*Supporting Information*

# Efficiently enantioselective synthesis of pyrazolines and isoxazolines enabled by iridium-catalyzed intramolecular allylic substitution reaction

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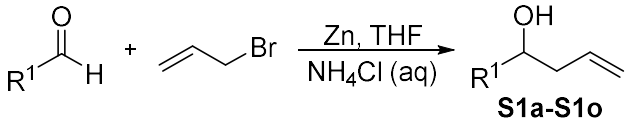
## 1. General information

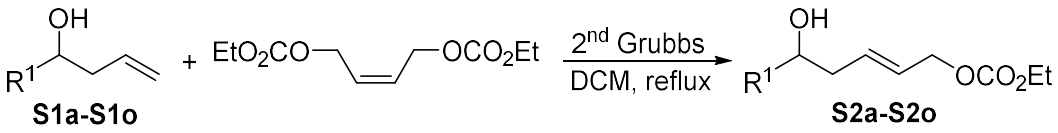
$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer using tetramethylsilane as internal reference, and chemical shifts ($\delta$) and coupling constants ($J$) were expressed in ppm and Hz, respectively. Optical rotation was measured by the Perkin Elmer 341 polarimeter. The HRMS analysis was obtained on a Bruker Apex II FT-ICR mass spectrometer with ESI ionization method. The *ee* value determination was carried out using HPLC with chiral Chirapak column on Agilent 1260 with a UV-detector. Melting points were taken on an XT–4 melting point apparatus and were uncorrected. Dichloromethane and acetonitrile were freshly distilled from phosphorous pentoxide. Toluene and THF were freshly distilled from a deep-blue solution of sodium-benzophenone under argon. Phosphoramidite ligand **$L_1$-$L_2$**, $[Ir(COD)Cl]_2$ and *n*-propylamine were purchased from commercial suppliers and used directly. All syntheses and manipulations were carried out under a dry argon atmosphere. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

## 2. General procedure for synthesis of substrates 1a–1s and 3a–3p

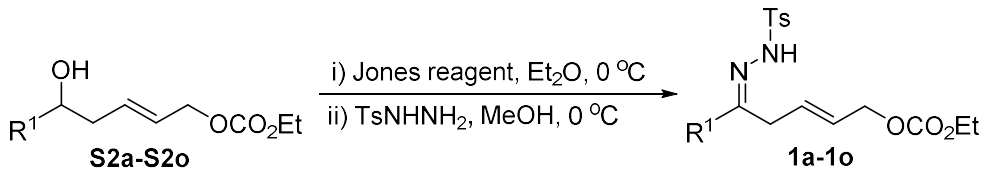
### 2.1 General procedure for synthesis of *β,γ*-allyl carbonate hydrazones 1a–1r




To a solution of aldehyde (20.0 mmol) in THF (30 mL) was added 3-bromoprop-1-ene (40.0 mmol, 3.46 mL, 2.0 equiv.) and saturated aqueous $NH_4Cl$ (30 mL). Then, zinc dust (40.0 mmol, 2.6 g, 2.0 equiv.) was slowly added to the solution at 0 °C and the resulting suspension was stirred overnight at room temperature. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered and extracted with ethyl acetate (20 mL×3). The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated in reduced pressure. The 1-substituted but-3-en-1-ol **S1** was directly used in next step without further purification.[1]




Under argon atmosphere, 1-substituted but-3-en-1-ol **S1** (8.0 mmol) and (*Z*)-but-2-ene-1,4-diyl diethyl dicarbonate (12 mmol, 2.79 g, 1.5 equiv.) were dissolved in anhydrous $CH_2Cl_2$ (20 mL) at room temperature. The solution of Grubbs catalyst 2$^{nd}$ generation (0.16 mmol, 136 mg, 2 mol %) in anhydrous $CH_2Cl_2$ (5 mL) was added and the mixture was refluxed overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 9/1) to afford product **S2** in 40–65% yields.[2]

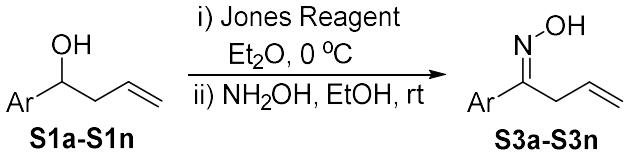



Compound **S2** (5 mmol) was dissolved in diethyl ether at 0 °C and Jones reagent (10 mmol, 4.0 mL, 2.5 M, 2 equiv.) was added dropwise at 0 °C. Then, the mixture was warmed to room temperature and stirred for another 2.5 h. After completion of the reaction (monitored by TLC), the ether layer was separated and the aqueous layer was extracted with ethyl acetate (20 mL×3). The combined organic phase was washed with brine, dried over $Na_2SO_4$, filtered, and concentrated in reduced pressure. The crude product was directly used in next step without further purification.[1]

To a solution of *β*,*γ*-unsaturated ketone (4 mmol) in MeOH (16 mL), *p*-toluenesulfonyl hydrazide (4.8 mmol, 0.894 g, 1.2 equiv.) was added at 0 °C. The mixture was stirred at 0 °C until the reaction was completed (monitored by TLC). The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford compounds **1a**–**1o** in 24–43% yield.

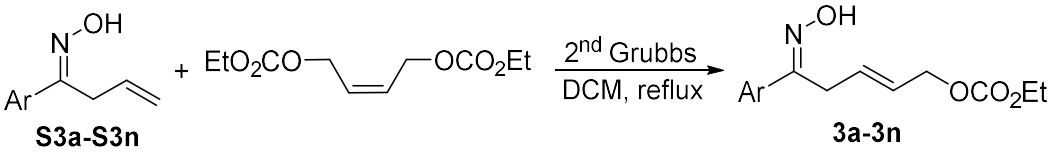
The substrates **1p**, **1r** and **1s** were synthesized using the similar methods.

### 2.2 General procedure for synthesis of *β*,*γ*-allyl carbonate oximes 3a–3p




1-Aryl-but-3-en-1-ol **S1** (20 mmol) was dissolved in diethyl ether at 0 °C and Jones reagent (40 mmol, 16.0 mL, 2.5 M, 2 equiv.) was added dropwise at 0 °C. The resulting mixture was warmed to room temperature and stirred for another 4 h. After completion of the reaction (monitored by TLC), the ether layer was separated and the aqueous layer was extracted with ethyl acetate (20 mL×3). The combined organic phase was washed with water and brine, dried over $Na_2SO_4$, filtered, and concentrated under reduce pressure. The crude *β*,*γ*-unsaturated ketone was directly used in next step without further purification.[1]

To a solution of hydroxylamine hydrochloride (50 mmol, 3.48 g, 5 equiv.) and sodium acetate (70 mmol, 5.74g, 7 equiv.) in ethanol (50 mL) was added *β*,*γ*-unsaturated ketone (10 mmol) in ethanol (8 mL). The reaction mixture was stirred overnight at room temperature and concentrated under reduced pressure. Then, the mixture was extracted with ethyl acetate (30 mL×3) and the combined organic phase was washed with water and brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1) to afford *β*,*γ*-unsaturated oxime **S3** in 50–70% yield.[3]

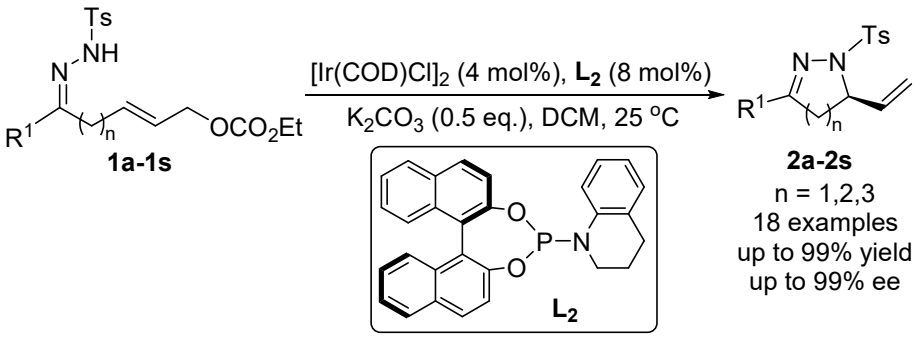



S3a-S3n 3a-3n

Under argon atmosphere, *β*,*γ*-unsaturated oxime **S3** (4.0 mmol) and (*Z*)-but-2-ene-1,4-diyl diethyl dicarbonate (6 mmol, 1.40 g, 1.5 equiv.) were dissolved in dry $CH_2Cl_2$ (10 mL). To the solution was added the solution of Grubbs catalyst 2nd generation (0.08 mmol, 68 mg, 2 mol %) in dry $CH_2Cl_2$ (3 mL). The mixture was refluxed overnight and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1) to afford the products **3a**–**3n** in 20–45% yield.

The substrates **3o**–**3p** were synthesized using the similar methods.

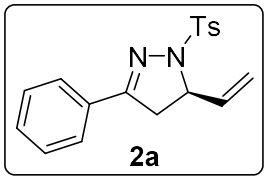
## 3. General procedure for enantioselective synthesis of 1*H*-pyrazolines 2a–2q, tetrahydro-pyridazine 2r and 1*H*-1,2-diazepine 2s enabled by iridium-catalyzed intramolecular allylic substitution reactions




1a-1s

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[Ir(COD)Cl]_2$ (0.004 mmol, 4 mol %), phosphoramidite ligand $\mathbf{L_2}$ (0.008 mmol, 8 mol %), *n*-propylamine (0.5 mL) and THF (0.5 mL). The reaction mixture was heated at 50 °C for 0.5 h and the volatile solvent was removed *in vacuo* to afford a pale-yellow solid. Then, $K_2CO_3$ (0.05 mmol, 0.5 equiv.) and a solution substrate **1** (0.1 mmol) in $CH_2Cl_2$ (2 mL) were added. The reaction mixture was stirred for another 20 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtrated with celite and washed with $CH_2Cl_2$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **2**.

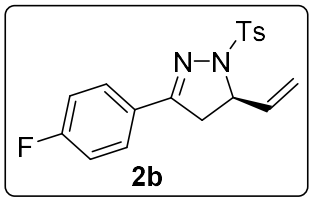
**(*R*)-3-phenyl-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2a)**




2a

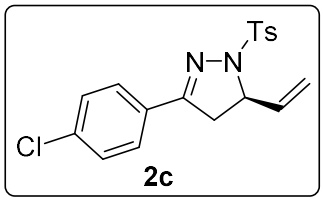
white solid, mp 107.2 – 107.8 °C, 32.0 mg, 98% yield, $[\alpha]_D^{26}$ +24.6 (c 0.57, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.65 (dd, $J$ = 7.6, 2.4 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.28 (d, $J$ = 8.0 Hz, 2H), 6.12 – 6.03 (m, 1H), 5.36 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.0 Hz, 1H), 4.35 – 4.28 (m, 1H), 3.21 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.96 (dd, $J$ = 17.2, 10.0 Hz, 1H), 2.39 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 157.04, 144.21, 136.45, 132.46, 130.79, 130.56, 129.50, 128.76, 128.62, 126.85, 117.73, 64.63, 40.22, 21.59. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O_2S$ $(M+H)^+$: 327.1162, Found: 327.1165. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 26.642 min, $t_{minor}$ = 33.923 min, 96% ee).

**(*R*)-3-(4-fluorophenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2b)**



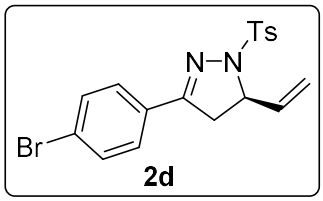

white solid, mp 161.7 – 162.9 °C, 32.0 mg, 93% yield, $[\alpha]_D^{26}$ +20.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.62 (dd, $J$ = 8.8, 5.6 Hz, 2H), 7.27 (d, $J$ = 8.0 Hz, 2H), 7.04 (t, $J$ = 8.4 Hz, 2H), 6.09 – 6.01 (m, 1H), 5.35 (d, $J$ = 16.8 Hz, 1H), 5.27 (d, $J$ = 10.4 Hz, 1H), 4.34 – 4.27 (m, 1H), 3.18 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.92 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.37 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 165.35, 162.85, 156.06, 144.30, 136.31, 132.39, 128.90, 128.82, 128.73, 127.08, 127.05, 117.84, 115.92, 115.70, 64.69, 40.26, 21.61. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{18}FN_2O_2S$ $(M+H)^+$: 345.1068, Found: 345.1072. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 23.365 min, $t_{minor}$ = 29.963 min, 97% ee).

**(*R*)-3-(4-chlorophenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2c)**




colorless oil, 32.5 mg, 90% yield, $[\alpha]_D^{26}$ –10.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 8.4 Hz, 2H), 7.58 (dd, $J$ = 6.8, 2.0 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 6.11 – 6.02 (m, 1H), 5.37 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 4.37 – 4.30 (m, 1H), 3.19 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.93 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.40 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.89, 144.29, 136.58, 136.19, 132.38, 129.49, 129.23, 128.88, 128.67, 128.01, 117.87, 64.71, 40.05, 21.56. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{18}ClN_2O_2S$ $(M+H)^+$: 361.0772, Found: 361.0777. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 27.728 min, $t_{minor}$ = 33.757 min, 93% ee).

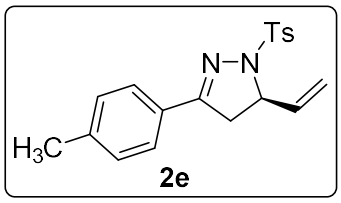
**(*R*)-3-(4-bromophenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2d)**



**2d**

white solid, mp 149.8 – 150.9 °C, 34.8 mg, 86% yield, $[\alpha]_D^{26}$ –55.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.49 (s, 4H), 7.28 (d, $J$ = 8.0 Hz, 2H), 6.10 – 6.01 (m, 1H), 5.35 (d, $J$ = 17.2 Hz, 1H), 5.28 (d, $J$ = 10.0 Hz, 1H), 4.36 – 4.29 (m, 1H), 3.18 (dd, $J$ = 17.2, 10.8 Hz, 1H), 2.92 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.38 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.01, 144.35, 136.22, 132.41, 131.89, 129.70, 129.54, 128.71, 128.25, 125.00, 117.94, 64.78, 40.04, 21.62. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{18}BrN_2O_2S$ $(M+H)^+$: 405.0267, Found: 405.0272. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 0.5 mL/min, retention time: $t_{major}$ = 28.883 min, $t_{minor}$ = 33.922 min, 90% ee).

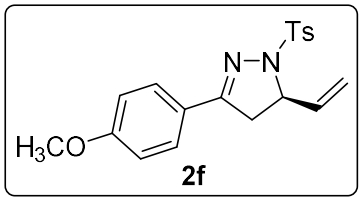
**(*R*)-3-(*p*-tolyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2e)**



**2e**

colorless oil, 31.3 mg, 92% yield, $[\alpha]_D^{26}$ –33.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.52 (d, $J$ = 8.4 Hz, 2H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.4 Hz, 2H), 6.10 – 6.01 (m, 1H), 5.34 (d, $J$ = 17.2 Hz, 1H), 5.26 (d, $J$ = 10.0 Hz, 1H), 4.29 – 4.22 (m, 1H), 3.17 (dd, $J$ = 16.8, 10.4 Hz, 1H), 2.92 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 157.22, 144.16, 140.99, 136.54, 132.33, 129.48, 129.33, 128.76, 128.00, 126.83, 117.64, 64.55, 40.26, 21.59, 21.48. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O_2S$ $(M+H)^+$: 341.1318, Found: 341.1323. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 30.452 min, $t_{minor}$ = 35.454 min, 97% ee).

**(*R*)-3-(4-methoxyphenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2f)**

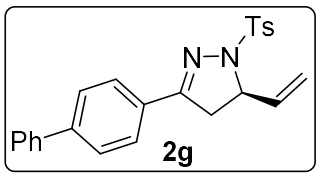


**2f**

white solid, mp 147.1 – 148.6 °C, 19.9 mg, 56% yield, $[\alpha]_D^{26}$ –56.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.0 Hz, 2H), 7.60 (d, $J$ = 8.8 Hz, 2H), 7.28 (d, $J$ = 8.0 Hz, 2H), 6.88 (d, $J$ = 9.2 Hz,

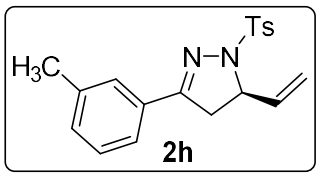
2H), 6.12 – 6.04 (m, 1H), 5.36 (d, $J$ = 17.2 Hz, 1H), 5.28 (d, $J$ = 10.0 Hz, 1H), 4.30 – 4.23 (m, 1H), 3.83 (s, 3H), 3.17 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.93 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.52, 156.88, 144.11, 136.60, 132.36, 129.45, 128.79, 128.49, 123.41, 117.58, 114.03, 64.48, 55.39, 40.31, 21.59. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O_3S$ $(M+H)^+$: 357.1267, Found: 357.1274. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 46.998 min, $t_{minor}$ = 66.760 min, 98% ee).

**(*R*)-3-(1,1'-biphenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2g)**



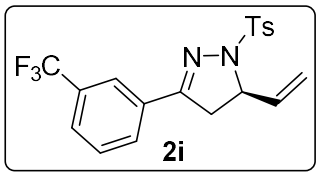

white solid, mp 158.6 – 159.4 °C, 35.4 mg, 88% yield, $[\alpha]_D^{26}$ –111.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.4 Hz, 2H), 7.61 – 7.58 (m, 4H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 7.30 (d, $J$ = 8.0 Hz, 2H), 6.14 – 6.05 (m, 1H), 5.38 (d, $J$ = 17.2 Hz, 1H), 5.30 (d, $J$ = 10.0 Hz, 1H), 4.37 – 4.29 (m, 1H), 3.25 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.99 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.76, 144.22, 143.30, 140.03, 136.46, 132.46, 129.65, 129.52, 128.93, 128.77, 127.94, 127.33, 127.26, 127.05, 117.76, 64.68, 40.23, 21.61. HRMS (ESI): Exact Mass Calcd. for $C_{24}H_{23}N_2O_2S$ $(M+H)^+$: 403.1475, Found: 403.1480. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 49.871 min, $t_{minor}$ = 59.985 min, 95% ee).

**(*R*)-3-(*m*-tolyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2h)**



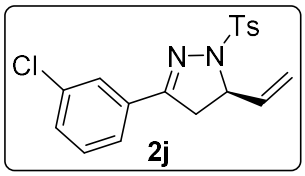

white solid, mp 163.5 – 164.8 °C, 32.0 mg, 94% yield, $[\alpha]_D^{26}$ –26.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.51 (s, 1H), 7.42 (d, $J$ = 7.6 Hz, 1H), 7.30 – 7.20 (m, 4H), 6.12 – 6.03 (m, 1H), 5.36 (d, $J$ = 16.8 Hz, 1H), 5.28 (d, $J$ = 10.4 Hz, 1H), 4.33 – 4.26 (m, 1H), 3.20 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.95 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 157.25, 144.17, 138.40, 136.51, 132.44, 131.40, 130.69, 129.49, 128.74, 128.50, 127.39, 124.07, 117.64, 64.53, 40.28, 21.58, 21.31. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O_2S$ $(M+H)^+$: 341.1318, Found: 341.1325. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 21.884 min, $t_{minor}$ = 28.315 min, 97% ee).

**(*R*)-1-tosyl-3-(trifluoromethyl)-5-vinyl-4,5-dihydro-1*H*-pyrazole (2i)**



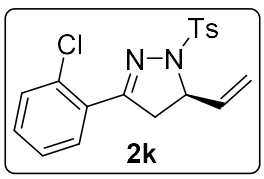

colorless oil, 38.2 mg, 97% yield, $[\alpha]_D^{26}$ +17.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 – 7.79 (m, 4H), 7.64 (d, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 7.6 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 2H), 6.11 – 6.02 (m, 1H), 5.38 (d, $J$ = 17.2 Hz, 1H), 5.30 (d, $J$ = 10.4 Hz, 1H), 4.41 – 4.34 (m, 1H), 3.26 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.98 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.39 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.63, 144.49, 136.07, 132.37, 131.64, 131.37, 131.05, 129.88, 129.61, 129.26, 128.68, 127.01, 126.98, 125.06, 123.56, 123.52, 122.35, 118.08, 64.87, 40.04, 21.60. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{18}F_3N_2O_2S$ $(M+H)^+$: 395.1036, Found: 395.1041. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 92/8, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 38.514 min, $t_{minor}$ = 41.838 min, 95% ee).

**(*R*)-3-(3-chlorophenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2j)**




colorless oil, 34.2 mg, 95% yield, $[\alpha]_D^{26}$ –7.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.64 (s, 1H), 7.51 (d, $J$ = 7.6 Hz, 1H), 7.37 (d, $J$ = 8.0 Hz, 1H), 7.33 – 7.30 (m, 3H), 6.11 – 6.02 (m, 1H), 5.37 (d, $J$ = 17.2 Hz, 1H), 5.30 (d, $J$ = 10.4 Hz, 1H), 4.38 – 4.31 (m, 1H), 3.21 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.94 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.41 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.72, 144.40, 136.16, 134.77, 132.54, 132.42, 130.49, 129.92, 129.59, 128.70, 126.78, 124.90, 117.98, 64.75, 40.06, 21.62. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{18}ClN_2O_2S$ $(M+H)^+$: 361.0772, Found: 361.0776. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 19.910 min, $t_{minor}$ = 24.079 min, 97% ee).

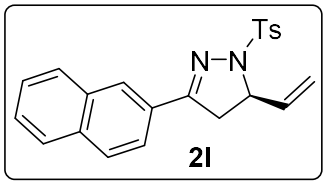
**(*R*)-3-(2-chlorophenyl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2k)**




colorless oil, 18.4 mg, 51% yield, $[\alpha]_D^{26}$ +83.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.73 (d, $J$ = 8.4 Hz, 2H), 7.50 (dd, $J$ = 7.6, 2.0 Hz, 1H), 7.27 – 7.14 (m, 5H), 6.03 – 5.95 (m, 1H), 5.25 (d, $J$ = 17.2 Hz,

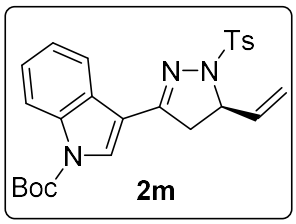
1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.24 (dd, *J* = 17.2, 10.4 Hz, 1H), 3.07 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 157.21, 144.37, 136.08, 132.80, 132.39, 131.08, 130.55, 130.54, 130.26, 129.51, 128.85, 126.91, 117.97, 65.48, 43.17, 21.63. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{18}ClN_2O_2S$ $(M+H)^+$: 361.0772, Found: 361.0778. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 21.507 min, $t_{major}$ = 26.629 min, 89% ee).

**(*R*)-3-(naphthaien-2-yl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2l)**



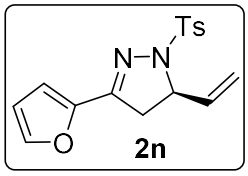

white solid, mp 124.6 – 125.3 ºC, 35.3 mg, 94% yield, $[\alpha]_D^{26}$ +5.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.85 – 7.80 (m, 6H), 7.54 – 7.47 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.16 – 6.07 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.40 – 4.33 (m, 1H), 3.34 (dd, *J* = 16.8, 10.8 Hz, 1H), 3.07 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 157.15, 144.25, 136.48, 134.25, 132.82, 132.43, 129.52, 128.77, 128.46, 128.45, 128.38, 127.84, 127.40, 127.34, 126.76, 123.53, 117.78, 64.76, 40.18, 21.59. HRMS (ESI): Exact Mass Calcd. for $C_{22}H_{21}N_2O_2S$ $(M+H)^+$: 377.1318, Found: 377.1322. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 33.806 min, $t_{minor}$ = 40.933 min, 99% ee).

**(*R*)-*tert*-butyl-3-(1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazol-3-yl)-1*H*-indole-1-carboxylate (2m)**



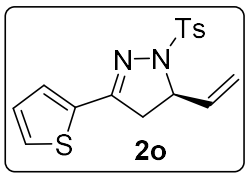

colorless oil, 46.0 mg, 99% yield, $[\alpha]_D^{27}$ –37.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.38 – 8.36 (m, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 1H), 7.43 – 7.36 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.15 – 6.06 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.32 – 4.25 (m, 1H), 3.23 (dd, *J* = 16.4, 10.4 Hz, 1H), 3.01 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.36 (s, 3H), 1.67 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.80, 149.17, 144.16, 136.48, 135.68, 132.26, 129.44, 128.76, 127.50, 127.08, 125.57, 123.98, 123.04, 117.75, 115.01, 113.27, 84.86, 63.67, 41.02, 28.13, 21.57. HRMS (ESI): Exact Mass Calcd. for $C_{25}H_{28}N_3O_4S$ $(M+H)^+$: 466.1795, Found: 466.1798. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 23.247 min, $t_{major}$ = 29.962 min, 97% ee).

**(*R*)-3-(furan-2-yl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2n)**



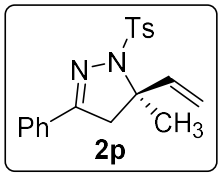

colorless oil, 25.9 mg, 82% yield, $[\alpha]_D^{27}$ +70.0 (c 0.5, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.0 Hz, 2H), 7.49 (d, $J$ = 1.2 Hz, 1H), 7.30 (d, $J$ = 8.0 Hz, 2H), 6.78 (d, $J$ = 3.2 Hz, 1H), 6.47 (dd, $J$ = 3.6, 2.0 Hz, 1H), 6.09 – 6.01 (m, 1H), 5.36 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 4.32 – 4.25 (m, 1H), 3.18 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.93 (dd, $J$ = 17.2, 10.0 Hz, 1H), 2.41 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 148.85, 146.41, 144.68, 144.25, 136.12, 132.38, 129.53, 128.79, 117.89, 112.44, 111.97, 64.08, 40.07, 21.62. HRMS (ESI): Exact Mass Calcd. for $C_{16}H_{17}N_2O_3S$ $(M+H)^+$: 317.0954, Found: 317.0960. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 20.299 min, $t_{minor}$ = 45.552 min, 94% ee).

**(*R*)-3-(thiophen-2-yl)-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2o)**




white solid, mp 145.1 – 146.9 °C, 32.2 mg, 97% yield, $[\alpha]_D^{27}$ –65.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 8.4 Hz, 2H), 7.41 (dd, $J$ = 5.2, 0.8 Hz, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.15 (dd, $J$ = 3.6, 0.8 Hz, 1H), 7.02 (dd, $J$ = 4.8, 3.6 Hz, 1H), 6.11 – 6.02 (m, 1H), 5.36 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 4.33 – 4.26 (m, 1H), 3.19 (dd, $J$ = 16.8, 10.8 Hz, 1H), 2.97 (dd, $J$ = 16.8, 10.0 Hz, 1H), 2.40 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 152.69, 144.25, 136.23, 134.33, 132.25, 129.49, 129.32, 128.93, 128.84, 127.44, 117.85, 64.70, 40.93, 21.60. HRMS (ESI): Exact Mass Calcd. for $C_{16}H_{17}N_2O_2S_2$ $(M+H)^+$: 333.0726, Found: 333.0732. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 29.916 min, $t_{minor}$ = 35.600 min, 98% ee).

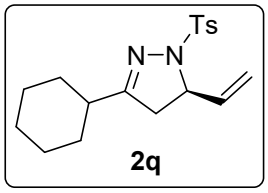
**(*R*)-5-methyl-3-phenyl-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2p)**




white solid, mp 120.1 – 120.8 °C, 31.9 mg, 94% yield, $[\alpha]_D^{27}$ +19.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (d, $J$ = 8.4 Hz, 2H), 7.67 – 7.65 (m, 2H), 7.39 – 7.37 (m, 3H), 7.27 (d, $J$ = 7.2 Hz, 2H), 6.04 (dd, $J$ = 17.2, 10.8 Hz, 1H), 5.28 (d, $J$ = 17.6 Hz, 1H), 5.15 (d, $J$ = 10.8 Hz, 1H), 3.21 (d, $J$ = 16.4 Hz, 1H),

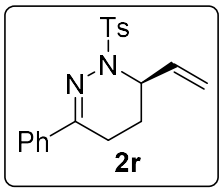
3.05 (d, $J$ = 16.8 Hz, 1H), 2.39 (s, 3H), 1.69 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 153.45, 143.50, 139.66, 137.03, 131.23, 130.17, 129.14, 128.59, 128.37, 126.53, 114.76, 71.49, 47.98, 23.65, 21.57. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O_2S$ $(M+H)^+$: 341.1318, Found: 341.1325. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 25.521 min, $t_{minor}$ = 30.528 min, 30% ee).

**(*R*)-3-cyclohexyl-1-tosyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (2q)**



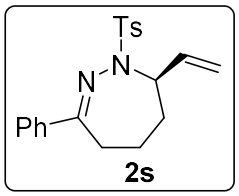

colorless oil, 30.6 mg, 92% yield, $[\alpha]_D^{26}$ +242.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (d, $J$ = 7.6 Hz, 2H), 7.31 (d, $J$ = 7.6 Hz, 2H), 6.03 – 5.95 (m, 1H), 5.28 (d, $J$ = 17.2 Hz, 1H), 5.22 (d, $J$ = 10.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 2.73 – 2.66 (m, 1H), 2.57 – 2.50 (m, 1H), 2.43 (s, 3H), 2.28 (s, 1H), 1.71 – 1.68 (m, 5H), 1.24 – 1.17 (m, 5H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.32, 144.04, 136.71, 131.96, 129.26, 128.87, 117.20, 63.75, 40.67, 39.22, 30.29, 29.91, 25.78, 25.64, 25.57, 21.61. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{25}N_2O_2S$ $(M+H)^+$: 333.1631, Found: 333.1629. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 12.270 min, $t_{major}$ = 14.196 min, 97% ee).

**(*R*)-3-phenyl-1-tosyl-6-vinyl-1,4,5,6-tetrahydropyridazine (2r)**




colorless oil, 30.9 mg, 91% yield, $[\alpha]_D^{27}$ +150.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 8.4 Hz, 2H), 7.69 (dd, $J$ = 7.6, 2.0 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.26 (d, $J$ = 8.0 Hz, 2H), 5.66 – 5.57 (m, 1H), 5.19 – 5.18 (m, 1H), 5.14 – 5.11 (m, 1H), 5.03 – 5.00 (m, 1H), 2.63 – 2.57 (m, 1H), 2.41 – 2.31 (m, 4H), 2.06 – 2.00 (m, 1H), 1.98 – 1.90 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.45, 143.58, 136.95, 135.92, 134.30, 129.21, 129.14, 128.41, 128.32, 125.24, 117.77, 53.99, 23.27, 21.57, 18.55. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O_2S$ $(M+H)^+$: 341.1318, Found: 341.1326. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 23.508 min, $t_{major}$ = 27.270 min, 96% ee).

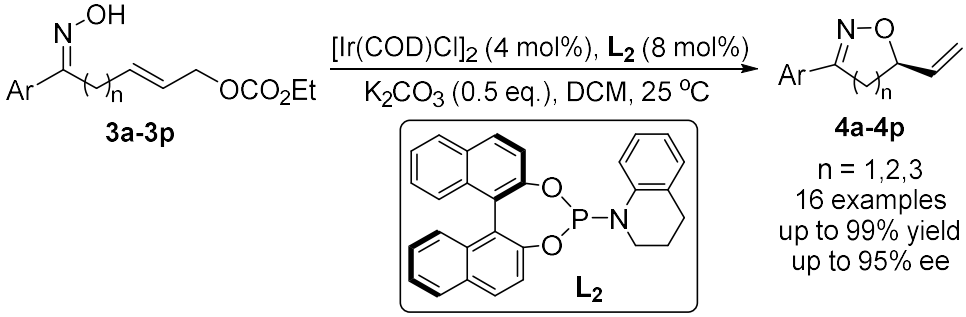
**(*R*)-3-phenyl-1-tosyl-7-vinyl-4,5,6,7-tetrahydro-1*H*-1,2-diazepine (2s)**




**2s**

white solid, mp 125.2 – 126.9 °C, 35.0 mg, 99% yield, $[\alpha]_D^{27}$ +678.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.93 (d, $J$ = 8.4 Hz, 2H), 7.72 (dd, $J$ = 8.0, 1.6 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.30 (d, $J$ = 8.0 Hz, 2H), 5.28 – 5.20 (m, 1H), 5.07 – 5.06 (m, 1H), 4.90 (d, $J$ = 17.2 Hz, 1H), 4.80 (d, $J$ = 10.8 Hz, 1H), 3.08 – 3.03 (m, 1H), 2.92 – 2.85 (m, 1H), 2.42 (s, 3H), 2.10 – 2.05 (m, 2H), 1.76 – 1.68 (m, 1H), 1.51 – 1.40 (m, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 168.71, 143.77, 137.29, 134.44, 133.64, 130.15, 129.41, 129.09, 128.41, 127.20, 117.13, 60.53, 33.96, 30.73, 21.63, 15.74. HRMS (ESI): Exact Mass Calcd. for $C_{20}H_{23}N_2O_2S$ $(M+H)^+$: 355.1475, Found: 355.1482. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 15.596 min, $t_{major}$ = 24.030 min, 92% ee).

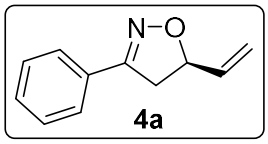
## 4. General procedure for enantioselective synthesis of dihydroisoxazoles 4a–4n, dihydro-4*H*-1,2-oxazine 4o, tetrahydro-1,2-oxazepine 4p enabled by iridium-catalyzed intramolecular allylic substitution reactions




**3a-3p** **4a-4p**

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[Ir(COD)Cl]_2$ (0.004 mmol, 4 mol %), phosphoramidite ligand **L₂** (0.008 mmol, 8 mol %), *n*-propylamine (0.5 mL) and THF (0.5 mL). The reaction mixture was heated at 50 °C for 0.5 h and the volatile solvents were removed *in vacuo* to afford a pale-yellow solid. Then, $K_2CO_3$ (0.05 mmol, 0.5 equiv.) and a solution of allylic carbonate **3** (0.1 mmol) in $CH_2Cl_2$ (2 mL) were added. The reaction mixture was stirred for another 20 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtrated with celite and washed with $CH_2Cl_2$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **4**.

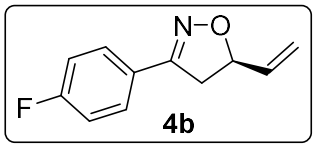
**(*R*)-3-phenyl-5-vinyl-4,5-dihydroisoxazole (4a)**




**4a**

white solid, mp 43.6 – 44.5 °C, 15.7 mg, 91% yield, $[\alpha]_D^{24}$ –110.0 (c 0.5, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 – 7.66 (m, 2H), 7.41 – 7.40 (m, 3H), 6.01 – 5.93 (m, 1H), 5.41 (d, $J$ = 17.2 Hz, 1H), 5.27 (d, $J$ = 10.0 Hz, 1H), 5.20 – 5.13 (m, 1H), 3.50 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.13 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.36, 136.10, 130.08, 129.57, 128.71, 126.68, 117.93, 82.03, 40.53. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{12}NO$ $(M+H)^+$: 174.0913, Found: 174.0916. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 28.121 min, $t_{minor}$ = 30.563 min, 92% ee).

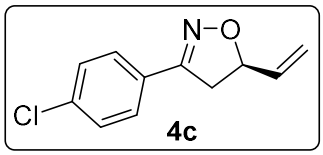
**(*R*)-3-(4-fluorophenyl)-5-vinyl-4,5-dihydroisoxazole (4b)**



**4b**

white solid, mp 67.0 – 67.7 °C, 18.9 mg, 99% yield, $[\alpha]_D^{25}$ –119.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (dd, $J$ = 8.8, 5.6 Hz, 2H), 7.09 (t, $J$ = 8.8 Hz, 2H), 6.00 – 5.92 (m, 1H), 5.41 (d, $J$ = 16.8 Hz, 1H), 5.27 (d, $J$ = 10.4 Hz, 1H), 5.19 – 5.13 (m, 1H), 3.48 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.10 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 165.00, 162.51, 155.39, 135.97, 128.65, 128.56, 125.87, 125.84, 118.04, 115.97, 115.75, 82.14, 40.58. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{11}FNO$ $(M+H)^+$: 192.0819, Found: 192.0821. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 19.721 min, $t_{minor}$ = 22.818 min, 76% ee).

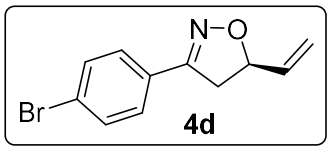
**(*R*)-3-(4-chlorophenyl)-5-vinyl-4,5-dihydroisoxazole (4c)**



**4c**

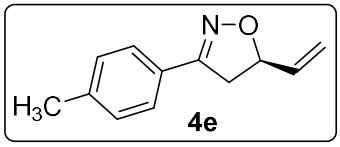
white solid, mp 84.5 – 85.4 °C, 19.3 mg, 93% yield, $[\alpha]_D^{25}$ –130.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (dd, $J$ = 6.8, 2.0 Hz, 2H), 7.37 (dd, $J$ = 6.8, 2.0 Hz, 2H), 6.00 – 5.92 (m, 1H), 5.41 (d, $J$ = 17.2 Hz, 1H), 5.28 (d, $J$ = 10.4 Hz, 1H), 5.20 – 5.14 (m, 1H), 3.47 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.09 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.45, 136.04, 135.87, 129.00, 128.09, 127.89, 118.13, 82.29, 40.35. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{11}ClNO$ $(M+H)^+$: 208.0524, Found: 208.0526. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 20.322 min, $t_{minor}$ = 22.814 min, 91% ee).

**(*R*)-3-(4-bromophenyl)-5-vinyl-4,5-dihydroisoxazole (4d)**



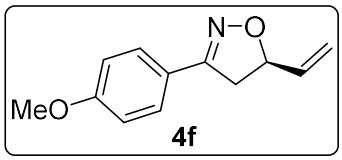

white solid, mp 100.1 – 101.2 °C, 22.9 mg, 91% yield, $[\alpha]_D^{22}$ –86.0 (c 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (s, 4H), 6.00 – 5.91 (m, 1H), 5.41 (d, $J$ = 16.8 Hz, 1H), 5.28 (d, $J$ = 10.0 Hz, 1H), 5.20 – 5.14 (m, 1H), 3.47 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.09 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.56, 135.85, 131.96, 128.52, 128.11, 124.35, 118.19, 82.34, 40.28. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{11}BrNO$ $(M+H)^+$: 252.0019, Found: 252.0022. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 22.617 min, $t_{minor}$ = 25.395 min, 93% ee).

**(*R*)-3-(*p*-tolyl)-5-vinyl-4,5-dihydroisoxazole (4e)**



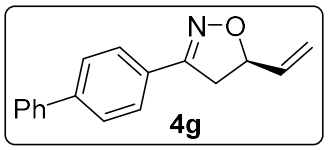

white solid, mp 68.2 – 70.1 °C, 17.2 mg, 92% yield, $[\alpha]_D^{25}$ –171.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.56 (d, $J$ = 8.4 Hz, 2H), 7.21 (d, $J$ = 8.0 Hz, 2H), 6.01 – 5.93 (m, 1H), 5.40 (d, $J$ = 16.8 Hz, 1H), 5.26 (d, $J$ = 10.4 Hz, 1H), 5.17 – 5.11 (m, 1H), 3.48 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.11 (dd, $J$ = 16.4, 8.4 Hz, 1H), 2.38 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.33, 140.31, 136.21, 129.41, 126.75, 126.63, 117.83, 81.87, 40.66, 21.43. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO$ $(M+H)^+$: 188.1070, Found: 188.1073. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 15.941 min, $t_{minor}$ = 17.777 min, 94% ee).

**(*R*)-3-(4-methoxyphenyl)-5-vinyl-4,5-dihydroisoxazole (4f)**




white solid, mp 77.4 – 77.8 °C, 20.1 mg, 99% yield, $[\alpha]_D^{25}$ –166.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 8.8 Hz, 2H), 6.90 (d, $J$ = 8.8 Hz, 2H), 5.99 – 5.91 (m, 1H), 5.38 (d, $J$ = 17.2 Hz, 1H), 5.24 (d, $J$ = 10.4 Hz, 1H), 5.14 – 5.08 (m, 1H), 3.82 (s, 3H), 3.45 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.08 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 161.06, 155.95, 136.25, 128.20, 122.14, 117.80, 114.13, 81.78, 55.35, 40.79. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO_2$ $(M+H)^+$: 204.1019, Found: 204.1022. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 19.754 min, $t_{major}$ = 22.778 min, 94% ee).

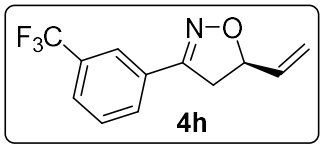
**(*R*)-3-([1,1'-biphenyl]-4-yl)-5-vinyl-4,5-dihydroisoxazole (4g)**




**4g**

white solid, mp 130.1 – 130.9 °C, 22.7 mg, 91% yield, $[\alpha]_D^{25}$ –158.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.72 (d, $J$ = 8.4 Hz, 2H), 7.63 – 7.59 (m, 4H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.38 – 7.34 (m, 1H), 6.01 – 5.93 (m, 1H), 5.41 (d, $J$ = 16.8 Hz, 1H), 5.26 (d, $J$ = 10.4 Hz, 1H), 5.20 – 5.13 (m, 1H), 3.51 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.14 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.13, 142.81, 140.17, 136.10, 128.92, 128.44, 127.83, 127.37, 127.15, 127.06, 118.00, 82.12, 40.55. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}NO$ $(M+H)^+$: 250.1226, Found: 250.1230. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 19.111 min, $t_{minor}$ = 25.833 min, 91% ee).

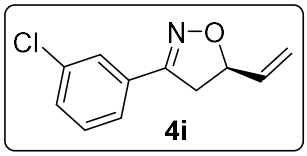
**(*R*)-3-(3-(trifluoromethyl)phenyl)-5-vinyl-4,5-dihydroisoxazole (4h)**




**4h**

white solid, mp 71.8 – 72.6 °C, 23.1 mg, 96% yield, $[\alpha]_D^{25}$ –148.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.89 – 7.87 (m, 2H), 7.66 (d, $J$ = 7.6 Hz, 1H), 7.54 (t, $J$ = 7.6 Hz, 1H), 6.01 – 5.93 (m, 1H), 5.43 (d, $J$ = 17.2 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 5.25 – 5.19 (m, 1H), 3.52 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.15 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.30, 135.70, 131.45, 131.12, 130.49, 129.71, 129.29, 126.59, 126.55, 123.45, 123.41, 123.38, 118.28, 82.51, 40.17. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{11}F_3NO$ $(M+H)^+$: 242.0787, Found: 242.0792. HPLC (Chiralpak IC column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 10.586 min, $t_{minor}$ = 12.380 min, 86% ee).

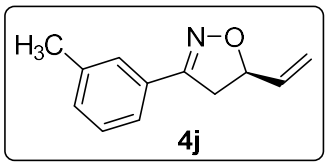
**(*R*)-3-(3-chlorophenyl)-5-vinyl-4,5-dihydroisoxazole (4i)**




**4i**

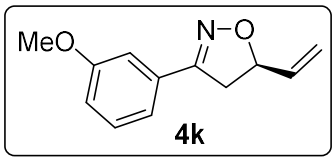
white solid, mp 69.6 – 71.1 °C, 19.7 mg, 95% yield, $[\alpha]_D^{25}$ –183.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (d, $J$ = 1.6 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.39 – 7.31 (m, 2H), 6.00 – 5.91 (m, 1H), 5.41 (d, $J$ = 17.2 Hz, 1H), 5.28 (d, $J$ = 10.0 Hz, 1H), 5.21 – 5.15 (m, 1H), 3.47 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.09 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.34, 135.79, 134.76, 131.35, 130.03, 129.99, 126.71, 124.72, 118.19, 82.35, 40.24. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{11}ClNO$ $(M+H)^+$: 208.0524, Found: 208.0527. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 12.181 min, $t_{minor}$ = 13.877 min, 89% ee).

**(*R*)-3-(*m*-tolyl)-5-vinyl-4,5-dihydroisoxazole (4j)**



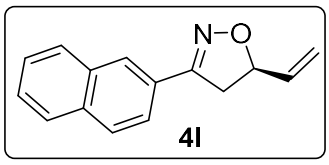

colorless oil, 18.5 mg, 99% yield, $[\alpha]_D^{26}$ –131.7 (c 0.6, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (s, 1H), 7.44 (d, $J$ = 7.6 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.01 – 5.92 (m, 1H), 5.40 (d, $J$ = 17.2 Hz, 1H), 5.26 (d, $J$ = 10.4 Hz, 1H), 5.18 – 5.12 (m, 1H), 3.49 (dd, $J$ = 16.4, 10.4 Hz, 1H), 3.12 (dd, $J$ = 16.4, 8.4 Hz, 1H), 2.38 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.47, 138.43, 136.16, 130.88, 129.46, 128.59, 127.25, 123.87, 117.85, 81.94, 40.60, 21.34. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO$ $(M+H)^+$: 188.1070, Found: 188.1073. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 19.703 min, $t_{major}$ = 21.050 min, 95% ee).

**(*R*)-3-(3-methoxyphenyl)-5-vinyl-4,5-dihydroisoxazole (4k)**



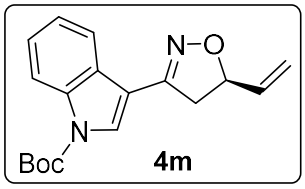

colorless oil, 17.5 mg, 86% yield, $[\alpha]_D^{26}$ –155.4 (c 0.65, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31 – 7.26 (m, 2H), 7.17 (d, $J$ = 7.6 Hz, 1H), 6.96 (dd, $J$ = 8.4, 1.6 Hz, 1H), 6.01 – 5.92 (m, 1H), 5.41 (d, $J$ = 17.2 Hz, 1H), 5.27 (d, $J$ = 10.0 Hz, 1H), 5.19 – 5.13 (m, 1H), 3.84 (s, 3H), 3.49 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.11 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.72, 156.36, 136.06, 130.82, 129.71, 119.36, 117.98, 116.47, 111.25, 82.11, 55.37, 40.58. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO_2$ $(M+H)^+$: 204.1019, Found: 204.1021. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 17.718 min, $t_{minor}$ = 19.856 min, 91% ee).

**(*R*)-3-(naphthalen-2-yl)-5-vinyl-4,5-dihydroisoxazole (4l)**



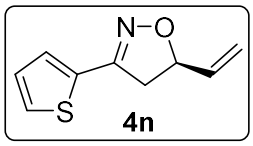

white solid, mp 93.3 – 95.1 °C, 19.6 mg, 88% yield, $[\alpha]_D^{26}$ –161.0 (c 1.0, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 – 7.95 (m, 1H), 7.88 – 7.82 (m, 4H), 7.51 – 7.49 (m, 2H), 6.03 – 5.95 (m, 1H), 5.43 (d, $J$ = 16.8 Hz, 1H), 5.28 (d, $J$ = 10.0 Hz, 1H), 5.23 – 5.17 (m, 1H), 3.60 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.24 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.54, 136.11, 134.04, 133.00, 128.55, 128.36, 127.86, 127.18, 127.12, 126.88, 126.69, 123.58, 118.04, 82.24, 40.49. HRMS (ESI): Exact Mass Calcd. for $C_{15}H_{14}NO$ $(M+H)^+$: 224.1070, Found: 224.1072. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 14.438 min, $t_{minor}$ = 16.774 min, 91% ee).

***tert*-butyl (*R*)-3-(5-vinyl-4,5-dihydroisoxazol-3-yl)-1*H*-indole-1-carboxylate (4m)**



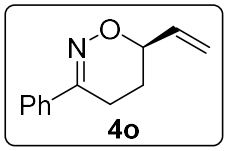

white solid, mp 95.1 – 95.9 °C, 23.7 mg, 76% yield, $[\alpha]_D^{26}$ –86.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 – 8.23 (m, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H), 7.70 (s, 1H), 7.40 – 7.30 (m, 2H), 6.01 – 5.93 (m, 1H), 5.42 (d, $J$ = 16.8 Hz, 1H), 5.27 (d, $J$ = 10.0 Hz, 1H), 5.15 – 5.08 (m, 1H), 3.52 (dd, $J$ = 16.0, 10.4 Hz, 1H), 3.15 (dd, $J$ = 16.0, 8.4 Hz, 1H), 1.69 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 151.82, 149.37, 136.11, 135.69, 127.11, 126.55, 125.50, 123.76, 123.10, 117.95, 115.00, 111.89, 84.70, 80.84, 41.47, 28.17. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{21}N_2O_3$ $(M+H)^+$: 313.1547, Found: 313.1549. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 14.169 min, $t_{minor}$ = 16.564 min, 85% ee).

**(*R*)-3-(thiophen-2-yl)-5-vinyl-4,5-dihydroisoxazole (4n)**




colorless oil, 16.1 mg, 90% yield, $[\alpha]_D^{26}$ –129.3 (c 0.75, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38 – 7.37 (m, 1H), 7.18 (d, $J$ = 2.8 Hz, 1H), 7.05 (dd, $J$ = 4.0, 4.8 Hz, 1H), 5.99 – 5.90 (m, 1H), 5.39 (d, $J$ = 17.2 Hz, 1H), 5.26 (d, $J$ = 10.0 Hz, 1H), 5.14 (q, $J$ = 8.4 Hz, 1H), 3.49 (dd, $J$ = 16.4, 10.8 Hz, 1H), 3.12 (dd, $J$ = 16.4, 8.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.13, 135.78, 132.07, 128.28, 128.25, 127.28, 118.18, 82.24, 41.32. HRMS (ESI): Exact Mass Calcd. for $C_9H_{10}NOS$ $(M+H)^+$: 180.0478, Found: 180.0481. HPLC (Chiralpak AD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 13.642 min, $t_{minor}$ = 15.135 min, 95% ee).

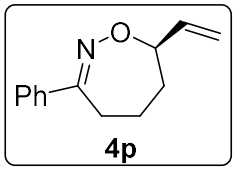
**(*R*)-3-phenyl-6-vinyl-5,6-dihydro-4*H*-1,2-oxazine (4o)**




colorless oil, 18.1 mg, 97% yield, $[\alpha]_D^{26}$ –237.7 (c 0.85, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 – 7.66 (m, 2H), 7.37 – 7.35 (m, 3H), 5.97 – 5.89 (m, 1H), 5.41 (d, $J$ = 17.6 Hz, 1H), 5.27 (d, $J$ = 10.4 Hz, 1H), 4.35 – 4.30 (m, 1H), 2.69 – 2.58 (m, 2H), 2.18 – 2.11 (m, 1H), 1.96 – 1.86 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 154.27, 135.89, 129.45, 128.45, 125.33, 117.72, 75.35, 24.09, 21.08. HRMS (ESI): Exact Mass Calcd. for

$C_{12}H_{14}NO$ $(M+H)^+$: 188.1070, Found: 188.1073. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 92/8, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 15.152 min, $t_{minor}$ = 16.377 min, 90% ee).

**(*R*)-3-phenyl-7-vinyl-4,5,6,7-tetrahydro-1,2-oxazepine (4p)**

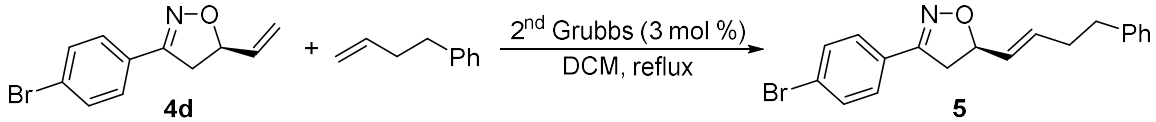



**4p**

colorless oil, 18.7 mg, 93% yield, $[\alpha]_D^{26}$ –57.0 (c 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 (d, $J$ = 6.4 Hz, 2H), 7.44 – 7.39 (m, 3H), 6.05 – 5.97 (m, 1H), 5.36 (d, $J$ = 17.6 Hz, 1H), 5.19 (d, $J$ = 10.4 Hz, 1H), 4.24 – 4.20 (m, 1H), 3.23 – 3.16 (m, 1H), 2.81 – 2.77 (m, 1H), 2.09 – 1.97 (m, 2H), 1.94 – 1.84 (m, 1H), 1.63 – 1.57 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 175.72, 138.07, 135.44, 130.35, 128.58, 126.92, 115.34, 80.30, 35.39, 29.44, 21.86. HRMS (ESI): Exact Mass Calcd. for $C_{13}H_{16}NO$ $(M+H)^+$: 202.1226, Found: 202.1230. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 12.350 min, $t_{major}$ = 18.285 min, 94% ee).

## 5. Synthetic transformation of products

### 5.1 Olefin metathesis of compound 4d



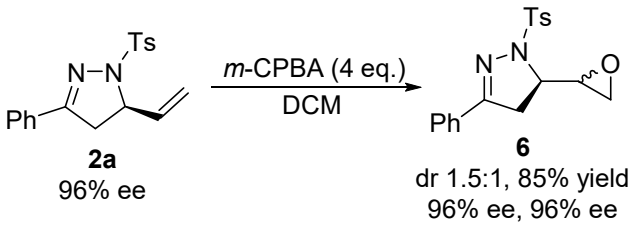

**4d**
93% ee

**5**
86% yield, 89% ee

Under argon atmosphere, a solution of compound **4d** (50.4 mg, 0.2 mmol) and but-3-en-1-ylbenzene (79.2 mg, 0.6 mmol, 3.0 equiv.) in dry DCM (2 mL) was treated with Grubbs 2$^{nd}$ catalyst (5.1 mg, 3 mol %). The reaction mixture was refluxed for 24 h. After cooling to room temperature, DCM was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 19/1) to afford product **5** (61.2 mg).

**(*R*,*E*)-3-(4-bromophenyl)-5-(4-phenylbut-1-en-1-yl)-4,5-dihydroisoxazole (5).** white solid, mp 67.7 – 68.8 °C, 86% yield, $[\alpha]_D^{23}$ –83.0 (c 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (s, 4H), 7.29 – 7.25 (m, 3H), 7.20 – 7.15 (m, 2H), 5.90 – 5.83 (m, 1H), 5.59 (dd, $J$ = 15.2, 7.6 Hz, 1H), 5.11 (dd, $J$ = 18.0, 8.8 Hz, 1H), 3.39 (dd, $J$ = 16.4, 10.4 Hz, 1H), 2.99 (dd, $J$ = 16.4, 8.8 Hz, 1H), 2.72 (t, $J$ = 7.2 Hz, 2H), 2.43 – 2.39 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 155.70, 141.40, 134.64, 131.93, 128.69, 128.45, 128.41, 128.36, 128.08, 125.96, 124.24, 82.41, 40.37, 35.24, 33.91. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{19}BrNO$ $(M+H)^+$: 356.0645, Found: 356.0646. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 37.630 min, $t_{minor}$ = 44.594 min, 89% ee).

### 5.2 Epoxidation of compound 2a




**2a**
96% ee

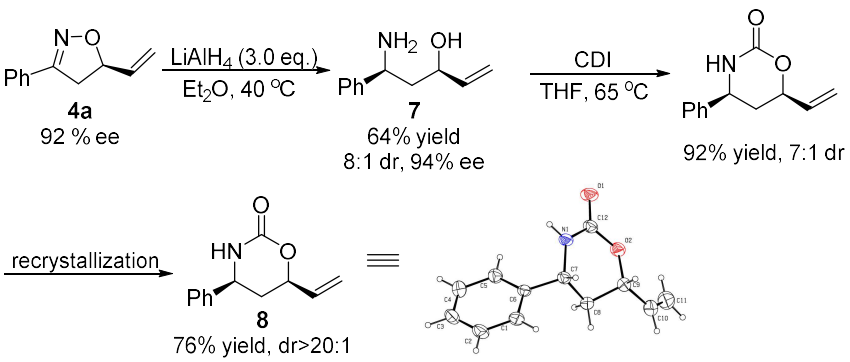
**6**
dr 1.5:1, 85% yield
96% ee, 96% ee

To a solution of compound **2a** (49.0 mg, 0.15 mmol) in $CH_2Cl_2$ (2 mL), *m*-CPBA (70%, 147.9 mg, 0.6 mmol, 4.0 equiv.) was added at 0 °C. The reaction mixture was stirred for 24 h at room temperature. Upon completion of the reaction (monitored by TLC), the reaction was quenched with saturated aqueous $Na_2SO_3$. The organic phase was separated, washed with saturated aqueous $NaHCO_3$, brine, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (9/1) to afford the product **6** (85% yield, 3:2 dr).

major **6**, white solid, mp 136.5 – 138.6 °C, 26.2 mg, 51% yield, $[\alpha]_D^{27}$ +6.0 (c 0.5, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.65 (d, $J$ = 8.0 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.27 (d, $J$ = 8.0 Hz, 2H), 3.76 – 3.70 (m, 1H), 3.43 – 3.40 (m, 1H), 3.19 – 3.05 (m, 2H), 2.99 (t, $J$ = 4.4 Hz, 1H), 2.79 (dd, $J$ = 4.4, 2.4 Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 157.85, 144.55, 132.07, 130.78, 130.49, 129.65, 128.67, 128.62, 126.97, 63.17, 53.32, 47.71, 36.54, 21.60. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$: 343.1111, Found: 343.1117. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 37.774 min, $t_{minor}$ = 41.754 min, 96% ee).

minor **6**, white solid, mp 88.4 – 90.1 °C, 17.4 mg, 34% yield, $[\alpha]_D^{27}$ +2.0 (c 0.5, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.65 (d, $J$ = 6.8 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.28 (d, $J$ = 8.0 Hz, 2H), 4.28 – 4.22 (m, 1H), 3.47 (dd, $J$ = 6.4, 4.0 Hz, 1H), 3.03 (d, $J$ = 10.0 Hz, 2H), 2.97 – 2.95 (m, 1H), 2.91 (t, $J$ = 4.4 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 157.97, 144.48, 132.17, 130.78, 130.46, 129.62, 128.65, 128.01, 126.97, 60.66, 52.35, 44.80, 35.47, 21.60. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$: 343.1111, Found: 343.1117. HPLC (Chiralpak IG column, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, retention time: $t_{major}$ = 25.022 min, $t_{minor}$ = 35.241 min, 96% ee).

### 5.3 Synthesis of *β*-amino alcohol 7 and 6-vinyl-1,3-oxazinan-2-one (8)




**4a**
92 % ee

**7**
64% yield
8:1 dr, 94% ee

92% yield, 7:1 dr

**8**
76% yield, dr>20:1

Under argon atmosphere, compound **4a** (34.6 mg, 0.2 mmol) was dissolved in dry $Et_2O$ (8.0 mL). Lithium aluminium hydride (22.8 mg, 0.6 mmol, 3.0 equiv.) was added to the above solution. The reaction mixture was refluxed for 36 h. After cooling to room temperature, the reaction was quenched with aqueous $NH_4Cl$ (20 mL), and then extracted with $CH_2Cl_2$ (10 mL×3). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (7:1) to afford the product **7** (8:1 dr).

**(3*R*,5*S*)-5-amino-5-phenylpent-1-en-3-ol (7).** white solid, mp 295.3 – 297.1 °C, 22.7 mg, 64% yield, $[\alpha]_D^{26}$ –135.4 (c 0.33, $CH_2Cl_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.48 – 7.30 (m, 5H), 6.62 (br s, 2H), 5.83 – 5.75 (m, 1H), 5.13 – 5.08 (m, 1H), 4.98 – 4.95 (m, 1H), 4.23 (dd, $J$ = 8.0, 6.4 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.34 (br s, 1H), 1.93 – 1.77 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 142.43, 140.87, 129.01, 128.44, 127.73, 113.79, 68.93, 53.45, 43.09. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{16}NO$ $(M+H)^+$: 178.1226, Found: 178.1230. HPLC (Chiralpak OD–H column, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, retention time: $t_{minor}$ = 11.600 min, $t_{major}$ = 13.077 min, 94% ee).

