Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Silver-Catalyzed Oxidative 1,2-Alkyletherification of Unactivated Alkenes with α-Bromoalkyl Carbonyls: Facile Access to Highly Substituted 2,3-Dihydrofurans

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(A) Typical experimental procedure

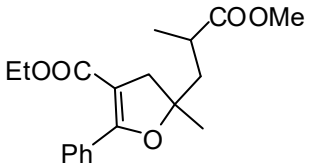
(a) Synthesis of Substrates 1:

Substrates **1**were prepared according to the known procedures.[1]

(b) Typical Experimental Procedure for the Silver-Catalyzed Oxidative Alkene Alkyletherification:

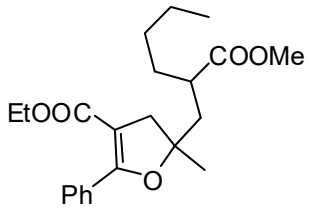
To a Schlenk tube were added alkenes **1** (0.2 mmol), α-bromoalkyl crbonyls **2** (0.4 mmol), Ag_2O (10 mol%), TBHP (2 equiv; 5 M in decane), Et_3N (2 equiv), and DMA (1 mL). Then the tube was charged with argon, and was stirred at 80 ºC for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

(B) Analytical data

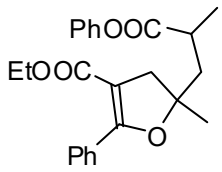


Ethyl 5-(3-methoxy-2-methyl-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3aa**)**:** dr = 1:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 6.4 Hz, 3H), 4.14-4.10 (m, 2H), 3.50 (s, 1.5H), 3.40 (s, 1.5H), 2.99-2.86 (m, 2H), 2.42-2.33 (m, 1H), 1.72-1.62 (m, 2H), 1.47 (s, 1.5H), 1.43 (s, 1.5H), 1.23-1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 177.1, 165.5, 165.4,

164.0, 163.9, 130.3, 130.2 (2), 130.1, 129.3 (2), 127.5, 127.4, 101.6, 101.5, 86.5, 86.4, 59.7, 59.6, 51.6, 51.5, 44.8 (2), 43.5, 43.0, 35.5, 35.4, 26.7, 26.1, 19.3, 14.2; IR (KBr, cm^{-1}): 1752, 1714; LRMS (EI, 70 eV) *m/z* (%): 332 (M^+, 10), 226 (58), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{25}O_5$ ($[M+H]^+$) 333.1697, found 333.1703.

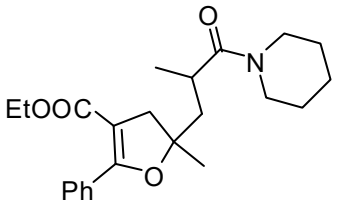


Ethyl 5-(2-(methoxycarbonyl)hexyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ab**)**:** dr = 2:1; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.71 (m, 2H), 7.39-7.34 (m, 3H), 4.15-4.11 (m, 2H), 3.45 (s, 1H), 3.34 (s, 2H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.60-2.55 (m, 1H), 2.36-2.30 (m, 1H), 1.78-1.75 (m, 1H), 1.46 (s, 1H), 1.43 (s, 2H), 1.28-1.26 (m, 6H), 1.23-1.19 (m, 3H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.0, 176.9, 165.4 (2), 164.0, 163.9, 130.4, 130.3, 130.1, 130.0, 129.4, 129.3, 127.4 (2), 101.6 (2), 86.5, 86.4, 59.6 (2), 51.4, 51.2, 43.8, 43.6, 43.4, 42.7, 41.2, 41.1, 33.8 (2), 29.4, 29.3, 27.0, 25.9, 22.5, 22.4, 14.2, 13.8; IR (KBr, cm^{-1}): 1745, 1718; LRMS (EI, 70 eV) *m/z* (%): 374 (M^+, 7), 230 (15), 105 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{31}O_5$ ($[M+H]^+$) 375.2166, found 375.2175.

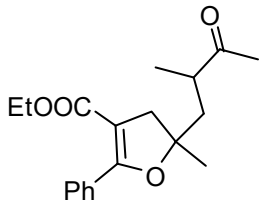


Ethyl 5-methyl-5-(2-methyl-3-oxo-3-phenoxypropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ac**)**:** dr = 1.5:1; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.68 (m, 2H), 7.39-7.34 (m, 3H), 7.32-7.23 (m, 2H), 7.21-7.14 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.13-4.10 (m, 2H), 3.07-2.92 (m, 3H), 2.55-2.49 (m, 1H), 1.87-1.78 (m, 1H), 1.55 (s, 1.8H), 1.51 (s, 1.2H), 1.41-1.38 (m, 3H), 1.22-1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.2, 175.0, 165.4 (2), 164.2, 164.1, 150.6 (2), 130.3, 130.2 (2),

130.1, 129.4 (2), 129.2, 129.1, 127.5 (2), 125.6, 125.5, 121.4, 121.3, 101.7 (2), 86.6, 86.5, 59.7 (2), 44.8, 44.3, 43.7, 43.0, 35.9, 35.8, 26.8, 26.2, 19.5, 14.2; IR (KBr, cm^{-1}): 1742, 1717; LRMS (EI, 70 eV) *m/z* (%): 394 (M^+, 1), 255 (19), 105 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{27}O_5$ ($[M+H]^+$) 395.1853, found 395.1865.

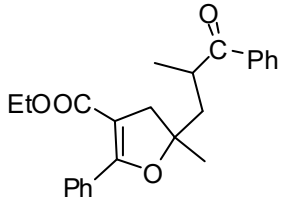


Ethyl 5-methyl-5-(2-methyl-3-oxo-3-(piperidin-1-yl)propyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ad**)**:** dr = 2:1; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.76 (t, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 3H), 4.16-4.11 (m, 2H), 3.72 (d, *J* = 7.6 Hz, 1H), 3.52-3.50 (m, 2H), 3.49-3.46 (m, 2H), 3.00-2.96 (m, 2H), 2.86 (d, *J* = 15.2 Hz, 1H), 2.62-2.58 (m, 1H), 1.68-1.50 (m, 6H), 1.45 (s, 1H), 1.39 (s, 2H), 1.22 (t, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 174.4, 165.7, 165.6, 163.8, 163.7, 130.3, 130.2, 129.4, 129.2, 127.5 (2), 101.4, 99.9, 87.2, 86.9, 59.7, 59.5, 46.6, 46.4, 44.6, 43.8, 43.6, 43.0, 42.9, 30.8, 26.6, 26.5, 25.4, 24.6, 20.1, 20.0, 14.2; IR (KBr, cm^{-1}): 1718, 1674; LRMS (EI, 70 eV) *m/z* (%): 385 (M^+, 13), 181 (36), 141 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{32}NO_4$ ($[M+H]^+$) 386.2325, found 386.2331.

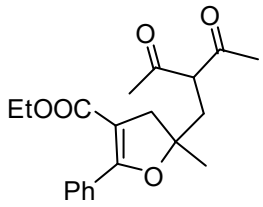


Ethyl 5-methyl-5-(2-methyl-3-oxobutyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ae**)**:** dr = 1:1; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.72 (t, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 3H), 4.14-4.09 (m, 2H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.93-2.83 (m, 3H), 2.42-2.40 (m, 1H), 2.12 (s, 1.5H), 2.09 (s, 1.5H), 1.46 (s, 1.5H), 1.39 (s, 1.5H), 1.20 (d, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 212.0, 211.9, 165.4

(2), 163.9, 163.8, 130.2 (2), 130.1 (2), 129.2 (2), 127.6, 127.5, 101.8, 101.7, 86.7, 86.6, 59.7 (2), 43.8, 43.5, 43.4, 43.2, 42.7 (2), 28.4, 28.3, 27.9, 26.9, 26.6, 18.8, 18.7, 14.2; IR (KBr, cm^{-1}): 1710, 1678; LRMS (EI, 70 eV) *m/z* (%): 316 (M^+, 7), 227 (32), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{25}O_4$ ($[M+H]^+$) 317.1747, found 317.1761.

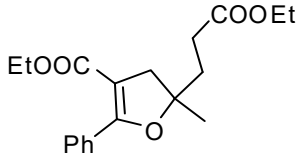


Ethyl 5-methyl-5-(2-methyl-3-oxo-3-phenylpropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3af**)**:** dr = 2:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.89 (m, 2H), 7.62-7.60 (m, 1H), 7.53-7.51 (m, 3H), 7.49-7.37 (m, 3H), 7.35-7.30 (m, 1H), 4.12-4.01 (m, 2H), 3.80-3.73 (m, 1H), 2.90 (d, *J* = 15.2 Hz, 1H), 2.83 (d, *J* = 15.6 Hz, 1H), 2.68-2.65 (m, 1H), 1.86-1.75 (m, 1H), 1.47 (s, 2H), 1.36 (s, 1H), 1.25 (d, *J* = 3.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.3, 203.6, 165.4, 165.2, 163.9, 163.3, 136.3, 132.9 (2), 130.2, 130.1, 130.0, 129.2, 129.1, 128.7, 128.6, 128.4, 128.3, 128.2, 127.4, 127.3, 101.8, 86.8 (2), 59.7, 59.5, 44.2, 43.2, 36.1, 36.0, 27.2, 26.8, 20.2, 20.1, 14.2 (2); IR (KBr, cm^{-1}): 1711, 1686; LRMS (EI, 70 eV) *m/z* (%): 378 (M^+, 5), 134 (16), 105 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{27}O_4$ ($[M+H]^+$) 379.1904, found 379.1910.

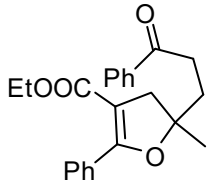


Ethyl 5-(2-acetyl-3-oxobutyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ag**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.54 (t, *J* = 6.0 Hz, 1H), 4.18-4.13 (m, 2H), 2.79-2.71 (m, 2H), 2.45 (t, *J* = 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,

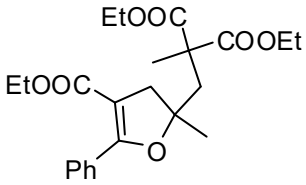
128.8, 128.7, 111.8, 86.8, 61.7, 49.8, 42.7, 39.4, 29.3, 26.4, 15.0, 13.9; IR (KBr, cm^{-1}): 1721, 1663; LRMS (EI, 70 eV) *m/z* (%): 344 (M^+, 4), 255 (22), 105 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{25}O_5$ ($[M+H]^+$) 345.1697, found 345.1705.



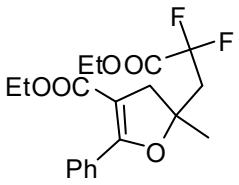
Ethyl 5-(3-ethoxy-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ah**)**:** Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.2 Hz, 2H), 7.41-7.36 (m, 3H), 4.13-4.09 (m, 4H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.88 (d, *J* = 15.2 Hz, 1H), 2.48-2.46 (m, 2H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.47 (s, 3H), 1.25-1.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 165.4, 163.9, 130.2, 129.2, 127.5, 101.6, 86.3, 60.5, 59.7, 42.5, 35.8, 29.1, 26.5, 14.2, 14.1; IR (KBr, cm^{-1}): 1748, 1712; LRMS (EI, 70 eV) *m/z* (%): 332 (M^+, 7), 286 (21), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{25}O_5$ ($[M+H]^+$) 333.1697, found 333.1700.



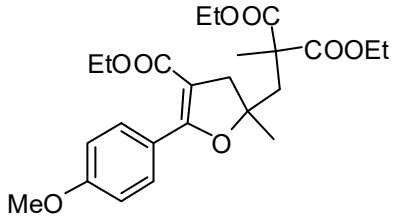
Ethyl 5-methyl-5-(3-oxo-3-phenylpropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3ai**)**:** Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47-7.41 (m, 2H), 7.39-7.36 (m, 3H), 4.15-4.10 (m, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 3.04 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.24-2.20 (m, 2H), 1.52 (s, 3H), 1.21 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 165.4, 164.0, 136.7, 133.1, 130.3, 130.2, 129.2, 128.6, 128.0, 127.6, 101.8, 86.7, 59.7, 42.7, 35.0, 33.1, 26.7, 14.2; IR (KBr, cm^{-1}): 1708, 1685; LRMS (EI, 70 eV) *m/z* (%): 364 (M^+, 5), 213 (44), 105 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{25}O_4$ ($[M+H]^+$) 365.1747, found 365.1756.



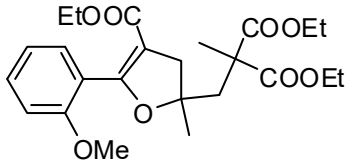
Diethyl 2-((4-(ethoxycarbonyl)-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3aj): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 6.8 Hz, 2H), 7.40-7.34 (m, 3H), 4.13-4.08 (m, 6H), 3.05 (d, *J* = 15.2 Hz, 1H), 2.87 (d, *J* = 15.2 Hz, 1H), 2.60-2.50 (m, 2H), 1.59 (s, 3H), 1.44 (s, 3H), 1.22-1.17 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 172.1, 165.4, 163.6, 130.2 (2), 129.3, 127.5, 101.5, 86.1, 61.5, 61.4, 59.7, 52.7, 45.6, 44.8, 27.0, 20.6, 14.2, 14.0, 13.9; IR (KBr, cm^{-1}): 1747, 1709; LRMS (EI, 70 eV) *m/z* (%): 418 (M^+, 5), 230 (16), 105 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{31}O_7$ ($[M+H]^+$) 419.2064, found 419.2073.



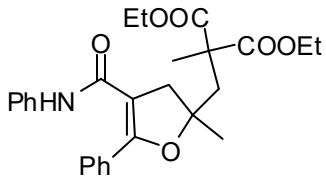
Ethyl 5-(3-ethoxy-2,2-difluoro-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ak): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (t, *J* = 4.0 Hz, 2H), 7.40-7.35 (m, 3H), 4.14-4.03 (m, 4H), 3.15 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.69-2.54 (m, 2H), 1.59 (s, 3H), 1.14-1.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 164.1 (t, *J* = 31.3 Hz, 1C), 163.0, 130.4, 129.8, 129.3, 127.5, 114.8 (d, *J* = 1.4 Hz, 1C), 101.9, 83.4, 62.9, 59.8, 48.6 (d, *J* = 29.9 Hz, 1C), 44.3 (t, *J* = 22.4 Hz, 1C), 26.4 (t, *J* = 12.6 Hz, 1C), 14.2, 13.6; ^{19}F NMR (375 MHz, $CDCl_3$) δ: -100.8, -101.5, -102.1, -102.8; IR (KBr, cm^{-1}): 1759, 1711; LRMS (EI, 70 eV) *m/z* (%): 368 (M^+, 1), 330 (21), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{23}F_2O_5$ ($[M+H]^+$) 369.1509, found 369.1523.



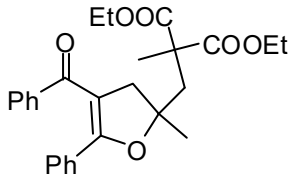
Diethyl 2-((4-(ethoxycarbonyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3bj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.15-4.07 (m, 6H), 3.83 (s, 3H), 3.03 (d, *J* = 14.8 Hz, 1H), 2.85 (d, *J* = 14.8 Hz, 1H), 2.59-2.49 (m, 2H), 1.59 (s, 3H), 1.42 (s, 3H), 1.25-1.19 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 172.2, 165.7, 163.5, 161.1, 131.1, 122.5, 112.9, 100.0, 85.7, 61.5 (2), 59.6, 55.3, 52.8, 45.8, 44.8, 27.0, 20.6, 14.4, 13.9 (2); IR (KBr, cm^{-1}): 1748, 1710; LRMS (EI, 70 eV) *m/z* (%): 448 (M^+, 10), 229 (38), 135 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{33}O_8$ ($[M+H]^+$) 449.2170, found 449.2176.



