Base-Promoted Domino Radical Cyclization of 1,6-Enynes

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Supporting Information

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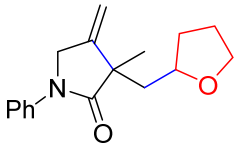
(A) Typical experimental procedure for the radical cyclization:

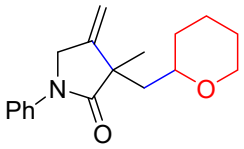
To a Schlenk tube were added 1,6-enynes **1** (0.2 mmol), ethers **2** (0.5 mL), TBPB (4.0 equiv) and Cs_2CO_3 (1.2 equiv). Then the tube was stirred at 85 °C sealed in air for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate) to afford the desired products **3**. All solvents were purchased from commercial sources and used without further purification.

Synthesis of **1a**: Step 1: The mixture of aniline (697.9 mg, 7.5 mmol) and K_2CO_3 (1382.1 mg, 10 mmol) was dissolved in the THF (10 mL) under the ice-bath followed by dropwise addition of 3-bromoprop-1-yne (589.5 mg, 5 mmol), Then, warming to room temperature and the reaction was stirred overnight. After the starting material was completely reacted as monitored by TLC analysis, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 15:1) to afford the *N*-(prop-2-yn-1-yl)aniline (4.5 mmol, 90% yield). Step 2: The *N*-(prop-2-yn-1-yl)aniline (589.9 mg, 4.5 mmol) and Et_3N (910.7 mg, 9 mmol) was dissolved in the anhydrous CH_2Cl_2 (10 mL), cooled to 0 °C and slowly add methacryloyl chloride (561.6 mg, 5.4 mmol), which react for 3 hours. 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 = 10:1) to afford the **1a** (4.0 mmol, 89% yield).

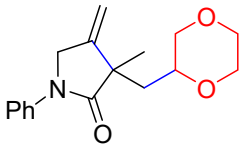
(B) Analytical data



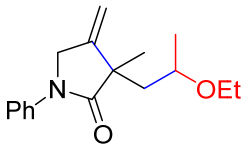
3-Methyl-4-methylene-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (3aa), yellow oil (0.0423 g, 78% yield, d.r. = 5.7: 1); ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 7.74 (d, *J* = 8.4 Hz, 0.3H), 7.69 (d, *J* = 8.0 Hz, 1.7H), 7.42-7.36 (m, 2H), 7.17-7.12 (m, 1H), 5.29-5.02 (m, 2H), 4.51 (d, *J* = 14.4 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 3.90-3.84 (m, 1H), 3.60-3.54 (m, 1H), 3.45-3.40 (m, 1H), 2.01-1.95 (m, 1H), 1.89-1.82 (m, 1H), 1.78-1.63 (m, 3H), 1.44-1.37 (m, 1H), 1.26 (s, 0.5H), 1.22 (s, 2.6H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 177.0, 176.6, 146.3, 139.9, 139.4, 129.3, 129.1, 124.7, 124.4, 120.3, 120.1, 108.4, 108.1, 76.0, 75.7, 66.9 (2), 52.0, 51.9, 48.4, 48.1, 45.1, 44.9, 32.0, 31.8, 26.5, 25.7, 25.4; IR (KBr, cm^{-1}): 1693 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{22}NO_2$ ($[M+H]^+$) 272.1645, found 272.1649.



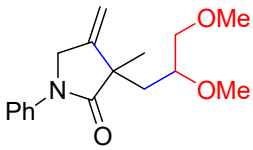
3-Methyl-4-methylene-1-phenyl-3-((tetrahydro-2H-pyran-2-yl)methyl)pyrrolidin-2-one (**3ab**), yellow oil (0.0371 g, 65% yield, d.r. > 20: 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 6.4 Hz, 2H), 7.35 (t, *J* = 6.4 Hz, 2H), 7.13 (t, *J* = 6.0 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.45-4.41 (m, 1H), 4.37-4.34 (m, 1H), 3.73-3.70 (m, 1H), 3.35 (t, *J* = 8.4 Hz, 1H), 3.19-3.14 (m, 1H), 2.23-2.18 (m, 1H), 1.78-1.71 (m, 2H), 1.54-1.43 (m, 4H), 1.40-1.38 (m, 1H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 177.2, 146.6, 139.9, 129.0, 124.4, 120.5, 108.4, 75.1, 68.1, 52.3, 47.5, 46.3, 32.1, 26.4, 25.8, 23.4; IR (KBr, cm^{-1}): 1691 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_2$ ($[M+H]^+$) 286.1802, found 286.1800.



3-((1,4-Dioxan-2-yl)methyl)-3-methyl-4-methylene-1-phenyl pyrrolidin-2-one (**3ac**), yellow oil (0.0350 g, 61% yield, d.r. > 20: 1); ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 7.65 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.14 (t, *J* = 6.8 Hz, 1H), 5.31 (s, 1H), 5.19 (s, 1H), 4.51 (d, J = 14.4 Hz, 1H), 4.38 (d, *J* = 14.0 Hz, 1H), 3.57-3.50 (m, 3H), 3.46-3.41 (m, 1H), 3.39-3.36 (m, 2H), 3.12 (t, *J* = 10.2 Hz, 1H), 1.87 (t, *J* = 12.0 Hz, 1H), 1.53 (d, *J* = 13.6 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 176.7, 146.2, 139.8, 129.1, 124.6, 120.6, 108.7, 73.1, 70.7, 66.5, 66.1, 52.2, 47.2, 26.3; IR (KBr, cm^{-1}): 1698 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{22}NO_3$ ([M+H]$^+$) 288.1594, found 288.1599.

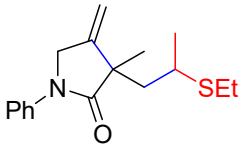


3-(2-Ethoxypropyl)-3-methyl-4-methylene-1-phenylpyrrolid in-2-one (**3ad**), colorless oil (0.0361 g, 66% yield, d.r. > 20: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 10.0 Hz, 2H), 7.36 (t, *J* = 10.0 Hz, 2H), 7.11 (t, *J* = 9.0 Hz, 1H), 5.28 (t, *J* = 2.5 Hz, 1H), 5.07 (t, *J* = 3.0 Hz, 1H), 4.52-4.47 (m, 1H), 4.39-4.35 (m, 1H), 3.58-3.53 (m, 1H), 3.48-3.42 (m, 1H), 3.08-3.01 (m, 1H), 2.30-2.24 (m, 1H), 1.61-1.57 (m, 1H), 1.32 (s, 3H), 1.11 (d, *J* =7.5 Hz, 3H), 0.81 (t, *J* =8.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.7, 145.9, 139.6, 128.8, 123.9, 119.2, 107.6, 71.9, 63.3, 51.7, 48.1, 46.2, 27.0, 19.5, 15.2; IR (KBr, cm^{-1}): 1683 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO_2$ ([M+H]$^+$) 274.1802, found 274.1800.

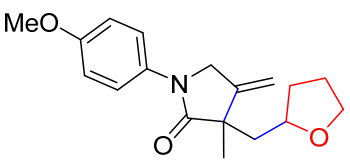


3-(2,3-Dimethoxypropyl)-3-methyl-4-methylene-1-phenylpy rrolidin-2-one (3ae), colorless oil (0.0399 g, 69% yield, d.r. = 1: 1); ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 7.74-7.62 (m, 2H), 7.40-7.36 (m, 2H), 7.16-7.11 (m, 1H), 5.32-5.16 (m, 2H), 4.58-4.37 (m, 2H), 3.30 (d, *J* = 3.6 Hz, 3H),

3.25 (t, *J* = 20.4 Hz, 3H), 3.09 (s, 1.5H), 3.03 (s, 1.5H), 2.06-1.96 (m, 1H), 1.79-1.65 (m, 1H), 1.25 (s, 1.5H), 1.22 (s, 1.5H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 177.0, 176.7, 146.1, 145.9, 139.8, 139.6, 129.3, 129.1, 124.5, 124.3, 120.2, 120.1, 108.5, 108.3, 77.0 (2), 74.4(2), 58.9, 58.4, 51.8 (2), 38.6 (2), 26.7, 26.1, 25.7; IR (KBr, cm^{-1}): 1679 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO_3$ ($[M+H]^+$) 290.1751, found 290.1755.

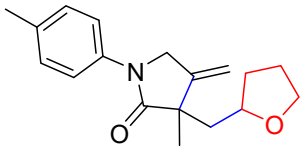


3-(2-(Ethylthio)propyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3af), yellow oil (0.0411 g, 71% yield, d.r. = 4: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72-7.69 (m, 1.6H), 7.67-7.62 (m, 0.4H), 7.41-7.36 (m, 2H), 7.19-7.13 (m, 1H), 5.30-5.25 (m, 1H), 5.20-5.14 (m, 0.8H), 5.09 (t, *J* = 3.0 Hz, 0.2H), 4.56-4.42 (m, 2H), 3.06-2.98 (m, 0.8H), 2.87-2.80 (m, 1H), 2.58-2.43 (m, 2H), 2.33-2.27 (m, 0.2H), 1.78-1.62 (m, 1H), 1.39 (s, 2.5H), 1.33 (s, 0.6H), 1.29-1.20 (m, 3H), 1.17 (t, *J* = 9.0 Hz, 2.4H), 1.08 (t, *J* = 9.0 Hz, 0.6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.9, 176.0, 145.7, 145.1, 139.4, 139.0, 128.9, 128.8, 124.8, 124.4, 120.1, 120.0, 108.8, 108.2, 52.6, 52.1, 52.0, 41.5, 36.5, 36.2, 24.3, 24.1, 23.0, 22.7, 15.0, 14.4; IR (KBr, cm^{-1}): 1691 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NOS$ ($[M+H]^+$) 290.1573, found 290.1569.

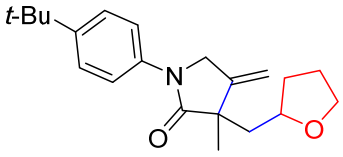


1-(4-Methoxyphenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (3ba), yellow oil (0.0506 g, 84% yield, d.r. = 14: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 9.0 Hz, 0.2H), 7.53 (d, *J* = 9.0 Hz, 1.9H), 6.91 (t, *J* = 8.5 Hz, 2H), 5.26 (t, *J* = 2.0 Hz, 1H), 5.09 (t, *J* = 2.5 Hz, 1H), 4.43-4.37 (m, 2H),

4.05-3.99 (m, 1H), 3.80 (s, 3H), 3.74 (t, *J* = 11.0 Hz, 1H), 3.58-3.54 (m, 1H), 2.19-2.14 (m, 1H), 1.95-1.85 (m, 2H), 1.79-1.74 (m, 1H), 1.63-1.59 (m, 1H), 1.50 (t, *J* = 8.5 Hz, 1H), 1.36 (s, 0.2H), 1.32 (s, 2.8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.1, 156.6, 146.5, 132.7, 122.4, 121.7, 114.1, 114.0, 107.8, 107.7, 75.8, 67.3, 55.5, 52.8, 48.0, 45.0, 31.9, 26.3, 25.3; IR (KBr, cm^{-1}): 1676 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_3$ ($[M+H]^+$) 302.1751, found 302.1753.

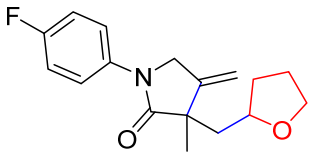


3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(p-tolyl)pyrrolidin-2-one (**3ca**), yellow oil (0.0462 g, 81% yield, d.r. = 2.3: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 5.0 Hz, 0.6H), 7.53 (d, *J* = 5.0 Hz, 1.4H), 7.18 (t, *J* = 9.5 Hz, 2H), 5.26-5.21 (m, 1H), 5.15-5.08 (m, 1H), 4.53-4.36 (m, 2H), 4.04-3.99 (m, 0.7H), 3.80-3.71 (m, 1.3H), 3.60-3.54 (m, 1H), 2.34 (s, 0.9H), 2.33 (s, 2.1H), 2.19-2.14 (m, 1H), 2.05-2.00 (m, 0.7H), 1.94-1.84 (m, 2.3H), 1.78-1.74 (m, 1H), 1.51-1.46 (m, 1H), 1.33 (s, 0.9H), 1.33 (s, 2.1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.2, 176.6, 146.4, 146.2, 137.0, 136.6, 134.4, 134.0, 129.5, 129.3, 120.5, 119.9, 107.8, 107.7, 76.4, 75.7, 67.3, 52.4, 52.3, 48.6, 48.2, 45.5, 44.9, 31.9 (2), 26.3, 25.9, 25.6, 25.3, 20.9; IR (KBr, cm^{-1}): 1677 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_2$ ($[M+H]^+$) 286.1802, found 286.1798.

