

Electronic Supplementary Information:

Efficient Bromination of Olefins, Alkynes, and Ketones with Dimethyl Sulfoxide and Hydrobromic Acid

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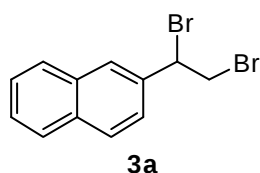
(A) General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography on silica gel. ^1H -NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced TMS in CDCl_3 (0 ppm). ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer.

(B) Experimental Procedure and Characterization Data of Products

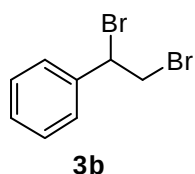
Typical procedure for dibromination of olefins and alkynes: Olefin **1** or alkyne **6** (0.5 mmol) and DMSO (43 μL , 0.6 mmol) were dissolved in EA (2 mL). Aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) was added to the solution at 60 $^\circ\text{C}$ and the mixture were stirred for 0.5 h under air at that temperature. After cooling down to room temperature and concentrating in vacuum, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the dibrominated product **3** or **7**.

2-(1,2-Dibromoethyl)naphthalene (**3a**)^[1]



The reaction of 2-vinylnaphthalene **1a** (77.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 125.4 mg (80%) of **3a** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.83 (m, 4H), 7.53–7.50 (m, 3H), 5.33 (dd, $J = 8.8, 7.2$ Hz, 1H), 4.16–4.13 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.7, 133.5, 132.9, 129.1, 128.2, 127.8, 127.4, 126.9, 126.7, 124.4, 51.3, 34.8.

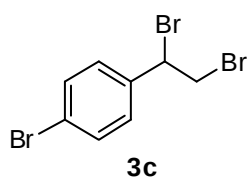
(1,2-Dibromoethyl)benzene (**3b**)^[2]



The reaction of styrene **1b** (52.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in

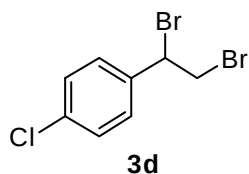
EA (2 mL) at 60 °C for 0.5 h, affords 93.6 mg (71%) of **3b** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.31 (m, 5H), 5.13 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.08–3.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 129.1, 128.8, 127.6, 50.9, 35.0.

1-Bromo-4-(1,2-dibromoethyl)benzene (**3c**)^[3]



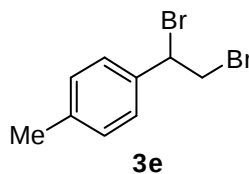
The reaction of 1-bromo-4-vinylbenzene **1c** (91.5 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 130.1 mg (76%) of **3c** as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.09 (dd, *J* = 11.2, 5.2 Hz, 1H), 4.06 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.99–3.94 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 137.7, 132.1, 129.3, 123.2, 49.5, 34.6.

1-Chloro-4-(1,2-dibromoethyl)benzene (**3d**)^[4]



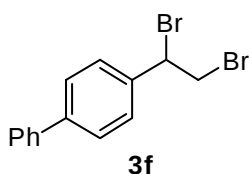
The reaction of 1-chloro-4-vinylbenzene **1d** (69.3 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 110.5 mg (74%) of **3d** as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.38–7.33 (m, 4H), 5.10 (dd, *J* = 11.0, 5.0 Hz, 1H), 4.06 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.99–3.94 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 137.1, 135.0, 129.1, 129.0, 49.5, 34.6.

1-(1,2-Dibromoethyl)-4-methylbenzene (**3e**)^[4]



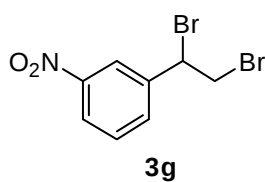
The reaction of 1-methyl-4-vinylbenzene **1e** (59.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 109.7 mg (79%) of **3e** as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.14 (dd, *J* = 10.6, 5.2 Hz, 1H), 4.07 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.05–3.99 (m, 1H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 139.2, 135.6, 129.6, 127.5, 51.0, 35.0, 21.3.

4-(1,2-Dibromoethyl)-1,1'-biphenyl (**3f**)^[5]



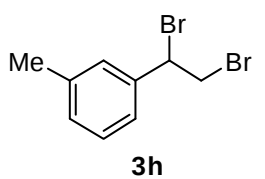
The reaction of 4-vinyl-1,1'-biphenyl **1f** (90.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 137.7 mg (81%) of **3f** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.65–7.63 (m, 4H), 7.52–7.41 (m, 5H), 5.25 (dd, *J* = 8.7, 5.9 Hz, 1H), 4.16–4.07 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 140.1, 137.4, 128.8, 128.0, 127.6, 127.5, 127.1, 50.7, 34.8.

1-(1,2-Dibromoethyl)-3-nitrobenzene (**3g**)^[6]



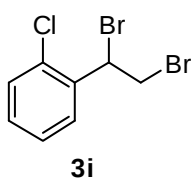
The reaction of 1-nitro-3-vinylbenzene **1g** (74.6 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 117.4 mg (76%) of **3g** as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.29 (t, J = 1.8 Hz, 1H), 8.23–8.21 (m, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 5.19 (dd, J = 11.2, 4.8 Hz, 1H), 4.11 (dd, J = 10.6, 5.0 Hz, 1H), 4.04–3.98 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.4, 140.8, 133.7, 129.9, 124.0, 122.8, 48.0, 34.1.

1-(1,2-Dibromoethyl)-3-methylbenzene (**3h**)^[7]



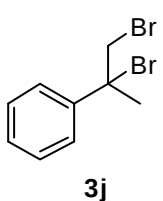
The reaction of 1-methyl-3-vinylbenzene **1h** (59.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 104.0 mg (75%) of **3h** as a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.29–7.25 (m, 1H), 7.20–7.19 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 5.11 (dd, J = 10.4, 5.6 Hz, 1H), 4.08–3.99 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 138.6, 138.5, 130.0, 128.7, 128.3, 124.7, 51.1, 35.0, 21.4.

1-Chloro-2-(1,2-dibromoethyl)benzene (**3i**)



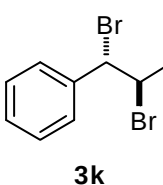
The reaction of 1-chloro-2-vinylbenzene **1i** (69.3 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 110.3 mg (74%) of **3i** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.27 (t, J = 8.2 Hz, 1H), 5.70 (t, J = 7.7 Hz, 1H), 4.12–4.07 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.0, 133.9, 130.1, 130.0, 128.3, 127.5, 45.5, 33.6.

(1,2-Dibromopropan-2-yl)benzene (**3j**)^[8]



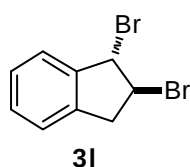
The reaction of α -methylstyrene **1j** (59.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 101.0 mg (73%) of **3j** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.54 (m, 2H), 7.38–7.30 (m, 3H), 4.35 (d, J = 10.2 Hz, 1H), 4.13 (d, J = 10.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 128.5, 128.4, 126.5, 63.7, 43.5, 29.9.

(1,2-Dibromopropyl)benzene (**3k**)^[8]



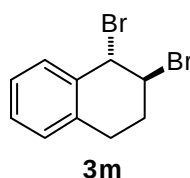
The reaction of (*E*)- β -methylstyrene **1k** (59.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 108.4 mg (78%) of **3k** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.32 (m, 5H), 5.05 (d, J = 10.4 Hz, 1H), 4.63–4.59 (m, 1H), 2.05 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 128.8, 126.6, 127.7, 59.1, 51.1, 25.8.

1,2-Dibromo-2,3-dihydro-1H-indene (**3l**)^[9]



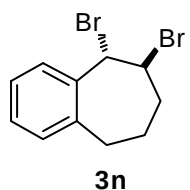
The reaction of indene **1l** (58.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 101.2 mg (73%) of **3l** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.44 (m, 1H), 7.34–7.27 (m, 3H), 5.62 (s, 1H), 4.86 (dt, J = 5.2, 1.2 Hz, 1H), 3.79 (dd, J = 17.5, 5.2 Hz, 1H), 3.25 (d, J = 17.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 140.5, 129.7, 127.9, 125.7, 125.4, 57.7, 54.4, 41.4.

1,2-Dibromo-1,2,3,4-tetrahydronaphthalene (**3m**)^[10]



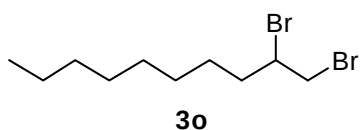
The reaction of 1,2-dihydronaphthalene **1m** (65.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 112.4 mg (78%) of **3m** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, J = 7.5, 1.4 Hz, 1H), 7.25–7.16 (m, 2H), 7.11 (d, J = 7.5 Hz, 1H), 5.64–5.63 (m, 1H), 4.93–4.90 (m, 1H), 3.25 (ddd, J = 17.7, 11.9, 6.2 Hz, 1H), 2.91 (dd, J = 17.4, 6.0 Hz, 1H), 2.84–2.76 (m, 1H), 2.20–2.13 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.4, 132.8, 131.2, 129.2, 128.9, 126.6, 51.52, 51.49, 25.1, 24.4.

5,6-Dibromo-6,7,8,9-tetrahydro-5H-benzo[7]annulene (**3n**)^[11]



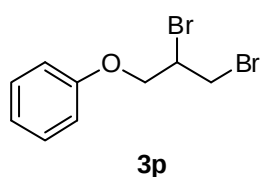
The reaction of 6,7-dihydro-5H-benzo[7]annulene **1n** (72.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 129.2 mg (85%) of **3n** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.12 (m, 4H), 5.49 (d, J = 5.3 Hz, 1H), 4.88–4.85 (m, 1H), 3.31–3.23 (m, 1H), 3.00–2.92 (m, 1H), 2.80–2.74 (m, 1H), 2.27–2.21 (m, 1H), 1.98–1.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 136.3, 131.3, 130.9, 129.3, 126.1, 58.4, 54.7, 35.3, 34.6, 22.8.

1,2-Dibromodecane (**3o**)^[8]



The reaction of 1-decene **1o** (70.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 141.0 mg (94%) of **3o** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.20–4.13 (m, 1H), 3.85 (dd, J = 10.2, 4.4 Hz, 1H), 3.63 (t, J = 10.0 Hz, 1H), 2.18–2.09 (m, 1H), 1.83–1.73 (m, 1H), 1.60–1.53 (m, 1H), 1.45–1.28 (m, 11H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 53.1, 36.3, 36.0, 31.8, 29.3, 29.1, 28.8, 26.7, 22.6, 14.1.

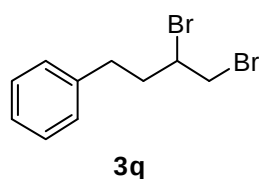
(2,3-Dibromopropoxy)benzene (**3p**)^[12]



The reaction of (allyloxy)benzene **1p** (67.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 119.1 mg (81%) of **3p** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.28 (m, 2H), 7.00 (t, J = 7.4 Hz, 1H),

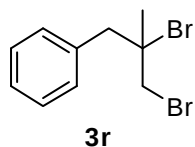
6.95–6.92 (m, 2H), 4.44–4.33 (m, 3H), 3.95–3.86 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.9, 129.6, 121.6, 114.8, 69.0, 47.7, 32.7.

(3,4-Dibromobutyl)benzene (**3q**)^[13]



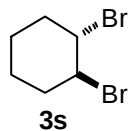
The reaction of (allyloxy)benzene **1q** (66.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 131.5 mg (90%) of **3q** as colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.29–7.21 (m, 5H), 4.09 (m, 1H), 3.83–3.81 (m, 1H), 3.64–3.59 (m, 1H), 2.92–2.90 (m, 1H), 2.75–2.73 (m, 1H), 2.46–2.45 (m, 1H), 2.07–2.06 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 140.2, 128.51, 128.47, 126.2, 52.0, 37.6, 36.2, 32.9.

(2,3-Dibromo-2-methylpropyl)benzene (**3r**)^[14]



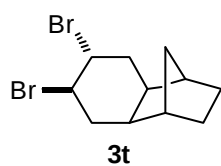
The reaction of (2-methylallyl)benzene **1r** (66.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 121.7 mg (83%) of **3r** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.31 (m, 5H), 3.81 (d, J = 10.2 Hz, 1H), 3.74 (d, J = 10.2 Hz, 1H), 3.33–3.21 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.0, 130.9, 128.0, 127.3, 66.6, 47.1, 42.2, 30.7.

1,2-Dibromocyclohexane (**3s**)^[15]



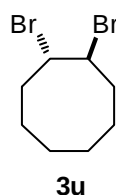
The reaction of cyclohexene **1s** (41.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 100.5 mg (83%) of **3s** as colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 4.46 (s, 2H), 2.49–2.43 (m, 2H), 1.91–1.79 (m, 4H), 1.55–1.50 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 55.2, 31.9, 22.4.

6,7-Dibromodecahydro-1,4-methanonaphthalene (**3t**)^[16]



The reaction of octahydro-1,4-methanonaphthalene **1t** (74.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 135.5 mg (88%) of **3t** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 4.70 (dt, J = 6.3, 3.1 Hz, 1H), 4.34–4.27 (m, 1H), 2.02 (dt, J = 12.9, 5.0 Hz, 1H), 1.96–1.87 (m, 5H), 1.72–1.66 (m, 1H), 1.60–1.50 (m, 4H), 1.29–1.19 (m, 2H), 1.12 (d, J = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 56.8, 54.8, 42.8, 41.9, 41.3, 36.4, 36.1, 33.5, 33.2, 29.3, 29.2.

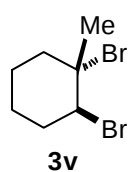
1,2-Dibromocyclooctane (**3u**)^[17]



The reaction of (Z)-cyclooctene **1u** (55.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ\text{C}$ for 0.5 h, affords 109.3 mg (81%) of **3u** as colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 4.61–4.56 (m, 2H), 2.45–2.38 (m, 2H),

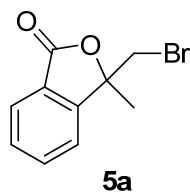
2.14–2.05 (m, 2H), 1.89–1.82 (m, 2H), 1.71–1.55 (m, 4H), 1.52–1.45 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 61.5, 33.2, 25.9, 25.4.

1,2-Dibromo-1-methylcyclohexane (**3v**)^[18]



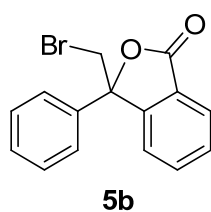
The reaction of 1-methylcyclohexene **1v** (48.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 107.7 mg (84%) of **3v** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.65 (s, 1H), 2.58–2.50 (m, 1H), 2.12–2.05 (m, 1H), 2.02–1.93 (m, 5H), 1.86–1.75 (m, 2H), 1.68–1.53 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 70.7, 61.9, 37.6, 34.0, 32.5, 22.7, 20.7.

3-(Bromomethyl)-3-methylisobenzofuran-1(3H)-one (**5a**)



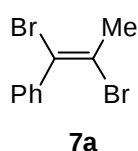
The reaction of 2-(prop-1-en-2-yl)benzoic acid **4a** (81.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 1 h, affords 105.4 mg (87%) of **5a** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 3.68 (d, J = 11.1 Hz, 1H), 3.65 (d, J = 11.1 Hz, 1H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 151.1, 134.3, 129.8, 126.2, 125.8, 121.4, 84.5, 37.8, 24.2. HRMS (ESI) Calcd for $[\text{C}_{10}\text{H}_{10}\text{BrO}_2, \text{M} + \text{H}]^+$: 240.9859, Found: 240.9863.

3-(Bromomethyl)-3-phenylisobenzofuran-1(3H)-one (**5b**)



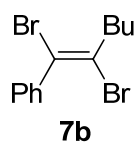
The reaction of 2-(1-phenylvinyl)benzoic acid **4b** (112.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 1 h, affords 148.2 mg (98%) of **5b** as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 7.6 Hz, 1H), 7.76–7.72 (m, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.61–7.56 (m, 3H), 7.42–7.36 (m, 3H), 4.15 (d, J = 11.4 Hz, 1H), 4.09 (d, J = 11.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 149.8, 137.5, 134.3, 129.9, 129.1, 129.0, 126.5, 126.0, 125.4, 122.5, 87.2, 37.9. HRMS (ESI) Calcd for $[\text{C}_{15}\text{H}_{12}\text{BrO}_2, \text{M} + \text{H}]^+$: 303.0015, Found: 303.0018.

(E)-(1,2-Dibromoprop-1-en-1-yl)benzene (**7a**)^[14]



The reaction of 1-phenyl-1-propyne **6a** (58.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 118.7 mg (86%) of **7a** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.32 (m, 5H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 129.1, 128.6, 128.2, 117.2, 116.8, 29.3.

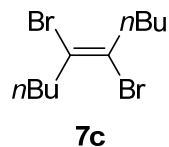
(E)-(1,2-Dibromohex-1-en-1-yl)benzene (**7b**)^[19]



The reaction of hex-1-yn-1-ylbenzene **6b** (79.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 108.3 mg (68%) of **7b** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.23 (m, 5H), 2.85 (t, J

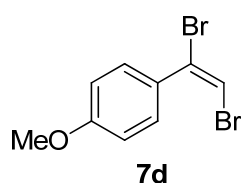
= 7.6 Hz, 2H), 1.72–1.64 (m, 2H), 1.50–1.42 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 129.1, 128.5, 128.2, 123.7, 116.2, 40.8, 29.6, 21.8, 14.0.

(E)-5,6-Dibromodec-5-ene (7c)^[20]



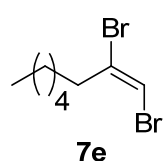
The reaction of dec-5-yne **6c** (69.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 123.2 mg (83%) of **7c** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 2.67 (t, J = 7.4 Hz, 4H), 1.59–1.52 (m, 4H), 1.40–1.31 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 121.6, 40.5, 29.6, 21.7, 13.9.

(E)-1-(1,2-Dibromovinyl)-4-methoxybenzene (7d)^[20]



The reaction of 1-ethynyl-4-methoxybenzene **6d** (66.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 5 h, affords 118.2 mg (81%) of **7d** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.73 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 130.8, 129.1, 121.5, 113.5, 101.9, 55.3.

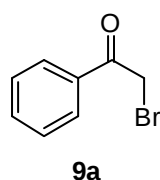
(E)-1,2-dibromooct-1-ene (7e)^[21]



The reaction of 1-phenyl-1-propyne **6e** (55.1 mg, 0.5 mmol), DMSO (43 μL , 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 86.6 mg (64%) of **7e** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.40 (s, 1H), 2.59 (t, J = 7.4 Hz, 2H), 1.59–1.55 (m, 2H), 1.36–1.31 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 127.0, 102.1, 36.9, 31.5, 28.0, 27.0, 22.5, 14.0.

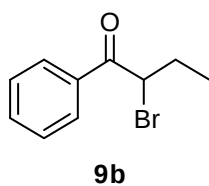
Typical procedure for bromination of ketones: Ketone **8** (0.5 mmol) and DMSO (43 μL , 0.6 mmol) in EA (2 mL) were added hydrobromic acid (48%, 0.6 mmol) at 60 °C under air. The mixture were stirred at that temperature. After cooling down to room temperature and concentrating in vacuum, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the brominated product **9**.

2-Bromoacetophenone (9a)^[22]



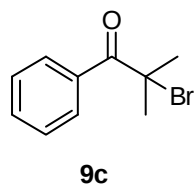
The reaction of acetophenone **8a** (60.1 mg, 0.5 mmol), DMSO (43 μL , 0.55 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 2 h, affords 72.3 mg (73%) of **9a** as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.99–7.97 (m, 2H), 7.62–7.59 (m, 1H), 7.50–7.47 (m, 2H), 4.45 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 133.9, 133.9, 128.9, 128.8, 30.9.

2-Bromo-1-phenylbutan-1-one (9b)^[23]



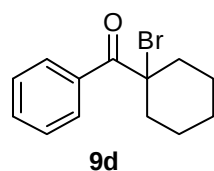
The reaction of butyrophenone **8b** (74.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 108.0 mg (94%) of **9b** as pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.02–8.01 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 5.08 (dd, J = 7.6, 6.4 Hz, 1H), 2.28–2.10 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 134.5, 133.6, 128.8, 128.7, 49.0, 26.9, 12.1.

2-Bromo-1-phenylbutan-1-one (**9c**)^[24]



The reaction of isobutyrophenone **8c** (74.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 102.6 mg (90%) of **9c** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.15–8.12 (m, 2H), 7.54–7.50 (m, 1H), 7.45–7.42 (m, 1H), 2.04 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 134.9, 132.3, 130.0, 128.1, 60.3, 31.5.

(1-Bromocyclohexyl)(phenyl)methanone (**9d**)^[25]

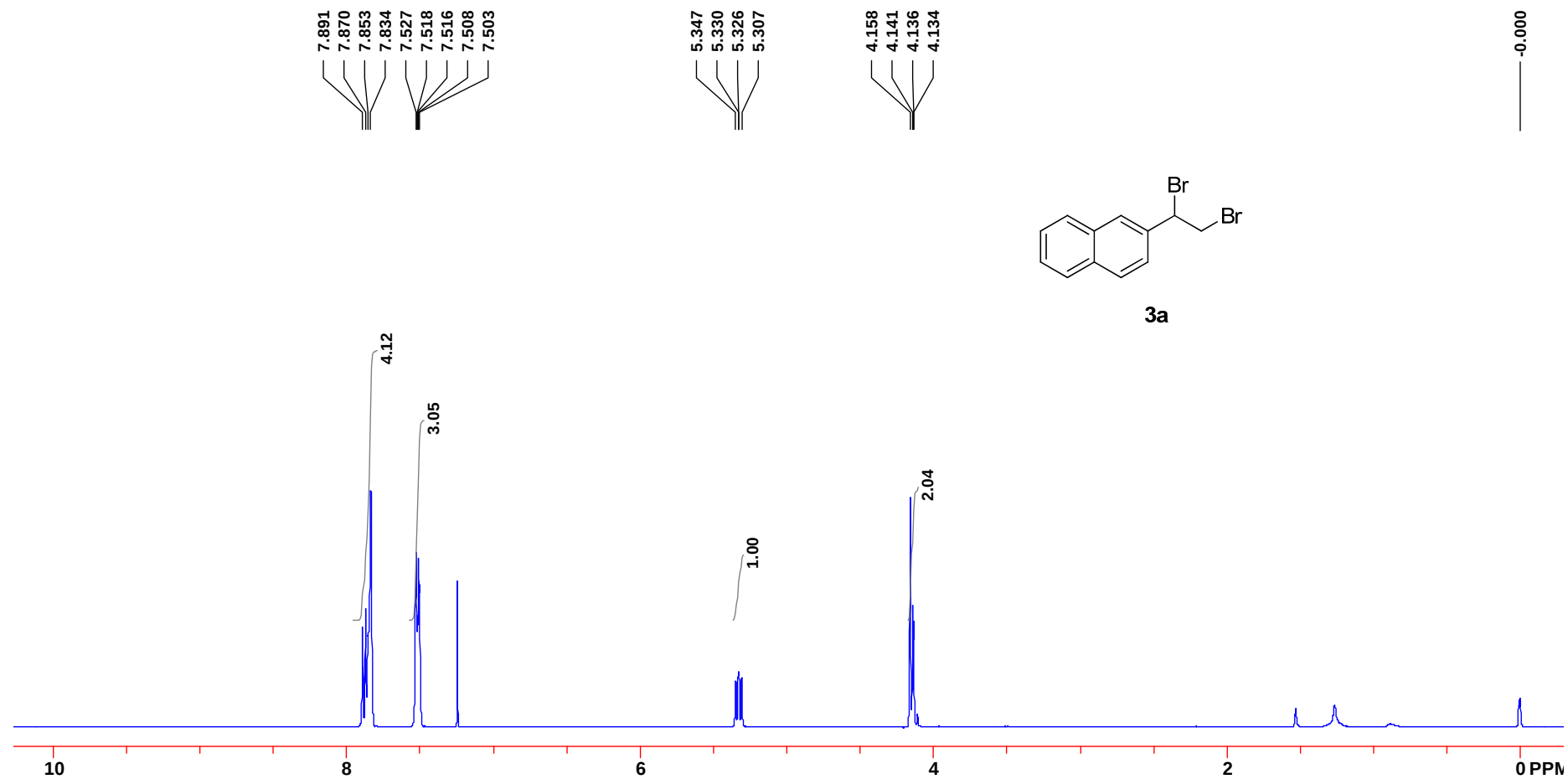


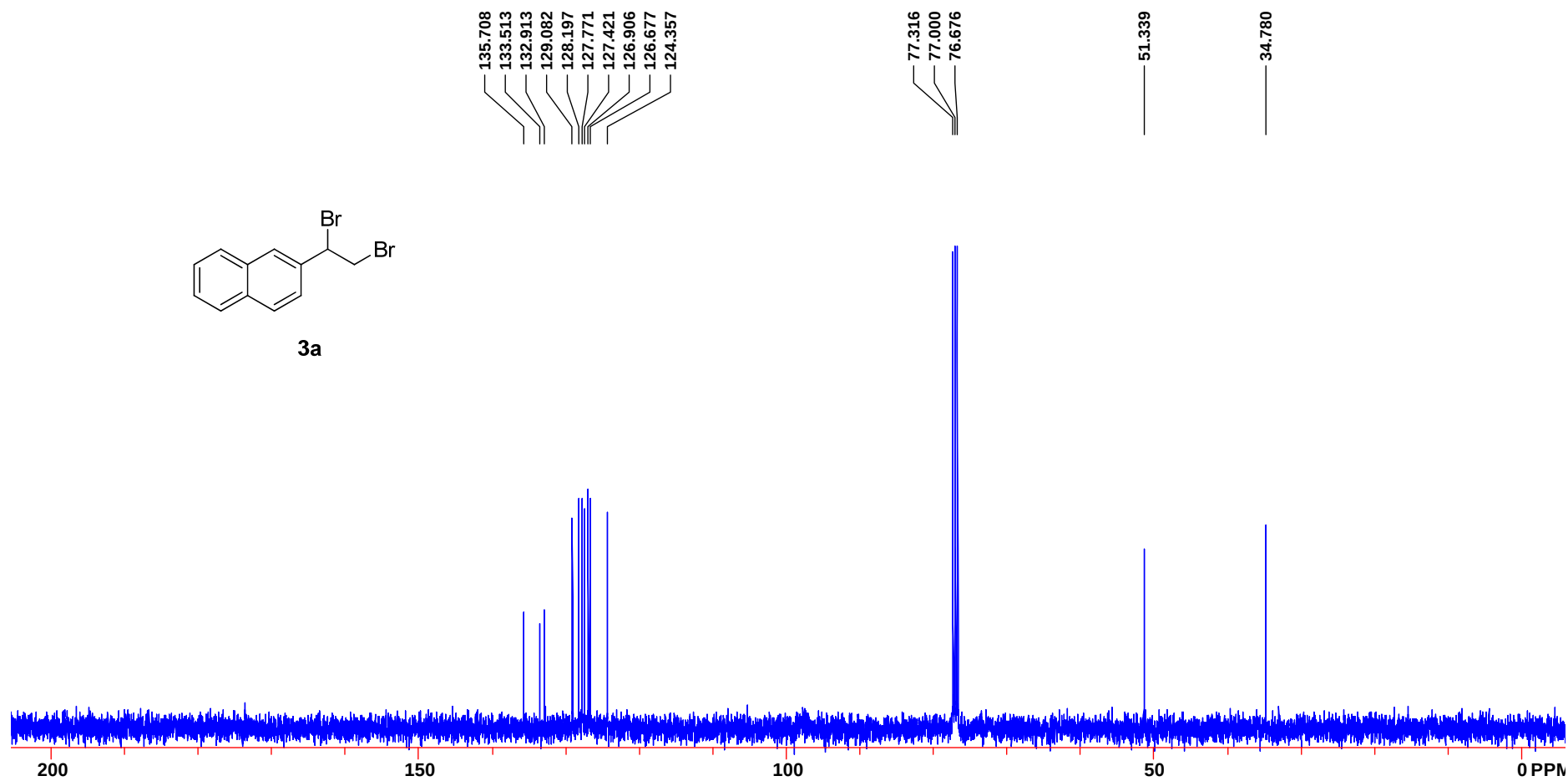
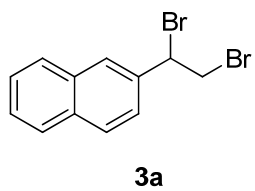
The reaction of cyclohexyl(phenyl)methanone **8d** (94.1 mg, 0.5 mmol), DMSO (43 μ L, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 122.9 mg (92%) of **9d** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.09–8.07 (m, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 2.38–2.32 (m, 2H), 2.22–2.17 (m, 2H), 1.83–1.77 (m, 2H), 1.59–1.52 (m, 3H), 1.41–1.38 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 135.8, 132.0, 129.7, 128.1, 67.9, 38.2, 24.9, 23.5.