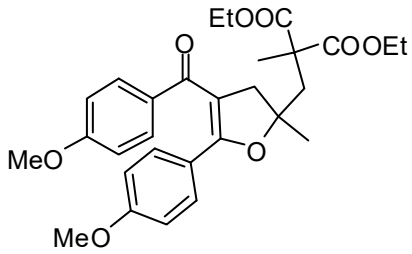
Diethyl 2-((4-(ethoxycarbonyl)-5-(2-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3cj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.32 (m, 1H), 7.32-7.26 (m, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.13-4.12 (m, 4H), 4.02-3.97 (m, 2H), 3.79 (s, 3H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.80 (d, *J* = 14.8 Hz, 1H), 2.62-2.51 (m, 2H), 1.57 (s, 3H), 1.44 (s, 3H), 1.22-1.18 (m, 6H), 1.03 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 172.2, 165.5, 161.7, 157.3, 130.8, 130.2, 120.7, 119.8, 110.8, 104.0, 87.3, 61.5, 61.4, 59.3, 55.5, 52.8, 44.5, 44.2, 26.8, 20.2, 14.0, 13.9, 13.8; IR (KBr, cm^{-1}): 1753, 1708; LRMS (EI, 70 eV) *m/z* (%): 448 (M^+, 7), 229 (37), 135 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{33}O_8$ ($[M+H]^+$) 449.2170, found 449.2174.



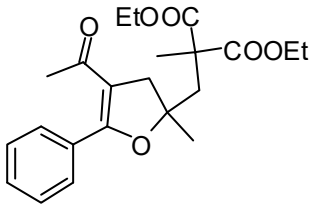
Diethyl 2-methyl-2-((2-methyl-5-phenyl-4-(phenylcarbamoyl)-2,3-dihydrofuran-2-yl)methyl)malonate (**3ej**): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63-7.53 (m, 2H), 7.52-7.46 (m, 4H), 7.25-7.22 (m, 3H), 7.02 (t, *J* = 4.0 Hz, 1H), 4.18-4.11 (m, 4H), 3.16 (d, *J* = 14.8 Hz, 1H), 2.98 (d, *J* = 14.8 Hz, 1H), 2.63-2.54 (m, 2H), 1.61 (s, 3H), 1.48 (s, 3H), 1.23-1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 172.1, 163.2, 158.5, 138.0, 130.6, 129.0, 128.9, 128.7, 123.6, 119.8, 119.1, 106.2, 86.2, 61.5, 61.4, 52.7, 45.8, 44.8, 27.2, 20.7, 14.0, 13.9; IR (KBr, cm^{-1}): 1746, 1682; LRMS (EI, 70 eV) *m/z* (%): 465 (M^+, 7), 207 (6), 105 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{32}NO_6$ ($[M+H]^+$) 466.2226, found 466.2233.



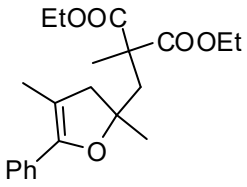
Diethyl 2-((4-benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3fj**): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 2H), 7.21-7.14 (m, 4H), 7.08-7.02 (m, 4H), 4.14-4.11 (m, 4H), 3.26 (d, *J* = 15.2 Hz, 1H), 3.04 (d, *J* = 14.8 Hz, 1H), 2.68-2.59 (m, 2H), 1.64 (s, 3H), 1.53 (s, 3H), 1.23-1.18 (m, 6H); ^{13}C NMR (100 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, 13.8; IR (KBr, cm^{-1}): 1742, 1681; LRMS (EI, 70 eV) *m/z* (%): 450 (M^+, 3), 259 (10), 105 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{31}O_6$ ($[M+H]^+$) 451.2115, found 451.2123.



Diethyl 2-((4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3gj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.64-6.59 (m, 4H), 4.16-4.10 (m, 4H), 3.74 (s, 3H), 3.72 (s, 3H), 3.23 (d, *J* = 14.8 Hz, 1H), 3.01 (d, *J* = 14.8 Hz, 1H), 2.66-2.56 (m, 2H), 1.64 (s, 3H), 1.51 (s, 3H), 1.24-1.19 (m, 6H); ^{13}C NMR (100 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; IR (KBr, cm^{-1}): 1738, 1672; LRMS (EI, 70 eV) *m/z* (%): 510 (M^+, 4), 323 (13), 135 (100); HRMS *m/z* (ESI) calcd for $C_{29}H_{35}O_8$ ($[M+H]^+$) 511.2326, found 511.2334.

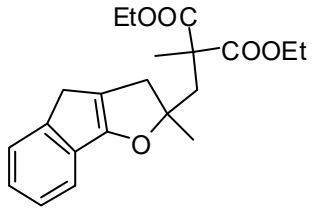


Diethyl 2-((4-acetyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3hj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (t, *J* = 4.0 Hz, 2H), 7.46-7.40 (m, 3H), 4.10-4.07 (m, 4H), 3.05 (d, *J* = 14.8 Hz, 1H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.59-2.51 (m, 2H), 1.93 (s, 3H), 1.57 (s, 3H), 1.44 (s, 3H), 1.21-1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.7, 172.2, 172.0, 164.9, 131.1, 130.4, 129.1, 128.2, 114.1, 87.0, 61.5, 61.4, 52.7, 45.2, 44.7, 28.8, 27.1, 20.6, 13.8 (2); IR (KBr, cm^{-1}): 1744, 1658; LRMS (EI, 70 eV) *m/z* (%): 388 (M^+, 8), 215 (19), 105 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{29}O_6$ ($[M+H]^+$) 389.1959, found 389.1971.

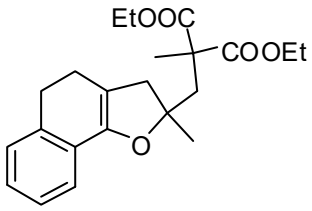


Diethyl 2-((2,4-dimethyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3ij**)**:** Yellow oil; ^{1}H NMR (400

MHz, $CDCl_3$) δ: 7.47 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 4.18-4.13 (m, 2H), 4.10-4.05 (m, 2H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.54-2.43 (m, 3H), 1.87 (s, 3H), 1.61 (s, 3H), 1.36 (s, 3H), 1.22-1.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 172.5, 146.5, 132.3, 128.0, 127.4, 126.9, 104.2, 81.8, 61.3, 61.2, 53.0, 52.0, 45.0, 27.7, 20.4, 13.9 (2), 12.9; IR (KBr, cm^{-1}): 1738; LRMS (EI, 70 eV) *m/z* (%): 360 (M^+, 17), 174 (100), 129 (16); HRMS *m/z* (ESI) calcd for $C_{21}H_{29}O_5$ ($[M+H]^+$) 361.2010, found 361.2023.

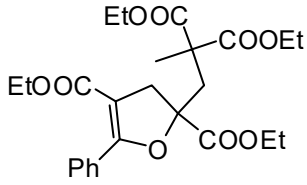


Diethyl 2-methyl-2-((2-methyl-3,4-dihydro-2*H*-indeno[1,2-b]furan-2-yl)methyl)malonate (**3jj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03-7.99 (m, 1H), 7.47-7.42 (m, 1H), 7.31-7.27 (m, 1H), 7.23 (t, *J* = 3.6 Hz, 1H), 4.21-4.14 (m, 4H), 2.99-2.96 (m, 2H), 2.76 (d, *J* = 14.4 Hz, 2H), 2.64 (d, *J* = 14.4 Hz, 2H), 1.44 (s, 3H), 1.26-1.22 (m, 6H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 172.1, 144.0, 142.1, 133.2, 132.4, 128.7, 127.4, 126.5, 104.3, 82.0, 61.5, 61.4, 53.2, 45.3, 40.1, 36.7, 26.8, 19.8, 14.0, 13.9; IR (KBr, cm^{-1}): 1742; LRMS (EI, 70 eV) *m/z* (%): 358 (M^+, 4), 221 (12), 185 (100); HRMS *m/z* (ESI) calcd for $C_{21}H_{27}O_5$ ($[M+H]^+$) 359.1853, found 359.1861.

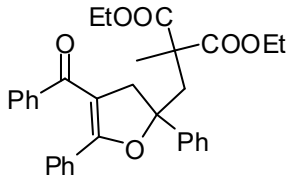


Diethyl 2-methyl-2-((2-methyl-2,3,4,5-tetrahydronaphtho[1,2-b]furan-2-yl)methyl)malonate (**3kj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04-7.99 (m, 1H), 7.48-7.43 (m, 1H), 7.32 (t, *J* = 5.6 Hz, 1H), 7.24 (t, *J* = 4.0 Hz, 1H), 4.22-4.17 (m, 4H), 3.00-2.97 (m, 2H), 2.77 (d, *J* = 14.4 Hz, 2H), 2.65 (d, *J* = 14.4 Hz, 2H),

2.47-2.33 (m, 2H), 1.44 (s, 3H), 1.27-1.24 (m, 6H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 172.1, 144.0, 142.1, 133.2, 132.4, 128.7, 127.4, 126.5, 103.4, 82.4, 61.5, 61.4, 53.2, 45.3, 40.1, 28.4, 27.6, 26.8, 19.8, 14.0, 13.9; IR (KBr, cm^{-1}): 1746; LRMS (EI, 70 eV) *m/z* (%): 372 (M^+, 7), 199 (100), 181 (16); HRMS *m/z* (ESI) calcd for $C_{22}H_{29}O_5$ ($[M+H]^+$) 373.2010, found 373.2014.

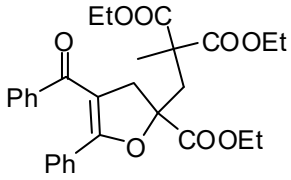


Diethyl 2-(3-ethoxy-2-(ethoxycarbonyl)-2-methyl-3-oxopropyl)-5-phenyl-2,3-dihydrofuran-2,4-dicarboxylate (**3lj**): Yellow oil; ^{1}H NMR (400 MHz) δ: 7.57 (t, *J* = 6.8 Hz, 1H), 7.48-7.45 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 4.28-4.20 (m, 8H), 3.33 (d, *J* = 15.6 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 2.89-2.84 (m, 2H), 1.48 (s, 3H), 1.33-1.26 (m, 12H); ^{13}C NMR (100 MHz) δ: 172.7, 171.1, 169.9, 169.5, 164.4, 130.5, 129.5, 129.1, 129.0, 101.1, 85.0, 61.6, 61.4, 61.2, 61.1, 52.3, 45.0, 42.1, 18.8, 14.2, 14.0, 13.8, 13.7; IR (KBr, cm^{-1}): 1751, 1748, 1712; LRMS (EI, 70 eV) *m/z* (%): 476 (M^+, 1), 311 (32), 229 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{33}O_9$ ($[M+H]^+$) 477.2119, found 477.2125.

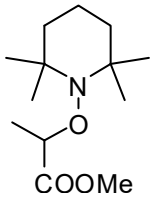


Diethyl 2-((4-benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3mj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 2H), 7.50-7.37 (m, 4H), 7.34-7.29 (m, 3H), 7.22-7.20 (m, 2H), 7.12-7.04 (m, 4H), 3.96-3.78 (m, 4H), 3.68 (d, *J* = 15.2 Hz, 1H), 3.43 (d, *J* = 15.2 Hz, 1H), 3.19 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 1.29 (s, 3H), 1.14-1.04 (m, 6H); ^{13}C NMR (100 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; IR (KBr, cm^{-1}):

1750, 1677; LRMS (EI, 70 eV) *m/z* (%): 512 (M^+, 3), 293 (40), 105 (100); HRMS *m/z* (ESI) calcd for $C_{32}H_{33}O_6$ ($[M+H]^+$) 513.2272, found 513.2283.



Diethyl 2-((4-benzoyl-2-(ethoxycarbonyl)-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (**3nj**)**:** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.6 Hz, 3H), 7.27-7.22 (m, 3H), 7.09-7.04 (m, 4H), 4.31-4.29 (m, 2H), 4.16-4.11 (m, 4H), 3.51-3.41 (m, 2H), 3.06 (d, *J* = 14.8 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 1.53 (s, 3H), 1.26-1.20 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 172.5, 171.7, 171.2, 164.5, 138.4, 131.4, 130.2, 129.5, 128.9, 128.3, 127.7, 127.5, 110.3, 85.7, 62.0, 61.6, 61.3, 52.4, 46.4, 41.9, 19.0, 14.0, 13.9, 13.7; IR (KBr, cm^{-1}): 1748, 1742, 1683; LRMS (EI, 70 eV) *m/z* (%): 508 (M^+, 1), 335 (10), 105 (100); HRMS *m/z* (ESI) calcd for $C_{29}H_{33}O_8$ ($[M+H]^+$) 509.2170, found 509.2176.



Methyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (**4a**)**:**[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.36-4.31 (m, 1H), 3.71 (s, 3H), 1.52-1.44 (m, 4H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.35-1.26 (m, 2H), 1.18 (s, 3H), 1.12 (s, 6H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 81.6, 60.0, 59.4, 51.4, 40.2, 40.0, 33.6, 32.8, 20.1, 20.0, 18.1, 17.1.

