Electronic Supplementary Material (ESI) for ChemComm.

Highly Efficient Oxidation of Alcohols Catalyzed by a Porphyrin-inspired Manganese Complex

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Supporting Information

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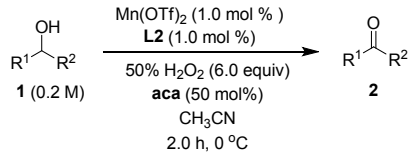
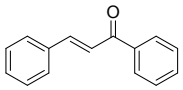
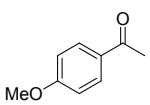
Representative Procedure for the oxidation of alcohols.



A solution of $Mn(OTf)_2$ (0.008 M solution in CH_3CN, 0.25 mL, 0.002 mmol) was added to **L2** (0.008 M solution in CH_3CN, 0.25 mL, 0.002 mmol) at room temperature. The reaction mixture was stirred at room temperature for 8 h. To the solution of manganese complex was directly added substrate (0.2 mmol) and CH_3CN (0.5 mL) and the mixture was cooled to 0 °C. Then 47% H_2O_2 (86.8 mg, 1.2 mmol, diluted with 1.0 mL CH_3CN) was added through syringe pump over 1 h and the mixture was stirred at 0 °C for another1.0 h. At this point, a saturated aqueous solution of $NaHCO_3$ (8 mL) was added and the resulting mixture was extracted with EtOAc (10 mL× 3). The organic layer was combined and washed with brine, dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding aldehydes or ketones.

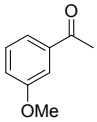


Chalcone (Table 3, entry 2). Yellow solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (38.3 mg, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.82 (m, 1H), 7.65 (m, 2H), 7.58 (m, 2H), 7.51 (m, 2H), 7.41 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 162.9, 158.8, 134.8, 132.3, 130.8, 128.4, 113.7, 113.5, 55.5, 55.3.



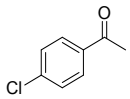
1-(4-Methoxyphenyl)ethanone (Table 3, entry 6). White solid, purified by column

chromatography on silica gel (10% EtOAc in petroleum ether) (28.5 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 2H), 7.00 – 6.83 (m, 2H), 3.94 – 3.78 (m, 3H), 2.62 – 2.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3.



1-(3-Methoxyphenyl)ethanone (Table 3, entry 7). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.2 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.40 – 7.31 (m, 1H), 7.15 – 7.01 (m, 1H), 4.00 – 3.73 (m, 3H), 2.70 – 2.50 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 159.8, 138.4, 129.5, 121.1, 119.5, 112.6, 55.6, 26.7.

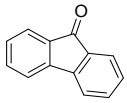
1-(O-tolyl)ethanone (Table 3, entry 8). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (23.3 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.25 (m, 2H), 2.57 (d, J = 0.6 Hz, 3H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 138.4, 137.6, 132.1, 131.5, 129.4, 125.7, 29.5, 21.6.



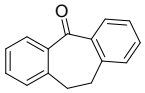
1-(4-Chlorophenyl)ethanone (Table 3, entry 9). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (21.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.76 (m, 2H), 7.39 (m, 2H), 2.76 – 2.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 139.4, 135.8, 129.7, 128.8, 26.5.

2,3-Hihydro-1H-inden-1-one (Table 3, entry 10). Brown solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (24.3 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.59 (m, 1H), 7.48 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.37 (m, 1H), 3.21 – 3.09 (m, 2H), 2.75 – 2.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 155.2, 137.1, 134.6, 127.3, 126.7, 123.7, 36.2, 25.8.

3,4-Hihydronaphthalen-1(2H)-one (Table 3, entry 11). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.2 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.43 (m, 1H), 7.26 (m, 2H), 3.04 – 2.89 (m, 2H), 2.61 (m, 2H), 2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 144.5, 133.4, 132.6, 128.8, 127.1, 126.6, 39.1, 29.7, 23.3.

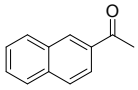


9H-fluoren-9-one (Table 3, entry 12). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (32.4 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.3 Hz, 2H), 7.49 (m, 4H), 7.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 144.4, 134.7, 134.2, 129.1, 124.3, 120.3.

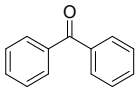


10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-one (Table 3, entry 13). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (38.7 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.42 (m, 2H), 7.31 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.19 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 142.0, 138.6, 132.4, 130.6, 129.3,

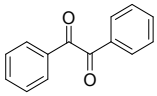
126.7, 35.0.



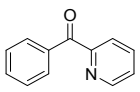
1-(Naphthalen-2-yl)ethanone (Table 3, entry 14). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (31.3 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.93 – 7.82 (m, 2H), 7.65 – 7.46 (m, 2H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 127.8, 126.8, 123.9, 26.7.



Benzophenone (Table 3, entry 15). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (32.4 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 4H), 7.62 – 7.55 (m, 2H), 7.52 – 7.44 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3.

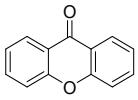


Benzil (Table 3, entry 16). Yellow solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (20.2 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 4H), 7.70 – 7.62 (m, 2H), 7.55 – 7.44 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 134.9, 133.0, 129.9, 129.0.



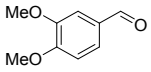
Phenyl(pyridin-2-yl)methanone (Table 3, entry 17). White solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (29.3 mg, 80% yield). ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.78 – 8.69 (m, 1H), 8.06 (m, 3H), 7.91 (m, 1H), 7.59 (m, 1H), 7.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 155.1, 148.6, 137.1, 136.3, 133.0 (s), 131.0, 128.2, 126.2, 124.7.

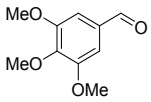


9H-xanthen-9-one (Table 3, entry 18). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (35.3 mg, 90% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 156.2, 134.8, 126.8, 123.9, 121.9, 118.0.

Chroman-4-one (Table 3, entry 19). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (26.0 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.83 (m, 1H), 7.47 (m, 1H), 7.12 – 6.80 (m, 2H), 4.68 – 4.41 (m, 2H), 2.93 – 2.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 161.9, 136.0, 127.2, 121.4, 117.9, 67.0, 37.8.

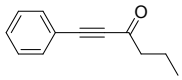


3,4-Dimethoxybenzaldehyde (Table 3, entry 23). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.6 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 10.06 – 9.76 (m, 1H), 7.45 (m, 2H), 6.98 (m, 1H), 3.96 (m, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 154.5, 149.6, 130.2, 126.9, 110.4, 108.9, 56.1.

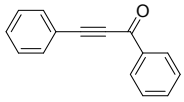


3,4,5-Trimethoxybenzaldehyde (Table 3, entry 24). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (29.4 mg, 75% yield). ^1H NMR (400

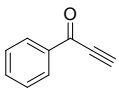
MHz, $CDCl_3$) δ 9.88 (d, *J* = 2.3 Hz, 1H), 7.14 (s, 2H), 3.94 (d, *J* = 2.8 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 153.7, 143.6, 131.7, 106.7, 61.0, 56.3.



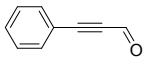
1-Phenylhex-1-yn-3-one (Table 3, entry 25). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (24.1 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.48 – 7.42 (m, 1H), 7.41 – 7.34 (m, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.71 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 133.0, 130.7, 128.6, 120.1, 90.5, 87.9, 47.4, 17.7, 13.6.



1,3-Diphenylprop-2-yn-1-one (Table 3, entry 26). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (37.5 mg, 91% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.63 (m, 1H), 7.54 – 7.46 (m, 3H), 7.45 – 7.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 136.9, 134.2, 133.1, 130.8, 129.6, 128.7, 127.8, 120.2, 93.2, 86.9.

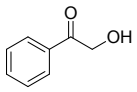


1-Phenylprop-2-yn-1-one (Table 3, entry 28). Yellow solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (21.8 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.12 (m, 2H), 7.75 – 7.59 (m, 1H), 7.55 – 7.45 (m, 2H), 3.45 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 136.2, 134.6, 129.7, 128.7, 80.8, 80.3.



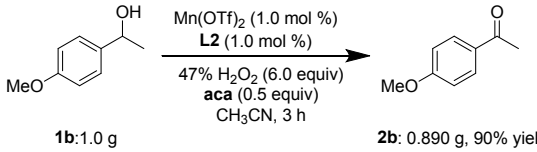
3-Phenylpropiolaldehyde (Table 3, entry 29). Colorless oil, purified by column

chromatography on silica gel (10% EtOAc in petroleum ether) (10.4 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.65 – 7.58 (m, 2H), 7.53 – 7.46 (m, 1H), 7.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 133.3, 131.3, 128.8, 119.5, 95.2, 88.4.



2-hydroxy-1-phenylethanone (Table 3, entry 30). Yellow solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (15.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 2H), 7.68 – 7.60 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 4.89 (s, 2H), 3.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 134.3, 133.4, 129.0, 127.7, 65.5.

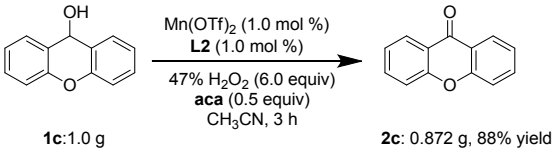
Experimental Procedure for the Gram Scale Synthesis of 2b.



1b:1.0 g **2b**: 0.890 g, 90% yield

A mixture of $Mn(OTf)_2$ (23.3 mg, 0.066 mmol) and **L2** (0.066 mmol) in CH_3CN (10 mL) was stirred at room temperature for 12 h. To the solution of manganese complex was added **1b** (1000 mg, 6.6 mmol) and adamantane carboxylic acid (594 mg, 3.3 mmol) and the temperature was cooled to 0 °C. Then 47 % H_2O_2 (2865 mg, 39.6 mmol, diluted with 10 mL CH_3CN) was added dropwise to the stirring reaction over 1 h and the mixture was stirred at room temperature for another 2 h, the reaction was quenched by adding the sat. aq. $NaHCO_3$ (20 mL), and extracted with EtOAc (20 mL× 5). The organic layer was separated and washed with brine, dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the **2b** (890 mg, 90% yield).

Experimental Procedure for the Gram Scale Synthesis of 2c.



1c:1.0 g **2c**: 0.872 g, 88% yield

A mixture of $Mn(OTf)_2$ (17.8 mg, 0.05 mmol) and **L2** (0.05 mmol) in CH_3CN (10 mL) was stirred at room temperature for 12 h. To the solution of manganese complex was added **1c** (1000 mg, 5.0 mmol) and adamantane carboxylic acid (450 mg, 2.5 mmol) and the temperature was cooled to 0 °C. Then 47 % H_2O_2 (2170 mg, 30.0 mmol, diluted with 10 mL CH_3CN) was added dropwise

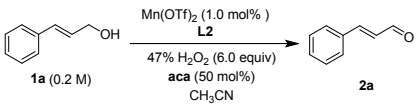
to the stirring reaction over 1 h and the mixture was stirred at room temperature for another 2 h, the reaction was quenched by adding the sat. aq. $NaHCO_3$ (20 mL), and extracted with EtOAc (20 mL× 5). The organic layer was separated and washed with brine, dried over $MgSO_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the **2c** (872 mg, 88% yield).

Determination of the KIE value.

A solution of $Mn(OTf)_2$ (0.008 M solution in CH $_3$CN, 0.25 mL, 0.002 mmol) was added to **L2** (0.008 M solution in CH_3CN, 0.25 mL, 0.002 mmol) at room temperature. The reaction mixture was stirred at room temperature for 8 h. To the solution of manganese complex was directly added 1-phenylethanol or (0.2 mmol) and CH_3CN (0.5 mL) and the mixture was cooled to 0 °C. Then 47% H_2O_2 (86.8 mg, 1.2 mmol, diluted with 1.0 mL CH_3CN) was directly added and the mixture was stirred at 0 °C for 10 min. At this point, decane was added to the mixture as the internal standard. Then the result was determined by GC and the k_H value could be calculated. The k_D was calculated by the same method as k_H. Finally, the KIE value was calculate by using the equations: KIE= k_H/ k_D.

Screening the ratio of $Mn(TOf)_2$ and ligand.

Table S1 Screening the ratio of $Mn(TOf)_2$ and ligand.



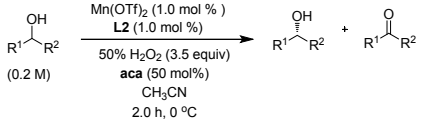
entry	Ligand (mol%)	% yield[a]
1	0.5	71
2	1.5	84

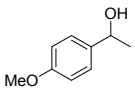
3	2.0	80

[a]Determined by GC.

Oxidative kinetic resolution of the secondary alcohols.

Table S2 Oxidative kinetic resolution of the secondary alcohol



entry	alcohol	conversion/%[a]	ee/%[b]
1		60	8
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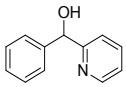
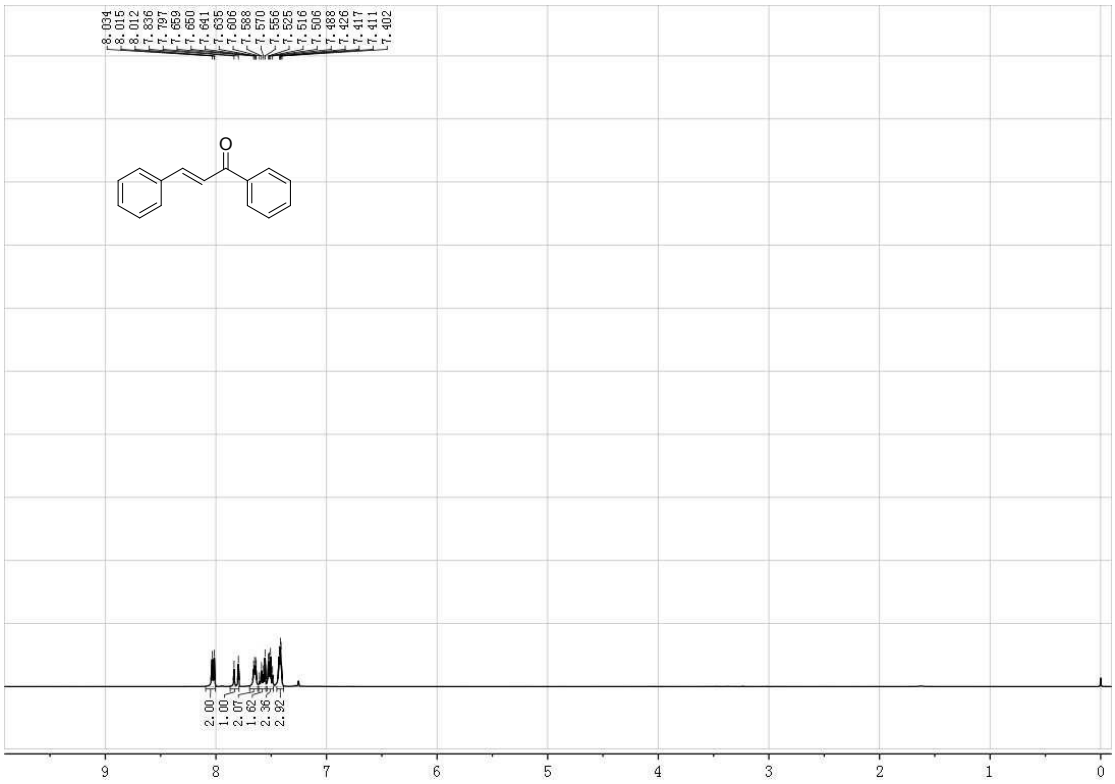
3		59	58

