Ammonium Iodide Promoted Cyclization of Aryl Substituted Carboxylic Acids

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Supporting Information

EXPERIMENTAL

Melting points were measured with an XT-4 melting point apparatus and are uncorrected, IR spectra were recorded on a Thermo-Nicolet 6700 instrument, ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AVANCE Ⅲ (500MHz) spectrometer, and mass spectra were determined on Thermo-ITQ 1100 mass spectrometer. Carboxylic acids, Oxone®, NH_4I and KBr were commercially available.

Typical Procedure for the NH_4I Promoted Cyclization of Carboxylic Acids

To a mixture of MeCN and CF_3CH_2OH (6:4) (5.0 mL), carboxylic acid **1** (0.5 mmol), NH_4I (0.25 mmol), KBr (0.4 mmol) and Oxone® (0.75 mmol) were added. The resulting solution was stirred at room temperature for 12 h and then solvents were removed under reduced pressure. Water (10 mL), sat. aq $Na_2S_2O_3$ (4 mL) and sat. aq Na_2CO_3 (4 mL) were added to the residue and the mixture was stirred for another 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel using (hexane-AcOEt 3:1) as eluant to give the pure product of aryl lactone **2**.

Dihydro-5-phenyl-2(3H)-furanone (2a)

White solid; mp 35−36°C (lit.[1] mp 35–36°C); Yield: 56 mg (69%).

IR (neat): 3070, 1754, 1616, 1493, 1297, 1216, 1176, 1140, 1022, 762, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.34 (*m*, 5 H), 5.53 (*t*, *J* = 5.0 Hz, 1 H), 2.72-2.64 (*m*, 3 H), 2.24-2.18 (*m*, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.87, 139.40, 128.77, 128.45, 125.28, 81.22, 30.95, 28.94.

MS (ESI): *m/z* (%) 162 (M^+, 47), 117 (100).

5-(4-Bromophenyl)-dihydro-2(3H)-furanone (2b)

White solid; mp 81−82°C (lit.[2] mp 81.5–82.5°C); Yield: 77 mg (64%).

IR (neat): 1763, 1592, 1490, 1178, 1142, 1008, 828, 804 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (*d*, *J* = 5.0 Hz, 2 H), 7.23 (*d*, *J* = 5.0 Hz, 2 H), 5.49-5.46 (*m*, 1 H), 2.68-2.65 (*m*, 3 H), 2.19-2.13 (*m*, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ =176.48, 138.44, 131.94, 126.96, 122.40, 80.42, 30.90, 28.83.

MS (ESI): *m/z* (%) 240 ($Br^{79}M^+$, 19), 242 ($Br^{81}M^+$, 20), 161 (100).

Dihydro-5-(4-methylphenyl)-2(3H)-furanone (2c)

White solid; mp 73−74°C (lit.[3] mp 71–72.5°C); Yield: 49 mg (56%).

IR (film): 3036; 2932; 1721; 1603; 1493; 1165; 1139; 1037; 1008; 852 cm^{-1}.

^{1}H-NMR: δ = 7.23 (*d*, *J* = 5.0 Hz, 4 H), 5.50 (*dd*, *J* = 10.0, 5.0 Hz, 1 H), 2.68-2.63 (*m*, 3 H), 2.37 (*s*, 3 H), 2.22-2.19 (*m*, 1 H).

^{13}C-NMR: δ = 176.96, 138.33, 136.35, 129.41, 125.35, 81.33, 30.94, 29.03, 21.13.

MS (ESI): *m/z* (%) 176 (M^+, 26); 91 (100).

Tetrahydro-6-phenyl-2H-pyran-2-one (2d)

White solid; mp 75−76°C (lit.[1] 76–78°C); Yield: 51 mg (58%).

IR (film): 3043, 2969, 2950, 1727, 1493, 1245, 1035, 764, 705 cm^{-1}.

^{1}H-NMR: 7.42-7.33 (*m*, 5 H), 5.38 (*dd*, *J* = 10.0, 5.0 Hz, 1 H), 2.76-2.69 (*m*, 1 H), 2.63-2.56 (*m*, 1 H), 2.21-2.17 (*m*, 1 H), 2.03-1.99 (*m*, 2 H), 1.93-1.86 (*m*, 1 H).

^{13}C-NMR: 171.31, 139.75, 128.61, 128.27, 125.70, 81.63, 30.52, 29.52, 18.61.

MS (ESI): *m/z* (%) 176 (M^+, 5.6), 104 (100).

7-Phenyl-2-oxepanone (2f)

White solid; mp 67−68°C (lit.[1] 66–67°C); Yield: 15 mg (18%).

IR (film): 2924, 1766, 1616, 1520, 1183, 1147, 1011, 940, 773, 723 cm^{-1}.

^{1}H-NMR: 7.41-7.36 (*m*, 5 H), 5.31 (*d*, *J* = 10.0 Hz, 1 H), 2.82-2.76 (*m*, 2 H), 2.16-2.02 (*m*, 4 H), 1.81-1.75 (*m*, 2 H).

^{13}C-NMR: 174.84, 140.79, 128.57, 128.10, 125.86, 82.11, 37.49, 34.98, 28.63, 22.86.

MS (ESI): *m/z* (%) 162 (M^+, 47), 117 (100).

Phthalide (2g)

White solid; mp 72−74°C (lit.[1] 73–74°C); Yield: 48 mg (72%).

IR (film): 3023, 2927, 2888, 1742, 1600, 1490, 1457, 1249, 1220, 1144, 1029, 752 cm^{-1}.

^{1}H-NMR: 7.93 (*d*, *J* = 10.0 Hz, 1 H), 7.71-7.68 (*m*, 1 H), 7.56-7.50 (*m*, 2 H), 5.34 (*s*, 2 H).

^{13}C-NMR: 171.08, 146.54, 134.00, 129.05, 125.79, 122.09, 69.64.

MS (ESI): *m/z* (%) 134 (M^+, 2.1), 105 (100).

6-Methylphthalide (2h)

White solid; mp 85−86°C (lit.[4] 88°C); Yield: 41 mg (55%).

IR (film): 3037, 2925, 1759, 1591, 1496, 1457, 1156, 1056, 996, 821, 770 cm^{-1}.

^{1}H-NMR: 7.67 (*s*, 1 H), 7.48 (*d*, *J* = 5.0 Hz, 1 H), 7.37 (*d*, *J* = 10.0 Hz, 1 H), 5.26 (*s*, 2 H), 2.44 (*s*, 3 H).

^{13}C-NMR: 171.16, 143.82, 139.14, 135.10, 125.75, 125.50, 121.73, 69.51, 21.12.

MS (ESI): *m/z* (%) 148 (M^+, 8.1), 91(100).

3H-2-Benzopyran-3-one (2i)

White solid; mp 80−81°C (lit.[5] 81–82°C); Yield: 50 mg (67%).