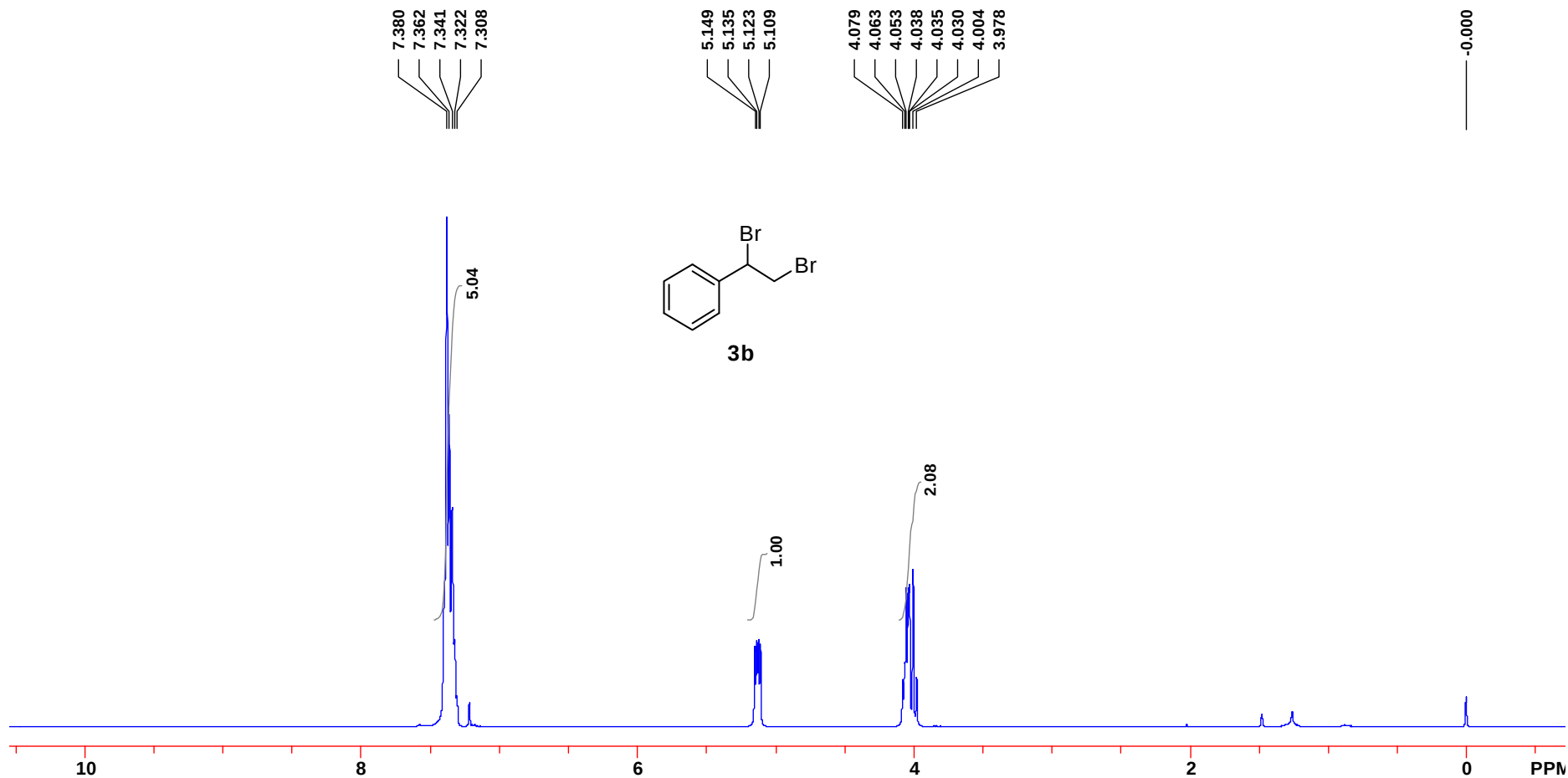
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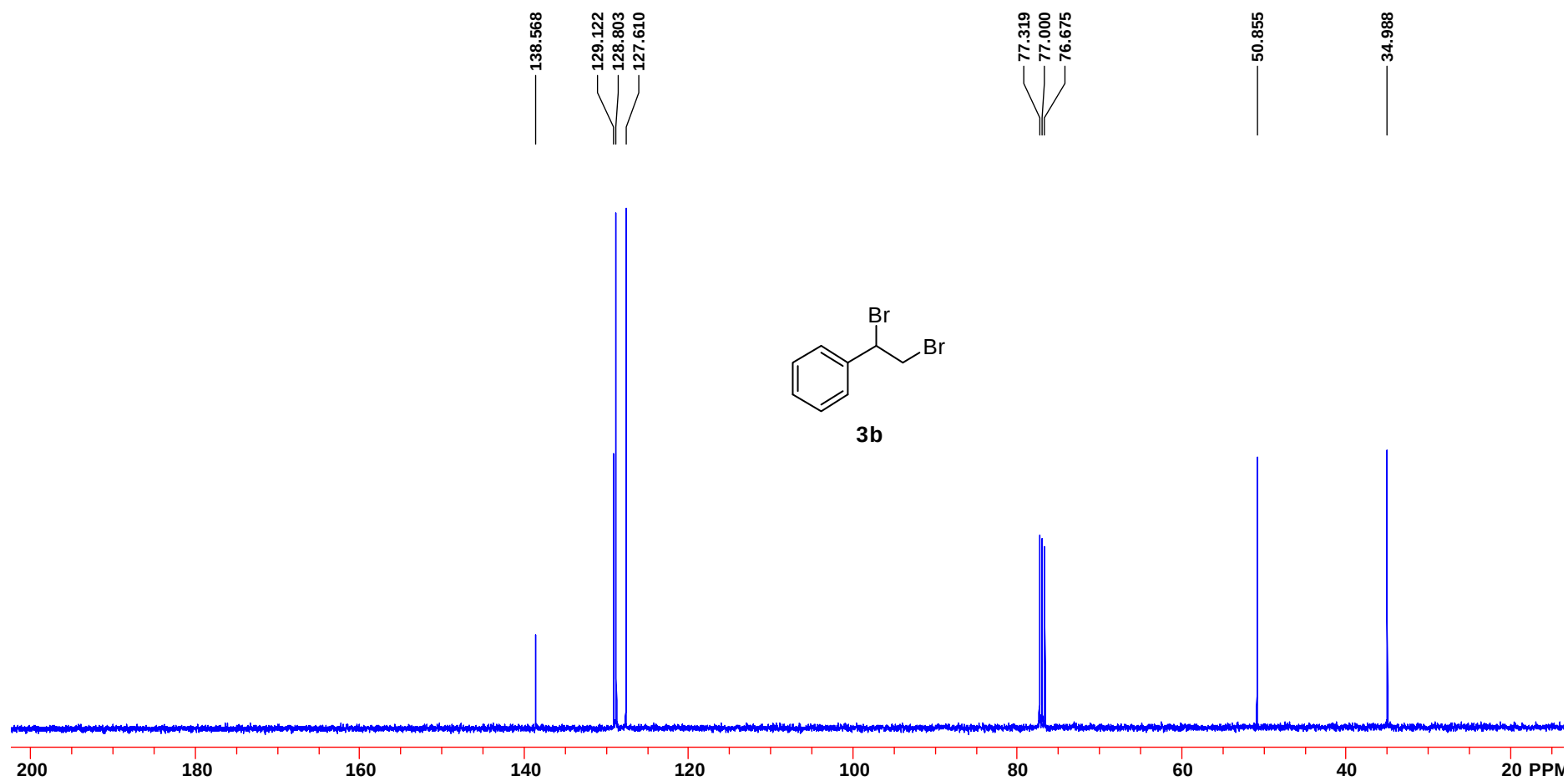
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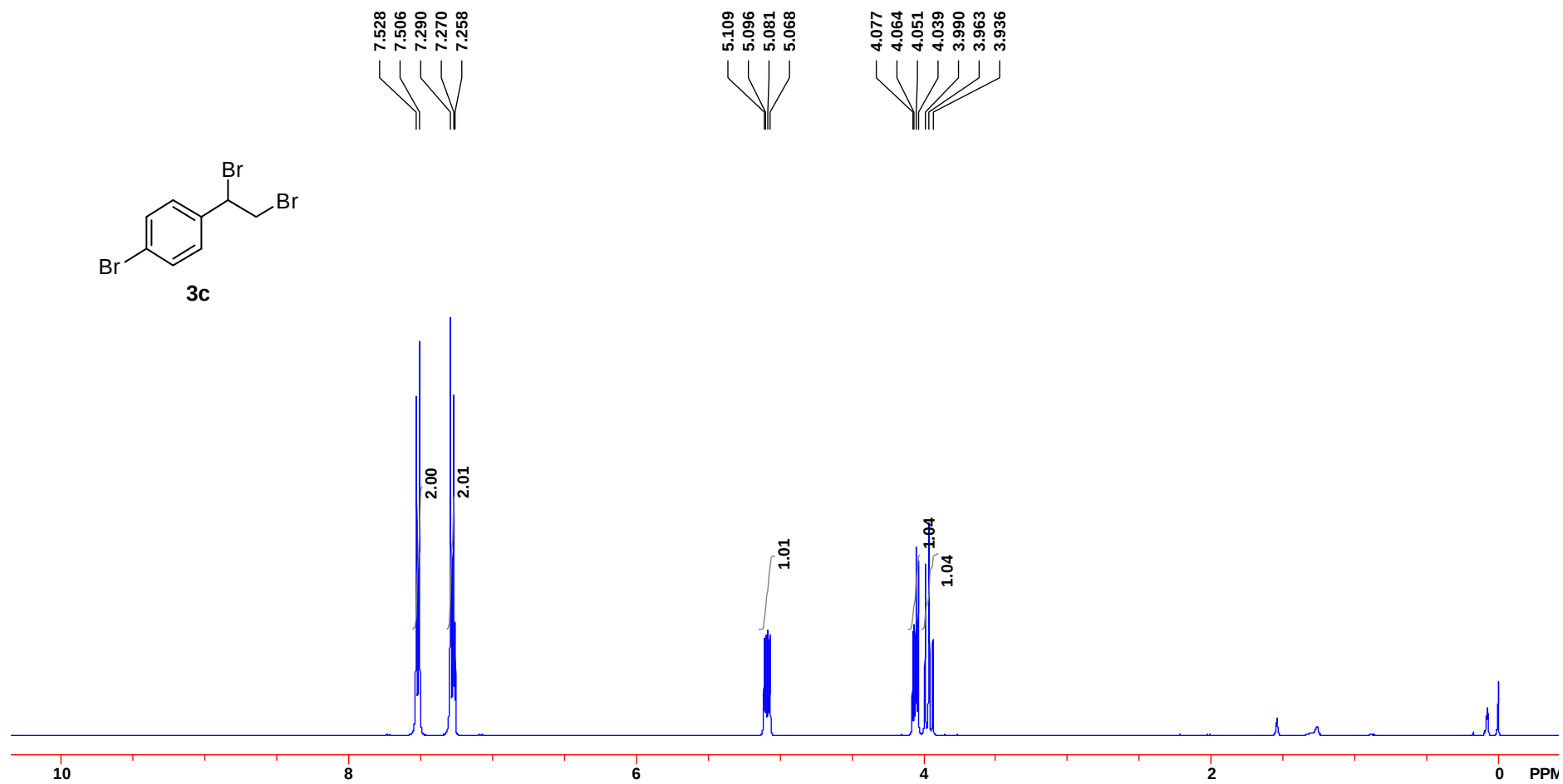
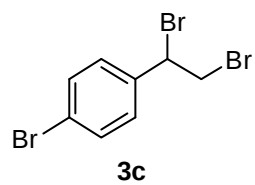
(G) ^1H NMR and ^{13}C NMR Spectra of Products

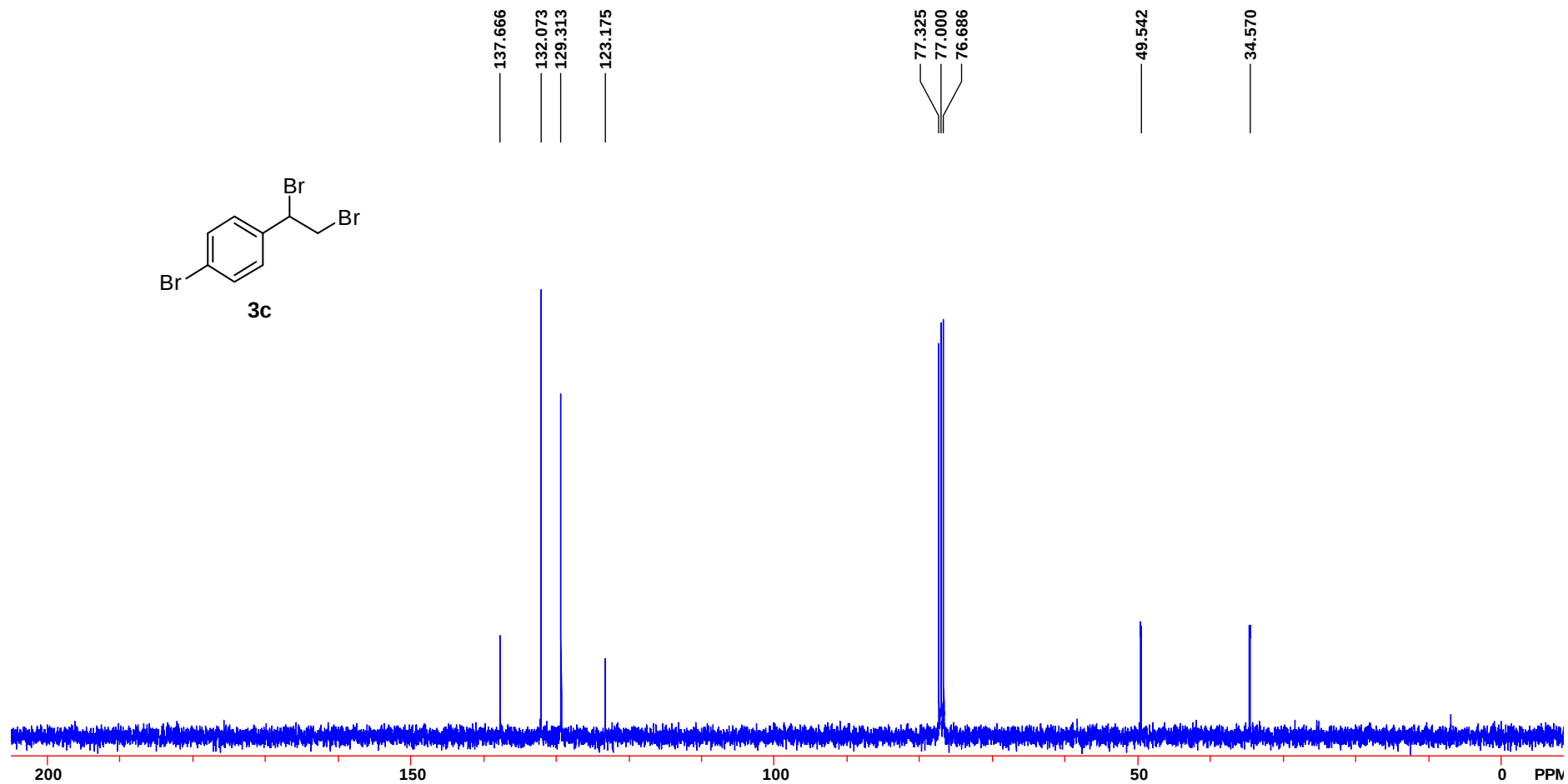
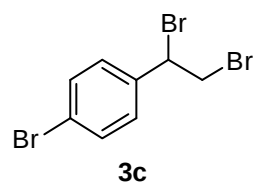


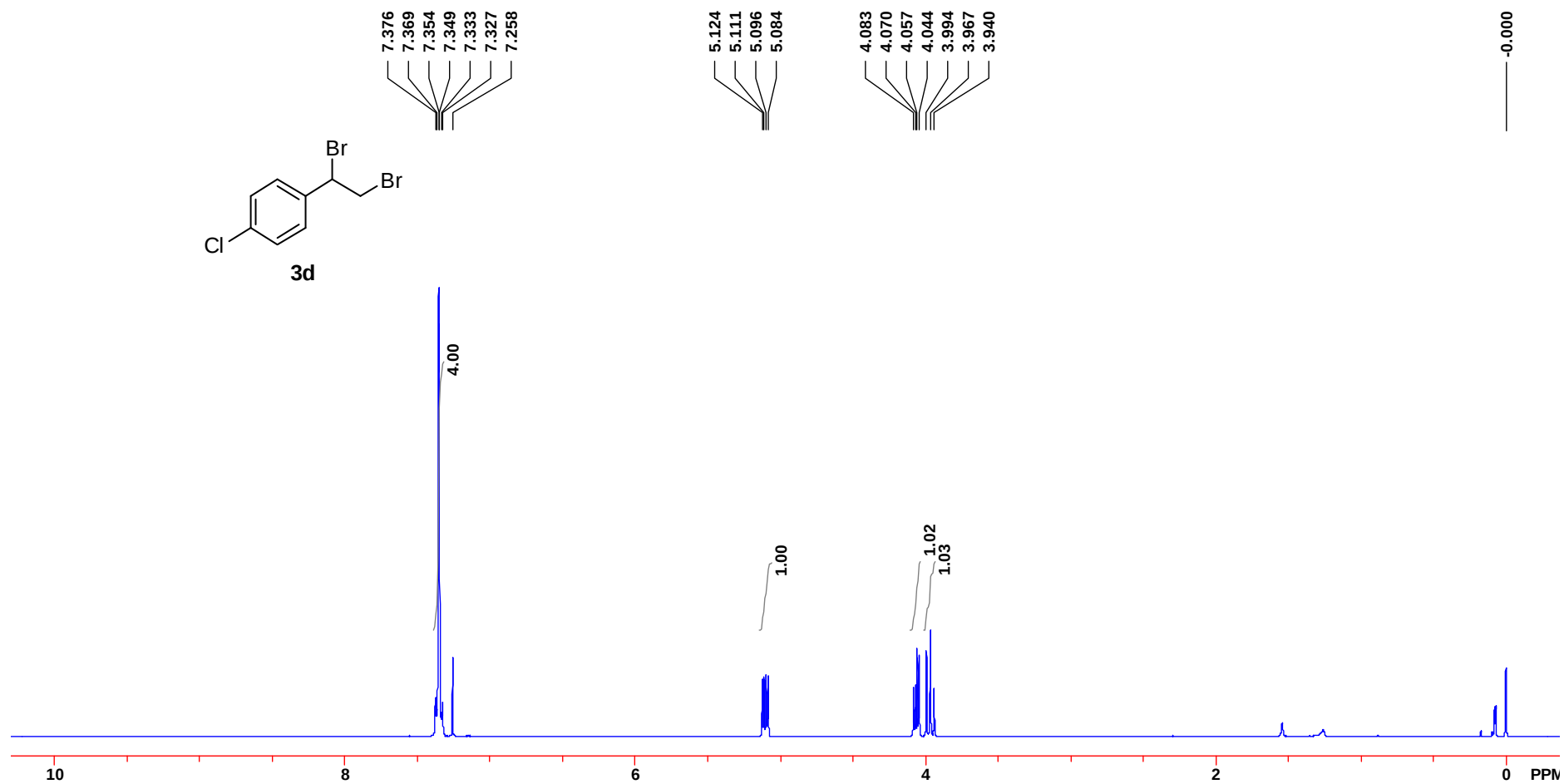


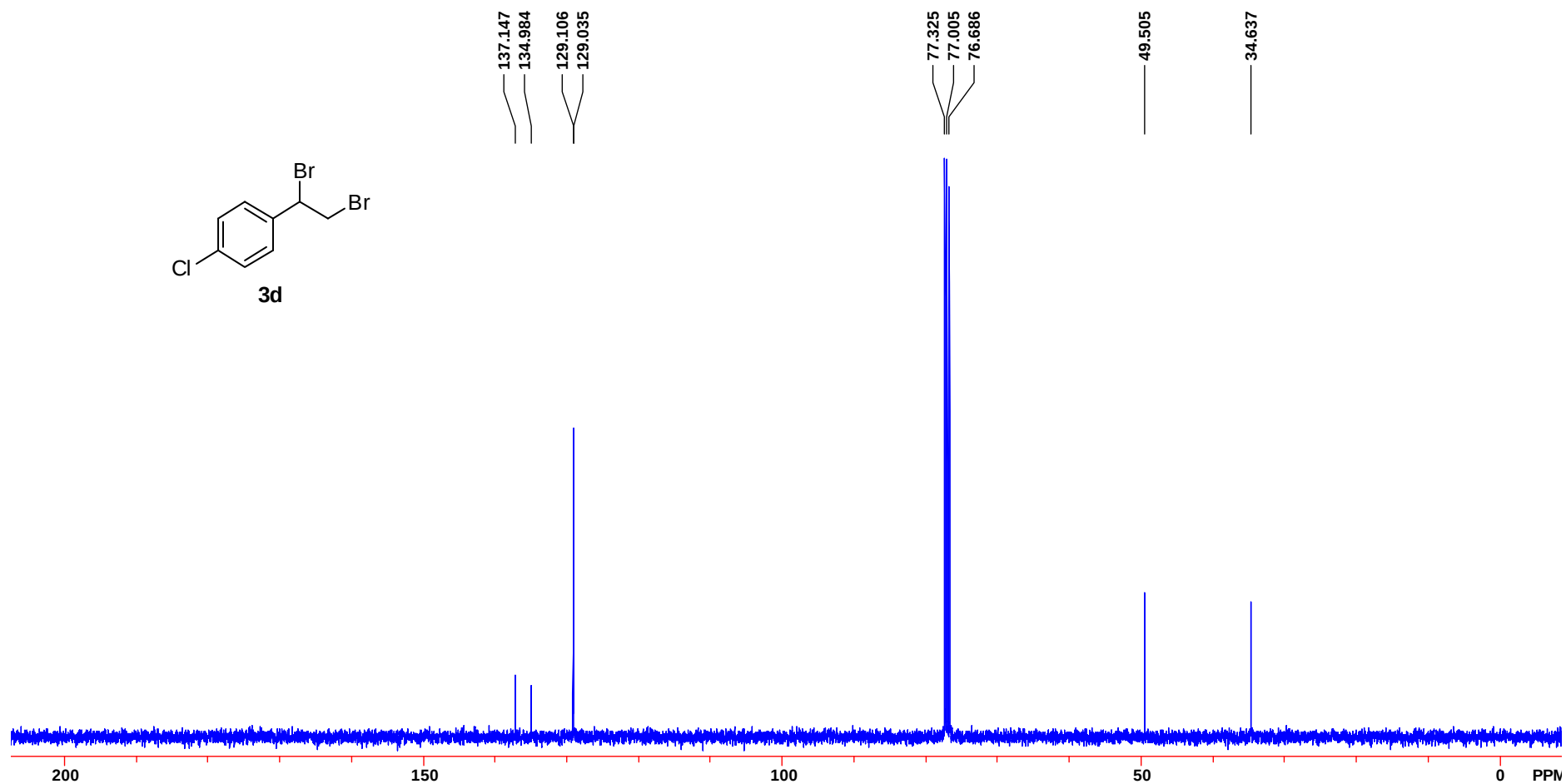
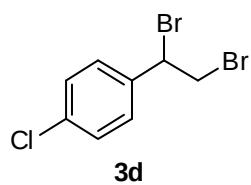


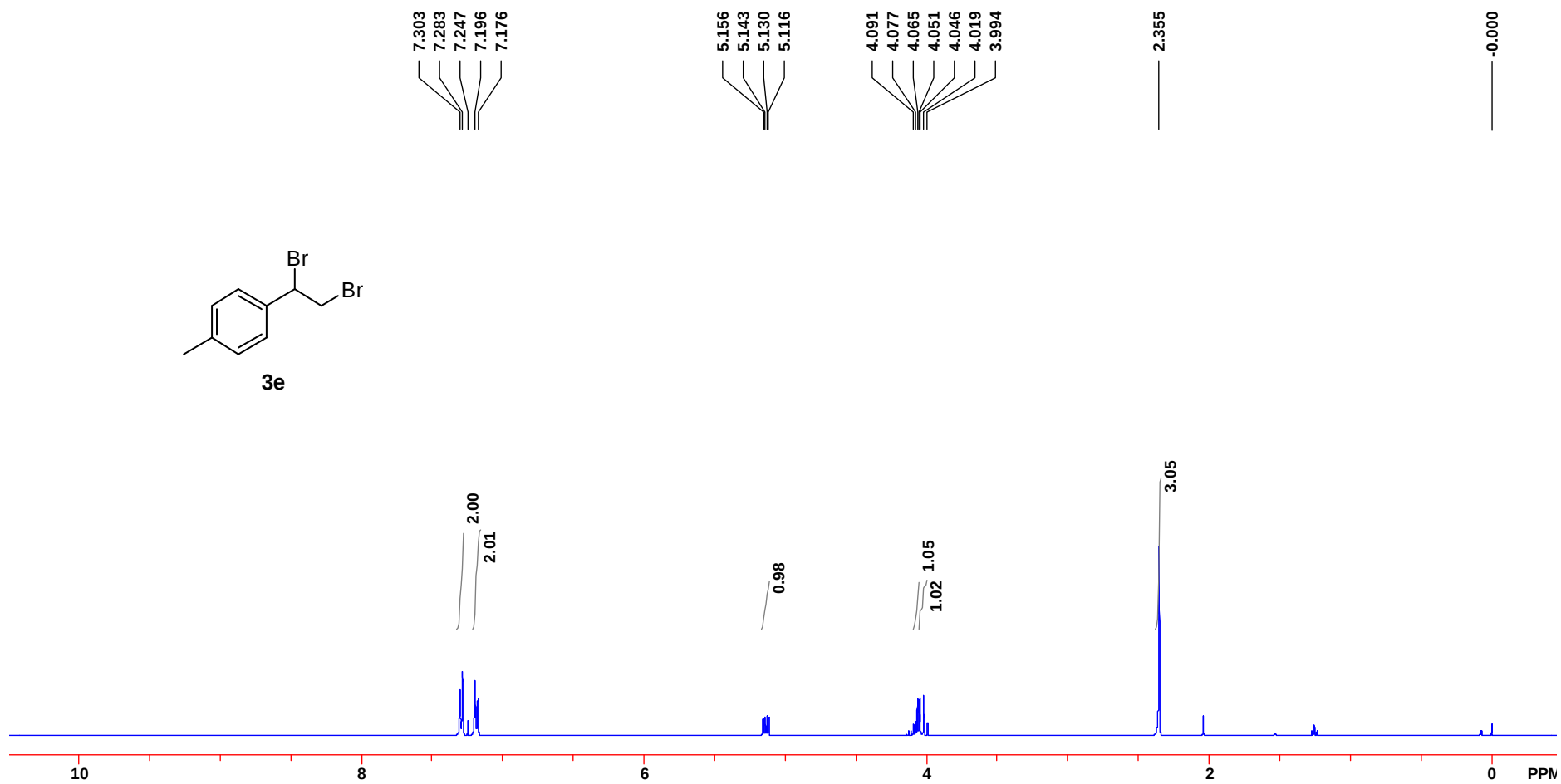
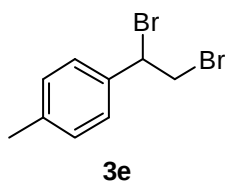


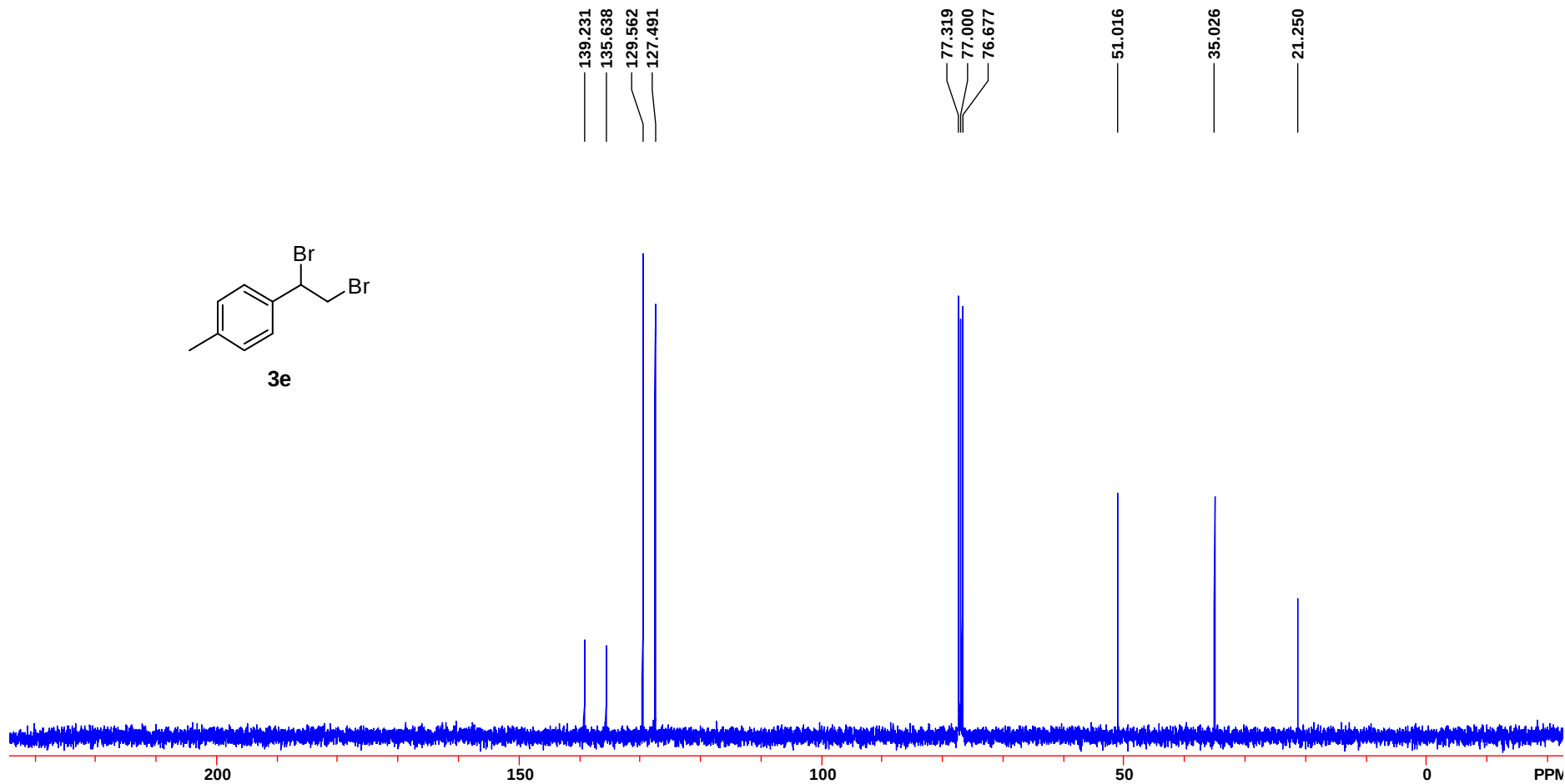
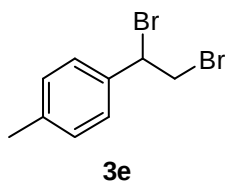


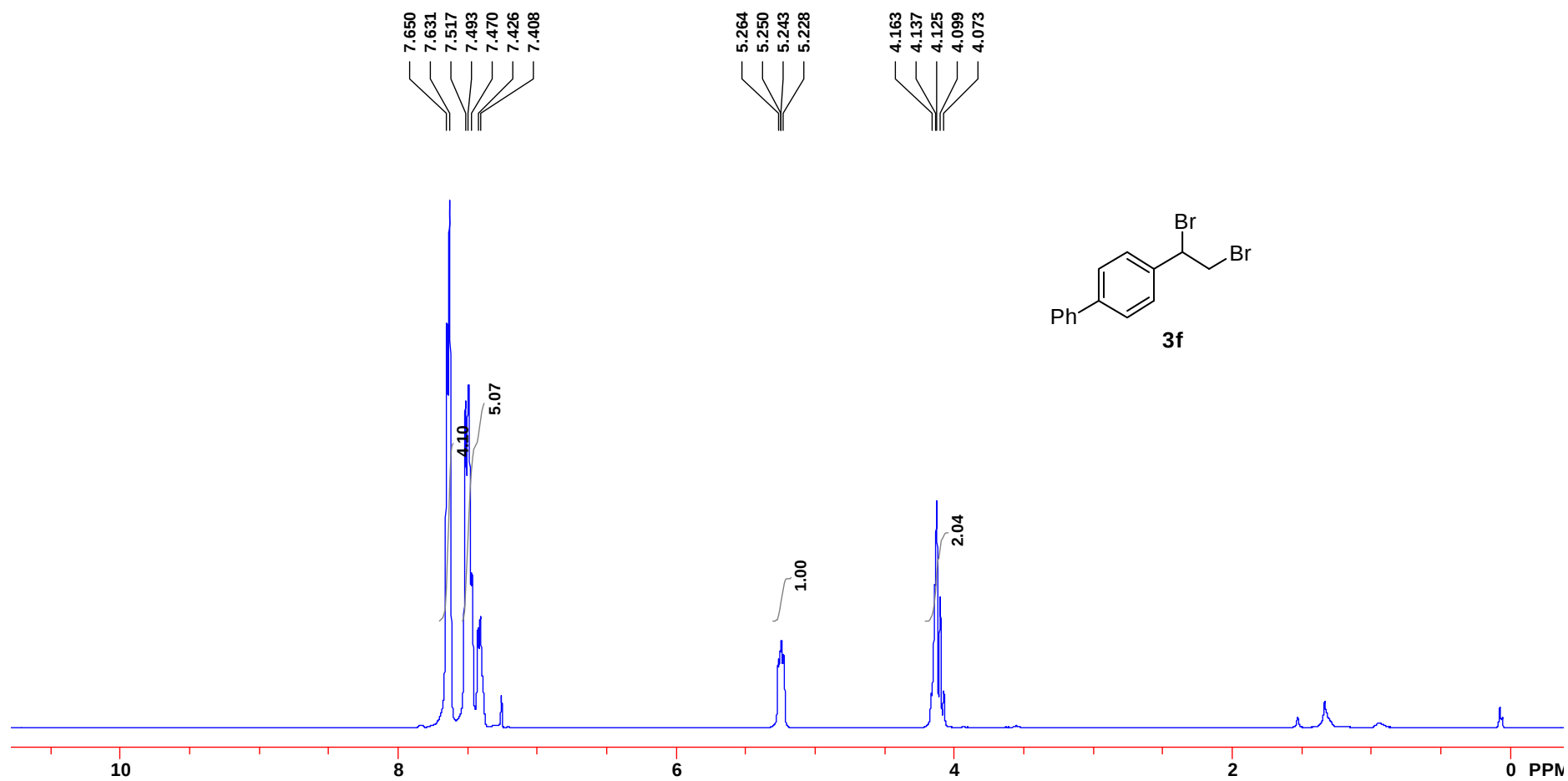


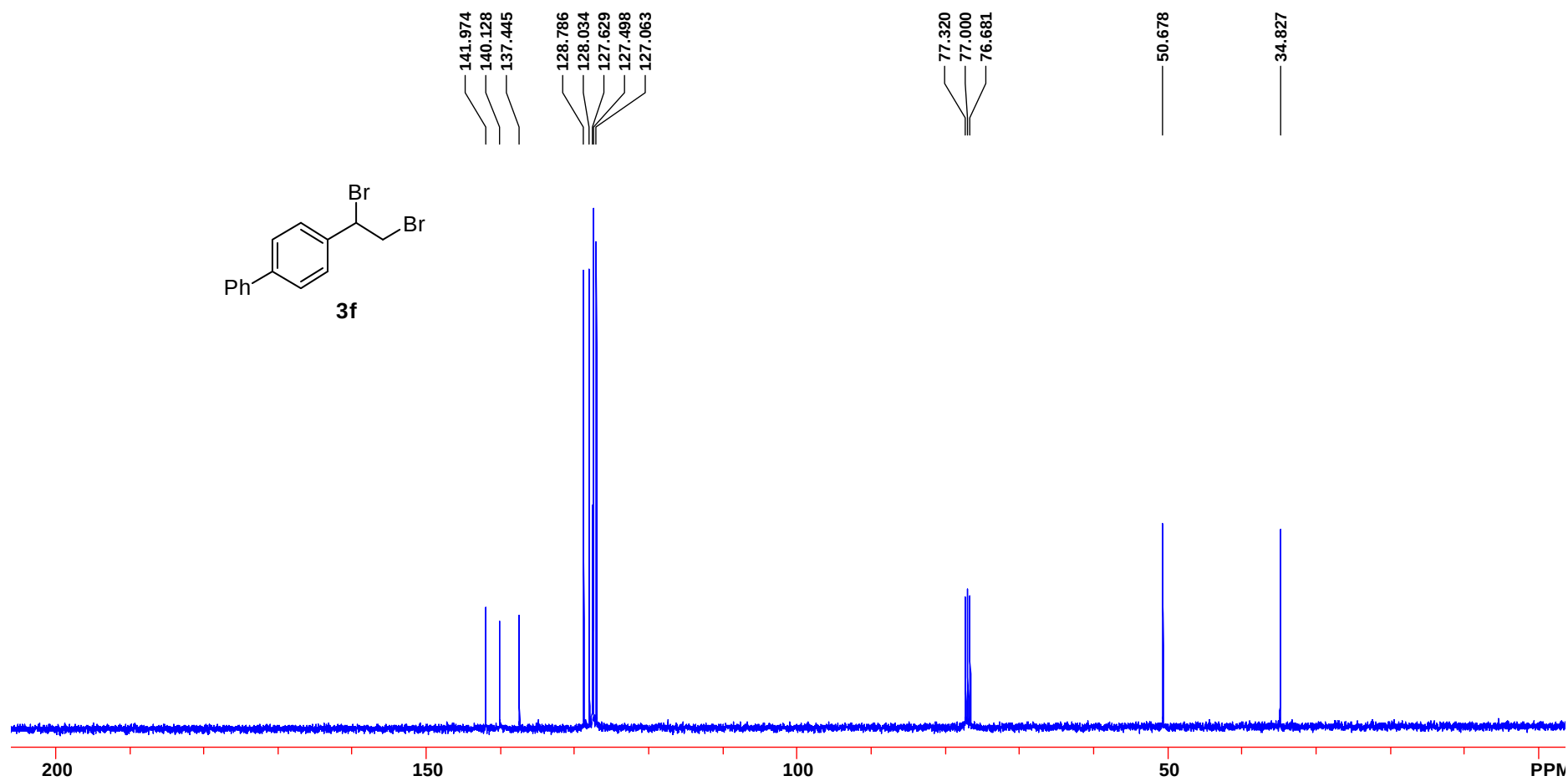
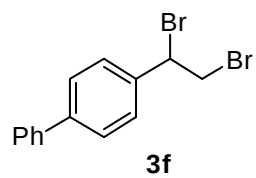


