

Supporting Information

Aerobic Copper Catalyzed α -Oxyacylation of Ketones with Carboxylic Acids

Xin Huang,[†] Xiao Liang,[†] Jun Yuan,[†] Zhangqin Ni,[†] Yifeng Zhou*[§] and Yuanjiang Pan*[†]

[†] Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, P. R. China 310027

[§] College of life sciences, China Jiliang University, Hangzhou, Zhejiang, P. R. China 310018

E-mail: panyuanjiang@zju.edu.cn and zhouyifeng@cjlzj.edu.cn

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1 General Information

All reagents used in the experiments were obtained from commercial sources and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE 400 for ^1H and ^{13}C NMR in CDCl_3 . The NMR chemical shift was reported in ppm relative to 7.26 and 77.20 ppm of CDCl_3 solvent as the standards of ^1H and ^{13}C NMR. The HRMS of products were tested on LCMS-IT-TOF. Melting points were obtained on a X-4 digital melting point apparatus without correction. IR was tested on Bruker ALPHA.

2 Characterization data for the products

1-oxo-1-phenylpropan-2-yl benzoate (3aa)¹.

A white solid (94.2 mg, 74%). mp 98-99 °C. Eluting with 10:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 7.2 Hz, 2H), 7.60-7.55 (m, 2H), 7.50-7.42 (m, 4H), 6.21 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 166.1, 134.5, 133.7, 133.4, 130.0, 129.6, 128.9, 128.6, 128.5, 72.0, 17.3. IR (KBr): ν = 2981, 1722, 1692, 1452, 1276, 1225, 1122, 968, 713. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{14}\text{NaO}_3$ ($\text{M}+\text{Na}$)⁺ 277.0835, found 277.0837.

1-oxo-1-phenylpropan-2-yl 2-chlorobenzoate (3ab)¹.

A colorless oil (119.5 mg, 83%). Eluting with 8:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 6.8 Hz, 2H), 7.96 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.52-7.41 (m, 4H), 7.33 (t, J = 7.2 Hz, 1H), 6.24 (q, J = 7.2 Hz, 1H),

1.66 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.6, 165.1, 134.5, 134.2, 133.9, 133.0, 132.0, 131.2, 129.4, 129.0, 128.7, 126.8, 72.5, 17.3. IR (KBr): $\nu = 3062$, 2989, 1732, 1698, 1252, 1121, 969, 748, 700. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{ClNaO}_3$ ($\text{M}+\text{Na}$) $^+$ 311.0445, found 311.0444.

1-oxo-1-phenylpropan-2-yl 2-bromobenzoate (3ac).

A light yellow oil (58.1 mg, 35%). Eluting with 8:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.39-7.31 (m, 2H), 6.24 (q, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 165.5, 134.5, 134.4, 133.8, 133.0, 131.9, 131.4, 128.9, 128.6, 127.3, 122.0, 72.5, 17.3. IR (KBr): $\nu = 3066$, 2989, 1732, 1697, 1250, 1029, 968, 745, 699. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{BrNaO}_3$ ($\text{M}+\text{Na}$) $^+$ 354.9940, found 354.9948.

1-oxo-1-phenylpropan-2-yl 2-iodobenzoate (3ad).

A colorless oil (140.6 mg, 74%). Eluting with 10:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.94 (m, 4H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.24 (q, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 165.8, 141.4, 134.3, 134.2, 133.8, 133.1, 131.6, 128.9, 128.6, 128.1, 94.4, 72.6, 17.6. IR (KBr): $\nu = 3063$, 2988, 1729, 1693, 1103, 1016, 742. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{INaO}_3$ ($\text{M}+\text{Na}$) $^+$ 402.9802, found 402.9816.

1-oxo-1-phenylpropan-2-yl 3-iodobenzoate (3ae).

A white solid (171.1 mg, 90%). mp 117-119 °C. Eluting with 10:1 petroleum ether/ethyl

acetate. ^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 8.04 (d, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 7.2$ Hz, 2H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 8.0$ Hz, 1H), 6.19 (q, $J = 7.2$ Hz, 1H), 1.67 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 164.6, 142.2, 138.7, 134.5, 133.8, 131.5, 130.2, 129.2, 129.0, 128.6, 94.0, 72.4, 17.4. IR (KBr): $\nu = 2983, 1719, 1702, 1306, 1126, 966, 744, 694$. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{INaO}_3$ ($\text{M}+\text{Na}$) $^+$ 402.9802, found 402.9816.

1-oxo-1-phenylpropan-2-yl 4-iodobenzoate (3af).

A white solid (153.9 mg, 81%). mp 109-111 $^\circ\text{C}$. Eluting with 10:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.83-7.78 (m, 4H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 6.19 (q, $J = 6.8$ Hz, 1H), 1.66 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 165.7, 138.0, 134.5, 133.9, 131.5, 129.1, 129.0, 128.7, 101.4, 72.3, 17.4. IR (KBr): $\nu = 3067, 2915, 1694, 1603, 1361, 1268, 1227, 1116$. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{13}\text{INaO}_3$ ($\text{M}+\text{Na}$) $^+$ 402.9802, found 402.9819.

1-oxo-1-phenylpropan-2-yl 2-methylbenzoate (3ag) 1 .

A colorless oil (101.9 mg, 76%). Eluting with 10:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 8.02-8.00 (m, 3H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.26 (t, $J = 8.0$ Hz, 2H), 6.20 (q, $J = 7.2$ Hz, 1H), 2.60 (s, 3H), 1.66 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 167.1, 140.7, 134.6, 133.7, 132.4, 131.8, 131.0, 129.1, 129.0, 128.7, 125.9, 71.9, 17.3. IR (KBr): $\nu = 3064, 2987, 1720, 1698, 1257, 1228, 1076, 968, 739$. HRMS (ESI, m/z) calcd. for $\text{C}_{17}\text{H}_{16}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 291.0992, found 291.0988.

1-oxo-1-phenylpropan-2-yl 4-acetylbenzoate (3ah).

A white solid (59.2 mg, 40%). mp 85-87 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.4 Hz, 2H), 8.01 (t, *J* = 7.2 Hz, 4H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.23 (q, *J* = 7.2 Hz, 1H), 2.65 (s, 3H), 1.69 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 196.6, 165.3, 140.7, 134.5, 133.9, 133.4, 130.3, 129.1, 128.7, 128.4, 72.5, 27.1, 17.4. IR (KBr): ν = 2955, 1724, 1690, 1274, 1243, 1123, 911, 700. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₆NaO₄ (M+Na)⁺ 319.0941, found 319.0946.

1-oxo-1-phenylpropan-2-yl 3-(dimethylamino)benzoate (3ai).

A light yellow solid (109.9 mg, 40%). mp 73-75 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 3H), 7.42 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.18 (q, *J* = 6.8 Hz, 1H), 2.96 (s, 6H), 1.67 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 166.8, 150.5, 134.7, 133.6, 130.2, 129.1, 128.9, 128.6, 117.9, 117.2, 113.5, 71.9, 40.6, 17.2. IR (KBr): ν = 3067, 2915, 1694, 1603, 1361, 1268, 1227, 1116. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₉NaO₃ (M+Na)⁺ 320.1257, found 320.1254.

1-oxo-1-phenylpropan-2-yl 4-(dimethylamino)benzoate (3aj).

A white solid (95.1 mg, 64%). mp 125-127 °C. Eluting with 3:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.15 (q, *J* = 7.2 Hz, 1H), 3.04 (s, 6H), 1.63 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 166.4, 153.6, 134.9, 133.5, 131.8, 128.9, 128.7, 116.6, 111.1, 71.3, 40.3, 17.3.

IR (KBr): ν = 3063, 1692, 1616, 1275, 1186, 1111, 966, 705. HRMS (ESI, m/z) calcd. for $C_{18}H_{19}NaO_3$ ($M+Na$)⁺ 320.1257, found 320.1263.

1-oxo-1-phenylpropan-2-yl 2,5-difluorobenzoate (3ak).

A white solid (89.9 mg, 62%). mp 54-56 °C. Eluting with 10:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.22-7.20 (m, 1H), 7.14-7.08 (m, 1H), 6.20 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 162.7, 159.7, 159.6, 159.3, 159.2, 157.1, 157.0, 156.9, 156.8, 134.3, 133.9, 129.0, 128.7, 121.9, 121.8, 121.7, 121.6, 119.3, 119.2, 119.1, 119.0, 118.7, 118.6, 118.5, 118.4, 72.8, 17.3. IR (KBr): ν = 3088, 2995, 1732, 1697, 1494, 1265, 1189, 1094, 969, 769, 696. HRMS (ESI, m/z) calcd. for $C_{16}H_{12}F_2NaO_3$ ($M+Na$)⁺ 313.0647, found 313.0638.

1-oxo-1-phenylpropan-2-yl 2,6-difluorobenzoate (3al).

A colorless oil (87.0 mg, 60%). Eluting with 10:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 8.4 Hz, 1H), 6.95 (t, J = 8.4 Hz, 2H), 6.25 (q, J = 6.8 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 162.4, 162.3, 161.1, 159.9, 159.8, 134.4, 133.9, 133.5, 133.4, 133.3, 129.0, 128.7, 112.4, 112.3, 112.1, 110.6, 110.5, 110.3, 73.1, 17.3. IR (KBr): ν = 3067, 2991, 1735, 1699, 1625, 1470, 1264, 1116, 1013, 699. HRMS (ESI, m/z) calcd. for $C_{16}H_{12}F_2NaO_3$ ($M+Na$)⁺ 313.0647, found 313.0646.

1-oxo-1-phenylpropan-2-yl 2,5-dichlorobenzoate (3am).

A white solid (140.1 mg, 87%). mp 78-80 °C. Eluting with 10:1 petroleum ether/ethyl

acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.93 (m, 3H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.42-7.37 (m, 2H), 6.23 (q, $J = 7.2$ Hz, 1H), 1.67 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.3, 163.8, 134.3, 134.0, 133.0, 132.8, 132.6, 132.4, 131.8, 130.6, 129.0, 128.7, 72.9, 17.3. IR (KBr): $\nu = 2990, 1737, 1698, 1251, 1148, 1127, 1047, 968, 696$. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 345.0056, found 345.0059.

1-oxo-1-phenylpropan-2-yl cinnamate (5aa)².

A white solid (98.0 mg, 70%). mp 67-68 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.6$ Hz, 2H), 7.75 (d, $J = 16.0$ Hz, 1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.52-7.45 (m, 4H), 7.38-7.36 (m, 3H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.12 (q, $J = 7.2$ Hz, 1H), 1.61 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 166.3, 145.9, 134.4, 134.4, 133.6, 130.5, 128.9, 128.8, 128.6, 128.2, 117.2, 71.5, 17.3. IR (KBr): $\nu = 3054, 3025, 1714, 1698, 1636, 1449, 1324, 1223, 1009, 770, 685$. HRMS (ESI, m/z) calcd. for $\text{C}_{18}\text{H}_{16}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 303.0992, found 303.0993.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(4-chlorophenyl)acrylate (5ab).

A white solid (95.8 mg, 61%). mp 104-106 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 7.2$ Hz, 2H), 7.69 (d, $J = 16.0$ Hz, 1H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.51-7.45 (m, 4H), 7.36 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.12 (q, $J = 6.8$ Hz, 1H), 1.61 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 166.2, 144.6, 136.6, 134.5, 133.8, 132.9, 129.5, 129.4, 129.0, 128.7, 118.0, 71.7, 17.4. IR (KBr): $\nu = 3066, 1710, 1695, 1635, 1324, 1191, 1178$. HRMS (ESI, m/z) calcd. for $\text{C}_{18}\text{H}_{15}\text{ClNaO}_3$ ($\text{M}+\text{Na}$) $^+$ 337.0602, found 337.0606.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(3-chlorophenyl)acrylate (5ac).

A white solid (80.1 mg, 51%). mp 103-105 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 16.0 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50-7.46 (m, 3H), 7.39-7.28 (m, 3H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.11 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 165.9, 144.3, 136.1, 135.0, 134.4, 133.7, 130.4, 130.3, 128.9, 128.6, 128.3, 128.0, 126.4, 118.8, 71.7, 17.3. IR (KBr): ν = 3066, 1712, 1695, 1636, 1327, 1190, 1006, 796, 699. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₅ClNaO₃ (M+Na)⁺ 337.0602, found 337.0605.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(4-nitrophenyl)acrylate (5ad).

A pale yellow solid (69.9 mg, 43%). mp 165-166 °C. Eluting with 3:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.14 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 165.5, 148.8, 143.0, 140.5, 134.4, 133.9, 129.0, 128.9, 128.7, 124.4, 121.7, 72.0, 17.4. IR (KBr): ν = 3072, 1711, 1692, 1517, 1347, 1334, 1196, 1178, 1008, 850, 702. HRMS (ESI, *m/z*) calcd. for C₁₈H₁₅NNaO₅ (M+Na)⁺ 348.0842, found 348.0851.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(4-methoxyphenyl)acrylate (5ae).

A white solid (48.1 mg, 31%). mp 106-108 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49-7.45 (m, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.10 (q, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H). ¹³C NMR

(100 MHz, CDCl₃) δ 197.1, 166.6, 161.6, 145.7, 134.6, 133.6, 130.0, 128.9, 128.6, 127.0, 114.7, 114.4, 71.3, 55.4, 17.3. IR (KBr): ν = 2961, 1712, 1695, 1633, 1513, 1286, 1175, 828, 702. HRMS (ESI, m/z) calcd. for C₁₉H₁₈NaO₄ (M+Na)⁺ 333.1097, found 333.1103.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(3-methoxyphenyl)acrylate (5af).

A colorless oil (68.2 mg, 44%). Eluting with 10:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 16.0 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 6.10 (q, J = 7.2 Hz, 1H), 3.78 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.9, 166.1, 159.9, 145.8, 135.6, 134.4, 133.6, 129.9, 128.8, 128.5, 120.9, 117.5, 116.5, 112.9, 71.5, 55.3, 17.2. IR (KBr): ν = 3063, 2989, 2939, 2837, 1697, 1636, 1250, 1170, 700. HRMS (ESI, m/z) calcd. for C₁₉H₁₈NaO₄ (M+Na)⁺ 333.1097, found 333.1102.

1-oxo-1-phenylpropan-2-yl(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylate (5ag).

A pale grey solid (105.3 mg, 65%). mp 120-122°C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 16.0 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.10 (q, J = 6.8 Hz, 1H), 5.99 (s, 2H), 1.59 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 166.5, 149.9, 148.5, 145.8, 134.6, 133.7, 128.9, 128.8, 128.7, 124.9, 115.2, 108.7, 106.6, 101.7, 71.4, 17.3. IR (KBr): ν = 3066, 2901, 1717, 1700, 1633, 1503, 1451, 1265, 1175, 693. HRMS (ESI, m/z) calcd. for C₁₉H₁₆NaO₅ (M+Na)⁺ 347.0890, found 347.0896.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(thiophen-2-yl)acrylate (5ah).

A white solid (65.8 mg, 46%). mp 93-95 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 15.6 Hz,

1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 5.2$ Hz, 1H), 7.23 (d, $J = 3.2$ Hz, 1H), 7.02 (t, $J = 4.4$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 6.09 (q, $J = 7.2$ Hz, 1H), 1.58 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 166.1, 139.4, 138.3, 134.4, 133.6, 131.4, 128.9, 128.8, 128.6, 128.2, 115.9, 71.5, 17.3. IR (KBr): $\nu = 3087, 1707, 1692, 1624, 1207, 1171, 702$. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{14}\text{NaO}_3\text{S}$ ($\text{M}+\text{Na}$) $^+$ 309.0556, found 309.0557.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(furan-2-yl)acrylate (5ai).

A pale red solid (36.5 mg, 27%). mp 73-75 °C. Eluting with 5:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.2$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 4H), 6.61 (d, $J = 3.2$ Hz, 1H), 6.45 (s, 1H), 6.39 (d, $J = 15.6$ Hz, 1H), 6.07 (q, $J = 7.2$ Hz, 1H), 1.58 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 166.4, 150.9, 145.1, 134.5, 133.7, 132.2, 128.9, 128.6, 115.4, 114.9, 112.5, 71.5, 17.3. IR (KBr): $\nu = 3122, 3038, 1712, 1699, 1634, 1320, 1282, 1213, 1170, 705$. HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{14}\text{NaO}_4$ ($\text{M}+\text{Na}$) $^+$ 293.0784, found 293.0788.

1-oxo-1-phenylpropan-2-yl (*E*)-3-(pyridin-3-yl)acrylate (5aj).