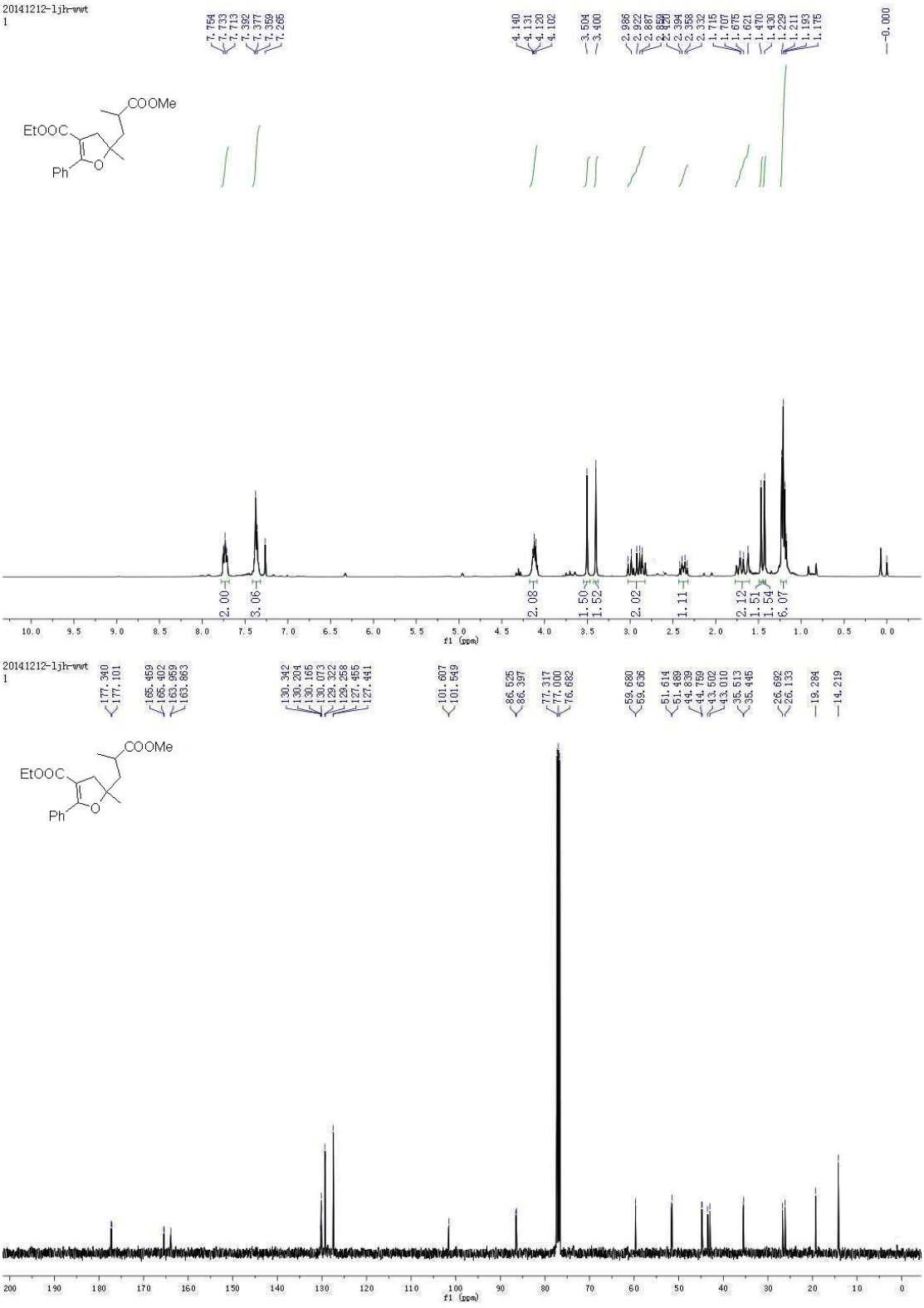
(C) References

1 Y. Zhao, X. Jiang and Y.-Y. Yeung, *Angew. Chem. Int. Ed.,* 2013, **52**, 8597.

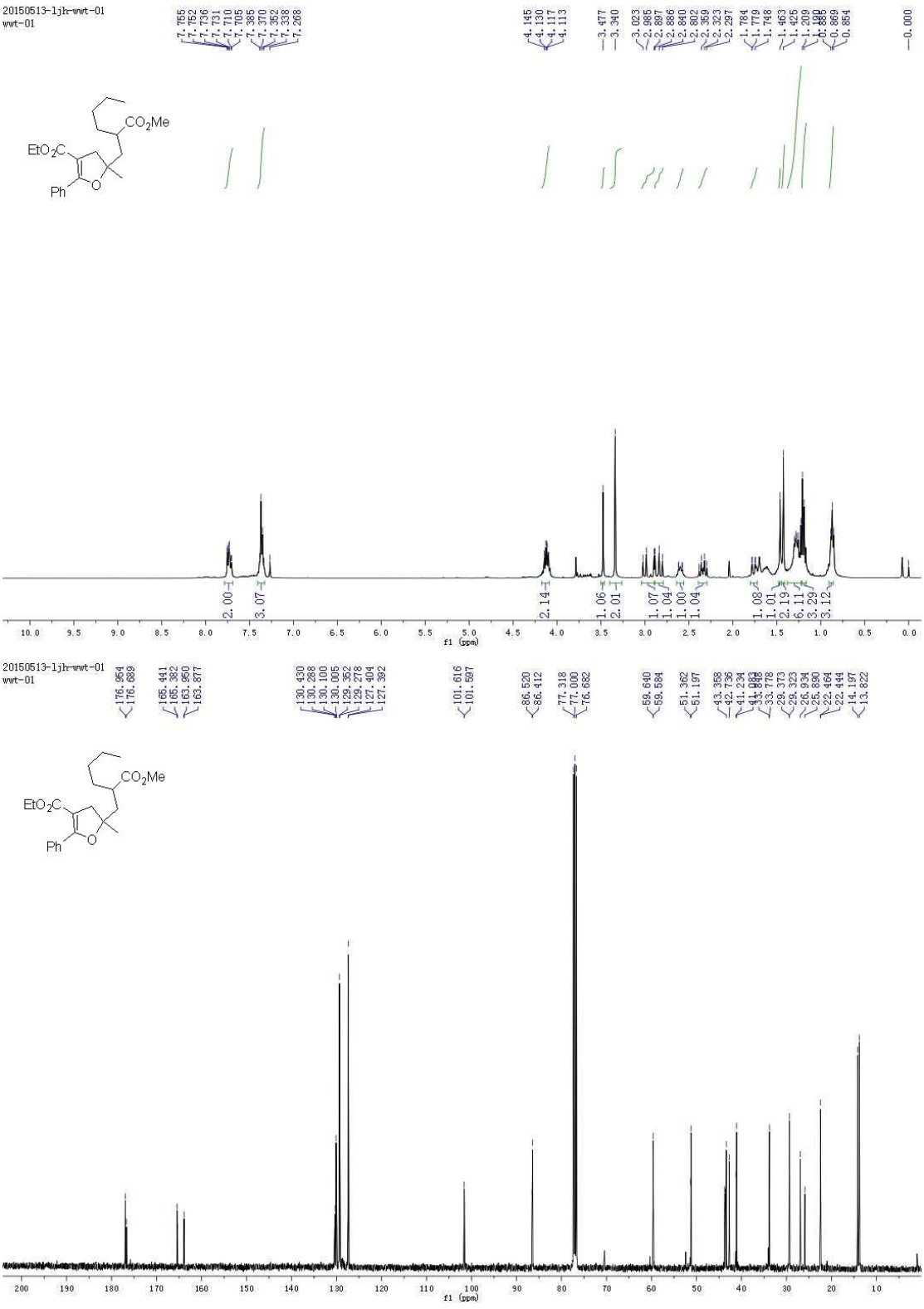
2 J.-H. Fan, W.-T. Wei, M.-B. Zhou, R.-J. Song and J.-H. Li**,** *Angew. Chem. Int. Ed.,* 2014, **53**, 6650.

(D) Spectra

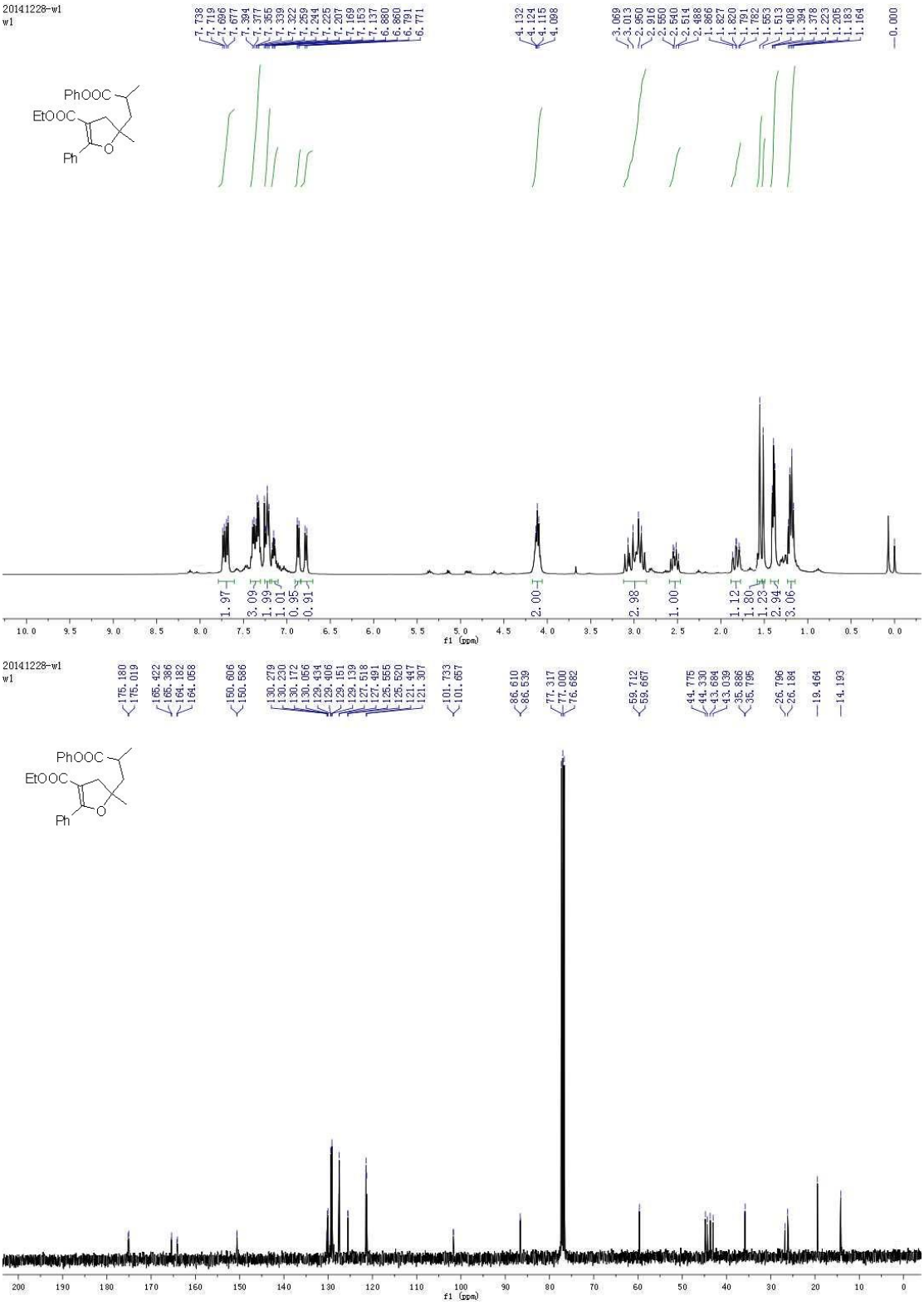
Ethyl 5-(3-methoxy-2-methyl-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3aa)



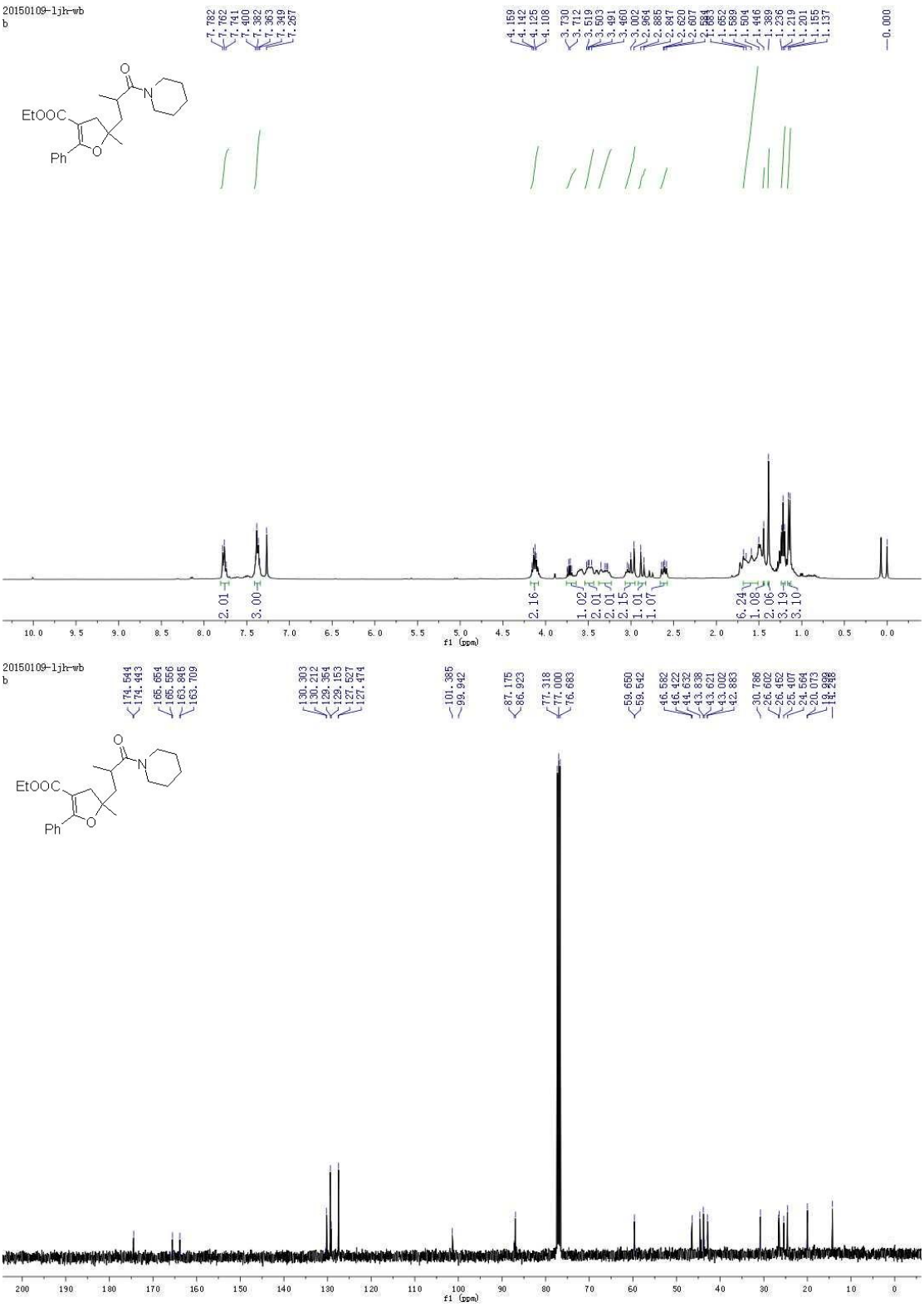
Ethyl 5-(2-(methoxycarbonyl)hexyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ab)



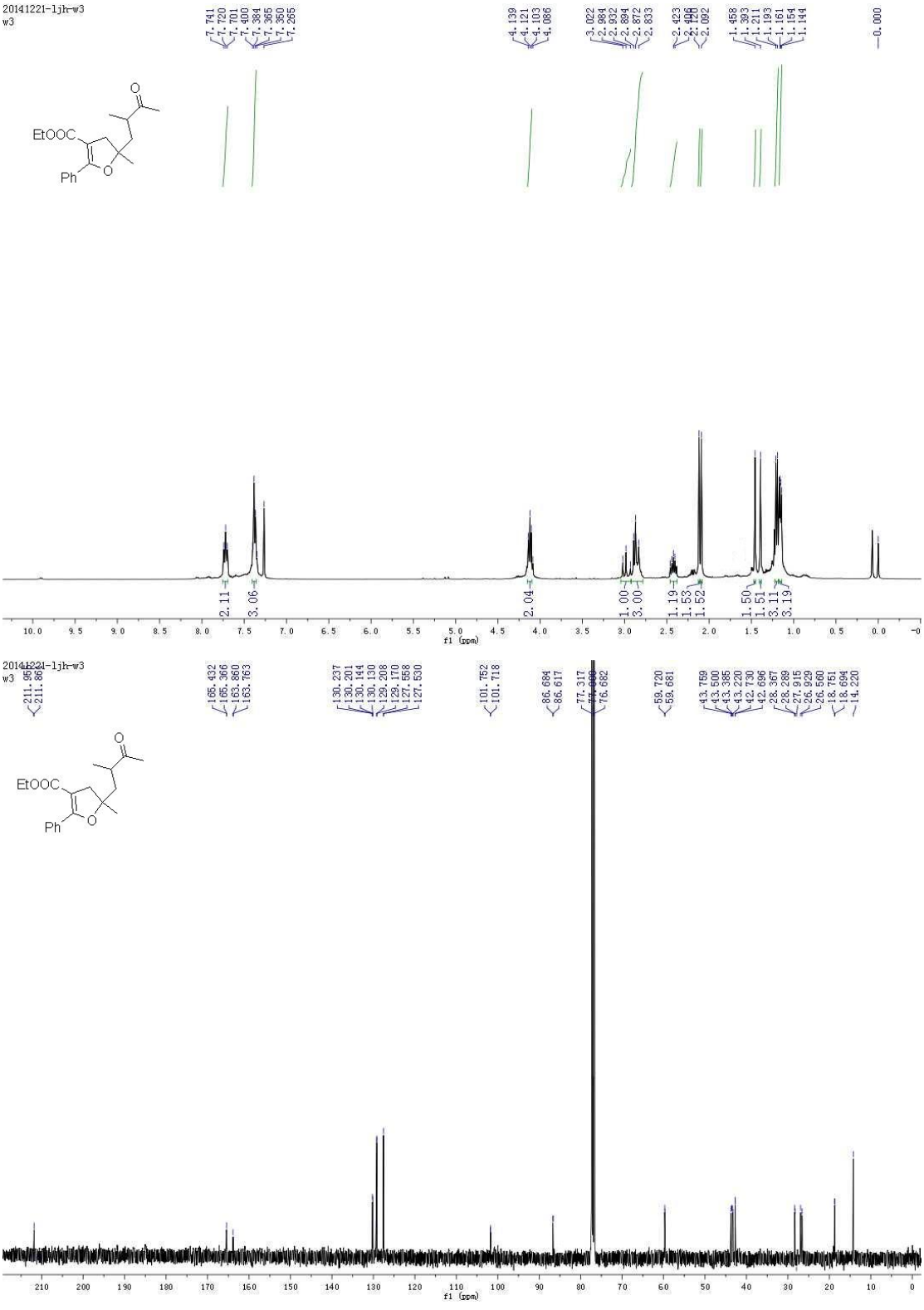
Ethyl 5-methyl-5-(2-methyl-3-oxo-3-phenoxypropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ac)



