Supporting Information

A Total Synthesis of the Tetracyclic Lupin Alkaloid (+)-Allomatrine

*Samuel V. Watkin, Nicholas P. Camp, Richard C. D. Brown**

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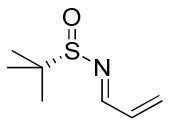
Experimental

(*S*,*E*)-*N*-Allylidene-2-methylpropane-2-sulfinamide (6)



$C_7H_{13}NOS$
Mol Wt: 159.2492

Sulfinimine **6** was prepared using a procedure adapted from Raghavan *et al.*[1a] To a solution of (*S*)-*tert*-butylsulfinamide (4.00 g, 33.00 mmol) and acrolein (2.32 mL, 33.00 mmol) in THF (50 mL) at rt under N_2 was added $Ti(OEt)_4$ (31.14 mL, 92.82 mmol) dropwise. During the addition the solution became yellow/orange. After 12 h the reaction was quenched with H_2O (40 mL) and diluted with EtOAc (30 mL). The biphasic mixture was stirred vigorously for 20 min and filtered through a pad of celite. The filter cake was washed with EtOAc (3 × 40 mL). The organics were combined and the solvent removed *in vacuo*. The crude material was purified by column chromatography (*eluent*: acetone/*n*-hexane - 1:9) to afford the title compound as a colourless oil (4.13 g, 25.90 mmol, 79%). Physical and spectroscopic data were consistent with reported values.[1]

$[\alpha]_D$: +566 (*c* = 0.37, $CHCl_3$, 26 °C).

R_f: 0.32 (*eluent*: EtOAc/*n*-hexane - 3:7).

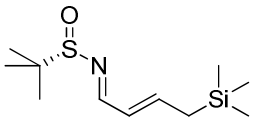
FT IR: 3487, 2977, 2960, 2926, 2868, 1624, 1575, 1080 cm^{-1}.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ 8.22 (1H, d, *J* = 10.1 Hz), 6.68 (1H, dt, *J* = 17.0, 10.1 Hz), 6.00 (1H, d, *J* = 17.0 Hz), 5.98 (1H, d, *J* = 10.1 Hz), 1.21 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 164.3, 134.6, 131.5, 57.4, 22.4 ppm.

[1] (a) S. Raghavan, V. Krishnaiah, B. Sridhar, *J. Org. Chem.* **2010**, *75*, 498–501. (b) M. Brichacek, M. Navarro Villalobos, A. Plichta, J. T. Njardarson, *Org. Lett.* **2011**, *13*, 1110–1113.

(*S*,*E*)-2-Methyl-*N*-((*E*)-4-(trimethylsilyl)but-2-en-1-ylidene)propane-2-sulfinamide (7)



$C_{11}H_{23}NOSSi$
Mol Wt: 245.4569

Sulfinimine **7** was prepared using a procedure adapted from BouzBouz *et al*.[2] To a solution of **6** (3.01 g, 18.38 mmol) and allyltrimethylsilane (6.31 mL, 37.68 mmol) in CH_2Cl_2 (50 mL) at rt under N_2 was added a solution of Hoveyda-Grubbs II catalyst (0.24 g, 0.37 mmol) in CH_2Cl_2 (8 mL) dropwise over 5 min. After 12 h, the reaction was concentrated *in vacuo* and the catalyst/ruthenium salts precipitated from *n*-hexane (40 mL). The precipitate was removed by filtering through celite. The filter cake was washed with *n*-hexane (2 × 75 mL) and the solvent removed *in vacuo* to give a pale brown oil. The crude material was purified by column chromatography (*eluent*: EtOAc/*n*-hexane - 2:8) to afford the title compound as a mixture of isomers (*E*:*Z* >25:1, ^{1}H NMR) as a colourless oil (4.46 g, 18.18 mmol, 97%).

$[\alpha]_D$: +407 (*c* = 0.61, $CHCl_3$, 29 °C).

R_f: 0.25 (*eluent*: EtOAc/*n*-hexane - 2:8).

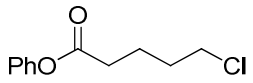
FT IR: 2955, 2925, 2898, 1625, 1575, 843 cm^{-1}.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ 8.15 (1H, d, *J* = 9.4 Hz), 6.60 (1H, dt, *J* = 15.2, 8.8 Hz), 6.29 (1H, ddt, *J* = 15.2, 9.4, 1.2 Hz), 1.83 (2H, dd, *J* = 8.8, 1.2 Hz), 1.19 (9H, s), 0.05 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 164.1, 150.7, 127.2, 57.0, 26.1, 22.4, −1.9 ppm.

[2] S. BouzBouz, E. De Lemos, J. Cossy, *Adv. Synth. Cat.* **2002**, *344*, 627–630.

Phenyl 5-chlorovalerate (8)



$C_{11}H_{13}ClO_2$
Mol Wt: 212.6727

To a solution of 5-chlorovaleric acid (10.80 g, 77.50 mmol) in CH_2Cl_2 (100 mL) at 0 °C under N_2 was added anhydrous DMF (0.10 mL, 1.30 mmol) followed by oxalyl chloride (9.44 mL, 96.87 mmol) dropwise. The reaction was stirred for 1 h at 0 °C and then warmed to rt. The reaction was stirred for 4 h at rt, then concentrated *in vacuo* giving a colourless oil. To the neat oil at rt under N_2, was added phenol (7.29 g, 77.46 mmol) in one portion, this was washed into the reaction with CH_2Cl_2 (15 mL) and the resulting solution was stirred for 24 h. The reaction was diluted with CH_2Cl_2 (100 mL) and quenched with *sat*. $NaHCO_3$ (100 mL). The phases were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 20 mL). The organics solutions were combined, washed with 10% K_2CO_3 (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The desired product was isolated by column chromatography (*eluent*: CH_2Cl_2/TEA - 500:1) yielding the title compound as a colourless oil (15.43 g, 72.55 mmol, 94%). Physical and spectroscopic data were consistent with reported values.[3]

R_f: 0.70 (*eluent*: CH_2Cl_2).

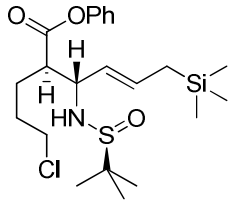
FT IR: 2957, 2872, 1754, 1593, 1491, 1454 cm^{-1}.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.45 - 7.34 (2H, m), 7.24 (1H, t, *J* = 7.6 Hz), 7.10 (2H, d, *J* = 7.6 Hz), 3.66 - 3.56 (2H, m), 2.68 - 2.57 (2H, m), 1.98 - 1.88 (4H, m) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 171.6, 150.6, 129.4, 125.8, 121.5, 44.4, 33.5, 31.8, 22.2 ppm.

[3] R. C. D. Brown, A. C. Cutter, I. R. Miller, J. F. Keily, R. K. Bellingham, M. E. Light, *Org. Lett.* **2011**, *13*, 3988–3991.

(2*R*,3*S*,*E*)-Phenyl 2-(3-chloropropyl)-3-((*S*)-1,1-dimethylethylsulfinamido)-6-(trimethylsilyl)hex-4-enoate (5)



$C_{22}H_{36}ClNO_3SSi$
Mol Wt: 458.1296

To a solution of *i*-Pr_2NH (4.56 mL, 32.59 mmol) in THF (120 mL) at 0 °C under N_2 was added a solution of *n*-BuLi (13.29 mL of 2.30 M in hexanes, 30.56 mmol) dropwise turning the solution pale yellow. The reaction was stirred for 30 min at 0 °C and cooled to −78 °C. To the LDA solution was added **8** (6.07 g, 28.52 mmol) in THF (15 mL) dropwise over 1.5 h via syringe pump. Upon complete addition, the reaction mixture was stirred for 30 min at −78 °C. To this was added sulfinimine **7** (5.00 g, 20.37 mmol) in THF (15 mL) dropwise over 1.5 h via syringe pump. The reaction was stirred for 1 h at −78 °C and quenched with *sat*. NH_4Cl (100 mL). The reaction was allowed to warm to rt, the phases were separated and the aqueous layer extracted with EtOAc (4 × 50 mL). The organic phases were combined and washed *with* brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The desired imino-aldol adduct was obtained by column chromatography (*eluent*: EtOAc/*n*-hexane - 1:1) as a colourless oil (6.99 g, 15.28 mmol, 75%).

$[\alpha]_D$: +54.5 (*c* = 0.54, $CHCl_3$, 25 °C).

R_f: 0.50 (*eluent*: EtOAc/ *n*-hexane - 1:1).

FT IR (cm^{-1}): 3466, 2955, 2871, 1754, 1656, 1592, 1492.

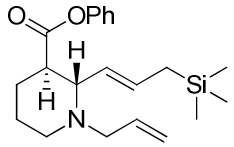
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.38 (2H, t, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.6 Hz), 7.06 (2H, d, *J* = 7.6 Hz), 5.81 (1H, dt, *J* = 15.2, 8.1 Hz), 5.30 (1H, dd, *J* = 15.2, 8.6 Hz), 4.10 (1H, dt, *J* = 8.6, 3.9 Hz), 3.92 (1H, d, *J* = 3.9 Hz), 3.58 (2H, t, *J* = 6.1 Hz), 2.90 (1H, dt, *J* = 8.6, 4.7 Hz), 2.03 - 1.74 (4H, m), 1.55 (2H, d, *J* = 8.1 Hz), 1.27 - 1.16 (9H, s), 0.03 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 171.9, 150.3, 133.5, 129.5, 126.0, 124.3, 121.4, 58.9, 55.5, 50.6, 44.3, 30.3, 26.0, 23.1, 22.6, –1.9 ppm.

LRMS: (ESI+) 480.2 and 482.2 $[M^{35/37}Cl+Na^+]^+$

HRMS: (ES+) for $C_{22}H_{36}{}^{35}ClNNaO_3SSi$: requires 480.1766; found 480.1771 Da.

(2*S*,3*R*)-Phenyl 1-allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidine-3-carboxylate (9)



$C_{21}H_{31}NO_2Si$
Mol Wt: 357.5618

To a solution of imino-aldol adduct **5** (4.01 g, 8.73 mmol) in dioxane (200 mL) at rt under N_2 was added *conc*. HCl (0.96 mL of ~36%, 9.60 mmol). The reaction was stirred for 1 h, then the solvent was removed *in vacuo*. The oily residue was dissolved in MeOH (15 mL) and evaporated (three times) giving a pale yellow oil. The yellow oil was re-dissolved in MeCN (200 mL) and K_2CO_3 (6.03 g, 43.66 mmol) was added. The reaction was stirred rapidly and NaI (0.13 g, 0.87 mmol) was added initially turning the solution yellow/orange, which became a colourless suspension. The reaction was stirred for 16 h and allyl bromide (0.84 mL, 9.60 mmol) was added to the reaction mixture. After a further 6 h, the solvent was removed *in vacuo*. The residue was partitioned between Et_2O/H_2O (200 mL - 1:1) and the phases separated. The aqueous was extracted with Et_2O (3 × 30 mL), the organic solutions combined, dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture was purified by column chromatography (*eluent*: Et_2O/CH_2Cl_2 - 3:7) to give the title piperidine as a colourless oil (2.53 g, 7.07 mmol, 81%).

$[\alpha]_D$: +33.8 (*c* = 0.63, $CHCl_3$, 25 °C).

R_f: 0.36 (*eluent*: Et_2O/CH_2Cl_2 - 3:7).

FT IR: 3074, 2947, 2864, 2798, 1755, 1492, 843 cm^{-1}.

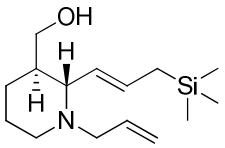
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.36 (2H, t, *J* = 7.6 Hz), 7.21 (1H, t, *J* = 7.6 Hz), 7.01 (2H, d, *J* = 7.6 Hz), 5.87 (1H, m), 5.72 (1H, ddd, *J* = 15.3, 8.8, 7.1 Hz), 5.27 (1H, dd, *J* = 15.3, 9.0 Hz), 5.21 - 5.11 (2H, m), 3.54 (1H, ddd, *J* = 13.6, 5.6, 1.0 Hz), 3.01 (1H, d, *J* = 12.1 Hz), 2.94 (1H, t, *J* = 9.0 Hz), 2.86 (1H, dd, *J* = 13.6, 7.6 Hz), 2.64 (1H, m), 2.10 (2H, m), 1.82 - 1.53 (4H, m), 1.48 (1H, m), 0.01 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 172.7, 150.7, 134.8, 131.7, 129.3, 128.5, 125.6, 121.5, 117.7, 66.6, 57.7, 51.6, 49.6, 27.7, 24.5, 23.0, −1.8 ppm.

LRMS: (ESI+) 358.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{21}H_{32}NO_2Si^+$: requires 358.2197; found 358.2202 Da.

((2*S*,3*R*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methanol (10)



$C_{15}H_{29}NOSi$
Mol Wt: 267.4824

To a solution of phenyl ester **9** (2.60 g, 7.27 mmol) in Et_2O (50 mL) at 0 °C under N_2 was added 1.0 M $LiAlH_4$ in Et_2O (7.27 mL, 7.27 mmol) dropwise over 15 min. The reaction was warmed to rt and stirred for 30 min. The reaction was cooled to 0 °C and 2 N NaOH (50 mL) added dropwise and the reaction stirred until all precipitates dissolved. The biphasic mixture was filtered through celite and the filter cake washed with Et_2O (3 × 10 mL). The phases were separated and the organic layer washed with 2 M NaOH (2 × 20 mL), *sat*. $NaHCO_3$ (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The desired material was purified by column chromatography (*eluent*: MeOH/EtOAc - 1:9) to give the title compound as a pale yellow oil (1.87 g, 7.01 mmol, 96%).

$[\alpha]_D$: +48.8 (*c* = 0.51, $CHCl_3$, 25 °C).

R_f: 0.20 (*eluent*: MeOH/EtOAc - 1:9).

FT IR: 3341, 2950, 2931, 2793, 1657, 1642, 1247, 839 cm^{-1}.

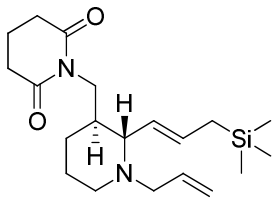
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.84 (1H, dddd, *J* = 16.6, 10.7, 7.6, 5.7 Hz), 5.59 (1H, dt, *J* = 15.4, 8.0 Hz), 5.25 (1H, dd, *J* = 15.4, 8.9 Hz), 5.17 - 5.06 (2H, m), 3.65 (1H, m), 3.55 (1H, m), 3.42 (1H, dd, *J* = 13.8, 5.7 Hz), 2.90 (1H, dt, *J* = 11.2, 4.0 Hz), 2.80 (1H, dd, *J* = 13.8, 7.6 Hz), 2.56 (1H, t, *J* = 8.9 Hz), 2.23 (1H, br. s.), 2.04 (1H, td, *J* = 11.2, 3.1 Hz), 1.85 (1H, dt, *J* = 12.8, 4.1 Hz), 1.77 (1H, dquin, *J* = 13.2, 4.1 Hz), 1.65 - 1.45 (4H, m), 1.23 (1H, m), 0.01 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 135.2, 131.0, 128.9, 117.5, 67.6, 66.7, 58.1, 51.2, 42.8, 27.0, 24.7, 22.9, –1.8 ppm.

LRMS: (ESI+) 268.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{15}H_{30}NOSi^+$: requires 268.2091; found 268.2093 Da.

1-(((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)piperidine-2,6-dione (11)



$C_{20}H_{34}N_2O_2Si$
Mol Wt: 362.5817

To a solution of alcohol **10** (1.77 g, 6.62 mmol), Ph_3P (4.34 g, 16.54 mmol) and glutarimide (3.74 g, 33.09 mmol) in THF/CH_2Cl_2 (5:1 – 120 mL) at 0 °C under N_2 was added DIAD (3.35 mL, 16.54 mmol) dropwise over 30 min. The reaction mixture was allowed to warm to rt and stirred for 12 h, then the solvent was removed *in vacuo* and the residue partitioned between EtOAc/H_2O (1:1 - 50 mL). The phases were separated and the aqueous phase extracted with EtOAc (3 × 20 mL). The organic solutions were combined and washed with 0.5 M HCl (4 × 10 mL). The combined acidic phases were basified with 35% NH_4OH to pH 14 and extracted with Et_2O (5 × 10 mL) and EtOAc (2 × 10 mL). The organic solutions were combined, dried ($MgSO_4$) and concentrated *in vacuo*. The crude material was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:193) to afford the title glutarimide as an off white/beige solid (1.79 g, 4.94 mmol, 75%).

$[\alpha]_D$: +69.1 (*c* = 0.60, $CHCl_3$, 25 °C).

R_f: 0.27 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:193).

MP: 44 - 46°C (35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:193).

FT IR: 2946, 2900, 2790, 1722, 1664, 1381, 1351, 838 cm^{-1}.

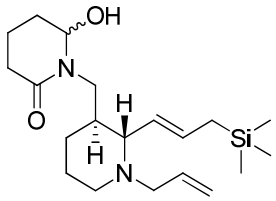
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.83 (1H, dddd, *J* = 17.2, 10.2, 7.8, 5.5 Hz), 5.56 (1H, dt, *J* = 15.4, 8.5 Hz), 5.19 (1H, dd, *J* = 15.4, 9.1 Hz), 5.14 - 5.04 (2H, m), 3.76 - 3.62 (2H, m), 3.50 (1H, m), 2.91 (1H, d, *J* = 11.2 Hz), 2.74 (1H, dd, *J* = 13.9, 7.8 Hz), 2.63 (4H, t, *J* = 6.5 Hz), 2.33 (1H, t, *J* = 8.5 Hz), 2.00 - 1.87 (3H, m), 1.80 (1H, m), 1.62 (1H, m), 1.56 - 1.34 (4H, m), 0.98 (1H, m), 0.00 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 172.6, 135.5, 131.0, 129.2, 117.1, 69.5, 57.9, 51.9, 42.7, 38.5, 33.0, 27.3, 24.7, 22.8, 17.2, −1.7 ppm.

