Supplementary Material (ESI) for Chemical Communications

Supporting information

Product-Selectivity Control by the Nature of Catalyst: Lewis Acid-Catalyzed Selective Formations of Ring-fused Tetrahydroquinolines and Tetrahydroazepines via Intramolecular Redox Reaction

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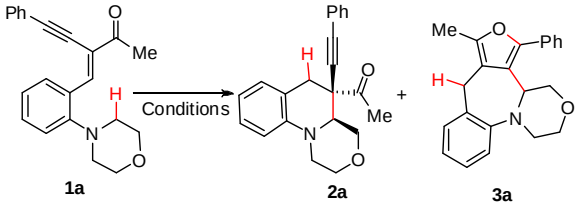
Table 1. Screening the reaction conditions of tuning the product selectivity.



1a **2a** **3a**

Entry	Conditions[a]	Yield (%)[b]	
		2a	**3a**
1	10 mol% $In(OTf)_3$, DCE, MS, reflux, 31 h	< 5	7
2	10 mol% $Mg(OTf)_2$, DCE, MS, reflux, 22 h	0	0
3	10 mol% $Cu(OTf)_2$, DCE, MS, reflux, 31 h	--	11
4	10 mol% $Ni(ClO_4)_2 \cdot 6H_2O$, DCE, MS, reflux, 16 h	< 5	< 5
5	10 mol% $Y(OTf)_3$, DCE, MS, reflux, 31 h	43	8
6	10 mol% $Yb(OTf)_3$, DCE, MS, reflux, 31 h	28	10
7	10 mol% $Bi(OTf)_3$, DCE, MS, reflux, 22 h	< 5	63
8	10 mol% $Sc(OTf)_3$, DCE, MS, reflux, 35 h	80[c]	< 5
9	**10 mol% $Sc(OTf)_3$, DCE, reflux, 35 h**	**86[d]**	**< 5**
10	10 mol% $Sc(OTf)_3$, DCM, MS, reflux, 35 h	29	< 5
11	10 mol% $Sc(OTf)_3$, TCE, MS, 80 °C, 36 h	43	< 5
12	10 mol% $Sc(OTf)_3$, $CHCl_3$, MS, reflux, 24 h	55	25
13	10 mol% $Sc(OTf)_3$, toluene, MS, 80 °C, 22 h	57	< 5
14	10 mol% $Sc(OTf)_3$, CH_3CN, MS, reflux, 35 h	0	0
15	5 mol% IPrAuCl/AgOTf, DCE, RT, 5 h	0	92
16	**5 mol% IPrAuCl/AgOTf, CH_3CN, RT, 3 h**	**0**	**92**
17	5 mol% IPrAuCl/AgOTf, toluene, RT, 10 h	0	89
18	5 mol% IPrAuCl/$AgSbF_6$, CH_3CN, RT, 6 h	0	79
19	5 mol% PPh_3AuCl/$AgSbF_6$, CH_3CN, RT, 1 h	0	64
20	5 mol% PPh_3AuCl/AgOTf, CH_3CN, RT, 4 h	0	71
21	5 mol% AuCl, CH_3CN, RT, 11.5 h	0	81

[a] Unless otherwise specified, the reaction was run with a 0.2-0.3 mmol scale (0.1 M) with (25-38 mg) or without 4Å molecular sieves. DCE = 1,2-dichloroethane, TCE = 1,1,2,2-tetrachloroethane; [b] isolated yield; [c] dr = 12:1; [d] dr = 15:1.

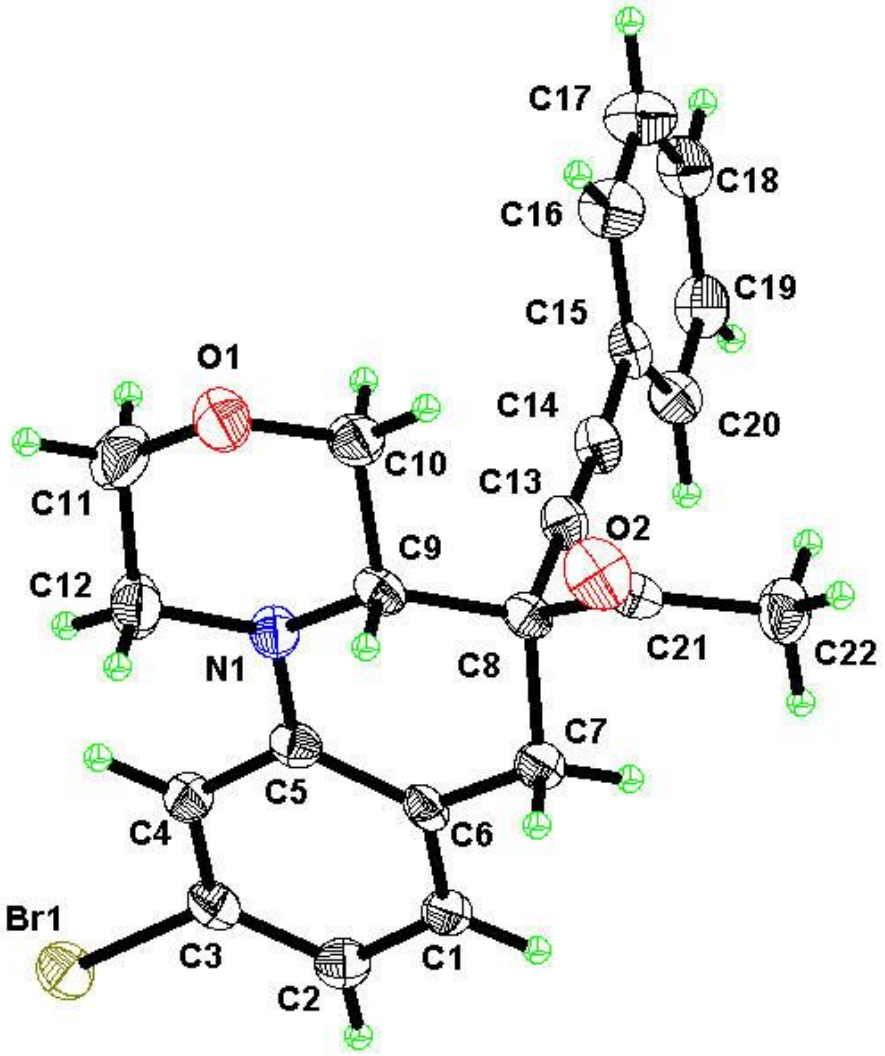


Figure 1. X-ray crystal structure of compound **2n**

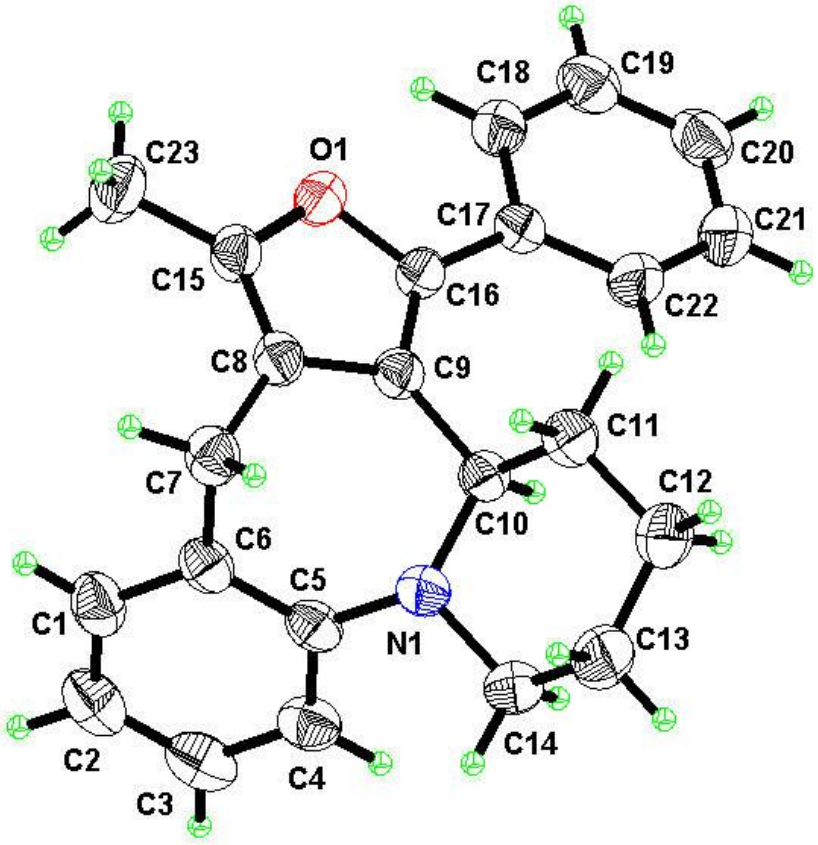
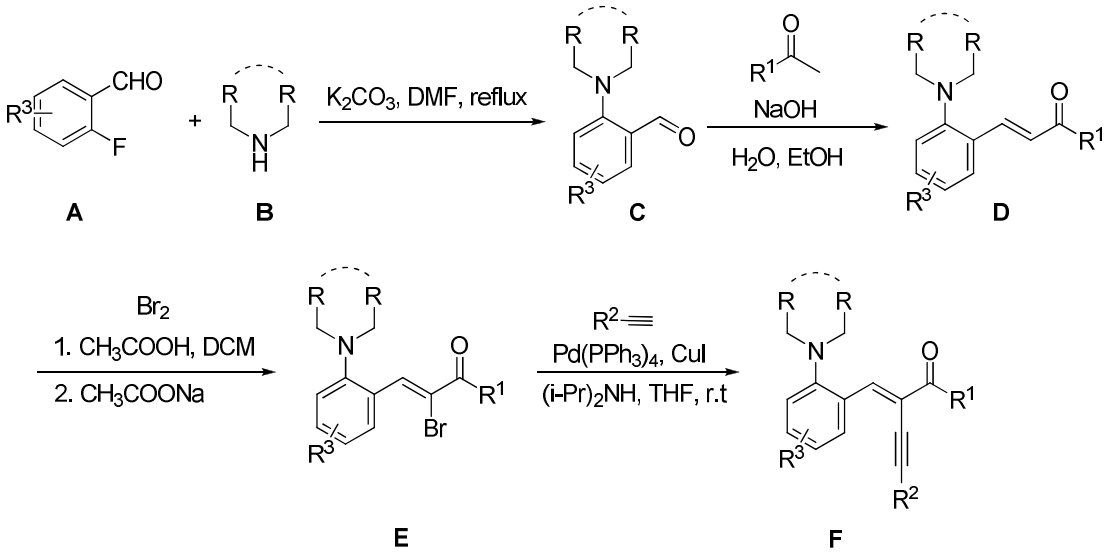


Figure 2. X-ray crystal structure of compound **3g**

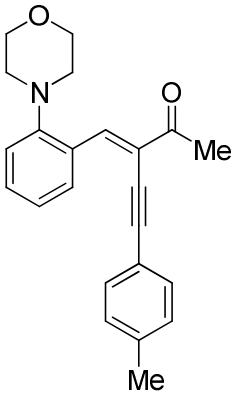
General procedure for the synthesis of yne-enones:



1. (*E*)-3-(2-morpholinobenzylidene)-5-phenylpent-4-yn-2-one

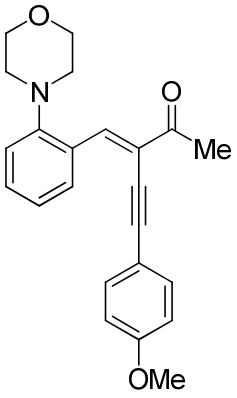
(*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.55 g), whichwas started from 2-fluorobenzaldehyde, ethynylbenzene (7.5 mmol, 0.765 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), and CuI (2 mol%, 19.1 mg) were taken up in THF at room temperature. Diisopropyl amine (15 mmol, 1.52 g) was added, and the resulting reaction mixture was stirred at room temperature till the complete consumption of the bromide as determined by TLC analysis. Water was added and the mixture was extracted three times with Et_2O, the combined organic layers were washed with brine and dried ($MgSO_4$). After filtration and concentration, the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1) to give the desired product **1a** (1.59 g) as a yellow solid in 96% yield. m.p: 92-94 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.44 (d, *J* = 7.8 Hz, 1 H), 8.23 (s, 1 H), 7.55-7.47 (m, 2 H), 7.45-7.30 (m, 4 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.08 (d, *J* = 7.8 Hz, 1 H), 3.90 (t, *J* = 4.5 Hz, 4 H), 2.99 (t, *J* = 4.5 Hz, 4 H), 2.62 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.23, 153.42, 140.46, 131.37, 129.78, 128.69, 128.46, 128.09, 122.93, 122.42, 119.57, 118.24, 98.15, 86.62, 67.15, 53.42, 28.12 ppm. MS (70 eV): m/z (%): 331 (M^+, 47.61), 230 (100). Anal, calcd for $C_{22}H_{21}NO_2$: C, 79.73, H, 6.39, N, 4.23, found: C, 79.93, H, 6.42. N, 4.19.

2. (*E*)-3-(2-morpholinobenzylidene)-5-p-tolylpent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.55 g), 1-ethynyl-4-methylbenzene (7.5 mmol, 0.87 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.515 g) in THF afforded **1b** (1.66 g) as a yellow solid in 96% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1); m.p: 127-128 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.45 (d, *J* = 7.8 Hz, 1 H), 8.21 (s, 1 H), 7.45-7.35 (m, 3 H), 7.20-7.00 (m, 4 H), 3.90 (t, *J* = 4.5 Hz, 4 H), 2.99 (t, *J* = 4.5 Hz, 4 H), 2.62 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.39, 153.33, 139.89, 138.95, 131.27, 131.24, 129.72, 129.21, 128.08, 122.37, 119.81, 119.63, 118.16, 98.39, 86.01, 67.12, 53.37, 28.16, 21.52 ppm; MS (70 eV): m/z (%): 345 (M^+, 69.82), 244 (100). HRMS calcd for $C_{23}H_{23}NO_2$: 345.1729, found: 345.1729.

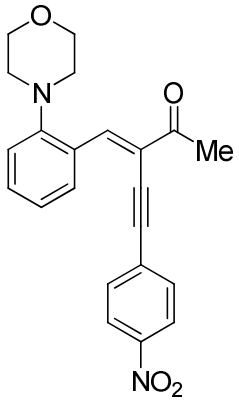
3.(*E*)-5-(4-methoxyphenyl)-3-(2-morpholinobenzylidene)pent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol,

1.55 g), 1-ethynyl-4-methoxybenzene (7.5 mmol, 0.99 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.515 g) in THF afforded **1c** (1.66 g) as a yellow solid in 92% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 8 : 1); m.p: 82-83 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.45 (d, *J* = 7.8 Hz, 1 H), 8.17 (s, 1 H), 7.50-7.35 (m, 3 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 3.90 (t, *J* = 4.5 Hz, 4 H), 3.83 (s, 3 H), 2.98 (t, *J* = 4.5 Hz, 4 H), 2.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.48, 159.95, 153.28, 139.45, 132.87, 131.19, 129.68, 128.17, 122.35, 119.80, 118.16, 115.00, 114.12, 98.30, 85.43, 67.14, 55.30, 53.36, 28.13 ppm; MS (70 eV): m/z (%): 361 (M^+, 35.80), 91 (100). Anal, calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88; found: C, 76.47, H, 6.62. N, 3.90.

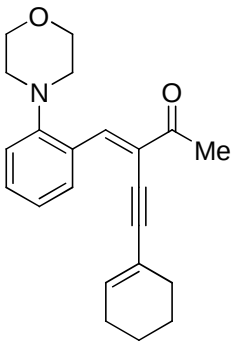
4. (*E*)-3-(2-morpholinobenzylidene)-5-(4-nitrophenyl)pent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.55 g), 1-ethynyl-4-nitrobenzene (7.5 mmol, 1.1025 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.515 g) in THF afforded **1d** (0.90 g) as an orange solid in 48% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 5 : 1); m.p: 158-159 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.40-8.25 (m, 2 H), 8.23 (d, *J* = 8.1 Hz, 2 H), 7.62 (d, *J* = 8.1 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 7.19-7.06 (m, 2 H), 3.90 (t, *J* = 4.2 Hz, 4 H), 3.00 (t, *J* = 4.2 Hz, 4 H), 2.62 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 195.42, 153.66, 147.15, 143.13, 132.06, 129.74, 129.66, 127.66, 123.76,

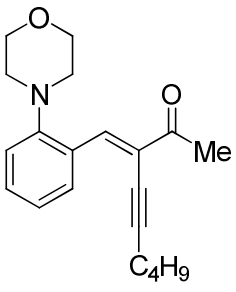
122.45, 118.88, 118.48, 95.81, 91.59, 67.13, 53.48, 28.03 ppm. MS (70 eV): m/z (%): 376 (M^+, 68.11), 43 (100). HRMS calcd for $C_{22}H_{20}N_2O_4$: 376.1423, found: 376.1423.

5. (*E*)-5-cyclohexenyl-3-(2-morpholinobenzylidene)pent-4-yn-2-one



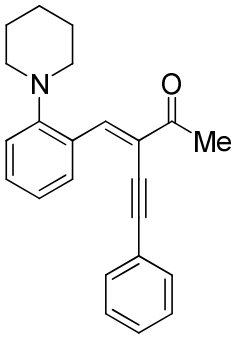
The reaction of (*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.55 g), 1-ethynylcyclohex-1-ene (7.5 mmol, 0.80 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.515 g) in THF afforded **1e** (1.36 g) as an yellow solid in 81% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 20 : 1); m.p: 113-114 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.36 (d, *J* = 7.8 Hz, 1 H), 8.09 (s, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.12-6.95 (m, 2 H), 6.19 (brs, 1 H), 3.86 (t, *J* = 4.5 Hz, 4 H), 2.93 (t, *J* = 4.5 Hz, 4 H), 2.52 (s, 3 H), 2.25-2.05 (m, 4 H), 1.70-1.50 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.48, 153.10, 138.78, 135.93, 130.97, 129.49, 128.06, 122.17, 120.65, 119.74, 118.00, 100.24, 84.06, 67.01, 53.24, 28.54, 27.93, 25.68, 22.07, 21.31 ppm. MS (70 eV): m/z (%): 335 (M^+, 45.95), 292 (100). HRMS calcd for $C_{22}H_{25}NO_2$: 335.1885, found: 335.1886.

6. (*E*)-3-(2-morpholinobenzylidene)non-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.55 g), hex-1-yne (7.5 mmol, 0.62 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1f** (1.51 g) as an yellow oil in 97% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 20 : 1); ^{1}H NMR (300 MHz, $CDCl_3$): 8.37 (dd, *J* = 7.8, 1.2 Hz, 1 H), 8.09 (s, 1 H), 7.37 (td, *J* =7.5, 1.2 Hz, 1 H), 7.12-6.95 (m, 2 H), 3.88 (t, *J* = 4.5 Hz, 4 H), 2.95 (t, *J* = 4.5 Hz, 4 H), 2.55-2.40 (m, 5 H), 1.70-1.55 (m, 2 H), 1.55-1.40 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 197.08, 152.95, 139.18, 130.93, 129.46, 128.06, 122.18, 120.28, 117.99, 99.95, 77.29, 67.08, 53.22, 30.39, 27.93, 22.01, 19.48, 13.54 ppm. MS (70 eV): m/z (%): 311 (M^+, 79.82), 268 (100). HRMS calcd for $C_{20}H_{25}NO_2$: 311.1884, found: 311.1885.

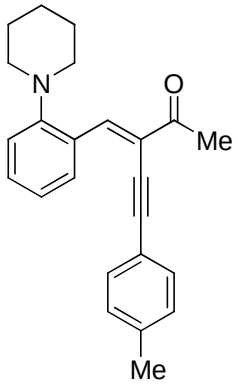
7. (*E*)-5-phenyl-3-(2-(piperidin-1-yl)benzylidene)pent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-(piperidin-1-yl)phenyl)but-3-en-2-one (5 mmol, 1.535 g), ethynylbenzene (7.5 mmol, 0.77 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1g** (1.58 g) as an yellow solid in 96% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 30 : 1); m.p.: 109-110 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.44 (d, *J* = 7.5 Hz, 1 H), 8.21 (s, 1 H), 7.60-7.45 (m, 2 H), 7.43-7.30 (m, 4 H), 7.15-7.10 (m, 2 H), 3.00-2.85 (m, 4 H), 2.63 (s, 3 H), 1.85-1.70 (m, 4 H), 1.65-1.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.50, 155.02, 141.45, 131.38, 131.27, 129.60, 128.54, 128.42, 127.98, 123.11, 121.48, 119.09, 118.39, 97.87, 86.76, 54.65, 28.04, 26.42,

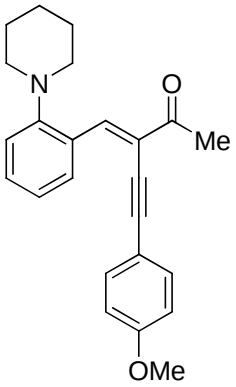
24.21 ppm. MS (70 eV): m/z (%): 329 (M^+, 63.14), 286 (100). Anal, calcd for $C_{23}H_{23}NO$: C, 83.85, H, 7.04, N, 4.25, found: C, 83.90, H, 6.98. N, 4.21.

8. (*E*)-3-(2-(piperidin-1-yl)benzylidene)-5-p-tolylpent-4-yn-2-one



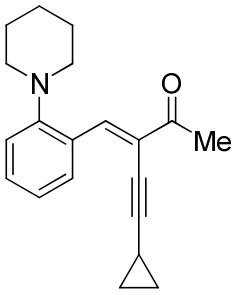
The reaction of (*Z*)-3-bromo-4-(2-(piperidin-1-yl)phenyl)but-3-en-2-one (5 mmol, 1.54 g), 1-ethynyl-4-methylbenzene (7.5 mmol, 0.87 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1h** (1.44 g) as an yellow solid in 84% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1); m.p.: 126-128 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.45 (d, *J* = 7.8 Hz, 1 H), 8.19 (s, 1 H), 7.45-7.30 (m, 3 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 7.10-7.00 (m, 2 H), 3.05-2.85 (m, 4 H), 2.62 (s, 3 H), 2.38 (s, 3 H), 1.80-1.70 (m, 4 H), 1.65-1.50 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.60, 155.00, 140.95, 138.78, 131.29, 131.16, 129.60, 129.19, 128.11, 121.49, 120.10, 119.29, 118.39, 98.18, 86.21, 54.65, 28.01, 26.44, 24.24, 21.52 ppm. MS (70 eV): m/z (%): 343 (M^+, 41.18), 149 (100). Anal, calcd for $C_{24}H_{25}NO$: C, 83.93, H, 7.34, N, 4.08, found: C, 83.79, H, 7.35. N, 4.06.

9. (*E*)-5-(4-methoxyphenyl)-3-(2-(piperidin-1-yl)benzylidene)pent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-(piperidin-1-yl)phenyl)but-3-en-2-one (5 mmol, 1.54 g), 1-ethynyl-4-methoxybenzene (7.5 mmol, 0.99 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1i** (1.60 g) as an yellow solid in 89% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 50 : 1); m.p.: 98-99 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.45 (d, *J* = 7.5 Hz, 1 H), 8.17 (s, 1 H), 7.55-7.40 (m, 2 H), 7.39-7.30 (m, 1 H), 7.10-7.00 (m, 2 H), 6.95-6.80 (m, 2 H), 3.83 (s, 3 H), 3.00-2.87 (m, 4 H), 2.62 (s, 3 H), 1.87-1.72 (m, 4 H), 1.65-1.55 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.65, 159.89, 154.94, 140.51, 132.88, 131.08, 129.55, 128.19, 121.47, 119.46, 118.38, 115.30, 114.12, 98.06, 85.61, 55.31, 54.63, 27.98, 26.44, 24.24 ppm. MS (70 eV): m/z (%): 359 (M^+, 93.29), 316 (100). HRMS calcd for $C_{24}H_{25}NO_2$: 359.1885, found: 359.1884.

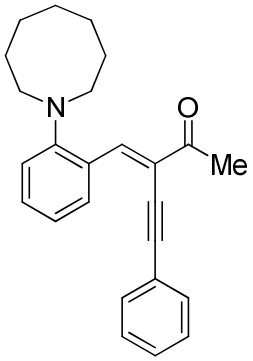
10. (*E*)-5-cyclopropyl-3-(2-(piperidin-1-yl)benzylidene)pent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-(piperidin-1-yl)phenyl)but-3-en-2-one (5 mmol, 1.54 g), ethynylcyclopropane (7.5 mmol, 0.495 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1j** (1.14 g) as an yellow solid in 78% yield by flash column

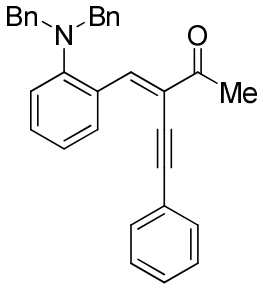
chromatography on silica gel (hexanes/ethyl acetate = 50 : 1); m.p.: 68-69 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.32 (d, *J* = 7.2 Hz, 1 H), 8.07 (s, 1 H), 7.36-7.28 (m, 1 H), 7.05-6.95 (m, 2 H), 2.95-2.85 (m, 4 H), 2.50 (s, 3 H), 1.80-1.70 (m, 4 H), 1.60-1.45 (m, 3 H), 0.95-0.75 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 197.10, 154.63, 140.23, 130.85, 129.14, 128.18, 121.31, 119.91, 118.27, 102.63, 72.71, 54.52, 27.71, 26.42, 24.21, 8.68, 0.71 ppm. MS (70 eV): m/z (%): 293 (M^+, 42.70), 250 (100). HRMS calcd for $C_{20}H_{23}NO$: 293.1780, found: 293.1779.

11. (*E*)-3-(2-(azocan-1-yl)benzylidene)-5-phenylpent-4-yn-2-one



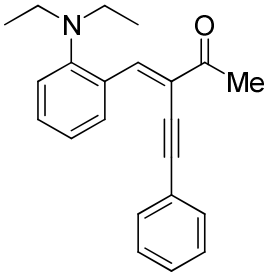
The reaction of (*Z*)-4-(2-(azocan-1-yl)phenyl)-3-bromobut-3-en-2-one (5 mmol, 1.68 g), ethynylbenzene (7.5 mmol, 0.77 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1k** (1.39 g) as an red oil in 78% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 70 : 1); ^{1}H NMR (300 MHz, $CDCl_3$): 8.39 (d, *J* = 7.8 Hz, 1 H), 8.31 (s, 1 H), 7.55-7.48 (m, 2 H), 7.40-7.30 (m, 4 H), 7.19 (d, *J* = 7.5 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 3.30-3.22(m, 4 H), 2.64 (s, 3 H), 1.77 (bs, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.26, 155.74, 142.97, 131.28, 131.08, 129.88, 128.46, 128.37, 128.06, 123.11, 120.72, 120.09, 118.35, 97.58, 87.00, 55.54, 28.21, 28.12, 27.45, 25.08 ppm; MS (70 eV): m/z (%): 357 (100). HRMS calcd for $C_{25}H_{27}NO$: 357.2093, found: 357.2092.

12. (*E*)-3-(2-(dibenzylamino)benzylidene)-5-phenylpent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-(dibenzylamino)phenyl)but-3-en-2-one (5 mmol, 2.10 g), ethynylbenzene (7.5 mmol, 0.77 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1l** (1.94 g) as an yellow oil in 88% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1); ^{1}H NMR (300 MHz, $CDCl_3$): 8.50 (s, 1 H), 8.42 (d, *J* = 7.8 Hz, 1 H), 7.55-7.45 (m, 2 H), 7.40-7.34 (m, 3 H), 7.32-7.15 (m, 11 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.98 (d, *J* = 8.1 Hz, 1 H), 4.17 (s, 3 H), 2.58 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.37, 152.03, 141.39, 137.64, 131.41, 130.74, 129.88, 129.28, 128.61, 128.45, 128.31, 127.17, 123.04, 122.38, 121.73, 119.81, 97.90, 86.74, 57.82, 28.06 ppm; MS (70 eV): m/z (%): 441 (M^+, 14.55), 91 (100). HRMS calcd for $C_{32}H_{27}NO$: 441.2093, found: 441.2094

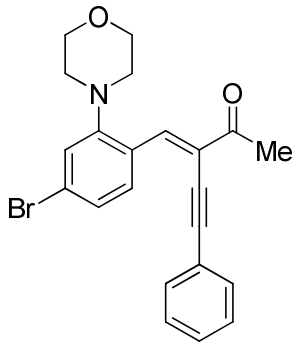
13. (*E*)-3-(2-(diethylamino)benzylidene)-5-phenylpent-4-yn-2-one



The reaction of (*Z*)-3-bromo-4-(2-(diethylamino)phenyl)but-3-en-2-one (5 mmol, 1.48 g), ethynylbenzene (7.5 mmol, 0.77 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.515 g) in THF afforded **1m** (0.97 g) as an yellow oil in 61% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 80 : 1); ^{1}H NMR (300 MHz, $CDCl_3$): 8.47 (d, *J* = 7.8 Hz, 1 H), 8.24 (s, 1 H), 7.55-7.45 (m, 2 H),

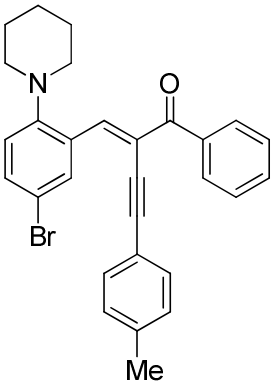
7.40-7.30 (m, 4 H), 7.15-7.00 (m, 2 H), 3.10 (q, *J* = 7.2 Hz, 4 H), 2.63 (s, 3 H), 1.07 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): 196.58, 152.60, 141.89, 131.34, 130.62, 129.78, 129.76, 128.52, 128.42, 123.13, 121.57, 120.82, 118.90, 97.75, 86.96, 47.94, 28.12, 12.45 ppm; MS (70 eV): m/z (%): 317 (M^+, 20.24), 288 (100). HRMS calcd for $C_{22}H_{23}NO$: 317.1780, found: 317.1779.

14. (*E*)-3-(4-bromo-2-morpholinobenzylidene)-5-phenylpent-4-yn-2-one



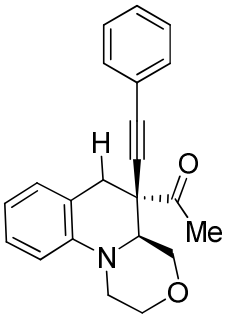
The reaction of (*Z*)-3-bromo-4-(4-bromo-2-morpholinophenyl)but-3-en-2-one (5 mmol, 1.95 g), ethynylbenzene (7.5 mmol, 0.765 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1n** (1.62 g) as an yellow solid in 79% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1); m.p: 144-145 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.28 (d, *J* = 8.4 Hz, 1 H), 8.08 (s, 1 H), 7.55-7.46 (m, 2 H), 7.40-7.30 (m, 3 H), 7.28-7.20 (m, 1 H), 7.19-7.11 (m, 1 H), 3.89 (t, *J* = 4.5 Hz, 4 H), 2.98 (t, *J* = 4.5 Hz, 4 H), 2.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 195.90, 154.33, 139.10, 131.33, 130.81, 128.88, 128.52, 126.81, 125.46, 125.40, 122.63, 121.80, 119.79, 98.73, 86.35, 66.93, 53.19, 28.14. MS (70 eV): m/z (%): 409 (M^+, 18.26), 411 (M^++2, 18.18), 43 (100). Anal, calcd for $C_{22}H_{20}BrNO_2$: C, 64.40, H, 4.91, N, 3.41, found: C, 64.29, H, 4.91. N, 3.41.

15. (*E*)-2-(5-bromo-2-(piperidin-1-yl)benzylidene)-1-phenyl-4-p-tolylbut-3-yn-1-one



The reaction of (Z)-2-bromo-3-(5-bromo-2-(piperidin-1-yl)phenyl)-1-phenyl-prop-2-en-1-one (5 mmol, 2.25 g), 1-ethynyl-4-methylbenzene (7.5 mmol, 0.87 g), $Pd(PPh_3)_4$ (1 mol%, 57.8 mg), CuI (2 mol%, 19.1 mg) and diisopropyl amine (15 mmol, 1.52 g) in THF afforded **1o** (2.06 g) as an yellow solid in 85% yield by flash column chromatography on silica gel (hexanes/ethyl acetate = 30 : 1); m.p: 122-123 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.83 (d, *J* = 2.4 Hz, 1 H), 7.99 (d, *J* = 8.7 Hz, 2 H), 7.87 (s, 1 H), 7.60-7.52 (m, 1 H), 7.52-7.40 (m, 3 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 6.92 (d, *J* = 8.7 Hz, 1 H), 2.95-2.80 (m, 4 H), 2.36 (s, 3 H), 1.70-1.60 (m, 4 H), 1.59-1.49 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.53, 153.46, 140.95, 139.05, 137.37, 133.47, 132.29, 132.00, 131.45, 130.21, 129.57, 129.18, 128.03, 120.76, 120.34, 119.68, 114.54, 101.14, 86.04, 54.44, 26.16, 23.98, 21.56 ppm. MS (70 eV): m/z (%): 483 (M^+, 22.11), 105 (100). HRMS calcd for $C_{29}H_{26}BrNO$: 483.1198, found: 483.1200.

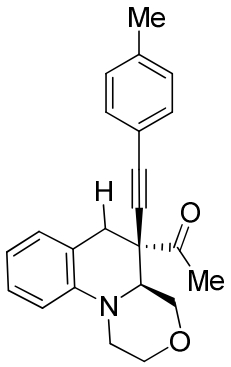
16. 1-((4aS,5R)-5-(phenylethynyl)-1,2,4,4a,5,6-hexahydro-[1,4]oxazino[4,3-a]quinolin-5-yl)ethanone



Synthesis of **2a**: A solution of **1a** (0.3 mmol, 99.3 mg) and $Sc(OTf)_3$ (10

mol%, 14.8 mg) in DCE (3.0 mL) was stirred under reflux for 34.5 h. The reaction was completed as determined by TLC analysis. After concentration of the reaction mixture under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1) to afford the pure product **2a** (85.3 mg, dr = 15 : 1) as a yellow oil in a yield of 86%; ^{1}H NMR (300 MHz, $CDCl_3$): major : 7.40-7.24 (m, 5 H), 7.20-7.10 (m, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 6.85-6.70 (m, 2 H), 4.10-3.90 (m, 2 H), 3.80-3.70 (m, 2 H), 3.69-3.60 (m, 2 H), 3.25 (d, *J* = 15.3 Hz, 1 H), 3.20-3.10 (m, 1 H), 3.05 (d, *J* = 15.3 Hz, 1 H), 2.53 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.61, 144.38, 131.61, 129.23, 128.40, 128.21, 127.66, 122.52, 120.59, 118.23, 112.26, 86.96, 86.84, 68.25, 66.38, 58.40, 49.36, 46.97, 38.05, 27.67 ppm. MS (70 eV): m/z (%): 331 (100). HRMS calcd for $C_{22}H_{21}NO_2$: 331.1572, found: 331.1570.

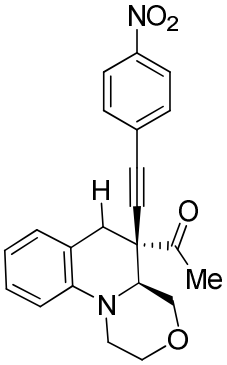
17. (1-((4aS,5R)-5-(p-tolylethynyl)-1,2,4,4a,5,6-hexahydro-[1,4]oxazino [4,3-a]quinolin-5-yl)ethanone)



The reaction of **1b** (0.3 mmol, 103.5 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2b** (70.4 mg, dr = 17 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1) as a light yellow oil in 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$): major : 7.30-7.00 (m, 6 H), 6.85-6.70 (m, 2 H), 4.05-3.90 (m, 2 H), 3.80-3.60 (m, 4 H), 3.23 (d, *J* = 15.3 Hz, 1 H), 3.20-3.00 (m, 2 H), 2.52 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.74, 144.35, 138.55, 131.49, 129.21, 128.94, 127.64, 120.70, 119.43, 118.21, 112.26, 87.05, 86.04, 68.26, 66.34, 58.39, 49.33, 47.01, 37.95, 27.59, 21.42 ppm. MS (70 eV): m/z (%): 345 (100). HRMS calcd for $C_{23}H_{23}NO_2$:

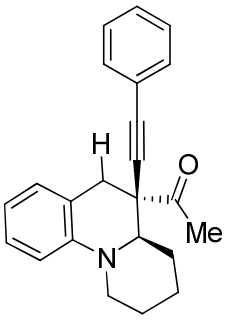
345.1729, found: 345.1729.

18. 1-((4aS,5R)-5-((4-nitrophenyl)ethynyl)-1,2,4,4a,5,6-hexahydro-[1,4]oxazino[4,3-a]quinolin-5-yl)ethanone



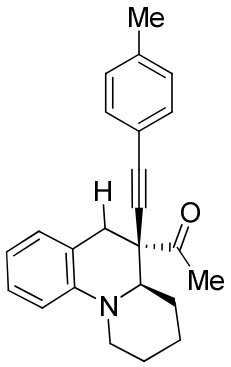
The reaction of **1d** (0.3 mmol, 112.8 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2d** (89.1 mg, dr = 10 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1) as a light yellow solid in 79% yield; m.p.: 109-110℃, ^{1}H NMR (300 MHz, $CDCl_3$): major: 8.13 (d, *J* = 8.7 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.17 (t, *J* = 7.8 Hz, 1 H), 7.03 (d, *J* = 7.2 Hz, 1 H), 6.85-6.70 (m, 2 H), 3.99 (d, *J* = 8.1 Hz, 2 H), 3.85-3.55 (m, 4 H), 3.27(d, *J* = 15.6 Hz, 1 H), 3.15-3.00 (m, 2 H), 2.53 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.77, 147.10, 144.31, 132.45, 129.33, 129.27, 127.84, 123.47, 120.05, 118.48, 112.42, 92.58, 85.27, 68.12, 66.50, 58.41, 49.56, 46.88, 38.20, 28.05 ppm. MS (70 eV): m/z (%): 376 (100). HRMS calcd for $C_{22}H_{20}N_2O_4$: 376.1423, found: 376.1425.

19. 1-((4aR,5R)-5-(phenylethynyl)-2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinolin-5-yl)ethanone



The reaction of **1g** (0.3 mmol, 98.7 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2g** (74.1 mg, dr = 11 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1) as a light yellow solid in 75% yield; m.p: 82-83 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): major: 7.40-7.35 (m, 2 H), 7.35-7.25 (m, 3 H), 7.15-7.00 (m, 2 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 4.05 (d, *J* = 7.2 Hz, 1 H), 3.69 (d, *J* = 10.5 Hz, 1 H), 3.36 (d, *J* = 15.6 Hz, 1 H), 3.10-2.85 (m, 2 H), 2.45 (s, 3 H), 1.94 (d, *J* = 10.8 Hz, 2 H), 1.75-1.50 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.37, 143.74, 131.64, 129.17, 128.29, 128.22, 127.39, 122.75, 121.06, 117.47, 113.01, 88.20, 86.09, 61.67, 51.31, 49.06, 34.40, 26.25, 25.78, 25.21, 23.07 ppm. MS (70 eV): m/z (%): 329 (100). HRMS calcd for $C_{23}H_{23}NO$: 329.1780, found: 329.1778.

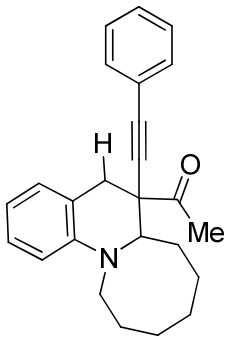
20. 1-((4aR,5R)-5-(p-tolylethynyl)-2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a] quinolin-5-yl)ethanone



The reaction of **1h** (0.3 mmol, 102.9 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2h** (75.1 mg, dr = 8 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 40 : 1) as a light yellow oil in 73% yield; ^{1}H NMR (300 MHz, $CDCl_3$): major: 7.26 (d, *J* = 7.2 Hz, 2 H), 7.15-7.00 (m, 4 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 6.68 (t, *J* = 8.2 Hz, 1 H), 4.04 (d, *J* = 13.8 Hz, 1 H), 3.68 (d, *J* = 10.5 Hz, 1 H), 3.34 (d, *J* = 15.9 Hz, 1 H), 3.00(d, *J* = 15.9 Hz, 1 H), 2.95-2.80 (m, 1 H), 2.43 (s, 3 H), 2.33 (s, 3 H), 1.93 (d, *J* = 11.7 Hz, 2 H), 1.70-1.50 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.42, 143.63, 138.44, 131.52, 129.18, 128.98, 127.35, 121.14, 119.64,

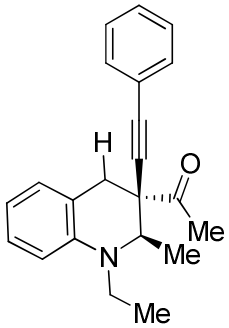
117.46, 113.00, 87.41, 86.12, 61.71, 51.19, 49.09, 34.14, 26.09, 25.62, 25.28, 22.93, 21.45 ppm. MS (70 eV): m/z (%): 343 (M^+, 1.83), 91 (100). HRMS calcd for $C_{24}H_{25}NO$: 343.1936, found: 343.1937.

21. 1-(6-(phenylethynyl)-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a] quinolin-6-yl)ethanone



The reaction of **1k** (0.3 mmol, 107.1 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2k** (85.7 mg, dr = 2 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1) as a light yellow oil in 80% yield; major : minor = 2:1, ^{1}H NMR (300 MHz, $CDCl_3$): [7.50-7.40 (m, 1.34 H), 7.27-7.20 (m, 1.66 H)], 7.37-7.30 (m, 2 H), 7.18-7.00 (m, 3 H), 6.80-6.50 (m, 2 H), 4.10-3.75 (m, 2 H), [3.55-3.32 (m, 1.33 H), 3.30-3.10 (m, 1.34 H), 2.85 (d, *J* = 16.8 Hz, 0.33 H)], 2.51 (s, 1 H), 2.29 (s, 2 H), 2.15-1.30 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.72, 202.88, 143.04, 142.59, 131.64, 131.57, 129.90, 128.83, 128.38, 128.28, 128.11, 128.08, 127.42, 127.17, 122.87, 122.64, 118.52, 118.23, 116.03, 115.90, 112.28, 111.55, 89.43, 88.87, 85.93, 84.23, 63.98, 62.92, 56.25, 53.96, 50.22, 49.37, 32.33, 30.81, 30.15, 30.12, 28.16, 27.96, 27.91, 27.57, 27.53, 27.23, 26.94, 26.70, 25.97, 24.89 ppm. MS (70 eV): m/z (%): 357 (100). HRMS calcd for $C_{25}H_{27}NO$: 357.2093, found: 357.2093.

22. (1-ethyl-2-methyl-3-(phenylethynyl)-1,2,3,4–tetrahydroquinolin-3-yl)ethanone

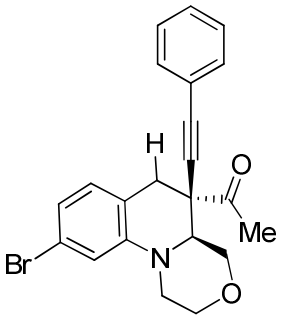


The reaction of **1m** (0.3 mmol, 95.1 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2m** (62.8 mg, dr = 1 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 30 : 1) in 66% yield.

The first fraction: Yellow solid in a yield of 35%; m.p: 110-111℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.45-7.35 (m, 2 H), 7.35-7.27 (m, 3 H), 7.15-7.00 (m, 2 H), 6.66 (t, *J* = 7.2 Hz, 1 H), 6.56 (d, *J* = 8.4 Hz, 1 H), 4.05 (q, *J* = 6.3 Hz, 1 H), 3.50-3.20 (m, 3 H), 3.15 (d, *J* = 6.3 Hz, 1 H), 2.35 (s, 3 H), 1.35 (d, *J* = 6.3 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 202.29, 142.00, 131.61, 128.84, 128.41, 128.29, 127.32, 122.58, 118.79, 116.28, 111.14, 88.57, 85.76, 57.57, 50.69, 44.77, 31.72, 24.36, 15.24, 13.09 ppm. MS (70 eV): m/z (%): 317 (100). HRMS calcd for $C_{22}H_{23}NO$: 317.1780, found: 317.1782.

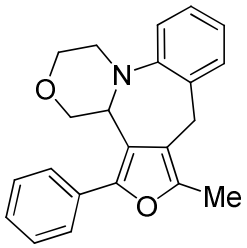
The second fraction: Yellow oil in a yield of 31%;^{1}H NMR (300 MHz, $CDCl_3$): 7.26-7.18 (m, 5 H), 7.15-7.05 (m, 2 H), 6.63 (t, *J* = 7.2 Hz, 1 H), 3.90-3.80 (m, 1 H), 3.72-3.60 (m, 1 H), 3.45-3.20 (m, 2 H), 2.87 (d, *J* = 16.5 Hz, 1 H), 2.50 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 0.95 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 204.55, 141.79, 131.53, 129.99, 128.10, 128.08, 127.27, 122.87, 117.97, 115.50, 110.71, 89.75, 84.48, 58.73, 49.81, 45.36, 30.26, 25.99, 15.81, 13.10 ppm.

23. 1-((4aS,5R)-9-bromo-5-(phenylethynyl)-1,2,4,4a,5,6-hexahydro-[1,4]ox-azino[4,3-a]quinolin-5-yl)ethanone



The reaction of **1o** (0.3 mmol, 122.7 mg) under the catalysis of $Sc(OTf)_3$ (10 mol%, 14.8 mg) in DCE (3.0 mL) afforded the **2o** (88.4 mg, dr = 12 : 1) by flash column chromatography on silica gel (hexanes/ethyl acetate = 10 : 1) as a light yellow solid in 72% yield. m.p: 121-123 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.40-7.24 (m, 5 H), 6.90-6.78 (m, 3 H), 4.05-3.90 (m, 2 H), 3.75-3.55 (m, 4 H), 3.20-3.05 (m, 2 H), 2.96 (d, *J* = 15.3 Hz, 1 H), 2.51 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 205.42, 145.51, 131.61, 130.42, 128.55, 128.26, 122.27, 121.37, 120.87, 119.38, 115.17, 87.25, 86.28, 68.17, 66.22, 58.11, 49.02, 46.77, 37.64, 27.74 ppm. MS (70 eV): m/z (%): 409 (M^+, 78.46), 43 (100). HRMS calcd for $C_{22}H_{20}BrNO_2$: 409.0677, found: 409.0677.