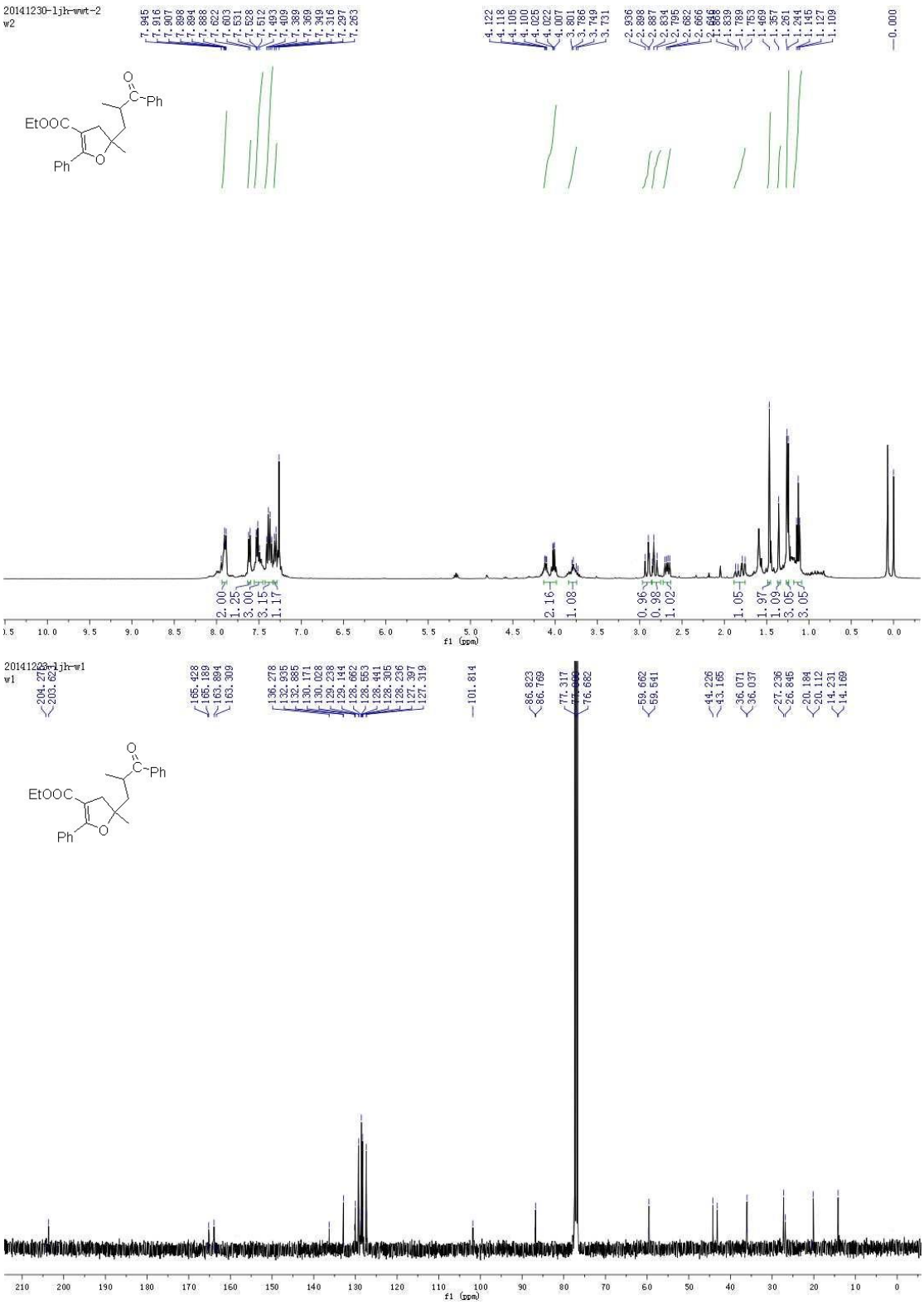
Ethyl 5-methyl-5-(2-methyl-3-oxo-3-(piperidin-1-yl)propyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ad)



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

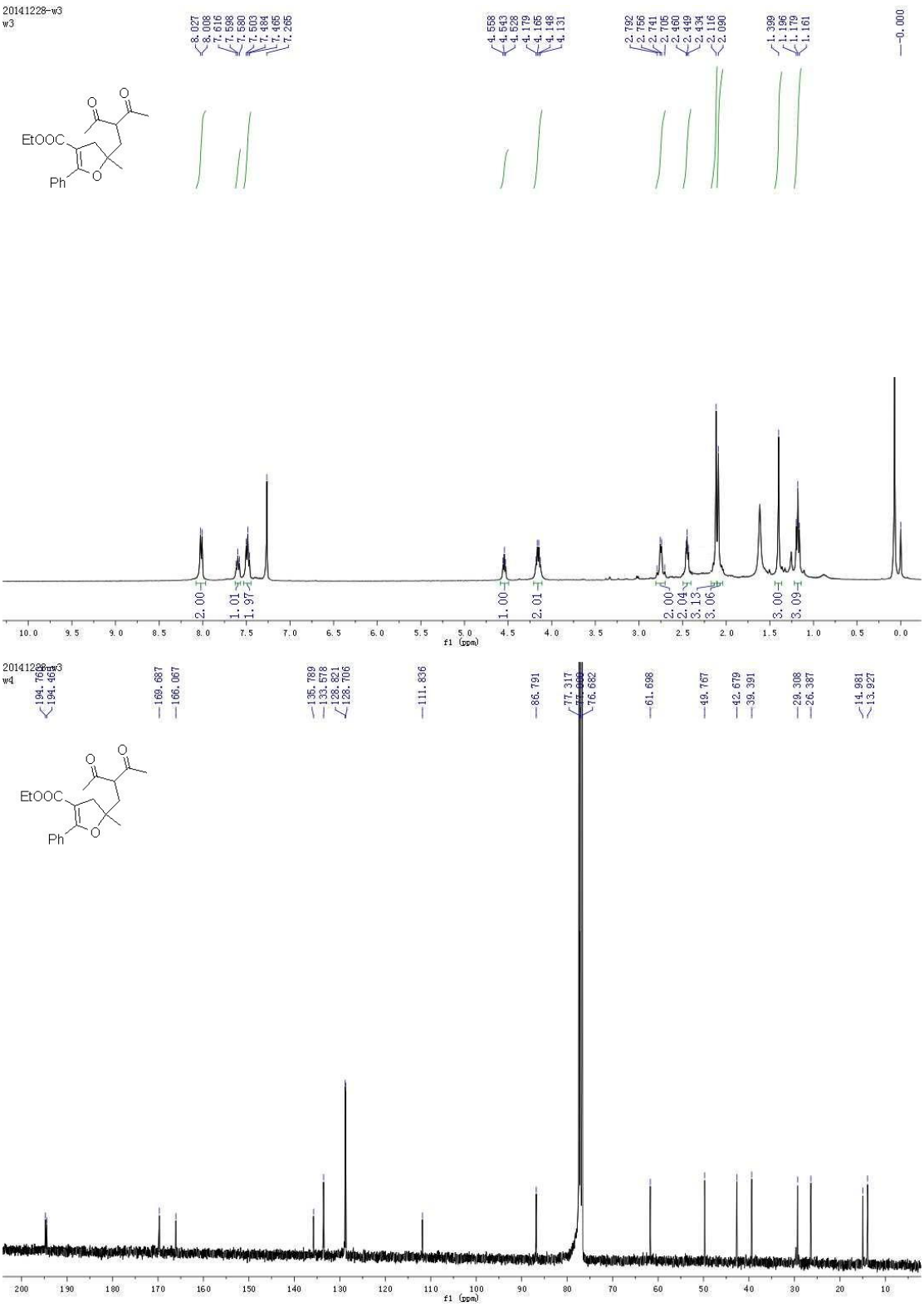


Ethyl 5-methyl-5-(2-methyl-3-oxo-3-phenylpropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3af)

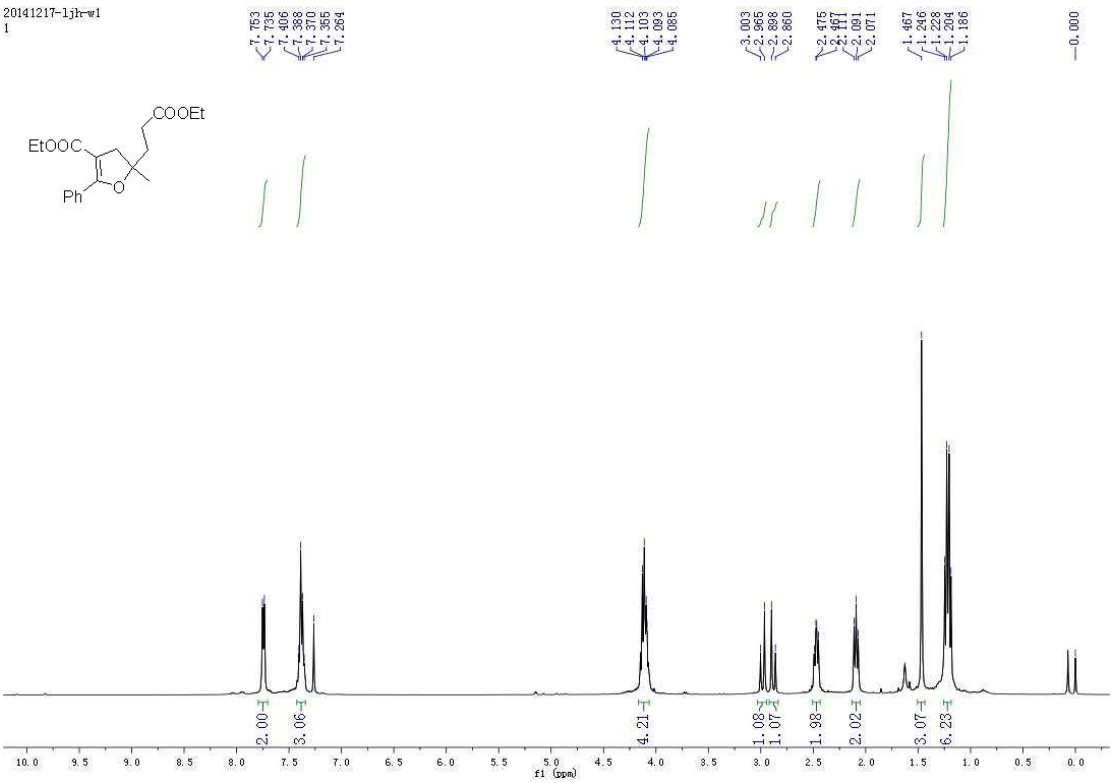


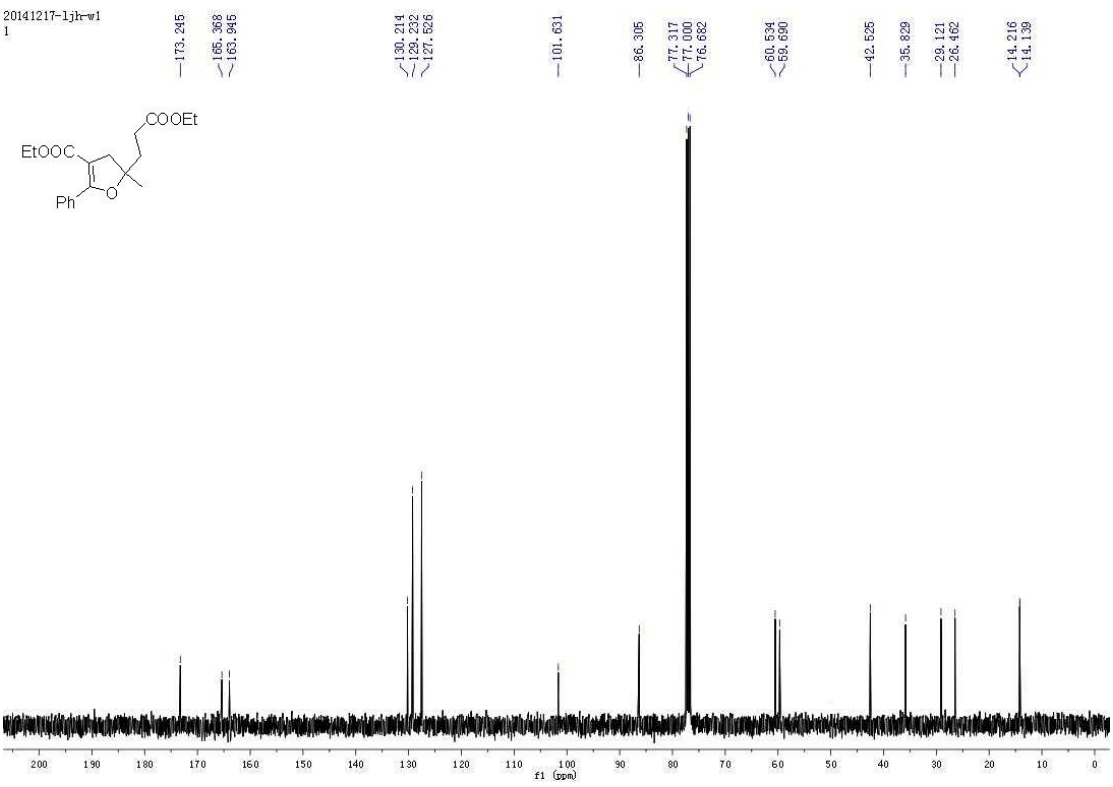
Ethyl 5-(2-acetyl-3-oxobutyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate

(3ag)

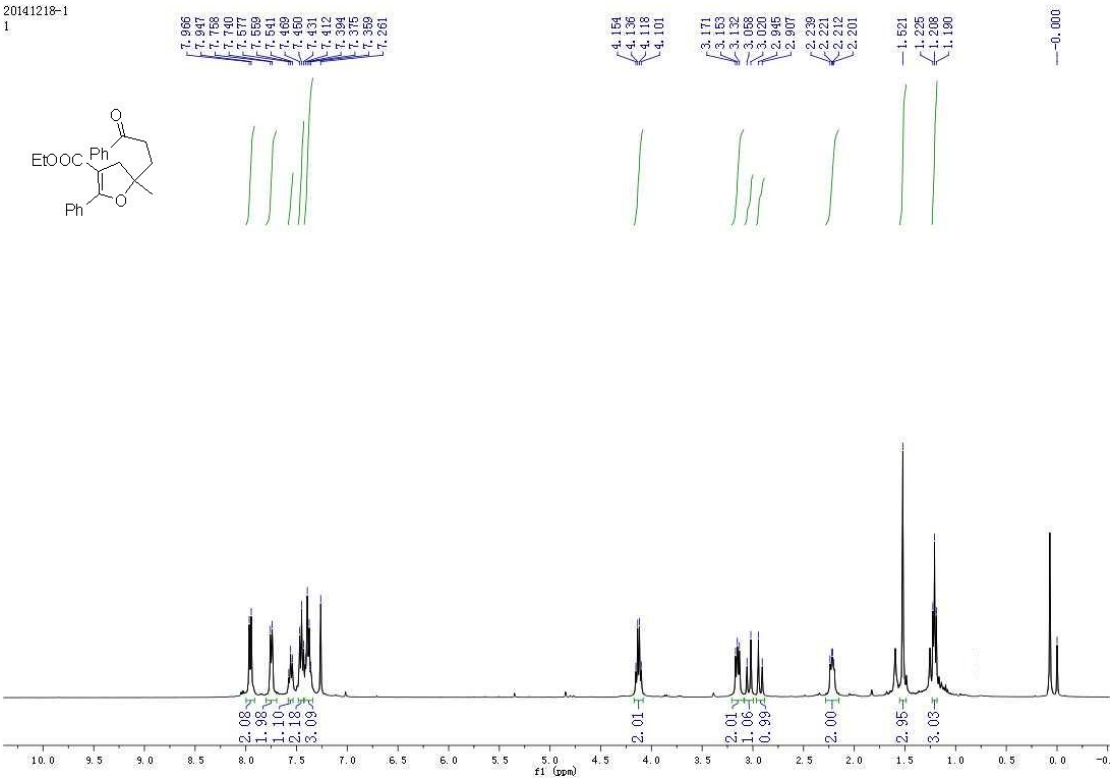


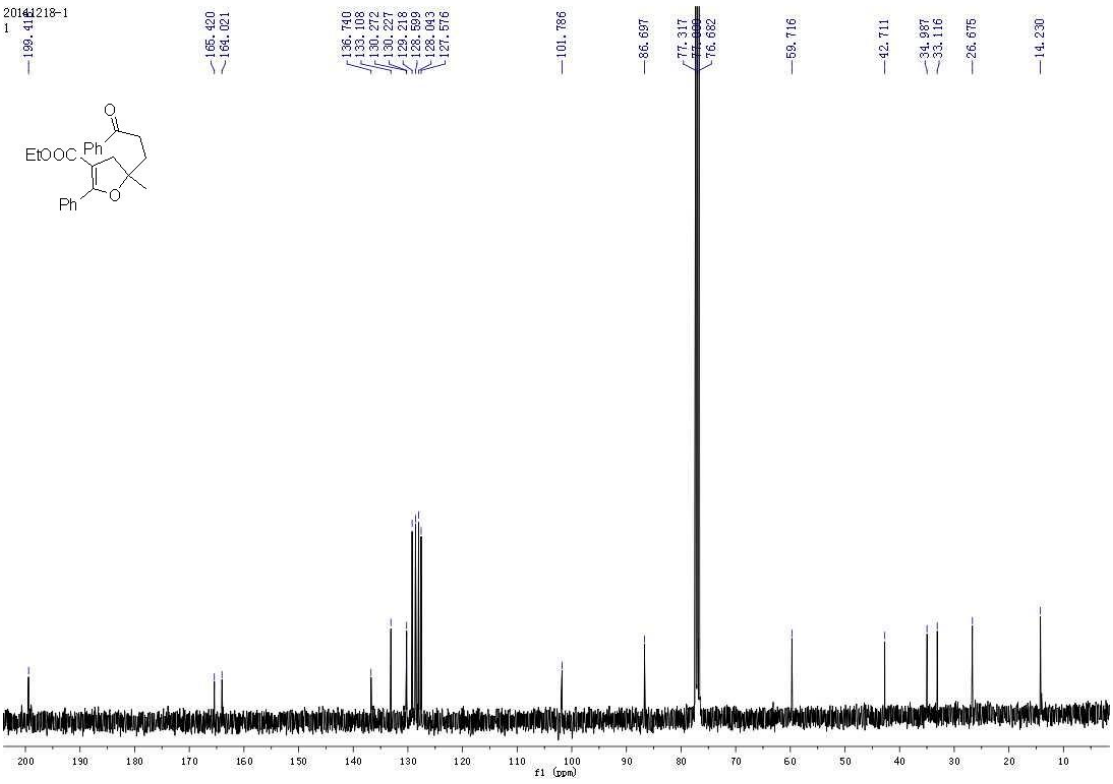
Ethyl 5-(3-ethoxy-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ah)



