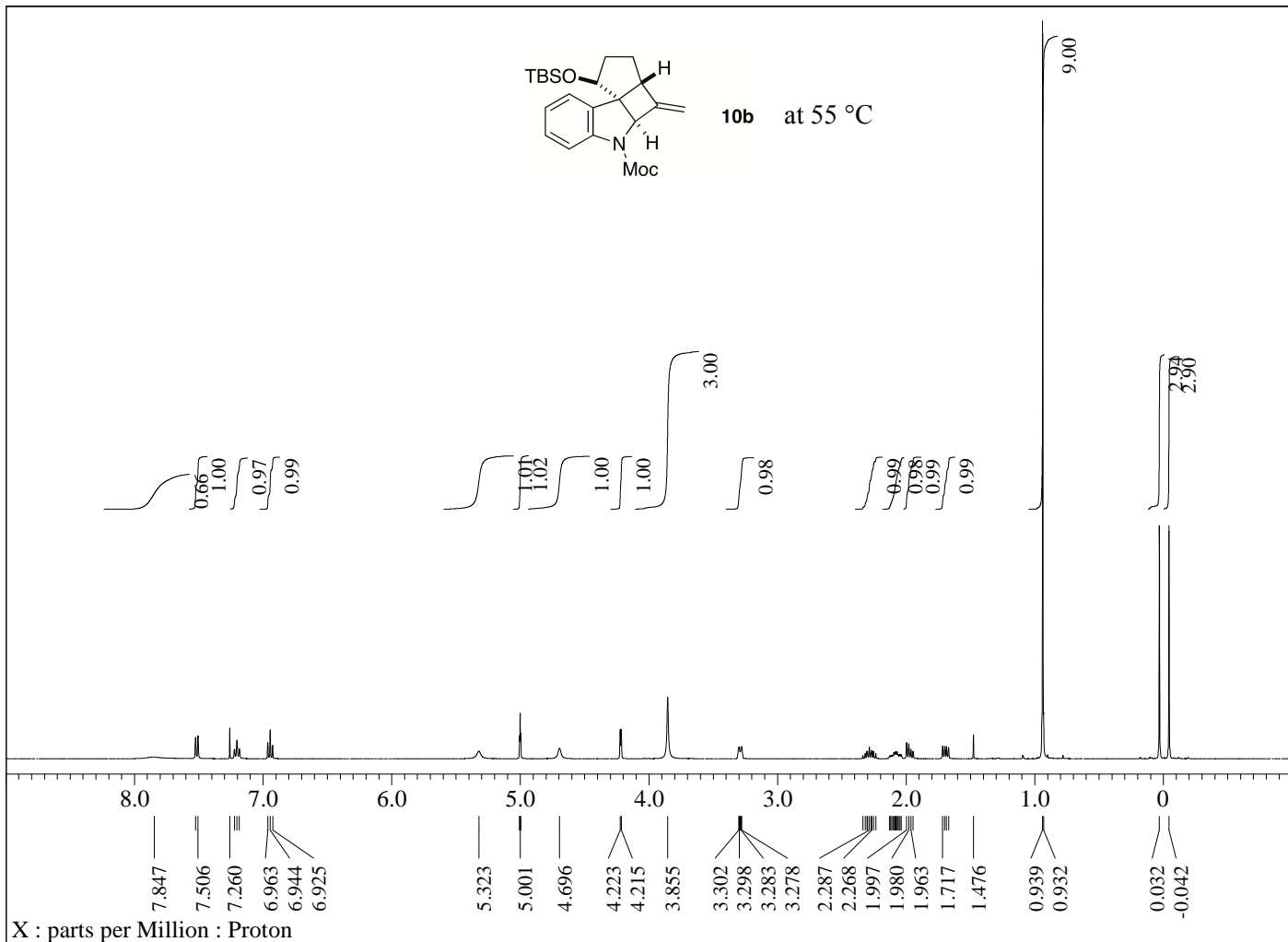


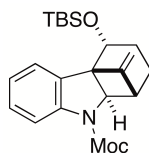
9b at 55 °C





10b at 55 °C





11b at 55 °C

