Electronic Supplementary Material (ESI) for RSC Advances.


# $I_2$/TBHP-Mediated Oxidative Coupling of Ketones and Toluene Derivatives: A Facile Method for the Preparation of α-Benzoyloxy Ketones

Cui Chen*[, a], Weibing Liu[a], Peng Zhou[a], and Hailing Liu[b, *]

[a] College of Chemical Engineering, Guangdong University of Petrochemical Technology, 2 Guandu Road, Maoming 525000, P. R. China

Email address: cc161002@gdupt.edu.cn

[b] College Analytical & Testing Centre, Beijing Normal University, No. 19 Xinjiekouwai St., Haidian District, Beijing 100875, People's Republic of China.

E-mail: liuhailing@bnu.edu.cn

*1-Oxo-1-phenylethyl benzoate (Scheme 1, 3aa)*[1]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.58 (q, *J* = 7.6 Hz, 2H), 7.48 (m, 4H), 5.59 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 192.1, 166.0, 134.3, 133.9, 133.3, 129.9, 129.4, 128.4, 127.8, 66.4.

*1-Oxo-1-(4-methylphenyl)ethyl benzoate (Scheme 1, 3ab)*[2]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.27 (m, 5H), 5.44 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 198.4, 166.8, 143.9, 134.3, 130.0, 129.5, 129.2, 129.1, 128.2, 127.9, 66.2, 21.6.

*1-Oxo-1-(4-chlorophenyl)ethyl benzoate (Scheme 1, 3ac)*[3]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.46 (m, 5H), 5.54 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 190.6, 165.1, 140.0, 132.5, 131.3, 129.9, 129.3, 129.2, 128.8, 128.5, 66.4.

*1-Oxo-1-(2-methylphenyl)ethyl benzoate (Scheme 1, 3ad)*[4]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.50 (m, 5H), 7.31 (m, 2H), 5.43 (s, 2H), 2.55 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 195.8, 165.7, 139.1, 133.3, 132.2, 132.1, 129.9, 129.4, 128.4, 128.1, 125.8, 122.1, 67.7, 21.8.

*1-Oxo-1-(4-fluorophenyl)ethyl benzoate (Scheme 1, 3ae)*[2]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.15 (m, 2H), 8.01 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.18 (m, 4H), 5.54 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 190.5, 167.7, 165.0, 164.5, 133.4, 132.6, 132.5, 130.6, 130.4, 129.9, 128.4, 116.3, 116.0, 115.8, 115.3, 66.3.

*1-Oxo-1-(3-fluorophenyl)ethyl benzoate (Scheme 1, 3af)*

Pale yellow crystals;; m.p. 91–93 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, *J* = 7.2 Hz, 1H), 7.91 (m, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.44 (m, 3H), 7.29 (m, 2H), 5.54 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 200.3, 164.3, 133.4, 130.7, 130.6, 130.2, 130.1, 129.9, 128.4, 125.7, 123.5, 121.2, 120.9, 120.7, 120.4, 117.0, 114.8, 66.6; HR-MS (ESI): calcd for $C_{15}H_{12}FO_3$: [M+H$^+$] 259.0765, found 259.0752.

*1-Oxo-1-(3-methylphenyl)ethyl benzoate (Scheme 1, 3ag)*

CAS: 587887-43-2; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.15 (d, *J* = 7.2 Hz, 1H), 7.97 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.42 (m, 5H), 5.57 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 192.2, 166.0, 128.7, 134.6, 133.3, 130.5, 130.0, 128.4, 128.3, 127.1, 125.0, 66.5, 21.3; HR-MS

(ESI): calcd for $C_{16}H_{15}O_3$: [M+H$^+$] 255.1015, found 255.1007.

*1-Oxo-1-(4-nitrophenyl)ethyl benzoate (Scheme 1, 3ah)*[5]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.26 (m, 4H), 7.42 (m, 4H), 5.41 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 202.1, 164.5, 150.6, 135.5, 135.2, 130.8, 128.7, 128.6, 128.4, 123.5, 67.6.

*2-(furan-2-yl)-2-oxoethyl benzoate (Scheme 1, 3ai)*[9]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 7.28 (m, 1H), 6.58 (m, 3H), 5.39 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 181.2, 157.8, 146.8, 146.7, 119.1, 117.9, 117.7, 112.5, 112.5, 112.0, 65.5.

*2-oxo-2-(thiophen-2-yl)ethyl benzoate (Scheme 1, 3aj)*

CAS: 326886-39-9; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.14 (dd, *J* = 1.5 Hz, *J* = 7.2 Hz, 2H), 7.83 (dd, *J* = 1.2 Hz, *J* = 7.2 Hz, 1H), 7.72 (dd, *J* = 1.2 Hz, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.19 (dd, *J* = 1.2 Hz, J = 7.2 Hz, 1H), 5.46 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 185.4, 165.9, 140.4, 134.3, 133.4, 132.0, 130.0, 129.2, 128.4, 128.3, 66.2; HR-MS (ESI): calcd for $C_{13}H_{11}O_3S$: [M+H$^+$] 247.0423, found 247.0438.

*2-cyclopropyl-2-oxoethyl benzoate (Scheme 1, 3ak)*[1]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 5.06 (s, 2H), 2.05 (m, 1H), 1.18 (m, 2H), 1.01 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 203.8, 166.1, 133.3, 129.9, 129.3, 128.4, 68.8, 17.2, 11.4.

*1-(4-fluorophenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3al)*[7]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m, 4H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 6.14 (q, *J* = 6.9 Hz, 1H), 1.68 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 195.2, 197.8, 166.0, 164.0, 133.4, 131.3, 131.1, 129.8, 129.3, 128.4, 116.1, 115.8, 115.5, 71.7, 17.1.

*1-(4-chlorophenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3am)*[7]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.35 (m, 5H), 5.11 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 201.2, 171.0, 140.9, 140.5, 131.5, 130.5, 129.2, 128.5, 127.6, 127.0, 69.3, 22.1 .

*1-(4-chlorophenyl)-1-oxobutan-2-yl benzoate (Scheme 1, 3an)*

Colorless crystals; m.p. 114–116 °C; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.45 (m, 4H), 5.97 (q, *J* = 7.2 Hz, 1H), 2.06 (m, 2H), 1.12 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 195.4, 166.2, 140.5, 133.4, 133.2, 129.8, 129.4, 129.1,

128.6, 128.4, 76.6, 26.2, 9.95; HR-MS (ESI): calcd for $C_{17}H_{16}ClO_3$: [M+H$^+$] 303.0782, found 303.0791.

*1-(4-methoxyphenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3ao)*[7]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.17 (q, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 1.65 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 195.1, 166.0, 163.9, 133.2, 130.9, 129.8, 129.6, 128.4, 127.3, 114.0, 71.6, 55.5, 17.4.

*1-oxo-1-(thiophen-2-yl)propan-2-yl benzoate (Scheme 1, 3ap)*[2]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 5.97 (q, *J* = 6.9 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 189.6, 165.9, 140.5, 134.4, 133.3, 132.7, 129.9, 129.4, 128.4, 128.2, 72.9, 17.6.

*1-Oxo-1-phenylethyl 4-methylbenzoate (Scheme 2, 3ba)*[2]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 5.56 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 192.3, 166.1, 144.1, 133.8, 130.0, 129.1, 128.9, 128.8, 128.4, 127.8, 66.3, 21.7.

*1-Oxo-1-phenylethyl 4-fluorobenzoate (Scheme 2, 3ca)*

CAS: 55153-22-5; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.48 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 5.59 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 192.1, 167.5, 166.0, 164.0, 133.9, 133.9, 133.3, 132.5, 132.4, 130.0, 128.9, 128.4, 127.8, 115.8, 115.5, 66.4; HR-MS (ESI): calcd for $C_{15}H_{12}FO_3$: [M+H$^+$] 259.0765, found 259.0781.

*1-Oxo-1-phenylethyl 4-chlorobenzoate (Scheme 2, 3da)*[2]

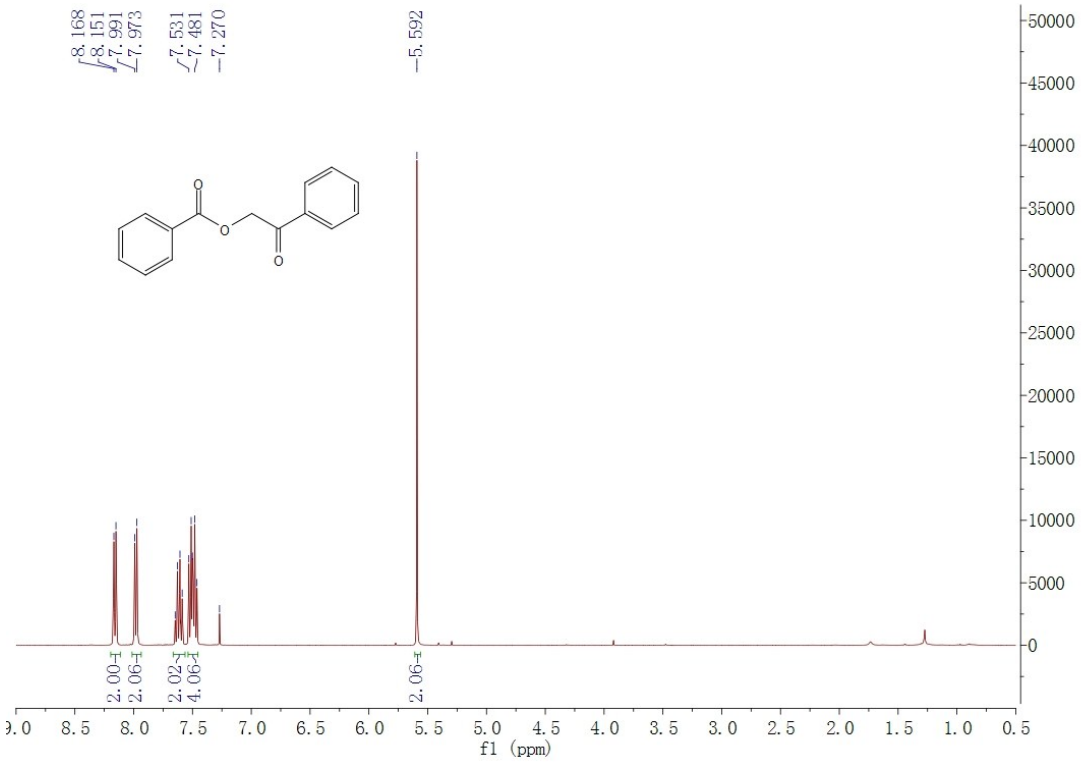
$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (m, 4H), 58 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 191.8, 165.2, 139.8, 134.2m 134.0m 131.3m 129.9m 128.9m 128.8m 127.8, 66.5.

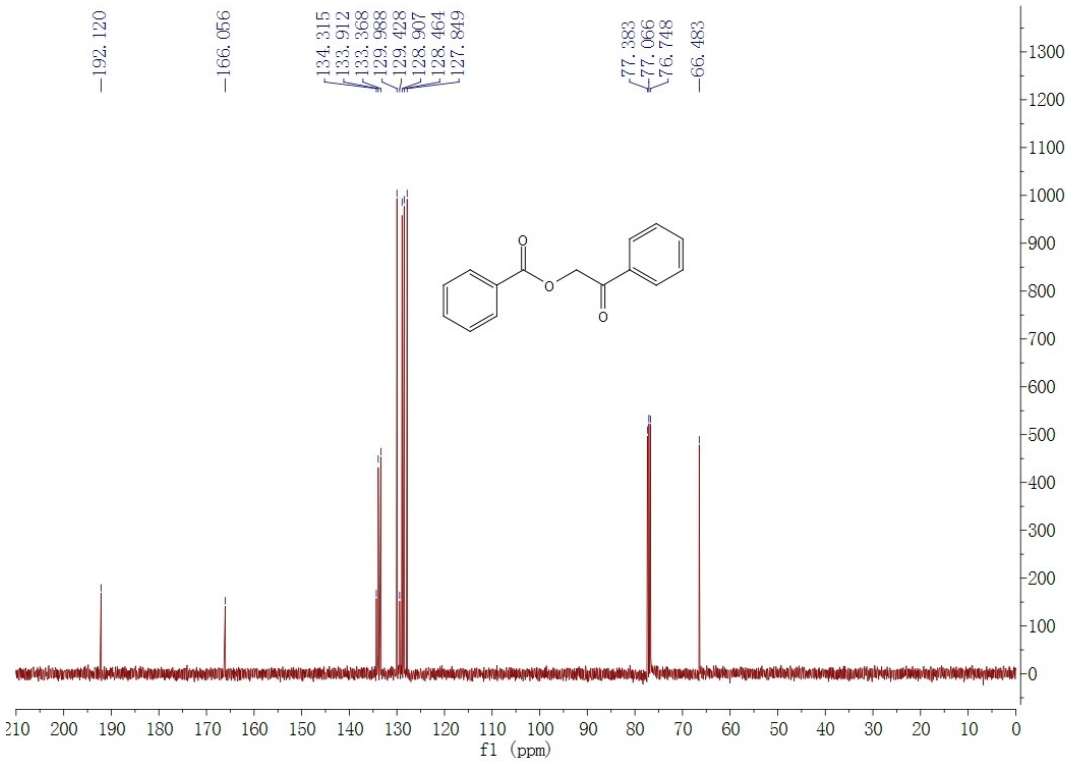
*1-Oxo-1-phenylethyl 2-naphthoate (Scheme 2, 3ea)*[2]

$^1$H NMR ($CDCl_3$, 400 MHz) δ 8.96 (d, *J* = 7.2 Hz, 1H), 8.39 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.96 (m, 3H), 7.89 (d, 1H), 7.53 (m, 5H), 5.69 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 192.3, 166.9, 133.9, 133.7, 133.3, 131.4, 130.7, 130.0, 128.9, 128.4, 127.8, 126.3, 125.8, 124.5, 66.