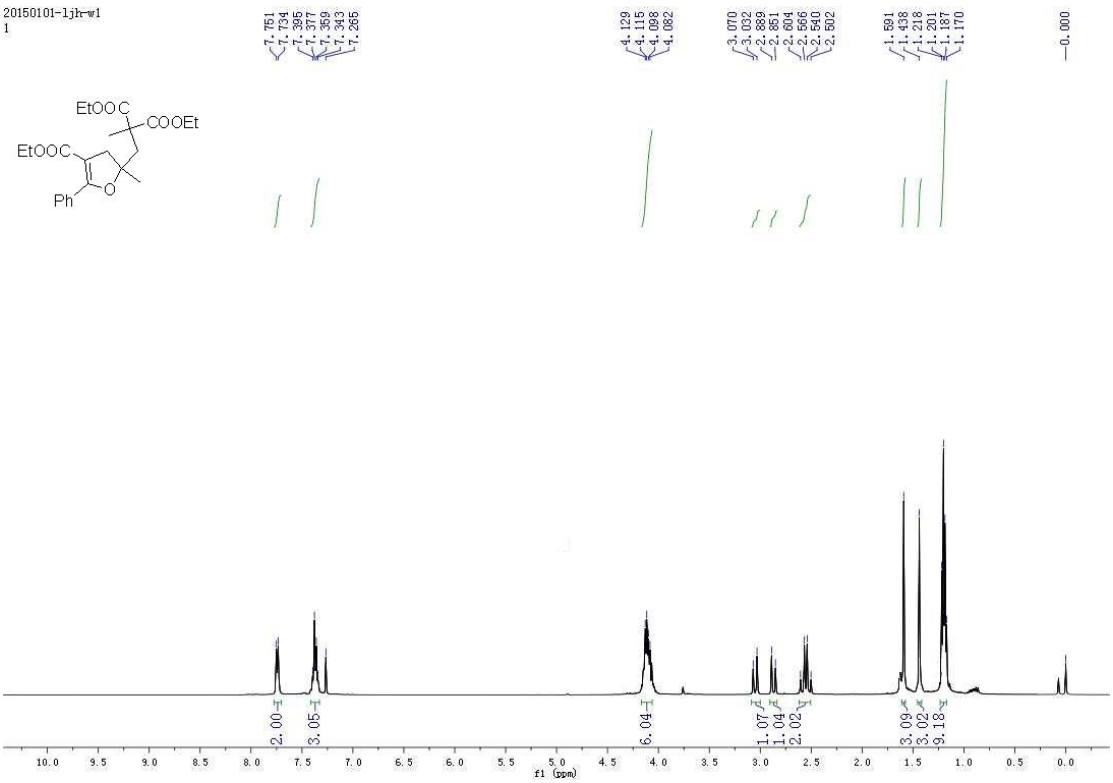


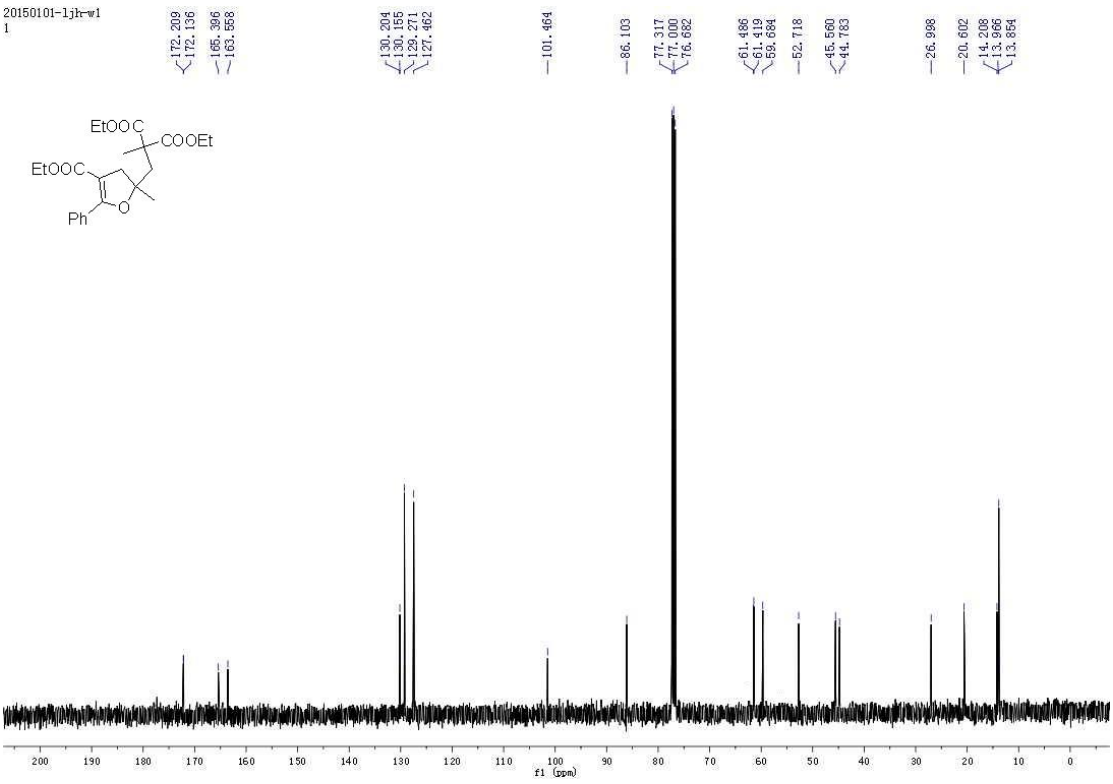
Ethyl 5-methyl-5-(3-oxo-3-phenylpropyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ai)



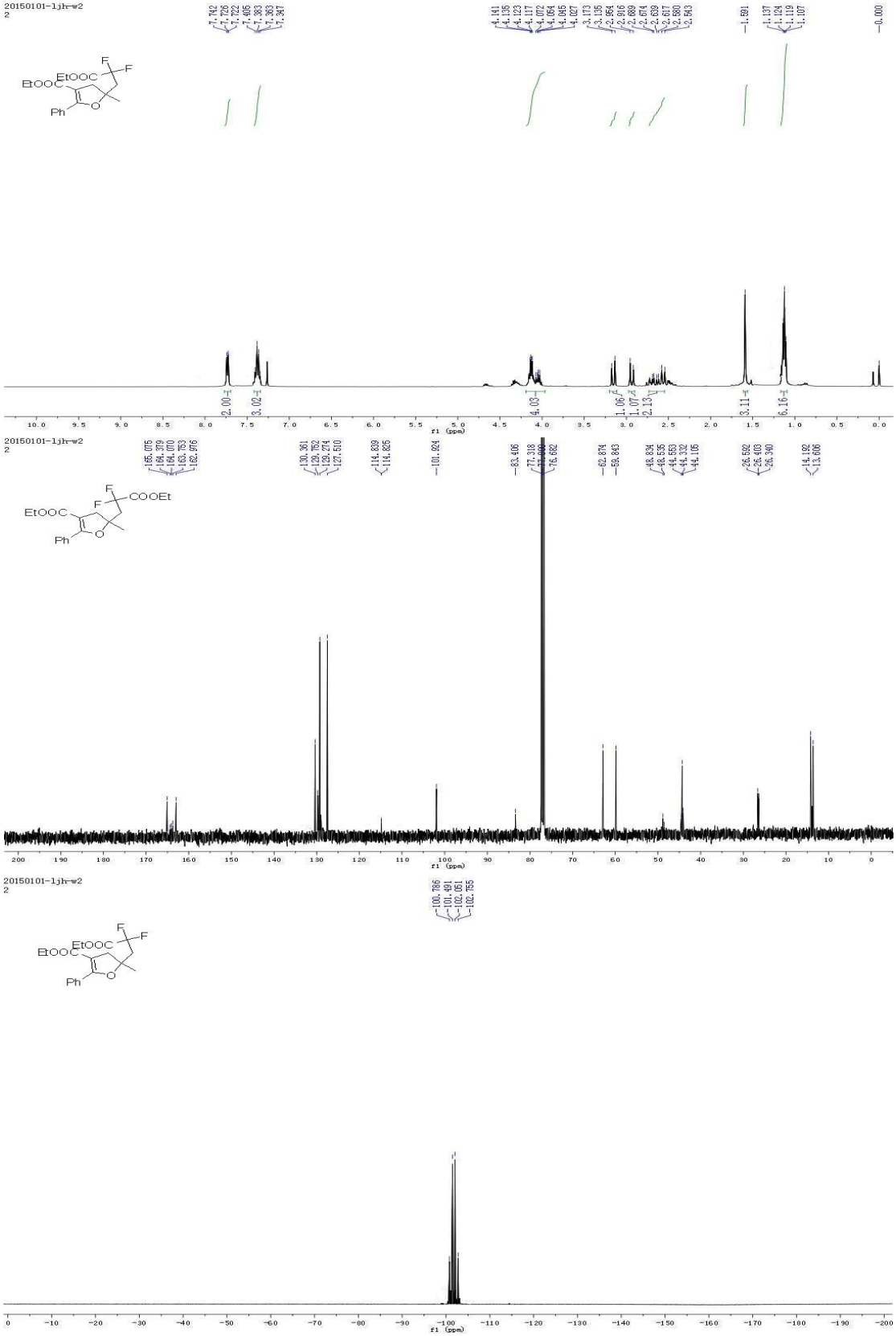


Diethyl 2-((4-(ethoxycarbonyl)-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3aj)

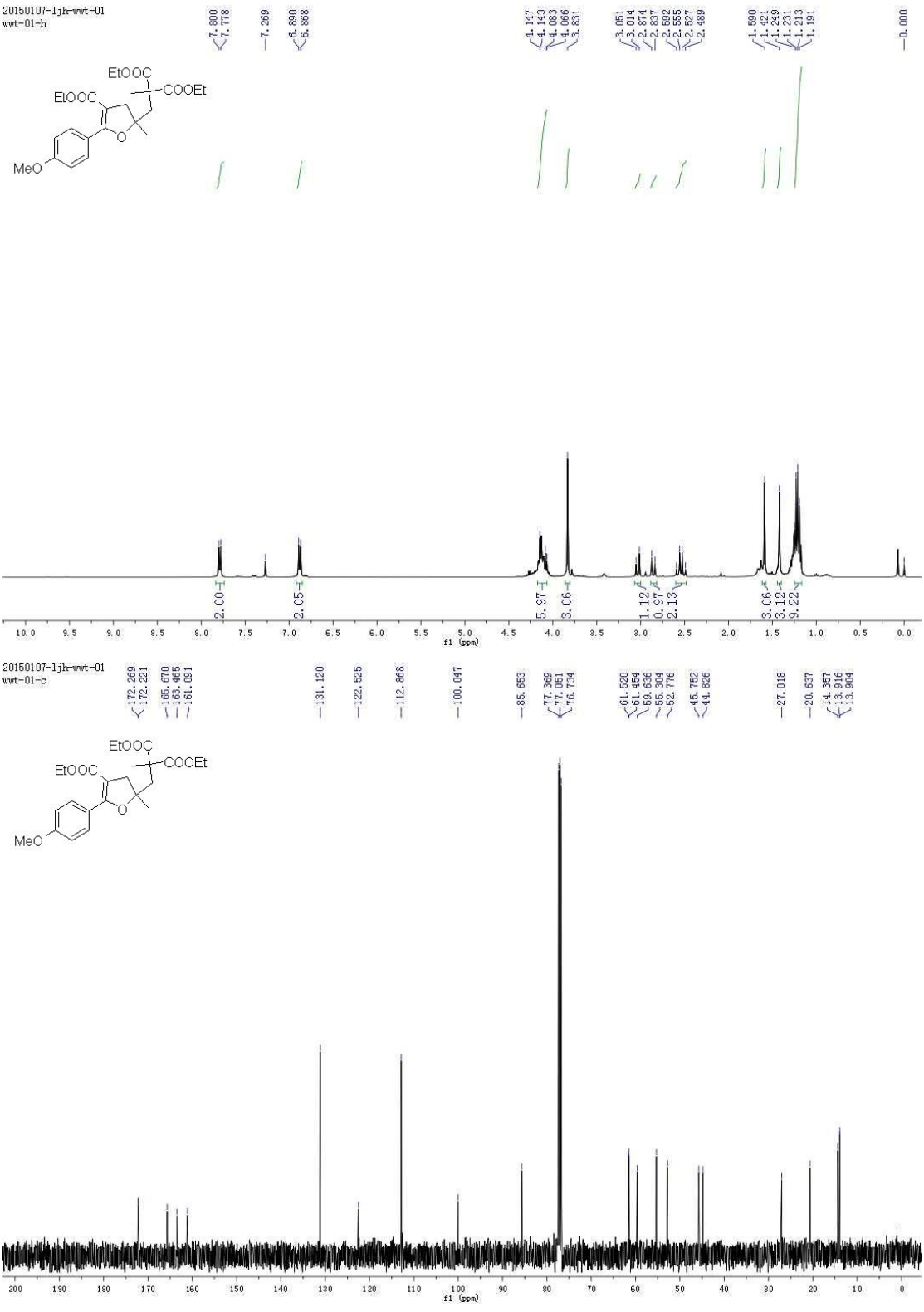




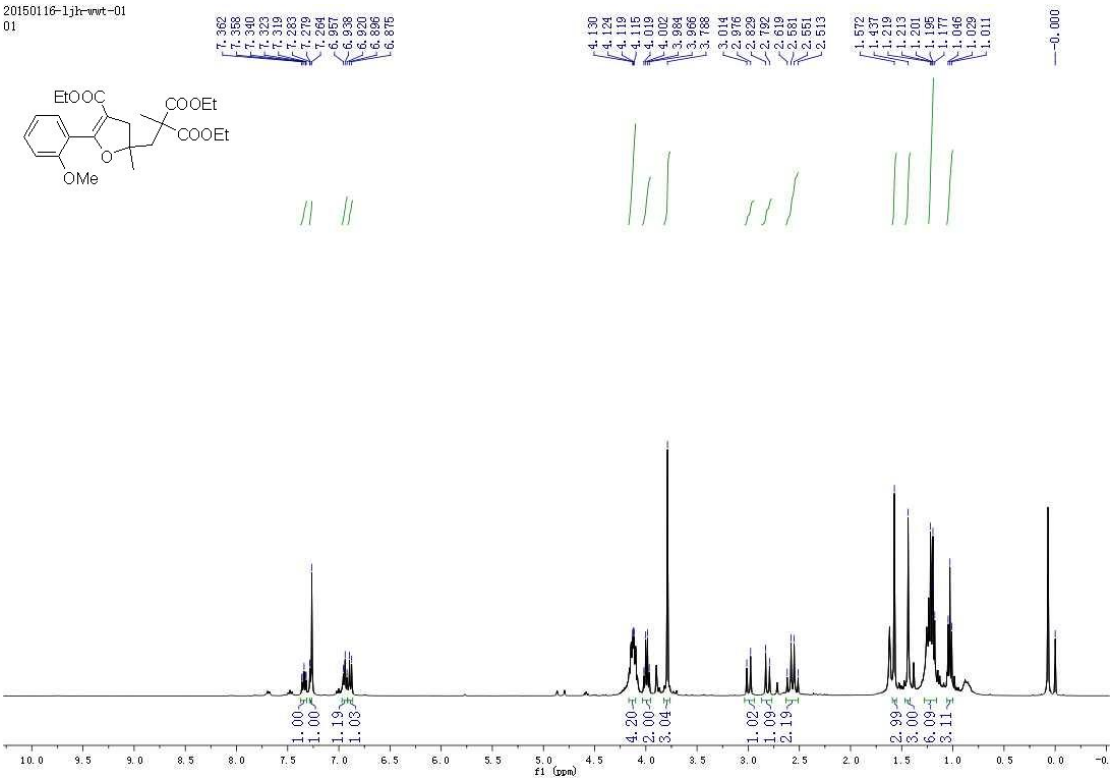
Ethyl 5-(3-ethoxy-2,2-difluoro-3-oxopropyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ak)