[a]Determined by GC. [b]Determined by chiral HPLC analysis.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7.516
7.506
7.488
7.426
7.417
7.411
7.402
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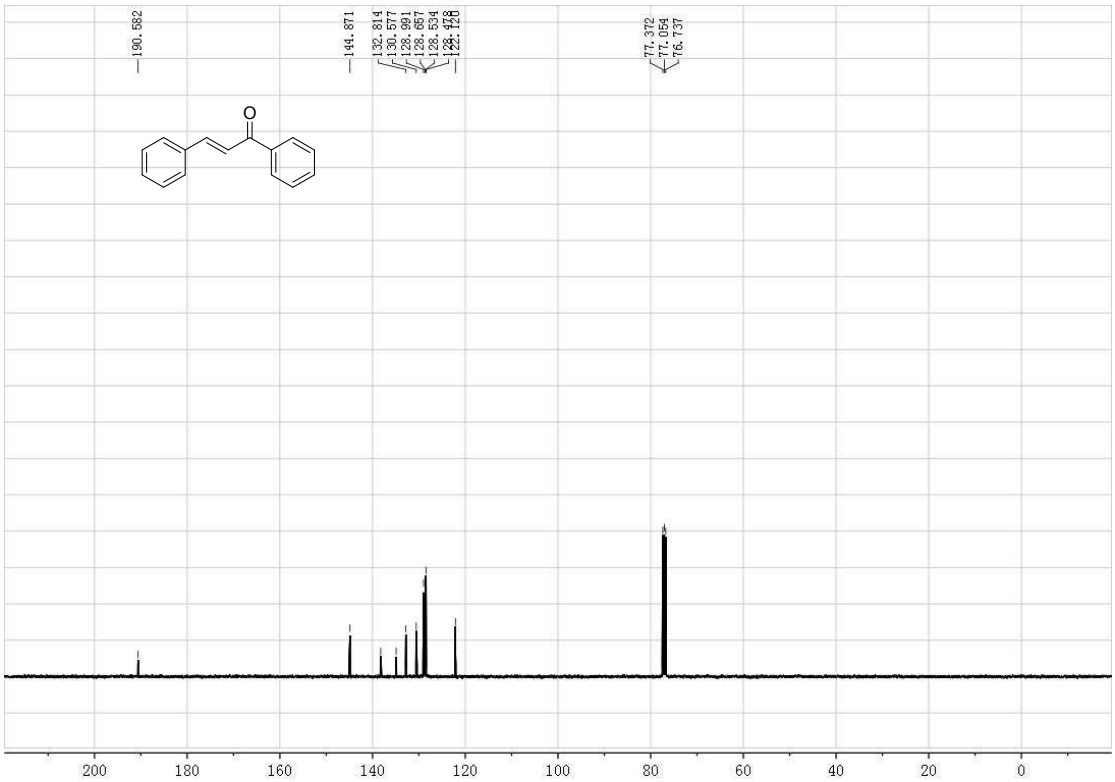
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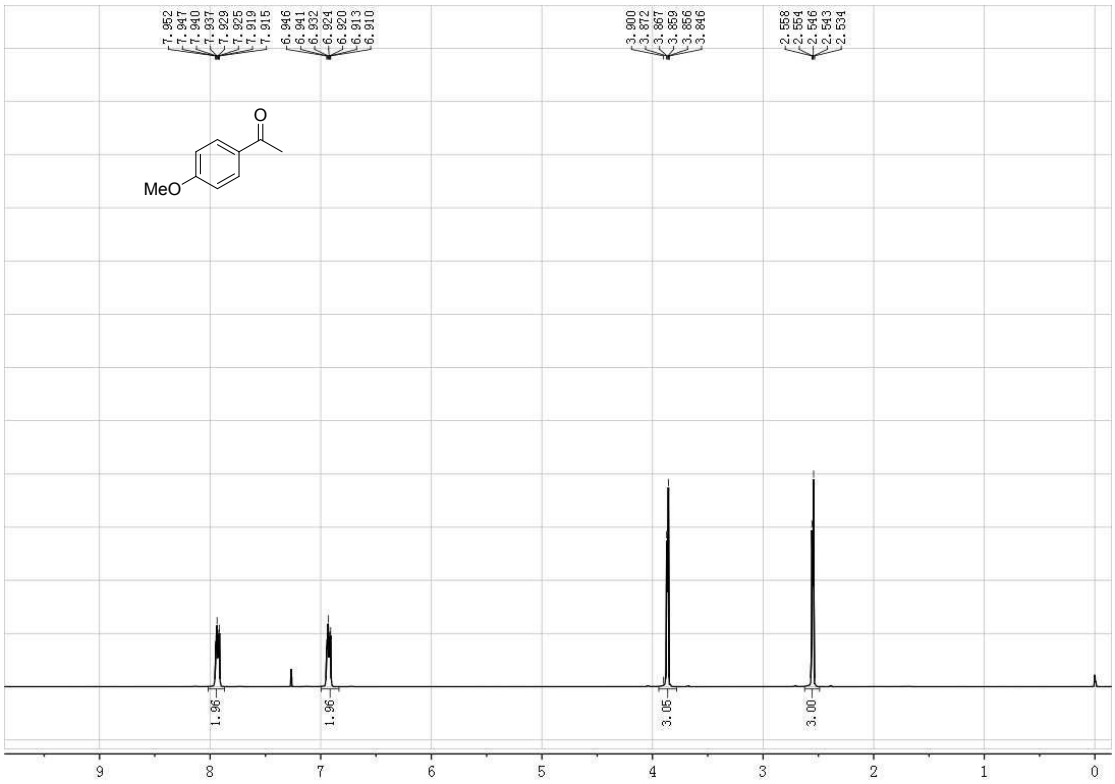
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6.910
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3.856
3.846
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2.554
2.546
2.543
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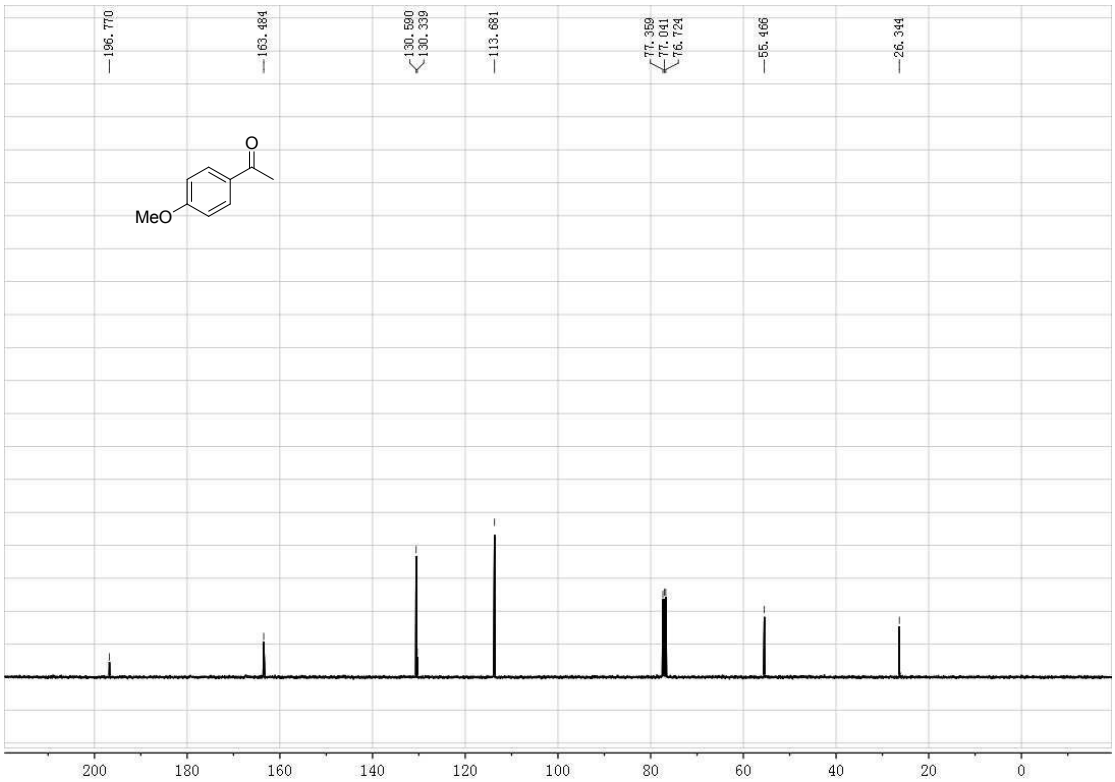
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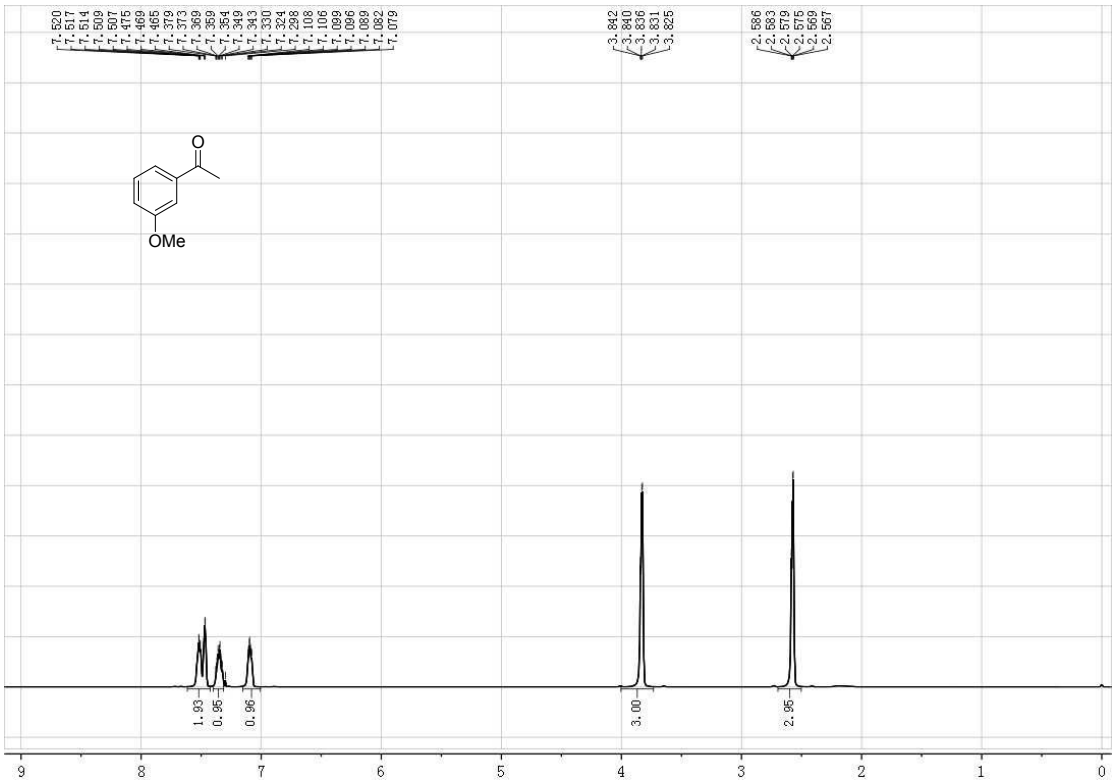
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7.106
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7.086
7.082
7.079
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3.840
3.836
3.831
3.825
2.586
2.583
2.579
2.575
2.569
2.567
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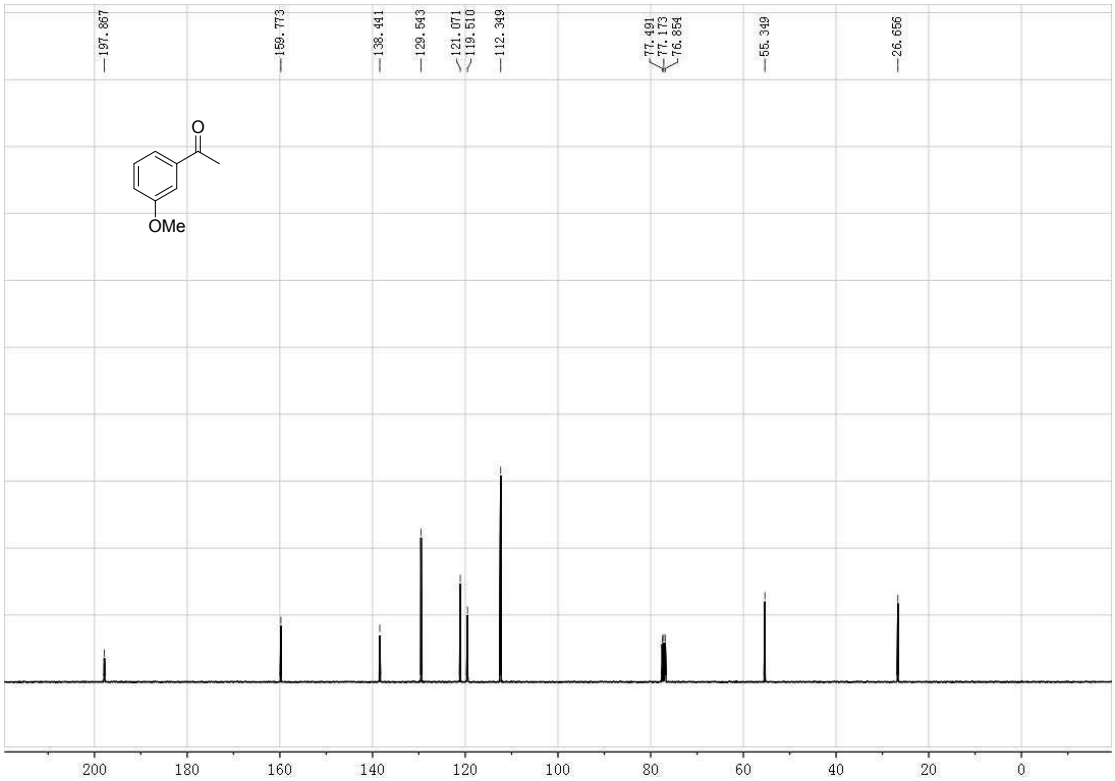
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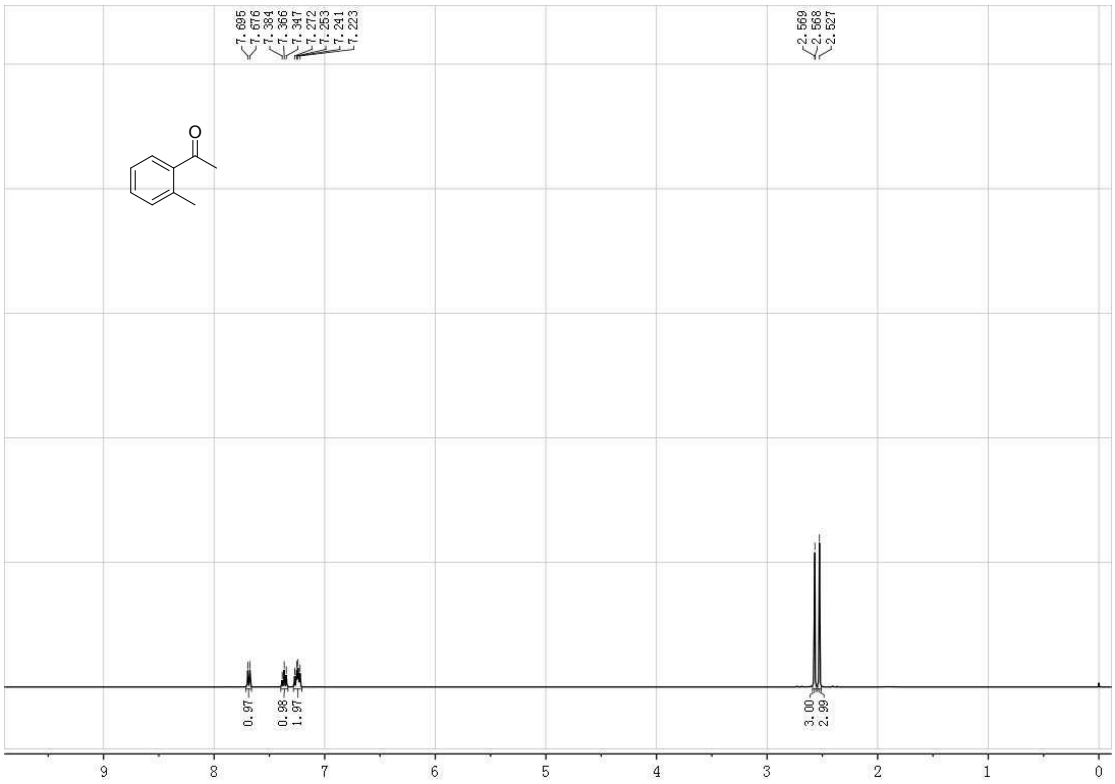
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7.241
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2.99
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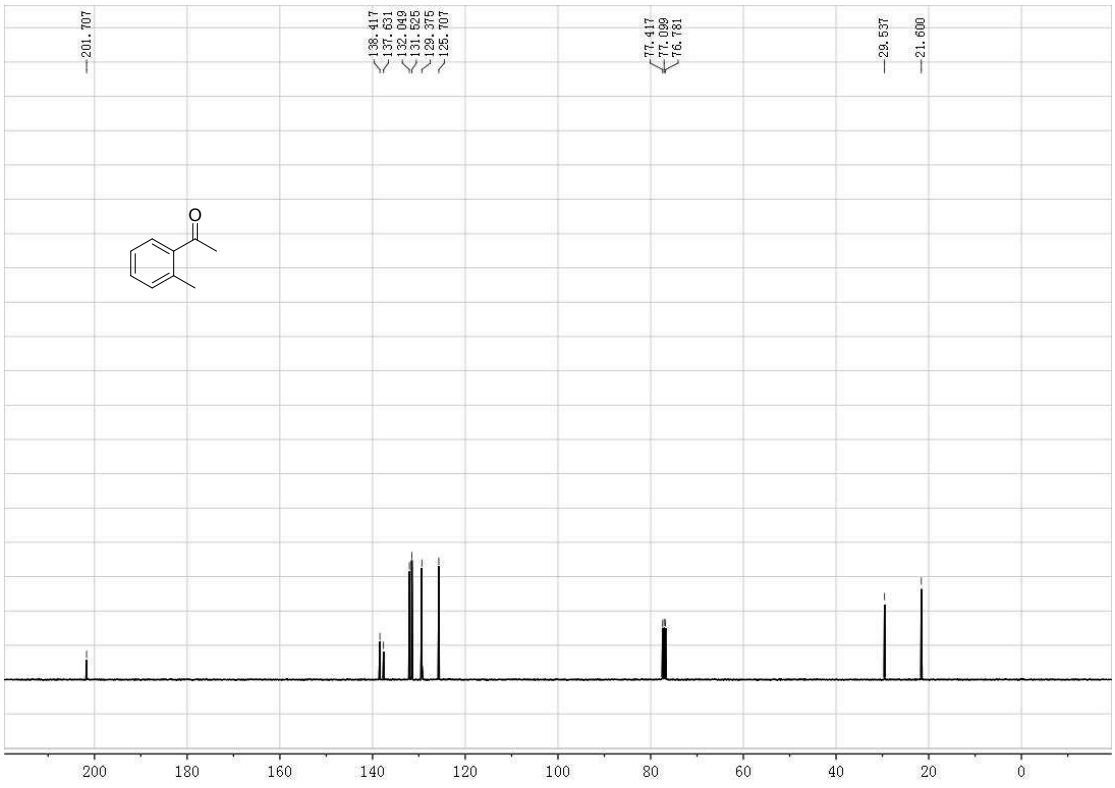
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77.099
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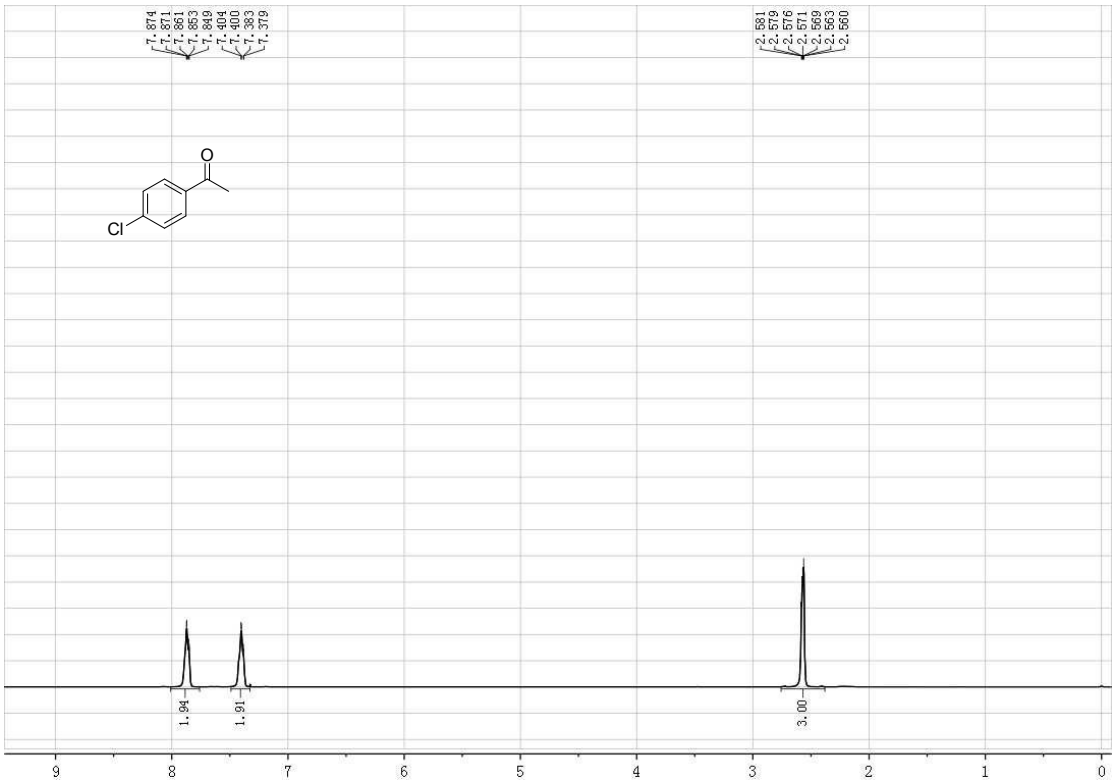
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2.569
2.563
2.560
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Cl
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1.91
3.00
9
8
7
6
5
4
3
2
1
0