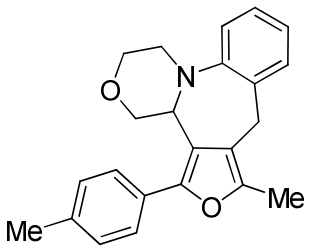
24. 11-methyl-13-phenyl-3,4,10,13b-tetrahydro-1H-benzo[f]furo[3,4-c][1,4] oxazino[4,3-a]azepine



To a dry Schlenk tube, IPrAuCl (5 mol%, 9.3 mg), AgOTf (5 mol%, 3.9 mg) and anhydrous CH_3CN (1.0 mL) were added and the mixture was stirred at room temperature for 10 min in dark. After which, the substrate **1a** (0.3 mmol, 99.3 mg) and anhydrous CH_3CN (2.0 mL) were added, and this reaction mixture was stirred for 3 h at room temperature and the reaction was complete as determined by TLC analysis. After concentration under reduced pressure, the residue was purified by flash column chromatography on silica gel

(hexanes/ethyl acetate = 20:1) to afford the pure product **3a** (91.4 mg) as a light yellow solid in 92% yield. m.p.: 163-165 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.59 (d, *J* = 7.8 Hz, 2 H), 7.37 (t, *J* = 7.5 Hz, 2 H), 7.30-7.10 (m, 4 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 4.44 (dd, *J* = 9.6, 2.4 Hz, 1 H), 4.28 (d, *J* = 13.5 Hz, 1 H), 4.15 (d, *J* = 9.6 Hz, 1 H), 3.95-3.75 (m, 2 H), 3.65-3.50 (m, 2 H), 3.30 (d, *J* = 13.5 Hz, 1 H), 3.10 (d, *J* = 11.4 Hz, 1 H), 2.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.29, 146.15, 144.44, 139.32, 131.34, 128.61, 127.38, 126.94, 126.69, 124.85, 123.46, 119.98, 119.29, 117.80, 71.44, 67.62, 60.76, 51.84, 28.81, 11.28 ppm. MS (70 eV): m/z (%):331 (M^+, 79.81), 273 (100). Anal, calcd for $C_{22}H_{21}NO_2$: C, 79.73, H, 6.39, N, 4.23, found: C, 79.74, H, 6.47. N, 4.27.

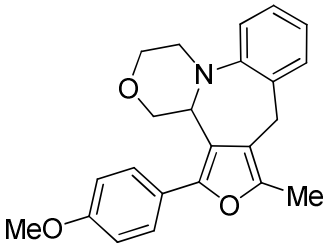
25. 11-methyl-13-p-tolyl-3,4,10,13b-tetrahydro-1H-benzo[f]furo[3,4-c][1,4] oxazino[4,3-a]azepine



The reaction of **1b** (0.3 mmol, 103.5 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3b** (88.0 mg) as a yellow solid in 85% yield; m.p.: 148-149 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (d, *J* = 7.8 Hz, 2 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.23-7.15 (m, 4 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 4.44 (dd, *J* = 9.9, 2.4 Hz, 1 H), 4.28 (d, *J* = 15.5 Hz, 1 H), 4.05 (d, *J* = 10.8 Hz, 1 H), 3.90-3.75 (m, 2 H), 3.65-3.45 (m, 2 H), 3.31 (d, *J* = 13.5 Hz, 1 H), 3.11 (d, *J* = 11.4 Hz, 1 H), 2.36 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.29, 146.34, 143.98, 139.30, 136.45, 129.29, 128.59, 127.32, 126.92, 124.80, 123.41, 119.94, 119.09, 116.98, 71.39, 67.58, 60.72, 51.81, 28.80, 21.11, 11.25 ppm. MS (70 eV): m/z (%): 345 (M^+, 72.87), 287(100). HRMS calcd for $C_{23}H_{23}NO_2$: 345.1729, found: 345.1730.

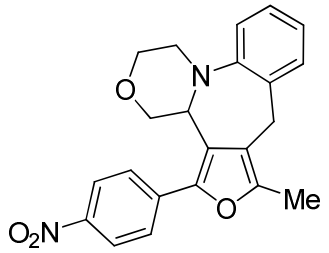
26. 13-(4-methoxyphenyl)-11-methyl-3,4,10,13b-tetrahydro-1H-benzo[f]

furo [3,4-c][1,4]oxazino[4,3-a]azepine



The reaction of **1c** (0.3 mmol, 108.3 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3c** (75.8 mg) as a light yellow solid in 70% yield; m.p.: 138-139 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (d, 2 H), 7.30-7.20 (m, 1 H), 7.20-7.10 (m, 2 H), 7.00 (td, *J* = 7.2, 0.9 Hz, 1 H), 6.95-6.85 (m, 2 H), 4.36 (dd, *J* = 9.9, 2.7 Hz, 1 H), 4.25 (d, *J* = 13.5 Hz, 1 H), 4.02 (d, *J* = 14.1 Hz, 1 H), 3.90-3.70 (m, 5 H), 3.60-3.40 (m, 2 H), 3.28 (d, *J* = 13.5 Hz, 1 H), 3.09 (d, *J* = 10.8 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.37, 149.31, 146.24, 143.68, 139.31, 127.33, 126.96, 126.37, 124.30, 123.43, 119.94, 118.96, 116.10, 114.07, 71.44, 67.61, 60.71, 55.21, 51.85, 28.83, 11.25 ppm. MS (70 eV): m/z (%): 361 (M^+, 71.09), 303 (100). HRMS calcd for $C_{23}H_{23}NO_3$: 361.1678, found: 361.1680.

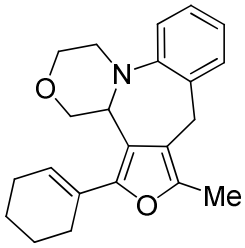
27. 11-methyl-13-(4-nitrophenyl)-3,4,10,13b-tetrahydro-1H-benzo[f]furo[3, 4-c][1,4]oxazino[4,3-a]azepine



The reaction of **1d** (0.3 mmol, 112.8 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3d** (111.7 mg) as a light yellow solid in 99% yield; m.p.: 273-274 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (d, *J* = 9.0 Hz, 2 H), 7.70 (d, *J* = 9.0 Hz, 2 H), 7.32-7.22 (m, 1 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 4.41 (dd, *J* = 14.7, 2.7 Hz, 1 H), 4.28 (d, *J* = 13.5 Hz, 1 H), 4.05 (d, *J* = 10.8 Hz, 1 H), 3.90-3.75 (m, 2 H), 3.55-3.45 (m, 2 H), 3.28 (d, *J* = 13.5

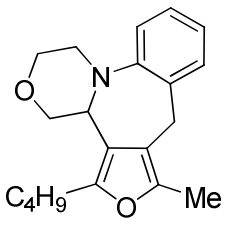
Hz, 1 H), 3.11 (d, *J* = 10.8 Hz, 1 H), 2.36 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 148.94, 147.21, 145.41, 144.01, 139.09, 136.91, 127.64, 126.97, 124.48, 124.40, 123.77, 122.50, 120.72, 120.14, 71.19, 67.63, 60.91, 51.72, 28.63, 11.48 ppm. MS (70 eV): m/z (%): 376 (M^+, 70.37), 318 (100). HRMS calcd for $C_{22}H_{20}N_2O_4$: 376.1423, found: 376.1424.

28. 13-cyclohexenyl-11-methyl-3,4,10,13b-tetrahydro-1H-benzo[f]furo[3,4-c] [1,4]oxazino[4,3-a]azepine



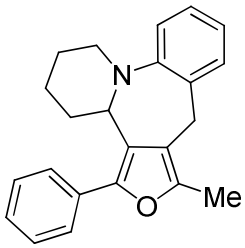
The reaction of **1e** (0.3 mmol, 100.5 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3e** (64.5 mg) as a light yellow solid in 64% yield; m.p: 52-53 ℃ ^{1}H NMR (300 MHz, $CDCl_3$): 7.19 (t, *J* = 7.8 Hz, 1 H), 7.08 (t, *J* = 8.4 Hz, 2 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 5.95 (s, 1 H), 4.20-4.05 (m, 2 H), 3.97 (d, *J* = 10.5 Hz, 1 H), 3.89 (d, *J* = 11.4 Hz, 1 H), 3.77 (t, *J* = 10.8 Hz, 1 H), 3.55-3.35 (m, 2 H), 3.89 (d, *J* = 13.2 Hz, 1 H), 3.02 (d, *J* = 10.4 Hz, 1 H), 2.45-2.30 (m, 1 H), 2.21 (s, 3 H), 2.13 (s, 3 H), 1.70-1.50 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.30, 148.56, 142.59, 139.35, 128.77, 127.17, 126.84, 125.02, 123.19, 119.79, 118.43, 115.63, 71.76, 67.57, 60.59, 51.79, 28.78, 26.05, 25.39, 22.48, 21.91, 11.09 ppm. MS (70 eV): m/z (%): 335 (100). HRMS calcd for $C_{22}H_{25}NO_2$: 335.1885, found: 335.1885.

29. 13-butyl-11-methyl-3,4,10,13b-tetrahydro-1H-benzo[f]furo[3,4-c][1,4] oxazino[4,3-a]azepine



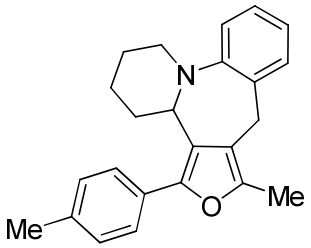
The reaction of **1f** (0.3 mmol, 93.3 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3f** (49.5 mg) as a yellow oil in 53% yield; ^{1}H NMR (300 MHz, $CDCl_3$): 7.11 (t, *J* = 7.5 Hz, 1 H), 6.99 (t, *J* = 8.7 Hz, 2 H), 6.85 (t, *J* = 7.5 Hz, 1 H), 4.03 (d, *J* = 13.2 Hz, 1 H), 3.89 (d, *J* = 10.5 Hz, 1 H), 3.76 (dd, *J* = 10.2, 2.7 Hz, 1 H), 3.67 (t, *J* = 10.4 Hz, 2 H), 3.46 (t, *J* = 10.5 Hz, 1 H), 3.34 (td, *J* = 10.4, 2.7 Hz, 1 H), 3.10 (d, *J* = 15.2 Hz, 1 H), 2.94 (d, *J* = 11.4 Hz, 1 H), 2.27 (t, *J* = 7.5 Hz, 2 H), 2.11 (s, 3 H), 1.52-1.32 (m, 2 H), 1.30-1.10 (m, 2 H), 0.79 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.31, 149.22, 142.48, 139.40, 127.14, 126.99, 123.18, 119.92, 117.11, 114.68, 72.81, 67.46, 59.72, 51.80, 30.48, 28.77, 26.40, 22.57, 13.79, 11.06 ppm. MS (70 eV): m/z (%): 311 (M^+, 79.81), 149 (100). HRMS calcd for $C_{20}H_{25}NO_2$: 311.1885, found: 311.1885.

30. 11-methyl-13-phenyl-1,2,3,4,10,13b-hexahydrobenzo[f]furo[3,4-c]pyrido[1,2-a]azepine



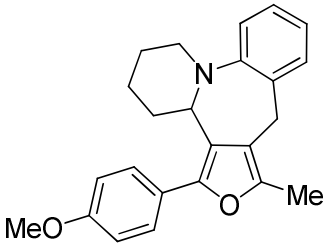
The reaction of **1g** (0.3 mmol, 98.7 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3g** (97.7 mg) as a light yellow solid in 99% yield; m.p.: 149-150 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (d, *J* = 7.8 Hz, 2 H), 7.40 (t, *J* = 7.5 Hz, 2 H), 7.27-7.17 (m, 2 H), 7.15 (d, *J* = 7.5 Hz, 2 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 4.32-4.16 (m, 2 H), 3.42-3.15 (m, 3 H), 2.36 (s, 3 H), 2.00-1.59 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): 150.48, 144.94, 143.81, 139.83, 131.88, 128.40, 127.05, 126.37, 126.14, 124.77, 123.92, 122.60, 120.55, 119.31, 61.45, 53.81, 35.52, 28.89, 26.80, 25.34, 11.28 ppm. MS (70 eV): m/z (%): 329 (100). Anal, calcd for $C_{23}H_{23}NO$: C, 83.85, H, 7.04, N, 4.25, found: C, 83.64, H, 6.97. N, 4.30.

31. 11-methyl-13-p-tolyl-1,2,3,4,10,13b-hexahydrobenzo[f]furo[3,4-c]pyrido[1,2-a]azepine



The reaction of **1h** (0.3 mmol, 102.9 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3h** (97.8 mg) as a light yellow solid in 95% yield; m.p.: 137-139 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.44 (d, *J* = 7.8 Hz, 2 H), 7.35-7.05 (m, 5 H), 7.00-6.85 (m, 1 H), 4.32-4.05 (m, 2 H), 3.42-3.05 (m, 3 H), 2.36 (s, 3 H), 2.33 (s, 3 H), 2.00-1.50 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): 150.55, 145.19, 143.40, 139.86, 135.88, 129.20, 129.12, 127.03, 126.40, 124.79, 123.12, 122.58, 120.55, 119.15, 61.48, 53.84, 35.50, 28.93, 26.83, 25.36, 21.14, 11.28 ppm. MS (70 eV): m/z (%): 343 (100). HRMS calcd for $C_{24}H_{25}NO$: 343.1936, found: 343.1936.

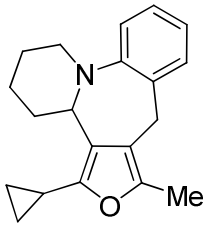
32. 13-(4-methoxyphenyl)-11-methyl-1,2,3,4,10,13b-hexahydrobenzo[f]furo[3,4-c]pyrido[1,2-a]azepine



The reaction of **1i** (0.3 mmol, 107.7 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3i** (100.2 mg) as a yellow solid in 93% yield; m.p.: 138-139 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.46 (d, *J* = 8.7 Hz, 2 H), 7.23-7.05 (m, 3 H), 7.00-6.80 (m, 3 H), 4.23 (d, *J* = 6.9 Hz, 1 H), 4.13 (d, *J* = 8.7 Hz, 1 H), 3.82 (s, 3 H), 3.40-3.10 (m, 3 H), 2.32 (s, 3 H), 2.00-1.50 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.04, 150.57, 145.09, 143.06, 139.87, 127.02, 126.42, 126.33, 124.99, 122.58, 122.23, 120.53, 119.05, 113.90, 61.47, 55.21, 53.85, 35.57, 28.96, 26.86, 25.37, 11.24 ppm. MS (70 eV): m/z (%): 359 (100).

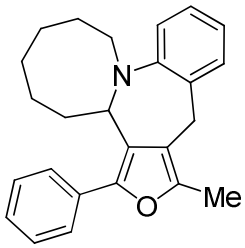
HRMS calcd for $C_{24}H_{25}NO_2$: 359.1885, found: 359.1884.

33. 13-cyclopropyl-11-methyl-1,2,3,4,10,13b-hexahydrobenzo[f]furo[3,4-c] pyrido[1,2-a]azepine



The reaction of **1j** (0.35 mmol, 102.6 mg) in anhydrous CH_3CN (3.5 mL) was catalyzed by IPrAuOTf, afforded **3j** (62.6 mg) as a light yellow oil in 61% yield; ^{1}H NMR (300 MHz, $CDCl_3$): 7.26-7.15 (m, 1 H), 7.11 (t, *J* = 7.5 Hz, 2 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 4.14 (d, *J* = 13.2 Hz, 1 H), 3.85-3.75 (m, 1 H), 3.35 (d, *J* = 4.2 Hz, 1 H), 3.25-3.10 (m, 2 H), 2.20 (s, 3 H), 2.05-1.87 (m, 2 H), 1.87-1.70 (m, 3 H), 1.69-1.55 (m, 2 H), 0.95-0.65 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): 150.71, 147.37, 140.75, 139.83, 126.89, 126.57, 122.44, 121.22, 120.55, 117.65, 60.61, 53.76, 36.77, 28.91, 26.86, 25.31, 11.02, 7.59, 6.31, 5.33 ppm. MS (70 eV): m/z (%): 293 (100). HRMS calcd for $C_{20}H_{23}NO$: 293.1780, found: 293.1780.

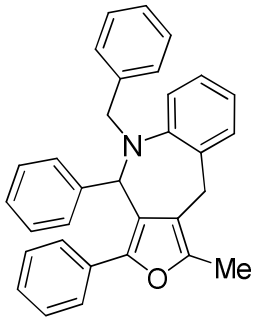
34. Synthesis of 3k.



The reaction of **1k** (0.3 mmol, 107.1 mg) in anhydrous CH_3CN (3.0 mL) was catalyzed by IPrAuOTf, afforded **3k** (100.7 mg) as a light yellow oil in 94% yield; ^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (d, *J* = 7.8 Hz, 2 H), 7.50-7.40 (m, 2 H), 7.35-7.25 (m, 1 H), 7.24-7.05 (m, 3 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 4.95 (dd, *J* = 10.2, 4.2 Hz, 1 H), 4.23 (d, *J* = 16.2 Hz, 1 H), 3.85 (d, *J* = 15.3 Hz, 1 H), 3.74 (d, *J* = 16.2 Hz, 1 H), 3.35-3.20 (m, 1 H), 2.37 (s, 3 H), 2.20-1.50 (m, 10 H); ^{13}C

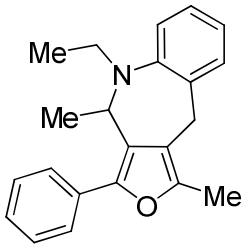
NMR (75 MHz, $CDCl_3$): 148.40, 145.10, 144.50, 131.83, 130.20, 130.08, 128.50, 127.10, 126.57, 125.57, 124.19, 120.09, 119.74, 118.50, 57.98, 54.67, 34.56, 31.23, 28.02, 27.26, 26.69, 23.91, 11.31 ppm. MS (70 eV): m/z (%): 357 (M^+, 47.25), 273 (100). HRMS calcd for $C_{25}H_{27}NO$: 357.2092, found: 357.2029.

35. 5-benzyl-1-methyl-3,4-diphenyl-5,10-dihydro-4H-benzo[b]furo[3,4-e] azepine



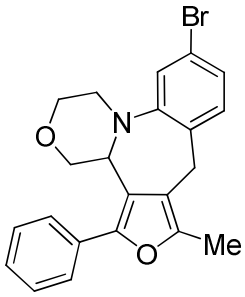
The reaction of **1l** (0.25 mmol, 110.3 mg) in anhydrous CH_3CN (2.5 mL) was catalyzed by IPrAuOTf, afforded **3l** (107.0 mg) as a yellow solid in 97% yield; m.p.: 62-63 ℃; ^1H NMR (300 MHz, $CDCl_3$): 7.48 (d, *J* = 7.5 Hz, 2 H), 7.29 (t, *J* = 7.5 Hz, 2 H), 7.23-7.11 (m, 4 H), 7.10-6.96 (m, 6 H), 6.95-6.88 (m, 2 H), 6.85-6.70 (m, 2 H), 6.50-6.35 (m, 1 H), 5.49 (s, 1 H), 4.42 (dd, *J* = 14.7, 2.7 Hz, 1 H), 4.28 (d, *J* = 14.7 Hz, 2 H), 3.57 (d, *J* = 14.7 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 147.86, 145.98, 144.69, 139.03, 138.97, 136.15, 131.15, 128.65, 128.48, 128.26, 128.17, 127.86, 127.27, 127.03, 126.77, 126.63, 126.20, 125.35, 124.31, 123.42, 122.27, 118.39, 61.37, 57.26, 30.19, 11.61 ppm. MS (70 eV): m/z (%): 441 (M^+, 27.47), 350 (100). HRMS calcd for $C_{32}H_{27}NO$: 441.2094, found: 441.2093.

36. 5-ethyl-1,4-dimethyl-3-phenyl-5,10-dihydro-4H-benzo[b]furo[3,4-e]az-epine



The reaction of **1m** (0.35 mmol, 111.0 mg) in anhydrous CH_3CN (3.5 mL) was catalyzed by IPrAuOTf, afforded **3m** (103.2 mg) as a yellow solid in 93% yield; ^{1}H NMR (300 MHz, $CDCl_3$): 7.54 (d, *J* = 8.4 Hz, 2 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.19 (t, *J* = 7.5 Hz, 3 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 6.99 (t, *J* = 7.2 Hz, 1 H), 4.82 (q, *J* = 6.6 Hz, 1 H), 4.12 (d, *J* = 14.4 Hz, 1 H), 3.55-3.30 (m, 2 H), 3.20-3.00 (m, 1 H), 2.33 (s, 3 H), 1.16 (t, *J* = 7.5 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 147.08, 144.66, 144.12, 137.77, 132.18, 128.42, 126.47, 126.26, 125.51, 125.09, 124.15, 123.47, 117.35, 54.33, 47.01, 29.95, 16.15, 14.51, 11.45 ppm. MS (70 eV): m/z (%): 317 (M^+, 15.18), 302 (100). HRMS calcd for $C_{22}H_{23}NO$: 317.1780, found: 317.1780.

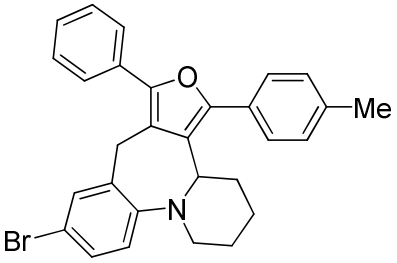
37. 7-bromo-11-methyl-13-phenyl-3,4,10,13b-tetrahydro-1H-benzo[f]furo [3,4-c][1,4]oxazino[4,3-a]azepine



The reaction of **1n** (0.25 mmol, 102.5 mg) in anhydrous CH_3CN (3.5 mL) was catalyzed by IPrAuOTf, afforded **3n** (71.8 mg) as a yellow solid in 70% yield; m.p.: 174-175 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.54 (d, *J* = 7.8 Hz, 2 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 7.25-7.15 (m, 2 H), 7.14-7.05 (m, 1 H), 7.00 (d, *J* = 8.1 Hz, 1 H), 4.40 (dd, *J* = 9.9, 2.7 Hz, 1 H), 4.14 (d, *J* = 13.5 Hz, 1 H), 4.00 (d, *J* = 10.8 Hz, 1 H), 3.90-3.70 (m, 2 H), 3.60-3.40 (m, 2 H), 3.24 (d, *J* = 13.5 Hz, 1 H), 3.05 (d, *J* = 10.8 Hz, 1 H), 2.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 150.59,

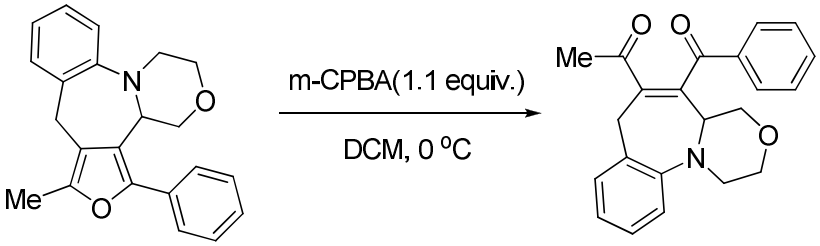
146.37, 144.59, 138.16, 131.12, 128.68, 128.17, 126.89, 126.31, 124.91, 123.61, 120.47, 118.58, 117.18, 71.41, 67.41, 60.74, 51.86, 28.32, 11.29 ppm. MS (70 eV): m/z (%): 409 (M^+, 96.87), 411 (100). Anal, calcd for $C_{22}H_{20}BrNO_2$: C, 64.40, H, 4.91, N, 3.41, found: C, 64.49, H, 4.99. N, 3.45.

38. 8-bromo-11-phenyl-13-p-tolyl-1,2,3,4,10,13b-hexahydrobenzo[f]furo[3, 4-c]pyrido[1,2-a]azepine)



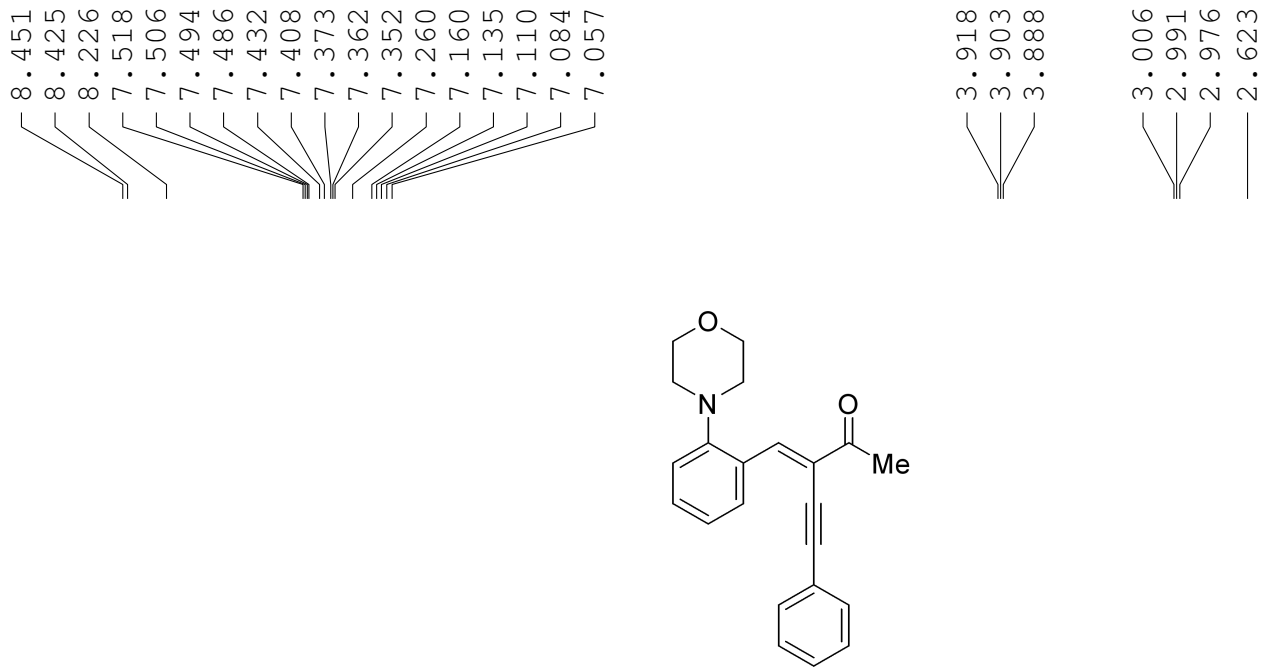
The reaction of **1o** (0.25 mmol, 120.8 mg) in anhydrous CH_3CN (3.5 mL) was catalyzed by IPrAuOTf, afforded **3o** (112.3 mg) as a yellow solid in 93% yield; m.p.: 257-258 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.69 (d, *J* = 7.5 Hz, 2 H), 7.60-7.40 (m, 4 H), 7.39-7.26 (m, 2 H), 7.26-7.15 (m, 3 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 4.41 (d, *J* = 13.2 Hz, 1 H), 4.22 (d, *J* = 9.6 Hz, 2 H), 3.74 (d, *J* = 13.2 Hz, 1 H), 3.32 (d, *J* = 10.8 Hz, 1 H), 3.25-3.10 (m, 1 H), 2.37 (s, 3 H), 2.00-1.60 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 149.43, 146.81, 145.90, 141.28, 136.79, 131.01, 129.99, 129.52, 129.25, 128.64, 127.27, 126.45, 125.36, 124.17, 122.04, 119.93, 115.26, 61.43, 53.67, 35.54, 29.03, 26.63, 25.25, 21.21 ppm. MS (70 eV): m/z (%): 483 (M^+, 8.63), 43 (100). HRMS calcd for $C_{29}H_{26}BrNO$: 483.1198, found: 483.1195.

39. 1-(5-benzoyl-2,4,4a,7-tetrahydro-1H-benzo[f][1,4]oxazino[4,3-a]azepin-6-yl)ethanone