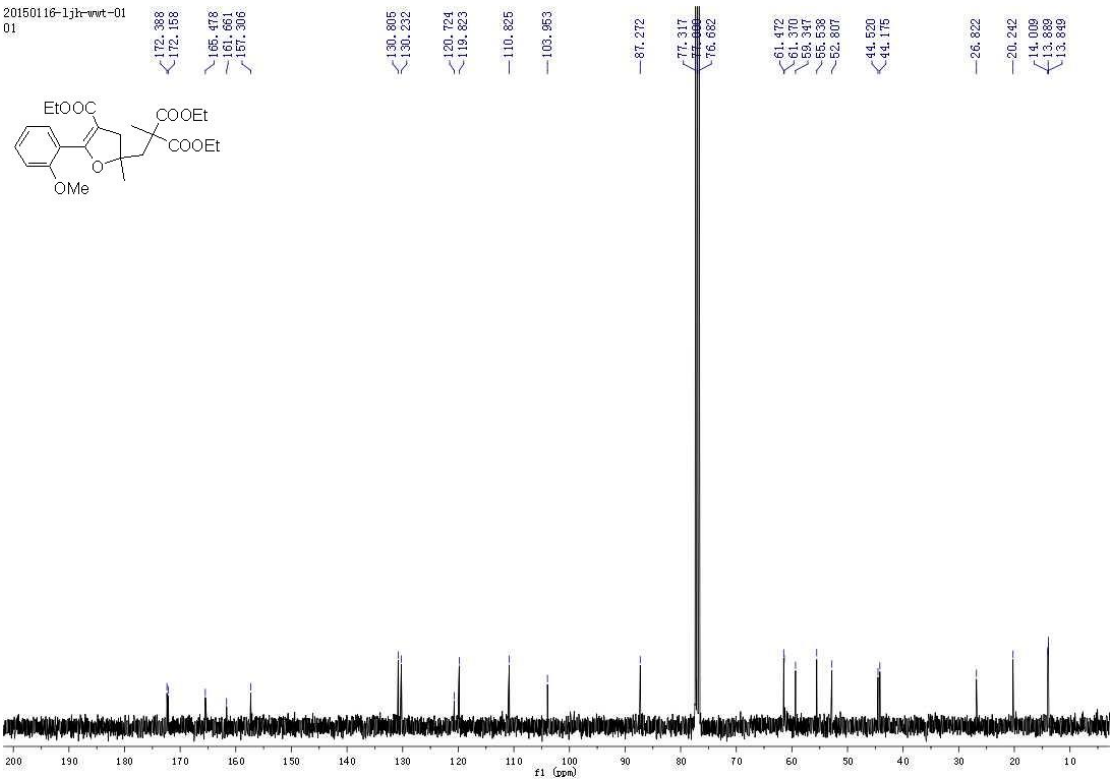


Diethyl 2-((4-(ethoxycarbonyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3bj)

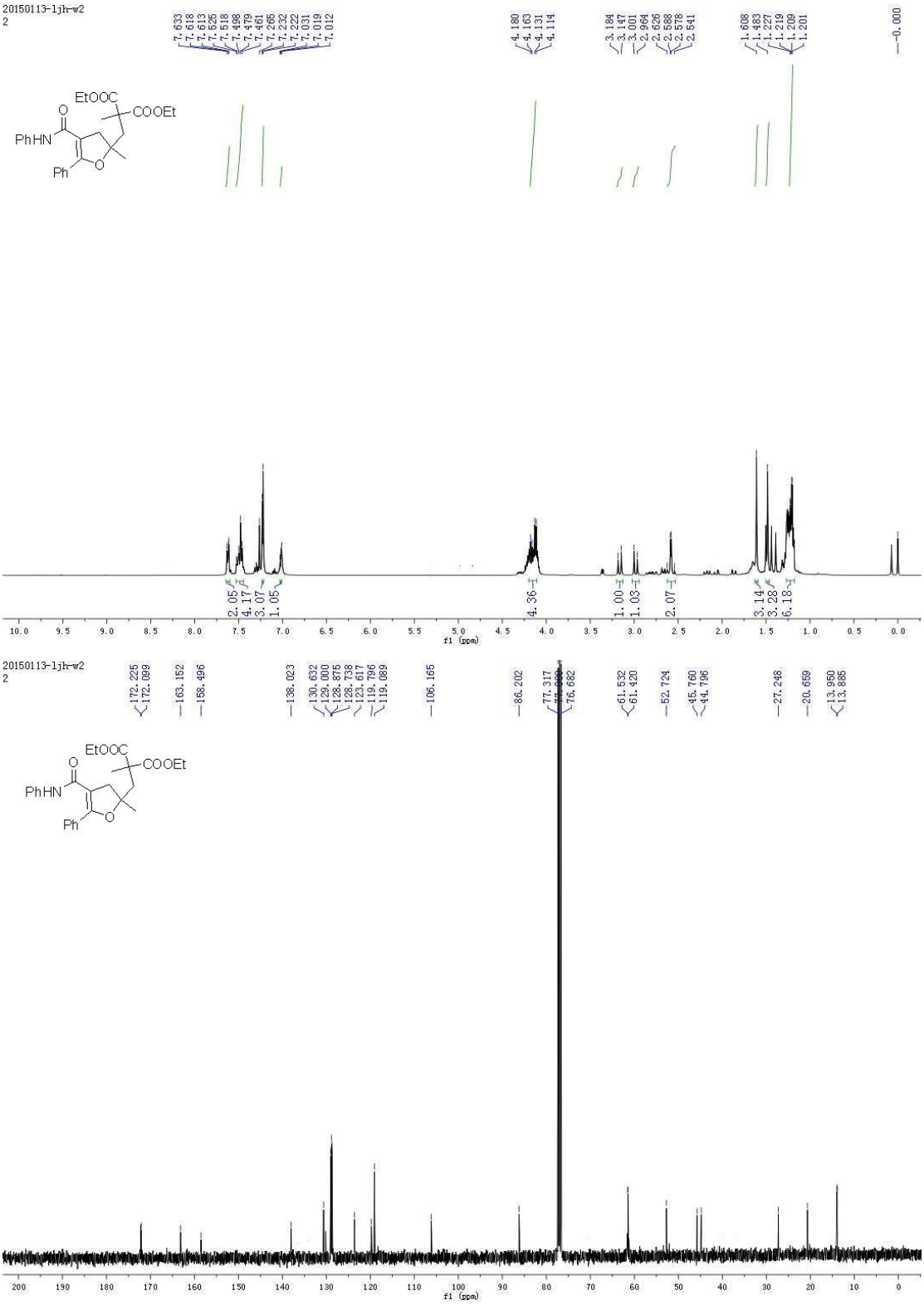


Diethyl 2-((4-(ethoxycarbonyl)-5-(2-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3cj)

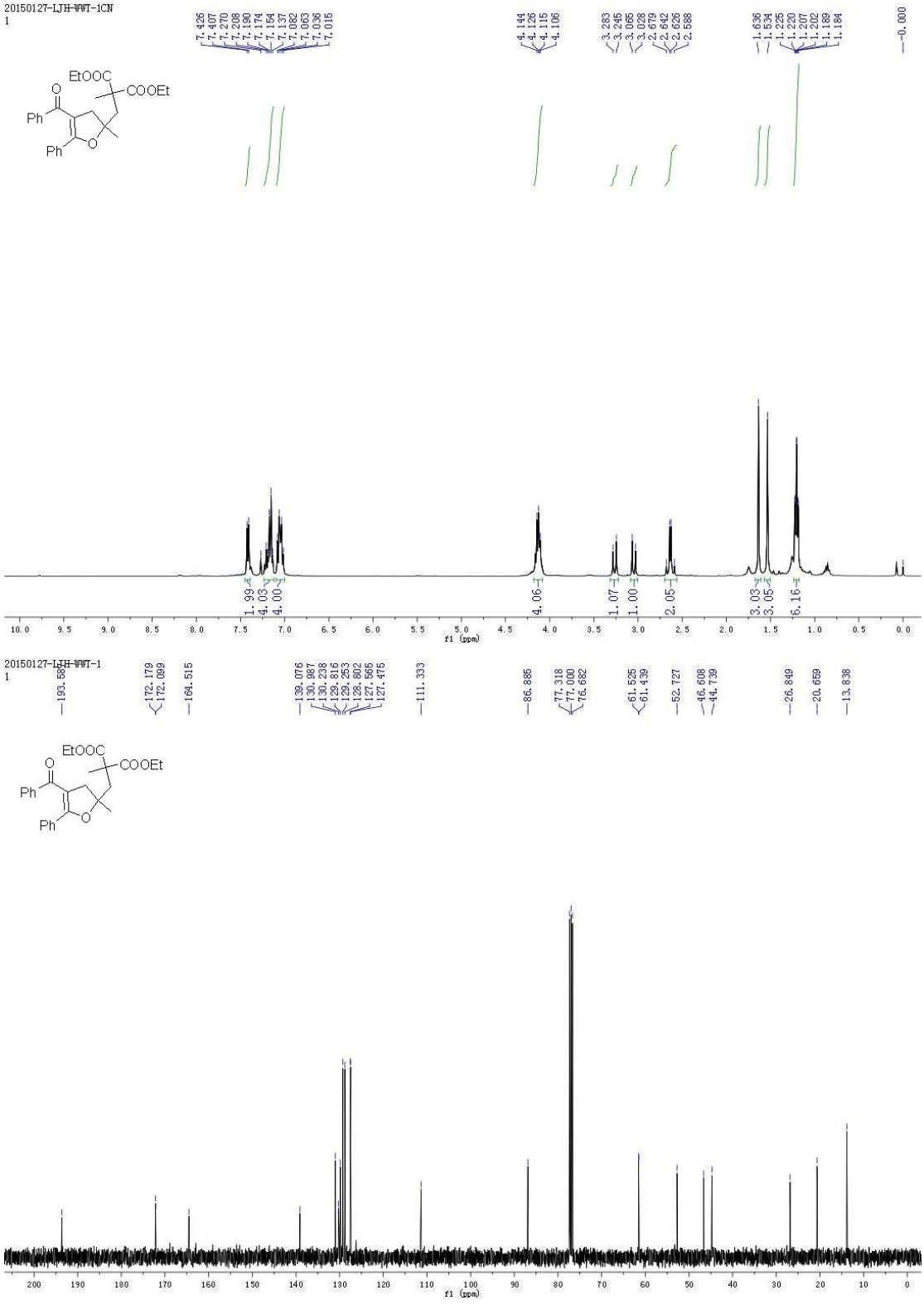




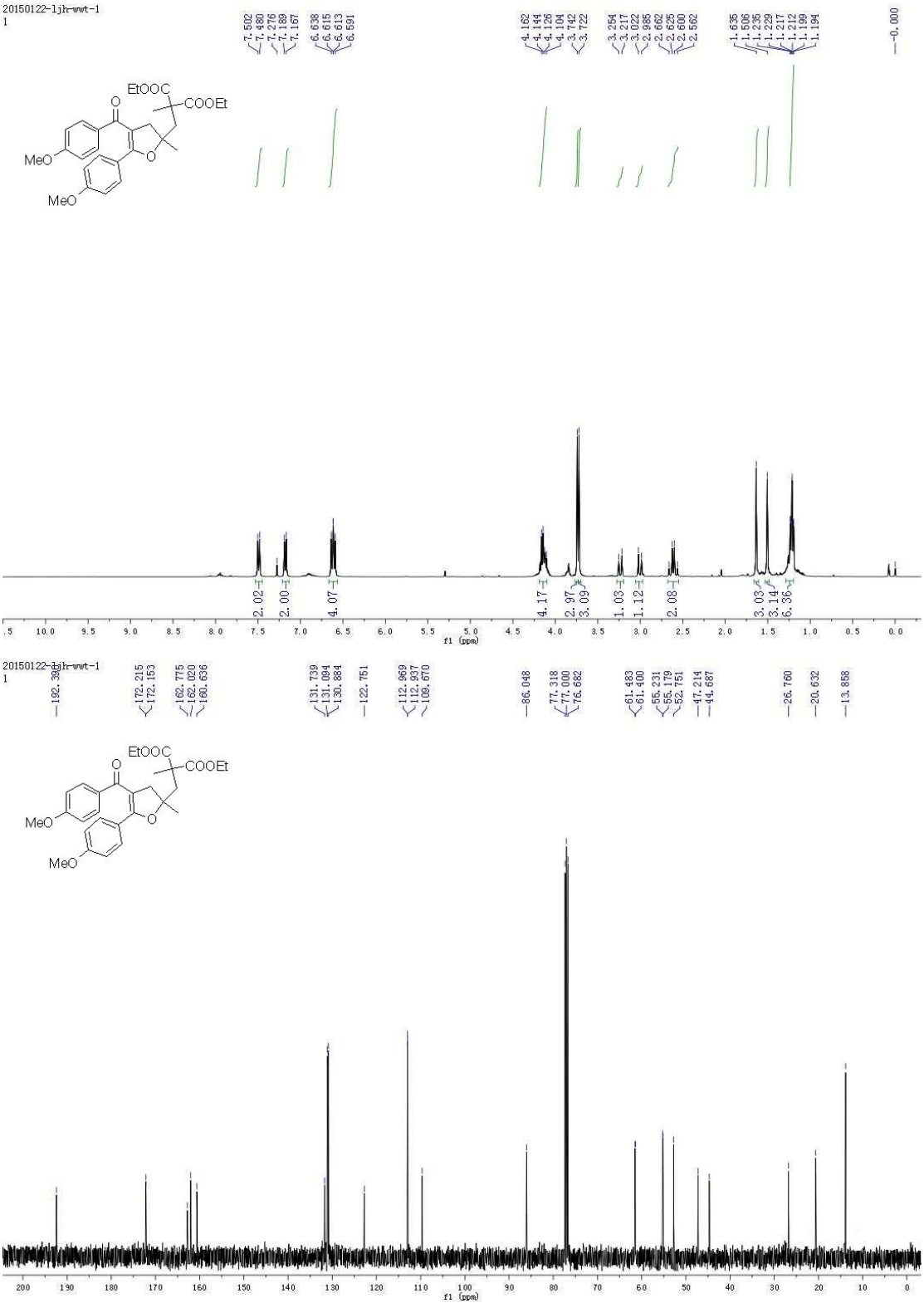
Diethyl 2-methyl-2-((2-methyl-5-phenyl-4-(phenylcarbamoyl)-2,3-dihydrofuran-2-yl)methyl)malonate (3ej)



