Visible-Light-Initiated Regioselective Sulfonylation/Cyclization of 1,6-Enynes under Photocatalyst- and Additive-Free Conditions

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Supporting Information

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(A) Typical experimental procedure for the sulfonylation/cyclization

To a Schlenk tube were added 1,6-enynes **1** (0.2 mmol), sulfonyl chlorides **2** (0.3 mmol) and 2-MeTHF (2.0 mL). Then the tube was stirred at R.T. opened in air under 3 W blue LED lamp (460-465 nm) 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) to a□ord the desired products **3**.

(B) Hammett correlation about 1 and 2.

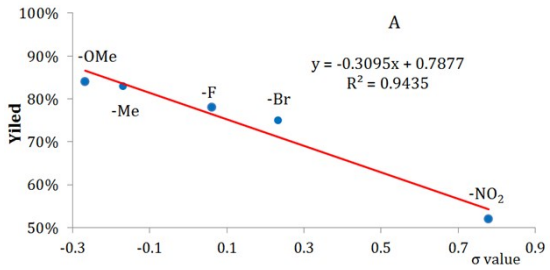


Figure 1. Hammett correlation using Hammett-Brown (σ) parameters about **2**.

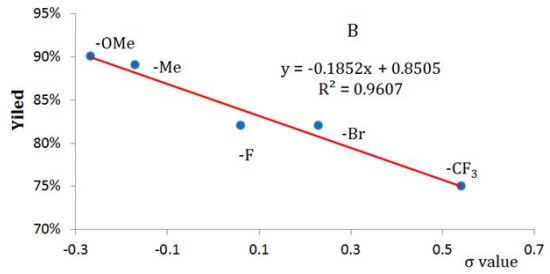
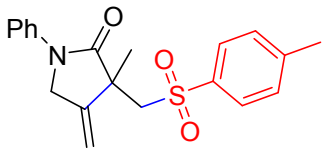


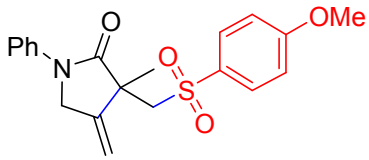
Figure 2. Hammett correlation using Hammett-Brown (σ) parameters about **1**.

(C) Analytical data

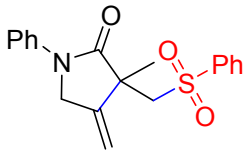


3-Methyl-4-methylene-1-phenyl-3-

(tosylmethyl)pyrrolidin-2-one (3aa), yellow solid (0.0582 g, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.26-7.24 (m, 2H), 7.20-7.17 (m, 1H), 5.43-5.41 (m, 1H), 5.36-5.35 (m, 1H), 4.69-4.66 (m, 1H), 4.51-4.47(m, 1H), 3.87 (d, J = 14.5 Hz, 1H), 3.48 (d, J = 14.5 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 144.6, 142.1, 138.8, 138.0, 129.7, 128.9, 127.7, 125.1, 120.6, 110.6, 63.4, 52.1, 47.8, 27.0, 21.6; HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_3S$ ([M+H]$^+$) 356.1315, found 356.1317.

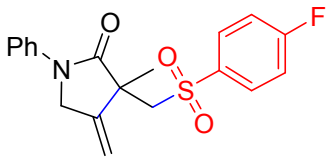


3-(((4-Methoxyphenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3ab), yellow solid (0.0623 g, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 9.0 Hz, 2H), 5.14 (s, 1H), 5.35 (s, 1H), 4.67 (d, J = 13.5 Hz, 1H), 4.47 (d, J = 14.0 Hz, 1H), 3.85 (d, J = 14.0 Hz, 1H), 3.79 (s, 3H), 3.45 (d, J = 14.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 163.6, 142.1, 138.8, 132.5, 129.9, 128.9, 125.0, 120.5, 114.2, 110.5, 63.6, 55.6, 52.1, 47.8, 27.0; HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_4S$ ([M+H]$^+$) 372.1264, found 372.1265.

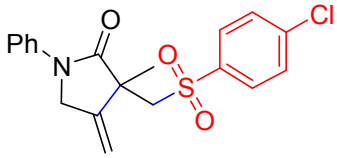


3-Methyl-4-methylene-1-phenyl-3-((phenylsulfonyl)methyl)pyrrolidin-2-one (3ac), yellow solid (0.0546 g, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 5.42 (s, 1H), 5.36 (s, 1H), 4.70 (d, J = 13.5 Hz, 1H), 4.50 (d, J = 14.0 Hz, 1H), 3.87 (d, J = 14.0 Hz, 1H), 3.50 (d, J = 14.0 Hz, 1H), 1.39 (s, 3H);

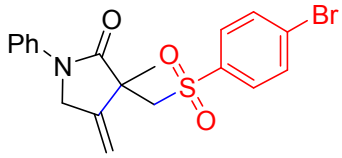
^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 142.2, 141.1, 138.8, 133.6, 129.1, 129.0, 127.7, 125.2, 120.7, 110.6, 63.3, 52.2, 47.8, 27.0; HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_3S$ ($[M+H]^+$) 342.1158, found 342.1159.



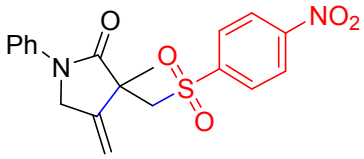
3-(((4-Fluorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3ad), yellow solid (0.0560 g, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88-7.85 (m, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 8.5 Hz, 2H), 5.41 (t, J = 2.5 Hz, 1H), 5.34 (t, J = 2.5 Hz, 1H), 4.69-4.66 (m, 1H), 4.52-4.48 (m, 1H), 3.86 (d, J = 14.0 Hz, 1H), 3.50 (d, J = 14.0 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 165.7 (d, $J_{C\text{-}F}$ = 254.5 Hz), 142.2, 138.8, 137.2, 130.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 129.0, 125.2, 120.5, 116.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 110.6, 63.5, 52.1, 47.9, 27.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -103.6; HRMS *m/z* (ESI) calcd for $C_{19}H_{19}FNO_3S$ ($[M+H]^+$) 360.1064, found 360.1066.



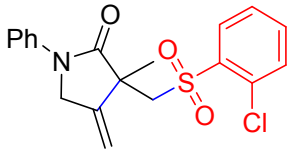
3-(((4-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3ae), yellow solid (0.0570 g, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.42-7.37 (m, 4H), 7.18 (t, J = 7.5 Hz, 1H), 5.40 (m, 1H), 5.33 (m, 1H), 4.67-4.64 (m, 1H), 4.51-4.48 (m, 1H), 3.85 (d, J = 14.5 Hz, 1H), 3.50 (d, J = 14.5 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.7, 141.9, 140.2, 139.3, 138.6, 129.3, 129.1, 128.9, 125.0, 120.3, 110.5, 63.2, 51.9, 47.8, 26.9; HRMS *m/z* (ESI) calcd for $C_{19}H_{19}ClNO_3S$ ($[M+H]^+$) 376.0769, found 376.0770.



3-(((4-Bromophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3af), yellow solid (0.0637 g, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (d, J = 9.0 Hz, 2H), 7.64 (d, J = 13.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 5.43 (s, 1H), 5.36 (s, 1H), 4.70-4.66 (m, 1H), 4.53-4.49 (m, 1H), 3.87 (d, J = 14.0 Hz, 1H), 3.50 (d, J = 14.5 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.8, 142.0, 139.9, 138.7, 132.4, 129.3, 129.0, 129.0, 125.2, 120.5, 110.6, 63.3, 52.1, 47.9, 27.1; HRMS *m/z* (ESI) calcd for $C_{19}H_{19}BrNO_3S$ ($[M+H]^+$) 420.0264, found 420.0267.

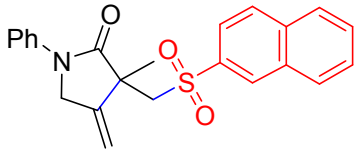


3-Methyl-4-methylene-3-(((4-nitrophenyl)sulfonyl)methyl)-1-phenylpyrrolidin-2-one (3ag), yellow solid (0.0401 g, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 2H), 8.05-8.04 (m, 2H), 7.65-7.63 (m, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.26-7.20 (m, 1H), 5.46 (t, J = 1.5 Hz, 1H), 5.38 (t, J = 1.0 Hz, 1H), 4.72-4.68 (m, 1H), 4.55-4.52 (m, 1H), 3.93 (d, J = 14.5 Hz, 1H), 3.57 (d, J = 14.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.6, 150.6, 146.2, 141.9, 138.5, 129.2, 129.1, 125.4, 124.3, 120.3, 110.7, 63.2, 52.0, 48.0, 27.1; HRMS *m/z* (ESI) calcd for $C_{19}H_{19}N_2O_5S$ ($[M+H]^+$) 387.1009, found 387.1011.

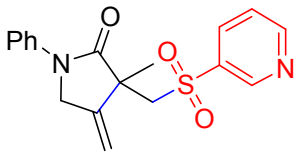


3-(((2-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3ah), yellow solid (0.0563 g, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 9.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.53-7.49 (m, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 7.19 (t,

J = 7.5 Hz, 1H), 5.30 (s, 1H), 5.27 (s, 1H), 4.65-4.62 (m, 1H), 4.48-4.46 (m, 1H), 4.08 (d, *J* = 15.0 Hz, 1H), 3.83 (d, *J* = 15.0 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 173.6, 142.3, 138.7, 138.5, 134.6, 132.5, 131.7, 130.9, 128.9, 127.2, 125.1, 120.4, 110.4, 61.7, 52.1, 47.6, 26.9; HRMS *m/z* (ESI) calcd for $C_{19}H_{19}ClNO_3S$ ($[M+H]^+$) 376.0769, found 376.0770.

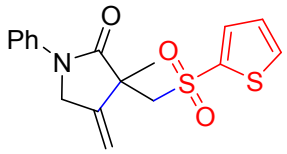


3-Methyl-4-methylene-3-((naphthalen-2-ylsulfonyl)methyl)-1-phenylpyrrolidin-2-one (3ai), white solid (0.0477 g, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.39 (s, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.88-7.84 (m, 3H), 7.64-7.62 (m, 3H), 7.57(t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 5.43 (s, 1H), 5.38 (s, 1H), 4.74-4.71 (m, 1H), 4.52-4.49 (m, 1H), 3.95 (d, *J* = 14.5 Hz, 1H), 3.54 (d, *J* = 14.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 173.9, 142.2, 138.8, 137.7, 135.3, 132.0, 129.6, 129.5, 129.5, 129.2, 129.0, 128.0, 127.5, 125.1, 122.5, 120.5, 110.7, 63.3, 52.2, 47.8, 27.1; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_3S$ ($[M+H]^+$) 392.1315, found 392.1319.

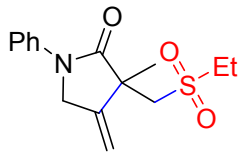


3-Methyl-4-methylene-1-phenyl-3-((pyridin-3-ylsulfonyl)methyl)pyrrolidin-2-one (3aj), yellow solid (0.0513 g, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 9.07 (s, 1H), 8.80 (d, *J* = 4.5 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.42-7.39 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.43 (s, 1H), 5.35 (s, 1H), 4.67 (d, *J* = 14.0 Hz, 1H), 4.53 (d, *J* = 14.0 Hz, 1H), 3.92 (d, *J* = 14.5 Hz, 1H), 3.57 (d, *J* = 14.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 173.8, 154.1, 148.7, 142.0, 138.6, 137.5, 135.6, 129.0, 125.3, 123.7,

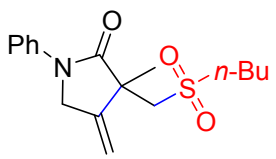
120.6, 110.7, 63.6, 52.1, 48.0, 27.0; HRMS *m/z* (ESI) calcd for $C_{18}H_{19}N_2O_3S$ ($[M+H]^+$) 343.1111, found 343.1112.



3-Methyl-4-methylene-1-phenyl-3-((thiophen-2-ylsulfonyl)methyl)pyrrolidin-2-one (3ak), white solid (0.0451 g, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 4.5 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 4.5 Hz, 1H), 5.41 (t, J = 2.0 Hz, 1H), 5.35 (t, J = 2.0 Hz, 1H), 4.70-4.66 (m, 1H), 4.52-4.48 (m, 1H), 4.00 (d, J = 14.5 Hz, 1H), 3.61 (d, J = 14.5 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.7, 142.3, 142.1, 138.8, 133.9, 133.8, 129.0, 127.8, 125.2, 120.6, 110.7, 64.8, 52.2, 47.9, 26.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{18}NO_3S_2$ ($[M+H]^+$) 348.0723, found 348.0725.

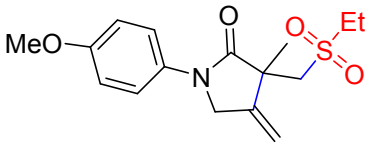


3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one （3al）, yellow solid (0.0510 g, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 5.39 (s, 1H), 5.33 (s, 1H), 4.68-4.65 (m, 1H), 4.50-4.47 (m, 1H), 3.73 (d, J = 14.5 Hz, 1H), 3.31 (d, J = 14.5 Hz, 1H), 3.04-2.99 (m, 2H), 1.43 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3, 143.1, 138.7, 129.0, 125.3, 120.8, 109.8, 59.3, 52.3, 50.4, 47.6, 27.1, 6.5; HRMS *m/z* (ESI) calcd for $C_{15}H_{20}NO_3S$ ($[M+H]^+$) 294.1158, found 294.1159.

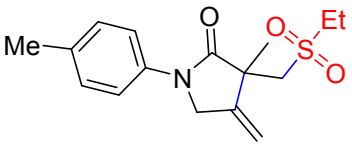


3-((Butylsulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3am), white solid (0.0546 g, 85% yield);^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H),

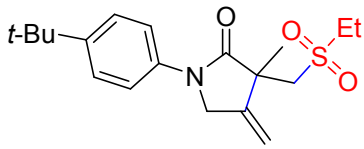
7.18 (t, J = 7.5 Hz, 1H), 5.38 (s, 1H), 5.32 (s, 1H), 4.66-4.63 (m, 1H), 4.49-4.46 (m, 1H), 3.72 (d, J = 14.5 Hz, 1H), 3.32 (d, J = 14.5 Hz, 1H), 3.00-2.95 (m, 2H), 1.78-1.73 (m, 2H), 1.78 (s, 3H), 1.77-1.73 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3, 143.1, 138.7, 129.0, 125.3, 120.8, 109.8, 60.3, 55.8, 52.3, 47.6, 27.1, 23.8, 21.6, 13.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO_3S$ ($[M+H]^+$) 322.1471, found 322.1473.



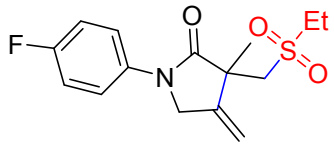
3-((Ethylsulfonyl)methyl)-1-(4-methoxyphenyl)-3-methyl-4-methylenepyrrolidin-2-one (3bl), yellow oil (0.0581 g, 90% yield);^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-7.51 (m, 2H), 6.93-6.91 (m, 2H), 5.37 (t, J = 1.5 Hz, 1H), 5.32 (t, J = 2.5 Hz, 1H), 4.62-4.60 (m, 1H), 4.45-4.42 (m, 1H), 3.81 (s, 3H), 3.73 (d, J = 14.5 Hz, 1H), 3.29 (d, J = 14.5 Hz, 1H), 3.04-2.99 (m, 2H), 1.42 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 157.3, 143.5, 131.8, 122.9, 114.3, 109.7, 59.4, 55.5, 52.9, 50.3, 47.3, 27.1, 6.5; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_4S$ ($[M+H]^+$) 324.1264, found 324.1268.



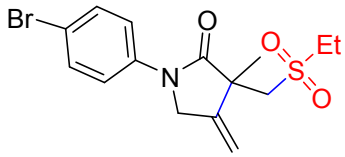
3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-(p-tolyl)pyrrolidin-2-one (3cl), white solid (0.0546 g, 89% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 5.37 (s, 1H), 5.32 (s, 1H), 4.64-4.61 (m, 1H), 4.67-4.43 (m, 1H), 3.71 (d, J = 14.5 Hz, 1H), 3.30 (d, J = 14.5 Hz, 1H), 3.03-2.96 (m, 2H), 2.33 (s, 3H), 1.42 (s, 3H), 1.34 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.1, 143.4, 136.2, 135.1, 129.6, 120.9, 109.7, 59.4, 52.5, 50.3, 47.5, 27.1, 20.9, 6.5; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_3S$ ($[M+H]^+$) 308.1315, found 308.1317.



1-(4-(*tert*-Butyl)phenyl)-3-((ethylsulfonyl)methyl)-3-methyl-4-methylenepyrrolidin-2-one (3dl), white solid (0.0614 g, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58-7.56 (m, 2H), 7.42-7.40 (m, 2H), 5.38 (s, 2H), 4.66-4.63 (m, 1H), 4.47-4.44 (m, 1H), 3.72 (d, J = 14.5 Hz, 1H), 3.30 (d, J = 14.5 Hz, 1H), 3.03-2.98 (m, 2H), 1.42 (s, 3H), 1.33 (t, J = 7.5 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.1, 148.3, 143.3, 136.1, 125.9, 120.5, 109.7, 59.4, 52.3, 50.3, 47.5, 34.4, 31.3, 27.2, 6.5; HRMS *m/z* (ESI) calcd for $C_{19}H_{28}NO_3S$ ([M+H]$^+$) 350.1784, found 350.1785.

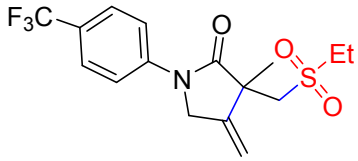


3-((Ethylsulfonyl)methyl)-1-(4-fluorophenyl)-3-methyl-4-methylenepyrrolidin-2-one (3el), white solid (0.0504 g, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62-7.59 (m, 2H), 7.10-7.06 (m, 2H), 5.39 (t, J = 1.5 Hz, 1H), 5.34 (t, J = 2.5 Hz, 1H), 4.63-4.60 (m, 1H), 4.48-4.44 (m, 1H), 3.72 (d, J = 14.5 Hz, 1H), 3.31 (d, J = 14.5 Hz, 1H), 3.02-2.97 (m, 2H), 1.42 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3, 160.0 (d, $J_{C\text{-}F}$ = 242.5 Hz), 143.0, 134.8, 122.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.3 Hz), 110.0, 59.4, 52.6, 50.4, 47.3, 27.1, 6.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -116.5; HRMS *m/z* (ESI) calcd for $C_{15}H_{19}FNO_3S$ ([M+H]$^+$) 312.1064, found 312.1066.

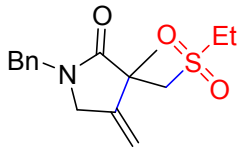


1-(4-Bromophenyl)-3-((ethylsulfonyl)methyl)-3-methyl-4-methylenepyrrolidin-2-one (3fl), white solid (0.0608 g, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58-7.56 (m, 2H), 7.50-7.48 (m, 2H), 5.40 (t, J = 2.0 Hz, 1H), 5.33 (t, J = 2.5 Hz, 1H), 4.62-4.59 (m, 1H), 4.47-4.43 (m, 1H), 3.72 (d, J = 14.5 Hz, 1H), 3.31 (d, J = 14.5 Hz, 1H), 3.00-2.96 (m, 2H), 1.41

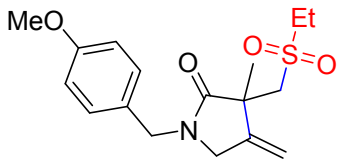
(s, 3H), 1.35 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.5, 142.6, 137.8, 132.0, 122.1, 118.1, 110.1, 59.3, 52.1, 50.4, 47.5, 27.1, 6.5; HRMS *m/z* (ESI) calcd for $C_{15}H_{19}BrNO_3S$ ([M+H]$^+$) 372.0264, found 372.0265.



