Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

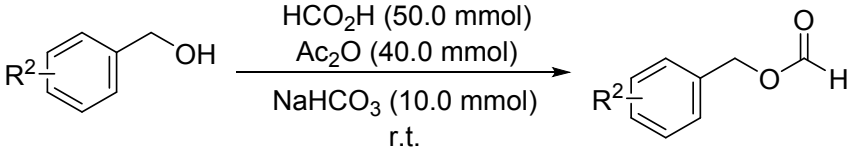
Table of Contents

1. General Information

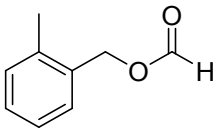
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. organic carbonates were from commercial sources and used as received without further purification. Benzyl formates that were not commercially available were synthesized according to existing method. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (Bp. 60-90 °C) and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.0) as solvent. All coupling constants (*J*) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quartet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with a FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV. IR spectra were collected with Bruker-VERTEX 70 spectrometer and only major peaks were reported in cm^{-1}.

2. General Procedure for the Syntheses of the Benzyl formates[1]

Formic acid (50.0 mmol) was added to acetic anhydride (40.0 mmol) at room temperature. The resulting mixture was stirred at 60 ºC for 1 h and then cooled at room temperature. Benzyl alcohols (5.0 mmol) and $NaHCO_3$ (10.0 mmol) were added to the solution, and the mixture was stirred until starting material was consumed. The reaction was quenched by adding a mixture of EA and water, and the biphasic system was stirred vigorously. Then the organic phase was separated, and the aqueous phase was extracted with EA for 2 times. The organic phases were combined and washed with water and brine, and then dried over anhydrous Na_2SO_4. The resulting mixture was concentrated by rotary evaporation. The crude mixture was purified by silica gel column chromatography to afford the desired product.

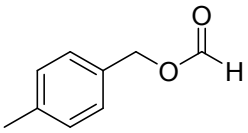


3. Characterization of the Benzyl formates



2-Methylbenzyl formate[2]

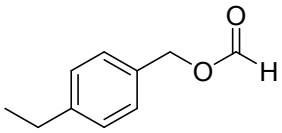
0.53 g, 70% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.26-7.14 (m, 3H), 5.19 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 136.9, 133.1, 130.3, 129.3, 128.7, 126.0, 63.9, 18.7.



4-Methylbenzyl formate[4]

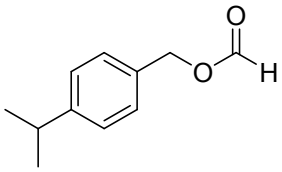
0.37 g, 49% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.9, 132.1, 128.9, 128.2,

65.1, 20.7.



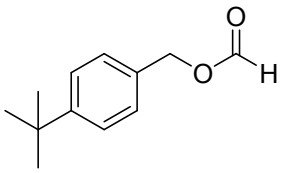
4-Ethylbenzyl formate

0.43 g, 52% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.15 (s, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.22 (td, *J* = 7.6, 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 144.6, 132.4, 128.5, 128.0, 65.5, 28.5, 15.4. HRMS (ESI): [M+Na$^+$] calcd. for $C_{10}H_{12}NaO_2^+$, 187.0730; found, 187.0745. IR (neat, cm^{-1}): 2966, 2932, 1726 , 1516, 1458, 1368, 1259, 1161, 1059, 1022, 821, 556.



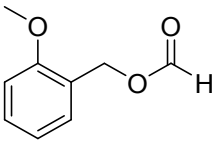
4-Isopropylbenzyl formate

0.40 g, 45% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.14 (s, 2H), 2.89 (hept, *J* = 6.8 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 149.2, 132.5, 128.5, 126.6, 65.4, 33.8, 23.8. HRMS (ESI): [M+H$^+$] calcd. for $C_{11}H_{15}O_2^+$, 179.1067; found, 179.1083. IR (neat, cm^{-1}): 2962, 1715, 1616, 1515, 1462, 1422, 1366, 1257, 1159, 1057, 1020, 921, 820, 700, 579, 541.



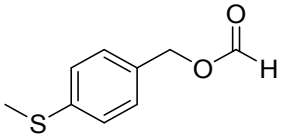
4-(*tert*-Butyl)benzyl formate[5]

0.53 g, 55% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.16 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 151.4, 132.1, 128.2, 125.4, 65.3, 34.4, 31.1.



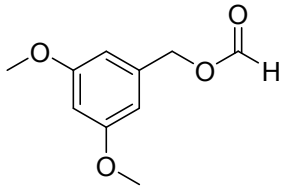
2-Methoxybenzyl formate

0.69 g, 83% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.32-7.25 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.22 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 157.2, 129.6, 129.6, 123.2, 120.1, 110.1, 60.9, 54.9. HRMS (ESI): [M+Na$^+$] calcd. for $C_9H_{10}NaO_3^+$, 189.0522; found, 189.0533. IR (neat, cm^{-1}): 3426, 3007, 2942, 2840, 1727, 1605, 1496, 1465, 1370, 1322, 1290, 1251, 1159, 1122, 1050, 1029, 915, 865, 756, 600, 567, 533, 489, 463.



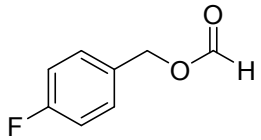
4-(Methylthio)benzyl formate

0.73 g, 80% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.28 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 5.14 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 139.1, 131.8, 128.9, 126.4, 65.2, 15.5. HRMS (ESI): [M+H$^+$] calcd. for $C_9H_{11}O_2S^+$, 183.0474; found, 183.0478. IR (neat, cm^{-1}): 3421, 3024, 2922, 1899, 1726, 1602, 1495, 1437, 1406, 1368, 1322, 1254, 1163, 1093, 1013, 968, 804, 727, 652, 527, 441.



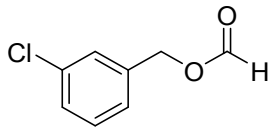
3,5-Dimethoxybenzyl formate

0.94 g, 96% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 8.12 (s, 1H), 6.50 (d, J = 2.2 Hz, 2H), 6.42 (t, J = 2.2 Hz, 1H), 5.11 (s, 2H), 3.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 160.5, 137.3, 105.8, 100.2, 65.4, 55.1. HRMS (ESI): [M+H$^+$] calcd. for $C_{10}H_{13}O_4^+$, 197.0808; found, 197.0807. IR (neat, cm^{-1}): 3427, 3003, 2942, 2842, 2121, 1730, 1612, 1470, 1370, 1323, 1299, 1205, 1069, 993, 919, 836, 692, 658, 592, 536, 485.



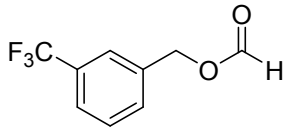
4-Fluorobenzyl formate[4]

0.48 g, 62% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.40-7.29 (m, 2H), 7.11-6.99 (m, 2H), 5.16 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 247.3 Hz), 160.6, 131.1, 130.4 (d, J = 8.3 Hz), 115.6 (d, J = 21.6 Hz), 64.9.



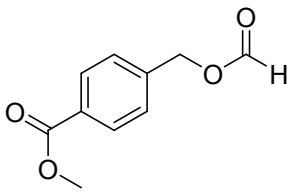
3-Chlorobenzyl formate

0.77 g, 90% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.37 (s, 1H), 7.34-7.23 (m, 3H), 5.17 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 137.0, 134.2, 129.7, 128.3, 128.0, 126.0, 64.4. HRMS (ESI): [M+Na$^+$] calcd. for $C_8H_7ClNaO_2^+$, 193.0027; found, 193.0049. IR (neat, cm^{-1}): 3066, 2938, 1729, 1602, 1577, 1478, 1434, 1367, 1252, 1157, 1097, 1080, 999, 873, 783, 683, 614, 519, 440.



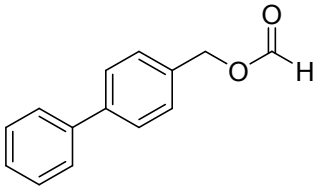
3-(Trifluoromethyl)benzyl formate

0.47 g, 46% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.64 (s, 1H), 7.62-7.46 (m, 3H), 5.24 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 136.3, 131.3, 130.9 (d, J = 32.4 Hz), 129.0, 125.0, 124.7, 123.9 (d, J = 272.2 Hz), 64.4. HRMS (ESI): [M+Na$^+$] calcd. for $C_9H_7F_3NaO_2^+$, 227.0290; found, 227.0281. IR (neat, cm^{-1}): 2943, 1731, 1620, 1494, 1454, 1369, 1332, 1257, 1126, 1075, 891, 801, 750, 702, 662, 576, 507, 419.



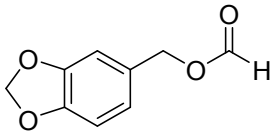
Methyl 4-((formyloxy)methyl)benzoate

0.76 g, 78% yield, white solid, Mp. 67.8-70.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 5.24 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 160.2, 139.9, 129.7, 129.4, 127.4, 64.3, 51.7. HRMS (ESI): [M+Na^+] calcd. for $C_{10}H_{10}NaO_4^+$, 217.0471; found, 217.0493. IR (neat, cm^{-1}): 3404, 3004, 2957, 1939, 1712, 1614, 1514, 1439, 1417, 1295, 1191, 1113, 1018, 925, 846, 758, 696, 511, 482.



[1,1'-Biphenyl]-4-ylmethyl formate

0.43 g, 41% yield, white solid, Mp. 55.9-57.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.67-7.30 (m, 9H), 5.23 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 141.5, 140.5, 134.1, 128.8, 128.8, 127.5, 127.3, 127.1, 65.4. HRMS (ESI): [M+H^+] calcd. for $C_{14}H_{13}O_2^+$, 213.0910; found, 213.0923. IR (neat, cm^{-1}): 3031, 1725, 1488, 1451, 1372, 1244, 1159, 1045, 1009, 827, 762, 698, 605, 501.

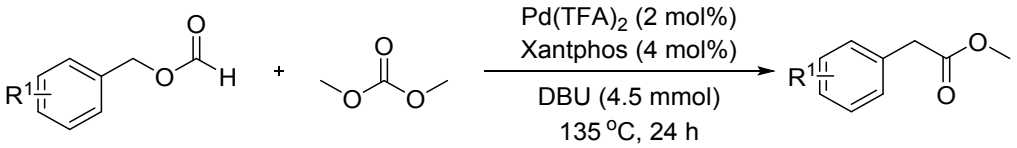


Benzo[*d*][1,3]dioxol-5-ylmethyl formate

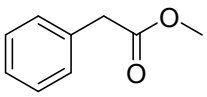
0.63 g, 70% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 2H), 5.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 147.5, 147.5, 128.7, 122.1, 108.7, 107.9, 100.9, 65.2. HRMS (ESI): [M+H^+] calcd. for $C_9H_9O_4^+$, 181.0495; found, 181.0489. IR (neat, cm^{-1}): 3422, 2894, 2781, 2038, 1851, 1724, 1610, 1510, 1450, 1379, 1249, 1100, 1040, 930, 861, 809, 769, 716, 644, 598, 519, 422.

4. General Procedure for the Syntheses of the 2-Methyl 2-arylacetates

Under nitrogen, $Pd(TFA)_2$ (2 mol%), Xantphos (4 mol%) was added to a 15 mL tube. After refill the tube with nitrogen, benzyl formates (1.0 mmol), DBU (4.5 mmol), and DMC (2.0 mL) were added by syringe. Then the tube was closed and the reaction mixture was stirred at 130-135 °C for 24 h. After the reaction was completed, the reaction mixture was concentrated by rotary evaporation. The crude mixture was purified by silica gel column chromatography (PE/EA = 50/1) to provide the desired pure products.

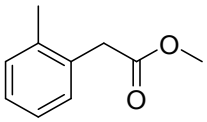


5. Characterization of the 2-methyl 2-arylacetates



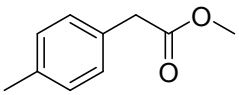
Methyl 2-phenylacetate[6]

118.5 mg, 79% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.14 (m, 5H), 3.59 (s, 3H), 3.54 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 133.9, 129.2, 128.5, 127.0, 51.9, 41.1.



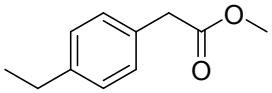
Methyl 2-(*o*-tolyl)acetate[6]

141.1 mg, 86% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 3.68 (s, 3H), 3.64 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 136.8, 132.7, 130.3, 130.1, 127.4, 126.1, 52.0, 39.0, 19.5.



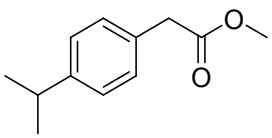
Methyl 2-(*p*-tolyl)acetate[7]

124.7 mg, 76% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 3.67 (s, 3H), 3.58 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 136.6, 130.9, 129.2, 129.0, 51.9, 40.7, 21.0.



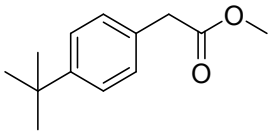
Methyl 2-(4-ethylphenyl)acetate

137.1 mg, 77% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.65 (s, 3H), 3.57 (s, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 142.9, 131.0, 129.0, 127.9, 51.7, 40.6, 28.3, 15.4. HRMS (ESI): [M+H$^+$] calcd. for $C_{11}H_{15}O_2^+$, 179.1067; found, 179.1071. IR (neat, cm^{-1}): 2965, 2874, 1741, 1515, 1435, 1259, 1157, 1015, 820, 710, 553.



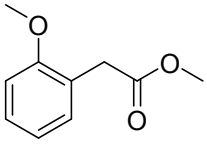
Methyl 2-(4-isopropylphenyl)acetate

146.0 mg, 76% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.12 (m, 4H), 3.64 (s, 3H), 3.56 (s, 2H), 2.92-2.82 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 147.4, 131.2, 129.0, 126.5, 51.7, 40.6, 33.6, 23.8. HRMS (ESI): [M+H$^+$] calcd. for $C_{12}H_{17}O_2^+$, 193.1223; found, 193.1229. IR (neat, cm^{-1}): 2960, 1741, 1515, 1435, 1384, 1257, 1157, 1056, 1019, 817, 774, 696, 554.



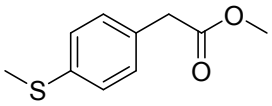
Methyl 2-(4-(*tert*-butyl)phenyl)acetate

162.8 mg, 79% yield, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 3.65 (s, 3H), 3.57 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 149.7, 130.8, 128.8, 125.4, 51.7, 40.5, 34.3, 31.2. HRMS (ESI): [M+H$^+$] calcd. for $C_{13}H_{19}O_2^+$, 207.1380; found, 207.1383. IR (neat, cm^{-1}): 2962, 2870, 1741, 1518, 1435, 1365, 1339, 1258, 1157, 1112, 1018, 814, 677, 555.



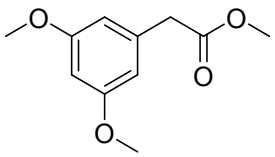
Methyl 2-(2-methoxyphenyl)acetate[6]

151.3 mg, 84% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.6 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 157.3, 130.6, 128.3, 122.8, 120.3, 110.3, 55.2, 51.5, 35.4.



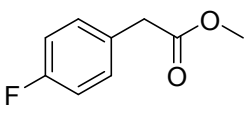
Methyl 2-(4-(methylthio)phenyl)acetate[8]

151.0 mg, 77% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 3.68 (s, 3H), 3.58 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 137.2, 130.8, 129.7, 126.9, 52.0, 40.6, 15.9.



Methyl 2-(3,5-dimethoxyphenyl)acetate

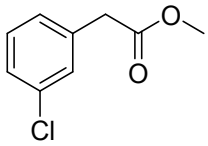
174.4 mg, 83% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, *J* = 2.2 Hz, 2H), 6.37 (t, *J* = 2.2 Hz, 1H), 3.78 (s, 6H), 3.69 (s, 3H), 3.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 160.9, 136.0, 107.3, 99.2, 55.3, 52.0, 41.4. HRMS (ESI): [M+H$^+$] calcd. for $C_{11}H_{15}O_4^+$, 211.0965; found, 211.0966. IR (neat, cm^{-1}): 3001, 2953, 2840, 1741, 1597, 1464, 1294, 1205, 1152, 1066, 1015, 953, 835, 790, 734, 686, 658, 540, 482.



Methyl 2-(4-fluorophenyl)acetate[6]

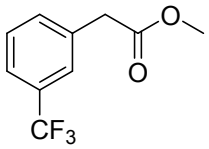
117.7 mg, 70% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.8, 5.7 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 3.69 (s, 3H), 3.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 162.0 (d, *J* = 245.4 Hz), 130.8 (d, *J* =

7.8 Hz), 129.6 (d, J = 3.2 Hz), 115.4 (d, J = 21.3 Hz), 52.0, 40.2.



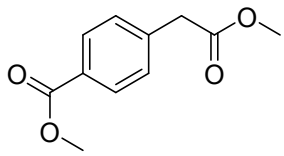
Methyl 2-(3-chlorophenyl)acetate

95.7 mg, 52% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.25-7.13 (m, 3H), 3.68 (s, 3H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 135.7, 134.2, 129.7, 129.3, 127.4, 127.2, 52.0, 40.5. HRMS (ESI): [M+H$^+$] calcd. for $C_9H_{10}ClO_2^+$, 185.0364; found, 185.0358. IR (neat, cm^{-1}): 3001, 2953, 2844, 1734, 1599, 1576, 1477, 1434, 1340, 1256, 1162, 1094, 1080, 1014, 939, 895, 868, 787, 725, 685, 637, 506, 437.



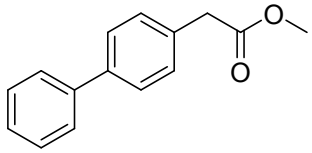
Methyl 2-(3-(trifluoromethyl)phenyl)acetate[6]

130.9 mg, 60% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.41 (m, 4H), 3.70 (s, 3H), 3.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 134.8, 132.7, 130.9 (q, J = 32.2 Hz), 129.0, 126.1 (d, J = 3.6 Hz), 124.0 (q, J = 272.2 Hz), 124.0 (d, J = 3.7 Hz), 52.1, 40.7.



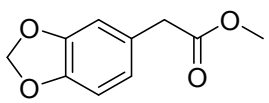
Methyl 4-(2-methoxy-2-oxoethyl)benzoate

95.7 mg, 46% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.90 (s, 3H), 3.70 (s, 3H), 3.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 166.7, 139.0, 129.8, 129.3, 129.0, 52.1, 52.0, 41.0. HRMS (ESI): [M+H$^+$] calcd. for $C_{11}H_{13}O_4^+$, 209.0808; found, 209.0811. IR (neat, cm^{-1}): 3001, 2954, 2845, 1935, 1751, 1737, 1723, 1713, 1613, 1577, 1511, 1436, 1281, 1020, 967, 901, 839, 809, 768, 742, 721, 694, 658, 578, 493, 427.



Methyl 2-([1,1'-biphenyl]-4-yl)acetate[7]

153.7 mg, 68% yield, white solid, Mp. 54.8-57.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.52 (m, 4H), 7.44-7.38 (m, 2H), 7.36-7.29 (m, 3H), 3.69 (s, 3H), 3.65 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 140.8, 140.1, 133.0, 129.7, 128.7, 127.3, 127.3, 127.1, 52.1, 40.8.

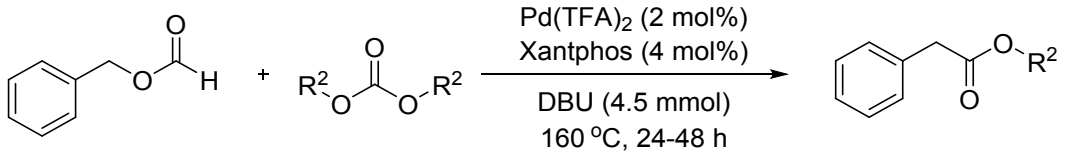


Methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate[6]

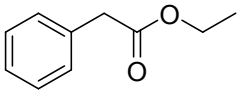
120.3 mg, 62% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79-6.69 (m, 3H), 5.93 (s, 2H), 3.68 (s, 3H), 3.53 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 147.7, 146.7, 127.5, 122.3, 109.7, 108.2, 101.0, 52.0, 40.7.

6. General Procedure for the Syntheses of the 2-Alkyl 2-phenylacetates

Under nitrogen, $Pd(TFA)_2$ (2 mol%), Xantphos (4 mol%) was added to a 15 mL tube. After refill the tube with nitrogen, benzyl formate (1.0 mmol), DBU (4.5 mmol), and organic carbonates (2.0 mL) were added by syringe. Then the tube was closed and the reaction mixture was stirred at 160 °C for 24-48 h. After the reaction was completed, the reaction mixture was concentrated by rotary evaporation. The crude mixture was purified by silica gel column chromatography (PE/EA = 50/1) to provide the desired pure products.

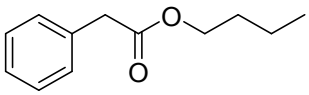


7. Characterization of the 2-Alkyl 2-phenylacetates



Ethyl 2-phenylacetate[6]

106.7 mg, 65% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 134.1, 129.1, 128.4, 126.9, 60.6, 41.3, 14.0.



Butyl 2-phenylacetate

86.4 mg, 45% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.58 (s, 2H), 1.64-1.52 (m, 2H), 1.39-1.26 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 134.1, 129.1, 128.3, 126.8, 64.5, 41.3, 30.5, 18.9, 13.5. HRMS (ESI): [M+H$^+$] calcd. for $C_{12}H_{17}O_2^+$, 193.1223; found, 193.1240. IR (neat, cm^{-1}): 3065, 3032, 2960, 2874, 1747, 1729, 1604, 1497, 1456, 1383, 1251, 1158, 1063, 1022, 723, 635, 532, 472.

8. References

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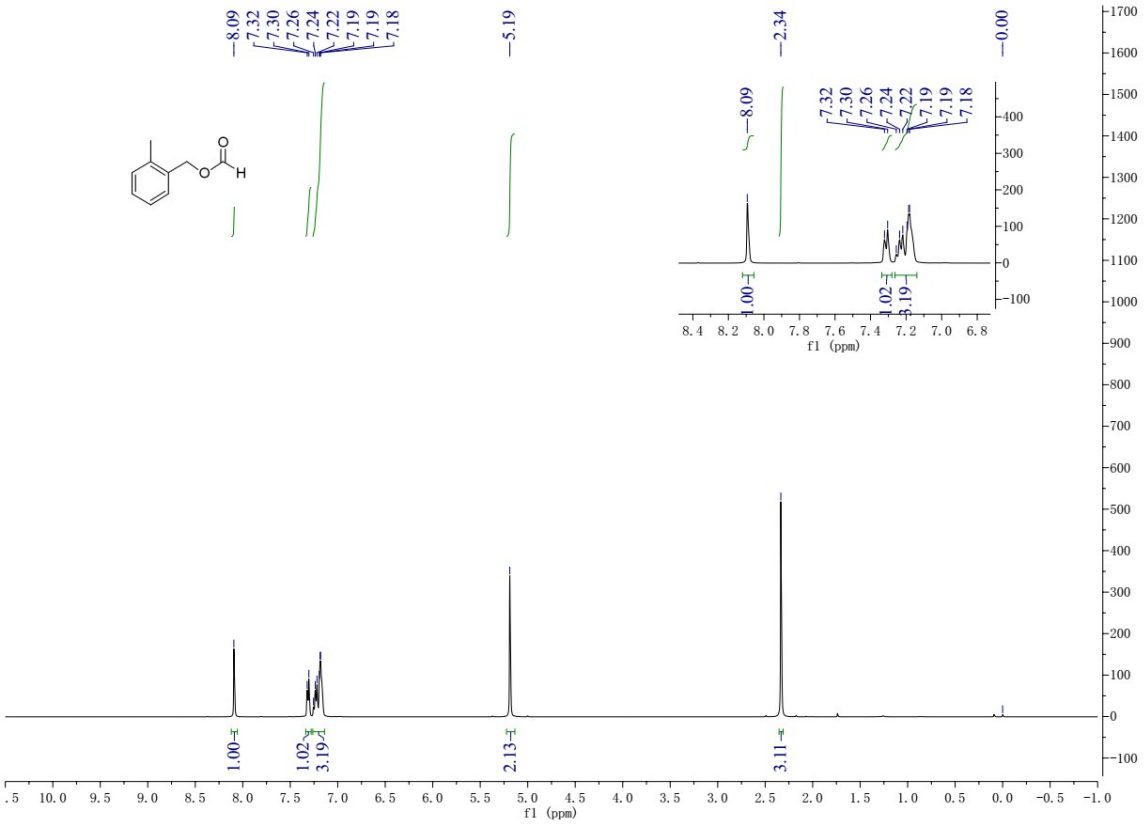
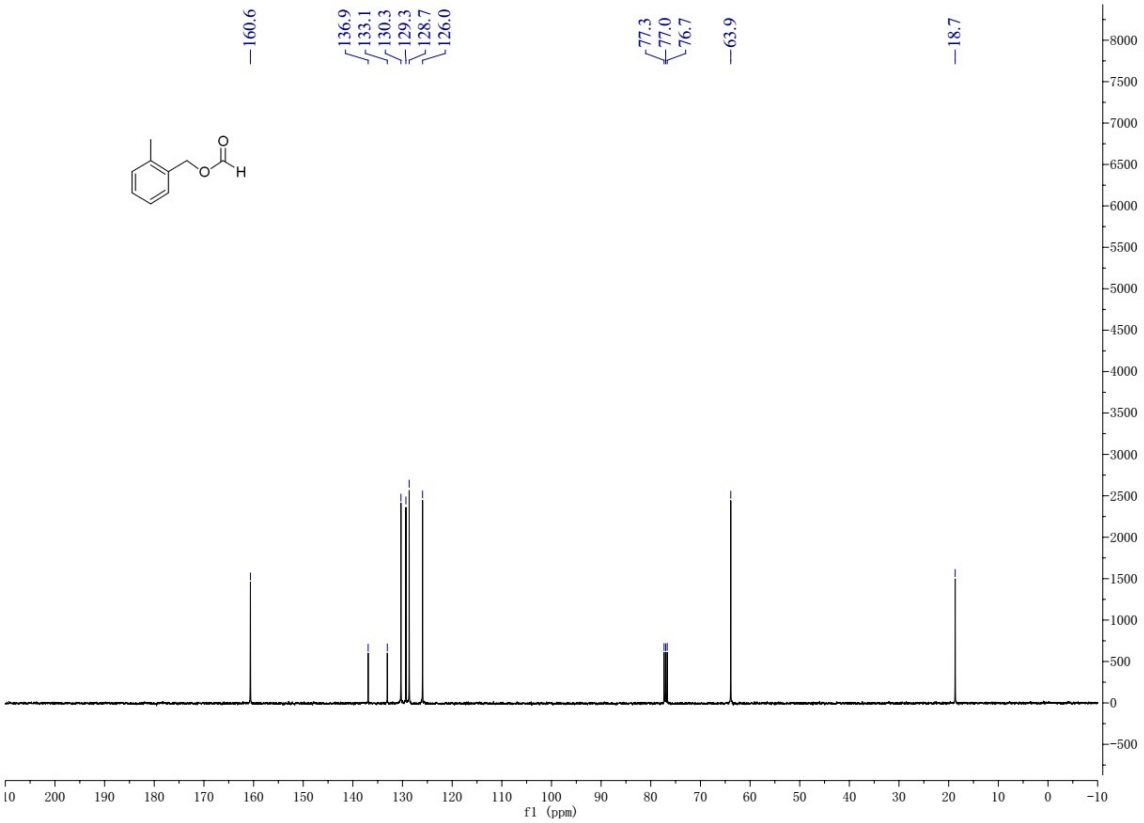
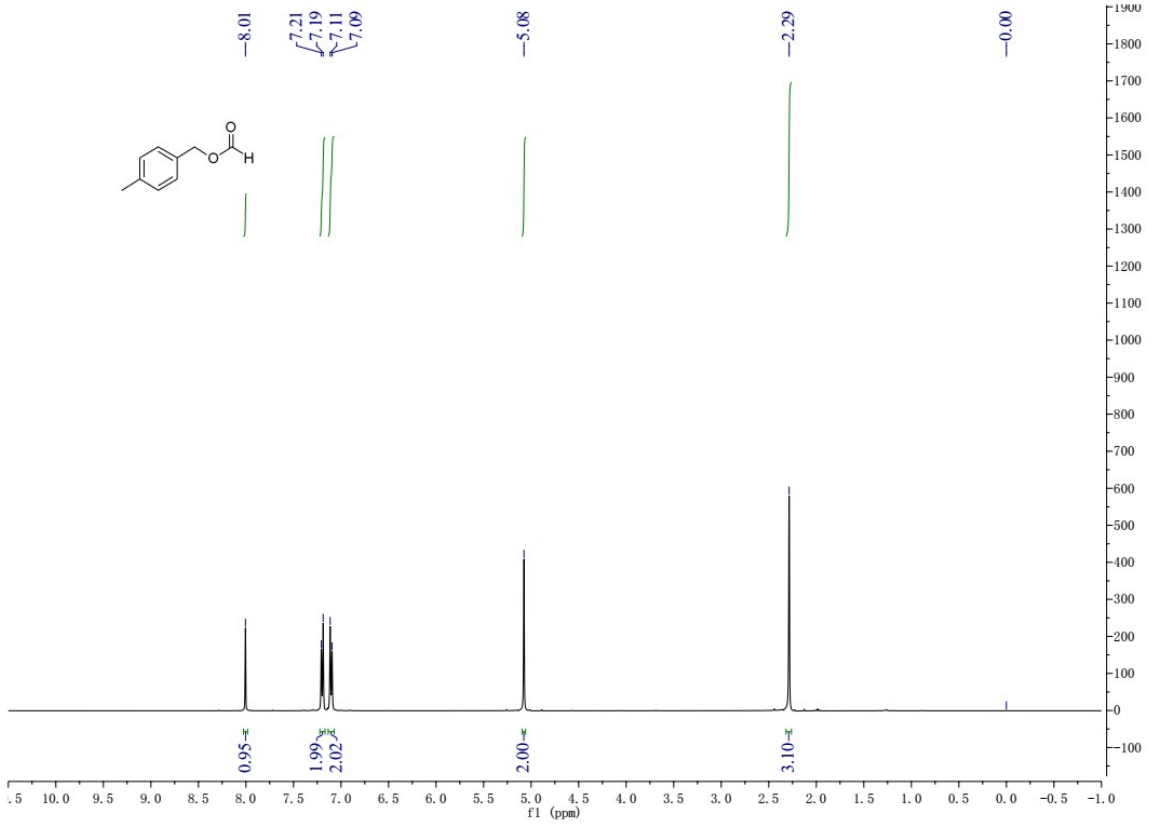
9. Spectra of Benzyl formates



