

Electronic Supplementary Information

Syntheses of Polynorbornadienes by Ring-Opening Metathesis Polymerizations (ROMP) of Symmetric and Non-symmetric 2,3-Bis(alkoxycarbonyl)norbornadienes and Their Conversion to Half-Ester Derivatives

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Diester **1** (isolated yield: 91%). Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ = 2.08 (1H, dt, J = 7.0 Hz and 2.0 Hz), 2.25 (1H, dt, J = 7.0 Hz and 2.0 Hz), 3.76 (6H, s), 3.92 (2H, m), 6.89 (2H, t, J = 1.5 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ = 52.11, 53.37, 73.06, 142.45, 152.52, 165.50.

Diester **2** (isolated yield: 89%). Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ = 1.29 (6H, t, J = 7.0 Hz), 2.07 (1H, d, J = 6.5 Hz), 2.27 (1H, d, J = 7.0 Hz), 3.92 (2H, m), 4.22 (4H, q, J = 7.0 Hz), 6.91 (2H, t, J = 2.0 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ = 14.25, 53.54, 61.11, 73.00, 142.53, 152.26, 165.40.

Diester **3** (isolated yield: 82%). Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ = 0.95 (6H, t, J = 7.0 Hz), 1.69 (4H, m), 2.08 (1H, d, J = 7.0 Hz), 2.28 (1H, d, J = 6.0 Hz), 3.92 (2H, m), 4.12 (4H, t, J = 6.0 Hz), 6.91 (2H, t, J = 1.5 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ = 10.54, 22.03, 53.58, 66.73, 72.94, 142.55, 152.24, 165.47.

Diester **4** (isolated yield: 86%). Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ = 1.28 (12H, d, J = 7.0 Hz), 2.05 (1H, dt, J = 6.5 Hz and 1.5 Hz), 2.27 (1H, dt, J = 6.5 Hz and 1.5 Hz), 3.89 (2H, m), 5.08 (2H, m), 6.90 (2H, t, J = 2.0 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ = 21.95, 53.56, 68.77, 72.87, 142.56, 152.07, 165.06.

Diester **5** (isolated yield: 79%). White solid. ^1H NMR (500 MHz, CDCl_3) δ = 1.48 (18H, s), 1.99 (1H, d, J = 7.0 Hz), 2.26 (1H, d, J = 7.0 Hz), 3.82 (2H, m), 6.87 (2H, t, J = 1.5 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ = 28.25, 53.61, 72.41, 81.53, 142.47, 152.06, 164.58.

Diester **6**. (isolated yield: 62%). Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ = 2.02 (1H, d, J = 5.5 Hz), 2.22 (1H, d, J = 5.5 Hz), 3.97 (2H, s), 5.03 (4H, m), 6.85 (2H, s), 7.25 (10H, m); ^{13}C NMR (125 MHz, CDCl_3) δ = 53.63, 66.89, 73.08, 128.39, 128.43, 128.63, 135.59, 142.53, 152.38, 165.12. HRMS Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4(\text{M}+\text{H})^+$: 360.1362. Found: 360.1366.

Polymer **1a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 5.41 (d, 2H, *trans* =CH), 3.94 (br, 2H, =CHCH), 3.74 (s, 6H, OCH_3), 2.50 and 1.44 (m, 2H, CHCH_2CH); ^{13}C NMR (125 MHz, CDCl_3) δ = 38.85 ($-\text{CH}_2-$), 44.34 ($\text{C}=\text{C}-\text{CH}$), 52.25 (CH_3), 131.57 ($\text{C}=\text{C}$), 142.40 ($\text{C}=\text{C}-\text{C}=\text{O}$), 165.40 ($\text{C}=\text{O}$).

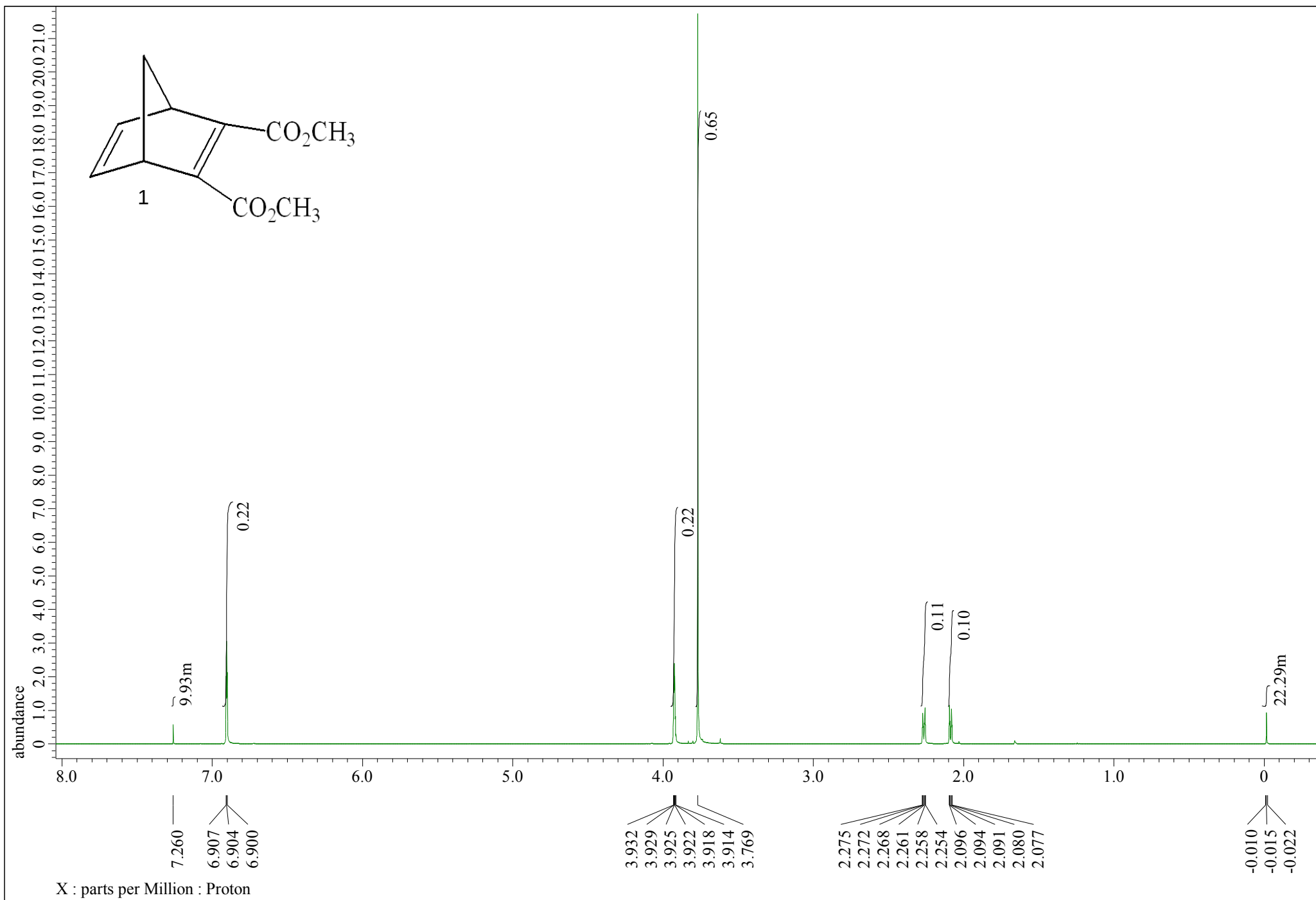
Polymer **2a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 5.45 (br, 2H, *trans* =CH), 4.20 (q, 4H, OCH_2-CH_3), 3.95 (br, 2H, =CHCH), 2.50 and 1.44 (m, 2H, CHCH_2CH), 1.26 (t, 6H, $-\text{CH}_2\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3) δ = 14.21 (CH_3), 38.94 ($-\text{CH}_2-$), 44.46 ($\text{C}=\text{C}-\text{CH}$), 61.09 (OCH_2), 131.60 ($\text{C}=\text{C}$), 142.17 ($\text{C}=\text{C}-\text{C}=\text{O}$), 164.95 ($\text{C}=\text{O}$).

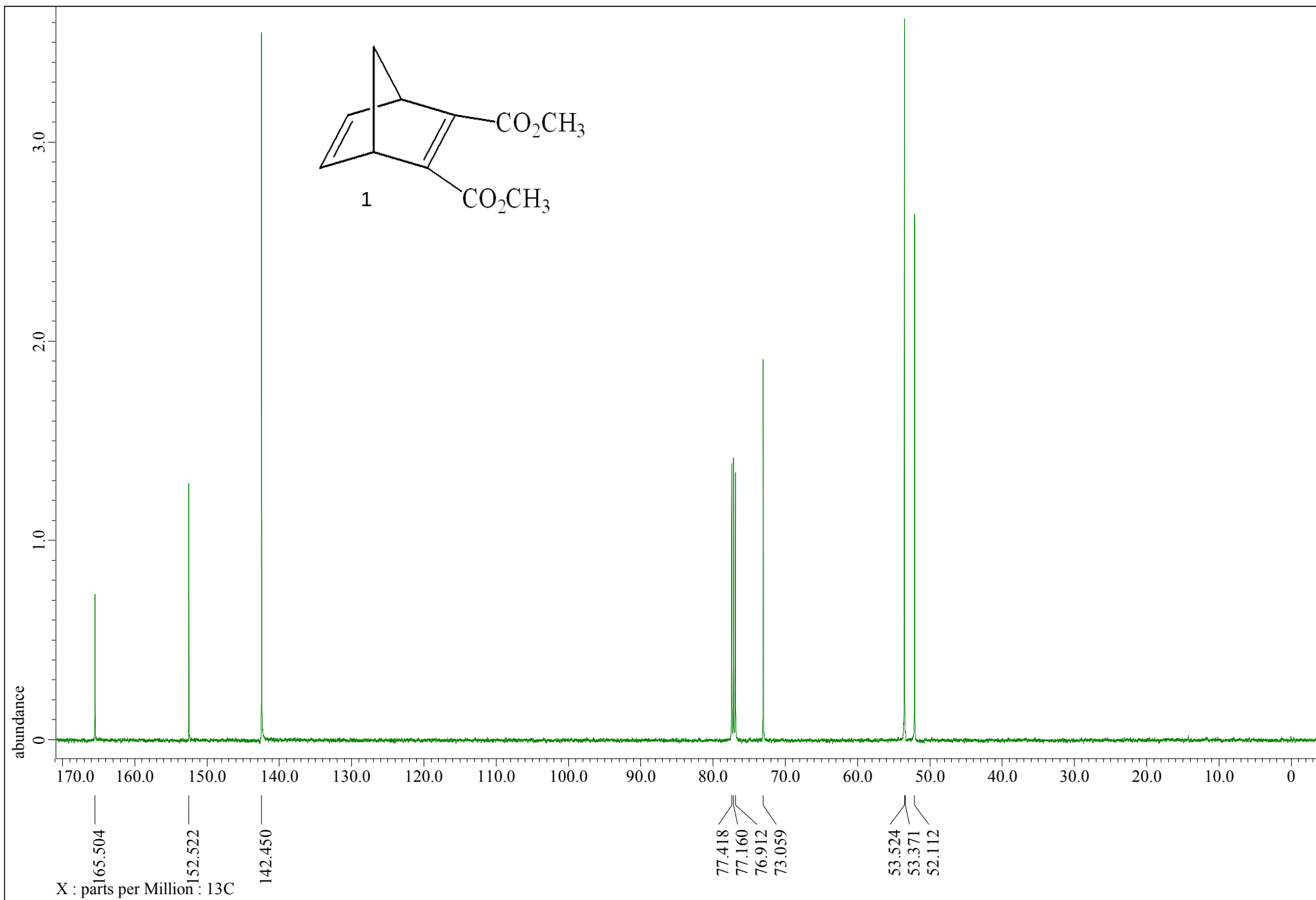
Polymer **3a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 5.57 and 5.43 (br, 2H, *cis* and *trans* =CH), 4.06 (m, 4H, OCH_2-CH_2), 3.94 (d, 2H, =CHCH), 2.50 and 1.44 (m, 2H, CHCH_2CH), 0.91 (t, 6H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ = 10.56 (CH_3), 21.92 ($-\text{CH}_2-\text{CH}_3$), 38.93 ($-\text{CH}_2-$), 44.48 ($\text{C}=\text{C}-\text{CH}$), 66.73 (OCH_2), 131.61 ($\text{C}=\text{C}$), 142.09 ($\text{C}=\text{C}-\text{C}=\text{O}$), 165.00 ($\text{C}=\text{O}$).

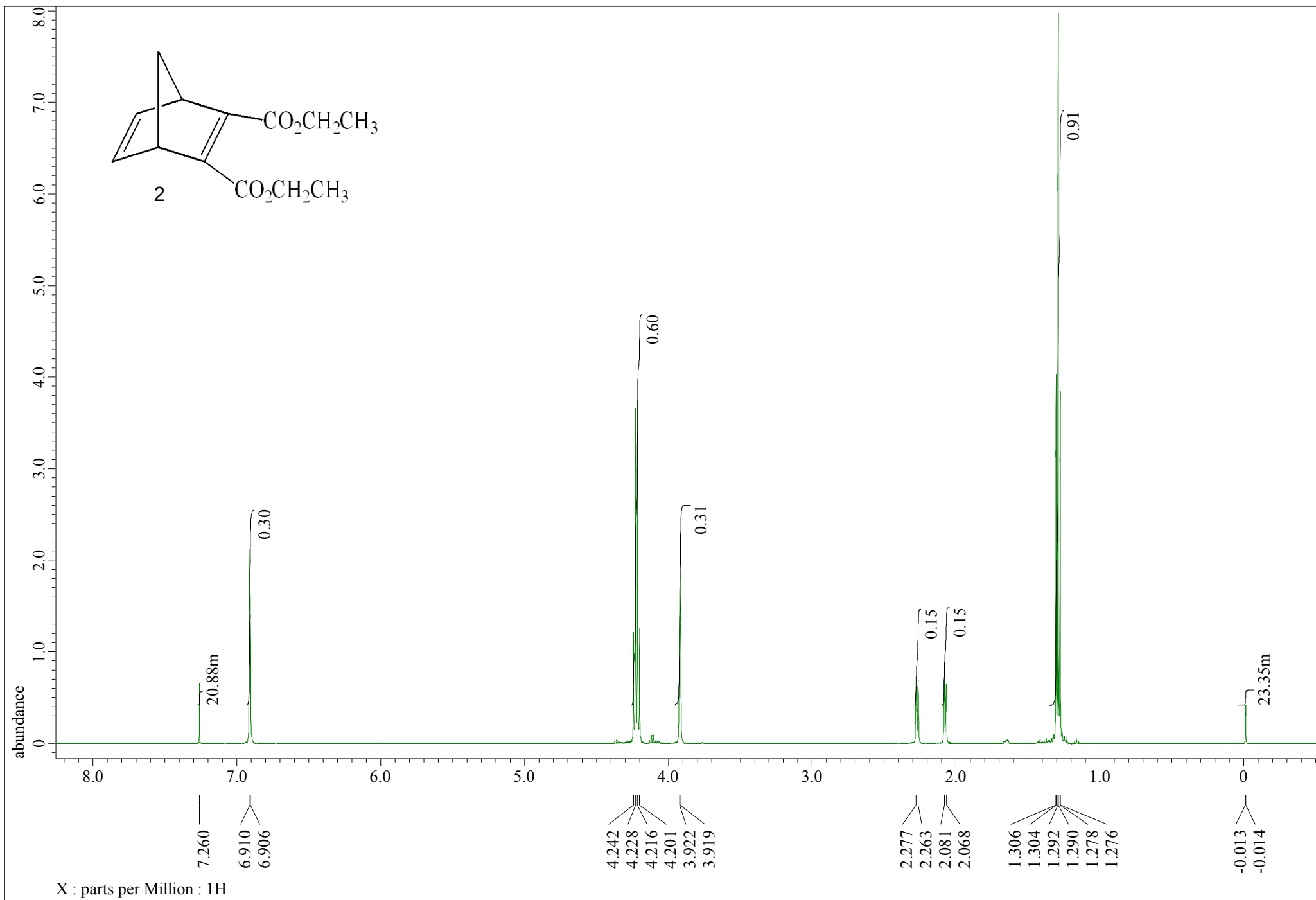
Polymer **4a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 5.57 and 5.46 (br, 2H, *cis* and *trans* =CH), 5.29 (m, 2H, $\text{OCH}(\text{CH}_3)_2$), 3.91 (d, 2H, =CHCH), 2.50 and 1.23 (d, 12H, $\text{OCH}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3) δ = 21.92 (CH_3), 39.21 ($-\text{CH}_2-$), 44.55 ($\text{C}=\text{C}-\text{CH}$), 68.80 ($\text{OCH}(\text{CH}_3)_2$), 131.61 ($\text{C}=\text{C}$), 142.05 ($\text{C}=\text{C}-\text{C}=\text{O}$), 164.48 ($\text{C}=\text{O}$).

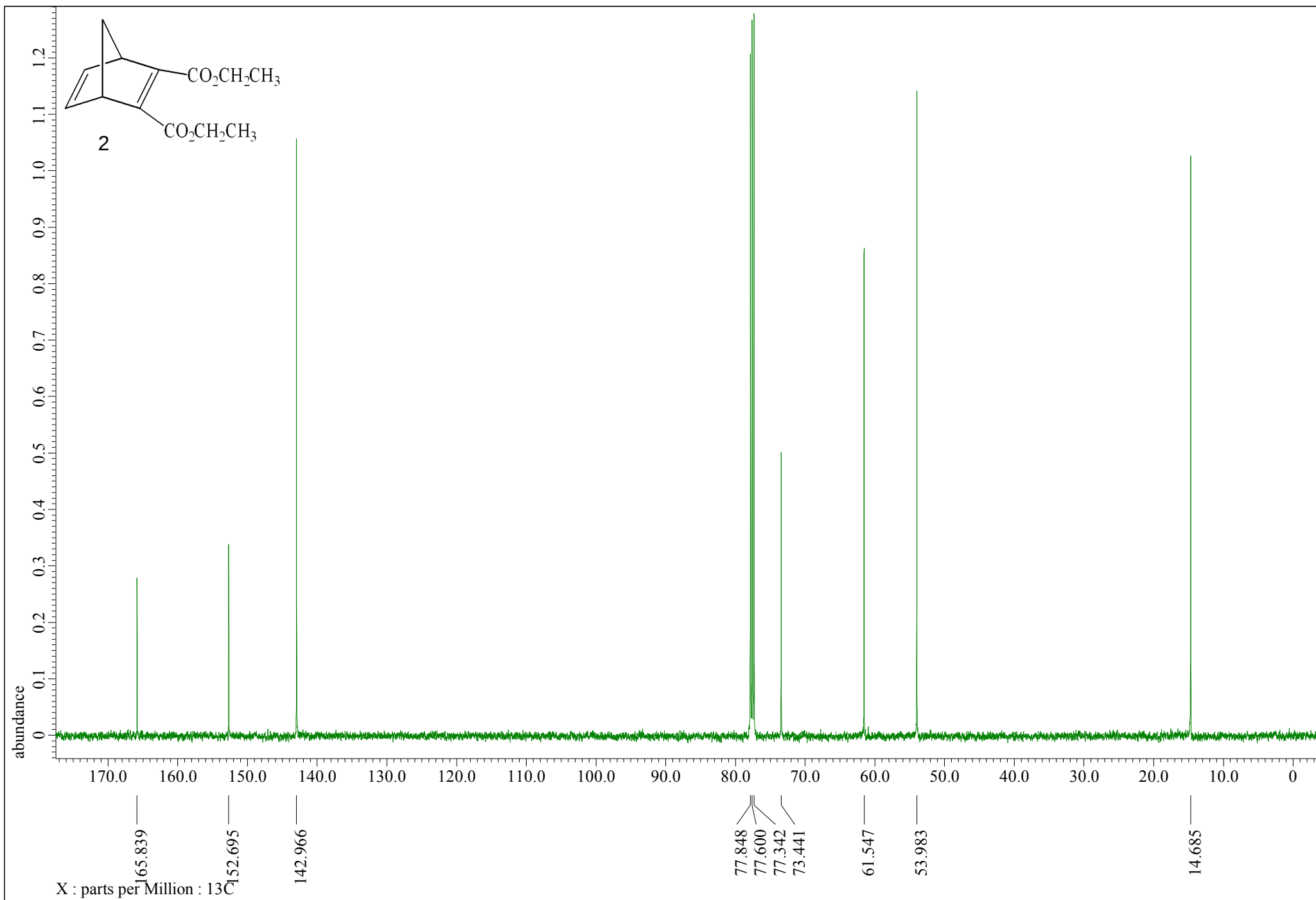
Polymer **5a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 5.54 and 5.50 (br, 2H, *cis* and *trans* =CH), 3.84 (d, 2H, =CHCH), 2.50 and 1.48 (m, 2H, CHCH_2CH), 1.45 (s, 18H, $\text{OC}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ = 28.34 ($\text{C}(\text{CH}_3)_3$), 39.75 ($-\text{CH}_2-$), 44.65 ($\text{C}=\text{C}-\text{CH}$), 81.79 ($\text{C}(\text{CH}_3)_2$), 131.71 ($\text{C}=\text{C}$), 142.25 ($\text{C}=\text{C}-\text{C}=\text{O}$), 164.35 ($\text{C}=\text{O}$).

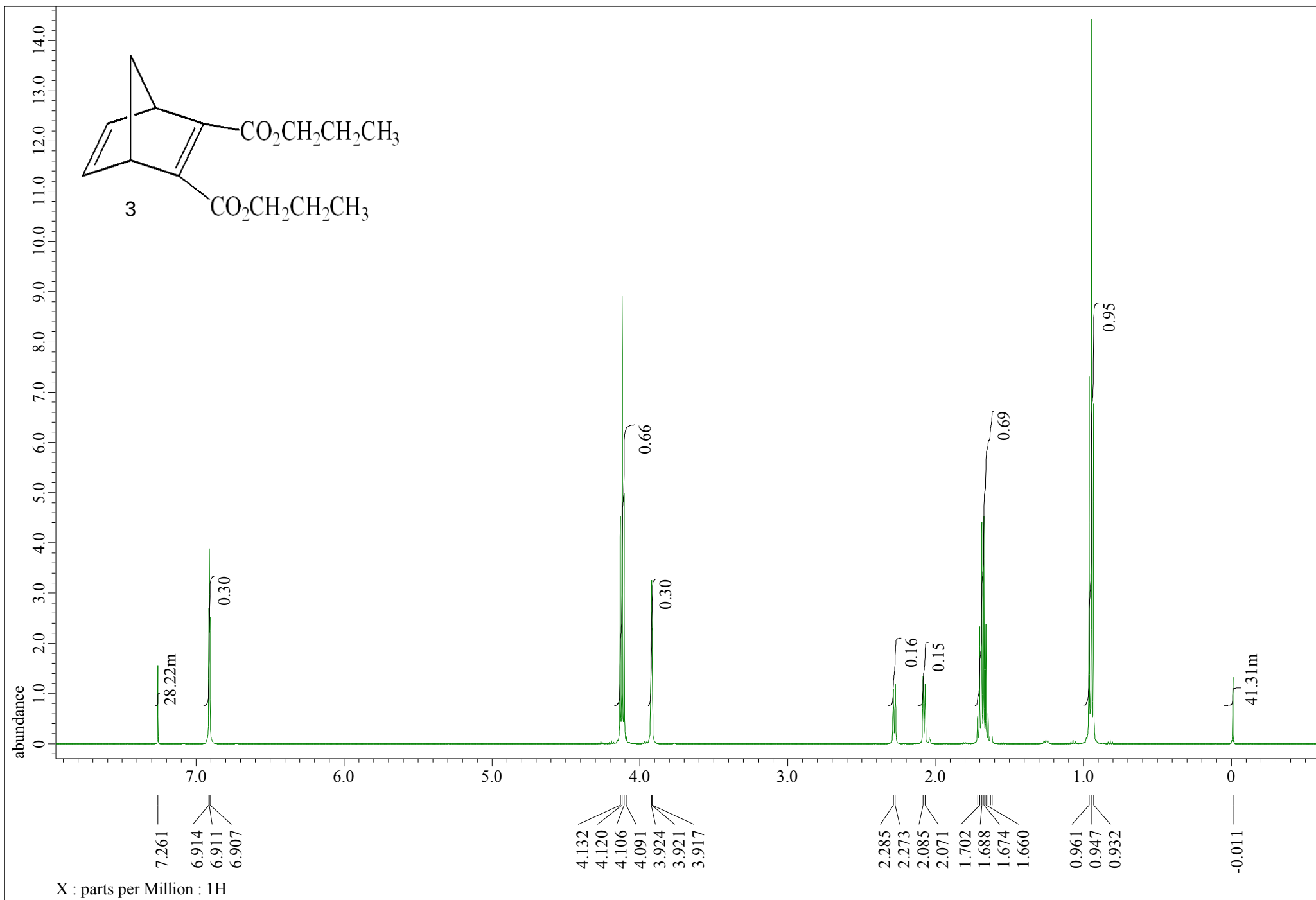
Polymer **6a**. Pale white solid. ^1H NMR (500 MHz, CDCl_3) δ = 7.22 (t, 10H, C_6H_5), 5.49 and 5.40 (br, 2H, *cis* and *trans* =CH), 4.94 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_5$), 3.91 (m, 2H, =CHCH), 2.36 and 1.38 (m, 2H, CHCH_2CH); ^{13}C NMR (125 MHz, CDCl_3) δ = 38.69 ($-\text{CH}_2-$), 44.50 ($\text{C}=\text{C}-\text{CH}$), 66.9 ($\text{C}-\text{C}_6\text{H}_5$), 128.43, 128.60, 128.72 (C_6H_5), 131.61 ($\text{C}=\text{C}$), 131.61 (C_6H_5), 135.50 ($\text{C}=\text{C}-\text{C}=\text{O}$), 164.82 ($\text{C}=\text{O}$).