IR (film): 3023, 2889, 1746, 1489, 1458, 1392, 1252, 1224, 1147, 1034, 761 cm^{-1}.

^{1}H-NMR: 7.37-7.31 (*m*, 2 H), 7.27-7.23 (*m*, 2 H), 5.33 (*s*, 2 H), 3.73 (*s*, 2 H).

^{13}C-NMR: 170.66, 131.55, 130.97, 128.82, 127.37, 127.07, 124.68, 70.08, 36.18.

MS (ESI): *m/z* (%) 148 (M^+, 5.0), 104 (100).

6-Methylisochroman-3-one (2j)

White solid; mp 70−71°C (lit.[5] 72–73°C); Yield: 35 mg (43%).

IR (film): 2921, 1725, 1616, 1590, 1501, 1461, 1255, 1216, 1157, 1126, 1021, 833, 780 cm^{-1}.

^{1}H-NMR: 7.13 (*dd*, *J* = 10.0, 5.0 Hz, 2 H), 7.05 (*s*, 1 H), 5.29 (*s*, 2 H), 3.68 (*s*, 2 H), 2.38 (*s*, 3 H).

^{13}C-NMR: 170.85, 138.81, 130.93, 128.60, 127.99, 127.70, 124.54, 70.01, 36.20, 21.19.

MS (ESI): *m/z* (%) 162 (M^+, 53), 117 (100).