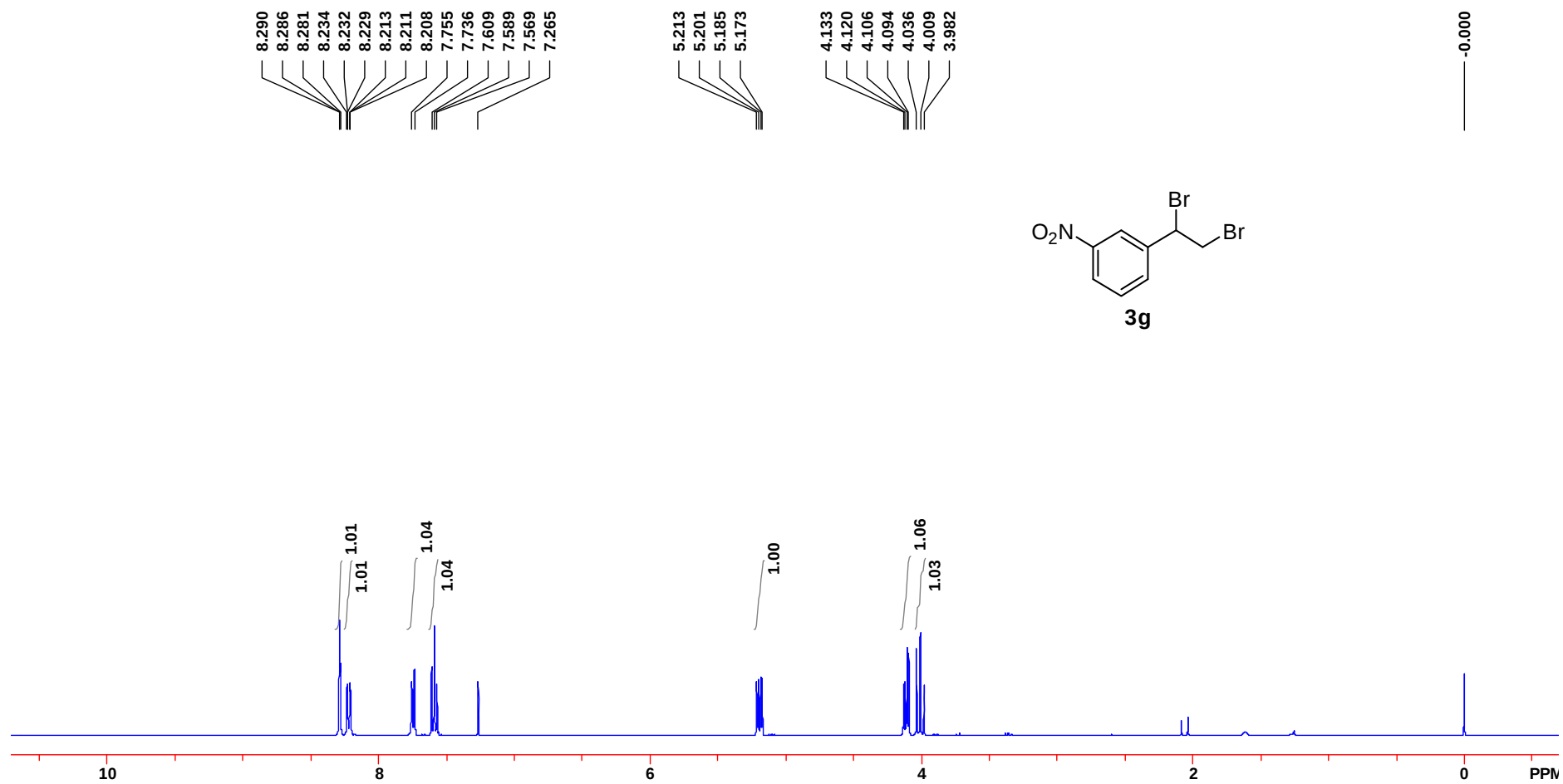


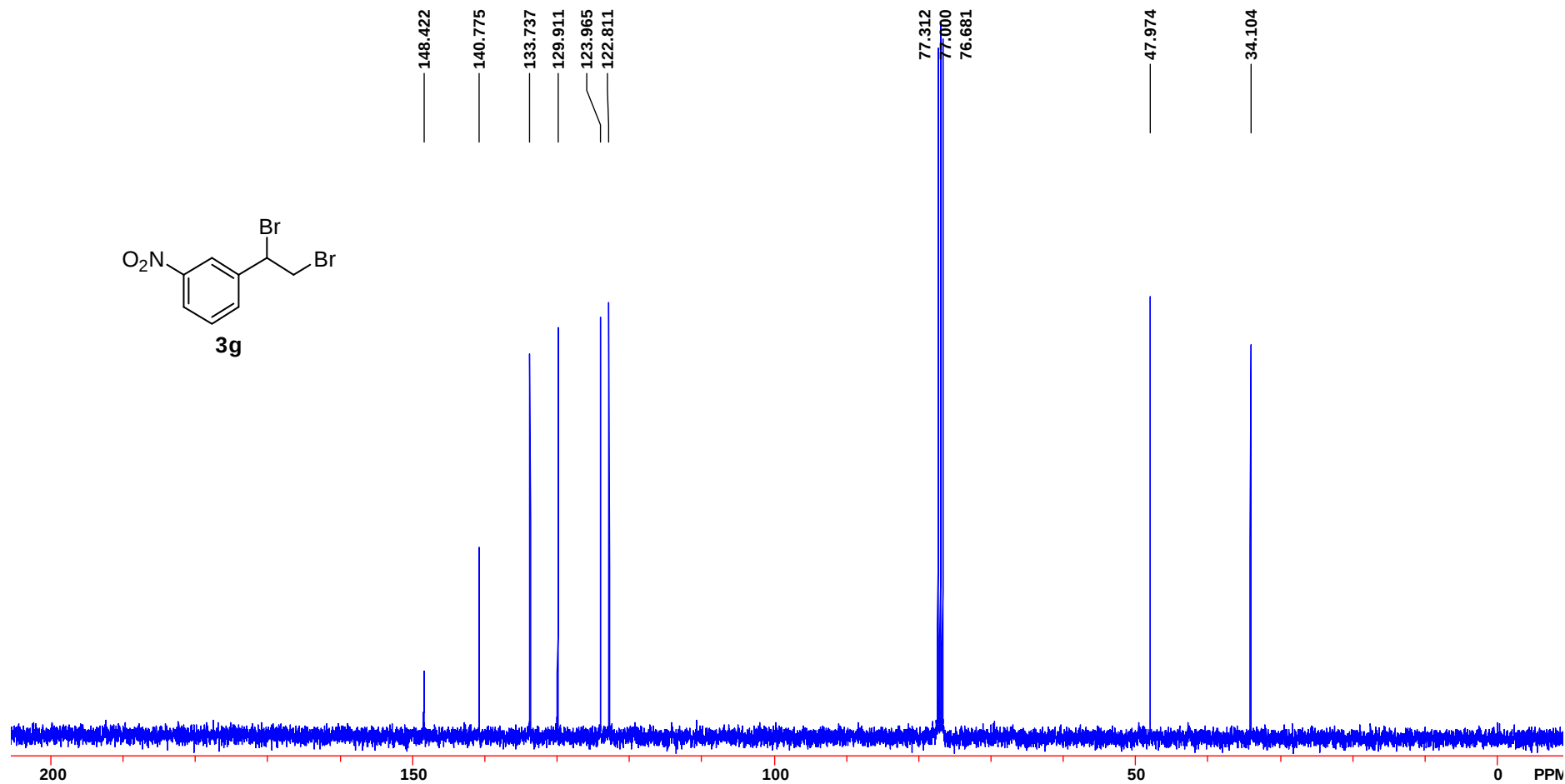
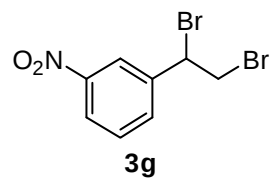


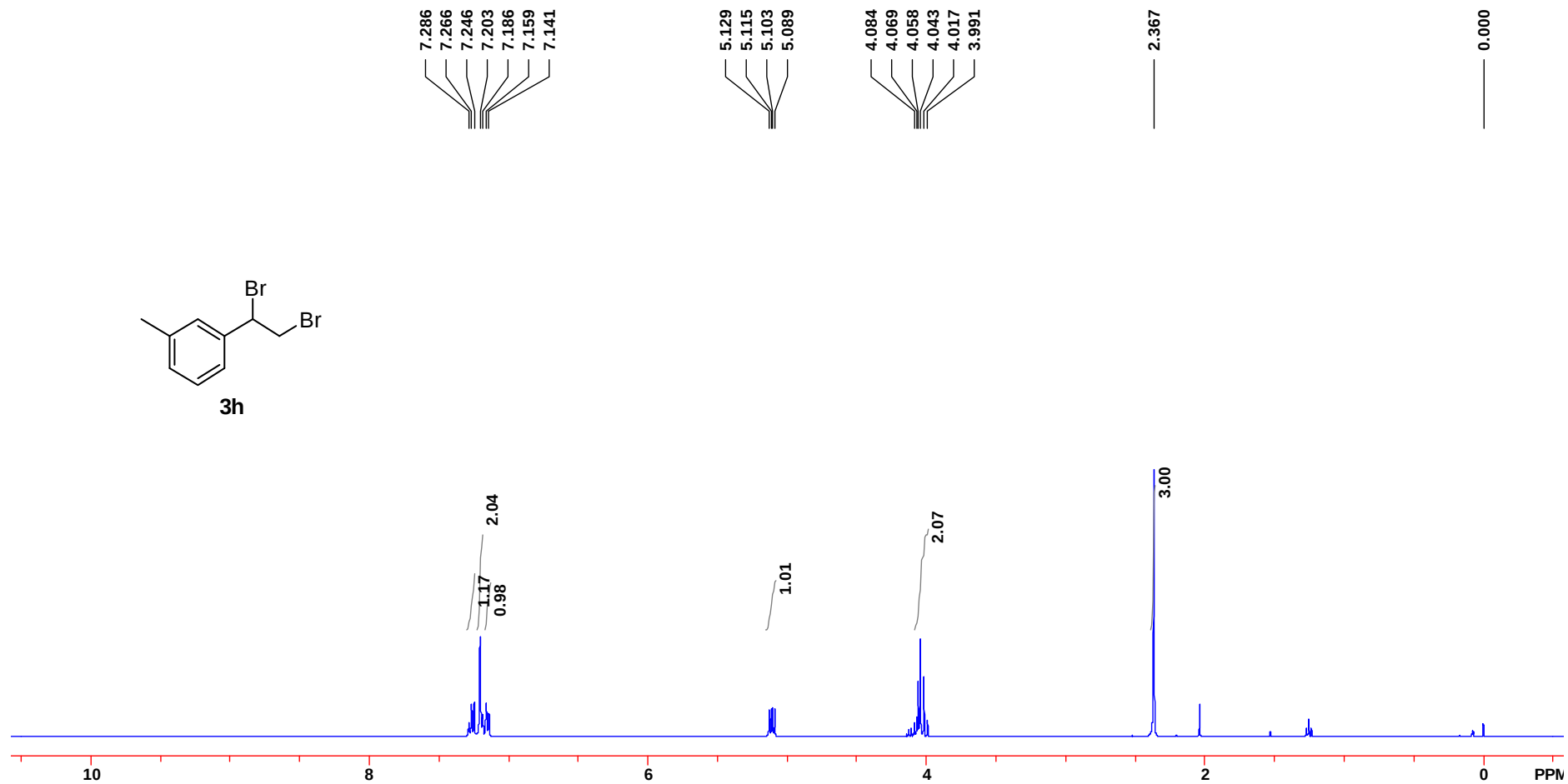
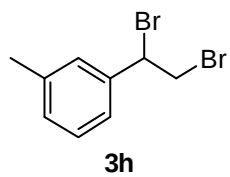


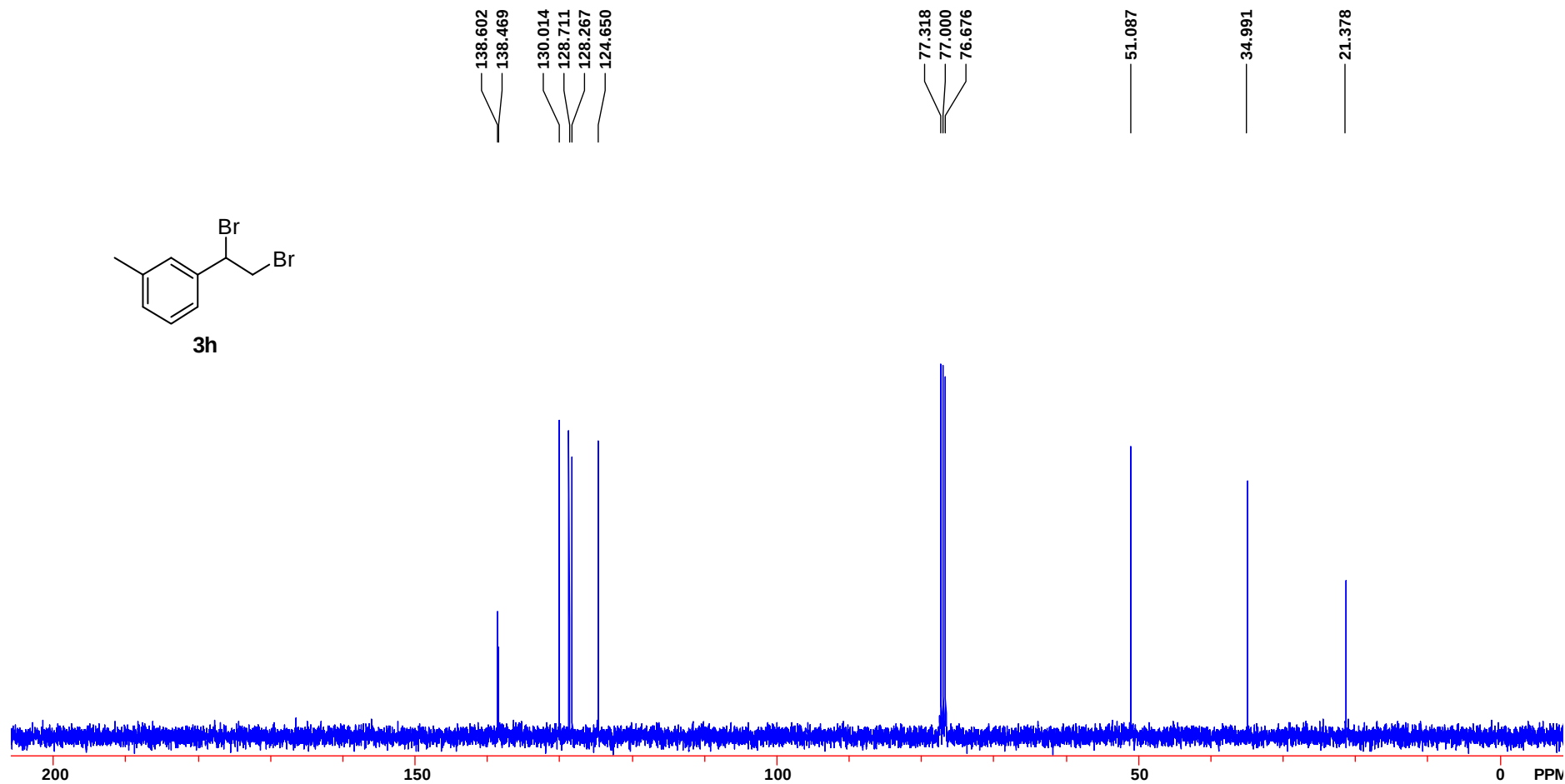
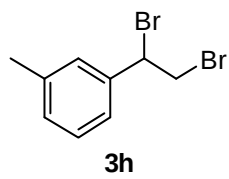


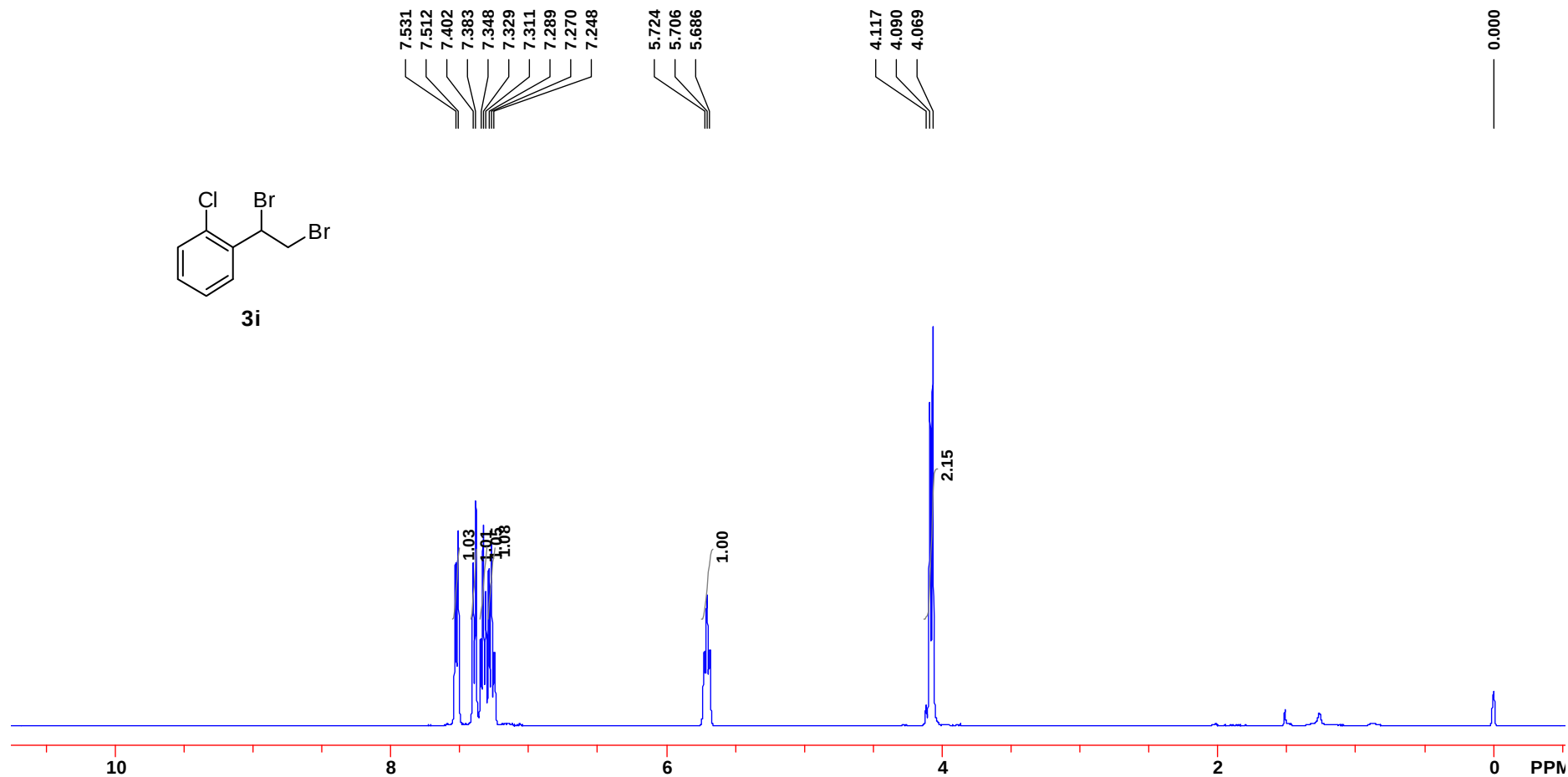
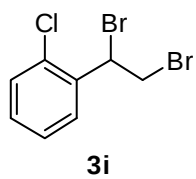


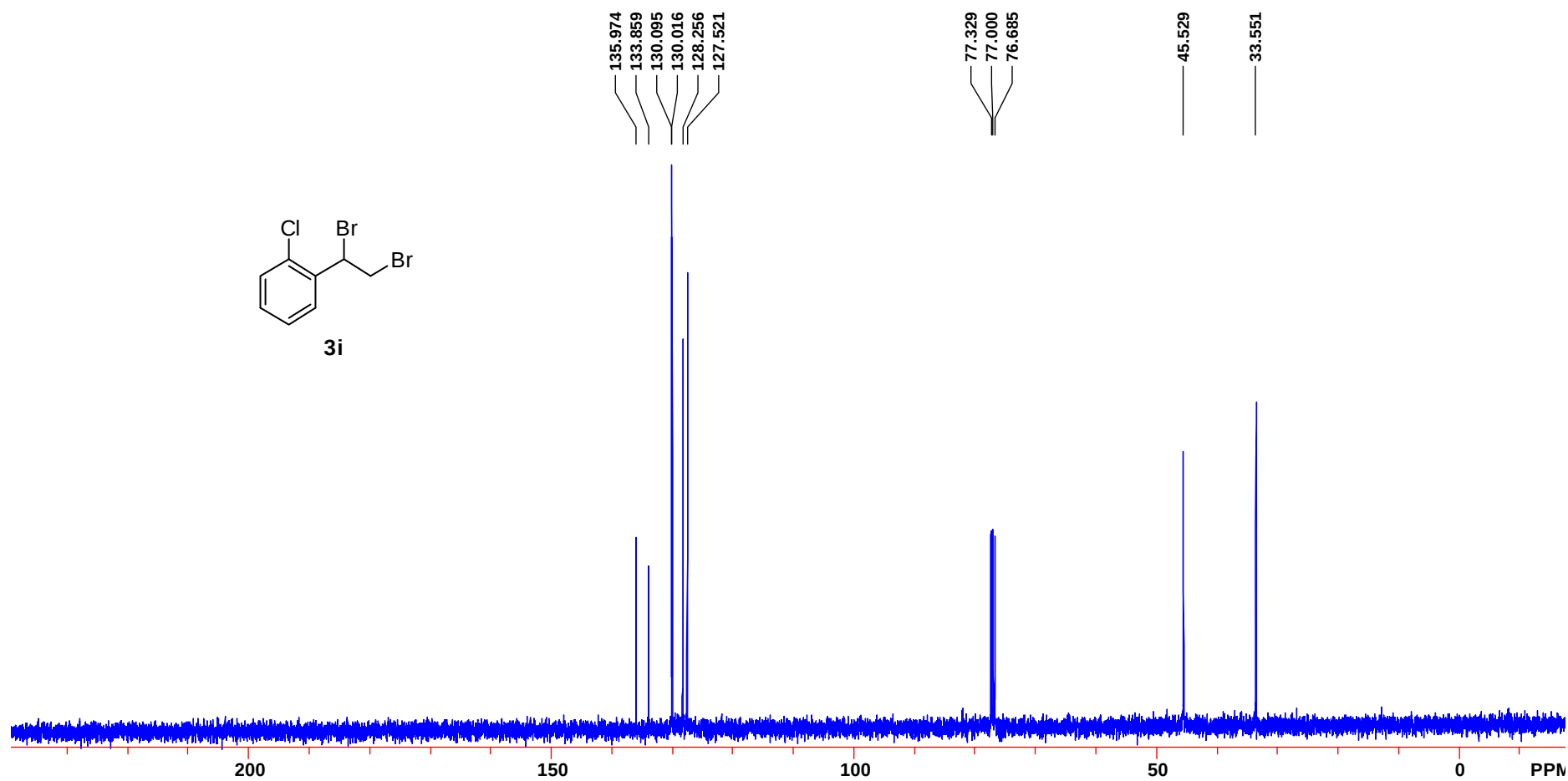
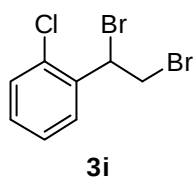