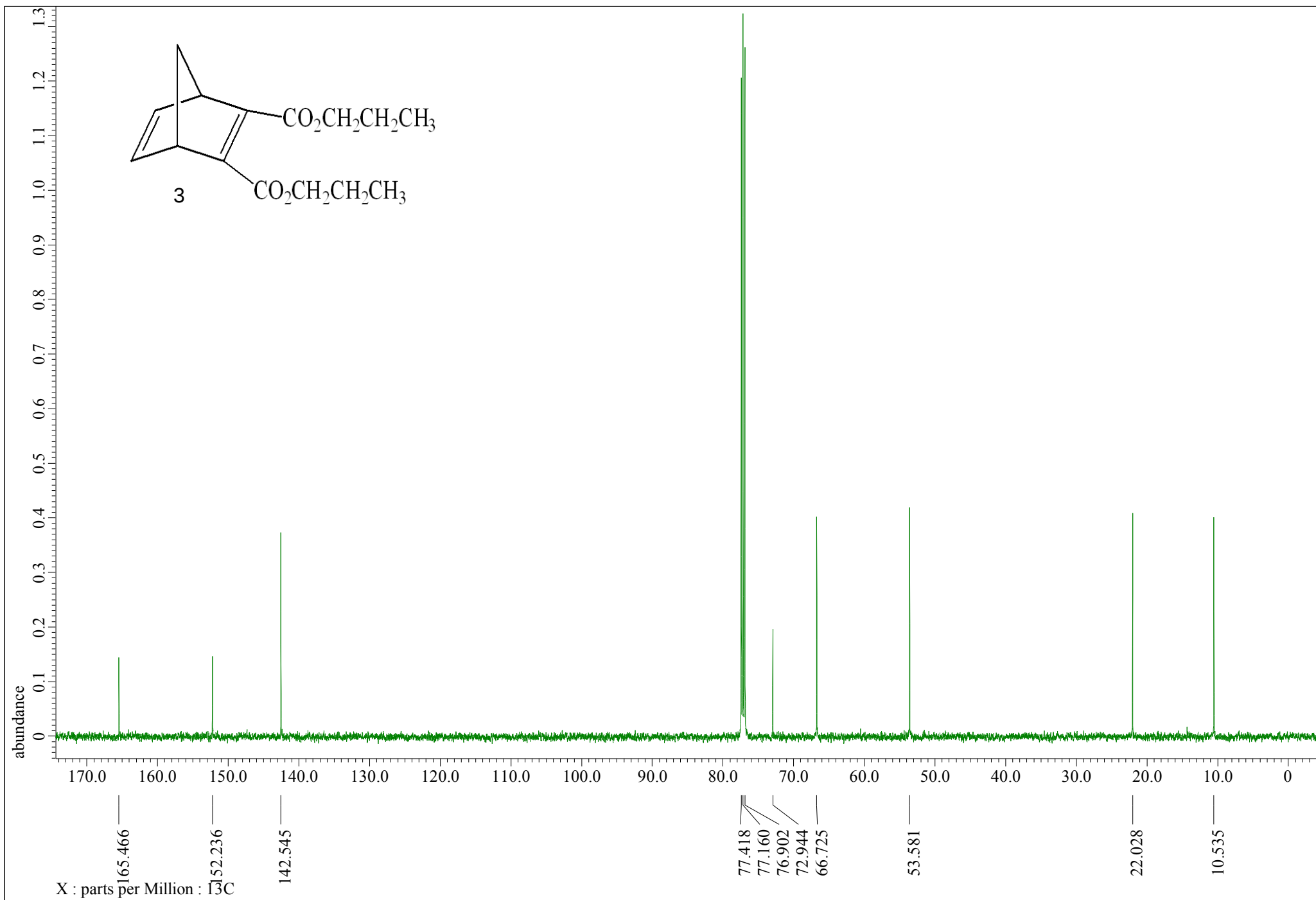


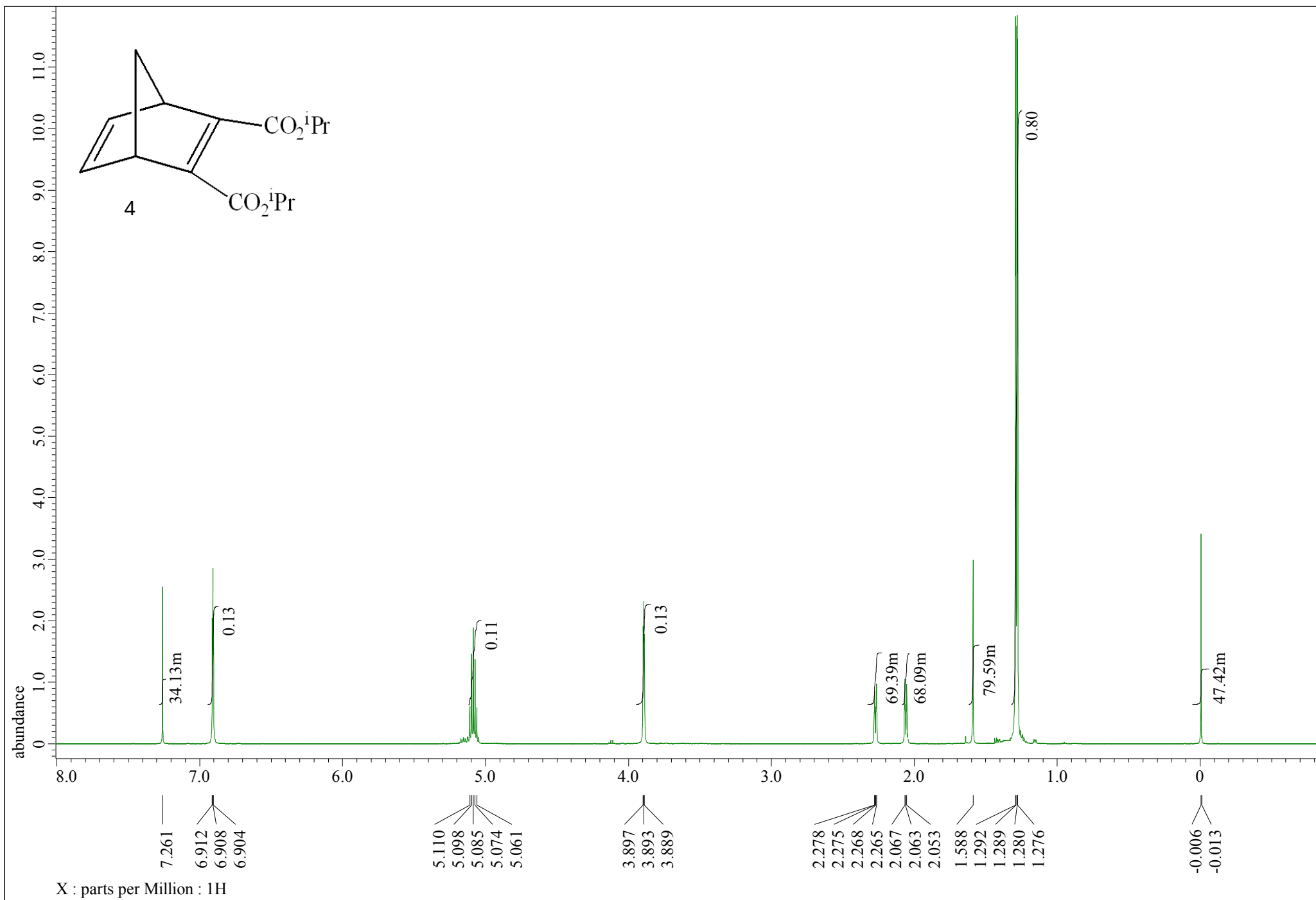


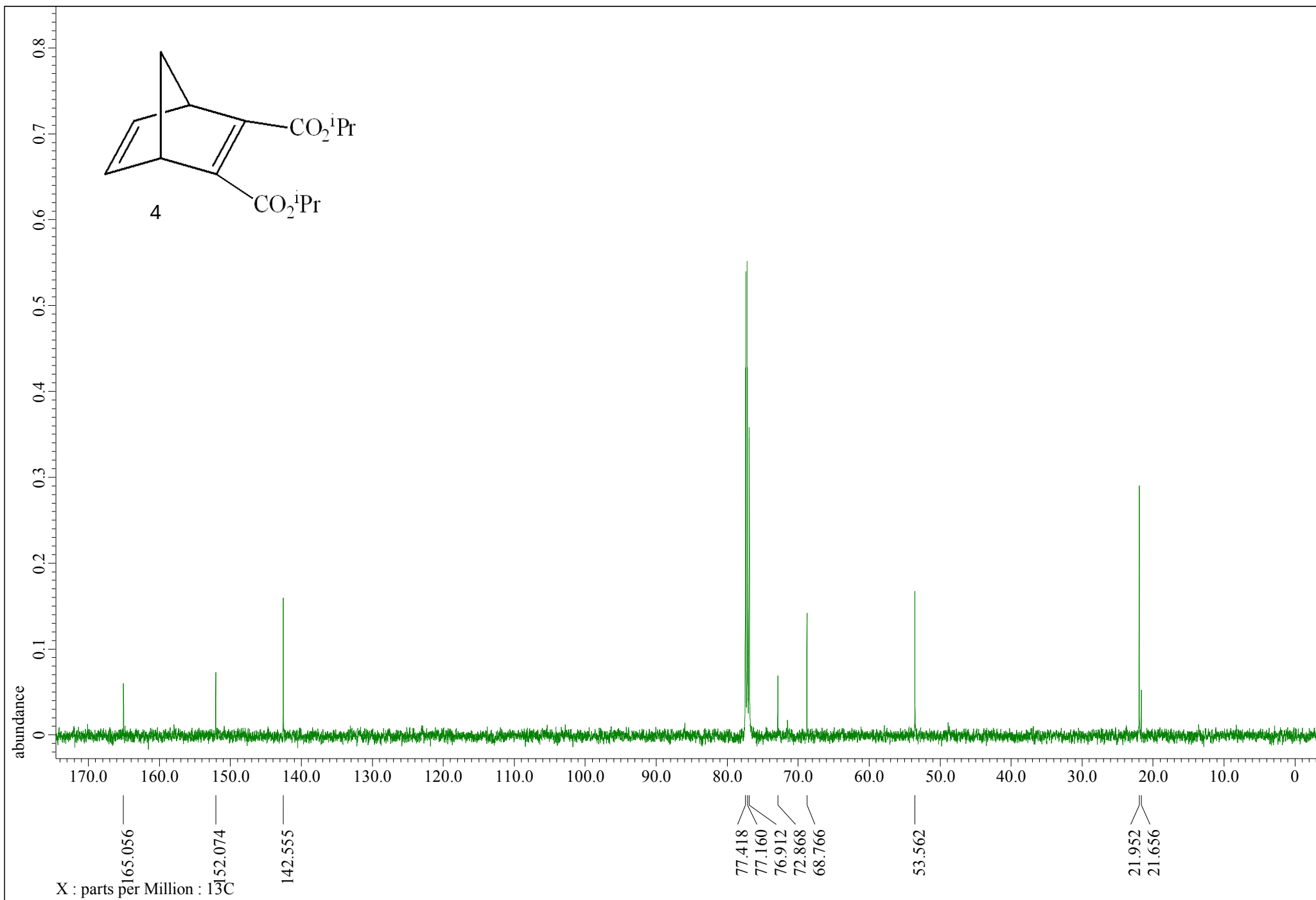


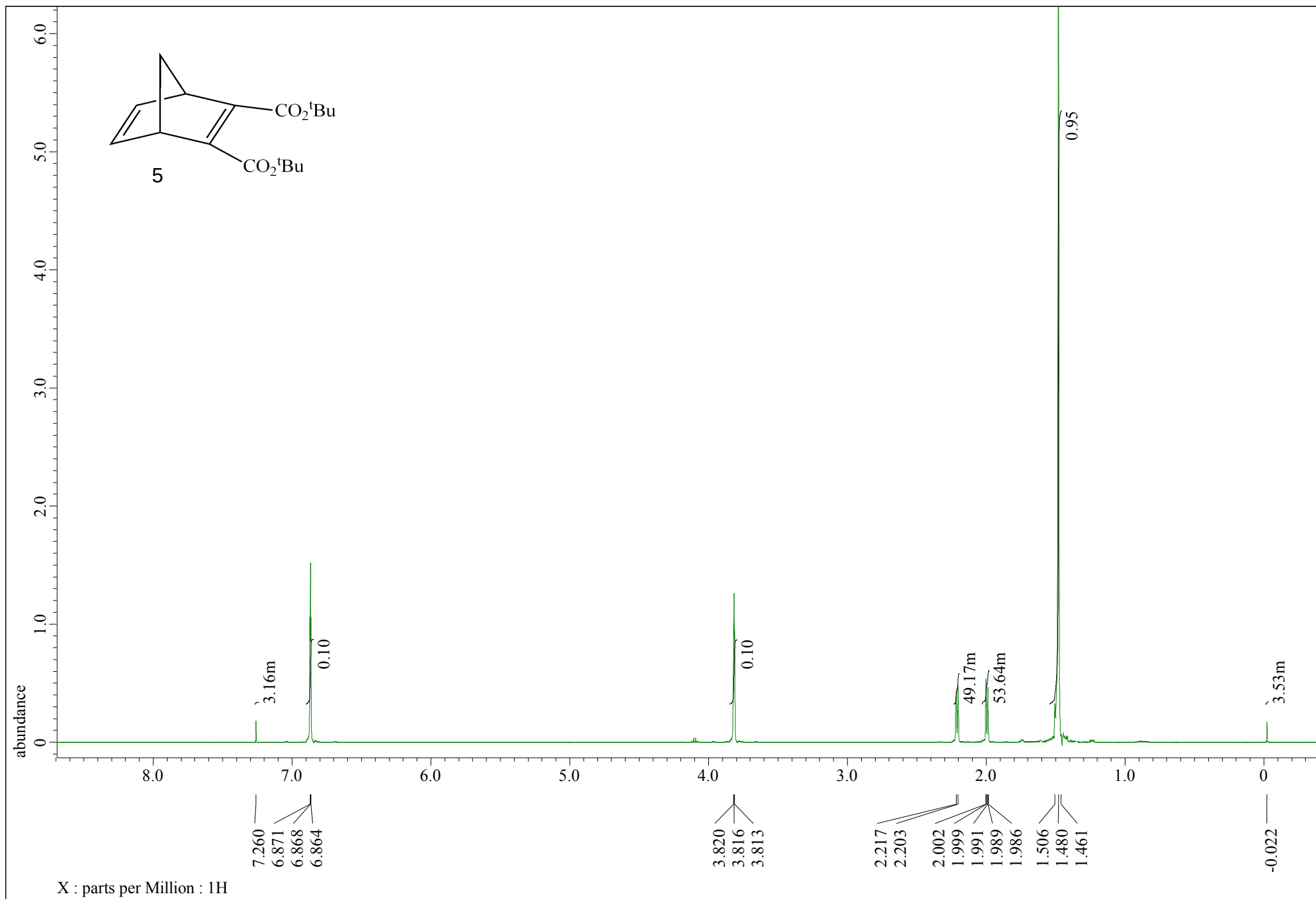


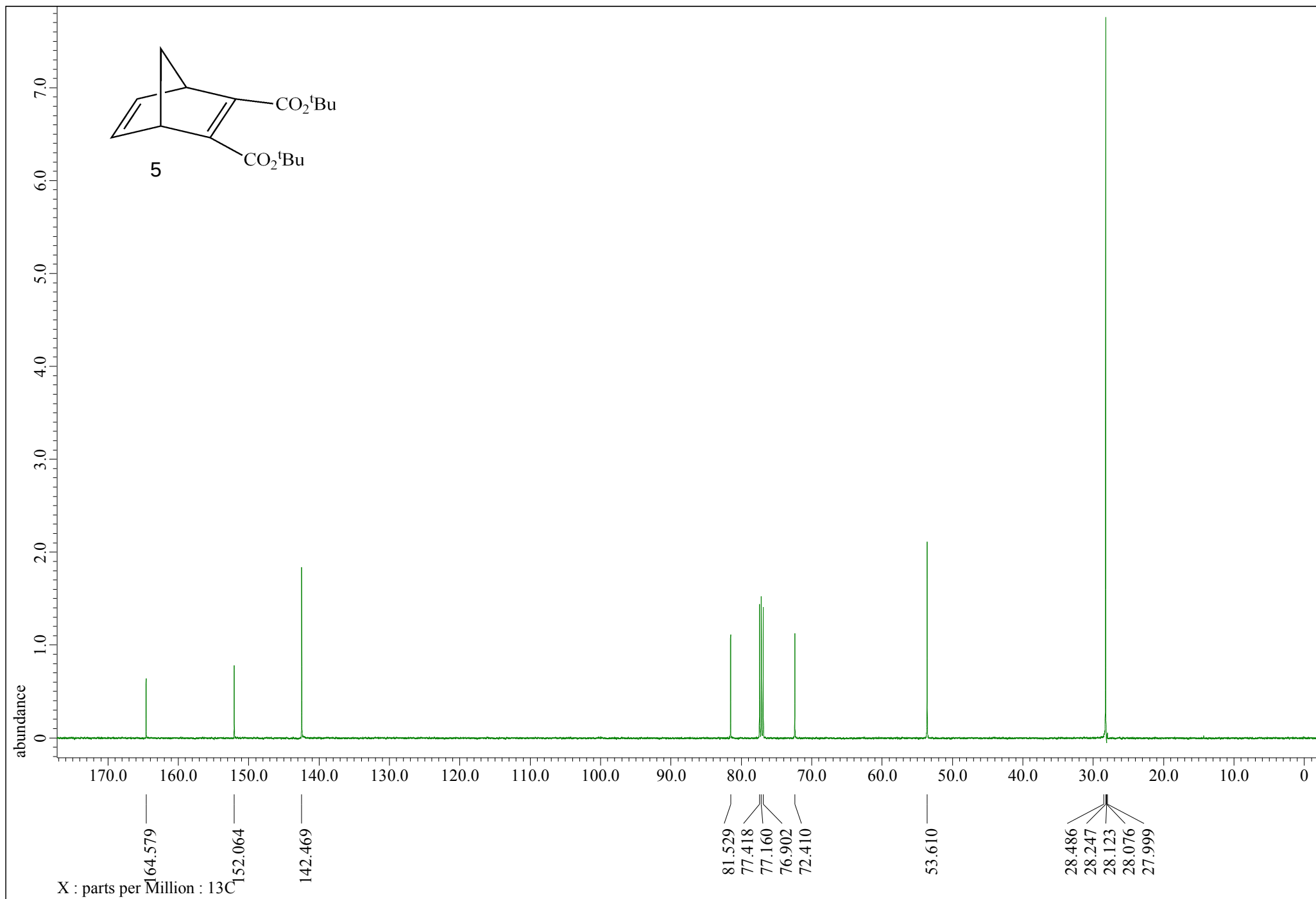


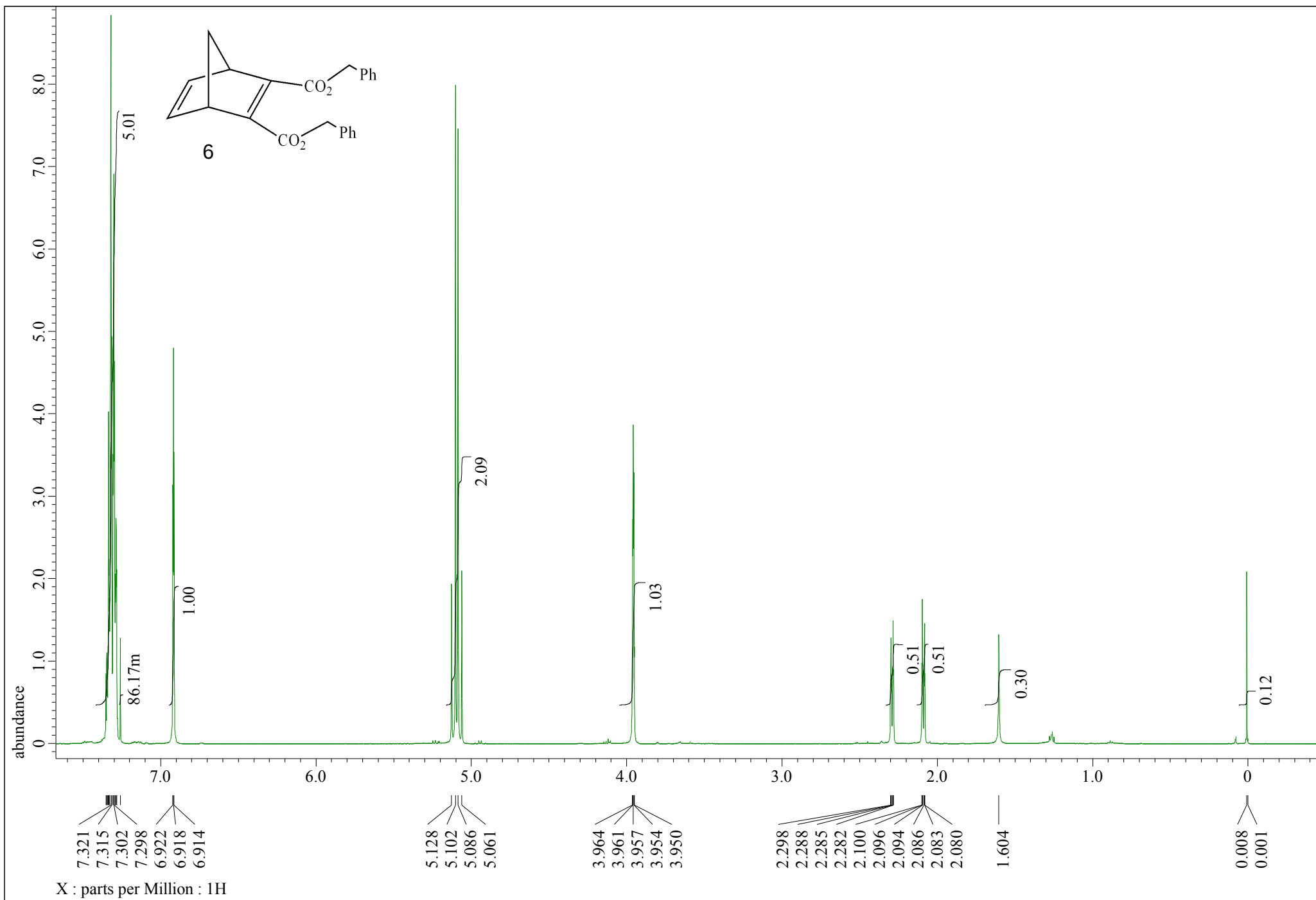


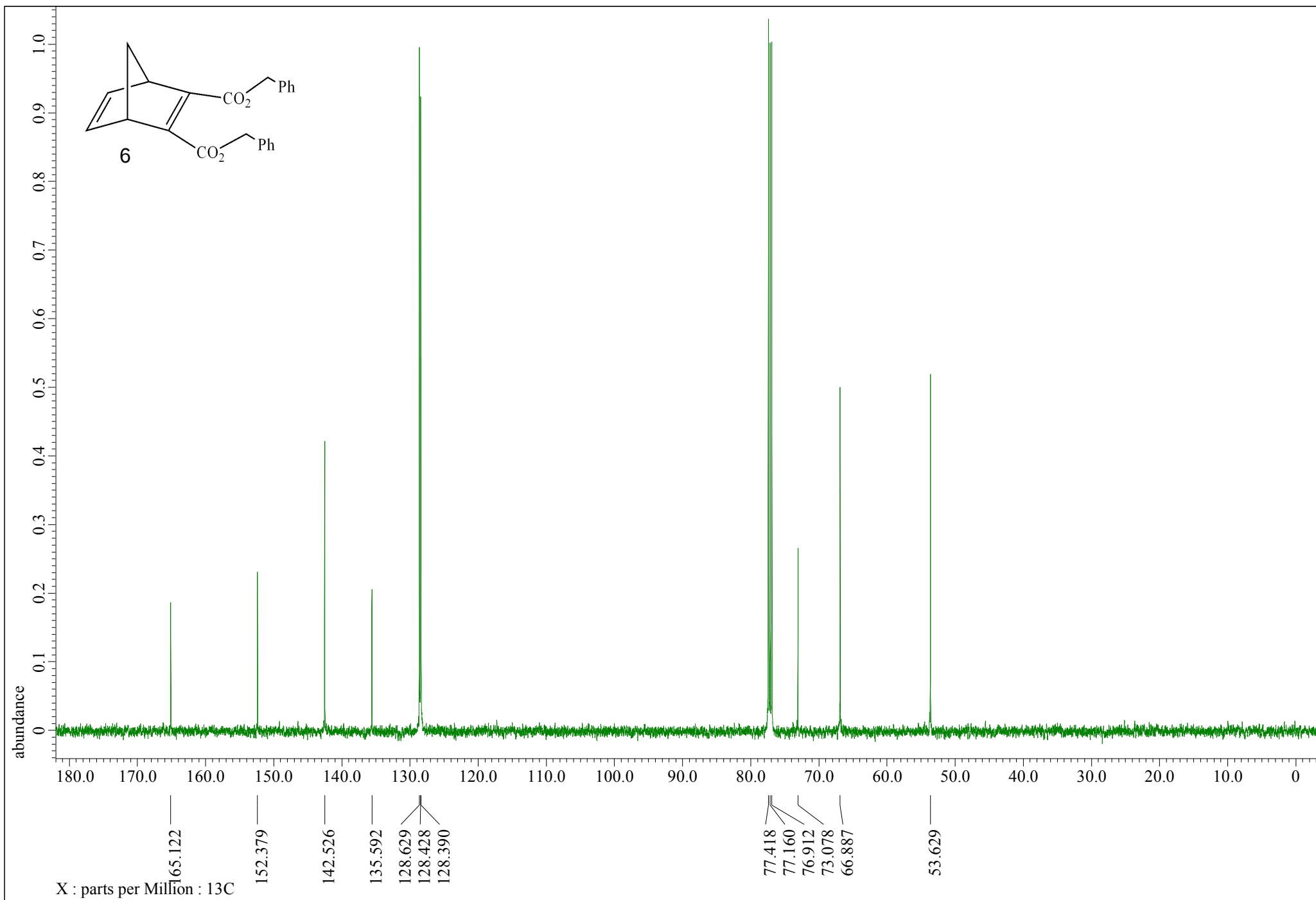


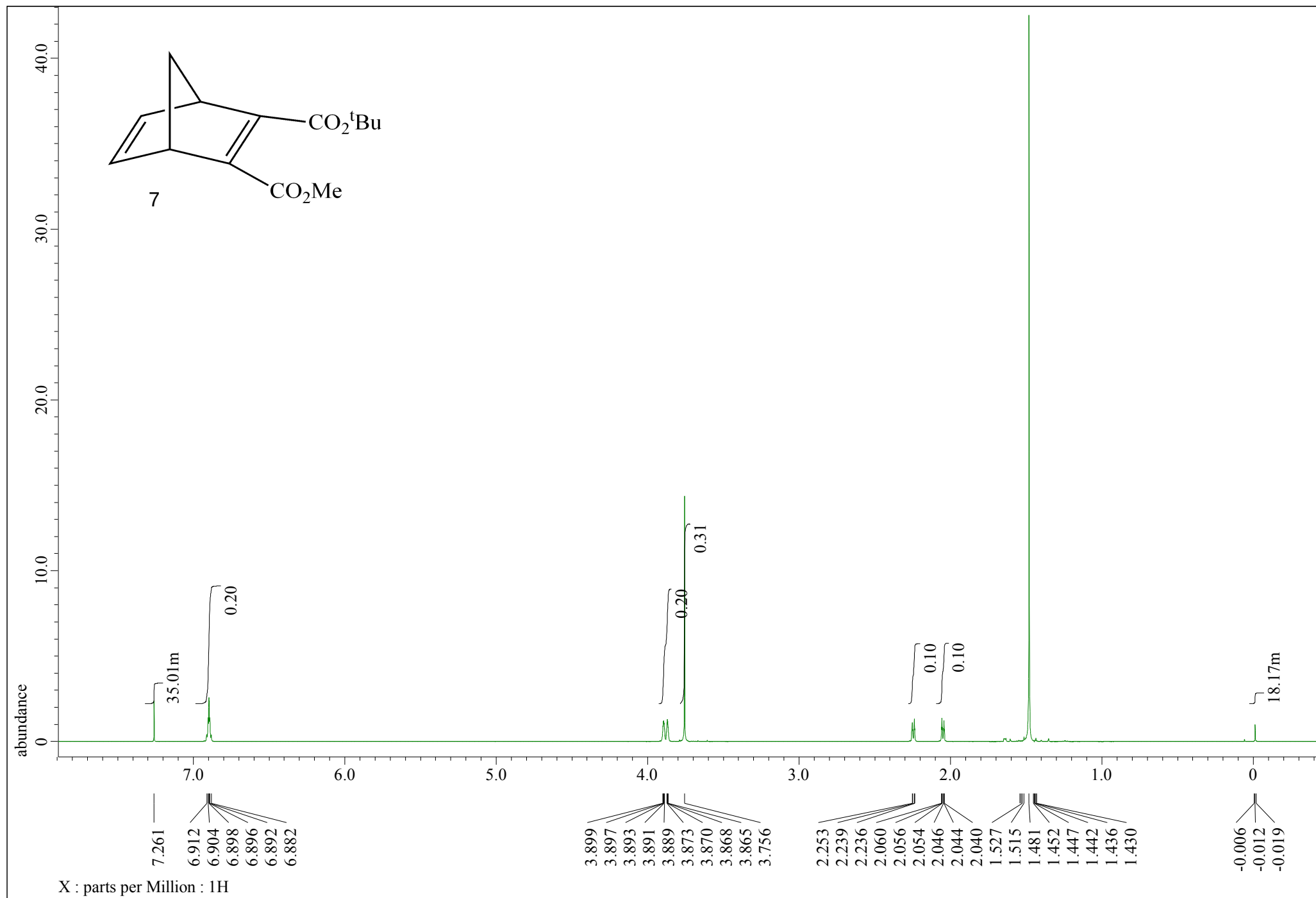


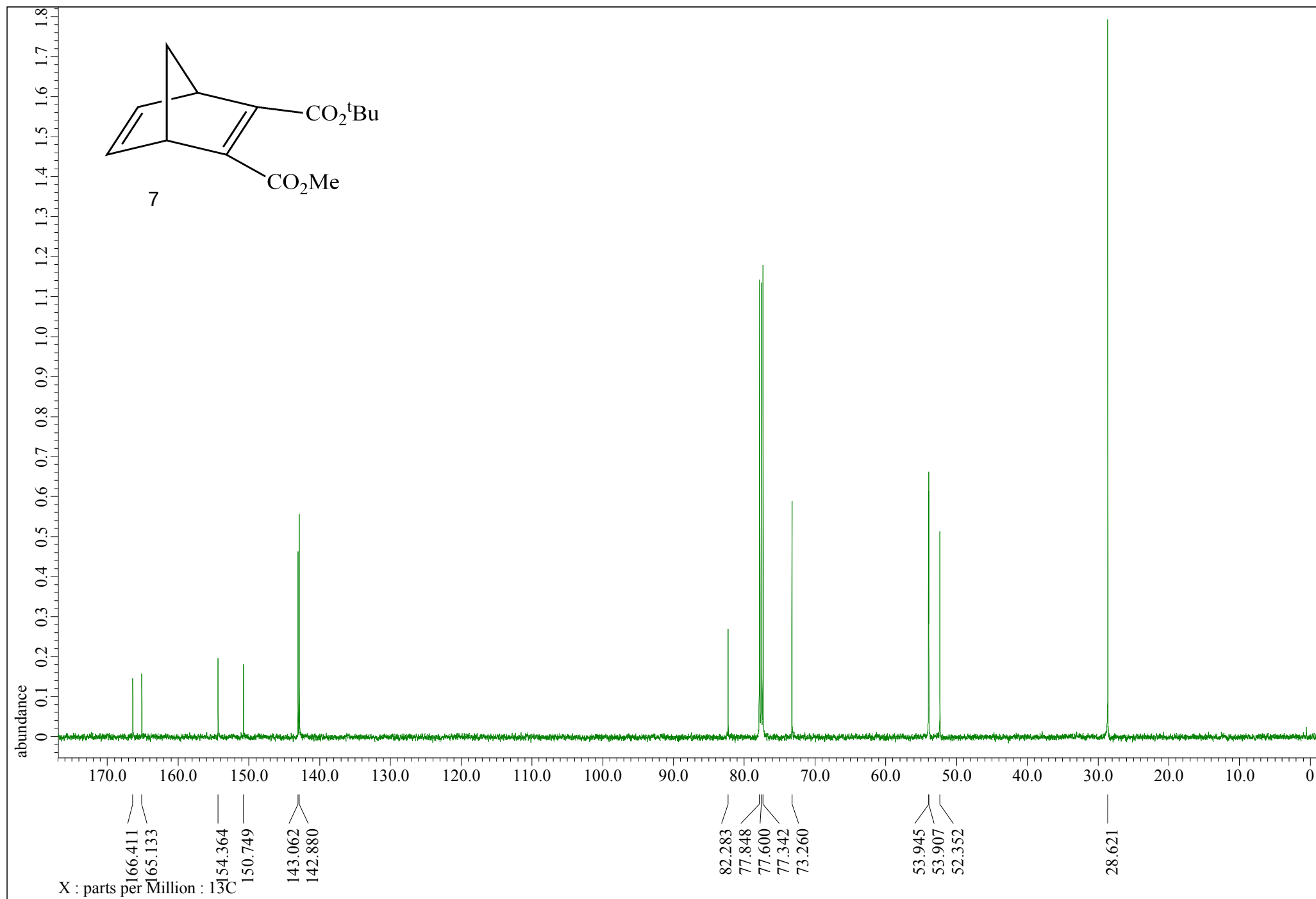


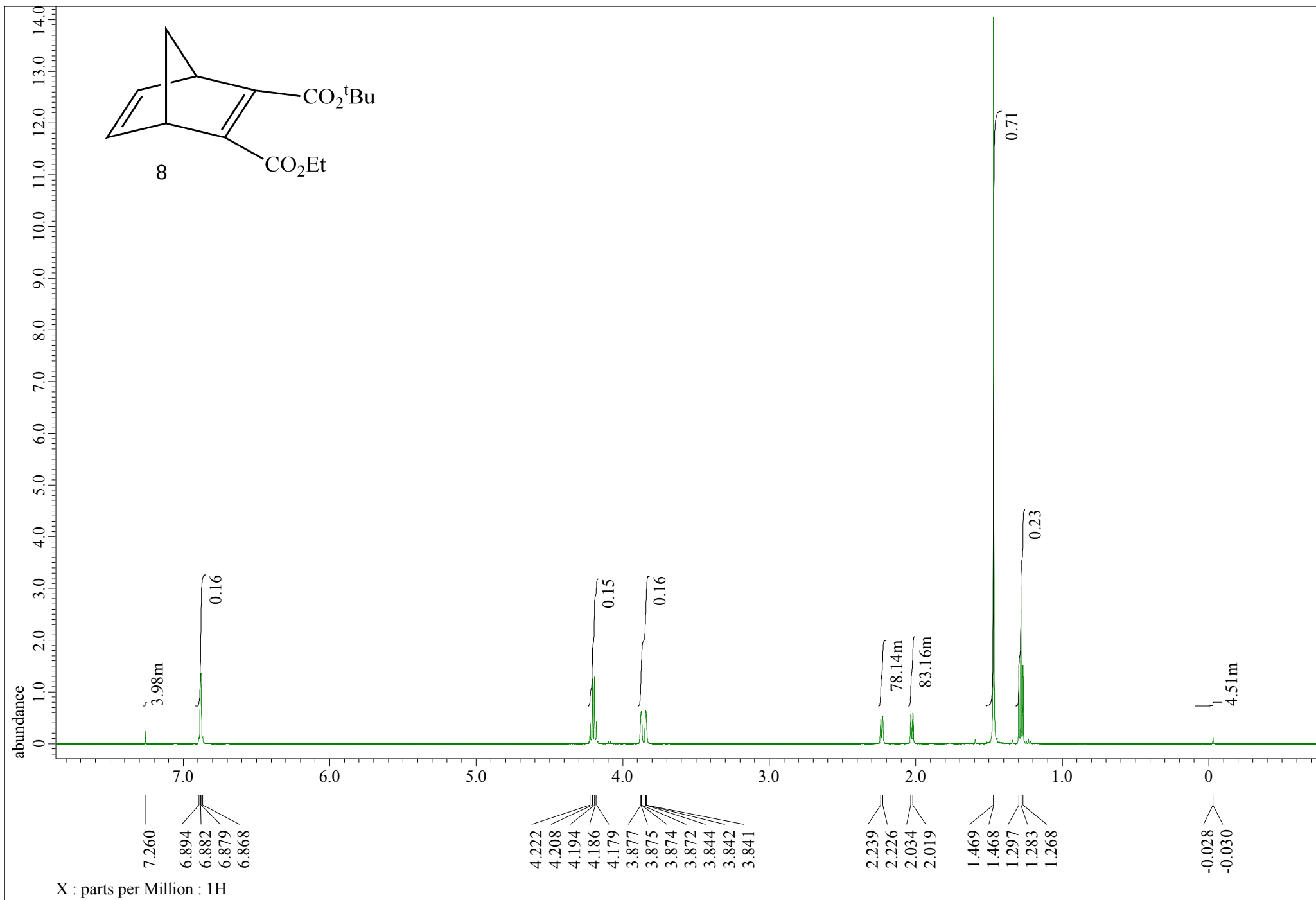


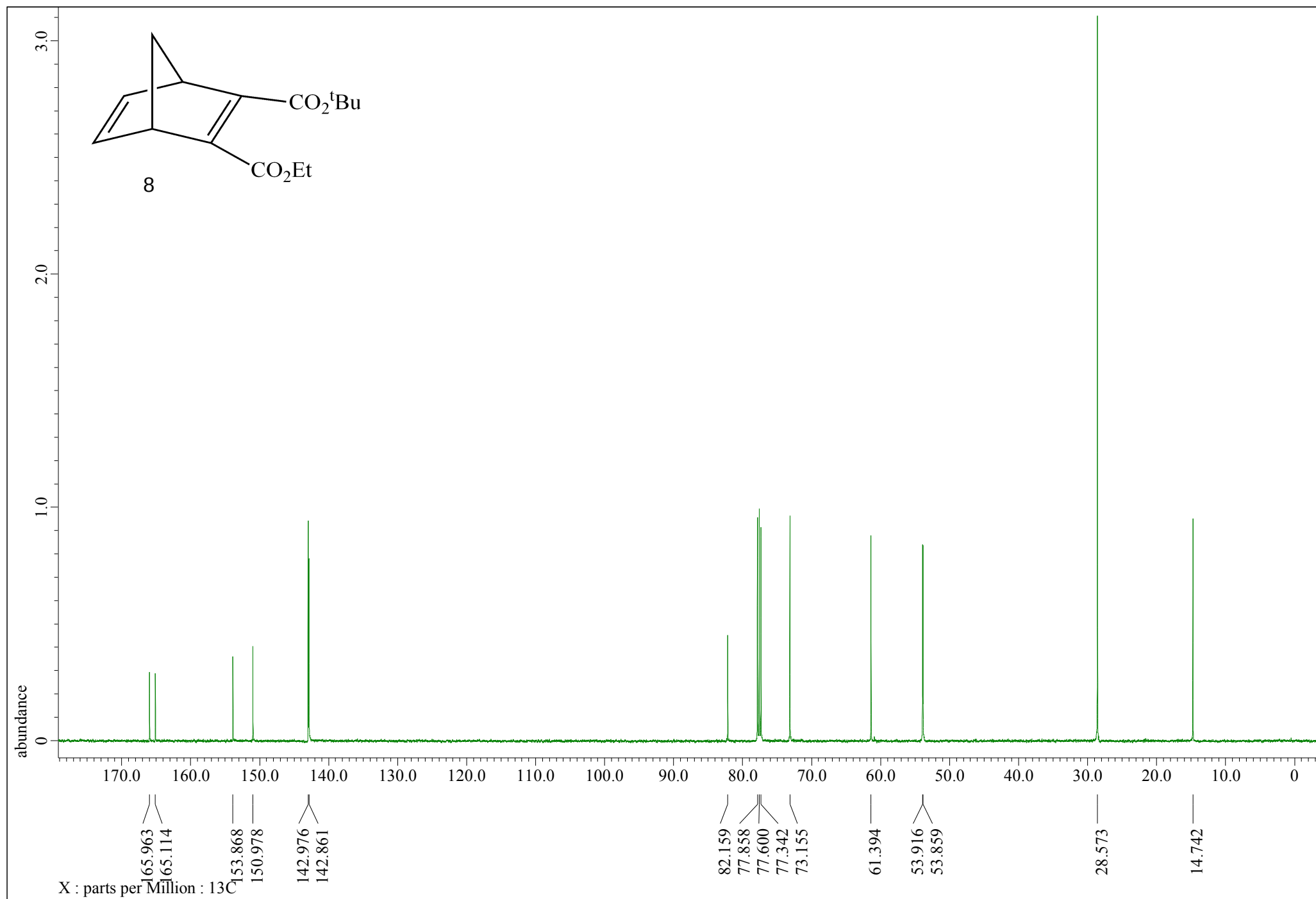


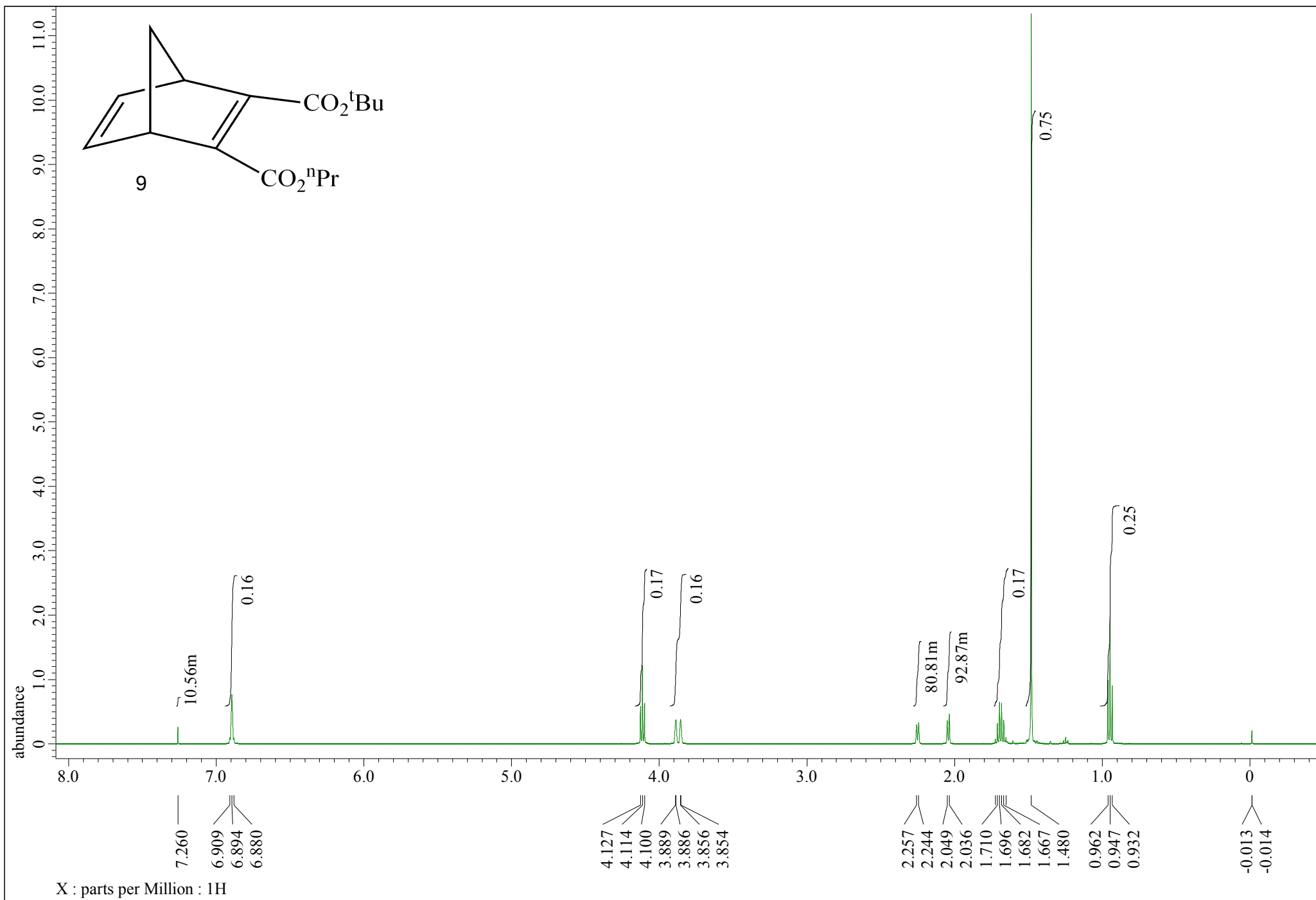


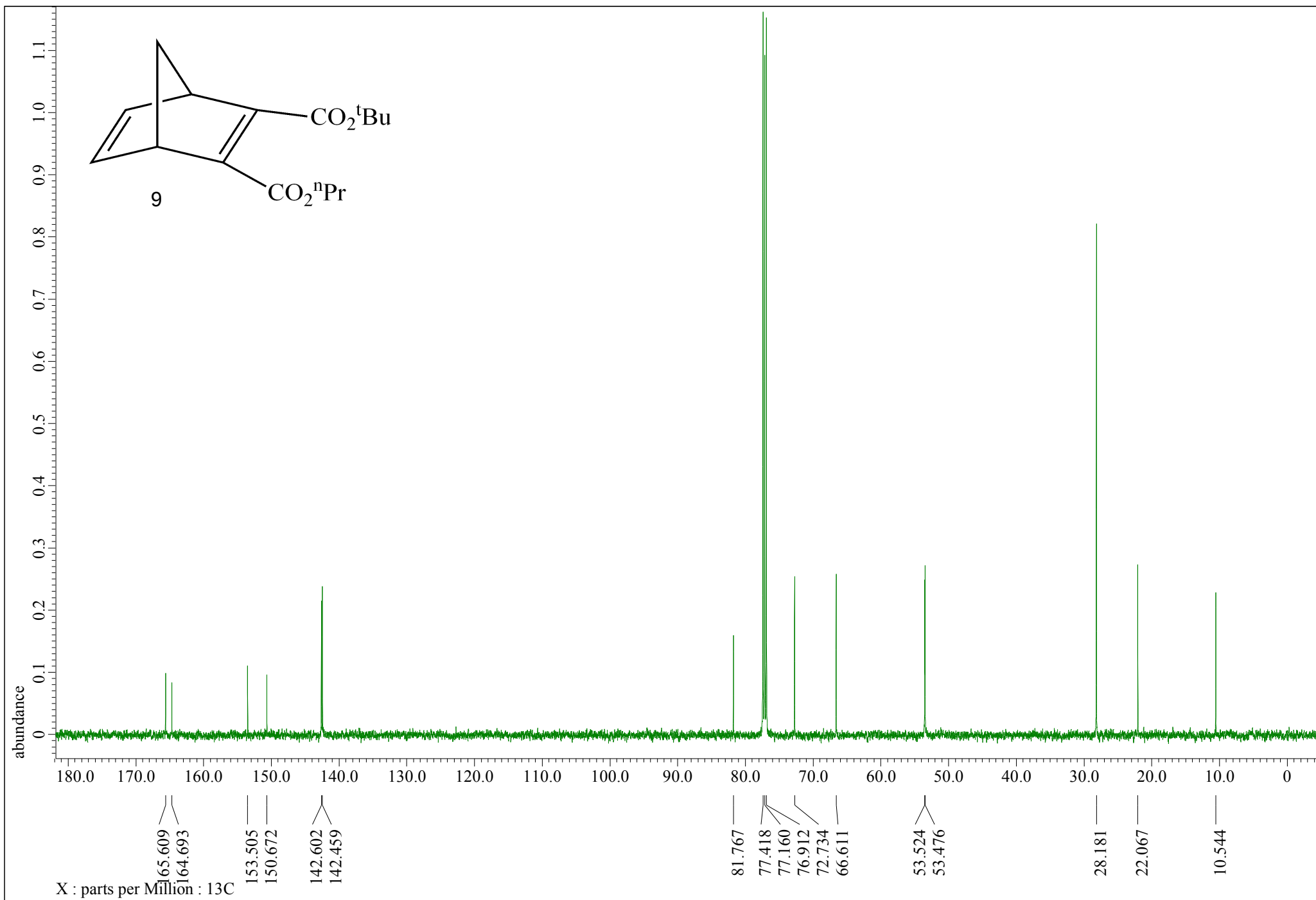


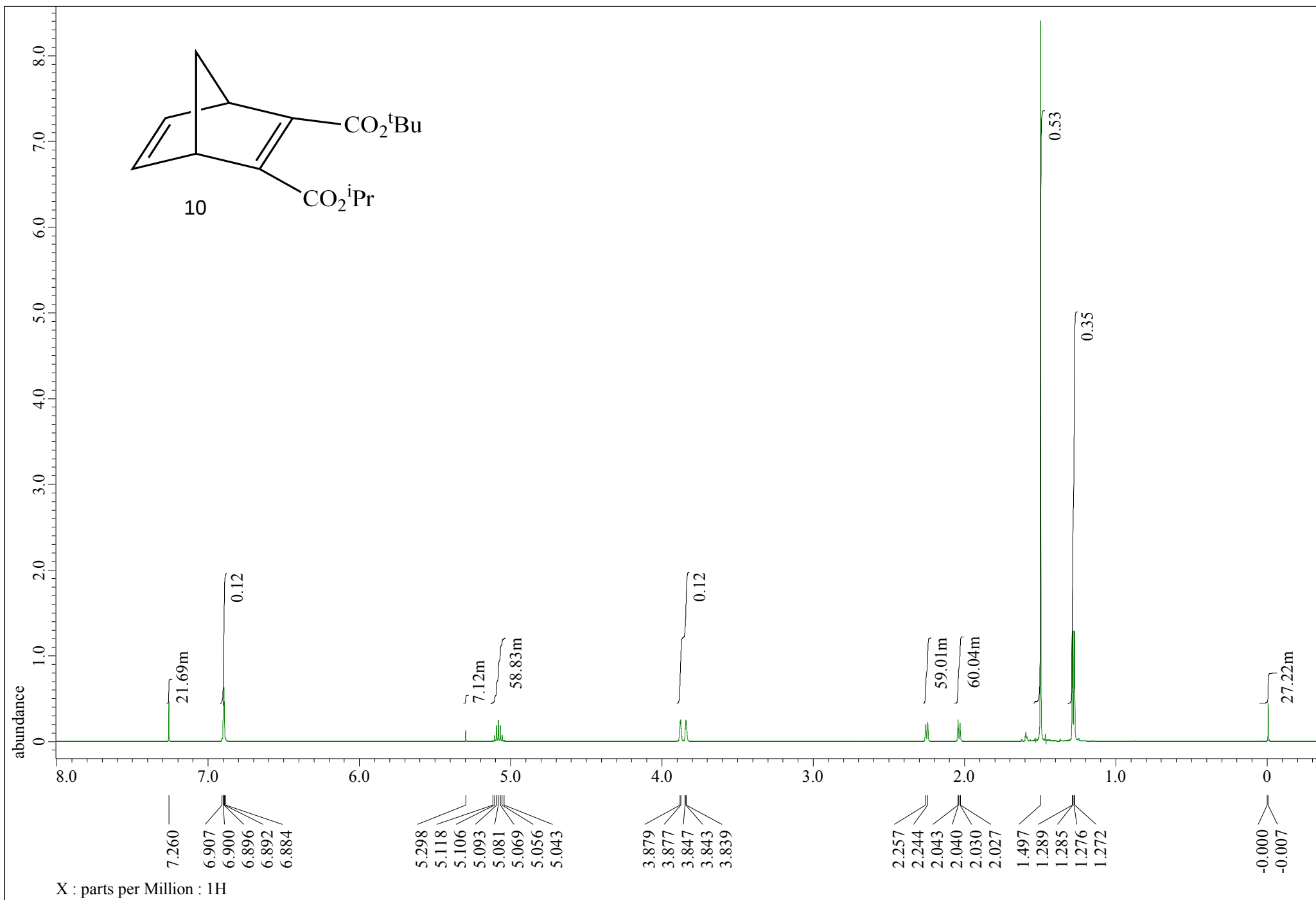


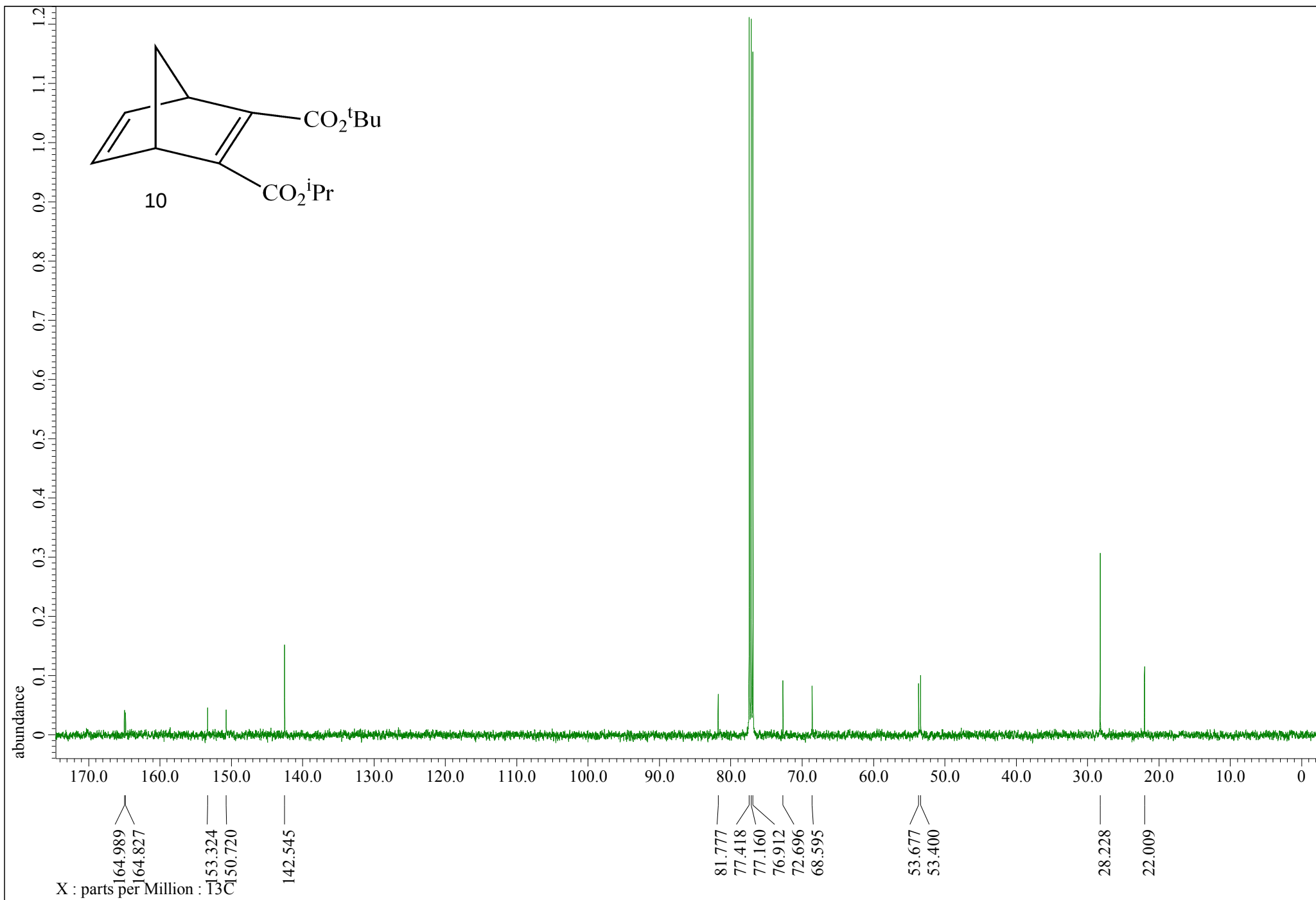