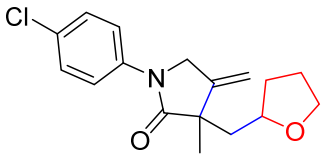


1-(4-(*tert*-Butyl)phenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3da**), yellow oil (0.0537 g, 82% yield, d.r. = 1: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65-7.62 (m, 0.5H), 7.58-7.57 (m, 1H), 7.42-7.35 (m, 2H), 7.14-7.12 (m, 0.5H), 5.27 (t, *J* = 2.0 Hz, 0.5H), 5.22-5.15 (m, 0.5H), 5.10-5.08 (m,

1H), 4.55-4.50 (m, 1H), 4.44-4.38 (m, 1.5H), 4.04-4.01 (m, 0.5H), 3.80-3.75 (m, 1H), 3.72-3.55 (m, 1H), 2.23-2.14 (m, 1H), 2.04-2.01 (m, 0.5H), 1.94-1.86 (m, 2H), 1.78-1.73 (m, 1.5H), 1.51-1.44 (m, 1H), 1.32 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.3, 176.7, 146.4, 146.1, 140.1, 139.8, 136.9, 136.5, 125.8, 125.7, 120.1, 119.6, 107.8 (2), 76.4, 75.7, 67.3 (2), 52.3, 52.2, 48.6, 48.2, 45.4, 44.8, 31.9 (2), 31.4 (2), 31.3, 26.8, 26.0, 25.6, 25.3; IR (KBr, cm^{-1}): 1685 (C=O); HRMS *m/z* (ESI) calcd for $C_{21}H_{30}NO_2$ ($[M+H]^+$) 328.2271, found 328.2275.

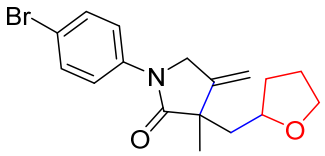


1-(4-Fluorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (3ea), yellow oil (0.0434 g, 75% yield, d.r. = 2.3: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69-7.66 (m, 0.6H), 7.62-7.59 (m, 1.4H), 7.09-7.04 (m, 2H), 5.29-5.22 (m, 1H), 5.16-5.11 (m, 1H), 4.55-4.35 (m, 2H), 4.03-3.99 (m, 0.7H), 3.88-3.84 (m, 0.3H), 3.80-3.70 (m, 1H), 3.62-3.52 (m, 1H), 2.19-2.14 (m, 1H), 1.94-1.85 (m, 3H), 1.63-1.60 (m, 1H), 1.52-1.46 (m, 1H), 1.36 (s, 0.9H), 1.33 (s, 2.1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.5, 176.8, 160.0 (d, $J_{C\text{-}F}$ = 242.3 Hz), 159.9 (d, $J_{C\text{-}F}$ = 242.9 Hz), 146.0, 145.9, 135.6 (2), 122.3 (d, $J_{C\text{-}F}$ = 7.9 Hz), 121.7 (d, $J_{C\text{-}F}$ = 7.9 Hz), 115.6 (d, $J_{C\text{-}F}$ = 19.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 19.4 Hz),108.0, 107.9, 76.3, 75.7, 67.4, 67.3, 52.6, 52.4, 48.5, 48.1, 45.5, 45.1, 32.0, 31.8, 26.4, 25.8, 25.5, 25.3; ^{19}F NMR (471 MHz, DMSO-*d6*) δ: -117.5, -118.0; IR (KBr, cm^{-1}): 1690 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{21}FNO_2$ ($[M+H]^+$) 290.1551, found 290.1553.

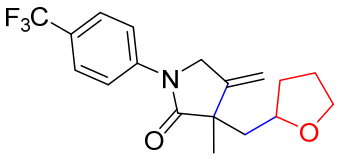


1-(4-Chlorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3fa**), yellow

oil (0.0445 g, 73% yield, d.r. = 9: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70-7.67 (m, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.36-7.32 (m, 2H), 5.29-5.23 (m, 1H), 5.16-5.09 (m, 1H), 4.54-4.35 (m, 2H), 4.13-4.01 (m, 1H), 3.79-3.69 (m, 1H), 3.61-3.51 (m, 1H), 2.00-1.84 (m, 3H), 1.76-1.58 (m, 2H), 1.51-1.42 (m, 1H), 1.33 (s, 2.7H), 1.29 (s, 0.3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.7, 177.0, 145.7, 145.1, 138.1, 137.5, 129.0, 128.9, 128.8, 121.4, 120.8, 108.2, 108.0, 76.3, 75.7, 67.4 (2), 52.2, 52.1, 48.6, 48.2, 45.5, 45.1, 32.0, 31.8, 26.4, 25.8, 25.5, 25.3; IR (KBr, cm^{-1}): 1699 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{21}ClNO_2$ ($[M+H]^+$) 306.1255, found 306.1251.

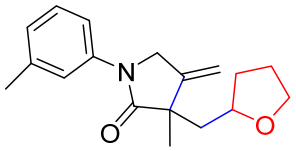


1-(4-Bromophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3ga**), yellow oil (0.0517 g, 74% yield, d.r. = 5: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64-7.62 (m, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.50-7.46 (m, 2H), 5.33-5.23 (m, 1H), 5.16-5.08 (m, 1H), 4.54-4.37 (m, 2H), 4.13-3.98 (m, 1H), 3.86-3.69 (m, 1H), 3.60-3.51 (m, 1H), 2.01-1.85 (m, 3H), 1.75-1.60 (m, 2H), 1.51-1.42 (m, 1H), 1.32 (s, 2.5H), 1.29 (s, 0.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.7, 177.2, 145.6, 145.1, 138.6, 138.0, 131.9, 131.7, 121.7, 121.1, 117.4, 117.1, 108.3, 108.2, 76.3, 75.6, 67.4, 67.0, 52.1, 52.0, 48.7, 48.3, 45.6, 45.1, 32.0, 31.8, 26.4, 25.8, 25.5, 25.3; IR (KBr, cm^{-1}): 1696 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{21}BrNO_2$ ($[M+H]^+$) 350.0750, found 350.0752.

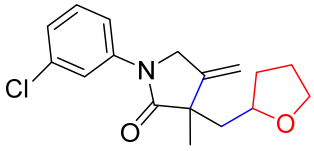


3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (**3ha**), yellow oil (0.0482 g, 71% yield, d.r. = 4: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.5 Hz, 0.4H), 7.82 (d, *J* = 8.5 Hz, 1.6H),

7.63 (t, J = 20.5 Hz, 2H), 5.33-5.26 (m, 1H), 5.18-5.13 (m, 1H), 4.60-4.40 (m, 2H), 4.05-4.00 (m, 0.8H), 3.82-3.67 (m, 1.2H), 3.60-3.49 (m, 1H), 2.17-1.85 (m, 3H), 1.76-1.62 (m, 2H), 1.52-1.44 (m, 1H), 1.38 (s, 0.6H), 1.34 (s, 2.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.2, 177.6, 145.4, 145.3, 142.5, 141.9, 126.1 (*q*, $J_{C\text{-}F}$ = 2.7 Hz), 126.0 (*q*, $J_{C\text{-}F}$ = 2.8 Hz), 125.8 (*q*, $J_{C\text{-}F}$ = 30.0 Hz), 119.5, 119.2, 119.1, 108.4, 108.2, 76.2, 75.6, 67.4, 52.0, 48.8, 48.4, 45.6, 45.2, 32.0, 31.7, 26.5, 25.8, 25.5, 25.3; ^{19}F NMR (471 MHz, DMSO-*d6*) δ: -62.1 (2); IR (KBr, cm^{-1}): 1687 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{21}F_3NO_2$ ([M+H]$^+$) 340.1519, found 340.1515.

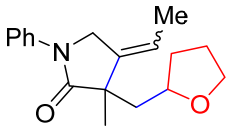


3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(m-tolyl)pyrrolidin-2-one (**3ia**), yellow oil (0.0456 g, 80% yield, d.r. = 4: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (s, 0.2H), 7.53 (s, 0.8H), 7.47 (d, J = 8.5 Hz, 0.2H), 7.41 (d, J = 8.0 Hz, 0.8H), 7.28-7.23 (m, 1H), 6.99-6.95 (m, 1H), 5.27-5.22 (m, 1H), 5.15-5.09 (m, 1H), 4.53-4.40 (m, 2H), 4.04-3.99 (m, 0.8H), 3.80-3.72 (m, 1.2H), 3.61-3.52 (m, 1H), 2.38 (s, 0.6H), 2.36 (s, 2.4H), 2.19-2.14 (m, 1H), 1.95-1.85 (m, 2H), 1.79-1.74 (m, 1H), 1.64-1.61 (m, 1H), 1.51-1.46 (m, 1H), 1.36 (s, 0.6H), 1.33 (s, 2.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.4, 176.9, 146.3, 146.1, 139.4, 139.0, 138.8, 138.6, 128.8, 128.6, 125.5, 125.3, 121.2, 120.7, 117.4, 117.0, 107.8, 107.7, 76.4, 75.7, 67.4, 67.3, 52.4, 52.3, 48.7, 48.3, 45.4, 44.9, 31.9 (2), 26.4, 25.9, 25.6, 25.3, 21.7 (2); IR (KBr, cm^{-1}): 1688 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_2$ ([M+H]$^+$) 286.1802, found 286.1800.

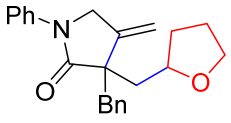


1-(3-Chlorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3ja**), yellow oil

(0.0433 g, 71% yield, d.r. = 4: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80 (s, 0.2H), 7.73 (s, 0.8H), 7.64 (d, *J* = 5.0 Hz, 0.2H), 7.58 (d, *J* = 10.0 Hz, 0.8H), 7.32-7.28 (m, 1H), 7.15-7.05 (m, 1H), 5.31-5.23 (m, 1H), 5.16-5.11 (m, 1H), 4.56-4.35 (m, 2H), 4.04-3.99 (m, 1H), 3.80-3.70 (m, 1H), 3.61-3.52 (m, 1H), 2.18-2.14 (m, 1H), 2.06-1.98 (m, 1H), 1.94-1.79 (m, 3H), 1.64-1.60 (m, 1H), 1.36 (s, 0.6H), 1.33 (s, 2.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.8 (2), 145.6, 140.2 (2), 134.5, 129.9, 129.8, 124.6, 124.3, 120.2, 119.8, 118.1, 117.6, 108.2, 108.0, 76.3, 75.6, 67.4 (2), 52.2, 52.1, 48.8, 48.3, 45.5, 45.1, 32.0, 31.8, 26.4, 25.8, 25.5, 25.3; IR (KBr, cm^{-1}): 1681 (C=O); HRMS *m/z* (ESI) calcd for $C_{17}H_{21}ClNO_2$ ($[M+H]^+$) 306.1255, found 306.1251.

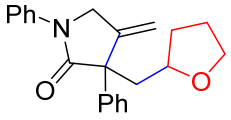


4-Ethylidene-3-methyl-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3la**), yellow oil (0.0359 g, 63% yield, d.r. = 5.7: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72-7.70 (m, 0.3H), 7.67-7.65 (m, 1.7H), 7.37 (t, *J* = 12.5 Hz, 2H), 7.16-7.11 (m, 1H), 5.64-5.60 (m, 1H), 4.42-4.34 (m, 2H), 4.02-3.97 (m, 0.8H), 3.79-3.69 (m, 1.2H), 3.63-3.52 (m, 1H), 2.26-2.21 (m, 1H), 2.07-2.01 (m, 1H), 1.95-1.83 (m, 4H), 1.78 (d, *J* = 5.0 Hz, 3H), 1.48 (s, 0.4H), 1.42 (s, 2.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.4, 139.7 (2), 135.3, 135.2, 128.9, 128.8, 124.6, 124.2, 120.3, 120.0, 119.8, 119.2, 76.1, 67.3, 67.2, 52.5, 52.4, 48.1, 48.0, 43.0, 42.8, 31.9, 31.5, 25.5, 25.4, 24.8 (2), 14.1, 13.7; IR (KBr, cm^{-1}): 1694 (C=O); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_2$ ($[M+H]^+$) 286.1802, found 286.1800.

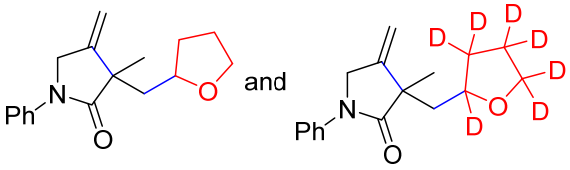


3-Benzyl-4-methylene-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (3na), yellow oil (0.0417 g, 60% yield,

d.r. > 20: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 2H), 7.18-7.09 (m, 6H), 5.33 (s, 1H), 5.24 (s, 1H), 4.14 (d, *J* = 13.5 Hz, 1H), 3.88-3.84 (m, 1H), 3.80-3.76 (m, 1H), 3.63-3.59 (m, 1H), 3.50 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 13.0 Hz, 1H), 2.74 (d, *J* = 12.5 Hz, 1H), 2.26-2.20 (m, 1H), 2.14-2.10 (m, 1H), 2.03-1.99 (m, 1H), 1.90-1.75 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.2, 142.9, 138.6, 136.4, 130.3, 128.8, 127.8, 126.6, 124.9, 120.6, 109.2, 76.3, 67.2, 54.8, 52.6, 46.8, 43.7, 31.8, 25.9; IR (KBr, cm^{-1}): 1698 (C=O); HRMS *m/z* (ESI) calcd for $C_{23}H_{26}NO_2$ ($[M+H]^+$) 348.1958, found 348.1960.