A pale yellow solid (16.9 mg, 12%). mp 74-76 °C. Eluting with 1:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 8.62 (s, 1H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 16.0$ Hz, 1H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.33 (dd, $J = 4.6, 3.2$ Hz, 1H), 6.63 (d, $J = 16.0$ Hz, 1H), 6.15 (q, $J = 6.8$ Hz, 1H), 1.63 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.6, 165.4, 151.0, 149.7, 142.0, 134.3, 134.2, 133.6, 129.9, 128.8, 128.4, 123.8, 119.4, 71.7, 17.2. IR (KBr): $\nu = 3056, 2951, 1712, 1696, 1638, 1327, 1198, 1008, 962, 811, 700$. HRMS (ESI, m/z) calcd. for $\text{C}_{17}\text{H}_{16}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 282.1125, found 282.1125.

1-oxo-1-phenylpropan-2-yl acetate (5ak)³.

A light yellow oil (49.0 mg, 51%). Eluting with 15:1 petroleum ether/ethyl acetate. ^1H

NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 5.94 (q, $J = 7.2$ Hz, 1H), 2.12 (s, 3H), 1.50 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 170.5, 134.4, 133.7, 128.9, 128.5, 71.5, 20.8, 17.2. IR (KBr): $\nu = 2989, 2938, 1719, 1601, 1451, 1269, 1111, 1071, 712$. HRMS (ESI, m/z) calcd. for $\text{C}_{11}\text{H}_{13}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 193.0859, found 193.0860.

1-oxo-1-phenylpropan-2-yl pivalate (5al).

A yellow oil (37.5 mg, 32%). Eluting with 20:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 5.91 (q, $J = 6.8$ Hz, 1H), 1.52 (d, $J = 7.2$ Hz, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 178.1, 134.8, 133.6, 128.9, 128.6, 71.3, 33.7, 27.2, 17.0. IR (KBr): $\nu = 2975, 2936, 1731, 1699, 1450, 1280, 1229, 1158, 970, 700$. HRMS (ESI, m/z) calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 235.1329, found 235.1331.

(2-(methacryloyloxy)-1-phenylpropylidene)oxonium (5am).

A pale yellow oil (40.3 mg, 37%). Eluting with 15:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.6$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 6.22 (s, 1H), 6.01 (q, $J = 7.2$ Hz, 1H), 5.63 (s, 1H), 1.96 (s, 3H), 1.57 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 166.9, 135.8, 134.6, 133.7, 128.9, 128.6, 126.7, 71.8, 18.4, 17.2. IR (KBr): $\nu = 2988, 1720, 1699, 1597, 1450, 1305, 1229, 1133, 1089, 971, 701$. HRMS (ESI, m/z) calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 219.1016, found 219.1014.

1-oxo-1-phenylpropan-2-yl 3-phenylpropanoate (5an).

A colorless oil (90.3 mg, 64%). Eluting with 15:1 petroleum ether/ethyl acetate. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.6$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.24-7.20 (m, 3H), 5.99 (q, $J = 7.2$ Hz, 1H), 3.00 (t, $J = 8.0$ Hz, 2H), 2.79-2.74 (m, 2H), 1.53 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100

MHz, CDCl₃) δ 196.9, 172.3, 140.4, 134.4, 133.6, 128.8, 128.6, 128.5, 128.4, 126.3, 71.5, 35.6, 30.8, 17.1. IR (KBr): ν = 3062, 2988, 2936, 1738, 1699, 1597, 1451, 1229, 1161, 699. HRMS (ESI, m/z) calcd. for C₁₈H₁₈NaO₃ (M+Na)⁺ 305.1148, found 305.1146.

1-(4-fluorophenyl)-1-oxopropan-2-yl benzoate (3ba)¹.

A white solid (119.7 mg, 88%). mp 87-88 °C. Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 8.4 Hz, 2H), 8.05-8.01 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 8.4 Hz, 2H), 6.14 (q, J = 7.2 Hz, 1H), 1.65 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.3, 167.3, 166.0, 164.7, 133.4, 131.3, 131.2, 130.9, 130.8, 129.9, 129.4, 128.5, 116.2, 115.9, 71.8, 17.2. IR (KBr): ν = 3055, 2997, 1715, 1684, 1600, 1280, 1239, 1120, 966, 714. HRMS (ESI, m/z) calcd. for C₁₆H₁₃FNaO₃ (M+Na)⁺ 295.0741, found 295.0746.

1-(4-chlorophenyl)-1-oxopropan-2-yl benzoate (3ca)¹.

A white solid (49.0 mg, 34%). mp 94-95 °C. Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45-7.41 (m, 4H), 6.12 (q, J = 7.2 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 166.0, 140.1, 133.5, 132.8, 130.0, 129.9, 129.4, 129.2, 128.5, 71.9, 17.1. IR (KBr): ν = 3069, 1717, 1693, 1270, 1116, 1092, 971, 720, 706. HRMS (ESI, m/z) calcd. for C₁₆H₁₃ClNaO₃ (M+Na)⁺ 311.0445, found 311.0442.

1-(3-chlorophenyl)-1-oxopropan-2-yl benzoate (3da).

A white solid (23.0 mg, 16%). mp 72-74 °C. Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 7.6 Hz, 2H), 7.98 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.61-7.55 (m, 2H), 7.47-7.41 (m, 3H), 6.11 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 166.2, 136.2, 135.4, 133.7, 133.6, 130.3, 130.1, 129.4, 128.8, 128.6, 126.7, 72.1, 17.2. IR (KBr): ν = 3064, 1720,

1696, 1273, 1220, 1114, 711. HRMS (ESI, m/z) calcd. for $C_{16}H_{13}ClNaO_3$ ($M+Na$)⁺ 311.0445, found 311.0443.

1-(4-bromophenyl)-1-oxopropan-2-yl benzoate (3ea)¹.

A pale yellow solid (76.4 mg, 46%). mp 90-92 °C. Eluting with 10:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 6.12 (q, J = 6.8 Hz, 1H), 1.65 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 166.1, 133.6, 133.3, 132.3, 130.1, 130.0, 129.4, 129.0, 128.6, 71.9, 17.2. IR (KBr): ν = 2989, 1708, 1692, 1319, 1276, 969, 718. HRMS (ESI, m/z) calcd. for $C_{16}H_{13}BrNaO_3$ ($M+Na$)⁺ 354.9940, found 354.9943.

1-oxo-1-(p-tolyl)propan-2-yl benzoate (3fa)^{10a}.

A white solid (85.8 mg, 64%). mp 77-79 °C. Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.20 (q, J = 7.2 Hz, 1H), 2.41 (s, 3H), 1.66 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 166.1, 144.7, 133.4, 132.0, 130.0, 129.7, 129.6, 128.8, 128.5, 72.0, 21.8, 17.4. IR (KBr): ν = 3063, 2990, 1718, 1687, 1301, 1273, 1114, 710. HRMS (ESI, m/z) calcd. for $C_{17}H_{16}NaO_3$ ($M+Na$)⁺ 291.0992, found 291.0984.

1-(4-methoxyphenyl)-1-oxopropan-2-yl benzoate (3ga)¹.

A white solid (45.5 mg, 32%). mp 96-97°C. Eluting with 5:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 6.8 Hz, 2H), 8.00 (d, J = 8.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.18 (q, J = 7.2 Hz, 1H), 3.84 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.2, 166.1, 164.0, 133.4, 131.0, 130.0, 129.7, 128.5, 127.3, 114.1, 71.8, 55.6, 17.5. IR (KBr): ν = 2964, 2840, 1709, 1684, 1600, 1280, 1239, 1120, 966, 714. HRMS (ESI,

m/z) calcd. for $C_{17}H_{16}NaO_4$ ($M+Na$)⁺ 307.0941, found 307.0936.

1-oxo-1-phenylbutan-2-yl benzoate (3ha)².

A colorless oil (73.7 mg, 55%). Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.58-7.56 (m, 2H), 7.50-7.43 (m, 4H), 6.07 (dd, J = 4.4, 3.6 Hz, 1H), 2.12-1.99 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 166.3, 135.0, 133.6, 133.4, 129.9, 129.7, 128.9, 128.5, 76.9, 25.0, 10.1. IR (KBr): ν = 2975, 2938, 1721, 1697, 1599, 1450, 1250, 1115, 712. HRMS (ESI, m/z) calcd. for $C_{17}H_{16}NaO_3$ ($M+Na$)⁺ 291.0992, found 291.0983.

1-oxo-1-phenylpentan-2-yl benzoate (3ia).

A pale yellow oil (64.9 mg, 46%). Eluting with 15:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.61-7.56 (m, 2H), 7.51-7.43 (m, 4H), 6.13 (dd, J = 5.2, 2.8 Hz, 1H), 2.01-1.99 (m, 2H), 1.61-1.59 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.6, 166.3, 134.9, 133.6, 133.4, 129.9, 129.7, 128.9, 128.6, 128.5, 75.7, 33.6, 19.1, 13.9. IR (KBr): ν = 3064, 2962, 2874, 1721, 1697, 1599, 1310, 1115, 1071, 711. HRMS (ESI, m/z) calcd. for $C_{18}H_{18}NaO_3$ ($M+Na$)⁺ 305.1148, found 305.1142.

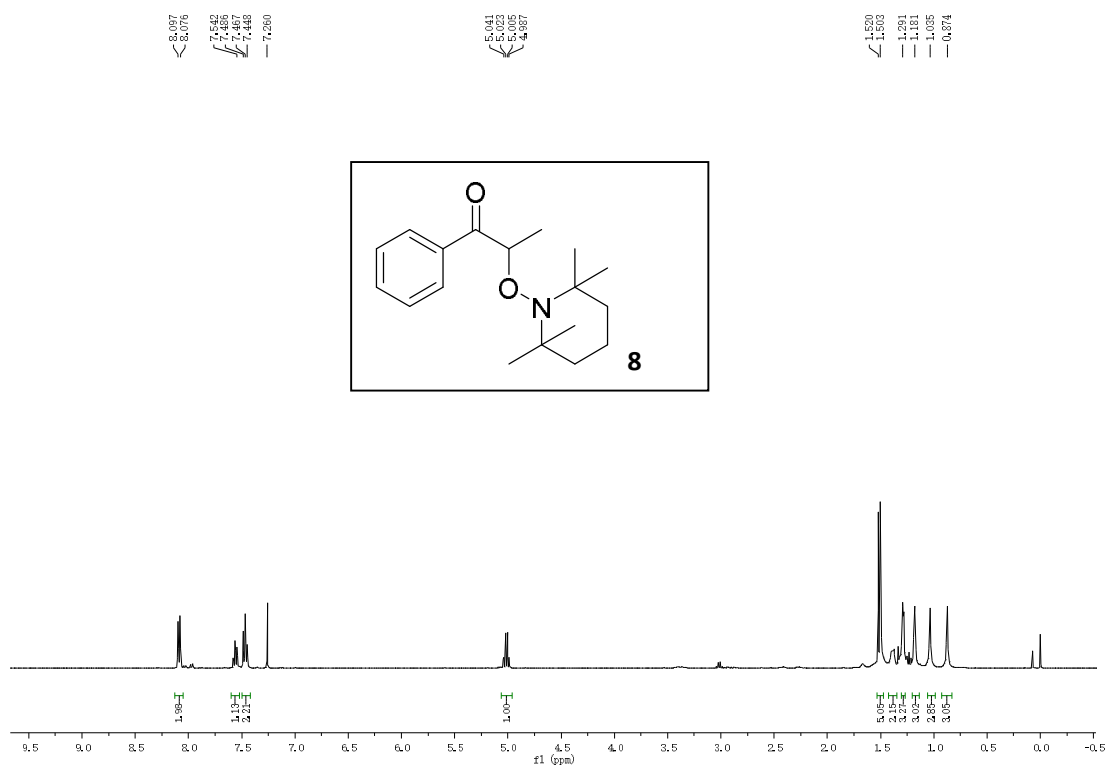
3-oxobutan-2-yl benzoate (3ma).

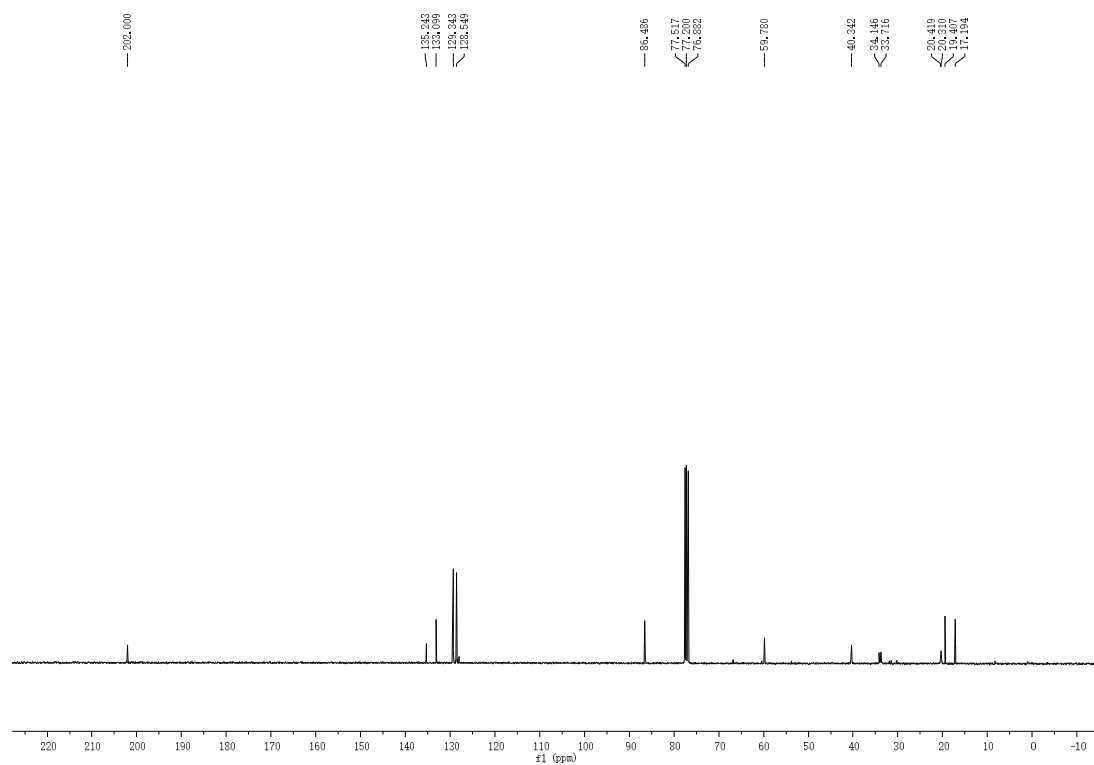
A pale yellow oil (30.7 mg, 32%). The experiment was carried out in 80 °C for 10 h. Eluting with 10:1 petroleum ether/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 5.32 (q, J = 7.2 Hz, 1H), 2.24 (s, 3H), 1.54 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 206.0, 166.1, 133.6, 130.0, 129.6, 128.7, 75.6, 25.9, 16.3. IR (KBr): ν = 2989, 2938, 1719, 1601, 1451, 1361, 1300, 1269, 1111, 1026, 712. HRMS (ESI, m/z) calcd. for $C_{11}H_{13}O_3$ ($M+H$)⁺ 193.0859, found 193.0856.