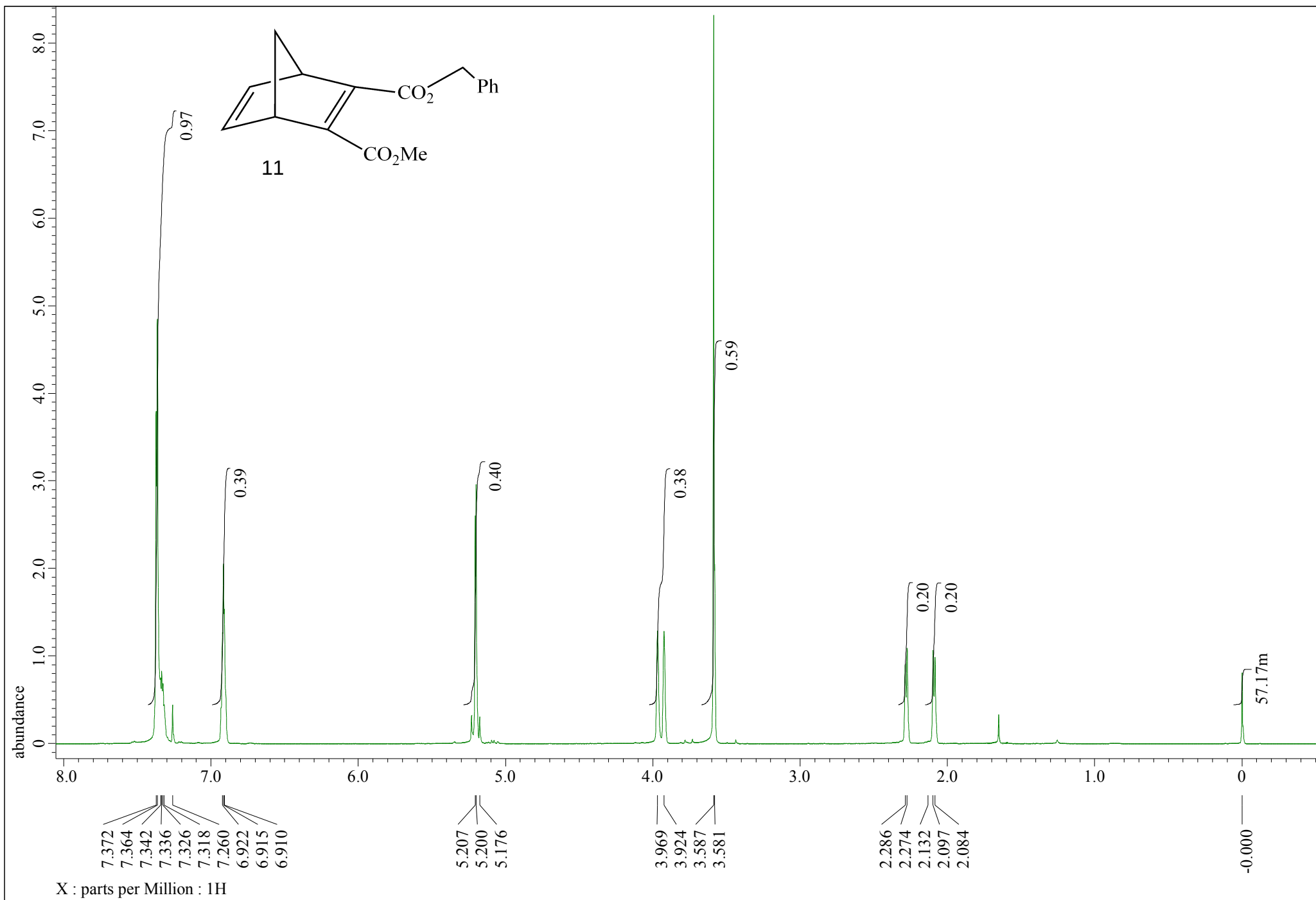


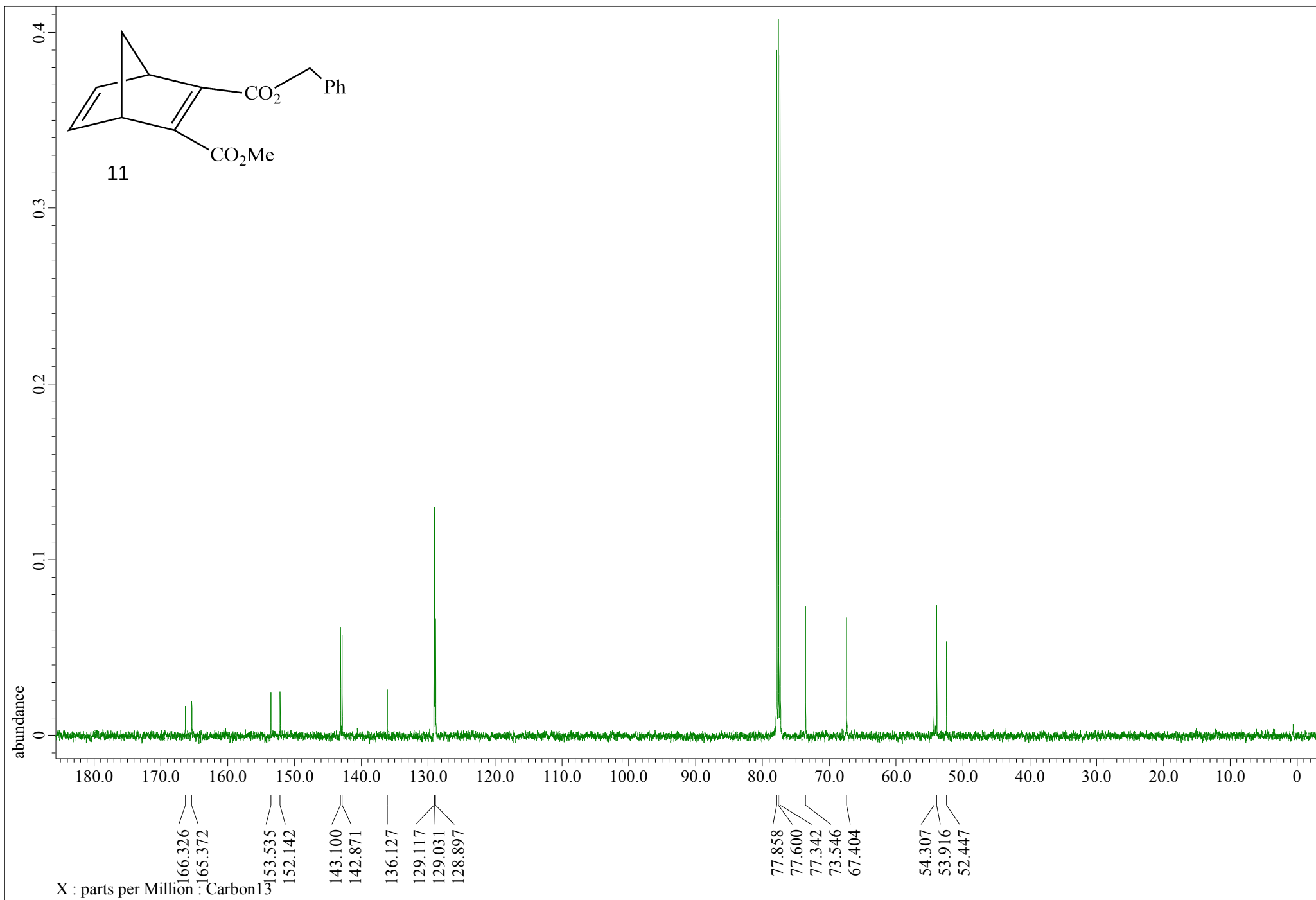


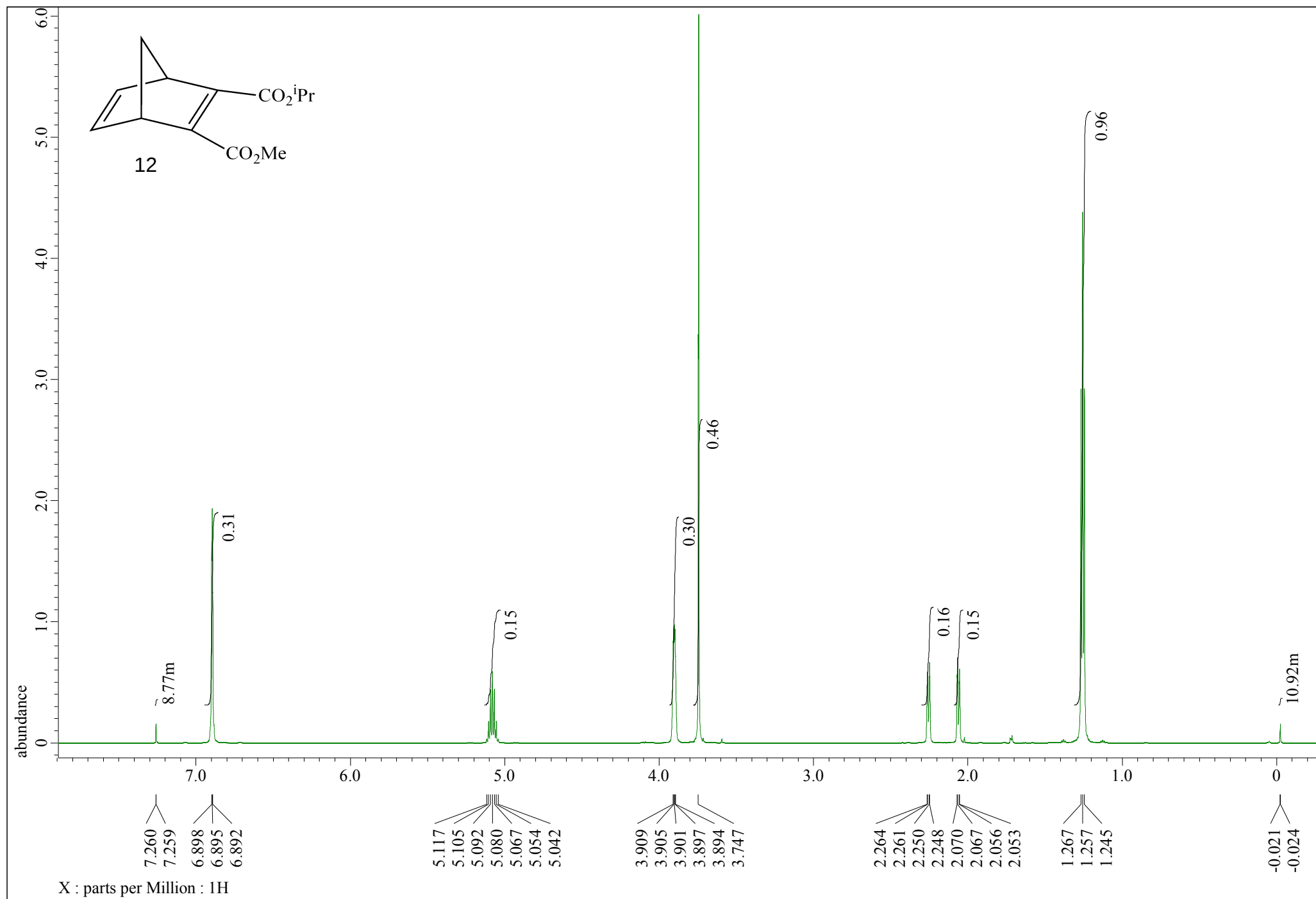


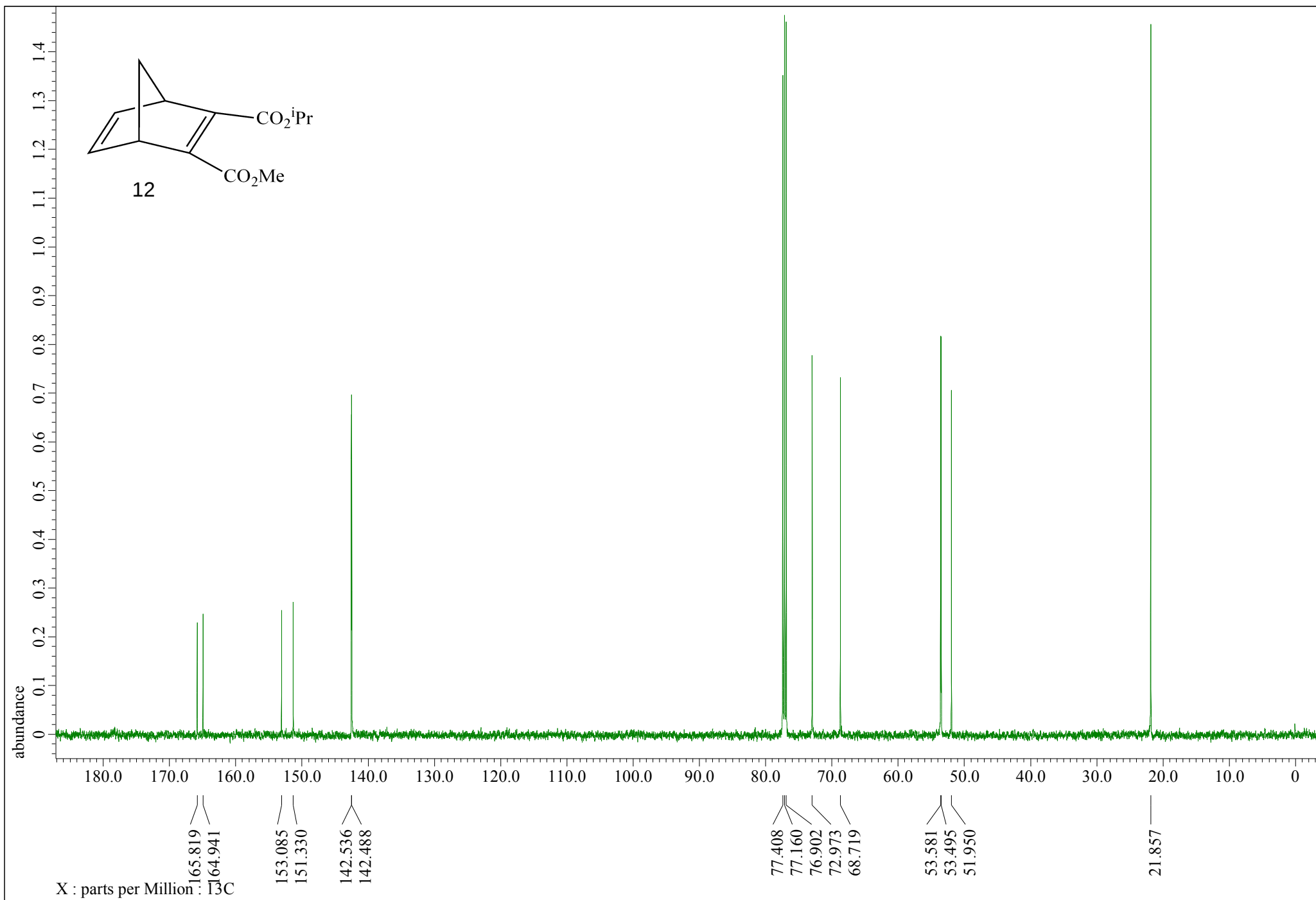


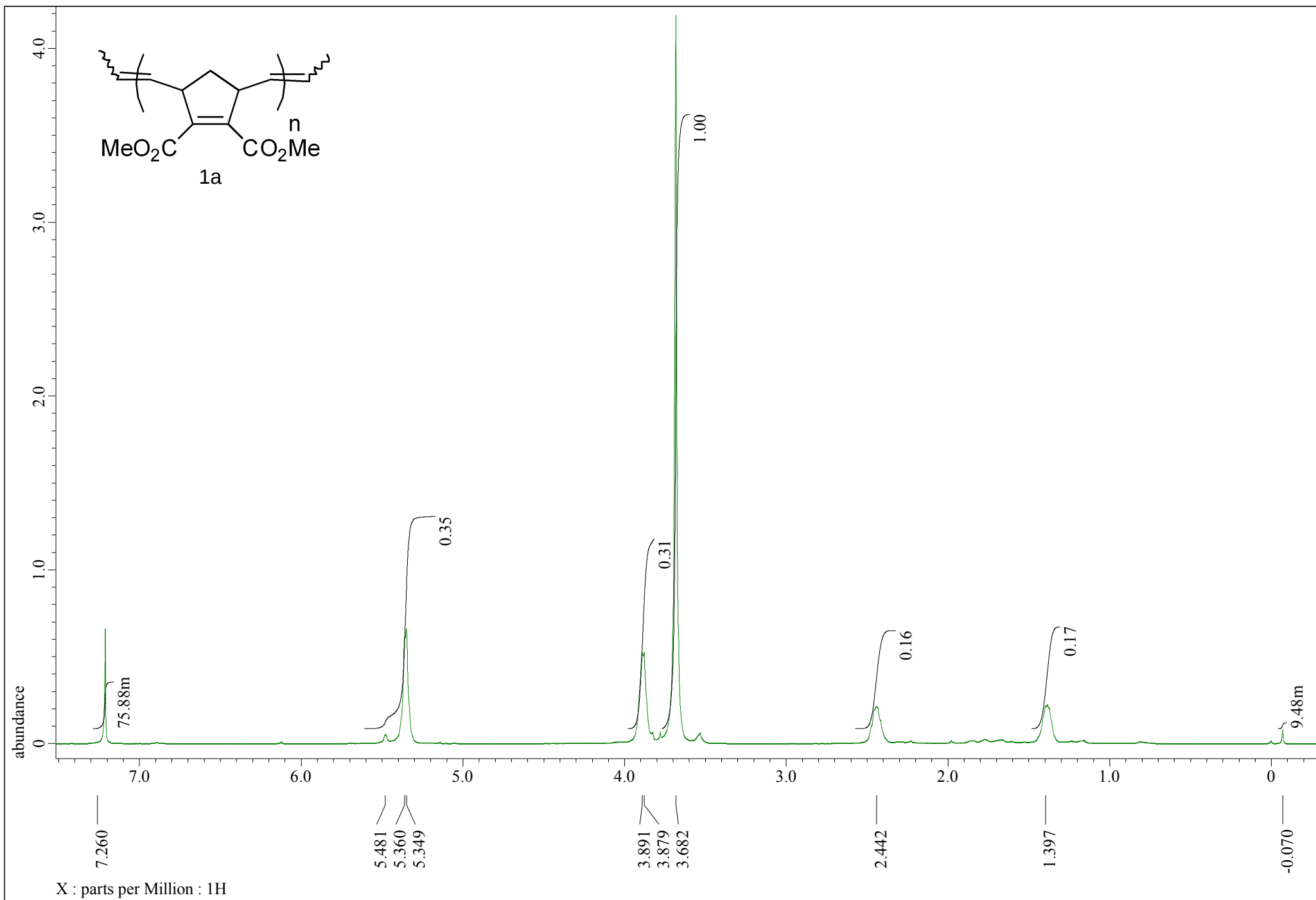


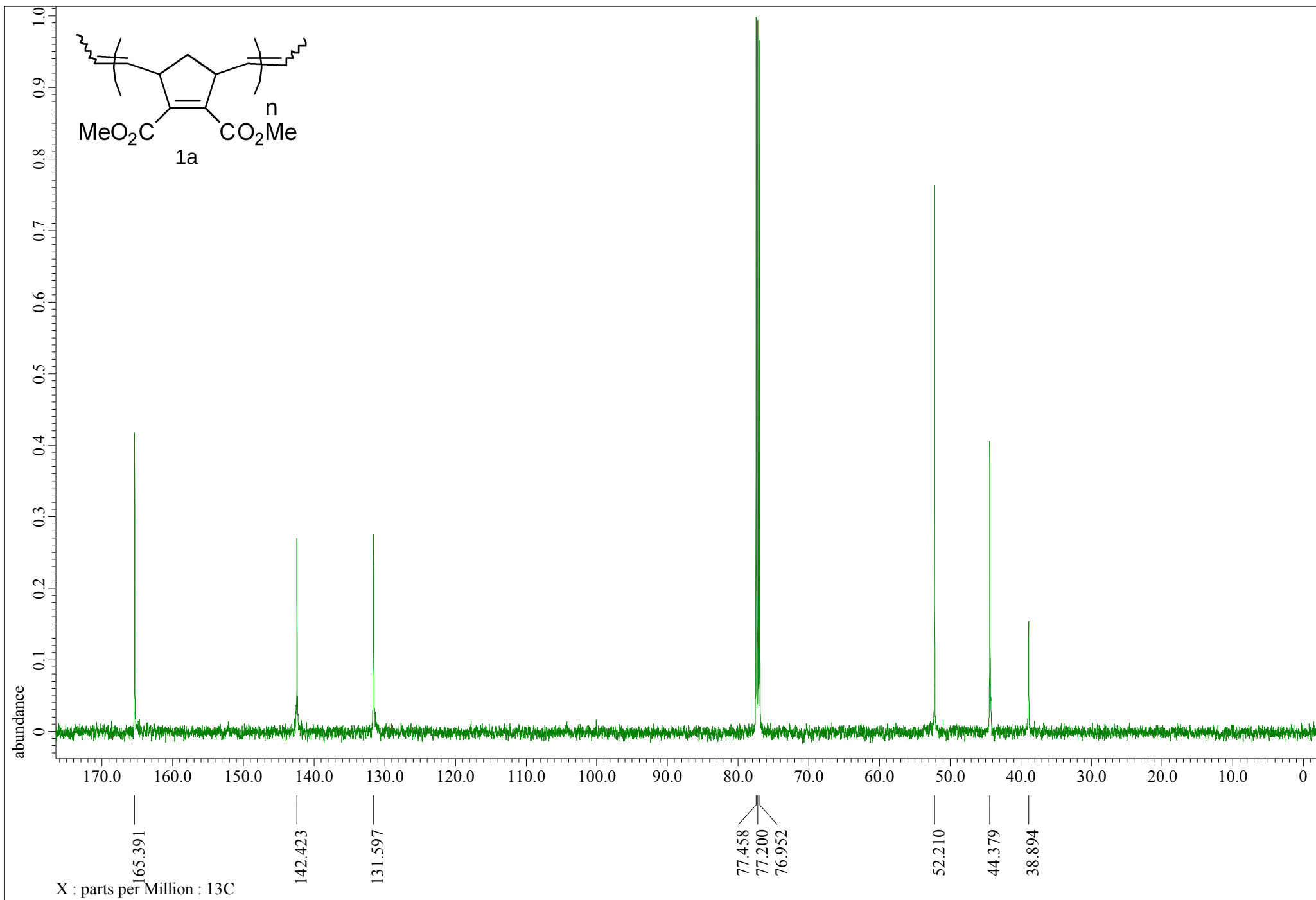


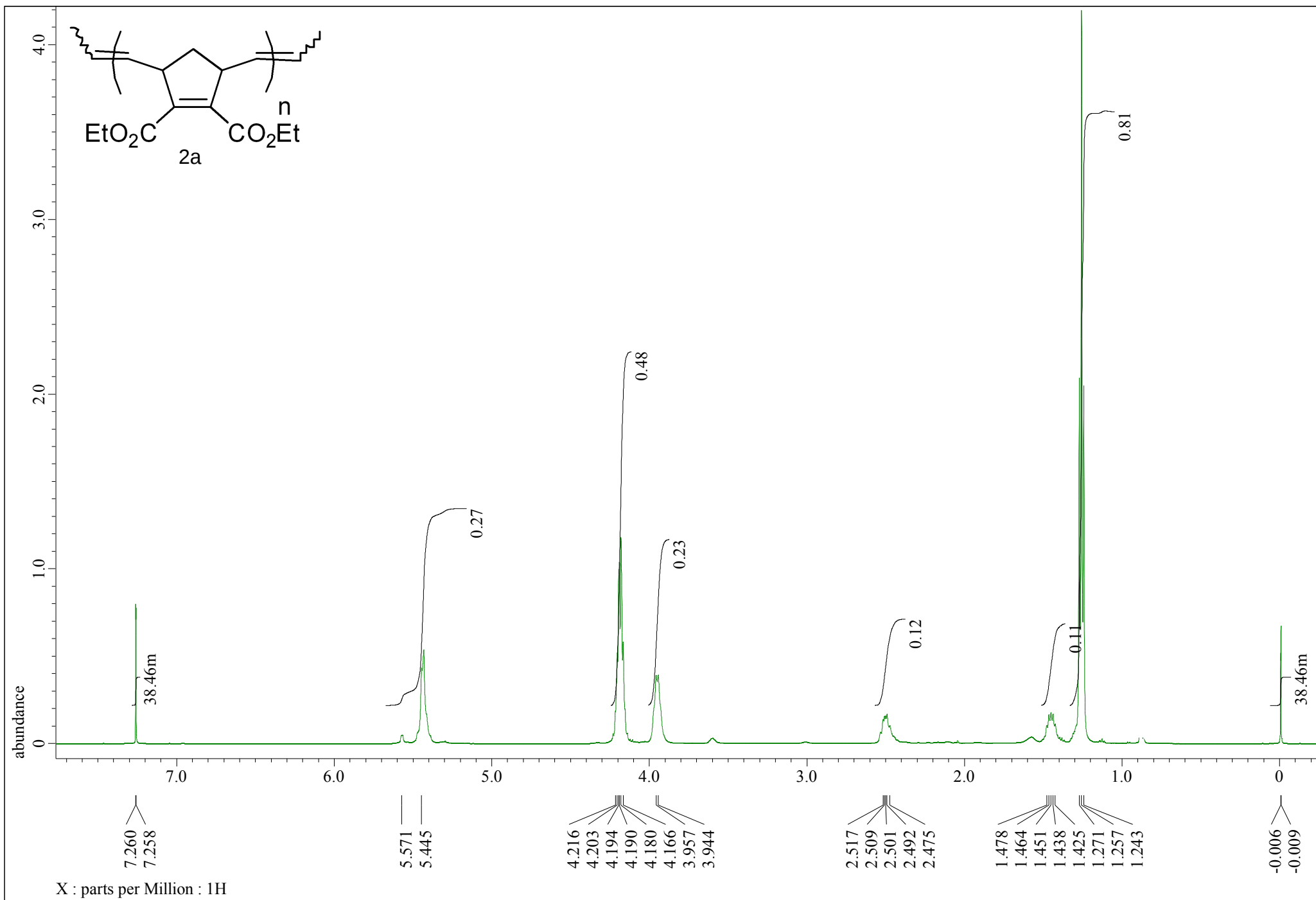


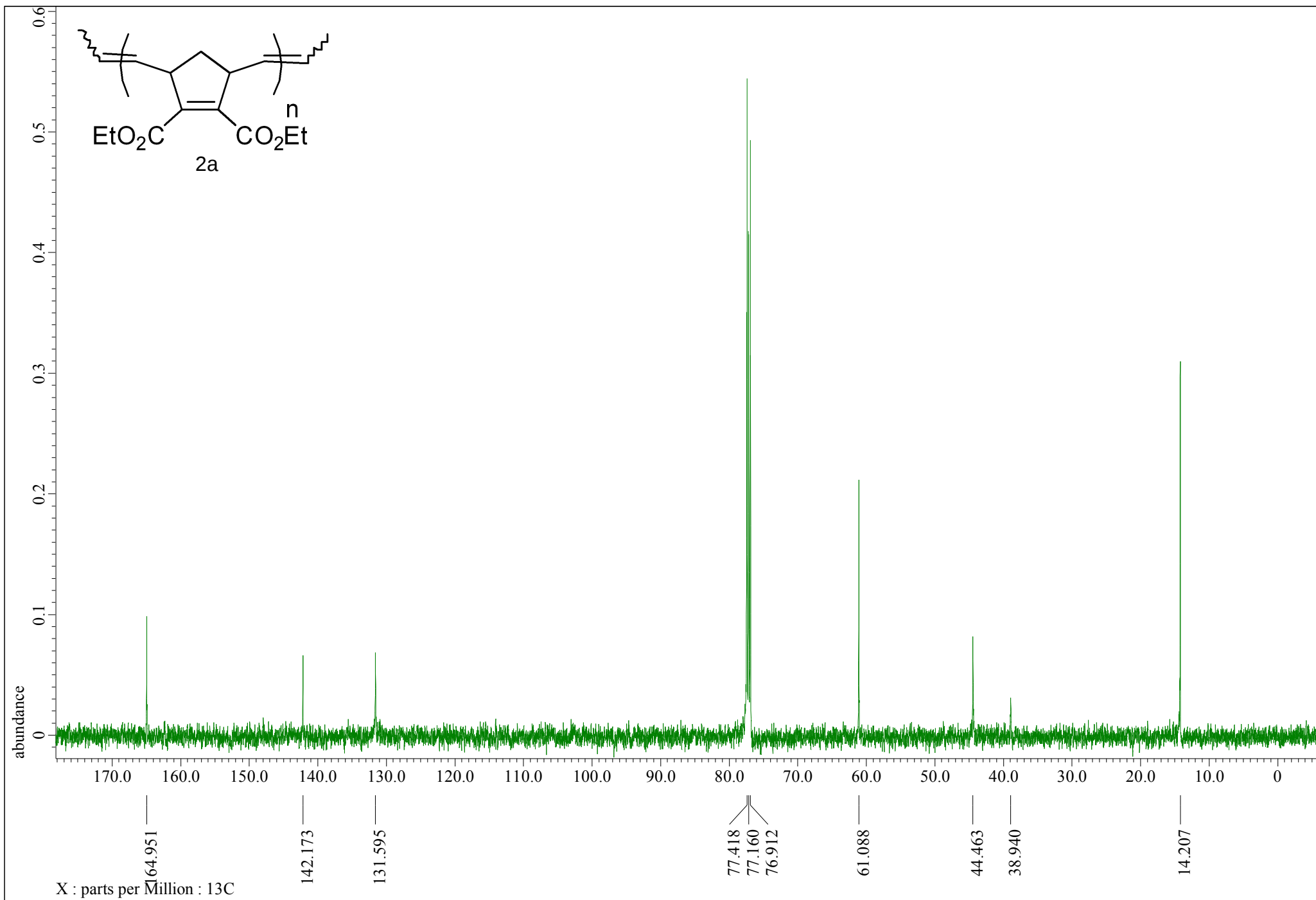


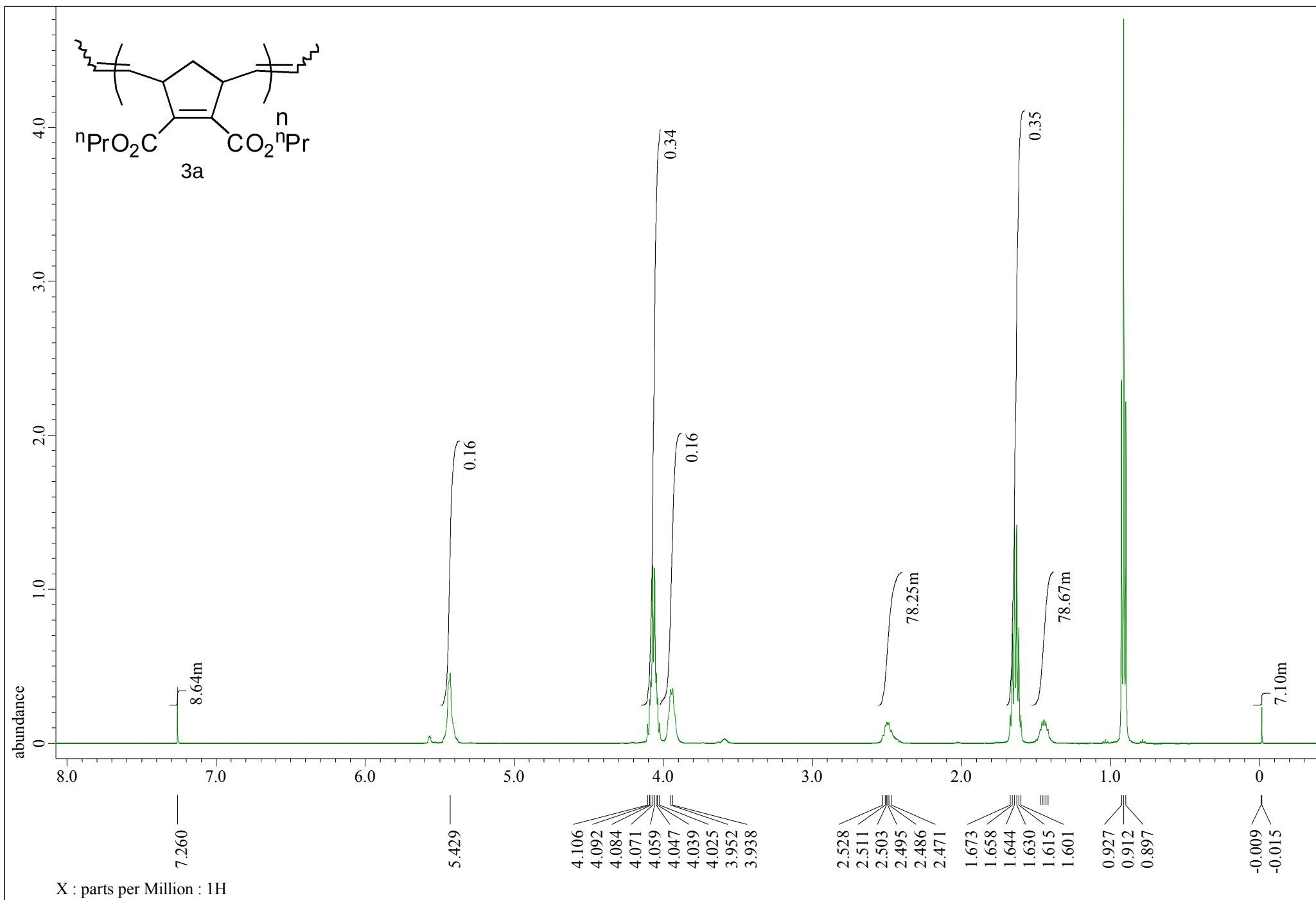


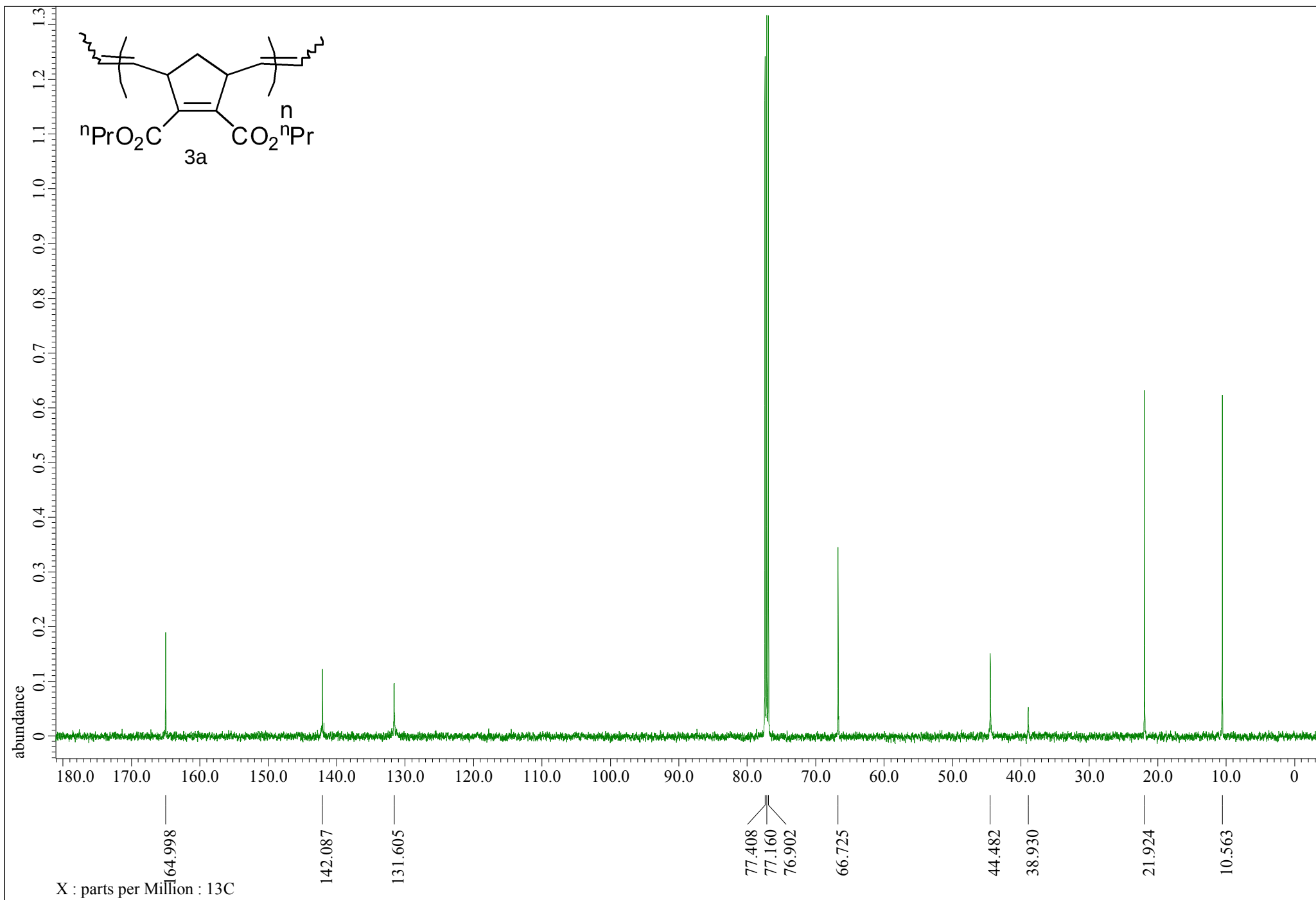


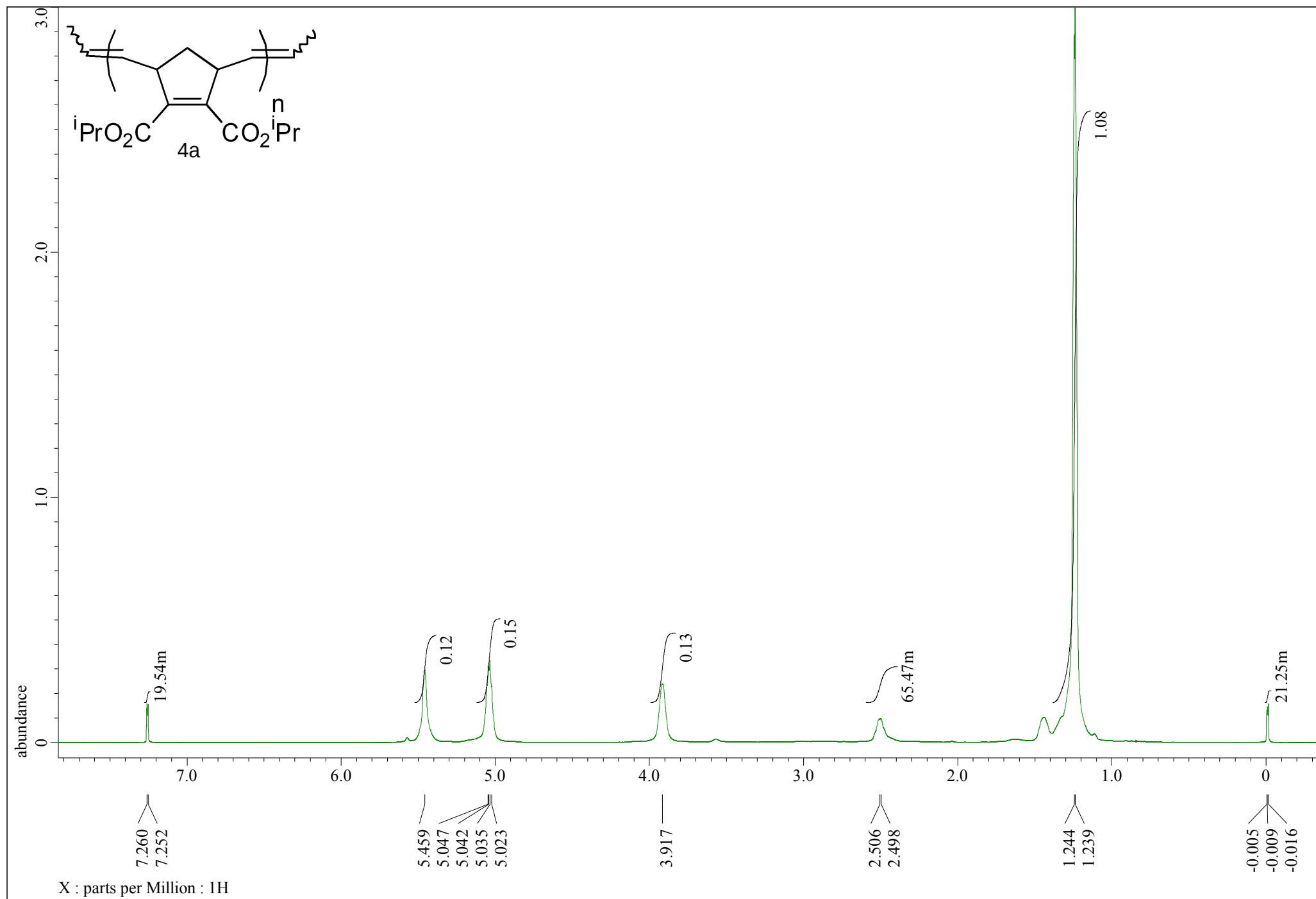


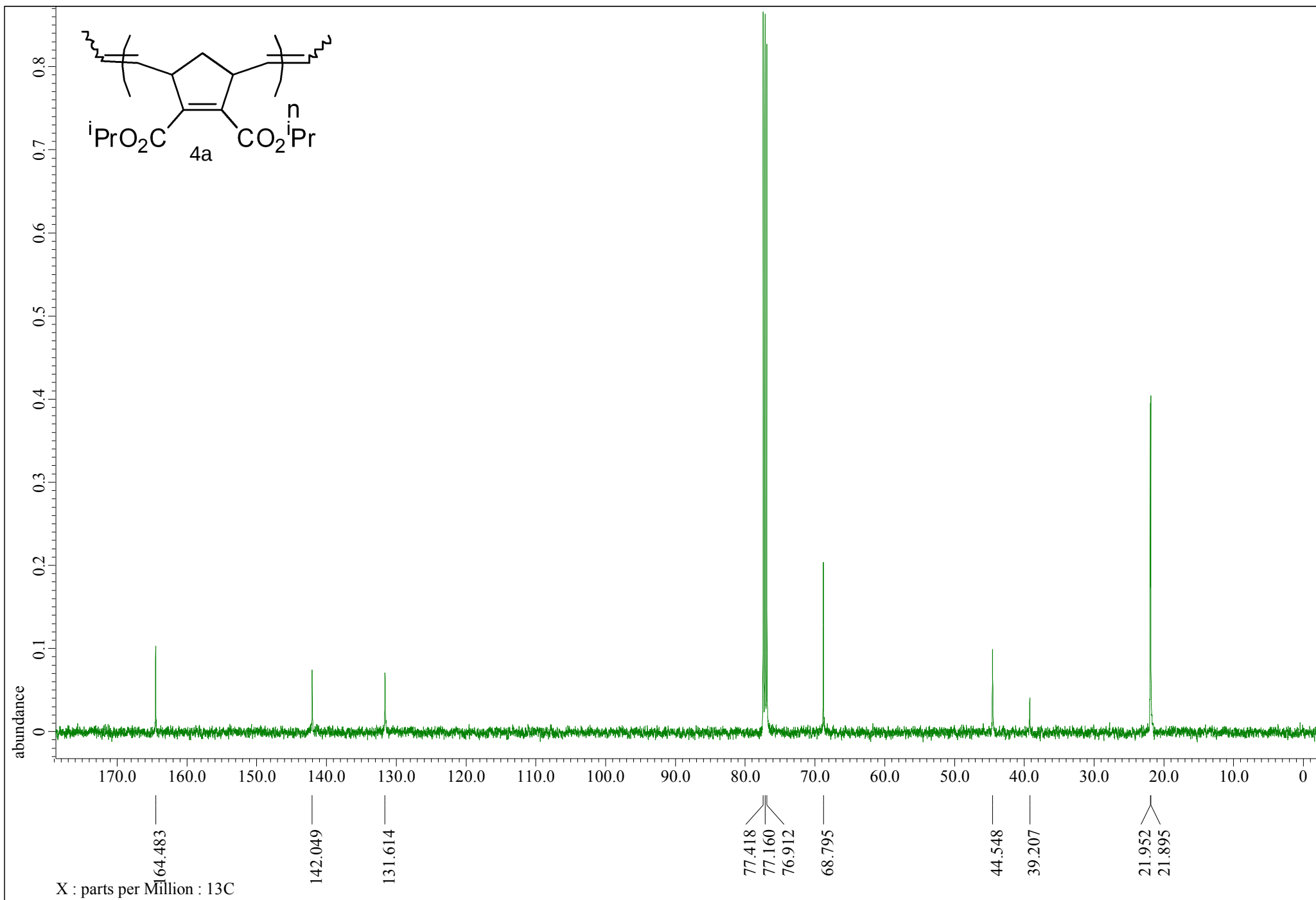


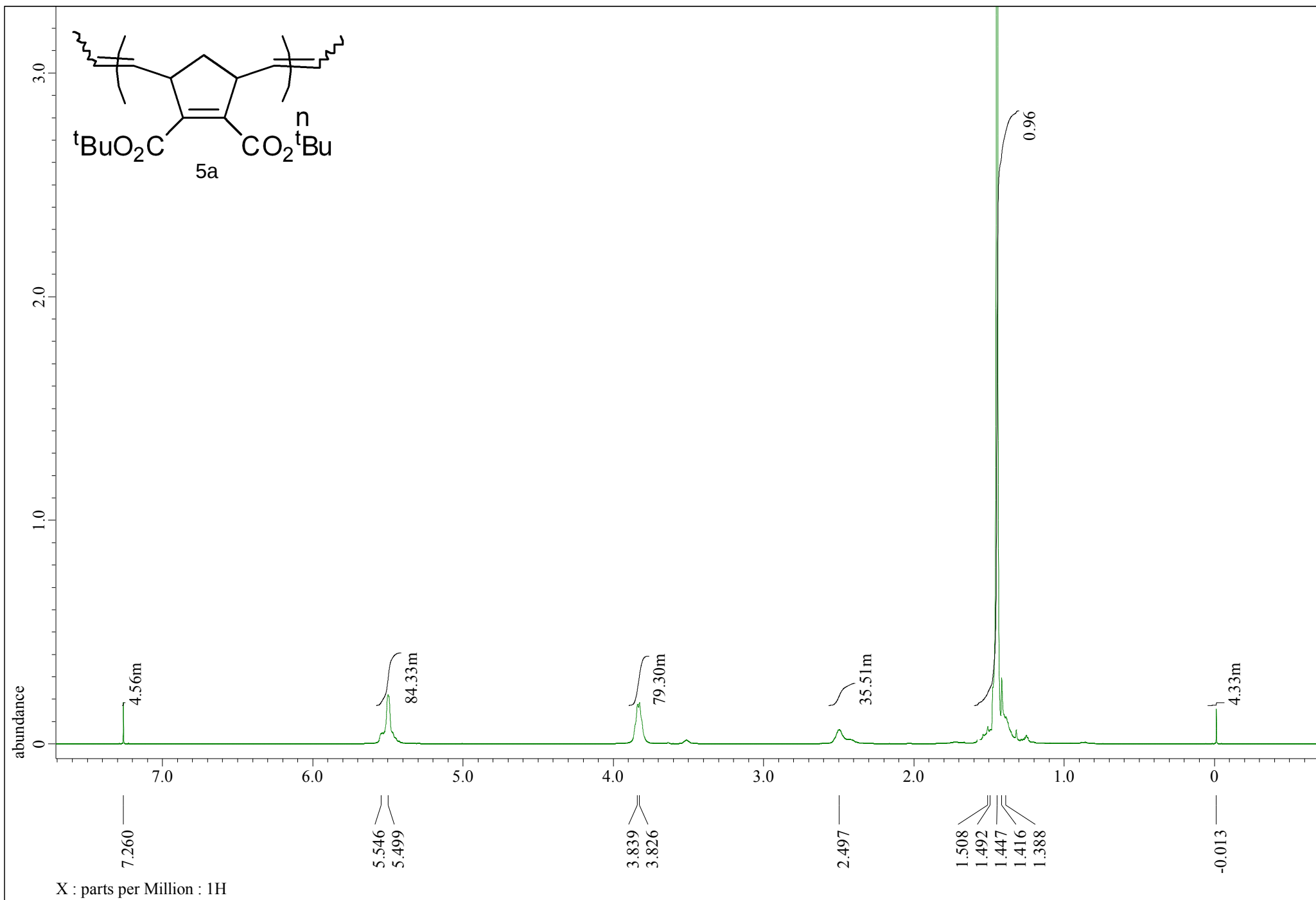


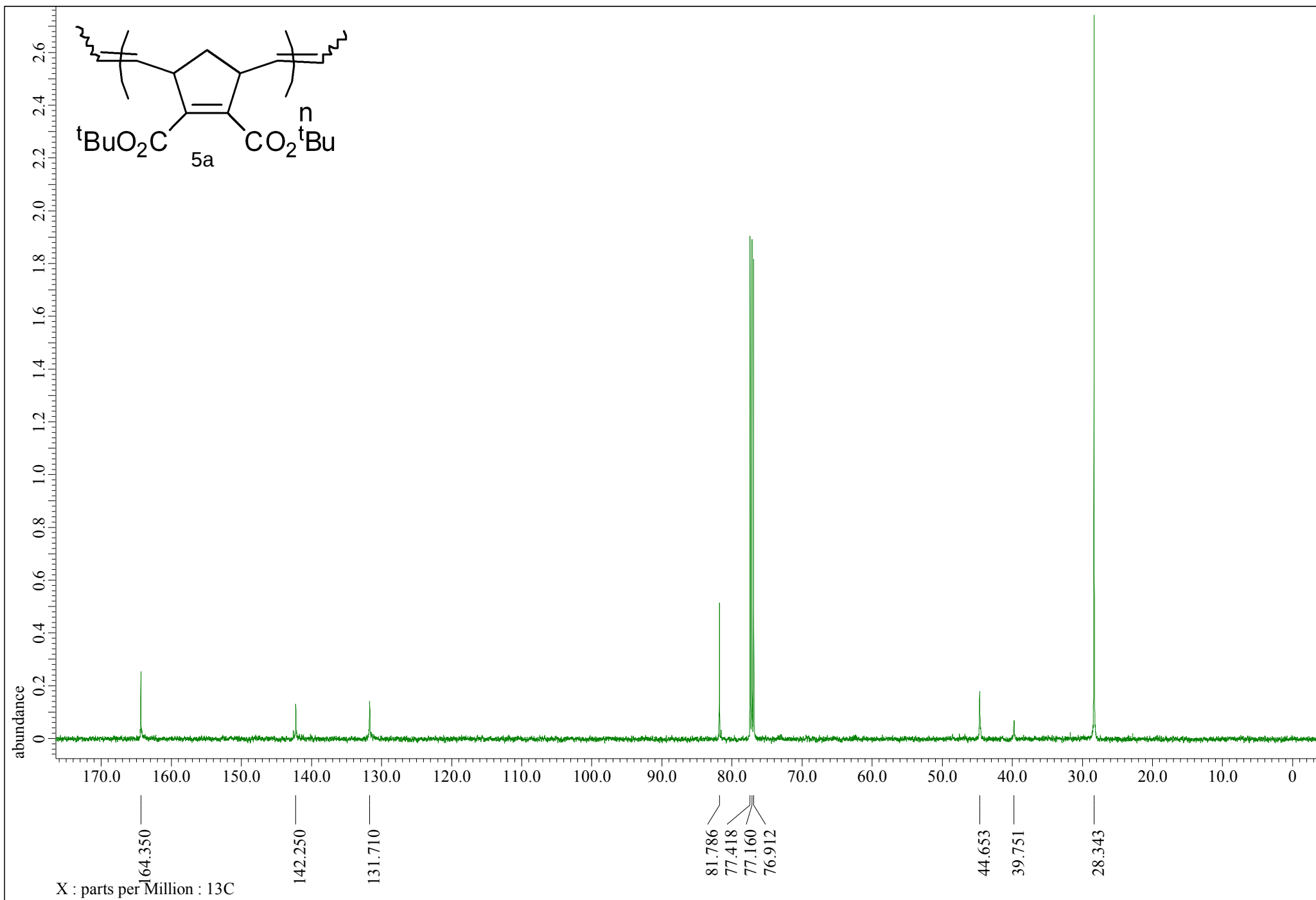


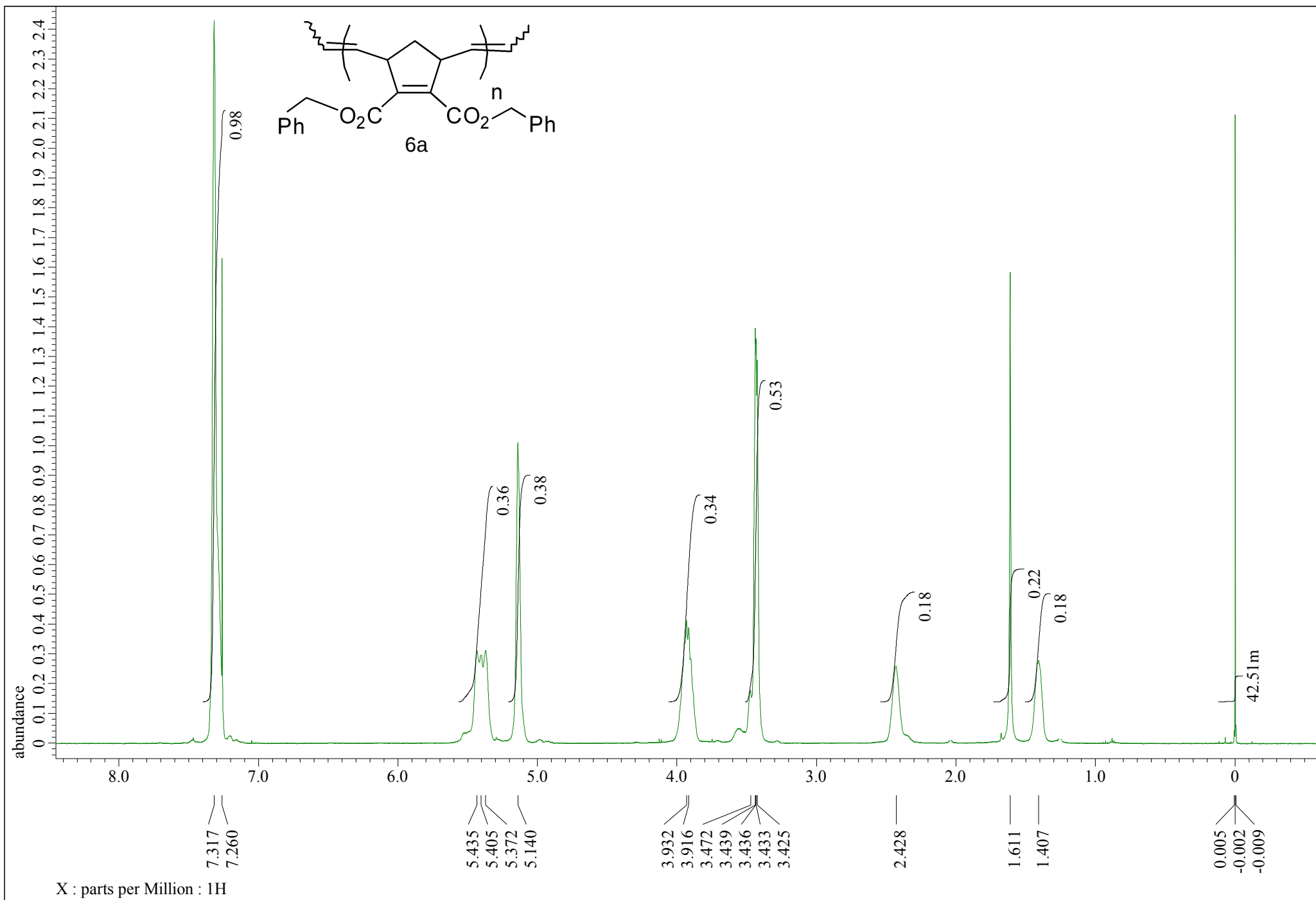