To a solution of **3a** (115.9 mg, 0.35 mmol) in DCM (3.5 mL) was added

m-CPBA (85%, 78.7 mg, 0.39 mmol) at 0 ℃, then the reaction mixture was allowed to stirred at 0 ℃ and monitored by TLC. Upon the complete consumption of **3a**, aqueous $Na_2S_2O_3$ solution (5 mL, 1 mol· L^{-1}) was added and the product was extracted with DCM three times, the organic layer was then washed with brine and dried with Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography to give compound **4** as a yellow solid in 81% yield (98.9 mg). m.p.: 192-193 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): 7.50-7.40 (m, 3 H), 7.38-7.23 (m, 3 H), 7.17 (d, *J* = 6.3 Hz, 1 H), 7.10-7.00 (m, 2 H), 4.58 (d, *J* = 13.8 Hz, 1 H), 4.10-3.90 (m, 2 H), 3.88-3.75 (m, 2 H), 3.68 (d, *J* = 9.0 Hz, 1 H), 3.32-3.20 (m, 2 H), 3.07 (d, *J* = 11.7 Hz, 1 H), 2.23 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 199.75, 196.17, 148.32, 142.93, 142.23, 138.75, 135.59, 133.17, 128.60, 128.57, 128.17, 126.42, 122.94, 119.11, 69.36, 67.38, 63.93, 50.98, 31.29, 28.90 ppm. MS (70 eV): m/z (%): 347 (M^+, 79.22), 105 (100). HRMS calcd for $C_{22}H_{21}NO_3$: 347.1521, found: 347.1520.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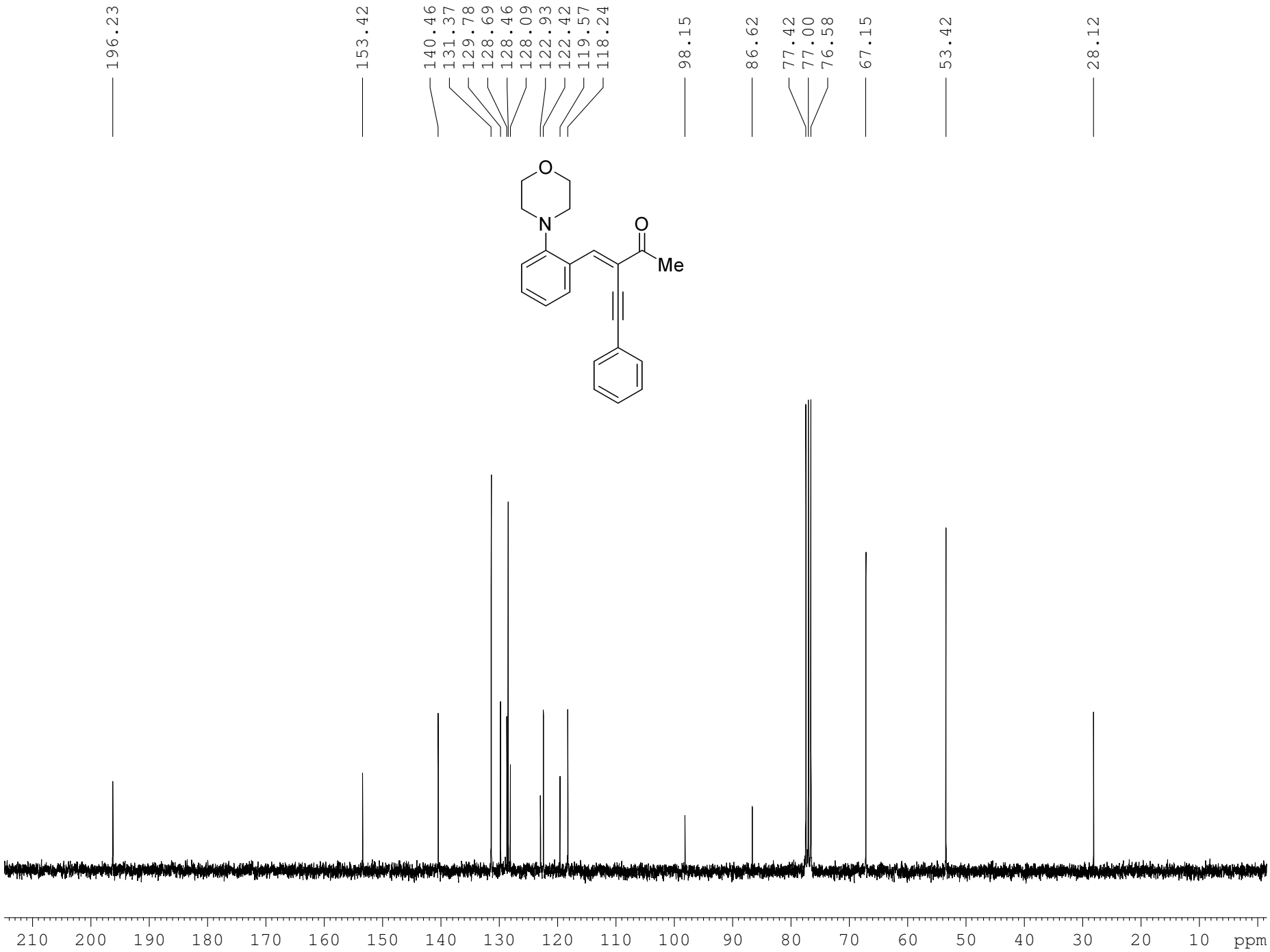
3.00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67.15
53.42
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Me
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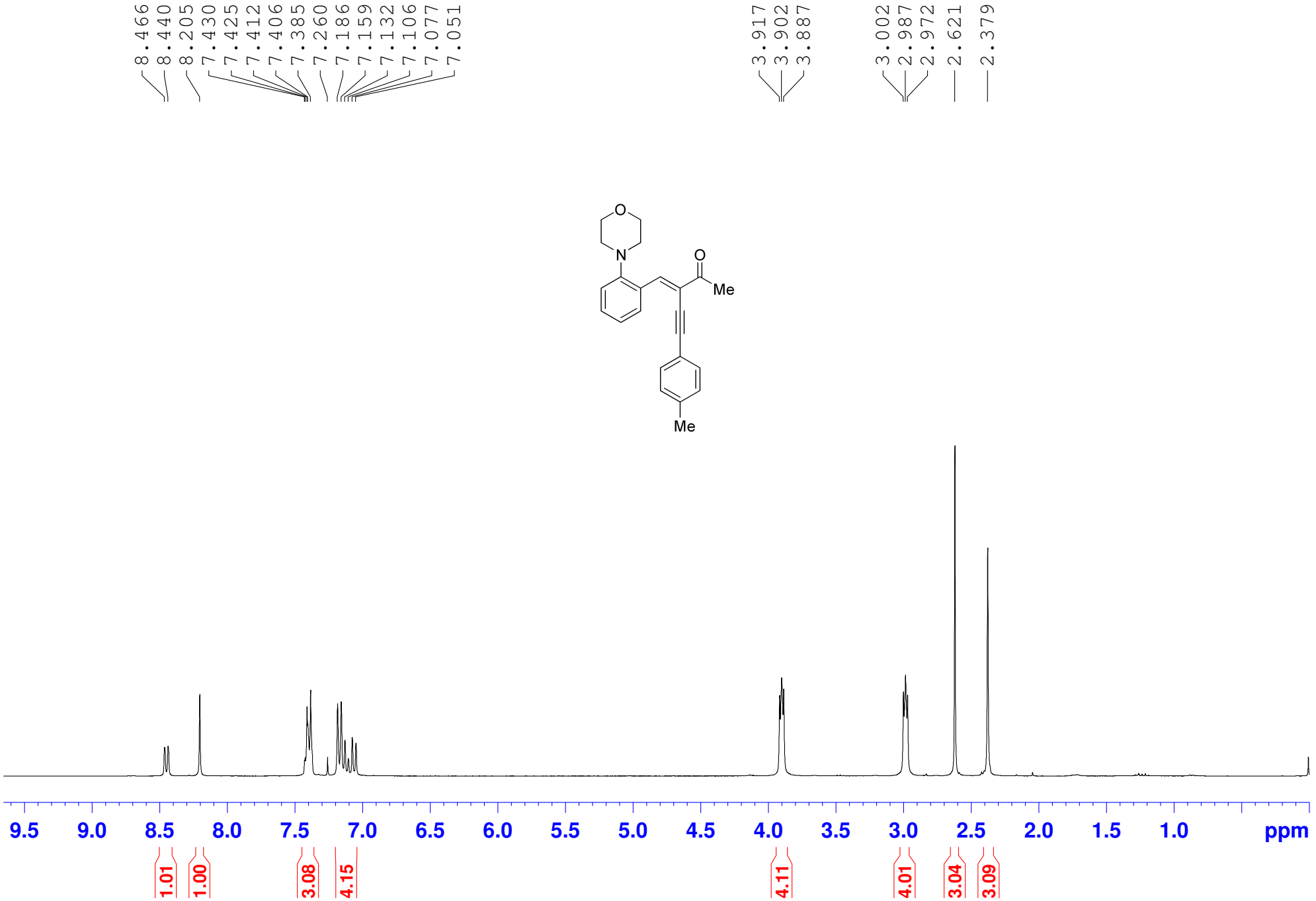
10
ppm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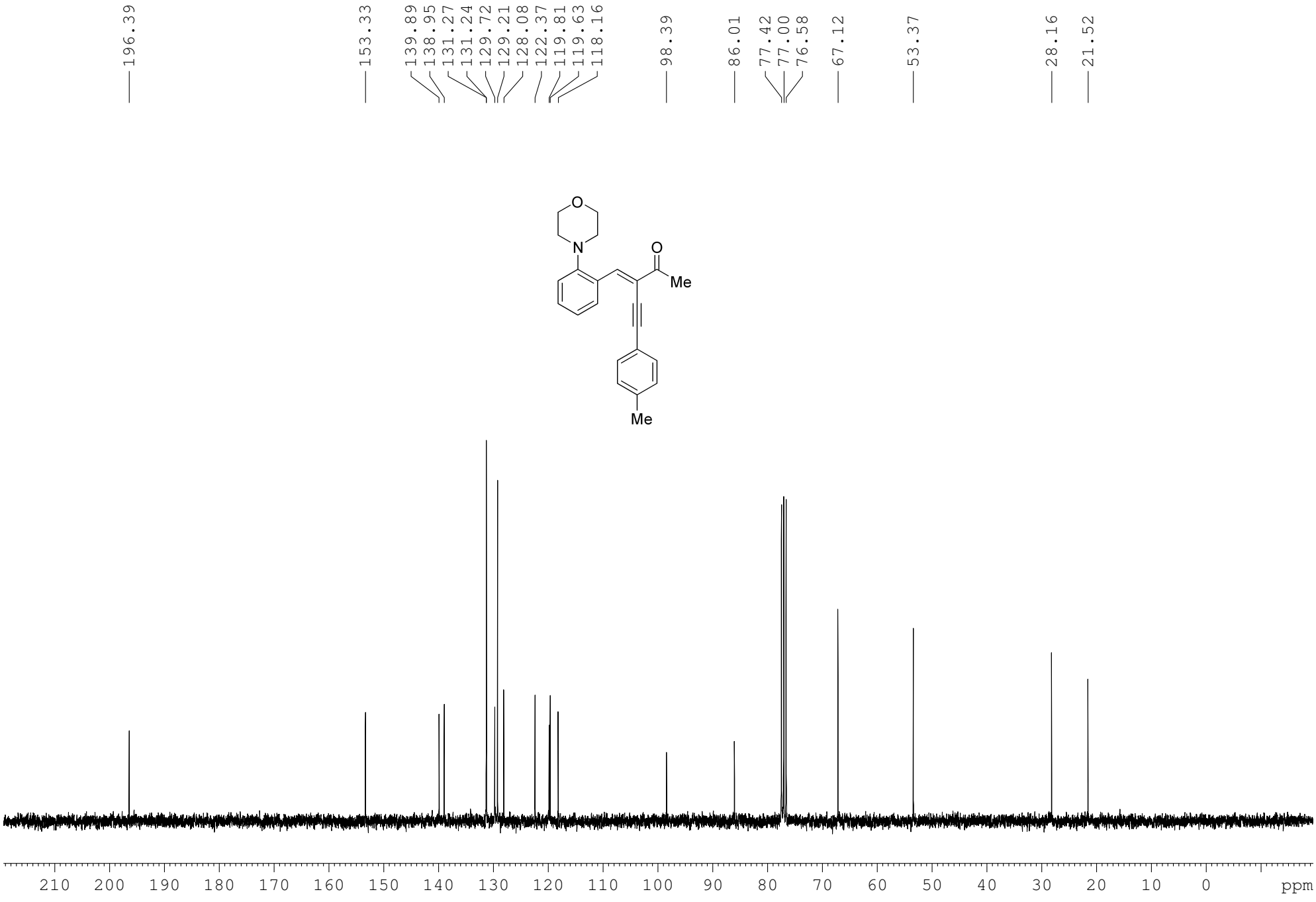
3.09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77.00
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53.37
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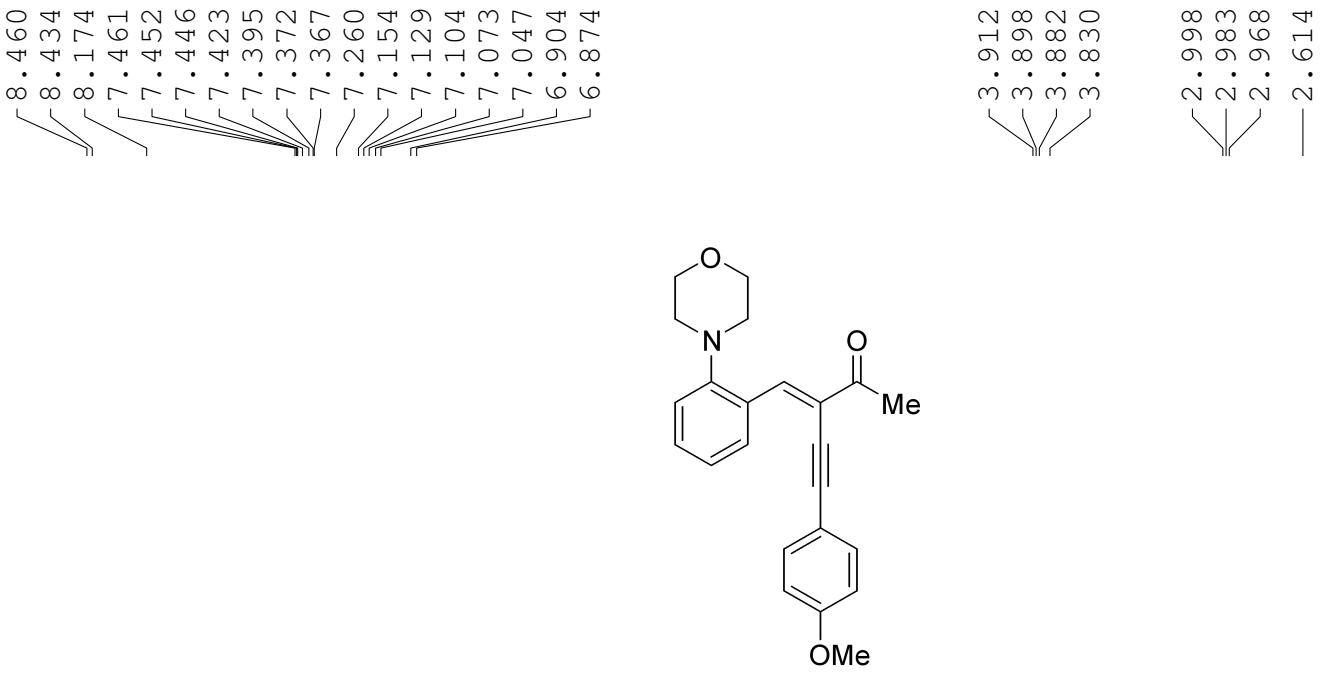
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7.104
7.073
7.047
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6.874
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3.898
3.882
3.830
2.998
2.983
2.968
2.614
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O
Me
OMe
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7.5
7.0
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5.5
5.0
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4.0
3.5
3.0
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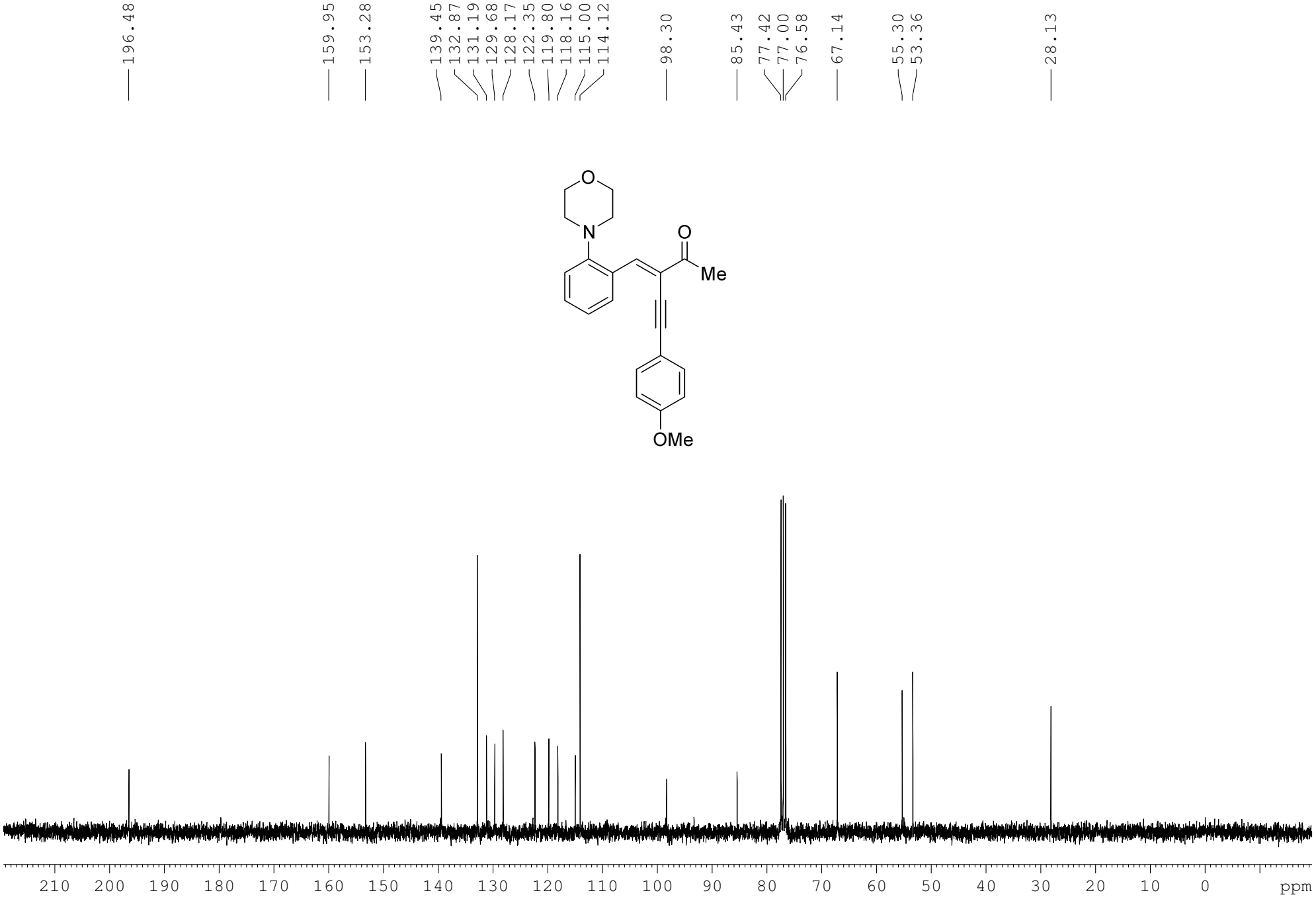
3.02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77.00
76.58
67.14
55.30
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28.13
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N
O
Me
OMe
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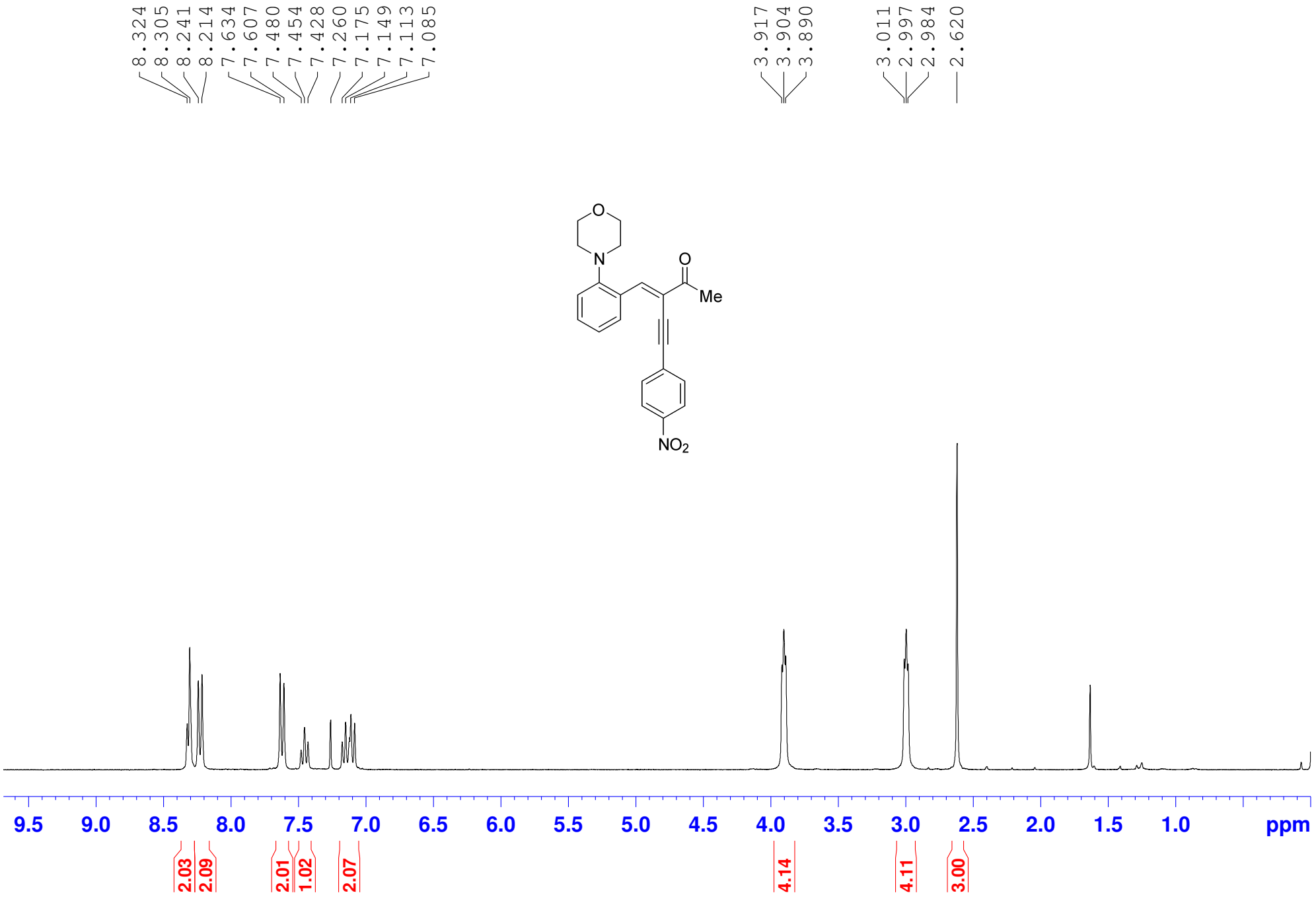
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3.904
3.890
3.011
2.997
2.984
2.620
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O
Me
NO2
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7.0
6.5
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1.02
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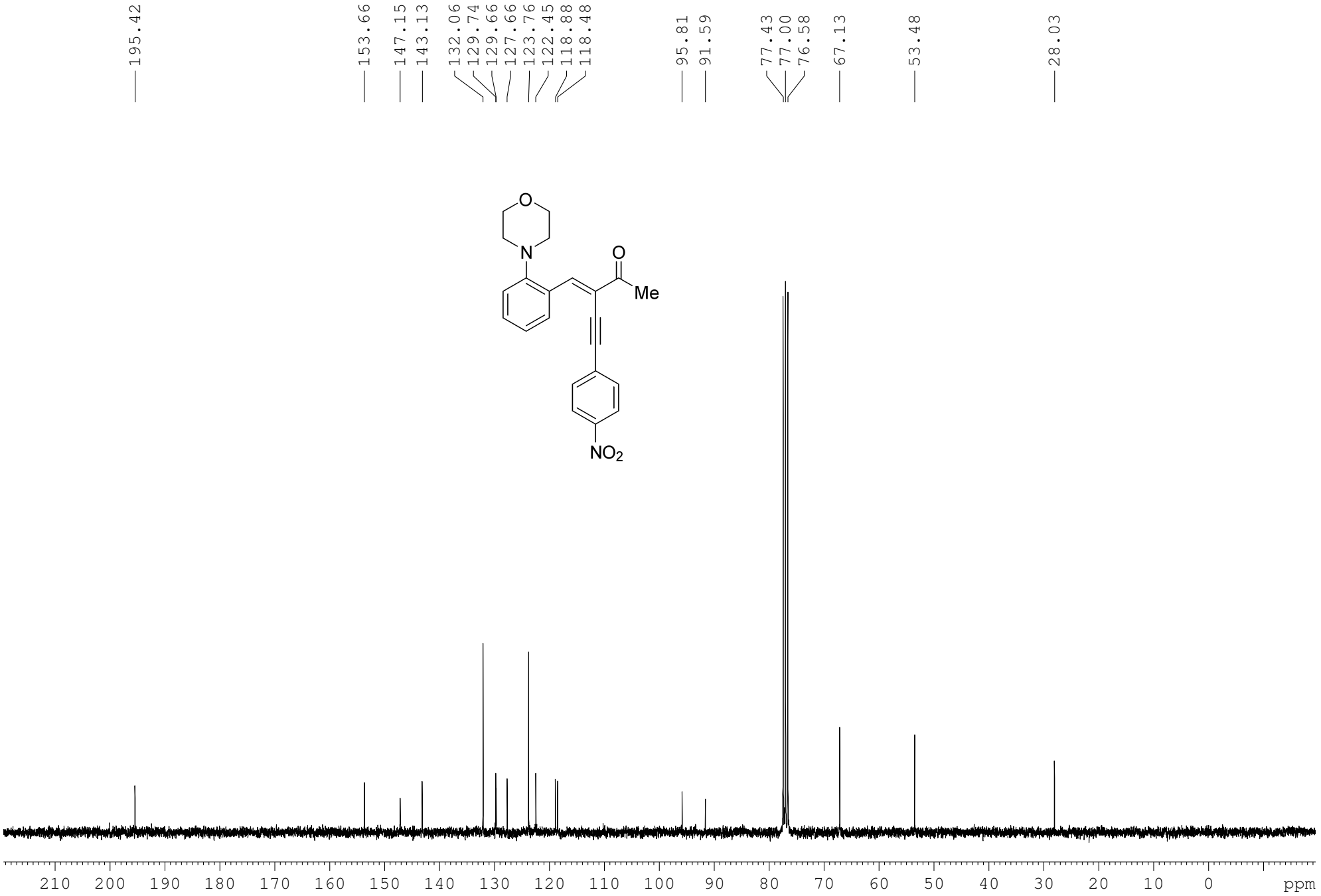
3.00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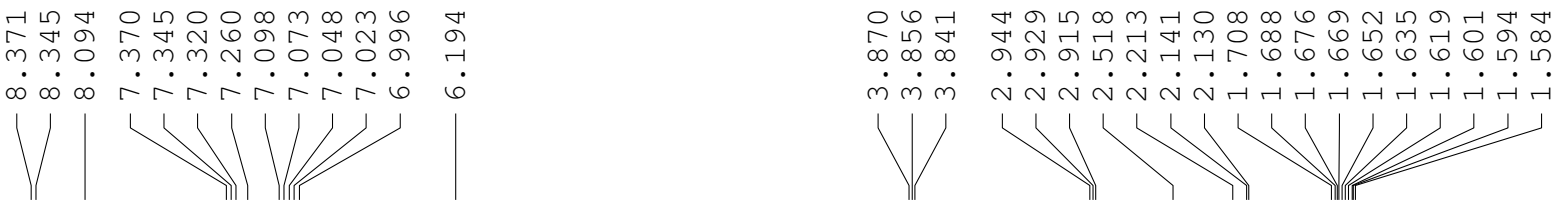
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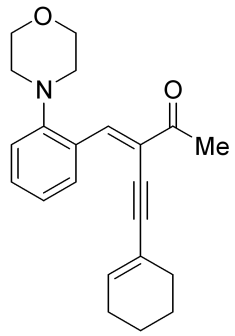
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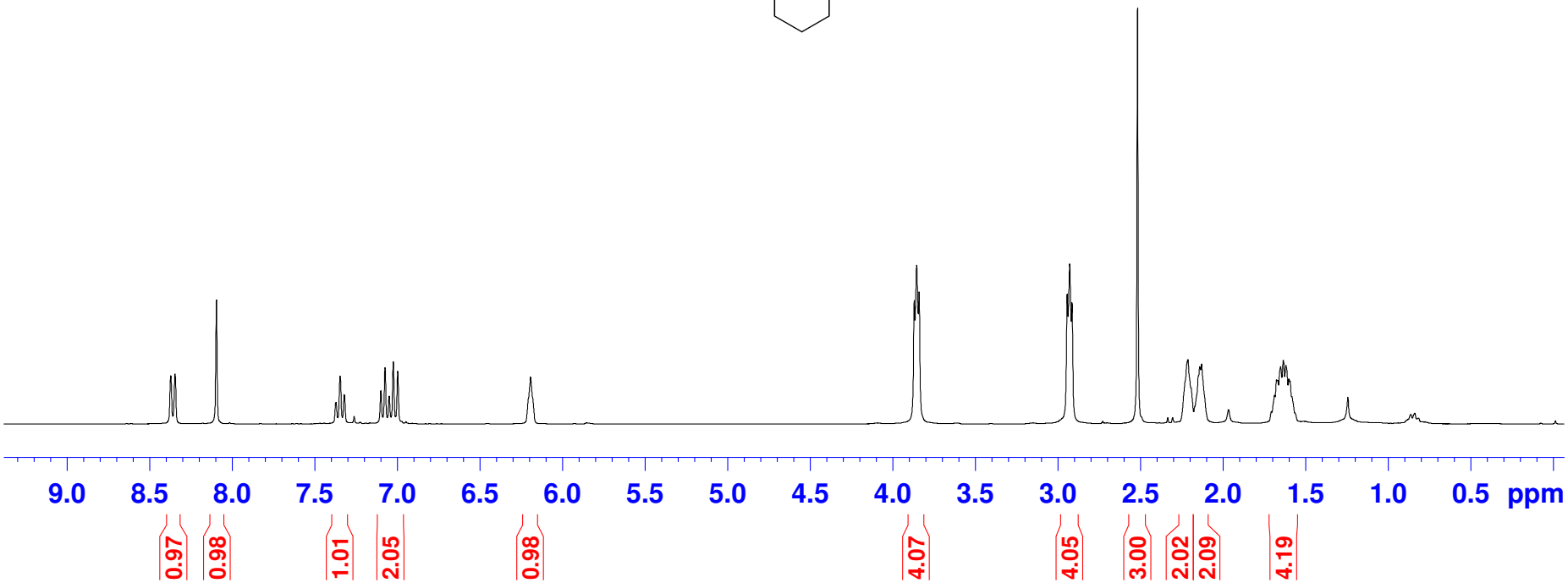
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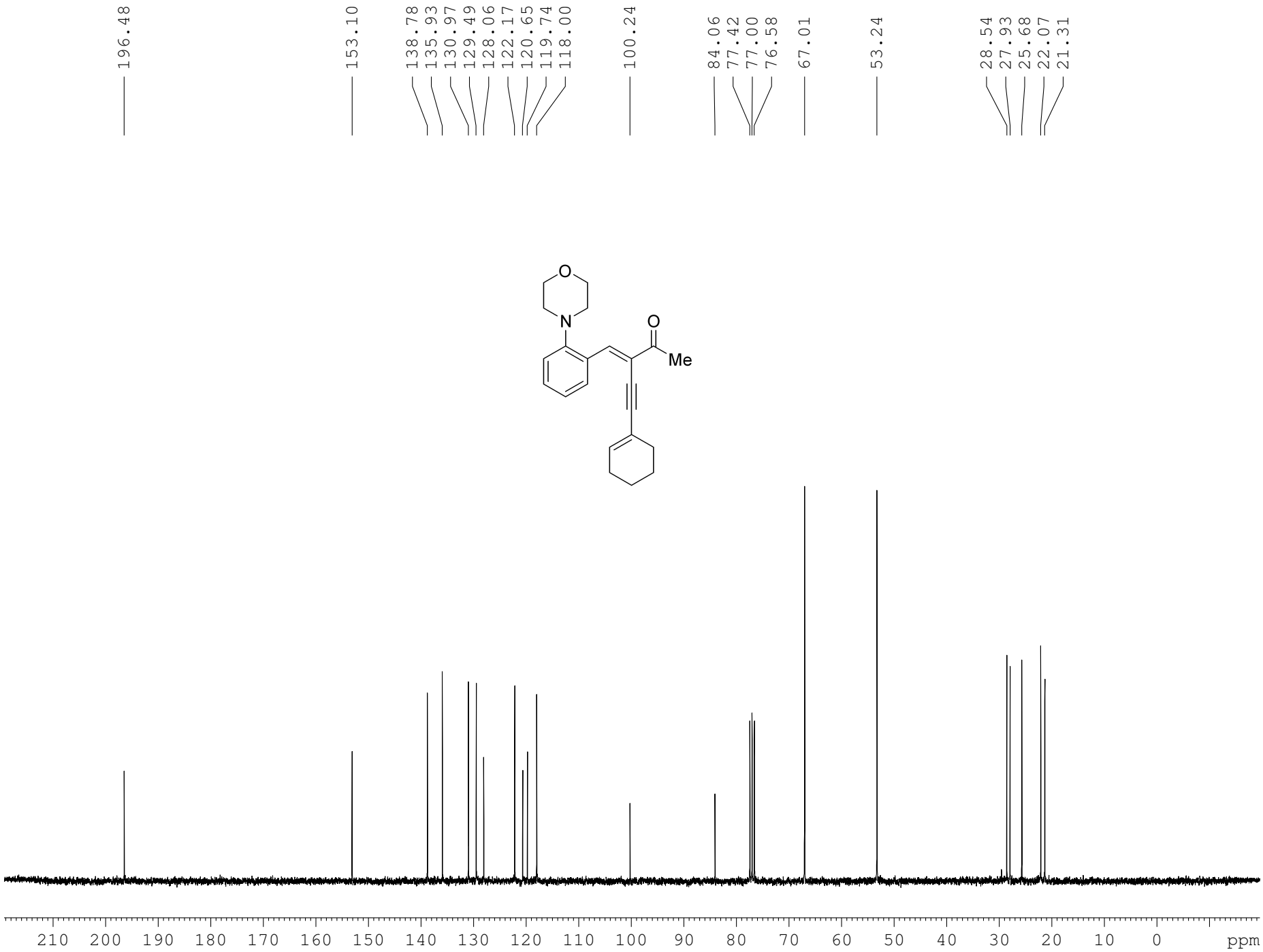
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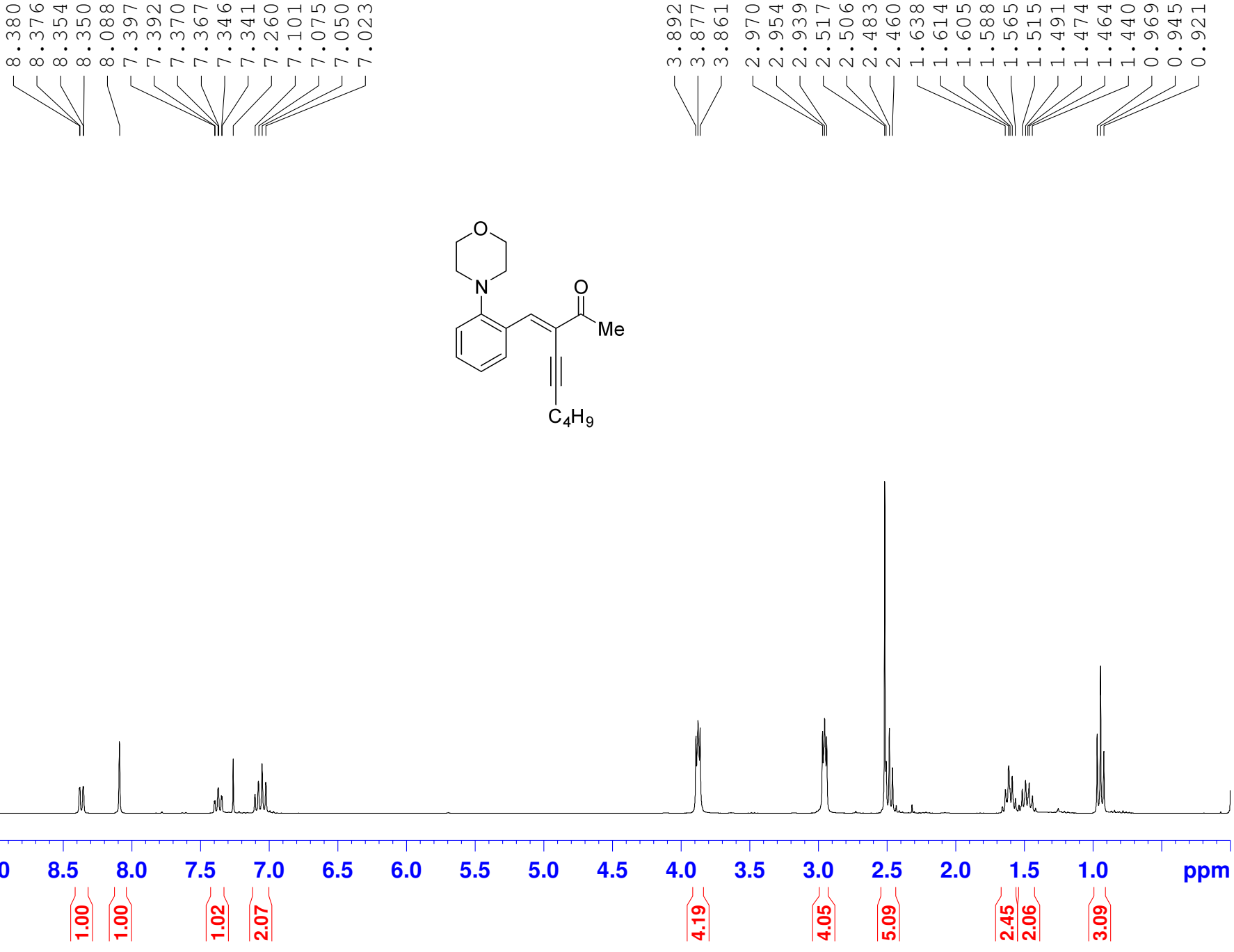
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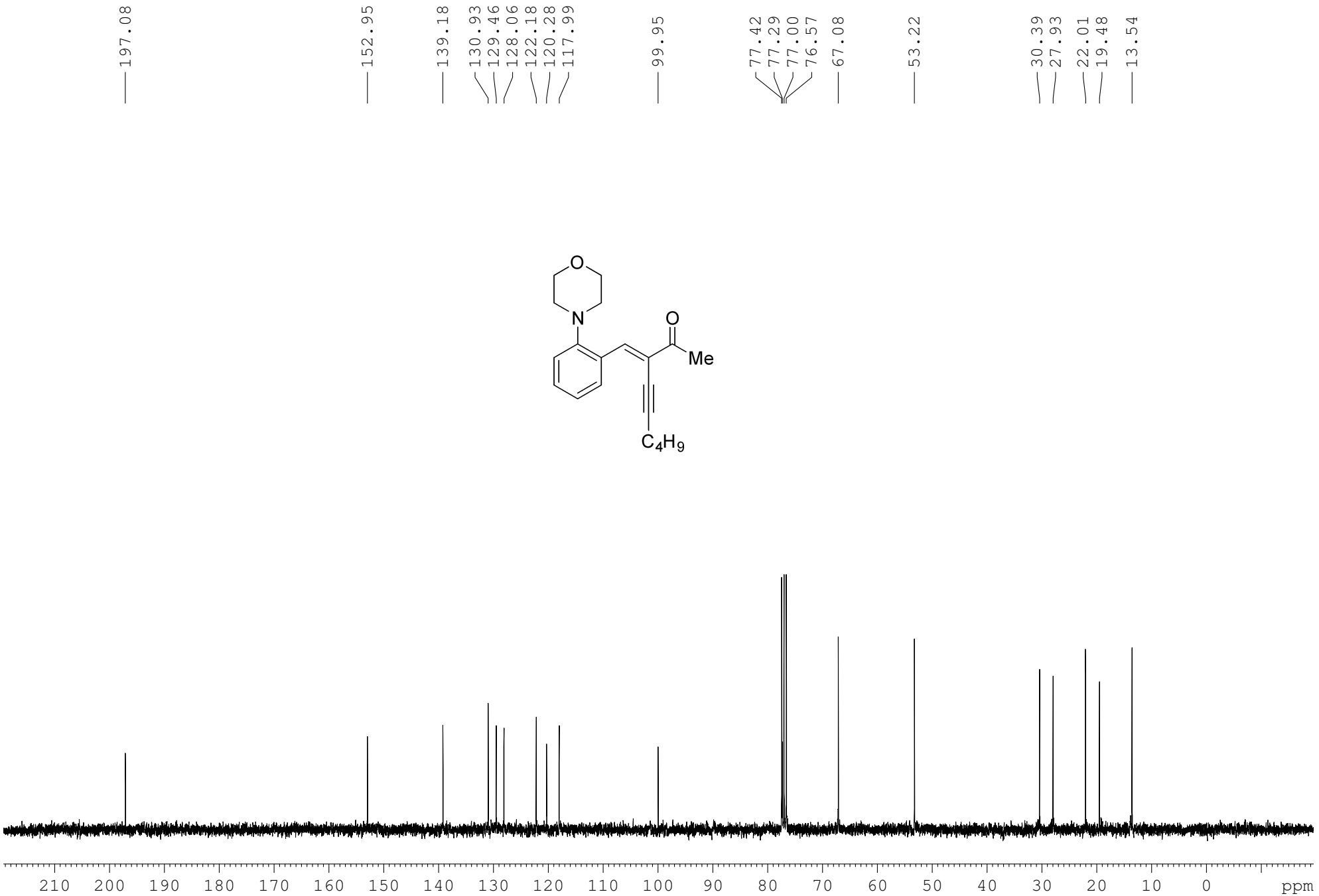
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30.39
27.93
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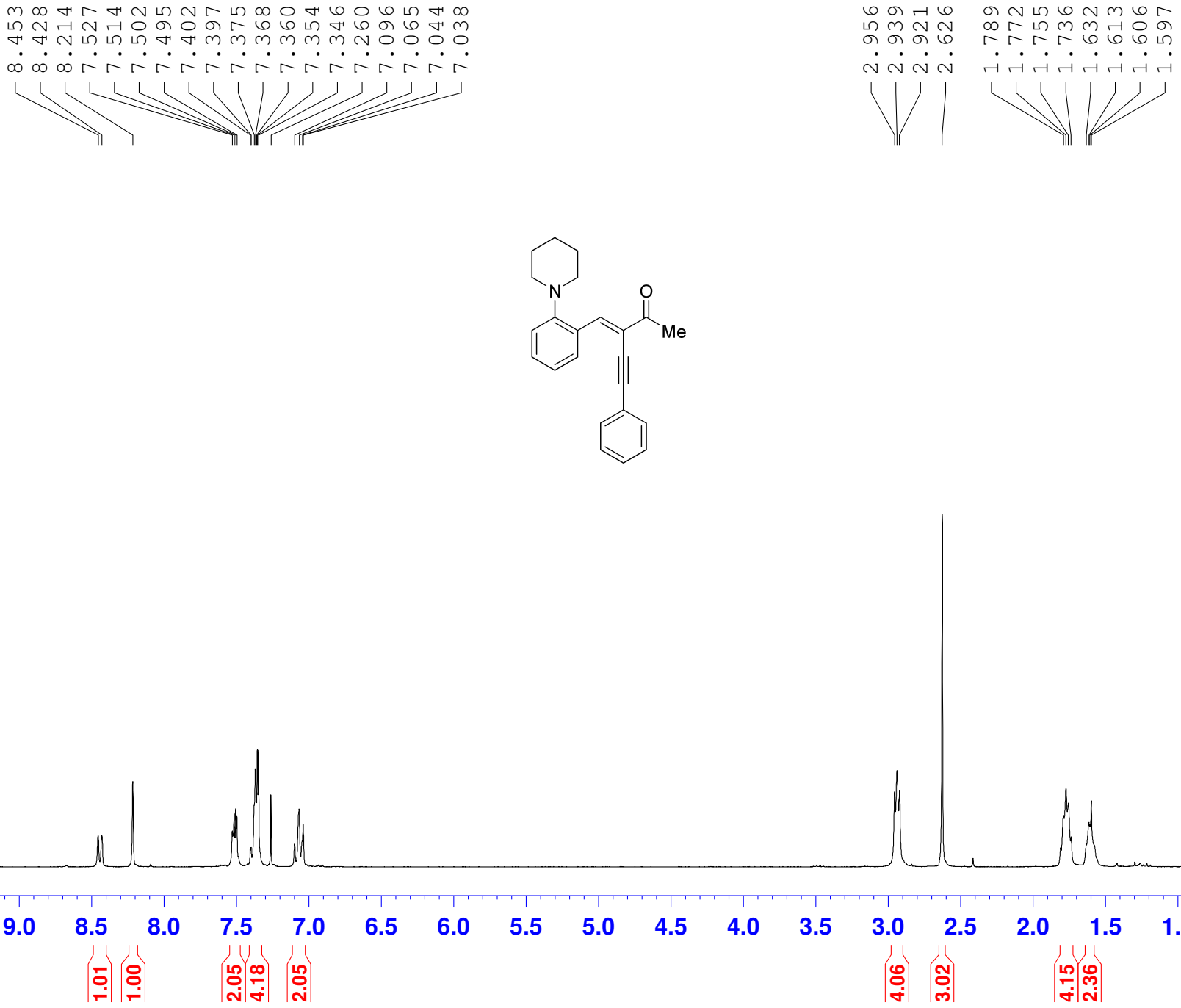
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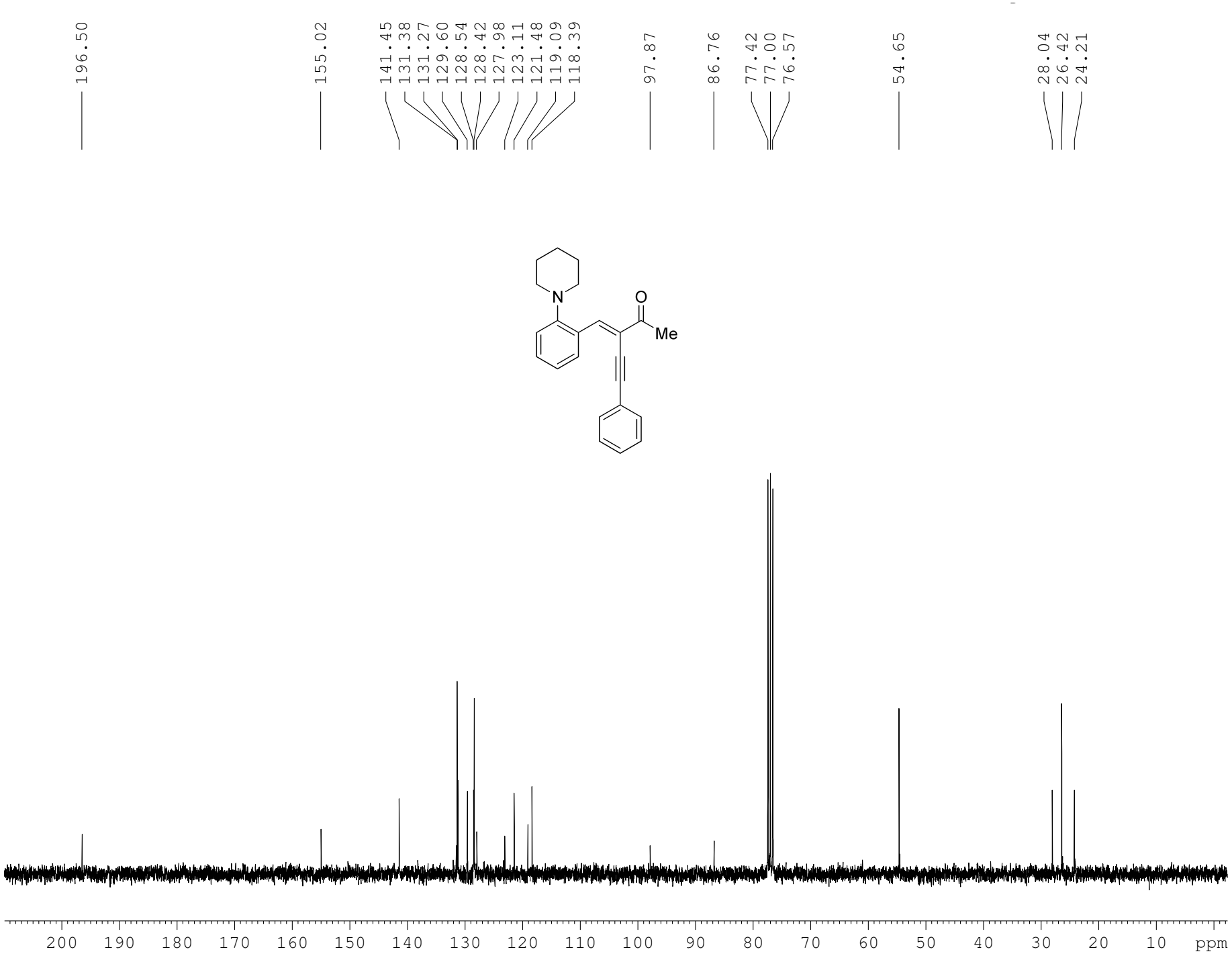
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131.38
131.27
129.60
128.54
128.42
127.98
123.11
121.48
119.09
118.39
97.87
86.76
77.42
77.00
76.57
54.65
28.04
26.42
24.21
N
O
Me
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110
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90
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30
20
10
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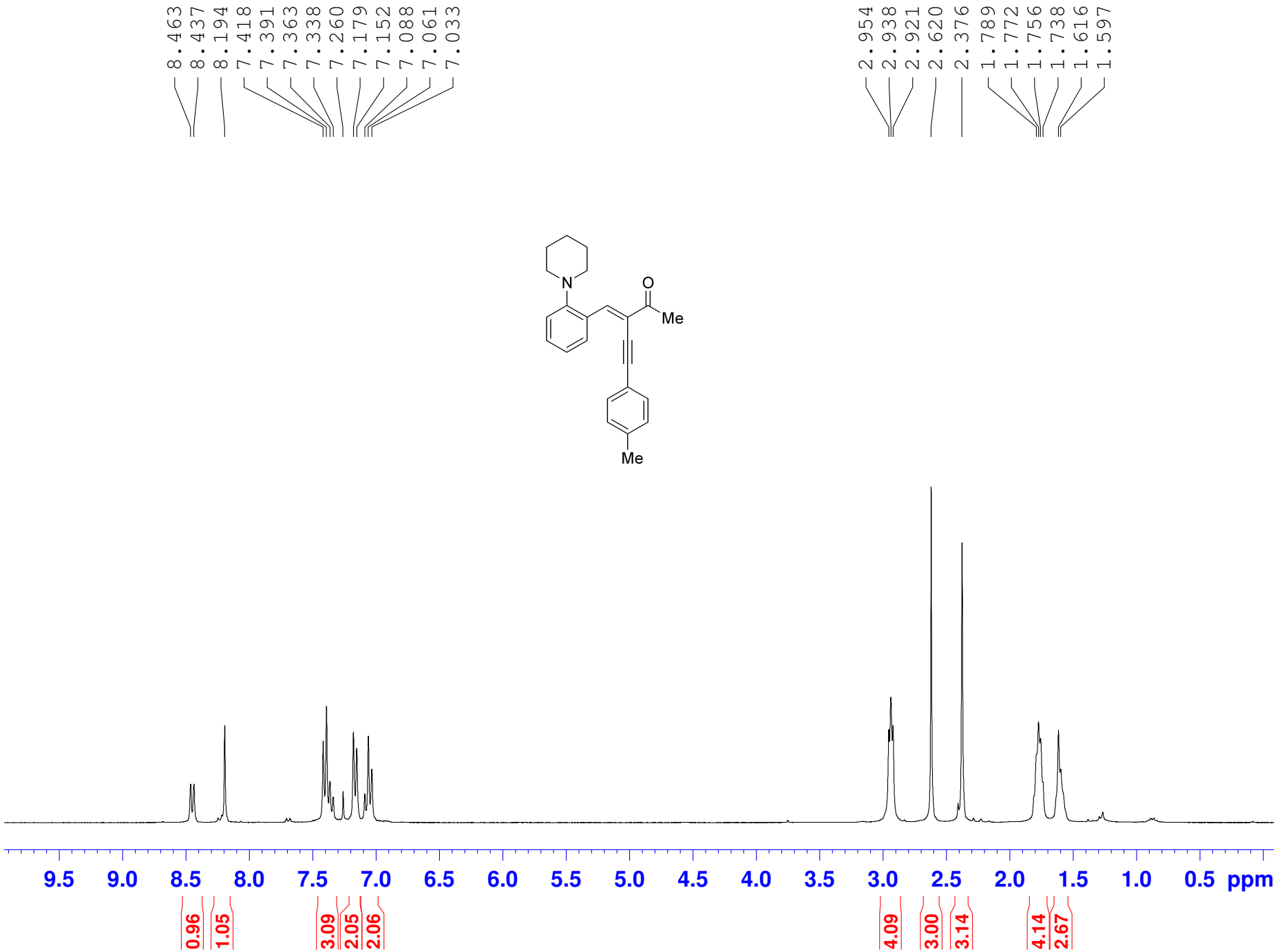
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7.061
7.033
2.954
2.938
2.921
2.620
2.376
1.789
1.772
1.756
1.738
1.616
1.597
N
O
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
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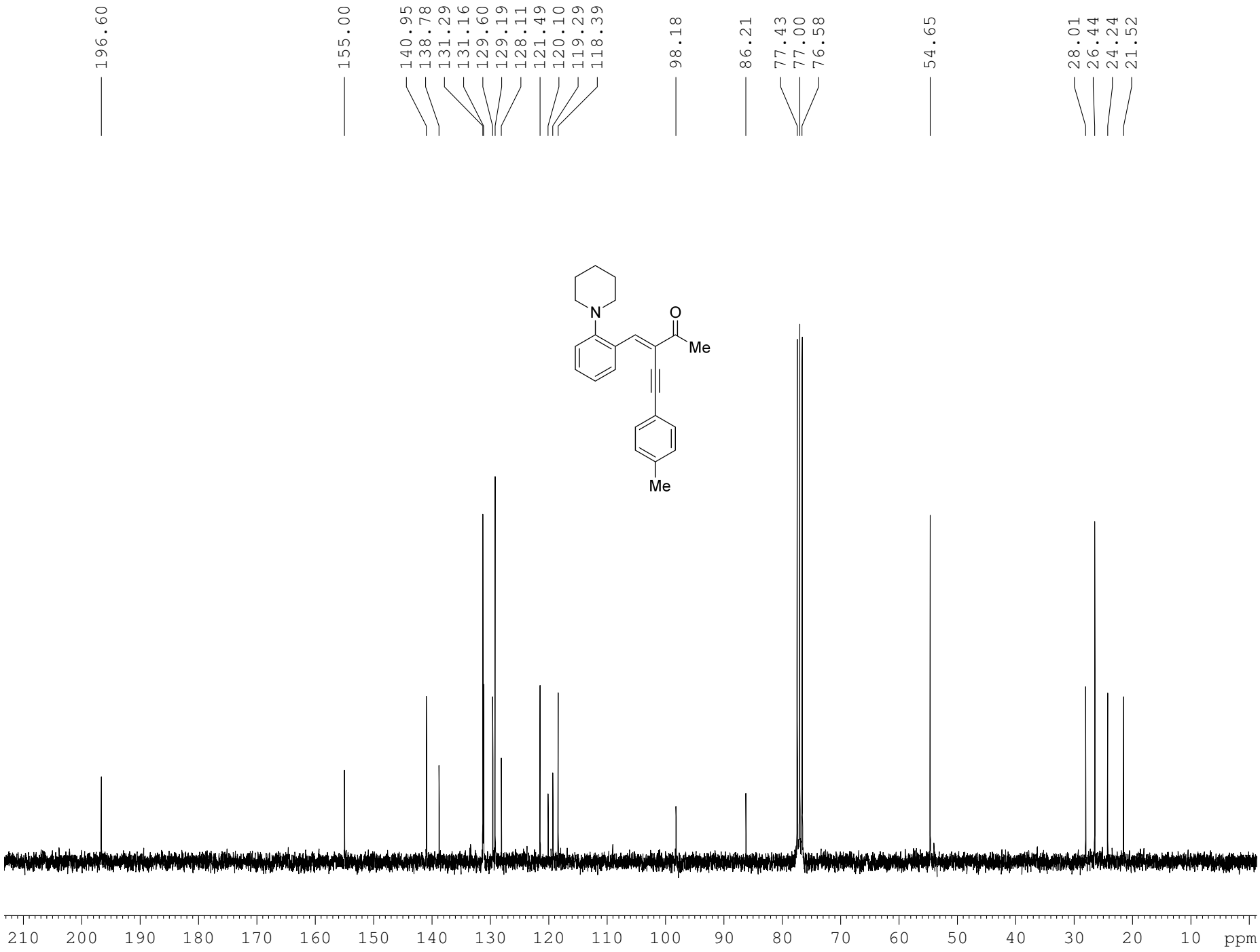
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98.18
86.21
77.43
77.00
76.58
54.65
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24.24
21.52
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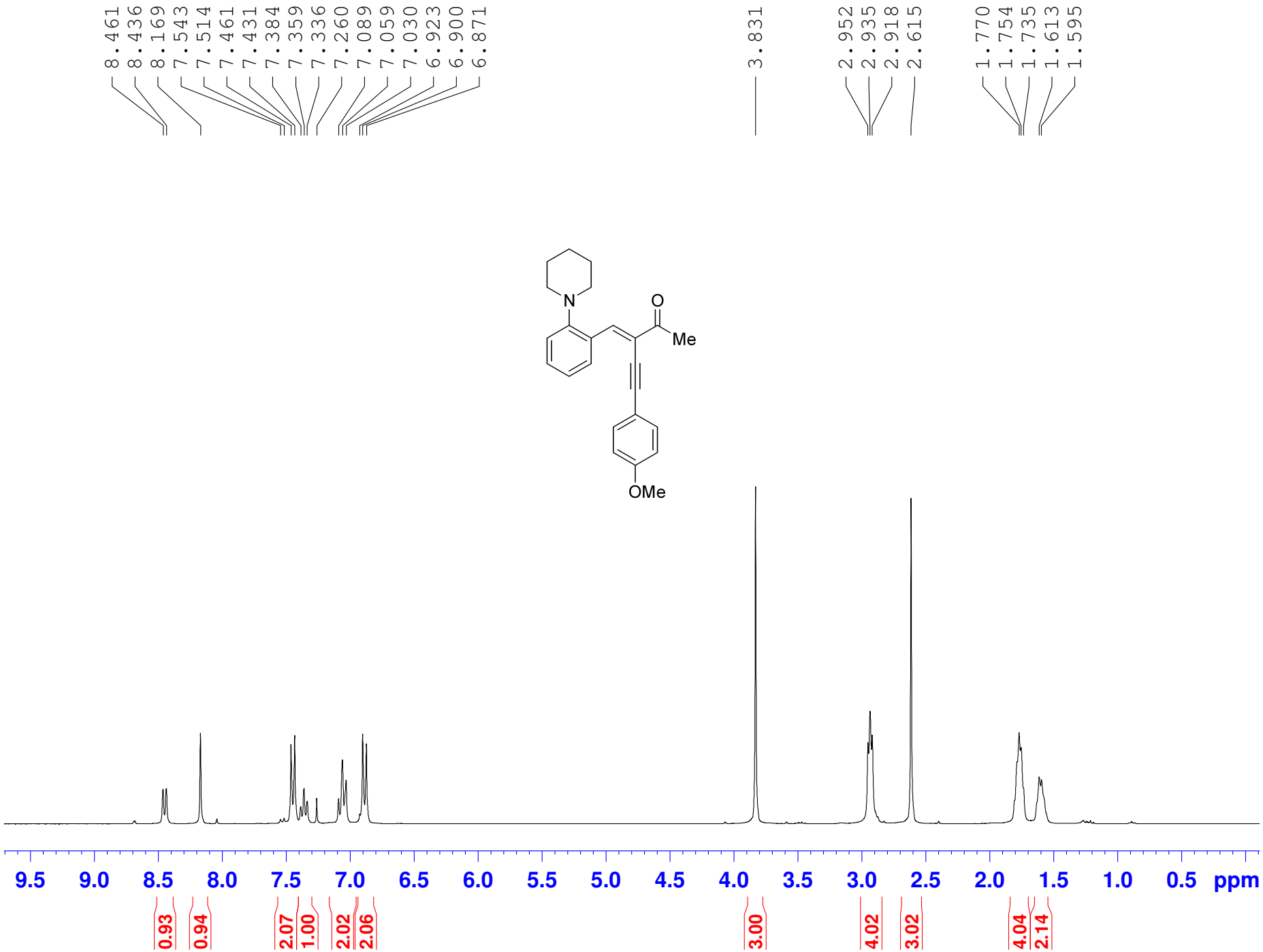
O
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.059
7.030
6.923
6.900
6.871
3.831
2.952
2.935
2.918
2.615
1.770
1.754
1.735
1.613
1.595
N
O
Me
OMe
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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3.00
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3.02
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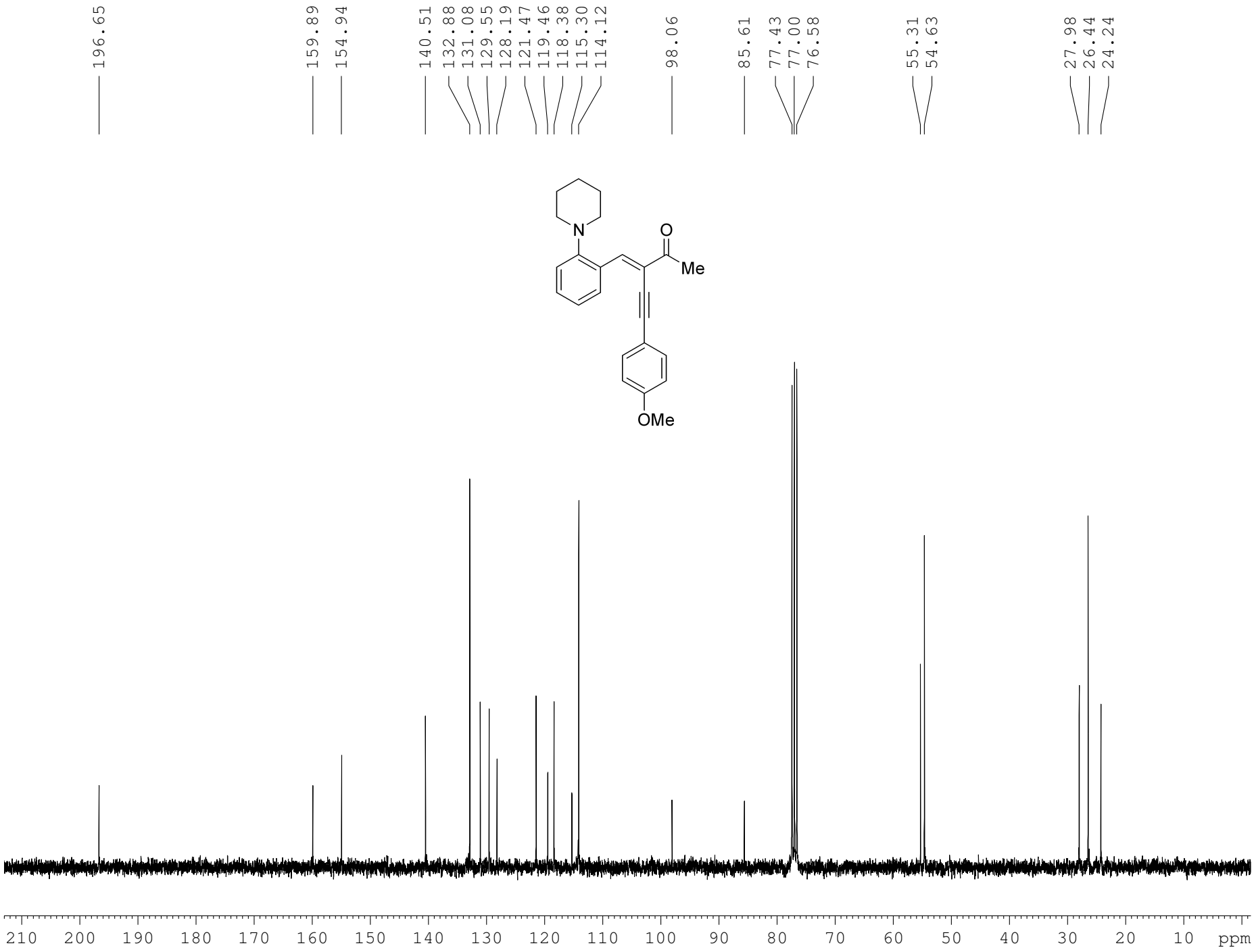
2.14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129.55
128.19
121.47
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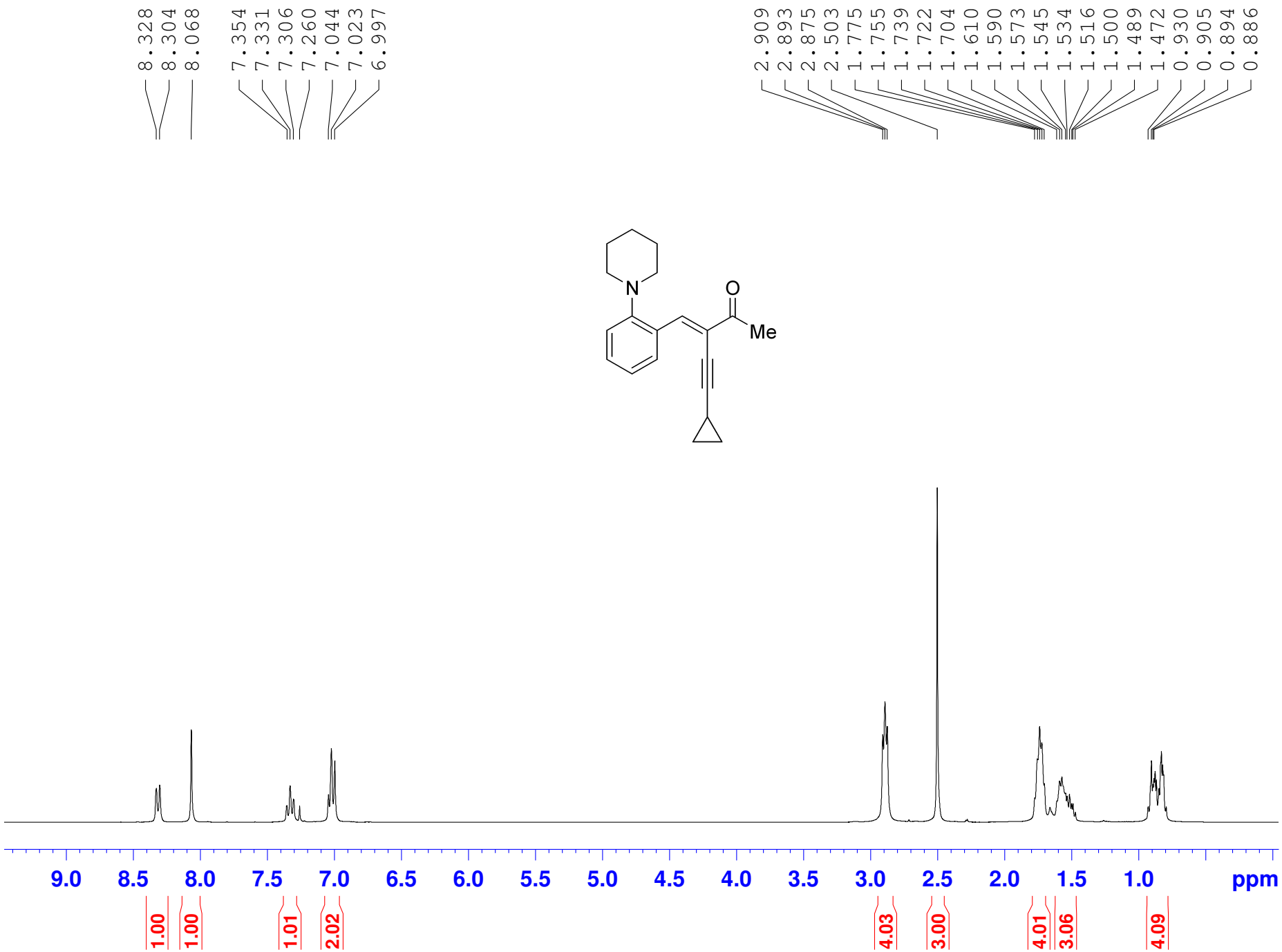
118.38
115.30
114.12
98.06
85.61
77.43
77.00
76.58
55.31
54.63
27.98
26.44
24.24
N
O
Me
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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2.503
1.775
1.755
1.739
1.722
1.704
1.610
1.590
1.573
1.545
1.534
1.516
1.500
1.489
1.472
0.930
0.905
0.894
0.886
N
O
Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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4.03
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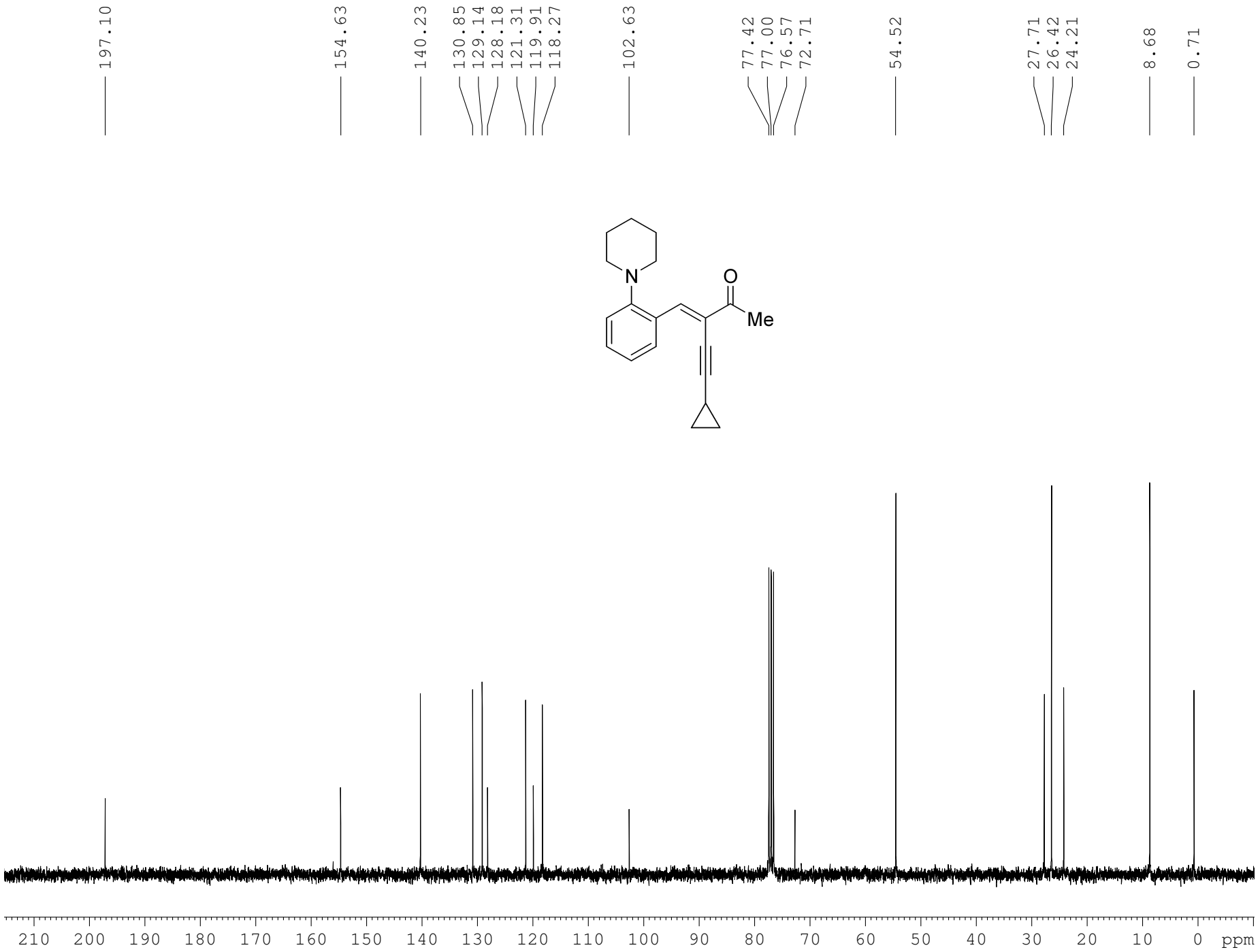