1 Dohi, T.; Takenaga, N.; Goto, A.; Maruyama, A.; Kita, Y. *Org. Lett.* **2007**, *9*, 3129.
2 Sato, M.; Kosasayama, A.; Uchimaru, F. *Chem. Pharm. Bull.* **1981**, *29*, 2885.
3 Fischer, A.; Leonard, D. R. A.; Roederer, R. *Can. J. Chem.* **1979**, *57*, 2527.
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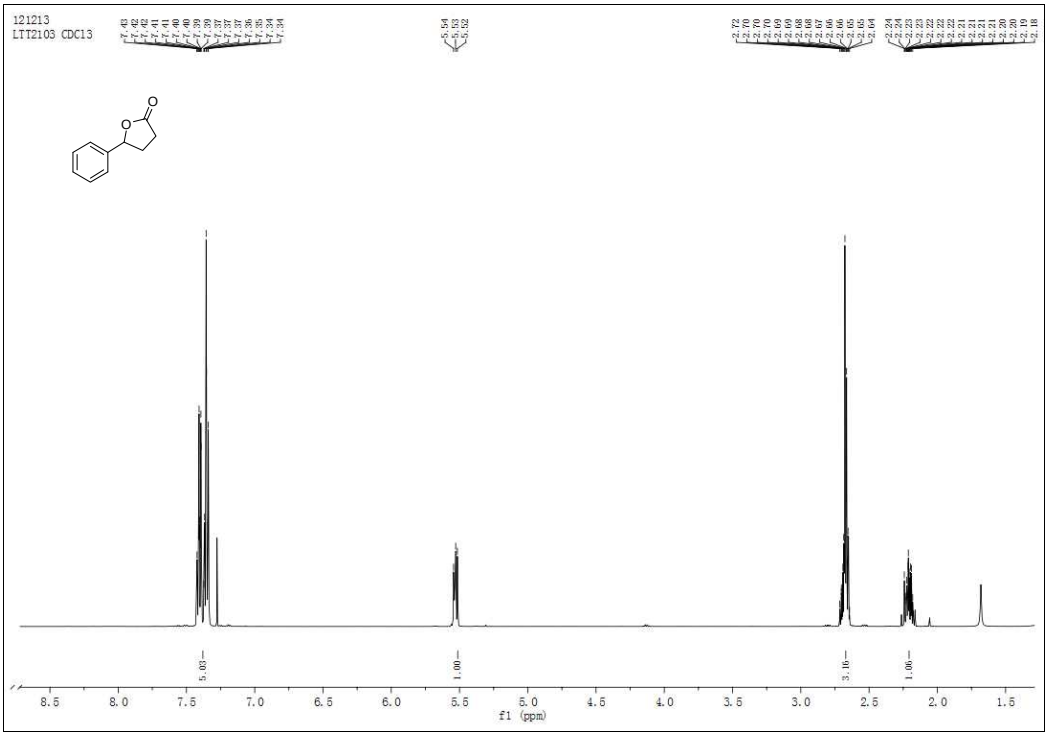