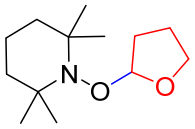


4-Methylene-1,3-diphenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3oa**), yellow oil (0.0446 g, 67% yield, d.r. = 1.5: 1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 9.0 Hz, 1.2H), 7.59 (d, *J* = 9.0 Hz, 0.8H), 7.47 (d, *J* = 8.5 Hz, 0.8H), 7.43 (d, *J* = 8.0 Hz, 1.2H), 7.33-7.28 (m, 2H), 7.26-7.22 (m, 2H), 7.16-7.05 (m, 2H), 5.50-5.40 (m, 1H), 5.19-5.16 (m, 1H), 4.48-4.40 (m, 2H), 4.14-4.09 (m, 0.4H), 3.91-3.88 (m, 0.6H), 3.76-3.72 (m, 1H), 3.58-3.51 (m, 1H), 2.63-2.49 (m, 1H), 2.35-2.31 (m, 1H), 2.04-1.82 (m, 3H), 1.75-1.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.8, 173.4, 142.7, 142.5, 141.1, 141.0, 138.5, 138.0, 127.9, 127.8, 127.5, 127.4, 126.1, 126.0, 125.6, 125.4, 123.8, 123.4, 119.2, 118.9, 110.5, 110.3, 74.5, 66.4, 66.3, 56.3, 55.7, 51.4, 42.6, 42.1, 31.3, 31.0, 24.8, 24.4; IR (KBr, cm^{-1}): 1676 (C=O); HRMS *m/z* (ESI) calcd for $C_{22}H_{24}NO_2$ ($[M+H]^+$) 334.1802, found 334.1804.



3aa and **3aa-*d7***, yellow oil (75% yield, d.r. = 5.7: 1); ^{1}H NMR (500

MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.5 Hz, 0.3H), 7.67 (d, *J* = 7.5 Hz, 1.7H), 7.40-7.35 (m, 2H), 7.17-7.12 (m, 1H), 5.28-5.22 (m, 1H), 5.16-5.10 (m, 1H), 4.54-4.39 (m, 2H), 4.05-3.99 (m, 0.6H), 3.77-3.72 (m, 0.6H), 3.59-3.53 (m, 0.6H), 2.20-2.15 (m, 1H), 2.03-2.00 (m, 0.6H), 1.93-1.85 (m, 1.8H), 1.52-1.46 (m, 1H), 1.37 (s, 0.5H), 1.33 (s, 2.5H).



2,2,6,6-Tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine

(4a) [1], yellow oil (0.1392 g, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.39-5.36 (m, 1H), 3.79-3.73 (m, 1H), 3.60-3.53 (m, 1H), 1.48-1.44 (m, 6H), 1.29 (d, *J* = 5.5 Hz, 3H), 1.20 (t, *J* = 8.0 Hz, 1H), 1.15 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 109.8, 66.8, 60.4, 59.0, 40.4, 40.0, 33.7, 33.6, 33.5, 20.4, 19.9, 19.2, 17.2.

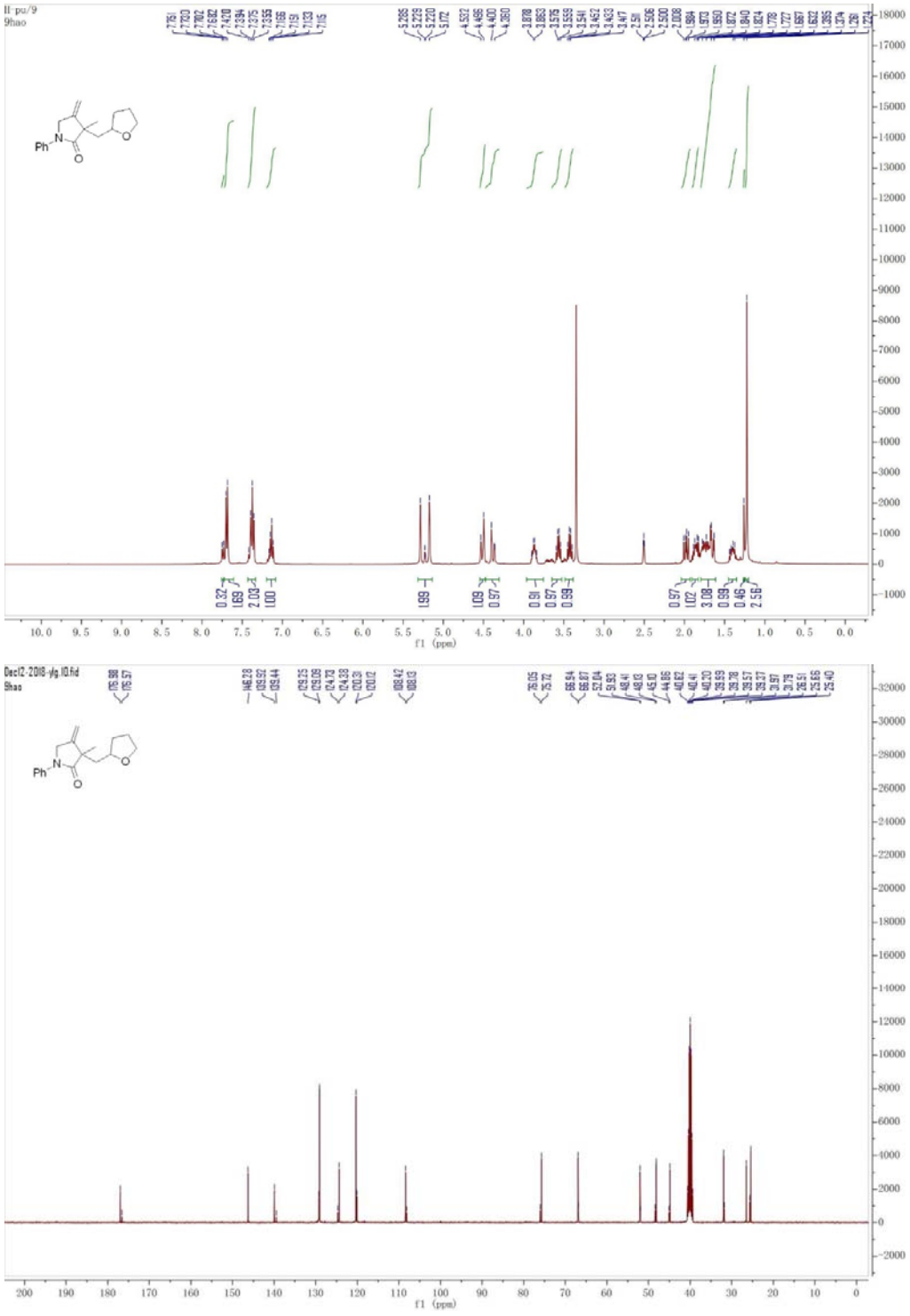
(C) Reference

[1] L. Li, Z. Yu and Z. Shen, *Adv. Synth. Catal.* 2015, **357**, 3495.

(D) Spectra

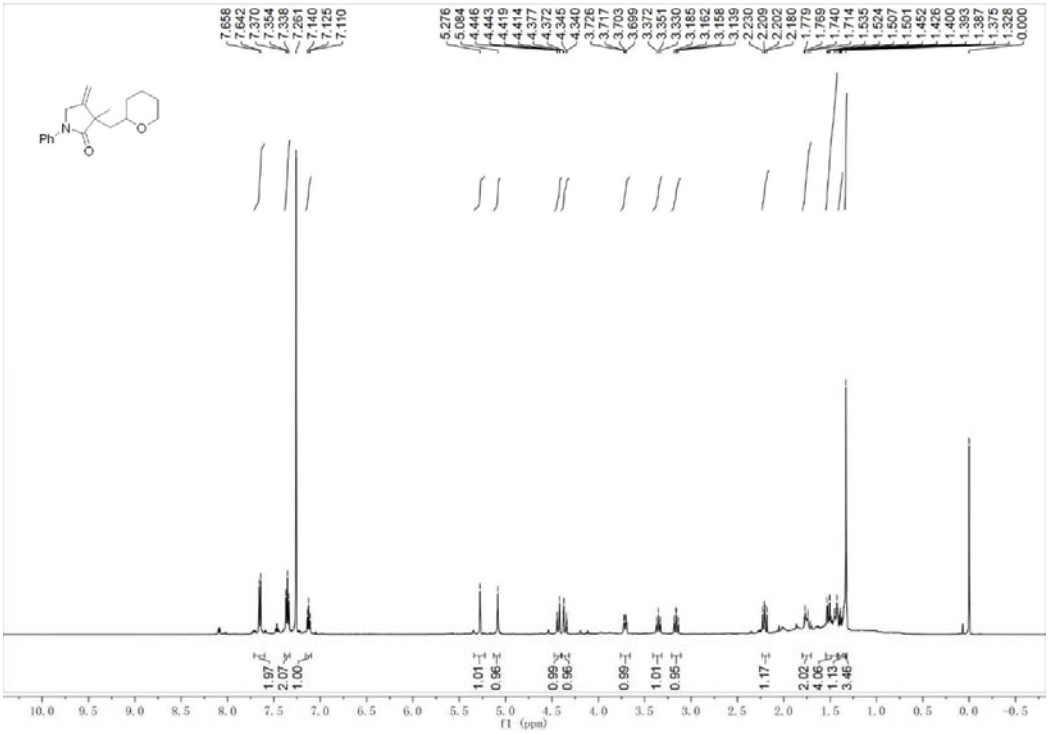
3-Methyl-4-methylene-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one

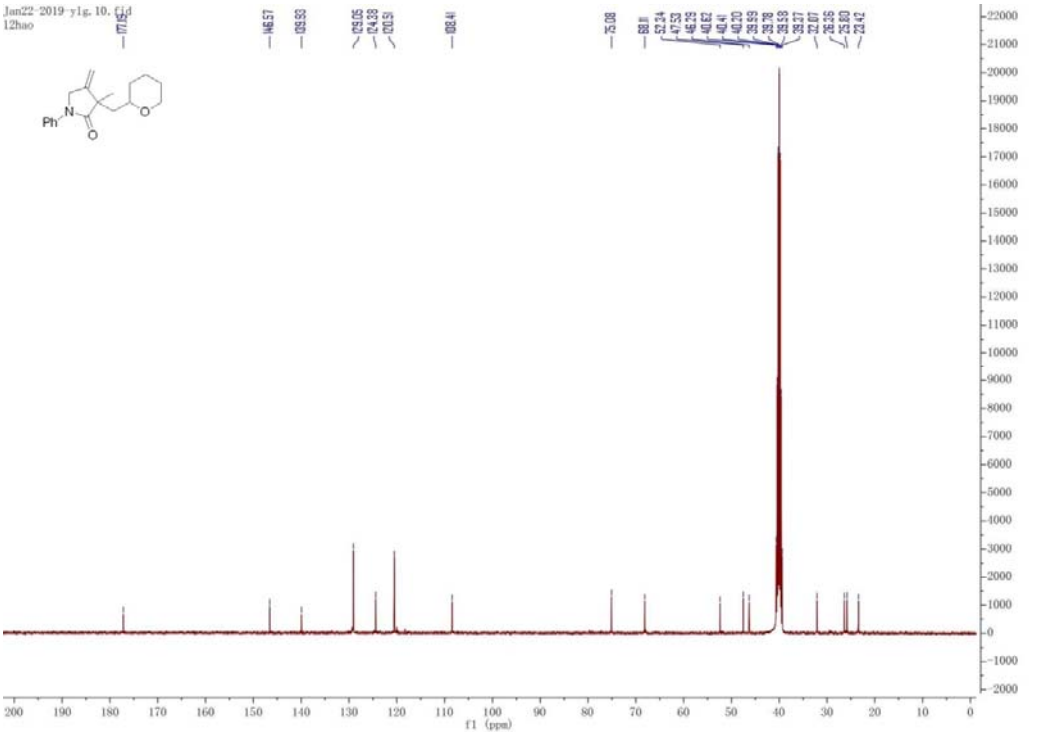
(**3aa**)