3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (3gl), white solid (0.0534 g, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 9.0 Hz, 2H), 5.43 (t, J = 2.5 Hz, 1H), 5.36 (t, J = 3.0 Hz, 1H), 4.69-4.66 (m, 1H), 4.53-4.50 (m, 1H), 3.74 (d, J = 14.5 Hz, 1H), 3.34 (d, J = 14.5 Hz, 1H), 3.01-2.95 (m, 2H), 1.44 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.0, 142,3, 141.7, 126.9 (q, $J_{C\text{-}F}$ = 21.8 Hz), 126.1 (q, $J_{C\text{-}F}$ = 2.8 Hz), 123.0, 120.0, 110.3, 59.3, 51.9, 50.5, 47.6, 27.2, 6.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.2; HRMS *m/z* (ESI) calcd for $C_{16}H_{19}F_3NO_3S$ ([M+H]$^+$) 362.1032, found 362.1034.

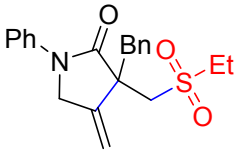


1-Benzyl-3-((ethylsulfonyl)methyl)-3-methyl-4-methylenepyrrolidin-2-one (3hl), white solid (0.0436 g, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 3H), 5.22 (t, J = 7.5 Hz, 2H), 4.70 (d, J = 14.5 Hz, 1H), 4.38 (d, J = 14.5 Hz, 1H), 4.06-4.02 (m, 1H), 3.89-3.86 (m, 1H), 3.68 (d, J = 14.5 Hz, 1H), 3.25 (d, J = 14.5 Hz, 1H), 3.03-2.99 (m, 2H), 1.37-1.34 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.9, 144.0, 135.7, 128.8, 128.2, 127.7, 109.5, 59.0, 50.4, 50.3, 46.8, 46.5, 27.2, 6.5; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_3S$ ([M+H]$^+$) 308.1315, found 308.1317.

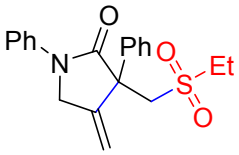


3-((Ethylsulfonyl)methyl)-1-(4-methoxybenzyl)-3-

methyl-4-methylenepyrrolidin-2-one (3il), white solid (0.0519 g, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 5.13 (d, J = 8.0 Hz, 2H), 4.52 (d, J = 14.5 Hz, 1H), 4.28 (d, J = 15.0 Hz, 1H), 3.93 (d, J = 15.0 Hz, 1H), 3.77 (d, J = 14.0 Hz, 1H), 3.71 (s, 3H), 3.60 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.5 Hz, 1H), 2.97-2.91 (m, 2H), 1.29 (t, J = 8.0 Hz, 3H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.6, 159.2, 144.1, 129.6, 127.7, 114.1, 109.4, 58.9, 55.3, 50.2 (2), 46.5, 46.1, 27.1, 6.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO_4S$ ($[M+H]^+$) 338.1421, found 338.1423.

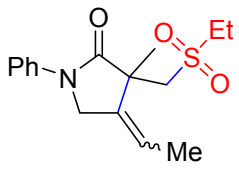


3-Benzyl-3-((ethylsulfonyl)methyl)-4-methylene-1-phenylpyrrolidin-2-one (3kl), white solid (0.0590 g, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.30 (m, 4H), 7.21-7.20 (m, 3H), 7.17-7.15 (m, 3H), 5.47 (s, 1H), 5.37 (s, 1H), 4.27 (d, J = 13.5 Hz, 1H), 3.91 (d, J = 14.5 Hz, 1H), 3.53-3.44 (m, 2H), 3.17 (d, J = 12.5 Hz, 1H), 3.10-3.04 (m, 2H), 2.75 (d, J = 12.5 Hz, 1H), 1.37 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.8, 141.1, 138.3, 134.1, 130.5, 128.9, 128.1, 127.4, 125.6, 121.5, 110.8, 58.7, 53.4, 52.9, 50.9, 46.1, 6.5; HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_3S$ ($[M+H]^+$) 370.1471, found 370.1473.

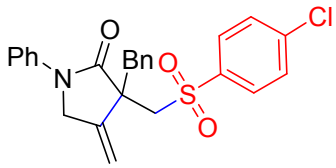


3-((Ethylsulfonyl)methyl)-4-methylene-1,3-diphenylpyrrolidin-2-one (3ll), white solid (0.0554 g, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.0 Hz, 2H), 5.57 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 8.0 Hz, 4H), 7.30 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 5.67 (s, 1H), 5.57 (s, 1H), 4.60-4.56 (m, 1H), 4.48-4.45 (m, 1H), 4.13 (d, J = 15.0 Hz, 1H), 3.69 (d, J = 15.0 Hz, 1H), 3.14-3.08 (m, 2H), 1.38 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ: 172.1, 140.9, 138.7, 138.0, 129.1, 129.0, 128.2, 126.4, 125.3, 120.7, 112.8, 59.0, 55.9, 52.4, 51.0, 6.6; HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_3S$ ($[M+H]^+$) 356.1315, found 356.1317.

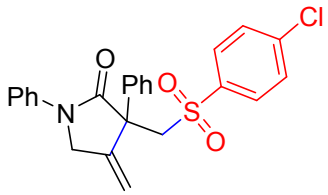


3-((Ethylsulfonyl)methyl)-4-methylene-1,3-diphenylpyrrolidin-2-one (3ml), white solid (0.0344 g, 56% yield, *E*:*Z* = 1.5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.68-7.64 (m, 2H), 7.41-7.36 (m, 2H), 7.21-7.16 (m, 1H), 5.73-5.68 (m, 1H), 4.59-4.56 (m, 1H), 4.46-4.37 (m, 1H), 3.79 (d, *J* = 14.5 Hz, 0.4H), 3.71 (d, *J* = 14.5 Hz, 0.6H), 3.55 (d, *J* = 14.5 Hz, 0.4H), 3.26 (d, *J* = 14.5 Hz, 0.6H), 2.99-2.94 (m, 2H), 1.88 (d, *J* = 7.5 Hz, 1.2H), 1.74 (d, *J* = 7.0 Hz, 1.8H), 1.51 (s, 1.2H), 1.39 (s, 1.8H), 1.35 (t, *J* = 5.0 Hz, 1.2H), 1.33 (t, *J* = 5.0 Hz, 1.8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.2, 174.9, 138.9, 138.8, 134.1, 132.0, 129.0, 129.0, 125.3, 125.2, 121.8, 121.0, 120.9, 120.0, 59.7, 57.7, 52.7, 50.6, 50.3, 50.0, 47.2, 46.5, 27.5, 24.8, 14.1, 13.7, 6.5 (2); HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_3S$ ($[M+H]^+$) 308.1315, found 308.1319.



3-Benzyl-3-(((4-chlorophenyl)sulfonyl)methyl)-4-methylene-1-phenylpyrrolidin-2-one (3ke), yellow solid (0.0613 g, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.36-7.33 (m, 3H), 7.32-7.26 (m, 2H), 7.22-7.18 (m, 4H), 7.14-7.11 (m, 2H), 5.51 (s, 1H), 5.40 (s, 1H), 4.28 (d, *J* = 17.5 Hz, 1H), 4.07 (d, *J* = 14.5 Hz, 1H), 3.65 (t, *J* = 13.0 Hz, 2H), 3.09 (d, *J* = 12.5 Hz, 1H), 2.71 (d, *J* = 12.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.7, 140.4, 140.0, 134.0, 130.4, 129.5, 129.3, 129.0 (2), 128.9, 128.5, 128.1, 125.6, 121.4, 111.7, 62.7, 53.8,

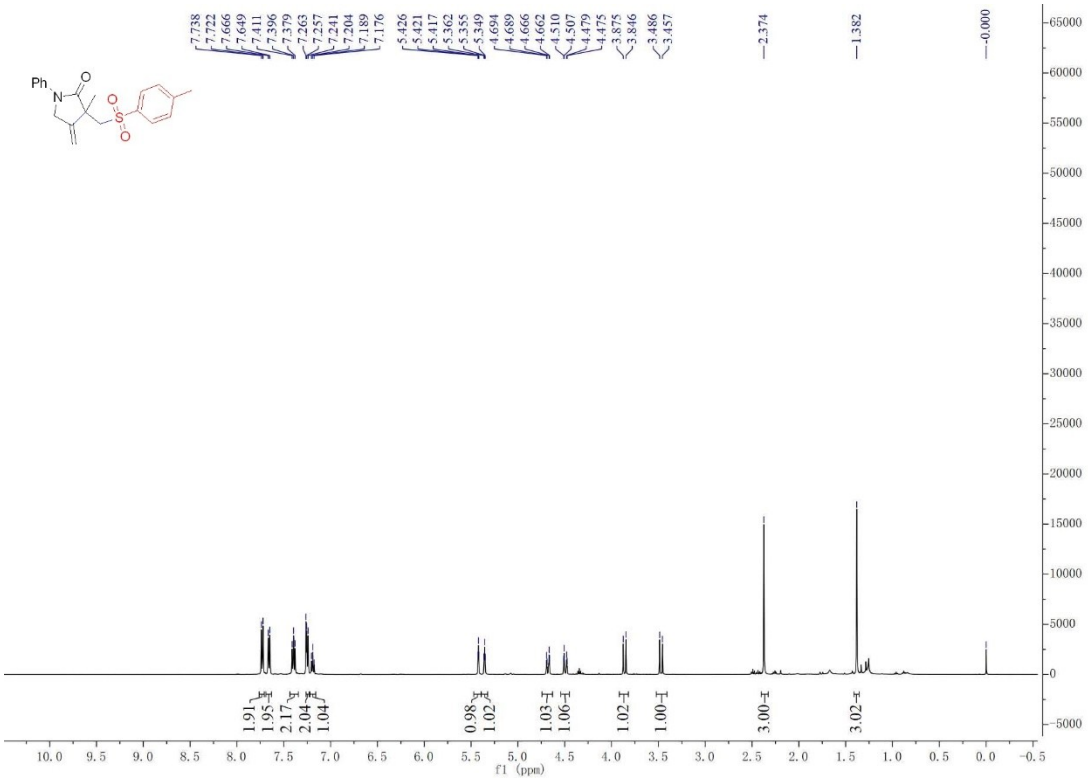
52.8, 46.1; HRMS *m/z* (ESI) calcd for $C_{25}H_{23}ClNO_3S$ ($[M+H]^+$) 452.1082, found 452.1084.

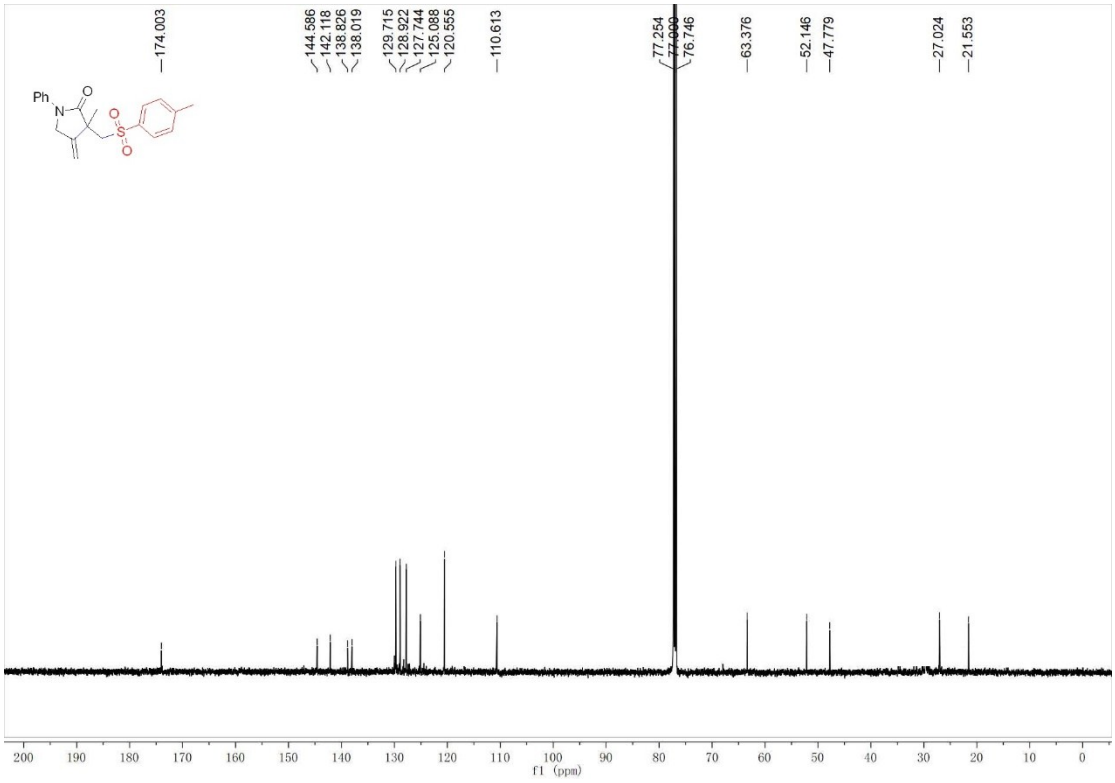


3-(((4-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3le), yellow solid (0.0586 g, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.52-7.48 (m, 4H), 7.38 (t, J = 8.0 Hz, 2H), 7.32-7.28 (m, 3H), 7.19 (t, J = 7.5 Hz, 1H), 5.76 (s, 1H), 5.68 (s, 1H), 4.62-4.59 (m, 1H), 4.52-4.48 (m, 1H), 4.29 (d, J = 14.5 Hz, 1H), 3.91 (d, J = 14.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9, 140.3, 140.0, 138.8, 137.4, 129.5, 129.3, 129.0 (2), 128.2, 126.4, 125.3, 120.6, 113.8, 63.3, 56.4, 52.3; HRMS *m/z* (ESI) calcd for $C_{24}H_{21}ClNO_3S$ ($[M+H]^+$) 438.0925, found 438.0927.

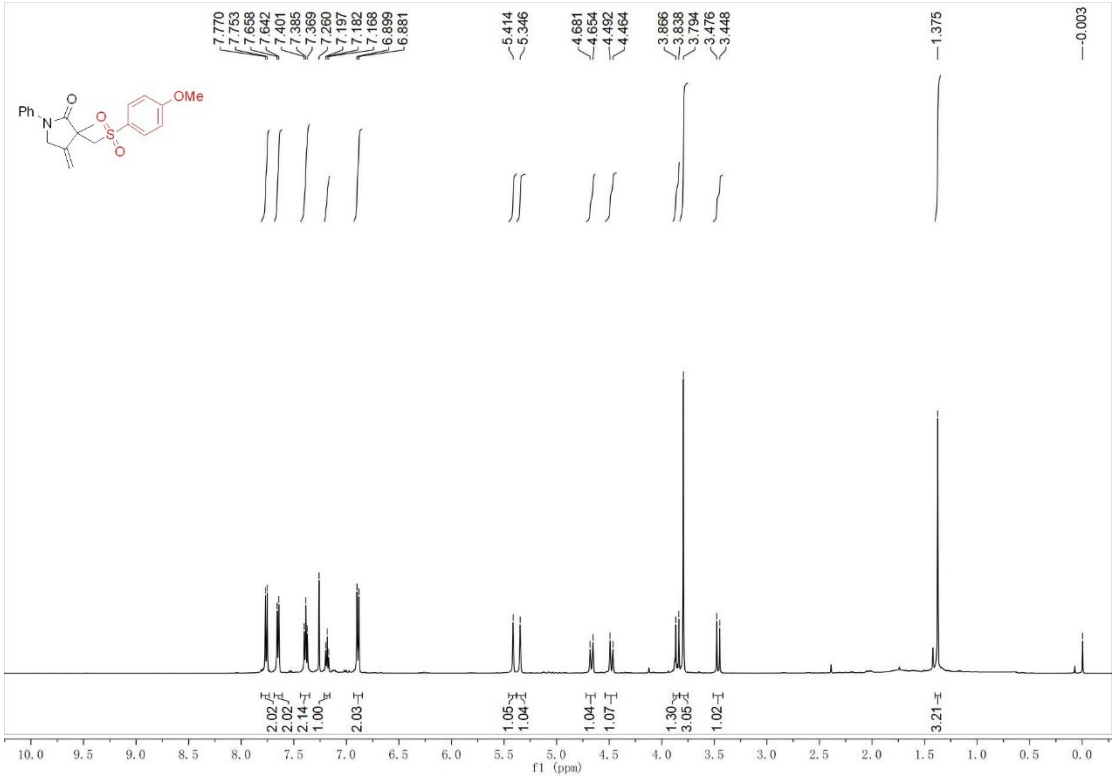
(D) Spectra

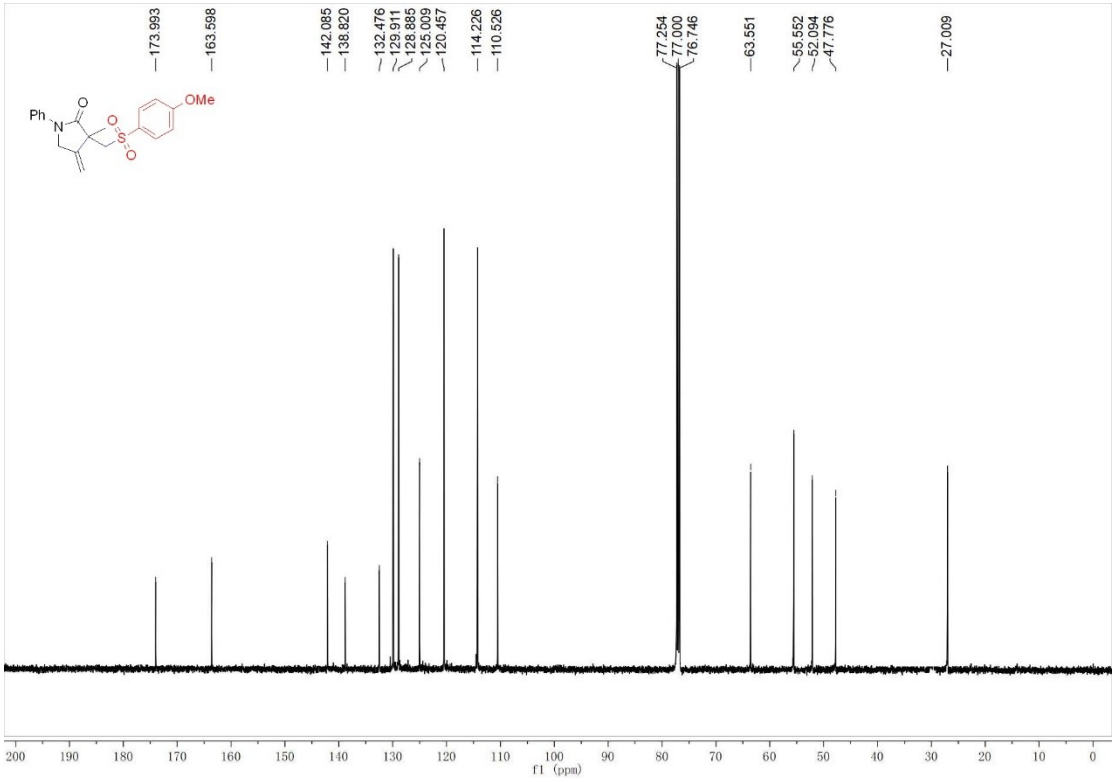
3-Methyl-4-methylene-1-phenyl-3-(tosylmethyl)pyrrolidin-2-one (3aa)