LRMS: (ESI+) 363.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{20}H_{35}N_2O_2Si^+$: requires 363.2462; found 363.2467 Da.

1-(((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)-6-hydroxypiperidin-2-one (12)



$C_{20}H_{36}N_2O_2Si$
Mol Wt: 364.5975

To a solution of glutarimide **11** (600 mg, 1.66 mmol) in EtOH (50 mL) at −15 °C under N_2 was added $NaBH_4$ (375 mg, 9.93 mmol) in one portion. At 15 min intervals 4-6 drops of 1.25 M HCl in EtOH were added over 6 h. After 16 h, the reaction was diluted with Et_2O (50 mL) and quenched with *sat*. $NaHCO_3$ (20 mL). The aqueous phase was extracted with Et_2O (5 × 10 mL), EtOAc (2 × 20 mL), and the combined organic solutions were dried ($MgSO_4$) and concentrated *in vacuo*. The material was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:93) giving the title hydroxypiperidin-2-one as a mixture of epimers (~1:1) as a colourless oil (209 mg, 0.58 mmol, 35%).

$[\alpha]_D$: +35.2 (*c* = 0.3, $CHCl_3$, 24 °C).

R_f: 0.44 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:10:90)**.**

FT IR: 3307, 3072, 2950, 2789, 2701, 1621, 1481, 848 cm^{-1}.

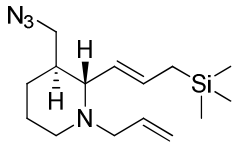
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.93 - 5.73 (2H, m), 5.55 (2H, tt, *J* = 15.8, 8.0 Hz), 5.19 - 5.03 (5H, m), 4.97 - 4.82 (2H, m), 3.80 (1H, dd, *J* = 13.7, 10.6 Hz,), 3.71 - 3.35 (4H, m), 3.25 - 3.02 (2H, m), 2.96 - 2.74 (4H, m), 2.69 (1H, m), 2.56 (1H, m), 2.51 - 2.15 (6H, m), 2.11 - 1.97 (4H, m), 1.93 - 1.37 (18H, m), 1.24 - 1.06 (2H, m), 0.00 (18H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 172.5, 172.4, 136.4, 136.3, 133.7, 133.4, 129.8, 119.8, 119.7, 83.9, 79.5, 70.7, 60.4, 59.7, 53.3, 51.6, 46.8, 40.3, 34.2, 34.1, 33.0, 32.9, 28.6, 26.2, 24.8, 24.8, 17.8, 17.4, 0.0 ppm.

LRMS: (ESI+) 365.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{20}H_{37}N_2O_2Si^+$: requires 365.2619; found 365.2625 Da.

(2*S*,3*S*)-1-Allyl-3-(azidomethyl)-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidine



$C_{15}H_{28}N_4Si$
Mol Wt: 292.4951

To a solution of alcohol **10** (751 mg, 2.80 mmol) and Ph_3P (1.47 g, 5.61 mmol) in THF (30 mL) at −10 °C under N_2 was added DIAD (1.16 mL, 5.61 mmol) dropwise over 40 min. DPPA (1.30 mL, 5.61 mmol) was added dropwise over 5 min and the reaction allowed to warm to rt. The reaction was stirred for 12 h and then concentrated *in vacuo*. The residue was partitioned between EtOAc (25 mL) and H_2O (25 mL), the phases separated and the organic solutions extracted with 2.0 M HCl (3 × 10 mL). The acidic aqueous solution was basified to pH 14 with an excess of aq. 35% NH_4OH. The aqueous layer was extracted with Et_2O (3 × 10 mL), EtOAc (2 x 10 mL), the organic solutions were combined, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was then purified by column chromatography (*eluent*: EtOAc/*n*-hexane - 1:1) to give the title azide as a colourless oil (0.58 g, 1.98 mmol, 71%).

$[\alpha]_D$: +60.6 (*c* = 0.67, $CHCl_3$, 28 °C).

R_f: 0.42 (*eluent*: EtOAc/*n*-hexane - 1:1).

FT IR: 2936, 2859, 2790, 2095, 1284, 1248, 845 cm^{-1}.

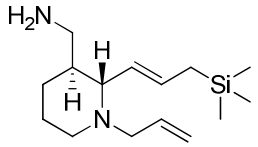
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.84 (1H, dddd, *J* = 16.8, 10.5, 7.8, 5.5 Hz), 5.59 (1H, dt, *J* = 15.3, 8.1 Hz), 5.17 - 5.03 (3H, m), 3.51 (1H, ddt, *J* = 13.9, 5.5, 1.6 Hz), 3.40 (1H, dd, *J* = 12.1, 3.6 Hz), 3.19 (1H, dd, *J* = 12.1, 6.8 Hz), 2.96 (1H, dtd, *J* = 11.9, 3.8, 1.2 Hz), 2.76 (1H, dd, *J* = 13.9, 7.8 Hz), 2.39 (1H, t, *J* = 9.2 Hz), 1.96 (1H, td, *J* = 11.9, 2.9 Hz), 1.86 (1H, m), 1.69 (1H, dquin, *J* = 13.1, 3.8 Hz), 1.63 - 1.48 (4H, m), 1.20 (1H, tdd, *J* = 12.5, 11.9, 3.8 Hz), 0.03 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 135.2, 131.7, 129.1, 117.4, 67.6, 58.2, 55.2, 51.9, 41.3, 28.0, 24.8, 23.0, −1.7 ppm.

LRMS: (ESI+) 293.4 $[M+H^+]^+$.

HRMS: (ES+) for $C_{15}H_{29}N_4Si^+$: requires 293.2156; found 293.2157 Da.

((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methanamine (14)



$C_{15}H_{30}N_2Si$
Mol Wt: 266.4976

To a solution of azide (490 mg, 1.68 mmol) in Et_2O (25 mL) under N_2 at 0 °C was added a solution of $LiAlH_4$ in Et_2O (1.68 mL of 1.0 M, 1.68 mmol) dropwise over 5 min. The reaction was allowed to warm to rt upon which vigorous effervescence was observed. The reaction was stirred for 1 h at rt and then quenched at 0 °C by dropwise addition of 2.0 M NaOH (25 mL). The reaction was stirred until all precipitates had dissolved. The biphasic mixture was filtered through a pad of celite under vacuum and the filter cake washed with Et_2O (3 × 15 mL) and EtOAc (20 mL). The phases were separated and the aqueous extracted with EtOAc (2 × 20 mL). The organic solutions were combined, washed with brine (20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude material was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:15:185 to 1:20:180) to give the title diamine as a colourless oil (388 mg, 1.47 mmol, 87%).

$[\alpha]_D$: +88.8 (*c* = 0.51, $CHCl_3$, 27 °C).

R_f: 0.54 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:20:180).

FT IR: 3290, 2929, 2950, 2784, 1580, 1247, 840 cm^{-1}.

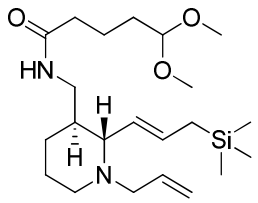
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.84 (1H, dddd, *J* = 16.7, 10.4, 7.9, 5.5 Hz), 5.52 (1H, dt, *J* = 15.1, 8.0 Hz), 5.20 - 4.98 (3H, m), 3.52 (1H, ddt, *J* = 13.9, 5.5, 1.5 Hz), 2.96 (1H, d, *J* = 11.5 Hz), 2.77 (1H, dd, *J* = 13.0, 3.9 Hz), 2.73 (1H, dd, *J* = 13.9, 7.9 Hz), 2.44 (1H, dd, *J* = 13.0, 7.2 Hz), 2.29 (1H, t, *J* = 9.3 Hz), 1.86 (1H, m), 1.92 (1H, td, *J* = 12.1, 3.3 Hz), 1.69 (1H, dquin, *J* = 12.9, 3.7 Hz), 1.56 (1H, qt, *J* = 12.9, 3.3 Hz), 1.50 (2H, ddd, *J* = 8.0, 2.5, 1.2 Hz), 1.39 - 1.14 (3H, m), 1.05 (1H, qd, *J* = 12.1, 3.7 Hz), 0.01 (9H, s) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 135.4, 130.5, 130.1, 117.3, 68.7, 58.3, 52.2, 45.5, 43.9, 27.9, 25.0, 22.8, –1.8 ppm.

LRMS: (ESI+) 267.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{15}H_{31}N_2Si^+$: requires 267.2251; found 267.2253 Da.

_N_-(((2_S_,3_S_)-1-Allyl-2-((_E_)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)-5,5-dimethoxypentanamide (15)



$C_{22}H_{42}N_2O_3Si$
Mol Wt: 410.6660

To a solution of diamine **14** (300 mg, 1.13 mmol), 5,5-dimethoxyvaleric acid (219 mg, 1.35 mmol)[4] and TEA (0.39 mL, 2.81 mmol) in EtOAc (15 mL) under N_2 at rt was added a solution of T3P (1.34 mL of 50 wt % in EtOAc, 2.25 mmol). After 6 h, an aqueous solution of NaOH (15 mL of 1 N) was added. The phases were separated and the aqueous extracted with EtOAc (3 × 10 mL), the organic solutions were combined, dried ($MgSO_4$) and concentrated *in vacuo*. The crude material was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 2:15:185) to give the title compound as a colourless oil (324 mg, 0.79 mmol, 69%).

$[\alpha]_D$: +37.7 (*c* = 0.53, $CHCl_3$, 26 °C).

R_f: 0.51 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:10:90).

FT IR: 3293, 2936, 2828, 2789, 1643, 1553, 1440, 1249, 848 cm^{-1}.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.83 (1H, dddd, *J* = 16.5, 10.8, 7.7, 5.6 Hz), 5.70 - 5.48 (2H, m), 5.26 - 5.01 (3H, m), 4.36 (1H, t, *J* = 5.3 Hz), 3.49 (1H, m), 3.32 (6H, s), 3.27 (1H, dt, *J* = 13.7, 4.9 Hz), 3.17 (1H, dt, *J* = 13.7, 7.1 Hz), 2.94 (1H, dt, *J* = 11.6, 3.5 Hz), 2.77 (1H, dd, *J* = 13.9, 7.7 Hz), 2.34 (1H, t, *J* = 9.1 Hz), 2.24 - 2.12 (2H, m), 1.98 (1H, td, *J* = 11.6, 2.8 Hz), 1.82 (1H, m), 1.75 - 1.59 (5H, m), 1.59 - 1.42 (4H, m), 1.06 (1H, qd, *J* = 12.2, 3.5 Hz), 0.02 (9H, s) ppm.

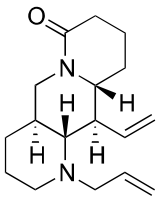
^{13}C NMR: ($CDCl_3$, 100 MHz) δ 174.1, 136.8, 133.1, 131.0, 119.3, 106.2, 70.7, 59.8, 54.6, 53.5, 44.6, 43.0, 38.1, 33.7, 29.9, 26.4, 24.7, 22.6, 0.0 ppm.

LRMS: (ESI+) 411.4 $[M+H^+]^+$.

HRMS: (ES+) for $C_{22}H_{43}N_2O_3Si^+$: requires 411.3037; found 411.3043 Da.

[4] Y. Nakamura, C. Shin, *Chem. Lett.* **1991**, *20*, 1953–1956. (b) J. Chen, J. Chen, Y. Xie, H. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 1024–1027.

(4a*S*,10a*R*,11*R*,11a*R*)-1-Allyl-11-vinyldecahydro-1H-pyrido[1,2-g][1,6]naphthyridin-7(2H)-one (13)



Chemical Formula: $C_{17}H_{26}N_2O$
Molecular Weight: 274.40

From cyclisation of aminal 12: To a solution of aminal **12** (170 mg, 0.47 mmol) in CH_2Cl_2 (5 mL) at 0 °C under N_2 was added TfOH (0.10 mL, 1.17 mmol) as a solution in CH_2Cl_2 (10 mL). After complete addition the reaction mixture was warmed to rt and stirred for 1 h. The reaction mixture was quenched with *sat*. $NaHCO_3$ (20 mL), the layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 × 15 mL), the organic solutions were combined, dried (Na_2SO_4) and concentrated *in vacuo*. The desired tricyclic product was isolated by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:7:92) as a colourless oil (95 mg, 0.35 mmol, 74%).

From cyclisation of acetal 15: To a solution of acetal **15** (265 mg, 0.65 mmol) in CH_2Cl_2 (15 mL) at 0 °C under N_2 was added BF_3•OEt_2 (0.20 mL, 1.61 mmol) dropwise. The reaction was warmed to rt and the reaction monitored by TLC (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:10:90). The reaction was stirred for 36 h. The reaction was quenched with *sat*. $NaHCO_3$ (15 mL) and the mixture stirred for 10 min. The phases were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 10 mL). The organic solutions were combined, washed with *sat*. brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude material was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:7:92) to afford the tricyclic product as a colourless oil (149 mg, 0.54 mmol, 84%).

$[\alpha]_D$: +32.5 (*c* = 1.30, $CHCl_3$, 24 °C).

R_f: 0.42 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:94).

FT IR: 3072, 2927, 2853, 1640, 1446 cm^{-1}.

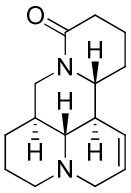
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.69 (1H, dddd, *J* = 17.1, 10.0, 8.9, 4.4 Hz), 5.54 (1H, dt, *J* = 17.1, 10.1 Hz), 5.24 (1H, dd, *J* = 10.1, 1.7 Hz), 5.17 - 5.08 (2H, m), 5.06 (1H, dt, *J* = 10.0, 1.5 Hz), 4.65 (1H, dd, *J* = 12.9, 4.4 Hz), 3.25 - 3.09 (3H, m), 3.04 (1H, dd, *J* = 13.2, 8.9 Hz), 2.63 (1H, td, *J* = 13.2, 2.1 Hz), 2.53 (1H, t, *J* = 10.1 Hz), 2.34 (2H, qt, *J* = 17.0, 6.1 Hz), 2.15 (1H, q, *J* = 10.1 Hz), 2.07 (1H, t, *J* = 12.5 Hz), 1.95 (1H, m), 1.86 - 1.51 (6H, m), 1.20 (1H, m), 1.06 (1H, m) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 169.2, 137.3, 136.6, 118.3, 116.8, 68.2, 59.1, 51.4, 49.8, 47.3, 46.9, 32.8, 31.7, 29.3, 27.7, 18.6, 17.5 ppm.

LRMS: (ESI+) 275.3 $[M+H^+]^+$.

HRMS: (ES+) for $C_{17}H_{27}N_2O^+$: requires 275.2118; found 275.2121 Da.

(+)-8,9-Didehydroallomatrine (16)



$C_{15}H_{22}N_2O$
Mol Wt: 246.3480

To a solution of diene **13** (110 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) under N_2 was added Hoveyda–Grubbs II catalyst (12.6 mg, 0.02 mmol) in three portions, after every 6 h at reflux. After 18 h (total reaction time), the reaction mixture was concentrated *in vacuo* and triturated with Et_2O (15 mL). The ruthenium salts were removed by filtration through a pad of celite. The pad was washed with Et_2O (2 × 10 mL). The organic solutions were combined and extracted with 1.0 M HCl (3 × 10 mL). The combined aqueous solution was basified with to pH 14 with 35% NH_4OH, then extracted with Et_2O (10 mL), EtOAc (10 mL) and $CHCl_3$ (2 × 10 mL). The organic solutions were combined, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by column chromatography (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:5:94) to give the tetracycle **16** as a white solid (69 mg, 0.28 mmol, 70%). Recrystallisation from *n*-hexane gave colourless platelets.

$[\alpha]_D$: +37.5 (*c* = 0.54, $CHCl_3$, 28 °C).

MP: 80.7 - 82.7 °C (*n*-hexane).

R_f: 0.25 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:6:93).

FT IR: 3037, 2927, 2855, 2749, 1621 cm^{-1}.

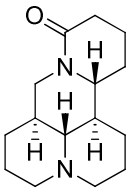
^{1}H NMR: ($CDCl_3$, 400 MHz) δ 5.78 (1H, dtt, *J* = 10.3, 2.5, 2.1 Hz), 5.67 (1H, ddt, *J* = 10.3, 2.5, 1.6 Hz), 4.76 (1H, dd, *J* = 13.3, 3.8 Hz), 3.33 (1H, dquin, *J* = 17.2, 2.5 Hz), 3.09 (1H, td, *J* = 9.8, 5.0 Hz), 2.99 (1H, dtd, *J* = 11.3, 2.9, 1.9 Hz), 2.71 (1H, ddt, *J* = 17.2, 4.4, 2.5 Hz), 2.45 (1H, m), 2.38 - 2.14 (3H, m), 2.08 - 1.97 (2H, m), 1.88 (1H, m), 1.78 - 1.39 (7H, m), 0.99 (1H, m) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 169.5, 127.3, 123.1, 66.4, 59.4, 55.7, 54.5, 46.9, 46.4, 39.1, 32.7, 27.7, 27.3, 24.5, 19.3 ppm.

LRMS: (ESI+) 247.3 $[M+H^+]^+$, 288.3 $[M+MeCN+H^+]^+$.

HRMS: (ES+) for $C_{15}H_{23}N_2O^+$: requires 247.1805; found 247.1801 Da.