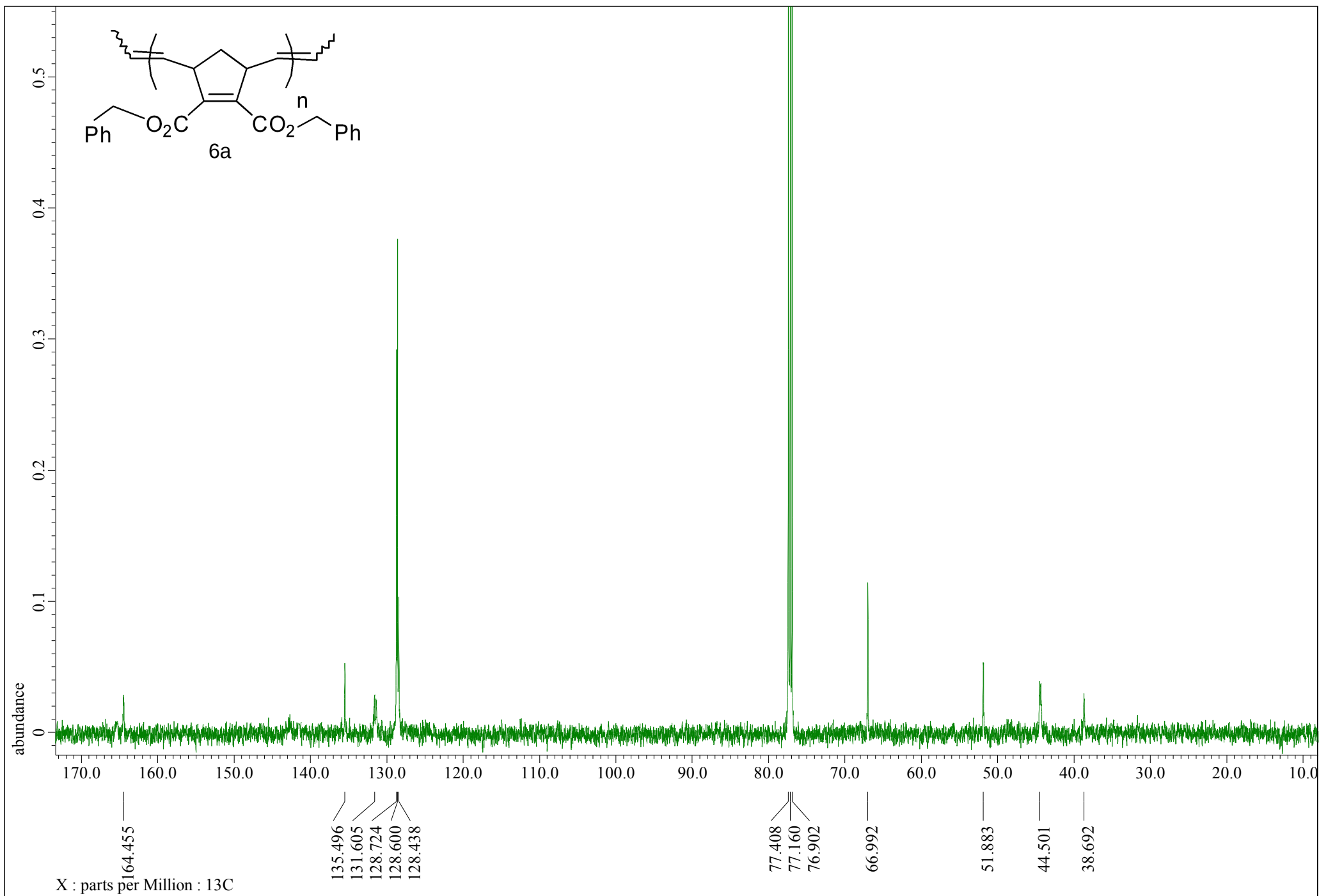


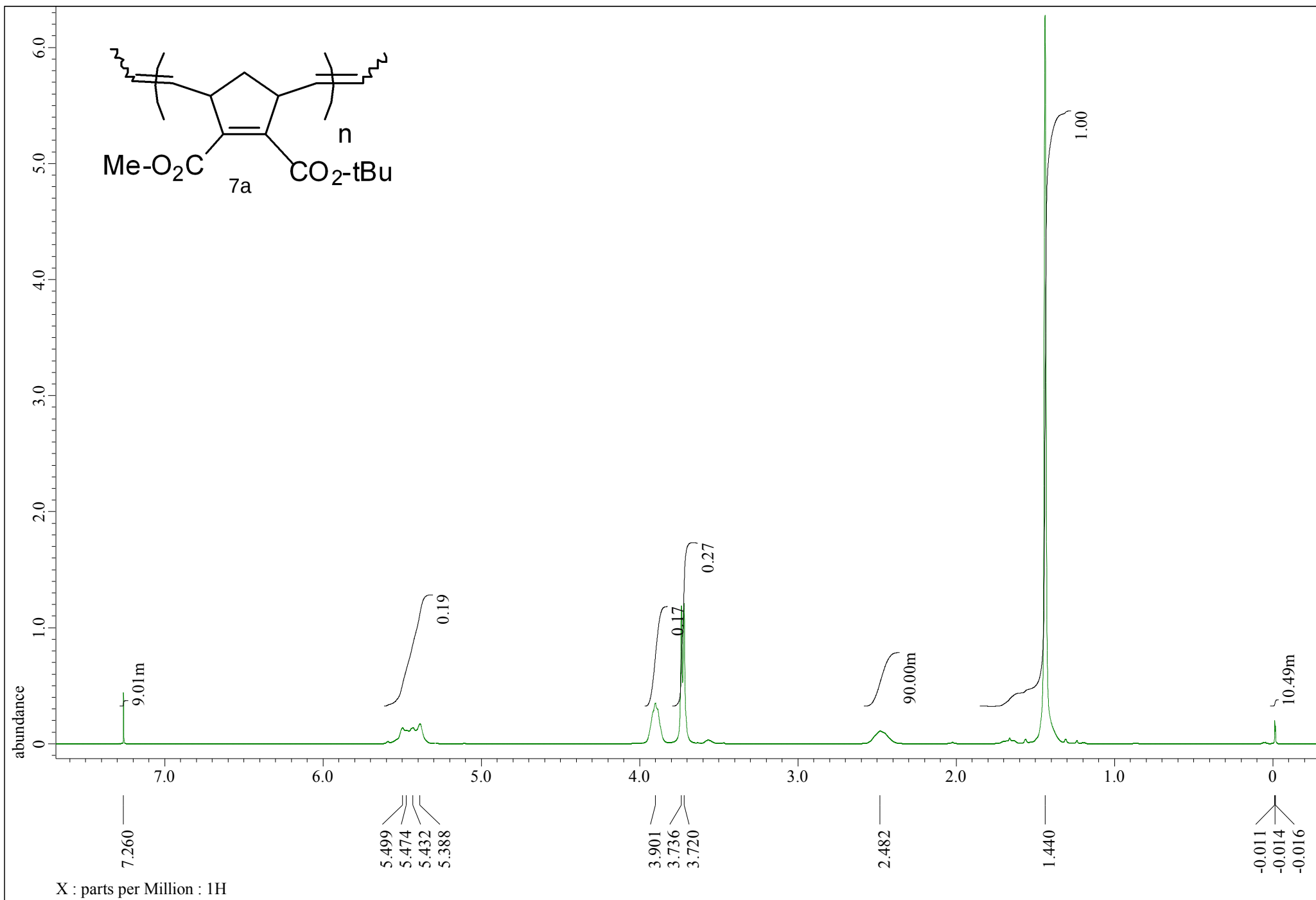


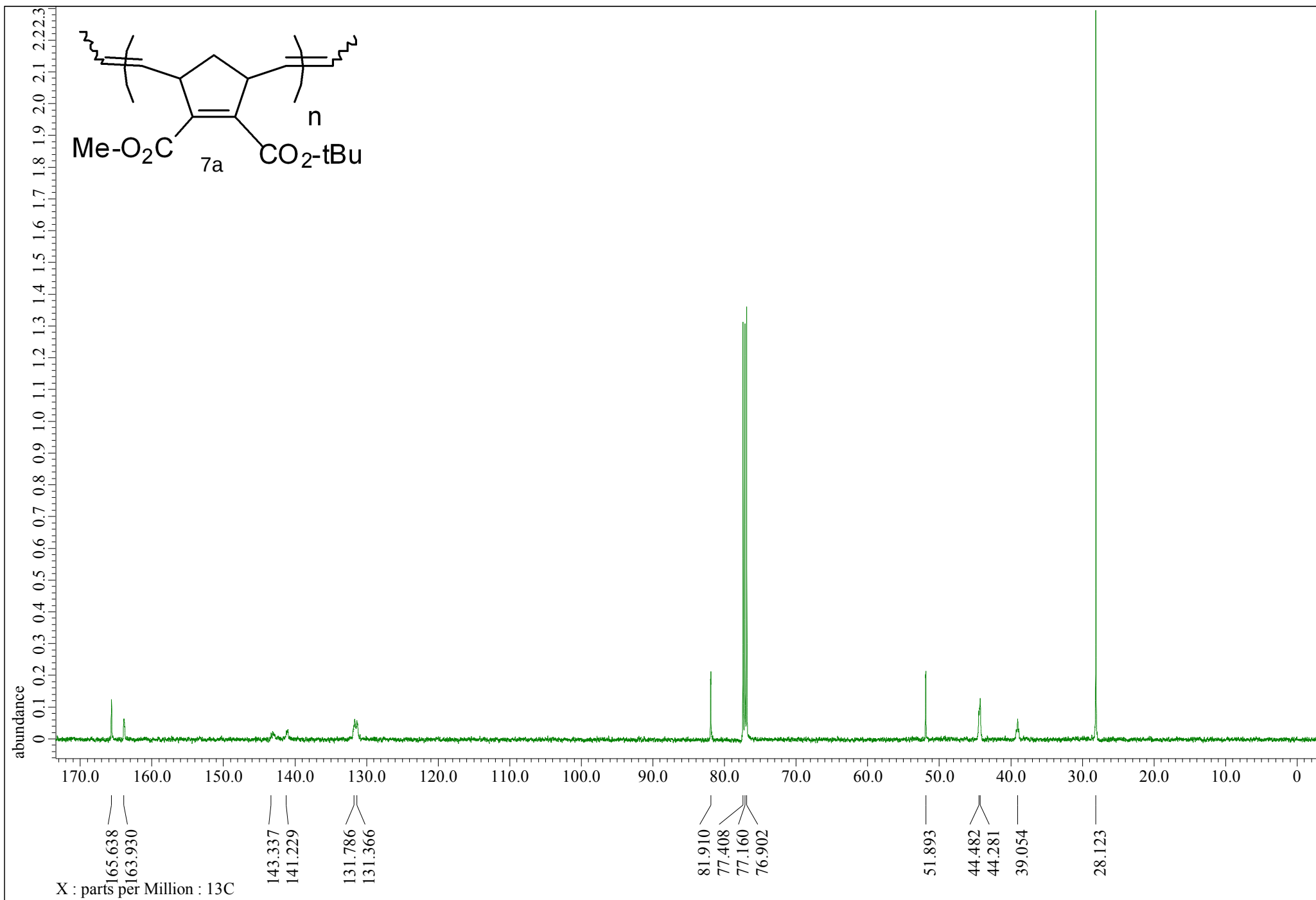


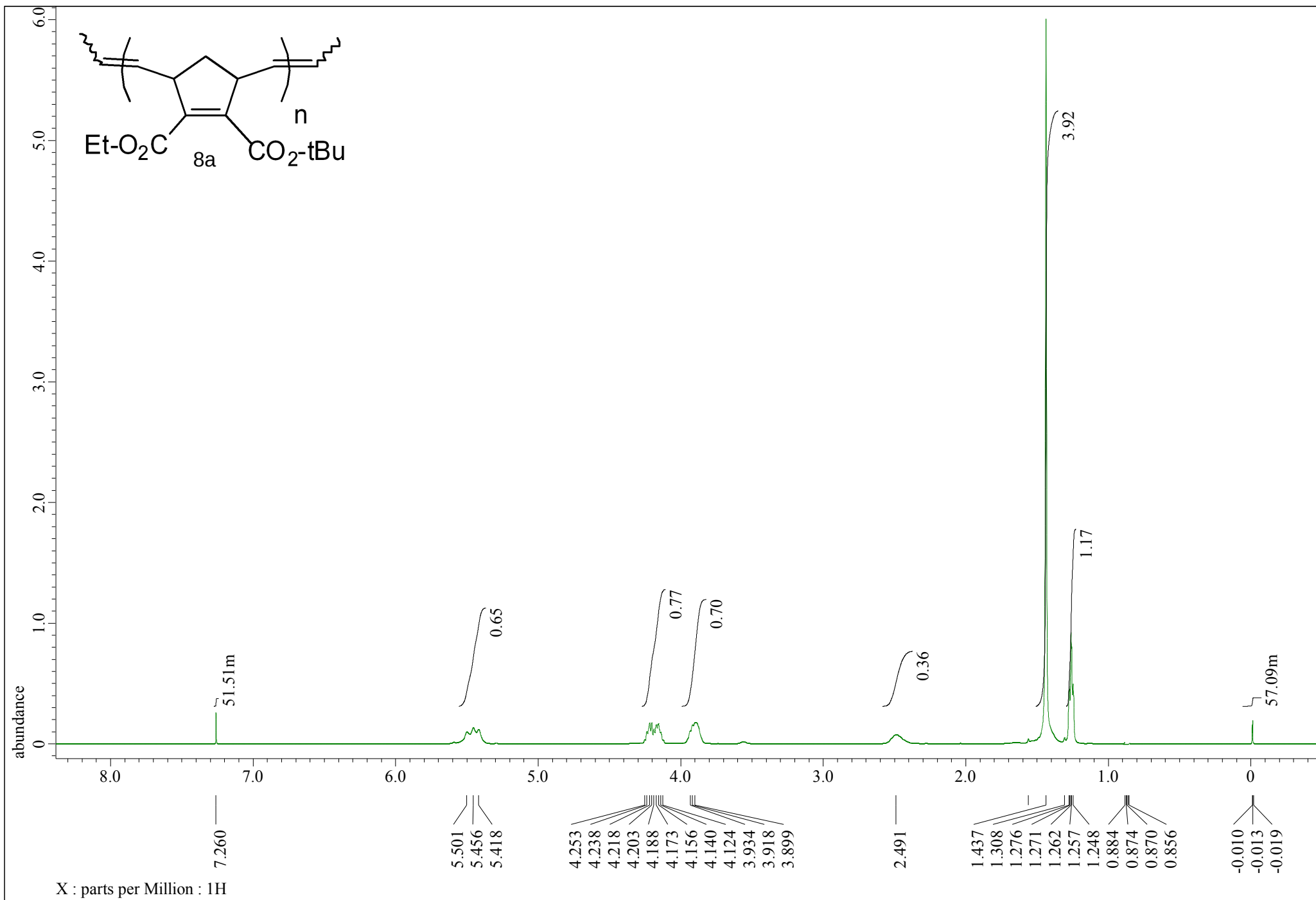


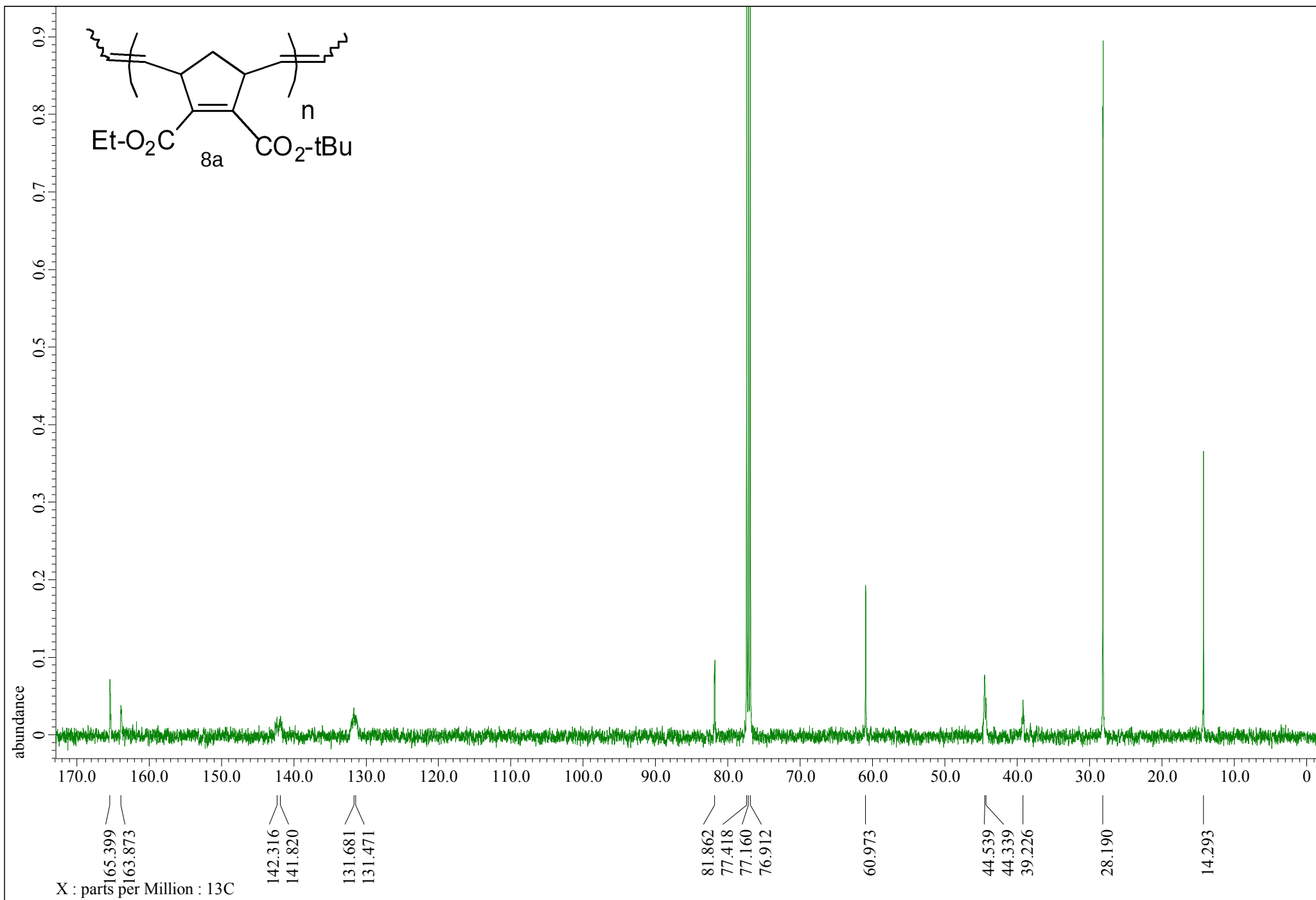


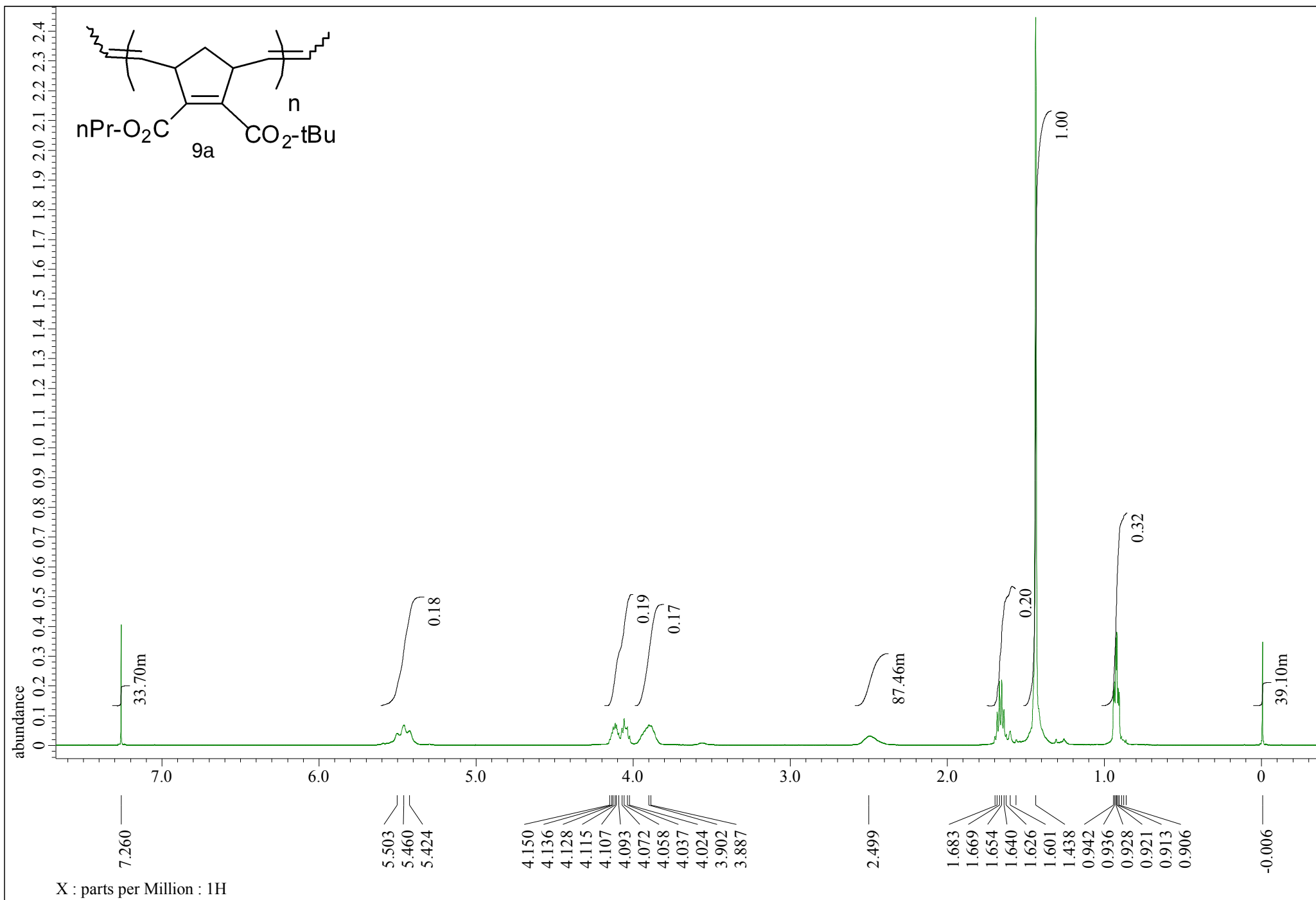


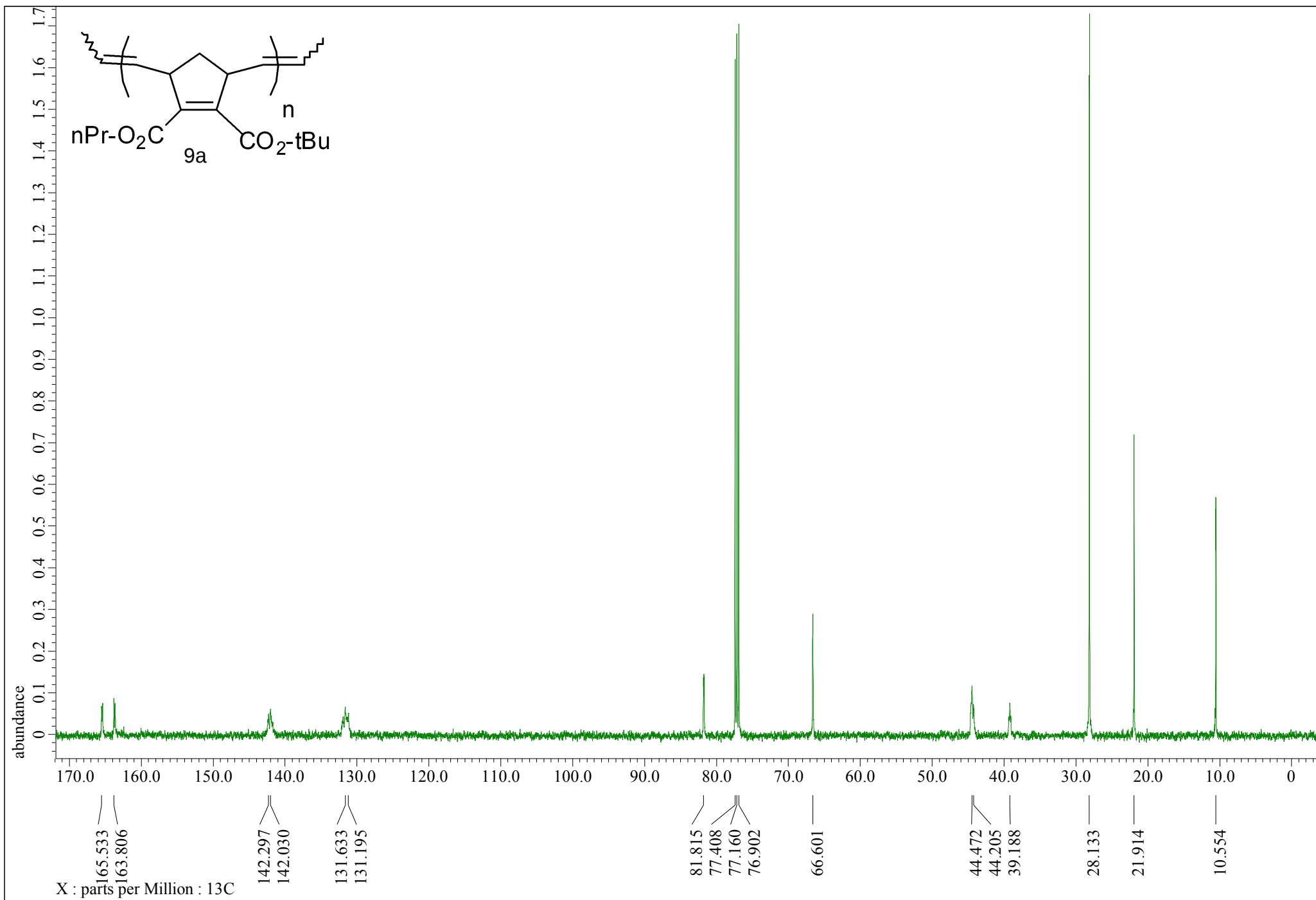


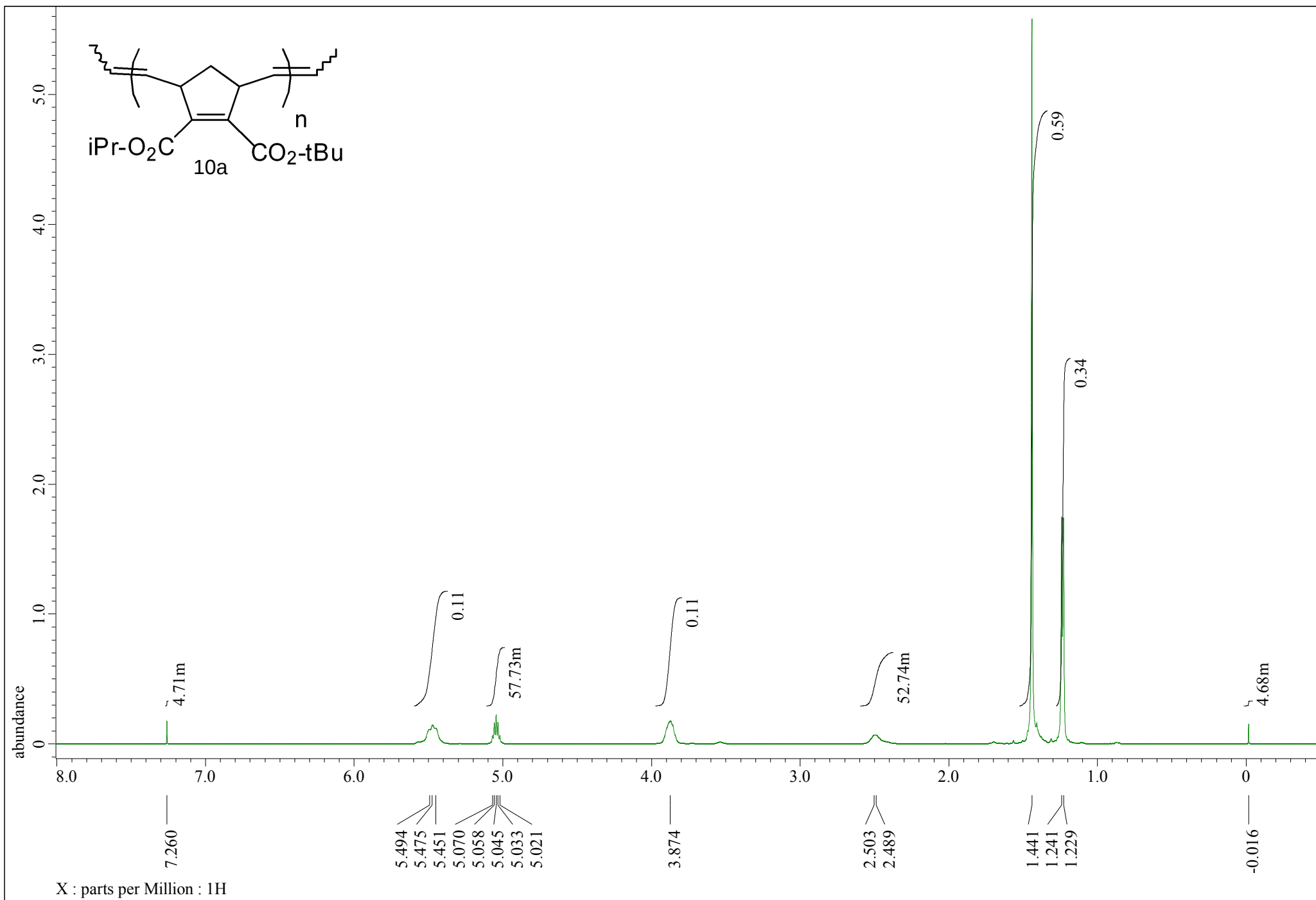


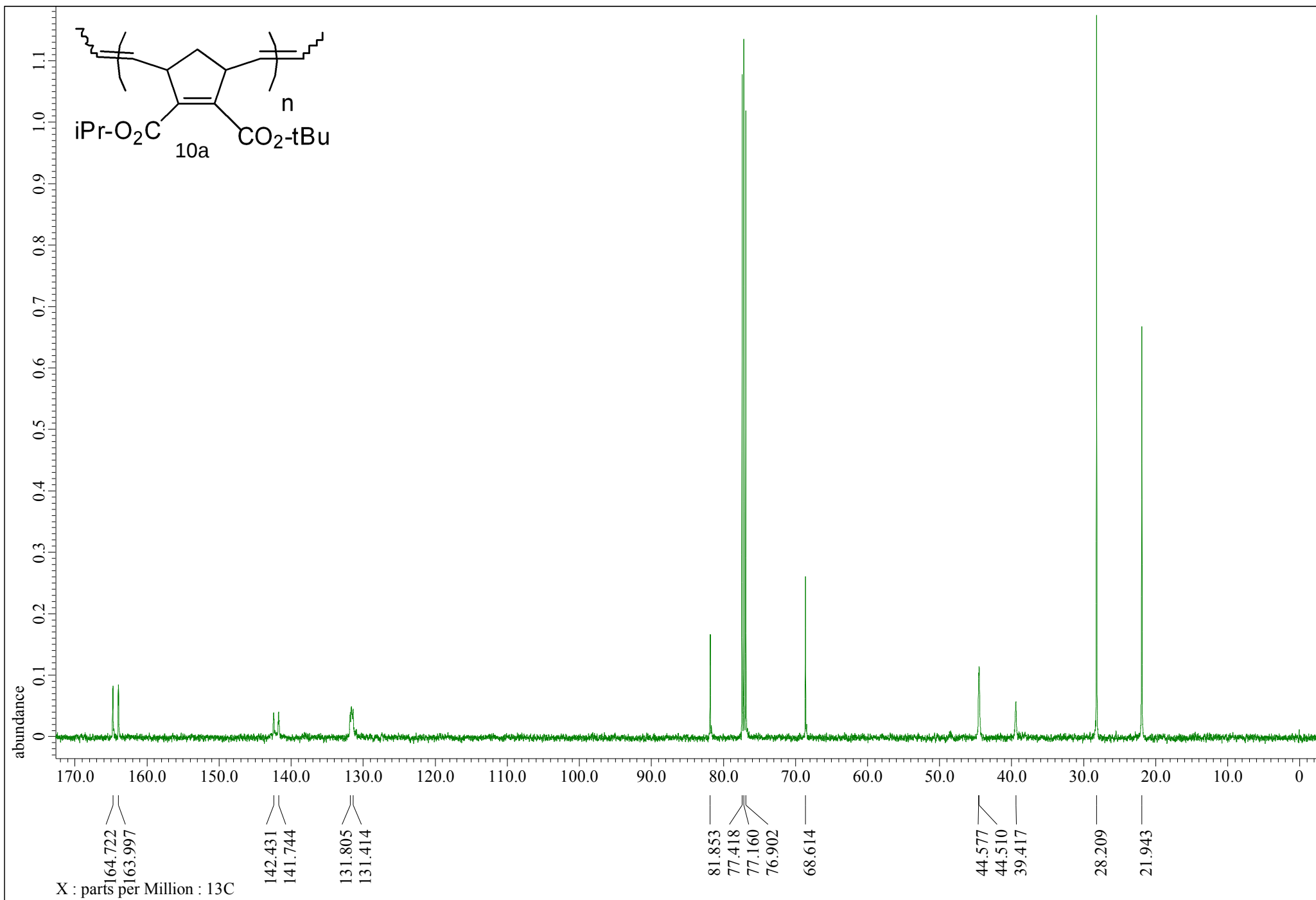


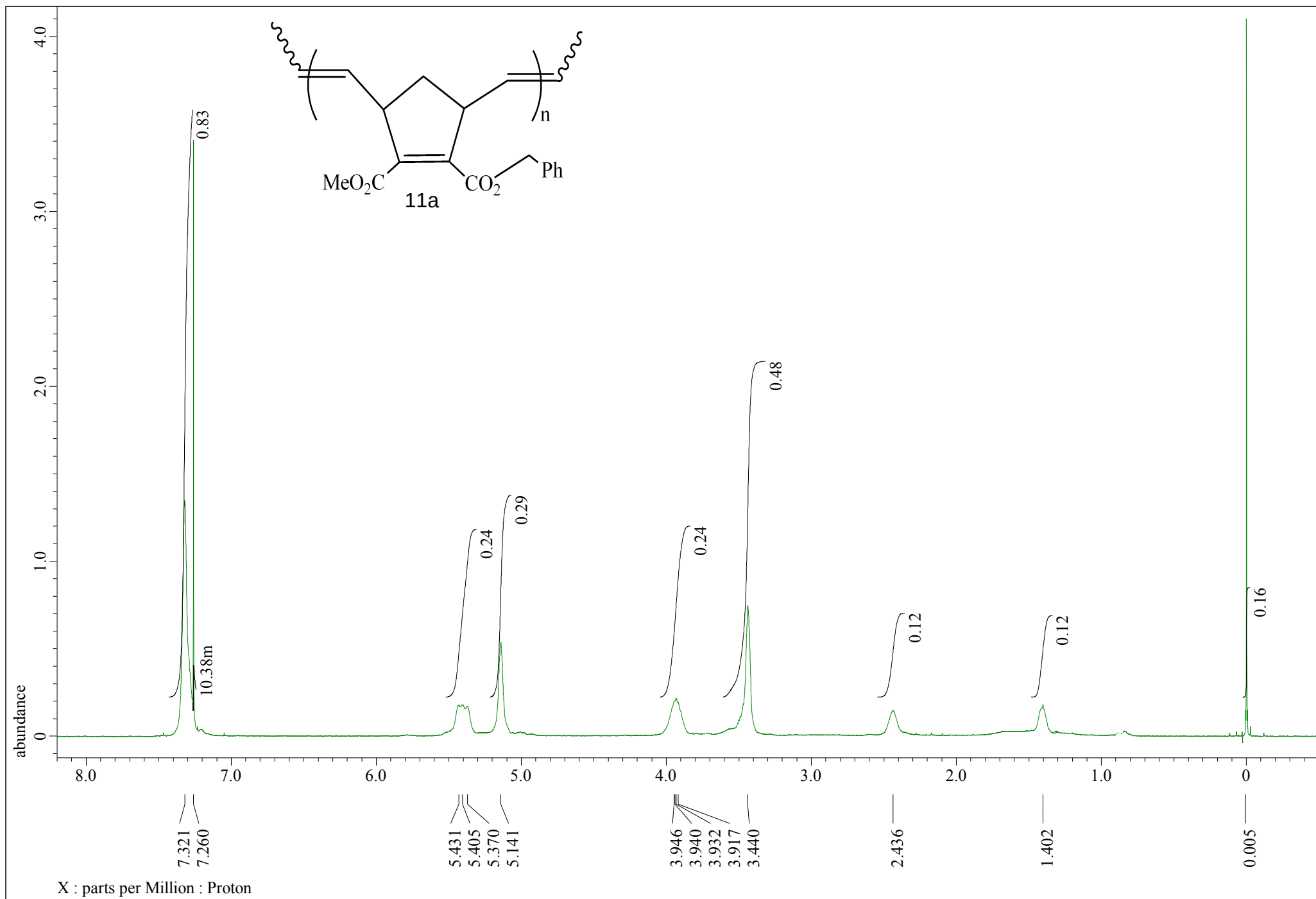


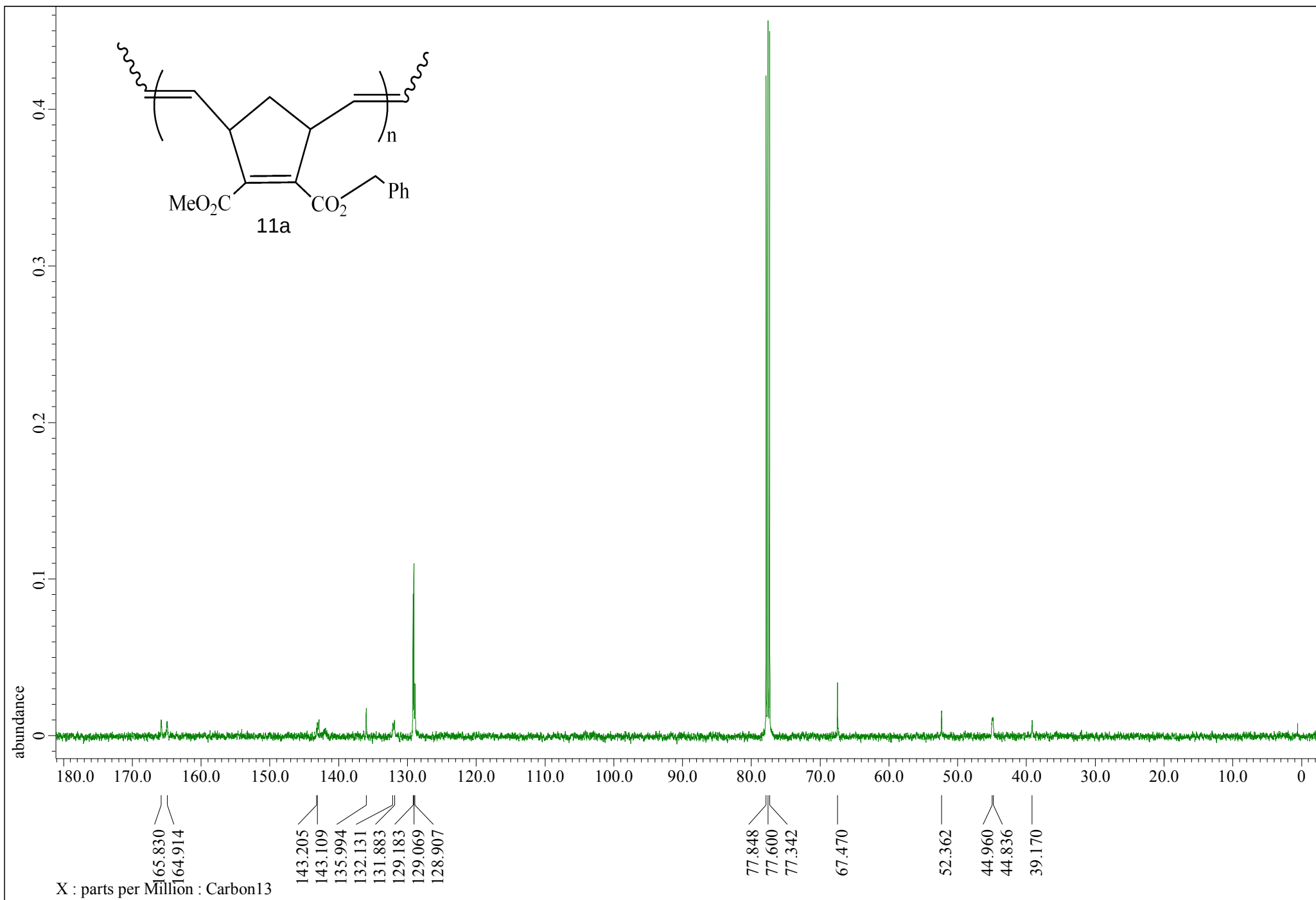


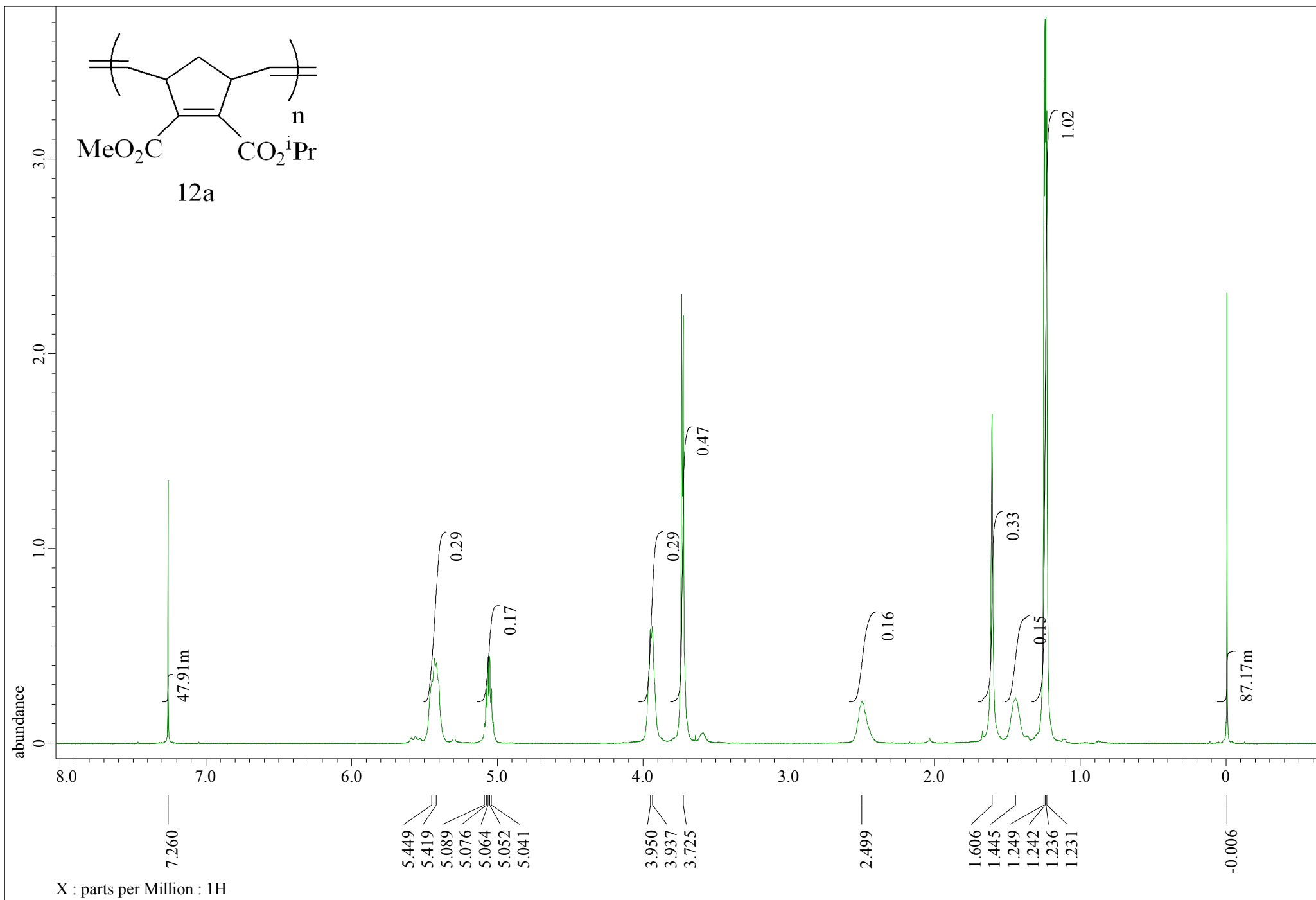


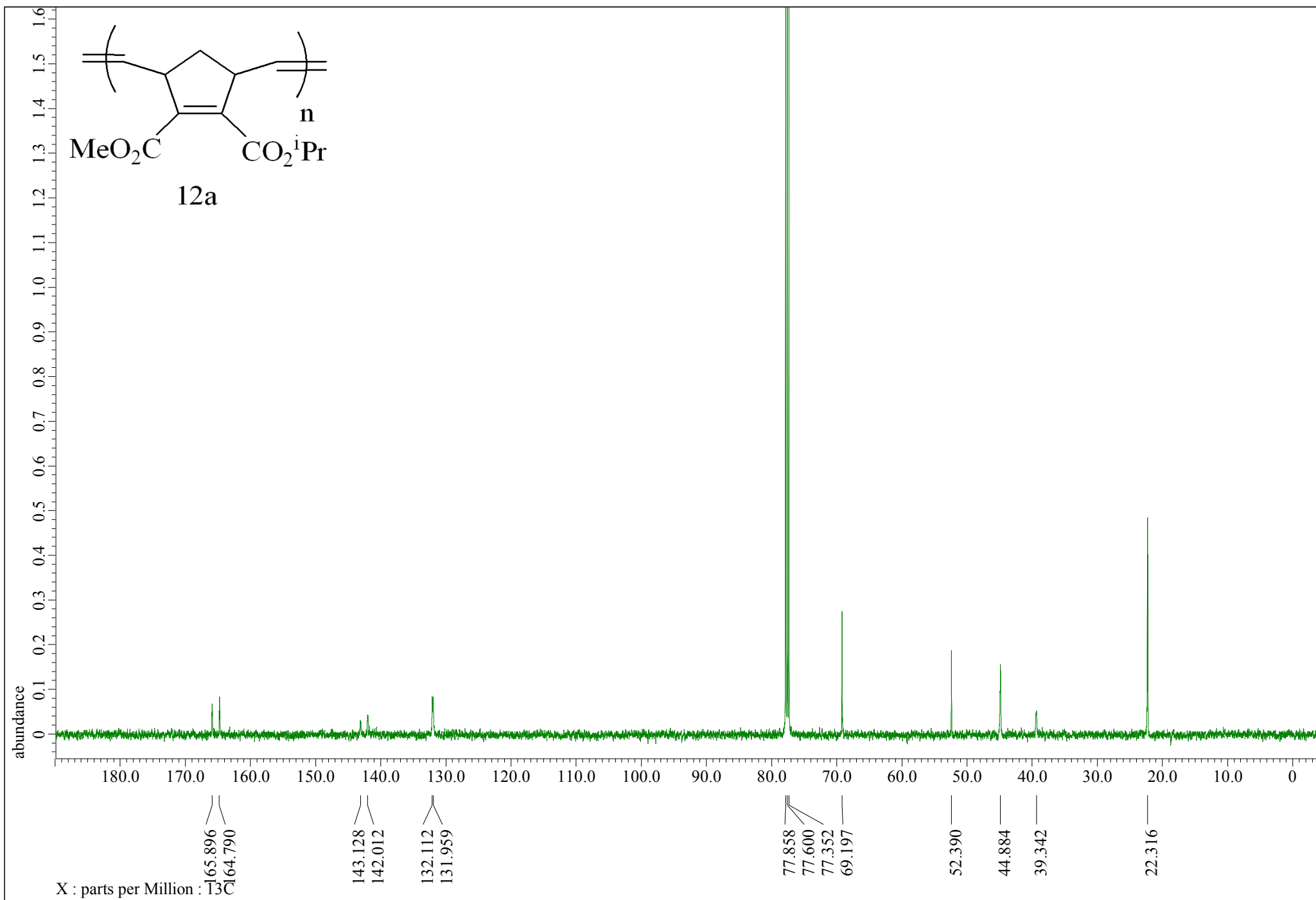


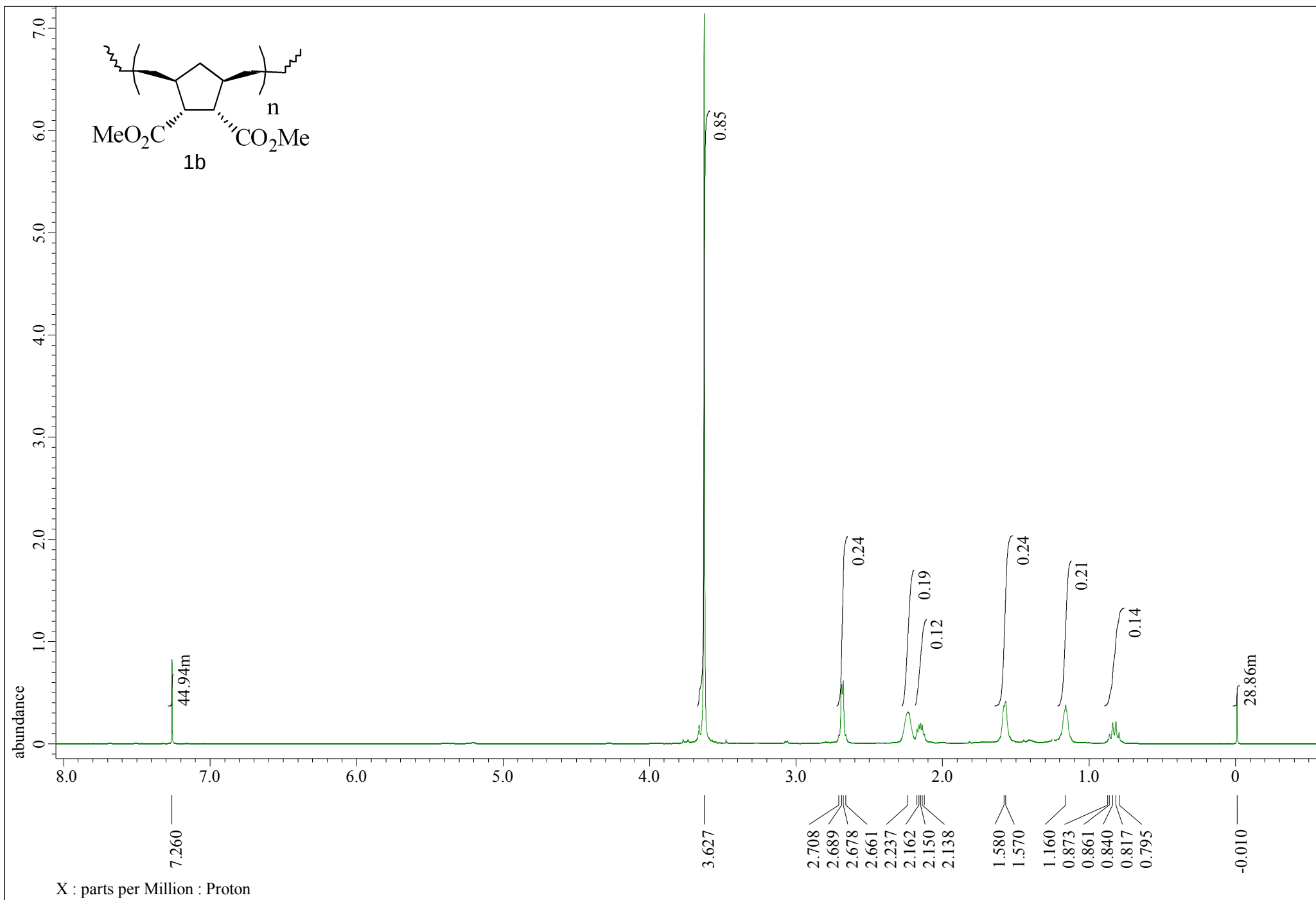


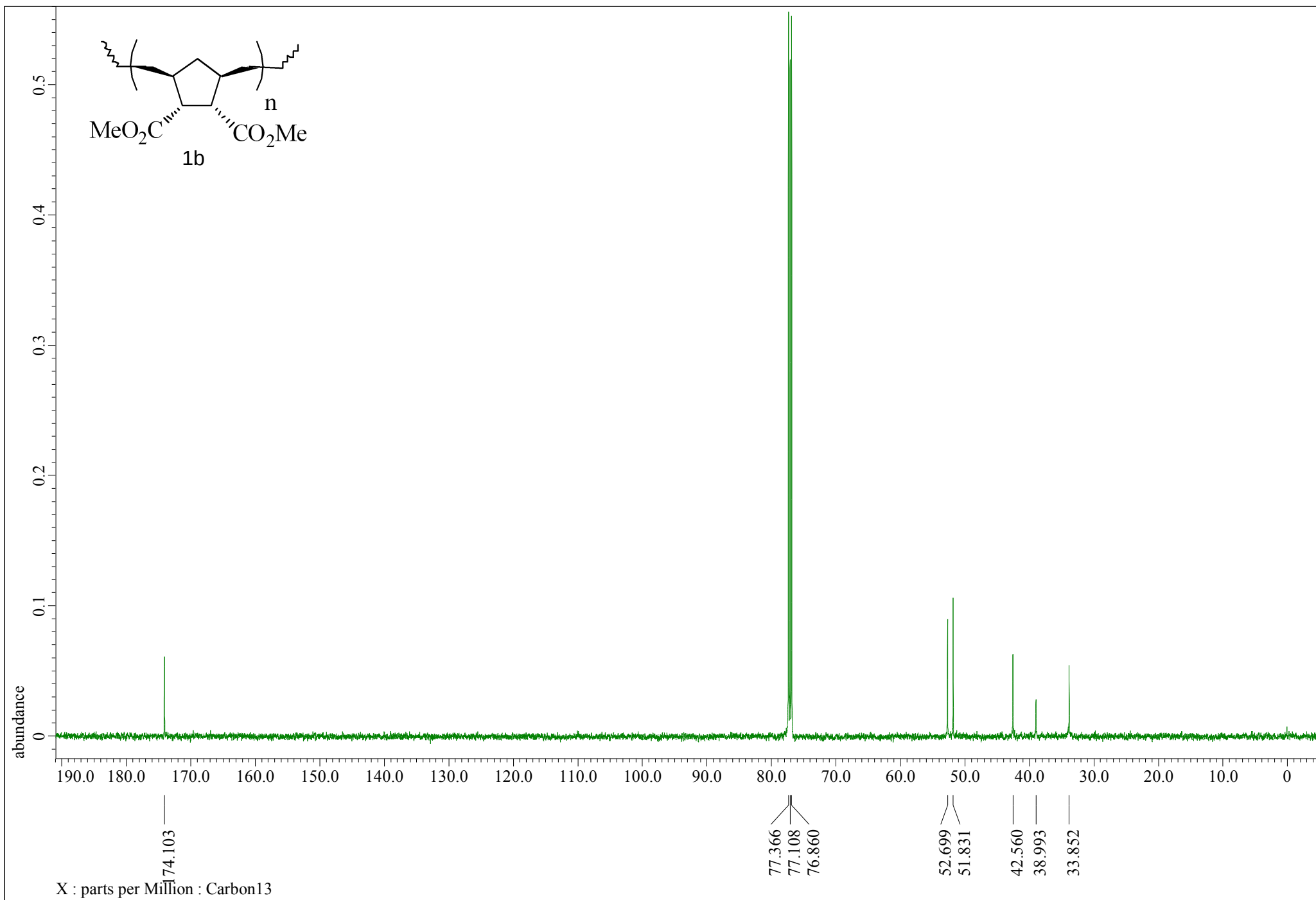