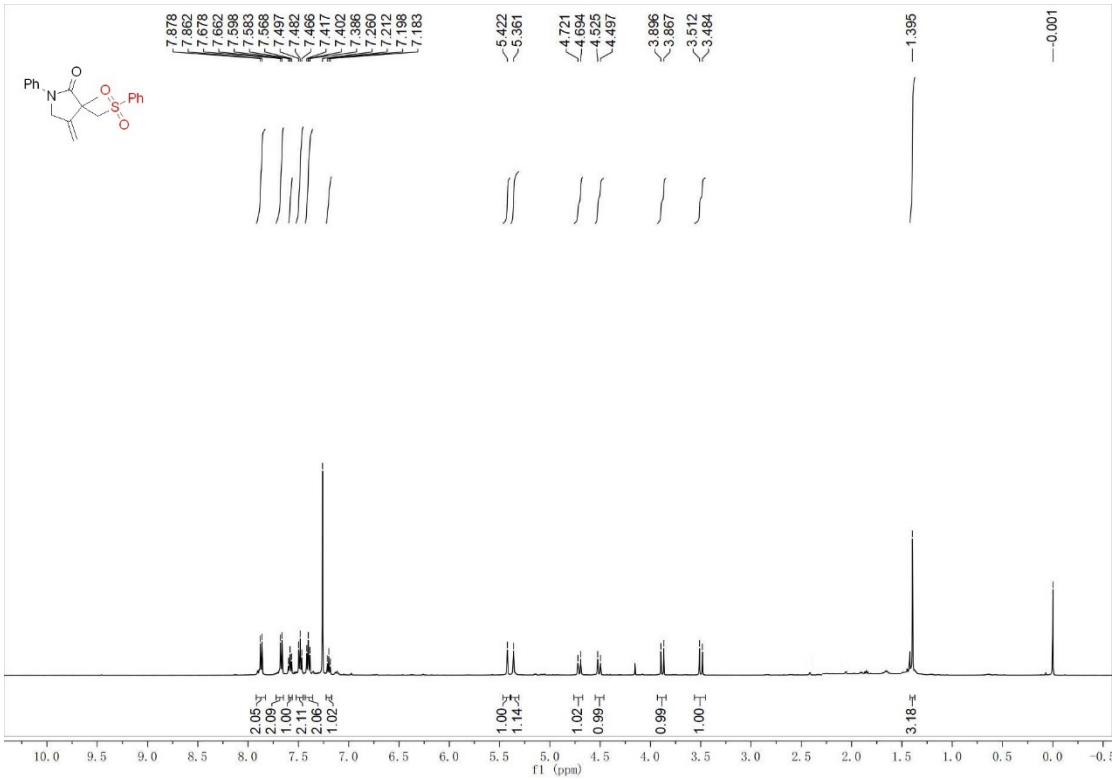


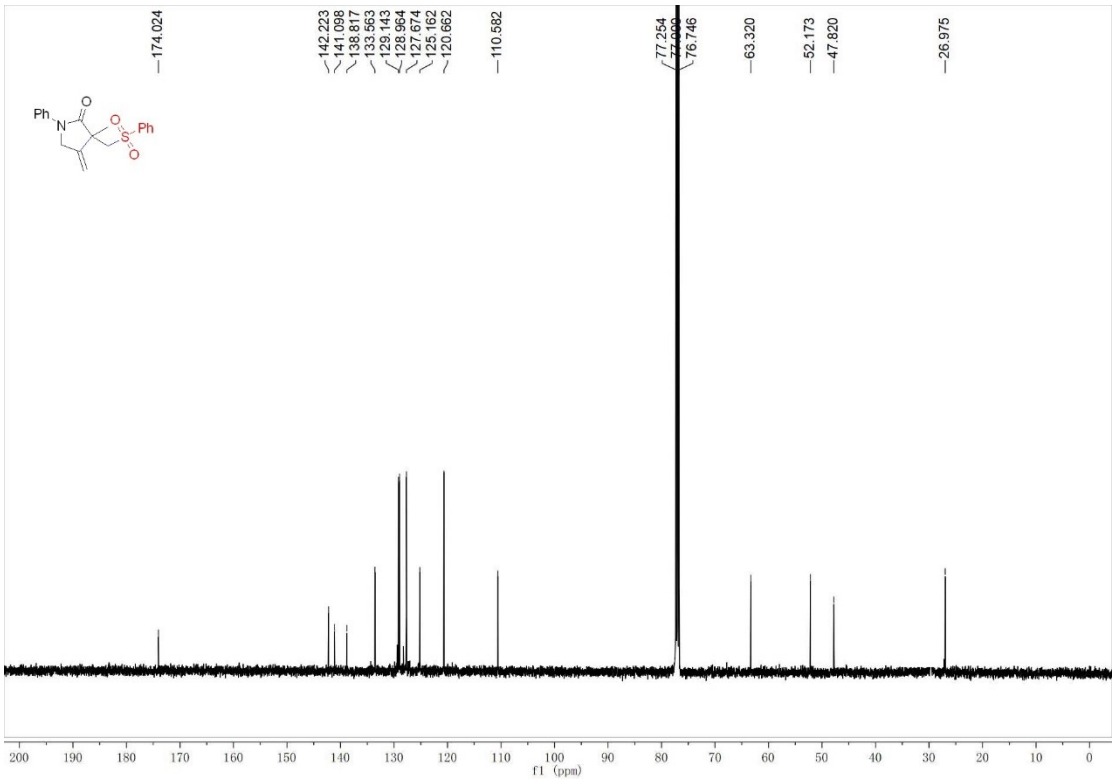
3-(((4-Methoxyphenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3ab)





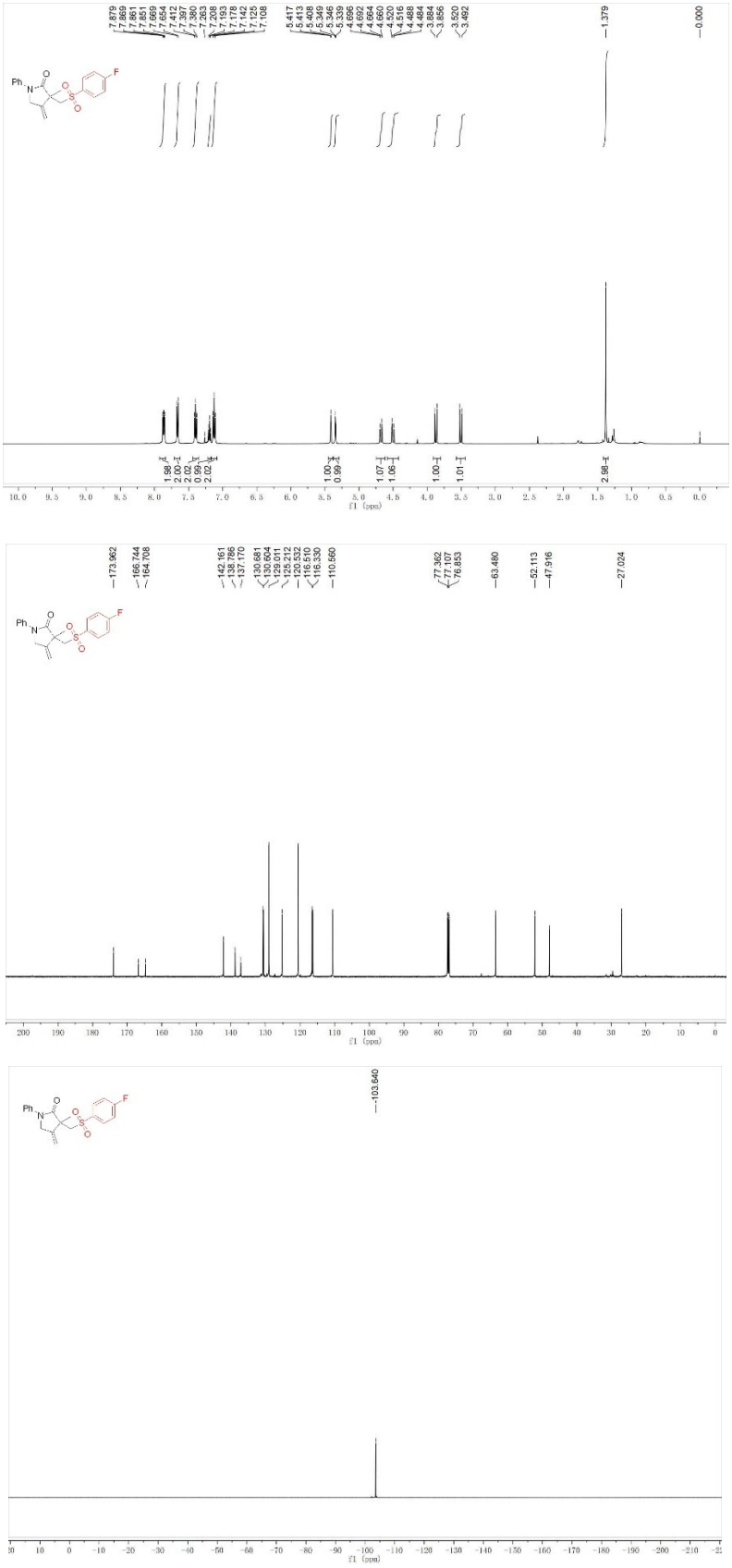
3-Methyl-4-methylene-1-phenyl-3-((phenylsulfonyl)methyl)pyrrolidin-2-one (3ac)





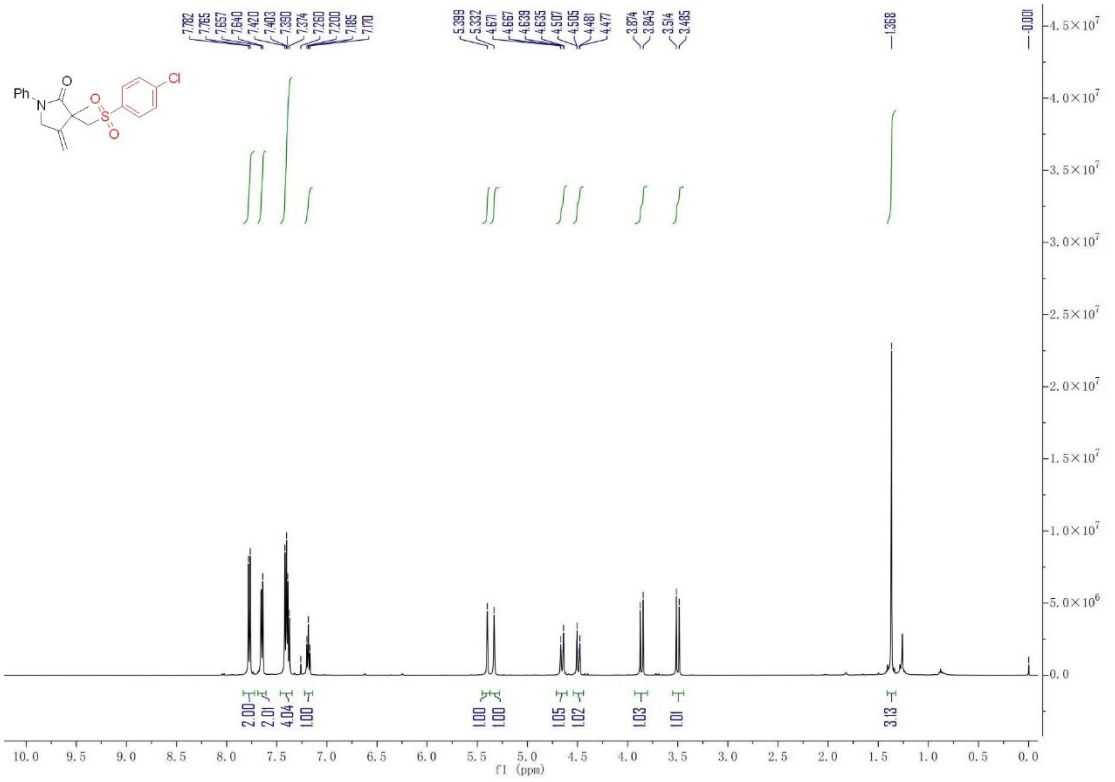
3-(((4-Fluorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-

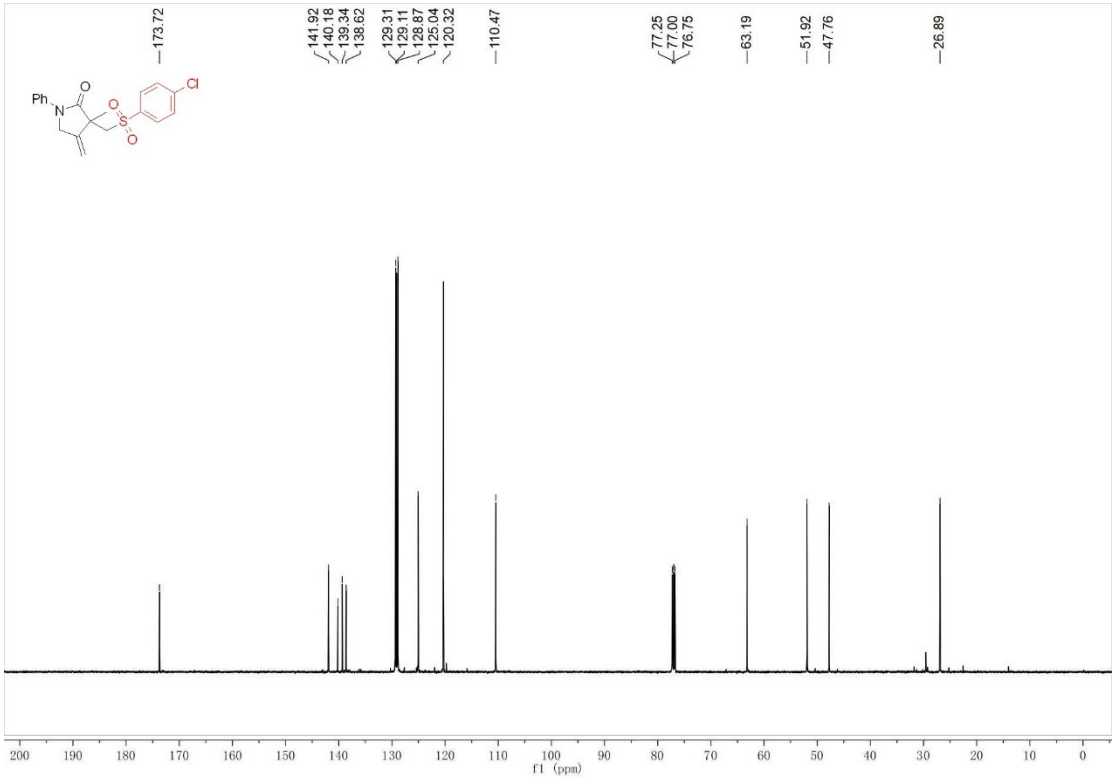
2-one (3ad)



3-(((4-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-

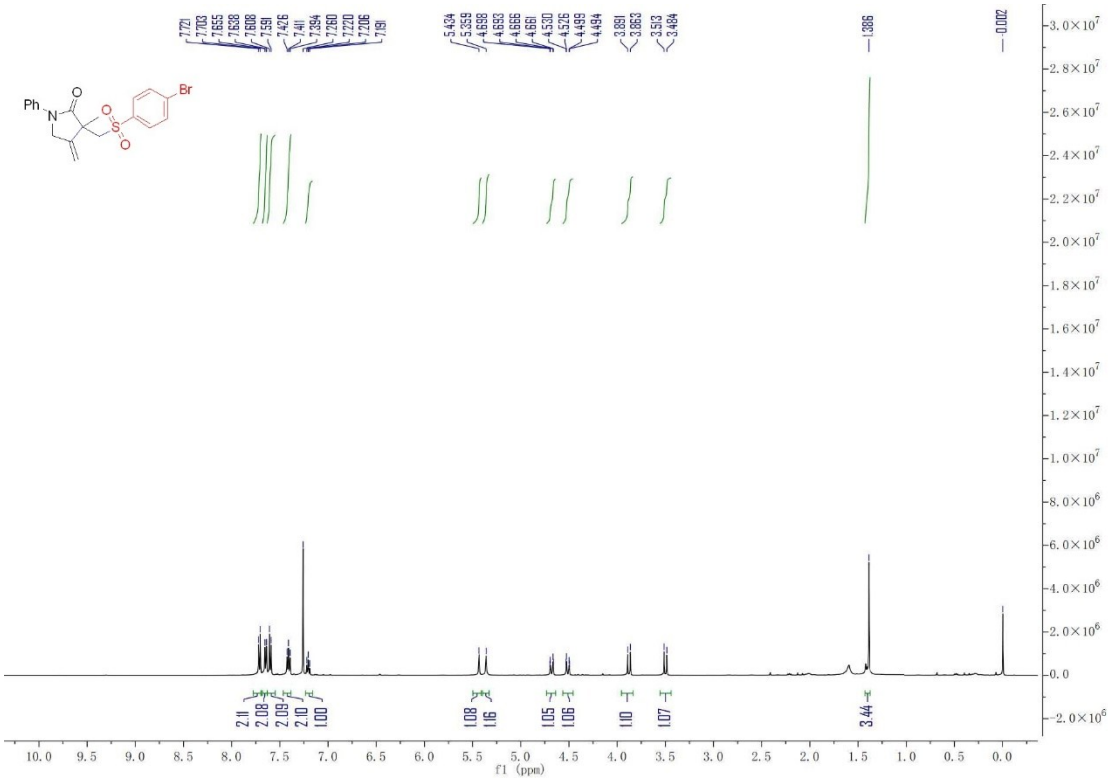
2-one (3ae)