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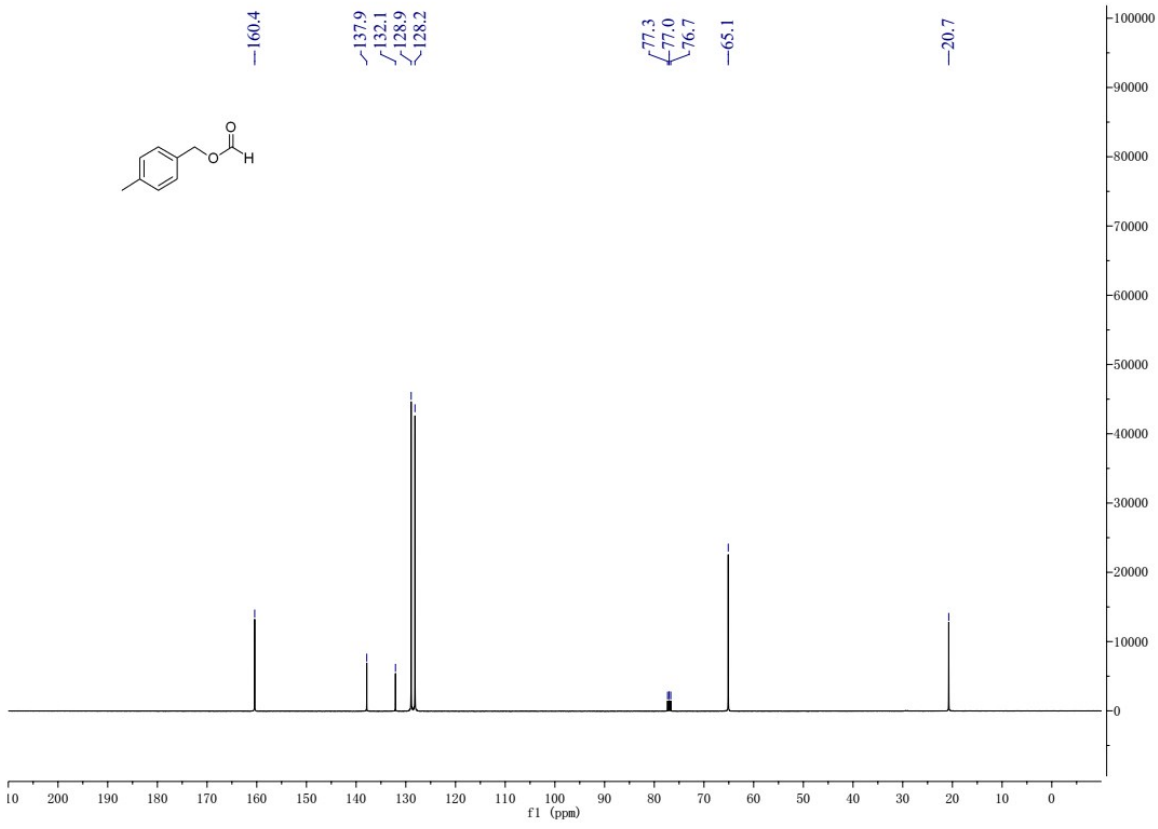
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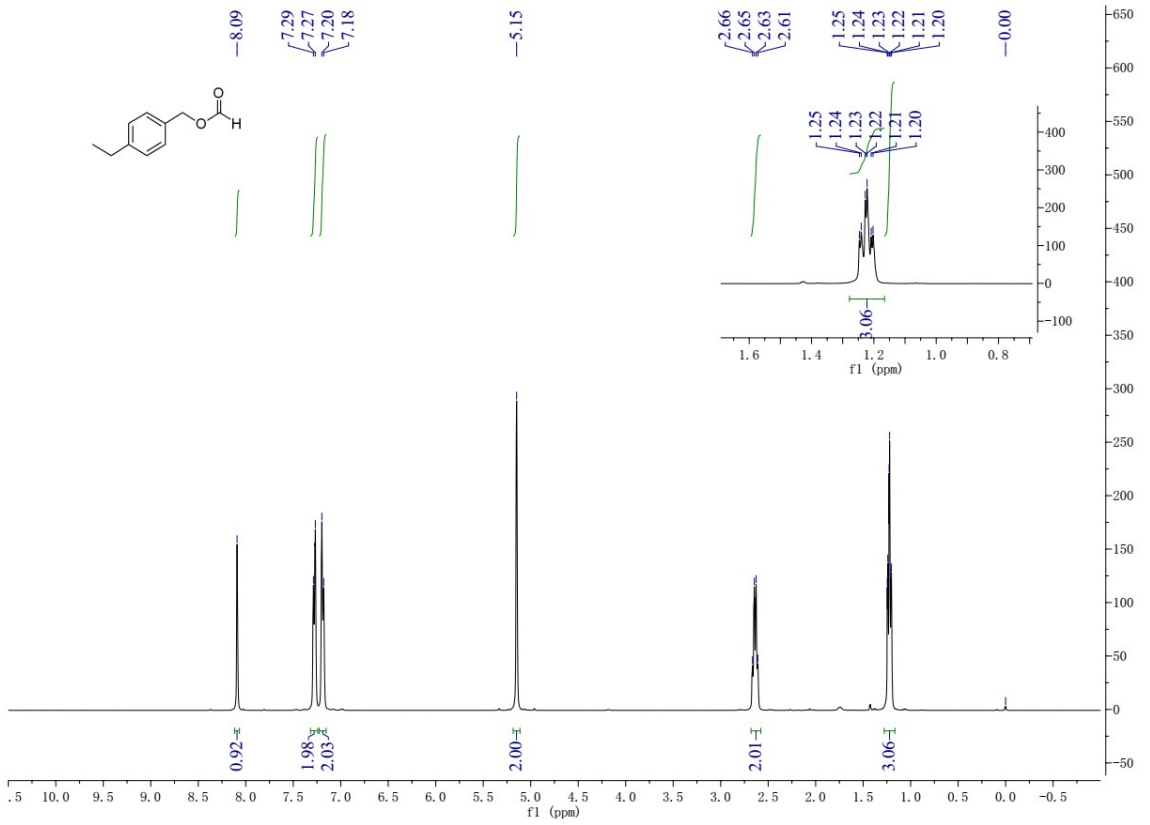
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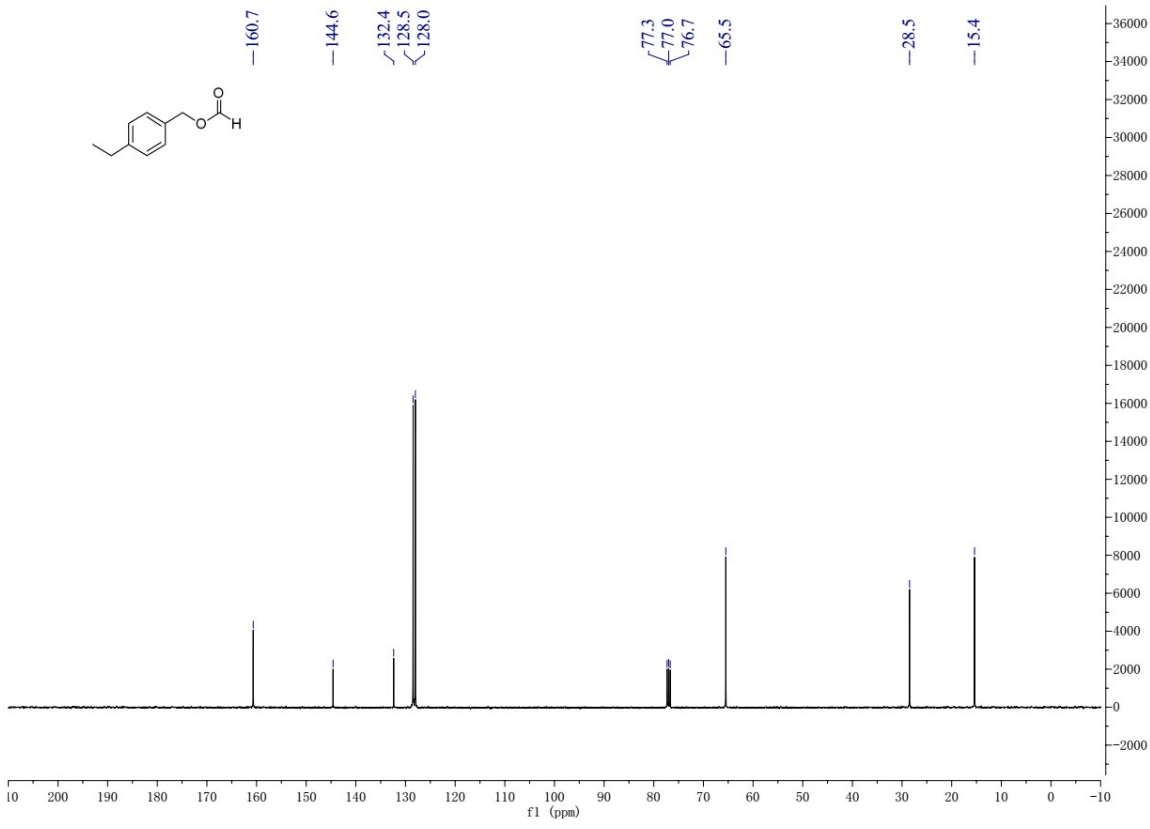
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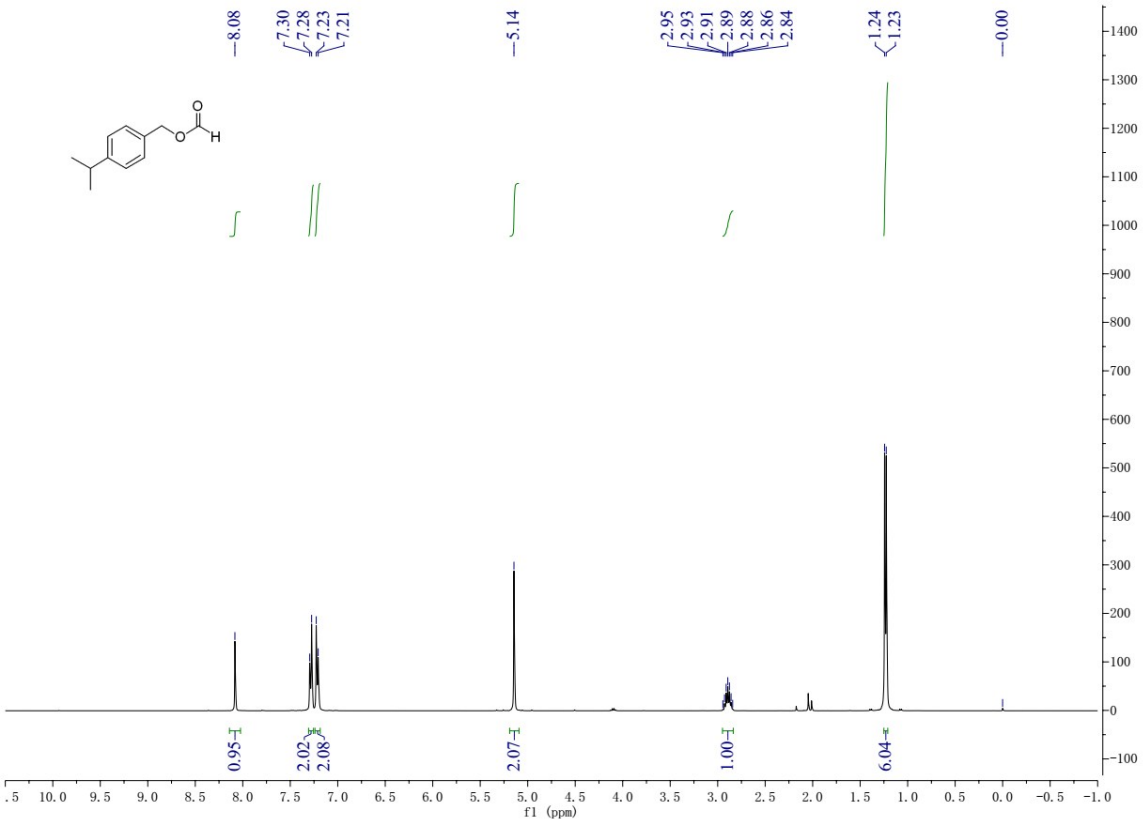
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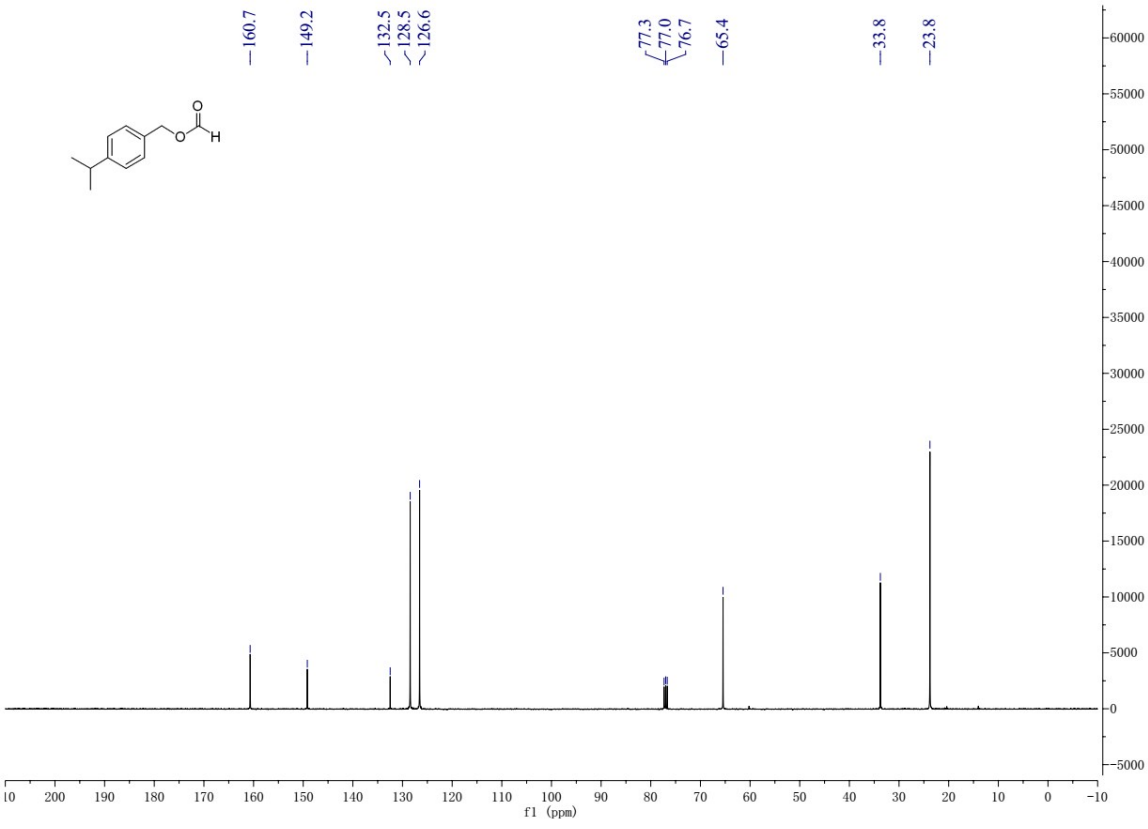
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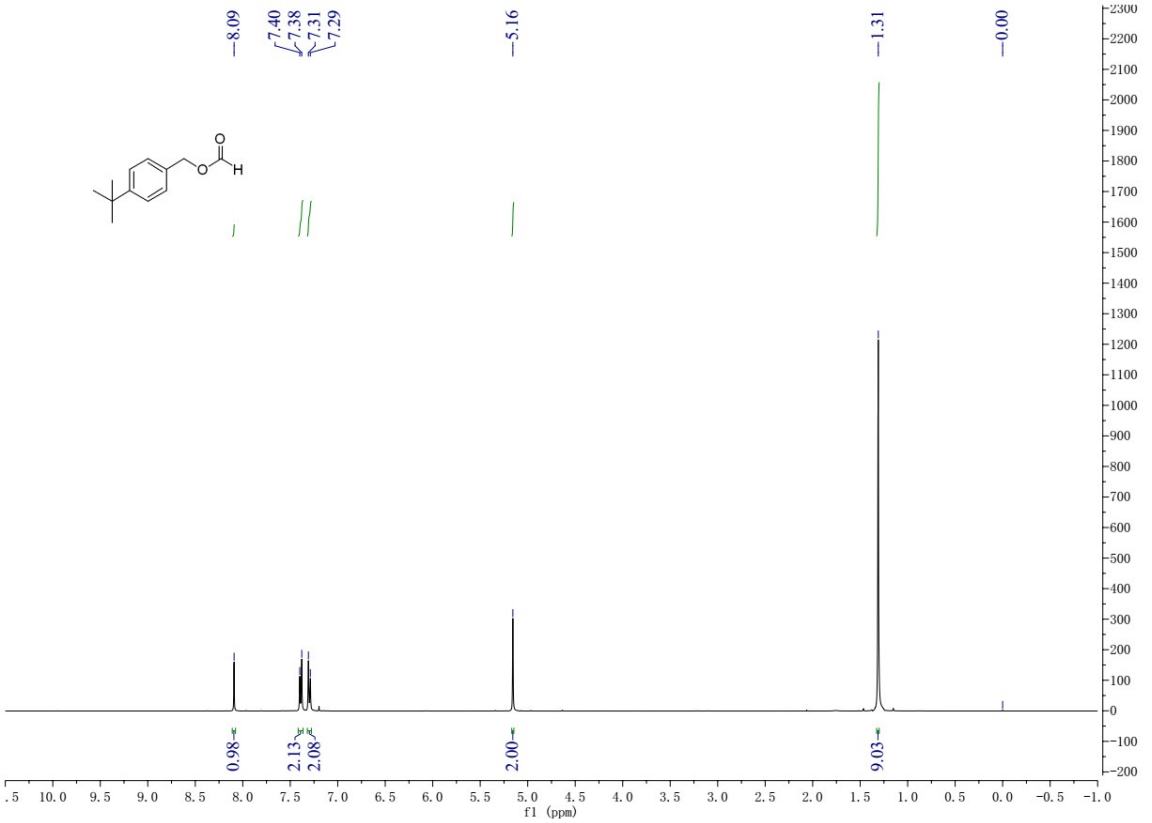
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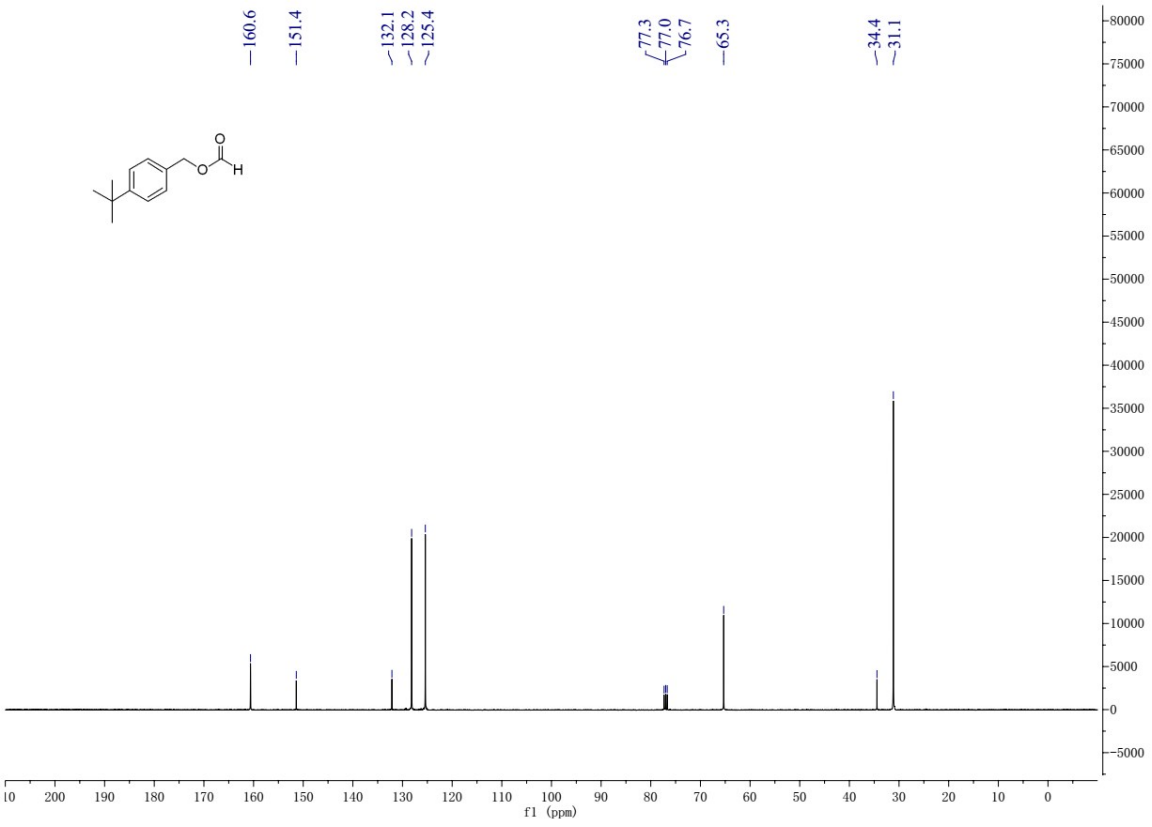
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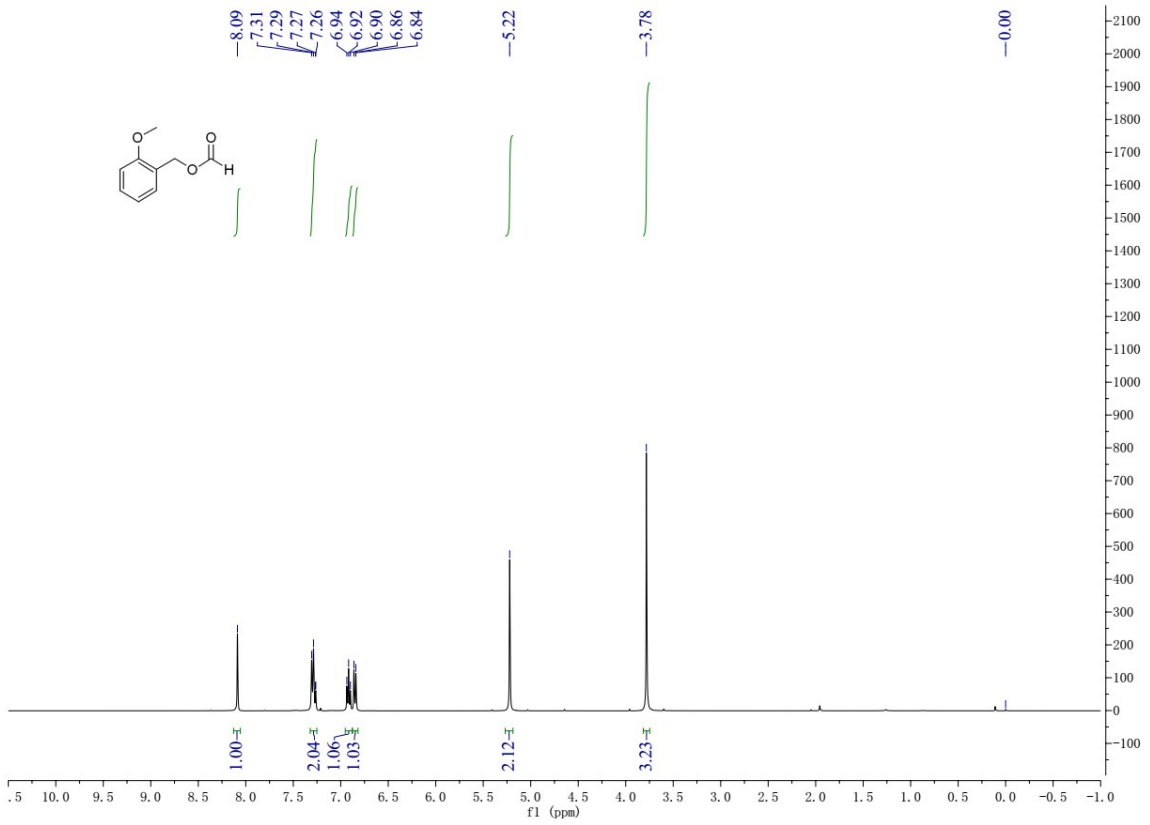
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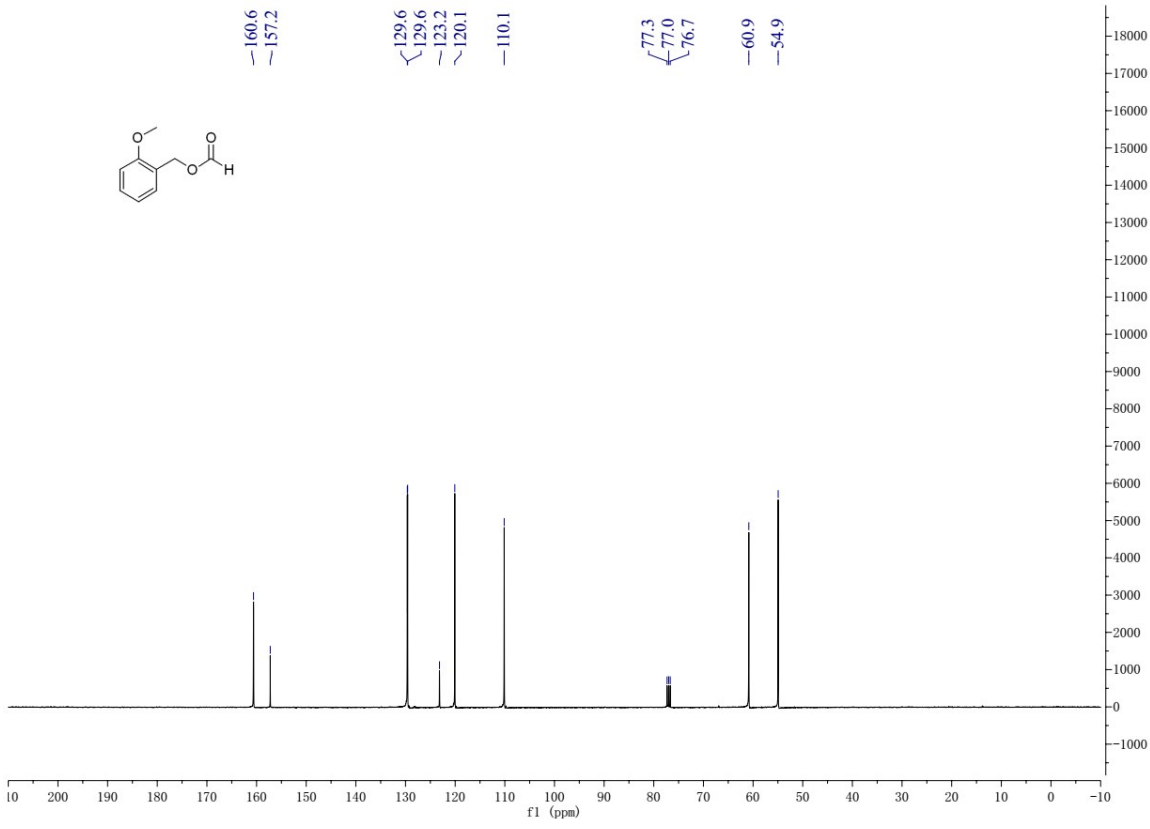
