

Efficient and Selective α -Bromination of Carbonyl Compounds with N-Bromosuccinimide under Microwave

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Supporting Information

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¹ H-NMR and ¹³ C-NMR data	S3

Supporting Information

General Information:

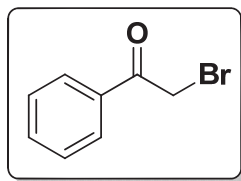
All solvents were purified by standard method. All ¹H NMR, and ¹³C NMR spectra were recorded using a Bruker AVIII 400 or AVIII 500 spectrometer in CDCl₃ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (δ = 0) for ¹H NMR, and CDCl₃ was used as internal standard (δ = 77.0) for ¹³C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). The NMR data were processed using the topspin program version 2.1. The α -bromination of carbonyl compounds with N-bromosuccinimide were performed in a CEM Matthews WC Discover microwave reactor (model no. 908010 DV9068 equipped with programmable pressure and temperature controller). Solvents were freshly dried and degassed according to the purification handbook "Purification of Laboratory Chemicals" before using. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

Experimental Section:**General Prodedure for the Microwave Promoted α -Bromination of Carbonyl Compounds with NBS Catalyzed by PTSA**

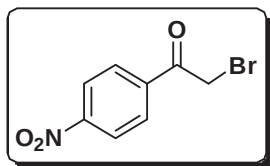
In a dry 10 mL flask with a Teflon stirring bar were introduced 0.2 mmol of the desired carbonyl compounds, NBS (0.2 mmol, 1 equiv), PTSA (0.02 mmol, 10 mol%). Anhydrous DCM (2 mL) was added, the flask was sealed and the mixture was stirred and irradiated at the corresponding temperature. After 30 min, the reaction mixture was treated with 10 mL of distilled water, extracted with 3*10 mL of CH₂Cl₂, dried over MgSO₄, and purified by flash chromatography to give the corresponding product.

General Prodedure for the α -Bromination of Carbonyl Compounds with NBS Catalyzed by PTSA Under Thermal condition.

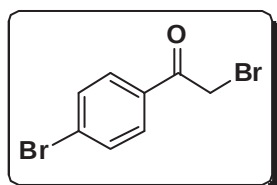
In a dry 10 mL flask with a Teflon stirring bar were introduced 0.2 mmol of the desired carbonyl compounds, NBS (0.2 mmol, 1 equiv), PTSA (0.02 mmol, 10 mol%). Anhydrous DCM (2 mL) was added, the flask was sealed and the mixture was stirred using thermostated oil-bath at the corresponding temperature. After 30 min, the reaction mixture was treated with 10 mL of distilled water, extracted with 3*10 mL of CH₂Cl₂, dried over MgSO₄, and purified by flash chromatography to give the corresponding product.

2-bromo-1-phenylethanone (1b)

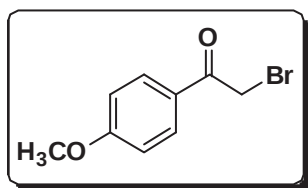
¹H NMR (500 MHz, CDCl₃) δ 4.46 (s, 2H), 7.47-7.51 (m, 2H), 7.59-7.72 (m, 1H), 7.97-7.99 (m, 2H). ¹³C NMR (125MHz, CDCl₃) δ 30.67, 128.51, 128.56, 133.52, 133.63, 190.93. HRMS (ESI) m/z 197.9680, calc.for [C₈H₇BrO] 197.9683.

2-bromo-1-(4-nitrophenyl)ethanone (2b)

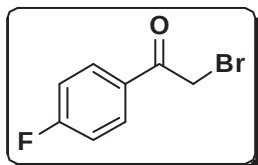
¹H NMR (500 MHz, CDCl₃) δ 4.46 (s, 2H), 8.15-8.17 (m, 2H), 8.34-8.35 (m, 2H). ¹³C NMR (125MHz, CDCl₃) δ 29.77, 123.69, 129.72, 137.94, 150.29, 189.52. HRMS (ESI) m/z 242.9531, calc.for [C₈H₆BrNO₃] 242.9536.

2-bromo-1-(4-bromophenyl)ethanone(3b)

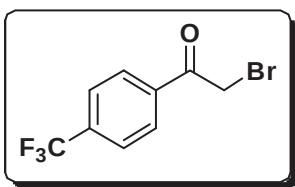
¹H NMR (500 MHz, CDCl₃) δ 4.40 (s, 2H), 7.63-7.65 (m, 2H), 7.84-7.86 (m, 2H). ¹³C NMR (125MHz, CDCl₃) δ 30.01, 128.97, 130.06, 131.86, 132.21, 190.07. HRMS (ESI) m/z 275.8785, calc.for [C₈H₆Br₂O] 275.8783.

2-bromo-1-(4-methoxyphenyl)ethanone (4b)

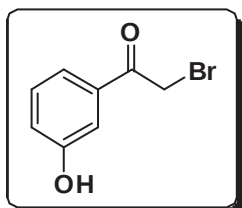
^1H NMR (500 MHz, CDCl_3) δ 3.88 (s, 3H), 4.40 (s, 2H), 6.94-6.96 (m, 2H), 7.96-7.97 (m, 2H). ^{13}C NMR (125MHz, CDCl_3) δ 30.38, 55.21, 113.68, 126.48, 131.00, 163.74, 189.61. HRMS (ESI) m/z 227.9786, calc. for $[\text{C}_9\text{H}_9\text{BrO}_2]$ 227.9790.

2-bromo-1-(4-fluorophenyl)ethanone (5b)

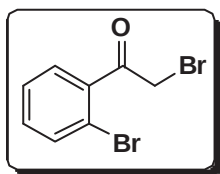
^1H NMR (500 MHz, CDCl_3) δ 4.41 (s, 2H), 7.14-7.18 (m, 2H), 8.00-8.03 (m, 2H). ^{13}C NMR (125MHz, CDCl_3) δ 30.13, 115.65, 115.83, 129.90, 129.92, 131.33, 131.40, 164.74, 166.78, 189.48. ^{19}F NMR (376MHz, CDCl_3) δ -103.19. HRMS (ESI) m/z 215.9589, calc. for $[\text{C}_8\text{H}_6\text{BrFO}]$ 215.9589.

2-bromo-1-(4-(trifluoromethyl)phenyl)ethanone (6b)

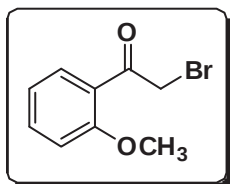
^1H NMR (500 MHz, CDCl_3) δ 4.40 (s, 2H), 7.70-7.72 (m, 2H), 8.04-8.05 (m, 2H). ^{13}C NMR (125MHz, CDCl_3) δ 30.00, 30.02, 121.91, 124.08, 125.55, 125.58, 128.96, 134.61, 134.87, 136.15, 190.05. ^{19}F NMR (376MHz, CDCl_3) δ -63.29. HRMS (ESI) m/z 265.9554, calc. for $[\text{C}_9\text{H}_6\text{BrF}_3\text{O}]$ 265.9559.

2-bromo-1-(3-hydroxyphenyl)ethanone (7b)

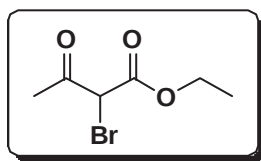
^1H NMR (500 MHz, CDCl_3) δ 4.46 (s, 2H), 6.11 (s, 1H), 7.12-7.14 (m, 1H), 7.35-7.38 (m, 1H), 7.52-7.53 (m, 2H). ^{13}C NMR (125MHz, CDCl_3) δ 30.83, 114.88, 121.09, 121.19, 129.82, 134.81, 155.92, 191.28. HRMS (ESI) m/z 213.9629, calc. for $[\text{C}_8\text{H}_7\text{BrO}_2]$ 213.9635.

2-bromo-1-(2-bromophenyl)ethanone (8b)

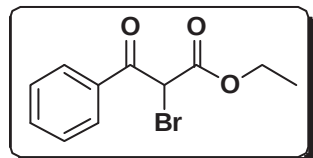
^1H NMR (500 MHz, CDCl_3) δ 4.49 (s, 2H), 7.35-7.37 (m, 1H), 7.39-7.42 (m, 1H), 7.46-7.48 (m, 1H), 7.62-7.64 (m, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 33.59, 118.72, 127.22, 129.36, 132.17, 133.34, 138.18, 194.58. HRMS (ESI) m/z 275.8785, calc. for $[\text{C}_8\text{H}_6\text{Br}_2\text{O}]$ 275.8788.

2-bromo-1-(2-methoxyphenyl)ethanone (9b)

^1H NMR (500 MHz, CDCl_3) δ 3.91 (s, 3H), 4.38 (s, 2H), 6.95-7.02 (m, 2H), 7.47-7.51 (m, 1H), 7.79-7.82 (m, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 37.46, 55.36, 111.20, 120.67, 124.39, 131.16, 134.43, 158.40, 191.92. HRMS (ESI) m/z 227.9786, calc. for $[\text{C}_9\text{H}_9\text{BrO}_2]$ 227.9792.

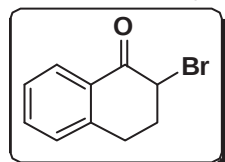
ethyl 2-bromo-3-oxobutanoate (10b)

^1H NMR (500 MHz, CDCl_3) δ 1.29-1.32 (t, J = 7.1 Hz, 3H), 2.34 (s, 2H), 4.26-4.30 (q, J = 7.1 Hz, 2H), 4.75 (s, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 13.53, 26.08, 48.74, 62.85, 164.78, 196.08. HRMS (ESI) m/z 207.9735, calc.for $[\text{C}_6\text{H}_9\text{BrO}_3]$ 207.9738.

ethyl 2-bromo-3-oxo-3-phenylpropanoate (11b)

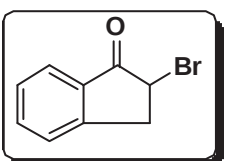
^1H NMR (500 MHz, CDCl_3) δ 1.23-1.26 (t, J = 7.1 Hz, 3H), 4.26-4.30 (q, J = 7.1 Hz, 2H), 5.65 (s, 1H), 7.48-7.51 (m, 2H), 7.61-7.62 (m, 1H), 7.98-8.00 (m, 2H). ^{13}C NMR (125MHz, CDCl_3) δ 13.51, 45.96, 62.97, 128.55, 128.83, 132.93, 133.94,

164.81, 187.75. HRMS (ESI) m/z 269.9892, calc.for $[\text{C}_{11}\text{H}_{11}\text{BrO}_3]$ 269.9896.

2-bromo-3,4-dihydronaphthalen-1(2H)-one (12b)

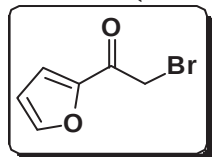
^1H NMR (500 MHz, CDCl_3) δ 2.45-2.54(m, 2H), 2.90-2.94 (m, 1H), 3.28-3.35(m, 1H), 4.73 (s, 1H), 7.27-7.29 (m, 1H), 7.34-7.37 (m, 1H), 7.51-7.54 (m, 1H), 8.08-8.10 (m, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 25.72, 31.50, 50.06, 126.75, 128.30, 128.39, 129.51, 133.78, 142.62, 190.26

HRMS (ESI) m/z 223.9837, calc.for $[\text{C}_{10}\text{H}_9\text{BrO}]$ 223.9843.

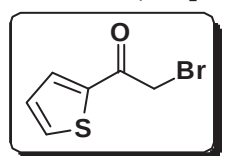
2-bromo-2,3-dihydro-1H-inden-1-one (13b)

^1H NMR (500 MHz, CDCl_3) δ 3.40-3.44(dd, J = 2.8, 18 Hz, 1H), 3.81-3.86(dd, J = 7.6, 18 Hz, 1H), 4.64-4.66 (m, 1H), 7.41-7.45 (m, 2H), 7.65-7.68 (m, 1H), 7.83-7.84 (m, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 37.59, 43.70, 124.72, 126.07, 127.93, 133.16, 135.63, 150.77, 199.32.

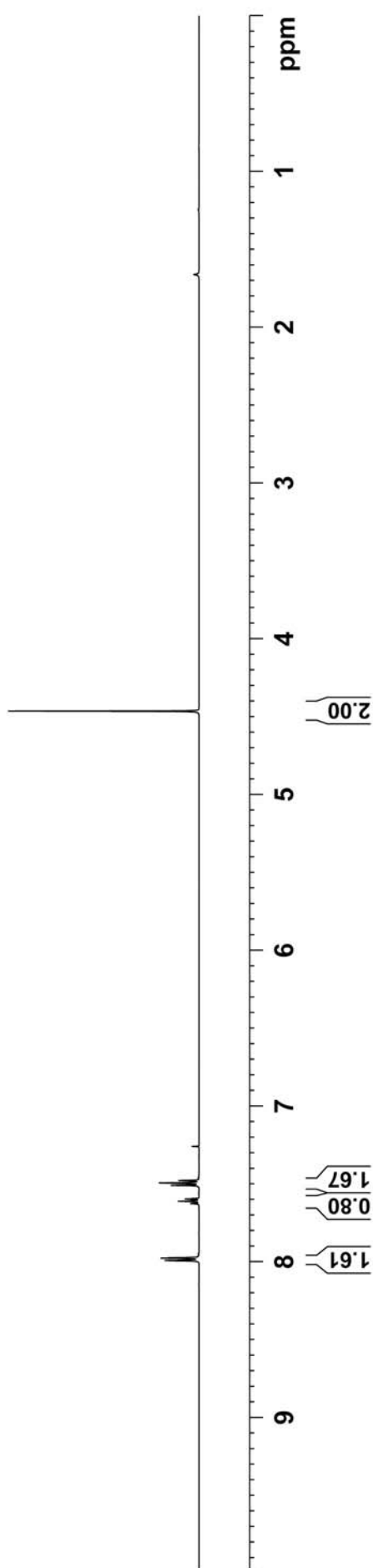
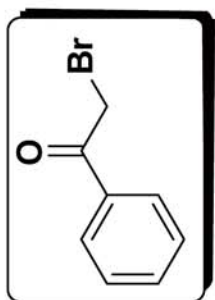
HRMS (ESI) m/z 209.9680, calc.for $[\text{C}_9\text{H}_7\text{BrO}]$ 209.9685.