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119.91
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102.63
77.42
77.00
76.57
72.71
54.52
27.71
26.42
24.21
8.68
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O
Me
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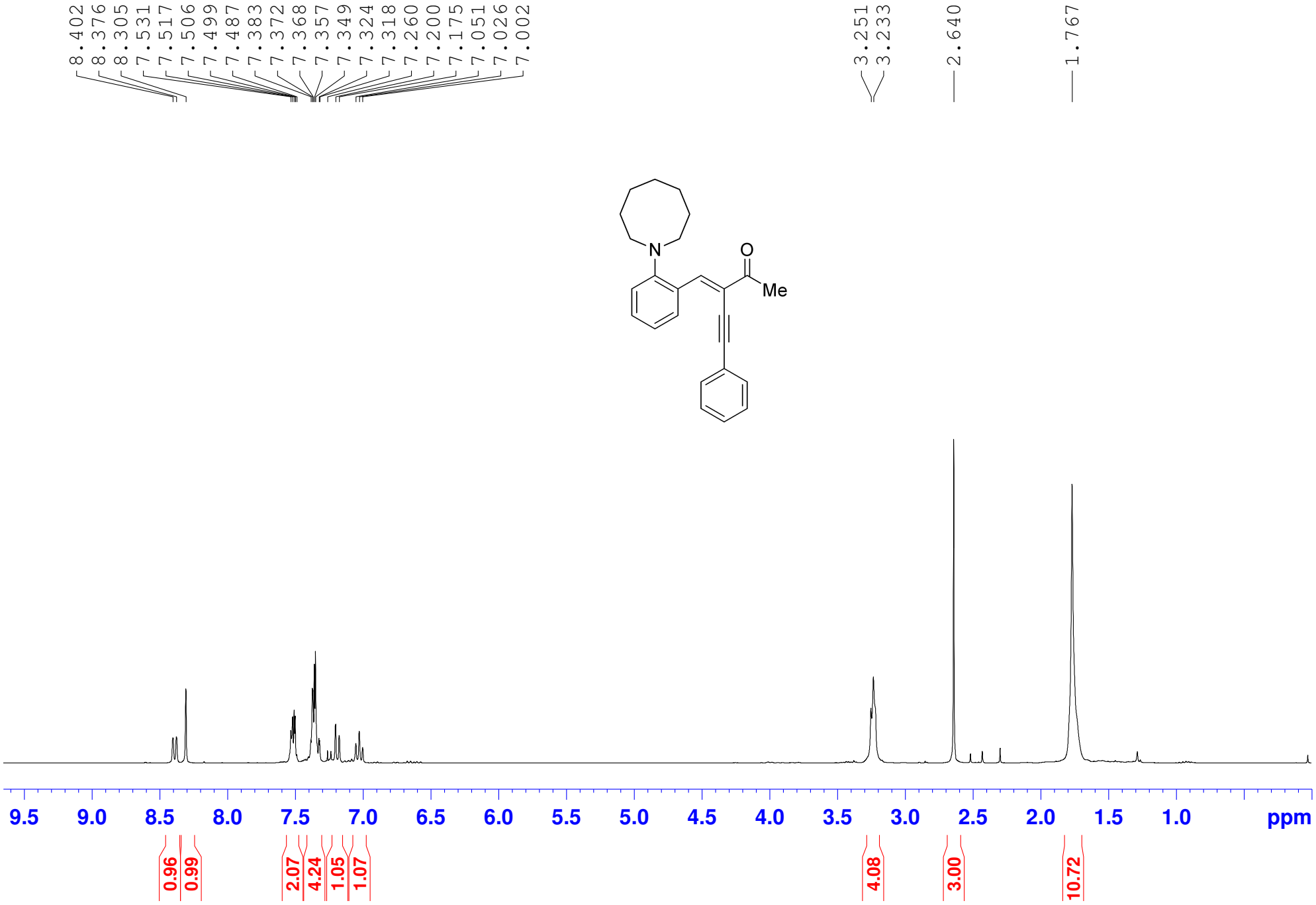
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7.506
7.499
7.487
7.383
7.372
7.368
7.357
7.349
7.324
7.318
7.260
7.200
7.175
7.051
7.026
7.002
3.251
3.233
2.640
1.767
N
O
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.05
1.07
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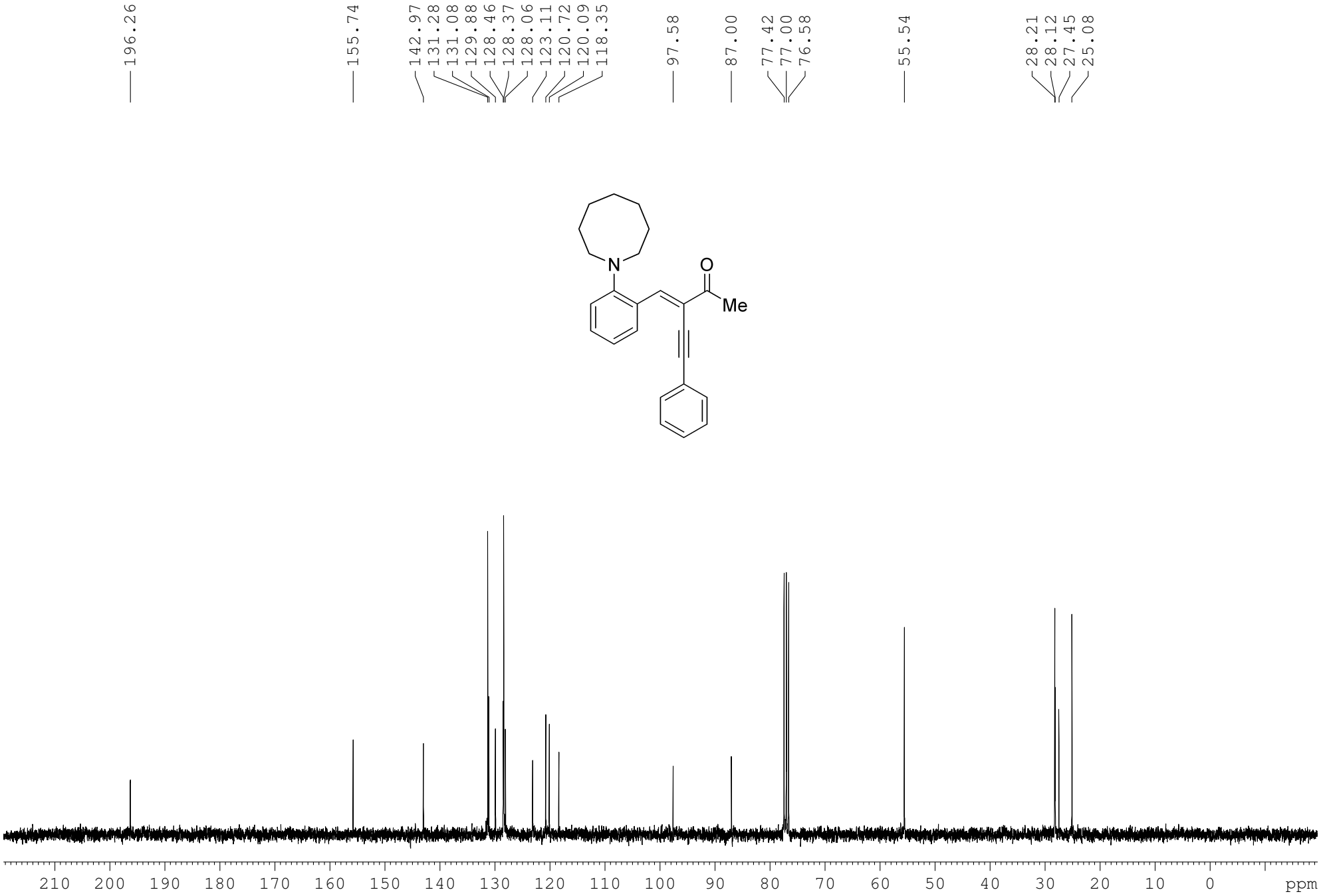
10.72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128.37
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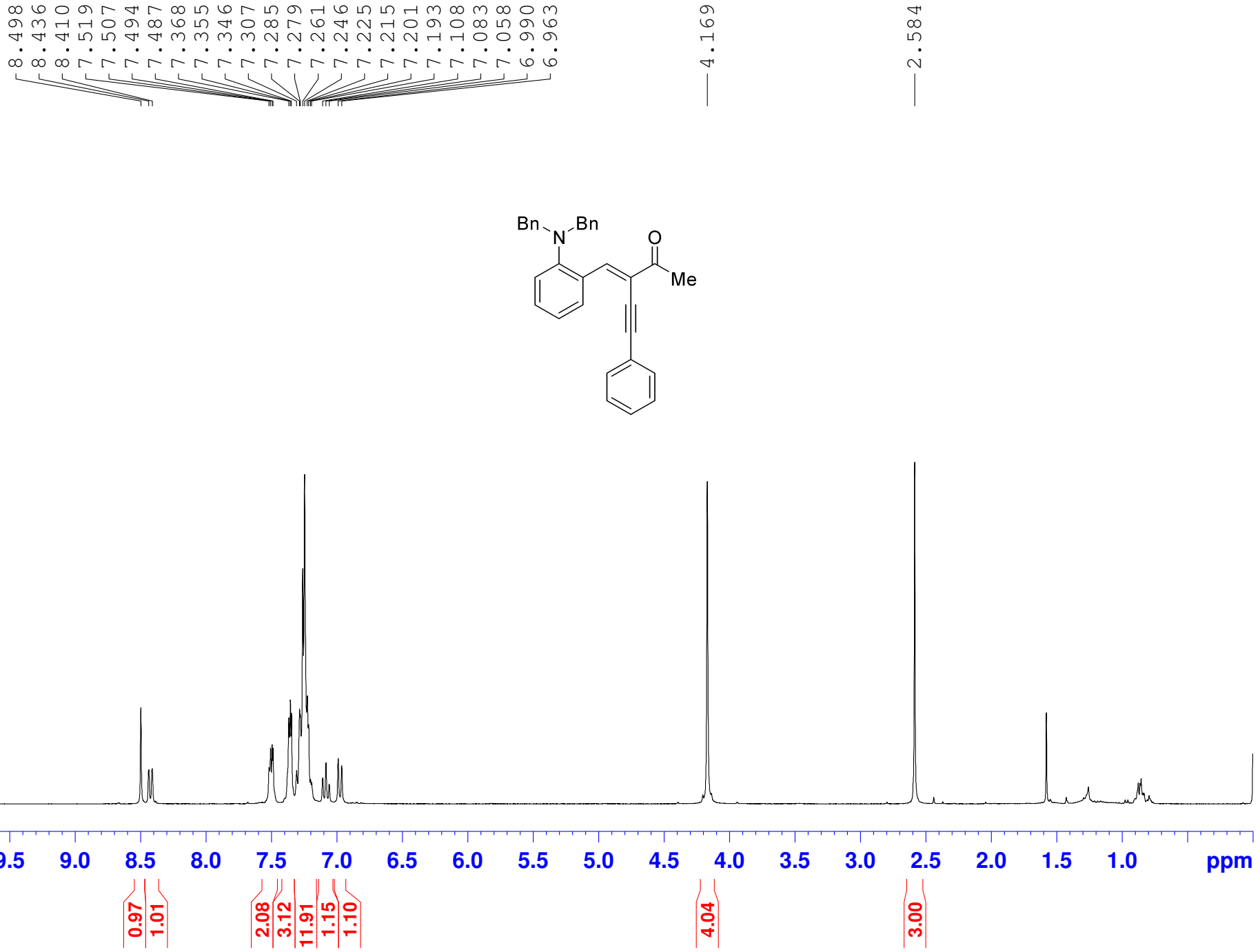
123.11
120.72
120.09
118.35
97.58
87.00
77.42
77.00
76.58
55.54
28.21
28.12
27.45
25.08
N
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.279
7.261
7.246
7.225
7.215
7.201
7.193
7.108
7.083
7.058
6.990
6.963
4.169
2.584
Bn
N
Bn
O
Me
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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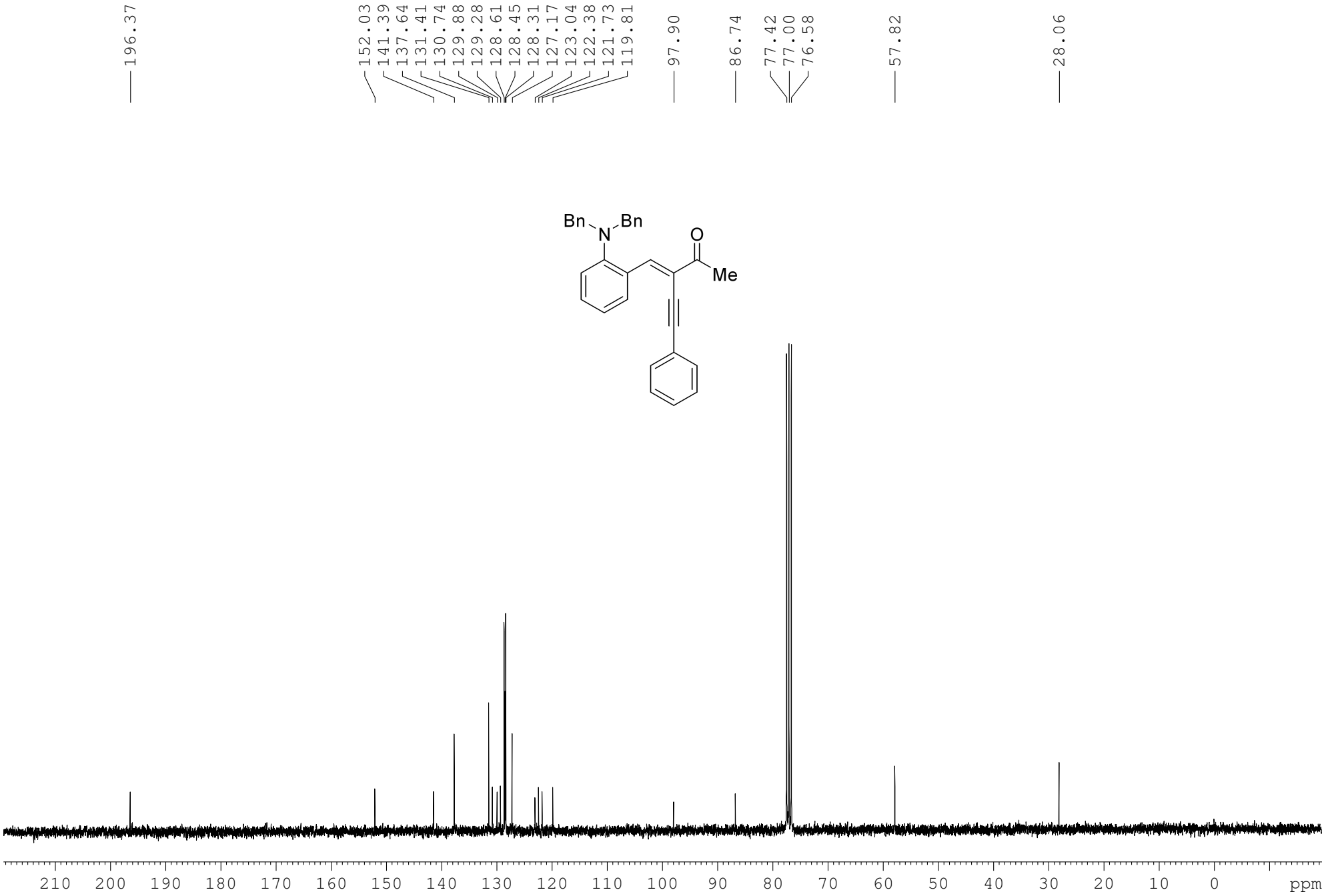
1.10
4.04
3.00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130.74
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129.28
128.61
128.45
128.31
127.17
123.04
122.38
121.73
119.81
97.90
86.74
77.42
77.00
76.58
57.82
28.06
Bn
N
Bn
O
Me
210
200
190
180
170
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150
140
130
120
110
100
90
80
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60
50
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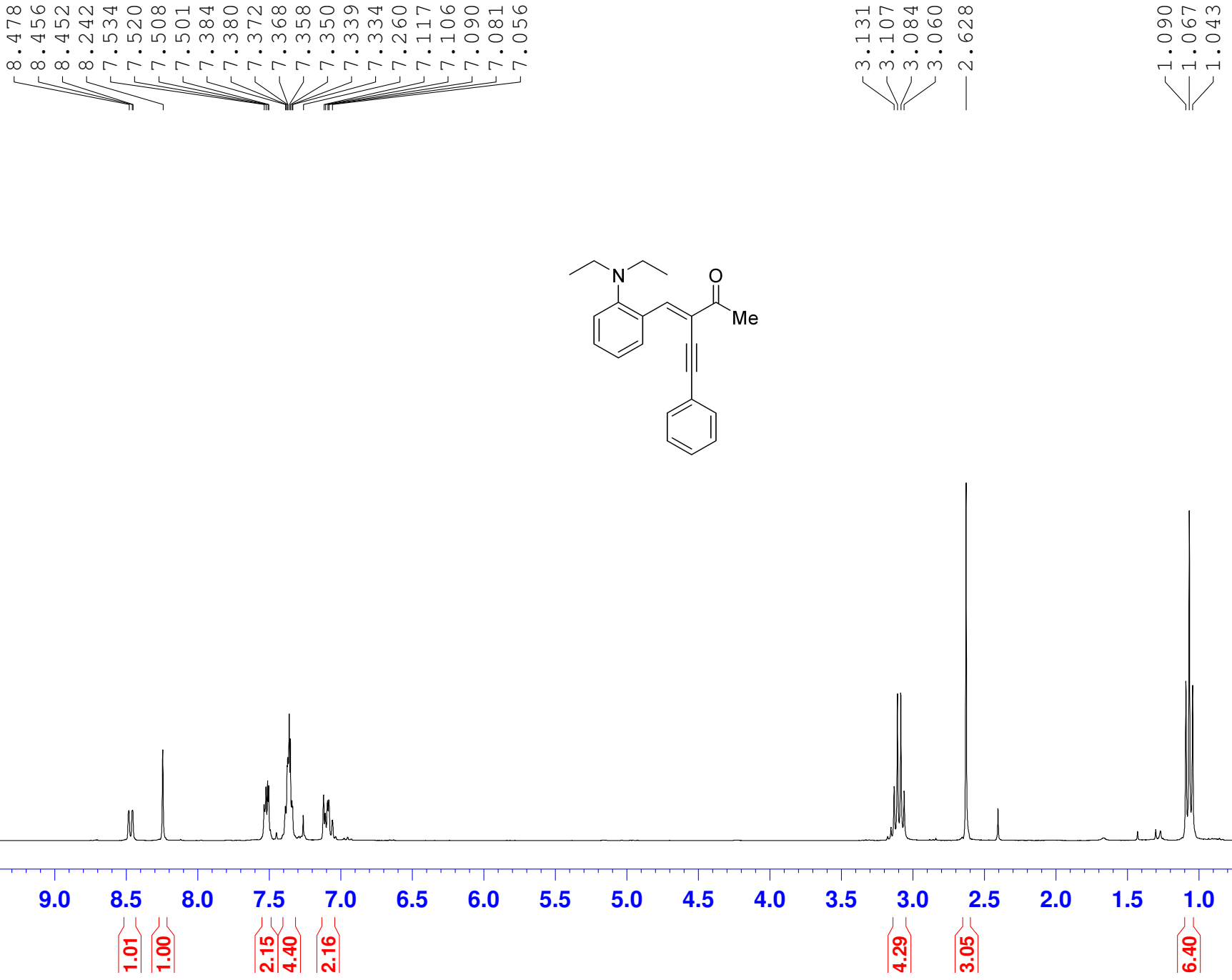
30
20
10
0
ppm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7.350
7.339
7.334
7.260
7.117
7.106
7.090
7.081
7.056
3.131
3.107
3.084
3.060
2.628
1.090
1.067
1.043
N
O
Me
9.5
9.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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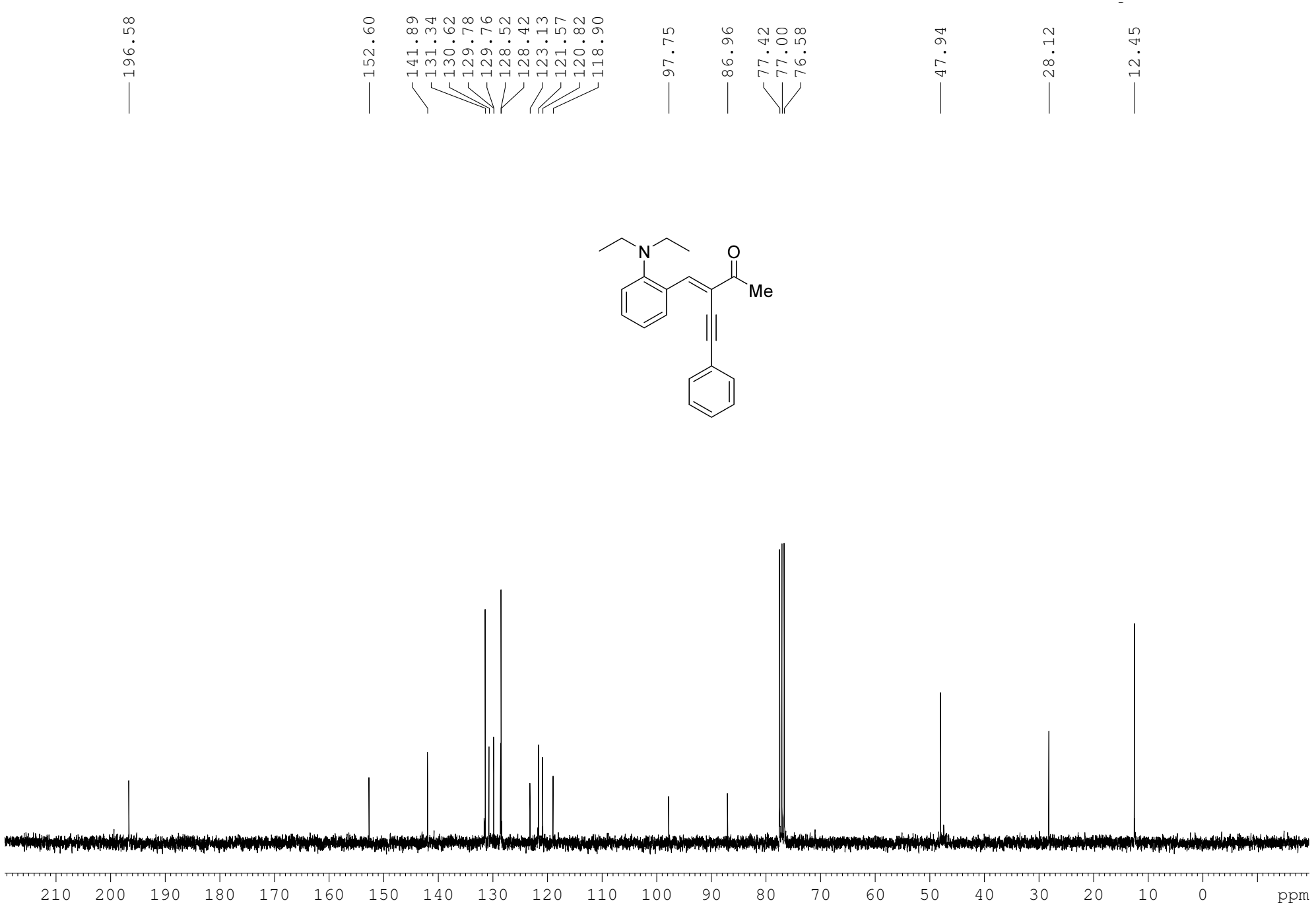
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129.78
129.76
128.52
128.42
123.13
121.57
120.82
118.90
97.75
86.96
77.42
77.00
76.58
47.94
28.12
12.45
N
O
Me
210
200
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140
130
120
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100
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60
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20
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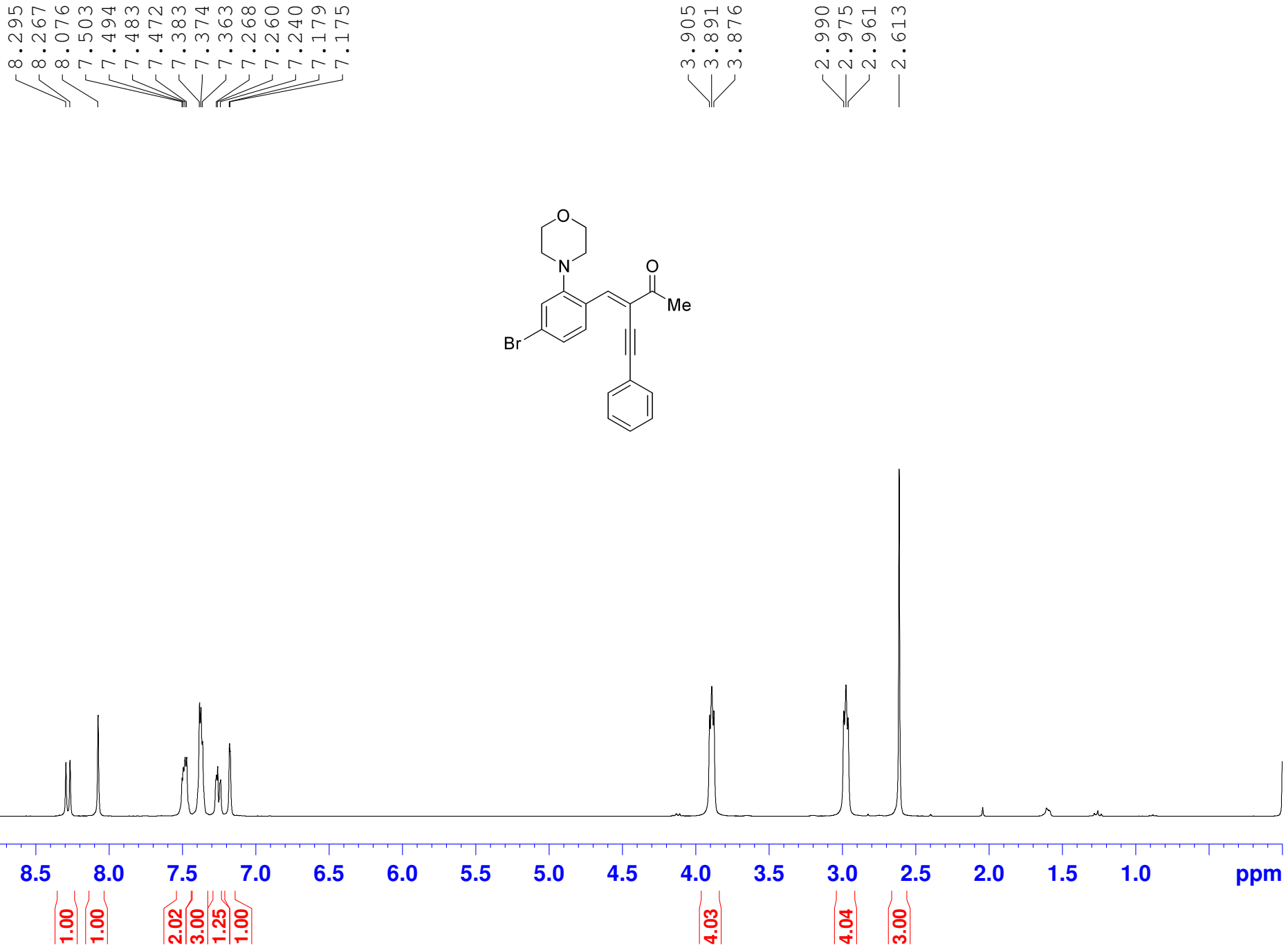
0
ppm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7.179
7.175
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3.891
3.876
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2.975
2.961
2.613
O
N
O
Me
Br
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.25
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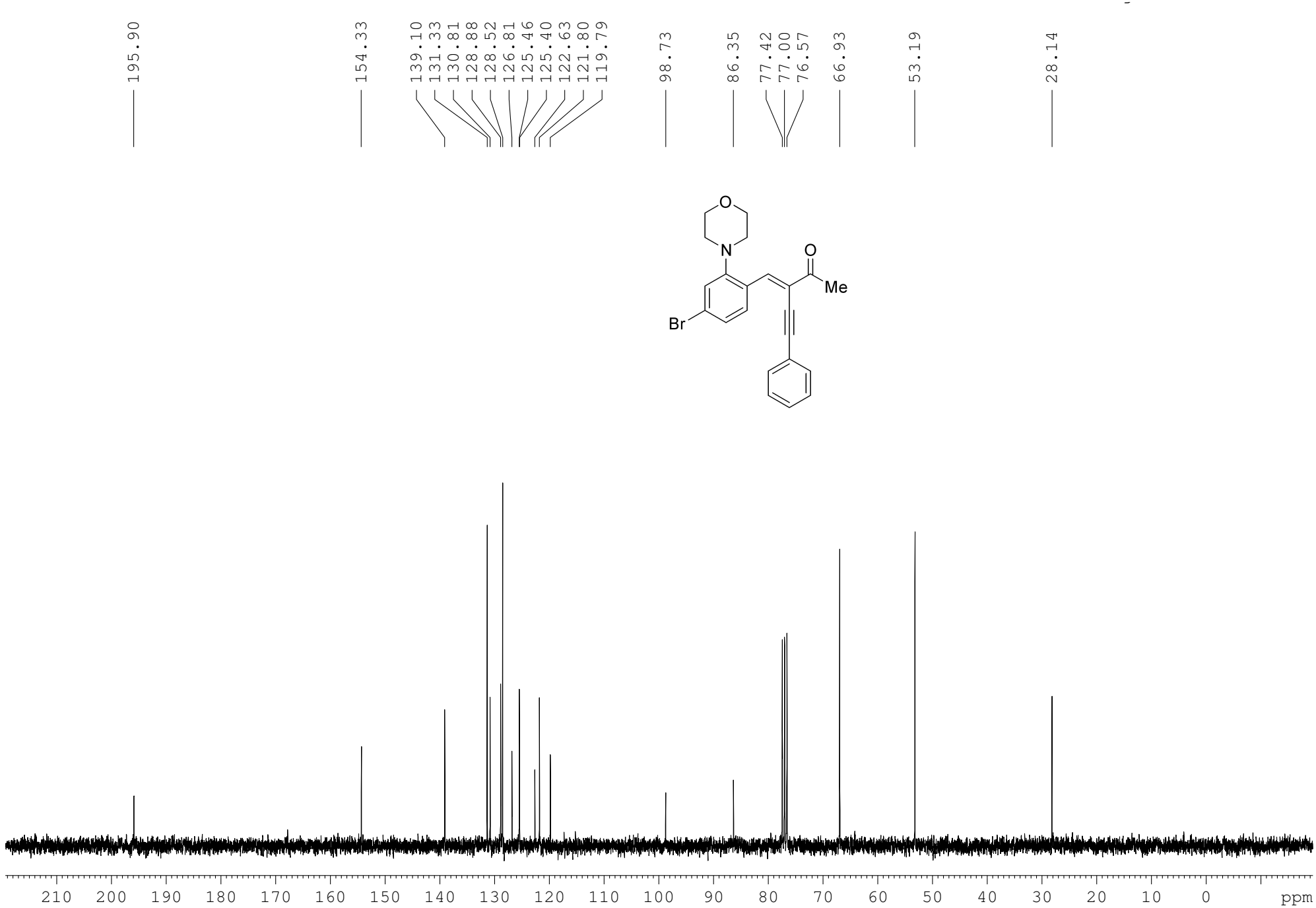
3.00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125.40
122.63
121.80
119.79
98.73
86.35
77.42
77.00
76.57
66.93
53.19
28.14
O
N
O
Me
Br
210
200
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180
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140
130
120
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100
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60
50
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30
20
10
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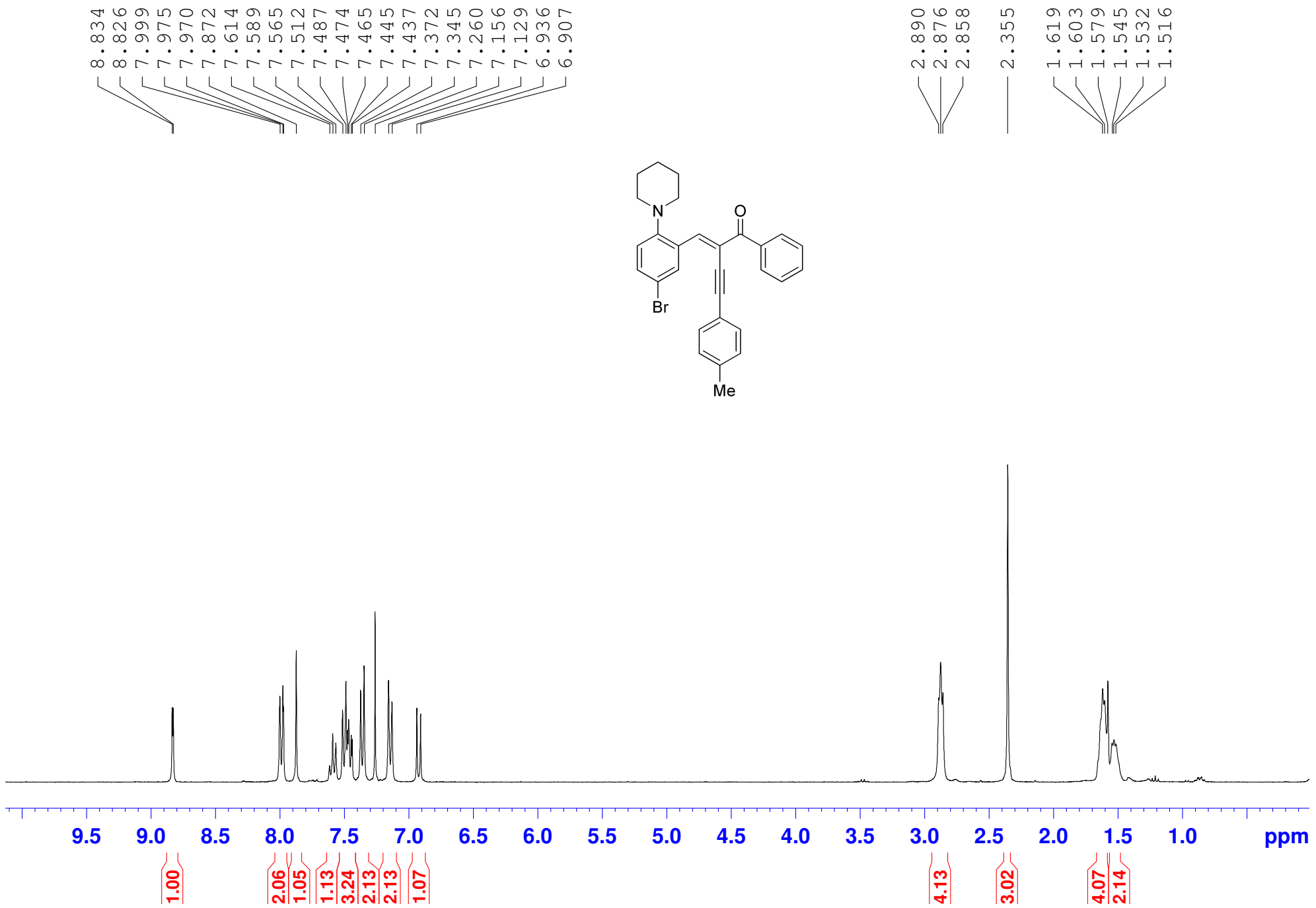
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7.512
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7.445
7.437
7.372
7.345
7.260
7.156
7.129
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6.907
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2.876
2.858
2.355
1.619
1.603
1.579
1.545
1.532
1.516
N
O
Br
Me
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
1.0
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1.07
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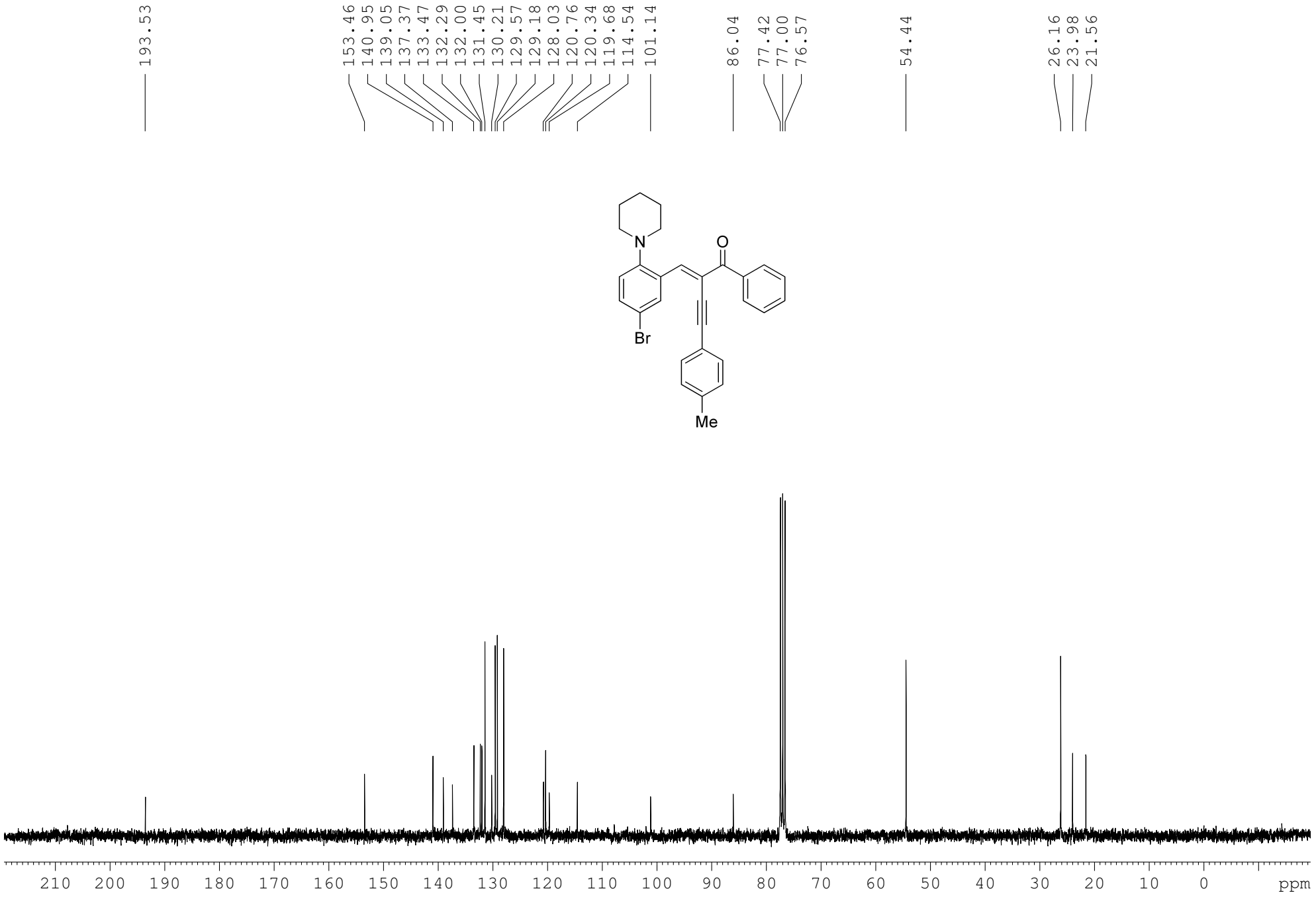
3.02
4.07
2.14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129.57
129.18
128.03
120.76
120.34
119.68
114.54
101.14
86.04
77.42
77.00
76.57
54.44
26.16
23.98
21.56
N
O
Br
Me
210
200
190
180
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140
130
120
110
100
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60
50
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20
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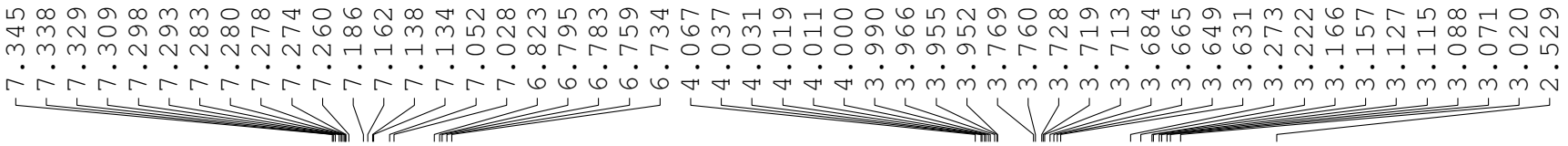
0
ppm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7.274
7.260
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7.162
7.138
7.134
7.052
7.028
6.823
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6.783
6.759
6.734
4.067
4.037
4.031
4.019
4.011
4.000
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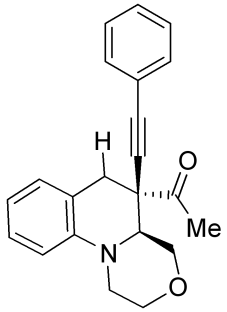
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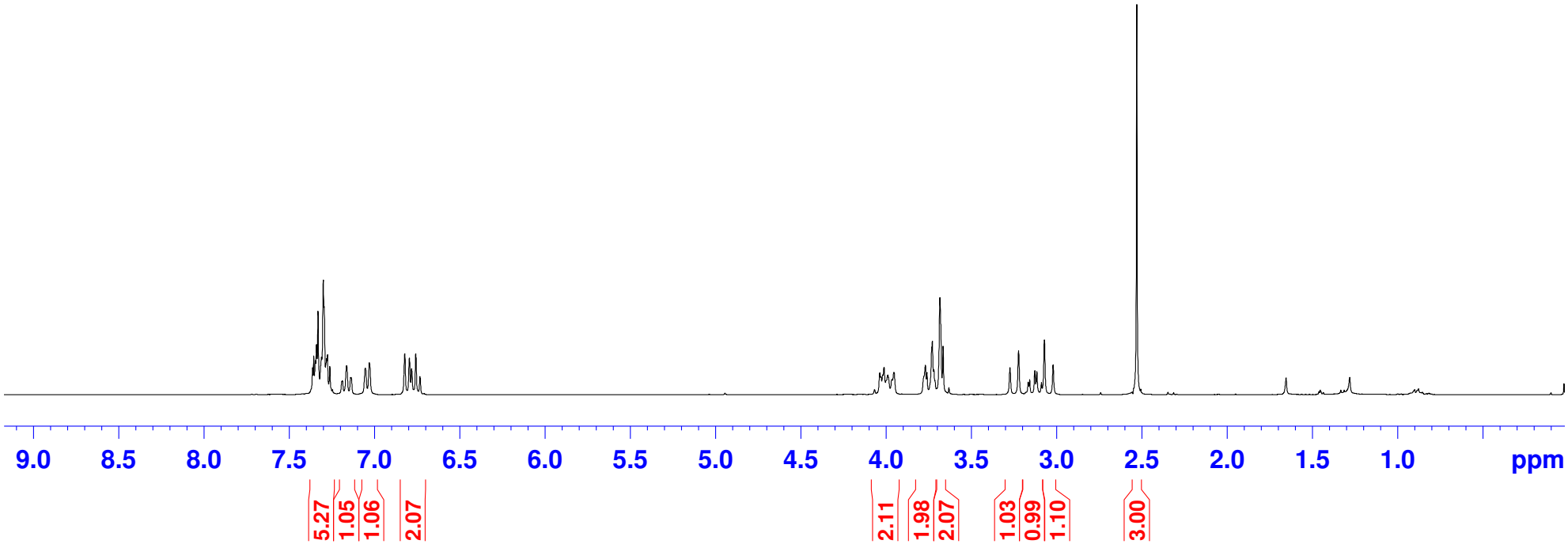
O
Me
N
O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5.5
5.0
4.5
4.0
3.5
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2.0
1.5
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1.06
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2.11
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2.07
1.03
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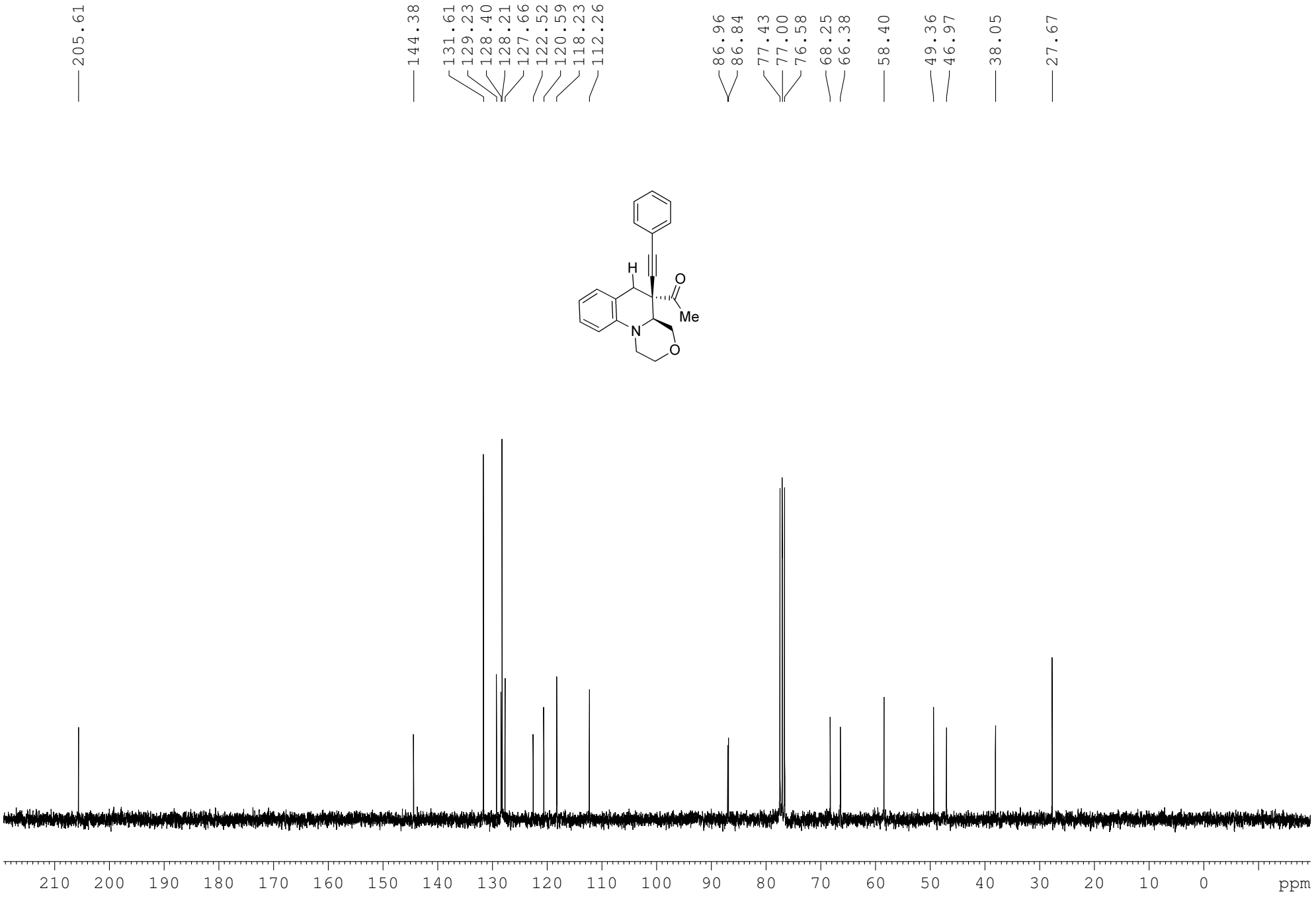
1.10
3.00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122.52
120.59
118.23
112.26
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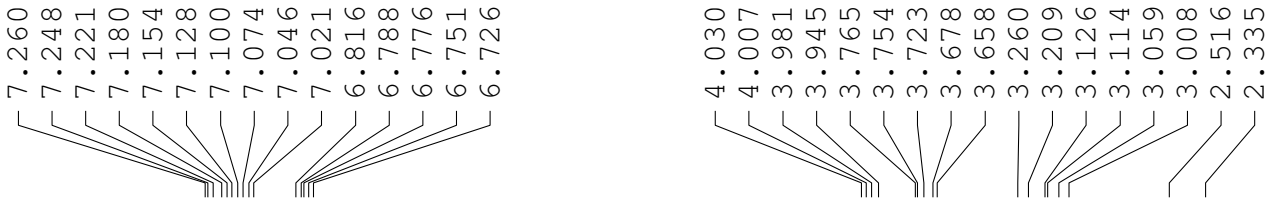
86.84
77.43
77.00
76.58
68.25
66.38
58.40
49.36
46.97
38.05
27.67
H
O
Me
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.021
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6.788
6.776
6.751
6.726
4.030
4.007
3.981
3.945
3.765
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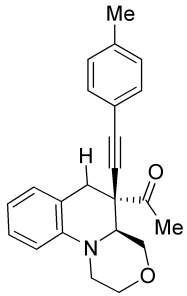
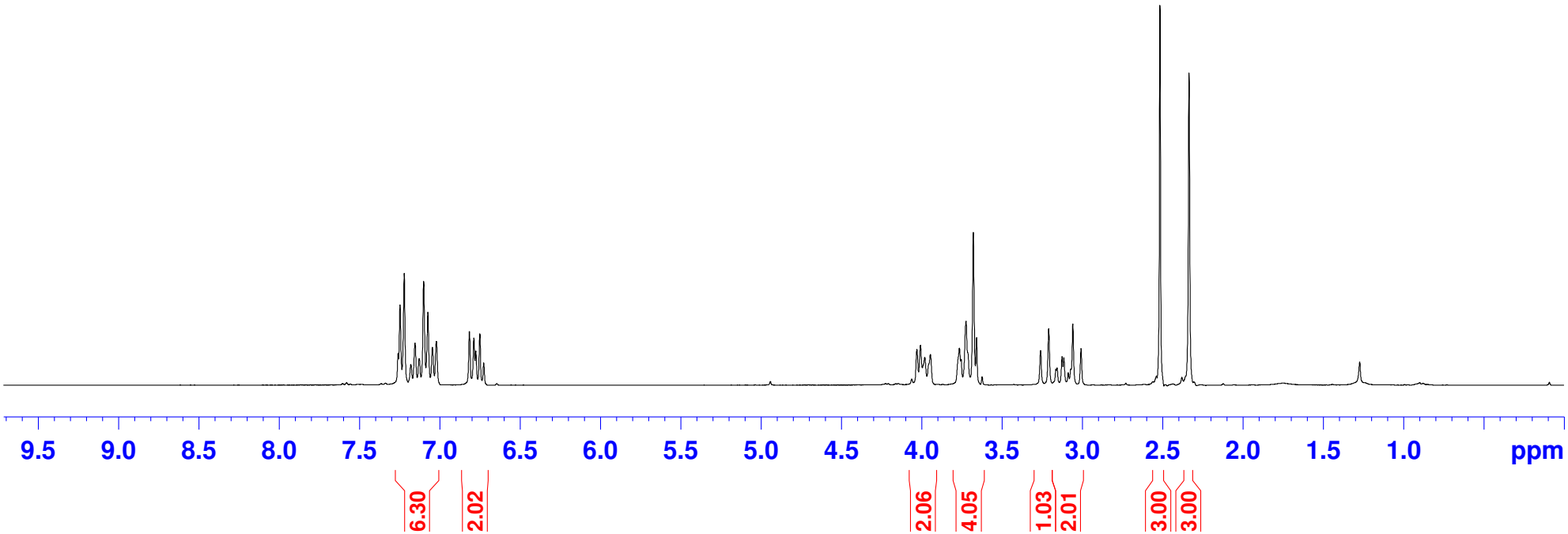