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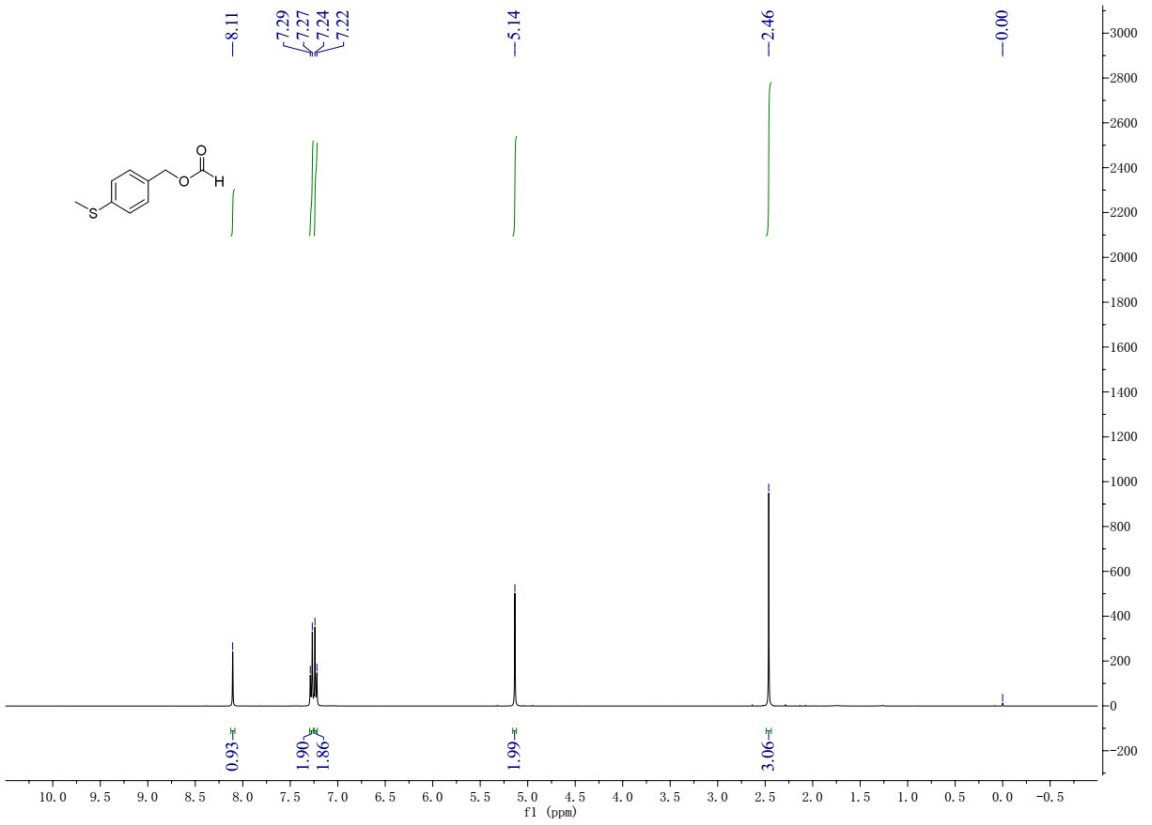
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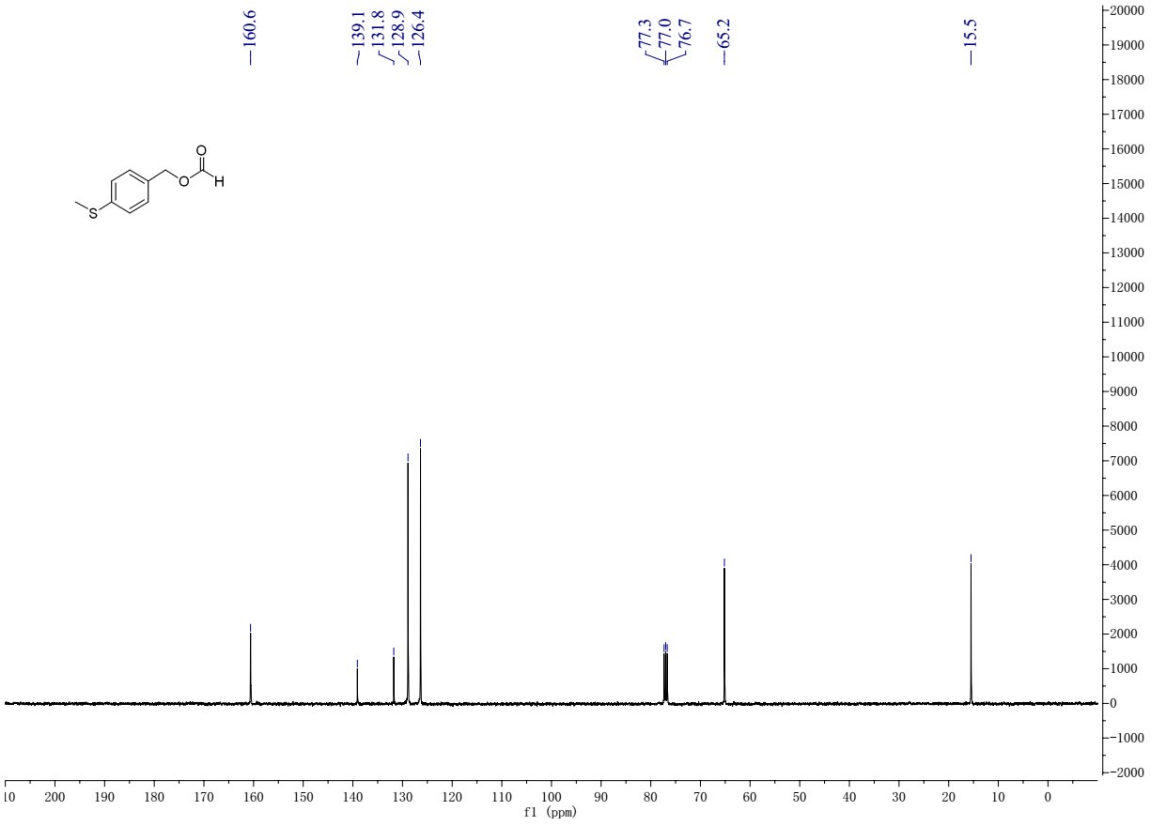
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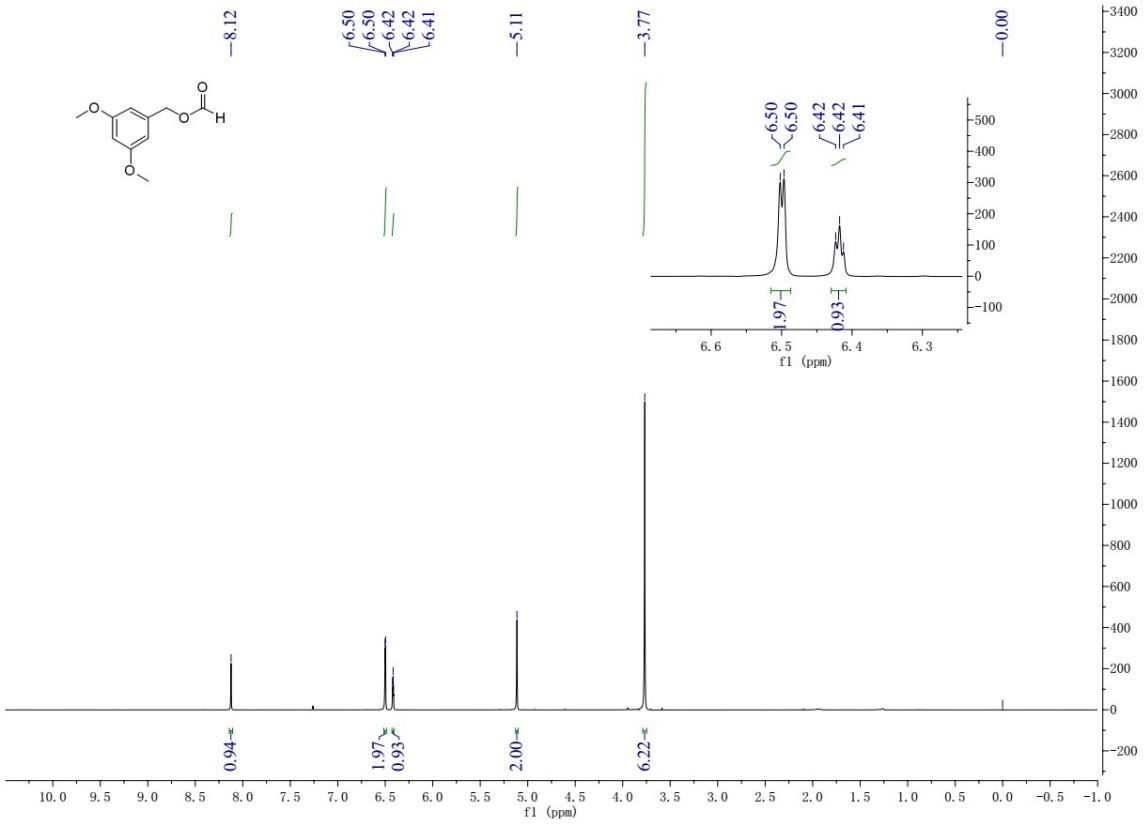
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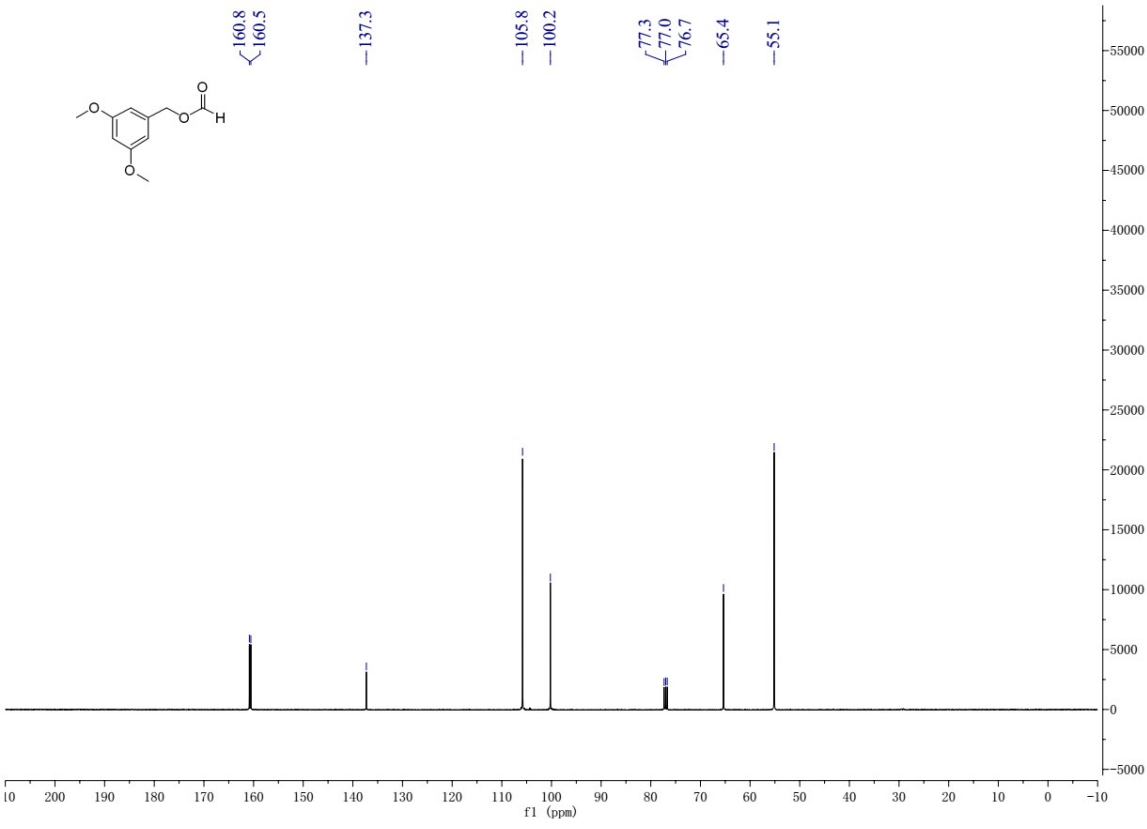
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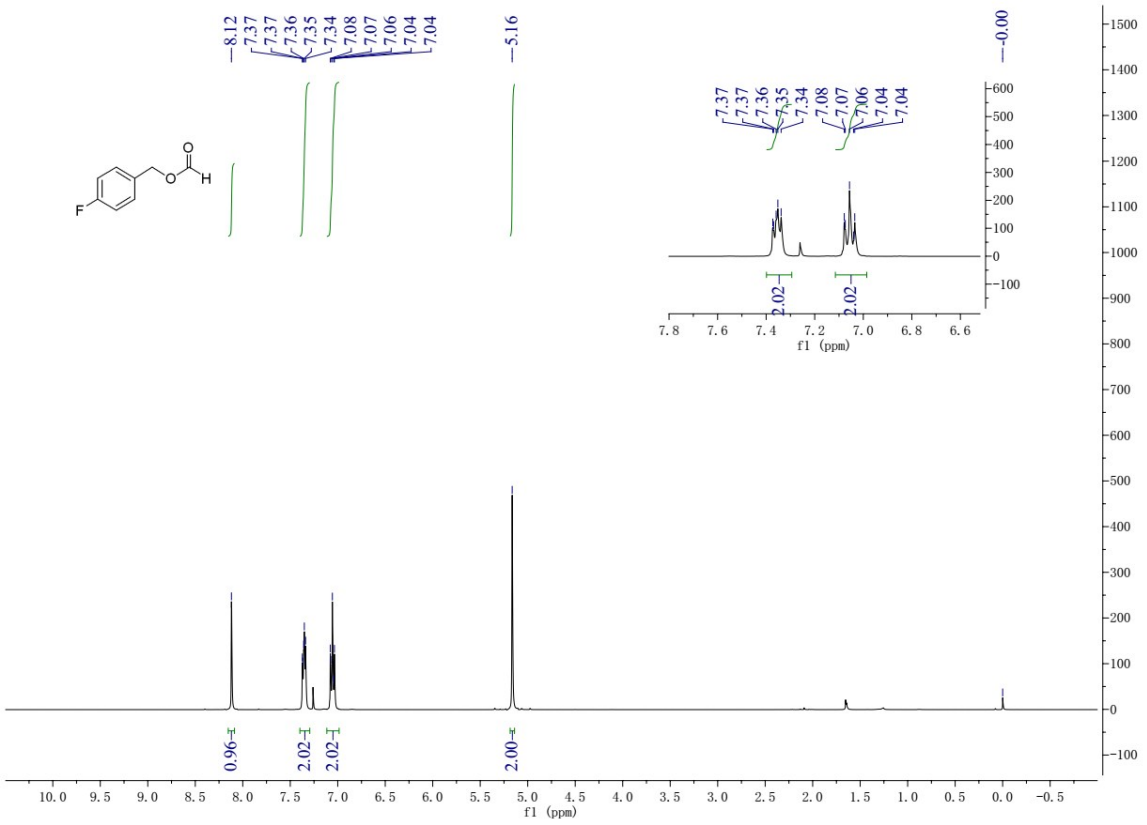
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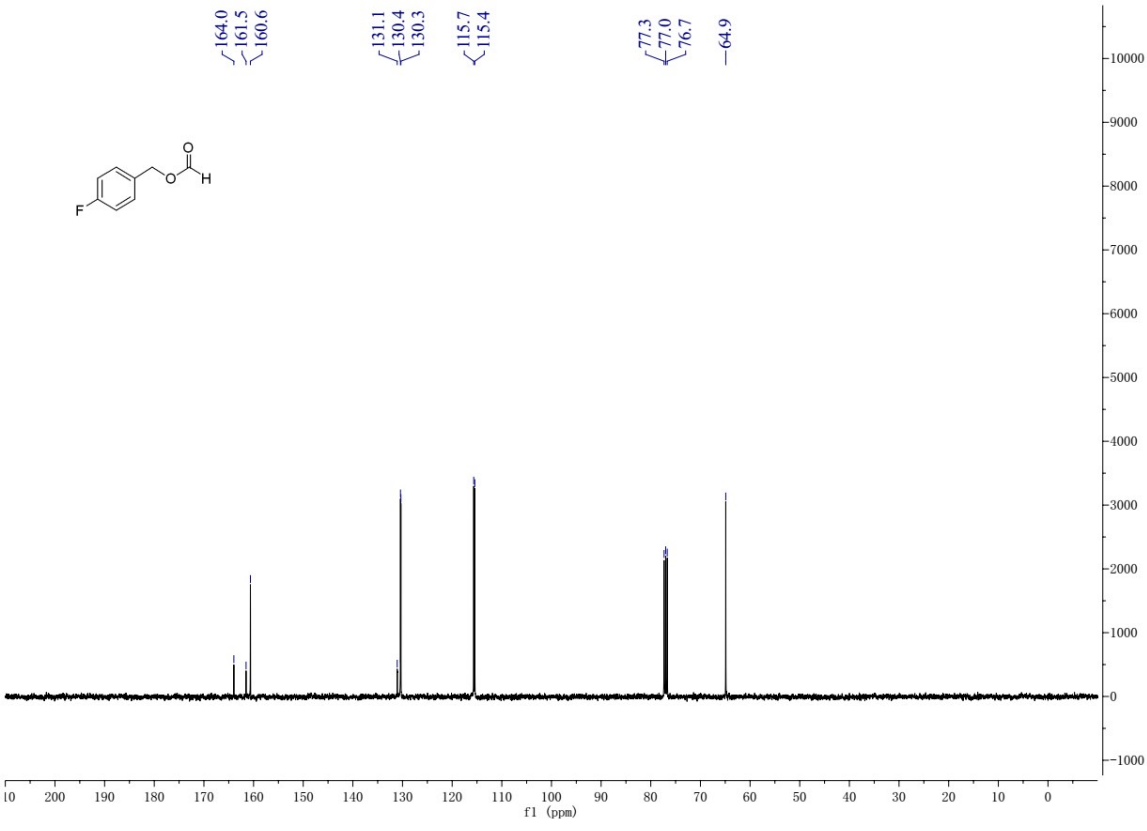
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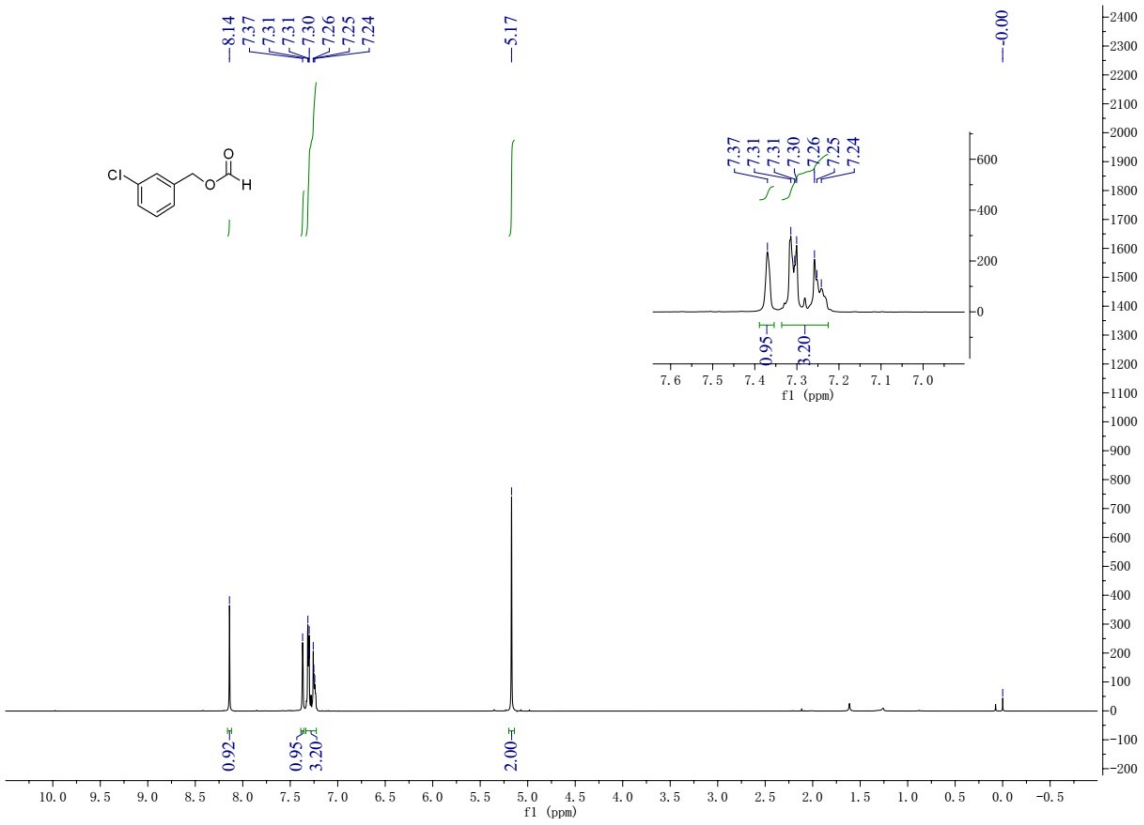
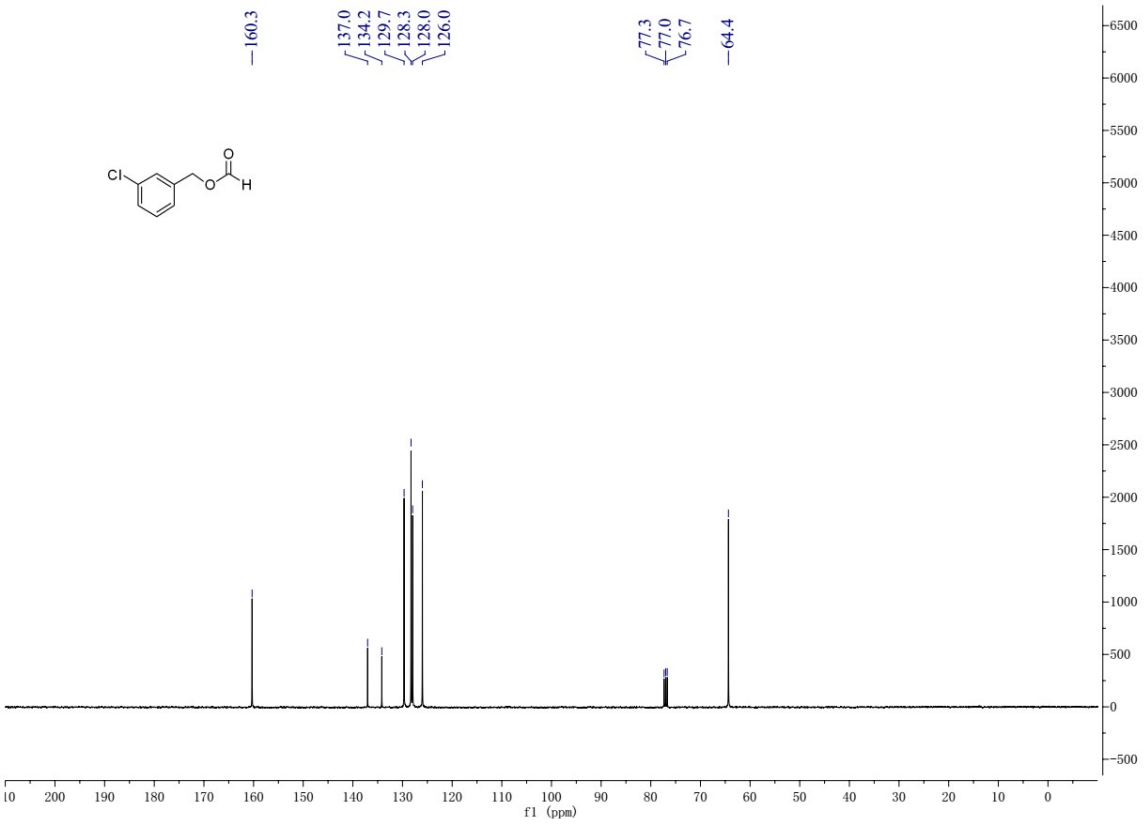
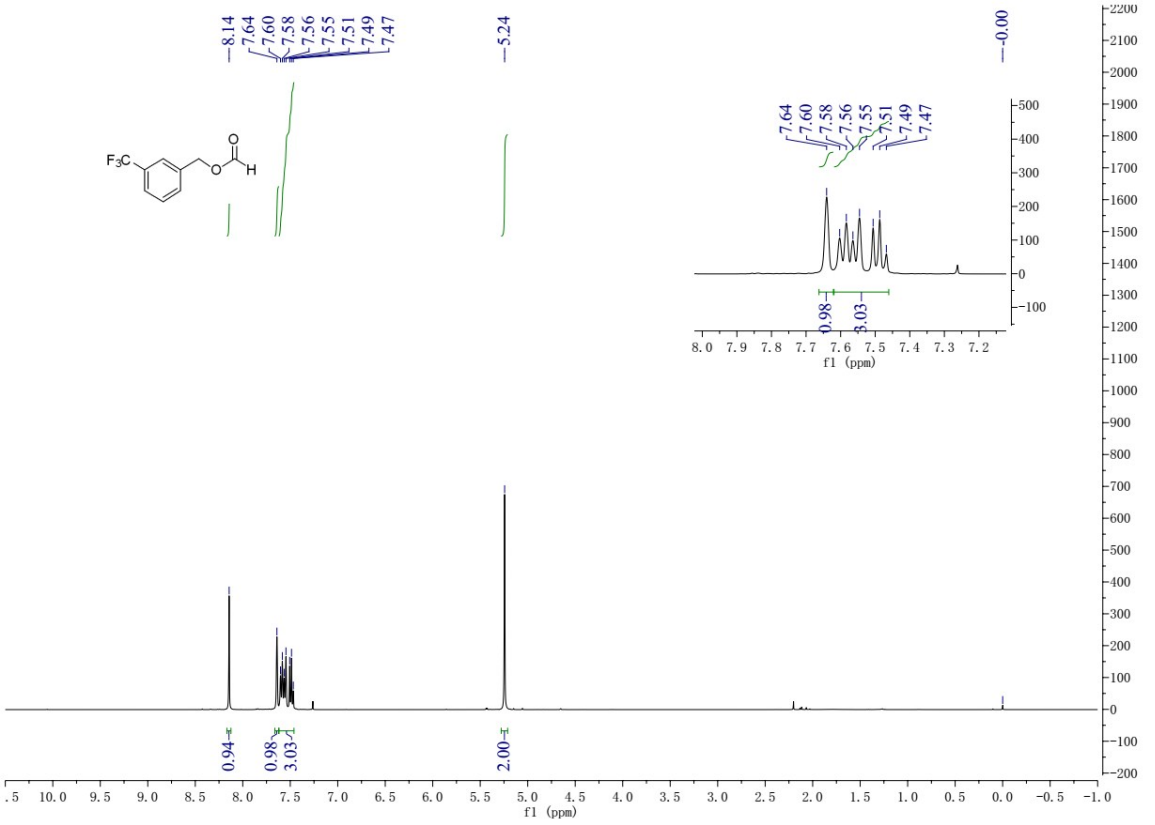
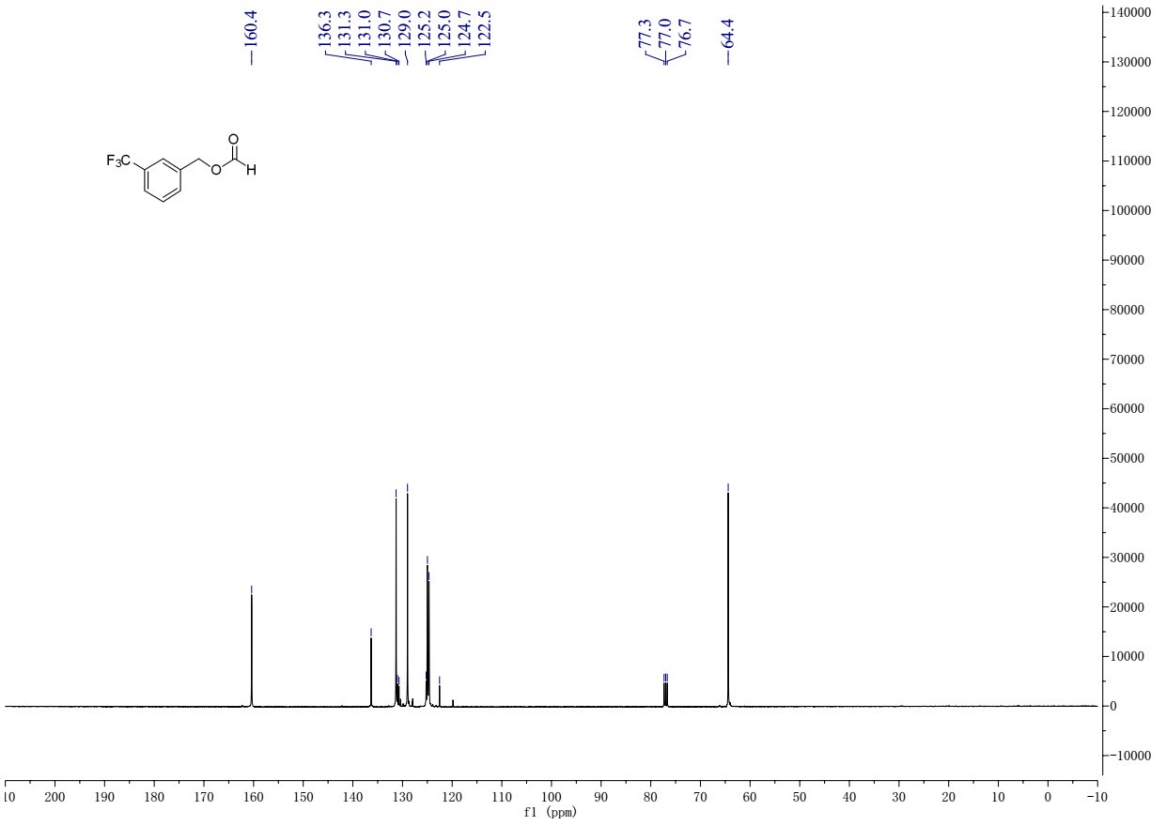
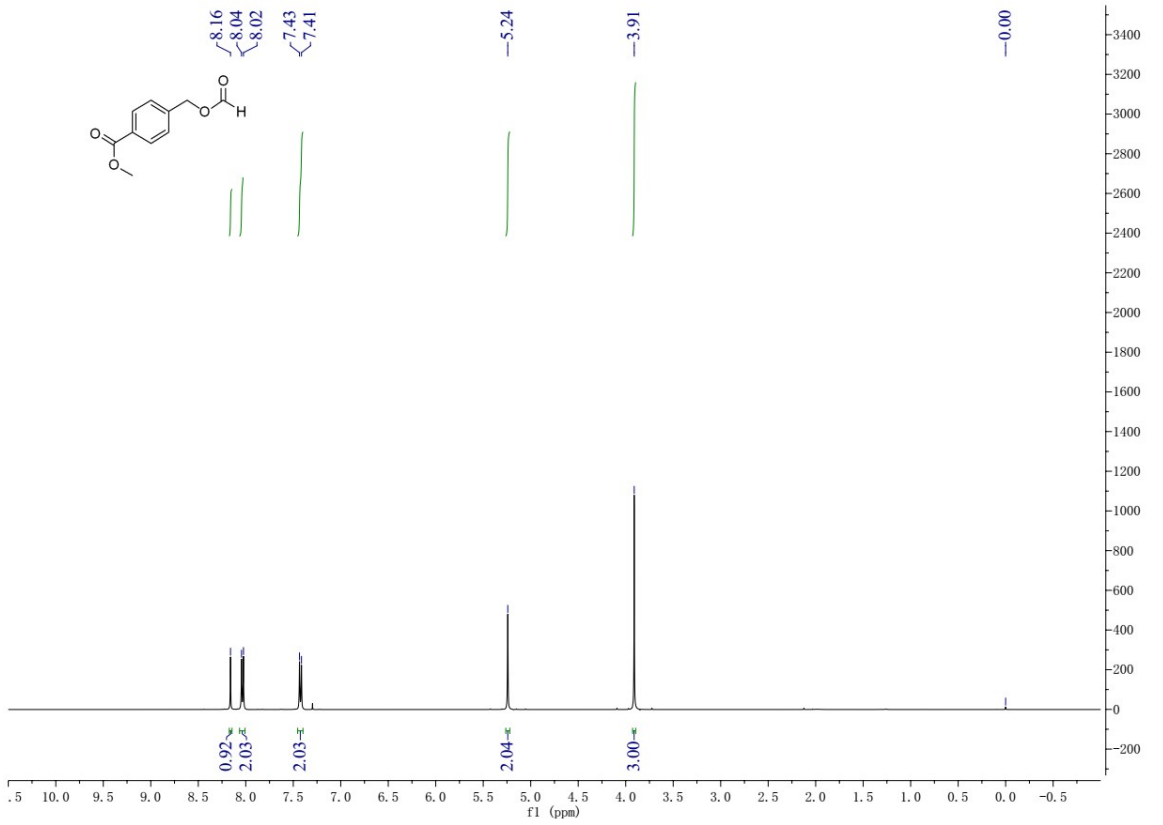
64.9
f1 (ppm)