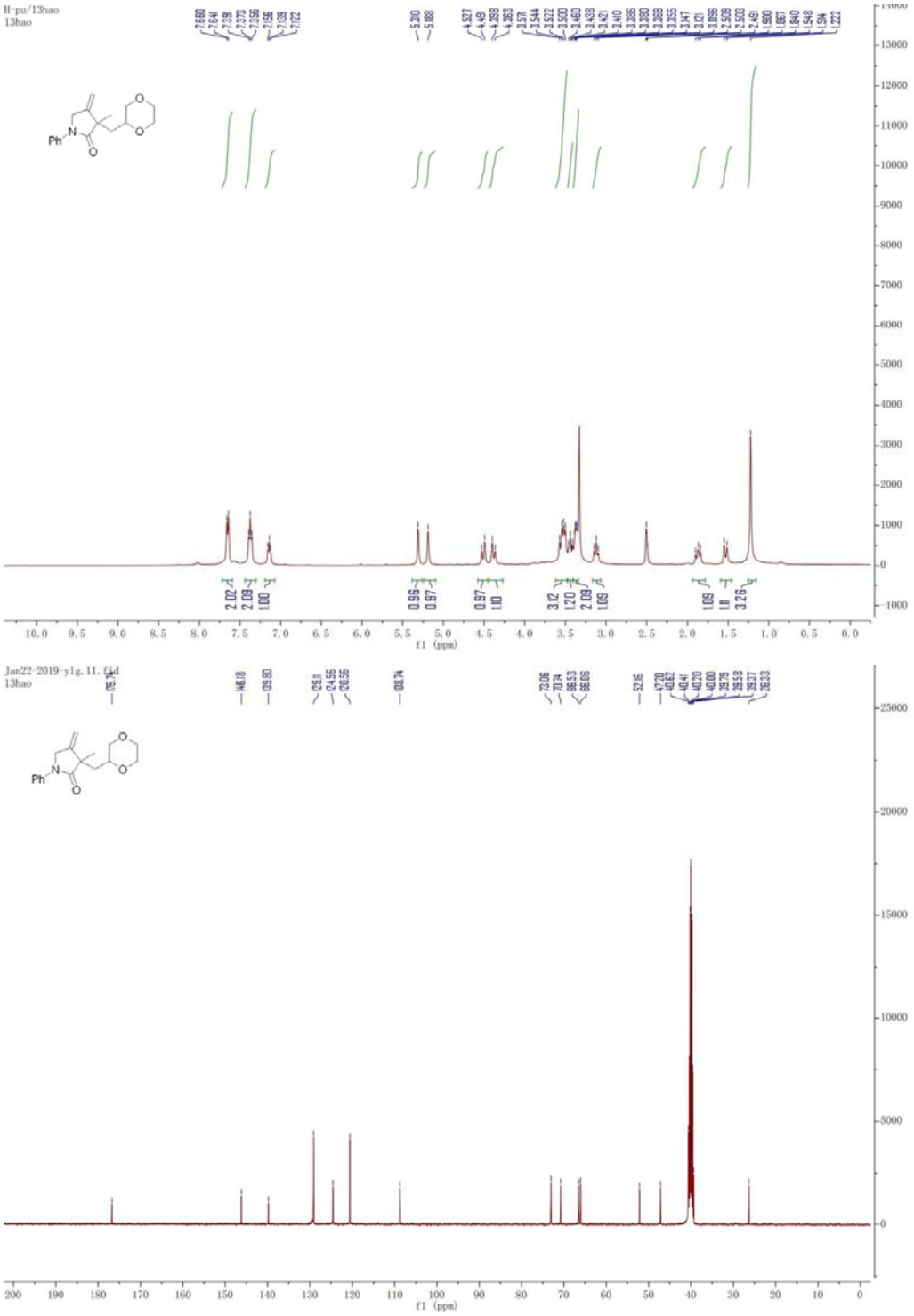
3-Methyl-4-methylene-1-phenyl-3-((tetrahydro-2H-pyran-2-yl)methyl)pyrrolidin-2-on

e (**3ab**)

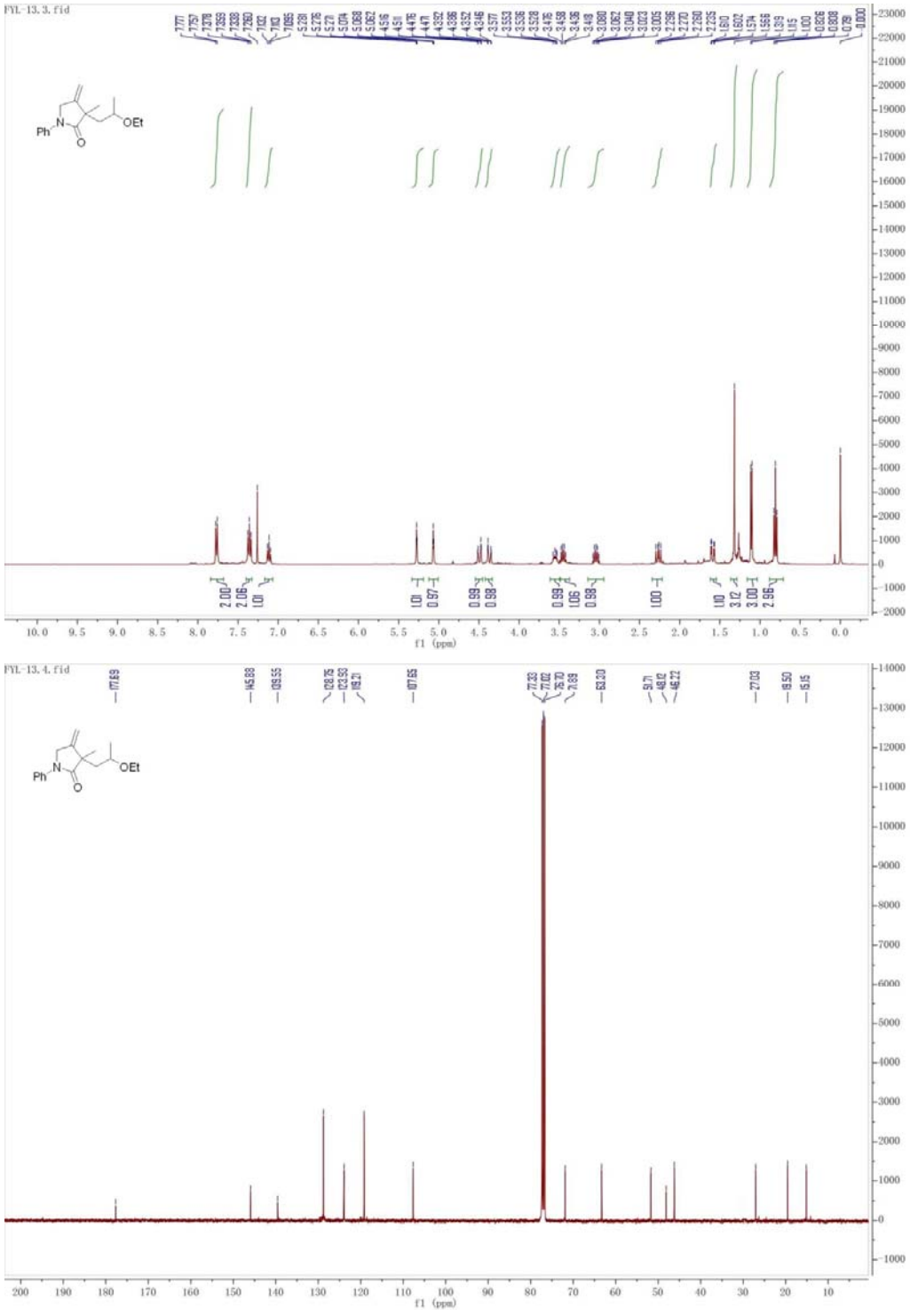




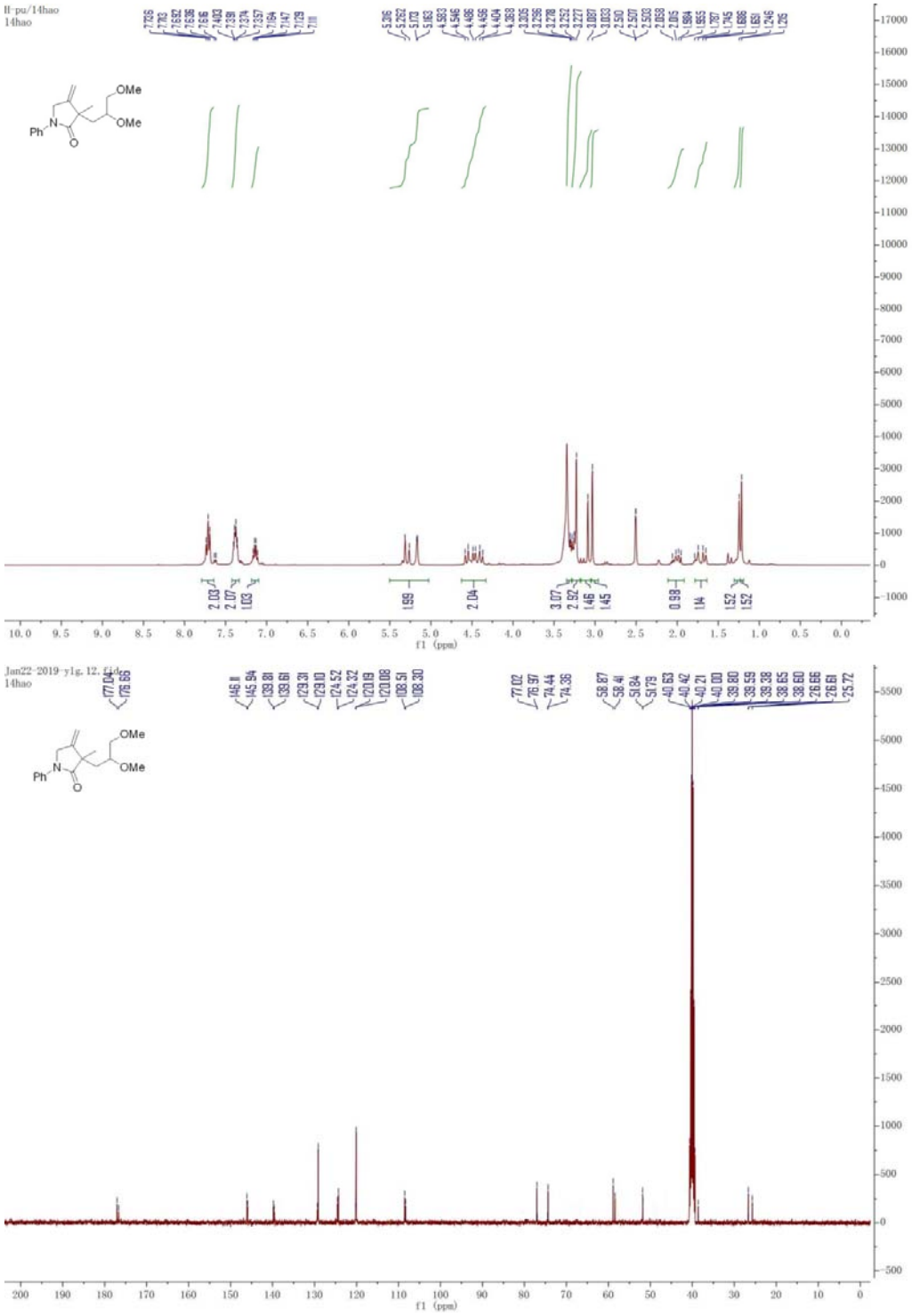
3-((1,4-Dioxan-2-yl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (**3ac**)



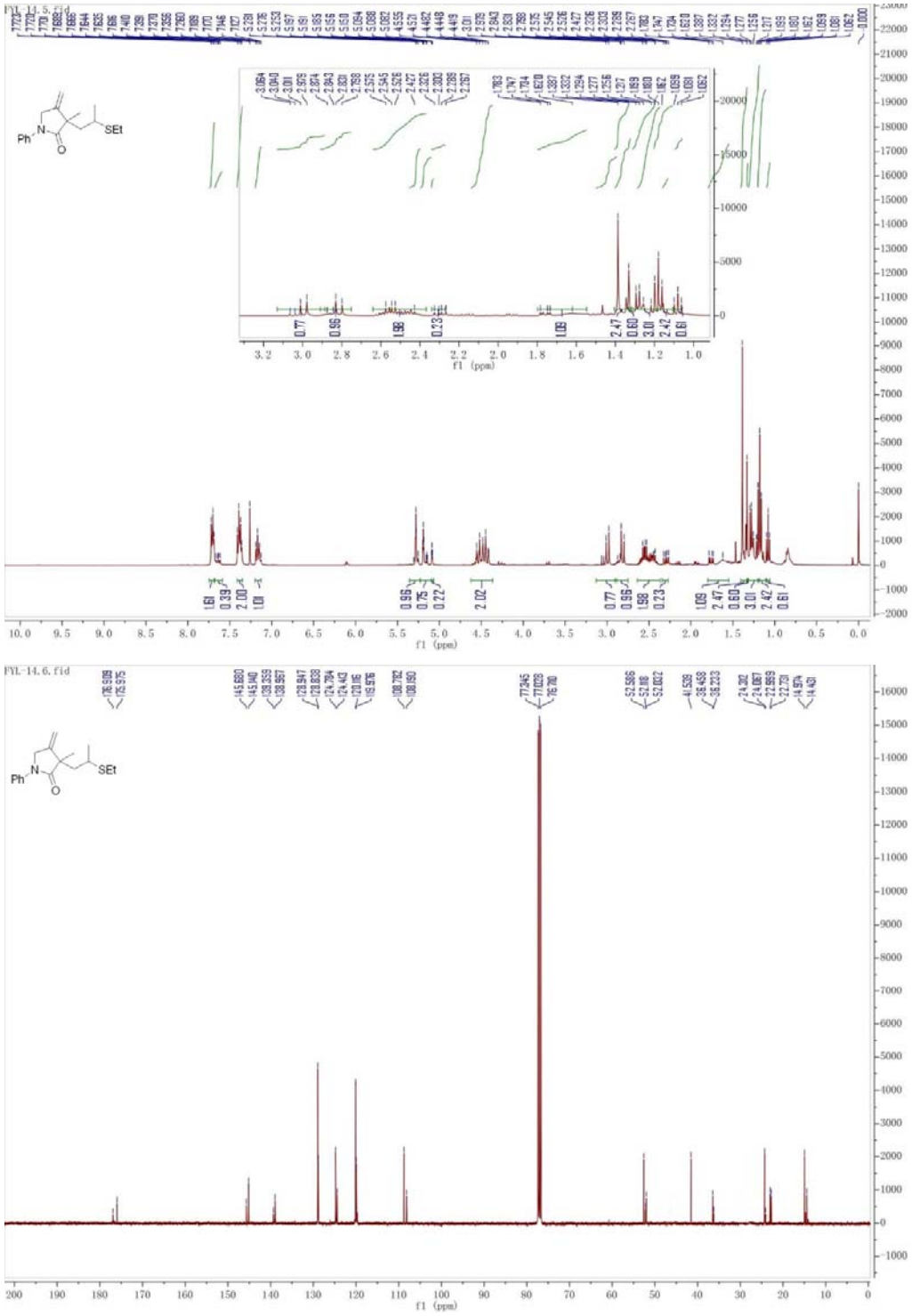
3-(2-Ethoxypropyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (**3ad**)



