Supporting Information

Iridium-catalyzed intramolecular allylic substitution reaction: efficiently enantioselective synthesis of 1,3,4-oxadiazine, oxazolines and 1,3-oxazine derivatives

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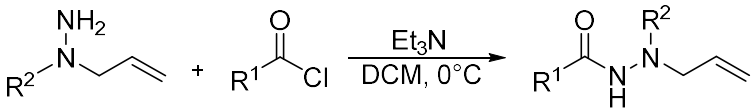
1. General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer using tetramethylsilane as internal reference, and chemical shifts (δ) 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 Thermo Scientific mass spectrometer (ESI) with an Orbitrap analyzer. The ee value determination was carried out using HPLC with chiral Chirapak column on Agilent 1260 and SHIMADZU LC-20AD with a UV detector. The X-ray data was detected by Agilent SuperNOVA X-ray single crystal diffractometer. Melting points were taken on an XT–4 melting point apparatus and were uncorrected. Dichloromethane was freshly distilled from phosphorous pentoxide. Toluene and THF were freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. Acetonitrile was dried by calcium hydride and freshly distilled. $[Ir(COD)Cl]_2$ 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.

S1a−**S1x** and **S4e** were prepared according to literature.[1-2]

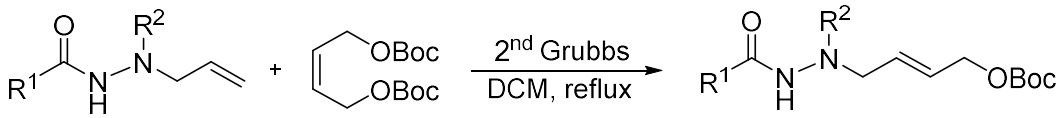
2. General procedure for synthesis of substrates

2.1 General procedure for synthesis of substrates 1a−1x



S1a-S1x **S2a-S2x**

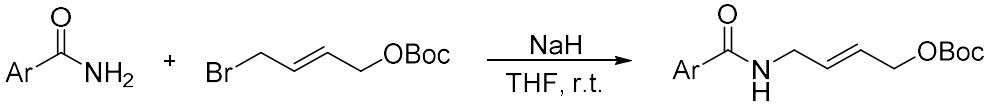
To a solution of 1-allyl-1-aryl hydrazine (10 mmol) in CH_2Cl_2 (30 mL) was added NEt_3 (30 mmol, 4.2 mL, 3.0 equiv.) and benzoyl chloride (15 mmol, 1.5 equiv.) at 0 ℃. The solution was stirred at 0 ℃ for 2 h (monitored by TLC). The reaction was quenched with water, extracted with CH_2Cl_2 (20 mL×3). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford products **S2** in 42−62% yields.



S2a-S2x **1a-1x**

Under argon atmosphere, a solution of 2nd Grubbs catalyst (0.06 mmol, 51 mg, 0.03 equiv.) in dry CH_2Cl_2 (2 mL) was added to a solution of **S2** (2 mmol) and (*Z*)-but-2-ene-1,4-diyl di-*tert*-butyl bis(carbonate) (2.4 mmol, 692 mg, 1.2 equiv.) in dry CH_2Cl_2 (10 mL) at room temperature. The solution was refluxed overnight and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford compounds **1**.

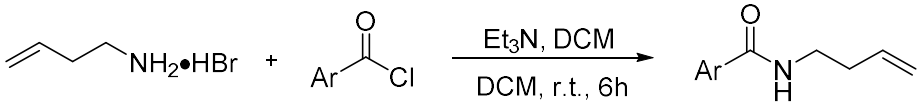
2.2 General procedure for synthesis of substrates 3a−3b



S3a-S3b **3a-3b**

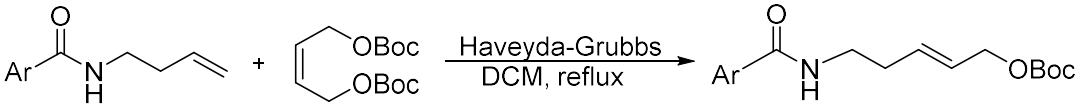
To a solution of argoncarboxamide (5.5 mmol, 1.1 equiv.) in THF (40 mL) was added NaH (10 mmol, 2.0 equiv.) at 0 ℃, the reaction mixture was stirred for 1 h. Then, 4-bromobut-2-en-1-yl *tert*-butyl carbonate (5 mmol, 1.26 g, 1.0 equiv.) was added. The solution was stirred at rt for 12 h (monitored by TLC) and was quenched with water, extracted with ethyl acetate (20 mL×3). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford compounds **3**.

2.3 General procedure for synthesis of substrates 3c−3d



S3c-S3d

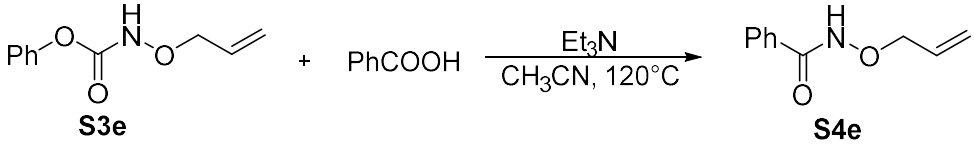
To a solution of 3-buten-1-amine hydrobromide (5 mmol, 0.76 g) in CH_2Cl_2 (40 mL) was added NEt_3 (15 mmol, 2.09 mL, 3.0 equiv.) and argoncarbonyl chloride (5.5 mmol, 1.1 equiv.) at 0 ℃. The solution was stirred at room temperature for 6 h (monitored by TLC). The reaction was quenched with water, extracted with CH_2Cl_2 (20 mL×3). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford products **S3c**−**S3d**.



S3c-S3d **3c-3d**

Under an argon atmosphere, a solution of Haveyda-Grubbs catalyst (0.1 mmol, 31 mg, 0.05 equiv.) in dry CH_2Cl_2 (2 mL) was added to a solution of **S3** (2 mmol) and (*Z*)-but-2-ene-1,4-diyl di-*tert*-butyl bis(carbonate) (2.4 mmol, 692 mg, 1.2 equiv.) in dry CH_2Cl_2 (10 mL) at room temperature. The solution was refluxed overnight and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford compounds **3c**−**3d**.

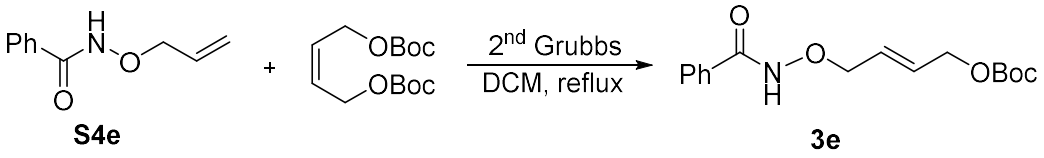
2.4 General procedure for synthesis of substrate 3e



S3e **S4e**

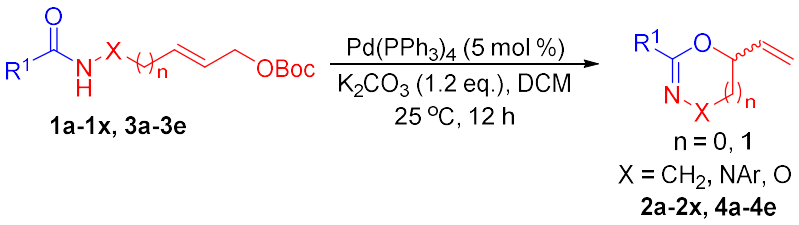
Compound **S4e** was synthesized according to literature method.[2]

A solution of benzoic acid (0.366 g, 3 mmol), **S3e** (1.737g, 9 mmol), NEt_3 (13.9 μL, 1 mmol) in acetonitrile (20 mL) was refluxed for 22 h at 120˚C. The crude mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to obtain compound **S4e**.



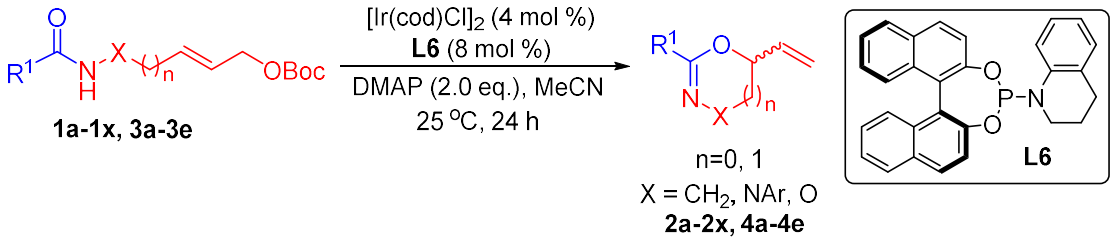
Under an argon atmosphere, a solution of 2nd Grubbs catalyst (0.06 mmol, 51 mg, 0.03 equiv.) in dry CH_2Cl_2 (2 mL) was added to a solution of **S4e** (2 mmol, 354 mg) and (*Z*)-but-2-ene-1,4-diyl di-*tert*-butyl bis(carbonate) (2.4 mmol, 692 mg, 1.2 equiv.) in dry CH_2Cl_2 (10 mL) at room temperature. The solution was refluxed overnight and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford compound **3e**.

2.5 General procedure for synthesis of racemic 2a−2x and 4a−4e



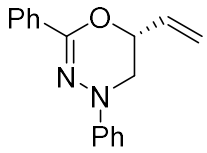
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Pd(PPh_3)_4$ (0.005 mmol, 5.8 mg, 5 mol %), K_2CO_3 (0.12 mmol, 16.6 mg, 1.2 equiv.). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. Subsequently, a solution of **1** (0.1 mmol) in DCM (2 mL) were added. The resulting solution was stirred at room temperature for 12 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was passed through a short pad of celite and washed with DCM (5 mL×3). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the racemic products **2** or **4**.

3. General procedure for enantioselective synthesis of 2a−2x and 4a−4e



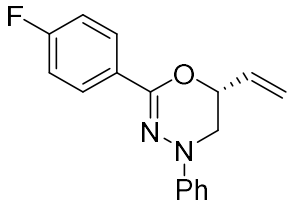
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $[Ir(COD)Cl]_2$ (0.004 mmol, 2.7 mg, 4 mol %), phosphoramidite ligand **L6** (0.008 mmol, 3.6 mg, 8 mol %). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. THF (0.5mL) and *n*-propylamine (0.5 mL) was added at 25 ºC and the reaction mixture was warmed to 50 ℃ for 0.5 h. The solvent was removed under reduced pressure to give a pale-yellow solid and DMAP (0.2 mmol, 24.4 mg, 2 equiv.), a solution of substrates **1** or **3** (0.1 mmol) in MeCN (2 mL) were added. The resulting solution was stirred for 24 h at 25 ℃. Upon completion of the reaction (monitored by TLC), the reaction mixture was passed through a short pad of celite and washed with ethyl acetate (5 mL×3). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the products **2** or **4**.

(*R*)-2,4-diphenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2a)



yellow oil, 23.2 mg, 88% yield, 94% ee, $[\alpha]_D^{24}$ −36.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 6.0, 2.0 Hz, 2H), 7.40 − 7.39 (m, 1H), 7.38 − 7.30 (m, 3H), 7.29 − 7.25 (m, 3H), 6.92 − 6.88 (m, 1H), 6.06 − 5.97 (m, 1H), 5.55 (d, J = 17.2 Hz, 1H), 5.40 (d, J = 10.4 Hz, 1H), 4.95 − 4.91 (m, 1H), 3.95 (dd, J = 12.0, 3.2 Hz, 1H), 3.37 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.10, 143.24, 133.98, 132.57, 129.12, 129.10, 128.15, 125.40, 119.96, 118.58, 113.46, 73.02, 46.69. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{17}N_2O$ (M+H): 265.1335, Found: 265.1338. HPLC (OD−H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.245 min (minor), 7.743 min (major).

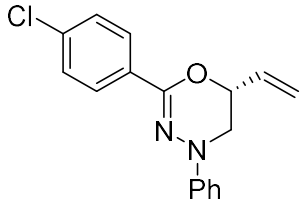
(*R*)-2-(4-fluorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2b)



yellow solid, mp 50.4 − 54.6 ºC, 20.3 mg, 72% yield, 92% ee, $[\alpha]_D^{23}$ −58.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.25 (m, 2H), 7.06 (t, J = 7.2 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.35 (d, J = 17.2 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 4.94 – 4.93 (m, 1H), 3.94 (dd, J = 11.6, 2.8 Hz, 1H), 3.34 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.49 (d, J = 247.0 Hz), 147.04, 142.61, 133.87, 129.14, 128.73 (d, J = 3.0 Hz), 127.32 (d, J = 8.2 Hz), 120.05, 118.72, 115.14 (d, J = 21.8 Hz), 113.46, 73.19, 46.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.25. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}FN_2O$ (M+H): 283.1241, Found: 283.1233. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.483 min (minor), 9.352 min (major).

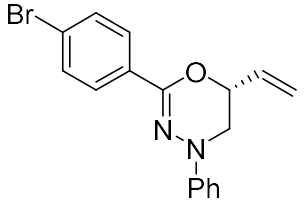
128.74

(*R*)-2-(4-chlorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2c)



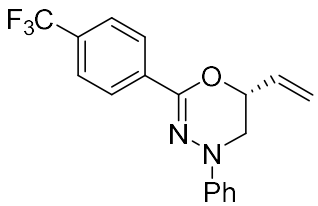
yellow solid, mp 64.2 – 66.4 °C, 22.4 mg, 75% yield, 93% ee, $[\alpha]_D^{23}$ –31.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.34 – 7.30 (m, 4H), 7.26 – 7.24 (m. 2H), 6.91 (t, J = 7.2 Hz, 1H), 6.04 – 5.95 (m, 1H), 5.52 (d, J = 17.2, 1H), 5.40 (d, J = 10.4 Hz, 1H), 4.93 – 4.89 (m, 1H), 3.93 (dd, J = 11.6, 2.8 Hz, 1H), 3.35 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.90, 142.40, 134.93, 133.80, 131.07, 129.15, 128.36, 126.66, 120.17, 118.77, 113.48, 73.07, 46.62. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}ClN_2O$ (M+H): 299.0946, Found: 299.0948. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.499 min (minor), 11.099 min (major).

(*R*)-2-(4-bromophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2d)



yellow solid, mp 82.8 – 84.6 °C, 26.8 mg, 78% yield, 94% ee, $[\alpha]_D^{23}$ –34.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.50 – 7.48 (m, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.25 (m, 2H), 6.92 (t, J = 7.2 Hz, 1H), 6.05 – 5.96 (m, 1H), 5.53 (d, J = 17.2 Hz, 1H), 5.41 (d, J = 10.4 Hz, 1H), 4.93 – 4.92 (m, 1H), 3.95 (dd, J = 12.0, 2.8 Hz, 1H), 3.37 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.87, 142.42, 133.77, 131.53, 131.29, 129.14, 126.91, 123.24, 120.18, 118.77, 113.48, 73.04, 46.60. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}BrN_2O$ (M+H): 343.0441, Found: 343.0434. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.469 min (minor), 13.204 min (major).

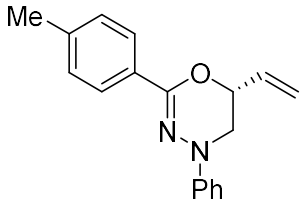
(*R*)-4-phenyl-2-(4-(trifluoromethyl) phenyl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2e)



yellow oil, 21.6 mg, 65% yield, 90% ee, $[\alpha]_D^{23}$ –12.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.06 – 5.97 (m, 1H), 5.54 (d, J = 17.2 Hz, 1H), 5.42 (d, J = 10.4 Hz, 1H), 4.96 – 4.92 (m, 1H), 3.97 (dd, J = 11.6, 2.8 Hz, 1H), 3.41 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

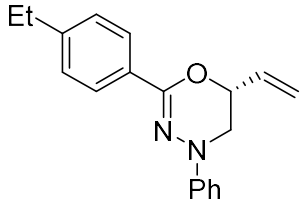
146.70, 141.90, 135.92, 133.66, 130.76, 130.43, 129.20, 125.49, 125.12 (q, J = 3.9 Hz), 120.44, 118.93, 113.57, 73.01, 46.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.54. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{16}F_3N_2O$ (M+H): 333.1209, Found: 333.1209. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R =10.453 min (minor), 12.019 min (major).

(*R*)-4-phenyl-2-(*p*-tolyl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2f)



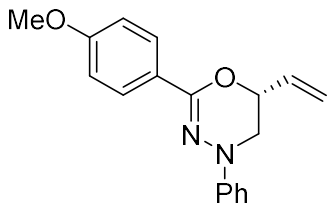
yellow solid, mp 72.1–74.4℃, 23.4 mg, 84% yield, 93% ee, $[\alpha]_D^{24}$ –30.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.16 Hz, 2 H), 7.34 – 7.30 (m, 2 H), 7.28 – 7.24 (m, 2 H), 7.18 (d, J = 8.1 Hz, 2 H), 6.90 – 6.87 (m, 1 H), 6.04 – 5.96 (m, 1 H), 5.53 (d, J = 17.2 Hz, 1 H), 5.38 (d, J = 10.6 Hz, 1 H), 4.93 – 4.90 (m, 1H), 3.92 (dd, J = 11.7, 3 Hz, 1 H), 3.37– 3.32 (q, J = 7.24 Hz, 1 H), 2.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.18, 143.46, 139.11, 134.05, 129.80, 129.08, 128.86, 125.36, 119.81, 118.49, 113.41, 73.00, 46.68, 21.42. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O$ (M+H): 279.1492, Found: 279.1483. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.028 min (minor), 9.590 min (major).

(*R*)-2-(4-ethylphenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2g)



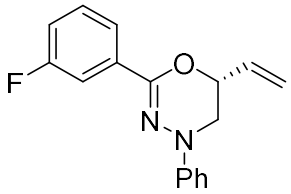
yellow oil, 21.9 mg, 75% yield, 73% ee, $[\alpha]_D^{24}$ –10.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.23 – 7.19 (m, 2H), 6.90 – 6.87 (m, 1H), 6.04 – 5.96 (m, 1H), 5.55 (d, J = 17.2 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 4.93 – 4.89 (m, 1H), 3.92 (dd, J = 11.6, 2.8 Hz, 1H), 3.33 (q, J = 7.2 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.19, 145.50, 143.48, 134.05, 130.04, 129.08, 127.68, 125.47, 119.80, 118.46, 113.41, 72.99, 46.69, 28.79, 15.56. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{21}N_2O$ (M+H): 293.1648, Found: 293.1653. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.736 min (minor), 8.872 min (major).

(R)-2-(4-methoxyphenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2h)



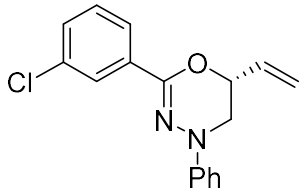
yellow solid, mp 59.6 – 63.5 °C, 19.1 mg, 65% yield, 85% ee, $[\alpha]_D^{24}$ –20.0 (c 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.33 – 7.23 (m, 4H), 6.91 – 6.86 (m, 3H), 6.04 – 5.95 (m, 1H), 5.52 (d, J = 17.6 Hz, 1H), 5.38 (d, J = 10.4 Hz, 1H), 4.92 – 4.88 (m, 1H), 3.91 (dd, J = 11.6, 2.8 Hz, 1H), 3.82 (s, 3H), 3.32 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.51, 147.25, 143.39, 134.07, 129.07, 126.92, 125.23, 119.71, 118.46, 113.53, 113.37, 73.11, 55.34, 46.69. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O_2$ (M+H): 295.1441, Found: 295.1439. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.062 min (minor), 16.379 min (major).

(*R*)-2-(3-fluorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2i)



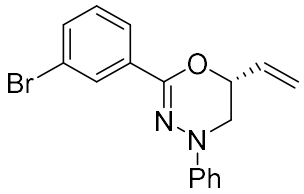
yellow oil, 21.1 mg, 75% yield, 93% ee, $[\alpha]_D^{22}$ –55.0 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 3.6 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.35 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.03 (dt, J = 8.0, 2.0 Hz, 1H), 6.91 (t, J = 3.2 Hz, 1H), 6.03 – 5.95 (m, 1H), 5.53 (d, J = 17.2 Hz, 1H), 5.40 (d, J = 10.4 Hz, 1H), 4.92 – 4.89 (m, 1H), 3.93 (dd, J = 11.6, 2.8 Hz, 1H), 3.36 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.83 (d, J = 242.9 Hz), 146.82, 142.10 (d, J = 3.5 Hz), 134.85 (d, J = 8.4 Hz), 133.73, 129.63 (d, J = 8.2 Hz), 129.15, 120.98 (d, J = 2.9 Hz), 120.22, 118.77, 115.85 (d, J = 21.3 Hz), 113.50, 112.29 (d, J = 23.9 Hz), 73.00, 46.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.43. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}FN_2O$ (M+H): 283.1241, Found: 283.1232. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.941 min (minor), 8.720 min (major).

(*R*)-2-(3-chlorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2j)



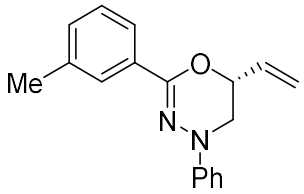
yellow oil, 22.9 mg, 77% yield, 95% ee, $[\alpha]_D^{21}$ –46.0 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.83 – 7.80 (m, 1H), 7.35 – 7.29 (m, 4H), 7.27 – 7.25 (m, 2H), 7.92 (t, J = 3.6 Hz, 1H), m (6.04 – 5.96, 1H), 5.54 (d, J = 1.2 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H), 4.93 – 4.90 (m, 1H), 3.94 (dd, J = 11.6, 2.8 Hz, 1H), 3.40 – 3.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.80, 141.94, 134.37, 134.24, 133.71, 129.40, 129.16, 128.95, 125.38, 123.45, 120.26, 118.85, 113.52, 73.04, 46.61. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}ClN_2O$ (M+H): 299.0946, Found: 299.0943. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 14.012 min (minor), 16.586 min (major).

(*R*)-2-(3-bromophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2k)



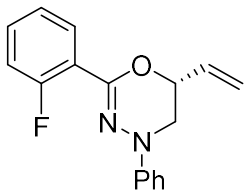
yellow oil, 24.9 mg, 73% yield, 94% ee, $[\alpha]_D^{22}$ –43.0 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.85 (d, J = 6.8 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 6.93 – 6.89 (m, 1H), 6.02 – 5.93 (m, 1H), 5.52 (d, J = 13.6 Hz, 1H), 5.39 (d, J = 10.4Hz, 1H), 4.90 – 4.86 (m, 1H), 3.91 (dd, J = 11.6, 3.2 Hz, 1H), 3.34 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.76, 141.75, 134.58, 133.69, 131.84, 129.66, 129.14, 128.24, 123.88, 122.35, 120.25, 118.84, 113.51, 73.01, 46.57. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}BrN_2O$ (M+H): 343.0441, Found: 343.0441. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.571 min (minor), 9.086 min (major).

(*R*)-4-phenyl-2-(*m*-tolyl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2l)



yellow oil, 16.7 mg, 60% yield, 93% ee. $[\alpha]_D^{24}$ –88.0 (c 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 7.17 – 7.15 (m, 1H), 6.9 – 6.87 (m, 1H), 6.02 – 5.94 (m, 1H), 5.54 – 5.49 (m, 1H), 5.39 – 5.36 (m, 1H), 4.90 – 4.86 (m, 1H), 3.89 (dd, J = 12.0, 3.2 Hz, 1H), 3.32 (q, J = 7.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.11, 143.34, 137.72, 133.99, 132.47, 129.89, 129.08, 128.05, 125.92, 122.60, 119.88, 118.52, 113.44, 72.96, 46.62, 21.52. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O$ (M+H): 279.1492, Found: 279.1491. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.789 min (minor), 7.377 min (major).

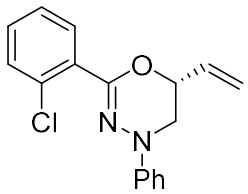
(*R*)-2-(2-fluorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2m)



yellow oil, 22.5 mg, 80% yield, 94% ee, $[\alpha]_D^{22}$ –35.0 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dt, J = 8.0, 1.6 Hz, 1H), 7.33 – 7.30 (m, 3H), 7.23 – 7.29 (m, 2H), 7.16 – 7.07 (m, 2H), 6.91 – 6.88 (m, 1H), 6.07 – 5.95 (m, 1H), 5.55 (d, J = 17.2 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H), 4.95 – 4.91 (m, 1H), 3.94 (dd, J = 11.6, 2.8 Hz, 1H), 3.37 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.30 (d, J = 254.2 Hz), 146.92, 140.96 (d, J = 5.4 Hz), 133.74, 130.45 (d, J = 8.3 Hz), 129.12, 123.73 (d, J = 3.8 Hz), 120.77 (d, J = 9.5 Hz), 120.12, 118.67, 116.77, 116.55, 113.42, 73.05, 46.65. ^{19}F NMR

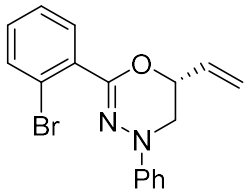
(376 MHz, $CDCl_3$) δ –111.74. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}FN_2O$ (M+H): 283.1241, Found: 283.1242. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.717 min (minor), 10.205 min (major).

(*R*)-2-(2-chlorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2n)



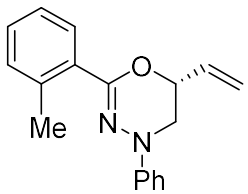
yellow oil, 21.7 mg, 73% yield, 92% ee, $[\alpha]_D^{23}$ –17.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 7.45 – 7.40 (m, 1H), 7.32 – 7.24 (m, 6H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.55 (d, *J* = 17.2 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), m (4.97 – 4.93, 1H), 3.97 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.38 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.96, 142.95, 133.72, 132.68, 131.80, 130.66, 130.51, 130.01, 129.11, 126.52, 120.18, 118.91, 113.57, 73.34, 46.83. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}ClN_2O$ (M+H): 299.0946, Found: 299.0941. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.137 min (minor), 11.233 min (major).

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



yellow oil, 24.7 mg, 72% yield, 92% ee, $[\alpha]_D^{22}$ –16.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.35 – 7.25 (m, 3H), 7.27 – 7.24 (m, 2H), 7.21 (dt *J* = 7.6, 1.6 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.06 – 5.98 (m, 1H), 5.55 (d, *J* = 17.2 Hz, 1H), 5.40 (d, *J* = 10.4 Hz, 1H), 4.97 – 4.93 (m, 1H), 3.97 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.37 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.95, 143.75, 133.86, 133.82, 133.70, 130.82, 130.26, 129.10, 127.13, 121.62, 120.18, 118.99, 113.61, 73.40, 46.87. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{16}BrN_2O$ (M+H): 343.0441, Found: 343.0442. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.548 min (minor), 11.412 min (major).

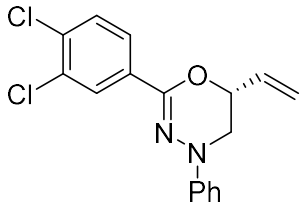
(*R*)-4-phenyl-2-(*o*-tolyl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2p)



yellow oil, 18.9 mg, 68% yield, 89% ee, $[\alpha]_D^{24}$ –16.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 5H), 6.88 (t, *J* = 3.2 Hz, 1H), 6.45 – 5.96

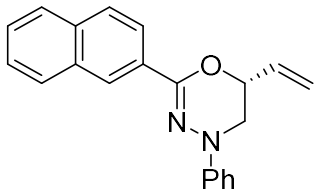
(m, 1H), 5.52 (d, *J* = 17.2 Hz, 1H), 5.38 (d, *J* = 10.8 Hz, 1H), 4.94 – 4.90 (m, 1H), 3.94 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.35 (q, *J* = 3.2 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.17, 144.55, 136.93, 134.03, 131.85, 131.29, 129.10, 128.83, 128.28, 125.61, 119.84, 118.61, 113.32, 73.09, 46.59, 22.44. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O$ (M+H): 279.1492, Found: 279.1486. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.492 min (minor), 8.428 min (major).

(*R*)-2-(3,4-dichlorophenyl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2q)



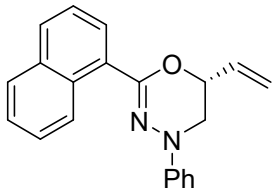
colorless oil, 20.6 mg, 62% yield, 75% ee, $[\alpha]_D^{24}$ +2.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.24 (m, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.04 – 5.95 (m, 1H), 5.53 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 10.8 Hz, 1H), 4.93 – 4.89 (m, 1H), 3.95 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.38 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.66, 141.28, 133.59, 132.86, 132.58, 132.46, 130.14, 129.20, 127.08, 124.52, 120.45, 119.03, 113.56, 73.12, 46.60. HRMS (ESI): Exact Mass Calcd. for $C_{17}H_{15}Cl_2N_2O$ (M+H): 333.0556, Found: 333.0556. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.274 min (minor), 11.611 min (major).

(*R*)-2-(naphthalen-2-yl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2r)



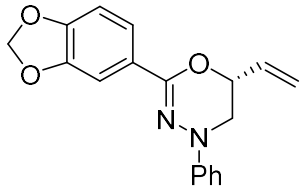
white solid, mp 108.2 – 113.0℃, 22.3 mg, 71% yield, 89% ee, $[\alpha]_D^{24}$ –18.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.15 (d, *J* = 12.0 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.50 – 7.46 (m, 2H), 7.38 – 7.32 (m, 4H), 6.95 – 6.90 (m, 1H), 6.11 – 6.03 (m, 1H), 5.60 (d, *J* = 17.2 Hz, 1H), 5.44 (d, *J* = 10.4 Hz, 1H), 5.01 – 4.98 (m, 1H), 3.99 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.44 (q, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.04, 143.26, 134.02, 133.76, 133.12, 129.93, 129.16, 128.57, 127.74, 126.44, 126.26, 124.52, 123.25, 120.06, 118.76, 113.50, 73.07, 46.72. HRMS (ESI): Exact Mass Calcd. for $C_{21}H_{19}N_2O$ (M+H): 315.1492, Found: 315.1488. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.098 min (minor), 19.502 min (major).

(*R*)-2-(naphthalen-1-yl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2s)



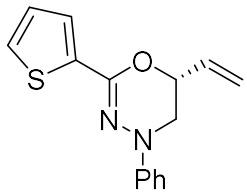
yellow oil, 21.6 mg, 69% yield, 94% ee, $[\alpha]_D^{24}$ –32.0 (c 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.4 Hz, 1H), 7.94 – 7.93 (m, 1H), 7.88 – 7.86 (m, 2H), 7.58 – 7.47 (m, 3H), 7.35 – 7.28 (m, 4H), 6.93 – 6.90 (m, 1H), 6.12 – 6.04 (m, 1H), 5.68 (d, J = 17.2 Hz, 1H), 5.43 (d, J = 10.4 Hz, 1H), 5.08 – 5.04 (m, 1H), 4.05 (dd, J = 11.6, 2.8 Hz, 1H), 3.49 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.14, 144.16, 134.09, 133.99, 130.02, 129.21, 128.48, 126.96, 126.66, 126.39, 125.82, 124.92, 120.03, 118.86, 113.42, 73.38, 46.73. HRMS (ESI): Exact Mass Calcd. for $C_{21}H_{19}N_2O$ (M+H): 315.1492, Found: 315.1487. HPLC (IF, *n*–hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm) t_R = 15.311 min (major), 16.658 min (minor).

(*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2t)



Colorless oil, 19.1 mg, 62% yield, 75% ee, $[\alpha]_D^{24}$ –2.0 (c 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.24 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 6.81 – 6.79 (m, 1H), 6.03 – 5.95 (m, 3H), 5.52 (d, J = 17.2 Hz, 1H), 5.39 (d, J = 10.4 Hz, 1H), 4.90 – 4.89 (m, 1H), 3.91 (dd, J = 11.6, 2.8 Hz, 1H), 3.32 (q, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.54, 147.65, 147.11, 143.06, 133.95, 129.10, 126.82, 119.84, 119.63, 118.57, 113.37, 107.87, 106.01, 101.26, 73.10, 46.65. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{17}N_2O_3$ (M+H): 309.1234, Found: 309.1236. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.696 min (minor), 15.502 min (major).

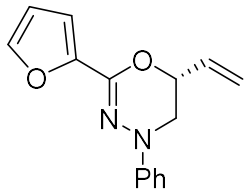
(*R*)-4-phenyl-2-(thiophen-2-yl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2u)



yellow oil, 19.7 mg, 73% yield, 92% ee, $[\alpha]_D^{23}$ –43.0 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.41 (m, 1H), 7.33 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 7.01 (t, J = 3.6 Hz, 1 H), 6.89 (dt J = 7.2, 0.8 Hz, 1H), 6.02 – 5.94 (m, 1H), 5.52 (d, J = 17.2 Hz, 1H), 5.39 (d, J = 10.4 Hz, 1H), 4.93 – 4.89 (m, 1H), 3.91 (dd, J = 11.6 Hz, 2.8 Hz, 1H), 3.38 – 3.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.75, 141.10, 136.36, 133.67, 129.10, 127.16, 126.48, 125.35, 120.04, 118.80, 113.43, 73.39, 46.80. HRMS (ESI): Exact Mass Calcd. for $C_{15}H_{15}N_2OS$ (M+H): 271.0900, Found: 271.0893. HPLC (OD–

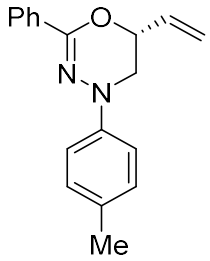
H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.576 min (minor), 10.188 min (major).

(*R*)-2-(furan-2-yl)-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2v)



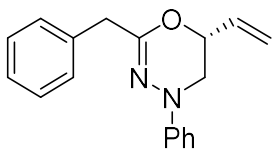
yellow oil, 16.2 mg, 64% yield, 92% ee, $[\alpha]_D^{24}$ –18.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.48 – 7.31 (m, 2H), 7.23 – 7.25 (m, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 6.46 – 6.45 (m, 1H), 6.03 – 5.95 (m, 1H), 5.53 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.4 Hz, 1H), 4.94 – 4.90 (m, 1H), 3.94 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.40 (q, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.82, 146.39, 143.29, 138.00, 133.60, 129.14, 120.25, 119.04, 113.67, 111.24, 109.32, 73.32, 47.08. HRMS (ESI): Exact Mass Calcd. for $C_{15}H_{15}N_2O_2$ (M+H): 255.1128, Found: 255.1121. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 11.214 min (minor), 12.568 min (major).

(*R*)-2-phenyl-4-(*p*-tolyl)-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2w)



yellow oil, 14.5 mg, 52% yield, 87% ee, $[\alpha]_D^{24}$ –2.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.39 – 7.36 (m, 3H), 7.19 – 7.11 (m, 4H), 6.05 – 5.97 (m, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.39 (d, *J* = 10.4 Hz, 1H), 4.94 – 4.93 (m, 1H), 3.90 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.32 (q, *J* = 2.8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.17, 143.07, 134.11, 132.67, 129.62, 129.37, 128.98, 128.13, 125.35, 118.46, 113.74, 73.13, 47.13, 20.54. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O$ (M+H): 279.1492, Found: 279.1489. HPLC (AD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.890 min (minor), 9.874 min (major).

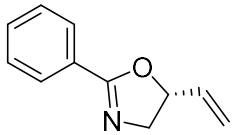
(*R*)-2-benzyl-4-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3,4-oxadiazine (2x)



yellow solid, mp 65.8 – 67.9°C, 16.4 mg, 59% yield, 87% ee, $[\alpha]_D^{24}$ –16.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.35 (m, 2H), 7.32 – 7.22 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* =

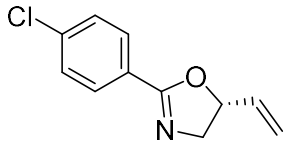
7.2 Hz, 1H), 5.89 – 5.80 (m, 1H), 5.28 (dd, *J* = 17.2, 10.8 Hz, 2H), 4.78 – 4.74 (m, 1H), 3.75 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.61 (s, 2H), 3.16 (q, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.63, 147.05, 136.88, 133.98, 129.05, 128.96, 128.39, 126.66, 119.87, 118.32, 113.68, 73.68, 46.71, 40.05. HRMS (ESI): Exact Mass Calcd. for $C_{18}H_{19}N_2O$ (M+H): 279.1492, Found: 279.1486. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 8.711 min (minor), 12.098 min (major).

(*R*)-2-phenyl-5-vinyl-4,5-dihydrooxazole (4a)



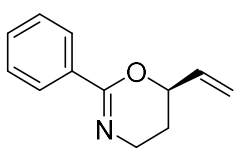
yellow oil, 11.9 mg, 69% yield, 91% ee, $[\alpha]_D^{25}$ +2 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.96 (m, 2H), 7.50 – 7.47 (m, 1H), 7.43 – 7.39 (m, 2H), 6.01 – 5.92 (m, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 5.16 – 5.10 (m, 1H), 4.22 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.79 (dd, *J* = 14.4, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.02, 136.42, 131.42, 128.40, 128.45, 127.71, 117.41, 80.56, 60.55. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{12}NO$ (M+H): 174.0913, Found: 174.0921. HPLC (OD–H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.896 min (minor), 14.120 min (major).

(*R*)-2-(4-chlorophenyl)-5-vinyl-4,5-dihydrooxazole (4b)



yellow oil, 14.1 mg, 68% yield, 90% ee, $[\alpha]_D^{26}$ –16 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.00 – 5.91 (m, 1H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.15 – 5.09 (m, 1H), 4.21 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.78 (dd, *J* =14.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.14, 137.60, 136.23, 129.59, 128.71, 126.23, 117.61, 80.79, 60.60. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{11}ClNO$ (M+H): 208.0524, Found: 208.0522. HPLC (OD–H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.600 min (minor), 9.323 min (major).

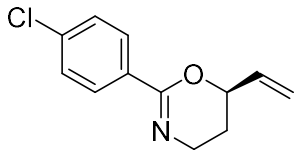
(*R*)-2-phenyl-6-vinyl-5,6-dihydro-4*H*-1,3-oxazine (4c)



yellow oil, 12.5 mg, 67% yield, 91% ee, $[\alpha]_D^{26}$ +2 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.44 – 7.35 (m, 3H), 6.01 – 5.92 (m, 1H), 5.39 (dt, *J* = 17.2,1.2 Hz, 1H), 5.28 (dt, *J* =

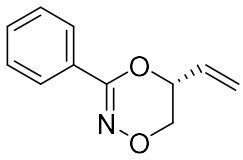
10.8, 1.6 Hz, 1H), 4.81 – 4.76 (m, 1H), 3.69 – 3.56 (m, 2H), 2.09 – 2.02 (m, 1H), 1.83 – 1.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.35, 136.76, 133.98, 130.41, 128.07, 127.00, 116.35, 74.90, 42.04, 27.04. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{14}NO$ (M+H): 188.1070, Found: 188.1079. HPLC (OD–H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.317 min (minor), 8.465 min (major).

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



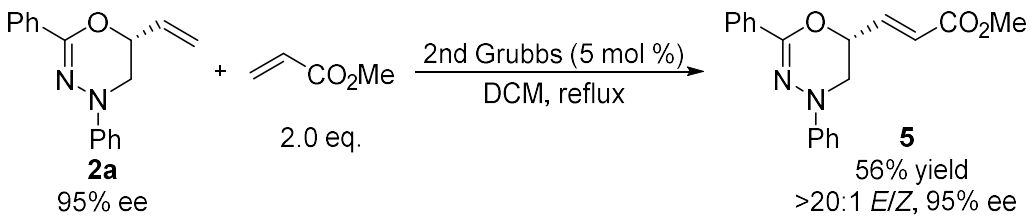
yellow oil, 12.2 mg, 55% yield, 95% ee, $[\alpha]_D^{25}$ +2 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.99 – 5.91 (m, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 4.78 – 4.75 (m, 1H), 3.68 – 3.55 (m, 2H), 2.08 – 2.02 (m, 1H), 1.83 – 1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.50, 136.58, 136.50, 132.45, 128.40, 128.29, 116.53, 75.04, 42.03, 26.95. HRMS (ESI): Exact Mass Calcd. for $C_{12}H_{13}ClNO$ (M+H): 222.0680, Found: 222.0690. HPLC (OD–H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.197 min (minor), 8.077 min (major).

(*R*)-3-phenyl-5-vinyl-5,6-dihydro-1,4,2-dioxazine (4e)



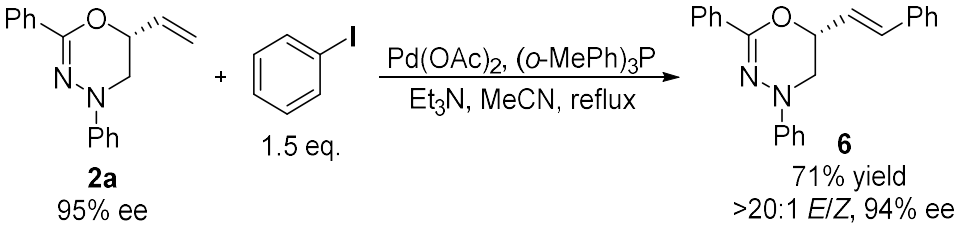
yellow oil, 11.7 mg, 62% yield, 54% ee, $[\alpha]_D^{26}$ –2 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.45 – 7.36 (m, 3H), 5.97 – 5.89 (m, 1H), 5.54 (d, *J* = 17.6 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 4.93 – 4.89 (m, 1H), 4.27 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.78 (dd, *J* = 11.6, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.99, 131.79, 130.54, 130.47, 128.30, 125.77, 119.65, 74.24, 67.47. HRMS (ESI): Exact Mass Calcd. for $C_{11}H_{12}NO_2$ (M+H): 190.0863, Found: 190.0864. HPLC (OD–H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.781 min (minor), 9.443 min (major).

4. Synthetic transformations of compound 2a



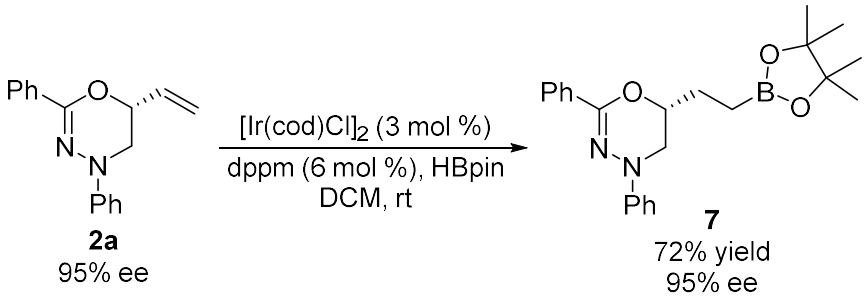
Under argon atmosphere, a solution of compound **2a** (26.4 mg, 0.1 mmol) and methyl acrylate (0.18 mL, 0.2 mmol, 2.0 equiv.) in DCM (2 mL) was treated with Grubbs 2nd catalyst (4.3 mg, 0.005 mmol, 5 mol %). The reaction mixture was refluxed for 12 h. After cooling to room temperature, DCM was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (15/1) to afford product **5** (18.0 mg, 56% yield, >20:1 *E*/*Z*, 94% ee).

methyl (*R*,*E*)-3-(2,4-diphenyl-5,6-dihydro-4*H*-1,3,4-oxadiazin-6-yl) acrylate (5). white solid, mp 109.4 – 113.2 °C, 18.0 mg, 56% yield, 94% ee, $[\alpha]_D^{24}$ –56.0 (c 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.40 – 7.38 (m, 3H), 7.36 – 7.28 (m, 4H), 7.05 (dd, J = 20.0, 3.6 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 6.28 (dd, J = 16.0, 1.6 Hz, 1H), 5.17 – 5.13 (m, 1H), 4.00 (dd, J = 12.0, 3.2 Hz, 1H), 3.78 (s, 3H), 3.42 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15, 146.90, 142.65, 142.20, 132.09, 129.35, 129.18, 128.25, 125.38, 123.12, 120.44, 113.70, 71.27, 51.97, 46.07. HRMS (ESI): Exact Mass Calcd. for $C_{19}H_{19}N_2O_3$ (M+H): 323.1390, Found: 323.1390. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 12.157 min (minor), 13.833 min (major).



A solution of **2a** (39.6 mg, 0.15 mmol), iodobenzene (25 μL, 0.225 mmol, 1.5 equiv.), palladium(II) acetate (2.03 mg, 0.009 mmol, 0.06 equiv.), tris(*o*-tolyl)phosphane (8.2 mg, 0.027 mmol, 0.18 equiv.) and triethylamine (31.2 μL, 0.225 mmol, 1.5 equiv.) in acetonitrile (3 mL) was refluxed for 4 h under an nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (10 mL) and washed with sodium bicarbonate solution (10 mL×3). The aqueous layer was extracted with ethyl acetate (10 mL×3) and the combined organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (19:1) as eluent to afford product **6** (36.2 mg, 71% yield, >20:1 *E*/*Z*, 94% ee).