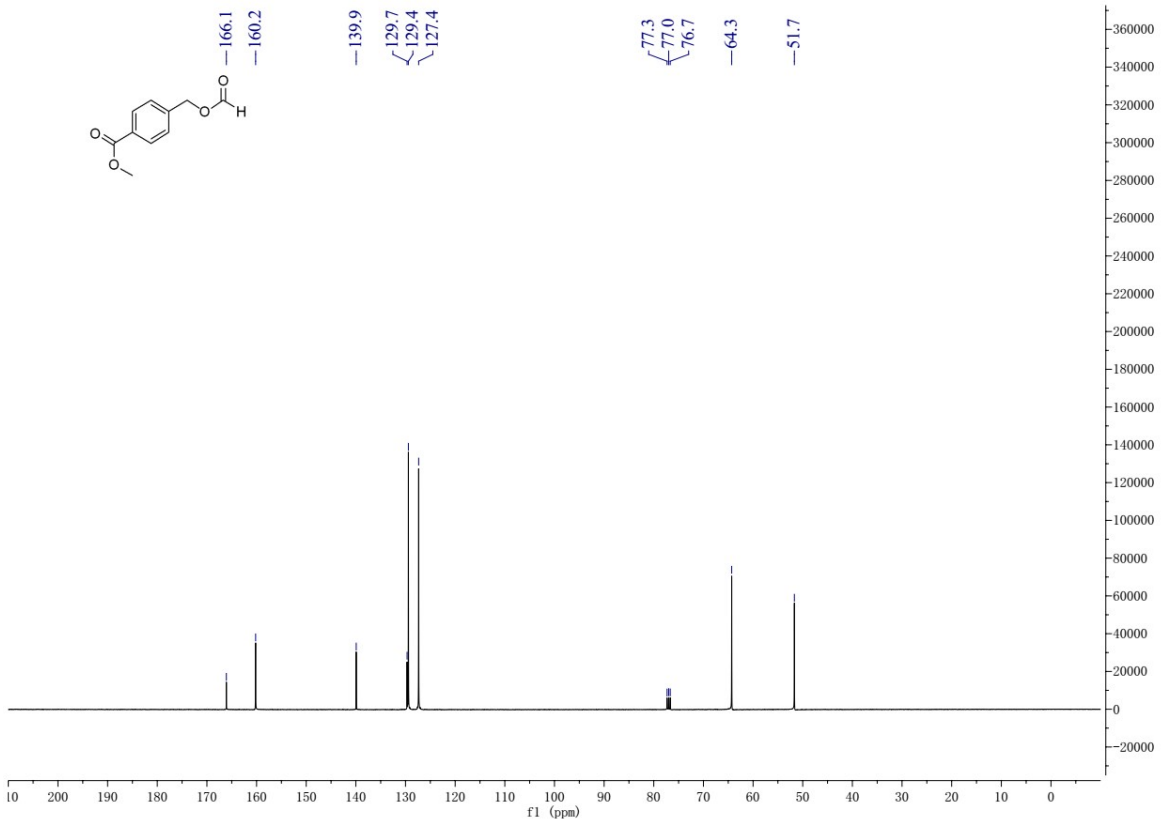

8.14
7.37
7.31
7.31
7.30
7.26
7.25
7.24
5.17
0.00
Cl
O
O
H
0.92
0.95
3.20
2.00
f1 (ppm)

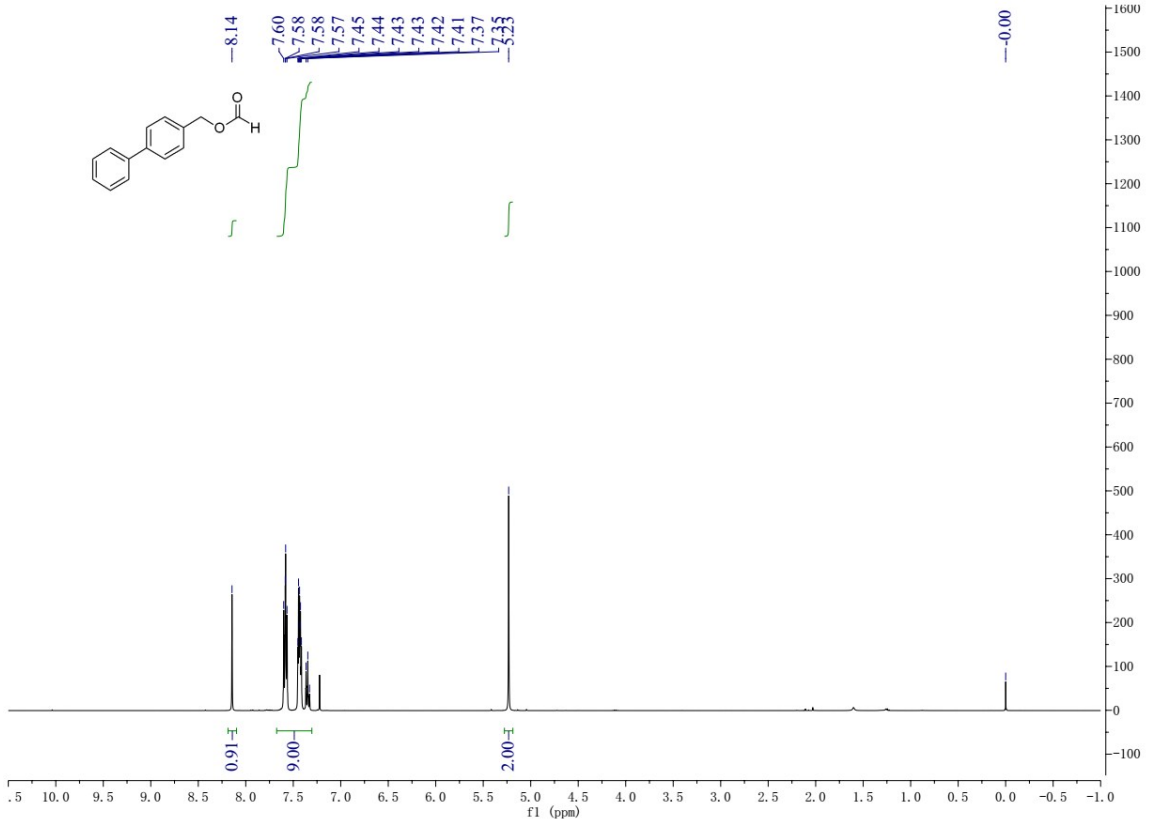

160.3
137.0
134.2
129.7
128.3
128.0
126.0
77.3
77.0
76.7
64.4
Cl
O
O
H
f1 (ppm)

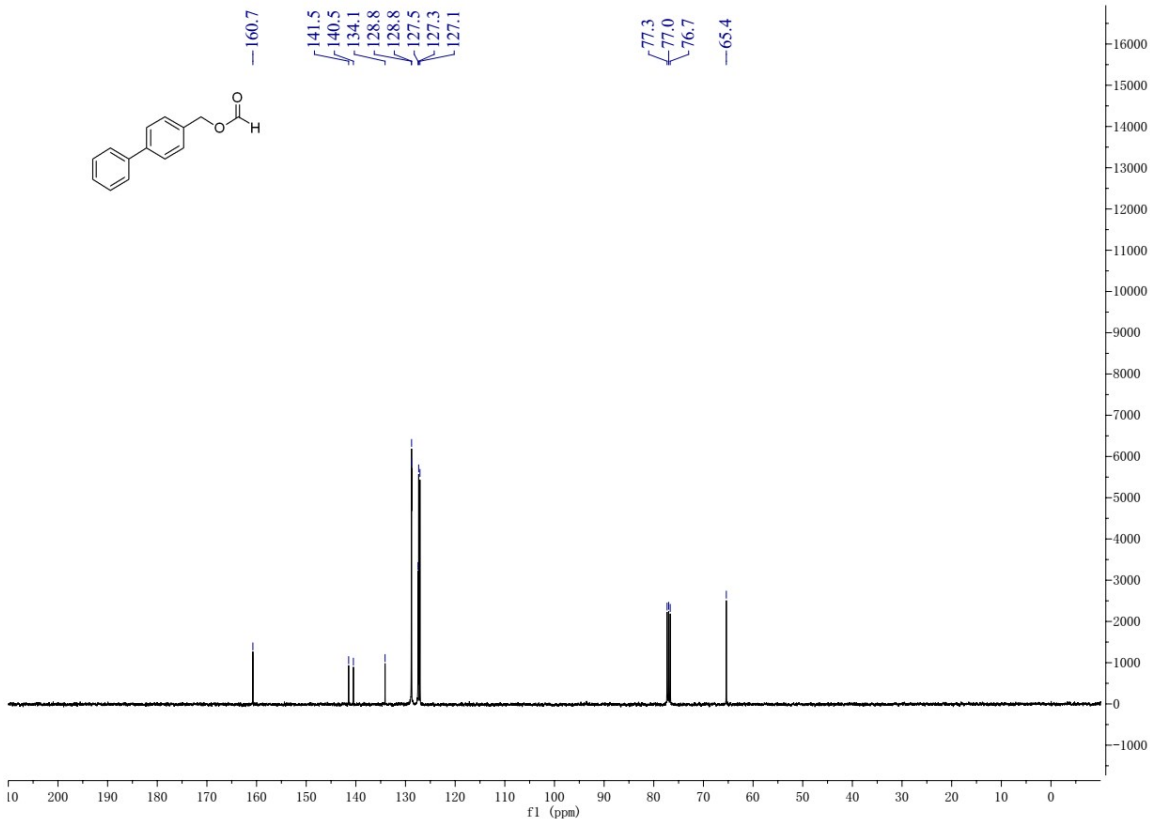

8.14
7.64
7.60
7.58
7.56
7.55
7.51
7.49
7.47
5.24
0.00
0.94
0.98
3.03
2.00
f1 (ppm)

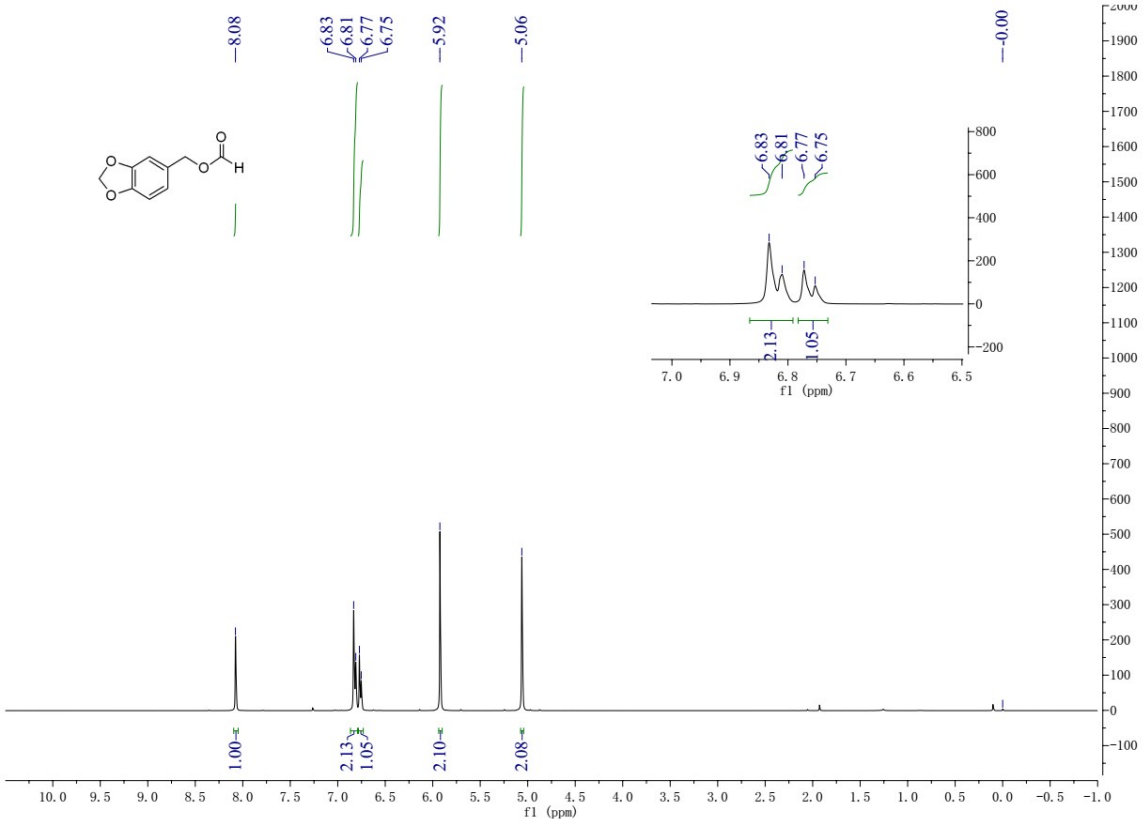

160.4
136.3
131.3
131.0
130.7
129.0
125.2
125.0
124.7
122.5
77.3
77.0
76.7
64.4
f1 (ppm)

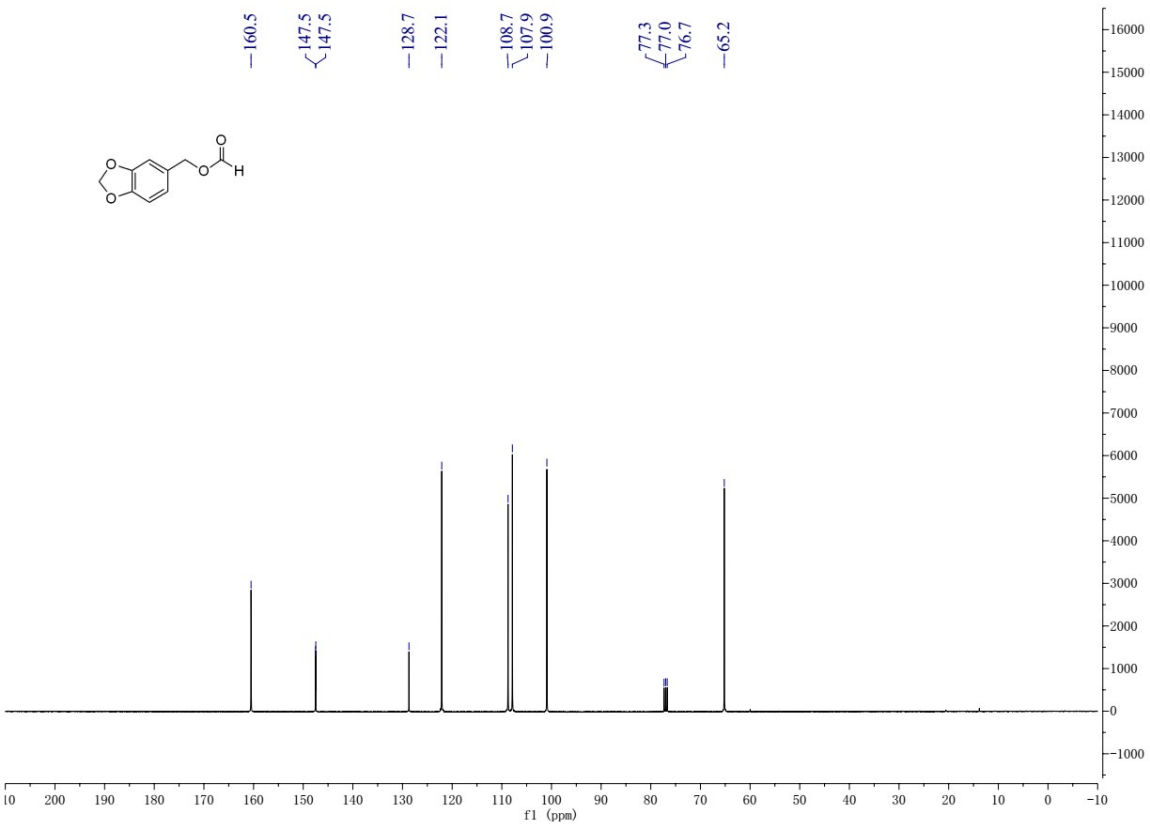

8.16
8.04
8.02
7.43
7.41
5.24
3.91
0.00
0.92
2.03
2.03
2.04
3.00
f1 (ppm)


166.1
160.2
139.9
129.7
129.4
127.4
77.3
77.0
76.7
64.3
51.7
f1 (ppm)