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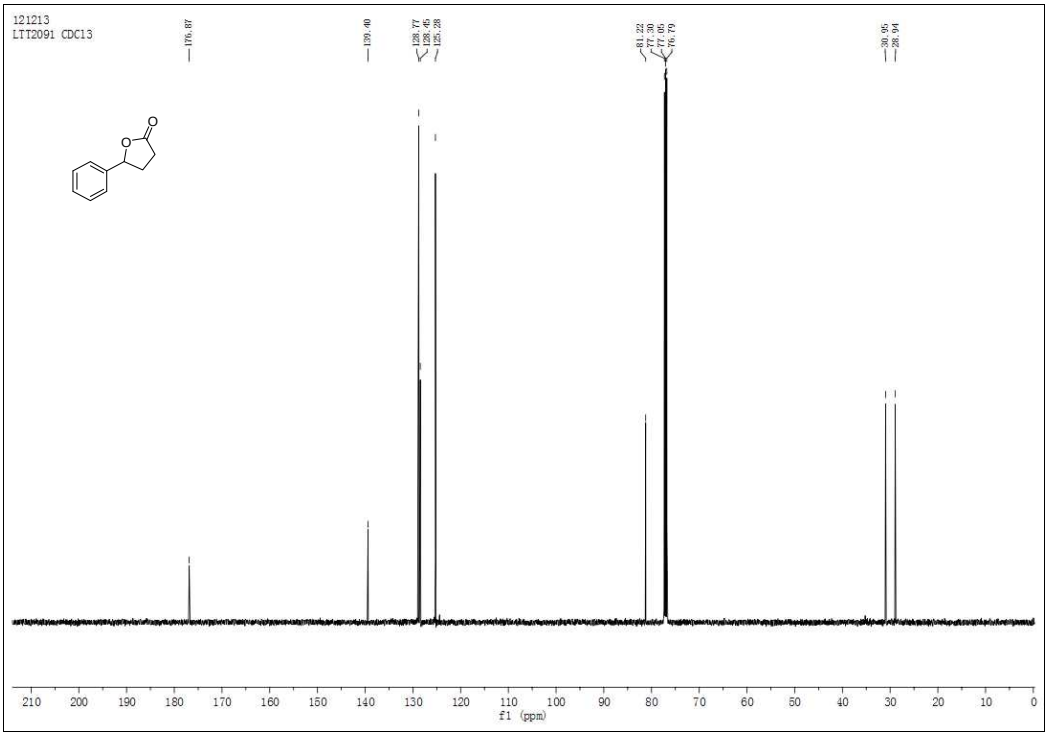
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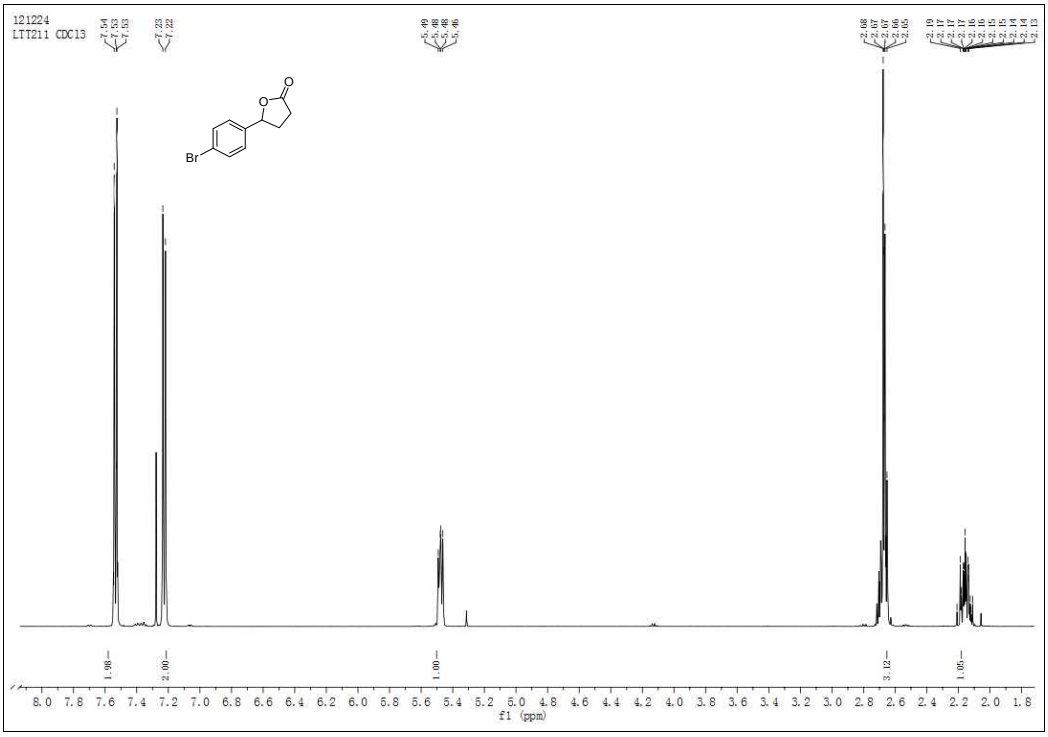
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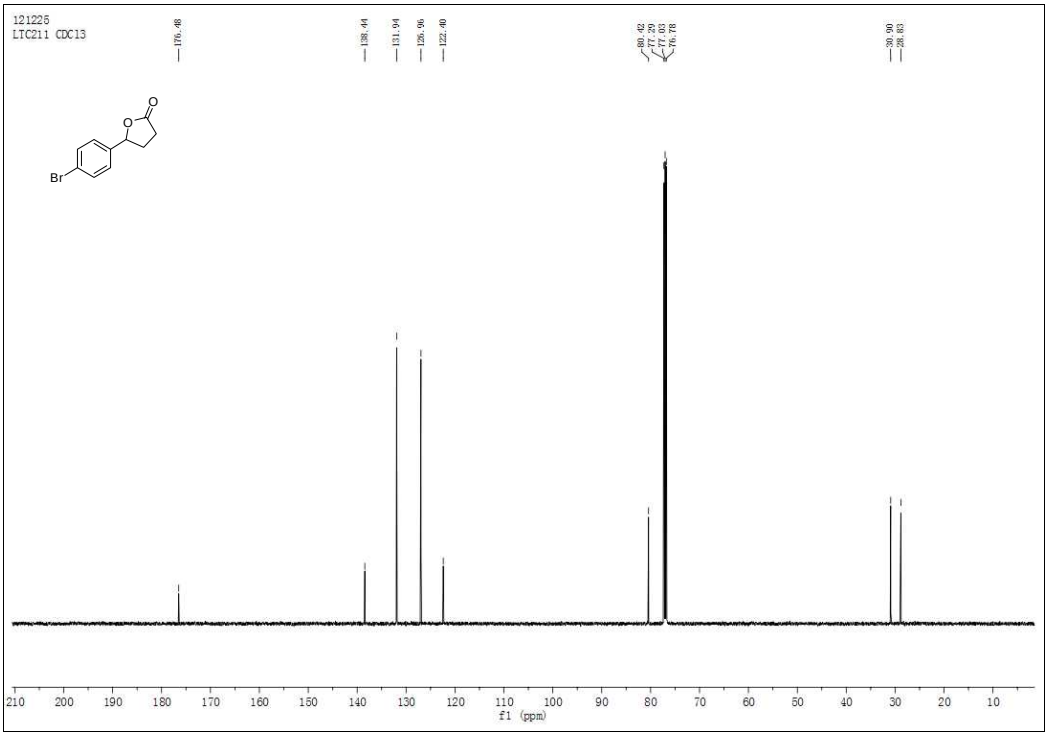