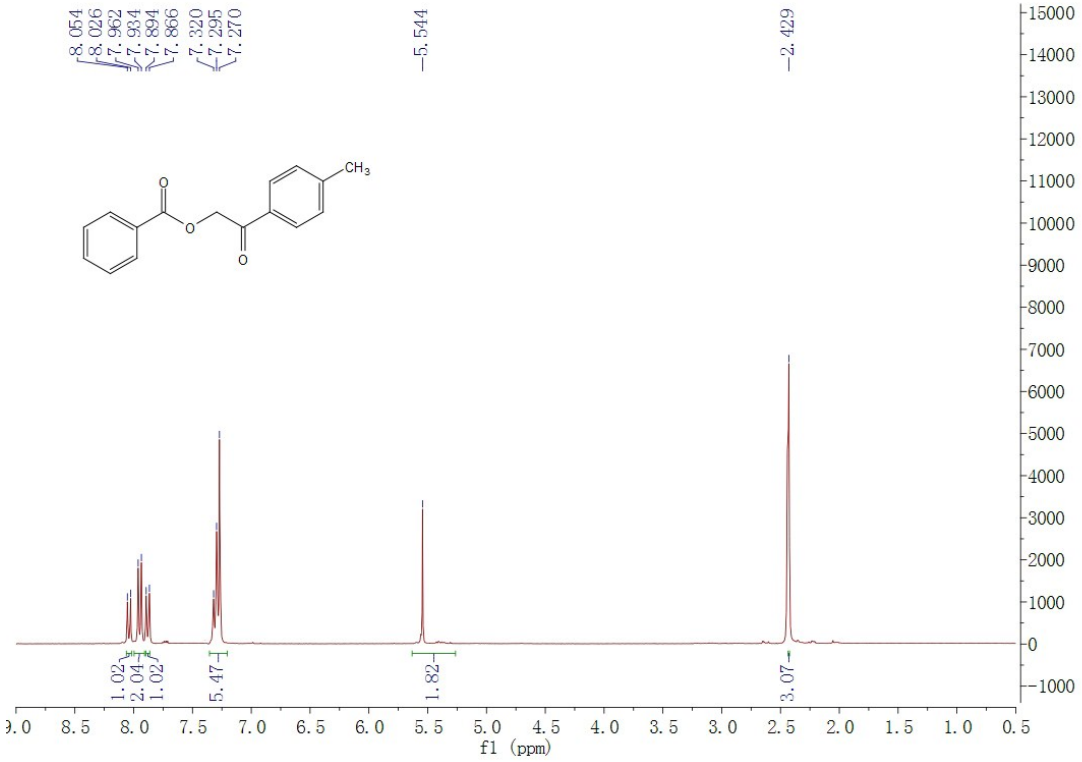
**NMR spectra**

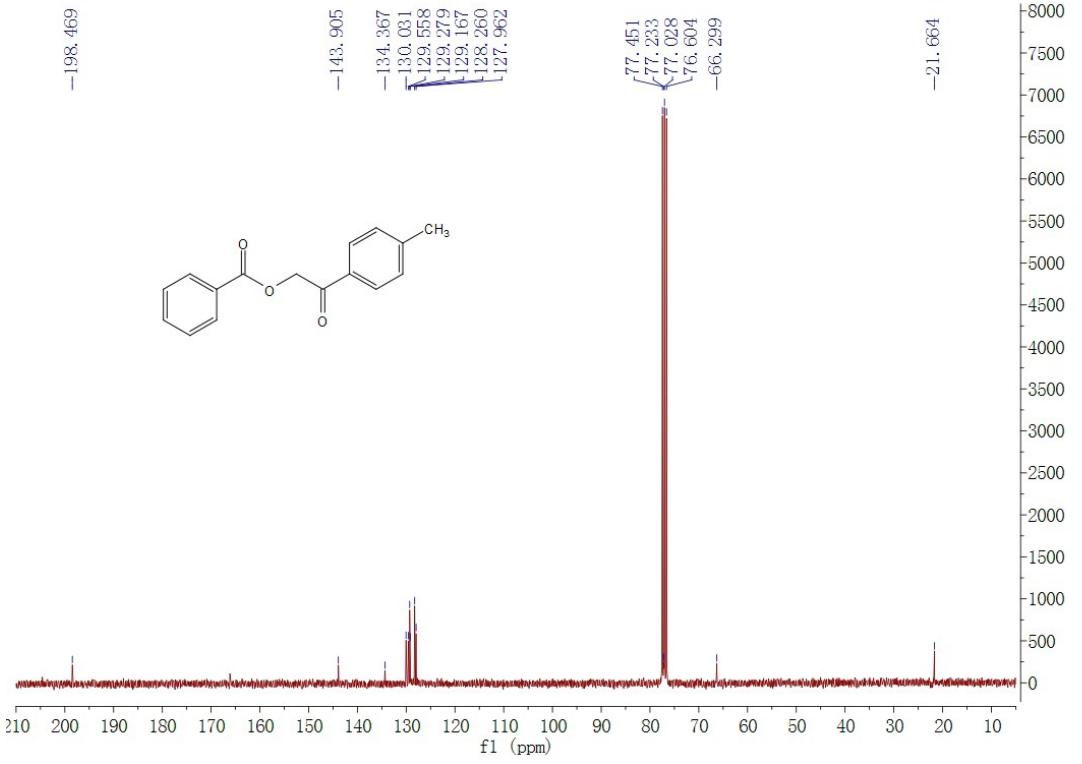
**1-Oxo-1-phenylethyl benzoate (Scheme 1, 3aa)**



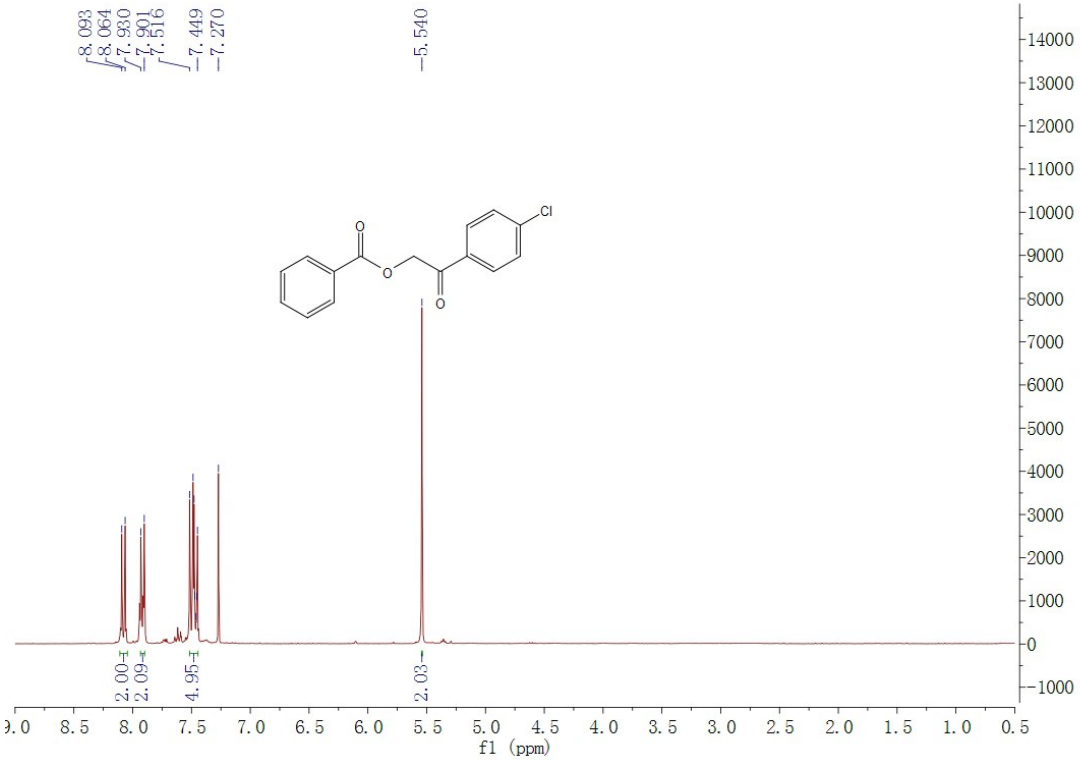



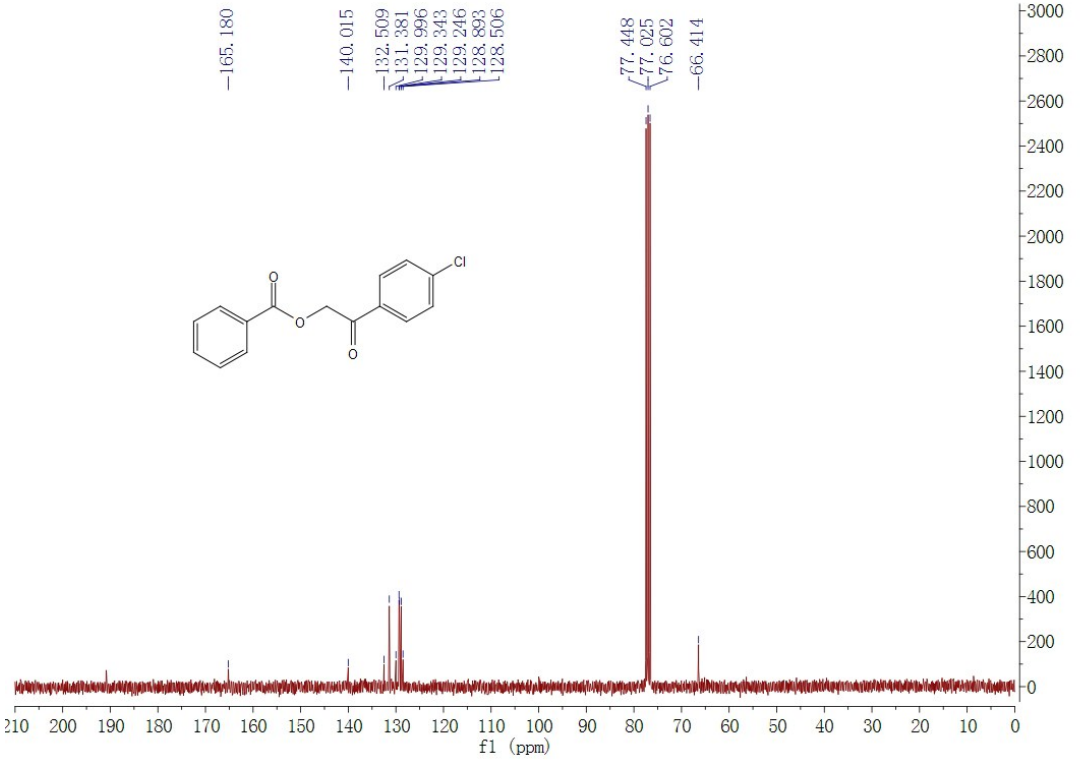
**1-Oxo-1-(4-methylphenyl)ethyl benzoate (Scheme 1, 3ab)**



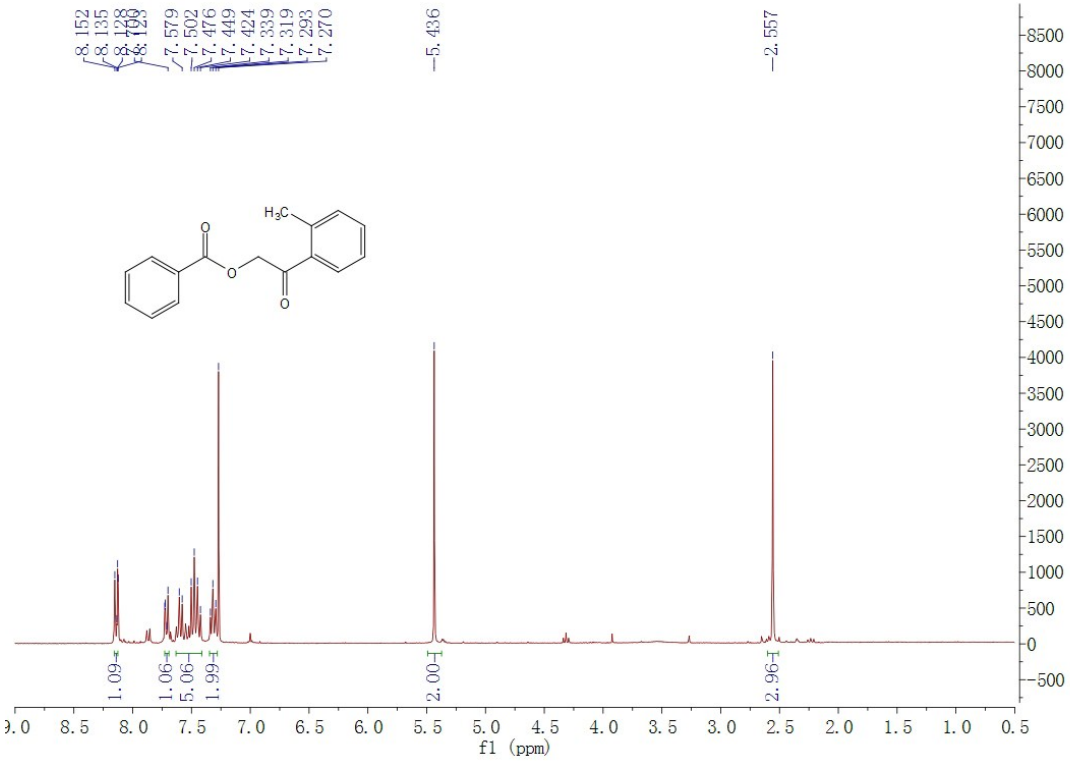



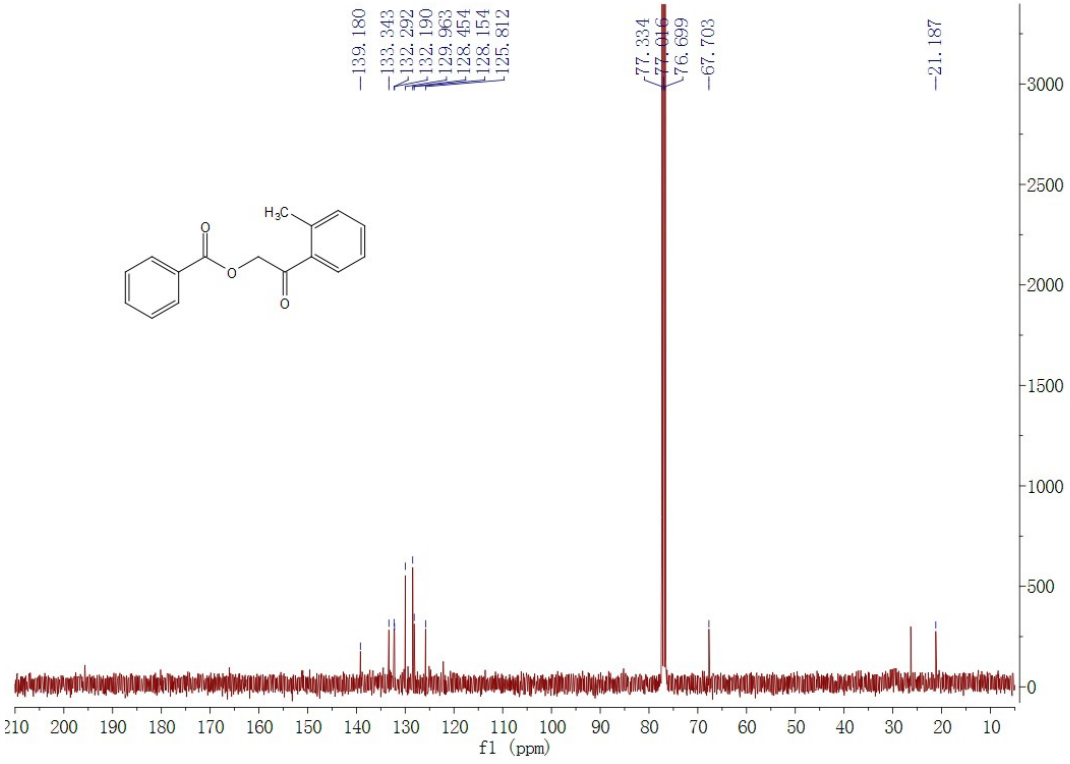
**1-Oxo-1-(4-chlorophenyl)ethyl benzoate (Scheme 1, 3ac)**