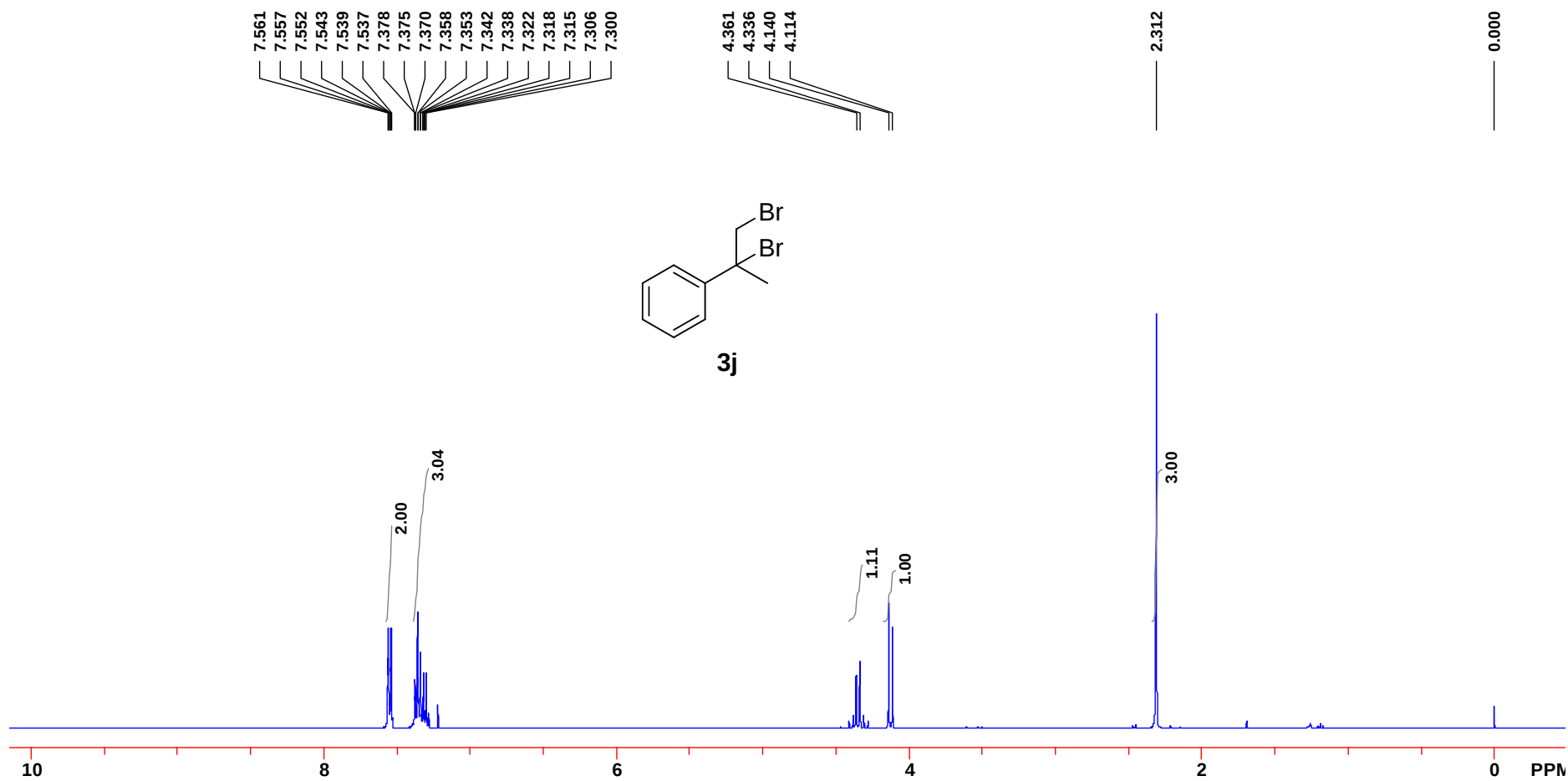


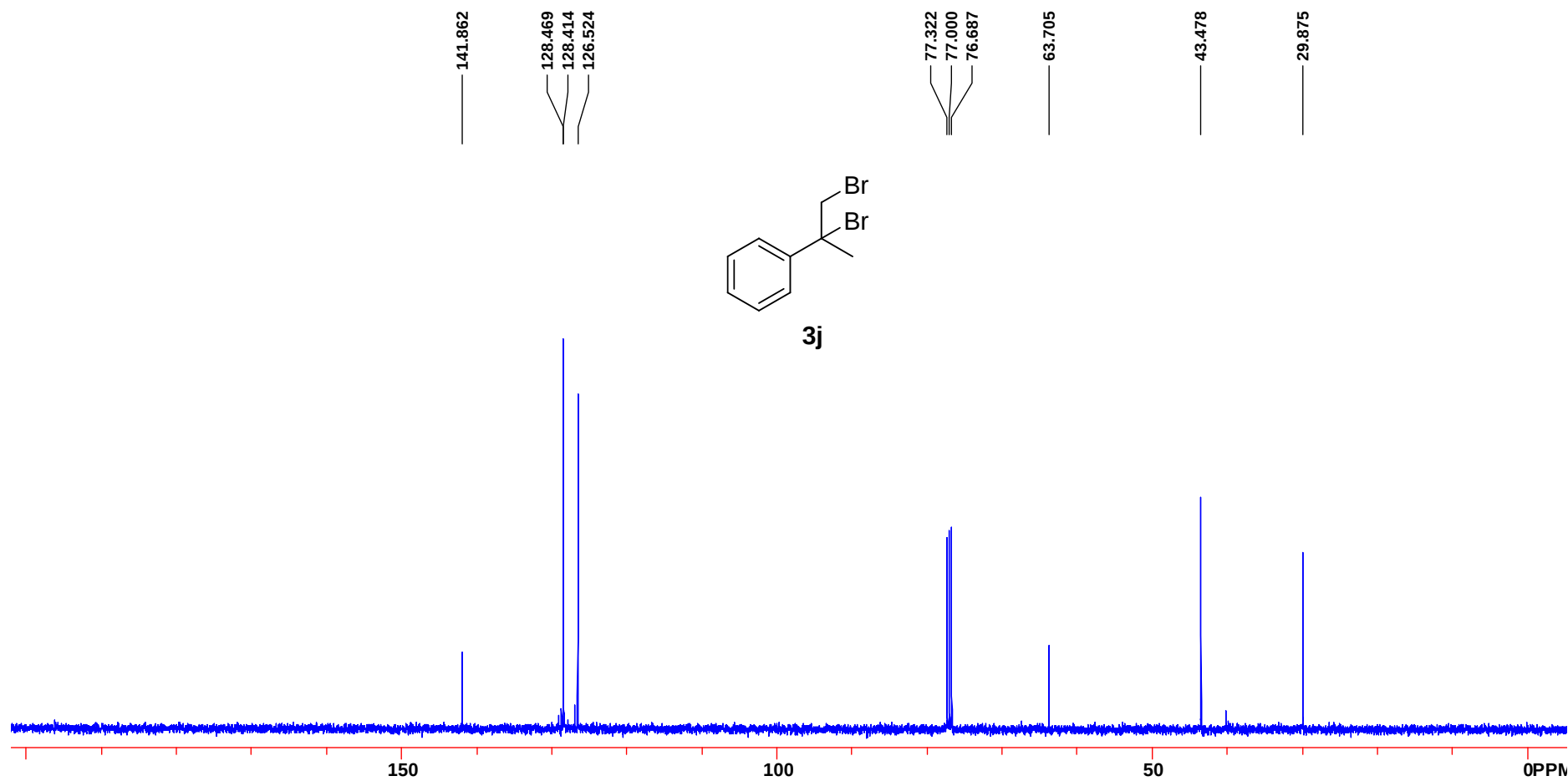


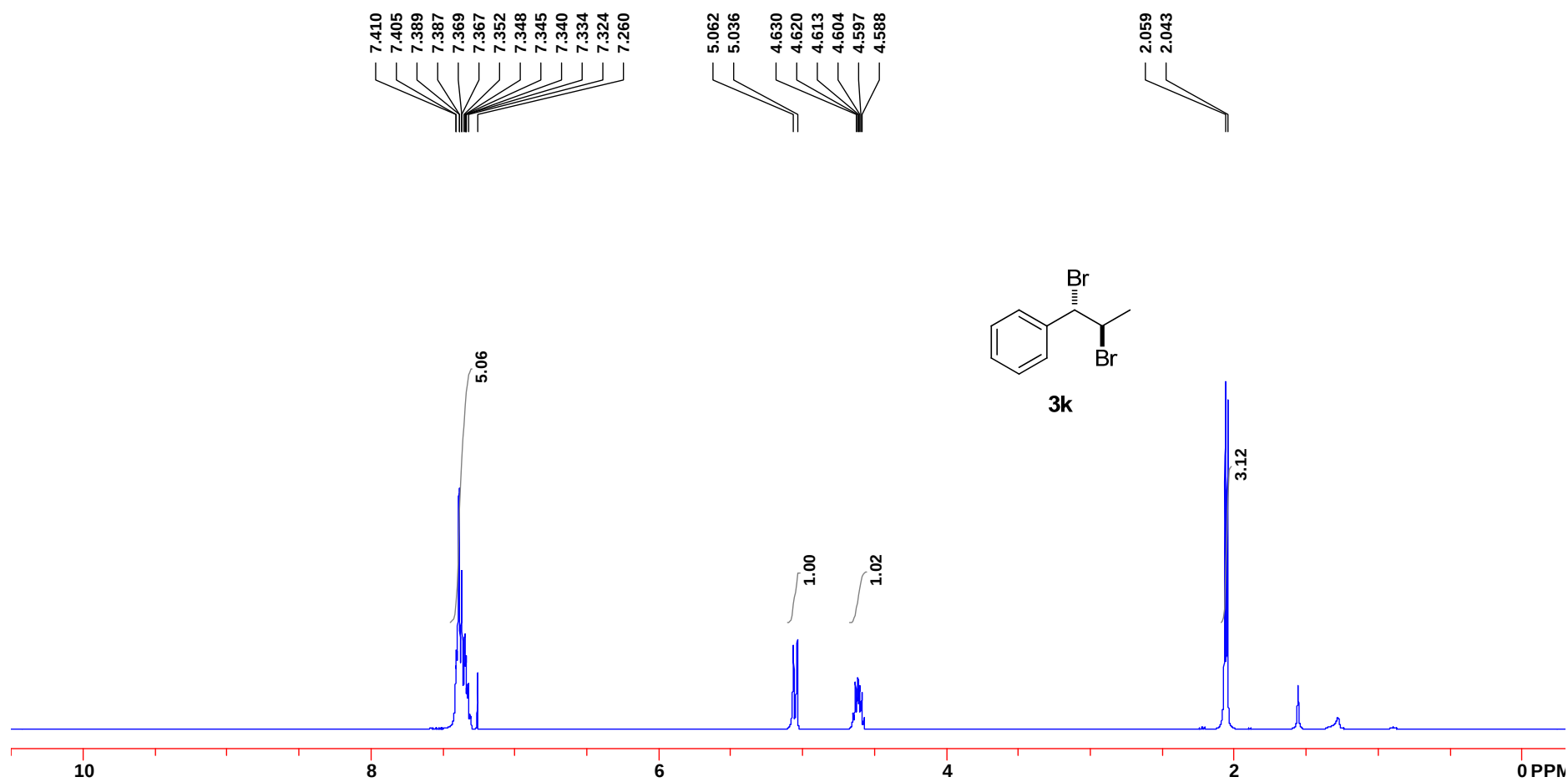


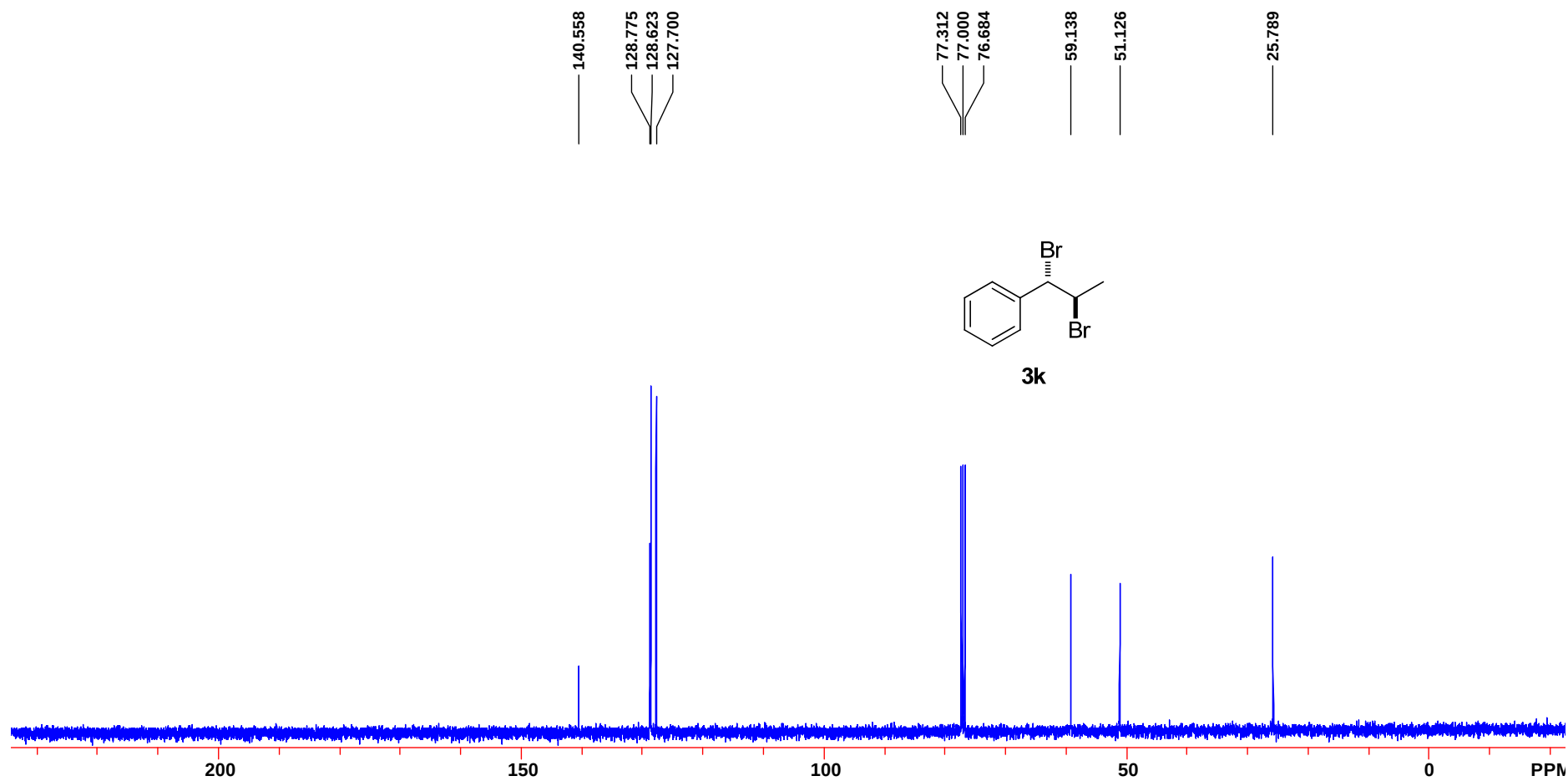


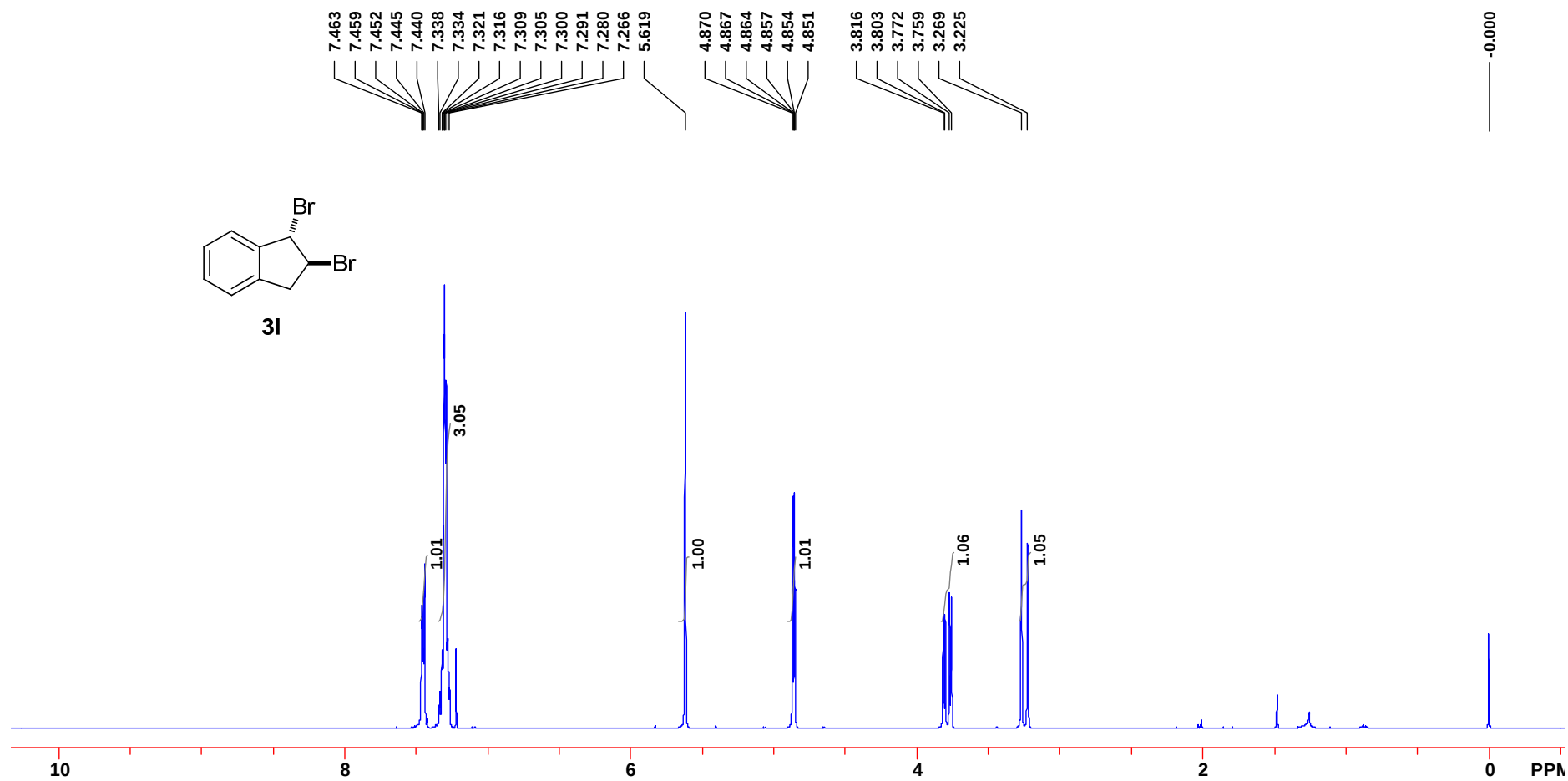


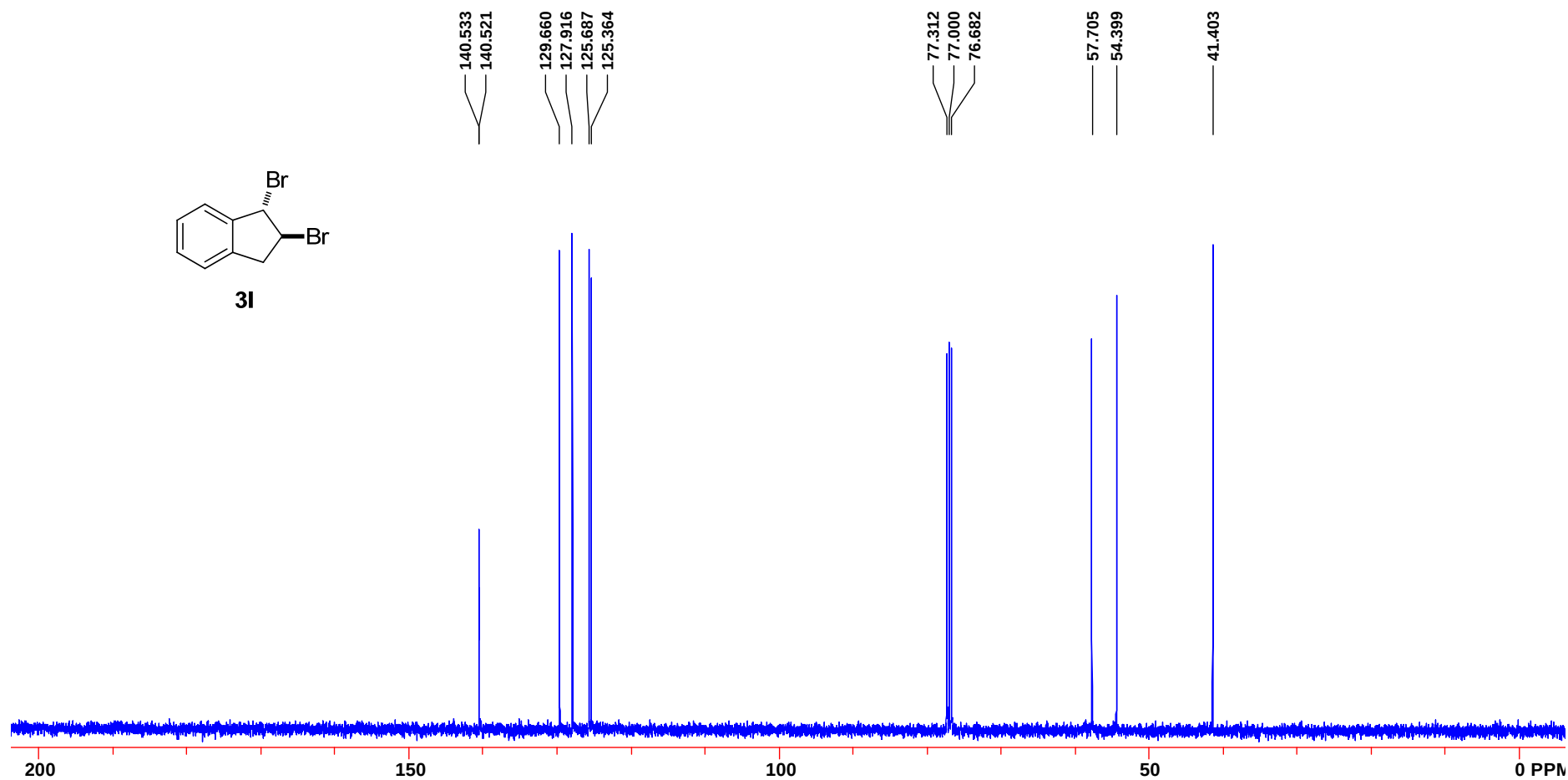
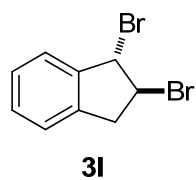


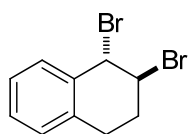
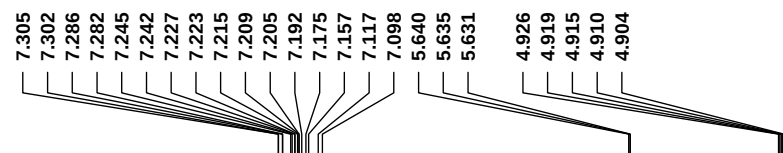




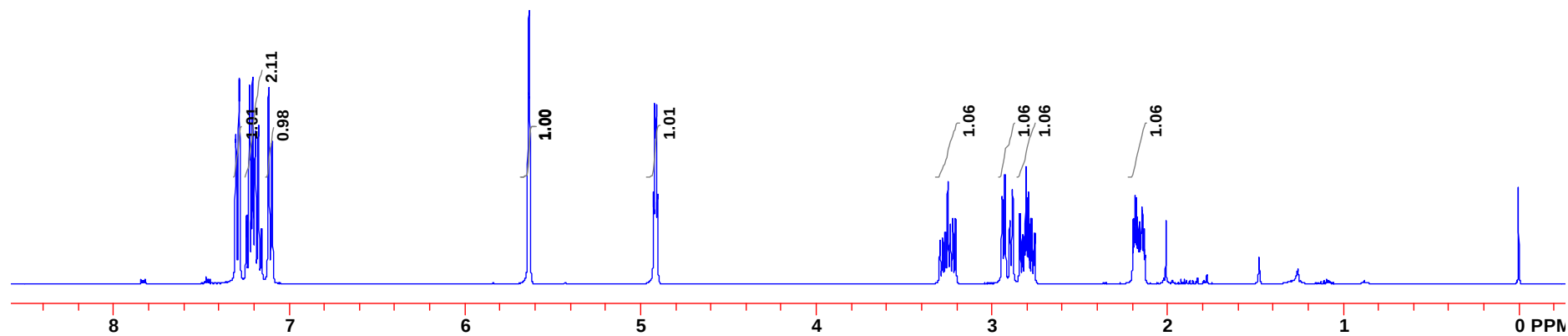
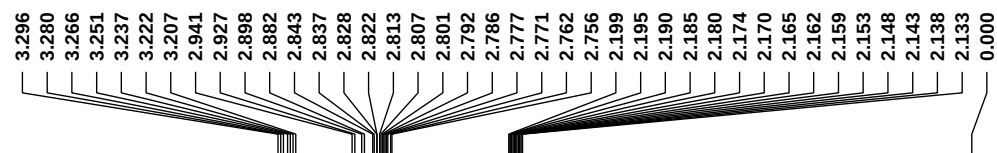


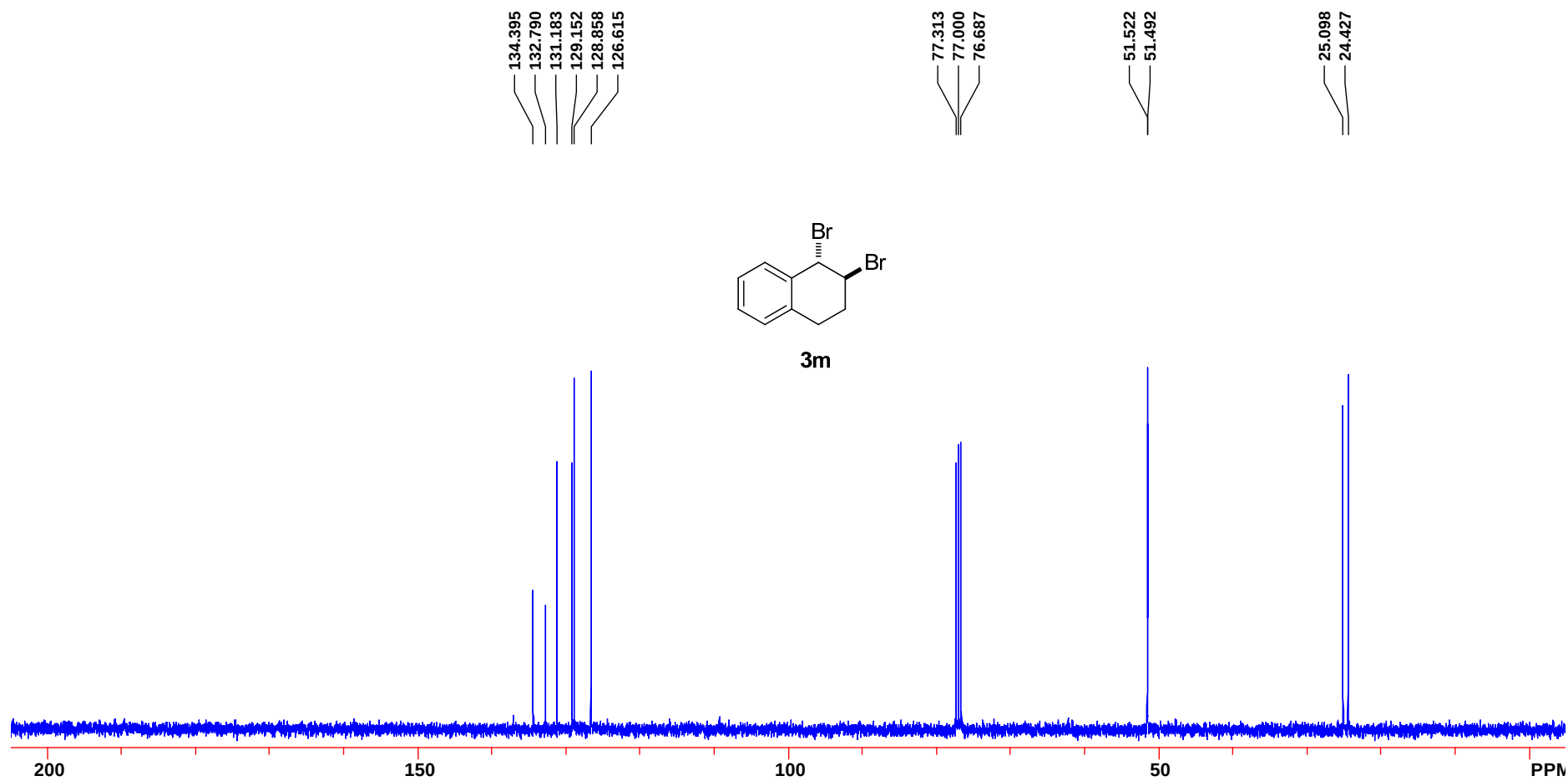


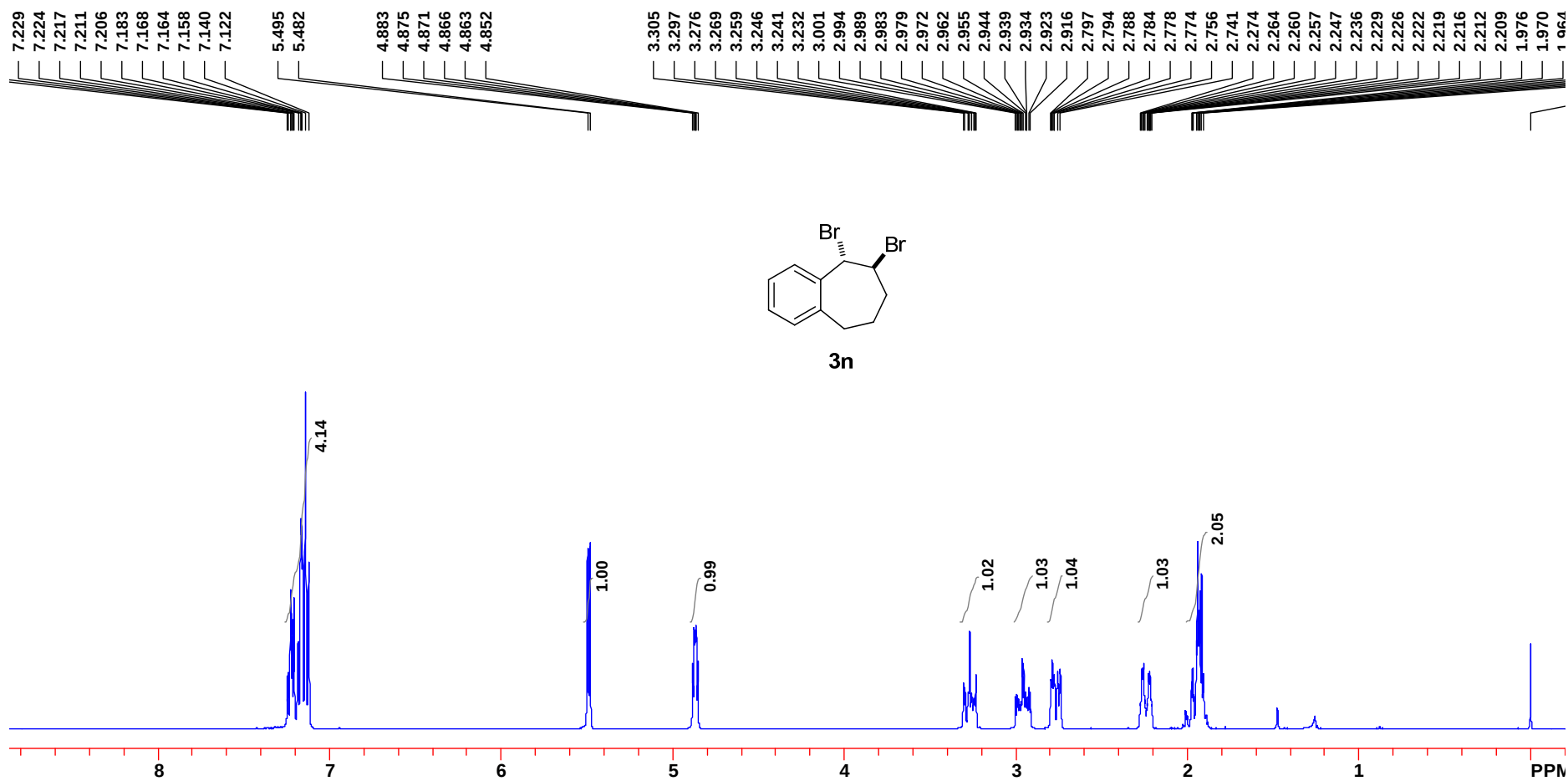


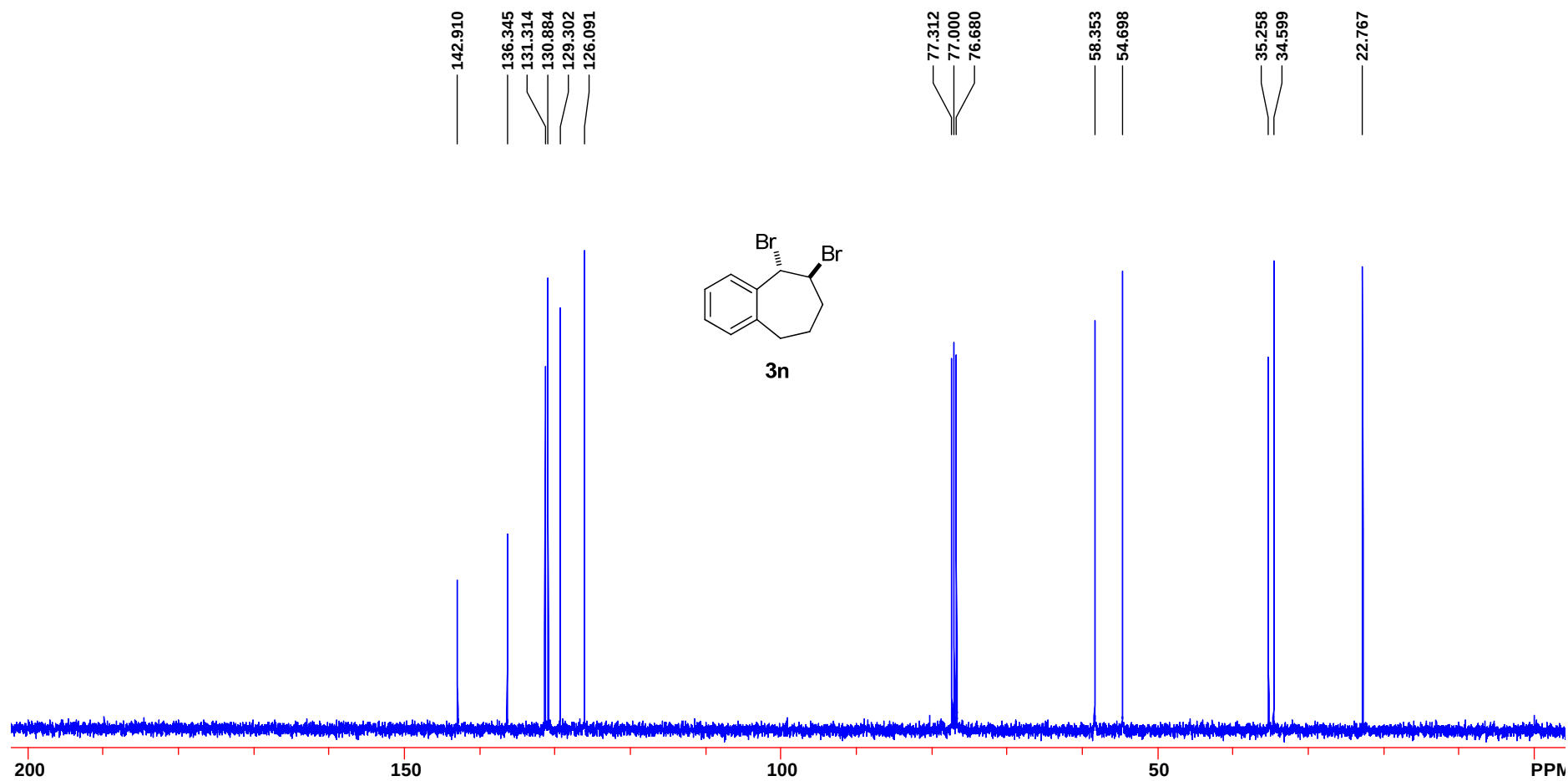


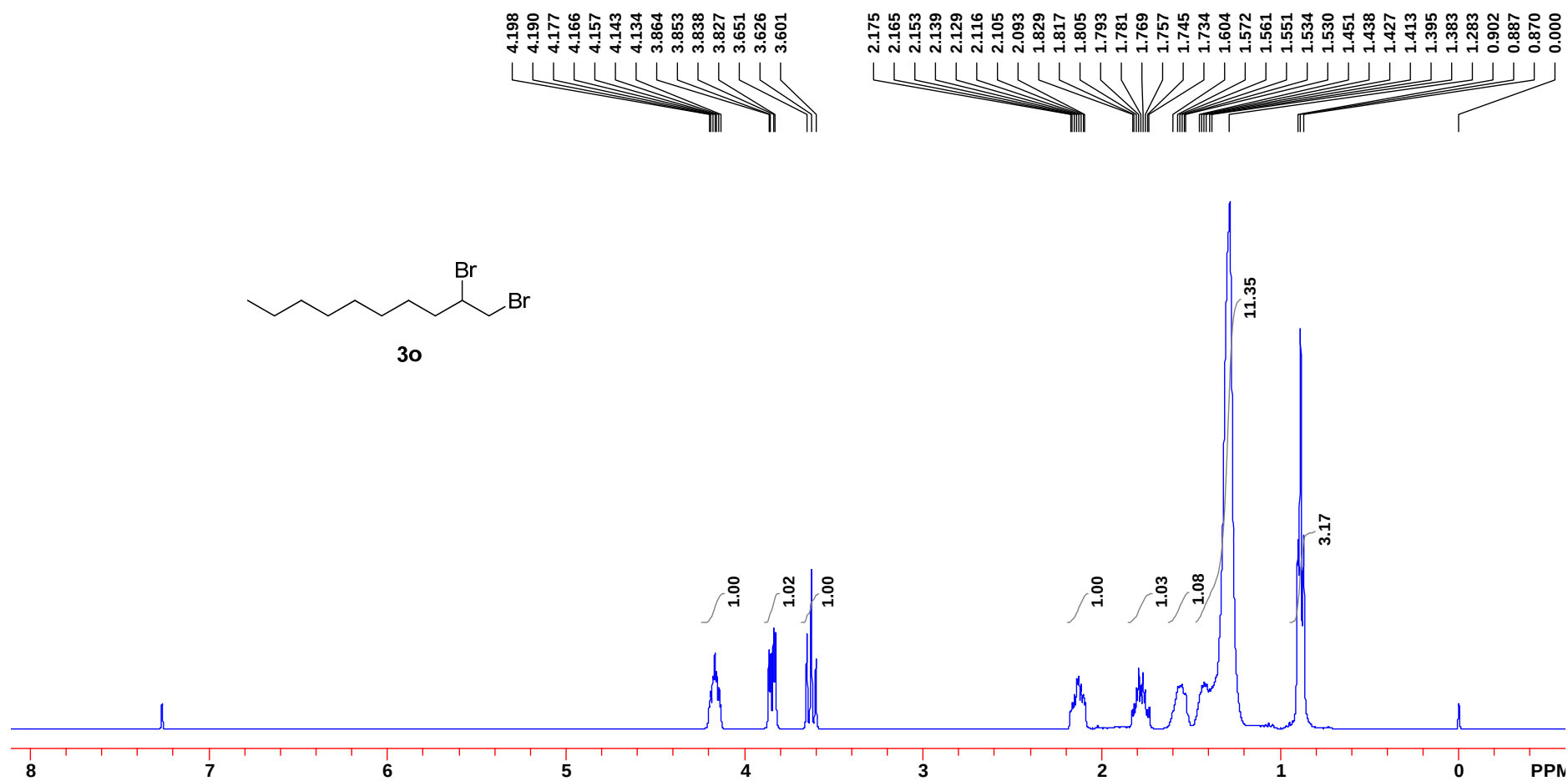
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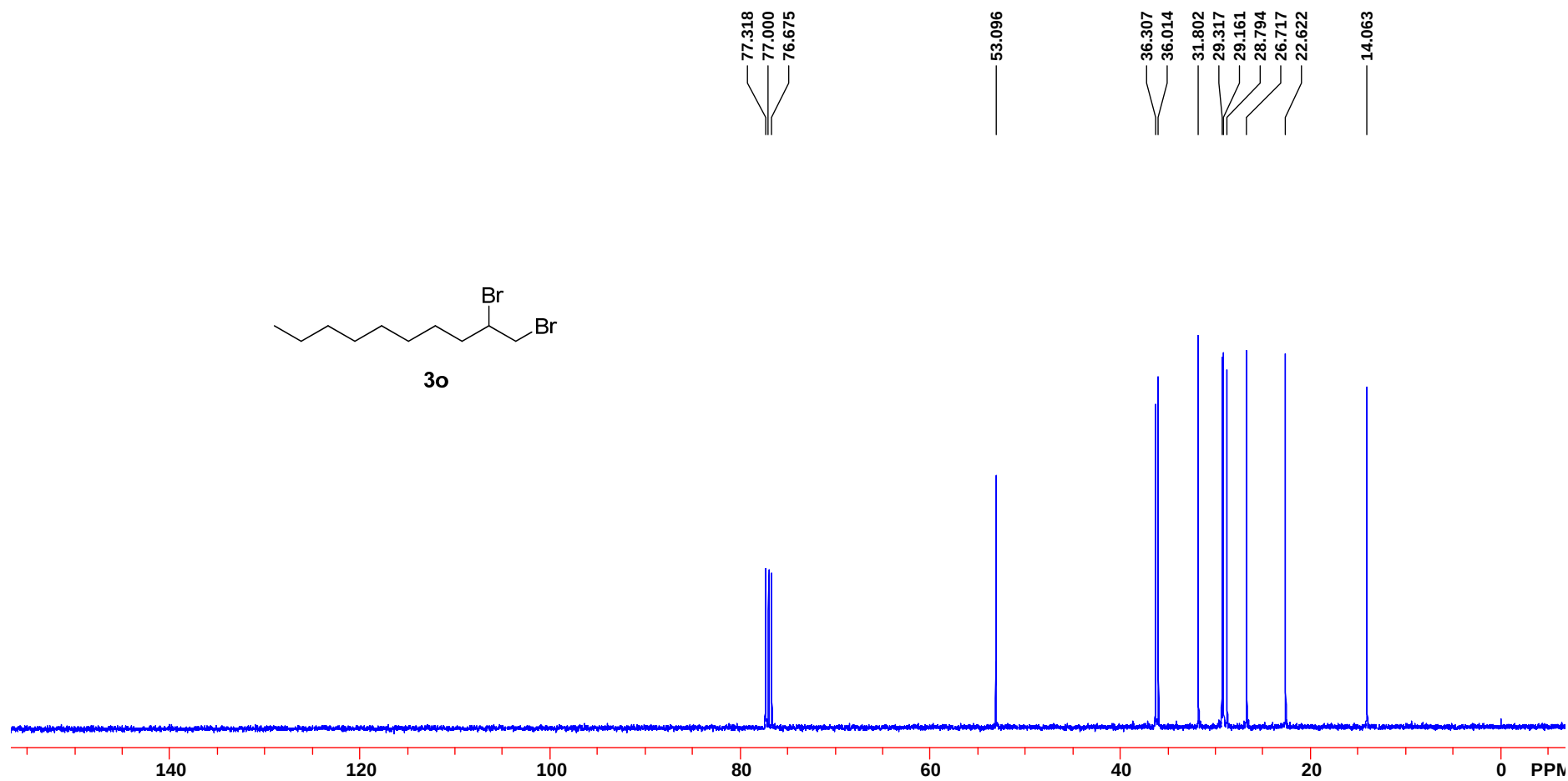
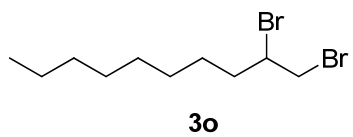