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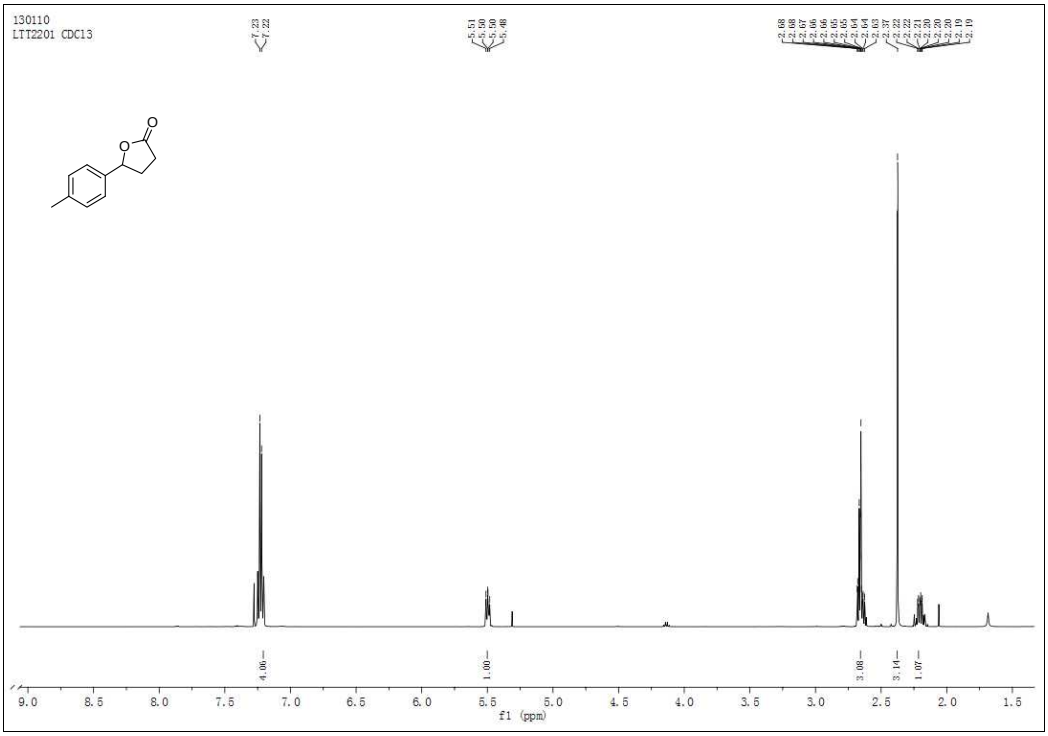
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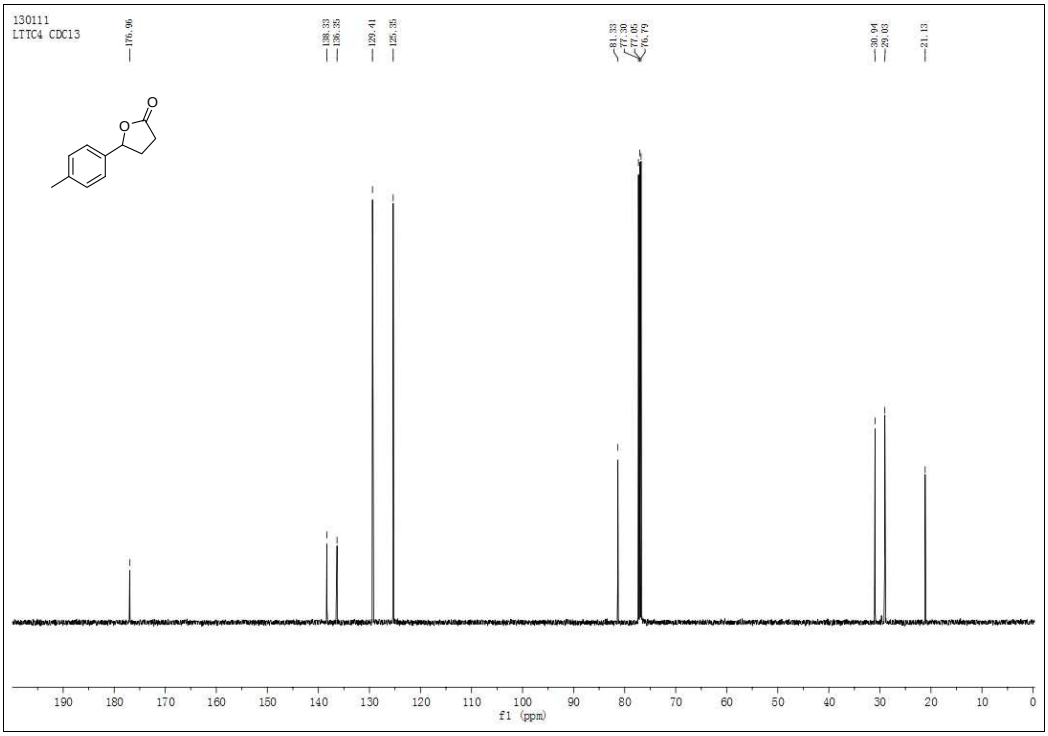
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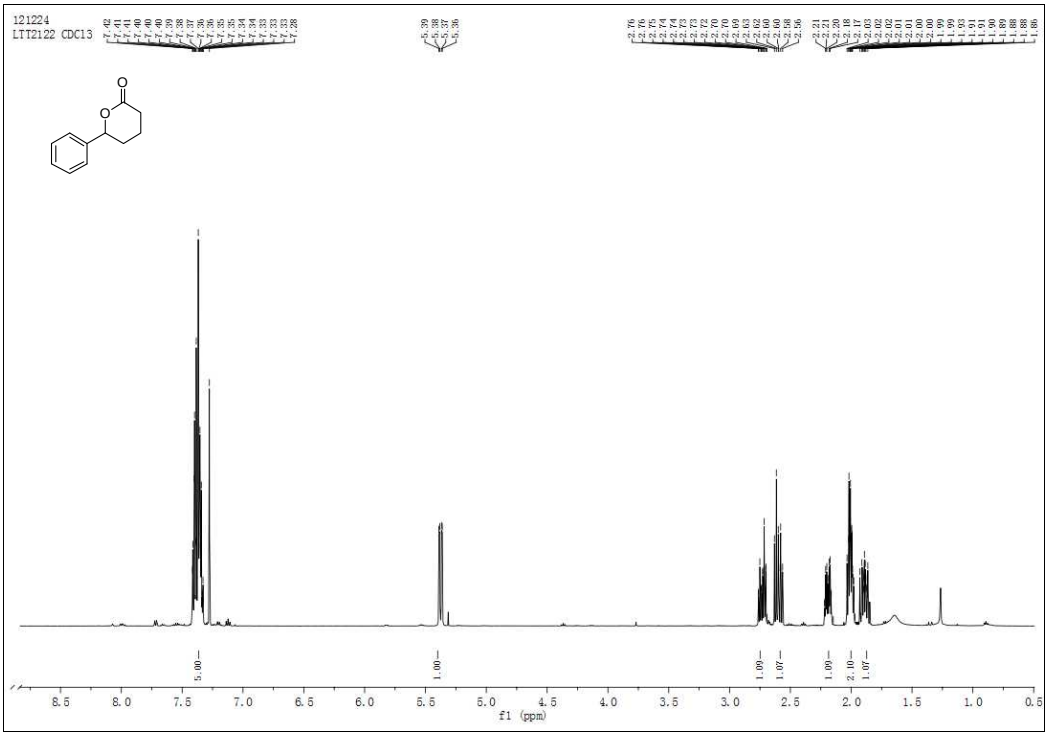
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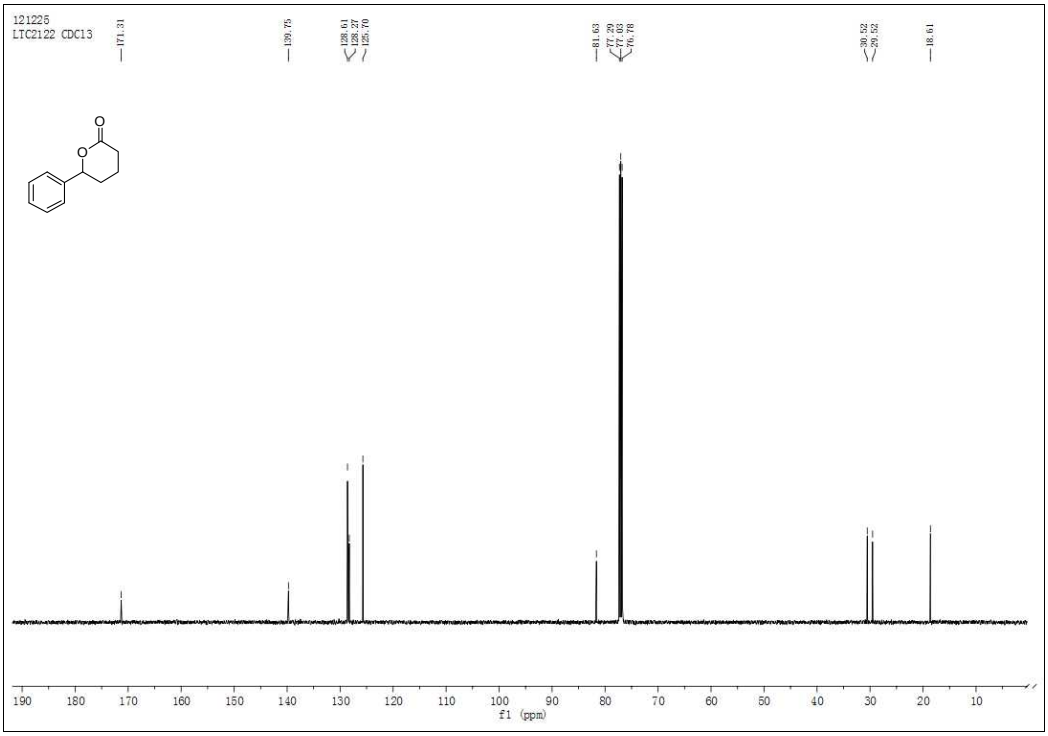