Me
H
O
Me
N
O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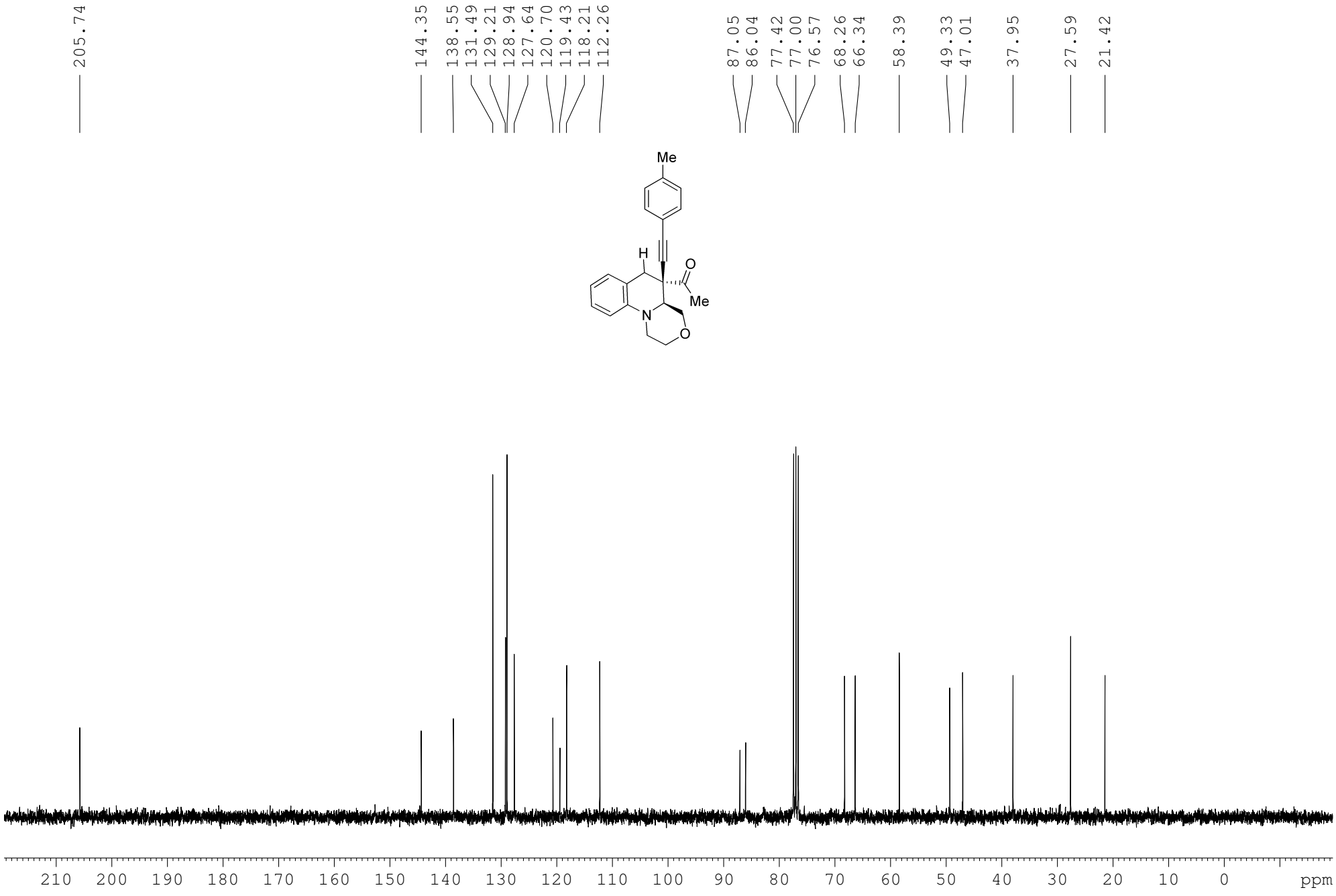
3.00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77.42
77.00
76.57
68.26
66.34
58.39
49.33
47.01
37.95
27.59
21.42
Me
H
O
Me
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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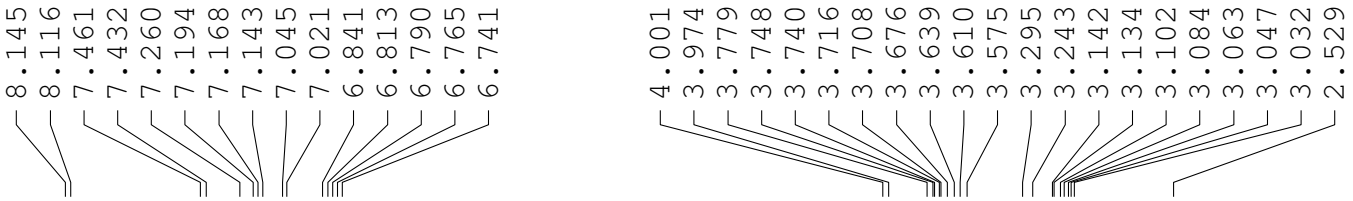
ppm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7.143
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6.765
6.741
4.001
3.974
3.779
3.748
3.740
3.716
3.708
3.676
3.639
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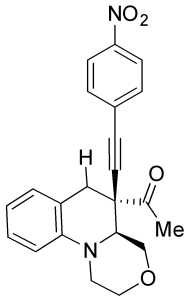
3.084
3.063
3.047
3.032
2.529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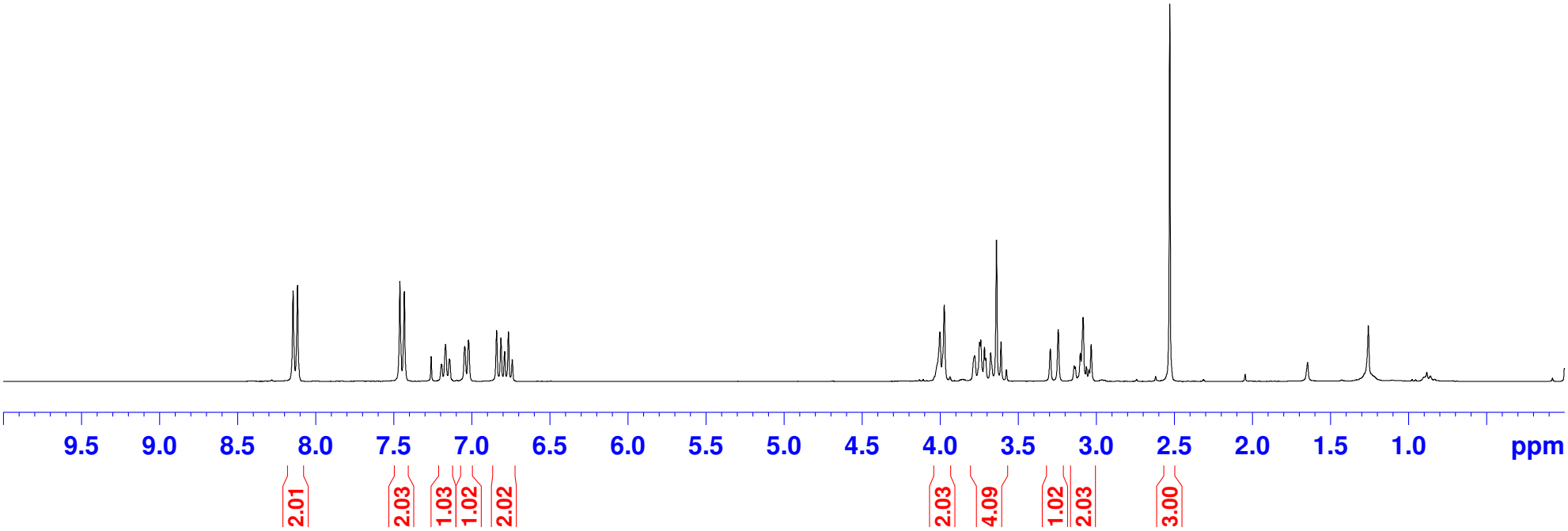
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6.0
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4.0
3.5
3.0
2.5
2.0
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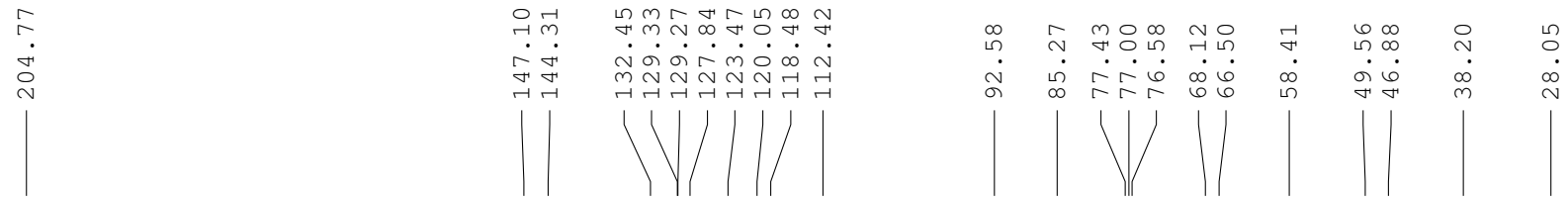
2.03
1.03
1.02
2.02
2.03
4.09
1.02
2.03
3.00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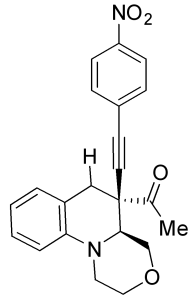
58.41
49.56
46.88
38.20
28.05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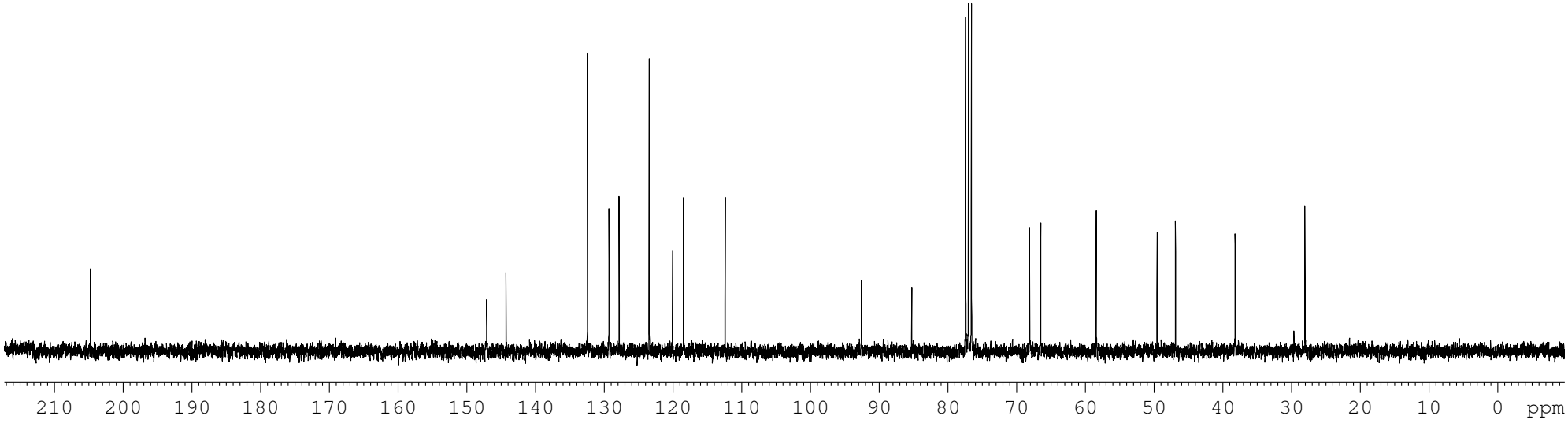
Me
N
O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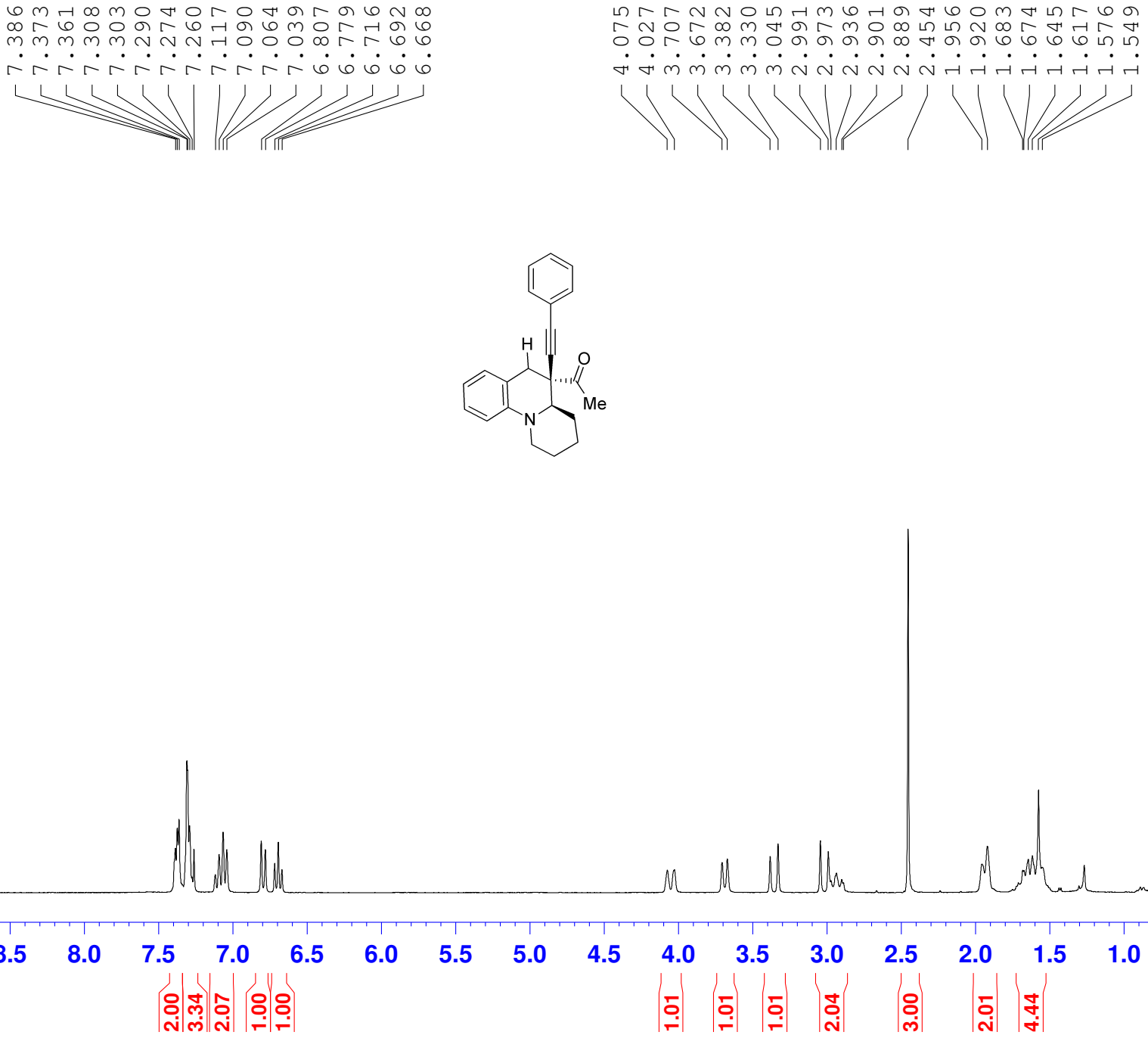
ppm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6.692
6.668
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4.027
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3.330
3.045
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2.936
2.901
2.889
2.454
1.956
1.920
1.683
1.674
1.645
1.617
1.576
1.549
H
O
Me
N
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.01
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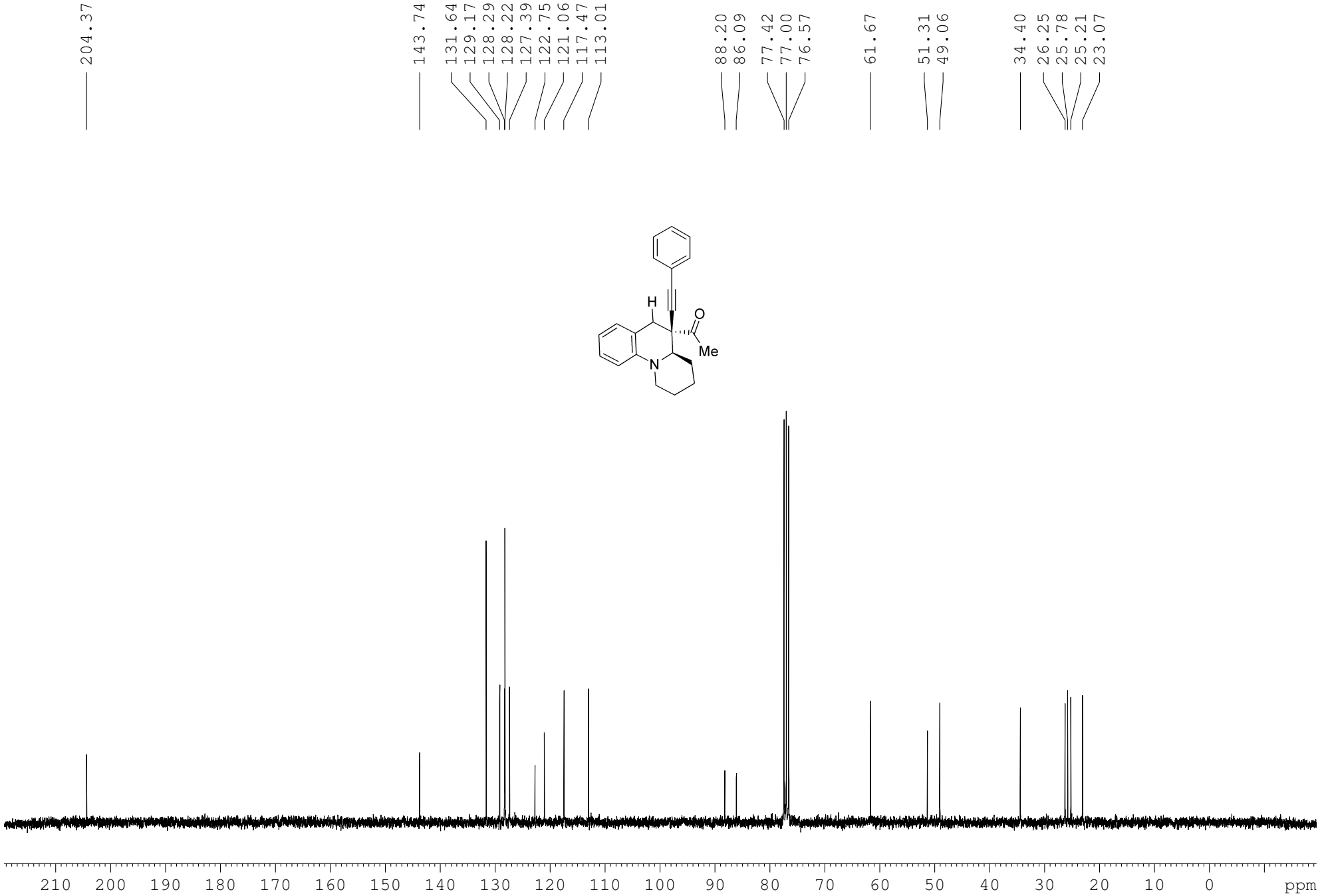
3.00
2.01
4.44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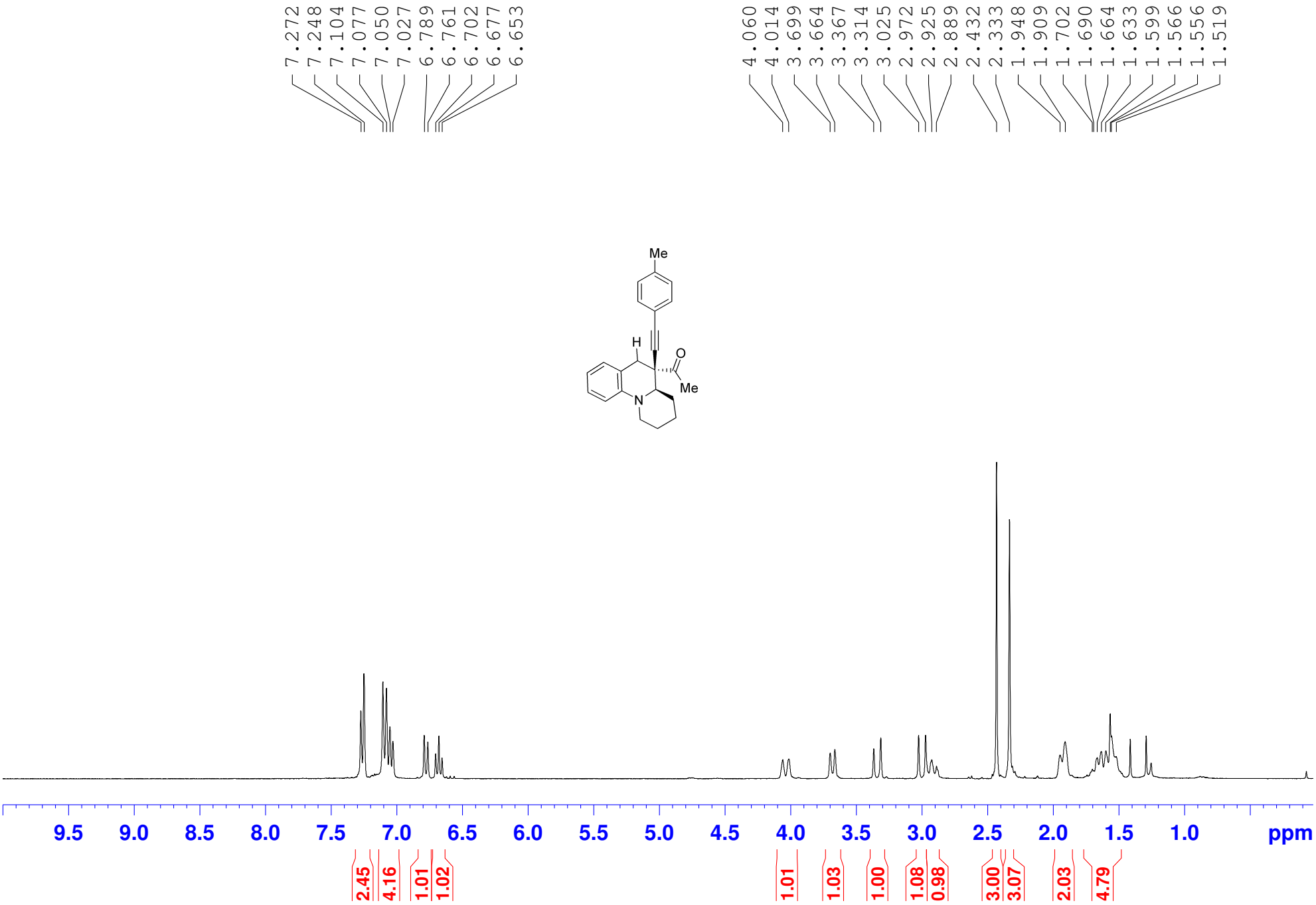
88.20
86.09
77.42
77.00
76.57
61.67
51.31
49.06
34.40
26.25
25.78
25.21
23.07
H
O
Me
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.027
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6.761
6.702
6.677
6.653
4.060
4.014
3.699
3.664
3.367
3.314
3.025
2.972
2.925
2.889
2.432
2.333
1.948
1.909
1.702
1.690
1.664
1.633
1.599
1.566
1.556
1.519
Me
H
O
Me
N
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9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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4.0
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2.0
1.5
1.0
ppm
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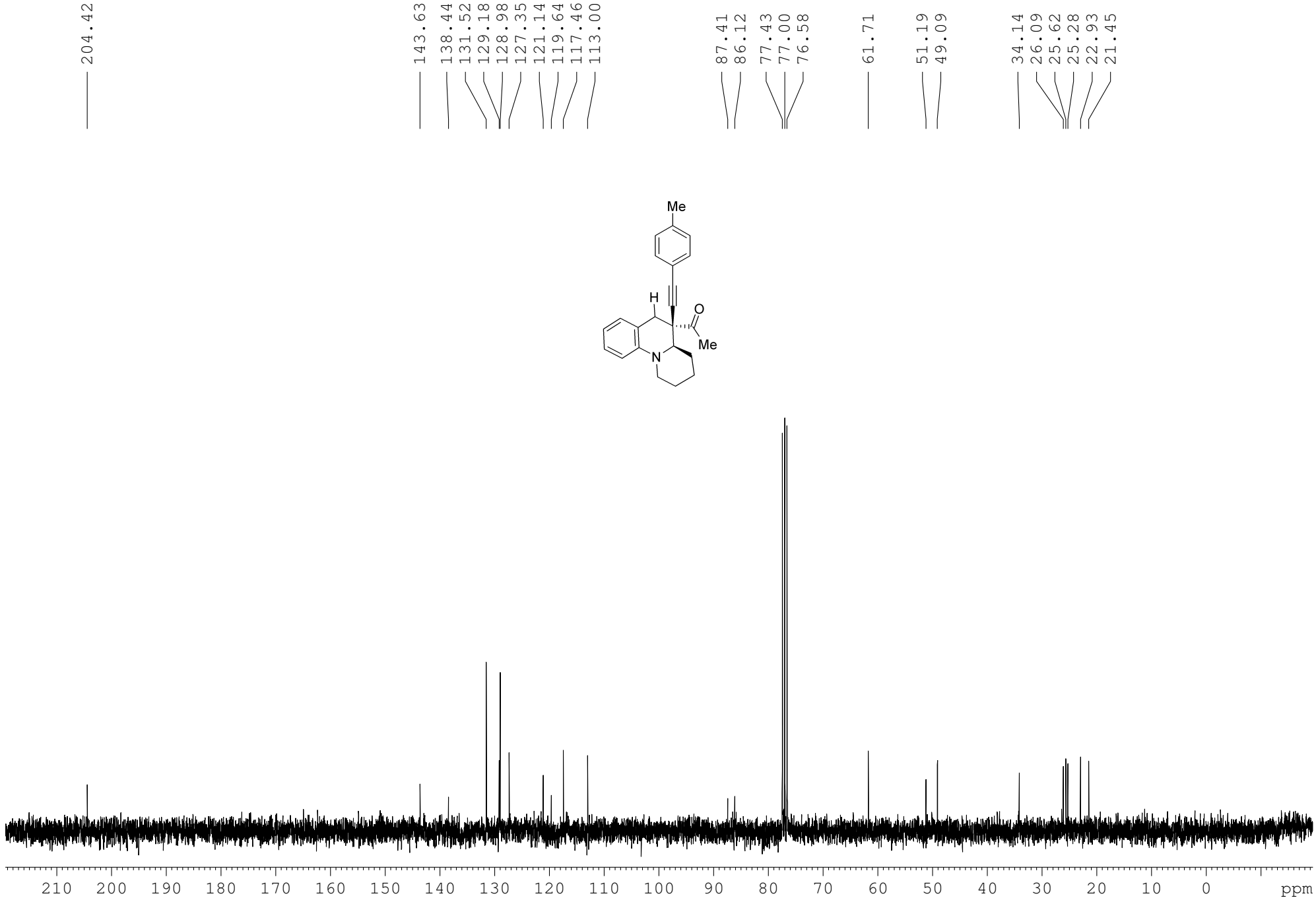
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87.41
86.12
77.43
77.00
76.58
61.71
51.19
49.09
34.14
26.09
25.62
25.28
22.93
21.45
Me
H
O
Me
N
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200
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180
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140
130
120
110
100
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60
50
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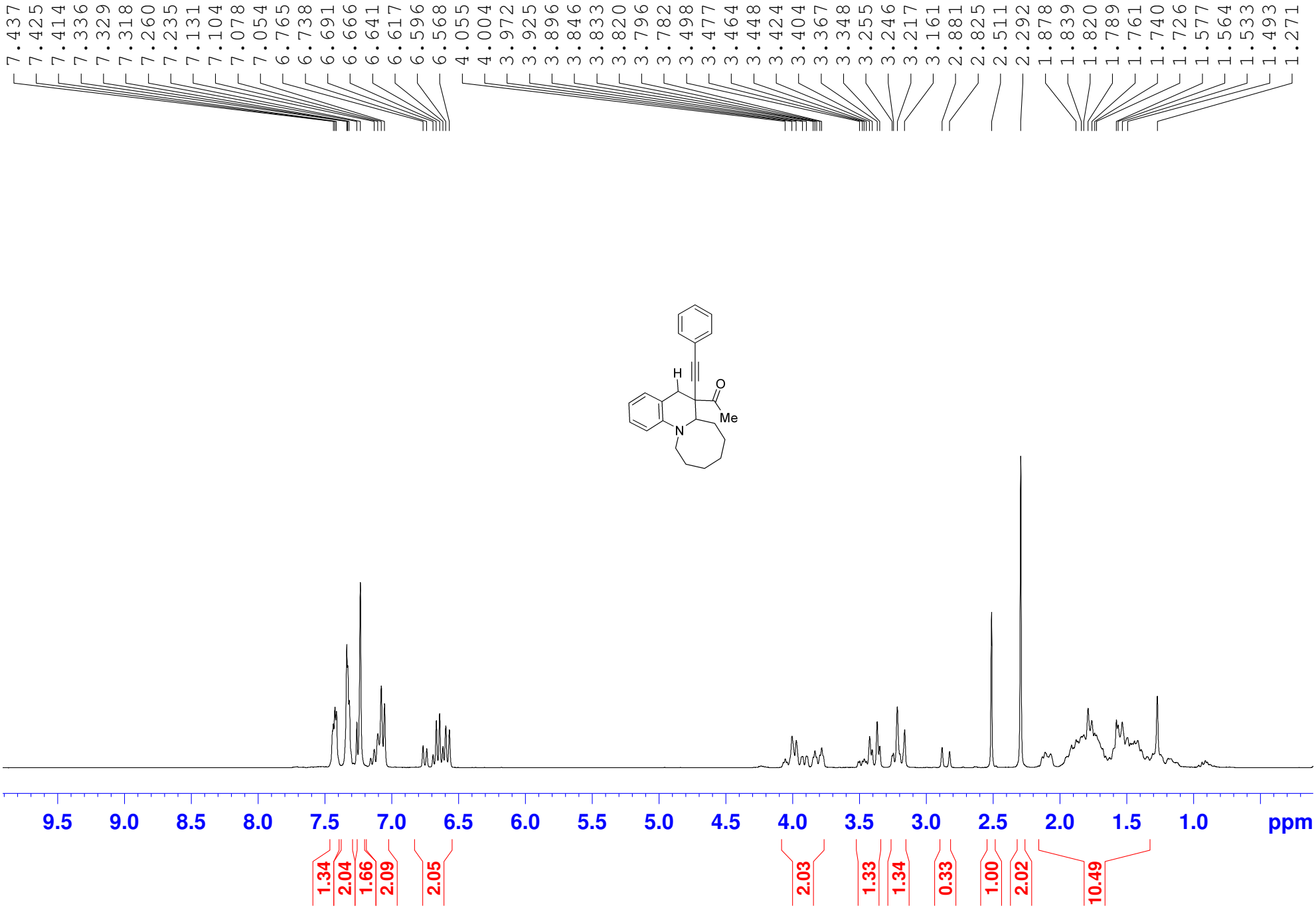
30
20
10
0
ppm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6.738
6.691
6.666
6.641
6.617
6.596
6.568
4.055
4.004
3.972
3.925
3.896
3.846
3.833
3.820
3.796
3.782
3.498
3.477
3.464
3.448
3.424
3.404
3.367
3.348
3.255
3.246
3.217
3.161
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2.825
2.511
2.292
1.878
1.839
1.820
1.789
1.761
1.740
1.726
1.577
1.564
1.533
1.493
1.271
H
O
Me
N
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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2.09
2.05
2.03
1.33
1.34
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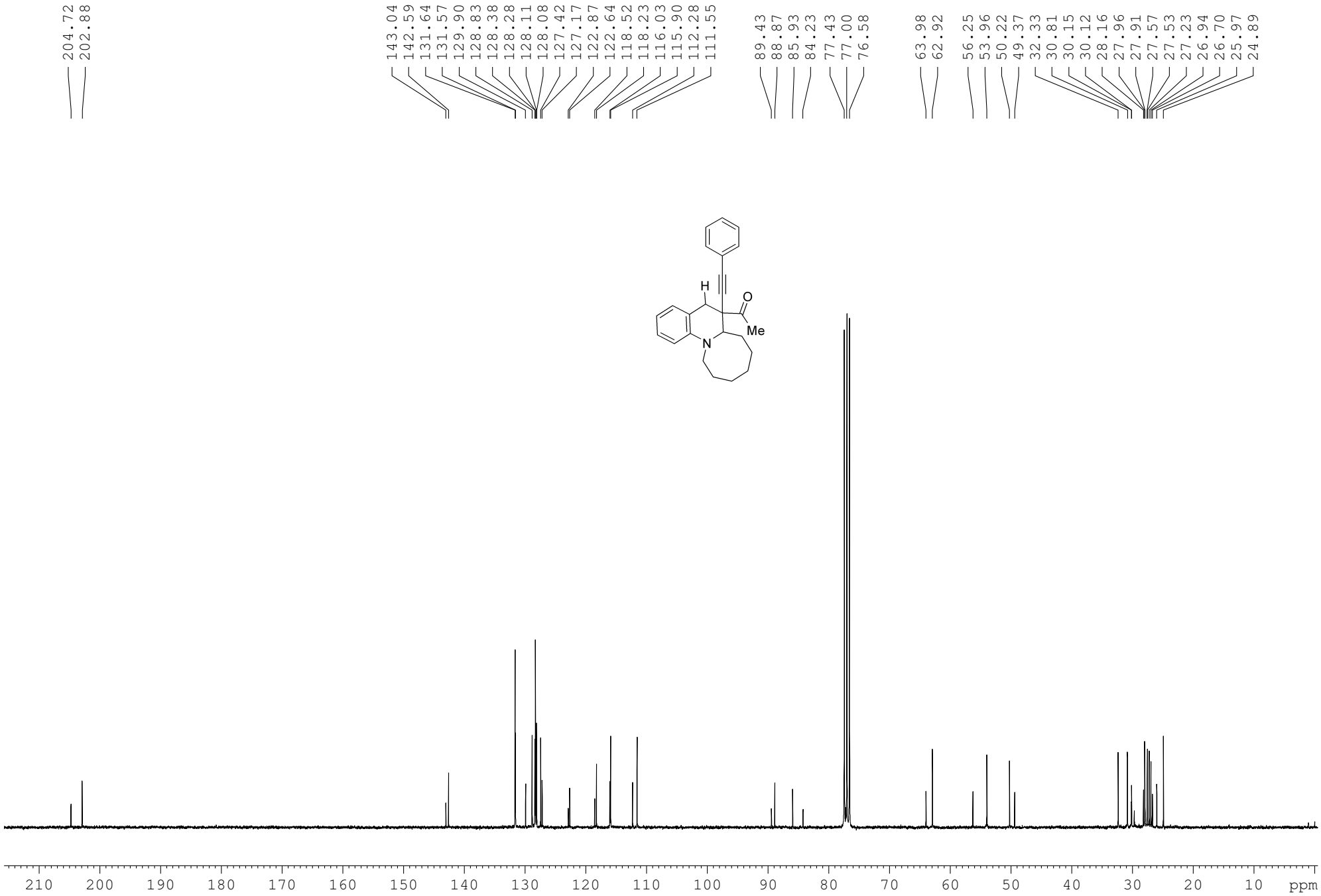
1.00
2.02
10.49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128.11
128.08
127.42
127.17
122.87
122.64
118.52
118.23
116.03
115.90
112.28
111.55
89.43
88.87
85.93
84.23
77.43
77.00
76.58
63.98
62.92
56.25
53.96
50.22
49.37
32.33
30.81
30.15
30.12
28.16
27.96
27.91
27.57
27.53
27.23
26.94
26.70
25.97
24.89
H
O
Me
N
210
200
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180
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150
140
130
120
110
100
90
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70
60
50
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30
20
10
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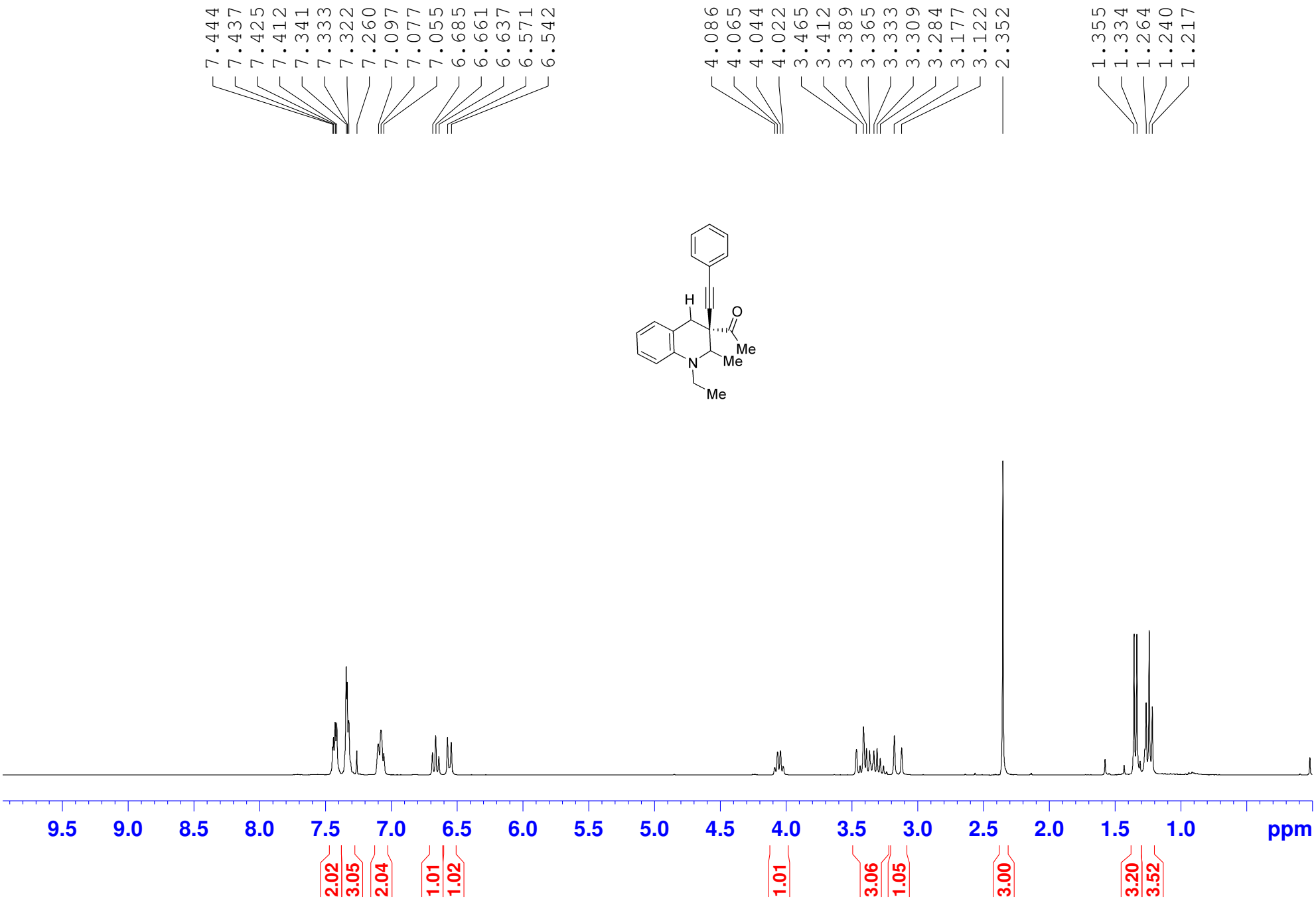
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7.077
7.055
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6.661
6.637
6.571
6.542
4.086
4.065
4.044
4.022
3.465
3.412
3.389
3.365
3.333
3.309
3.284
3.177
3.122
2.352
1.355
1.334
1.264
1.240
1.217
H
O
Me
Me
N
Me
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8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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2.04
1.01
1.02
1.01
3.06
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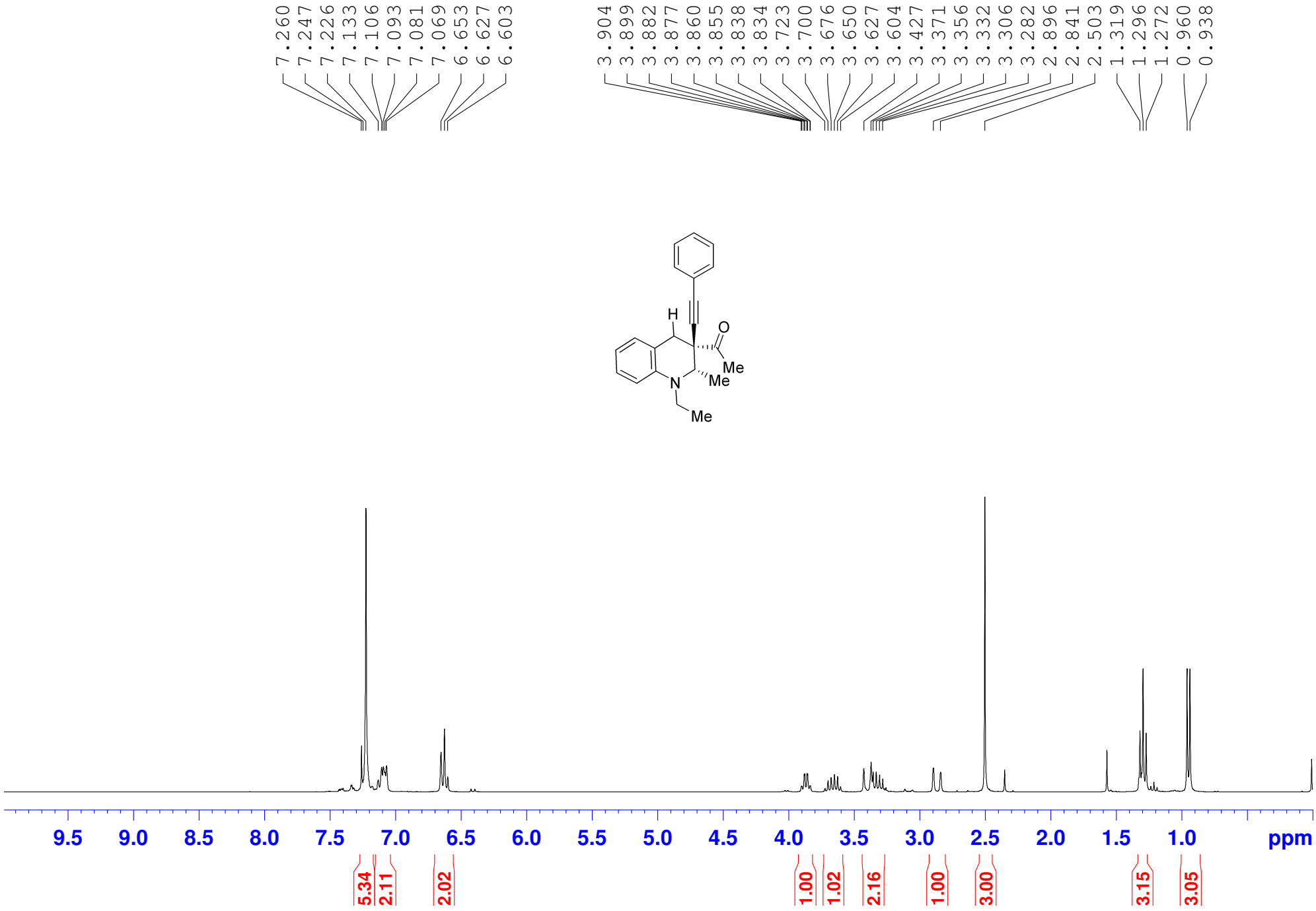
3.52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7.069
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6.627
6.603
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3.899
3.882
3.877
3.860
3.855
3.838
3.834
3.723
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3.676
3.650
3.627
3.604
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2.503
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1.296
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0.938
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O
Me
Me
N
Me
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6.0
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5.0
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4.0
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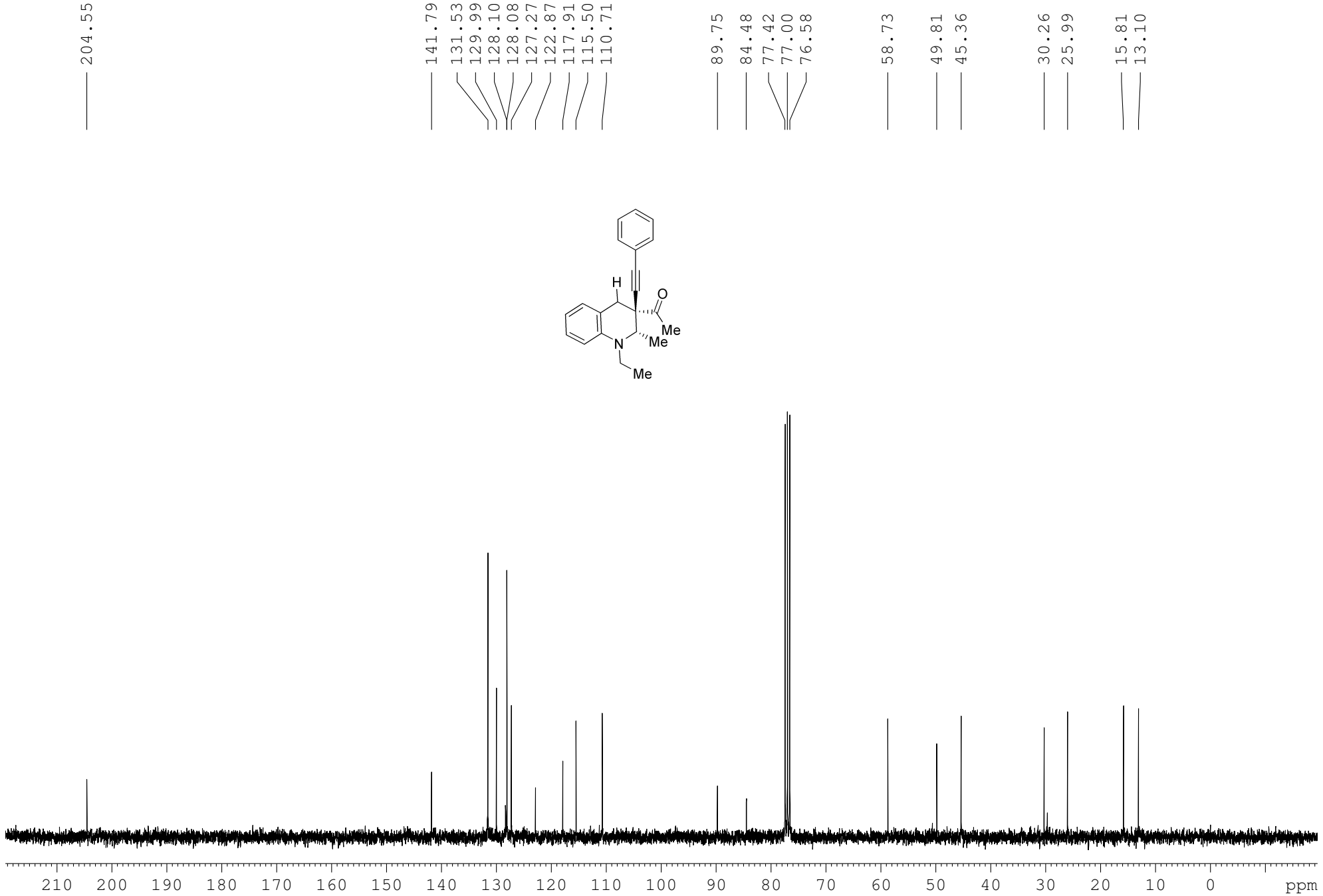
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84.48
77.42
77.00
76.58
58.73
49.81
45.36
30.26
25.99
15.81
13.10
H
O
Me
Me
N
Me
210
200
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140
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120
110
100
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60
50
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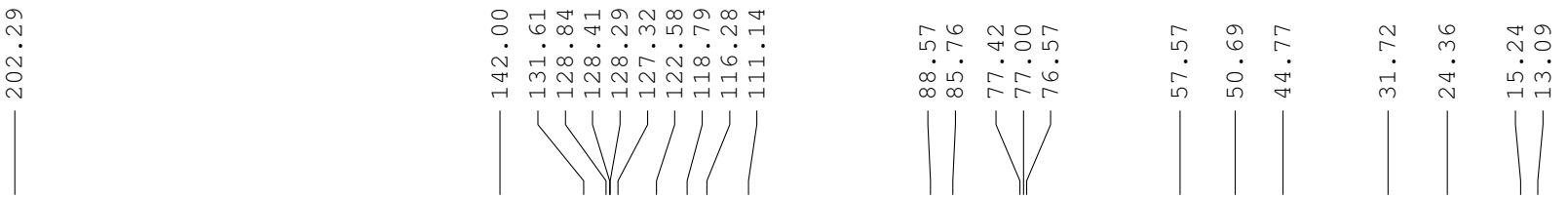
20
10
0
ppm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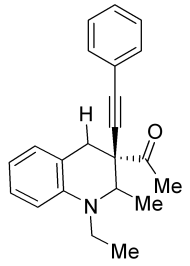
13.09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Me
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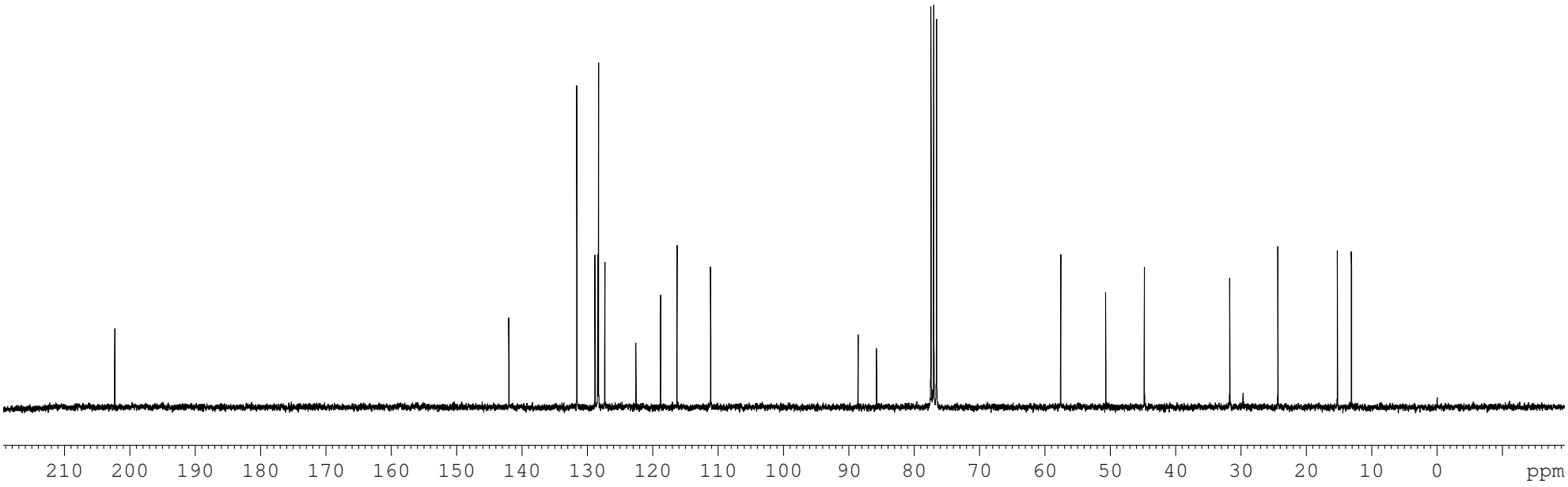
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200
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180
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100
90
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60
50
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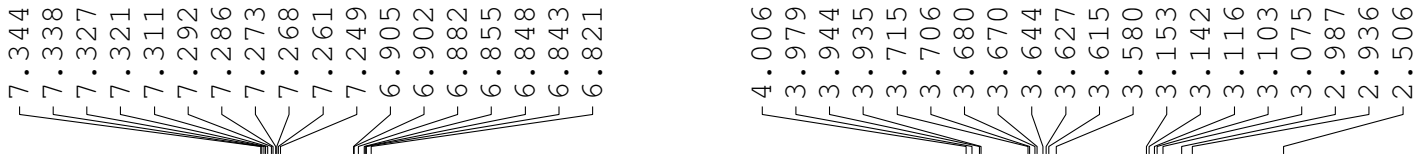
20
10
0
ppm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6.882
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6.843
6.821
4.006
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3.935
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3.706
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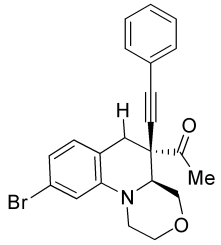
2.506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Br
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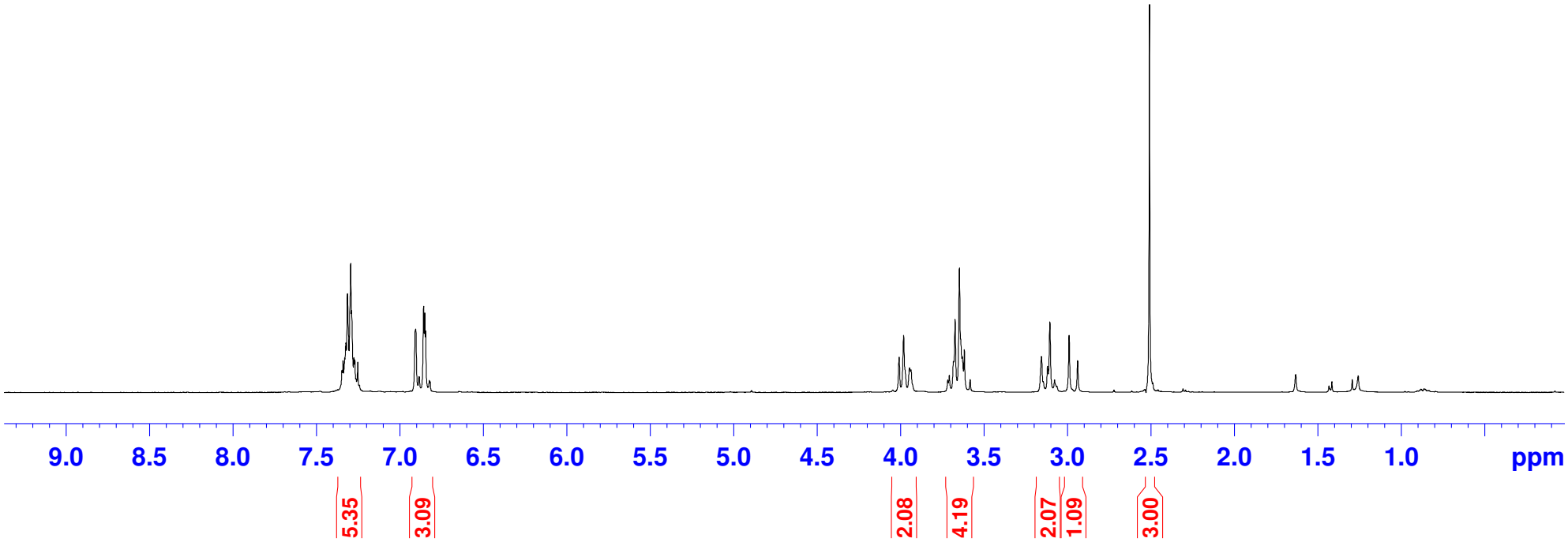
O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1.5
1.0
ppm
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2.08
4.19
2.07
1.09
3.00

