# Supporting Information

# A cooperative Pd/Co catalysis for the asymmetric (4+2) cycloaddition of vinyl benzoxazinones with *N*-acylpyrazoles

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## 1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. $^{1}H$ NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. $^{13}C$ NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). $^{19}F$ NMR spectra were recorded on Bruker DPX-400 376 MHz spectrophotometers. HRMS was recorded on Bruker micrOTOFII ESI-TOF using a positive electrospray inonization (ESI+). Measured values are reported to 4 decimal places of the calculated value. Enantiomeric ratio (ee) values were determined by chiral HPLC with AD-H, AZ-H and OD-H columns with hexane and *i*-PrOH as solvents.

## 2. Preparation of Materials

Substrates(**1a-n** and **2**) were prepared according to the reported procedures[1,2]. Ligands were synthesized according to the literature[3,4] or commercially available.

References

[1] (a) C. Wang, J. A. Tunge, *J. Am. Chem. Soc.,* 2008, **130**, 8118; (b) C. Wang, J. A. Tunge, *Tetrahedron.*, 2009, **65**, 5102; (c) T.-R. Li, F. Tan, L.-Q, Lu, Y, Wei, Y.-N. Wang, Y.-Y. Liu, Q.-Q. Yang, J.-R. Chen, D.-Q. Shi, W.-J. Xiao, *Nat. Commun.*, 2014, **5**, 5500; (d) Y. Wei, L.-Q, Lu, T.-R. Li, B. Feng, Q. Wang, W.-J. Xiao, H. Alper, *Angew. Chem., Int. Ed.*, 2016, **55**, 2200; (e) Q. Wang, X.-T. Qi, L.-Q. Lu, T.-R. Li, Z.-G. Yuan, K. Zhang, B.-J. Li, Y. Lan, W.-J. Xiao, *Angew. Chem., Int., Ed.*, 2016, **55**, 2840.

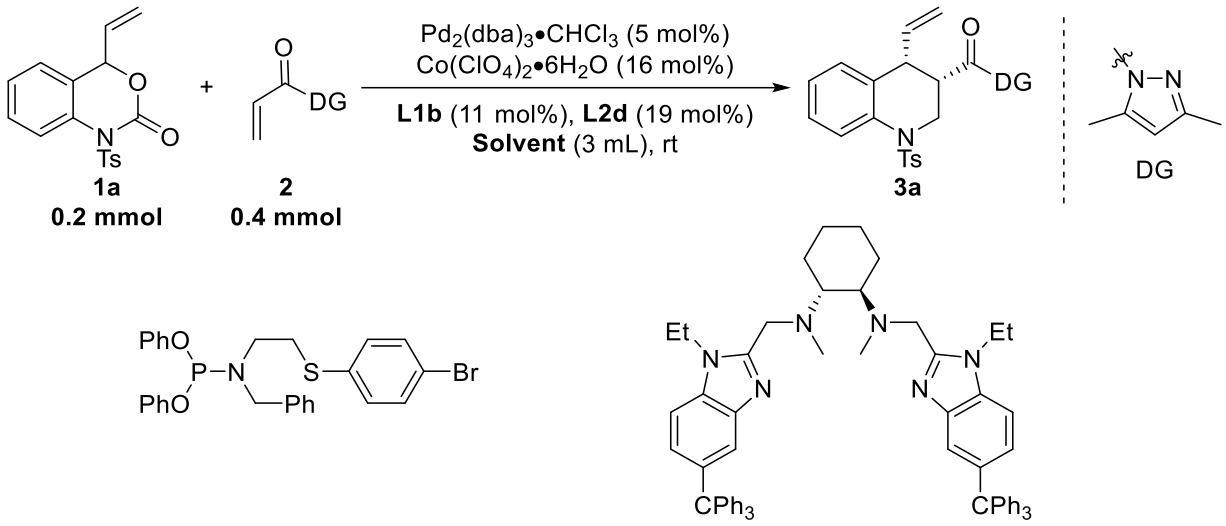
[2] M. P. Sibi, H. Miyable, *Org. Lett.,* 2002, **4**, 3435.

[3] J. Liu, M.-M. Li, B.-L. Qu, L.-Q. Lu, W.-J. Xiao, *Chem. Commun.,* 2019, **55**, 2031

[4] K. Zhang, L.-Q. Lu, Y. Jia, Y. Wang, F.-D. Lu, F.-F. Pang, W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2019, **58**, 13375.

## 3. Optimization of the Reaction Conditions

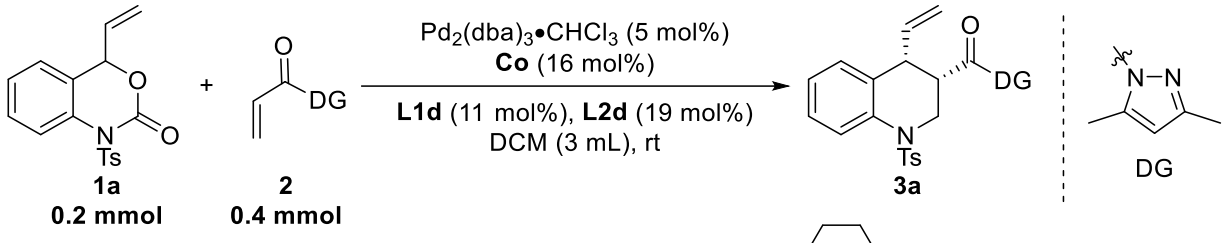
### 3.1 The effect of solvents[a)]

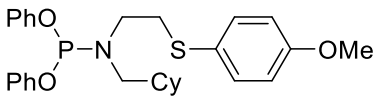



| entry | solvent | yield (%)[b)] | er[c)] | dr[d)] |
|---|---|---|---|---|
| 1 | DCE | 72 | 91.5:8.5 | 14:1 |
| 2 | THF | 89 | 82:18 | 14:1 |
| 3 | MeCN | 85 | 86:14 | 14:1 |
| 4 | $CHCl_3$ | 13 | 86:14 | 10:1 |
| 5 | $CCl_4$ | trace | -- | -- |
| 6 | PhCl | 8 | 93.5:6.5 | >19:1 |
| 7 | DCM | 80 | 92:8 | 16:1 |

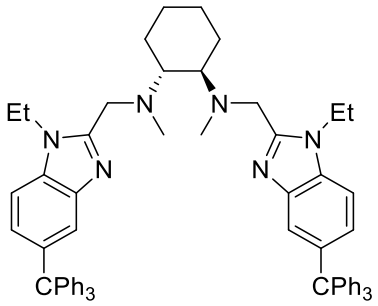
a) Reaction Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), $Pd_2(dba)_3$•$CHCl_3$ (0.01 mmol, 10 mol% Pd), **L1b** (0.022 mmol, 11 mol%), $Co(ClO_4)_2$•$6H_2O$ (0.032 mmol, 16 mol%), **L2d** (0.038 mmol, 19 mol%) at room temperature; b) Determined by $^1H$ NMR of the reaction mixture with 1,3,5-trimethoxybenzene; c) Determined by Chiral HPLC. d) Determined by $^1H$ NMR analysis of the reaction mixture.

### 3.2 The effect of cobalt salts[a)]



L1d



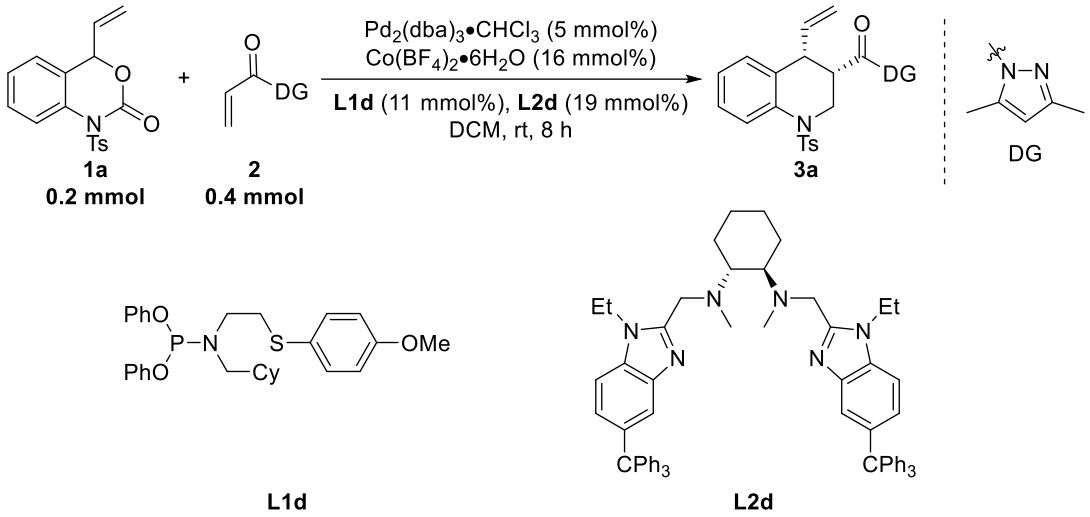
L2d

| entry | cobalt salt | yield (%)[b)] | er[c)] | dr[d)] |
|---|---|---|---|---|
| 1 | $Co(BF_4)_2·6H_2O$ | 87 | 96.5:3.5 | >19:1 |
| 2 | $CoCl_2·6H_2O$ | NR | -- | -- |
| 3 | $CoCl_2$ | NR | -- | -- |
| 4 | $Co(OAc)_2·4H_2O$ | NR | -- | -- |
| 5 | $Co(ClO_4)_2·6H_2O$ | 81 | 96:4 | >19:1 |

a) Reaction Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), $Pd_2(dba)_3$•$CHCl_3$ (0.01 mmol, 10 mol% Pd), **L1d** (0.022 mmol, 11 mol%), Co salt (0.032 mmol, 16 mol%) **L2d** (0.038 mmol, 19 mol%) and DCM (3 mL) at room temperature; b) Determined by $^1$H NMR of the reaction mixture with 1,3,5-trimethoxybenzene; c) Determined by Chiral HPLC; d) Determined by $^1$H NMR analysis of the reaction mixture.

## 4. General Procedure and Spectral Data of the Products

### 4.1 General procedure for the synthesis of the 3a-3n




**Procedure A:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Co(BF_4)_2·6H_2O$ (0.032 mmol, 16 mol%), **L2d** (0.038 mmol, 19 mol%) and anhydrous DCM (1.5 mL). The resulting solution was stirred for 12 h at room temperature to prepare the cobalt complex (solution A). Then, another a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3·CHCl_3$ (0.01 mmol, 5 mol%), **L1d** (0.022 mmol, 11 mol%) and anhydrous DCM (1.5 mL) under argon atmosphere, the resulting solution was stirred for 30 min at rt. Then **1a** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv) and solution A were added. The resulting solution was stirred until complete conversion of 1a (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1 to 10/1) to give product.

**Procedure B:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Co(BF_4)_2·6H_2O$ (0.016 mmol, 16 mol%), **L2d** (0.019 mmol, 19 mol%) and anhydrous DCM (1.0 mL). The resulting solution was stirred for 12 h at room temperature to prepare the cobalt complex (solution A). Then, another a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3·CHCl_3$ (0.005 mmol, 5 mol%), **L1d** (0.011 mmol, 11 mol%) and anhydrous DCM (1.0 mL) under argon atmosphere, the resulting solution was stirred for 30 min at rt. Then **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv) and solution A were added. The resulting solution was stirred until complete conversion of Sub a (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1 to 10/1) to give product.

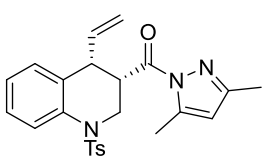
**Procedure C:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged

with $Co(BF_4)_2 \cdot 6H_2O$ (0.016 mmol, 16 mol%), **L2d** (0.019 mmol, 19 mol%) and anhydrous DCM (1.5 mL). The resulting solution was stirred for 12 h at room temperature to prepare the cobalt complex (solution A). Then, another a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5 mol%), **L1d** (0.011 mmol, 11 mol%) and anhydrous DCM (1.5 mL) under argon atmosphere, the resulting solution was stirred for 30 min at rt. Then **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv) and solution A were added. The resulting solution was stirred until complete conversion of Sub a (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1 to 10/1) to give product.

**Procedure D:** Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Co(BF_4)_2 \cdot 6H_2O$ (0.016 mmol, 16 mol%), **L2d** (0.019 mmol, 19 mol%) and anhydrous DCM (2.0 mL). The resulting solution was stirred for 12 h at room temperature to prepare the cobalt complex (solution A). Then, another a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5 mol%), **L1d** (0.011 mmol, 11 mol%) and anhydrous DCM (2.0 mL) under argon atmosphere, the resulting solution was stirred for 30 min at rt. Then **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv) and solution A were added. The resulting solution was stirred until complete conversion of Sub a (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1 to 10/1) to give product.

### 4.2 Spectral data of the desired products 3a-3n

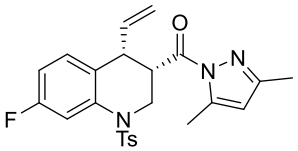
**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3a (Procedure A)**




White solid, 83% yield, $[\alpha]_D^{25}$ = 67.4 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr > 95:5, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 9.08 min, $t_R$ (minor) = 11.29 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.12 – 7.01 (m, 2H), 5.94 (s, 1H), 5.59 (ddd, *J* = 17.8, 10.0, 8.1 Hz, 1H), 4.86 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.54 (d, *J* = 16.8 Hz, 1H), 4.46 – 4.39 (m, 1H), 3.95 (m, *J* = 11.5, 5.7, 2.9 Hz, 2H), 3.63 (dd, *J* = 14.0, 11.5 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H), 2.18 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.02, 152.25, 143.86,

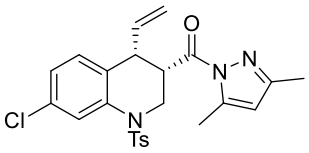
143.80, 137.04, 136.34, 136.03, 130.65, 129.76, 129.25, 127.22, 127.19, 124.46, 123.35, 117.45, 111.15, 43.68, 43.54, 41.27, 21.52, 14.20, 13.81. **HRMS (ESI)** for $C_{24}H_{25}N_3O_3S$ [M + H]$^+$: calcd 436.1698, found 436.1690.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-7-fluoro-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3b (Procedure B)**



Colourless oil, 80% yield, $[\alpha]_D^{25}$ = 10.9 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr = 8:1 (0.1 mmol, 2mL DCM), determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 12.14 min, $t_R$ (minor) = 21.38 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (s, 1H, minor) 7.69 - 7.59 (m, 3H, major), 7.25 (d, *J* = 8.2 Hz, 2H, major), 7.00 (dd, *J* = 8.6, 6.5 Hz, 1H, major), 6.79 (m, *J* = 8.2, 2.6 Hz, 1H, major), 5.95 (s, 1H, major), 5.58 (m, *J* = 17.5, 10.0, 7.9 Hz, 1H, major), 4.88 (dd, *J* = 10.1, 1.5 Hz, 1H, major), 4.51 (d, *J* = 16.8 Hz, 1H, major), 4.46 - 4.38 (m, 1H, major), 4.03 – 3.88 (m, 2H, major), 3.61 (dd, *J* = 13.7, 11.6 Hz, 1H, major), 2.50 (s, 1H, minor), 2.48 (s, 3H, major), 2.40 (s, 3H, major+minor), 2.36 (s, 1H, minor), 2.19 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.77, 144.17, 143.96, 136.88, 135.90, 131.83, 129.89, 127.22, 124.60, 117.82, 111.66, 111.44, 111.28, 109.95, 109.69, 43.36, 43.25, 41.29, 21.57, 14.25, 13.84. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ = -113.47. **HRMS (ESI)** for $C_{24}H_{24}FN_3O_3S$ [M + H]$^+$: calcd 454.1595, found 454.1591.

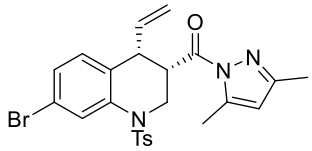
**((3S,4R)-7-Chloro-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone 3c (Procedure C)**



White solid, 90% yield, $[\alpha]_D^{25}$ = 15.3 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr = 11:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 10.41 min, $t_R$ (minor) = 17.04 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (s, 1H, minor), 7.91 (d, *J* = 2.1 Hz, 1H, major), 7.72 (d, *J* = 8.1 Hz, 2H, minor), 7.62 (d, *J* = 8.0 Hz, 2H, major), 7.29 – 7.23 (m, 2H, major), 7.04 (dd, *J* = 8.3, 2.1 Hz, 1H, major), 6.97 (d, *J* = 8.3 Hz, 1H, major), 6.01 (s, 1H, minor), 5.95 (s, 1H, major), 5.56 (m, *J* = 17.4, 10.0, 7.9 Hz, 1H, major), 4.88 (dd, *J* = 10.0, 1.5 Hz, 1H, major), 4.52 (d, *J* = 16.8 Hz, 1H, major), 4.40 (dd, *J* = 14.3, 3.0 Hz, 1H, major), 4.03 – 3.88 (m, 2H, major), 3.59 (dd, *J* = 13.8, 11.6 Hz, 1H, major), 2.50 (s, 3H, minor), 2.47 (s, 3H, major), 2.40 (s, 3H, major), 2.38 (s, 3H, minor), 2.36

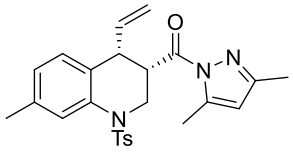
(s, 3H, minor), 2.18 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 144.18, 143.94, 137.06, 136.61, 135.86, 132.73, 131.64, 129.90, 127.54, 127.24, 124.54, 122.92, 117.99, 111.28, 43.39, 43.30, 41.15, 21.58, 14.24, 13.84. **HRMS (ESI)** for $C_{24}H_{24}ClN_3O_3S$ $[M + H]^+$: calcd 470.1300, found 470.1305.

**((3S,4R)-7-Bromo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone 3d (Procedure B)**



Colourless oil, 83% yield, $[\alpha]_D^{25}$ = 3.2 (*c* = 1.00 in $CHCl_3$); er = 95:5, dr = 10:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 11.34 min, $t_R$ (minor) = 21.45 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 1.9 Hz, 1H, major), 7.61 (d, *J* = 8.2 Hz, 2H, major), 7.29 – 7.24 (m, 2H, major), 7.19 (dd, *J* = 8.2, 2.0 Hz, 1H, major), 6.91 (d, *J* = 8.3 Hz, 1H, major), 5.95 (s, 1H, major), 5.64 – 5.45 (m, 1H, major), 4.88 (dd, *J* = 10.1, 1.5 Hz, 1H, major), 4.52 (d, *J* = 16.8 Hz, 1H, major), 4.45 – 4.33 (m, 1H), 4.01 – 3.86 (m, 2H, major), 3.68 – 3.49 (m, 1H, major), 2.50 (s, 3H, minor), 2.47 (s, 3H, major), 2.40 (s, 3H, major+minor), 2.36 (s, 3H, minor), 2.19 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.69, 152.48, 144.24, 143.95, 137.27, 136.52, 135.78, 131.97, 129.93, 128.10, 127.48, 127.28, 125.85, 120.59, 118.07, 111.31, 43.38, 43.36, 41.07, 21.62, 14.29, 13.89. **HRMS (ESI)** for $C_{24}H_{24}BrN_3O_3S$ $[M + H]^+$: calcd 514.0795, found 514.0783.

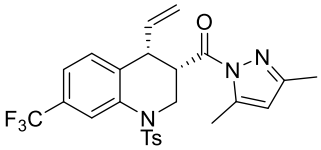
**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-7-methyl-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3e (Procedure B)**



Colourless oil, 73% yield. $[\alpha]_D^{25}$ = 18.4 (*c* = 1.00 in $CHCl_3$); er = 95.5:4.5, dr = 8:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 9.88 min, $t_R$ (minor) = 17.74 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.68 (s, 1H, major), 7.58 (d, *J* = 8.1 Hz, 2H, major), 7.22 (d, *J* = 8.1 Hz, 2H, major), 6.97 – 6.82 (m, 2H, major), 5.93 (s, 1H, major), 5.57 (m, *J* = 17.2, 10.0, 7.8 Hz, 1H, major), 4.84 (dd, *J* = 10.0, 1.7 Hz, 1H, major), 4.53 (dd, *J* = 16.9, 1.7 Hz, 1H, major), 4.46 – 4.28 (m, 1H), 3.90 (m, *J* = 6.1, 3.4 Hz, 2H, major), 3.67 – 3.53 (m, 1H, major), δ 2.49 (s, 3H, minor), 2.46 (s, 3H, major), 2.39 (s, 3H, major+minor), 2.37 (s, 3H, minor), 2.35 (s, 3H, major+minor), 2.17 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.19, 152.18, 143.83, 143.76, 137.26, 137.04, 136.39, 135.81, 130.41, 129.75, 127.22, 126.32, 125.59, 123.90, 117.19, 111.12, 43.58, 43.34, 41.20,

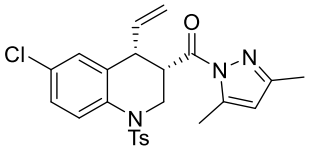
21.56, 21.41, 14.23, 13.84. **HRMS (ESI)** for $C_{25}H_{27}N_3O_3S$ $[M + H]^+$: calcd 450.1846, found 450.1845.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-1-tosyl-7-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3f (Procedure B)**



Colourless oil, 73% yield. $[\alpha]_D^{25}$ = 97.1 (*c* = 3.00 in $CHCl_3$); er = 95:5, dr = 10:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 9.00 min, $t_R$ (minor) = 17.29 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.23 (m, 3H), 7.18 (d, *J* = 8.1 Hz, 1H), 6.03 – 5.89 (m, 1H), 5.59 (m, *J* = 16.9, 10.1, 8.3 Hz, 1H), 4.92 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.54 (m, *J* = 16.9, 1.2 Hz, 1H), 4.44 (m, *J* = 13.8, 3.4, 1.2 Hz, 1H), 4.06 (t, *J* = 7.1 Hz, 1H), 3.97 (m, *J* = 12.0, 5.8, 3.4 Hz, 1H), 3.65 (dd, *J* = 13.8, 12.0 Hz, 1H), 2.48 (s, 3H), 2.39 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.45, 152.60, 144.38, 144.02, 136.55, 136.22, 135.69, 132.80, 131.28, 129.93, 127.31, 120.64, 120.60, 120.01, 119.97, 118.48, 111.37, 43.71, 43.47, 41.15, 21.55, 14.22, 13.83. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ = -62.59. **HRMS (ESI)** for $C_{25}H_{24}F_3N_3O_3S$ $[M + H]^+$: calcd 504.1563, found 504.1559.

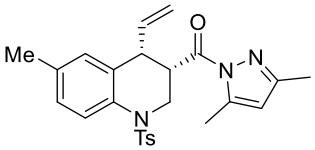
**((3S,4R)-6-Chloro-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)(3,5-dimethyl-1H-pyrazol-1-yl)methanone 3g (Procedure C)**



Colourless oil, 81% yield. $[\alpha]_D^{25}$ = 14.6 (*c* = 1.00 in $CHCl_3$); er = 91:9, dr = 5:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 13.39 min, $t_R$ (minor) = 17.85 min. **$^1$H NMR** (400 MHz, $CDCl_3$) 7.87 (d, *J* = 9.0 Hz, 1H, minor), δ = 7.83 (d, *J* = 8.9 Hz, 1H, major), 7.68 (d, *J* = 8.1 Hz, 1H, minor), 7.62 (d, *J* = 4.3 Hz, 1H, minor), 7.45 – 7.38 (m, 1H, minor), 7.57 (d, *J* = 8.0 Hz, 2H, major), 7.24 (d, *J* = 8.0 Hz, 2H, major), 7.19 (dd, *J* = 9.0, 2.6 Hz, 1H, major), 7.15 (d, 1H, minor), 7.09 (d, *J* = 15.9 Hz, 1H, minor), 7.03 (d, *J* = 2.5 Hz, 1H, major), 6.01 (s, 1H, minor), 5.94 (s, 1H, major), 5.66 – 5.38 (m, 1H, major), 4.95 (d, *J* = 4.8 Hz, 1H, minor), 4.89 (d, *J* = 10.0 Hz, 1H, major), 4.54 (d, *J* = 16.9 Hz, 1H, major), 4.39 (dd, *J* = 13.9, 3.3 Hz, 1H, major), 4.01 – 3.81 (m, 2H, major), 3.60 (dd, *J* = 13.9, 11.9 Hz, 1H, major), 2.49 (s, 3H, minor), 2.47 (s, 3H, major), 2.39 (s, 3H, major+minor), 2.36 (s, 3H, minor), 2.18 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.61, 152.43, 144.11, 143.92, 136.33, 135.91, 134.68, 131.12, 130.24, 129.90, 127.40,

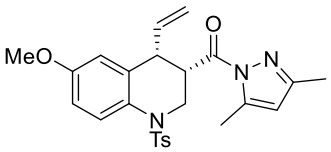
127.21, 124.82, 118.16, 111.27, 43.58, 43.51, 40.92, 21.57, 14.21, 13.83. **HRMS (ESI)** for $C_{24}H_{24}ClN_3O_3S$ $[M + H]^+$: calcd 470.1300, found 470.1295.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-6-methyl-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3h (Procedure C)**




Colourless oil, 78% yield. $[\alpha]_D^{25}$ = 53 (*c* = 1.00 in $CHCl_3$); er = 92.5:7.5, dr = 5:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 14.02 min, $t_R$ (major) = 15.20 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.4 Hz, 1H, minor), 7.75 (d, *J* = 8.5 Hz, 1H, major), 7.69 – 7.65 (m, 2H, minor), 7.56 (d, *J* = 8.3 Hz, 2H, major), 7.42 (m, *J* = 4.6, 2.9 Hz, 2H, minor), 7.22 (d, *J* = 7.9 Hz, 2H, major), 7.14 – 7.06 (m, 1H, minor), 7.03 (dd, *J* = 8.6, 2.2 Hz, 1H, major), 6.96 (d, 1H, minor), 6.84 (d, *J* = 2.1 Hz, 1H, major), 6.00 (s, 1H, minor), 5.93 (s, 1H, major), 5.66 – 5.44 (m, 1H, major), 5.07 – 4.88 (m, 2H, minor), 4.85 (dd, *J* = 10.0, 1.7 Hz, 1H, major), 4.73 (dd, *J* = 13.7, 3.9 Hz, 1H, minor), 4.53 (dd, *J* = 16.9, 1.6 Hz, 1H, major), 4.39 (m, *J* = 13.9, 3.0, 1.7 Hz, 1H, major), 3.89 (m, *J* = 8.5, 2.3 Hz, 2H, major), 3.70 – 3.55 (m, 1H, major), 2.50 (s, 3H, minor), 2.46 (s, *J* = 1.0 Hz, 3H, major), 2.36 (d, *J* = 1.8 Hz, 6H, minor), 2.38 (s, 3H, major), 2.30 (s, 3H, minor), 2.27 (s, 3H, major), 2.17 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.16, 152.20, 143.83, 143.72, 137.14, 136.26, 134.21, 133.41, 130.95, 129.76, 129.11, 128.11, 127.22, 123.46, 117.28, 111.13, 43.65, 43.55, 41.12, 21.57, 20.72, 14.24, 13.84. **HRMS (ESI)** for $C_{25}H_{27}N_3O_3S$ $[M + H]^+$: calcd 450.1846, found 450.1841.

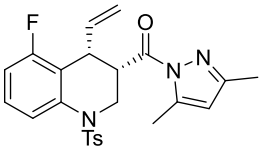
**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-6-methoxy-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3i (Procedure C)**




Colourless oil, 73% yield. $[\alpha]_D^{25}$ = 3.63 (*c* = 1.00 in $CHCl_3$); er = 94.5:5.5, dr = 4:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 21.68 min, $t_R$ (major) = 26.65 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 9.1 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.81 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H), 5.93 (s, 1H), 5.64 – 5.43 (m, 1H), 4.84 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.54 (dd, *J* = 16.9, 1.6 Hz, 1H), 4.37 (dt, *J* = 14.1, 1.9 Hz, 1H), 3.84 (dt, *J* = 8.6, 2.2 Hz, 2H), 3.77 (s, 3H), 3.60 (ddd, *J* = 14.1, 8.9, 3.0 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.17 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.11, 156.61, 152.15, 143.82, 143.69, 136.98, 136.16, 131.09,

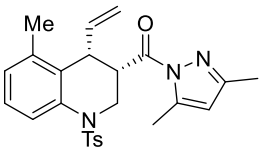
129.77, 129.03, 127.27, 125.58, 117.32, 114.97, 113.23, 111.11, 55.40, 43.73, 43.67, 40.72, 21.57, 14.21, 13.84. **HRMS (ESI)** for $C_{25}H_{27}N_3O_4S$ $[M + H]^+$: calcd 466.1795, found 466.1792.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-5-fluoro-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3j (Procedure A)**




White solid, 96% yield. $[\alpha]_D^{25}$ = 39.4 (*c* = 1.00 in $CHCl_3$); er = 96:4, dr = 10:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 11.25 min, $t_R$ (minor) = 13.30 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.5 Hz, 1H, major), 7.68 (d, *J* = 8.4 Hz, 1H, minor), 7.60 (d, *J* = 8.0 Hz, 2H, major), 7.44 – 7.38 (m, 2H, minor), 7.24 (d, *J* = 8.1 Hz, 3H, major+minor), 7.10 (d, *J* = 16.0 Hz, 1H, minor), 6.80 (t, *J* = 8.7 Hz, 1H, major), 6.01 (s, 1H, minor), 5.96 (s, 1H, major), 5.51 (m, *J* = 17.2, 10.1, 7.4 Hz, 1H, major), 4.94 (d, *J* = 10.1 Hz, 1H, major), 4.80 (d, *J* = 10.1 Hz, 1H, minor), 4.69 (d, *J* = 17.1 Hz, 1H, minor), 4.57 (dd, *J* = 13.6, 4.2 Hz, 1H, minor), 4.53 – 4.40 (m, 2H, major), 4.29 (t, *J* = 6.4 Hz, 1H, major), 3.84 (m, *J* = 12.4, 5.4, 3.1 Hz, 1H, major), 3.63 (t, *J* = 13.0 Hz, 1H, major), 2.50 (s, 3H, major+minor), 2.39 (s, 3H, major), 2.37 (s, 6H, minor), 2.19 (s, 3H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.56, 161.86, 159.41, 152.58, 144.16, 143.91, 137.47, 135.76, 134.69, 129.86, 127.85, 127.24, 118.42, 118.26, 117.31, 111.40, 110.76, 42.93, 40.53, 37.60, 37.56, 21.57, 14.28, 13.85. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ = 114.65. **HRMS (ESI)** for $C_{24}H_{24}FN_3O_3S$ $[M + H]^+$: calcd 454.1595, found 454.1583.