(+)-Allomatrine (1)



$C_{15}H_{24}N_2O$
Mol Wt: 248.3639

A suspension of **16** (45 mg, 0.18 mmol) and 5 wt % Pd/C (20 mg) in EtOH (5 mL) was placed under a H_2 atmosphere (CAUTION! Explosive gas) and stirred for 16 h. Upon completion, the reaction was filtered through a plug of celite, taking care not to allow the Pd residues to dry out. The plug was washed with EtOH (3 × 5 mL) and the solvent removed from the filtrate *in vacuo* to give a white solid. The crude material was purified by recrystallisation from *n*-hexane to give (+)-allomatrine (**1**) as a white crystalline solid (43 mg, 0.17 mmol, 94%). Physical and spectroscopic data were consistent with reported values.[5]

Recorded data:

$[\alpha]_D$: +76.1 (*c* = 1.05, EtOH, 30 °C); [Lit. +77.9[5c] (EtOH, 22 °C), +82.3[5d] (*c* = 1.53, EtOH, 26 °C) and +78.1[6] (*c* = 3.30, EtOH, 25 °C)]. +51.2 (*c* = 1.07, $CHCl_3$, 32 °C); [Lit.[6] for leontine ((–)-allomatrine, (**3**)): −78.0 (EtOH).

MP: 98 - 101 °C (pet. ether); [Lit.[5c,d] 103 - 105 °C (pet. ether); 103 - 104 °C (pet. ether)].

R_f: 0.30 (*eluent*: 35% NH_4OH/MeOH/CH_2Cl_2 - 1:10:90).

FT IR: 2925, 2854, 2804, 2755, 2677, 1622, 1445, 1418 cm^{-1}.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ 4.69 (1H, dd, *J* = 12.9, 3.9 Hz), 3.00 (1H, td, *J* = 9.4, 5.4 Hz), 2.85 (2H, m), 2.42 (1H, m), 2.27 (1H, m), 2.17 (1H, t, *J* = 12.9 Hz), 2.11 - 1.92 (3H, m), 1.89 - 1.78 (2H, m), 1.77 - 1.52 (6H, m), 1.52 - 1.39 (2H, m), 1.35 (1H, t, *J* = 9.4 Hz), 1.27 (1H, m), 1.03 - 0.83 (2H, m) ppm.

^{13}C NMR: ($CDCl_3$, 100 MHz) δ 169.1, 70.7, 60.1, 56.4, 55.8, 46.1, 46.0, 38.9, 32.7, 28.2, 27.4, 26.7, 24.5, 19.3 ppm .

LRMS: (ESI+) 249.4 $[M+H^+]^+$, 312.4 $[M+MeCN+Na^+]^+$.

HRMS: (ES+) for $C_{15}H_{25}N_2O^+$: requires 249.1961; found 249.1959 Da. For $C_{15}H_{24}N_2NaO$: requires 271.1781; found 271.1779 Da.

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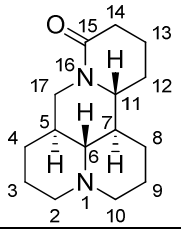
[5] Allomatrine: (a) F. Bohlmann, R. Zeisberg, *Chem. Ber.* **1975**, *108*, 1043–1051. (b) V. Galasso, F. Asaro, F. Berti, B. Pergolese, B. Kovac, F. Pichierri, *Chem. Phys.* **2006**, *330*, 457–468. (c) E. Ochiai, S. Okuda, H. Minato, *Yakugaku Zasshi.* **1952**, *72*, 781–784. (d) S. Okuda, M. Yoshimoto, K. Tsuda, *Chem. Pharm. Bull.* **1966**, *14*, 275–279. (e) F. Bohlmann, D. Schumann, *Tetrahedron Lett.* **1965**, 2435.

[6] Leontine: F. Rulko, N. F. Proskurnina, *Zh. Obshch. Khim.* **1961**, *31*, 308–313.

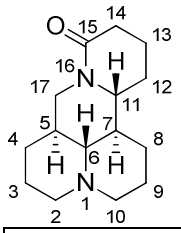
Supporting Information

Table 1: ^{13}C NMR Data for (+)-allomatrine (**1**), and comparison with reported data



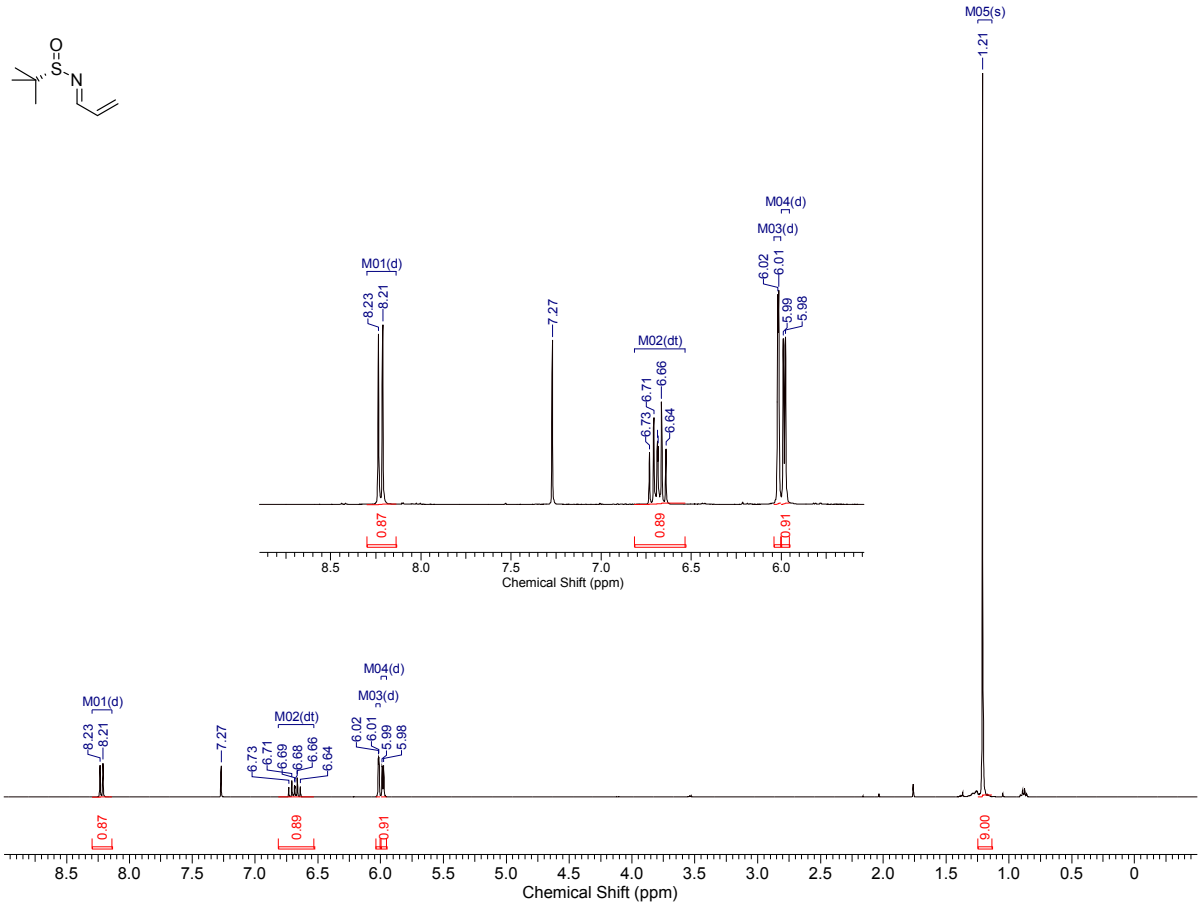
Assignment	Recorded data (100 MHz, $CDCl_3$) δ (ppm)	Ref. 5a: ^{13}C NMR (20 MHz, $CDCl_3$) δ (ppm)	Ref. 5b: ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)
C-2	55.8	55.9	56.3
C-3	24.5	24.7	24.5
C-4	27.4	27.5	27.4
C-5	38.9	39.1	38.8
C-6	70.7	70.9	70.0
C-7	46.0	46.2	46.0
C-8	26.7	26.9	26.6
C-9	24.5	24.7	24.5
C-10	56.4	56.0	55.7
C-11	60.1	60.3	60.1
C-12	28.2	28.4	28.2
C-13	19.3	19.4	19.2
C-14	32.7	32.8	32.7
C-15	169.1	-	169.2
C-17	46.1	46.2	46.1

Table 2: ^{1}H NMR Data for (+)-allomatrine (**1**), and comparison with available reported data

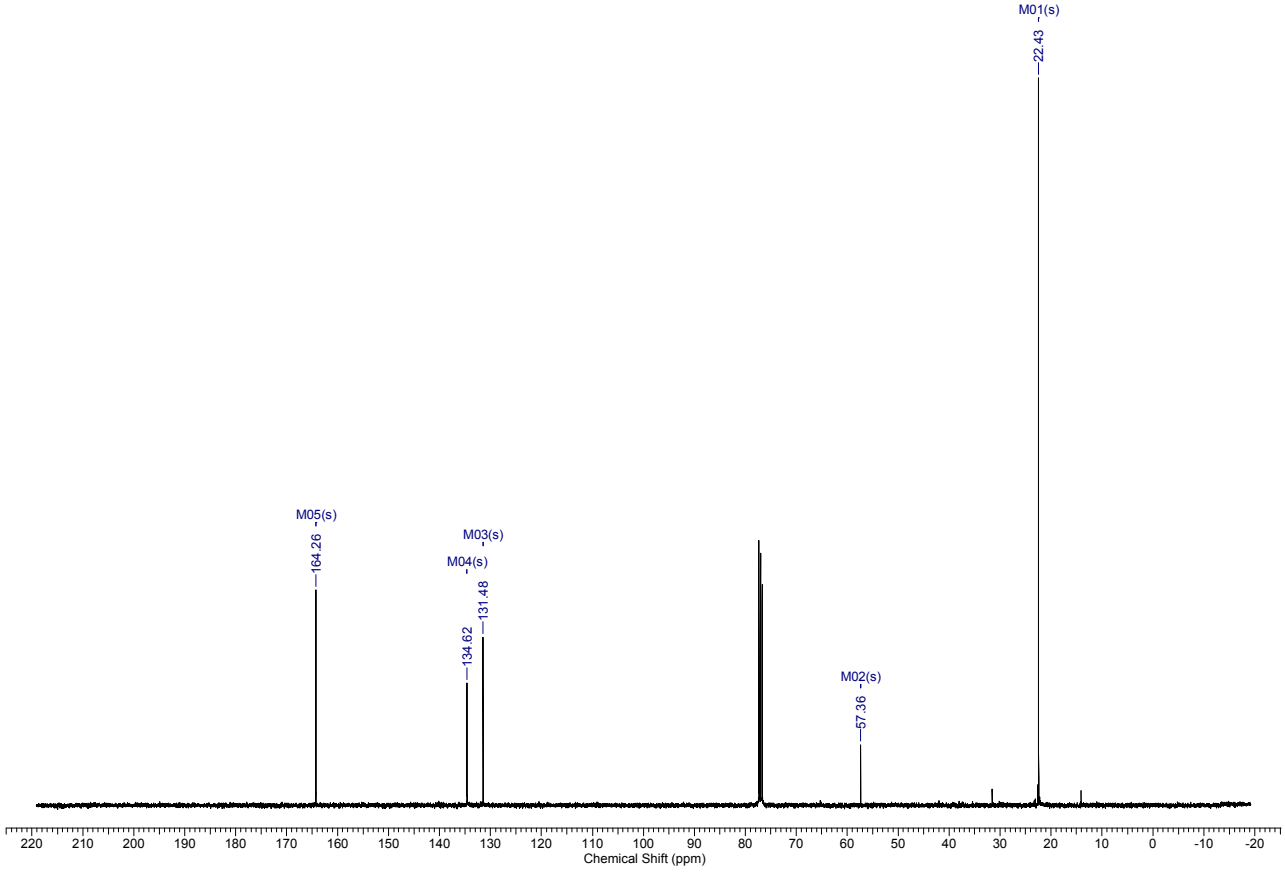


Recorded data (400 MHz, $CDCl_3$) δ (ppm)	Ref. 5e: ^{1}H NMR (100 MHz, $CDCl_3$)	Ref. 5b: Reported *J* values (400 MHz, $CDCl_3$)
4.69 (1H, dd, J = 12.9, 3.9 Hz, H_{17eq})	4.69 (1H, dd, J = 12.6, 3.2 Hz, H_{17eq})	$^{3}J(H_5H_{17eq})$ = 3.8 Hz $^{2}J(H_{17ax}H_{17eq})$ = –13.2 Hz
3.00 (1H, td, J = 9.4, 5.4 Hz, H_{11})	2.9 (m, H_{11})	$^{3}J(H_7H_{11})$ = 9.5 Hz
2.85 (2H, m, H_{2ax} & H_{10ax})		
2.42 (1H, m, H_{14eq})		
2.27 (1H, ddd, J = 17.0, 11.1, 5.5 Hz, H_{14ax})		
2.17 (1H, t, J = 12.9 Hz, H_{17ax})		$^{3}J(H_5H_{17ax})$ = 13.3 Hz $^{2}J(H_{17ax}H_{17eq})$ = –13.2 Hz
2.11 - 1.92 (3H, m, H_{2eq}, H_{4eq} & H_{10eq})		
1.89 - 1.78 (2H, m, H_{8eq} & H_{13eq})		
1.75 - 1.58 (5H, m, H_3, H_9 & H_{12eq})		
1.58 (1H, m, H_{13ax})		
1.52 - 1.39 (2H, m, H_5 & H_{4ax})		
1.35 (1H, t, J = 9.4 Hz, H_6)		$^{3}J(H_5H_6)$ = 9.5 Hz $^{3}J(H_6H_7)$ = 9.5 Hz
1.27 (1H, m, H_7)		
1.03 - 0.83 (2H, m, H_{8ax} & H_{12ax})		

(*S,E*)-*N*-Allylidene-2-methylpropane-2-sulfinamide (6). ^{1}H NMR (400 MHz, $CDCl_3$)

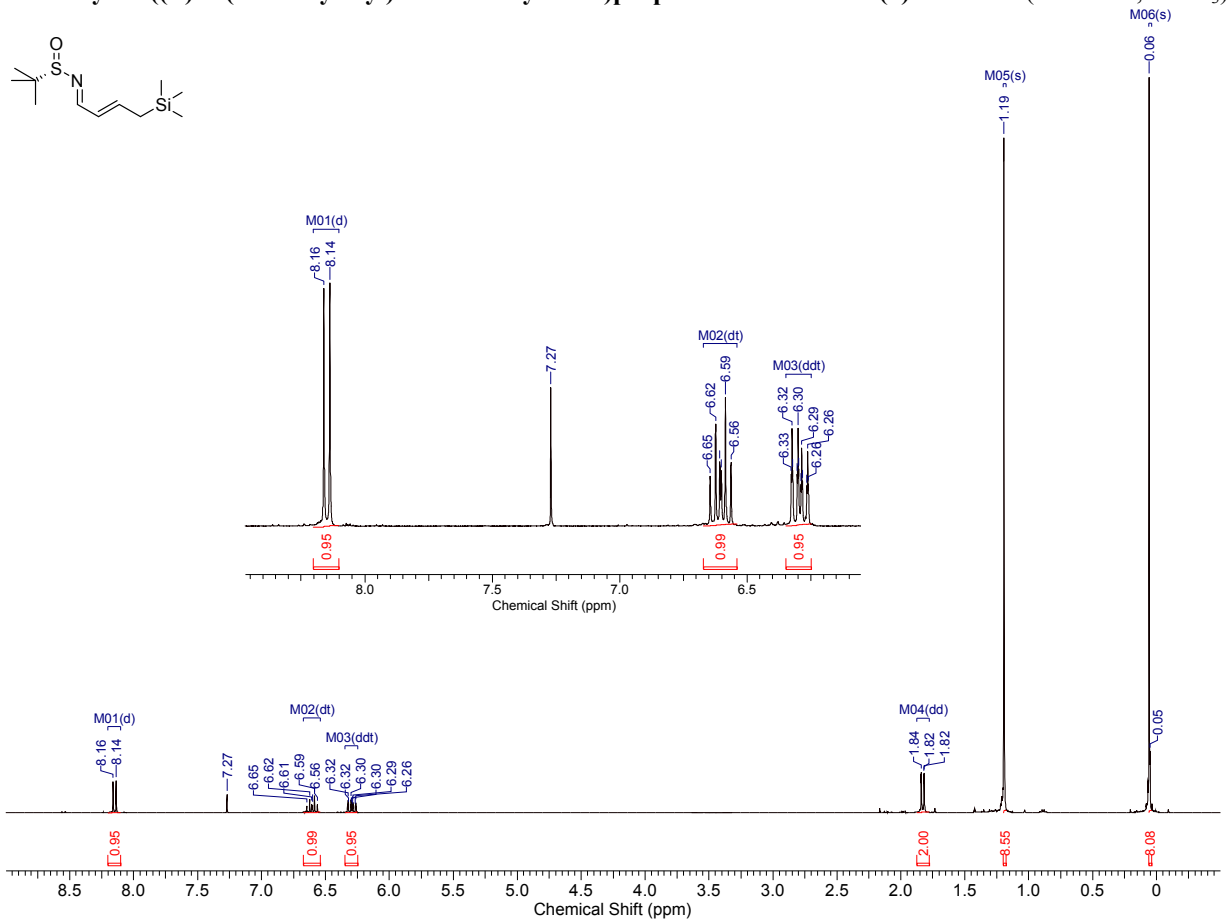


^{13}C NMR (100 MHz, $CDCl_3$)