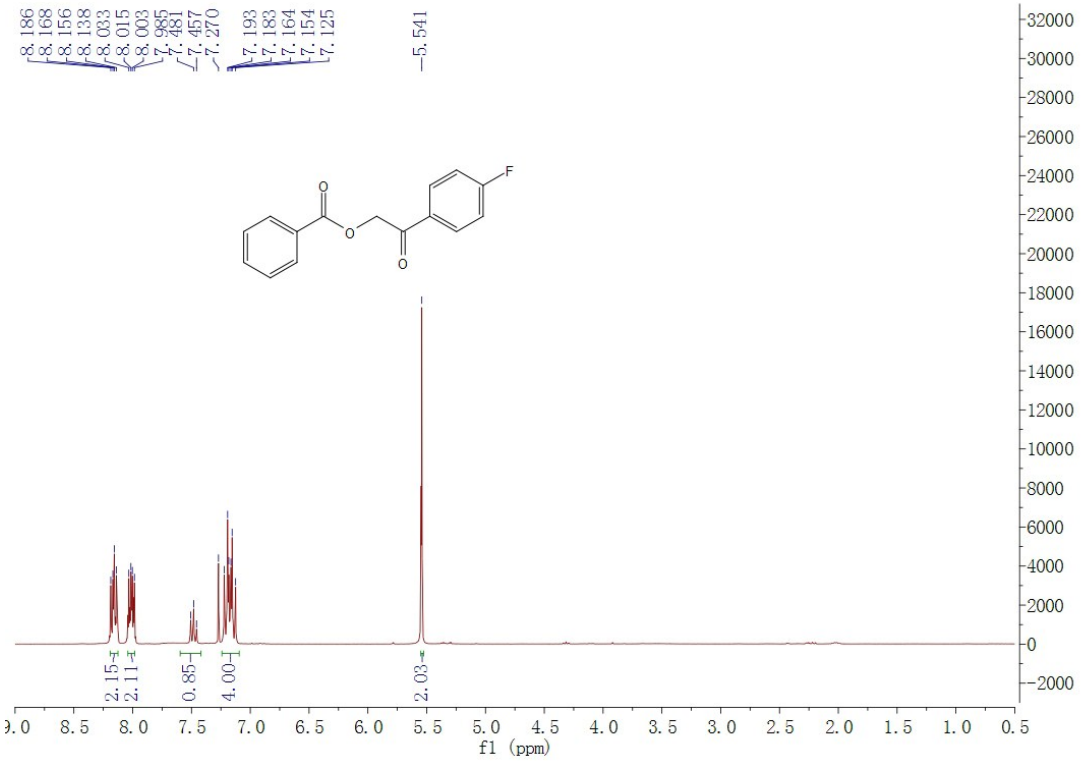



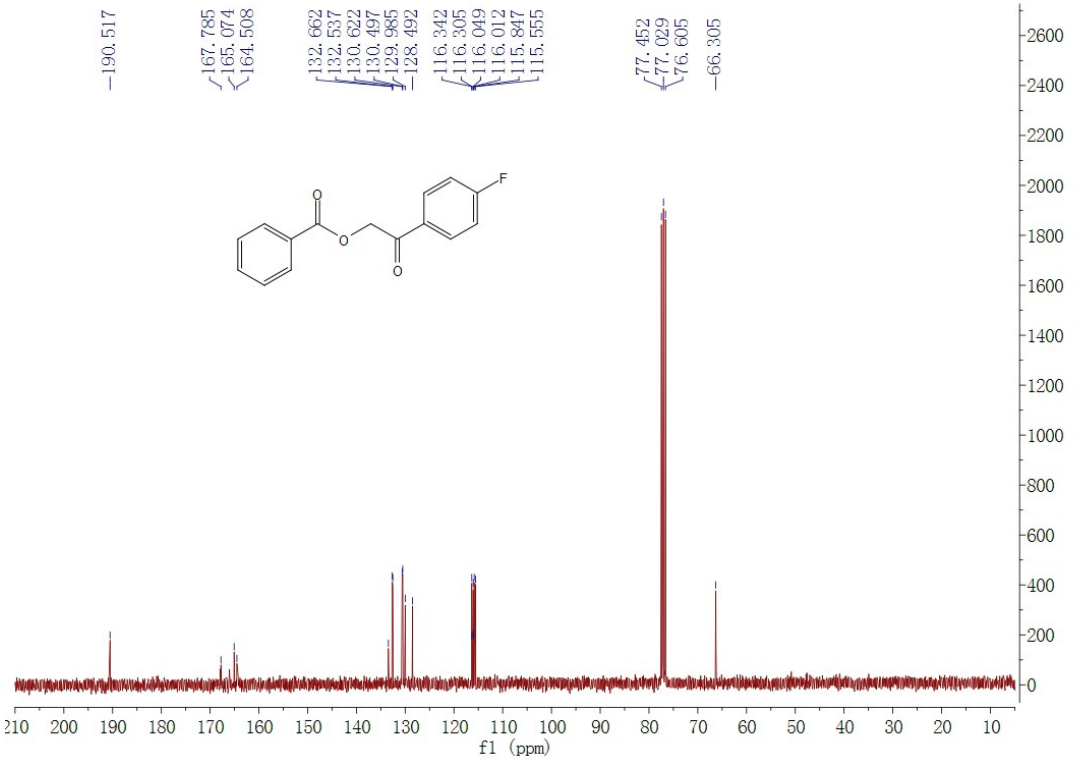
**1-Oxo-1-(2-methylphenyl)ethyl benzoate (Scheme 1, 3ad)**



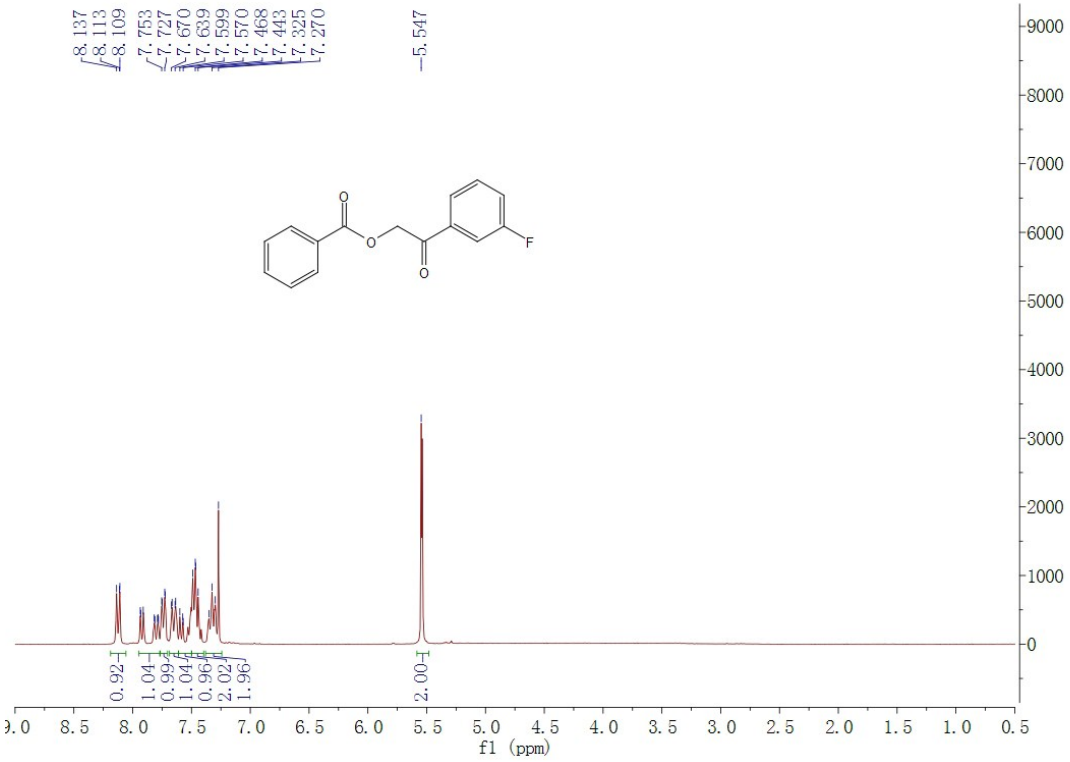



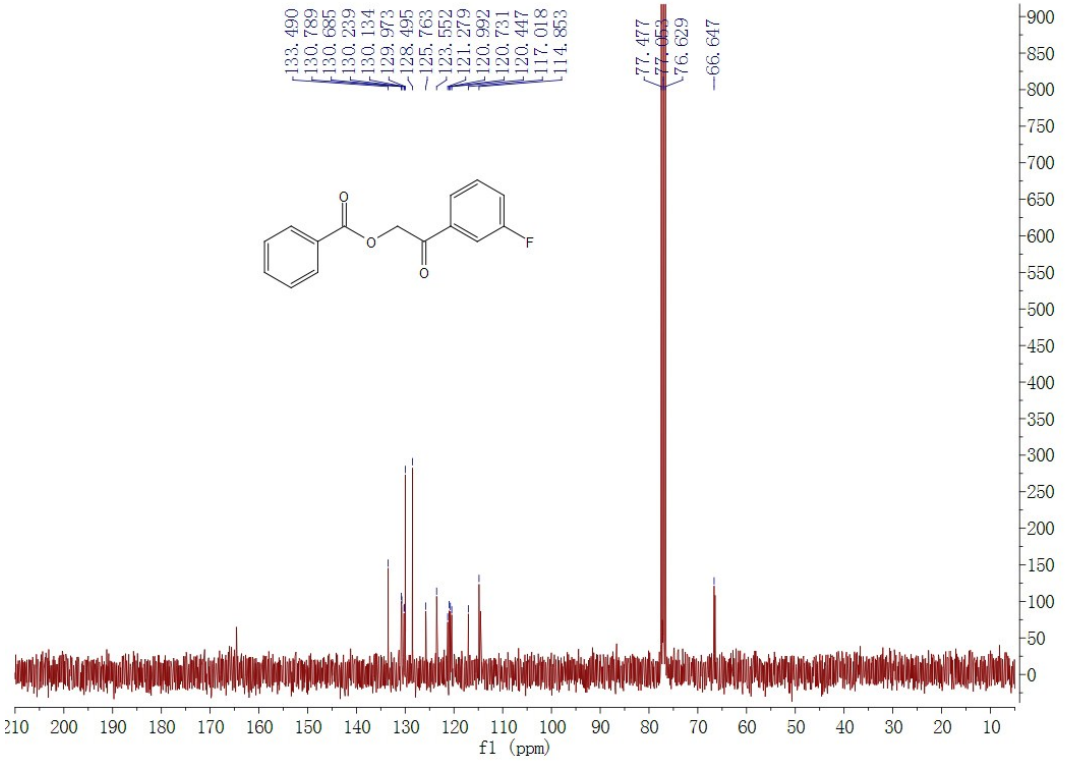
**1-Oxo-1-(4-fluorophenyl)ethyl benzoate (Scheme 1, 3ae)**



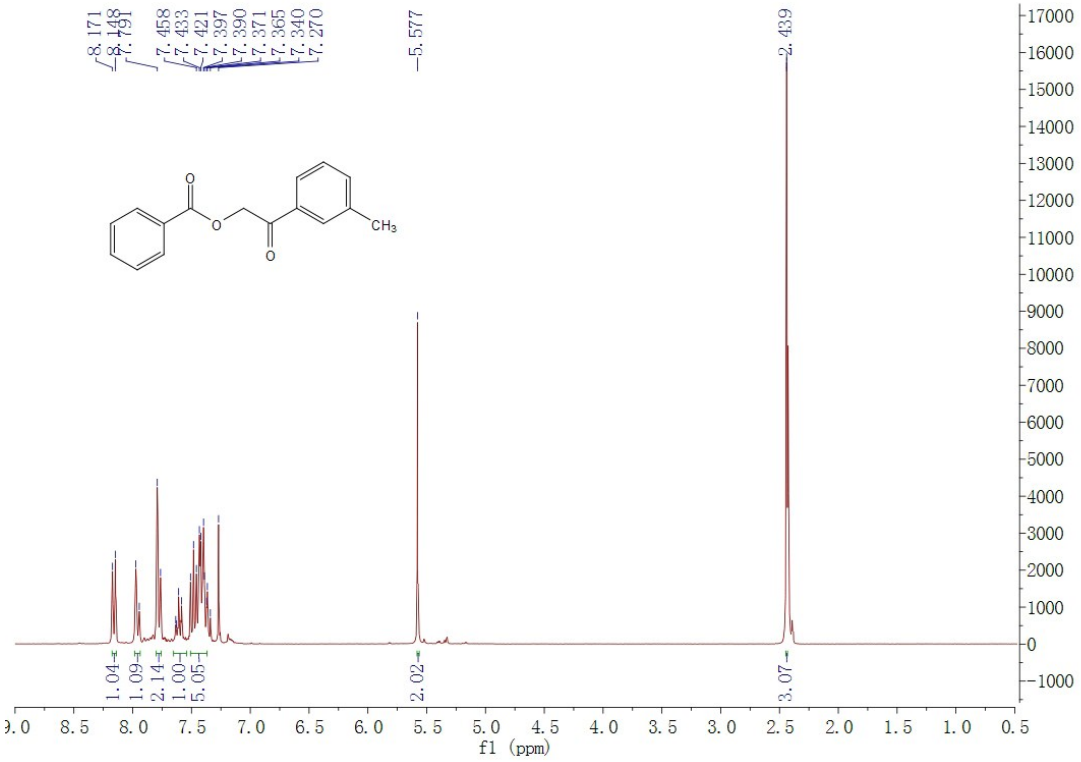



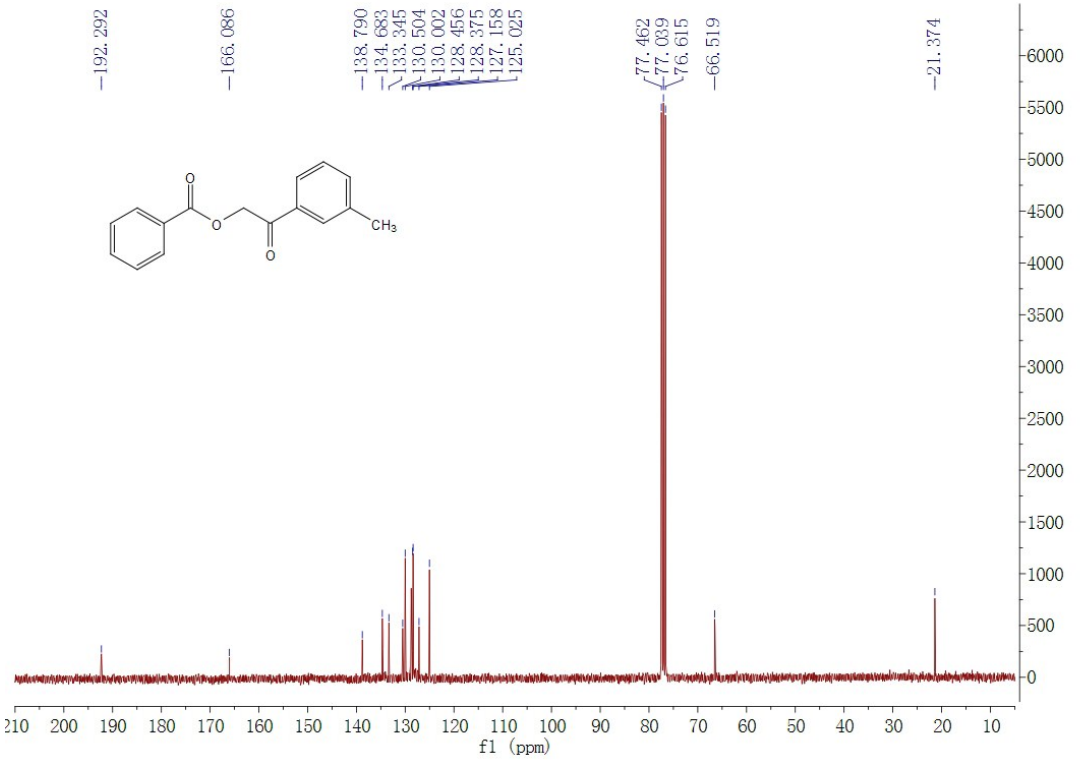
**1-Oxo-1-(3-fluorophenyl)ethyl benzoate (Scheme 1, 3af)**