2-bromo-1-(furan-2-yl)ethanone (14b)

^1H NMR (500 MHz, CDCl_3) δ 4.32 (s, 2H), 6.59-6.60 (m, 1H), 7.33-7.34 (m, 1H), 7.64 (s, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 30.07, 112.91, 119.20, 147.34, 150.33, 180.40. HRMS (ESI) m/z 187.9473, calc.for $[\text{C}_6\text{H}_5\text{BrO}_2]$ 187.9476.

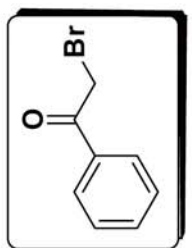
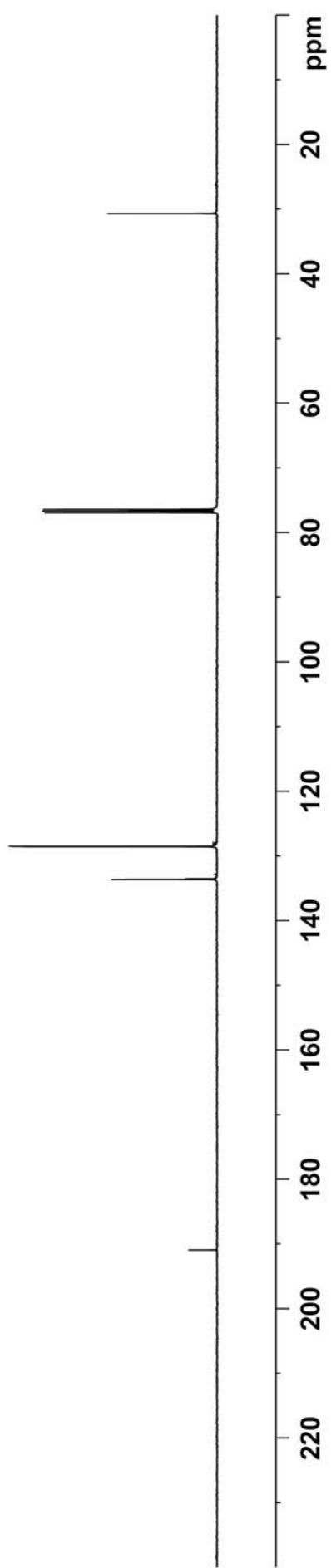
2-bromo-1-(thiophen-2-yl)ethanone (15b)

^1H NMR (500 MHz, CDCl_3) δ 4.36 (s, 2H), 7.16-7.18 (m, 1H), 7.72-7.73 (m, 1H), 7.80-7.81 (m, 1H). ^{13}C NMR (125MHz, CDCl_3) δ 30.24, 128.05, 133.19, 134.93, 140.37, 184.07. HRMS (ESI) m/z 203.9244, calc.for $[\text{C}_6\text{H}_5\text{BrOS}]$ 203.9250.



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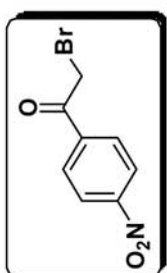
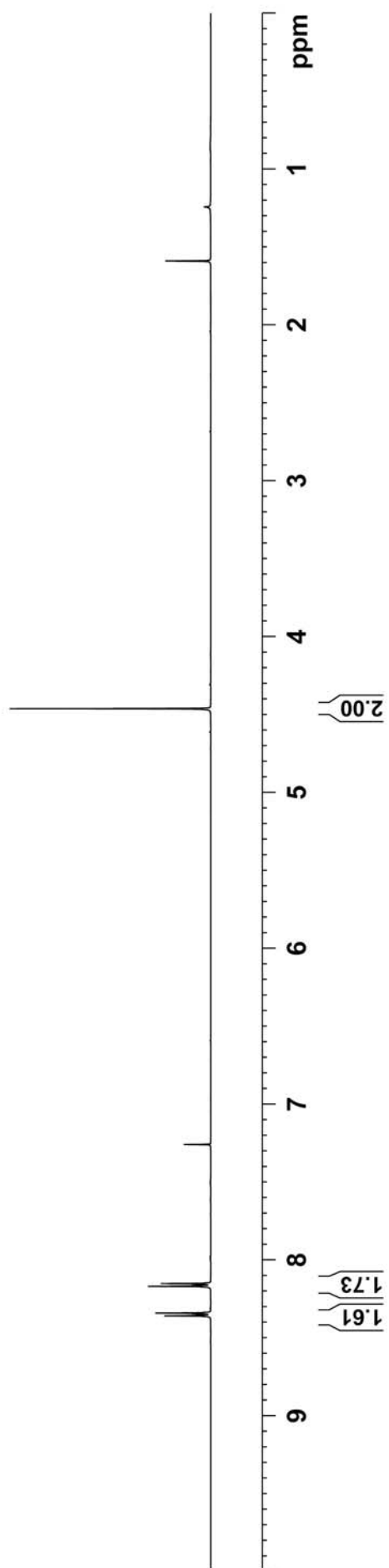


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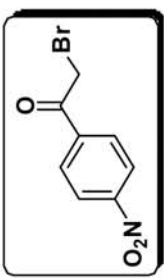
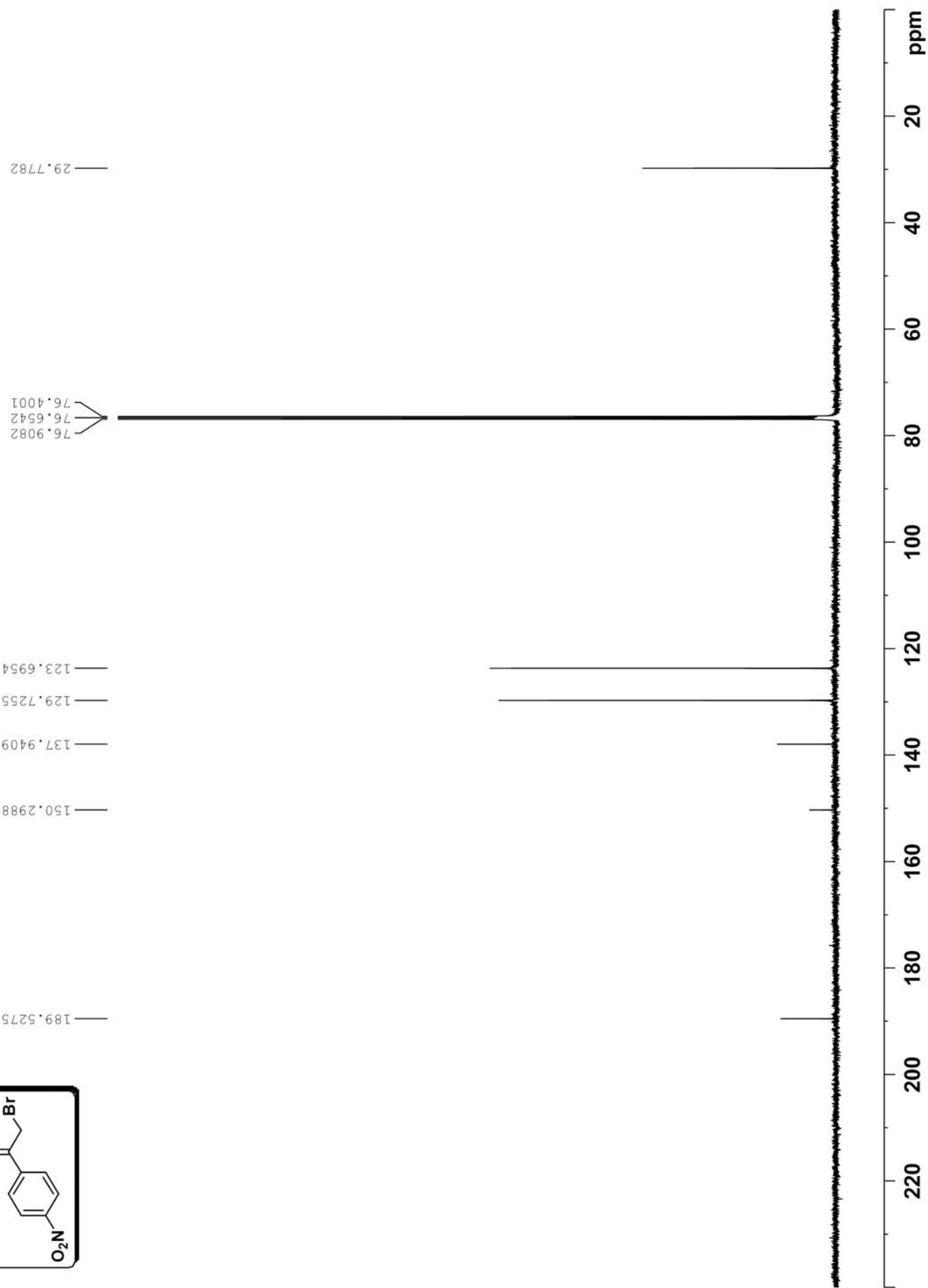
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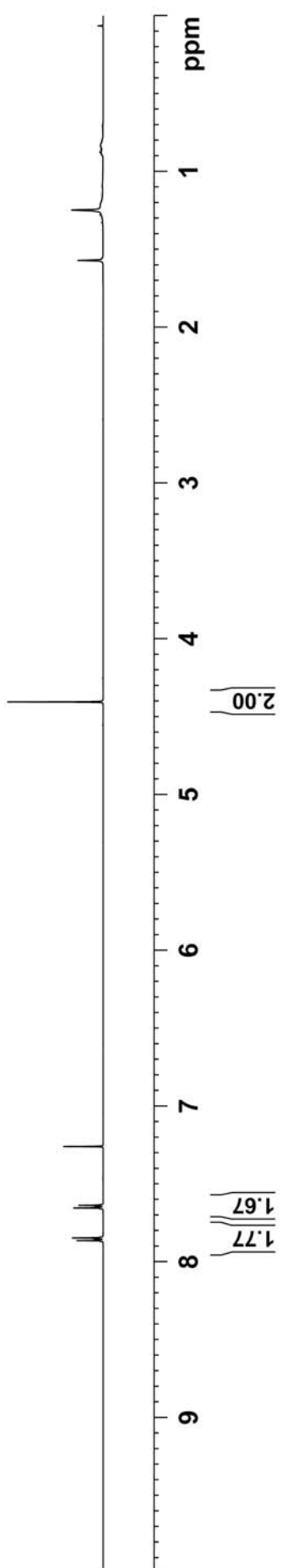