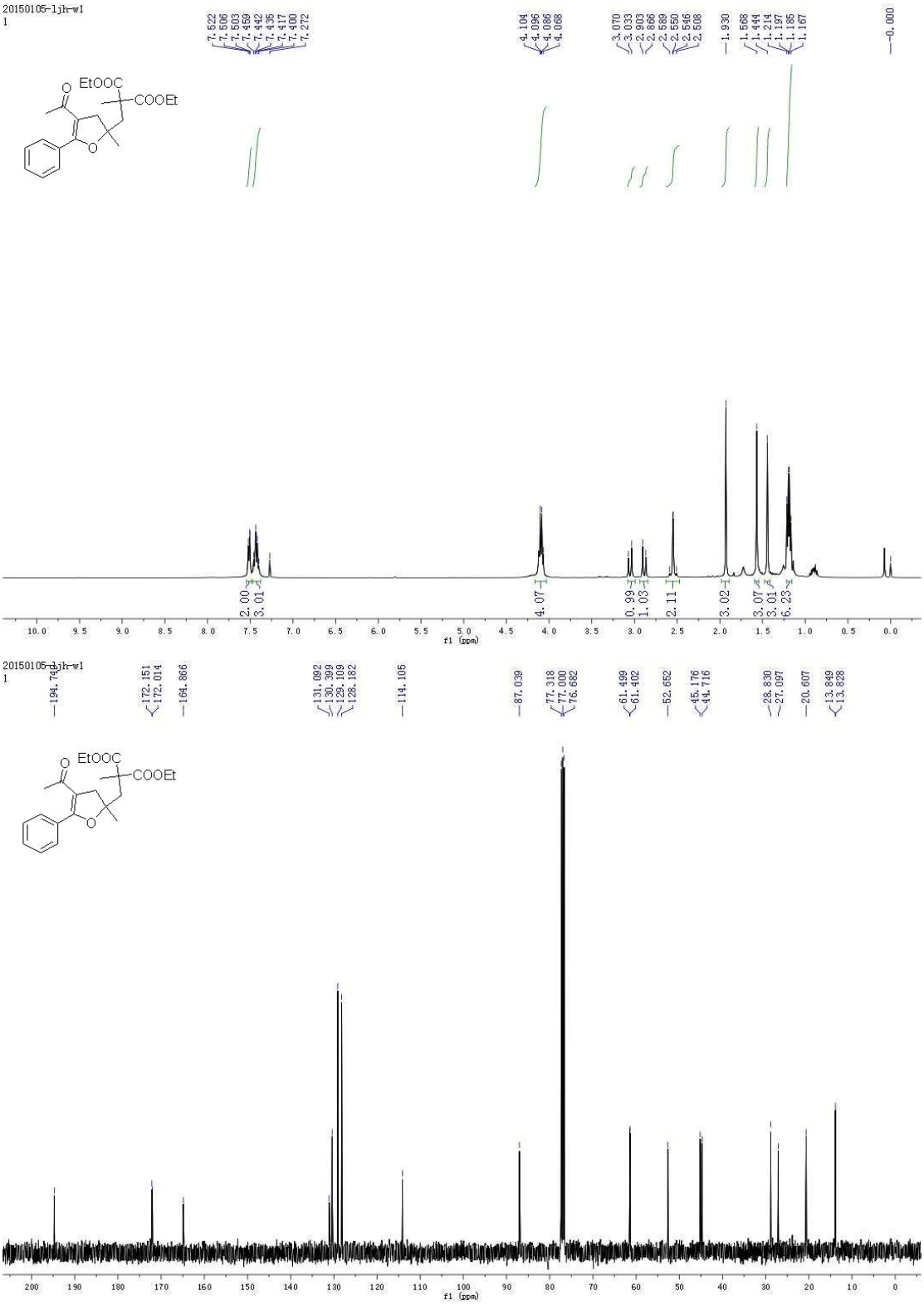
Diethyl 2-((4-benzoyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3fj)



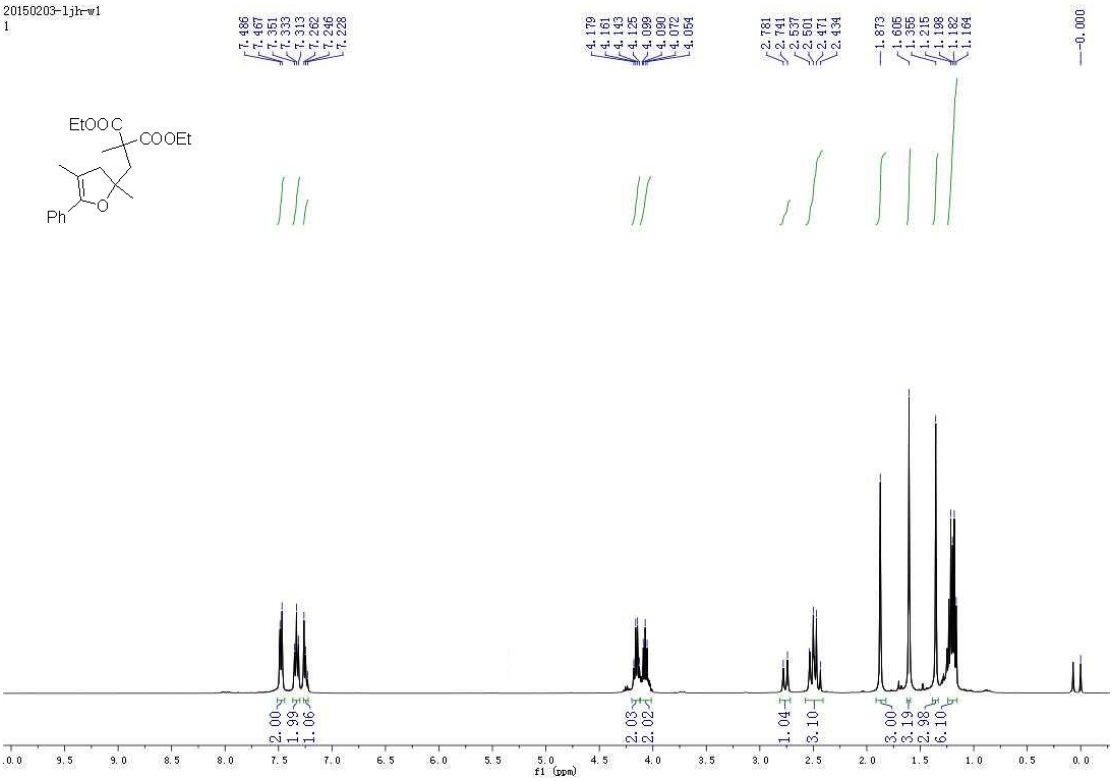
Diethyl 2-((4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2-methyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3gj)

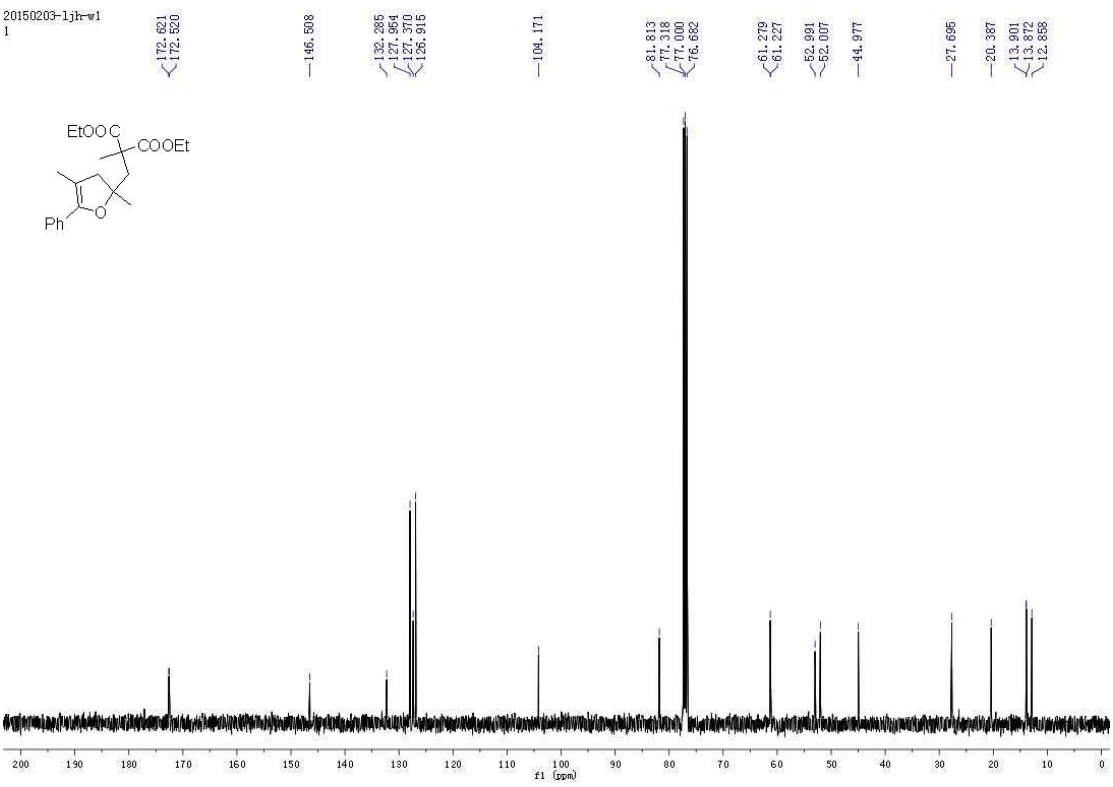


Diethyl 2-((4-acetyl-2-methyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3hj)

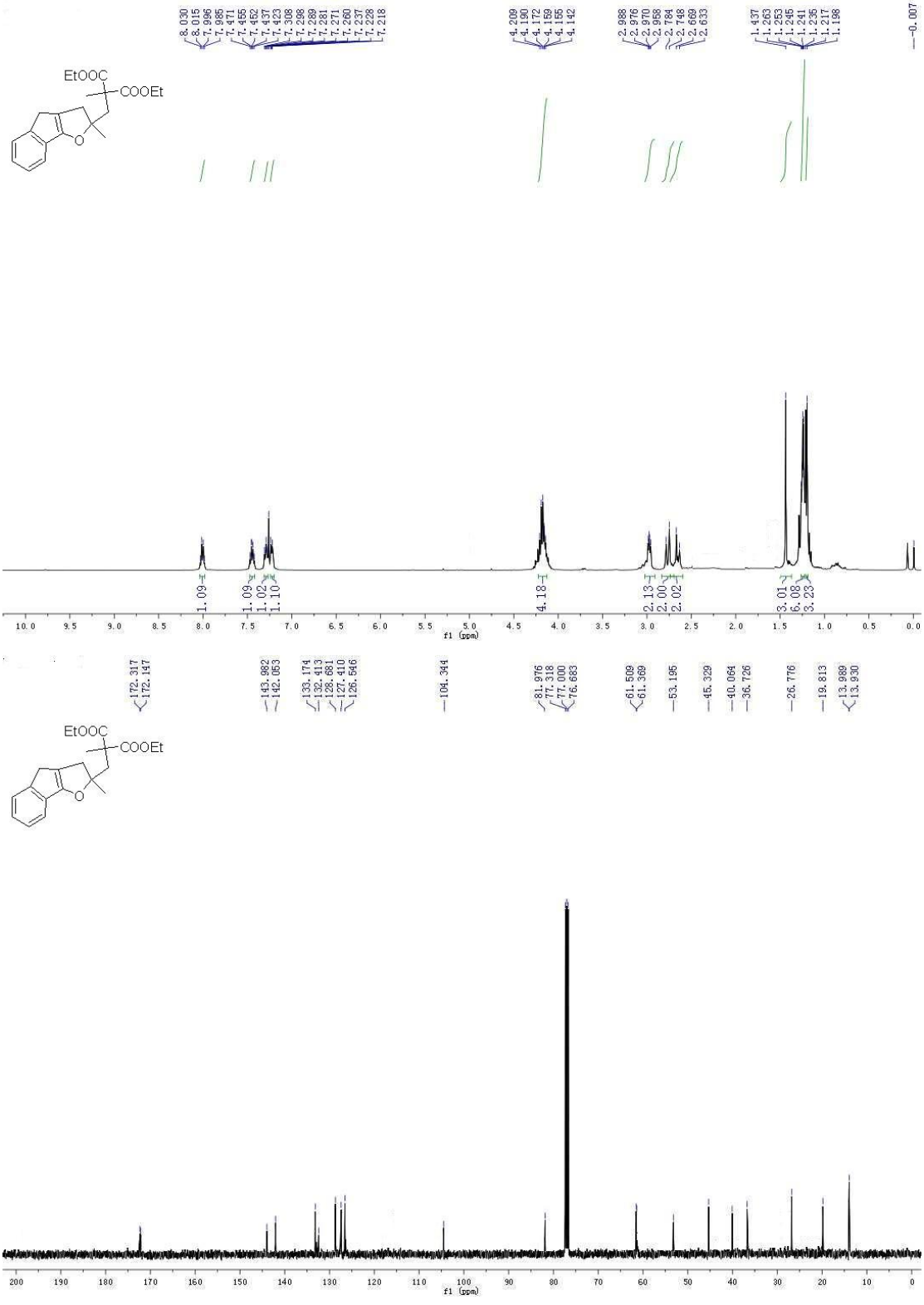


Diethyl 2-((2,4-dimethyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3ij)