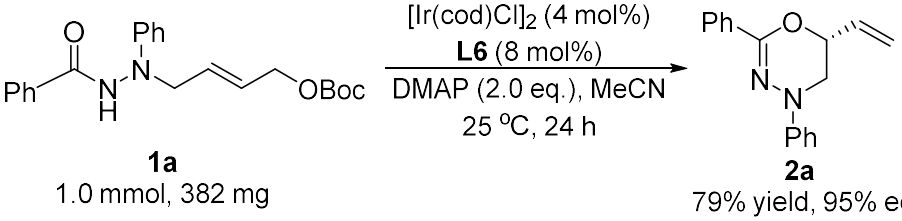
(*R*,*E*)-2,4-diphenyl-6-styryl-5,6-dihydro-4*H*-1,3,4-oxadiazine (6). yellow oil, 36.2 mg, 71% yield, 94% ee, $[\alpha]_D^{23}$ –7.0 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.96 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.24 (m, 10H), 6.93 – 6.89 (m, 1H), 6.84 (d, J = 16.0 Hz, 1H), 6.35 (q, J = 6.8 Hz, 1H), 5.10 – 5.06 (m, 1H), 4.01 (dd, J = 12.0, 3.2 Hz, 1H), 3.44 (q, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.11, 143.42, 135.84, 133.97, 132.59, 129.13, 128.75, 128.47, 128.17, 126.84, 125.45, 124.76, 119.98, 113.50, 73.27, 47.02. HRMS (ESI): Exact Mass Calcd. for $C_{23}H_{21}N_2O$ (M+H): 341.1648, Found:341.1647. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 21.585 min (minor), 22.757 min (major).



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **2a** (26.4 mg, 0.1 mmol), $[Ir(cod)Cl]_2$ (2.01 mg, 0.003 mmol, 3 mol %) and dppm (2.3 mg, 0.006 mmol, 6 mol %). The flask tube was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. DCM (2.0 mL) and HBpin (29 μL, 0.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, the reaction was quenched with 2M HCl (2 mL) and extracted with EtOAc (10 mL×3). The combined organic fractions were washed with brine (10 mL×3), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate (9/1) to afford the product **7** (28.2 mg, 72% yield, 95% ee).

(*R*)-2,4-diphenyl-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) ethyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine (7). yellow oil, 28.2 mg, 72% yield, 95% ee, $[\alpha]_D^{24}$ –10.0 (c 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.39 – 7.28 (m, 7H), 6.90 – 6.86 (m, 1H), 4.40 – 4.34 (m, 1H), 3.93 (dd, J = 11.6 Hz, 1H), 3.26 (q, J = 3.6 Hz, 1H), 2.00 – 1.80 (m, 2H), 1.26 (s, 12H), 1.16 – 0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.21, 143.39, 132.80, 129.07, 128.92, 128.08, 125.40, 119.58, 113.22, 83.38, 73.80, 46.51, 27.63, 24.90, 24.88. HRMS (ESI): Exact Mass Calcd. for $C_{23}H_{30}BN_2O_3$ (M+H): 393.2348, Found: 393.2353. HPLC (OD–H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 7.263 min (minor), 11.591 min (major).

5. Scale-up synthesis of compound 2a



To a 50 mL Schlenk tube equipped with a magnetic stir bar was added $[Ir(COD)Cl]_2$ (27 mg, 0.04 mmol, 4 mol %), phosphoramidite ligand **L6** (36 mg, 0.08 mmol, 8 mol %). The flask was sealed, evacuated, and backfilled with argon three times using standard Schlenk techniques. THF (5 mL) and *n*-propylamine (5 mL) was added at 25 °C and the reaction mixture was warmed to 50 °C for 0.5 h. The solvent was removed under reduced pressure to give a pale-yellow solid and DMAP (244 mg, 2 mmol, 2 equiv.), a solution of **1a** (1 mmol) in MeCN (20 mL) were then added. The resulting solution was stirred for 24 h at 25 °C. Upon completion of the reaction (monitored by TLC), the reaction

mixture was passed through a short pad of celite and washed with ethyl acetate (10 mL×3). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **2a**.

Table 1. Crystal data and structure refinement for compound 2a

Identification code	lixiy_0320_auto
Empirical formula	$C_{17}H_{15}N_2O$
Formula weight	263.31
Temperature/K	300.61(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6196(3)
b/Å	10.1794(2)
c/Å	16.4222(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1440.92(7)
Z	4
ρ_{calc}g/cm^3	1.214
μ/mm^{-1}	0.607
F(000)	556.0
Crystal size/mm^3	0.19 × 0.18 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	10.224 to 152.592
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 7$, $-20 \le l \le 20$
Reflections collected	7439
Independent reflections	2816 [R_{int} = 0.0292, R_{sigma} = 0.0345]
Data/restraints/parameters	2816/2/190
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1092
Largest diff. peak/hole / e Å^{-3}	0.18/-0.12
Flack parameter	0.09(16)

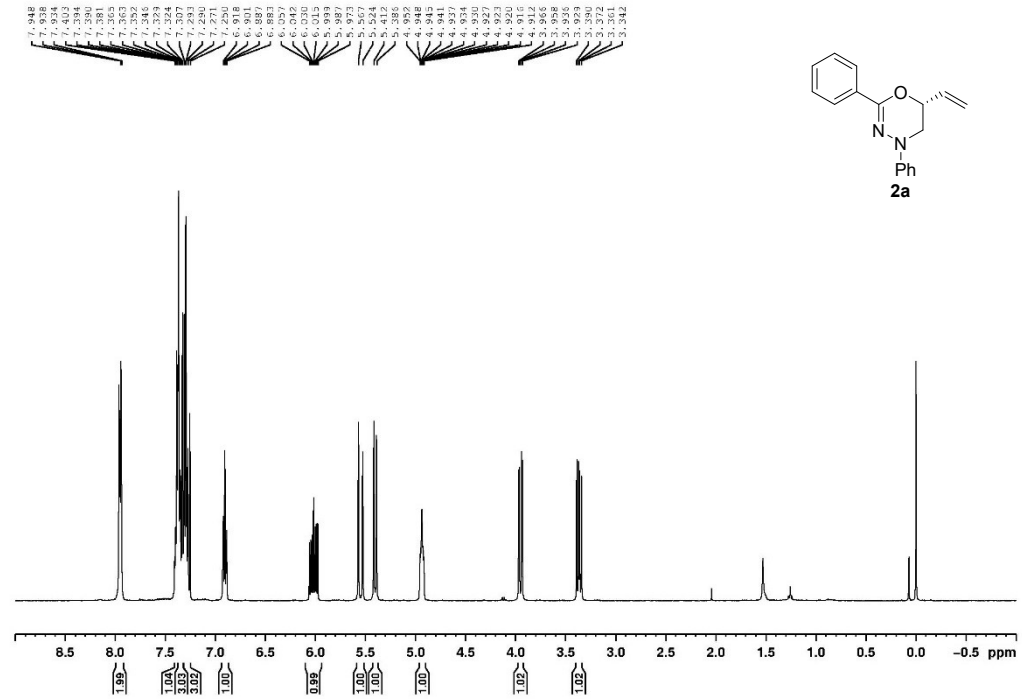
6. References

[1] F. Zhan, G. Liang, *Angew. Chem., Int. Ed*. **2013**, *52*, 1266–1269.

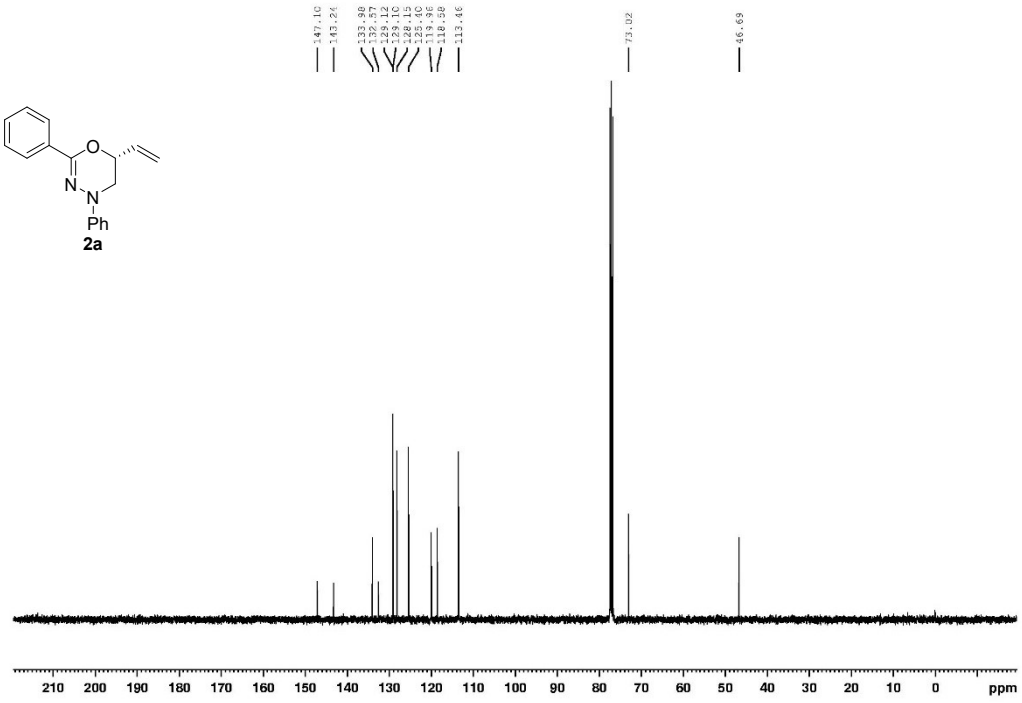
[2] J. S. Derasp, E. A. Barbera, N. R. Séguin, D. D. Brzezinski, A. M. Beauchemin, *Org. Lett*. **2020**, *22*, 7403–7407.

7. NMR spectra of compounds 2a−2x, 4a−4e and 5−7

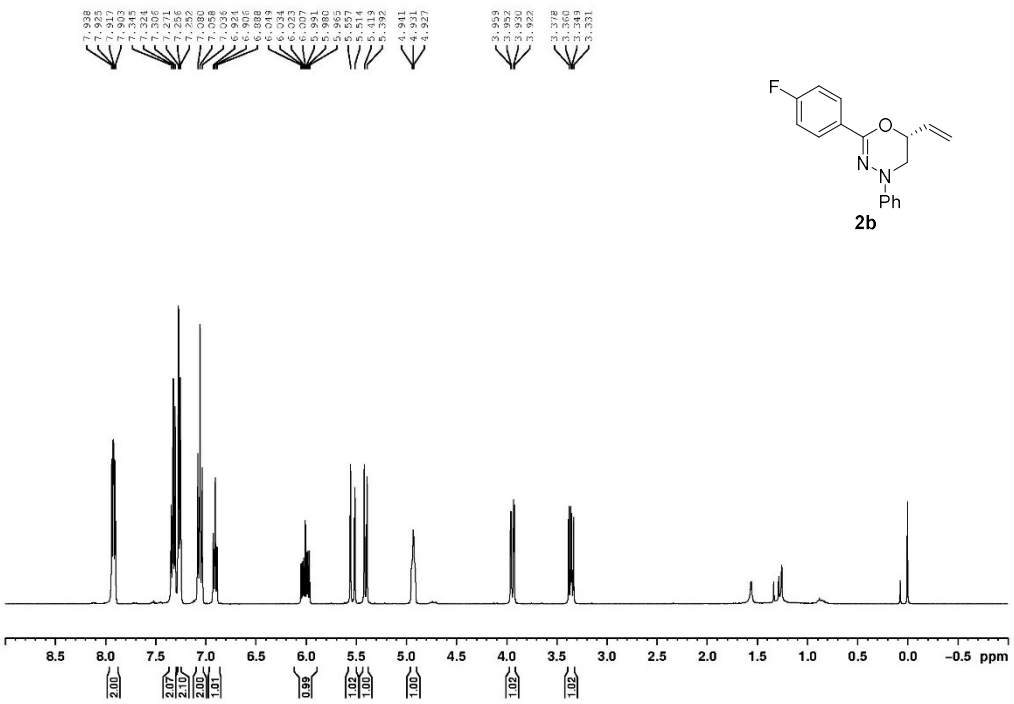
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz)



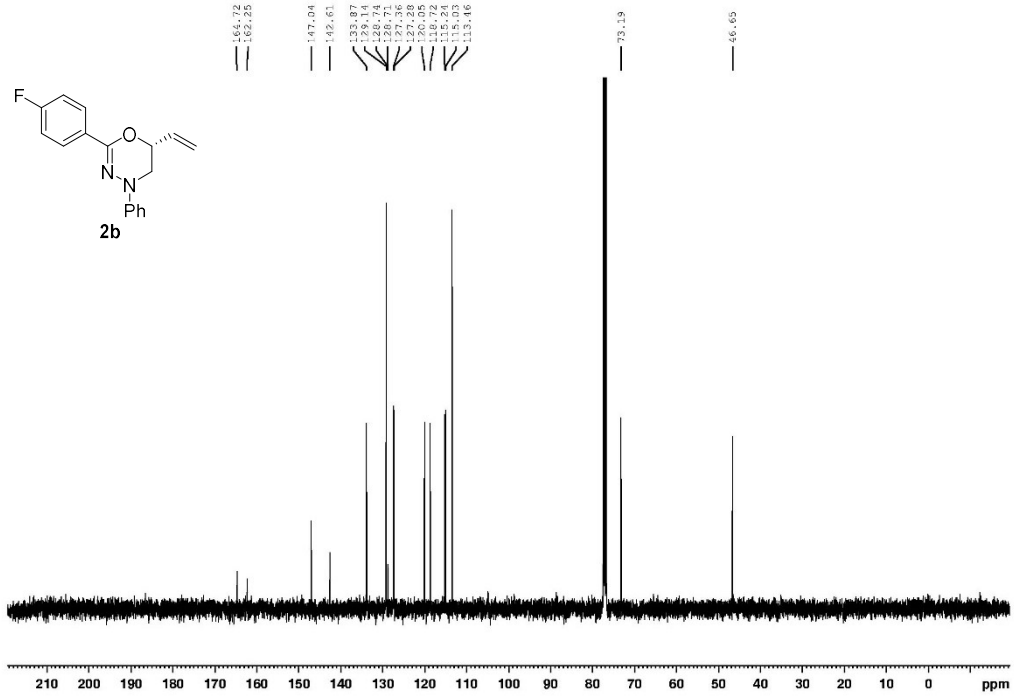
^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz)



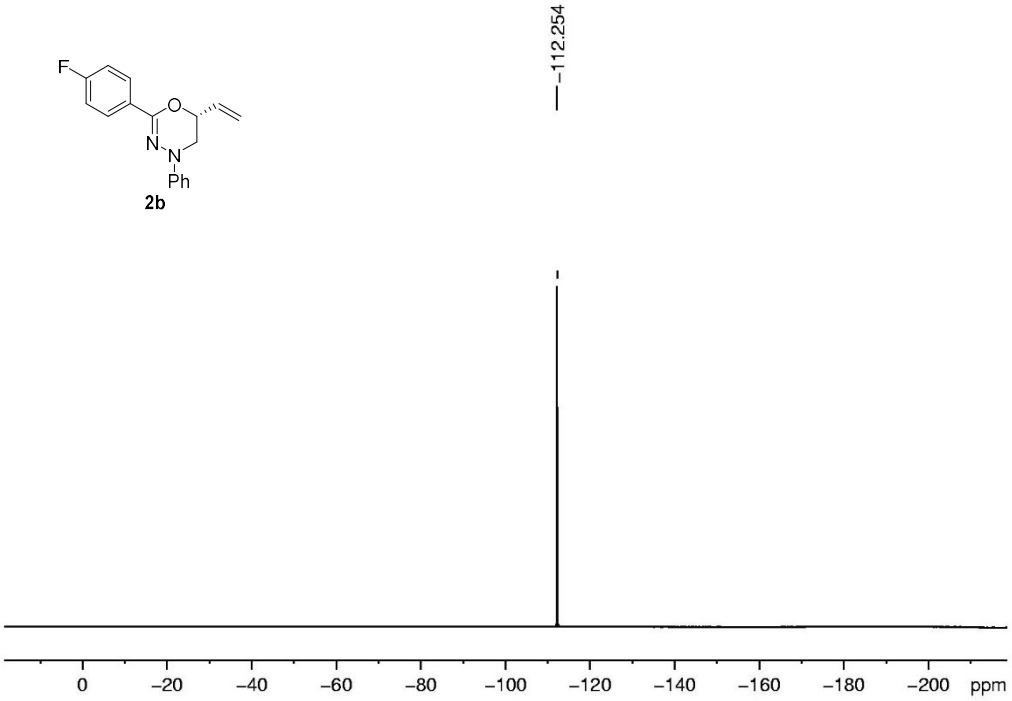
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz)



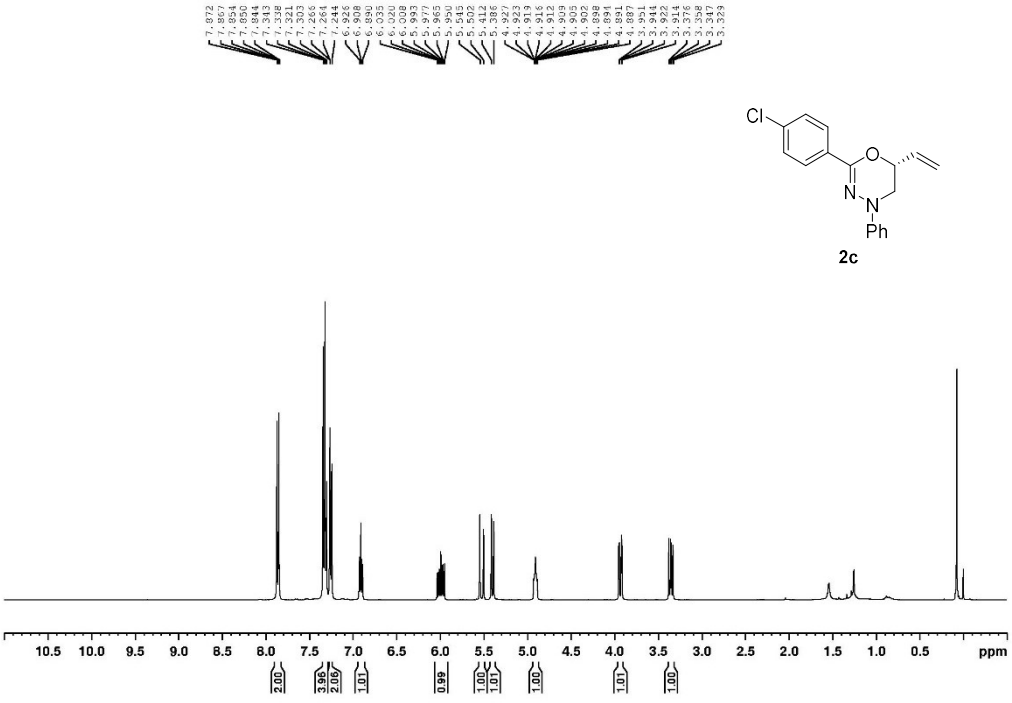
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz)



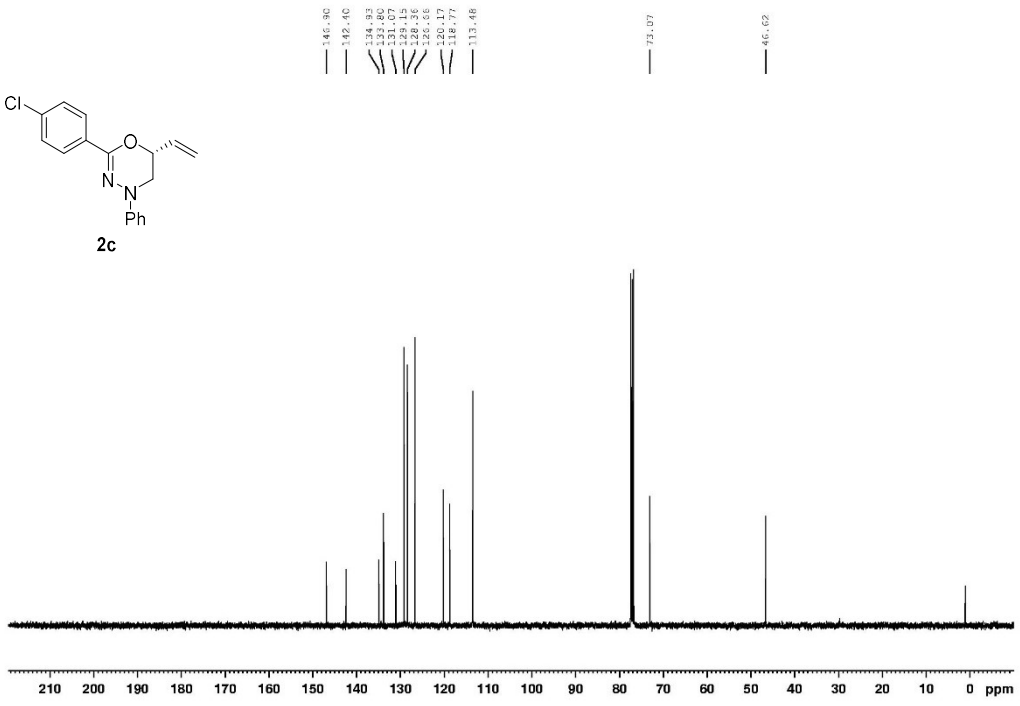
^{19}F NMR spectrum of compound **2b** ($CDCl_3$, 376 MHz)



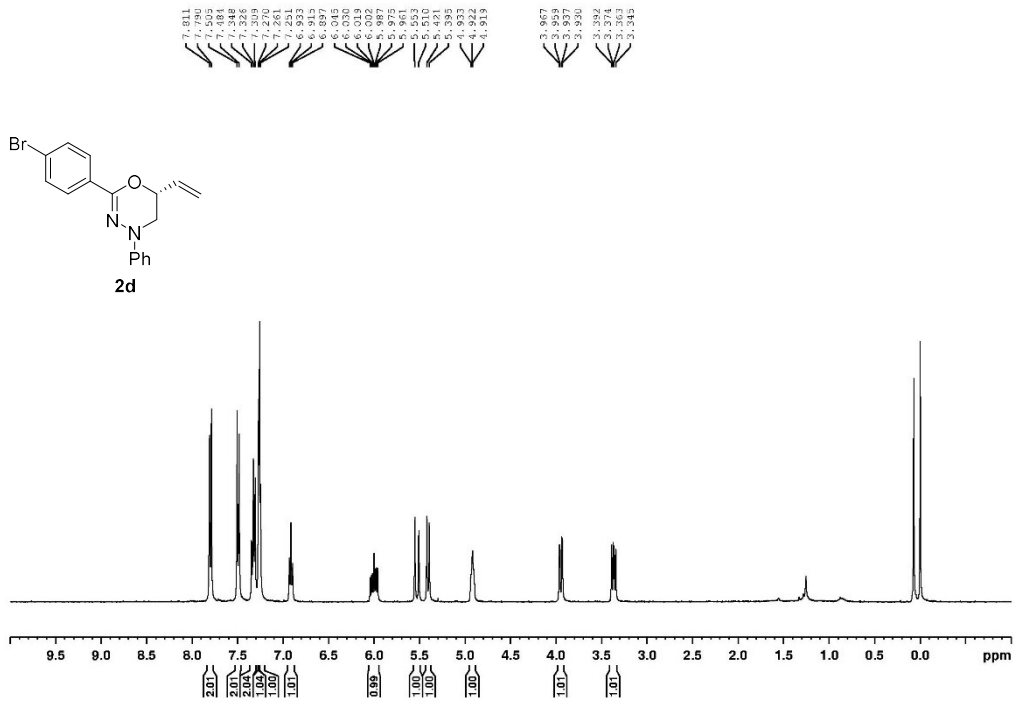
^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz)



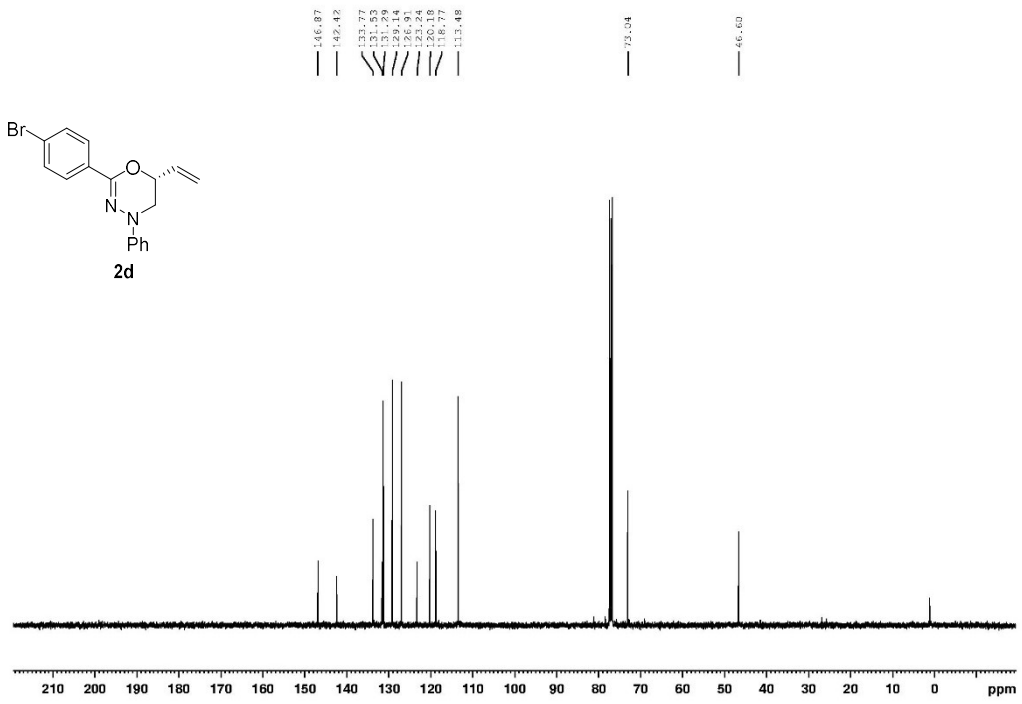
^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz)



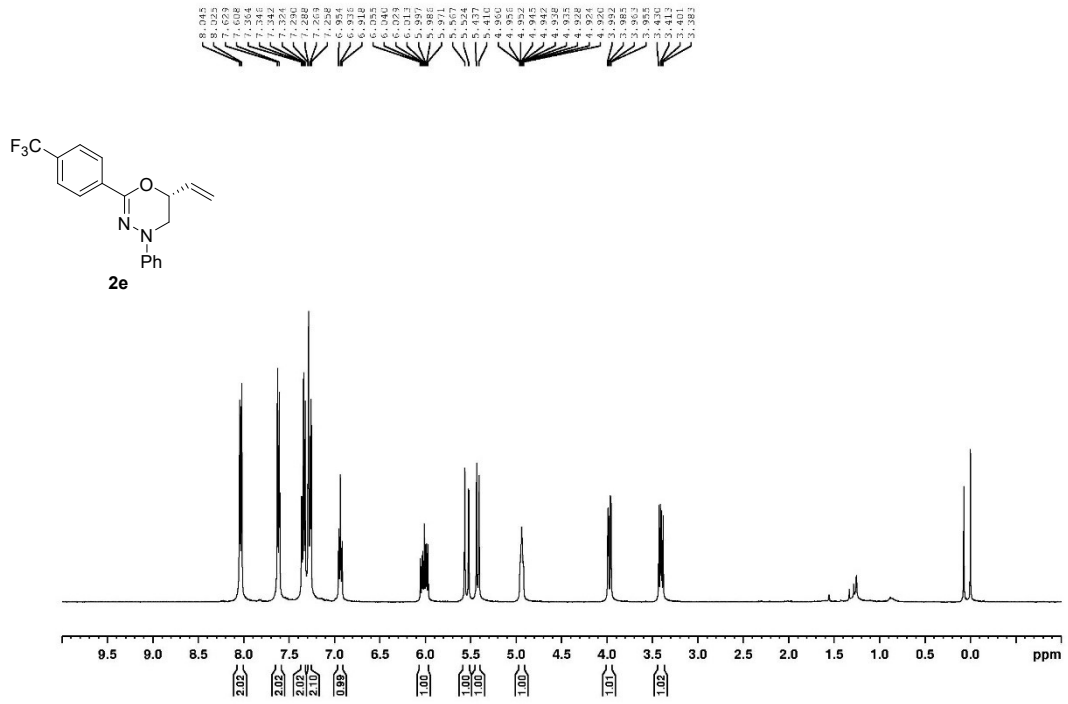
^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz)



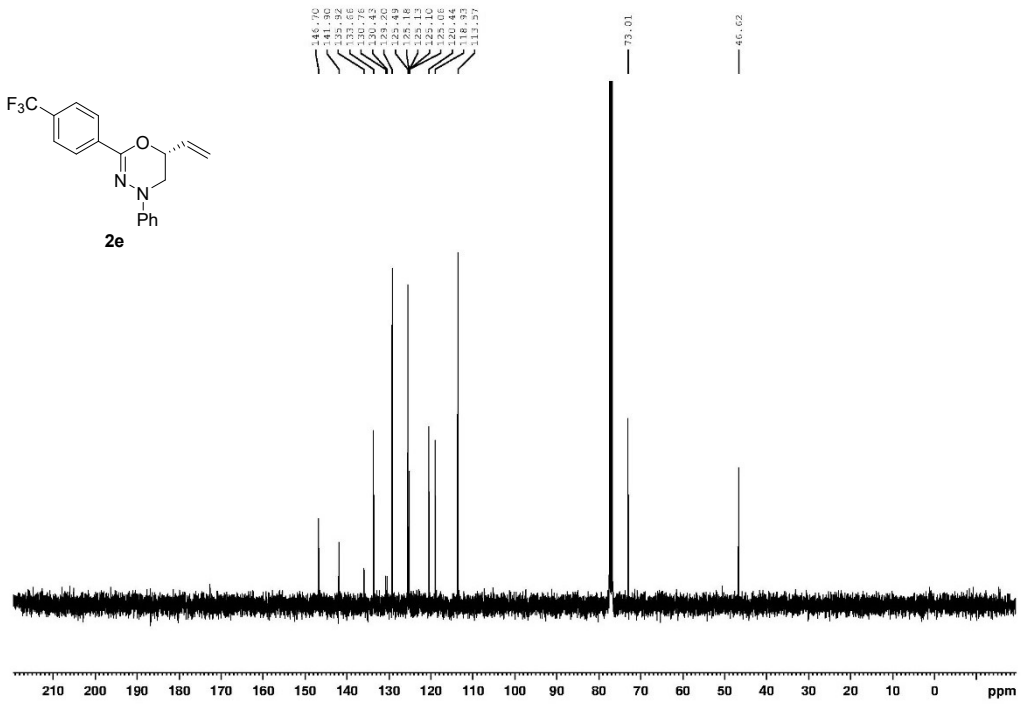
^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz)



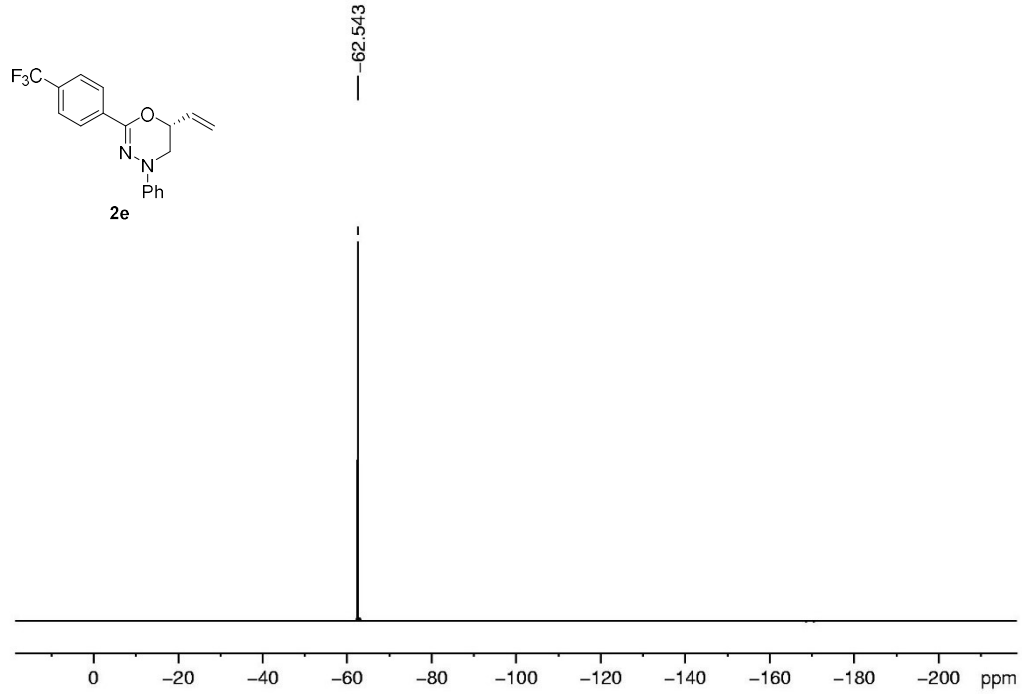
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz)



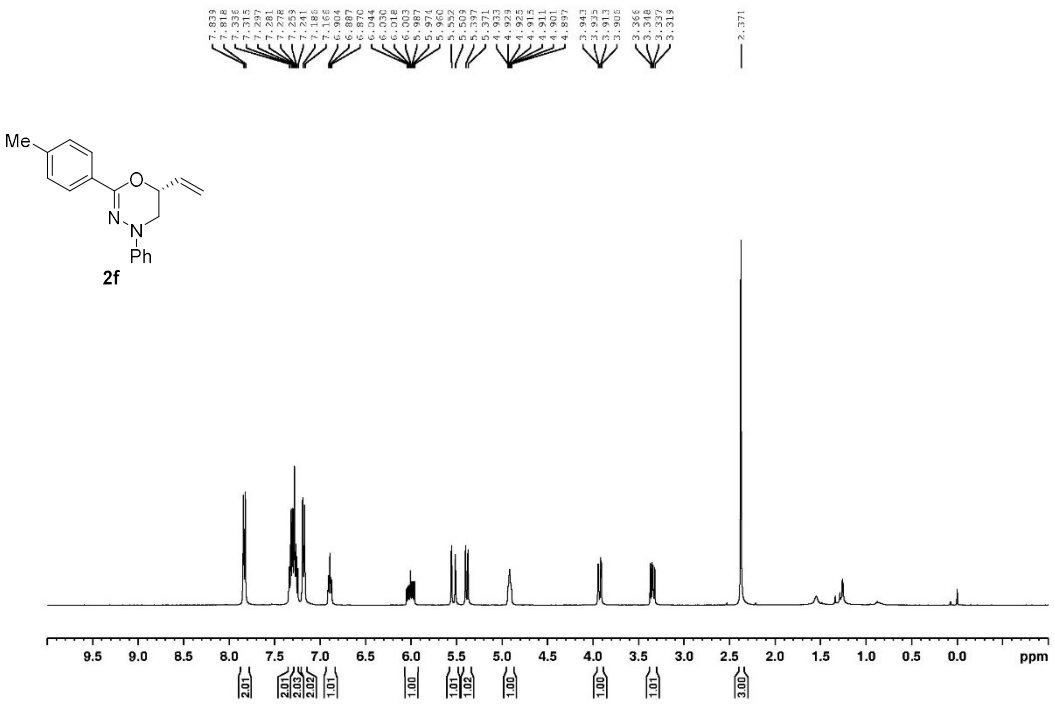
^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz)



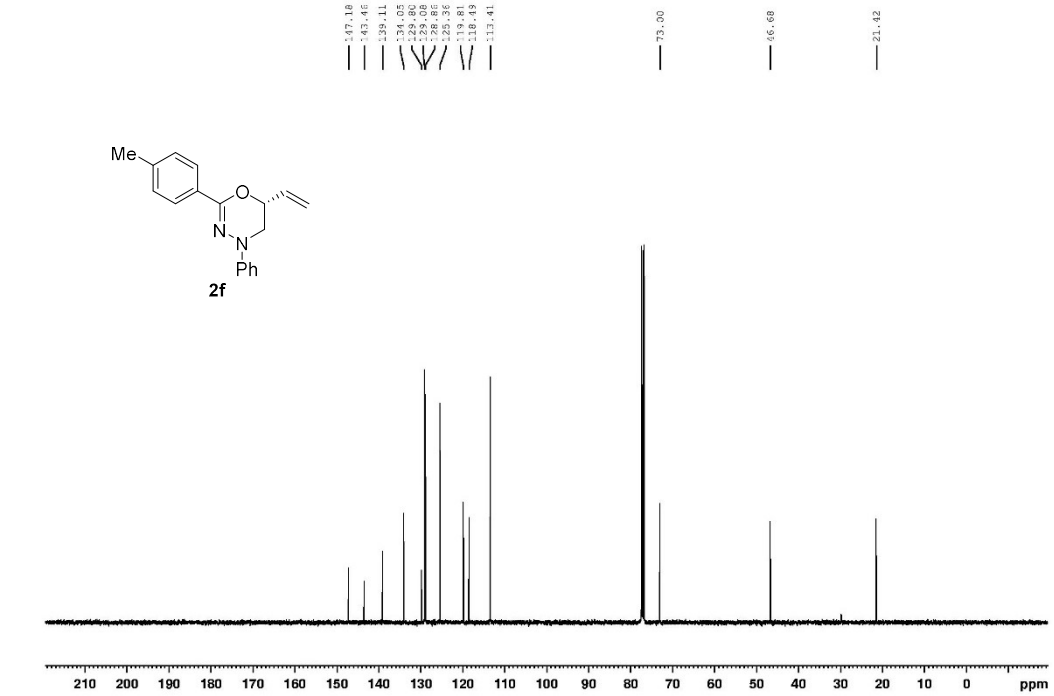
^{19}F NMR spectrum of compound **2e** ($CDCl_3$, 376 MHz)



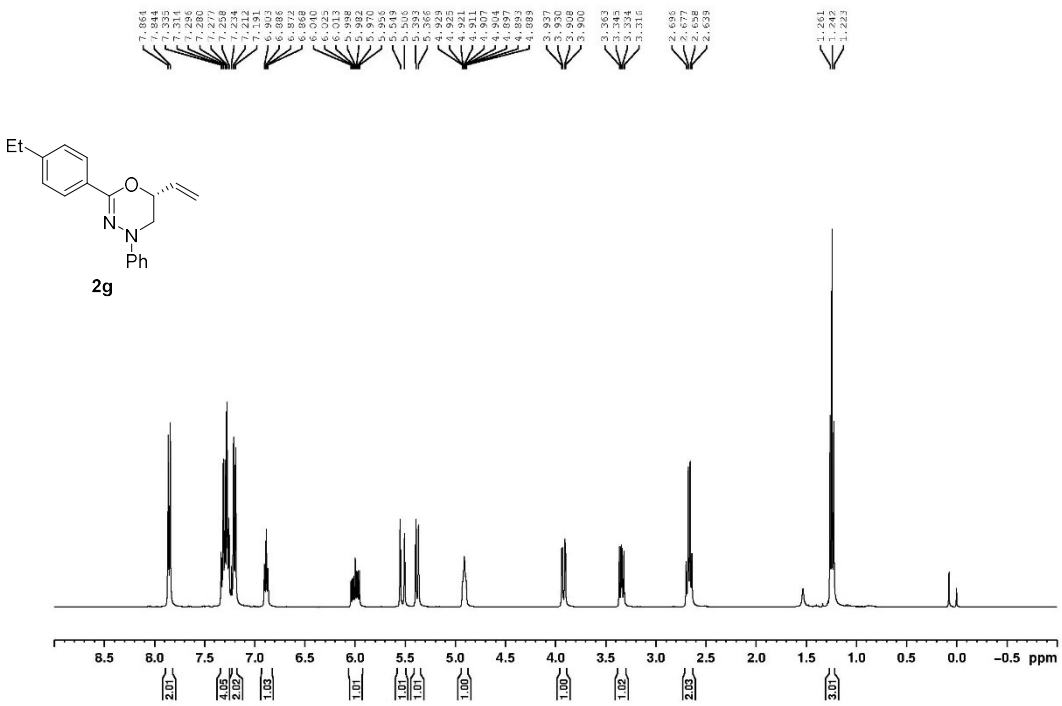
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)



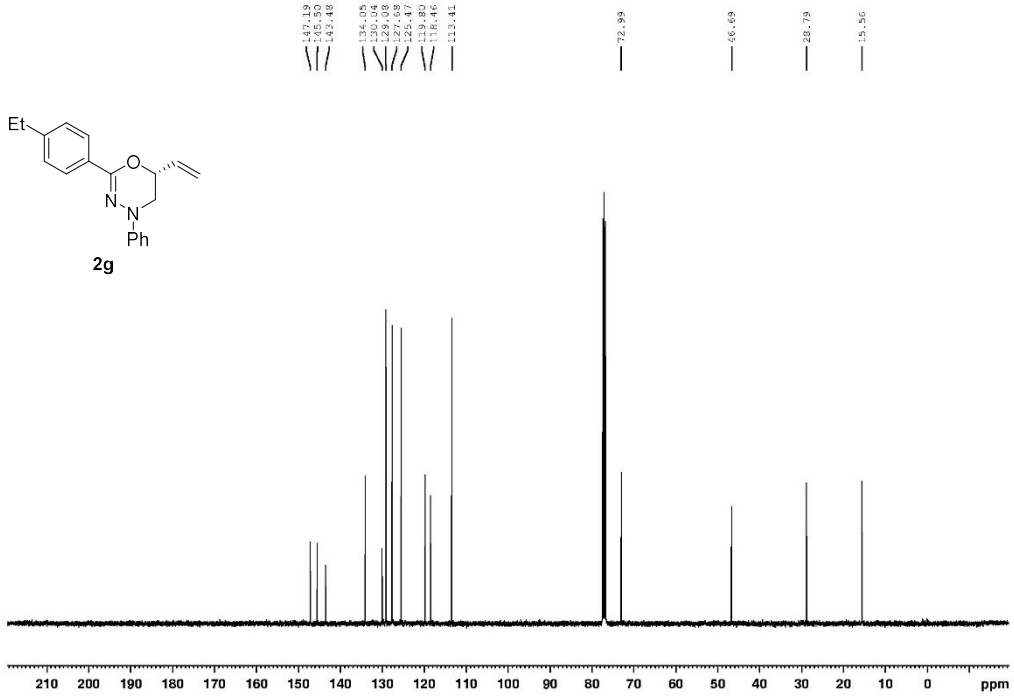
^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz)



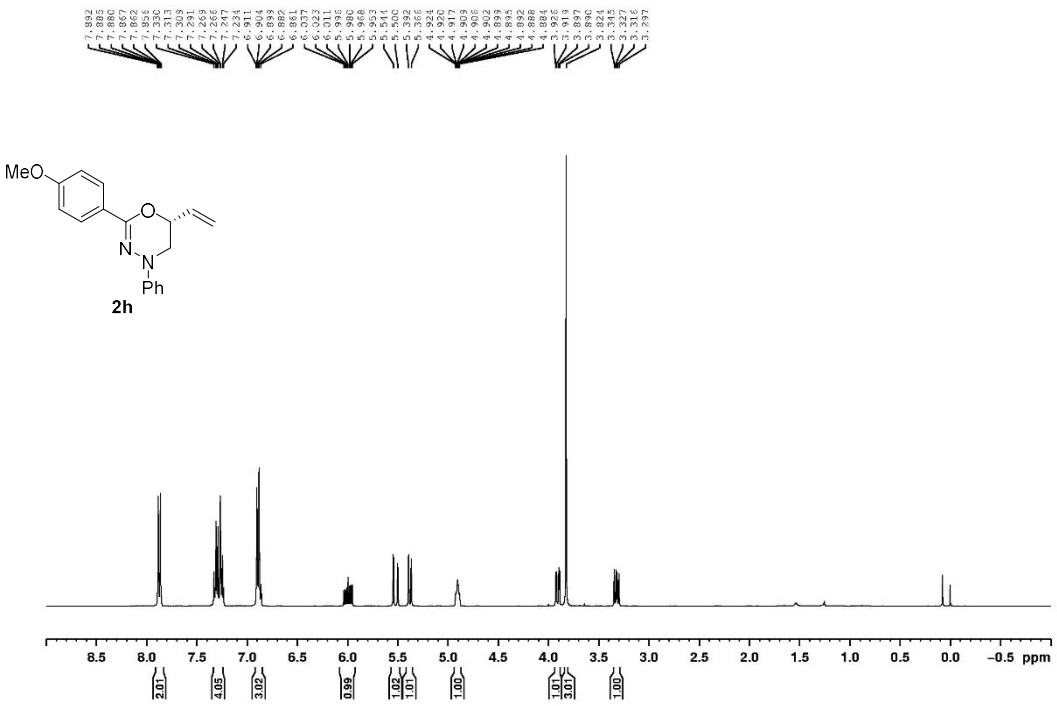
^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz)