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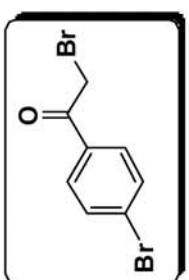
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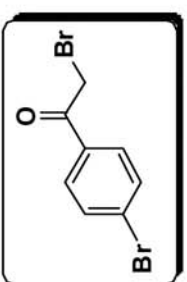
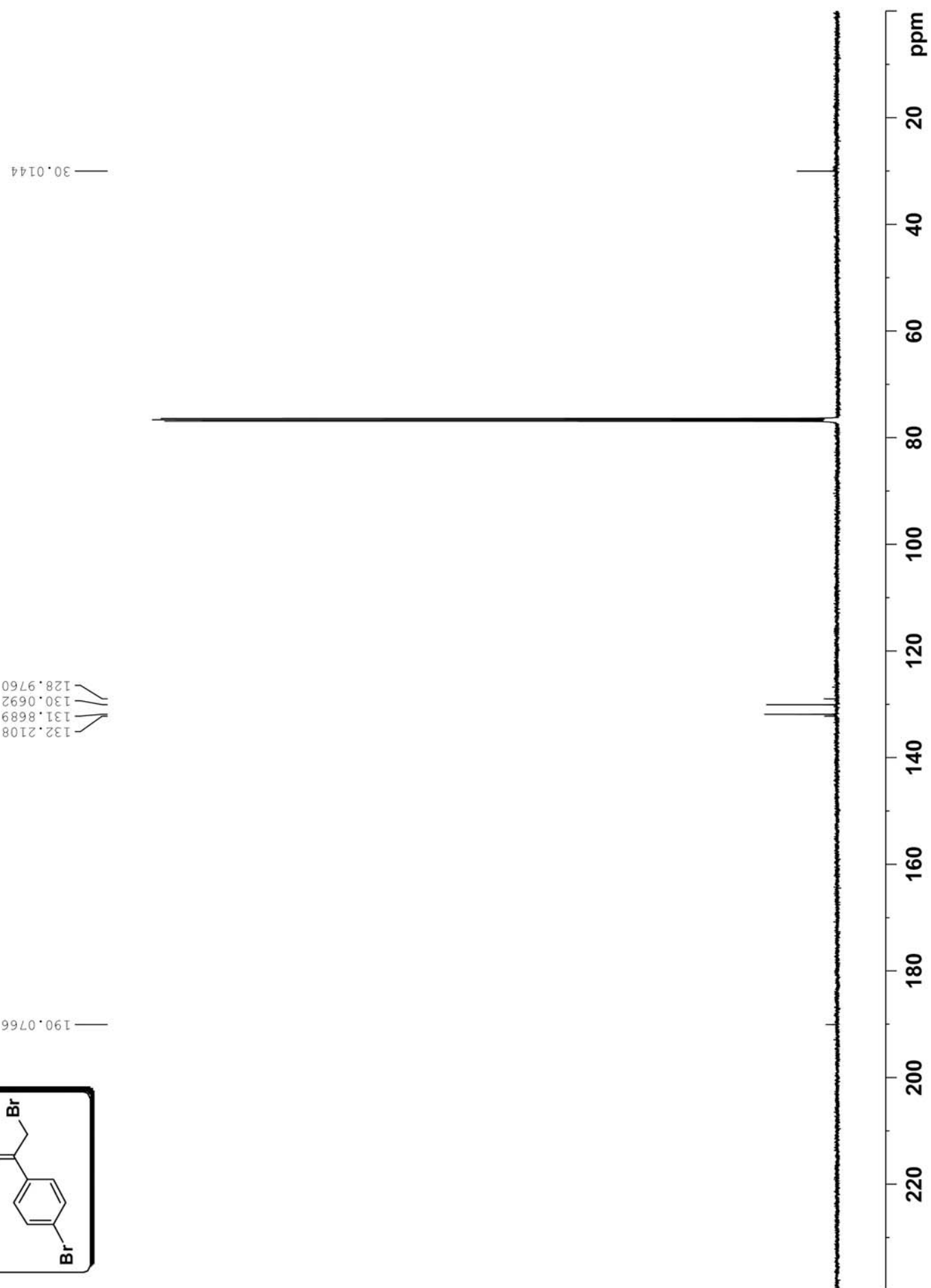


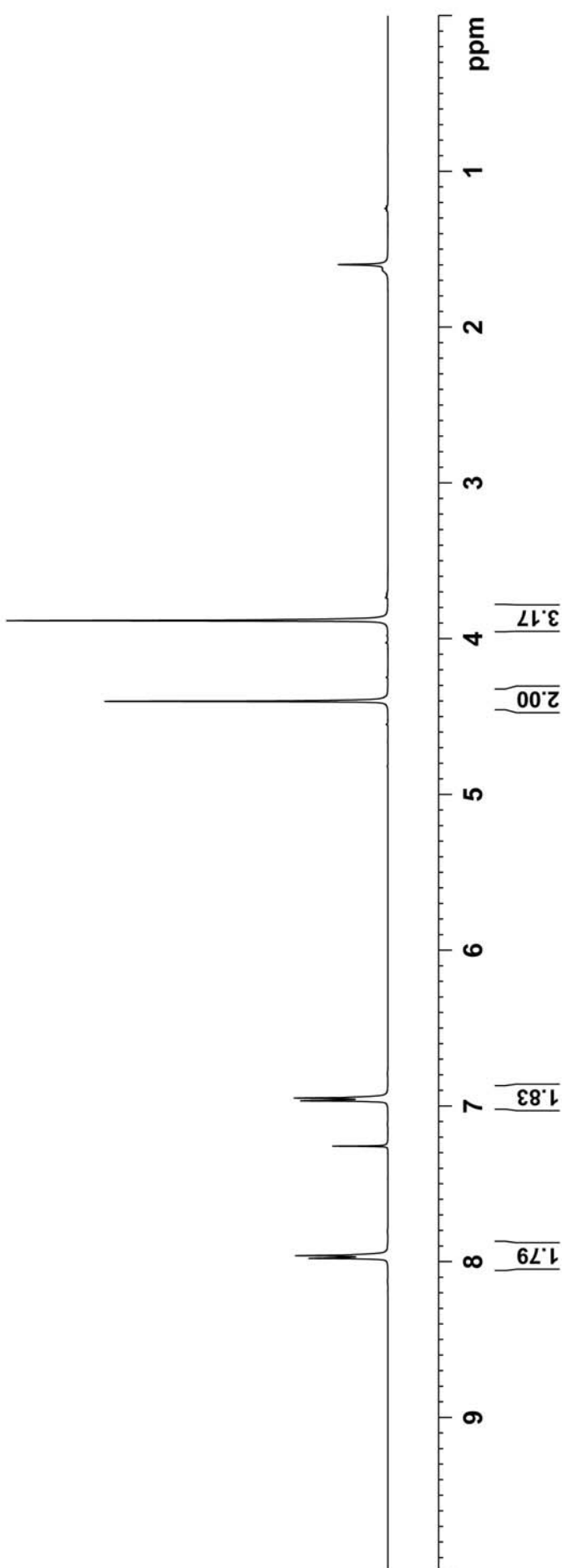
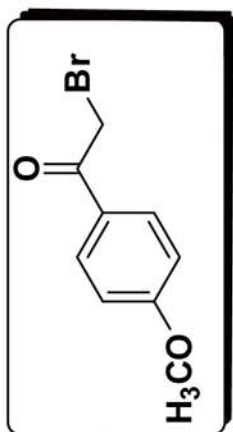


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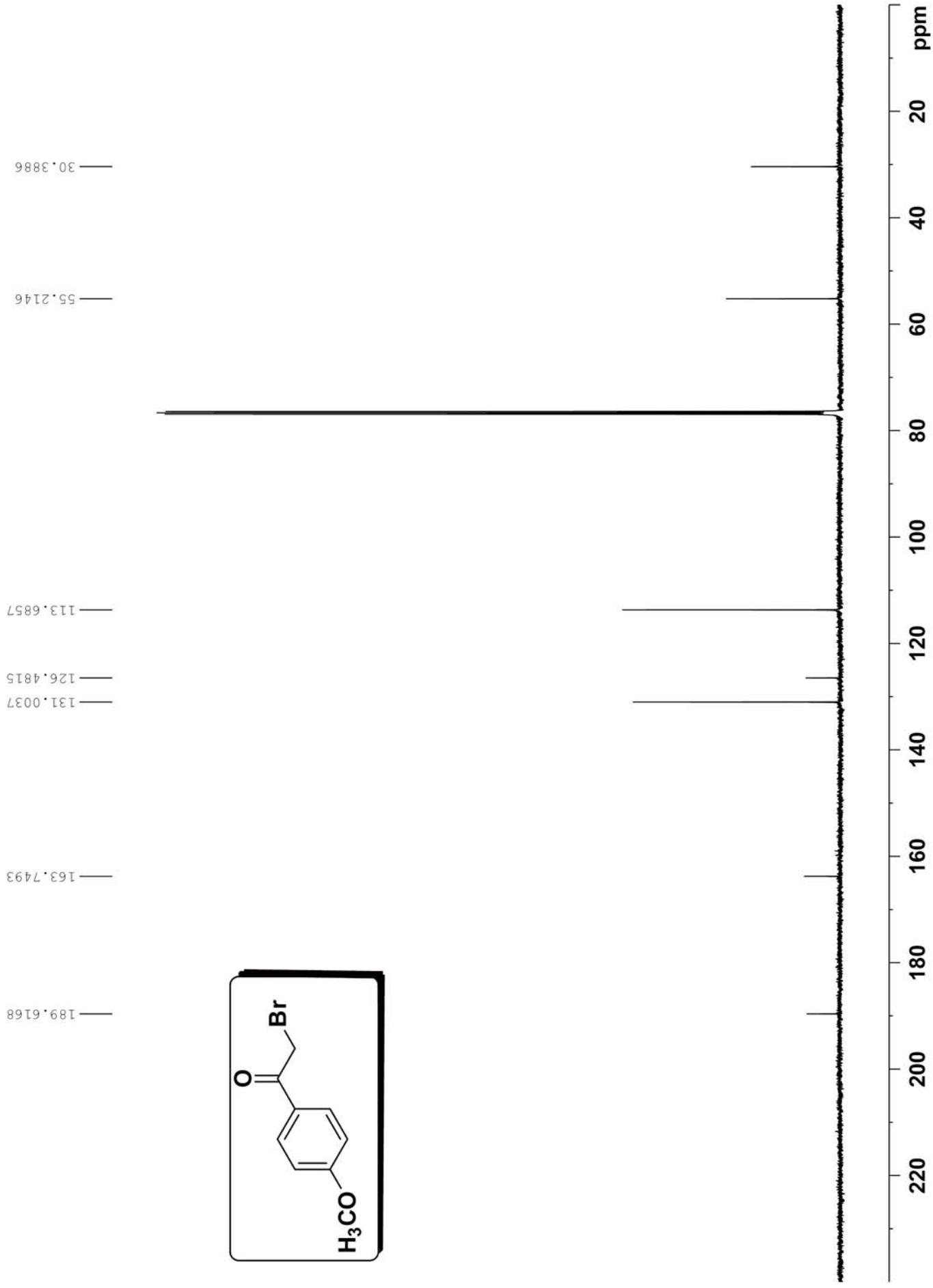
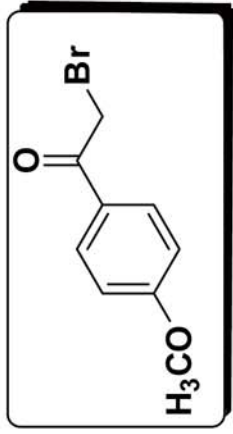
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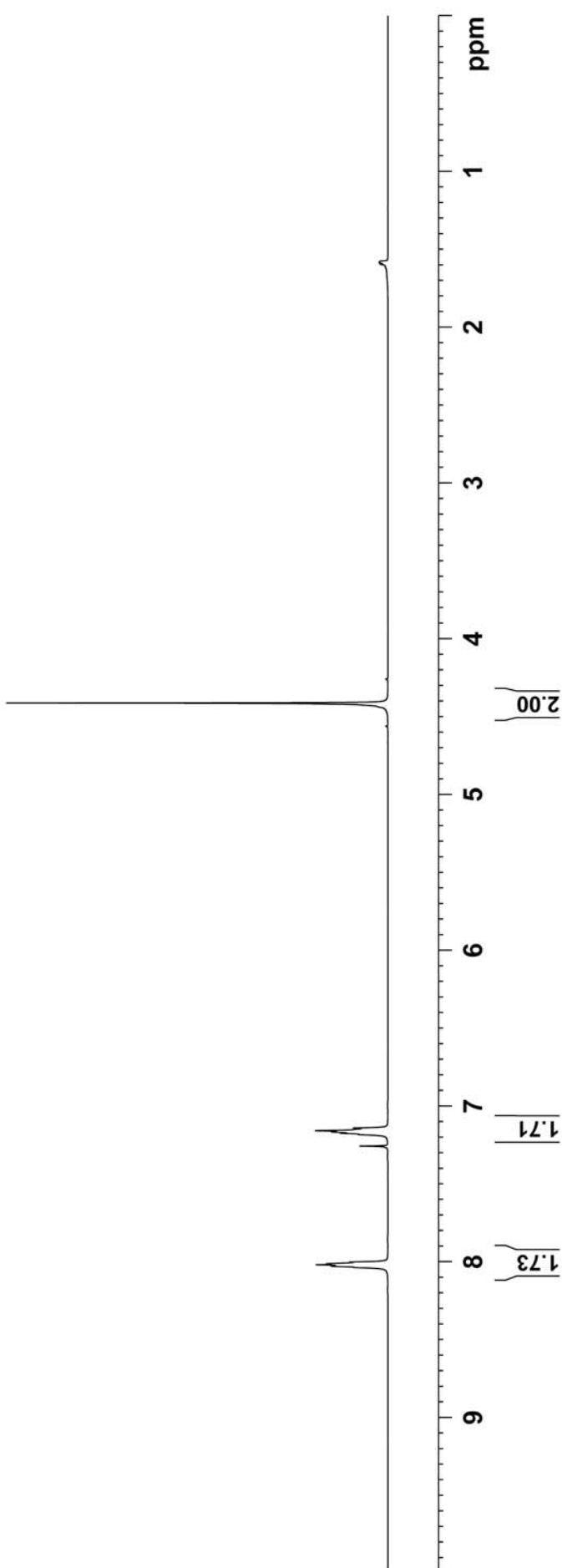
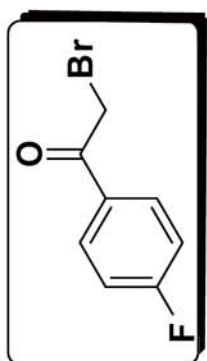
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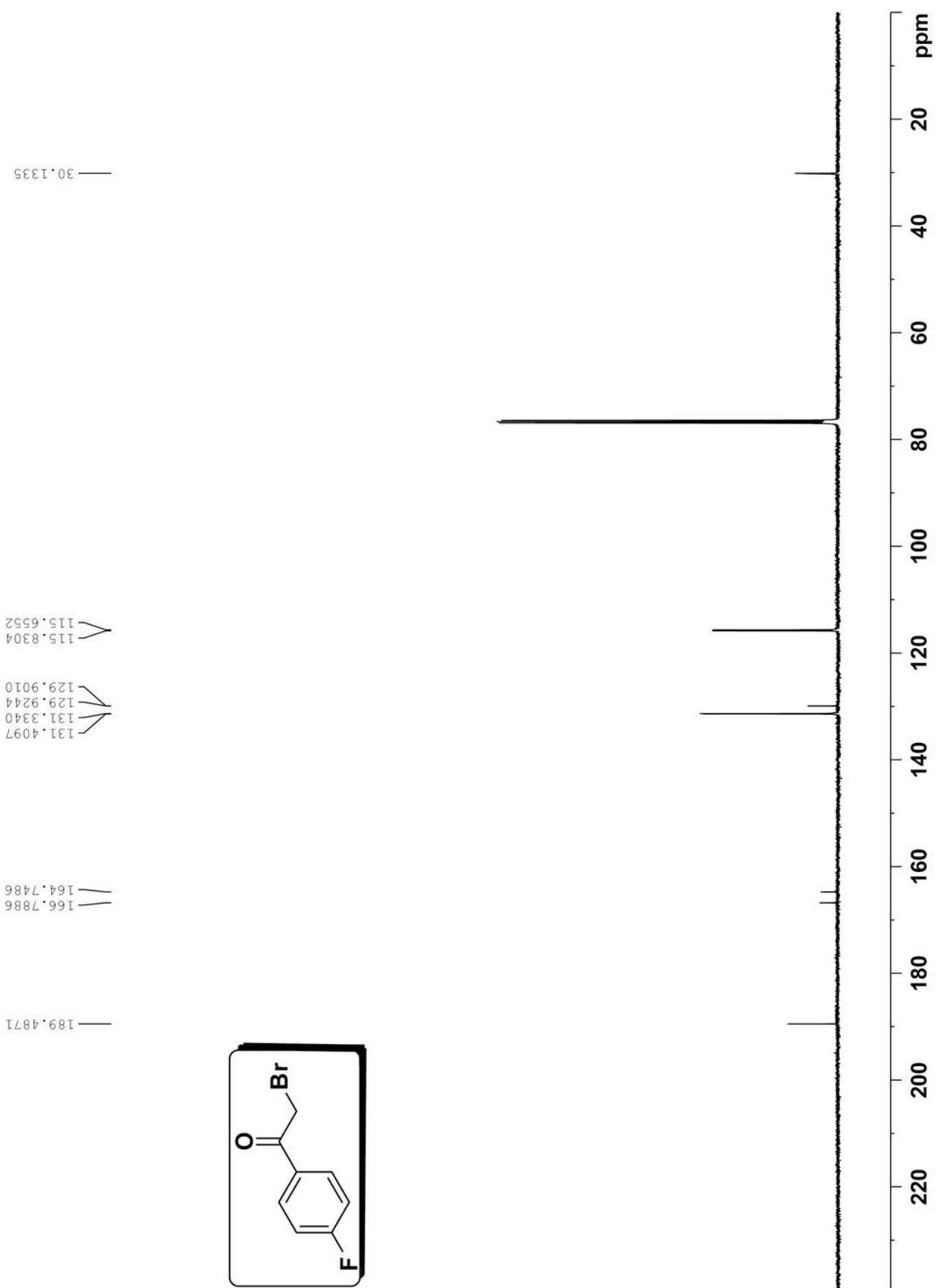
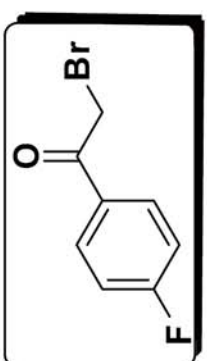
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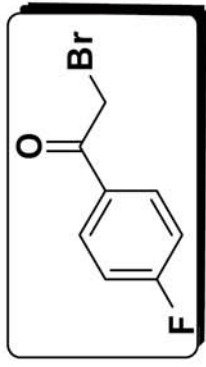