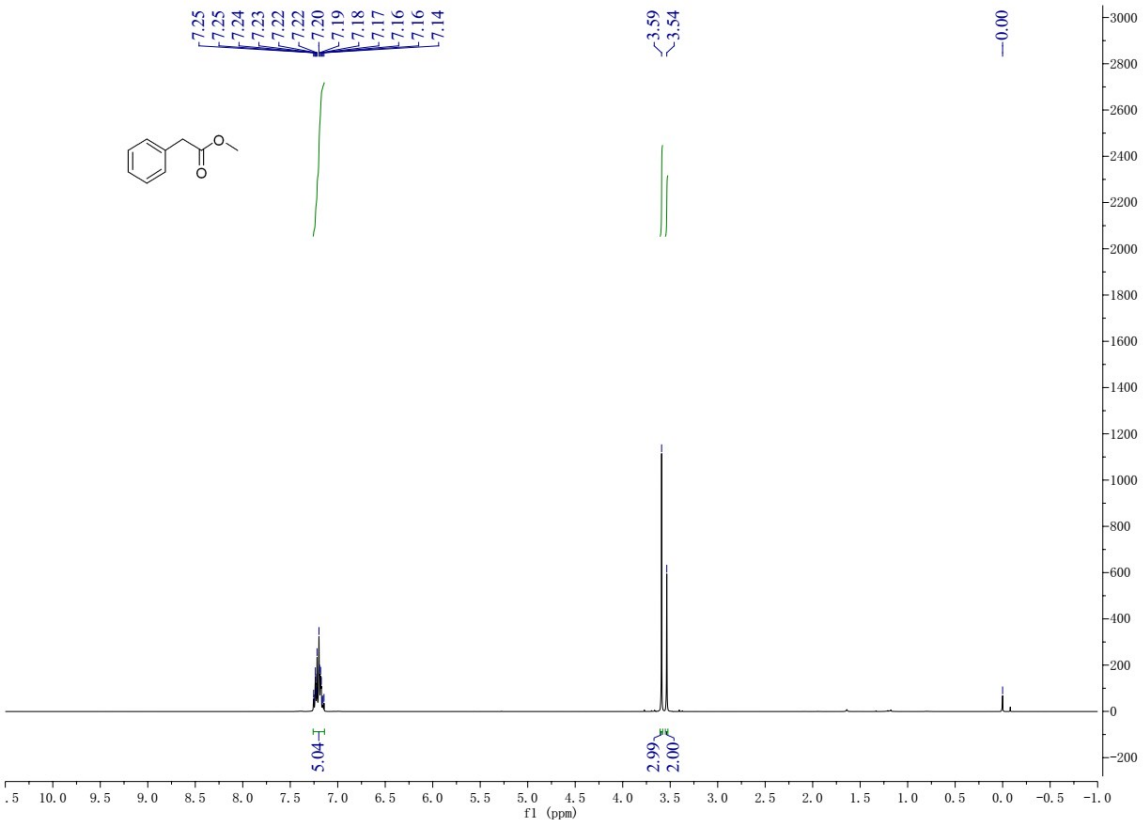

8.14
7.60
7.58
7.58
7.57
7.45
7.44
7.43
7.43
7.42
7.41
7.37
7.35
5.23
0.00
0.91
9.00
2.00
f1 (ppm)

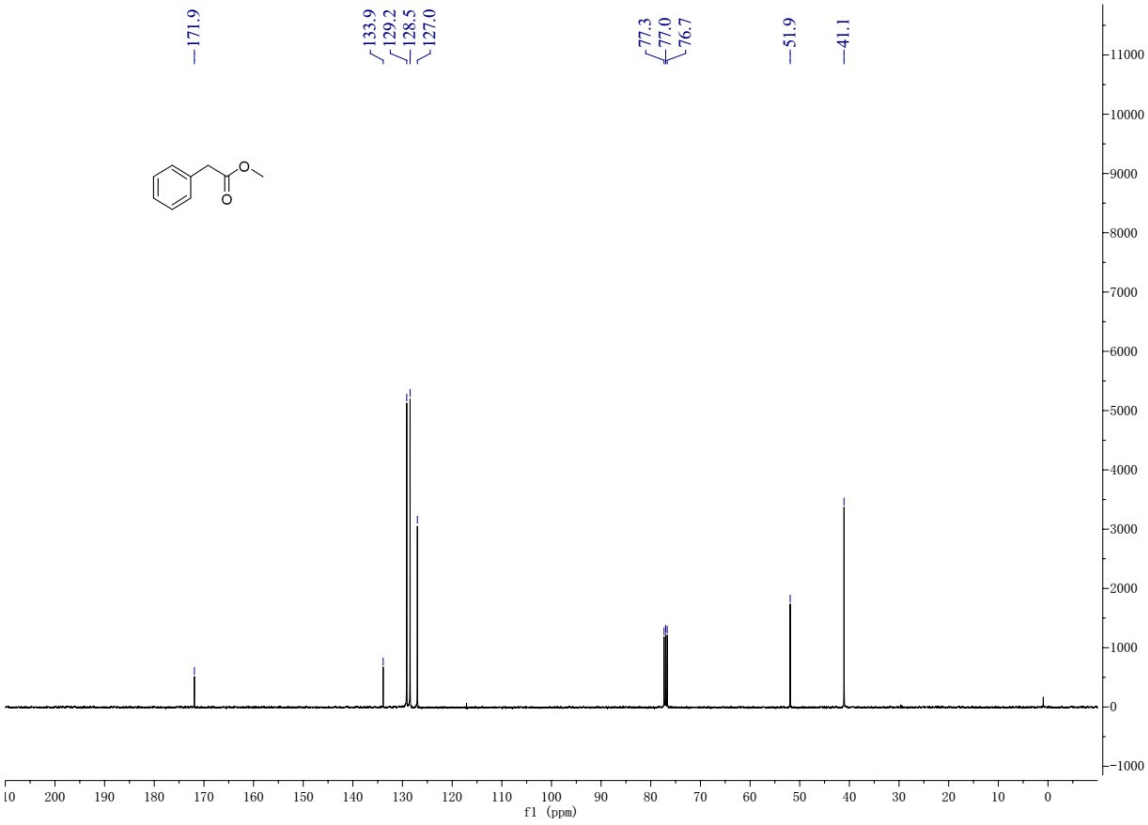

160.7
141.5
140.5
134.1
128.8
128.8
127.5
127.3
127.1
77.3
77.0
76.7
65.4
f1 (ppm)

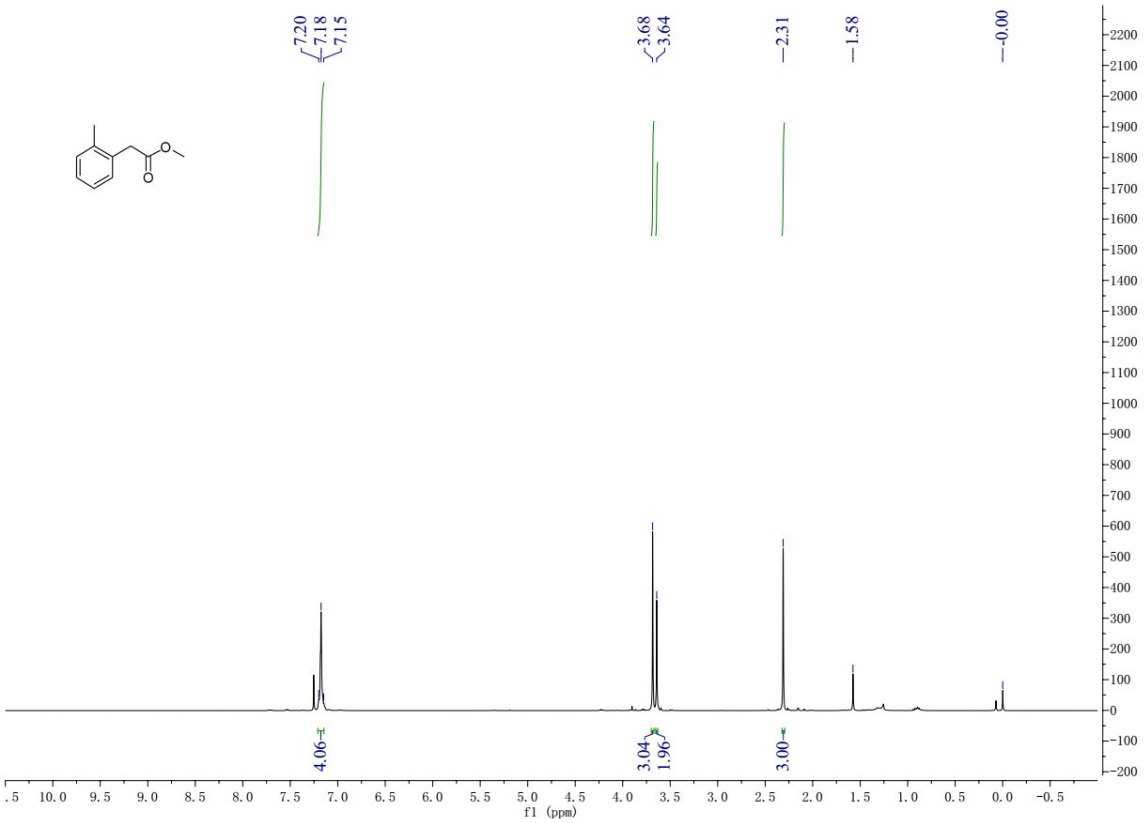

8.08
6.83
6.81
6.77
6.75
5.92
5.06
0.00
1.00
2.13
1.05
2.10
2.08
f1 (ppm)

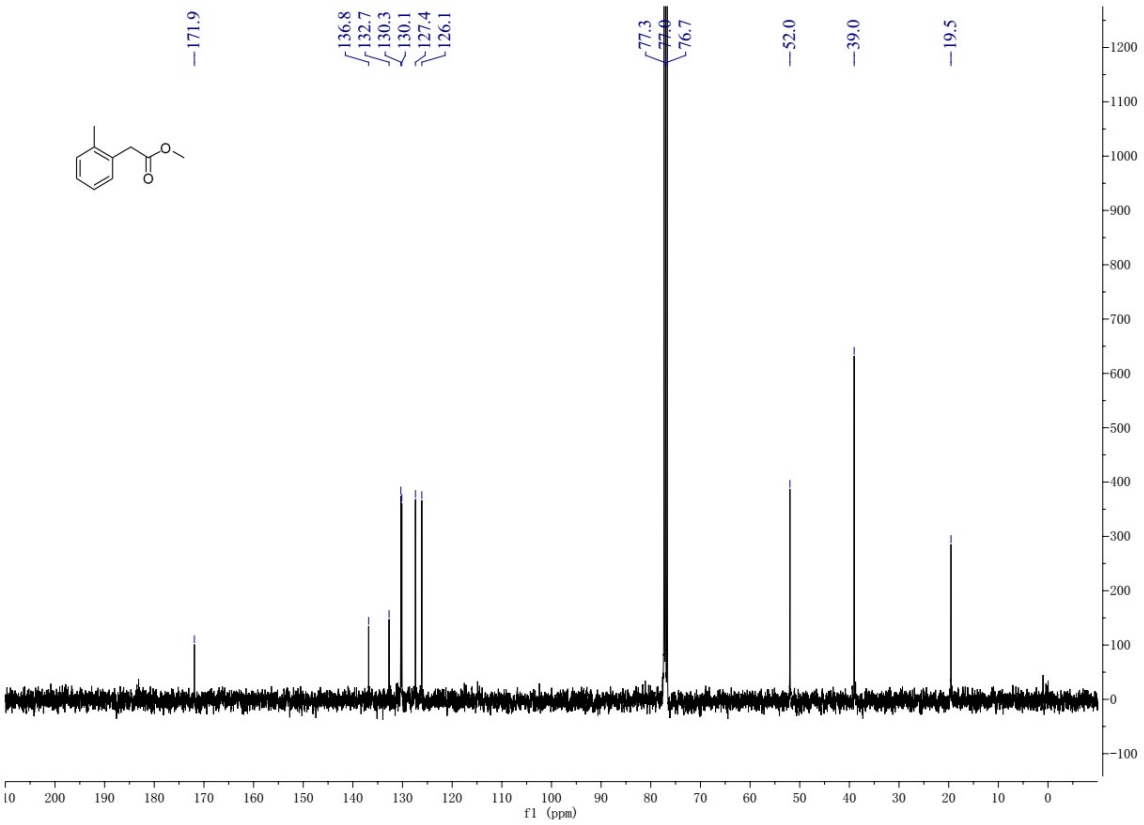

160.5
147.5
147.5
128.7
122.1
108.7
107.9
100.9
77.3
77.0
76.7
65.2
f1 (ppm)

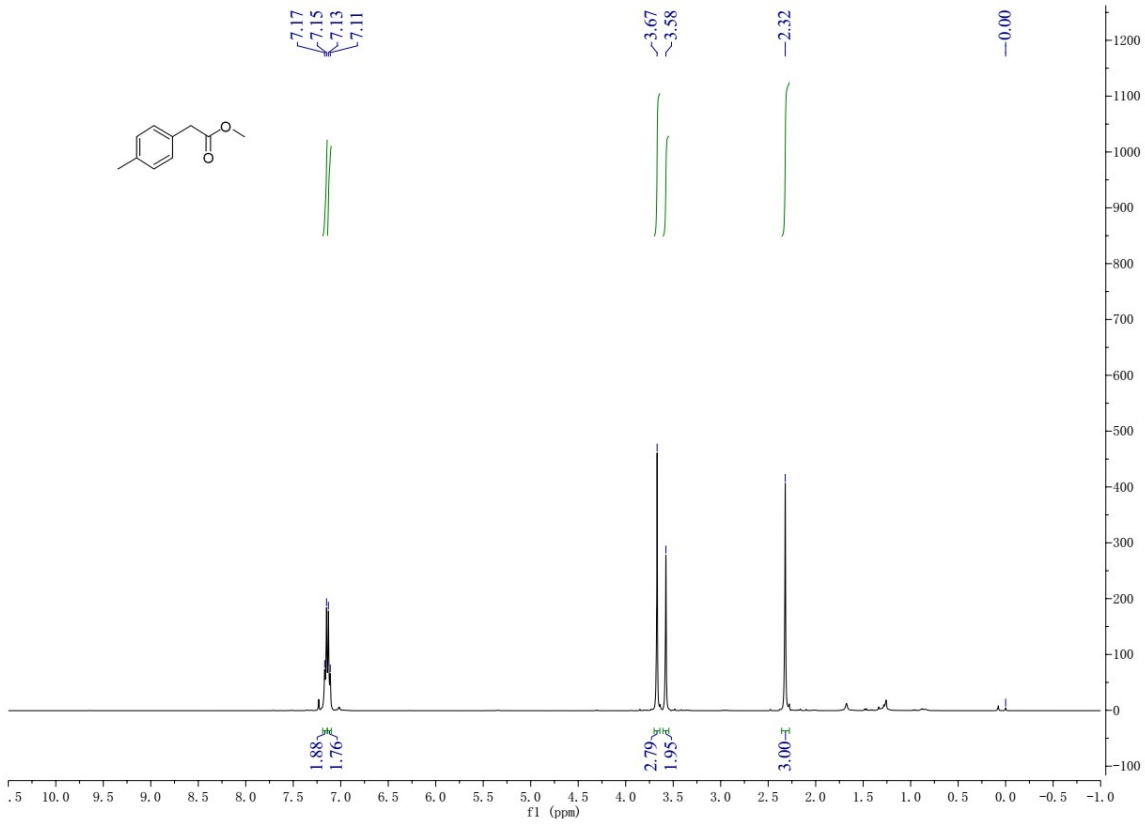
10. Spectra of 2-Methyl 2-arylacetates

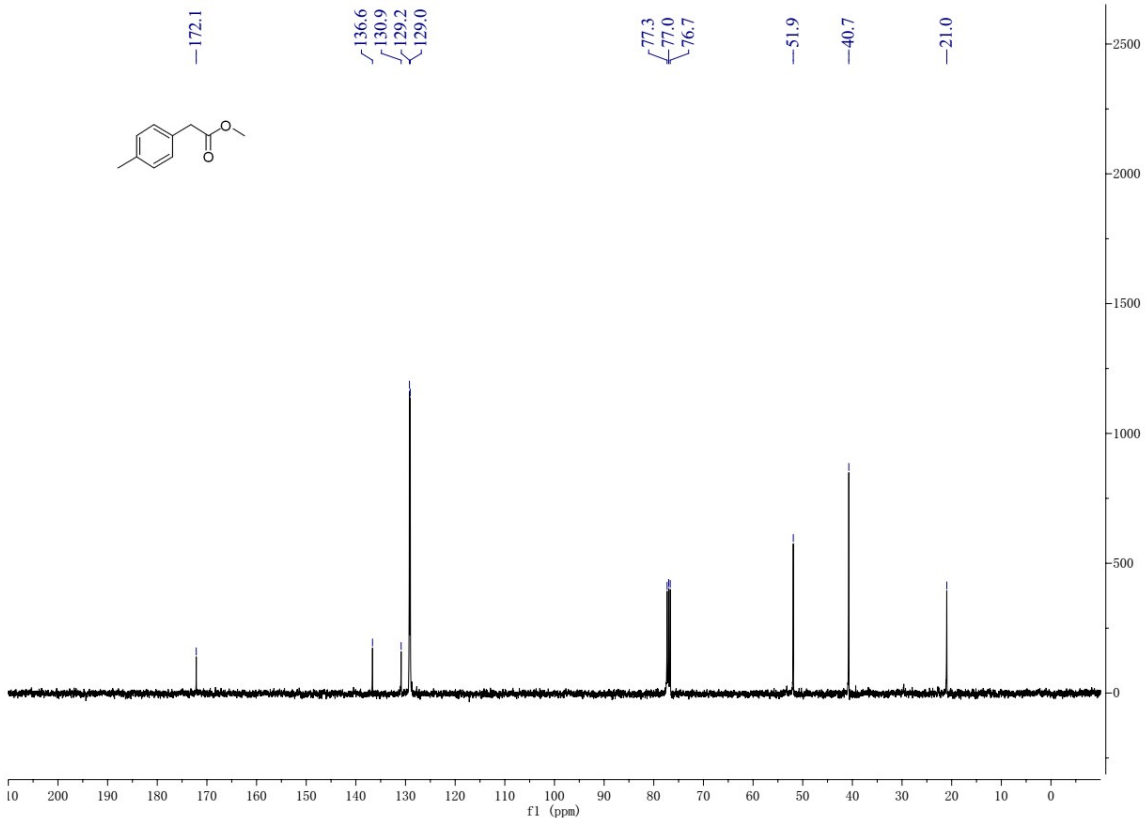


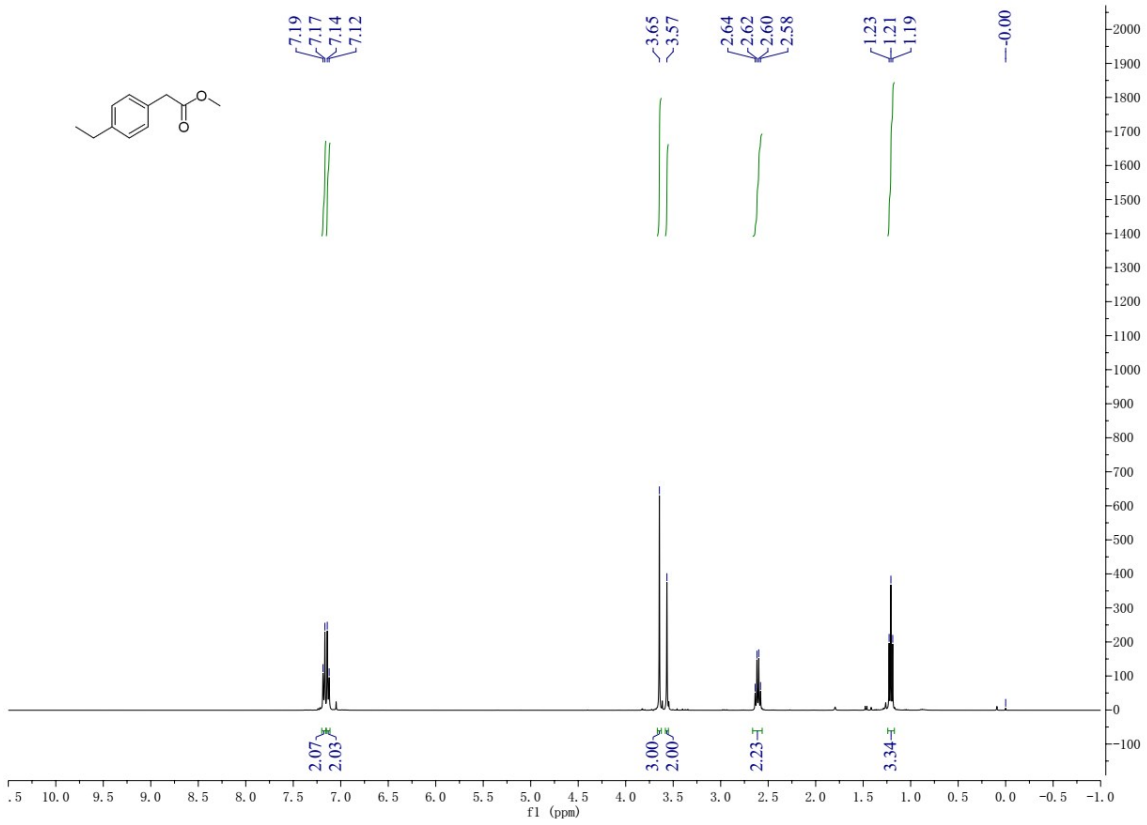


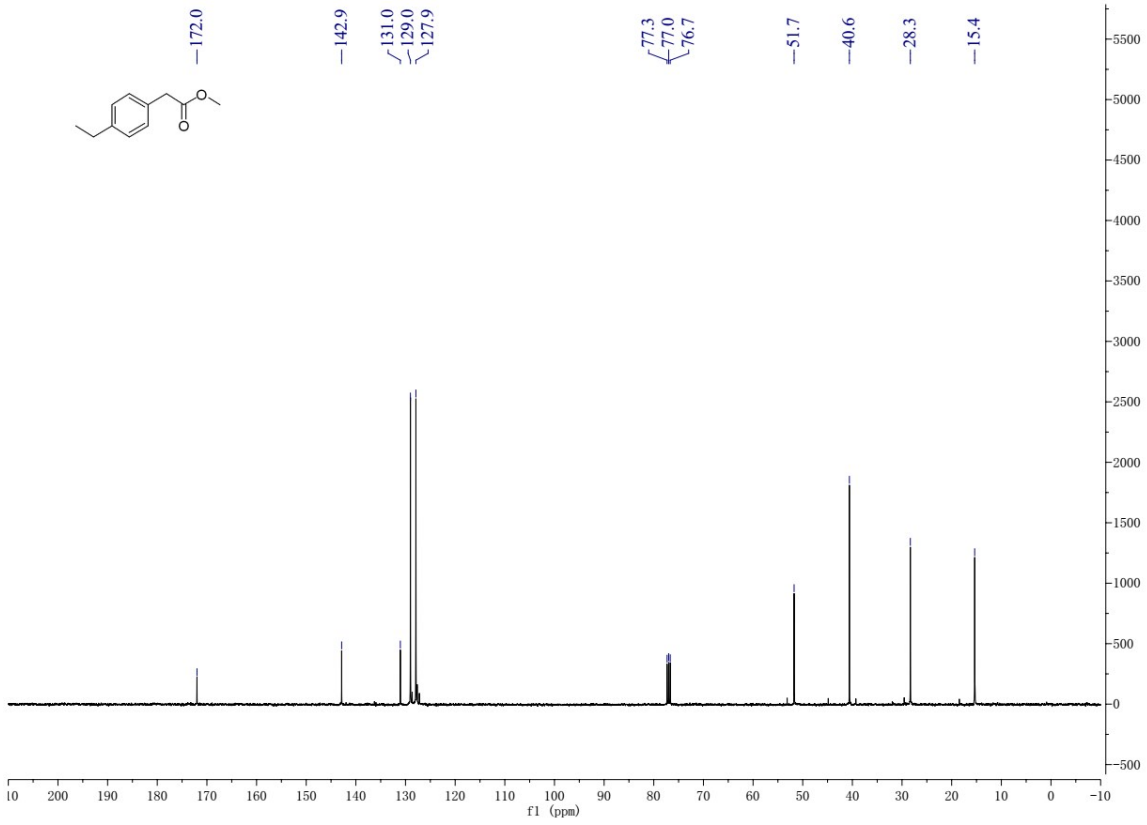

7.20
7.18
7.15
3.68
3.64
2.31
1.58
0.00
4.06
3.04
1.96
3.00
f1 (ppm)

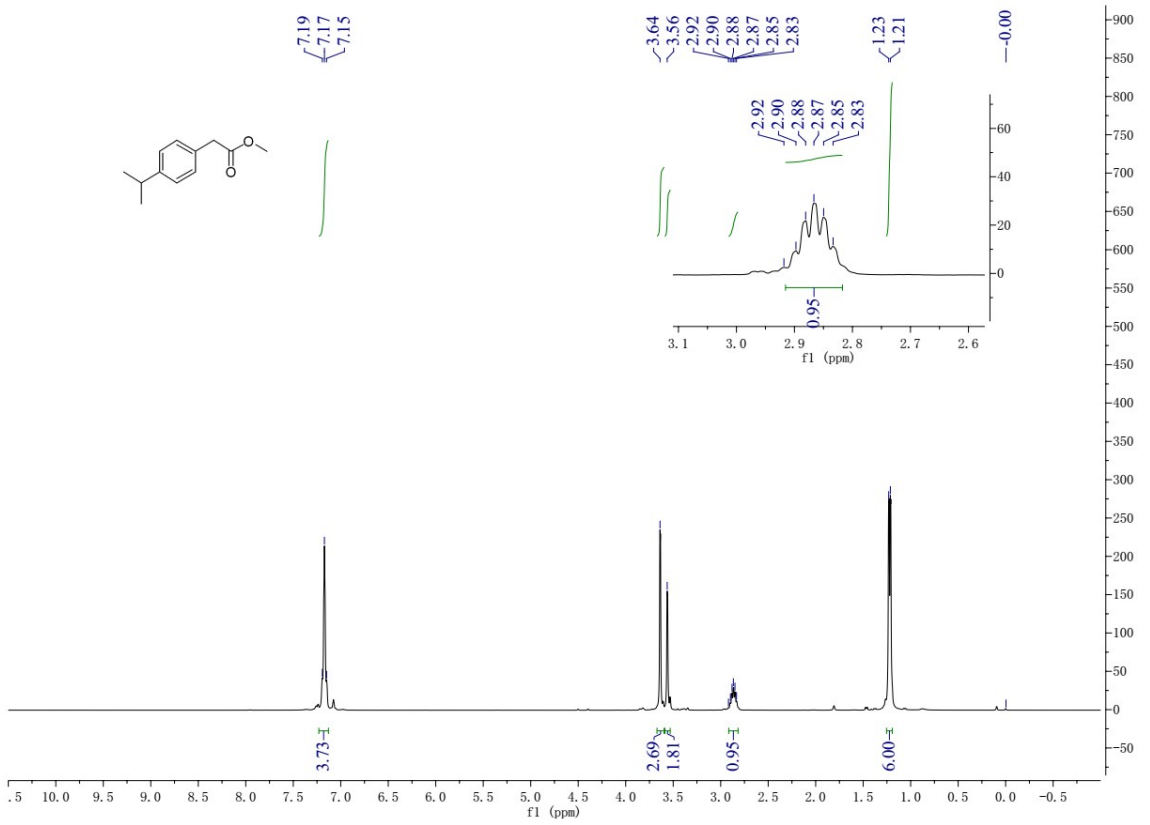

171.9
136.8
132.7
130.3
130.1
127.4
126.1
77.3
77.0
76.7
52.0
39.0
19.5
f1 (ppm)