3-(2,3-Dimethoxypropyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (**3ae**)

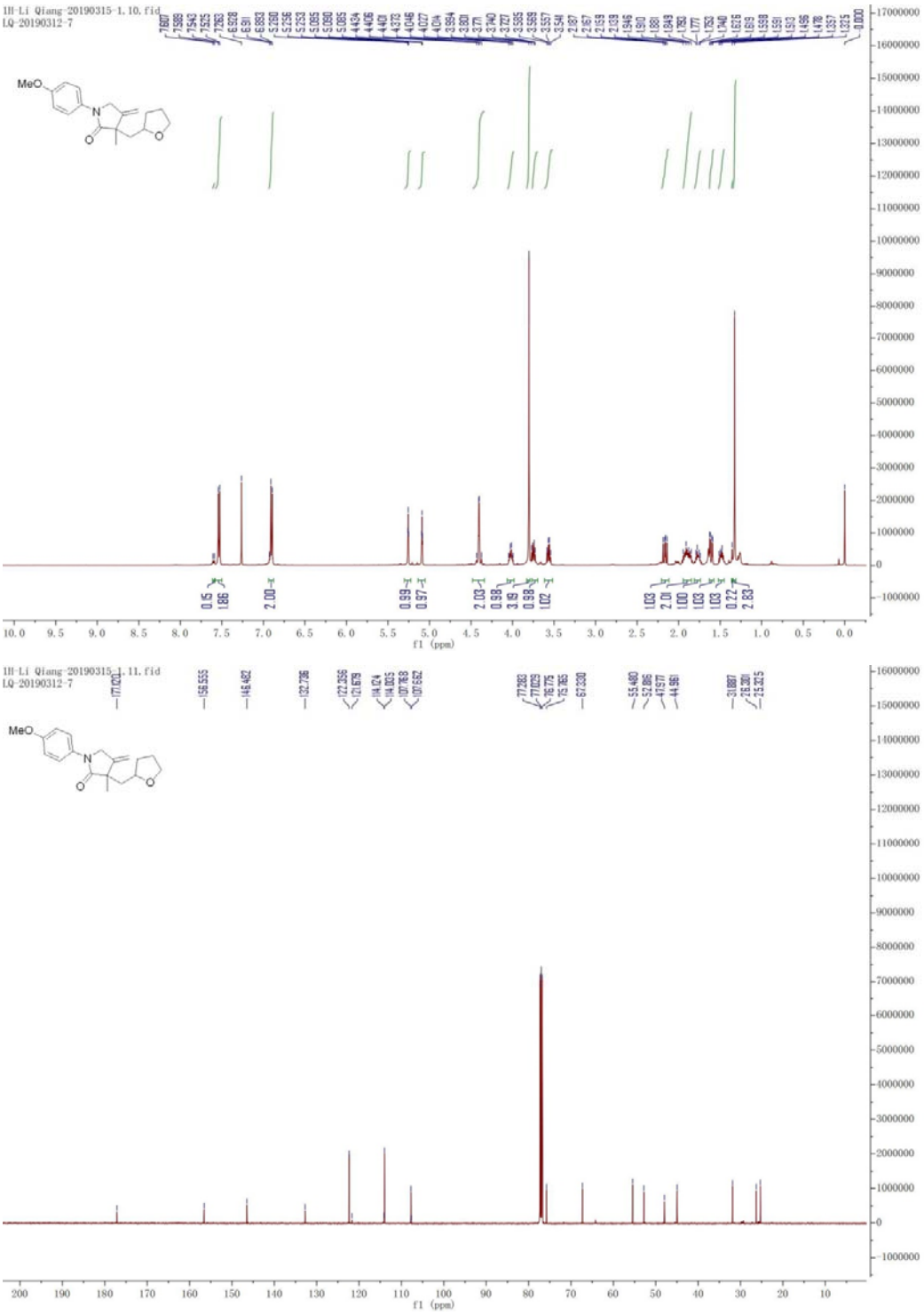


3-(2-(Ethylthio)propyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (**3af**)



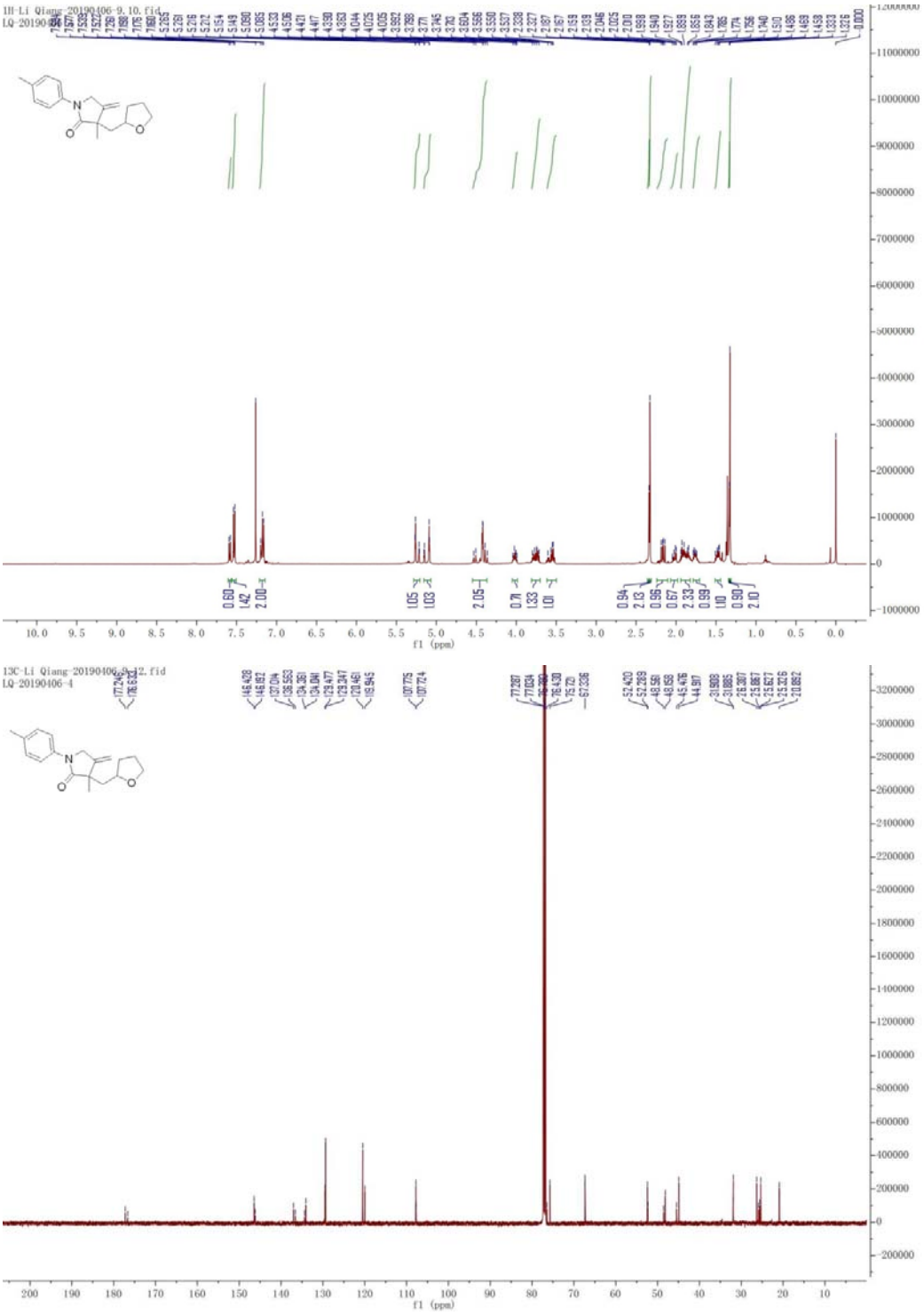
1-(4-Methoxyphenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolid

in-2-one (**3ba**)



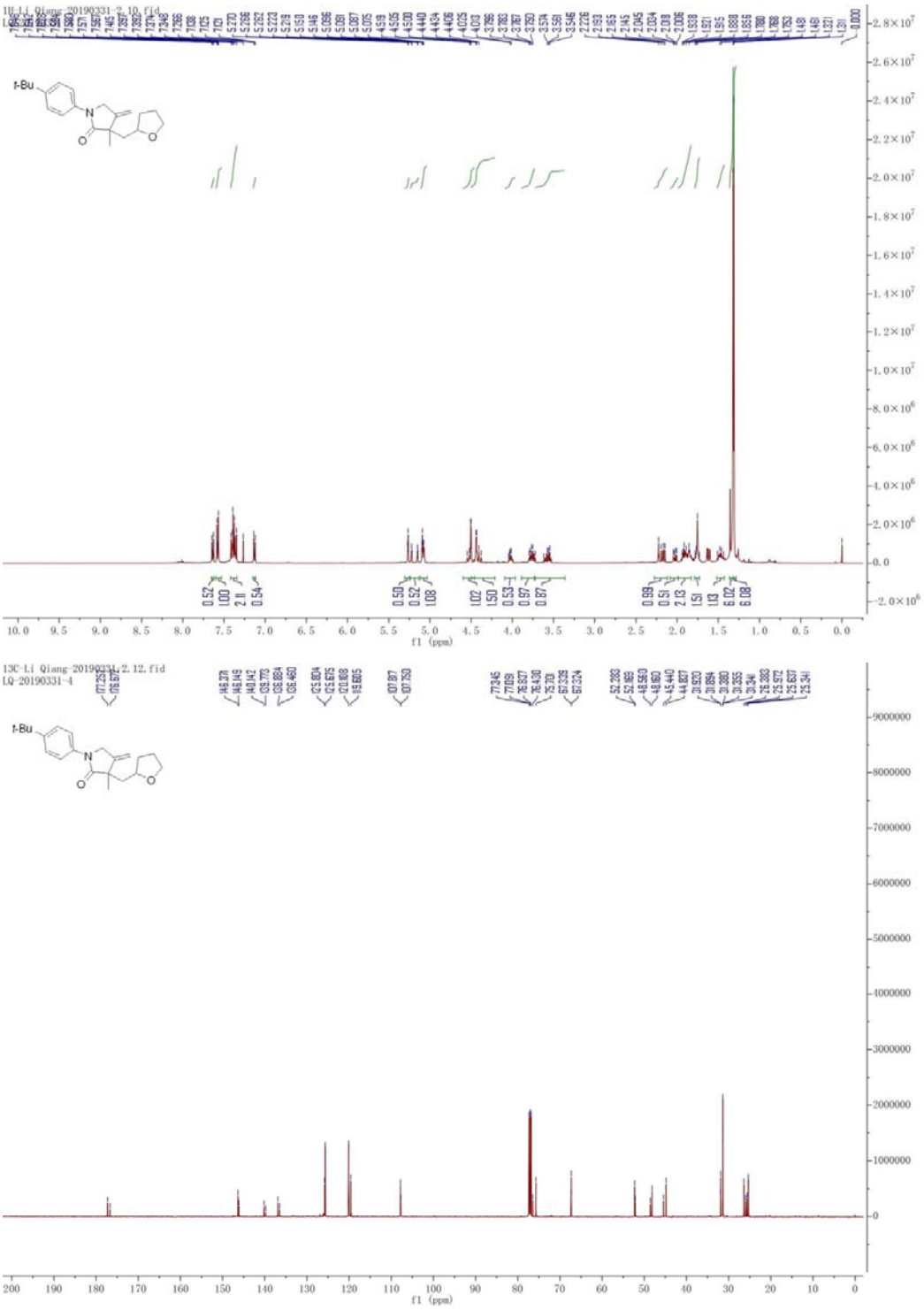
3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(p-tolyl)pyrrolidin-2-one