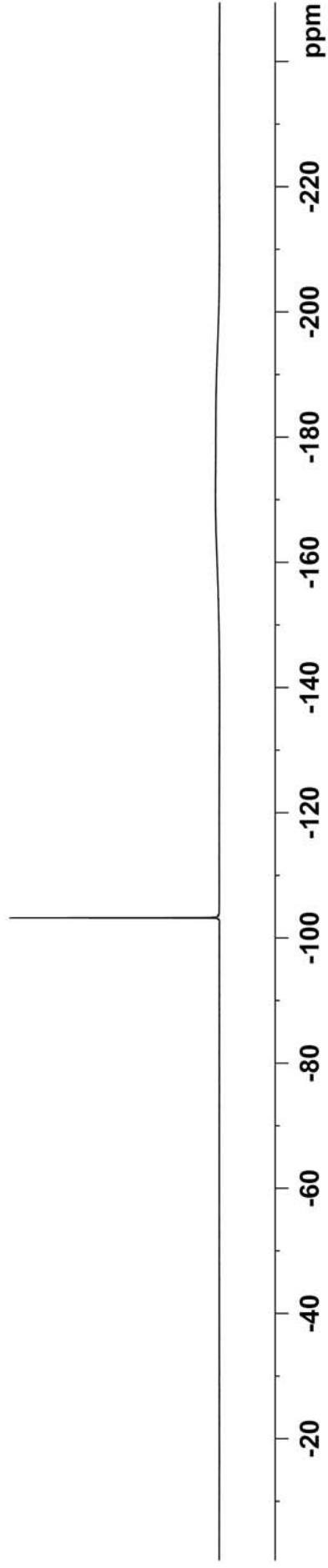
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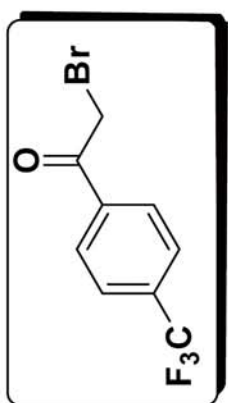
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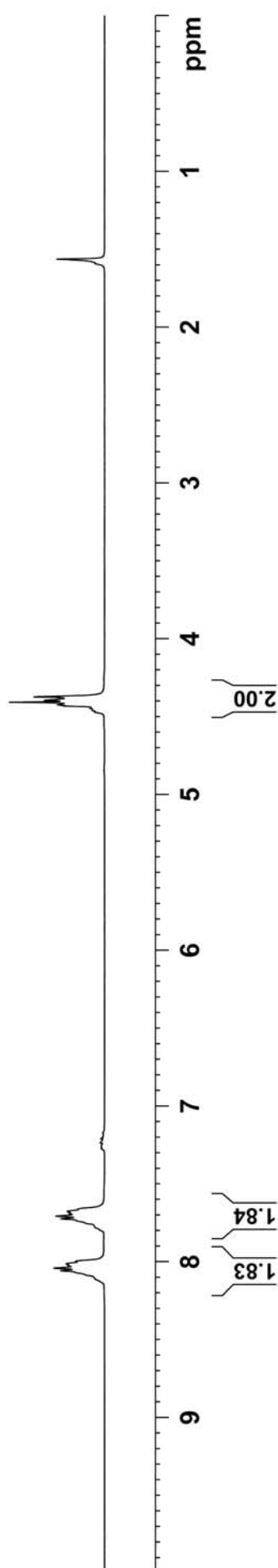
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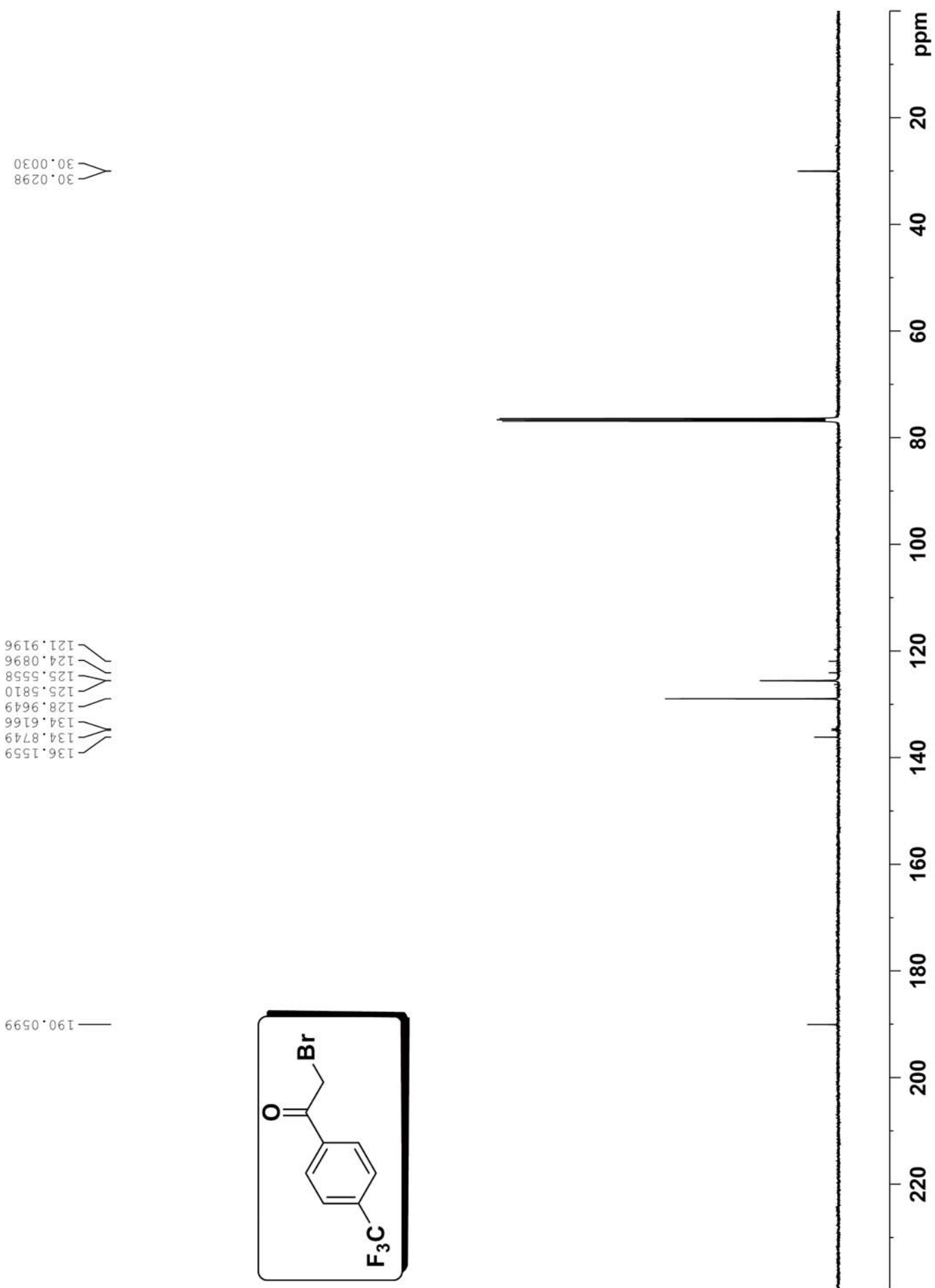
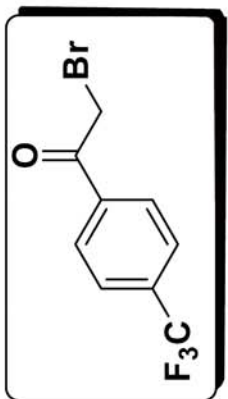