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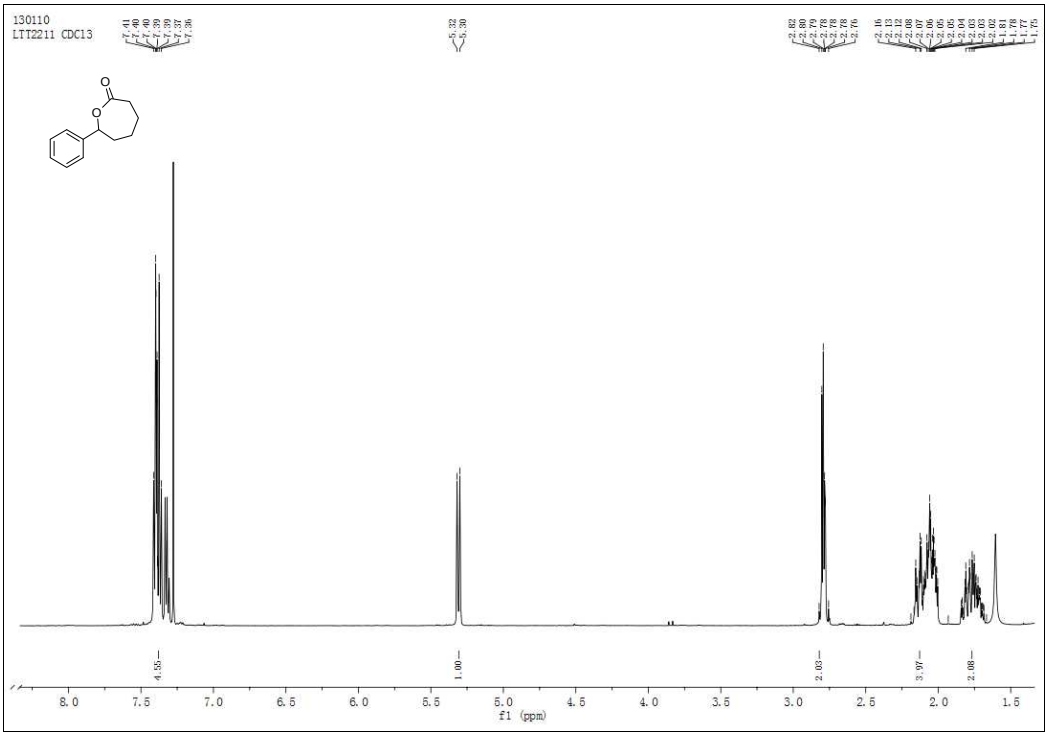
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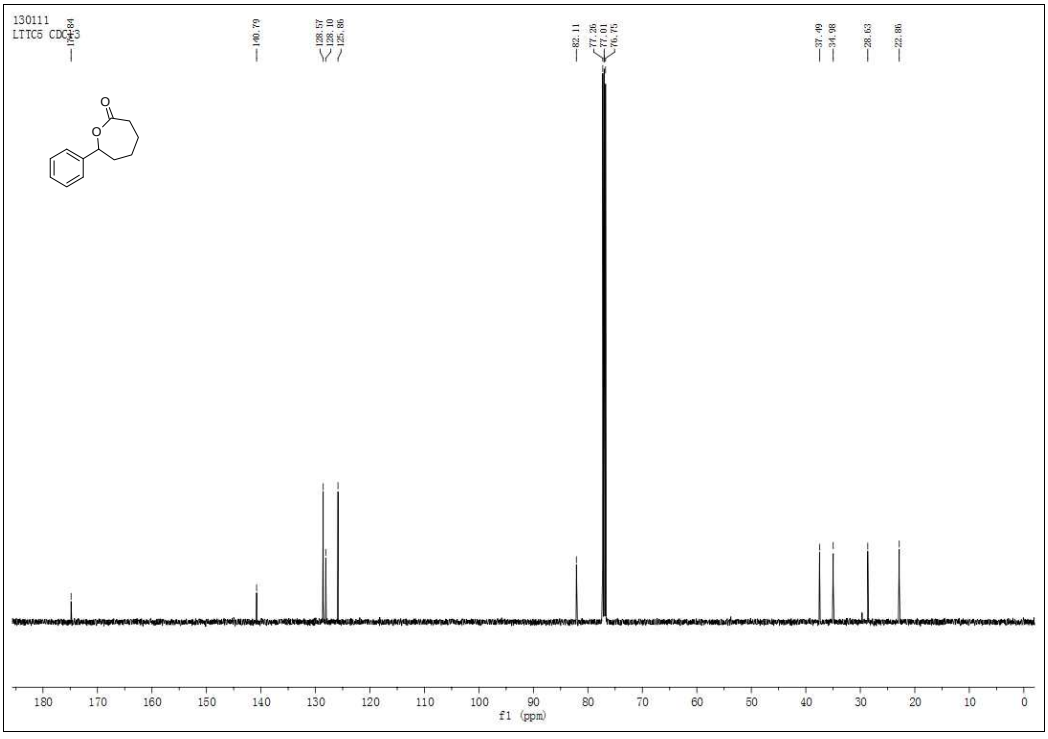
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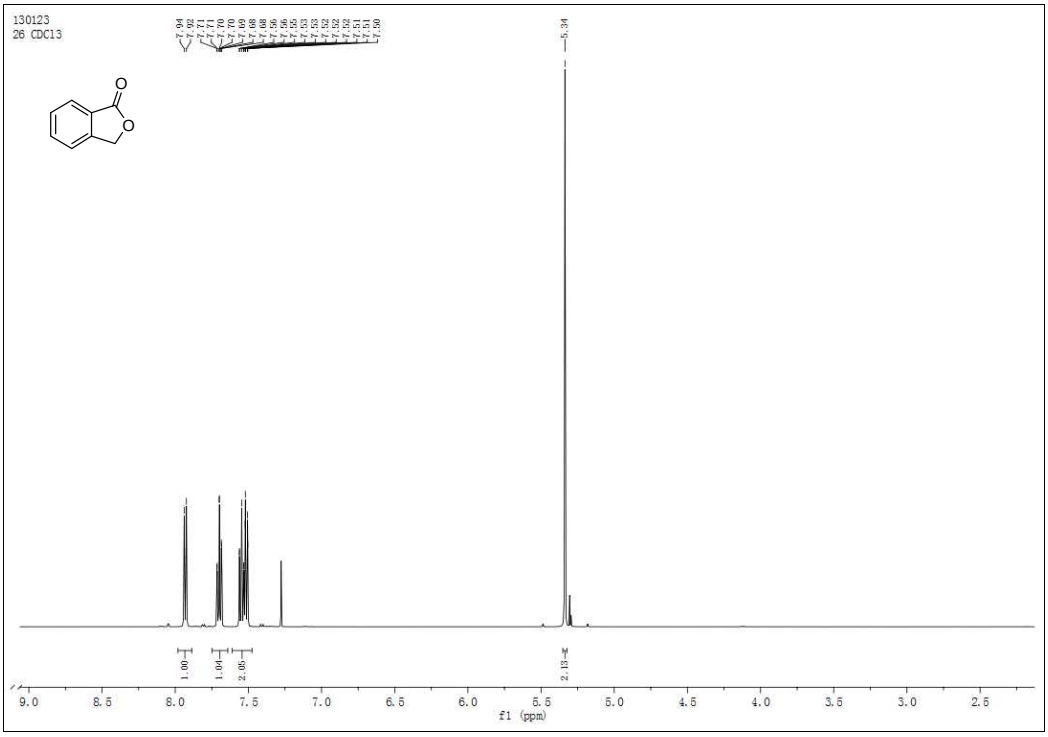