(**3ca**)



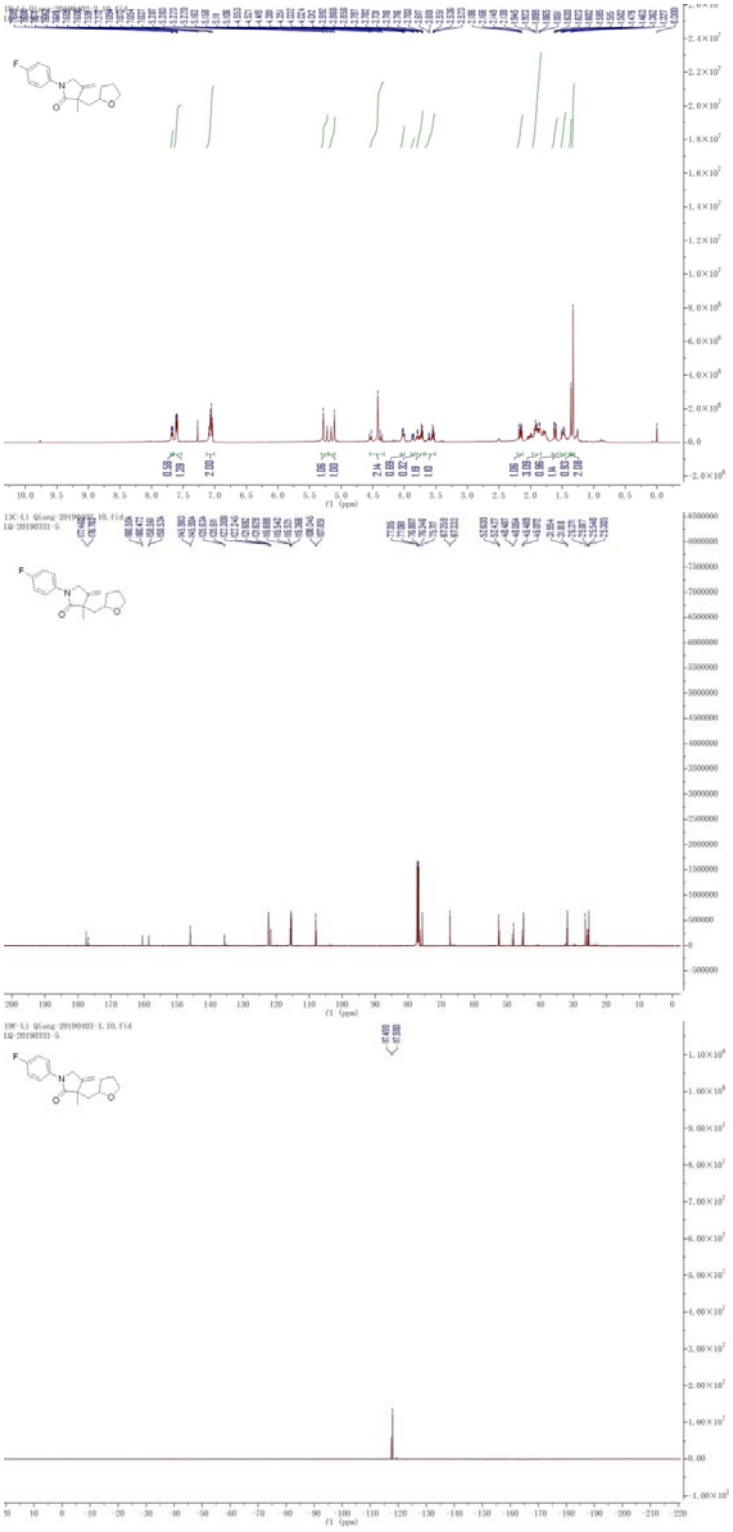
1-(4-(*tert*-Butyl)phenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrro

lidin-2-one (**3da**)



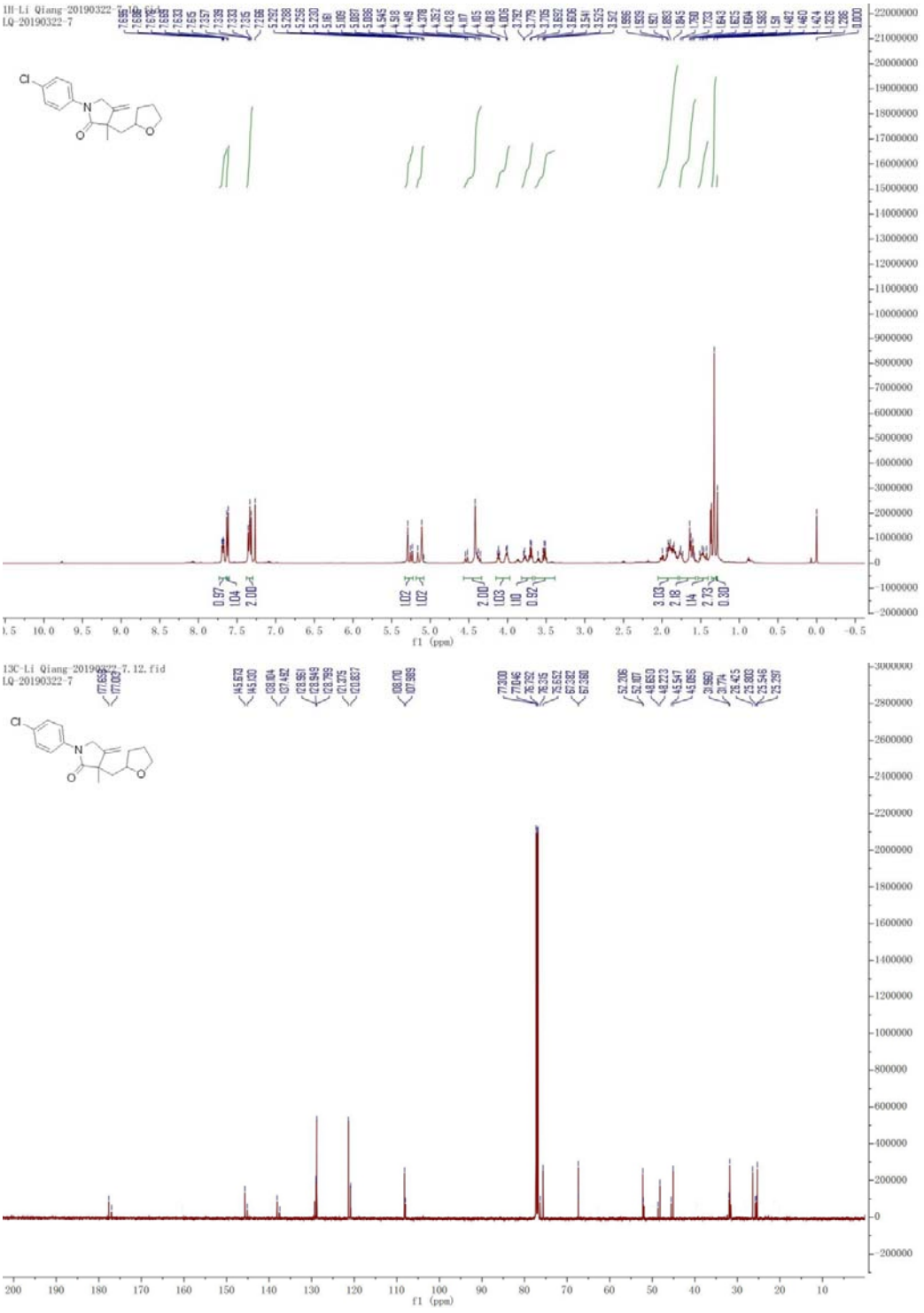
1-(4-Fluorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin

-2-one (**3ea**)



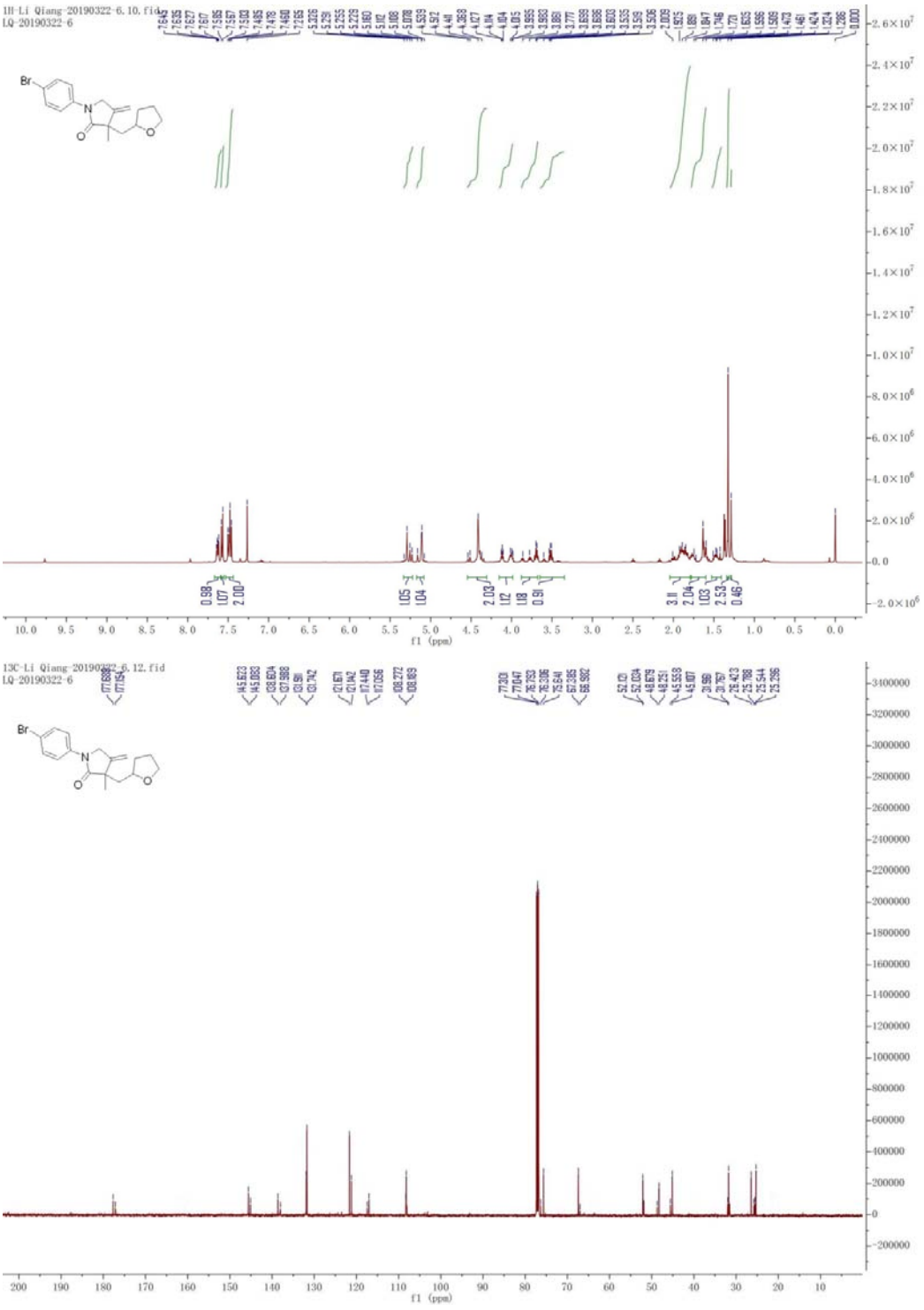
1-(4-Chlorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin

-2-one (**3fa**)