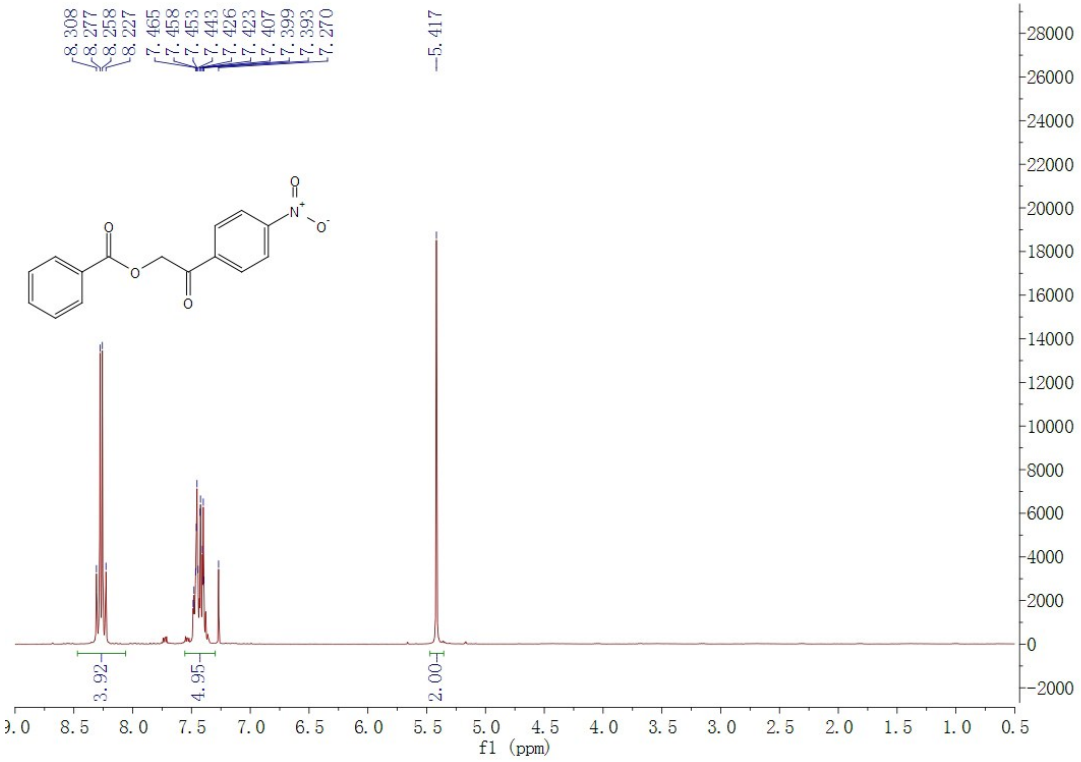



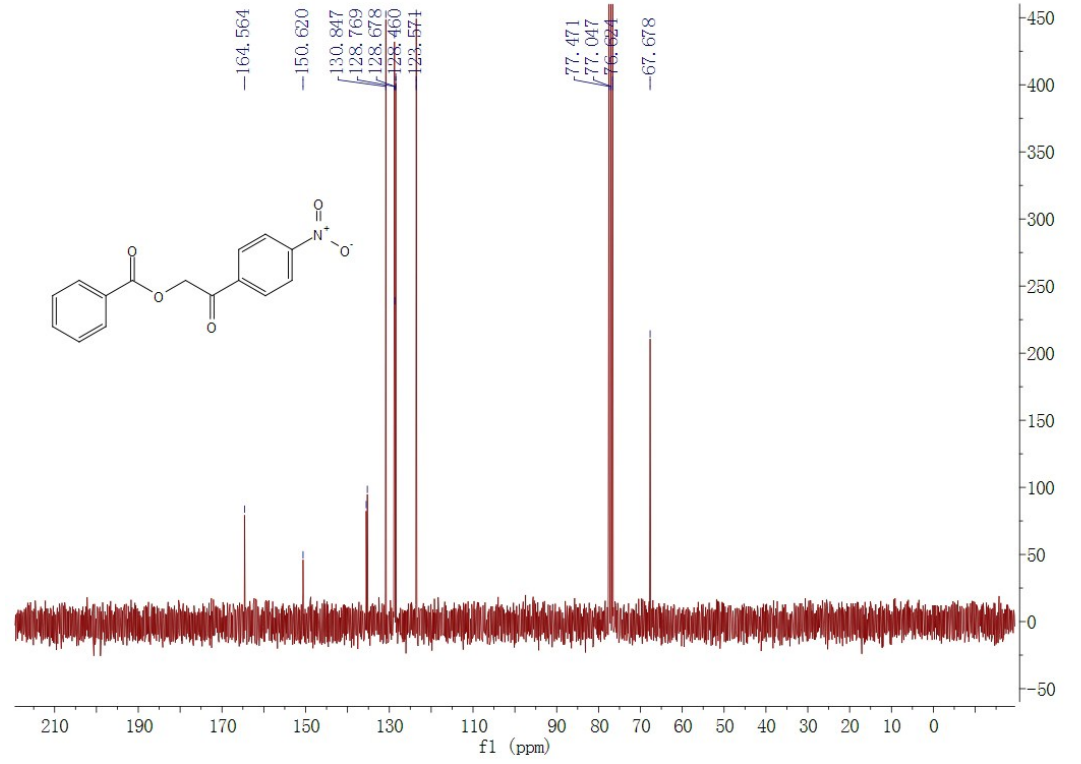
**1-Oxo-1-(3-methylphenyl)ethyl benzoate (Scheme 1, 3ag)**



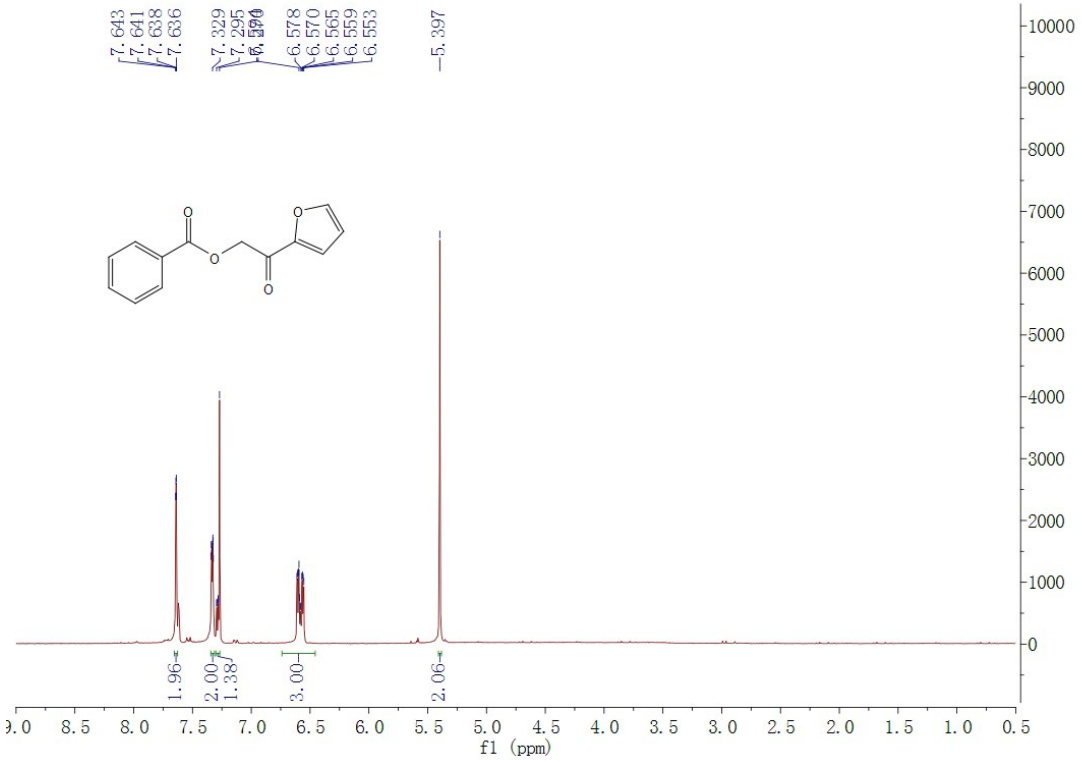



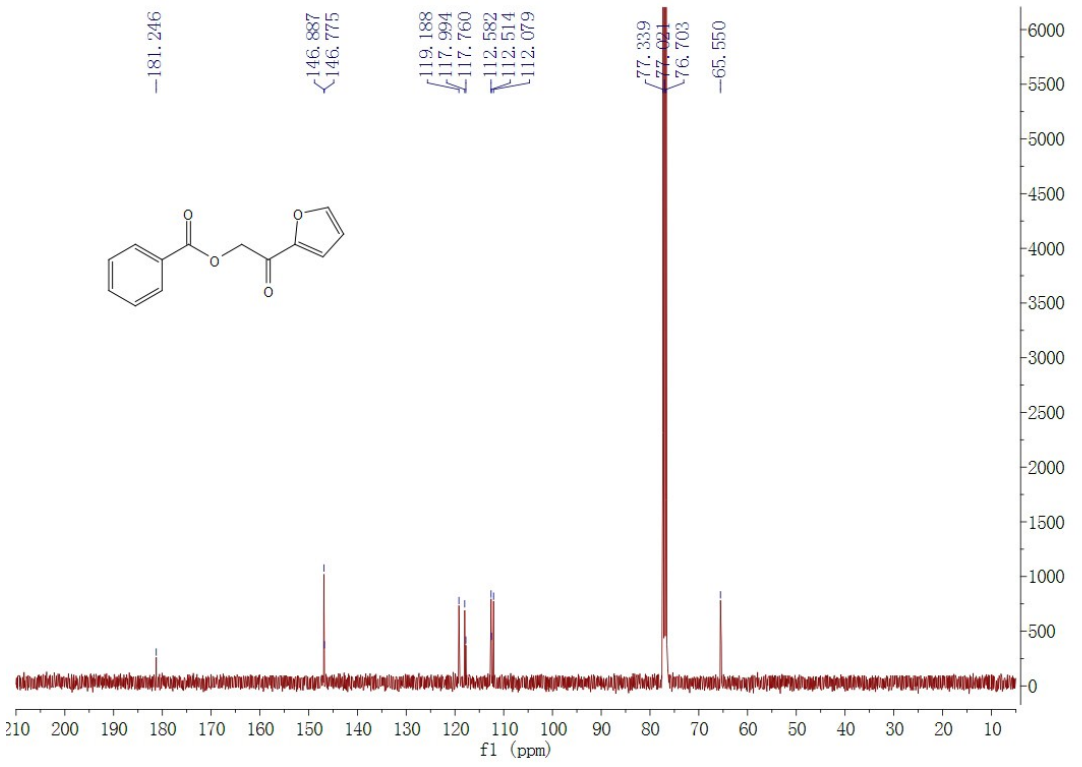
**1-Oxo-1-(4-nitrophenyl)ethyl benzoate (Scheme 1, 3ah)**