3 References

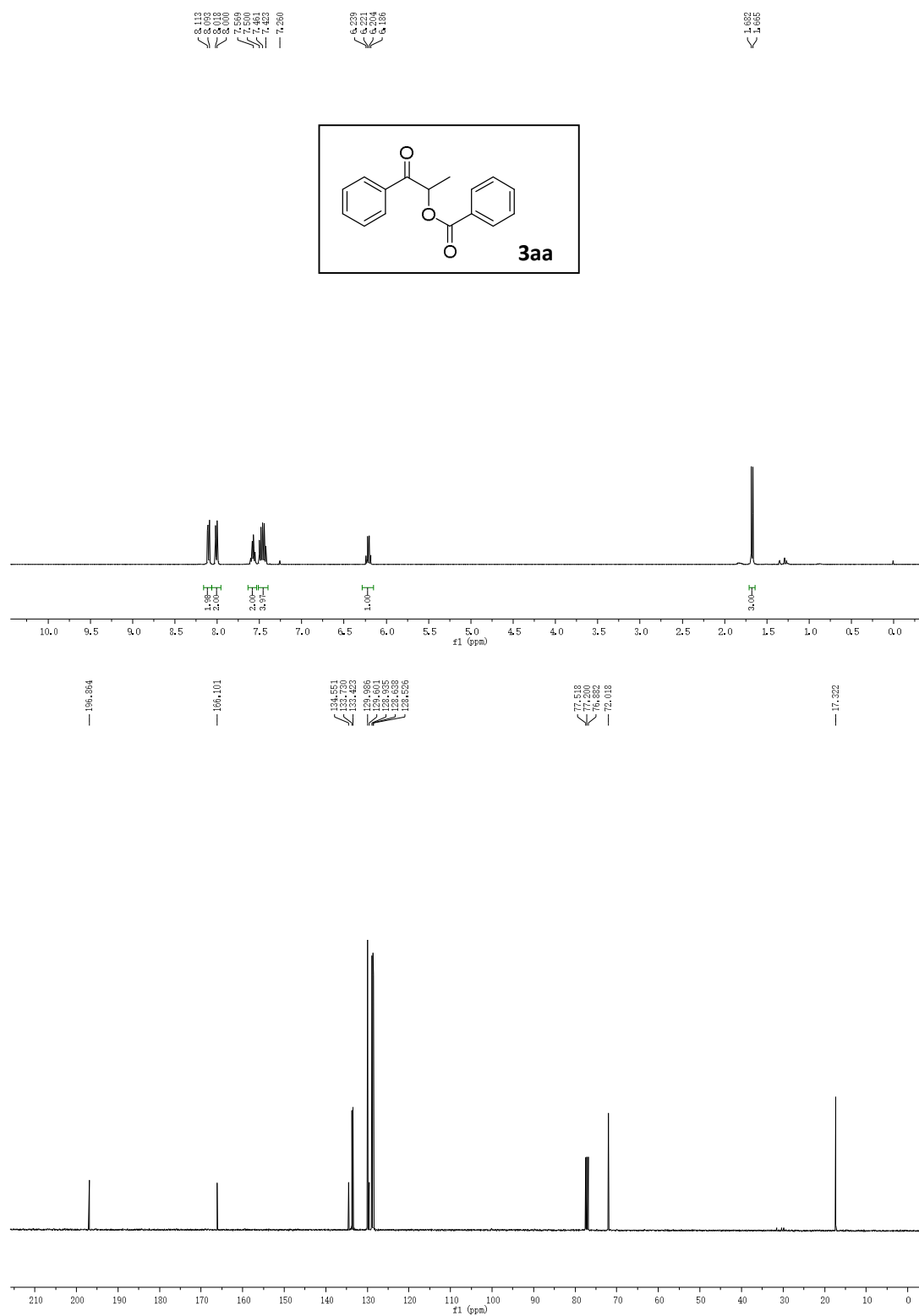
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- (2) S. Guo, J.-T. Yu, Q. Dai, H. Yang and J. Cheng, *Chem. Commun.* 2014, **50**, 6240.
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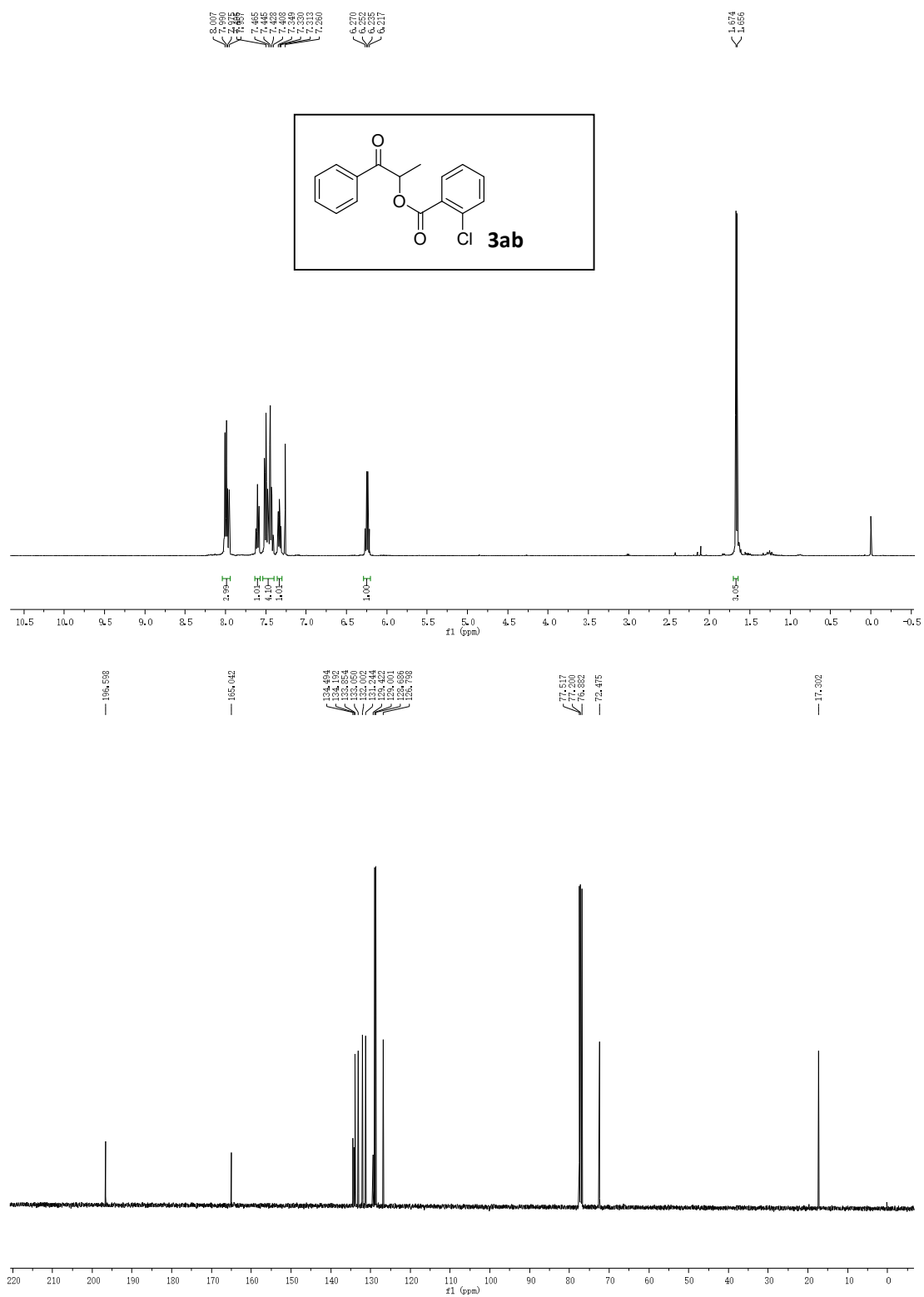
4 NMR Spectra of key intermediate 8

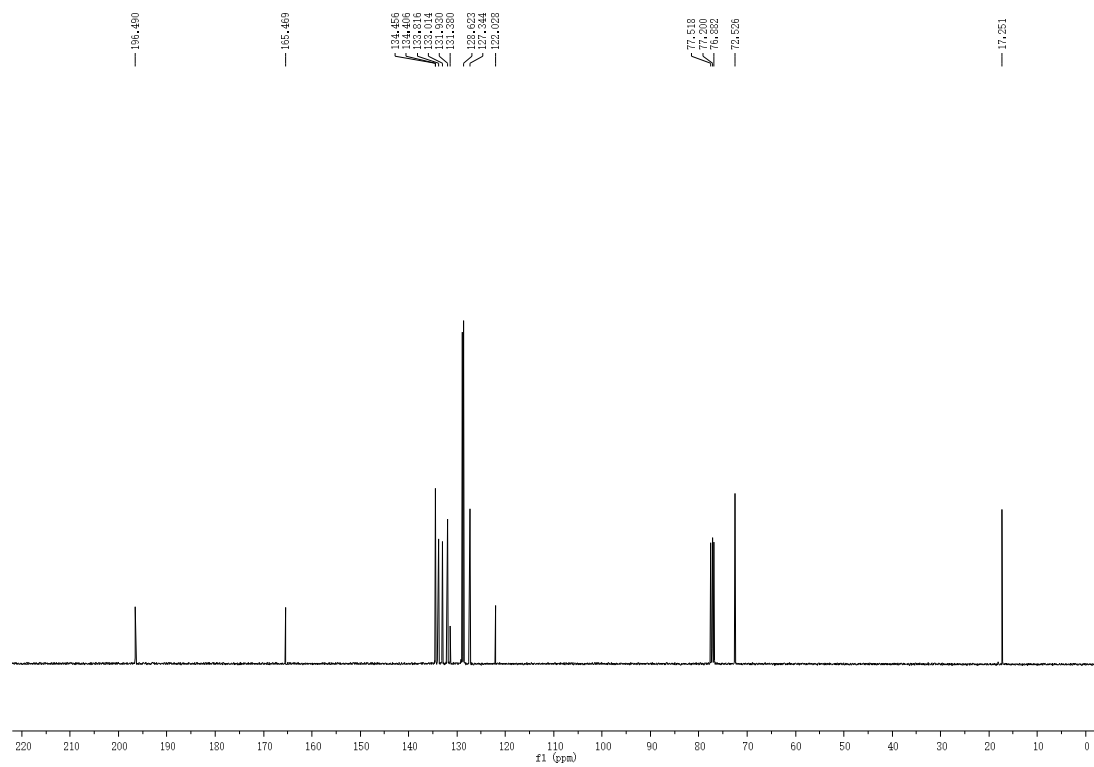
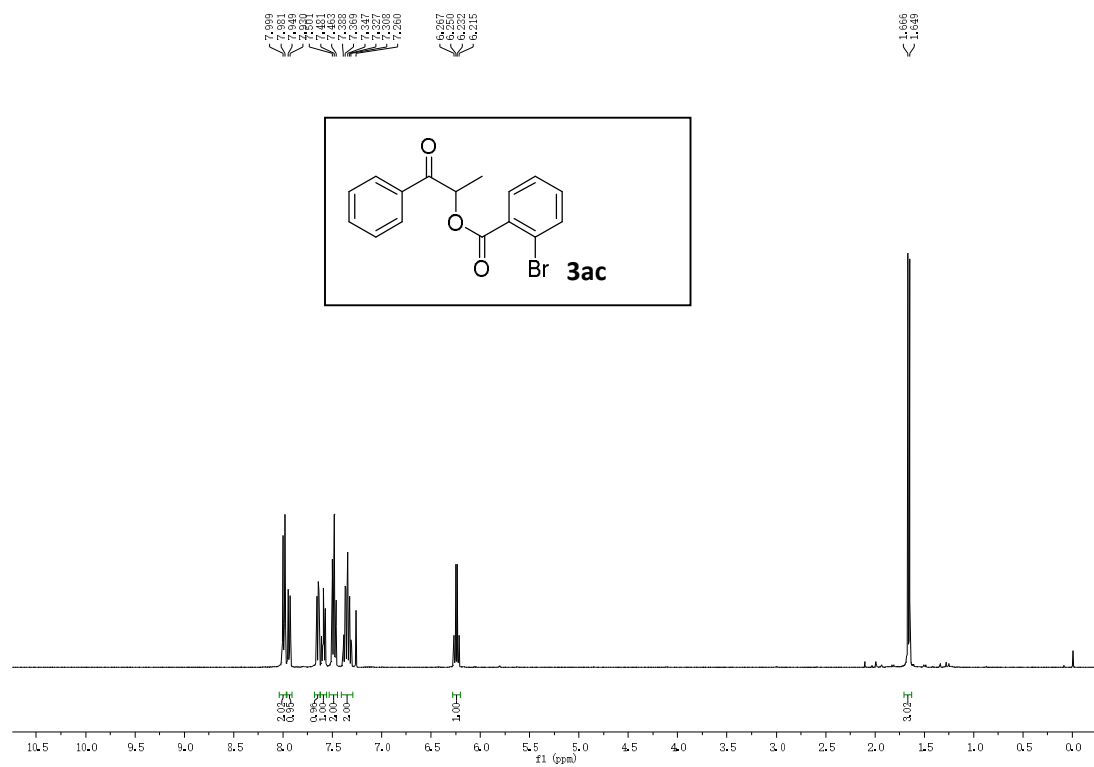


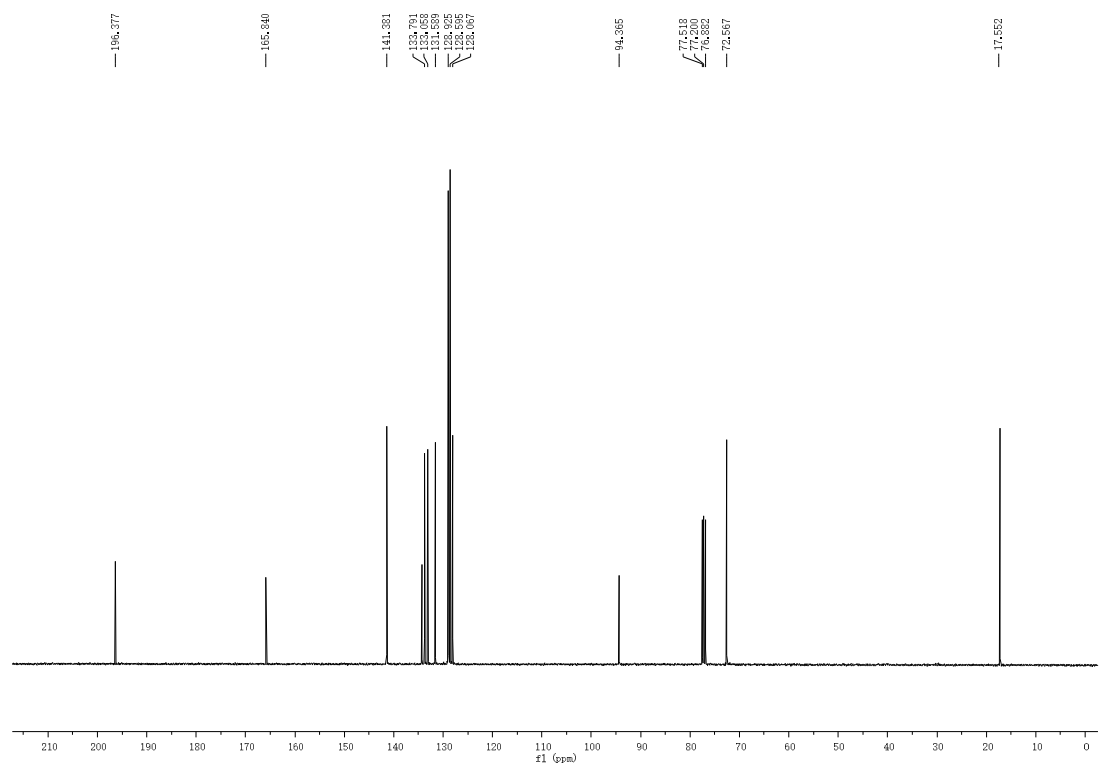
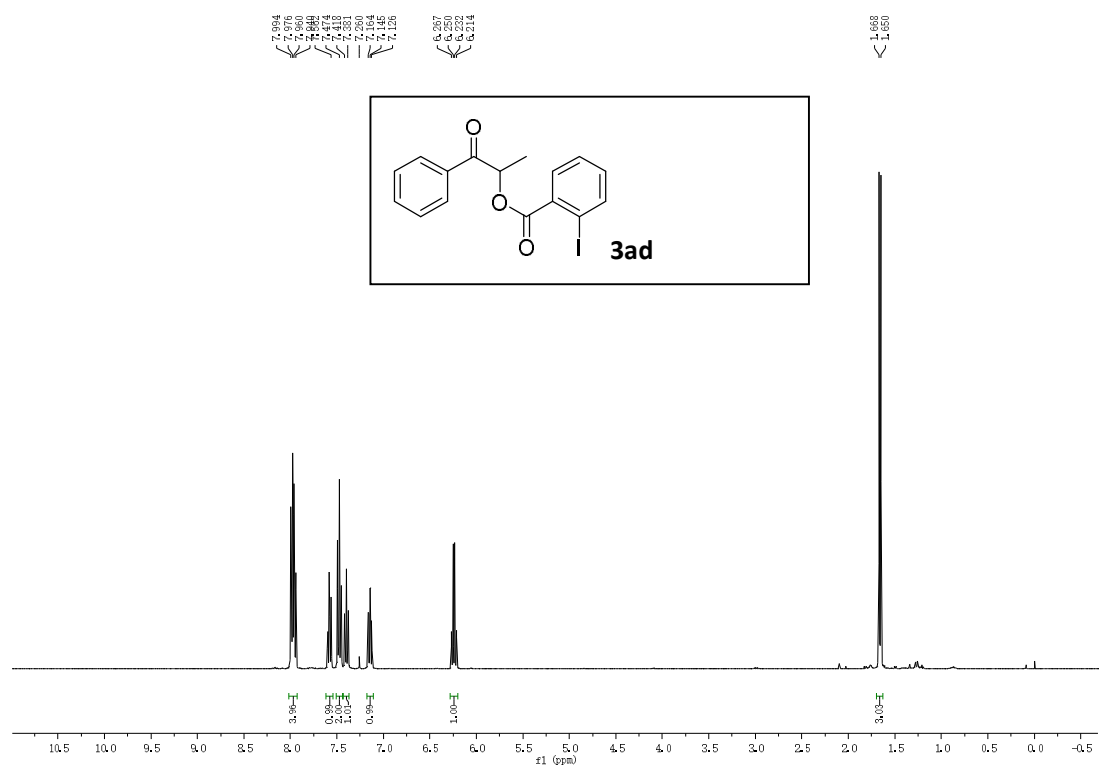