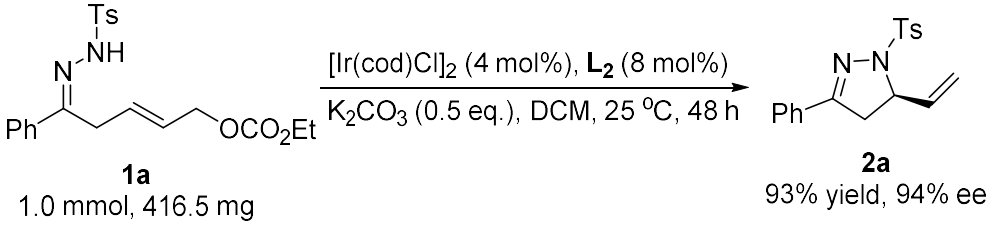
An oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was charged with compound **7** (17.7 mg, 0.1 mmol) in anhydrous THF (2 mL), followed by the addition of 1,1'-carbonyldiimidazole (CDI) (32.4 mg, 0.2 mmol). The reaction was refluxed for 6 h under argon. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure. The residue was dissolved in EtOAc, and washed with sat. aqueous $NH_4Cl$ and brine. The organic phase was dried over anhydrous $Na_2SO_4$, concentrated and purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1:1) to afford the product **8** (92% yield, 7:1 dr). The (4*S*,6*R*)-**8** was obtained in 76% yield by recrystallization from dichloromethane.

**(4*S*,6*R*)-4-phenyl-6-vinyl-1,3-oxazinan-2-one (8)**. White solid, 76% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.33 (m, 5H), 5.95 – 5.86 (m, 1H), 5.44 (d, $J$ = 17.2 Hz, 1H), 5.35 (br s, 1H), 5.28 (d, $J$ = 10.8 Hz, 1H), 4.91 – 4.87 (m, 1H), 4.64 (dd, $J$ = 11.6, 4.4, 1H), 2.27 – 2.22 (m, 1H), 1.89 – 1.80 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 153.68, 140.51, 134.83, 129.20, 128.74, 126.09, 117.68, 77.32, 55.59, 36.91. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO_2$ $(M+H)^+$: 204.1019, Found: 204.1021.

**Table 1. Crystal data and structure refinement for compound 8.**

| | |
|---|---|
| Identification code | hufang-hxp_0302_auto |
| Empirical formula | $C_{12}H_{13}NO_2$ |
| Formula weight | 203.23 |
| Temperature/K | 274.64(16) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.2864(3) |
| b/Å | 10.8028(3) |
| c/Å | 11.5140(4) |
| α/° | 90 |
| β/° | 109.190(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1090.89(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.237 |
| μ/mm$^{-1}$ | 0.685 |
| F(000) | 432.0 |
| Crystal size/mm$^3$ | 0.15 × 0.12 × 0.08 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2θ range for data collection/° | 11.546 to 153.276 |
| Index ranges | -11 ≤ h ≤ 11, -13 ≤ k ≤ 11, -14 ≤ l ≤ 14 |
| Reflections collected | 6938 |
| Independent reflections | 2192 [$R_{int}$ = 0.0386, $R_{sigma}$ = 0.0363] |
| Data/restraints/parameters | 2192/1/136 |
| Goodness-of-fit on F$^2$ | 1.091 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0666, $wR_2$ = 0.1928 |
| Final R indexes [all data] | $R_1$ = 0.0747, $wR_2$ = 0.2035 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.42/-0.28 |

## 6. Scale-up synthesis of compound 2a




**1a**
1.0 mmol, 416.5 mg

**2a**
93% yield, 94% ee

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added [Ir(COD)Cl]$_2$ (0.04 mmol, 4 mol %), phosphoramidite ligand **L$_2$** (0.08 mmol, 8 mol %), *n*-propylamine (1.0

mL) and THF (1.0 mL). The reaction mixture was heated at 50 °C for 0.5 h and the volatile solvent was removed *in vacuo* to afford a pale-yellow solid. Then, $K_2CO_3$ (0. 5 mmol, 0.5 equiv.), a solution of **1a** (1.0 mmol) in $CH_2Cl_2$ (20 mL) were added and the reaction mixture was stirred for 48 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtrated with celite and washed with $CH_2Cl_2$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **2a** (93% yield, 93% ee).

## 7. References

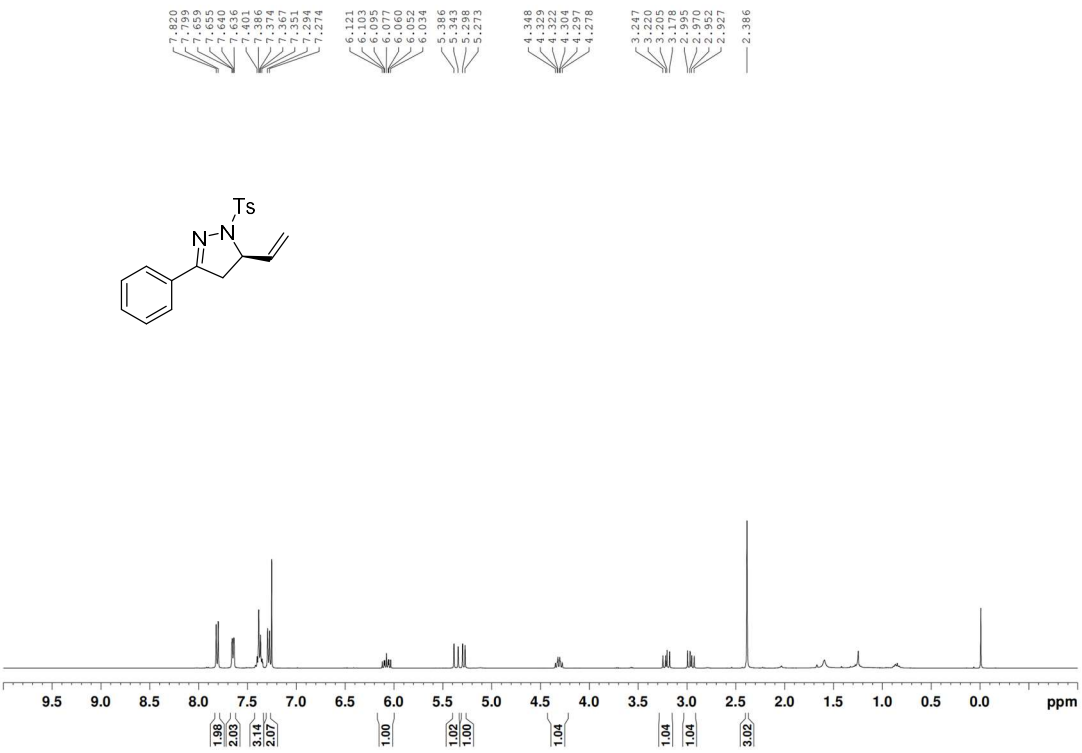

[1] Guo, Y.-Q.; Zhao, M.-N.; Ren, Z.-H.; Guan, Z.-H. *Org. Lett*. **2018**, *20*, 3337–3340.

[2] Wang, L.; Li, P.; Menche, D. *Angew. Chem. Int. Ed*. **2010**, *49*, 9270–9273.

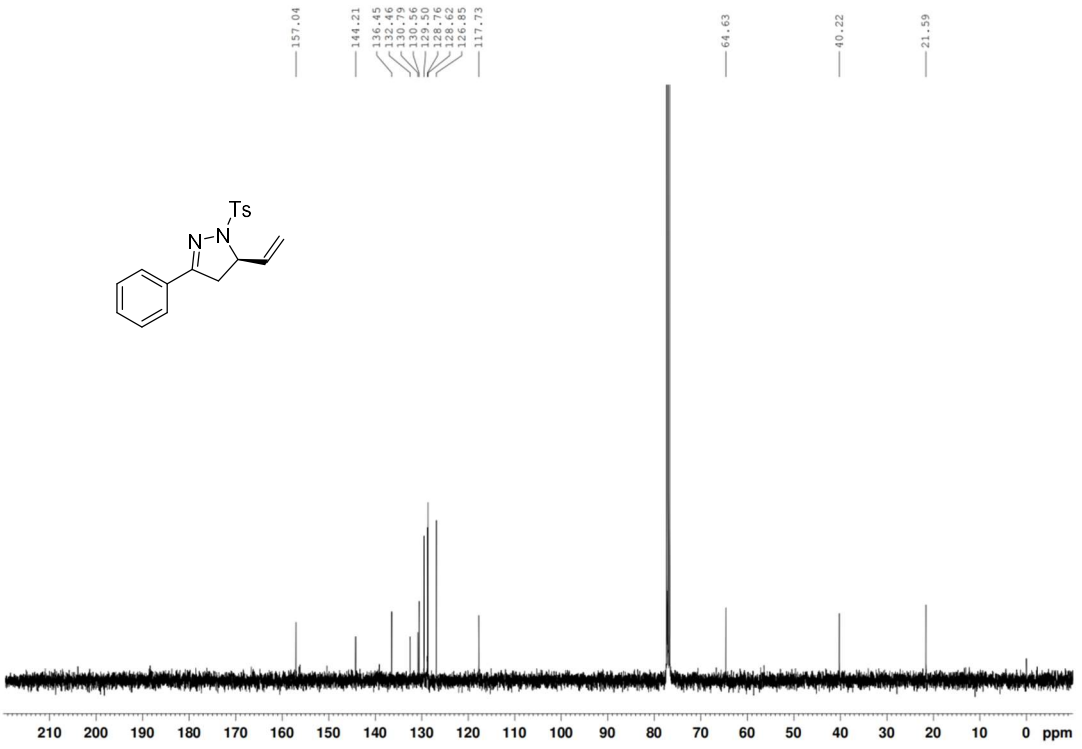
[3] Wang, L.; Zhang, K.; Wang, Y.; Li, W.; Chen, M.; Zhang, J. *Angew. Chem. Int. Ed*. **2020**, *59*, 4421–4427.

## 8. NMR spectra of compounds 2a–2s, 4a–4p and 5–8

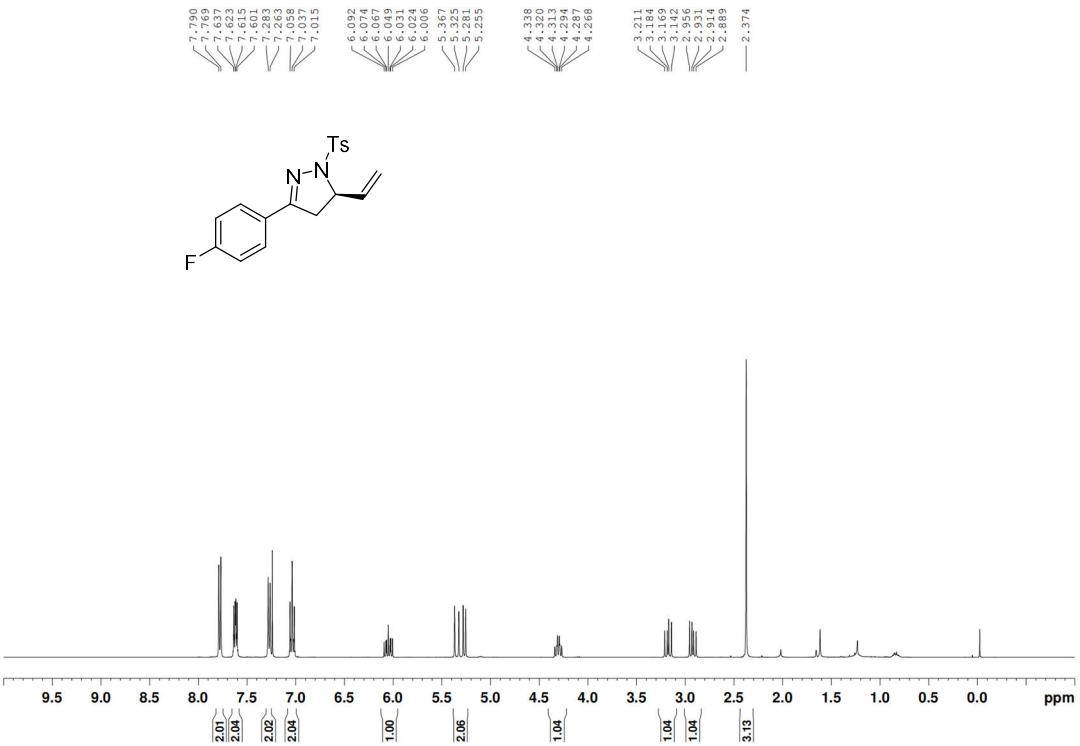
$^{1}$H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz)



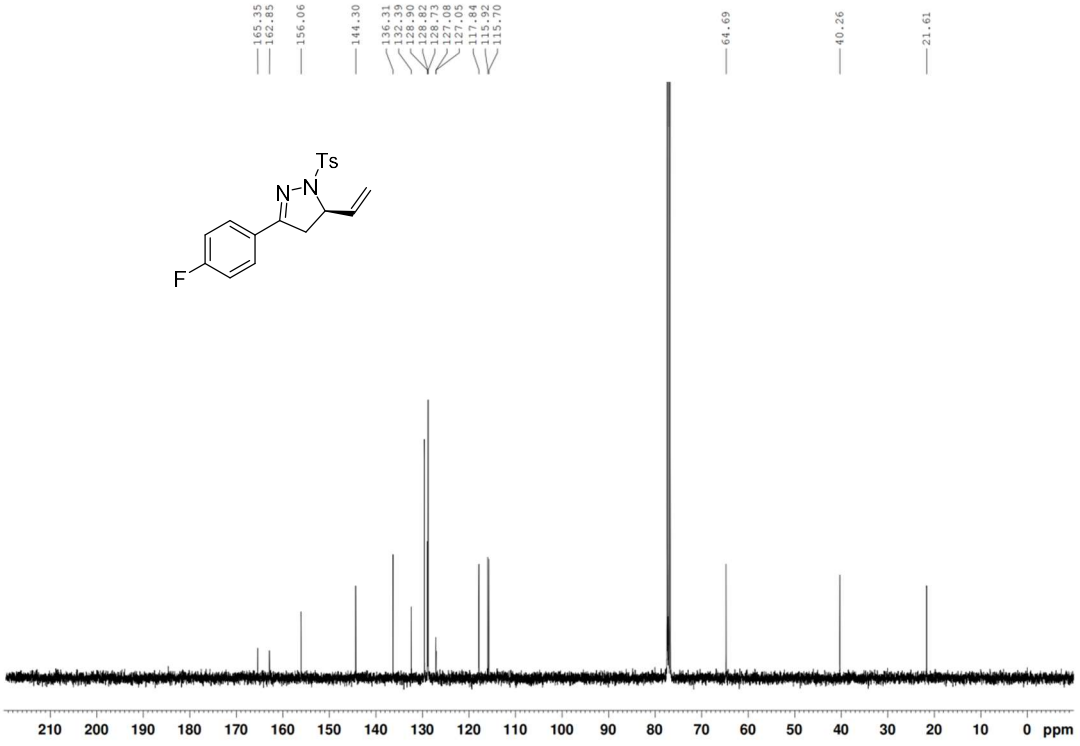

$^{13}$C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz)



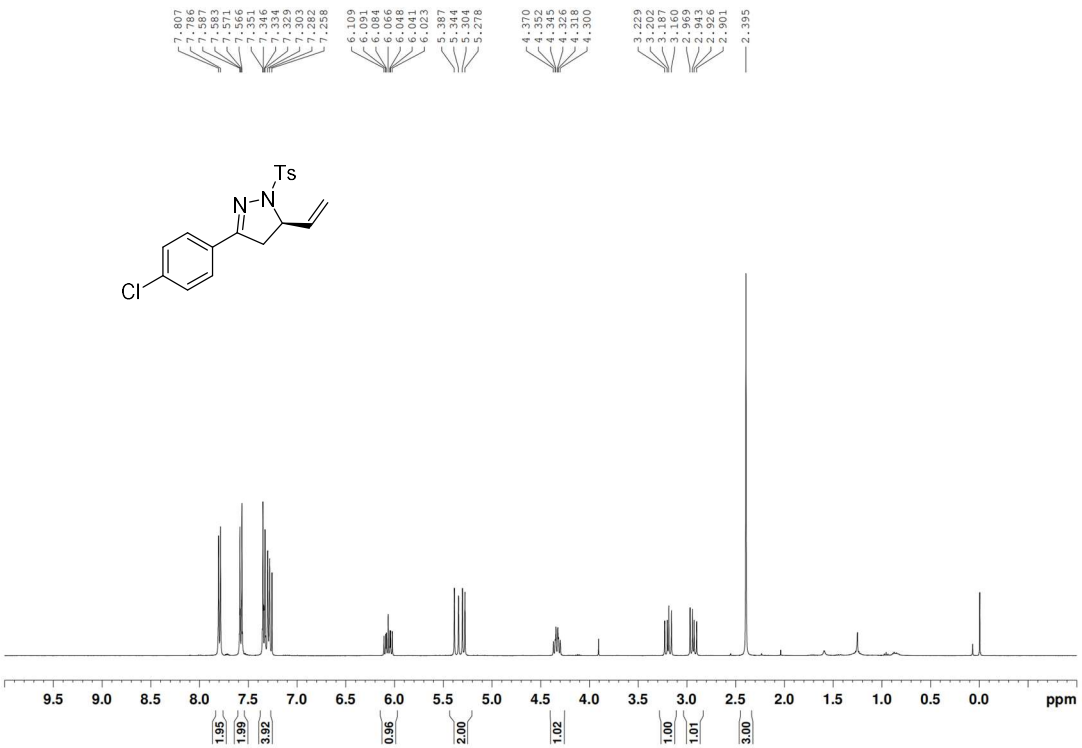
$^{1}$H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz)



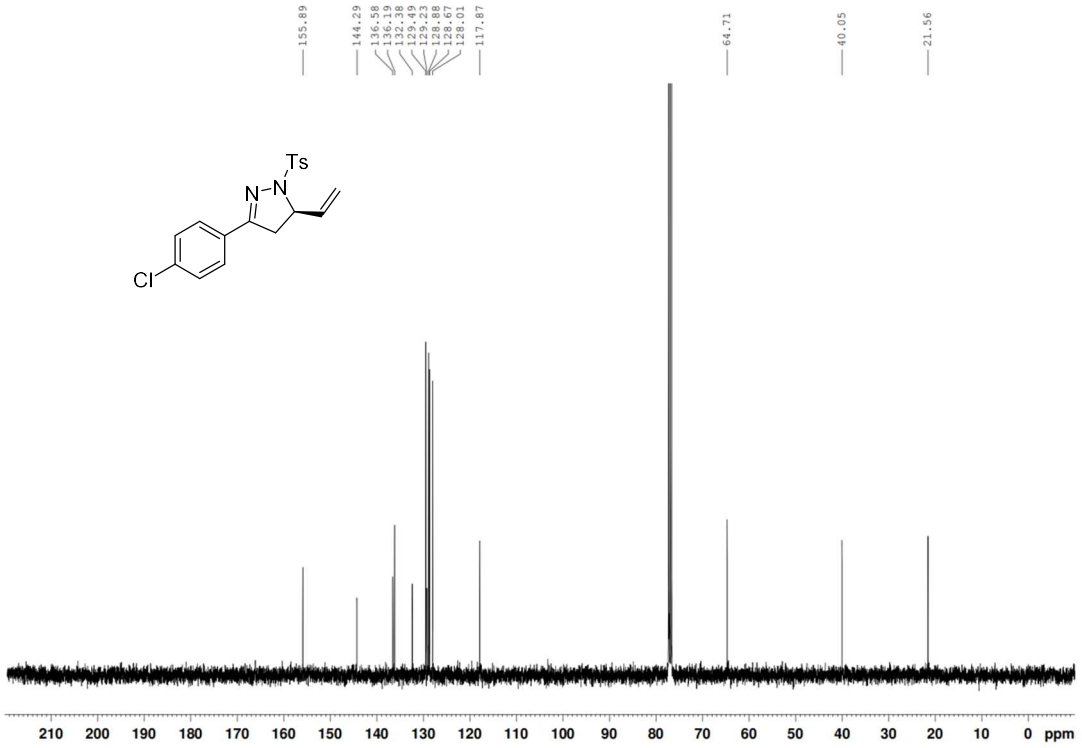

$^{13}$C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz)



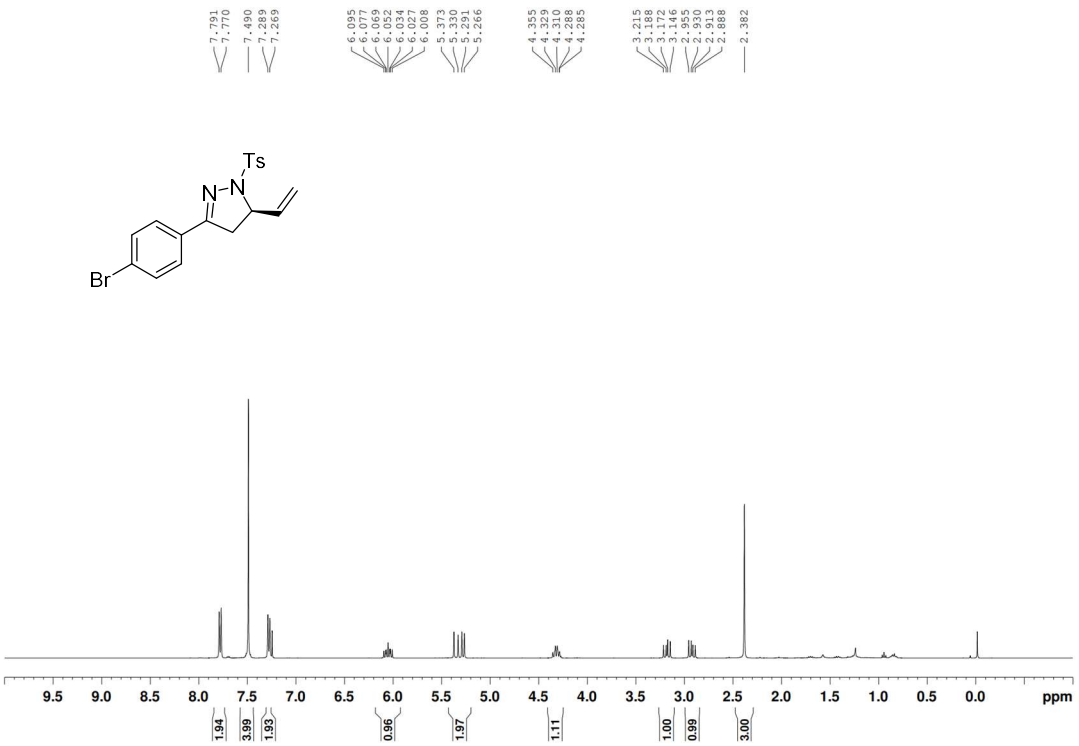
$^{1}$H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz)



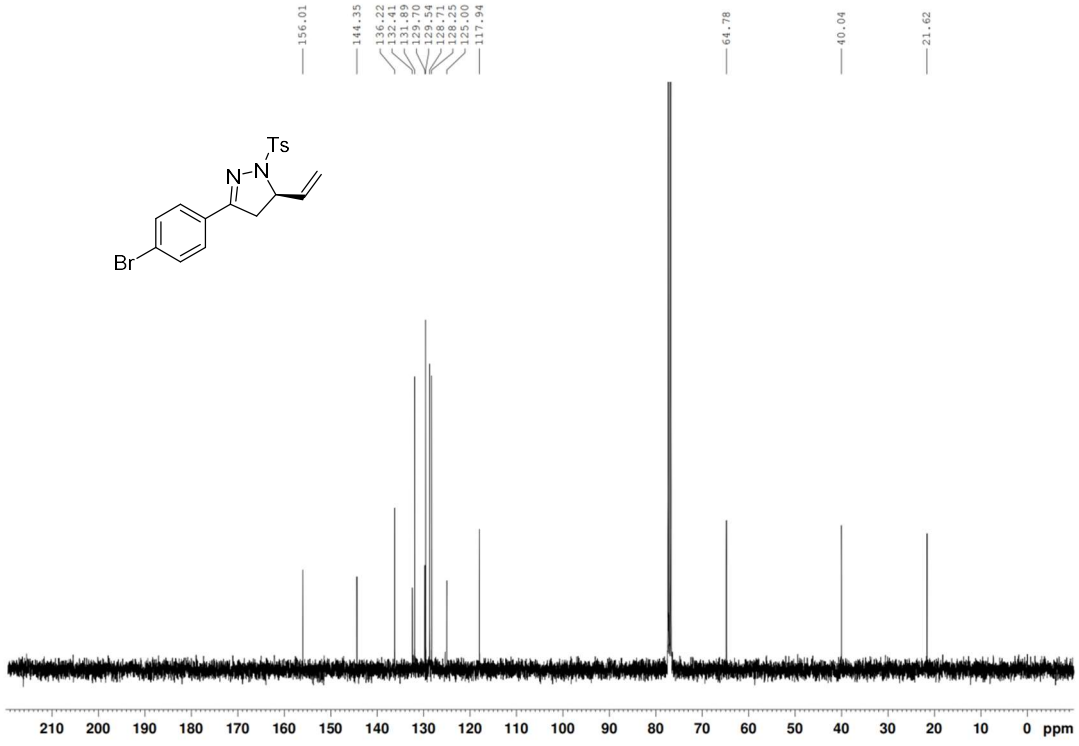

$^{13}$C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz)



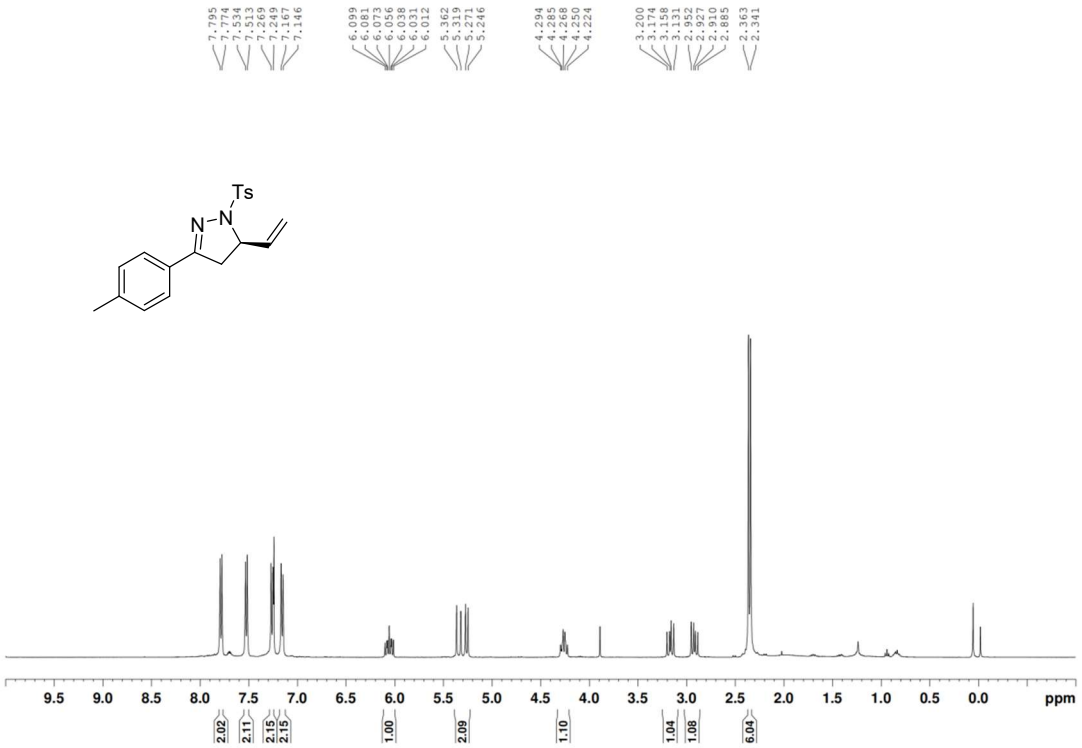
$^{1}$H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz)



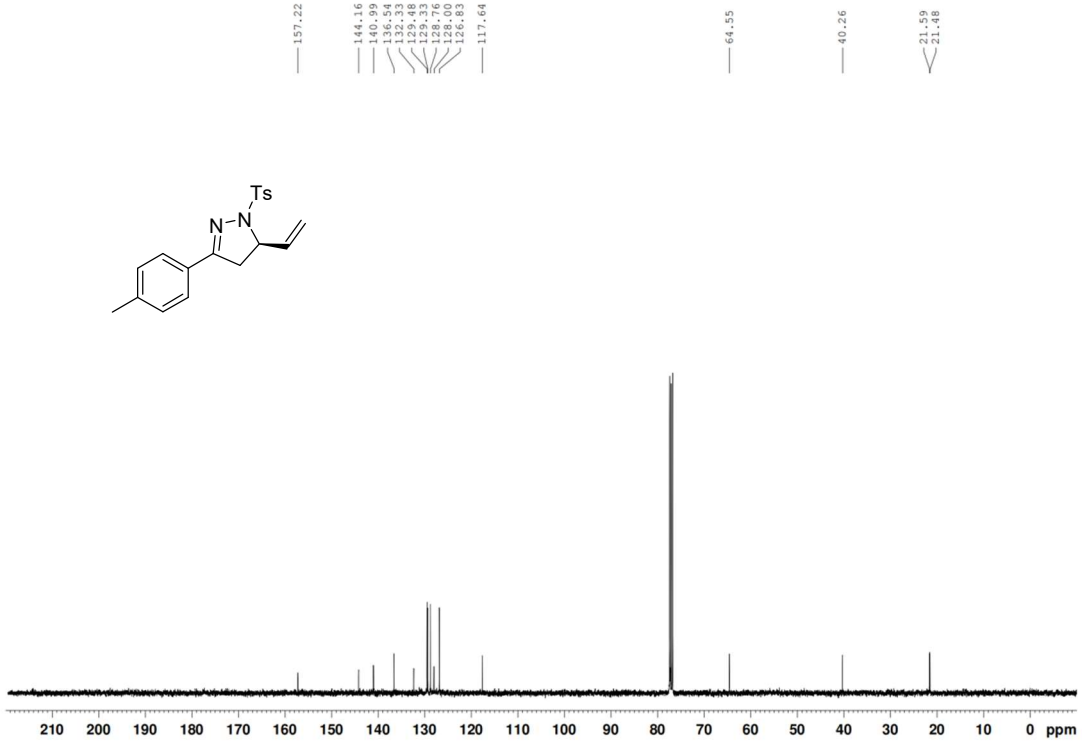

$^{13}$C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz)



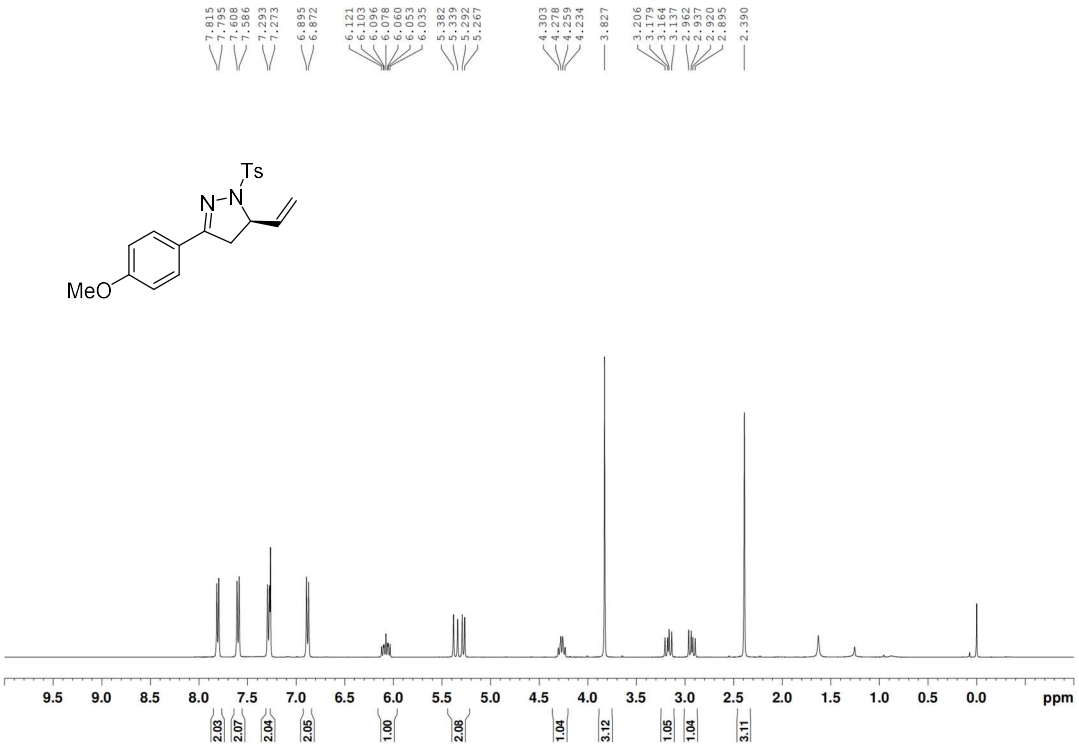
$^{1}$H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz)



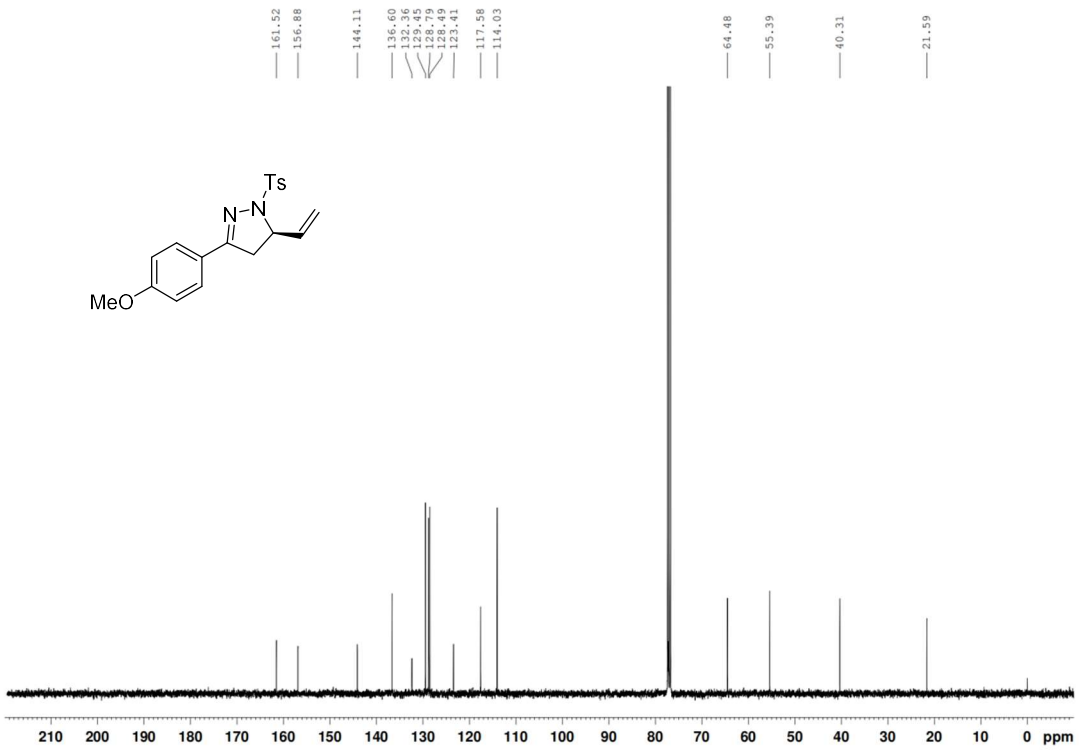

$^{13}$C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz)



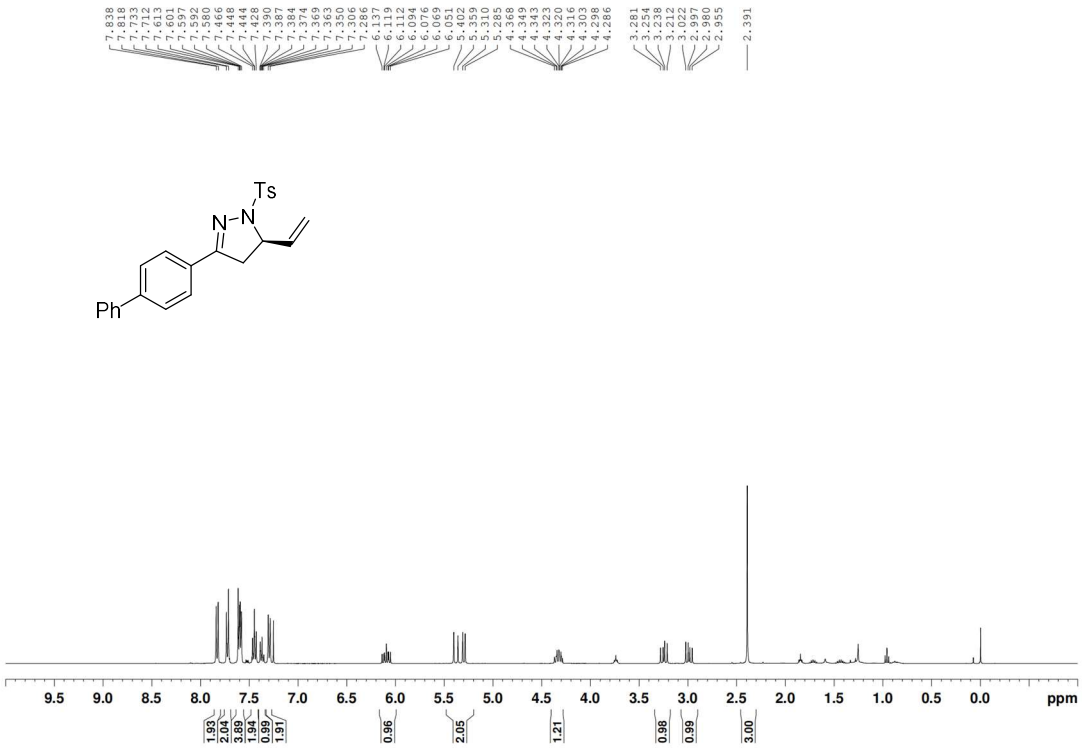
$^{1}$H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)



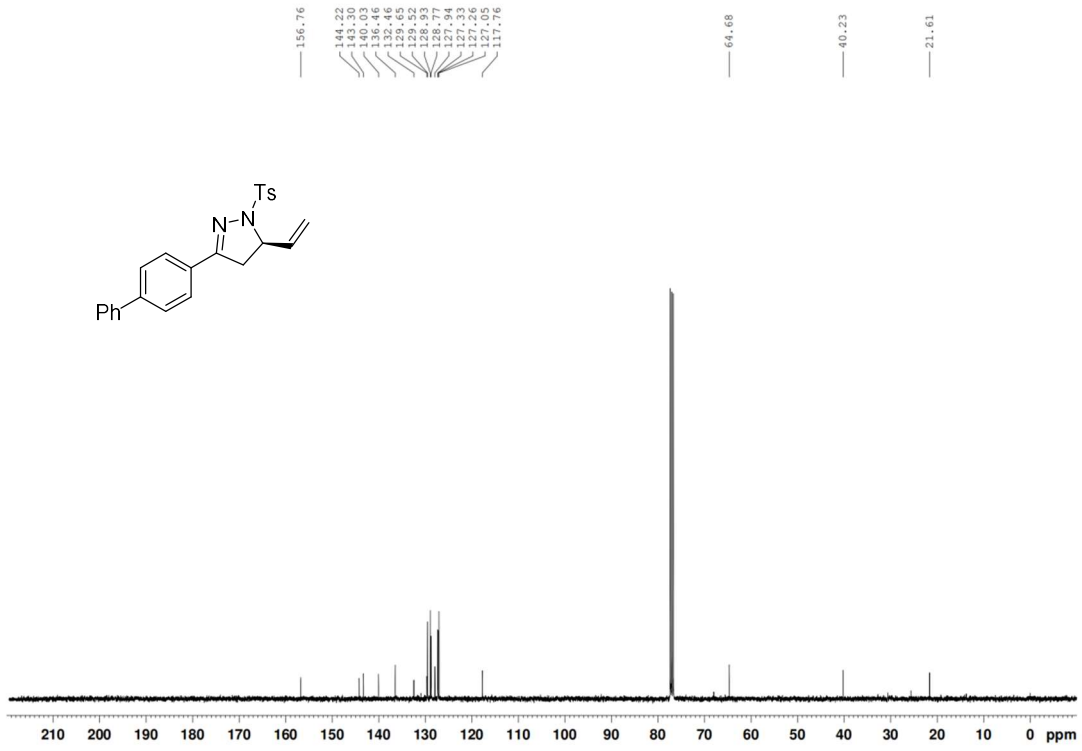

$^{13}$C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz)



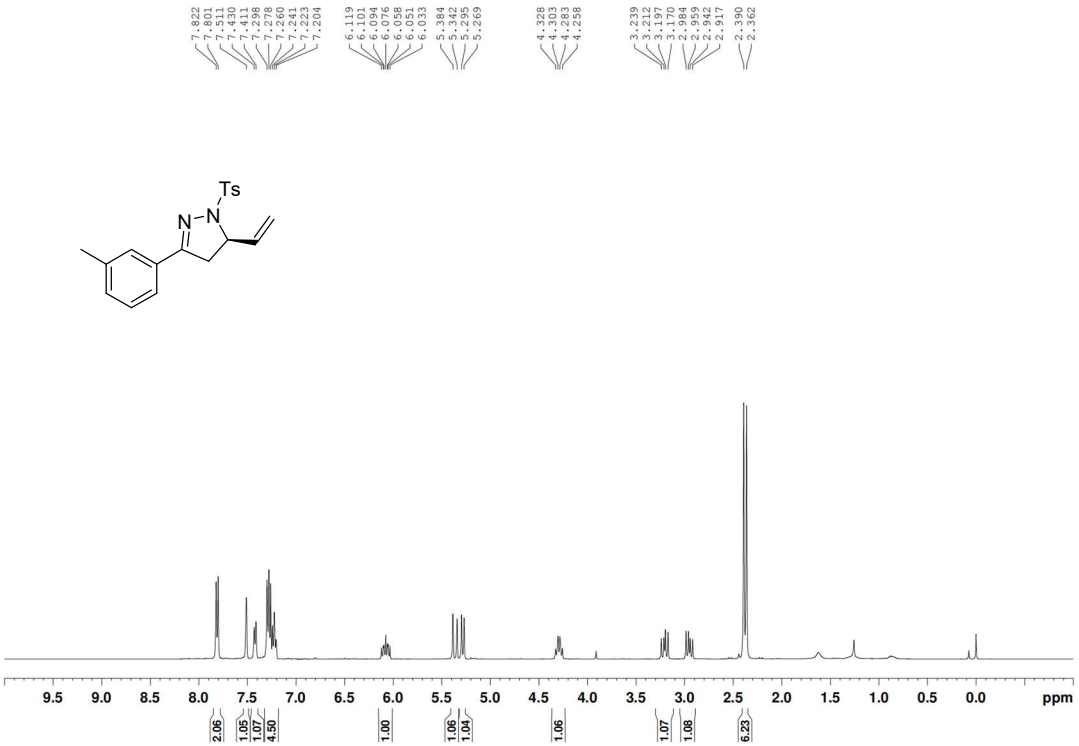
$^{1}$H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz)



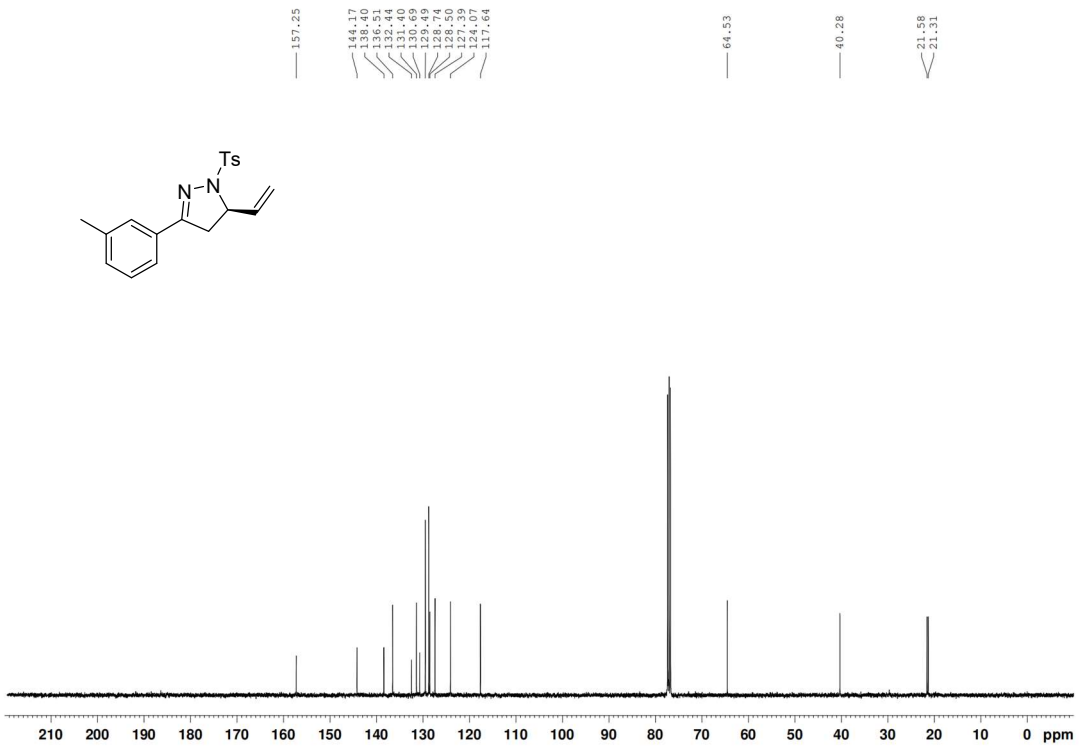

$^{13}$C NMR spectrum of compound **2g** ($CDCl_3$, 100 MHz)



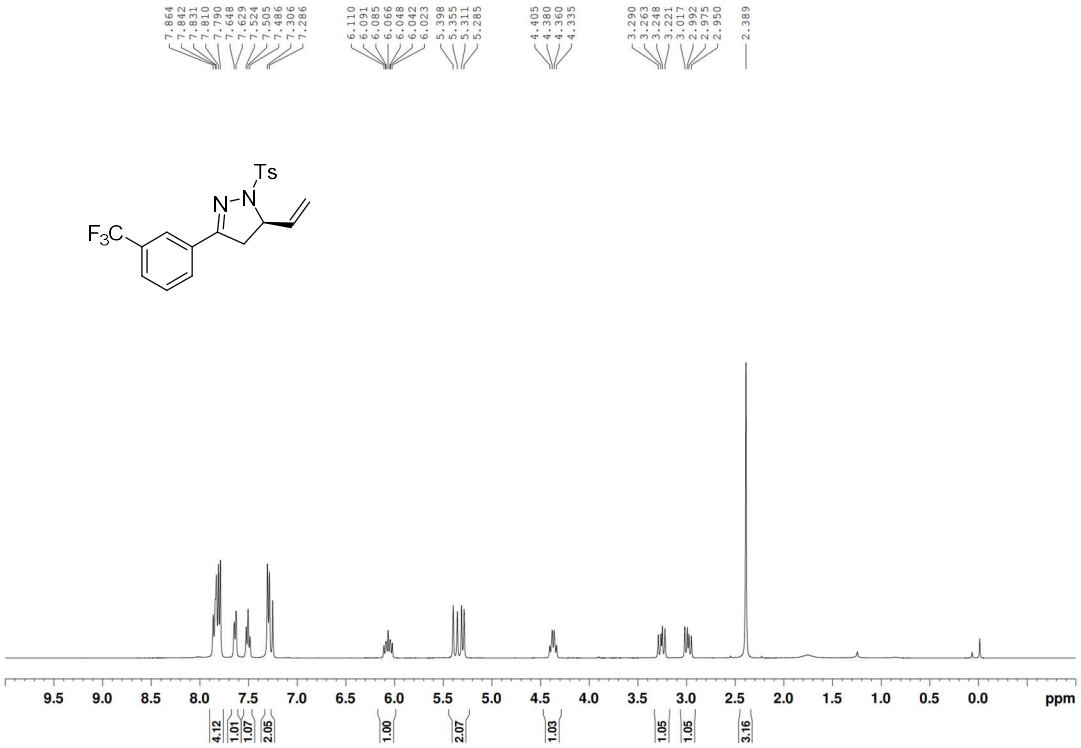
$^{1}$H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz)



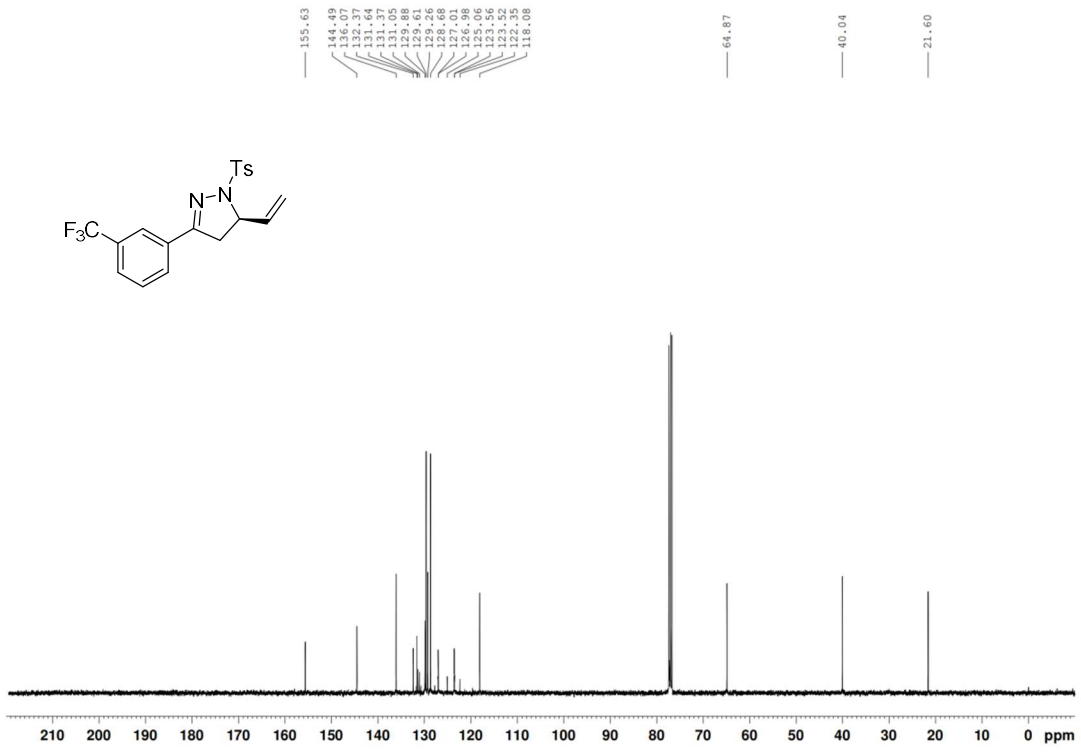

$^{13}$C NMR spectrum of compound **2h** ($CDCl_3$, 100 MHz)



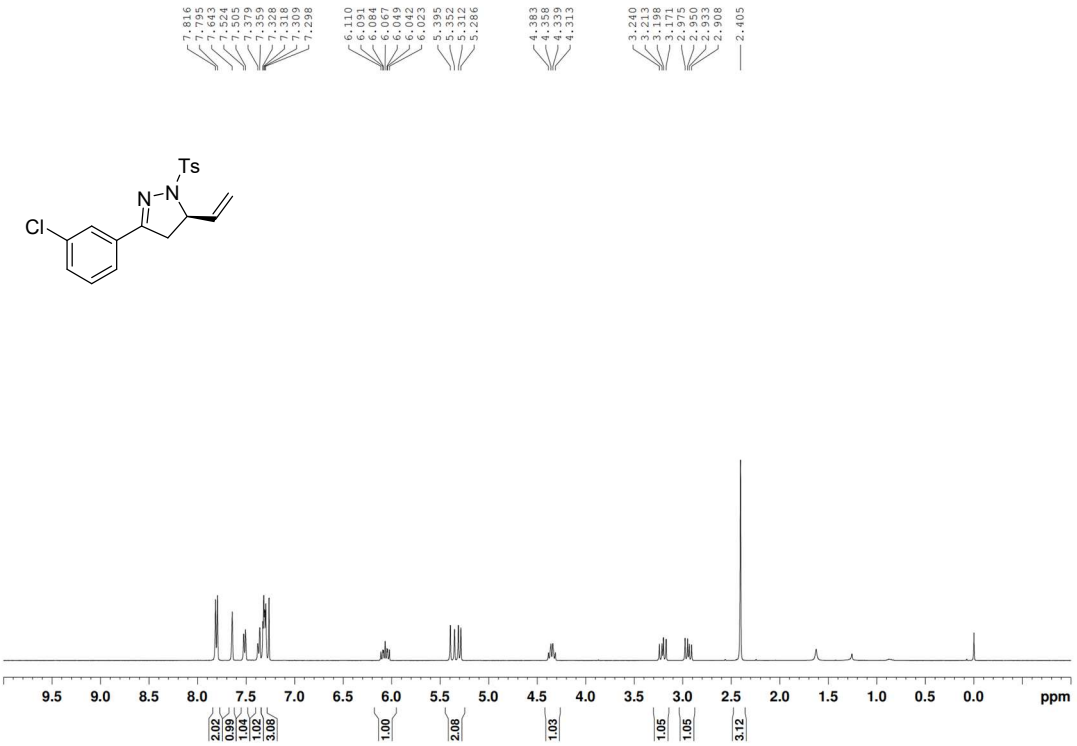
$^{1}$H NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz)



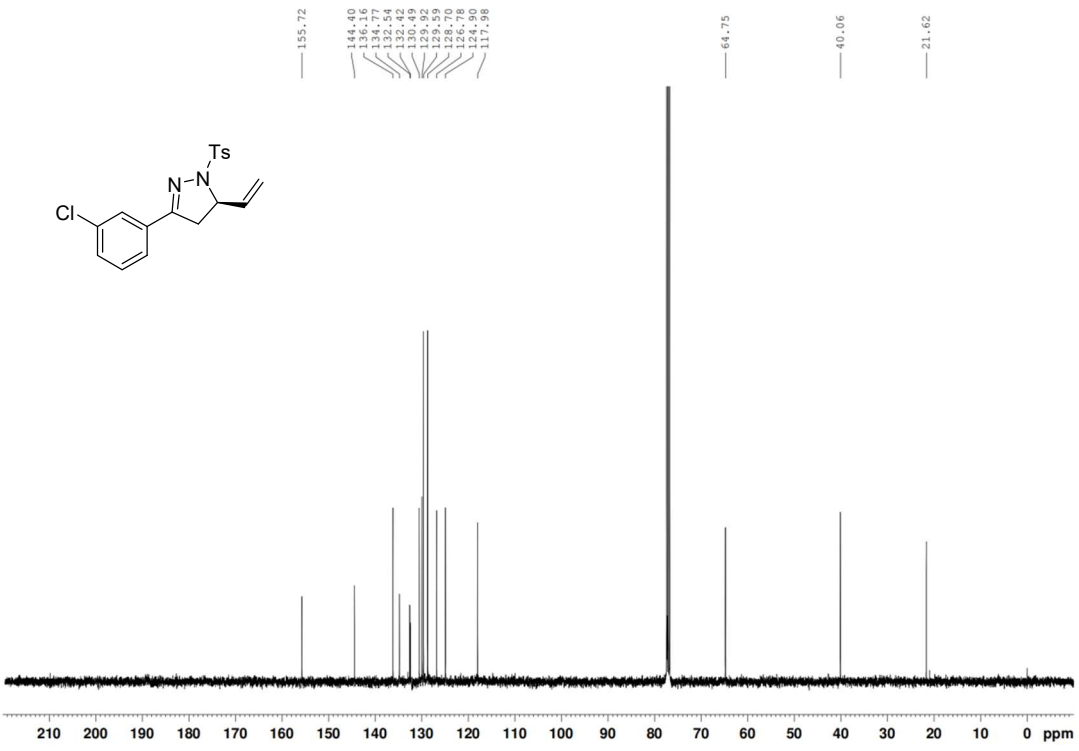

$^{13}$C NMR spectrum of compound **2i** ($CDCl_3$, 100 MHz)



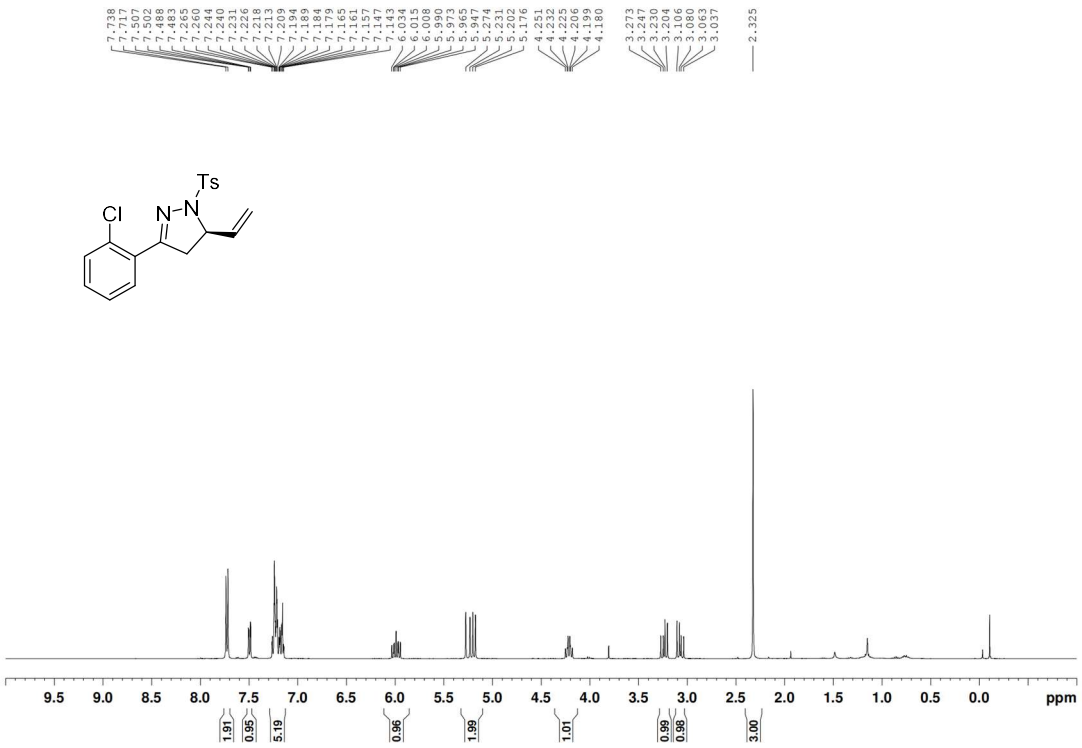
$^{1}$H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz)