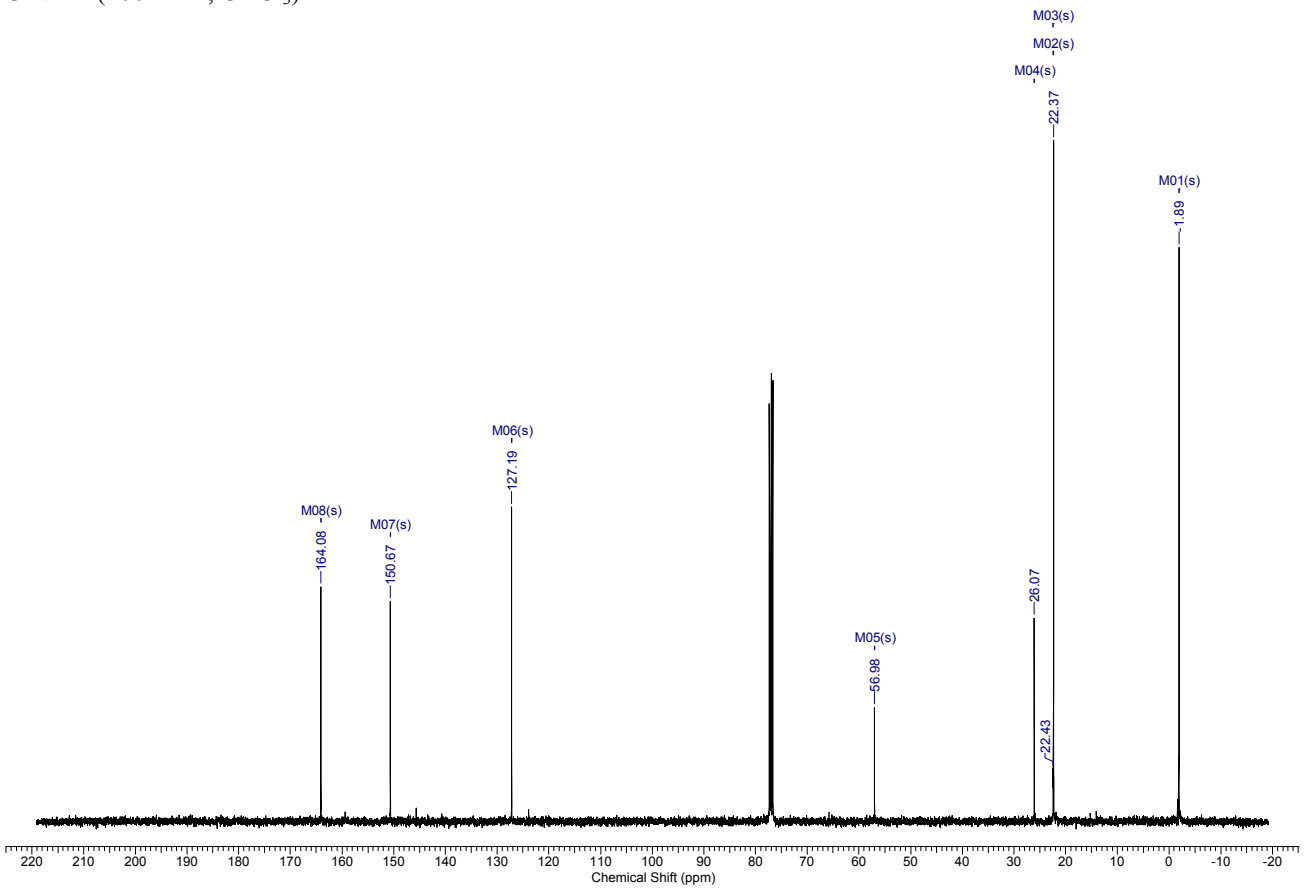


Supporting Information

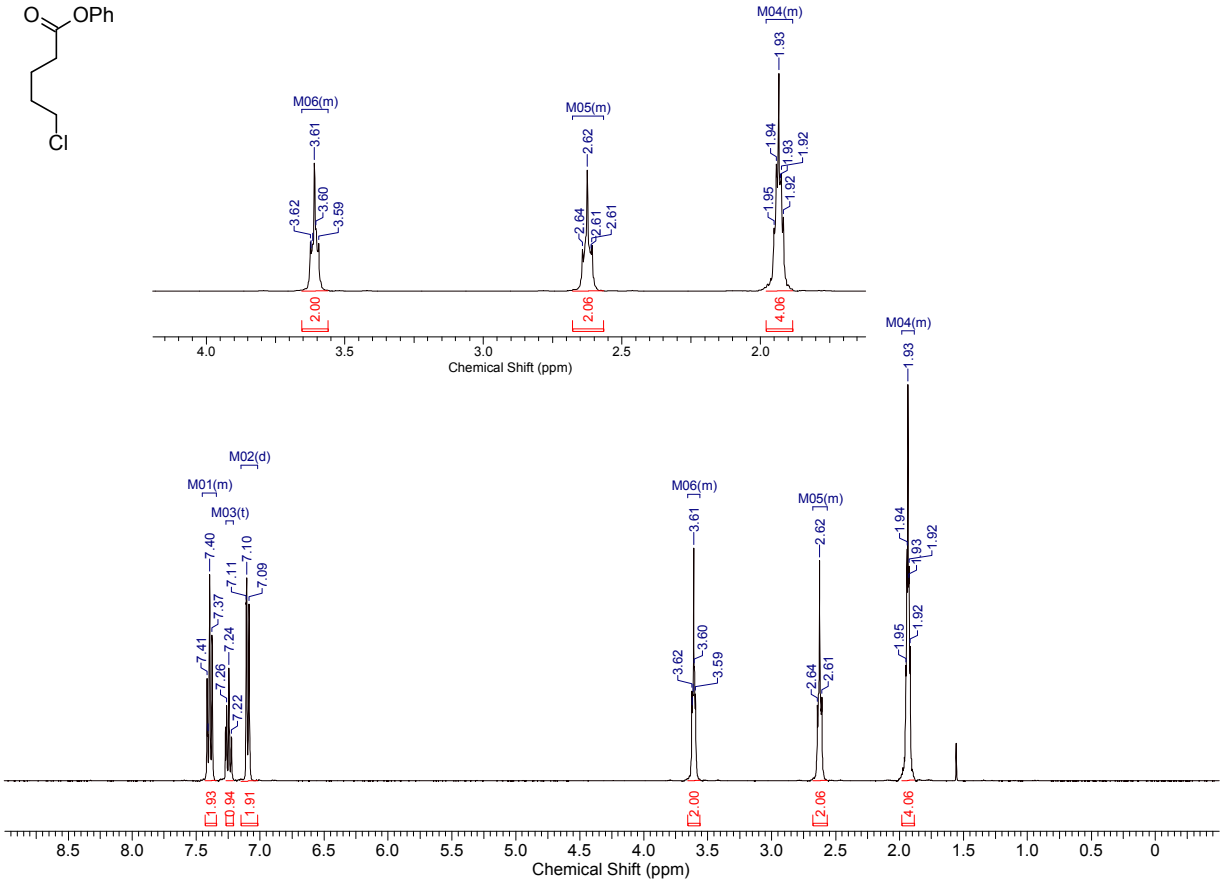
(*S*,*E*)-2-Methyl-*N*-((*E*)-4-(trimethylsilyl)but-2-en-1-ylidene)propane-2-sulfinamide (7). ^{1}H NMR (400 MHz, $CDCl_3$)



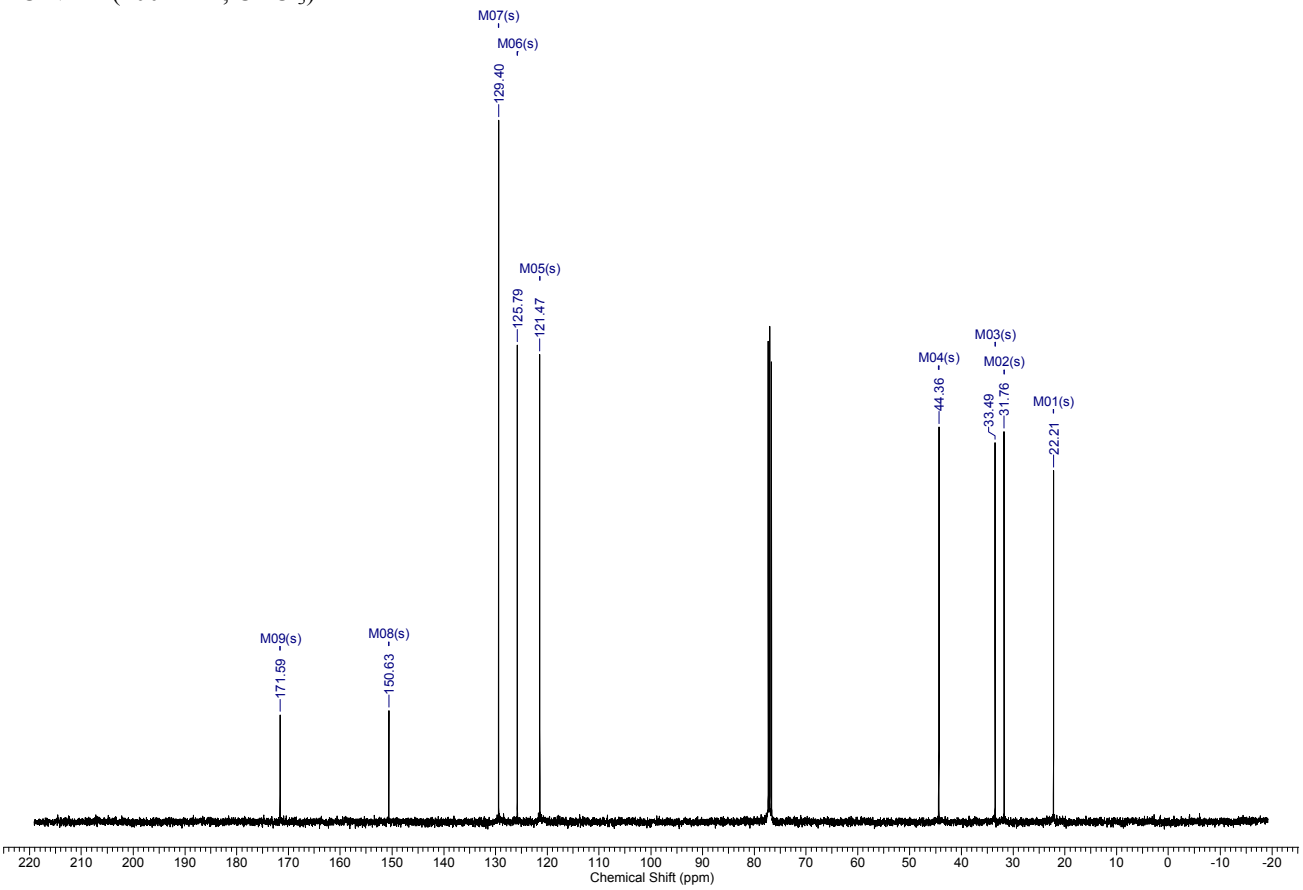
^{13}C NMR (100 MHz, $CDCl_3$)



Phenyl 5-chlorovalerate (8). ^{1}H NMR (400 MHz, $CDCl_3$)

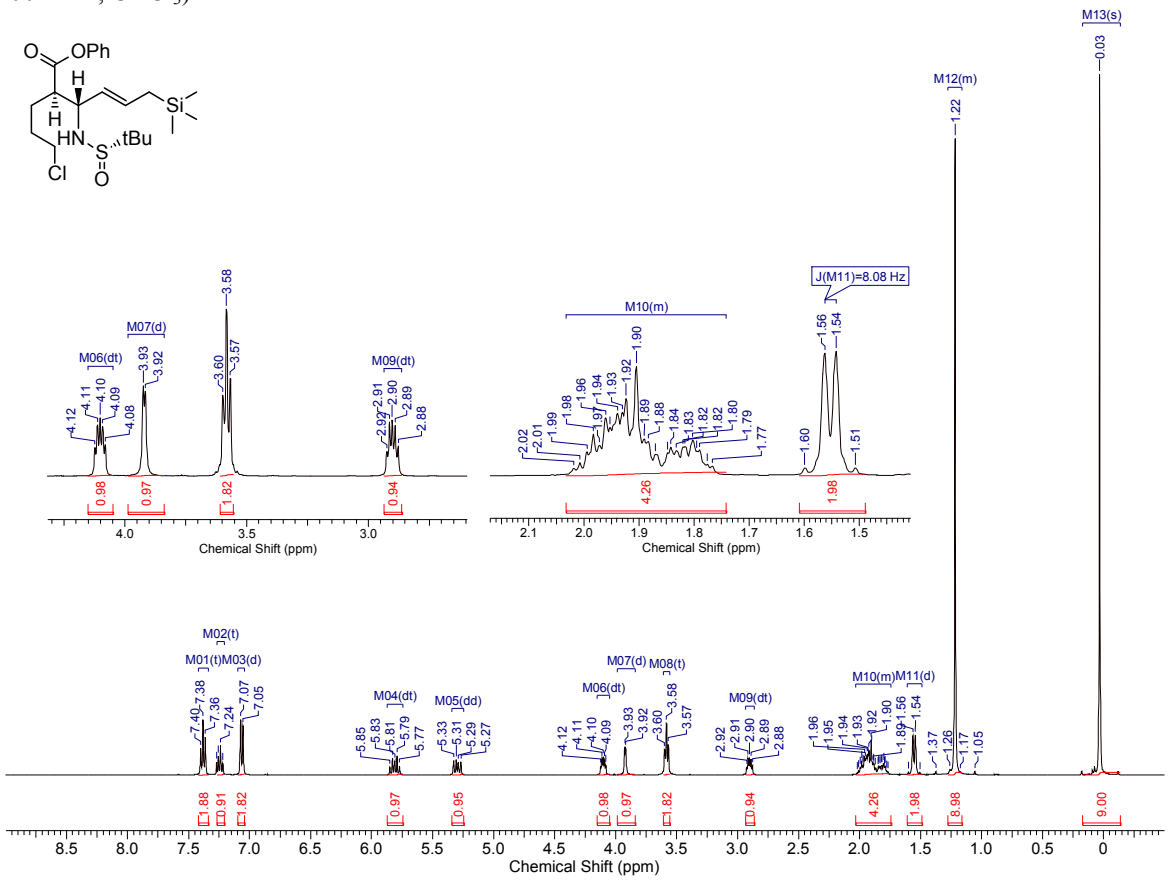


^{13}C NMR (100 MHz, $CDCl_3$)

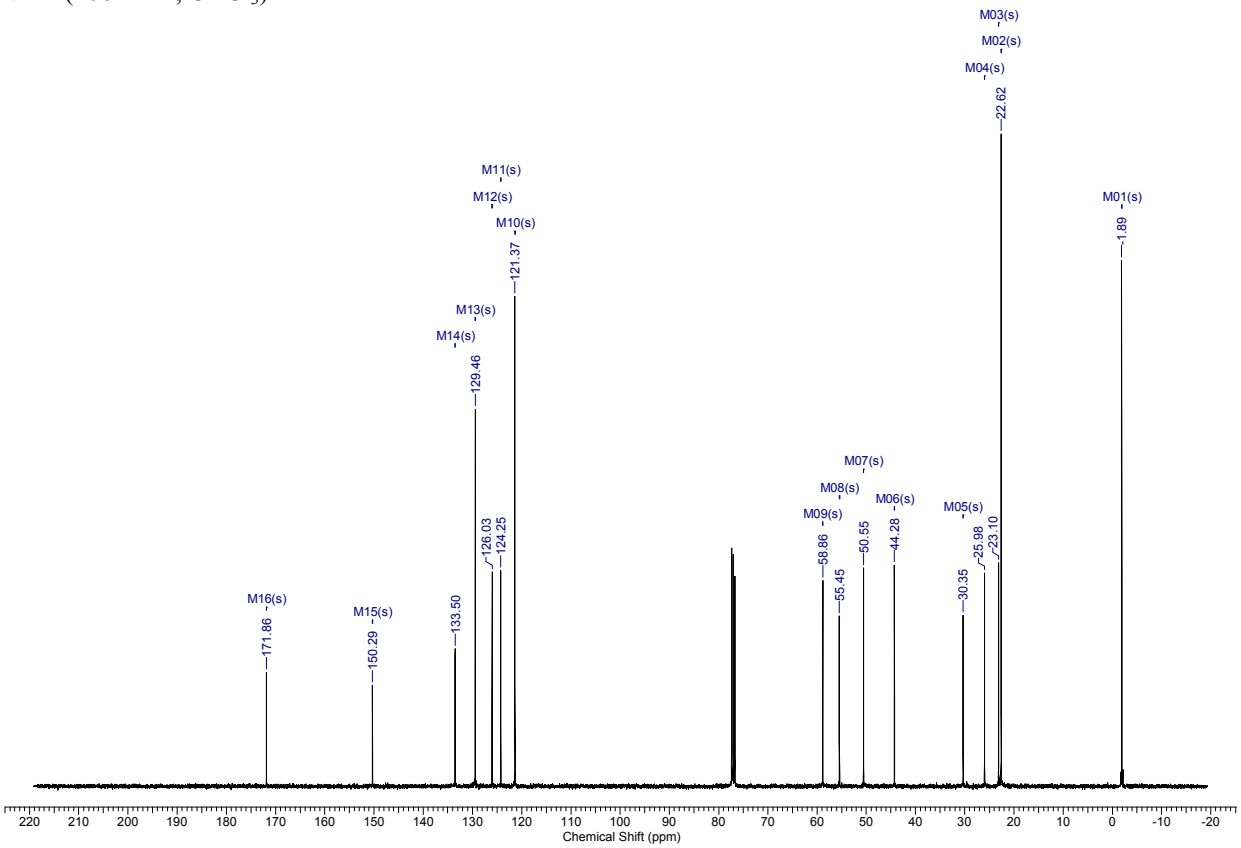


Supporting Information

(2*R*,3*S*,*E*)-Phenyl 2-(3-chloropropyl)-3-((*S*)-1,1-dimethylethylsulfinamido)-6-(trimethylsilyl)hex-4-enoate (5). ^{1}H NMR (400 MHz, $CDCl_3$)