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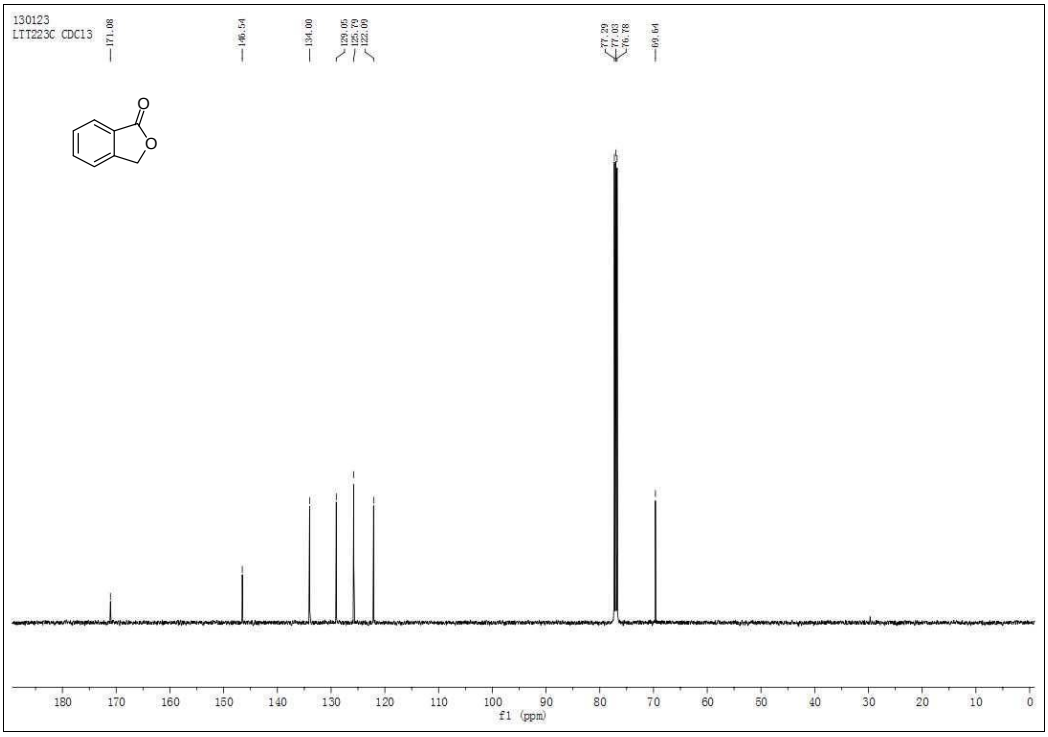
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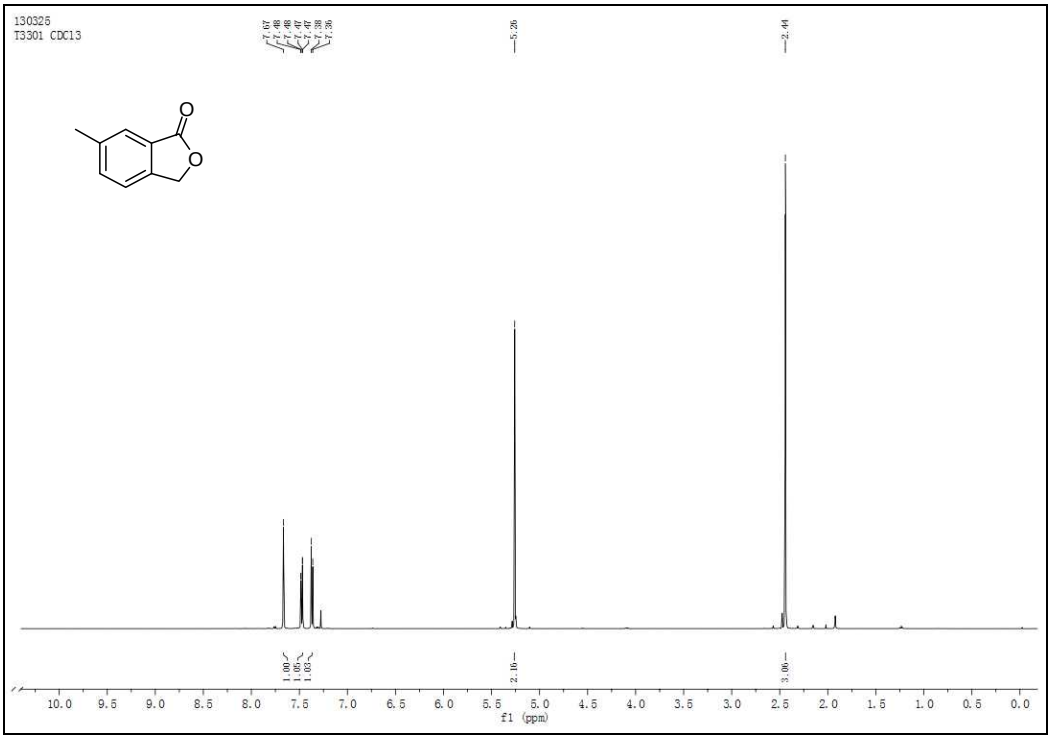
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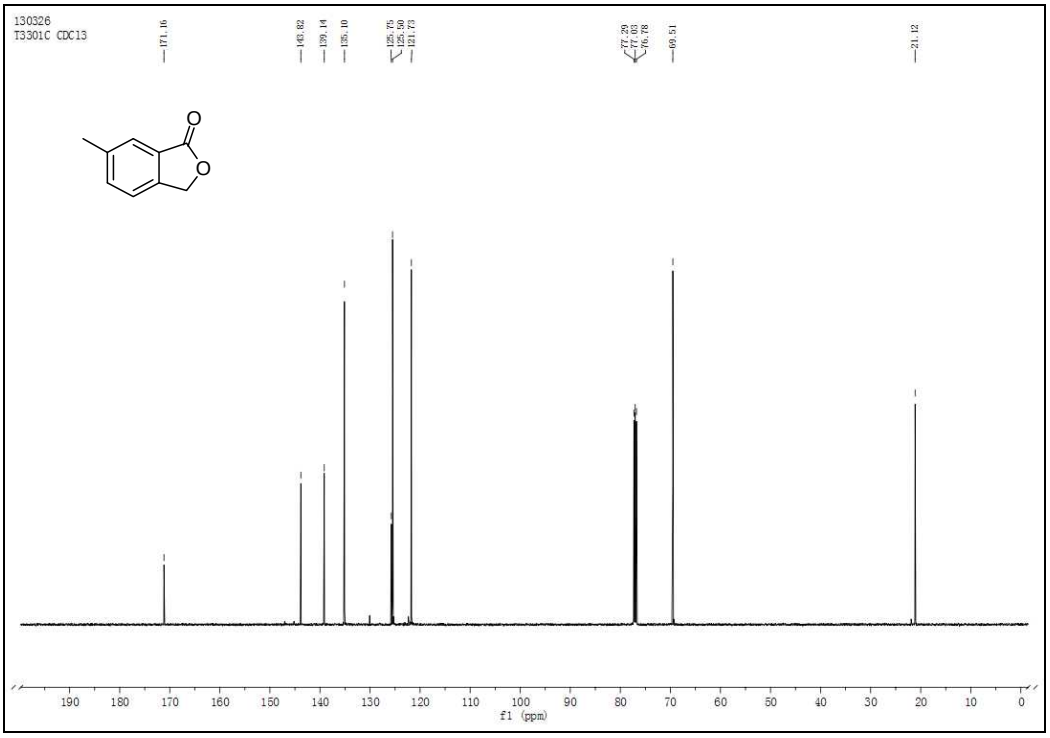
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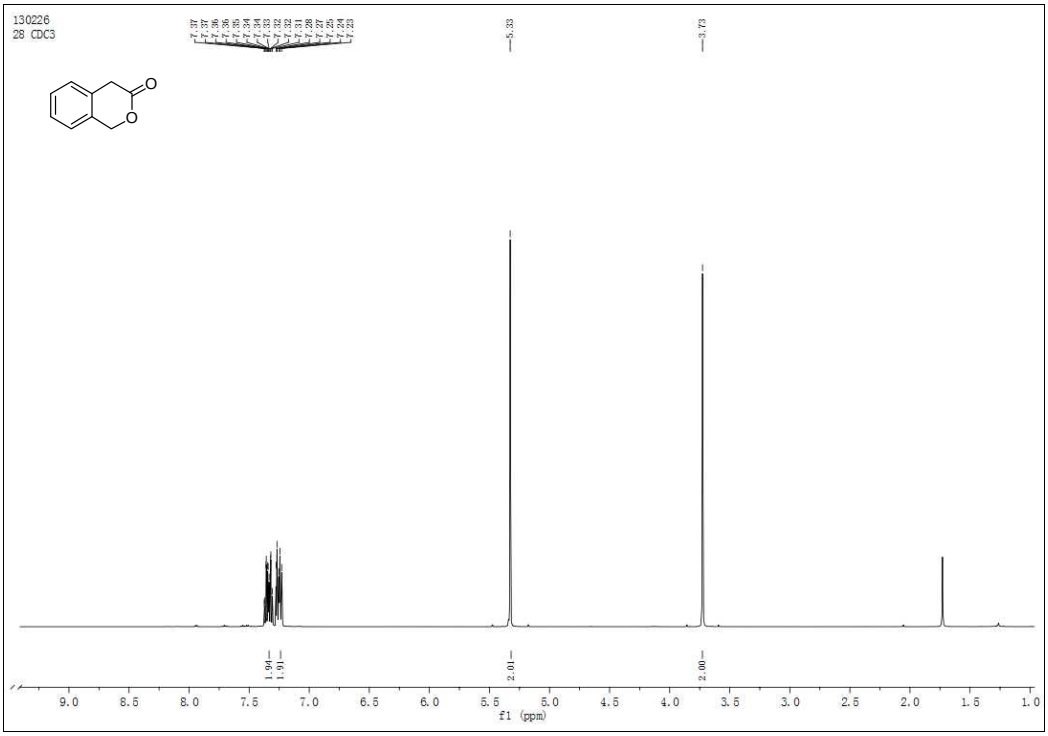