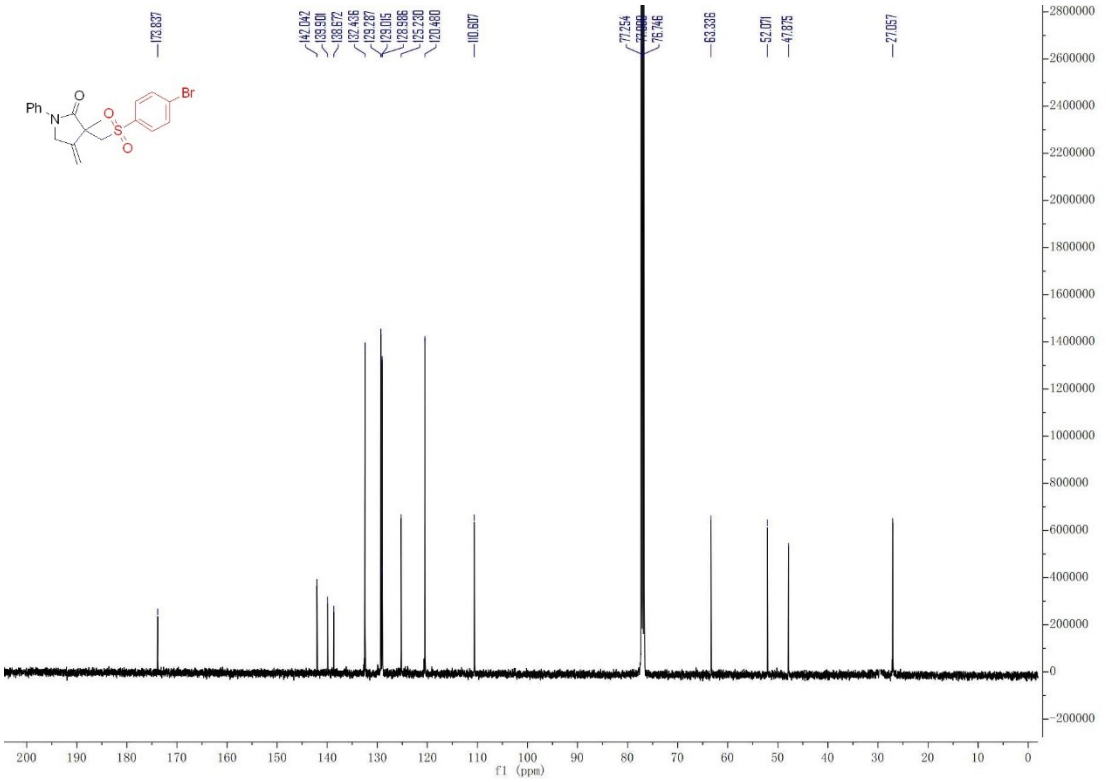




3-(((4-Bromophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-

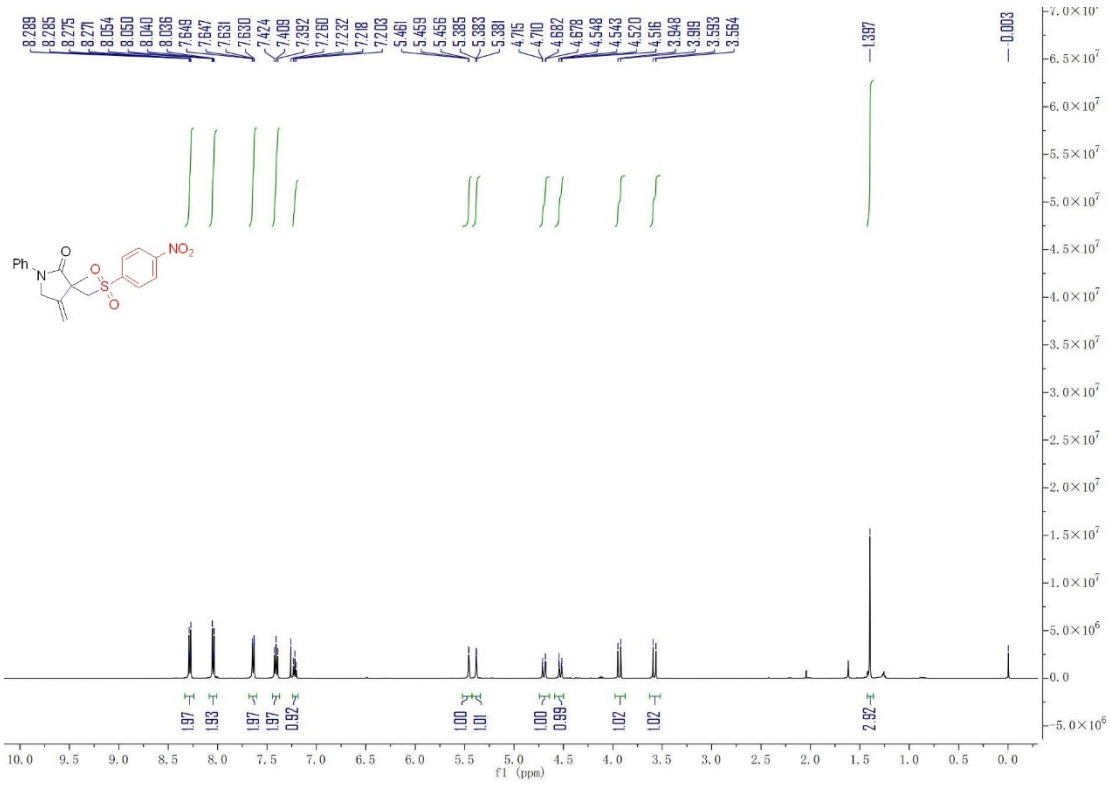
2-one (3af)

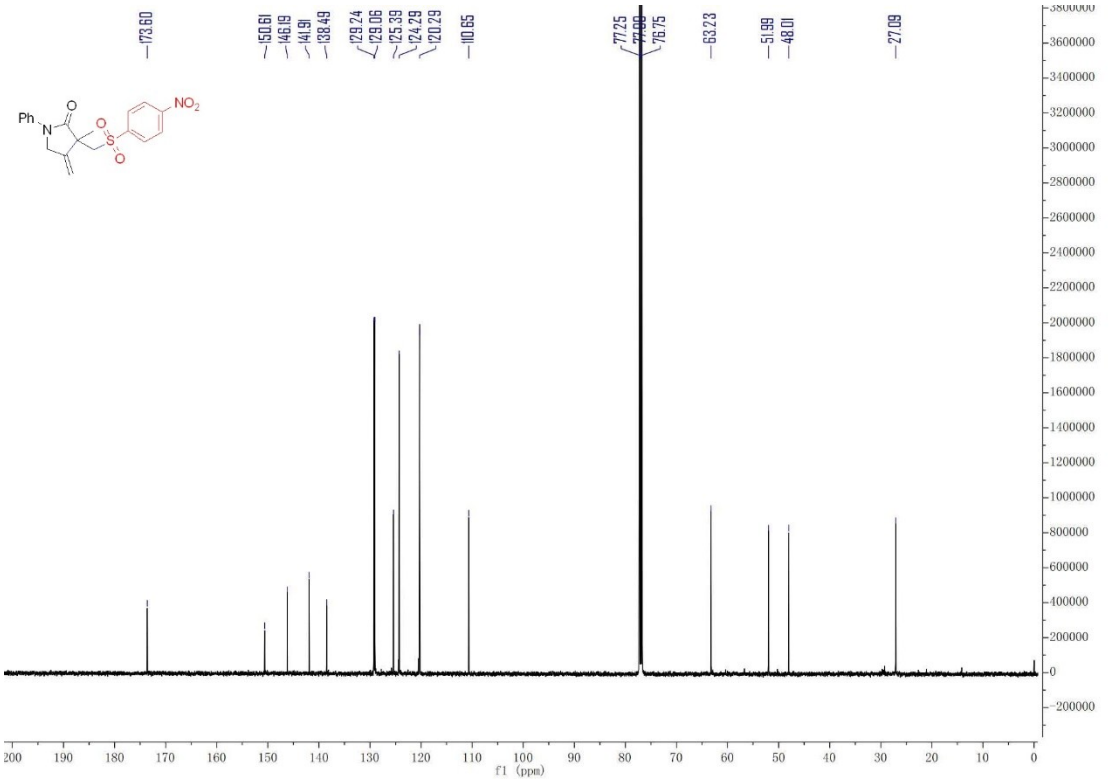




3-Methyl-4-methylene-3-(((4-nitrophenyl)sulfonyl)methyl)-1-phenylpyrrolidin-2-

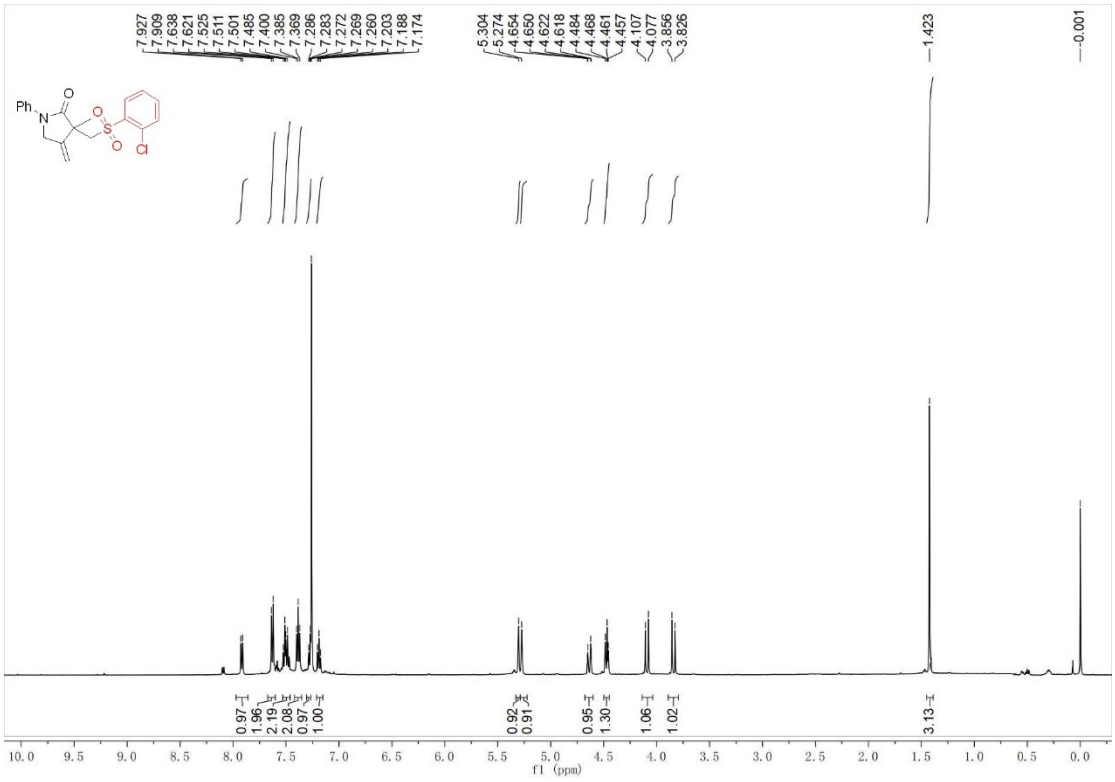
one (3ag)

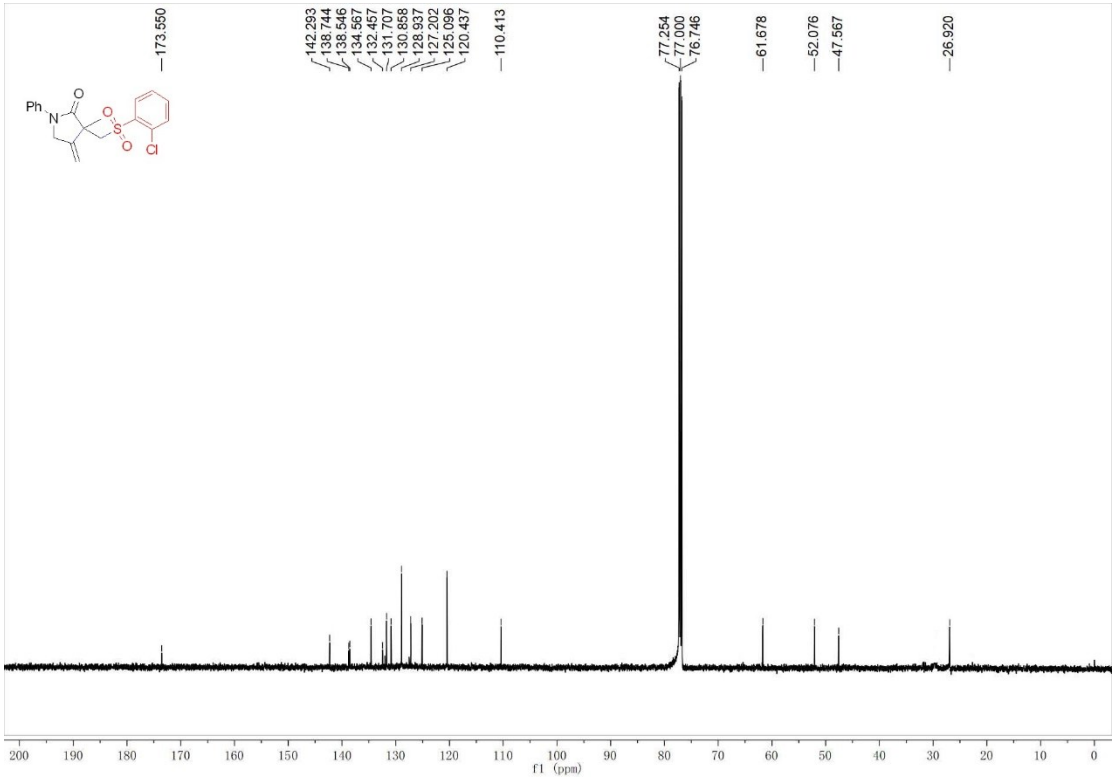




3-(((2-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-

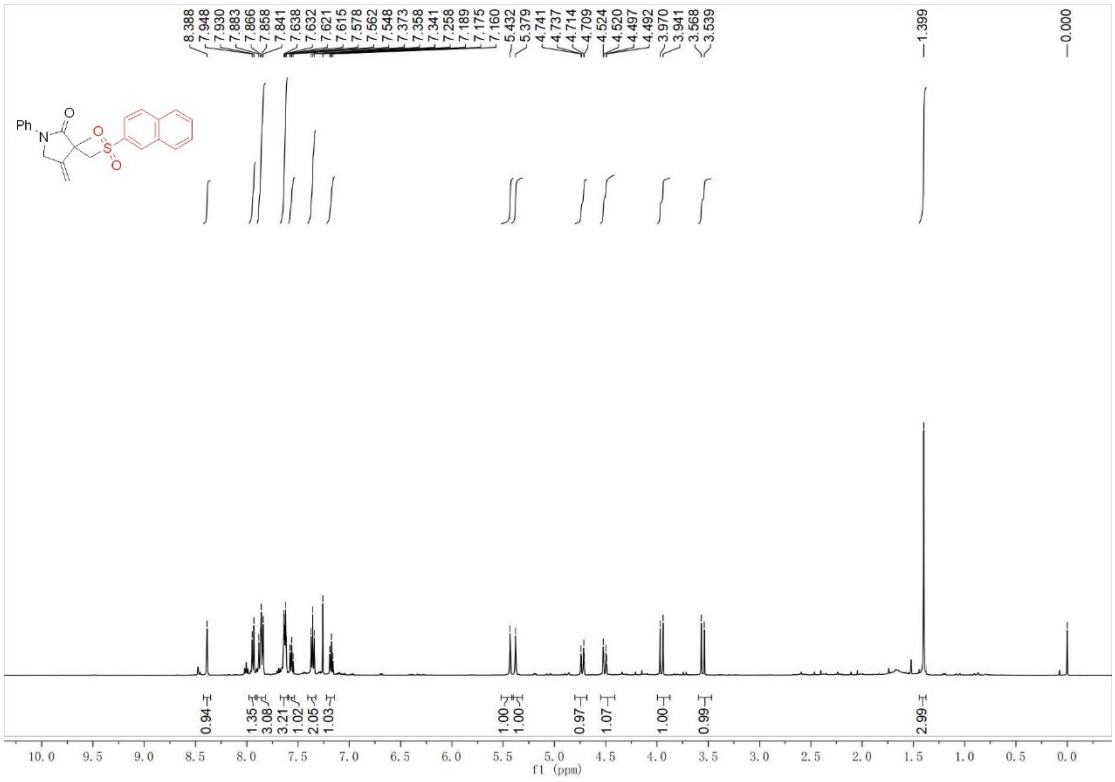
phenylpyrrolidin-2-one (3ah)