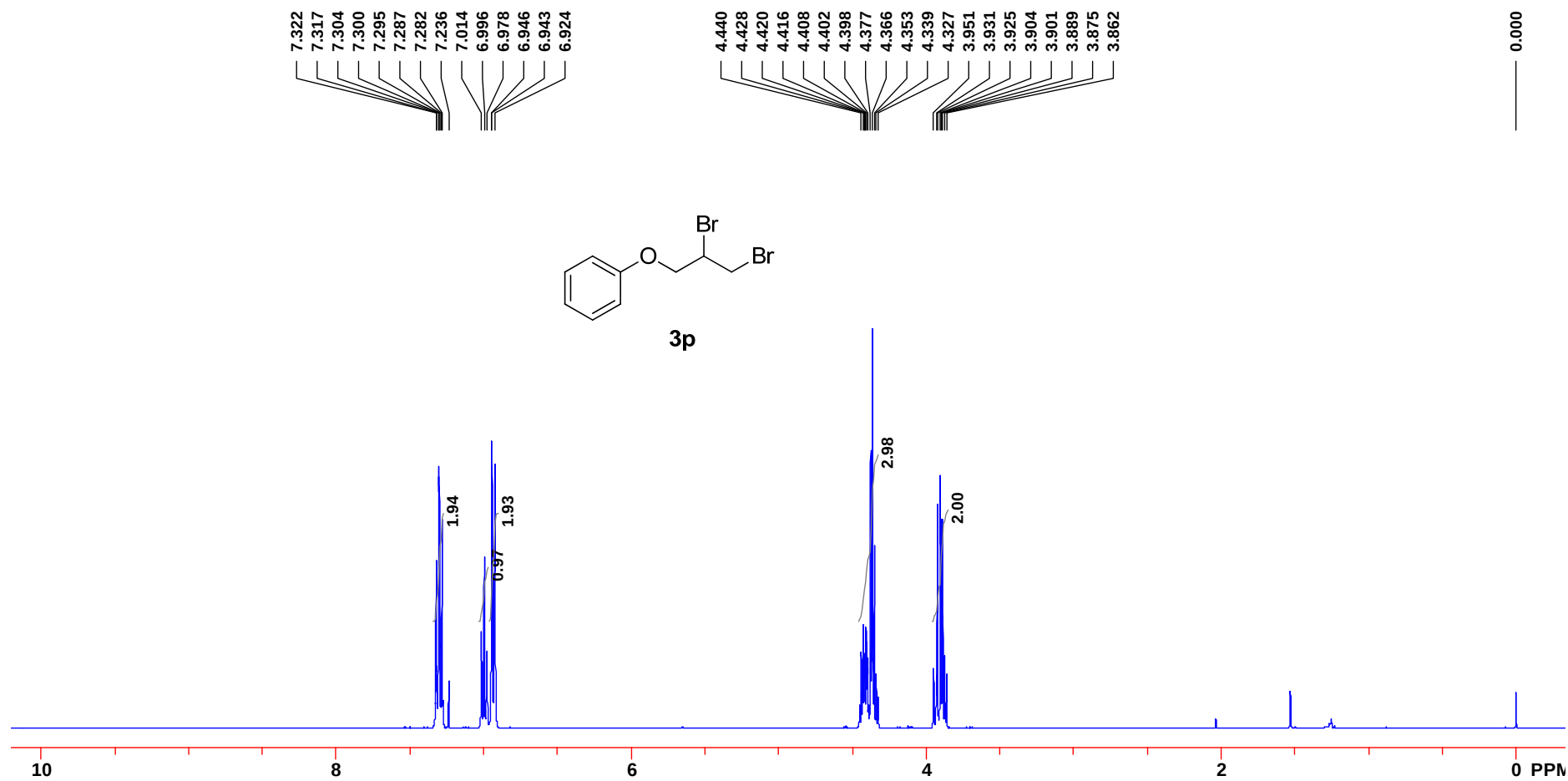


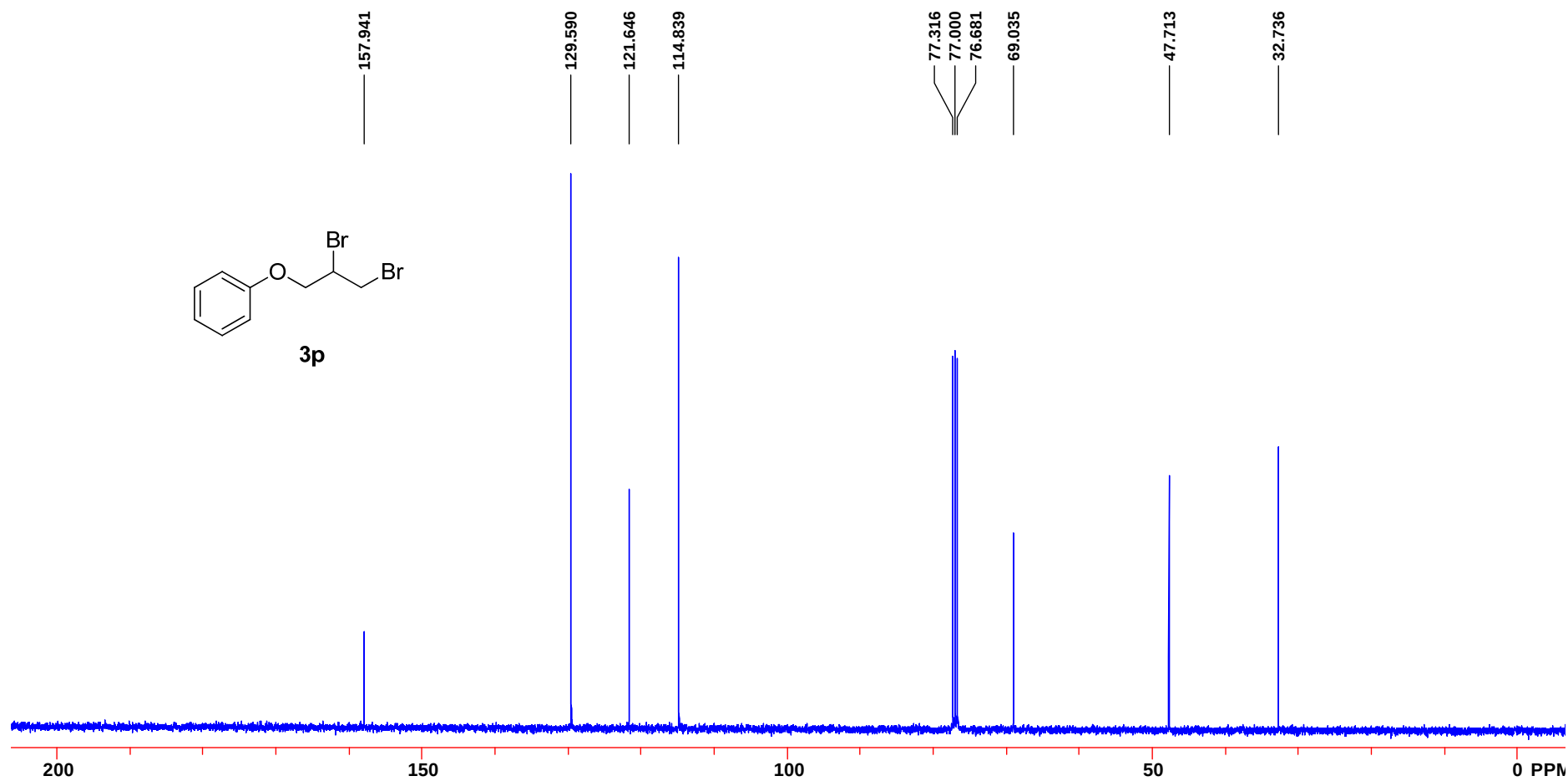


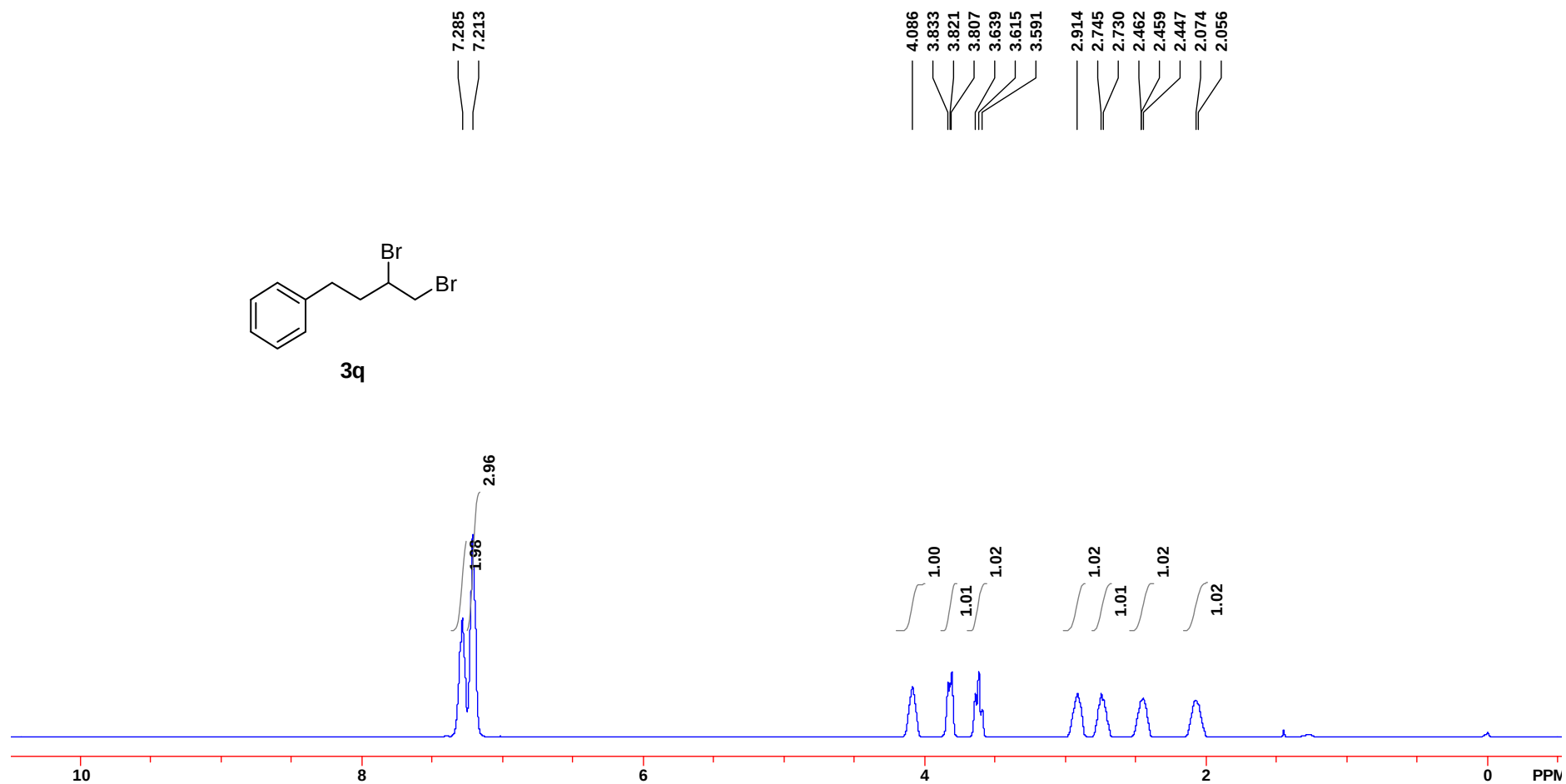
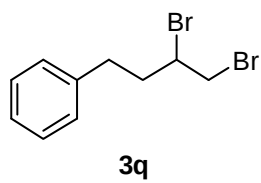


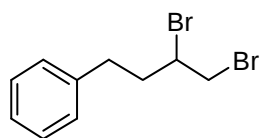




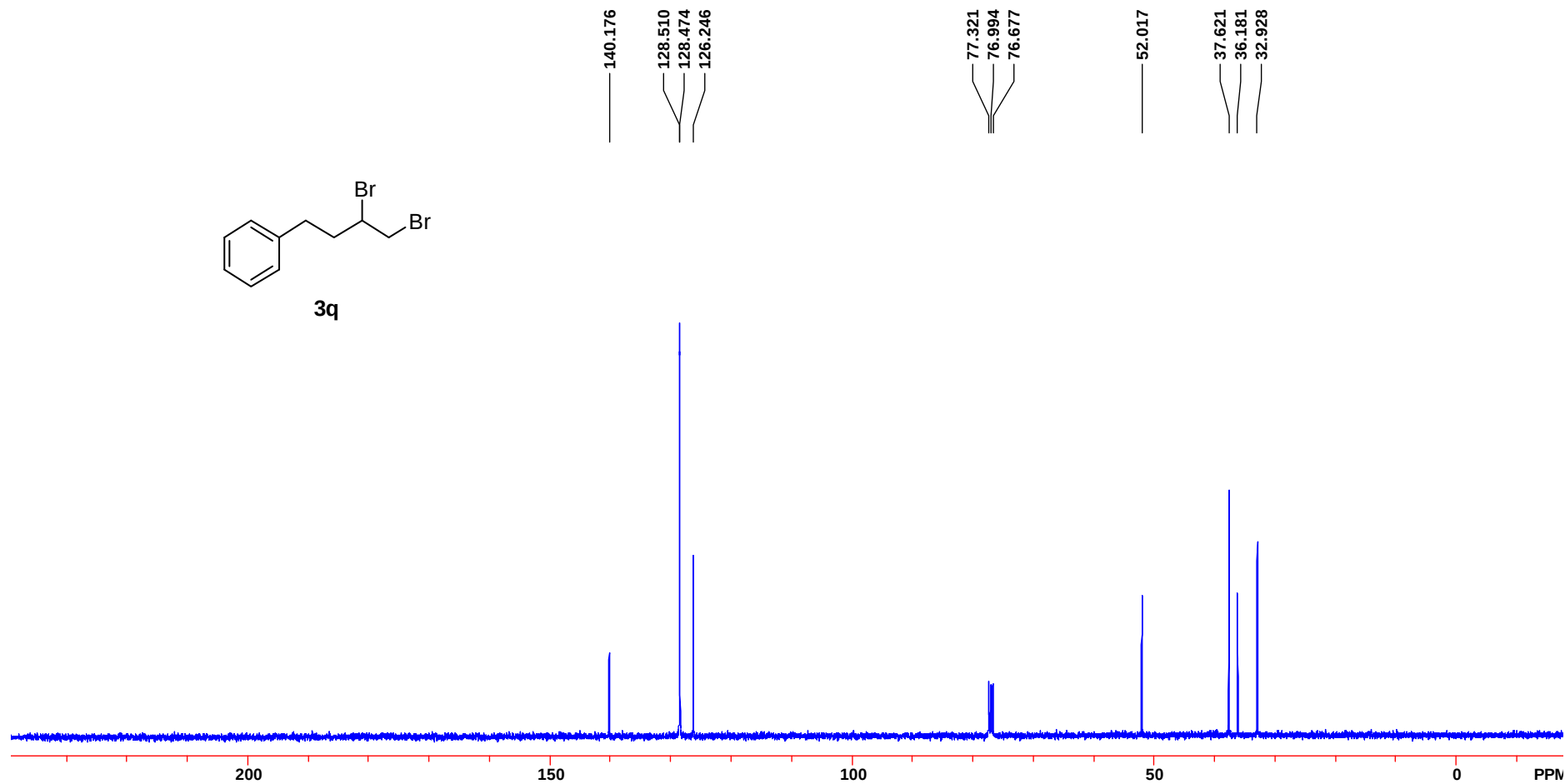


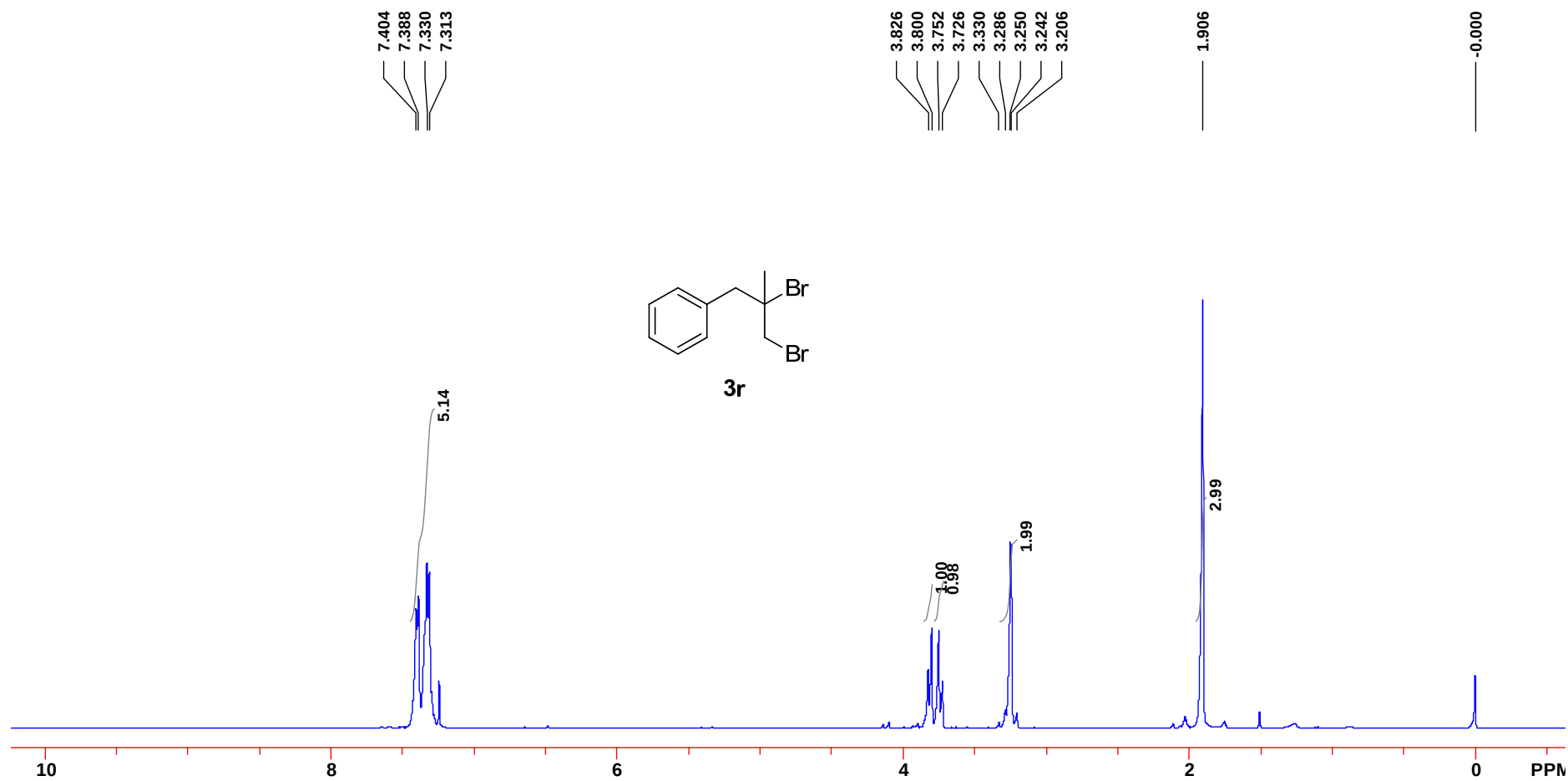


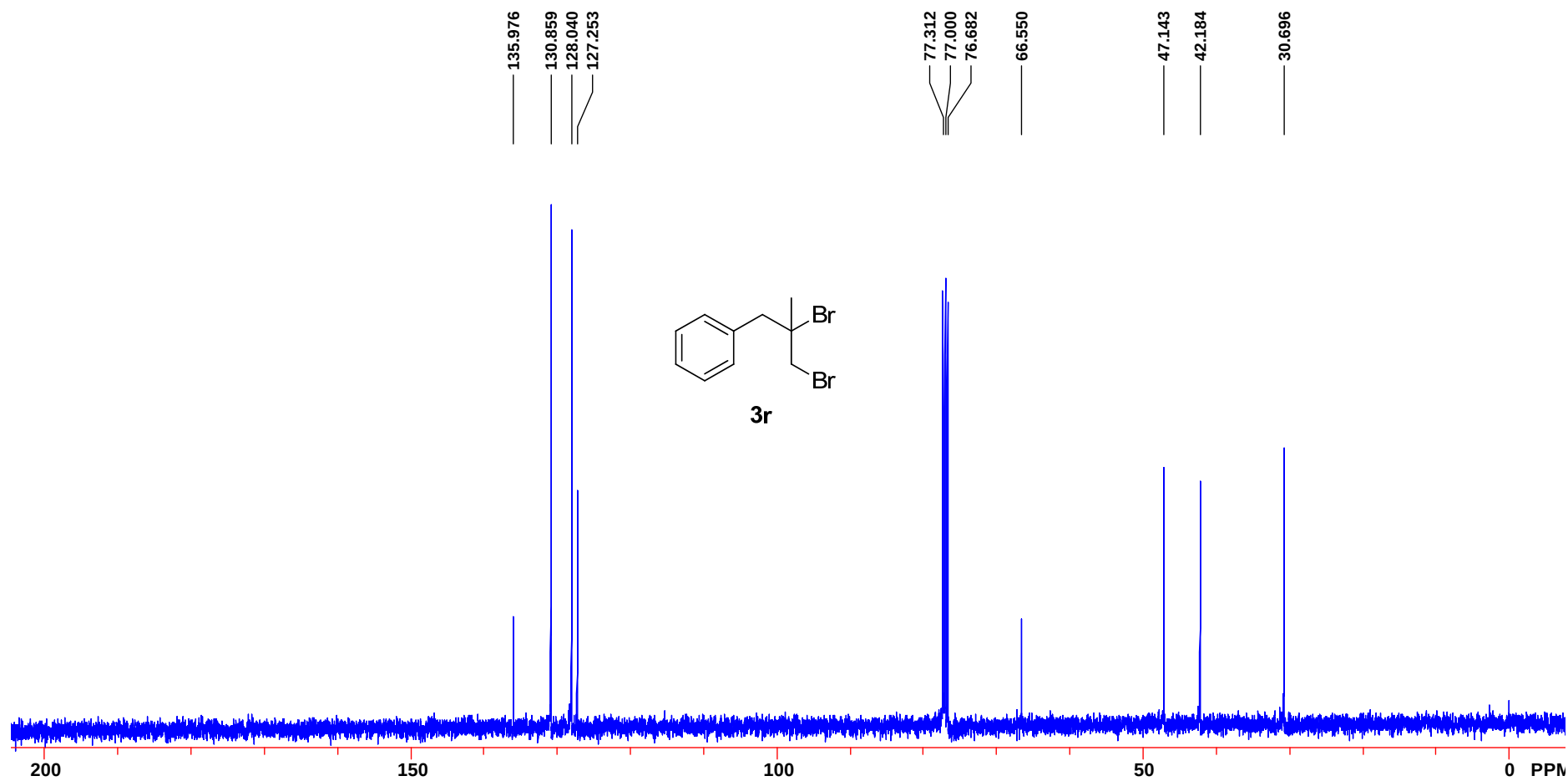


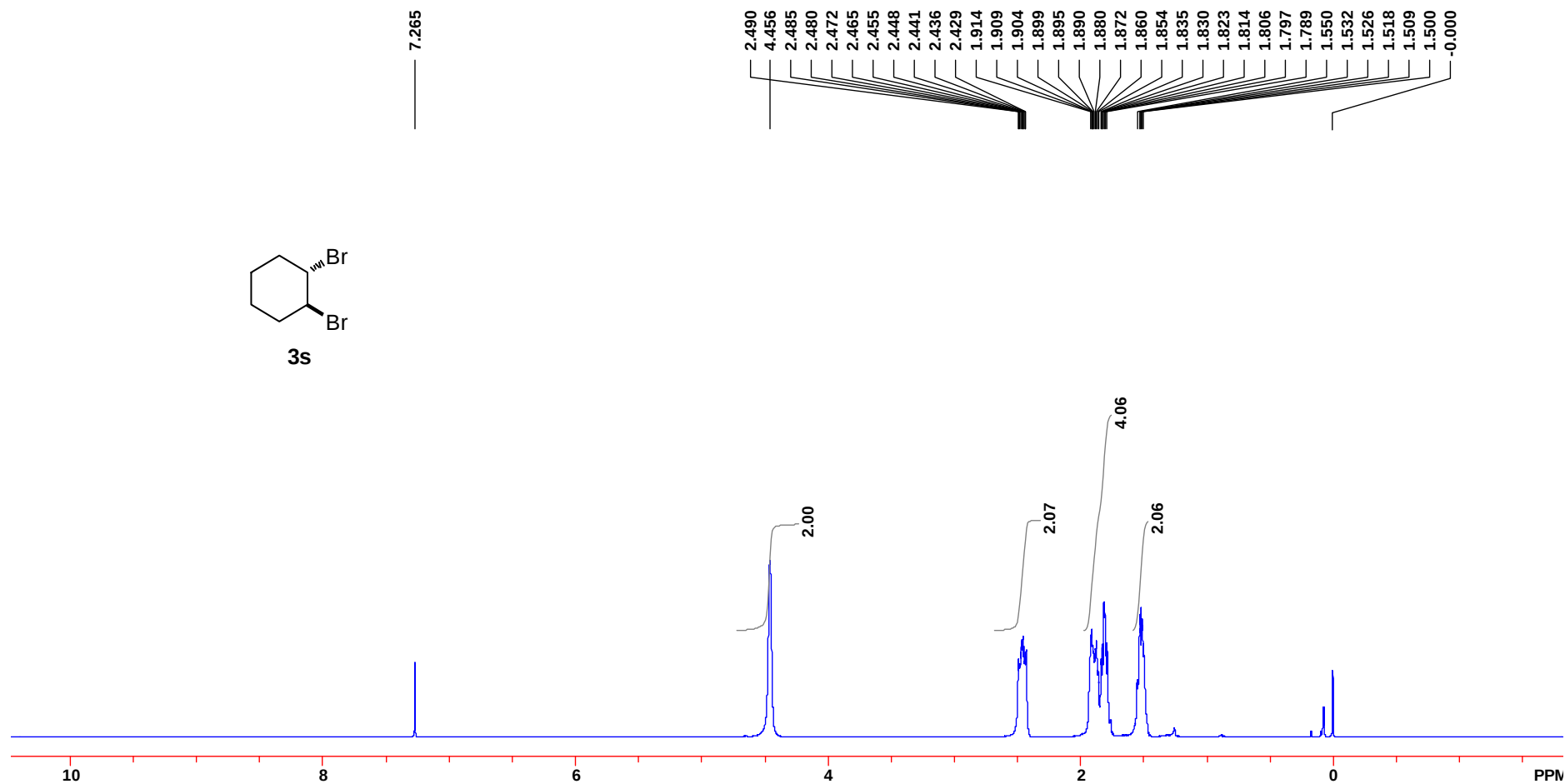
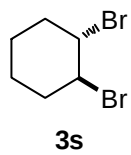


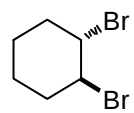
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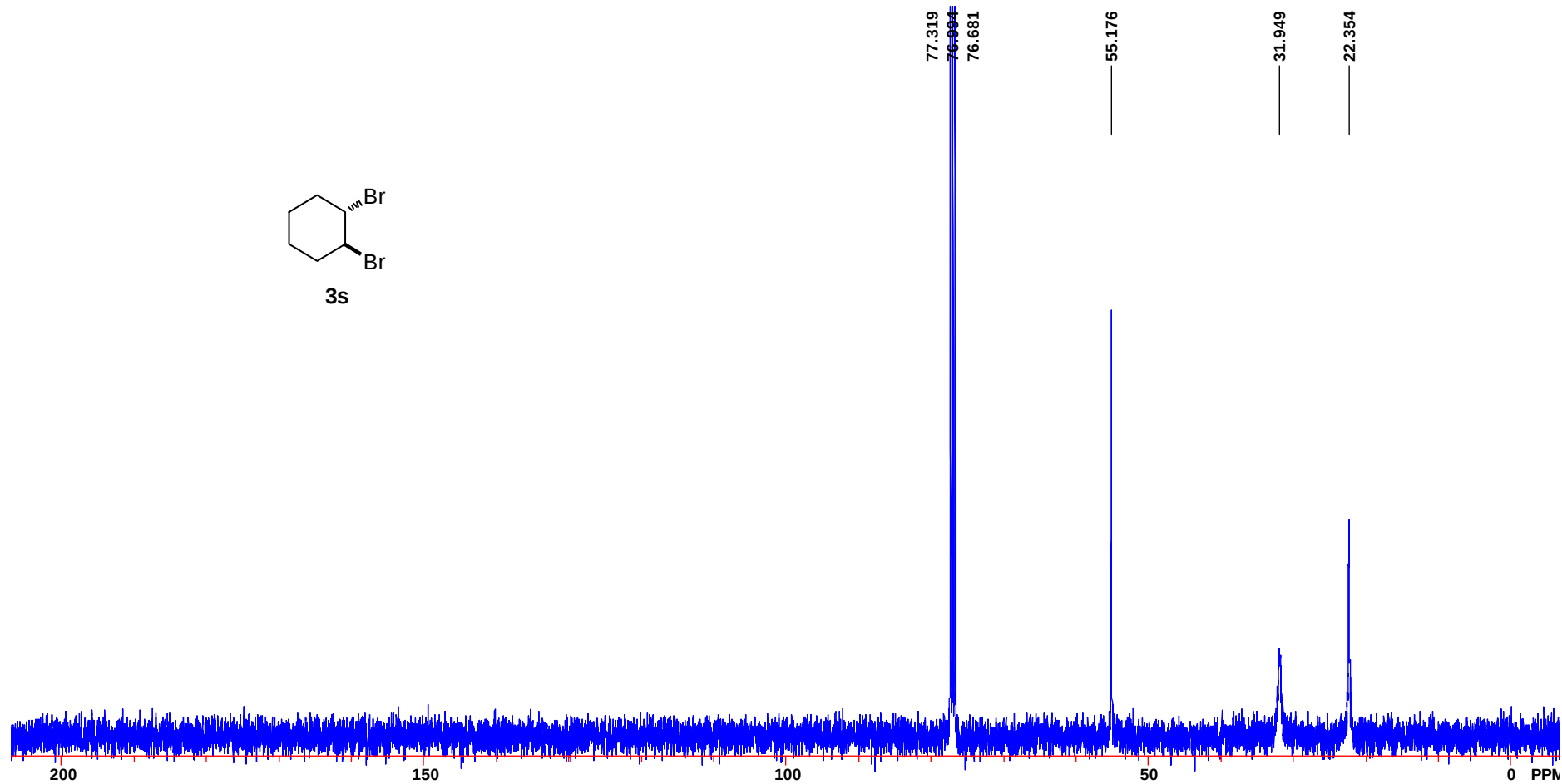