196.655
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129.678
128.794
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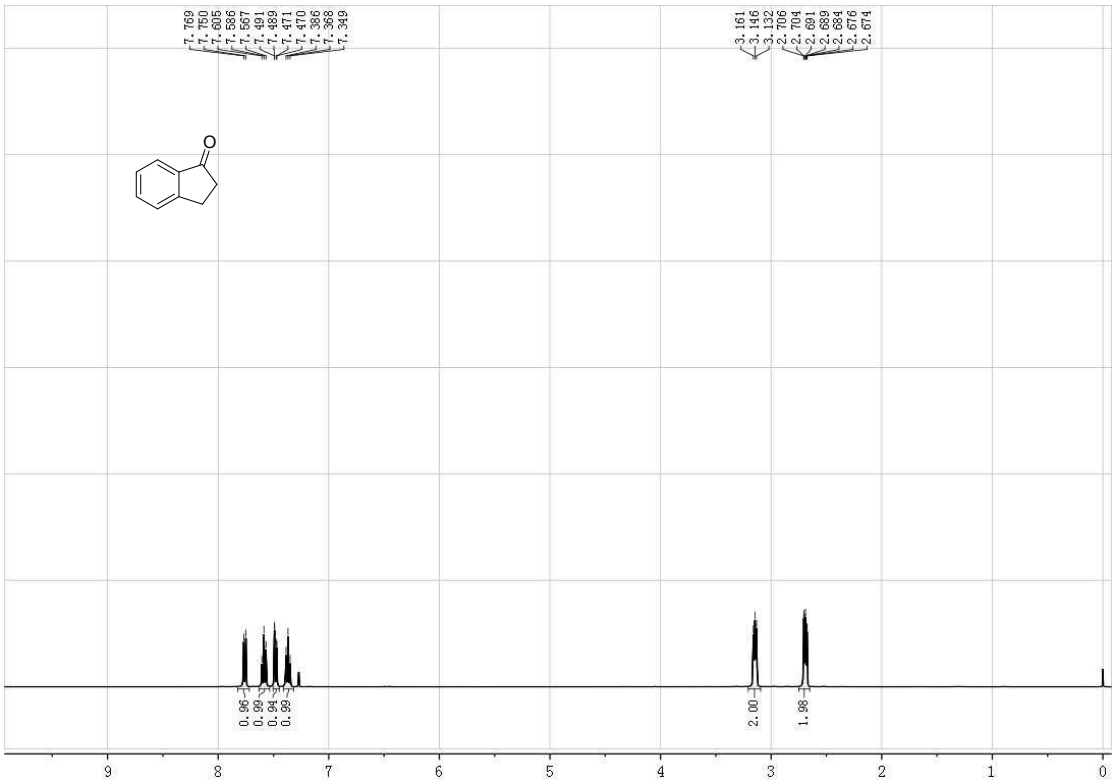
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3.146
3.132
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2.704
2.691
2.689
2.684
2.676
2.674
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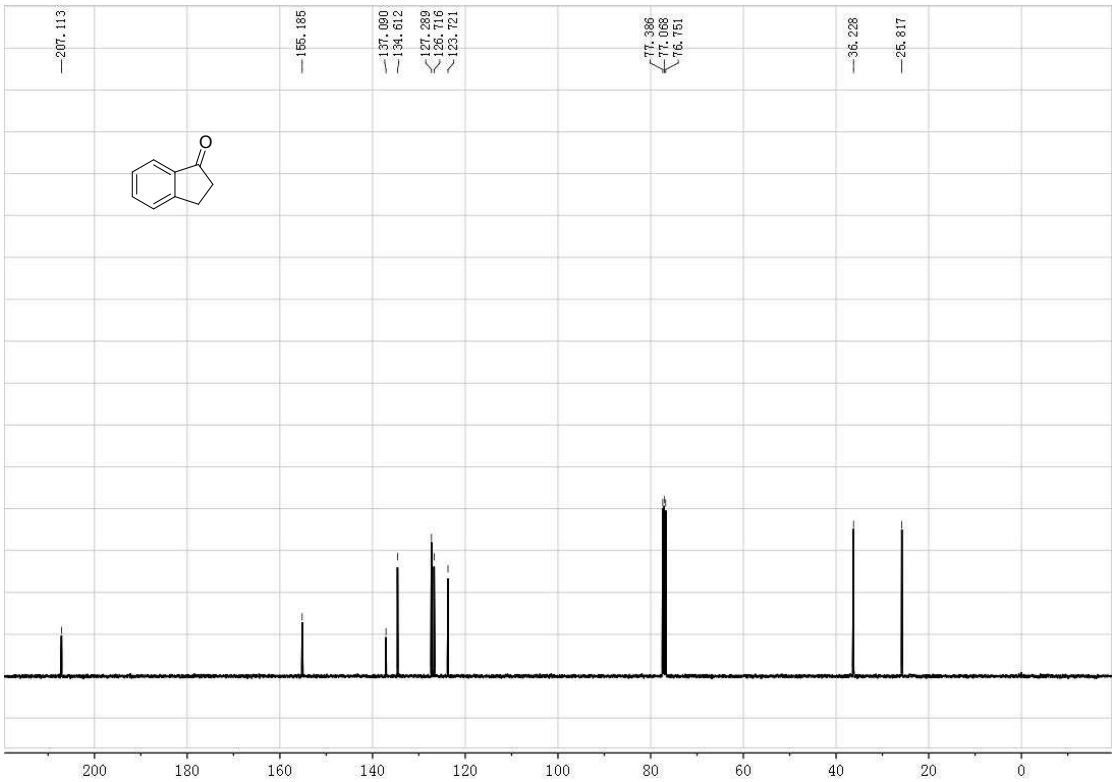
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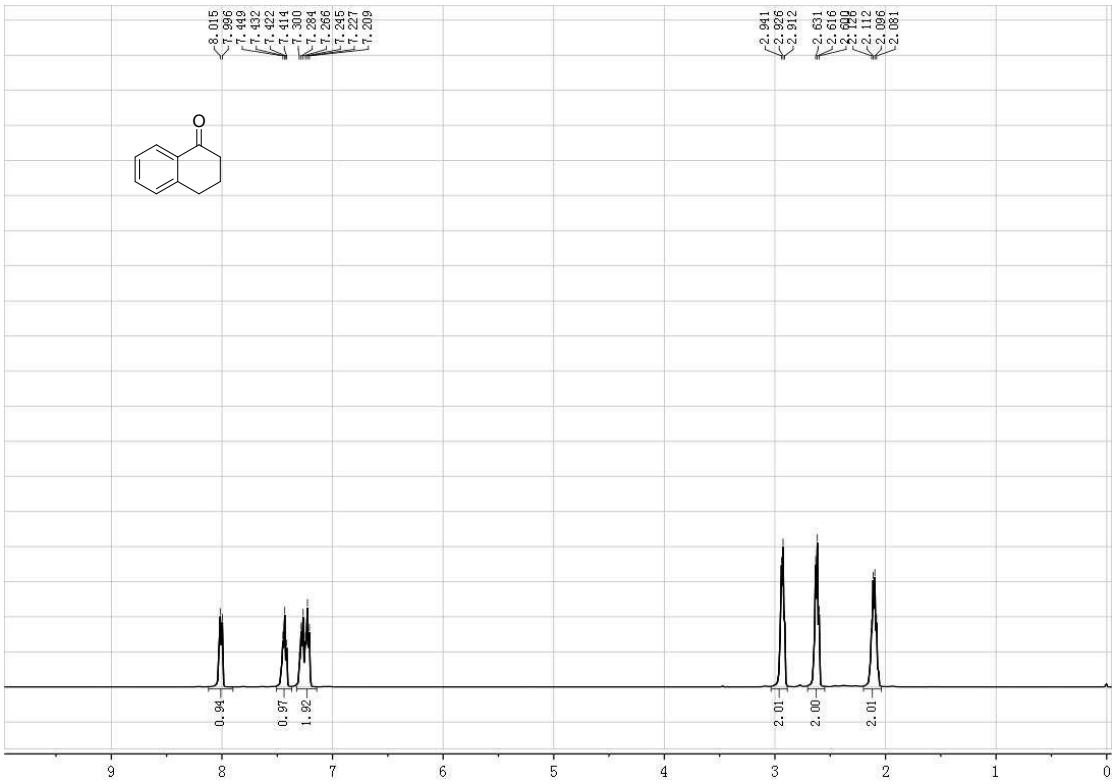
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2.926
2.912
2.631
2.616
2.112
2.096
2.081