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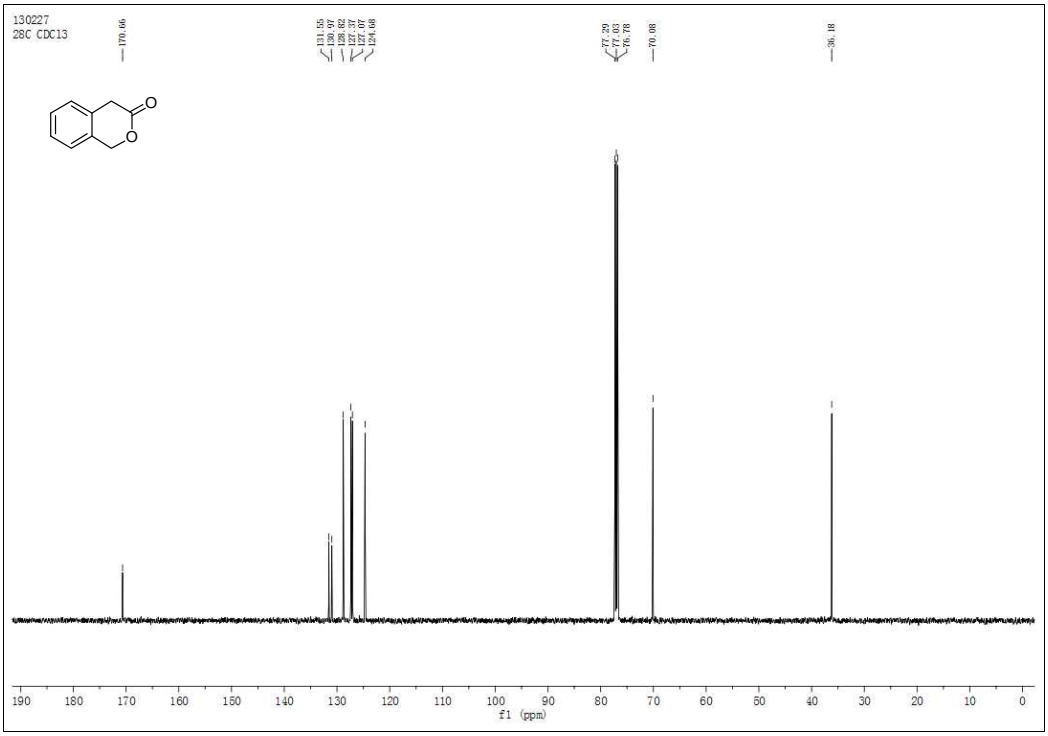
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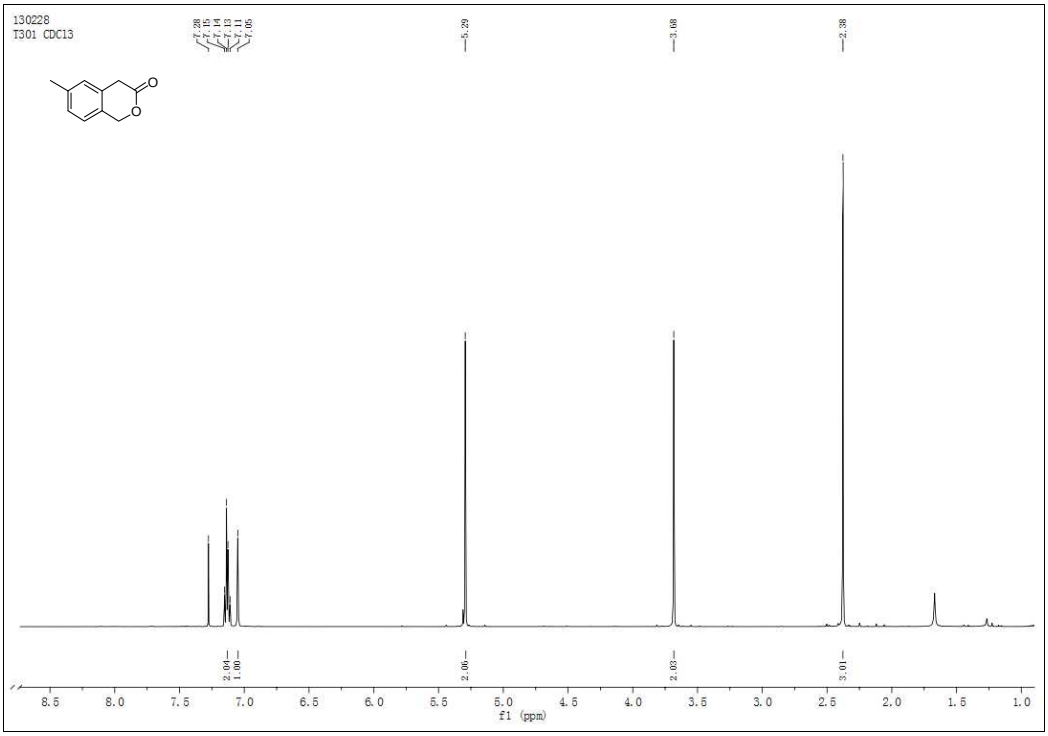
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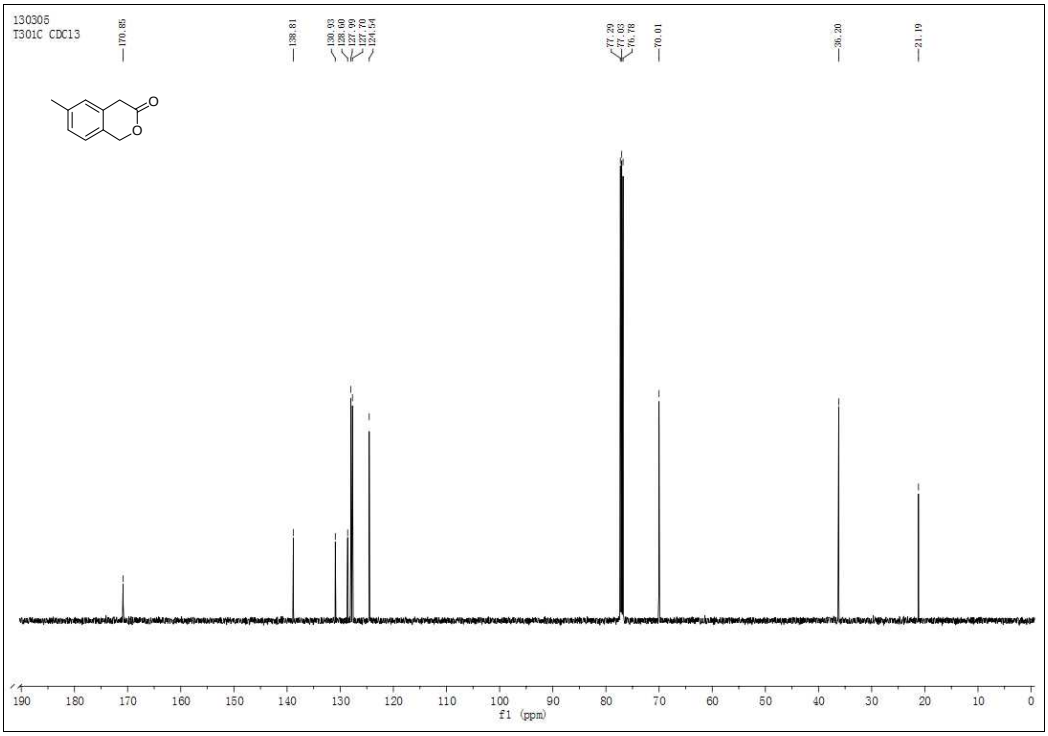
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