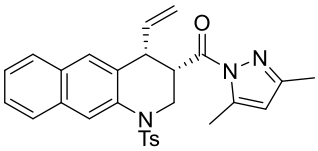
**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-5-methyl-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3k (Procedure D)**




Colourless oil, 90% yield. $[\alpha]_D^{25}$ = 5.5 (*c* = 1.00 in $CHCl_3$); er = 94.5:5.5, dr = 1:1, determined by HPLC analasis (Chiralpak AZ column, hexane/i-PrOH, 98:2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 29.55 min, $t_R$ (minor) = 34.51 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.4 Hz, 1H, minor), 7.76 (d, *J* = 8.0 Hz, 2H, major), 7.70 (d, *J* = 8.3 Hz, 1H, minor), 7.58 (d, *J* = 8.0 Hz, 1H, major+minor), 7.21 (m, *J* = 8.1, 4.1 Hz, 3H, minor), 7.14 (m, *J* = 7.9, 5.7 Hz, 3H, major), 6.99 (d, *J* = 7.5 Hz, 1H, major), 6.94 (d, *J* = 7.5 Hz, 1H, minor), 6.01 (s, 1H, major), 5.97 (s, 1H, minor), 5.34 (m, J = 17.0, 10.2, 6.8 Hz, 1H, minor), 4.99 (m, *J* = 17.0, 10.1, 6.6 Hz, 1H, major), 4.84 (d, *J* = 10.2 Hz, 1H, minor), 4.74 (d, *J* = 10.1 Hz, 1H, major), 4.60 – 4.51 (m, 2H, major), 4.33 – 4.20 (m, 2H, minor), 4.15 (m, *J* = 7.7, 3.6 Hz, 2H, major), 4.12 – 4.08 (m, 1H,

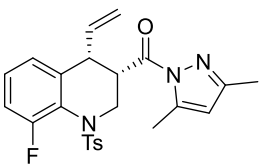
minor), 3.94 (m, *J* = 12.6, 4.2 Hz, 1H, major), 3.72 (m, *J* = 12.7 Hz, 1H, minor), 3.60 (dd, *J* = 13.3, 8.6 Hz, 1H, major), 2.52 (s, 3H, minor), 2.47 (s, 3H, major), 2.37 (s, 6H, major+minor), 2.21 (s, 3H, major), 2.18 (s, 3H, minor), 2.15 (s, 3H, minor, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.69, 152.50, 144.32, 143.61, 138.49, 137.10, 136.92, 134.44, 129.50, 128.79, 127.72, 127.40, 126.60, 122.45, 116.26, 111.57, 44.90, 41.90, 39.51, 21.56, 20.32, 14.50, 14.06. **HRMS (ESI)** for $C_{25}H_{27}N_3O_3S$ $[M + H]^+$: calcd 450.1846, found 450.1841.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-1-tosyl-4-vinyl-1,2,3,4-tetrahydrobenzo[g]quinolin-3-yl)methanone 3l (Procedure C)**




Colourless oil, 81% yield. $[\alpha]_D^{25}$ = 65.2 (*c* = 1.00 in $CHCl_3$); er = 95:5, dr = 6:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 16.48 min, $t_R$ (minor) = 21.38 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 1H), 7.42 (m, *J* = 20.8, 8.1, 6.8, 1.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.96 (s, 1H), 5.62 (m, *J* = 17.2, 10.1, 7.5 Hz, 1H), 4.89 – 4.80 (m, 1H), 4.52 (d, *J* = 17.0 Hz, 1H), 4.45 (m, *J* = 13.2, 2.9 Hz, 1H), 4.18 – 4.07 (m, 2H), 3.83 (dd, *J* = 13.4, 11.5 Hz, 1H), 2.50 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.74, 152.43, 144.01, 143.86, 136.64, 136.11, 133.86, 132.69, 130.44, 129.72, 129.26, 127.87, 127.31, 126.93, 126.18, 125.54, 120.58, 117.63, 111.30, 44.17, 43.96, 41.74, 21.52, 14.30, 13.85. **HRMS (ESI)** for $C_{28}H_{27}N_3O_3S$ $[M + H]^+$: calcd 486.1846, found 486.1830.

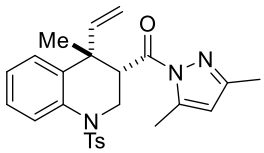
**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-8-fluoro-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3m (Procedure A)**




Colourless oil, 93% yield. $[\alpha]_D^{25}$ = 127.5 (*c* = 1.00 in $CHCl_3$); er = 95.5:4.5, dr = 14:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 99:1 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 21.64 min, $t_R$ (minor) = 42.77 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 (m, *J* = 8.0, 5.1 Hz, 1H), 7.03 – 6.91 (m, 2H), 5.95 (s, 1H), 5.69 (m, *J* = 16.8, 9.7 Hz, 1H), 4.95 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.72 (m, *J* = 16.9, 1.2 Hz, 1H), 4.62 (m, *J* = 11.4, 6.6, 3.5 Hz, 1H), 4.37 (dd, *J* = 9.3, 6.7 Hz, 1H), 4.20 (dd, *J* = 14.2, 3.5 Hz, 1H), 3.51 (dd, *J* = 14.3, 11.4 Hz, 1H), 2.48 (s, 1H), 2.44 (s, 3H), 2.25 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.60, 157.49, 155.00, 152.54, 143.86, 137.74,

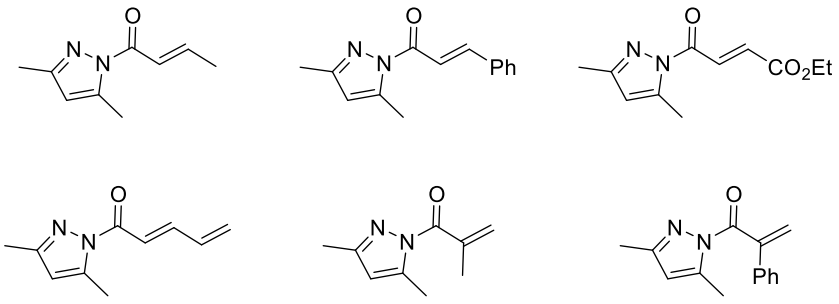
137.09, 133.77, 129.58, 127.41 (d, *J* = 16.0 Hz), 126.04, 125.93 (d, *J* = 24.0 Hz), 124.80 (d, *J* = 48.0 Hz), 117.50, 114.20 (d, *J* = 84.0), 111.22, 44.16, 43.69, 42.94, 21.61, 14.25, 13.91. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ = -114.67. **HRMS (ESI)** for $C_{24}H_{24}FN_3O_3S$ $[M + H]^+$: calcd 454.1595, found 454.1583.

**(3,5-Dimethyl-1H-pyrazol-1-yl)((3S,4R)-4-methyl-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanone 3n (Procedure A)**



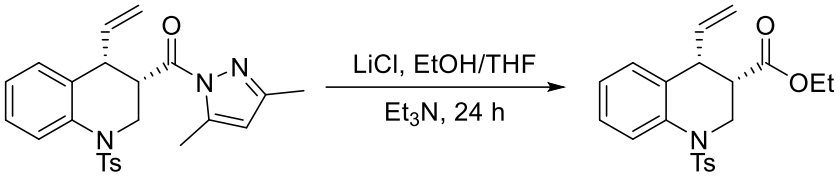

Colourless oil, 88% yield. $[\alpha]_D^{25}$ = -2.9 (*c* = 1.00 in $CHCl_3$); er = 85.5:14.5, dr = 4.6:1, determined by HPLC analasis (Chiralpak AZ column, hexane/i-PrOH, 99.5:0.5 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 60.50 min, $t_R$ (major) = 71.51 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.6 Hz, 1H, major), 7.58 (d, *J* = 8.2 Hz, 2H, major+minor), 7.22 (d, *J* = 8.6 Hz, 3H, major), 7.18 (d, *J* = 2.1 Hz, 3H, minor), 7.10 (m, 2H, minor), 7.00 – 6.99 (m, 2H, major), 6.08 – 5.96 (m, 2H, minor), 5.94 (s, 1H, major), 5.59 (dd, *J* = 17.3, 10.6 Hz, 1H, major), 4.89 (d, *J* = 10.6 Hz, 1H, major), 4.79 (d, *J* = 17.3 Hz, 1H, major), 4.44 (s, 1H, minor), 4.39 (dd, *J* = 10.8, 3.9 Hz, 1H, major), 4.34 (m, *J* = 3.0 Hz, 1H, minor), 4.30 (dd, *J* = 13.4, 3.9 Hz, 1H, major), 3.97 (dd, *J* = 13.2, 10.7 Hz, 1H, major), 2.50 (s, 3H, minor), 2.47 (s, 3H, major), 2.39 (s, 3H, major), 2.21 (s, 3H, minor), 2.18 (s, 3H, major), 1.17 (s, 3H, major), 1.16 (s, 3H, minor). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.84, 151.40, 144.40, 143.80, 143.67, 136.09, 135.34, 134.59, 129.64, 128.13, 127.34, 127.05, 124.35, 122.70, 113.96, 111.73, 45.01, 43.95, 43.14, 21.75, 21.58, 14.49, 13.78. **HRMS (ESI)** for $C_{25}H_{27}N_3O_3S$ $[M + H]^+$: calcd 450.1846, found 450.1845.

**4.3 Unsuccessful Substrates**



## 5. Synthetic Transformation

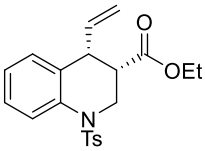
### 5.1 Synthesis of Product 5




**3a** **5**

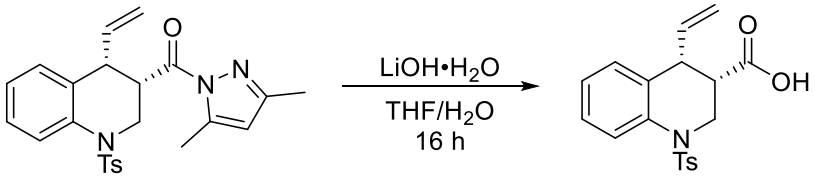
**Procedure E:** Compound **3a** (43.5 mg, 0.1 mmol) was dissolved into 1mL EtOH/THF (4:1) in an oven-dried 10 mL flask containing a stir bar under Ar atmosphere. Then, LiCl (21.2 mg, 0.5 mmol) and $Et_3N$ (50.5 mg, 0.5 mmol) were added and the resulting solution was stirring at this temperature for 24 h. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1 to 10/1) to give product **5**. The diastereomer ration (dr value) was determined by $^1$H NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

**Ethyl (3S,4R)-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate 5**




Colourless oil, 94% yield. $[\alpha]_D^{25}$ = 56.3 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr = 18:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 22.14 min, $t_R$ (major) = 22.45 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.10 – 6.97 (m, 2H), 5.53 (m, *J* = 17.3, 10.1, 7.7 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.70 (d, *J* = 16.9 Hz, 1H), 4.39 (dd, *J* = 13.6, 3.8 Hz, 1H), 4.15 (m, *J* = 6.0, 2.9 Hz, 2H), 3.69 (t, *J* = 6.5 Hz, 1H), 3.52 (dd, *J* = 13.7, 12.1 Hz, 1H), 2.70 (m, *J* = 12.1, 5.3, 3.8 Hz, 1H), 2.38 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 170.83, 144.00, 136.46, 135.94, 135.88, 130.43, 129.74, 128.77, 127.52, 127.19, 124.42, 123.06, 118.46, 60.90, 43.43, 43.18, 41.37, 21.55, 14.24. **HRMS (ESI)** for $C_{21}H_{23}NO_4S$ [M + H]$^+$: calcd 386.1421, found 386.1417.

### 5.2 Synthesis of Product 6

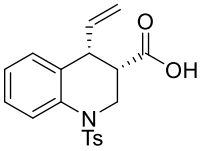



**3a** **6**

**Procedure F:** Compound **3a** (57.5 mg, 0.13 mmol) was dissolved into 1mL THF/$H_2O$ (2:1)

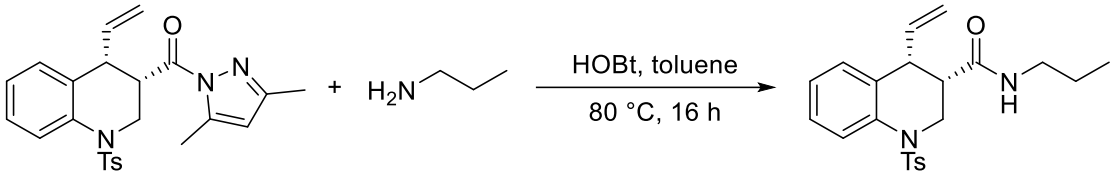
in an oven-dried 10 mL flask containing a stir bar under Ar atmosphere. Then, $LiOH·H_2O$ (11.1 mg, 0.26 mmol) was added and the resulting solution was stirring at this temperature for 16 h. The reaction mixture was quenched with two drops of $CH_3COOH$. Then the crude product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 7/1 to 5/1) to give product **6**. The diastereomer ration (dr value) was determined by $^1H$ NMR of the reaction mixture.

**(3S,4R)-1-Tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid 6**




Colourless oil, 94% yield. $[\alpha]_D^{25}$ = 40.2 (*c* = 1.00 in $CHCl_3$); dr >19:1, **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 3H), 7.17 – 6.98 (m, 2H), 5.59 (m, *J* = 17.3, 10.1, 7.6 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 4.74 (d, *J* = 16.8 Hz, 1H), 4.40 (dd, *J* = 13.7, 3.7 Hz, 1H), 3.73 (t, *J* = 6.4 Hz, 1H), 3.51 (dd, *J* = 13.6, 12.1 Hz, 1H), 2.77 (m, *J* = 12.1, 4.4 Hz, 1H), 2.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 176.5, 144.15, 136.09, 135.87, 135.81, 130.49, 129.81, 128.41, 127.69, 127.19, 124.56, 123.15, 119.08, 43.11, 42.77, 41.26, 21.58. **HRMS (ESI)** for $C_{19}H_{19}NO_4S$ $[M + H]^+$: calcd 358.1107, found 358.1101.

**5.3 Synthesis of Product 7**

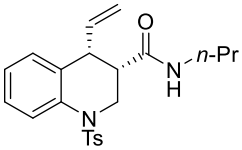



**3a** **7**

**Procedure G:** To a mixture of **3a** (43.5 mg, 0.1 mmol), n-propylamine (11.8 mg, 0.2 mmol) in PhMe (1.5 mL) was added 1-hydroxybenzotriazole (27.0 mg, 0.2 mmol). The reaction mixture was stirred for 16 h at 80 ºC. Afterwards, the volatiles were removed by evaporation and the resulted material was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 3/1 to 1/1) to give product **8**. The diastereomer ration (dr value) was determined by $^1H$ NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

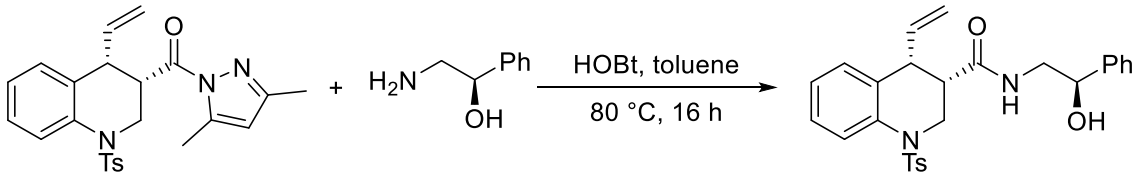
**(3S,4R)-*N*-Propyl-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxamide 7**

Colourless oil, 90% yield. $[\alpha]_D^{25}$ = -0.7 (*c* = 1.00 in $CHCl_3$); er = 95.5:4.5, dr >19:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 80:20 v/v, flow rate 1 mL/min, λ =



254 nm, 25 ºC), $t_R$ (major) = 6.34 min, $t_R$ (minor) = 6.94 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 13.9, 8.3 Hz, 3H), 7.07 – 6.95 (m, 2H), 5.74 (s, 1H), 5.60 (m, *J* = 17.2, 10.1, 7.5 Hz, 1H), 4.90 (d, *J* = 10.1 Hz, 1H), 4.60 (d, *J* = 16.9 Hz, 1H), 4.25 (dd, *J* = 13.3, 3.9 Hz, 1H), 3.65 – 3.47 (m, 2H), 3.19 (m, *J* = 27.1, 6.3 Hz, 2H), 2.60 (m, *J* = 11.9, 4.5 Hz, 1H), 2.38 (s, 3H), 1.49 (p, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 170.36, 144.08, 136.41, 135.87, 135.72, 130.41, 129.78, 128.99, 127.49, 127.25, 124.31, 122.76, 118.12, 44.50, 43.86, 42.57, 41.19, 22.85, 21.60, 11.45. **HRMS (ESI)** for $C_{22}H_{26}N_2O_3S$ $[M + H]^+$: calcd 399.1737, found 399.1735.

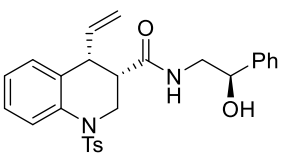
### 5.4 Synthesis of Product 8




**3a** **8**

**Procedure H:** To a mixture of **3a** (43.5 mg, 0.1 mmol), (R)-(+)-2-Phenylglycinol (27.4 mg, 0.2 mmol) in PhMe (1.5 mL) was added 1-hydroxybenzotriazole (27.0 mg, 0.2 mmol). The reaction mixture was stirred for 16 h at 80 ºC. Afterwards, the volatiles were removed by evaporation and the resulted material was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 3/1 to 1/1) to give product **8**. The diastereomer ration (dr value) was determined by $^1$H NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

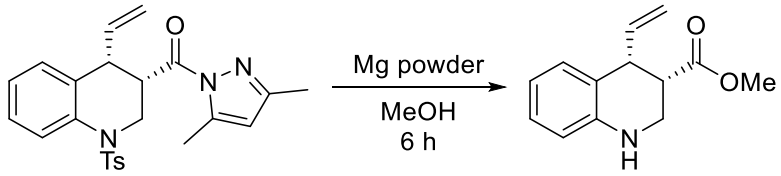
**(3S,4R)-N-((R)-2-Hydroxy-2-phenylethyl)-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxamide 8**



Colourless oil, 76% yield. $[\alpha]_D^{25}$ = 57 (*c* = 1.00 in $CHCl_3$); er = 95:5, dr >19:1, determined by HPLC analasis (Chiralpak OD column, hexane/i-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 29.93 min, $t_R$ (minor) = 62.94 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.36 (d, *J* = 4.5 Hz, 5H), 7.30 (t, *J* = 4.4 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 3H), 7.08 – 6.94 (m, 2H), 5.55 (m, *J* = 17.2, 10.0, 7.3 Hz, 1H), 4.86 (dd, *J* = 17.2, 9.2 Hz, 2H), 4.53 (d, *J* = 16.9 Hz, 1H), 4.25 (dd, *J* = 13.3, 3.6 Hz, 1H), 3.69 (m, *J* = 14.3, 6.8, 3.3 Hz,

1H), 3.54 (d, *J* = 12.2 Hz, 1H), 3.49 (t, *J* = 6.4 Hz, 1H), 3.38 – 3.24 (m, 2H), 2.63 (m, *J* = 11.9, 4.5 Hz, 1H), 2.38 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.59, 144.14, 141.49, 136.34, 135.85, 135.69, 130.37, 129.80, 128.80, 128.63, 127.99, 127.57, 127.25, 125.79, 124.34, 122.69, 118.34, 73.38, 47.17, 44.38, 43.86, 42.69, 21.60. **HRMS (ESI)** for $C_{27}H_{28}N_2O_4S$ [M + H]$^+$: calcd 477.1843, found 477.1850.

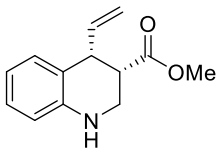
### 5.5 Synthesis of Product 9




**3a** **9**

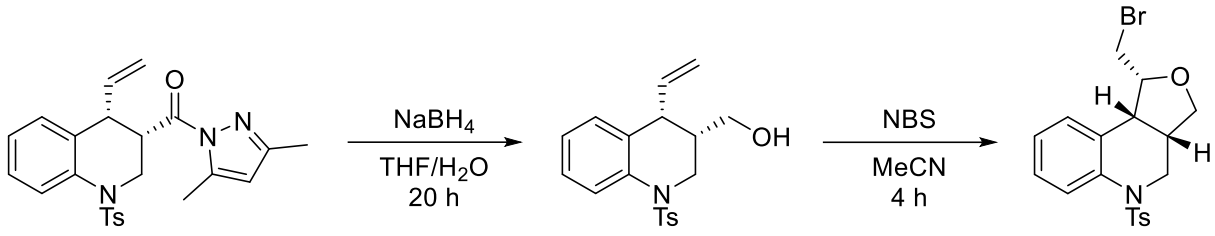
**Procedure I:** To a mixture of **3a** (43.6 mg, 0.10 mmol) in MeOH (2.0 mL) was added Mg powder (180.0 mg, 7.5 mmol). The reaction mixture was stirred for 6 h at 60 ºC. Afterwards, the mixture was quenched with 0.5 mL aqueous $NH_4Cl$ and extracted with EtOAc (2 x 5 mL). The combined EtOAc layers were died over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product was performed with flash column chromatography on silica gel (petrol ether/ EtOAc = 10/1 to 8/1) to give product **9**. The diastereomer ration (dr value) was determined by $^1$H NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

**Methyl (3S,4R)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate 9**




Colourless oil, 83% yield. $[\alpha]_D^{25}$ = -36.1 (c = 1.00 in $CHCl_3$); er = 95.5:4.5, dr = 5:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 99:1 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 29.64 min, $t_R$ (major) = 44.40 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.05 – 6.91 (m, 2H, major), 6.64 (t, *J* = 7.5 Hz, 1H, major), 6.53 (d, *J* = 8.0 Hz, 1H, major), 5.86 (m, *J* = 17.3, 10.2, 7.7 Hz, 1H, major), 5.76 (dd, *J* = 17.7, 9.3 Hz, 1H, minor), 5.25 – 5.12 (m, 2H, minor), 5.13 – 5.08 (m, 1H, major), 4.94 (m, *J* = 16.9, 1.5 Hz, 1H, major), 3.96 – 3.83 (m, 2H, major), 3.79 (m, *J* = 8.2 Hz, 1H, minor), 3.73 (s, 3H, major), 3.44 (d, *J* = 8.4 Hz, 2H, major), 3.09 – 2.97 (m, 1H, major). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 172.75, 143.45, 138.35, 130.40, 127.74, 120.87, 117.46, 117.19, 114.23, 51.66, 43.32, 42.26, 38.60. **HRMS (ESI)** for $C_{13}H_{15}NO_2$ [M + H]$^+$: calcd 218.1176, found 218.1183.

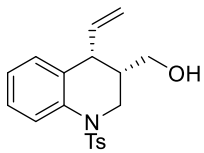
## 5.6 Synthesis of Product 10




**Procedure J:** To a mixture of **3a** (74.3 mg, 0.17 mmol) in THF/$H_2O$ (4:1, 1.7 mL) was added $NaBH_4$ (66.0 mg, 1.74 mmol) in one portion. The reaction mixture was stirred for 20 h at room temperature. Afterwards, the reaction mixture was quenched with 1.3 mL HCl (2 N) and extracted with DCM (2 x 5 mL). The combined organic phase was died over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulted material was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 5/1 to 1/1) to give product **S1**. The diastereomer ration (dr value) was determined by $^1$H NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

To a mixture of **S1** (34.3 mg, 0.10 mmol) in MeCN (2.0 mL) was added NBS (19.6 mg, 0.11 mmol). The reaction mixture was stirred for 4 h at room temperature. Afterwards, the mixture was poured into 10% $Na_2S_2O_3$ solution (5 mL) and extracted with EtOAc (2 x 5 mL). The combined EtOAc layers were washed with saturated aqueous $KHCO_3$ solution (5 mL) and brine (5 mL), died over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product was performed with flash column chromatography on silica gel (petrol ether/ EtOAc = 15/1 to 10/1) to give product **10**. The diastereomer ration (dr value) was determined by $^1$H NMR of the reaction mixture and the enantiomeric excess (ee value) of purified product was determined by chiral HPLC.

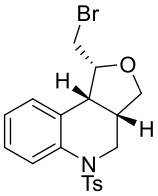
**((3S,4R)-1-Tosyl-4-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)methanol S1**




Colourless oil, 83% yield. $[\alpha]_D^{25}$ = -28.1 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr >19:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (minor) = 61.59 min, $t_R$ (major) = 69.43 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.13 (m, 3H), 7.07 – 6.94 (m, 2H), 5.47 (m, *J* = 16.9, 10.1, 8.6 Hz, 1H),

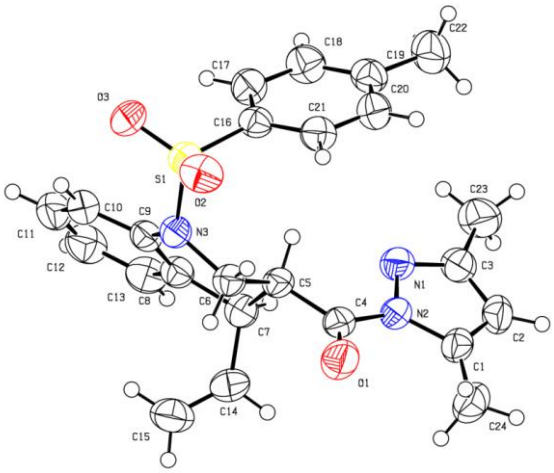
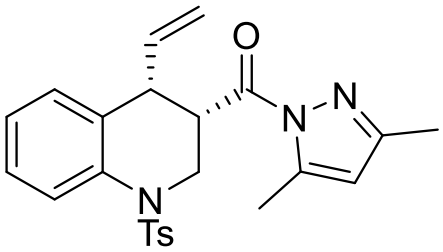
4.97 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.85 (m, *J* = 16.9, 1.2 Hz, 1H), 4.12 (dd, *J* = 12.9, 3.7 Hz, 1H), 3.65 – 3.49 (m, 2H), 3.46 – 3.32 (m, 2H), 2.38 (s, 3H), 2.04 – 1.93 (m, 1H), 1.79 (d, *J* = 5.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 143.89, 136.81, 136.23, 136.10, 130.31, 129.98, 129.70, 127.28, 127.16, 124.26, 122.58, 117.72, 62.13, 45.38, 43.88, 38.36, 21.57. **HRMS (ESI)** for $C_{19}H_{21}NO_3S$ $[M + H]^+$: calcd 344.1315, found 344.1318.

**(1S,3aS,9bR)-1-(bromomethyl)-5-tosyl-1,3,3a,4,5,9b-hexahydrofuro[3,4-c]quinoline 10**

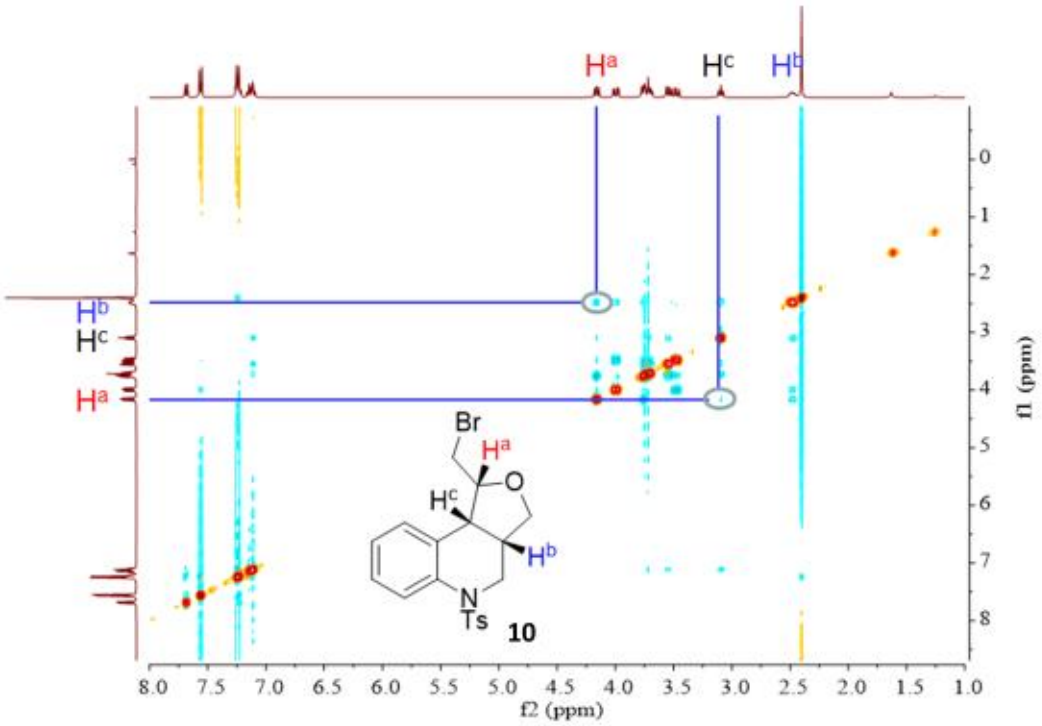


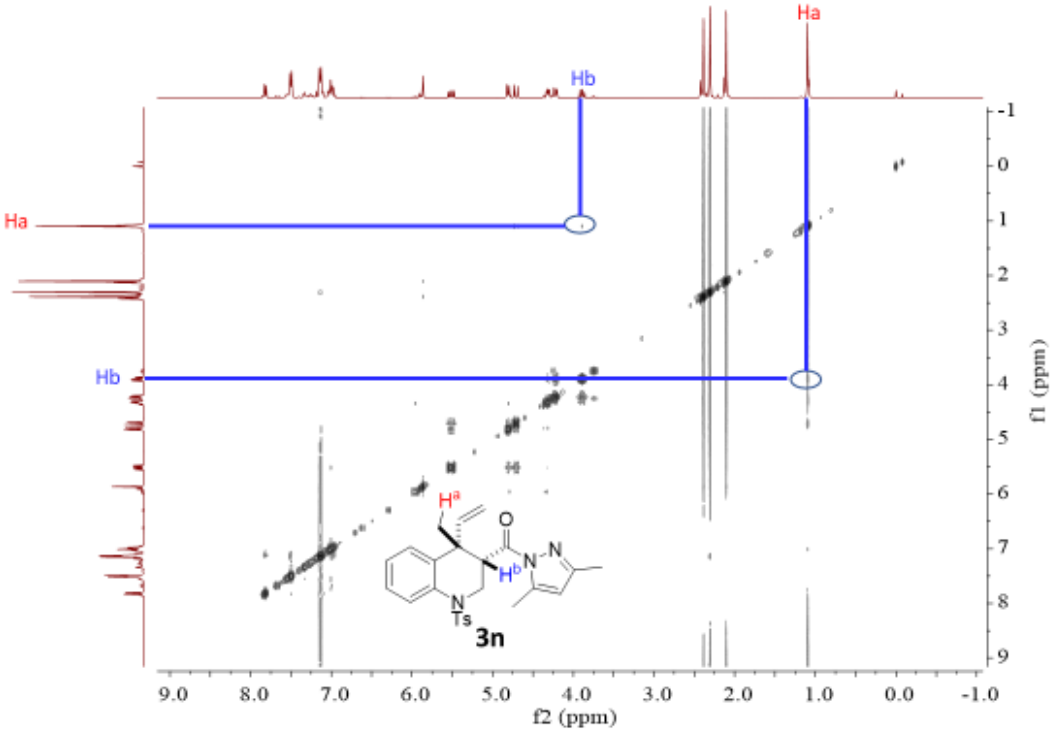

Colourless oil, 68% yield. $[\alpha]_D^{25}$ = -88.1 (*c* = 1.00 in $CHCl_3$); er = 96.5:3.5, dr >19:1, determined by HPLC analasis (Chiralpak AD column, hexane/i-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 ºC), $t_R$ (major) = 36.71 min, $t_R$ (minor) = 41.76 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 8.4, 2.2 Hz, 3H), 7.11 – 6.95 (m, 2H), 5.53 (m, *J* = 17.4, 10.1, 7.7 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.70 (d, *J* = 16.9 Hz, 1H), 4.47 – 4.31 (m, 1H), 3.69 (m, 4H), 3.52 (dd, *J* = 13.7, 12.2 Hz, 1H), 2.73 (m, *J* = 12.2, 5.4, 3.7 Hz, 1H), 2.38 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ = 171.29, 144.04, 136.57, 135.92, 135.84, 130.49, 129.77, 128.67, 127.57, 127.18, 124.49, 123.12, 118.48, 51.94, 43.35, 43.10, 41.39, 21.58. **HRMS (ESI)** for $C_{19}H_{20}BrNO_3S$ $[M + Na]^+$: calcd 422.0420, found 422.0415.