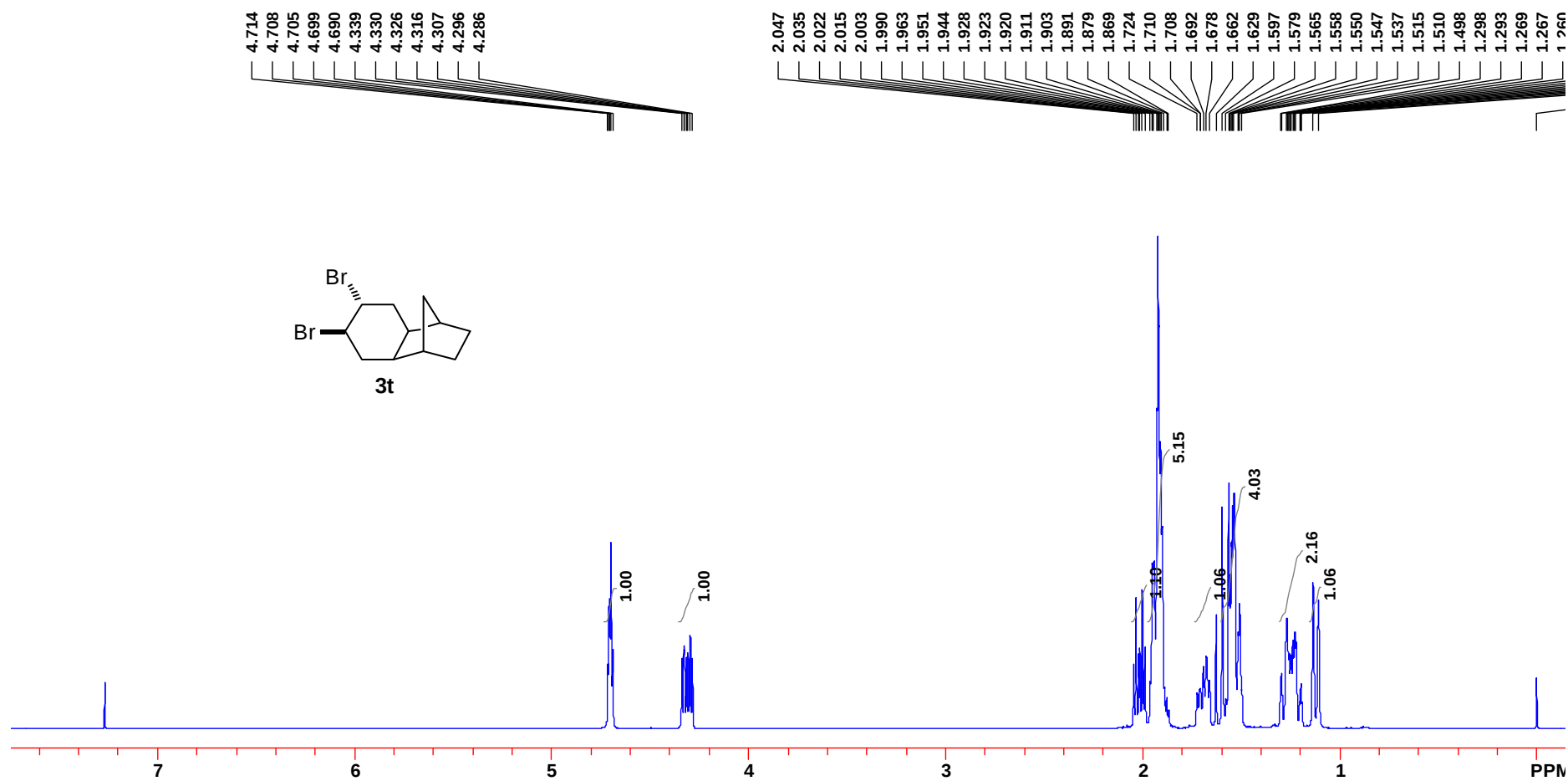


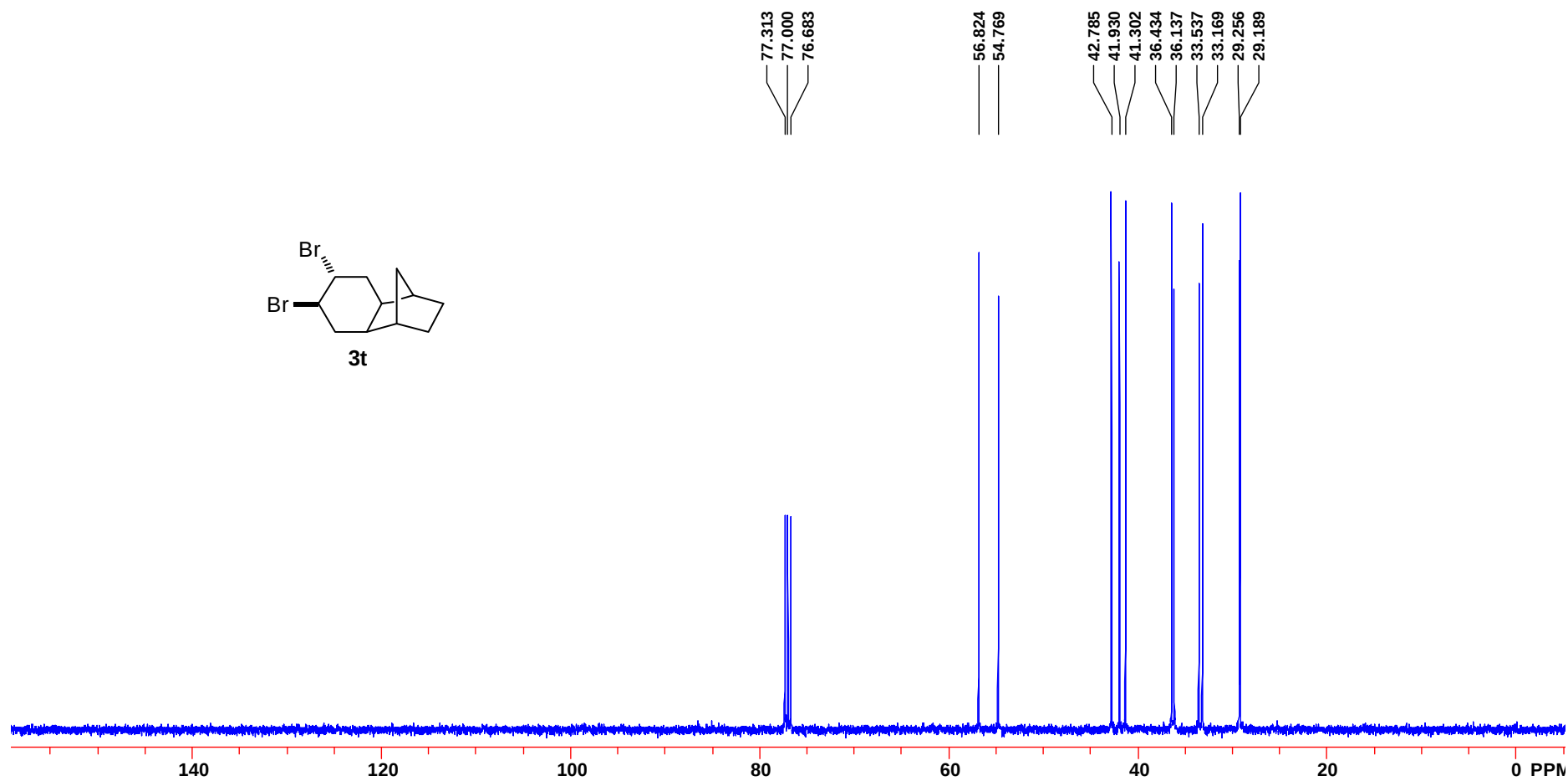
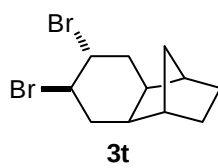


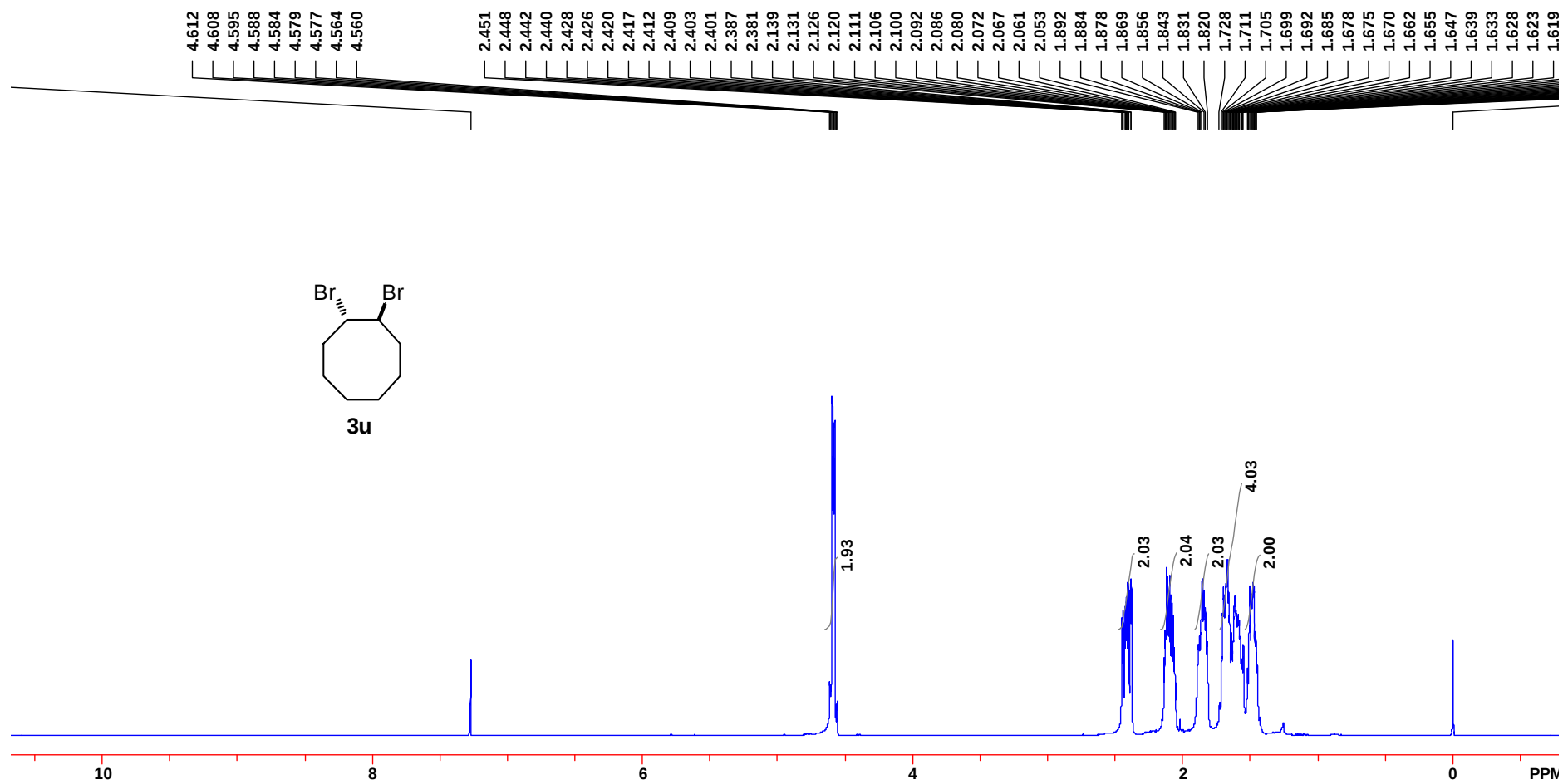


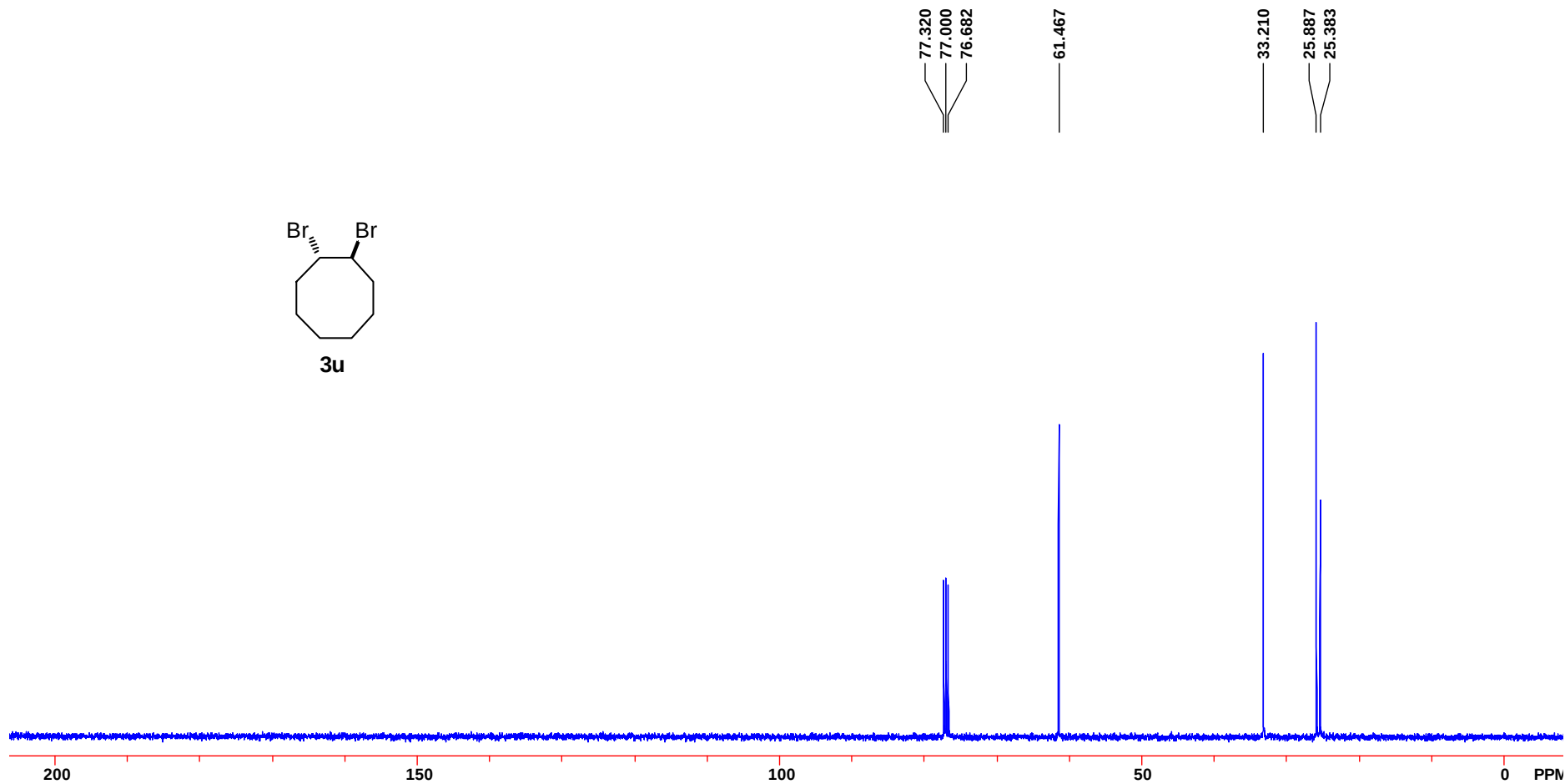
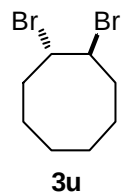
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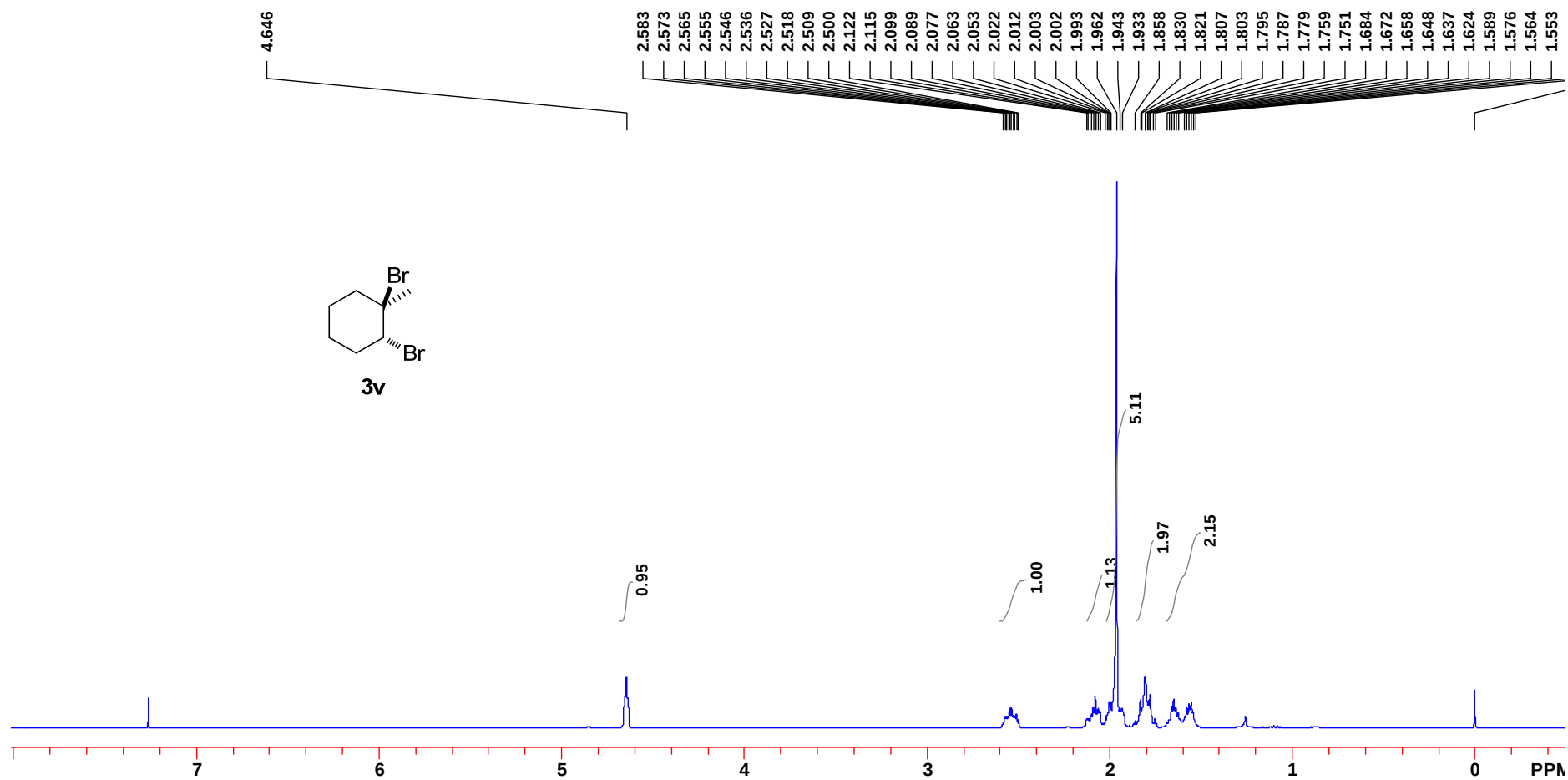


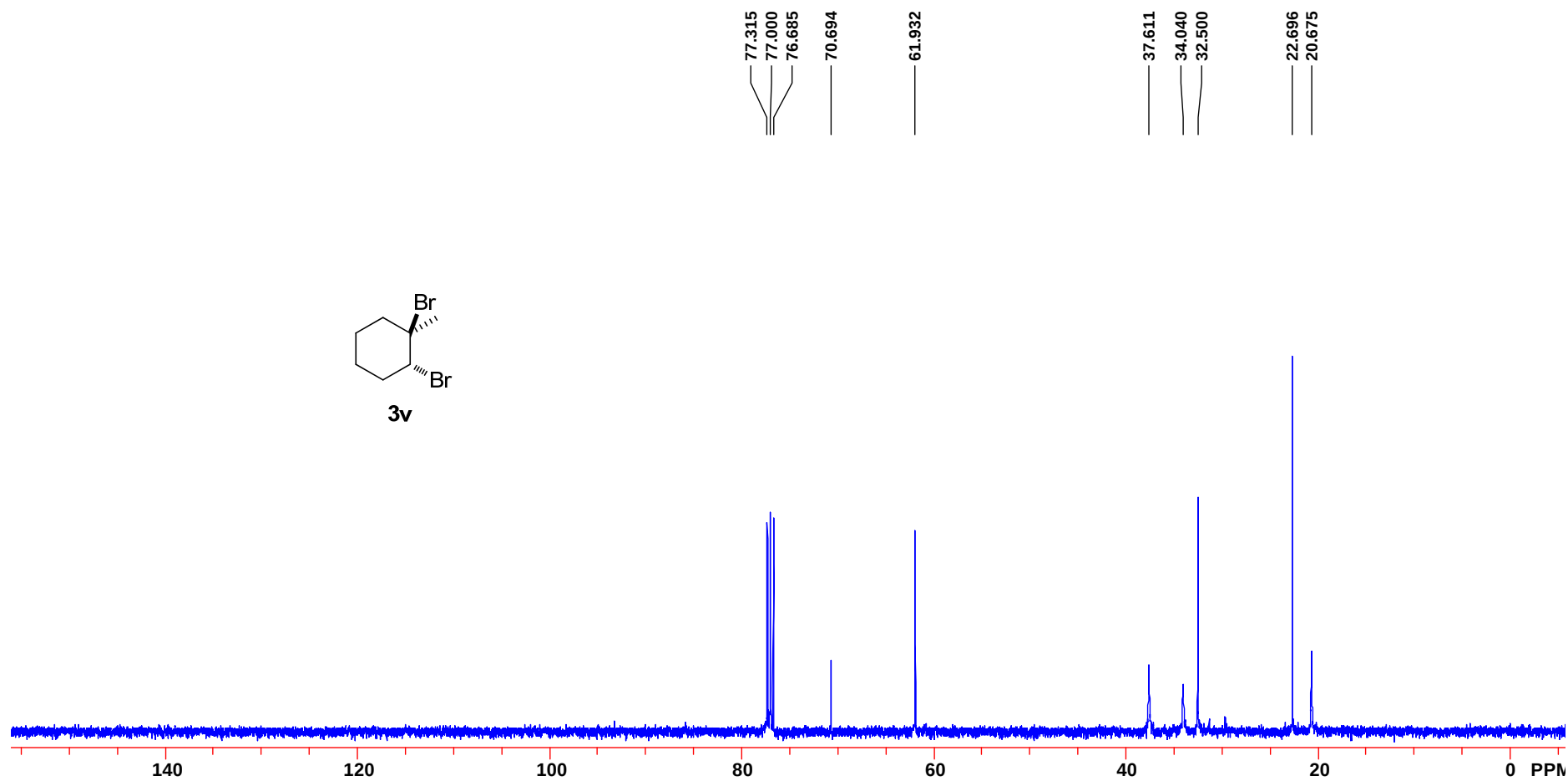
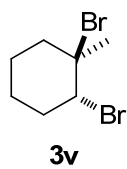