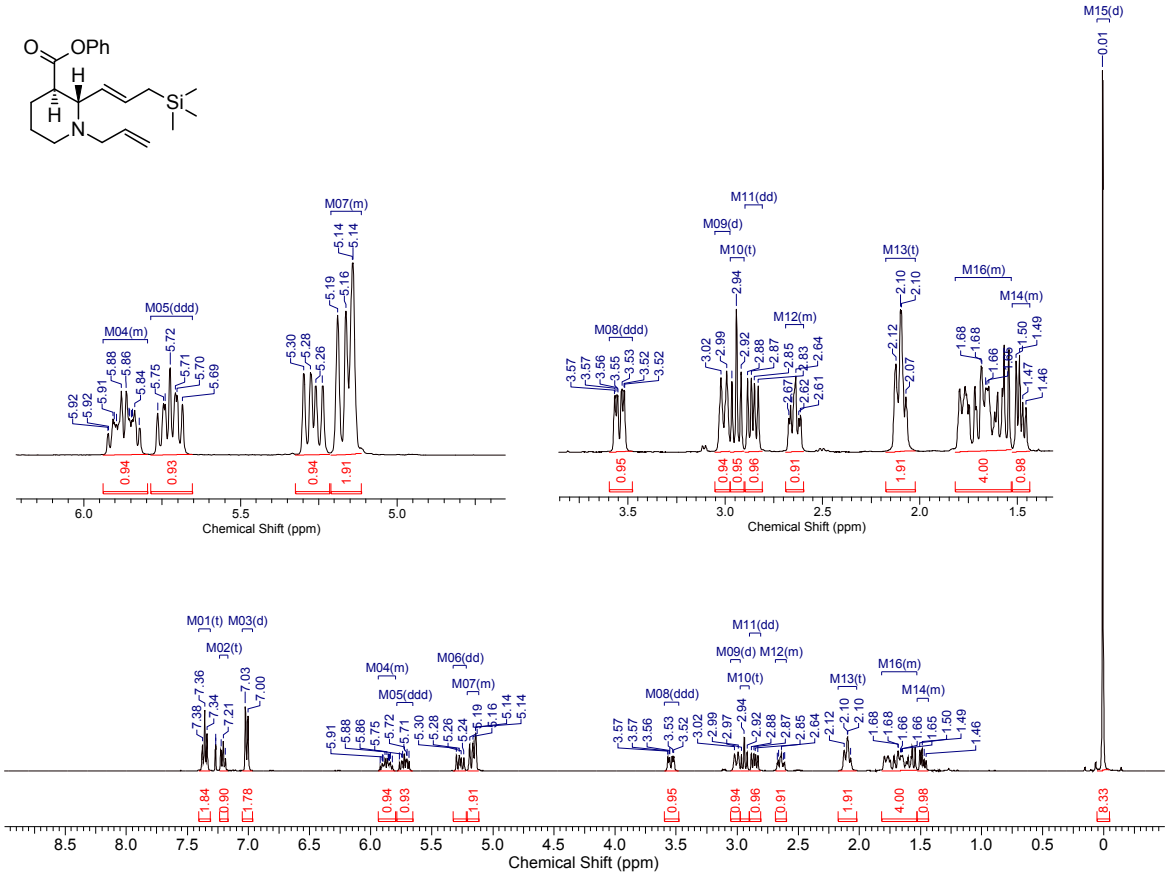


^{13}C NMR (100 MHz, $CDCl_3$)

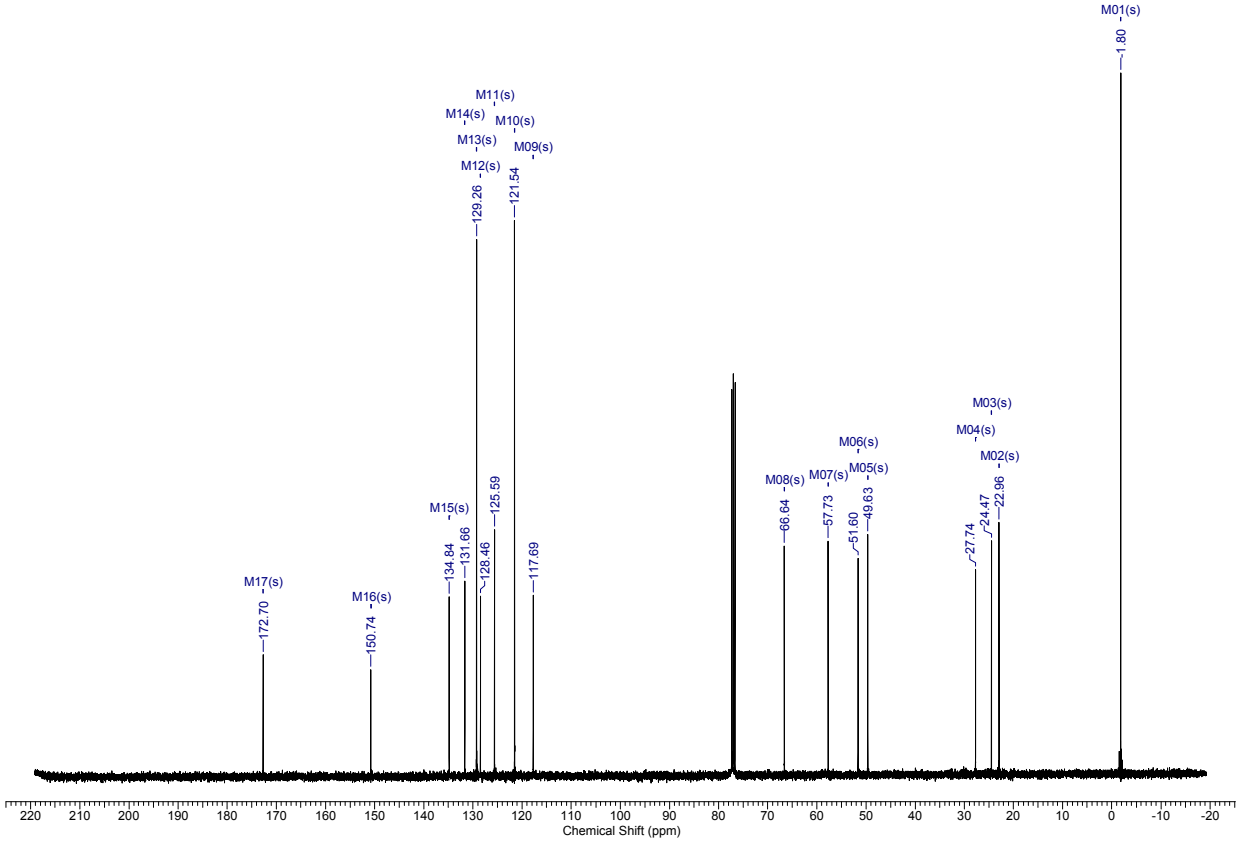


Supporting Information

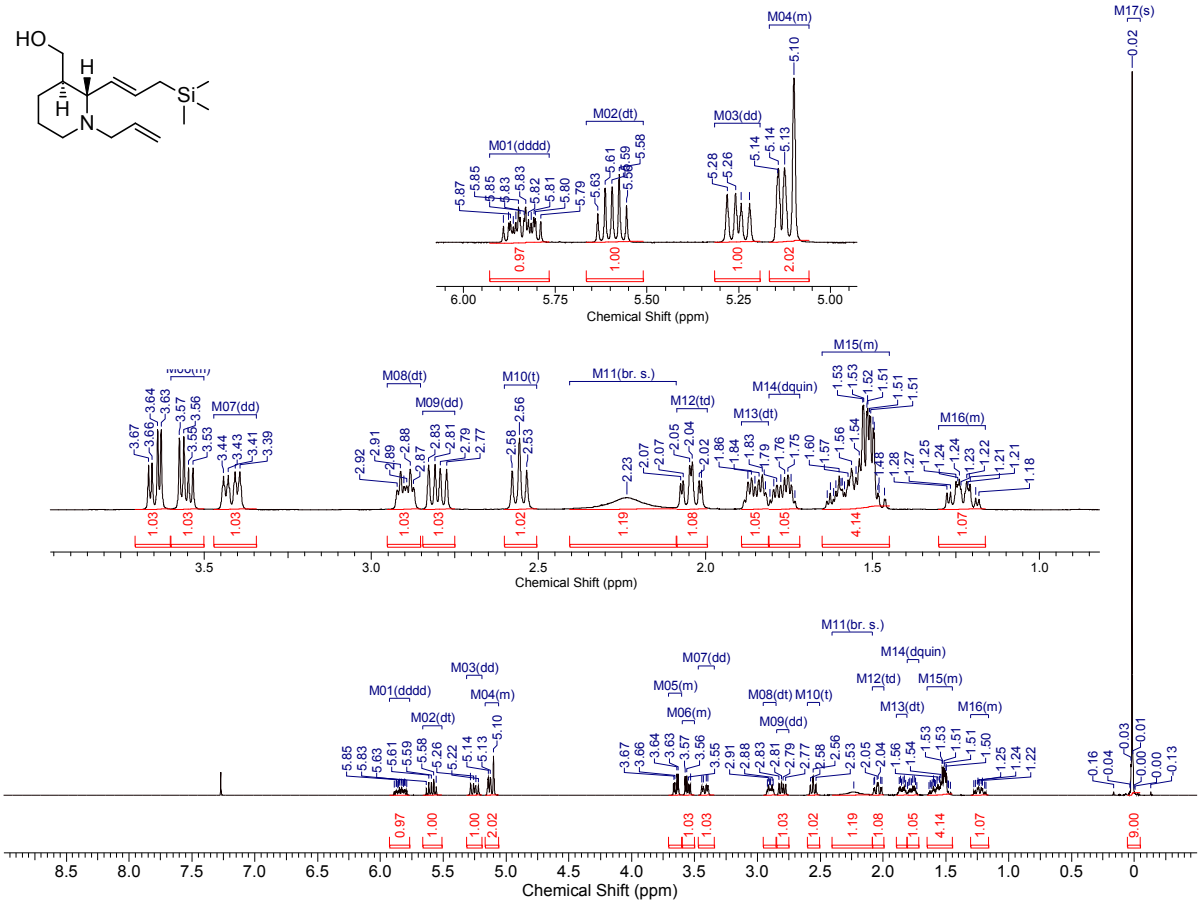
(2*S*,3*R*)-Phenyl 1-allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidine-3-carboxylate (9). ^{1}H NMR (400 MHz, $CDCl_3$)



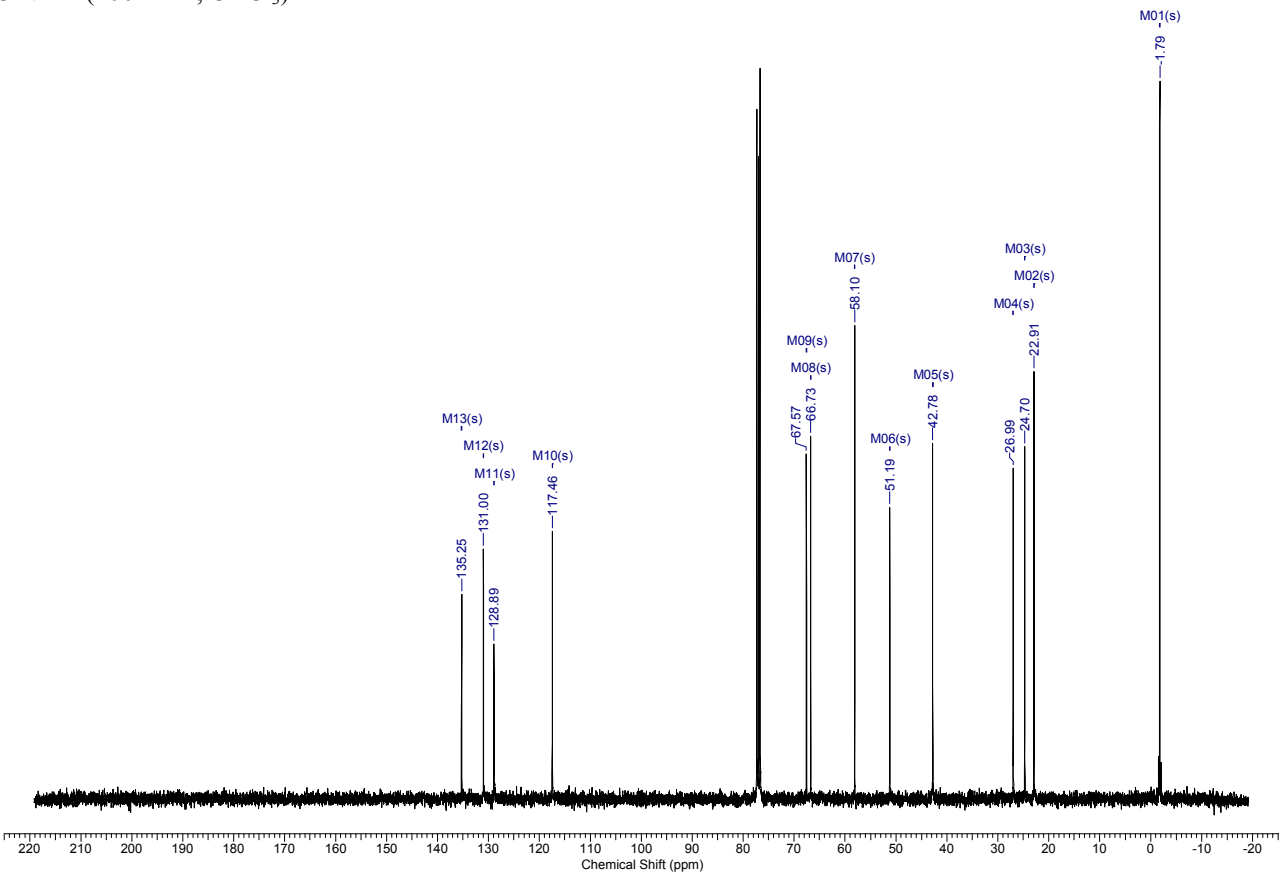
^{13}C NMR (100 MHz, $CDCl_3$)



((2*S*,3*R*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methanol (10). ^{1}H NMR (400 MHz, $CDCl_3$)

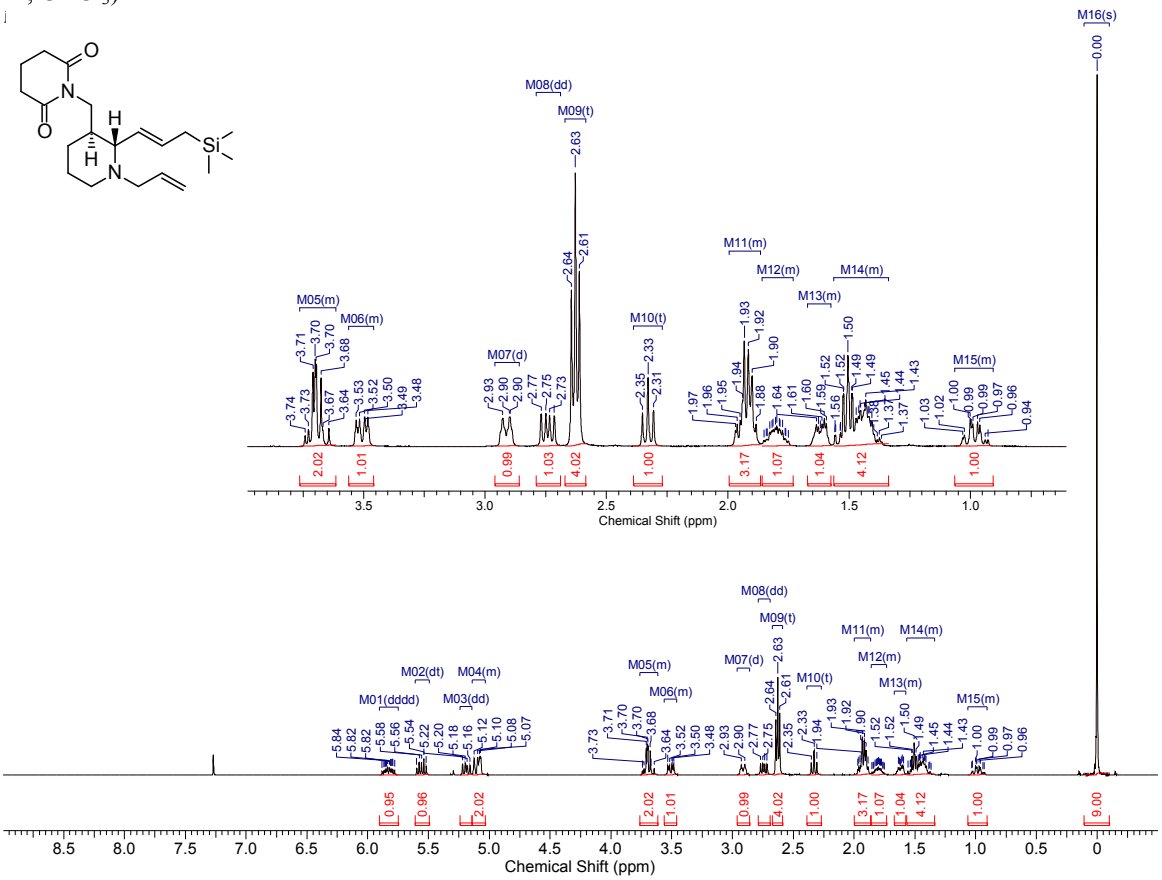


^{13}C NMR (100 MHz, $CDCl_3$)