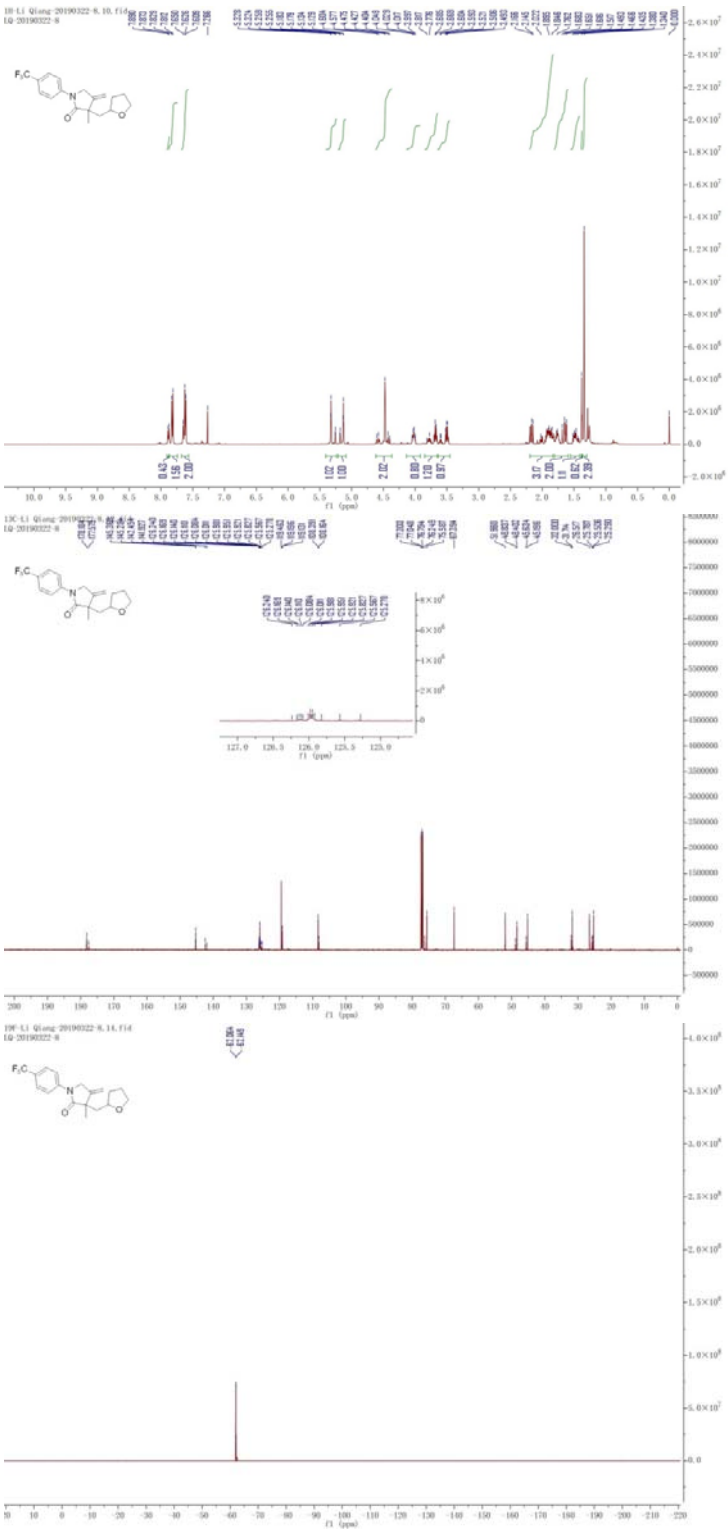
1-(4-Bromophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin

-2-one (**3ga**)



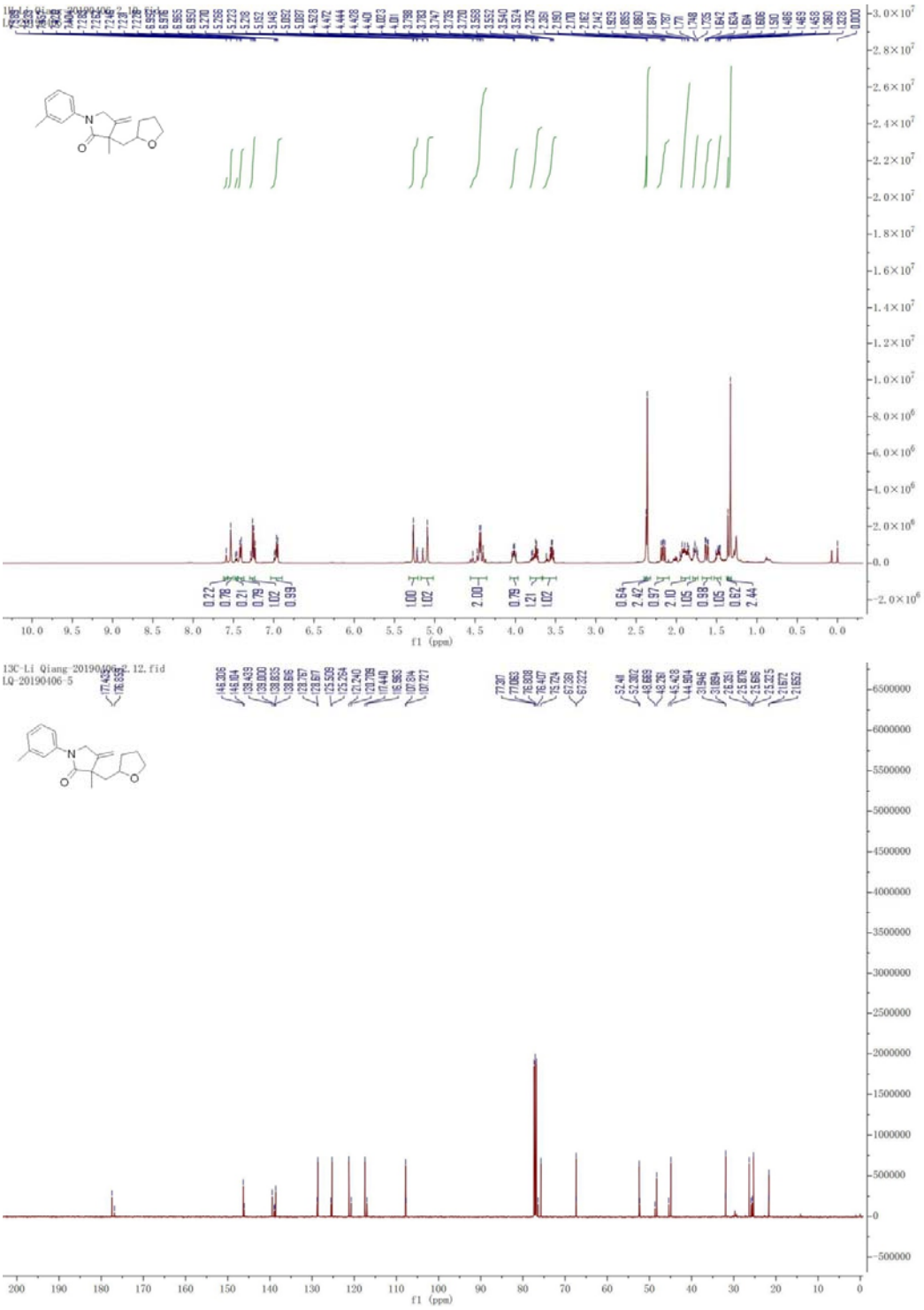
3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(4-(trifluoromethyl)phenyl

)pyrrolidin-2-one (**3ha**)



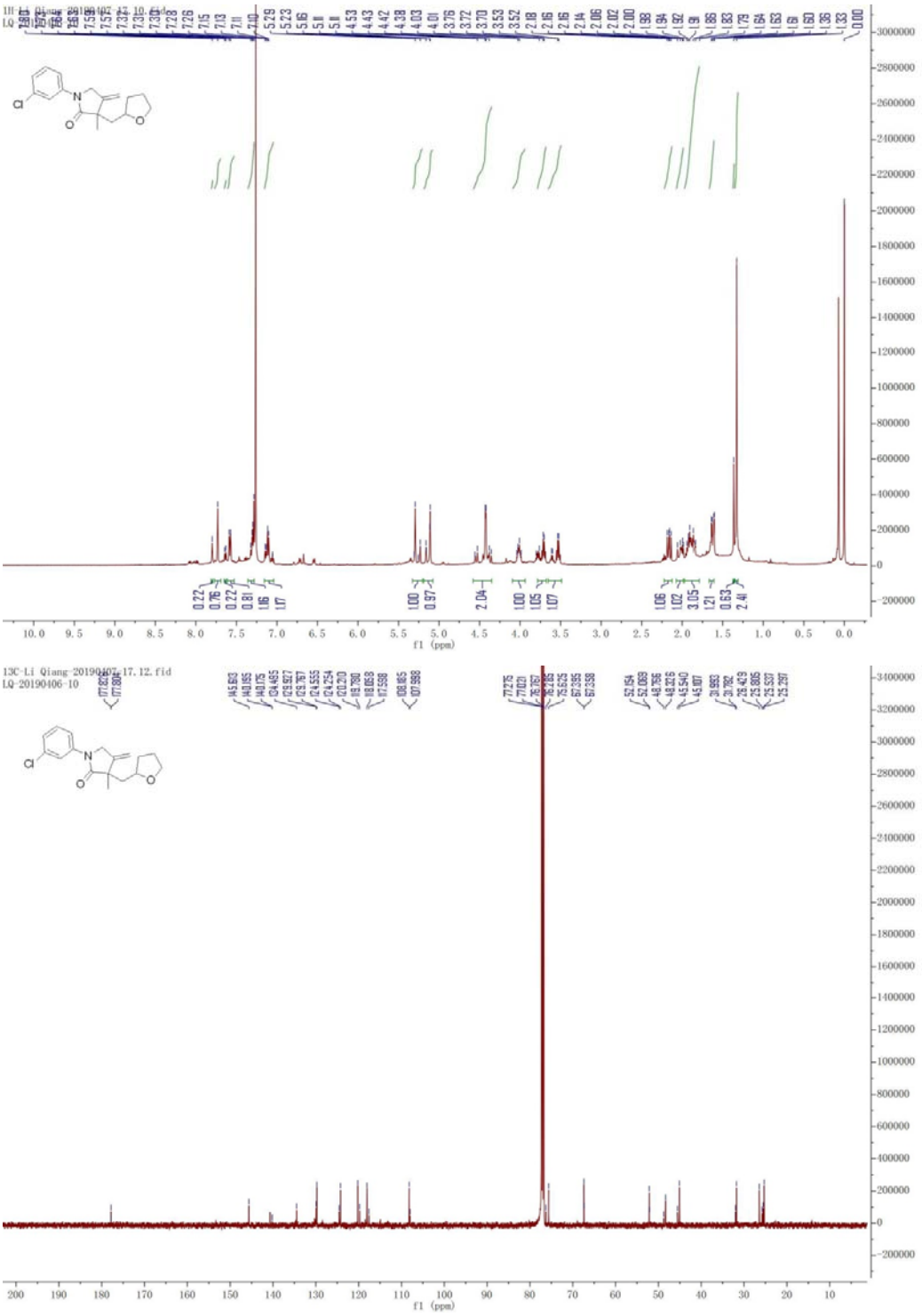
3-Methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)-1-(m-tolyl)pyrrolidin-2-one

(**3ia**)



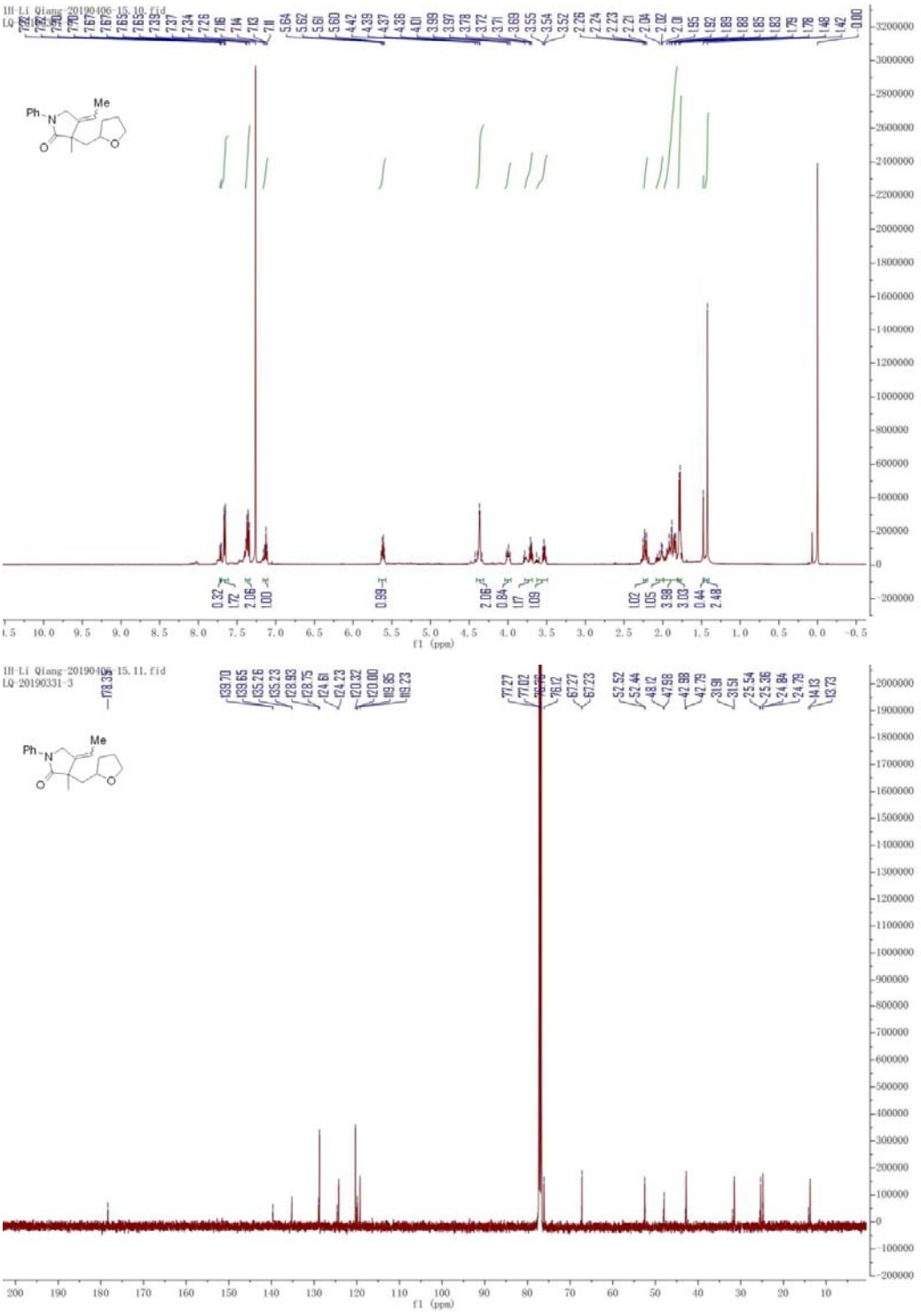
1-(3-Chlorophenyl)-3-methyl-4-methylene-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin