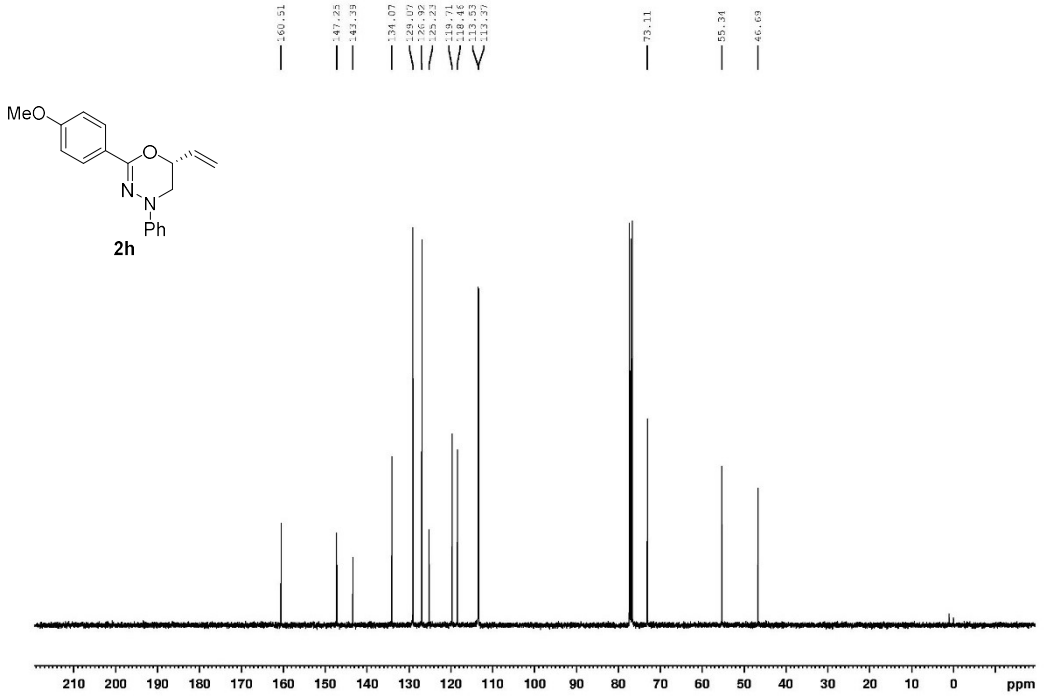
^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 100 MHz)



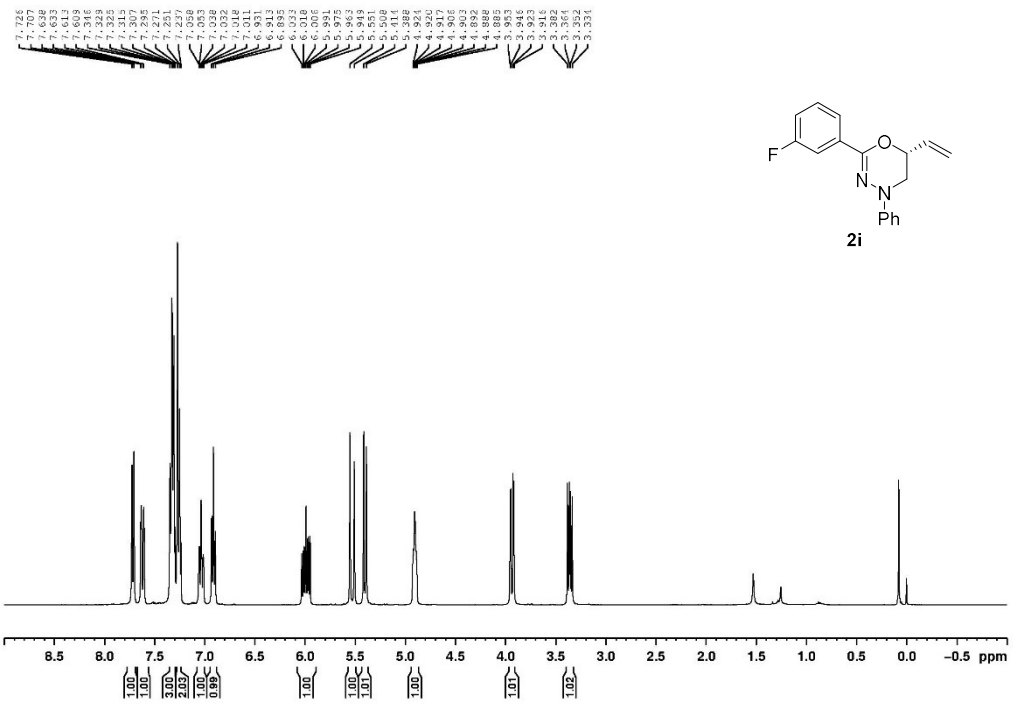
^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz)



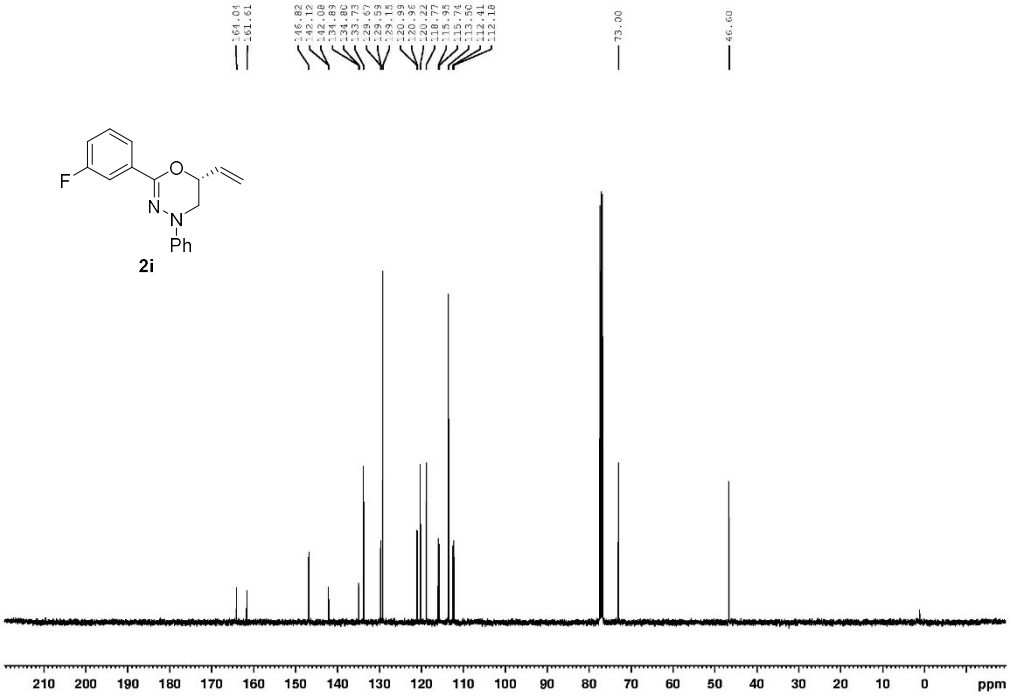
^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 100 MHz)



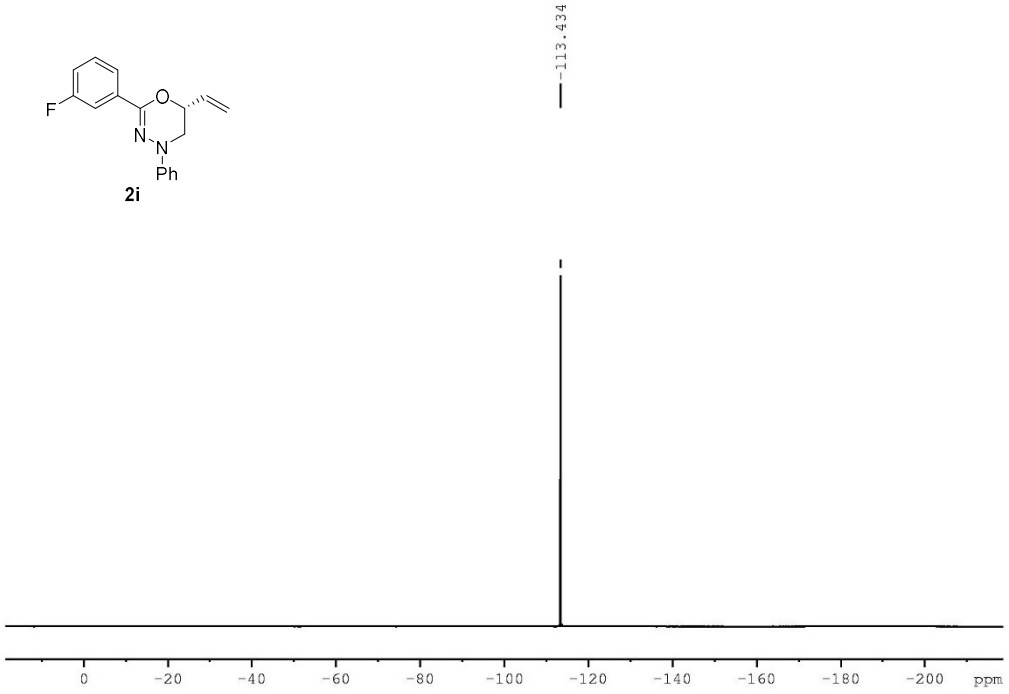
^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz)



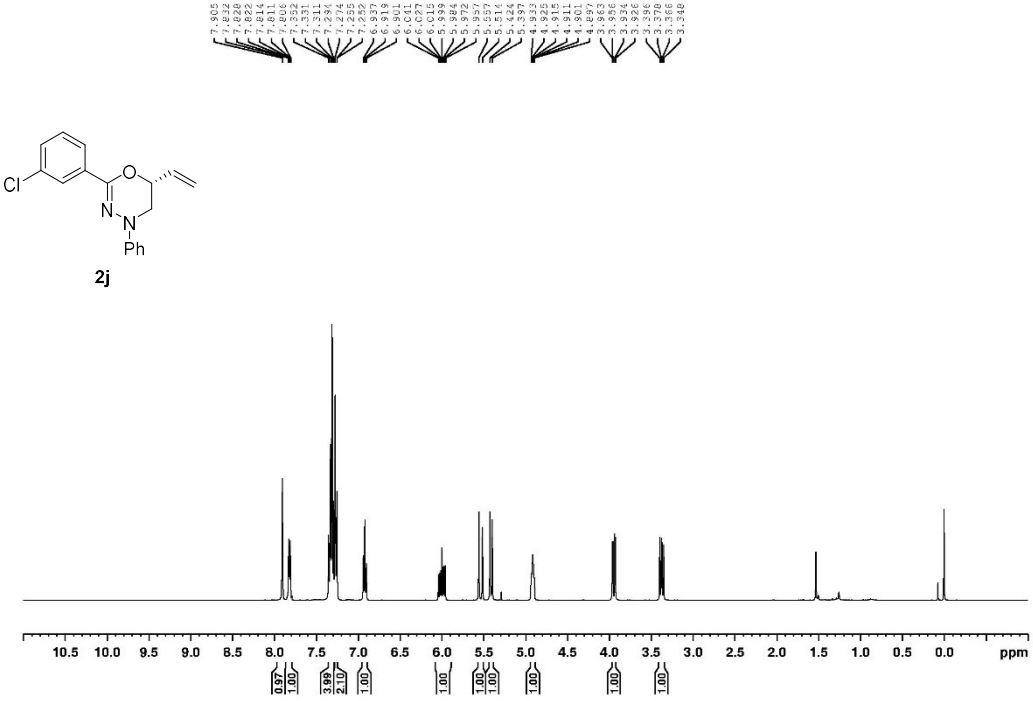
^{13}C NMR spectrum of compound **2i** ($CDCl_3$, 100 MHz)



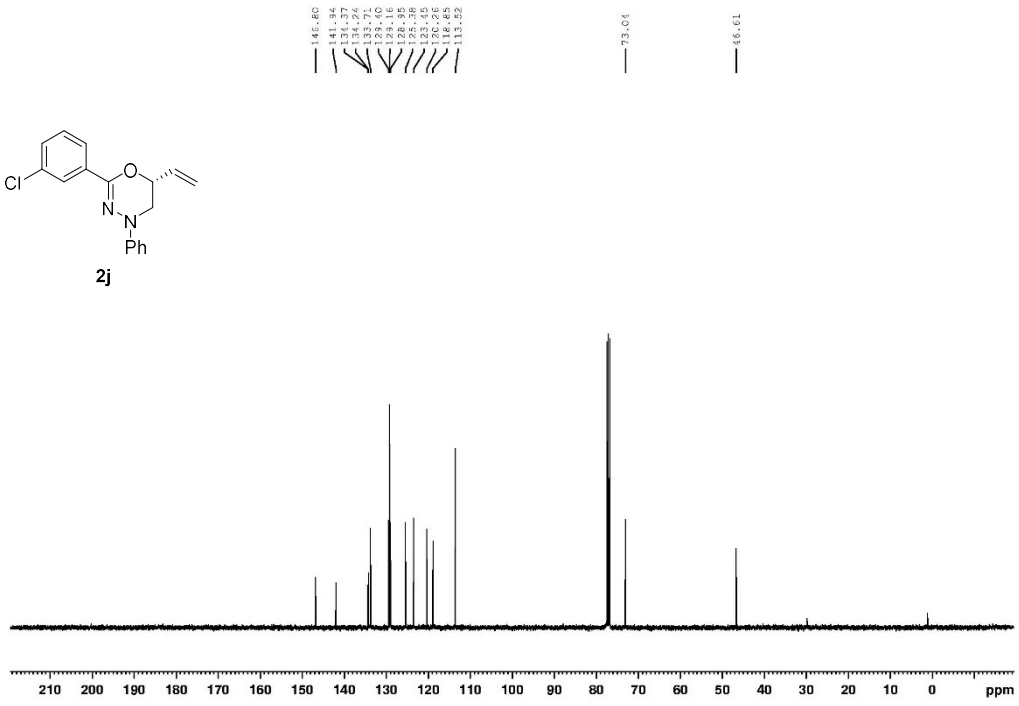
^{19}F NMR spectrum of compound **2i** ($CDCl_3$, 376 MHz)



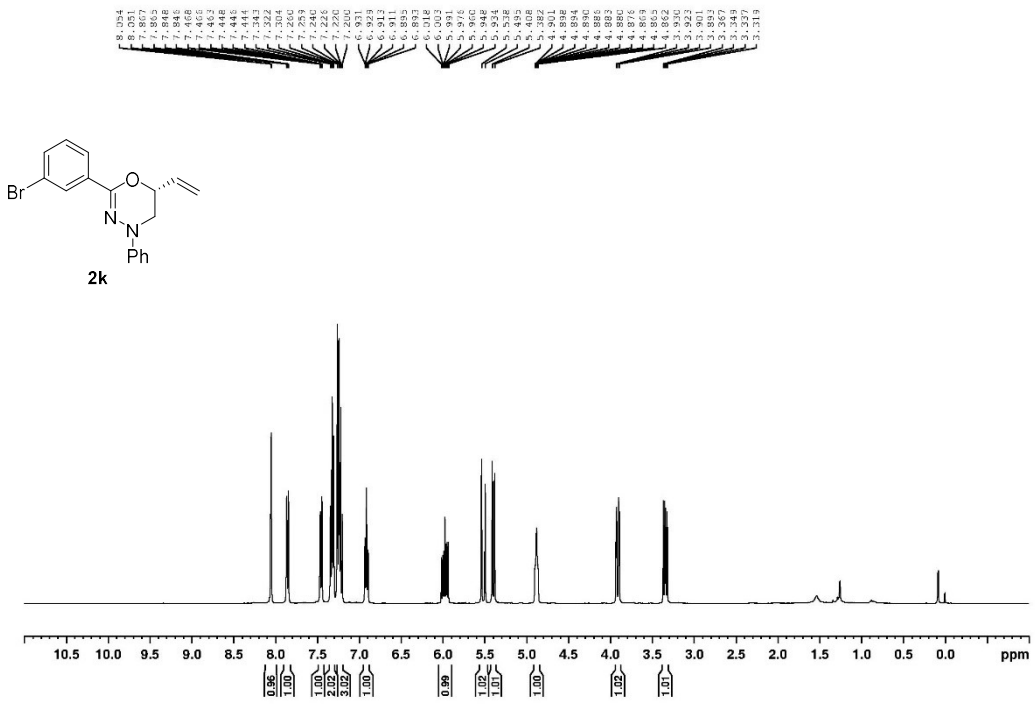
^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz)



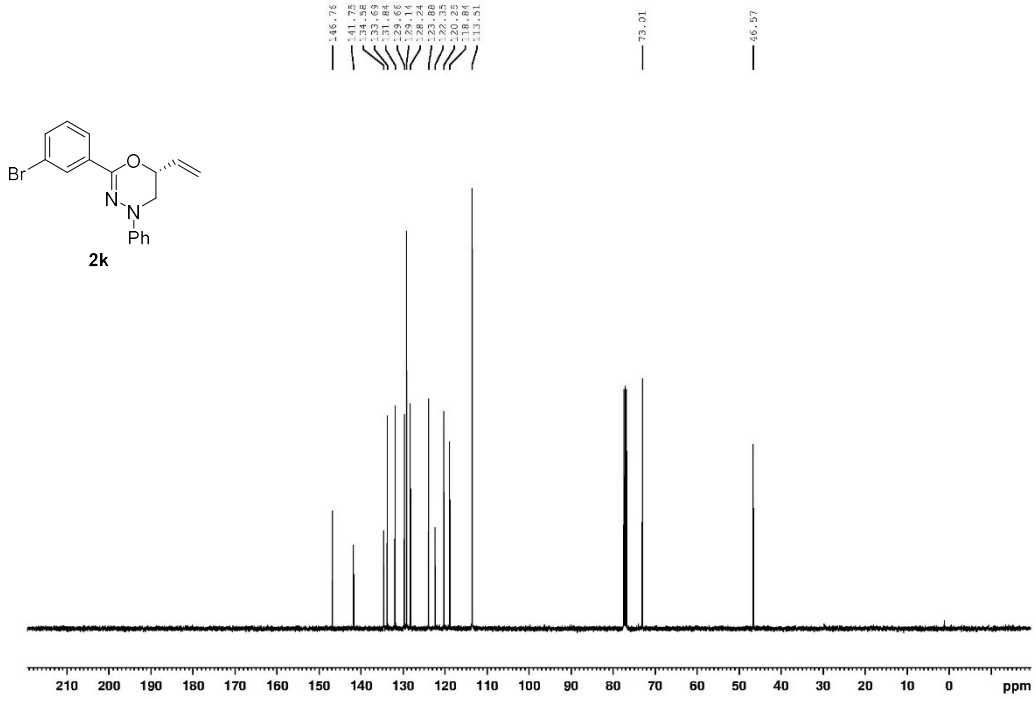
^{13}C NMR spectrum of compound **2j** ($CDCl_3$, 100 MHz)



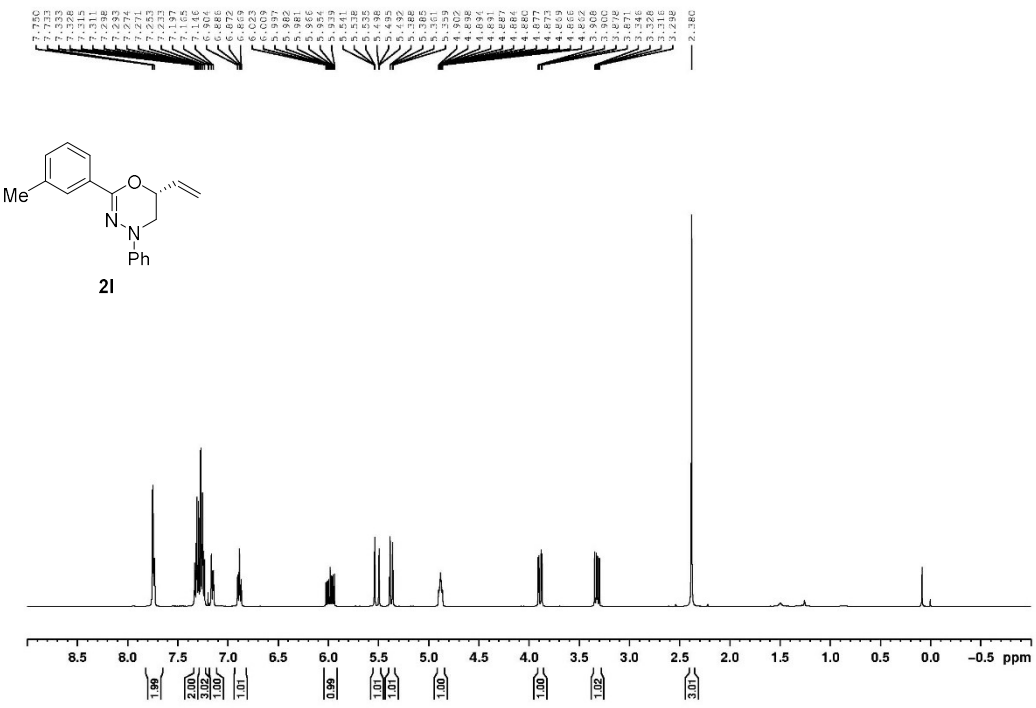
^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz)



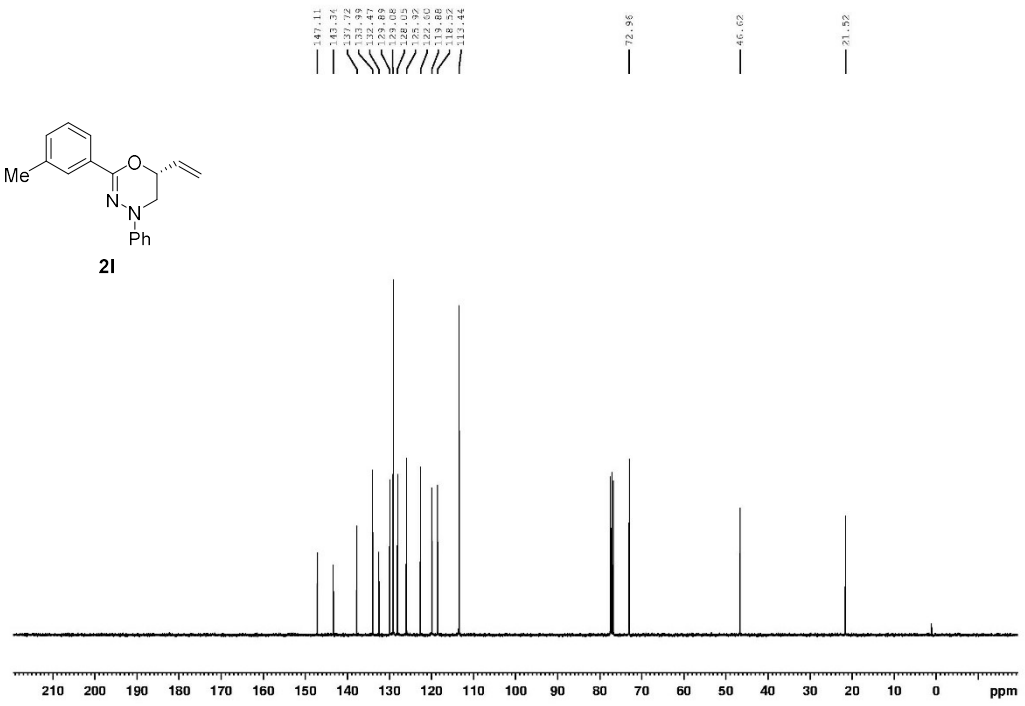
^{13}C NMR spectrum of compound **2k** ($CDCl_3$, 100 MHz)



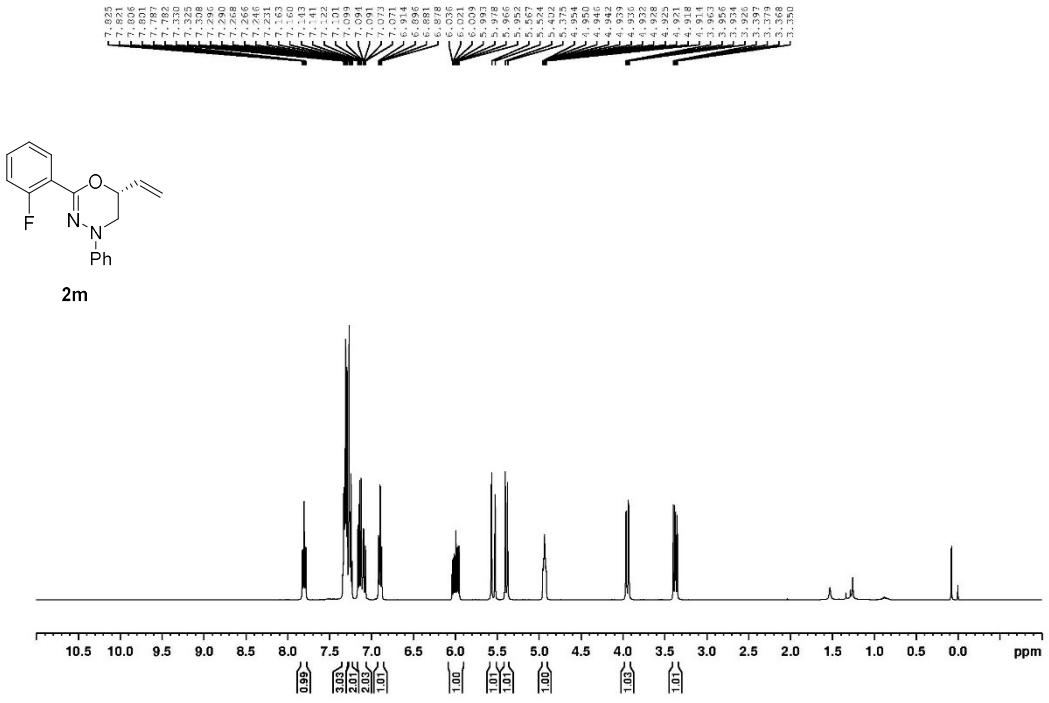
^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz)



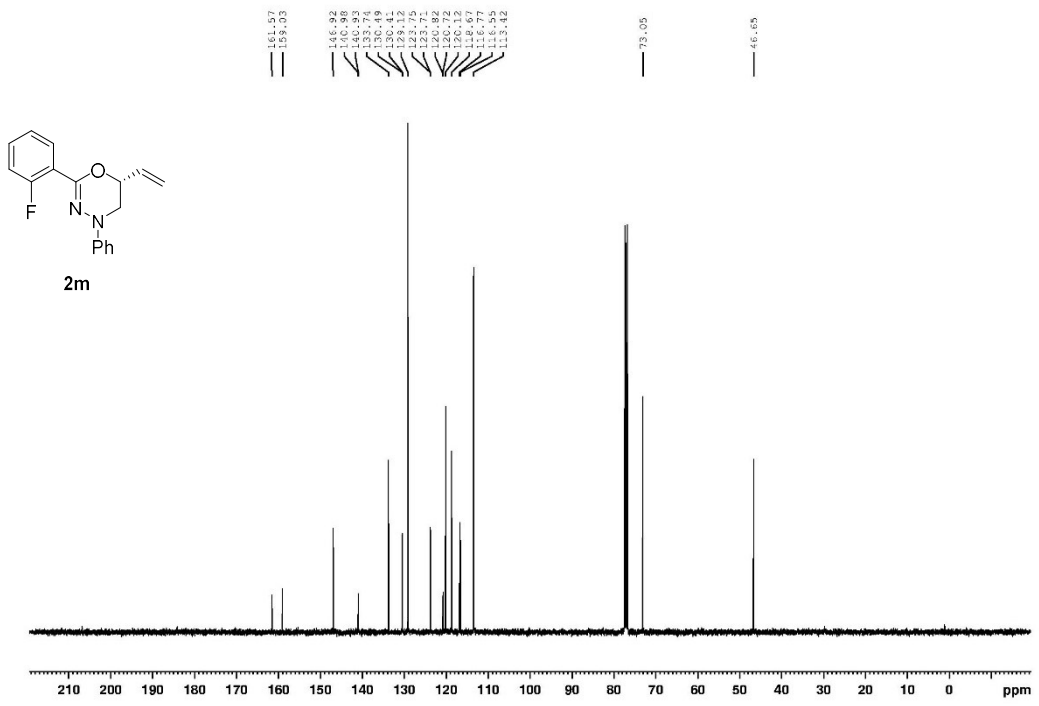
^{13}C NMR spectrum of compound **2l** ($CDCl_3$, 100 MHz)



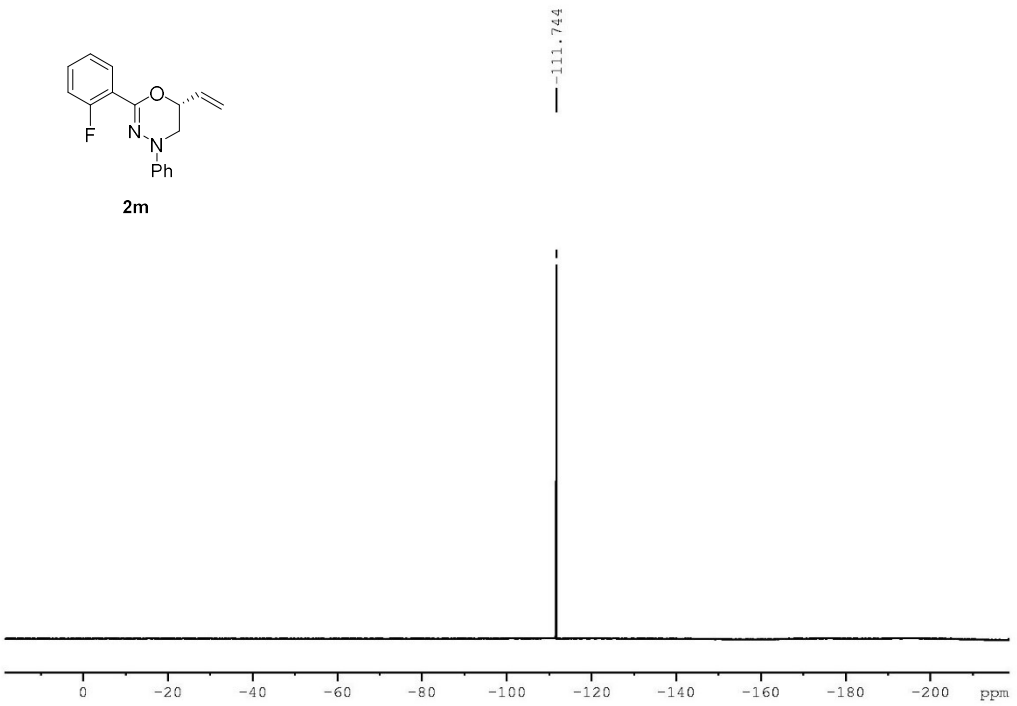
^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz)



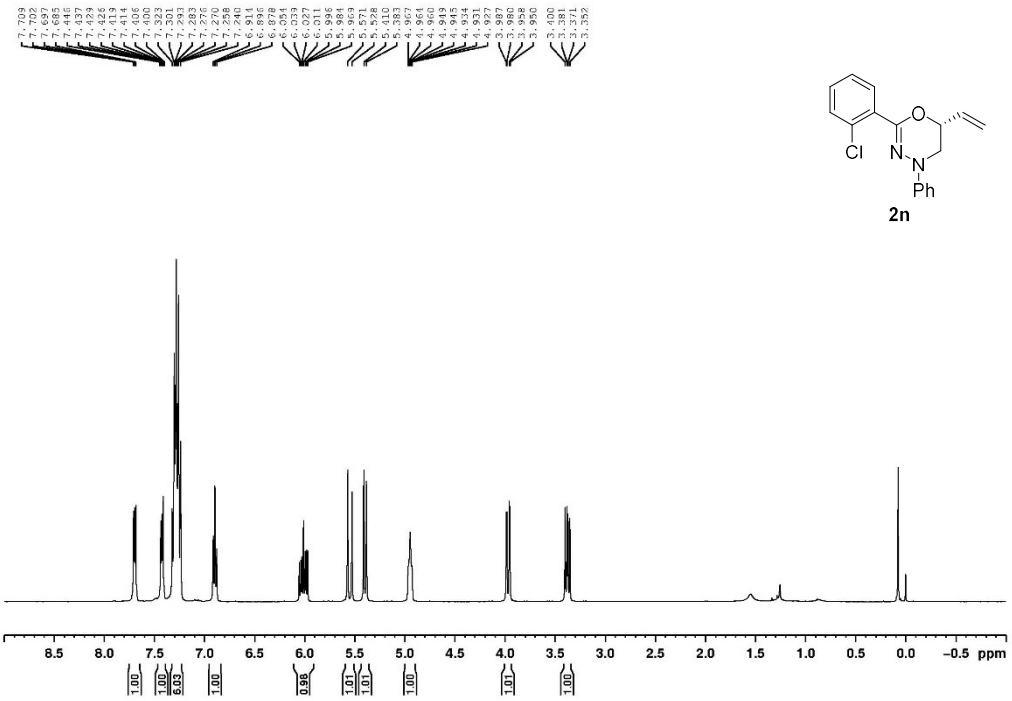
^{13}C NMR spectrum of compound **2m** ($CDCl_3$, 100 MHz)



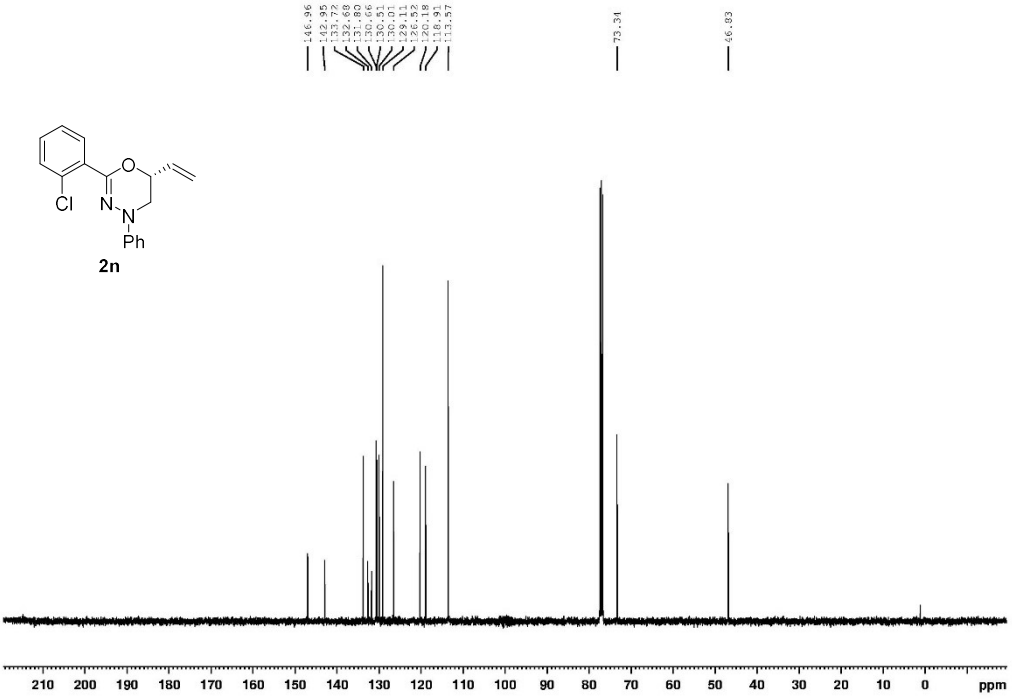
^{19}F NMR spectrum of compound **2m** ($CDCl_3$, 376 MHz)



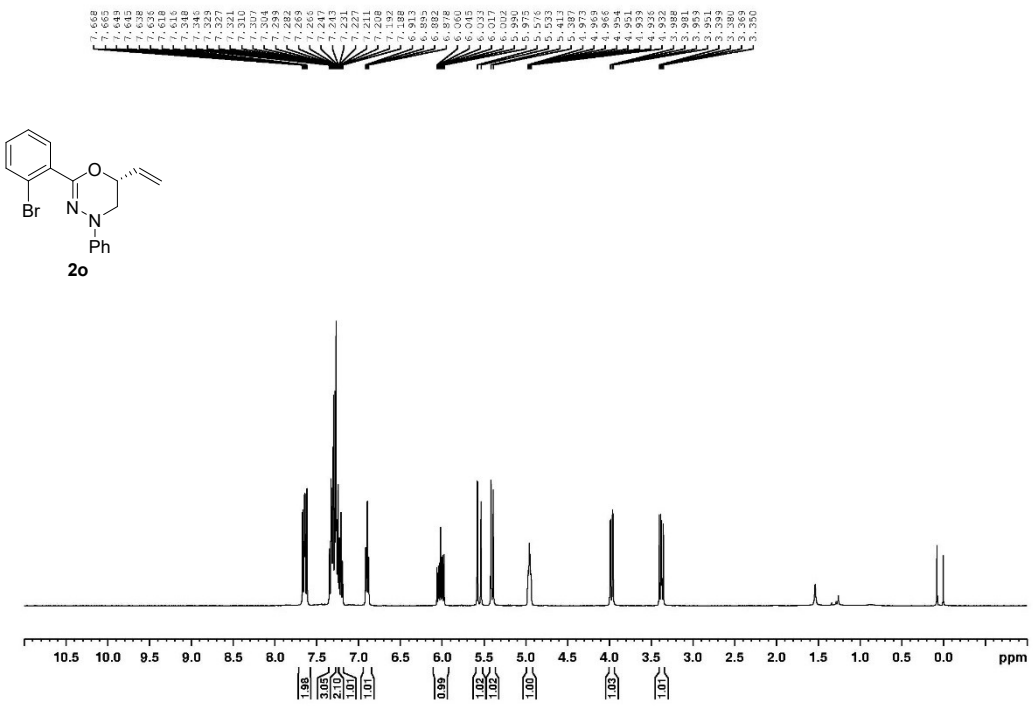
^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 400 MHz)



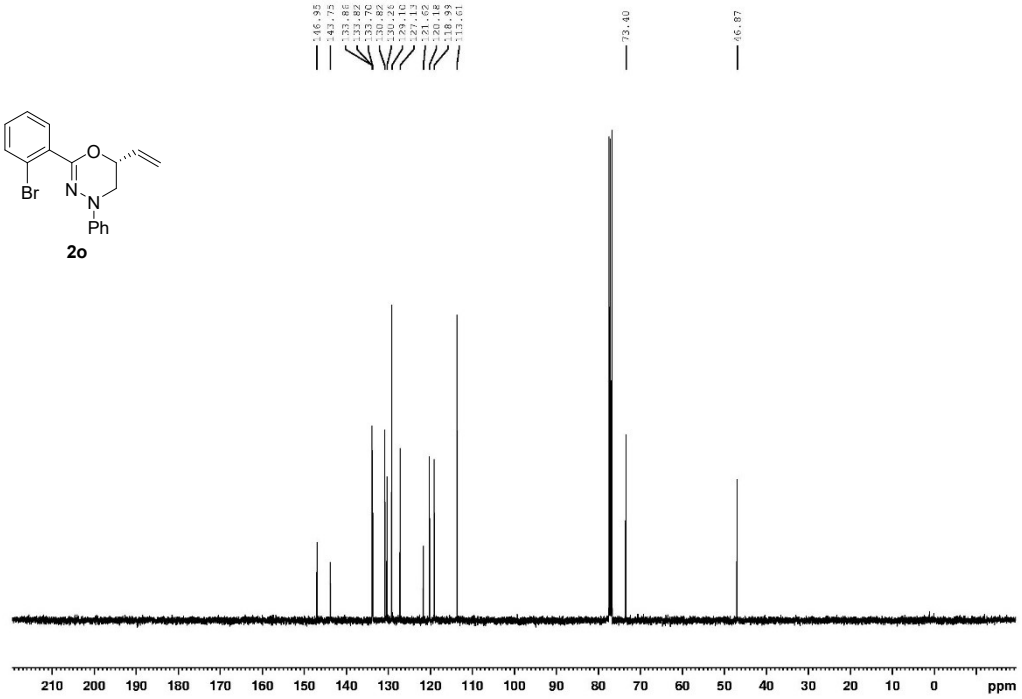
^{13}C NMR spectrum of compound **2n** ($CDCl_3$, 100 MHz)



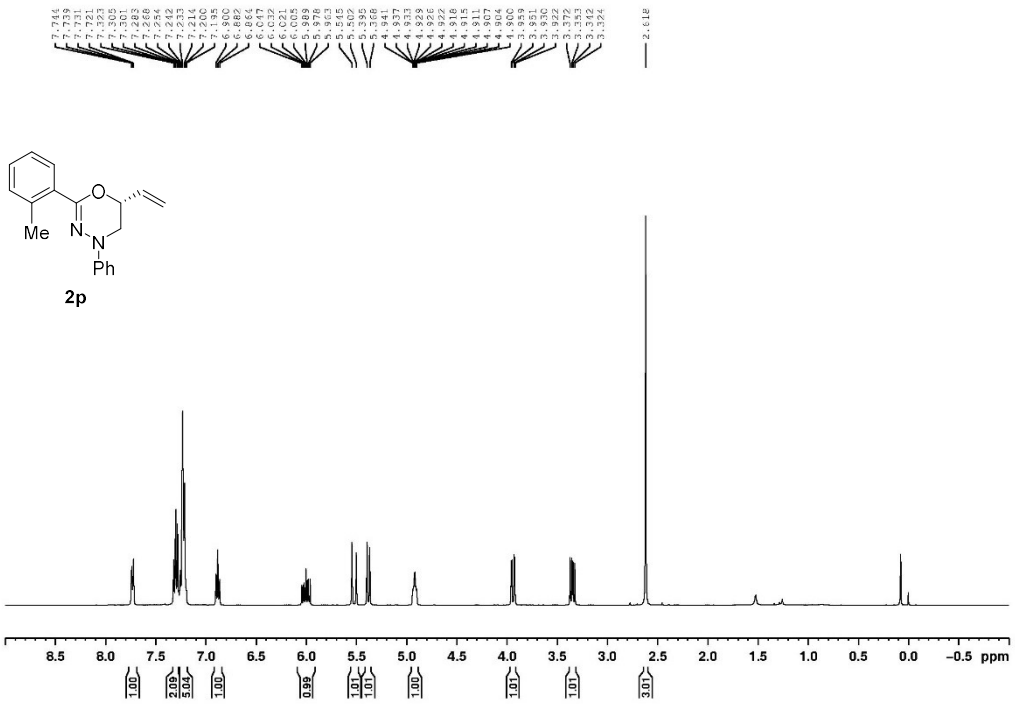
^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz)



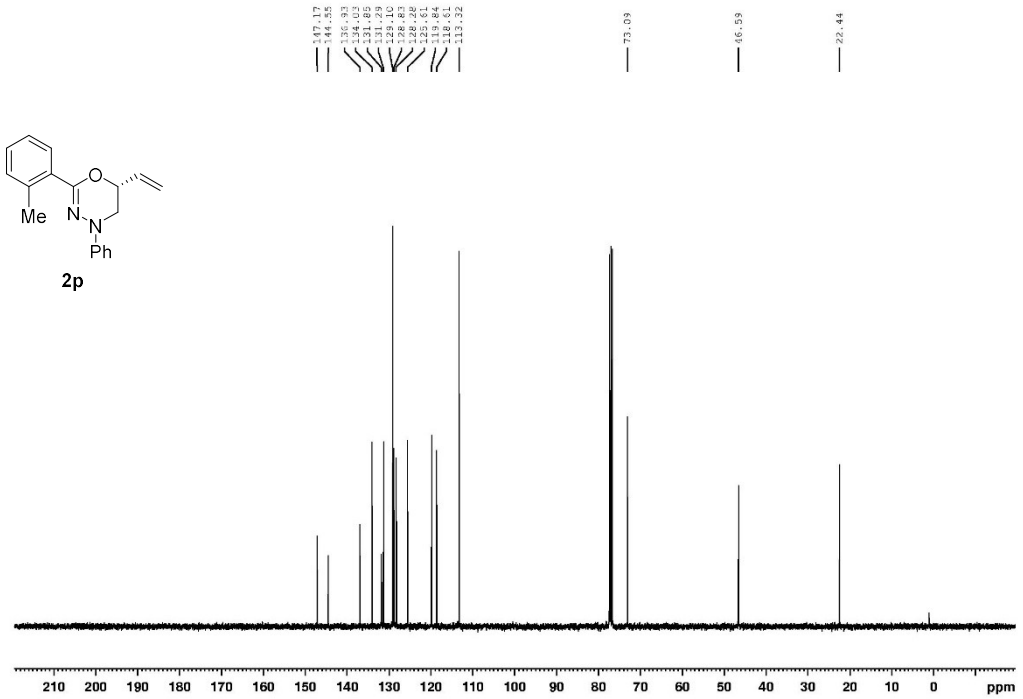
^{13}C NMR spectrum of compound **2o** ($CDCl_3$, 100 MHz)