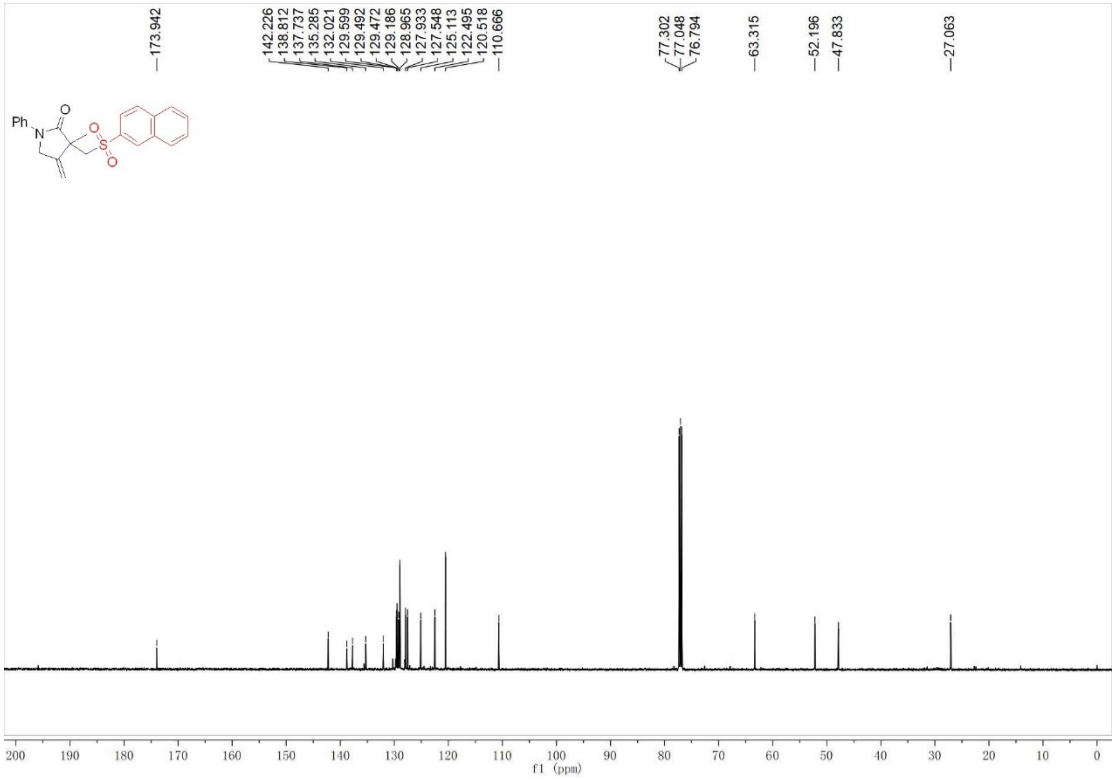




3-Methyl-4-methylene-3-((naphthalen-2-ylsulfonyl)methyl)-1-phenylpyrrolidin-

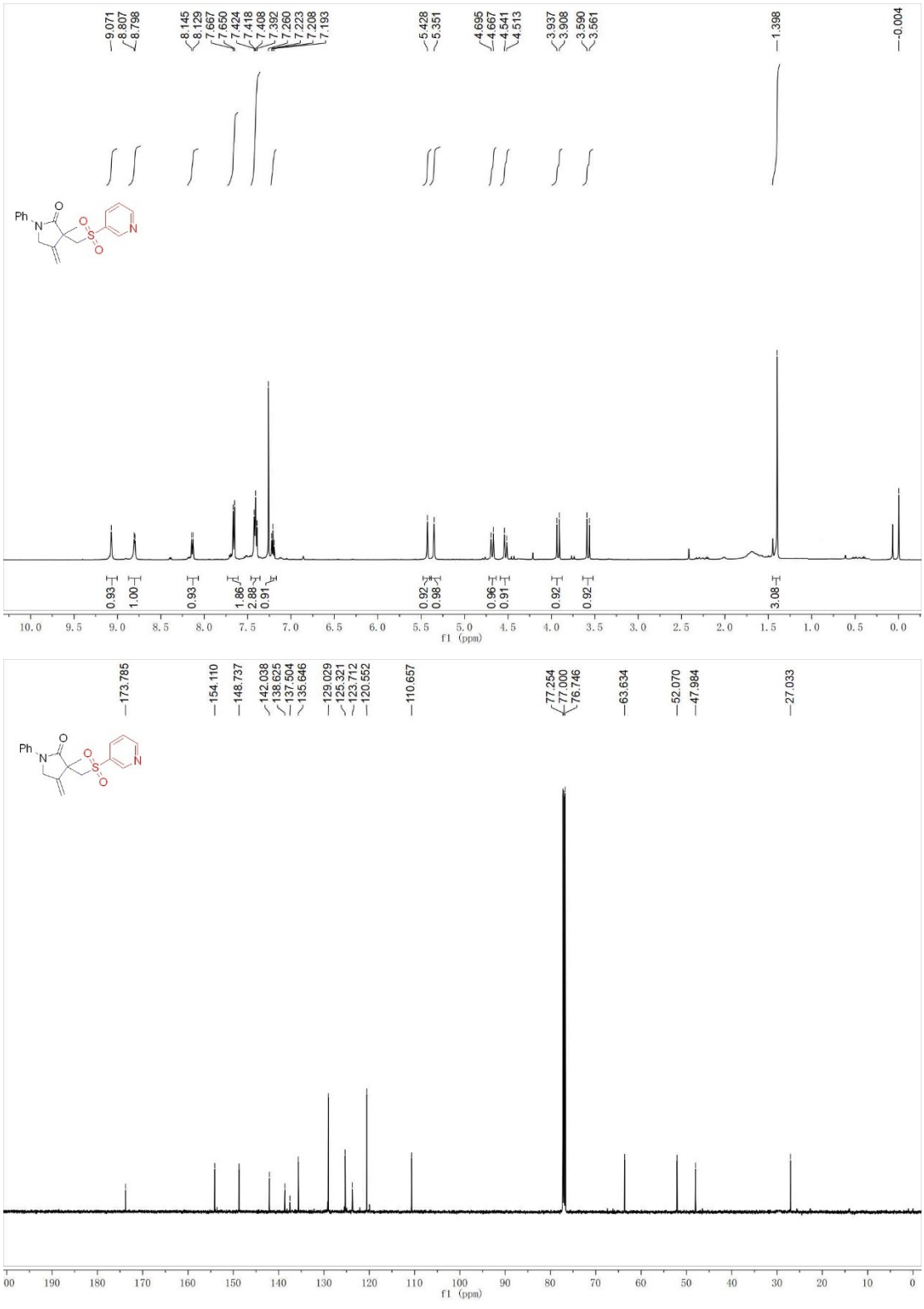
2-one (3ai)





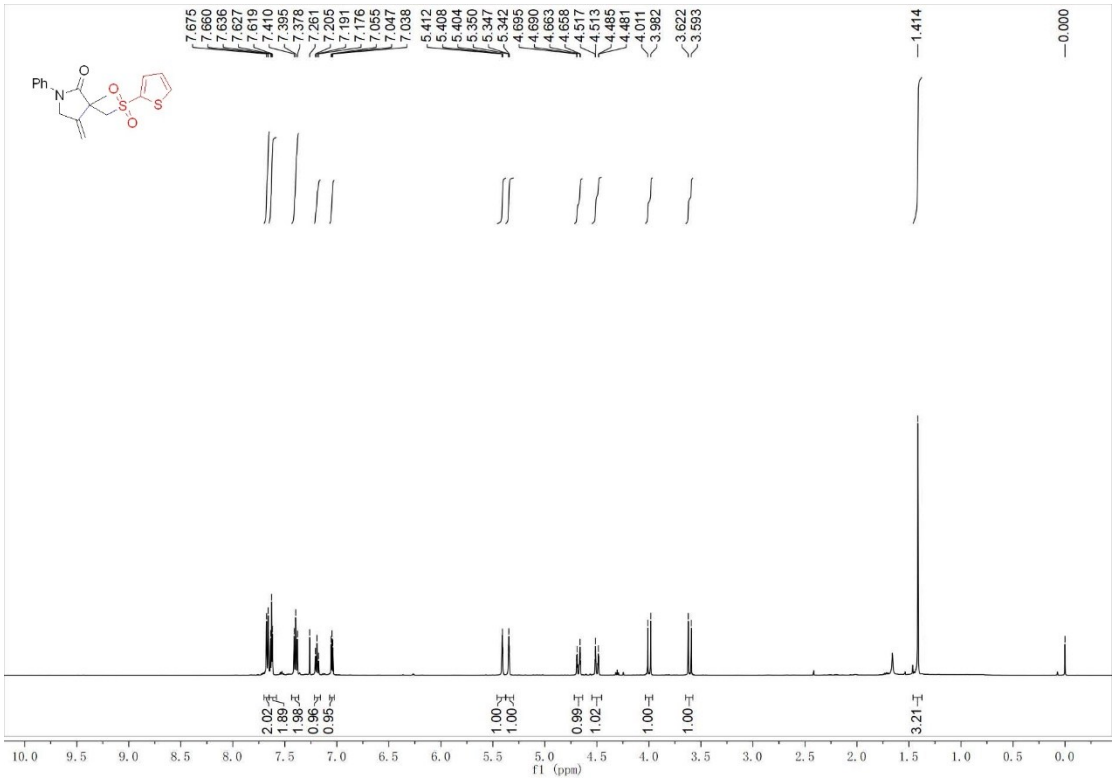
3-Methyl-4-methylene-1-phenyl-3-((pyridin-3-ylsulfonyl)methyl)pyrrolidin-2-one

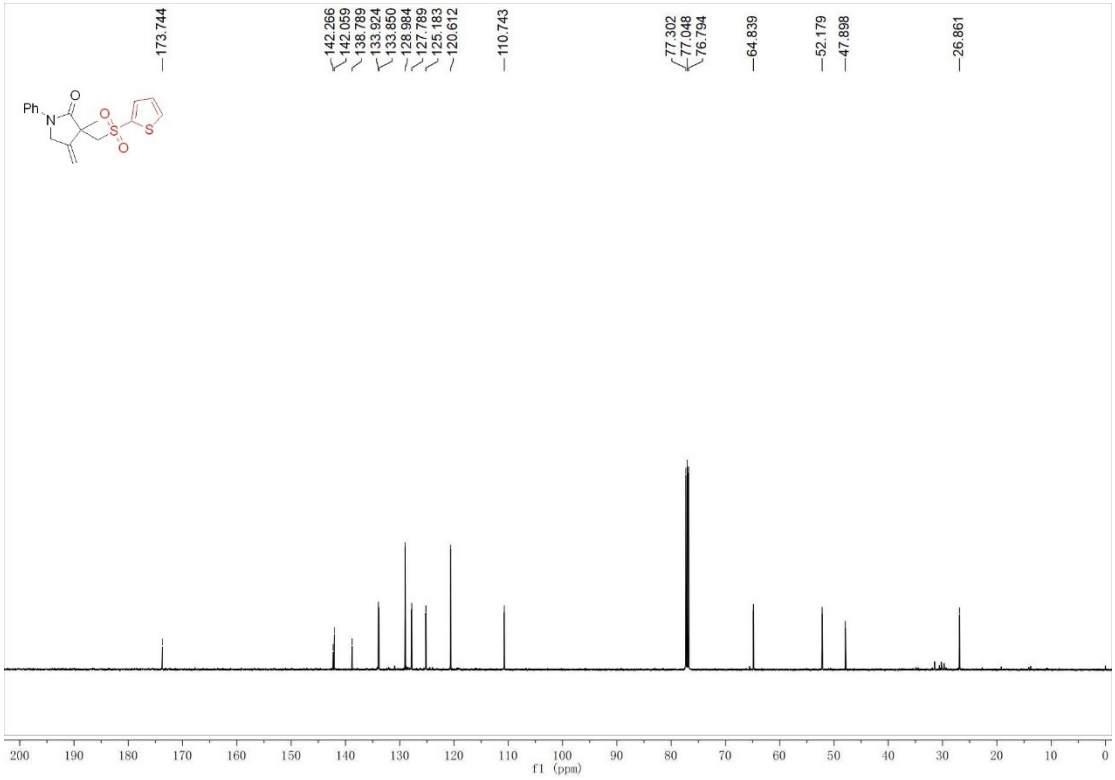
(3aj)



3-Methyl-4-methylene-1-phenyl-3-((thiophen-2-ylsulfonyl)methyl)pyrrolidin-2-

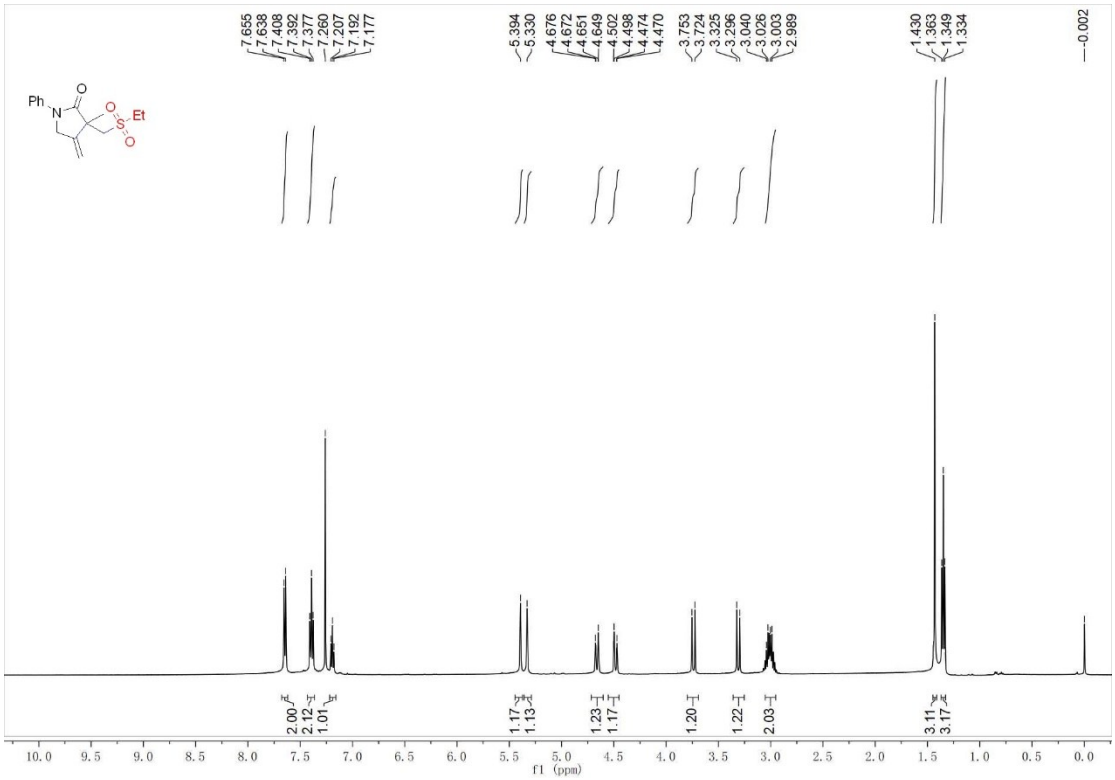
one (3ak)

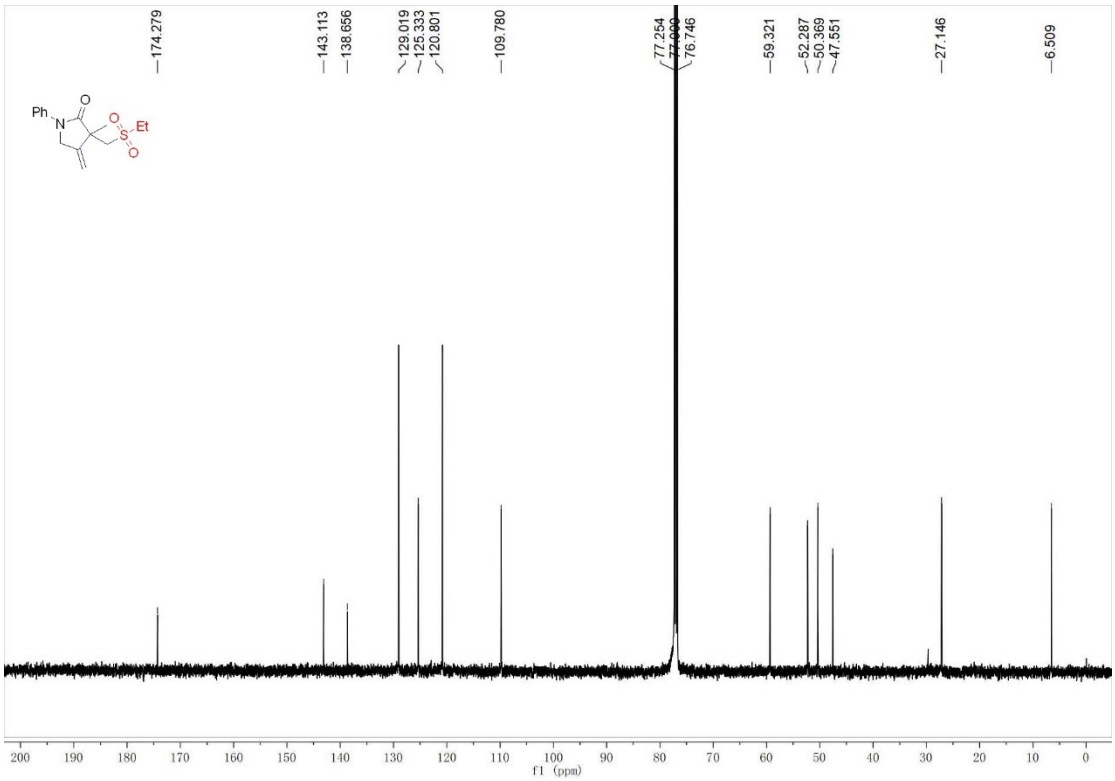




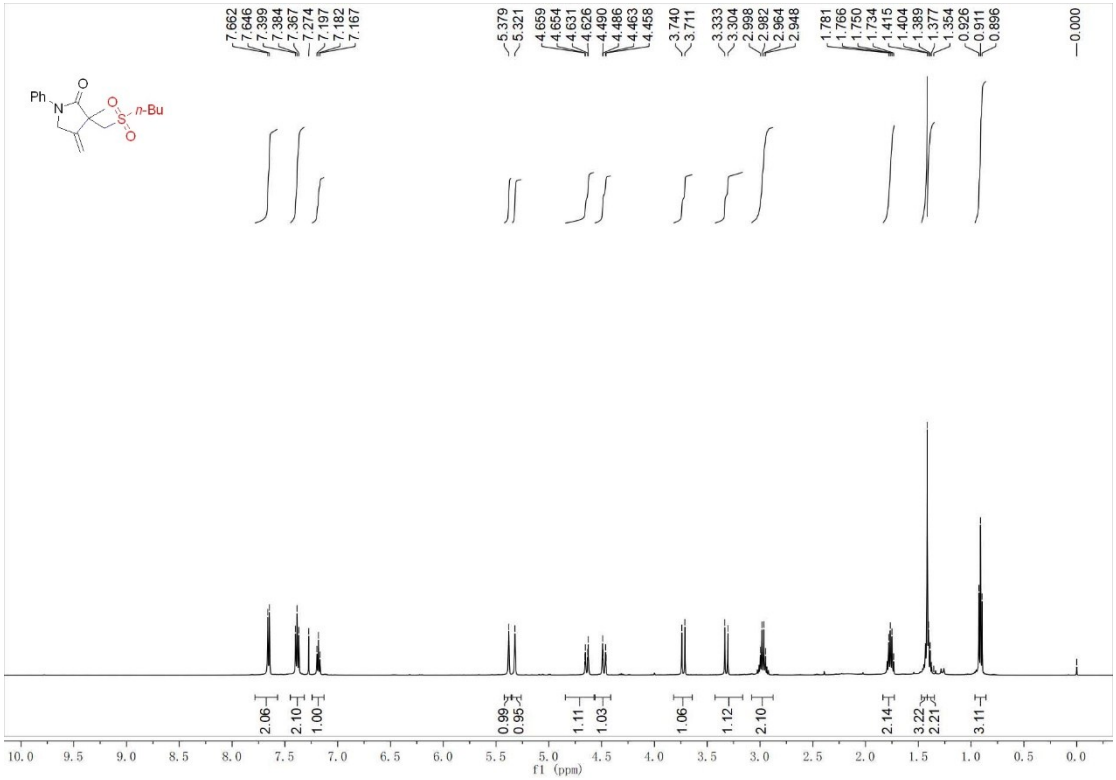
3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one