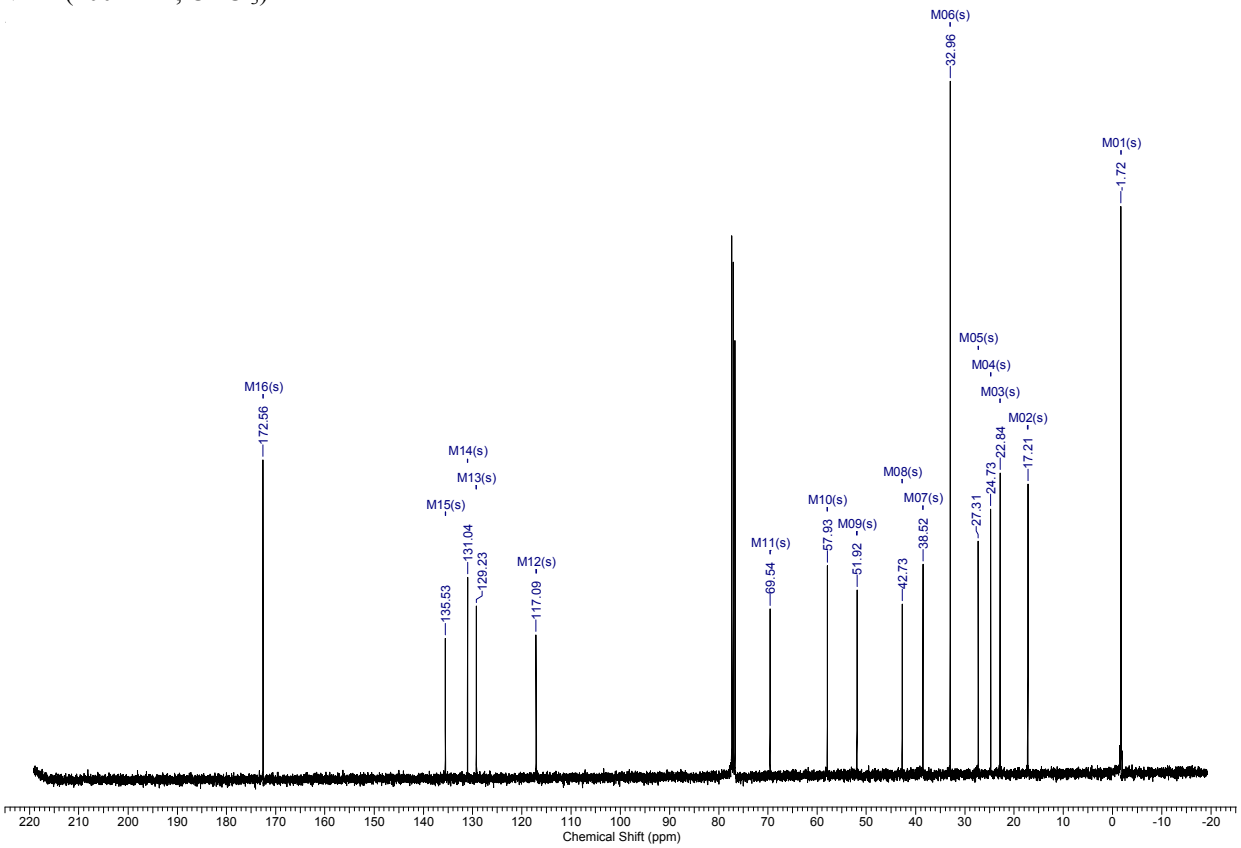


Supporting Information

1-(((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)piperidine-2,6-dione (11). ^{1}H NMR (400 MHz, $CDCl_3$)

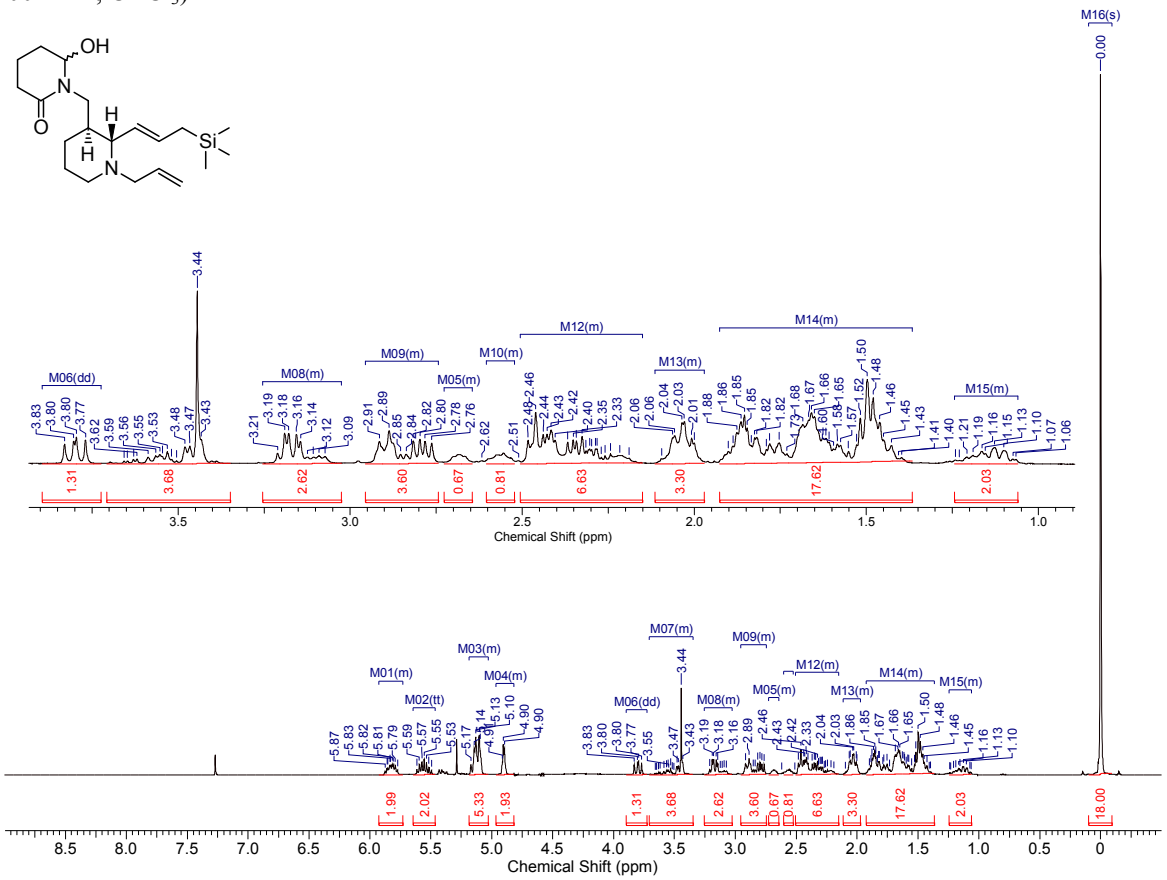


^{13}C NMR (100 MHz, $CDCl_3$)

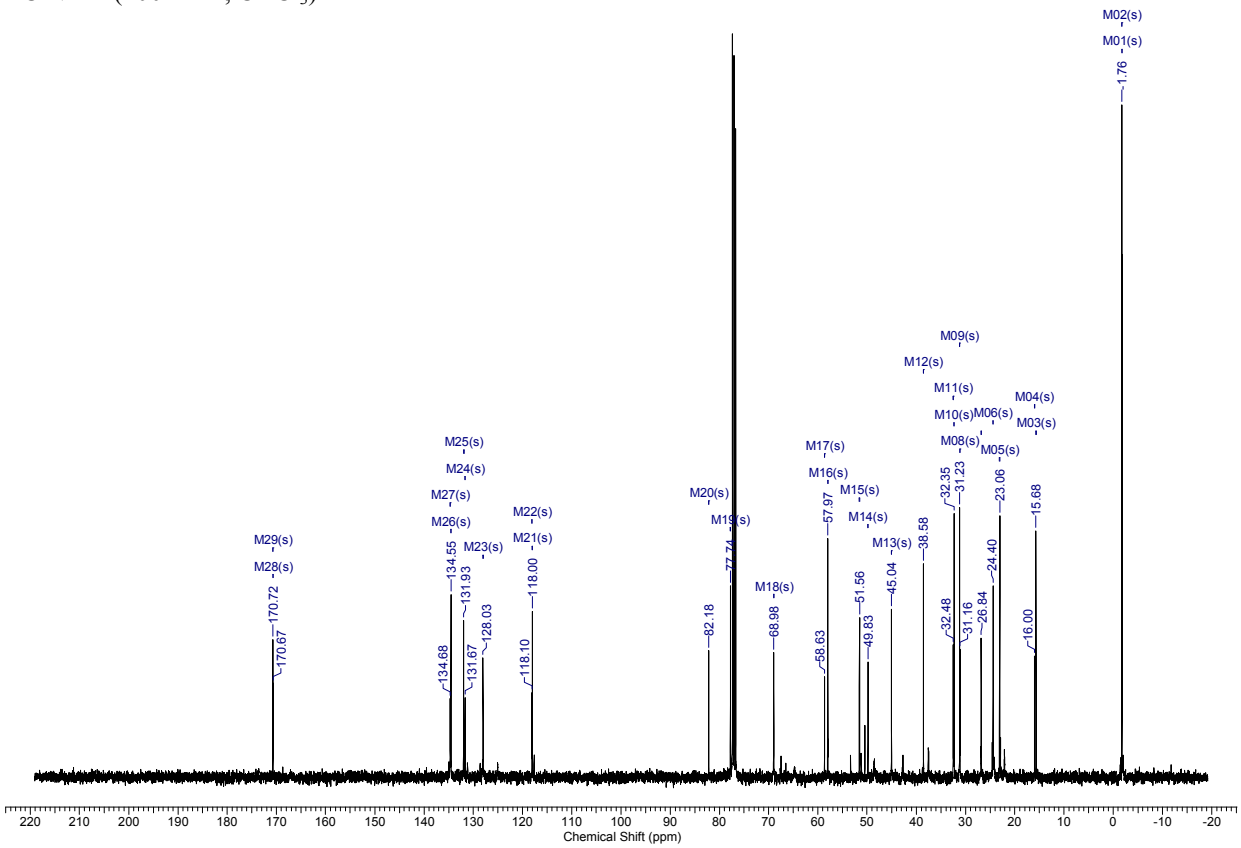


Supporting Information

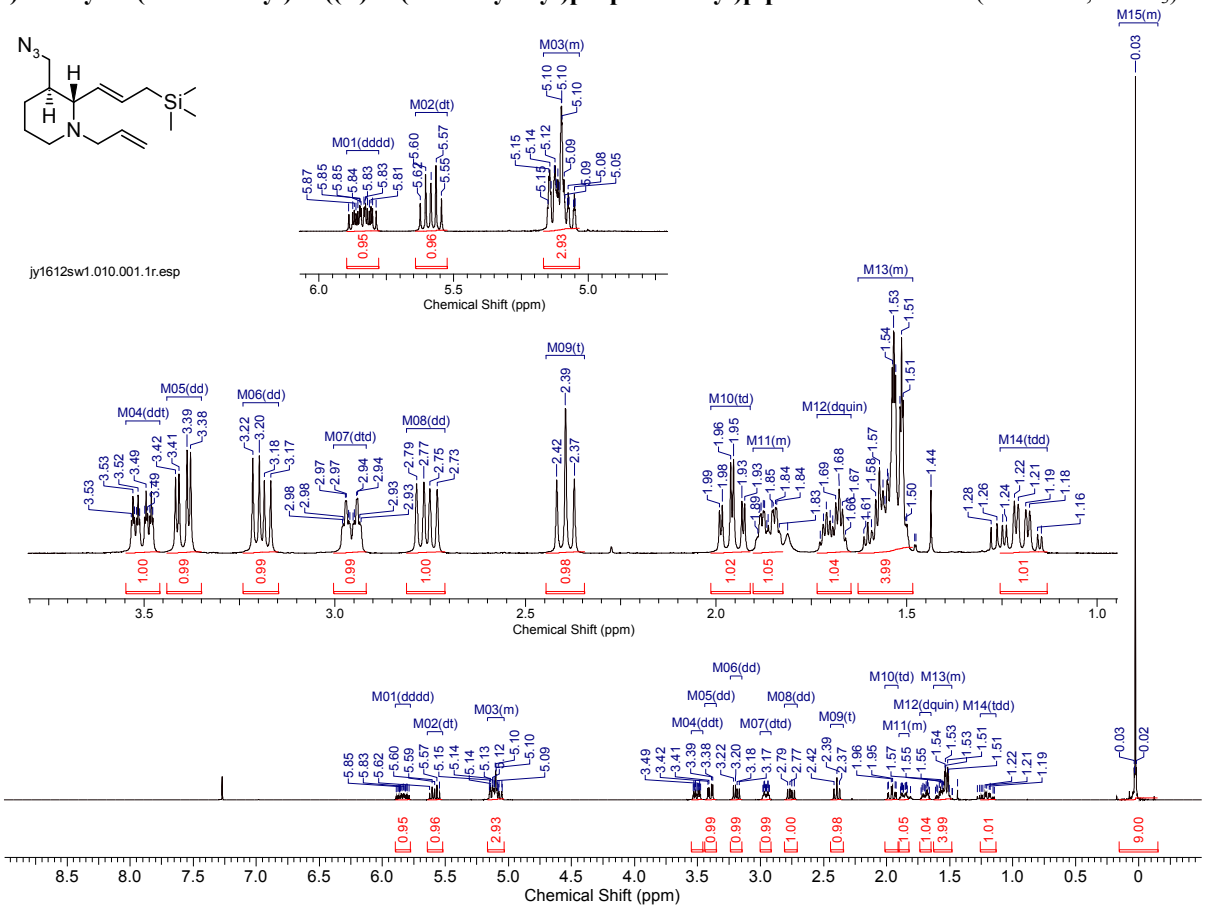
1-(((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)-6-hydroxypiperidin-2-one (12). ^{1}H NMR (400 MHz, $CDCl_3$)



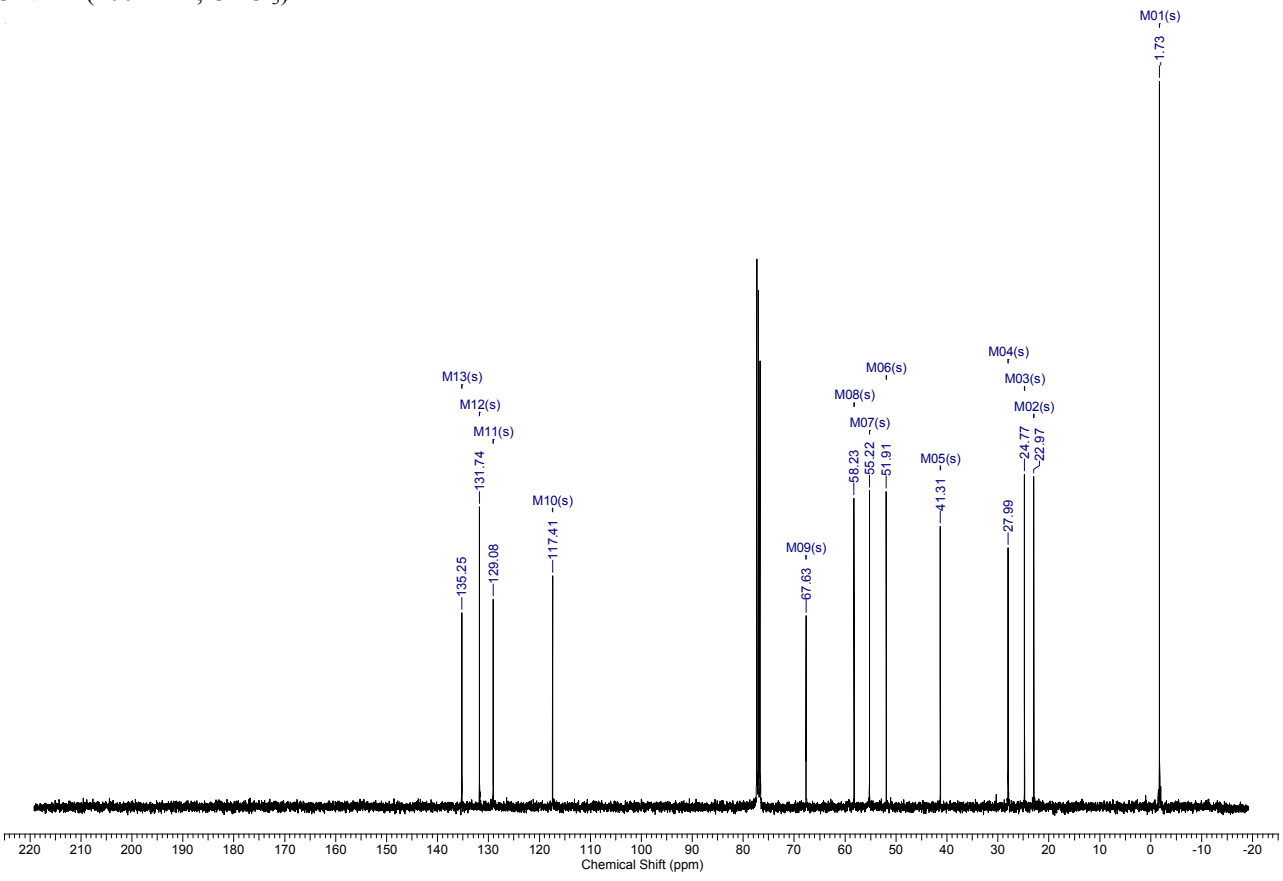
^{13}C NMR (100 MHz, $CDCl_3$)