## 6. X-ray Crystal Structure Determination of Product 3a

| | | |
|---|---|---|
| **3a** |  |  **(*3S*,*4R*)-3a** **CCDC 2114293** |

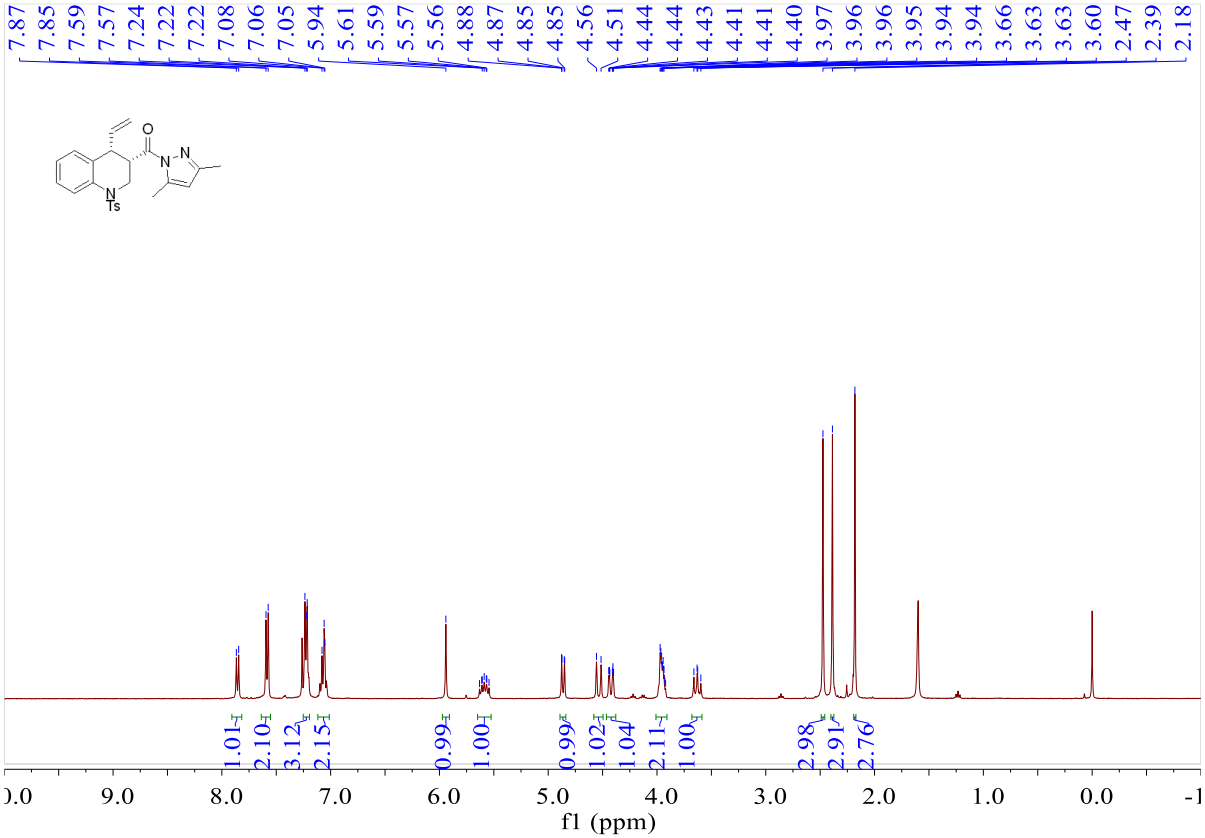
## 7. Copy of the NOESY Spectroscopy of Product 10 and 3n



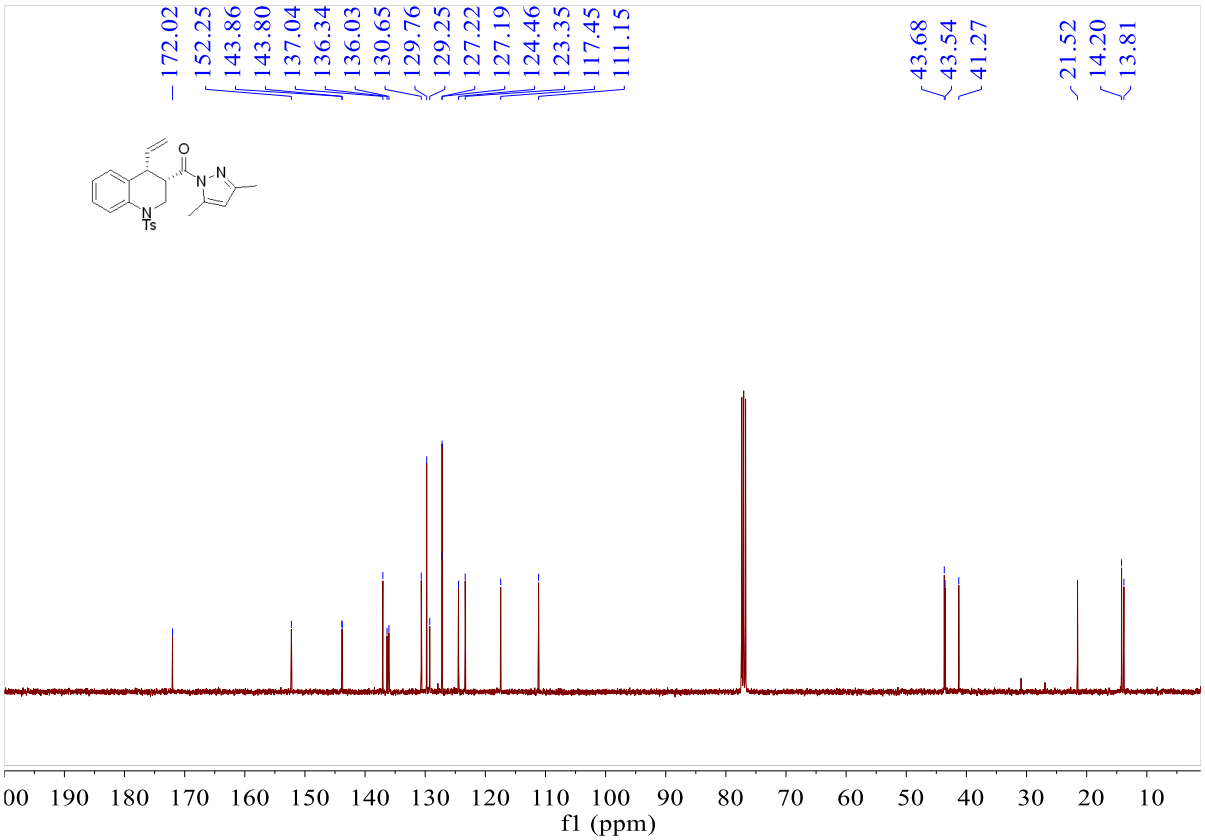



## 8. Copies of $^{1}H$ NMR, $^{13}C$ NMR and $^{19}F$ NMR Spectra

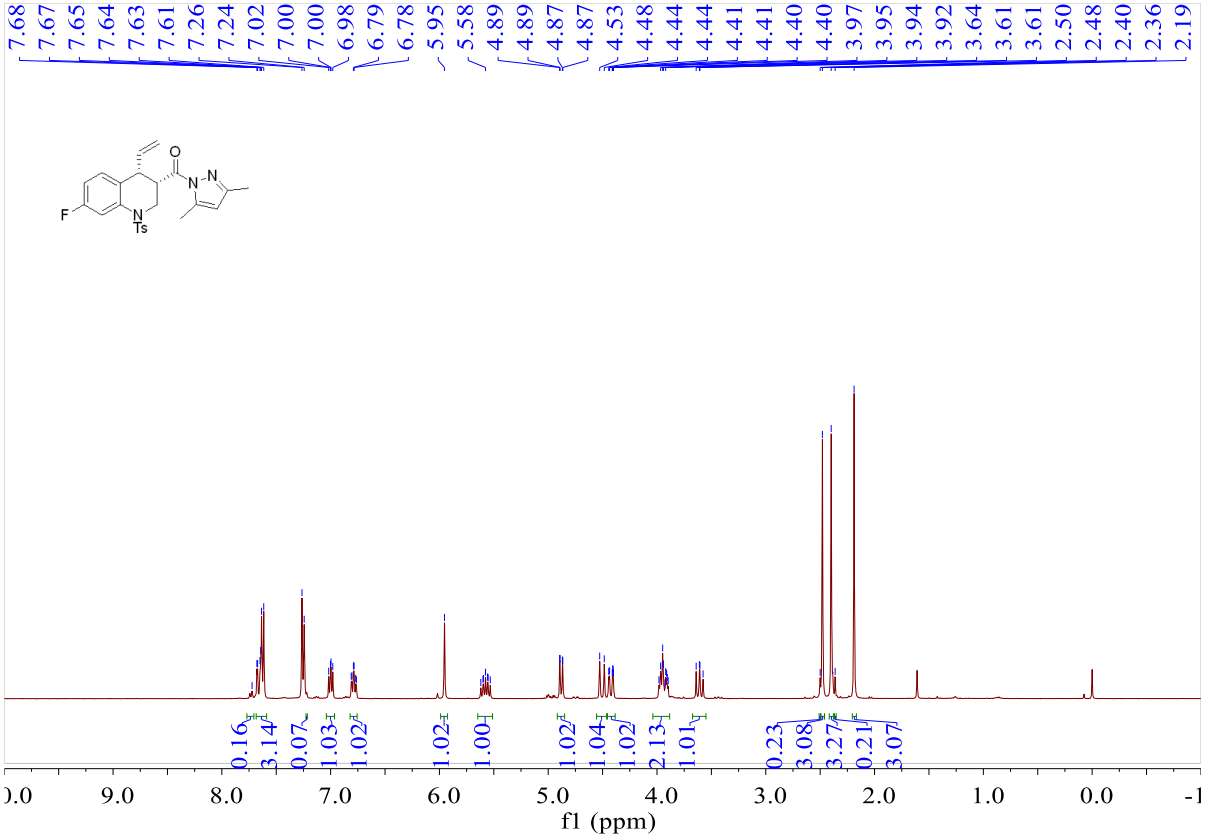
$^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of product **3a**



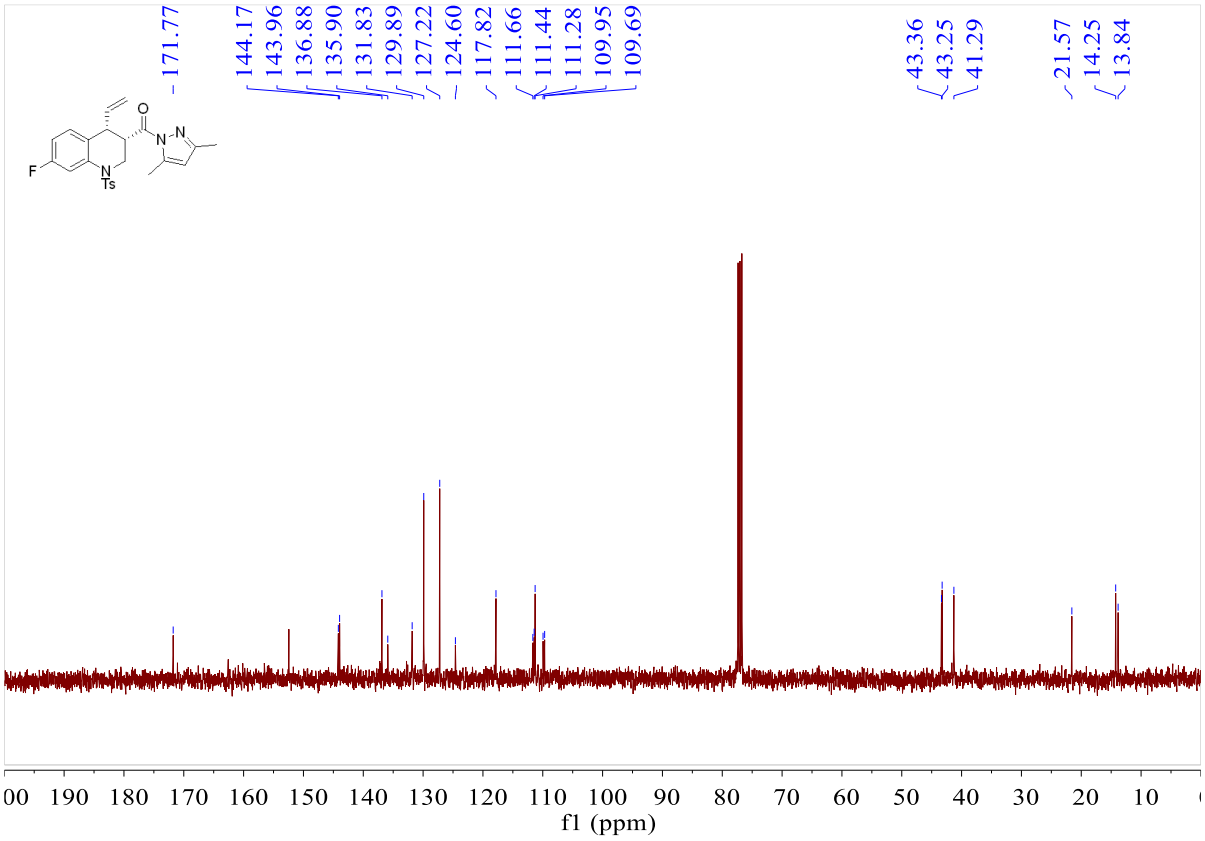

$^{13}C$ NMR (100 MHz, $CDCl_3$) spectrum of product **3a**



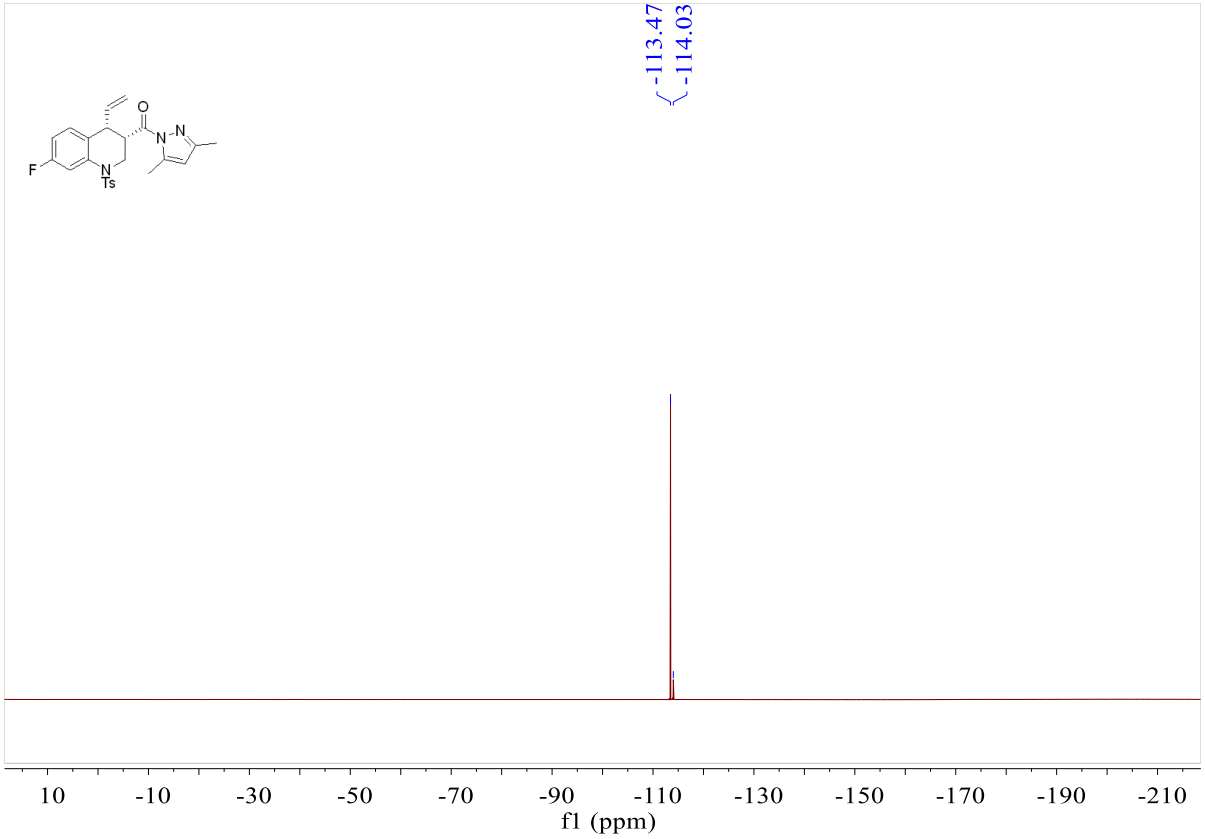
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3b**



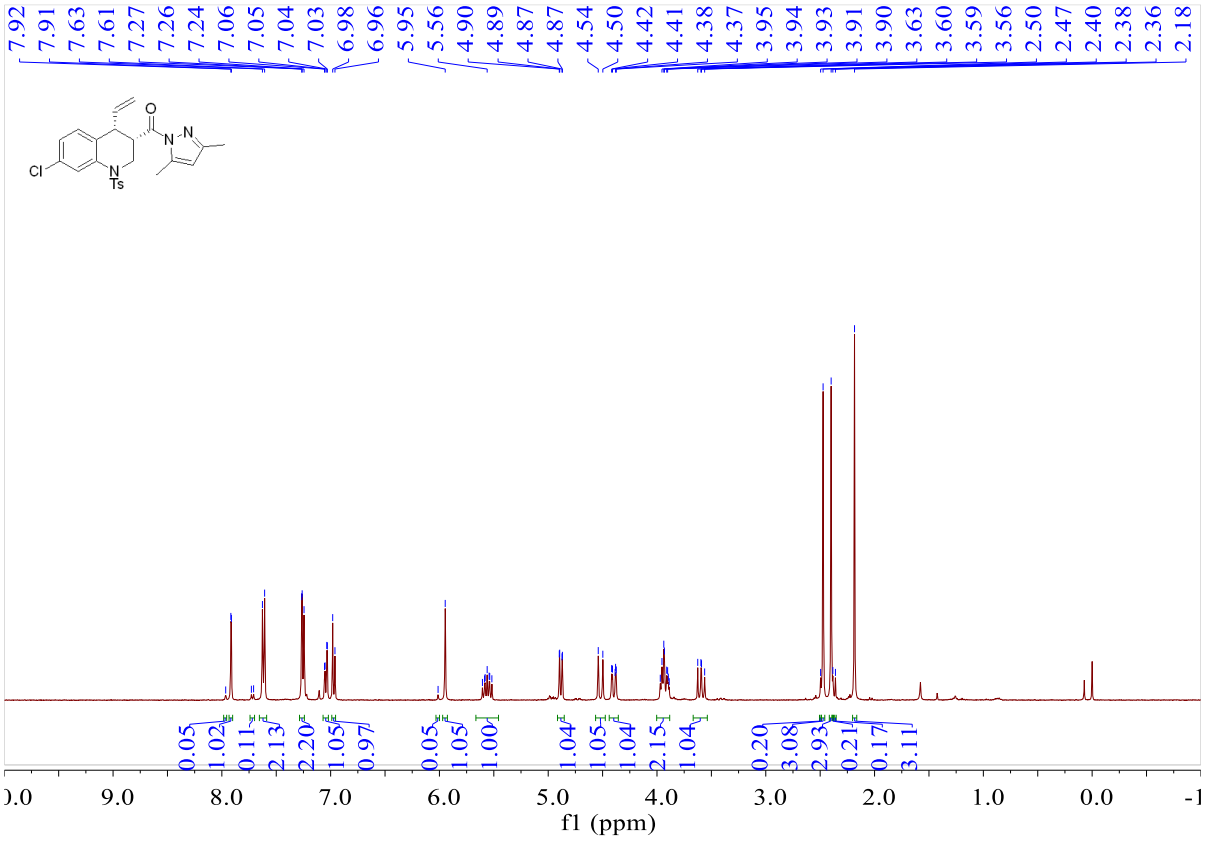

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3b**



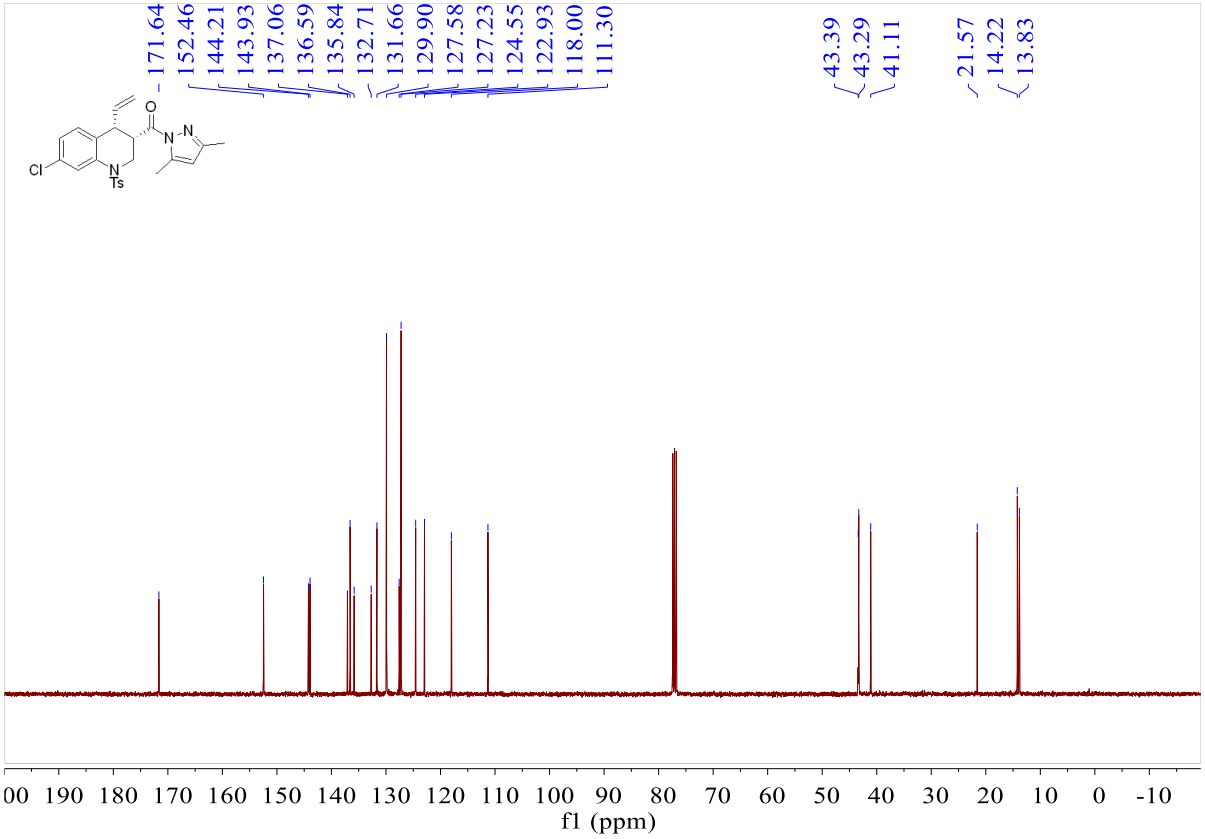
$^{19}$F NMR (376 MHz, $CDCl_3$) of product **3b**



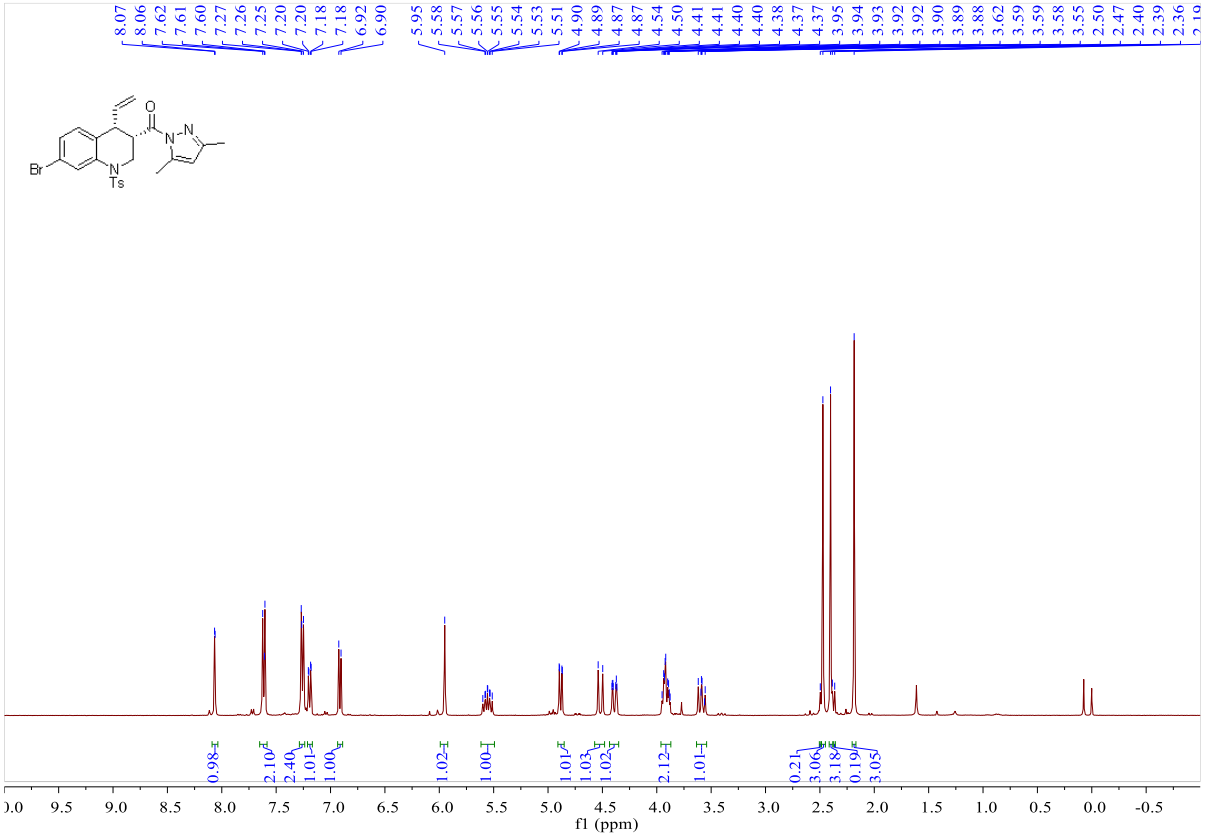

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3c**



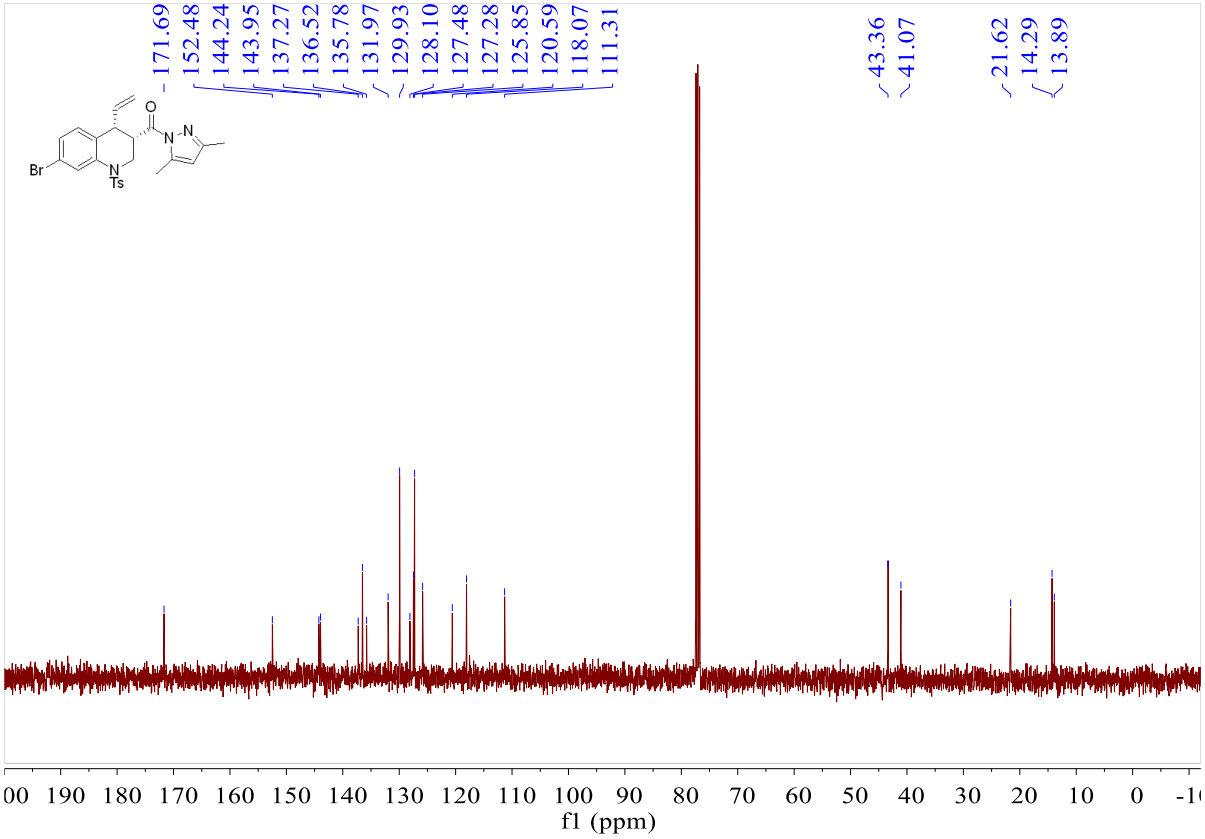
$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3c**