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2.01
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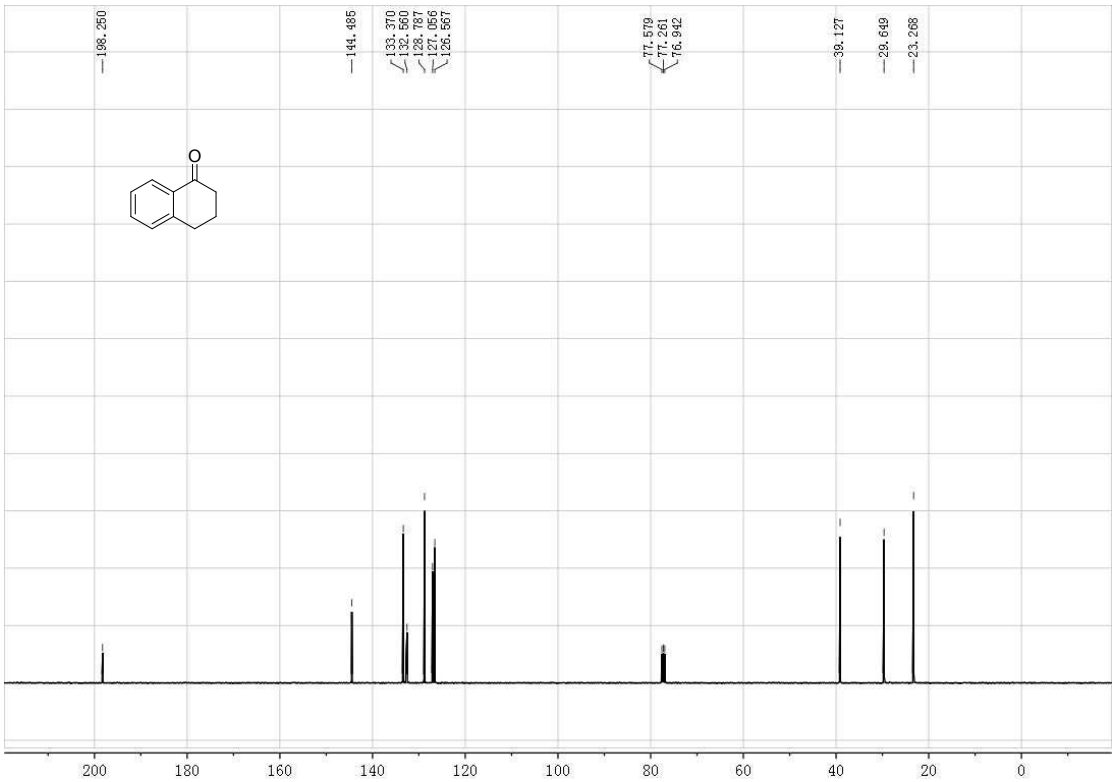
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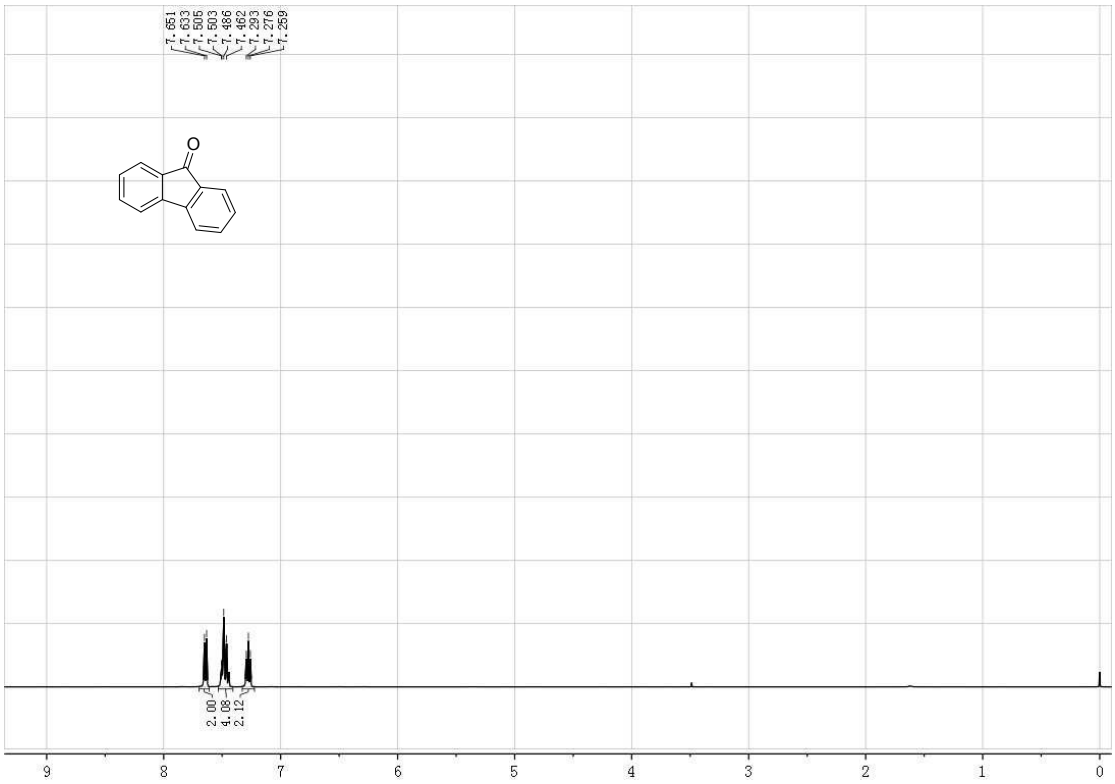
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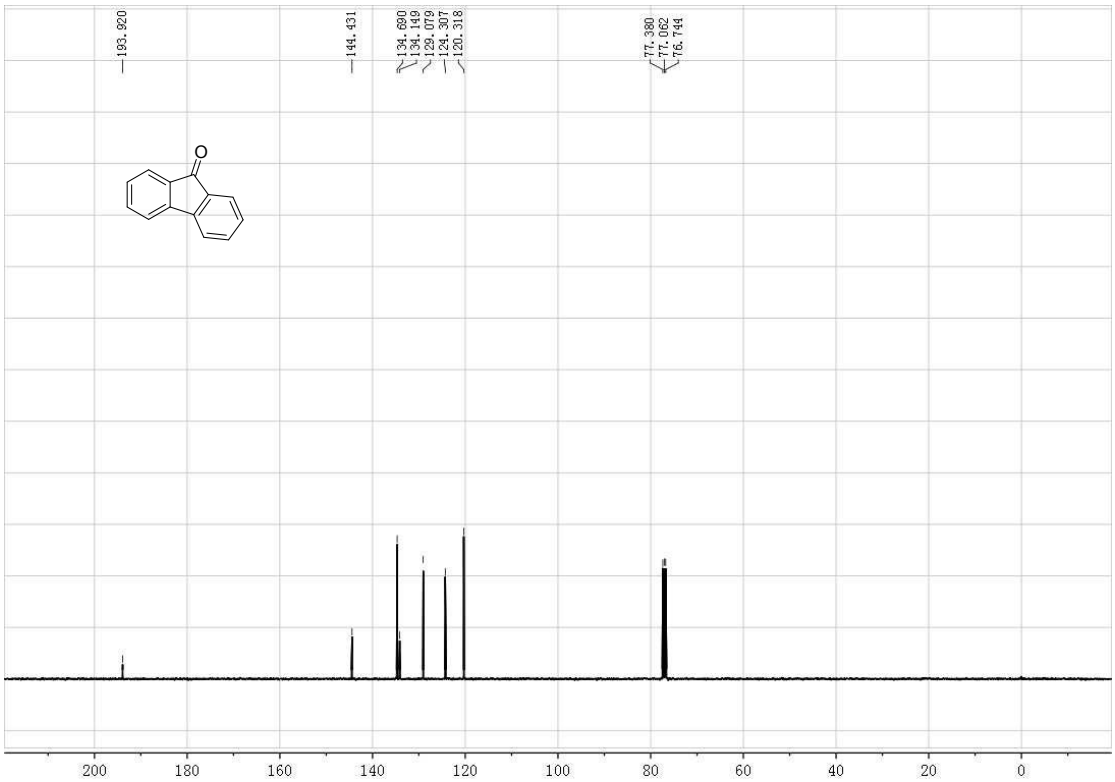
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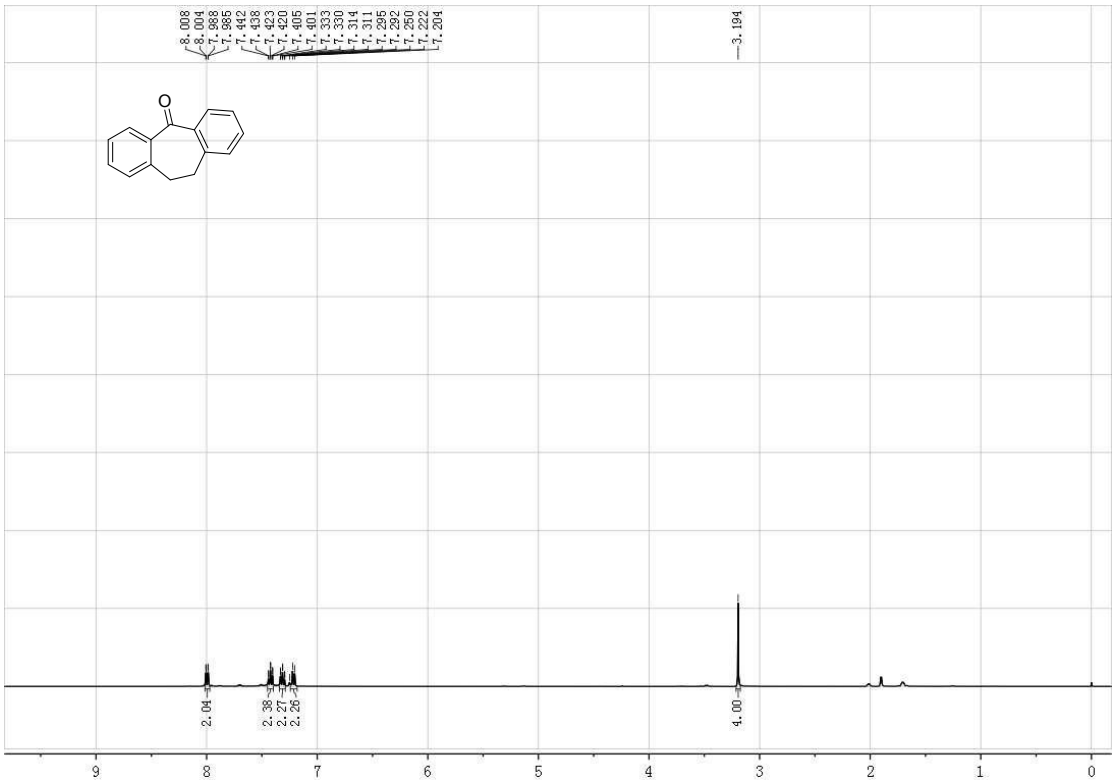
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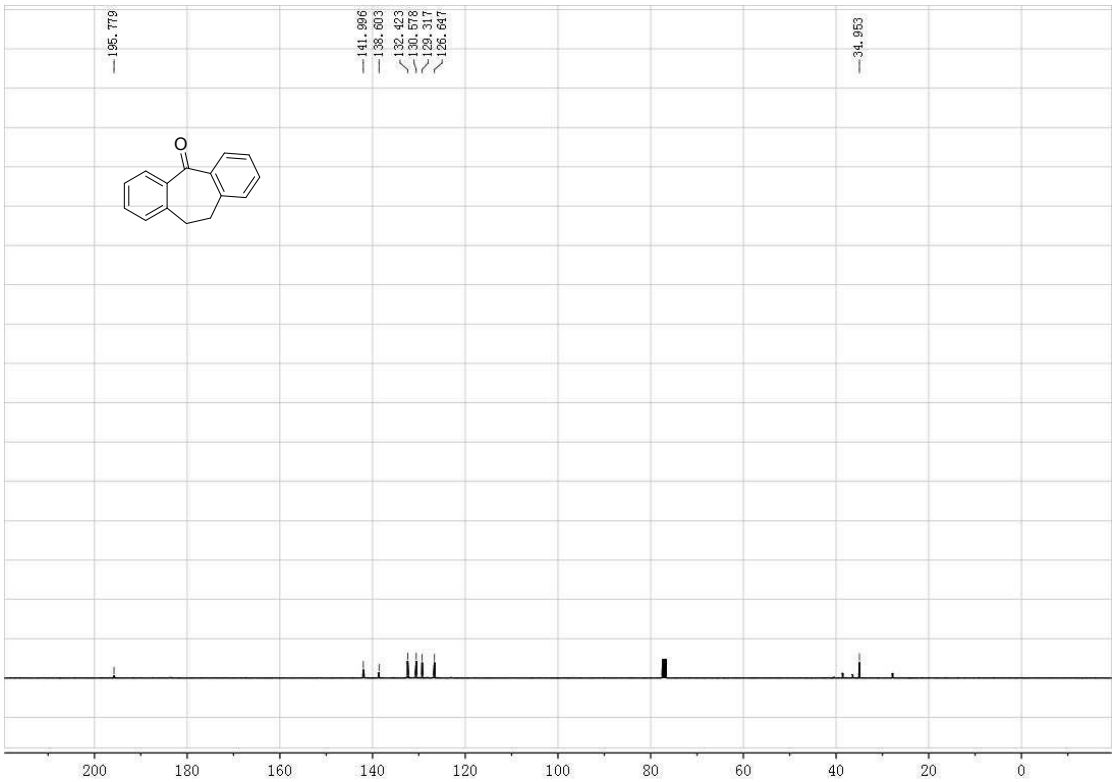
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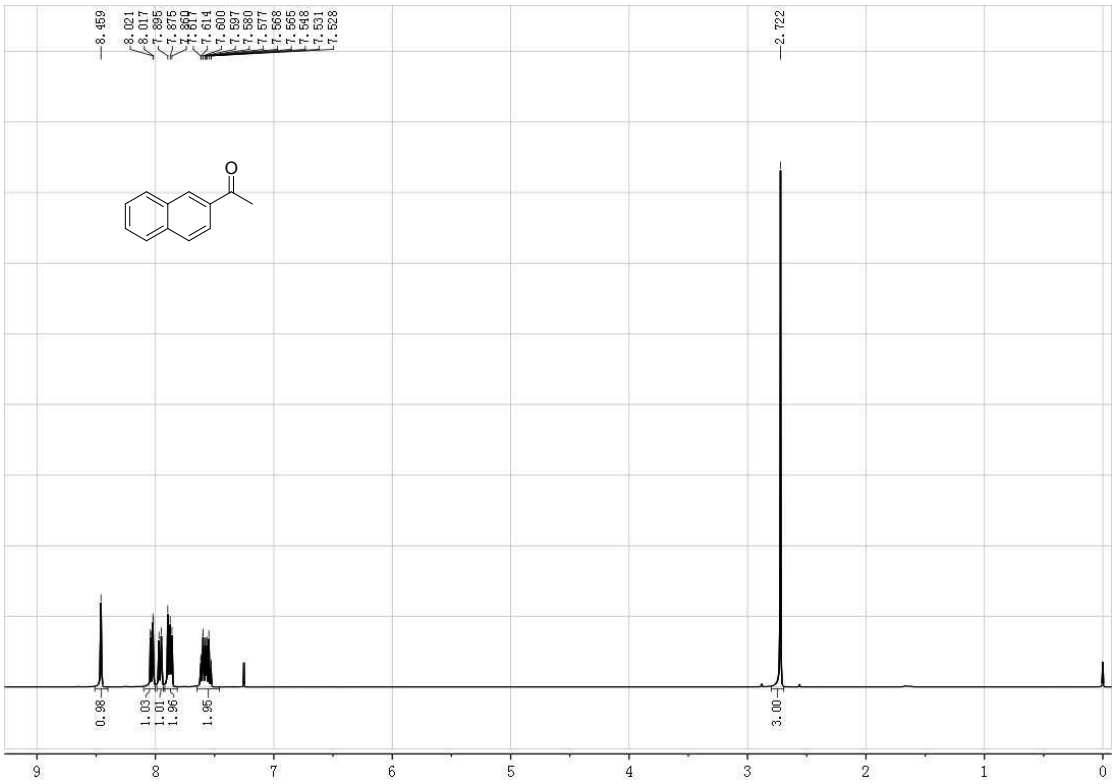
