

Supplementary Information

Bu₄Ni-catalyzed direct α -oxyacylation of diarylethanones with acyl peroxides

Zhou Zhou, Jiang Cheng and Jin-Tao Yu*

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

Email: yujintao@cczu.edu.cn

Table of Contents

1. General Considerations	S2
2. Experimental Procedures	S2
3. Mechanism Studies	S2-S4
4. Characterization Data for the Products	S5-S13
5. References	S14
6. Copies of the ¹H NMR and ¹³C NMR Spectra	S15-S39

1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. Acyl peroxides were synthesized according to the literature (W. Y. Yu, W. N. Sit, Z. Zhou and A. S. C. Chan, *Org. Lett.*, 2009, **11**, 3174.). ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer (100 MHz for ¹³C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl₃ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

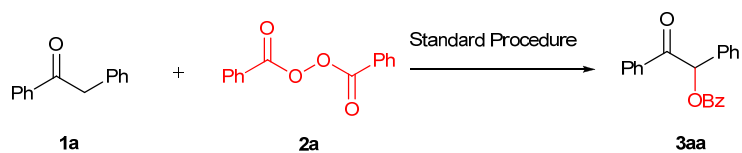
2. Experimental Procedures.

Under N₂, a Schlenk tube equipped with a stir bar was charged with diarylethanone **1** (0.2 mmol), acyl peroxide **2** (0.2 mmol, 1 equiv.), Bu₄NI (14.8 mg, 20 mol%) and 1,4-dioxane (2 mL) and sealed. The reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

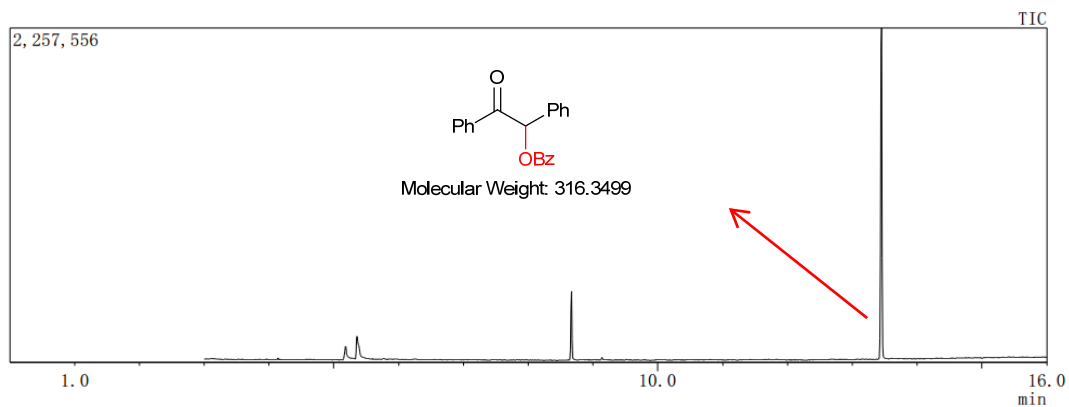
3. Mechanism Studies.

Under N₂, a Schlenk tube equipped with a stir bar was charged with 1,2-diphenylethanone **1a** (0.2 mmol), benzoyl peroxide **2a** (0.2 mmol, 1 equiv.), Bu₄NI (14.8 mg, 20 mol%), TEMPO (62.5 mg, 0.4 mmol, 2 equiv.) (or BHT (0.8 mmol, 4 equiv.)) in 1,4-dioxane (2 mL) and sealed. The reaction mixture was stirred at room temperature for 12 h. The mixture was analyzed using GC-MS spectrometer, as shown in Figure S2, no product of **3aa** was detected.

Standard Procedure



GC



MS (Residual time of 3aa: 13.450 min)

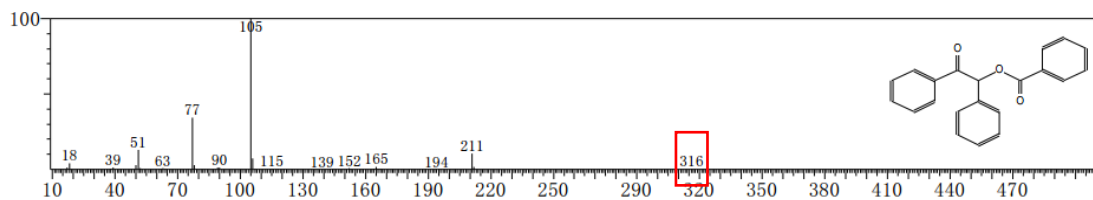
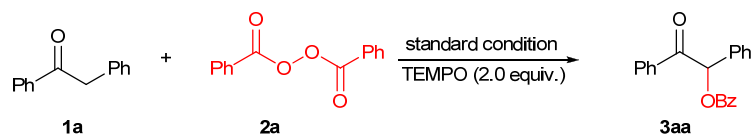


Figure S1 GC-MS spectra of the standard procedure results

Standard Procedure + TEMPO (2.0 equiv)



GC

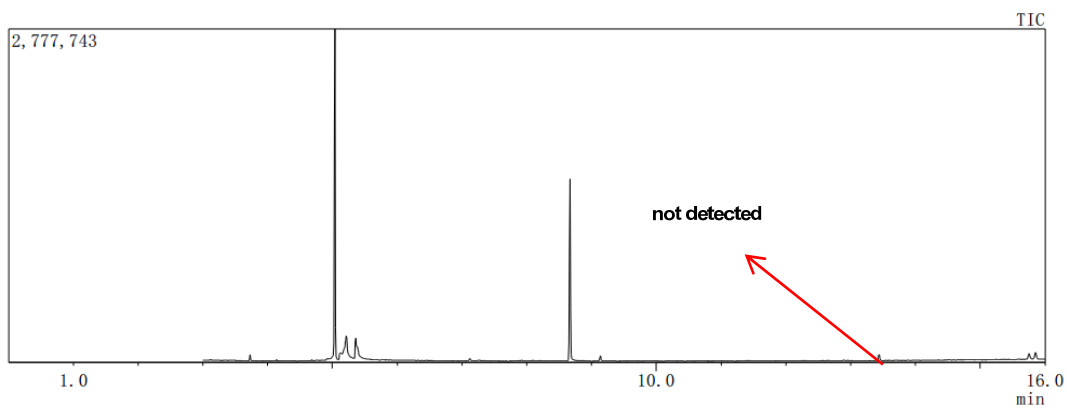
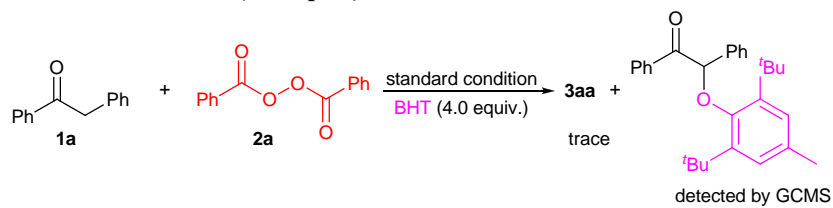
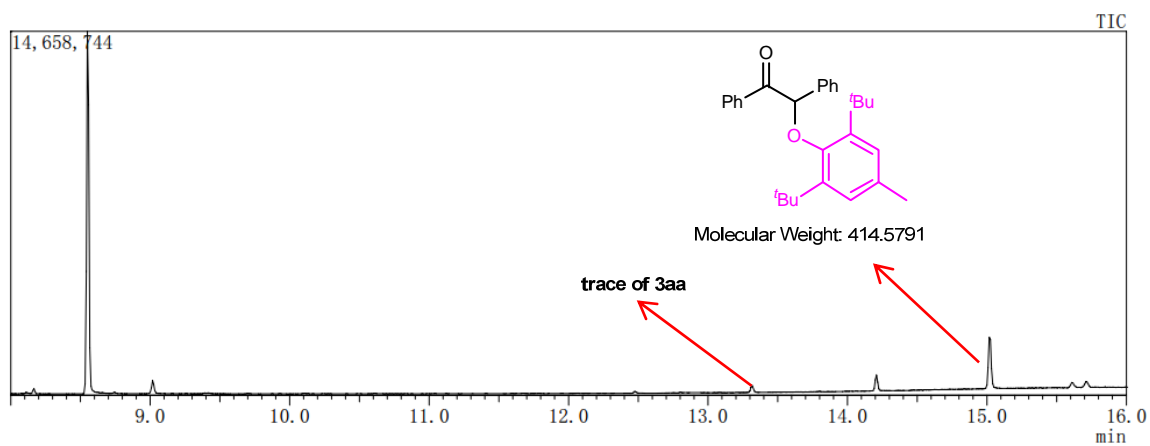


Figure S2 GC spectra of the free radical capture results

Standard Procedure + BHT (4.0 equiv)



GC



MS (Residual time of adduct: 15.017 min)

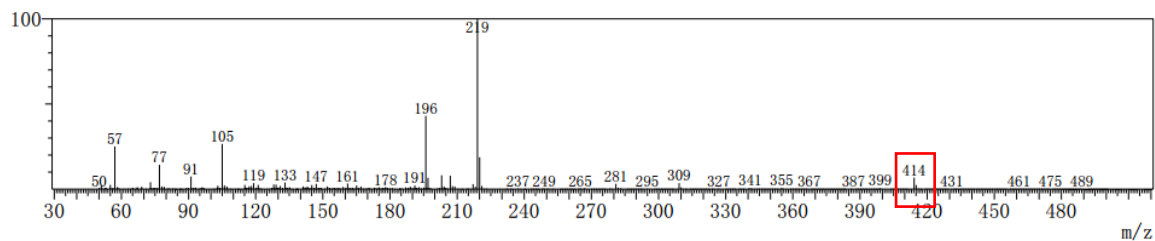
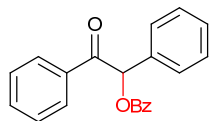


Figure S3 GC-MS spectra of the free radical capture results

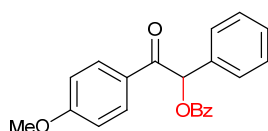
4. Characterization Data for the Products

2-oxo-1,2-diphenylethyl benzoate (**3aa**)¹



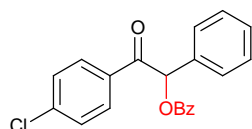
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3aa** (55.6mg, 88% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.15 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.61-7.51 (m, 4H), 7.47-7.35 (m, 7H), 7.12 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.6, 166.0, 134.6, 133.7, 133.5, 133.3, 129.9, 129.3, 129.3, 129.1, 128.8, 128.6, 128.6, 128.4, 77.9.

2-(4-methoxyphenyl)-2-oxo-1-phenylethyl benzoate (**3ba**)²



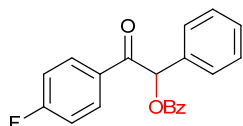
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) gave **3ba** (51.9 mg, 75% yield) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.59-7.55 (m, 3H), 7.46-7.38 (m, 5H), 7.08 (s, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 192.0, 166.0, 163.8, 134.2, 133.3, 131.2, 130.0, 129.5, 129.2, 129.1, 128.6, 128.3, 127.5, 113.9, 77.6, 55.4.

2-(4-chlorophenyl)-2-oxo-1-phenylethyl benzoate (**3ca**)²



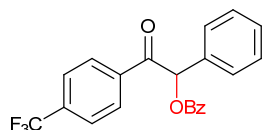
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ca** (56.7 mg, 81% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (d, *J* = 7.3 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.60-7.56 (m, 3H), 7.47-7.38 (m, 7H), 7.04 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 192.6, 166.0, 139.9, 133.4, 133.4, 132.9, 130.2, 129.9, 129.4, 129.2, 129.2, 129.0, 128.6, 128.4, 77.9.

2-(4-fluorophenyl)-2-oxo-1-phenylethyl benzoate (**3da**)



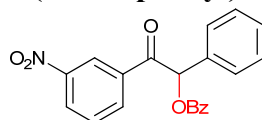
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3da** (47.4 mg, 71% yield) as a white solid. Mp. 97-99 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (d, *J* = 7.2 Hz, 2H), 8.07-8.03 (m, 2H), 7.59-7.57 (m, 3H), 7.47-7.36 (m, 5H), 7.12-7.06 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 192.2, 165.9 (d, *J*_{C-F} = 254.4 Hz), 133.6, 133.5, 131.6 (d, *J*_{C-F} = 9.4 Hz), 131.1 (d, *J*_{C-F} = 3.1 Hz), 130.0, 129.5, 129.3, 129.3, 128.7, 128.5, 116.1, 115.8, 77.9. HRMS (ESI) *m/z* calcd for C₂₁H₁₅FNaO₃ (M+Na)⁺ 357.0897, found 357.0898. IR (KBr) ν 3063, 2925, 2853, 1708, 1690, 1286, 1242, 1229, 1114 cm⁻¹.

2-oxo-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl benzoate (**3ea**)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ea** (66.8 mg, 87% yield) as a white solid. Mp. 71-72 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.13-8.09 (m, 4H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.61-7.56 (m, 3H), 7.48-7.38 (m, 5H), 7.05 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.0, 166.0, 137.5, 134.8, 133.5, 133.0, 130.0, 129.6, 129.3, 129.1, 129.1, 129.1, 128.6, 128.5, 125.7 (q, *J*_{C-F} = 3.8 Hz), 78.1. HRMS (ESI) *m/z* calcd for C₂₂H₁₅F₃NaO₃ (M+Na)⁺ 407.0866, found 407.0867. IR (KBr) ν 3065, 2922, 2851, 1715, 1698, 1326, 1283, 1250, 1180, 1170, 1114, 1067 cm⁻¹.

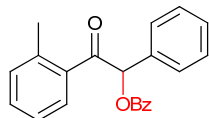
2-(3-nitrophenyl)-2-oxo-1-phenylethyl benzoate (**3fa**)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) gave **3fa** (60.6 mg, 84% yield) as a white solid. Mp. 115-116 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.85 (s, 1H), 8.37 (d, *J* = 8.2 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.1 Hz, 2H), 7.65-7.58 (m, 4H), 7.48-7.39 (m, 5H), 7.06 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 191.9, 166.0, 148.3, 135.8, 134.2, 133.6, 132.6, 130.0, 129.9, 129.8, 129.4, 128.9, 128.6, 128.5, 127.6, 123.7, 78.1. HRMS (ESI) *m/z* calcd for

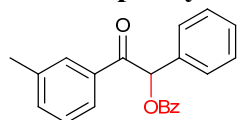
$C_{21}H_{15}NNaO_5(M+Na)^+$ 384.0842, found 384.0842. IR (KBr) ν 3066, 2924, 2855, 1733, 1702, 1536, 1494, 1344, 1284, 1253, 1220, 1108, 1089, 1071 cm^{-1} .

2-oxo-1-phenyl-2-(o-tolyl)ethyl benzoate (3ga)



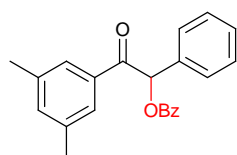
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ga** (46.9 mg, 71% yield) as a yellow solid. Mp. 114-115 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, $J = 7.1$ Hz, 2H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.59-7.55 (m, 1H), 7.49-7.43 (m, 4H), 7.38-7.31 (m, 4H), 7.26-7.22 (m, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 6.88 (s, 1H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.4, 166.1, 138.4, 136.1, 133.3, 132.9, 131.5, 131.4, 130.0, 129.4, 129.1, 128.9, 128.4, 128.2, 128.1, 125.5, 79.8, 20.1. HRMS (ESI) m/z calcd for $C_{22}H_{18}NaO_3 (M+Na)^+$ 353.1148, found 353.1149. IR (KBr) ν 3065, 2963, 2927, 1709, 1694, 1281, 1243, 1118 cm^{-1} .

2-oxo-1-phenyl-2-(m-tolyl)ethyl benzoate (3ha)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ha** (40.9 mg, 62% yield) as a yellow solid. Mp. 124-125 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 8.14 (d, $J = 7.4$ Hz, 2H), 7.82 (d, $J = 12.2$ Hz, 2H), 7.60-7.56 (m, 3H), 7.47-7.29 (m, 7H), 7.11 (s, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.9, 166.0, 138.5, 134.7, 134.3, 133.8, 133.3, 129.9, 129.4, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 126.0, 77.8, 21.3. HRMS (ESI) m/z calcd for $C_{25}H_{18}NaO_3 (M+Na)^+$ 353.1148, found 353.1147. IR (KBr) ν 3067, 3037, 2962, 2920, 2855, 1720, 1638, 1277, 1262, 1239, 1108 cm^{-1} .

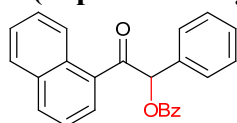
2-(3,5-dimethylphenyl)-2-oxo-1-phenylethyl benzoate (3ia)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave

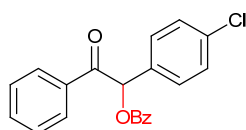
3ia (39.2 mg, 57% yield) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.14 (d, $J = 7.2$ Hz, 2H), 7.63 (s, 2H), 7.60-7.56 (m, 3H), 7.47-7.34 (m, 5H), 7.17 (s, 1H), 7.10 (s, 1H), 2.33 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 194.1, 166.0, 138.3, 135.2, 134.8, 133.9, 133.3, 129.9, 129.4, 129.2, 129.0, 128.6, 128.3, 126.6, 77.8, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{20}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 367.1305, found 367.1304. IR (KBr) ν 3051, 2955, 2919, 1719, 1692, 1600, 1452, 1282, 1273, 1246, 1108, 1096 cm^{-1} .

2-(naphthalen-1-yl)-2-oxo-1-phenylethyl benzoate (**3ja**)



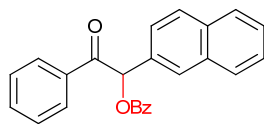
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ja** (47.6 mg, 65% yield) as a white solid. Mp. 142-143 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): δ 8.26 (d, $J = 8.2$ Hz, 1H), 8.17 (d, $J = 7.8$ Hz, 2H), 8.06 (d, $J = 7.1$ Hz, 1H), 7.91 (d, $J = 8.2$ Hz, 1H), 7.78 (d, $J = 7.4$ Hz, 1H), 7.58-7.42 (m, 8H), 7.32-7.27 (m, 3H), 7.07 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.1, 166.1, 134.0, 133.7, 133.4, 133.0, 132.7, 130.5, 129.9, 129.4, 129.1, 129.0, 128.4, 128.2, 128.2, 127.9, 127.6, 126.5, 125.2, 124.2, 80.1. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{18}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 389.1148, found 389.1148. IR (KBr) ν 3084, 3057, 3008, 2925, 2855, 1698, 1281, 1242, 1115, 1097 cm^{-1} .

1-(4-chlorophenyl)-2-oxo-2-phenylethyl benzoate (**3ka**)²



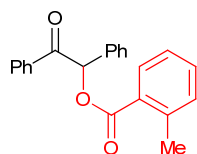
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ka** (46.9 mg, 67% yield) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.12 (d, $J = 7.2$ Hz, 2H), 7.99 (d, $J = 7.4$ Hz, 2H), 7.60-7.51 (m, 4H), 7.47-7.42 (m, 4H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.08 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.4, 165.9, 135.4, 134.5, 133.7, 133.5, 132.3, 129.9, 129.4, 129.1, 128.8, 128.7, 128.4, 99.9, 77.0.

1-(naphthalen-2-yl)-2-oxo-2-phenylethyl benzoate (**3la**)



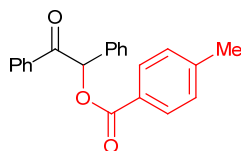
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **31a** (38.8 mg, 53% yield) as a white solid. Mp. 171-173 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.16 (d, *J* = 7.2 Hz, 2H), 8.06 (d, *J* = 7.2 Hz, 3H), 7.91-7.83 (m, 3H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.60-7.56 (m, 1H), 7.53-7.50 (m, 3H), 7.47-7.40 (m, 4H), 7.28 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.6, 166.0, 134.7, 133.5, 133.4, 133.2, 131.1, 130.0, 129.4, 129.1, 128.9, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.9, 126.6, 125.6, 78.1. HRMS (ESI) *m/z* calcd for C₂₅H₁₈NaO₃ (M+Na)⁺ 389.1148, found 389.1150. IR (KBr) ν 3057, 2923, 2849, 1705, 1686, 1596, 1450, 1317, 1287, 1273, 1252, 1115 cm⁻¹.