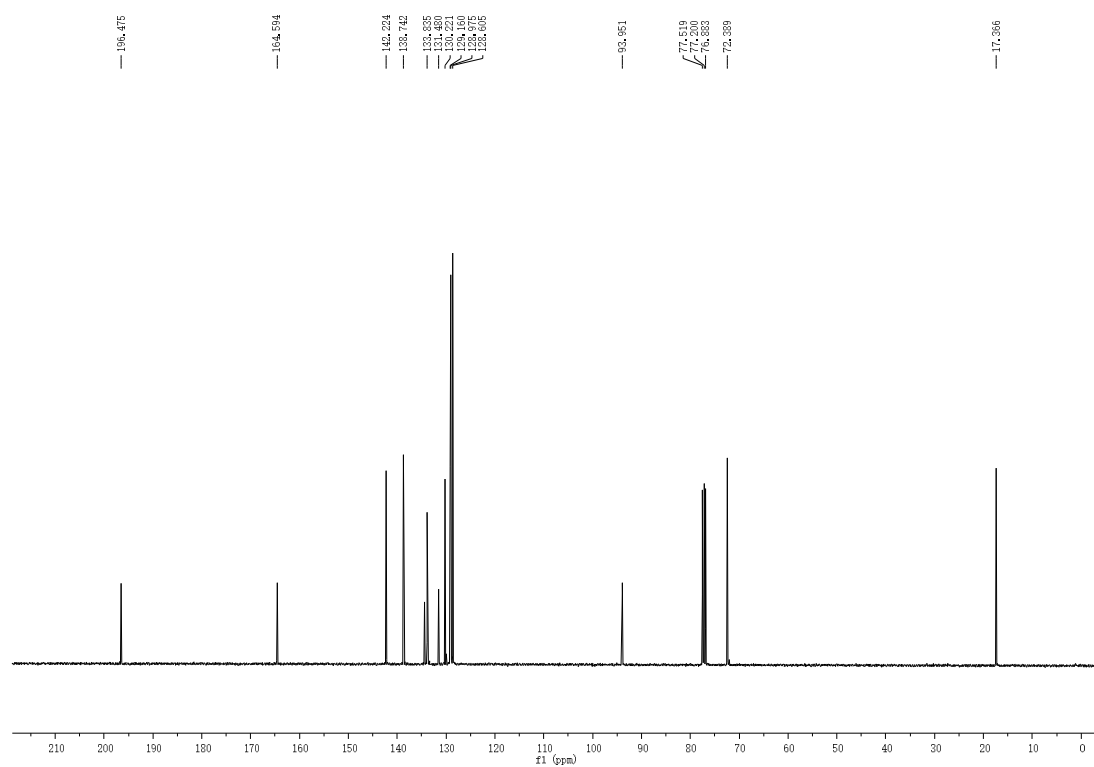
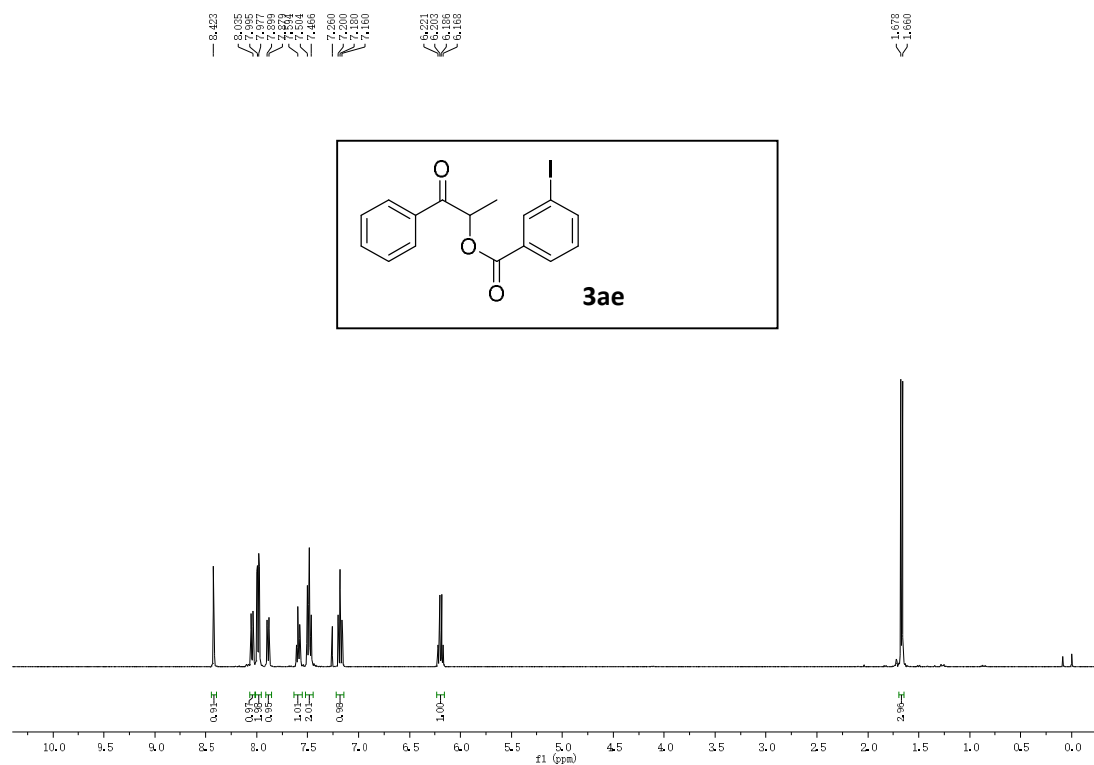
5 NMR Spectra of product 3aa-3am