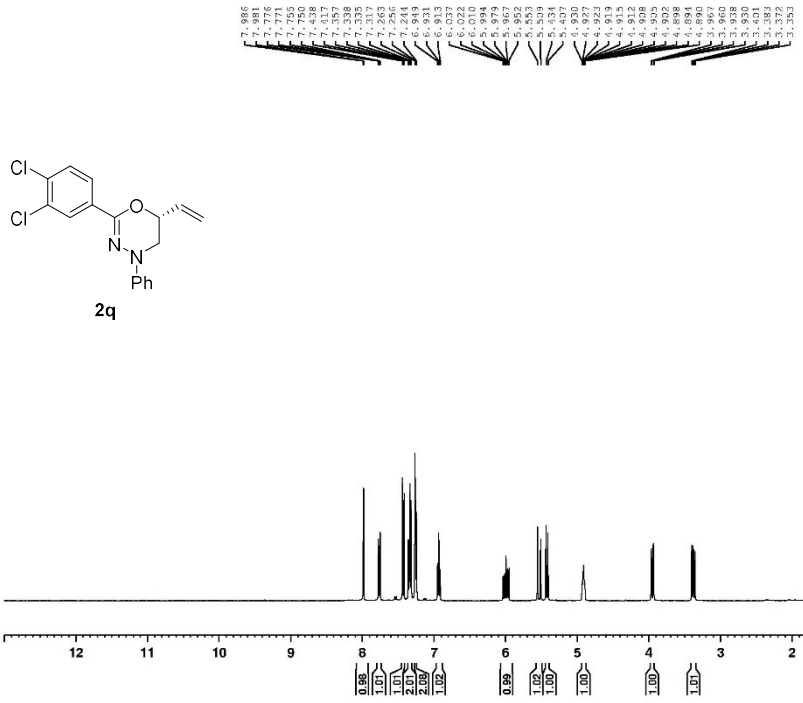
^{1}H NMR spectrum of compound **2p** ($CDCl_3$, 400 MHz)



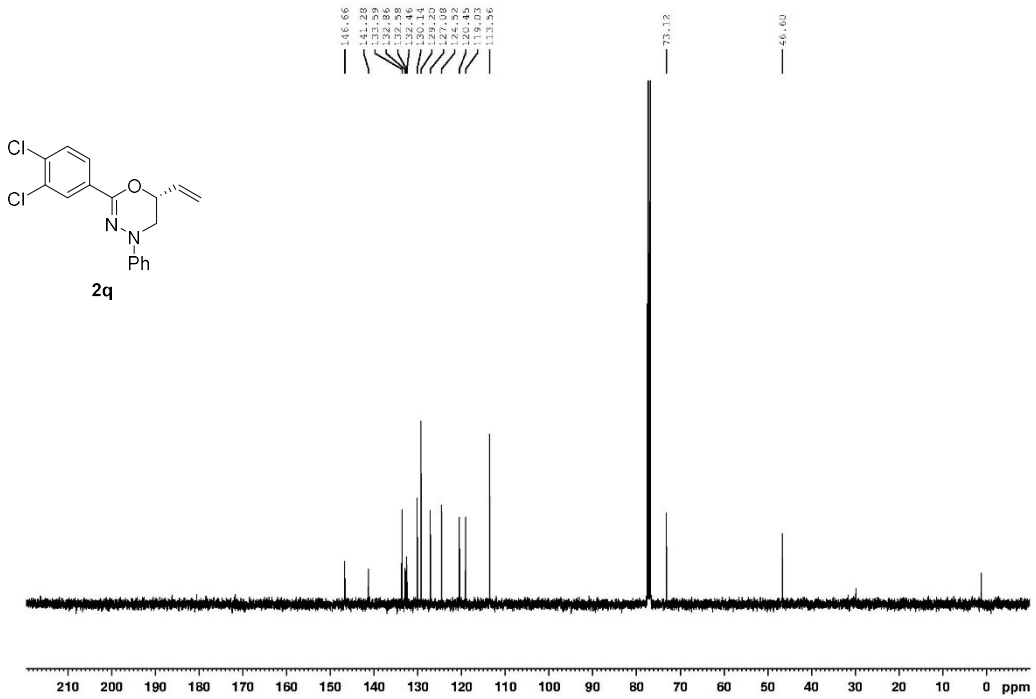
^{13}C NMR spectrum of compound **2p** ($CDCl_3$, 100 MHz)



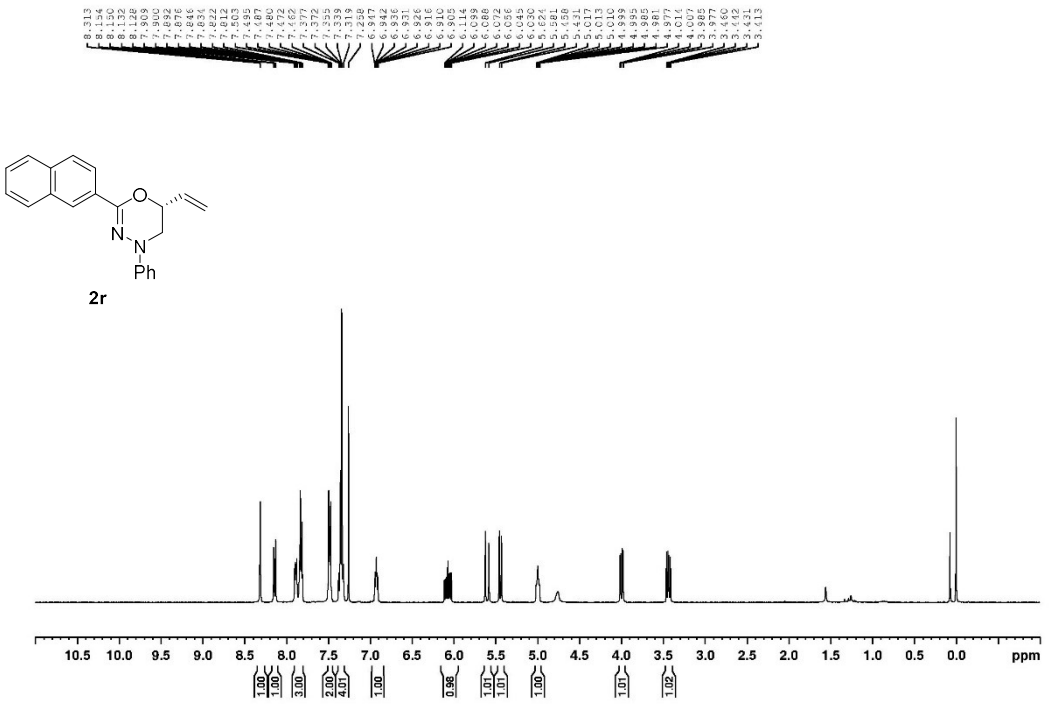
^{1}H NMR spectrum of compound **2q** ($CDCl_3$, 400 MHz)



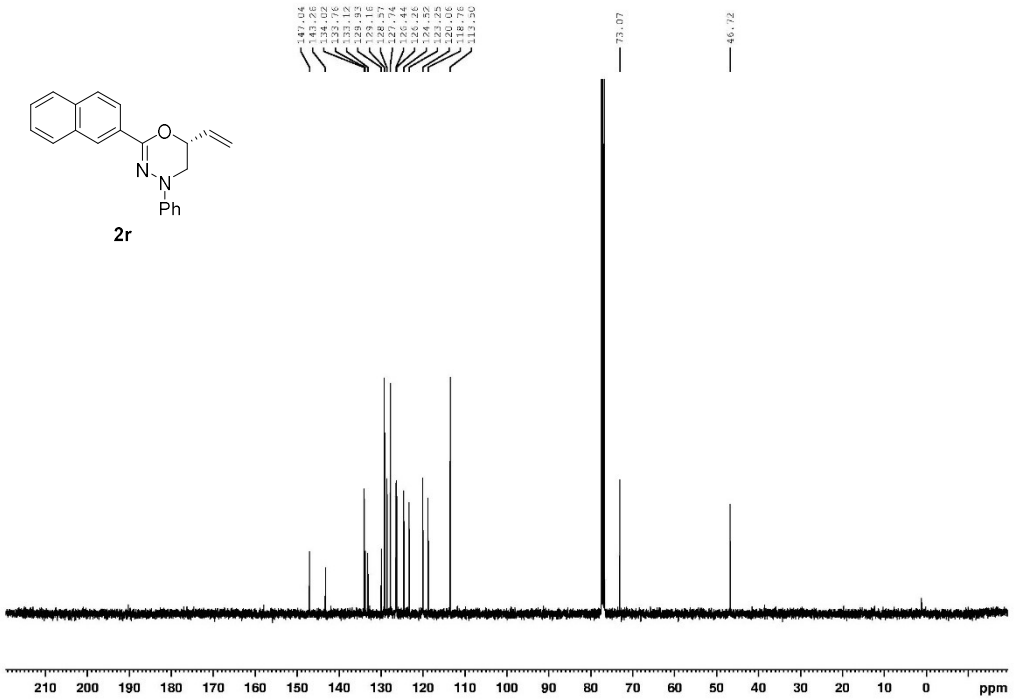
^{13}C NMR spectrum of compound **2q** ($CDCl_3$, 100 MHz)



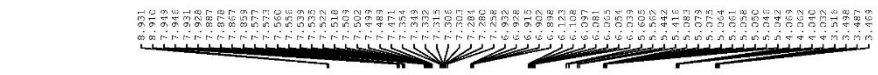
^{1}H NMR spectrum of compound **2r** ($CDCl_3$, 400 MHz)

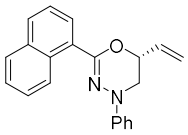


^{13}C NMR spectrum of compound **2r** ($CDCl_3$, 100 MHz)

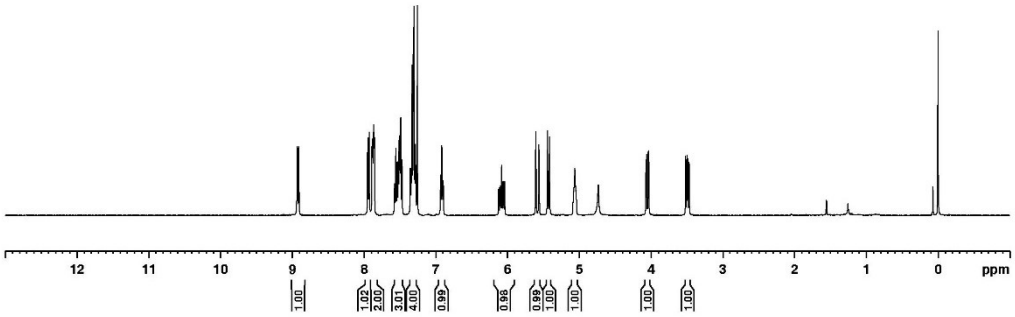


^{1}H NMR spectrum of compound **2s** ($CDCl_3$, 400 MHz)

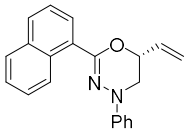




2s

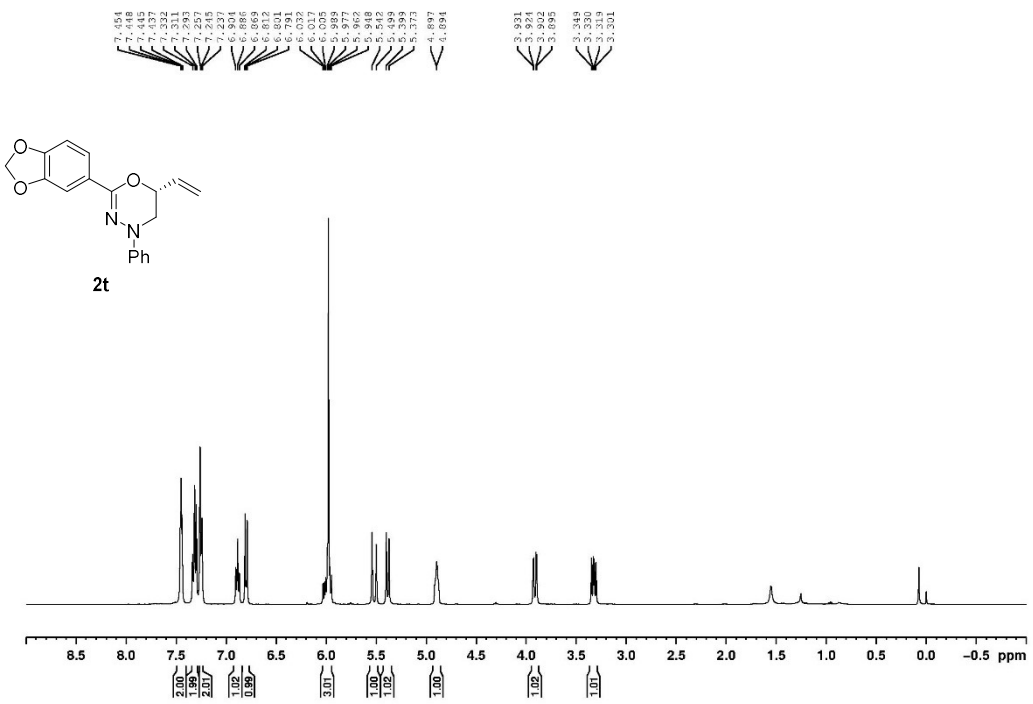


^{13}C NMR spectrum of compound **2s** ($CDCl_3$, 100 MHz)

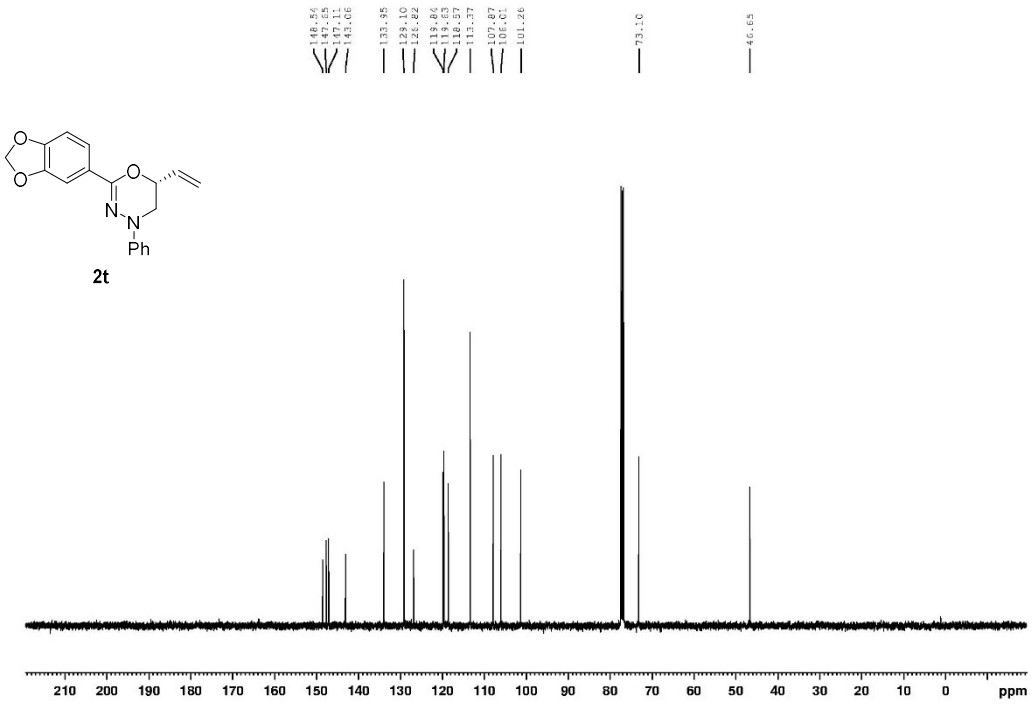


2s

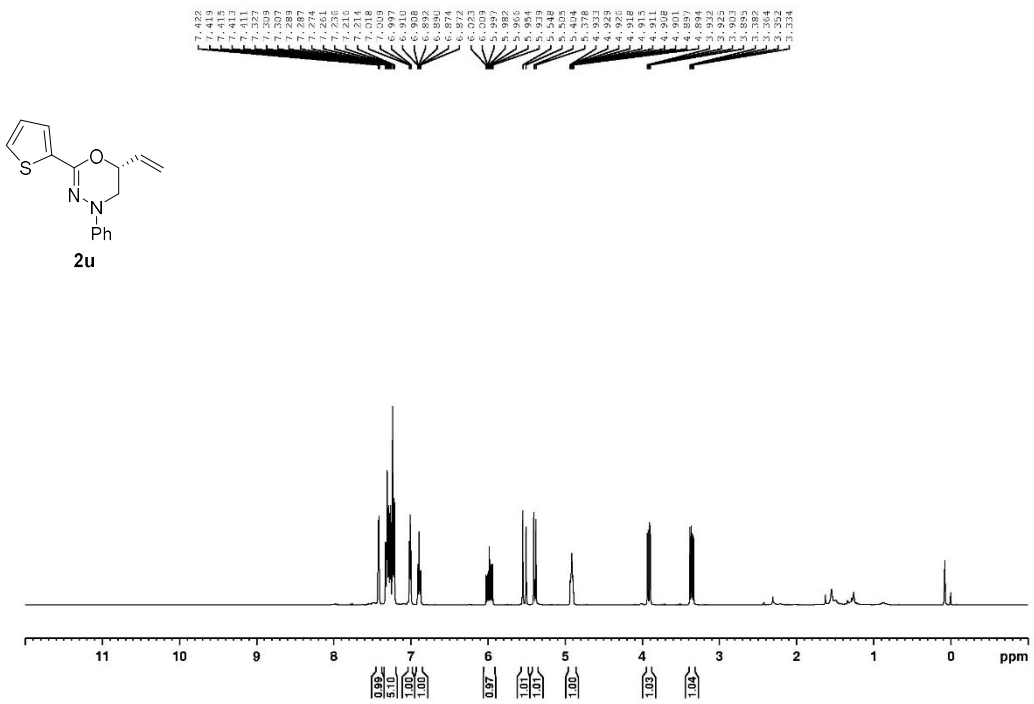
^{1}H NMR spectrum of compound **2t** ($CDCl_3$, 400 MHz)



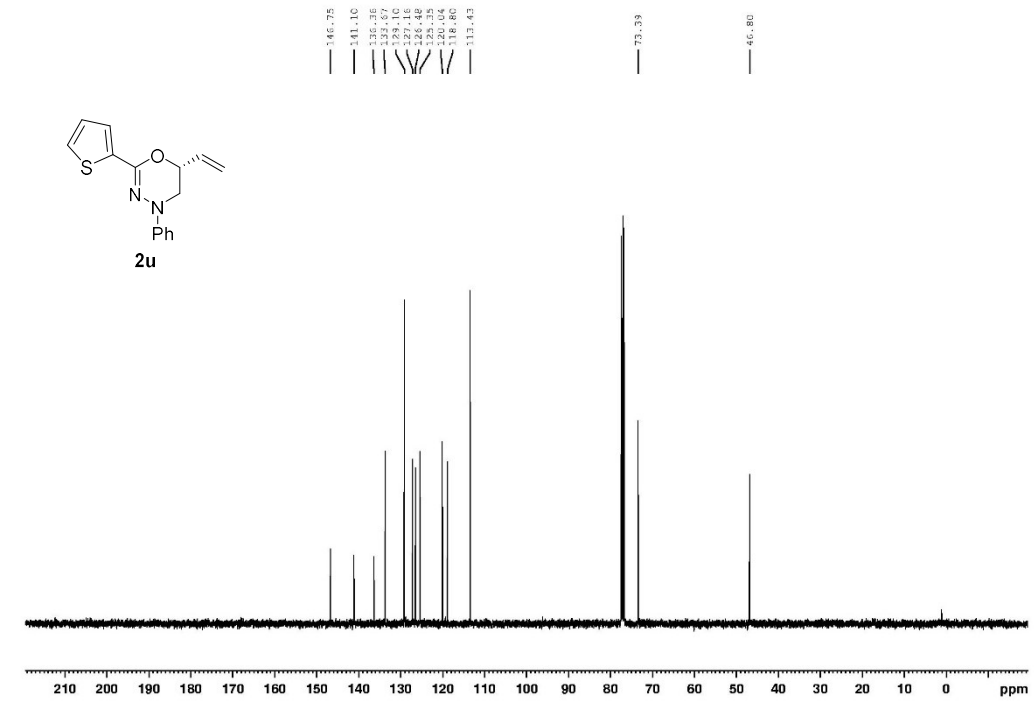
^{13}C NMR spectrum of compound **2t** ($CDCl_3$, 100 MHz)



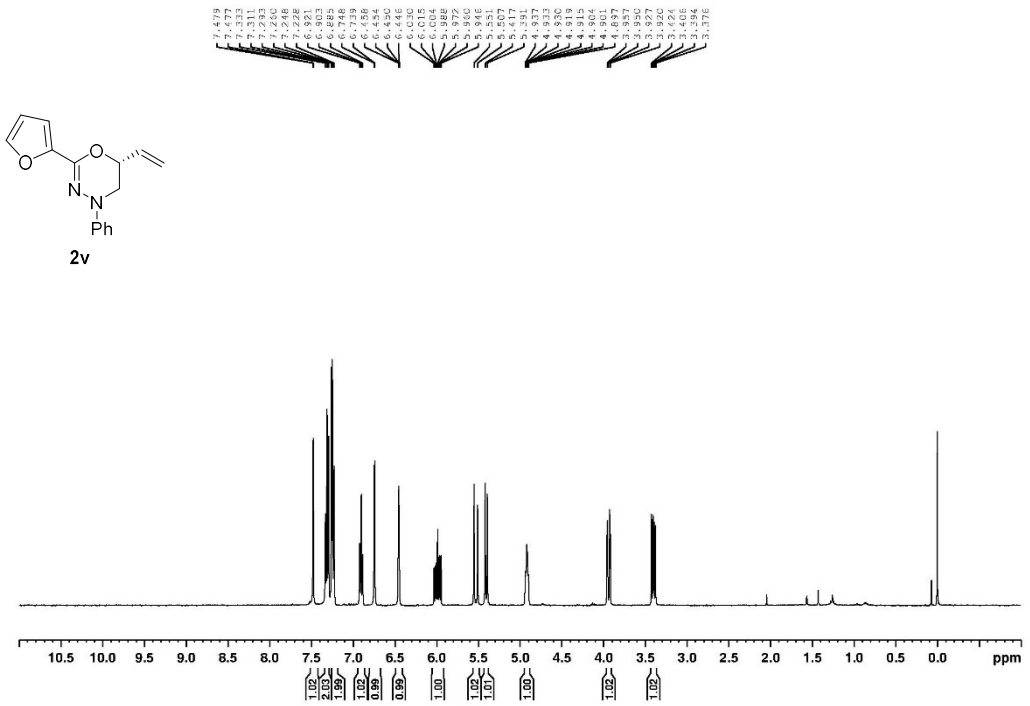
^{1}H NMR spectrum of compound **2u** ($CDCl_3$, 400 MHz)



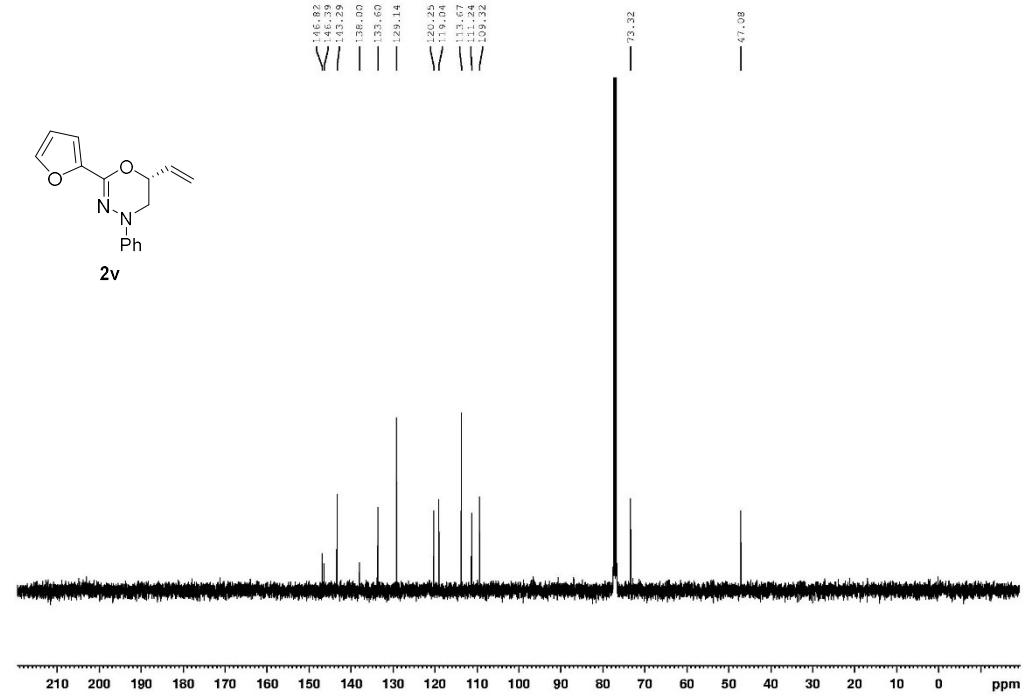
^{13}C NMR spectrum of compound **2u** ($CDCl_3$, 100 MHz)



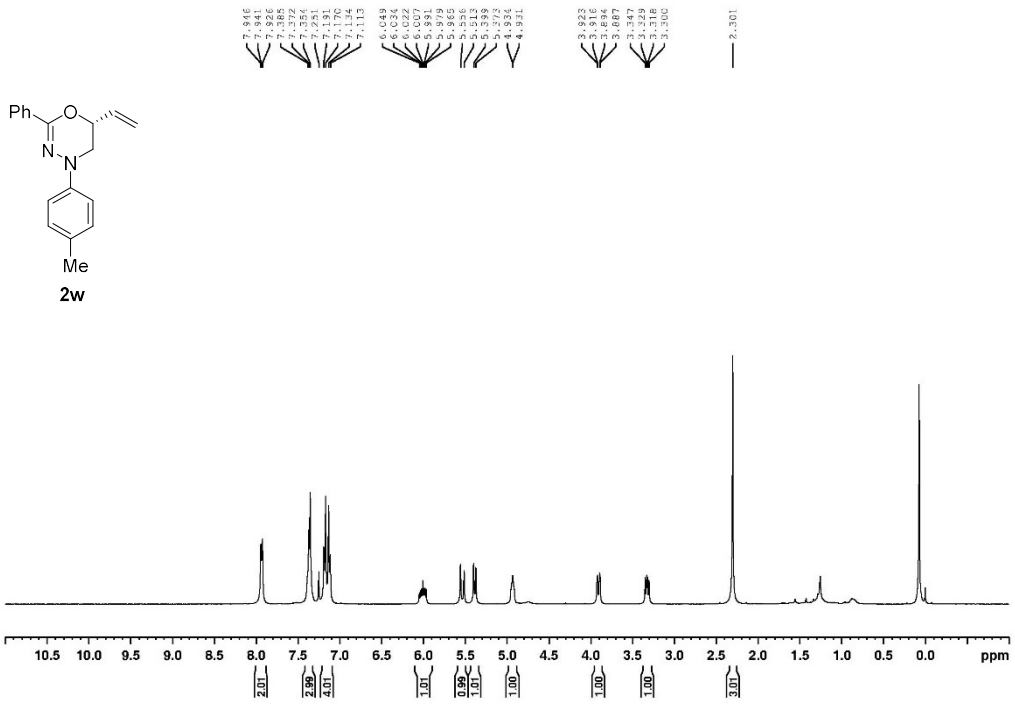
^{1}H NMR spectrum of compound **2v** ($CDCl_3$, 400 MHz)



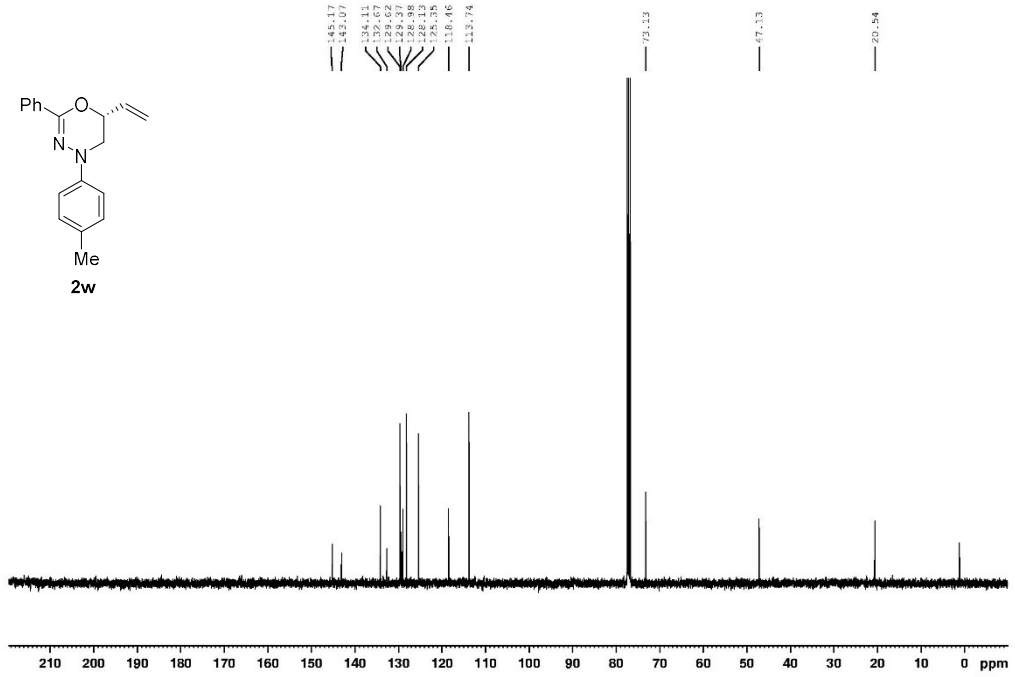
^{13}C NMR spectrum of compound **2v** ($CDCl_3$, 100 MHz)



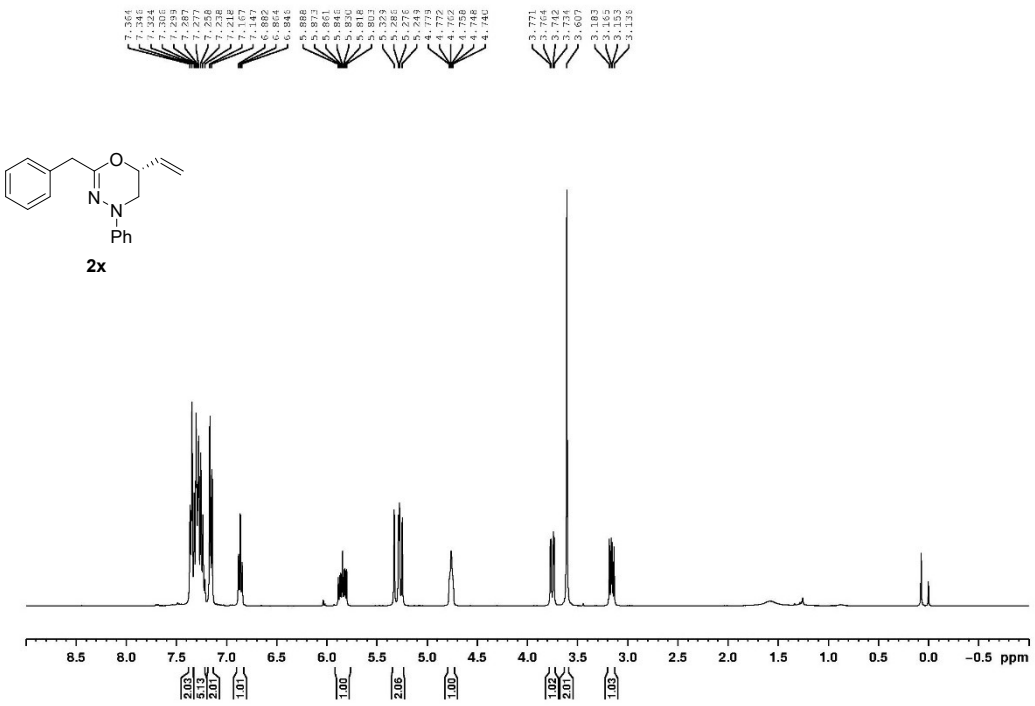
^{1}H NMR spectrum of compound **2w** ($CDCl_3$, 400 MHz)



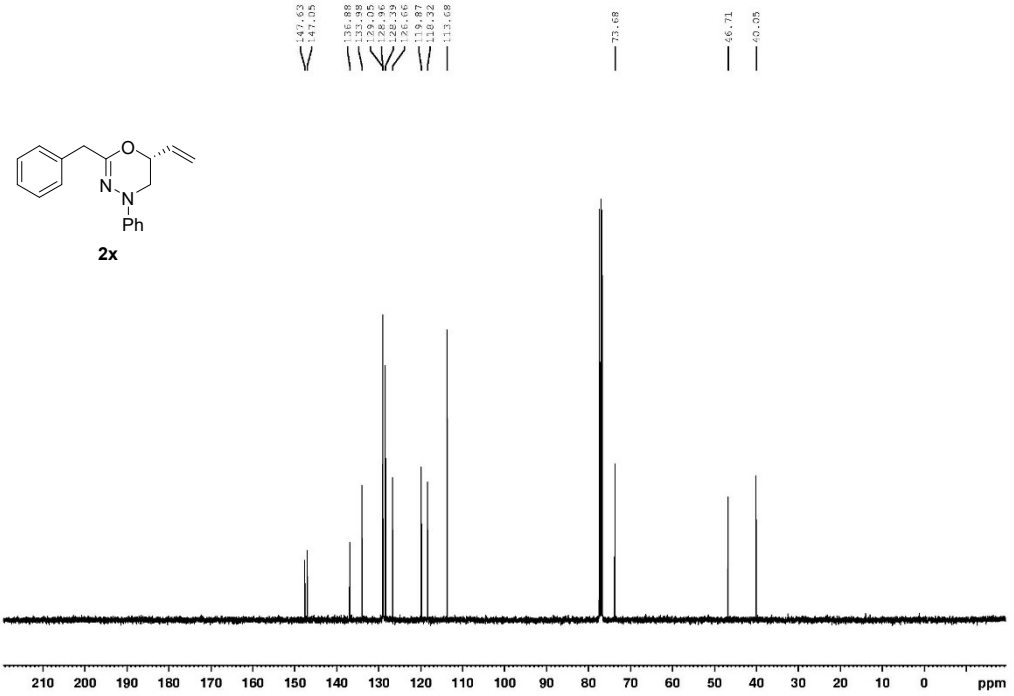
^{13}C NMR spectrum of compound **2w** ($CDCl_3$, 100 MHz)



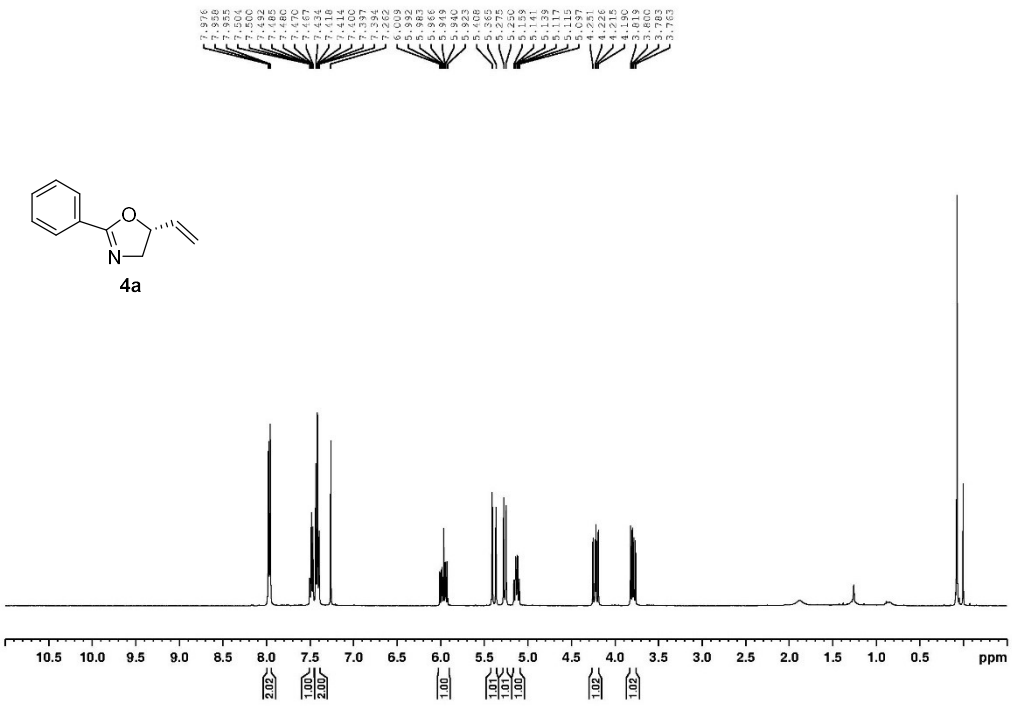
^{1}H NMR spectrum of compound **2x** ($CDCl_3$, 400 MHz)



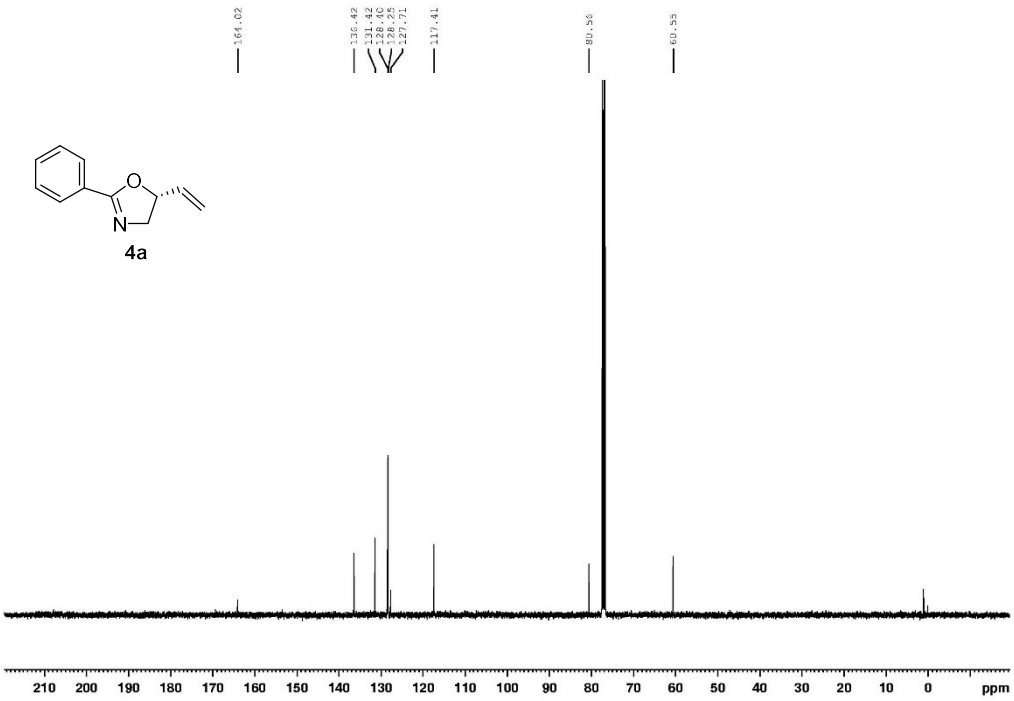
^{13}C NMR spectrum of compound **2x** ($CDCl_3$, 100 MHz)



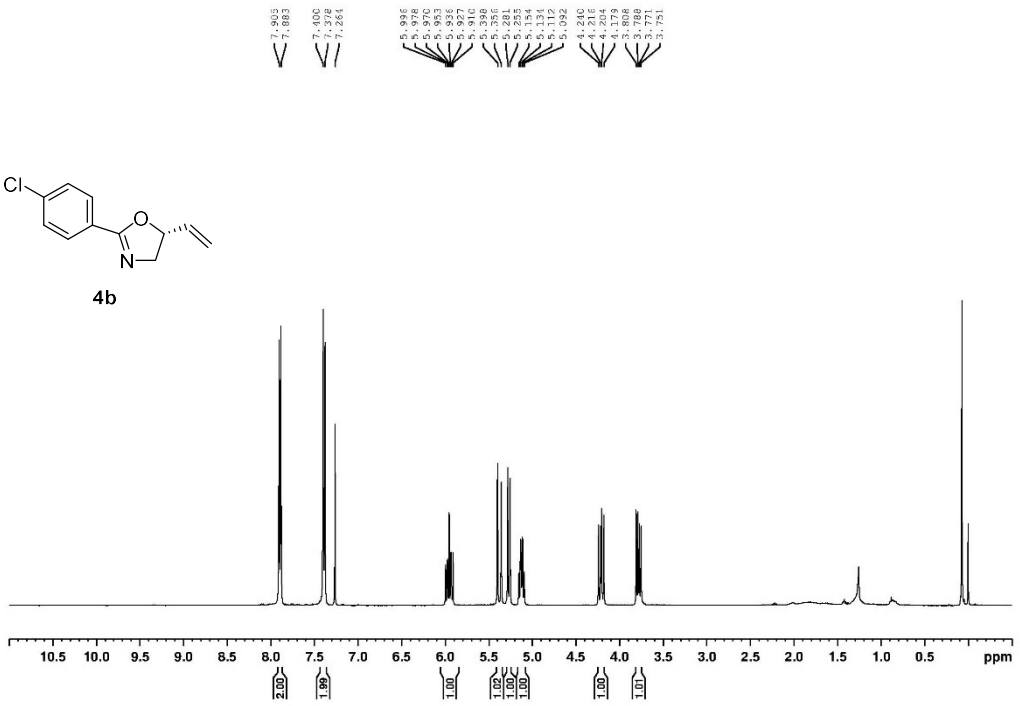
^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



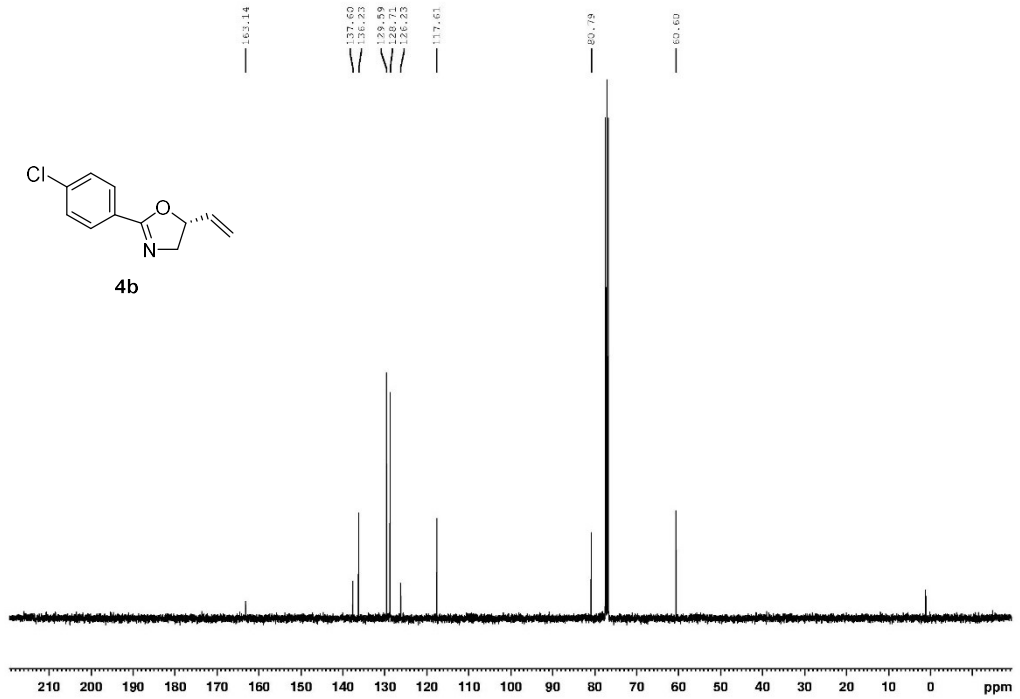
^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 100 MHz)



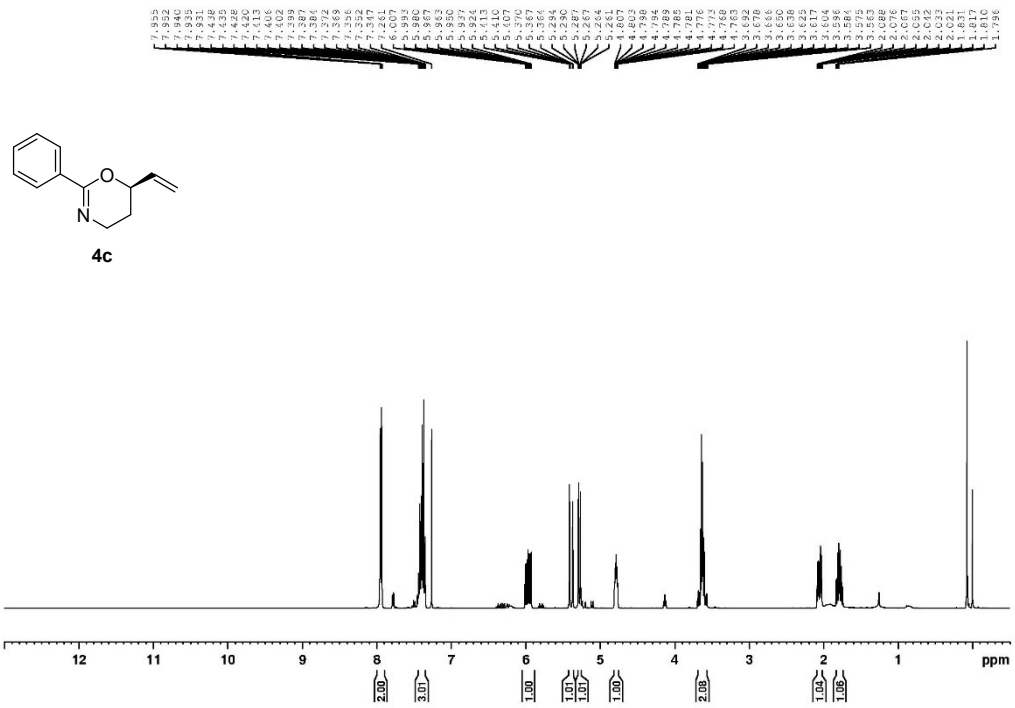
^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