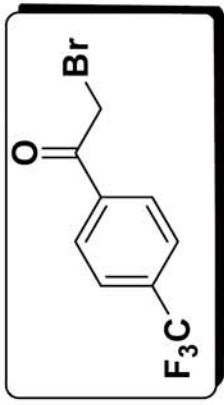


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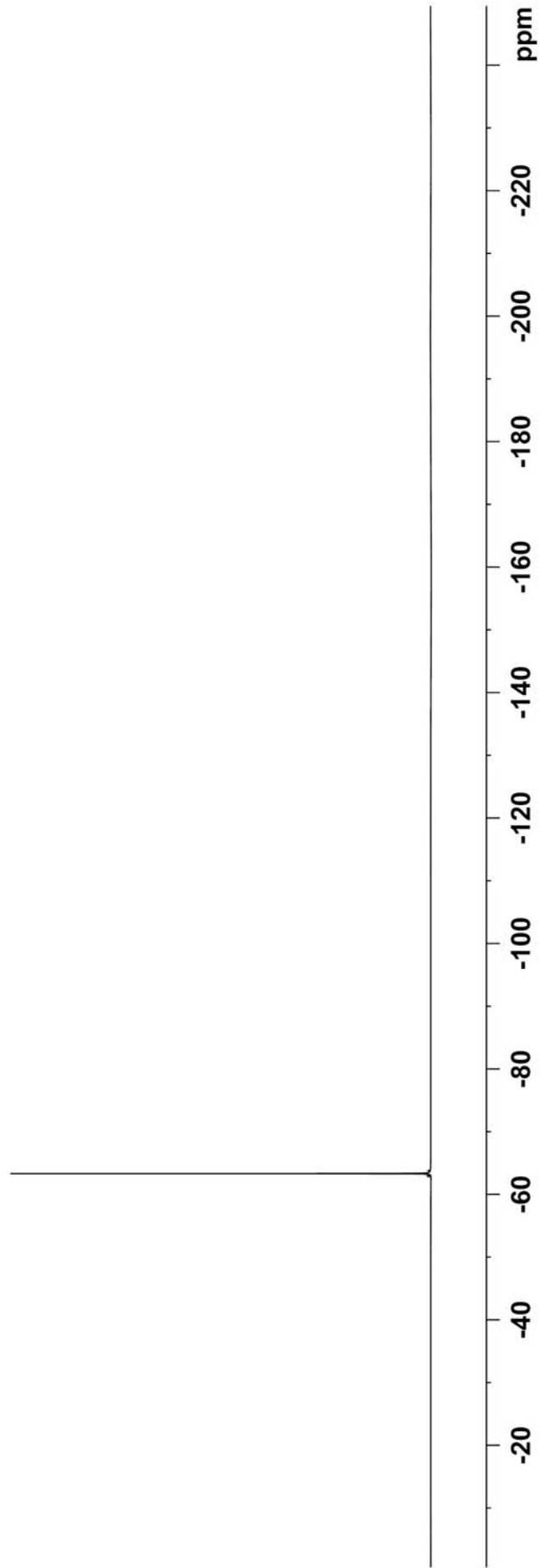
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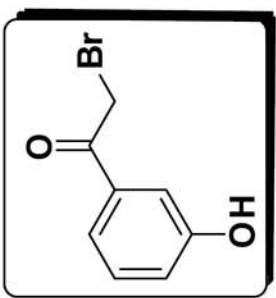
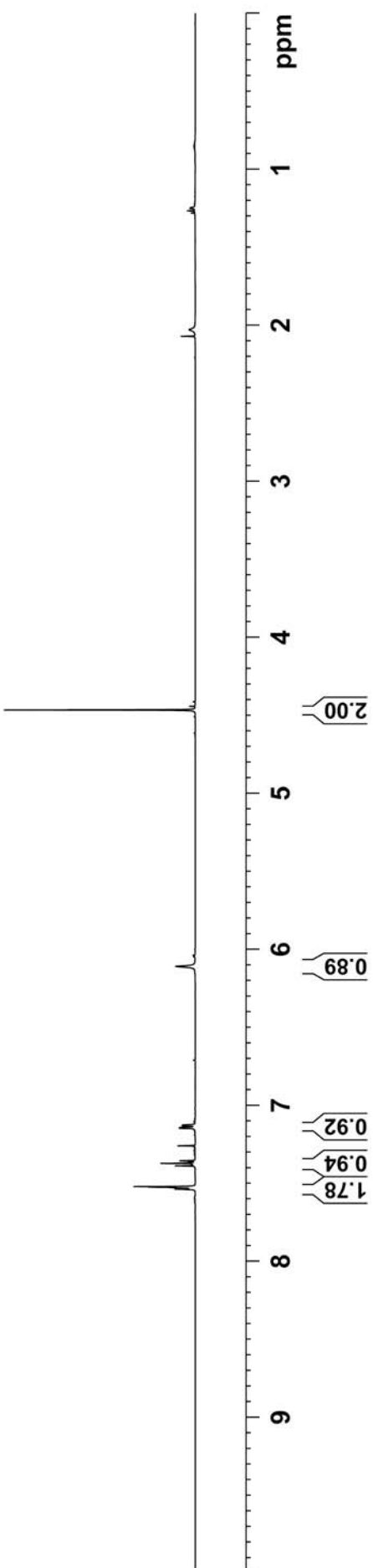






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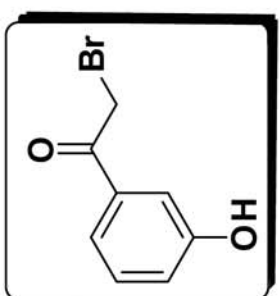
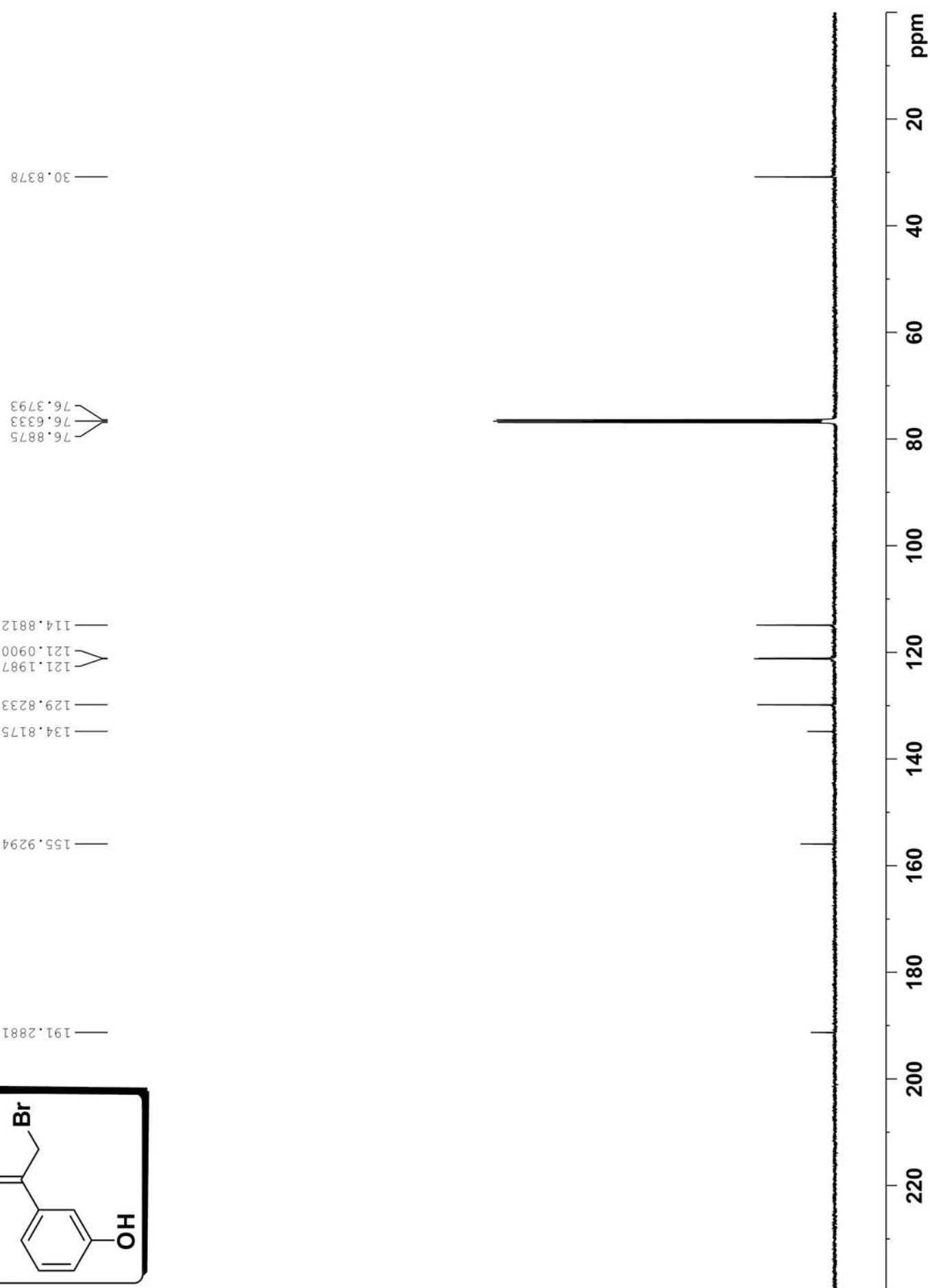


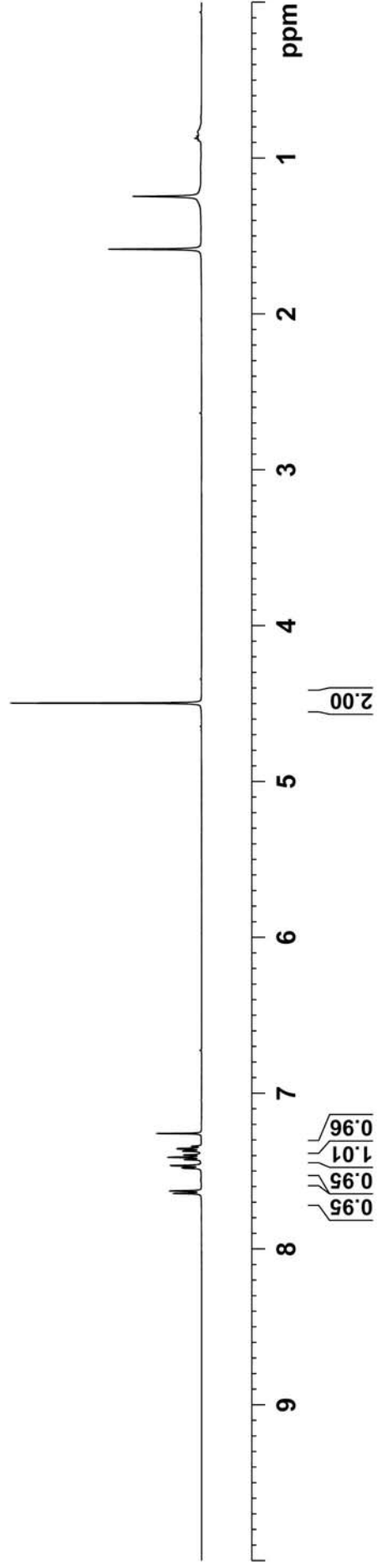
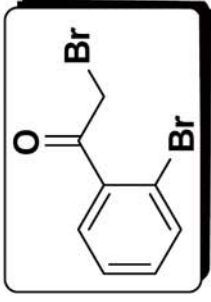


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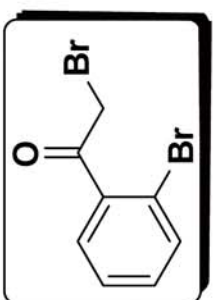
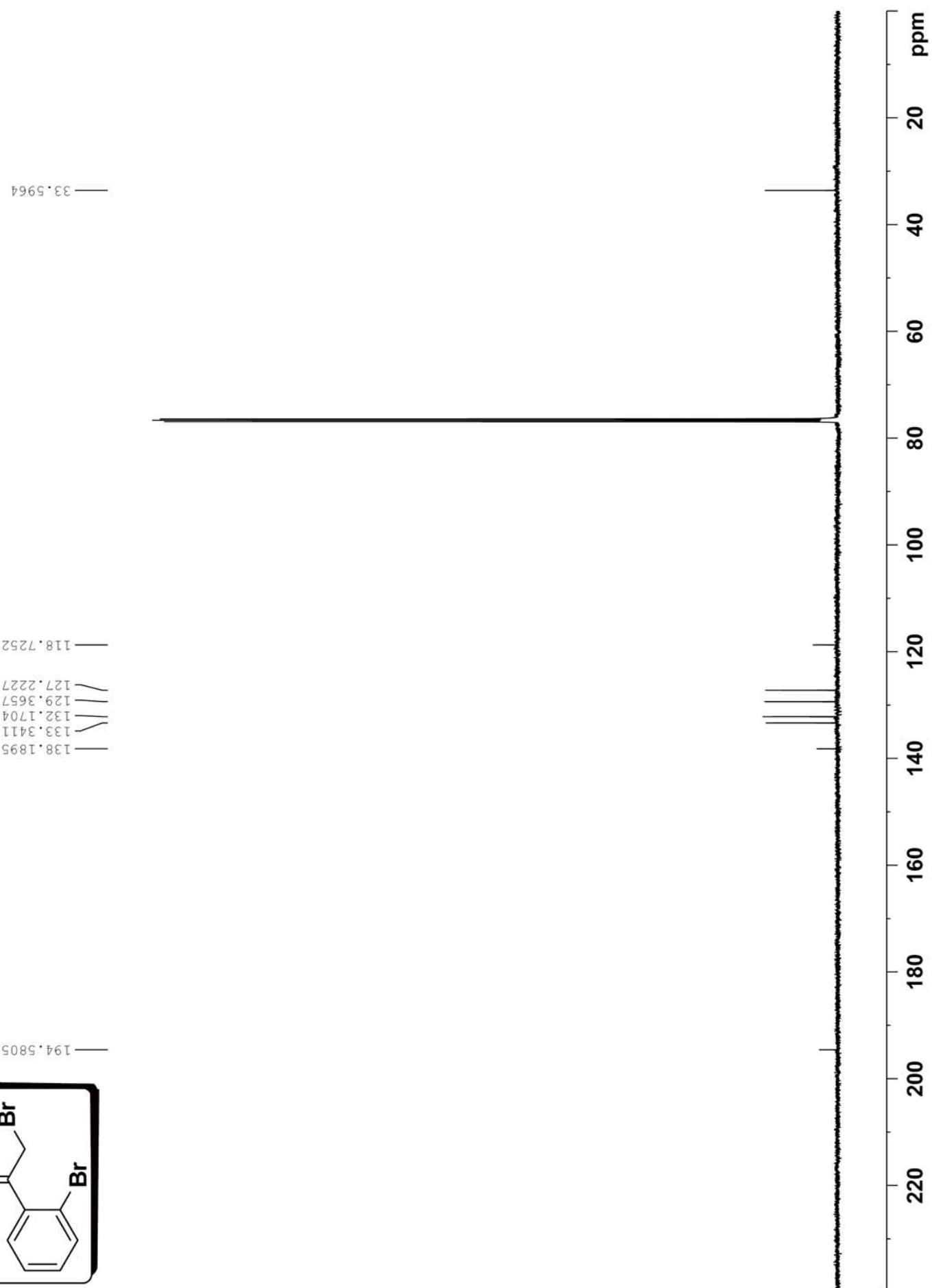
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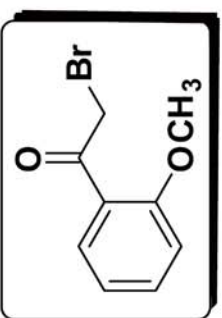
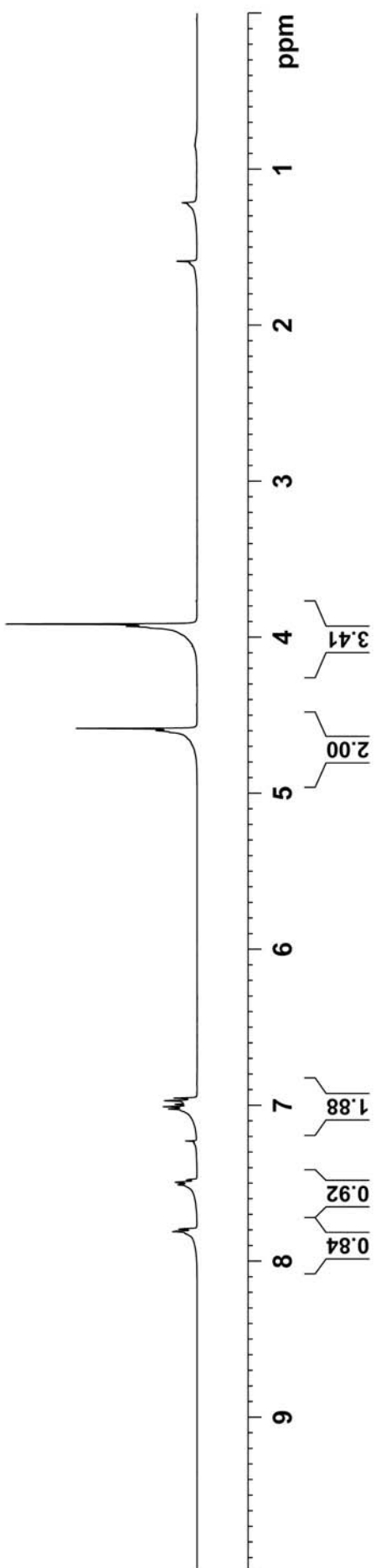