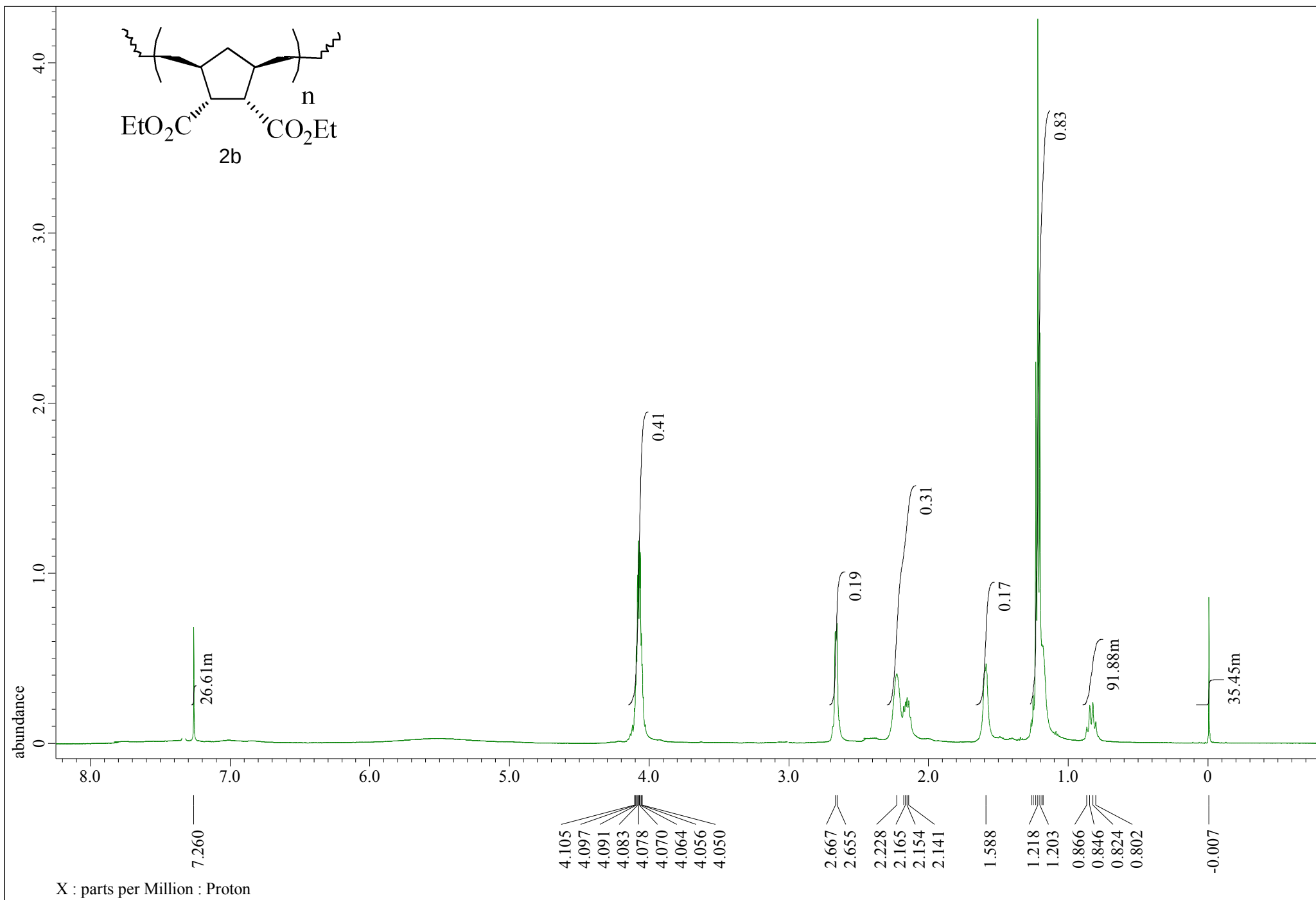


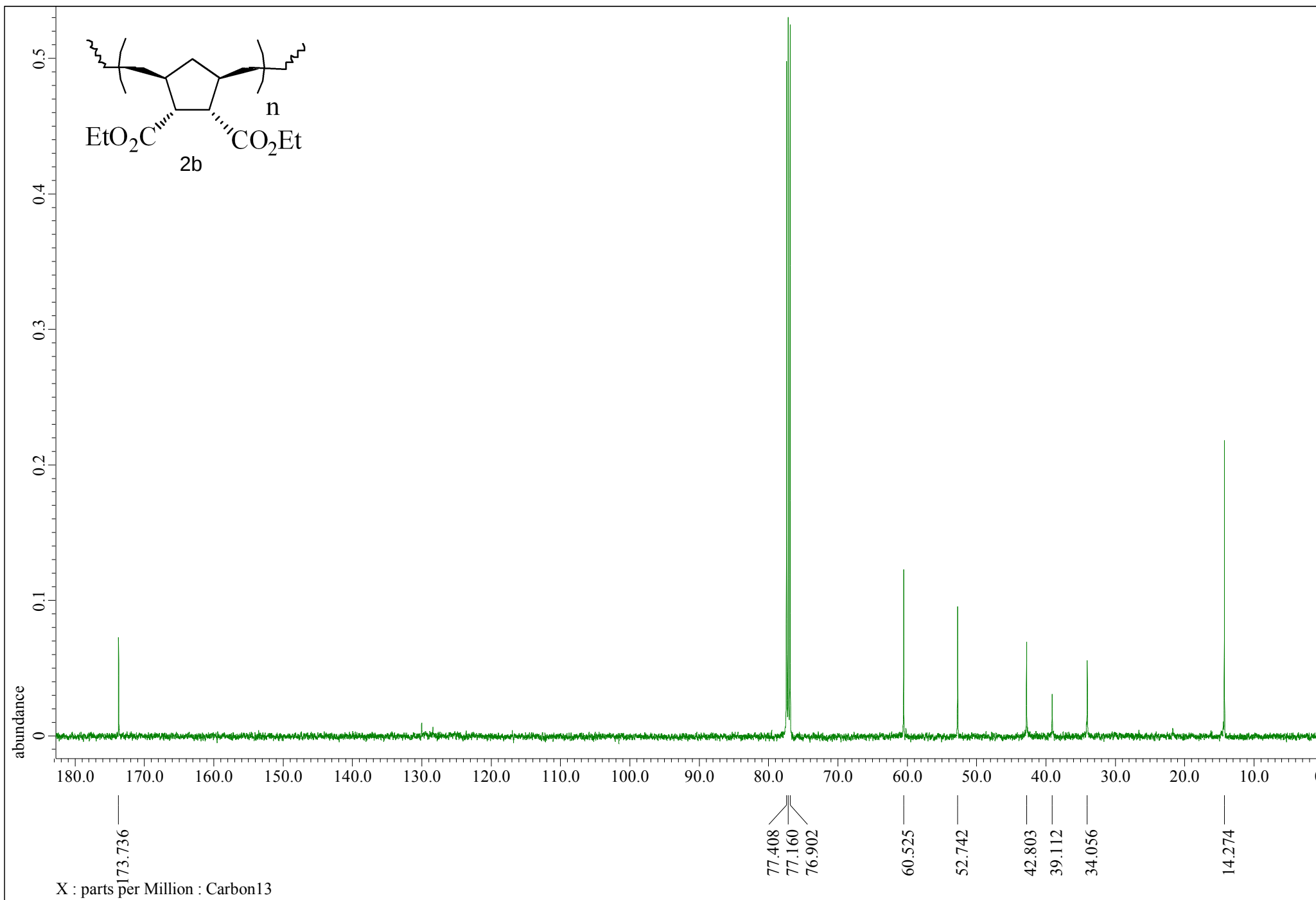


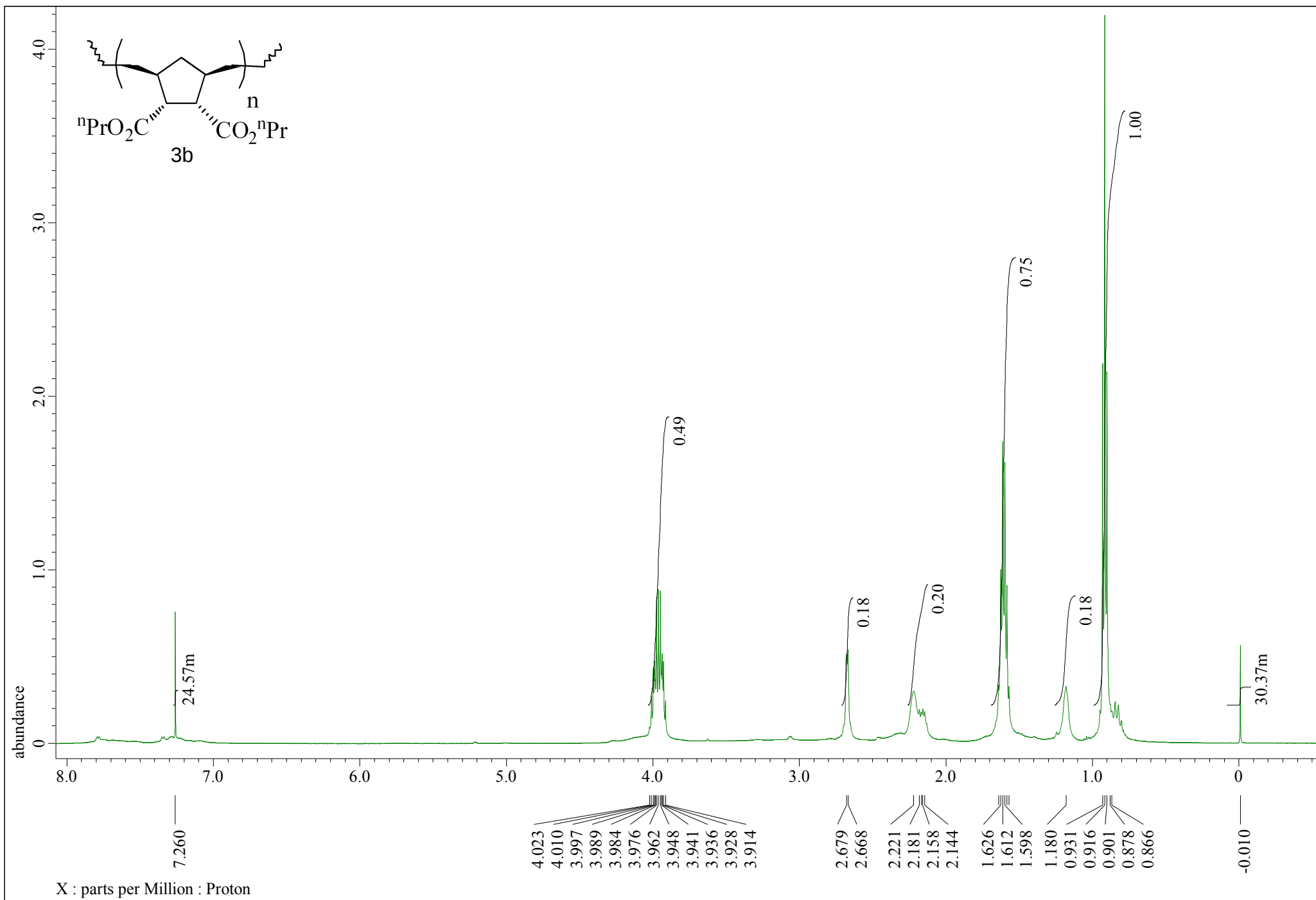


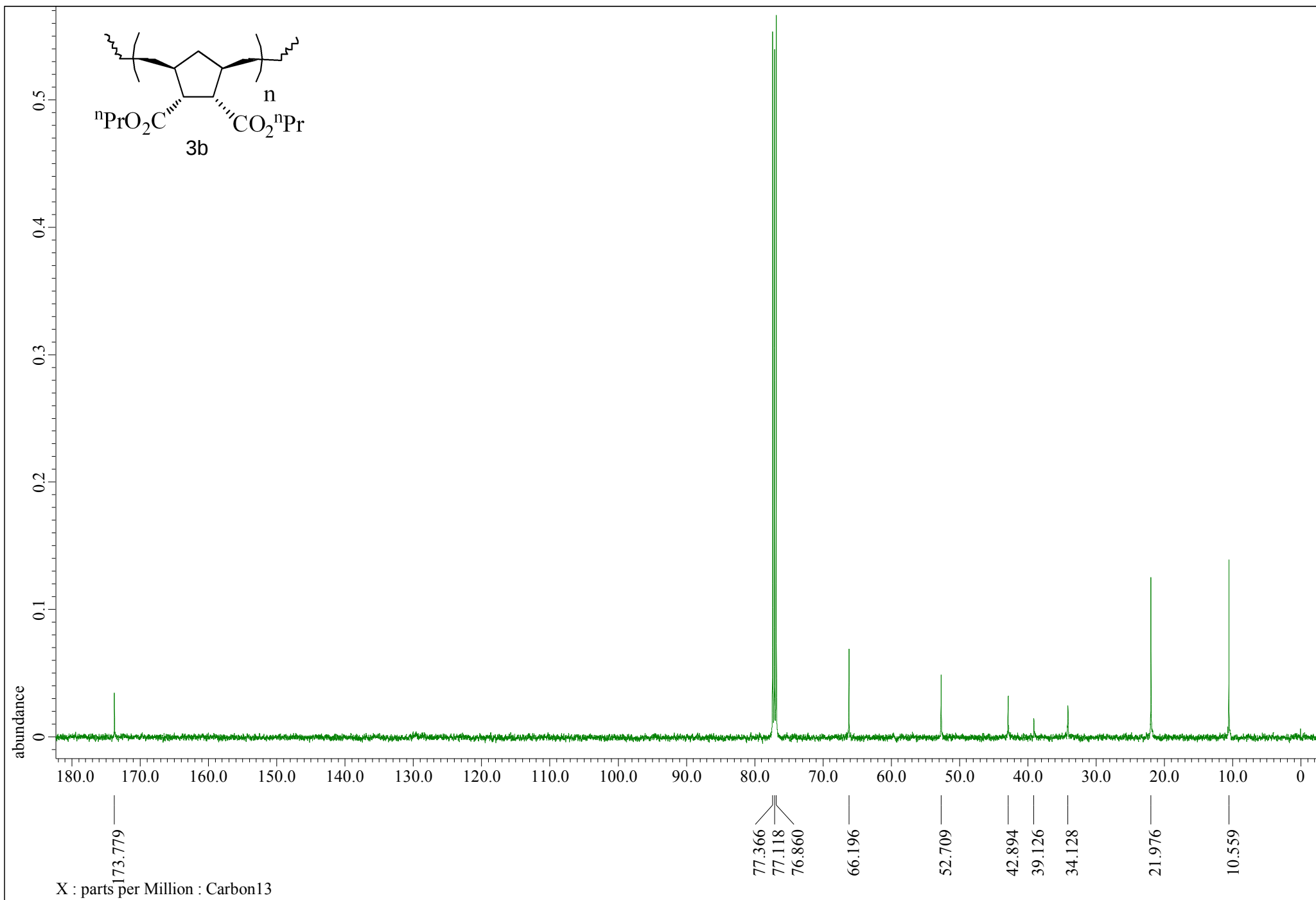


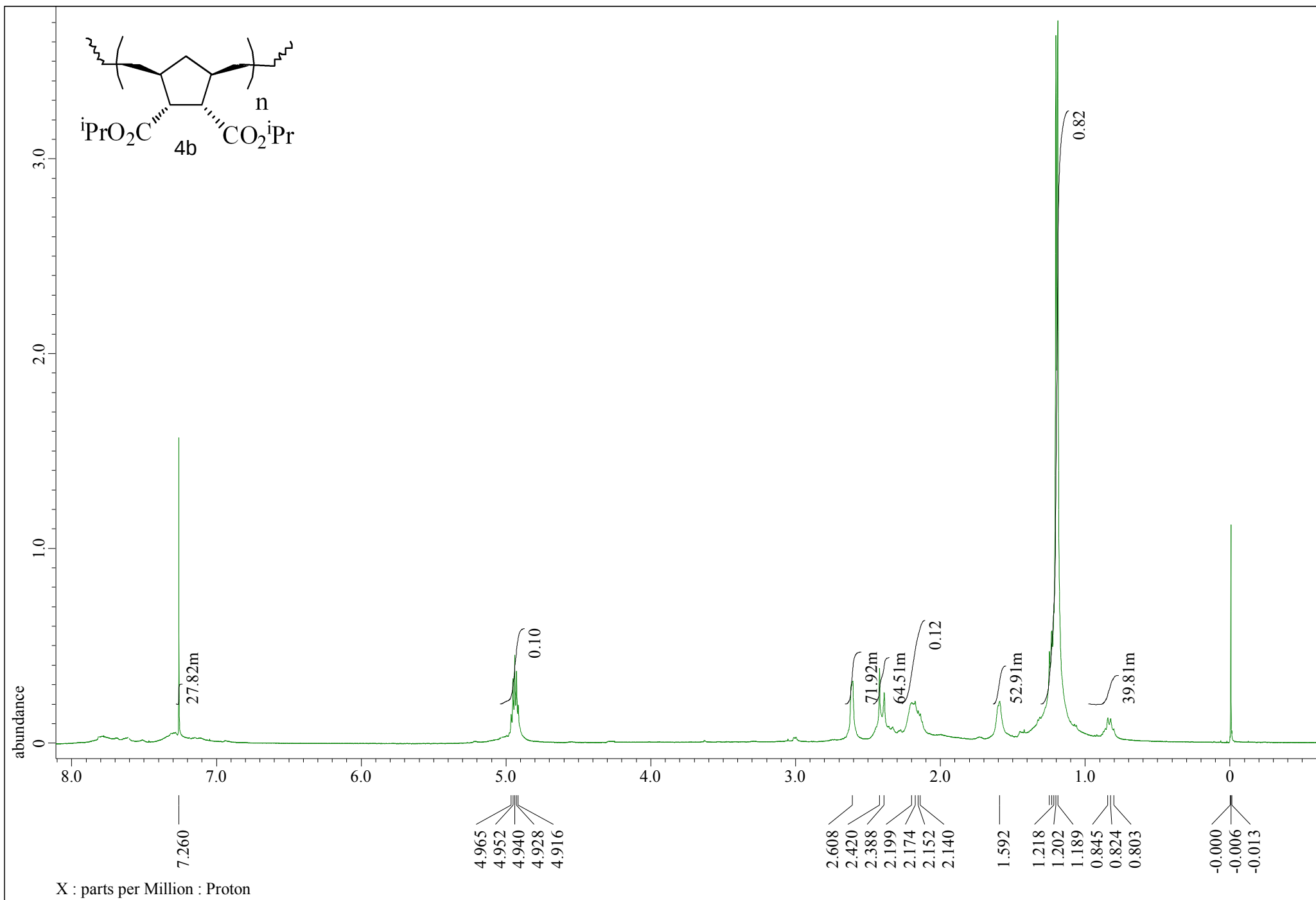


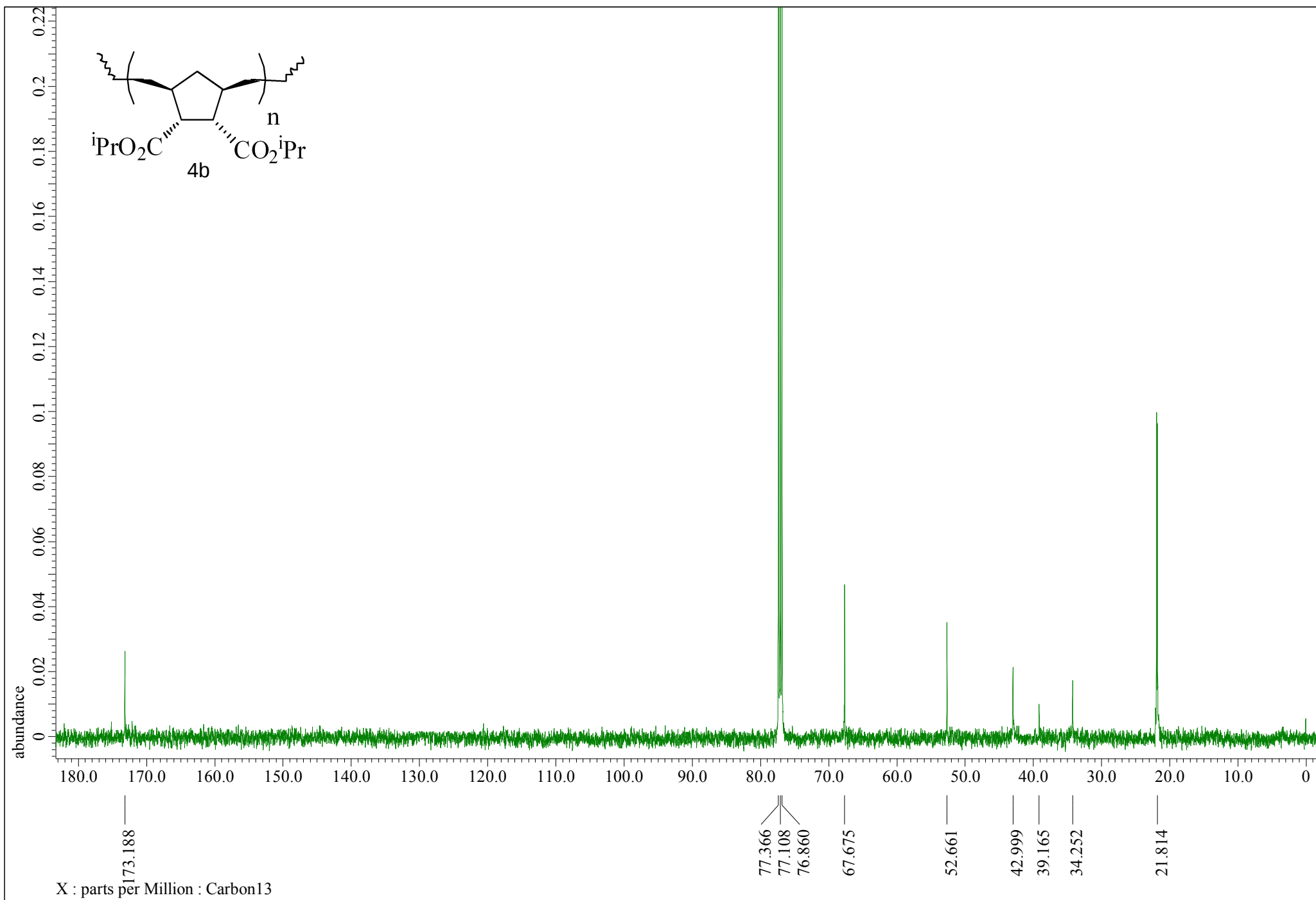


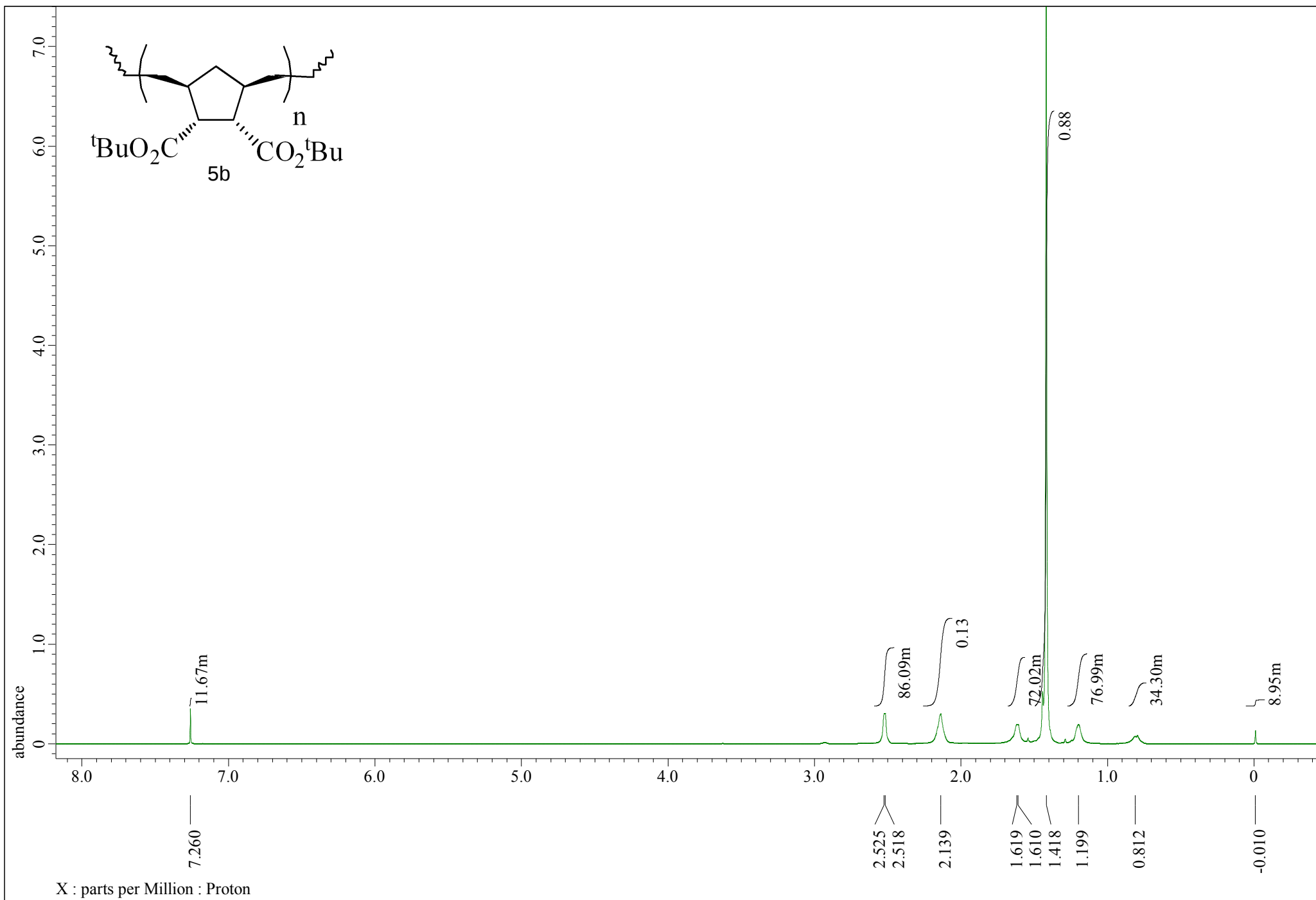


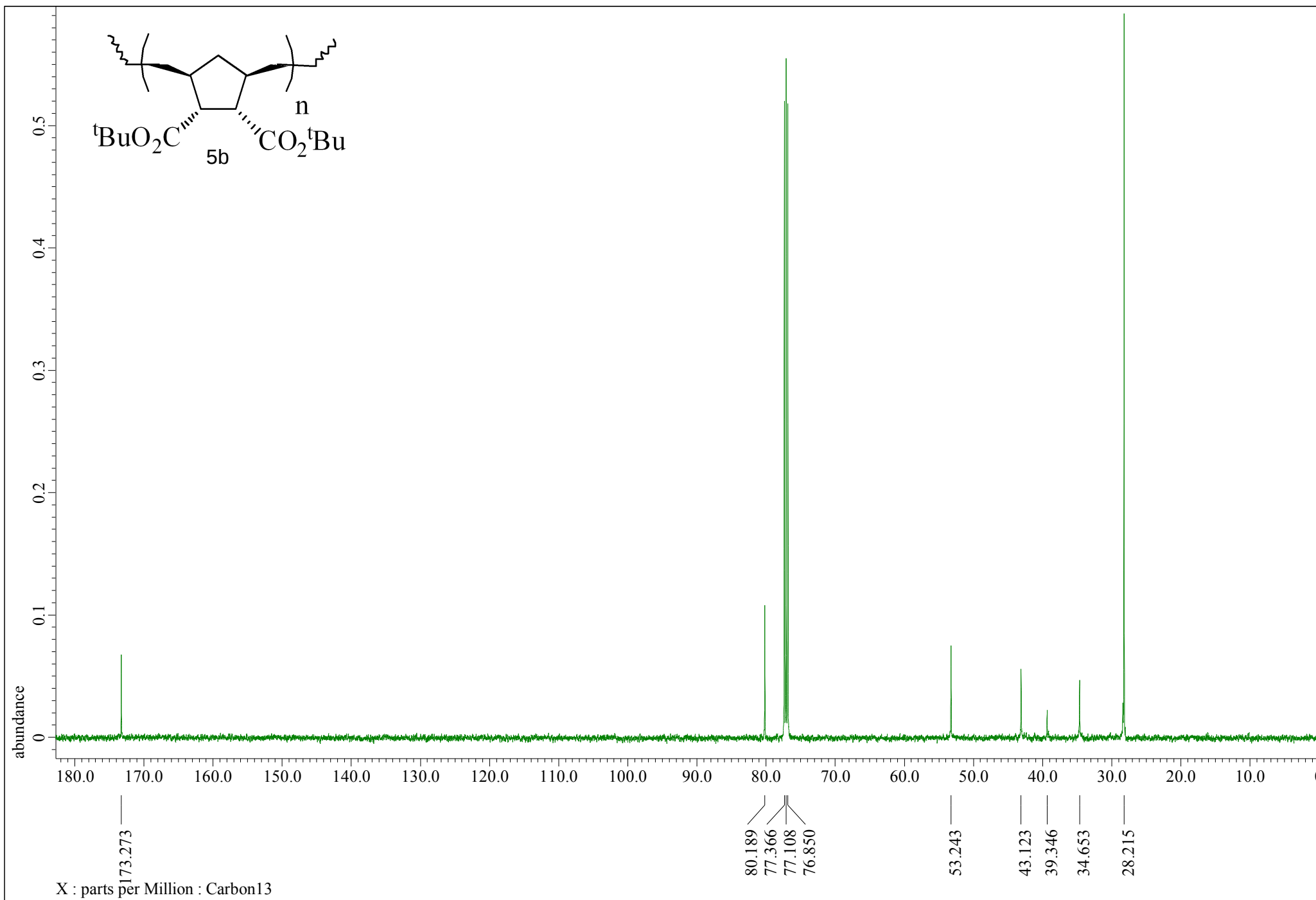


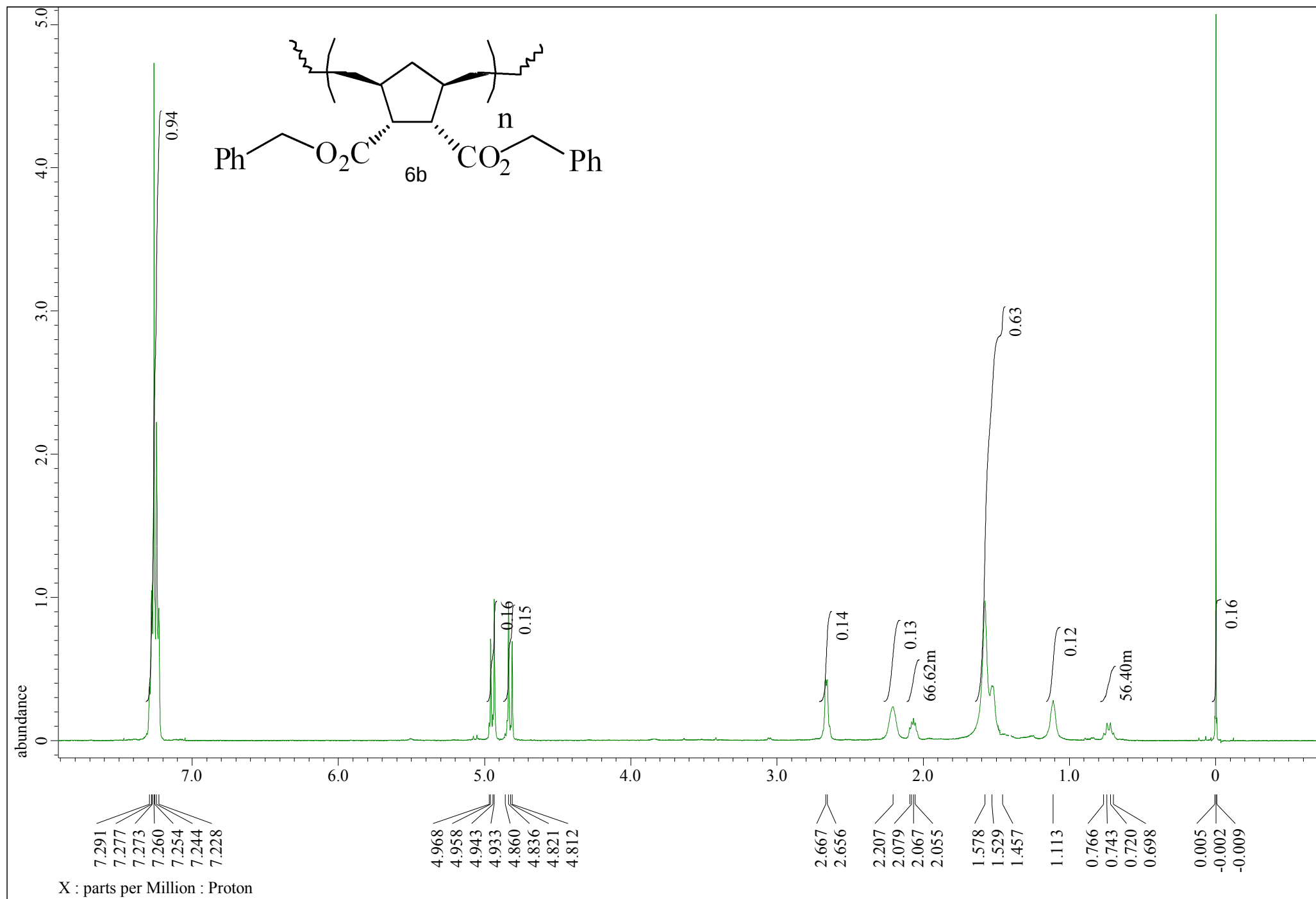


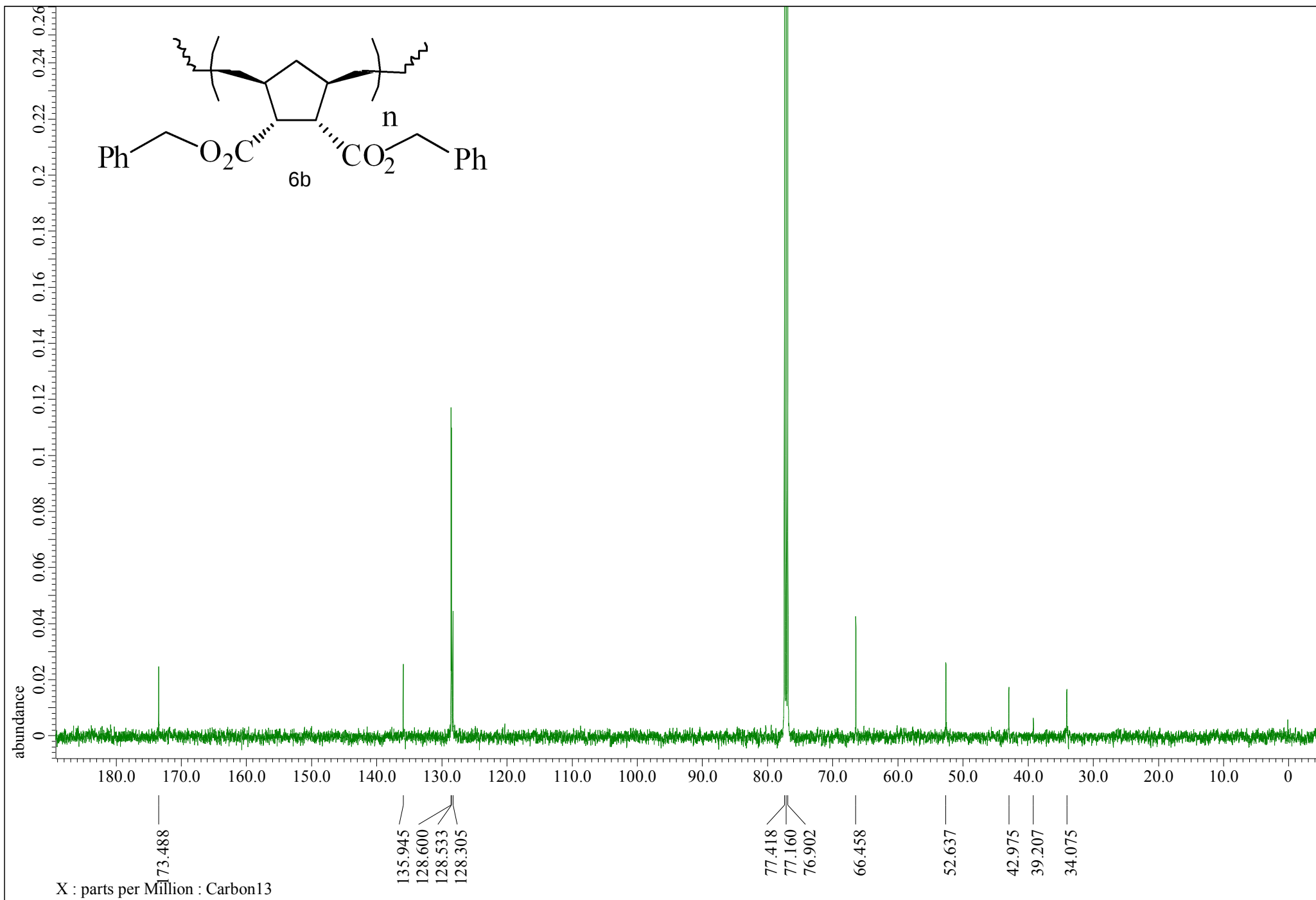


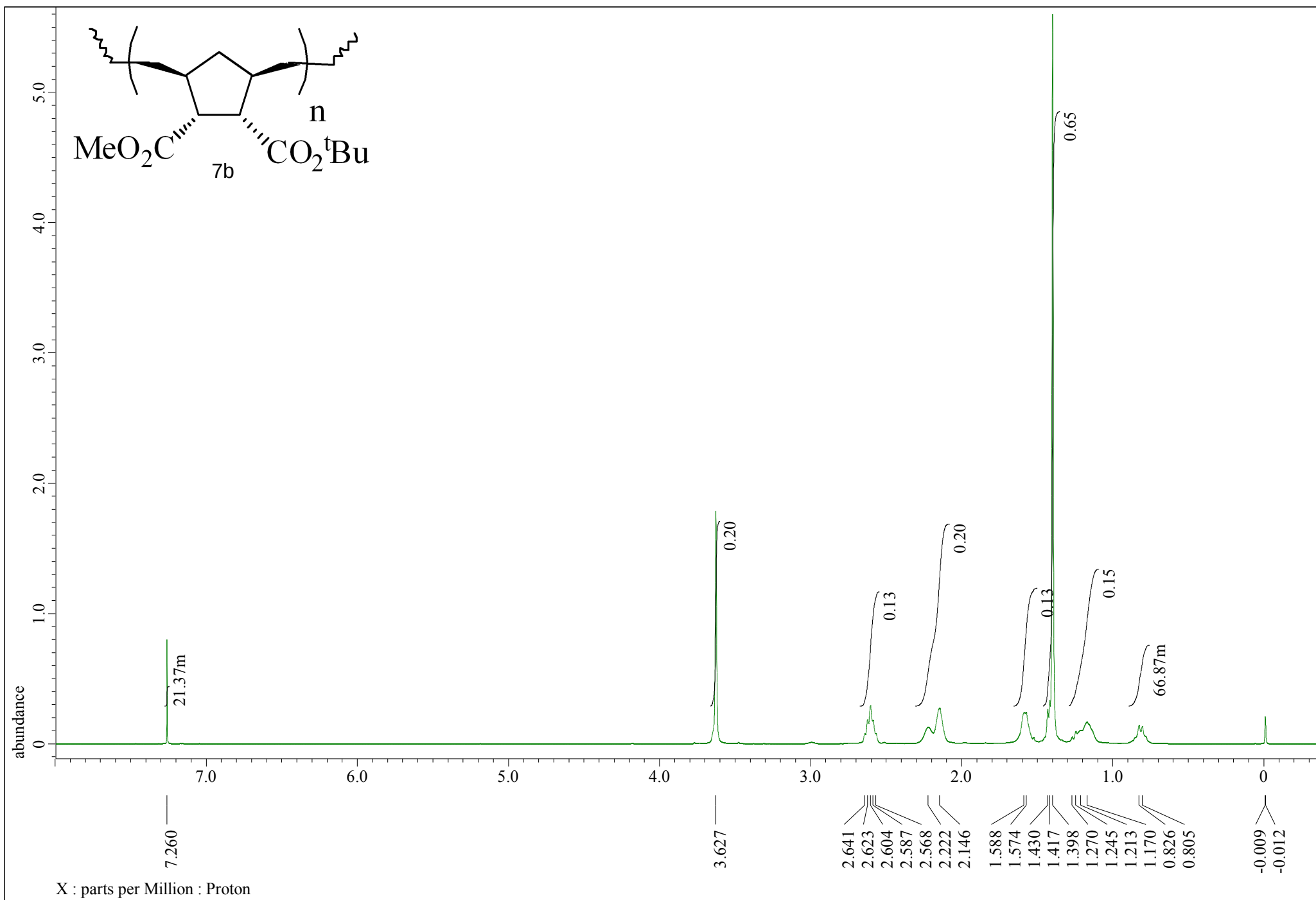


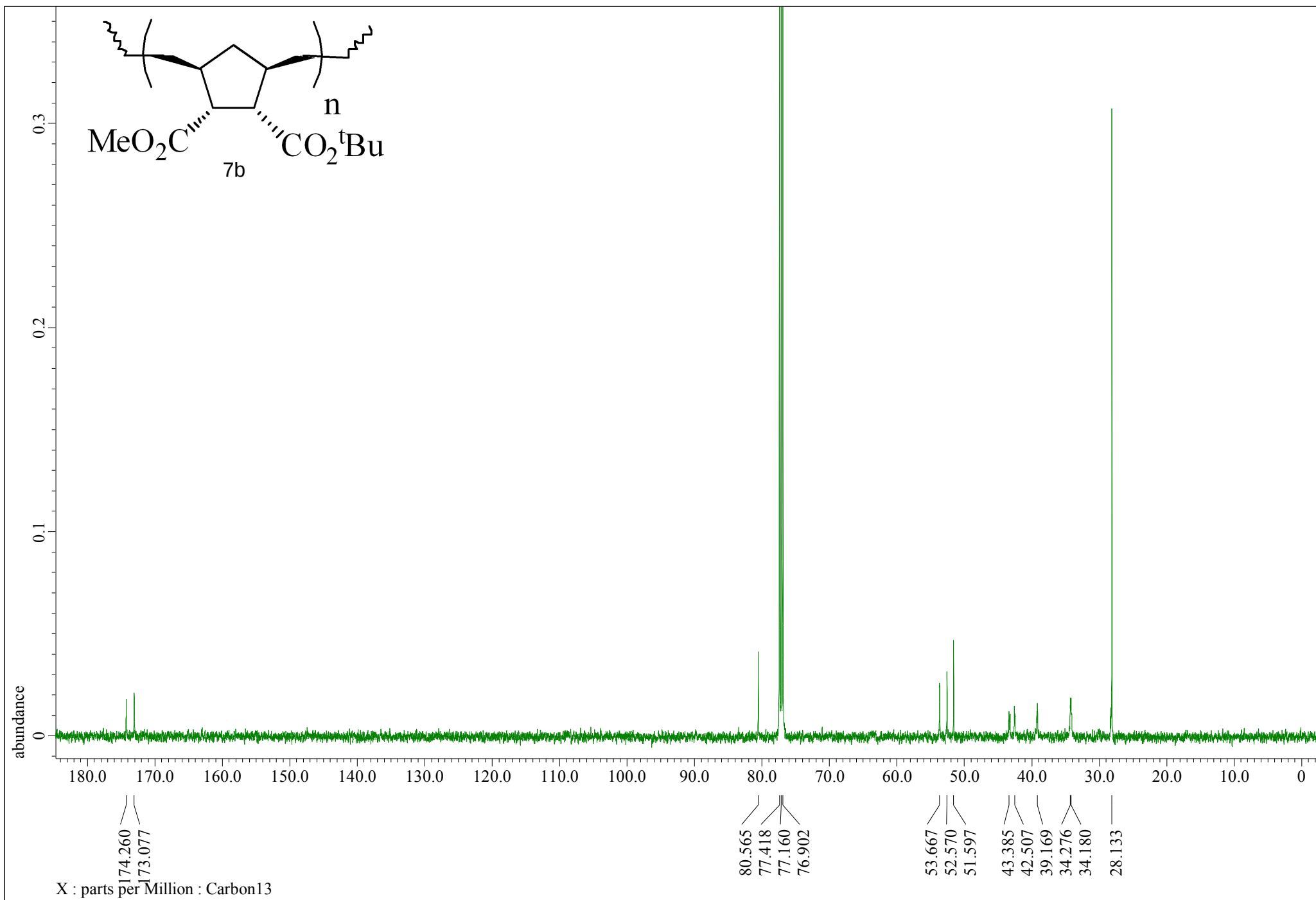


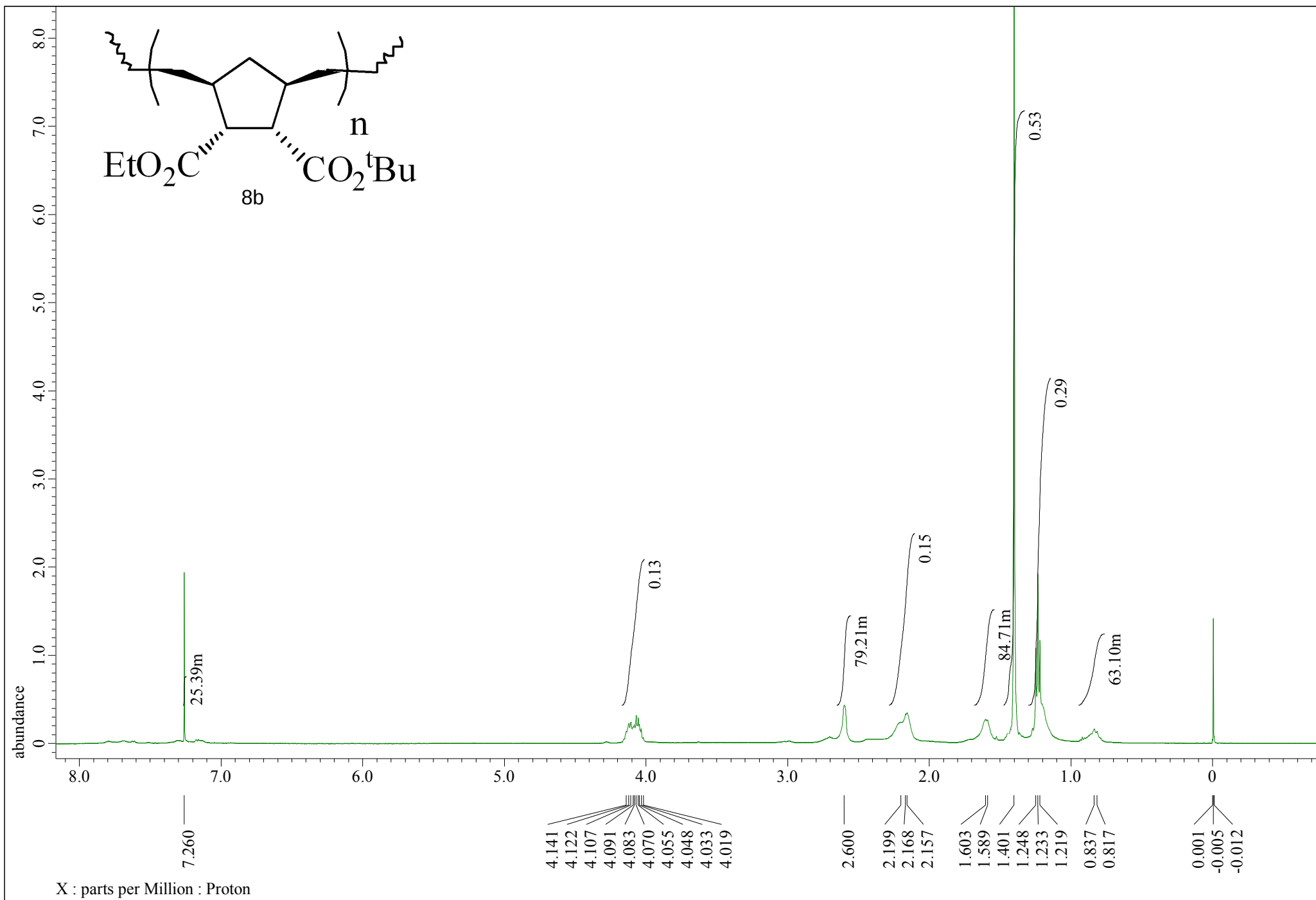


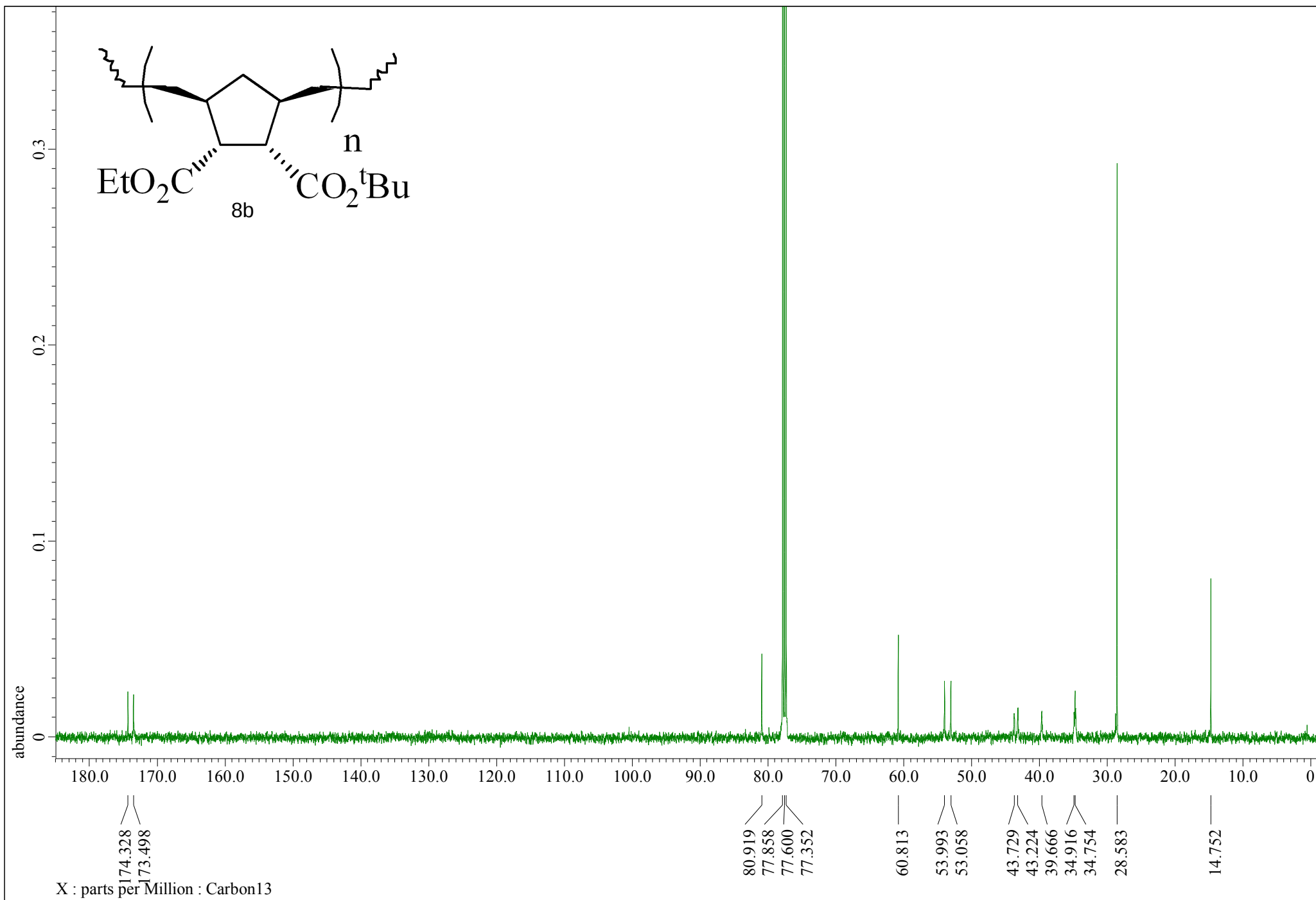