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122.27
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77.00
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66.22
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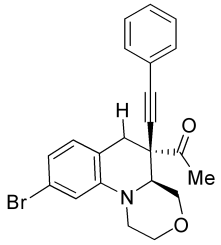
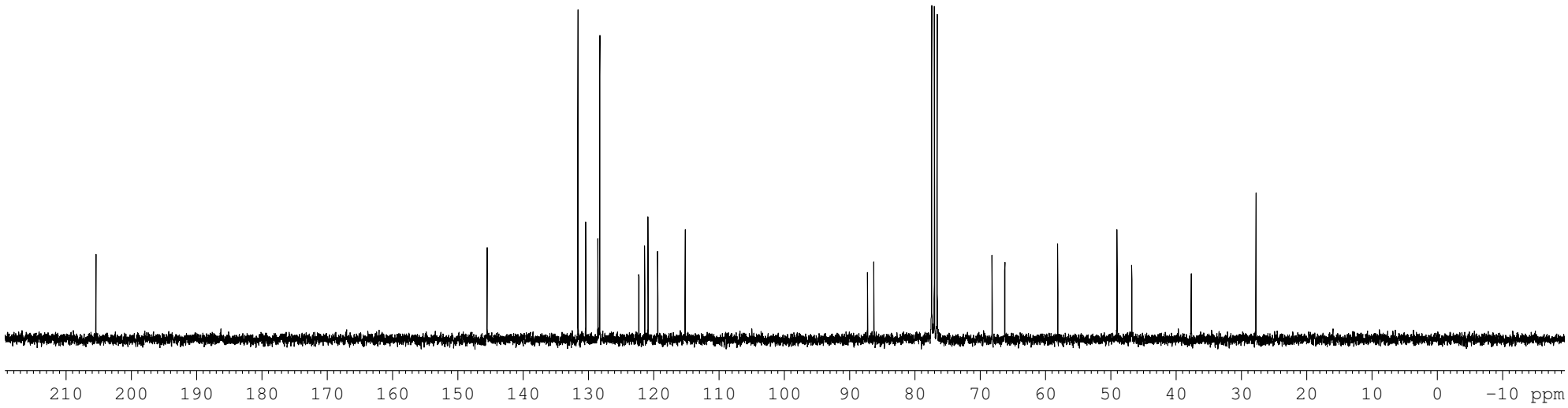
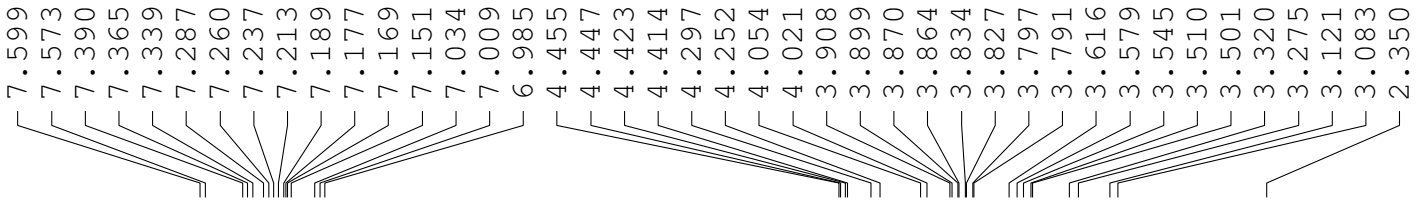
27.74