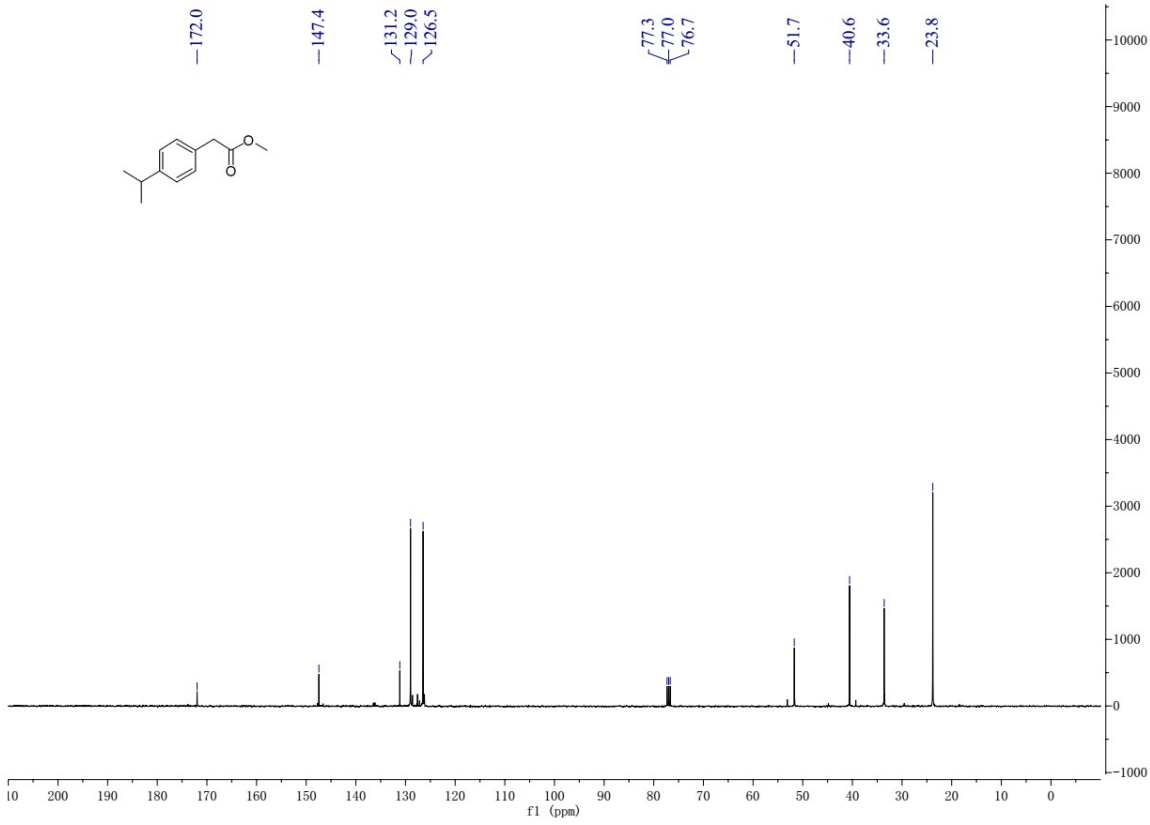

7.17
7.15
7.13
7.11
3.67
3.58
2.32
0.00
1.88
1.76
2.79
1.95
3.00
f1 (ppm)

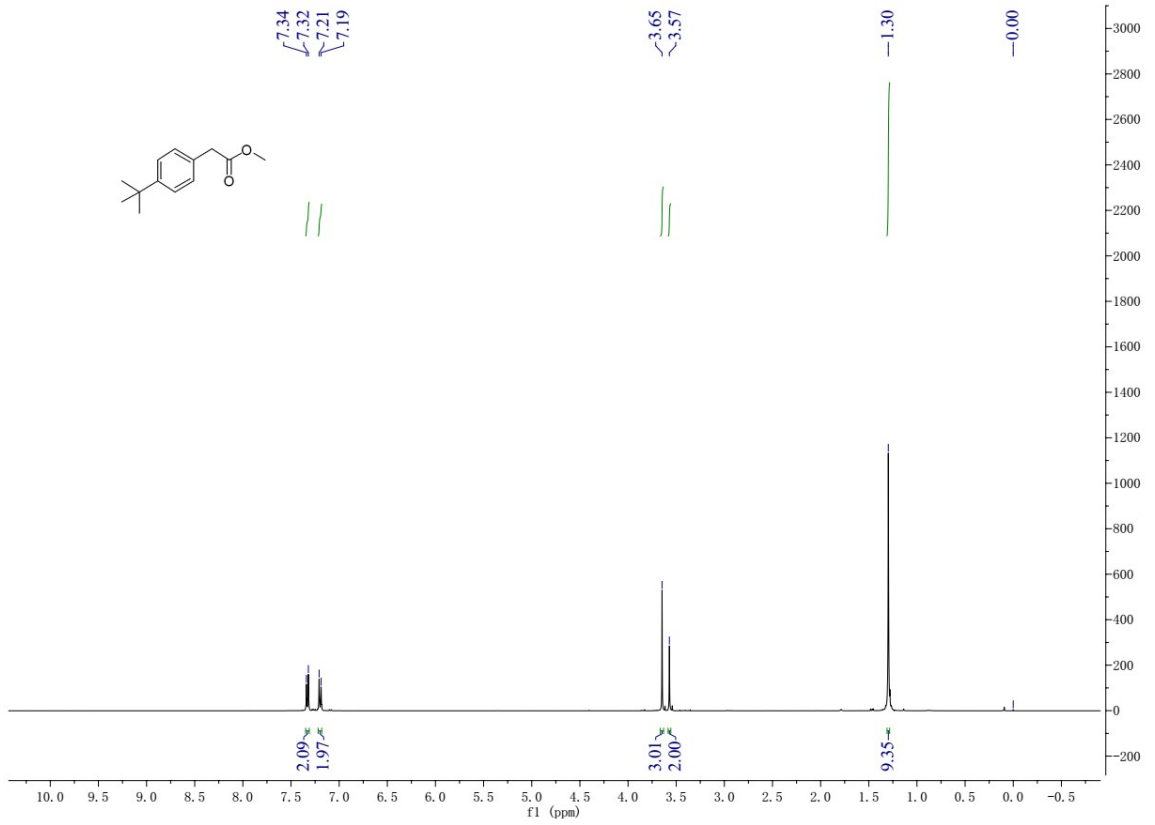

172.1
136.6
130.9
129.2
129.0
77.3
77.0
76.7
51.9
40.7
21.0
f1 (ppm)

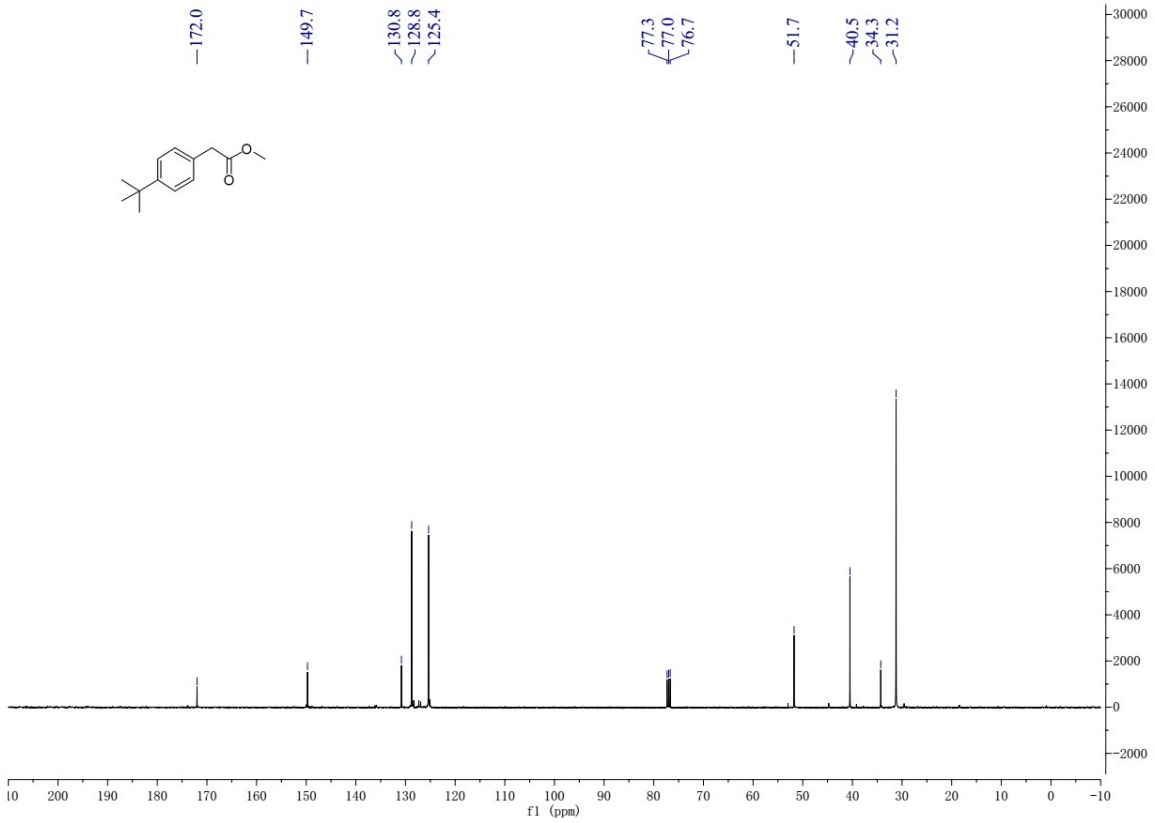

7.19
7.17
7.14
7.12
3.65
3.57
2.64
2.62
2.60
2.58
1.23
1.21
1.19
0.00
2.07
2.03
3.00
2.00
2.23
3.34
f1 (ppm)

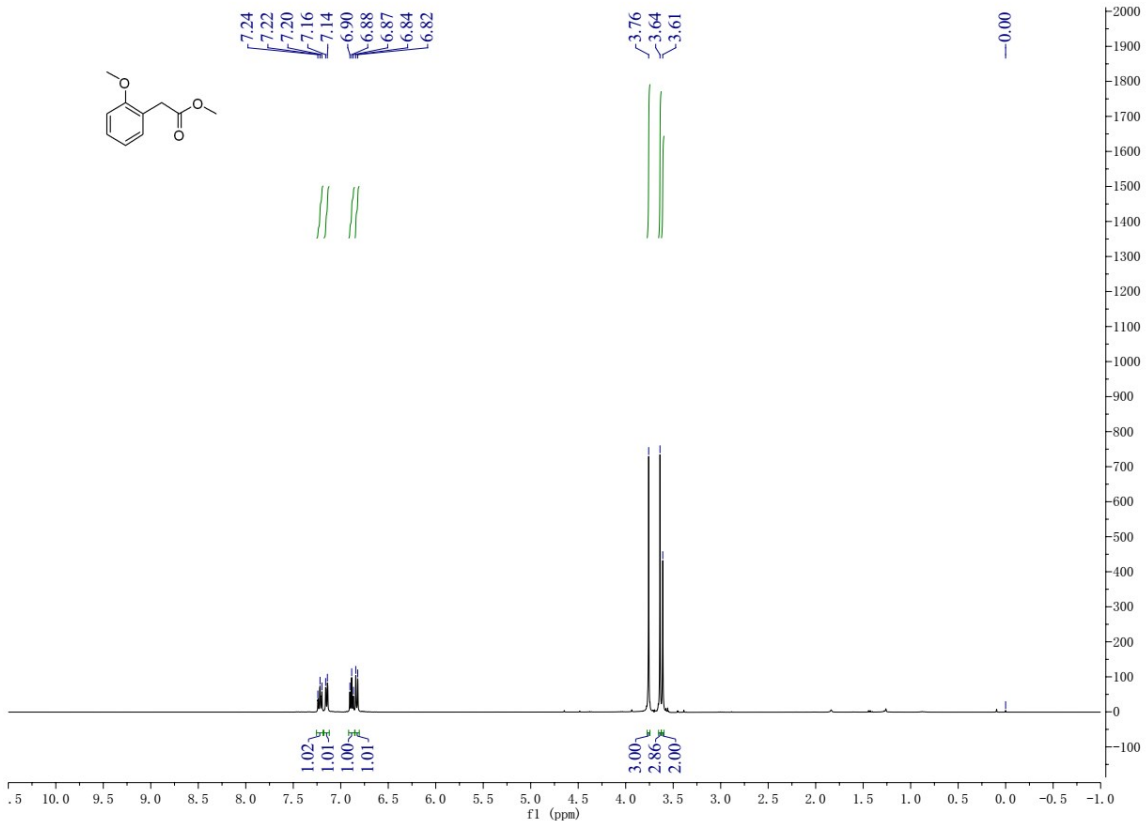

172.0
142.9
131.0
129.0
127.9
77.3
77.0
76.7
51.7
40.6
28.3
15.4
f1 (ppm)

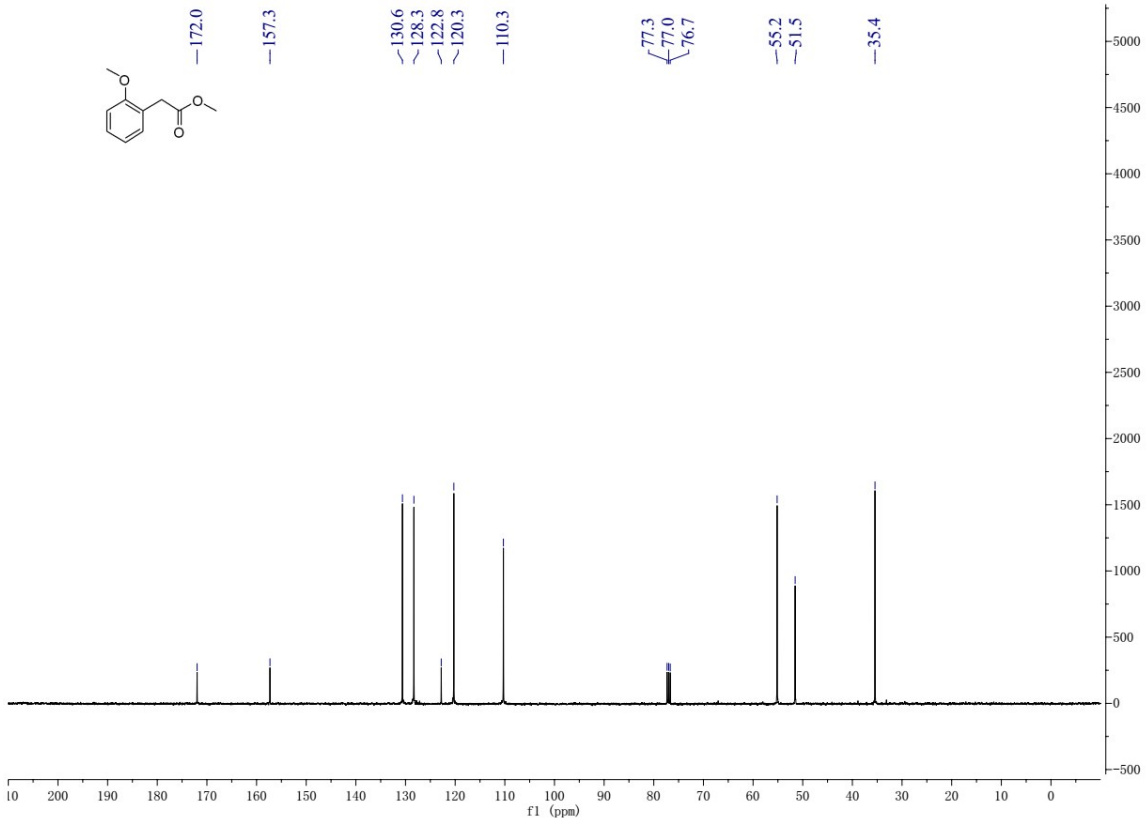

7.19
7.17
7.15
3.64
3.56
2.92
2.90
2.88
2.87
2.85
2.83
1.23
1.21
0.00
0.95
3.73
2.69
1.81
0.95
6.00
f1 (ppm)

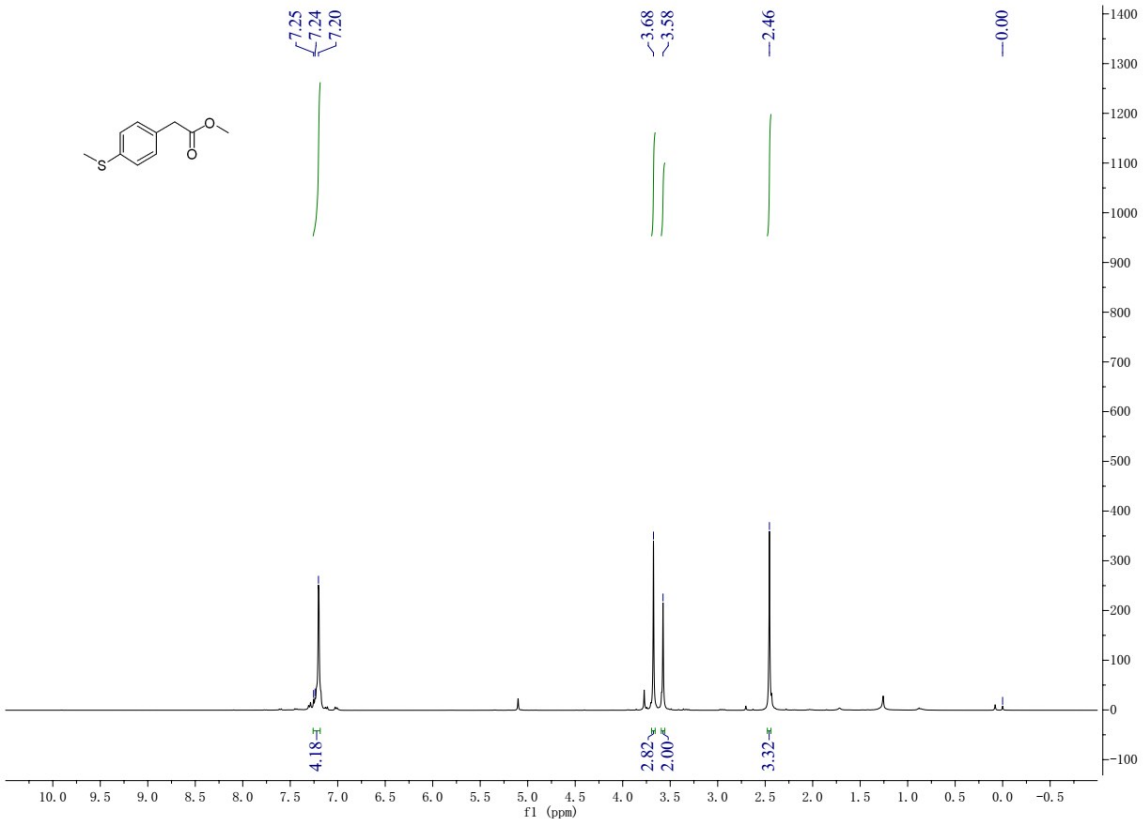

172.0
147.4
131.2
129.0
126.5
77.3
77.0
76.7
51.7
40.6
33.6
23.8
f1 (ppm)

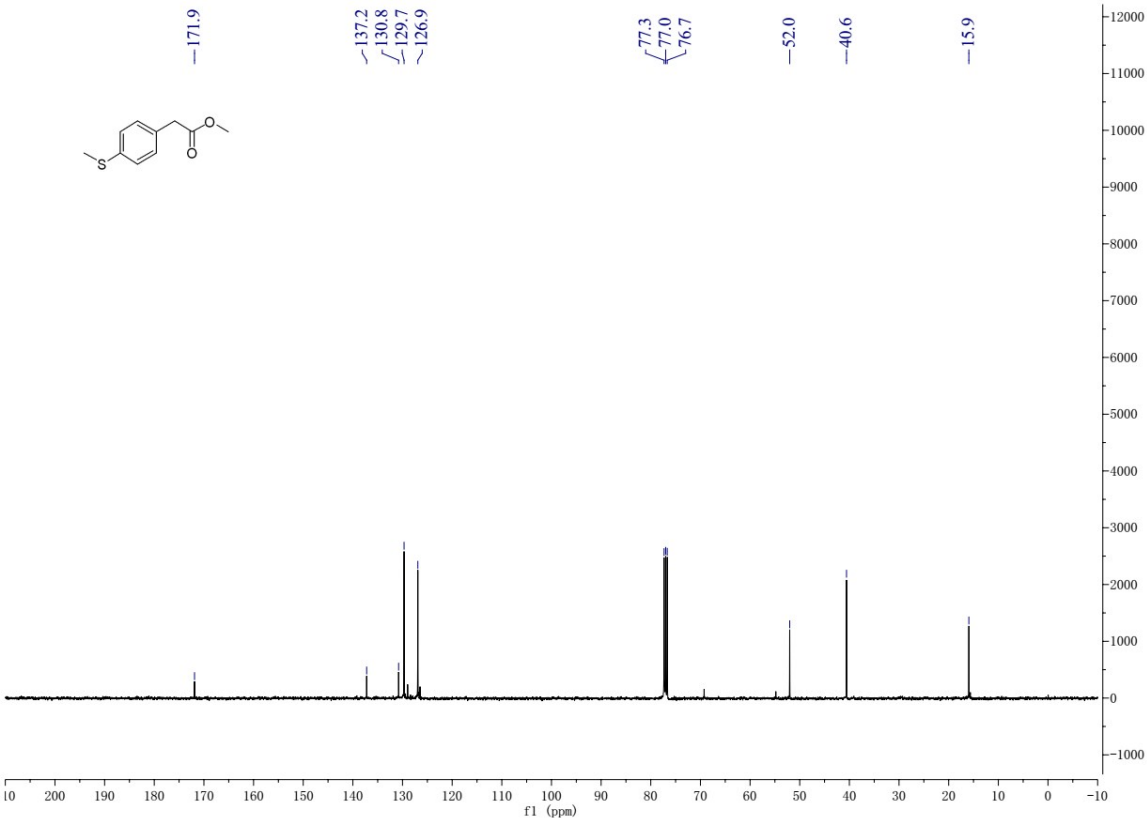

7.34
7.32
7.21
7.19
3.65
3.57
1.30
0.00
2.09
1.97
3.01
2.00
9.35
f1 (ppm)

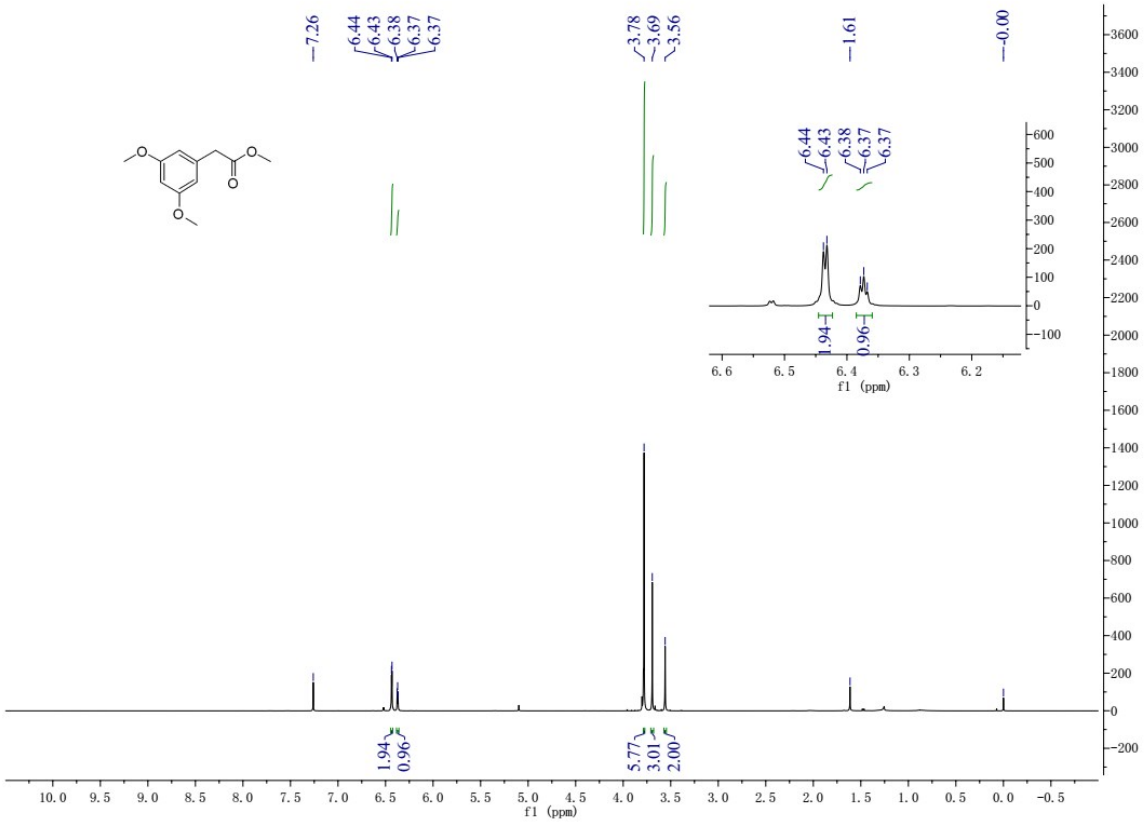

172.0
149.7
130.8
128.8
125.4
77.3
77.0
76.7
51.7
40.5
34.3
31.2
f1 (ppm)