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7.548
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7.528
2.722
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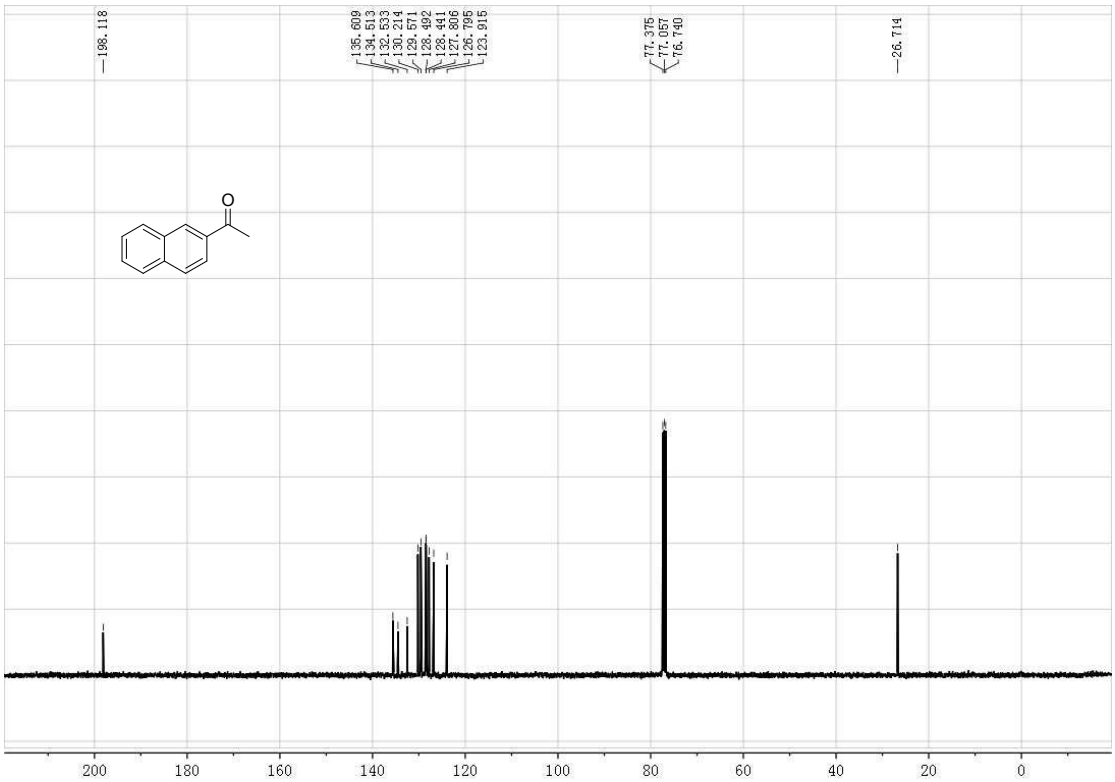
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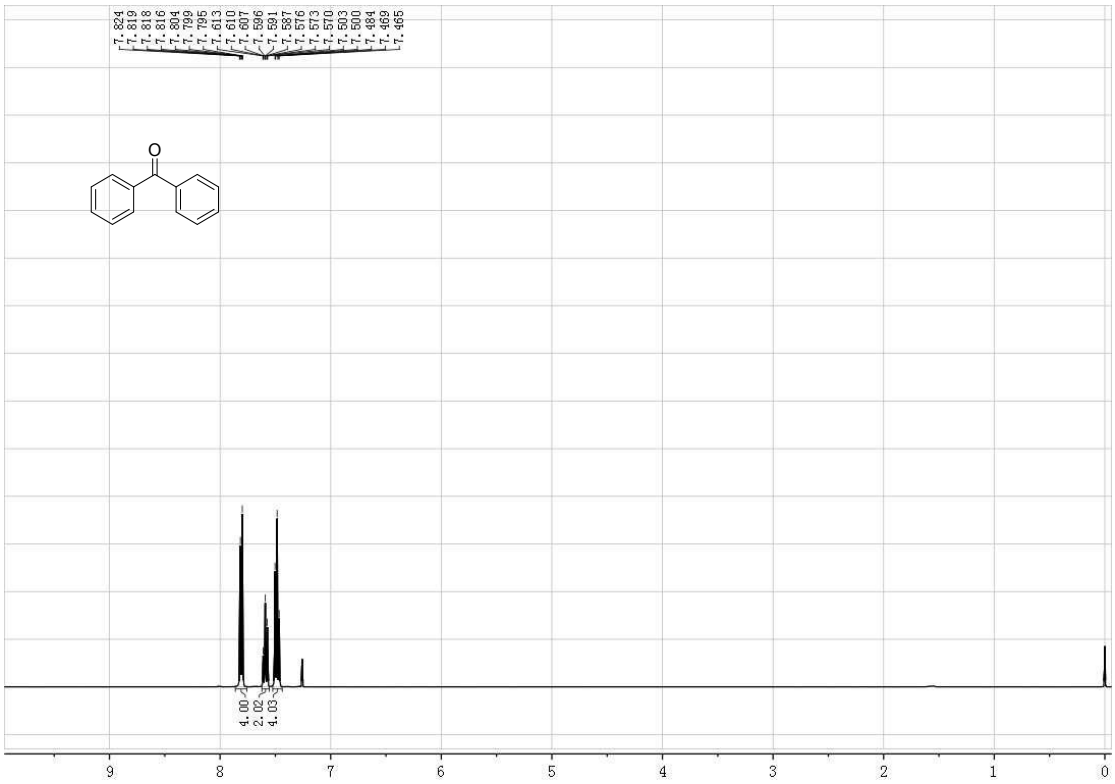
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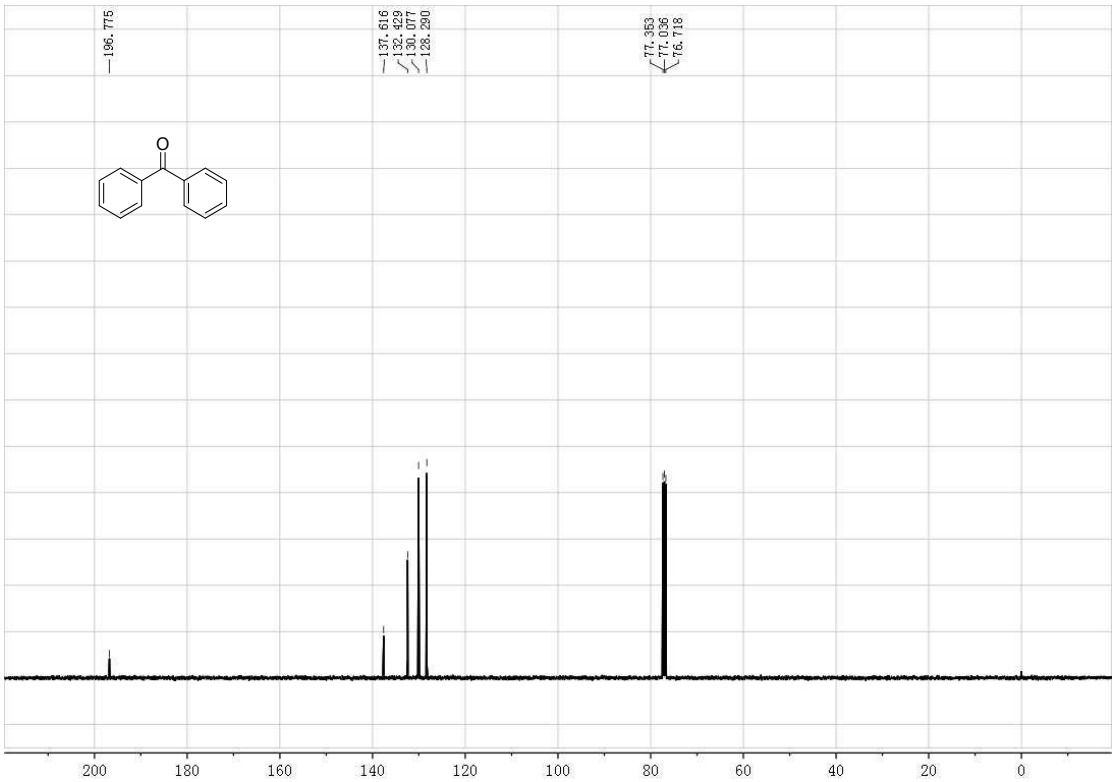
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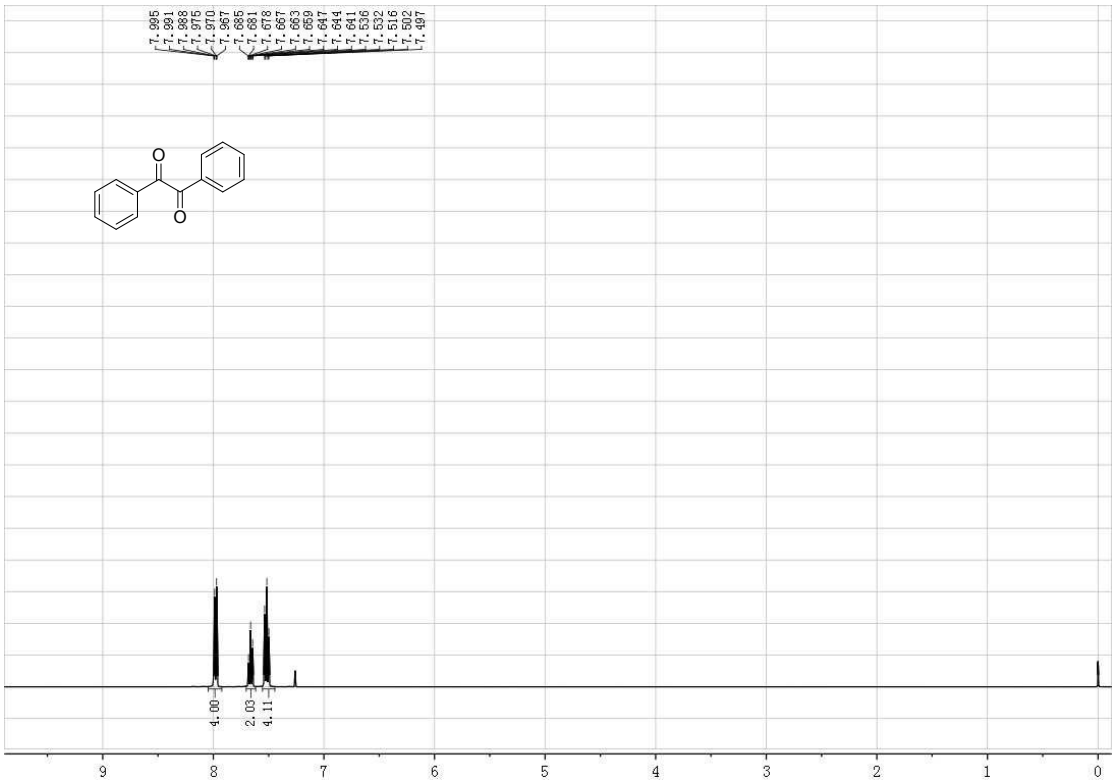
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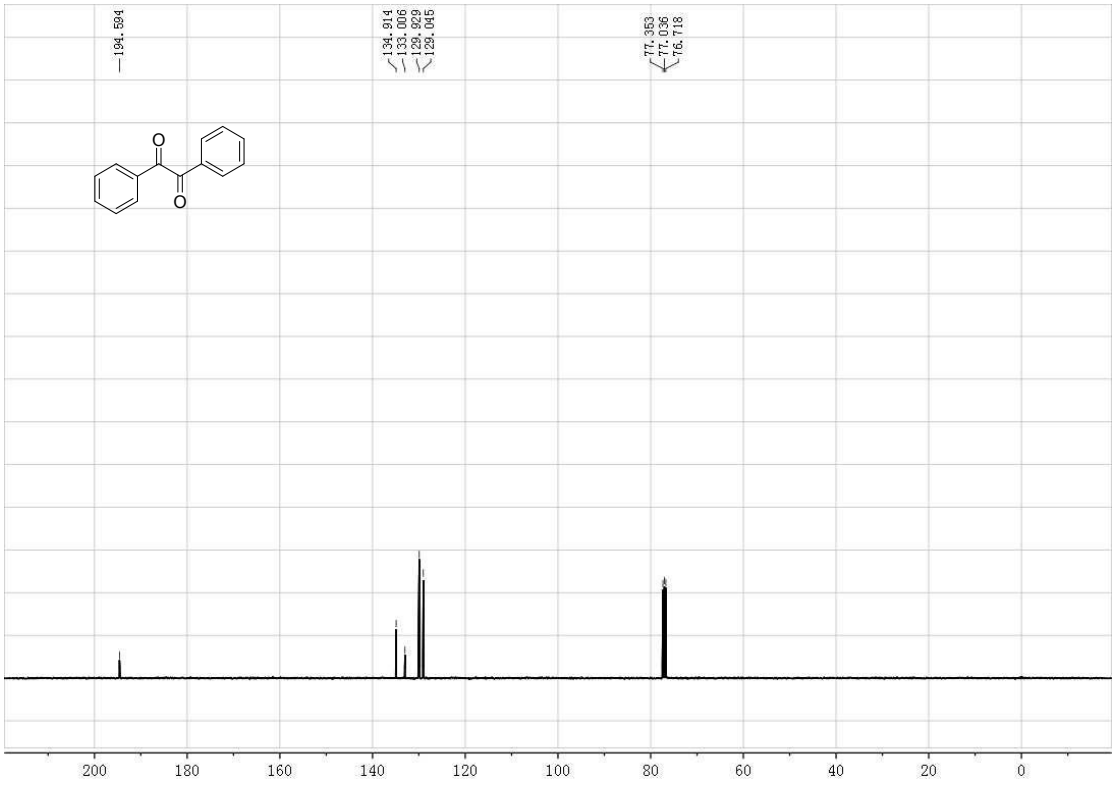