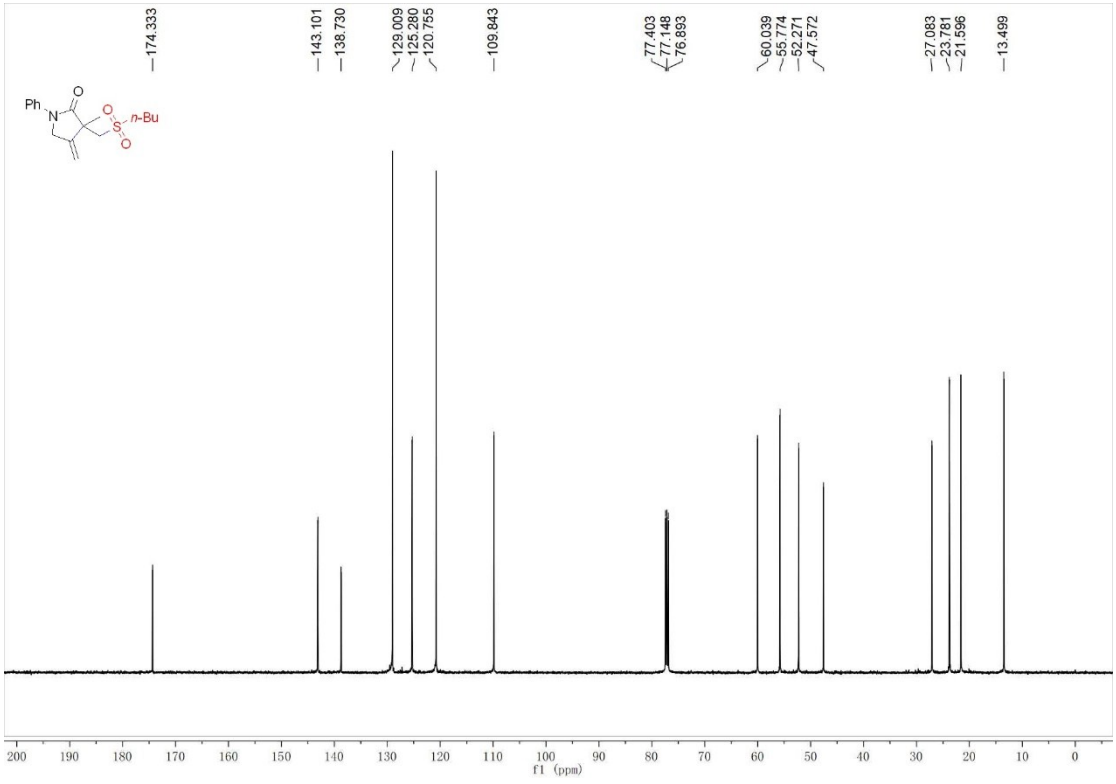
（3al）





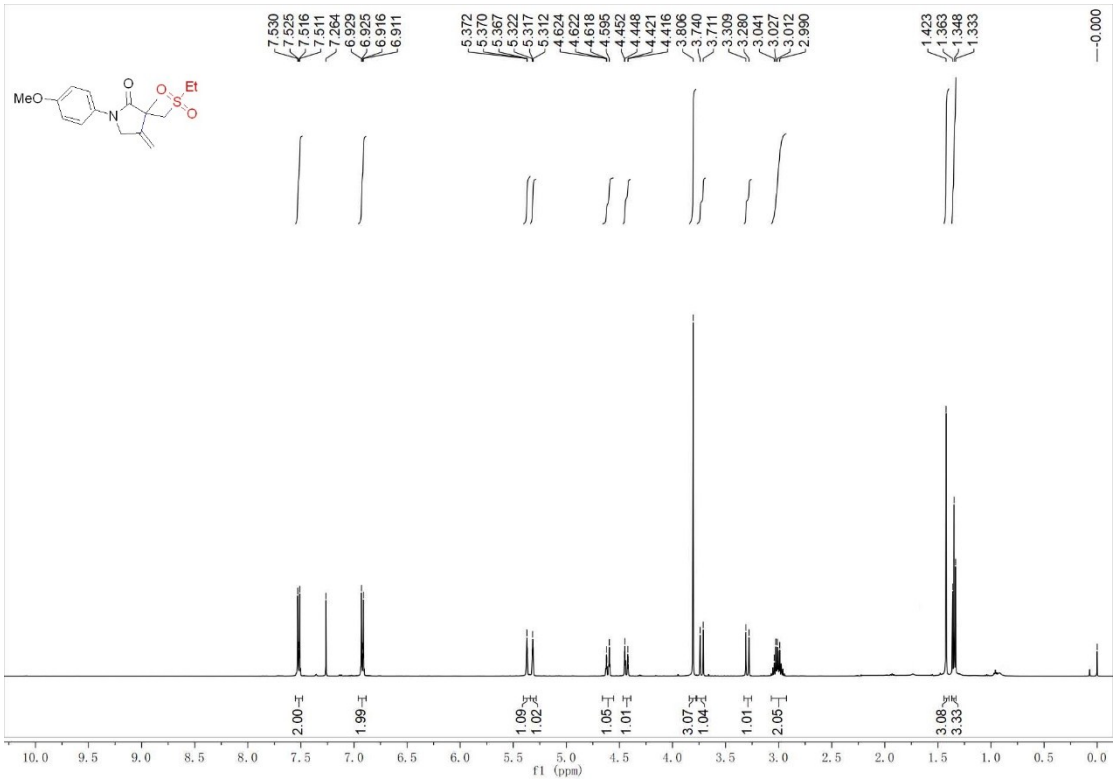
3-((Butylsulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3am)

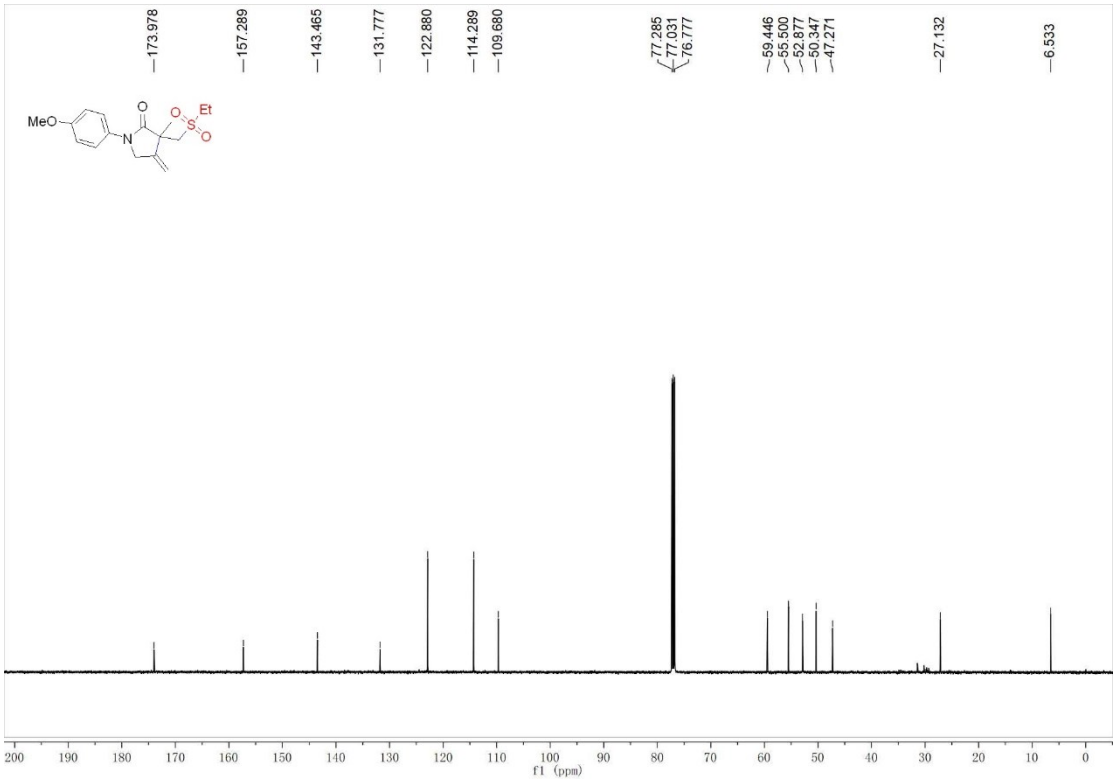




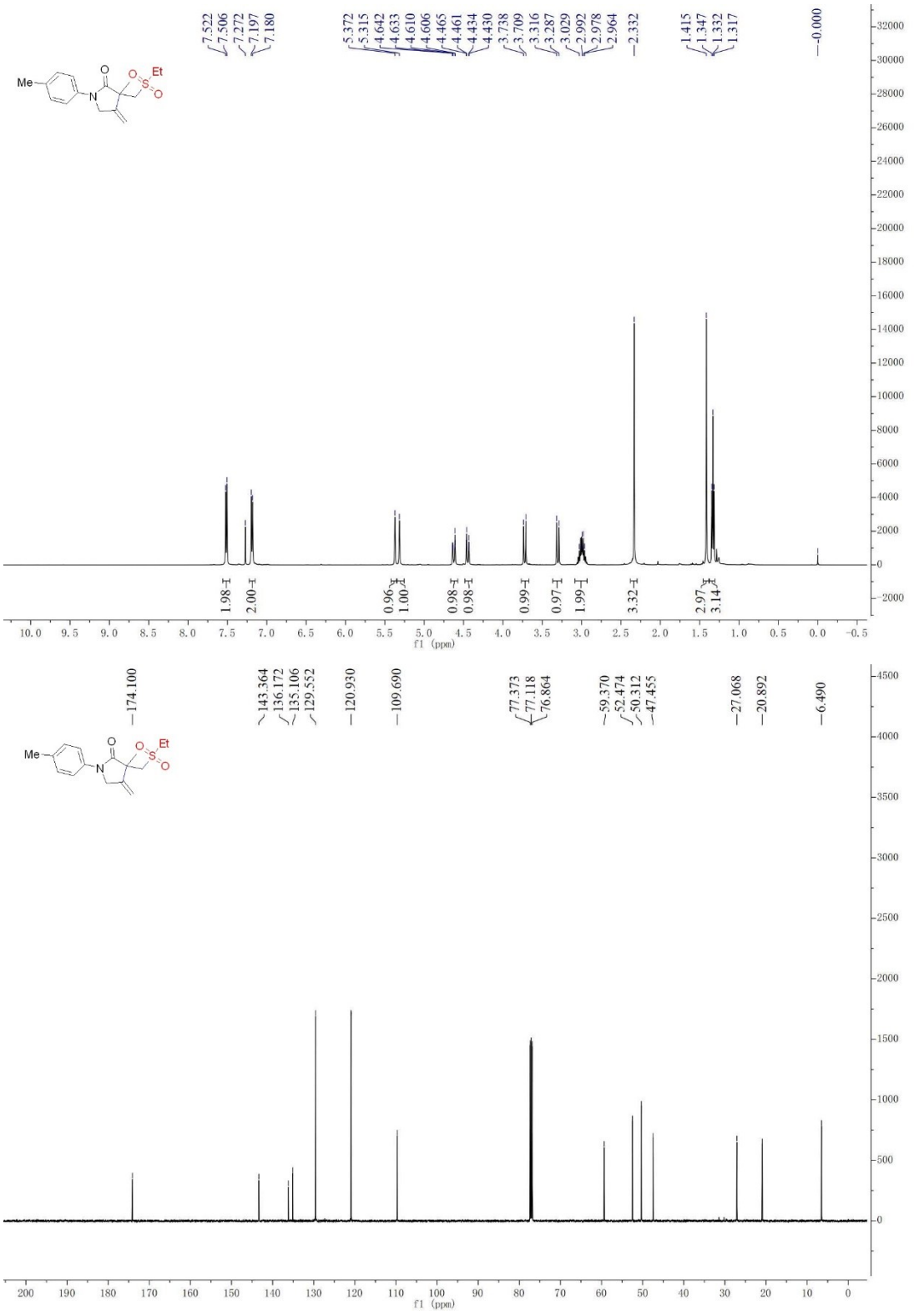
3-((Ethylsulfonyl)methyl)-1-(4-methoxyphenyl)-3-methyl-4-methylenepyrrolidin-

2-one (3bl)



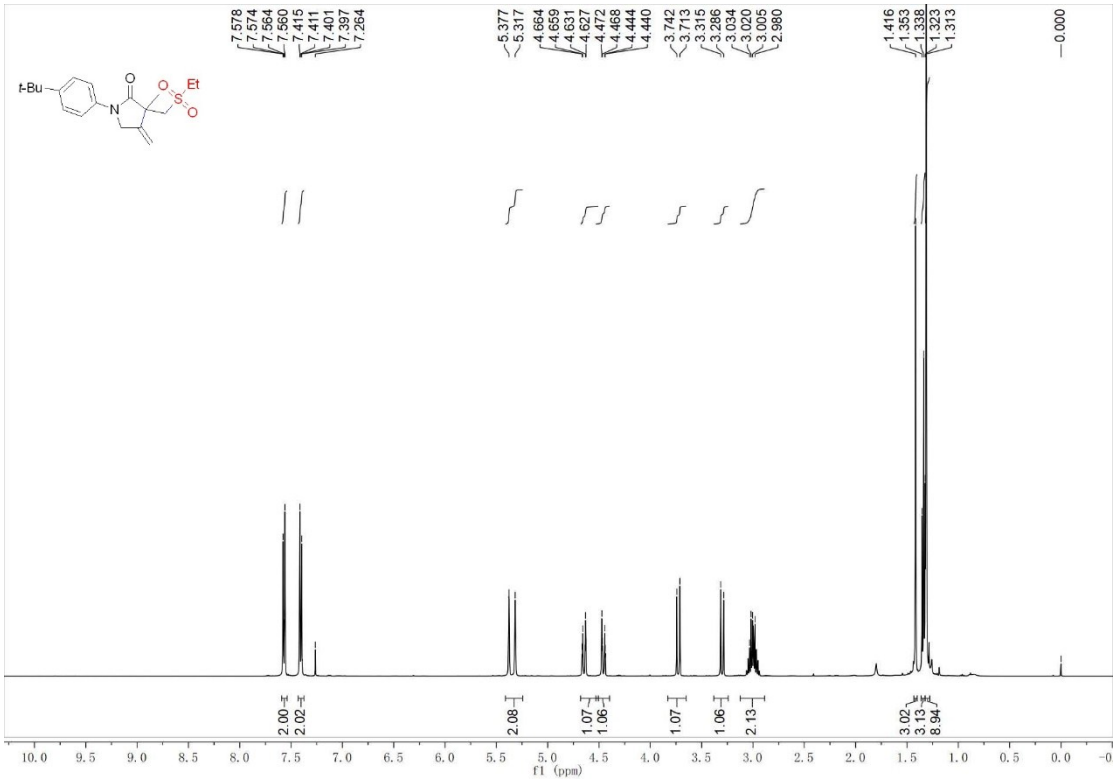


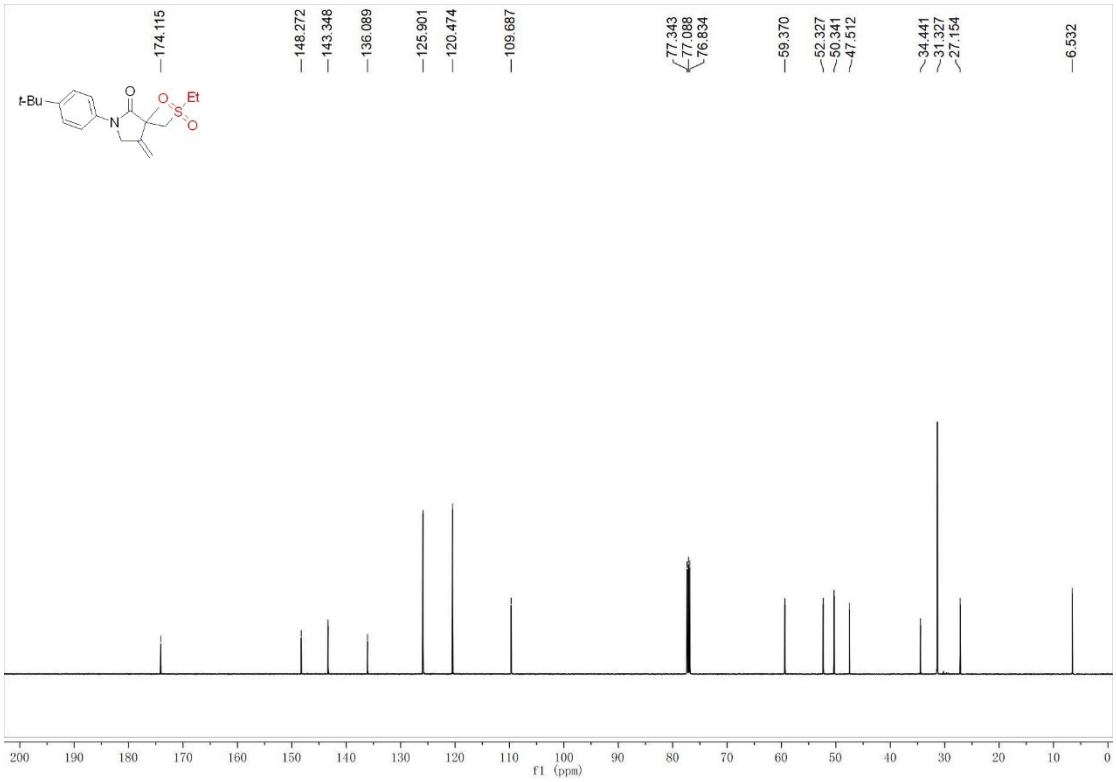
3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-(p-tolyl)pyrrolidin-2-one (3cl)



1-(4-(*tert*-Butyl)phenyl)-3-((ethylsulfonyl)methyl)-3-methyl-4-

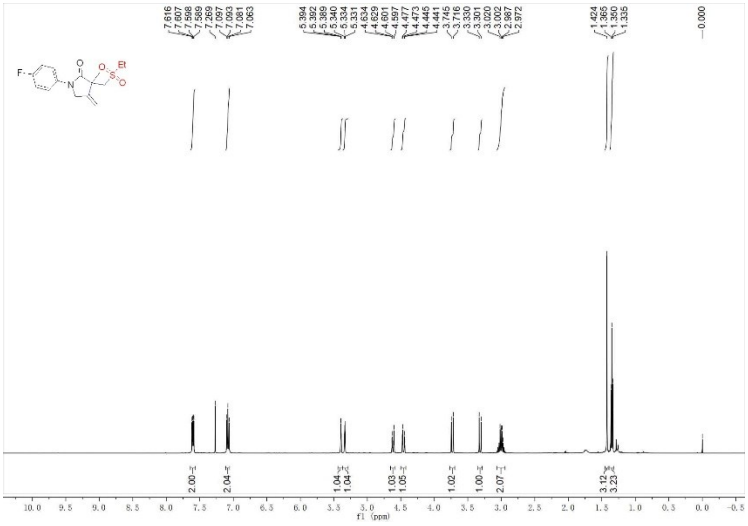
methylenepyrrolidin-2-one (3dl)