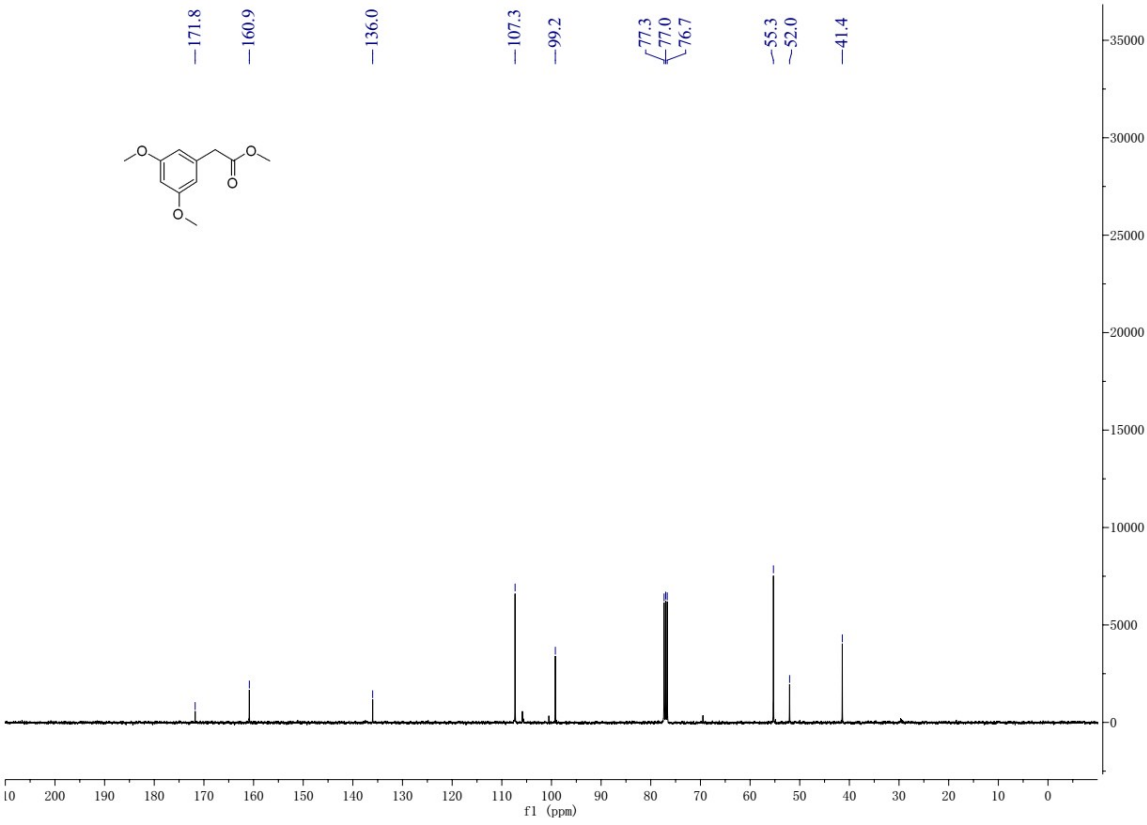

7.24
7.22
7.20
7.16
7.14
6.90
6.88
6.87
6.84
6.82
3.76
3.64
3.61
0.00
1.02
1.01
1.00
1.01
3.00
2.86
2.00
f1 (ppm)

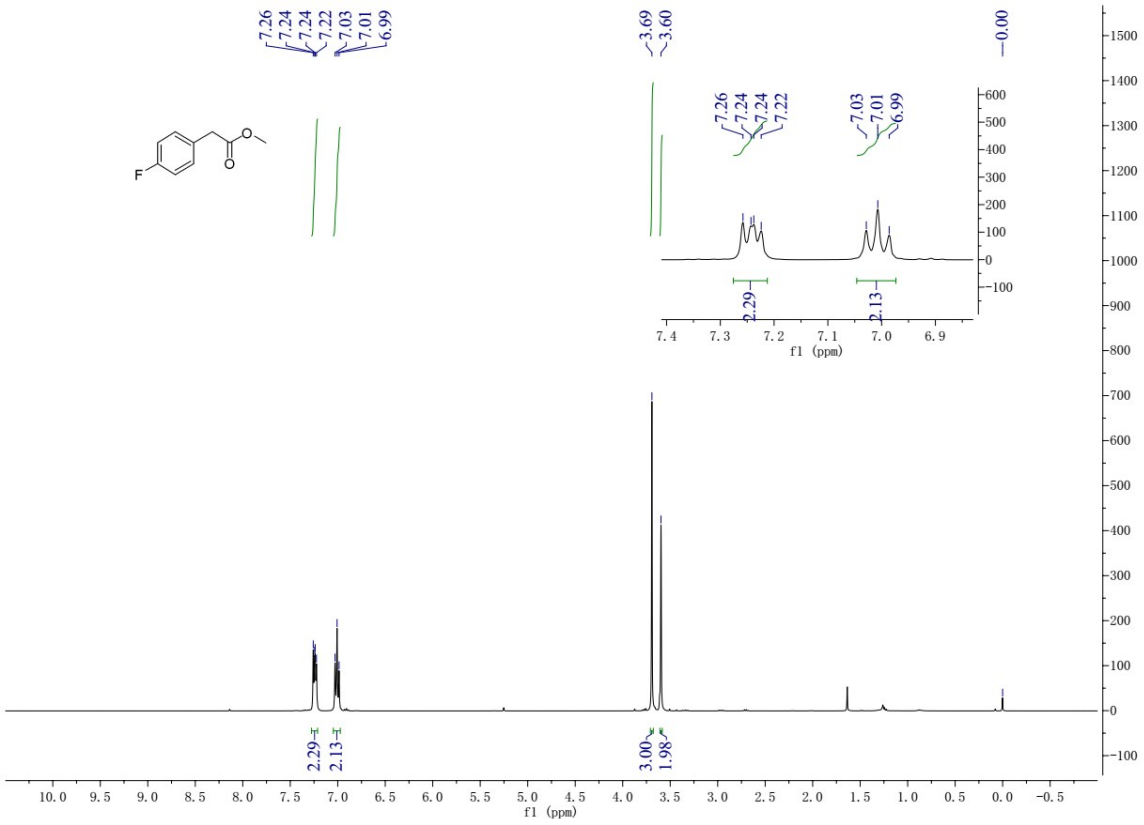

172.0
157.3
130.6
128.3
122.8
120.3
110.3
77.3
77.0
76.7
55.2
51.5
35.4
f1 (ppm)

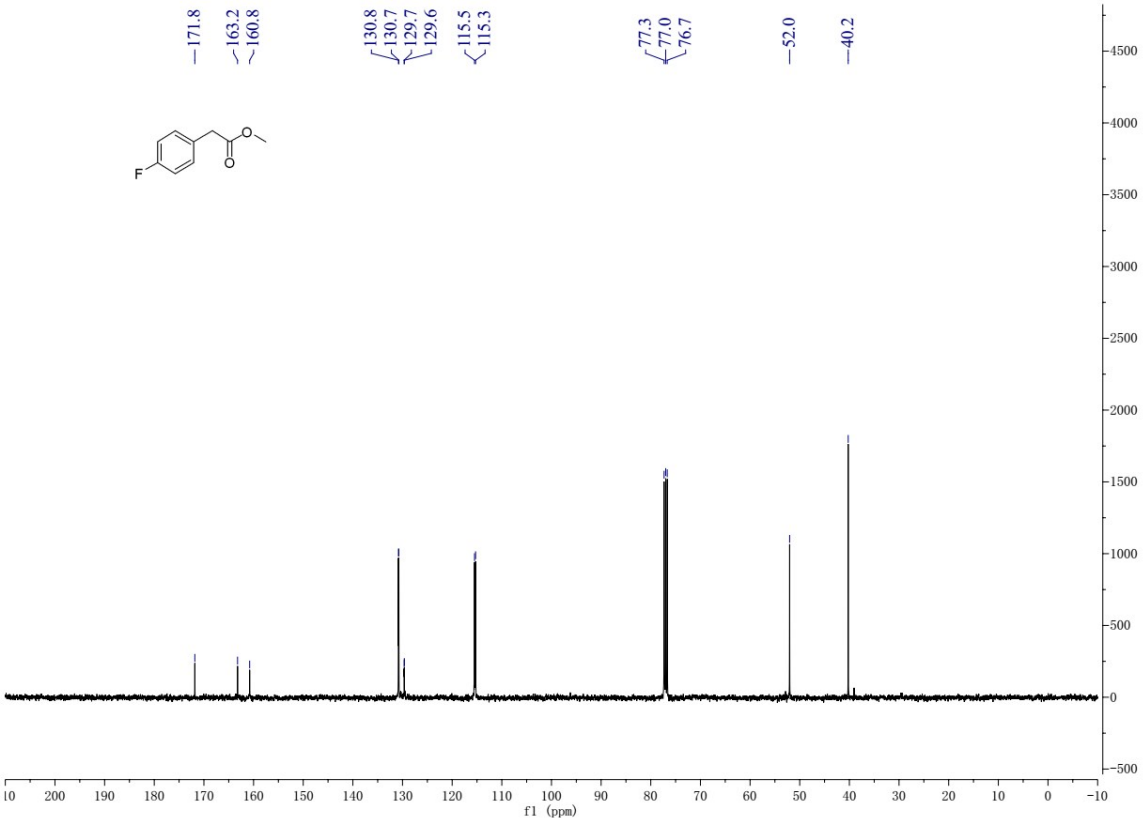

7.25
7.24
7.20
3.68
3.58
2.46
0.00
4.18
2.82
2.00
3.32
f1 (ppm)

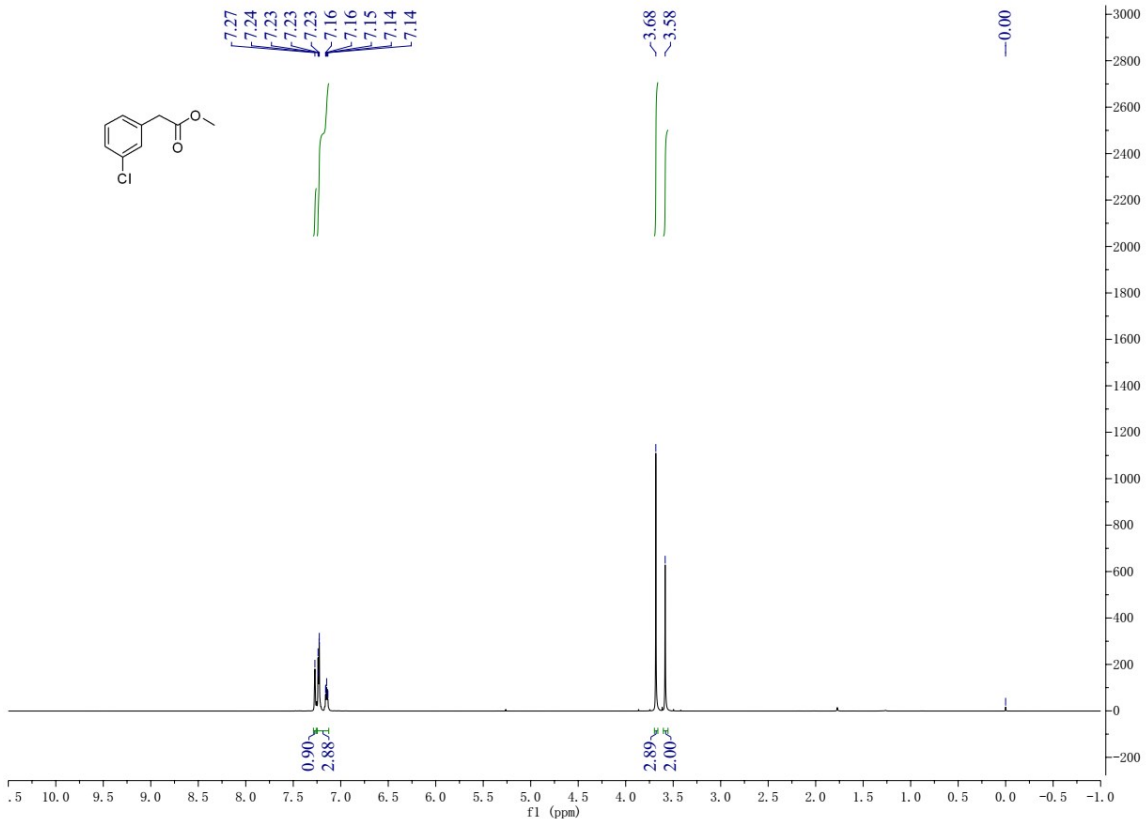

171.9
137.2
130.8
129.7
126.9
77.3
77.0
76.7
52.0
40.6
15.9
f1 (ppm)

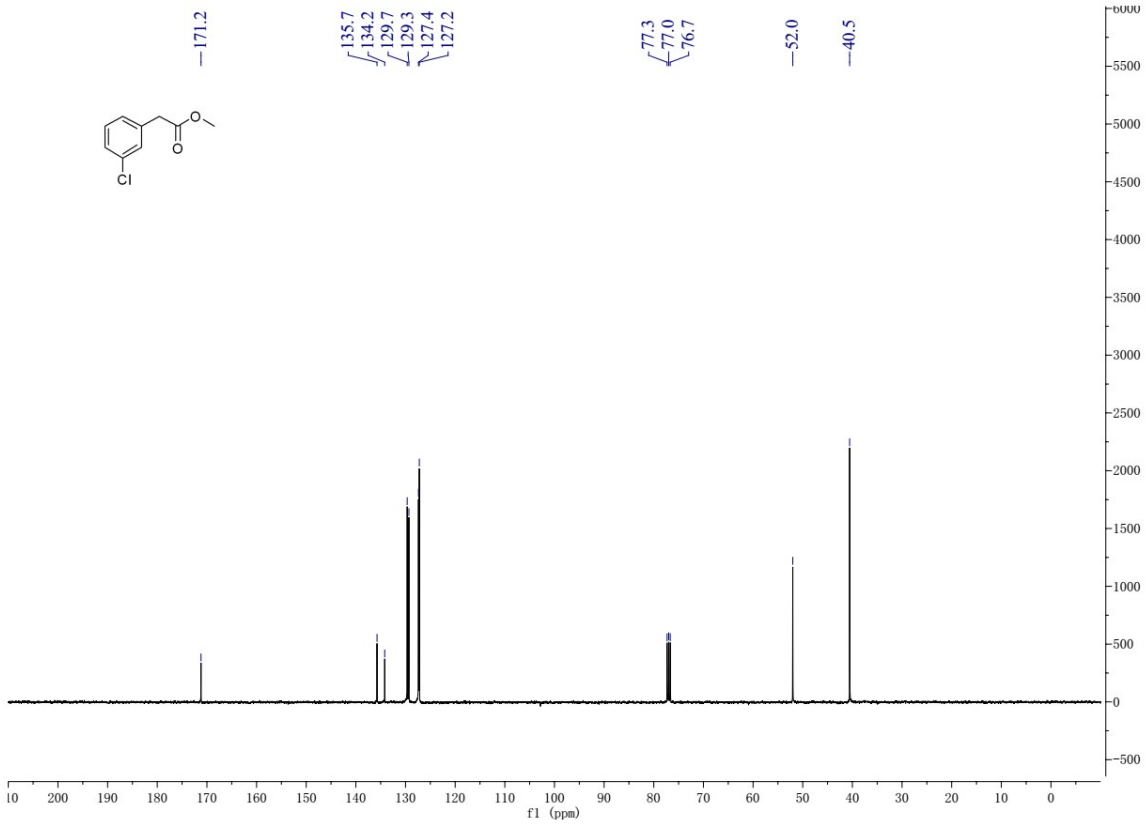

7.26
6.44
6.43
6.38
6.37
6.37
3.78
3.69
3.56
1.61
0.00
1.94
0.96
5.77
3.01
2.00
f1 (ppm)

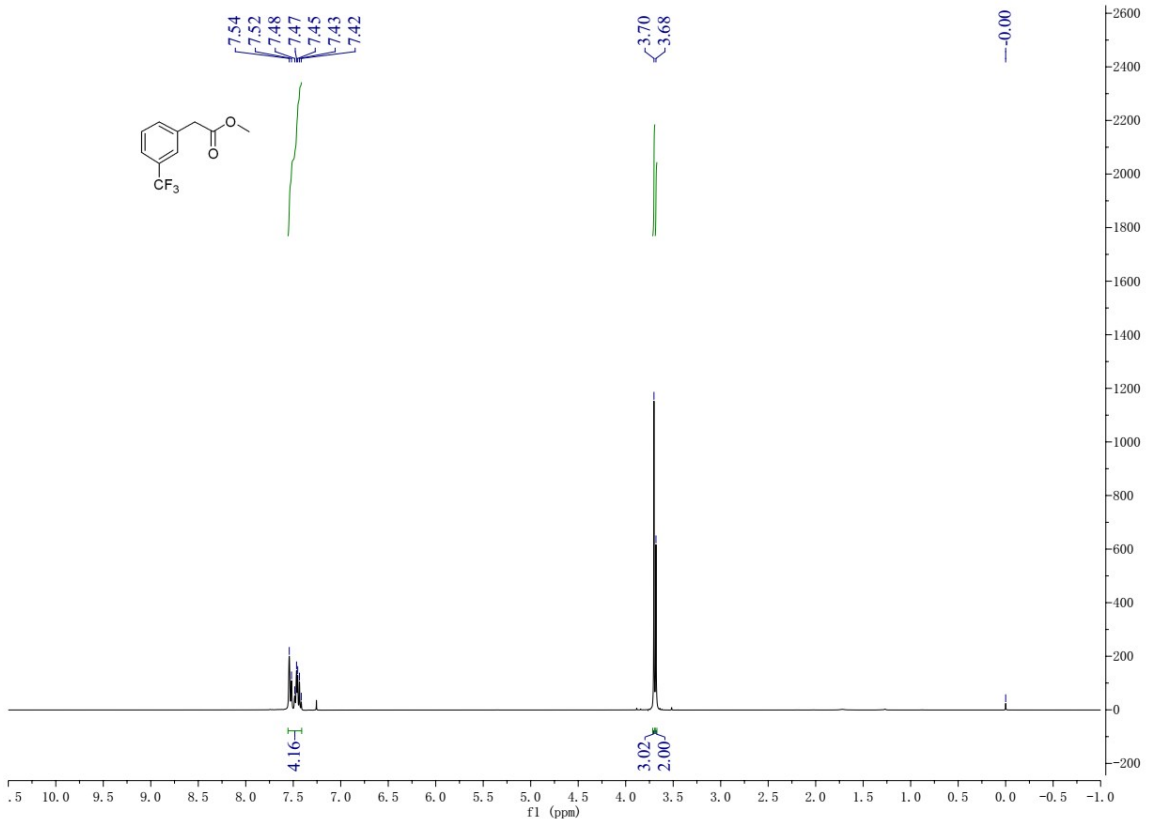

171.8
160.9
136.0
107.3
99.2
77.3
77.0
76.7
55.3
52.0
41.4
f1 (ppm)

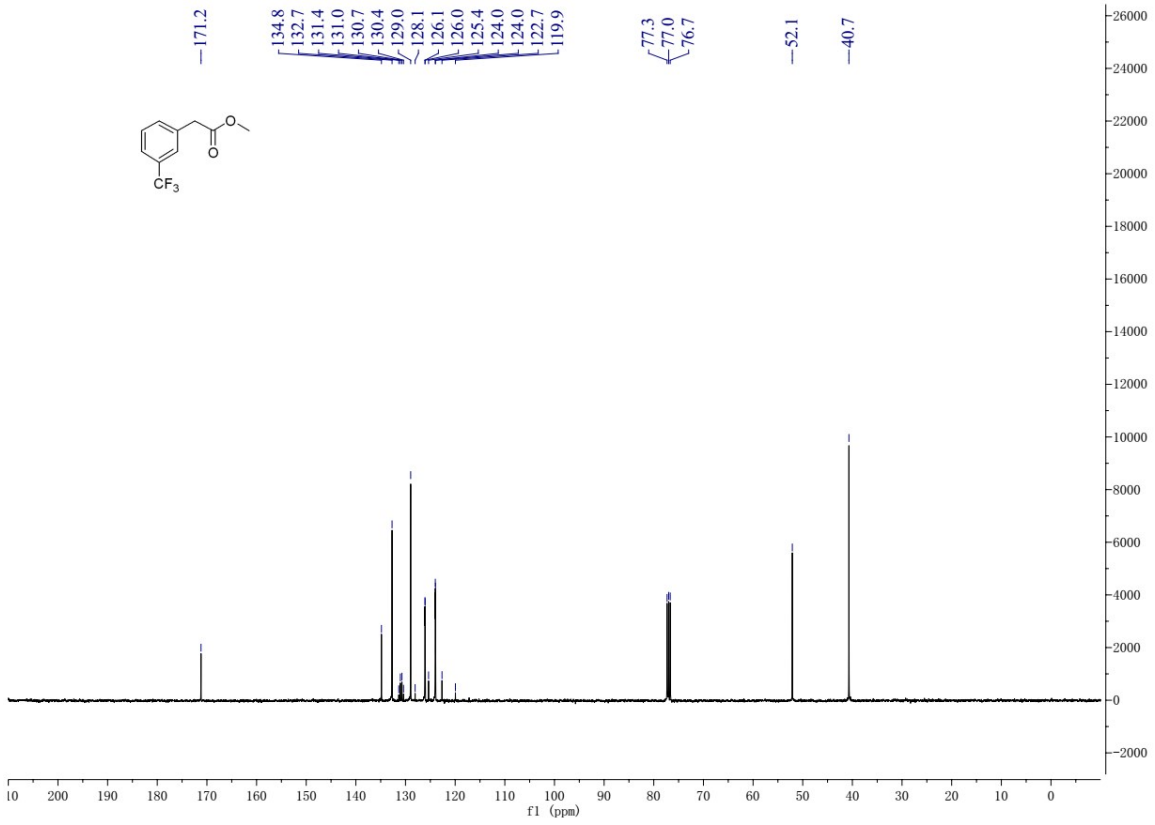

7.26
7.24
7.24
7.22
7.03
7.01
6.99
3.69
3.60
0.00
F
O
O
2.29
2.13
3.00
1.98
f1 (ppm)

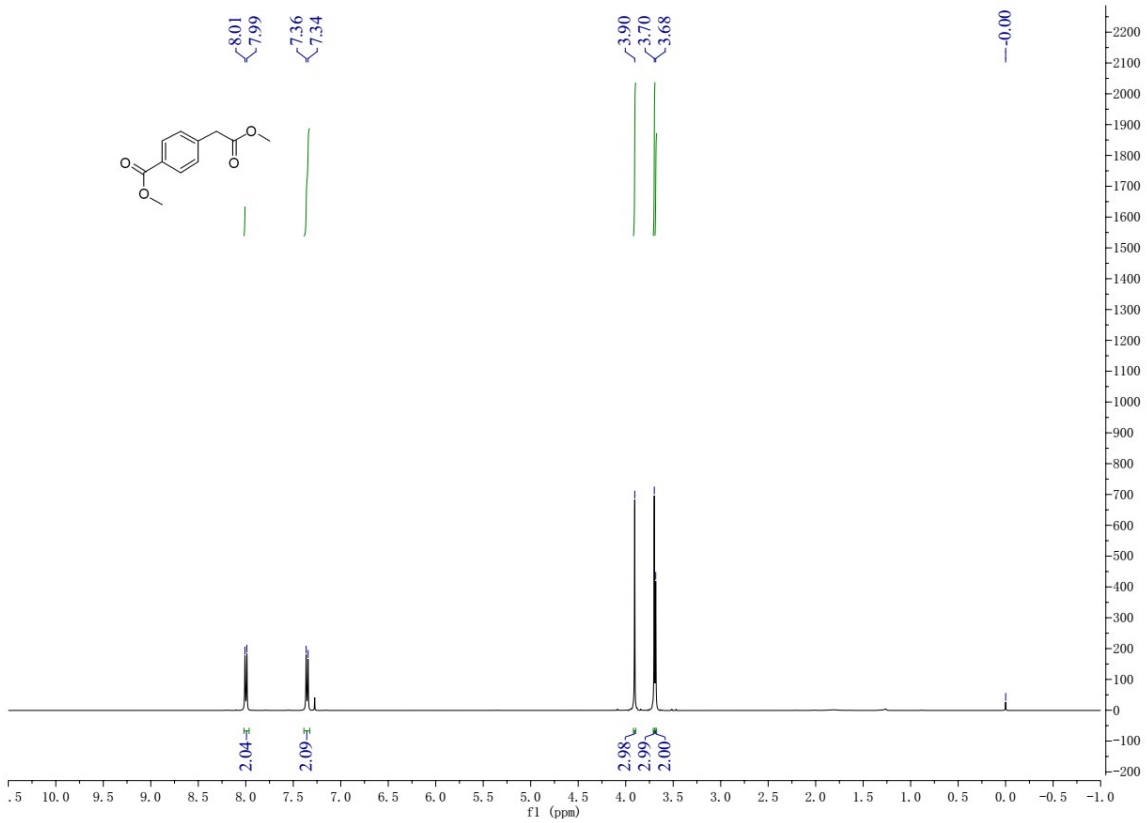

171.8
163.2
160.8
130.8
130.7
129.7
129.6
115.5
115.3
77.3
77.0
76.7
52.0
40.2
F
O
O
f1 (ppm)

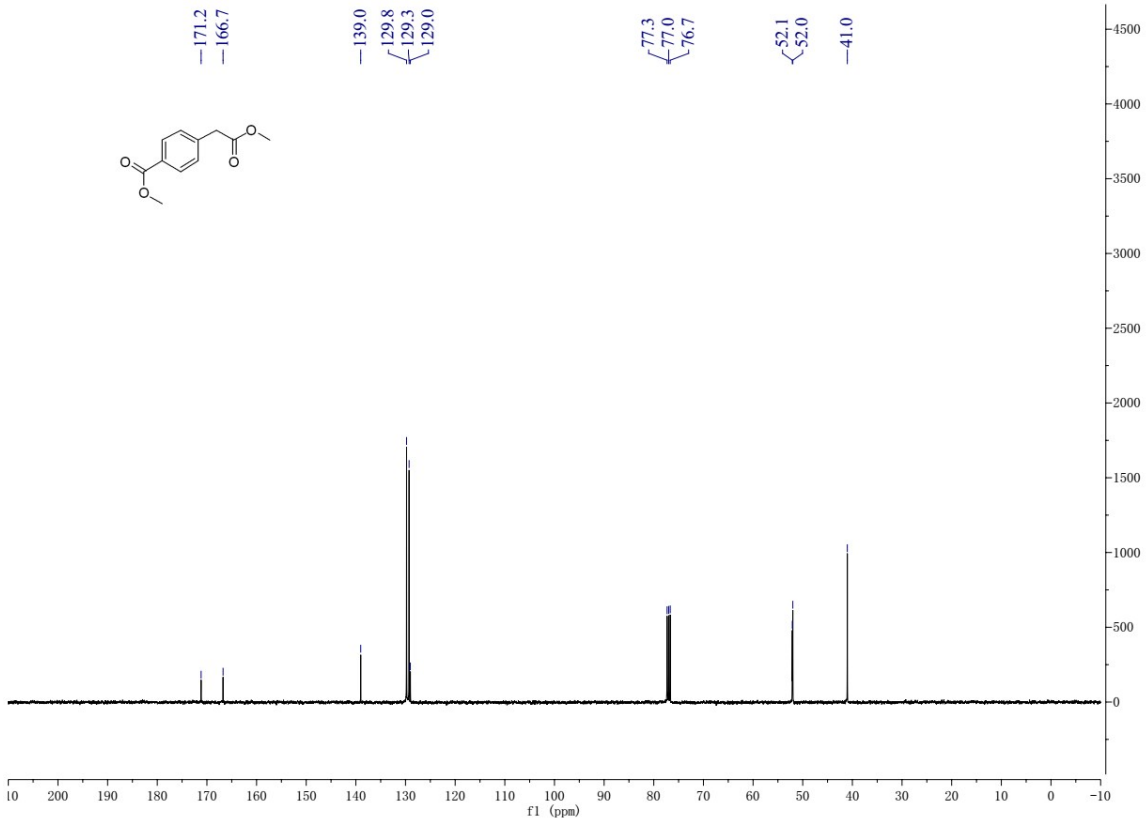

7.27
7.24
7.23
7.23
7.23
7.16
7.16
7.15
7.14
7.14
3.68
3.58
0.00
0.90
2.88
2.89
2.00
f1 (ppm)