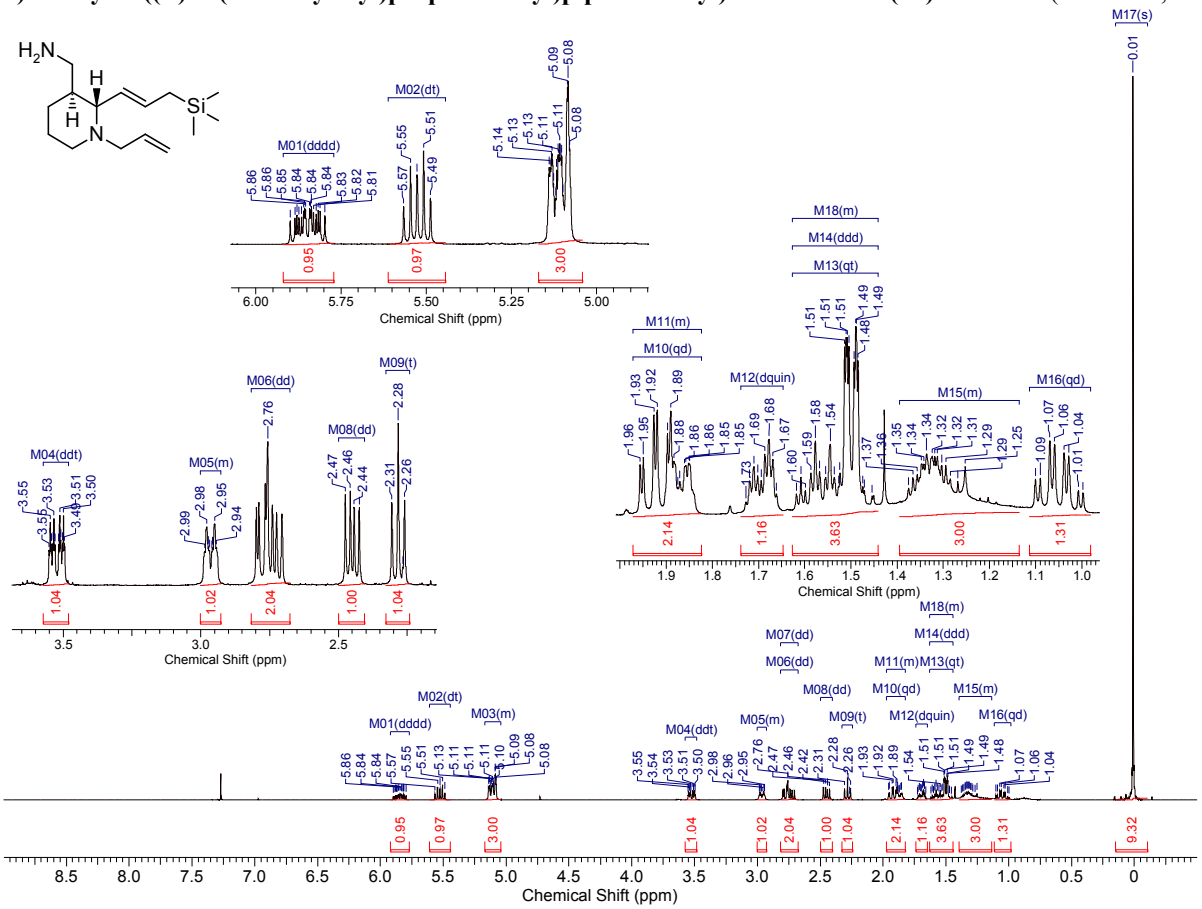
(2*S*,3*S*)-1-Allyl-3-(azidomethyl)-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidine. ^{1}H NMR (400 MHz, $CDCl_3$)



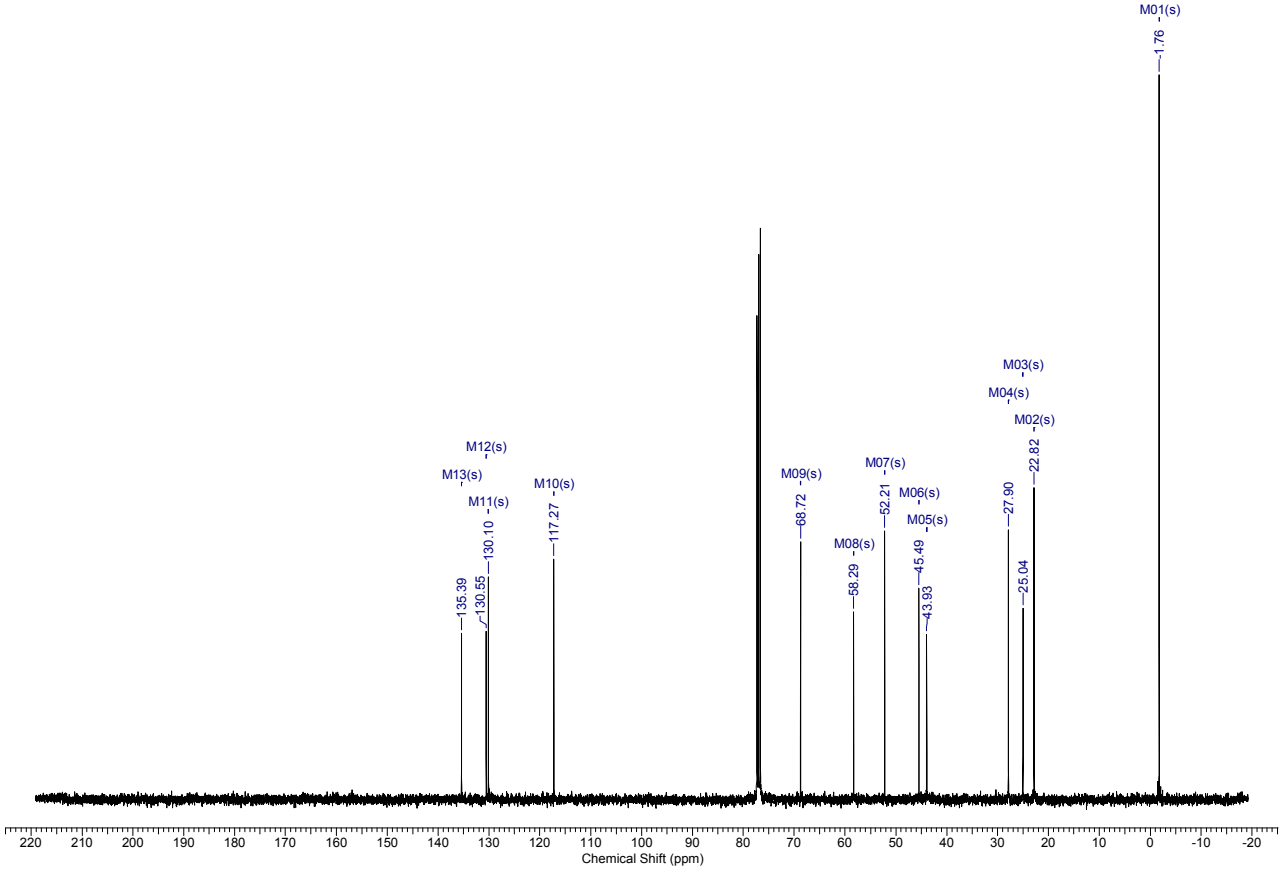
^{13}C NMR (100 MHz, $CDCl_3$)



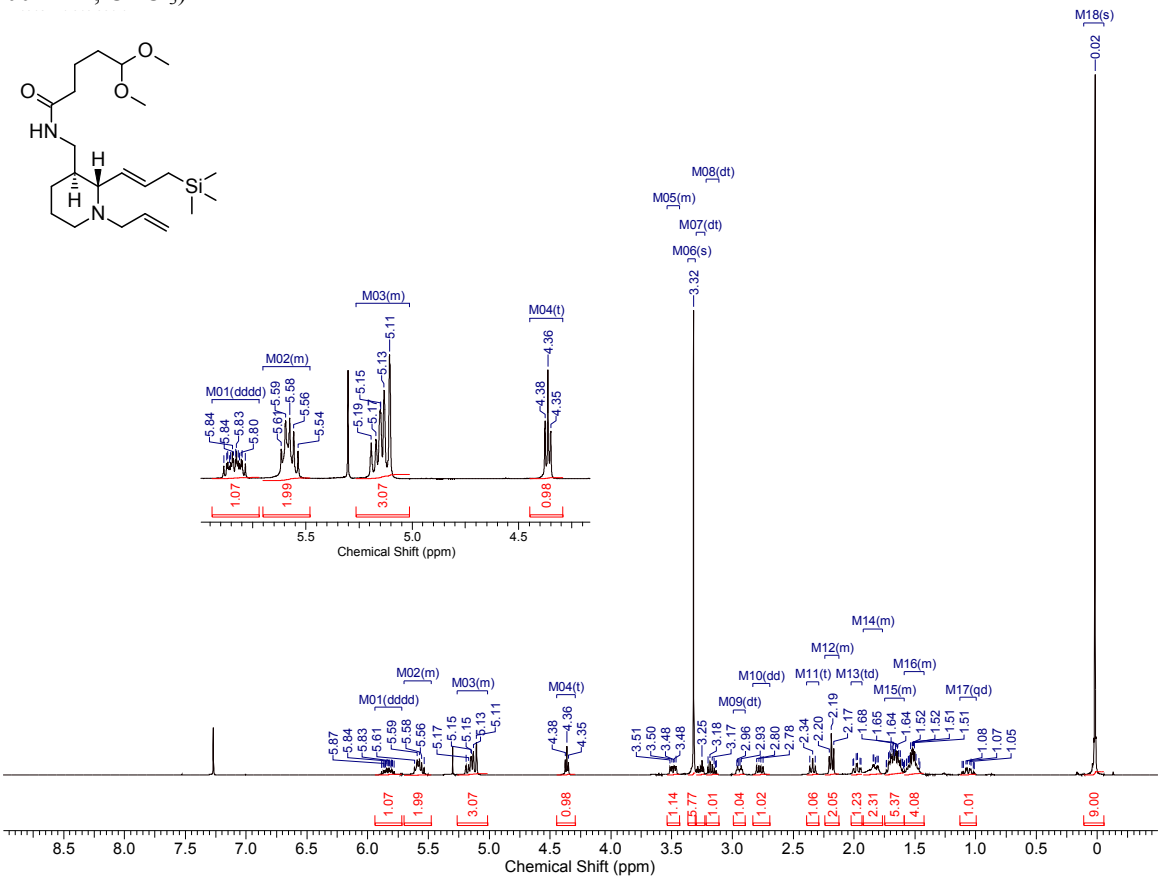
((2*S*,3*S*)-1-Allyl-2-((*E*)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methanamine (14). ^{1}H NMR (400 MHz, $CDCl_3$)



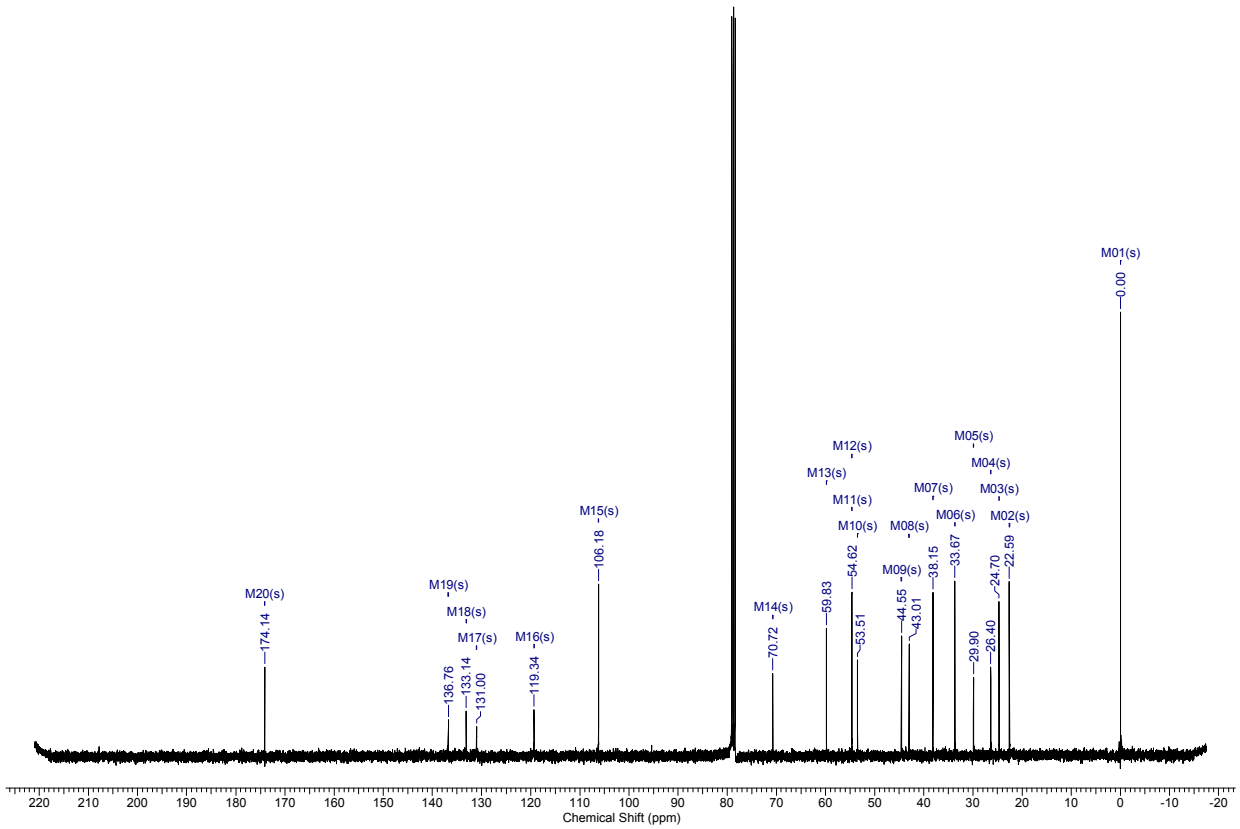
^{13}C NMR (100 MHz, $CDCl_3$)



_N_-(((2_S_,3_S_)-1-Allyl-2-((_E_)-3-(trimethylsilyl)prop-1-en-1-yl)piperidin-3-yl)methyl)-5,5-dimethoxypentanamide (15). ^{1}H NMR (400 MHz, $CDCl_3$)

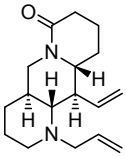


^{13}C NMR (100 MHz, $CDCl_3$)