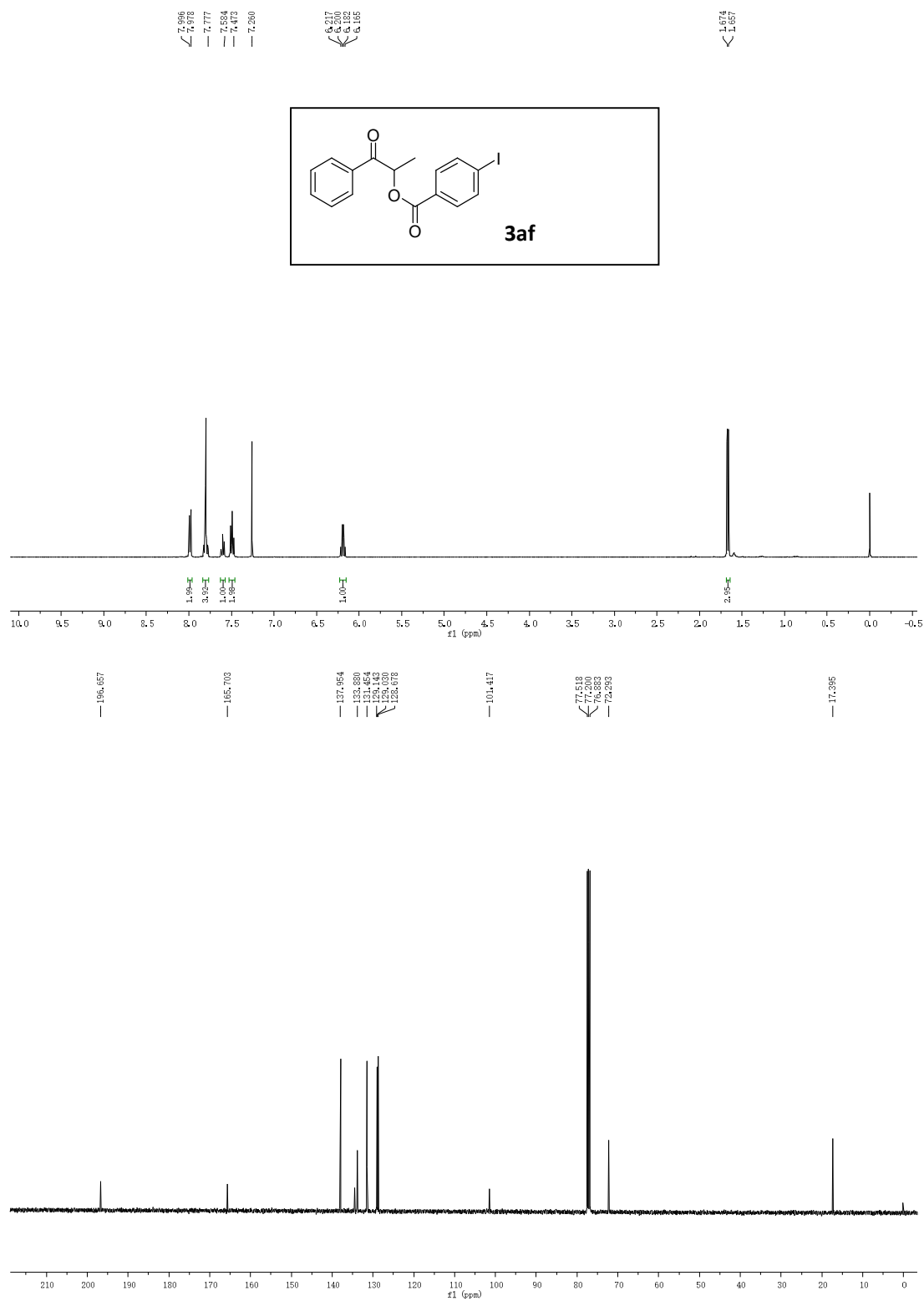


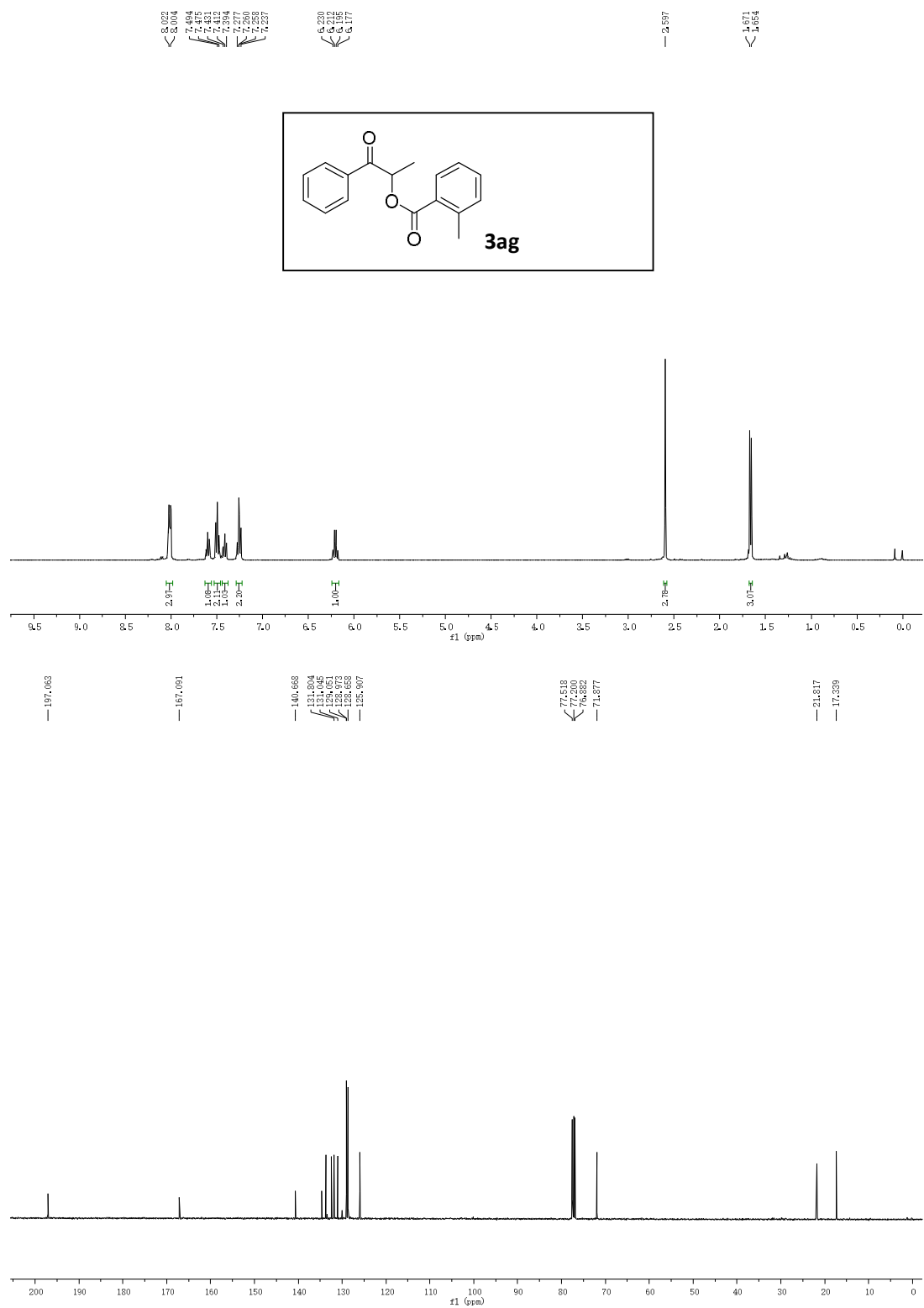


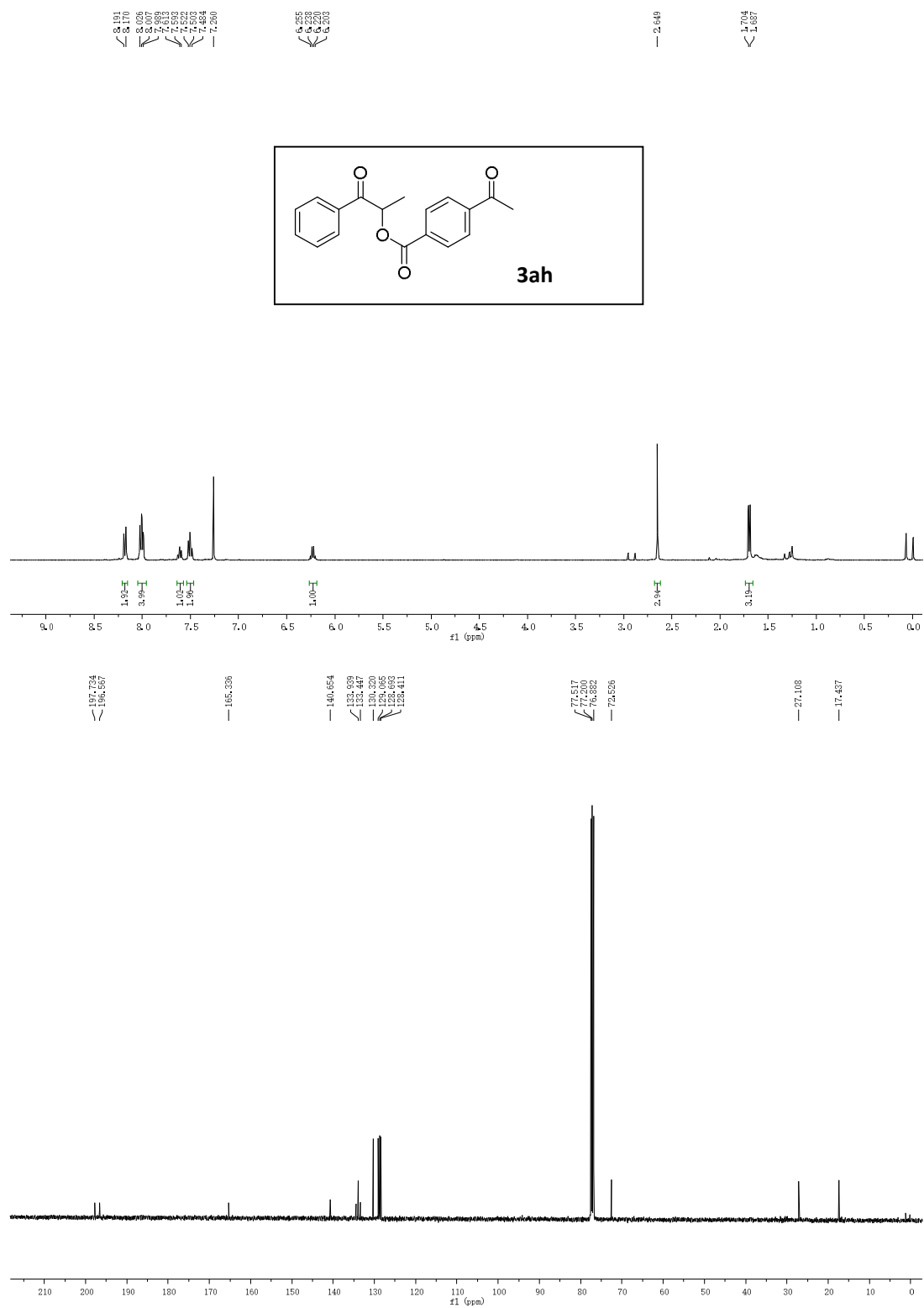


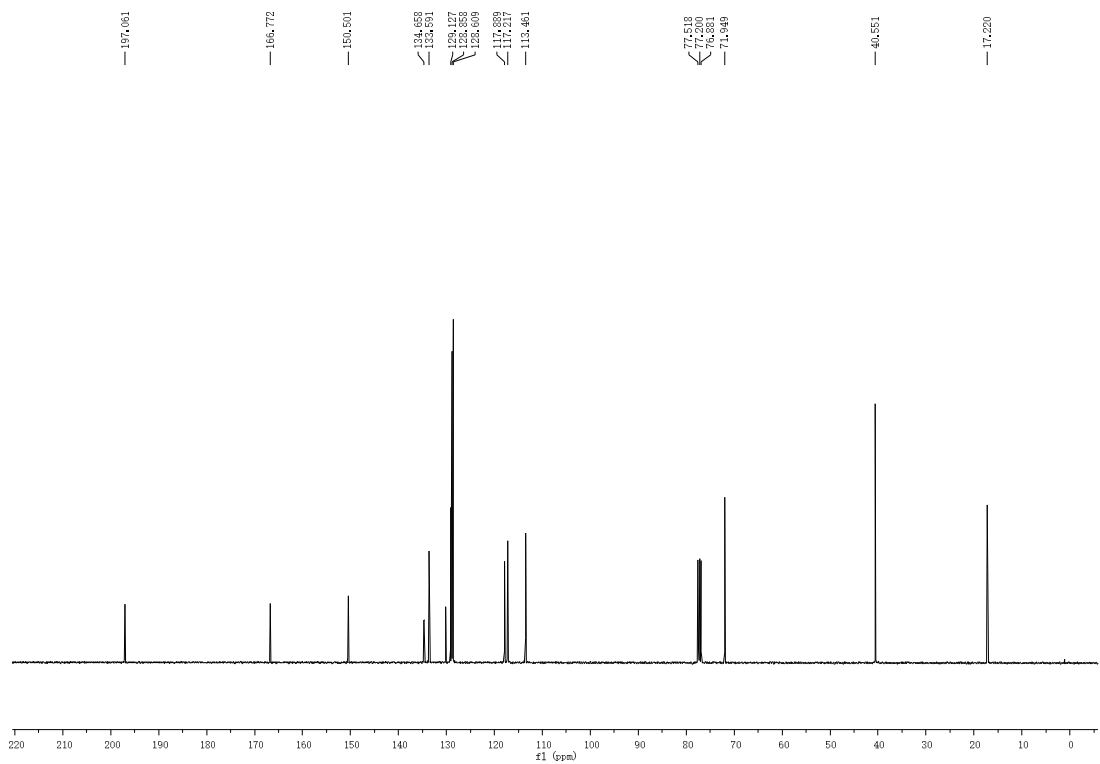


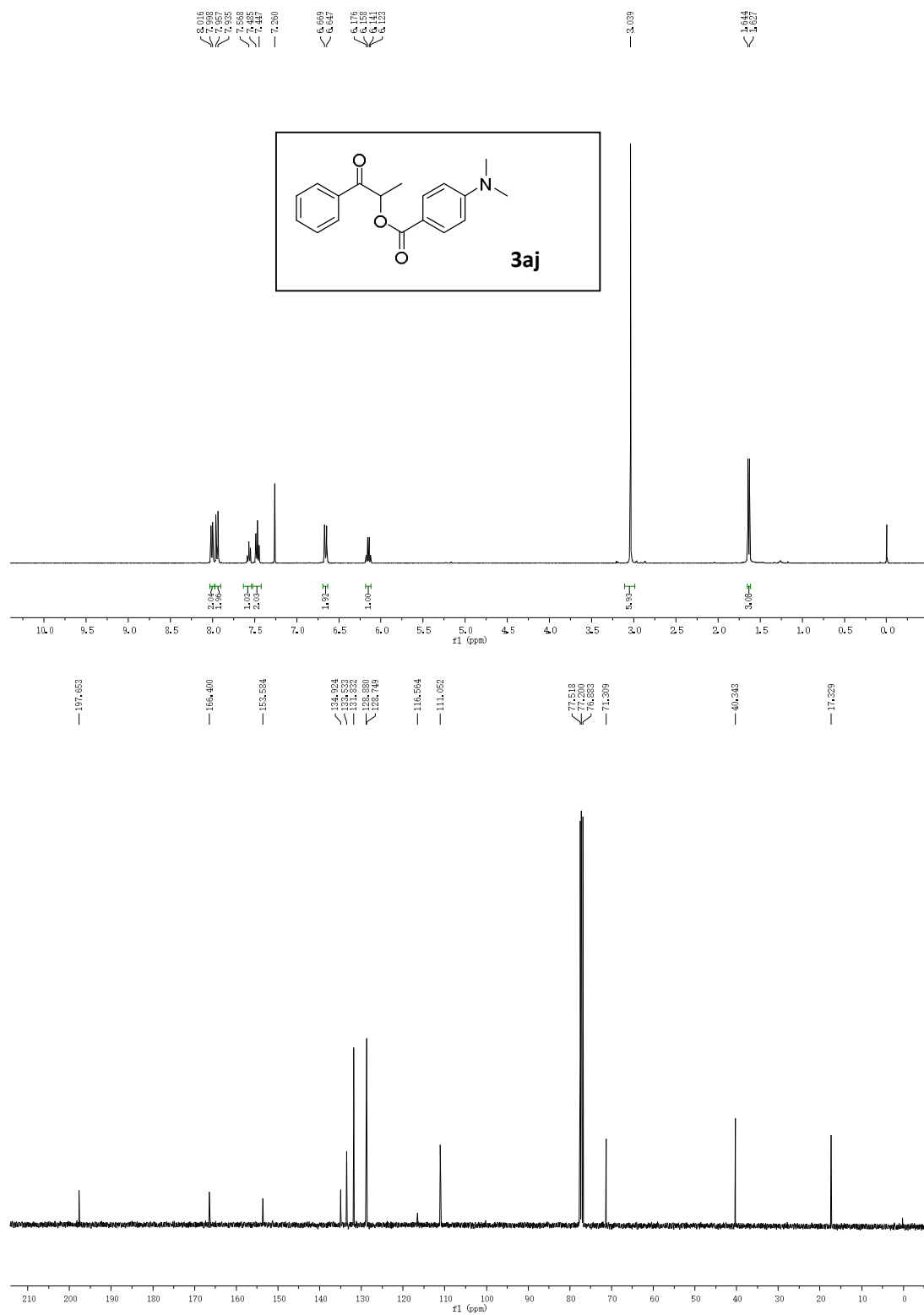


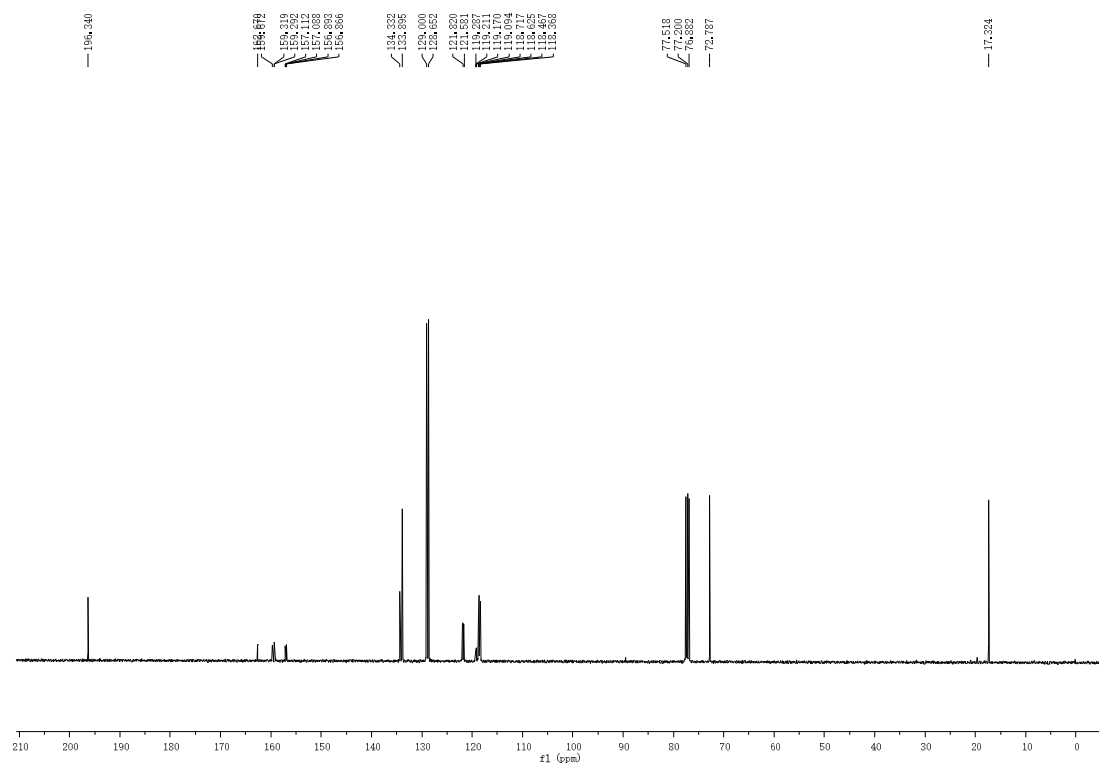




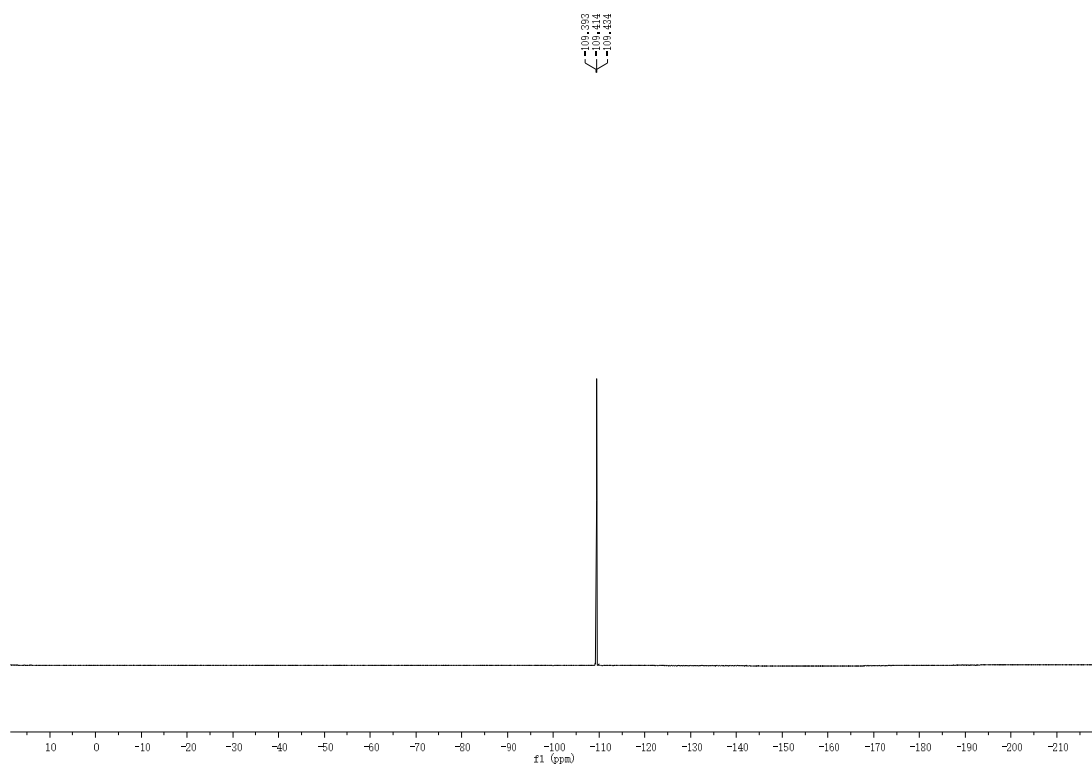


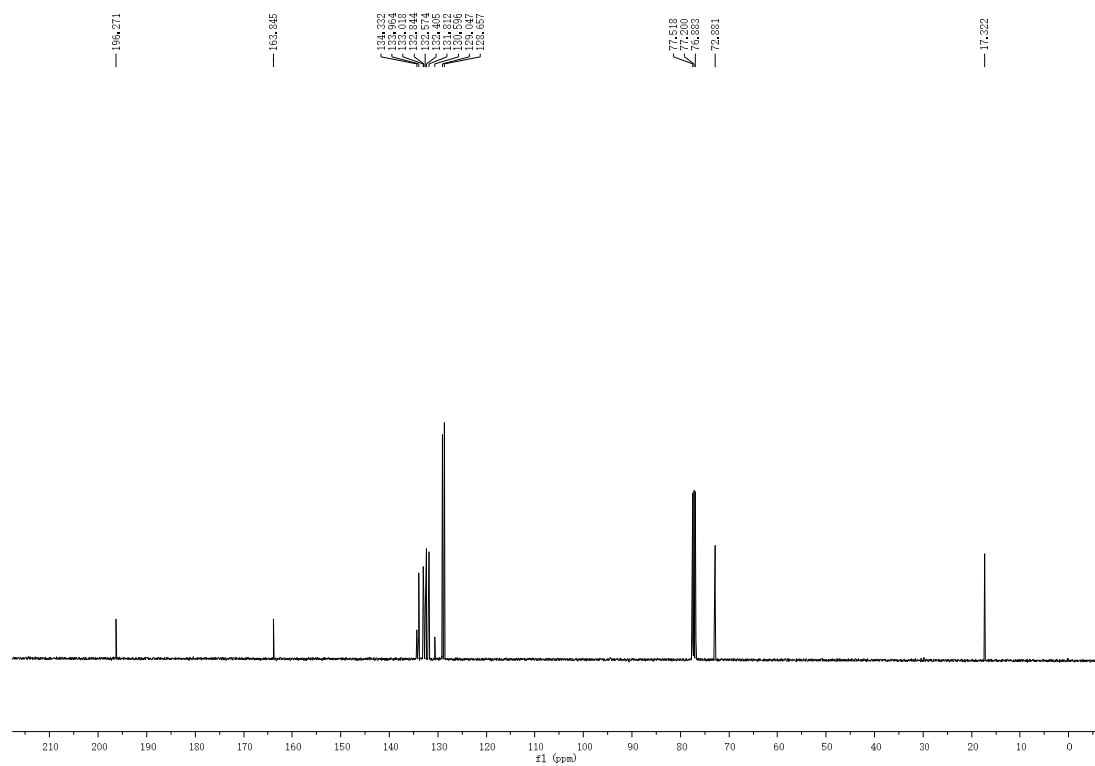
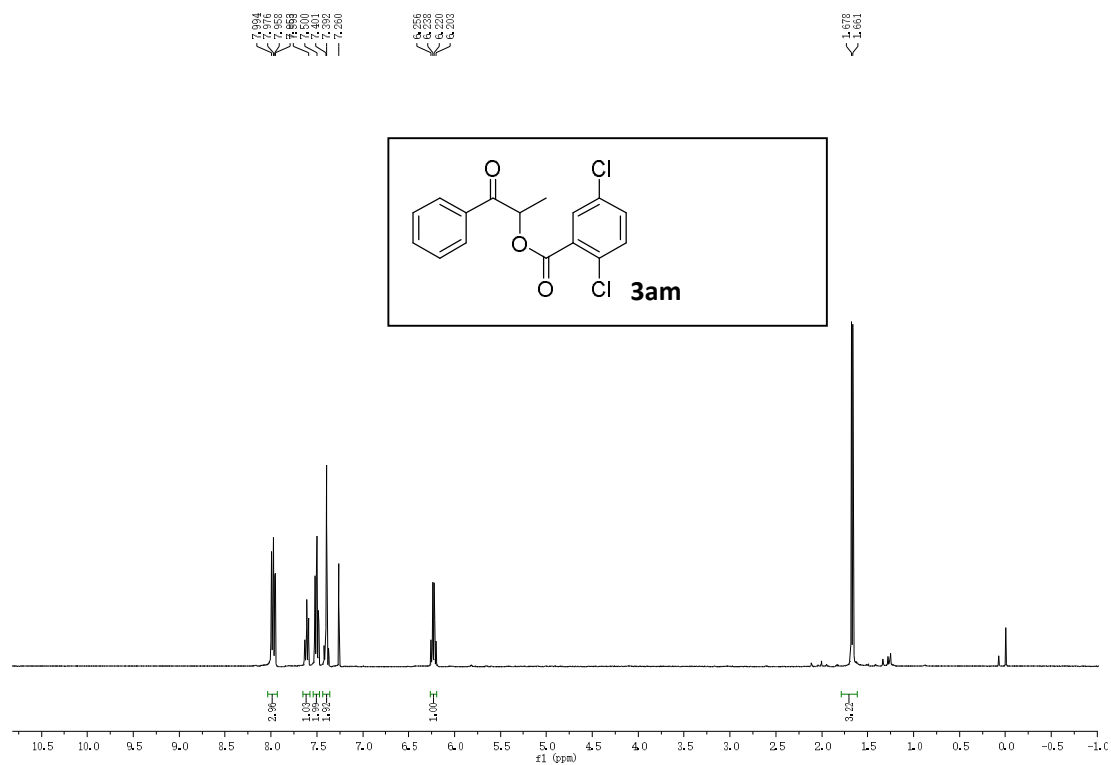