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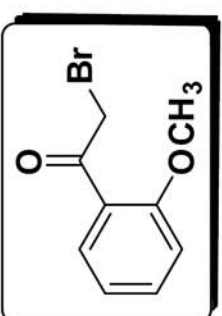
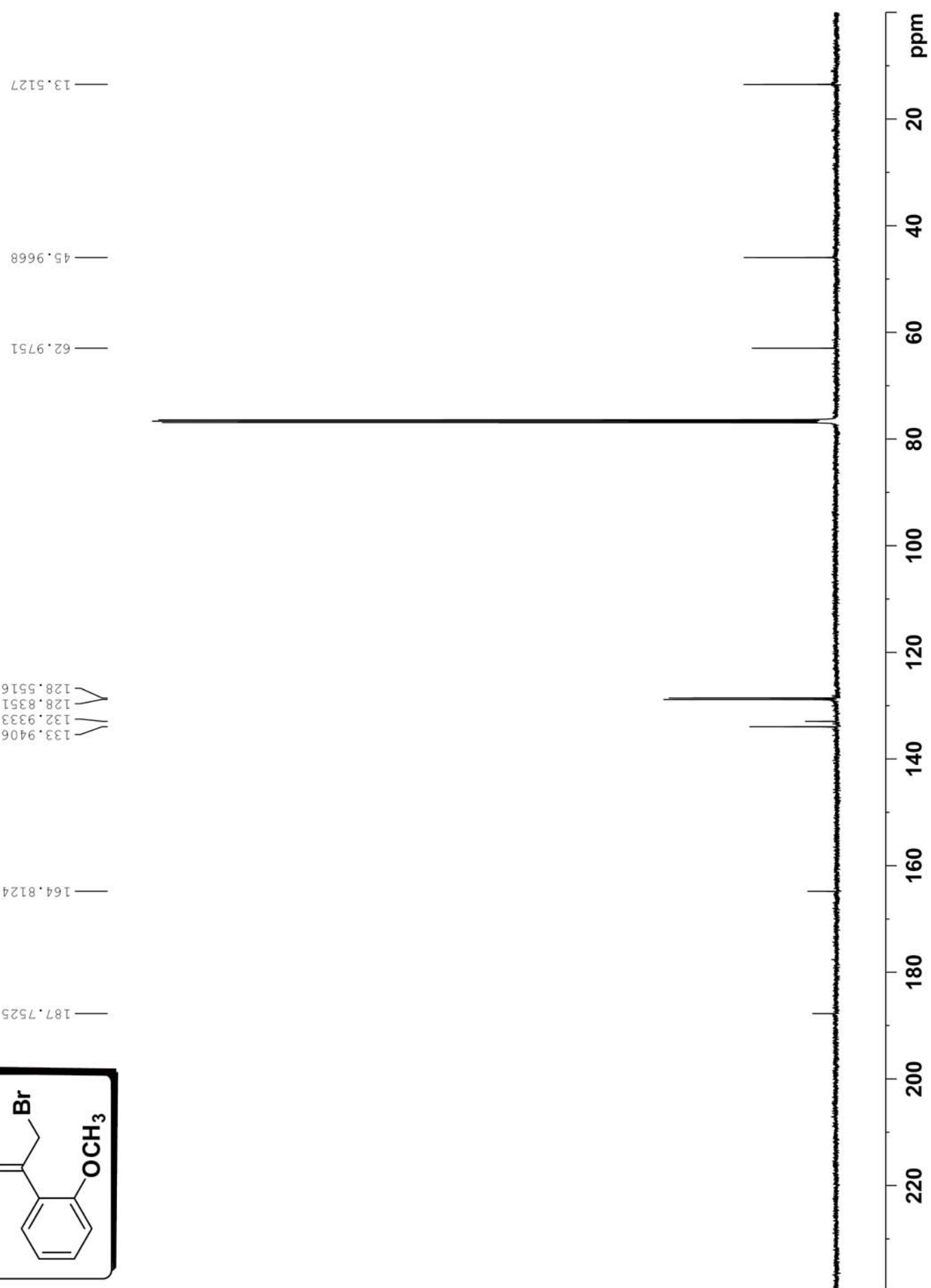


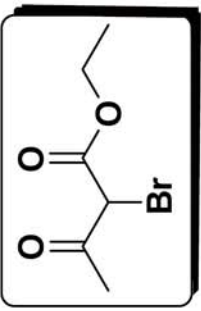


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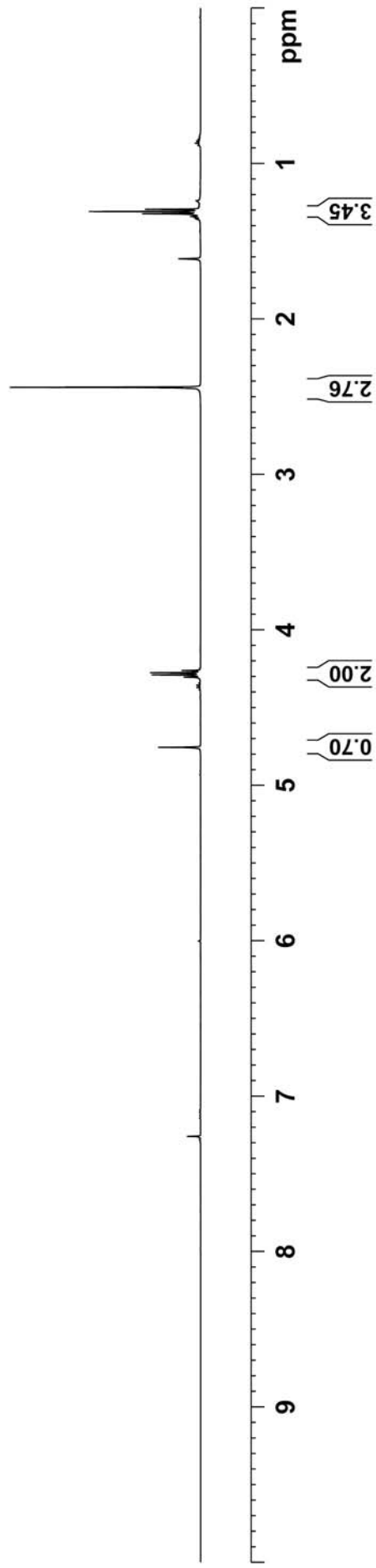
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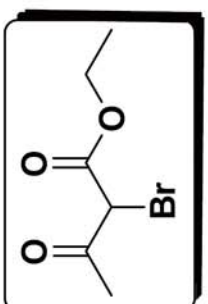
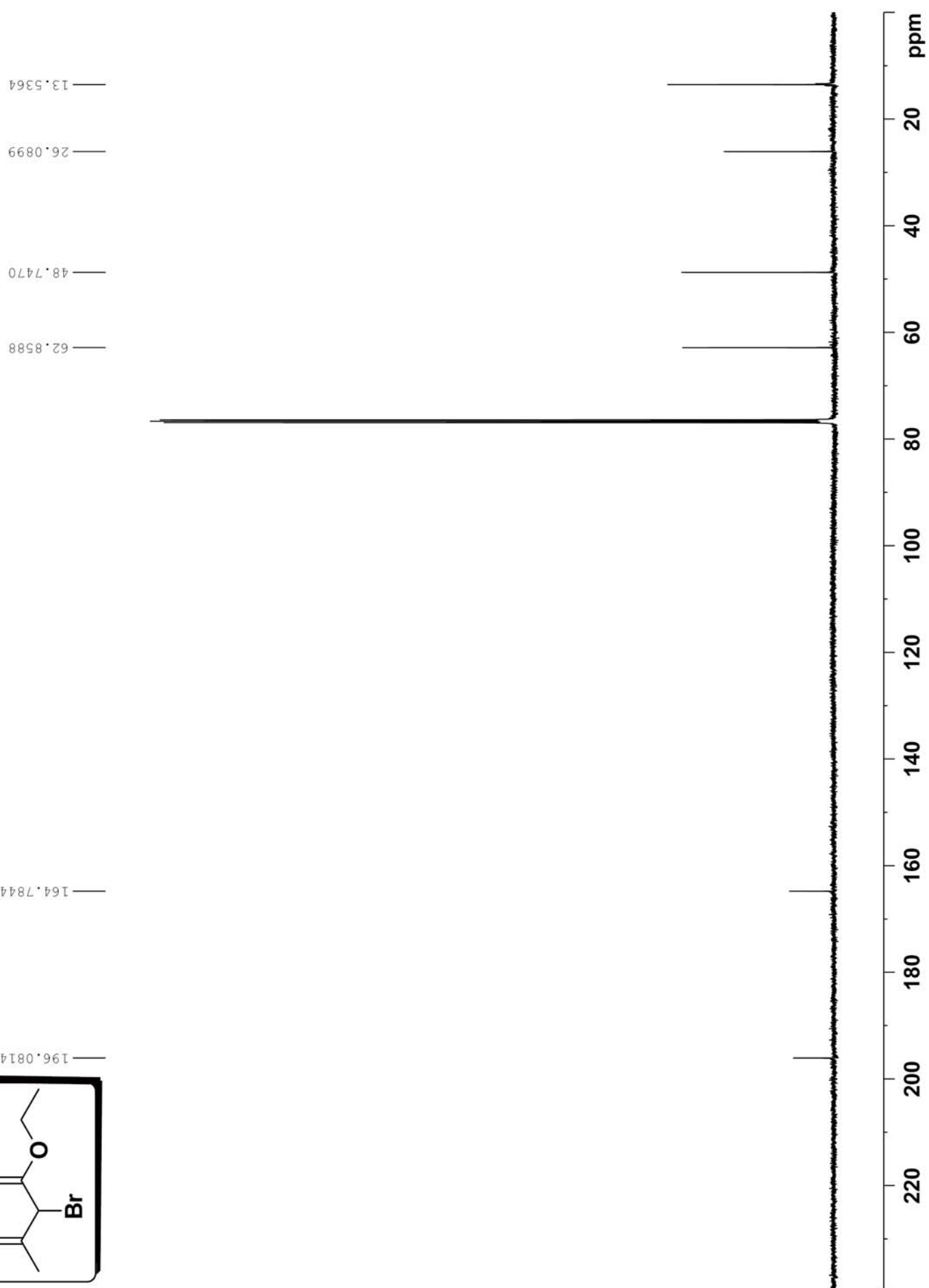
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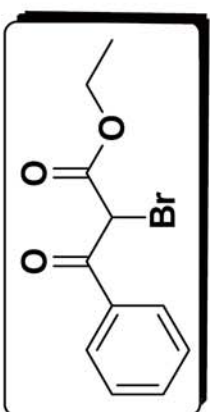
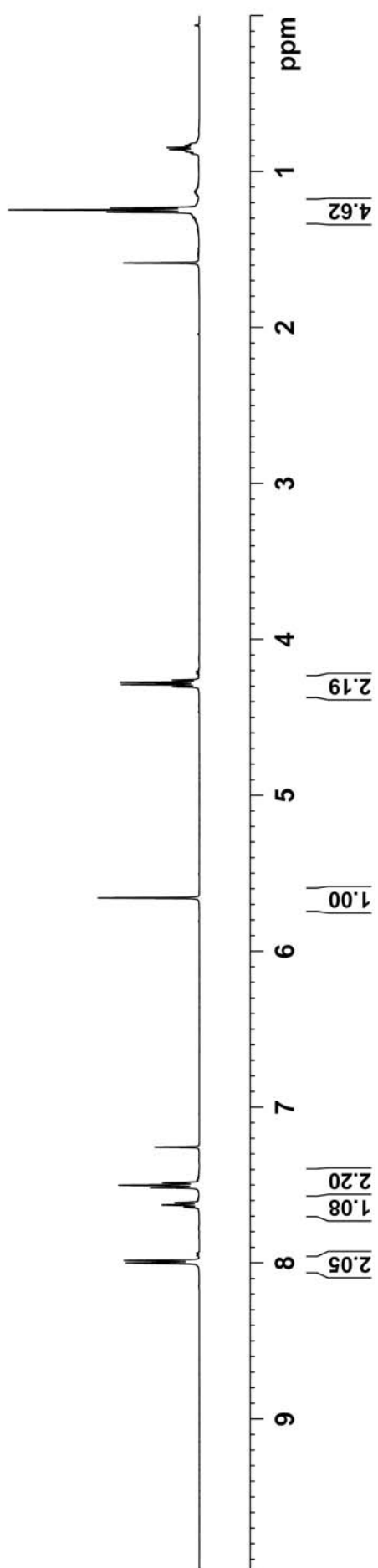
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1.3091
1.2949