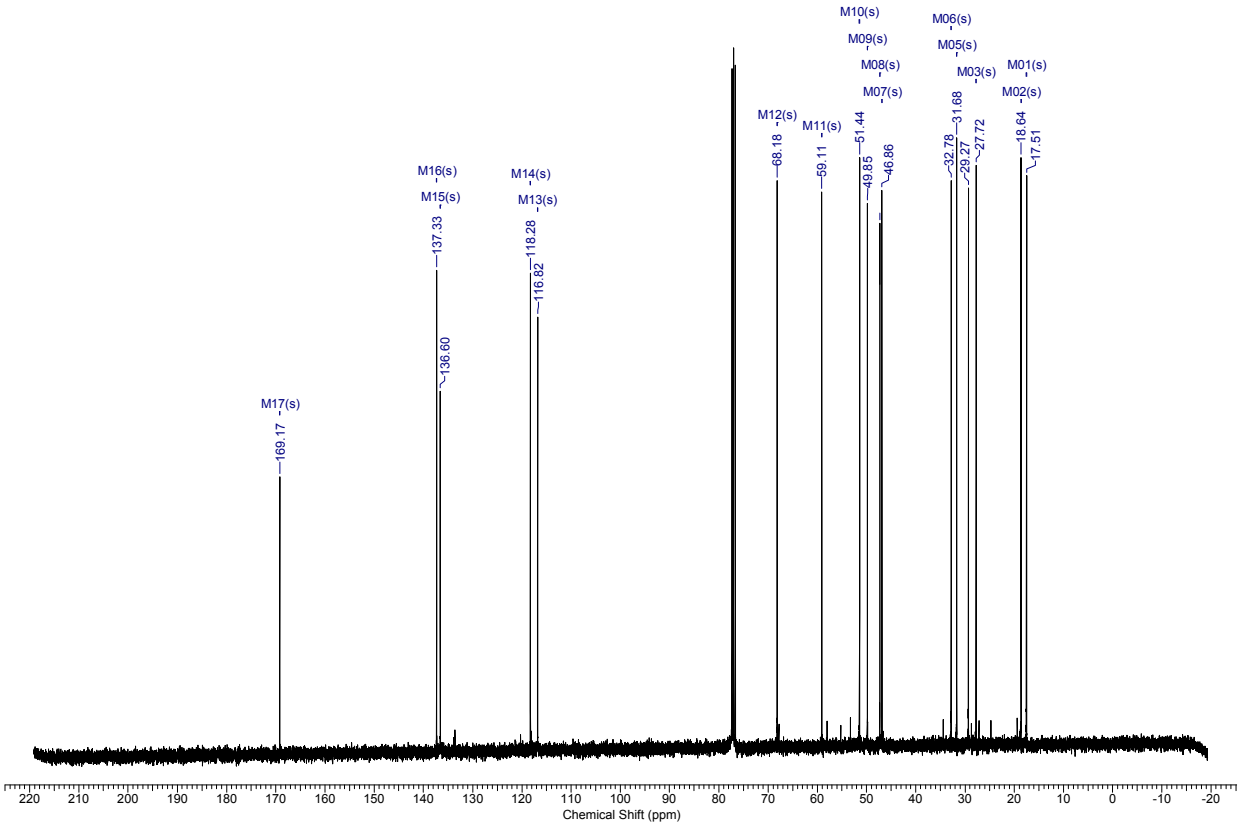


Supporting Information

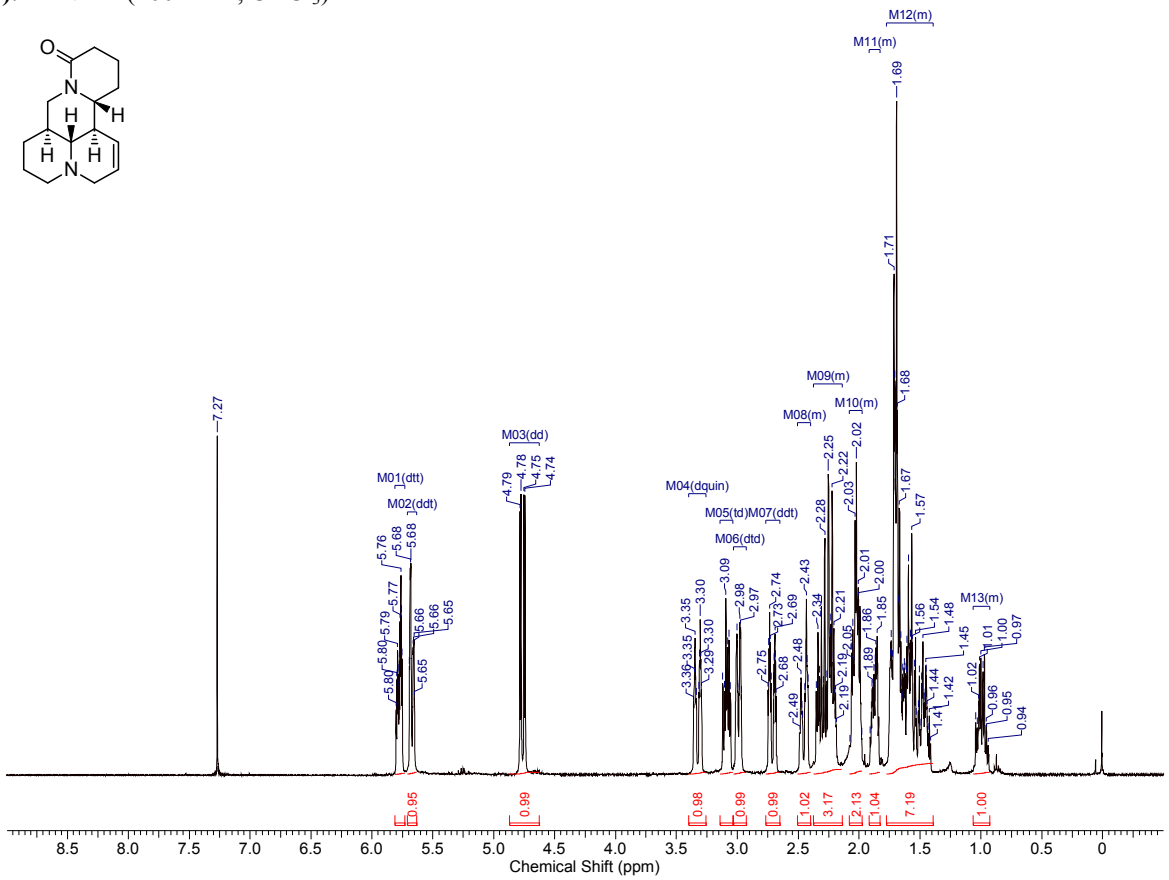
(4a*S*,10a*R*,11*R*,11a*R*)-1-Allyl-11-vinyldecahydro-1H-pyrido[1,2-g][1,6]naphthyridin-7(2H)-one (13). ^{1}H NMR (400 MHz, $CDCl_3$)



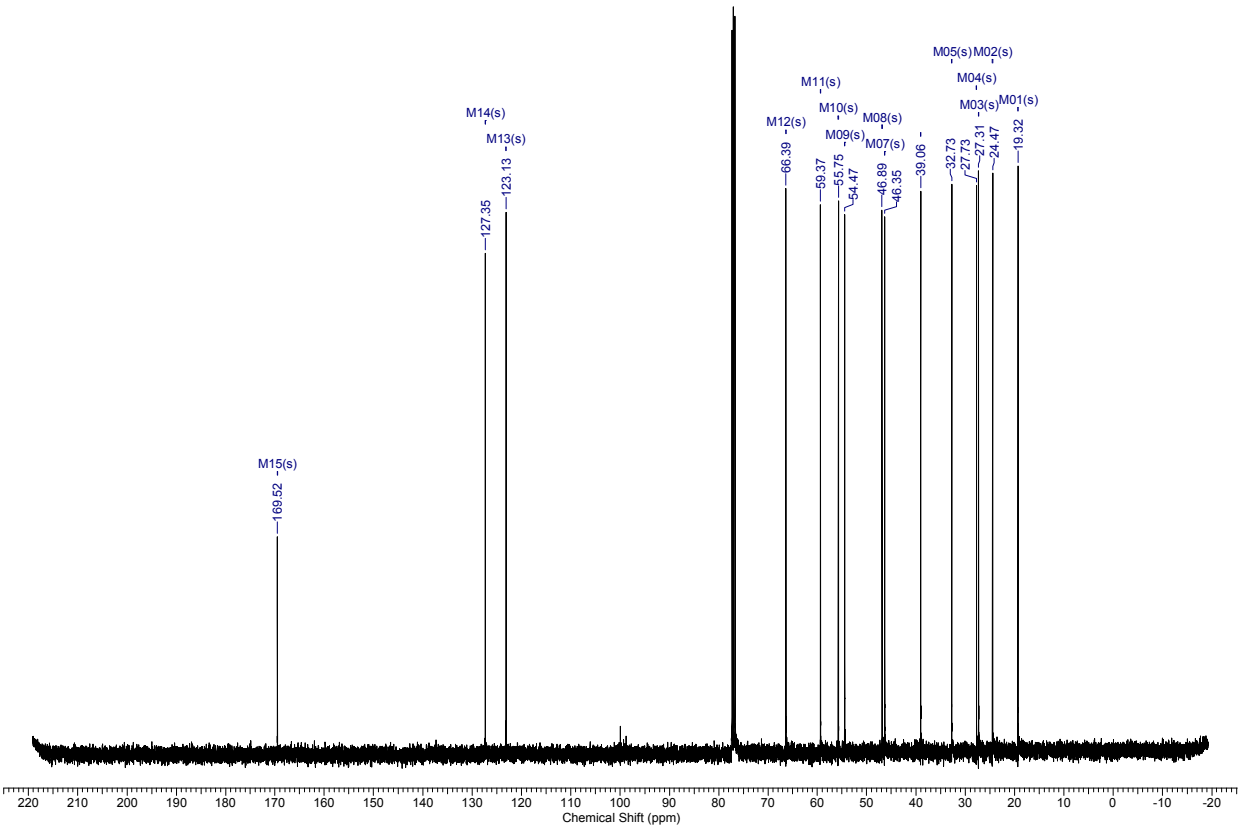
^{13}C NMR (100 MHz, $CDCl_3$)



(41*R*,7a*S*,13a*R*,13b*R*)-5,6,7,7a,8,11,12,13,13a,13b-Decahydro-3H-dipyrido[2,1-f:3',2',1'-ij][1,6]naphthyridin-10(41H)-one (16). ^{1}H NMR (400 MHz, $CDCl_3$)

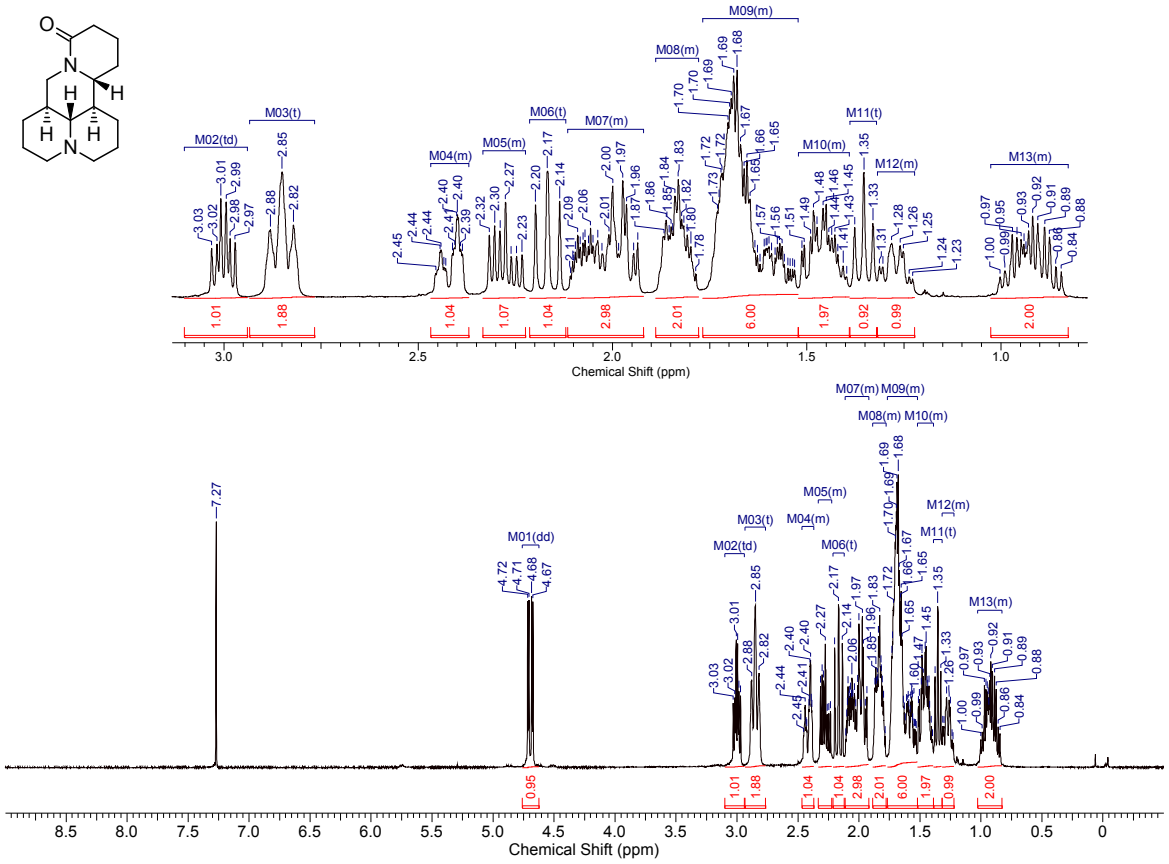


^{13}C NMR (100 MHz, $CDCl_3$)

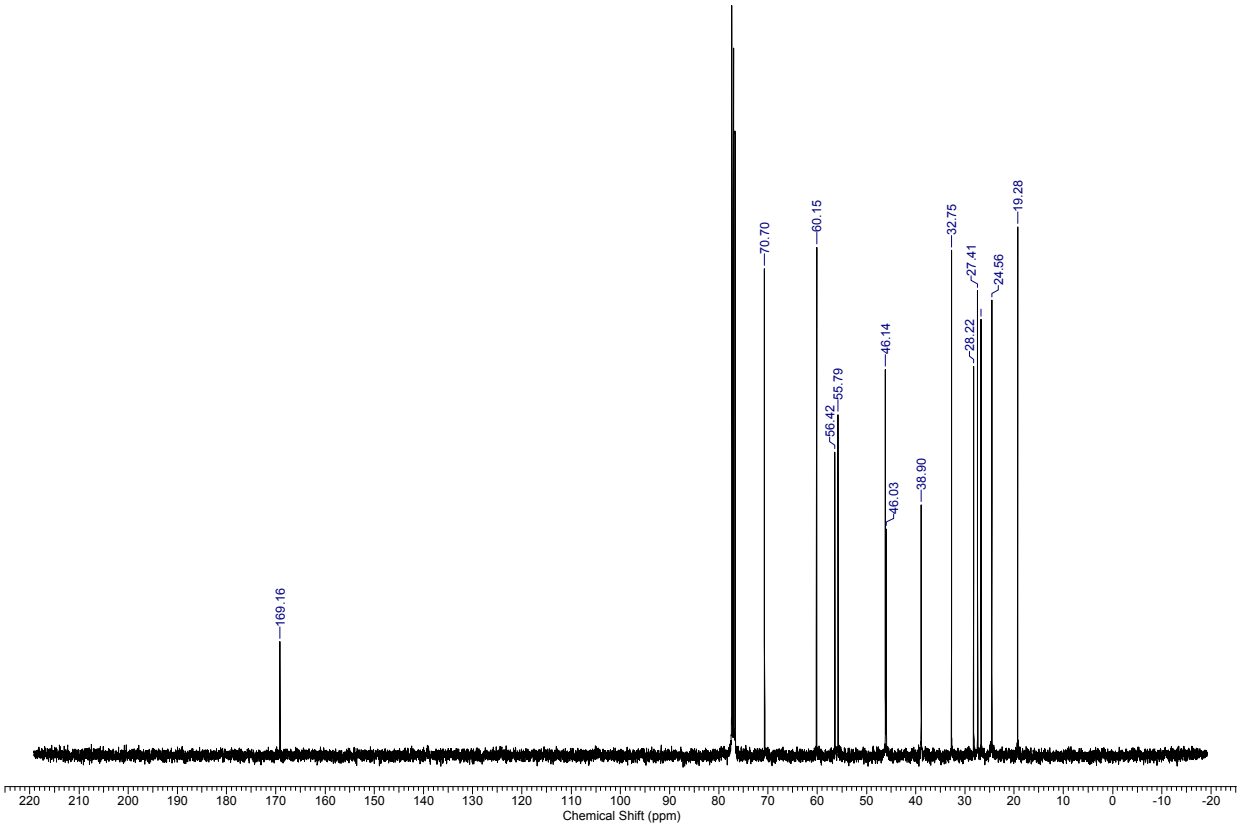


Supporting Information

(+)-Allomatrine (1). ^{1}H NMR (400 MHz, $CDCl_3$)

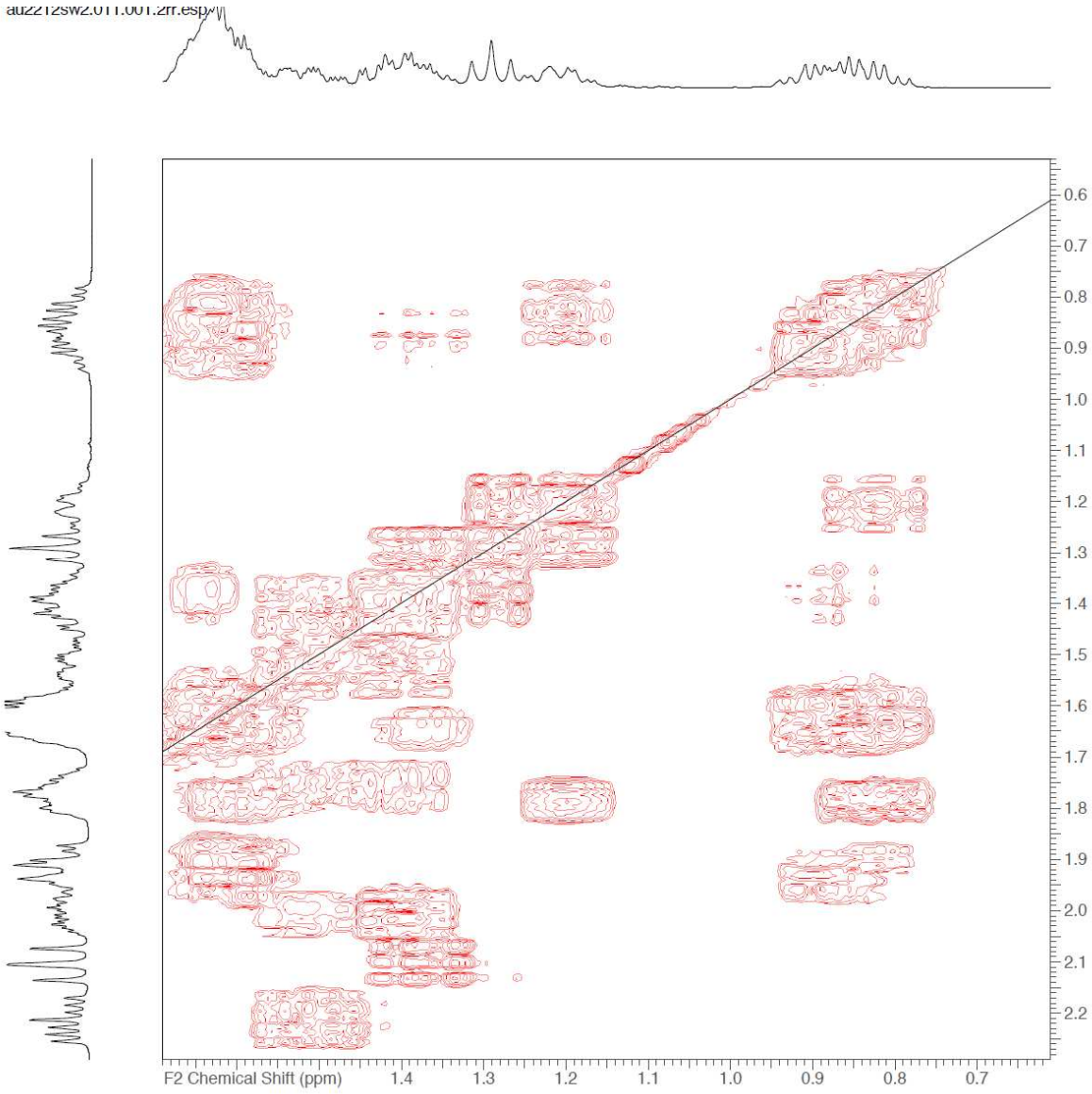


^{13}C NMR (100 MHz, $CDCl_3$)



Supporting Information

(+)-Allomatrine (1). ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)



(+)-Allomatrine (1). HMQC NMR ($CDCl_3$)