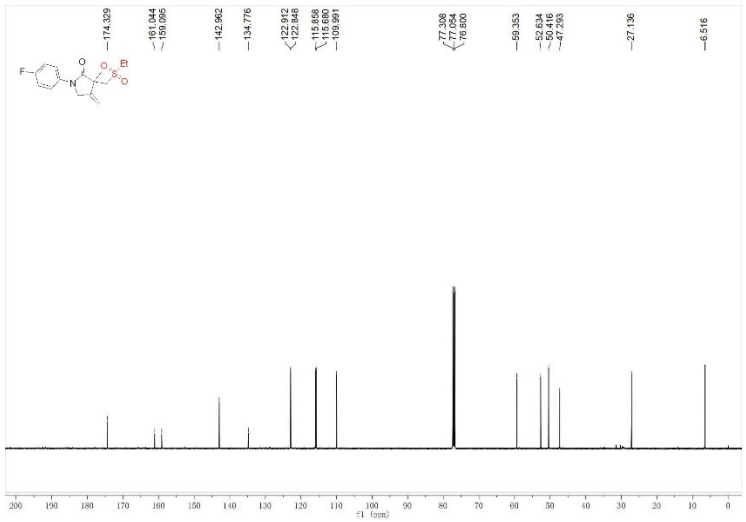


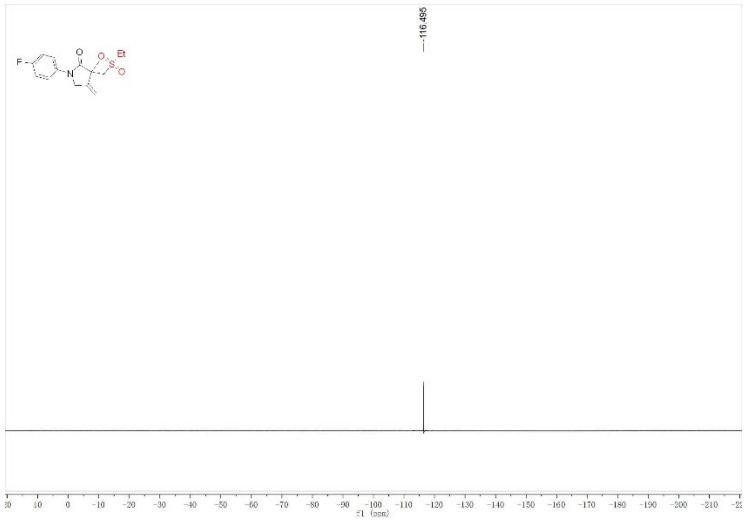


3-((Ethylsulfonyl)methyl)-1-(4-fluorophenyl)-3-methyl-4-methylenepyrrolidin-2-

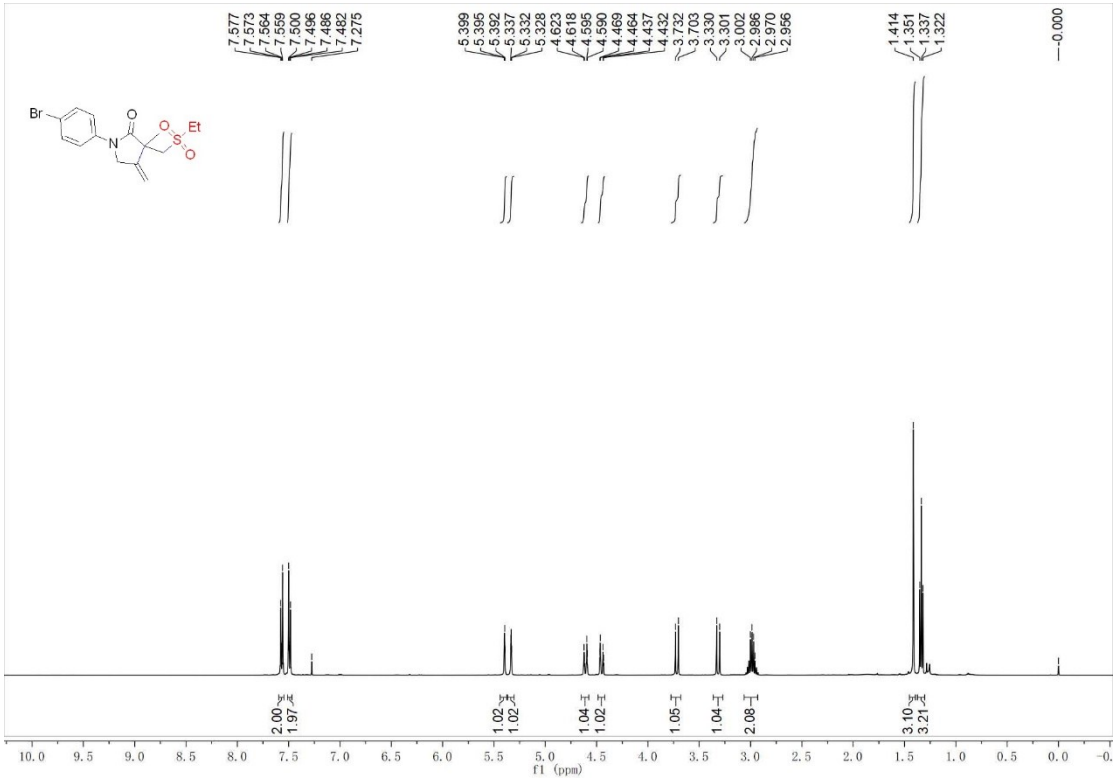
one (3el)

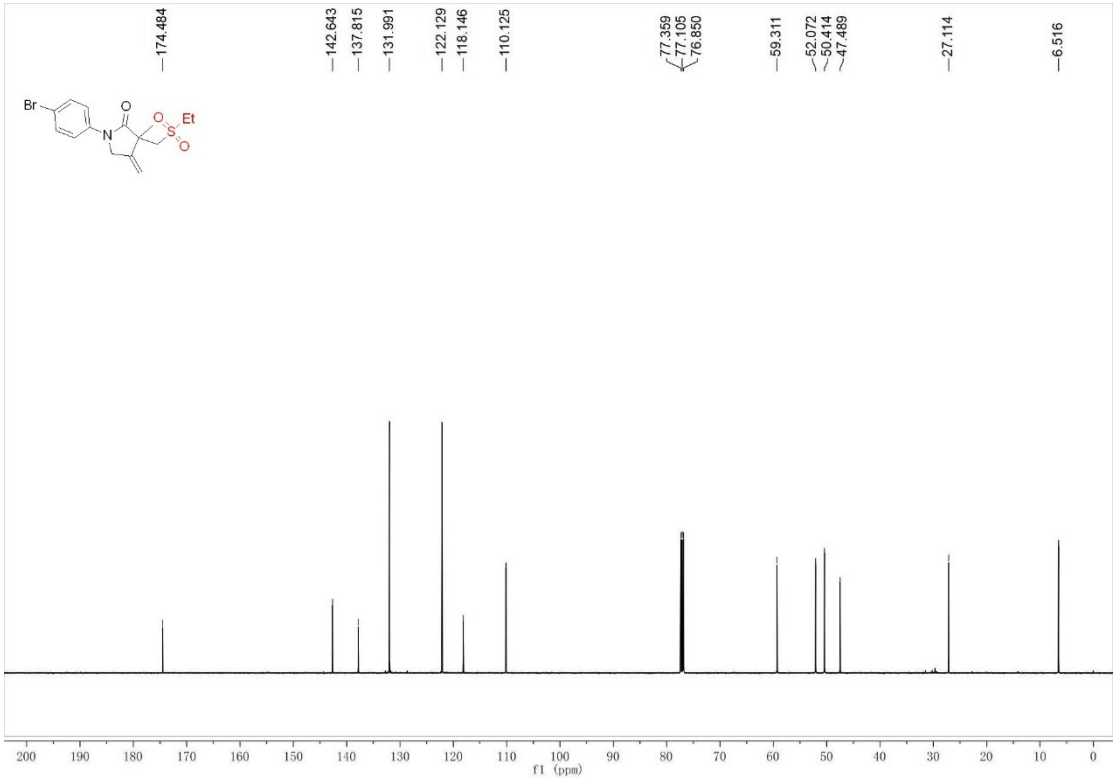




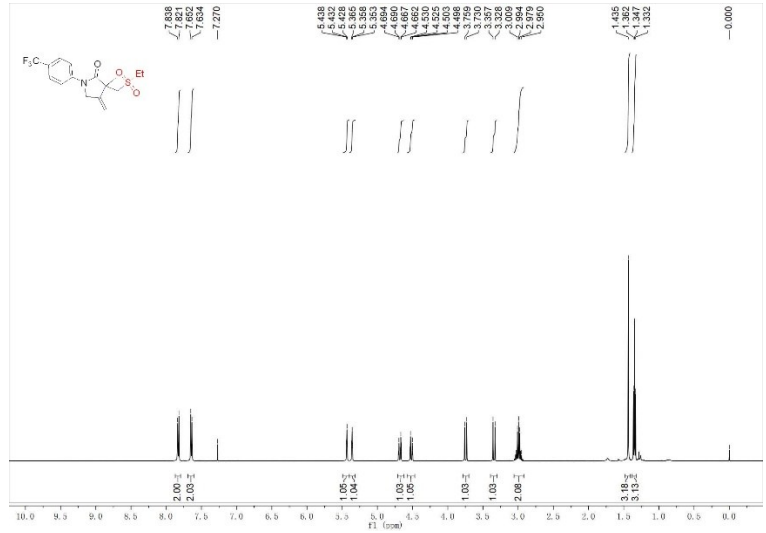


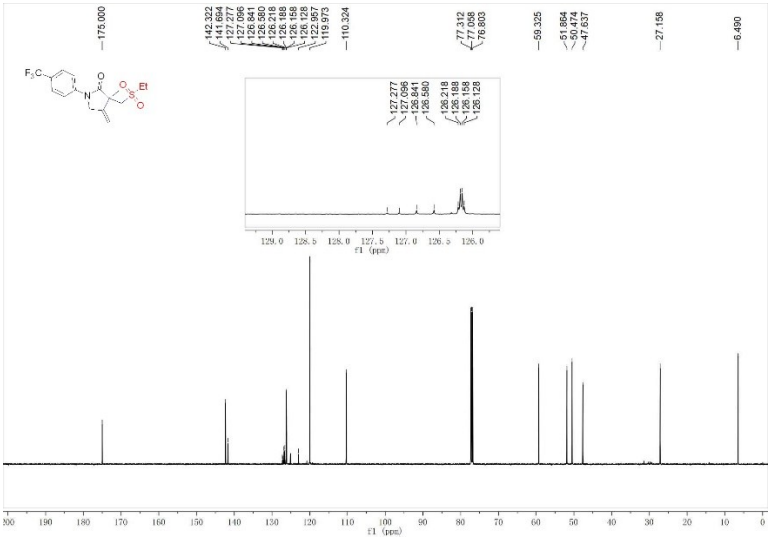
1-(4-Bromophenyl)-3-((ethylsulfonyl)methyl)-3-methyl-4-methylenepyrrolidin-2-one (3fl)

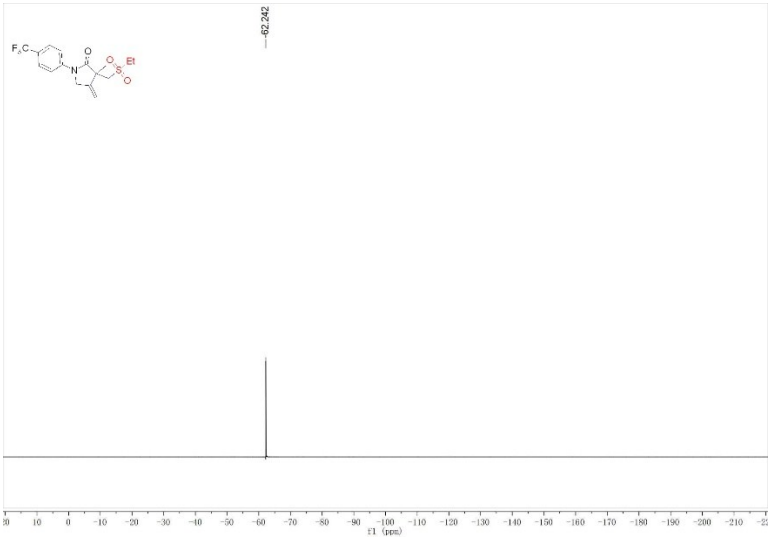




3-((Ethylsulfonyl)methyl)-3-methyl-4-methylene-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (3gl)

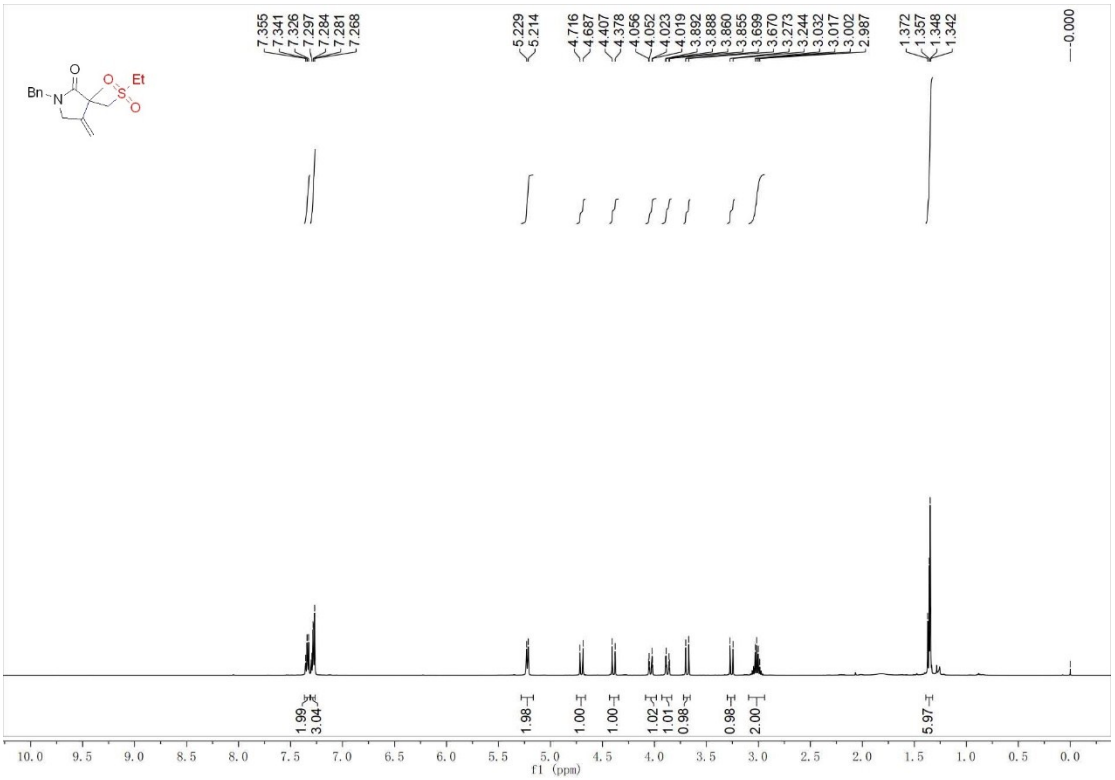


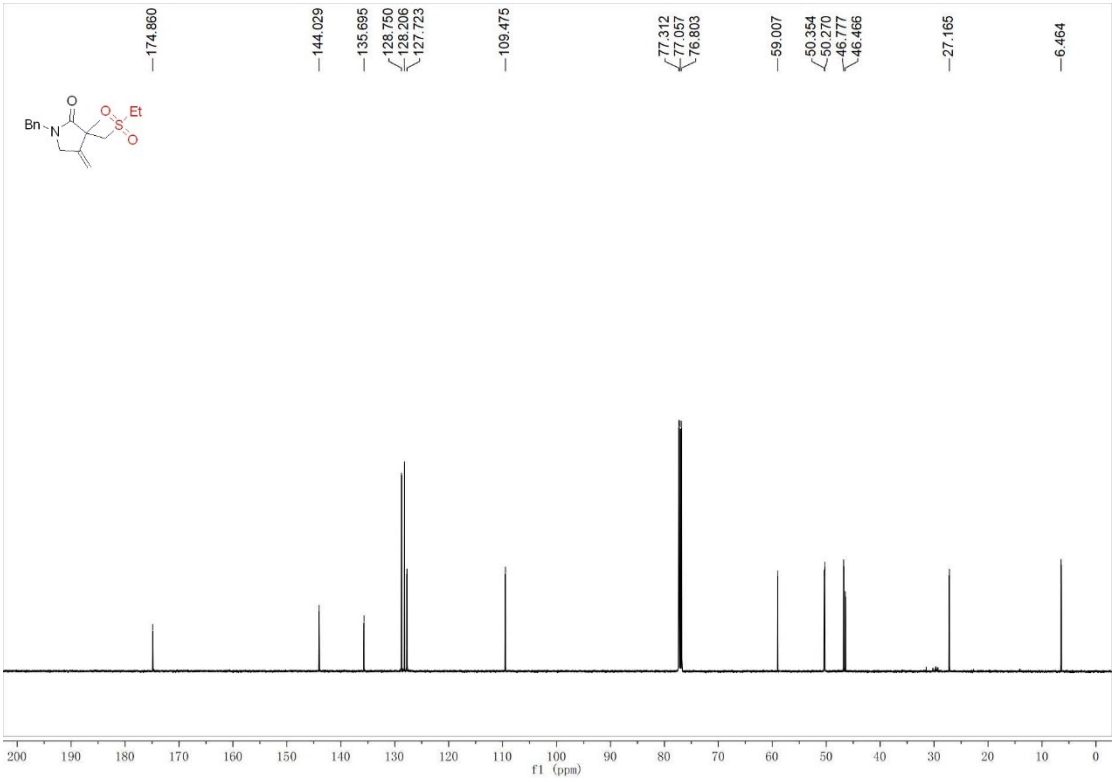




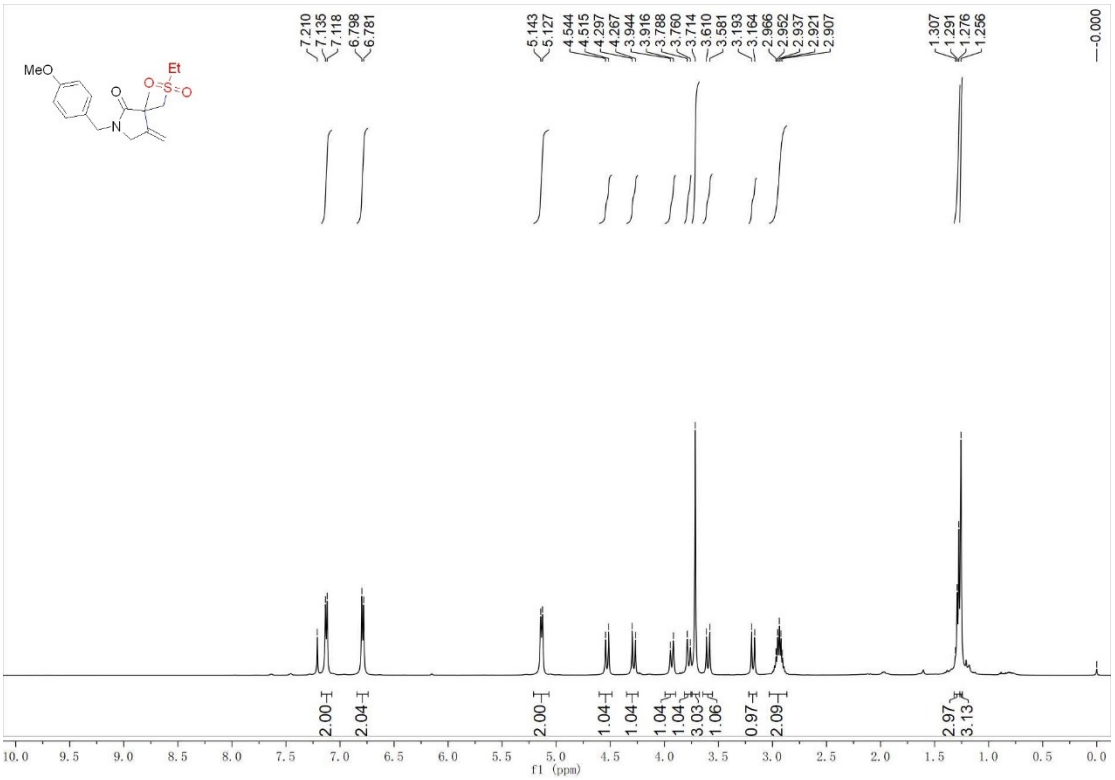
1-Benzyl-3-((ethylsulfonyl)methyl)-3-methyl-4-methylenepyrrolidin-2-one