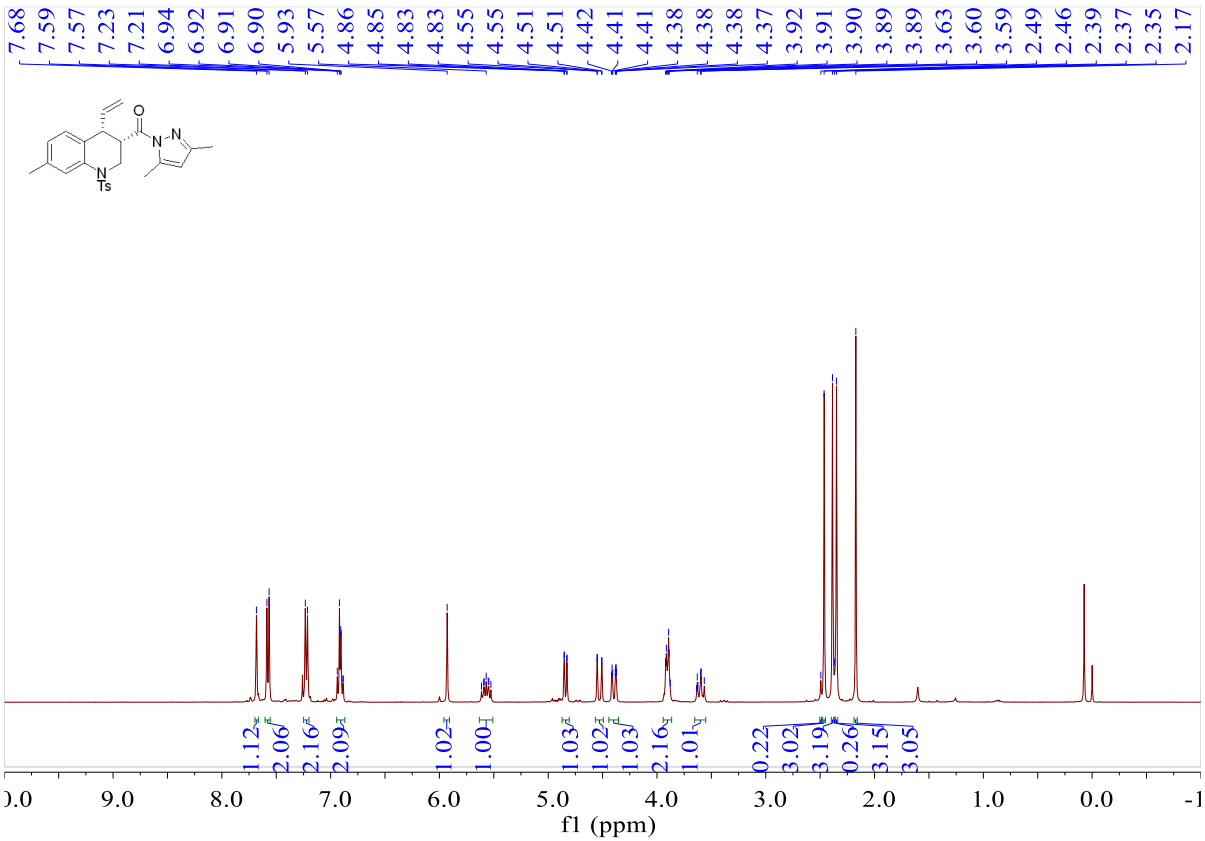

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3d**



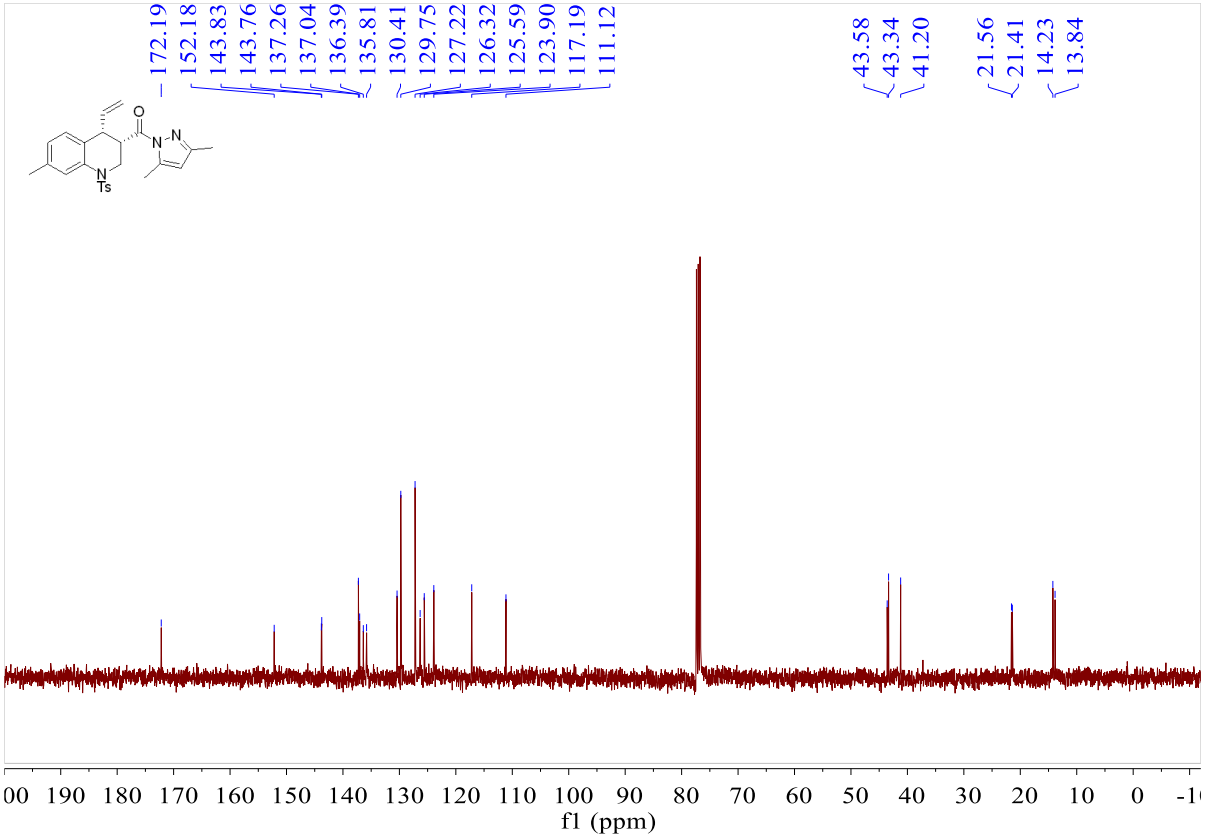
$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3d**



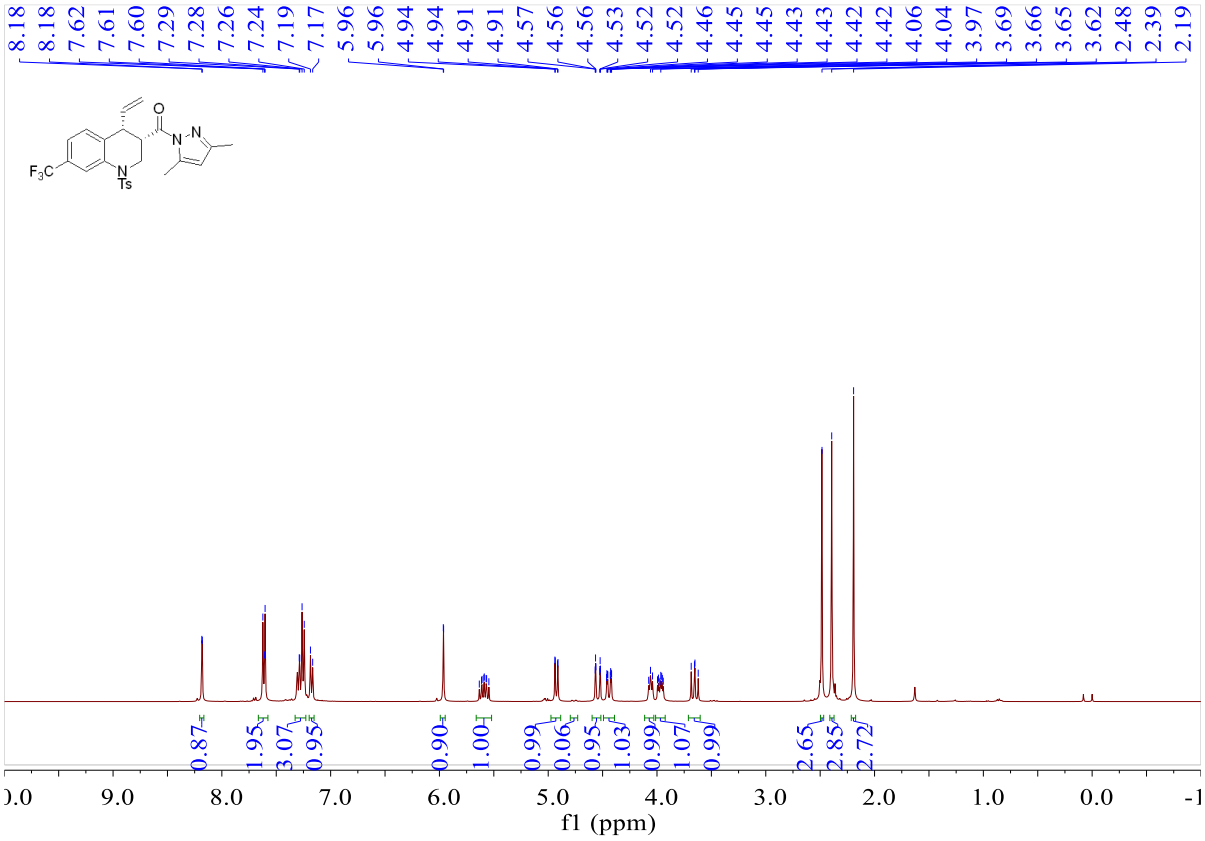

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3e**



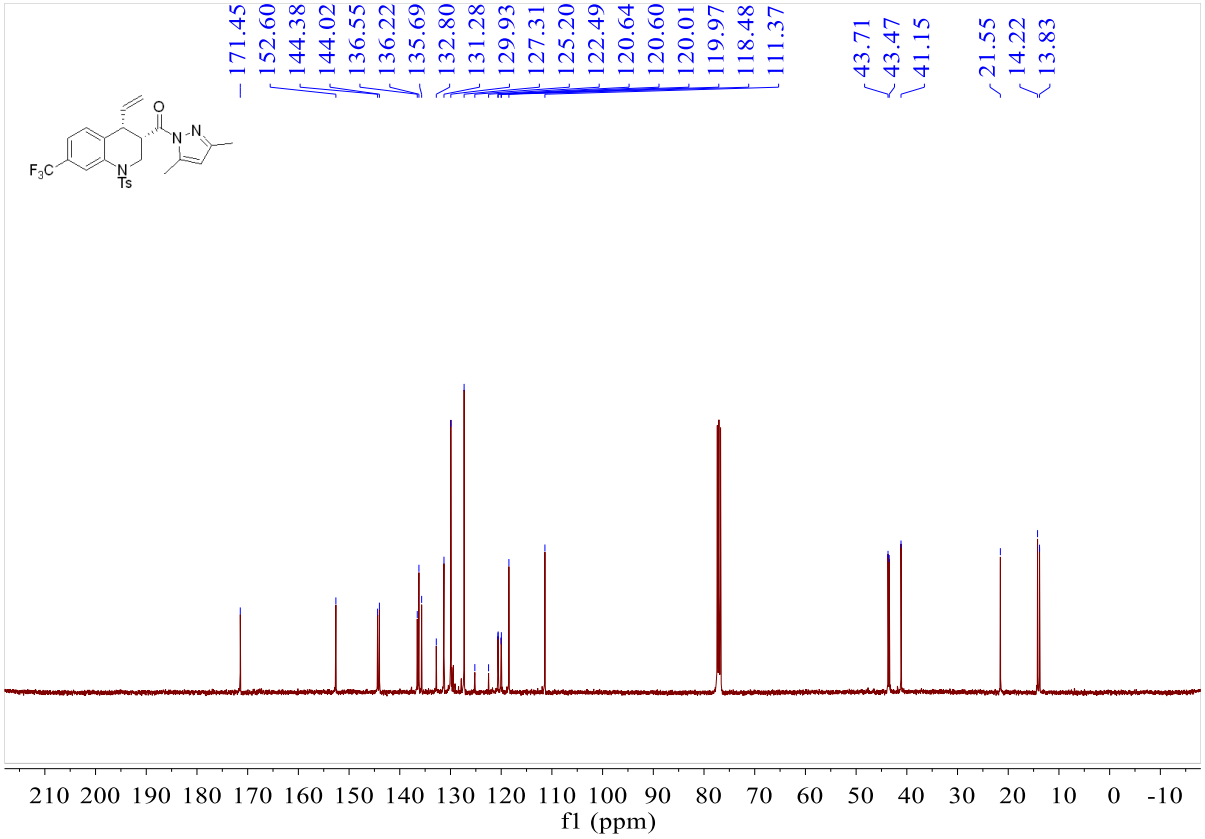
$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3e**



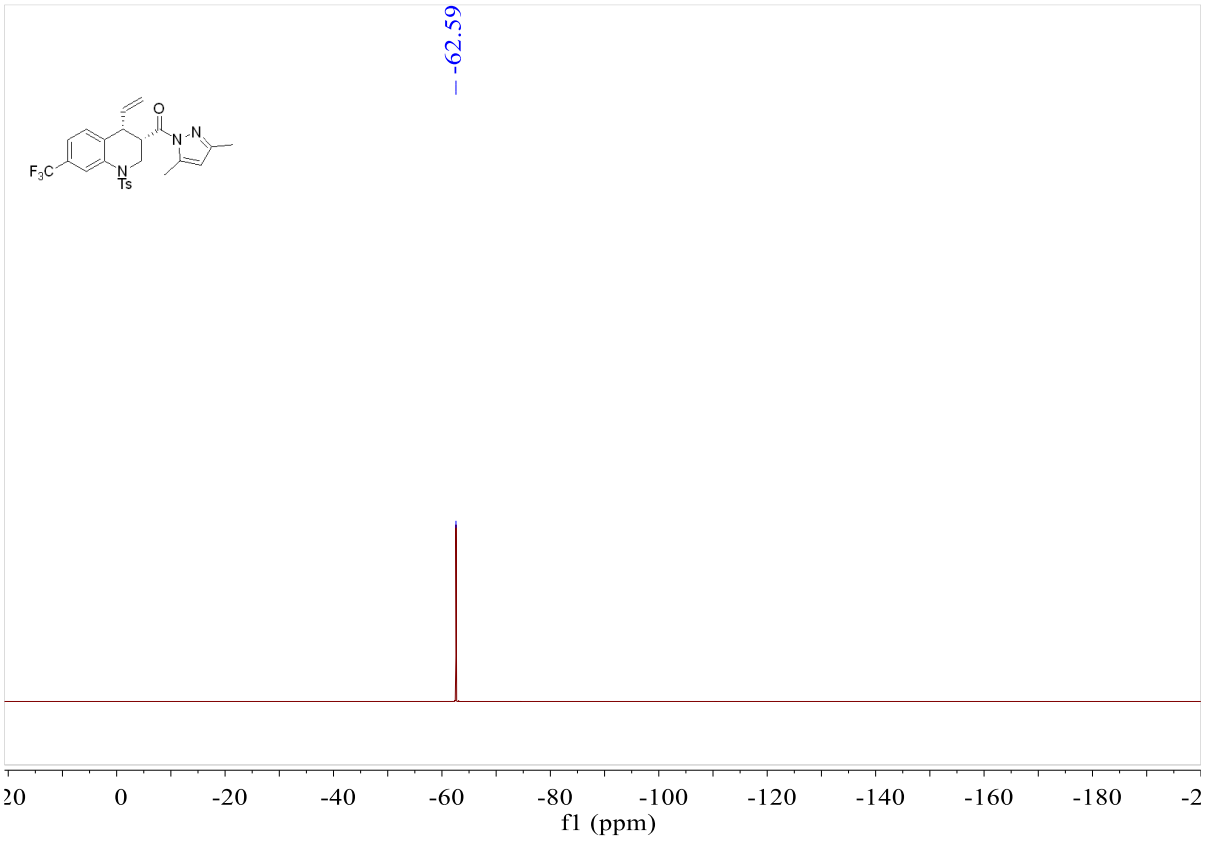

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3f**



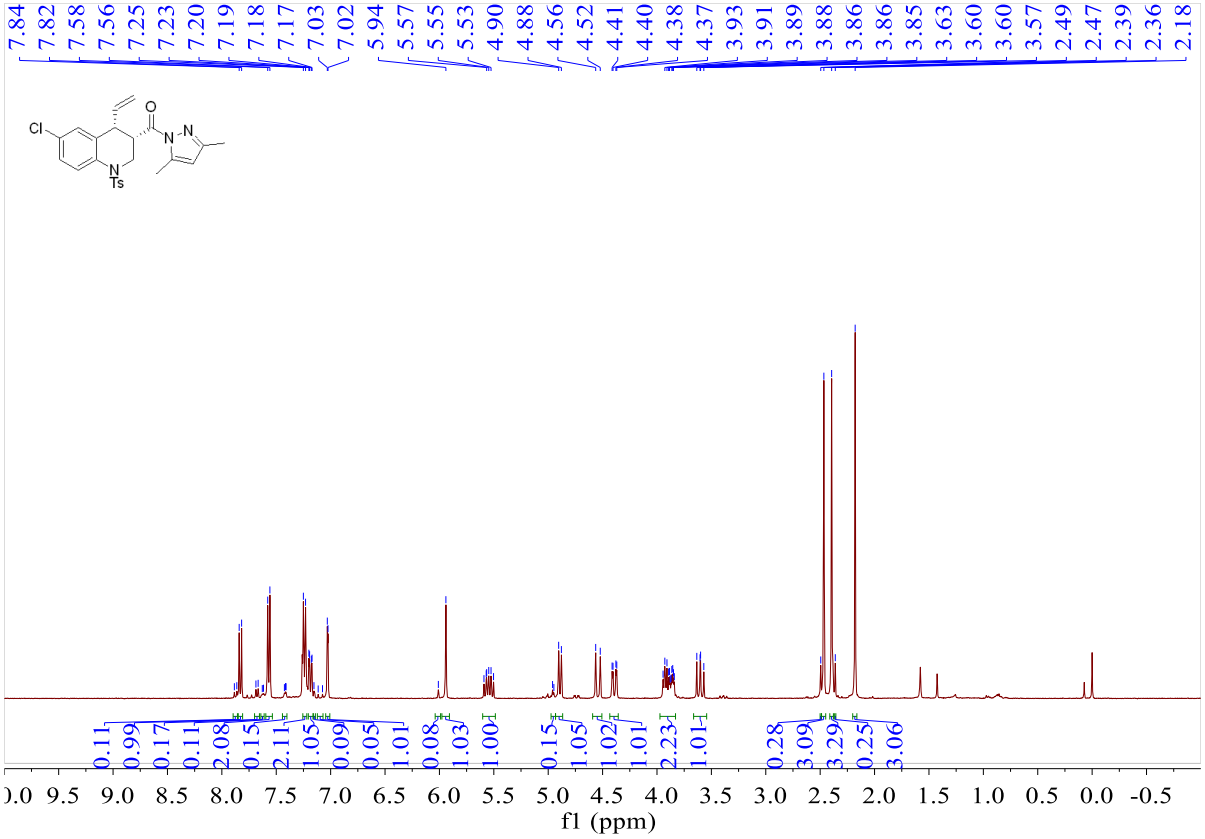
$^{13}C$ NMR (100 MHz, $CDCl_3$) of product **3f**



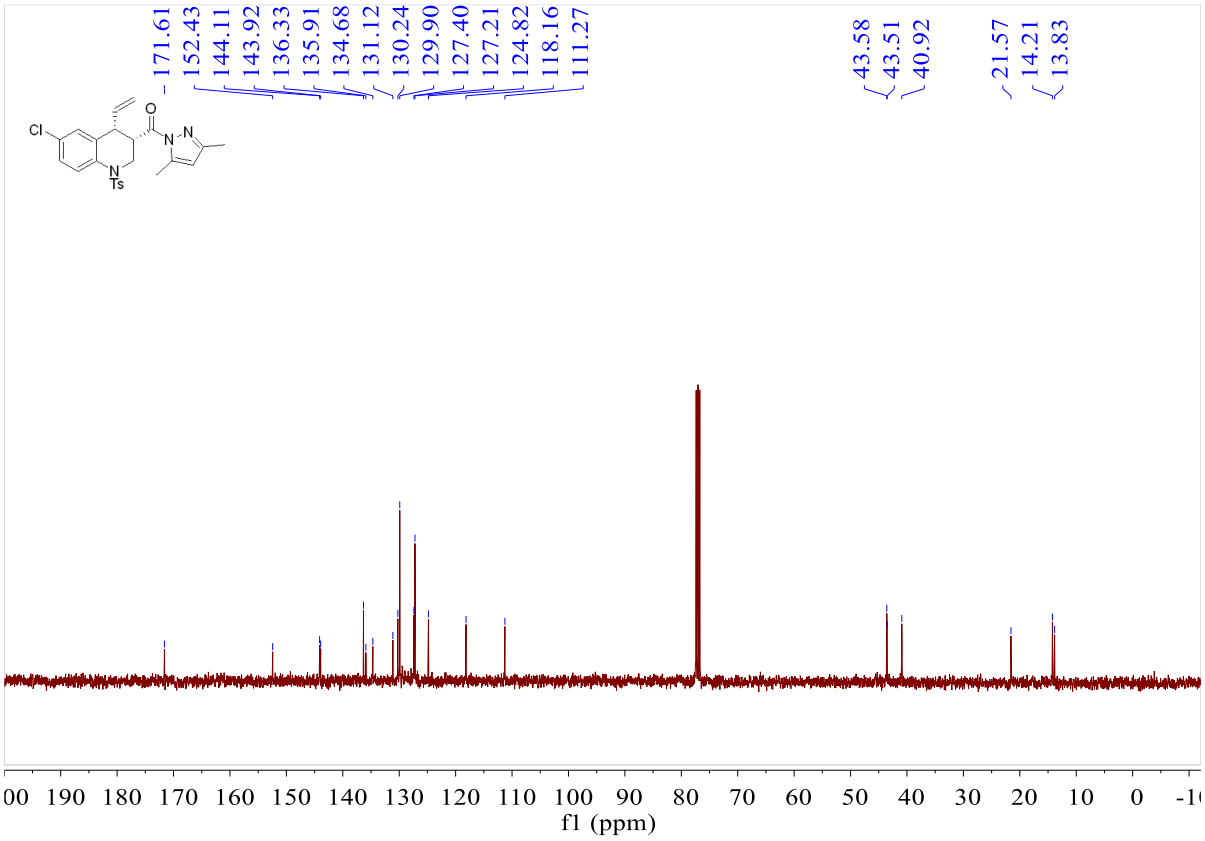

$^{19}F$ NMR (376 MHz, $CDCl_3$) of product **3f**



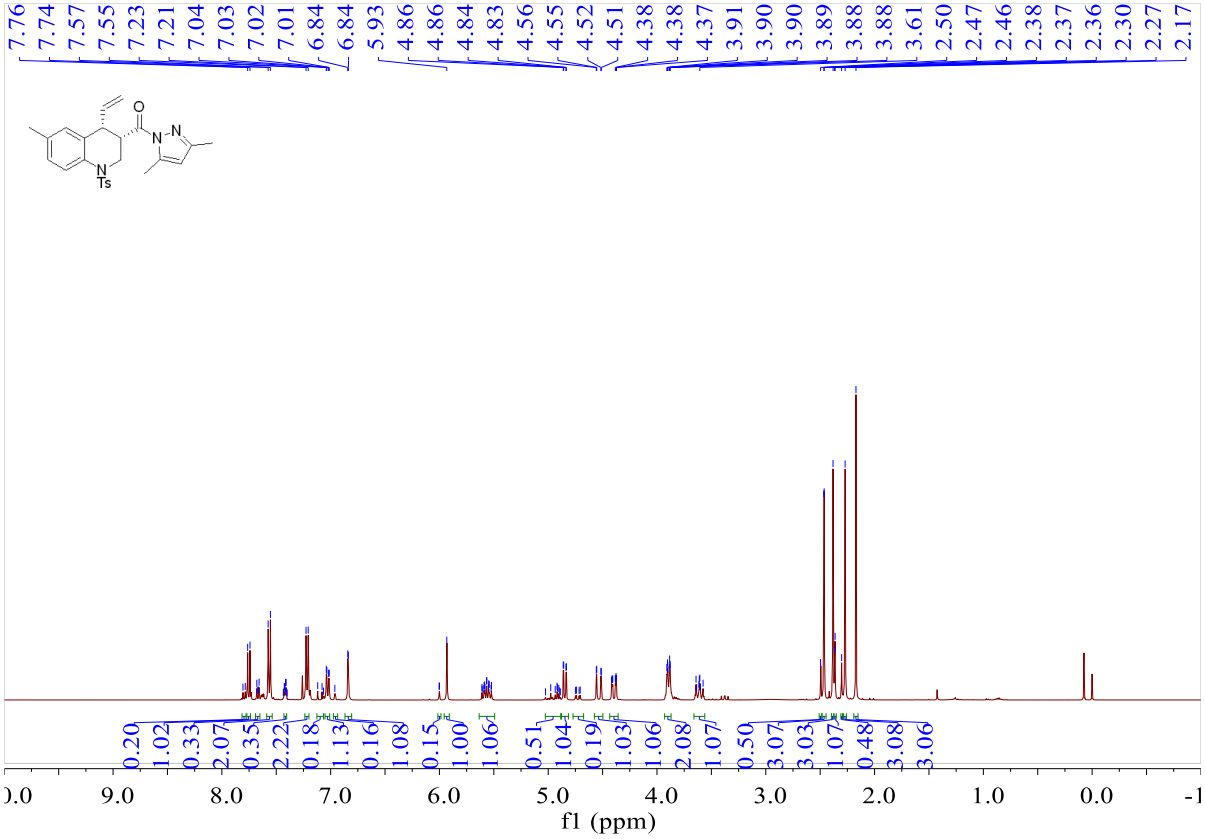
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3g**



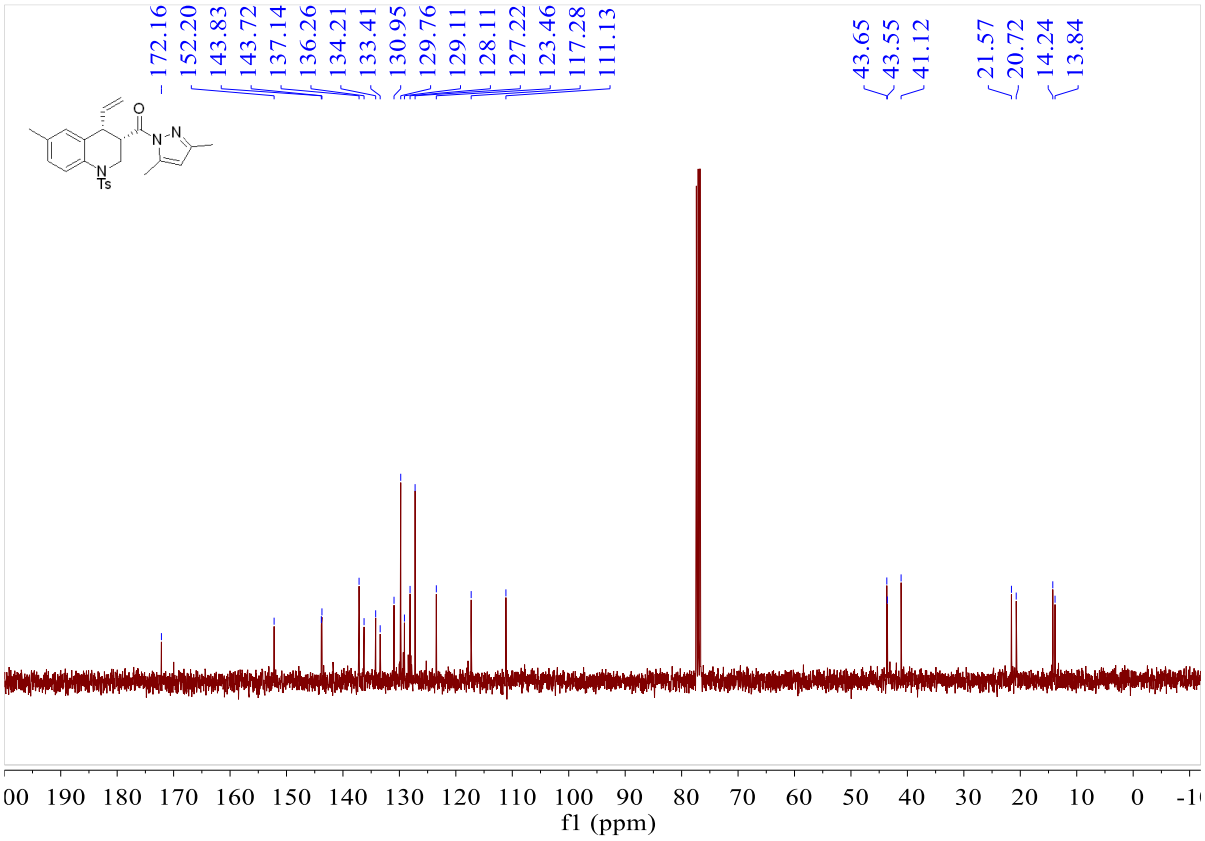

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3g**



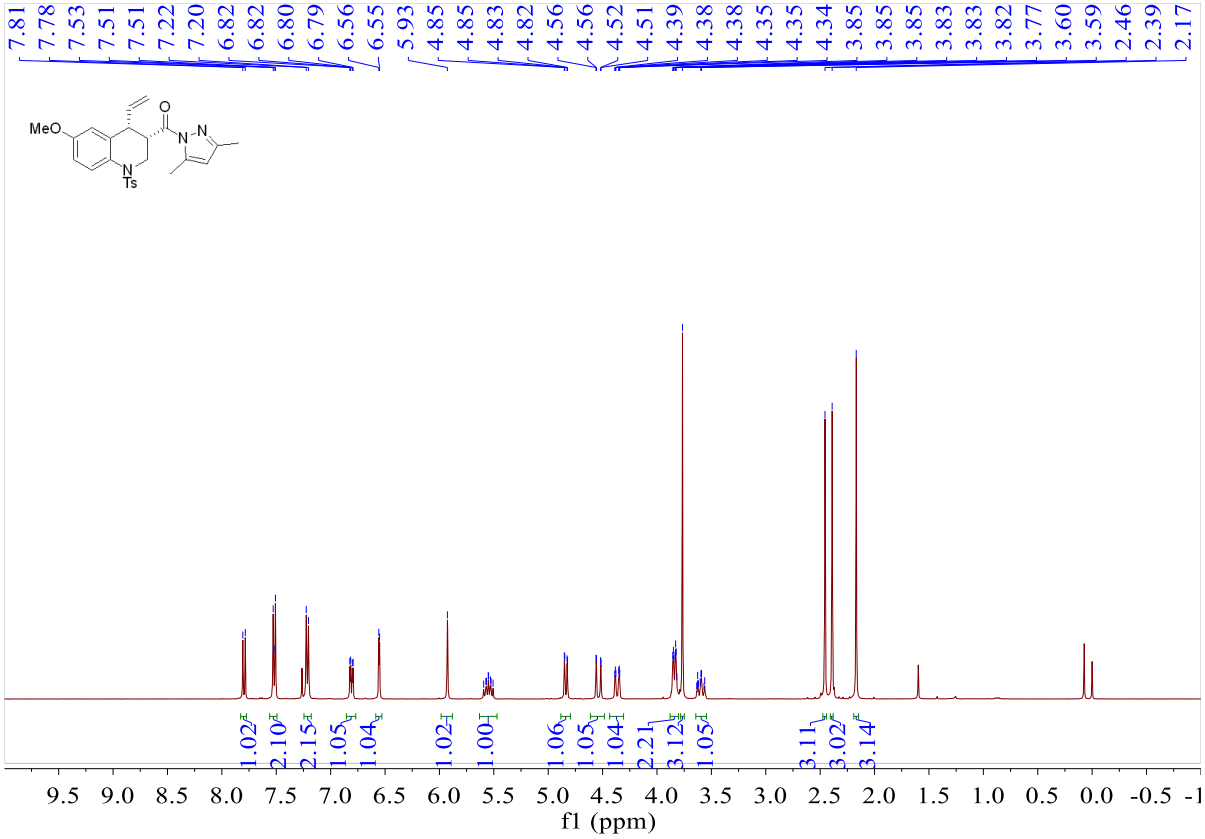
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3h**