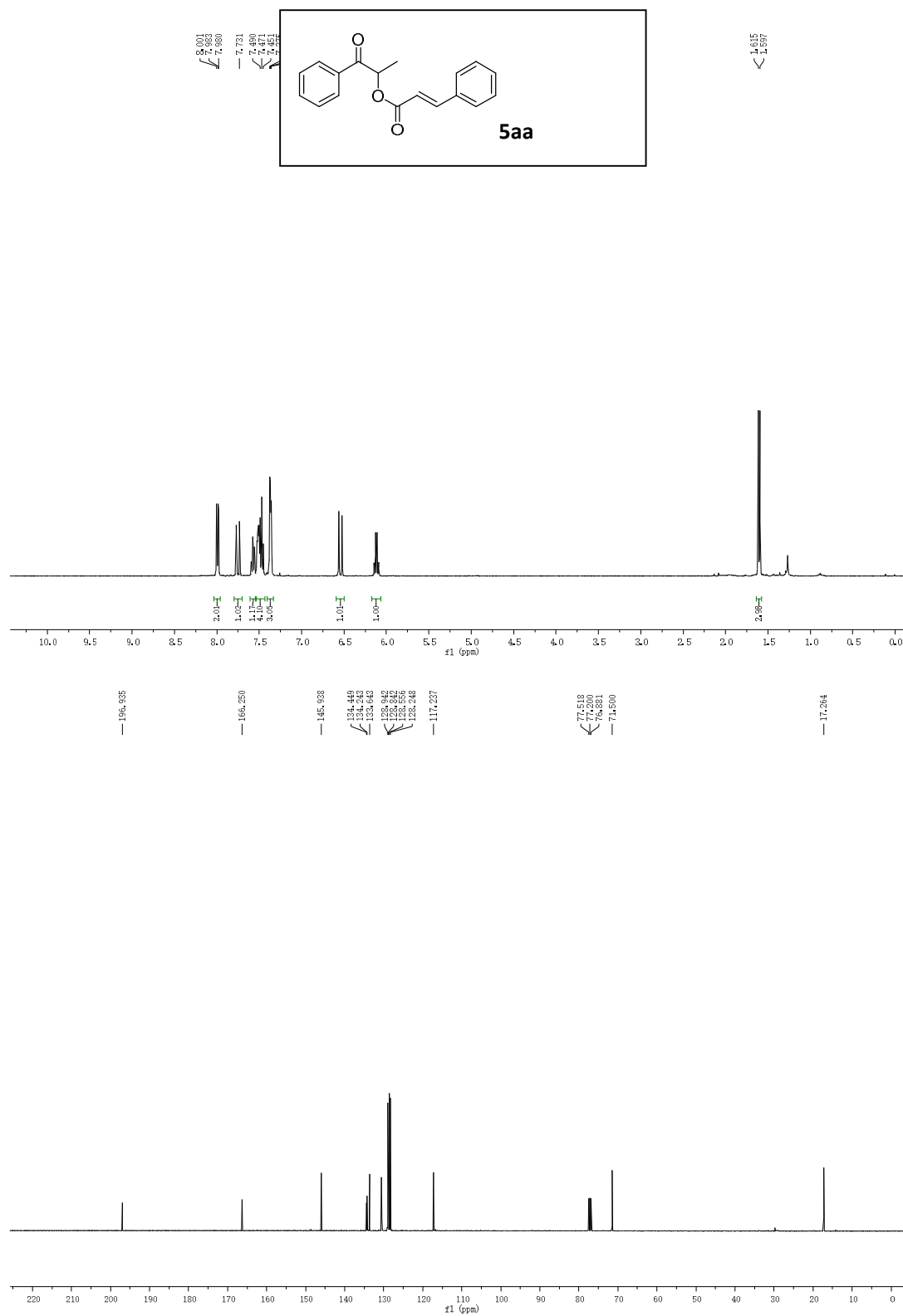


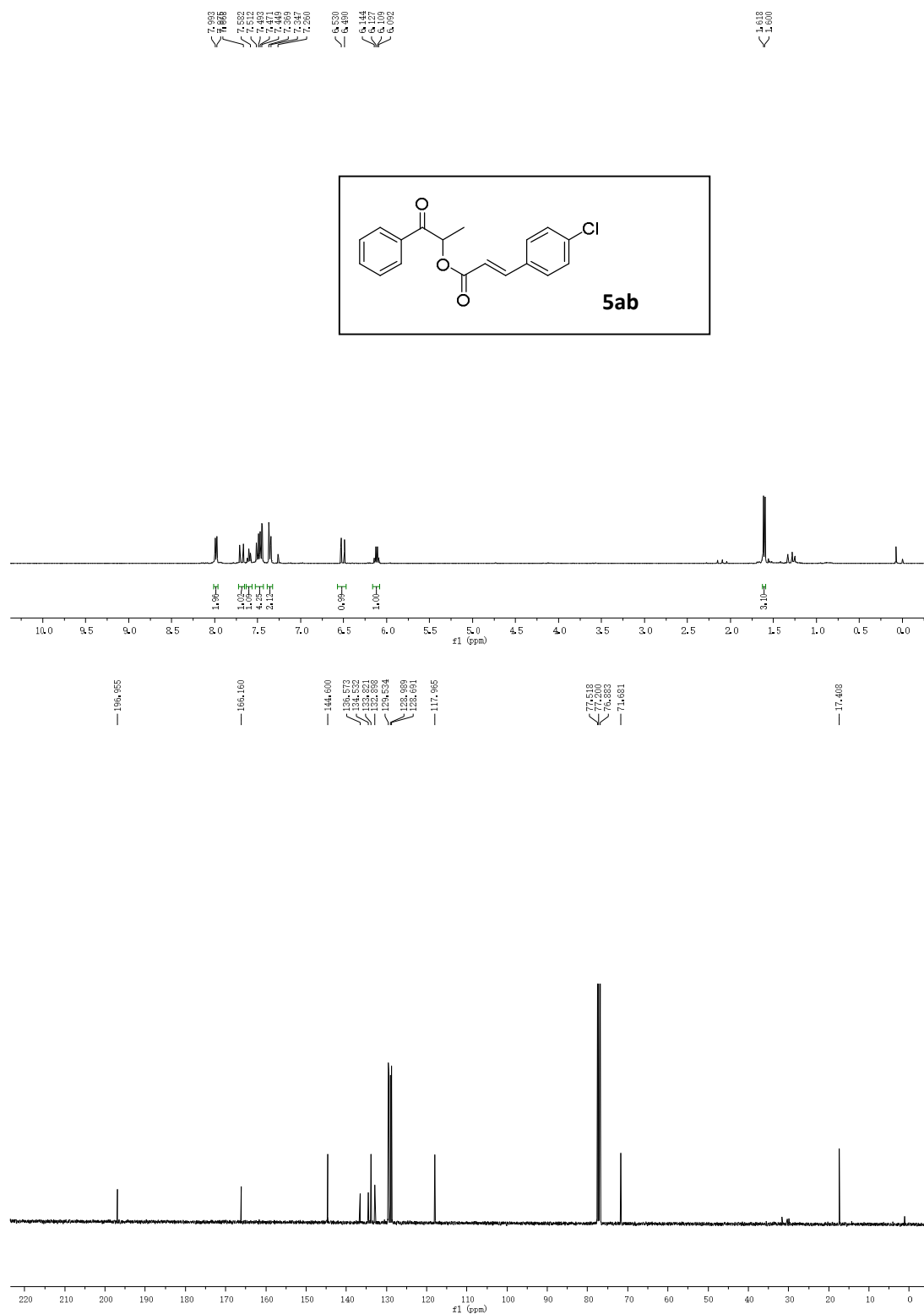




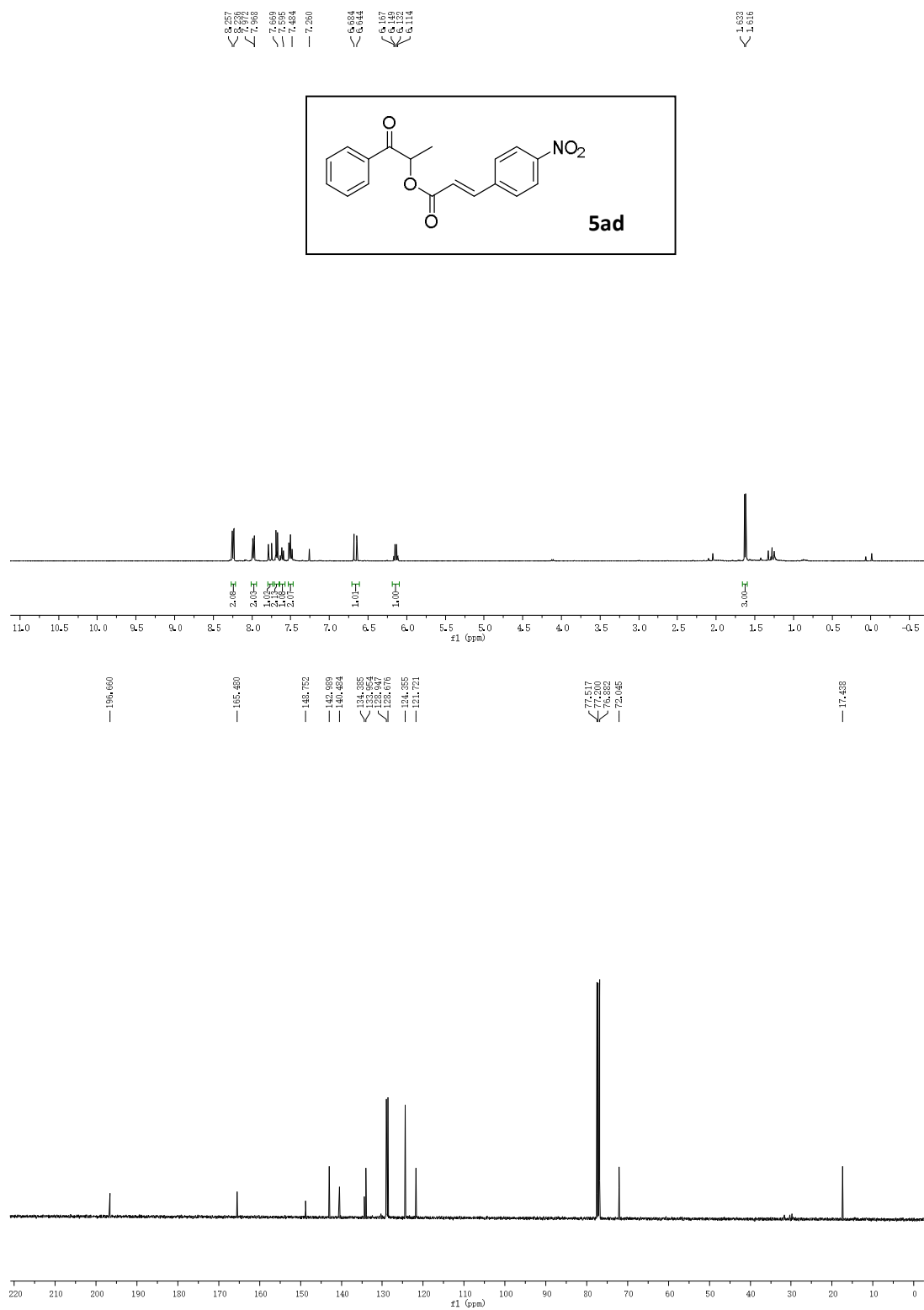


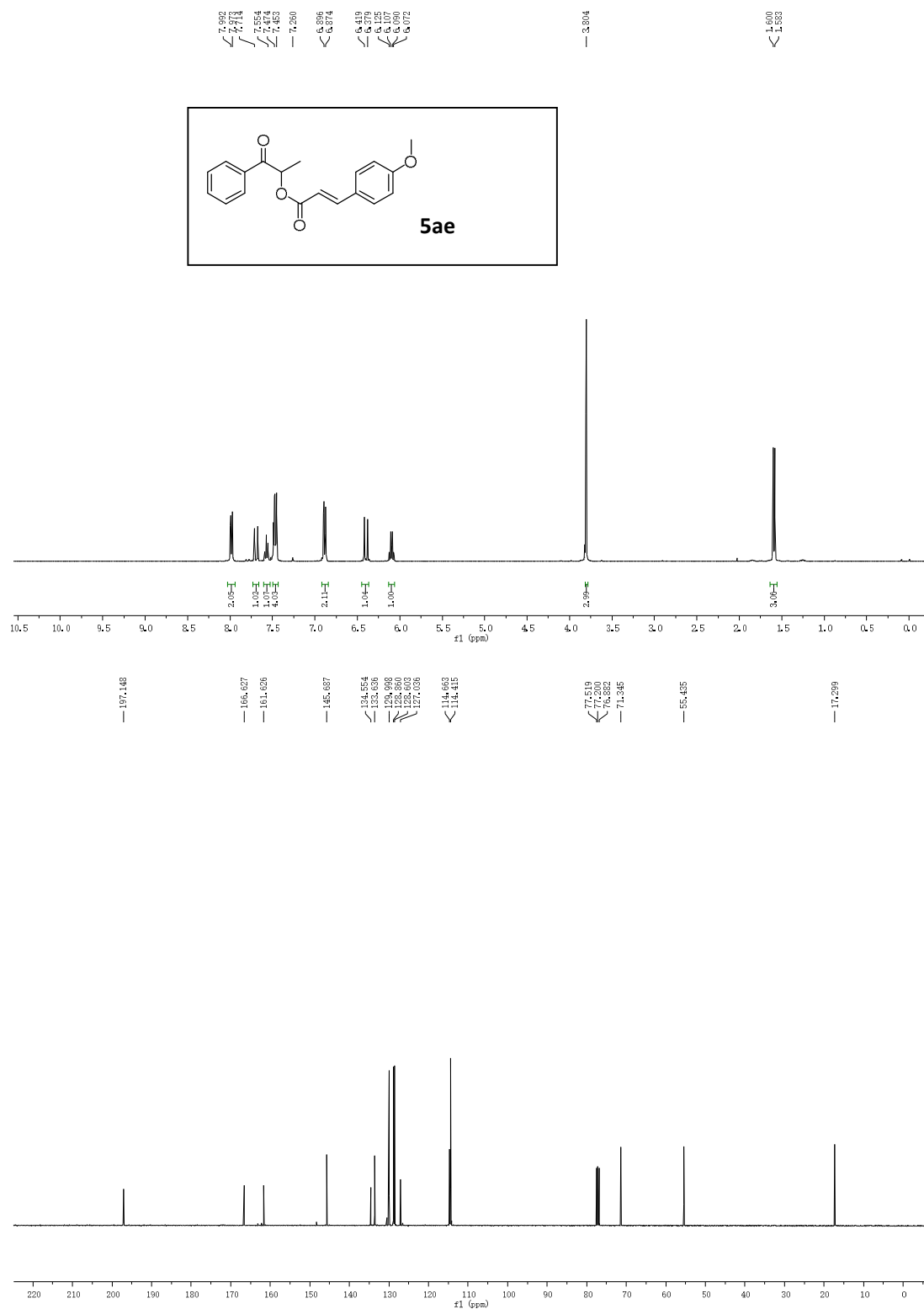
6 NMR Spectra of product 5aa-5an