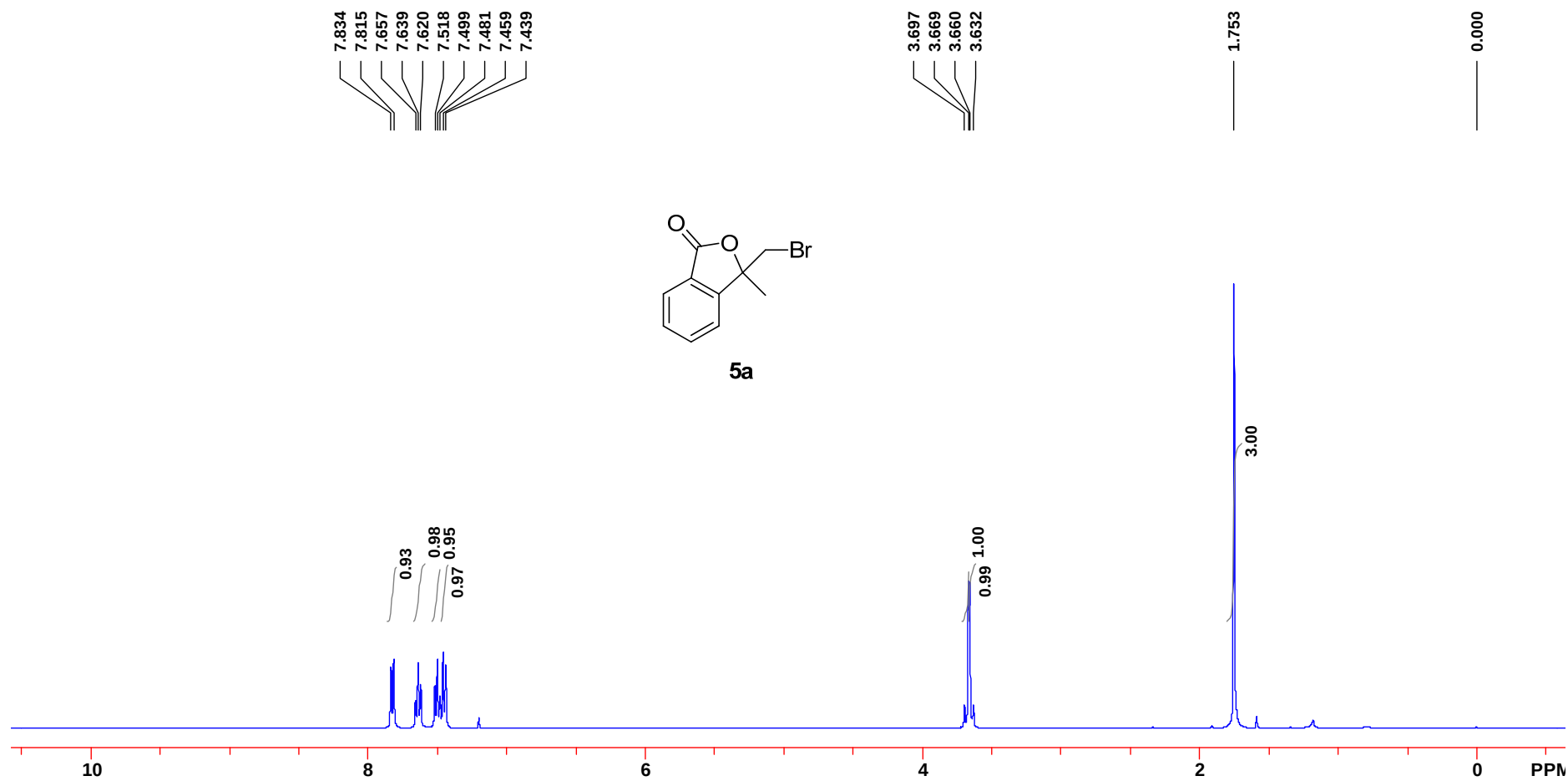


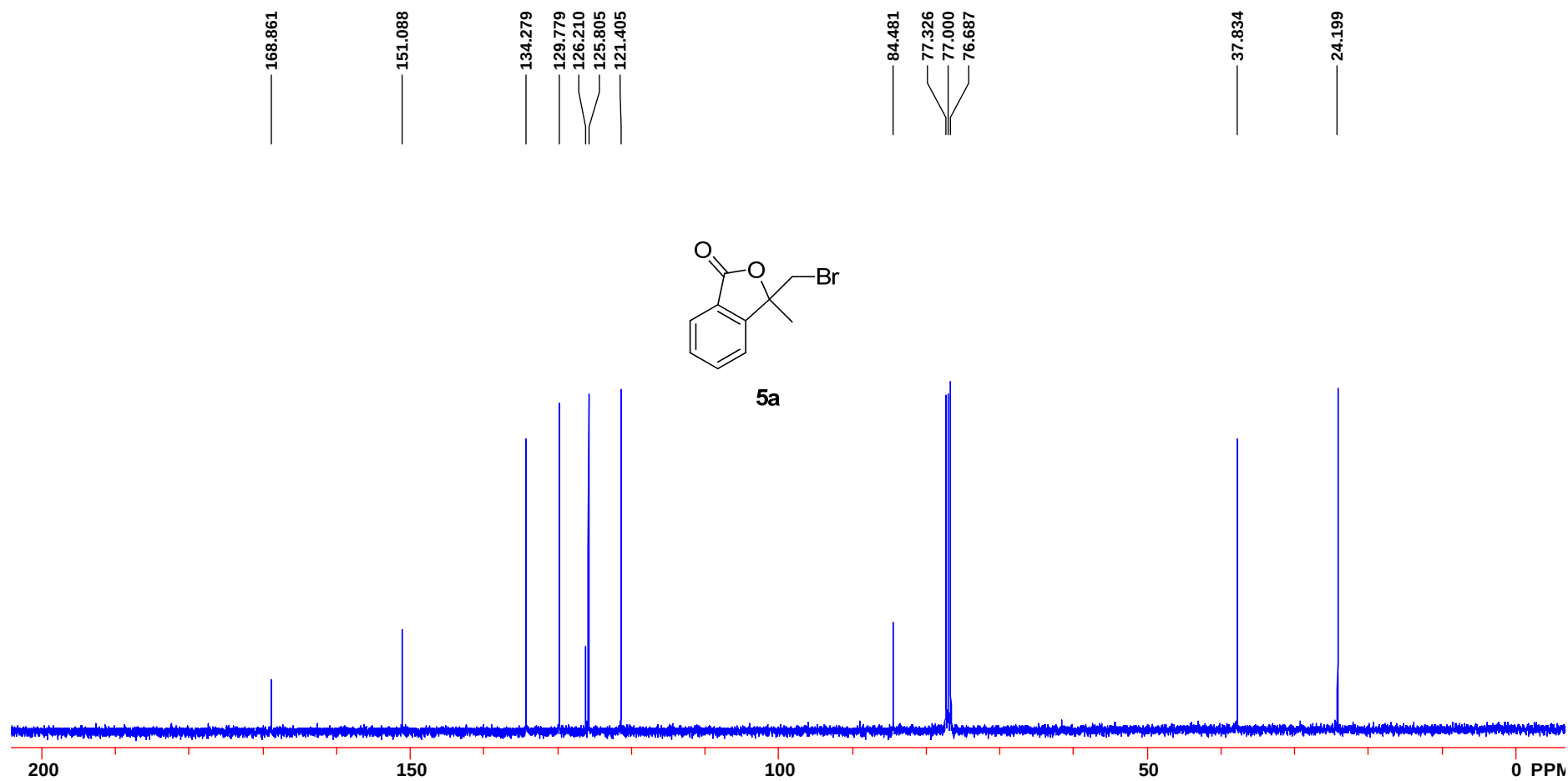


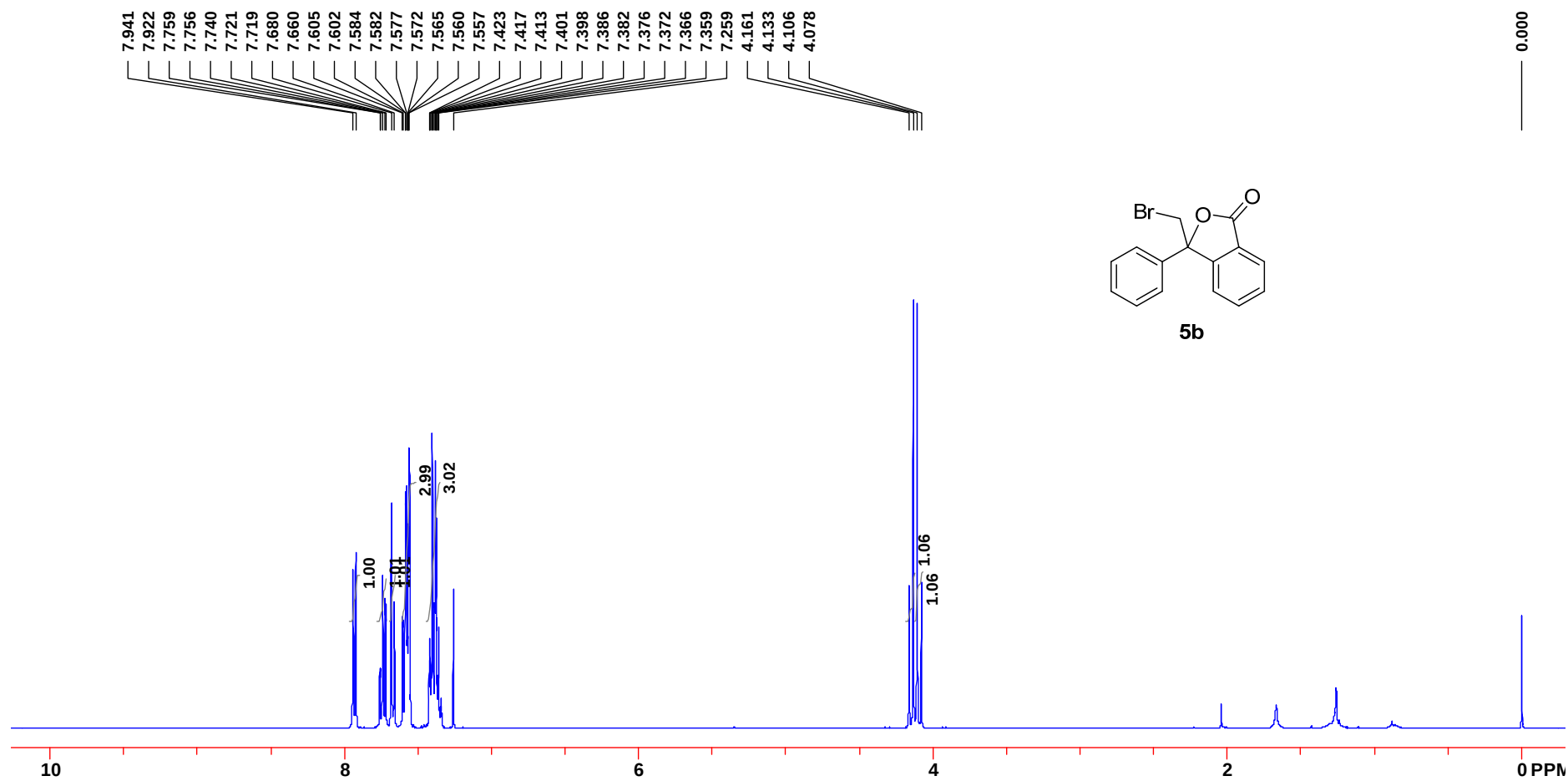


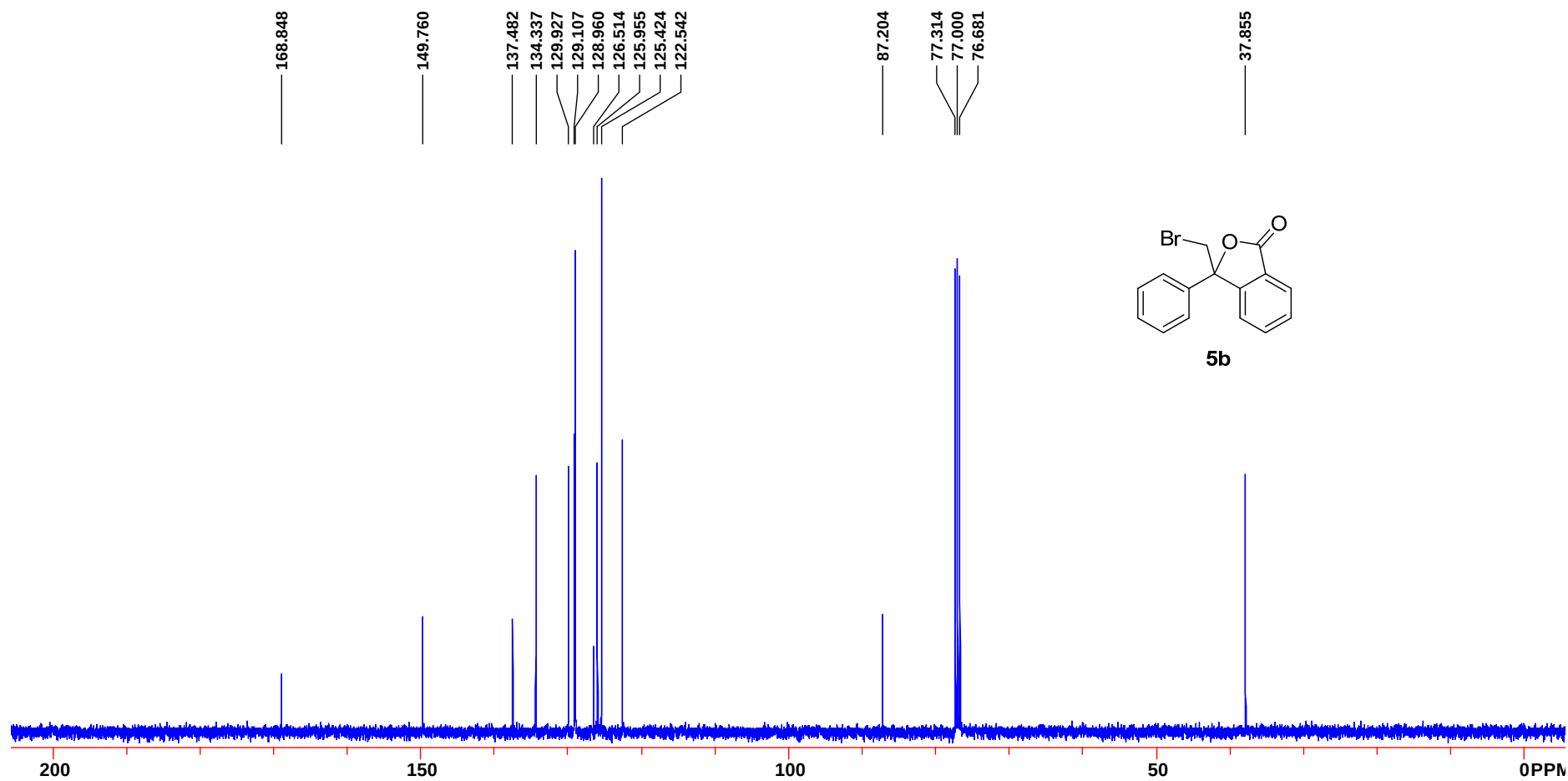


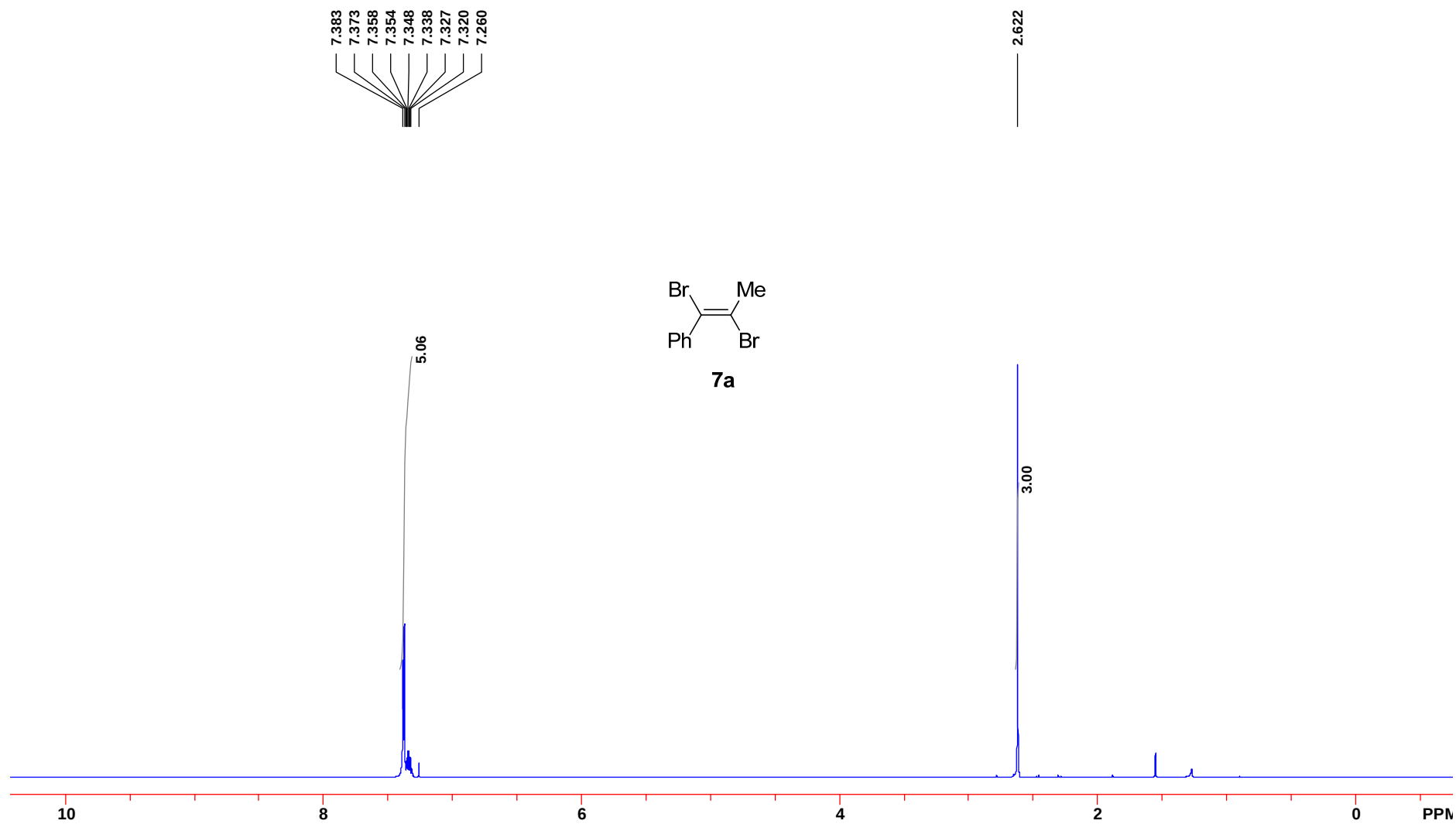


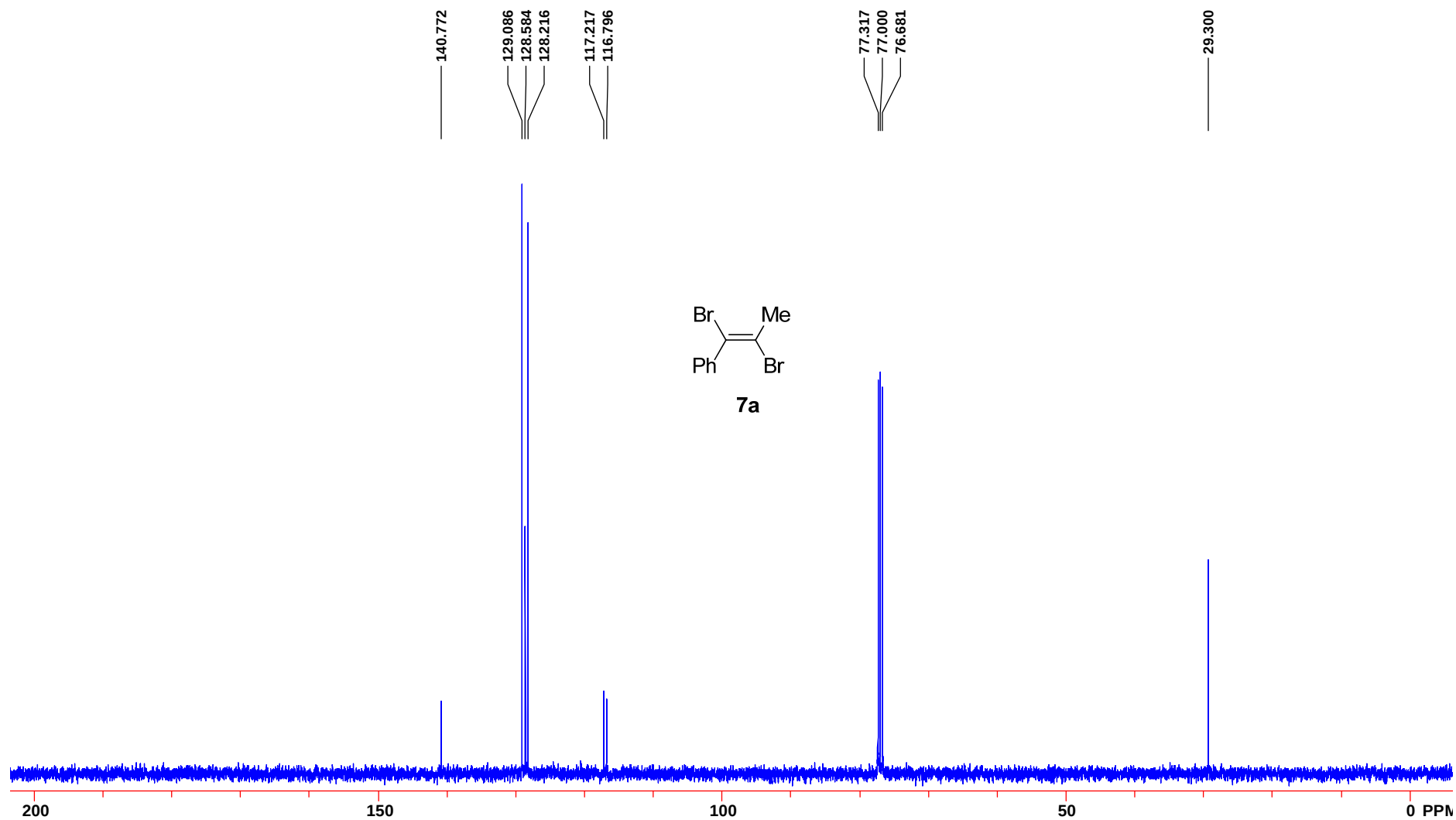


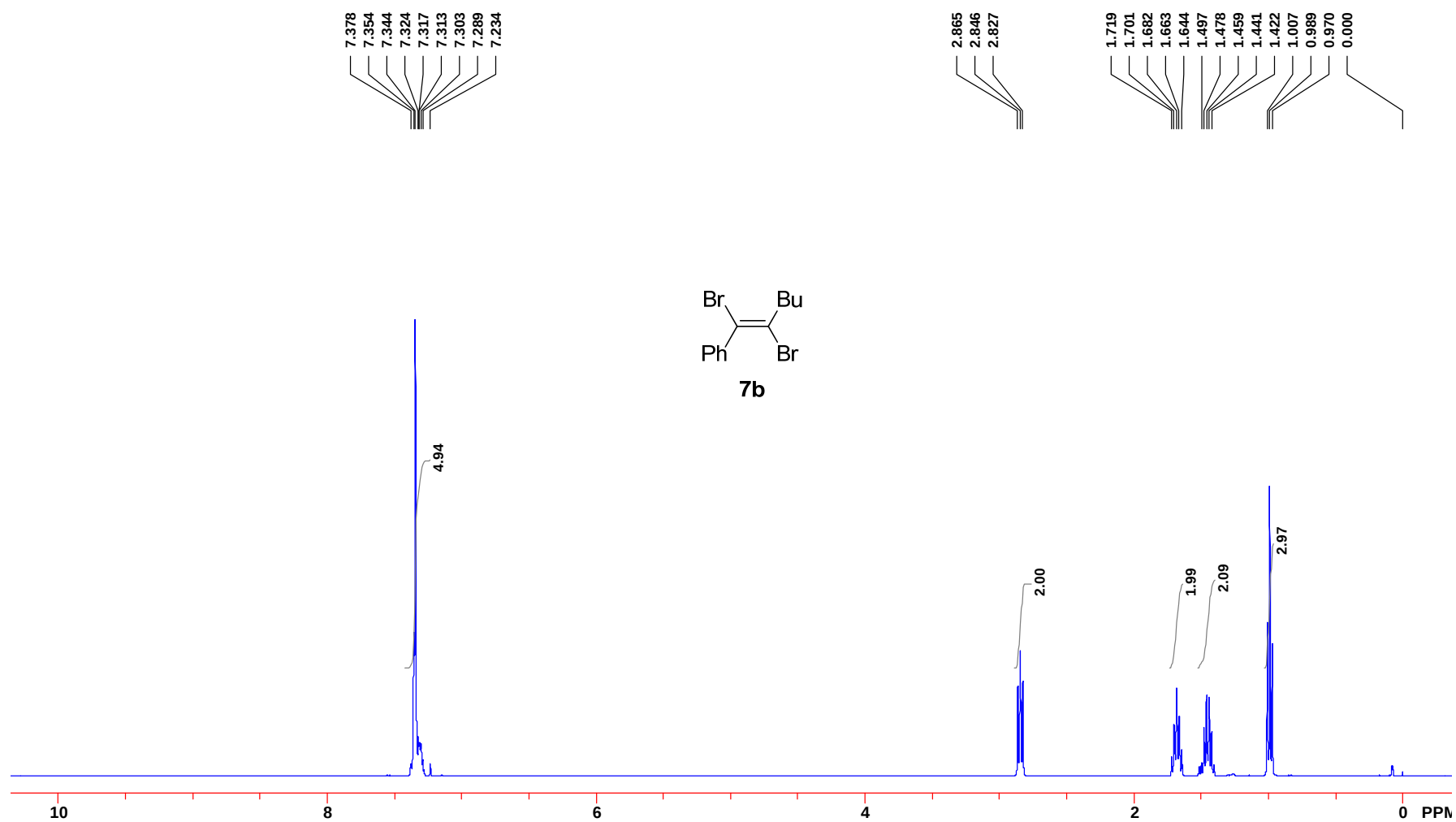


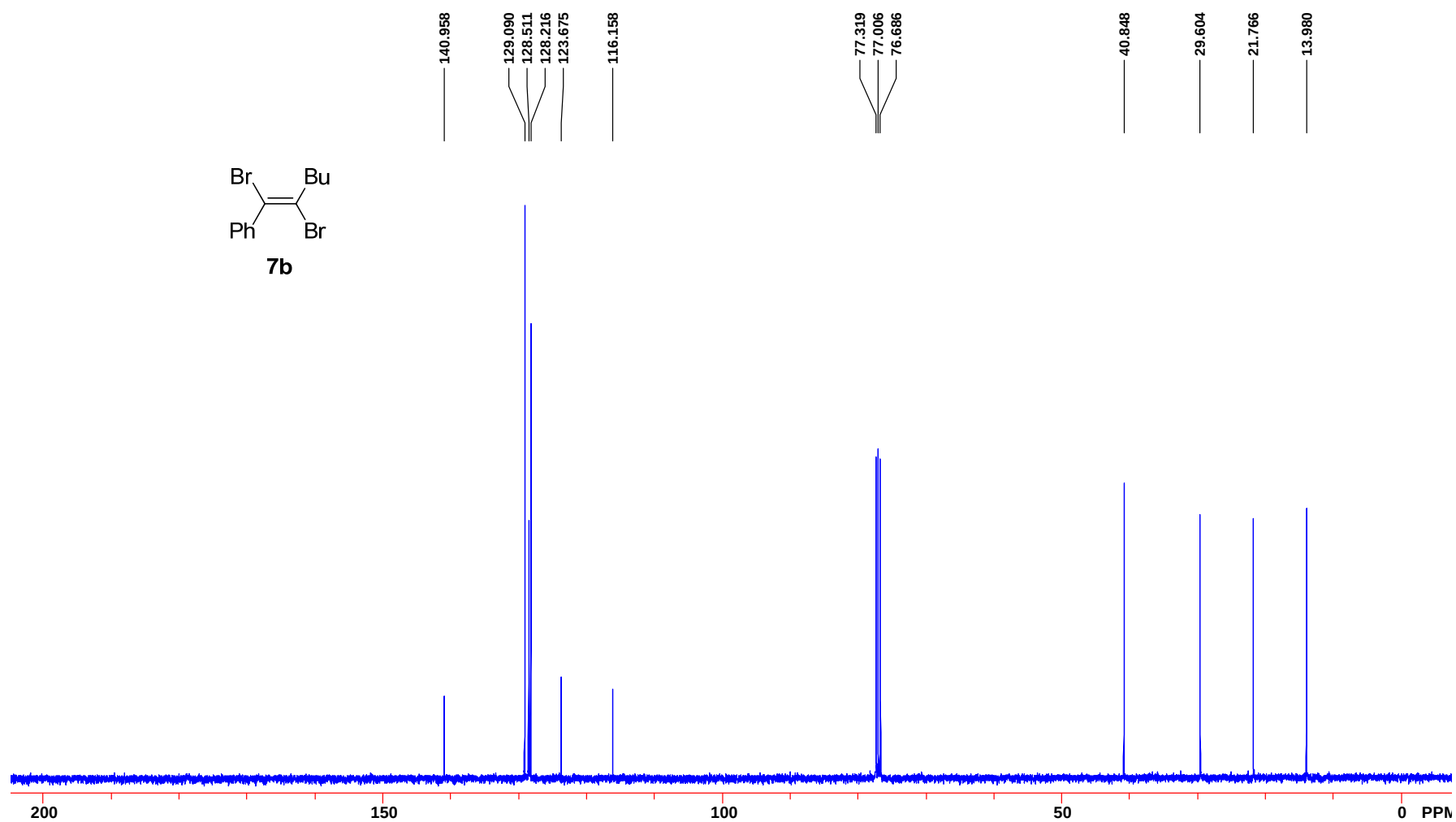


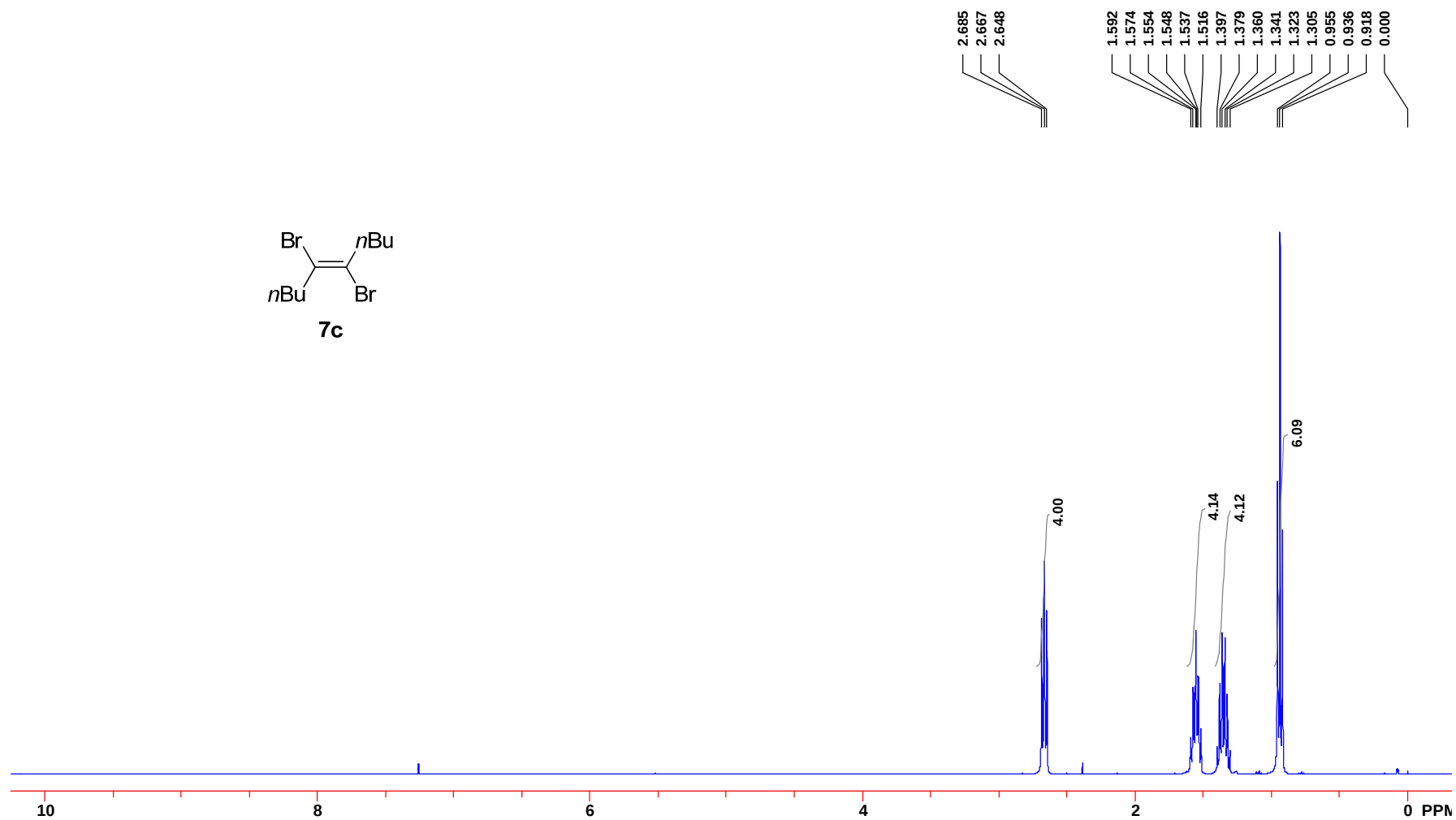
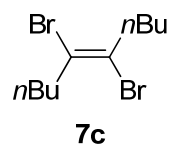


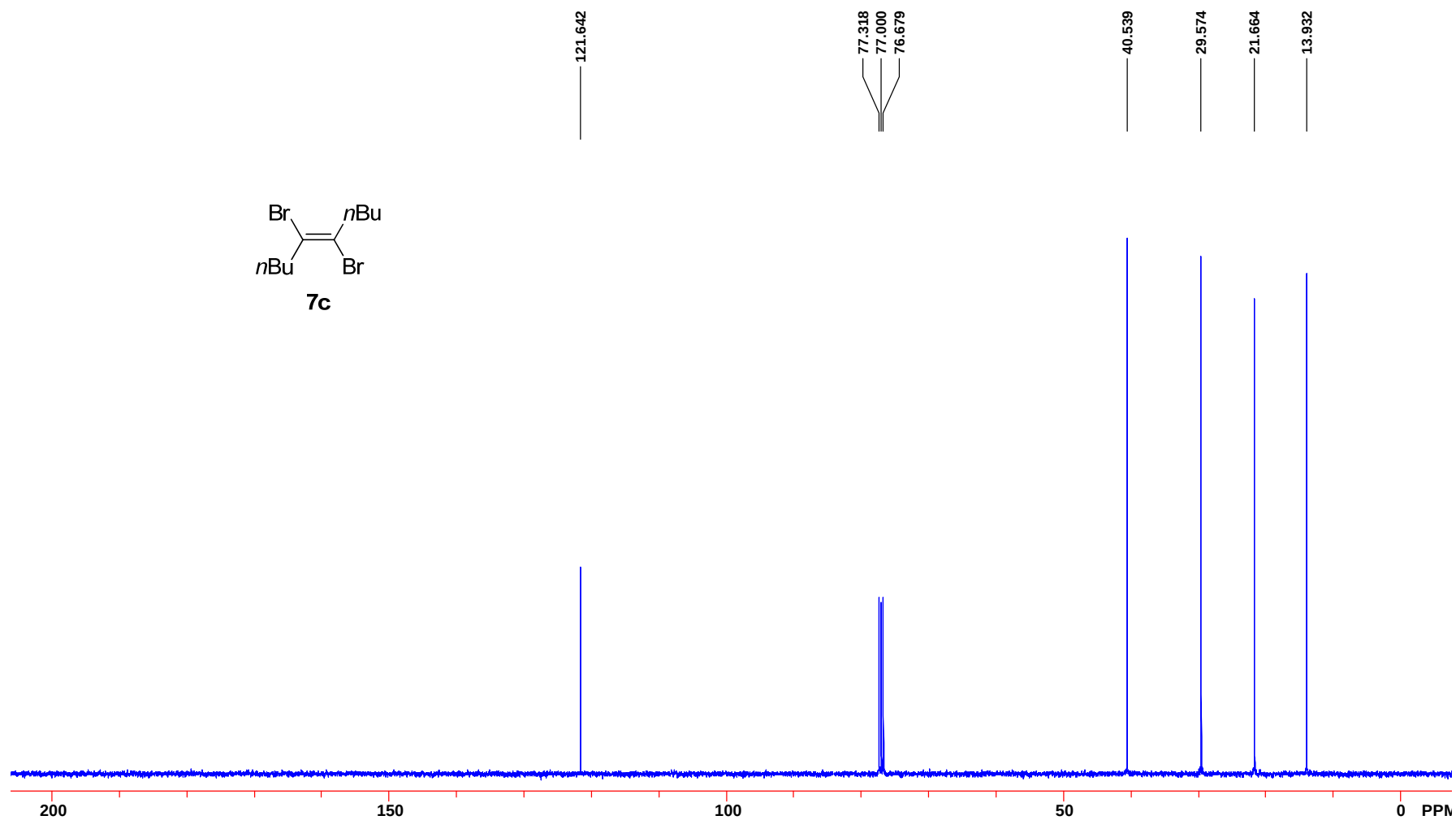
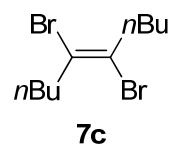


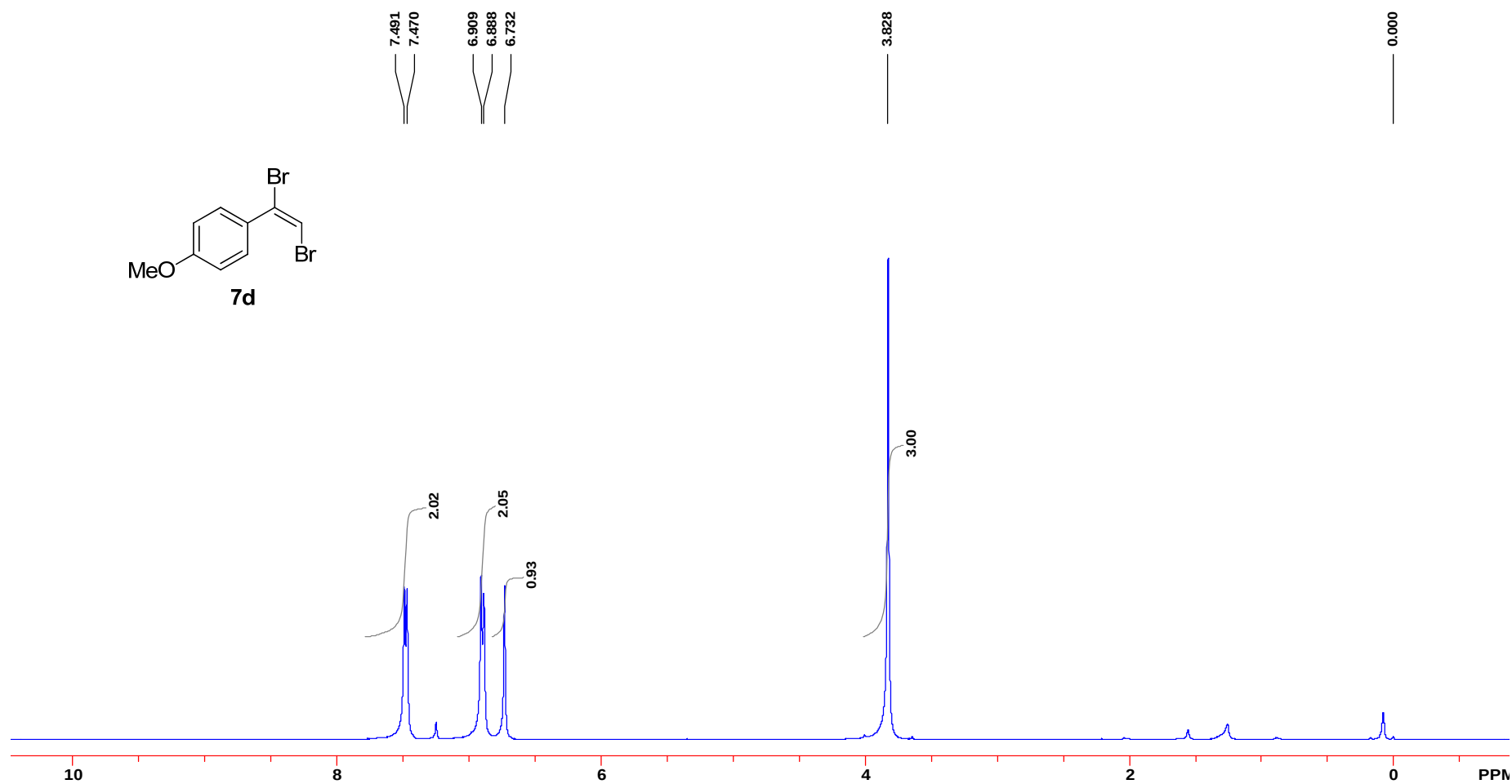
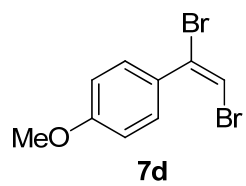


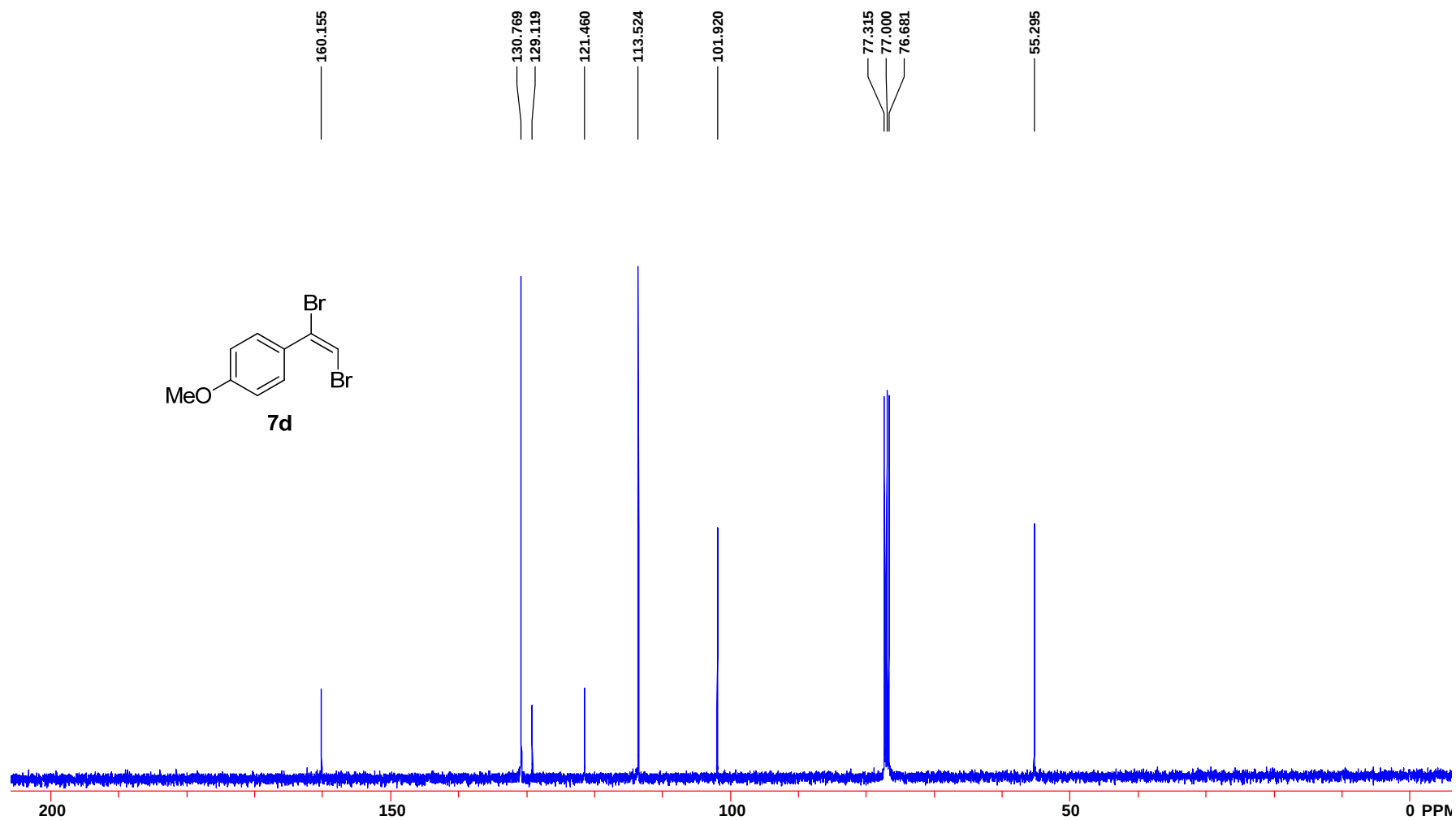
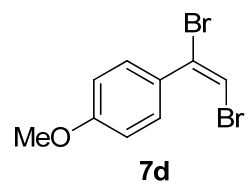