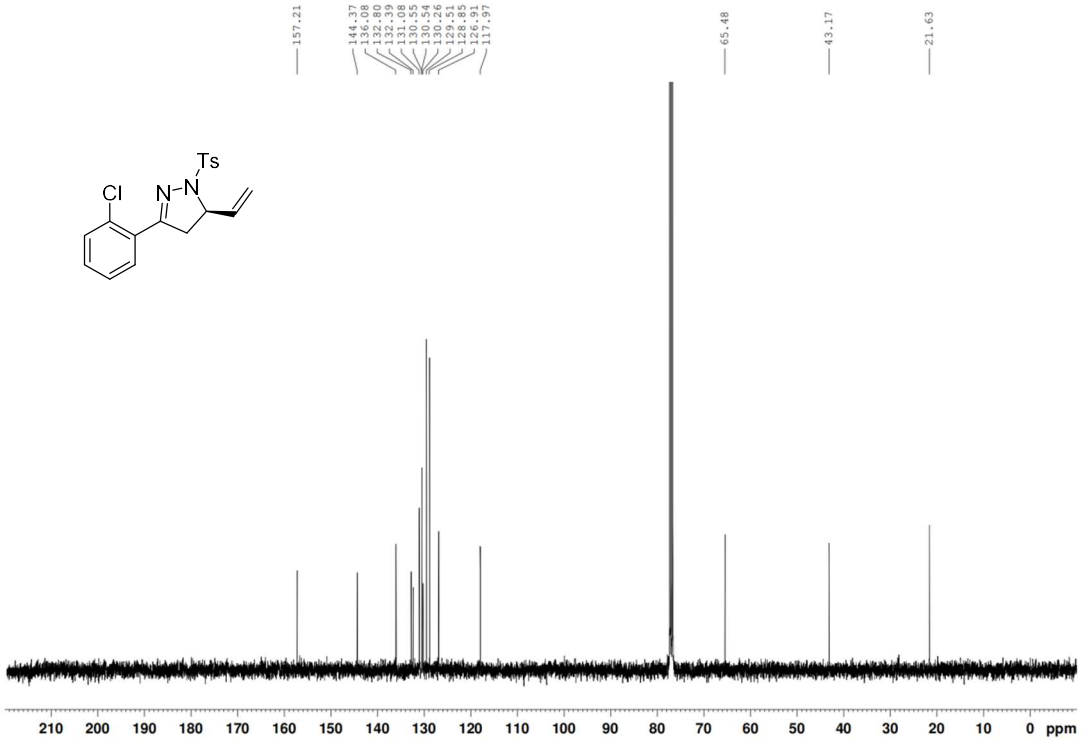

$^{13}$C NMR spectrum of compound **2j** ($CDCl_3$, 100 MHz)



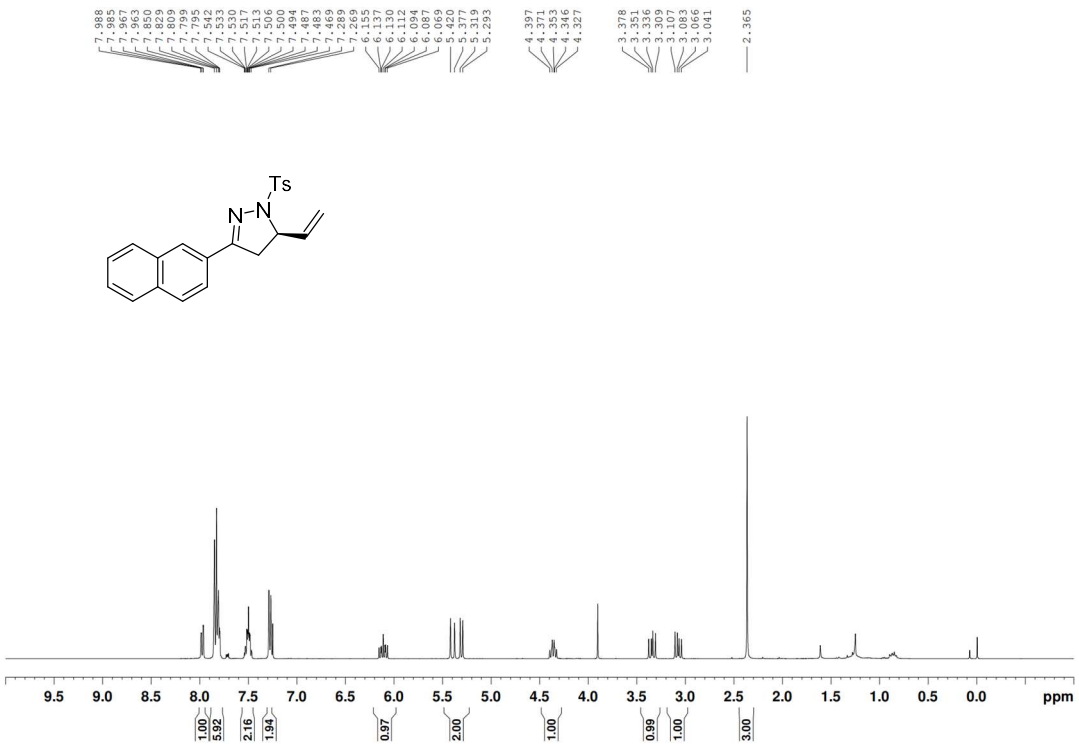
$^{1}$H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz)



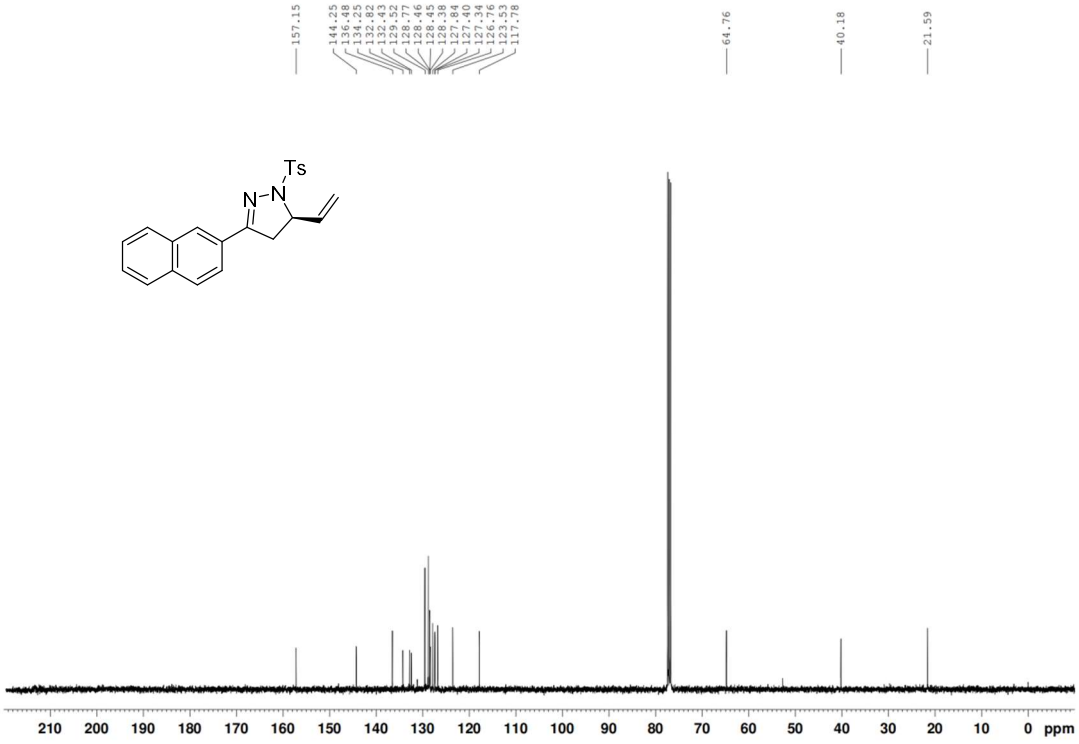

$^{13}$C NMR spectrum of compound **2k** ($CDCl_3$, 100 MHz)



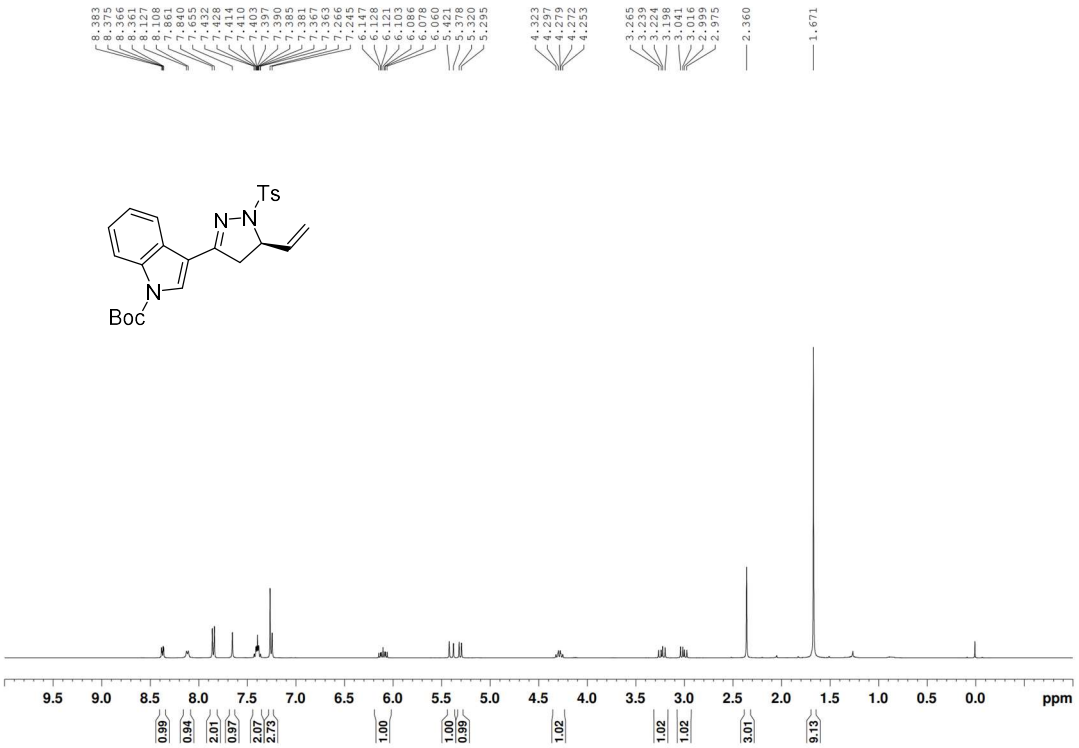
$^{1}$H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz)



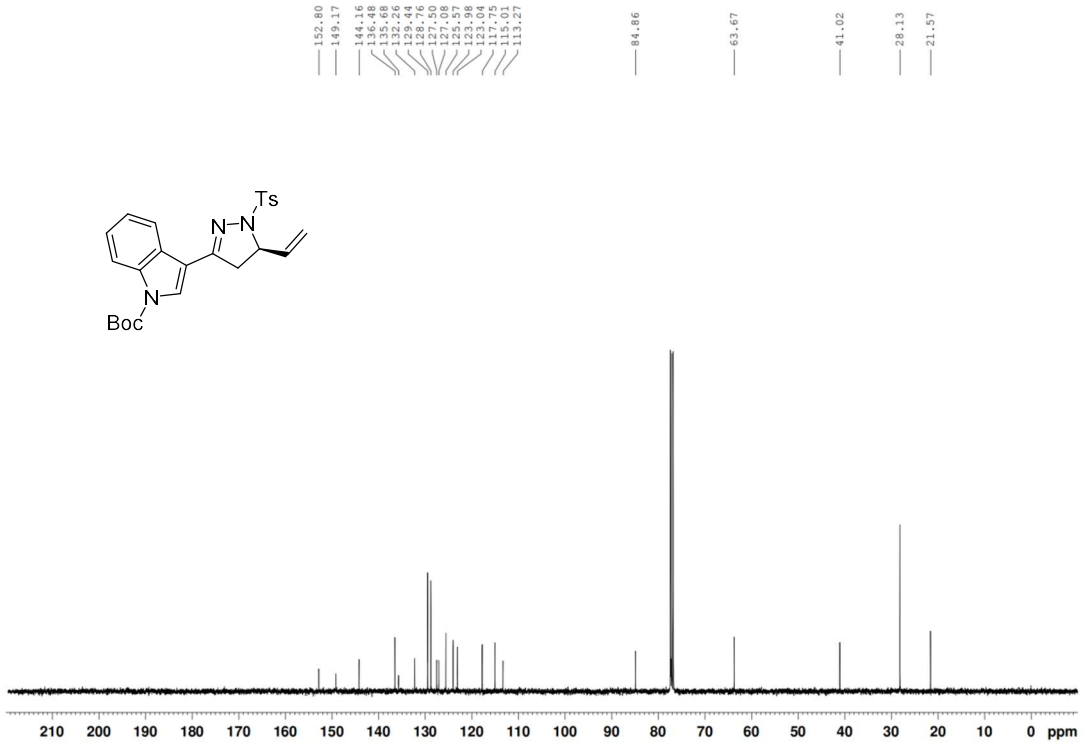

$^{13}$C NMR spectrum of compound **2l** ($CDCl_3$, 100 MHz)



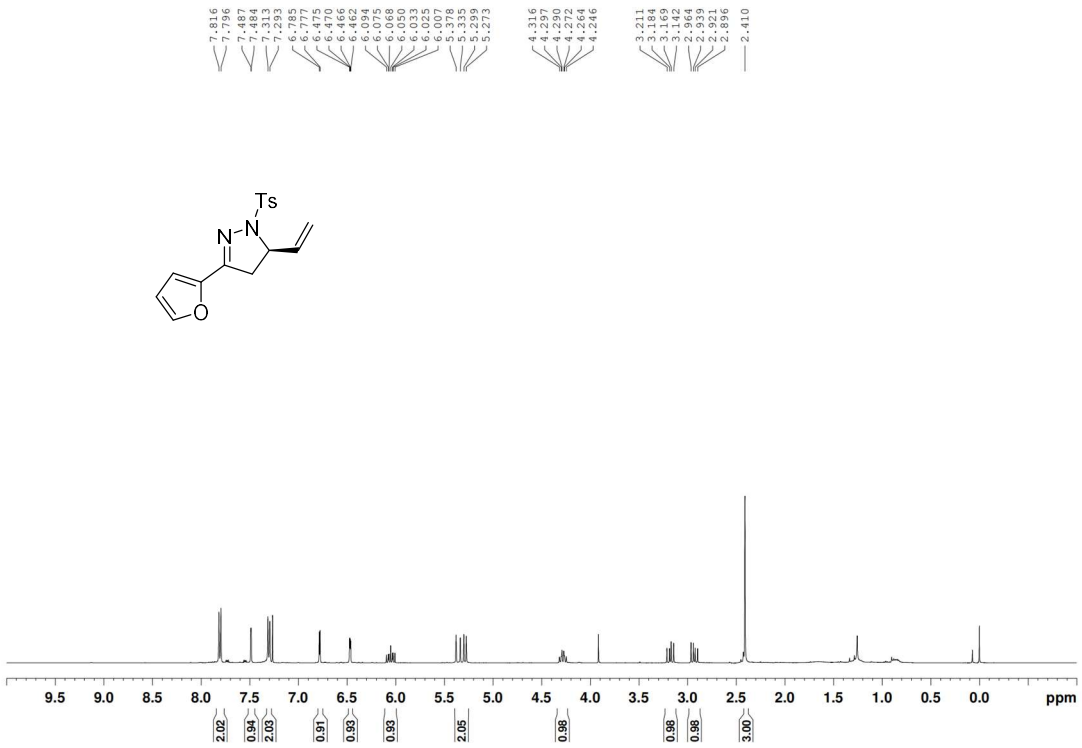
$^{1}$H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz)



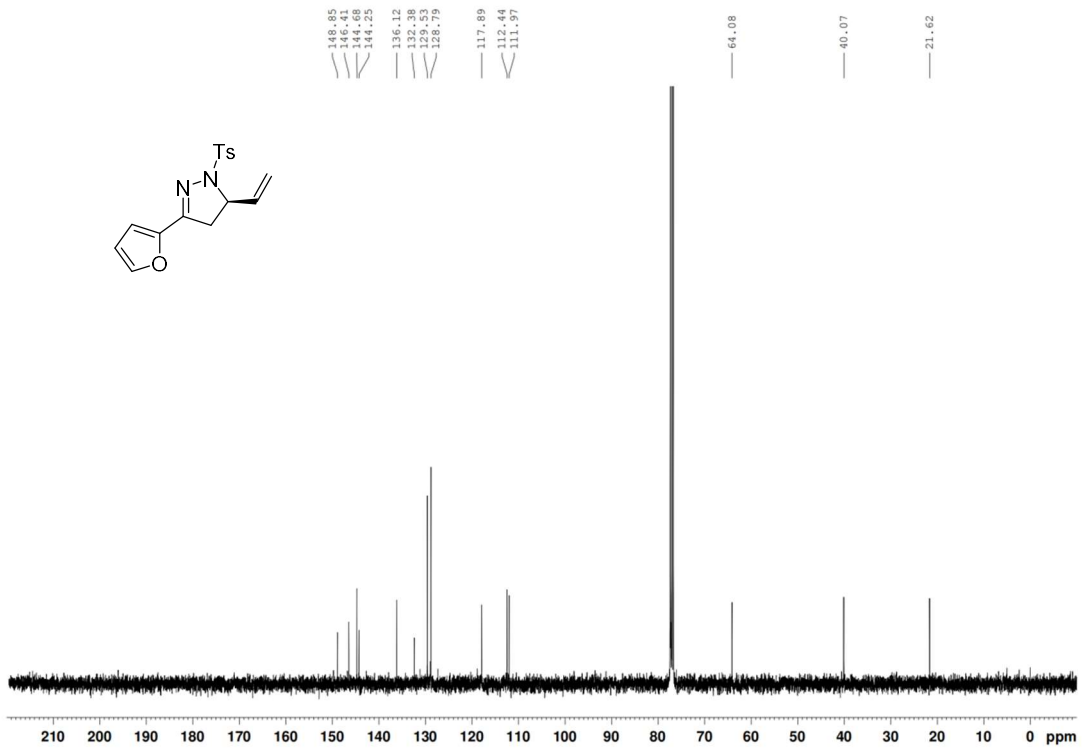

$^{13}$C NMR spectrum of compound **2m** ($CDCl_3$, 100 MHz)



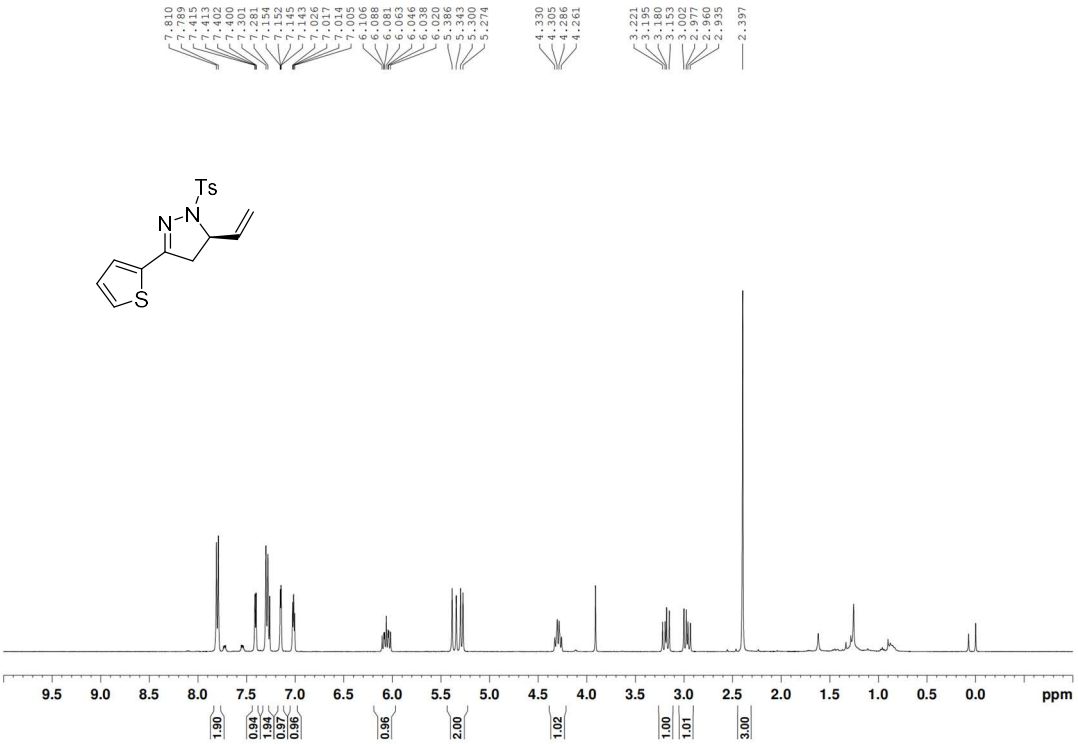
$^{1}$H NMR spectrum of compound **2n** ($CDCl_3$, 400 MHz)



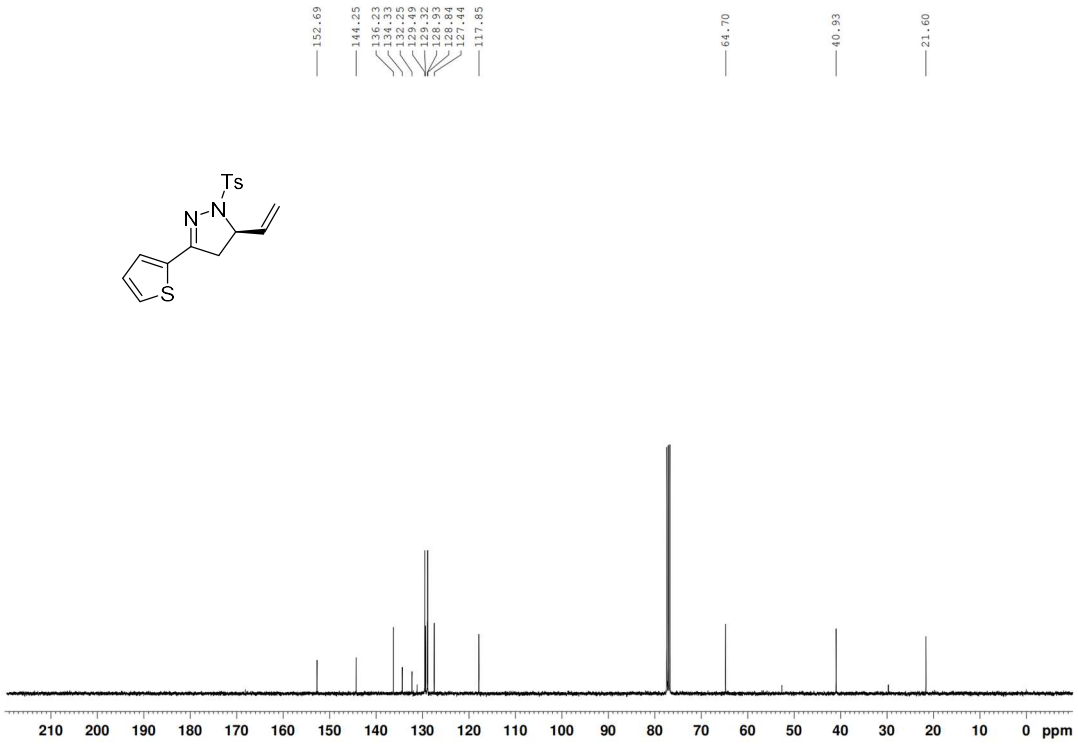

$^{13}$C NMR spectrum of compound **2n** ($CDCl_3$, 100 MHz)



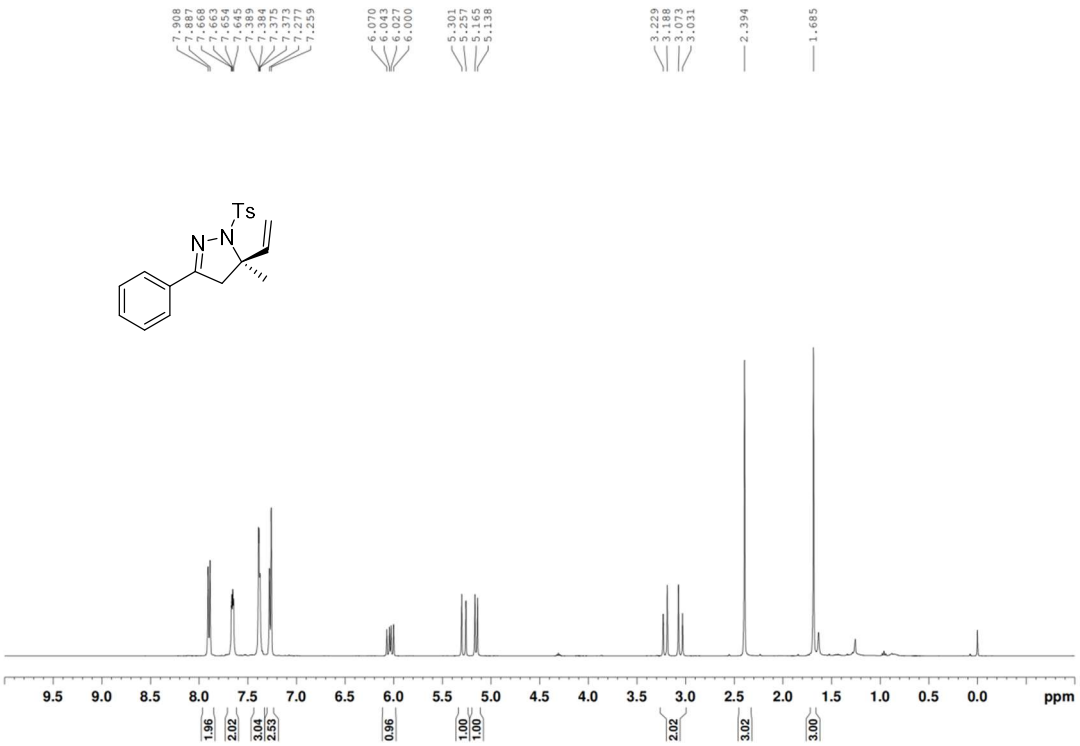
$^{1}$H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz)



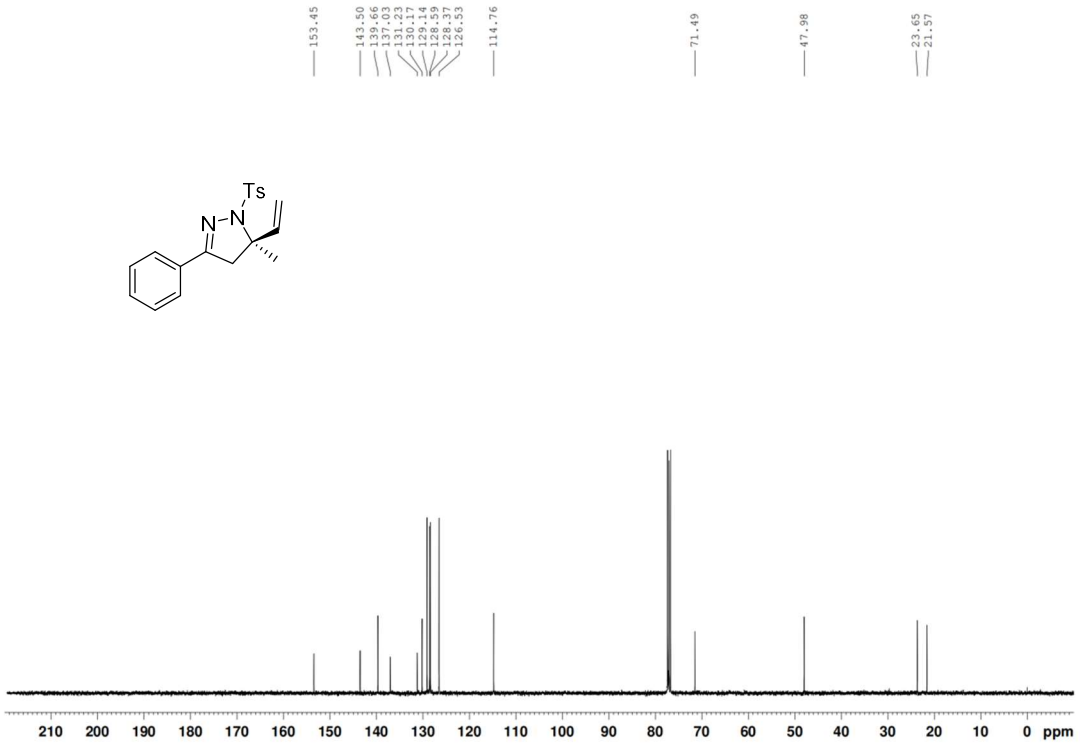

$^{13}$C NMR spectrum of compound **2o** ($CDCl_3$, 100 MHz)



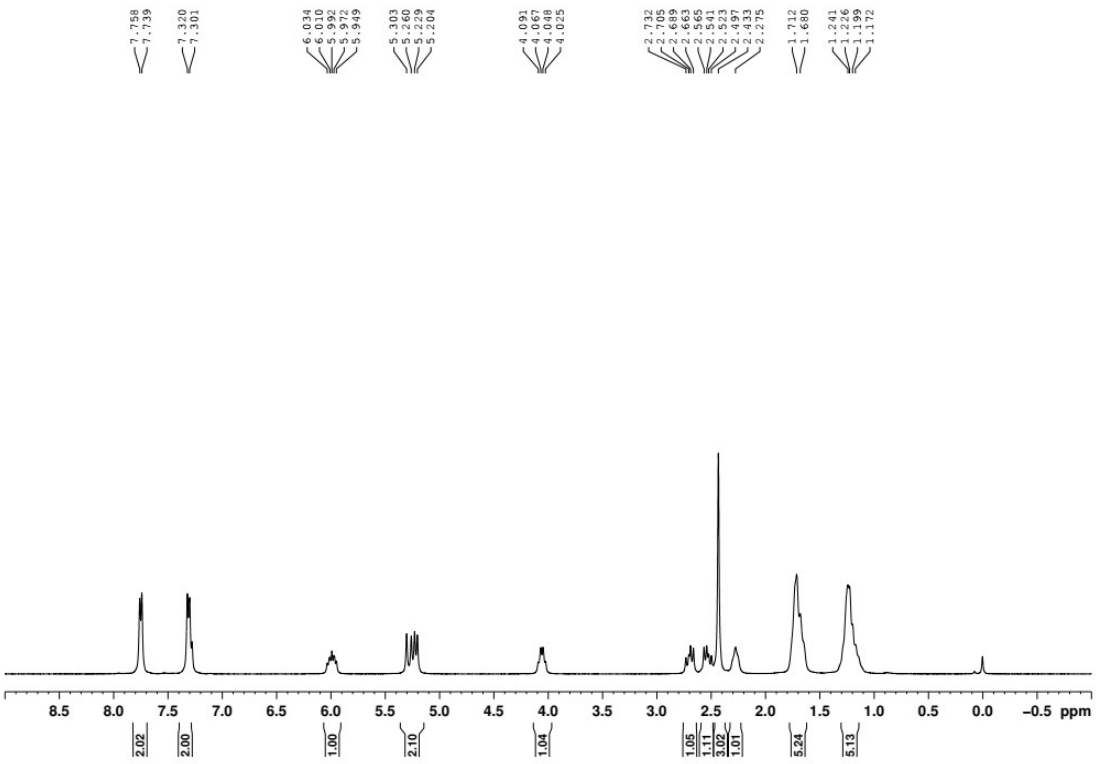
$^{1}$H NMR spectrum of compound **2p** ($CDCl_3$, 400 MHz)



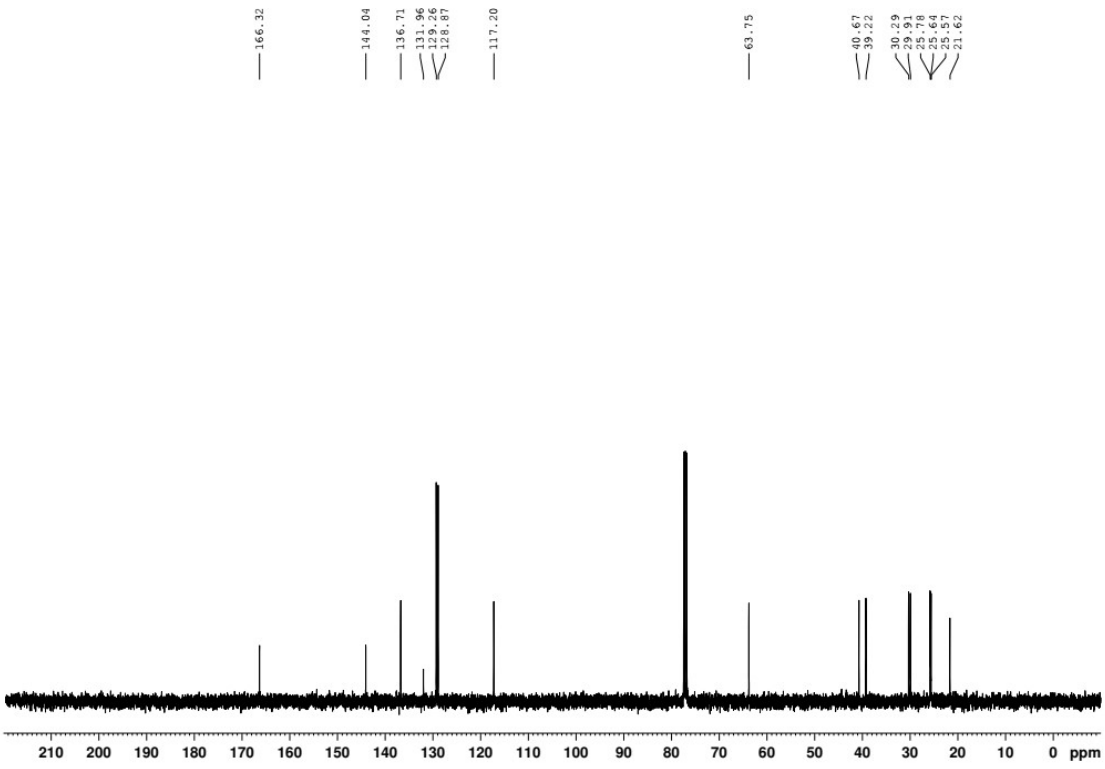

$^{13}$C NMR spectrum of compound **2p** ($CDCl_3$, 100 MHz)



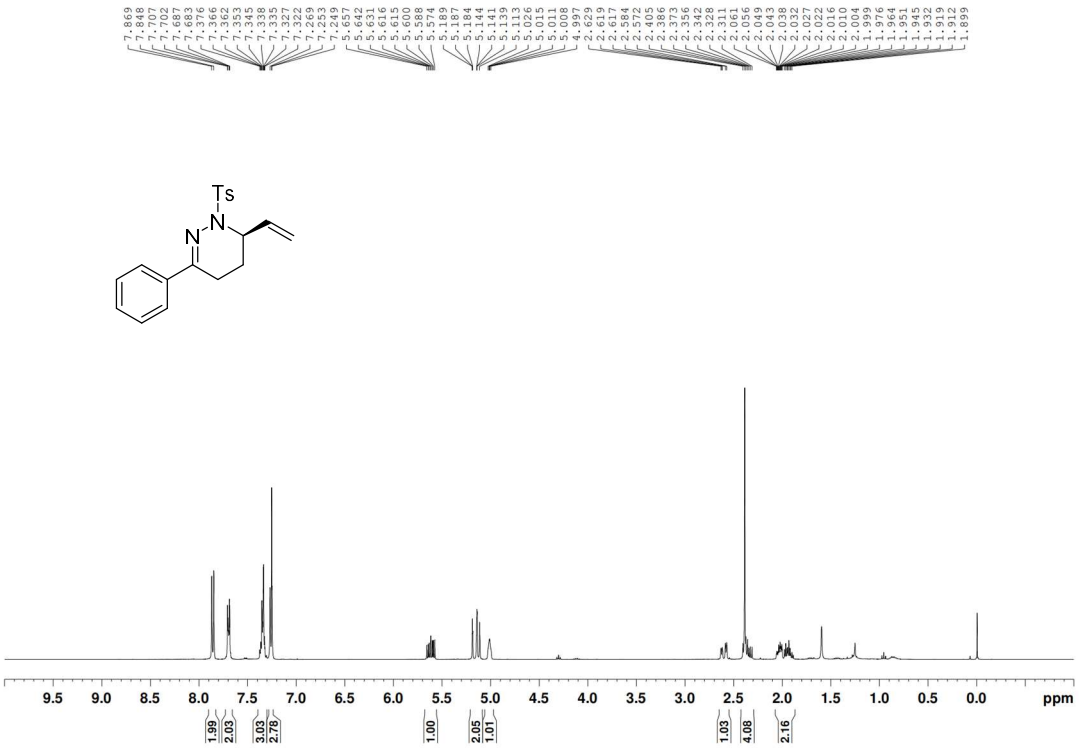
$^{1}$H NMR spectrum of compound **2q** ($CDCl_3$, 400 MHz)



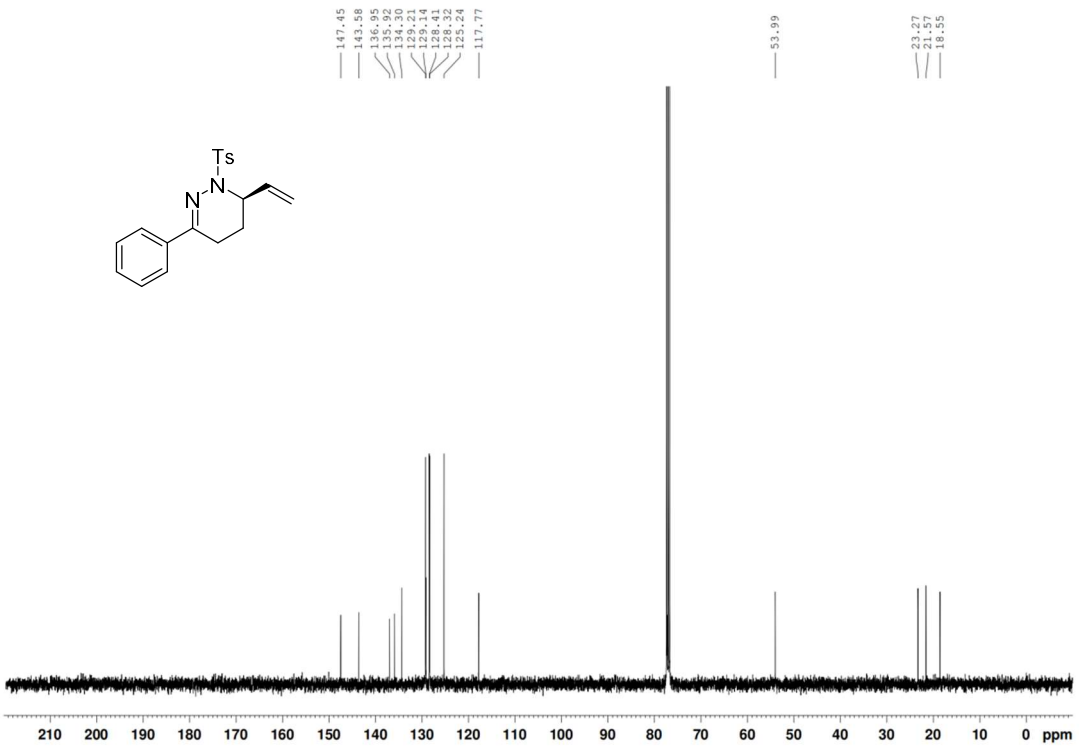

$^{13}$C NMR spectrum of compound **2q** ($CDCl_3$, 100 MHz)



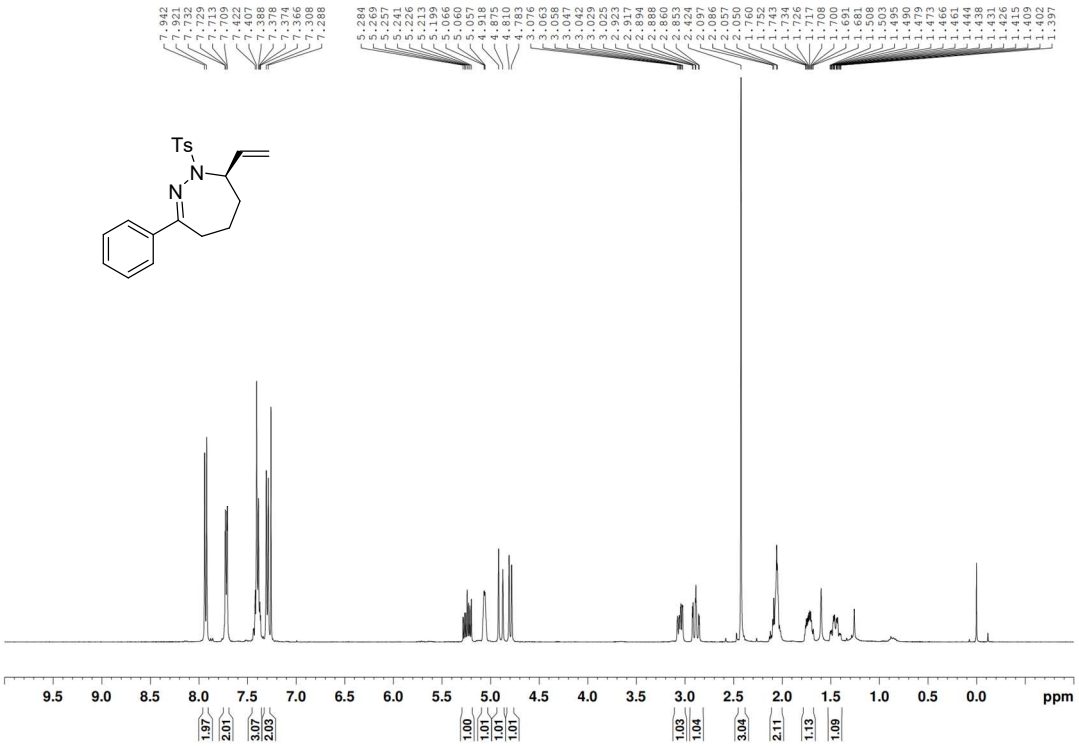
$^{1}$H NMR spectrum of compound **2r** ($CDCl_3$, 400 MHz)



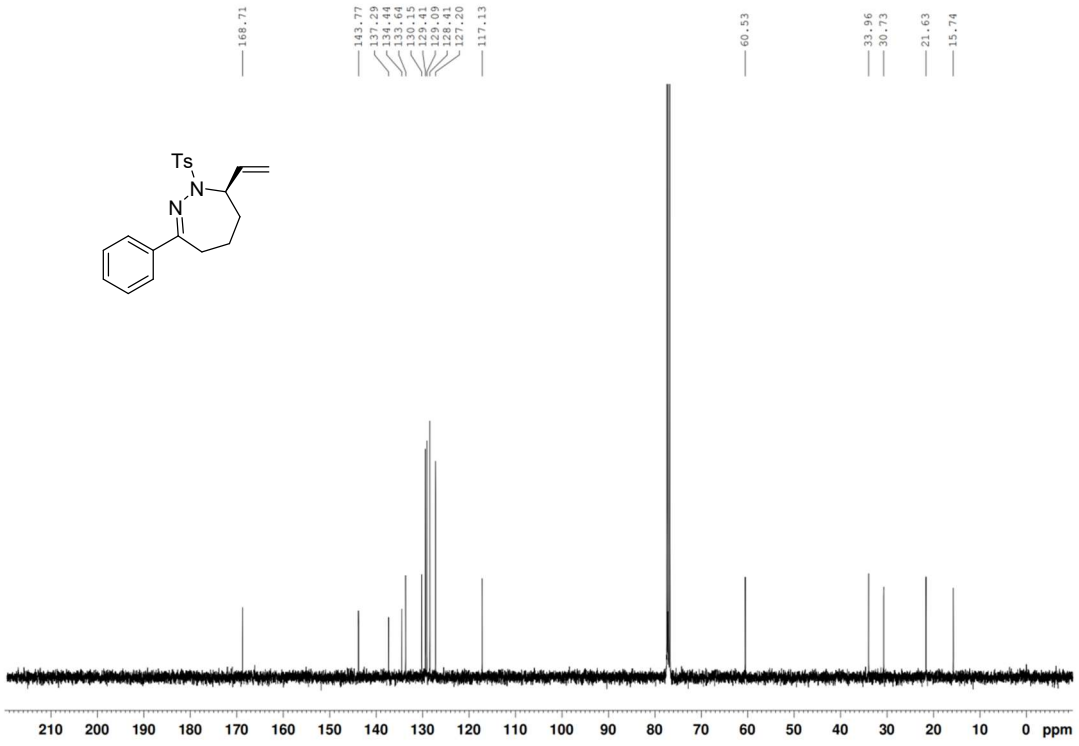

$^{13}$C NMR spectrum of compound **2r** ($CDCl_3$, 100 MHz)



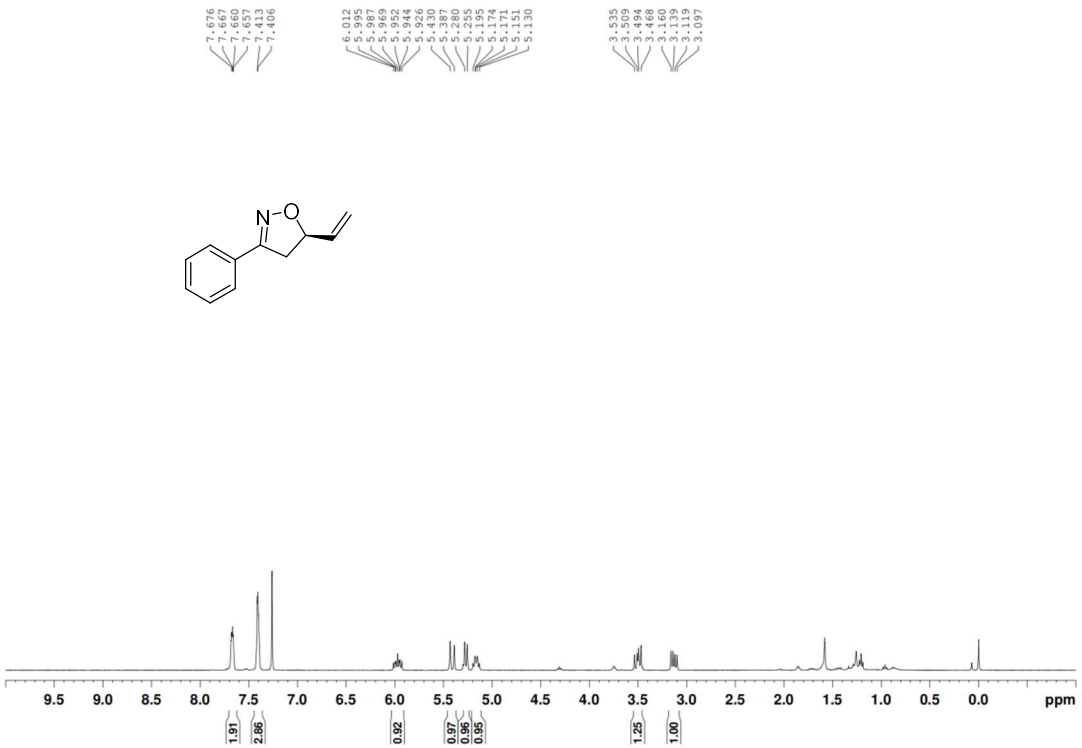
$^{1}$H NMR spectrum of compound **2s** ($CDCl_3$, 400 MHz)



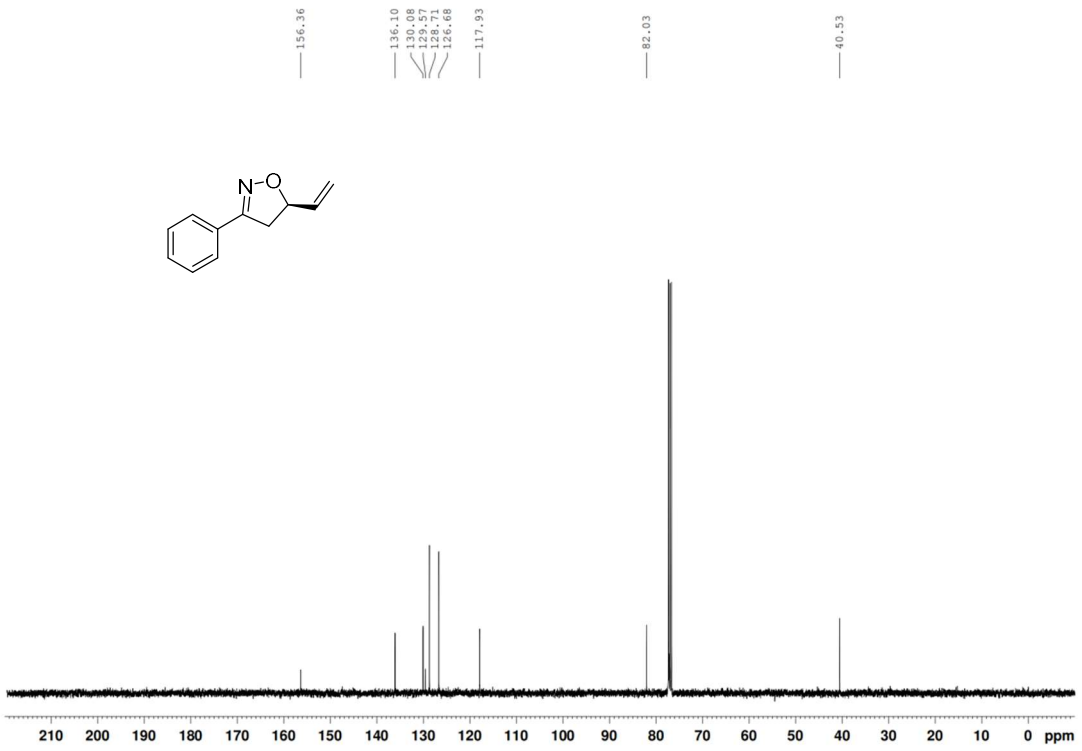

$^{13}$C NMR spectrum of compound **2s** ($CDCl_3$, 100 MHz)



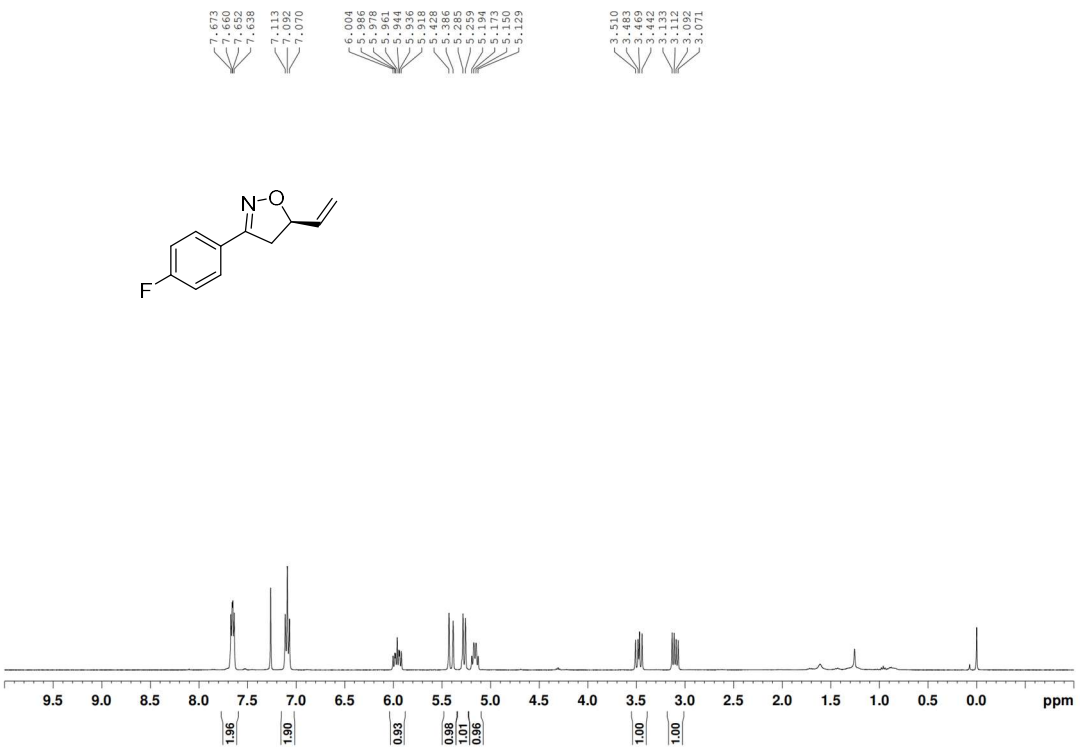
$^{1}$H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



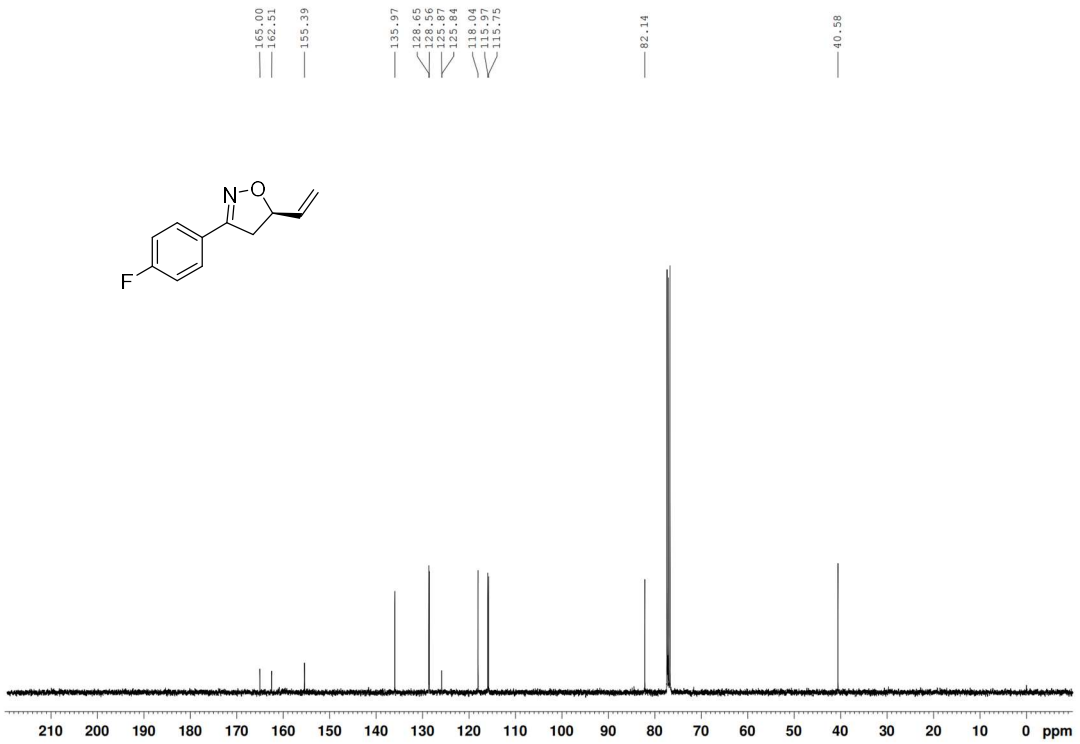

$^{13}$C NMR spectrum of compound **4a** ($CDCl_3$, 100 MHz)



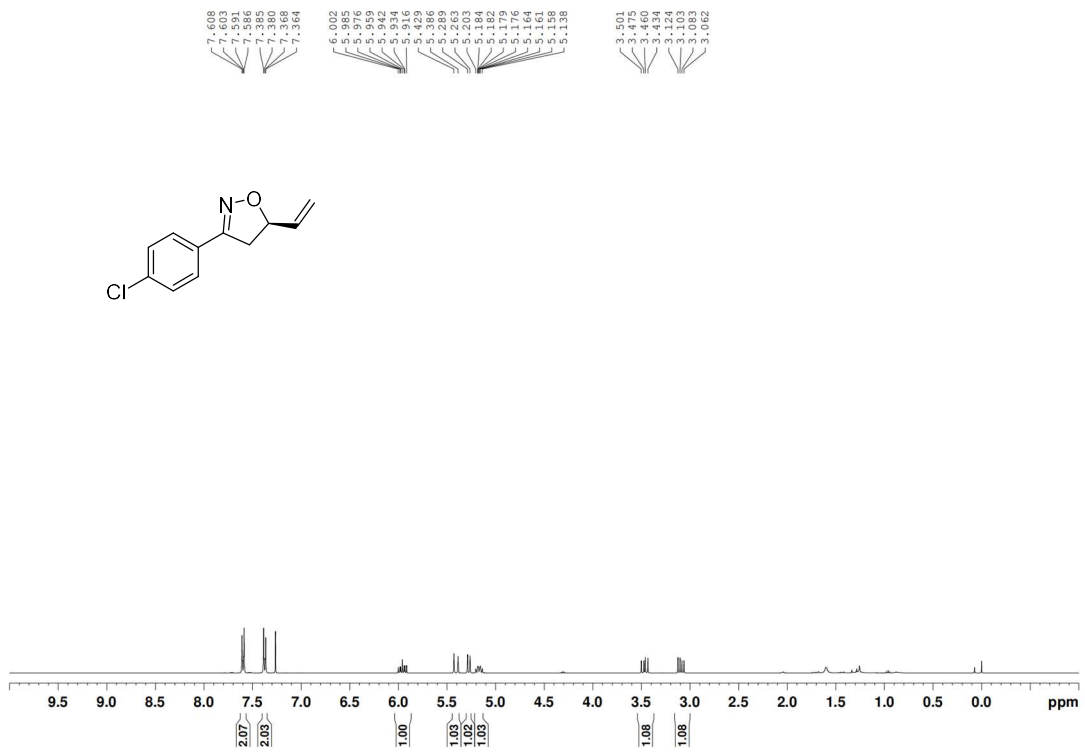
$^{1}$H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



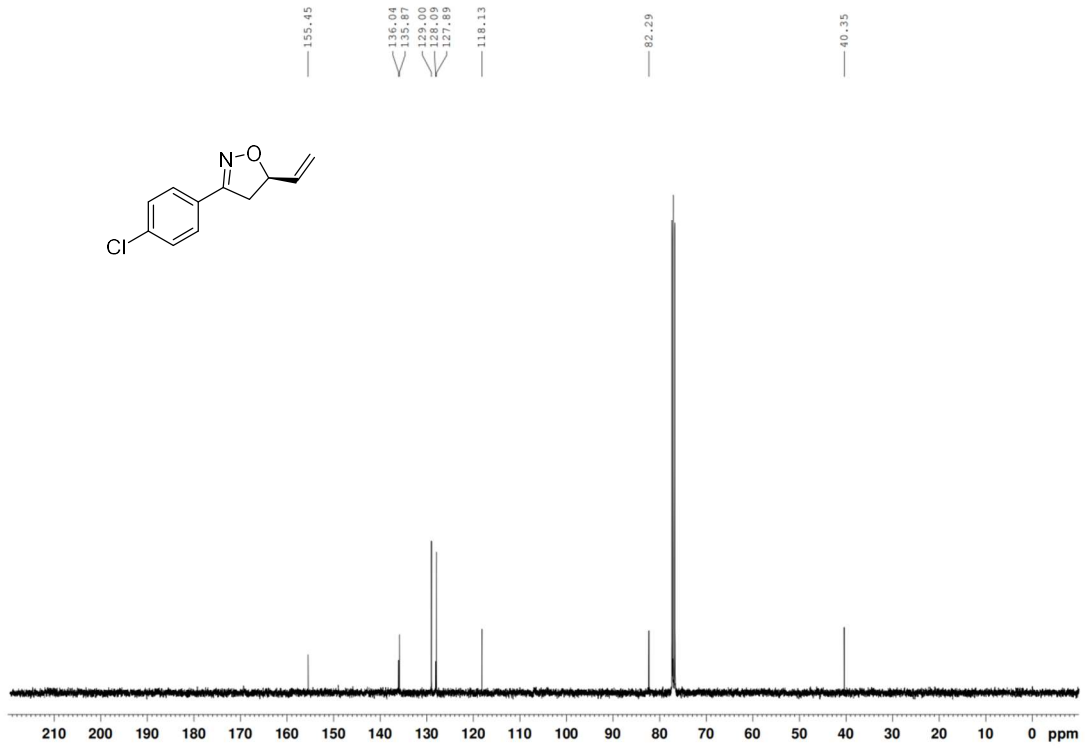

$^{13}$C NMR spectrum of compound **4b** ($CDCl_3$, 100 MHz)