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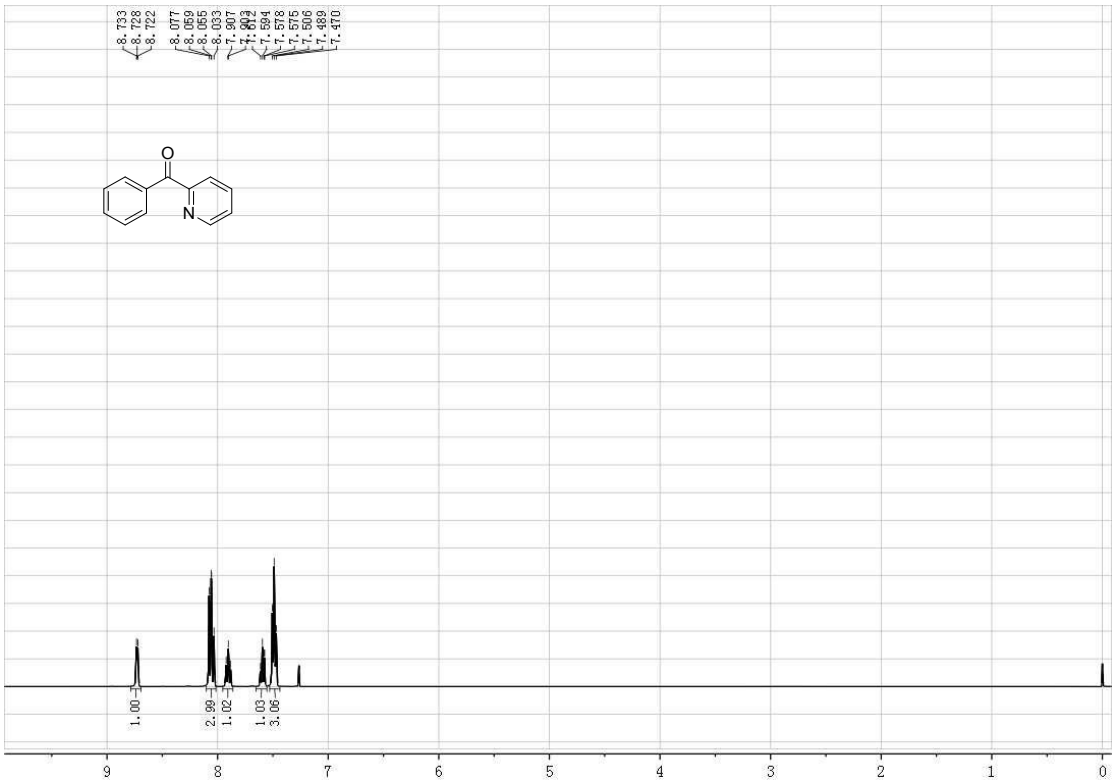
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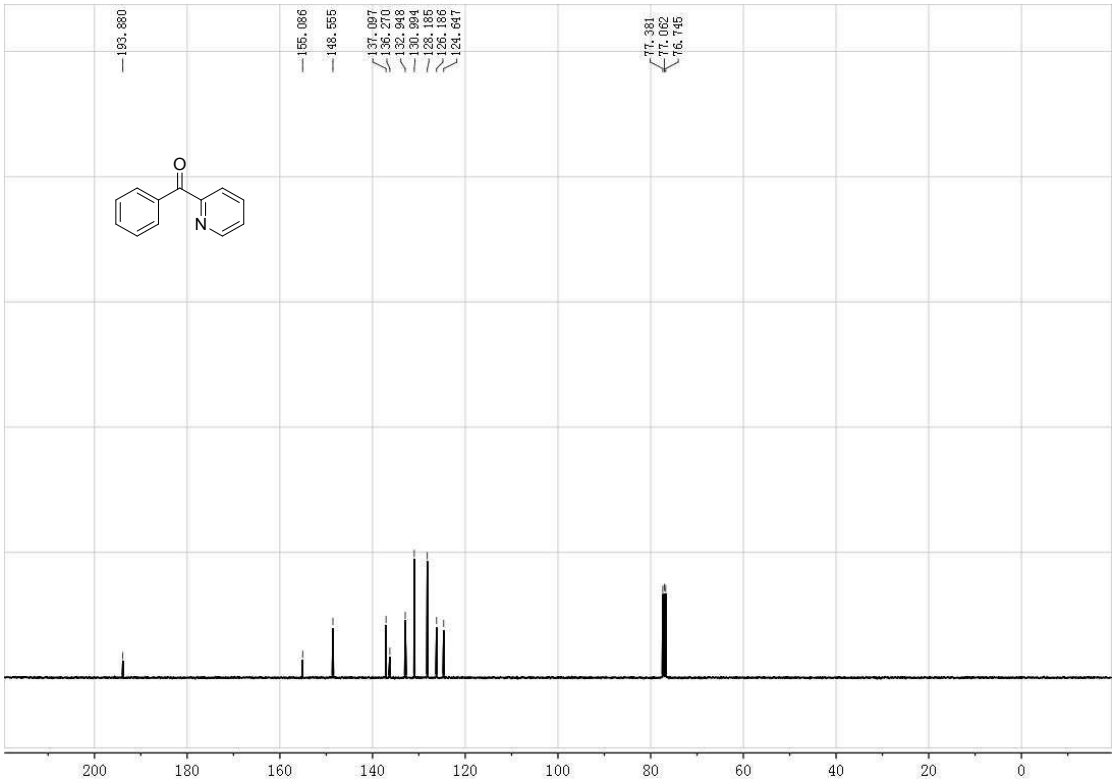
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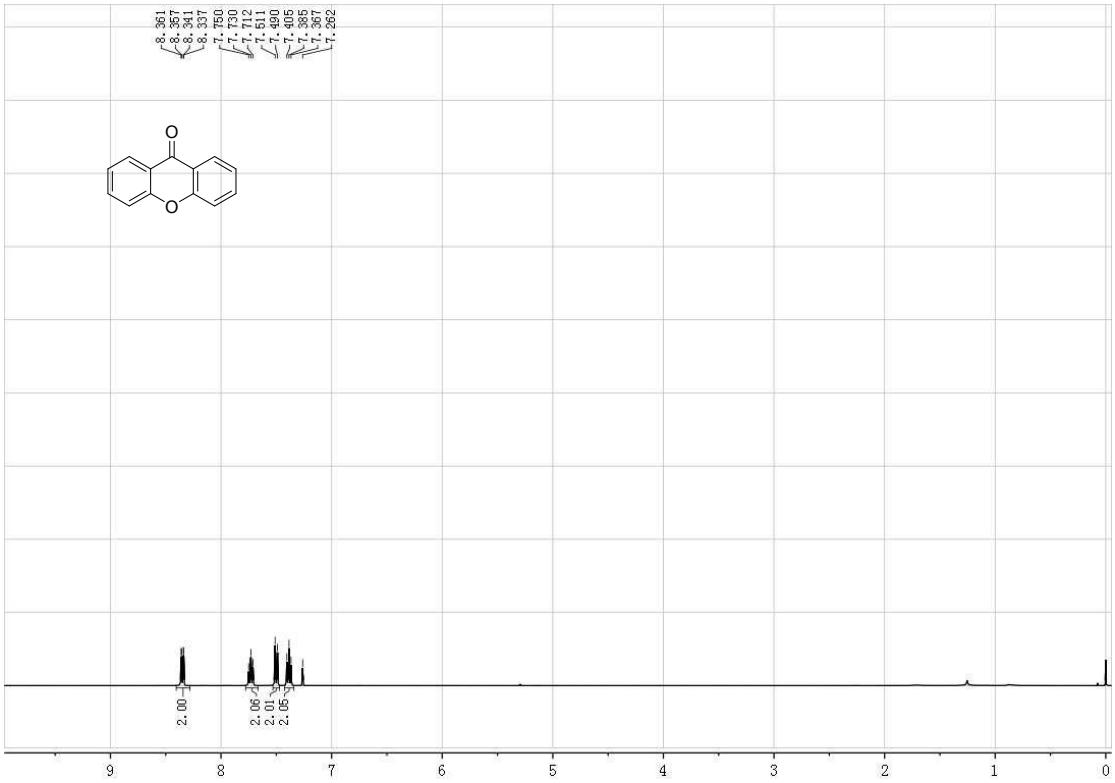
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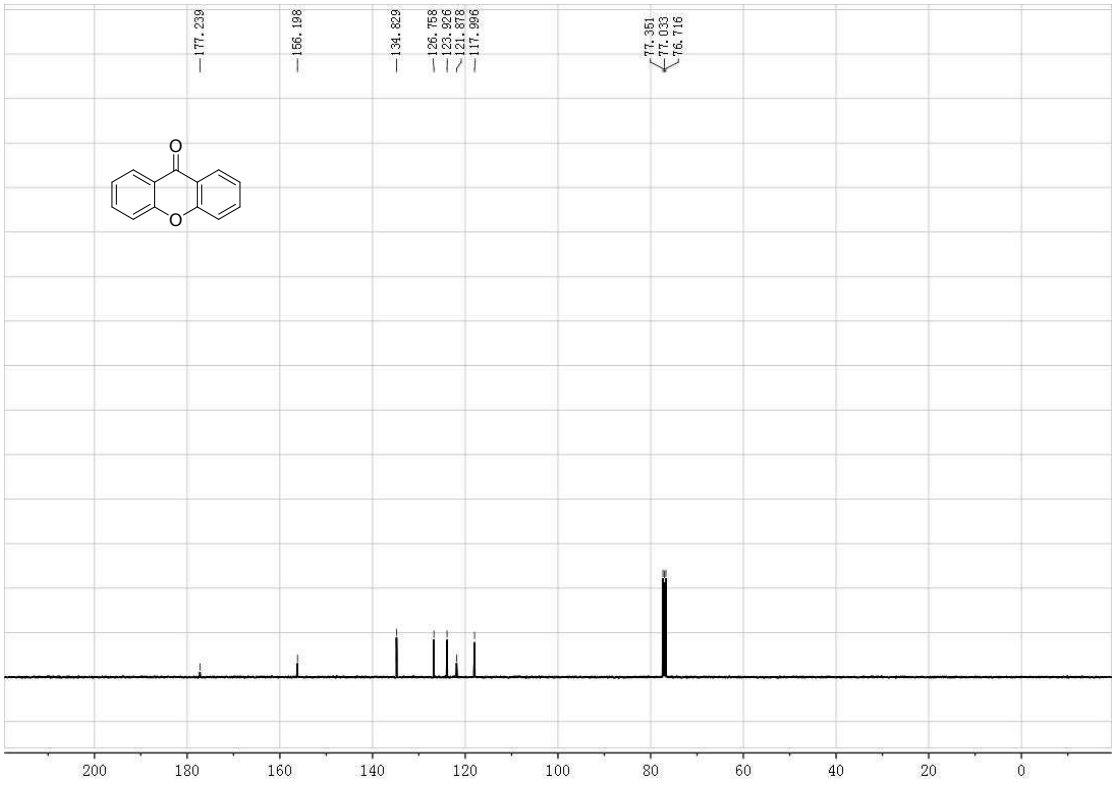
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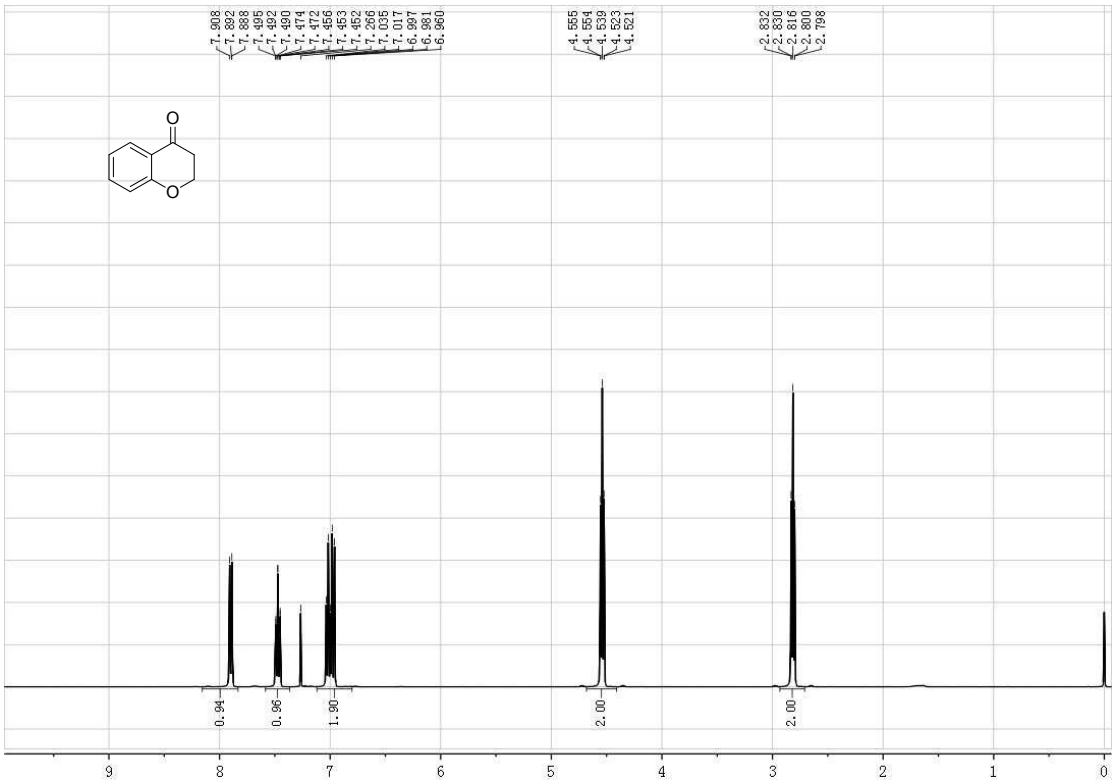
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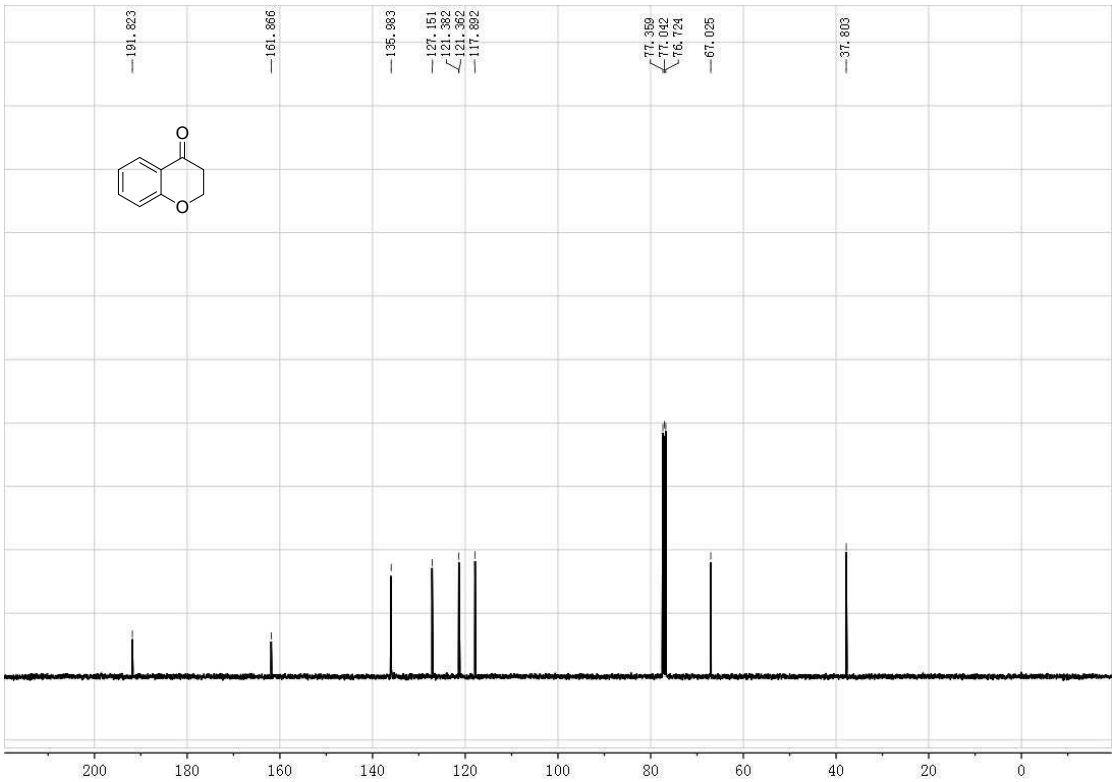
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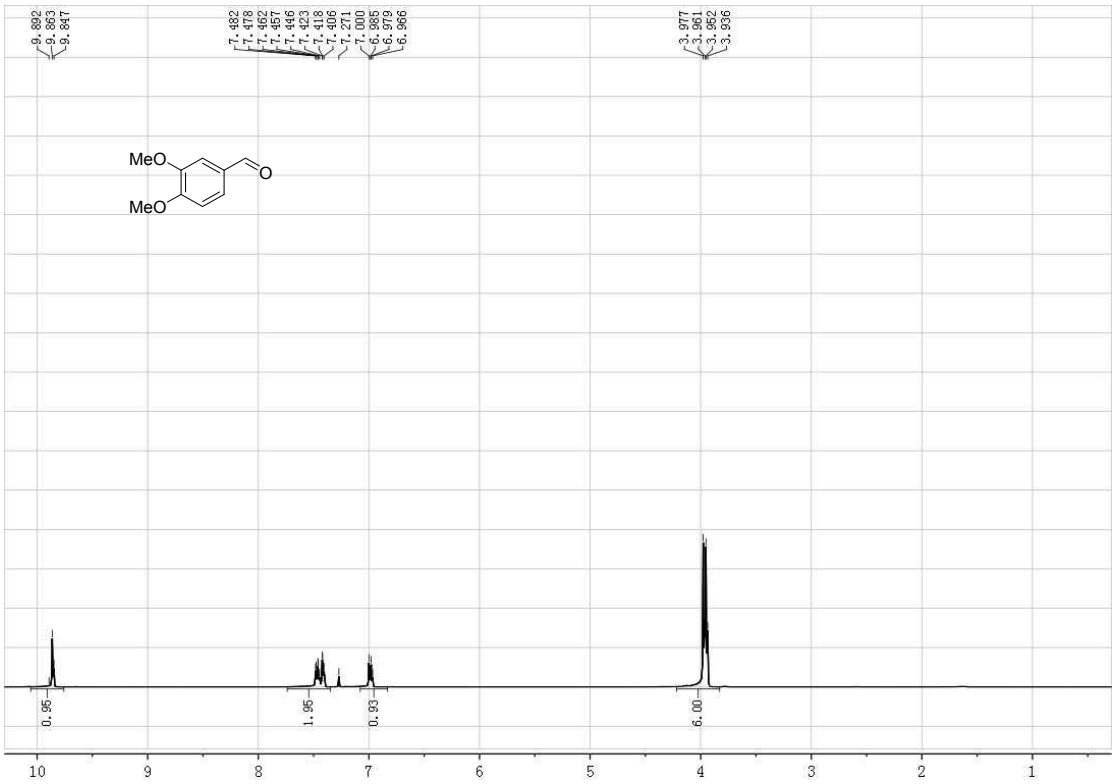