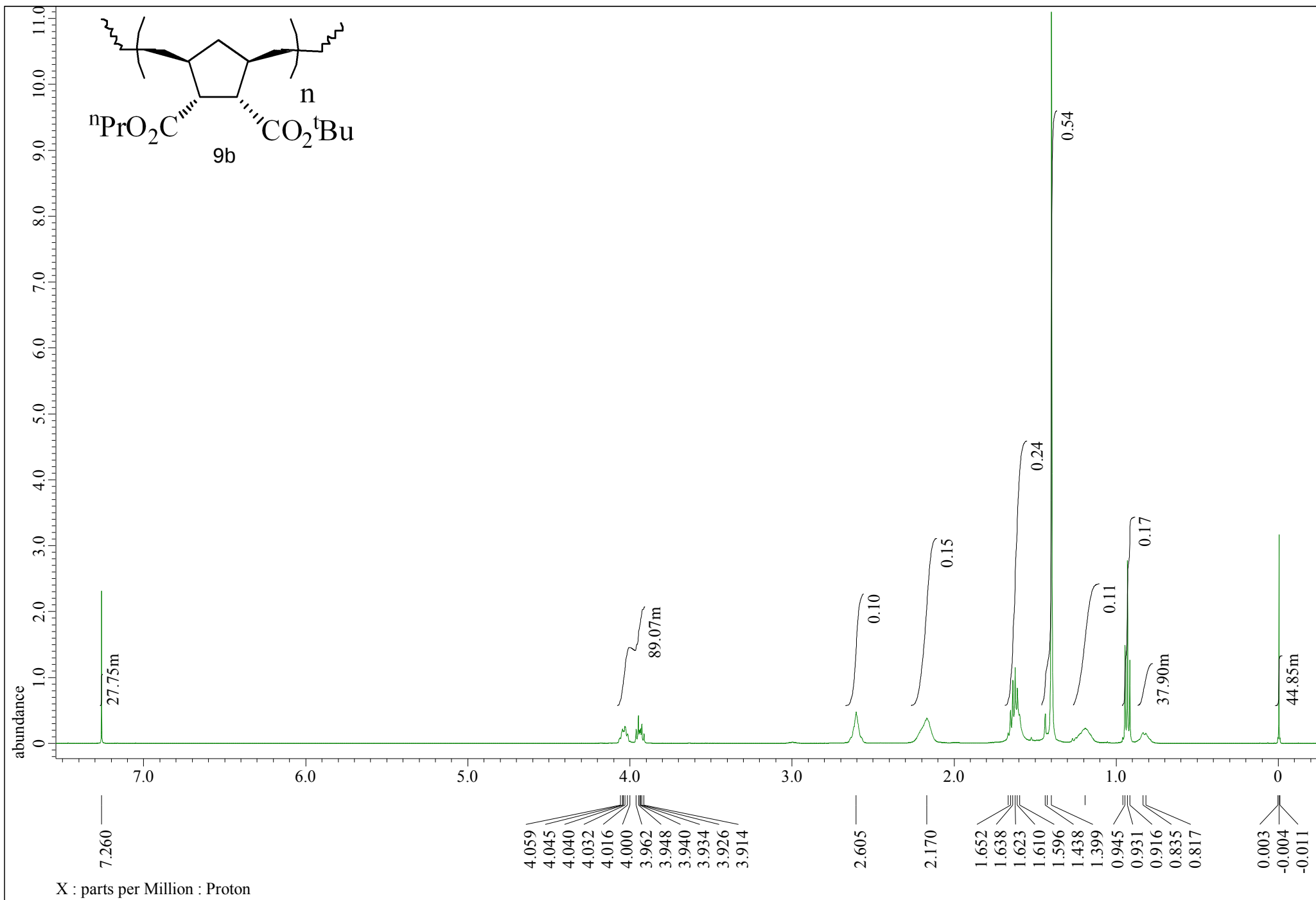


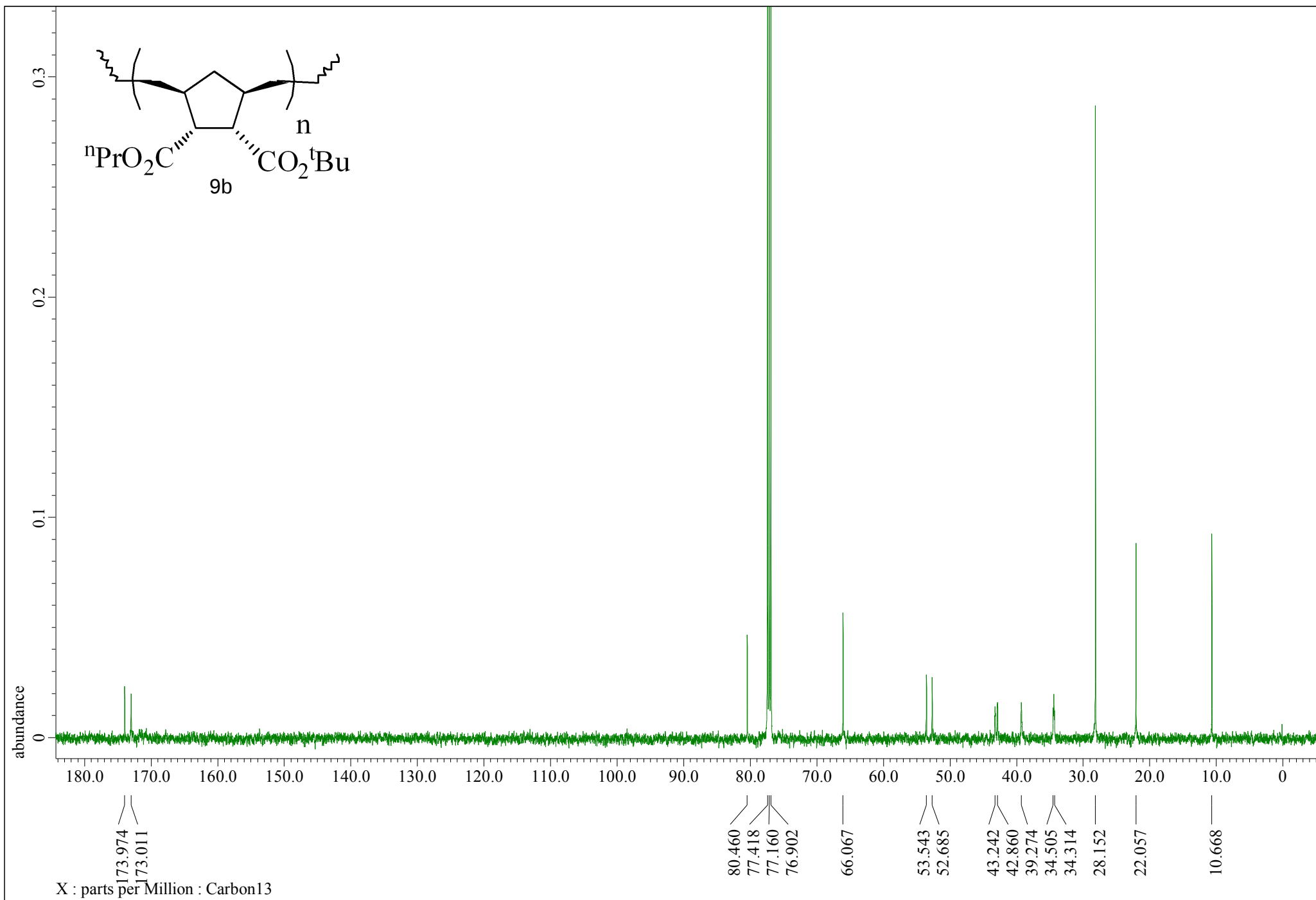


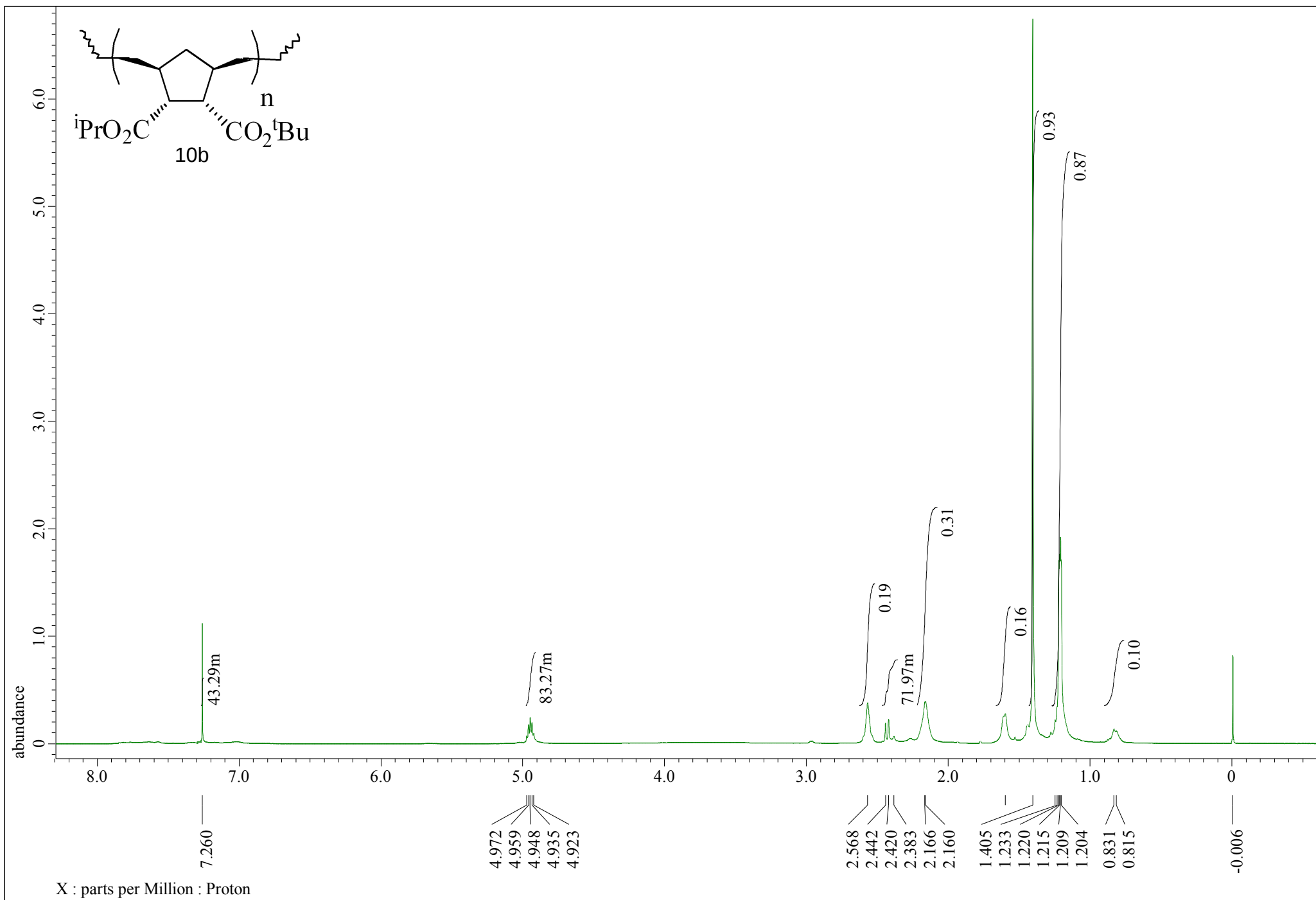


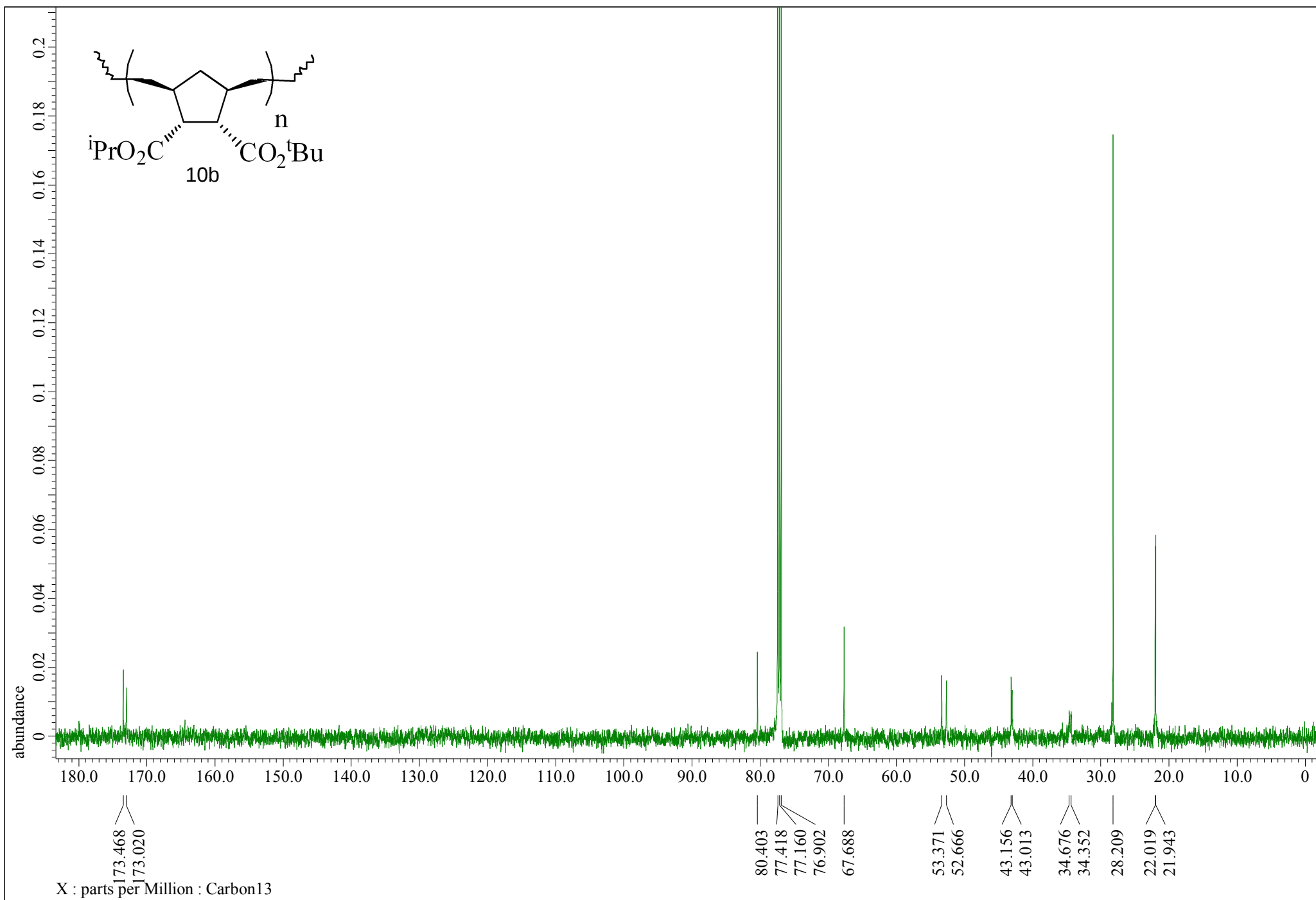


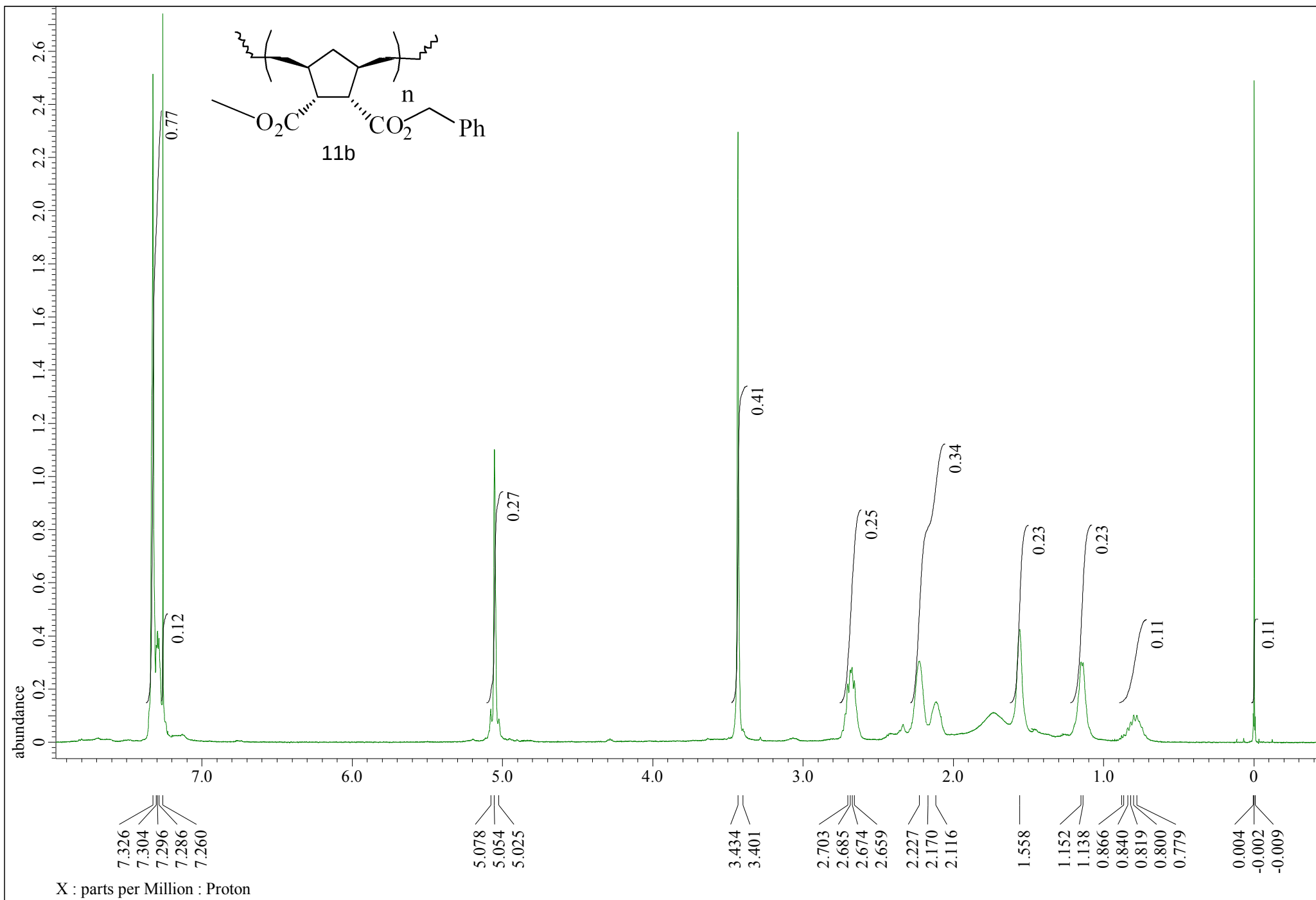


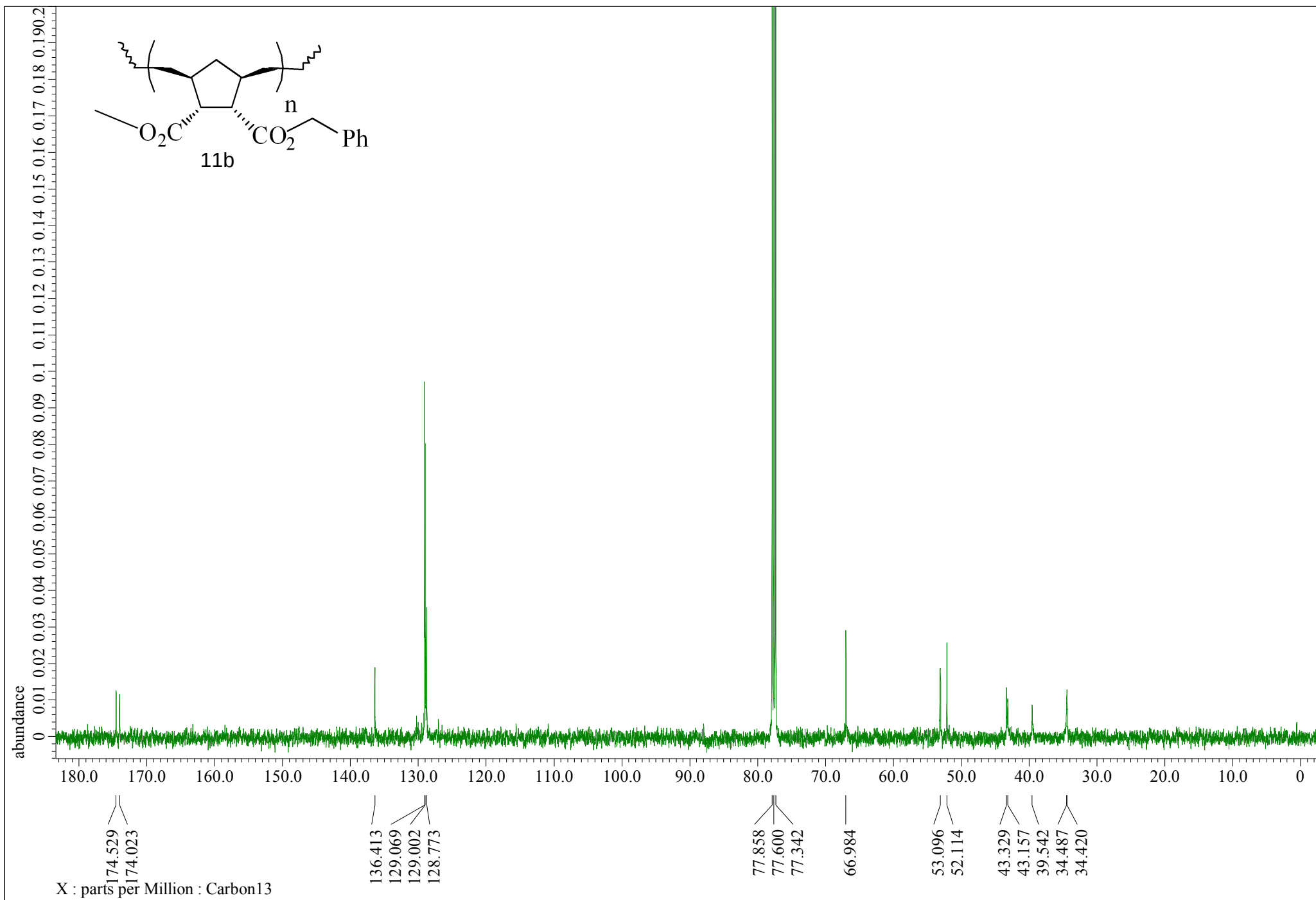


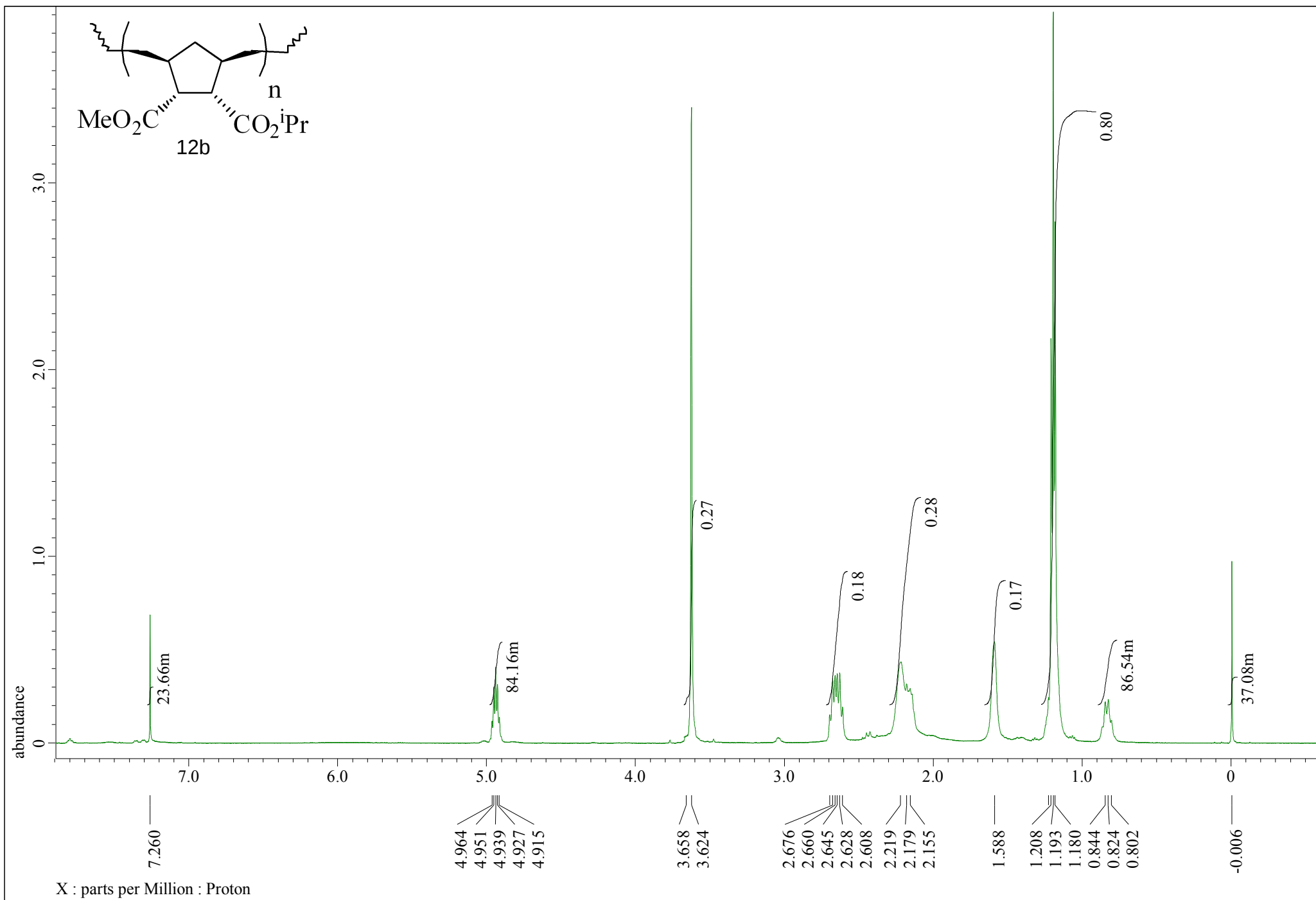


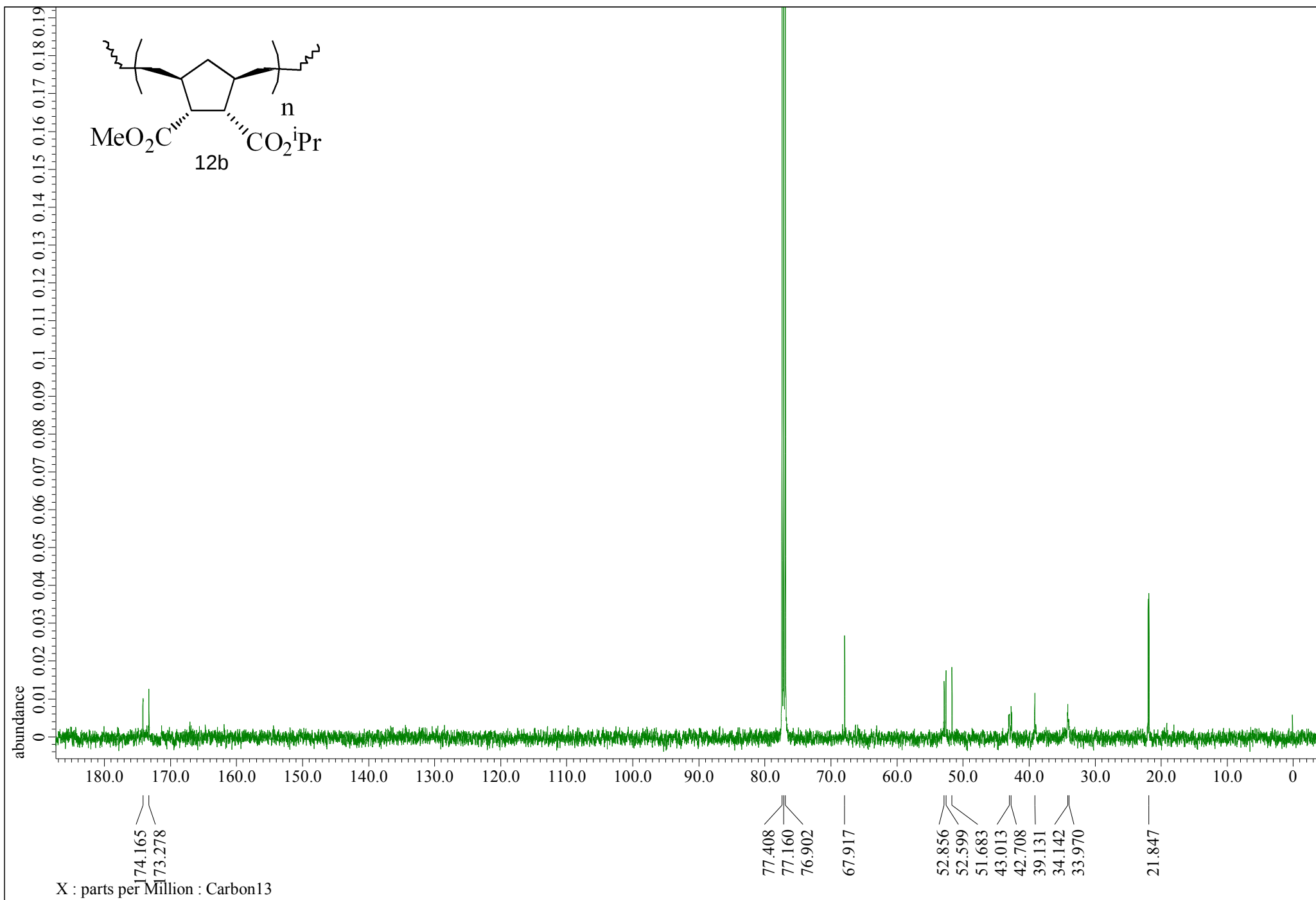


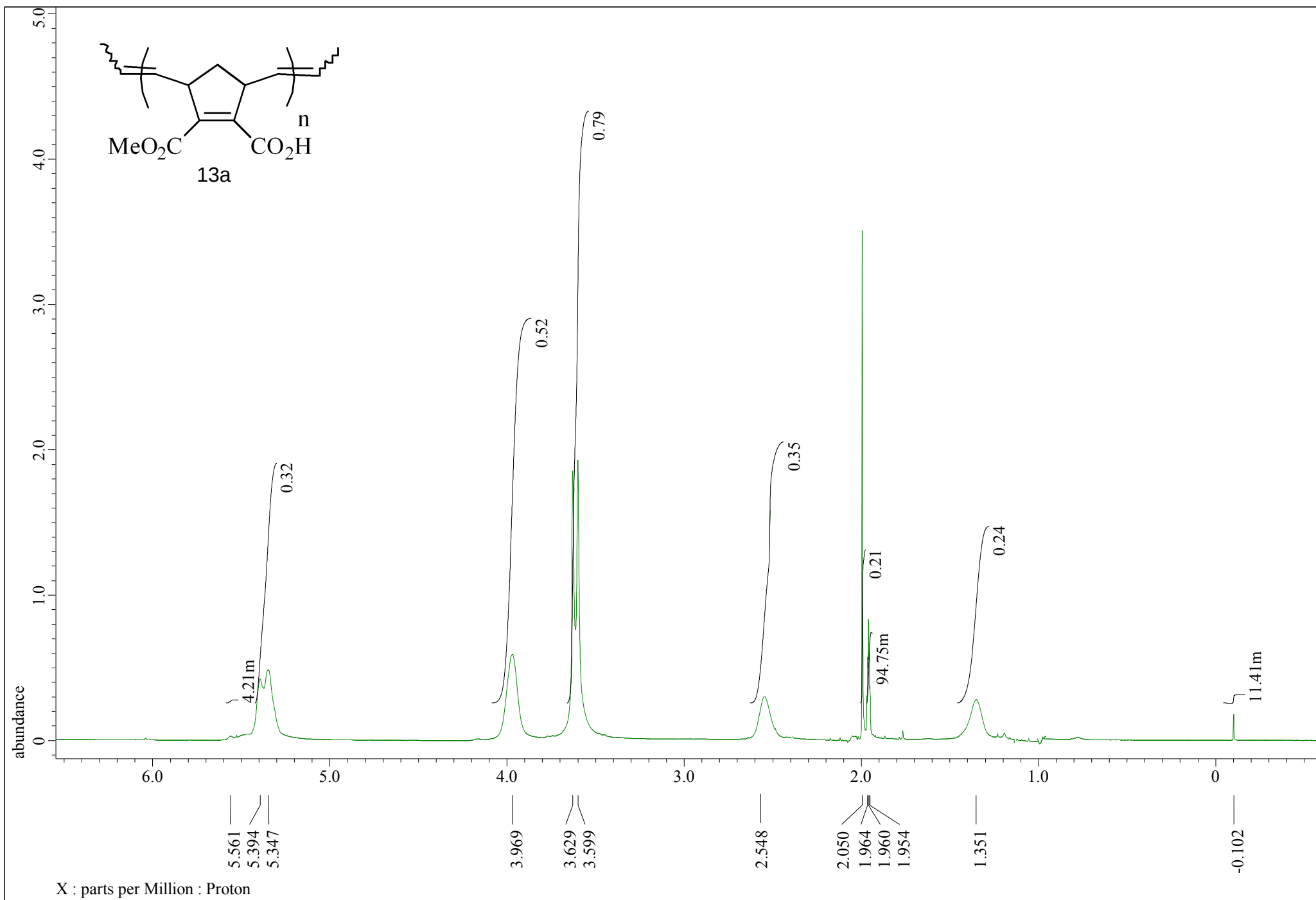


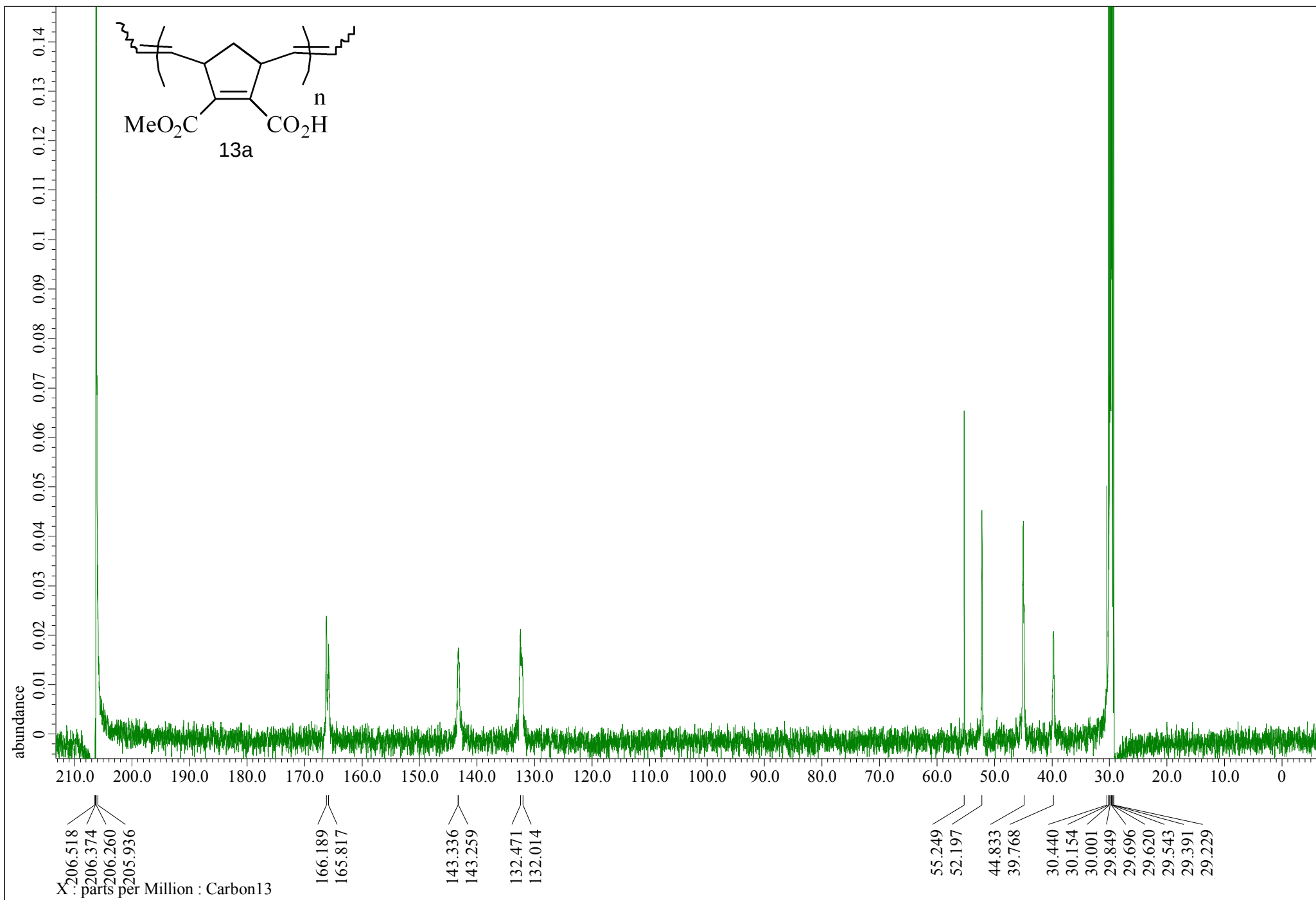


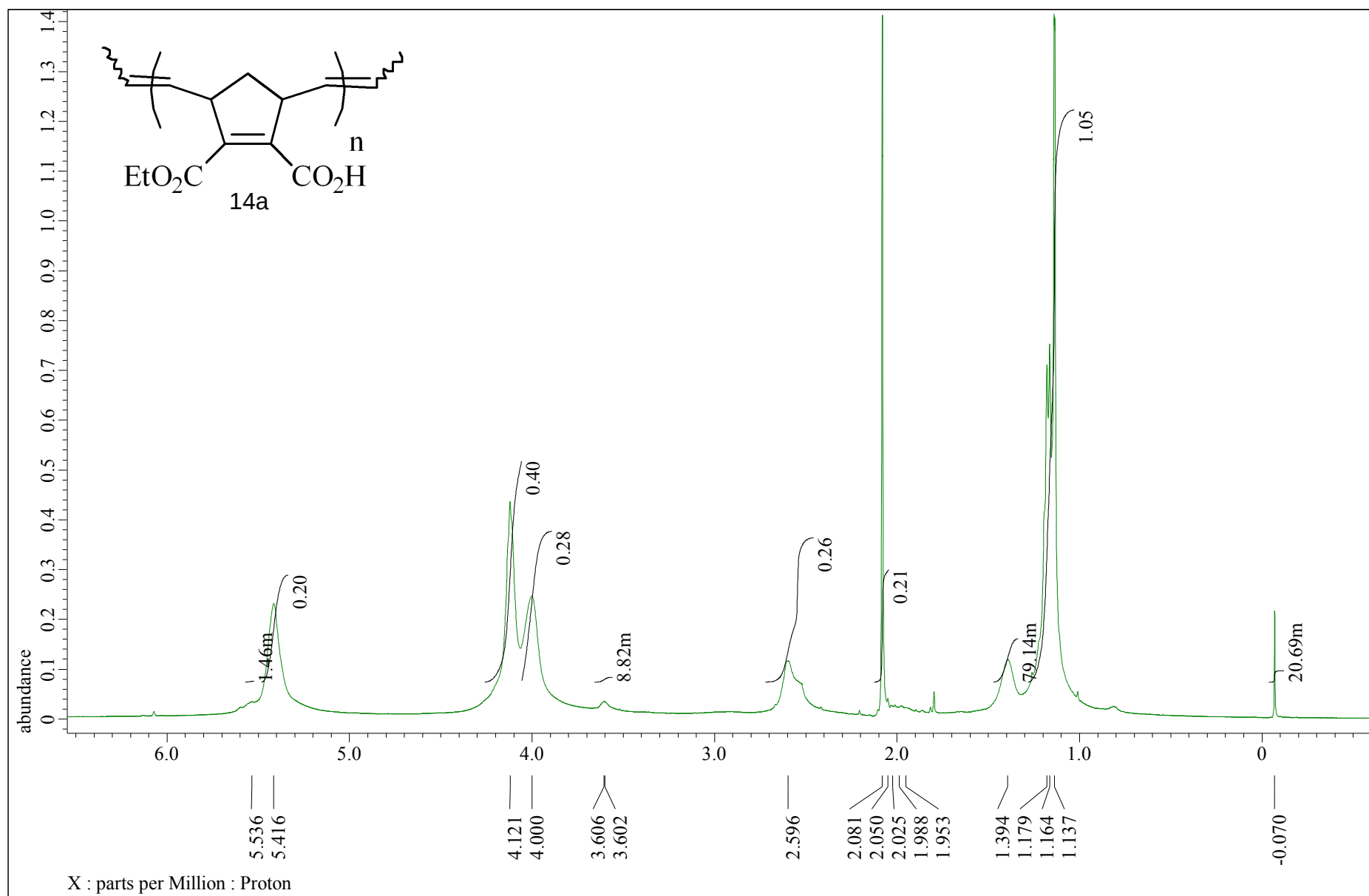


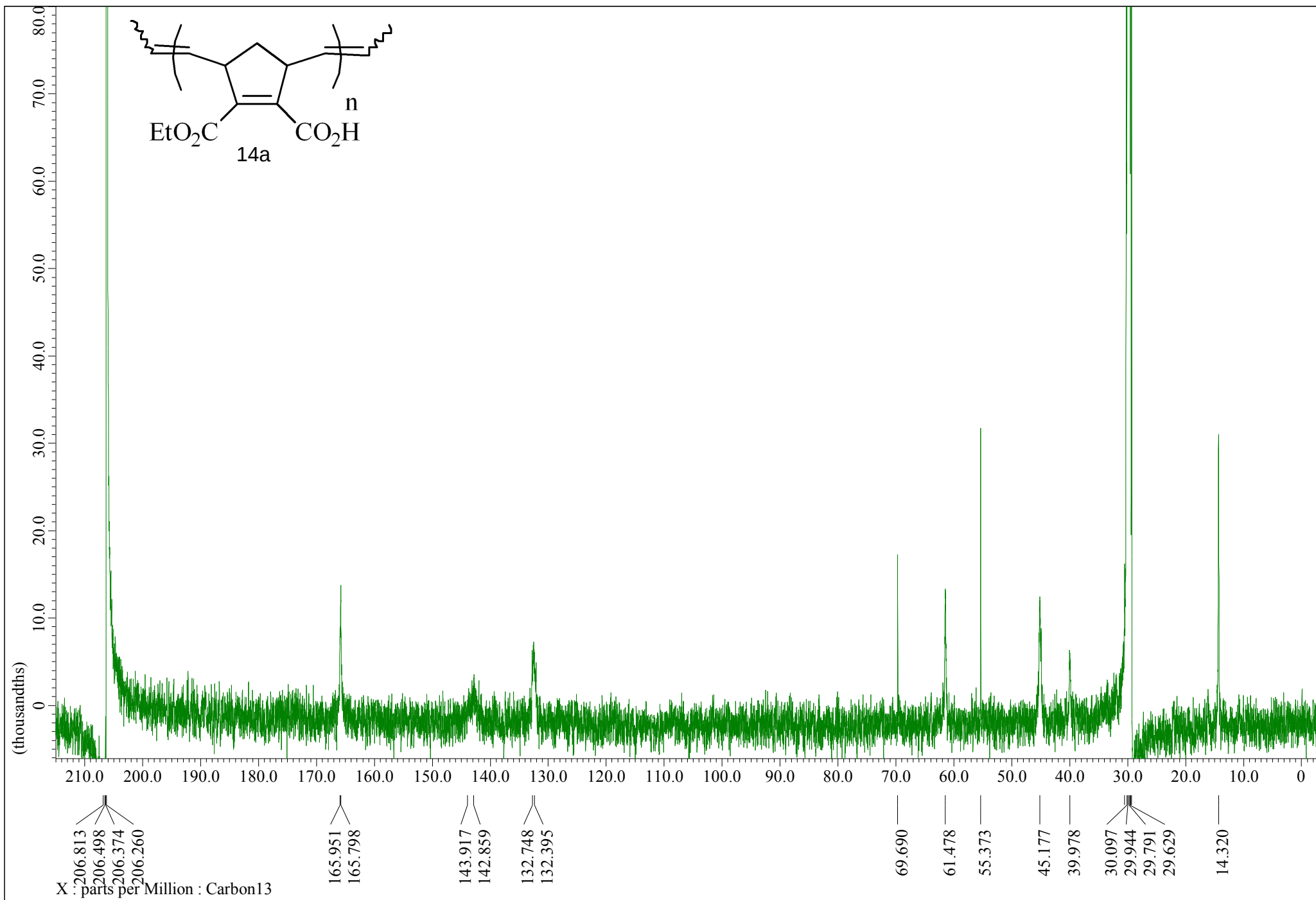


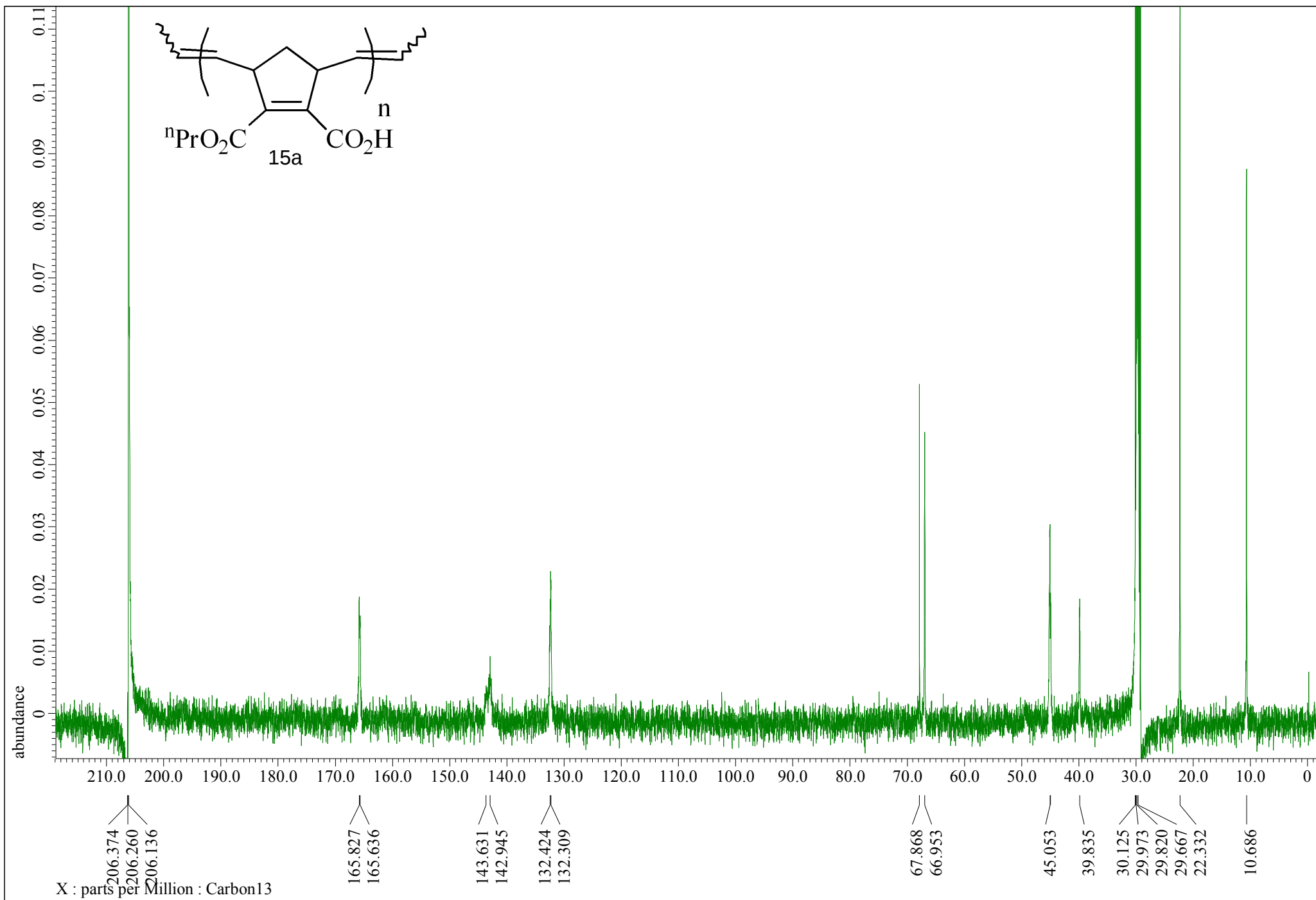


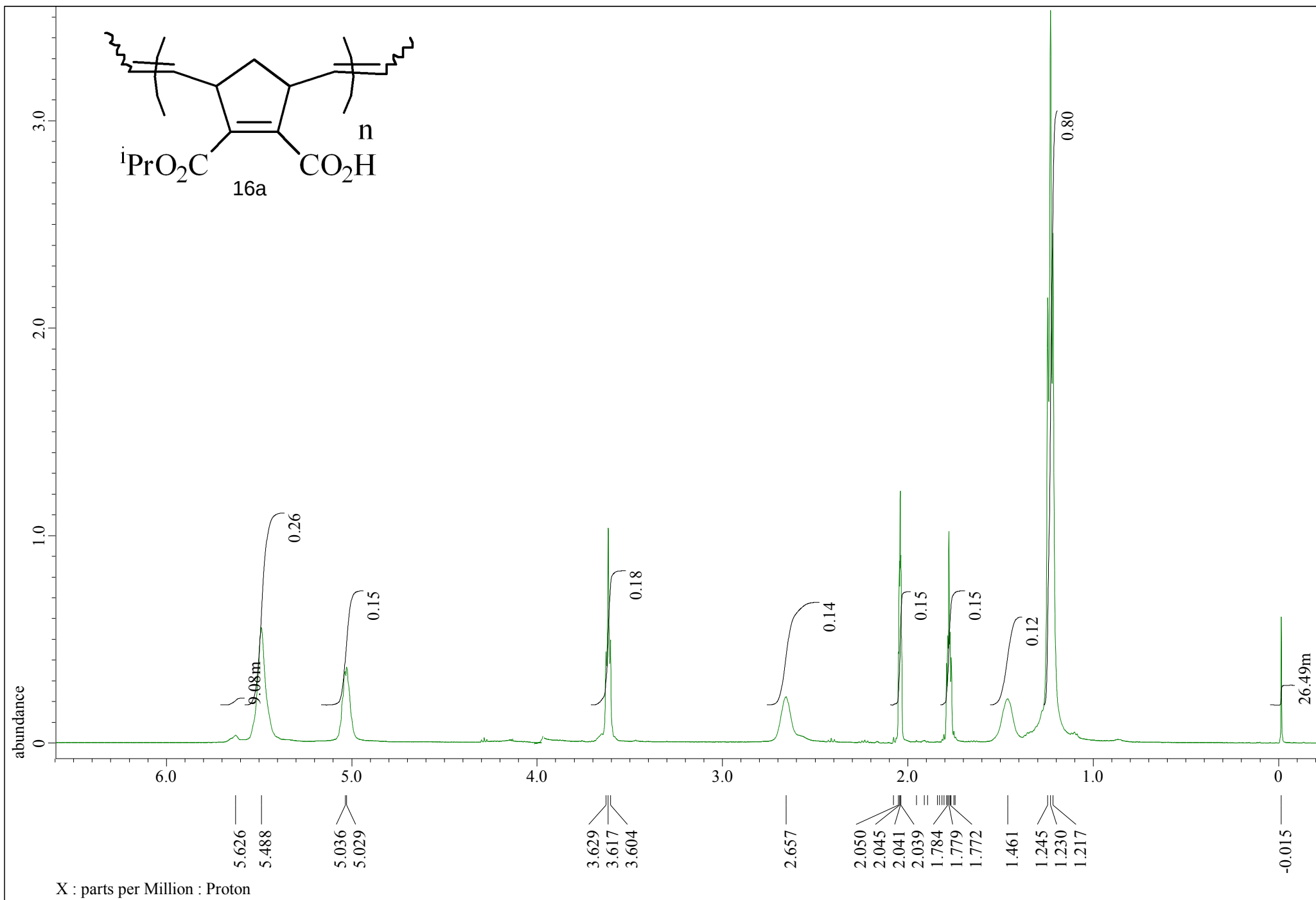


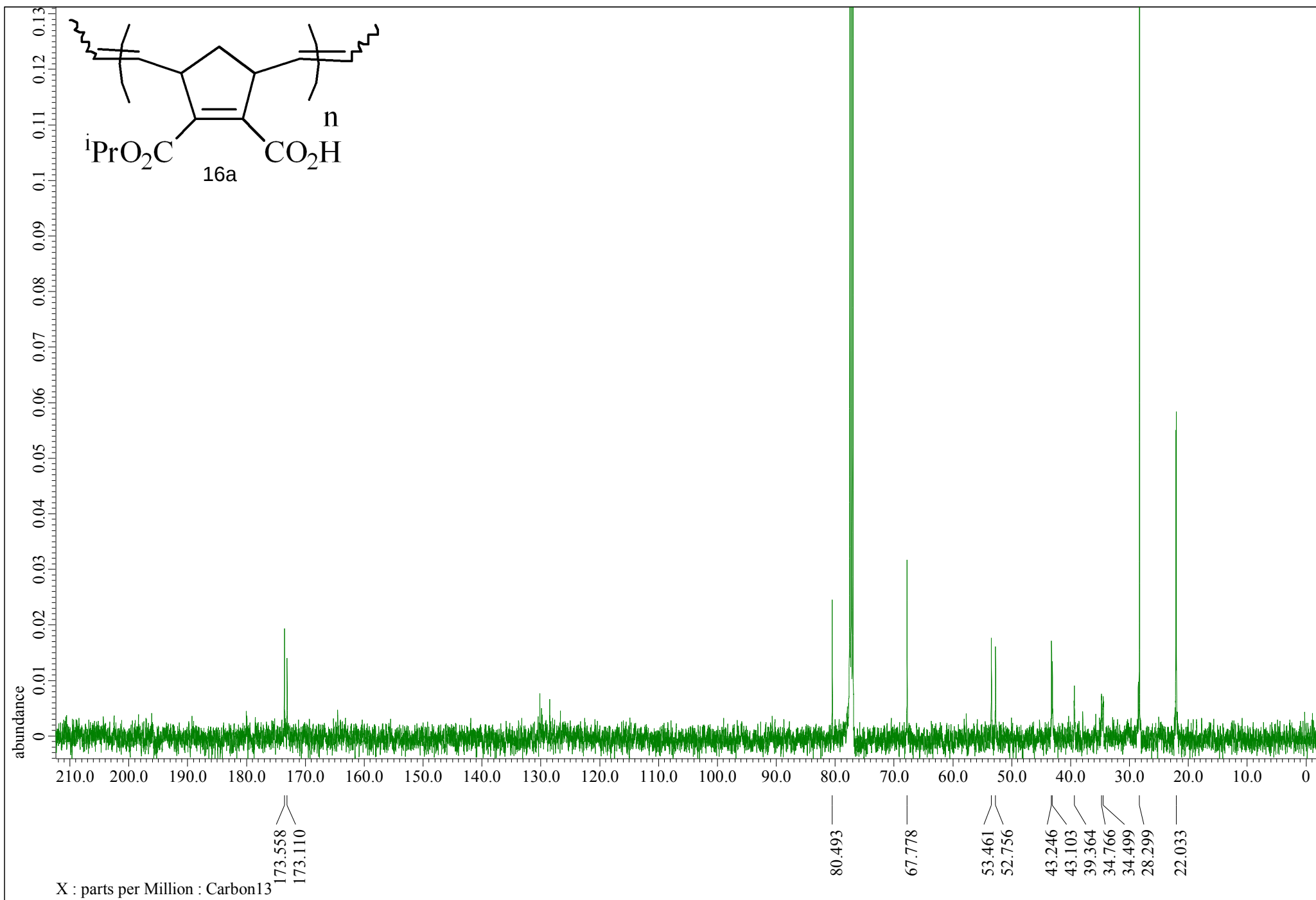