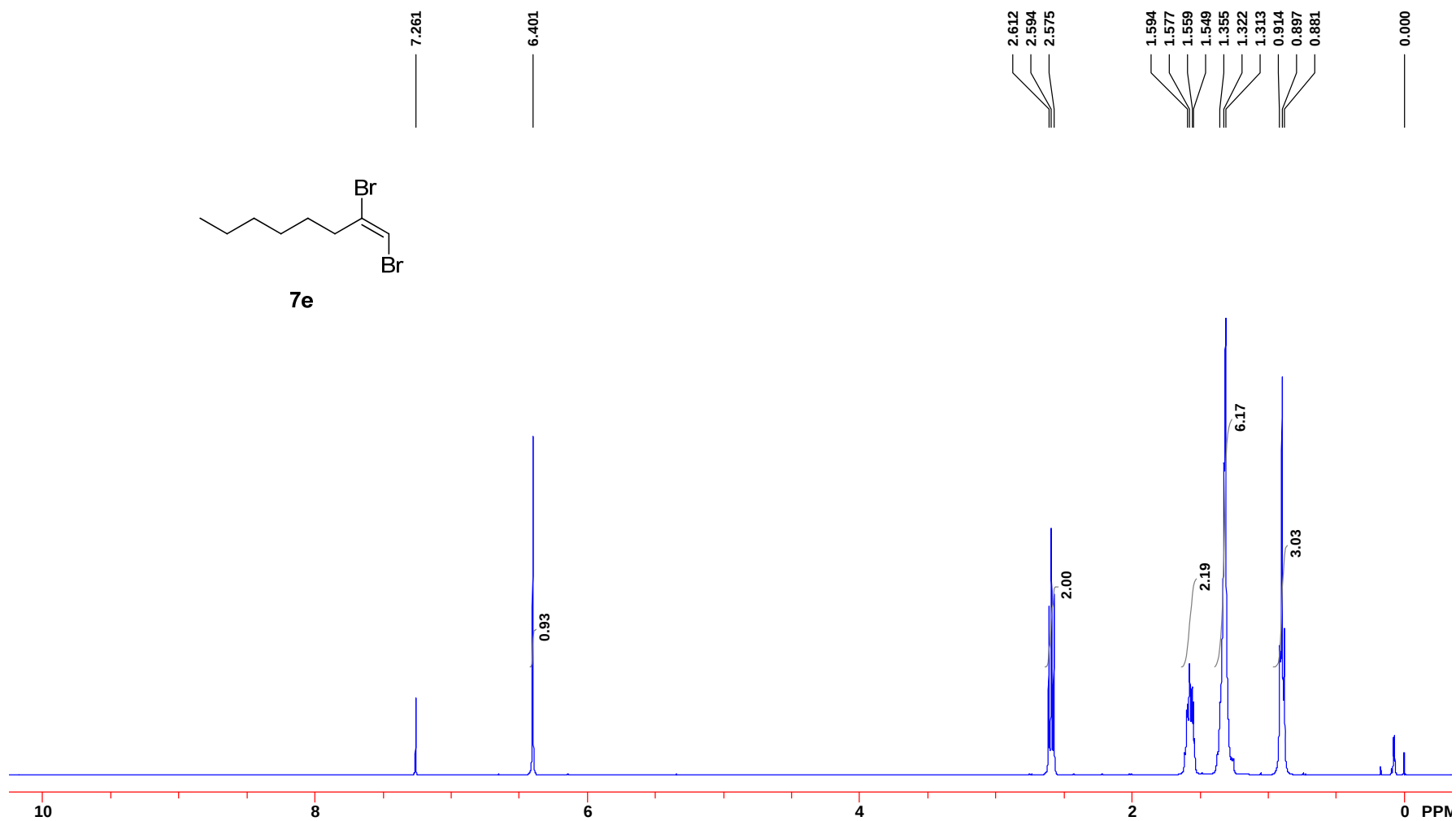
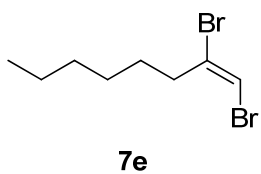


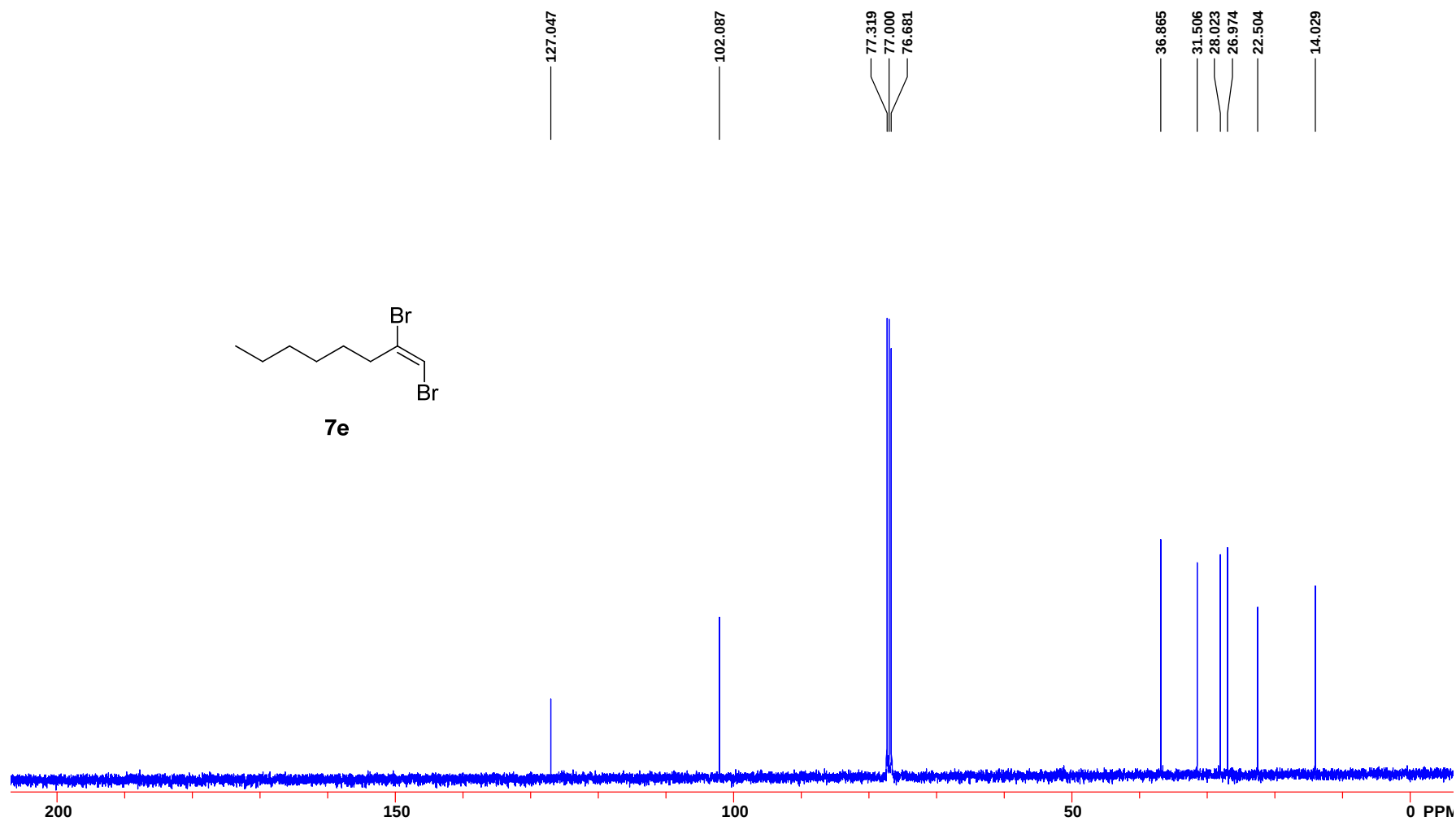
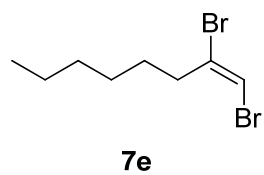


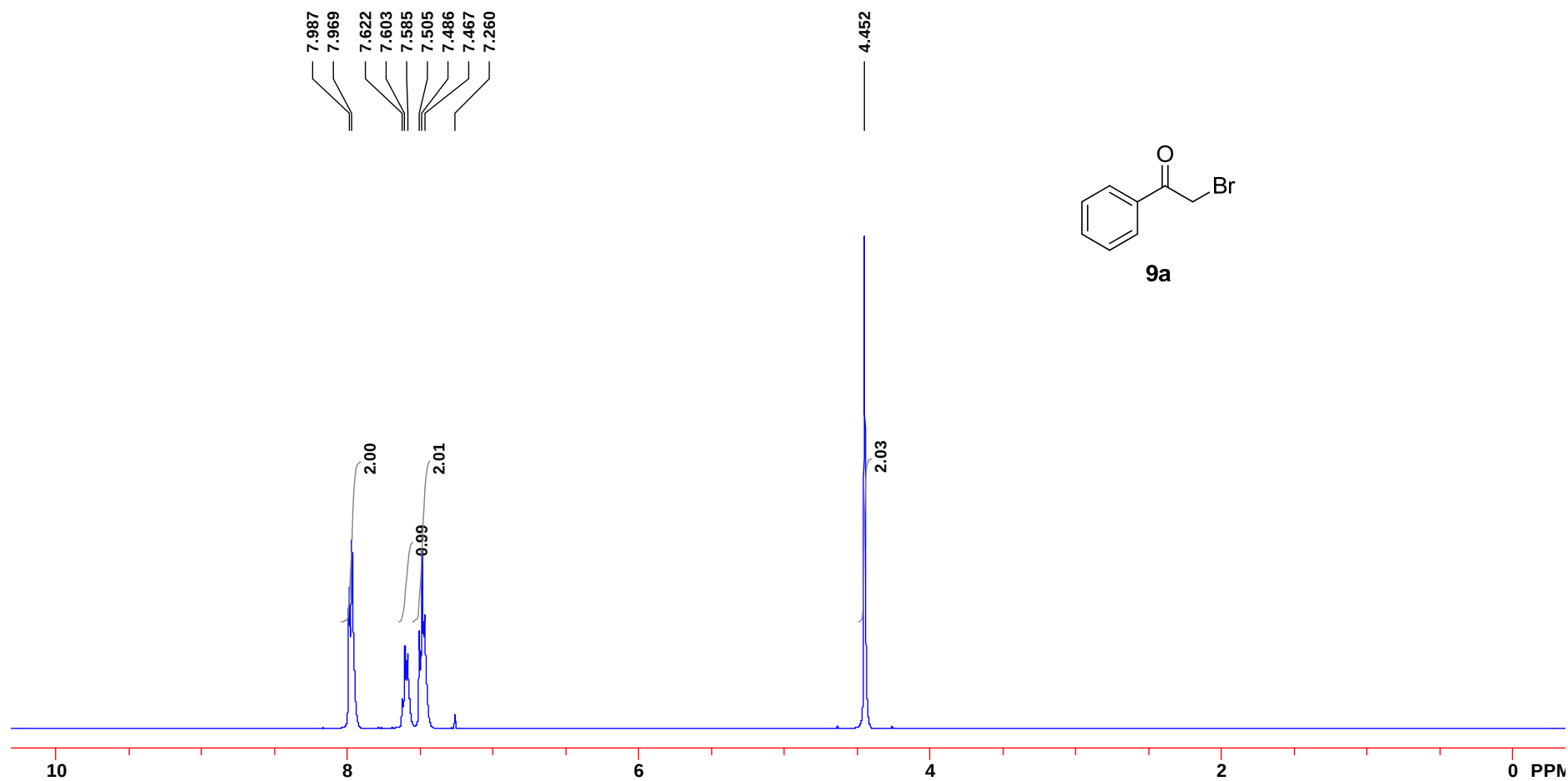


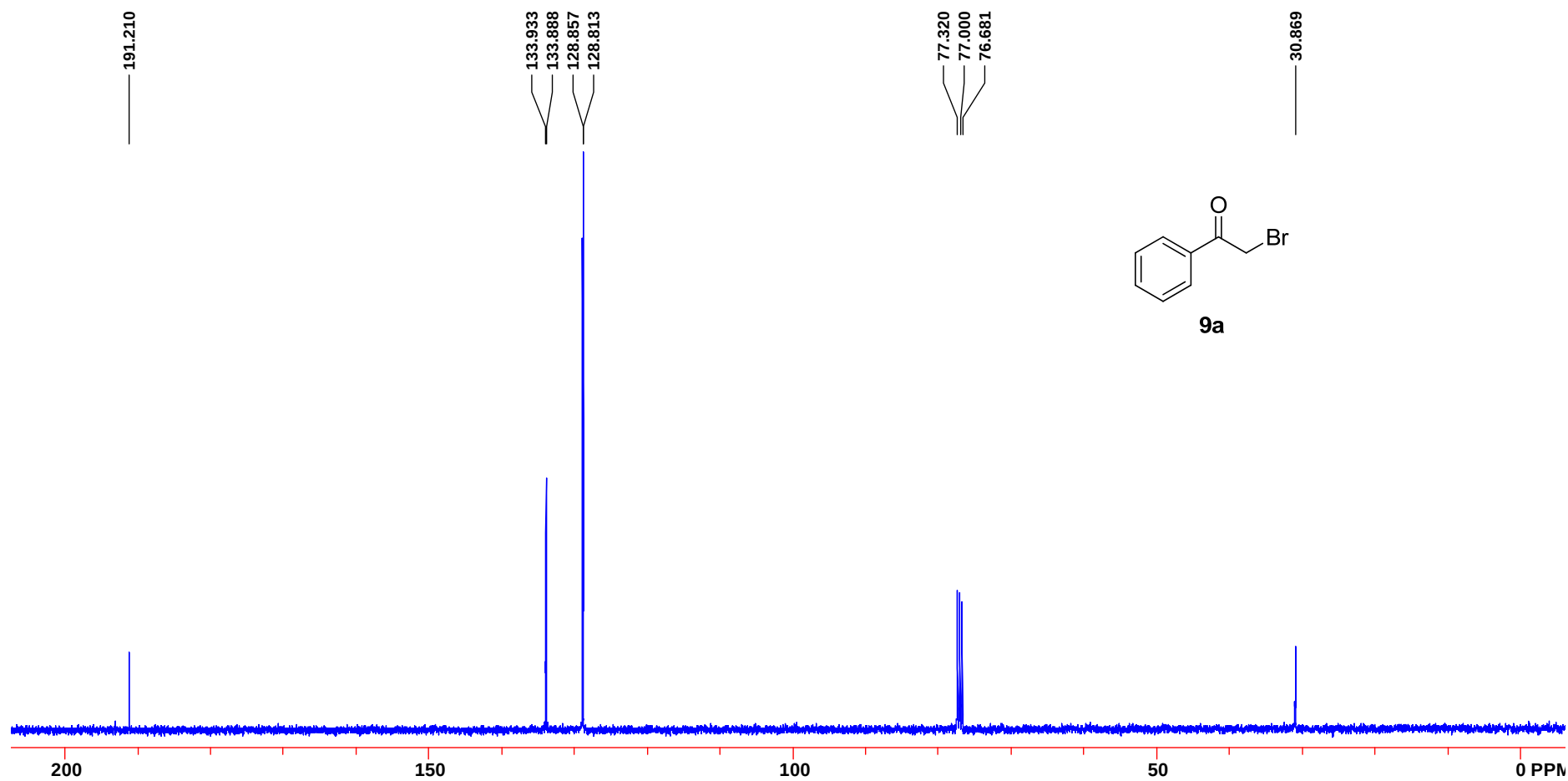


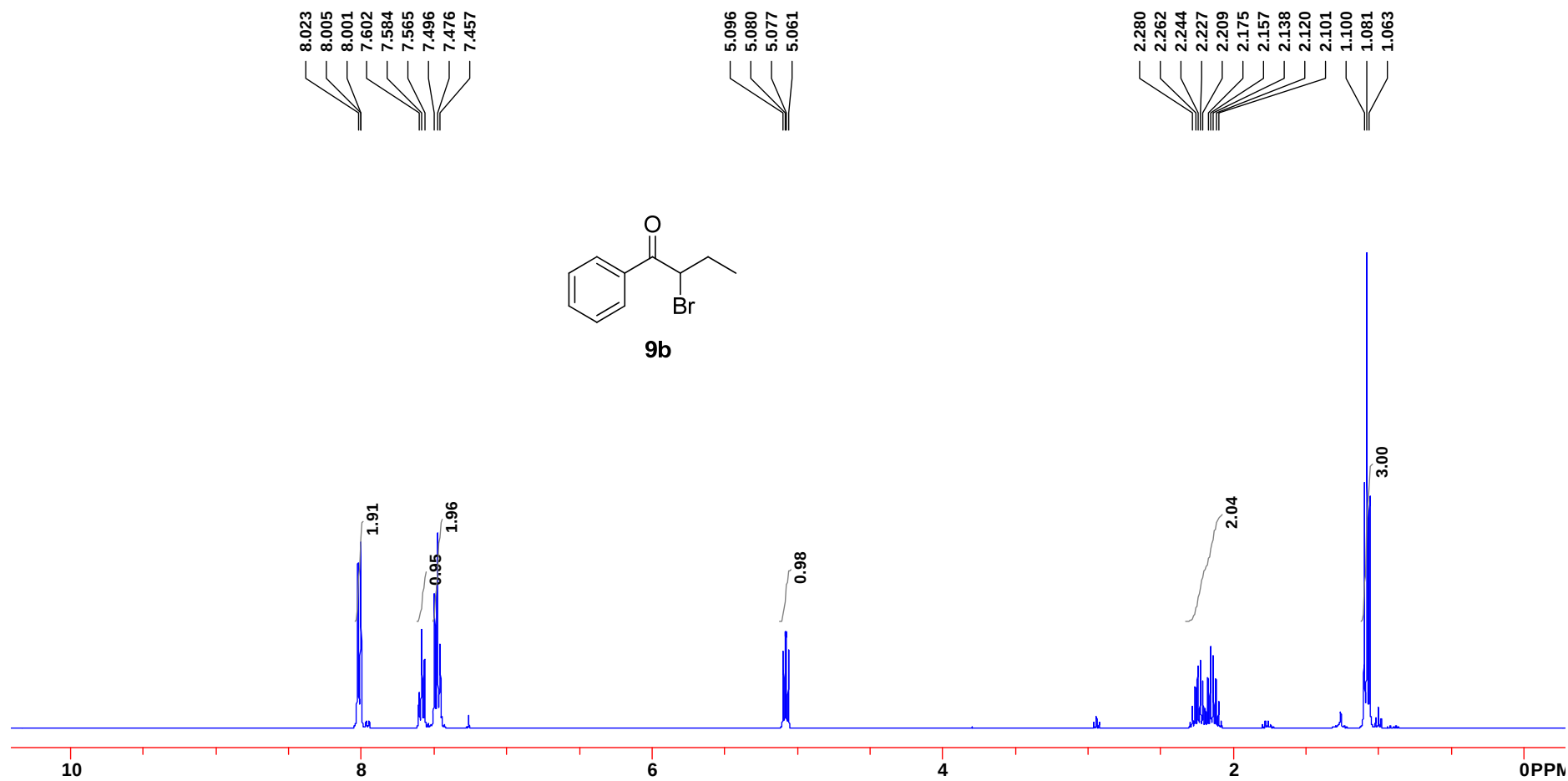


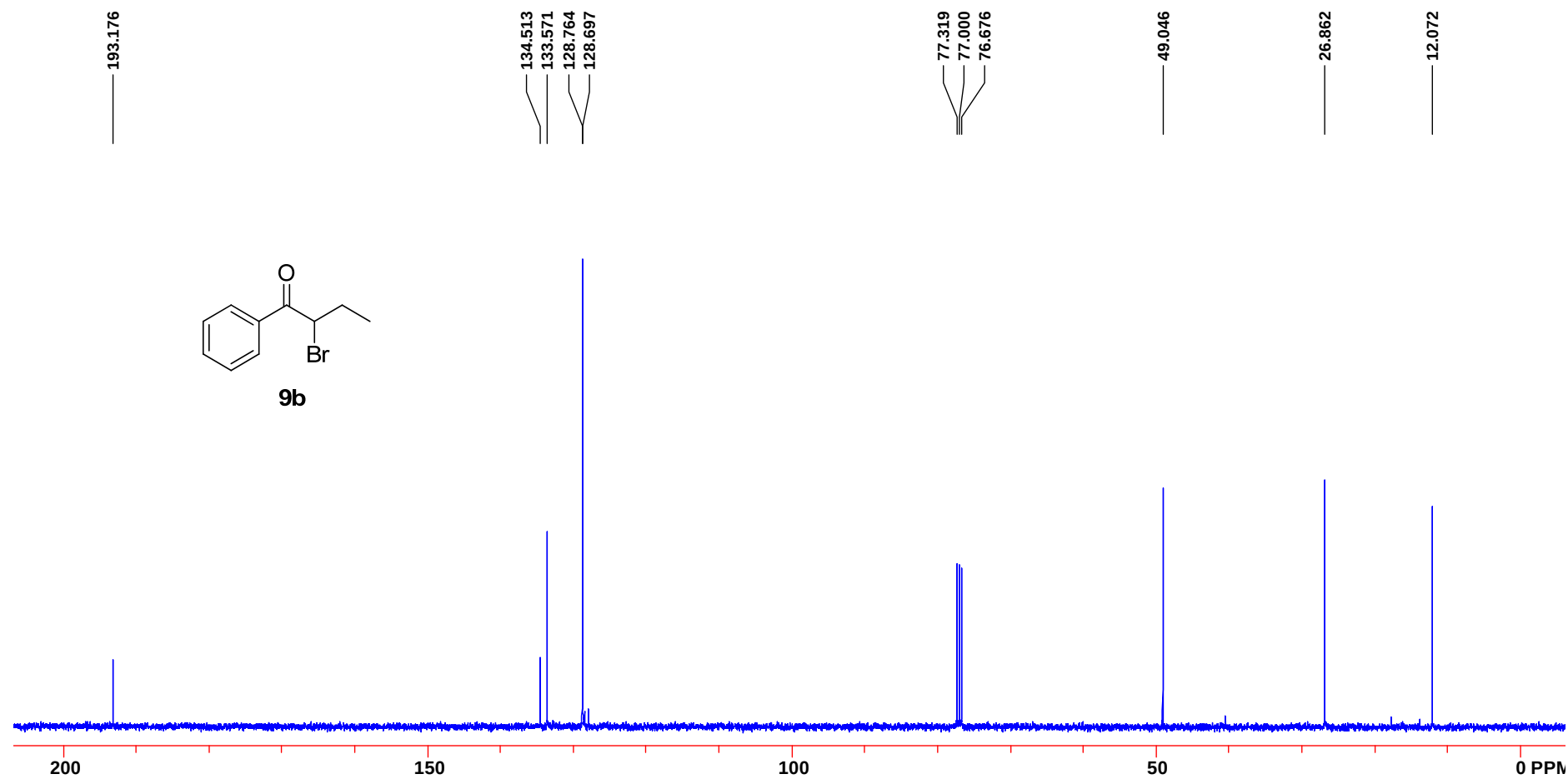
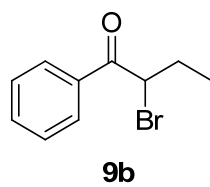


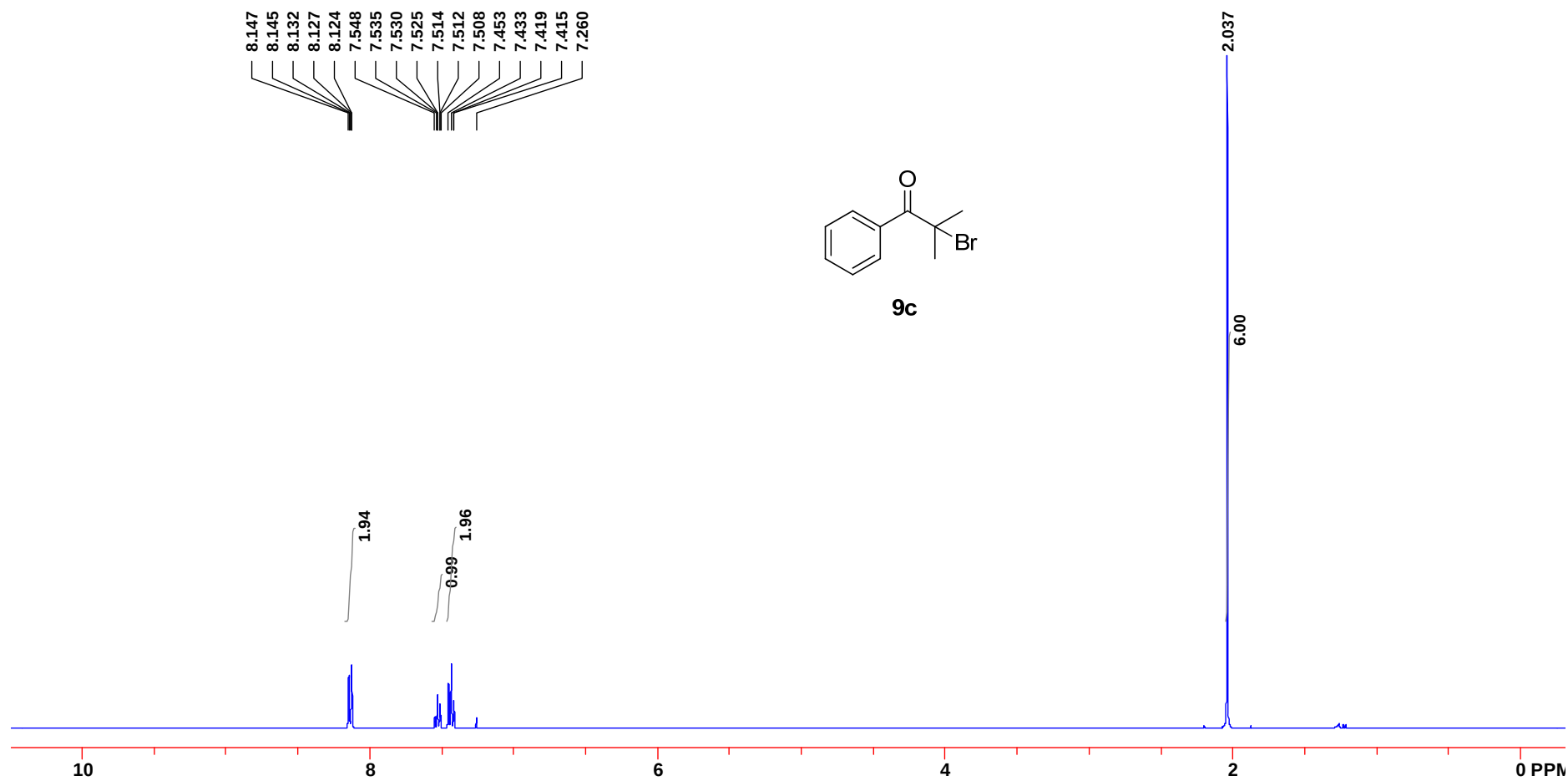


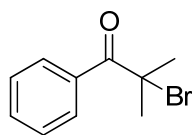




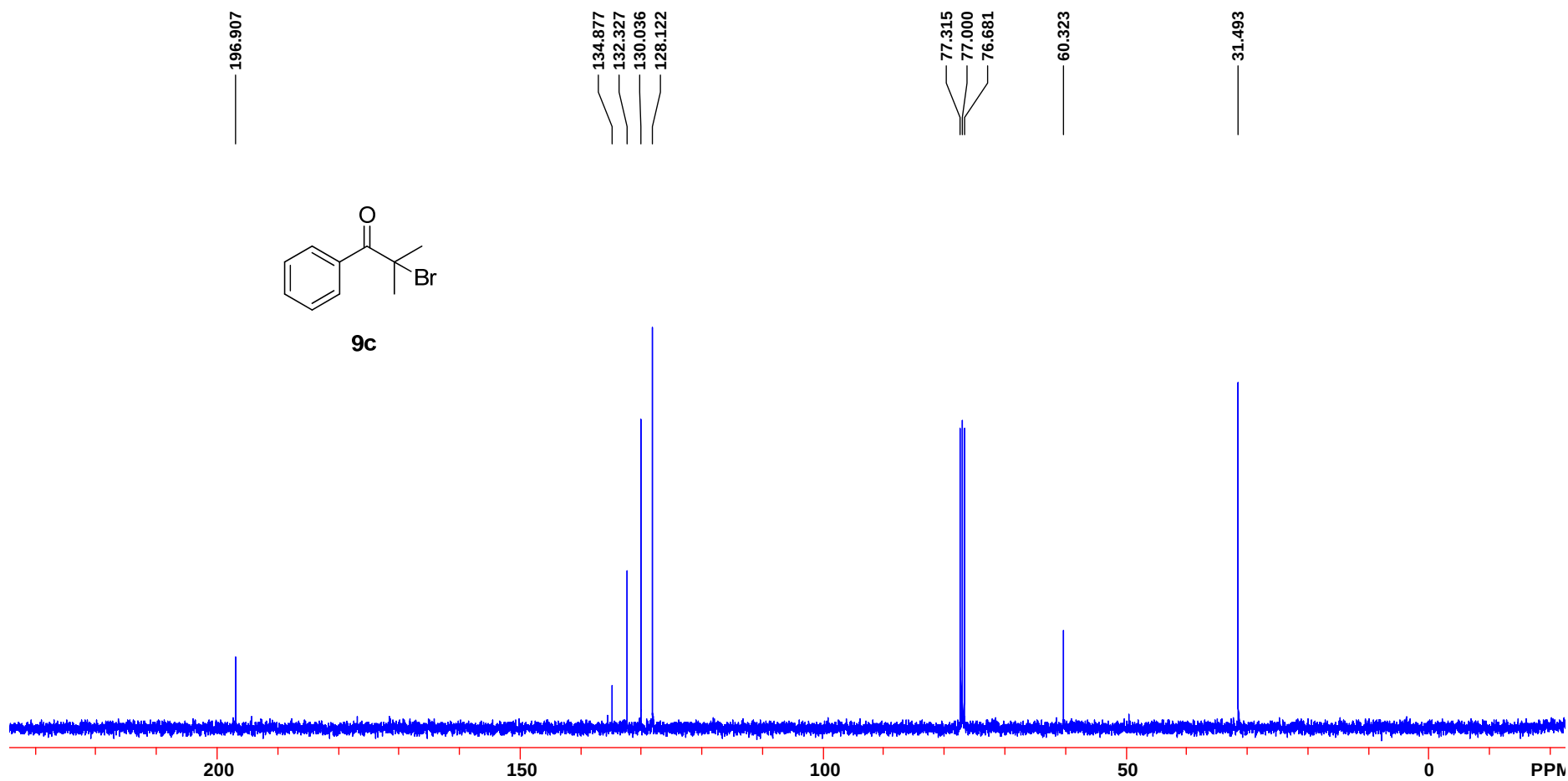


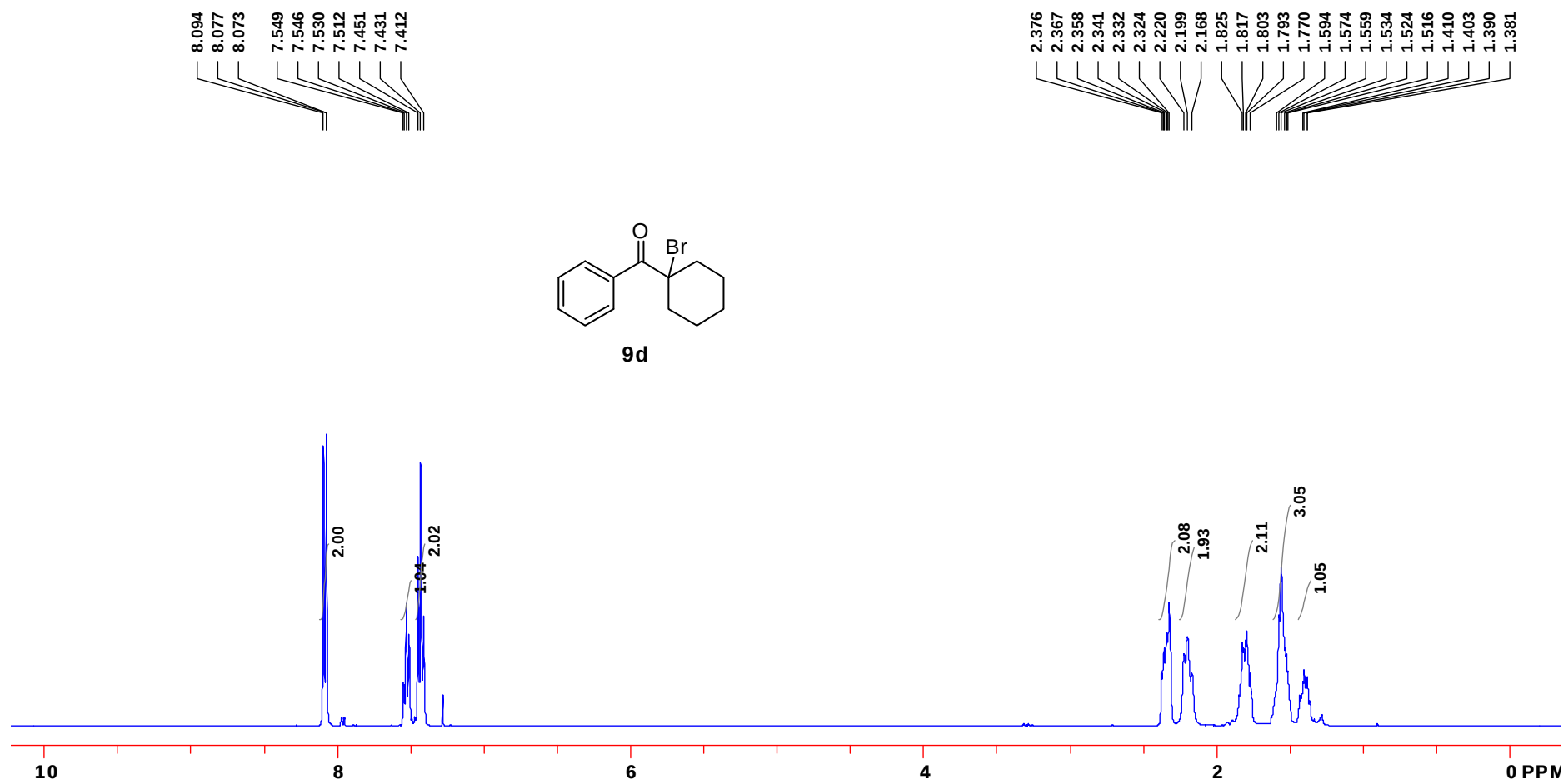


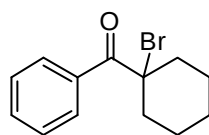




9c







9d

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