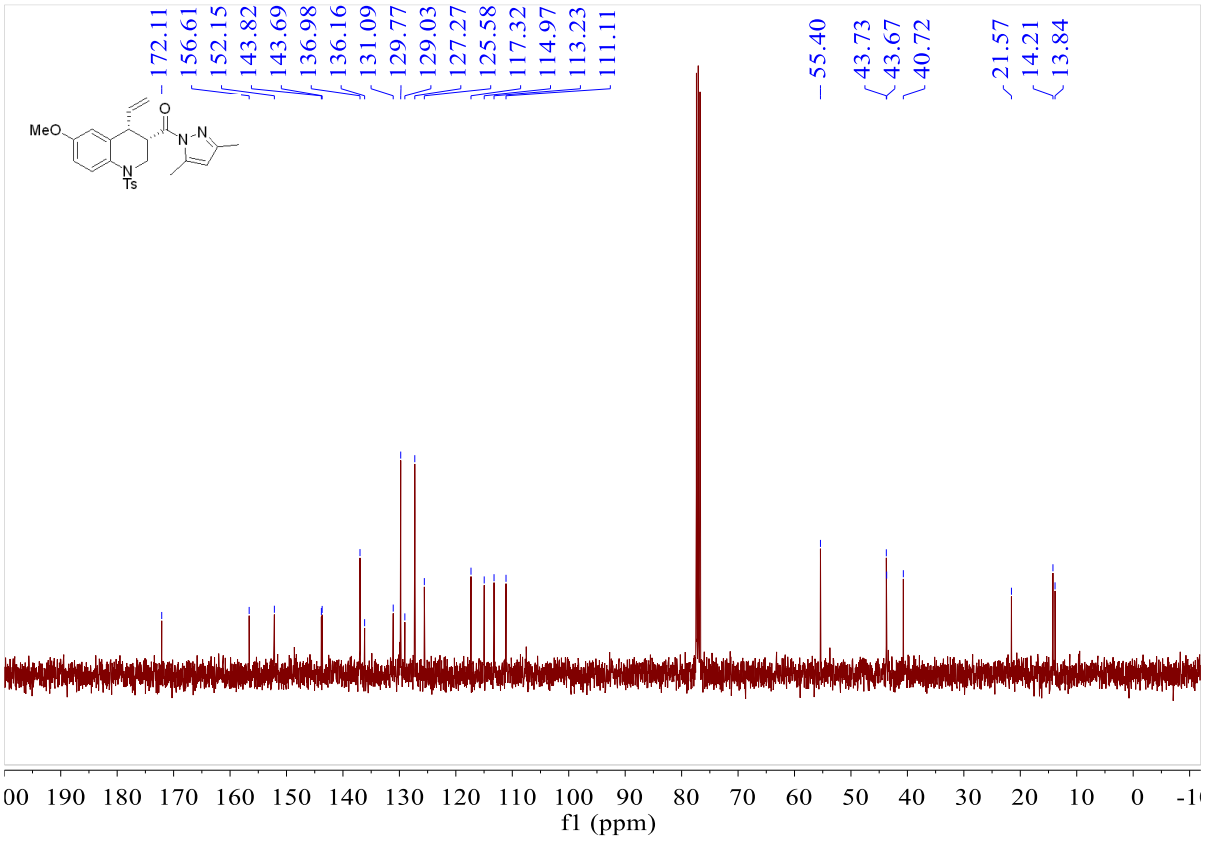

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3h**



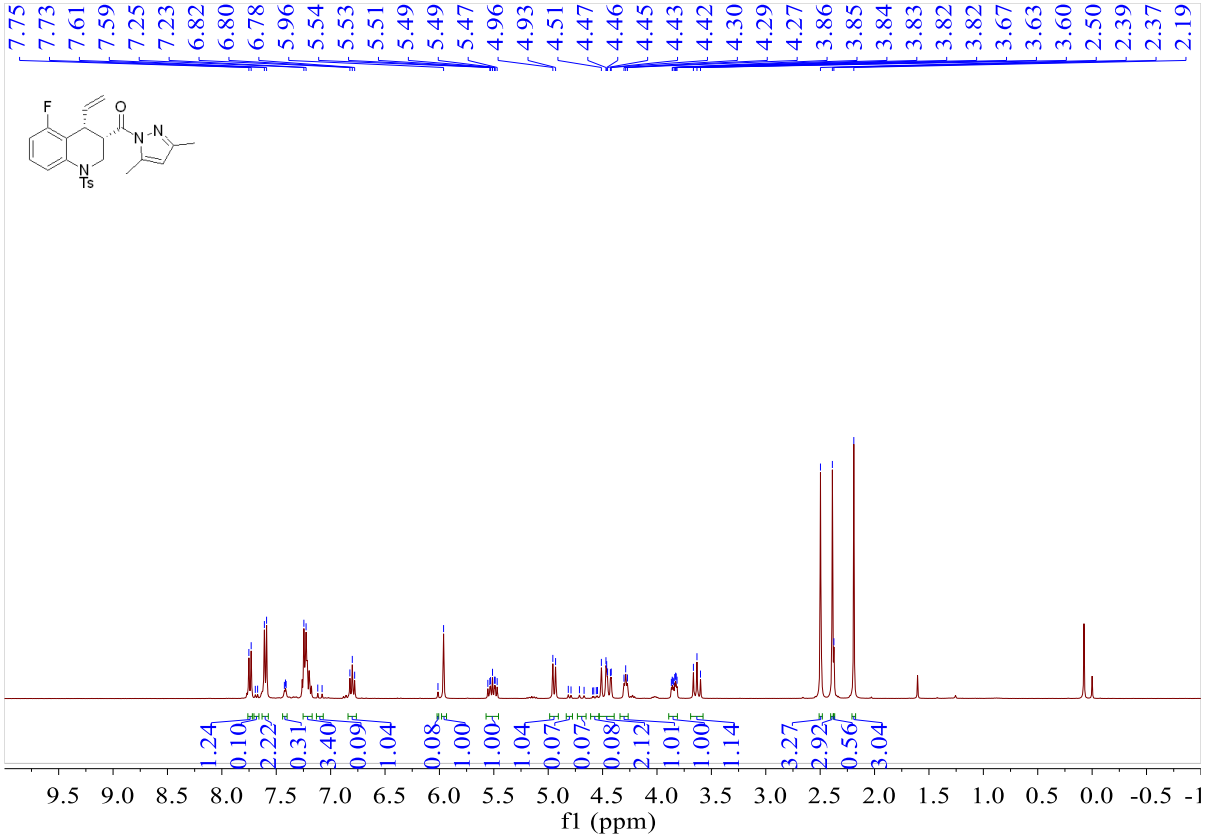
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3i**



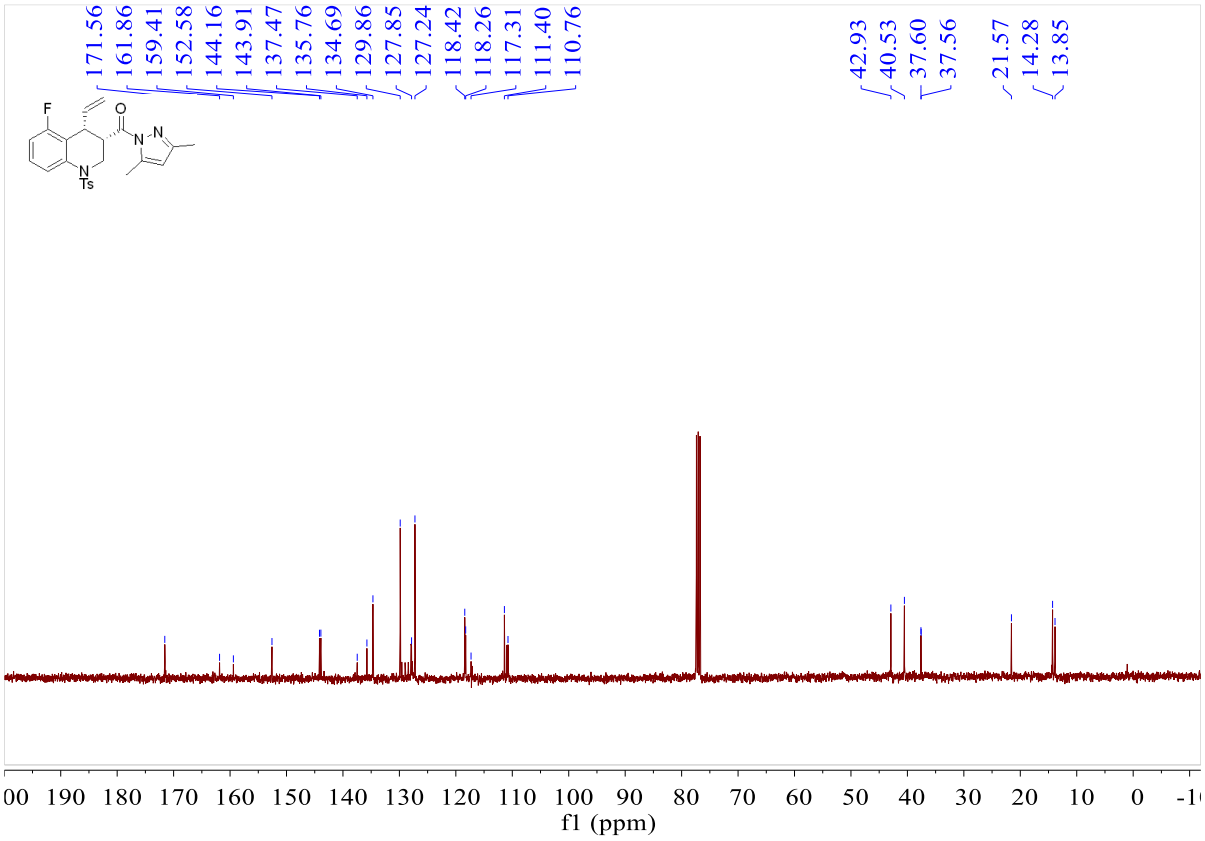

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3i**



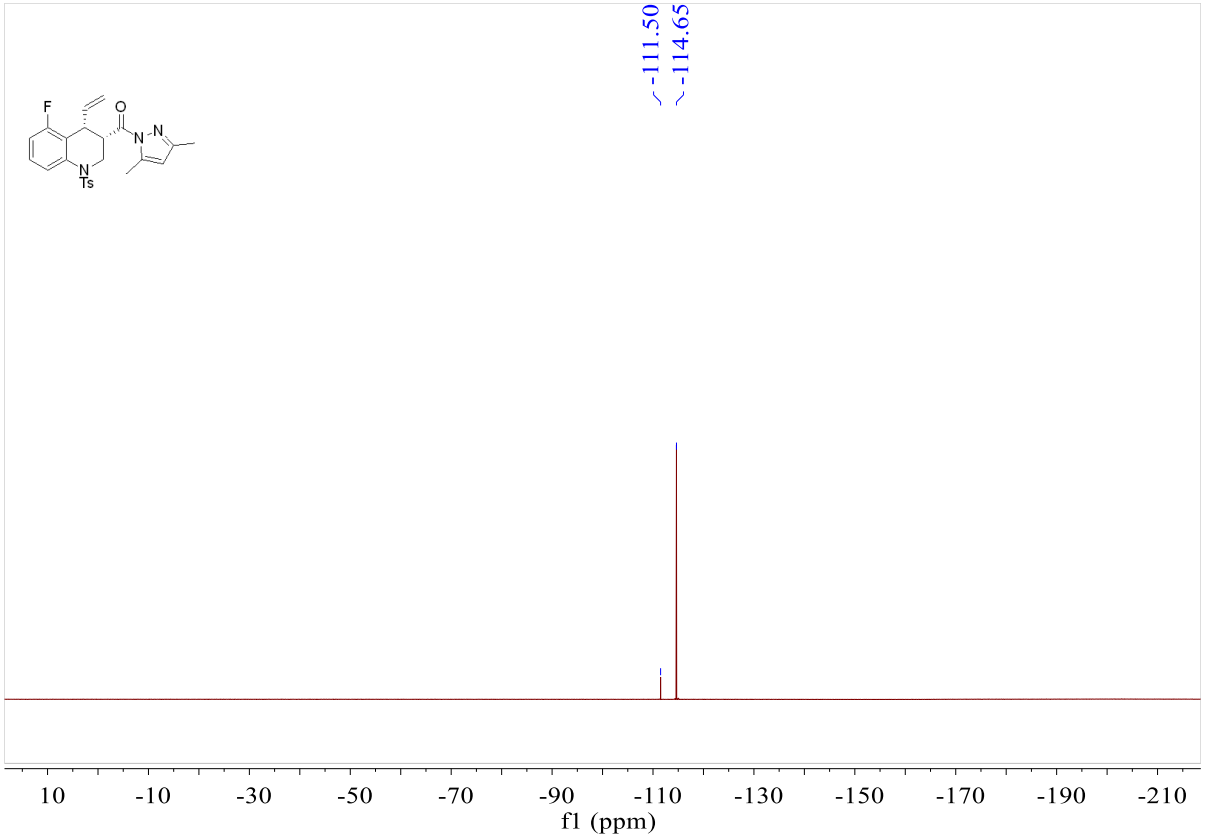
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3j**



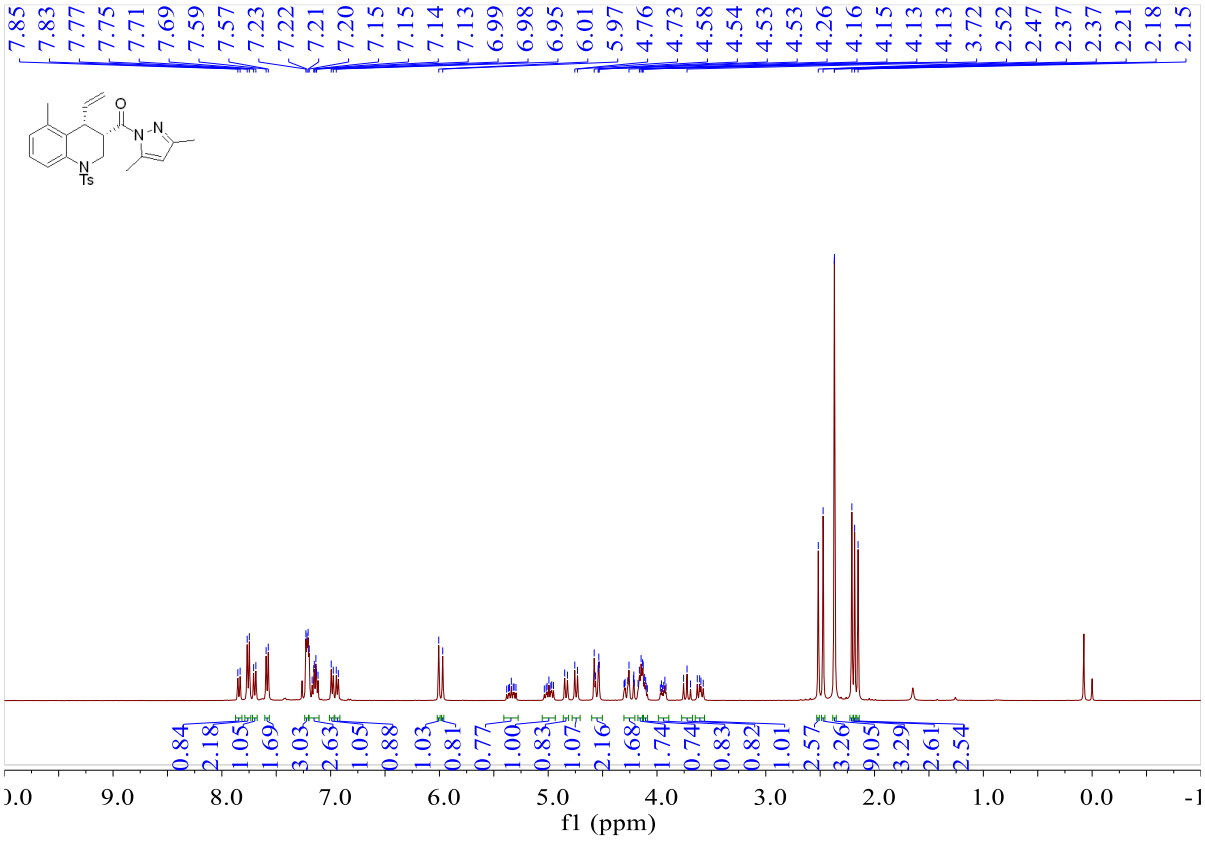

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3j**



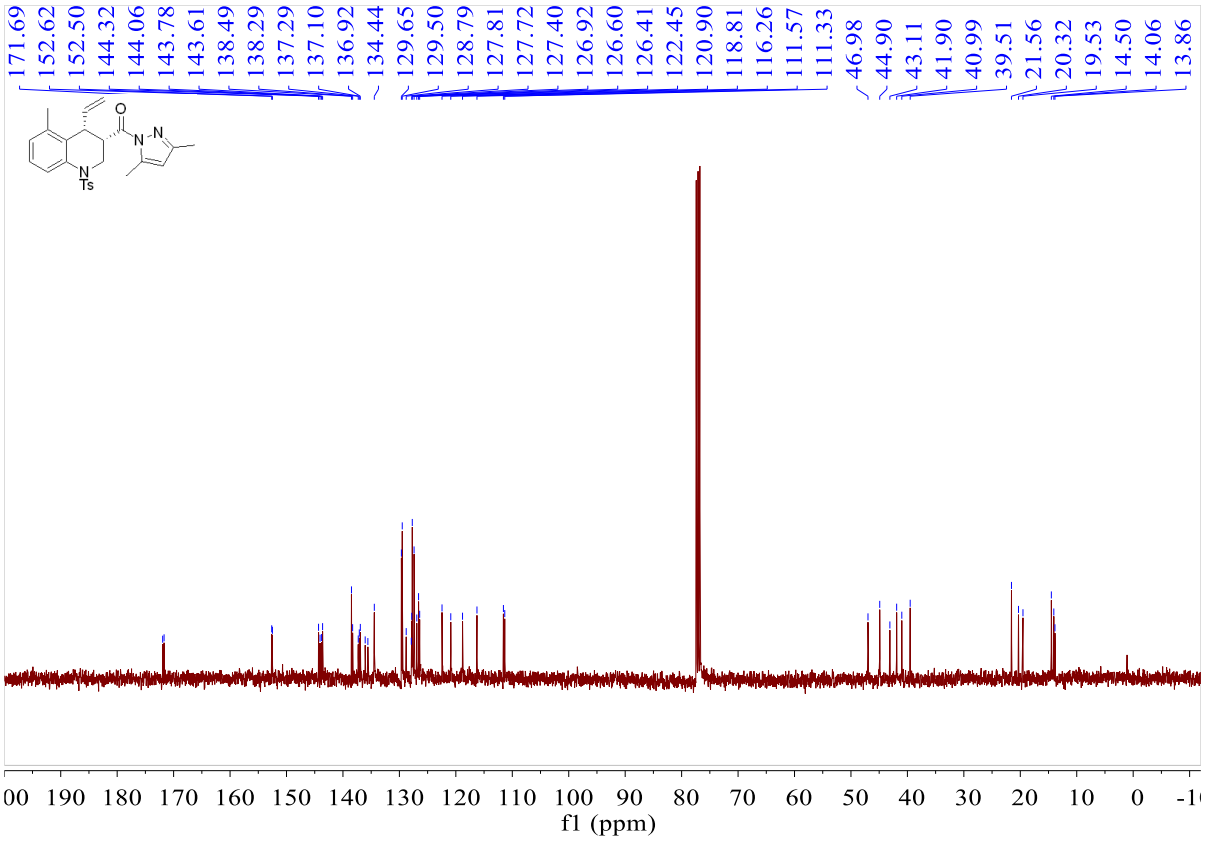
$^{19}$F NMR (376 MHz, $CDCl_3$) of product **3j**



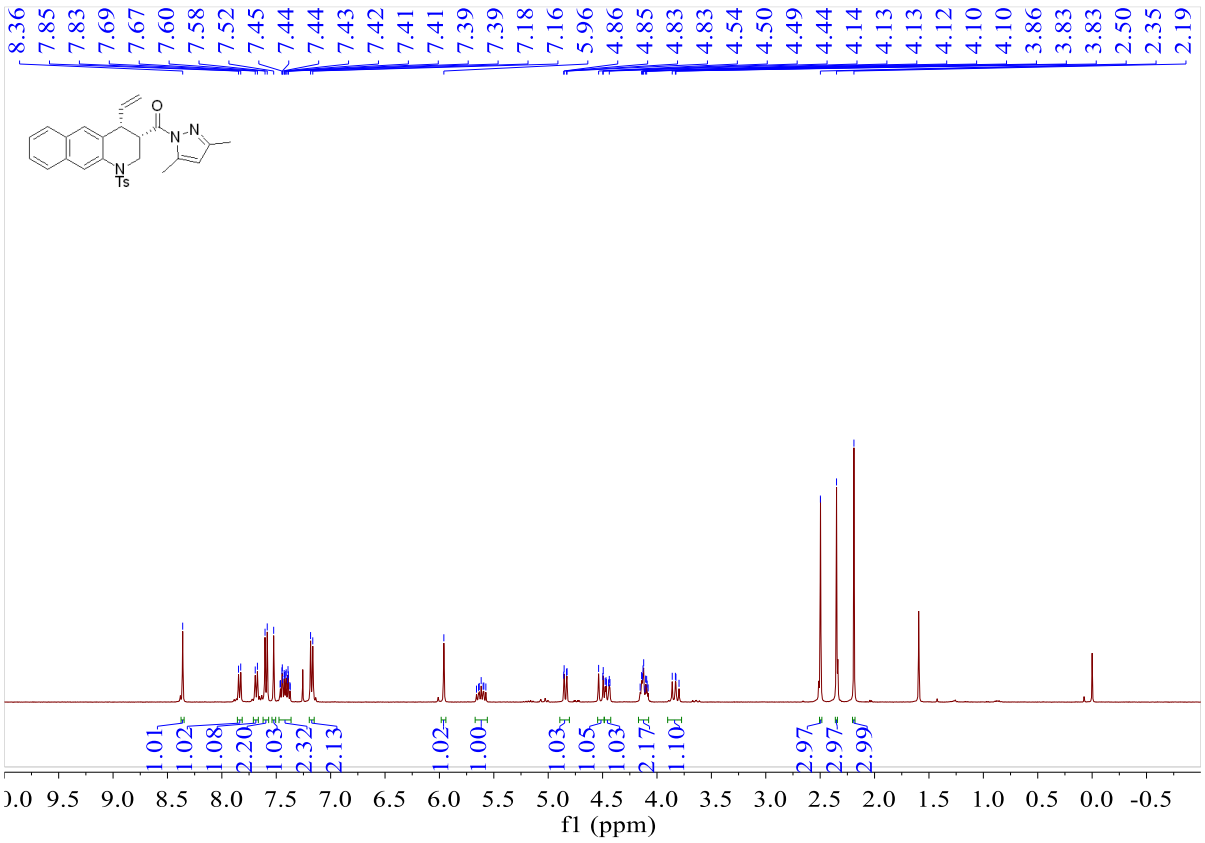

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3k**



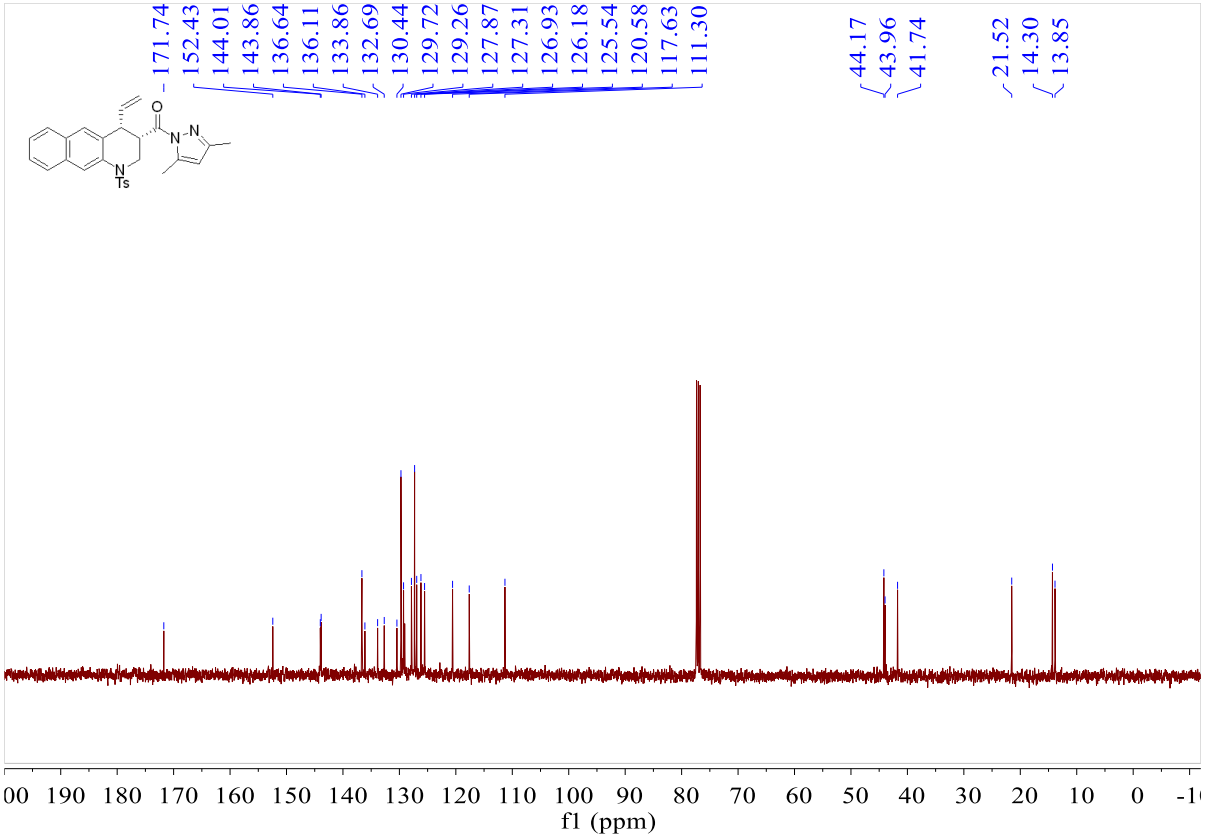
$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3k**



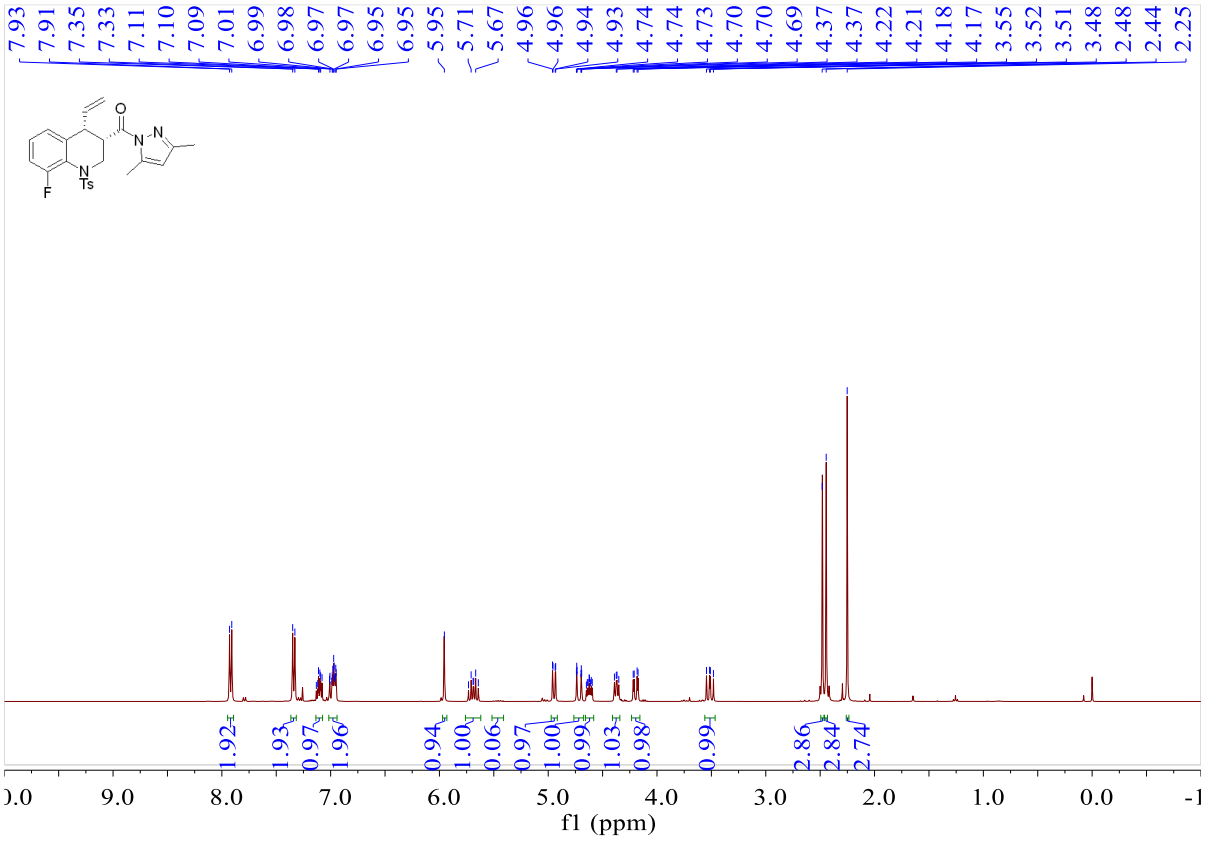

$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3l**



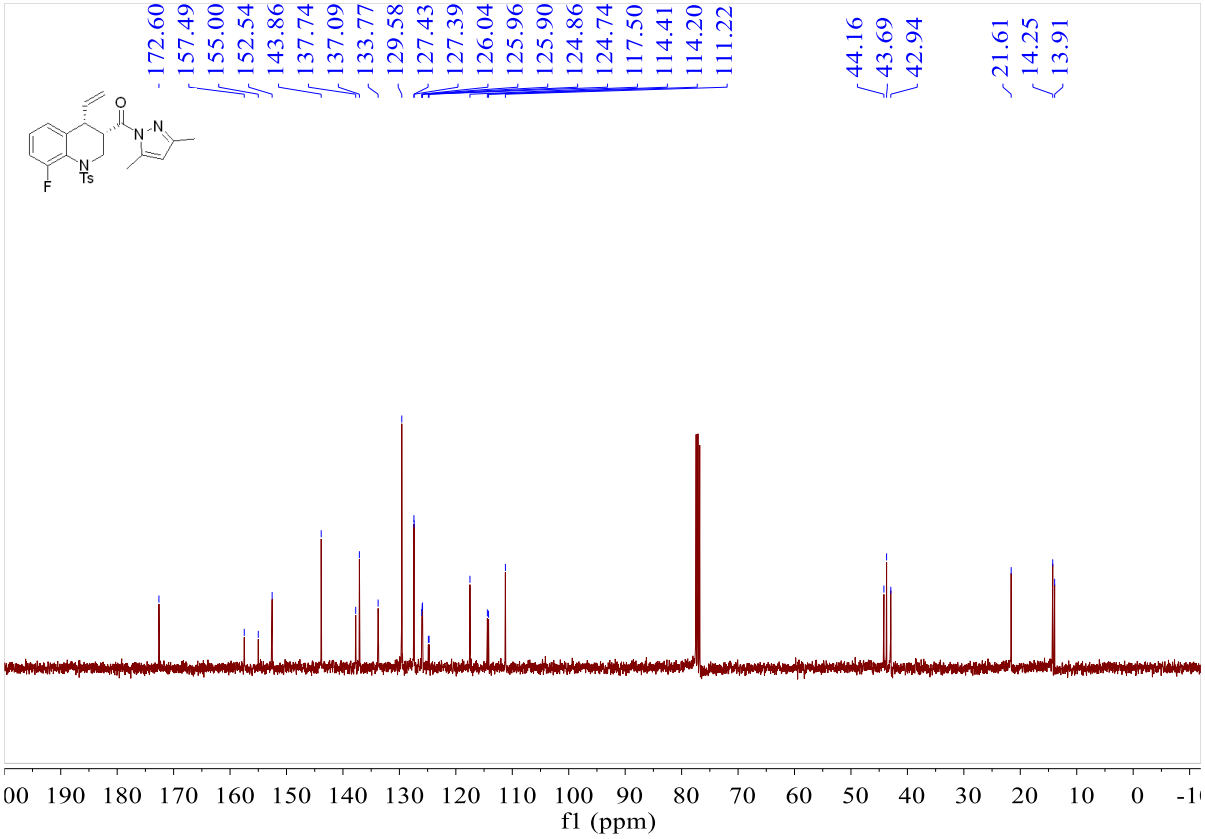
$^{13}C$ NMR (100 MHz, $CDCl_3$) of product **3l**