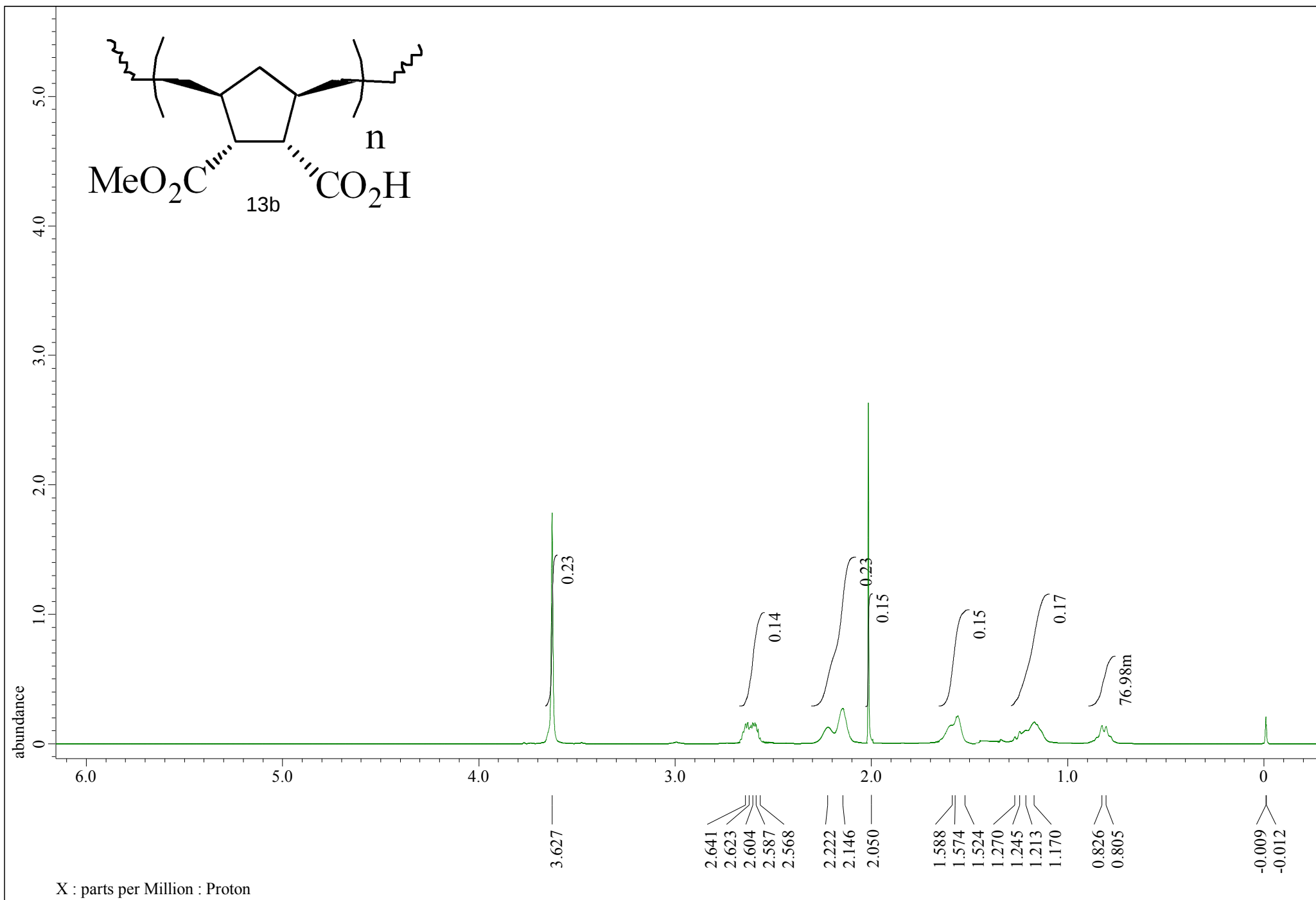


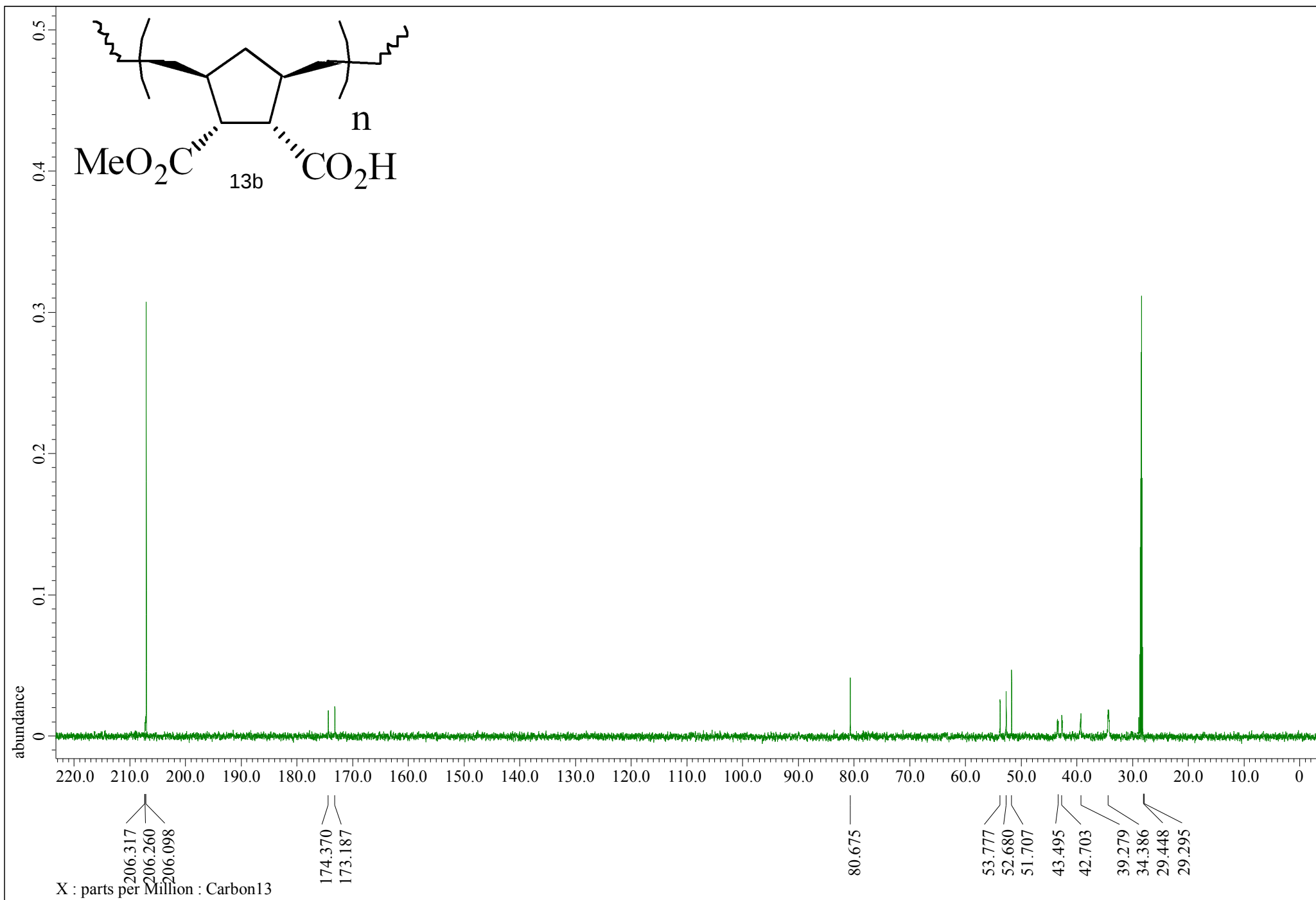


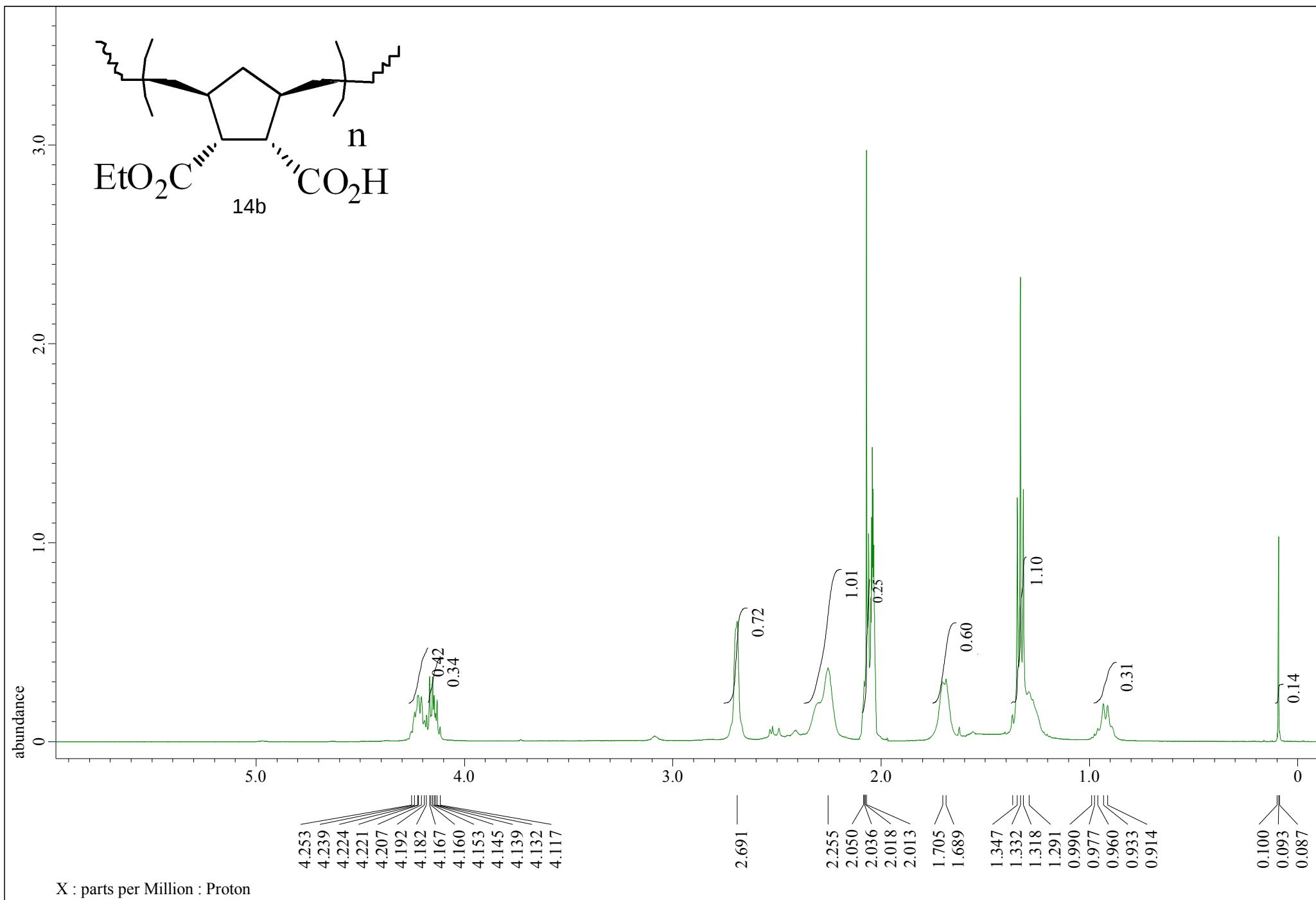


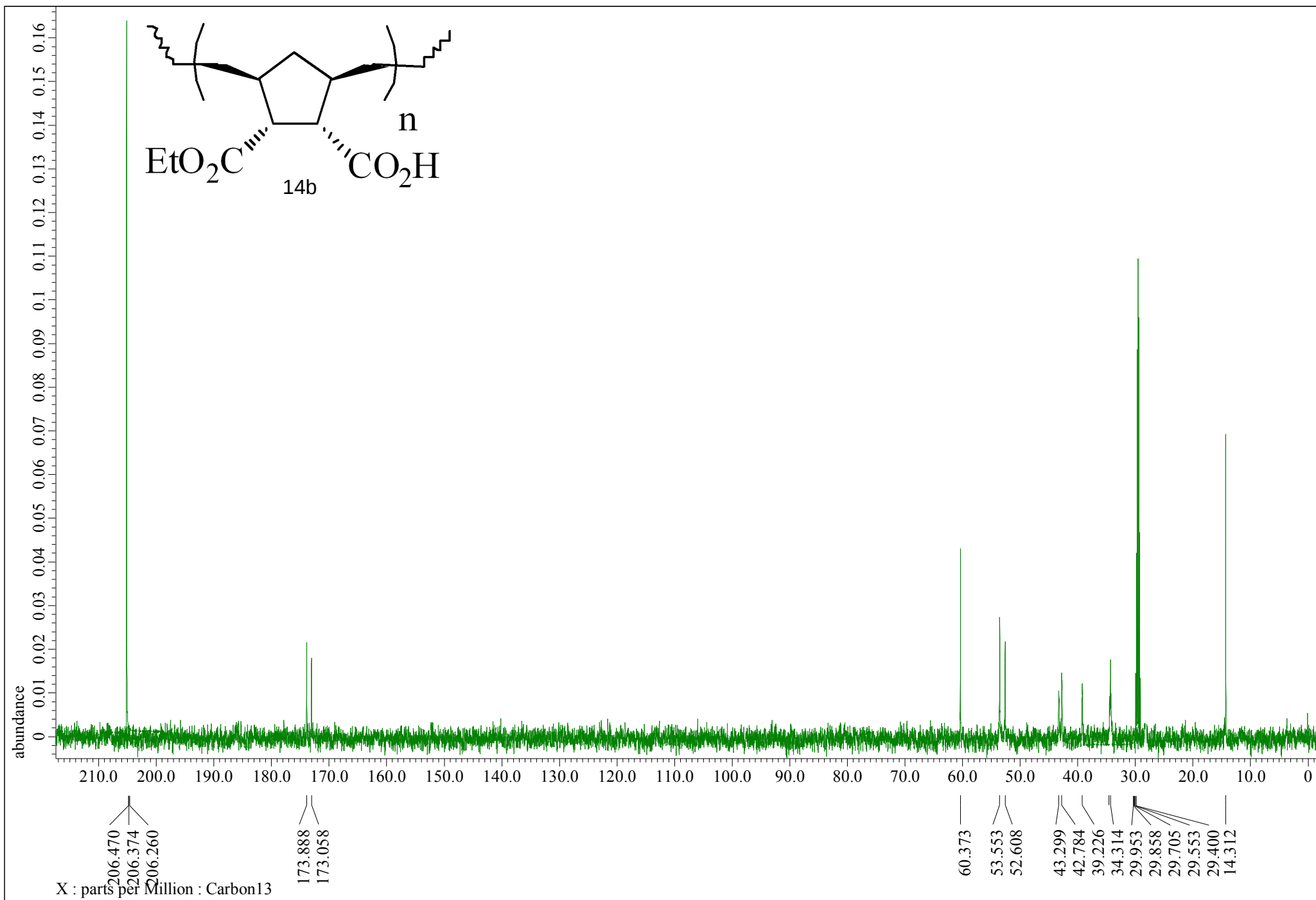


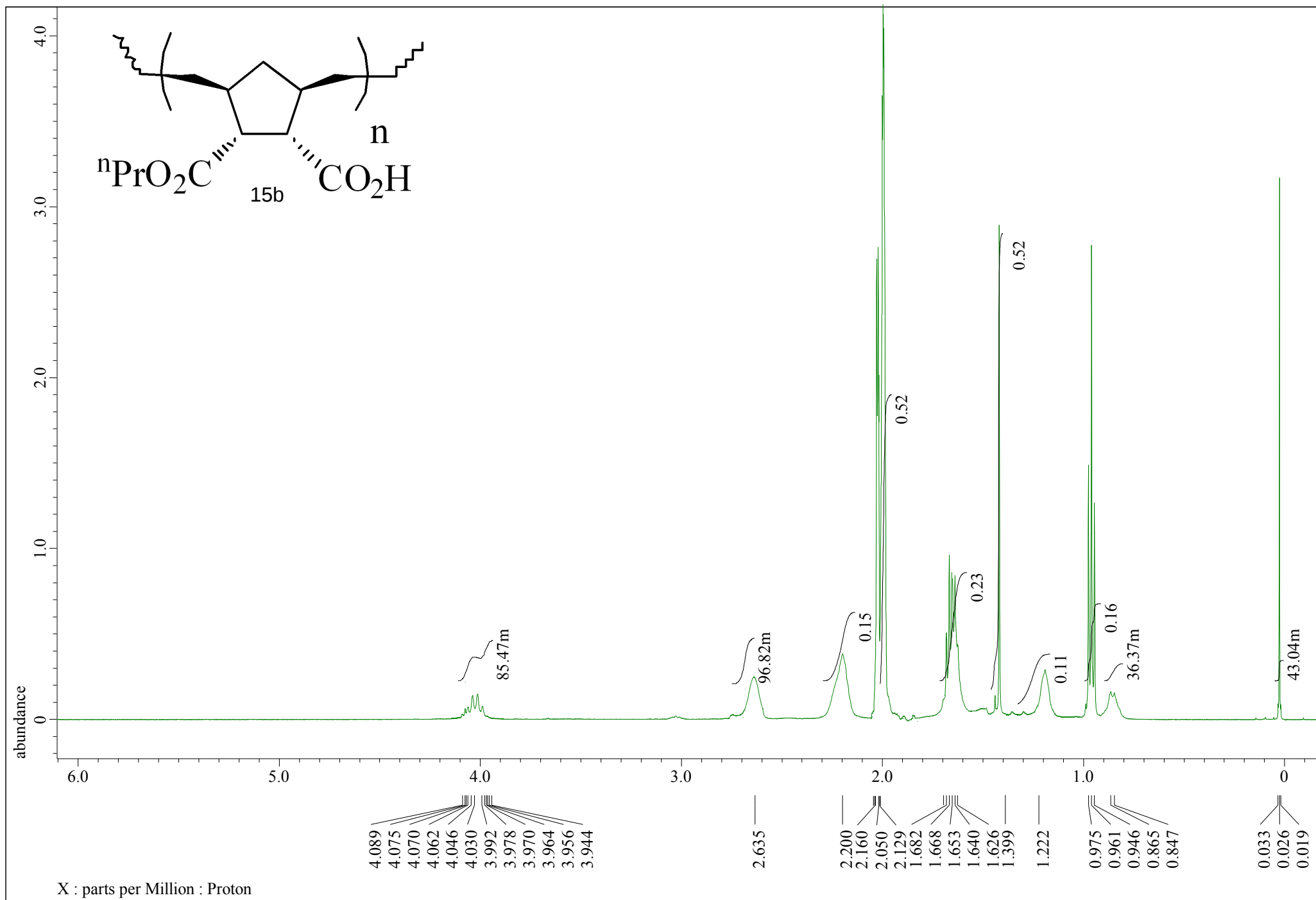


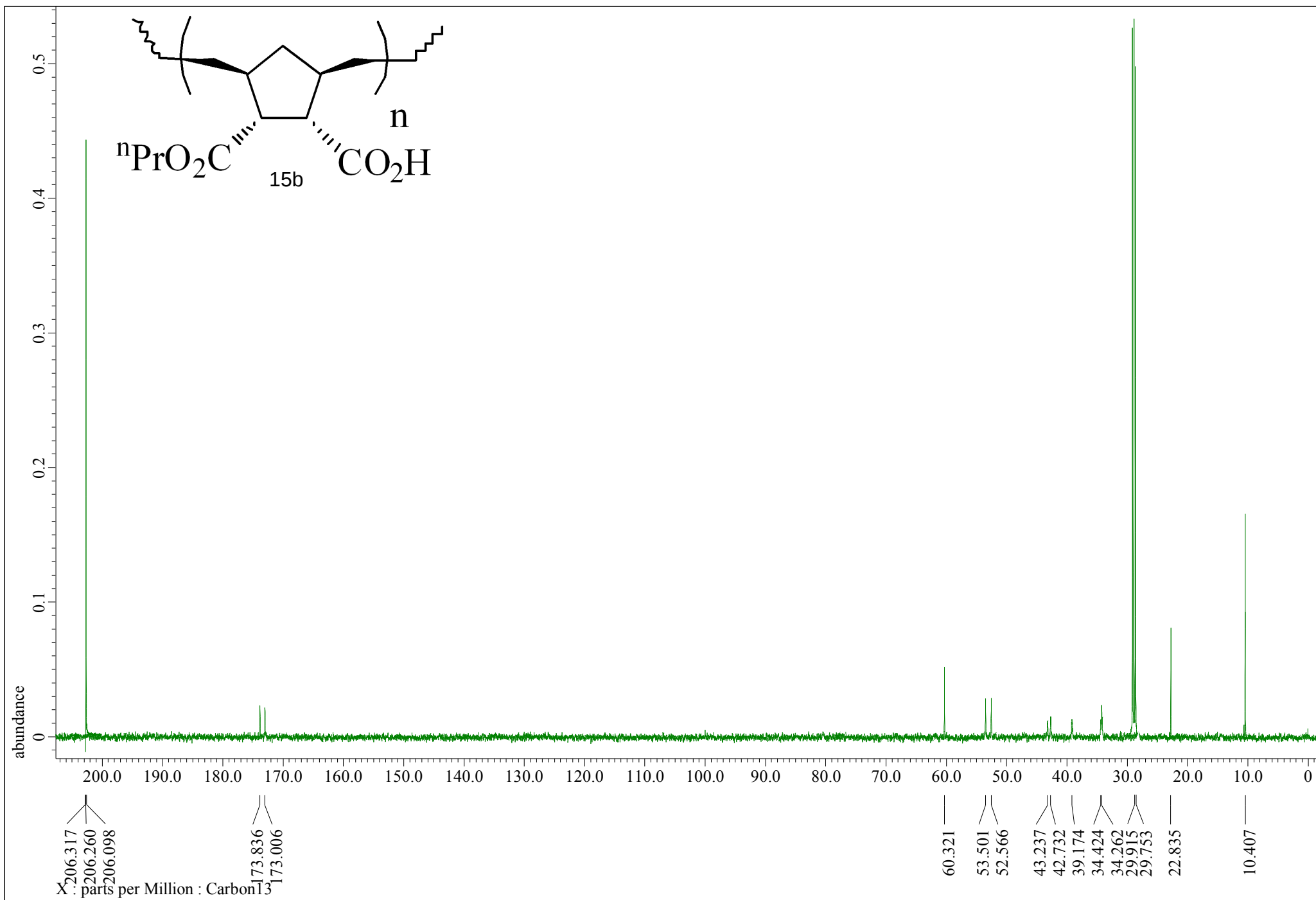


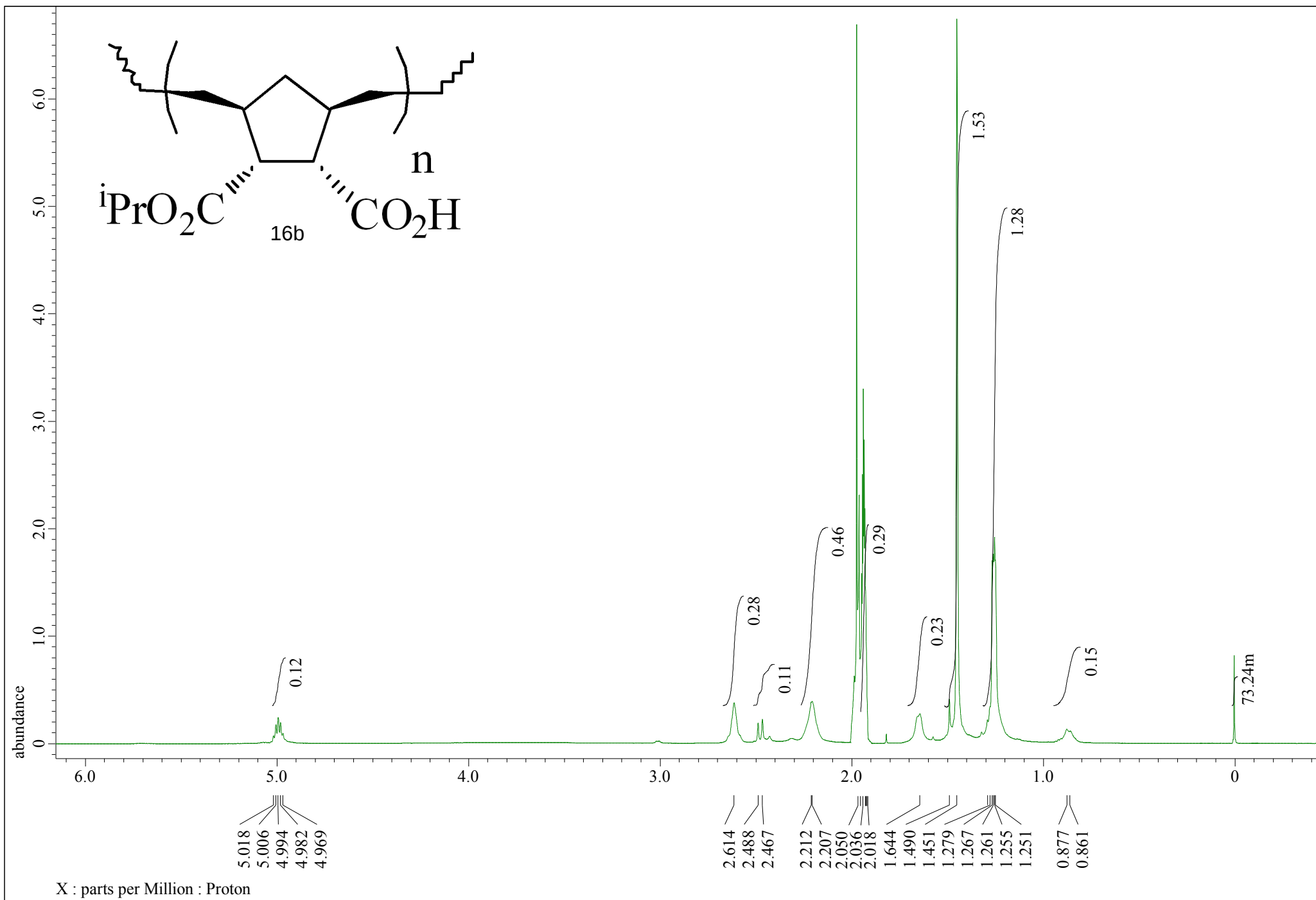


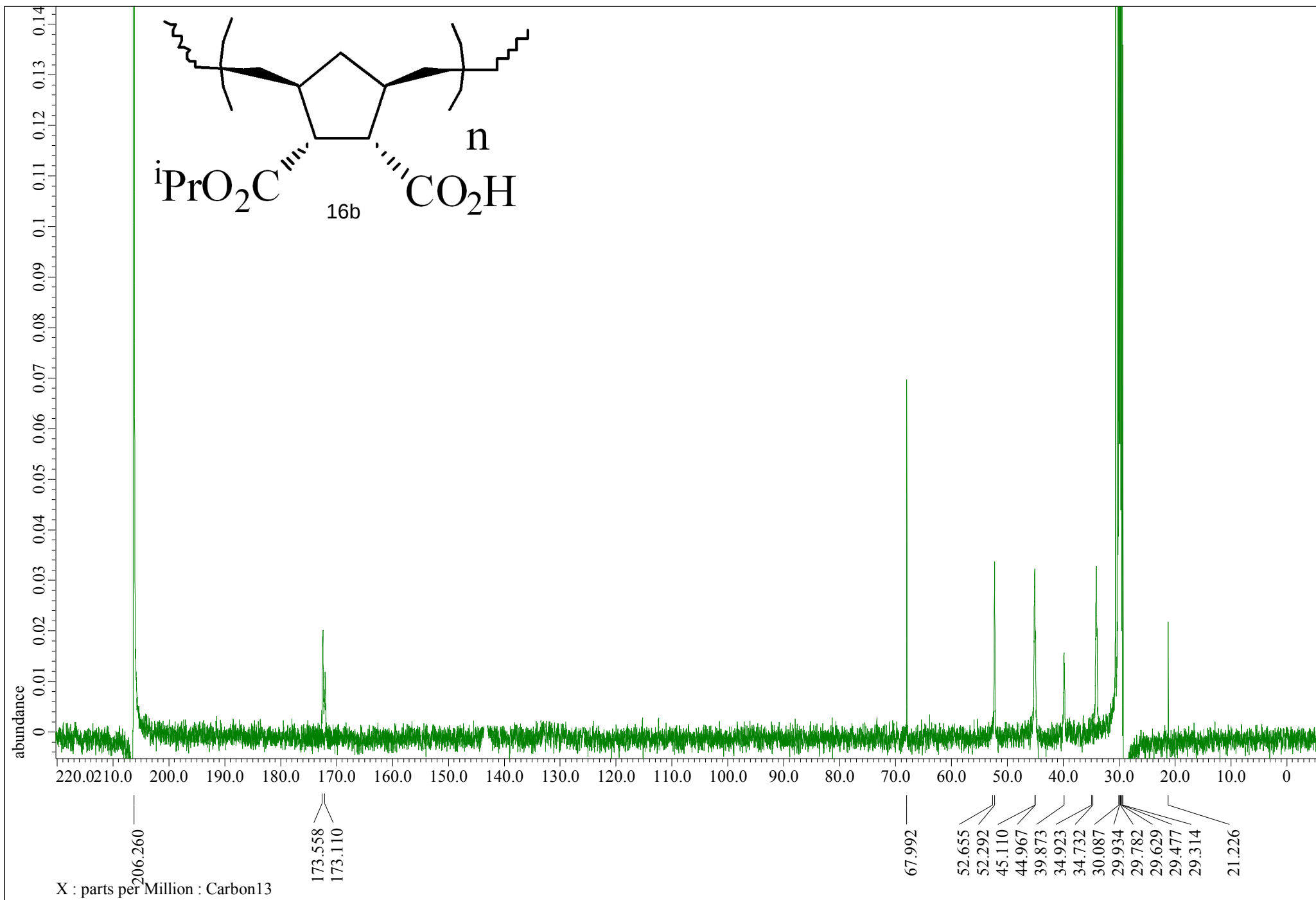


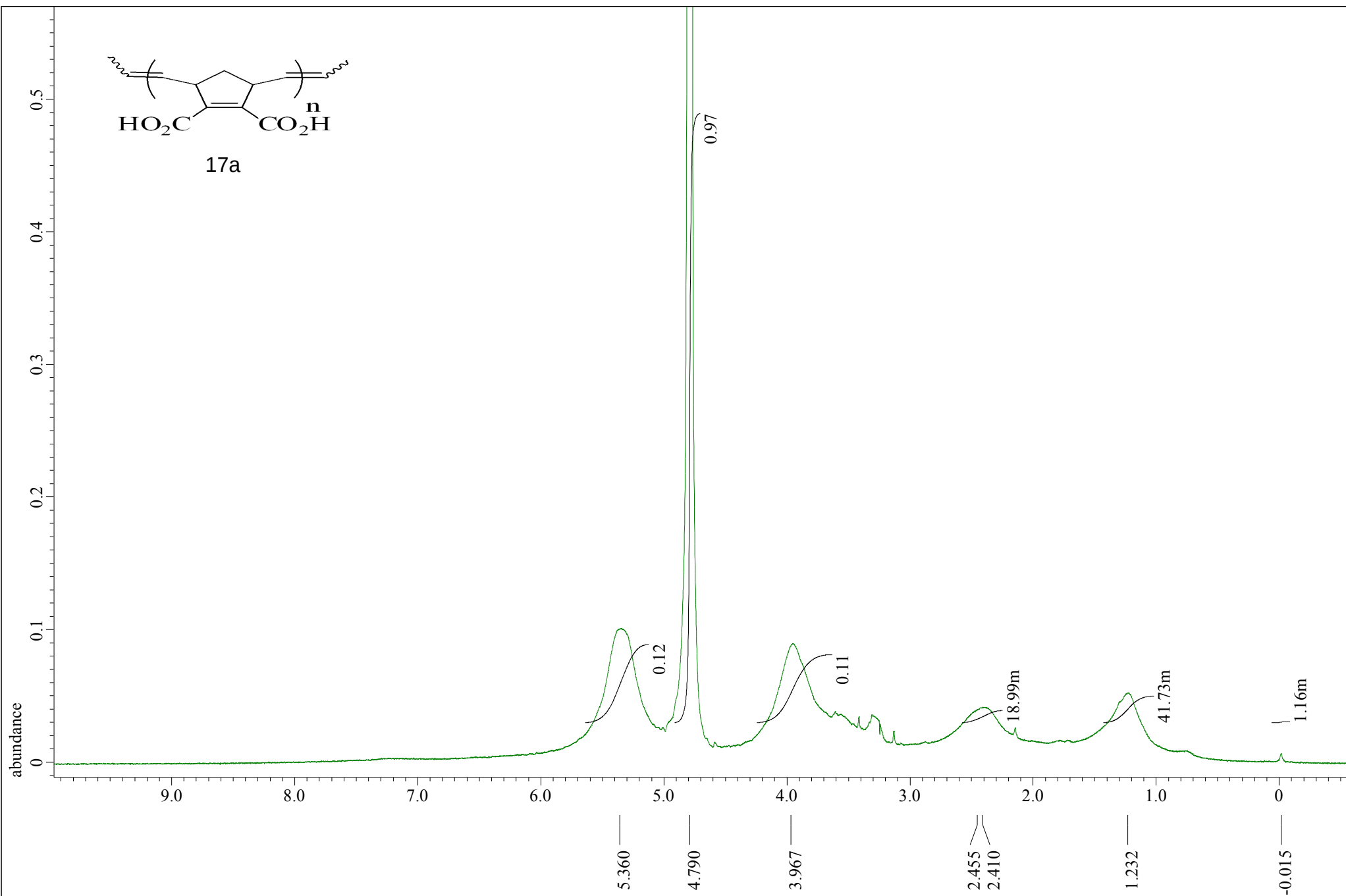
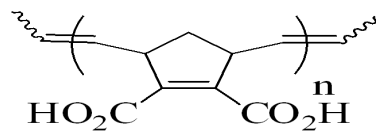




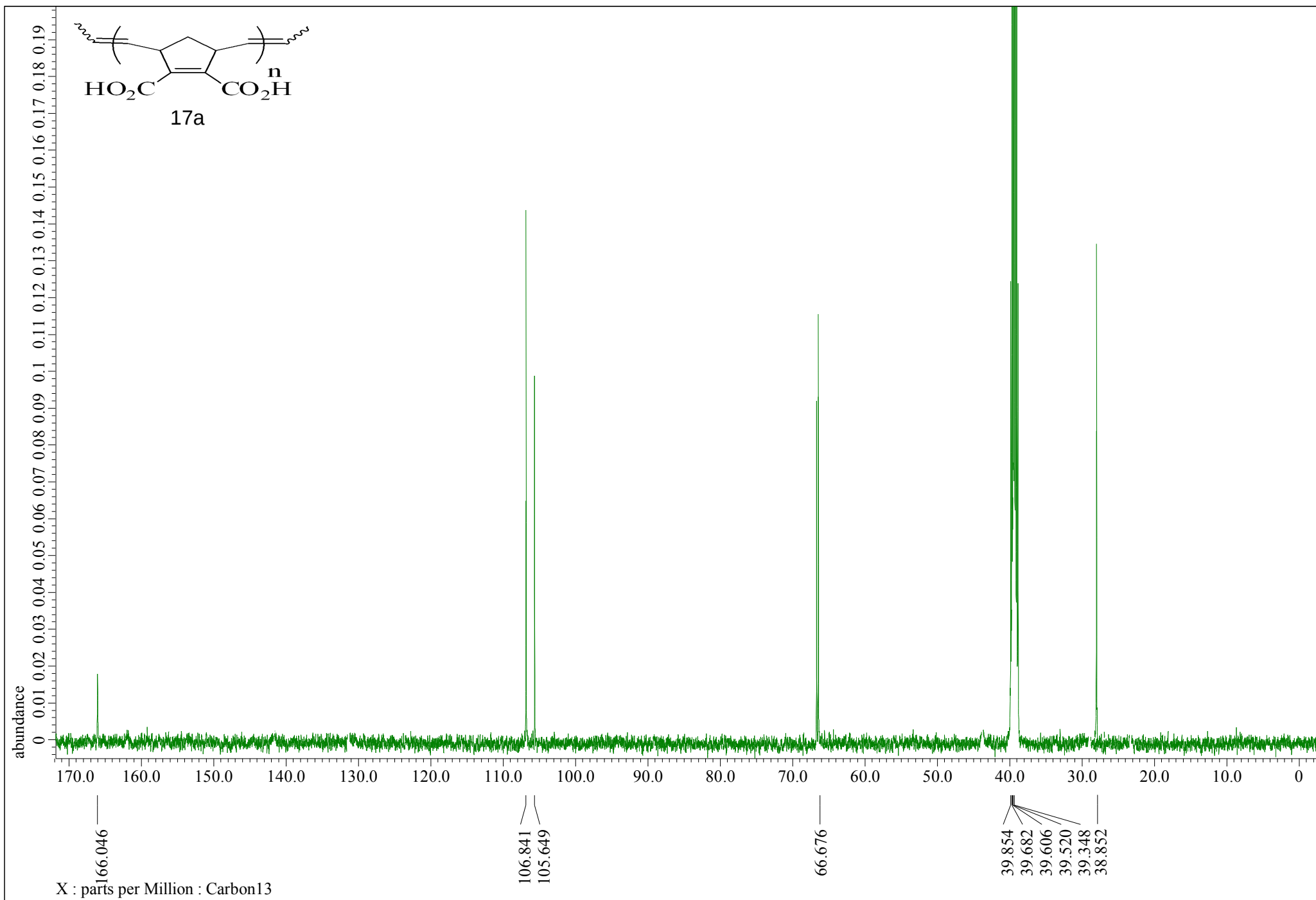


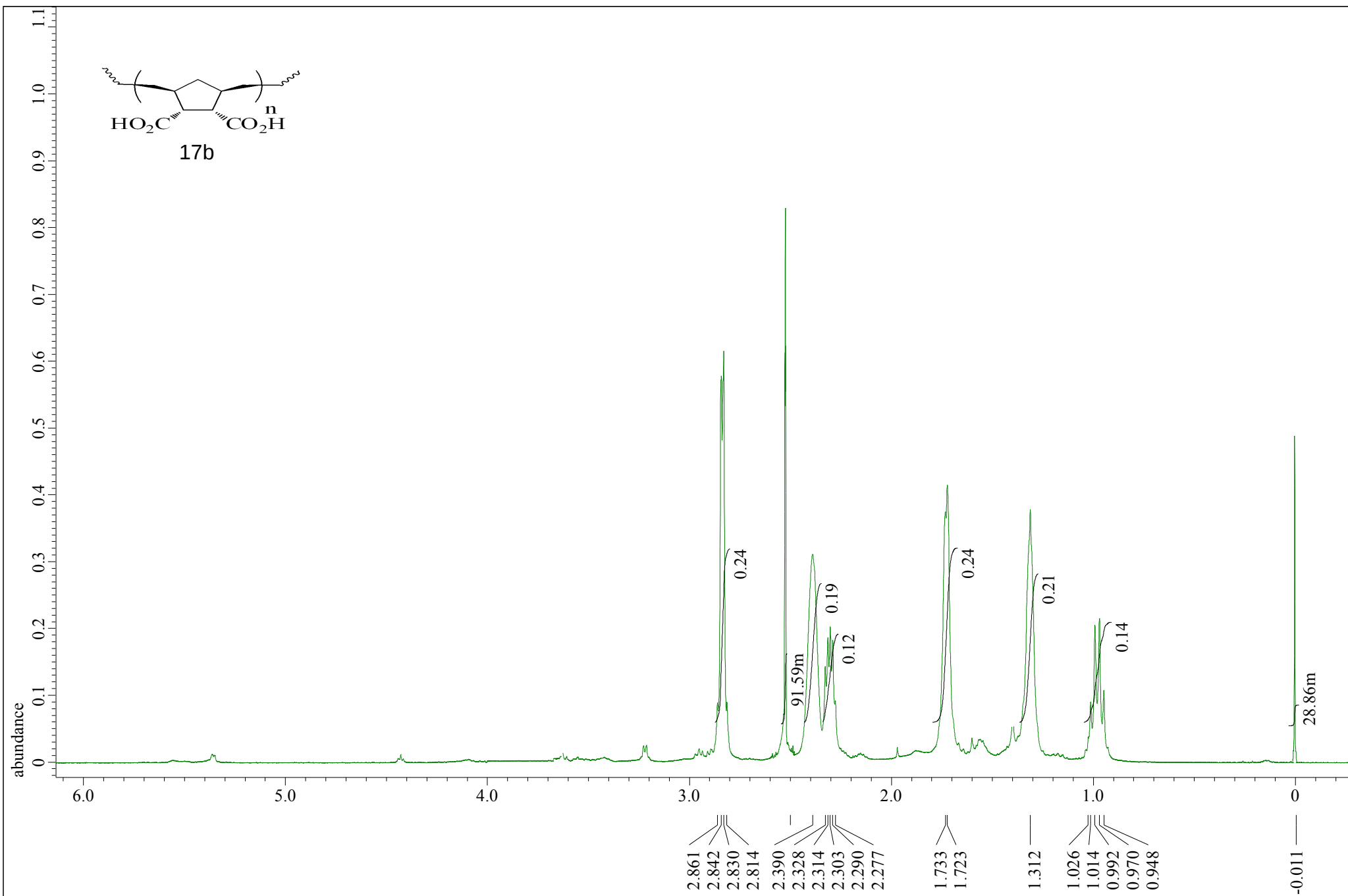
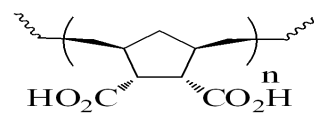




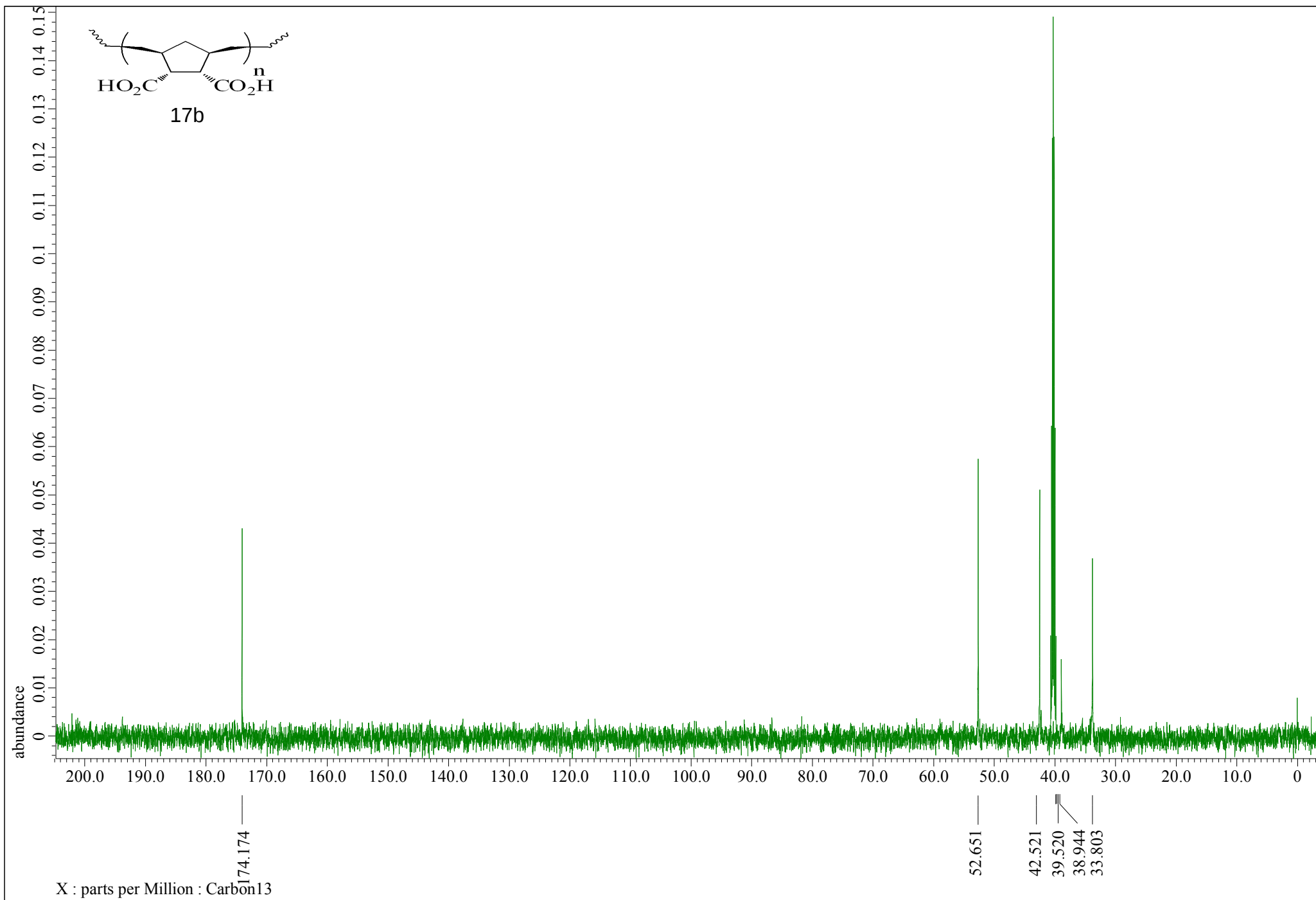


X : parts per Million : Proton