-2-one (**3ja**)



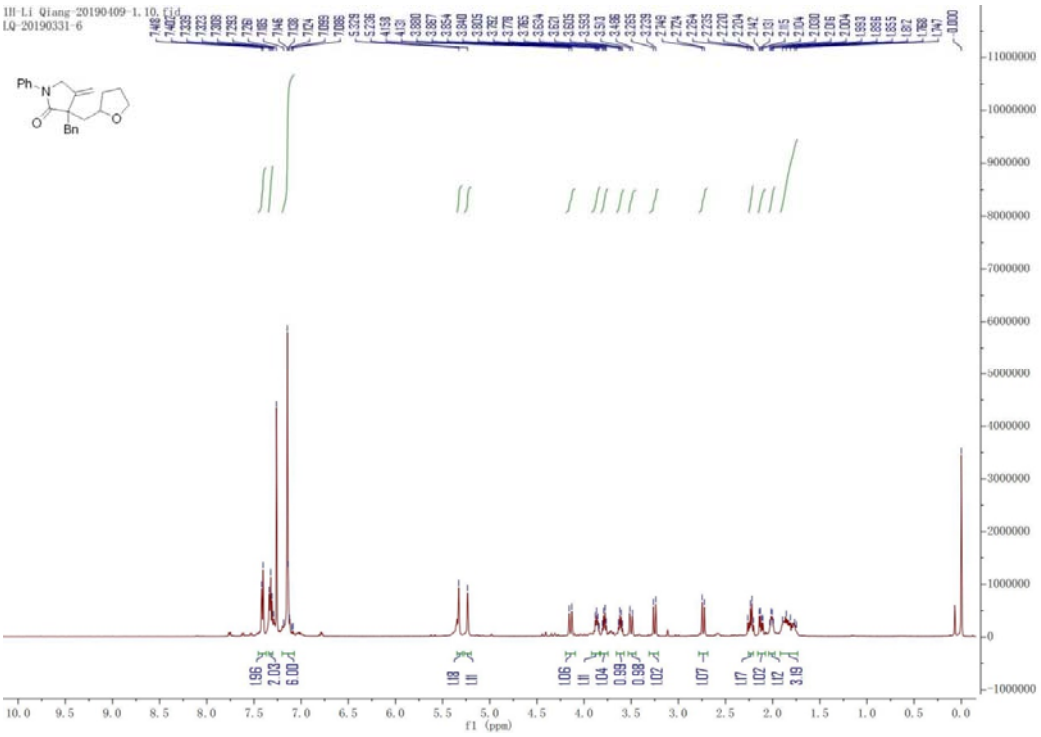
4-Ethylidene-3-methyl-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one

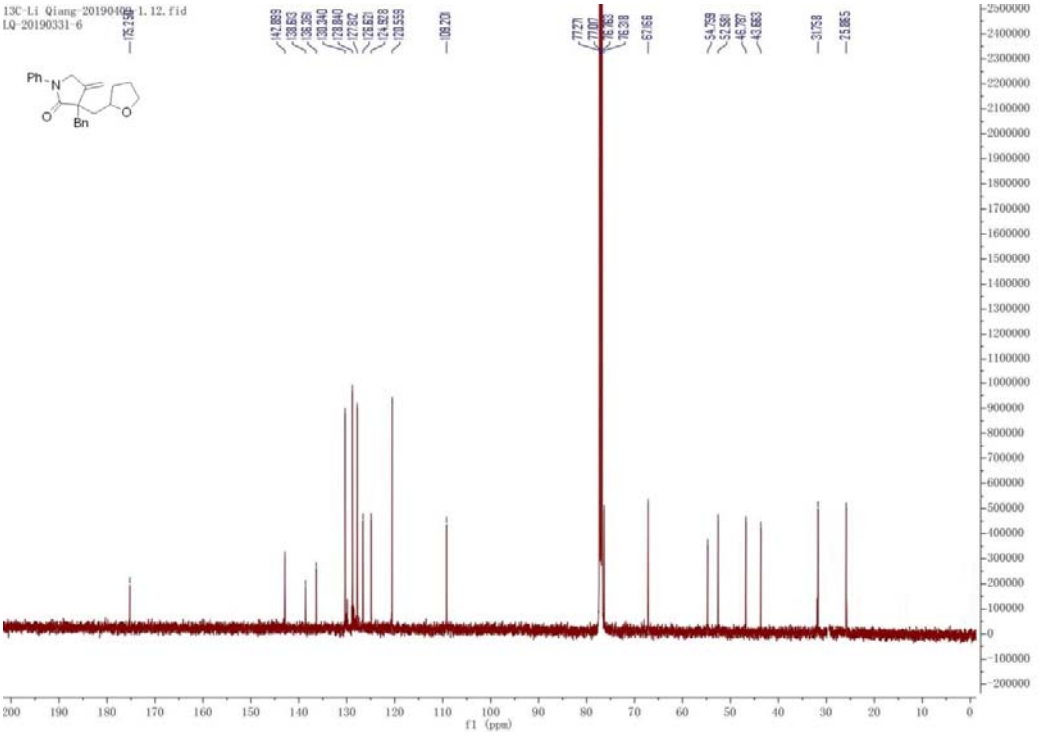
(**3la**)



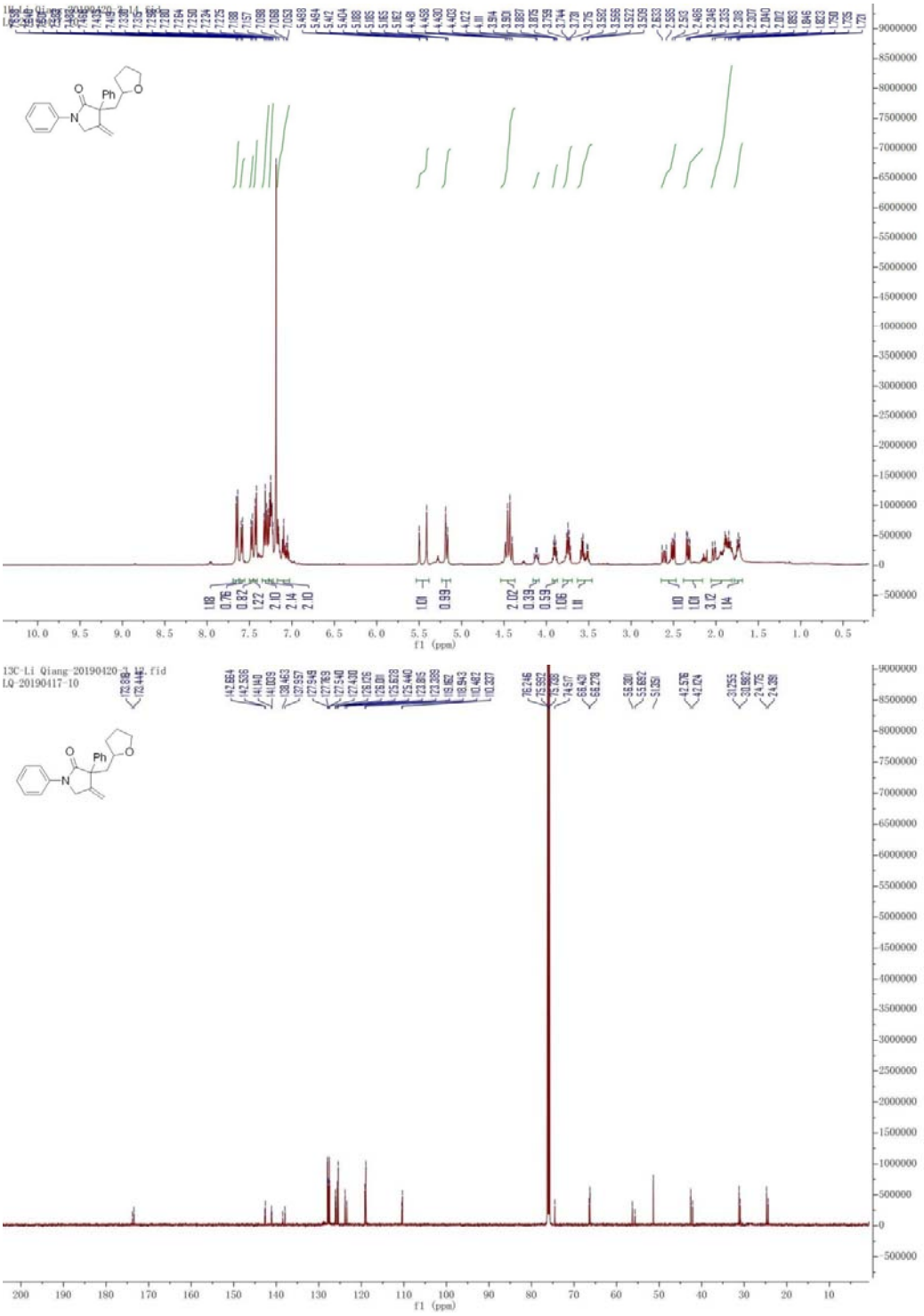
3-Benzyl-4-methylene-1-phenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one

(**3na**)

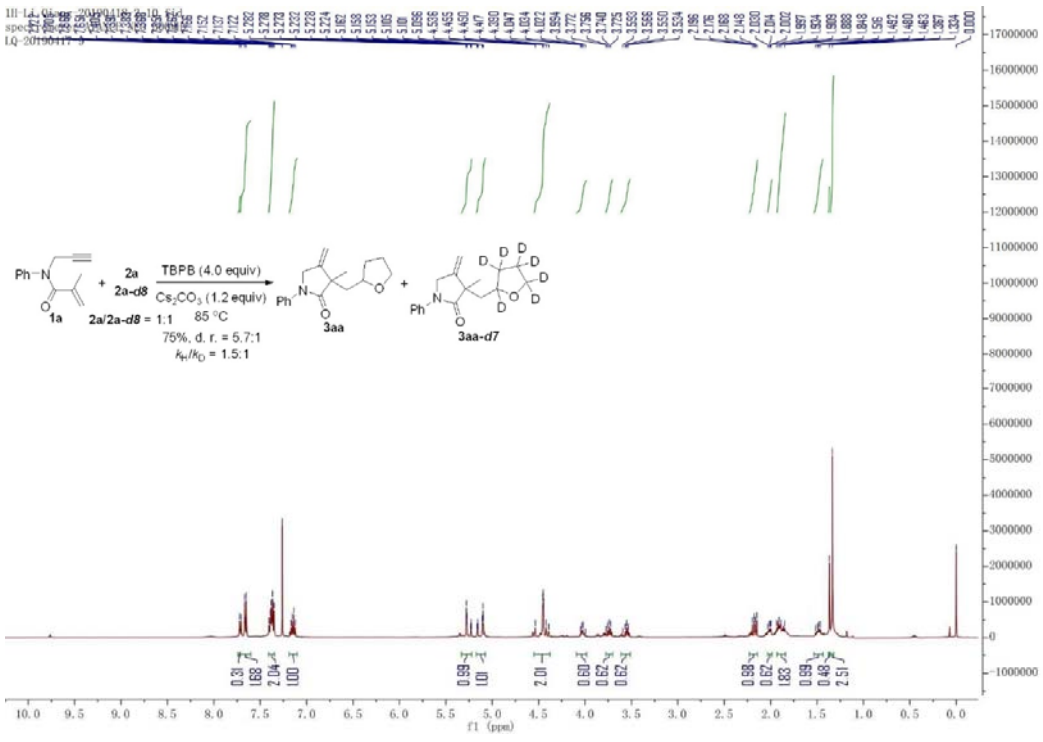




4-Methylene-1,3-diphenyl-3-((tetrahydrofuran-2-yl)methyl)pyrrolidin-2-one (**3oa**)



3aa and **3aa-*d7***



2,2,6,6-Tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine (**4a**)