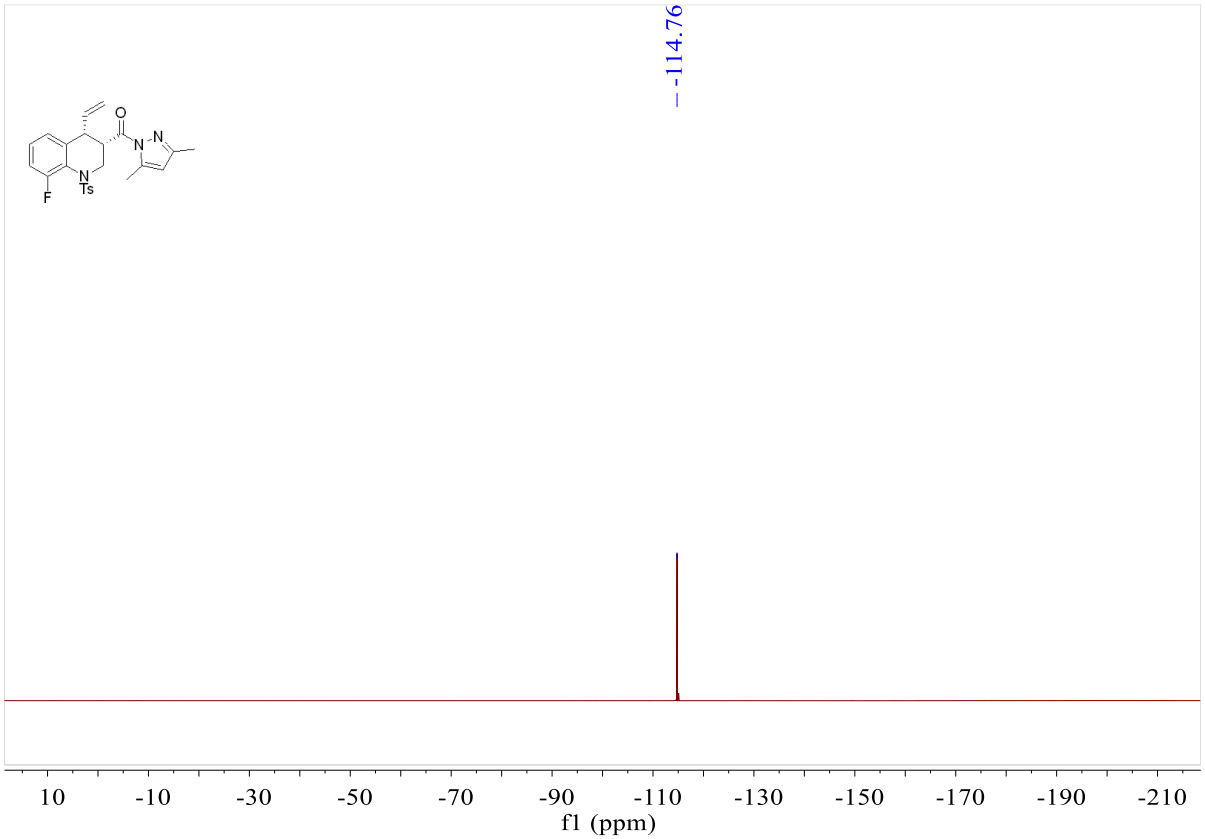

$^{1}H$ NMR (400 MHz, $CDCl_3$) of product **3m**



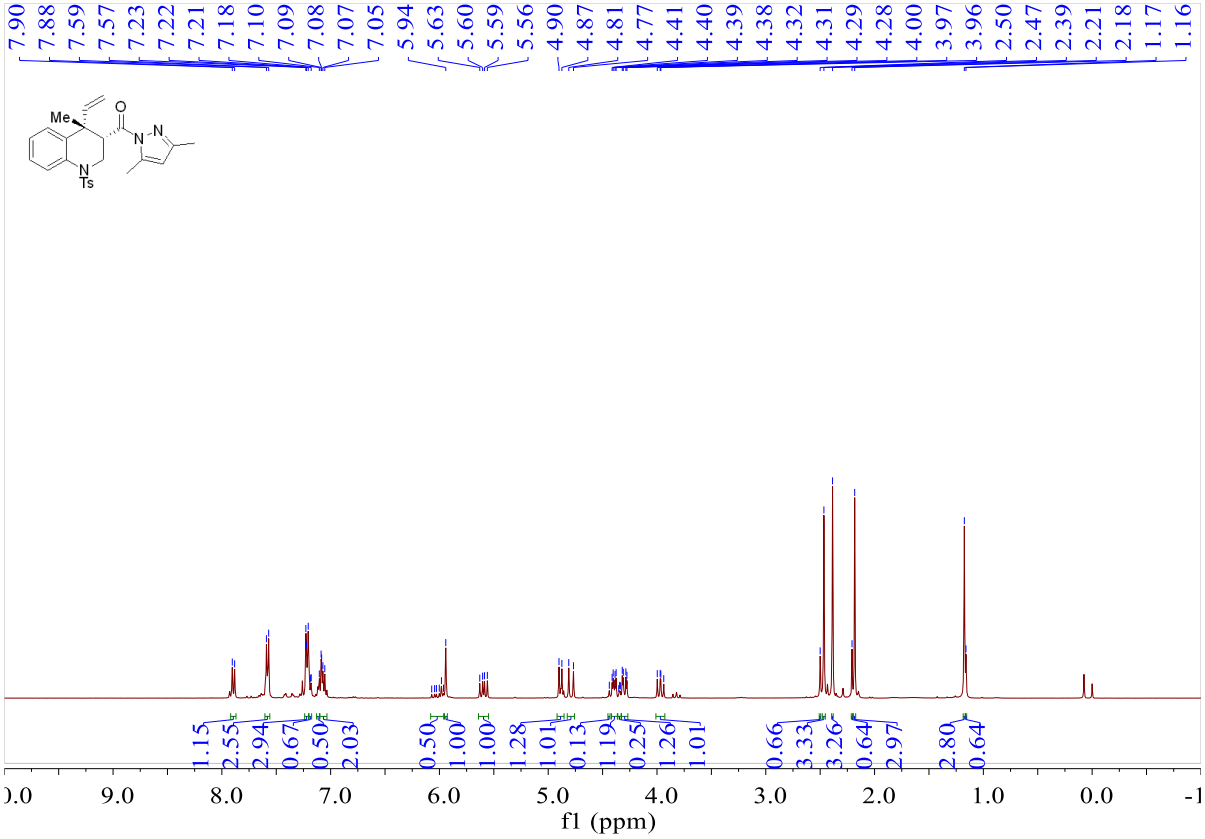
$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3m**



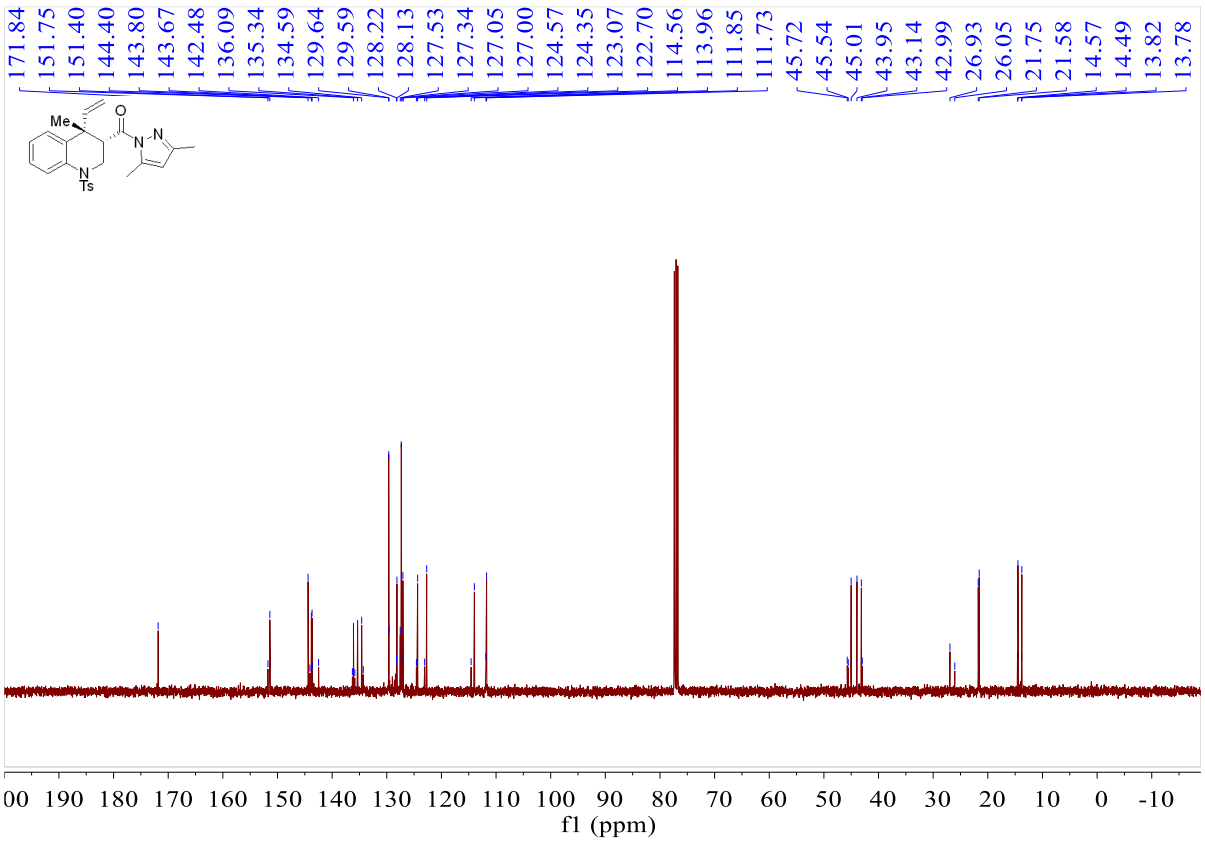

$^{19}$F NMR (376 MHz, $CDCl_3$) of product **3m**



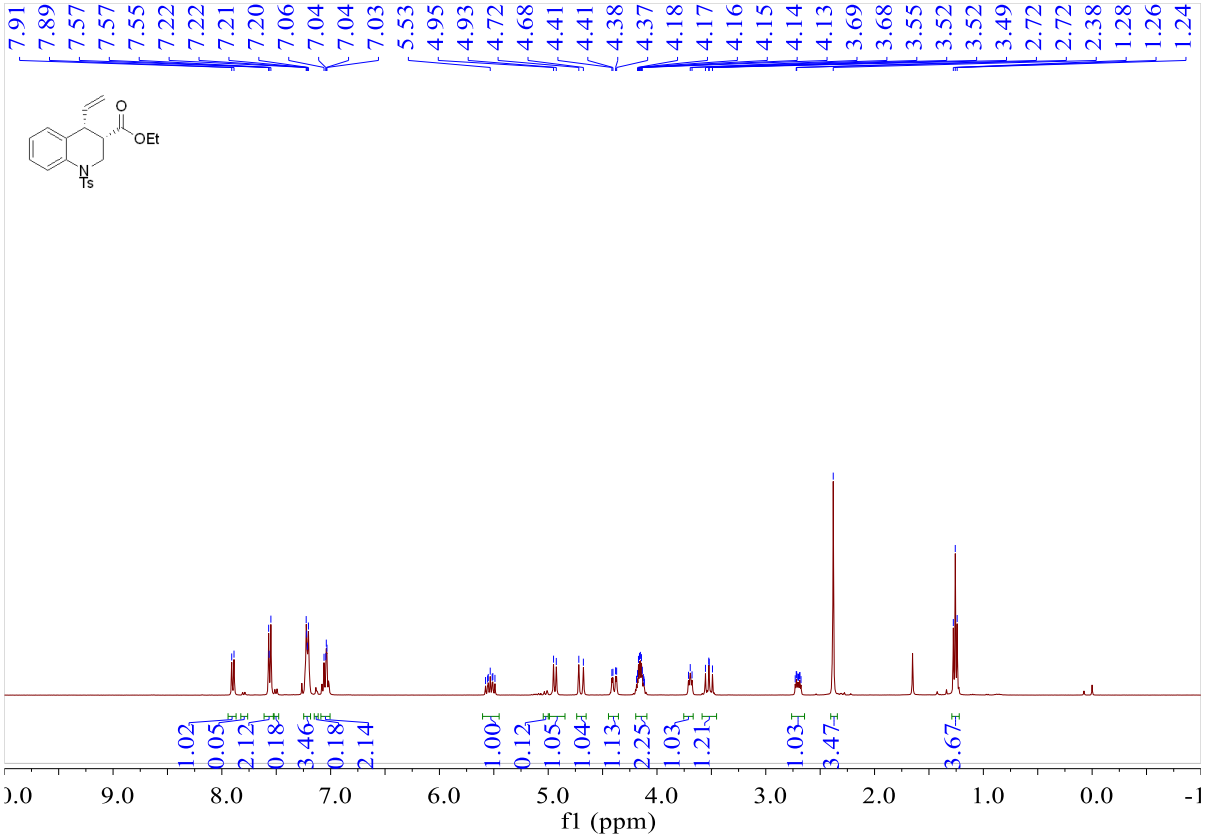
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **3n**



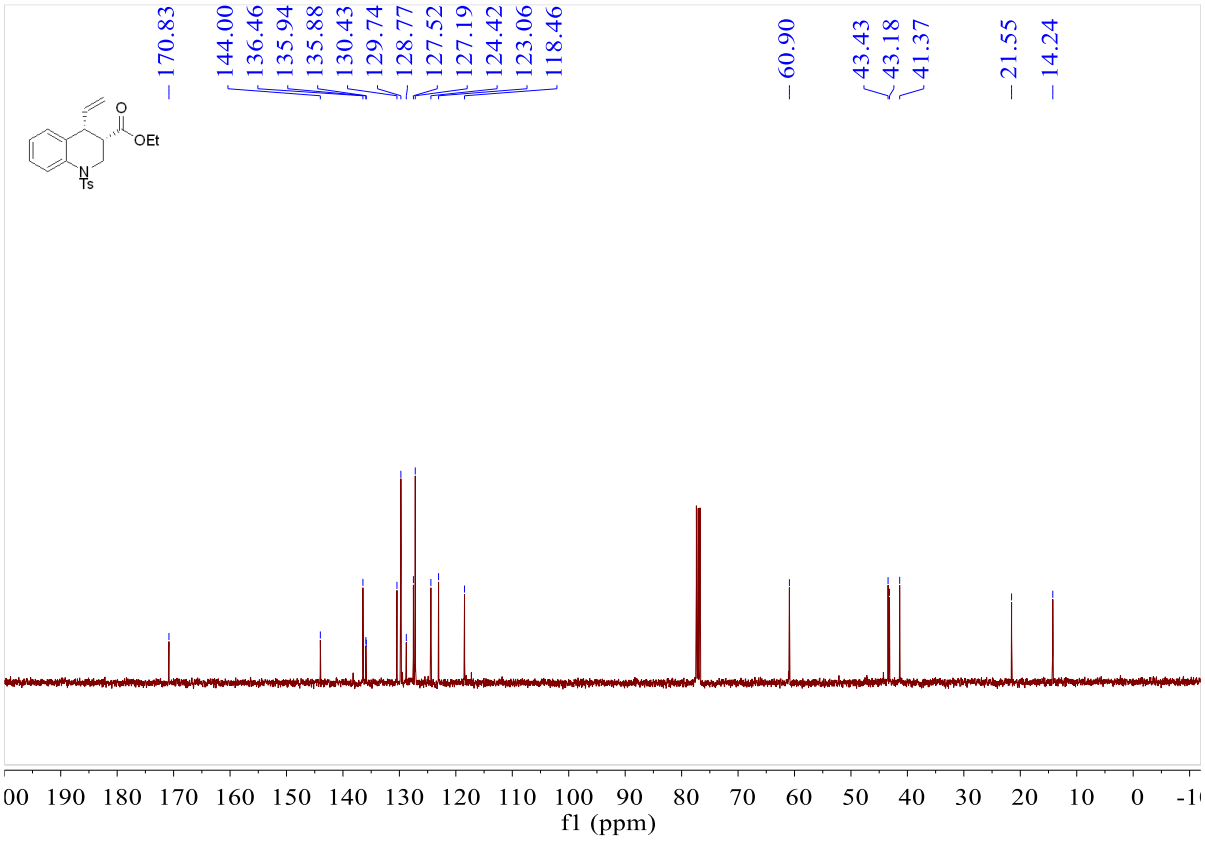

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **3n**



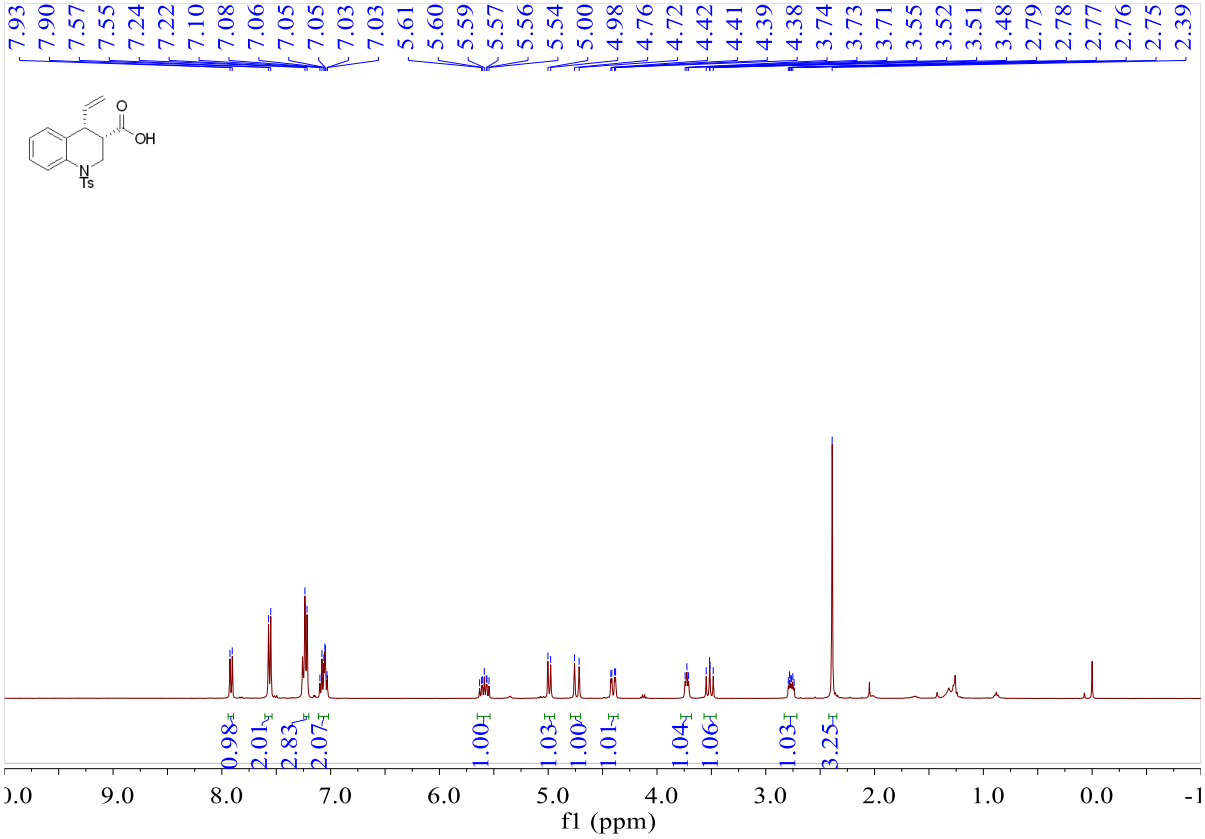
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **5**



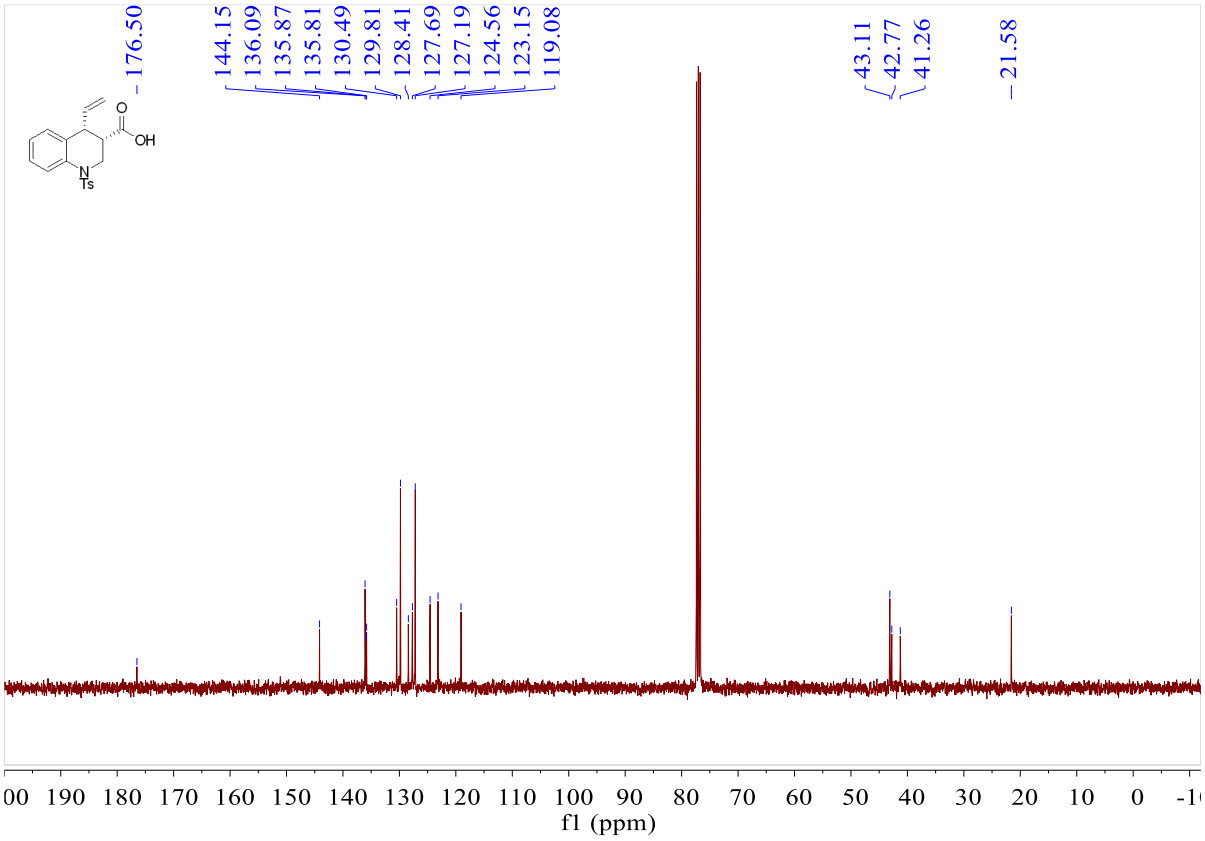

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **5**



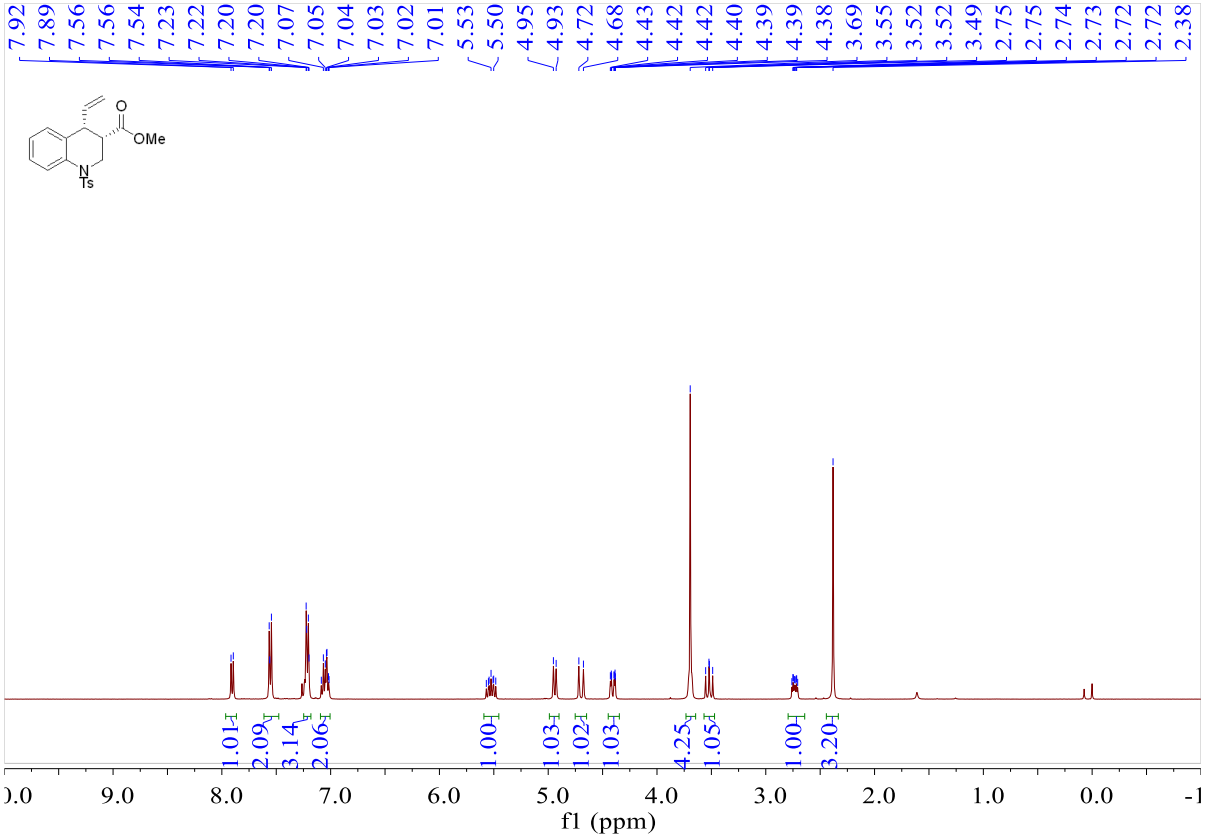
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **6**



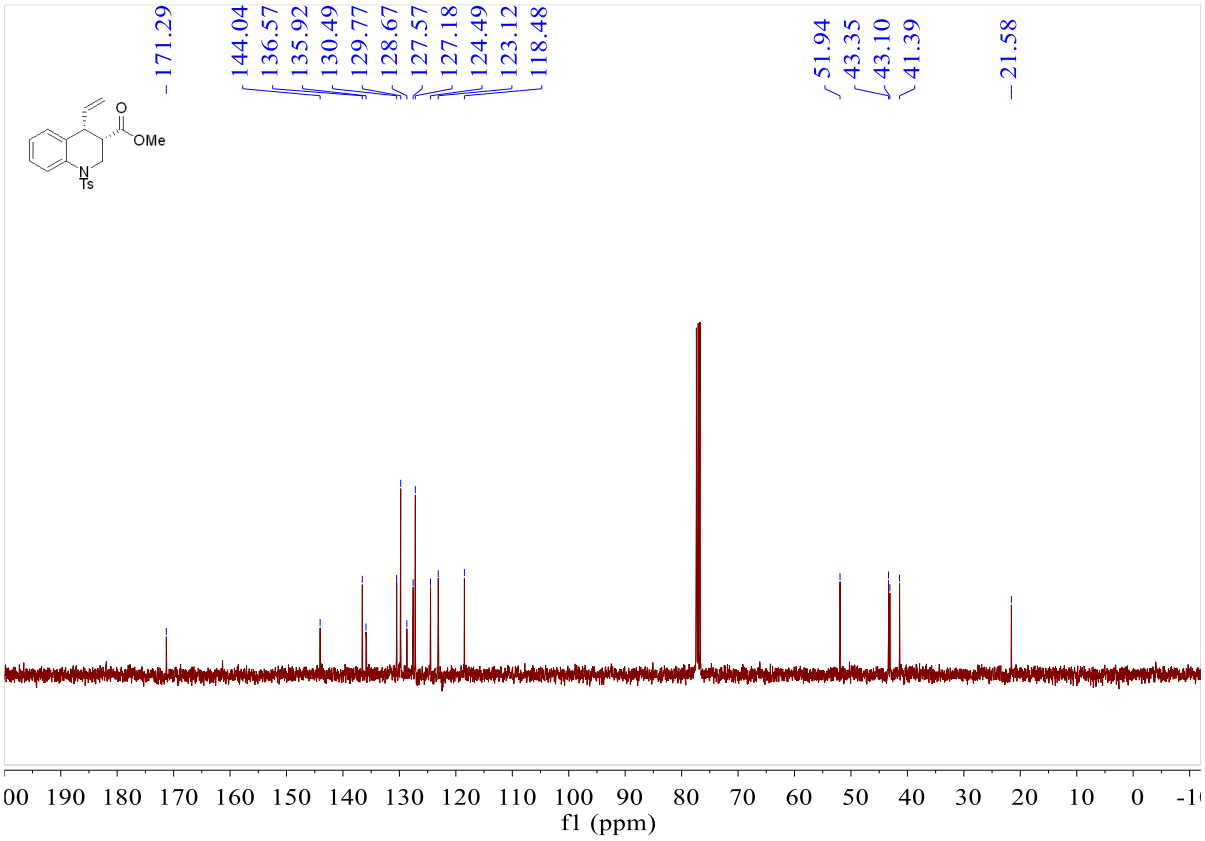

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **6**



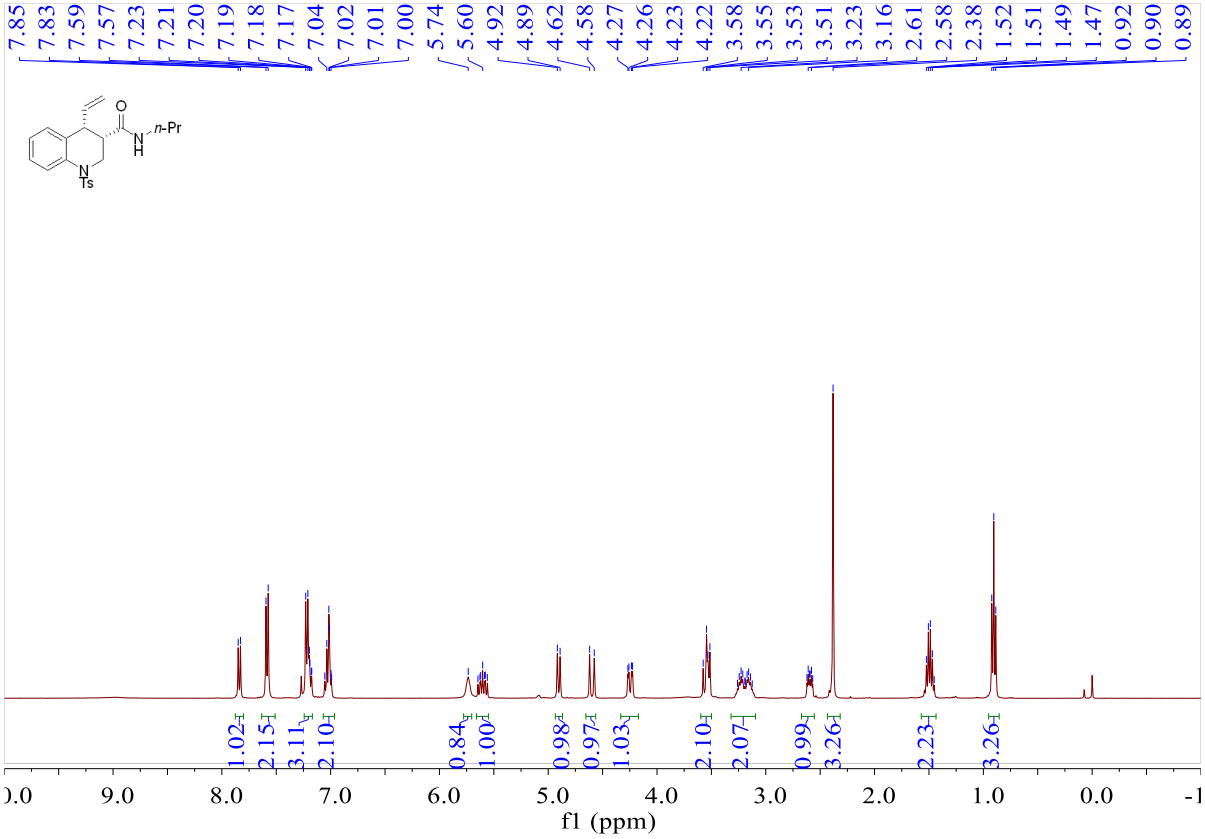
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **S0**