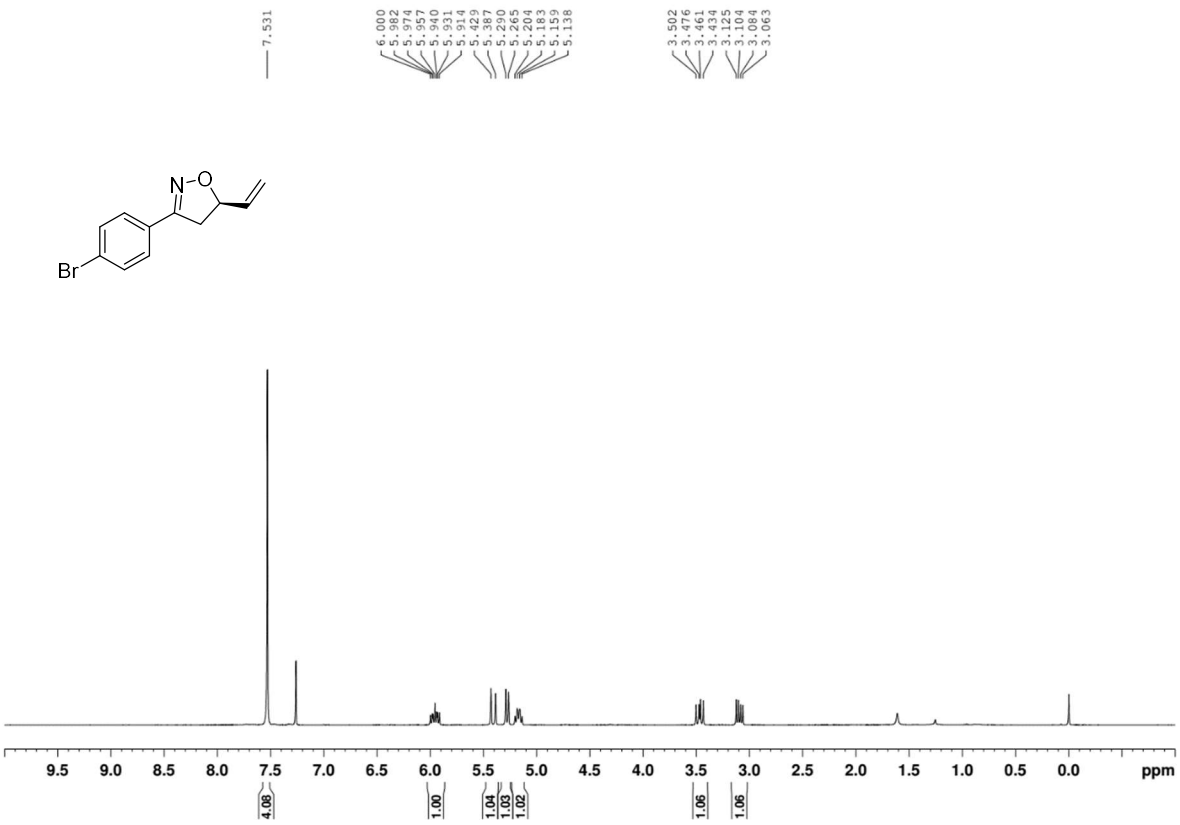
$^{1}$H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



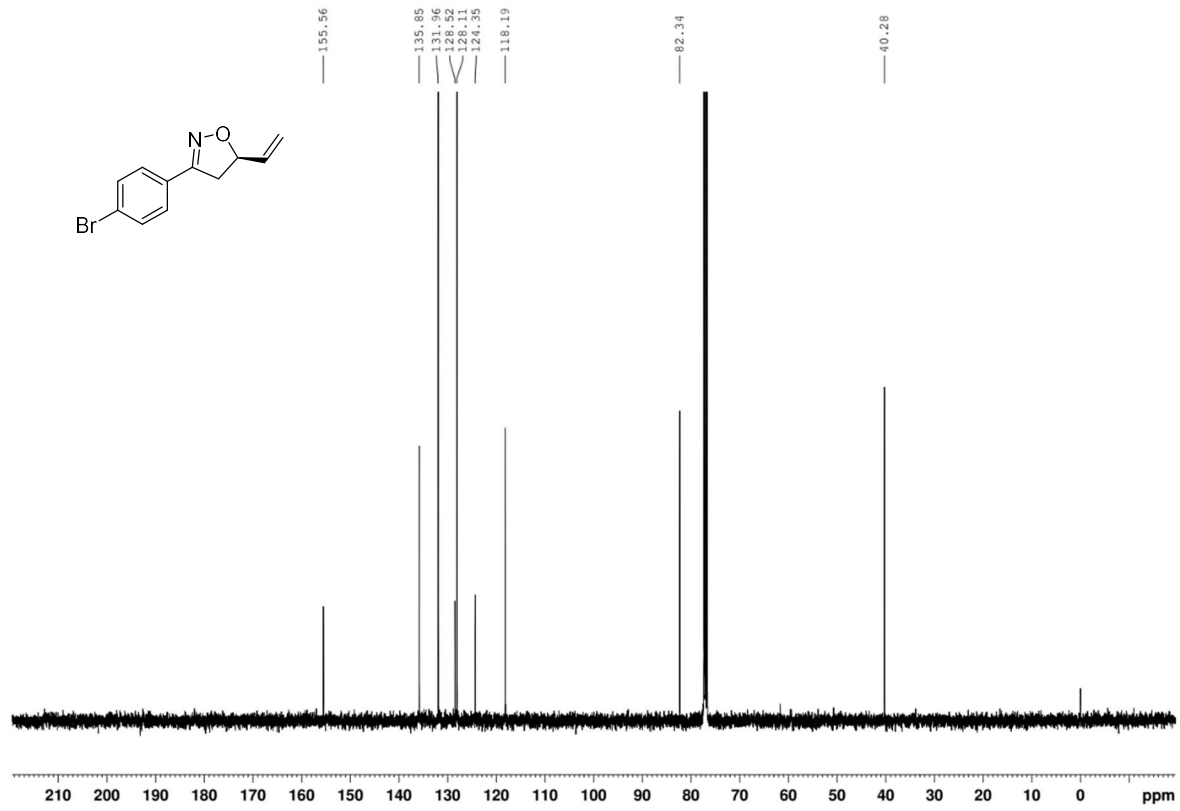

$^{13}$C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)



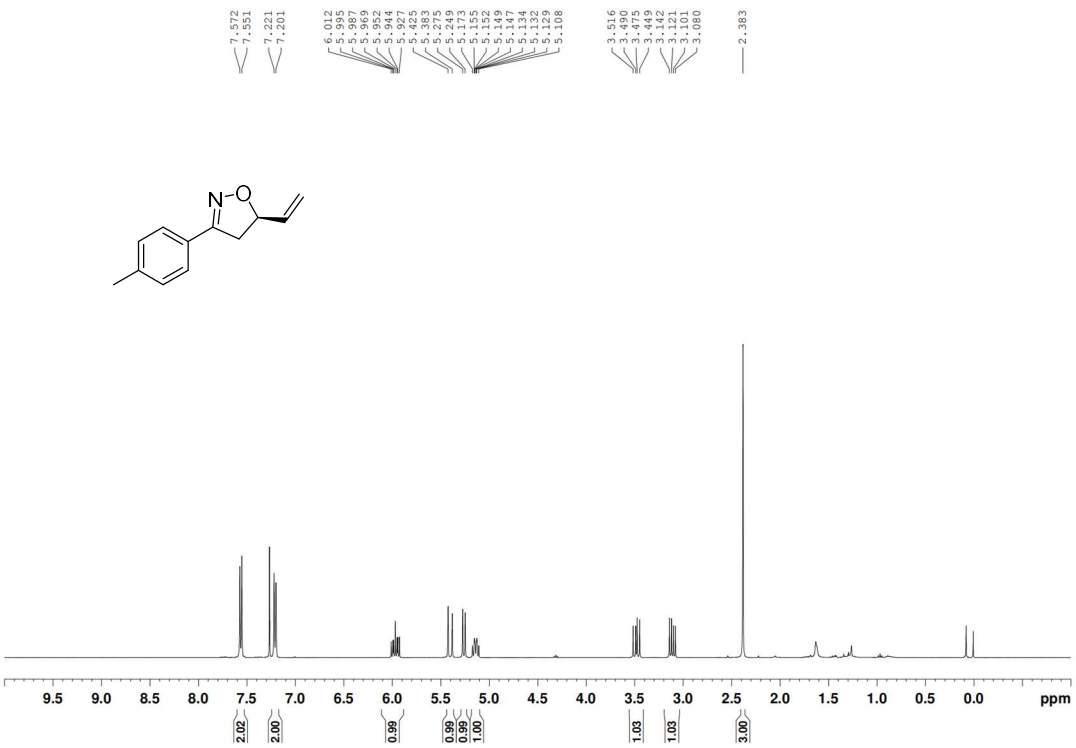
$^{1}$H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



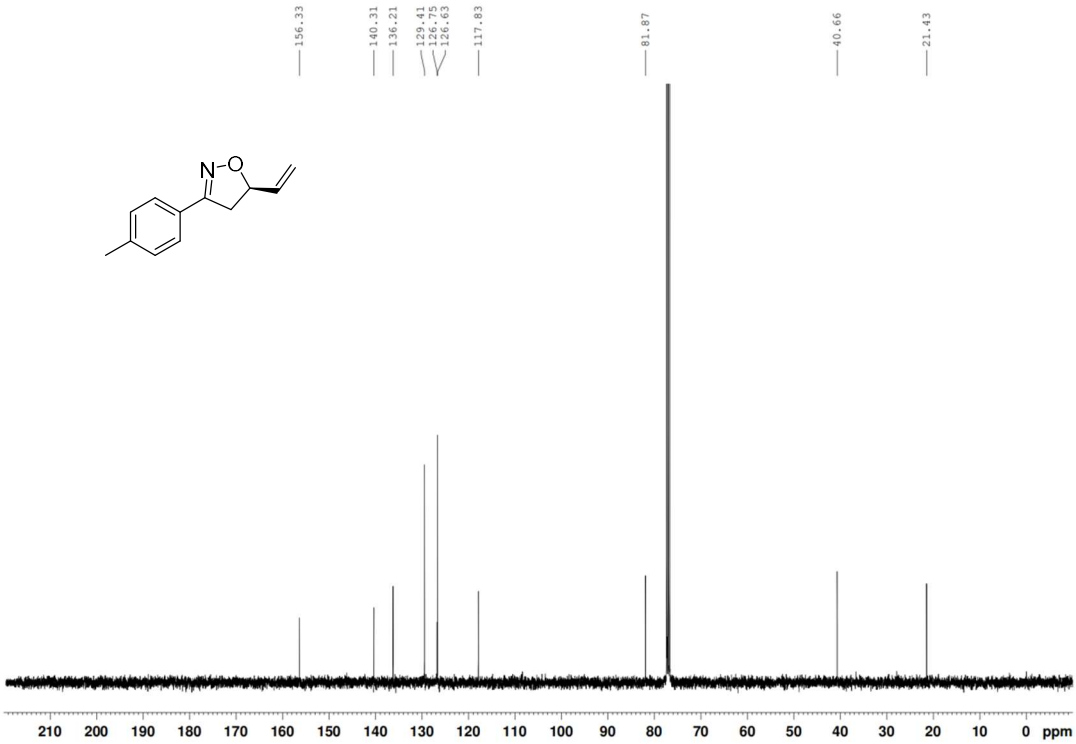

$^{13}$C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)



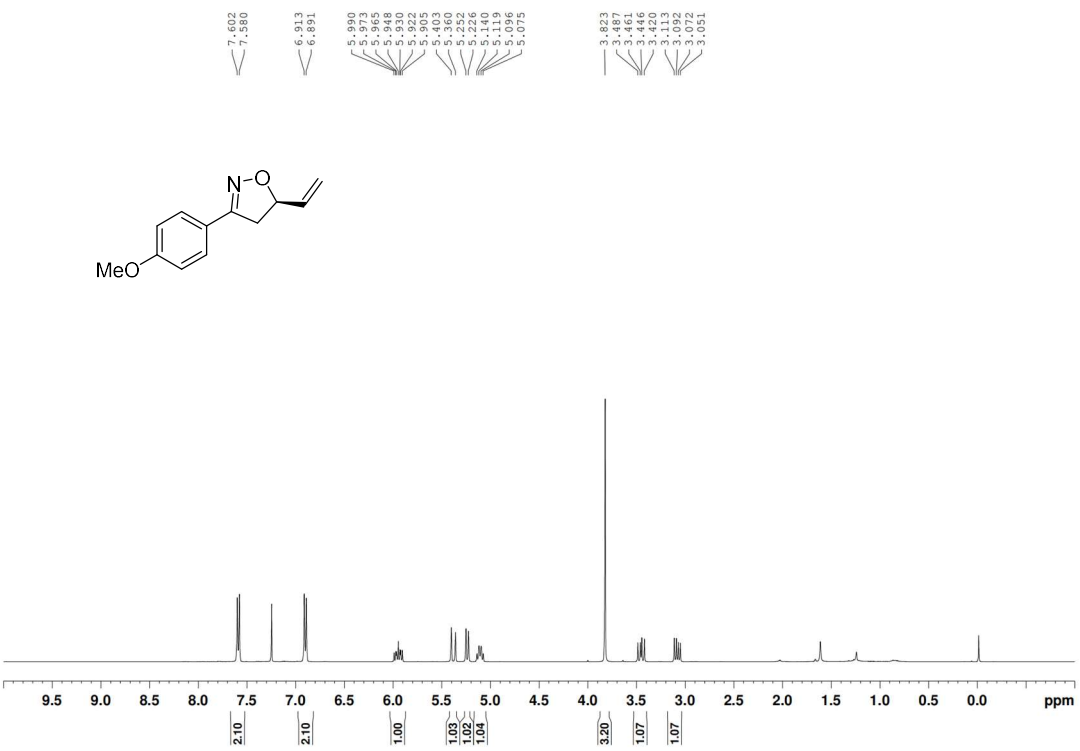
$^{1}$H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



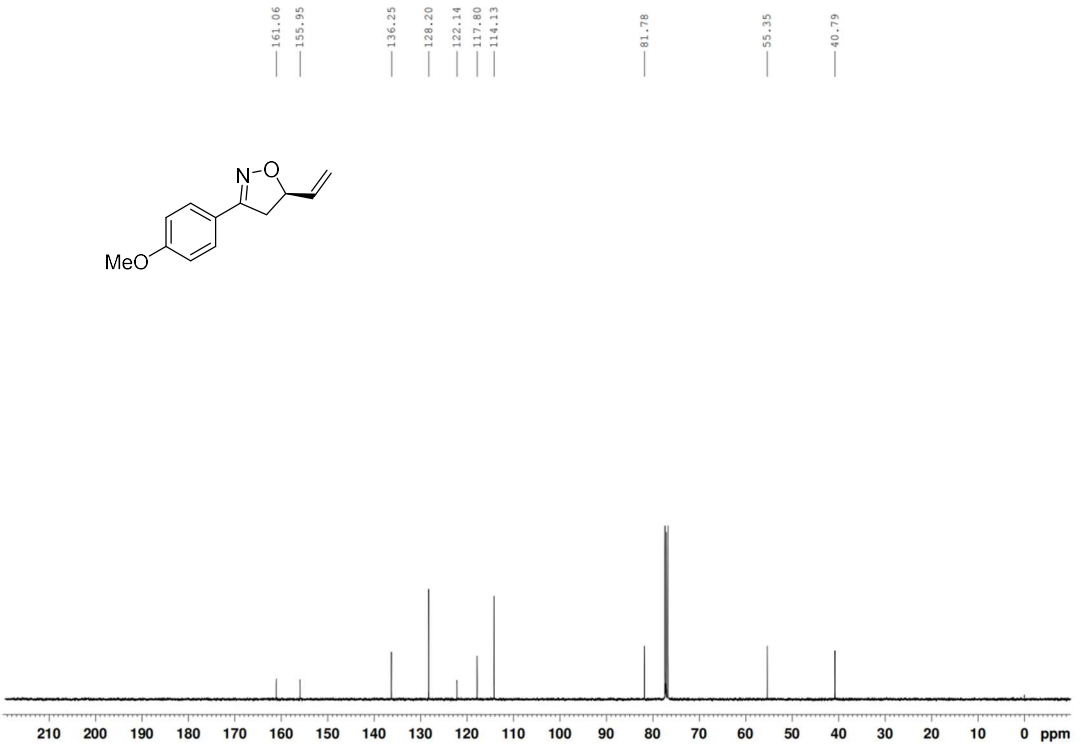

$^{13}$C NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)



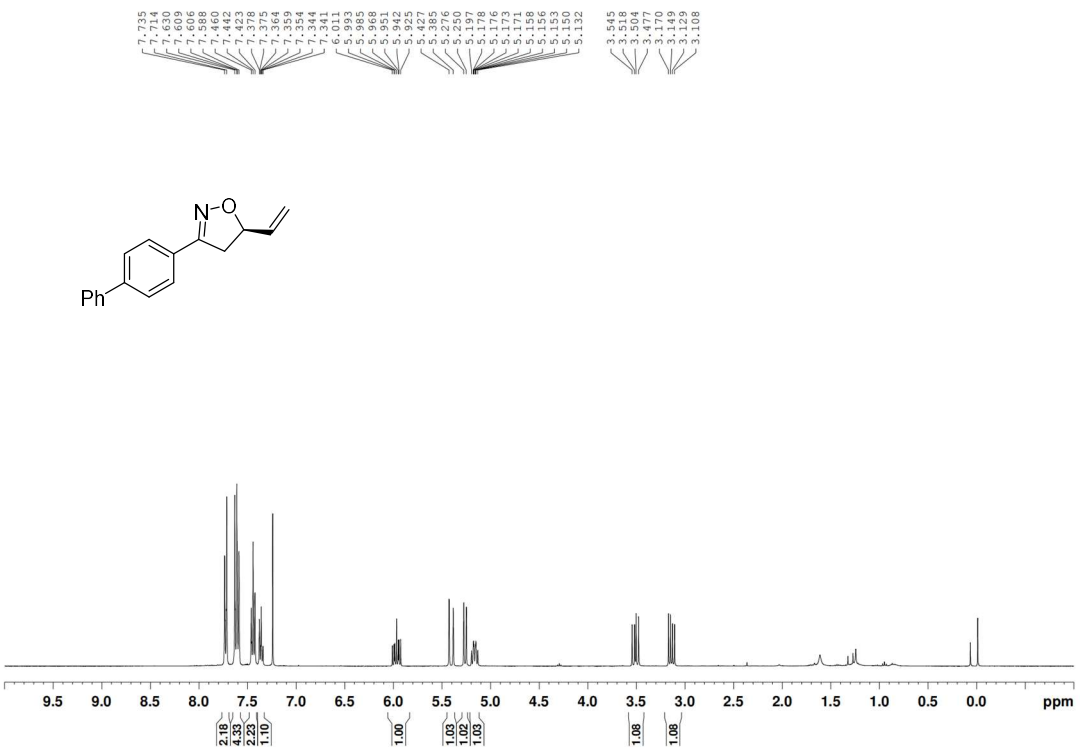
$^{1}$H NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



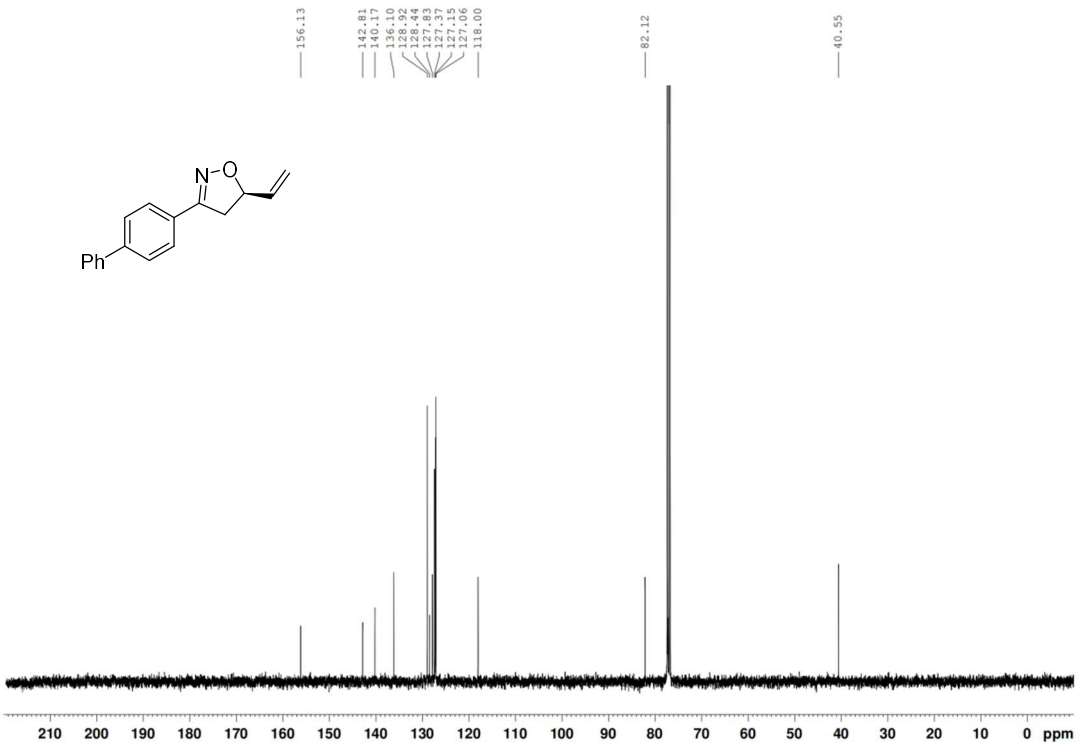

$^{13}$C NMR spectrum of compound **4f** ($CDCl_3$, 100 MHz)



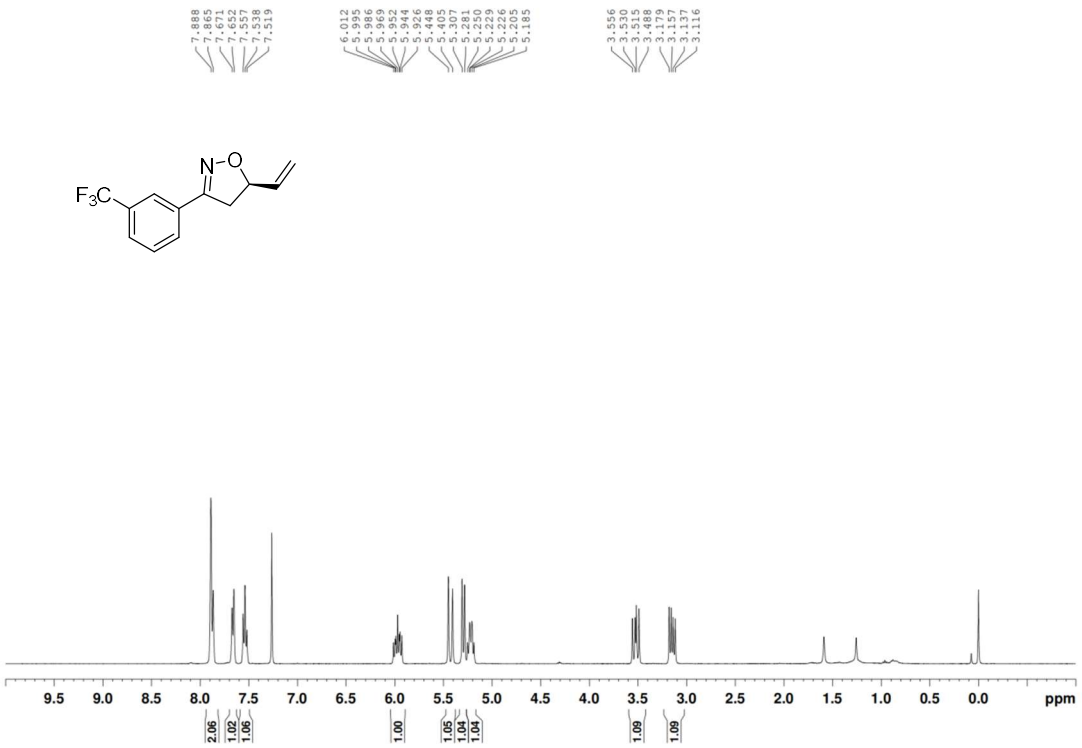
$^{1}$H NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



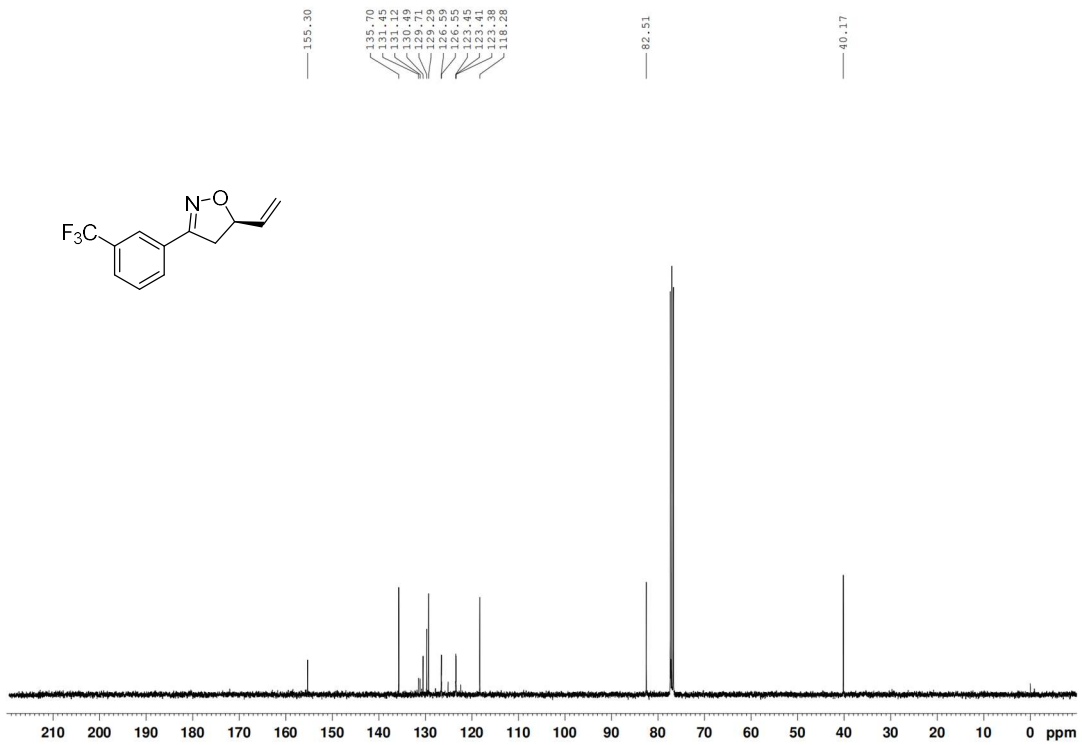

$^{13}$C NMR spectrum of compound **4g** ($CDCl_3$, 100 MHz)



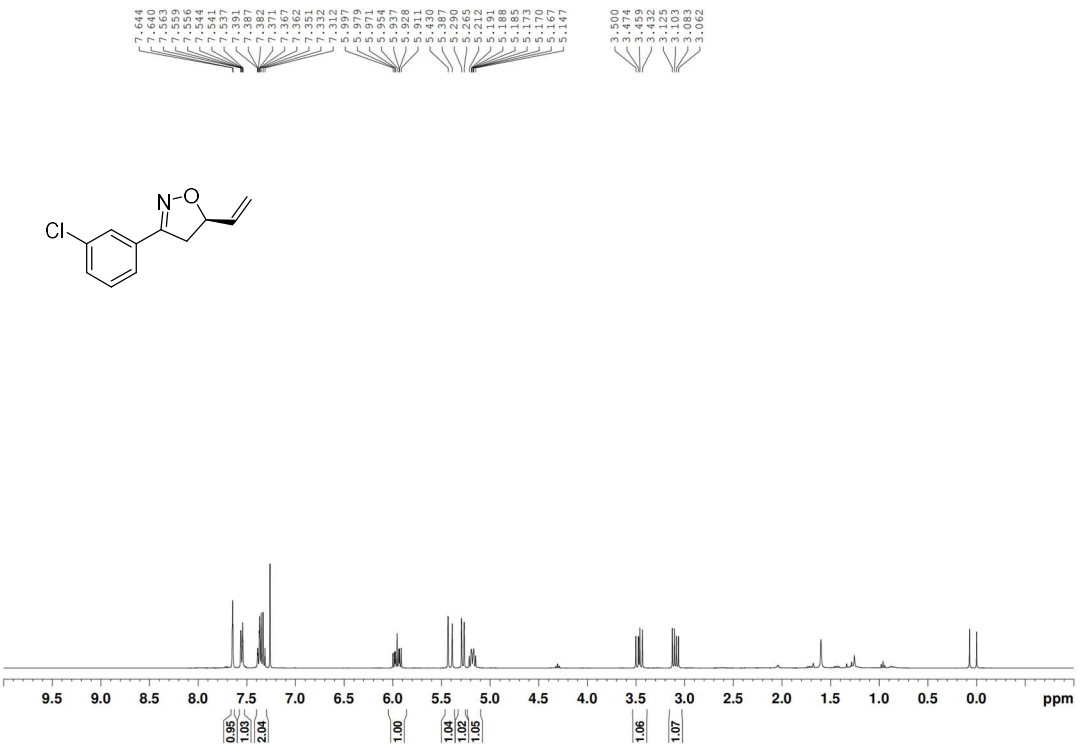
$^{1}$H NMR spectrum of compound **4h** ($CDCl_3$, 400 MHz)



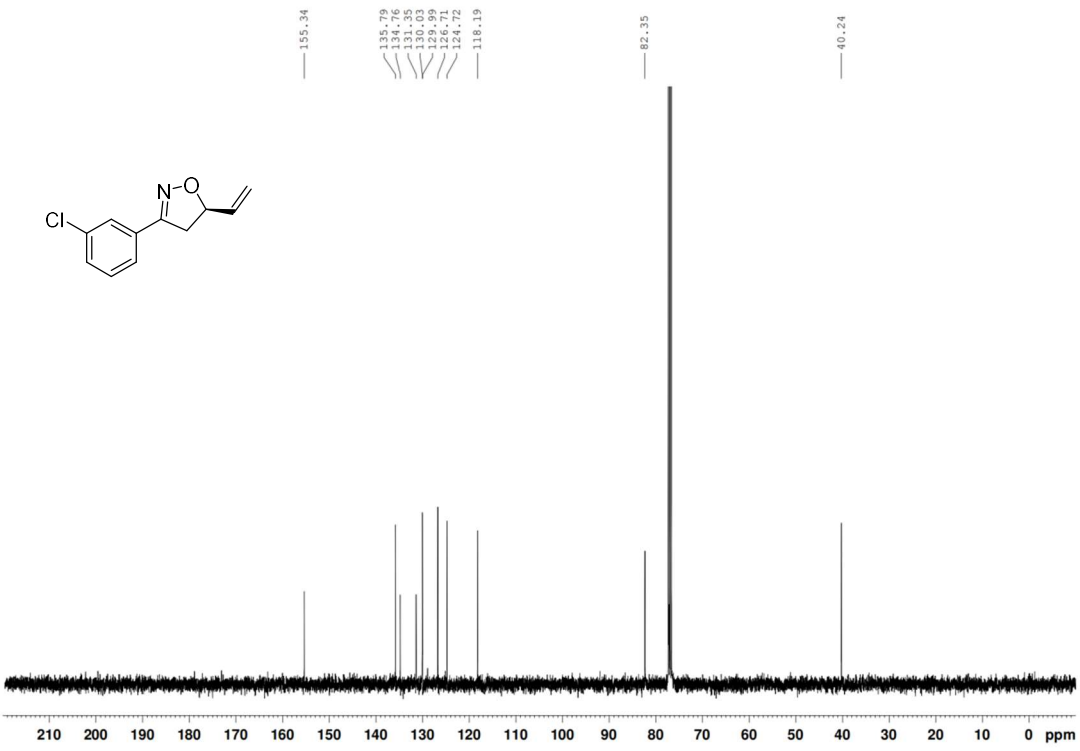

$^{13}$C NMR spectrum of compound **4h** ($CDCl_3$, 100 MHz)



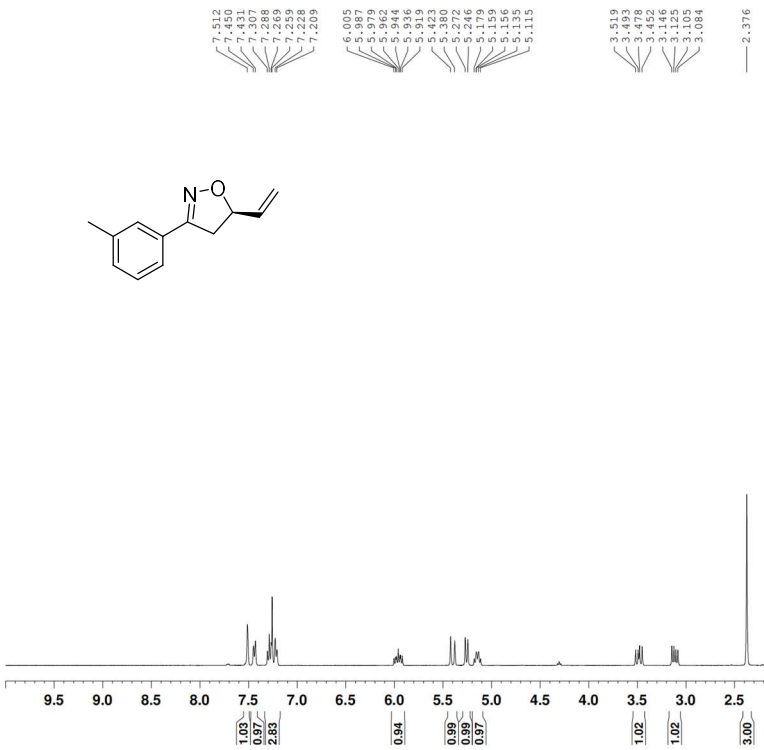
$^{1}$H NMR spectrum of compound **4i** ($CDCl_3$, 400 MHz)



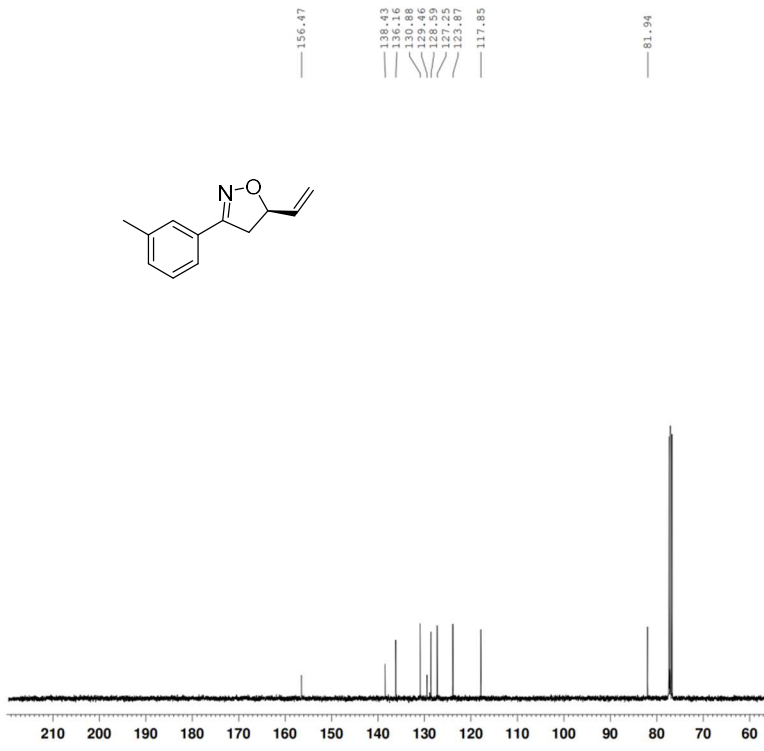

$^{13}$C NMR spectrum of compound **4i** ($CDCl_3$, 100 MHz)



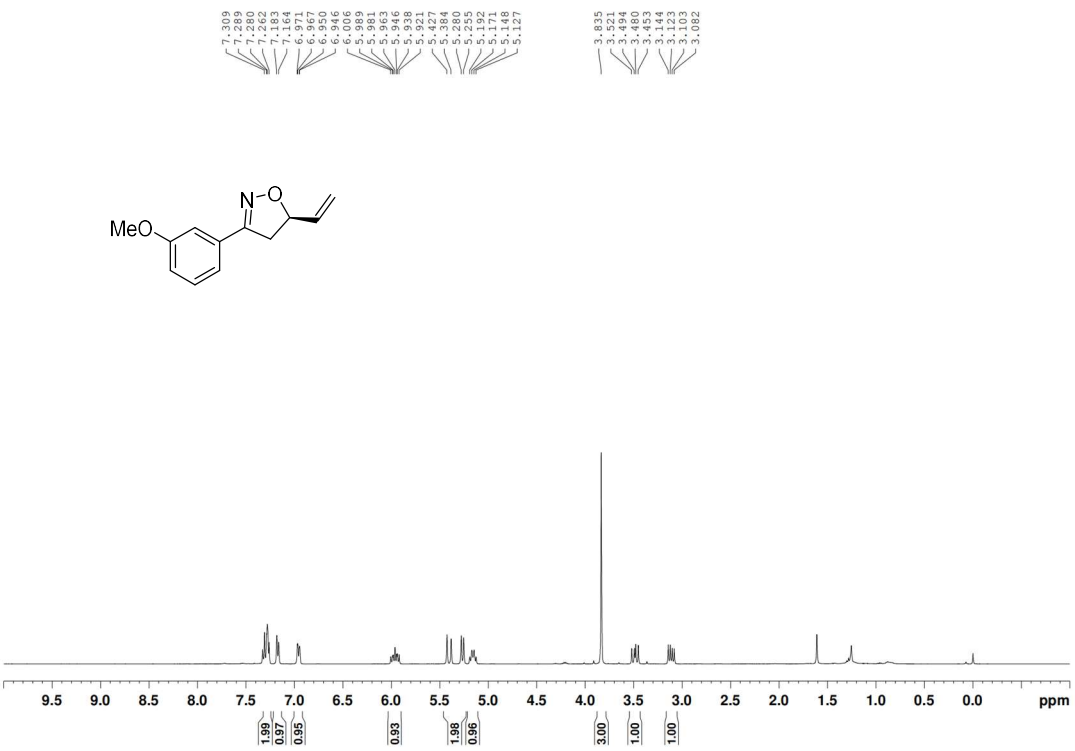
$^{1}$H NMR spectrum of compound **4j** ($CDCl_3$, 400 MHz)



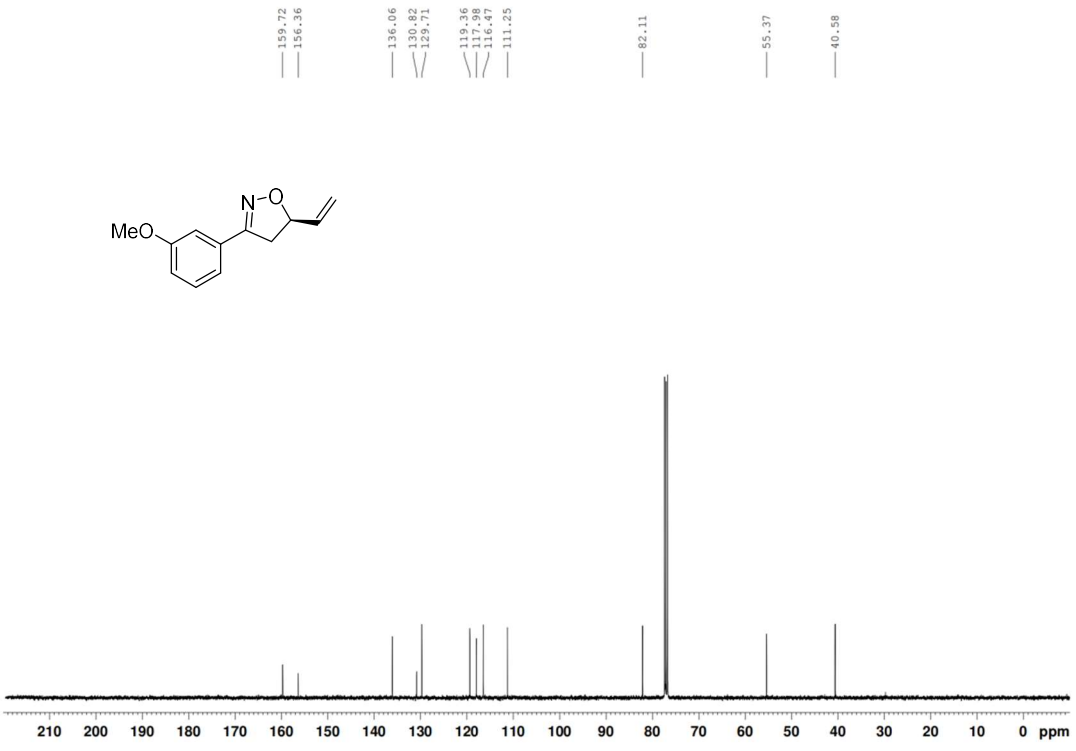

$^{13}$C NMR spectrum of compound **4j** ($CDCl_3$, 100 MHz)



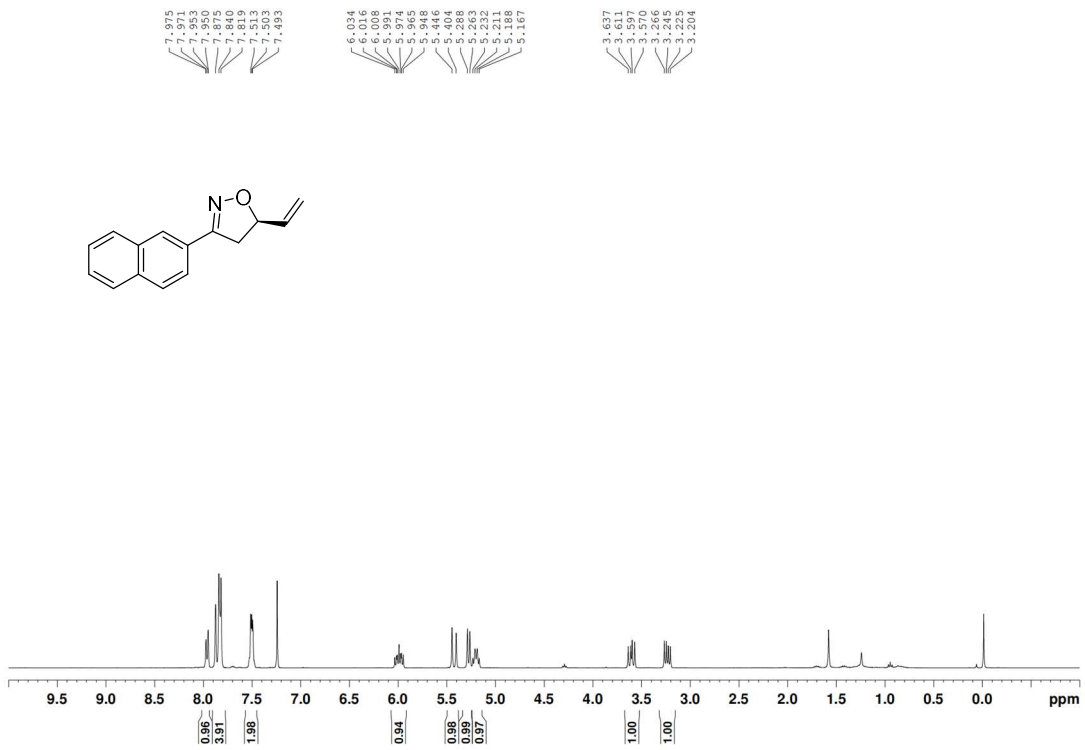
$^{1}$H NMR spectrum of compound **4k** ($CDCl_3$, 400 MHz)



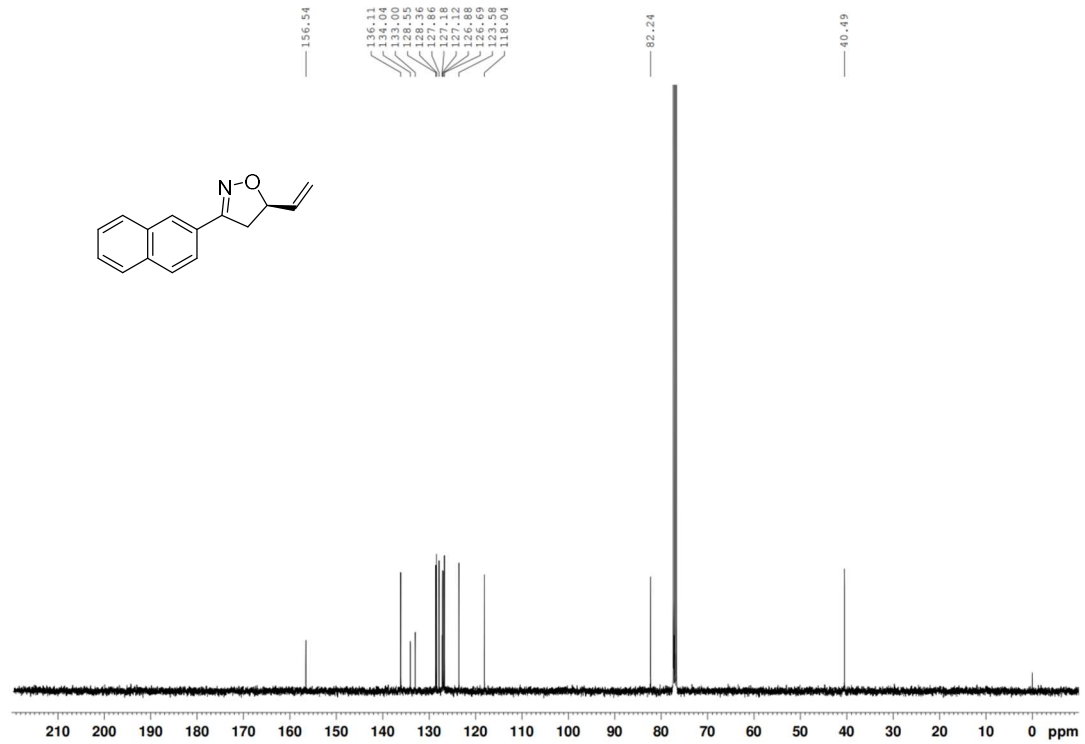

$^{13}$C NMR spectrum of compound **4k** ($CDCl_3$, 100 MHz)



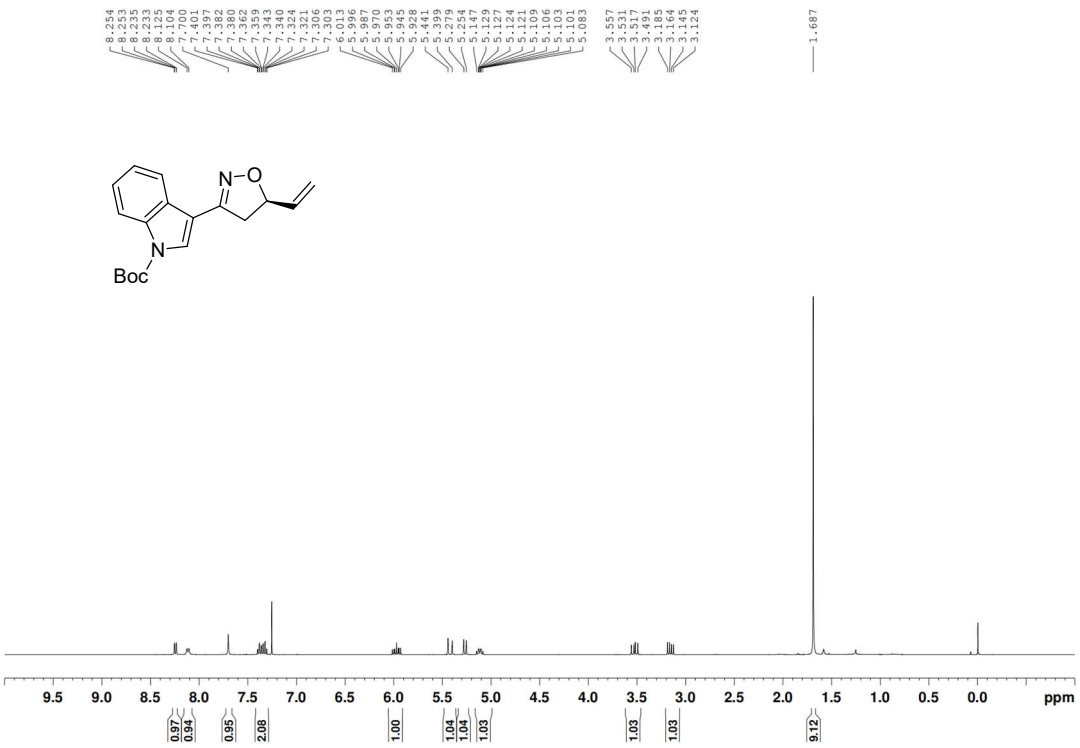
$^{1}$H NMR spectrum of compound **4l** ($CDCl_3$, 400 MHz)



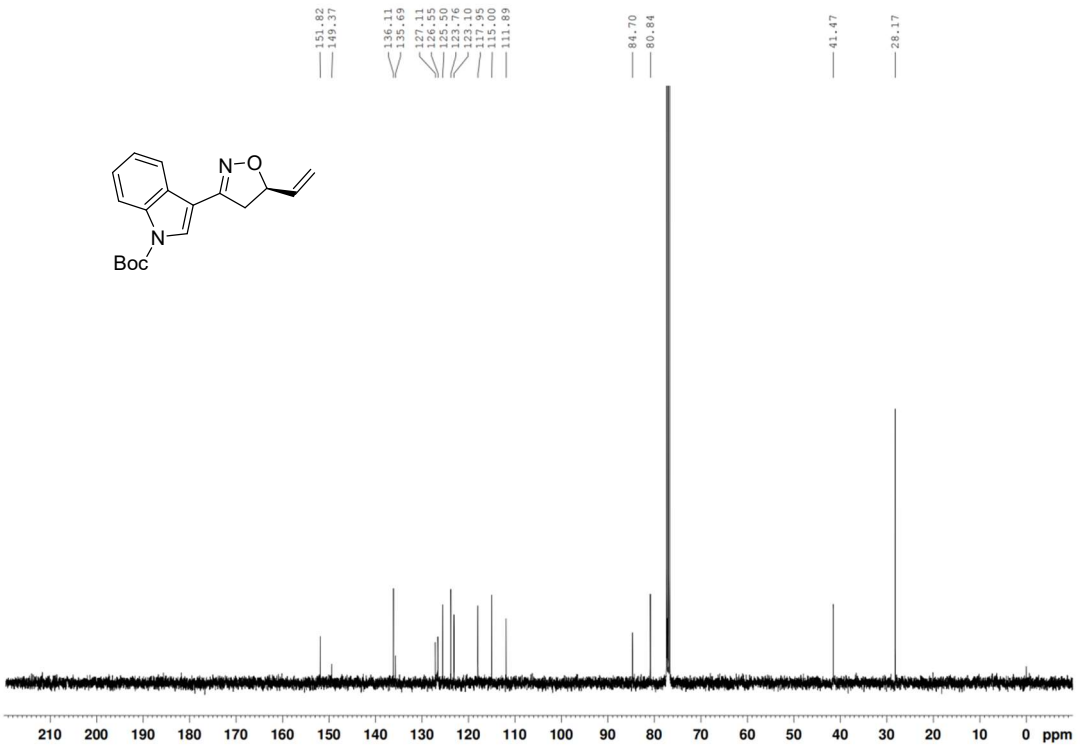

$^{13}$C NMR spectrum of compound **4l** ($CDCl_3$, 100 MHz)



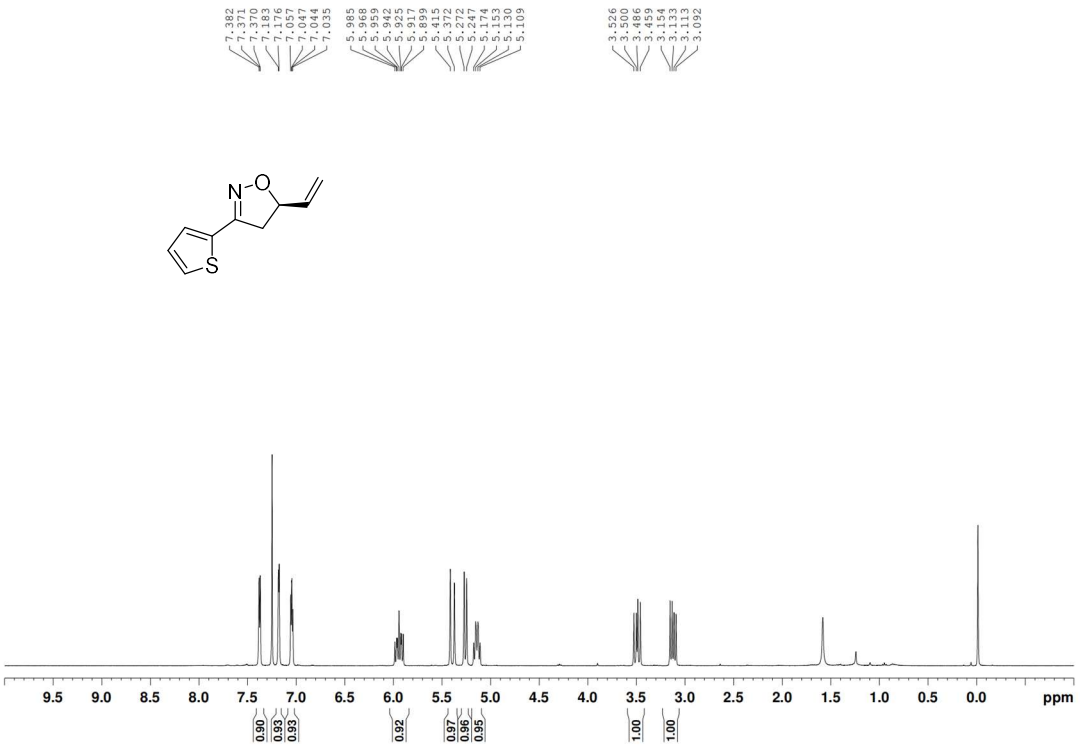
$^{1}$H NMR spectrum of compound **4m** ($CDCl_3$, 400 MHz)



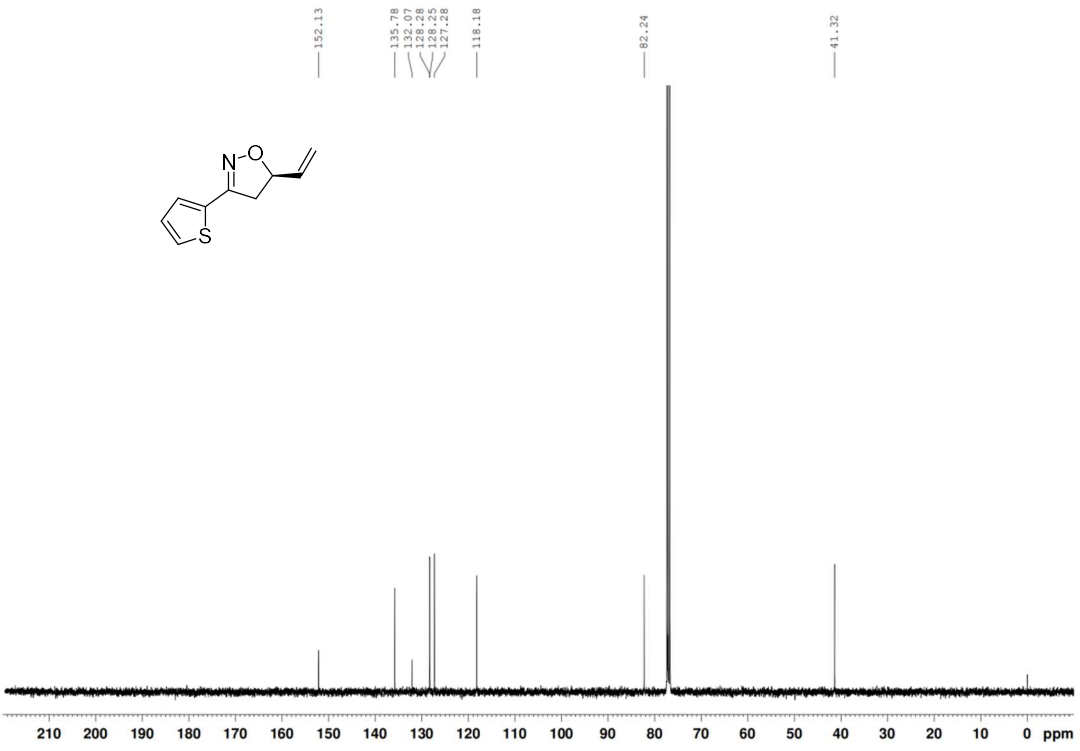

$^{13}$C NMR spectrum of compound **4m** ($CDCl_3$, 100 MHz)



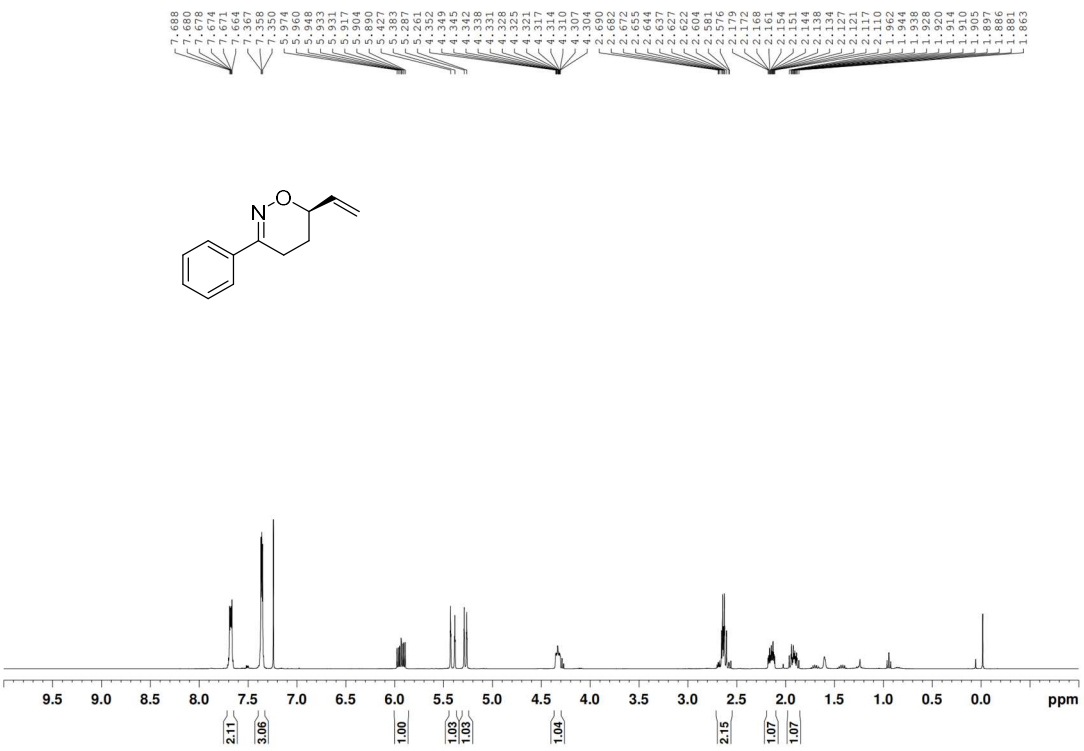
$^{1}$H NMR spectrum of compound **4n** ($CDCl_3$, 400 MHz)