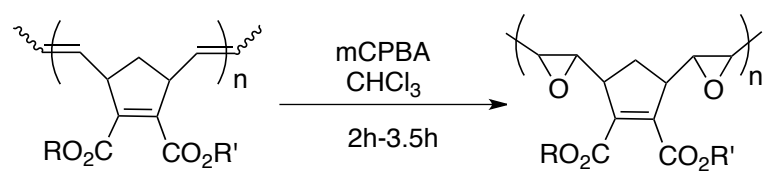




X : parts per Million : Proton



Epoxidation of polymers



R and R' ^a		Yield ^b (%)	M _n (GPC) ^c kDa	M _w /M _n ^c	T _g (°C)	T _d ^{5d} (°C)
Me	Me	>99	13.1	1.51	88	169
Et	Et	>99	14.6	1.69	71	174
ⁿ P	ⁿ P	>99	18.7	1.40	45	175
ⁱ P	ⁱ P	>99	17.3	1.39	86	197
^t Bu	^t Bu	>99	20.7	1.52	95	139
Bn	Bn	>99	45.1	1.40	60	197
Me	^t Bu	>99	21.2	1.51	89	161
Et	^t Bu	>99	24.9	1.42	76	155
ⁿ P	^t Bu	>99	29.0	1.36	70	150
ⁱ P	^t Bu	>99	28.6	1.55	34	156
Me	ⁱ P	>99	19.7	1.73	84	202

a: Interchangeable. b: Isolated yield after precipitation.

c: Determined by GPC with a polystyrene standard.

d: Temperature at 5% weight loss.