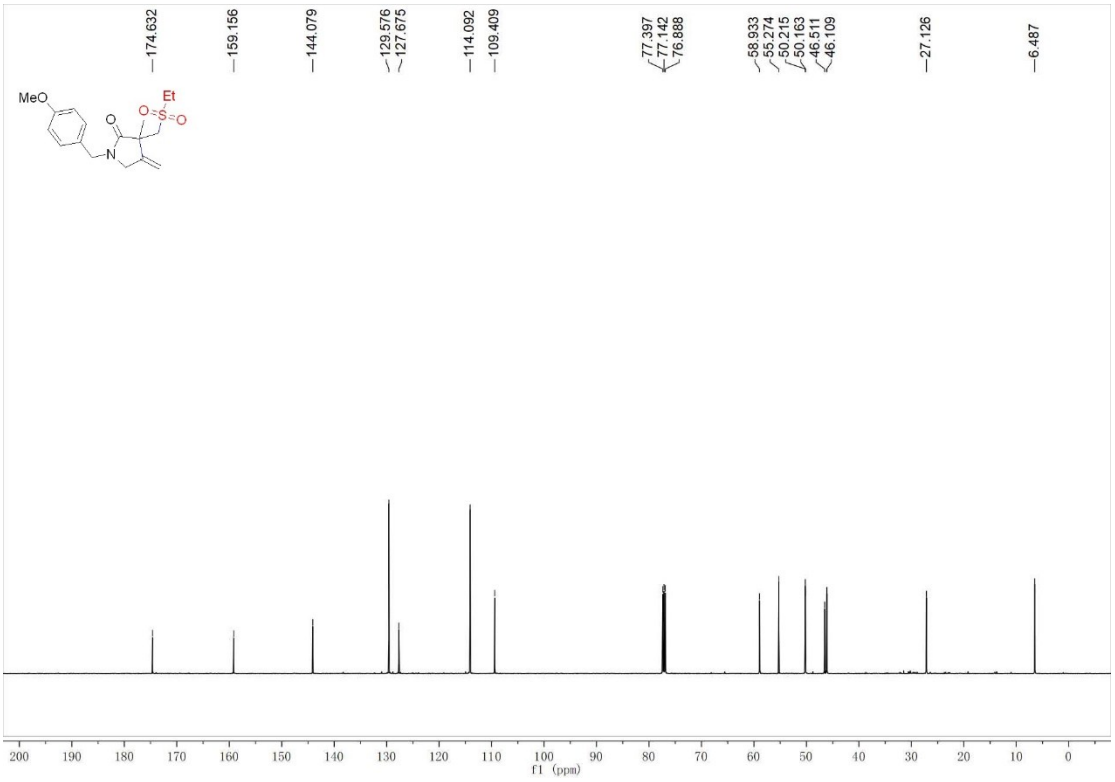
(3hl)



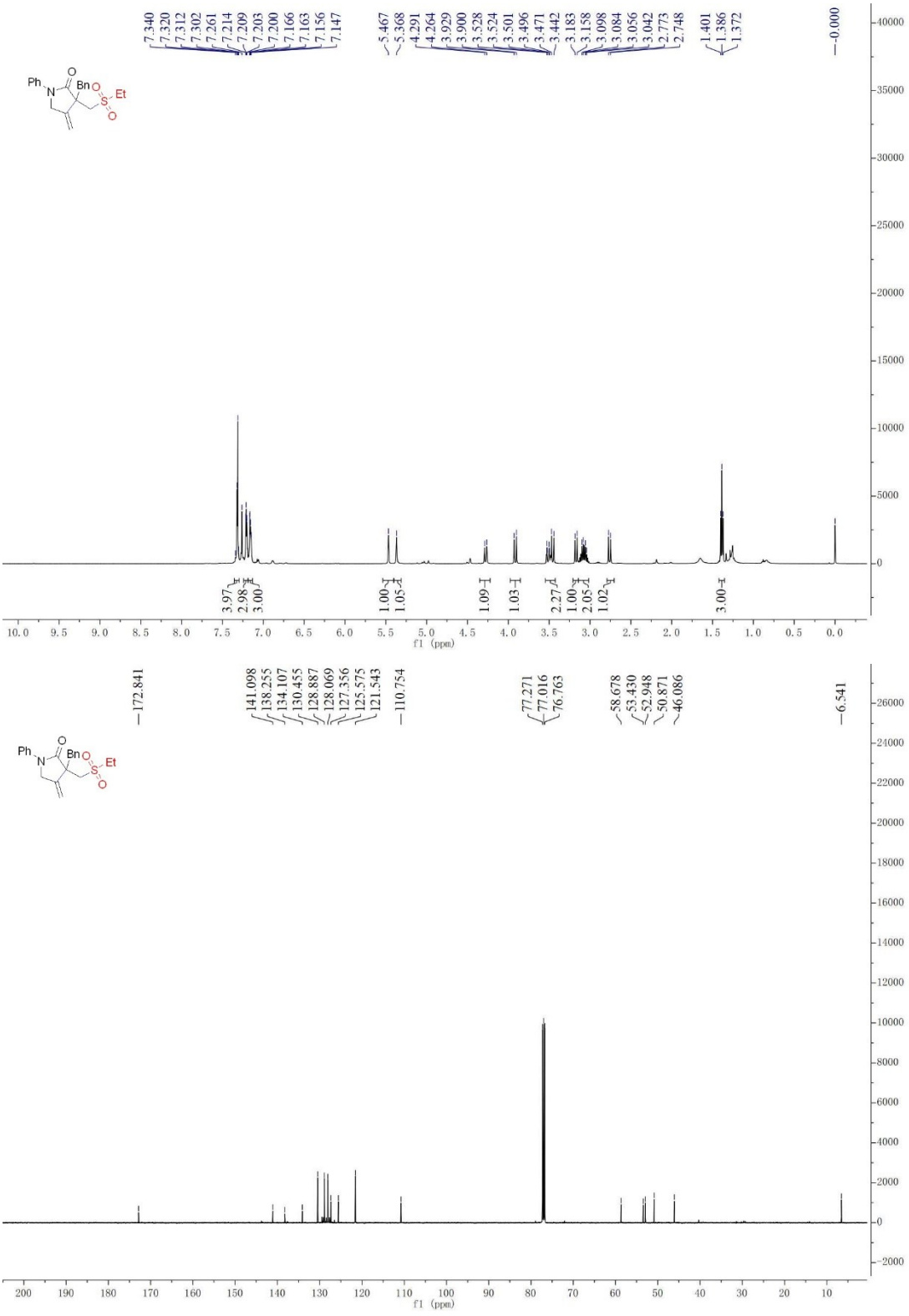


3-((Ethylsulfonyl)methyl)-1-(4-methoxybenzyl)-3-methyl-4-methylenepyrrolidin-2-one (3il)

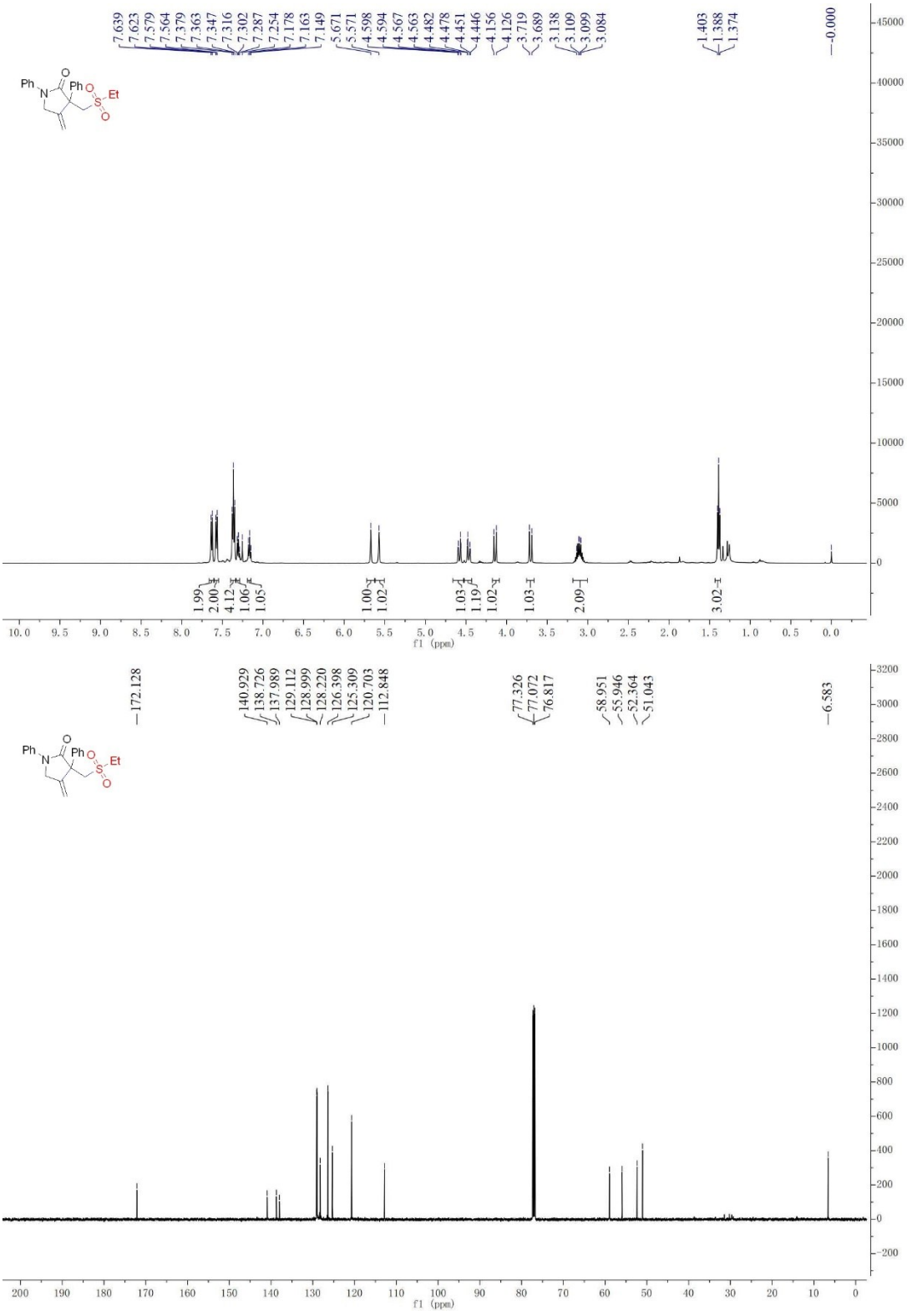




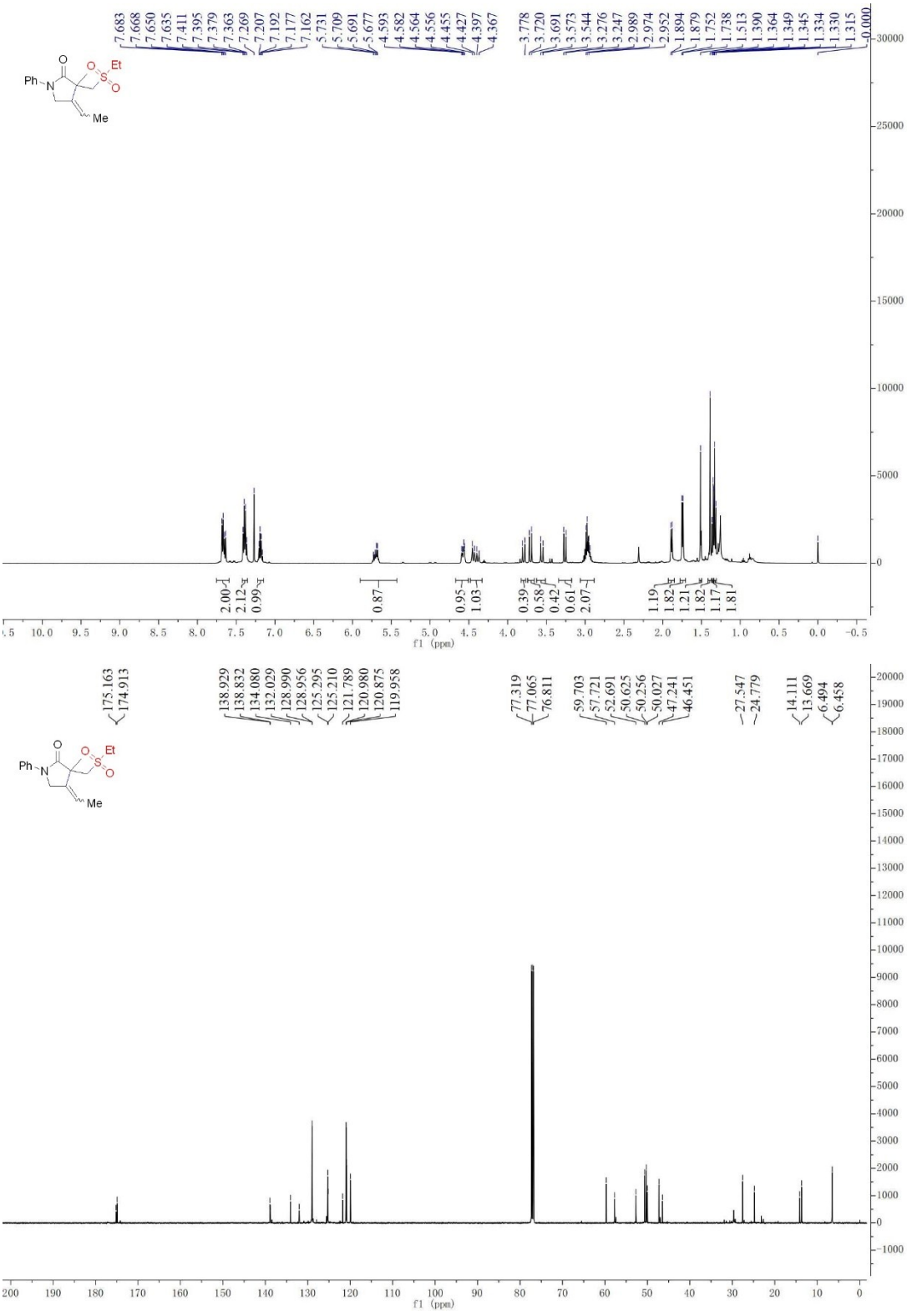
1-Benzyl-3-((ethylsulfonyl)methyl)-4-methylene-1-phenylpyrrolidin-2-one (3kl)



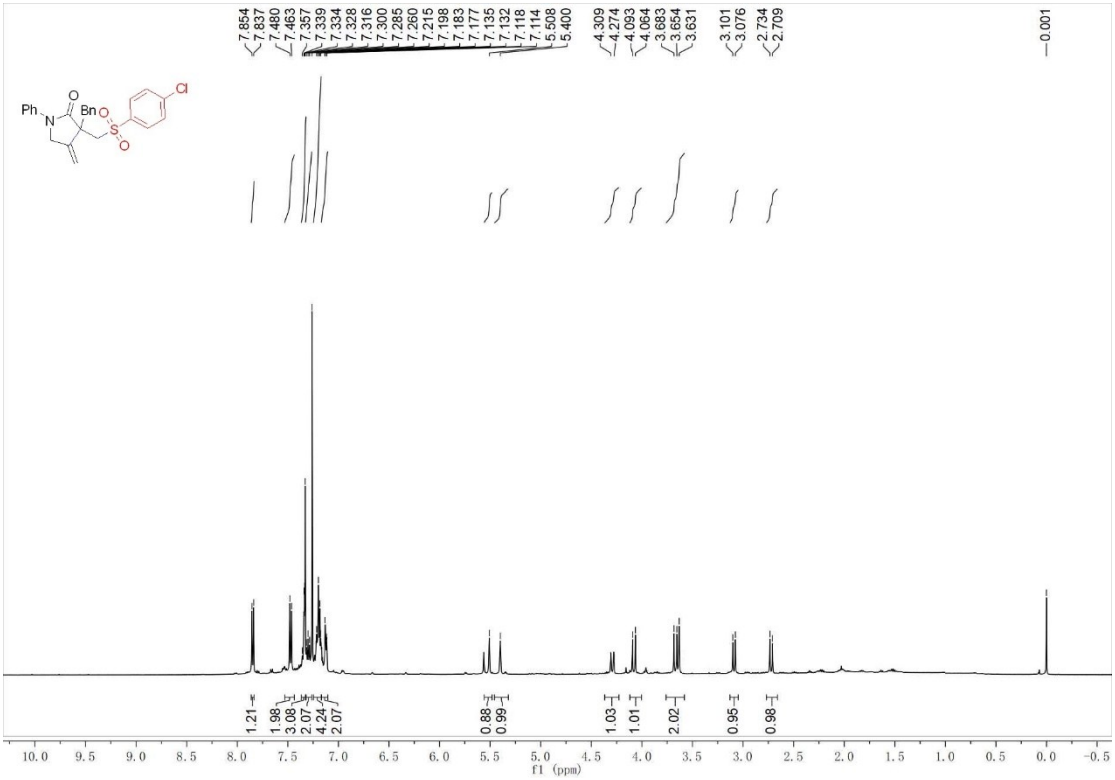
3-((Ethylsulfonyl)methyl)-4-methylene-1,3-diphenylpyrrolidin-2-one (3ll)

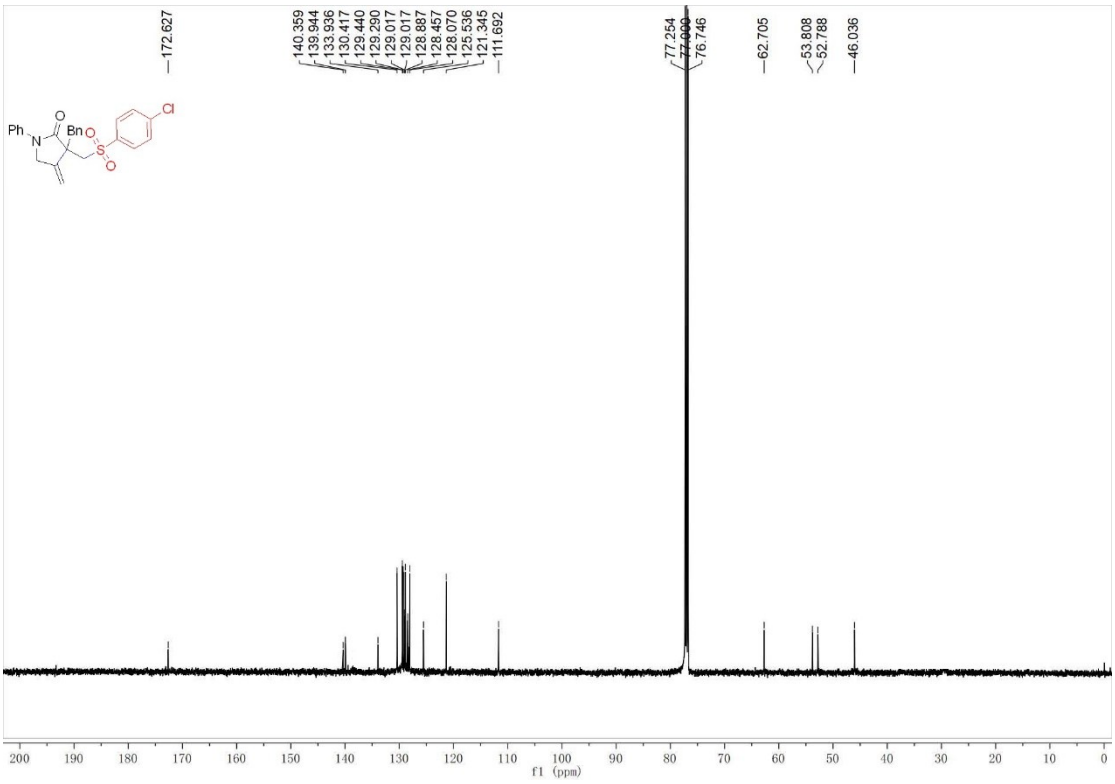


3-((Ethylsulfonyl)methyl)-4-methylene-1,3-diphenylpyrrolidin-2-one (3ml)



3-Benzyl-3-(((4-chlorophenyl)sulfonyl)methyl)-4-methylene-1-phenylpyrrolidin-2-one (3ke)





3-(((4-Chlorophenyl)sulfonyl)methyl)-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (3le)