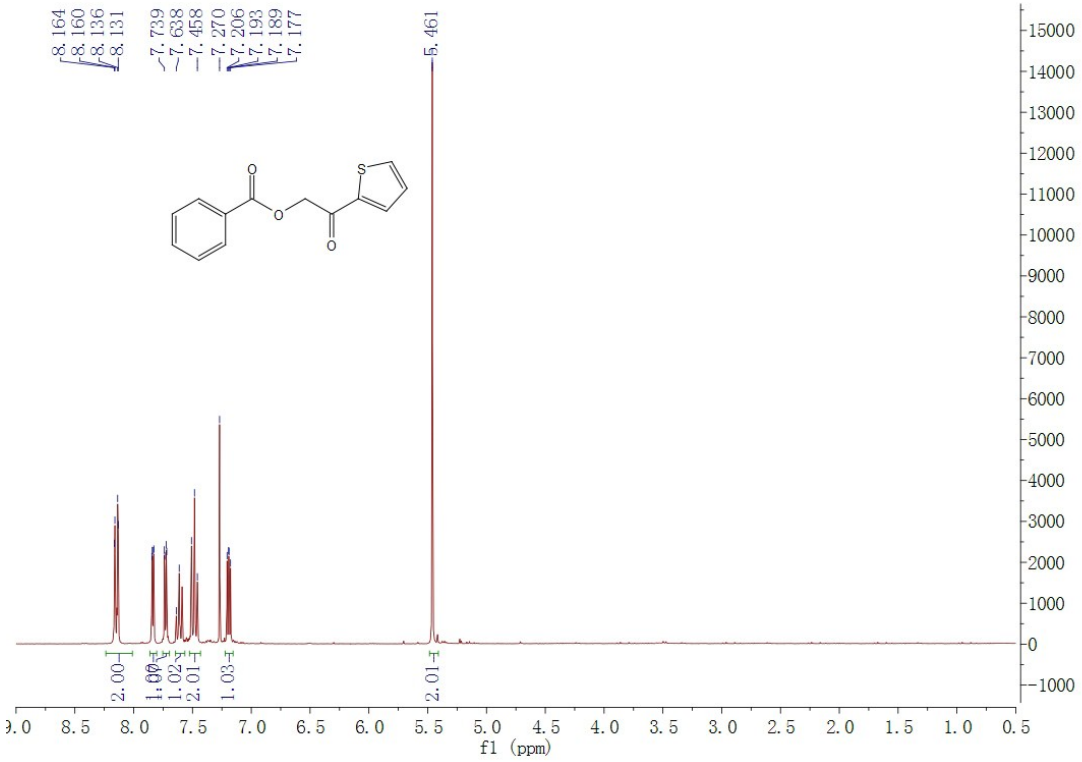



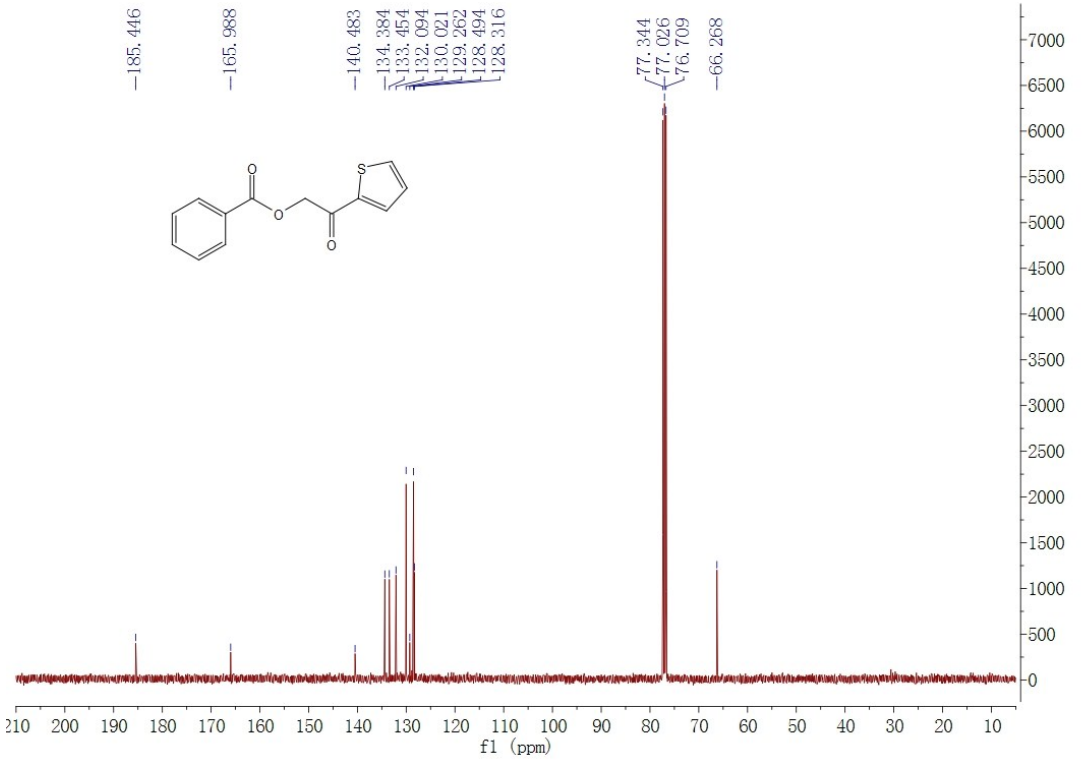
**2-(furan-2-yl)-2-oxoethyl benzoate (Scheme 1, 3ai)**



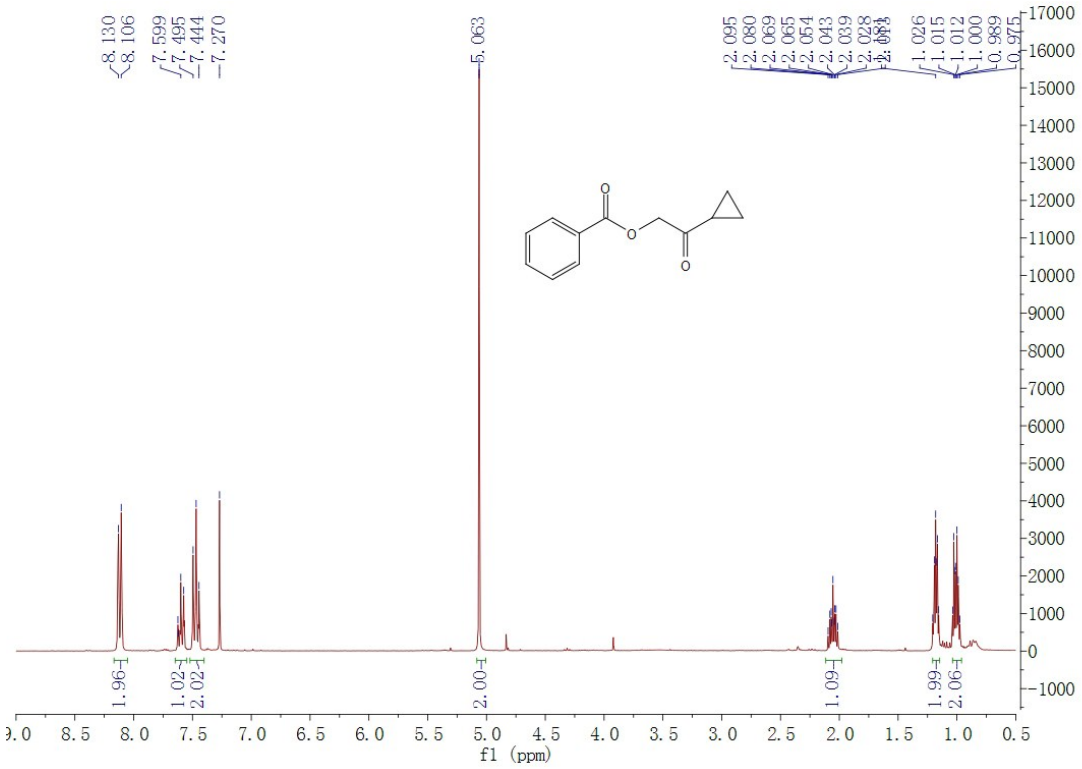



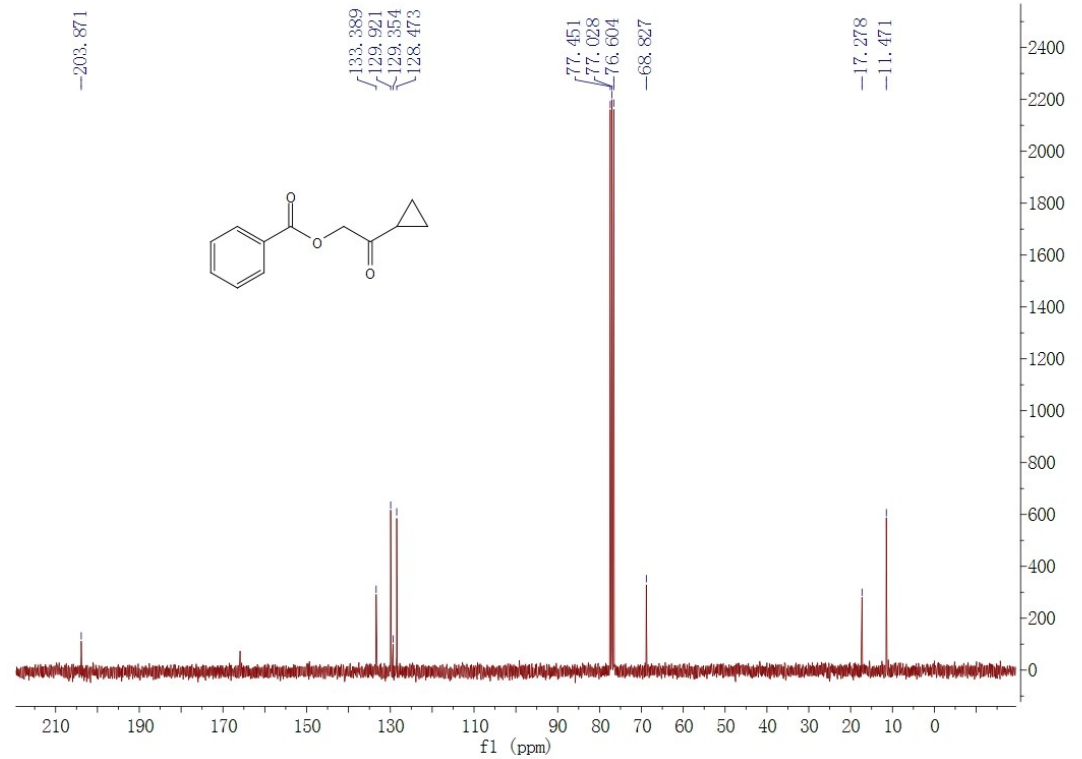
**2-oxo-2-(thiophen-2-yl)ethyl benzoate (Scheme 1, 3aj)**



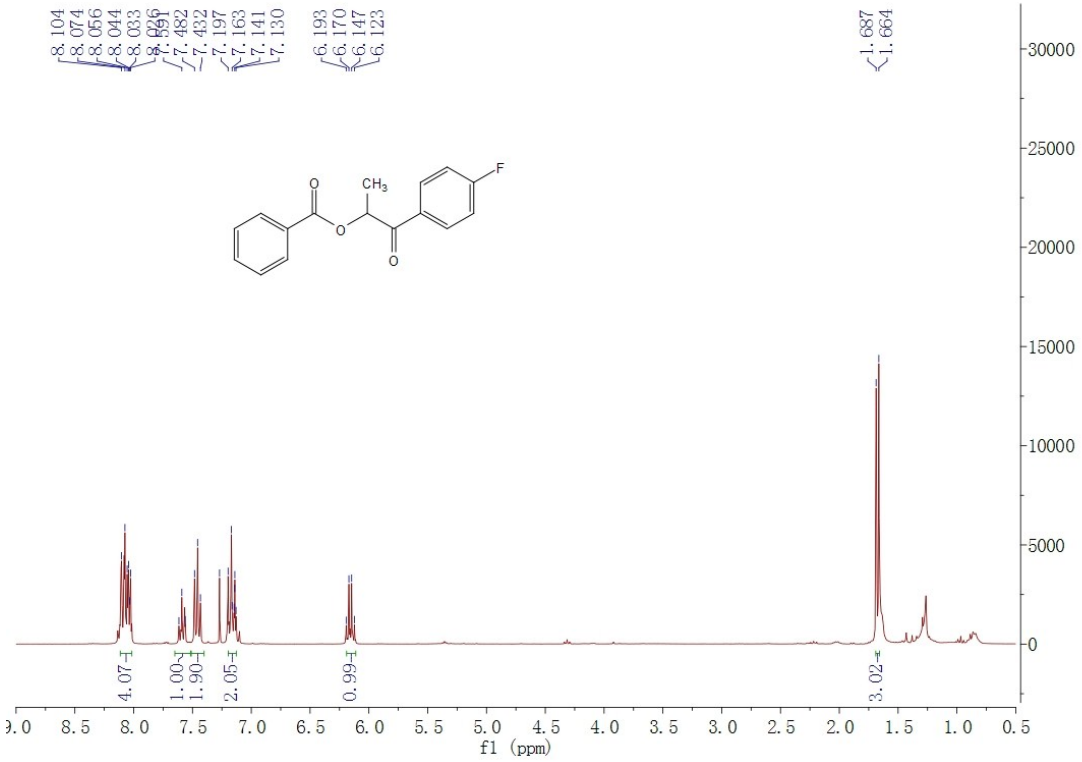



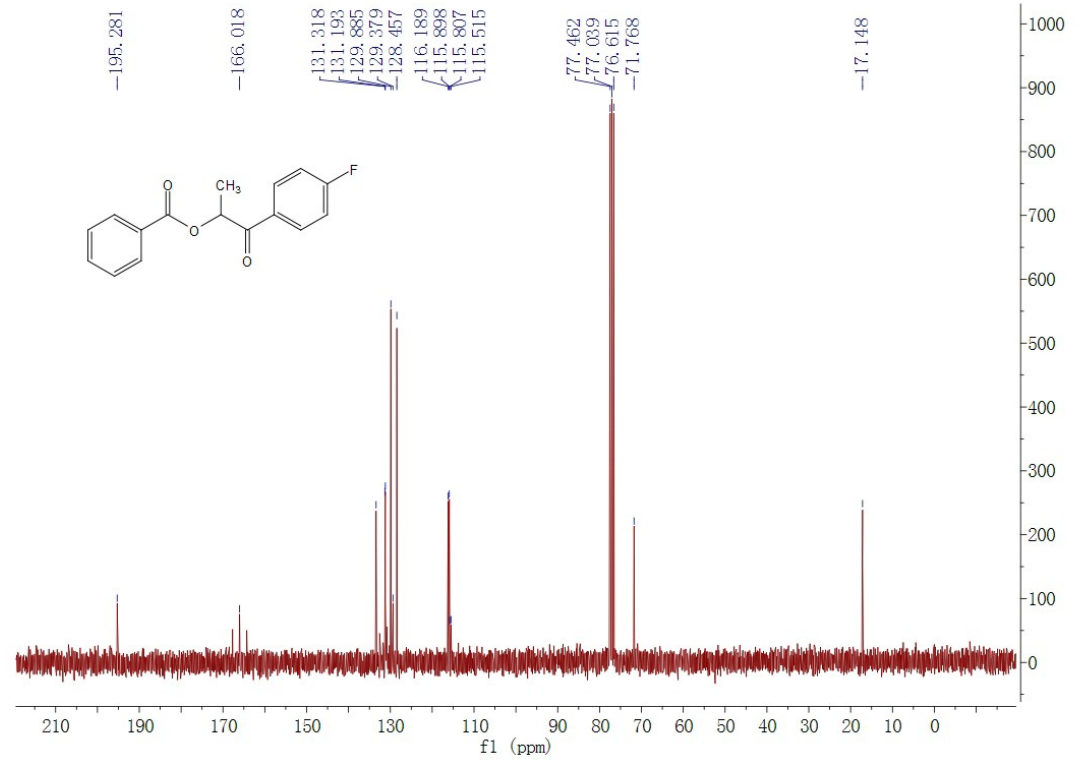
**2-cyclopropyl-2-oxoethyl benzoate (Scheme 1, 3ak)**