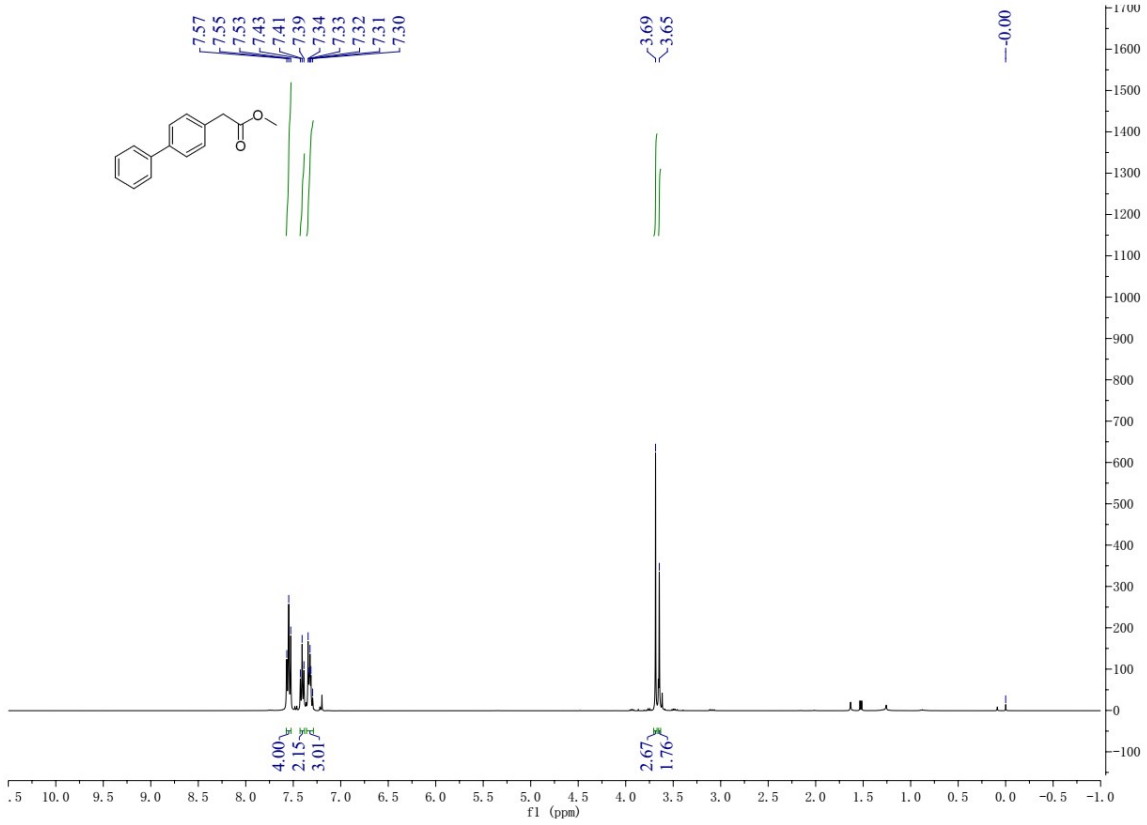

171.2
135.7
134.2
129.7
129.3
127.4
127.2
77.3
77.0
76.7
52.0
40.5
f1 (ppm)

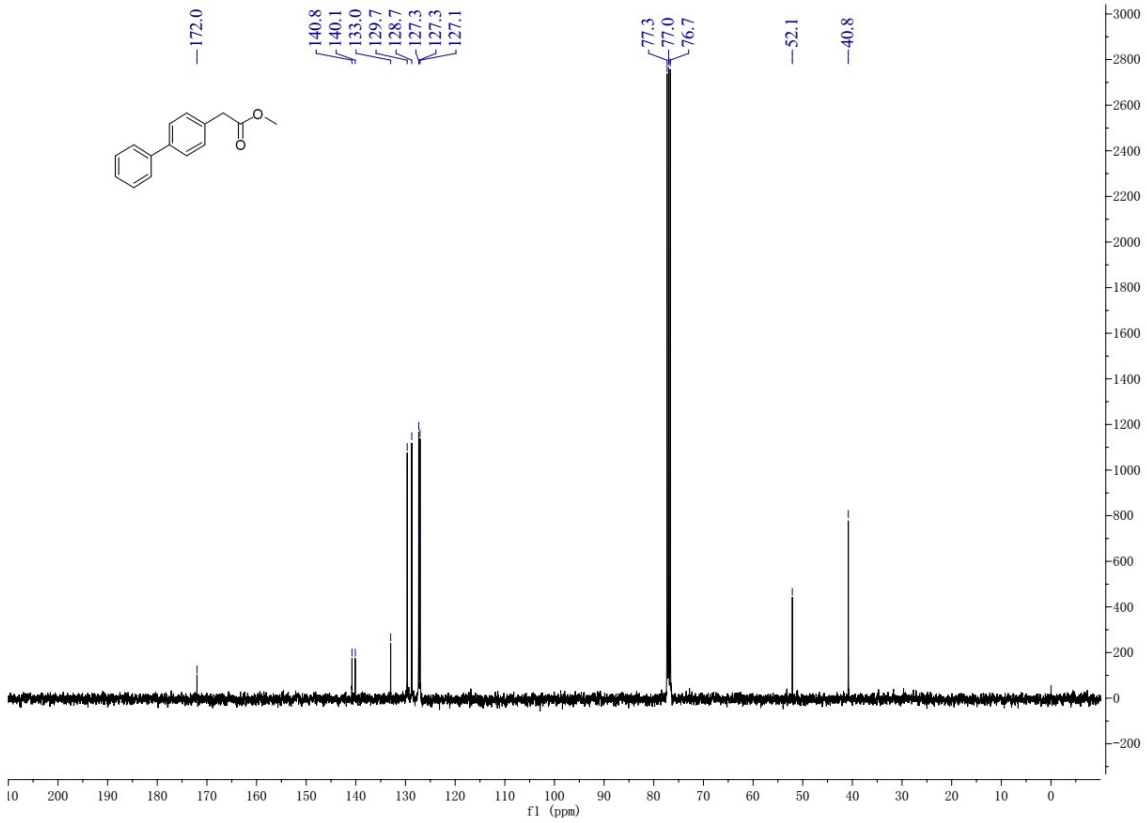

7.54
7.52
7.48
7.47
7.45
7.43
7.42
3.70
3.68
0.00
4.16
3.02
2.00
f1 (ppm)

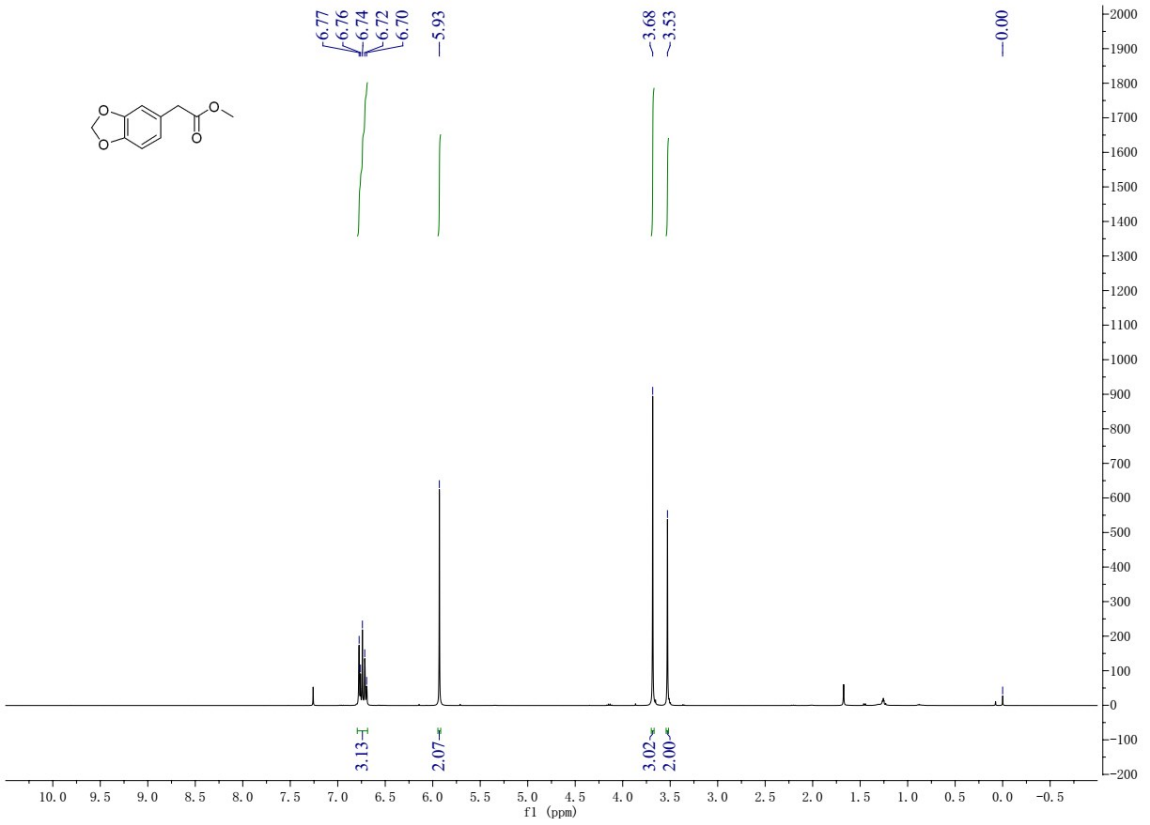

171.2
134.8
132.7
131.4
131.0
130.7
130.4
129.0
128.1
126.1
126.0
125.4
124.0
124.0
122.7
119.9
77.3
77.0
76.7
52.1
40.7
f1 (ppm)

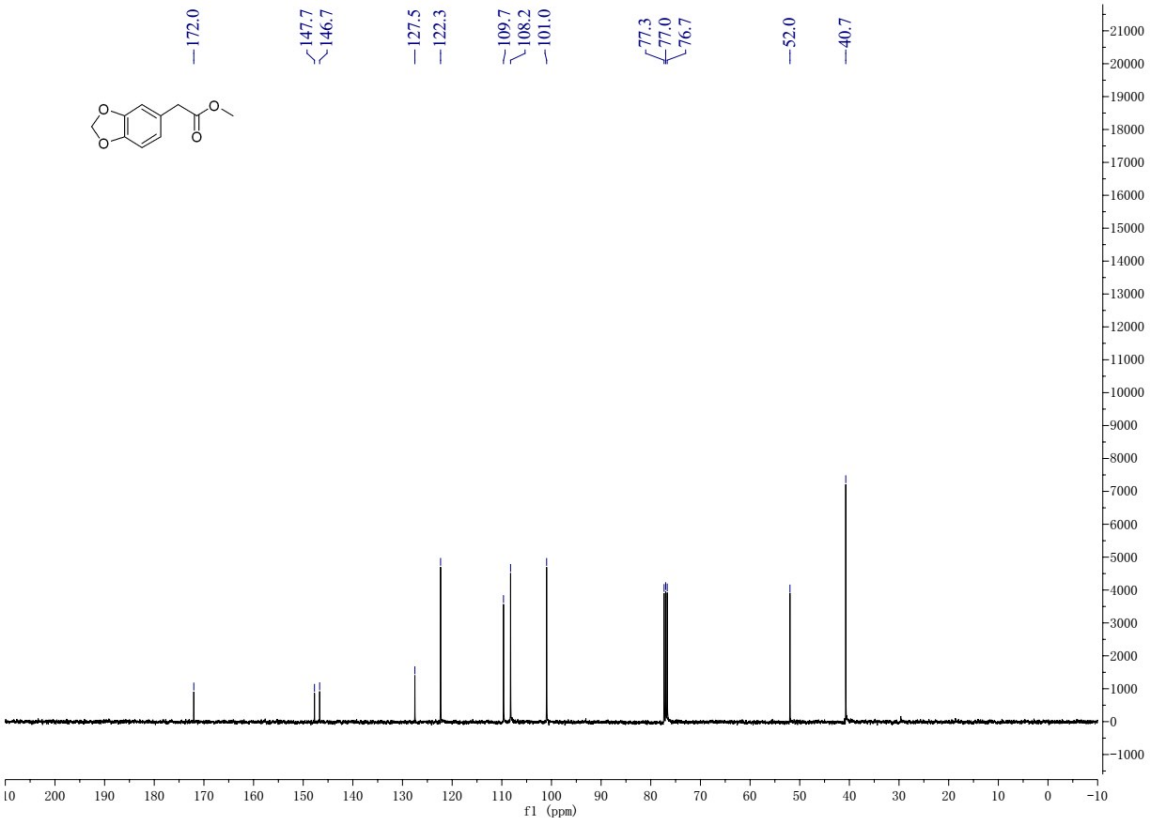

8.01
7.99
7.36
7.34
3.90
3.70
3.68
0.00
2.04
2.09
2.98
2.99
2.00
f1 (ppm)


171.2
166.7
139.0
129.8
129.3
129.0
77.3
77.0
76.7
52.1
52.0
41.0
f1 (ppm)

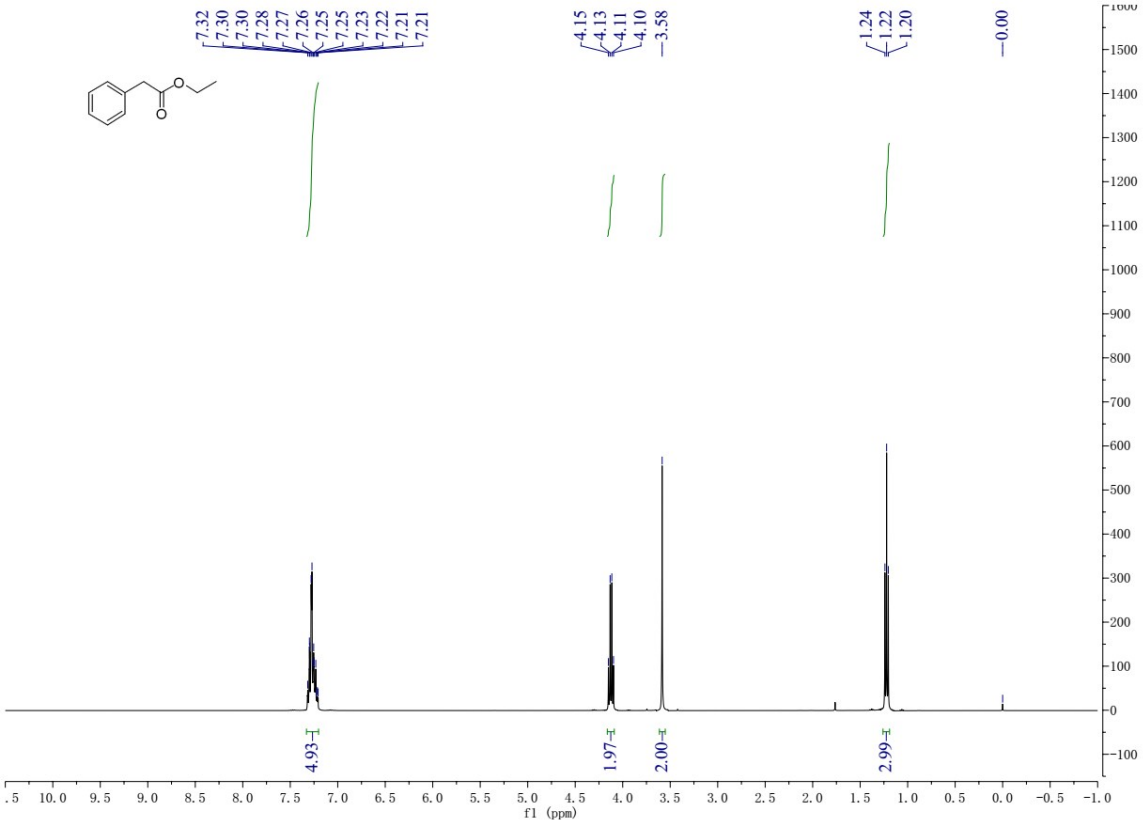

7.57
7.55
7.53
7.43
7.41
7.39
7.34
7.33
7.32
7.31
7.30
3.69
3.65
0.00
4.00
2.15
3.01
2.67
1.76
f1 (ppm)

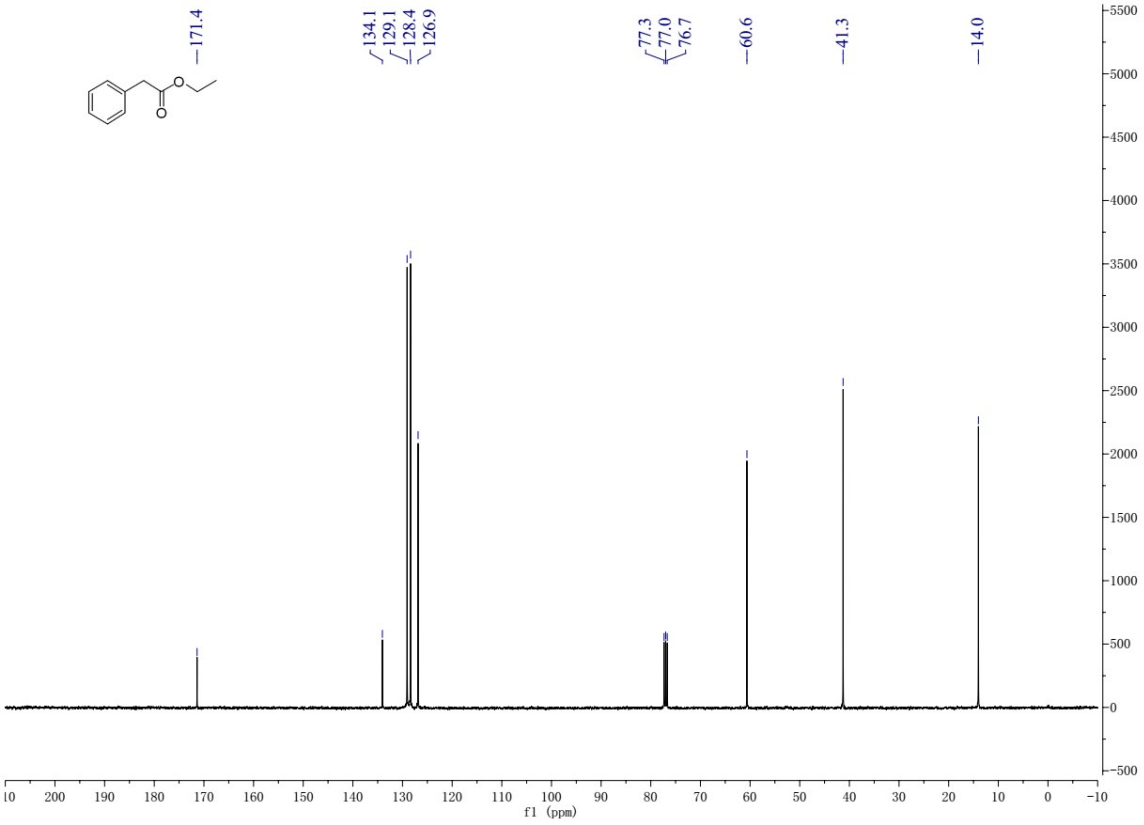

172.0
140.8
140.1
133.0
129.7
128.7
127.3
127.3
127.1
77.3
77.0
76.7
52.1
40.8
f1 (ppm)

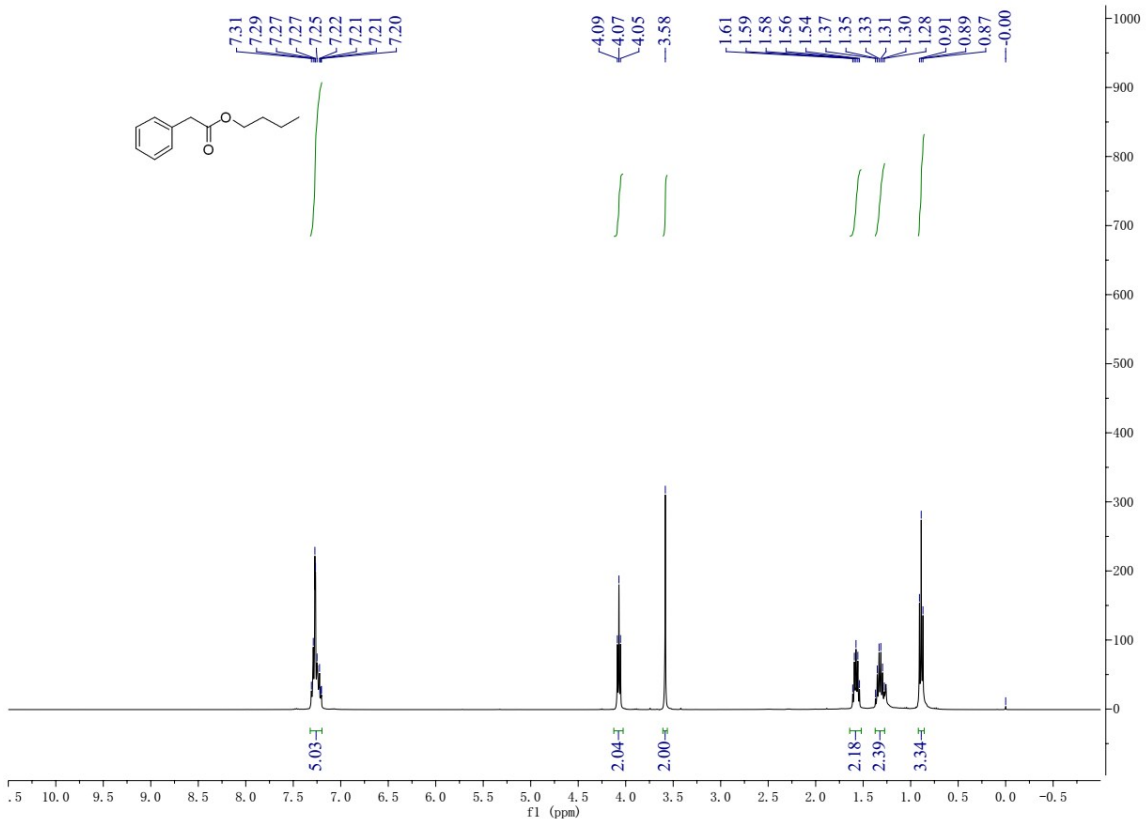

6.77
6.76
6.74
6.72
6.70
5.93
3.68
3.53
0.00
3.13
2.07
3.02
2.00
f1 (ppm)

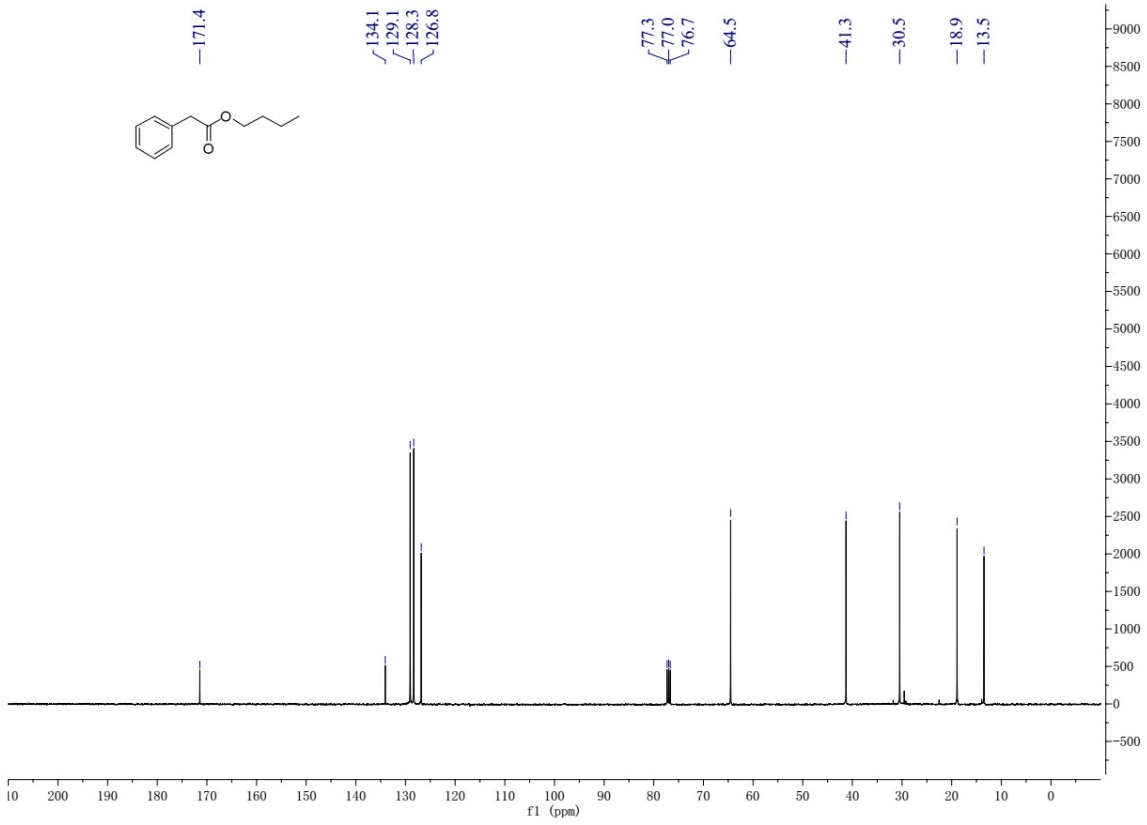

172.0
147.7
146.7
127.5
122.3
109.7
108.2
101.0
77.3
77.0
76.7
52.0
40.7
f1 (ppm)

11. Spectra of 2-Alkyl 2-phenylacetates






7.31
7.29
7.27
7.27
7.25
7.22
7.21
7.21
7.20
4.09
4.07
4.05
3.58
1.61
1.59
1.58
1.56
1.54
1.37
1.35
1.33
1.31
1.30
1.28
0.91
0.89
0.87
0.00
5.03
2.04
2.00
2.18
2.39
3.34
f1 (ppm)


171.4
134.1
129.1
128.3
126.8
77.3
77.0
76.7
64.5
41.3
30.5
18.9
13.5
f1 (ppm)