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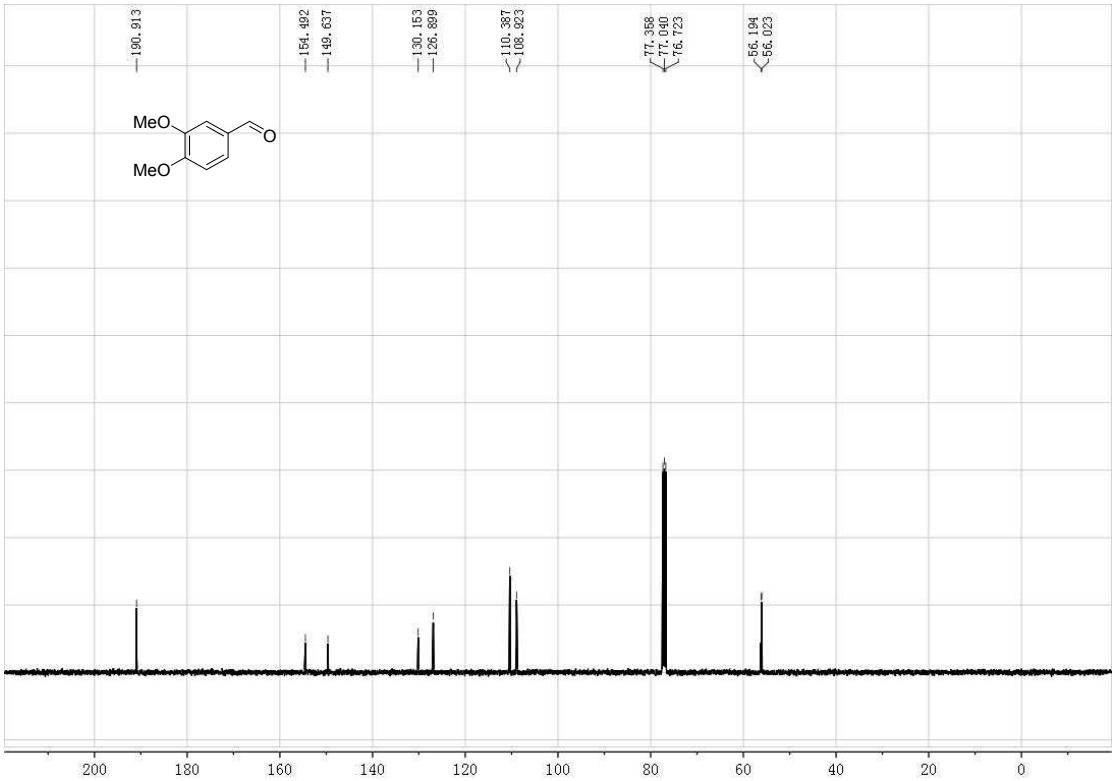
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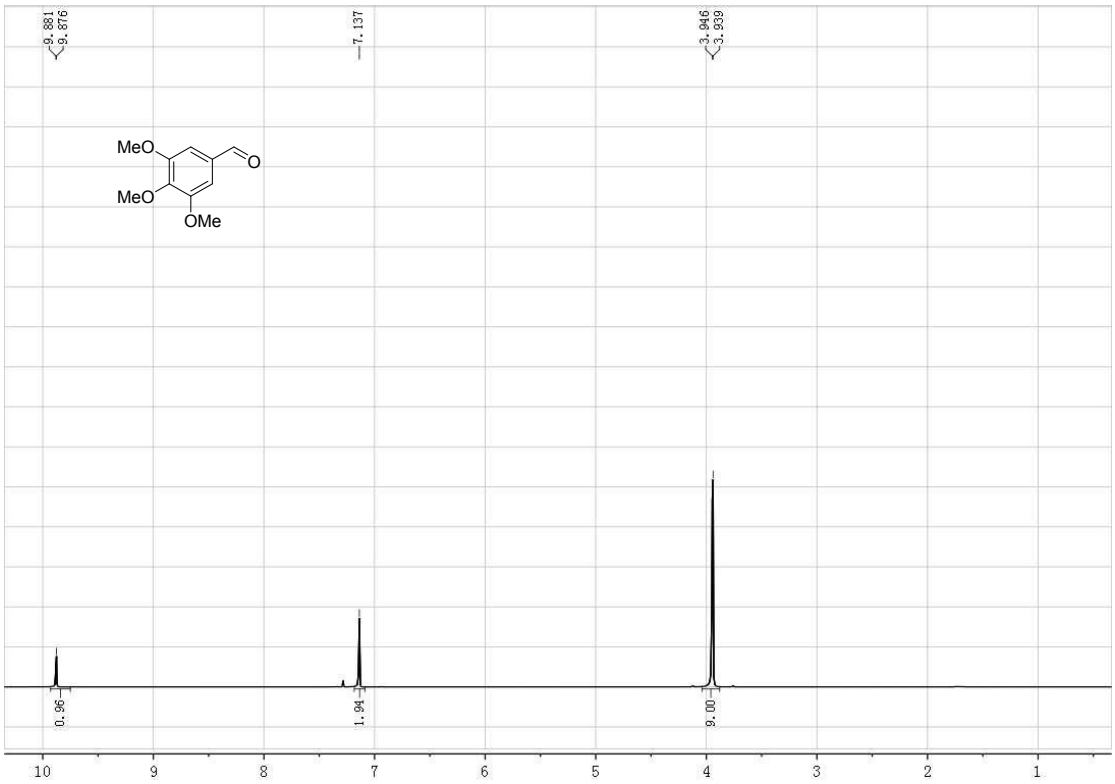
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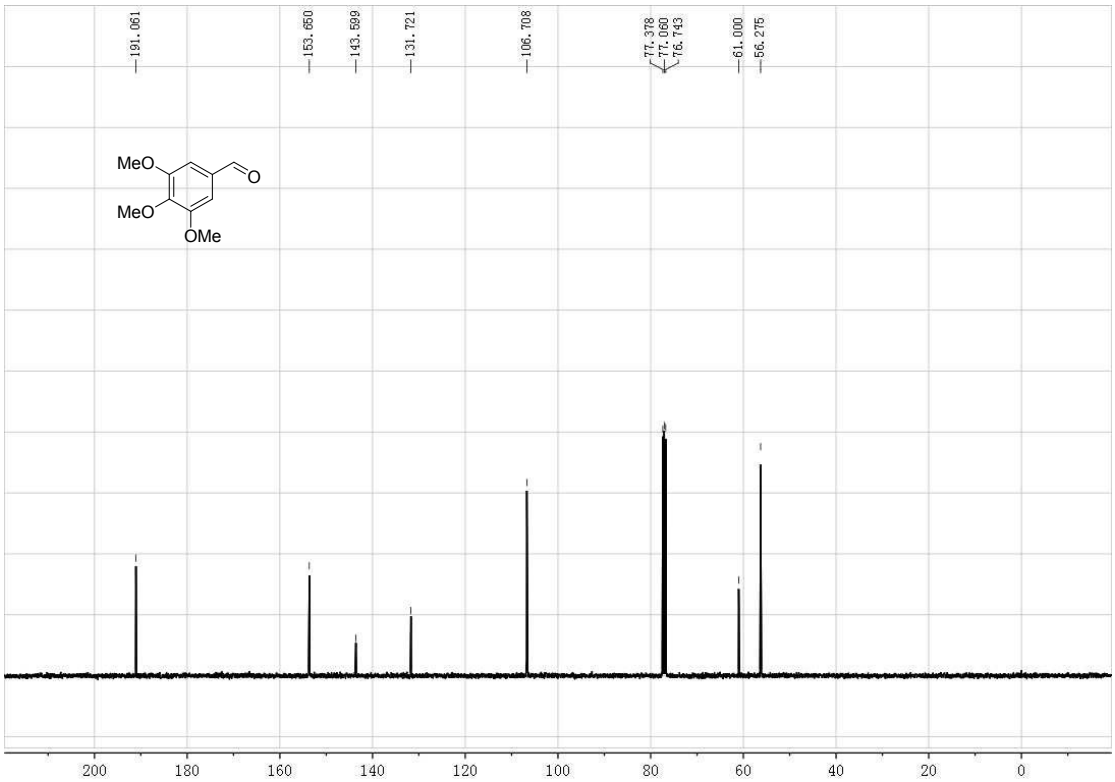
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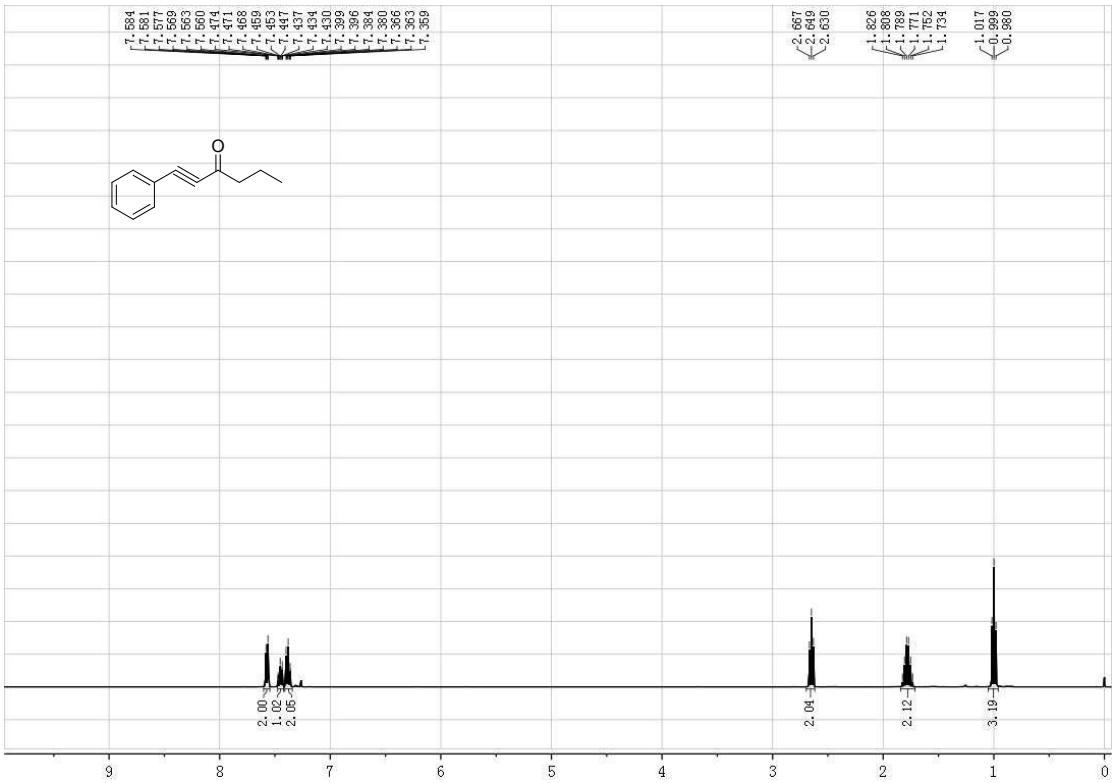
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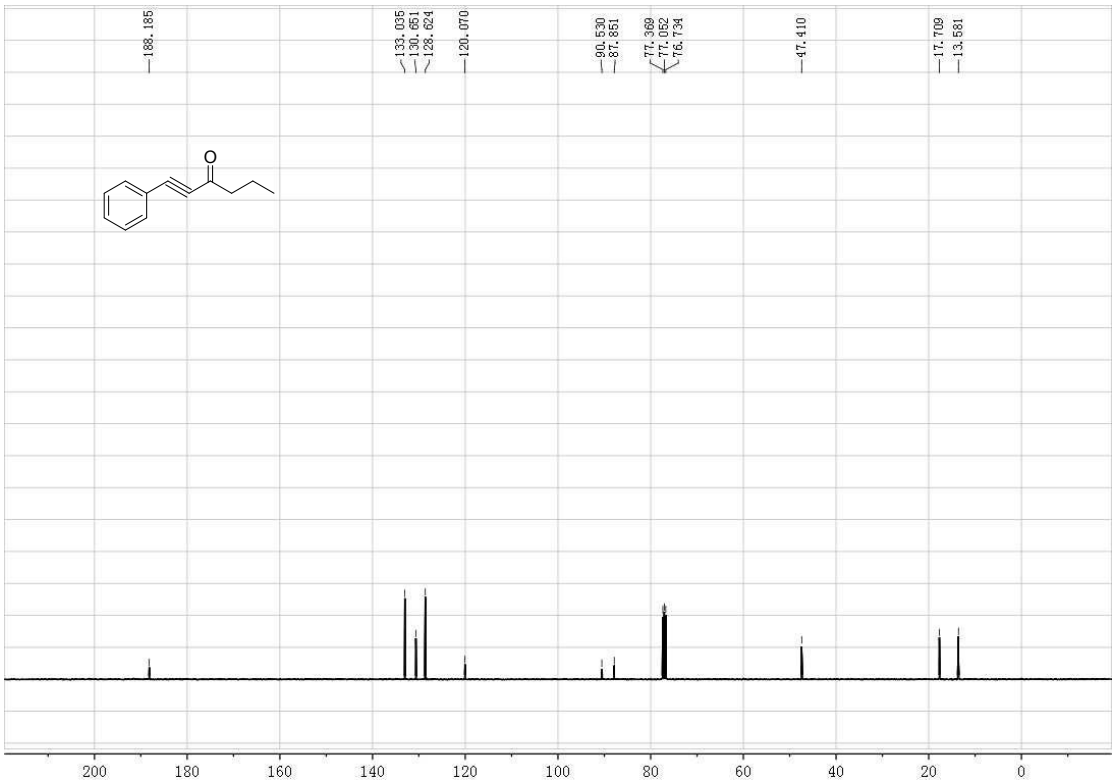
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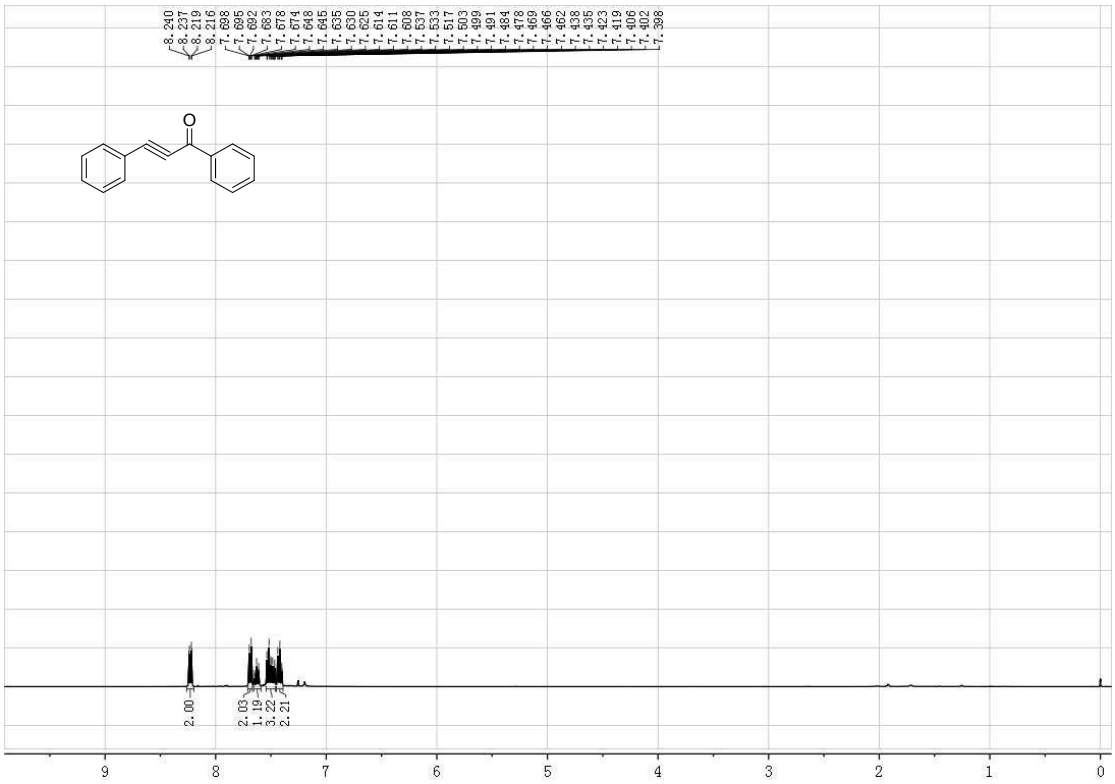