2-oxo-1,2-diphenylethyl 2-methylbenzoate (**3ab**)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ab** (59.4 mg, 90% yield) as a white solid. Mp. 104-105 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.07 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 6.6 Hz, 2H), 7.52-7.48 (m, 1H), 7.42-7.31 (m, 6H), 7.25-7.21 (m, 2H), 7.09 (s, 1H), 2.61 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.8, 166.9, 140.6, 134.7, 133.7, 133.4, 132.3, 131.6, 131.0, 129.2, 129.1, 128.8, 128.7, 128.7, 128.6, 125.7, 77.9, 21.7. IR (KBr) ν 3065, 3028, 2969, 2927, 1719, 1683, 1597, 1448, 1296, 1251, 1225, 1129, 1094 cm⁻¹.

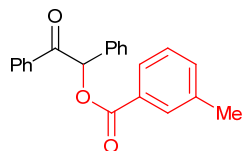
2-oxo-1,2-diphenylethyl 4-methylbenzoate (**3ac**)³



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ac** (40.3 mg, 61% yield) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.02-7.99 (m, 4H), 7.57 (d, *J* = 6.6 Hz, 2H), 7.53-7.49 (m, 1H), 7.42-7.33 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.08 (s, 1H), 2.39 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.8, 166.1,

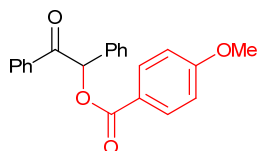
144.1, 134.7, 133.8, 133.4, 130.0, 129.2, 129.1, 129.1, 128.8, 128.6, 128.6, 126.6, 77.7, 21.7.

2-oxo-1,2-diphenylethyl 3-methylbenzoate (**3ad**)



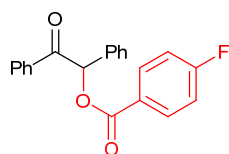
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ad** (57.4 mg, 87% yield) as a white solid. Mp. 119-121 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.94 (d, *J* = 5.4 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.55-7.51 (m, 1H), 7.44-7.31 (m, 7H), 7.12 (s, 1H), 2.39 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.7, 166.2, 138.2, 134.7, 134.1, 133.8, 133.4, 130.4, 129.3, 129.1, 128.8, 128.8, 128.7, 128.6, 128.3, 127.1, 77.8, 21.2. IR (KBr) ν 3062, 3037, 2980, 2922, 1708, 1688, 1595, 1448, 1289, 1199, 1109.

2-oxo-1,2-diphenylethyl 4-methoxybenzoate (**3ae**)²



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:20) gave **3ae** (59.5 mg, 86% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 6.7 Hz, 2H), 7.54-7.50 (m, 1H), 7.43-7.34 (m, 5H), 7.09 (s, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.9, 165.7, 163.7, 134.7, 133.9, 133.4, 132.0, 129.2, 129.0, 128.8, 128.6, 128.6, 121.7, 113.6, 77.6, 55.4.

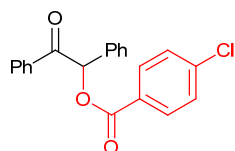
2-oxo-1,2-diphenylethyl 4-fluorobenzoate (**3af**)⁴



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3af** (62.1 mg, 93% yield) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.17-8.13

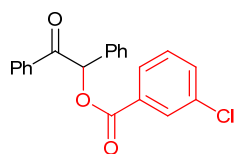
(m, 2H), 8.01 (d, $J = 7.3$ Hz, 2H), 7.59-7.51 (m, 3H), 7.44-7.35 (m, 5H), 7.14-7.09 (m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.6, 166.1 (d, $J_{\text{C-F}} = 252.9$ Hz), 134.7, 133.7, 133.6, 132.6 (d, $J_{\text{C-F}} = 9.4$ Hz), 129.5, 129.2, 128.9, 128.8, 128.7, 125.7 (d, $J_{\text{C-F}} = 2.9$ Hz), 115.8, 115.5, 78.1.

2-oxo-1,2-diphenylethyl 4-chlorobenzoate (**3ag**)⁴



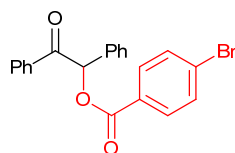
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ag** (59.5 mg, 85% yield) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.07 (d, $J = 8.6$ Hz, 2H), 8.01 (d, $J = 7.3$ Hz, 2H), 7.59-7.51 (m, 3H), 7.44-7.36 (m, 7H), 7.11 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.5, 165.2, 139.9, 134.6, 133.6, 133.6, 131.4, 129.5, 129.3, 128.9, 128.8, 128.8, 128.8, 127.9, 78.2.

2-oxo-1,2-diphenylethyl 3-chlorobenzoate (**3ah**)⁵



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ah** (53.2 mg, 76% yield) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.10 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 3H), 7.59-7.51 (m, 4H), 7.44-7.36 (m, 6H), 7.11 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.2, 164.8, 134.5, 134.5, 133.6, 133.4, 133.3, 131.1, 129.9, 129.7, 129.5, 129.2, 128.8, 128.7, 128.7, 128.1, 78.3.

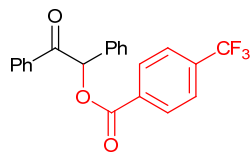
2-oxo-1,2-diphenylethyl 4-bromobenzoate (**3ai**)⁶



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ai** (67.8 mg, 86% yield) as a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 8.02-7.98 (m, 4H), 7.58 (d, $J = 8.7$ Hz, 4H), 7.54-7.51 (m, 1H), 7.44-7.35 (m, 5H), 7.11 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.5, 165.4, 134.6, 133.7, 133.6, 131.8, 131.5, 129.5,

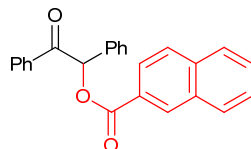
129.3, 128.9, 128.8, 128.8, 128.6, 128.4, 78.2.

2-oxo-1,2-diphenylethyl 4-(trifluoromethyl)benzoate (**3aj**)⁴



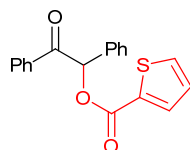
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3aj** (27.6 mg, 36% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.24 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.59-7.52 (m, 3H), 7.45-7.37 (m, 5H), 7.12 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.2, 164.8, 134.9, 134.5, 133.6, 133.4, 132.7, 130.4, 129.6, 129.3, 128.8, 128.8, 128.8, 128.7, 125.4 (q, *J*_{C-F} = 3.6 Hz), 78.4.

2-oxo-1,2-diphenylethyl 2-naphthoate (**3ak**)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3ak** (50.5 mg, 69% yield) as a white solid. Mp. 119-120 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.72 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.90-7.87 (m, 2H), 7.66-7.52 (m, 5H), 7.46-7.38 (m, 5H), 7.20 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 193.8, 166.3, 135.8, 134.8, 133.9, 133.6, 132.5, 131.7, 129.5, 129.4, 129.3, 128.9, 128.8, 128.8, 128.5, 128.3, 127.8, 126.7, 126.7, 125.4, 78.1. HRMS (ESI) *m/z* calcd for C₂₅H₁₈NaO₃ (M+Na)⁺ 389.1148, found 389.1150. IR (KBr) ν 3056, 2924, 1695, 1597, 1449, 1367, 1356, 1288, 1255, 1229, 1193, 1130, 1084 cm⁻¹.

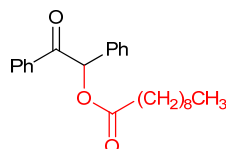
2-oxo-1,2-diphenylethyl thiophene-2-carboxylate (**3al**)⁷



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3al** (38.6 mg, 60% yield) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.00 (d, *J* =

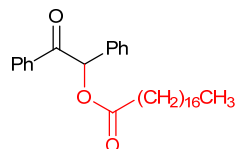
7.4 Hz, 2H), 7.90 (d, $J = 3.7$ Hz, 1H), 7.59-7.50 (m, 4H), 7.43-7.34 (m, 5H), 7.11-7.09 (m, 1H), 7.07 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.5, 161.5, 134.5, 134.3, 133.5, 133.1, 132.7, 129.3, 129.1, 128.8, 128.8, 128.6, 128.6, 127.8, 78.0.

2-oxo-1,2-diphenylethyl decanoate (**3am**)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3am** (61.5 mg, 84% yield) as a pale-yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.95 (d, $J = 7.5$ Hz, 2H), 7.52-7.47 (m, 3H), 7.41-7.31 (m, 5H), 6.87 (s, 1H), 2.55-2.40 (m, 2H), 1.72-1.65 (m, 2H), 1.42-1.18 (m, 12H), 0.90-0.87 (m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 193.9, 173.3, 134.7, 133.7, 133.4, 129.2, 129.0, 128.7, 128.6, 128.6, 77.3, 33.9, 31.8, 29.3, 29.2, 29.2, 29.0, 24.8, 22.6, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{30}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 389.2087, found 389.2089. IR (KBr) ν 3065, 3033, 2926, 2855, 1739, 1698, 1598, 1449, 1226, 1157, 1112 cm^{-1} .

2-oxo-1,2-diphenylethyl stearate (**3an**)



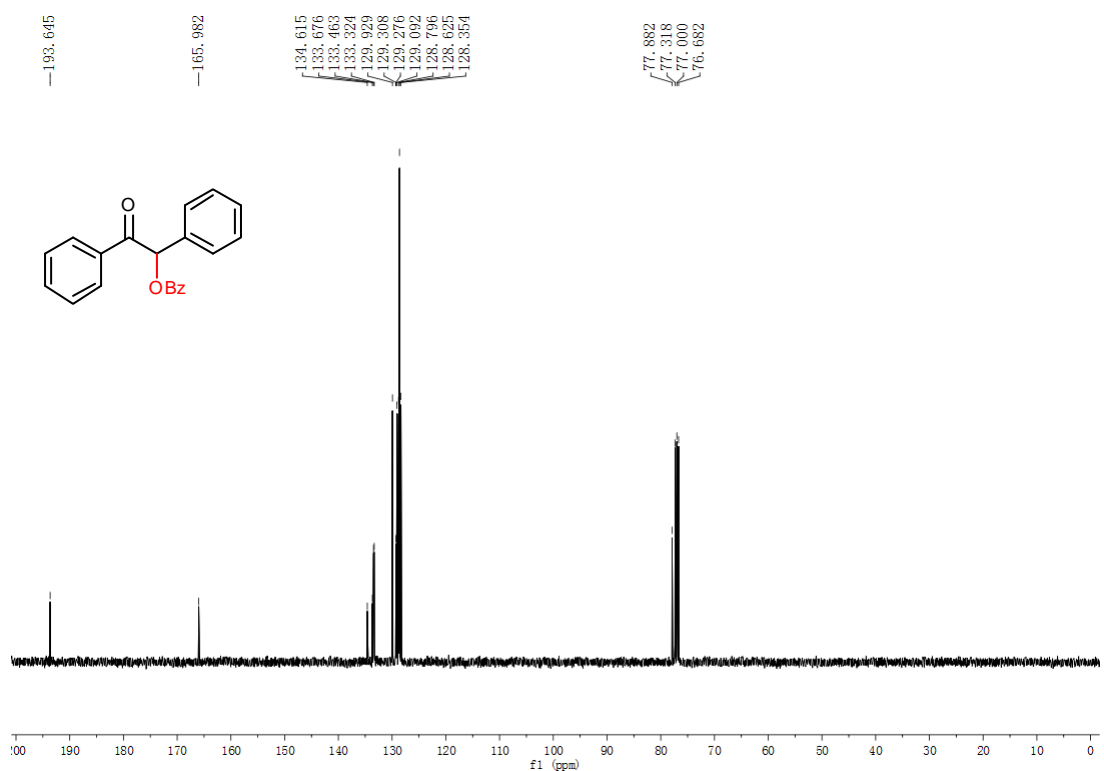
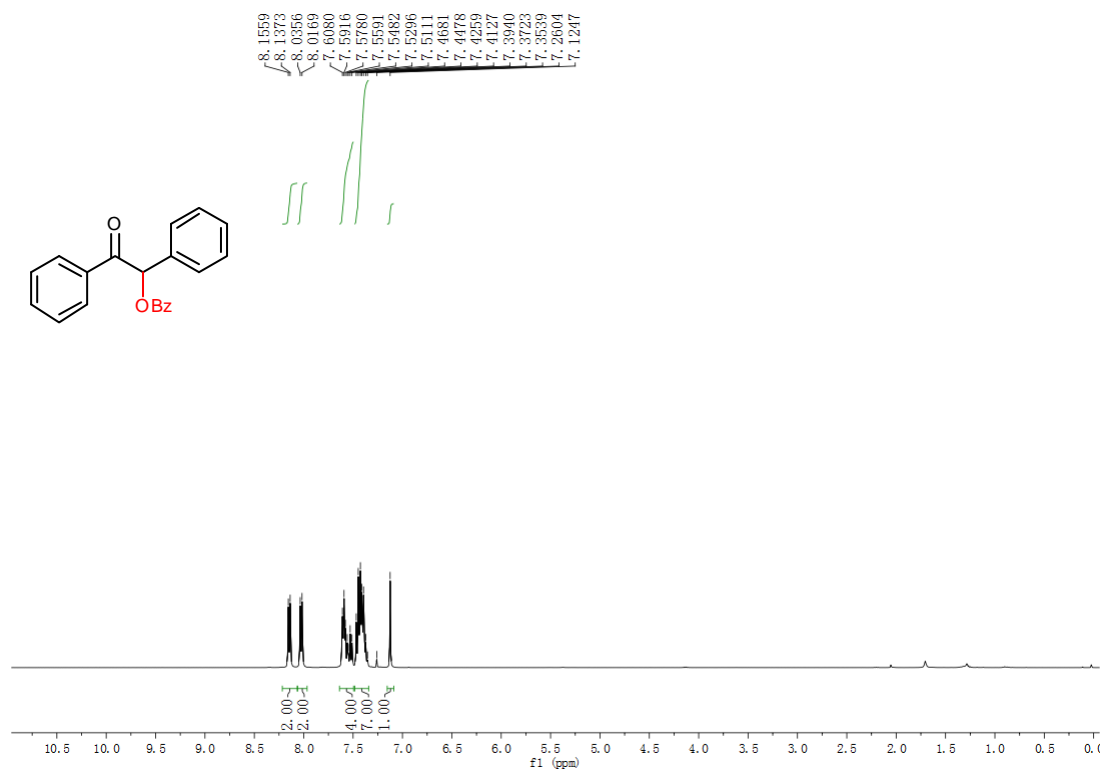
Flash column chromatography on silica gel (ethyl acetate/petroleum ether 1:40) gave **3an** (85.1 mg, 89% yield) as a white solid. mp 37-39 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.53-7.46 (m, 3H), 7.42-7.31 (m, 5H), 6.86 (s, 1H), 2.54-2.39 (m, 2H), 1.71-1.61 (m, 2H), 1.39-1.15 (m, 28H), 0.90-0.87 (m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.1, 156.7, 145.7, 138.0, 136.8, 136.3, 135.4, 134.8, 129.0, 129.0, 126.8, 125.7, 125.7, 123.8, 123.2, 123.0, 117.2, 116.8, 106.7, 92.8, 27.9, 27.9, 27.8, 23.2, 23.2, 23.2, 22.4, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{46}\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 501.3339, found 501.3338. IR (KBr) ν 3056, 3031, 2925, 2853, 1741, 1699, 1598, 1449, 1226, 1160, 972, 757, 721, 696, 586, 528 cm^{-1} .

5. References

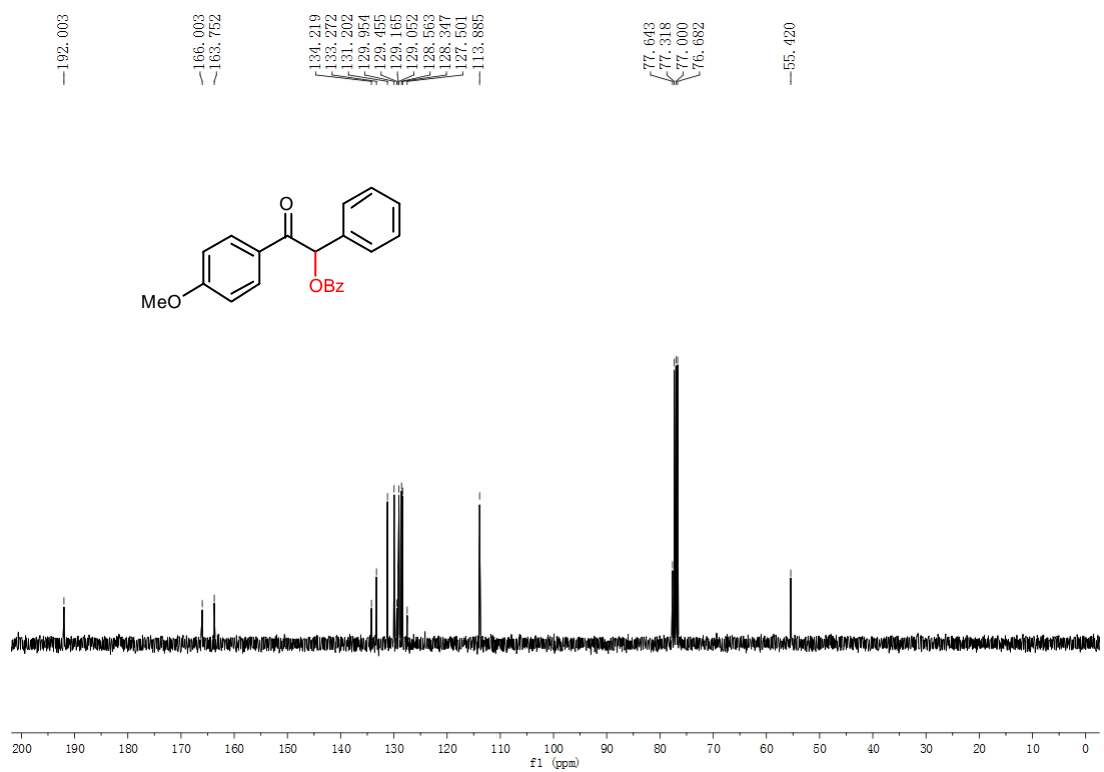
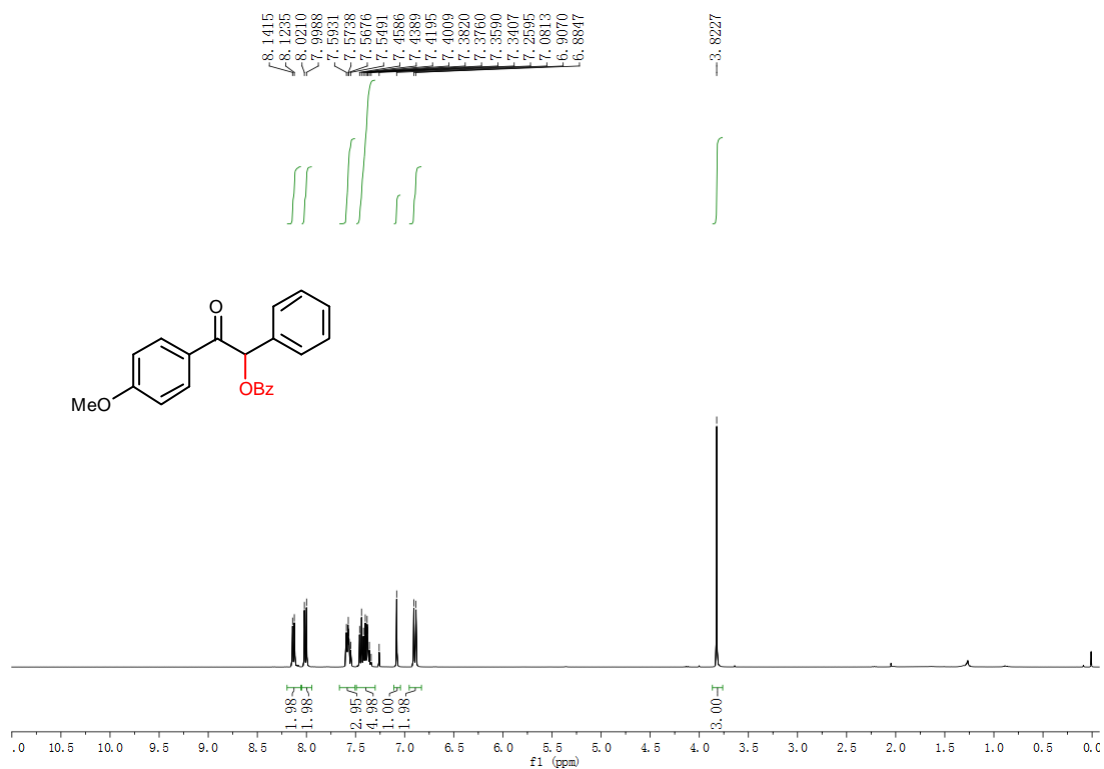
- 1 Y.-J. Kim, N. Y. Kim and C.-H. Cheon, *Org. Lett.*, 2014, **16**, 3171.
- 2 M. B. Rubin and S. Inbar, *J. Org. Chem.*, 1988, **53**, 3355.
- 3 B. Li, Q. Gu, T. Zhao, Y. He and Y. Zhang, *Chin. J. Org. Chem.*, 2012, **32**, 1459.
- 4 J. E. Pickett, *Tetrahedron Lett.*, 2015, **56**, 3023.
- 5 J. K. Stille and D. D. Whitehurst, *J. Am. Chem. Soc.*, 1964, **86**, 4871.
- 6 D. R. Demuth and F. A. Luzzio, *PCT Int. Appl.* WO 201316206, 2013.
- 7 M. Sreenivasulu, K. A. Kumar, K. S. Reddy, K. S. Kumar, P. R. Kumar, K. B. Chandrasekhar, and M. Pal, *Tetrahedron Lett.* 2011, **52**, 727.