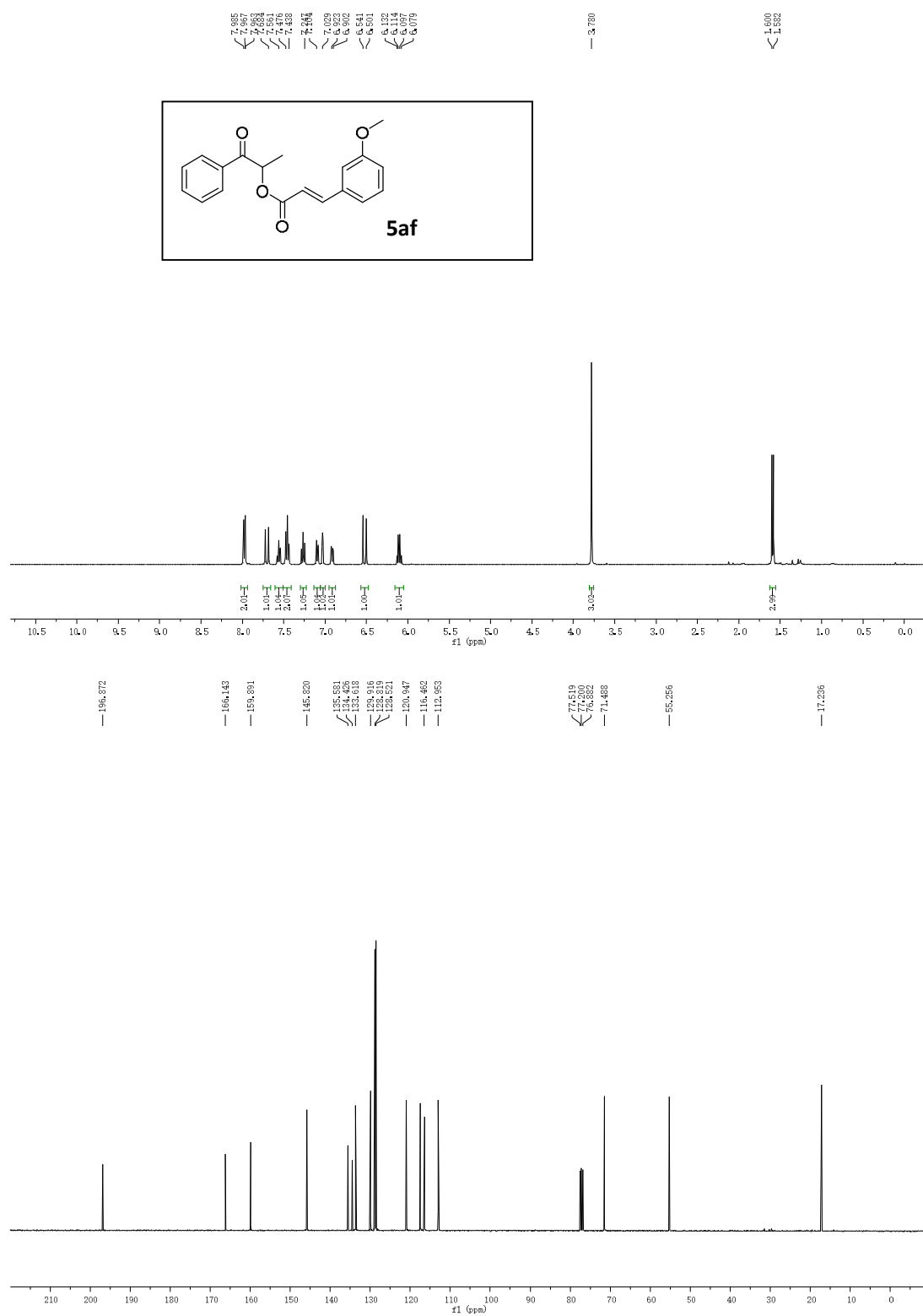


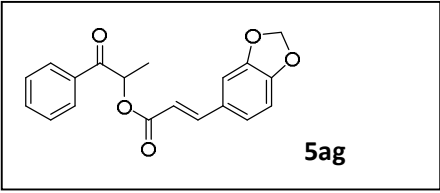


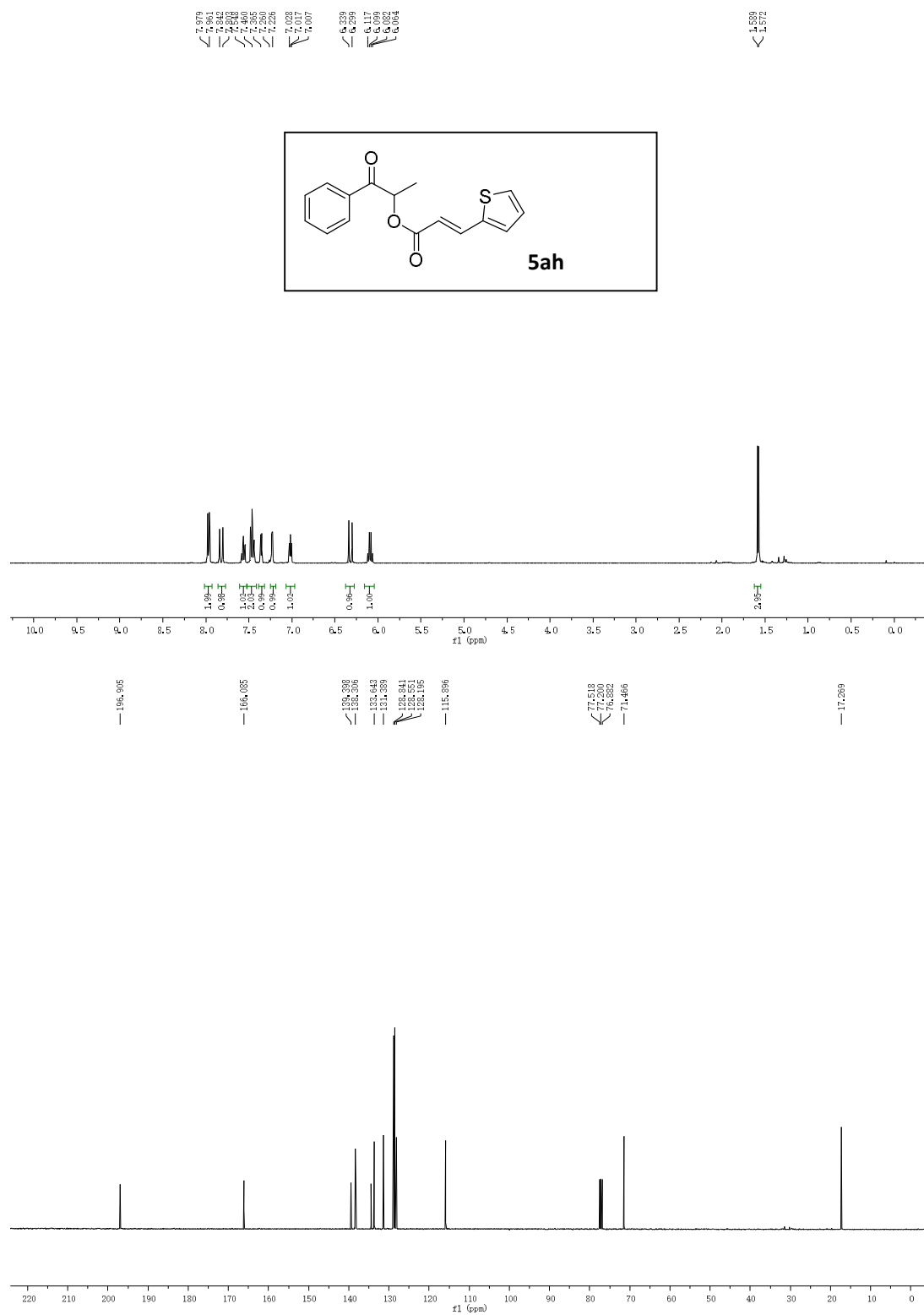


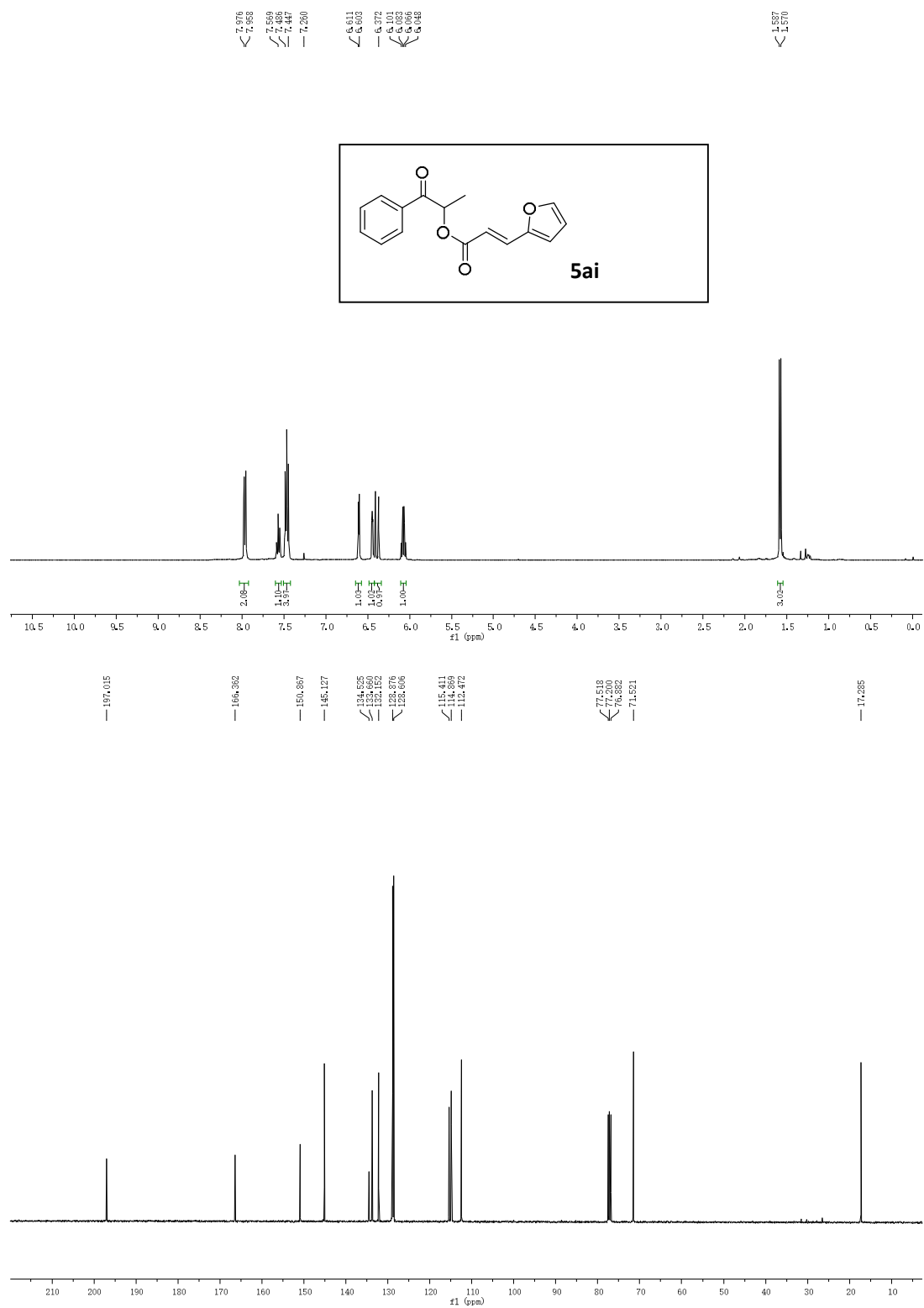


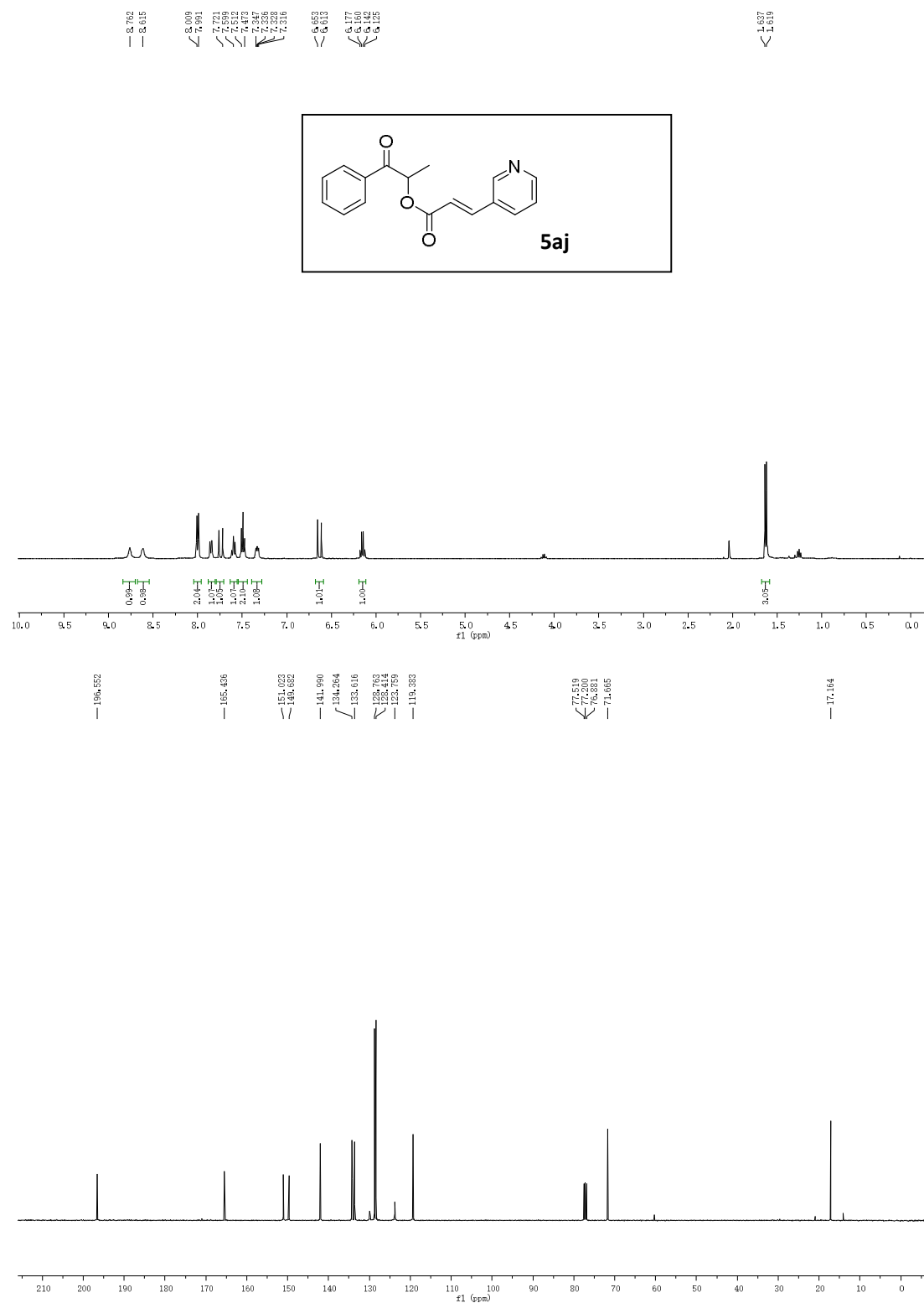


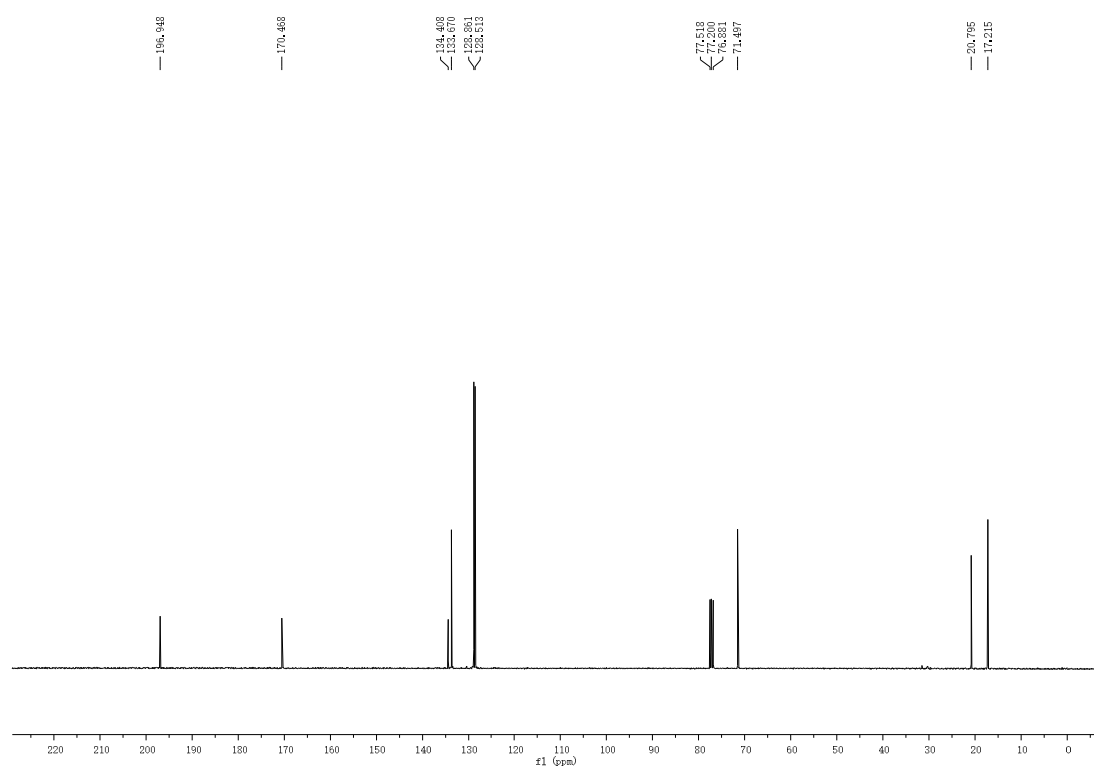