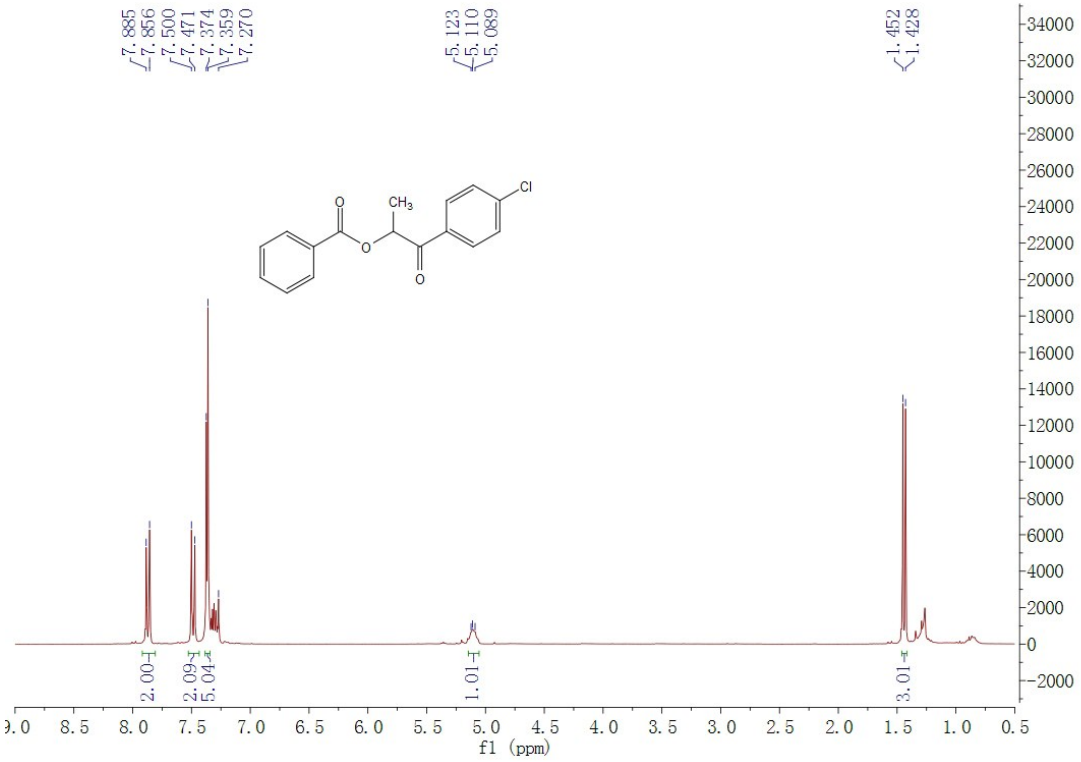



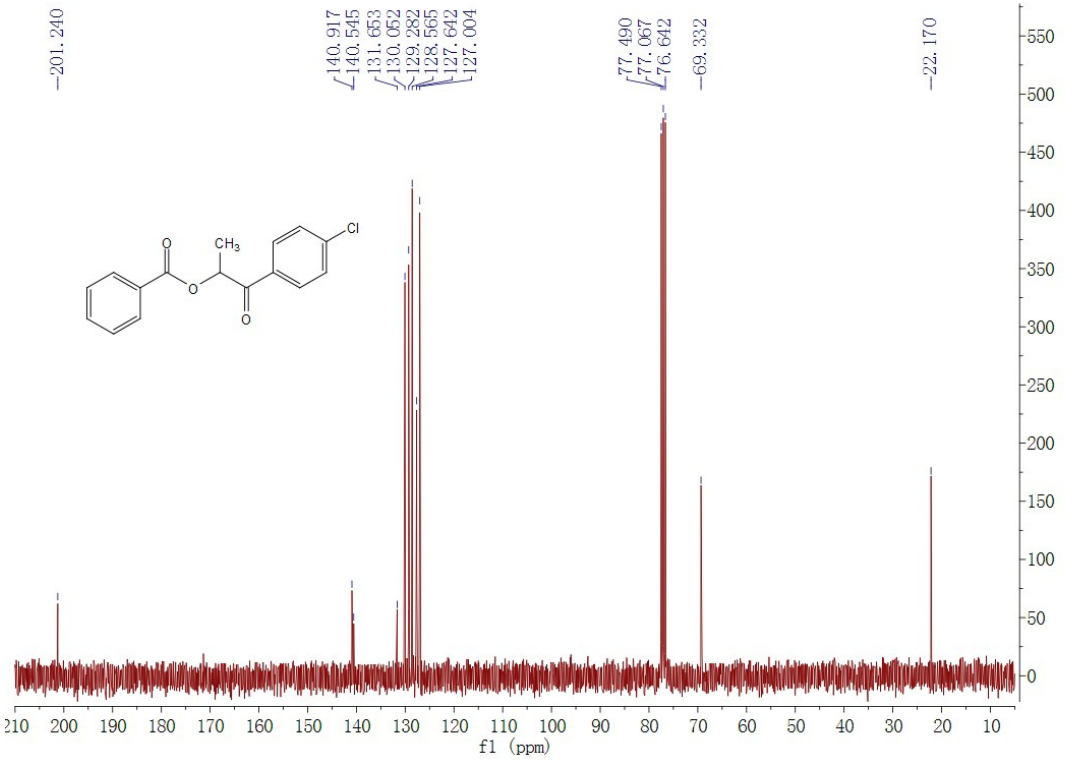
**1-(4-fluorophenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3al)**



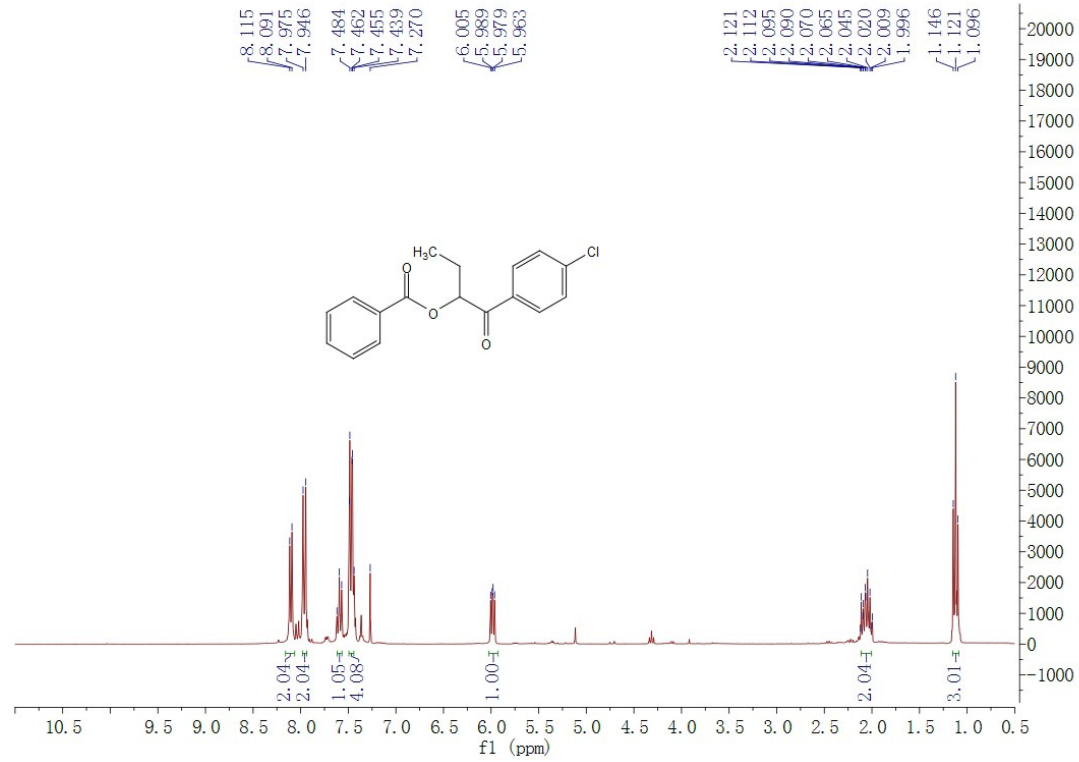



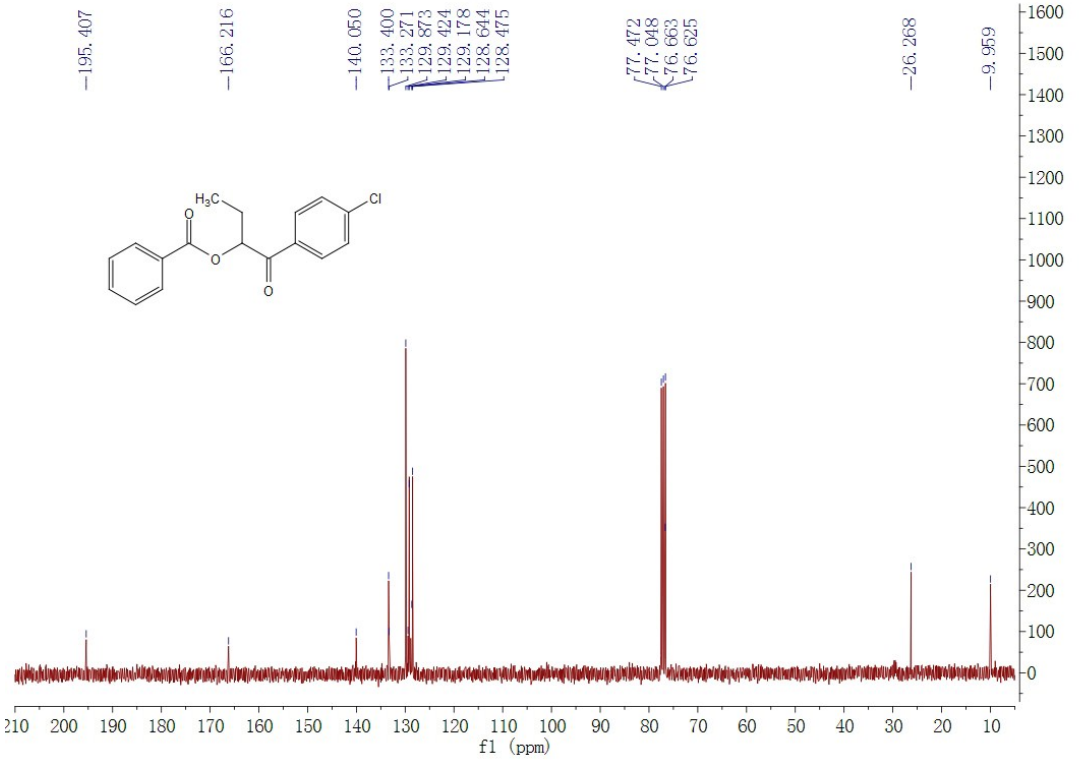
**1-(4-chlorophenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3am)**



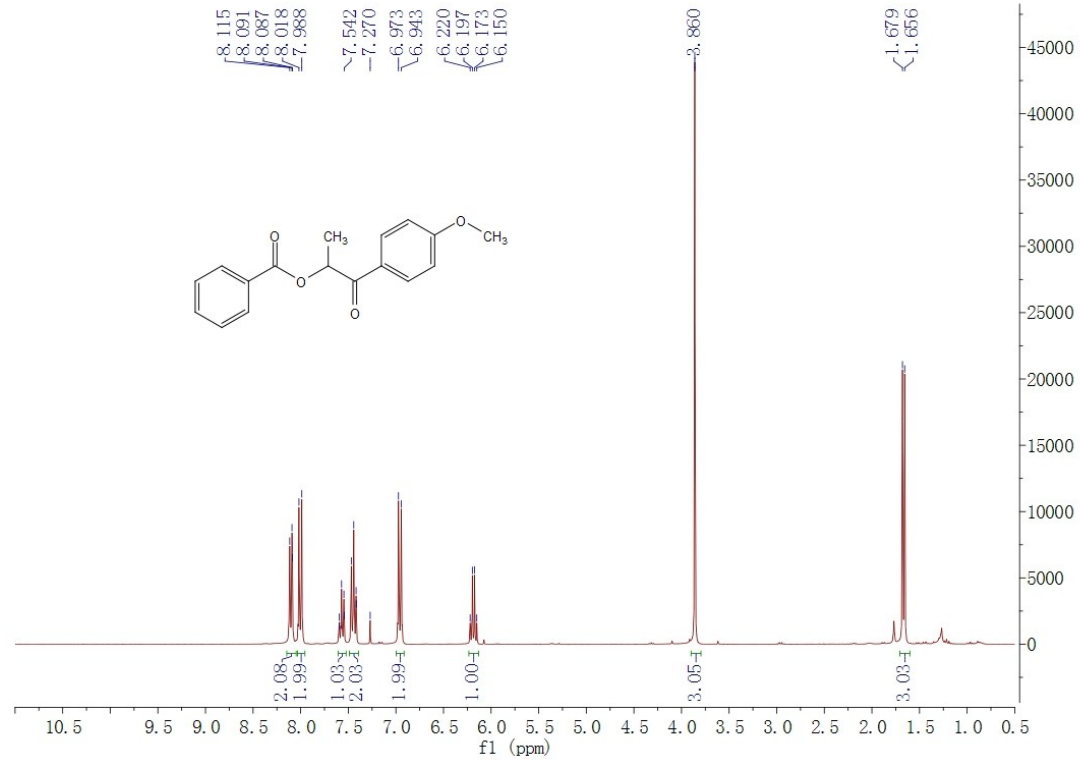



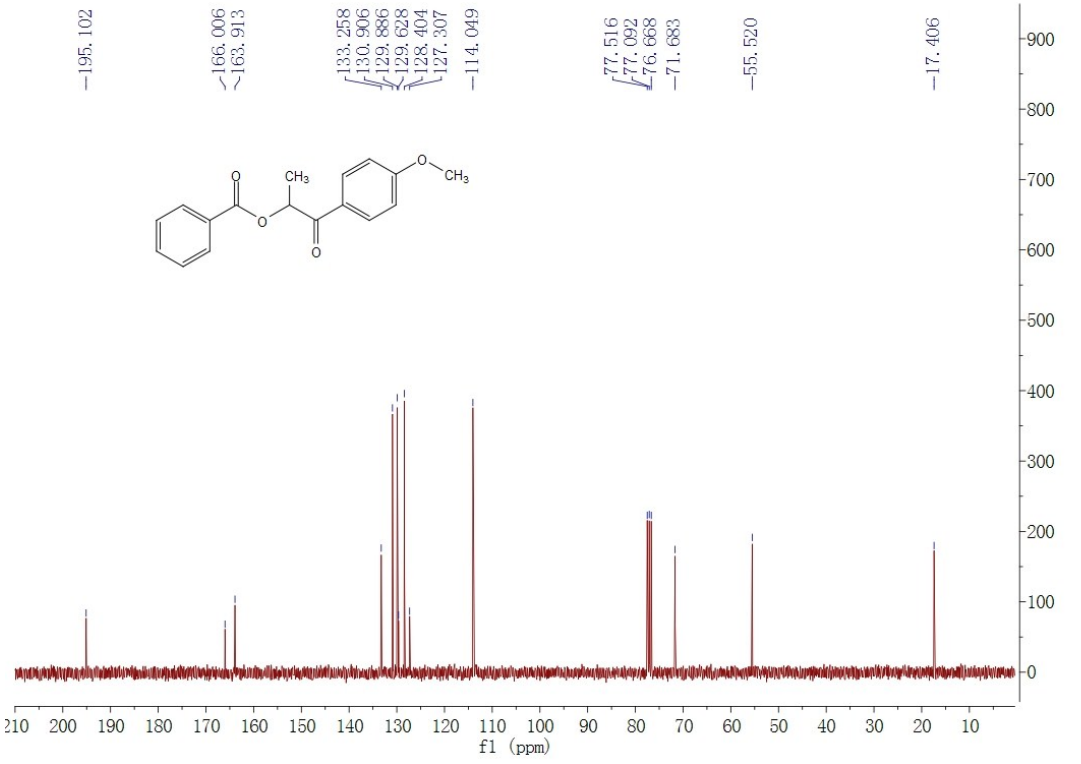
**1-(4-chlorophenyl)-1-oxobutan-2-yl benzoate (Scheme 1, 3an)**