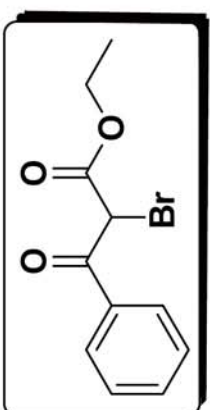
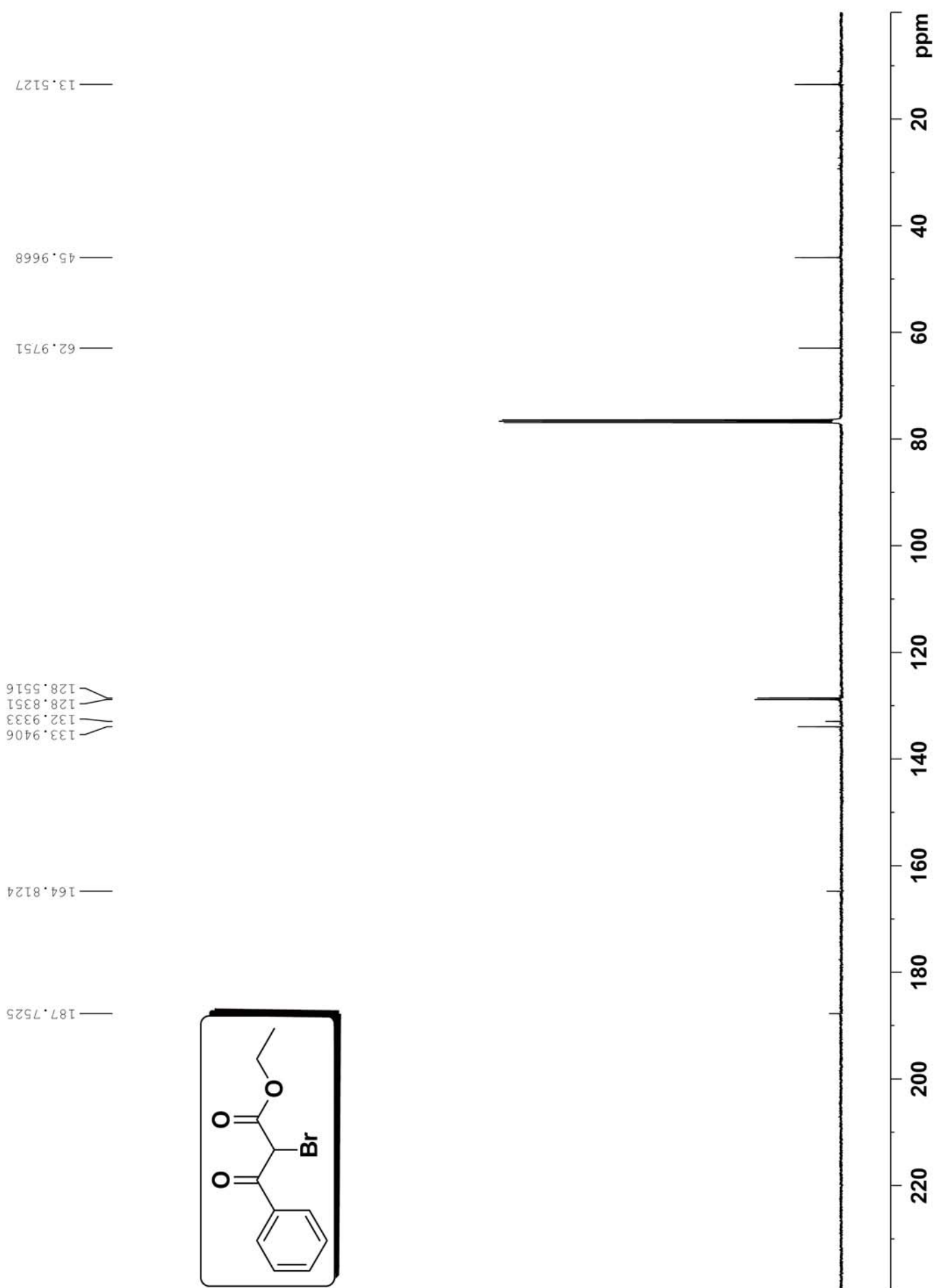


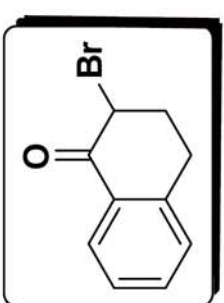
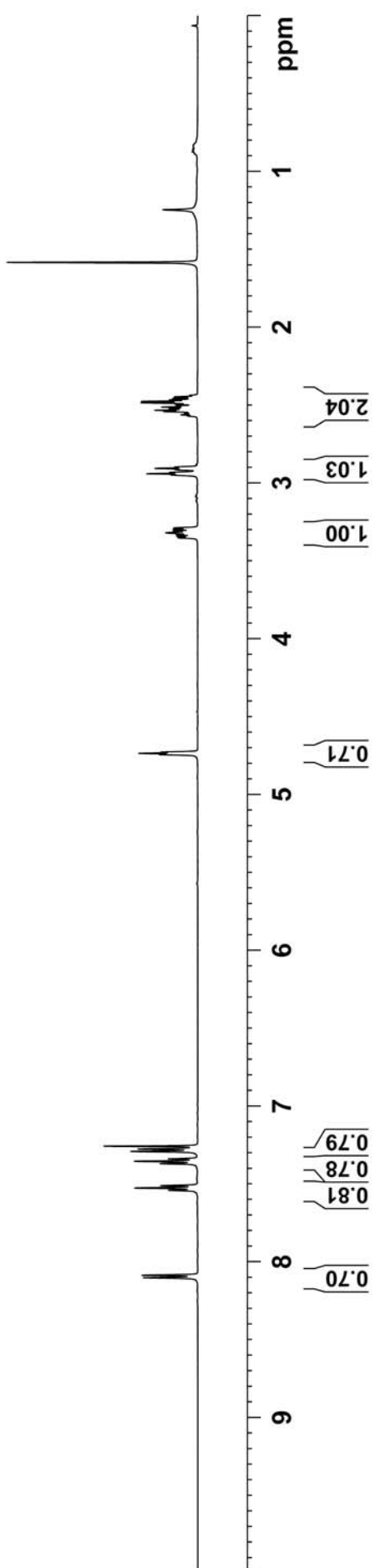
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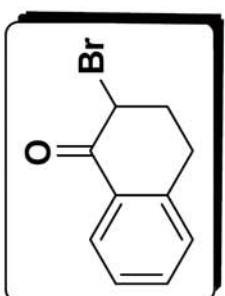
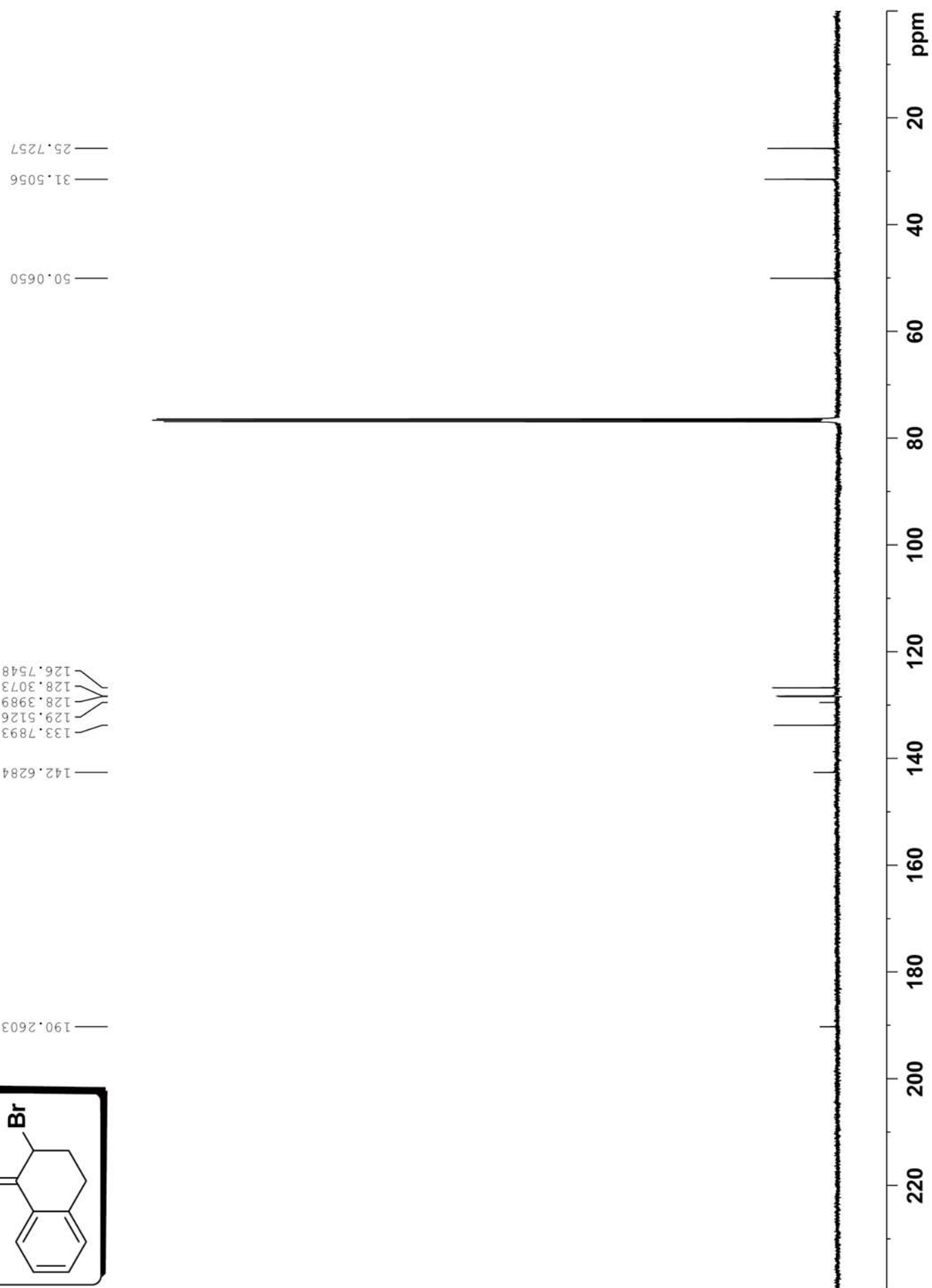