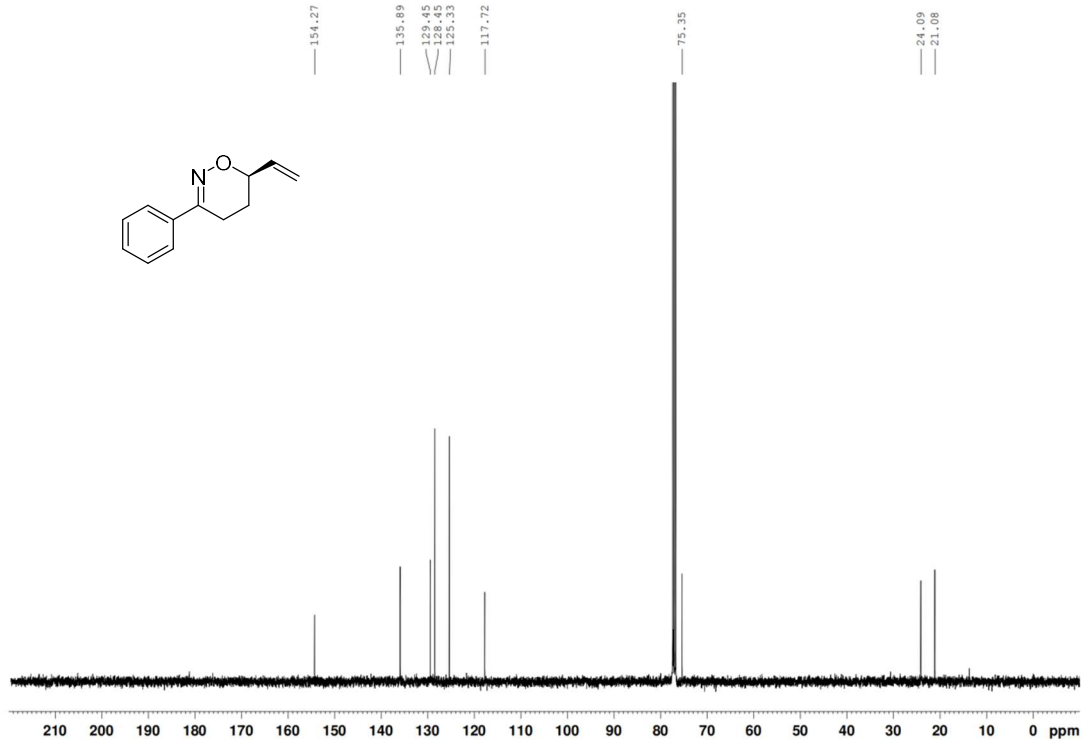

$^{13}$C NMR spectrum of compound **4n** ($CDCl_3$, 100 MHz)



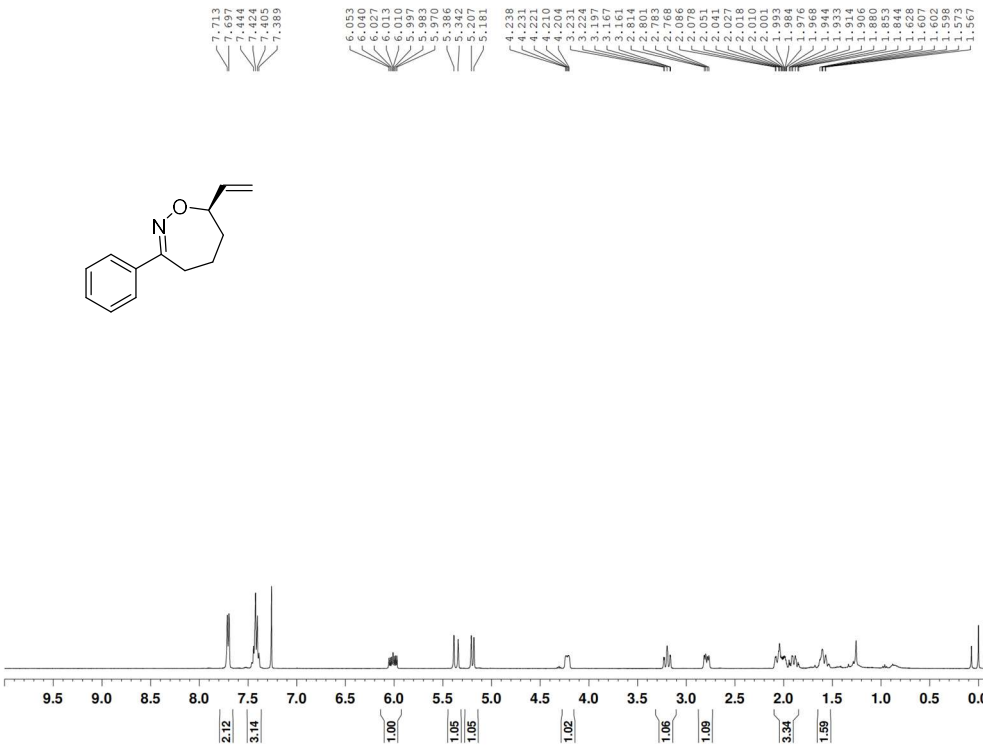
$^{1}$H NMR spectrum of compound **4o** ($CDCl_3$, 400 MHz)



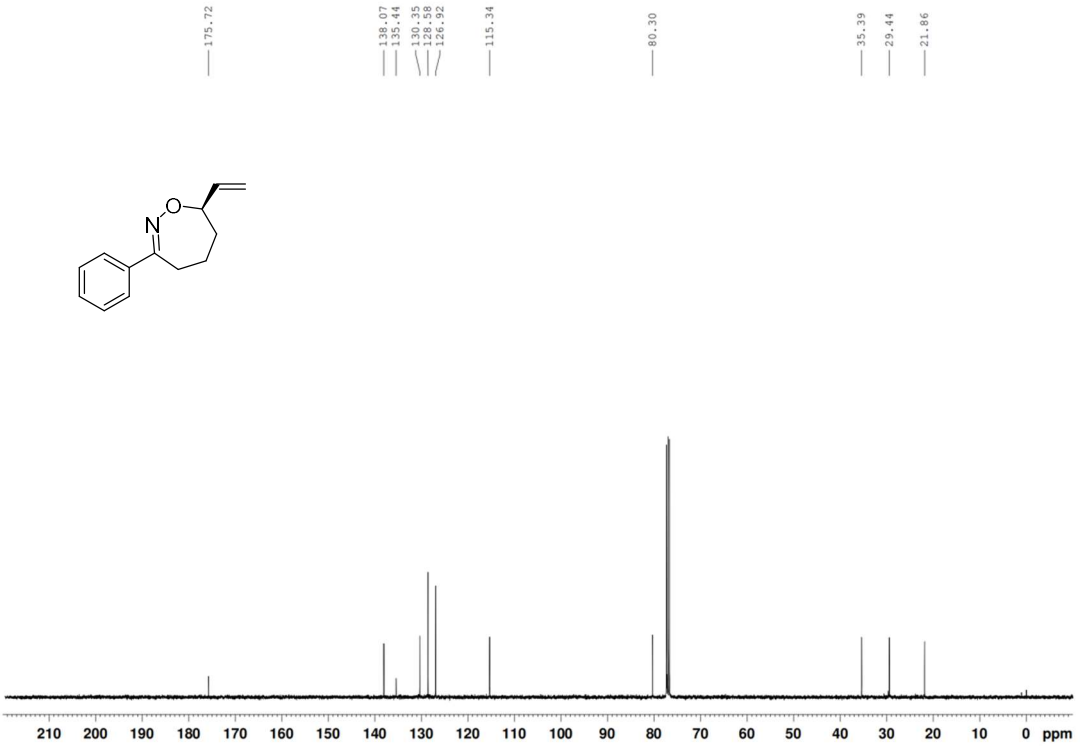
$^{13}$C NMR spectrum of compound **4o** ($CDCl_3$, 100 MHz)



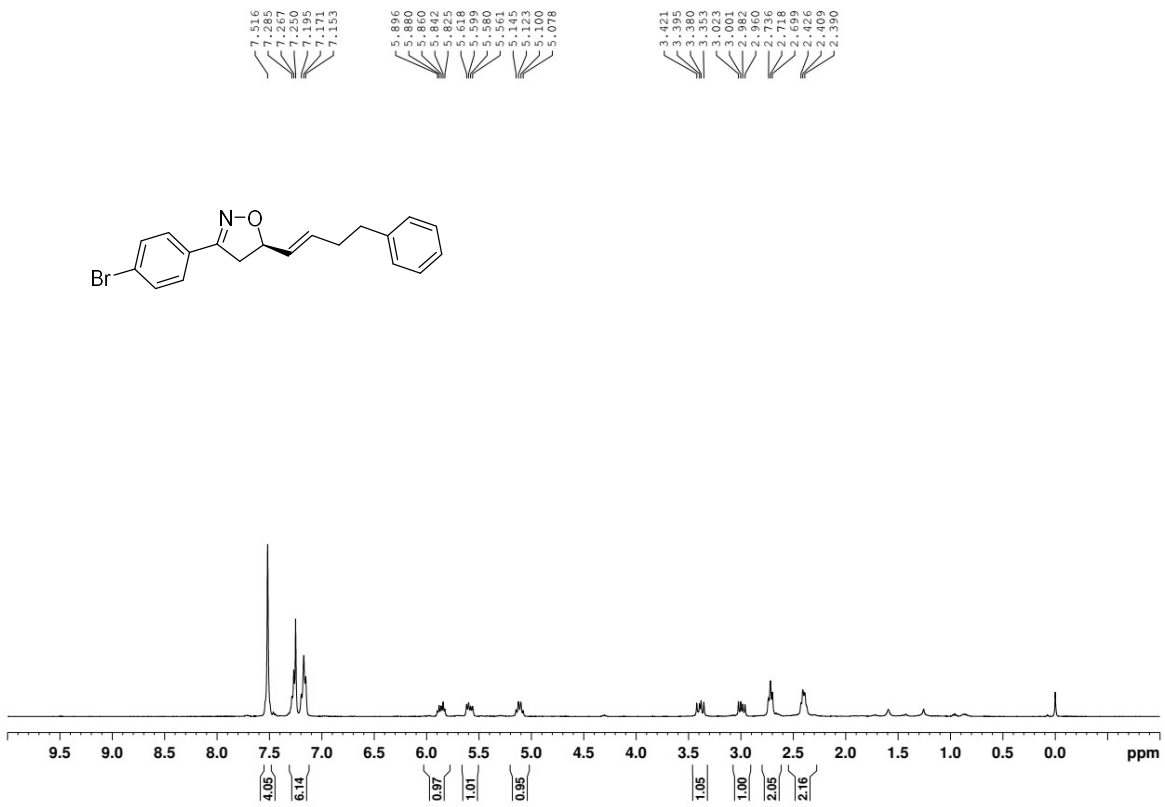
$^{1}$H NMR spectrum of compound **4p** ($CDCl_3$, 400 MHz)



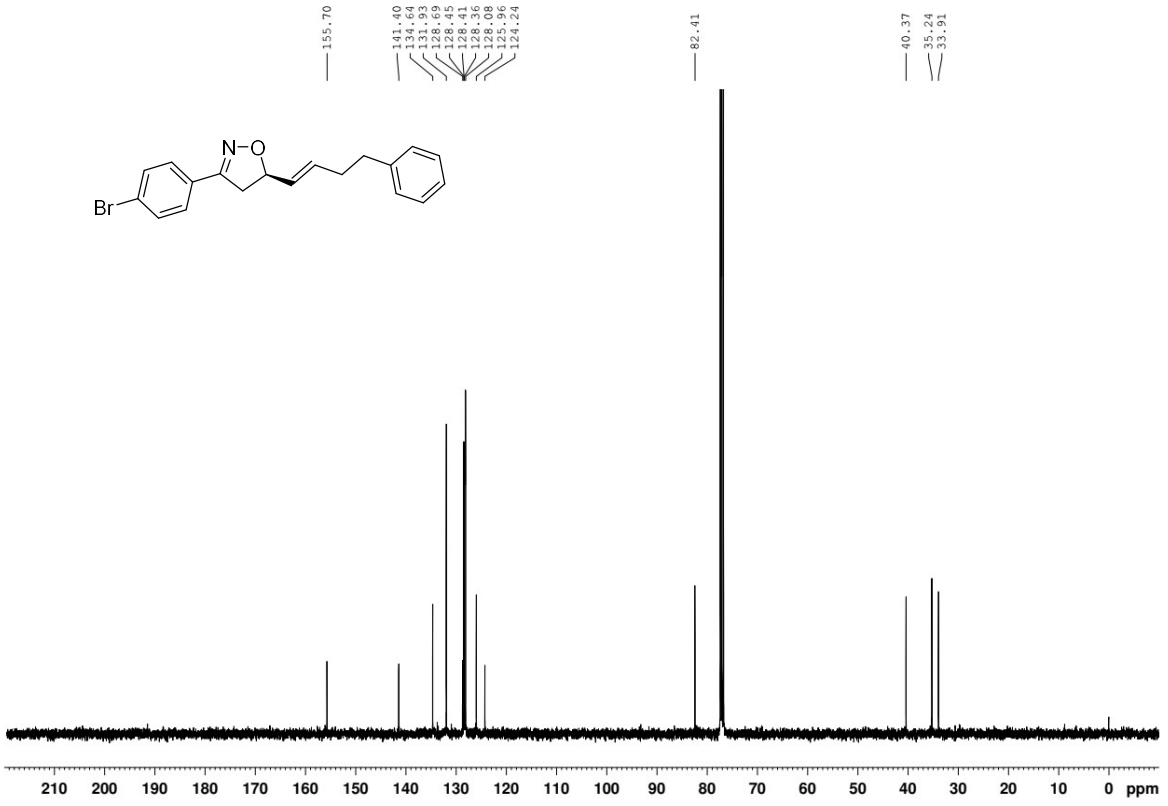

$^{13}$C NMR spectrum of compound **4p** ($CDCl_3$, 100 MHz)



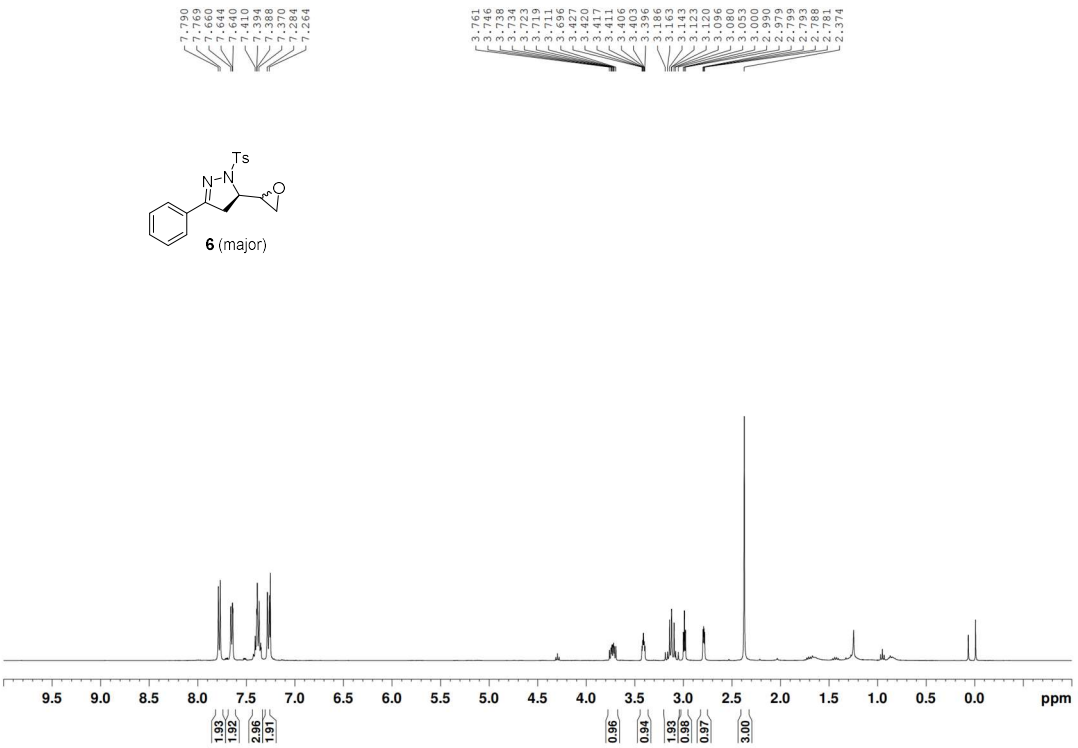
$^{1}$H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)



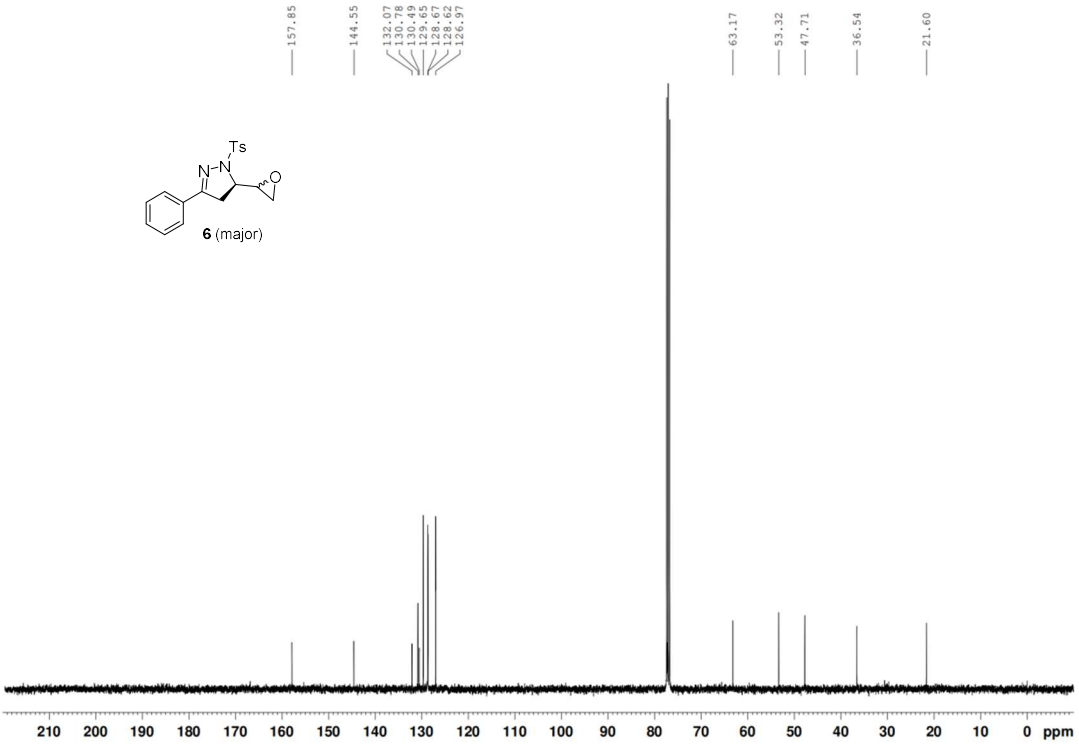

$^{13}$C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)



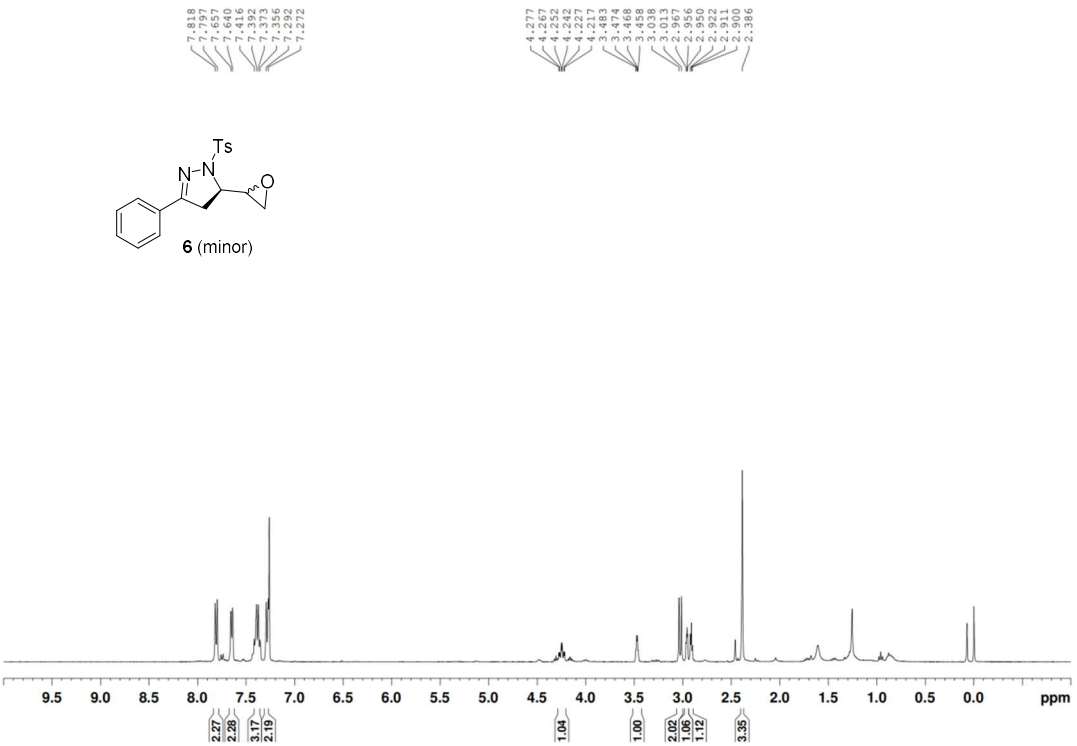
$^{1}$H NMR spectrum of compound **6** (major) ($CDCl_3$, 400 MHz)



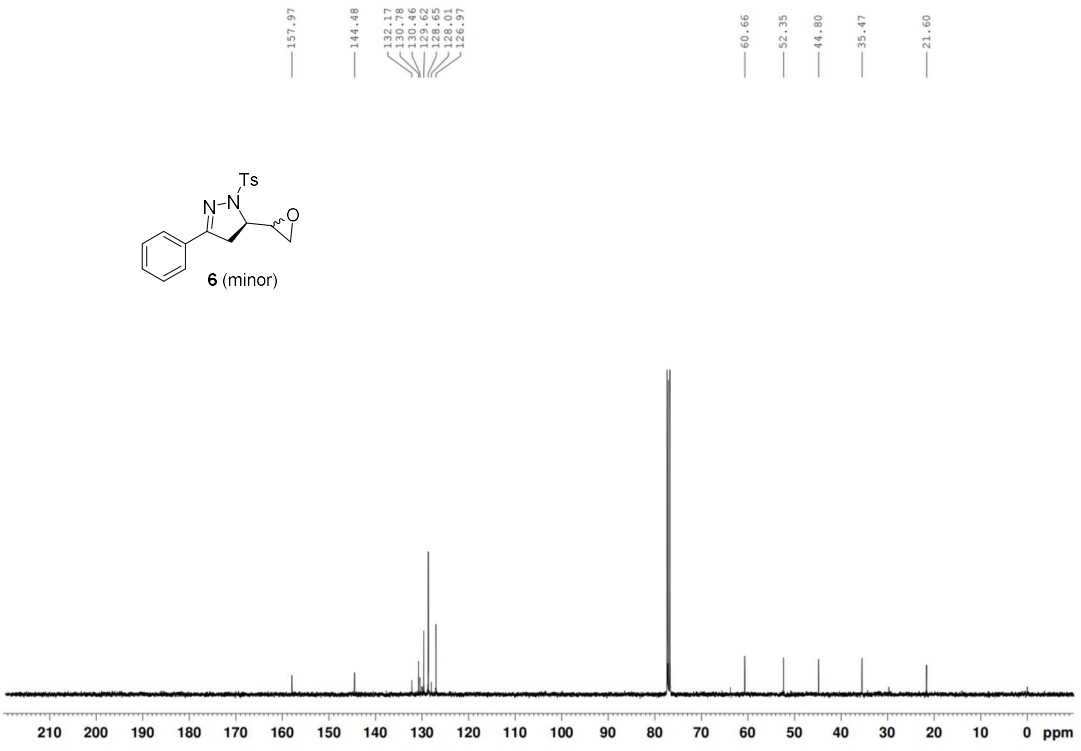

$^{13}$C NMR spectrum of compound **6** (major) ($CDCl_3$, 100 MHz)



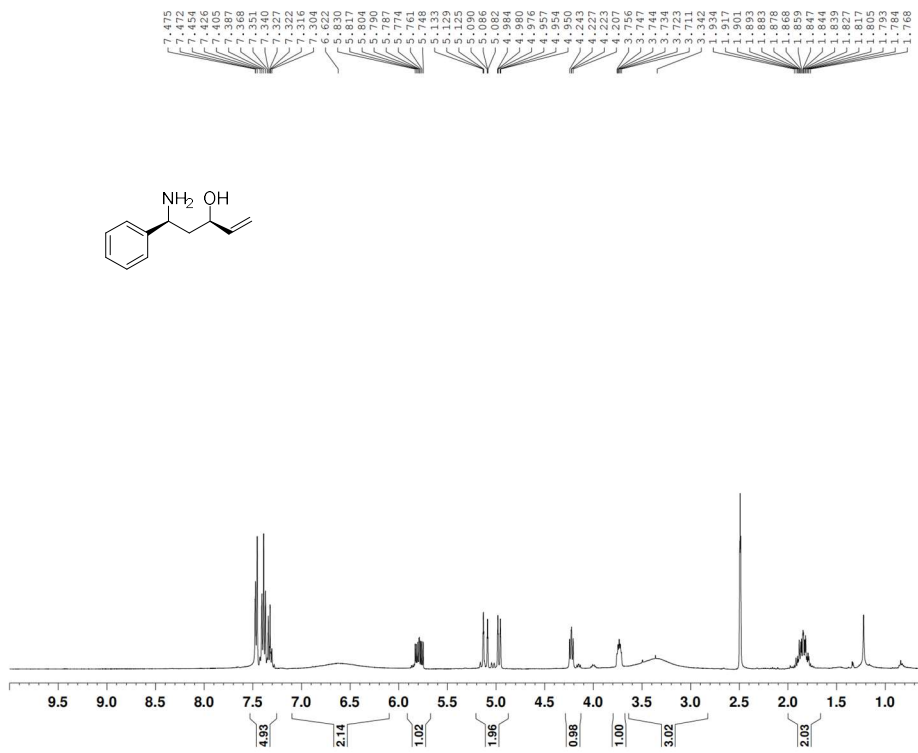
$^{1}$H NMR spectrum of compound **6** (minor) ($CDCl_3$, 400 MHz)



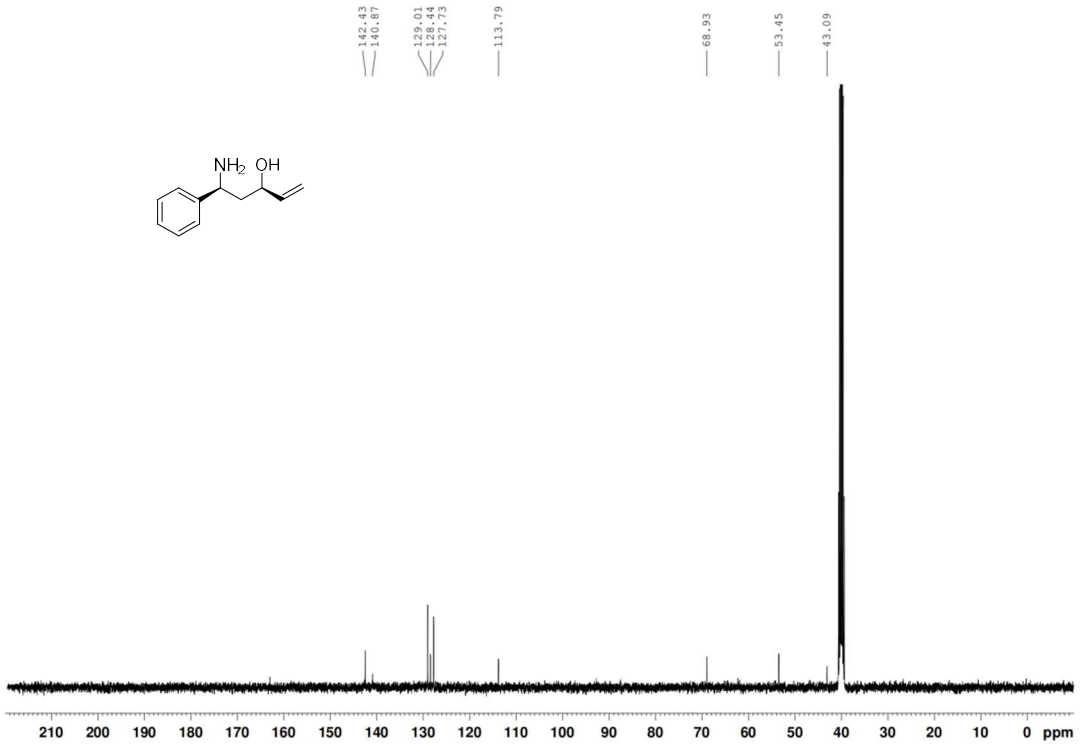

$^{13}$C NMR spectrum of compound **6** (minor) ($CDCl_3$, 100 MHz)



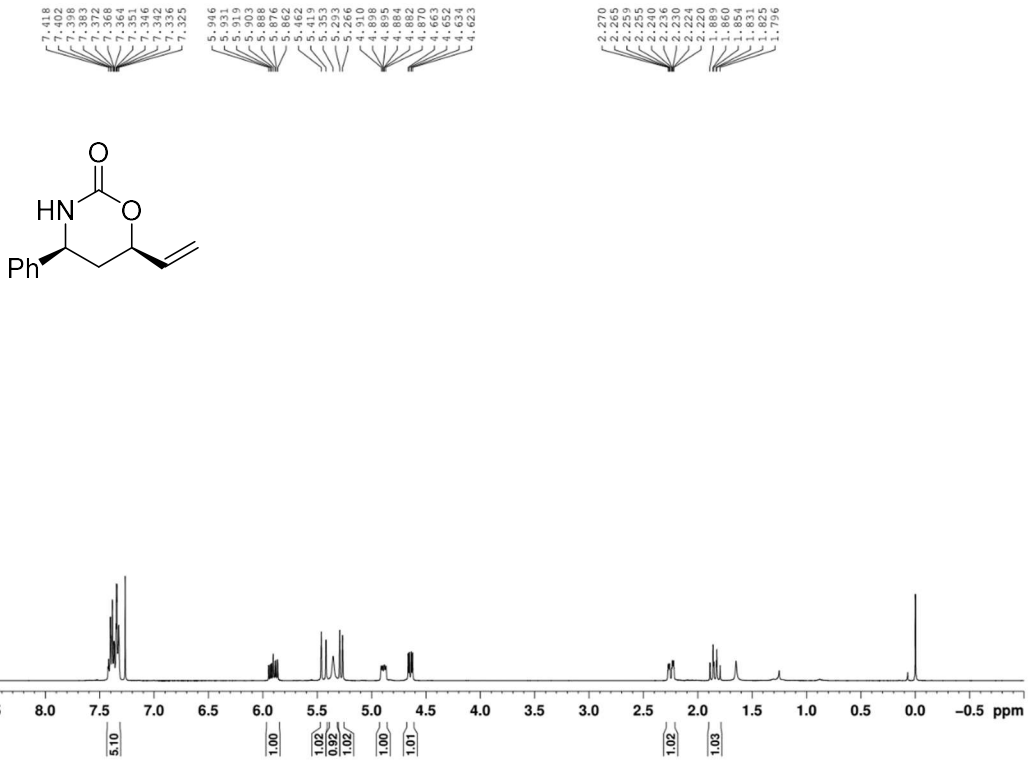
$^{1}$H NMR spectrum of compound **7** (DMSO-$d_6$, 400 MHz)



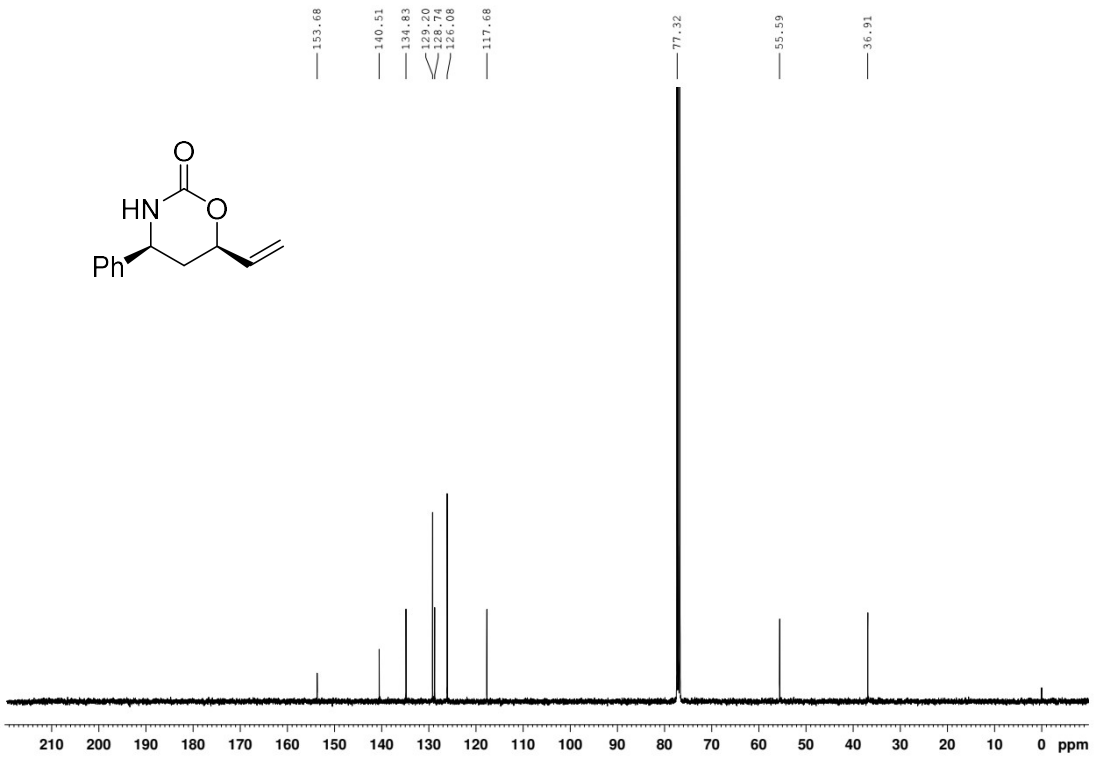

$^{13}$C NMR spectrum of compound **7** (DMSO-$d_6$, 100 MHz)



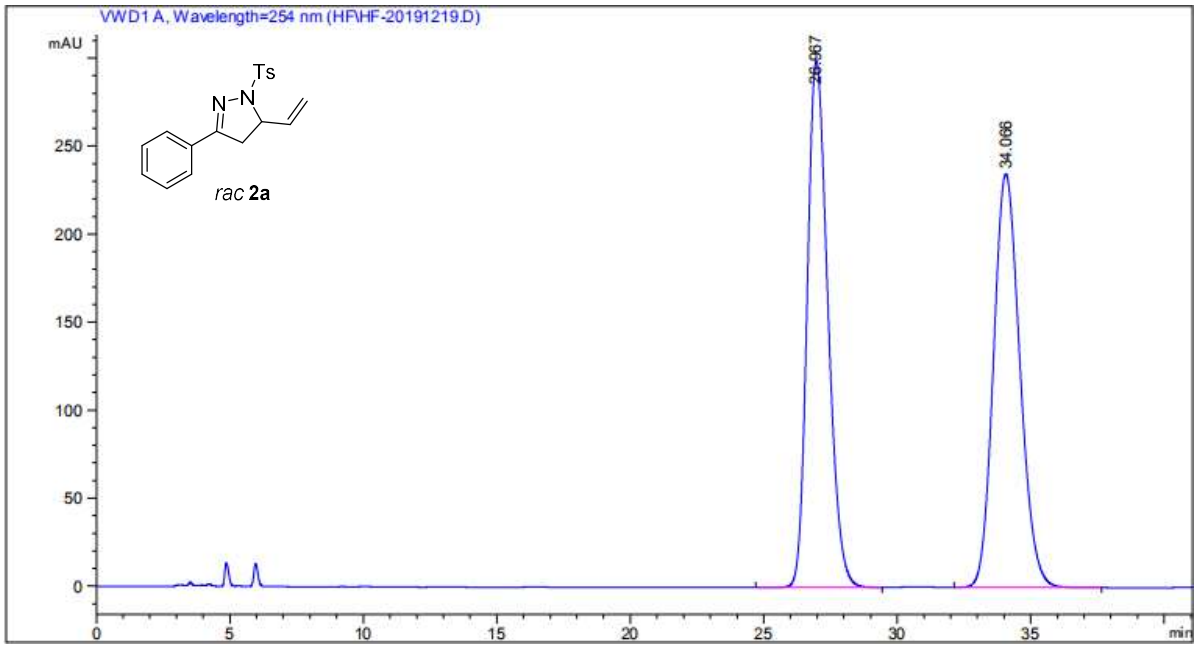
$^{1}$H NMR spectrum of compound **8** ($CDCl_3$, 400 MHz)



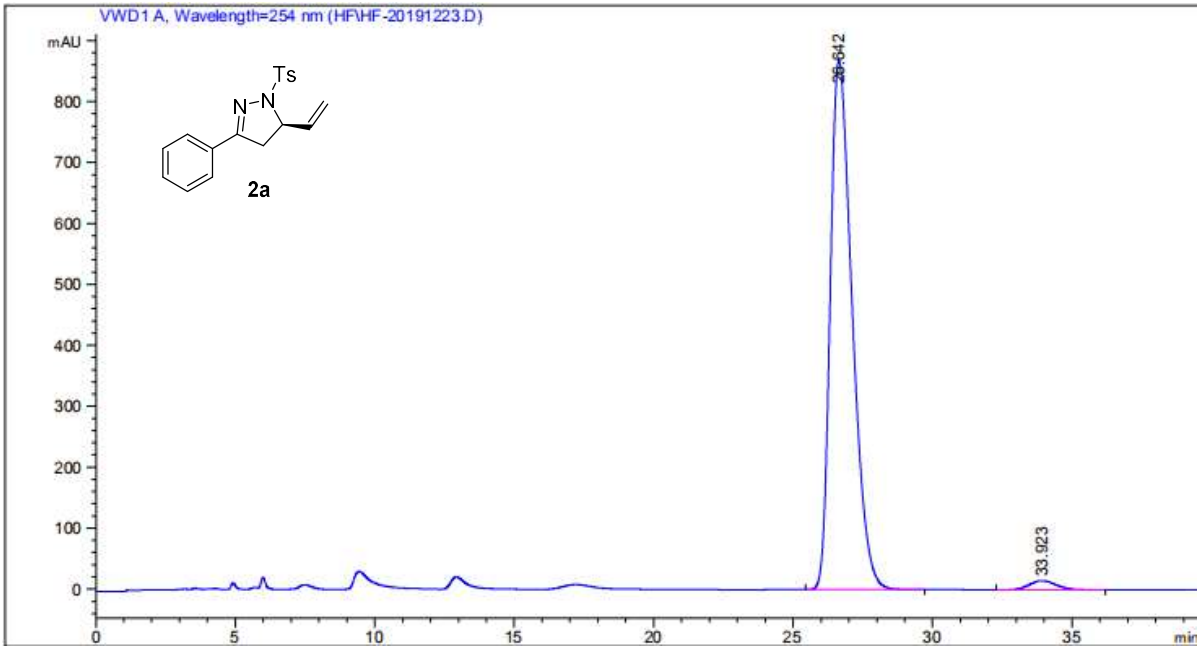

$^{13}$C NMR spectrum of compound **8** ($CDCl_3$, 100 MHz)



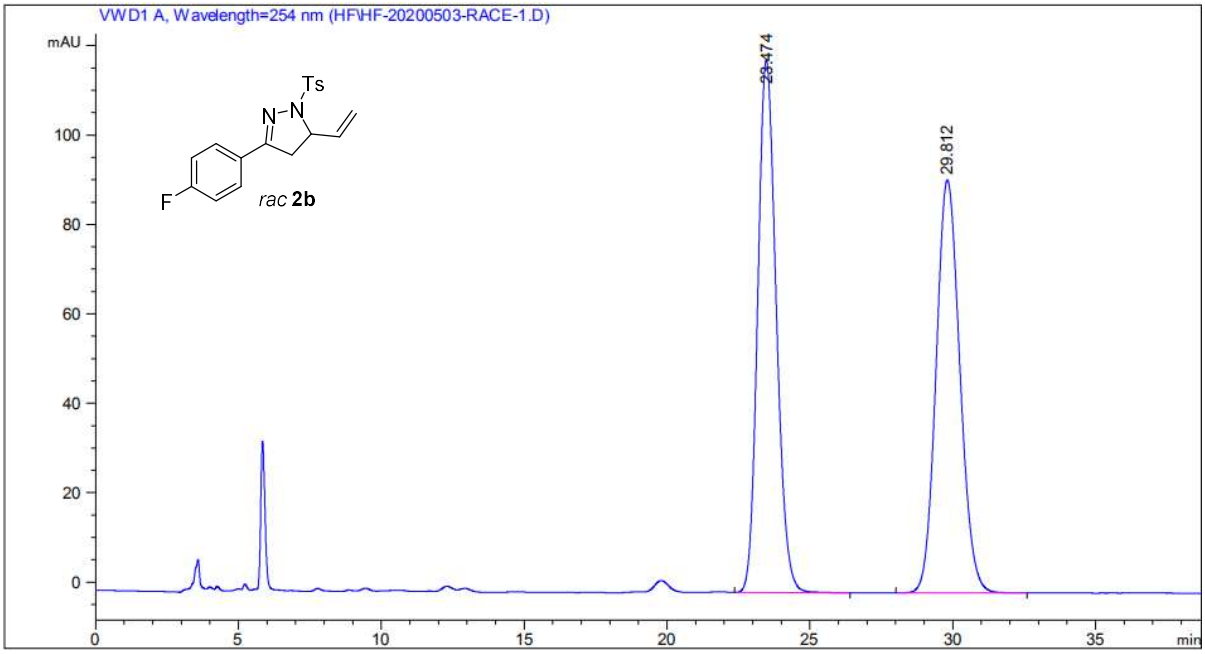
## 9. HPLC spectra for compounds 2a–2s, 4a–4p and 5–6



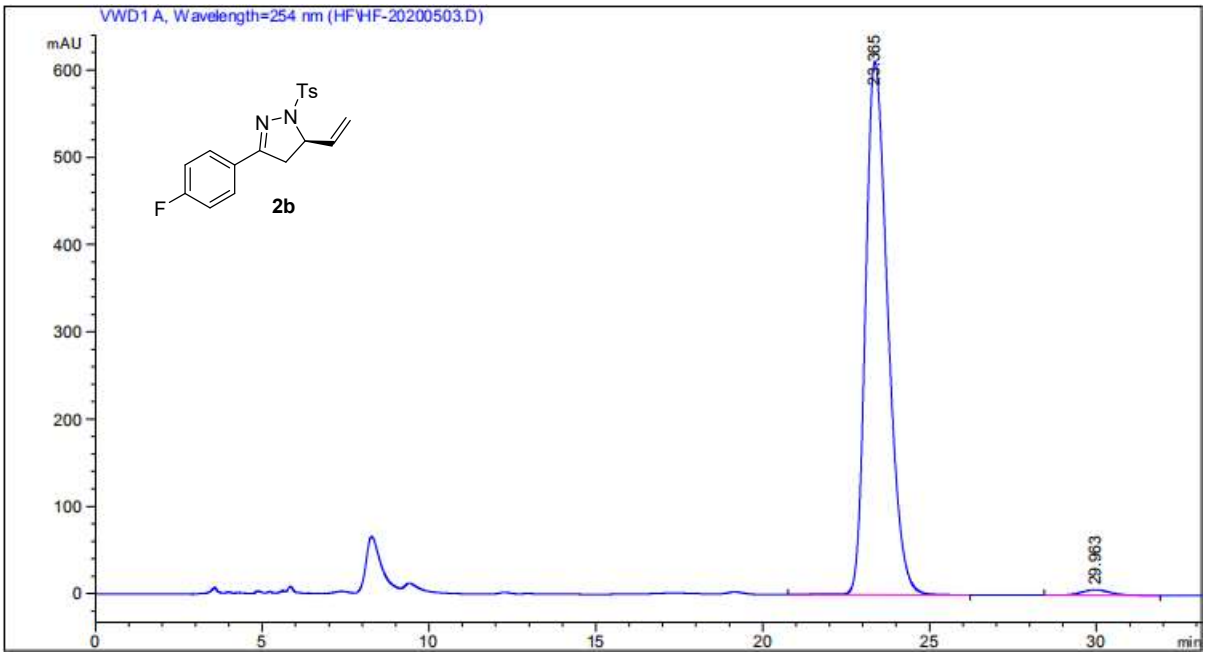

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 26.967 | 1.60612e4 | 299.27985 | 49.9391 |
| 2 | PDA 254 nm | 34.066 | 1.61004e4 | 234.97787 | 50.0609 |



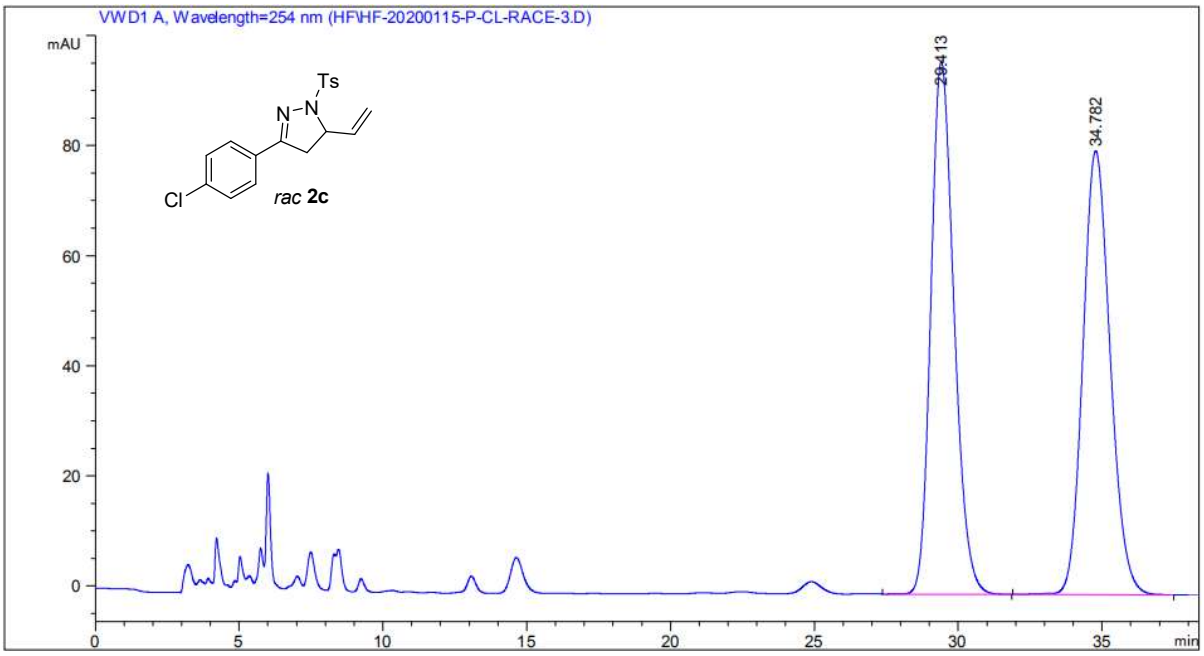

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 26.642 | 4.72158e4 | 868.20557 | 97.9137 |
| 2 | PDA 254 nm | 33.923 | 1006.04779 | 15.00314 | 2.0863 |



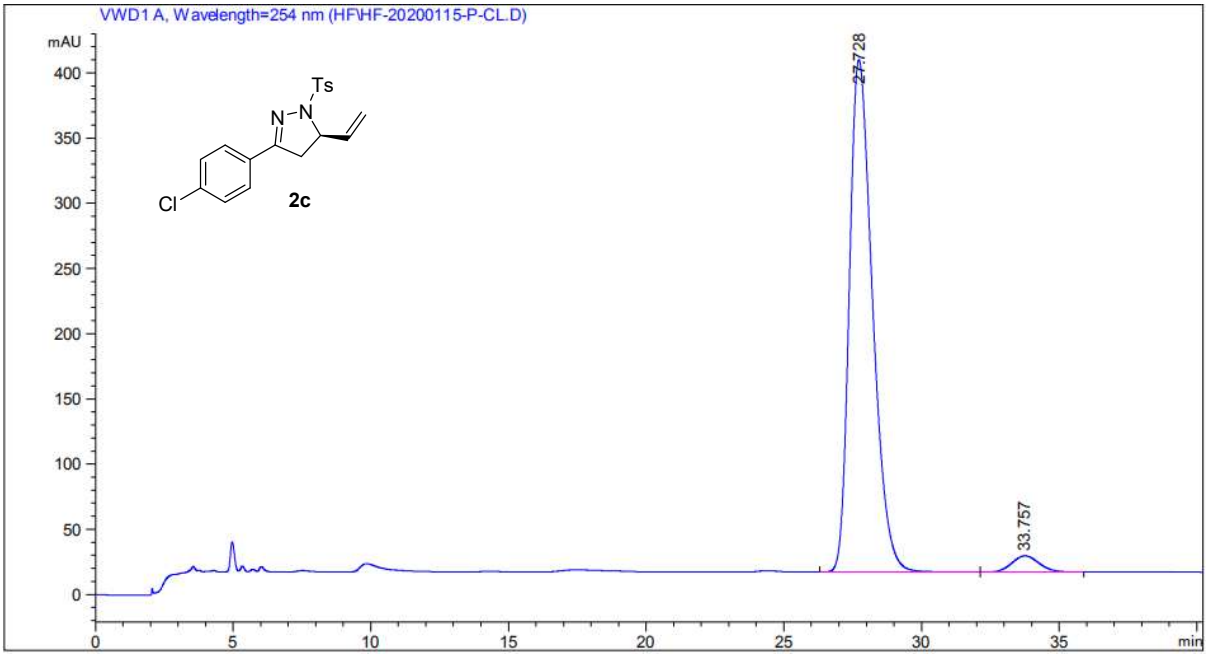

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.474 | 5355.04980 | 119.09879 | 50.0918 |
| 2 | PDA 254 nm | 29.812 | 5335.42188 | 92.39308 | 49.9082 |



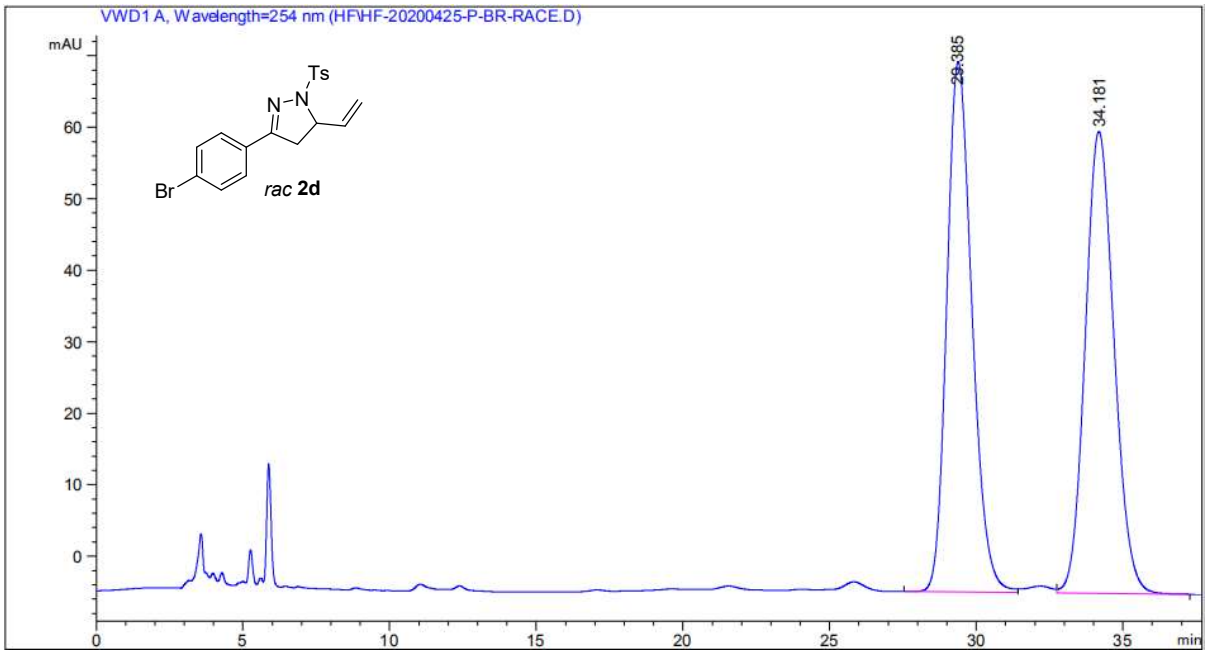

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.365 | 2.81806e4 | 611.02057 | 98.7030 |
| 2 | PDA 254 nm | 29.963 | 370.31766 | 6.33330 | 1.2970 |



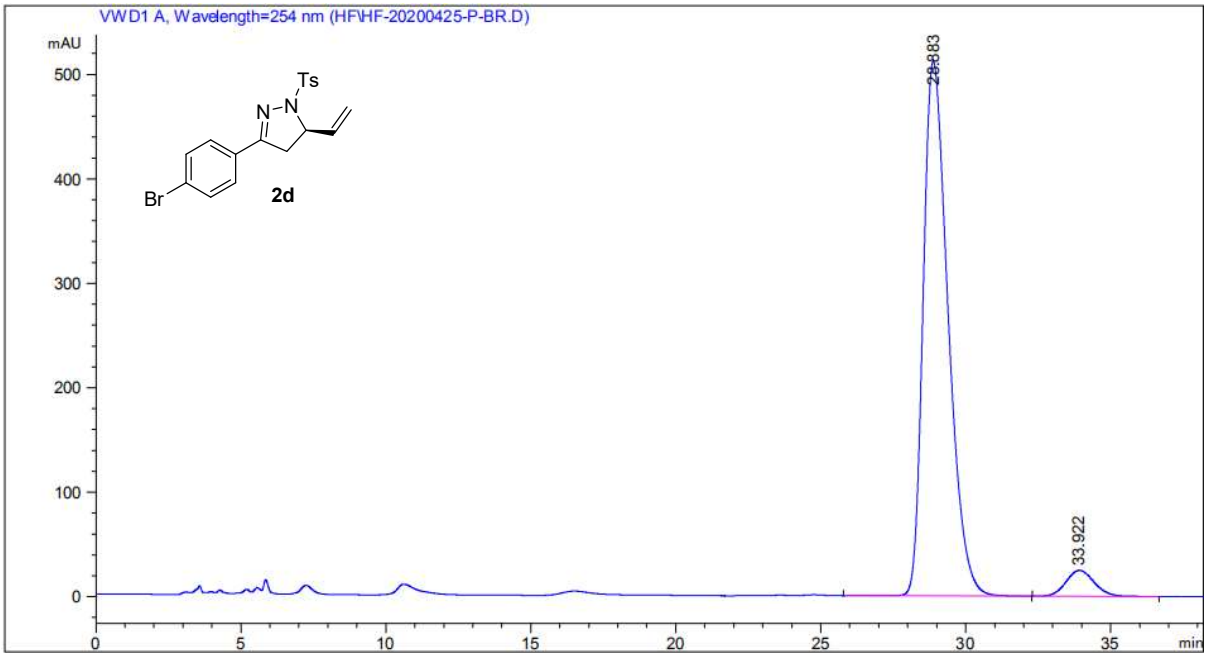

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 29.413 | 5405.50049 | 96.68369 | 50.4443 |
| 2 | PDA 254 nm | 34.782 | 5310.28223 | 80.60548 | 49.5557 |



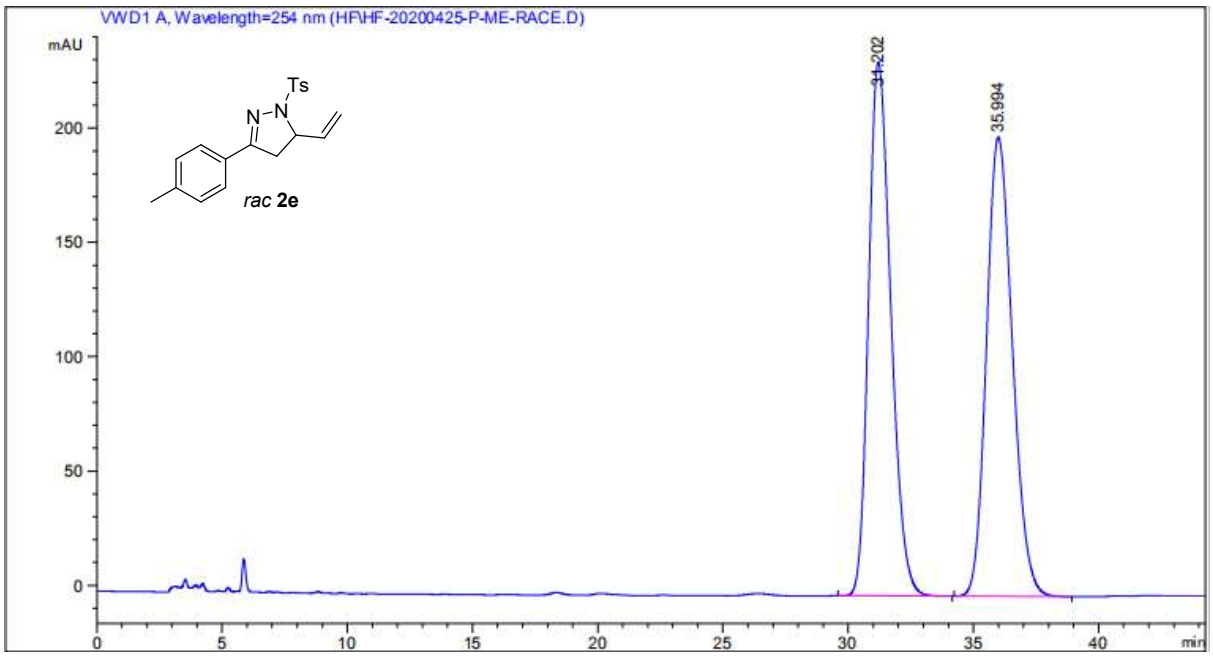

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 27.728 | 2.29153e4 | 392.76523 | 96.4258 |
| 2 | PDA 254 nm | 33.757 | 849.40820 | 12.43409 | 3.5742 |



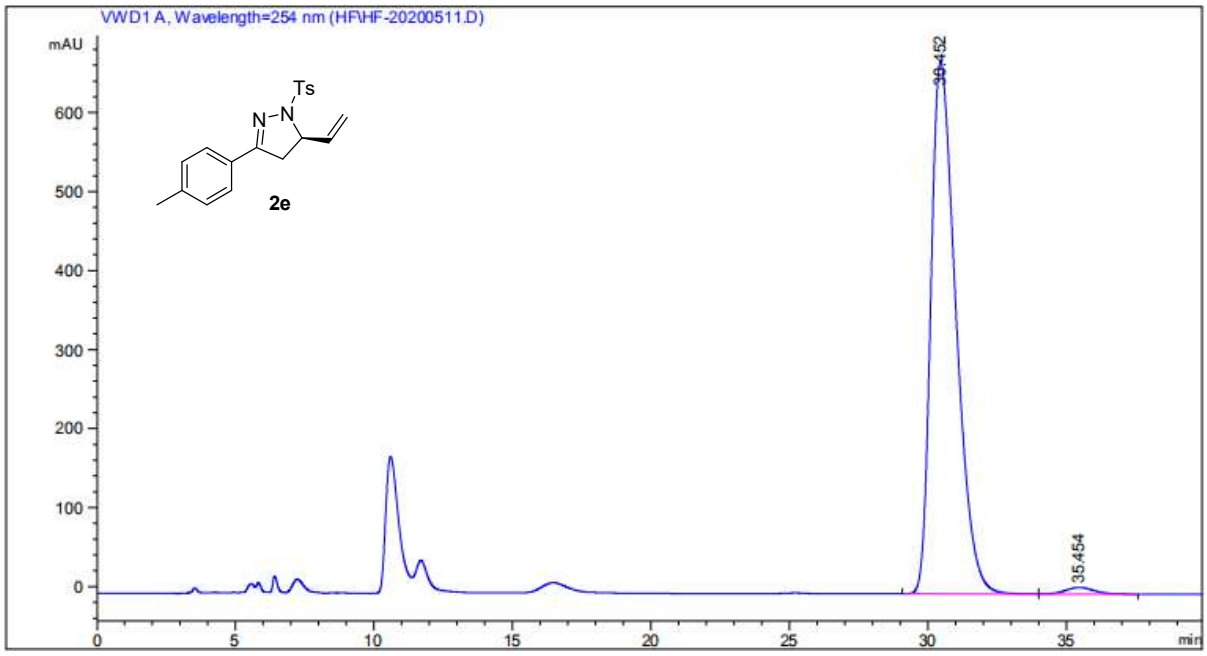

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 29.385 | 4422.99707 | 74.17055 | 50.0298 |
| 2 | PDA 254 nm | 34.181 | 4417.71924 | 64.60667 | 49.9702 |