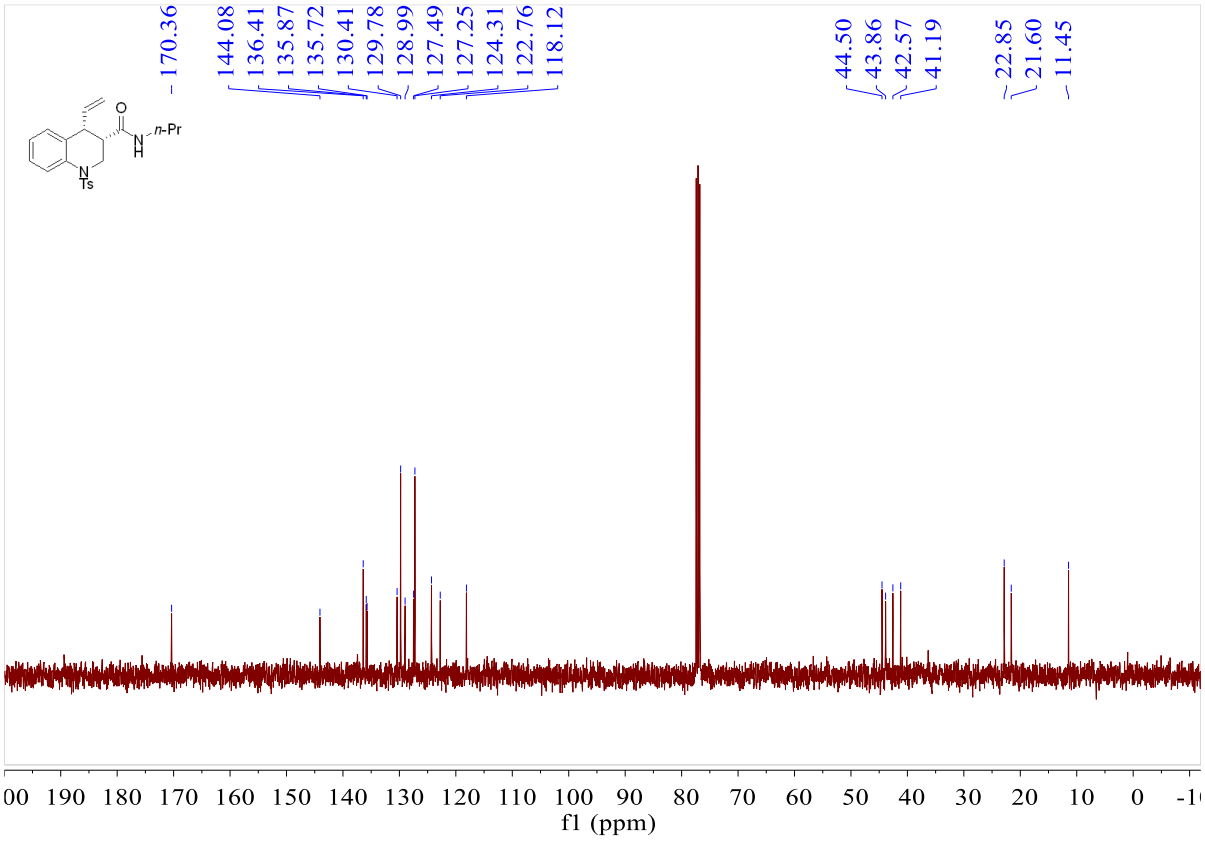

$^{13}$C NMR (400 MHz, $CDCl_3$) of product **S0**



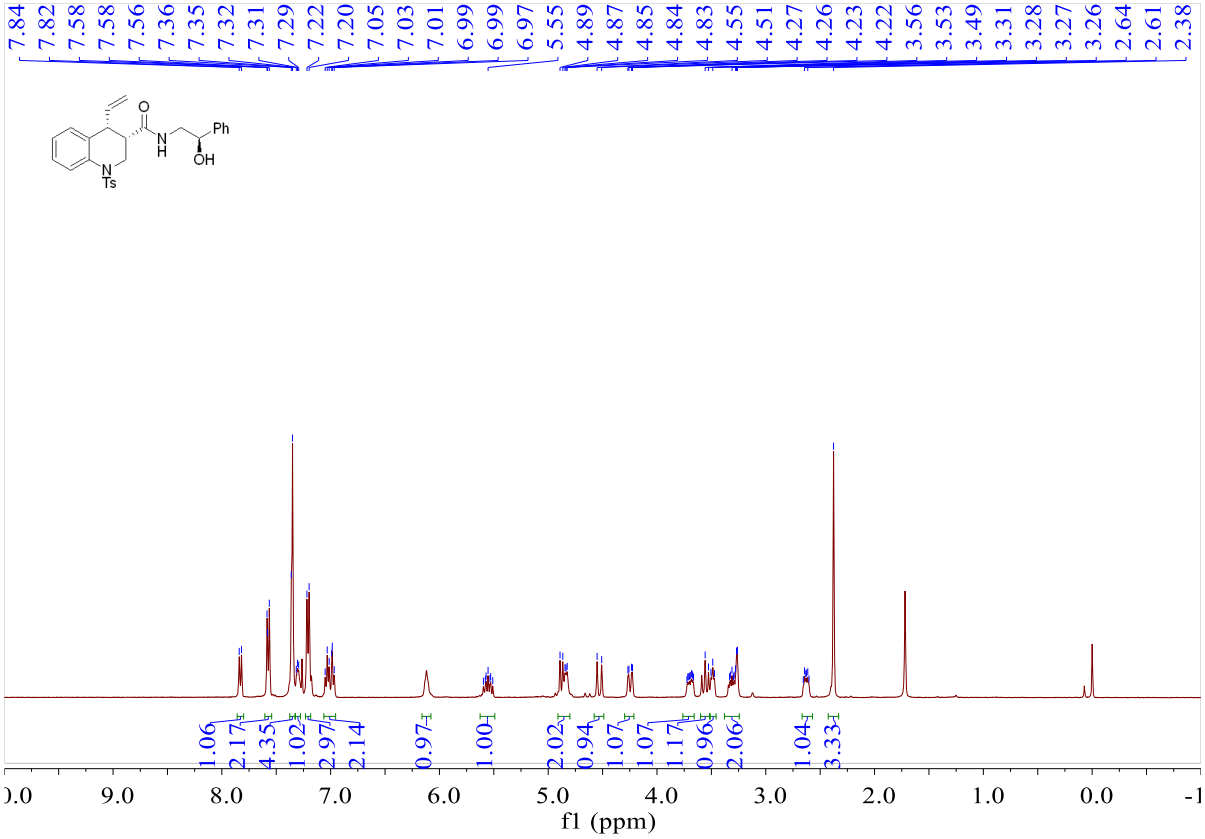
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **7**



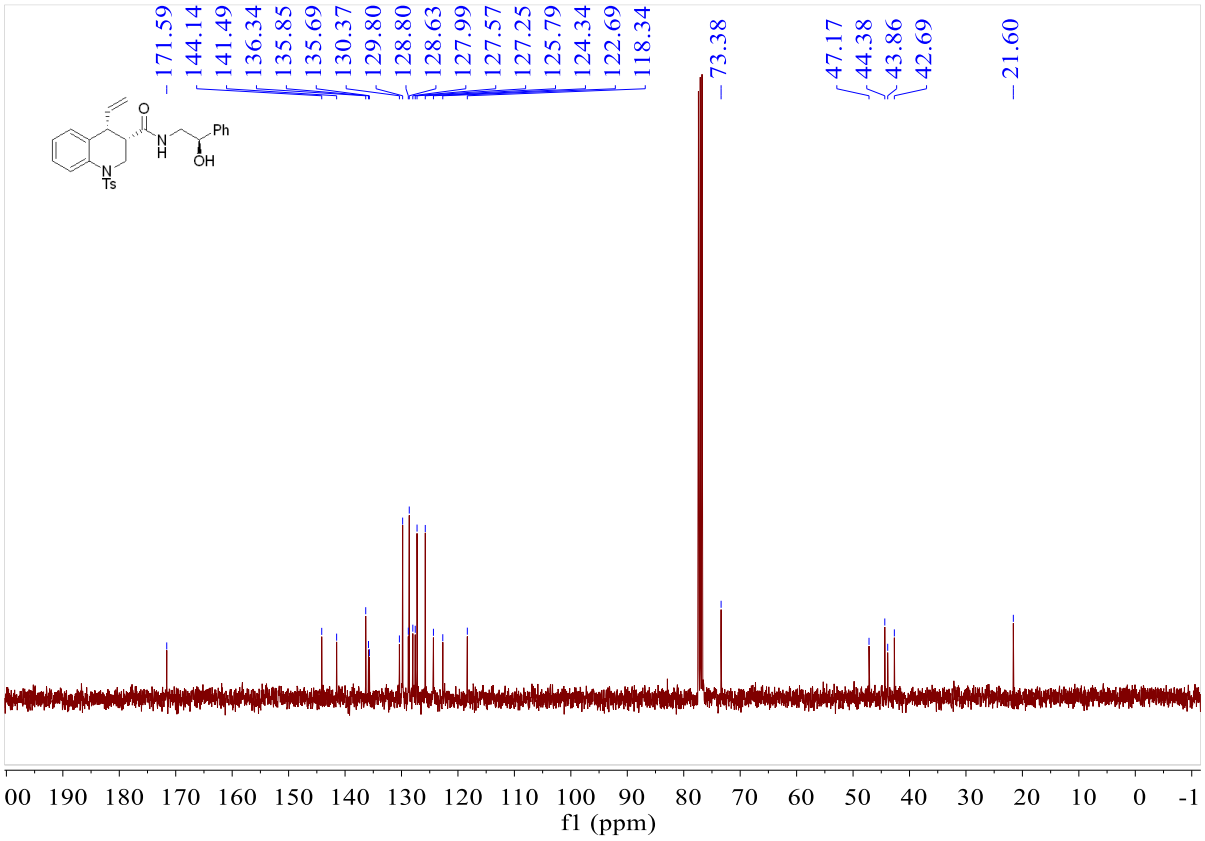

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **7**



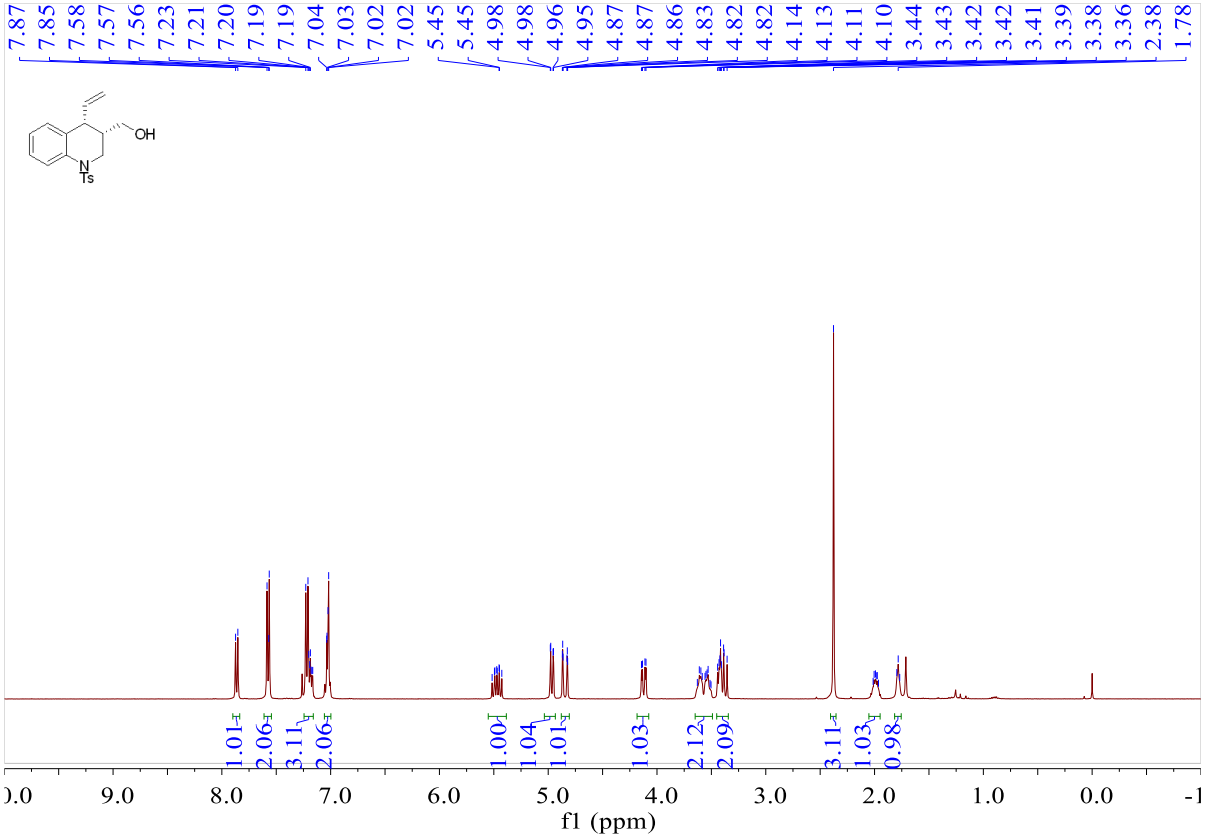
$^{1}$H NMR (100 MHz, $CDCl_3$) of product **8**



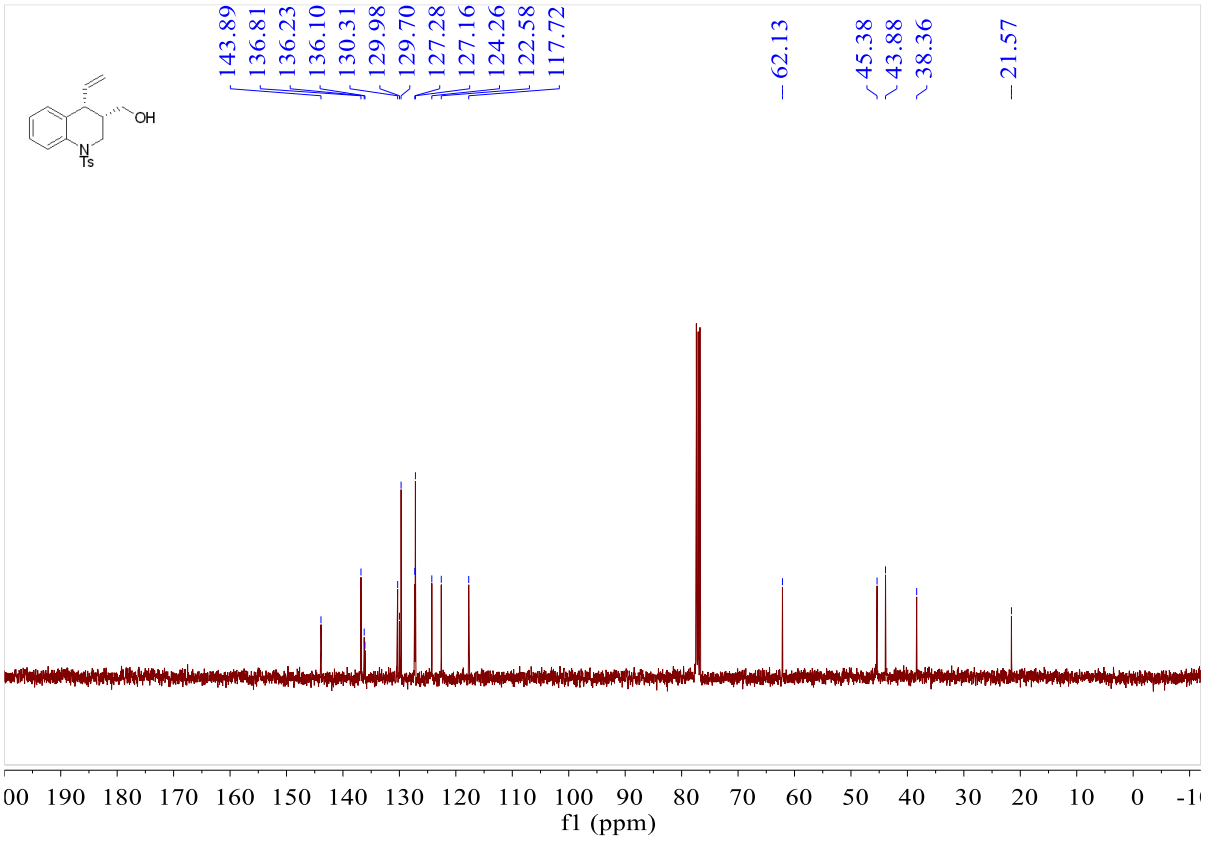

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **8**



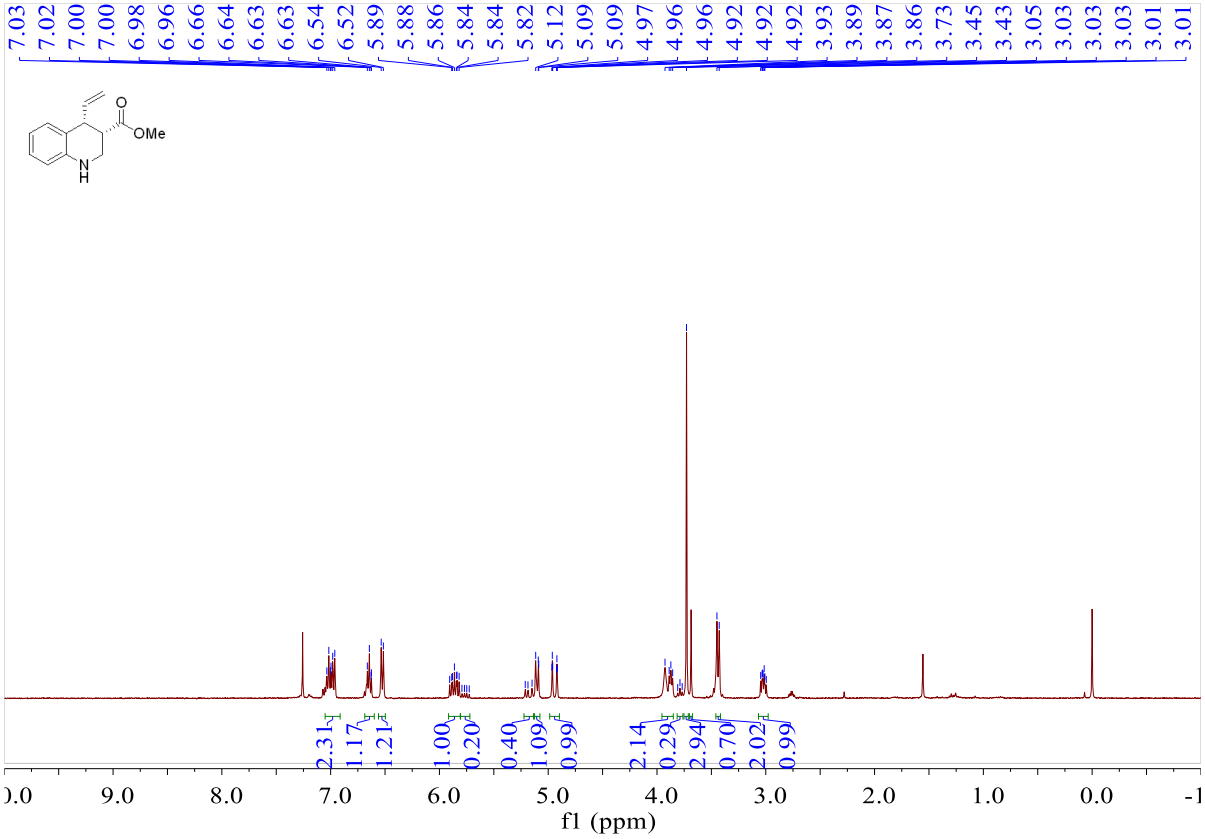
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **S1**



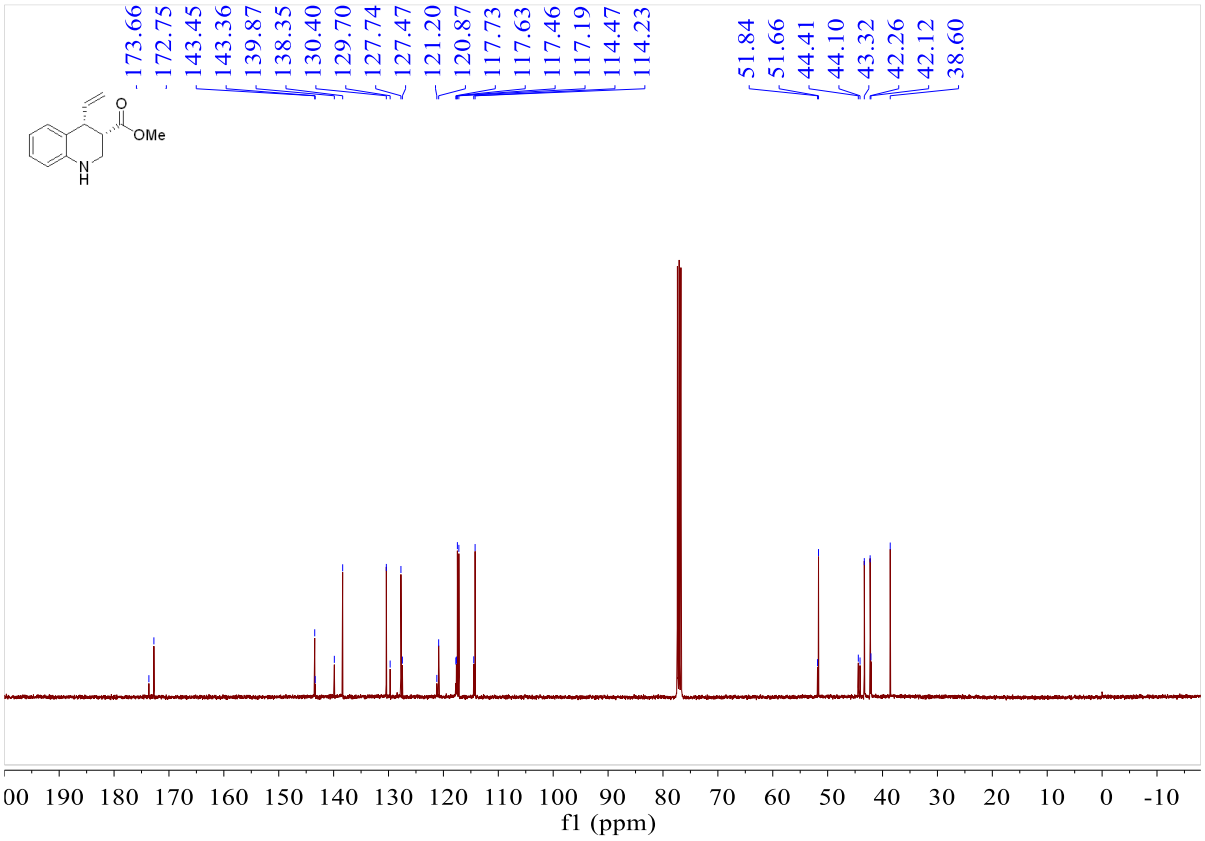

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **S1**



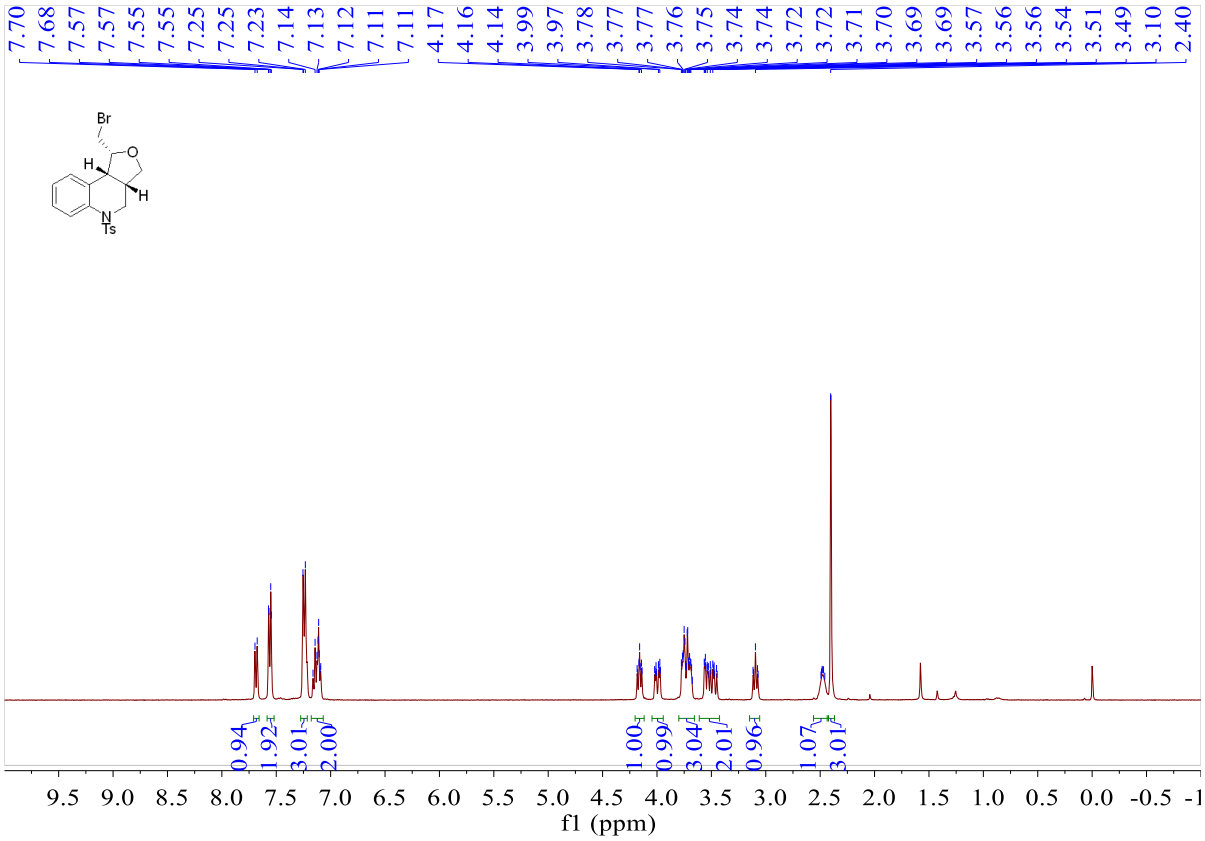
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **9**



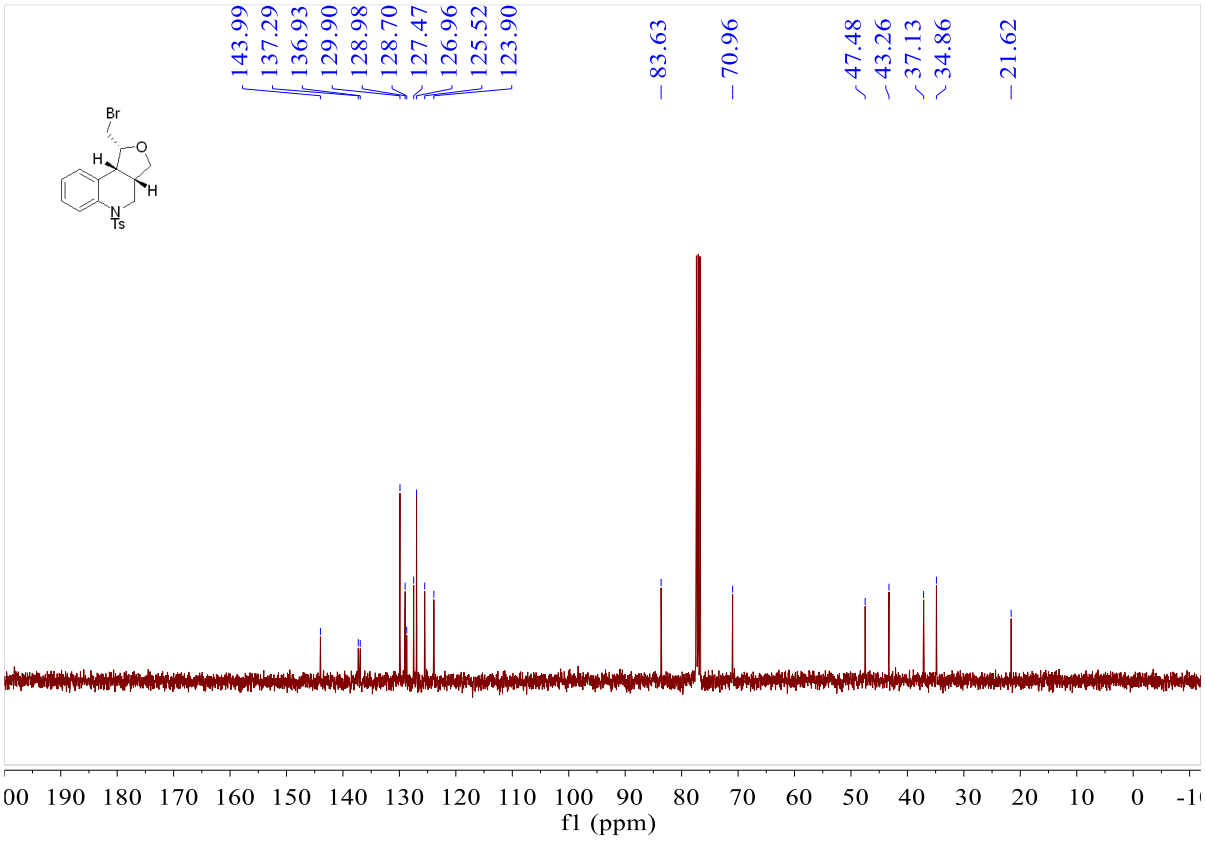

$^{13}$C NMR (100 MHz, $CDCl_3$) of product **9**



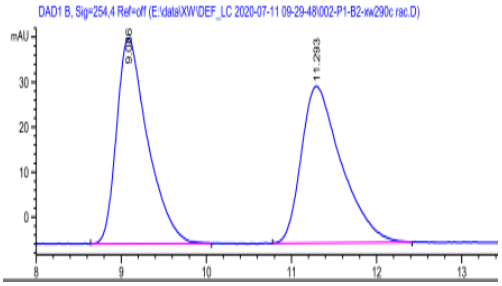
$^{1}$H NMR (400 MHz, $CDCl_3$) of product **10**

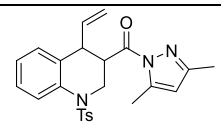



$^{13}$C NMR (100 MHz, $CDCl_3$) of product **10**



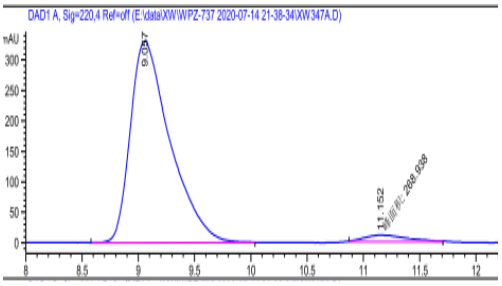
## 9. HPLC Data of Products

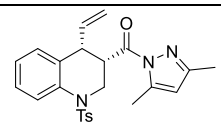



***rac*-3a**

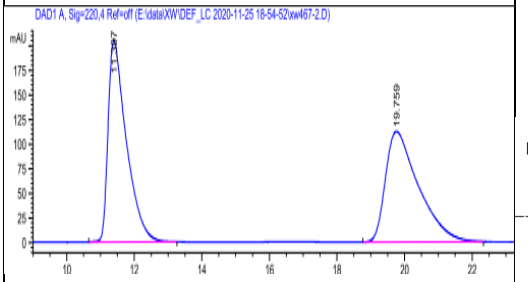
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.086 | BB | 0.3655 | 1158.82629 | 45.75510 | 50.4496 |
| 2 | 11.293 | BB | 0.4688 | 1138.17053 | 34.86823 | 49.5504 |

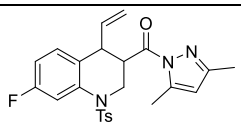



**3a**

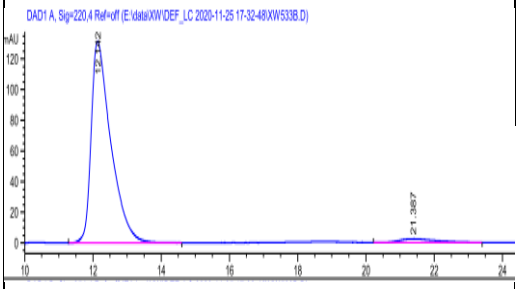
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.057 | BV R | 0.3618 | 8103.18506 | 330.81461 | 96.7877 |
| 2 | 11.152 | MM | 0.4173 | 268.93768 | 10.74025 | 3.2123 |

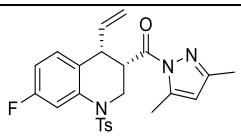



***rac*-3b**

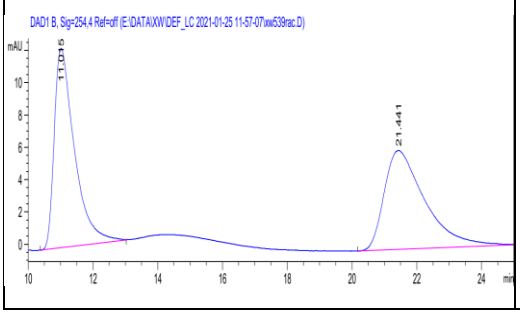
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.397 | BB | 0.5490 | 7715.66943 | 205.04381 | 50.2551 |
| 2 | 19.759 | BB | 0.9584 | 7637.32373 | 112.45216 | 49.7449 |