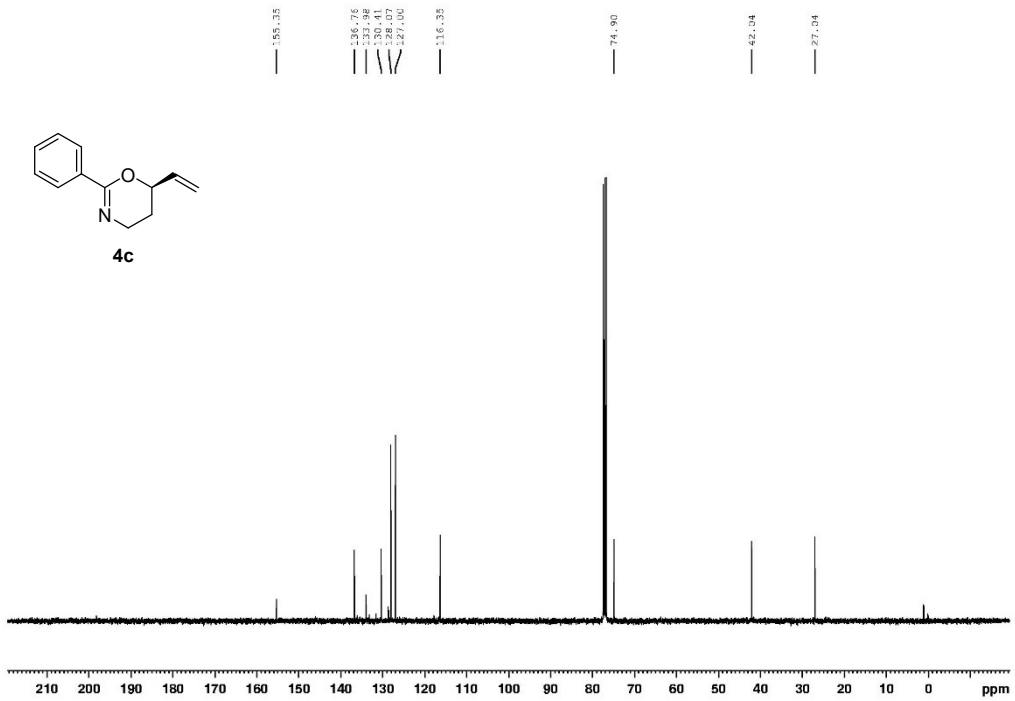
^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 100 MHz)



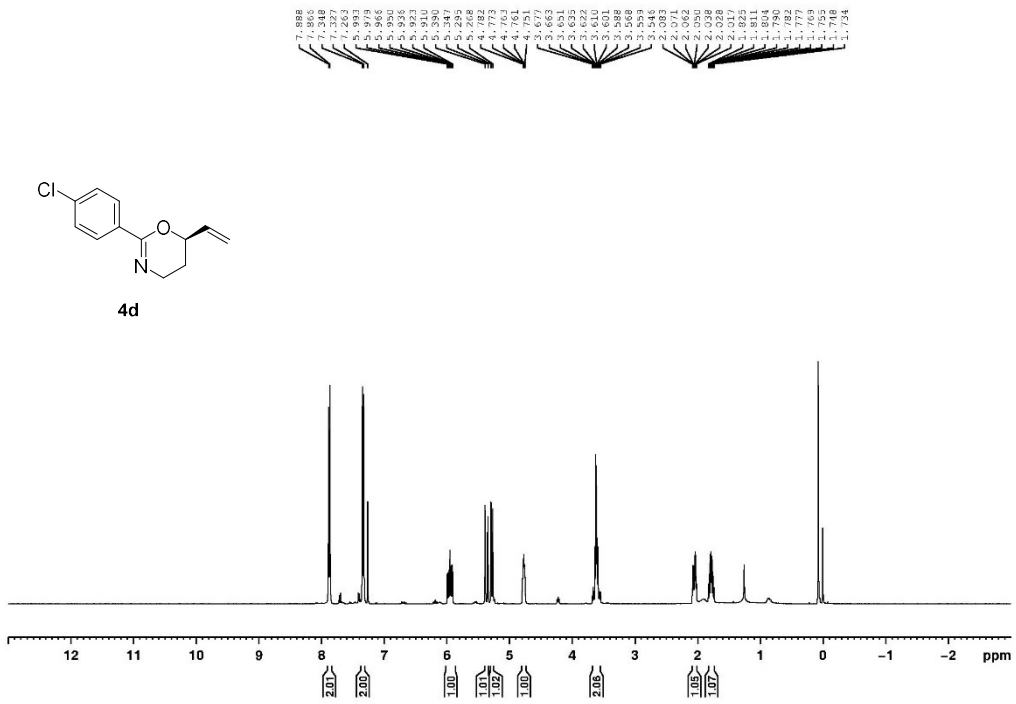
^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



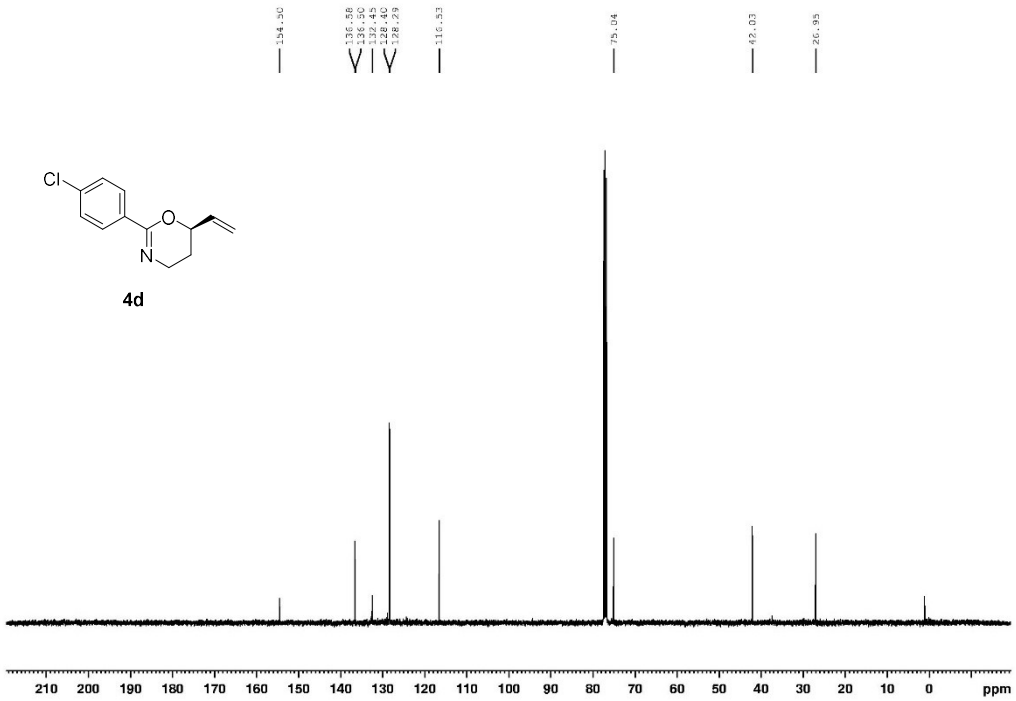
^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)



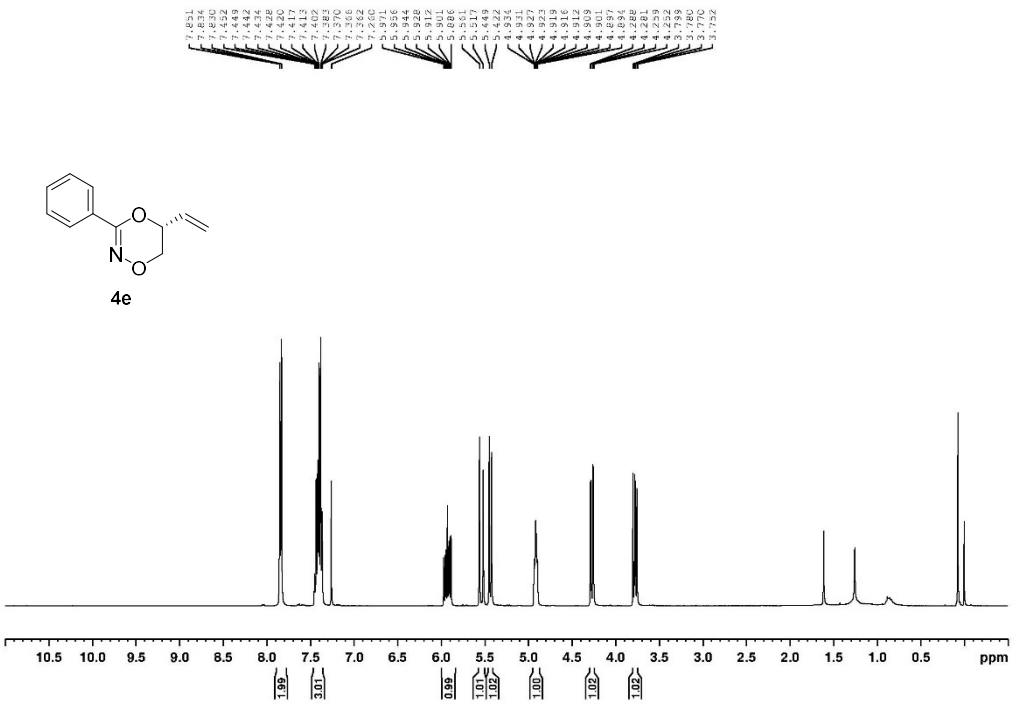
^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



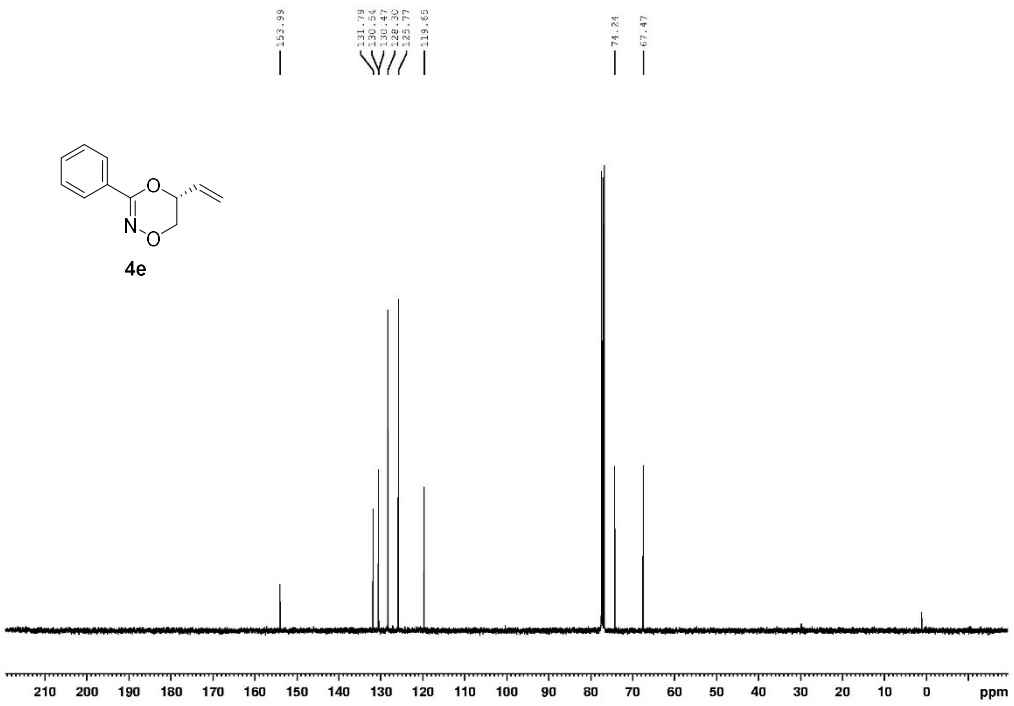
^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)



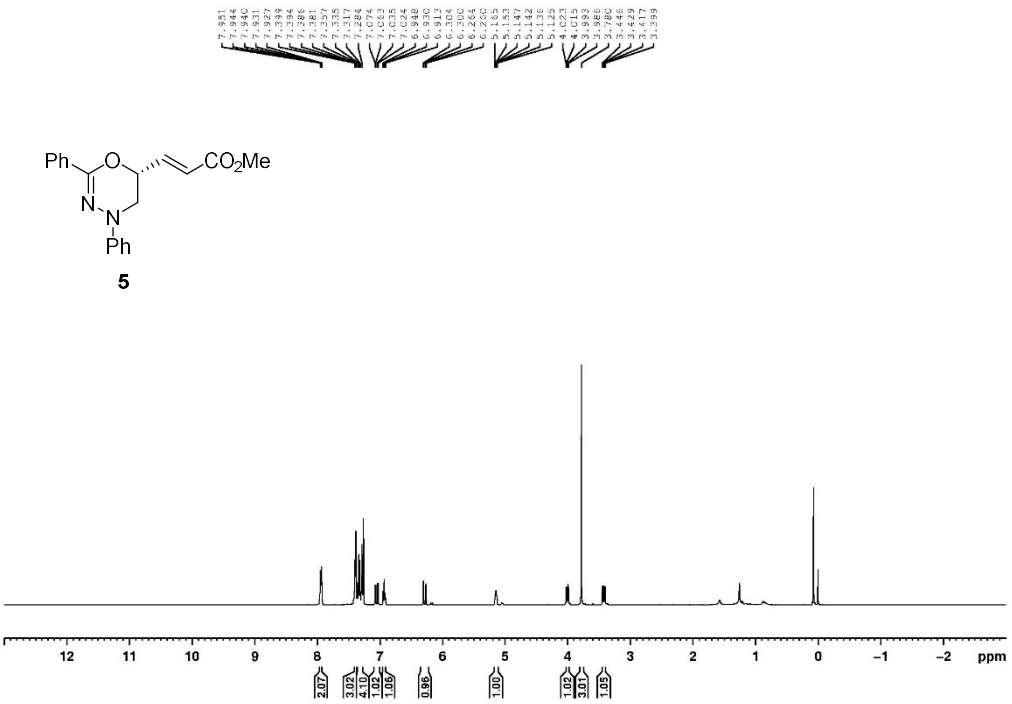
^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



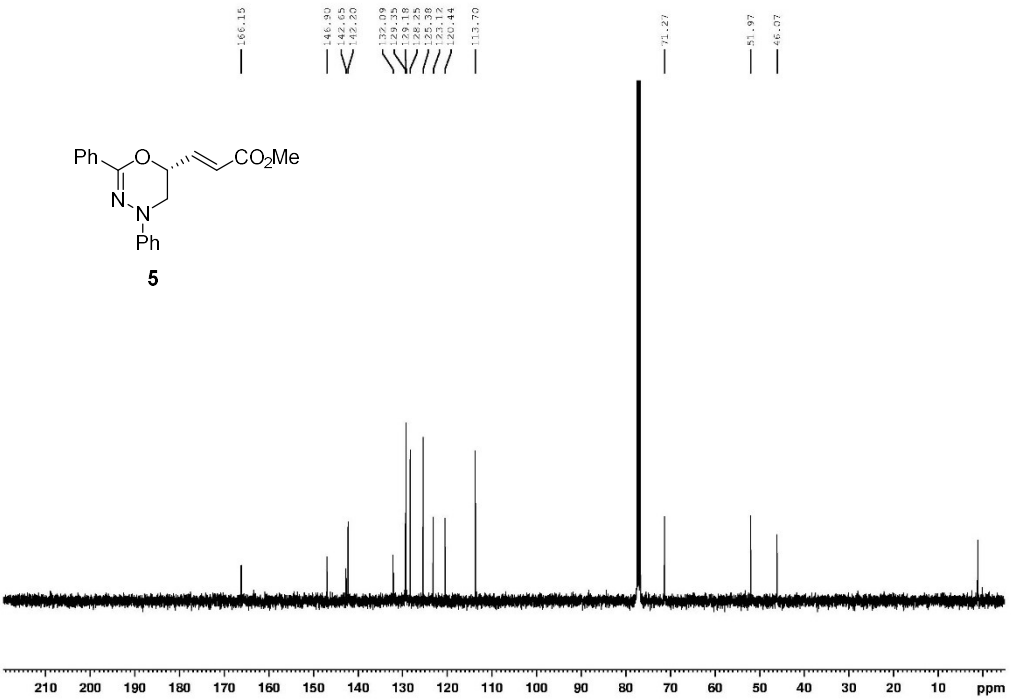
^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)



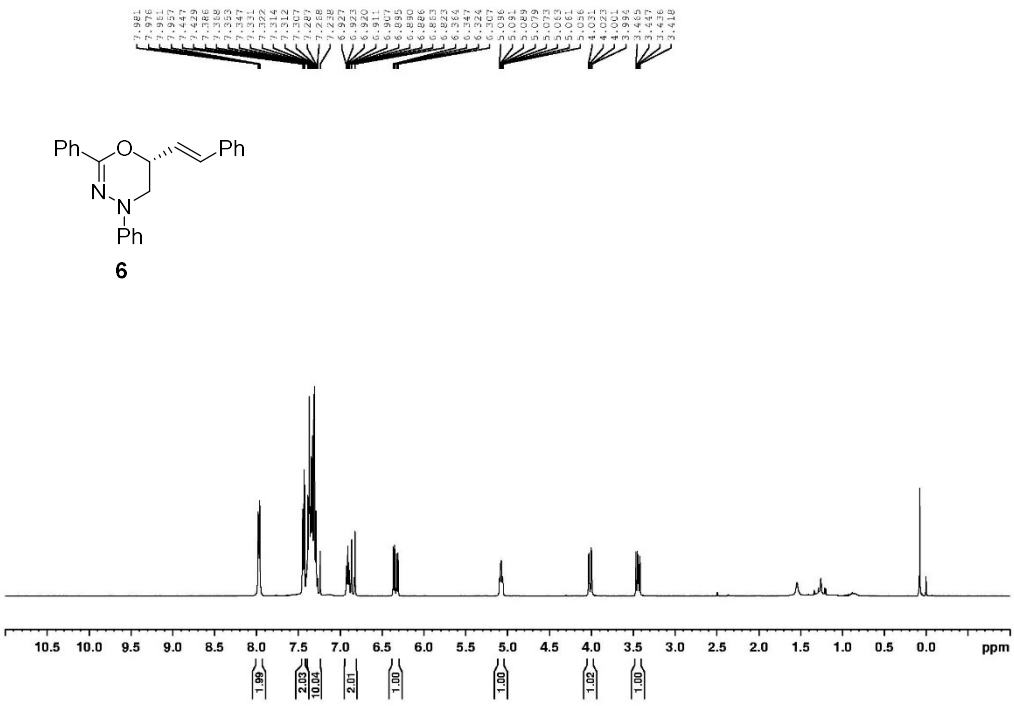
^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)



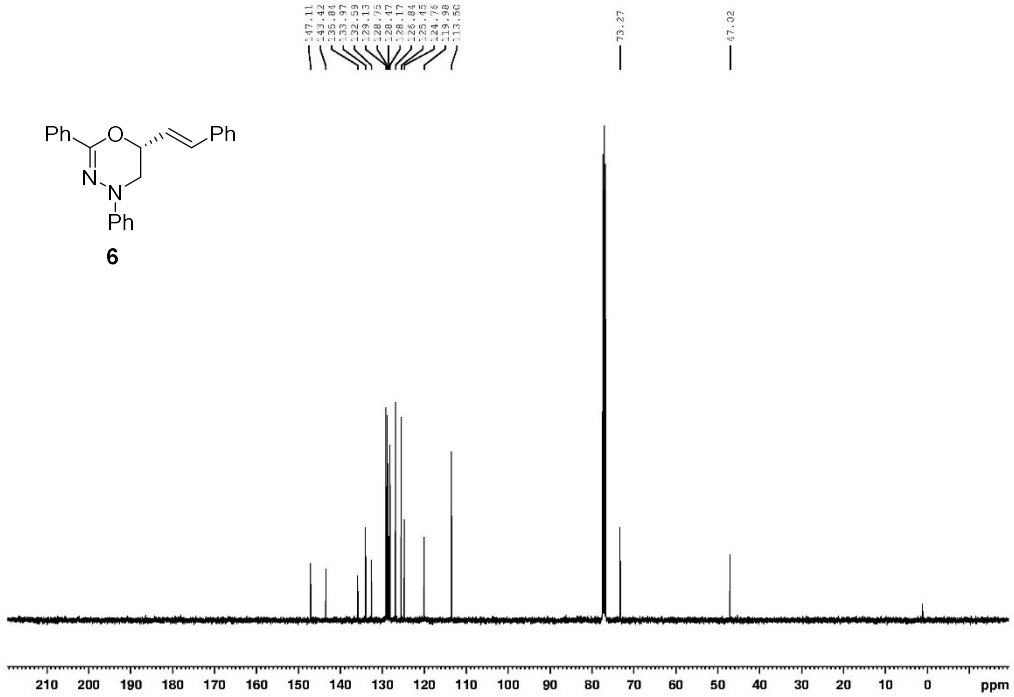
^{13}C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)



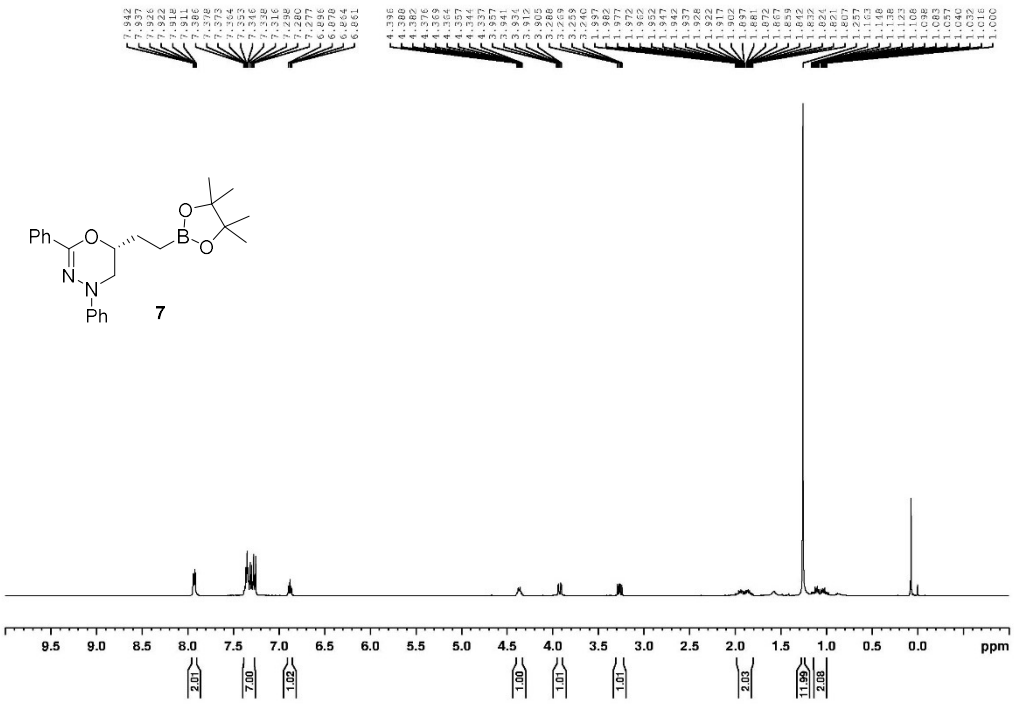
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz)



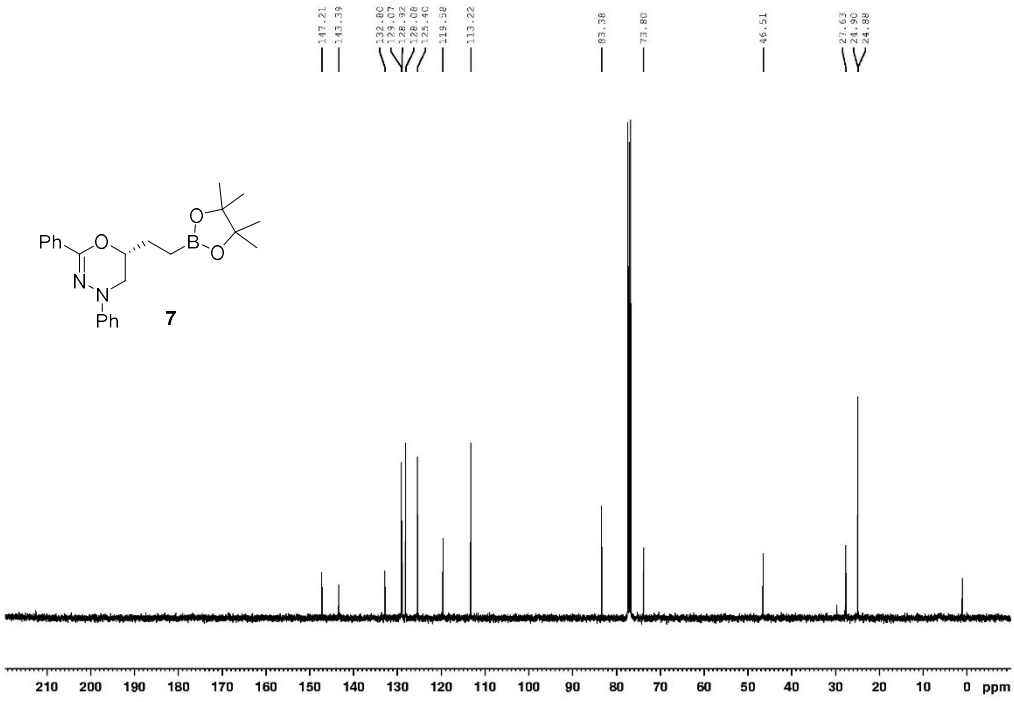
^{13}C NMR spectrum of compound **6** ($CDCl_3$, 100 MHz)



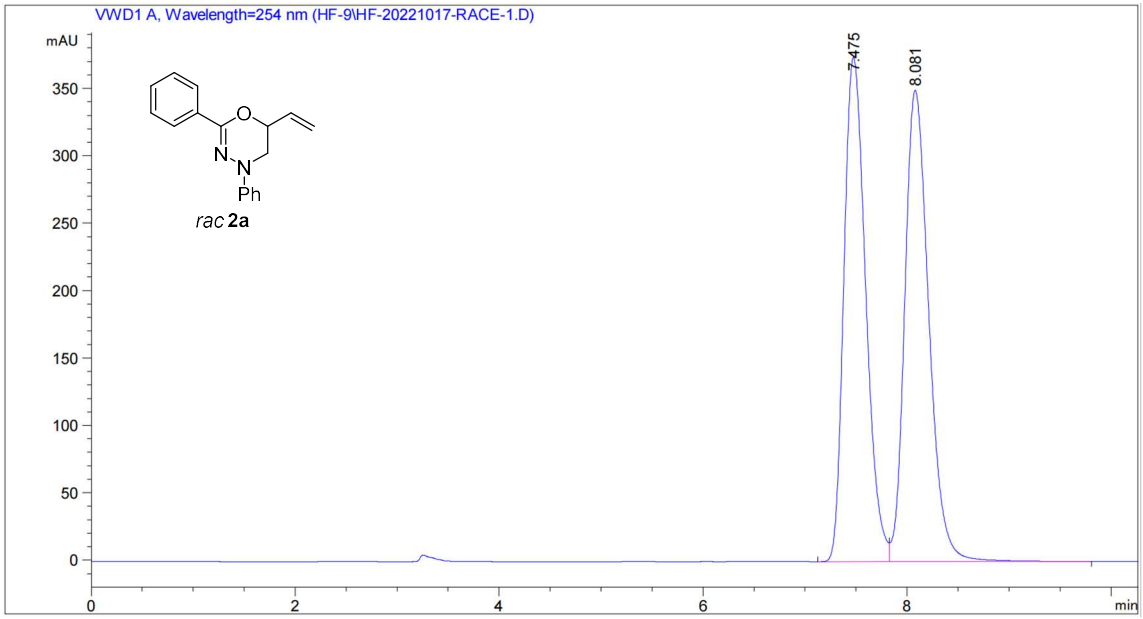
^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



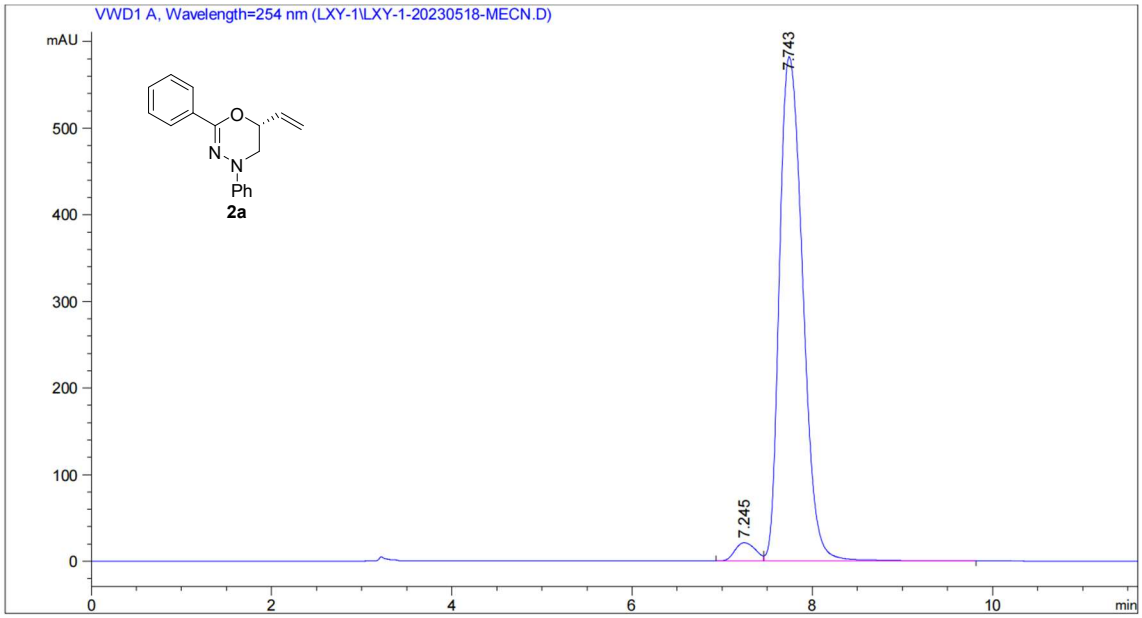
^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)



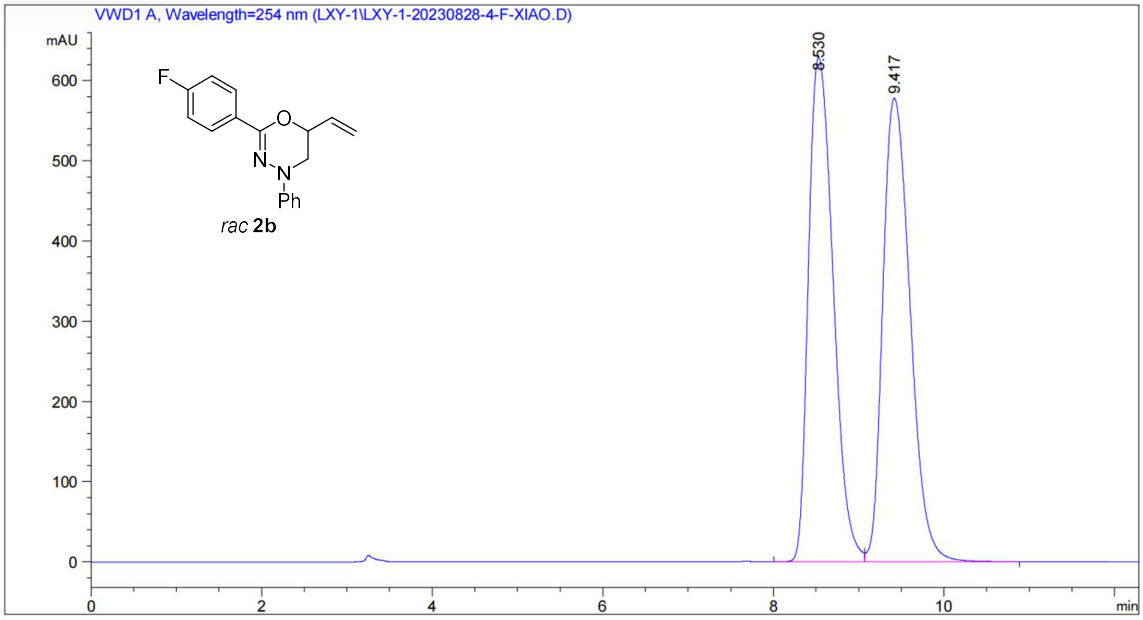
8. HPLC spectra of compounds 2a−2x, 4a−4e and 5−7



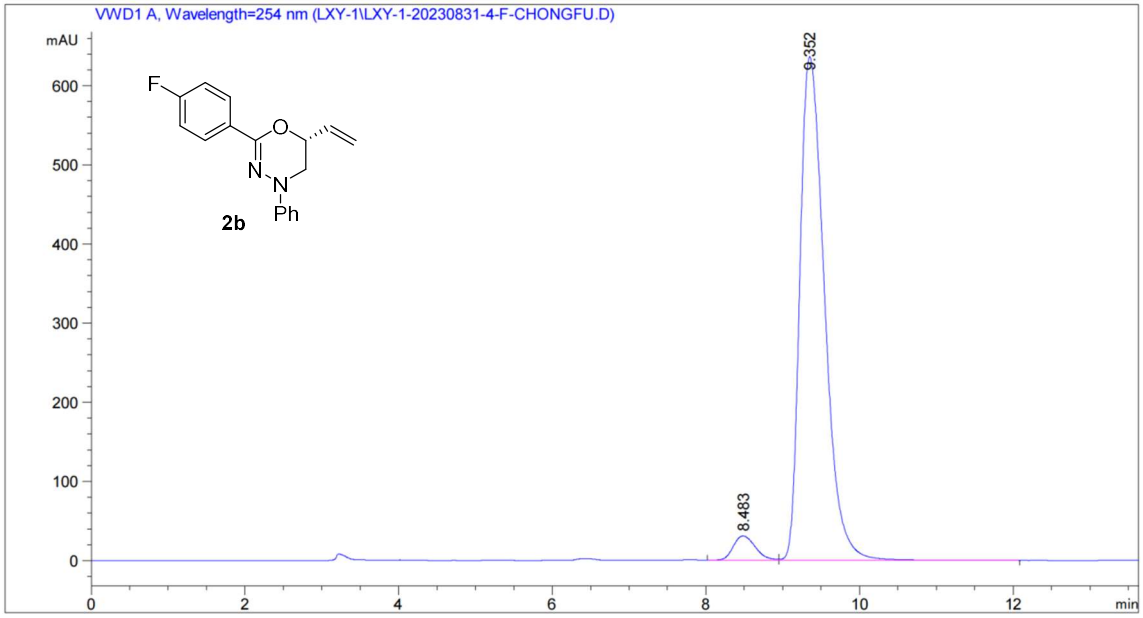
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.475	5545.14697	374.06250	49.1919
2	PDA 254 nm	8.081	5727.32813	349.65039	50.8081



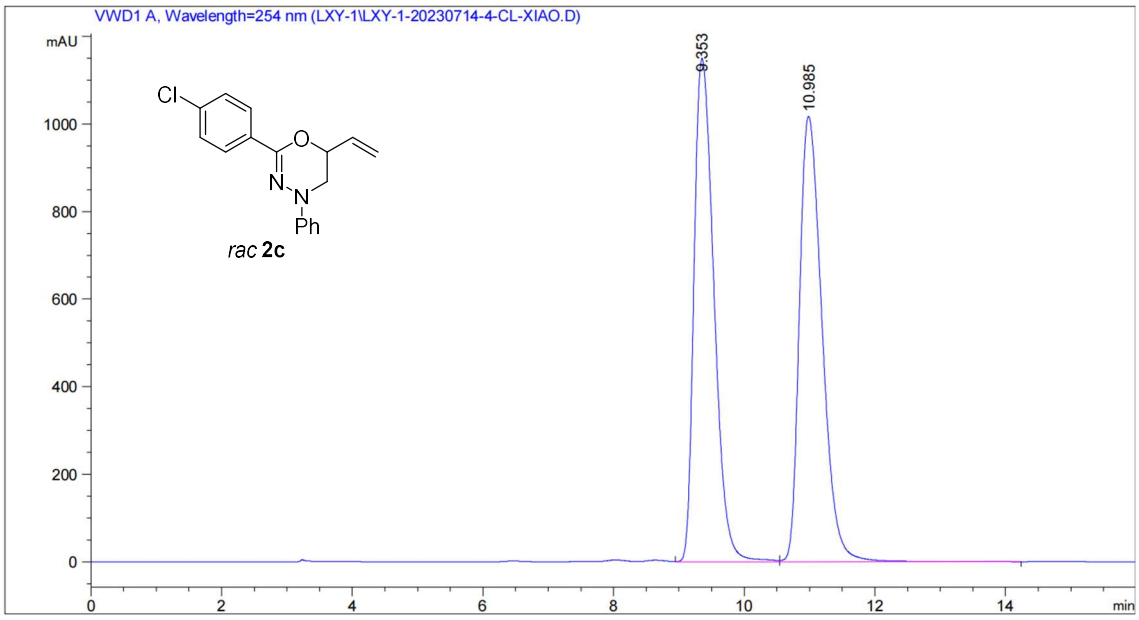
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.245	332.31720	21.01497	3.0923
2	PDA 254 nm	7.743	1.04141e4	582.07324	96.9077



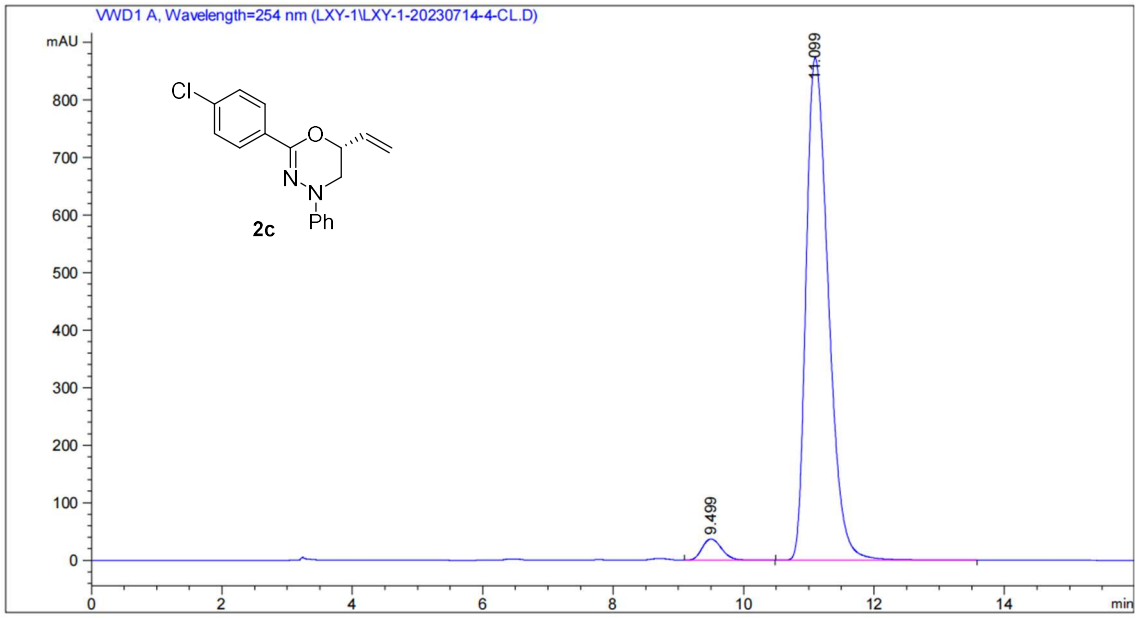
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.530	1.26431e4	629.00000	49.6082
2	PDA 254 nm	9.417	1.28428e4	578.00677	50.3918



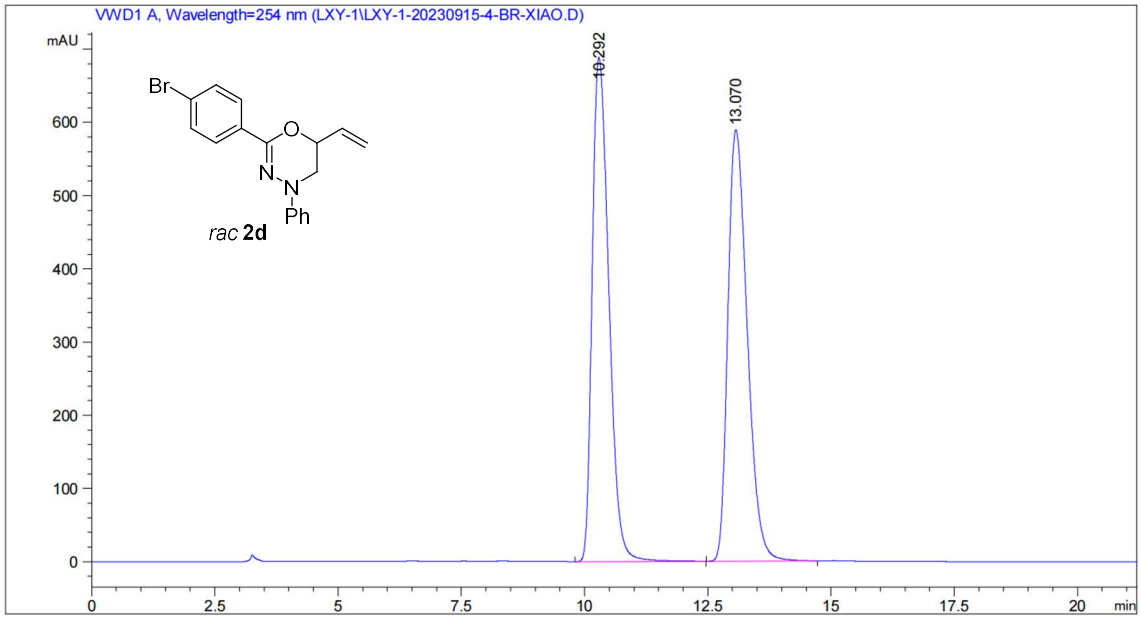
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.483	615.55981	30.74235	4.1811
2	PDA 254 nm	9.352	1.41068e4	636.29492	95.8189



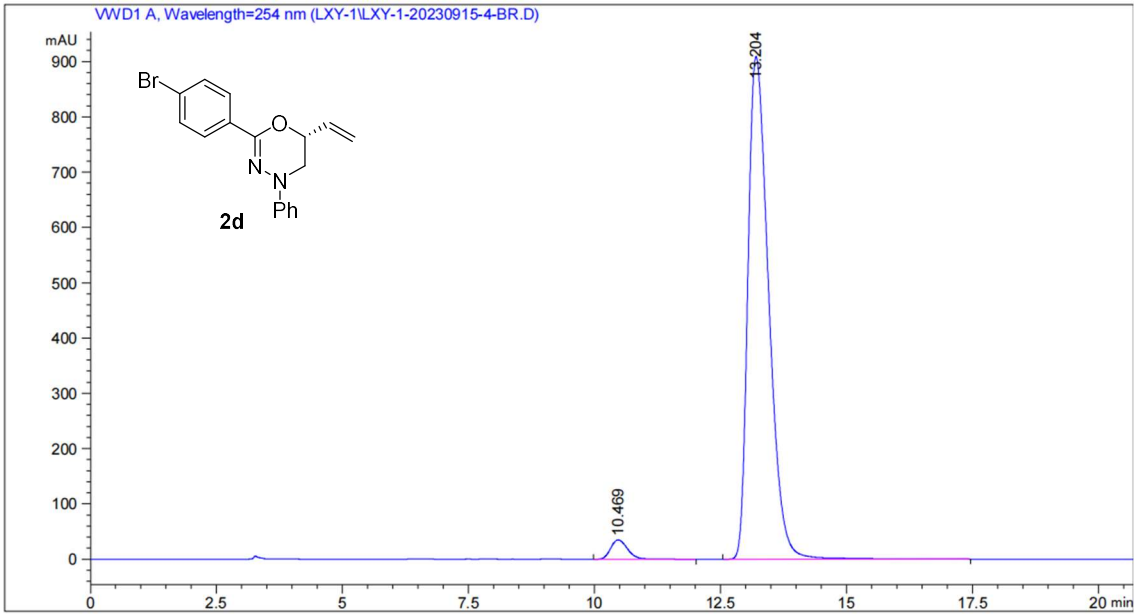
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.353	2.42744e4	1149.64050	49.8422
2	PDA 254 nm	10.985	2.44282e4	1017.78400	50.1578