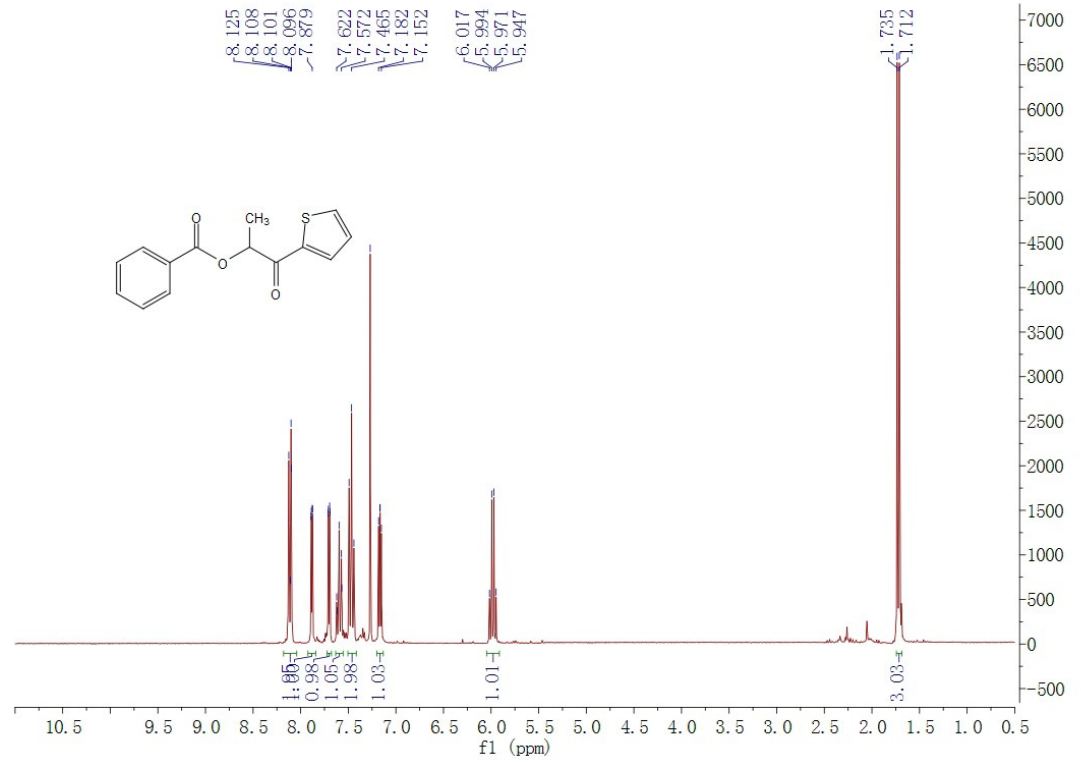



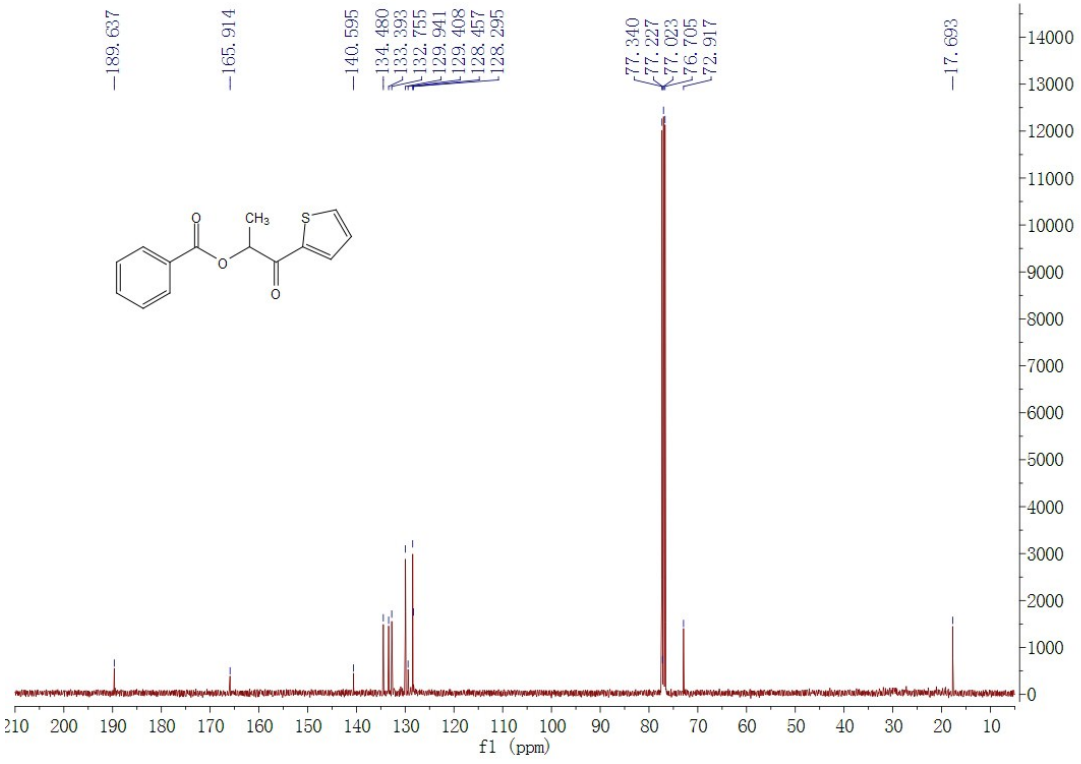
**1-(4-methoxyphenyl)-1-oxopropan-2-yl benzoate (Scheme 1, 3ao)**



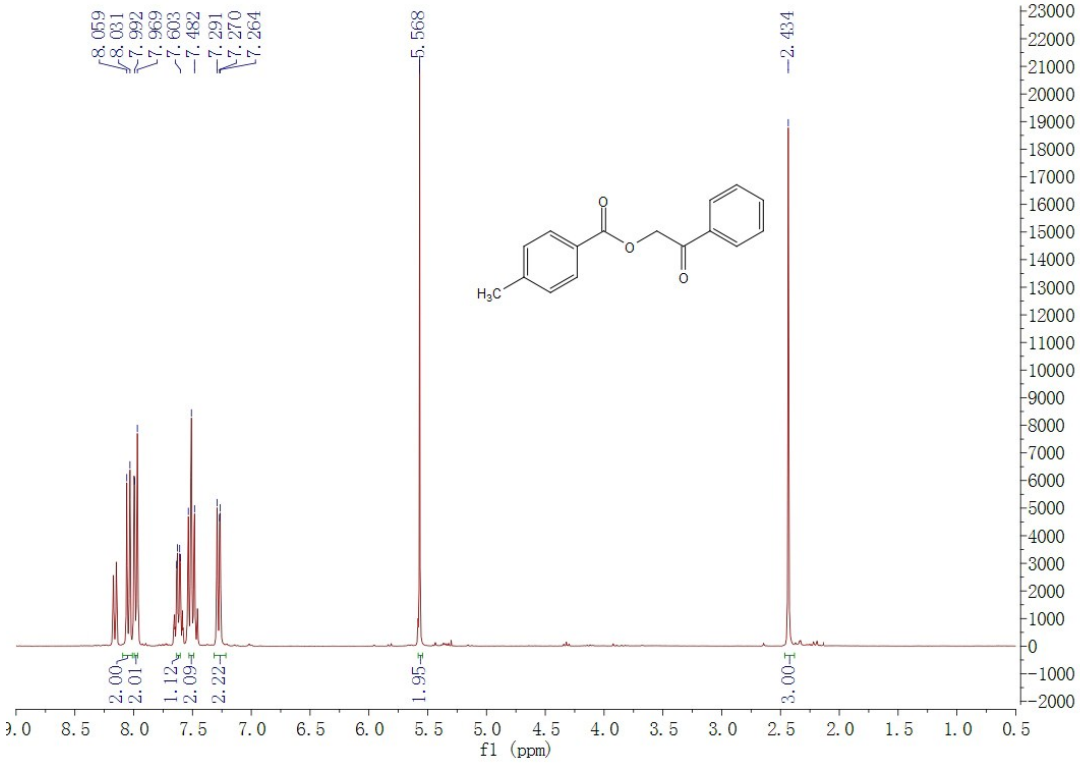



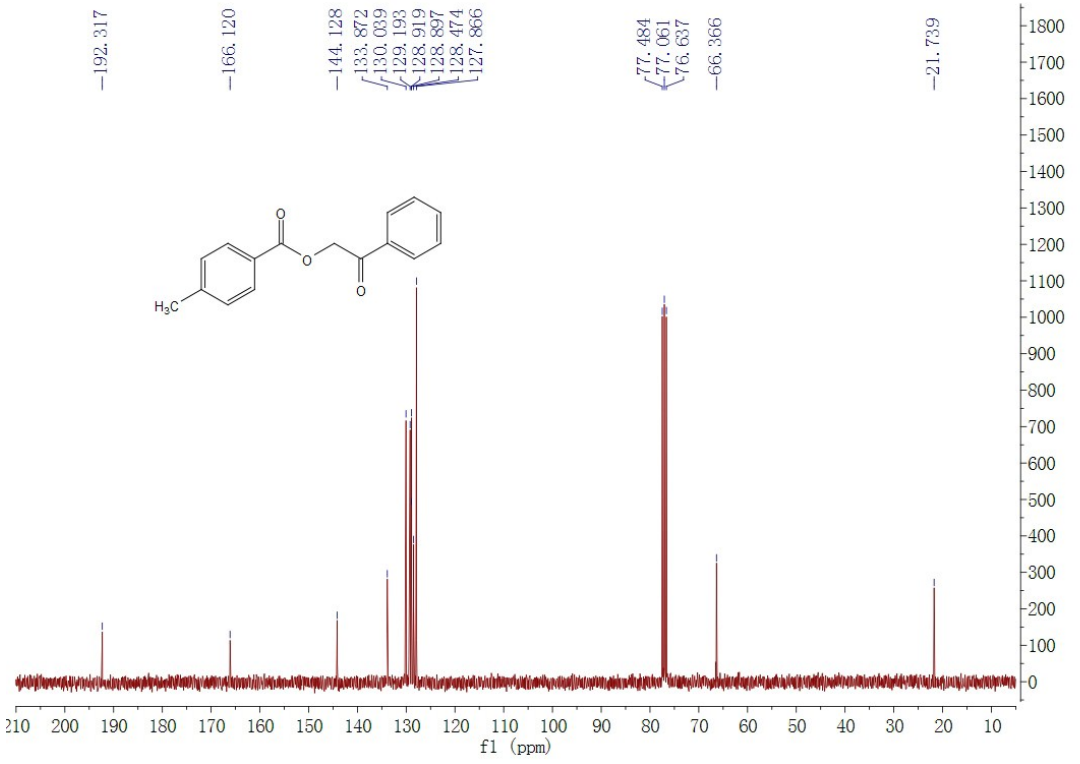
**1-Oxo-1-(thiophen-2-yl)propan-2-yl benzoate (Scheme 1, 3ap)**