6. Copies of the ^1H NMR and ^{13}C NMR Spectra

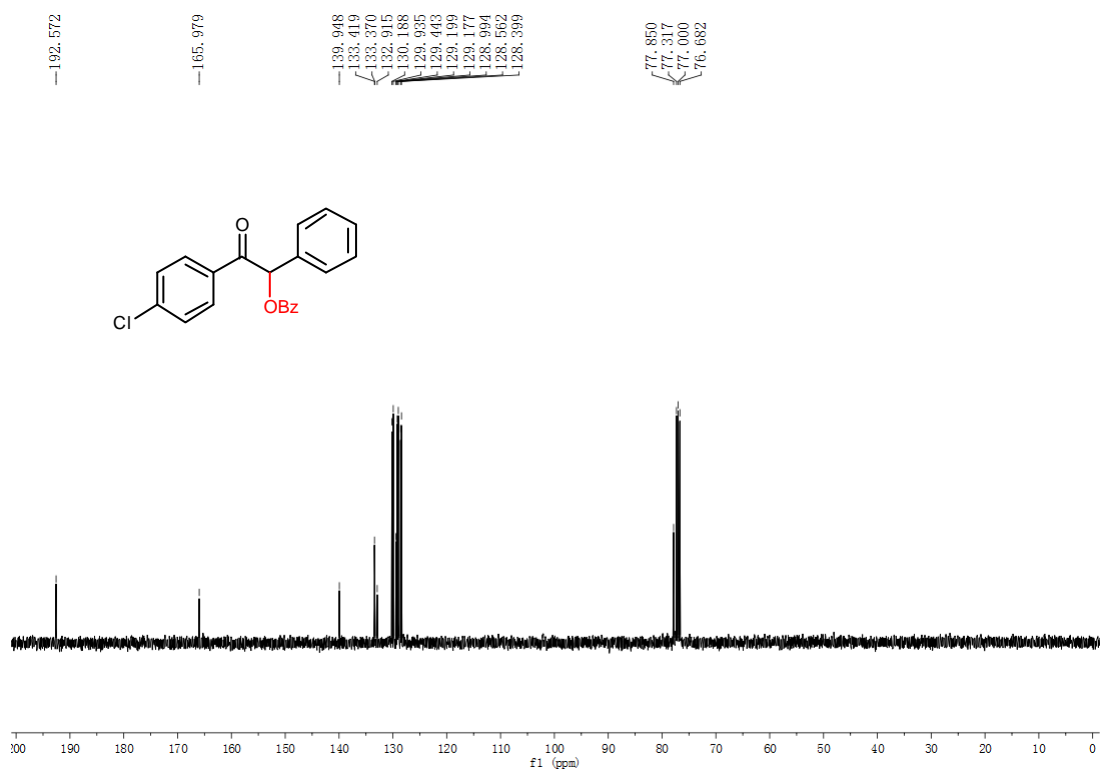
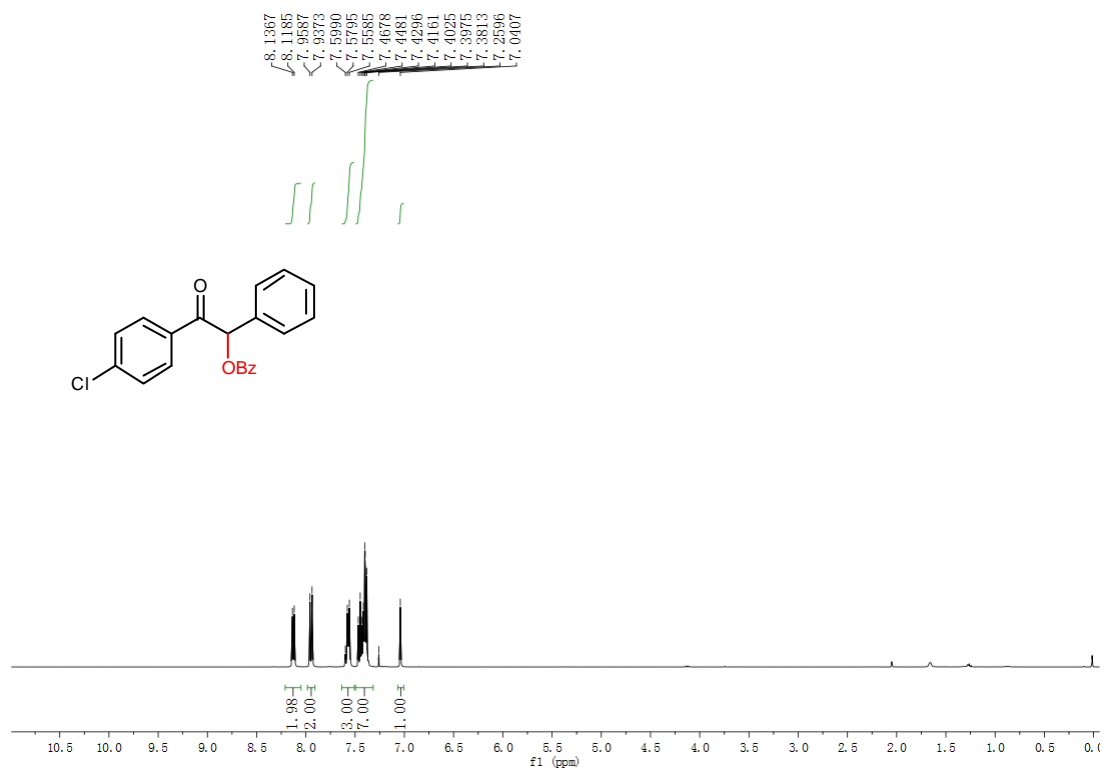
2-oxo-1,2-diphenylethyl benzoate (3aa)



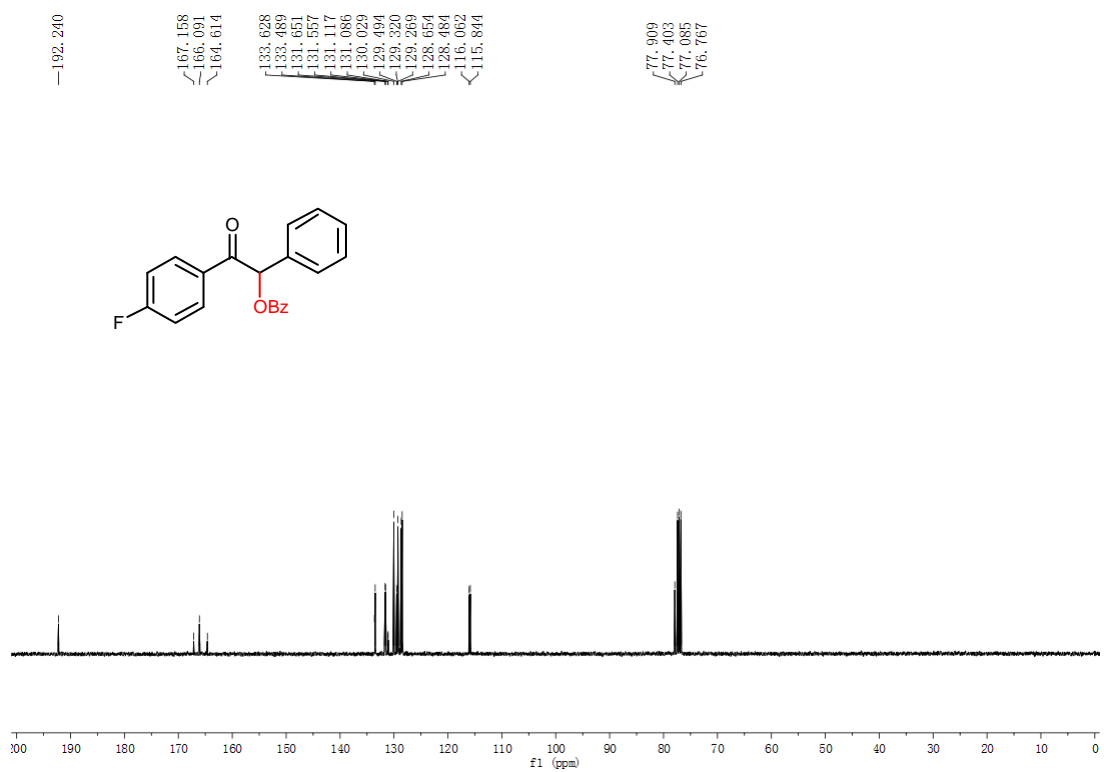
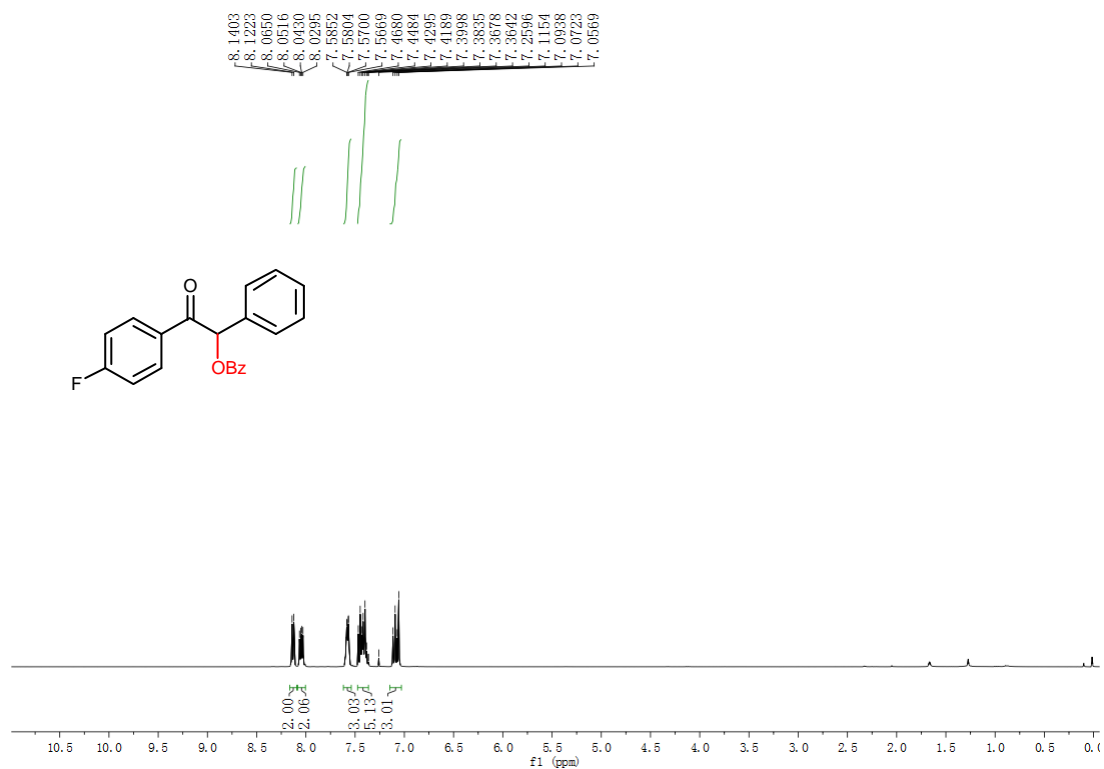
2-(4-methoxyphenyl)-2-oxo-1-phenylethyl benzoate (3ba)



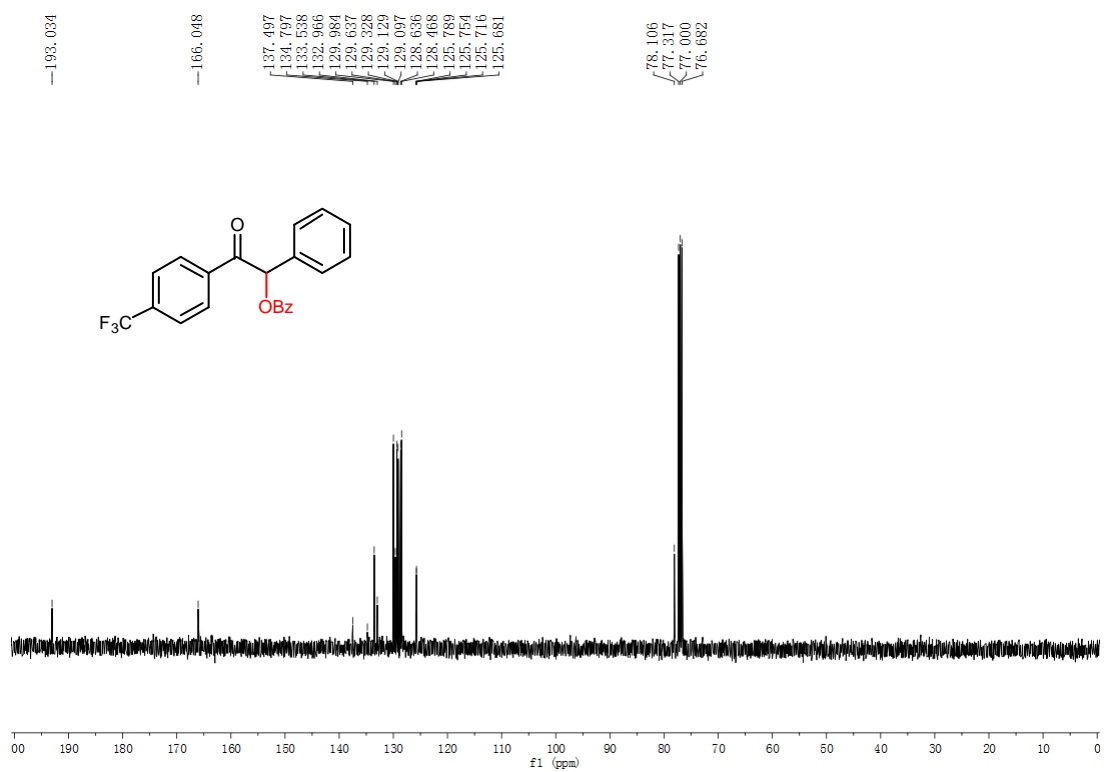
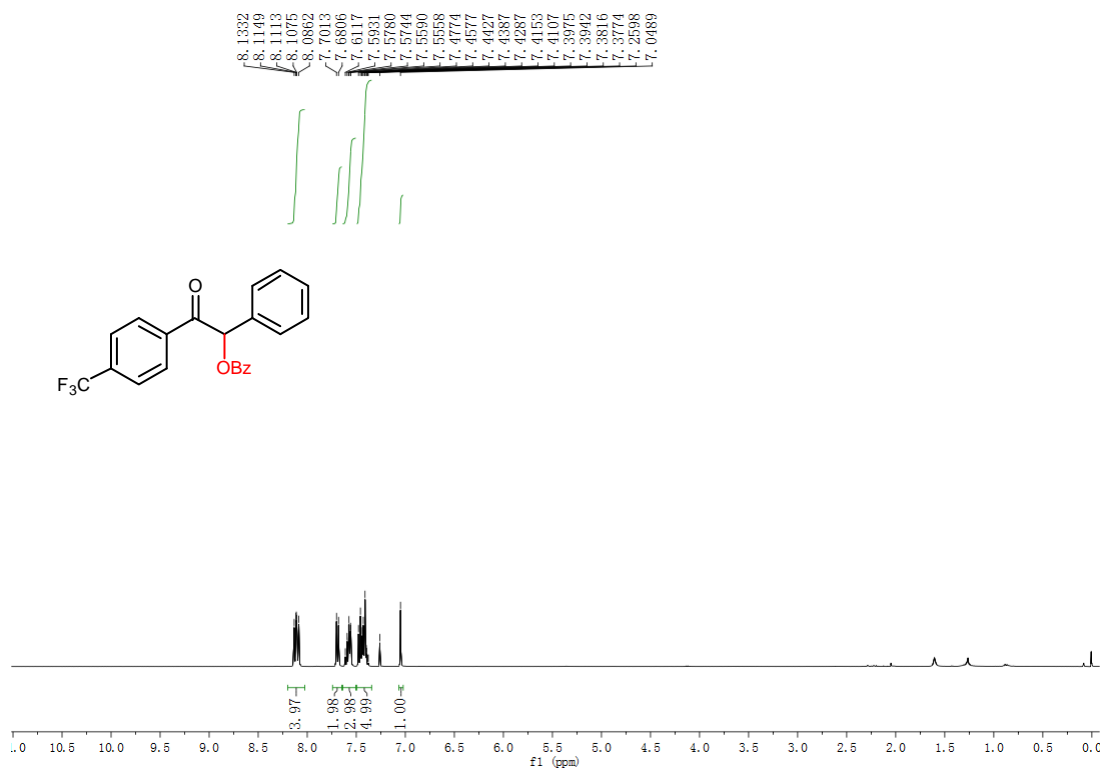
2-(4-chlorophenyl)-2-oxo-1-phenylethyl benzoate (3ca)



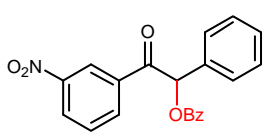
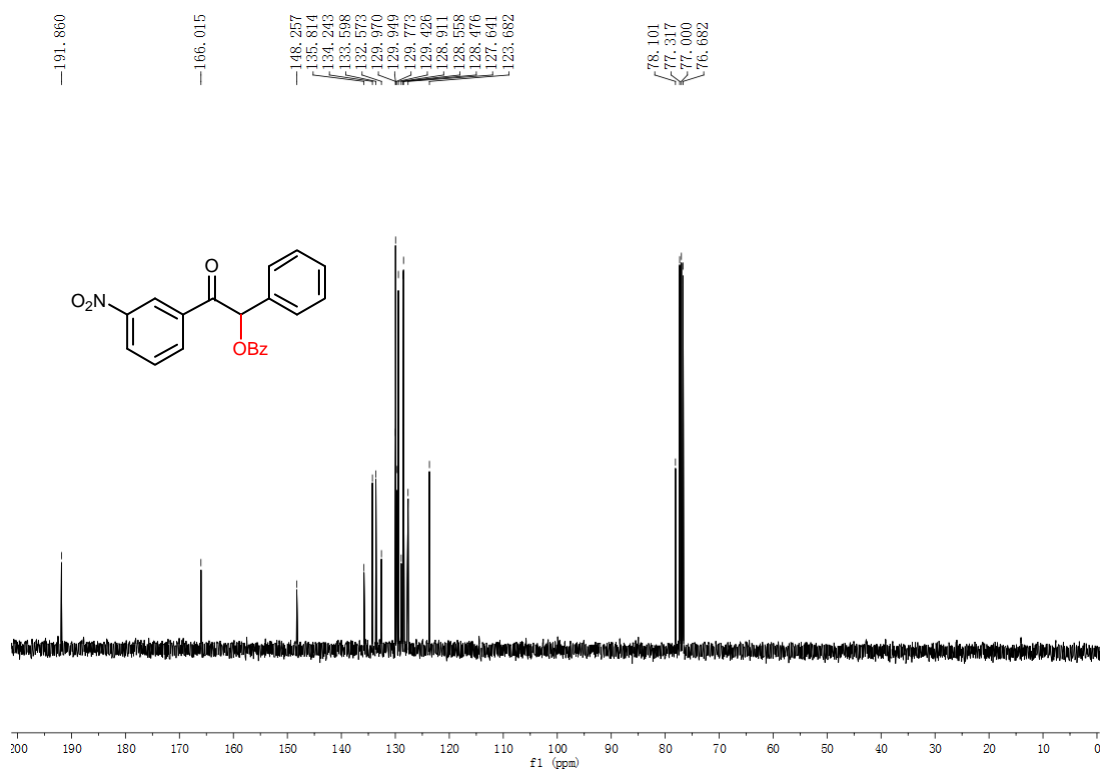
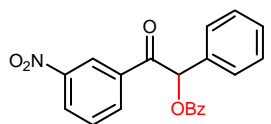
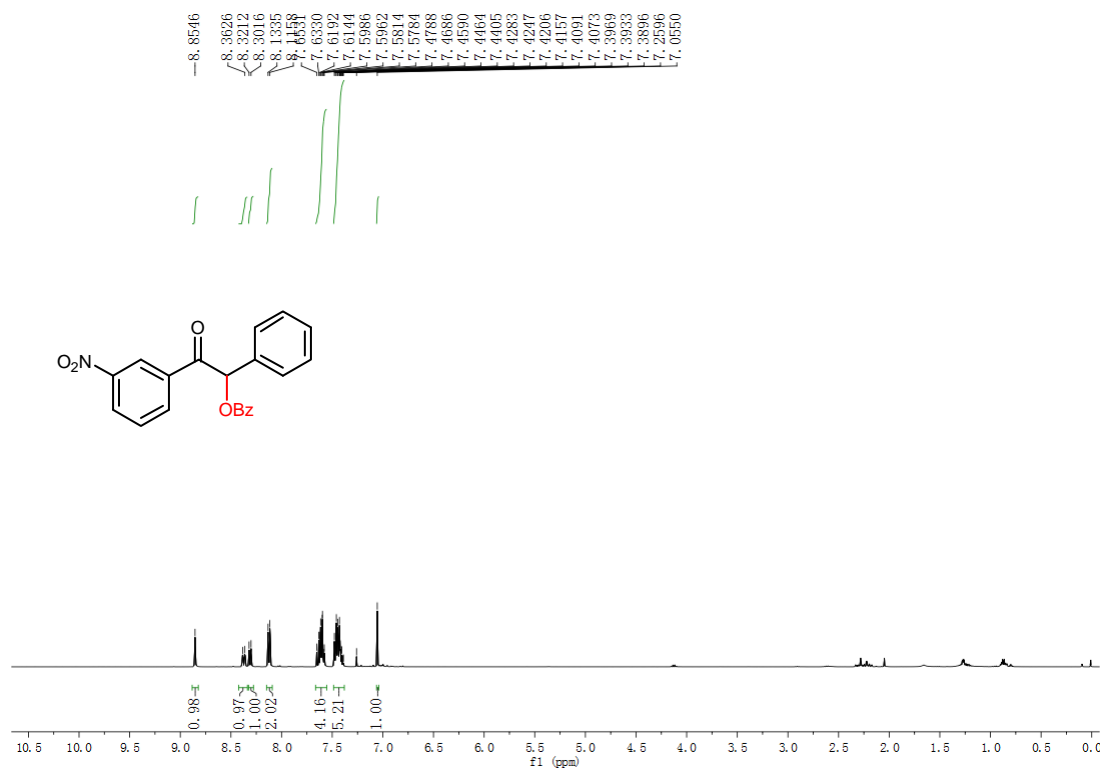
2-(4-fluorophenyl)-2-oxo-1-phenylethyl benzoate (3da)