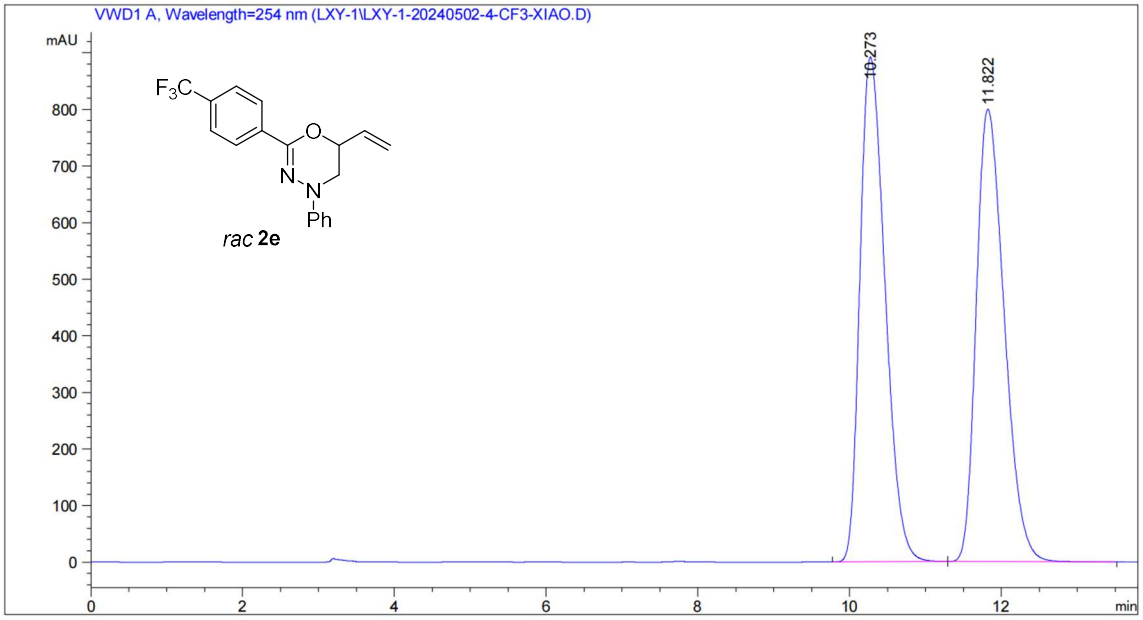
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.499	768.92975	36.85627	3.5948
2	PDA 254 nm	11.099	2.06211e4	873.04706	96.4052



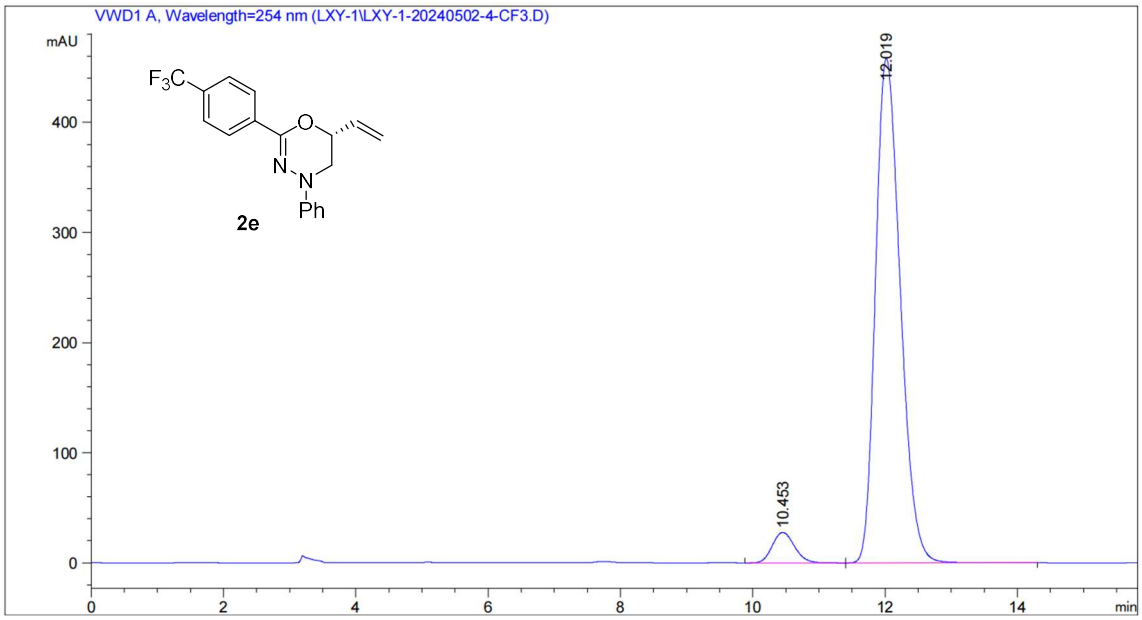
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.292	1.61252e4	688.62372	50.0844
2	PDA 254 nm	13.070	1.60709e4	589.25421	49.9156



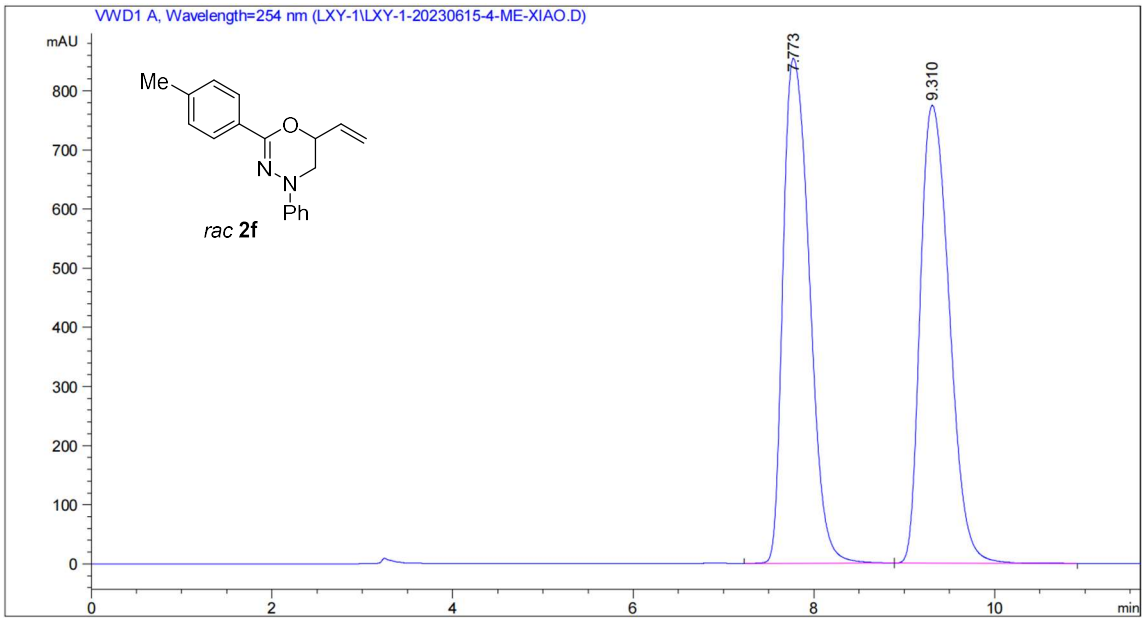
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.469	816.56934	34.80510	3.0537
2	PDA 254 nm	13.204	2.59237e4	908.76636	96.9463



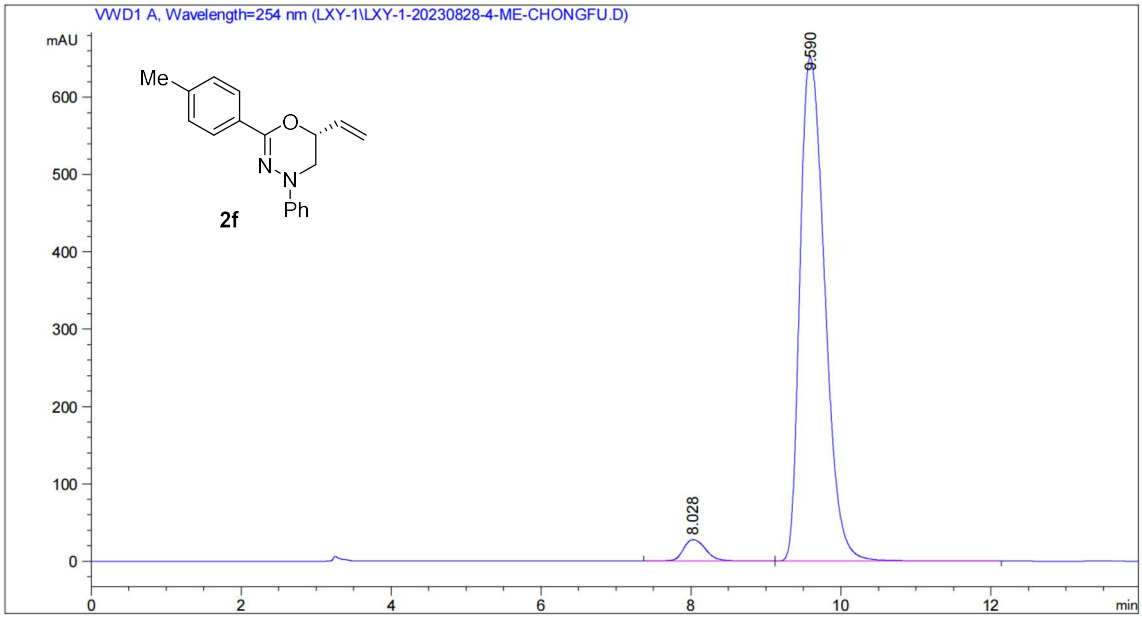
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.273	2.05265e4	892.02057	50.0244
2	PDA 254 nm	11.822	2.05065e4	799.69580	49.9756



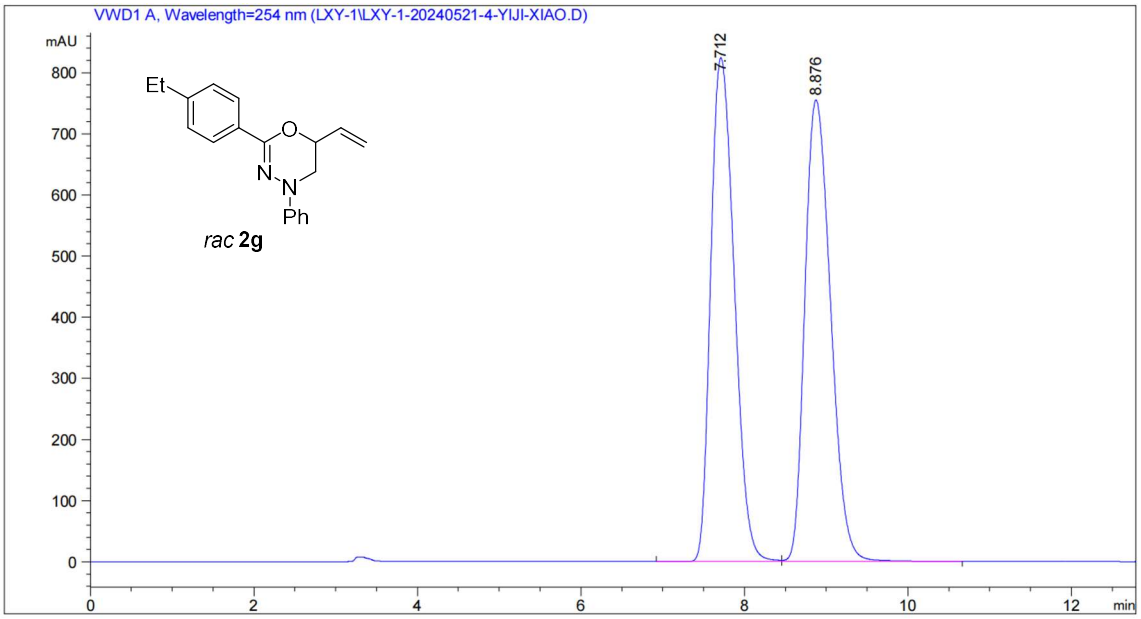
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.453	644.01263	27.65059	5.1367
2	PDA 254 nm	12.019	1.18935e4	458.16492	94.8633



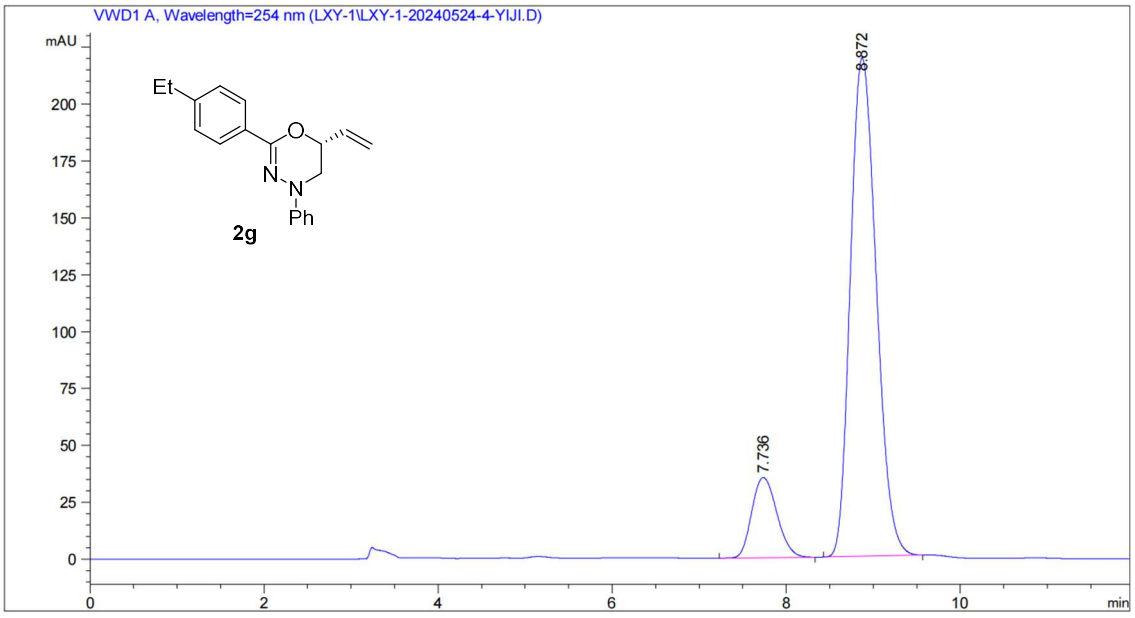
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.773	1.73006e4	853.76013	50.0599
2	PDA 254 nm	9.310	1.72592e4	773.94482	49.9401



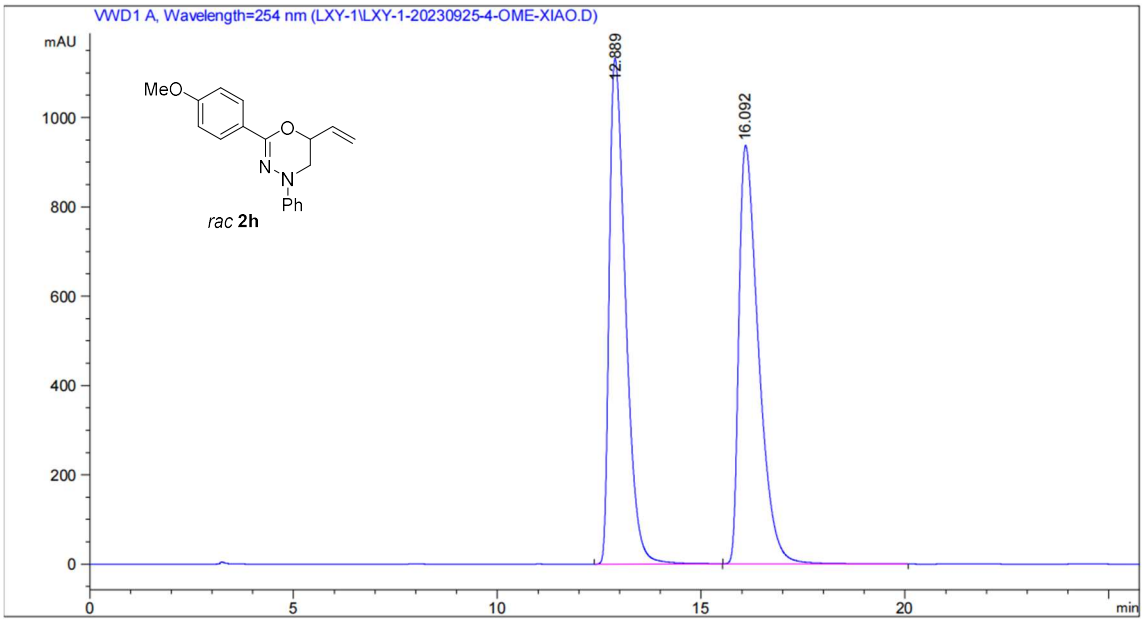
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.028	578.40607	27.75815	3.7344
2	PDA 254 nm	9.590	1.49104e4	651.65027	96.2656



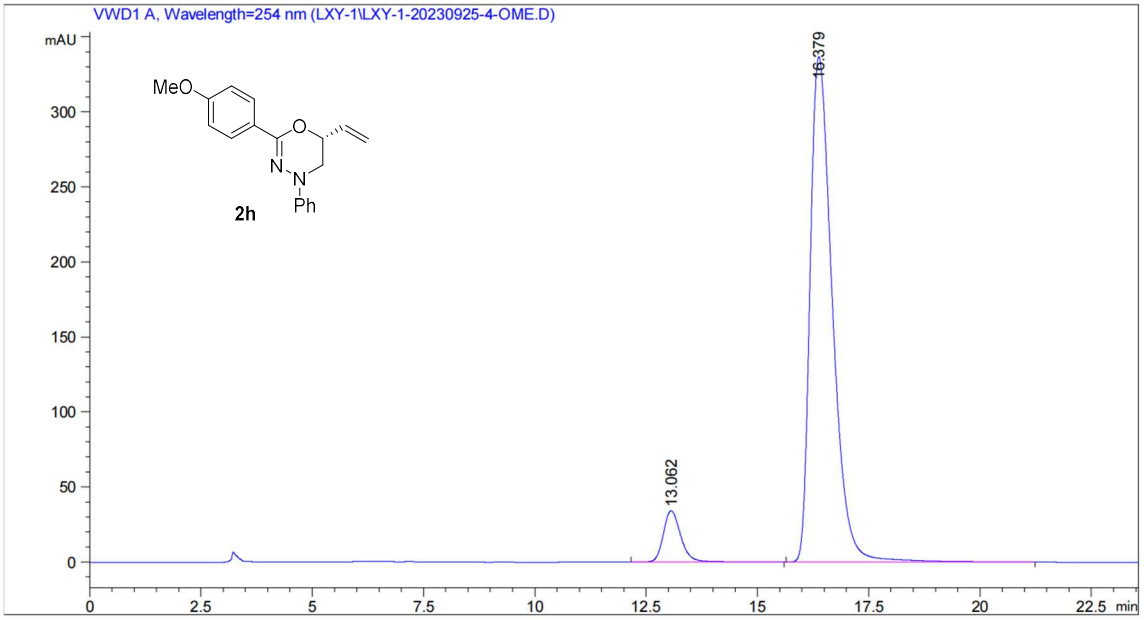
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.712	1.64330e4	824.05835	49.9172
2	PDA 254 nm	8.876	1.64875e4	755.10284	50.0828



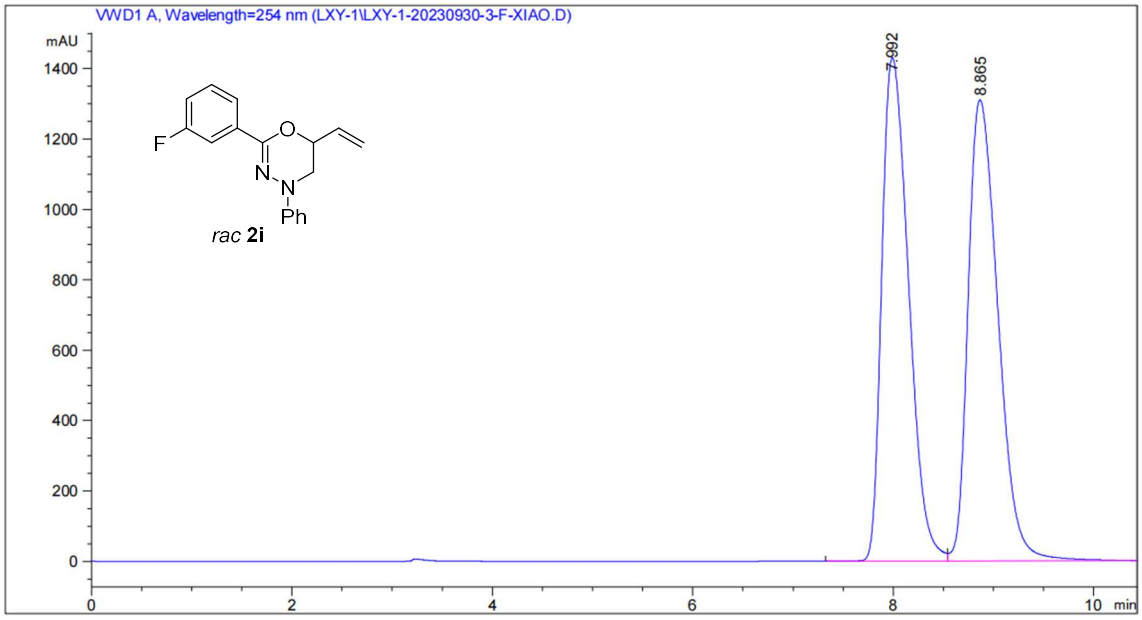
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.736	707.58521	35.23243	13.5323
2	PDA 254 nm	8.872	4521.28662	219.14201	86.4677



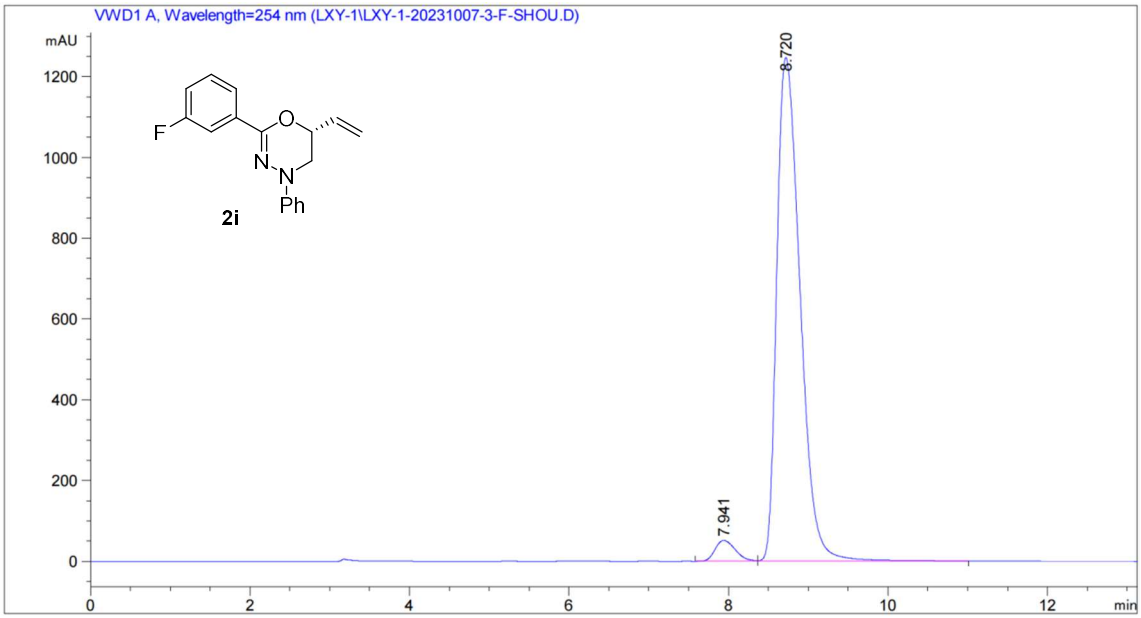
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	12.889	3.12966e4	1132.35571	49.9736
2	PDA 254 nm	16.092	3.13297e4	936.52216	50.0264



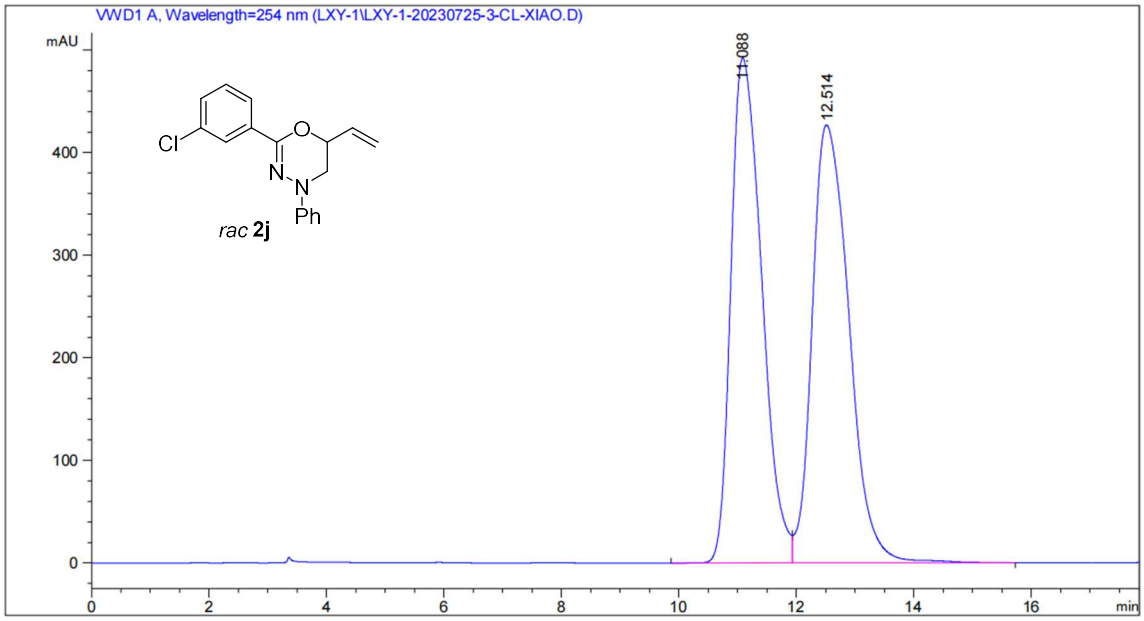
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	13.062	933.61298	34.20802	7.3887
2	PDA 254 nm	16.379	1.17021e4	336.72079	92.6113



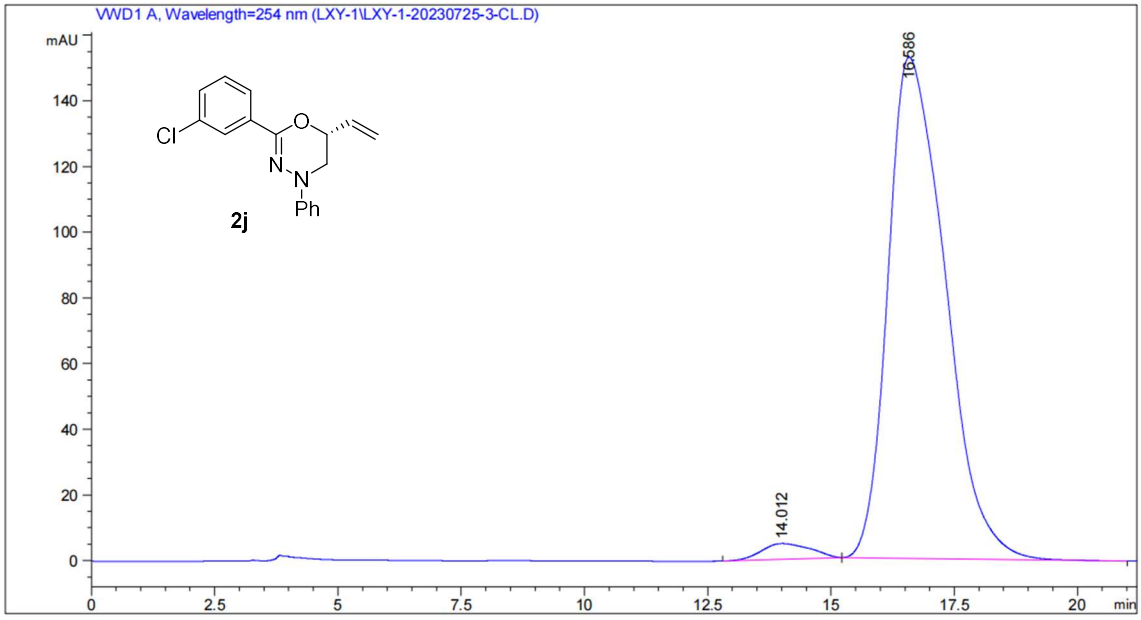
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.992	2.65009e4	1430.52295	49.4613
2	PDA 254 nm	8.865	2.70781e4	1310.23792	50.5387



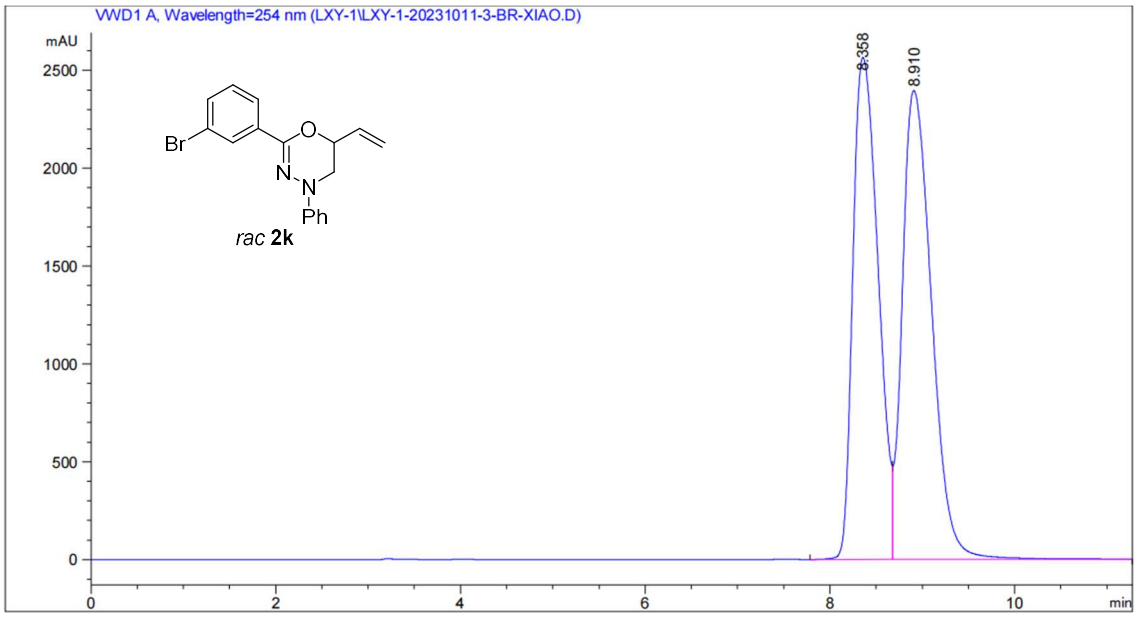
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.941	908.20709	51.38763	3.4721
2	PDA 254 nm	8.720	2.52493e4	1247.12488	96.5279



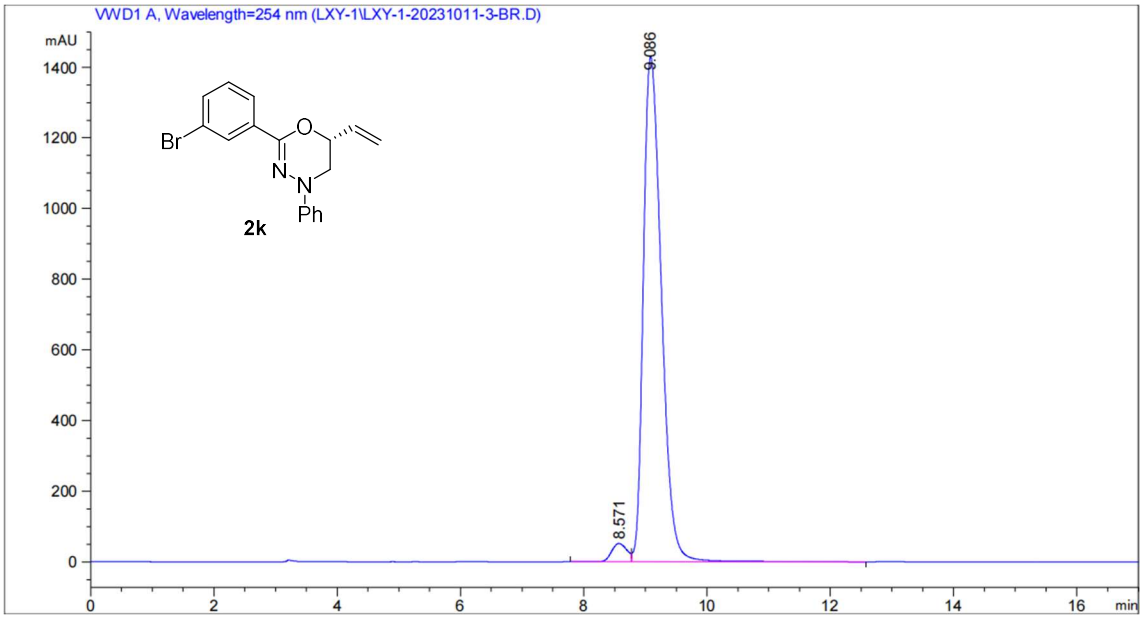
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	11.088	1.79578e4	492.42206	49.1083
2	PDA 254 nm	12.514	1.86099e4	426.89667	50.8917



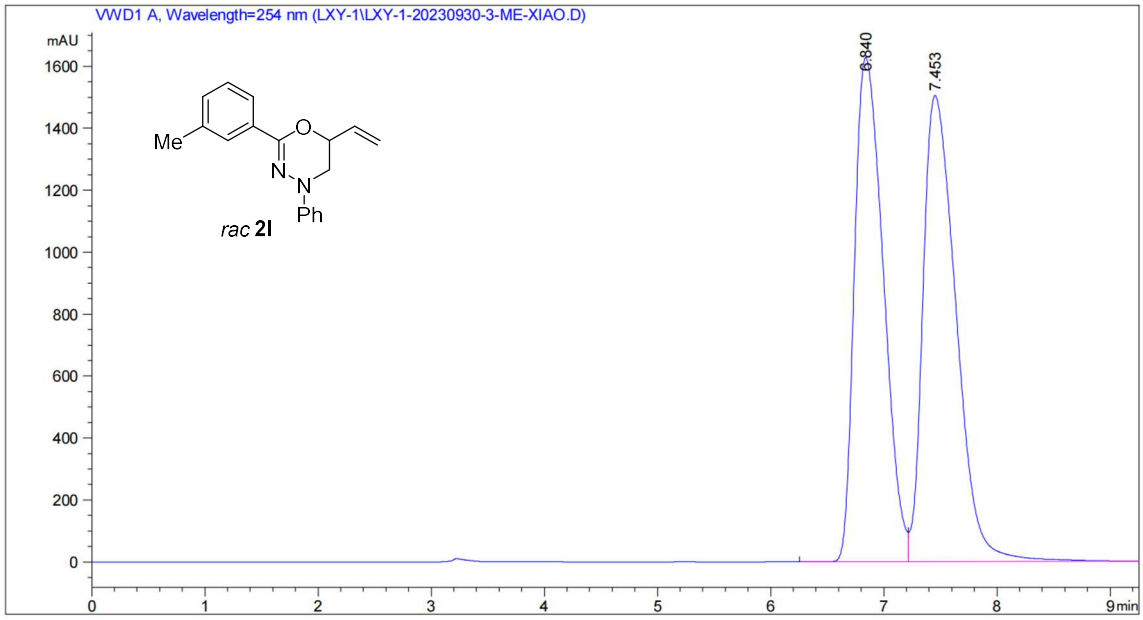
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	14.012	327.98294	4.80960	2.6002
2	PDA 254 nm	16.586	1.22856e4	152.63437	97.3998



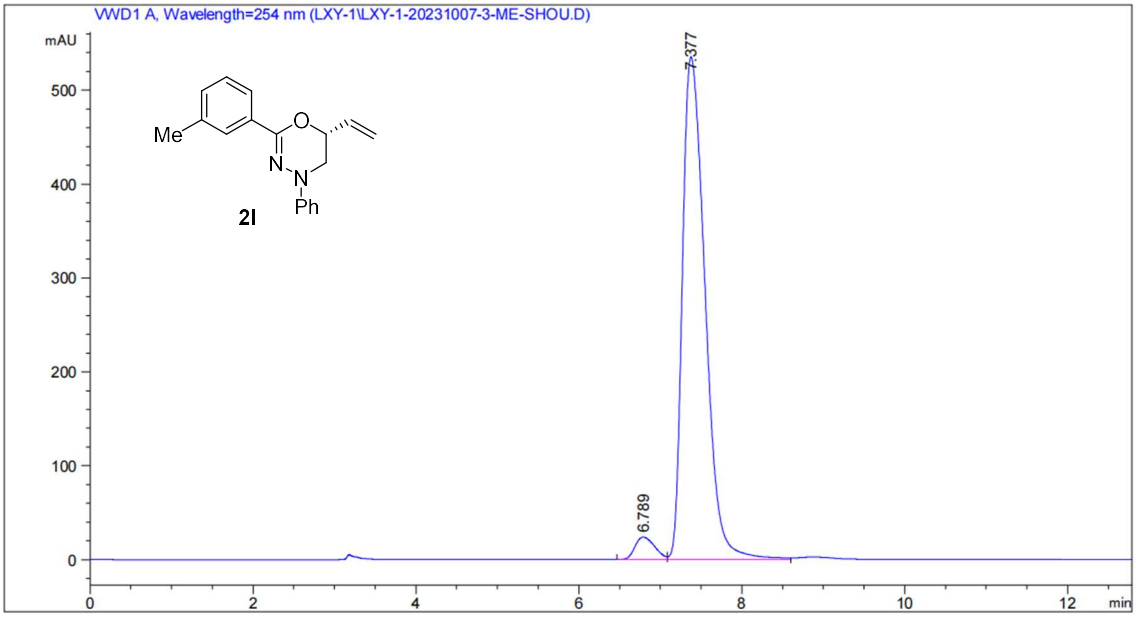
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.358	4.84731e4	2565.29932	47.8449
2	PDA 254 nm	8.910	5.28400e4	2395.82495	52.1551



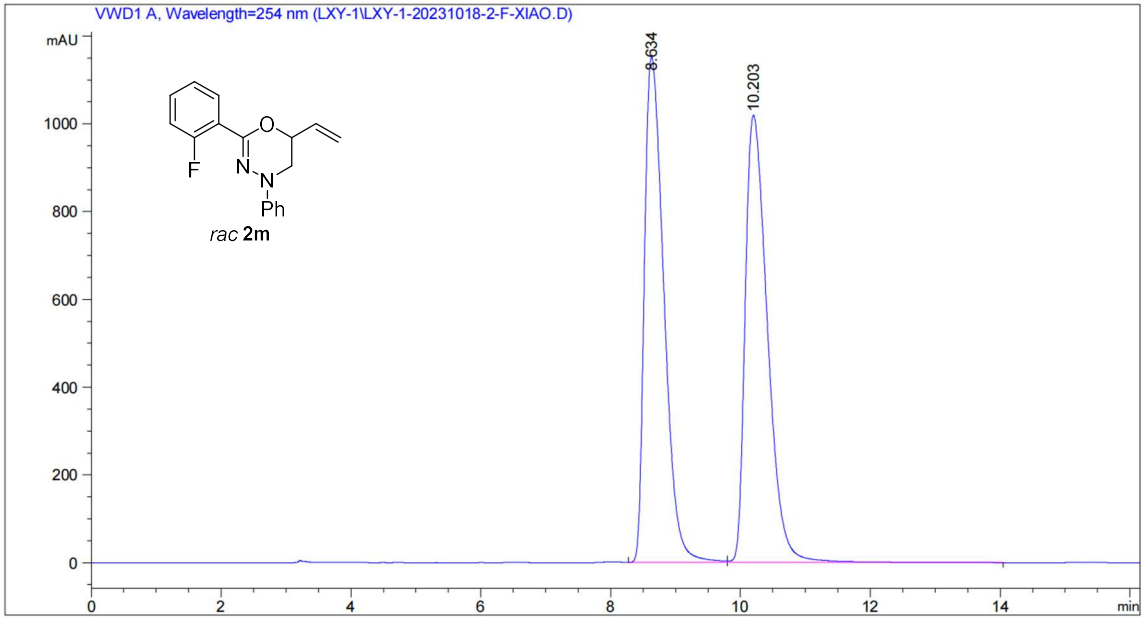
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.571	887.73608	51.71880	2.9675
2	PDA 254 nm	9.086	2.90274e4	1428.66882	97.0325



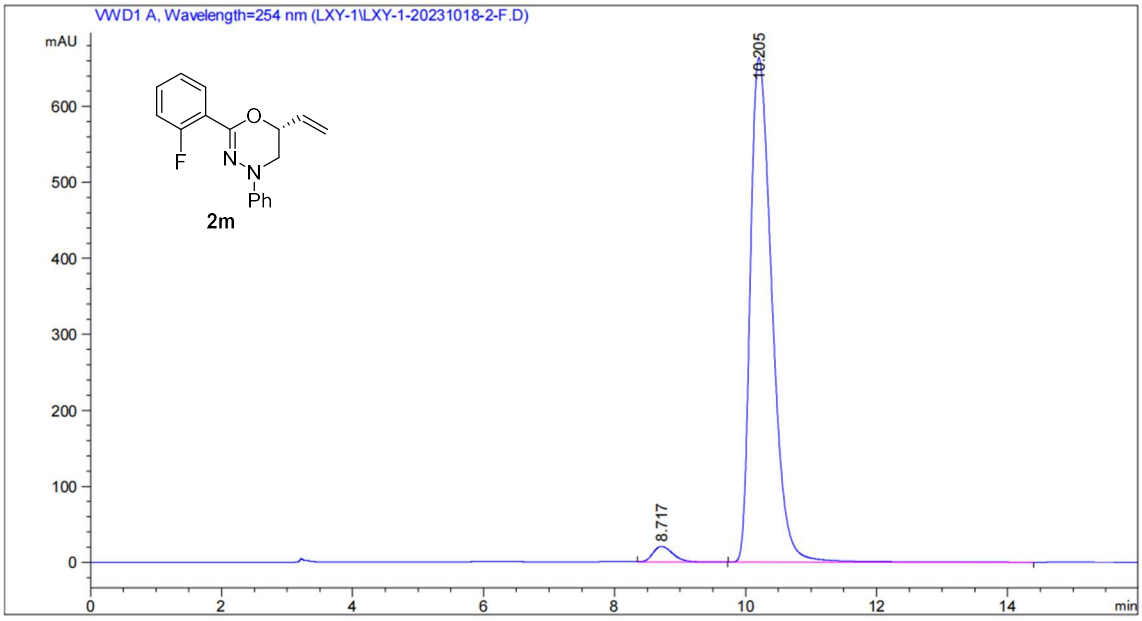
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	6.840	2.88443e4	1627.63770	48.5837
2	PDA 254 nm	7.453	3.05261e4	1504.26550	51.4163



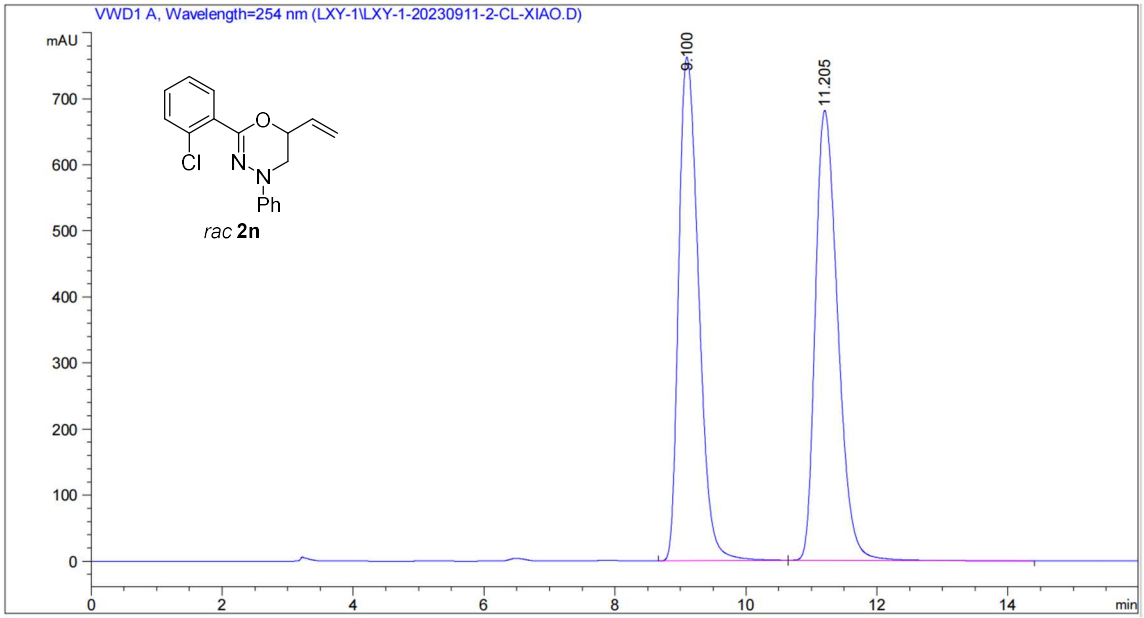
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	6.789	399.13583	23.87334	3.7338
2	PDA 254 nm	7.377	1.02908e4	535.27081	96.2662