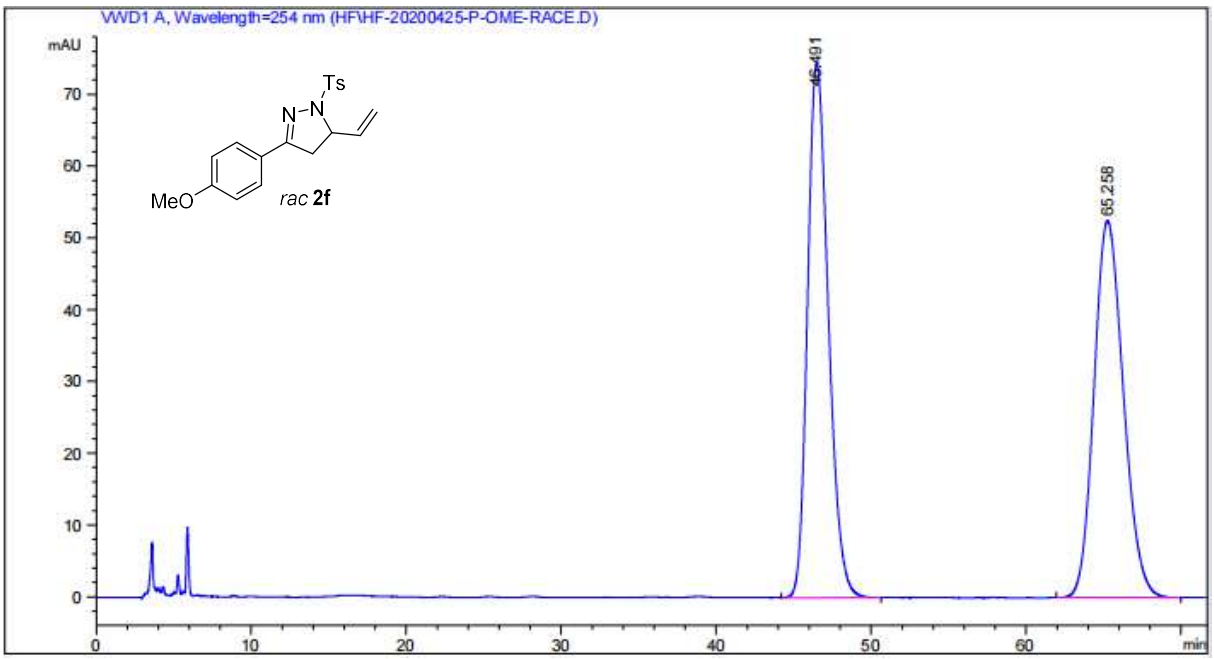

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 28.883 | 3.05136e4 | 512.06750 | 94.7941 |
| 2 | PDA 254 nm | 33.922 | 1675.75439 | 24.77319 | 5.2059 |



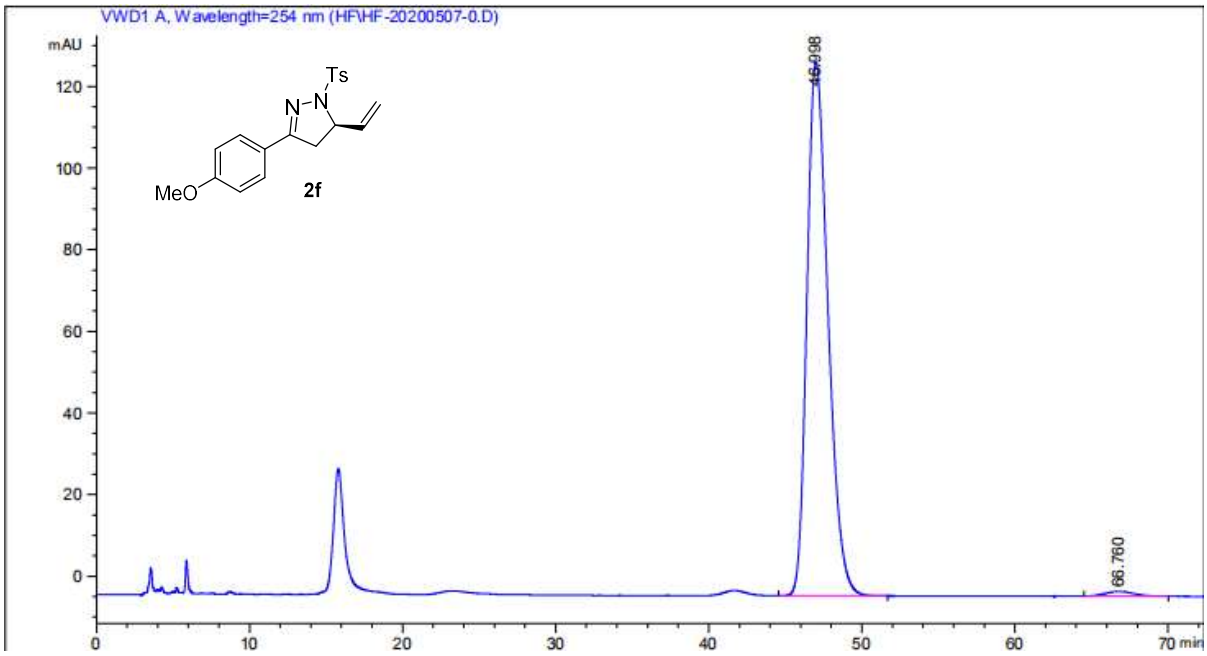

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254.16 nm | 31.202 | 1.44315e4 | 233.45490 | 50.0013 |
| 2 | PDA 254.16 nm | 35.994 | 1.44307e4 | 200.96352 | 49.9987 |



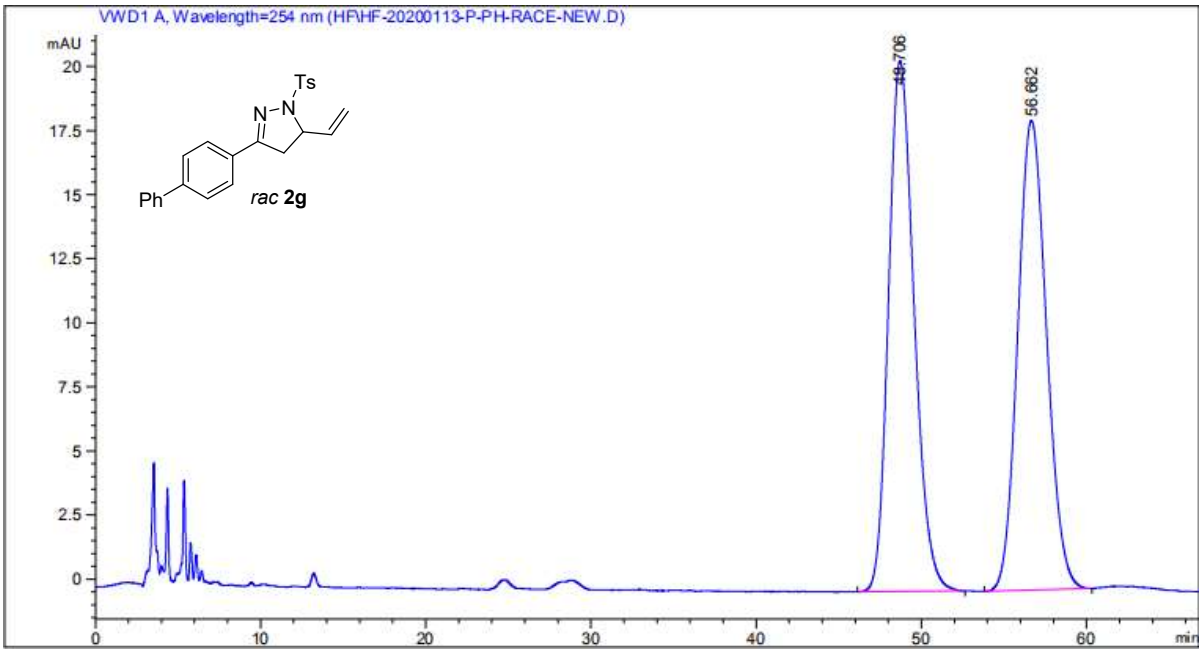

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254.16 nm | 30.452 | 4.22524e4 | 673.70184 | 98.6412 |
| 2 | PDA 254.16 nm | 35.454 | 582.02930 | 8.25200 | 1.3588 |



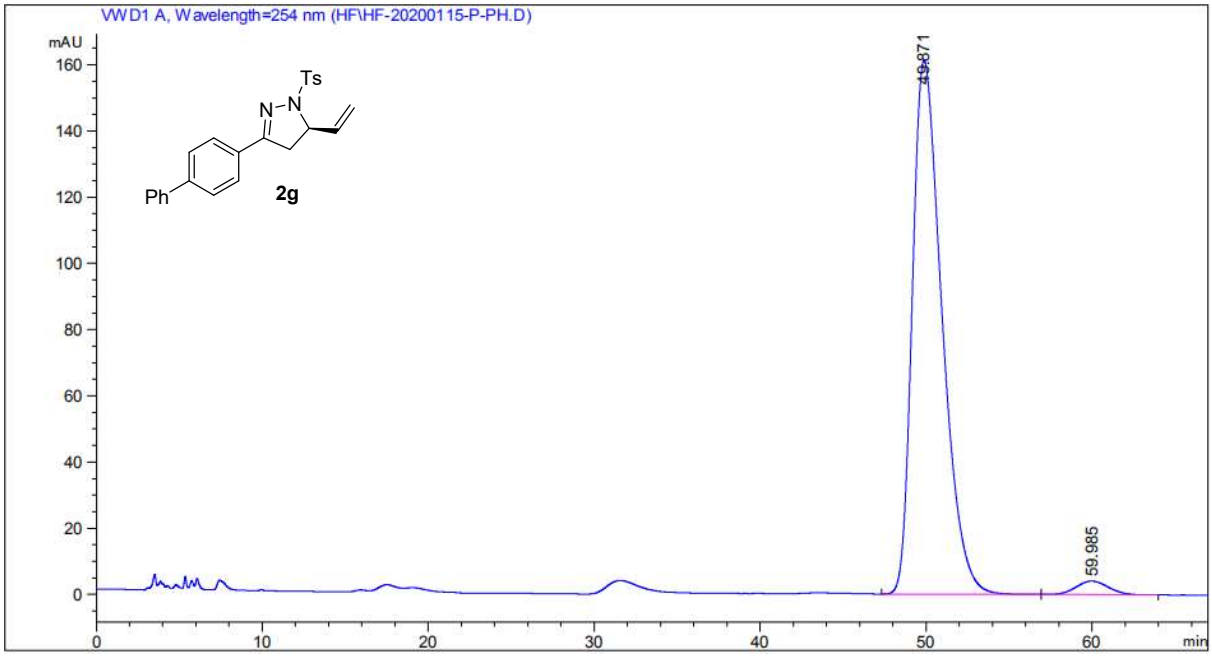

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 46.491 | 6932.46191 | 74.45089 | 50.0669 |
| 2 | PDA 254 nm | 65.258 | 6913.93311 | 52.52824 | 49.9331 |



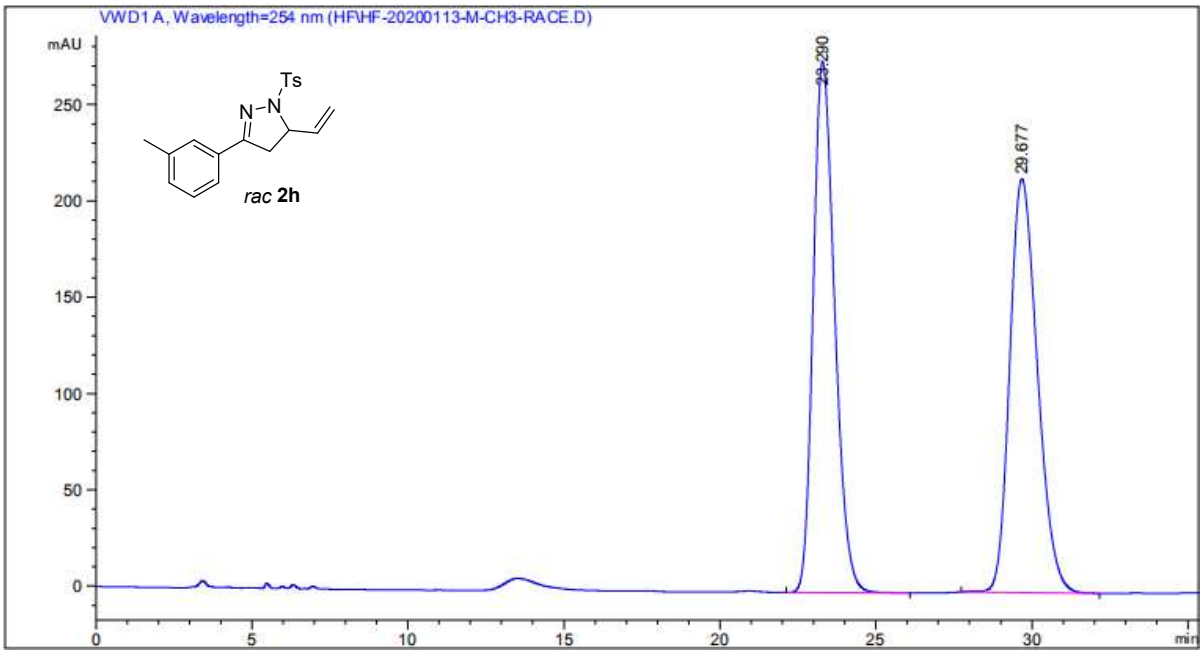

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 46.998 | 1.24963e4 | 130.80913 | 98.7595 |
| 2 | PDA 254 nm | 66.760 | 156.96873 | 1.19828 | 1.2405 |



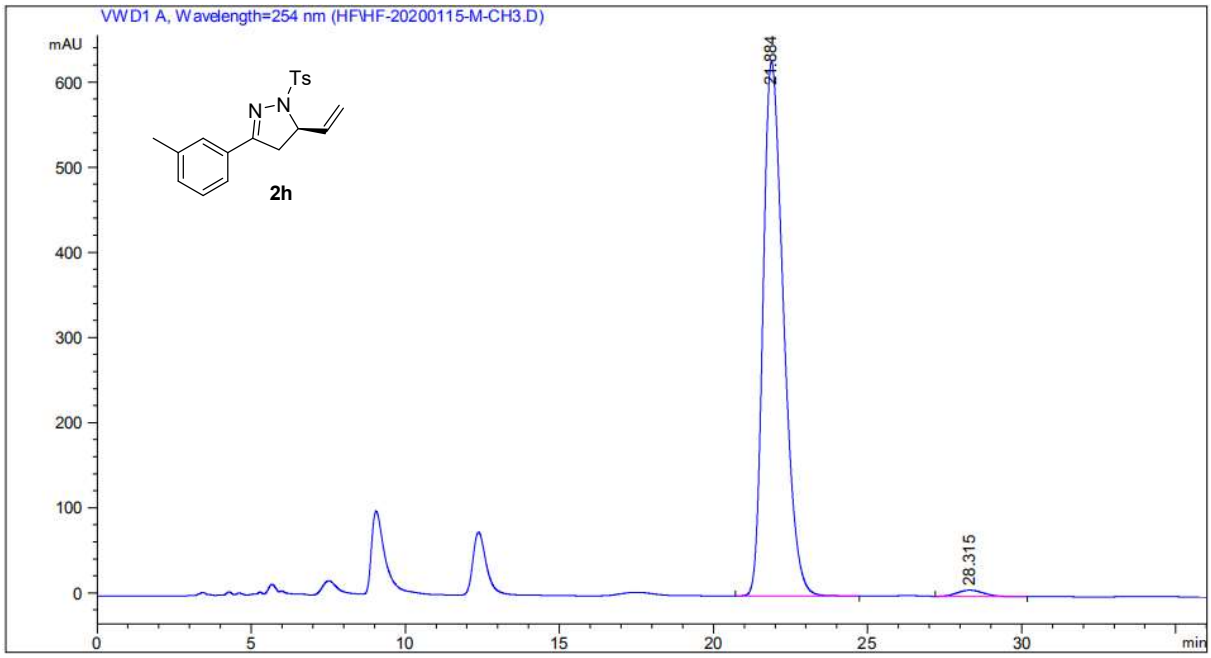

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 48.706 | 2224.79419 | 20.70044 | 50.1387 |
| 2 | PDA 254 nm | 56.662 | 2212.48779 | 18.31616 | 49.8613 |



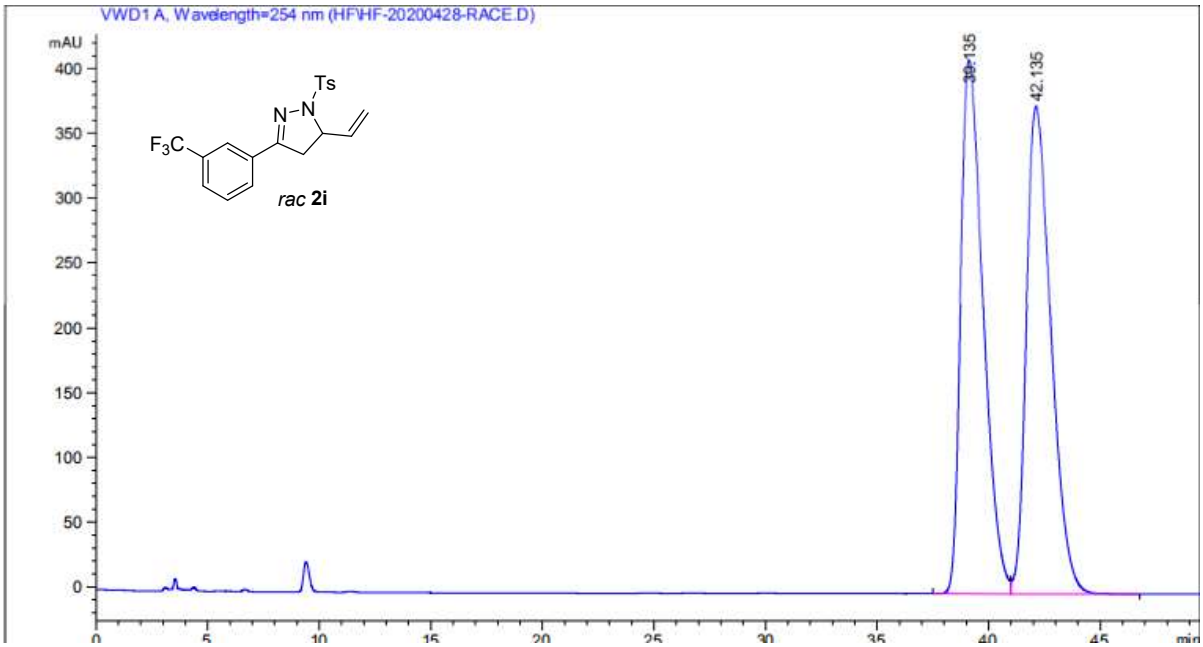

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 49.871 | 1.99476e4 | 161.25204 | 97.2849 |
| 2 | PDA 254 nm | 59.985 | 556.72223 | 4.10839 | 2.7151 |



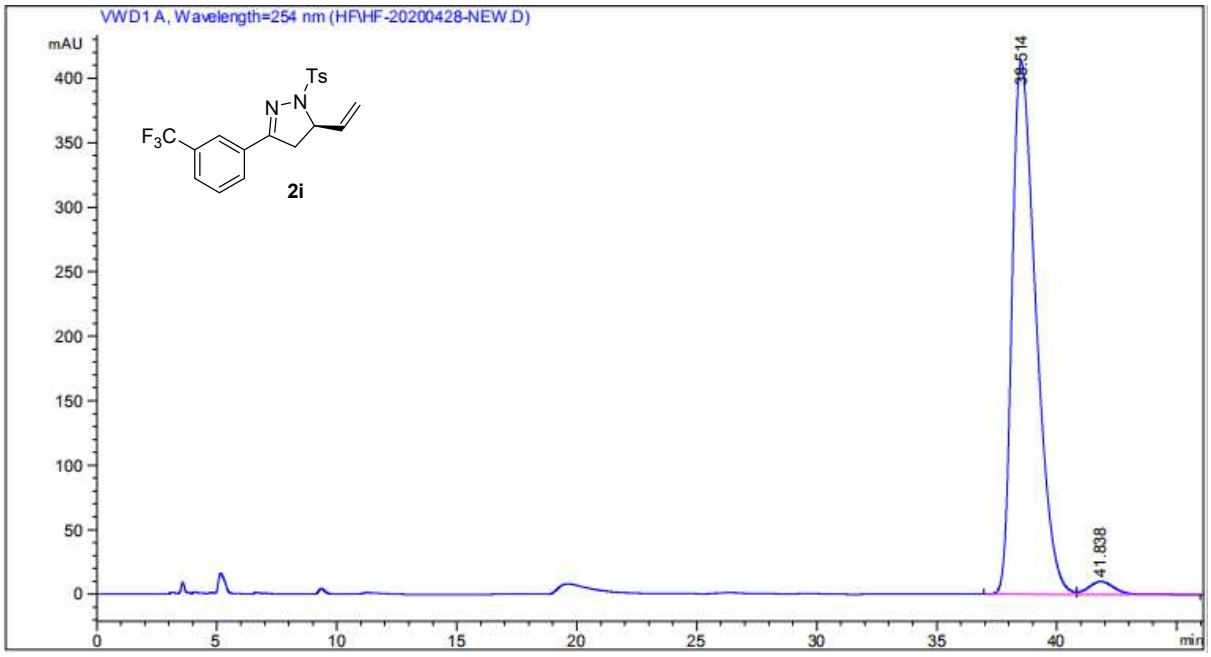

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.290 | 1.31609e4 | 275.59933 | 49.8838 |
| 2 | PDA 254 nm | 29.677 | 1.32222e4 | 214.83112 | 50.1162 |



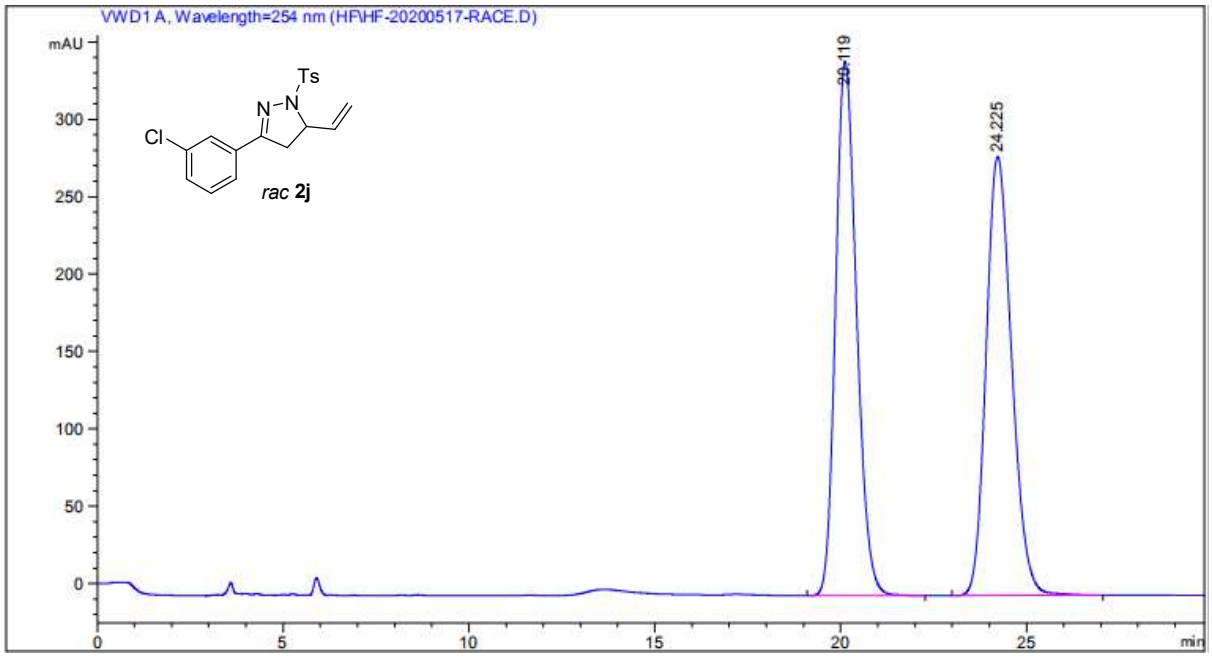

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 21.884 | 2.88562e4 | 627.56708 | 98.4812 |
| 2 | PDA 254 nm | 28.315 | 445.03397 | 7.46473 | 1.5188 |



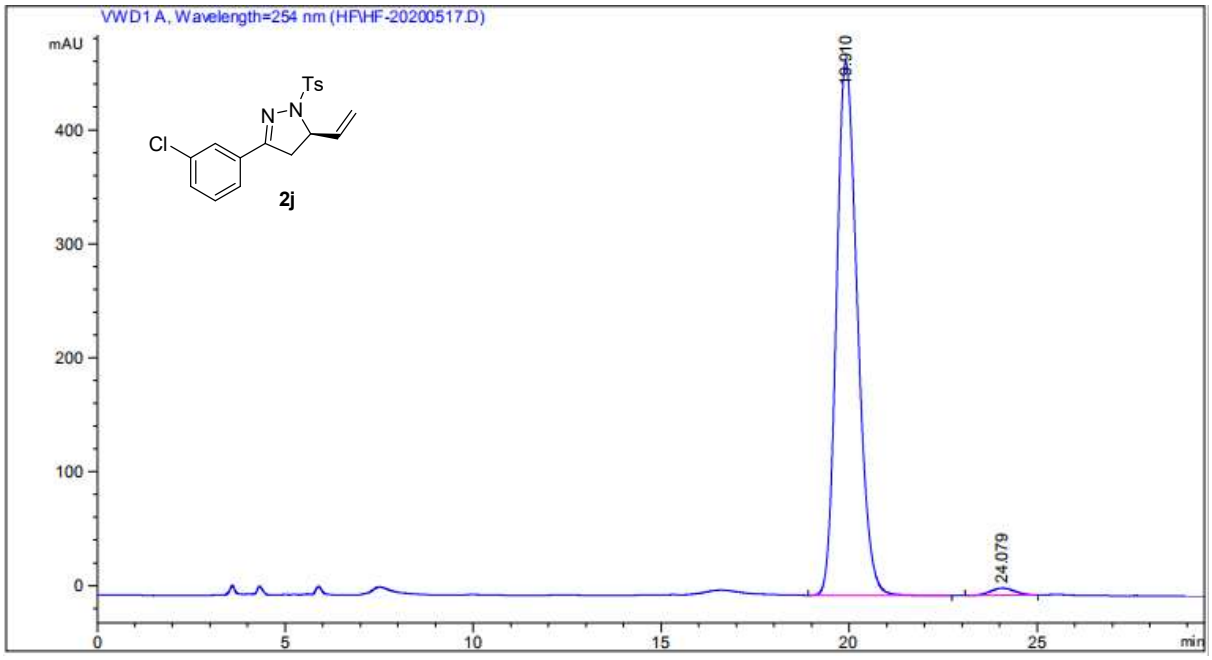

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 39.135 | 2.88280e4 | 412.03534 | 49.9263 |
| 2 | PDA 254 nm | 42.135 | 2.89131e4 | 376.51834 | 50.0737 |



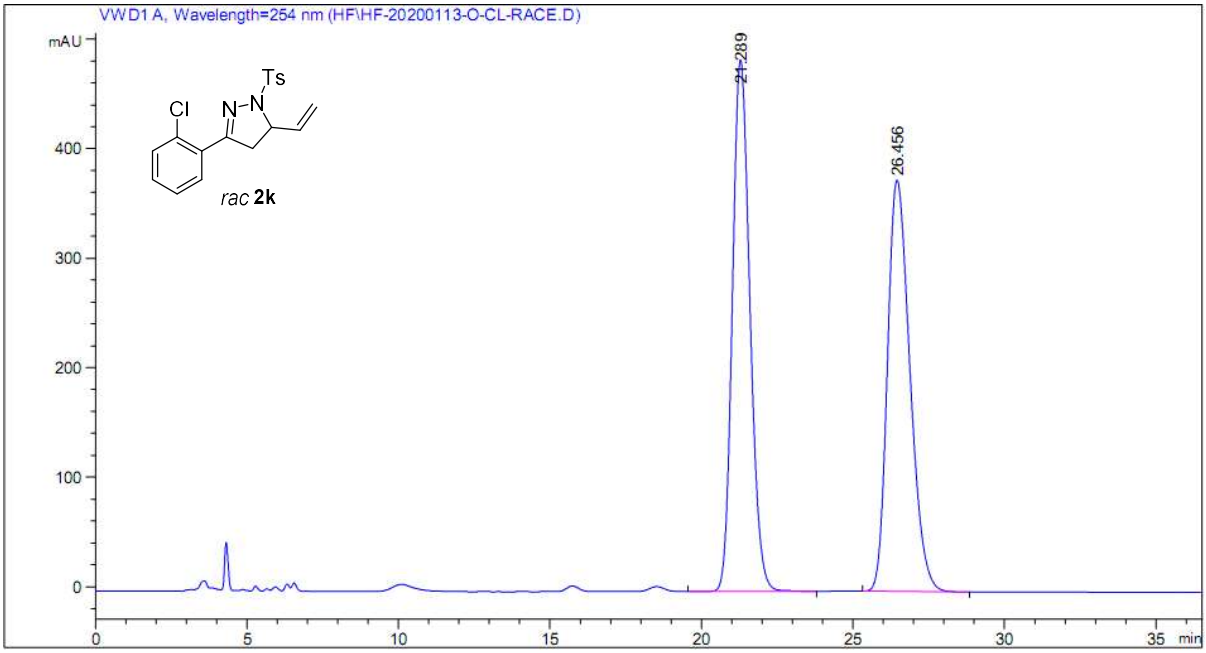

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 38.514 | 2.84698e4 | 413.26364 | 97.4970 |
| 2 | PDA 254 nm | 41.838 | 730.88403 | 9.93582 | 2.5030 |



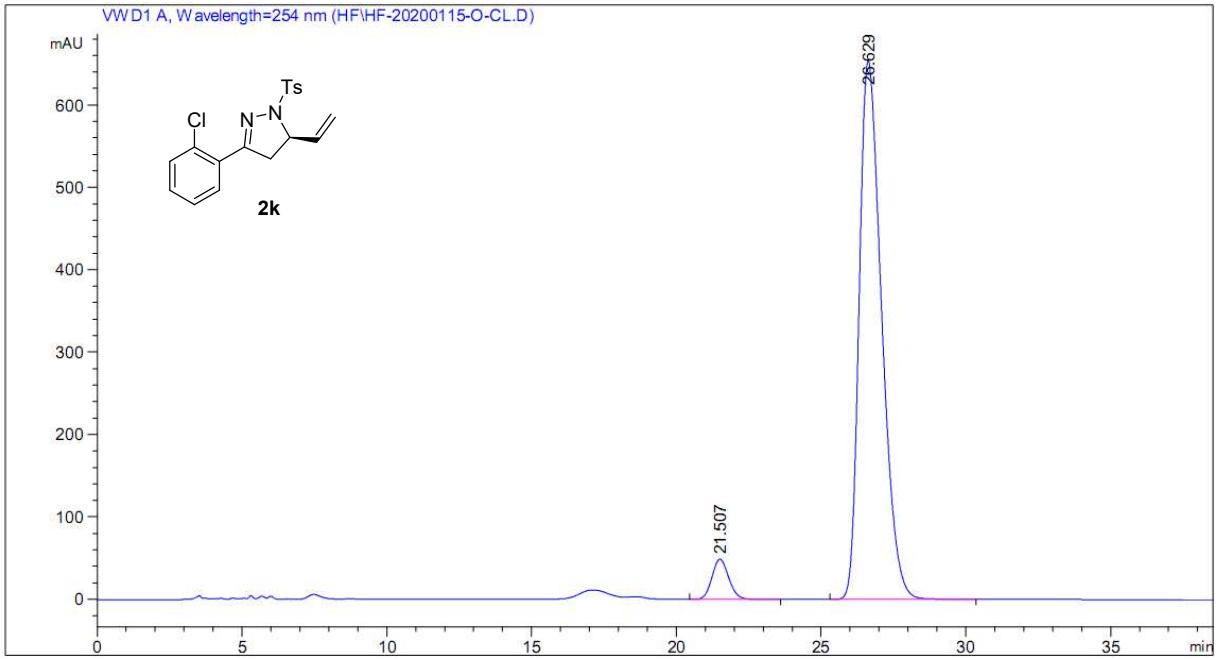

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 20.119 | 1.35099e4 | 345.16788 | 49.9352 |
| 2 | PDA 254 nm | 24.225 | 1.35450e4 | 283.78735 | 50.0648 |



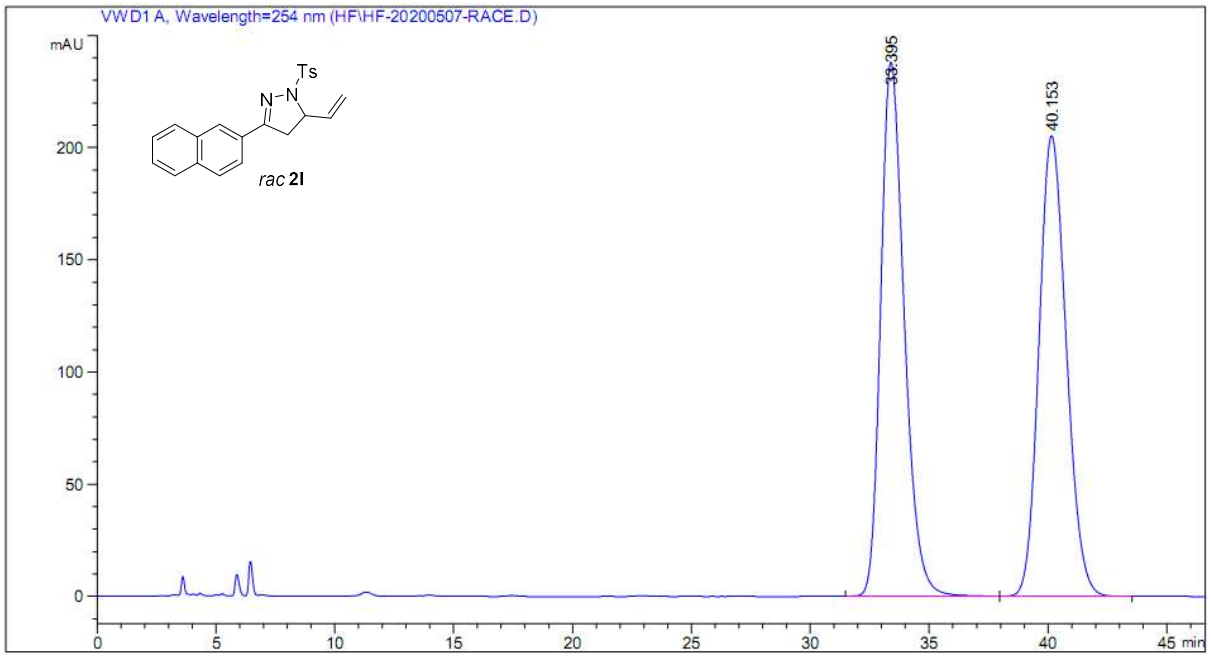

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.910 | 1.80977e4 | 468.50916 | 98.4584 |
| 2 | PDA 254 nm | 24.079 | 283.35599 | 6.34157 | 1.5416 |



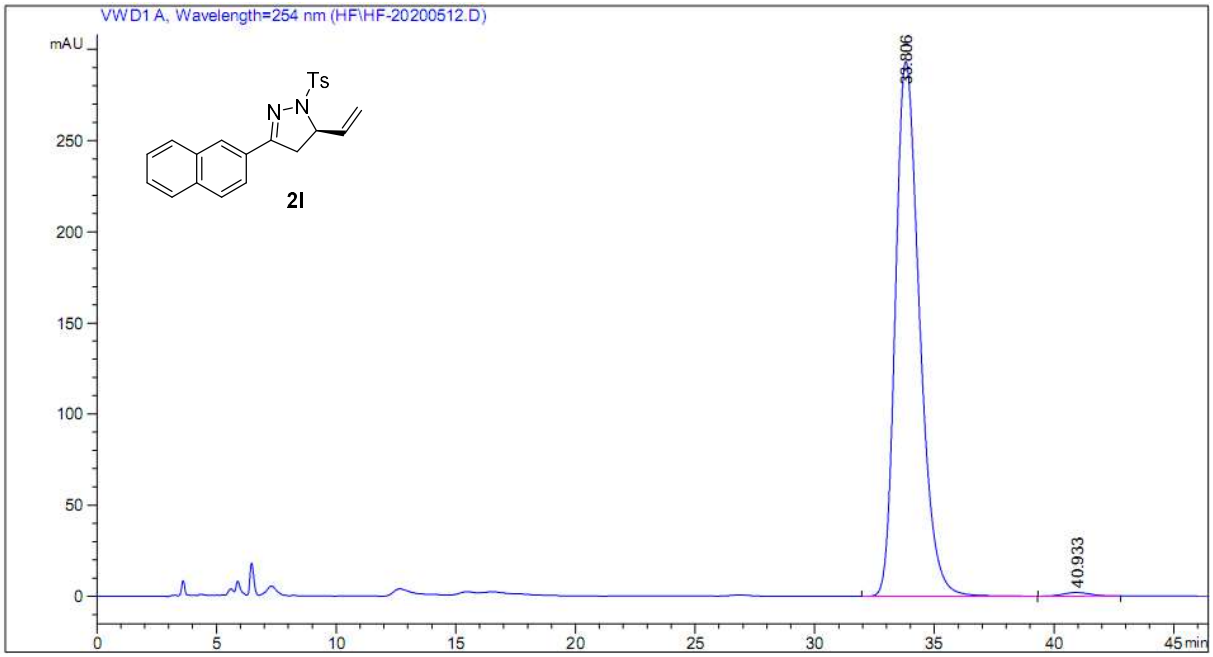

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 21.289 | 1.94571e4 | 485.52396 | 50.1488 |
| 2 | PDA 254 nm | 26.456 | 1.93416e4 | 375.70361 | 49.8512 |



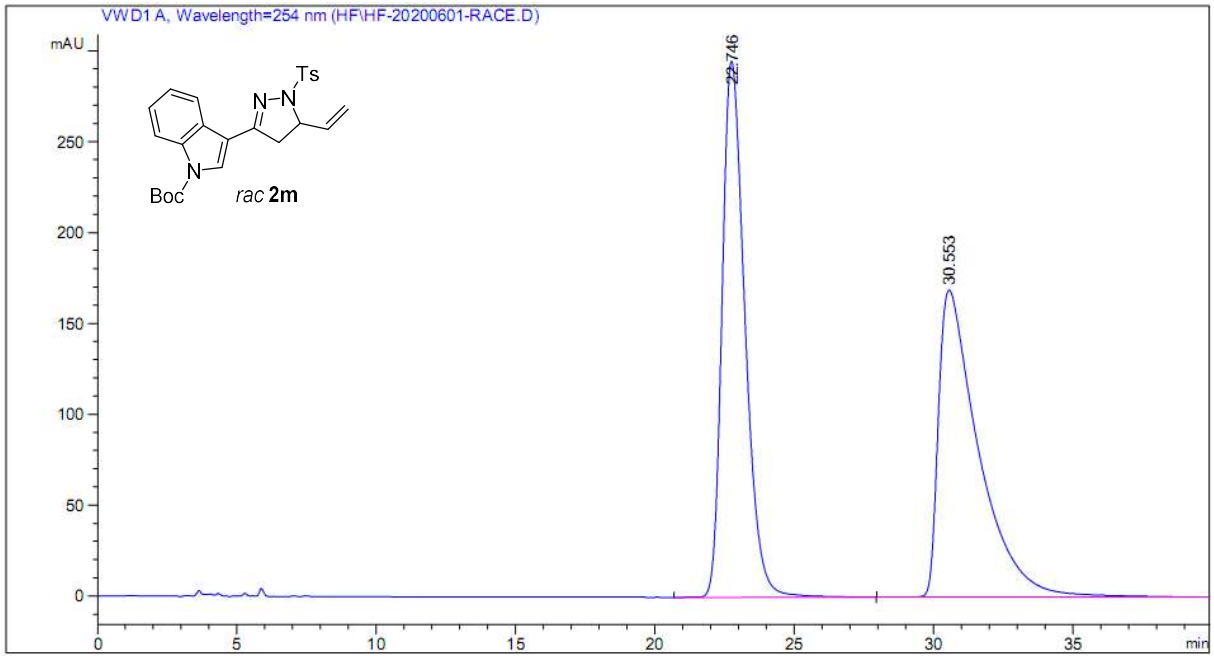

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 21.507 | 1966.74353 | 48.81145 | 5.3143 |
| 2 | PDA 254 nm | 26.629 | 3.50416e4 | 653.60272 | 94.6857 |



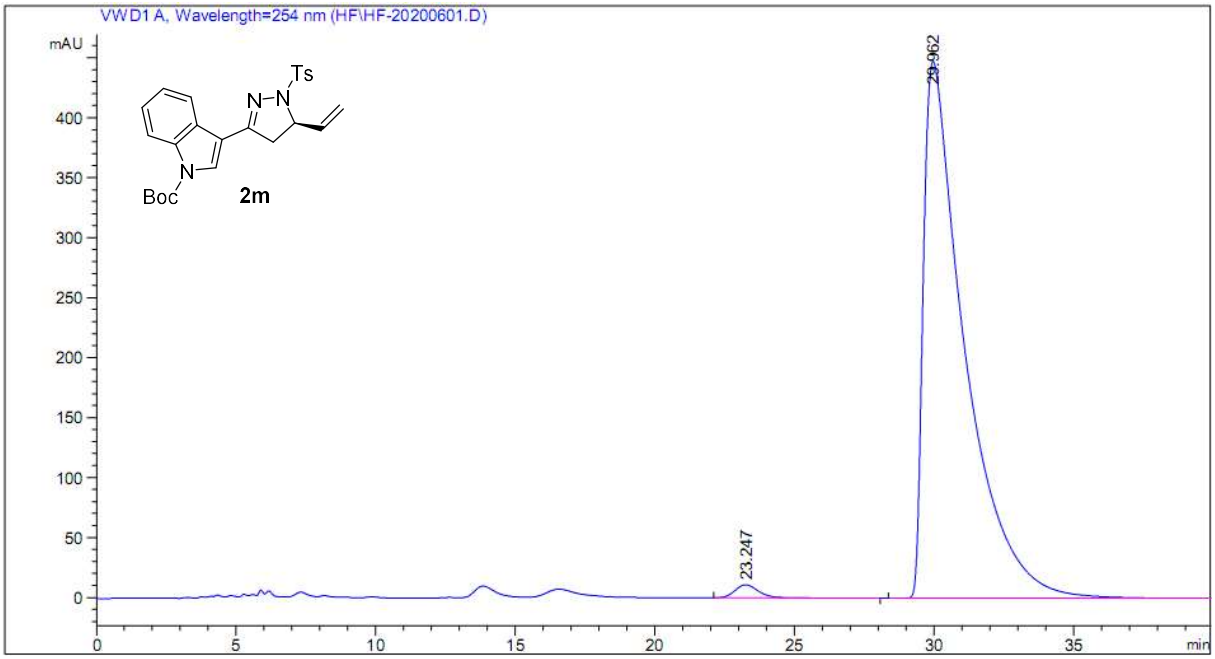

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 33.395 | 1.63527e4 | 238.01045 | 49.9865 |
| 2 | PDA 254 nm | 40.153 | 1.63616e4 | 205.29463 | 50.0135 |



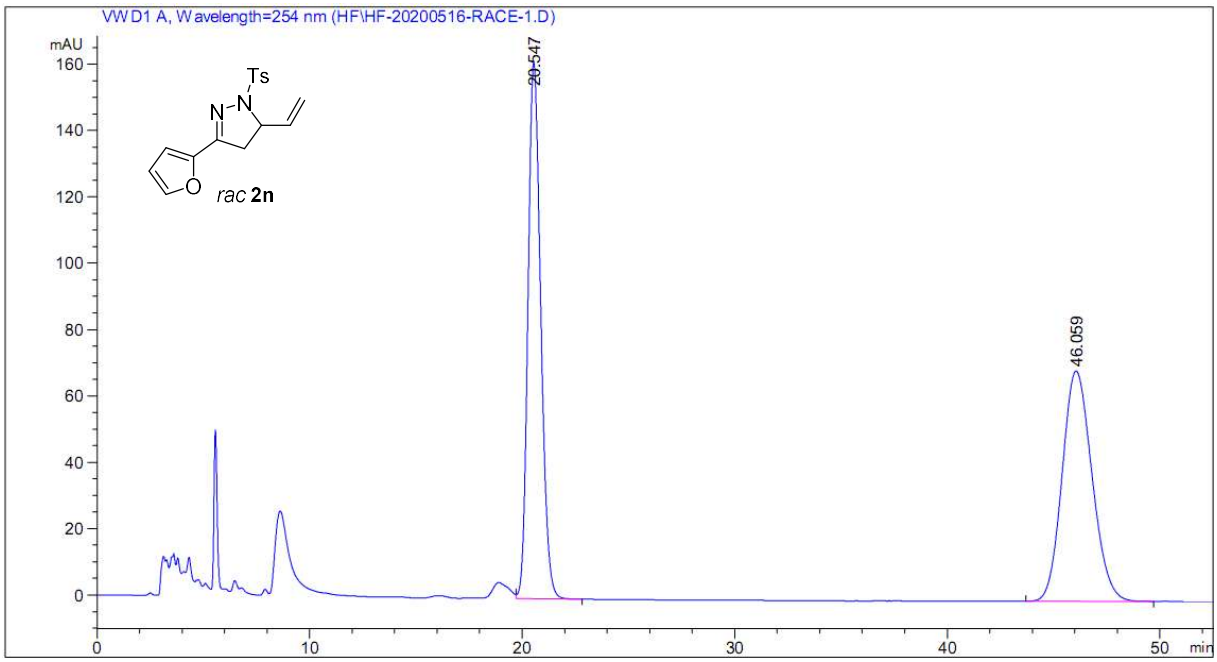

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 33.806 | 2.05620e4 | 293.59781 | 99.2595 |
| 2 | PDA 254 nm | 40.933 | 157.57225 | 2.00664 | 0.7405 |



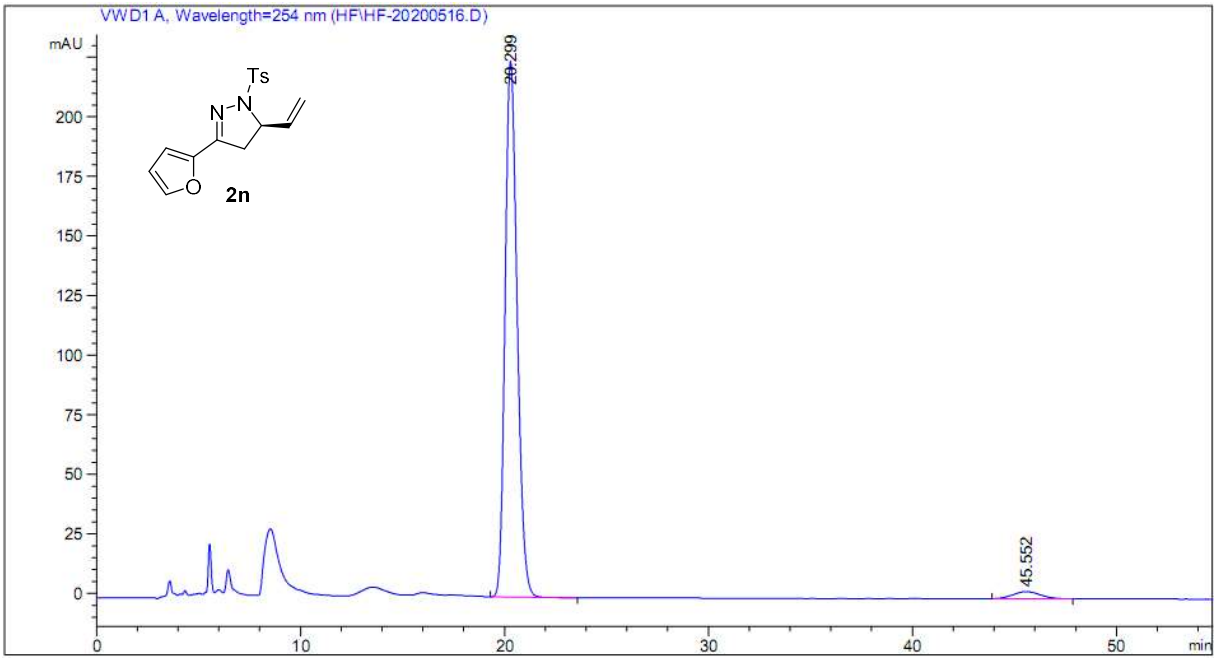

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 22.746 | 1.67712e4 | 294.92230 | 49.6924 |
| 2 | PDA 254 nm | 30.553 | 1.69788e4 | 169.03539 | 50.3076 |



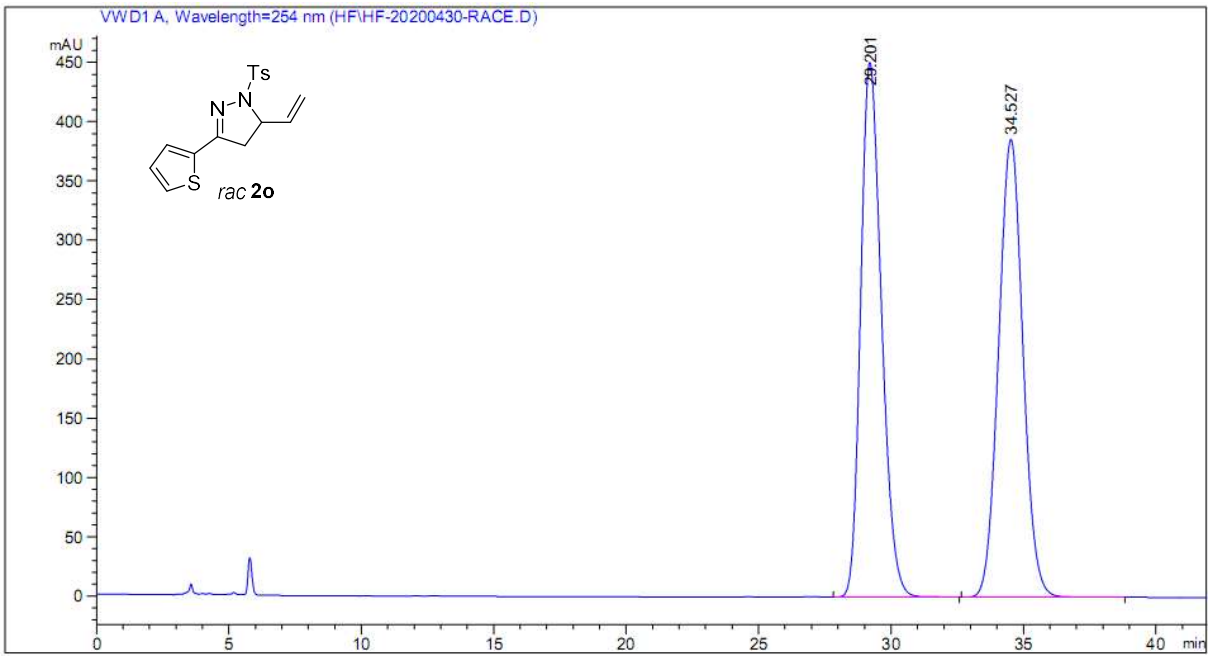

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.247 | 673.65228 | 10.97509 | 1.4463 |
| 2 | PDA 254 nm | 29.962 | 4.59040e4 | 447.61475 | 98.5537 |



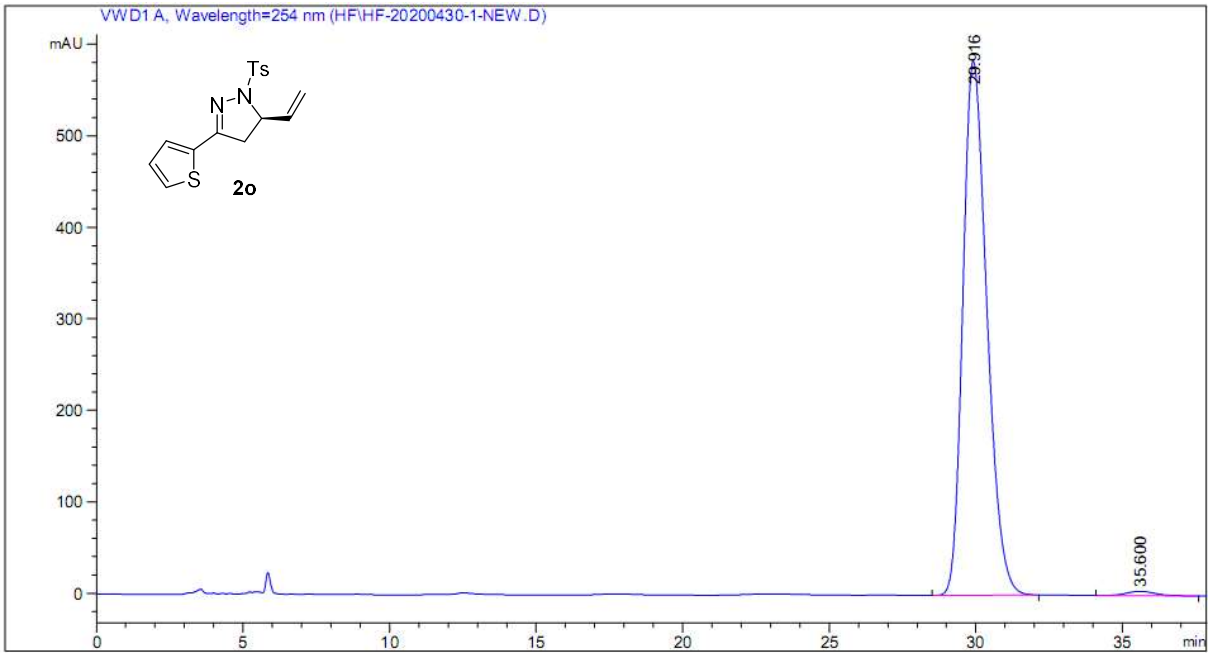

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 20.547 | 6756.59326 | 161.55437 | 49.9021 |
| 2 | PDA 254 nm | 46.059 | 6783.09131 | 69.43627 | 50.0979 |



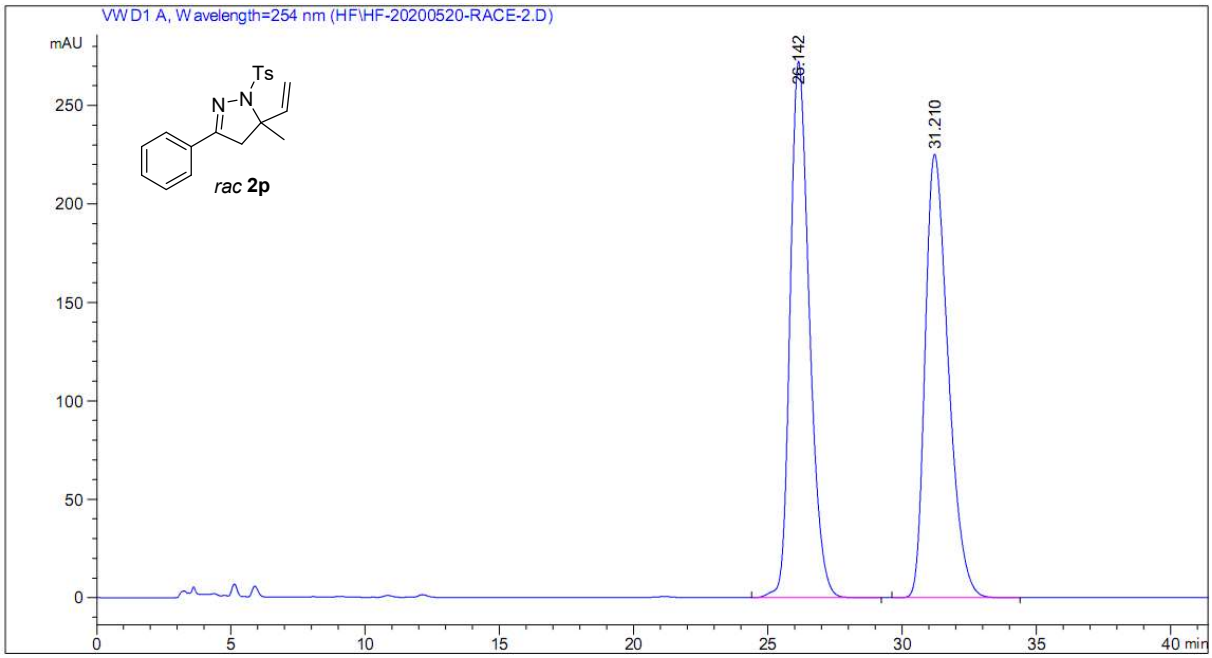

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 20.299 | 9243.96484 | 224.88922 | 97.0548 |
| 2 | PDA 254 nm | 45.552 | 280.51703 | 2.98567 | 2.9452 |



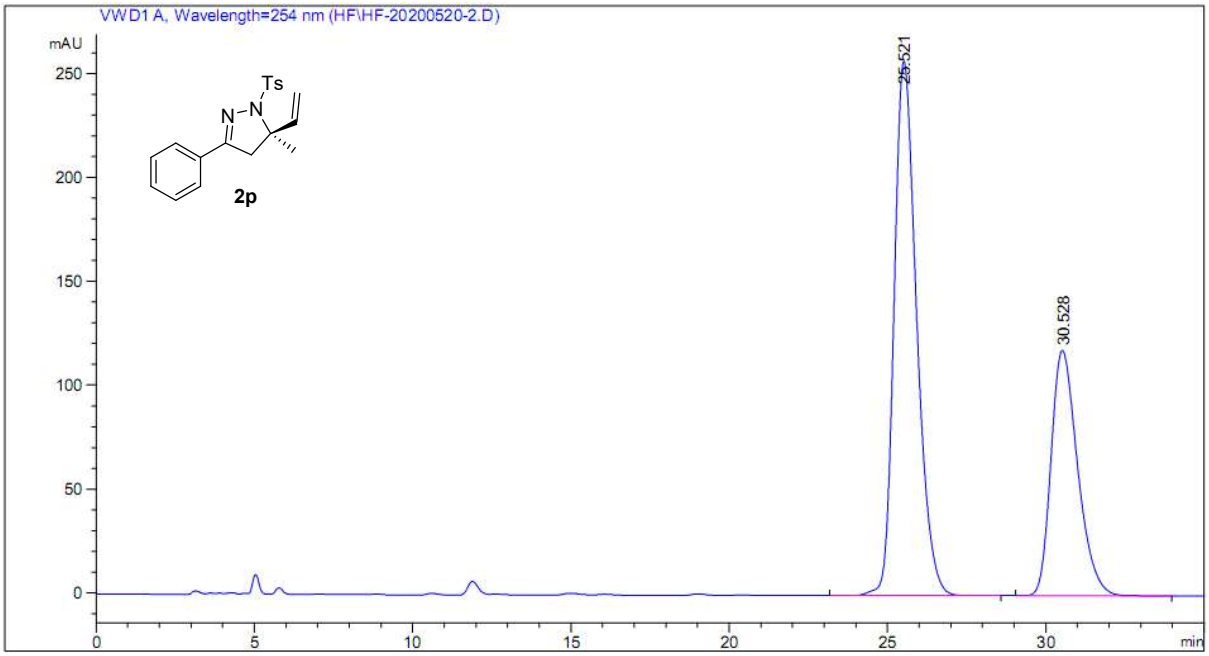

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 29.201 | 2.46311e4 | 450.95746 | 49.9760 |
| 2 | PDA 254 nm | 34.527 | 2.46548e4 | 386.06219 | 50.0240 |



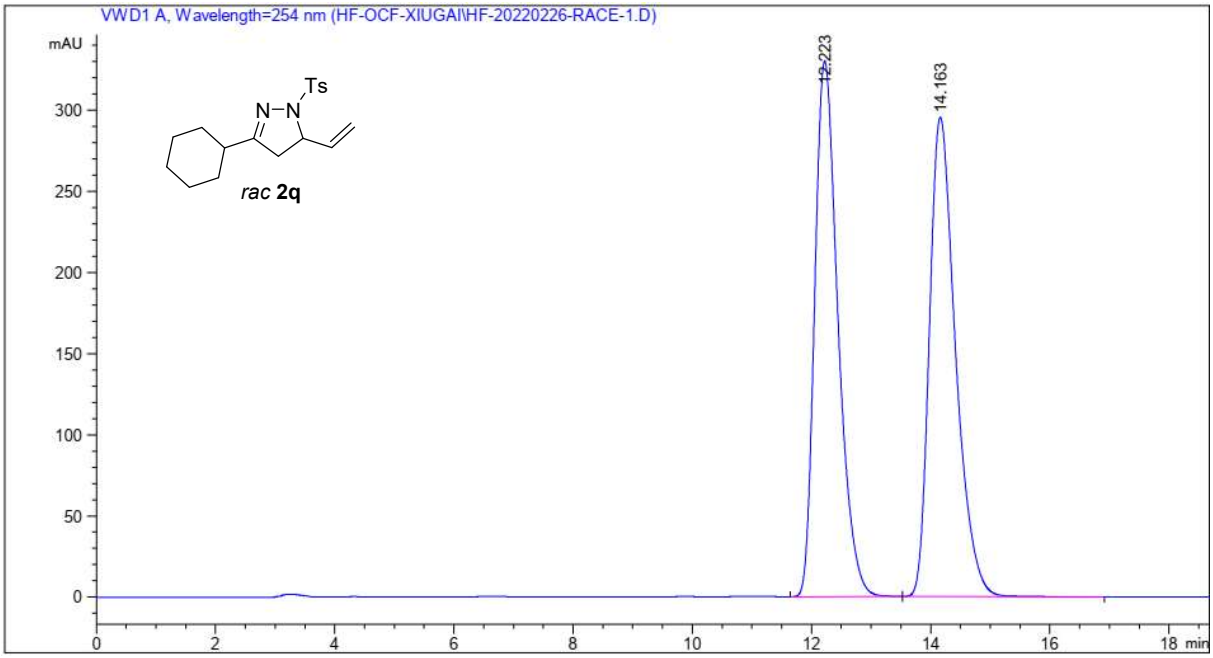

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 29.916 | 3.32195e4 | 583.60968 | 99.0617 |
| 2 | PDA 254 nm | 35.600 | 314.63745 | 4.75592 | 0.9383 |



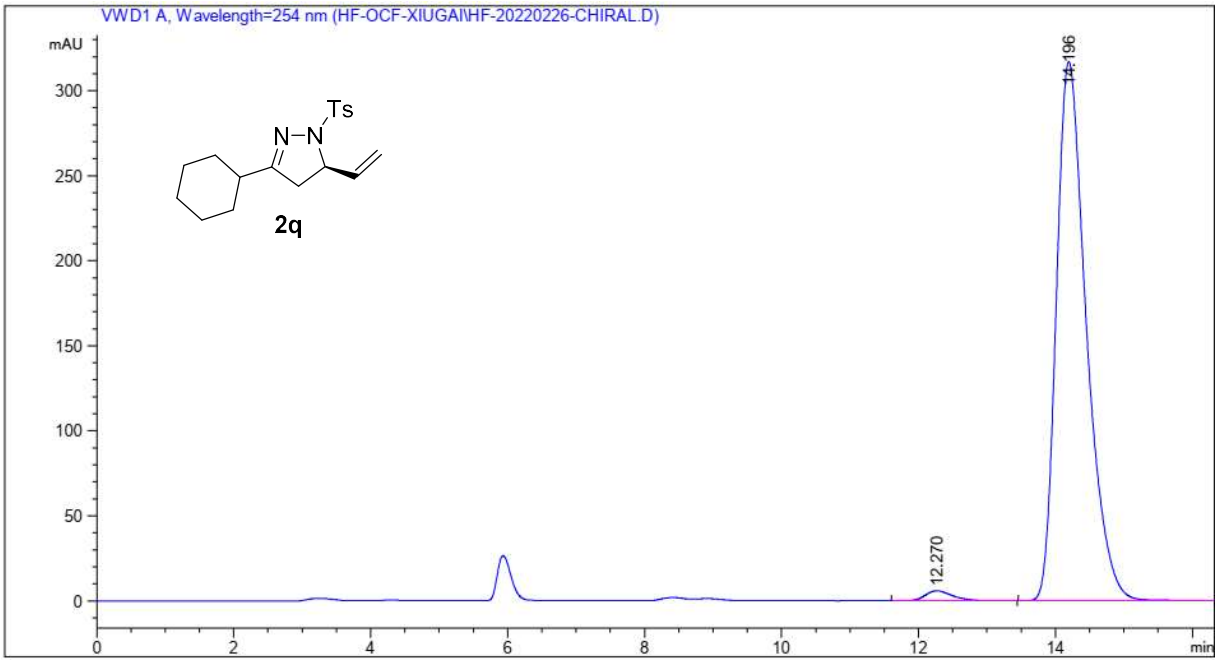

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 26.142 | 1.35700e4 | 272.39581 | 50.2693 |
| 2 | PDA 254 nm | 31.210 | 1.34246e4 | 225.19232 | 49.7307 |



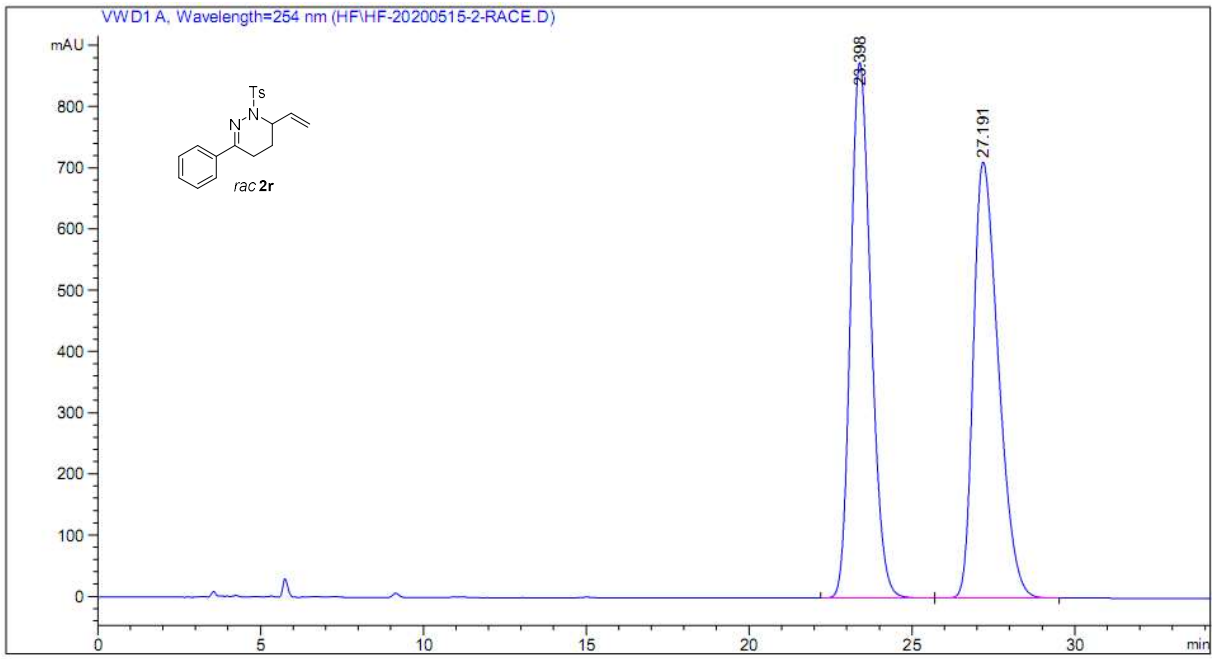

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 25.521 | 1.26995e4 | 257.25595 | 64.8141 |
| 2 | PDA 254 nm | 30.528 | 6894.23584 | 118.05122 | 35.1859 |



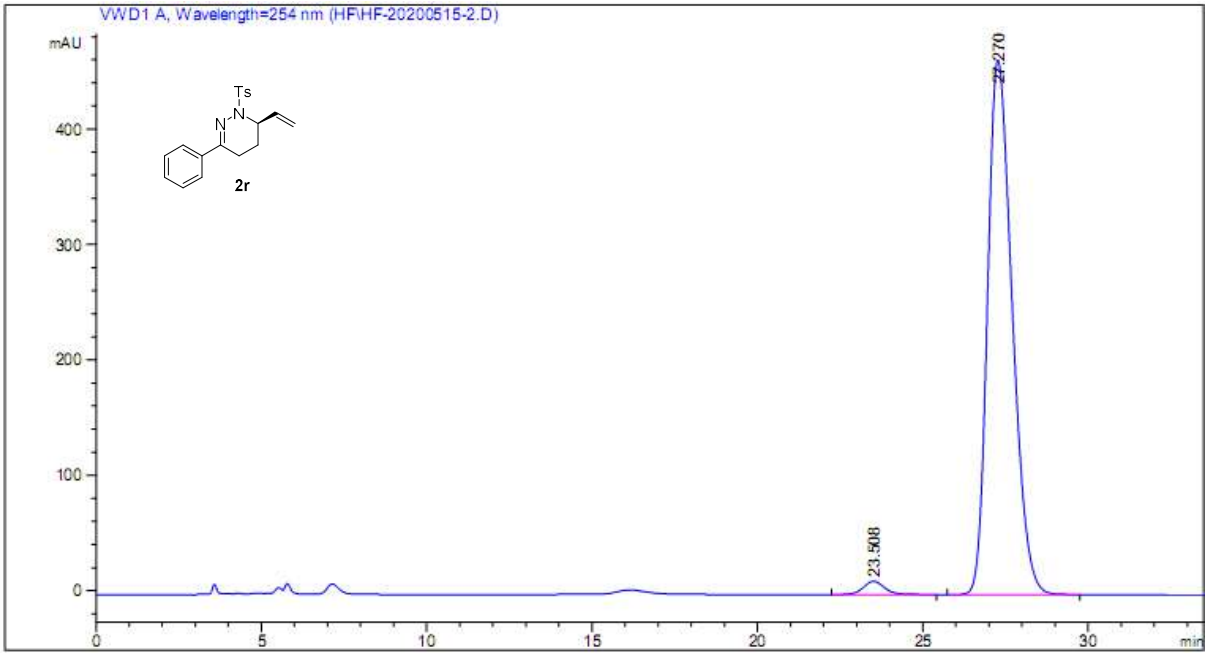

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 12.223 | 8919.99414 | 329.77625 | 49.8827 |
| 2 | PDA 254 nm | 14.163 | 8961.94141 | 295.20792 | 50.1173 |



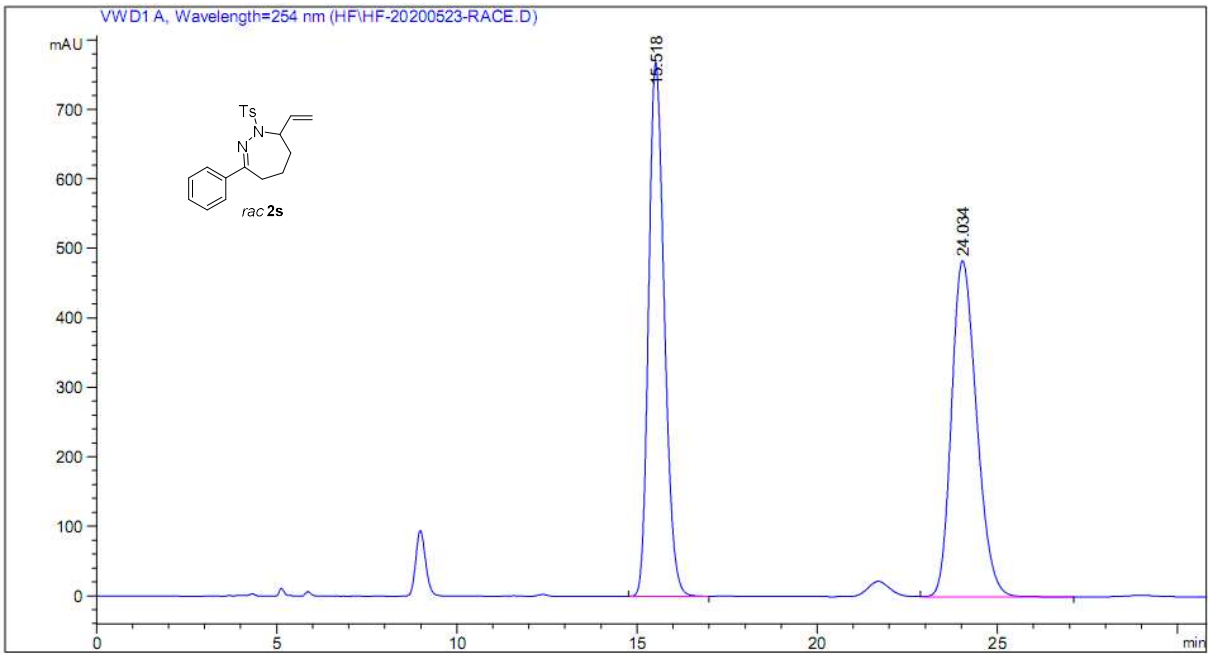

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 12.270 | 163.08018 | 5.88615 | 1.6670 |
| 2 | PDA 254 nm | 14.196 | 9620.04199 | 316.98193 | 98.3330 |



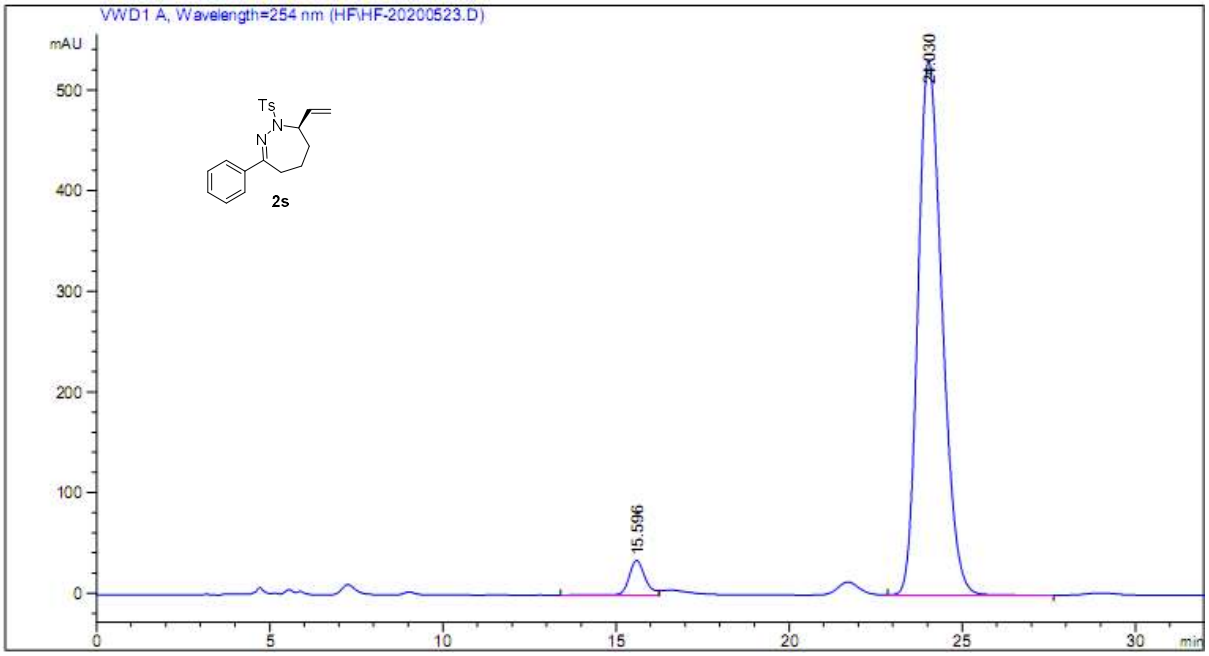

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.398 | 3.80032e4 | 874.99371 | 50.0360 |
| 2 | PDA 254 nm | 27.191 | 3.79485e4 | 712.33801 | 49.9640 |



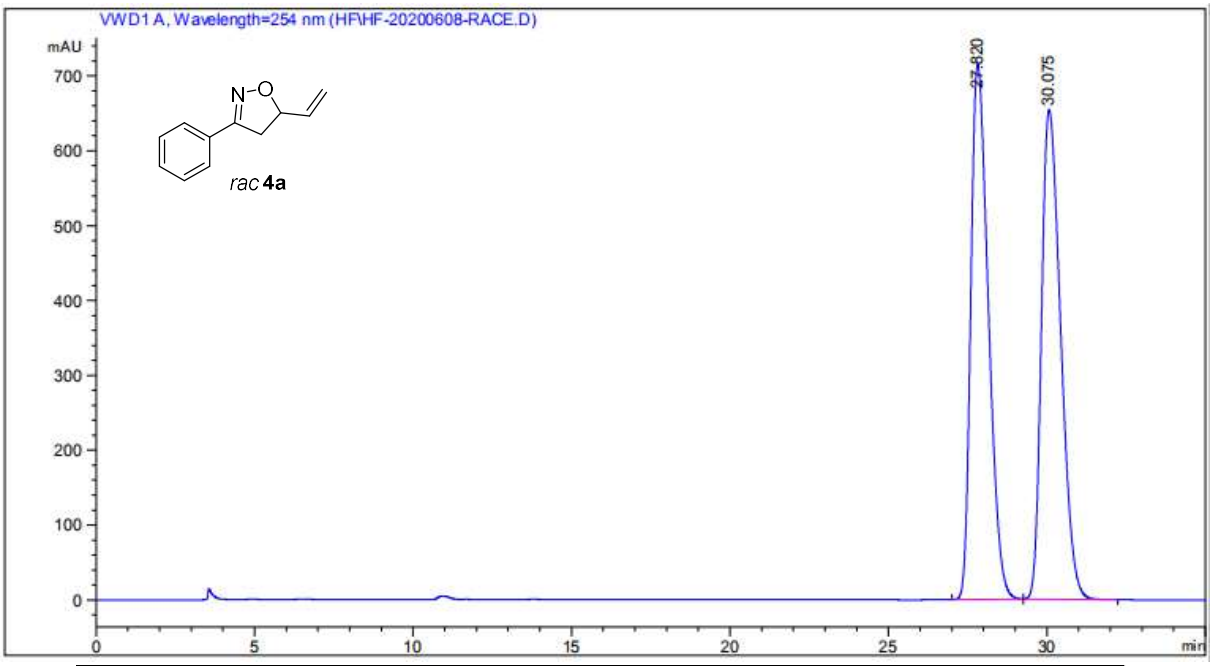

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 23.508 | 515.29761 | 11.50023 | 2.1125 |
| 2 | PDA 254 nm | 27.270 | 2.38773e4 | 462.84125 | 97.8875 |



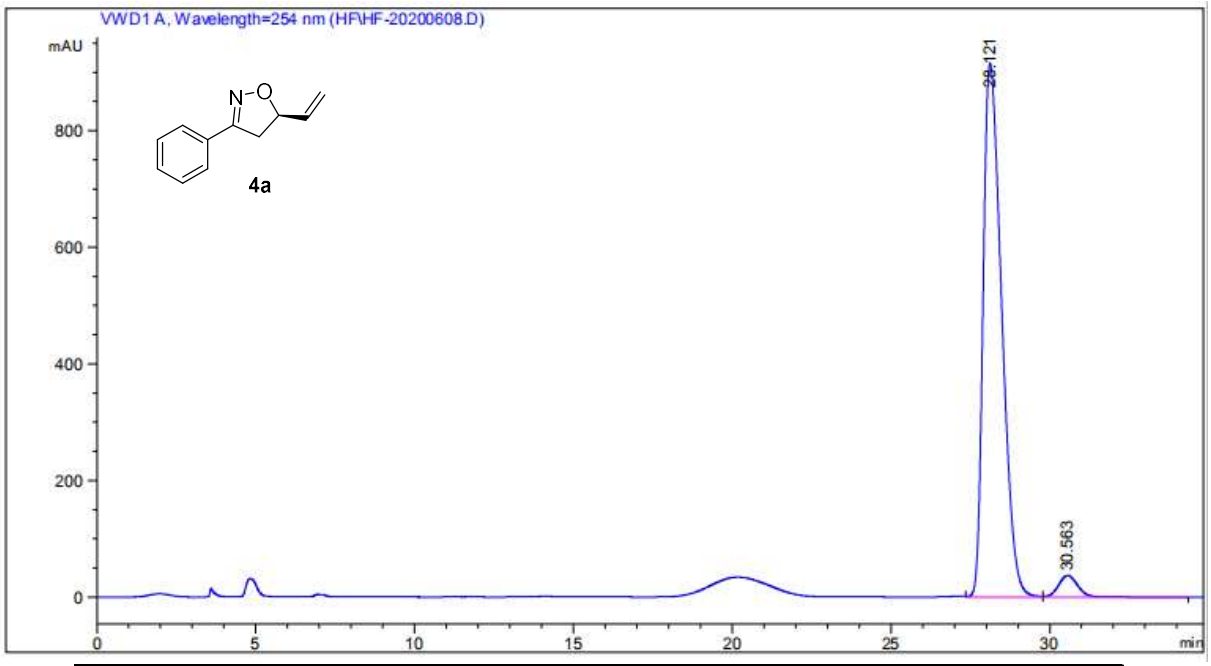

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 15.518 | 2.32929e4 | 769.38062 | 49.8565 |
| 2 | PDA 254 nm | 24.034 | 2.34271e4 | 483.71106 | 50.1435 |



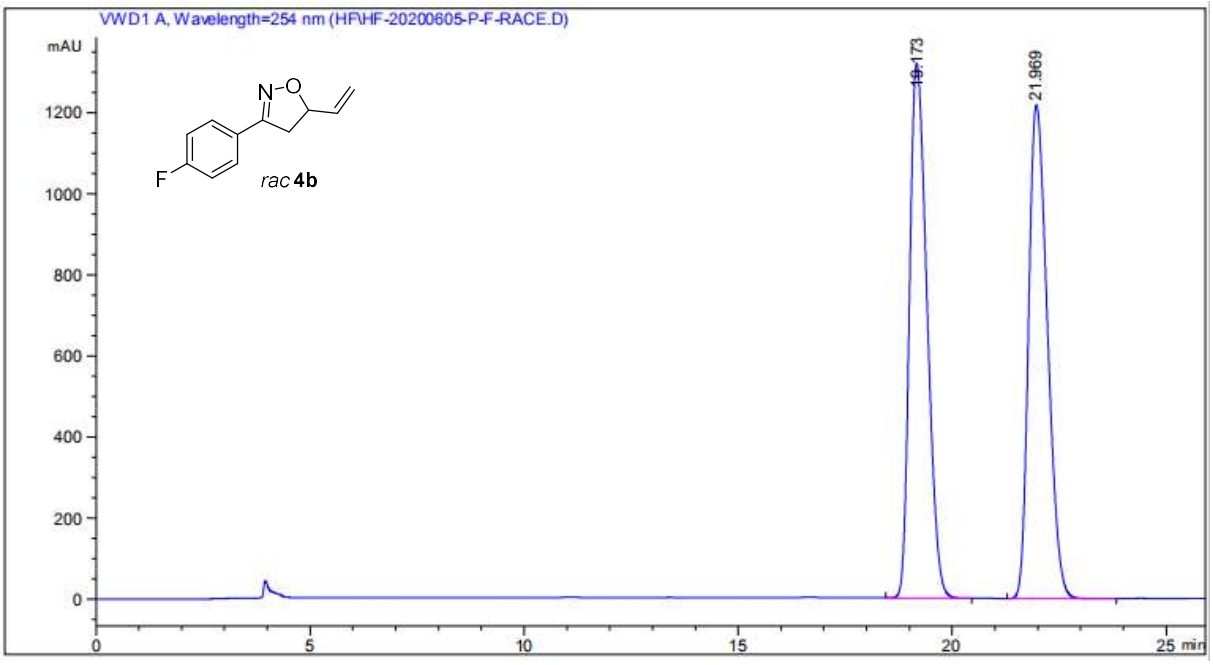

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 15.596 | 1096.22339 | 34.38272 | 4.1008 |
| 2 | PDA 254 nm | 24.030 | 2.56357e4 | 530.39777 | 95.8992 |



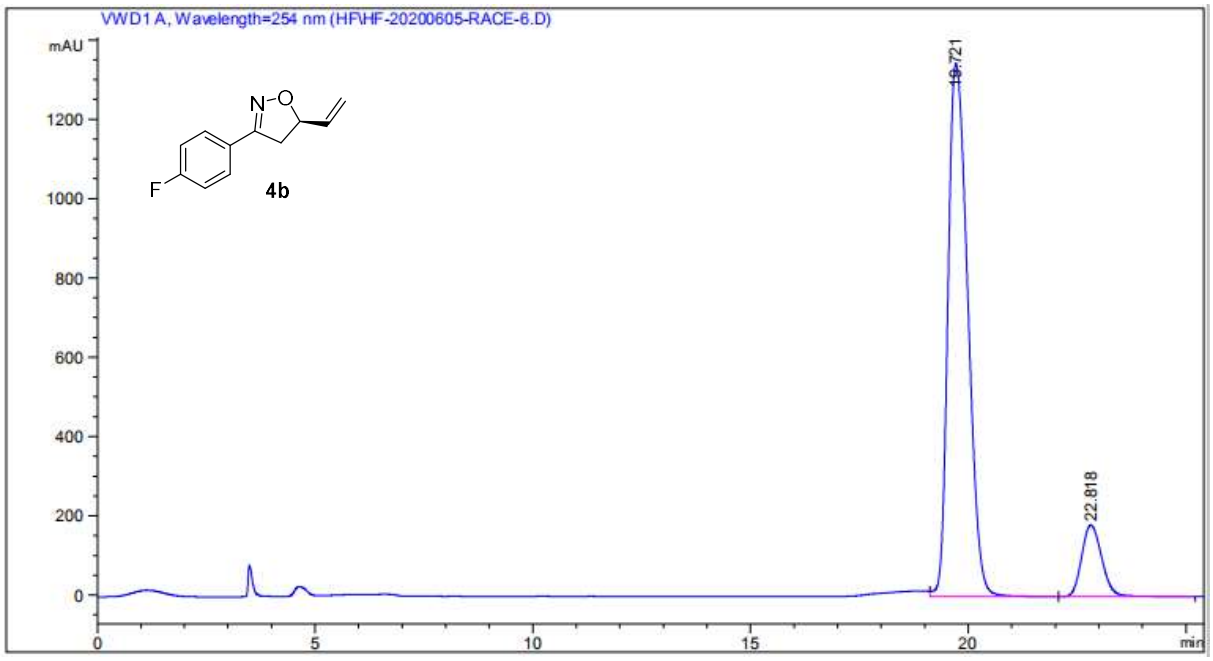

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 27.820 | 2.74864e4 | 714.84052 | 49.9697 |
| 2 | PDA 254 nm | 30.075 | 2.75197e4 | 653.80774 | 50.0303 |



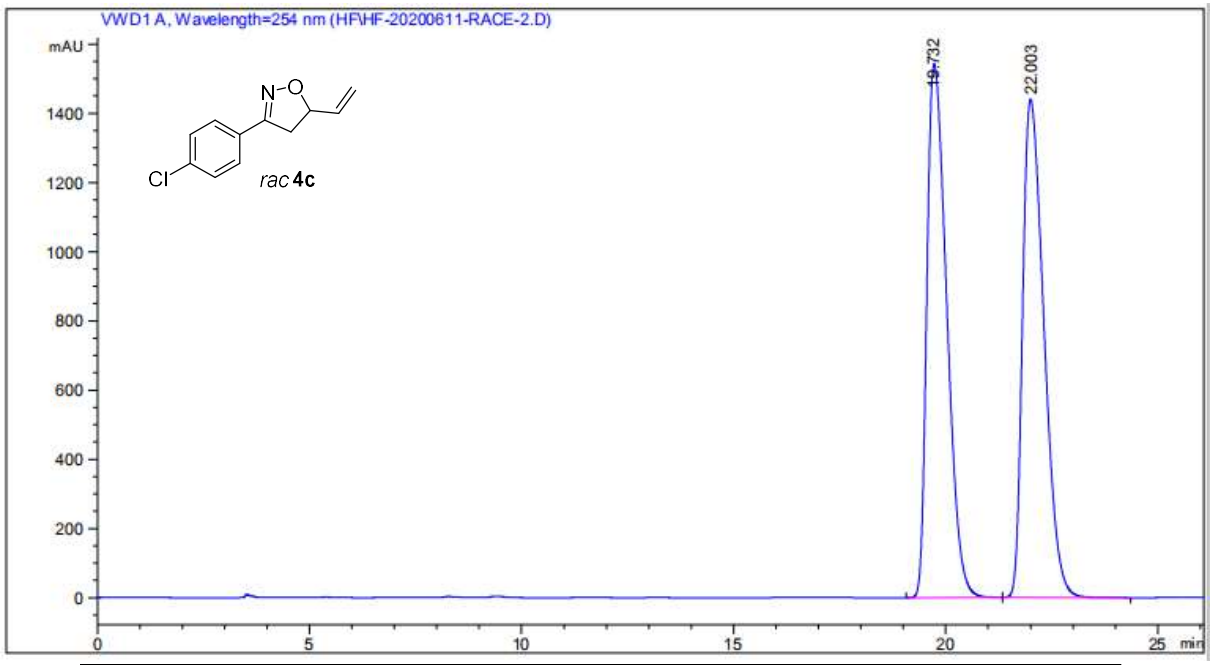

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 28.121 | 3.69333e4 | 914.74957 | 95.9805 |
| 2 | PDA 254 nm | 30.563 | 1546.69250 | 37.05835 | 4.0195 |



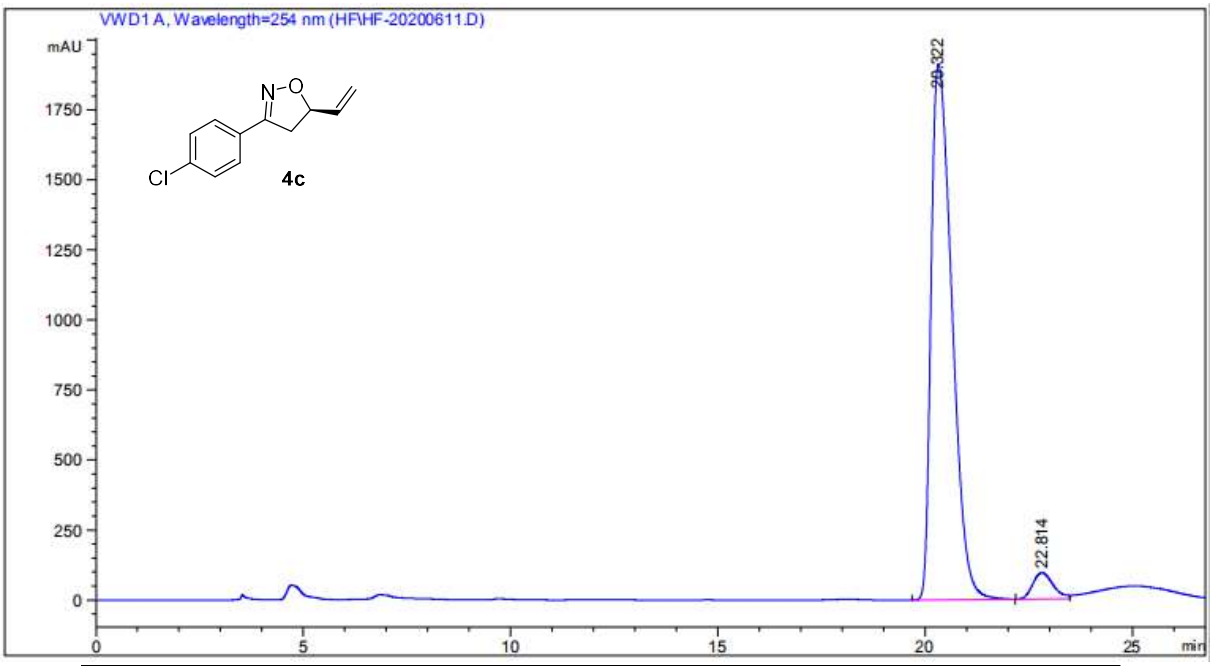

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.173 | 3.73125e4 | 1318.24670 | 50.1081 |
| 2 | PDA 254 nm | 21.969 | 3.71515e4 | 1218.15845 | 49.8919 |



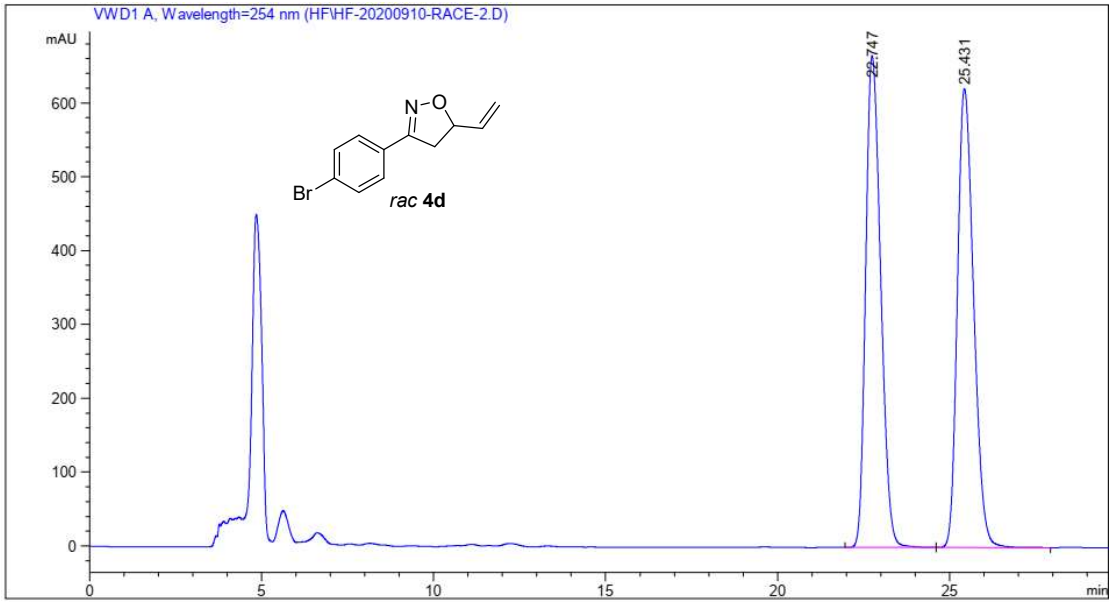

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.721 | 4.22978e4 | 1344.04138 | 87.9115 |
| 2 | PDA 254 nm | 22.818 | 5816.25781 | 180.42314 | 12.0885 |



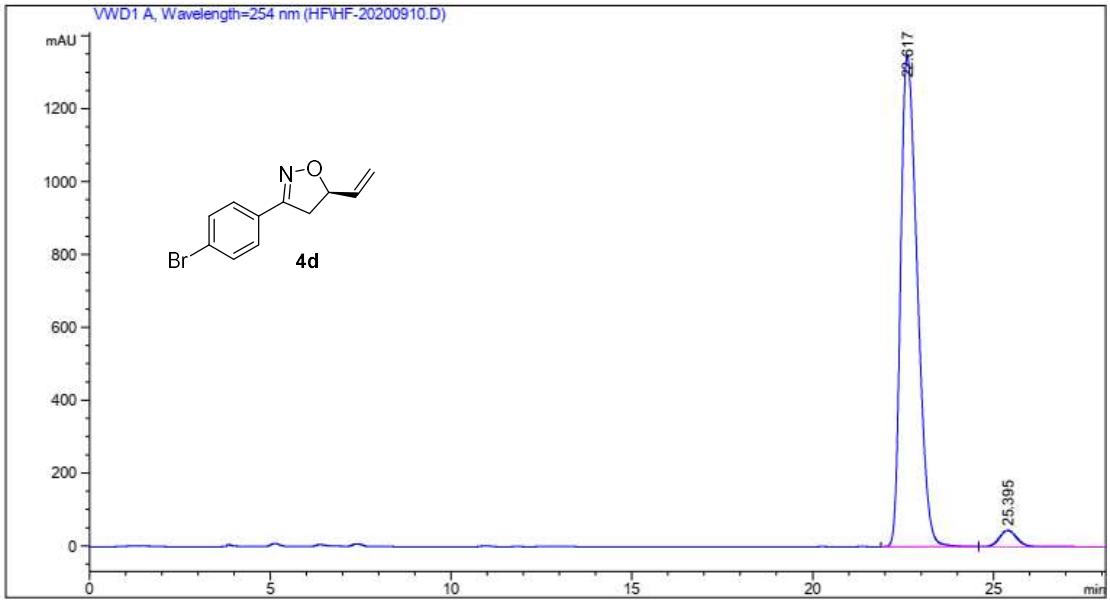

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.732 | 4.99934e4 | 1541.91064 | 49.9507 |
| 2 | PDA 254 nm | 22.003 | 5.00921e4 | 1439.00488 | 50.0493 |



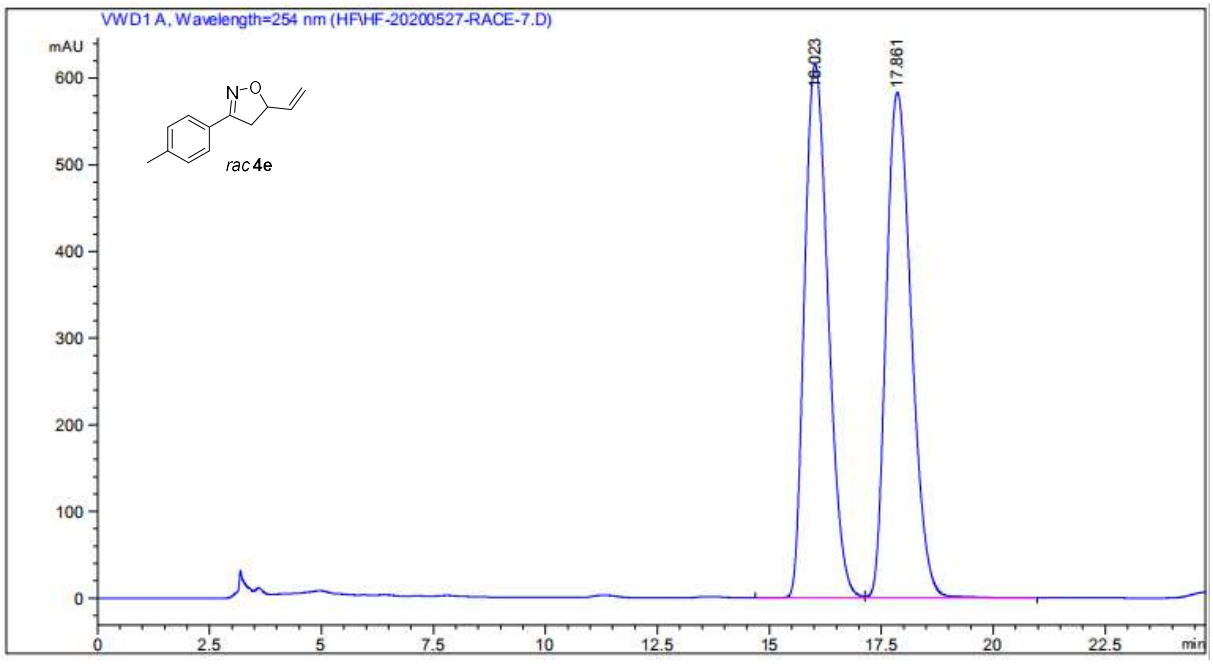

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 20.322 | 6.67856e4 | 1911.61597 | 95.3578 |
| 2 | PDA 254 nm | 22.814 | 3251.25952 | 94.14796 | 4.6422 |



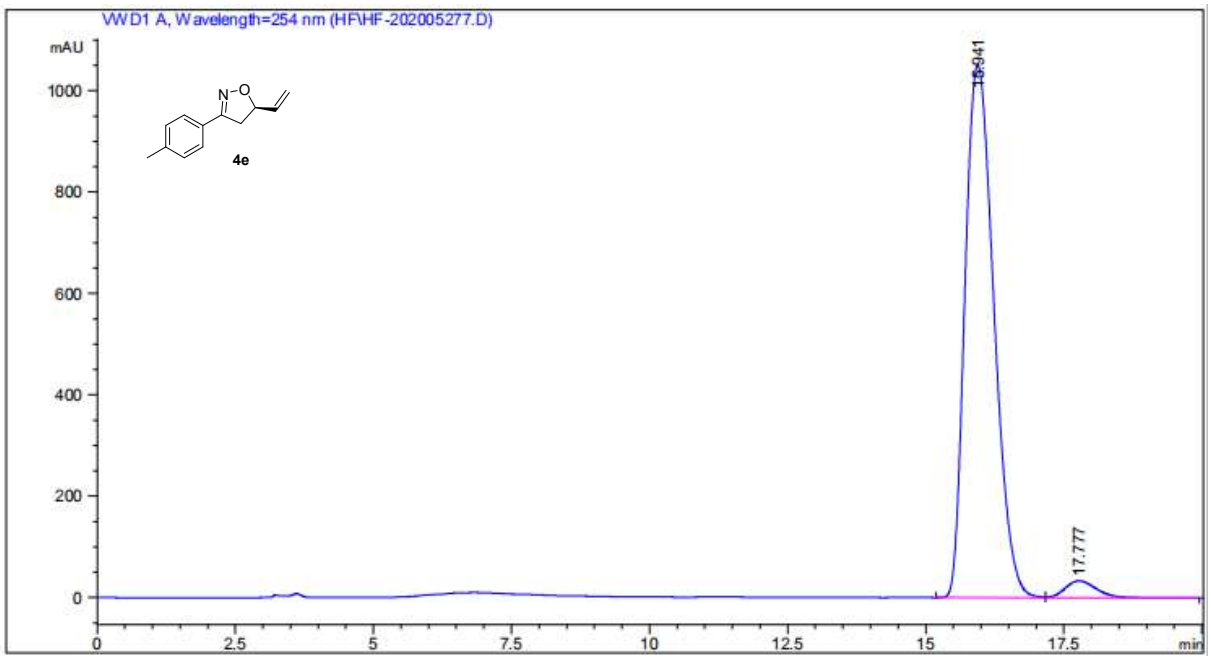

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 22.747 | 2.01724e4 | 665.94897 | 49.8013 |
| 2 | PDA 254 nm | 25.431 | 2.03334e4 | 621.40747 | 50.1987 |



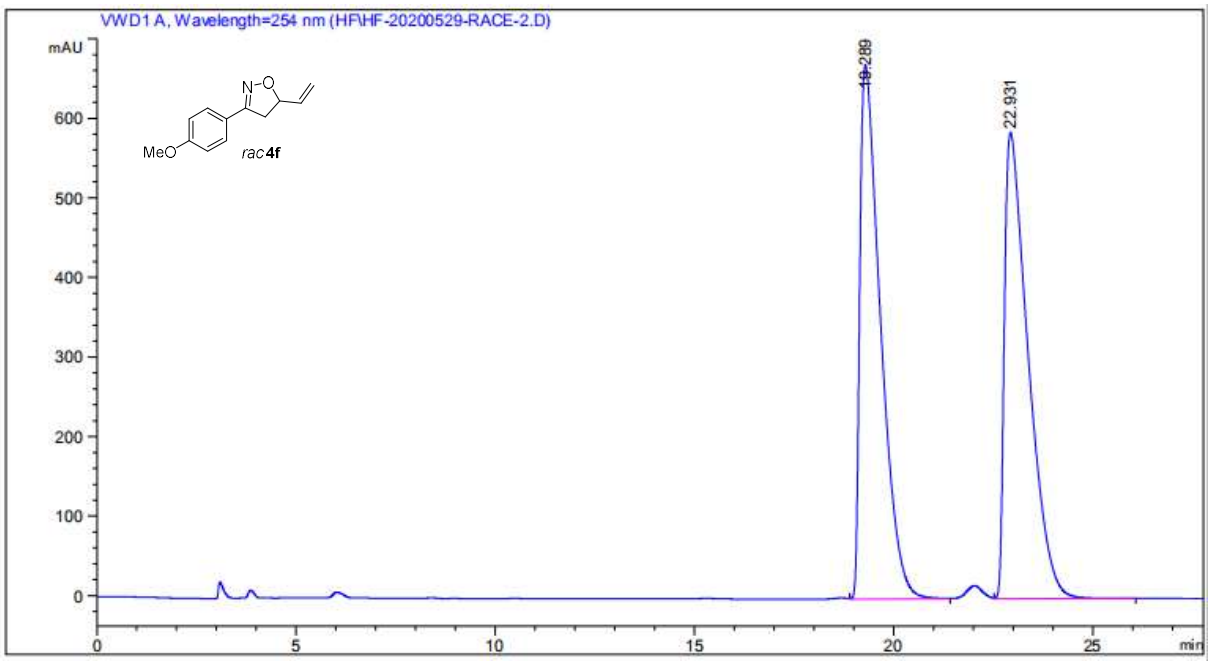

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 22.617 | 4.30791e4 | 1345.97412 | 96.6043 |
| 2 | PDA 254 nm | 25.395 | 1514.24365 | 44.72794 | 3.3957 |



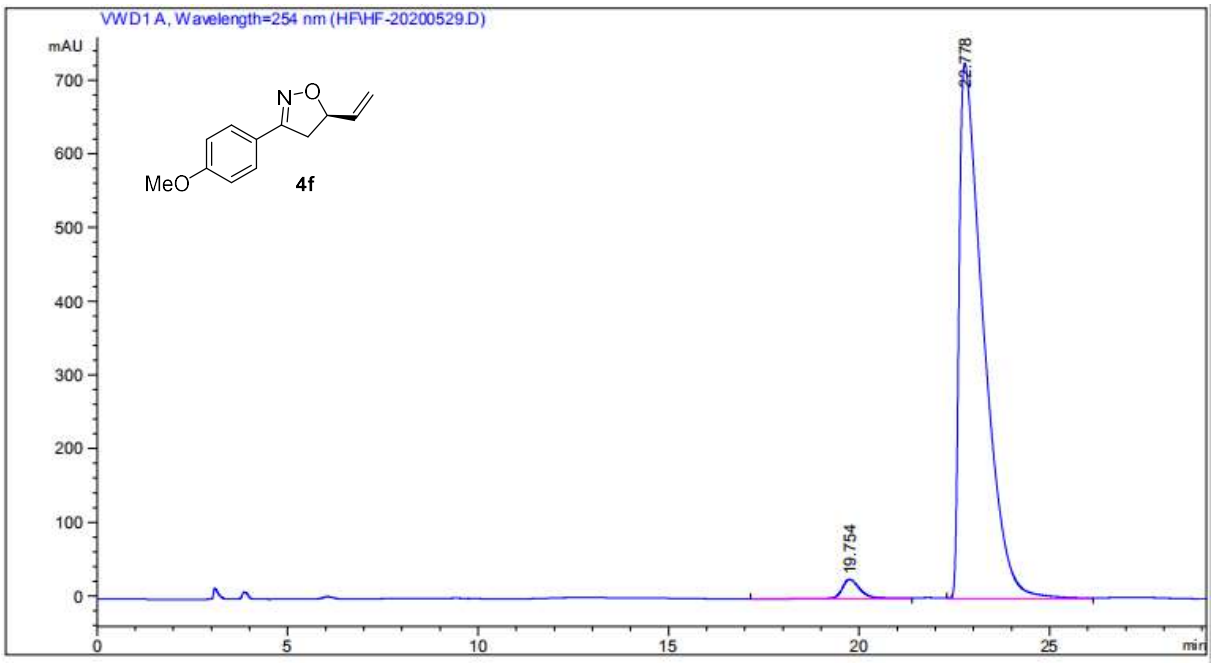

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 16.023 | 2.25727e4 | 616.26129 | 49.8096 |
| 2 | PDA 254 nm | 17.861 | 2.27453e4 | 583.22217 | 50.1904 |



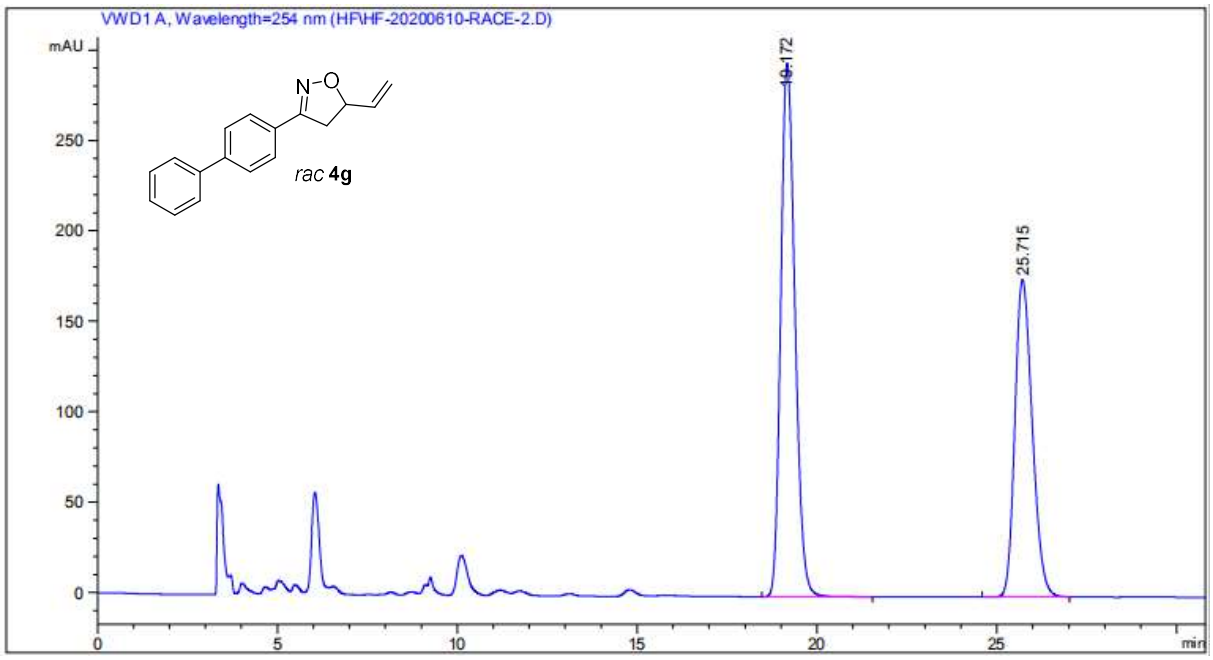

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 15.941 | 3.79763e4 | 1050.81470 | 96.7582 |
| 2 | PDA 254 nm | 17.777 | 1284.52844 | 33.05643 | 3.2418 |



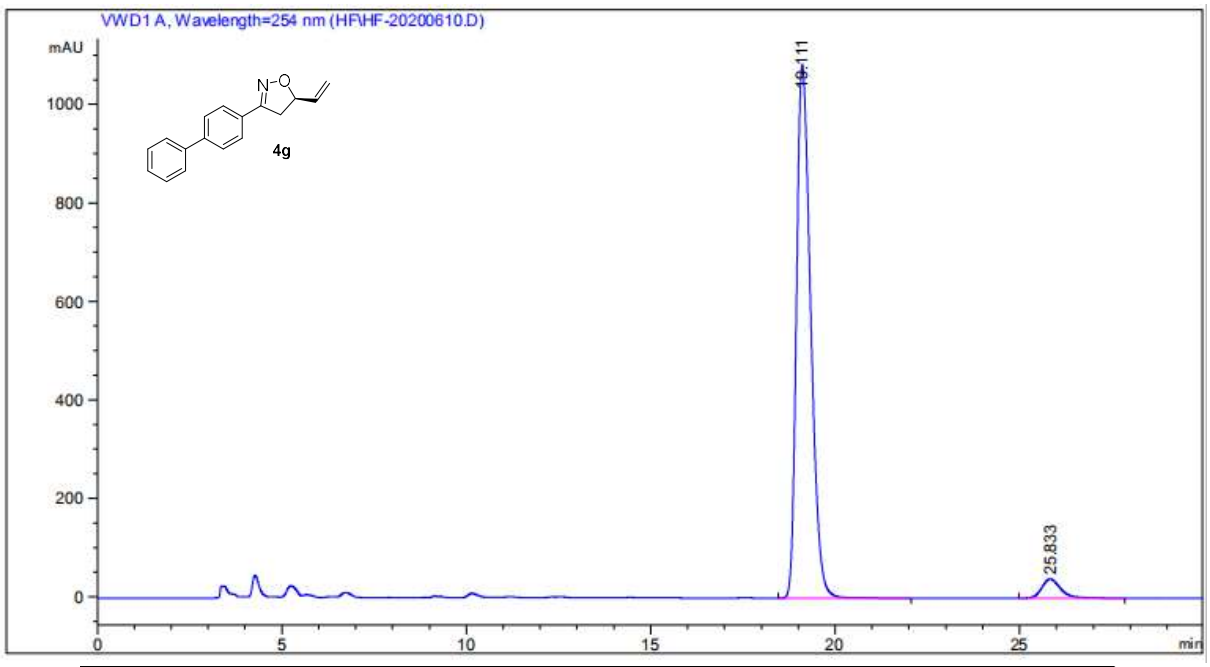

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.289 | 2.41663e4 | 671.07513 | 49.9955 |
| 2 | PDA 254 nm | 22.931 | 2.41707e4 | 585.51563 | 50.0045 |



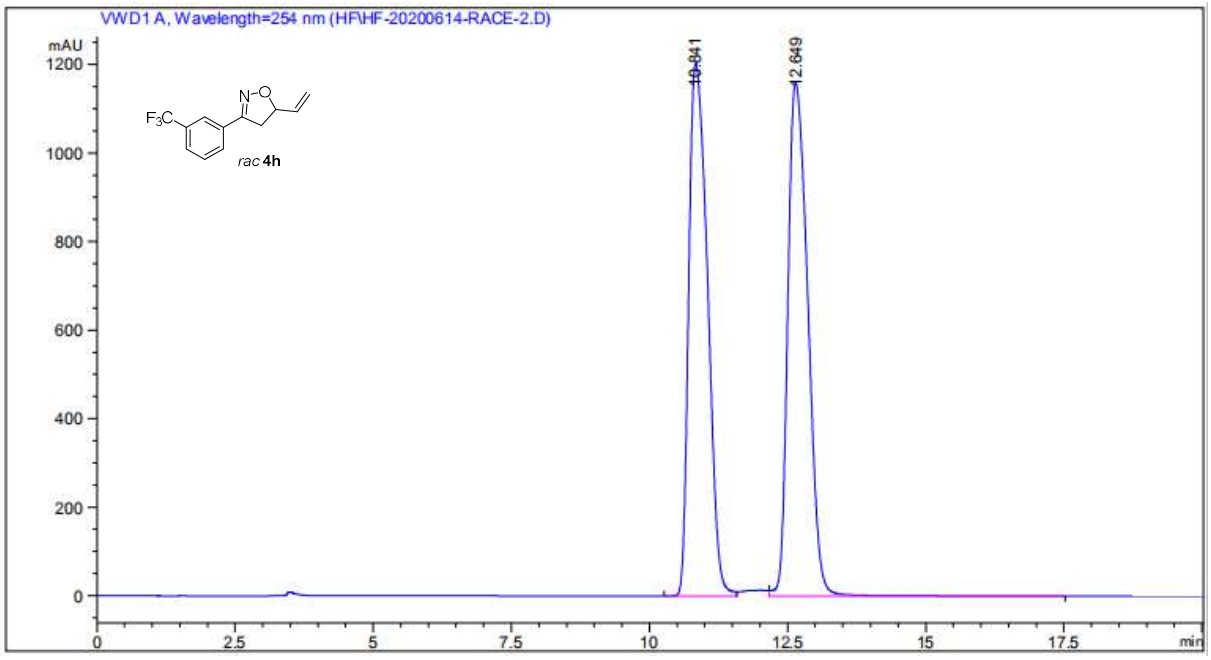

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.754 | 977.97791 | 26.58458 | 2.9630 |
| 2 | PDA 254 nm | 22.778 | 3.20280e4 | 726.07227 | 97.0370 |



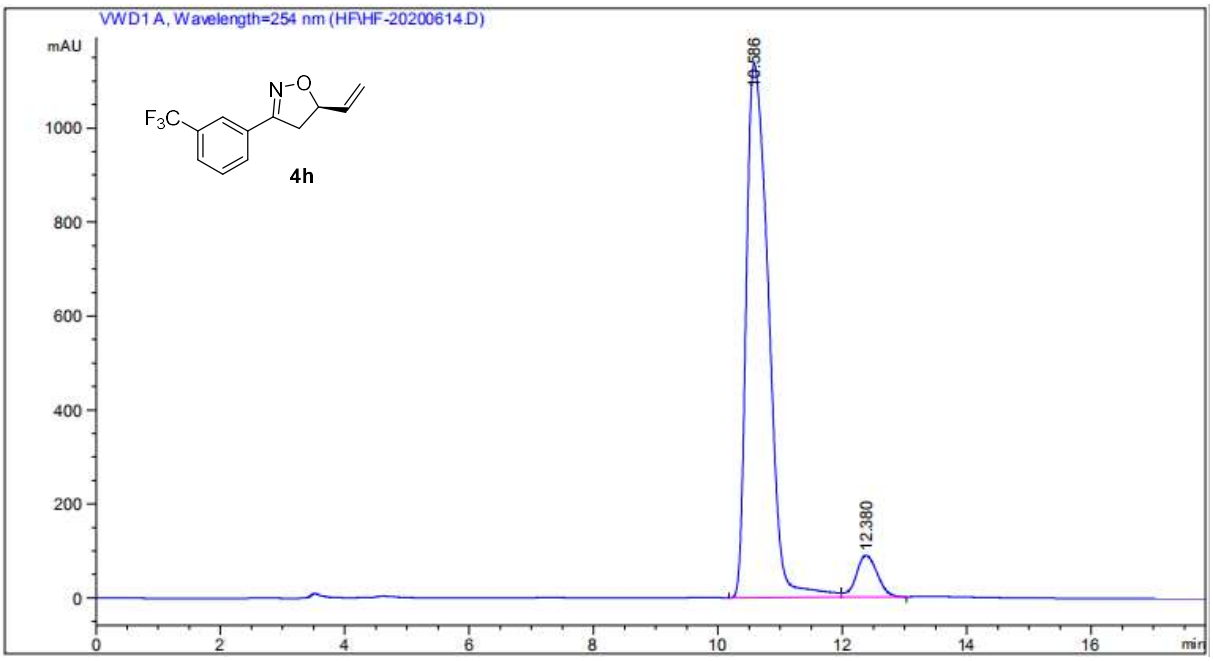

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.172 | 8072.64502 | 294.77164 | 57.7978 |
| 2 | PDA 254 nm | 25.715 | 5894.39160 | 175.55519 | 42.2022 |



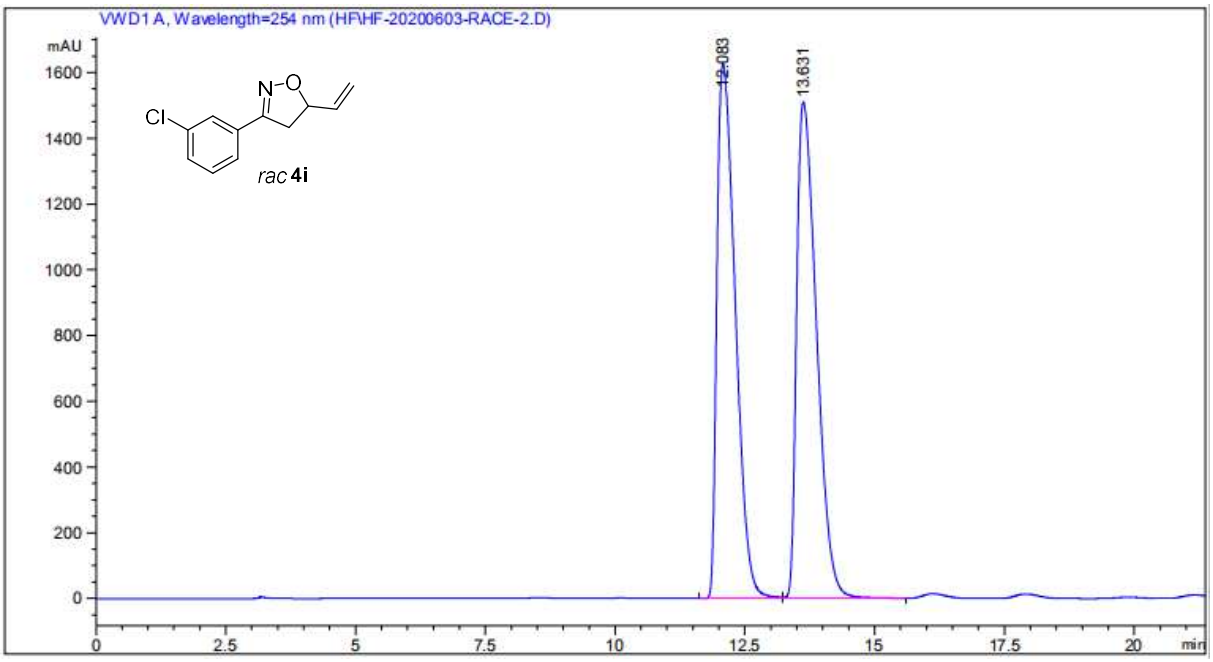

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 19.111 | 2.88379e4 | 1082.38330 | 95.4989 |
| 2 | PDA 254 nm | 25.833 | 1359.19348 | 38.61534 | 4.5011 |



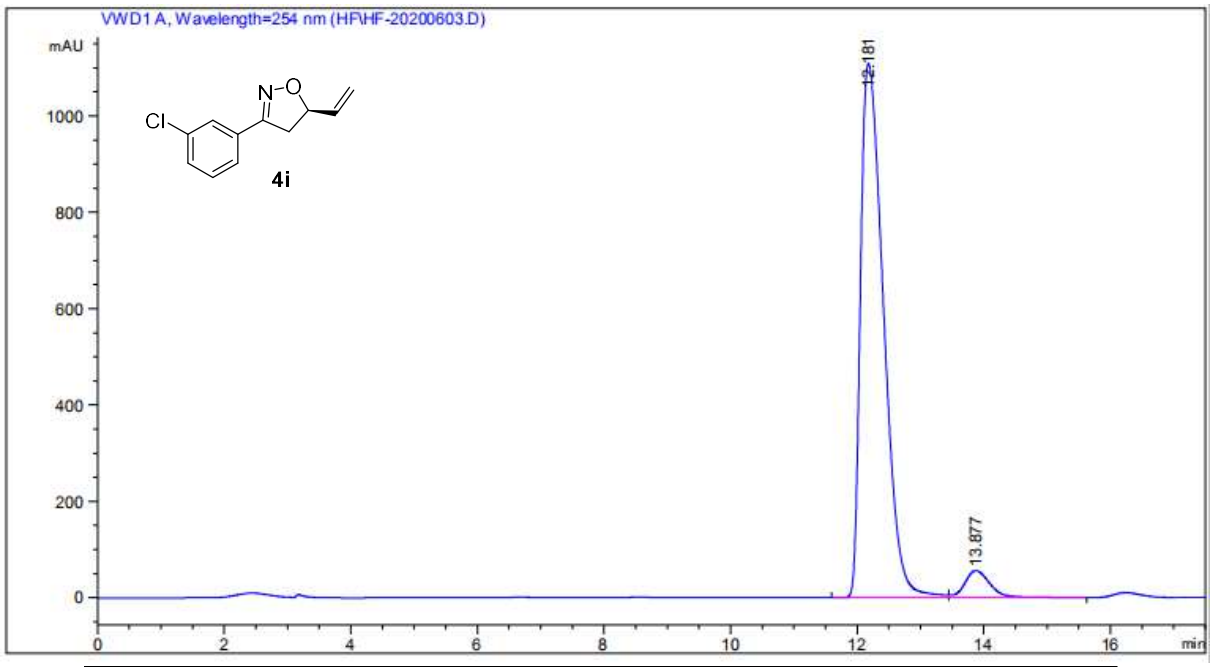

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254.16 nm | 10.841 | 2.83099e4 | 1202.91553 | 49.3771 |
| 2 | PDA 254.16 nm | 12.649 | 2.90241e4 | 1159.57361 | 50.6229 |



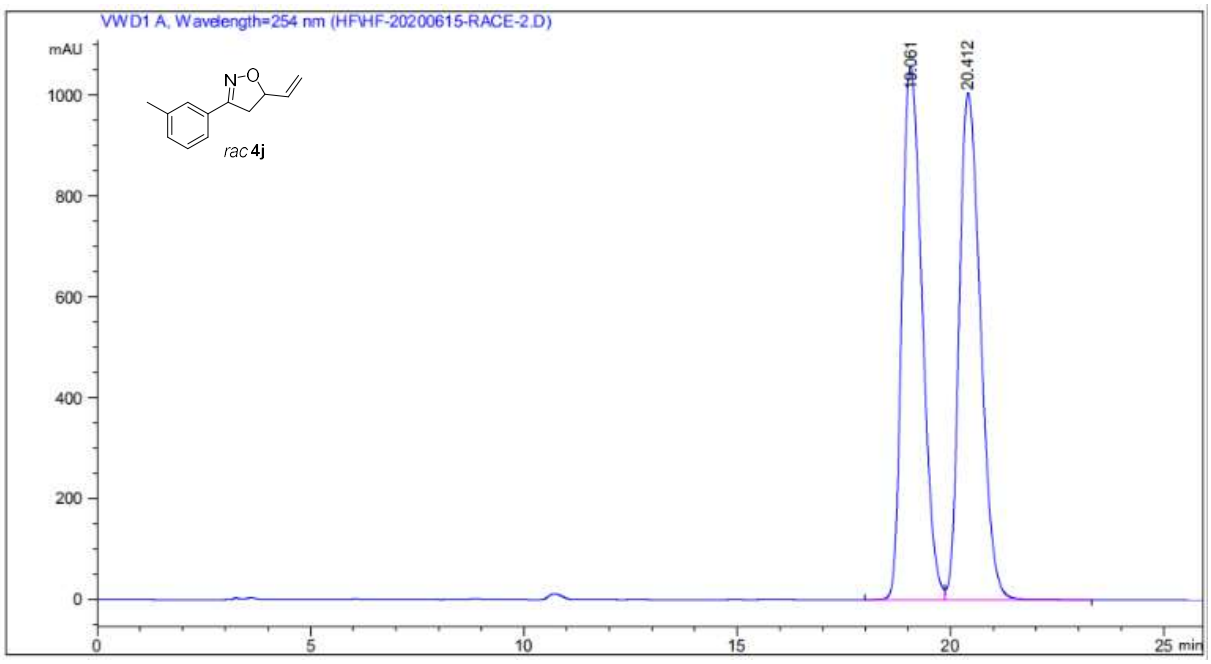

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254.16 nm | 10.586 | 2.80144e4 | 1135.48071 | 93.0330 |
| 2 | PDA 254.16 nm | 12.380 | 2097.93384 | 88.99281 | 6.9670 |



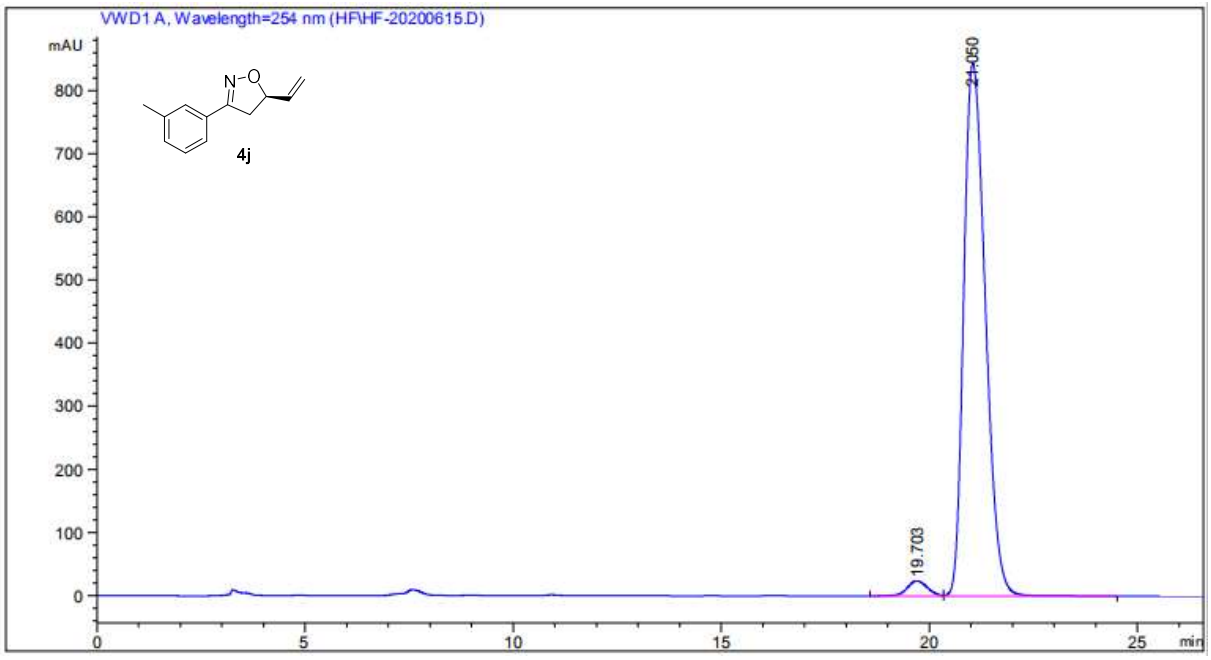

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 12.083 | 3.99314e4 | 1626.16687 | 49.8125 |
| 2 | PDA 254 nm | 13.631 | 4.02319e4 | 1510.26746 | 50.1875 |



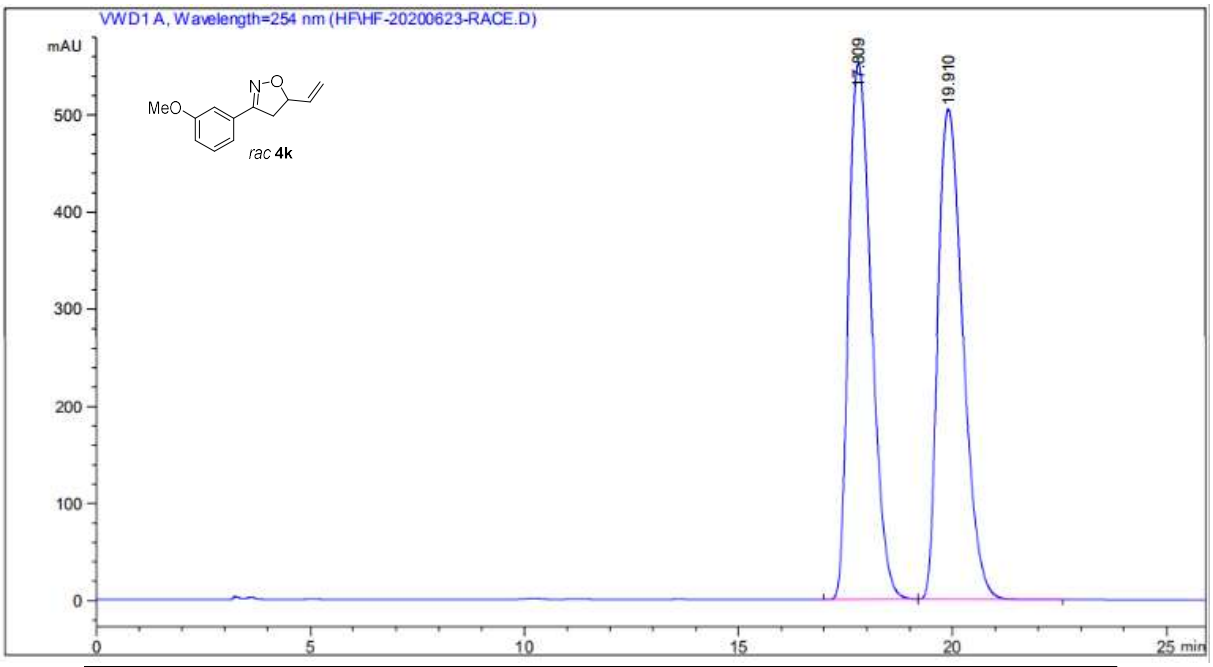

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 12.181 | 2.79276e4 | 1108.96167 | 94.5672 |
| 2 | PDA 254 nm | 13.877 | 1604.41321 | 56.15255 | 5.4328 |



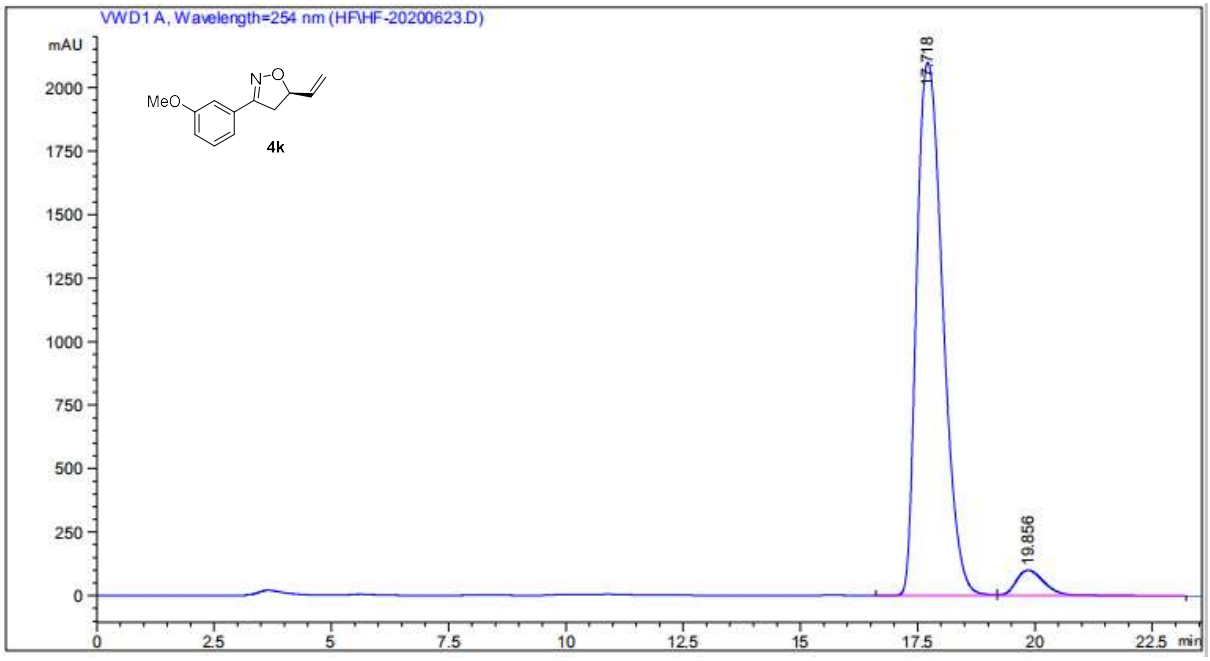

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 19.061 | 3.45227e4 | 1056.47290 | 49.8475 |
| 2 | PDA 254 nm | 20.412 | 3.47340e4 | 1004.29309 | 50.1525 |



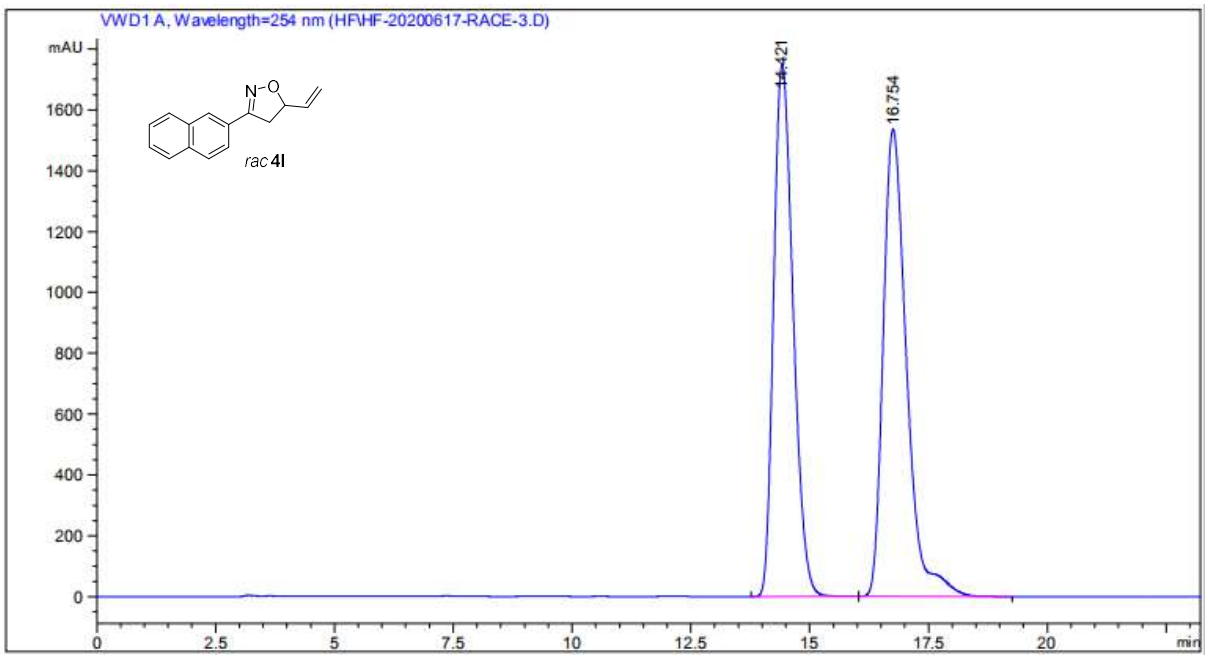

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 19.703 | 801.50470 | 23.7144 | 2.5779 |
| 2 | PDA 254 nm | 21.050 | 3.02900e4 | 844.37195 | 97.4221 |



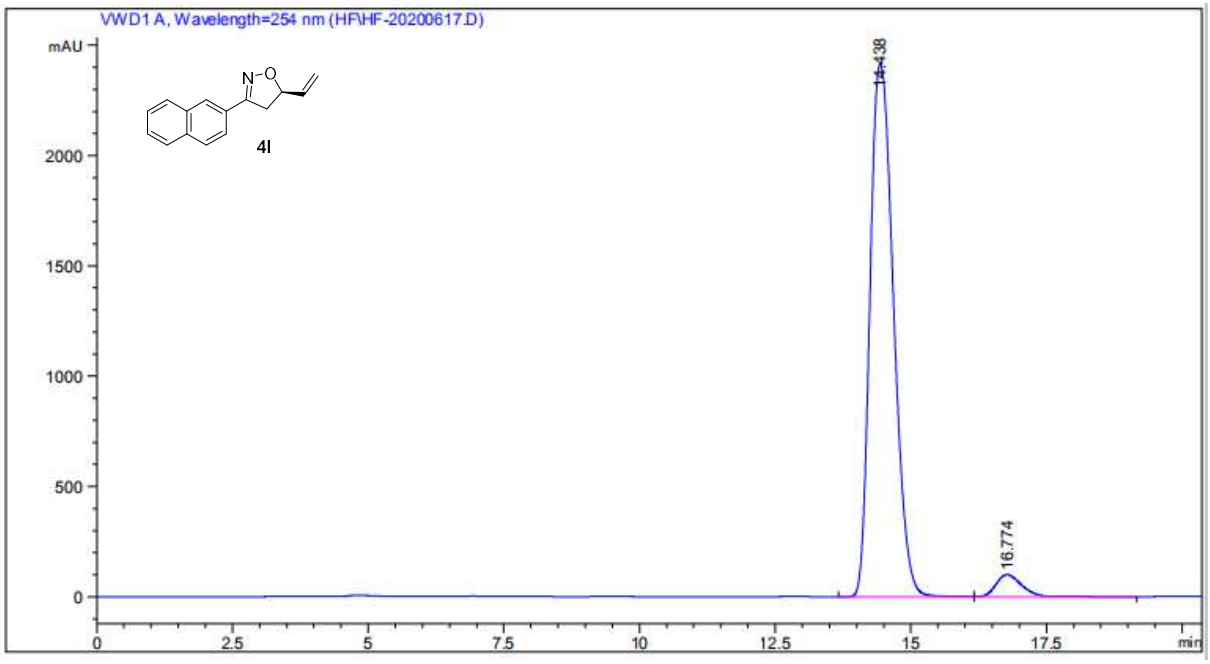

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 17.809 | 2.04057e4 | 551.24860 | 50.0101 |
| 2 | PDA 254 nm | 19.910 | 2.03975e4 | 504.31970 | 49.9899 |



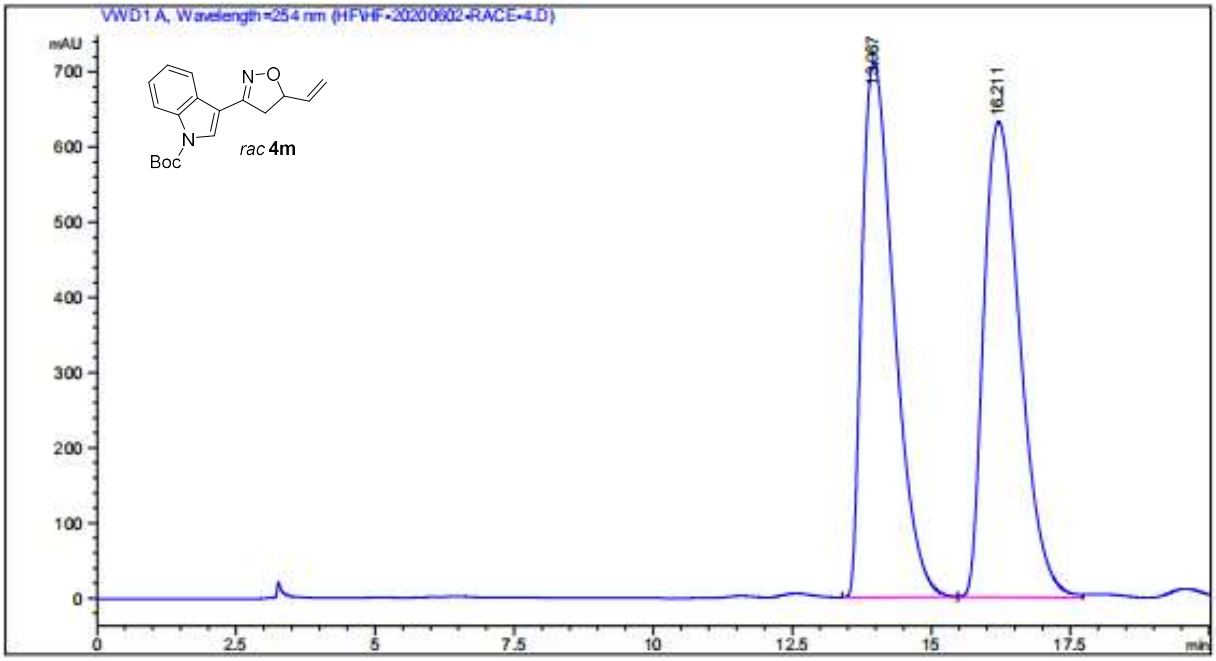

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 17.718 | 8.08922e4 | 2097.40063 | 95.2545 |
| 2 | PDA 254 nm | 19.856 | 4065.62109 | 99.07423 | 4.7455 |



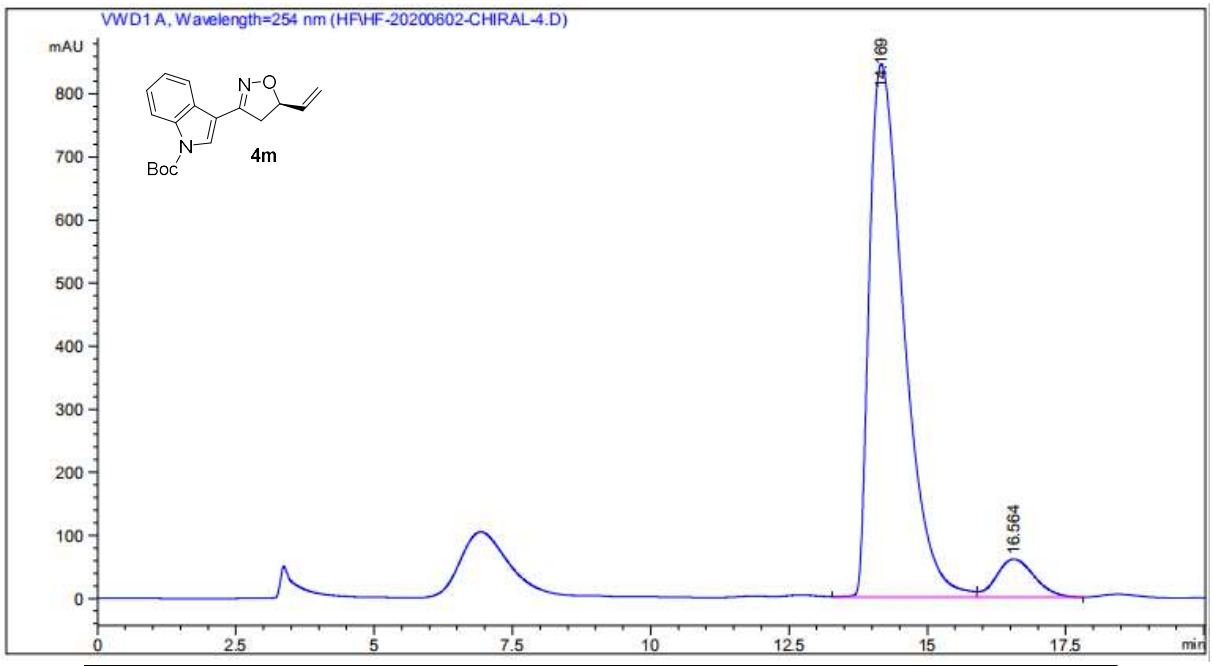

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 14.421 | 4.97738e4 | 1747.43677 | 48.7469 |
| 2 | PDA 254 nm | 16.754 | 5.23329e4 | 1535.21460 | 51.2531 |



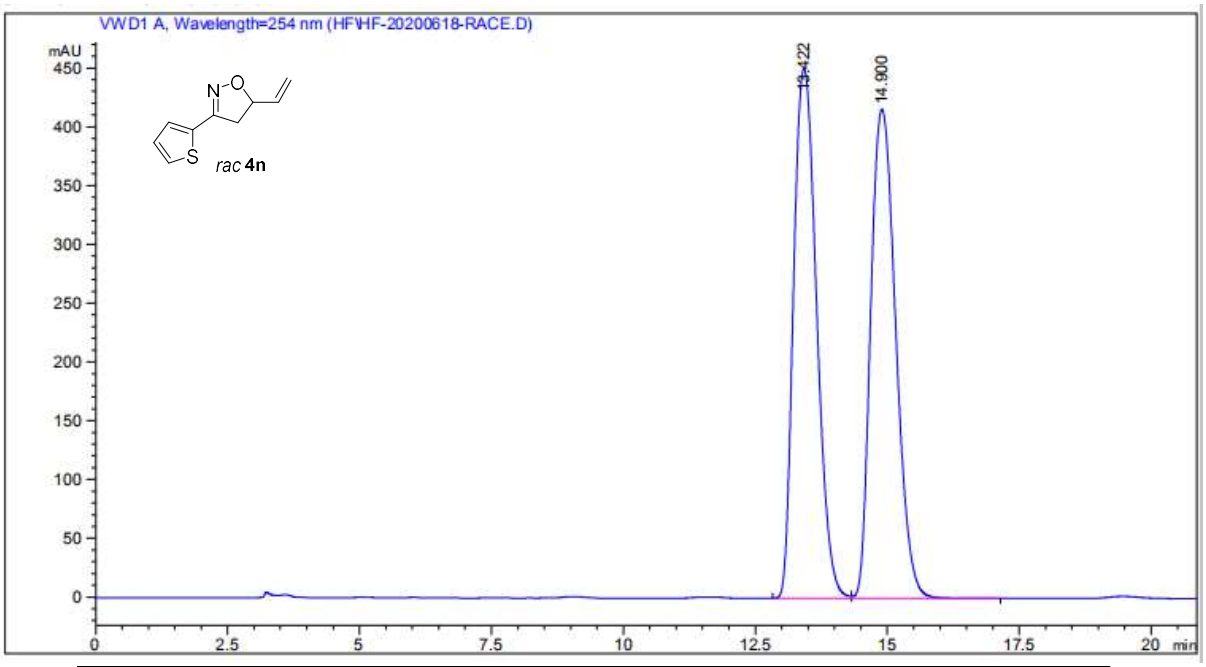

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 14.438 | 7.23118e4 | 2414.40845 | 95.6843 |
| 2 | PDA 254 nm | 16.774 | 3261.49048 | 99.86243 | 4.3157 |



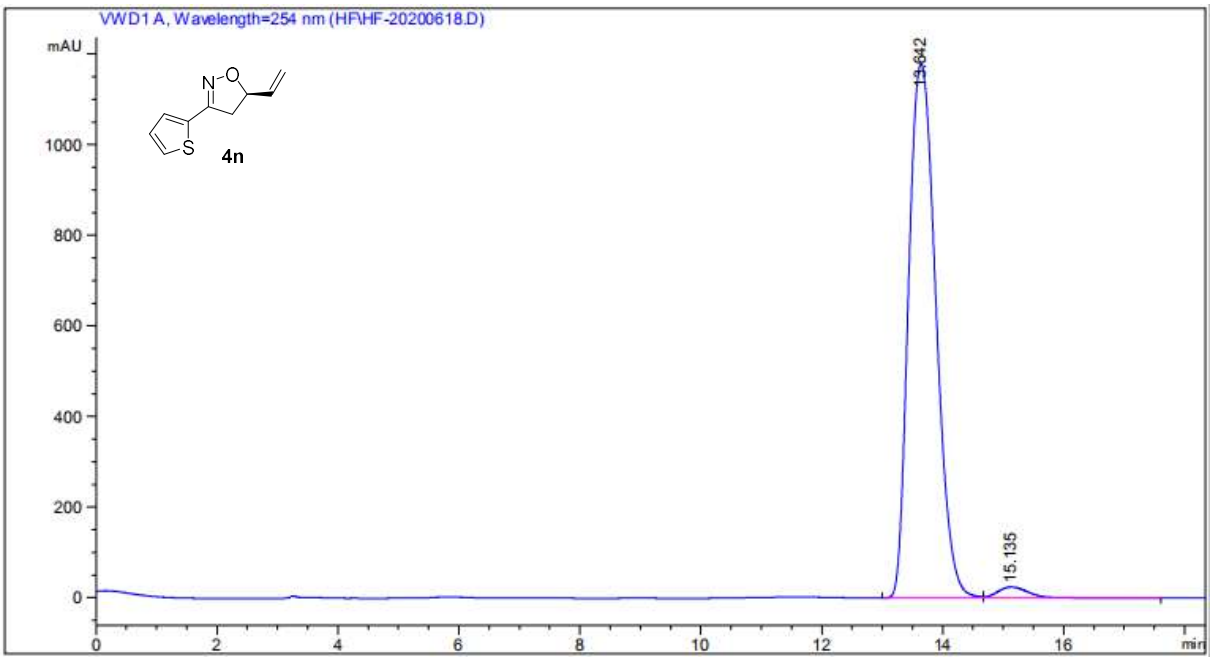

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 13.967 | 2.85029e4 | 712.03992 | 49.8842 |
| 2 | PDA 254 nm | 16.211 | 2.86352e4 | 632.05792 | 50.1158 |



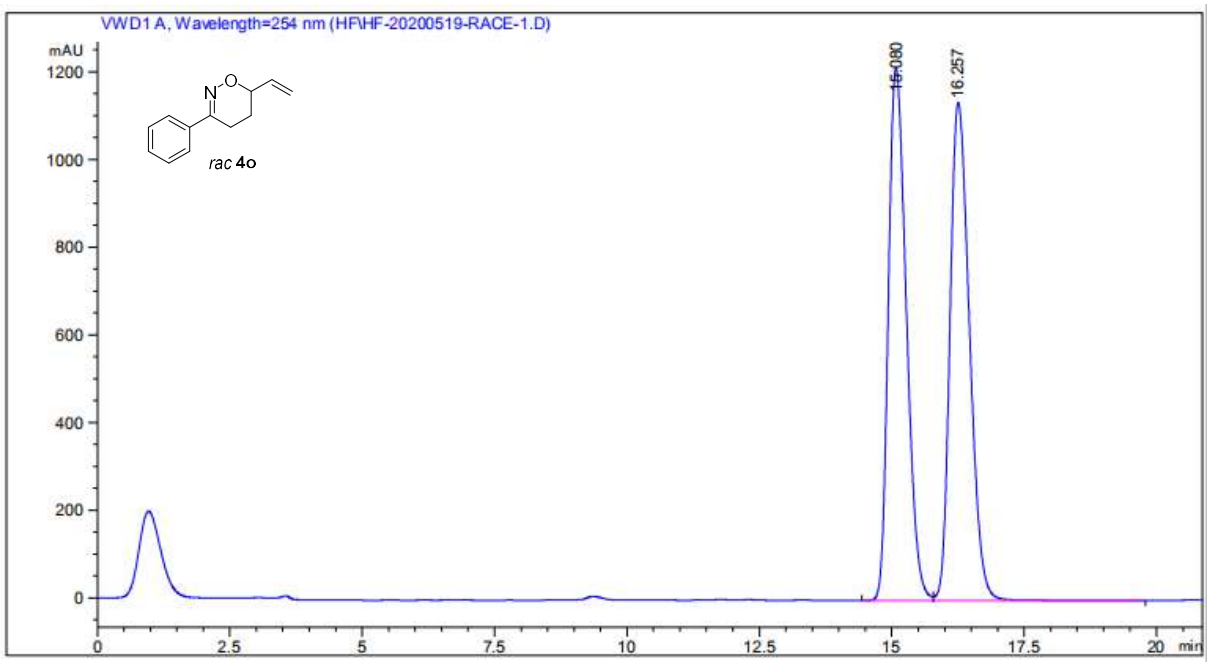

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 14.169 | 3.65472e4 | 845.72095 | 92.6744 |
| 2 | PDA 254 nm | 16.564 | 2888.92163 | 60.38203 | 7.3256 |



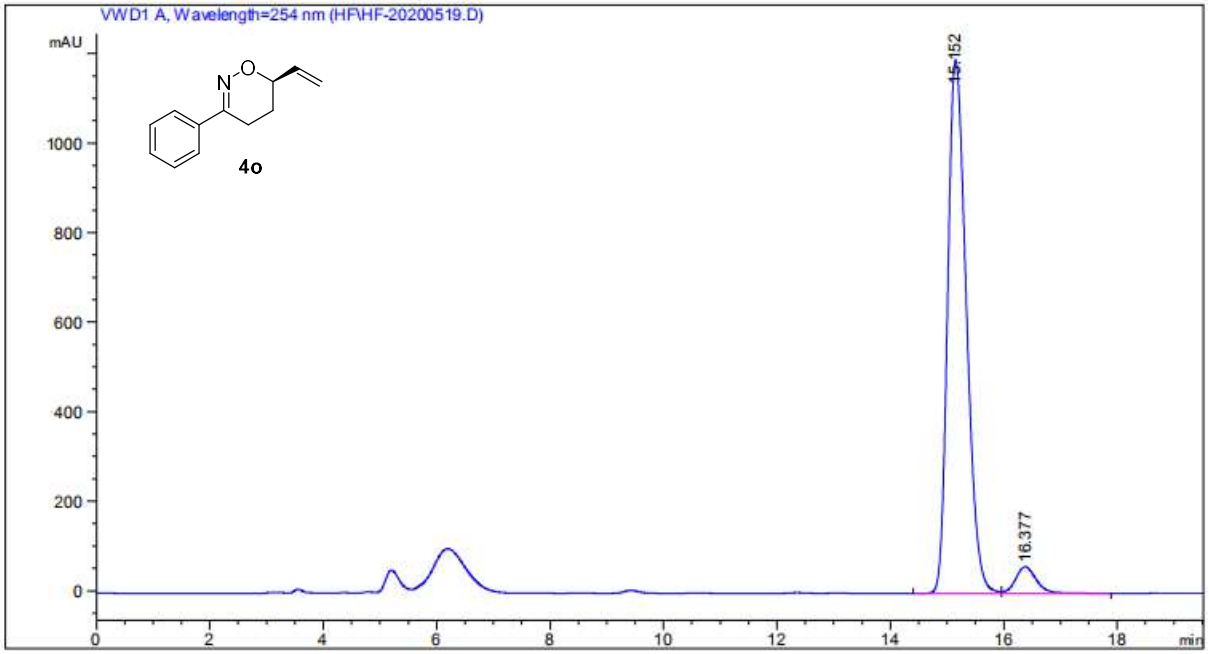

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 13.422 | 1.36113e4 | 450.63660 | 49.9075 |
| 2 | PDA 254 nm | 14.900 | 1.36617e4 | 415.72729 | 50.0925 |



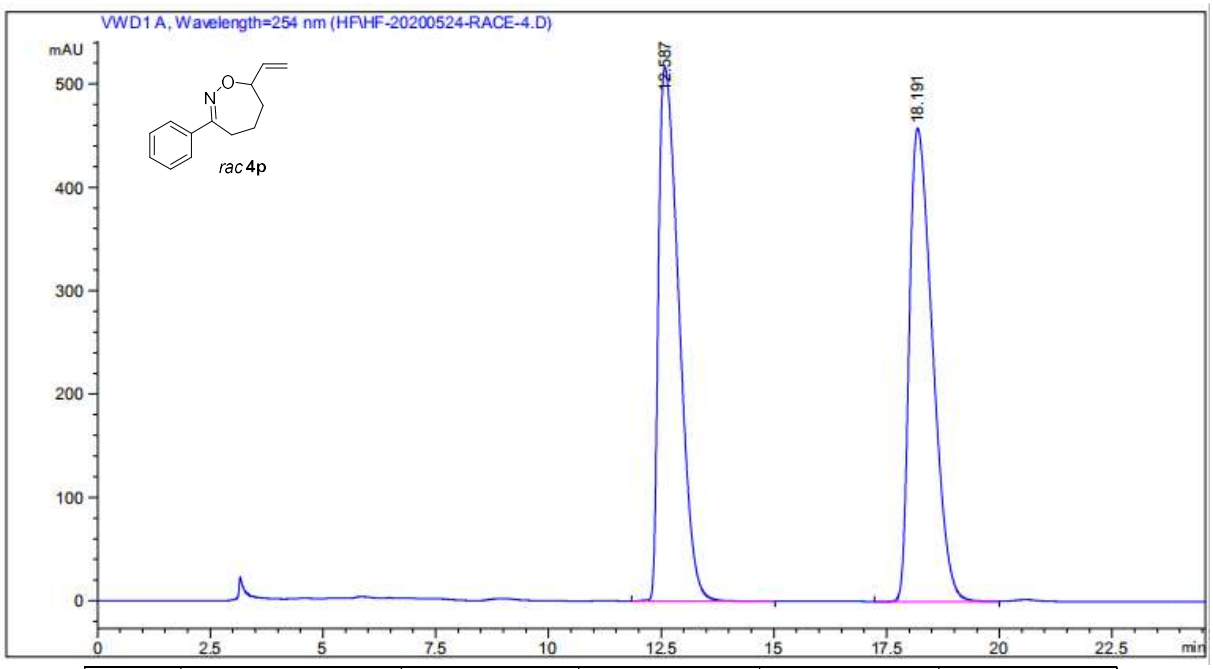

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 13.642 | 3.68070e4 | 1179.10706 | 97.6831 |
| 2 | PDA 254 nm | 15.135 | 873.02716 | 24.12109 | 2.3169 |



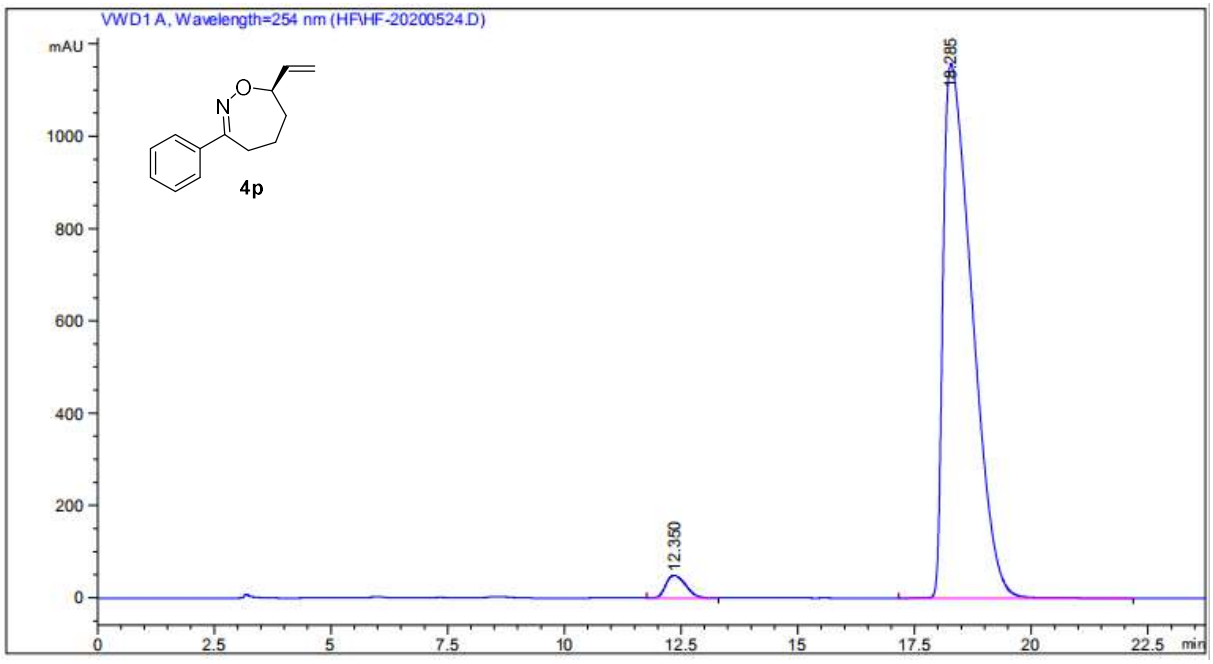

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 15.080 | 2.85420e4 | 1213.61987 | 49.6673 |
| 2 | PDA 254 nm | 16.257 | 2.89244e4 | 1135.31262 | 50.3327 |



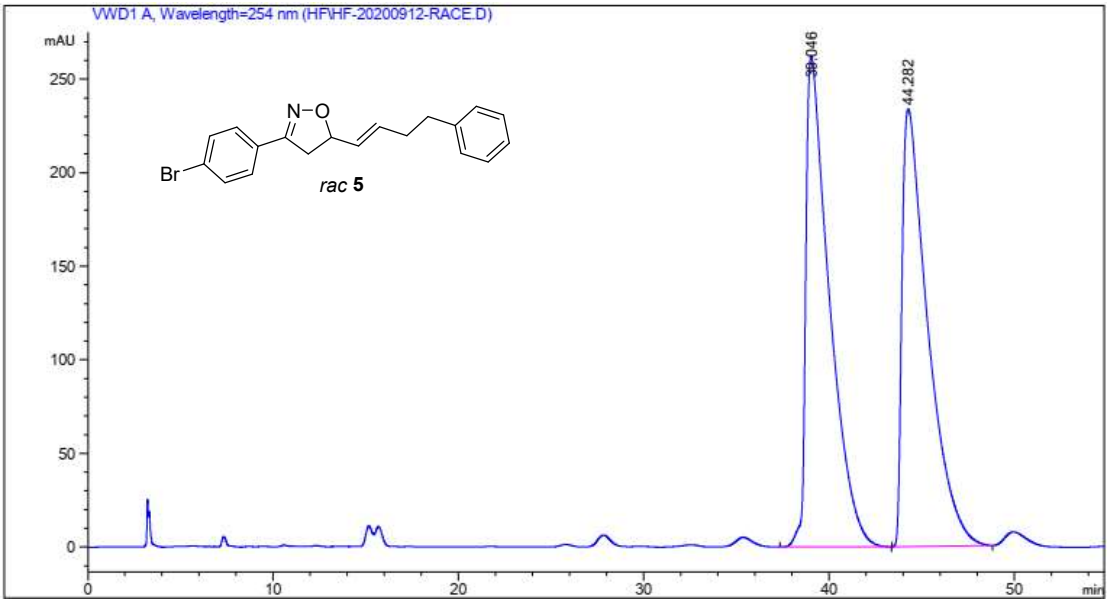

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 15.152 | 2.70595e4 | 1190.66467 | 94.7531 |
| 2 | PDA 254 nm | 16.377 | 1498.40527 | 59.29599 | 5.2469 |



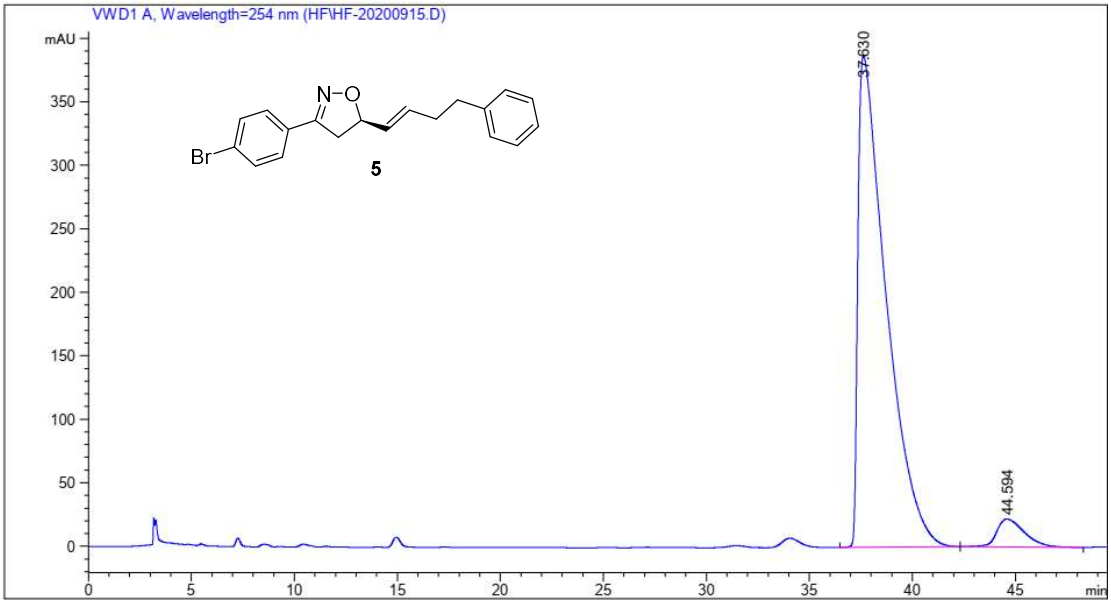

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 12.587 | 1.61958e4 | 516.27911 | 49.8943 |
| 2 | PDA 254 nm | 18.191 | 1.62644e4 | 457.71677 | 50.1057 |



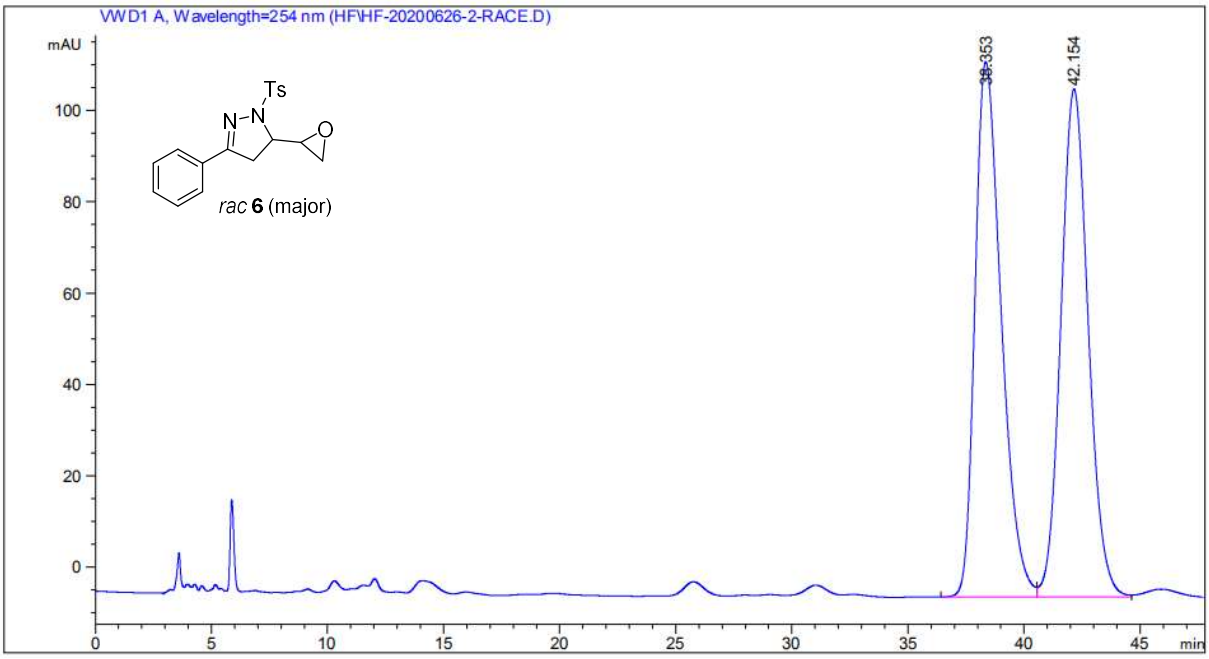

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254. nm | 12.350 | 1461.34460 | 48.88551 | 2.8608 |
| 2 | PDA 254 nm | 18.285 | 4.96206e4 | 1156.93945 | 97.1392 |



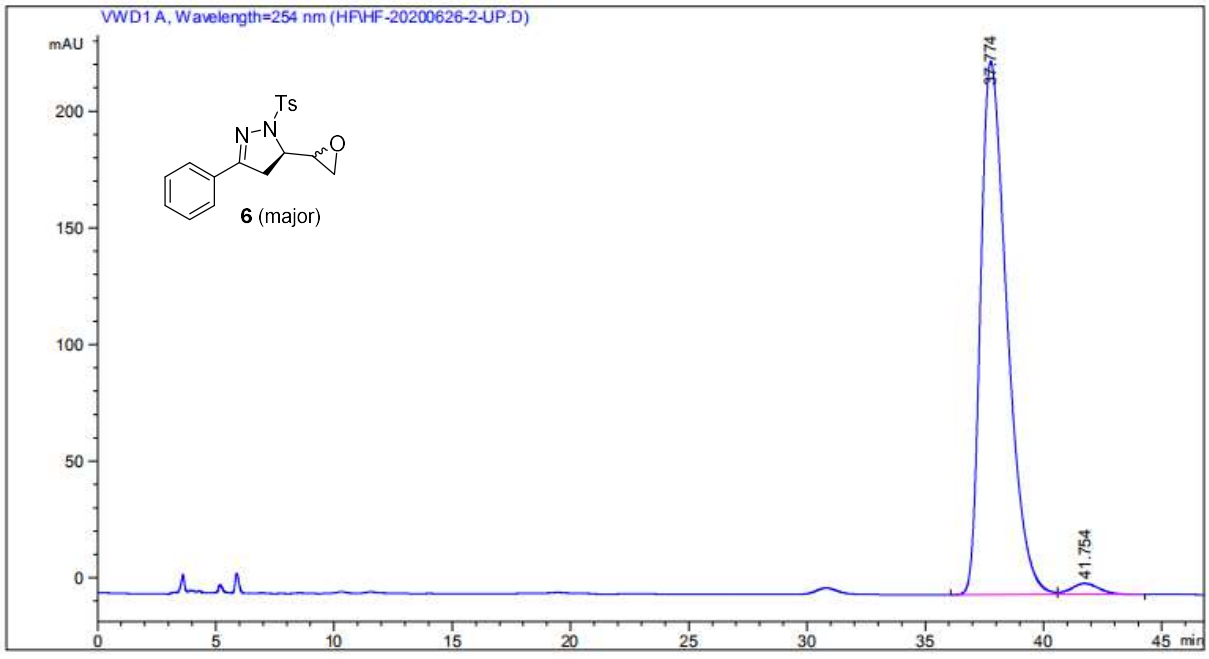

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 39.046 | 2.32221e4 | 262.10471 | 50.6208 |
| 2 | PDA 254 nm | 44.282 | 2.26525e4 | 233.82022 | 49.3792 |



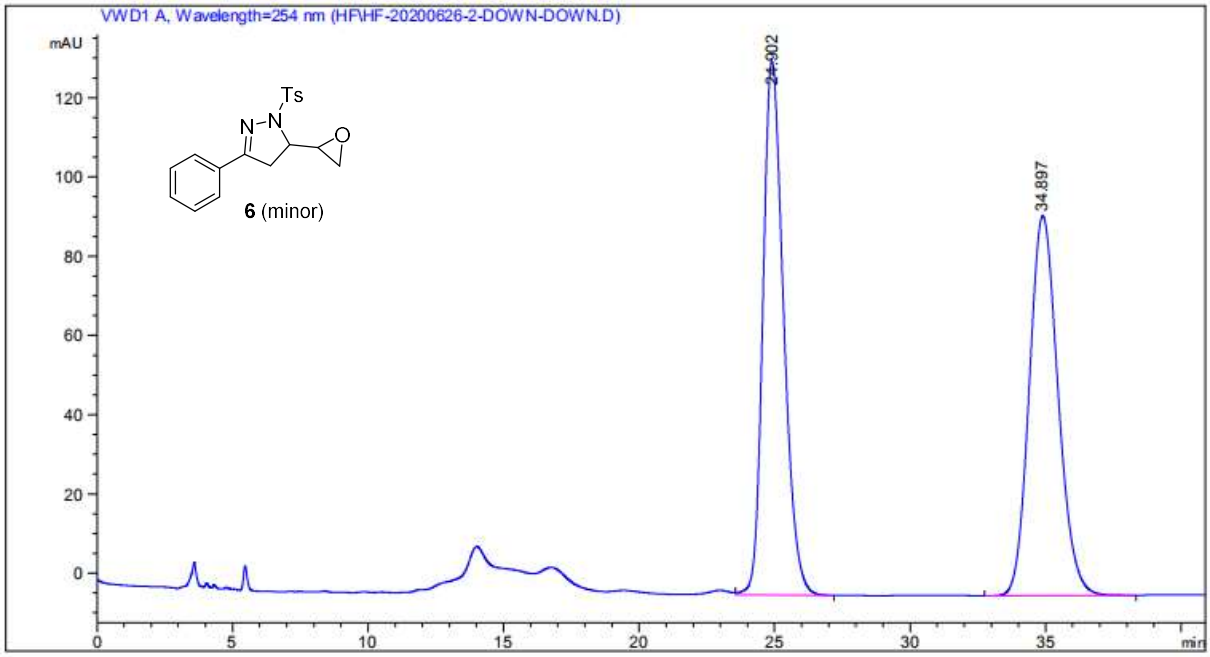

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 37.630 | 3.66823e4 | 386.96817 | 94.6748 |
| 2 | PDA 254 nm | 44.594 | 2063.28394 | 21.97522 | 5.3252 |



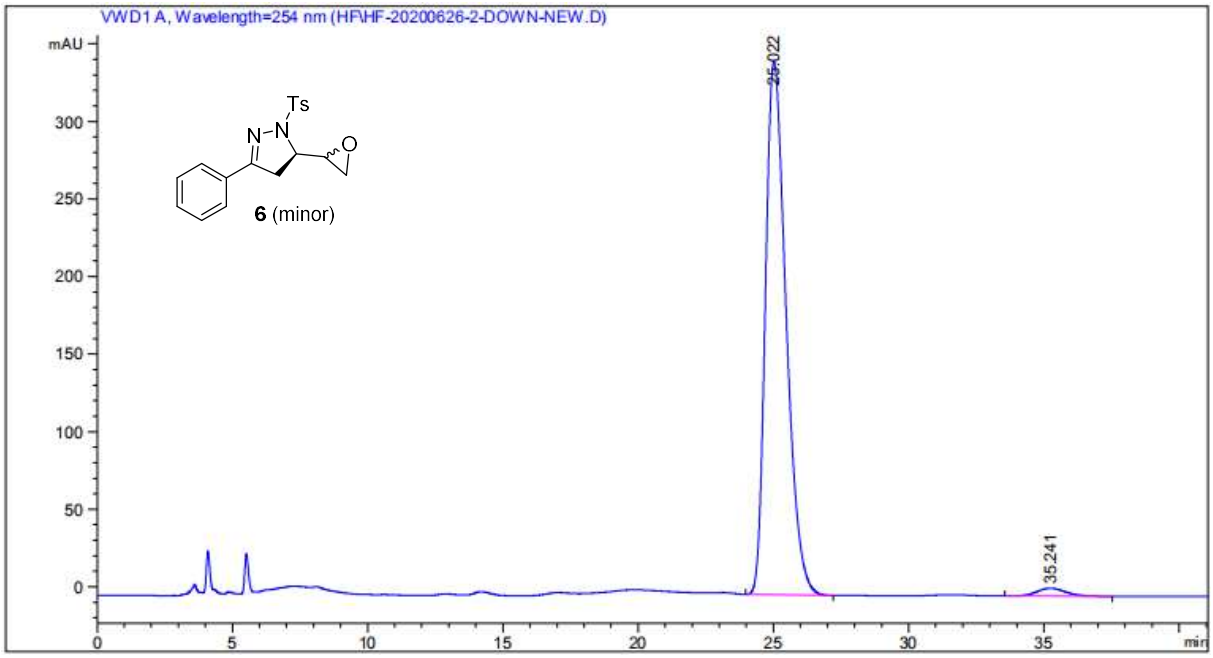

| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 280.16 nm | 38.353 | 9200.17578 | 117.25249 | 50.2860 |
| 2 | PDA 280.16 nm | 42.154 | 9095.52148 | 111.29817 | 49.7140 |




| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 280.16 nm | 37.774 | 1.77595e4 | 228.48381 | 97.8749 |
| 2 | PDA 280.16 nm | 41.754 | 385.60281 | 4.72605 | 2.1251 |




| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 280.16 nm | 24.902 | 7120.41455 | 134.75426 | 50.1862 |
| 2 | PDA 280.16 nm | 34.897 | 7067.57031 | 95.82932 | 49.8138 |




| Peak | Processed channel | Retention time (min) | Peak area (mAU*s) | Peak height (mAU) | Peak area (%) |
|---|---|---|---|---|---|
| 1 | PDA 254 nm | 25.022 | 1.81723e4 | 343.74432 | 97.9537 |
| 2 | PDA 254 nm | 35.241 | 379.63364 | 5.14803 | 2.0463 |