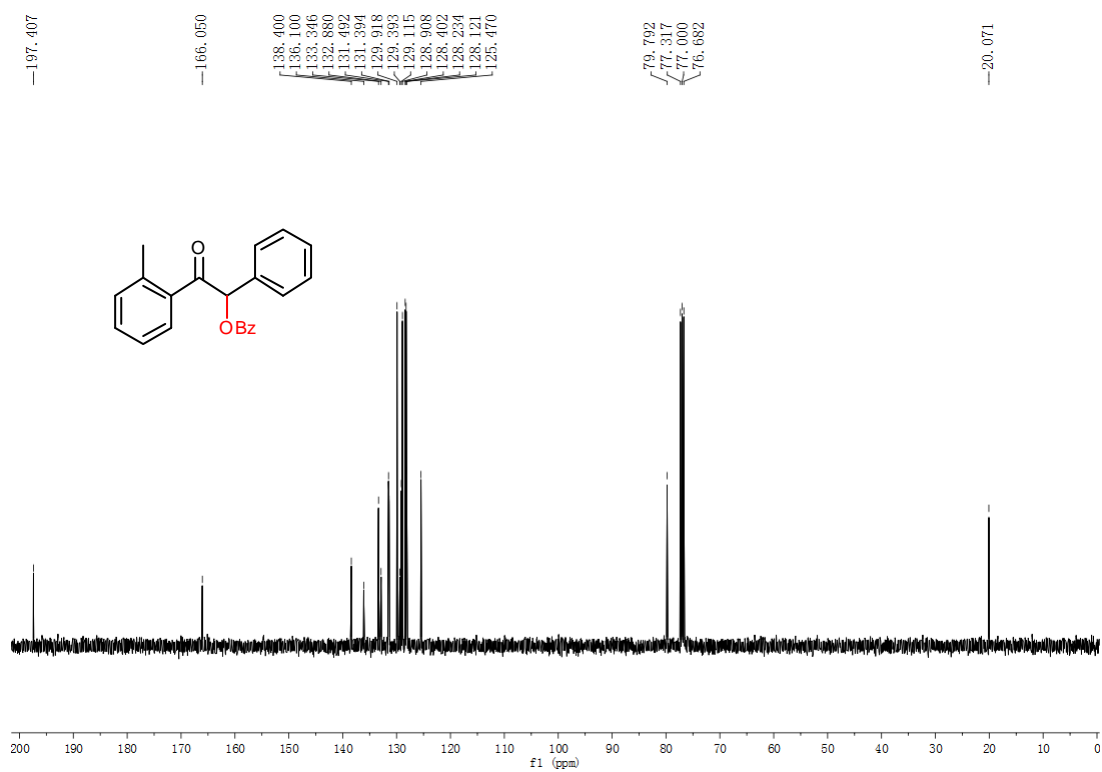
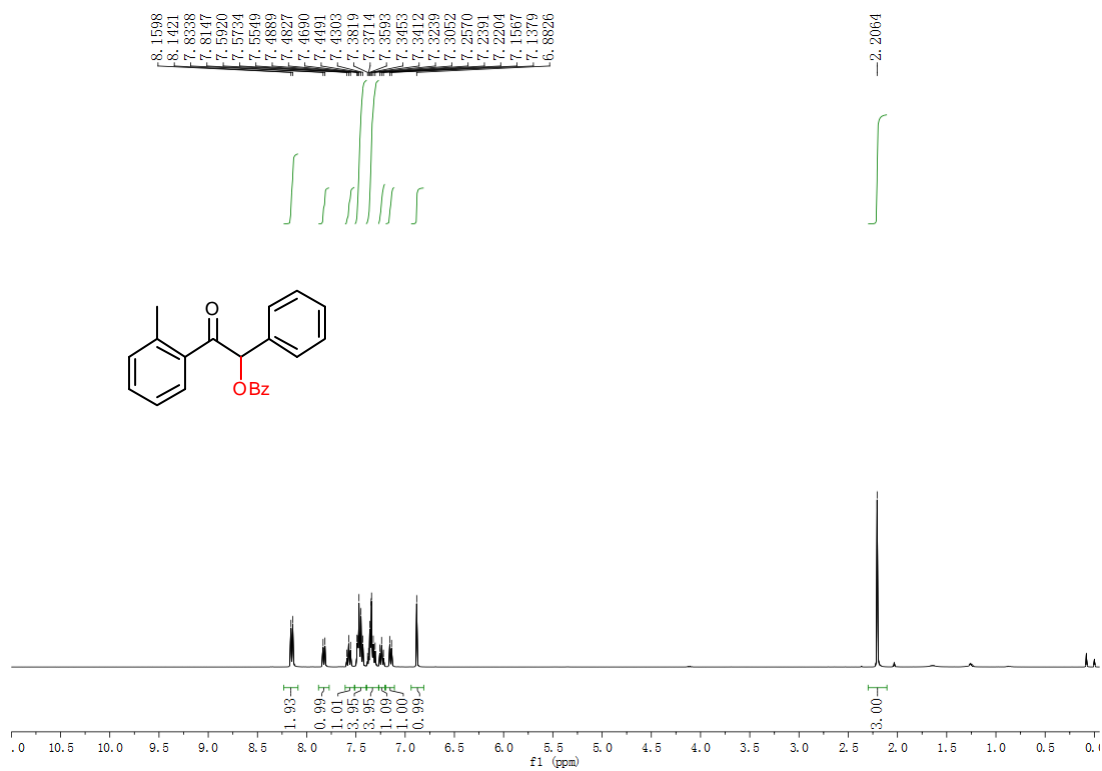
2-oxo-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl benzoate (3ea)



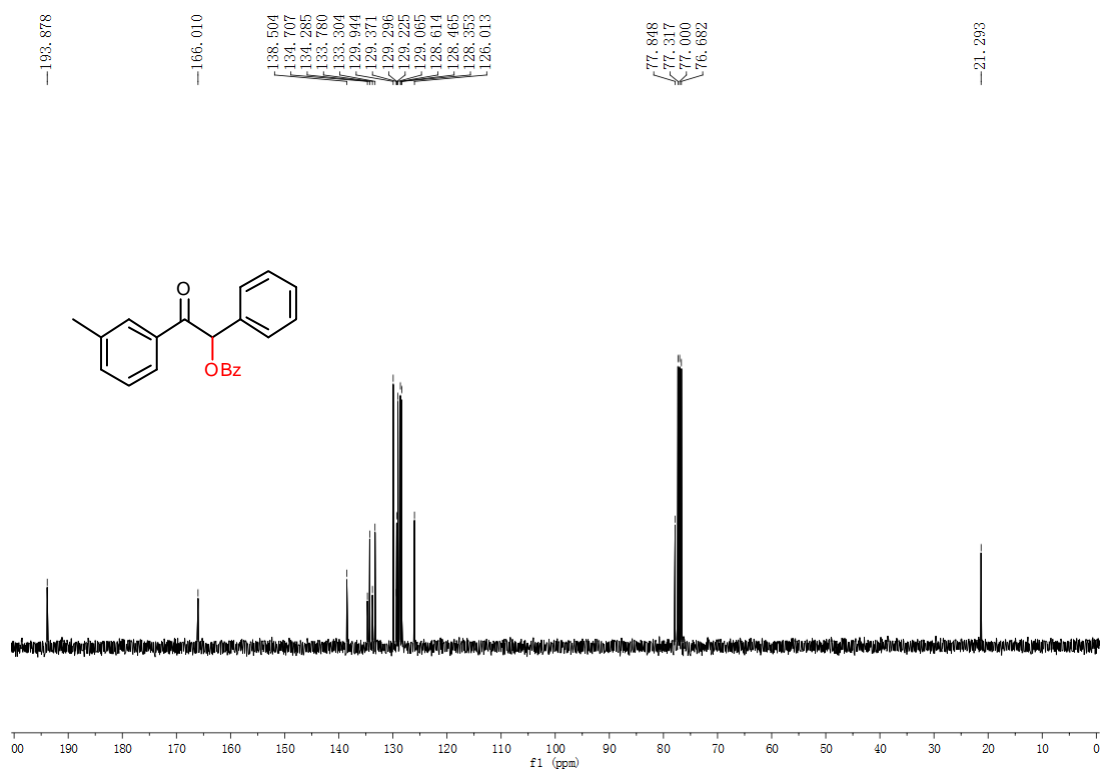
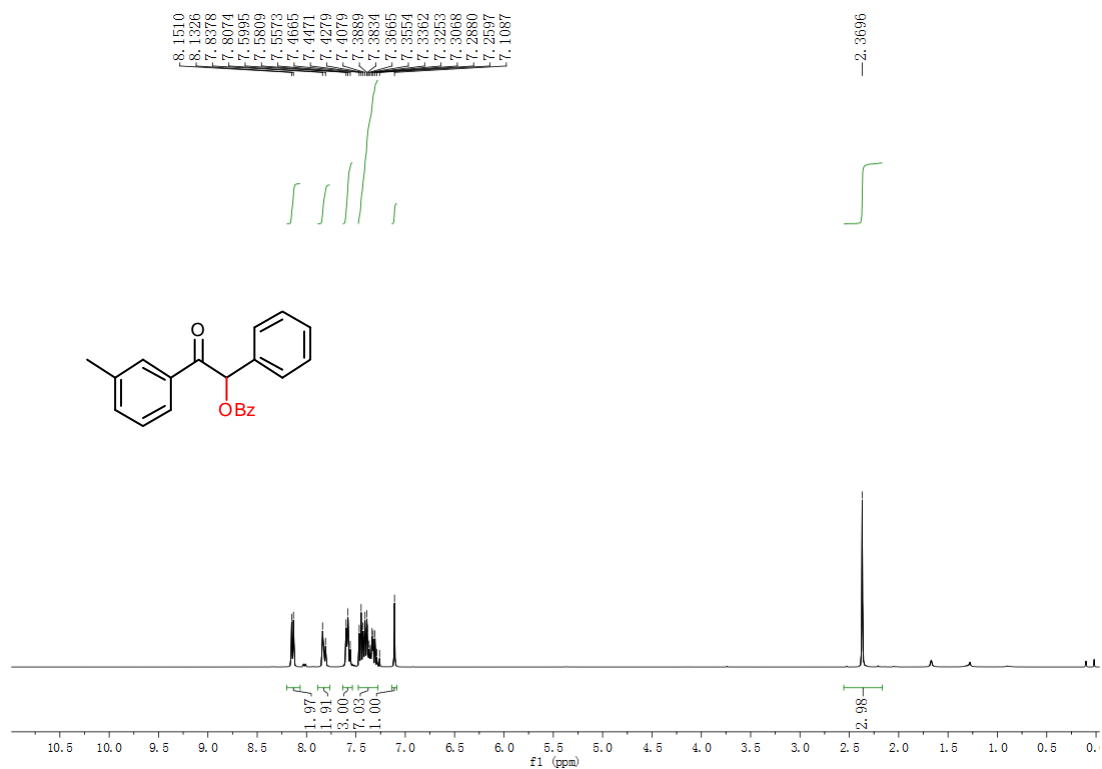
2-(3-nitrophenyl)-2-oxo-1-phenylethyl benzoate (3fa)



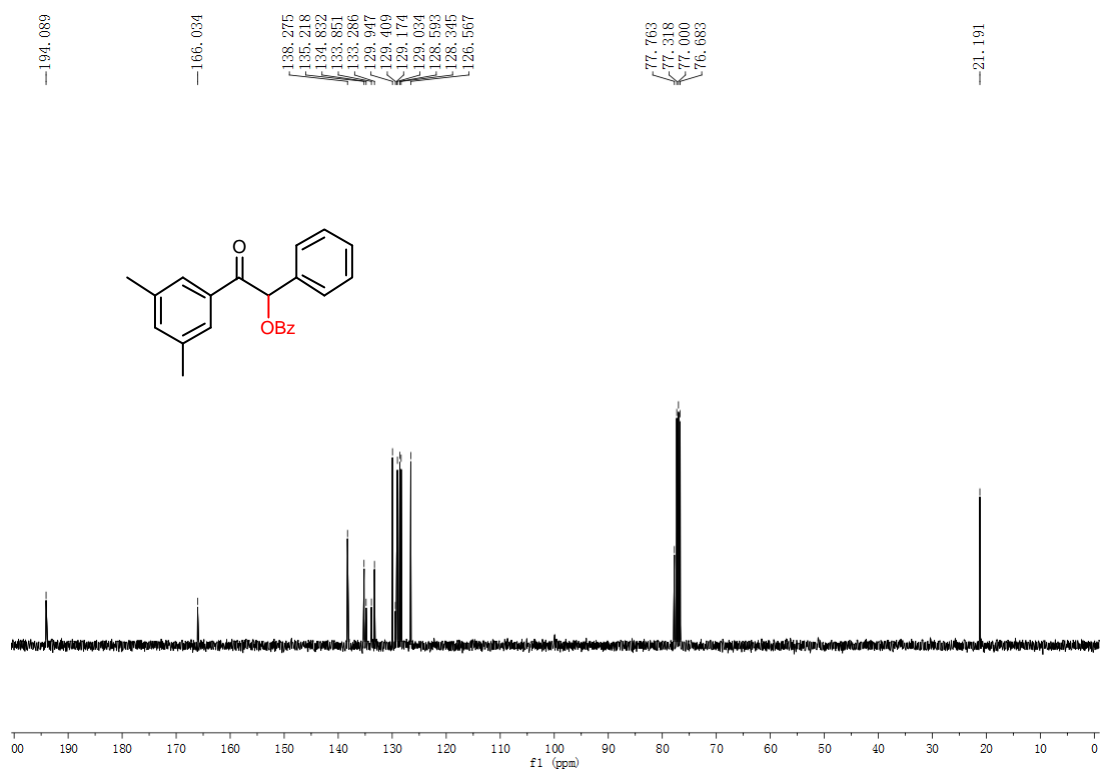
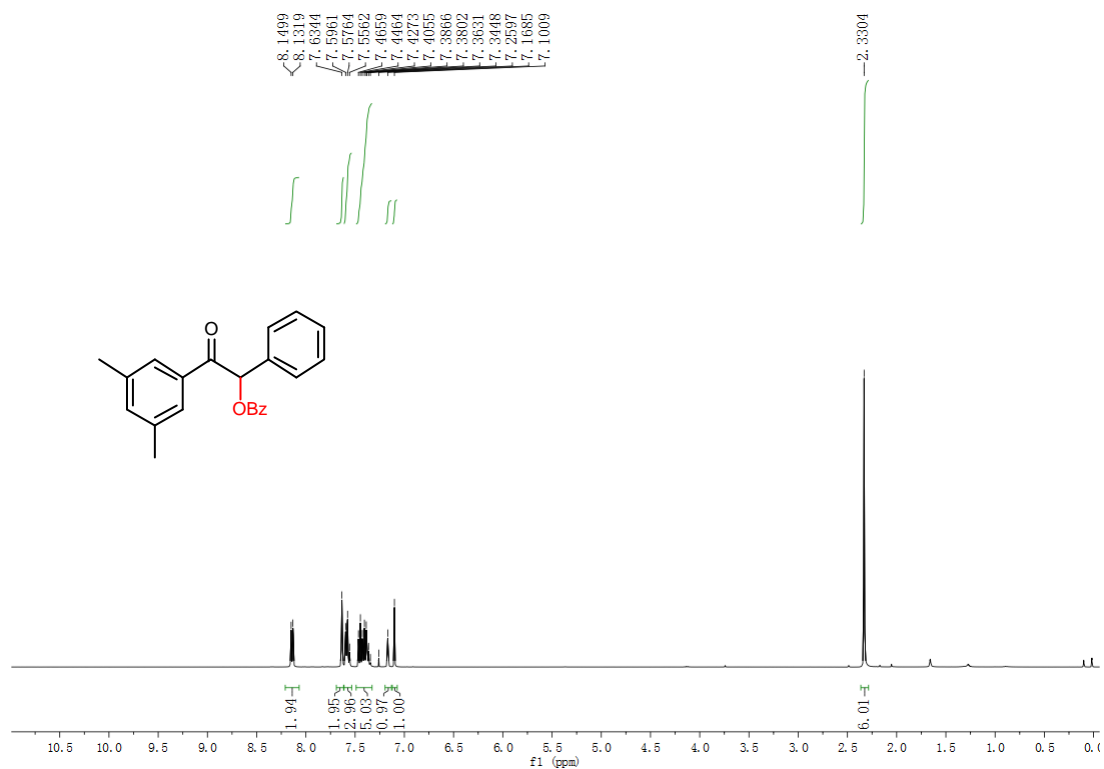
2-oxo-1-phenyl-2-(o-tolyl)ethyl benzoate (3ga)