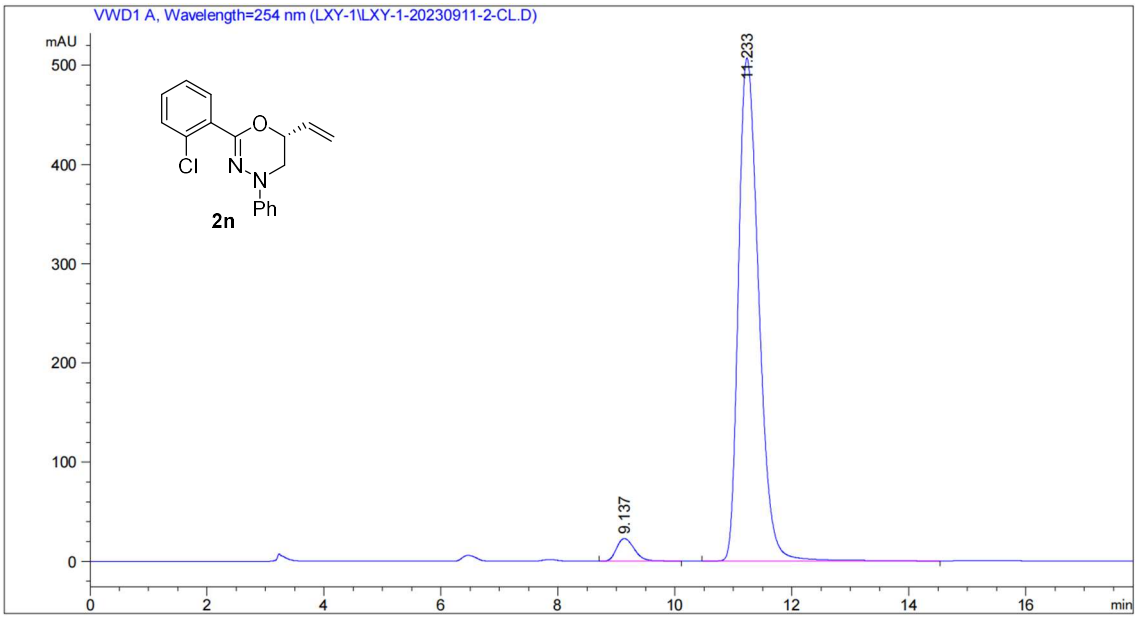
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.634	2.39585e4	1151.67090	49.7244
2	PDA 254 nm	10.203	2.42241e4	1018.17126	50.2756



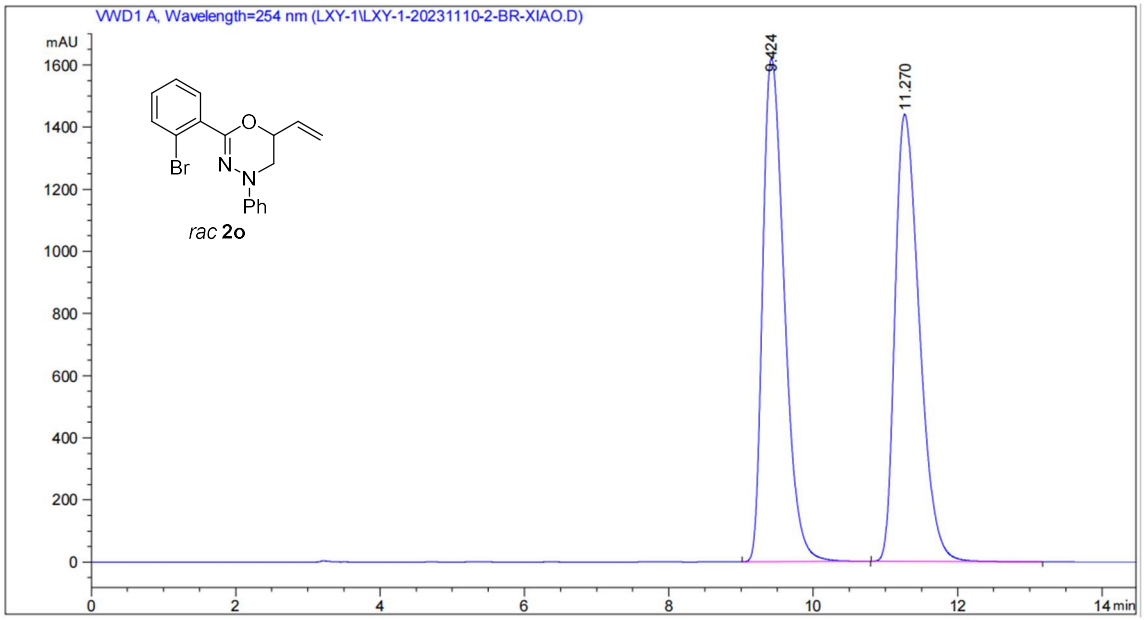
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.717	449.92065	20.65696	2.8739
2	PDA 254 nm	10.205	1.52055e4	663.66449	97.1261



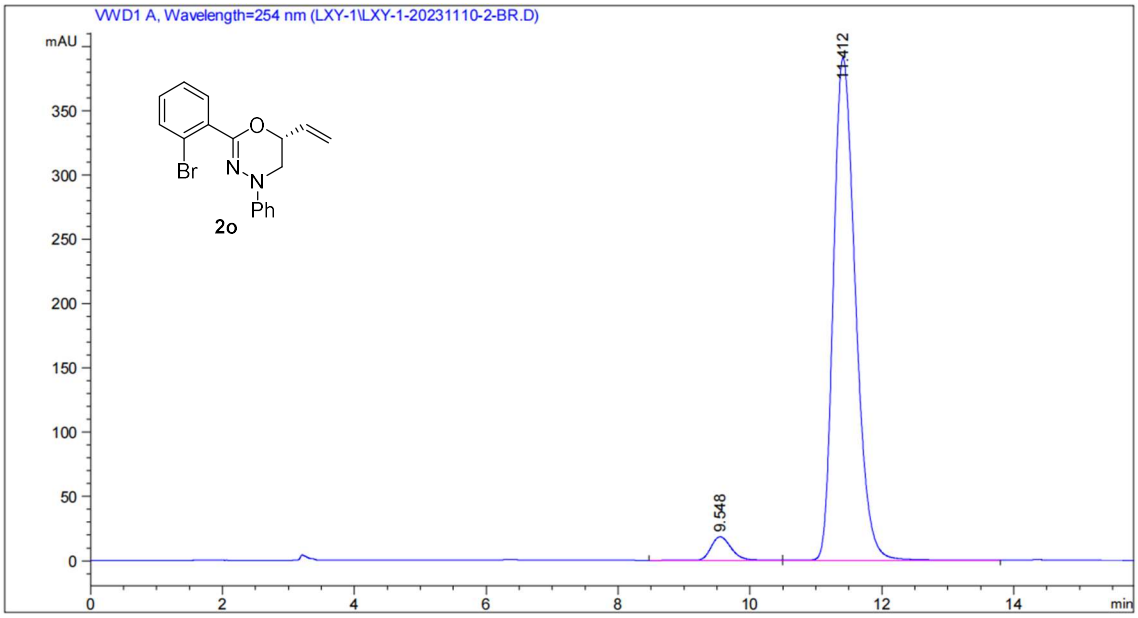
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.100	1.61168e4	762.38074	49.9159
2	PDA 254 nm	11.205	1.61711e4	680.71802	50.0841



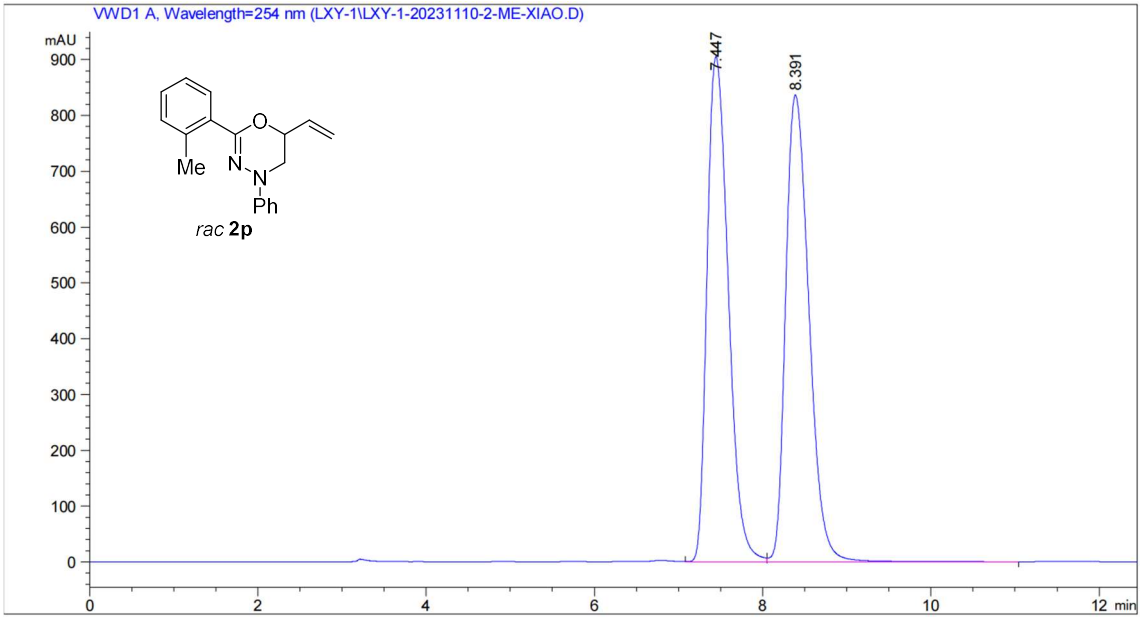
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.137	477.09335	22.70747	3.7673
2	PDA 254 nm	11.233	1.21870e4	506.64859	96.2327



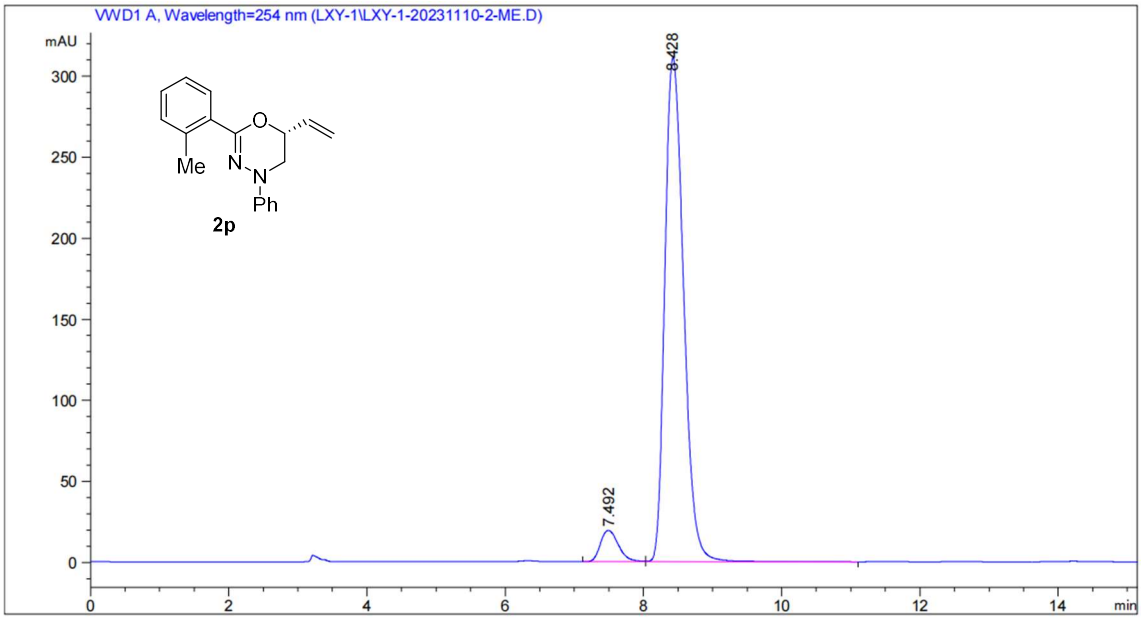
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.424	3.36028e4	1620.06213	49.9528
2	PDA 254 nm	11.270	3.36663e4	1438.41309	50.0472



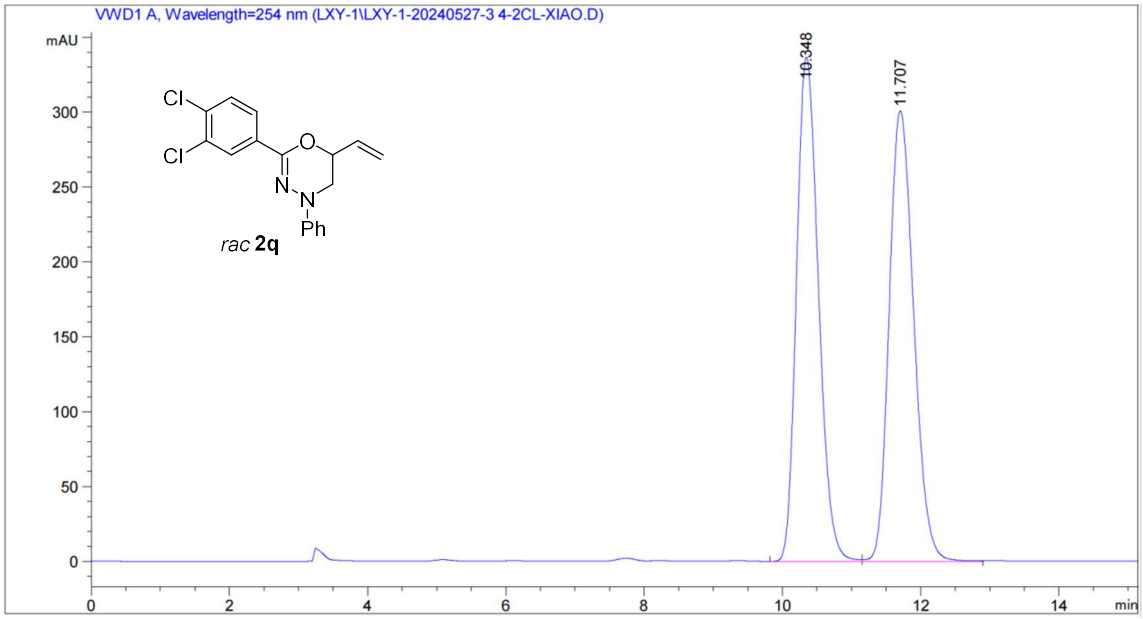
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.548	390.91885	18.28398	4.1342
2	PDA 254 nm	11.412	9064.72363	390.72415	95.8658



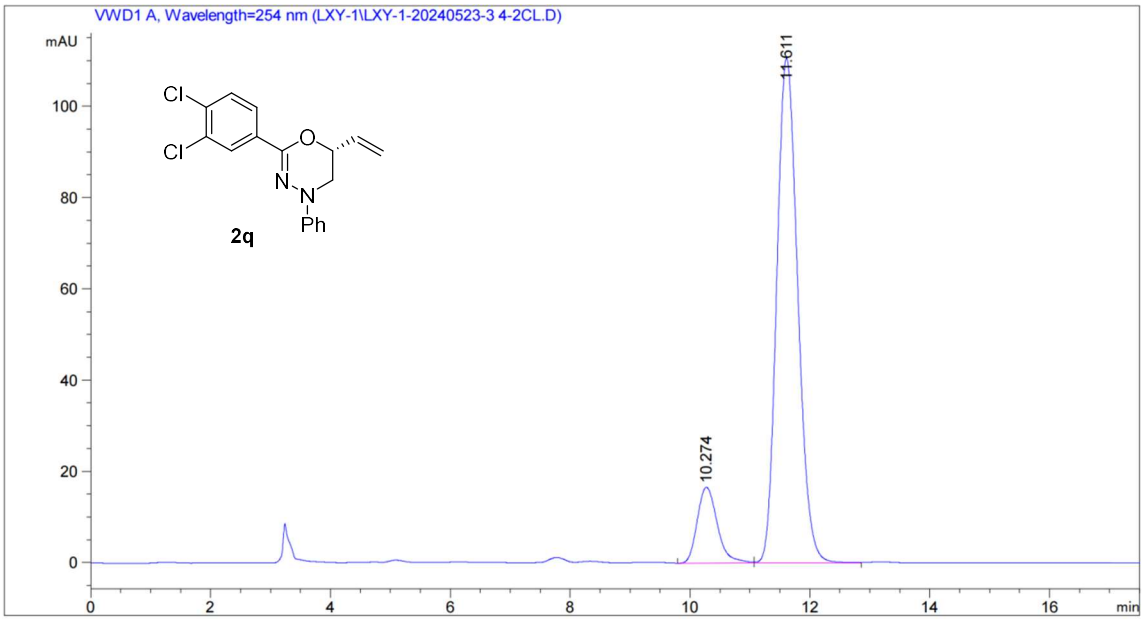
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.447	1.58199e4	904.30792	49.6682
2	PDA 254 nm	8.391	1.60313e4	835.67712	50.3318



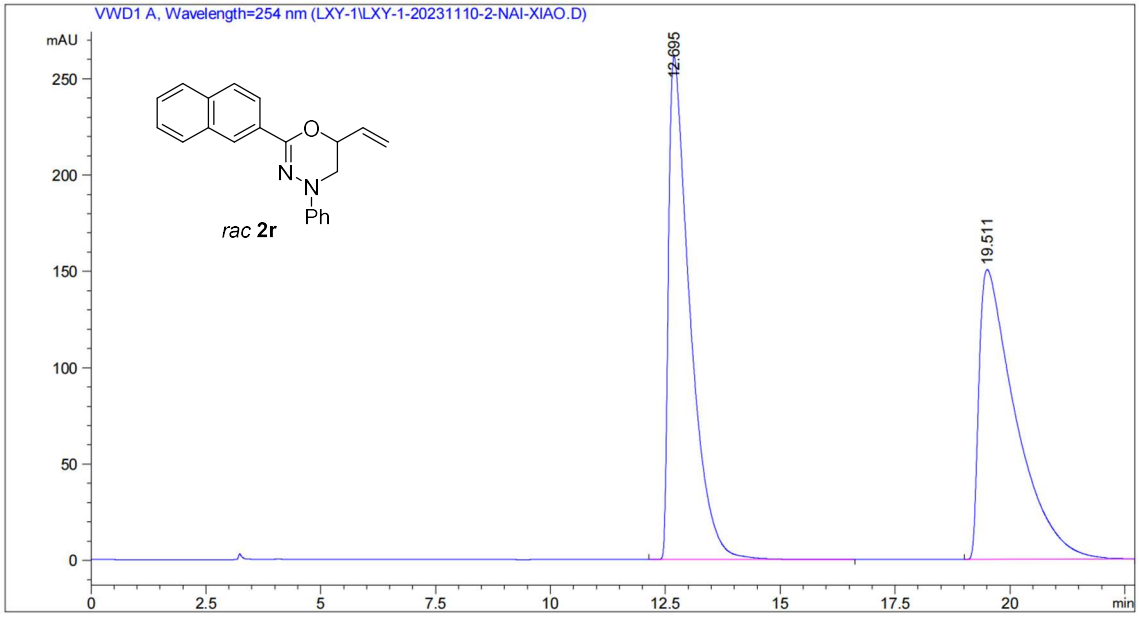
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.492	352.69107	19.37277	5.6812
2	PDA 254 nm	8.428	5855.30957	310.72833	94.3188



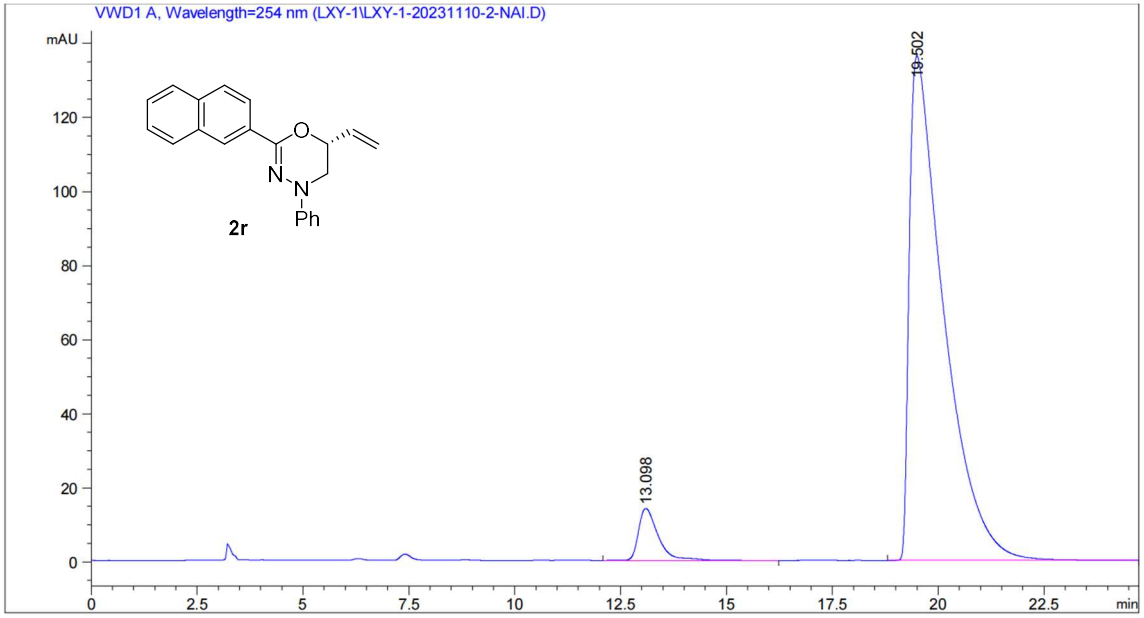
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.348	7408.49512	336.55316	49.9542
2	PDA 254 nm	11.707	7422.08447	300.71606	50.0458



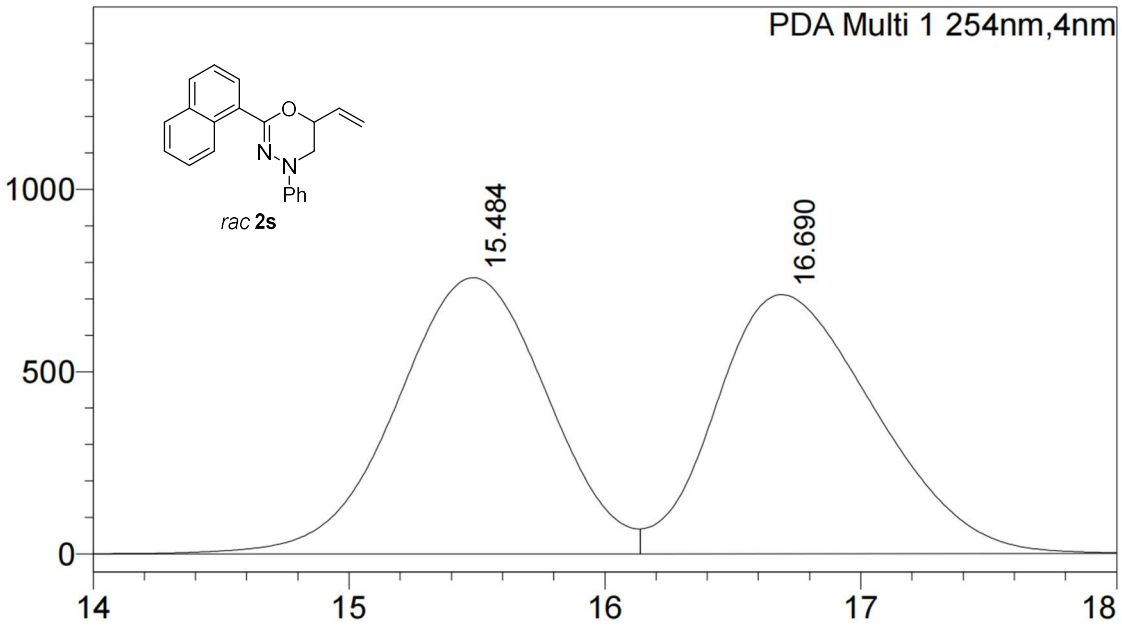
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	10.274	387.62274	16.63267	12.5782
2	PDA 254 nm	11.611	2694.07861	110.66516	87.4218



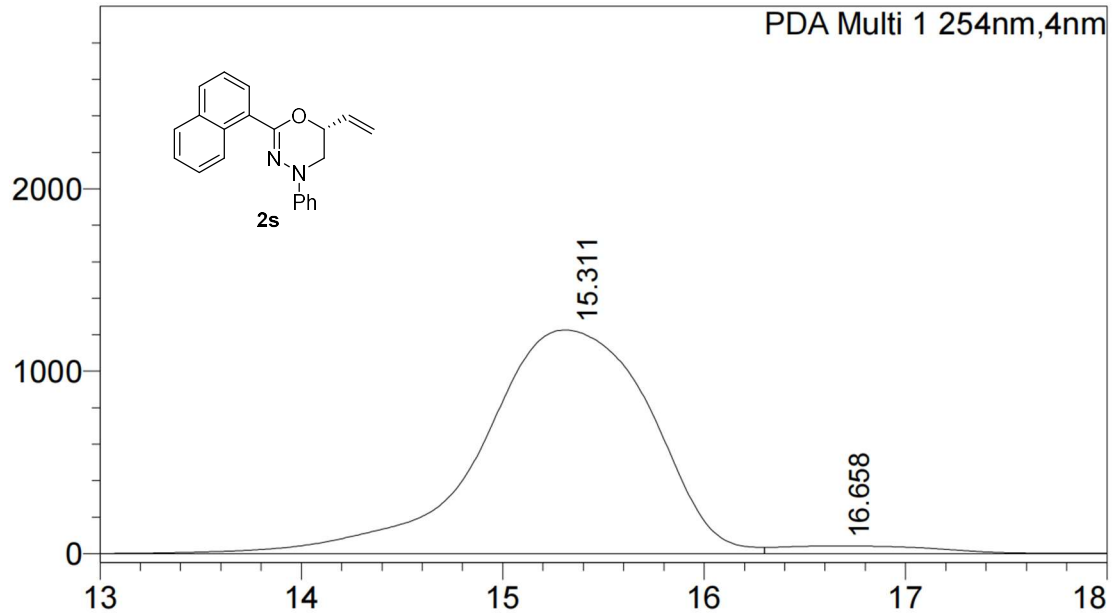
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	12.695	8435.94629	260.84421	50.1843
2	PDA 254 nm	19.511	8373.97656	150.48225	49.8157



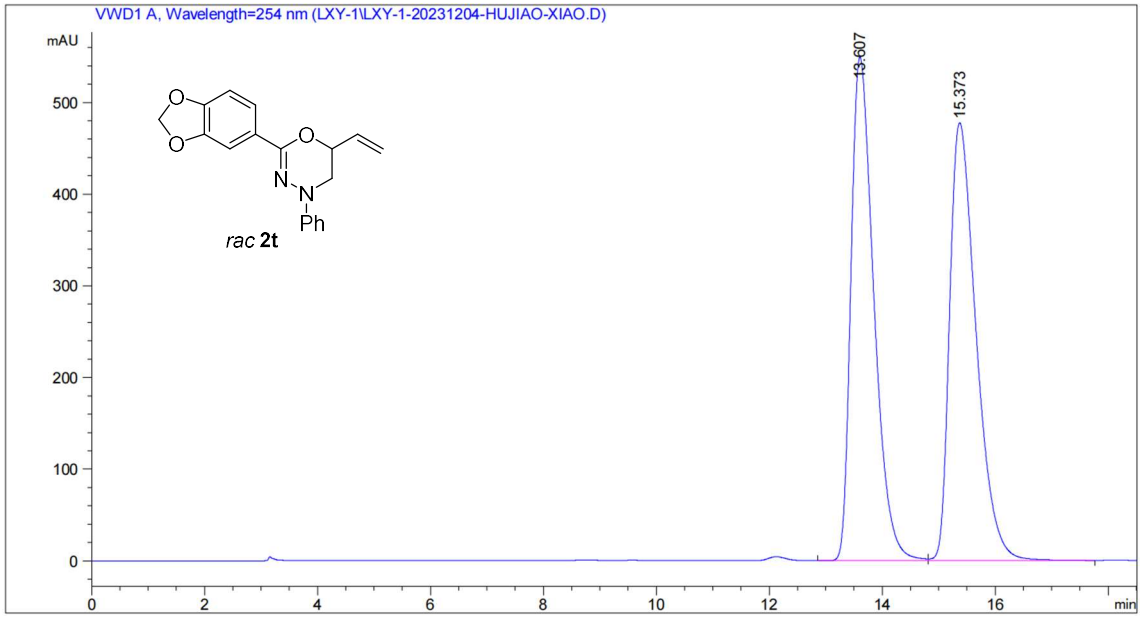
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	13.098	453.17133	14.05922	5.5786
2	PDA 254 nm	19.502	7670.21338	136.24324	94.4214



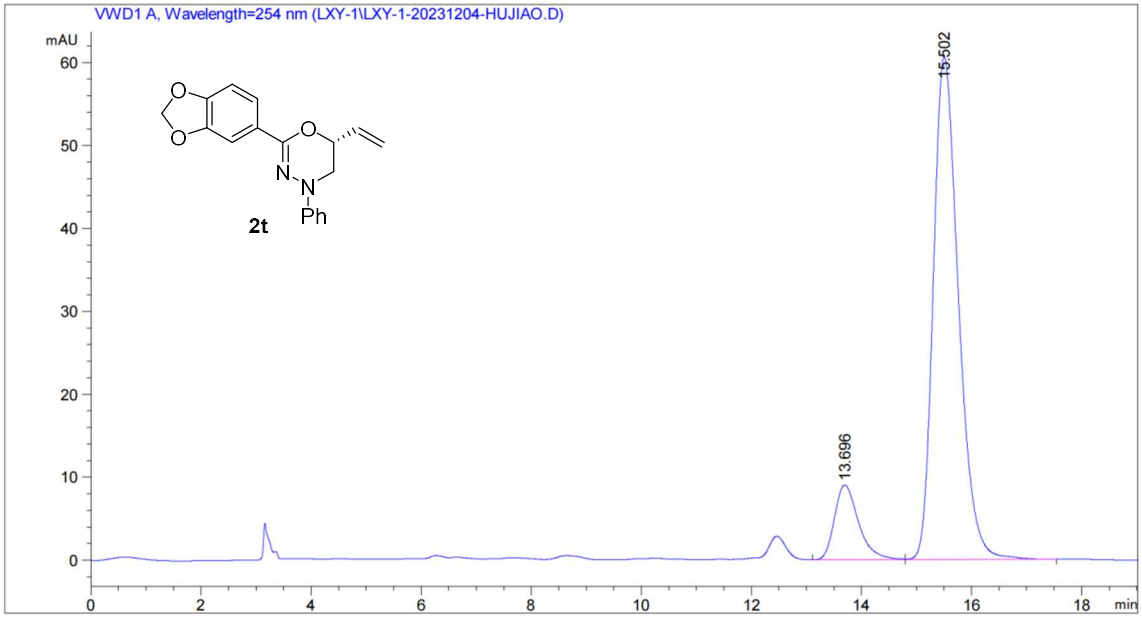
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak area (%)
1	PDA 254 nm	15.484	51.98585e4	50.291
2	PDA 254 nm	16.690	51.383265e4	49.709



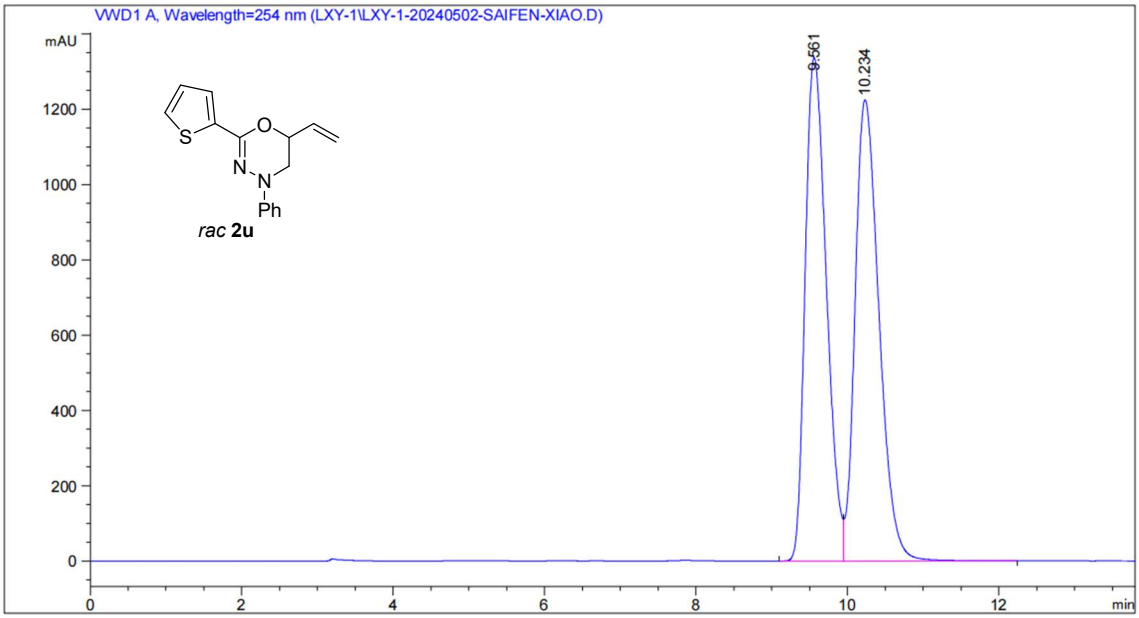
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak area (%)
1	PDA 254 nm	15.311	120.32799e4	96.865
2	PDA 254 nm	16.658	3.8938483e4	3.135



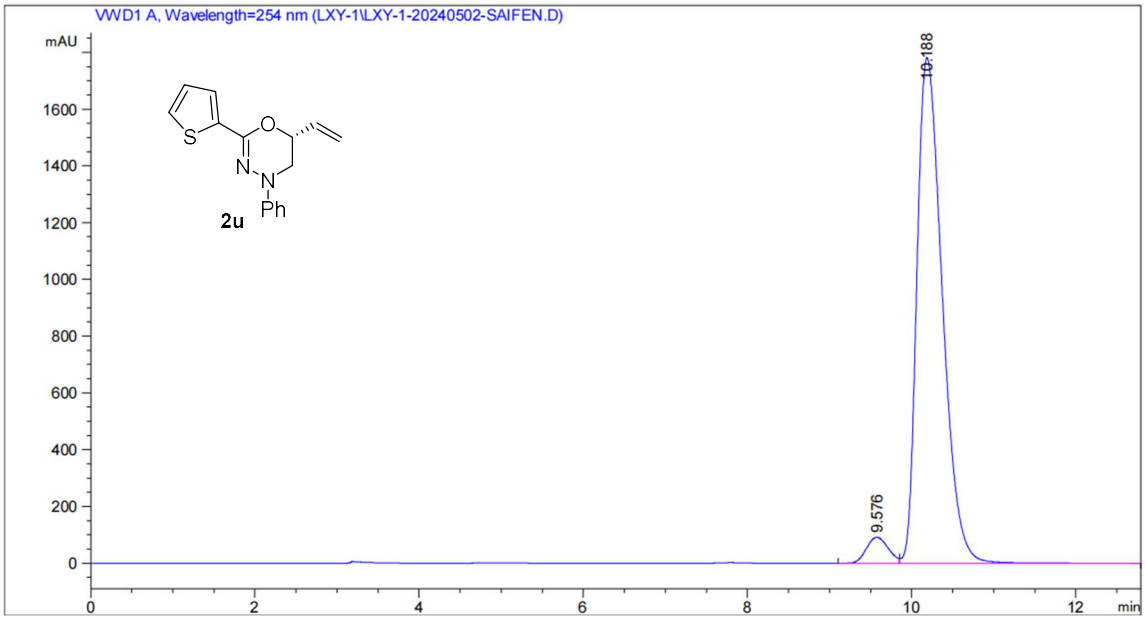
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	13.607	1.54510e4	549.31787	49.9152
2	PDA 254 nm	15.373	1.55035e4	477.48062	50.0848



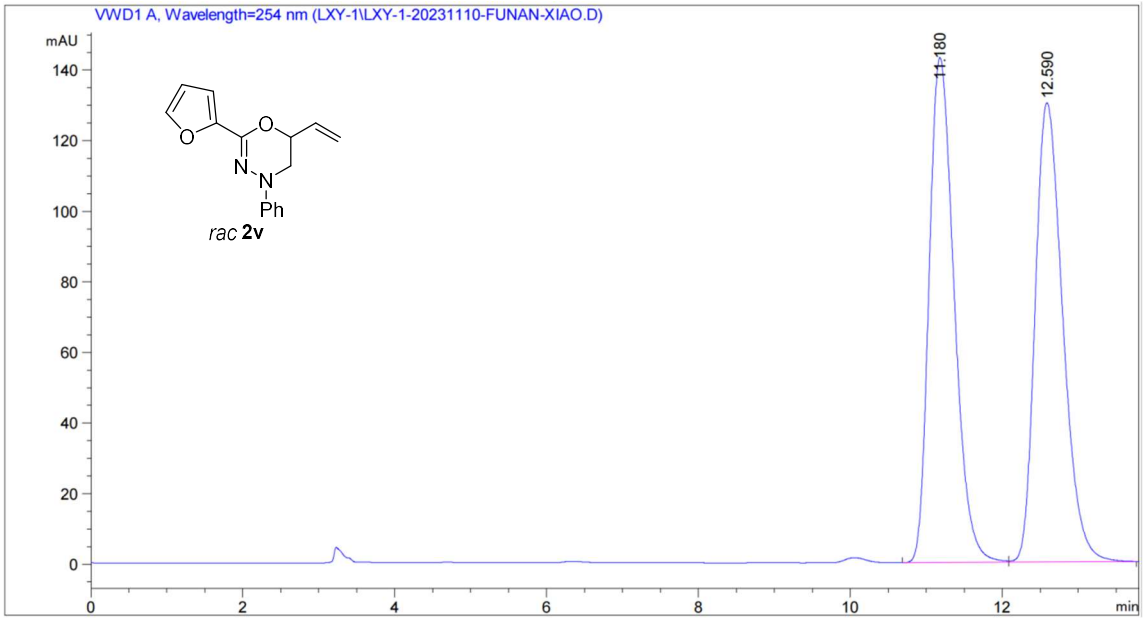
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	13.696	274.33865	9.01824	12.5148
2	PDA 254 nm	15.502	1917.78259	60.62328	87.4852



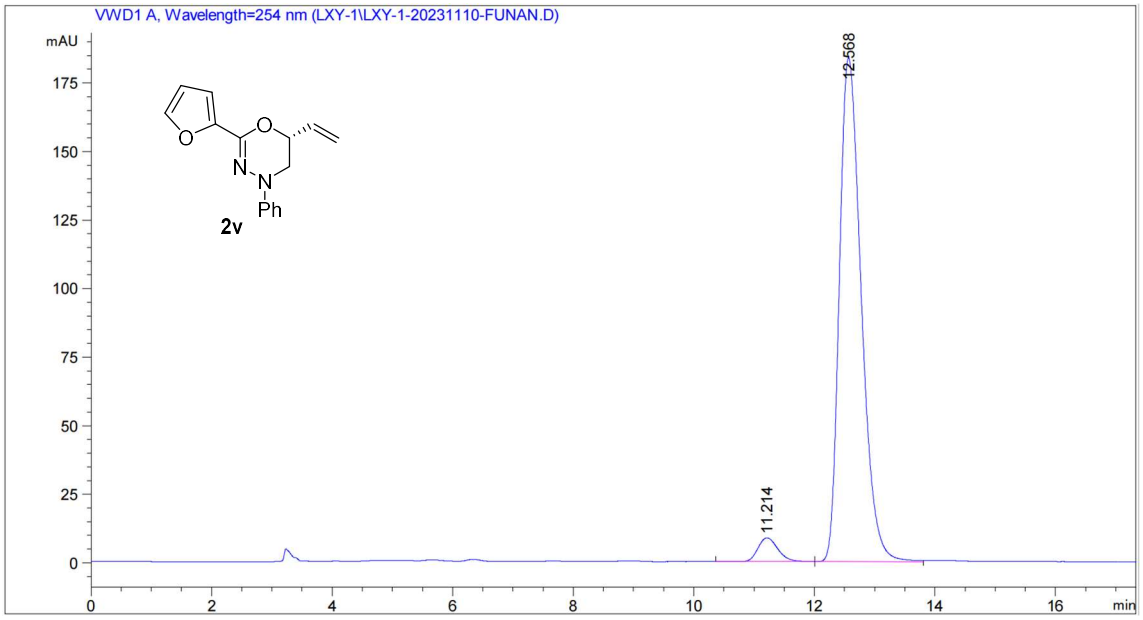
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.561	2.59236e4	1335.97803	49.0598
2	PDA 254 nm	10.234	2.69172e4	1224.49683	50.9402



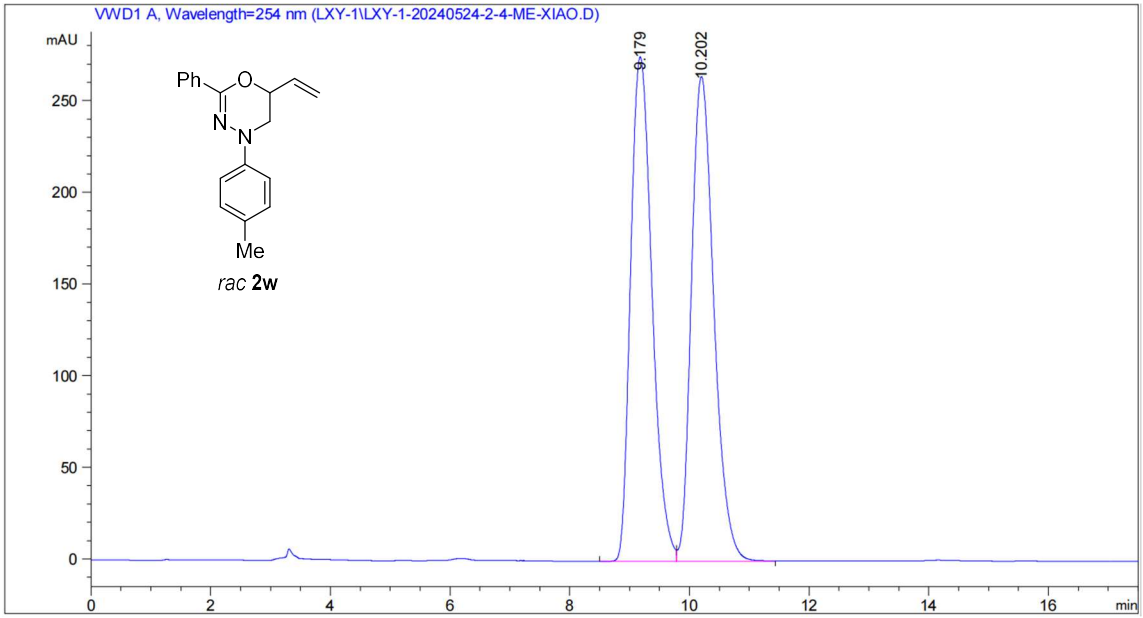
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.576	1685.50574	91.39238	4.2376
2	PDA 254 nm	10.188	3.80895e4	1779.38586	95.7624