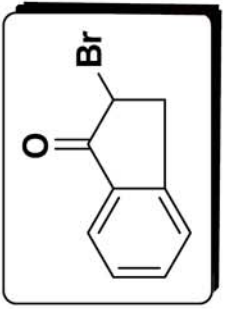


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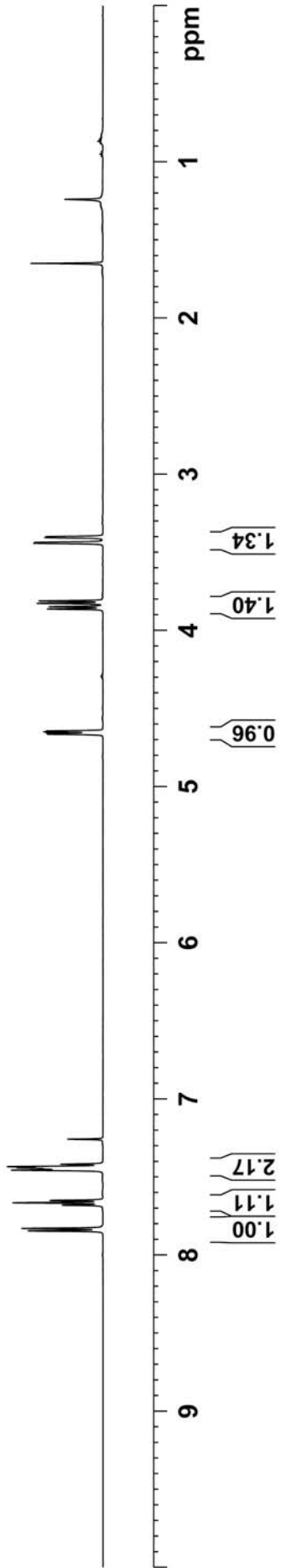


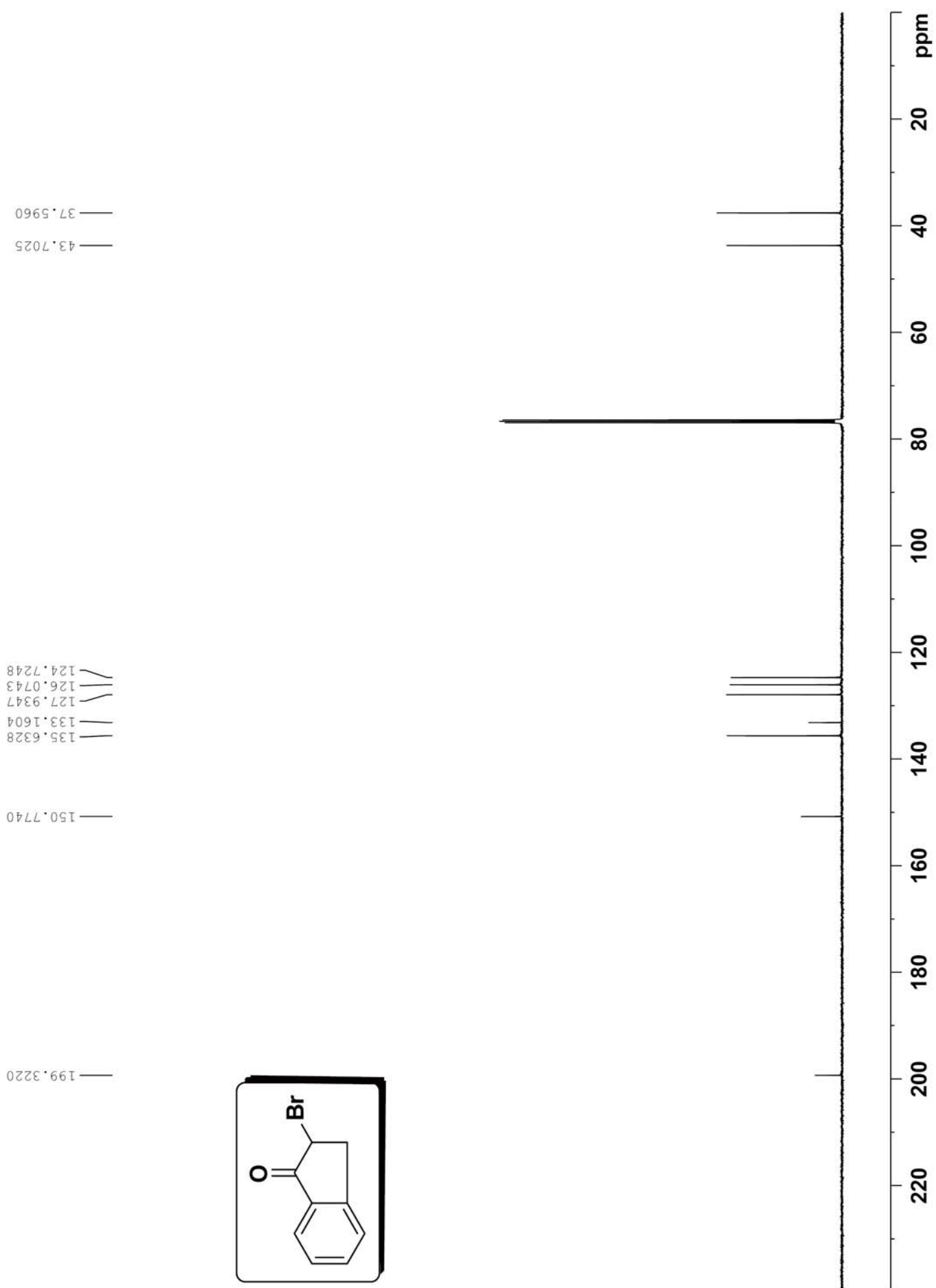


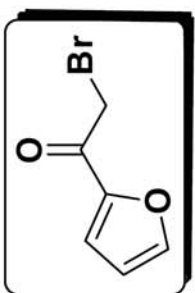
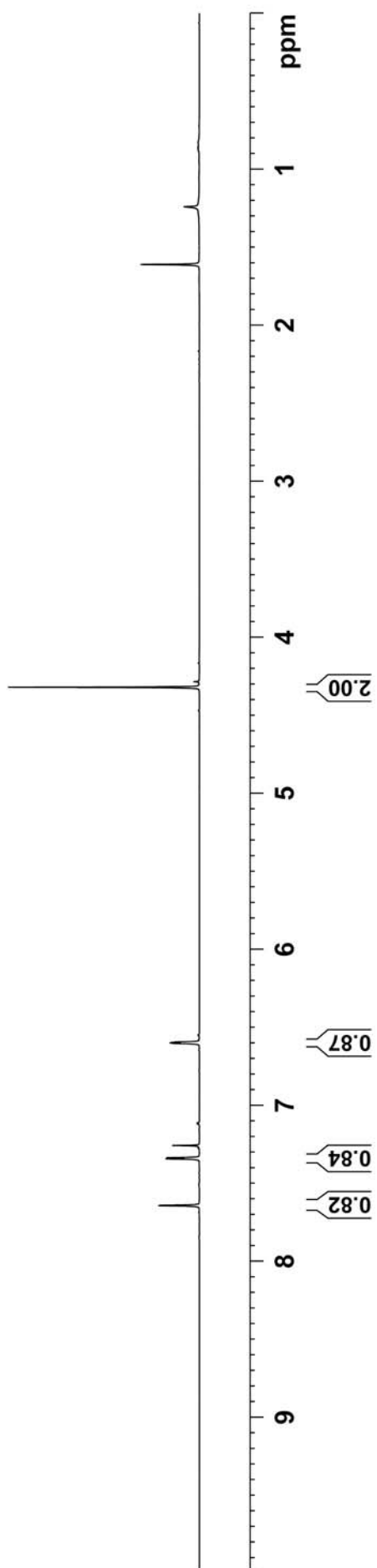
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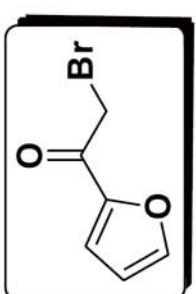
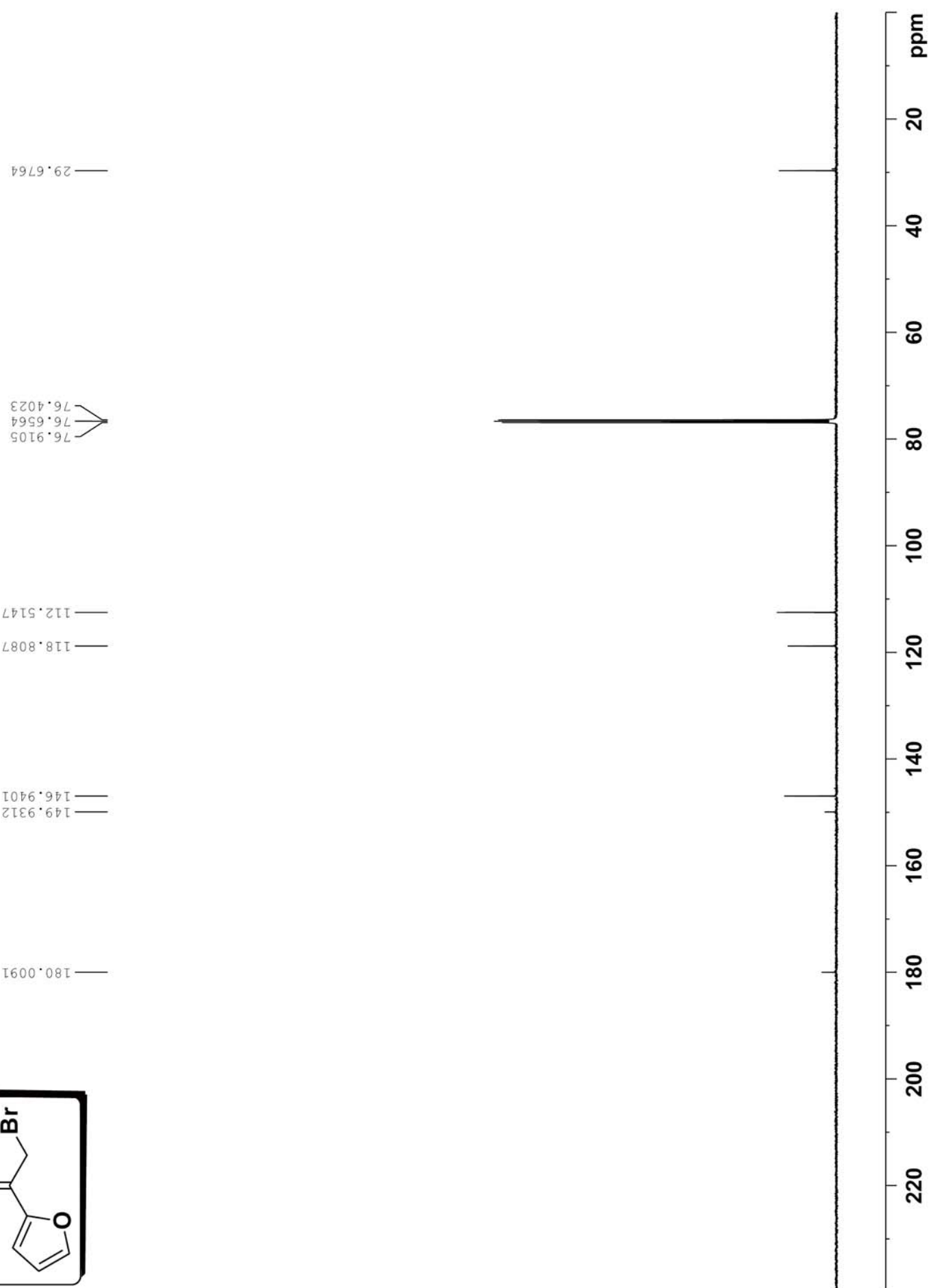


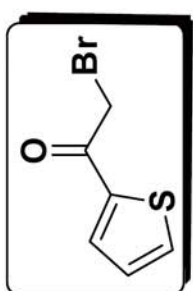
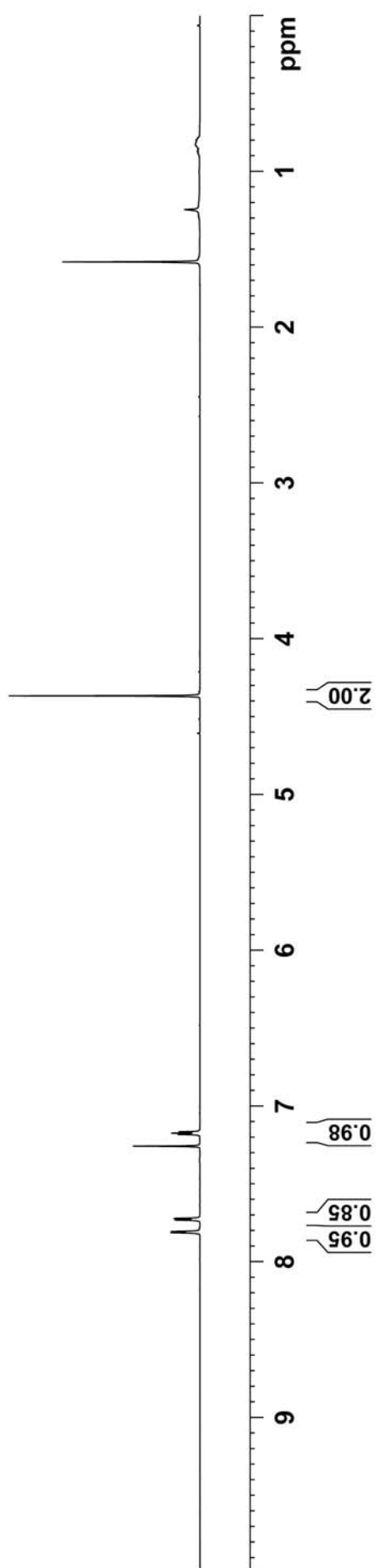


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