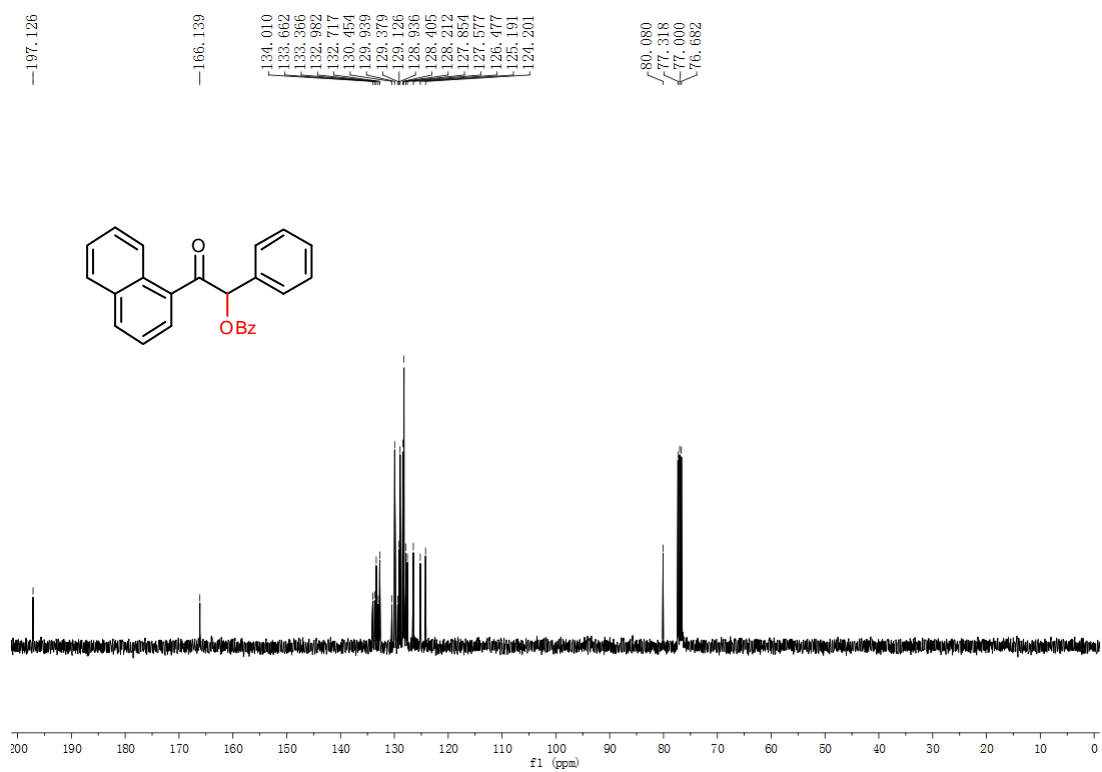
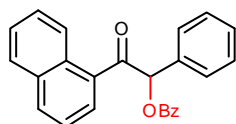
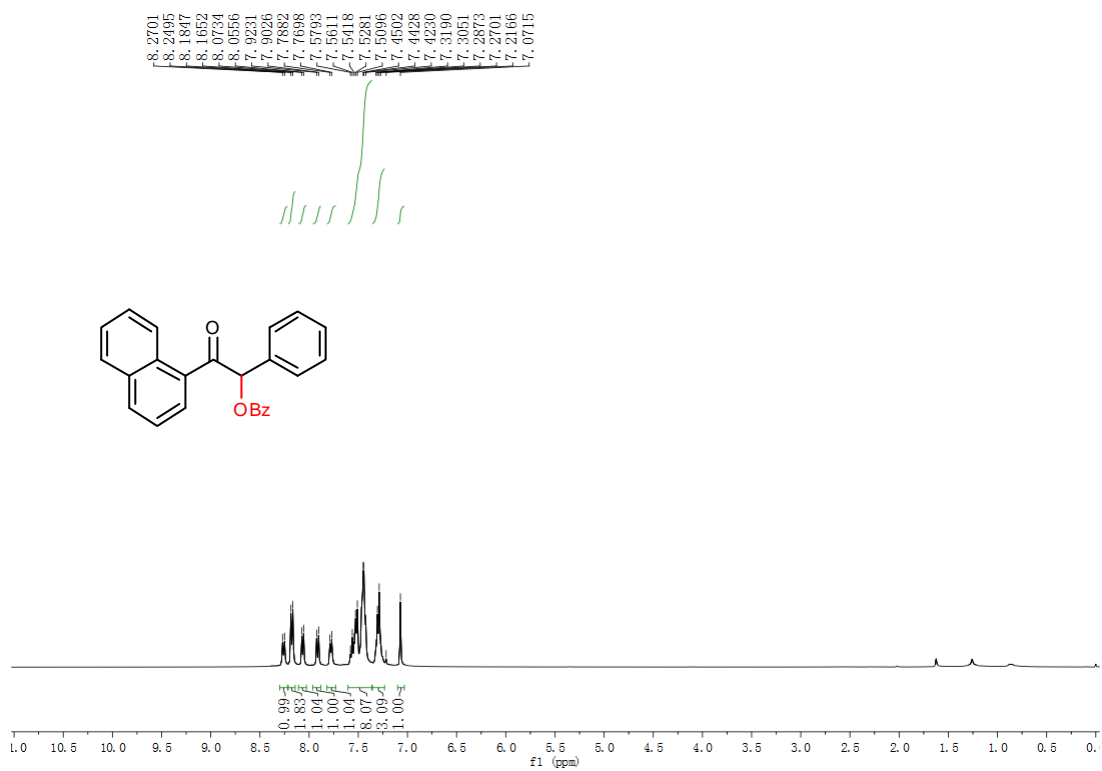
2-oxo-1-phenyl-2-(m-tolyl)ethyl benzoate (3ha)



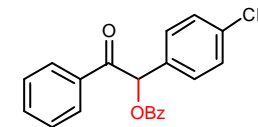
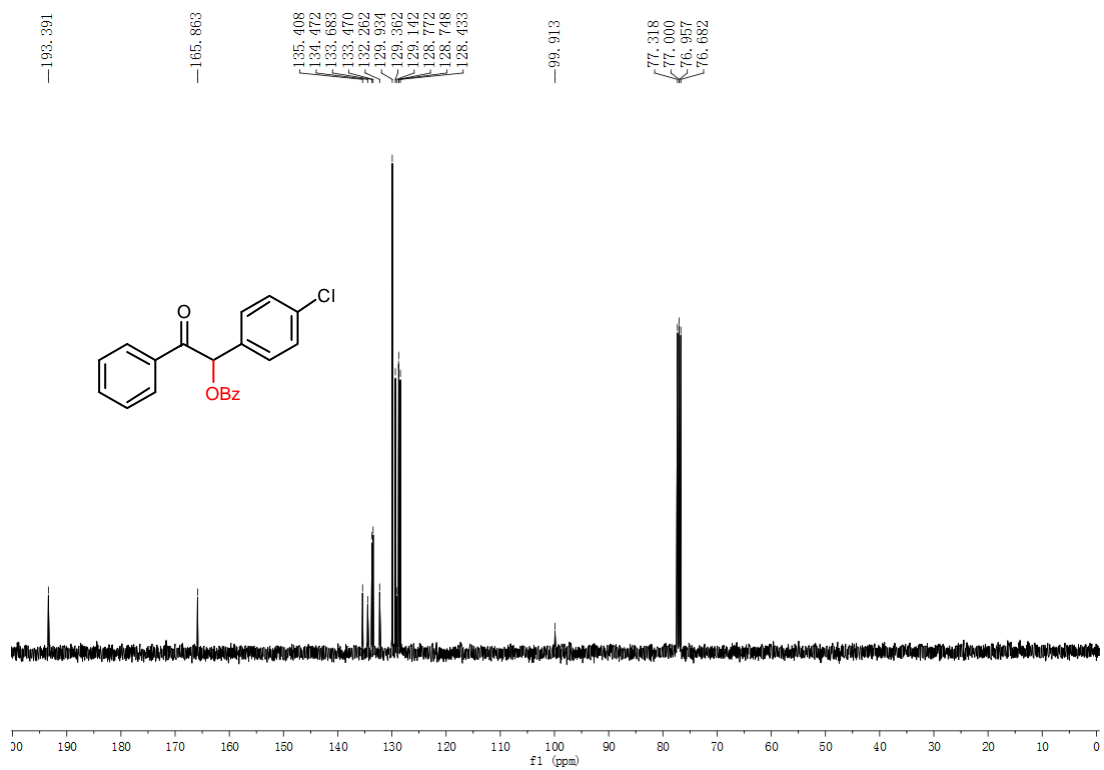
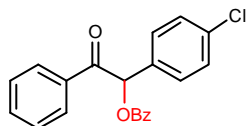
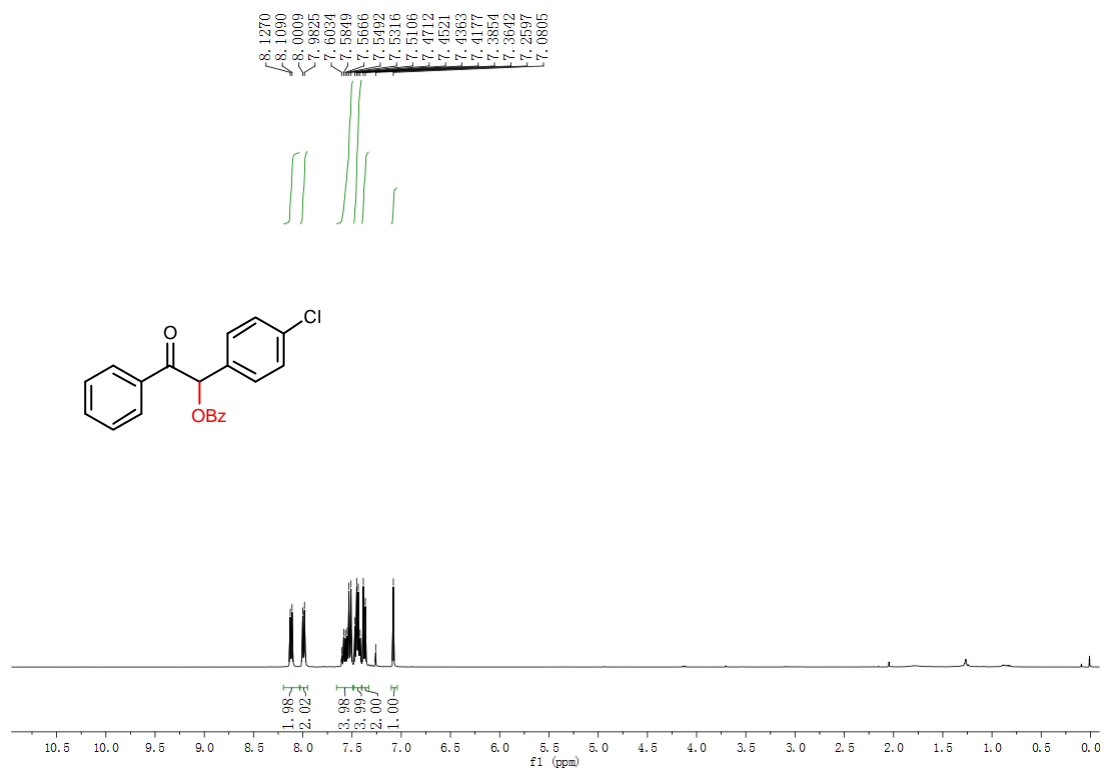
2-(3,5-dimethylphenyl)-2-oxo-1-phenylethyl benzoate (3ia)



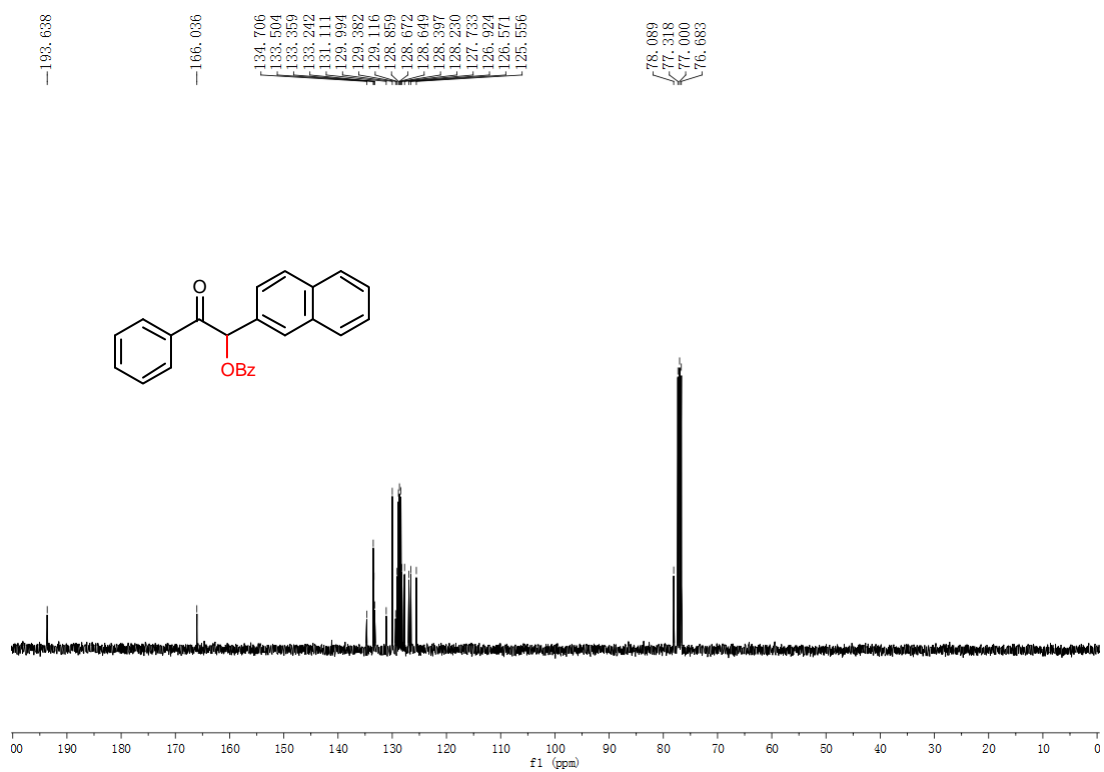
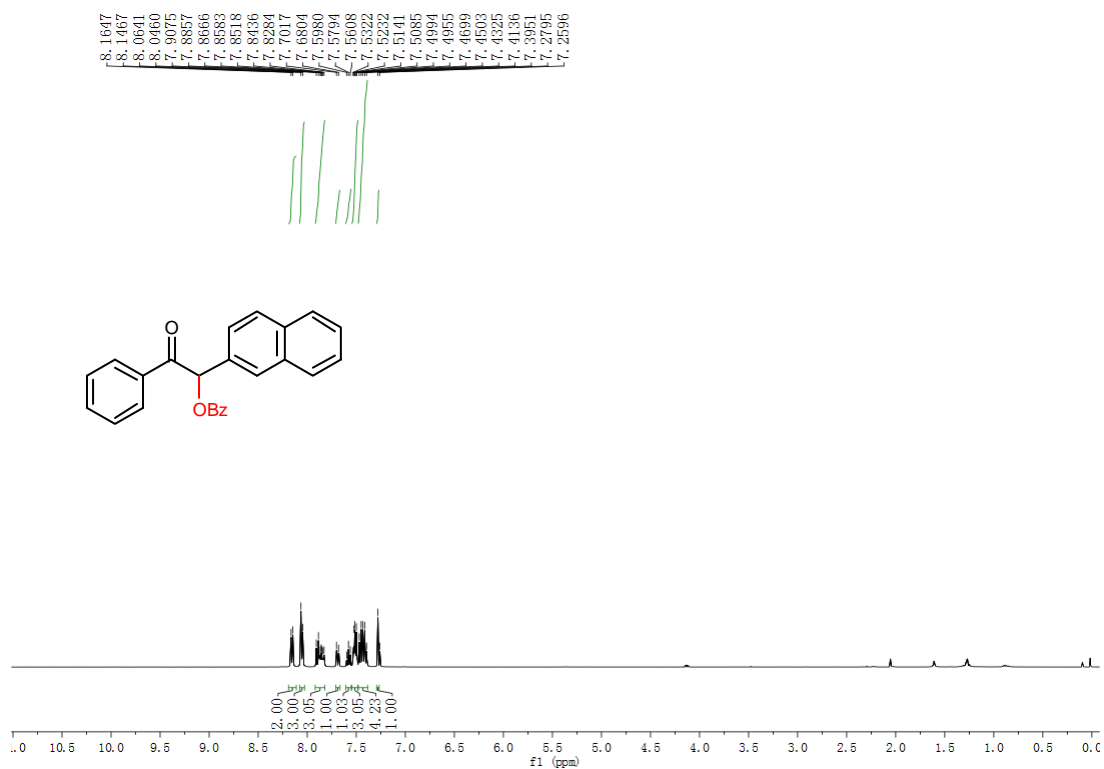
2-(naphthalen-1-yl)-2-oxo-1-phenylethyl benzoate (3ja)



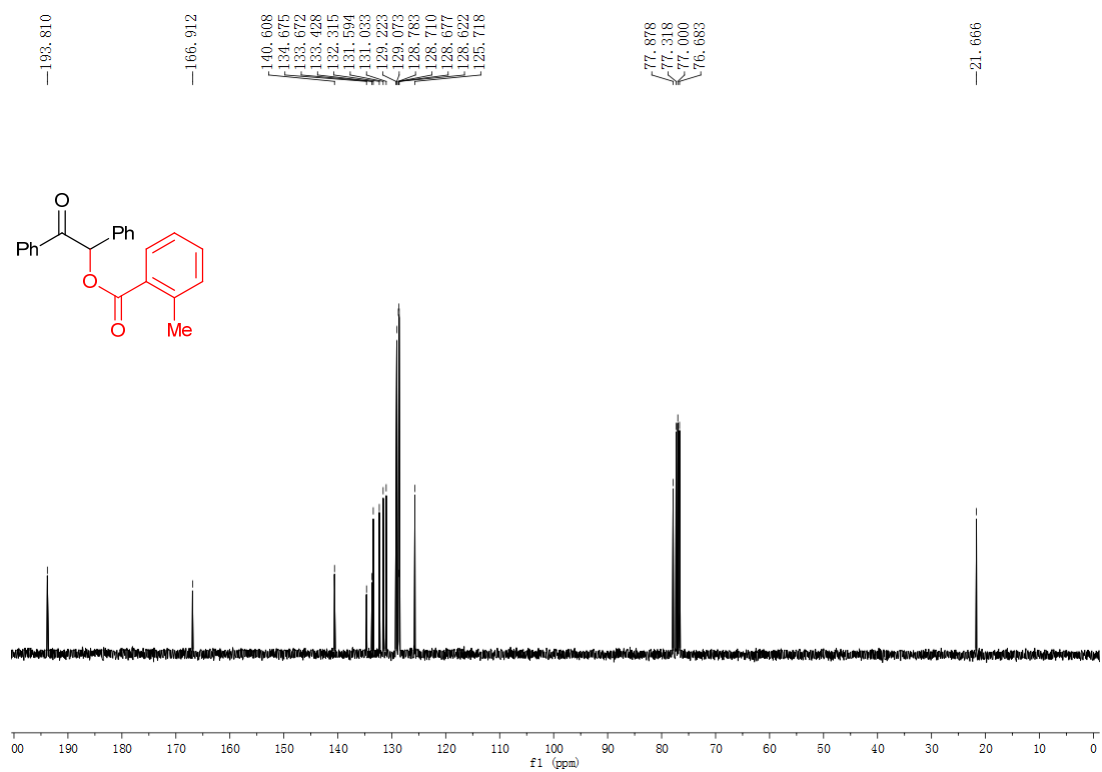
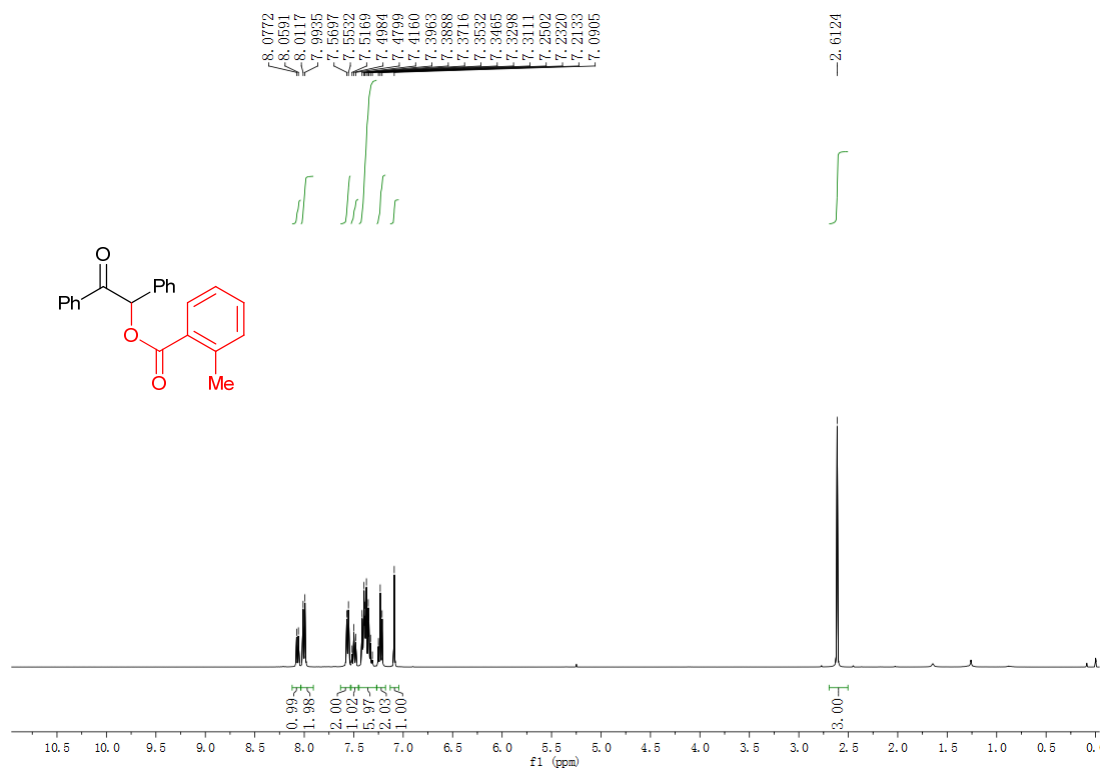
1-(4-chlorophenyl)-2-oxo-2-phenylethyl benzoate (3ka)



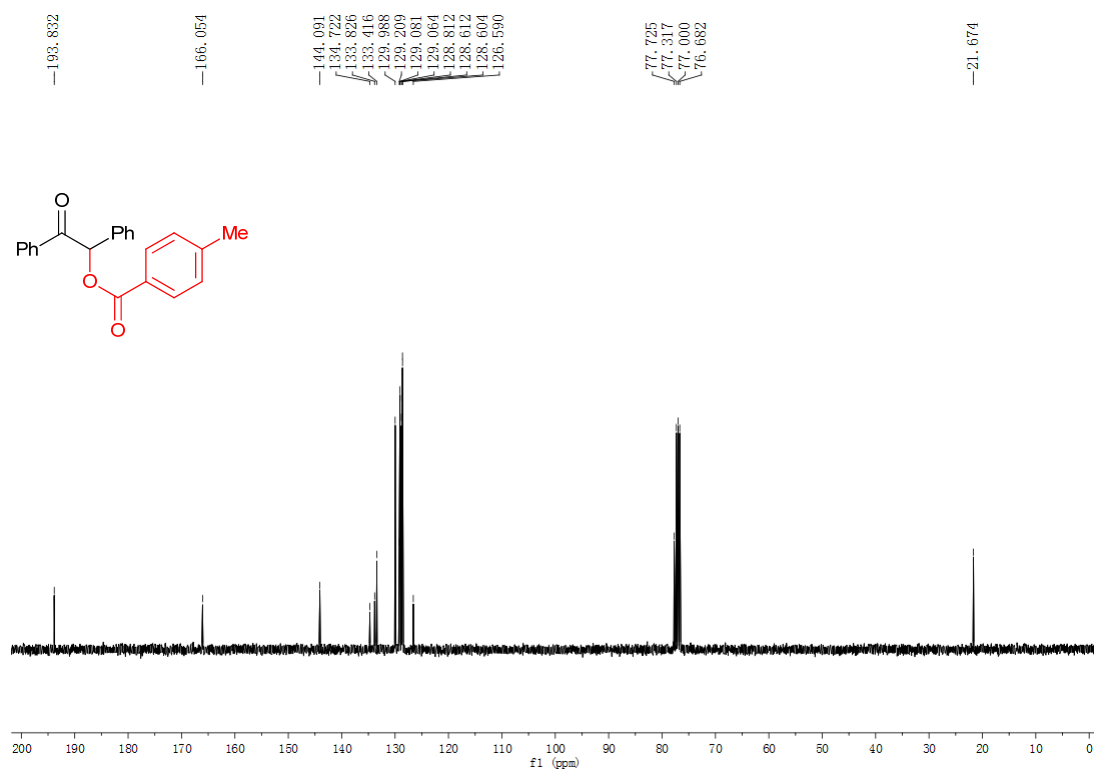
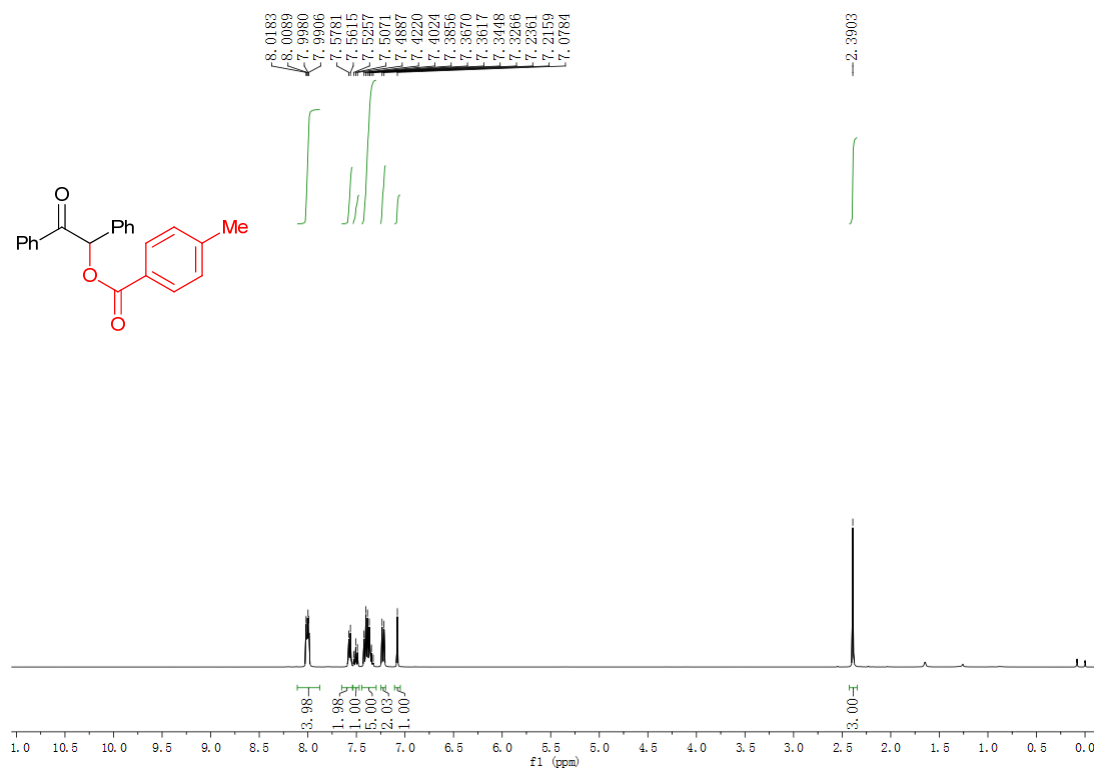
1-(naphthalen-2-yl)-2-oxo-2-phenylethyl benzoate (3la)



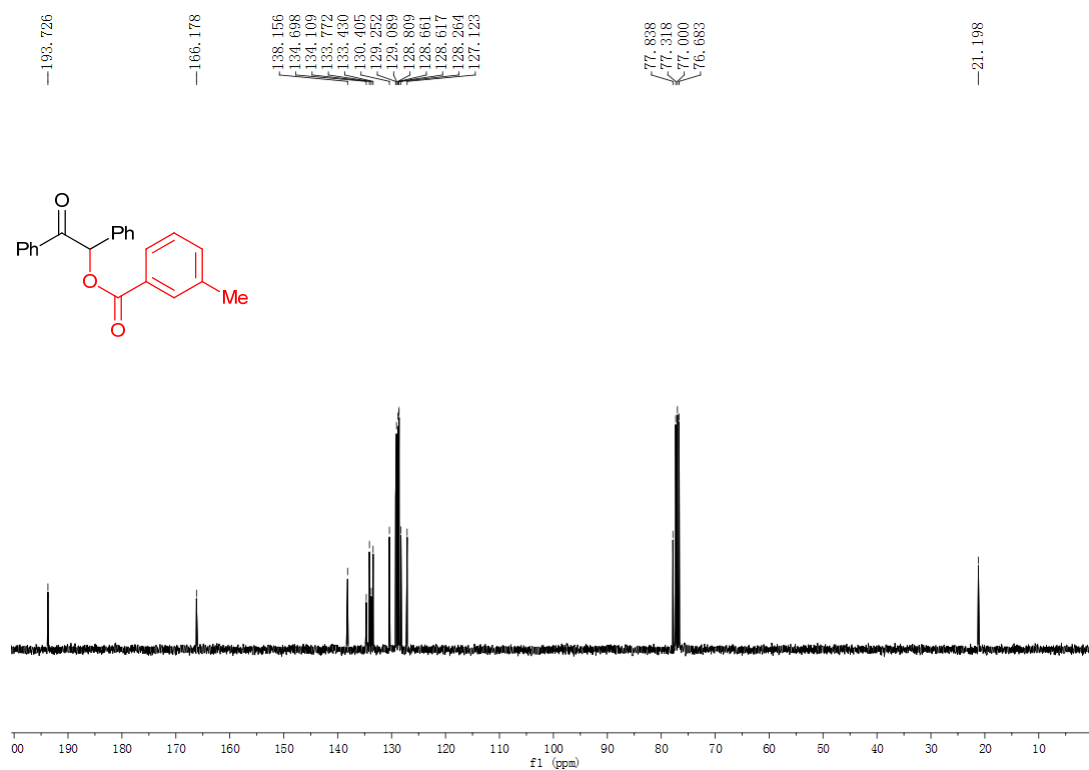
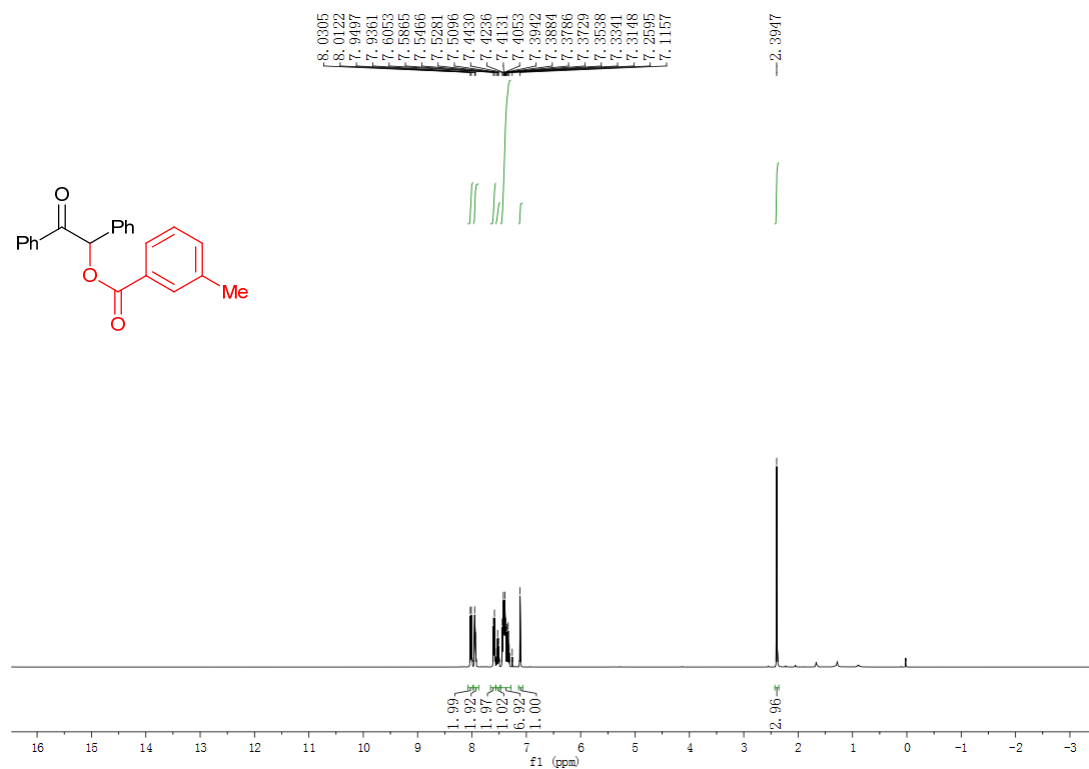
2-oxo-1,2-diphenylethyl 2-methylbenzoate (3ab)



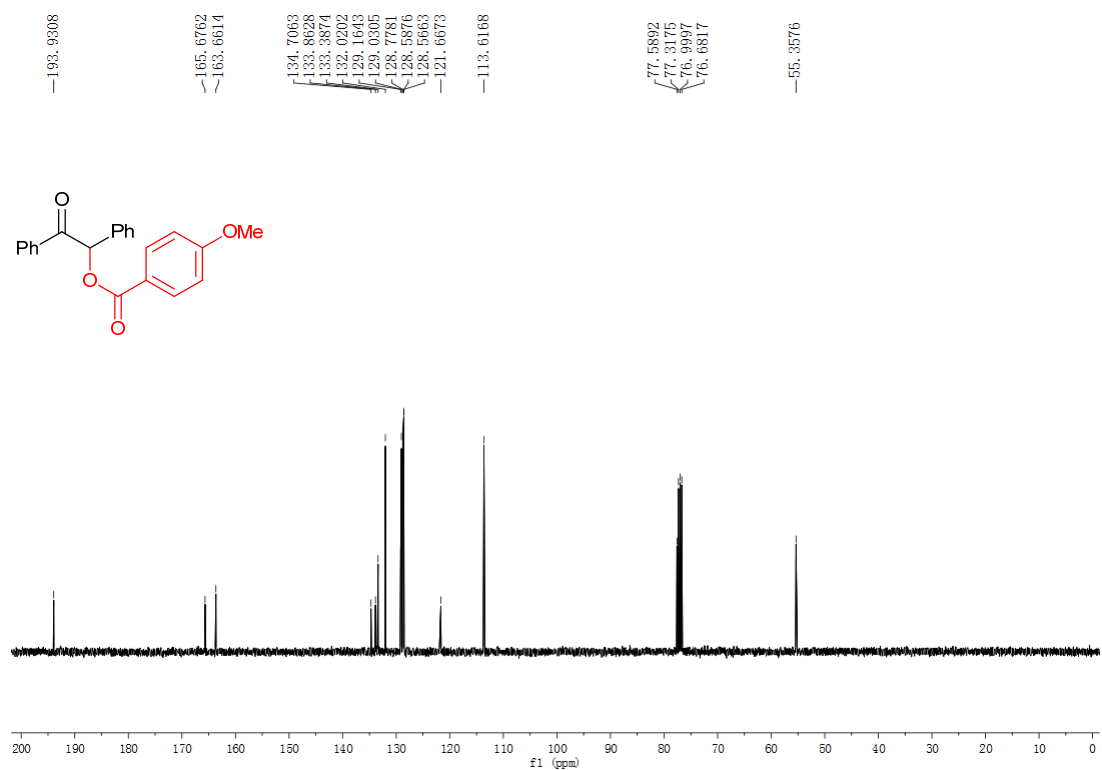
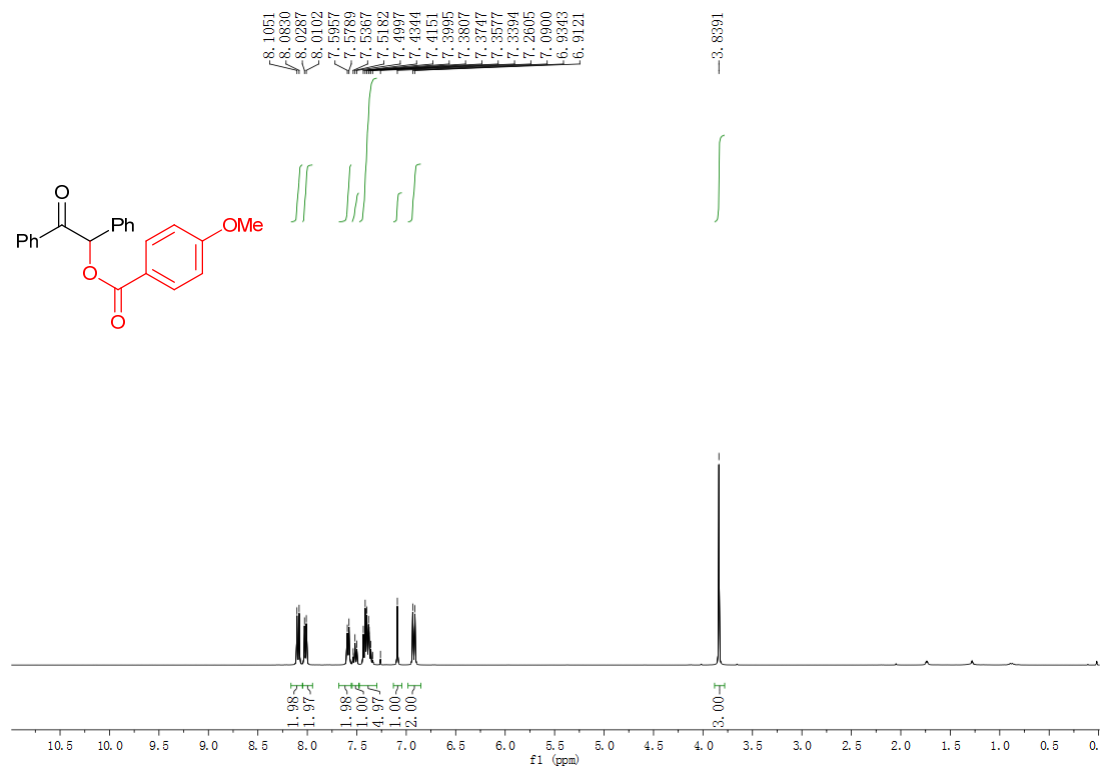
2-oxo-1,2-diphenylethyl 4-methylbenzoate (3ac)



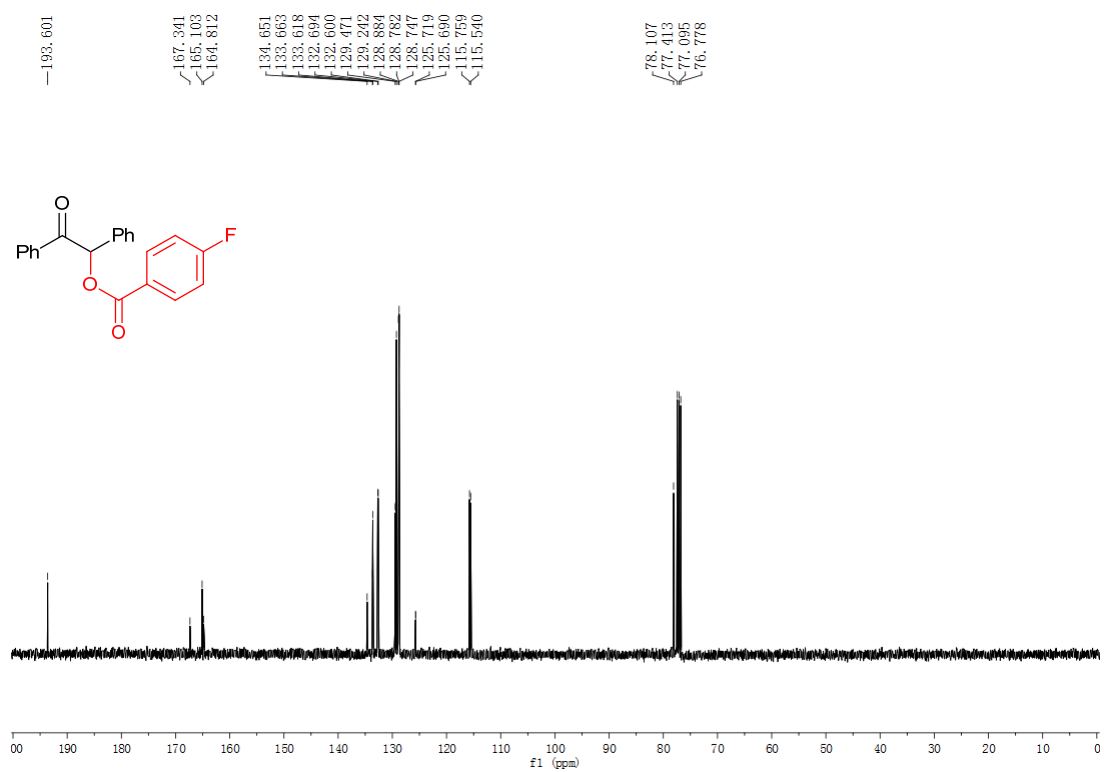
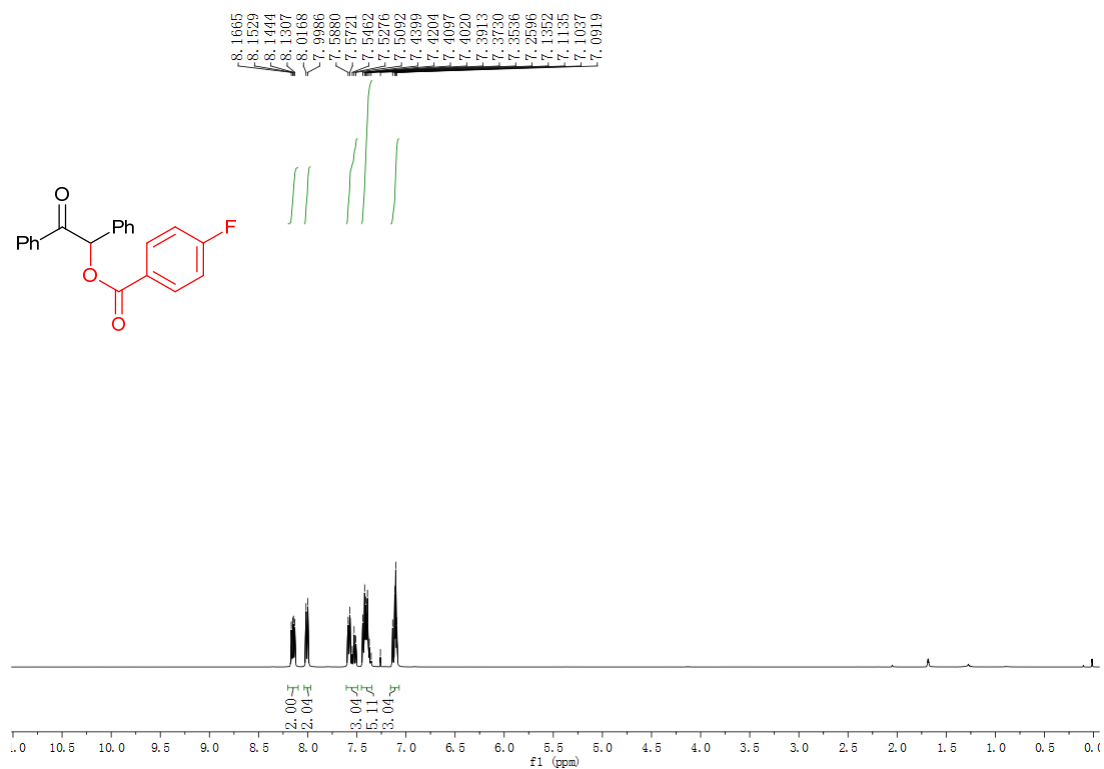
2-oxo-1,2-diphenylethyl 3-methylbenzoate (3ad)



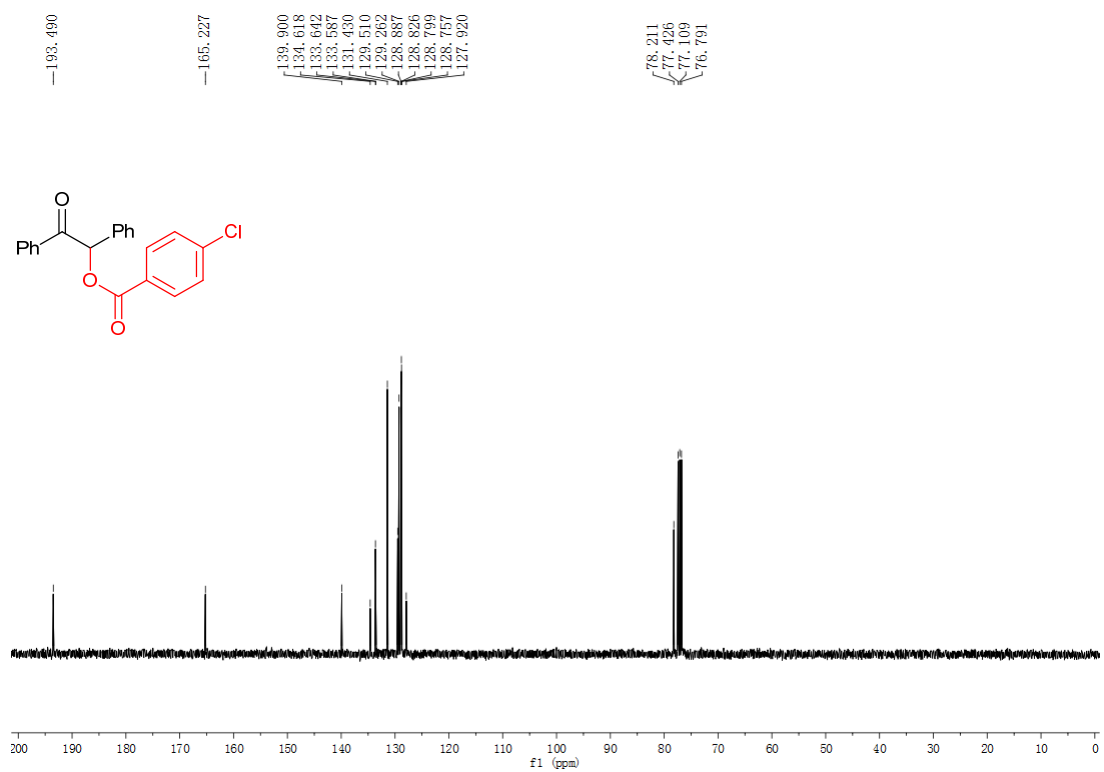
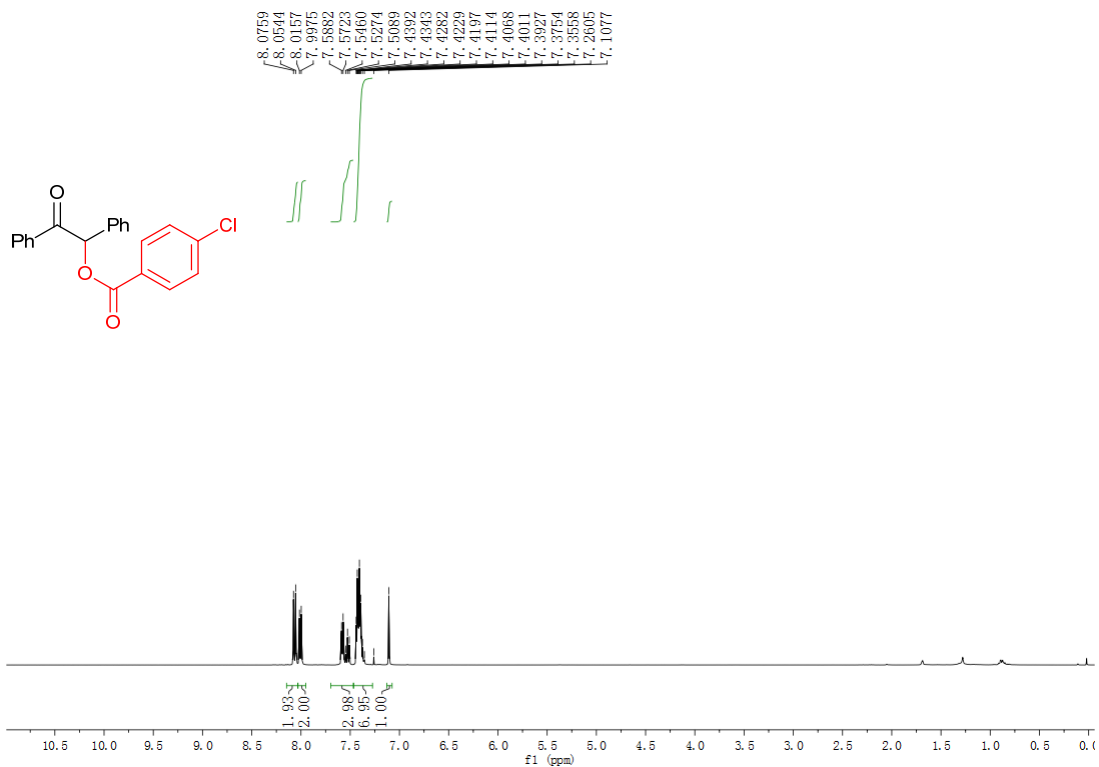
2-oxo-1,2-diphenylethyl 4-methoxybenzoate (3ae)



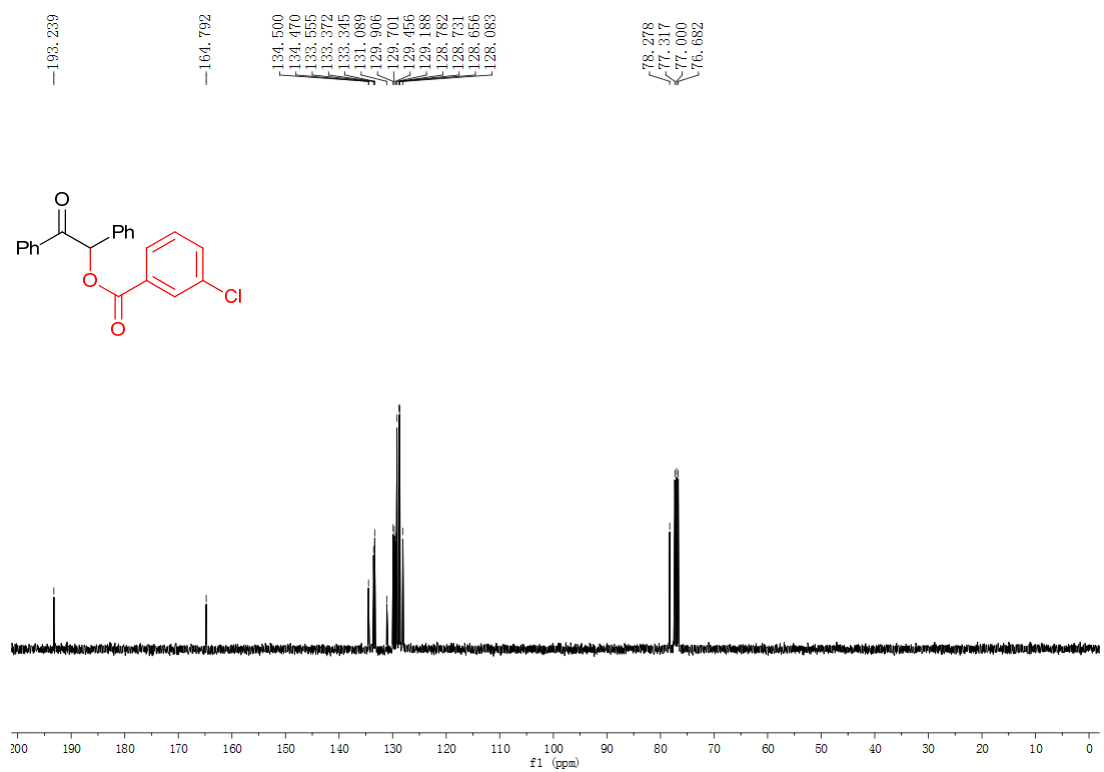
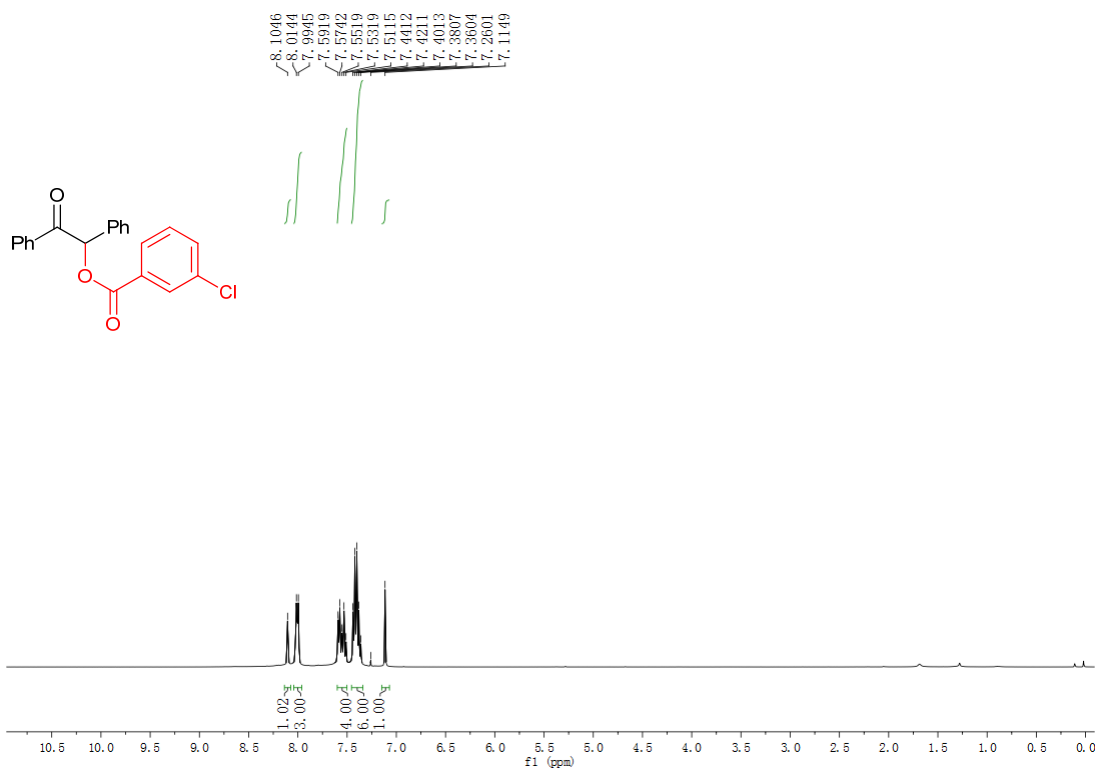
2-oxo-1,2-diphenylethyl 4-fluorobenzoate (3af)



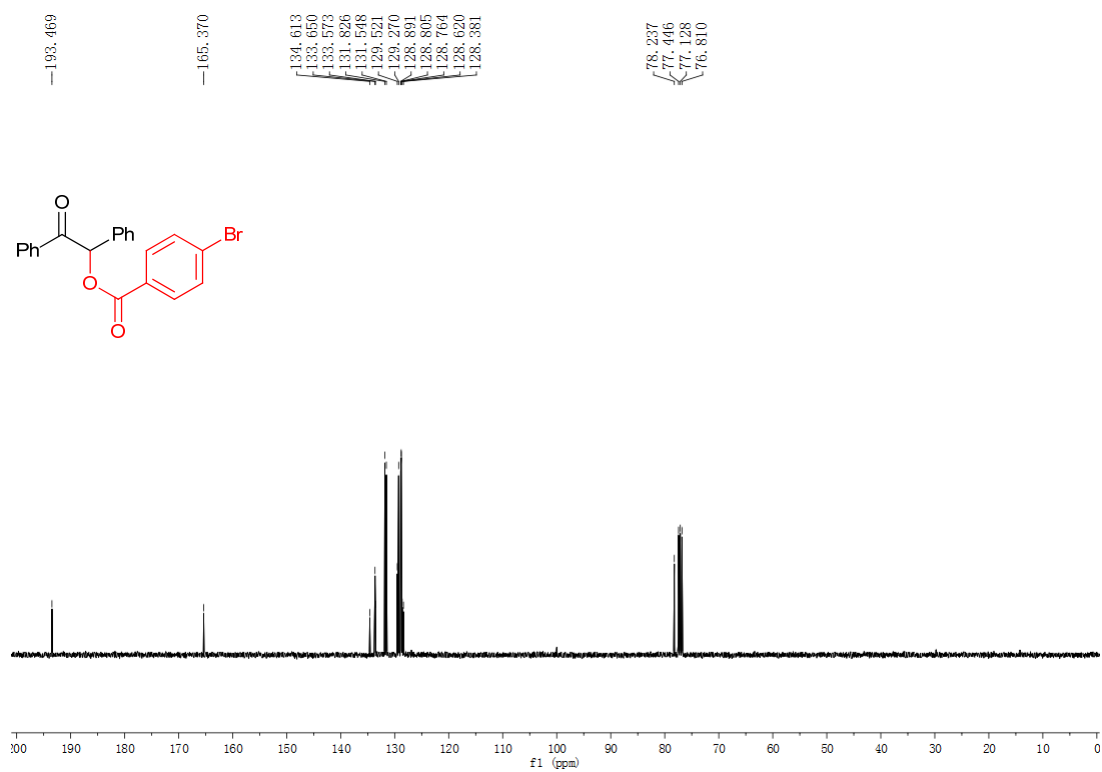
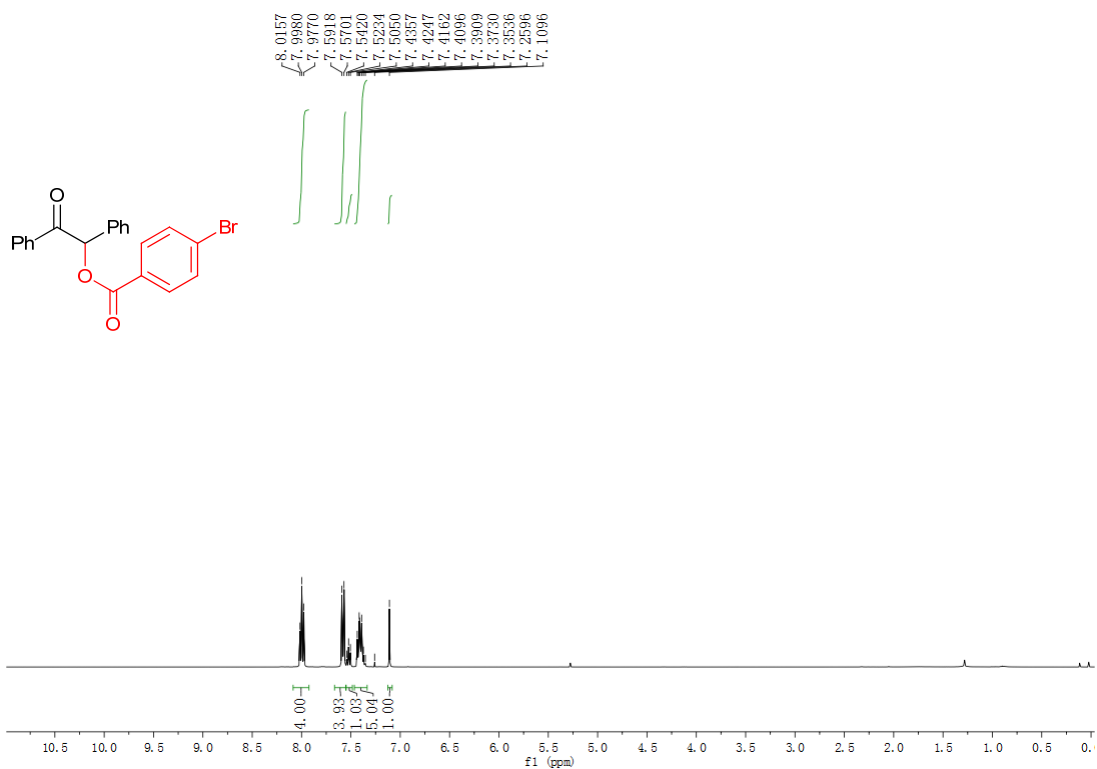
2-oxo-1,2-diphenylethyl 4-chlorobenzoate (3ag)



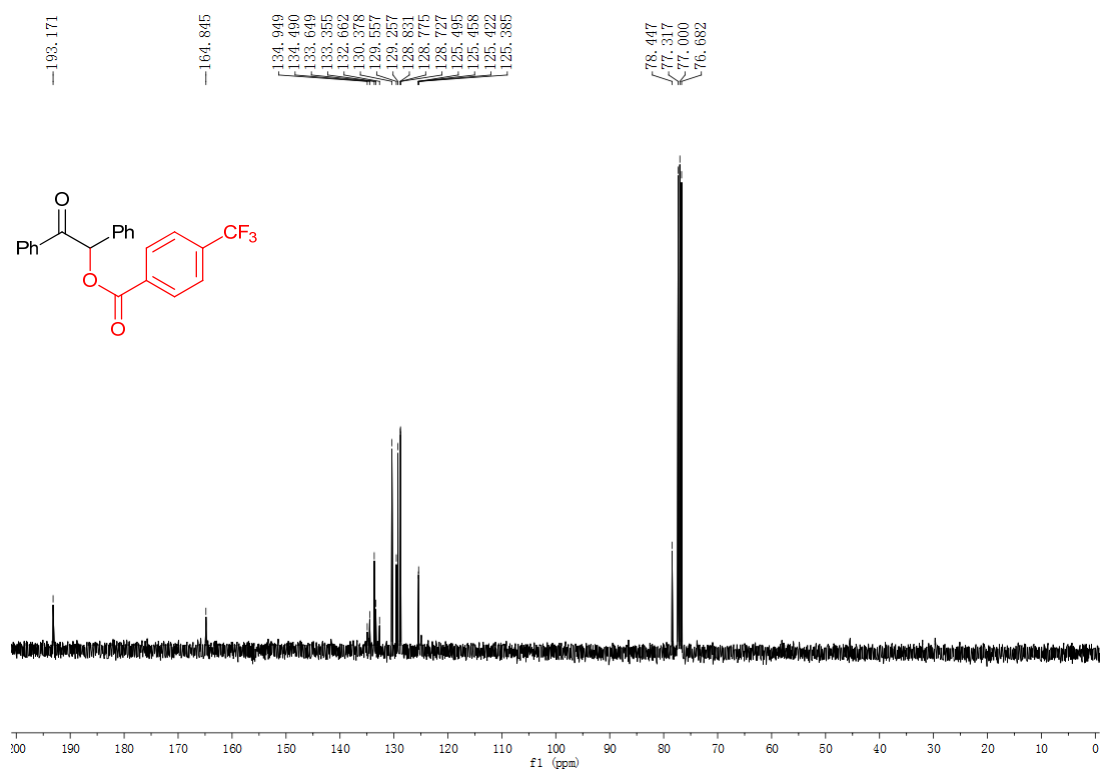
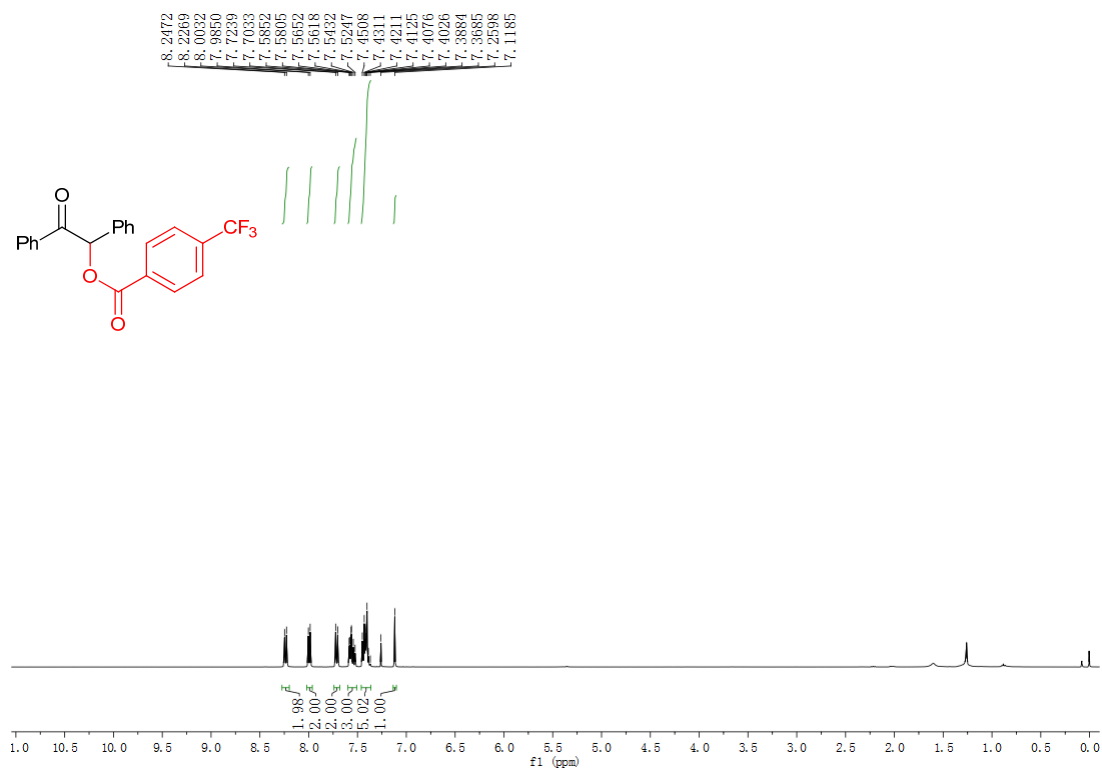
2-oxo-1,2-diphenylethyl 3-chlorobenzoate (3ah)



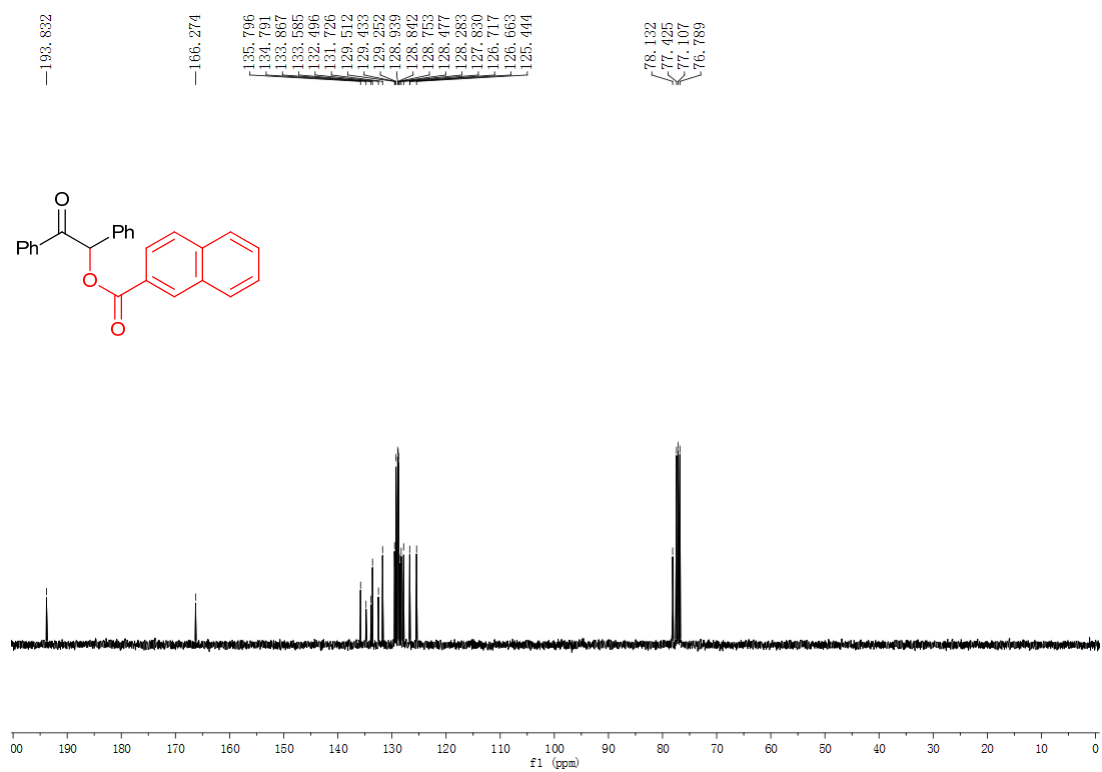
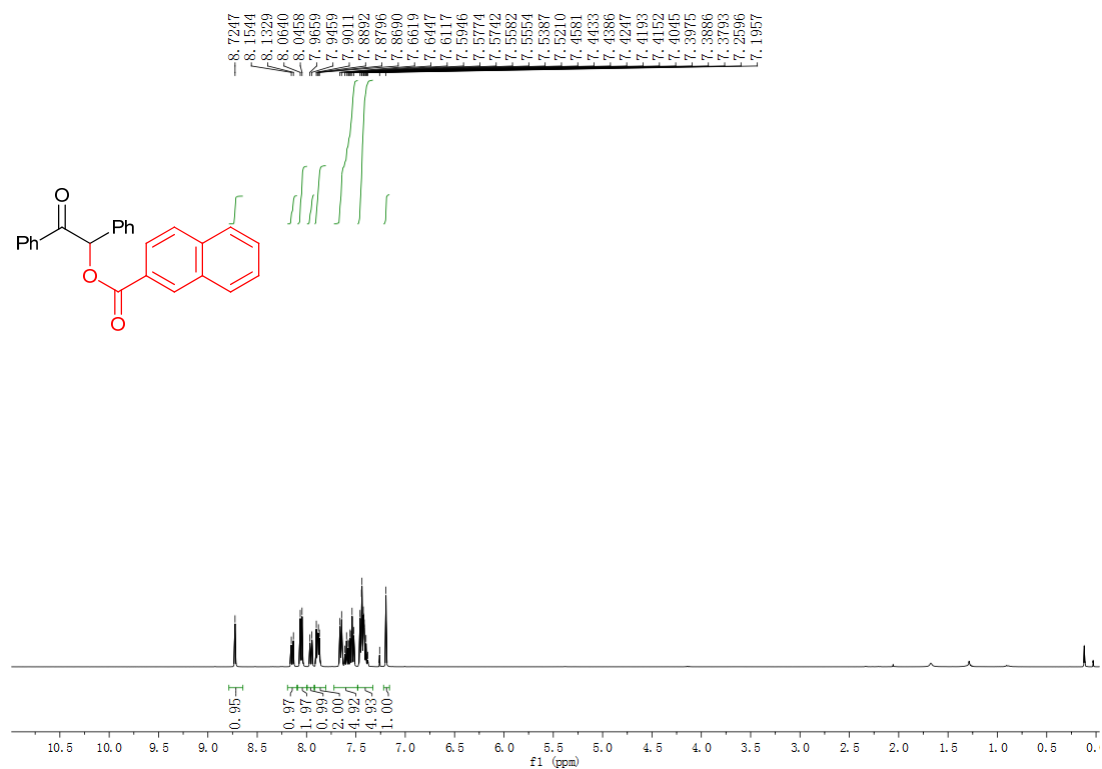
2-oxo-1,2-diphenylethyl 4-bromobenzoate (3ai)



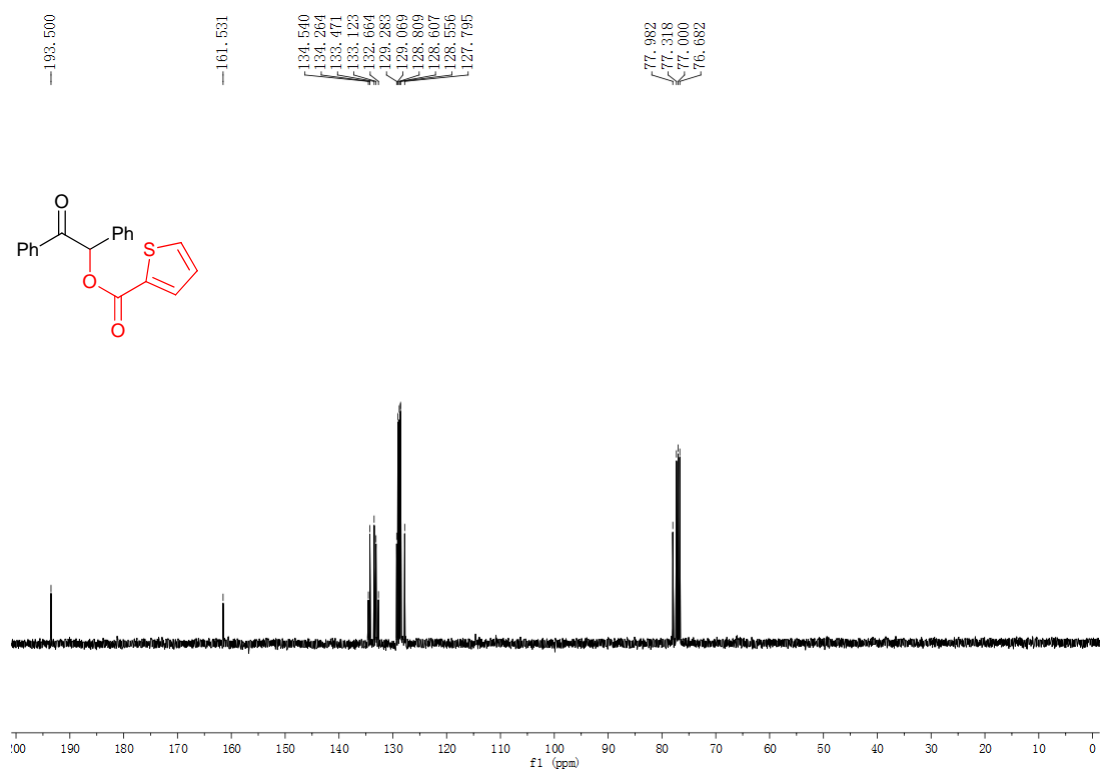
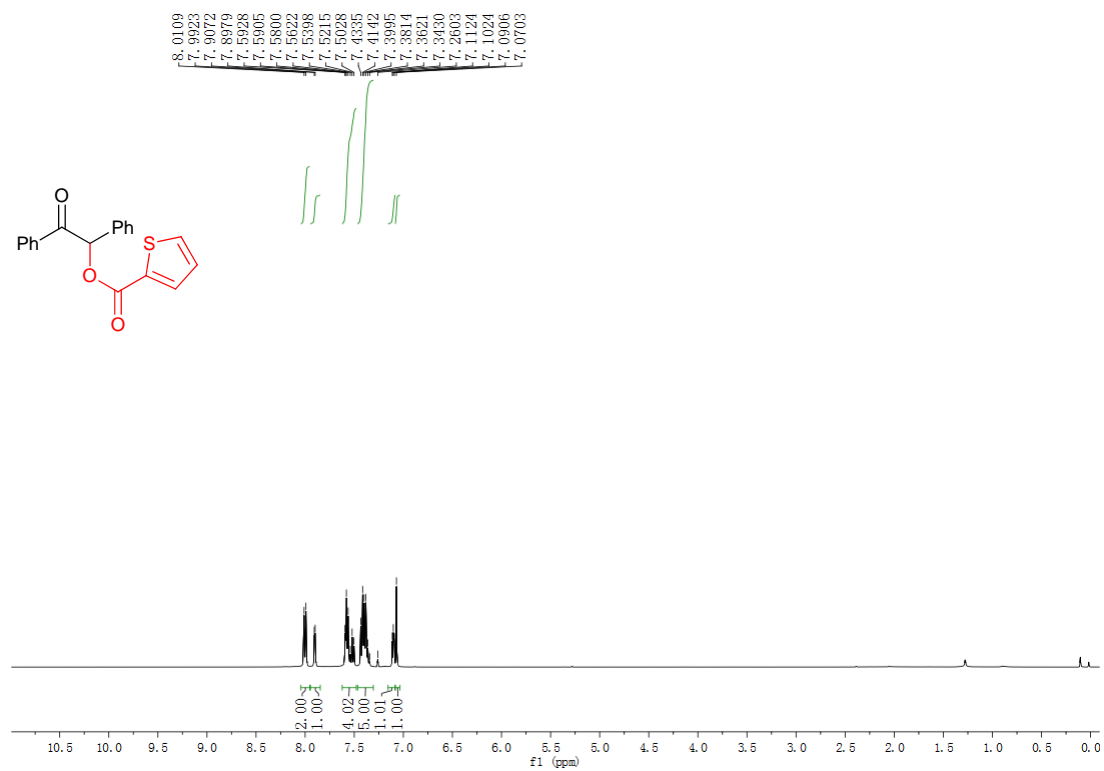
2-oxo-1,2-diphenylethyl 4-(trifluoromethyl)benzoate (3aj)



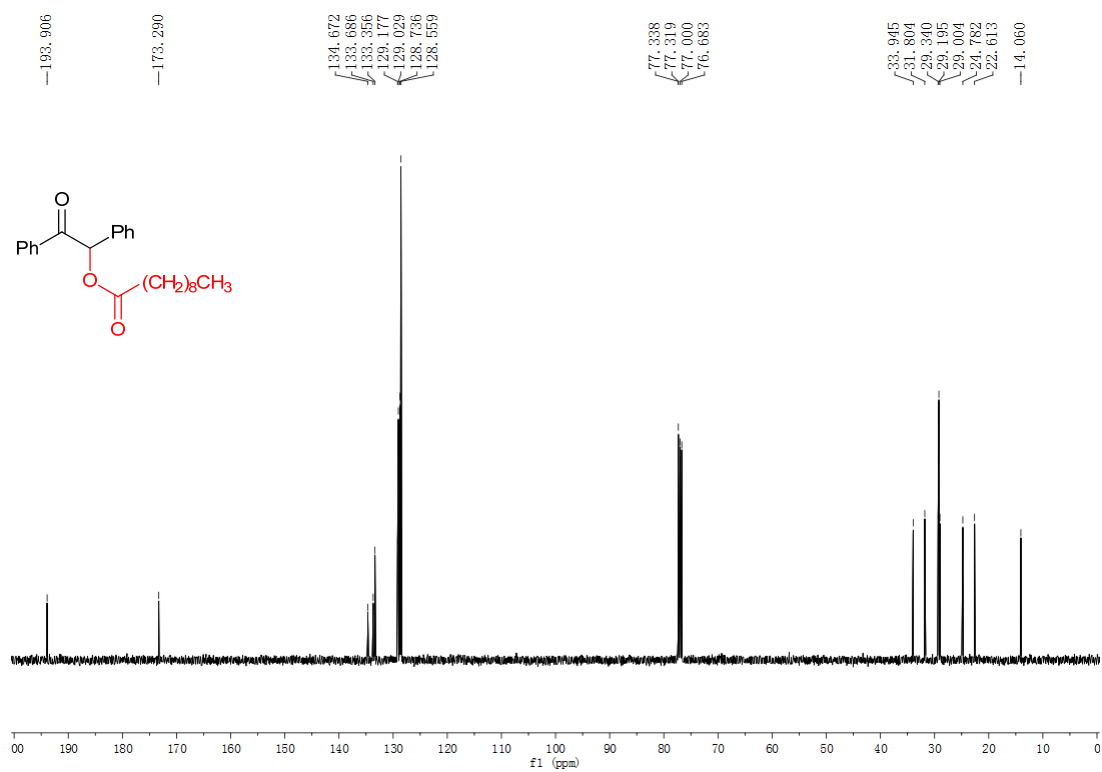
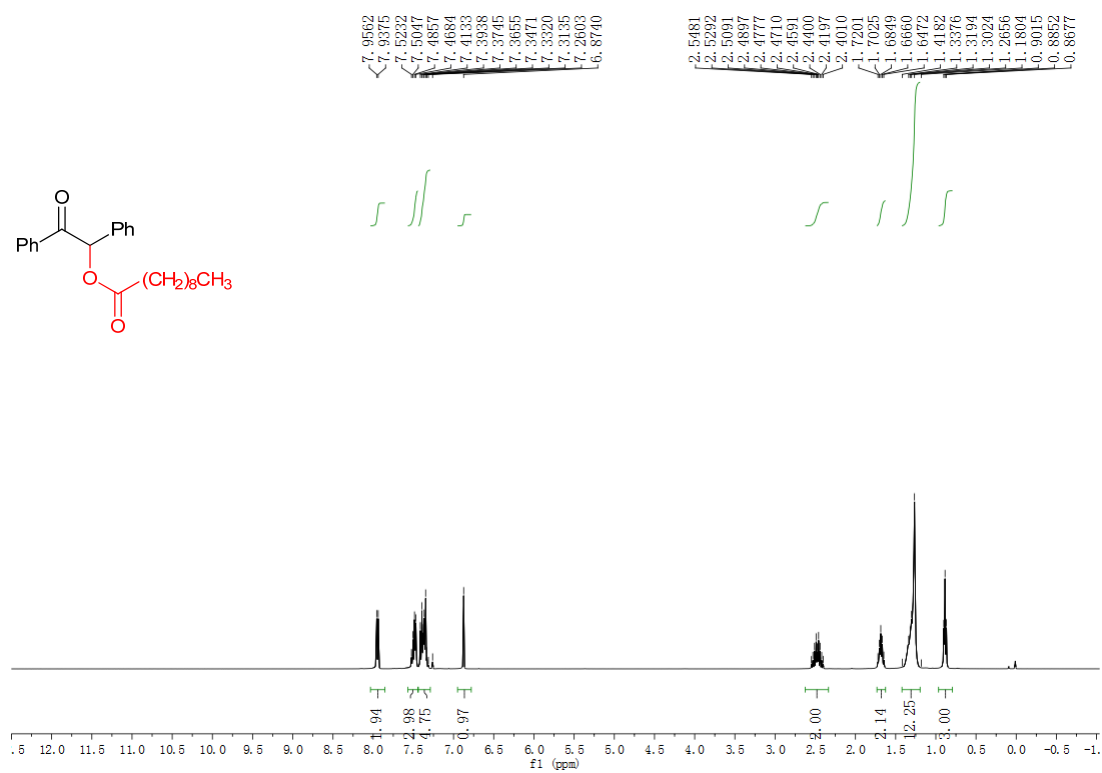
2-oxo-1,2-diphenylethyl 2-naphthoate (3ak)



2-oxo-1,2-diphenylethyl thiophene-2-carboxylate (3a)



2-oxo-1,2-diphenylethyl decanoate (3am)



2-oxo-1,2-diphenylethyl stearate (3an)