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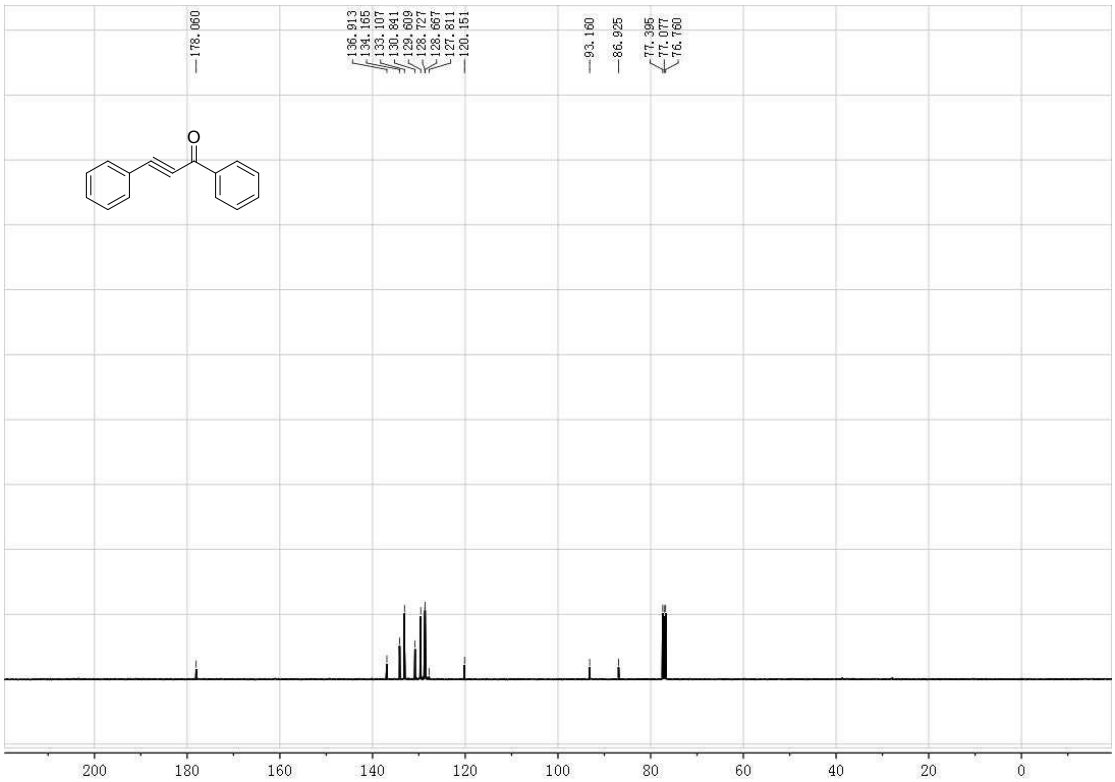
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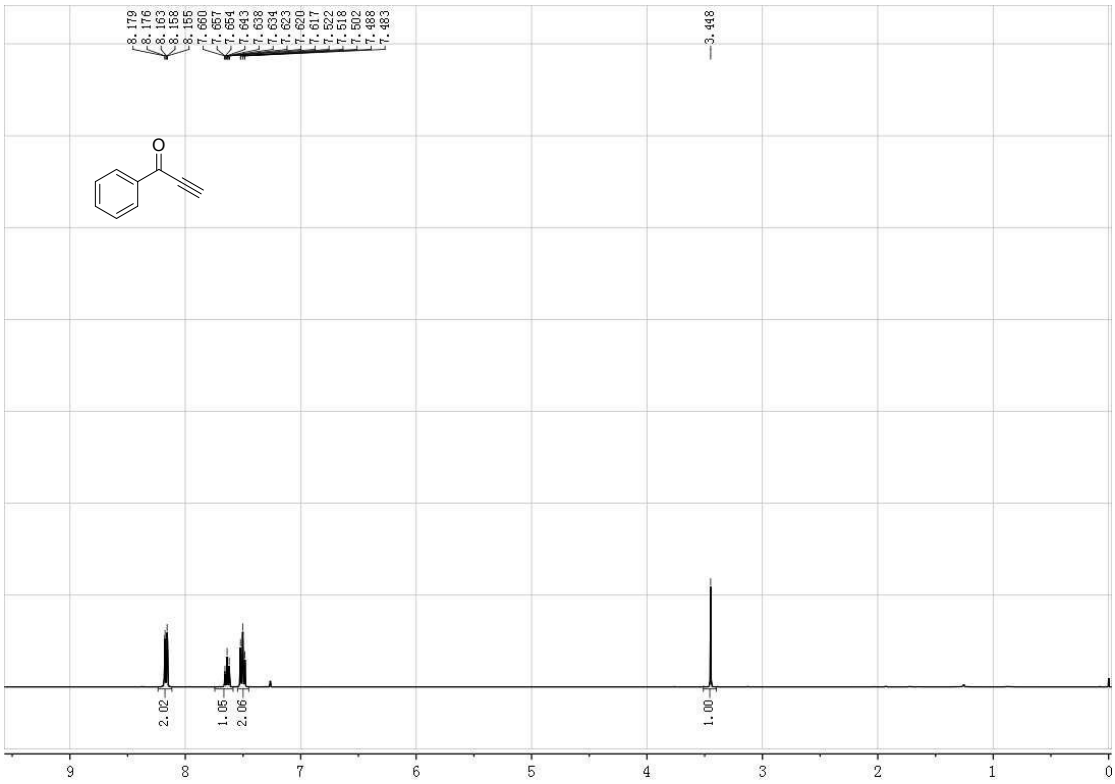
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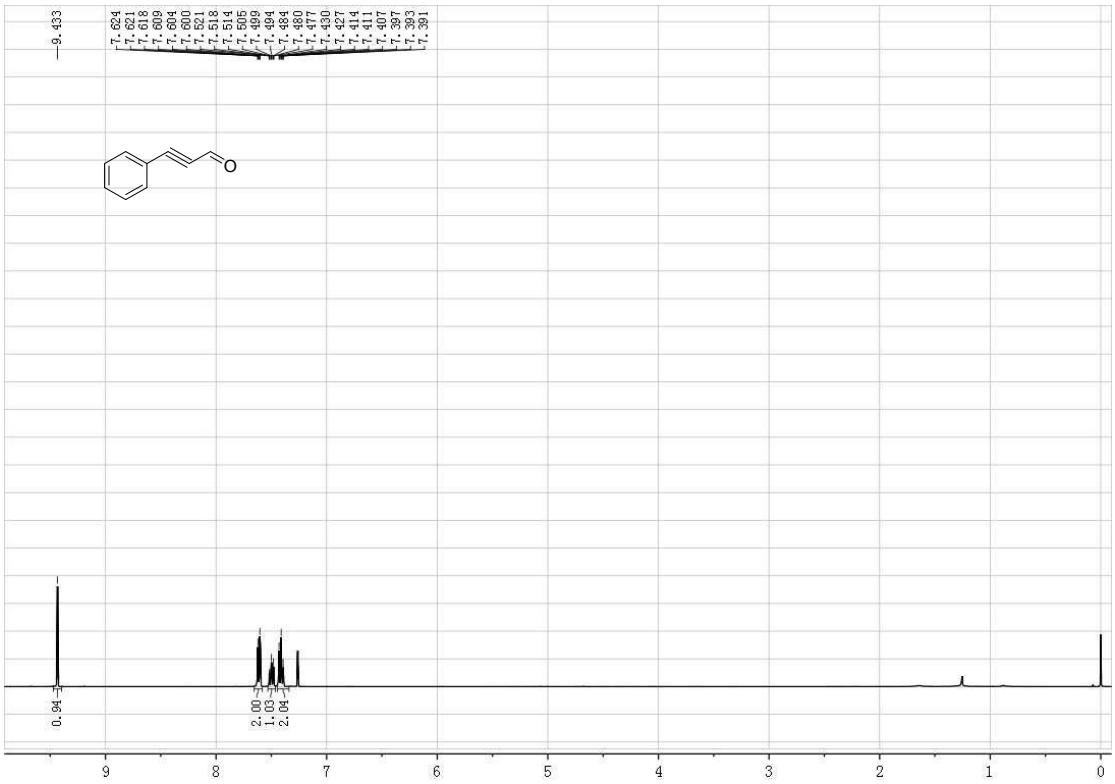
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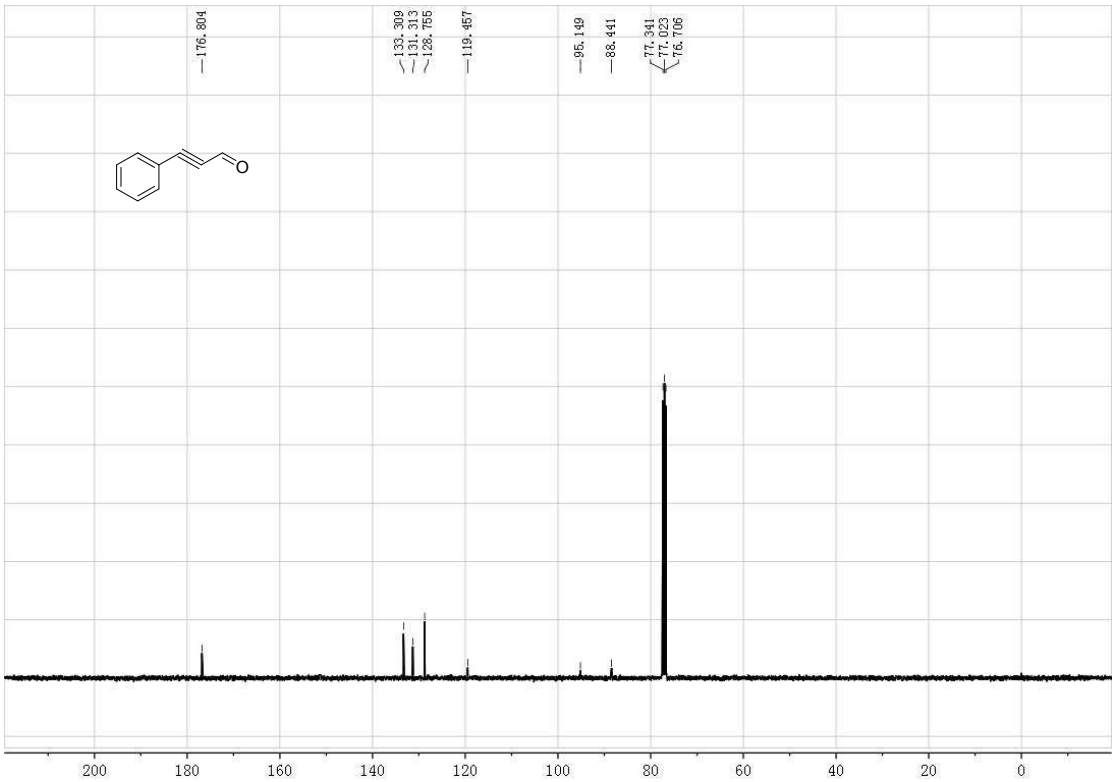
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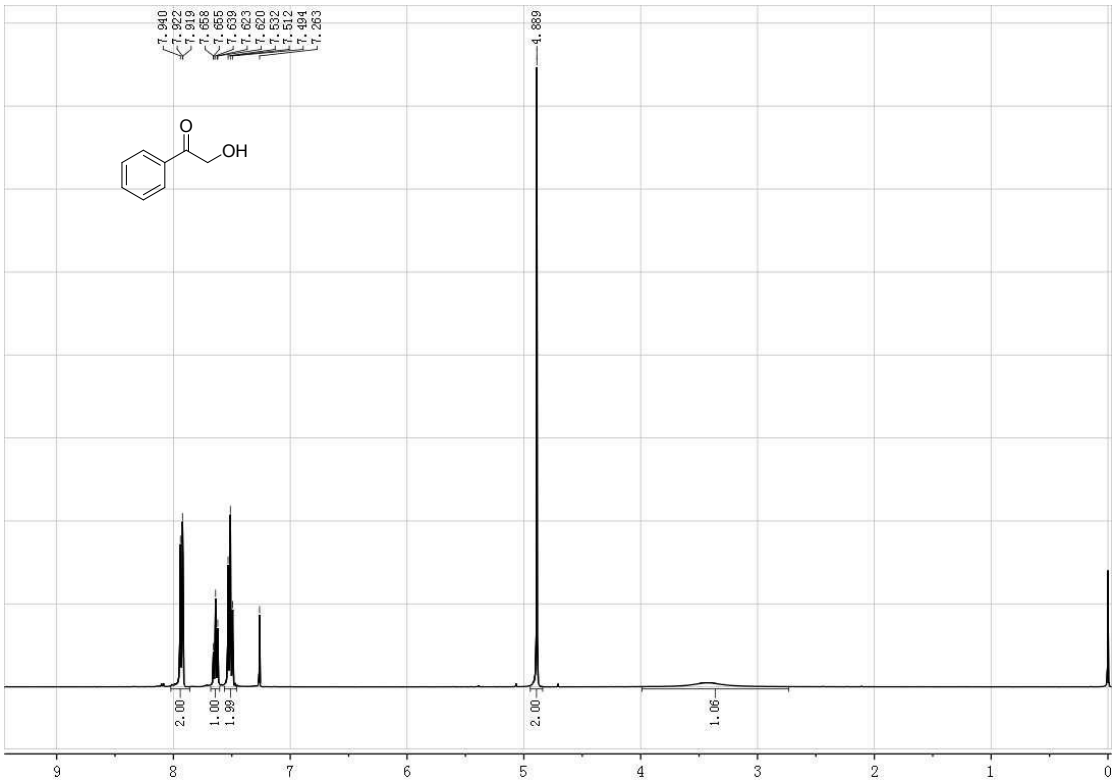
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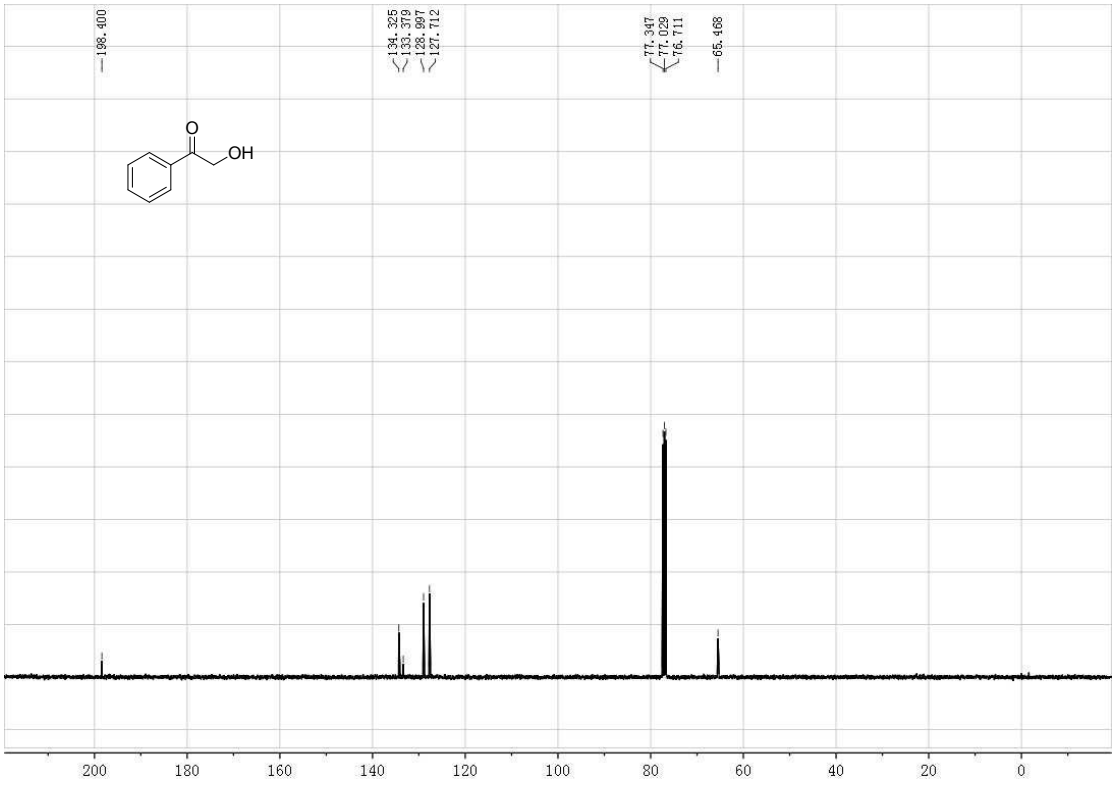
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