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7.189
7.177
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7.151
7.034
7.009
6.985
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4.447
4.423
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4.252
4.054
4.021
3.908
3.899
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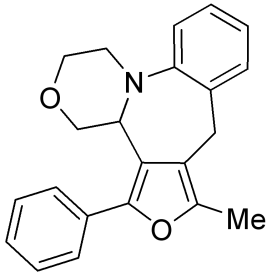
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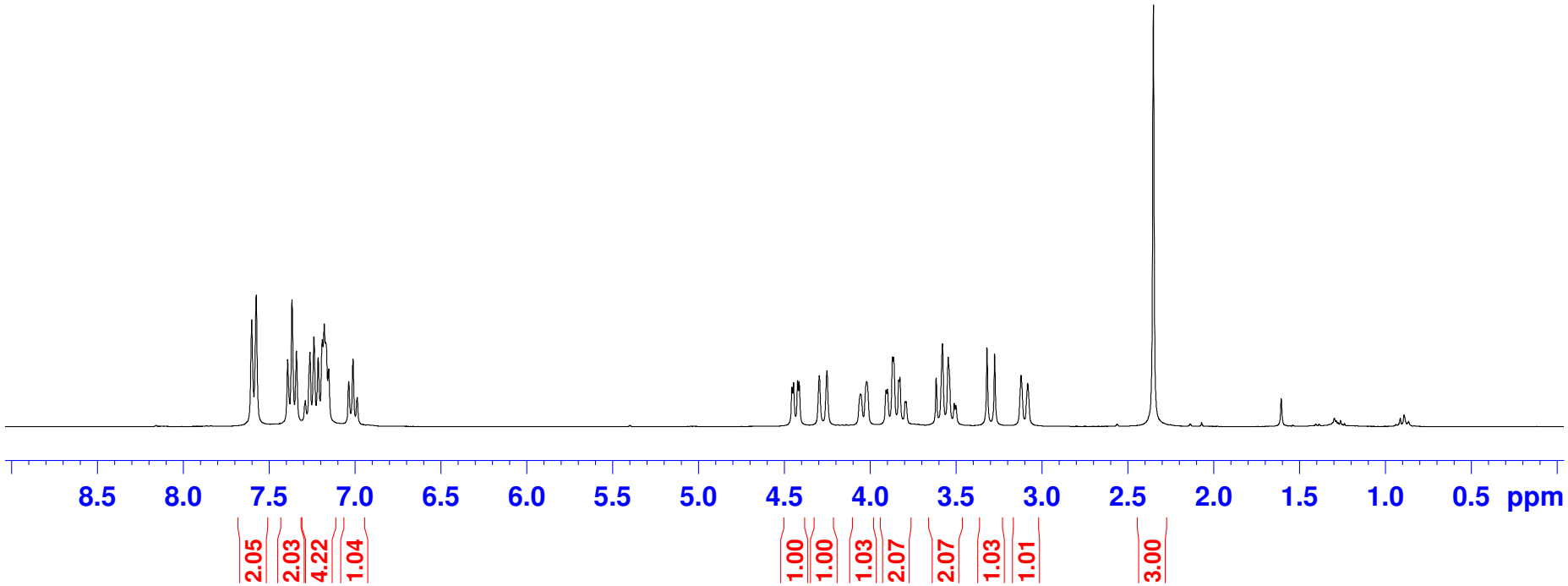
O
Me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1.0
0.5
ppm
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1.00
1.03
2.07
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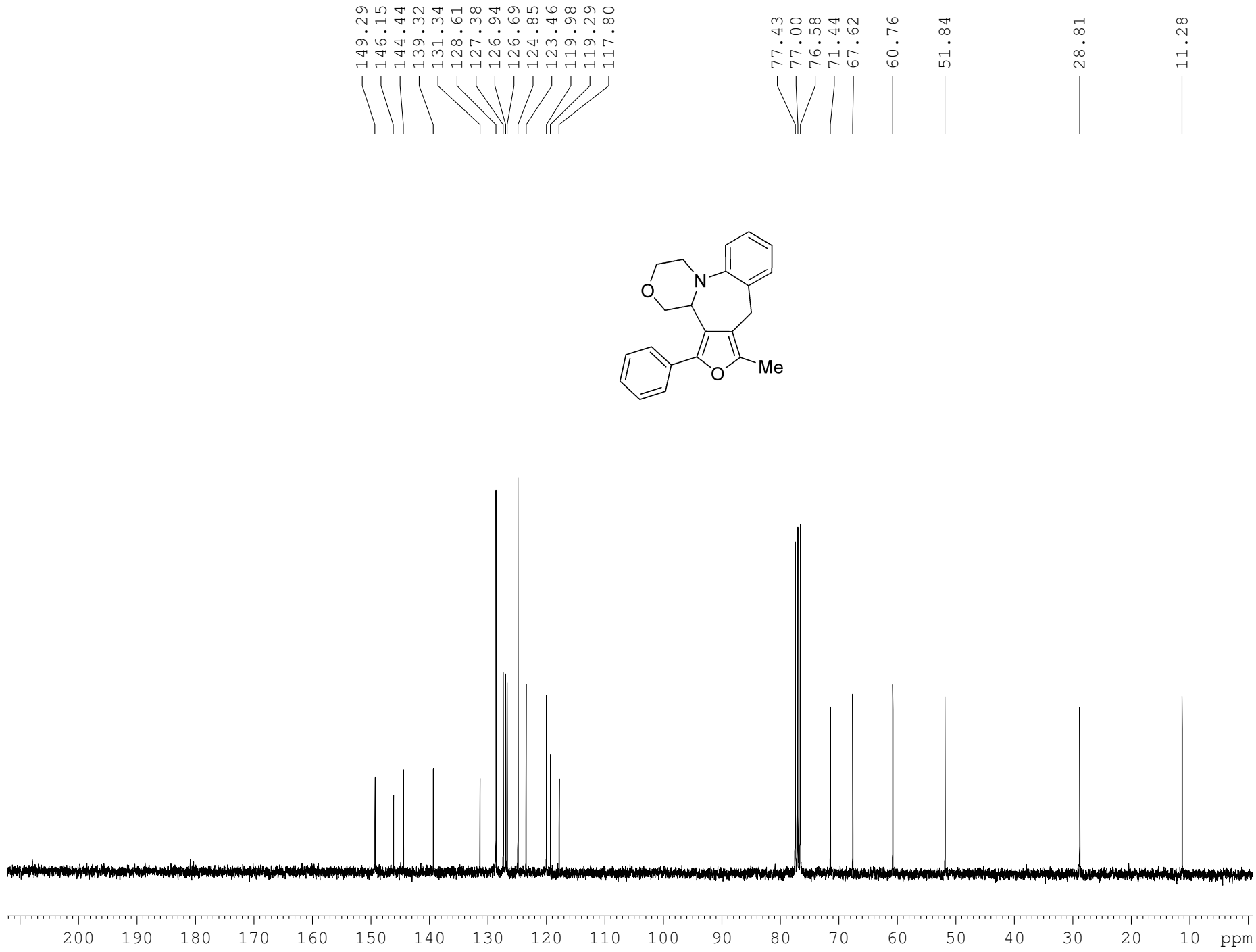
1.03
1.01
3.00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123.46
119.98
119.29
117.80
77.43
77.00
76.58
71.44
67.62
60.76
51.84
28.81
11.28
O
N
O
Me
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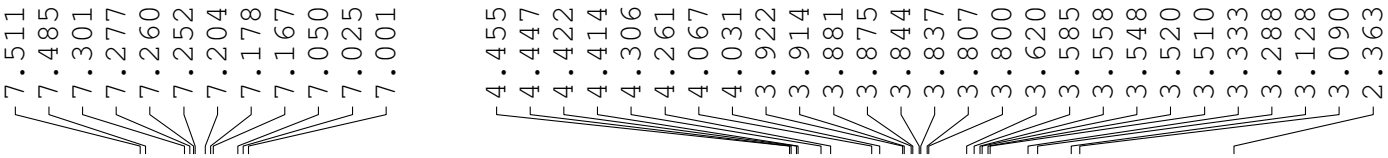
20
10
ppm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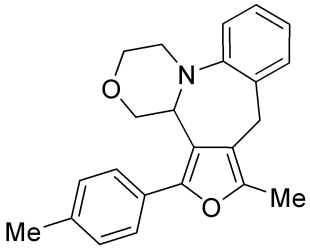
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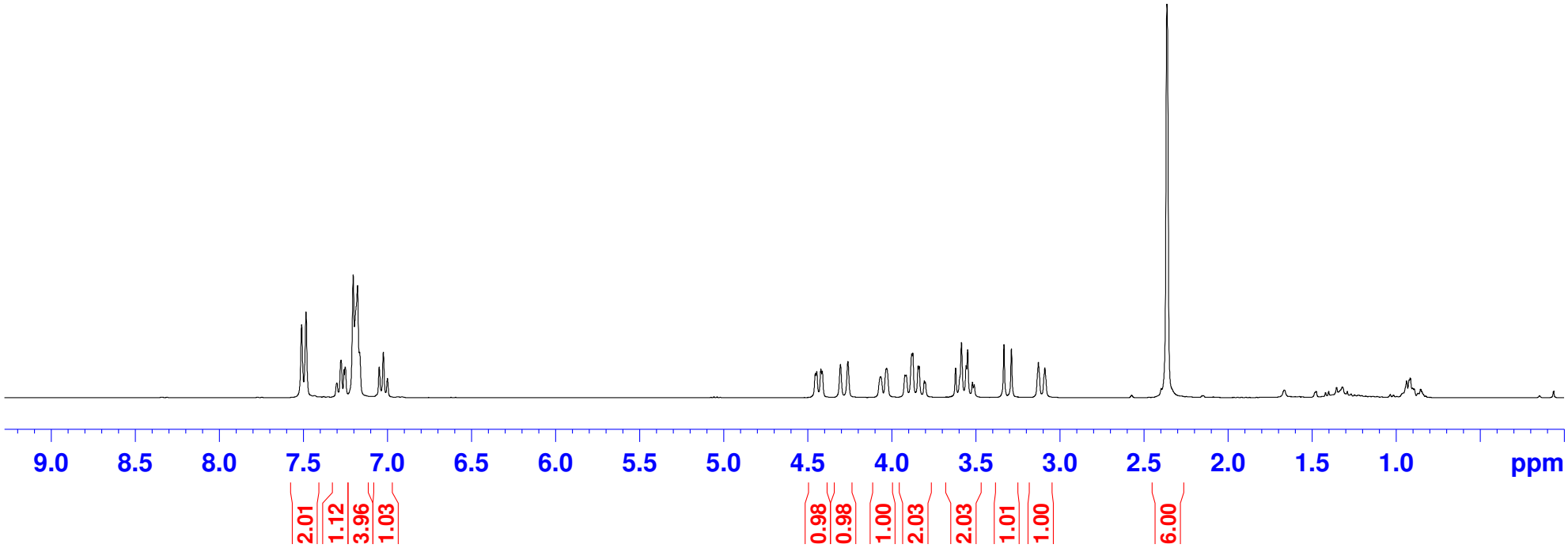
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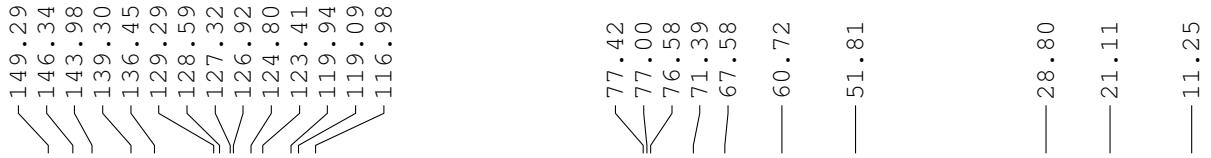
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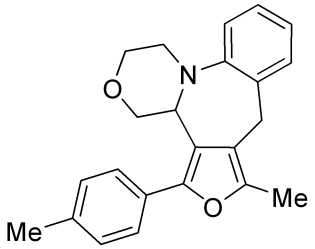
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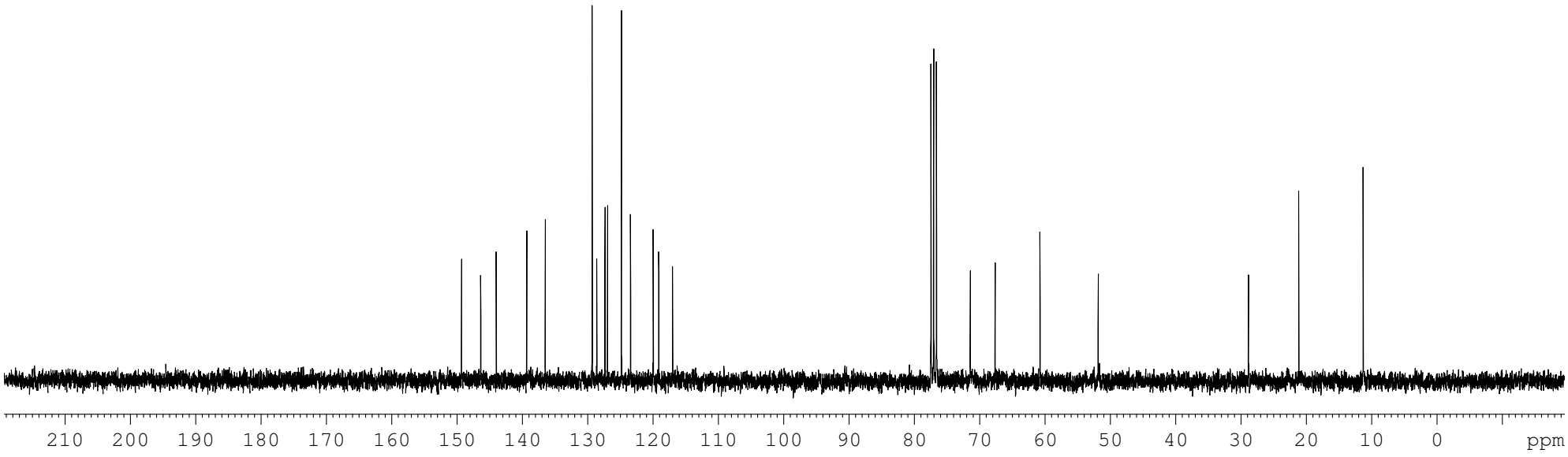
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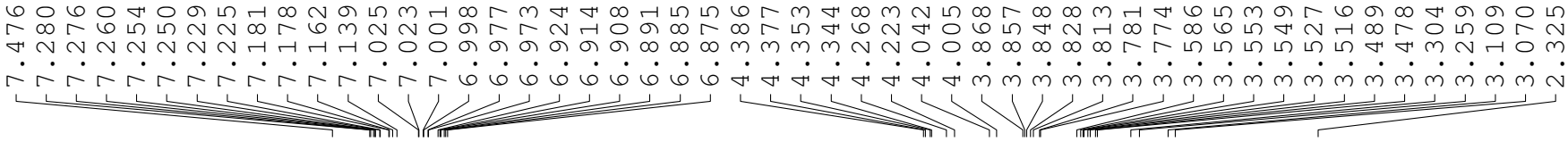
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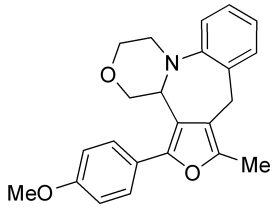
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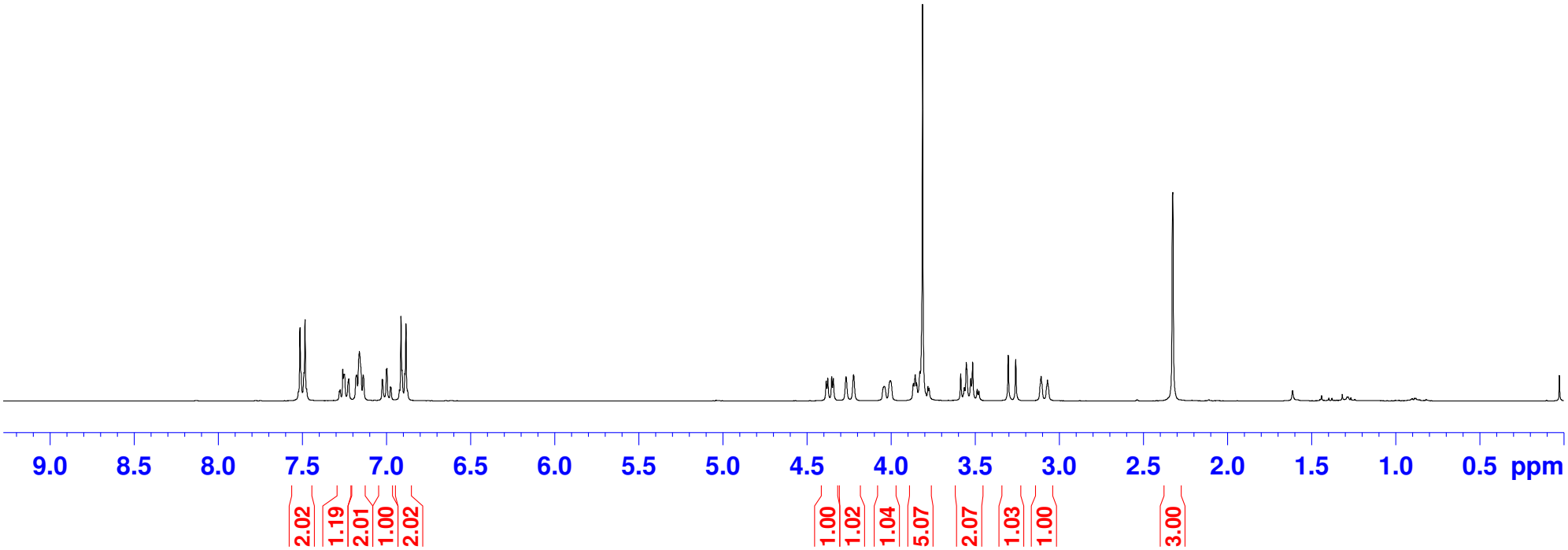
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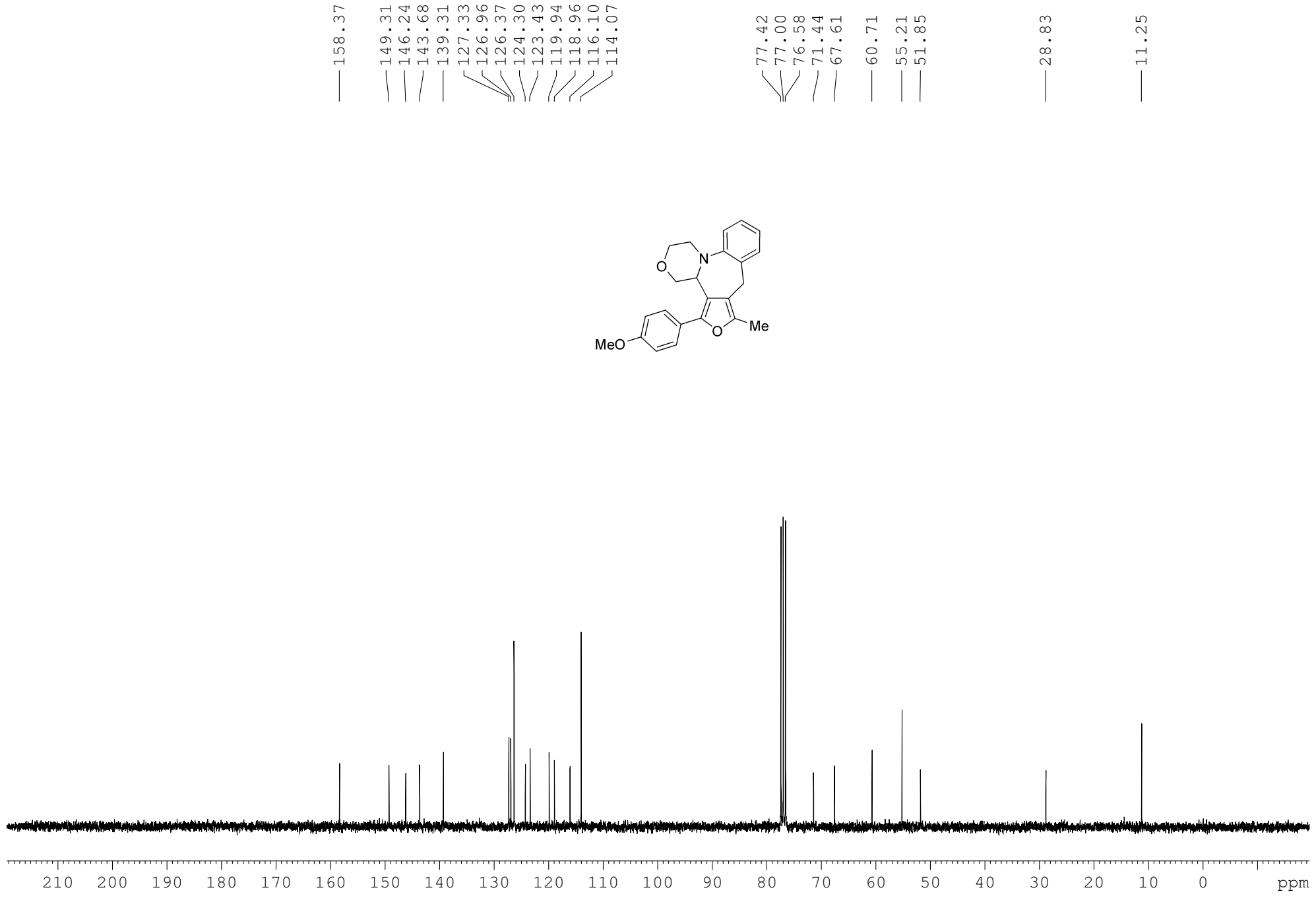
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O
O
Me
MeO
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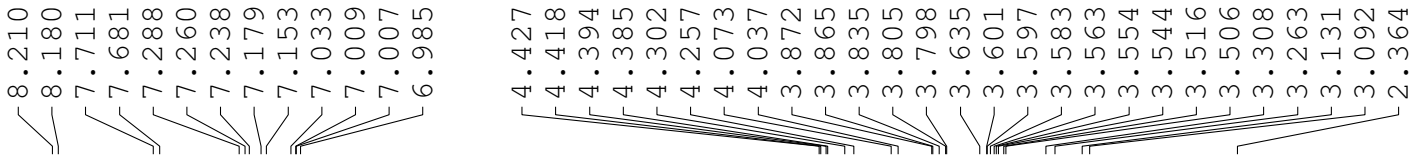
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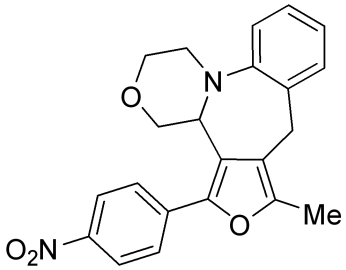
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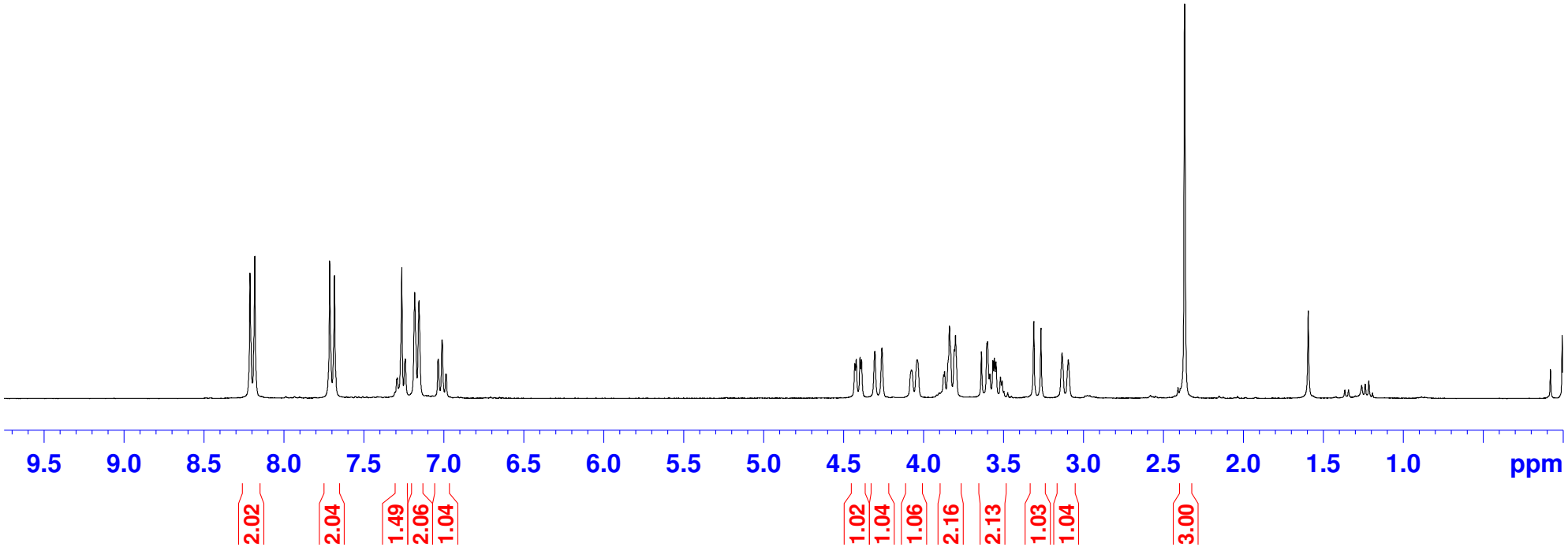
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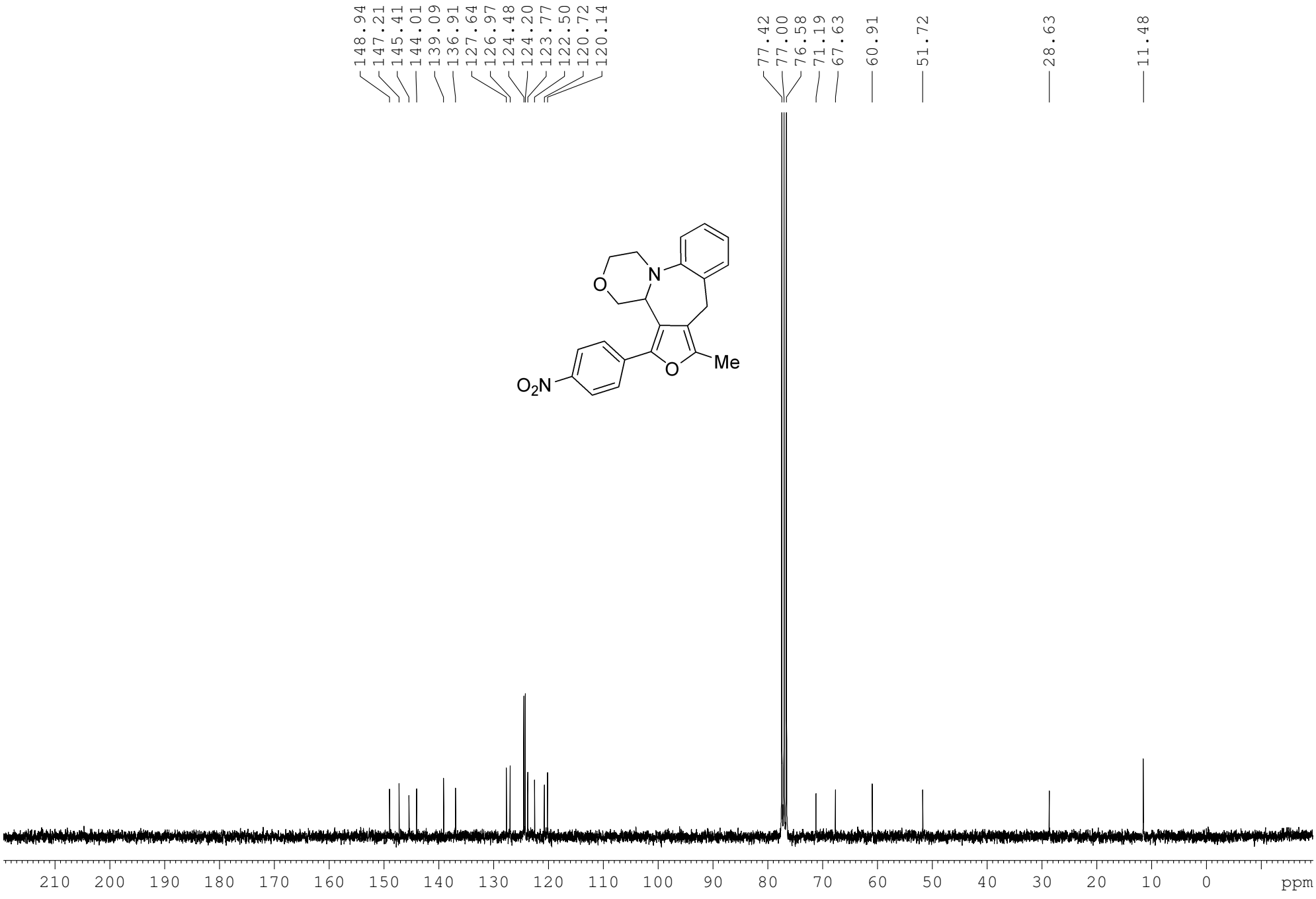
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O
Me
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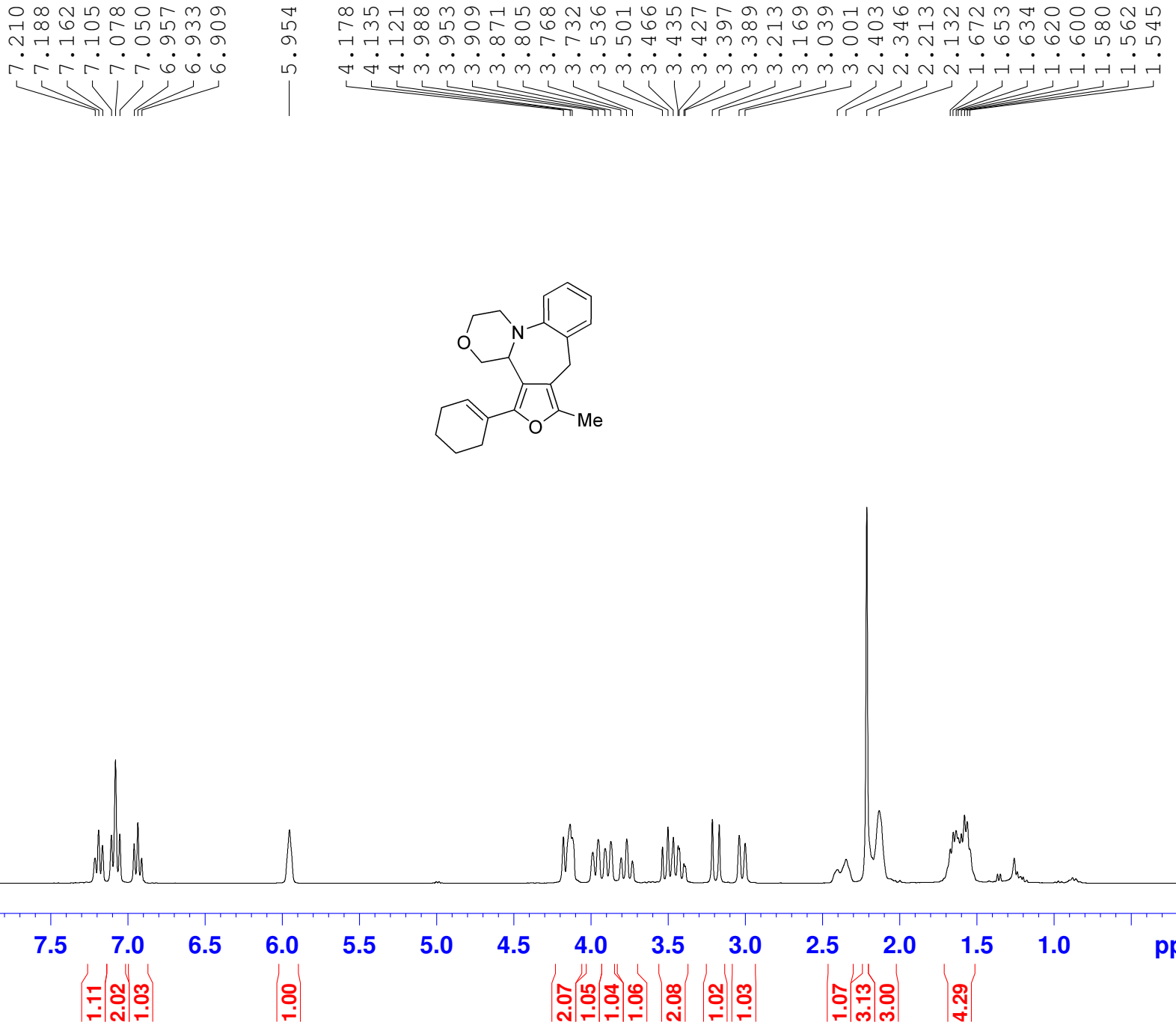
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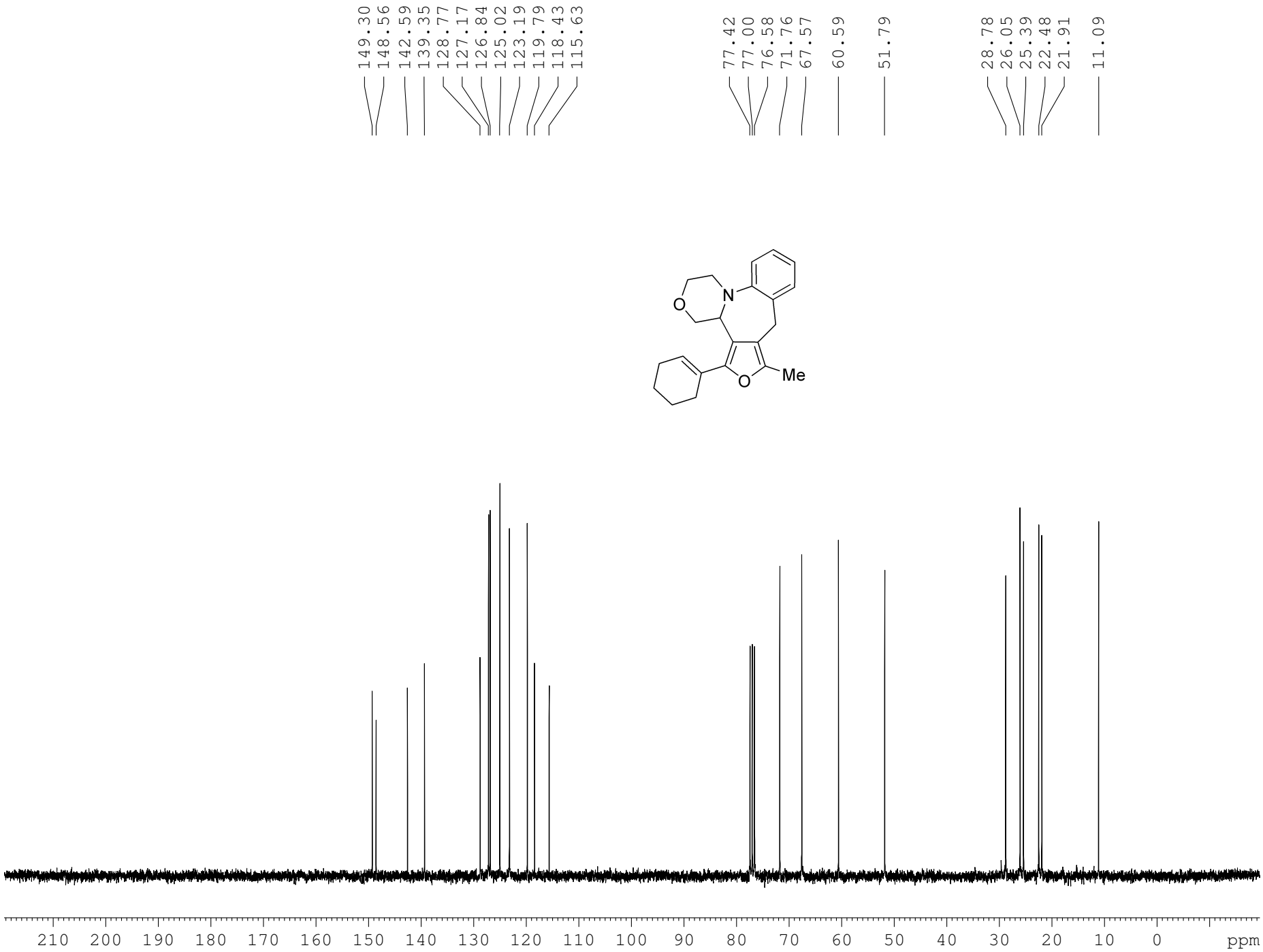
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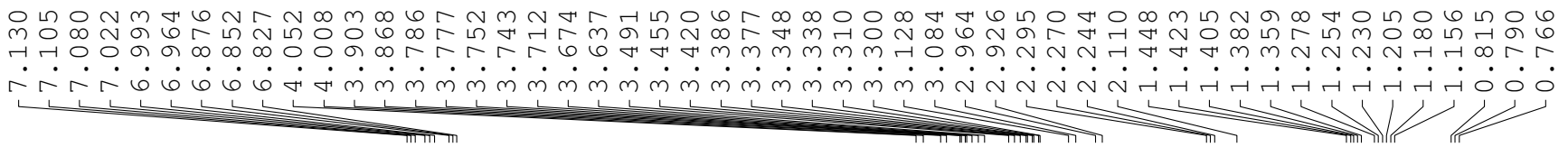
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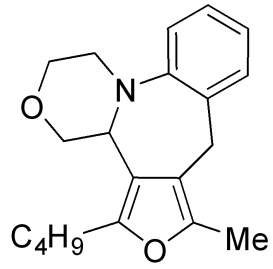
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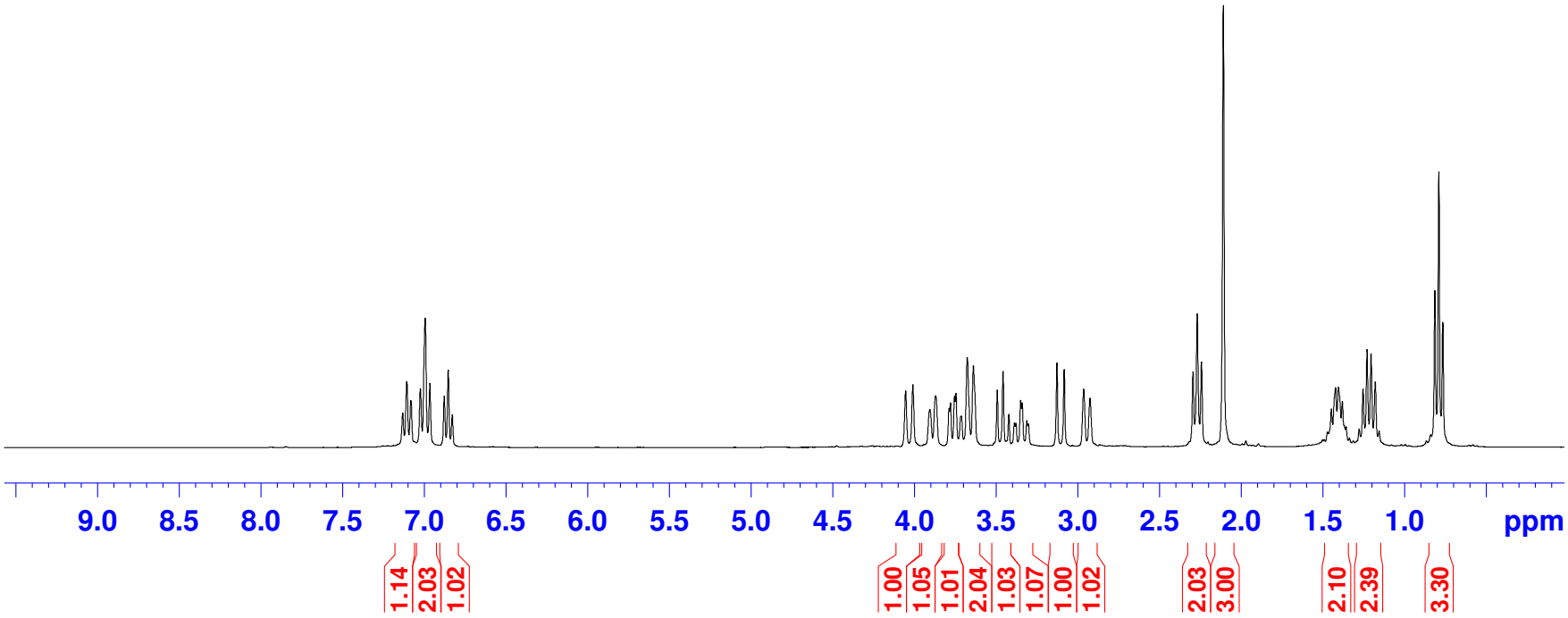
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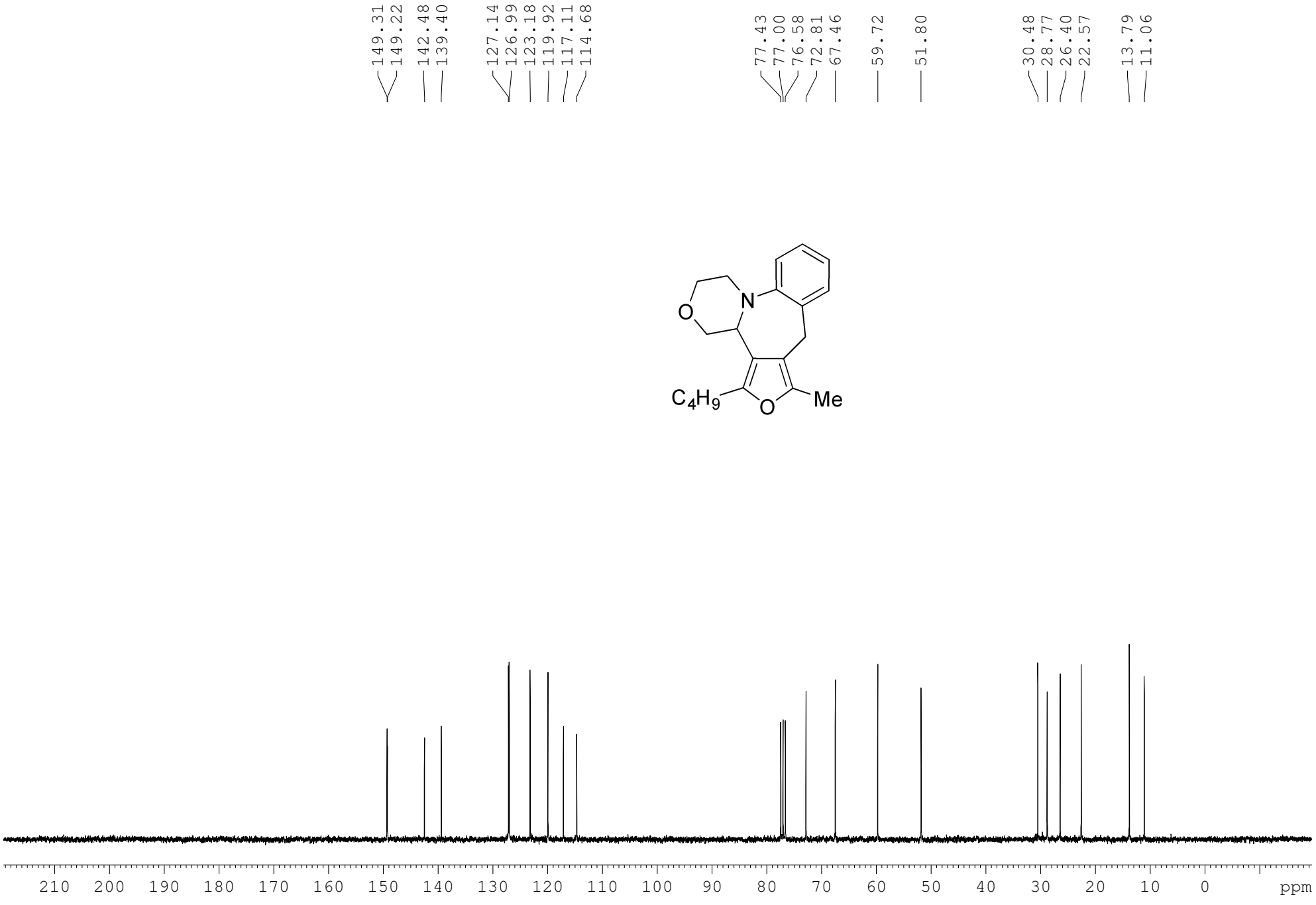
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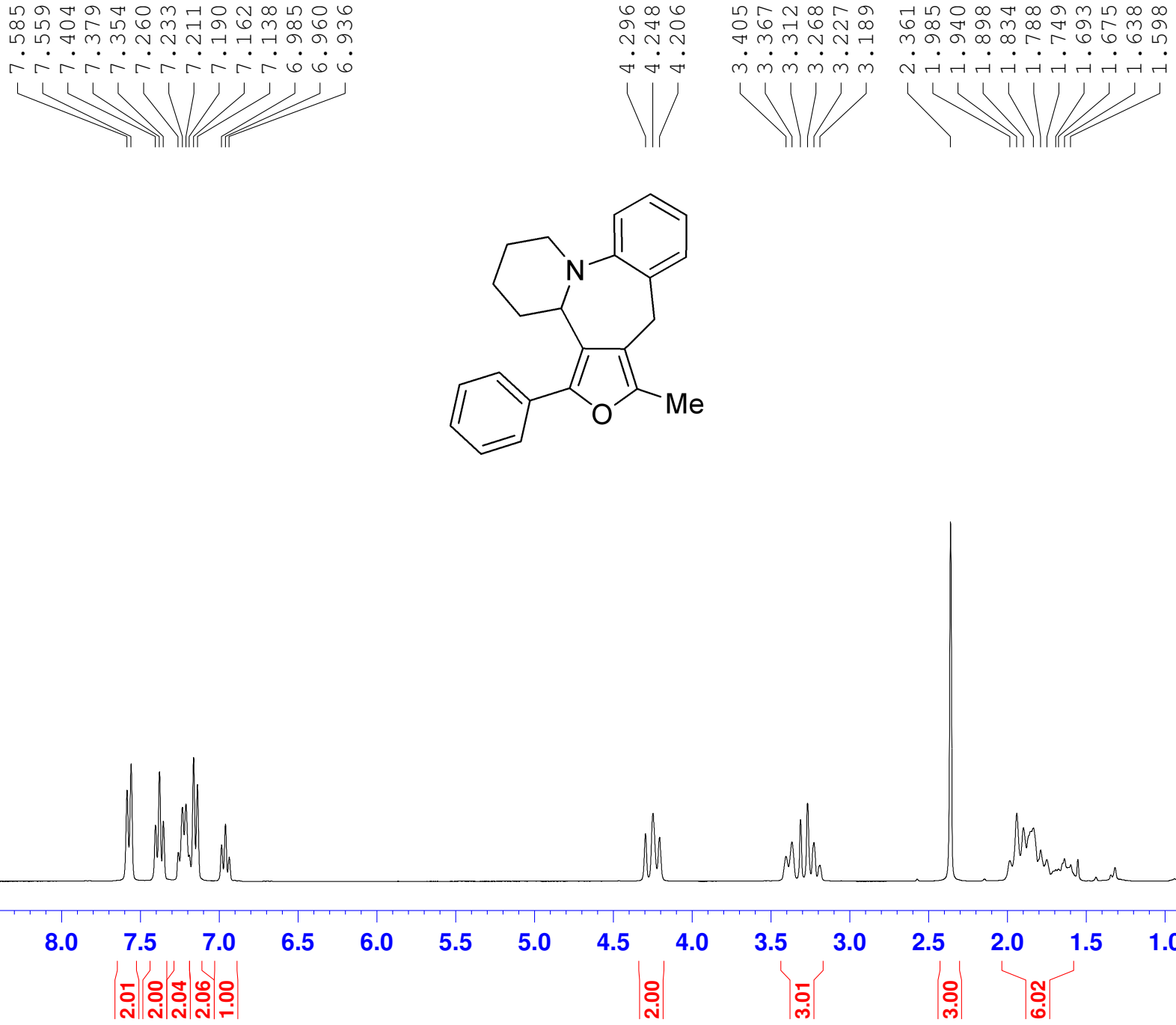
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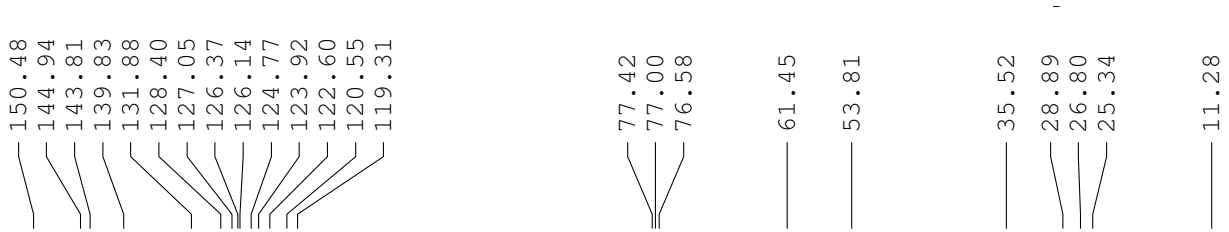
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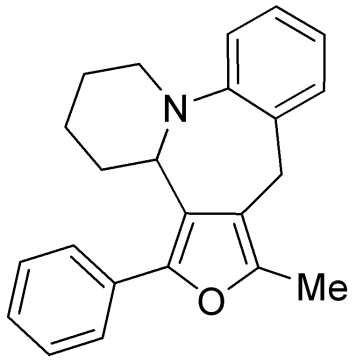
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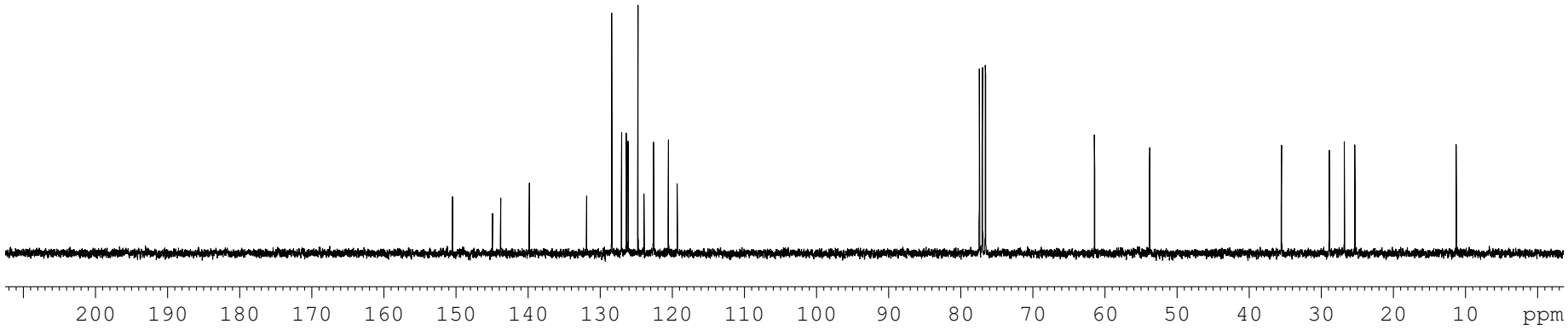
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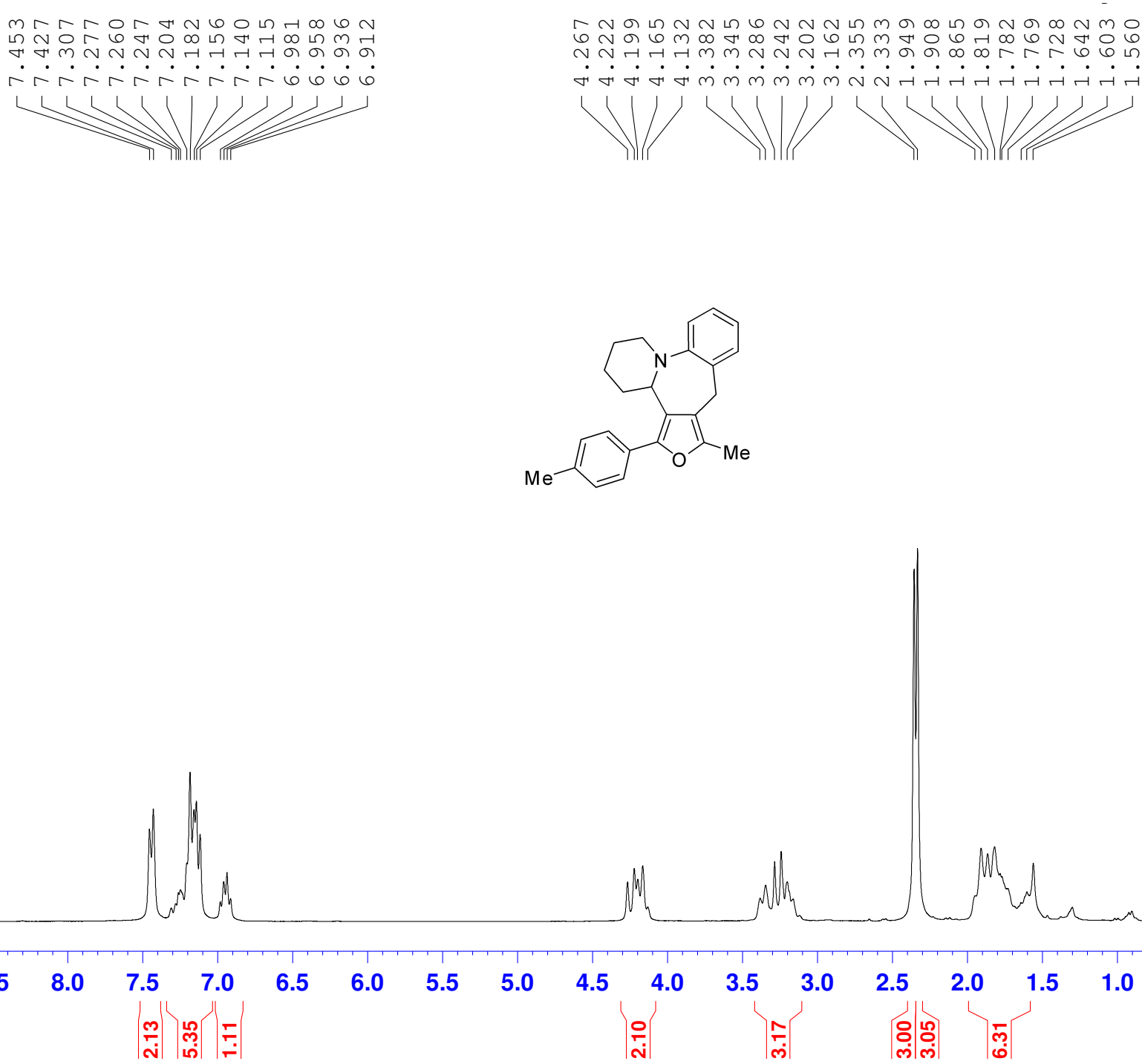
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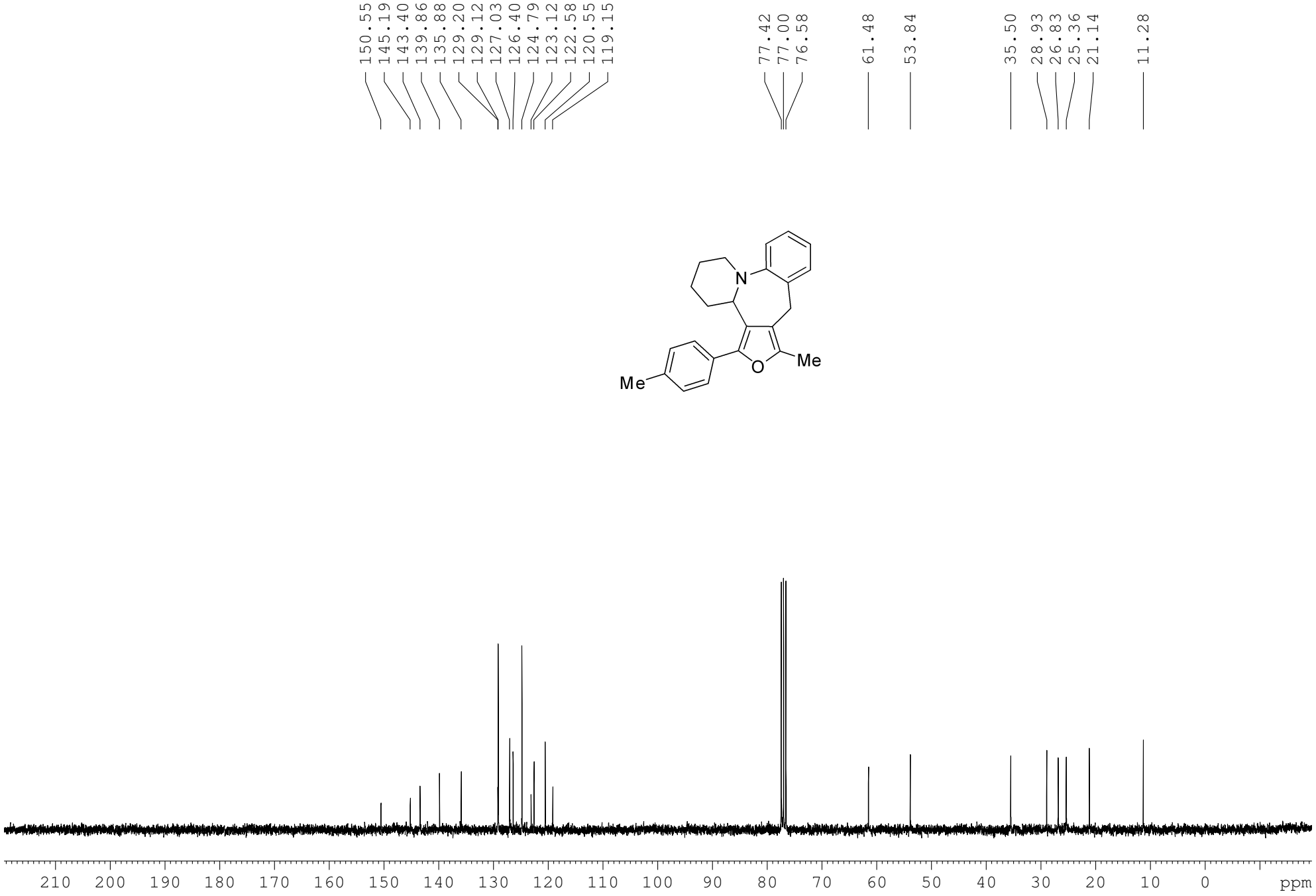
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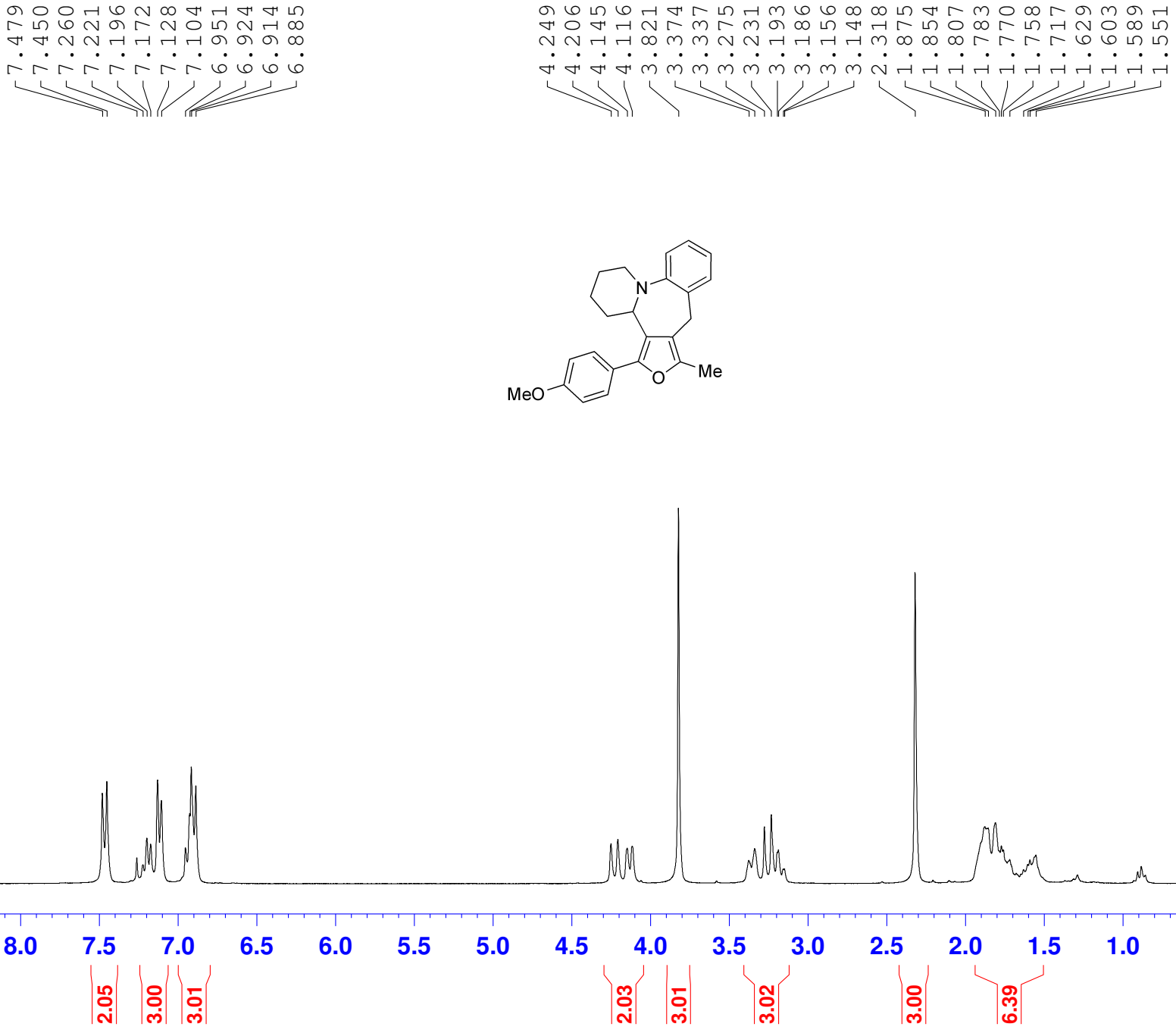
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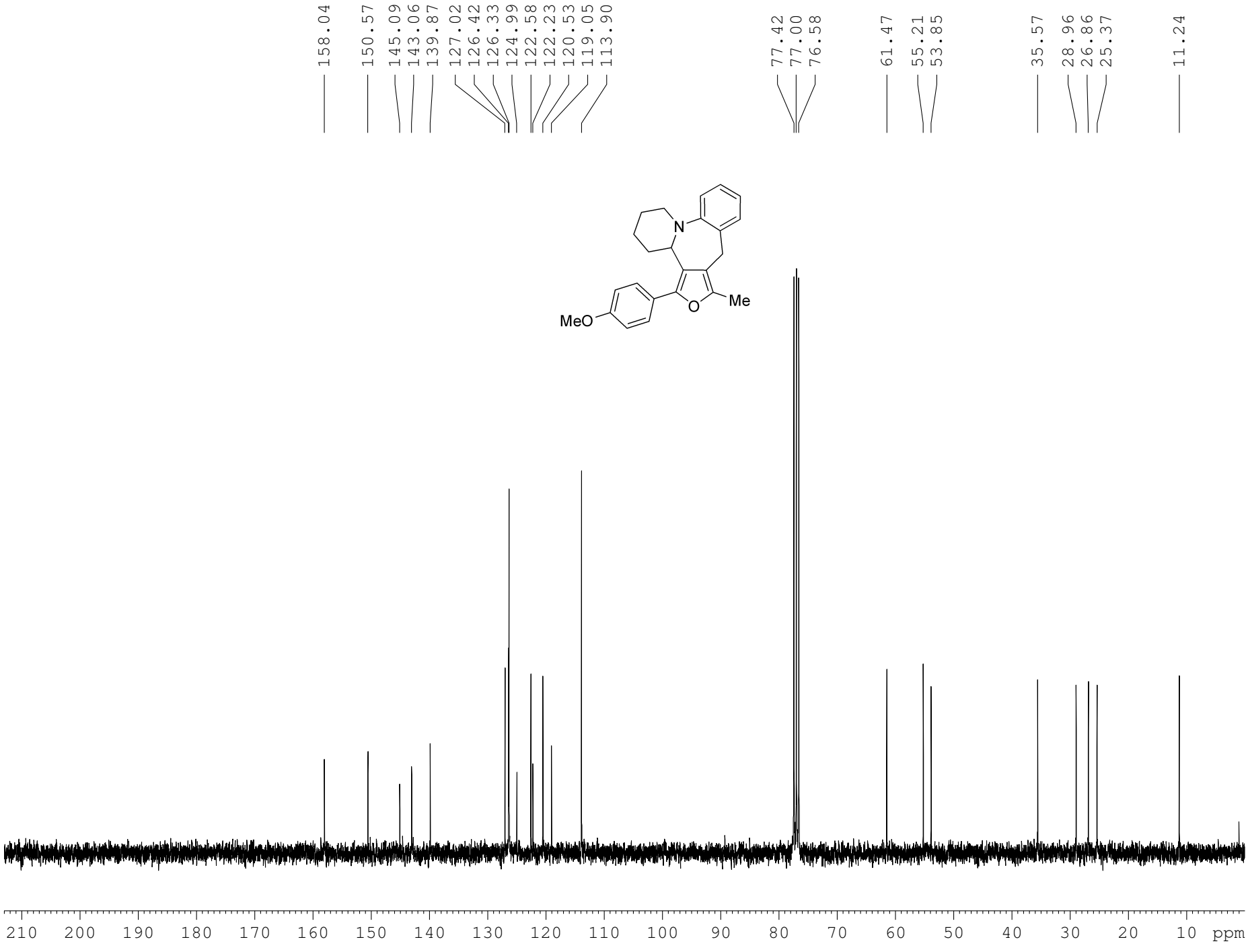
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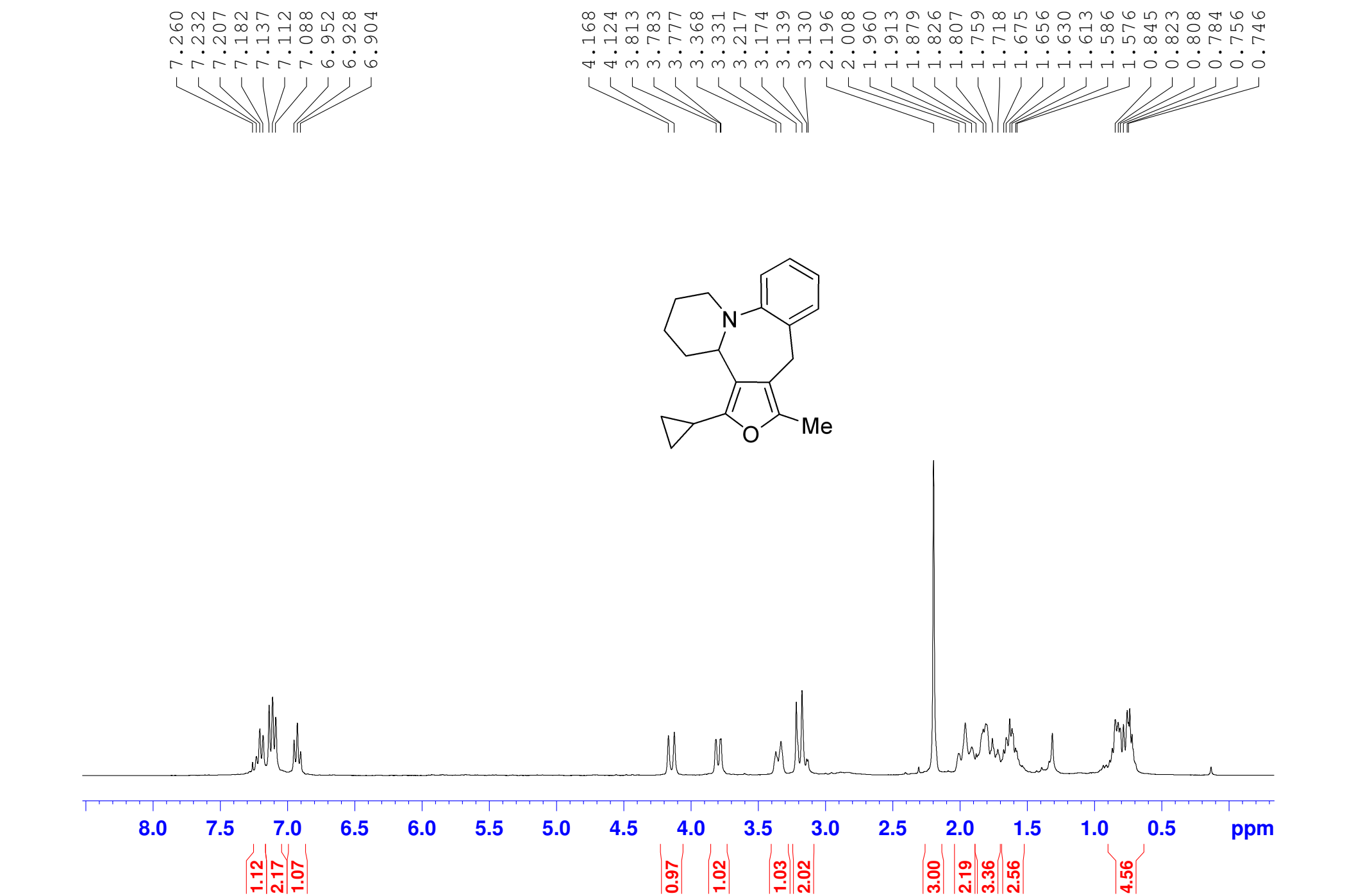
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7.182
7.137
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3.777
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3.217
3.174
3.139
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O
Me
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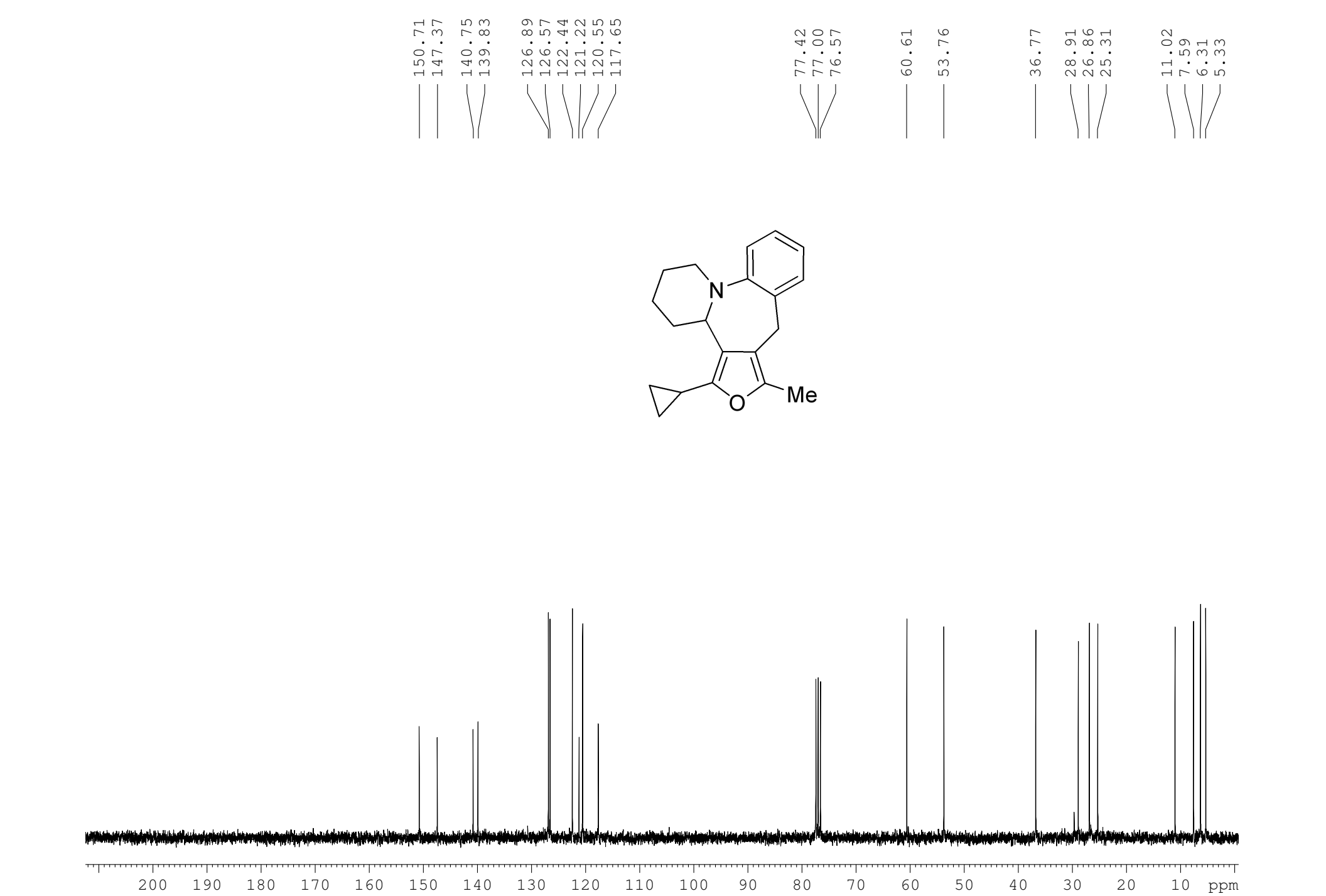
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76.57
60.61
53.76
36.77
28.91
26.86
25.31
11.02
7.59
6.31
5.33
N
O
Me
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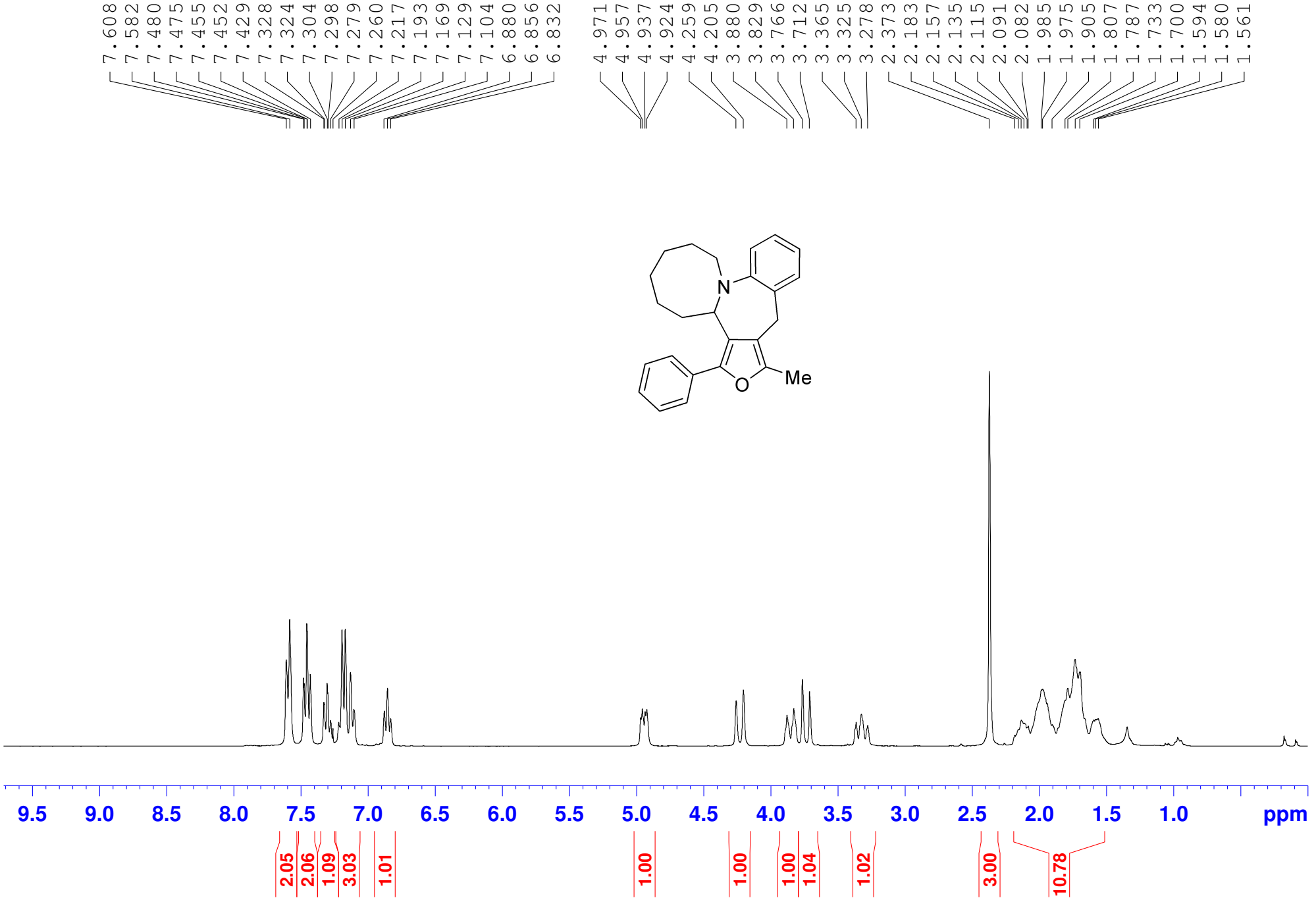
ppm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7.217
7.193
7.169
7.129
7.104
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6.856
6.832
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4.957
4.937
4.924
4.259
4.205
3.880
3.829
3.766
3.712
3.365
3.325
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2.373
2.183
2.157
2.135
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2.091
2.082
1.985
1.975
1.905
1.807
1.787
1.733
1.700
1.594
1.580
1.561
N
O
Me
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7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.05
2.06
1.09
3.03
1.01
1.00
1.00
1.00
1.04
1.02
3.00
10.78