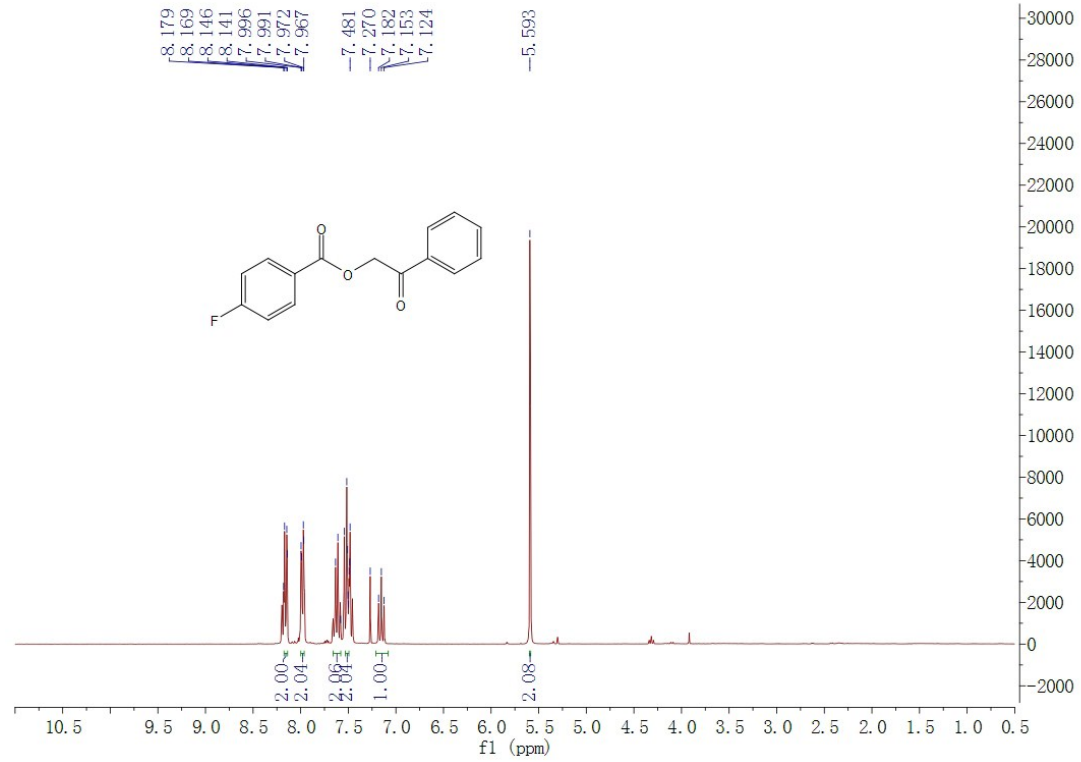



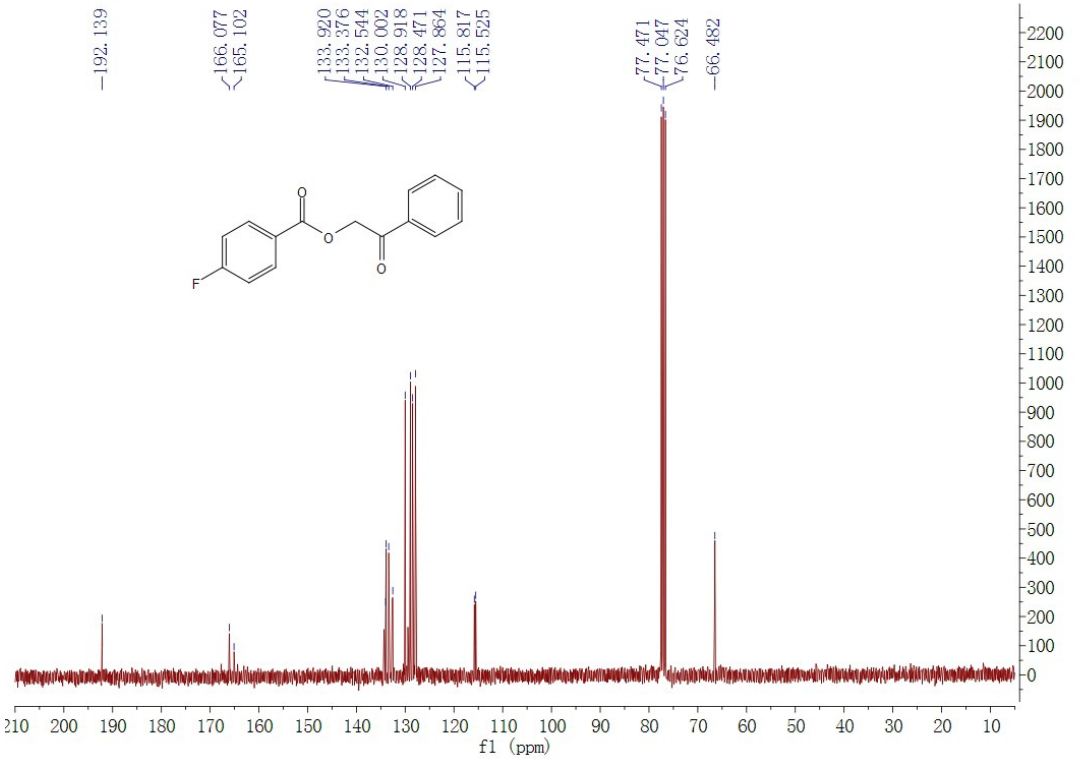
**1-Oxo-1-phenylethyl 4-methylbenzoate (Scheme 2, 3ba)**



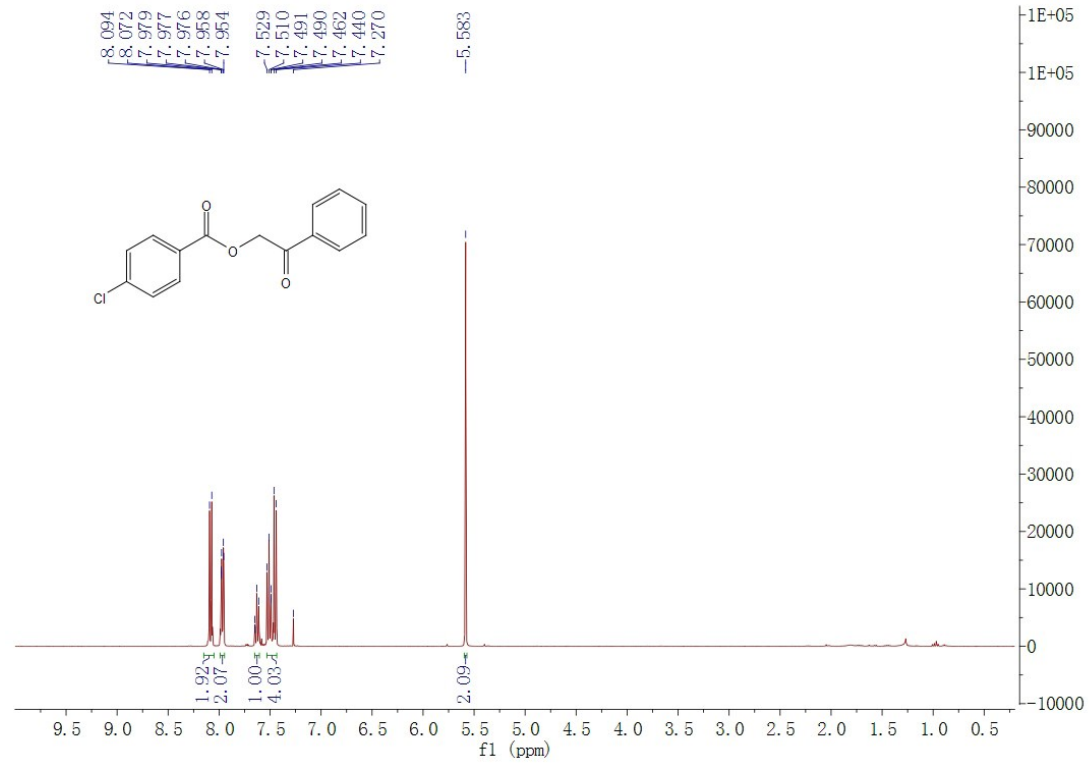



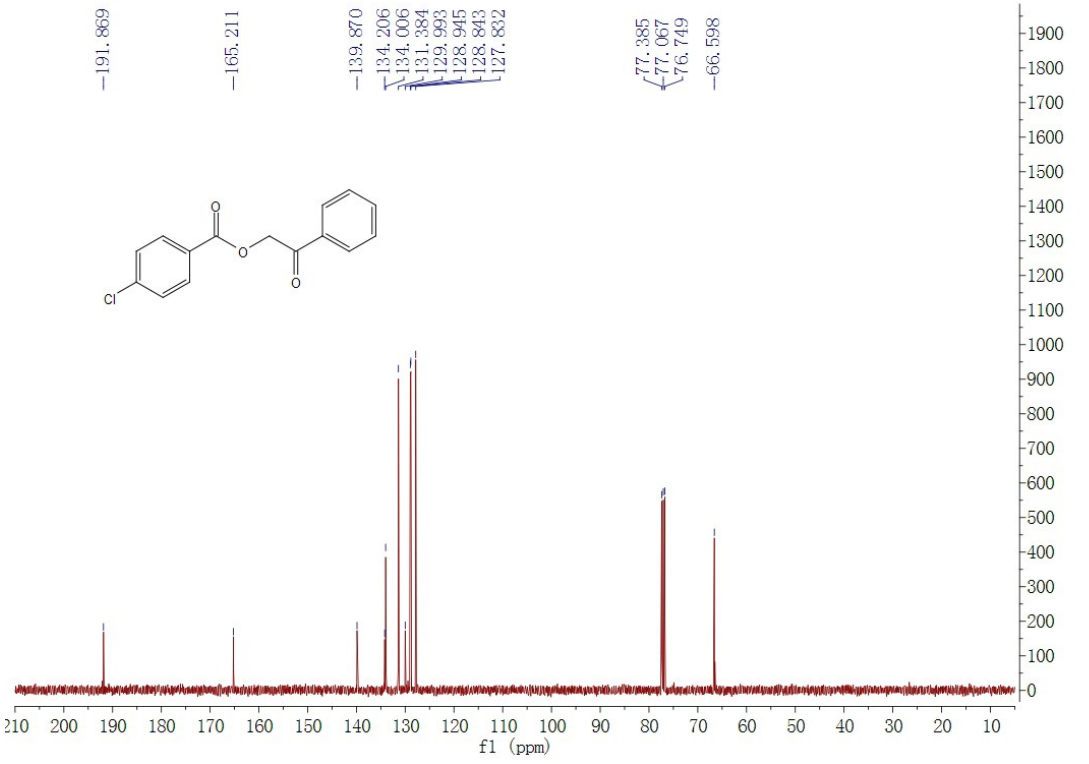
**1-Oxo-1-phenylethyl 4-fluorobenzoate (Scheme 2, 3ca)**



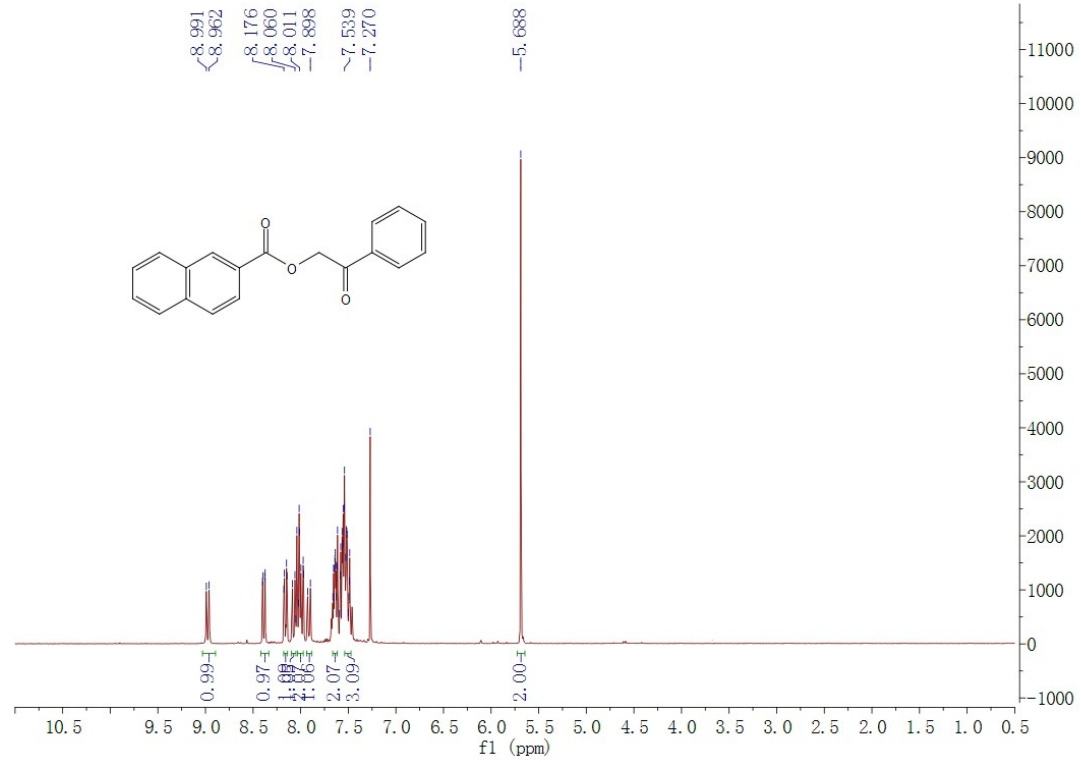



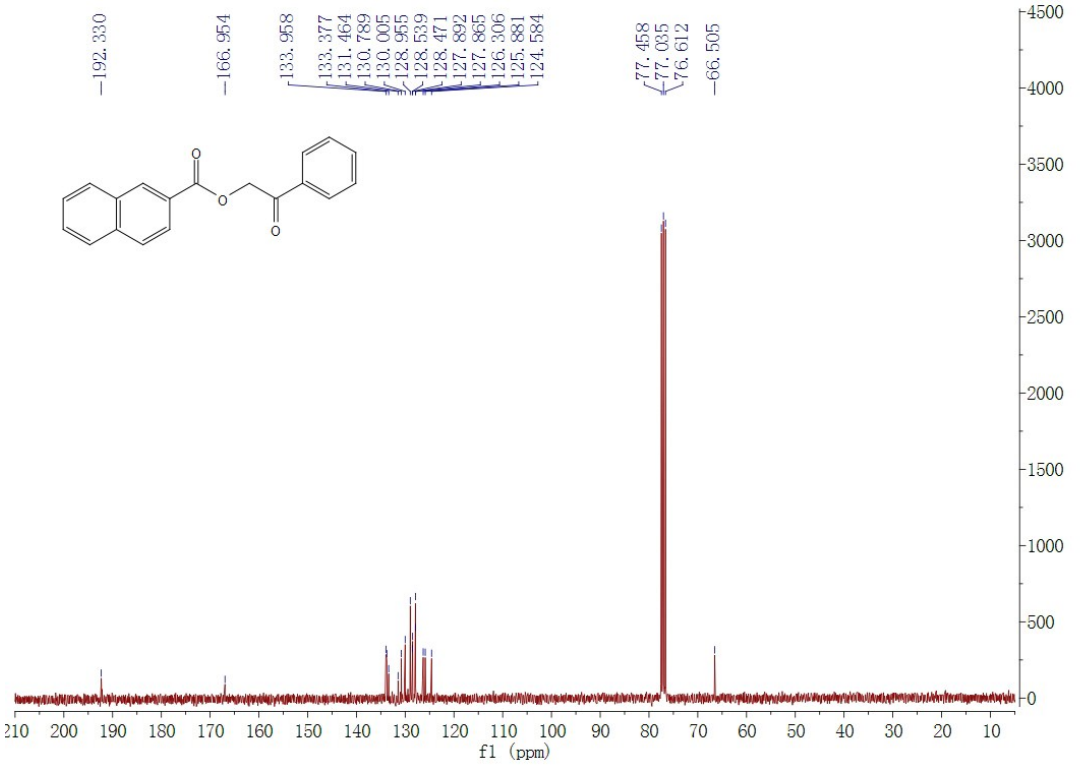
**1-Oxo-1-phenylethyl 4-chlorobenzoate (Scheme 2, 3da)**



**1-Oxo-1-phenylethyl 2-naphthoate (Scheme 2, 3ea)**



**References**

[1] Ji, K. G.; Zhao, Y. L.; Zhang, L. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 6508–6512.

[2] Mondal, B.; Sahoo, S. C.; Pan, S. C. *Eur. J. Org. Chem.* **2015**, 3135–3140.

[3] Dighe, S. N.; Bhattad, R. V.; Kulkarni, R. R.; Jain, K. S.; Srinivasan, K. V. *Synthetic. Commun.* **2010**, *40*, 3522–3527.

[4] Jang, M.; Lim, B. H.; Ryu, H. J.; Park, B. S. *Tetrahedron Lett.* **2013**, *54*, 7175–7179.

[5] Le, Z. G.; Xie, Z. B.; Xu, J. P. *Synthetic. Commun.* **2009**, *39*, 743–747.

[6] Shanmuganathan, S.; Natalia, D.; Greiner, L.; María, P. D. *Green Chem.* **2012**, *14*, 94–97.

[7] Li, C. L.; Jin, T.; Zhang, X. L.; Li, C. J.; Jia, X. S.; Li, J. *Org. Lett.* **2016**, *18*, 1916−1919.