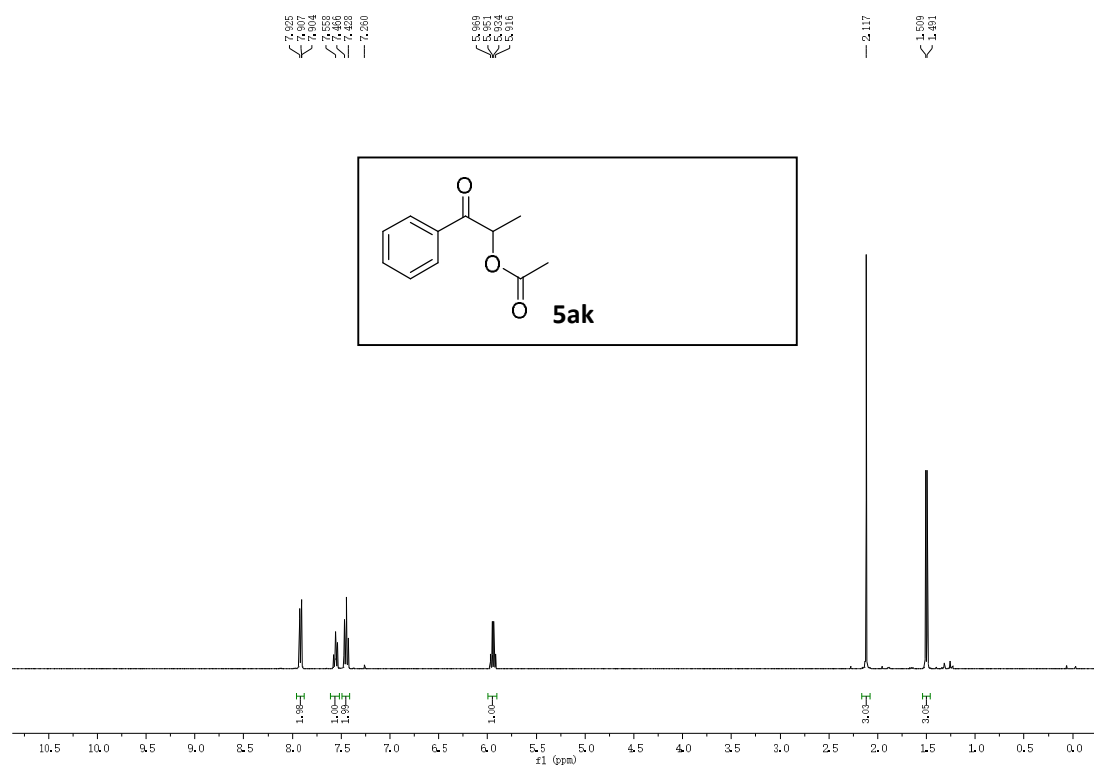


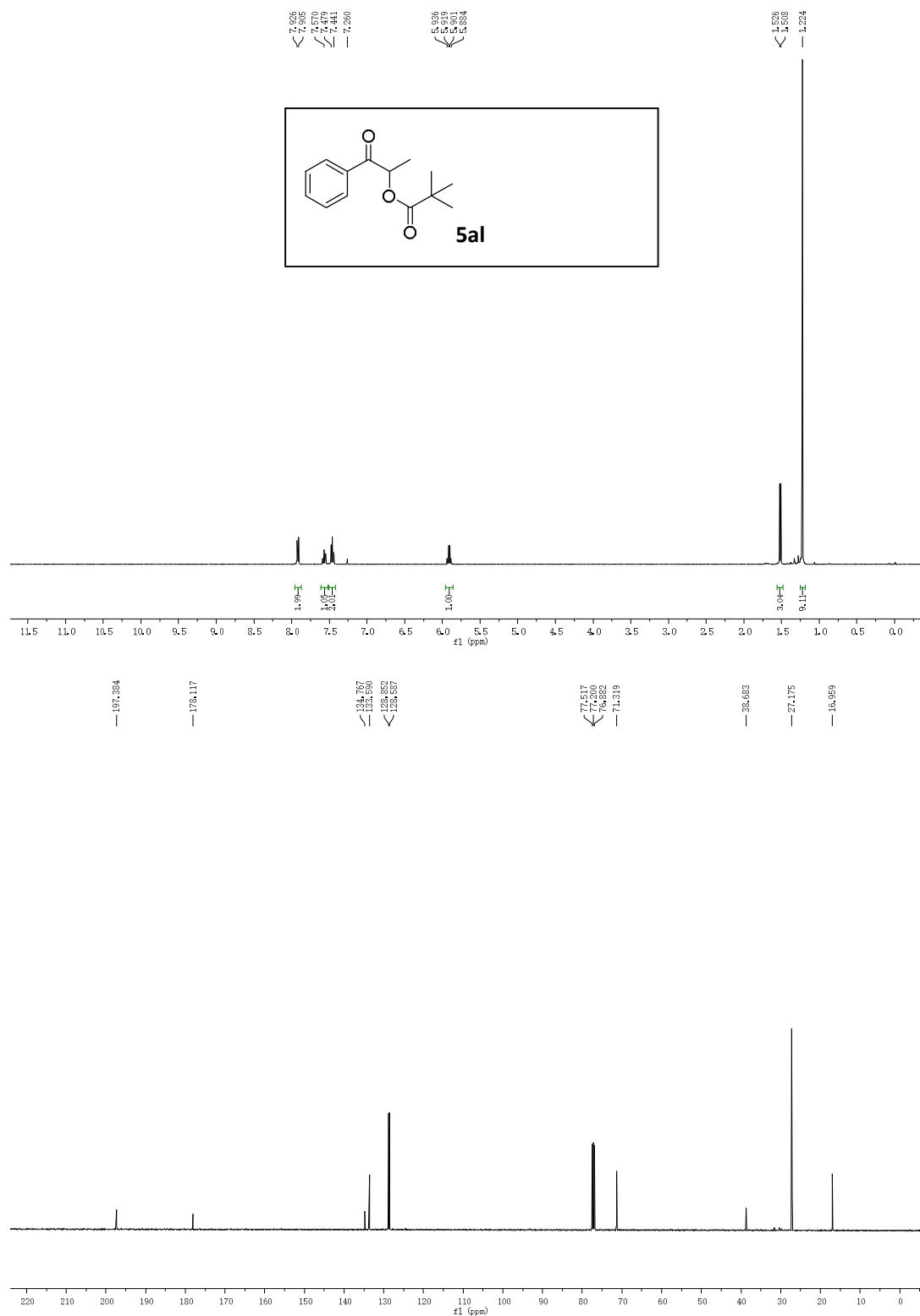


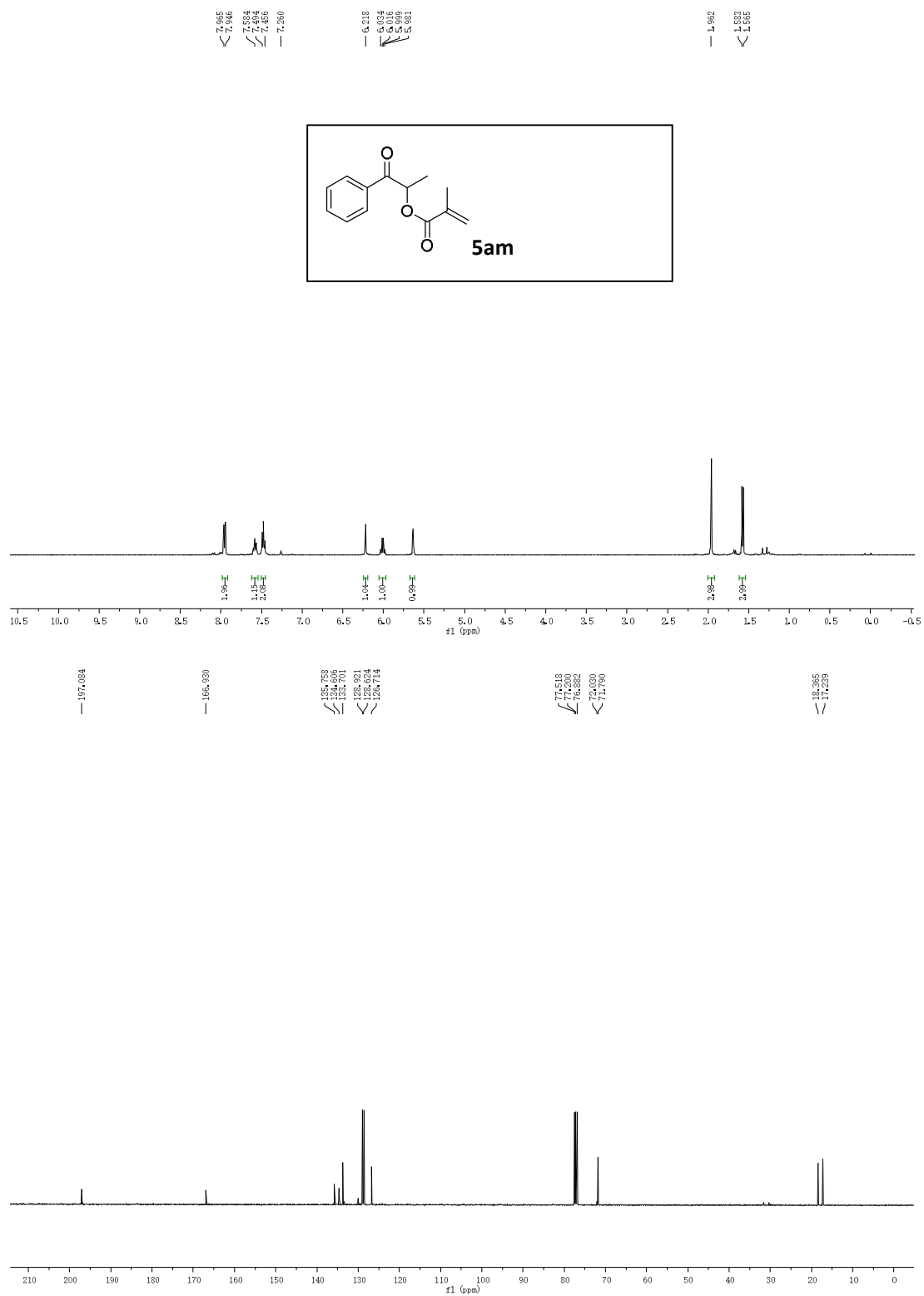


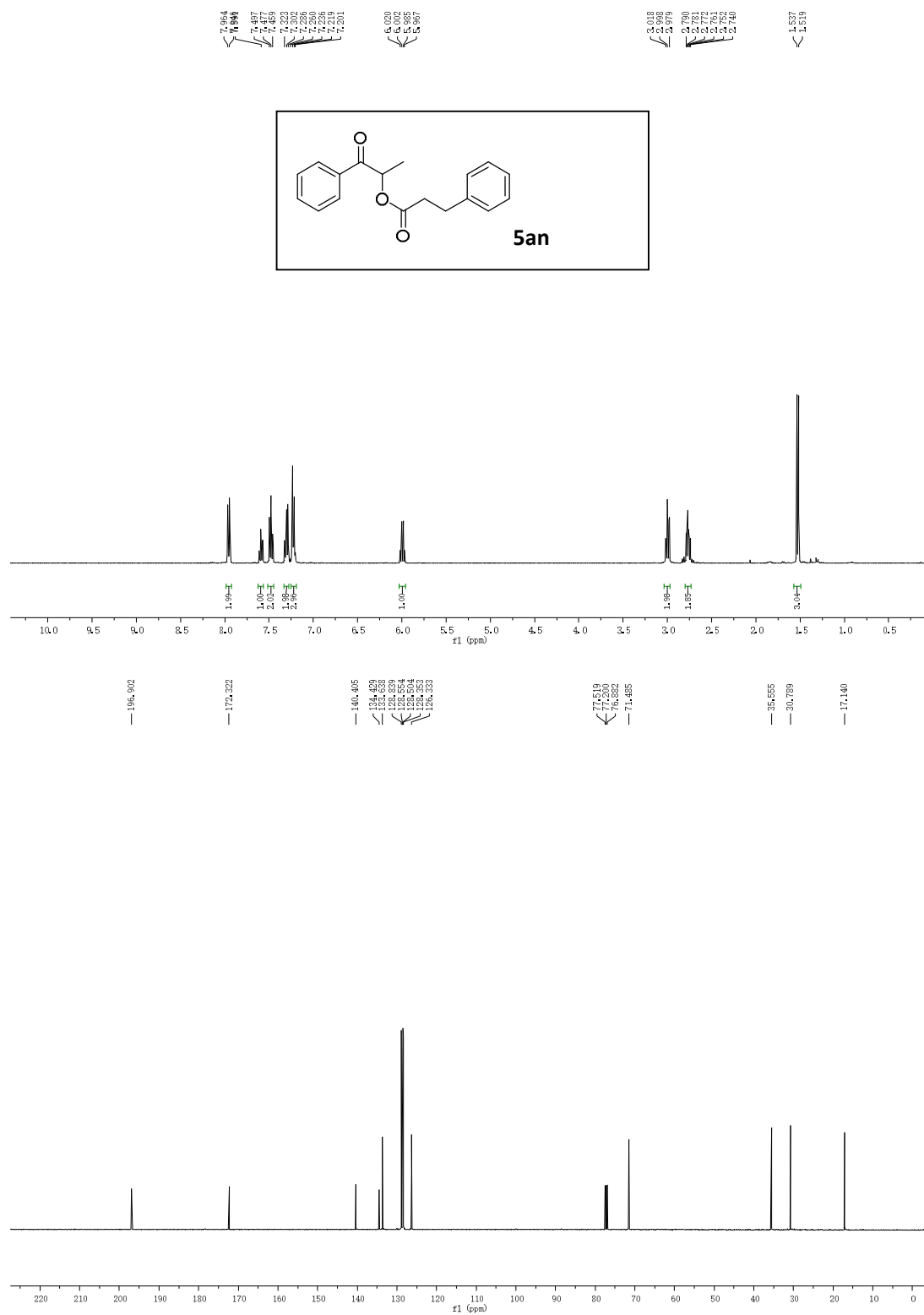












7 NMR Spectra of product 3ba-3ma