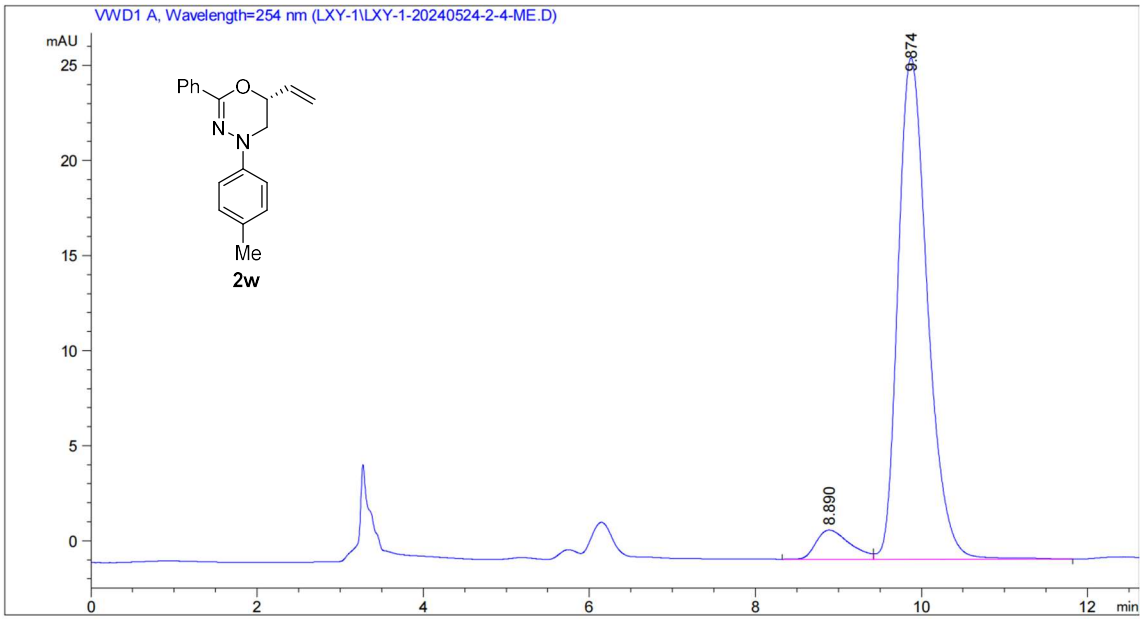
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	11.180	3267.55103	142.98737	49.9103
2	PDA 254 nm	12.590	3279.29419	130.03745	50.0897



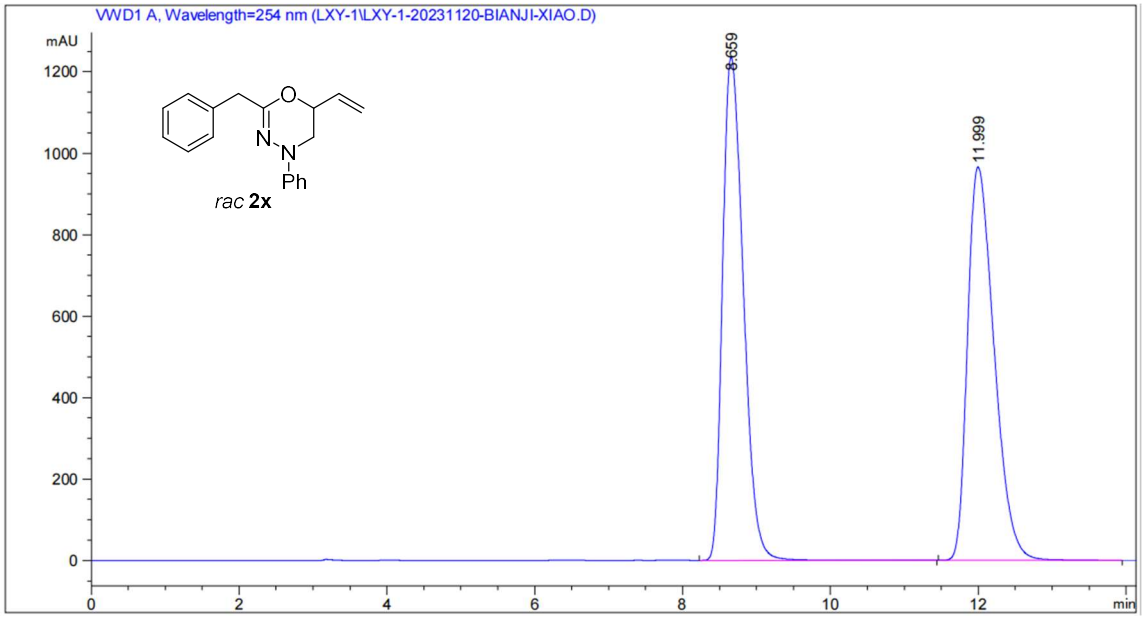
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	11.214	200.44565	8.67041	4.1608
2	PDA 254 nm	12.568	4616.99756	183.66676	95.8392



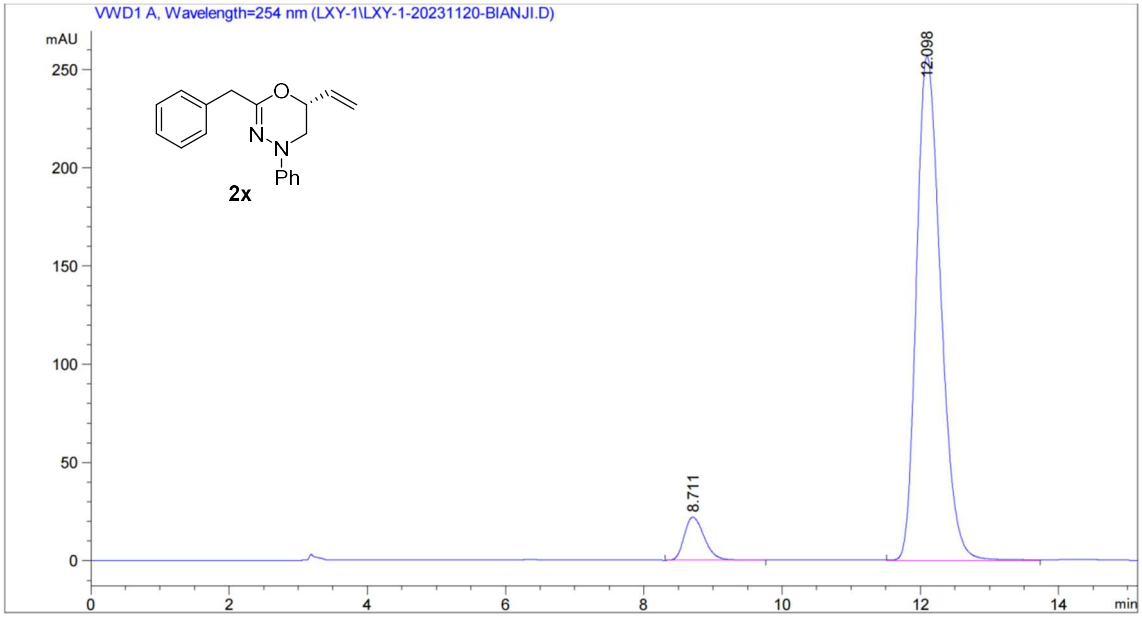
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	9.179	6829.65918	275.14215	49.7925
2	PDA 254 nm	10.202	6886.58545	264.34167	50.2075



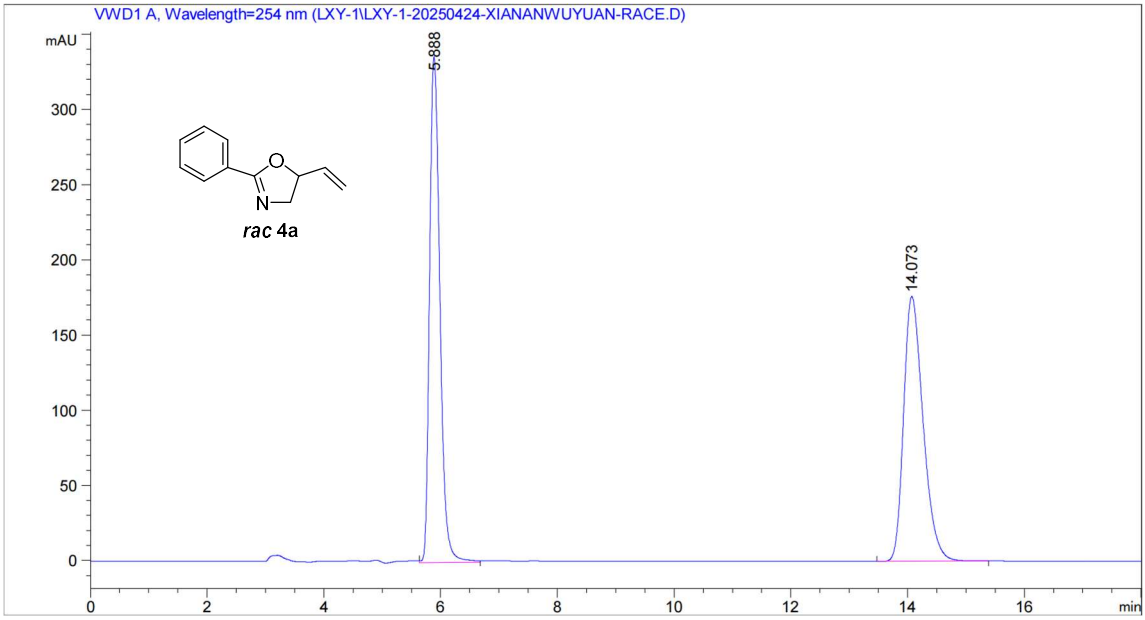
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.890	43.44970	1.53697	6.2648
2	PDA 254 nm	9.874	650.10718	26.36923	93.7352



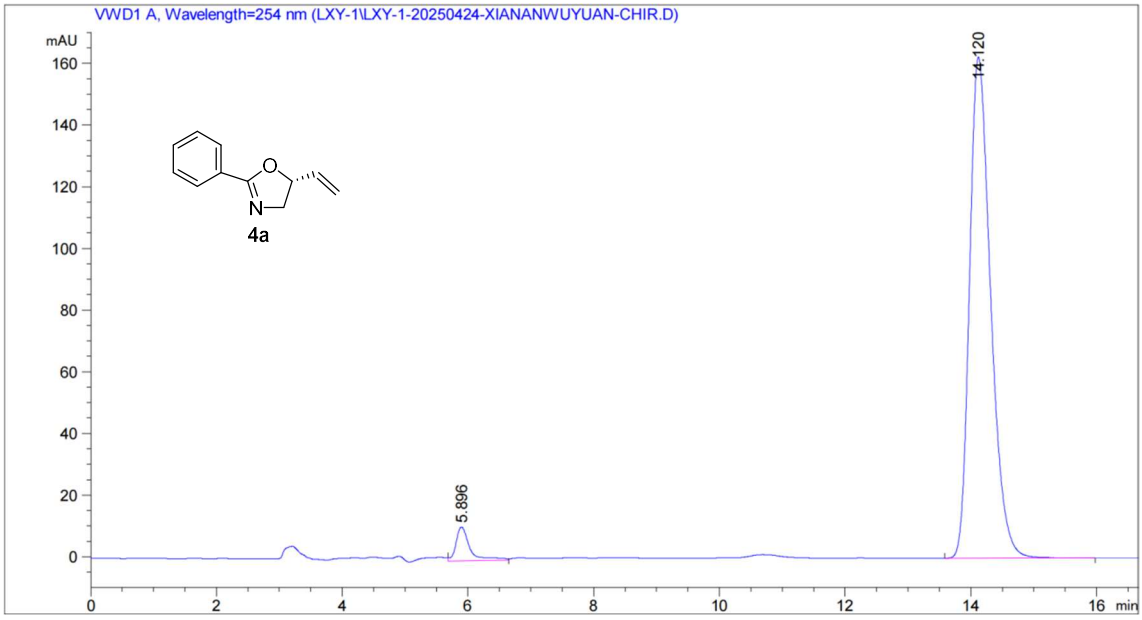
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.659	2.40789e4	1234.37024	49.9331
2	PDA 254 nm	11.999	2.41434e4	965.33820	50.0669



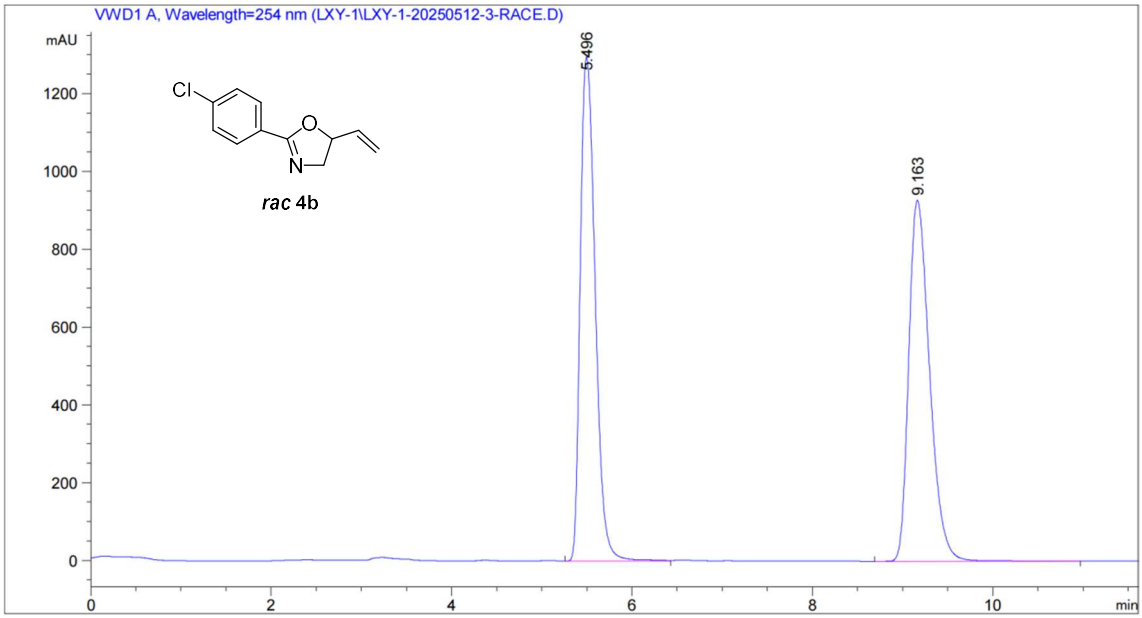
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	8.711	443.25421	21.94311	6.6360
2	PDA 254 nm	12.098	6236.26514	256.69135	93.3640



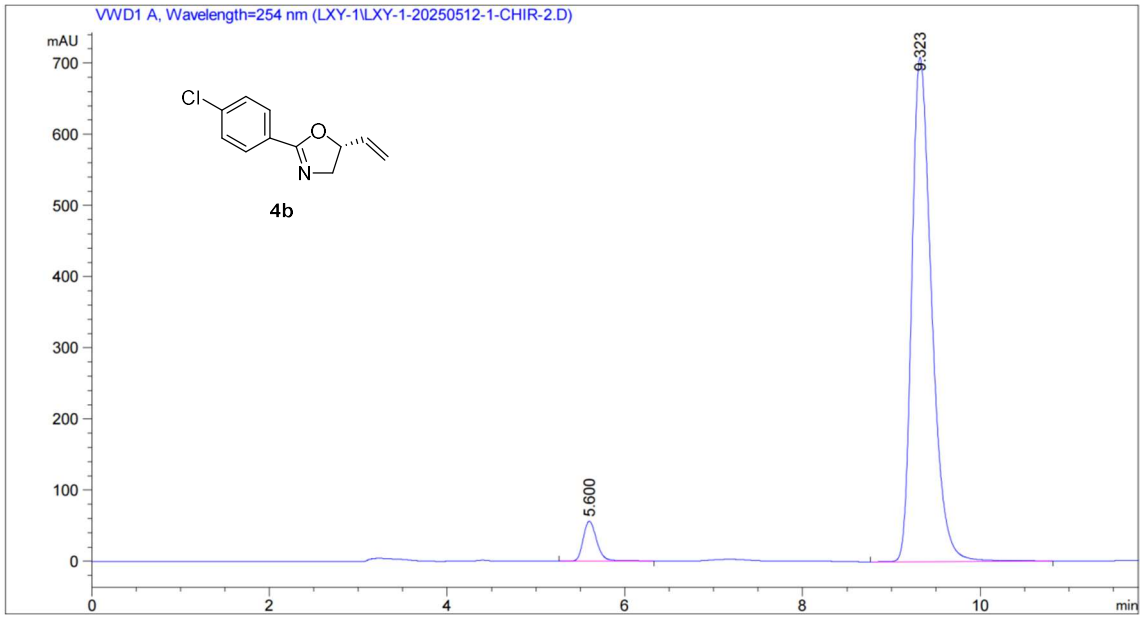
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.888	4125.52588	336.19339	50.2732
2	PDA 254 nm	14.073	4080.68774	176.01389	49.7268



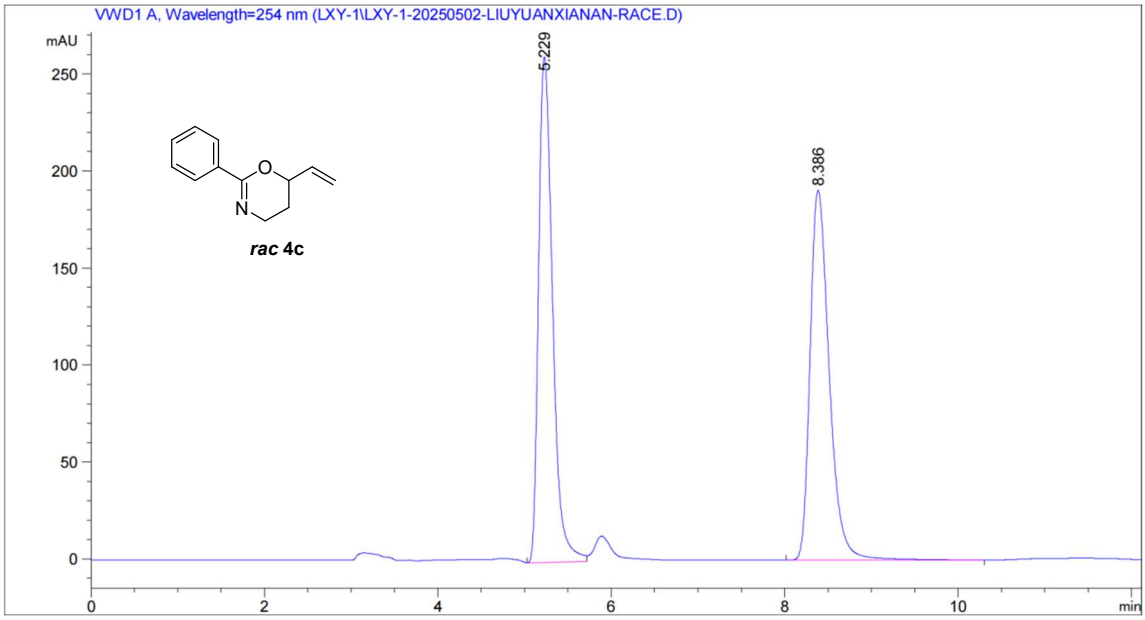
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.896	175.14236	11.08113	4.4211
2	PDA 254 nm	14.120	3786.38989	162.44640	95.5789



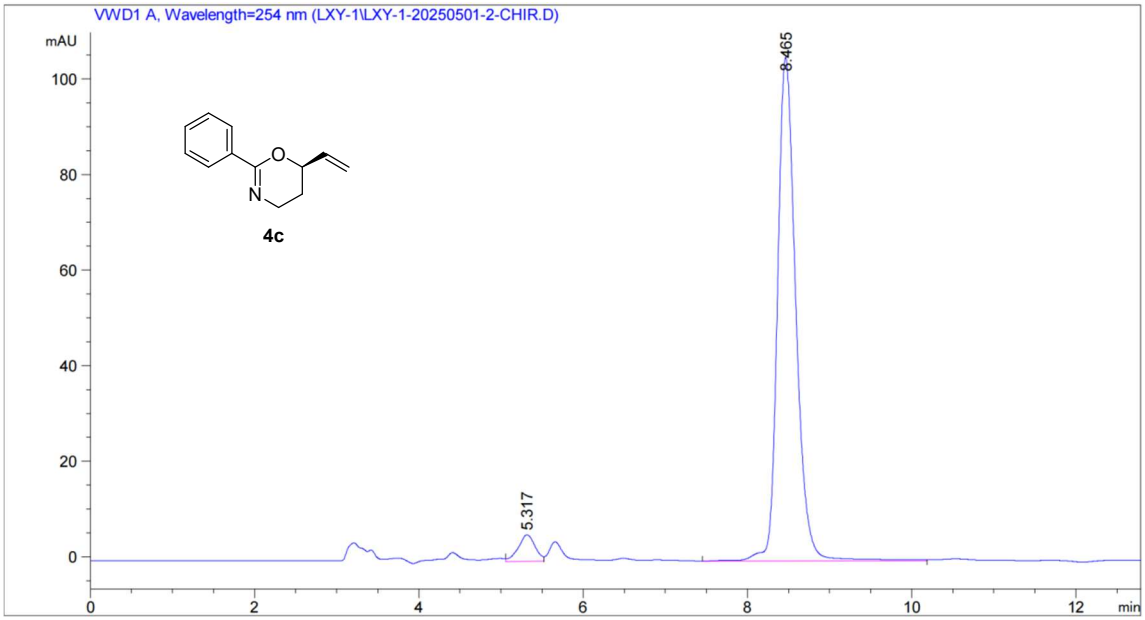
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.496	1.49185e4	1295.70142	50.0619
2	PDA 254 nm	9.163	1.48817e4	928.4371	49.9381



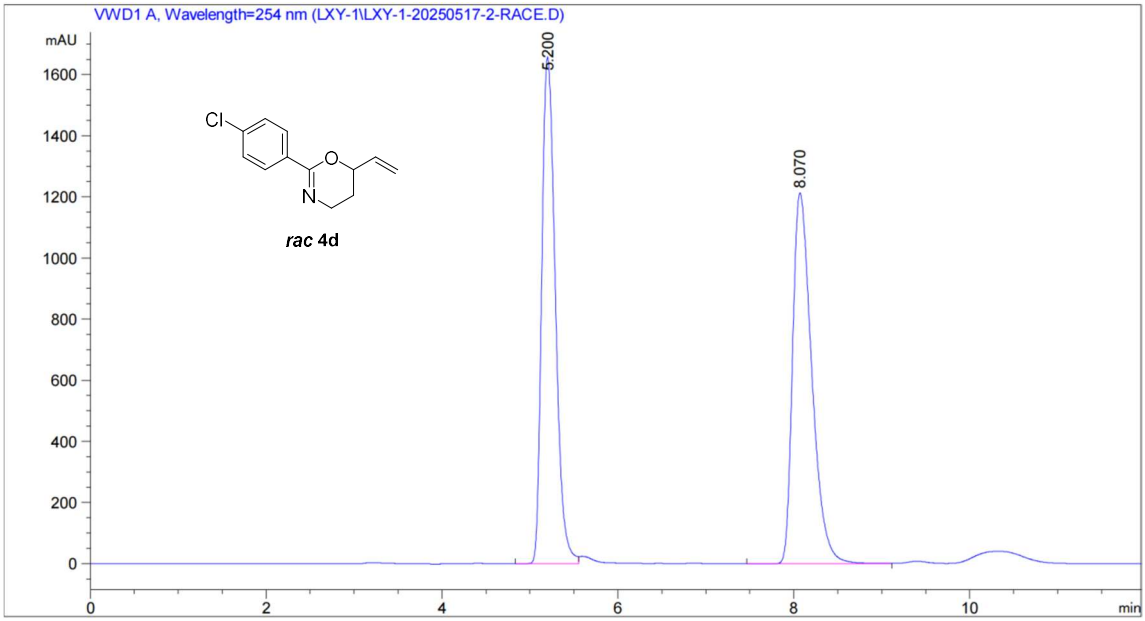
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.600	598.02081	56.08037	5.1663
2	PDA 254 nm	9.323	1.09773e4	708.38879	94.8337



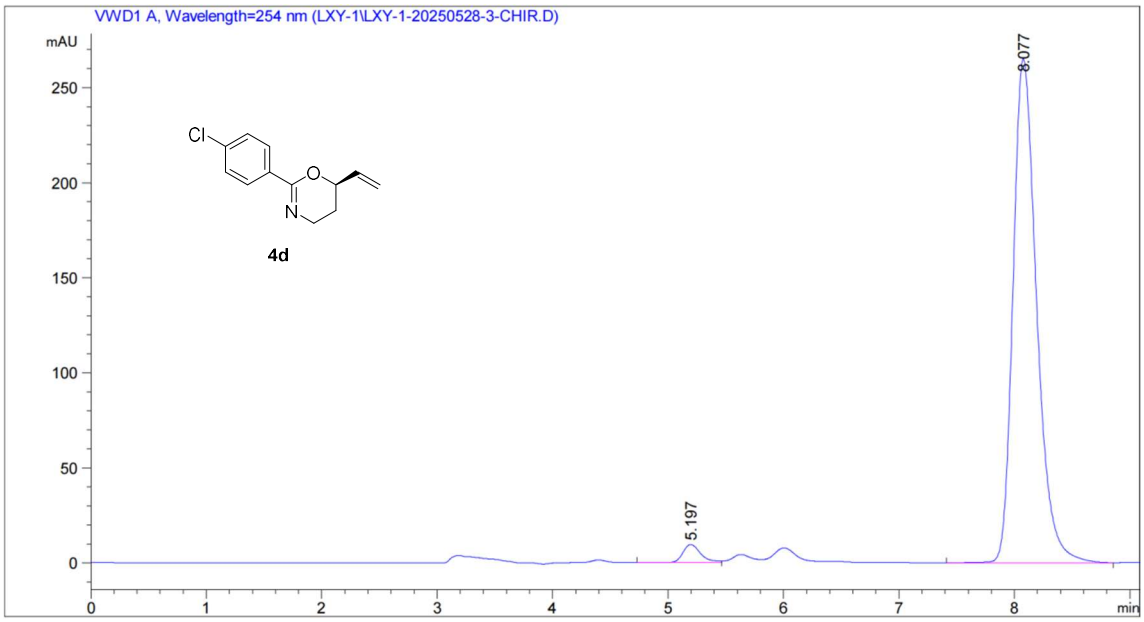
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.229	2916.52612	260.33728	49.9496
2	PDA 254 nm	8.386	2922.40967	190.48338	50.0504



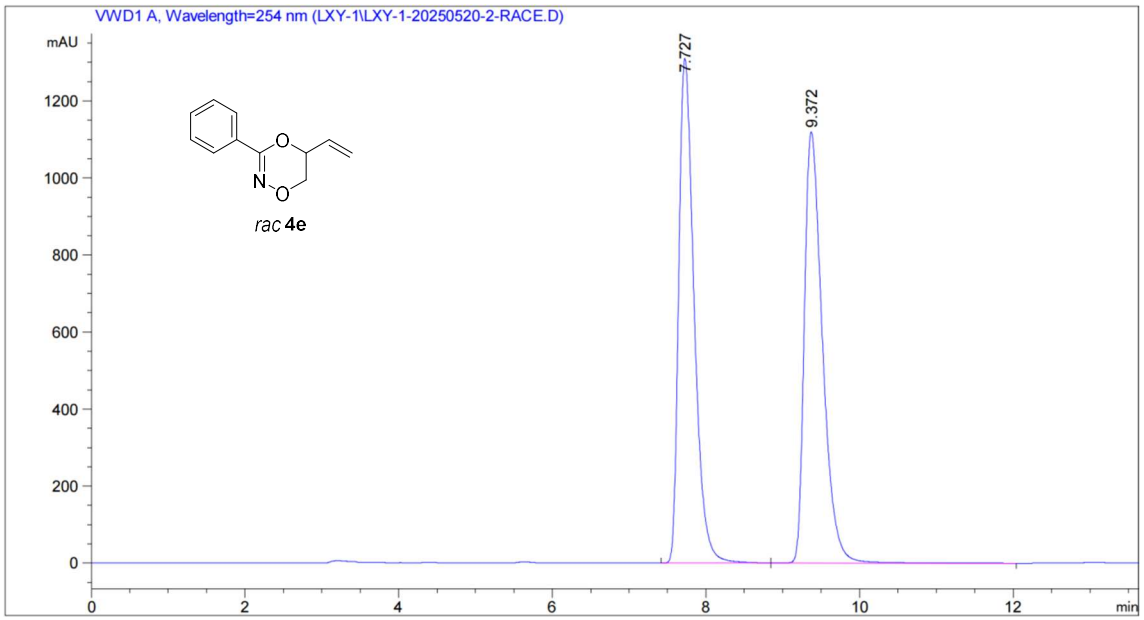
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.317	80.11609	5.59061	4.6668
2	PDA 254 nm	8.465	1636.60779	105.32313	95.3332



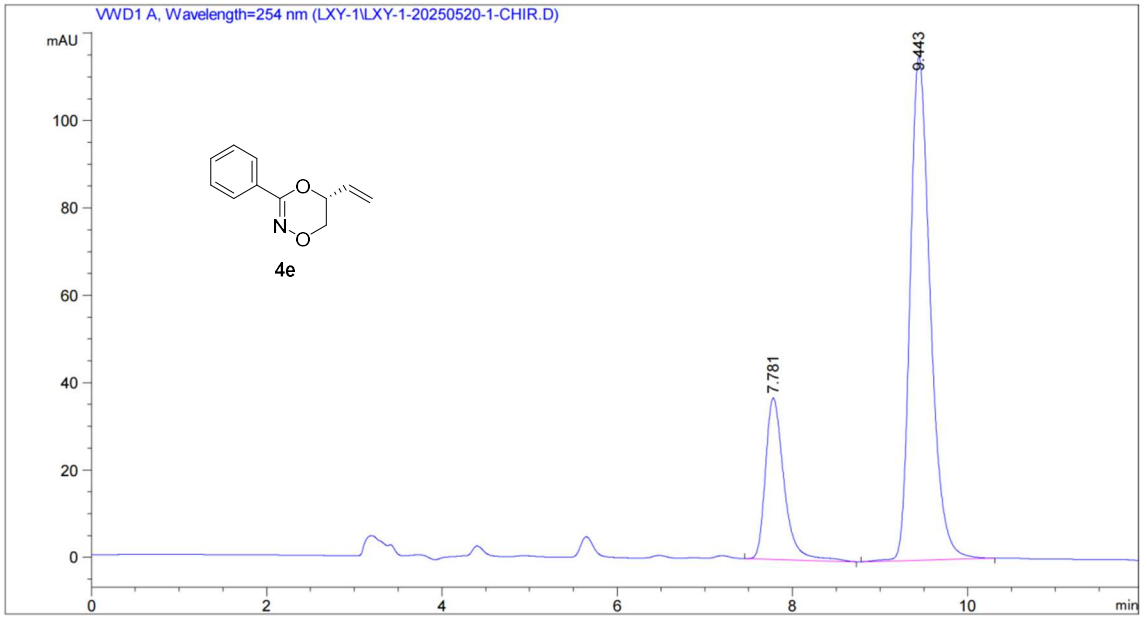
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.200	1.77705e4	1656.84241	49.2104
2	PDA 254 nm	8.070	1.83408e4	1213.04858	50.7896



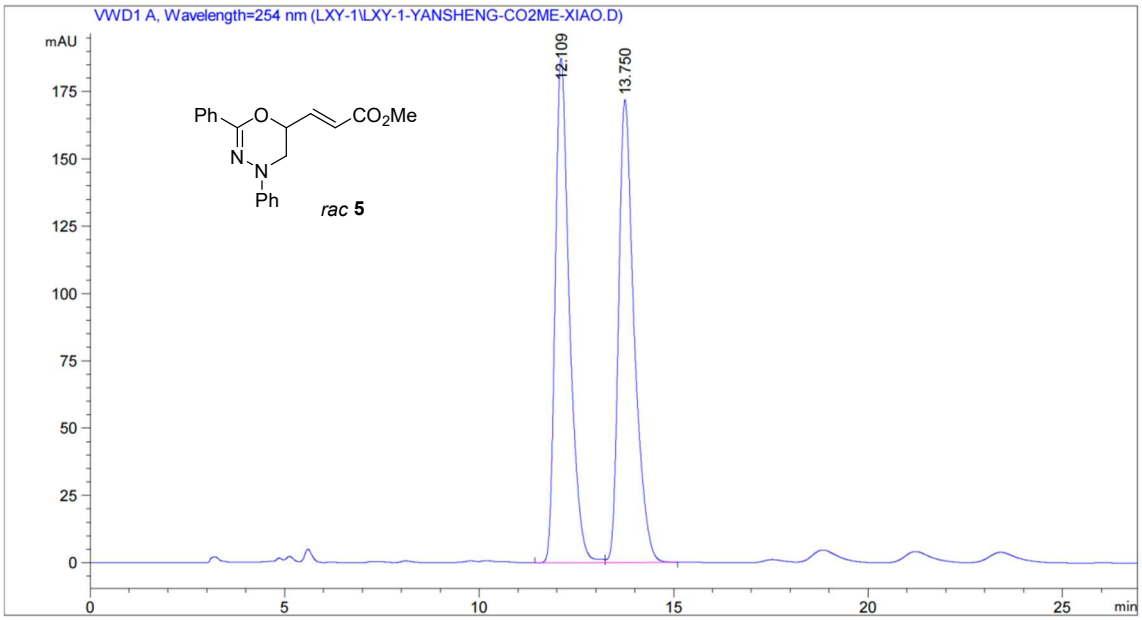
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	5.197	103.05188	9.49268	2.6666
2	PDA 254 nm	8.077	3761.44092	265.09888	97.3334



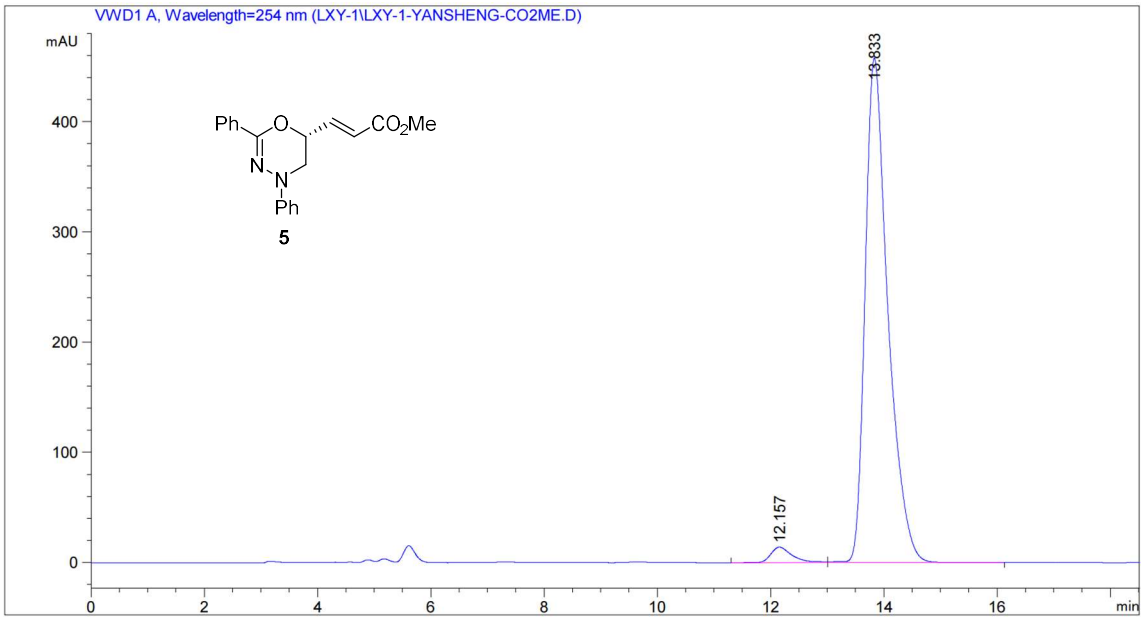
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.727	1.81730e4	1309.41895	49.8411
2	PDA 254 nm	9.372	1.82889e4	1118.37268	50.1589



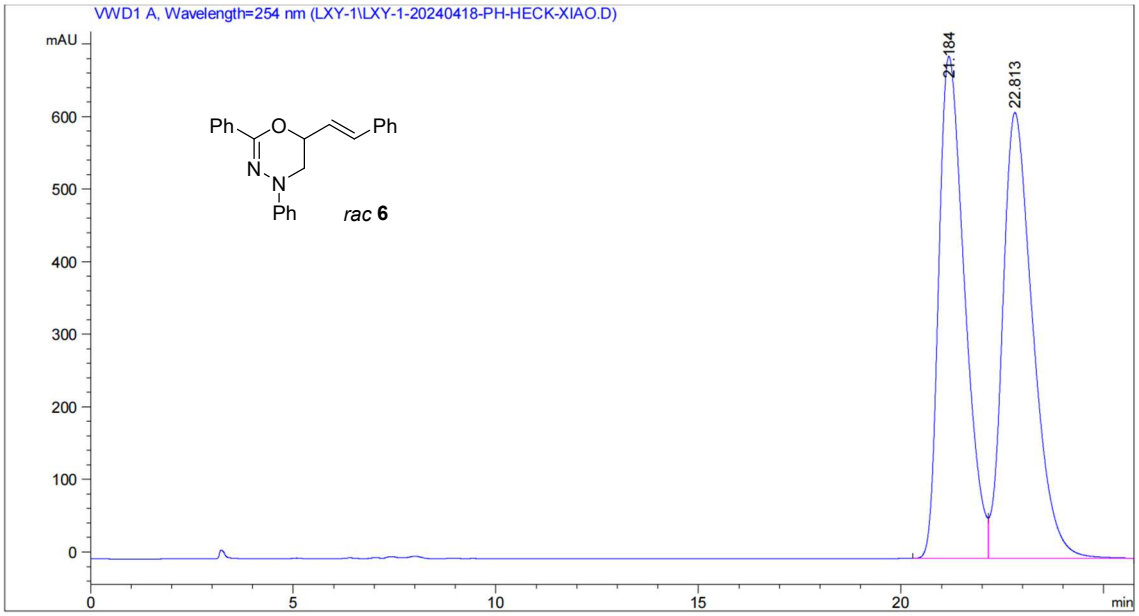
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.781	544.44464	36.93044	22.8017
2	PDA 254 nm	9.443	1843.29077	115.21226	77.1983



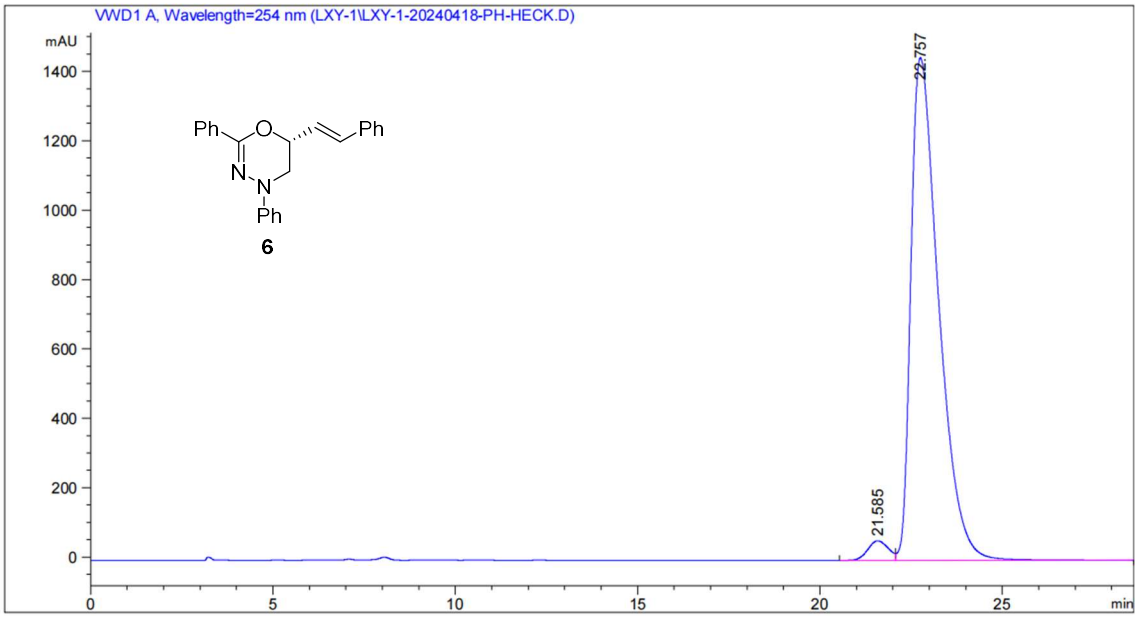
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	12.109	4775.67432	187.33482	49.9847
2	PDA 254 nm	13.750	4778.60547	171.94154	50.0153



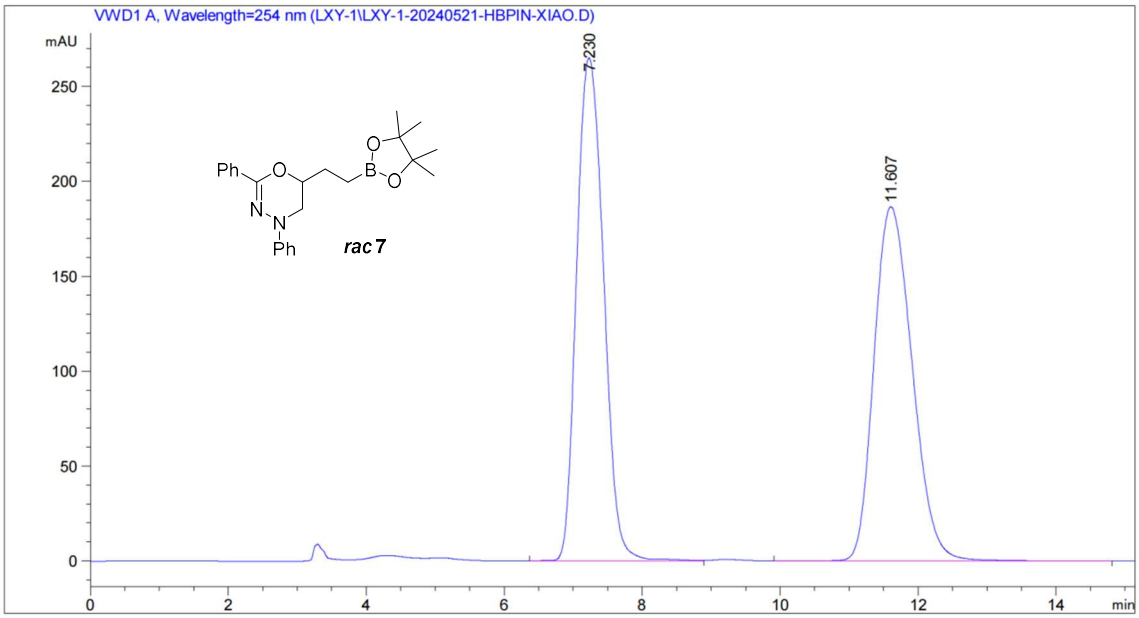
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	12.157	374.43576	14.11616	2.8444
2	PDA 254 nm	13.833	1.27894e4	457.64883	97.1556



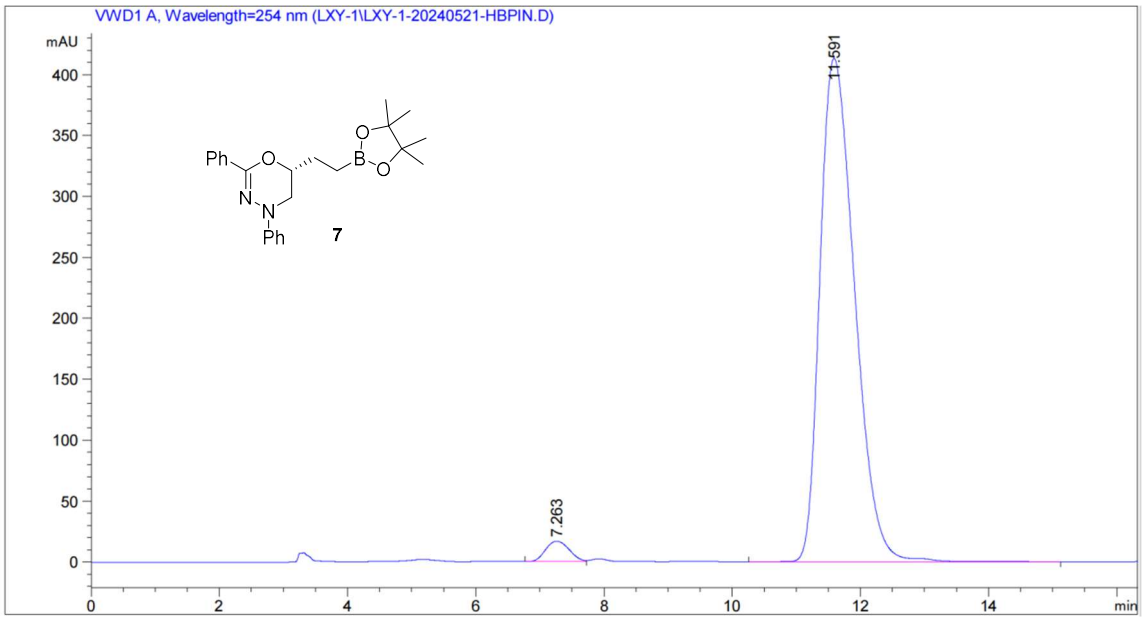
Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	21.184	3.05890e4	691.50647	49.0853
2	PDA 254 nm	22.813	3.17290e4	613.99219	50.9147



Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	21.585	2188.78540	56.39798	2.7776
2	PDA 254 nm	22.757	7.66125e4	1448.94678	97.2224



Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.230	7192.04590	264.79297	50.1011
2	PDA 254 nm	11.607	7163.01318	186.49080	49.8989



Peak	Processed channel	Retention time (min)	Peak area (m AU*s)	Peak height (m AU)	Peak area (%)
1	PDA 254 nm	7.263	429.49326	16.72911	2.6992
2	PDA 254 nm	11.591	1.54823e4	413.18597	97.3008