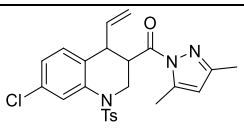



**3b**

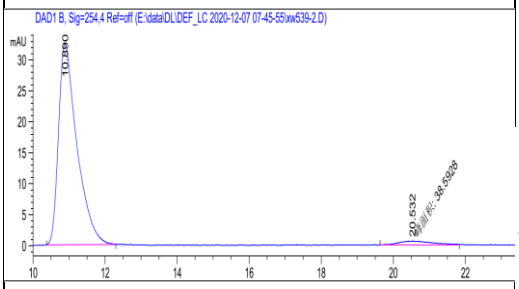
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 12.142 | BB | 0.5880 | 5274.13818 | 131.47530 | 96.6484 |
| 2 | 21.387 | BB | 0.9187 | 182.89757 | 2.47339 | 3.3516 |

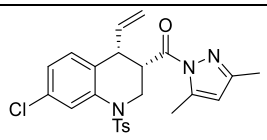



***rac*-3c**

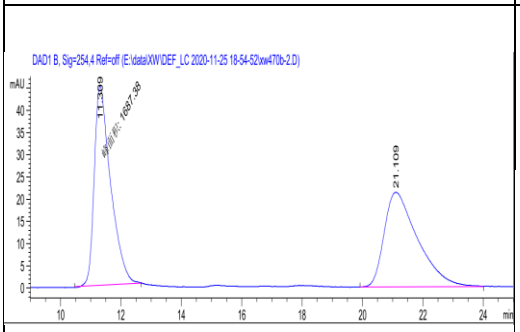
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.015 | BB | 0.6336 | 535.10706 | 12.34658 | 50.0737 |
| 2 | 21.441 | BBA | 1.0873 | 533.53253 | 6.13062 | 49.9263 |

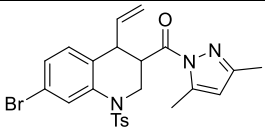



**3c**

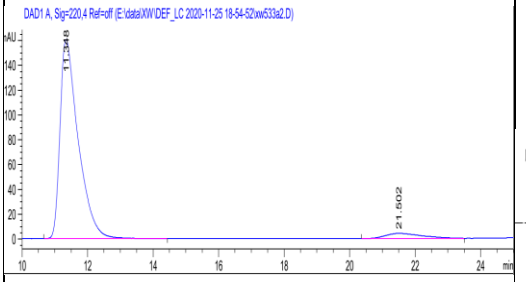
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 10.890 | BB | 0.5161 | 1151.13525 | 32.43196 | 96.7562 |
| 2 | 20.532 | MM | 1.0434 | 38.59284 | 6.16436e-1 | 3.2438 |

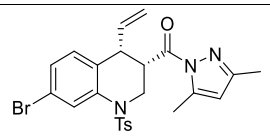



***rac*-3d**

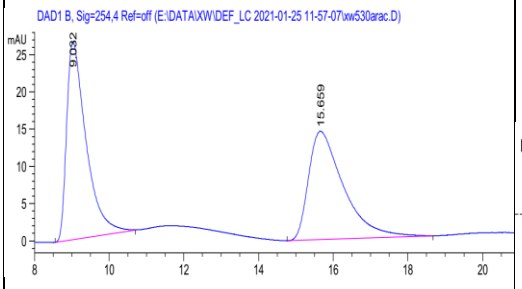
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.309 | MM | 0.6270 | 1687.38452 | 44.85280 | 50.7363 |
| 2 | 21.109 | BB | 1.0644 | 1638.40808 | 21.32492 | 49.2637 |

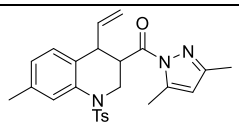



**3d**

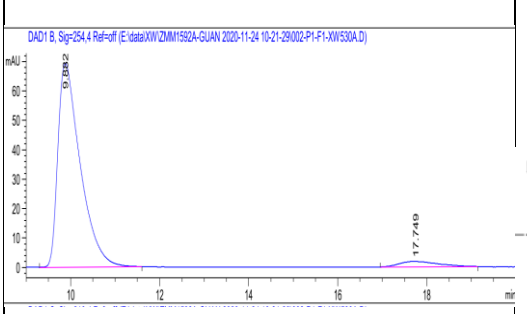
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.348 | BB | 0.5647 | 6174.82910 | 160.54295 | 95.0464 |
| 2 | 21.502 | BB | 0.9595 | 321.81894 | 4.15544 | 4.9536 |

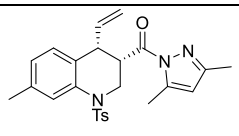



***rac*-3e**

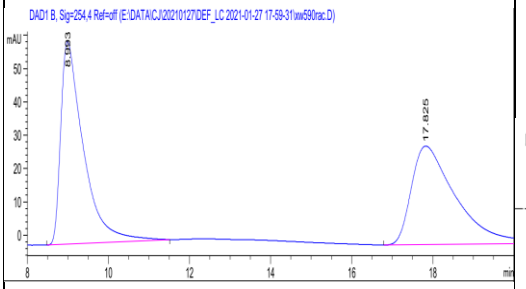
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.032 | BB | 0.5235 | 959.01959 | 26.54596 | 50.3091 |
| 2 | 15.659 | BB | 0.9352 | 947.23407 | 14.55627 | 49.6909 |

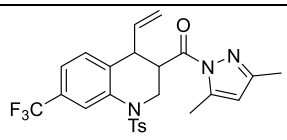



**3e**

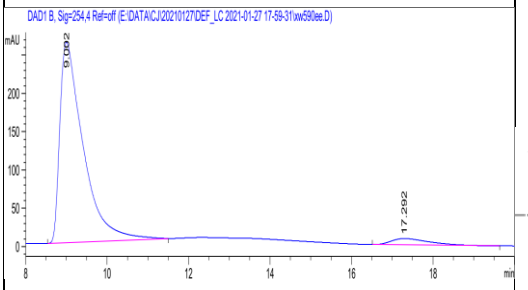
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.882 | BB | 0.5159 | 2414.60815 | 69.40131 | 95.5199 |
| 2 | 17.749 | BB | 0.7243 | 113.25111 | 1.86551 | 4.4801 |

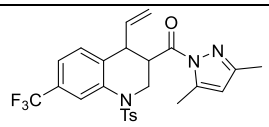



***rac*-3f**

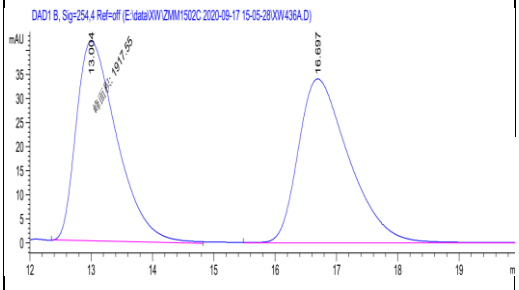
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 8.993 | BB | 0.5531 | 2362.22217 | 60.81805 | 50.6583 |
| 2 | 17.825 | BB | 1.0697 | 2300.82935 | 29.57315 | 49.3417 |

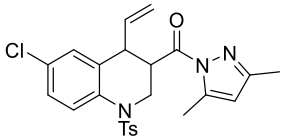



**3f**

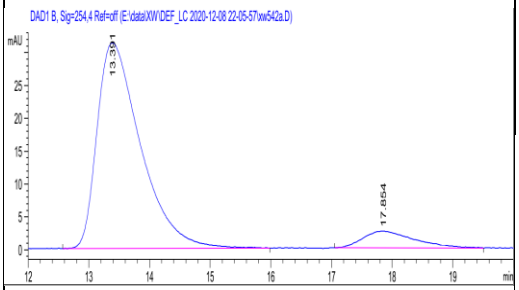
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.002 | BB | 0.5665 | 1.04195e4 | 261.72162 | 95.0986 |
| 2 | 17.292 | BB | 0.8339 | 537.02032 | 8.31027 | 4.9014 |

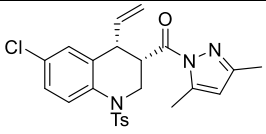



***rac*-3g**

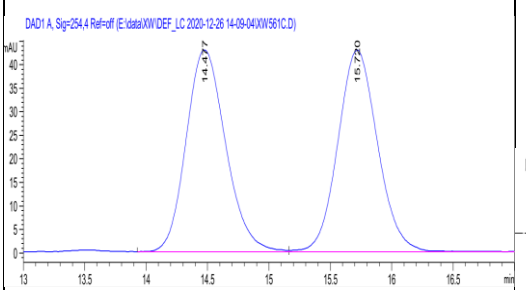
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 13.004 | MM | 0.7698 | 1917.55054 | 41.51402 | 49.5223 |
| 2 | 16.697 | VB | 0.8647 | 1954.54114 | 34.10003 | 50.4777 |

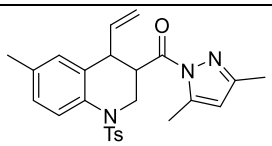



**3g**

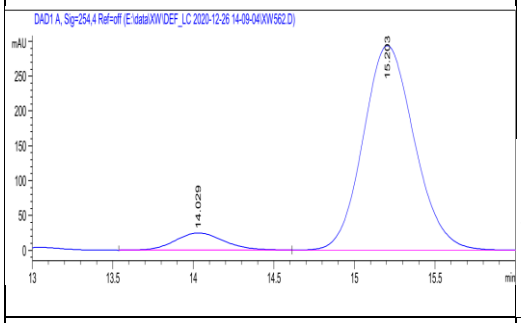
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 13.391 | BB | 0.7259 | 1556.65454 | 31.31947 | 91.2838 |
| 2 | 17.854 | BB | 0.6923 | 148.63721 | 2.56422 | 8.7162 |

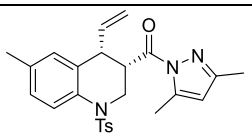



***rac*-3h**

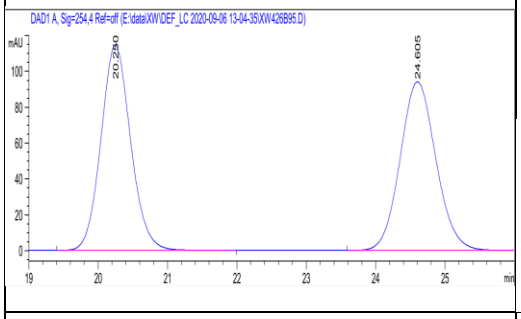
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 14.477 | BV | 0.3493 | 961.94330 | 42.94325 | 49.8563 |
| 2 | 15.720 | VB | 0.3511 | 967.49030 | 42.90529 | 50.1437 |

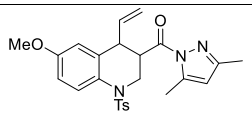



**3h**

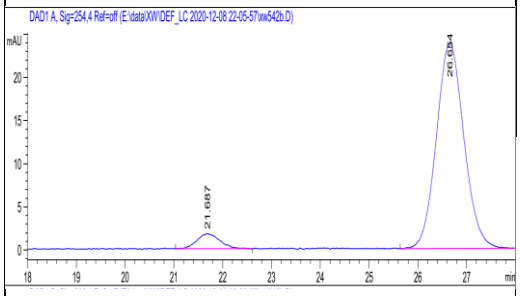
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 14.029 | BV | 0.3297 | 530.17383 | 24.77539 | 7.5479 |
| 2 | 15.203 | VB | 0.3459 | 6493.90576 | 293.74512 | 92.4521 |

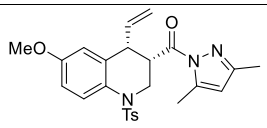



***rac*-3i**

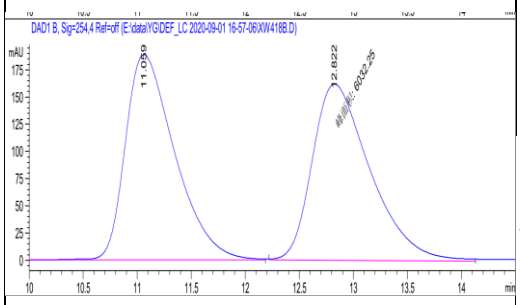
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 20.250 | BB | 0.4568 | 3403.59546 | 114.49046 | 50.2475 |
| 2 | 24.605 | BB | 0.5562 | 3370.06323 | 94.00637 | 49.7525 |

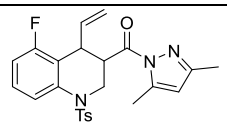



**3i**

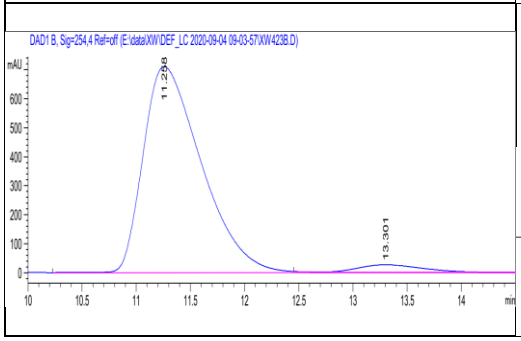
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 21.687 | BB | 0.4084 | 58.10890 | 1.76352 | 5.8412 |
| 2 | 26.654 | BB | 0.6026 | 936.69550 | 23.82941 | 94.1588 |

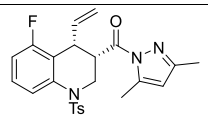



***rac*-3j**

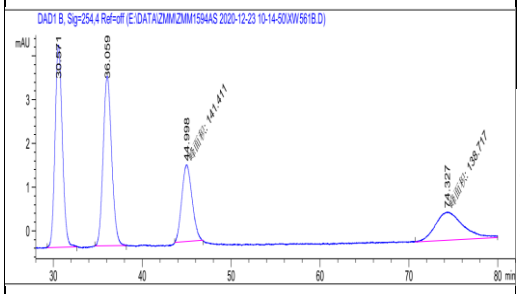
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.059 | BV | 0.4836 | 6016.21143 | 188.89915 | 49.9334 |
| 2 | 12.822 | MM | 0.6207 | 6032.25195 | 161.97853 | 50.0666 |

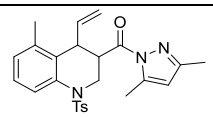



**3j**

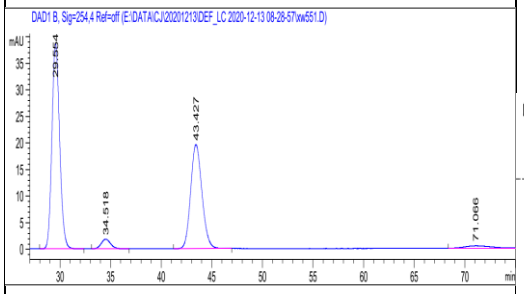
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.258 | BV R | 0.5709 | 2.64708e4 | 710.17780 | 95.8640 |
| 2 | 13.301 | VB E | 0.6475 | 1142.07959 | 26.88867 | 4.1360 |

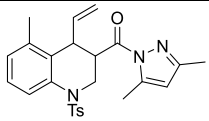


***rac*-3k**

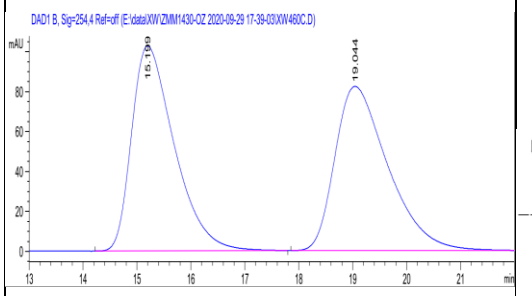
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 30.571 | BB | 0.8208 | 262.78906 | 4.62572 | 32.7611 |
| 2 | 36.059 | BB | 0.9746 | 259.21994 | 3.88433 | 32.3162 |
| 3 | 44.998 | MM | 1.3440 | 141.41104 | 1.75363 | 17.6293 |
| 4 | 74.327 | MM | 3.6325 | 138.71669 | 6.36470e-1 | 17.2934 |

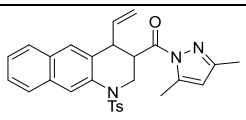


**3k**

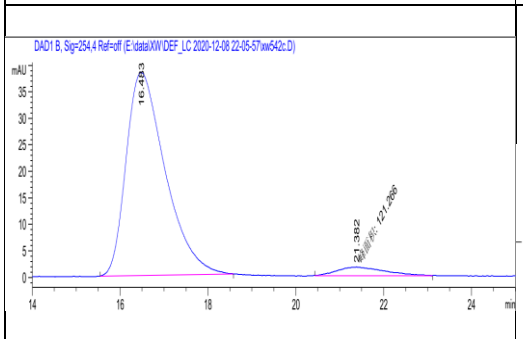
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 29.554 | BB | 0.8221 | 2046.38477 | 38.62733 | 54.3311 |
| 2 | 34.518 | BB | 0.9357 | 116.26343 | 1.80448 | 3.0868 |
| 3 | 43.427 | BB | 1.2185 | 1521.61060 | 19.58356 | 40.3985 |
| 4 | 71.066 | BB | 2.0915 | 82.24789 | 4.62332e-1 | 2.1837 |

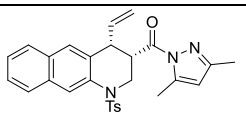


***rac*-3l**

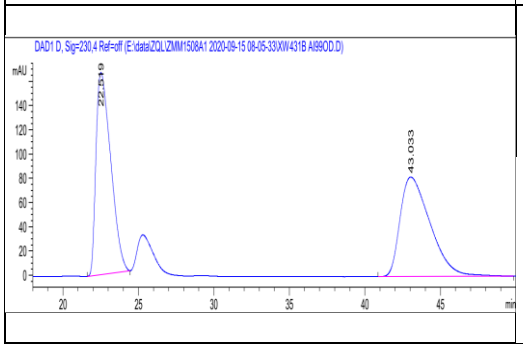
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 15.199 | BB | 0.8319 | 5647.47656 | 102.63880 | 50.0624 |
| 2 | 19.044 | BB | 1.0136 | 5633.40918 | 82.19961 | 49.9376 |

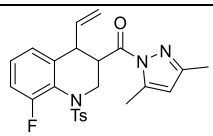


**3l**

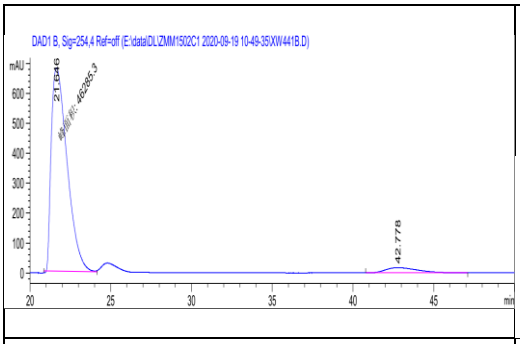
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 16.483 | BB | 0.8471 | 2361.26465 | 38.30870 | 95.1152 |
| 2 | 21.382 | MM | 1.2406 | 121.26585 | 1.62911 | 4.8848 |

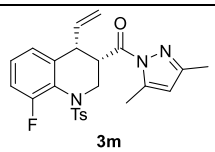


***rac*-3m**

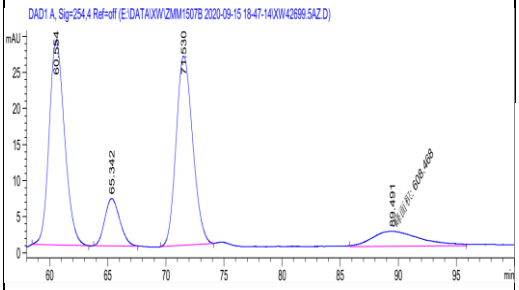
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 22.519 | BB | 1.0475 | 1.13193e4 | 166.43382 | 49.8852 |
| 2 | 43.033 | BB | 1.8951 | 1.13714e4 | 82.03735 | 50.1148 |

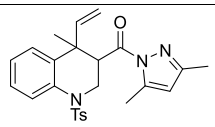



**3m**

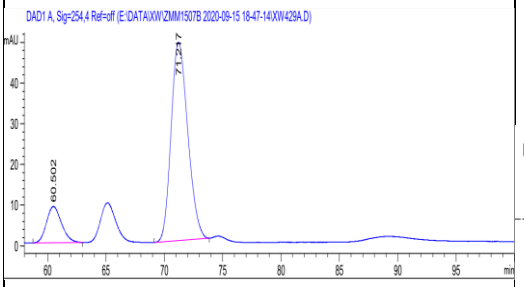
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 21.646 | MM | 1.1355 | 4.62853e4 | 679.38843 | 95.1229 |
| 2 | 42.778 | BB | 1.6174 | 2373.11743 | 17.20288 | 4.8771 |

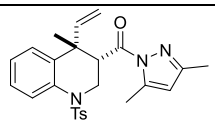



***rac*-3n**

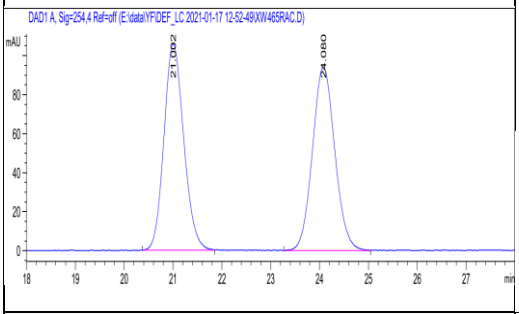
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 60.554 | BB | 1.1650 | 2618.62305 | 28.31404 | 40.8161 |
| 2 | 65.342 | BB | 1.0584 | 584.92310 | 6.55886 | 9.1171 |
| 3 | 71.530 | BB | 1.2641 | 2603.64966 | 26.22963 | 40.5827 |
| 4 | 89.491 | MM | 4.8705 | 608.46796 | 2.08217 | 9.4841 |

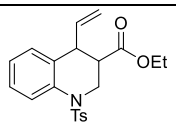



**3n**

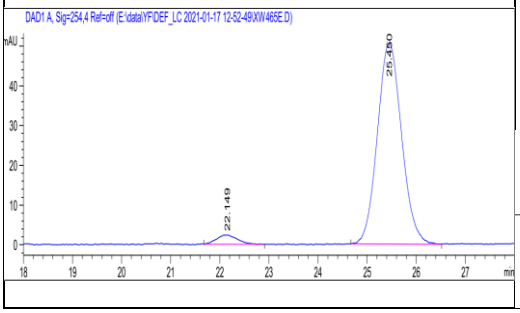
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 60.502 | BB | 1.0553 | 800.24365 | 8.93162 | 14.1629 |
| 2 | 71.217 | BB | 1.4220 | 4850.03076 | 48.77853 | 85.8371 |

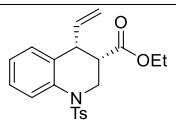



***rac*-5**

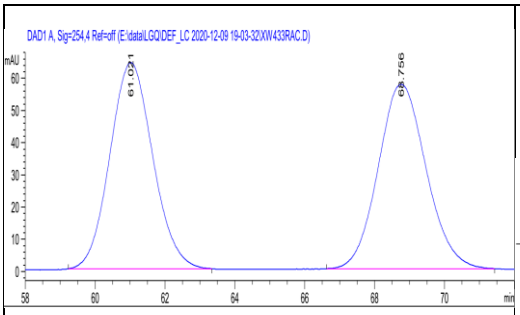
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 21.002 | BB | 0.4301 | 2969.31909 | 105.59761 | 49.8328 |
| 2 | 24.080 | BB | 0.4824 | 2989.24072 | 94.15453 | 50.1672 |

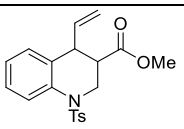



**5**

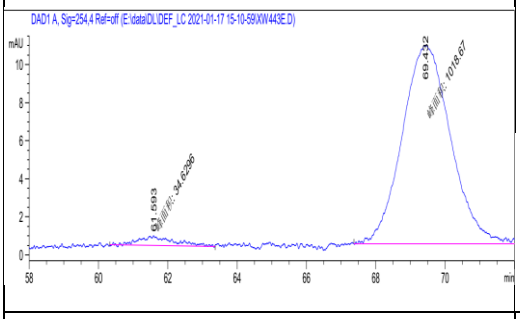
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 22.149 | BB | 0.3626 | 69.42024 | 2.32313 | 3.8555 |
| 2 | 25.450 | BB | 0.5179 | 1731.12390 | 50.50021 | 96.1445 |

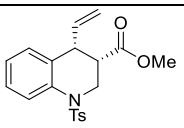



***rac*-S0**

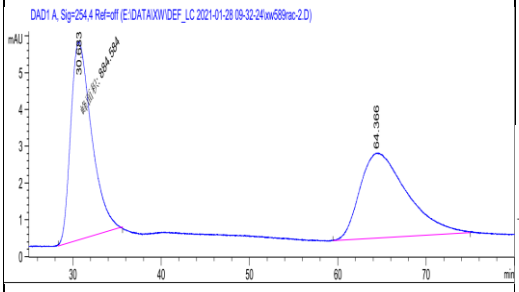
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 61.021 | BB | 1.1401 | 5460.07080 | 64.08046 | 49.9136 |
| 2 | 68.756 | BB | 1.1802 | 5478.97070 | 57.26724 | 50.0864 |

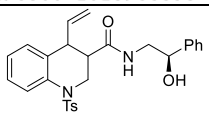



**S0**

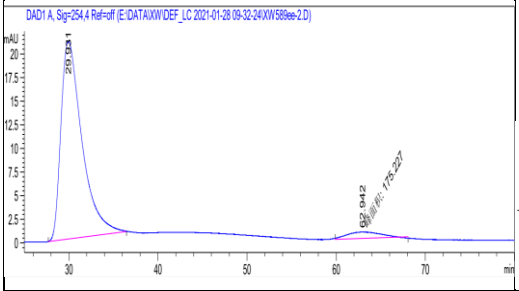
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 61.593 | MM | 1.1341 | 34.62959 | 5.08932e-1 | 3.2877 |
| 2 | 69.432 | MM | 1.6300 | 1018.66595 | 10.41585 | 96.7123 |

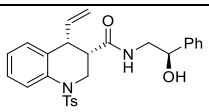



***rac*-8**

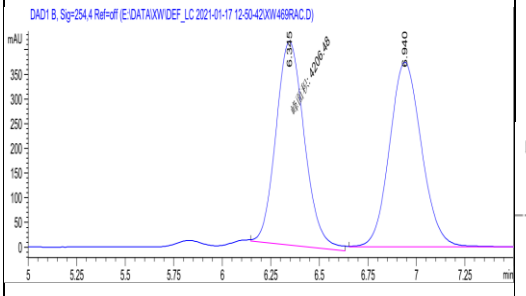
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 30.683 | MM | 2.7329 | 884.58423 | 5.39467 | 50.8366 |
| 2 | 64.366 | BB | 4.3490 | 855.46838 | 2.31189 | 49.1634 |

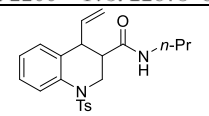



**8**

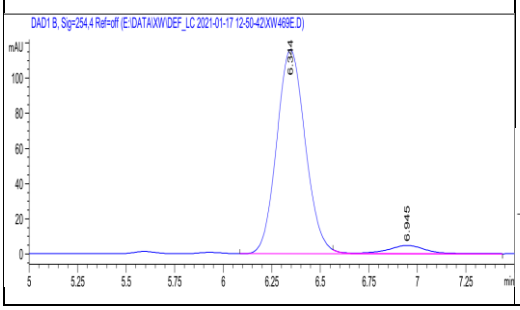
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 29.931 | BB | 1.9524 | 3420.72388 | 20.93444 | 95.1271 |
| 2 | 62.942 | MM | 4.2200 | 175.22673 | 6.92045e-1 | 4.8729 |

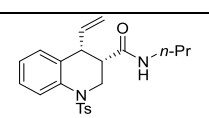



***rac*-7**

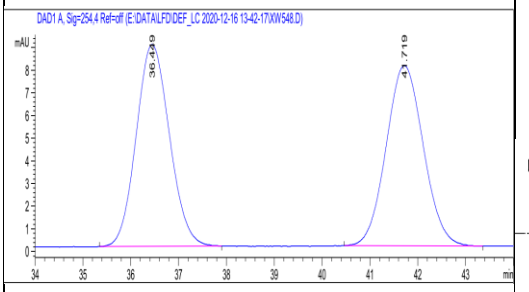
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 6.345 | MM | 0.1697 | 4206.48096 | 413.05505 | 49.3953 |
| 2 | 6.940 | VB | 0.1802 | 4309.47998 | 374.50867 | 50.6047 |

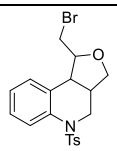



**7**

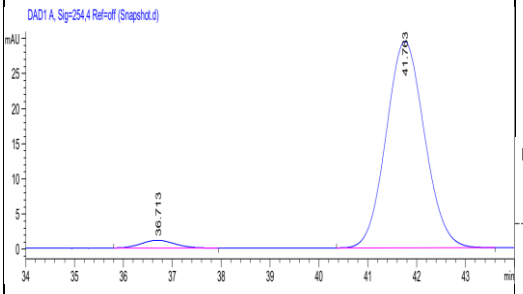
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 6.344 | BV R | 0.1595 | 1189.64709 | 116.17513 | 94.8953 |
| 2 | 6.945 | VB E | 0.2028 | 63.99529 | 4.70021 | 5.1047 |

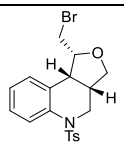



***rac*-10**

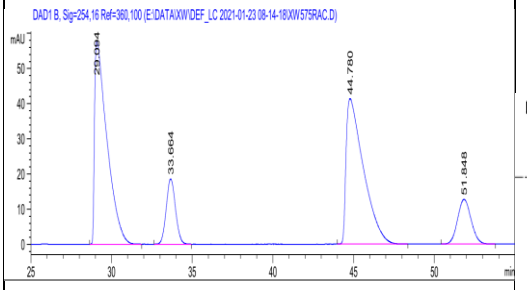
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 36.449 | BB | 0.7339 | 430.41171 | 8.90488 | 49.9697 |
| 2 | 41.719 | BB | 0.7919 | 430.93454 | 7.95633 | 50.0303 |

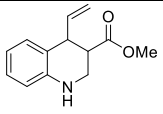



**10**

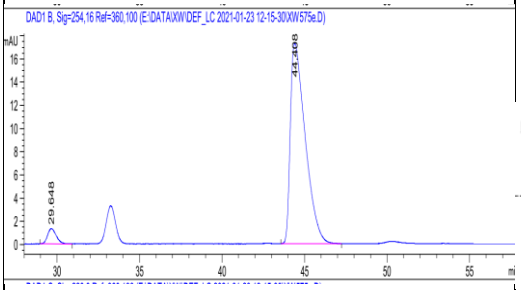
| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 36.713 | BB | 0.5783 | 53.81527 | 1.10861 | 3.2431 |
| 2 | 41.763 | BB | 0.8525 | 1605.55212 | 29.33435 | 96.7569 |

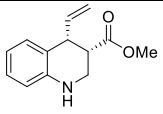



***rac*-9**

| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 29.094 | BB | 0.7609 | 3091.18457 | 57.70707 | 40.3124 |
| 2 | 33.664 | BB | 0.6241 | 741.50812 | 18.55898 | 9.6701 |
| 3 | 44.780 | BB | 1.0761 | 3093.11084 | 41.37868 | 40.3375 |
| 4 | 51.848 | BB | 0.9110 | 742.26953 | 12.71574 | 9.6800 |




**9**

| 峰 # | 保留时间 [min] | 类型 | 峰宽 [min] | 峰面积 [mAU*s] | 峰高 [mAU] | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 29.648 | BB | 0.5262 | 48.63472 | 1.32517 | 4.2916 |
| 2 | 44.408 | BB | 0.9039 | 1084.60693 | 17.28784 | 95.7084 |