zgh-03-60-1 C

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145.10
144.50
131.83
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130.08
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124.19
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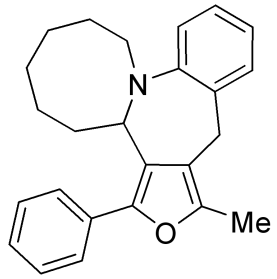
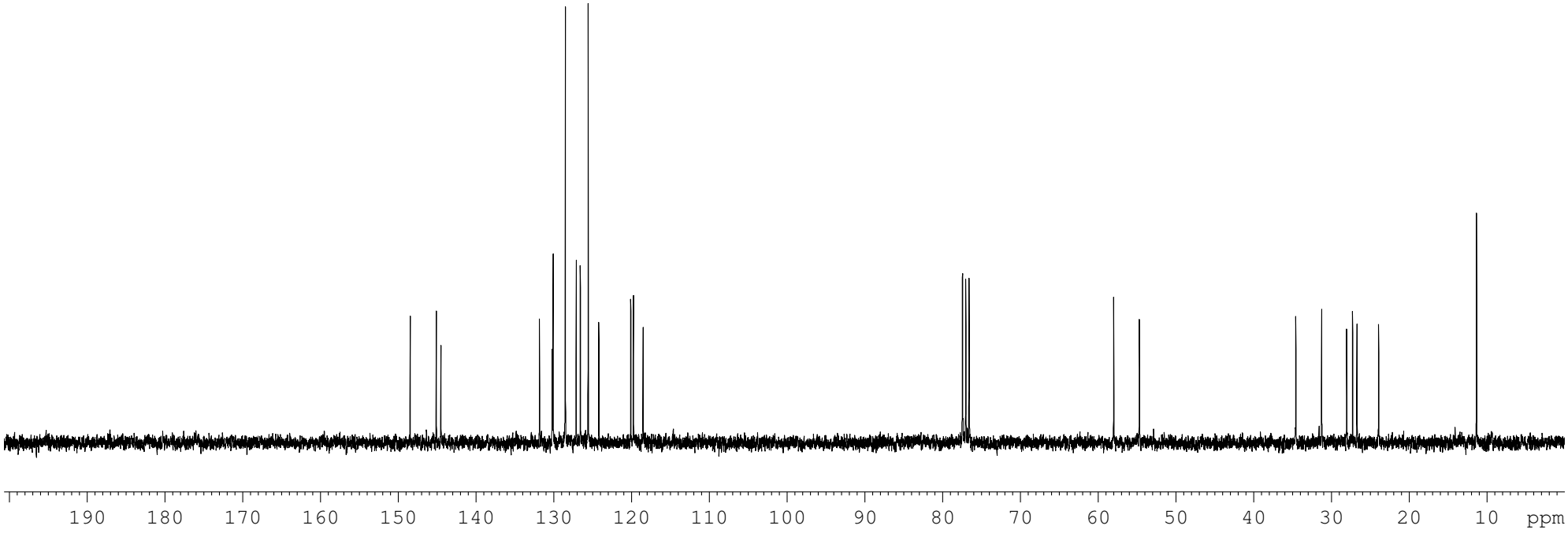
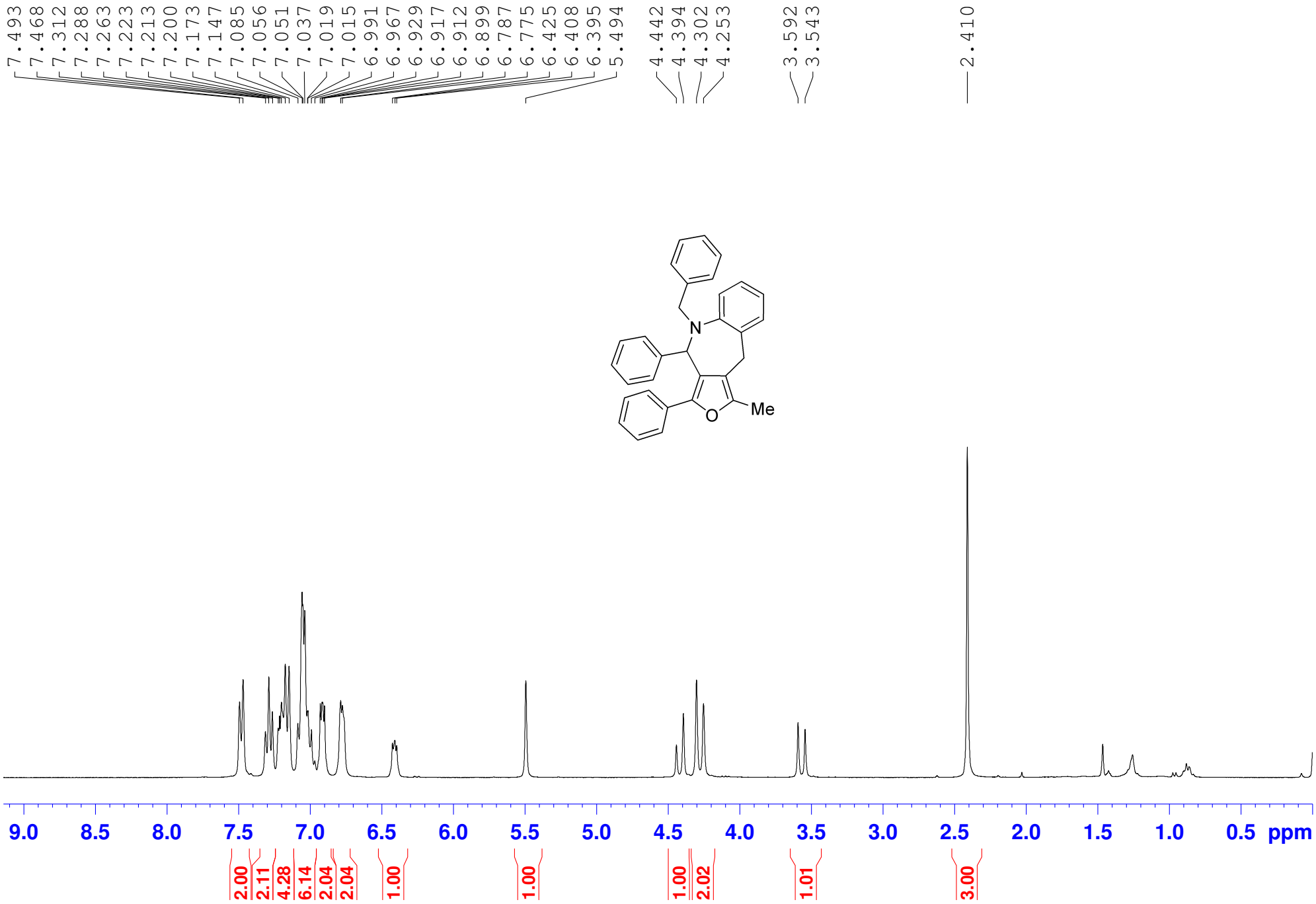
11.31



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7.051
7.037
7.019
7.015
6.991
6.967
6.929
6.917
6.912
6.899
6.787
6.775
6.425
6.408
6.395
5.494
4.442
4.394
4.302
4.253
3.592
3.543
2.410
N
O
Me
9.0
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8.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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2.04
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1.00
1.00
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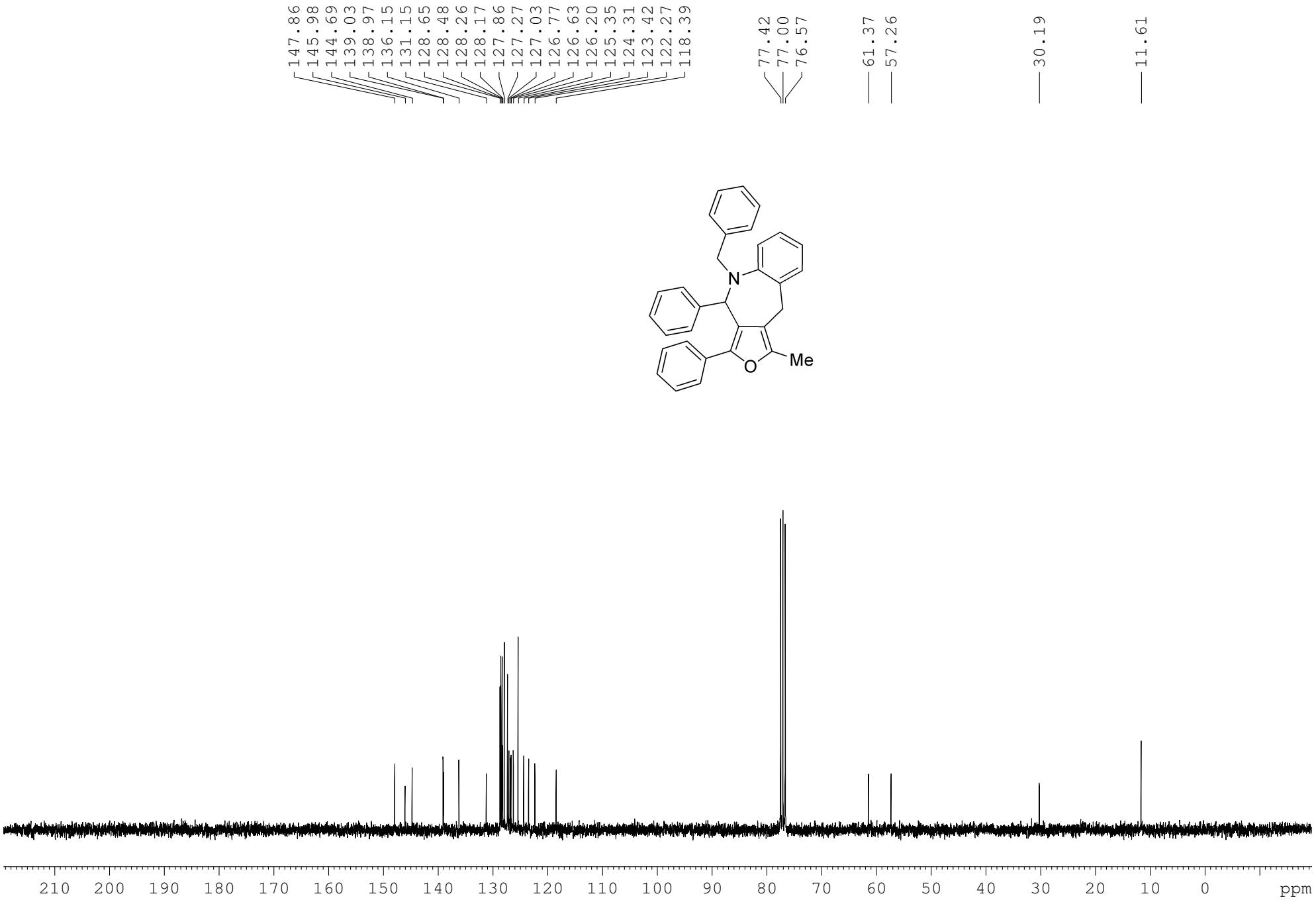
1.01
3.00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127.03
126.77
126.63
126.20
125.35
124.31
123.42
122.27
118.39
77.42
77.00
76.57
61.37
57.26
30.19
11.61
N
O
Me
210
200
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140
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120
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100
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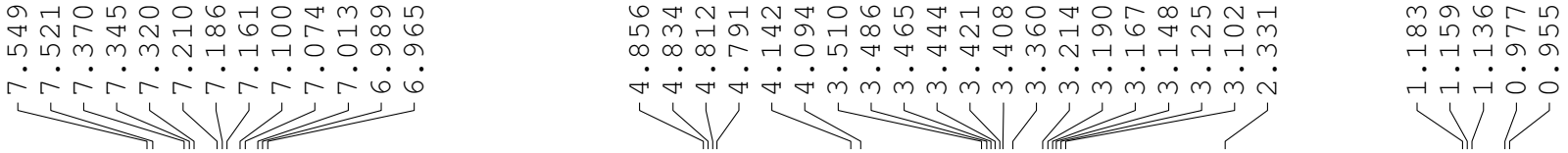
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6.965
4.856
4.834
4.812
4.791
4.142
4.094
3.510
3.486
3.465
3.444
3.421
3.408
3.360
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3.148
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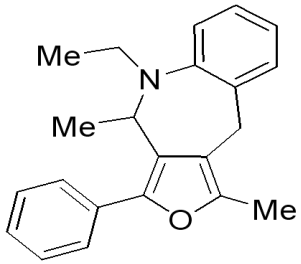
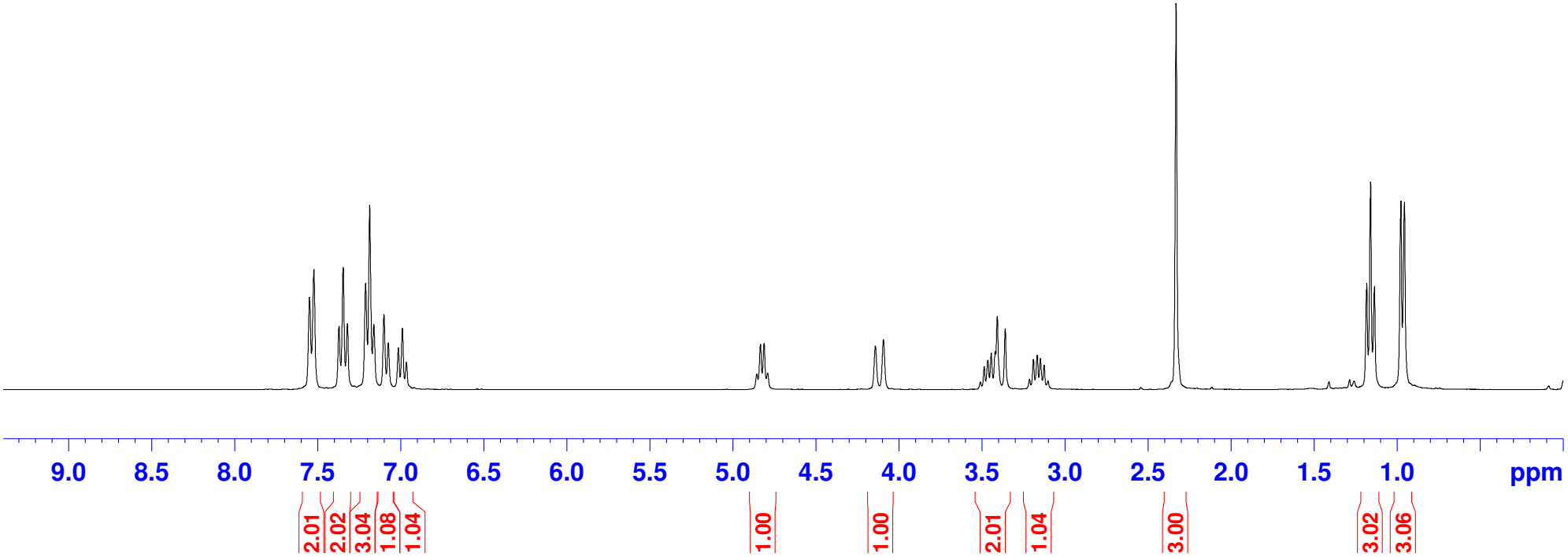

Me
N
Me
O
Me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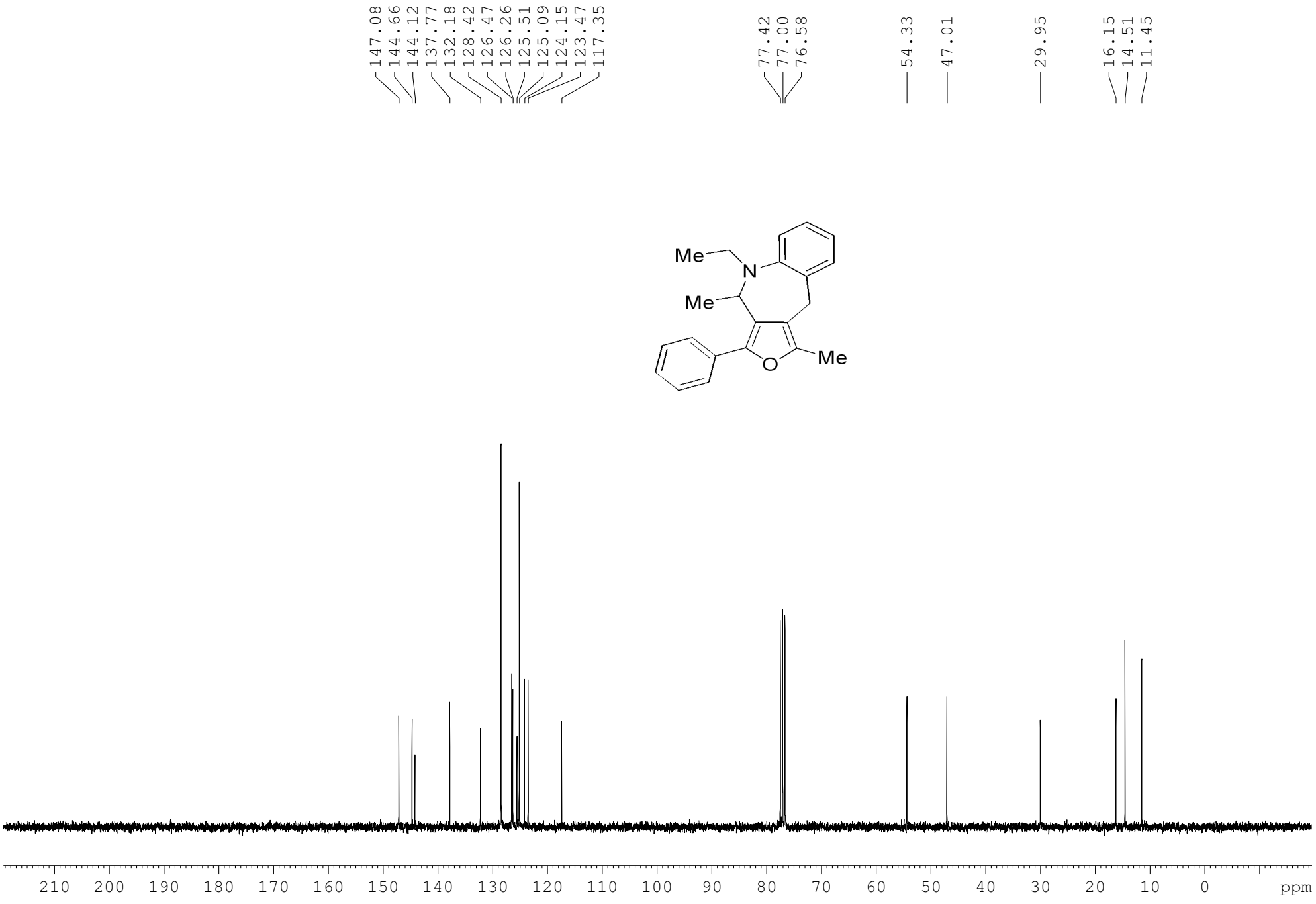
3.02
3.06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123.47
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77.42
77.00
76.58
54.33
47.01
29.95
16.15
14.51
11.45
Me
N
Me
O
Me
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200
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140
130
120
110
100
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80
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60
50
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20
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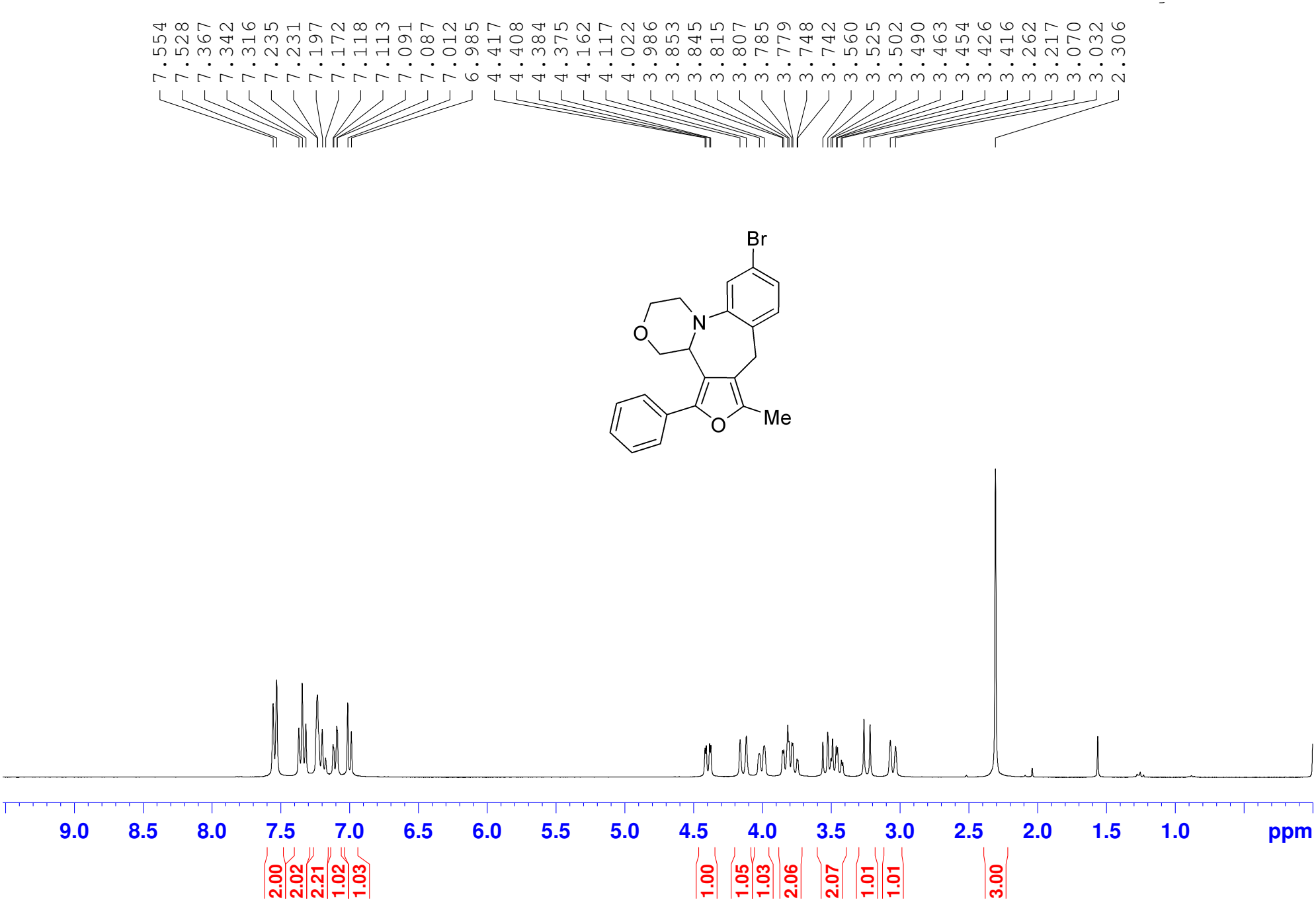
0
ppm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7.012
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4.408
4.384
4.375
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4.117
4.022
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3.853
3.845
3.815
3.807
3.785
3.779
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3.742
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3.525
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3.426
3.416
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3.032
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O
O
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6.5
6.0
5.5
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4.0
3.5
3.0
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2.0
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1.0
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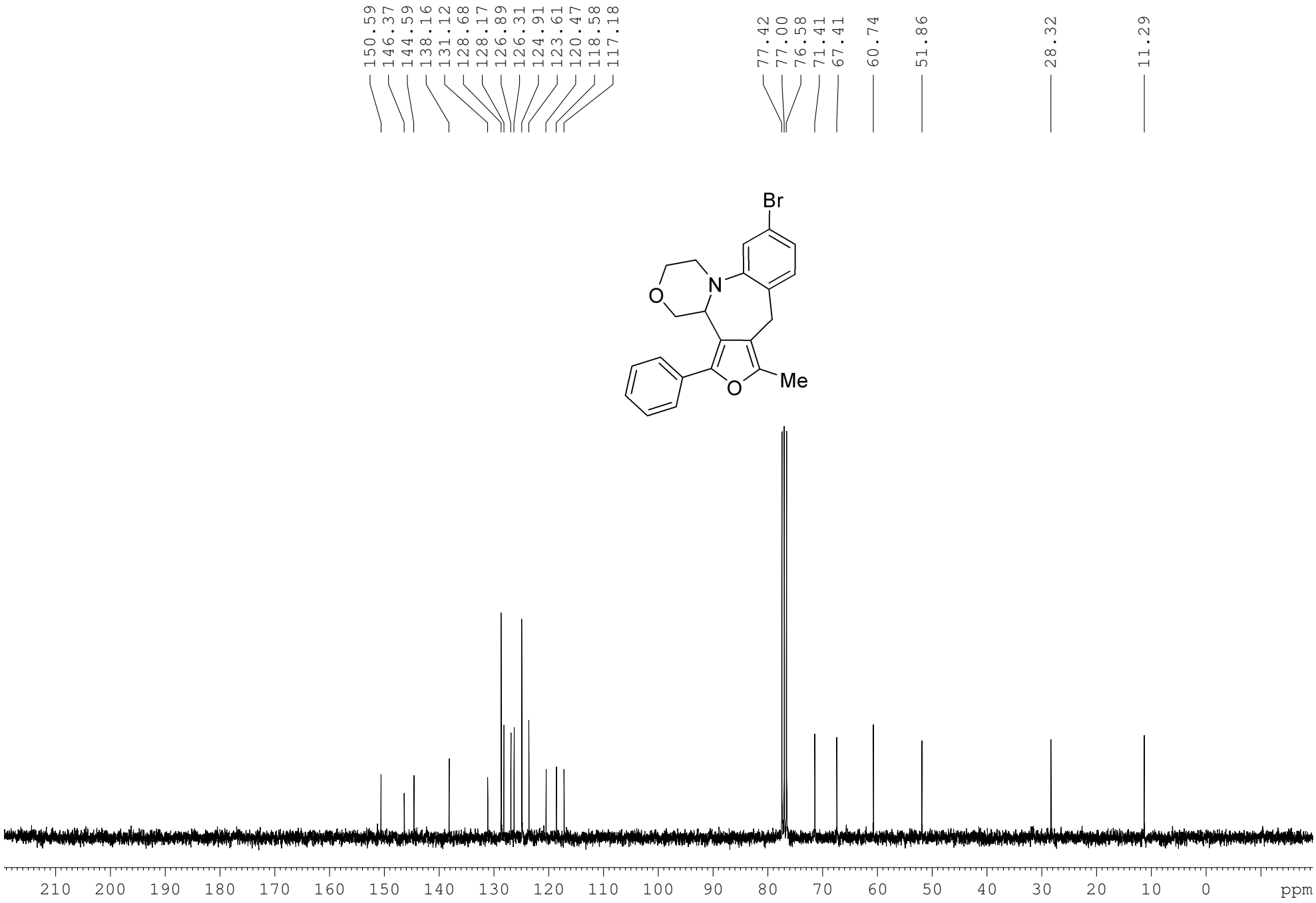
1.03
2.06
2.07
1.01
1.01
3.00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120.47
118.58
117.18
77.42
77.00
76.58
71.41
67.41
60.74
51.86
28.32
11.29
Br
N
O
O
Me
210
200
190
180
170
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140
130
120
110
100
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80
70
60
50
40
30
20
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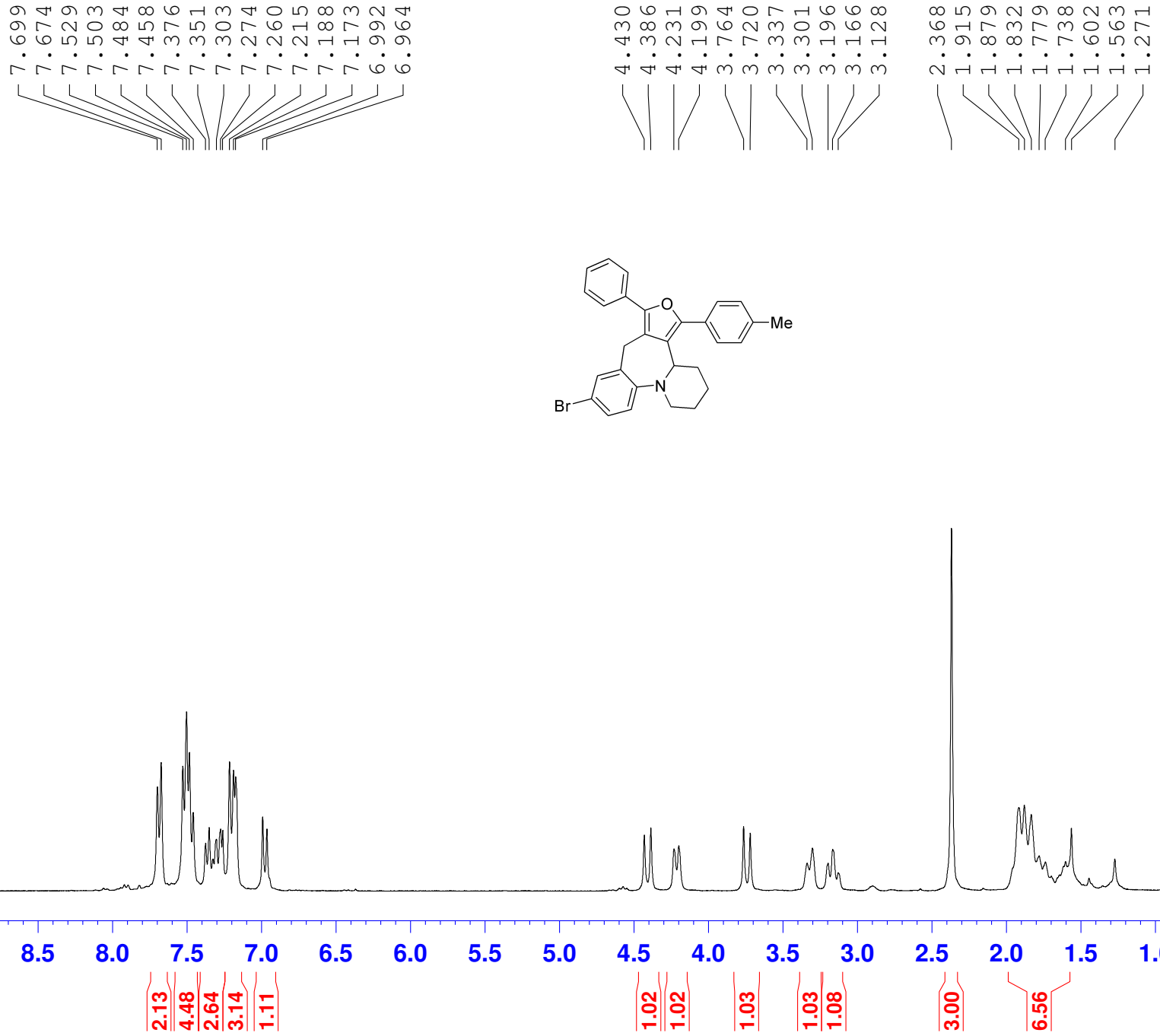
0
ppm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4.231
4.199
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3.301
3.196
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3.128
2.368
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1.879
1.832
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1.271
O
Me
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Br
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1.03
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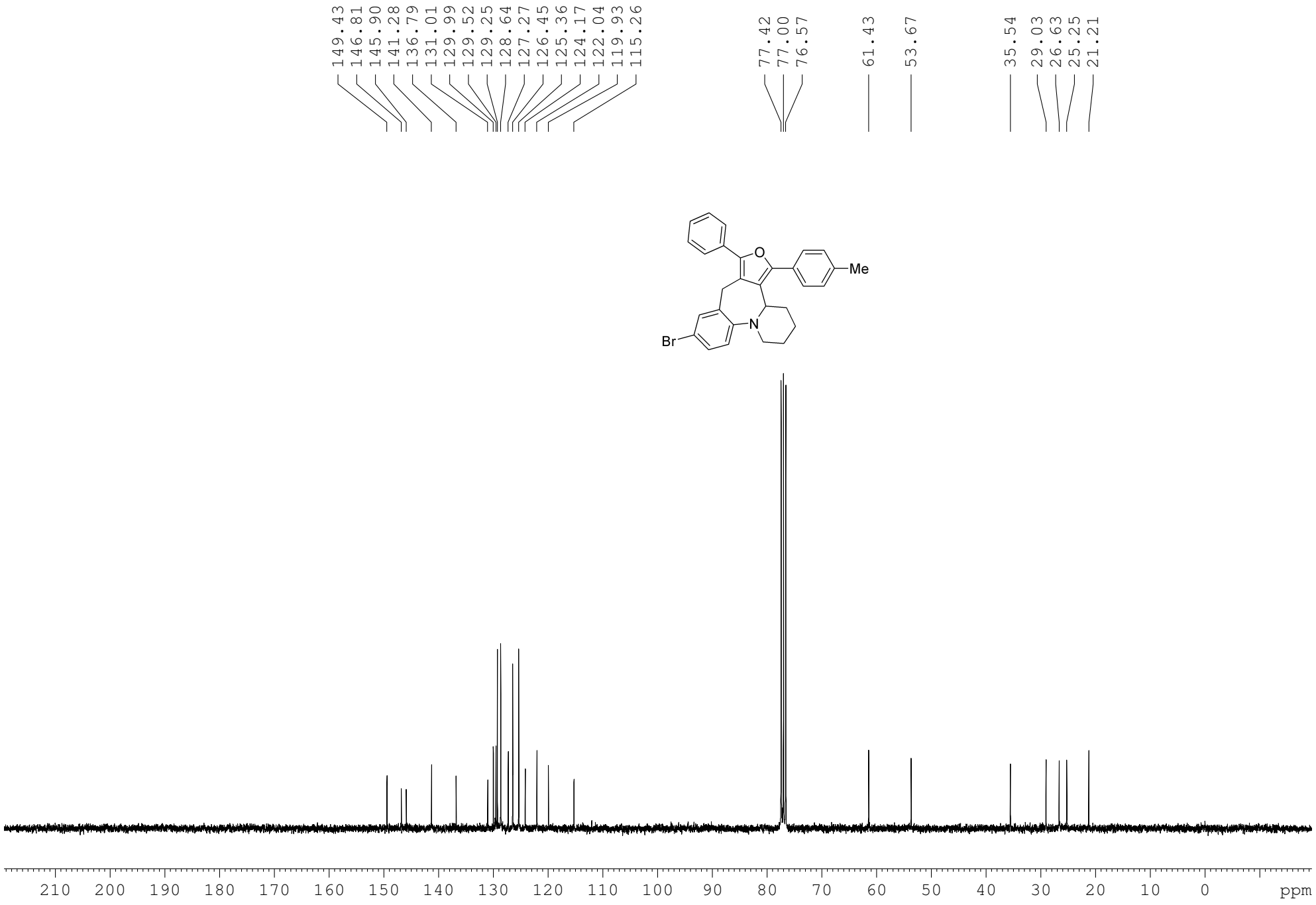
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127.27
126.45
125.36
124.17
122.04
119.93
115.26
77.42
77.00
76.57
61.43
53.67
35.54
29.03
26.63
25.25
21.21
O
Me
N
Br
210
200
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180
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140
130
120
110
100
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60
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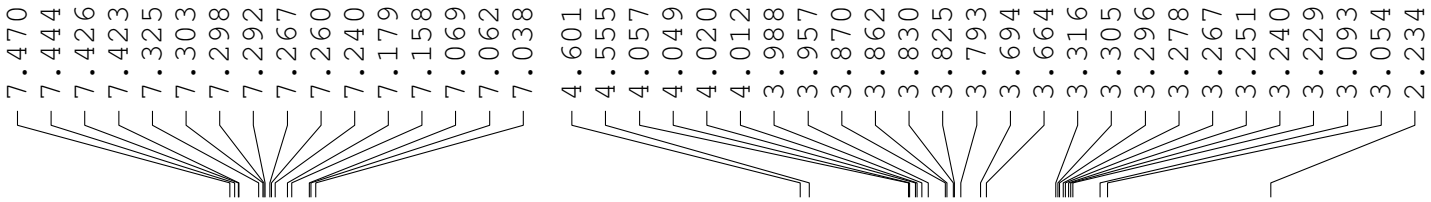
ppm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7.062
7.038
4.601
4.555
4.057
4.049
4.020
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3.957
3.870
3.862
3.830
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3.240
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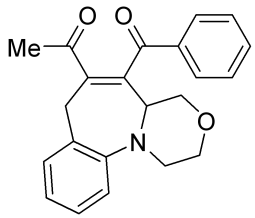
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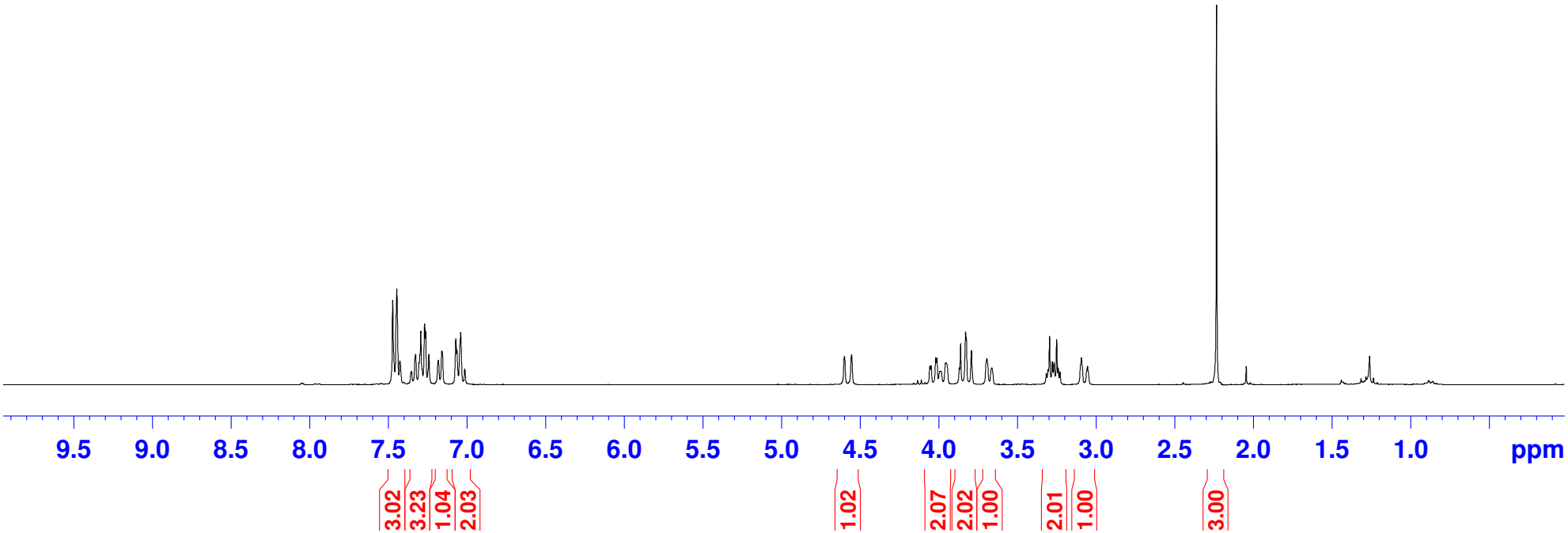
O
N
O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4.0
3.5
3.0
2.5
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1.5
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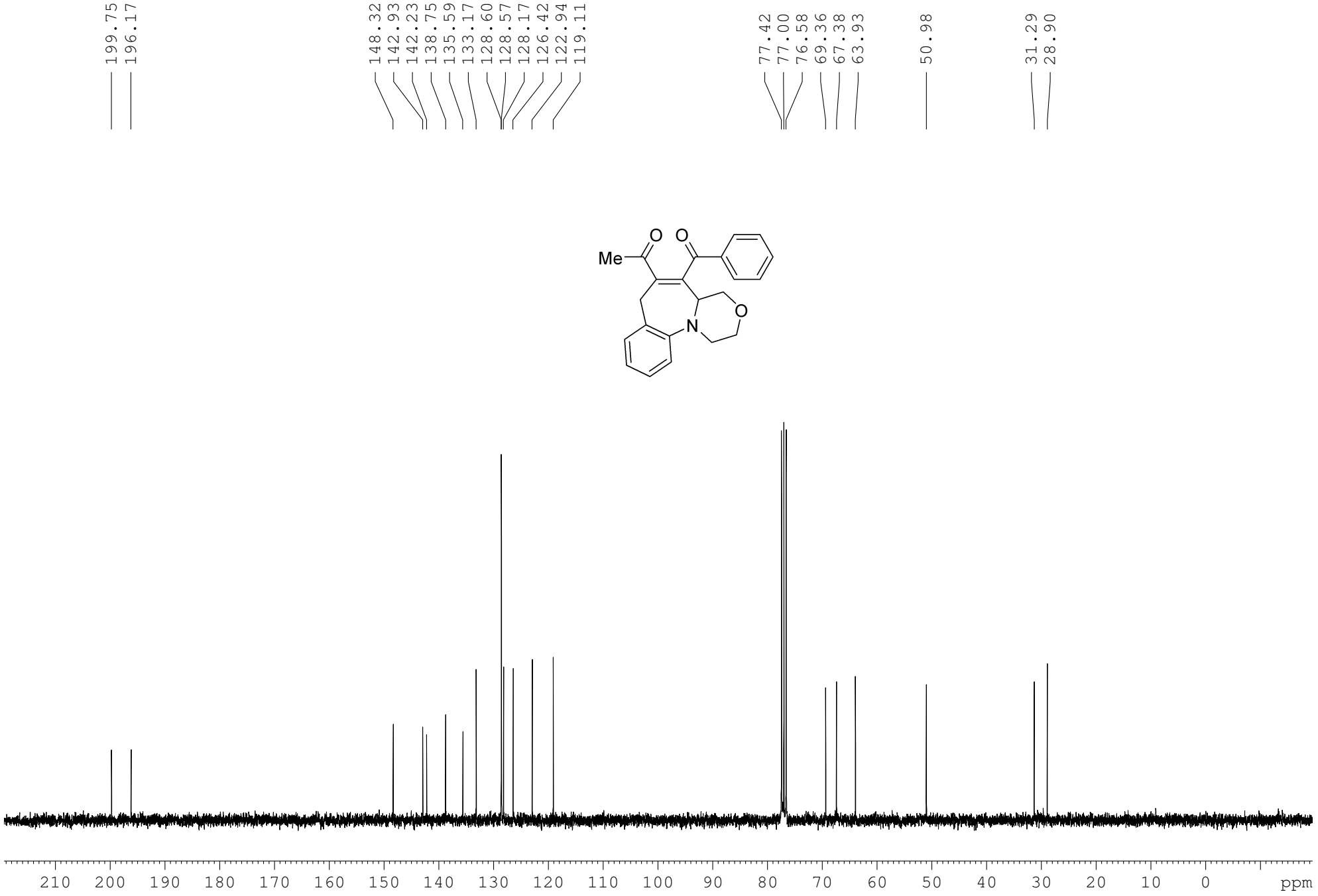
2.03
1.02
2.07
2.02
1.00
2.01
1.00
3.00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138.75
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133.17
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128.17
126.42
122.94
119.11
77.42
77.00
76.58
69.36
67.38
63.93
50.98
31.29
28.90
Me
O
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm