Supporting Information
Iron-Catalyzed Oxidative Cyclization of Olefinic 1,3-Dicarbonyls with Ketone C(sp^3)–H Bonds: Facile Access to 2,3-Dihydrofurans

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List of Contents

(A) Typical experimental procedure for the synthesis of 1 and oxidative cyclization

The dicarbonyl compounds (10 mmol) was dissolved in DMF (20 mL) in a dried round bottom flask, followed by addition of the corresponding allyl bromide (11 mmol) and K_2CO_3 (15 mmol). The mixture was stirred at 65 °C for 6 h under an Aratmosphere. Then diluted with Water (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography to give the corresponding **1**.

To a Schlenk tube were added olefinic 1,3-dicarbonyls **1** (0.2 mmol), ketones **2** (0.5 mL), $FeCl_3$ (10 mol%) and TBPB (2.0 equiv). Then the tube was stirred at 90 ^oC sealed in air for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 5:1) to afford the desired product **3**.

(B) Electron paramagnetic resonance (EPR) experiment

The EPR experiment was monitored under following conditions: DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) (5.6 uL) was dissolved in acetylacetone (1 mL) to form a 50 mM solution, then $FeCl_3$ (10 mol%) and TBPB (2.0 equiv) was added. The mixture was stirred at 90 ^oC for 2 min, after that 40 uL of the mixture was transferred to a flat cell and was measured, a strong signal with a g = 2.0036, AN = 1.467 mT,

AH = 2.254 mT, which was coincident with a carbon-centered radical was observed (Figure 1).

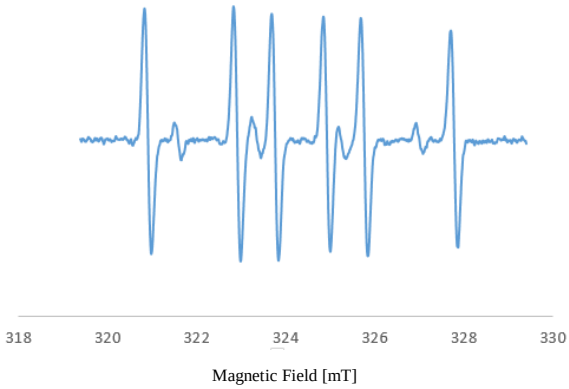
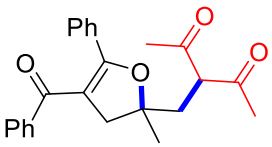


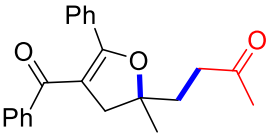
Figure 1. EPR experiment.

Measurement conditions: Power 1 mW, Frequency 9.439 GHz, Center field 336.638 mT, Sweep width 10mT, Modulation width 0.1 mT, Sweep time 1.0 min, Time constant 0.1s, Amplitude 400.

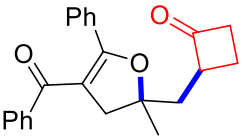
(C) Analytical data



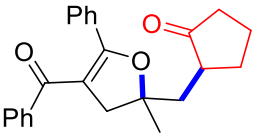
3-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl) methyl)pentane-2,4-dione (3aa), yellow oil (0.0609 g, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.60-7.55 (m, 2H), 7.48-7.44 (m, 4H), 5.52-5.50 (m, 1H), 2.85-2.76 (m, 2H), 2.73-2.69 (m, 1H), 2.46-2.43 (m, 1H), 2.11 (s, 6H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.5, 194.9, 194.8, 166.1, 135.9, 135.4, 133.8, 133.6, 130.1, 128.9 (2), 128.6, 112.0, 87.6, 52.5, 42.7, 39.0, 29.4, 26.6, 15.1; HRMS *m/z* (ESI) calcd for $C_{24}H_{25}O_4$ ($[M+H]^+$) 377.1747, found 377.1743.



4-(4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)butan-2-one (3ab), yellow oil (0.0575 g, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 2H), 7.22-7.19 (m, 1H), 7.18-7.15 (m, 3H), 7.08-7.03 (m, 4H), 3.16 (d, J = 15.0 Hz, 1H), 3.05 (d, J = 15.0 Hz, 1H), 2.68-2.64 (m, 2H) 2.19 (s, 3H), 2.15-2.10 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 207.8, 193.7, 165.0, 139.1, 133.5, 131.0, 130.3, 129.9, 129.3, 128.9, 127.6, 111.7, 87.3, 43.8, 38.3, 34.3, 30.1, 26.3; HRMS *m/z* (ESI) calcd for $C_{22}H_{23}O_3$ ($[M+H]^+$) 335.1642, found 335.1648.

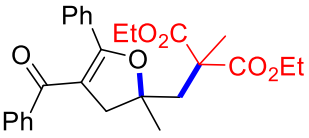


2-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)cyclobutan-1-one (3ac), yellow oil (0.0388 g, 56% yield, d.r. = 1.5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99-7.94 (m, 4H), 7.59-7.54 (m, 2H), 7.47-7.42 (m, 4H), 3.56-3.48 (m, 1H), 3.11-3.06 (m, 2H), 2.94-2.89 (m, 1H), 2.52-2.44 (m, 2H), 2.34-2.22 (m, 3H), 1.67 (s, 1.2H), 1.62 (s, 1.8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 211.0, 210.1, 199.3, 195.4, 165.6, 133.6 (2), 133.2, 133.1, 132.9, 131.3, 129.5, 129.4, 128.9 (2), 128.6 (2), 128.4, 128.1, 112.4, 83.9, 83.6, 56.2, 55.6, 45.4, 45.3, 44.6, 38.2, 38.0 19.2, 19.0, 17.3; HRMS *m/z* (ESI) calcd for $C_{23}H_{23}O_3$ ($[M+H]^+$) 347.1642, found 347.1638.

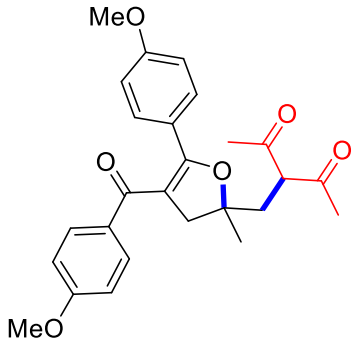


2-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)cyclopentan-1-one (3ad), yellow oil (0.0367 g, 51% yield, d.r. = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12-8.10 (m, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.42-7.40 (m, 2H), 7.20-7.16 (m, 3H), 7.07-7.03 (m, 3H), 3.23-3.03 (m, 2H), 2.54-2.49 (m, 1H), 2.40-2.27 (m, 3H), 2.15-2.05 (m, 2H), 1.81-1.74 (m, 2H),

1.69-1.63 (m, 1H), 1.57 (s, 1.5H), 1.56 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.8, 193.7, 171.2, 165.2, 165.0, 139.2 (2), 133.6, 131.0, 130.2, 129.9, 129.3 (2), 128.9 (2), 128.5, 127.6, 111.9, 111.6, 87.9, 87.8, 46.3, 46.2, 45.2, 43.5, 40.8, 40.4, 37.3, 37.2, 31.9, 31.8, 27.3, 26.0, 20.9 (2); HRMS *m/z* (ESI) calcd for $C_{24}H_{25}O_3$ ($[M+H]^+$) 361.1798, found 361.1794.

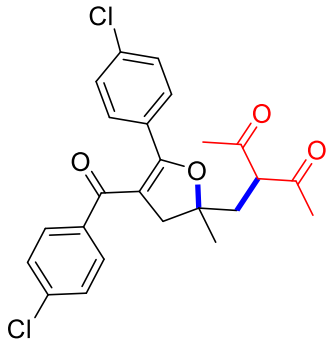


Diethyl 2-((4-benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl) methyl)-2-methylmalonate (3af)[1], 0.0684 g, 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, J = 9.5 Hz, 2H), 7.20-7.13 (m, 4H), 7.07-7.01 (m, 4H), 4.15-4.10 (m, 4H), 3.25 (d, J = 19.0 Hz, 1H), 3.04 (d, J = 18.5 Hz, 1H), 2.67-2.58 (m, 2H), 1.63 (s, 3H), 1.52 (s, 3H), 1.22-1.18 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.6, 172.2, 172.1, 164.5, 139.1, 131.0, 130.2, 129.8, 129.3, 128.8, 127.6, 127.5, 111.3, 86.9, 61.5, 61.4, 52.7, 46.6, 44.7, 26.8, 20.7, 13.9.

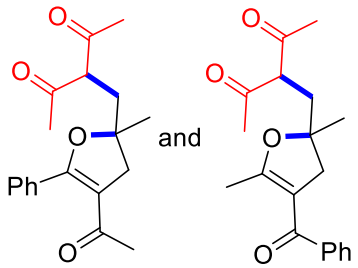


3-((4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ba), yellow oil (0.0724 g, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 9.0 Hz, 2H), 6.89 (t, J = 9.5 Hz, 4H), 5.35-5.33 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.81 (d, J = 14.5 Hz, 1H), 2.74-2.65 (m, 2H), 2.42-2.39 (m, 1H), 2.09 (s, 6H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.0, 194.1, 193.6, 166.4, 164.0, 163.8, 131.3, 131.0, 130.1, 128.9, 128.4, 114.0, 111.9, 87.8, 55.5 (2),

52.4, 42.6, 39.2, 29.3, 26.6, 15.1; HRMS *m/z* (ESI) calcd for $C_{26}H_{29}O_6$ ($[M+H]^+$) 437.1959, found 437.1955.

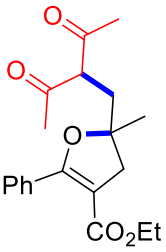


3-((4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ca), yellow oil (0.0675 g, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.45-7.41 (m, 4H), 5.35-5.33 (m, 1H), 2.83-2.76 (m, 2H), 2.70-2.65 (m, 1H), 2.46-2.42 (m, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.4, 194.1, 193.5, 165.5, 140.5, 140.3, 134.0, 133.6, 130.2, 130.0, 129.3, 129.2, 112.0, 87.3, 53.0, 42.7, 39.0, 29.3, 26.5, 15.0; HRMS *m/z* (ESI) calcd for $C_{24}H_{23}Cl_2O_4$ ($[M+H]^+$) 445.0968, found 445.0970.

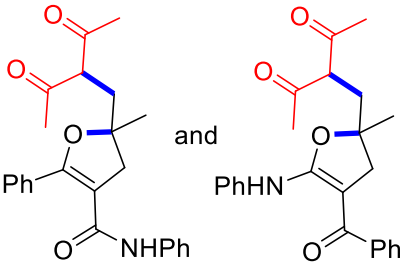


3-((4-Acetyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3da) and **3-((4-Benzoyl-2,5-dimethyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3da') (3da:3da' = 1:1)**, yellow oil (0.0465 g, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.02 (d, *J* = 7.5 Hz, 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 2H), 4.69-4.67 (m, 1H), 2.91-2.84 (m, 0.5H), 2.76-2.70 (m, 1H), 2.63-2.58 (m, 0.5H), 2.44-2.41 (m, 1H), 2.38-2.33 (m, 1H), 2.17 (s, 1.5H), 2.15 (s, 1.5H), 2.15 (s, 1.5H), 2.12 (s, 1.5H), 2.06 (s, 1.5H), 1.82 (s, 1.5H), 1.38 (s, 1.5H), 1.35 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 202.9, 202.6, 195.8, 195.5, 194.4, 194.3, 166.3, 165.9, 136.0, 135.8, 133.8, 128.9, 128.8 (2), 128.7, 111.9,

86.8, 86.7, 58.7, 58.2, 42.4, 42.0, 39.7, 39.2, 29.3, 29.2, 28.1, 28.0, 27.1, 26.7, 14.8, 14.7; HRMS *m/z* (ESI) calcd for $C_{19}H_{23}O_4$ ($[M+H]^+$) 315.1591, found 315.1587.

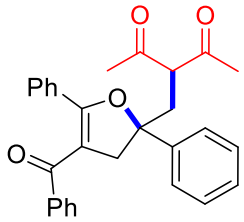


Ethyl 5-(2-acetyl-3-oxobutyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ea), yellow oil (0.0482 g, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.54 (t, *J* = 6.0 Hz, 1H), 4.18-4.13 (m, 2H), 2.79-2.71 (m, 2H), 2.45 (t, *J* = 5.2 Hz, 2H), 2.12 (s, 3H), 2.09 (s, 3H), 1.40 (s, 3H), 1.18 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.8, 194.5, 169.7, 166.1, 135.8, 133.6, 128.8, 128.7, 111.8, 86.8, 61.7, 49.8, 42.7, 39.4, 29.3, 26.4, 15.0, 13.9; HRMS *m/z* (ESI) calcd for $C_{20}H_{25}O_5$ ($[M+H]^+$) 345.1697, found 345.1705.

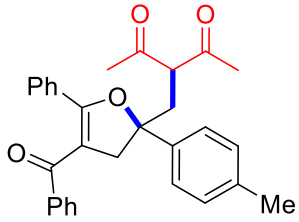


5-(2-Acetyl-3-oxobutyl)-5-methyl-*N*,2-diphenyl-4,5-dihydrofuran-3-carboxamide (3fa) and **3-((4-Benzoyl-2-methyl-5-(phenylamino)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3fa') (3fa:3fa' = 1:1)**, yellow oil (0.0555 g, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.18 (d, *J* = 11.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51-7.48 (m, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.68-4.64 (m, 1H), 2.77-2.69 (m, 2H), 2.46-2.36 (m, 2H), 2.12 (s, 1.5H), 2.10 (s, 1.5H), 1.99 (s, 1.5H), 1.64 (s, 1.5H), 1.45 (s, 1.5H), 1.37 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 198.9, 198.8, 194.5, 194.4, 166.5, 166.2, 166.1, 166.0, 137.4 (2), 136.1, 135.9, 134.2, 134.1, 128.9 (2), 128.7 (2), 124.6, 124.5, 119.7, 111.9 (2), 86.8, 86.6, 52.7, 52.4, 43.1, 42.6,

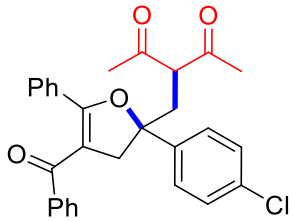
42.5, 41.6, 29.3, 29.2, 27.4, 26.2, 14.8, 14.6; HRMS *m/z* (ESI) calcd for $C_{24}H_{26}NO_4$ ($[M+H]^+$) 392.1856, found 392.1860.



3-((4-Benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ga), yellow oil (0.0684 g, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92-7.90 (m, 2H), 7.57-7.54 (m, 1H), 7.48-7.42 (m, 5H), 7.40-7.37 (m, 2H), 7.35-7.33 (m, 3H), 7.27-7.23 (m, 2H), 5.33-5.30 (m, 1H), 3.23-3.16 (m, 3H), 2.56-2.52 (m, 1H), 2.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 194.5, 194.2, 165.5, 143.7, 136.1, 135.2, 133.3, 128.8, 128.6, 128.5, 128.4, 127.7, 125.1, 112.4, 89.8, 51.7, 44.6, 41.0, 29.3, 14.8; HRMS *m/z* (ESI) calcd for $C_{19}H_{27}O_4$ ($[M+H]^+$) 439.1904, found 439.1900.

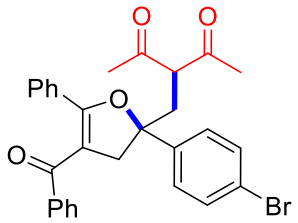


3-((4-Benzoyl-5-phenyl-2-(*p*-tolyl)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ha), yellow oil (0.0714 g, 79% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.48-7.43 (m, 5H), 7.26-7.22 (m, 4H), 7.17 (d, J = 8.5 Hz, 2H), 5.32-5.30 (m, 1H), 3.23-3.13 (m, 3H), 2.54-2.50 (m, 1H), 2.38 (s, 3H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.9, 194.6, 194.3, 165.6, 140.7, 137.4, 136.2, 135.3, 133.3 (2), 130.1, 129.4, 128.8, 128.6, 128.5, 125.0, 112.4, 89.9, 51.9, 44.6, 41.1, 29.3, 21.0, 14.8; HRMS *m/z* (ESI) calcd for $C_{30}H_{29}O_4$ ($[M+H]^+$) 453.2060, found 453.2056.

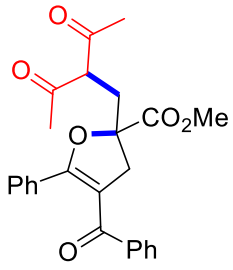


3-((4-Benzoyl-2-(4-chlorophenyl)-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ia), yellow oil (0.0680 g, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91

(d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.48-7.43 (m, 5H), 7.26-7.22 (m, 4H), 7.17 (d, J = 8.5 Hz, 2H), 5.32-5.30 (m, 1H), 3.23-3.13 (m, 3H), 2.54-2.50 (m, 1H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.9, 194.6, 194.3, 165.7, 140.7, 137.5, 136.2, 135.3, 133.3 (2), 130.1, 129.4, 128.8, 128.6, 128.5, 125.0, 112.4, 89.9, 51.9, 44.6, 41.1, 29.3, 14.9; HRMS m/z (ESI) calcd for $C_{29}H_{26}ClO_4$ ($[M+H]^+$) 473.1514, found 473.1518.

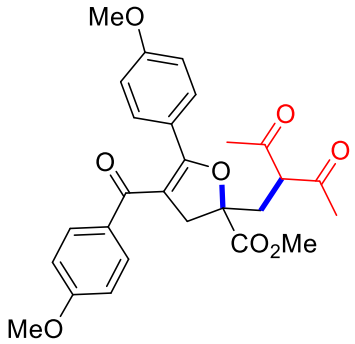


3-((4-Benzoyl-2-(4-bromophenyl)-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ja), yellow oil (0.0733 g, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91-7.89 (m, 2H), 7.47-7.41 (m, 5H), 7.39-7.36 (m, 2H), 7.34-7.32 (m, 3H), 7.26-7.23 (m, 2H), 5.32-5.30 (m, 1H), 3.23-3.15 (m, 3H), 2.55-2.51 (m, 1H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.8, 194.5, 194.2, 165.5, 143.7, 136.2, 135.2, 133.3, 128.8, 128.6, 128.5, 128.4, 127.7, 125.1, 112.5, 89.8, 51.7, 44.6, 41.0, 29.3, 14.8; HRMS m/z (ESI) calcd for $C_{29}H_{26}BrO_4$ ($[M+H]^+$) 517.1009, found 517.1001.

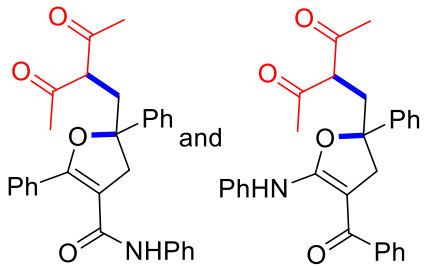


Methyl 2-(2-acetyl-3-oxobutyl)-4-benzoyl-5-phenyl-2,3-dihydrofuran-2-carboxylate (3ka), yellow oil (0.0529 g, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.60-7.54 (m, 2H), 7.48-7.42 (m, 4H), 5.60 (t, J = 5.5 Hz, 1H), 3.67 (s, 3H), 3.38-3.35 (m, 1H), 2.95-2.88 (m, 2H), 2.69-2.65 (m, 1H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.8, 194.3, 193.9, 171.5, 165.3, 135.6, 135.4, 133.7, 133.6, 128.9,

128.8 (2), 128.6, 111.8, 87.2, 52.8, 51.9, 40.5, 36.8, 29.7, 14.6; HRMS *m/z* (ESI) calcd for $C_{25}H_{25}O_6$ ([M+H]$^+$) 421.1646, found 421.1640.

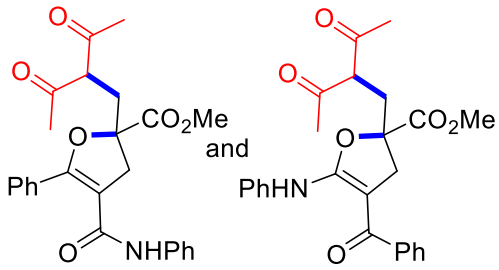


Methyl 2-(2-acetyl-3-oxobutyl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydrofuran-2-carboxylate (3ma), yellow oil (0.0615 g, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, J = 9.0 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 6.93-6.88 (m, 4H), 5.46 (t, J = 5.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.67 (s, 3H), 3.37-3.34 (m, 1H), 2.96-2.88 (m, 2H), 2.68-2.64 (m, 1H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.0, 193.4, 192.8, 171.6, 165.4, 163.9, 163.8, 131.2, 131.0, 128.7, 128.4, 114.0 (2), 111.7, 87.4, 55.5 (2), 52.8, 51.8, 40.5, 37.0, 29.4, 14.7; HRMS *m/z* (ESI) calcd for $C_{27}H_{29}O_8$ ([M+H]$^+$) 481.1857, found 481.1853.

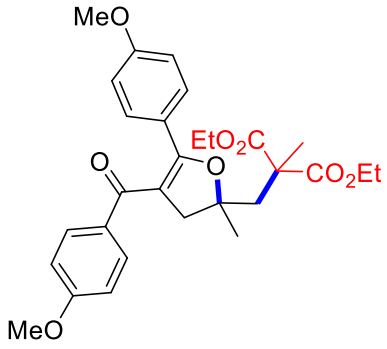


5-(2-Acetyl-3-oxobutyl)-*N*,2,5-triphenyl-4,5-dihydrofuran-3-carboxamide (3na) and **3-((4-Benzoyl-2-phenyl-5-(phenylamino)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3na')** **(3na:3na' = 1:1)**, yellow oil (0.0589 g, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, J = 14.0 Hz, 1H), 7.93 (d, J = 7.0 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.0 Hz, 3H), 7.42-7.37 (m, 3H), 7.28-7.23 (m, 6H), 7.10-7.05 (m, 1H), 4.58-4.56 (m, 0.5H), 4.39-4.36 (m, 0.5H), 3.20-3.09 (m, 2H), 2.94-2.89 (m, 1H), 2.81-2.77 (m, 1H), 2.14 (s, 3H), 2.08 (s, 1.5H), 1.97 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 199.1, 198.3, 194.3, 194.2, 166.1, 166.0, 165.7 (2), 143.7, 143.0, 137.5, 137.3, 136.2, 135.8,

134.0, 133.9, 133.4, 130.1, 128.9 (2), 128.8 (2), 128.6 (2), 128.4, 127.8, 127.7, 124.7, 124.6, 124.5, 119.7, 112.1, 89.8, 89.5, 52.7, 52.5, 44.9, 44.3, 44.2, 44.1, 29.3 (2), 14.7, 14.6; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}NO_4$ ($[M+H]^+$) 454.2013, found 454.2017.

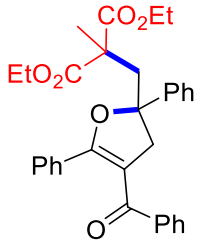


Methyl 2-(2-acetyl-3-oxobutyl)-5-phenyl-4-(phenylcarbamoyl)-2,3-dihydrofuran-2-carboxylate (3oa) and **Methyl 2-(2-acetyl-3-oxobutyl)-4-benzoyl-5-(phenylamino)-2,3-dihydrofuran-2-carboxylate (3oa') (3oa:3oa' = 1:1)**, yellow oil (0.0531 g, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.05 (d, J = 7.5 Hz, 3H), 7.61 (t, J = 7.5 Hz, 1H), 7.51-7.46 (m, 4H), 7.30-7.26 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 4.63-4.59 (m, 1H), 3.76 (s, 1.5H), 3.68 (s, 1.5H), 3.32-3.25 (m, 1H), 3.05-2.86 (m, 2H), 2.77-2.63 (m, 1H), 2.16 (s, 3H), 2.06 (s, 1.5H), 1.88 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.7, 197.4, 193.7 (2), 171.7, 171.6, 166.0, 165.6 (2), 165.5, 137.4, 135.9, 135.7, 134.2, 134.1, 129.0, 128.9, 128.8 (2), 124.7, 124.6, 119.8, 119.7, 111.8 (2), 87.0, 86.7, 53.1, 52.9, 52.5, 52.1, 40.9, 40.4, 39.0, 29.4, 29.3, 14.6, 14.5; HRMS *m/z* (ESI) calcd for $C_{25}H_{26}NO_6$ ($[M+H]^+$) 436.1755, found 436.1759.

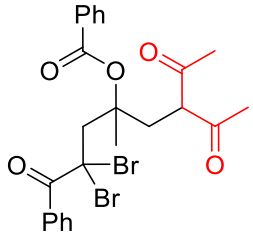


Diethyl 2-((4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3pf)[1], 0.0786 g, 77% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, J = 11.0 Hz, 2H), 7.16 (d, J

= 11.0 Hz, 2H), 6.60 (t, *J* = 12.0 Hz, 4H), 4.15-4.09 (m, 4H), 3.73 (s, 3H), 3.71 (s, 3H), 3.22 (d, *J* = 18.5 Hz, 1H), 3.00 (d, *J* = 18.5 Hz, 1H), 2.65-2.55 (m, 2H), 1.62 (s, 3H), 1.49 (s, 3H), 1.21-1.18 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 192.4, 172.2 (2), 162.8, 162.0, 160.6, 131.7, 131.1, 130.9, 122.8, 113.0, 112.9, 109.7, 86.0, 61.5, 61.4, 55.2 (2), 52.8, 47.2, 44.7, 26.8, 20.6, 13.9.

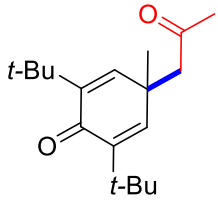


Diethyl 2-((4-benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3qf)[1], 0.0727 g, 71% yield; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.49 (d, *J* = 9.5 Hz, 2H), 7.39 (t, *J* = 9.0 Hz, 4H), 7.34-7.29 (m, 3H), 7.21 (t, *J* = 9.0 Hz, 2H), 7.12-7.06 (m, 4H), 3.96-3.87 (m, 3H), 3.82-3.76 (m, 1H), 3.69 (d, *J* = 19.0 Hz, 1H), 3.43 (d, *J* = 19.0 Hz, 1H), 3.09 (d, *J* = 19.0 Hz, 1H), 2.93 (d, *J* = 19.0 Hz, 1H), 1.29 (s, 3H), 1.12 (t, *J* = 9.0 Hz, 3H), 1.06 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 193.3, 171.9, 171.7, 163.5, 144.9, 138.8, 131.2, 130.1, 129.8, 129.4, 128.9, 128.4, 127.7, 127.6, 127.4, 124.8, 111.0, 89.0, 61.2, 52.8, 50.1, 45.9, 20.2, 13.7.



6-Acetyl-2,2-dibromo-4-methyl-1,7-dioxo-1-phenyloctan-4-yl benzoate (5a), yellow oil (0.0792 g, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.05 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.56-7.52 (m, 2H), 7.47-7.42 (m, 4H), 5.48 (t, *J* = 5.5 Hz, 1H), 3.47-3.37 (m, 2H), 2.69 (s, 2H), 1.88 (s, 6H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 195.5, 195.1, 187.8, 169.9, 135.8, 135.7, 133.6 (2), 129.0, 128.8, 124.5, 124.0, 83.3, 64.1,

54.0, 50.1, 31.4, 25.1, 24.1, 22.3; HRMS *m/z* (ESI) calcd for $C_{24}H_{25}Br_2O_5$ ($[M+H]^+$) 551.0063, found 551.0071.



2,6-di-*tert*-Butyl-4-methyl-4-(2-oxopropyl)cyclohexa-2,5-dien-1-one (7a)[2], 0.0387 g, 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.58 (s, 2H), 2.61 (s, 2H), 2.01 (s, 3H), 1.42 (s, 3H), 1.22 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 205.6, 186.0, 146.3, 144.9, 53.8, 38.6, 34.7, 31.3, 29.4, 26.5.

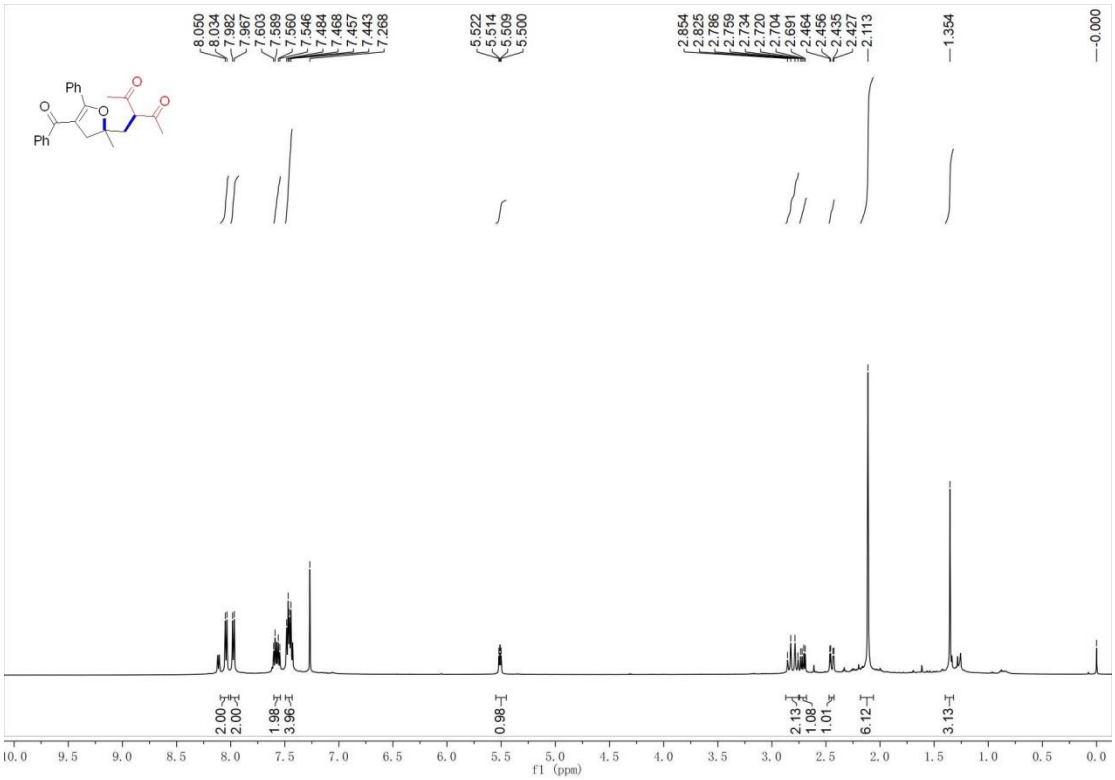
(D) References

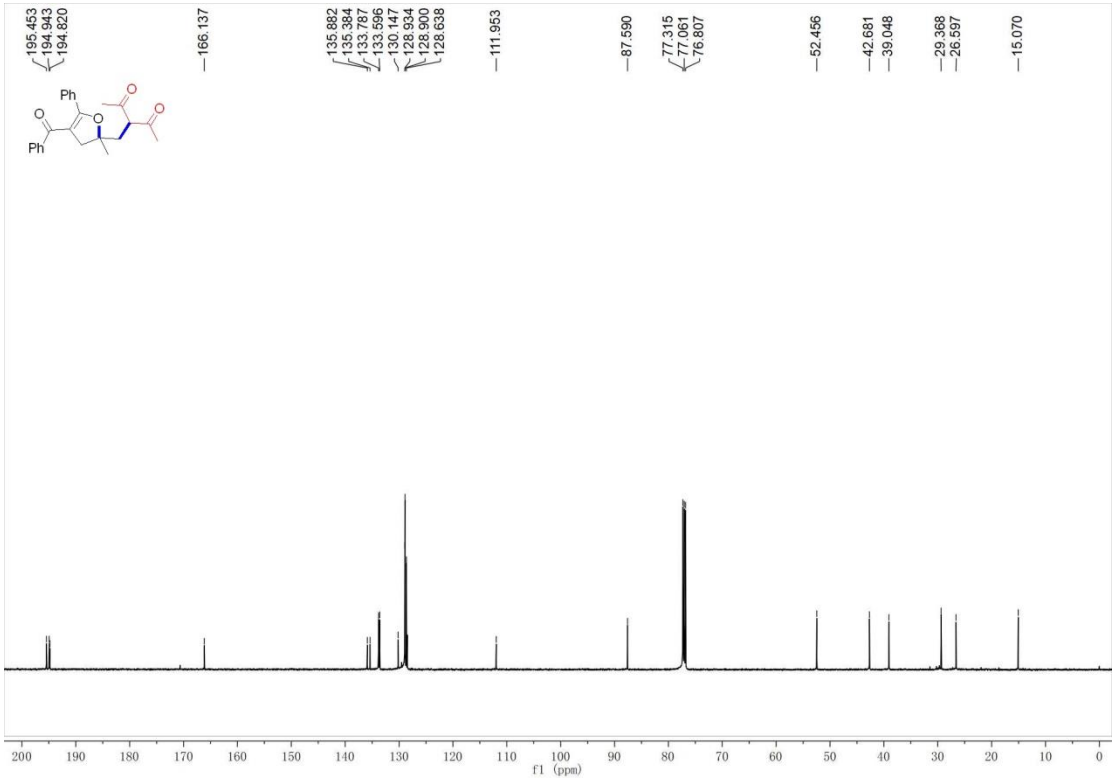
[1] W.-T. Wei, M.-J. Luo, F. Teng, R.-J. Song and J.-H. Li, *Chem. Commun.*, 2019, **55,** 11111.

[2] X. Wang, X. Zhao, X. Li, B. Huo, Y. Dong, D. Liang and Y. Ma, *Tetrahedron Lett.*, 2019, **60**, 1306.

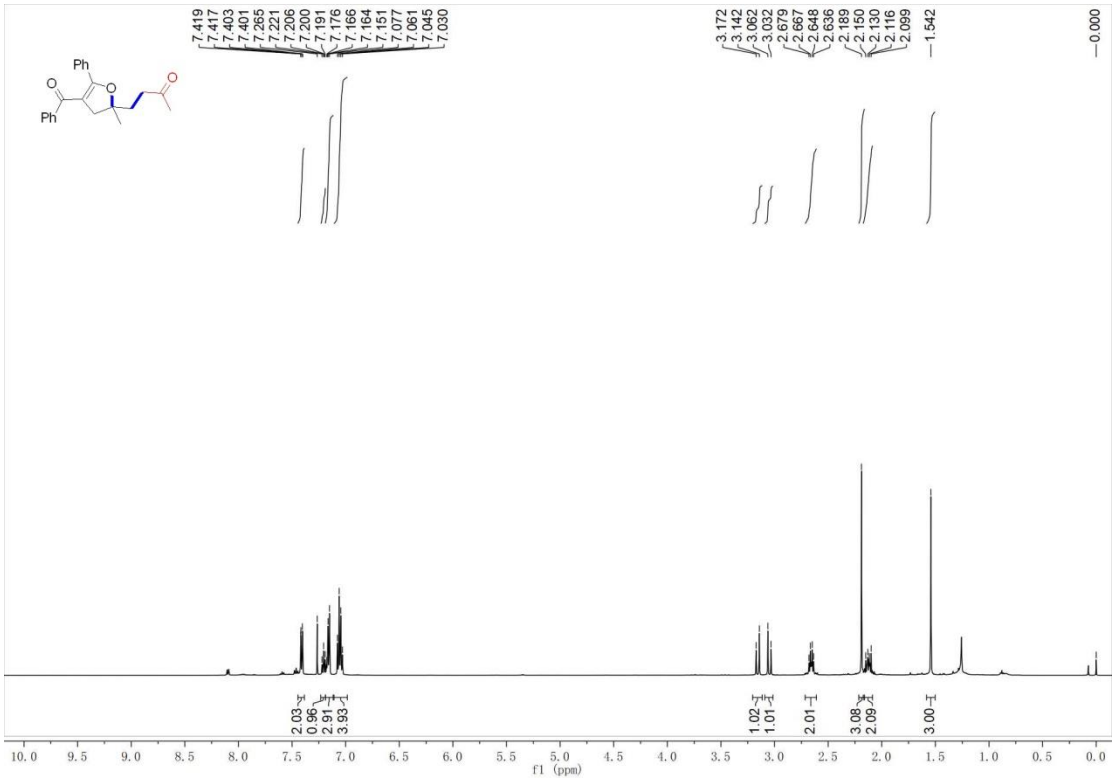
(E) Spectra

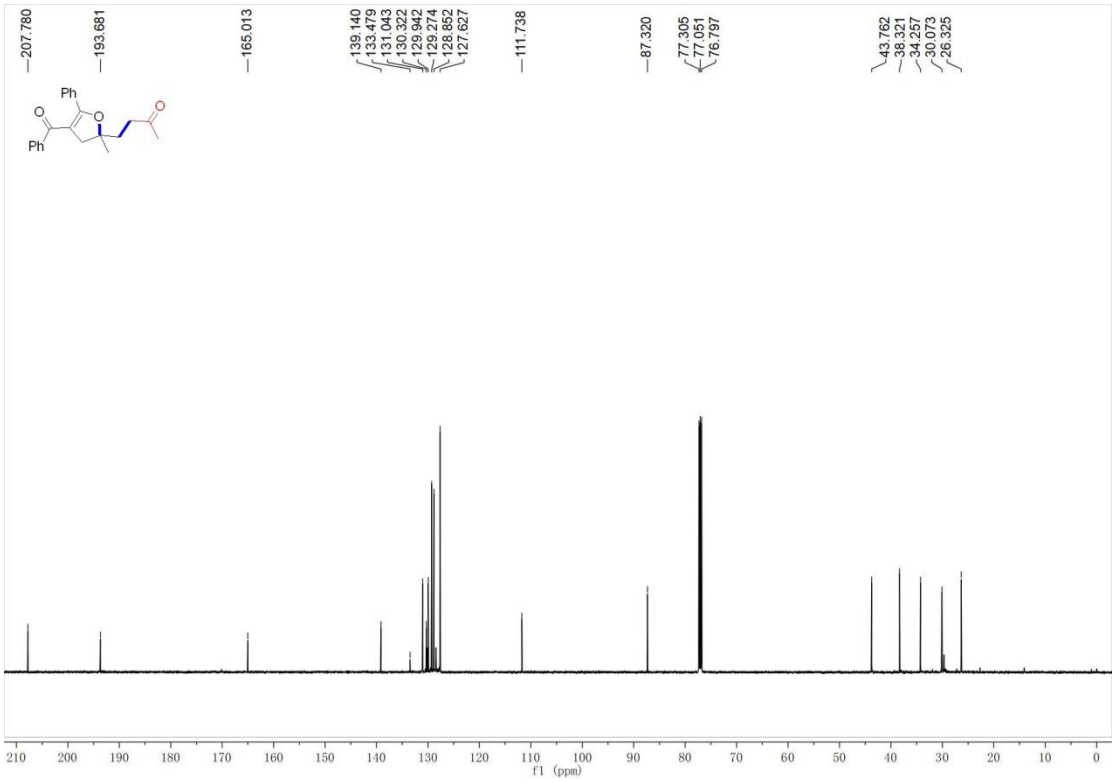
3-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3aa)



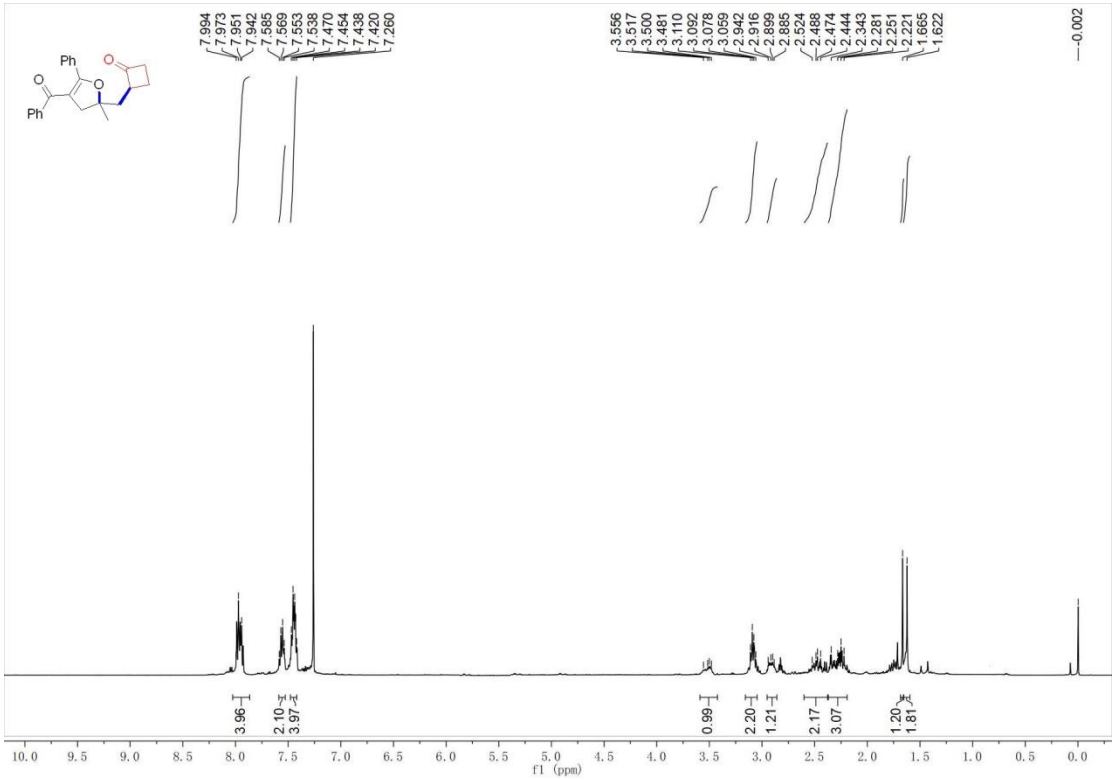


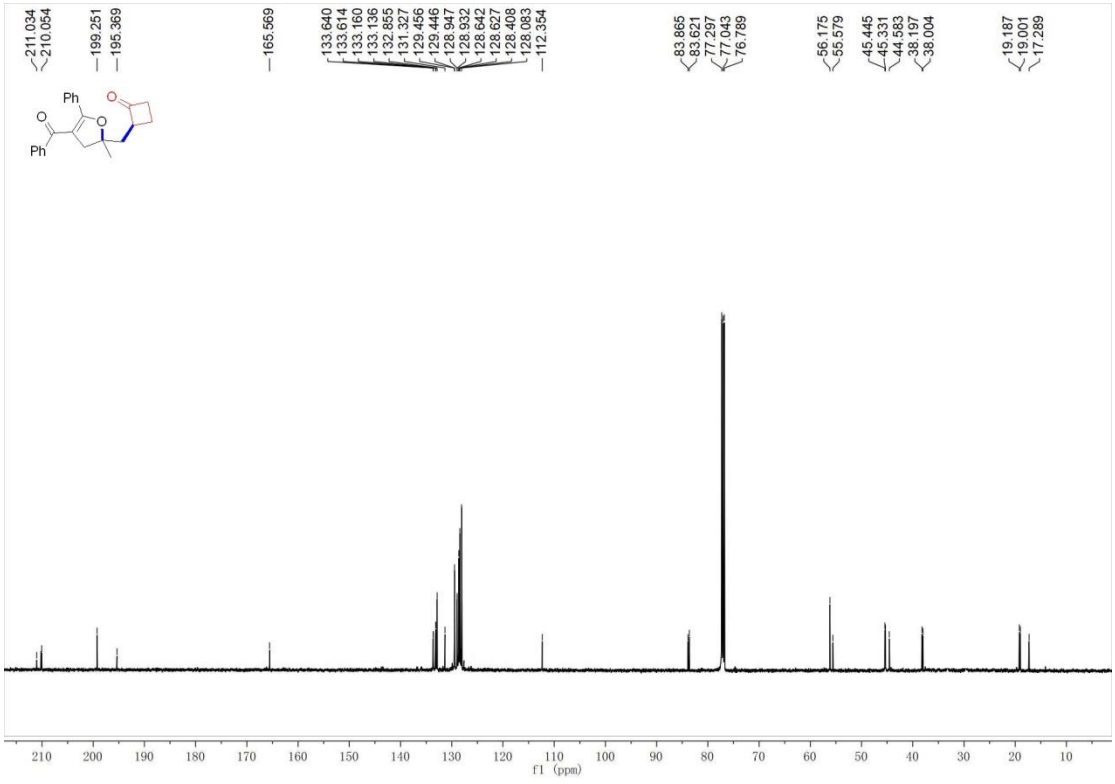
4-(4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)butan-2-one (3ab)



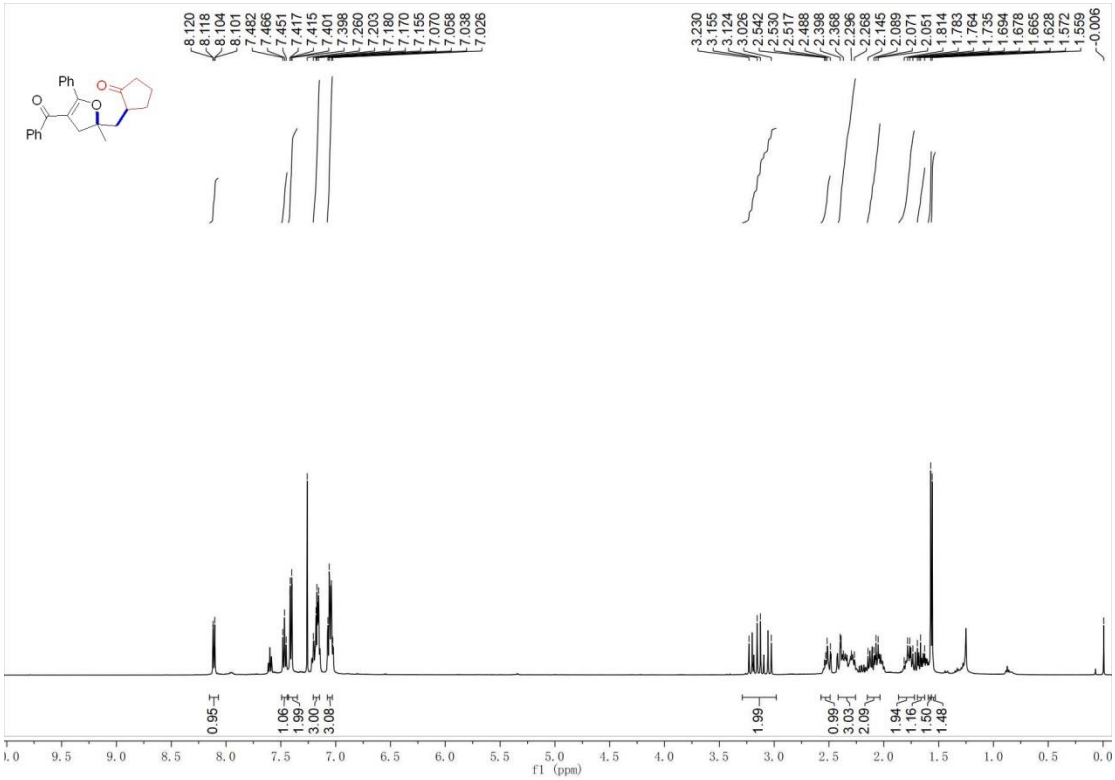


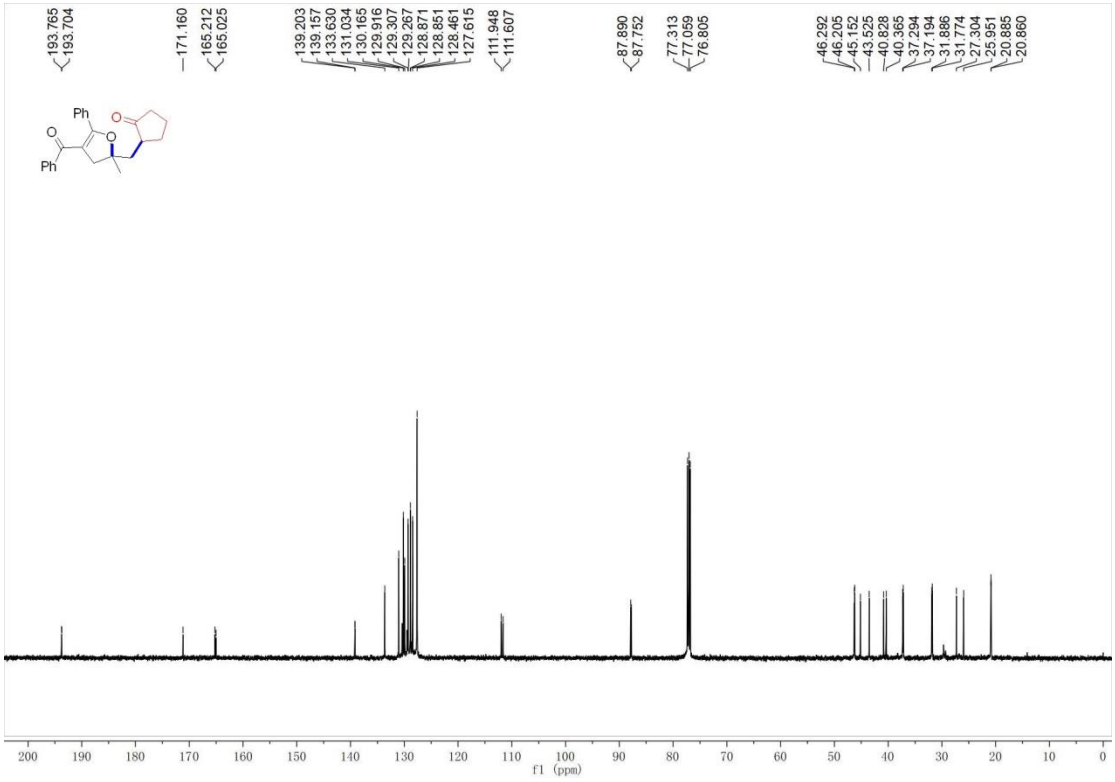
2-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)cyclobutan-1-one (3ac)



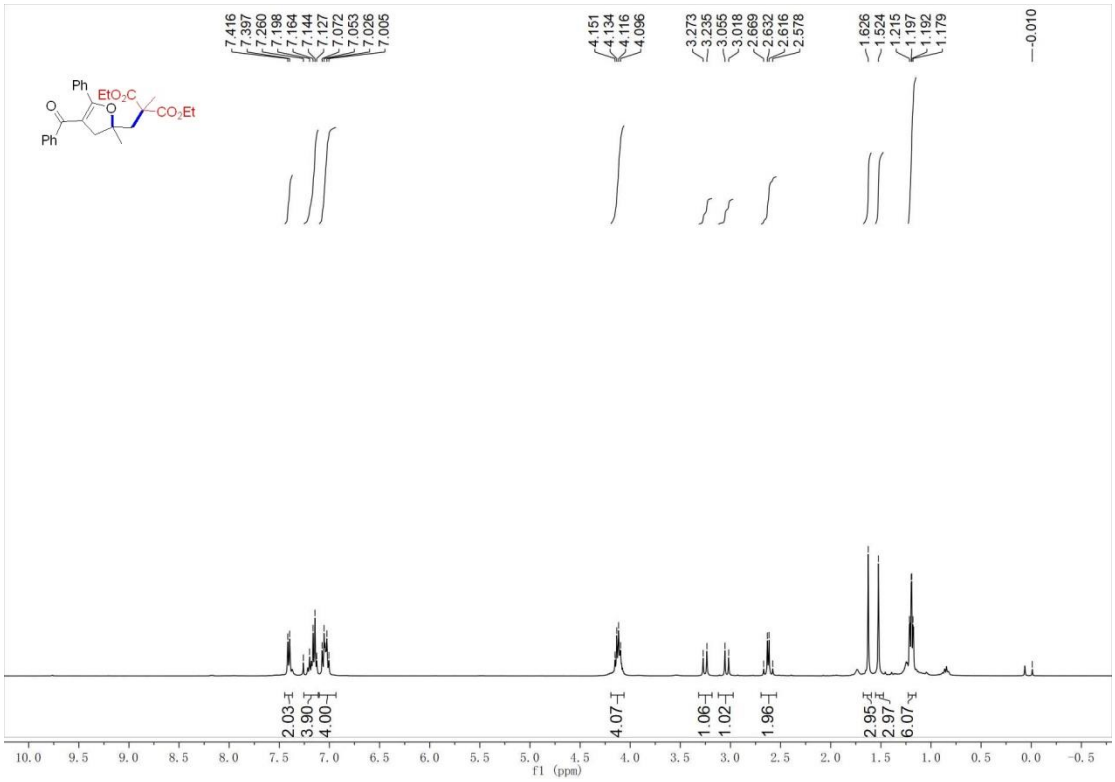


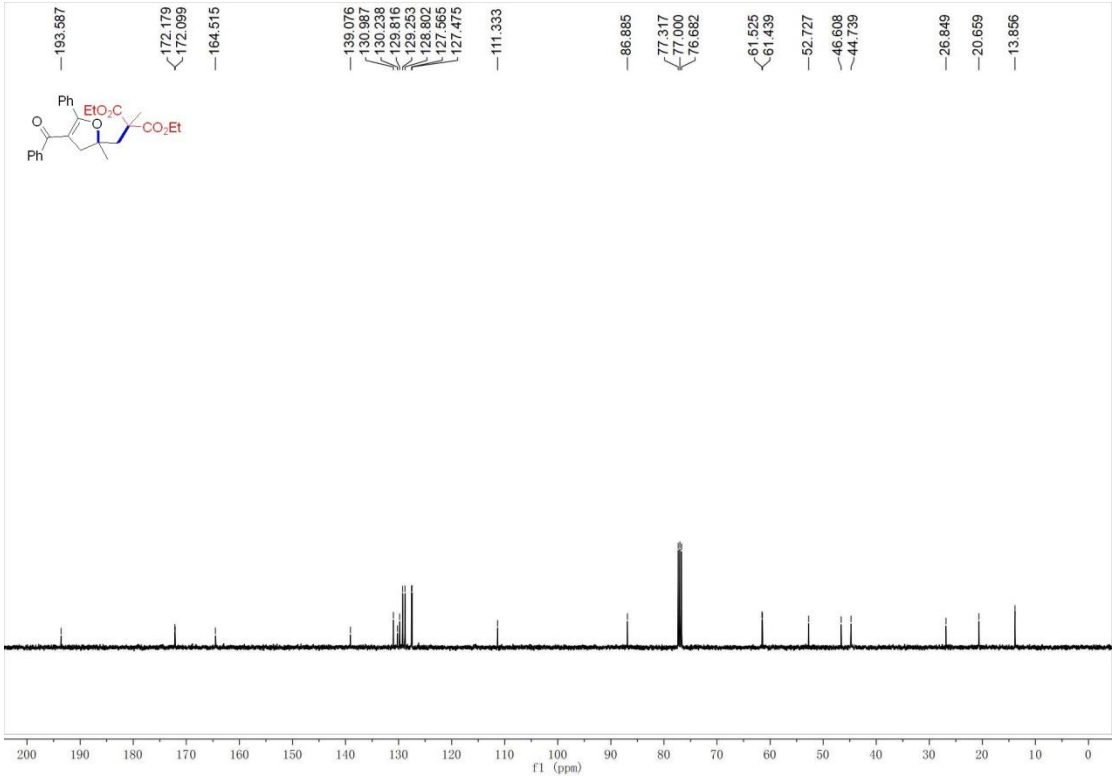
2-((4-Benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)cyclopentan-1-one (3ad)



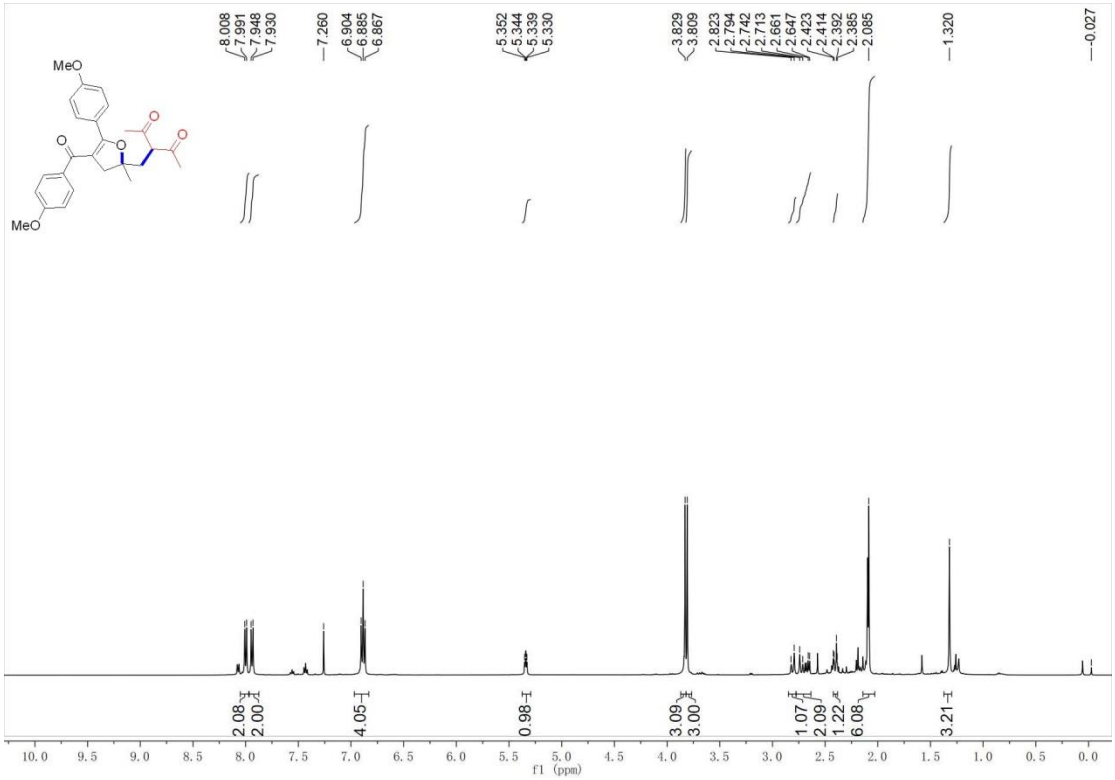


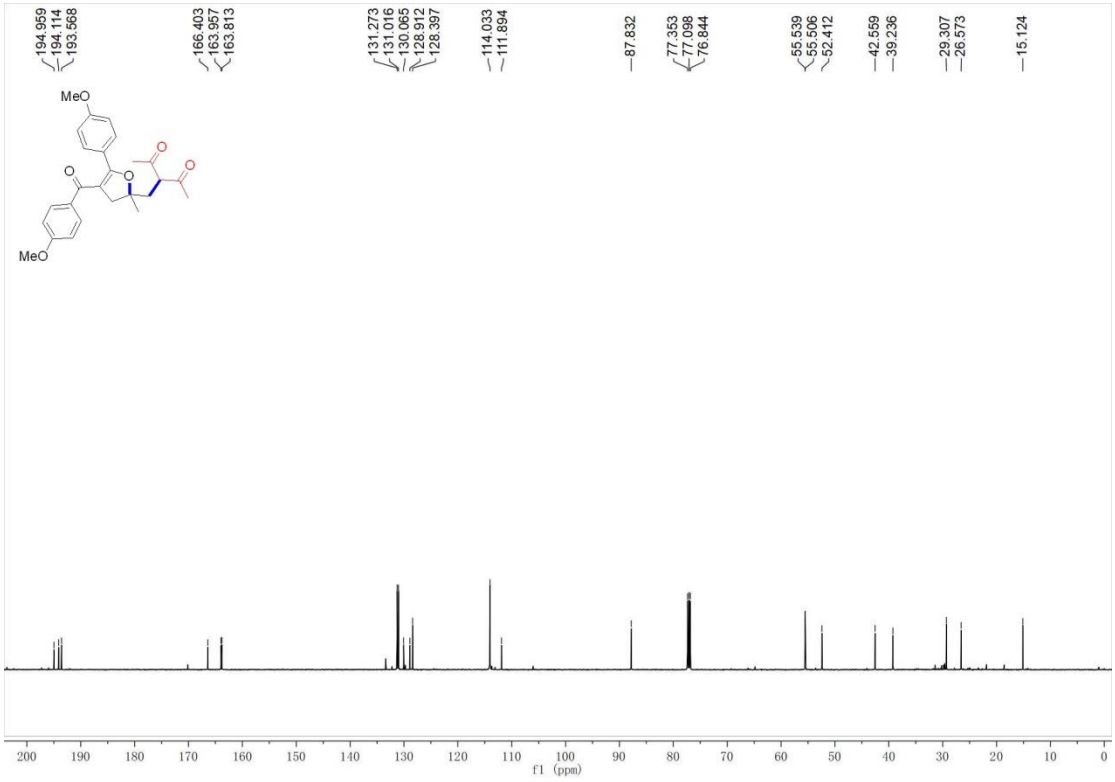
Diethyl 2-((4-benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3af)



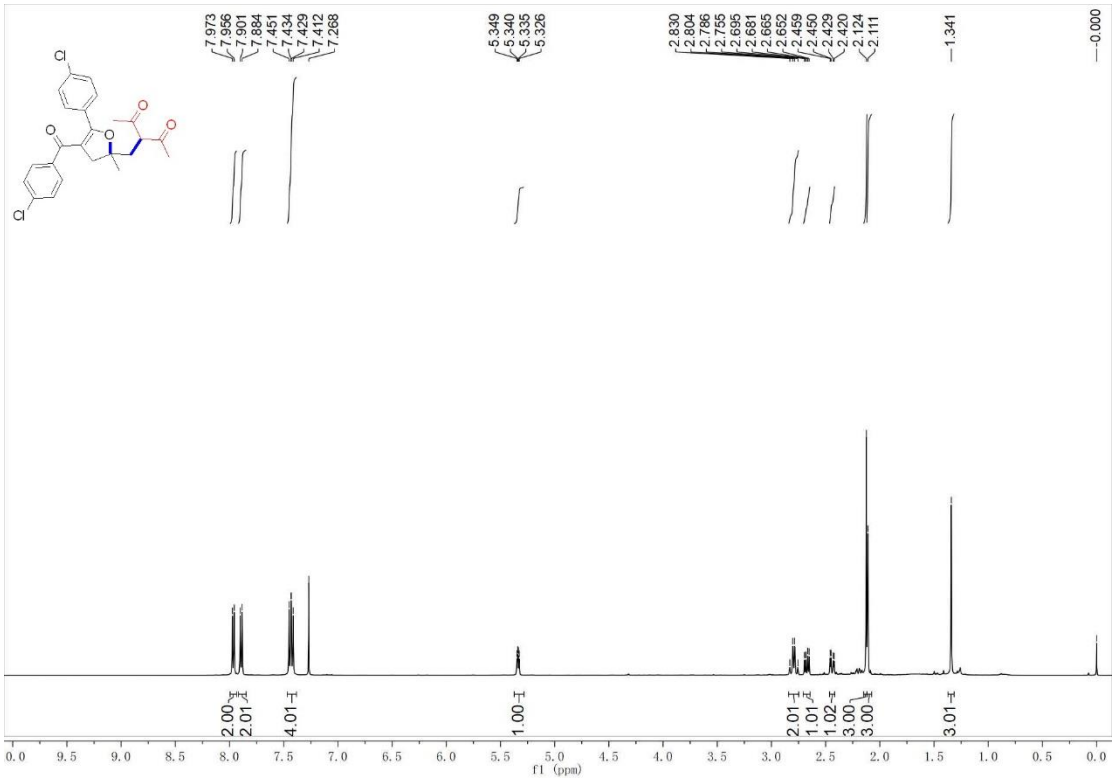


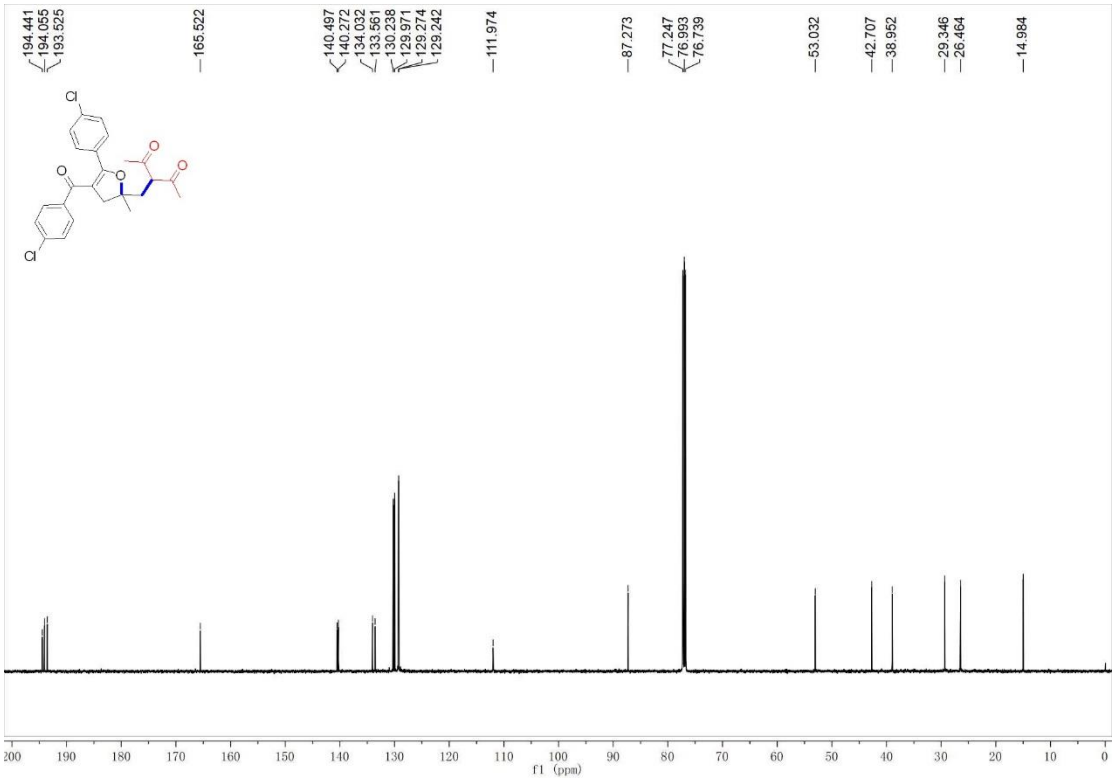
3-((4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl) methyl)pentane-2,4-dione (3ba)



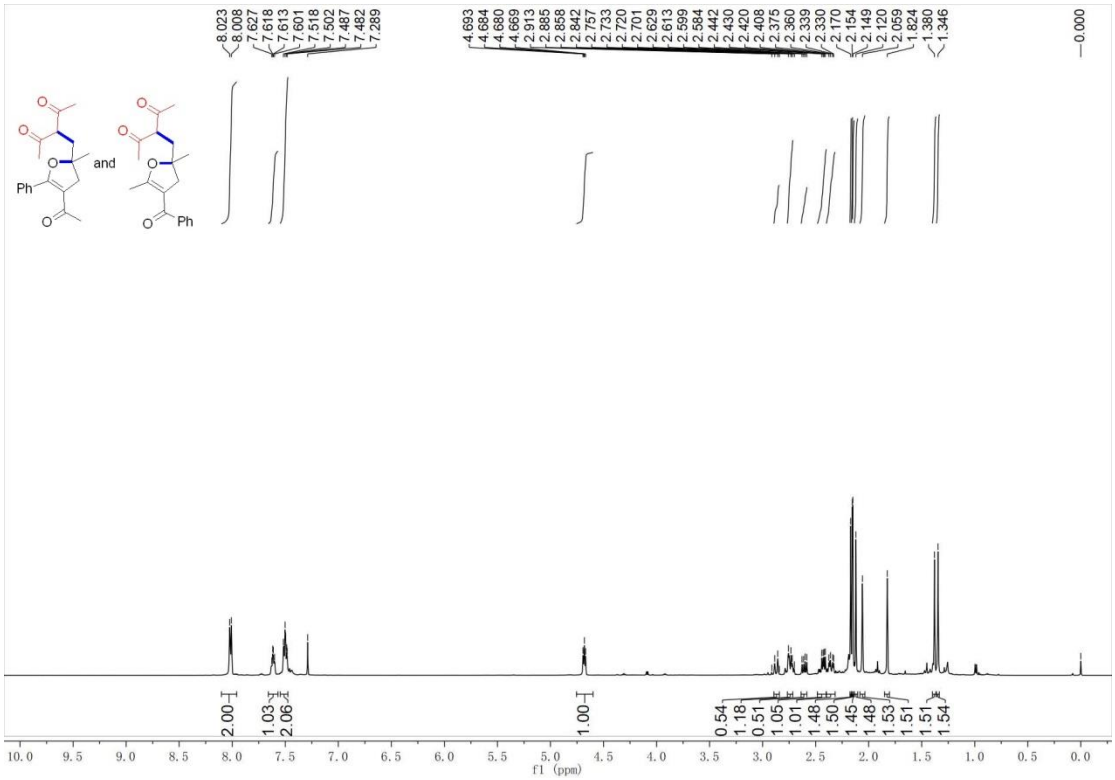


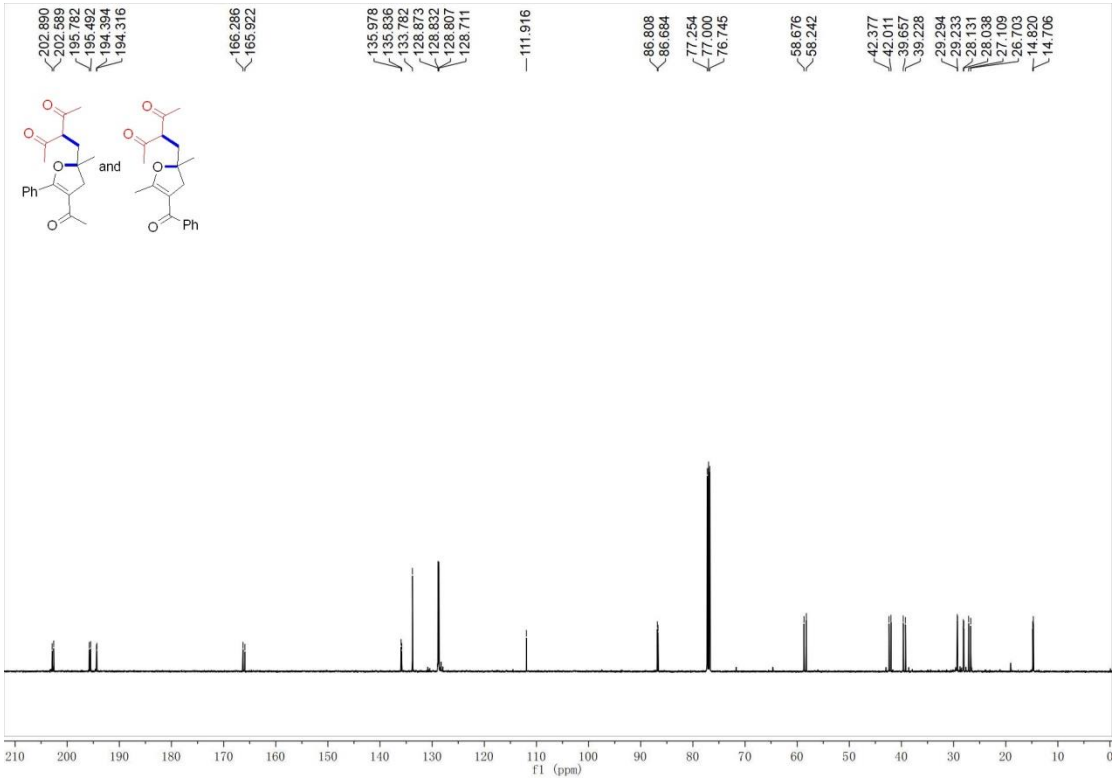
3-((4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ca)



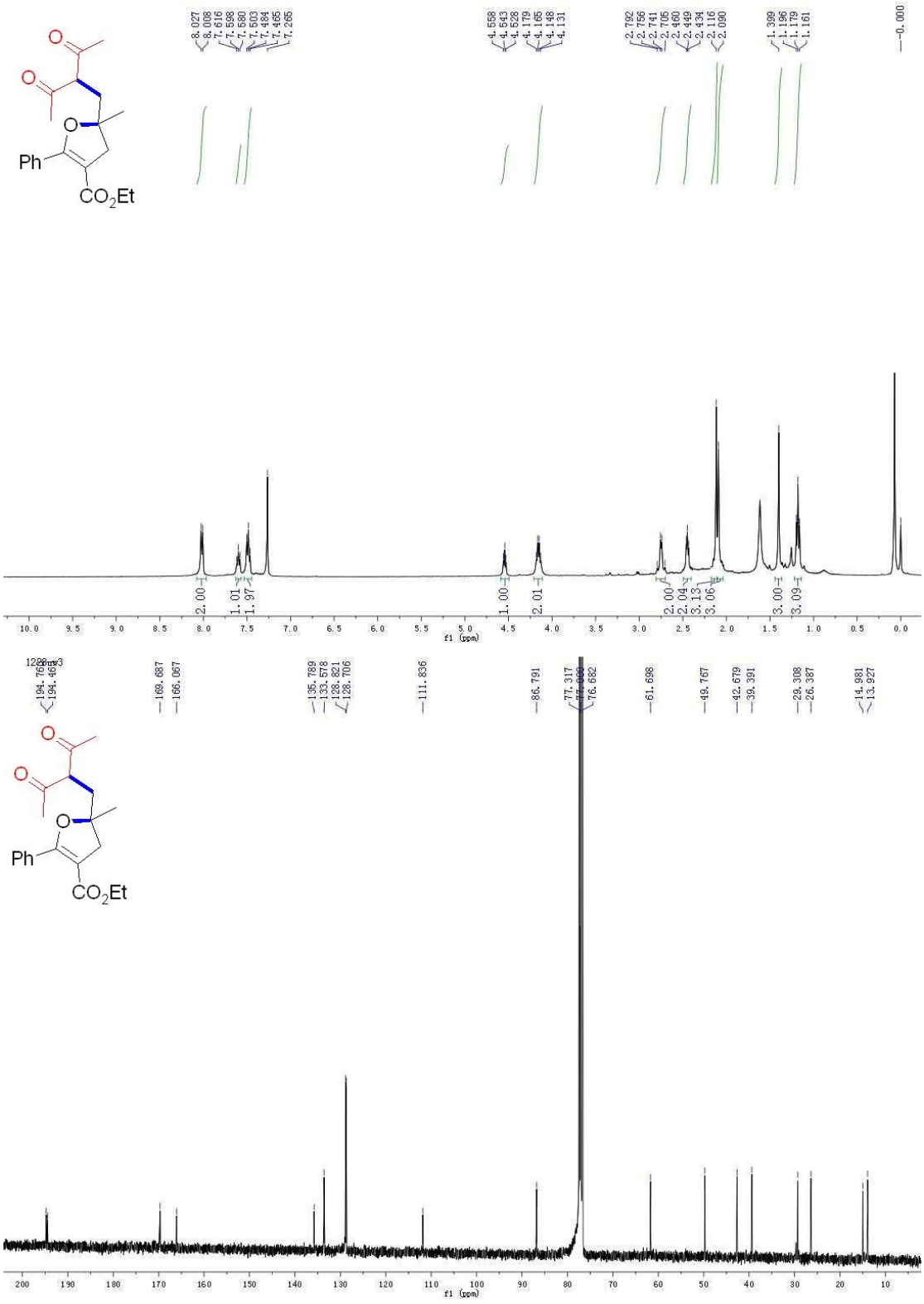


3-((4-Acetyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3da) and
3-((4-Benzoyl-2,5-dimethyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3da') (3da:3da' = 1:1**)**

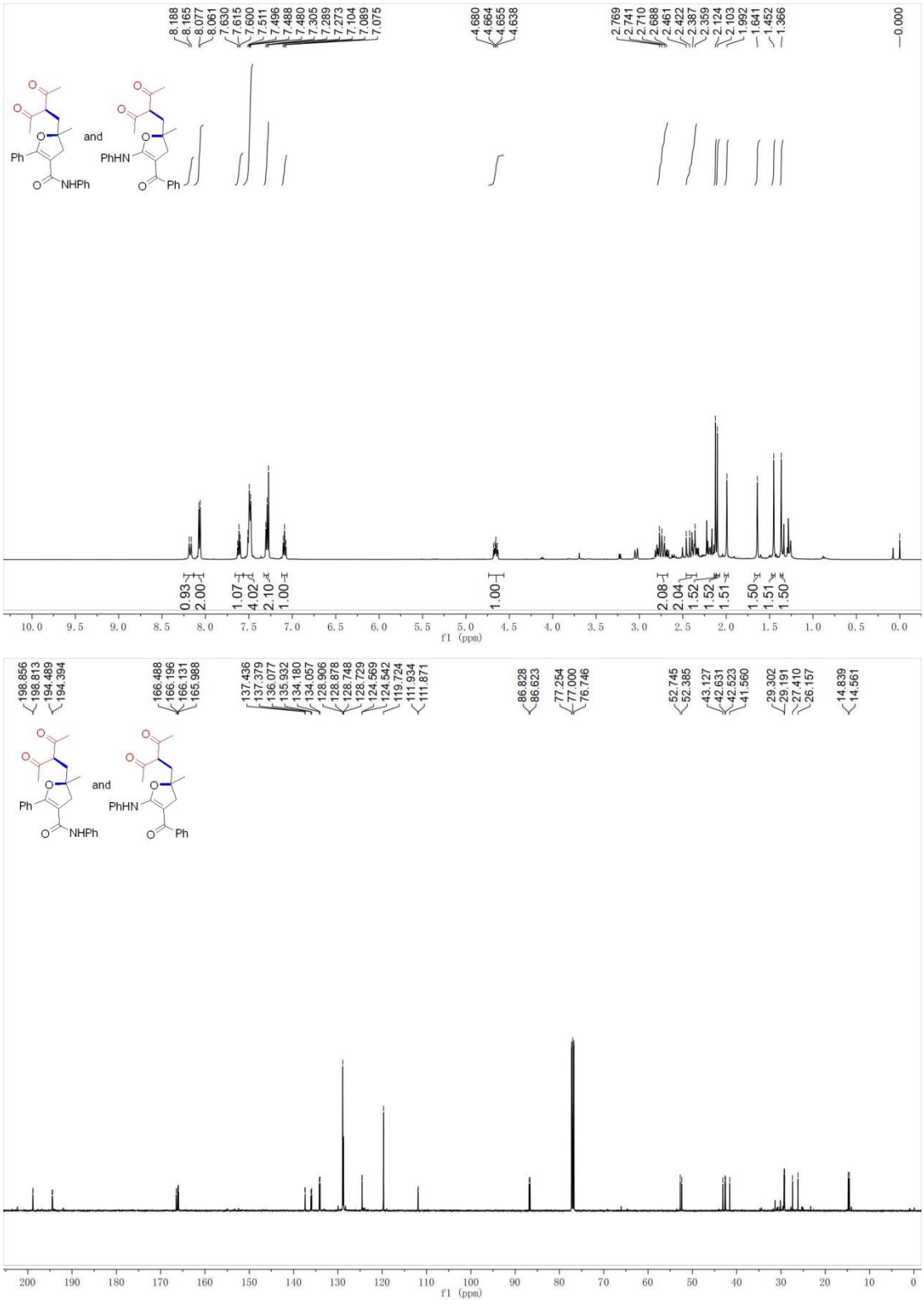




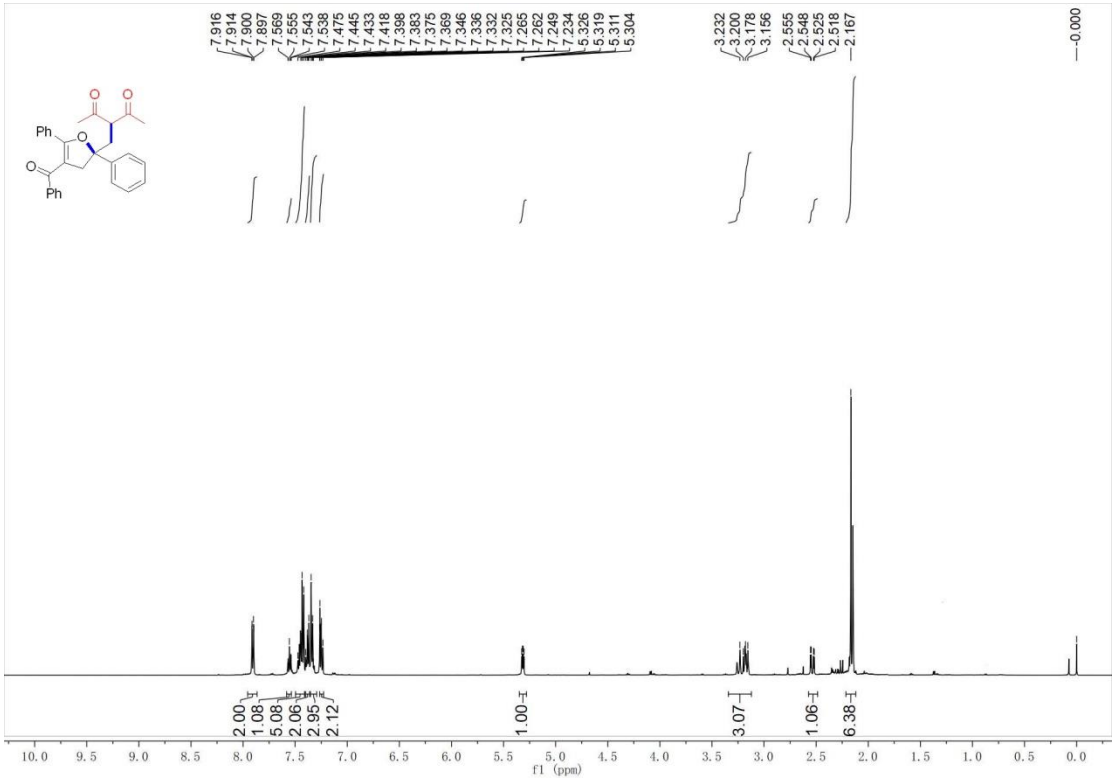
Ethyl 5-(2-acetyl-3-oxobutyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ea)

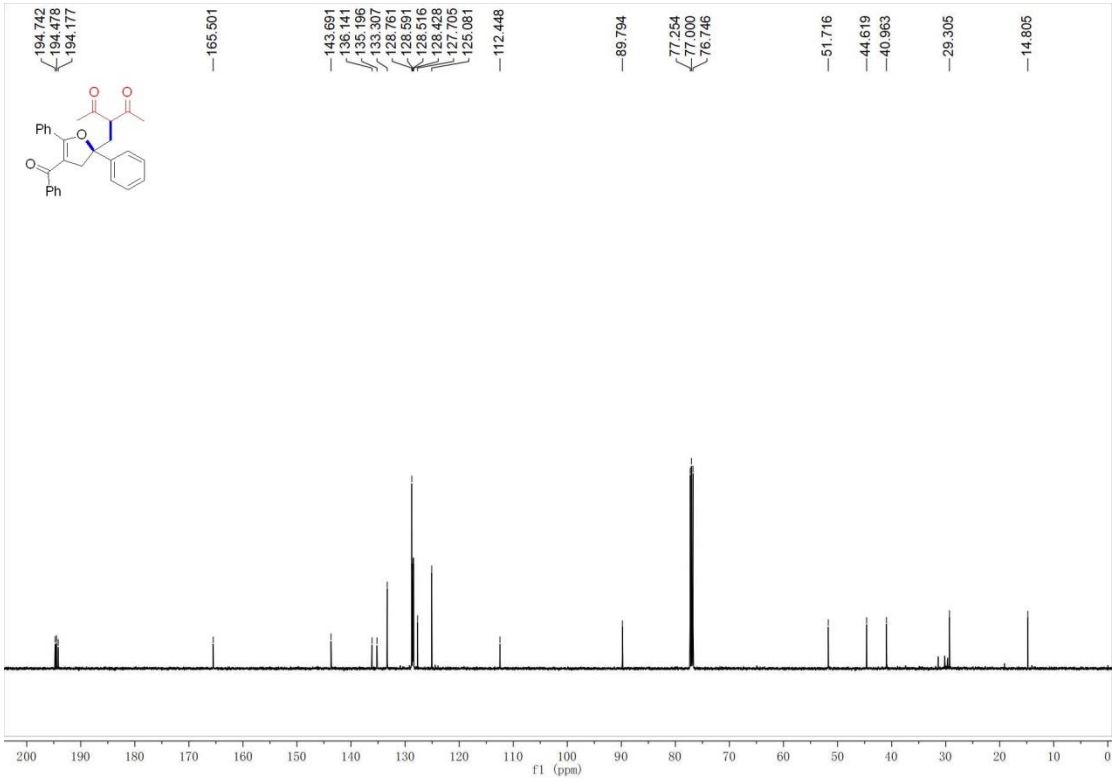


5-(2-Acetyl-3-oxobutyl)-5-methyl-*N*,2-diphenyl-4,5-dihydrofuran-3-carboxamide (3fa) and
3-((4-Benzoyl-2-methyl-5-(phenylamino)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3fa') (3fa:3fa' = 1:1**)**

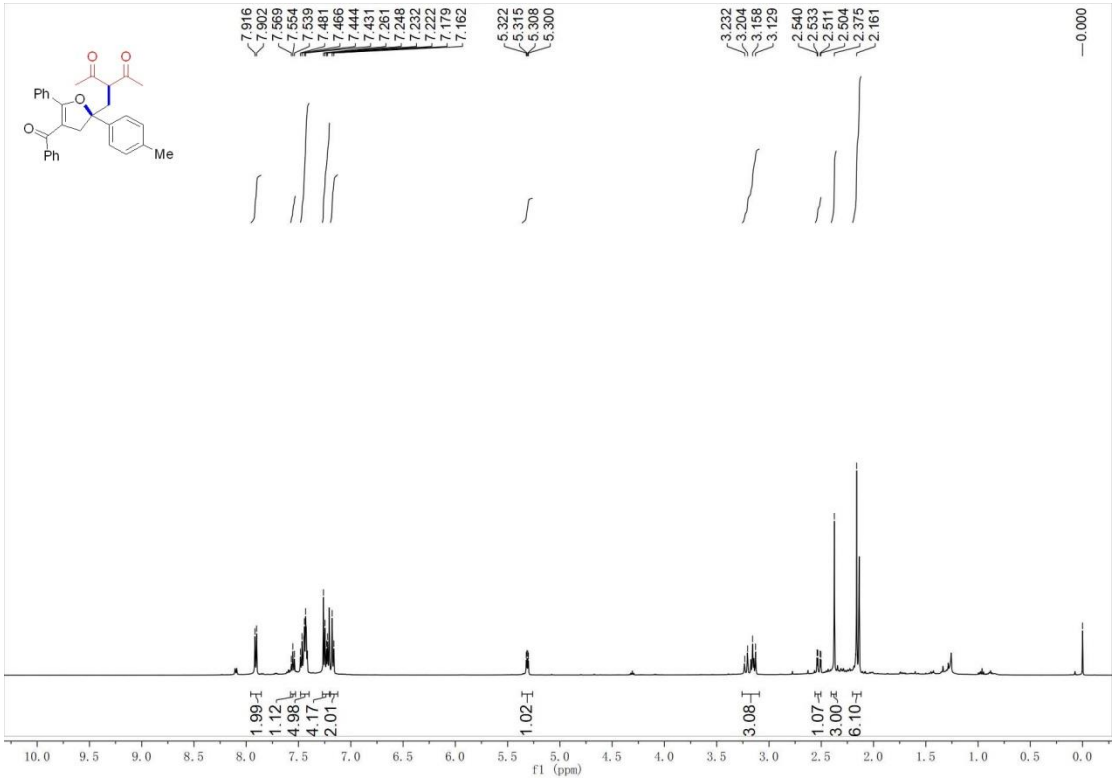


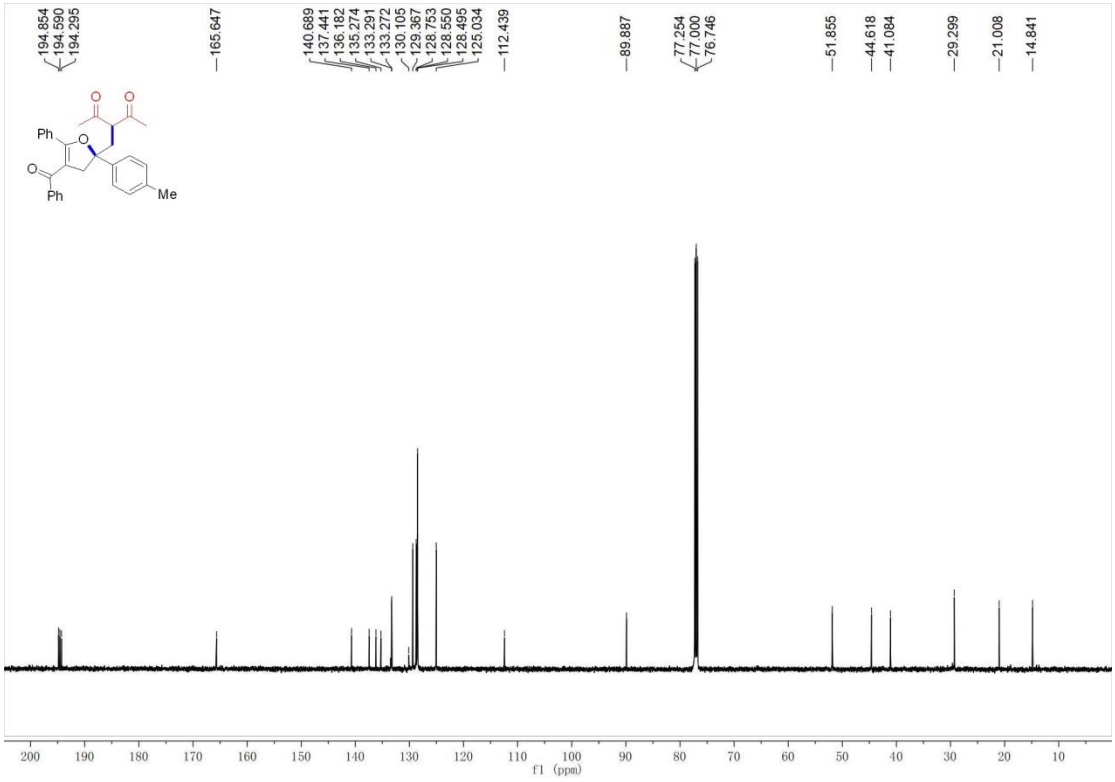
3-((4-Benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ga)



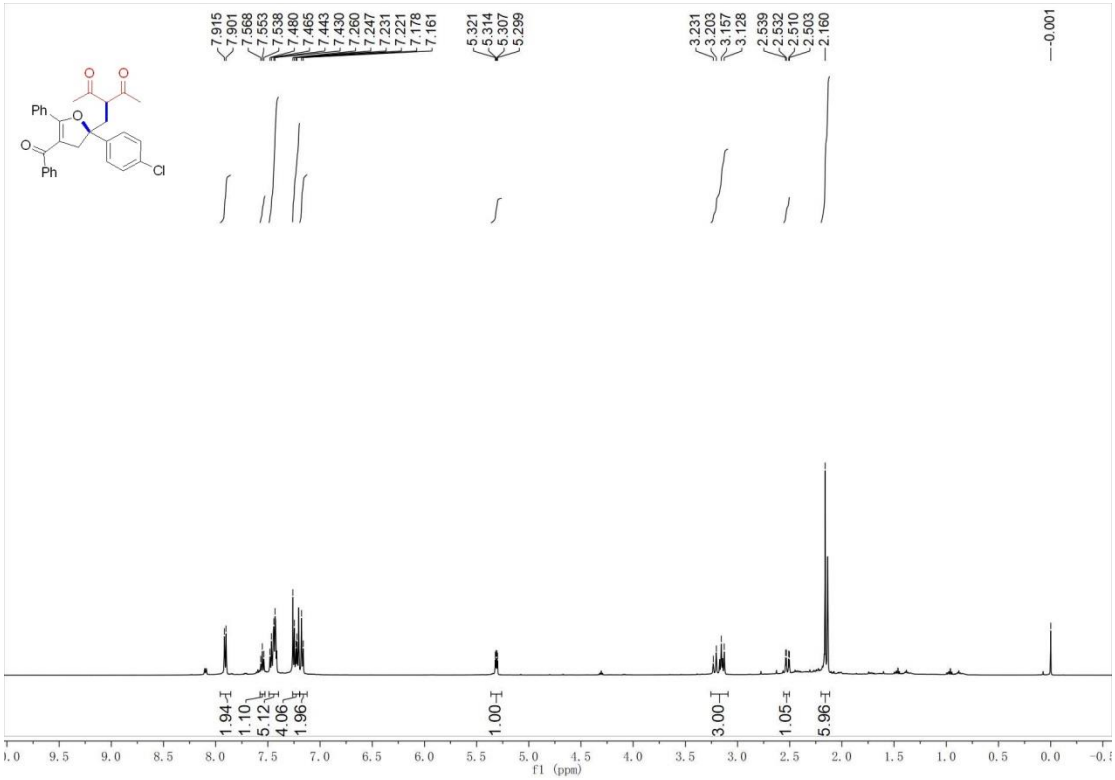


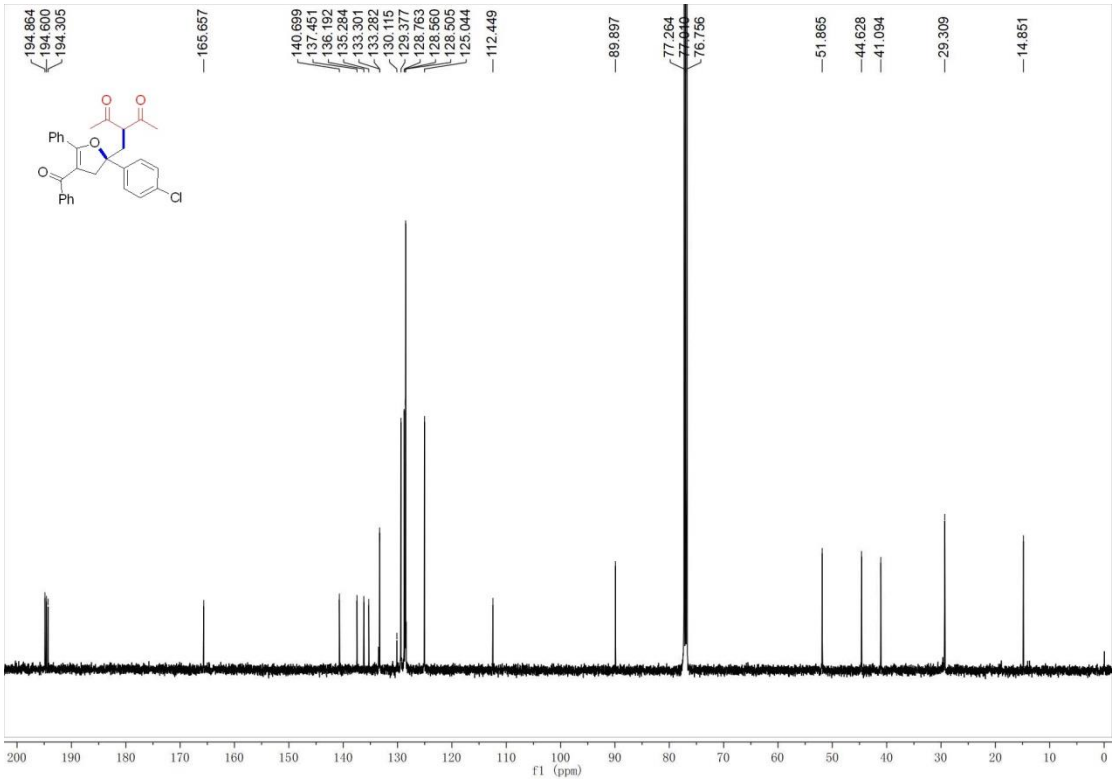
3-((4-Benzoyl-5-phenyl-2-(*p*-tolyl)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ha)



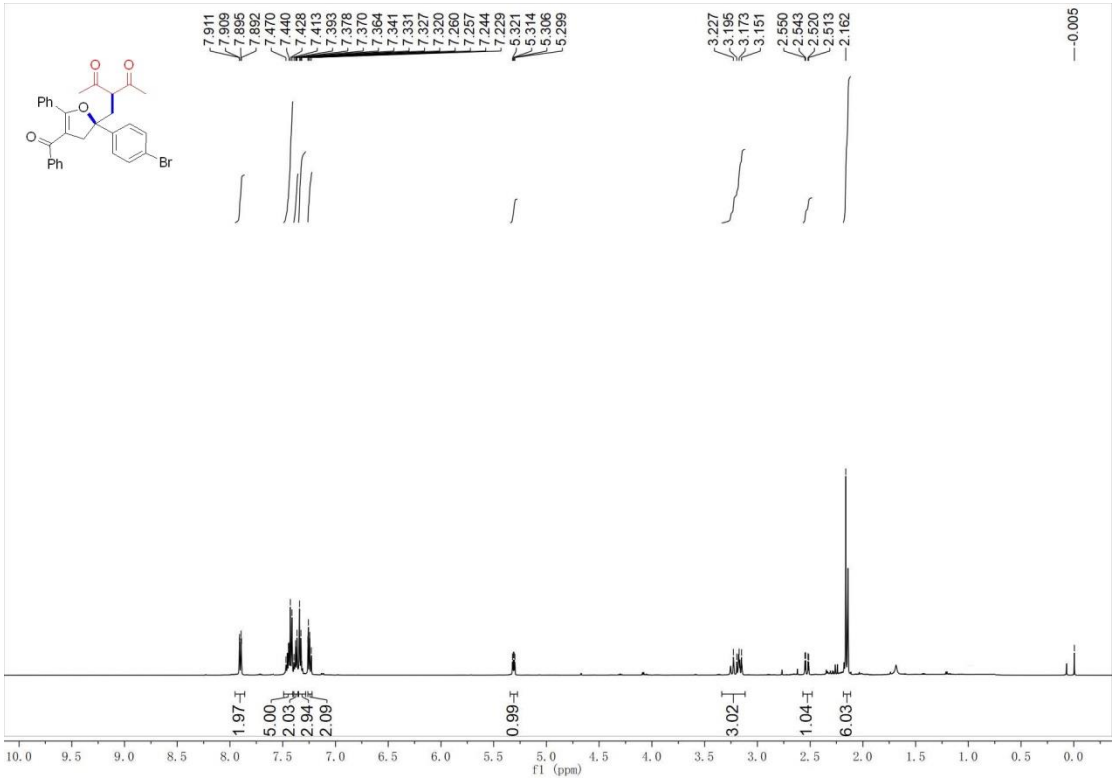


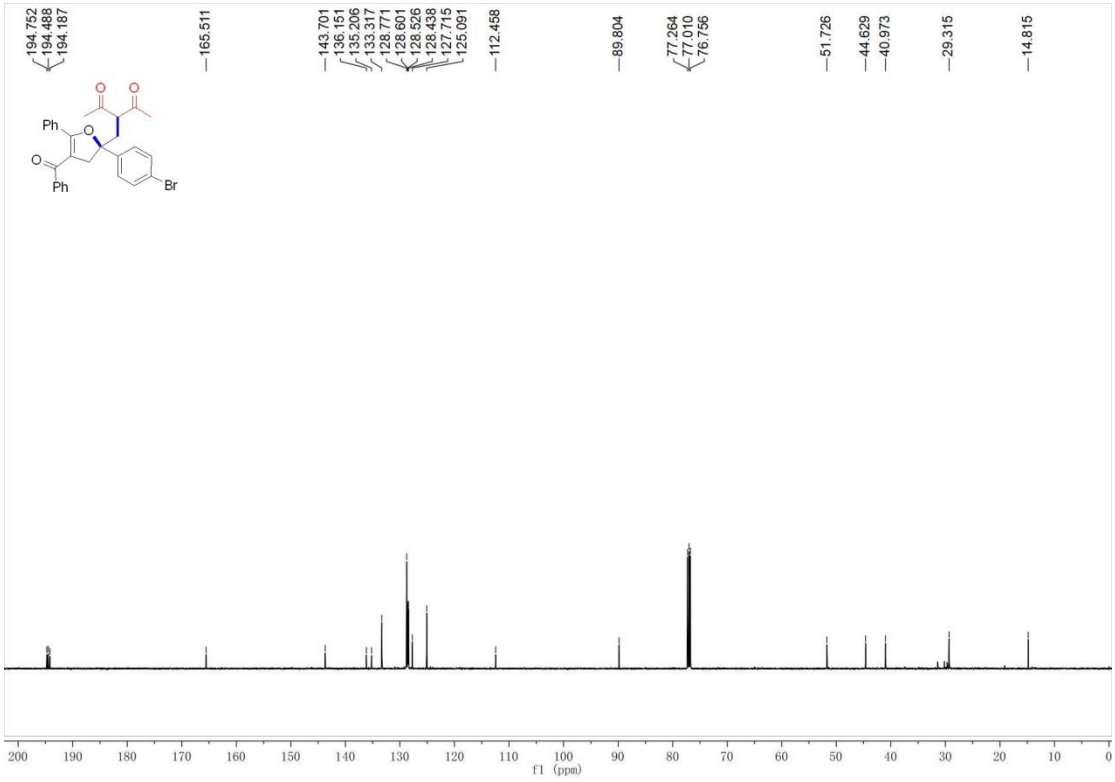
3-((4-Benzoyl-2-(4-chlorophenyl)-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ia)



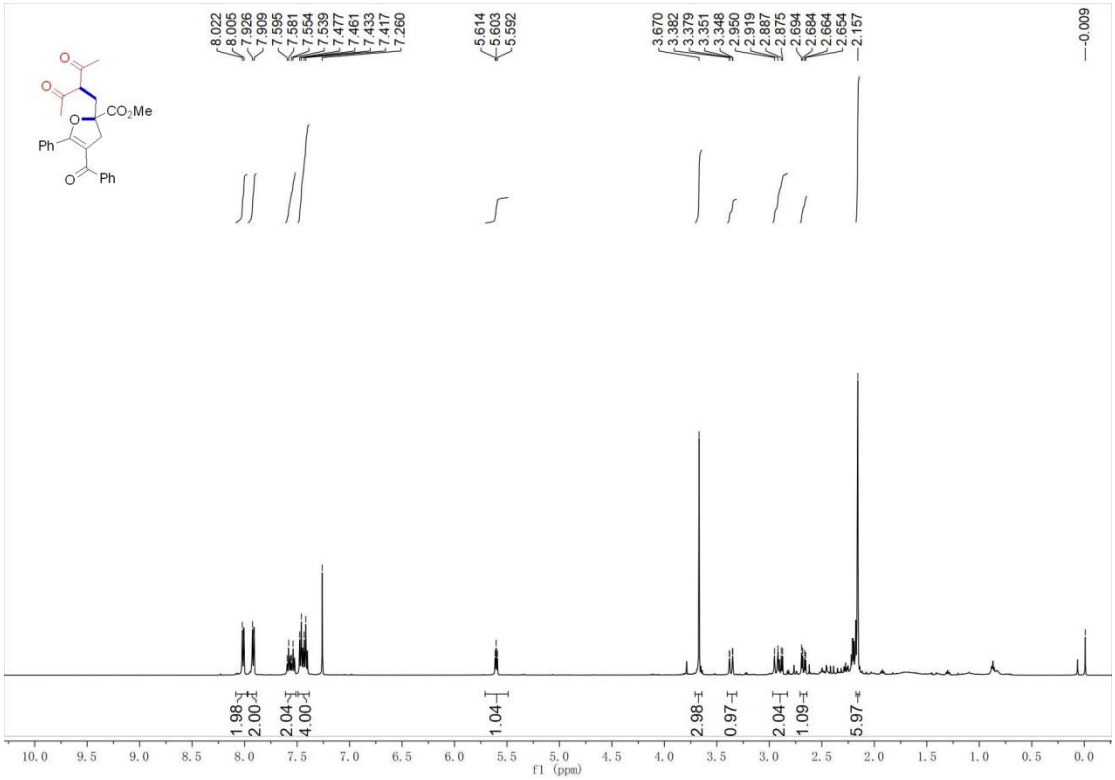


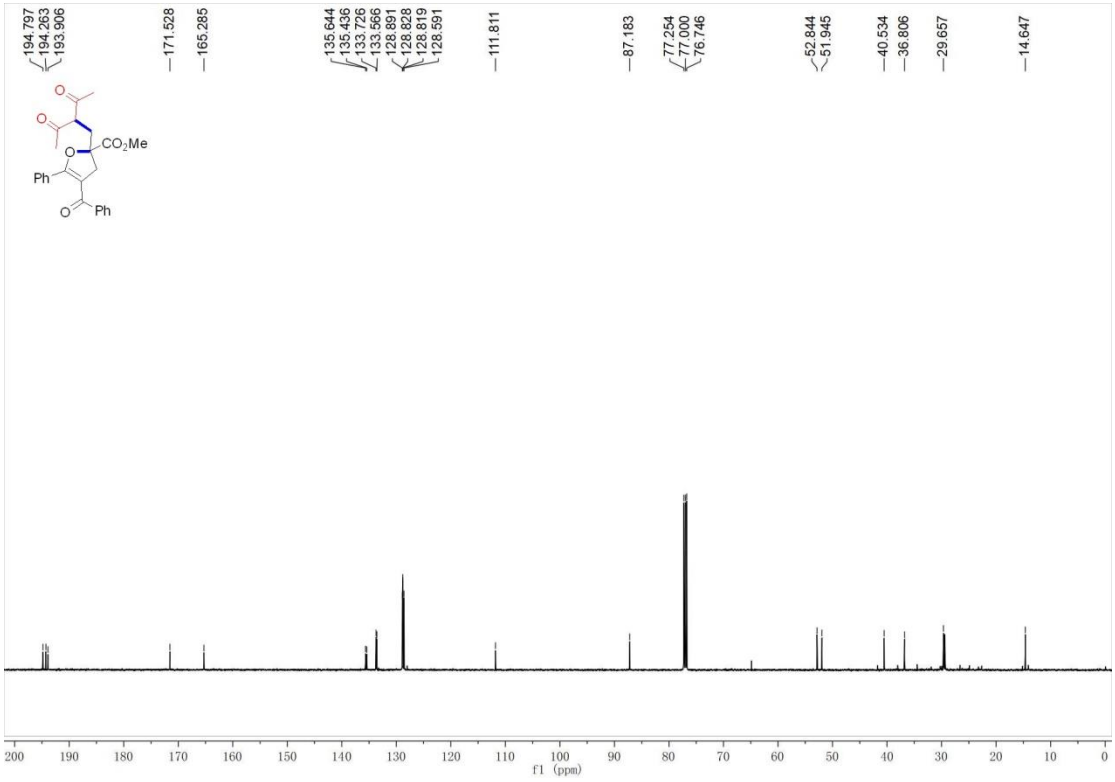
3-((4-Benzoyl-2-(4-bromophenyl)-5-phenyl-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3ja)



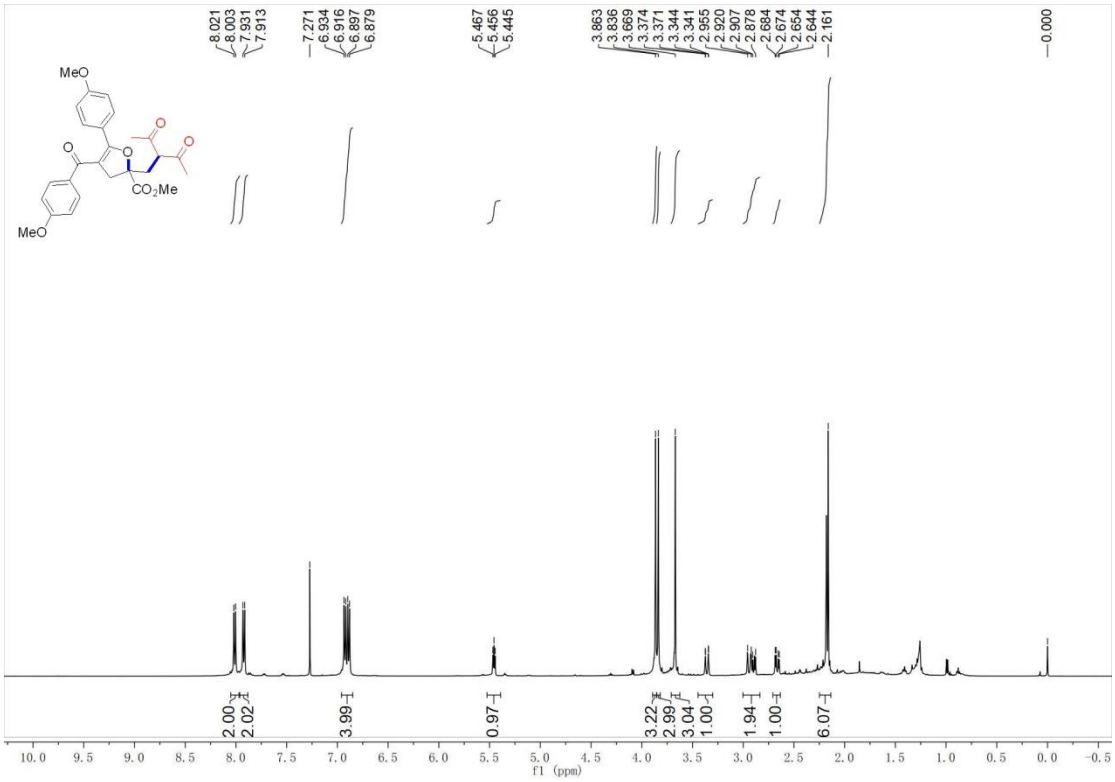


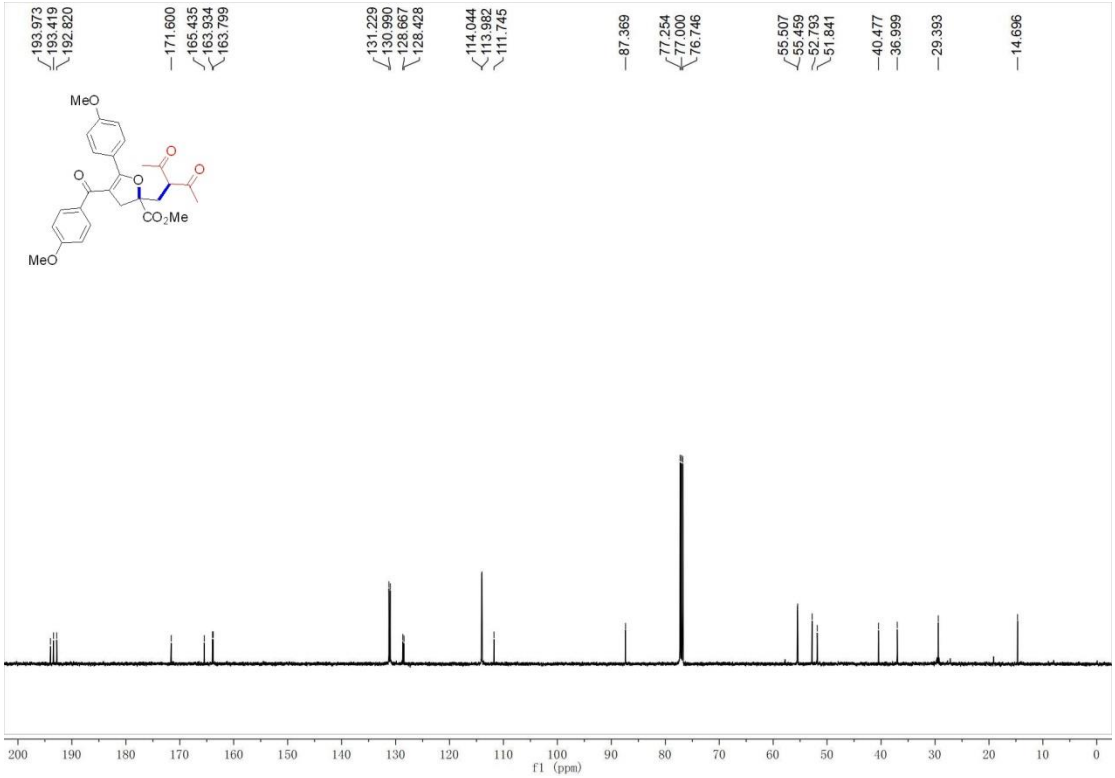
Methyl
2-(2-acetyl-3-oxobutyl)-4-benzoyl-5-phenyl-2,3-dihydrofuran-2-carboxylate (3ka)





Methyl 2-(2-acetyl-3-oxobutyl)-4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydrofuran-2-carboxylate (3ma)

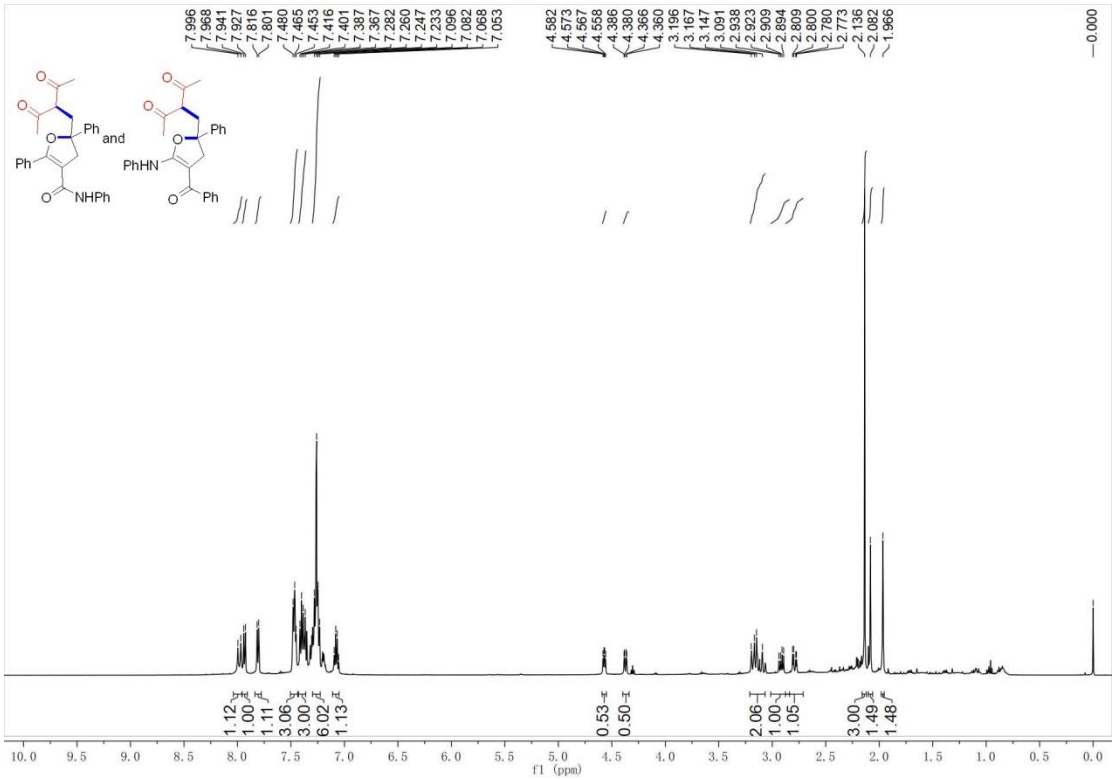


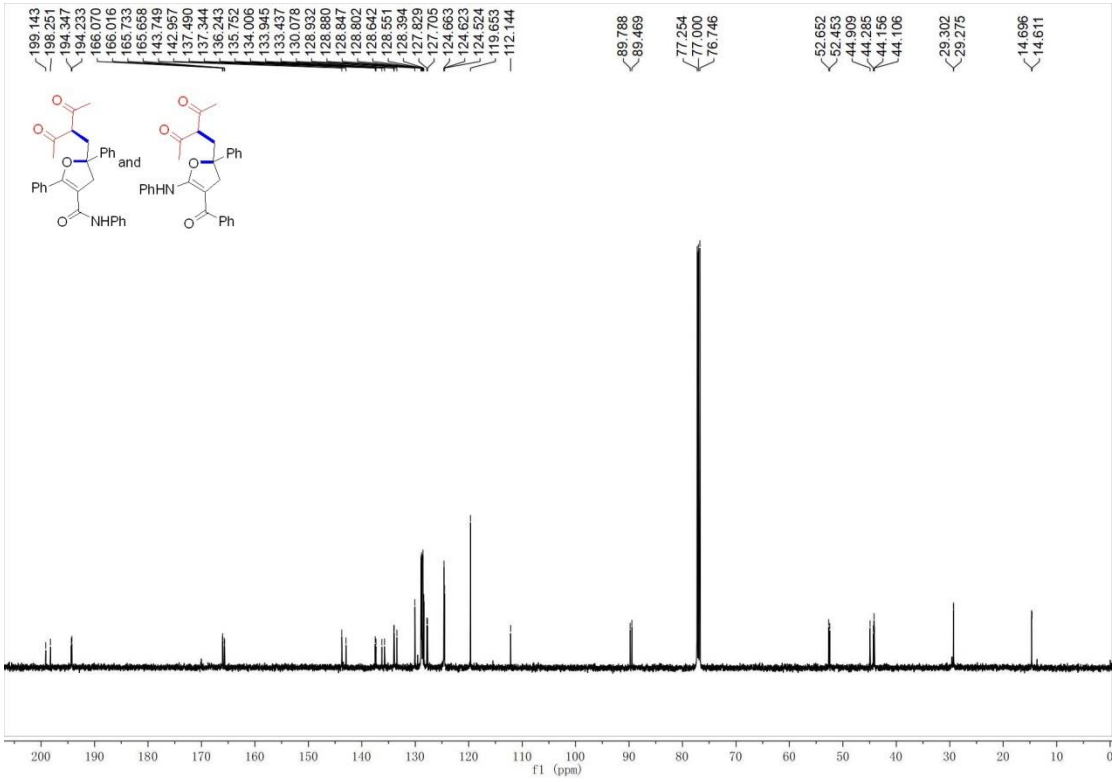


5-(2-Acetyl-3-oxobutyl)-*N*,2,5-triphenyl-4,5-dihydrofuran-3-carboxamide (3na)

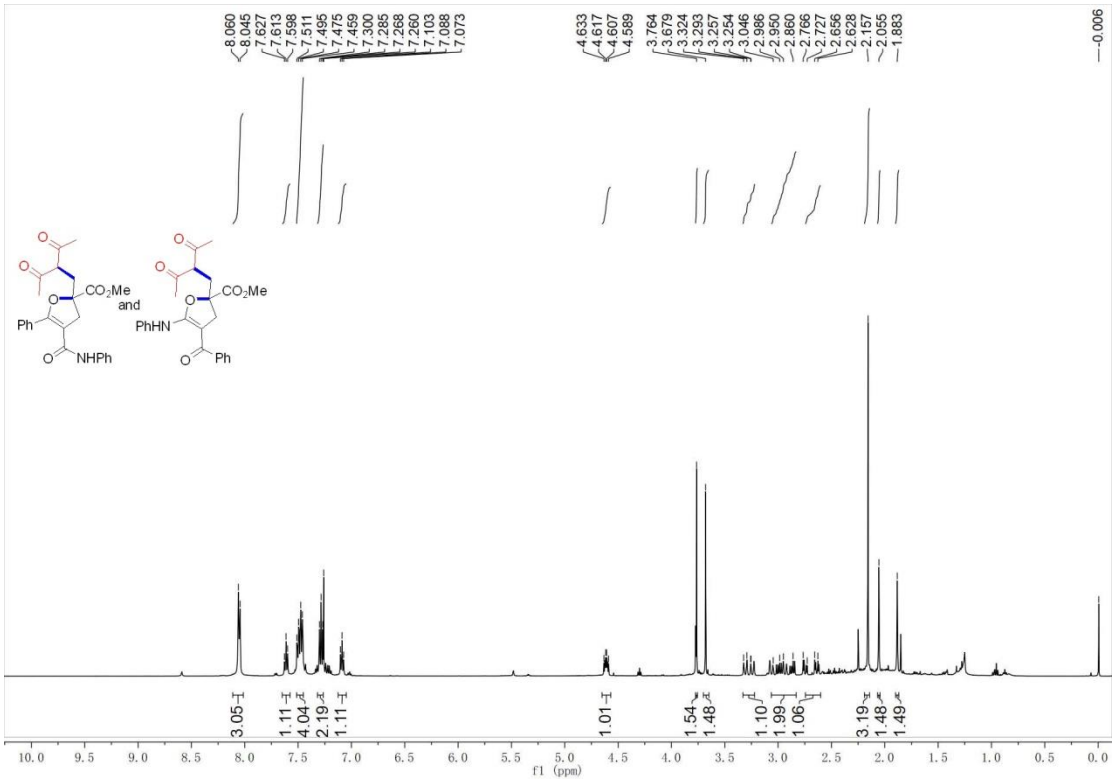
and

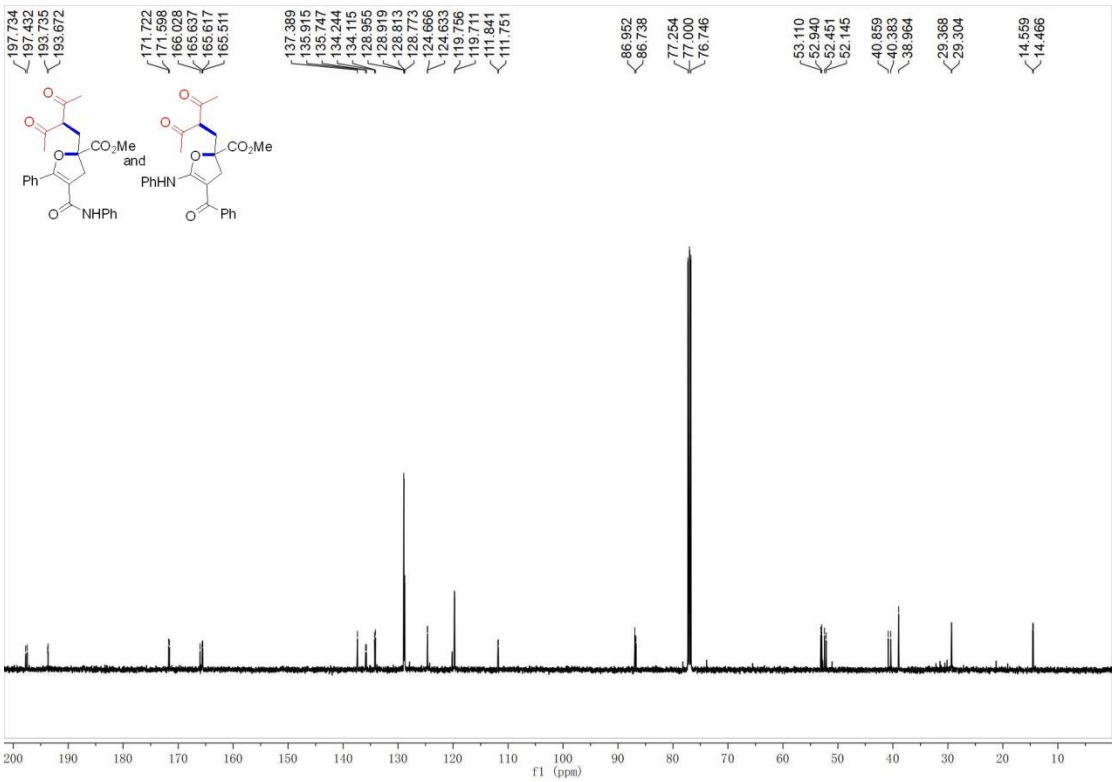
3-((4-Benzoyl-2-phenyl-5-(phenylamino)-2,3-dihydrofuran-2-yl)methyl)pentane-2,4-dione (3na') (3na:3na' = 1:1**)**



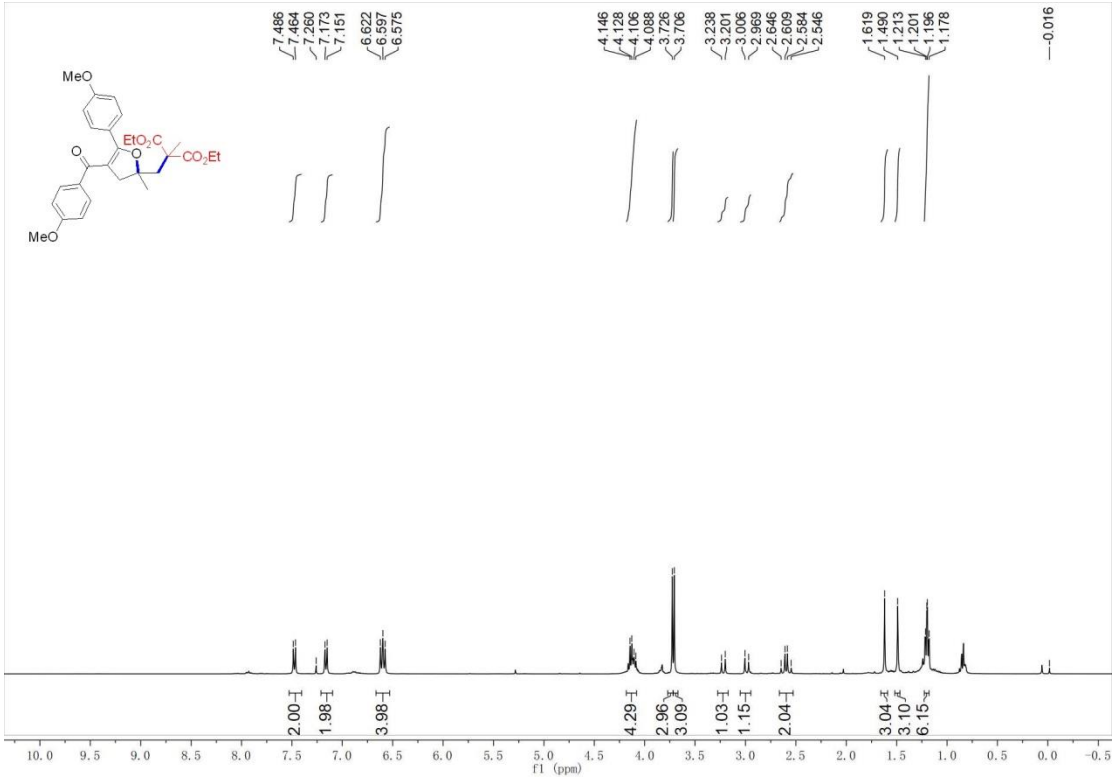


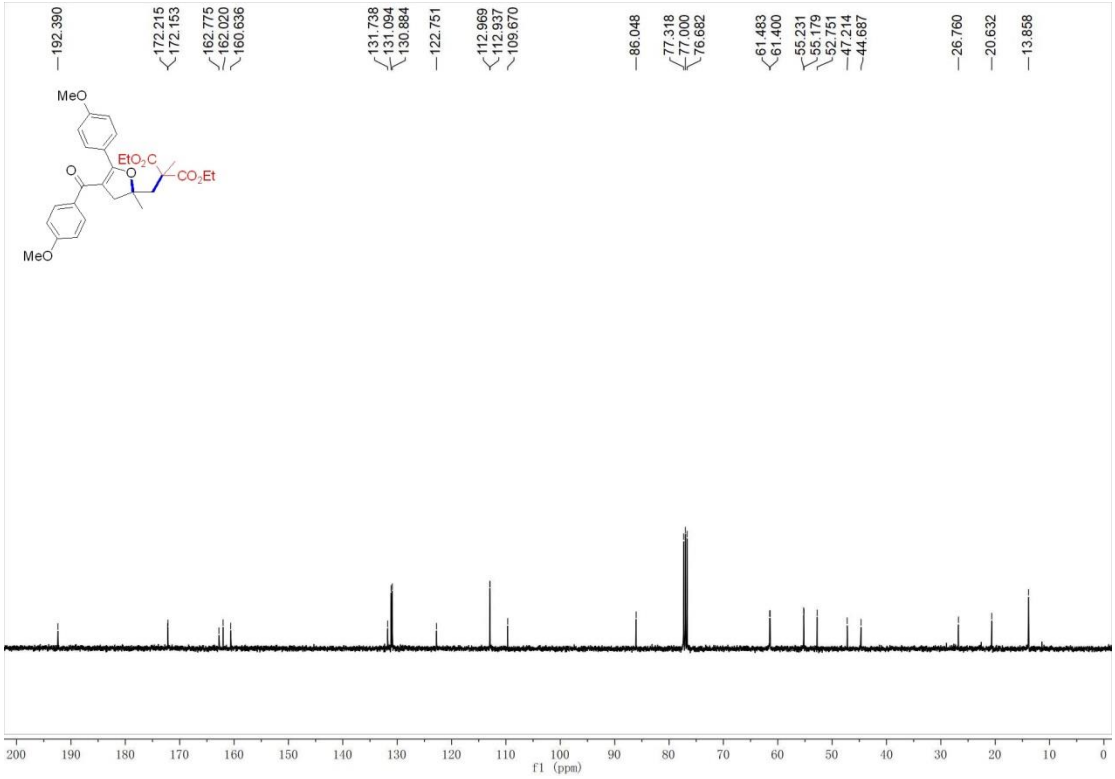
Methyl 2-(2-acetyl-3-oxobutyl)-5-phenyl-4-(phenylcarbamoyl)-2,3-dihydrofuran-2-carboxylate (3oa) and **Methyl 2-(2-acetyl-3-oxobutyl)-4-benzoyl-5-(phenylamino)-2,3-dihydrofuran-2-carboxylate (3oa') (3oa:3oa' = 1:1)**



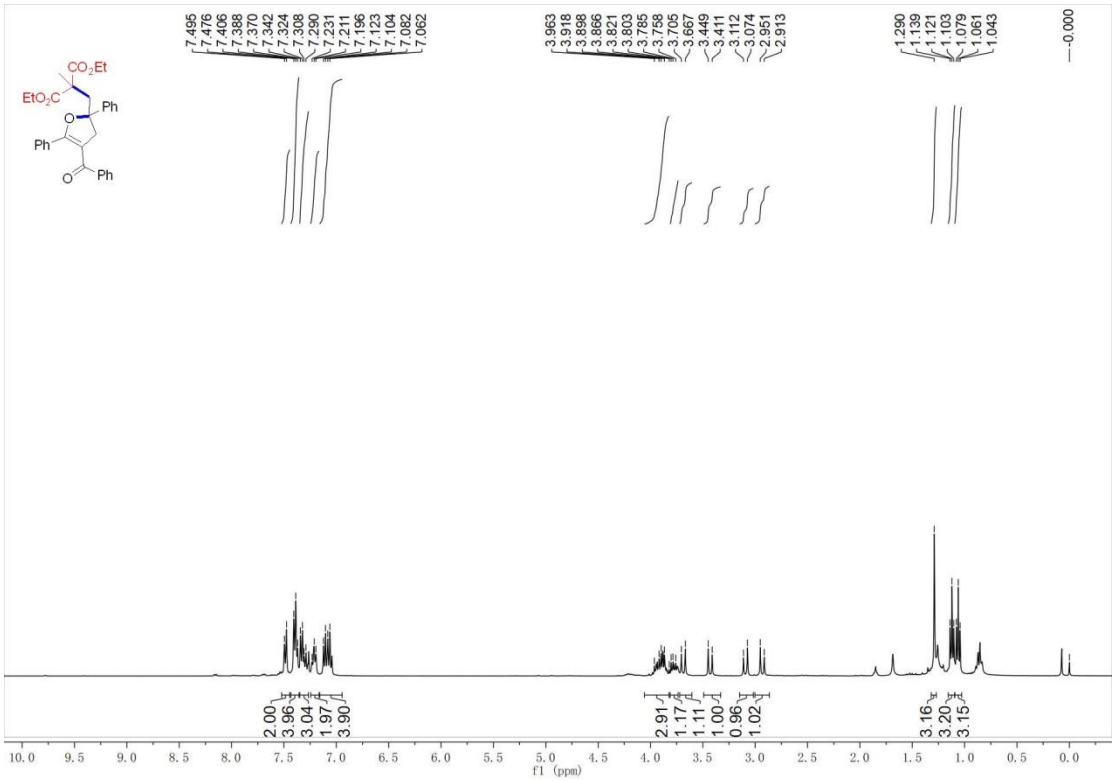


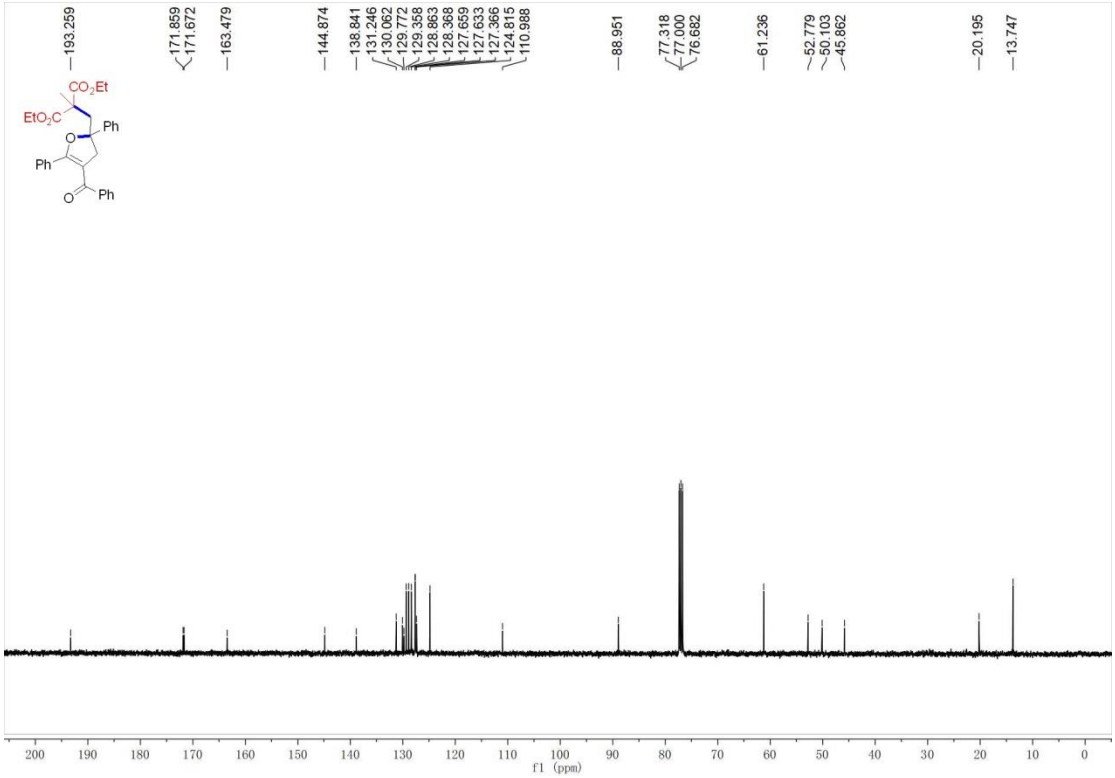
Diethyl
2-((4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl) methyl)-2-methylmalonate (3pf)



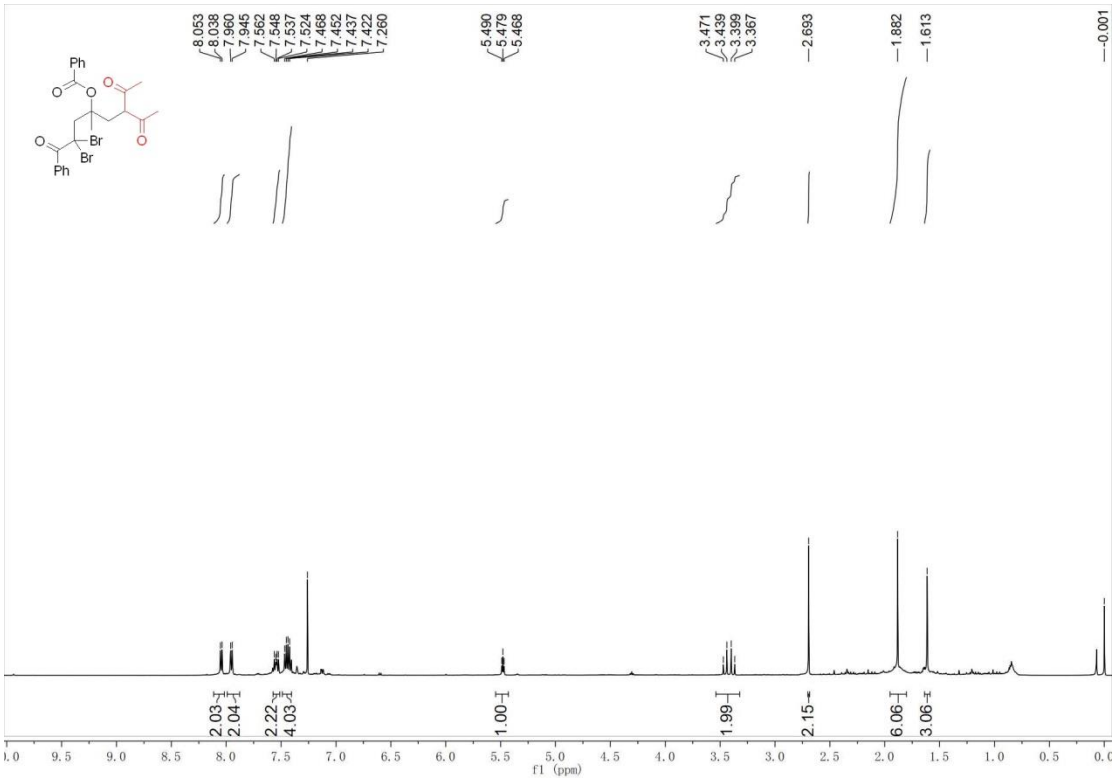


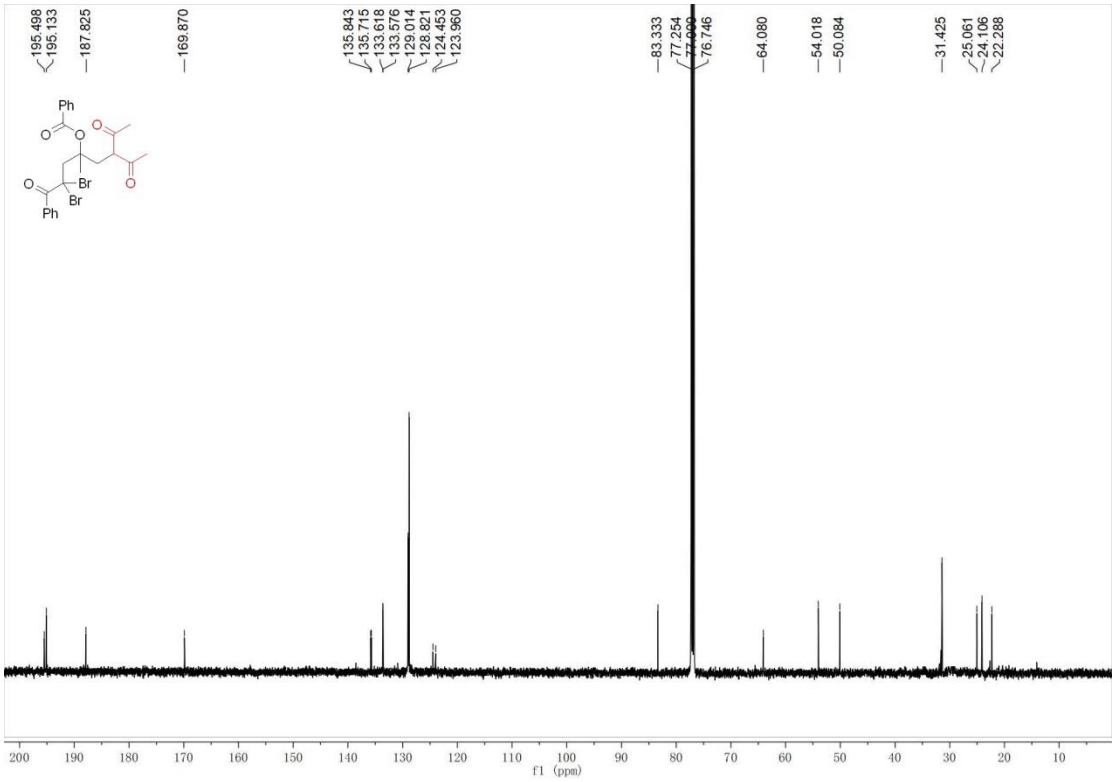
Diethyl
2-((4-benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate
(3qf)





6-Acetyl-2,2-dibromo-4-methyl-1,7-dioxo-1-phenyloctan-4-yl benzoate (5a)





2,6-di-*tert*-Butyl-4-methyl-4-(2-oxopropyl)cyclohexa-2,5-dien-1-one (7a)