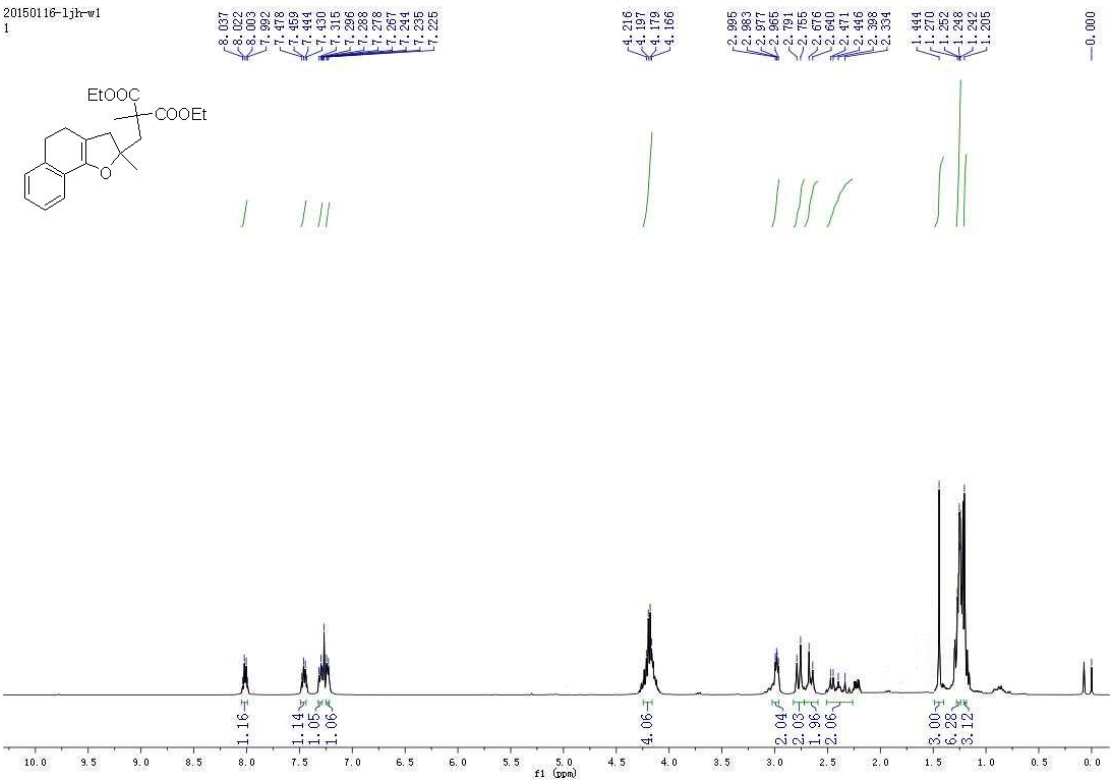


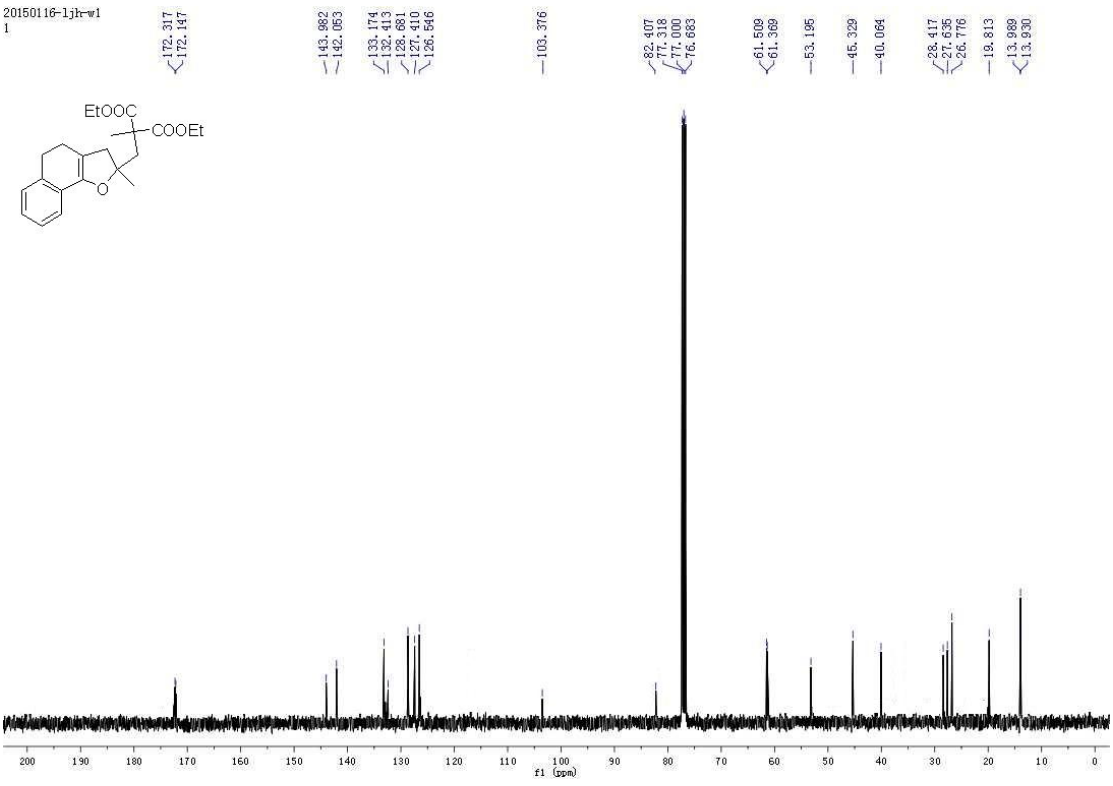


Diethyl 2-methyl-2-((2-methyl-3,4-dihydro-2*H*-indeno[1,2-b]furan-2-yl)methyl)malonate (3jj)

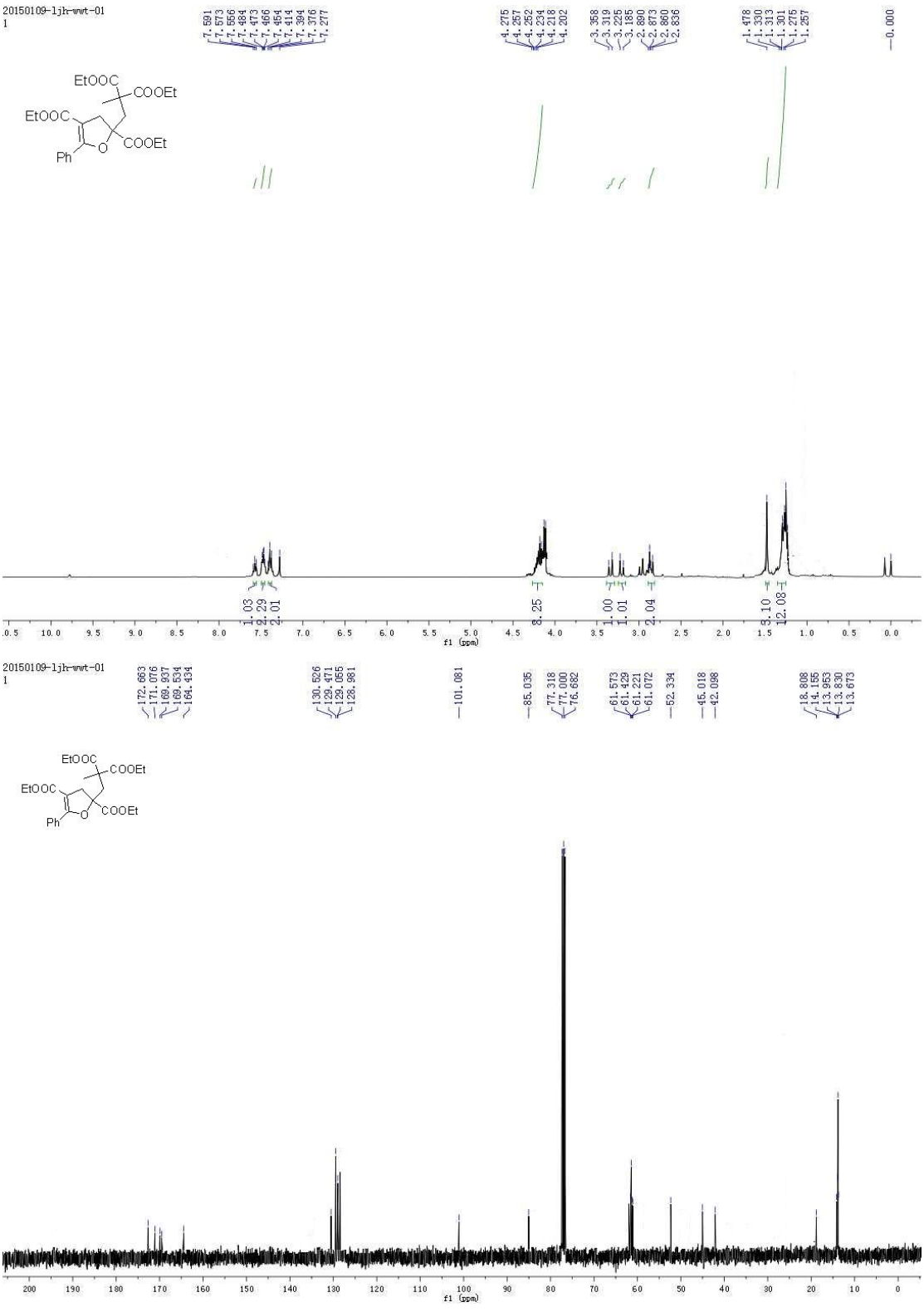


Diethyl 2-methyl-2-((2-methyl-2,3,4,5-tetrahydronaphtho[1,2-b]furan-2-yl)methyl)malonate (3kj)

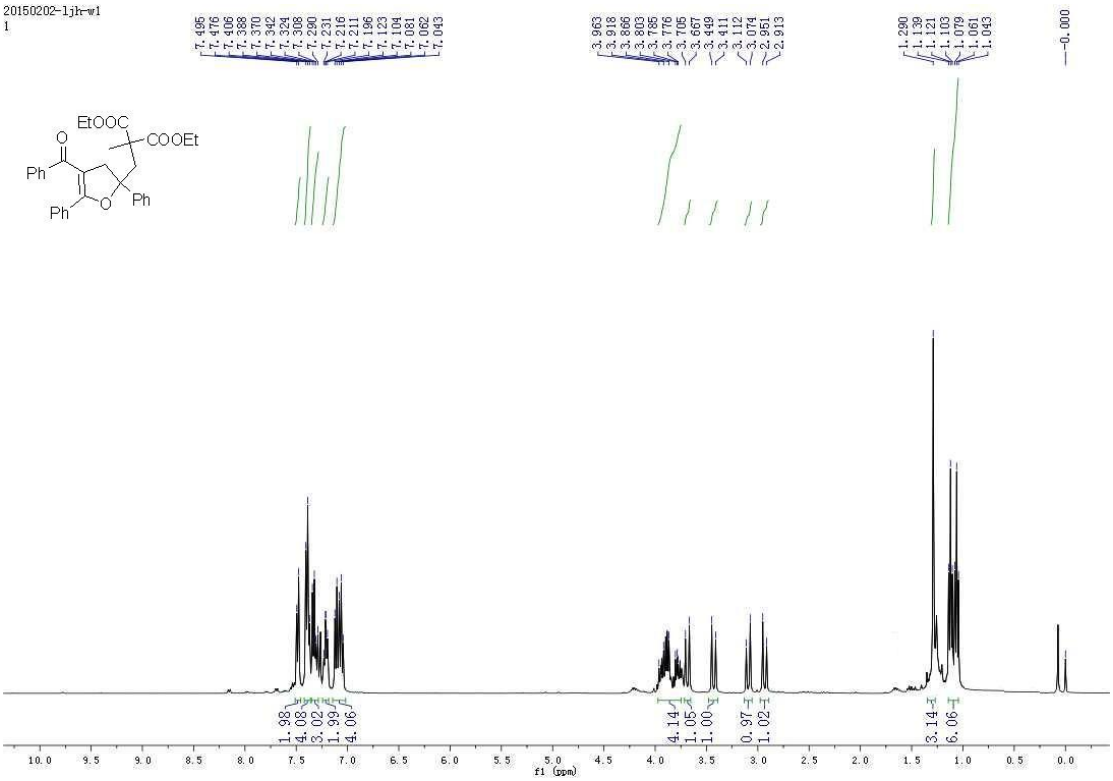


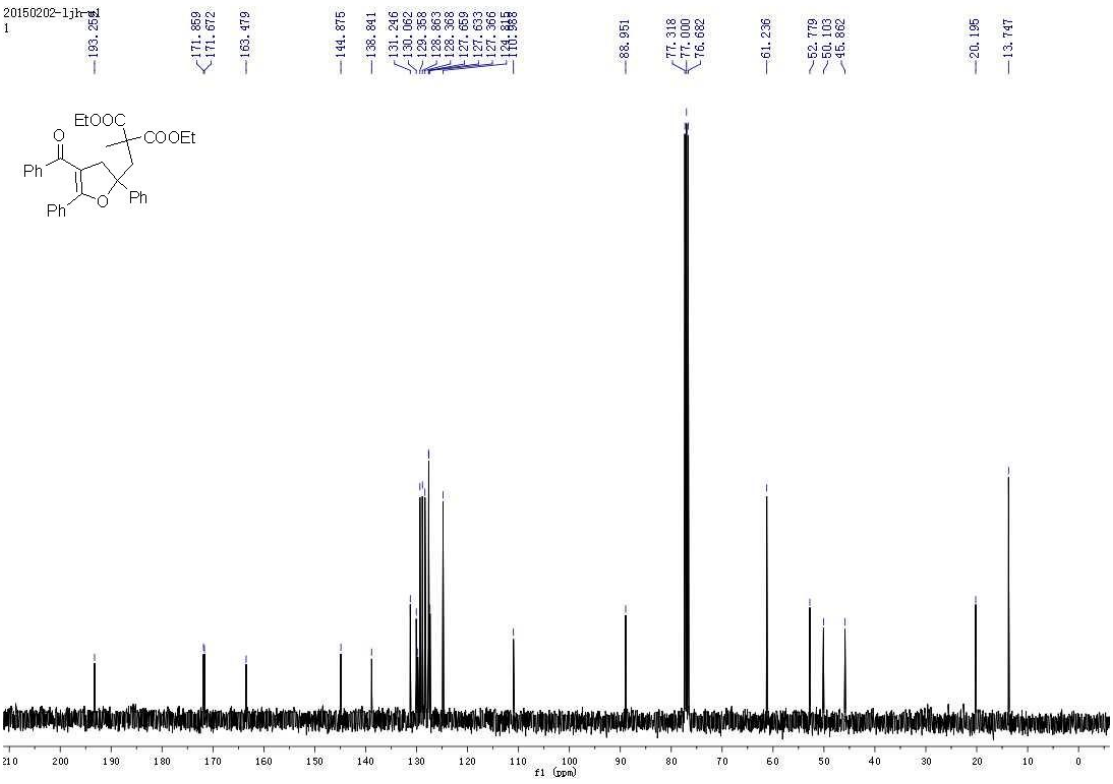


Diethyl 2-(3-ethoxy-2-(ethoxycarbonyl)-2-methyl-3-oxopropyl)-5-phenyl-2,3-dihydrofuran-2,4-dicarboxylate (3lj)

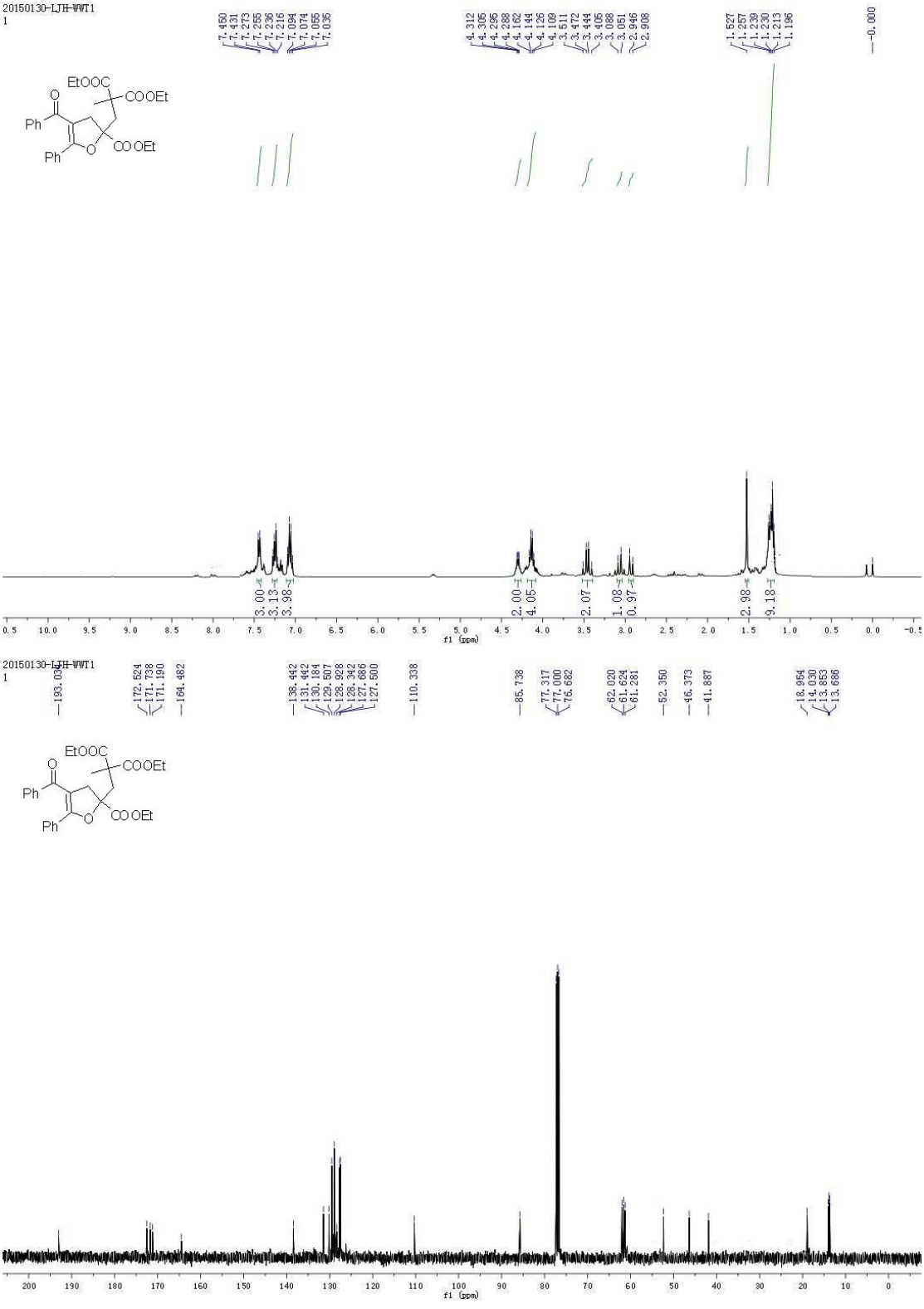


Diethyl 2-((4-benzoyl-2,5-diphenyl-2,3-dihydrofuran-2-yl)methyl)-2-methylmalonate (3mj)





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



Methyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (4a)