Supporting Information

Rhodium-Catalyzed Tandem Asymmetric Allylic Decarboxylative Addition and Cyclization of Vinylethylene Carbonates with N-Nosylimines

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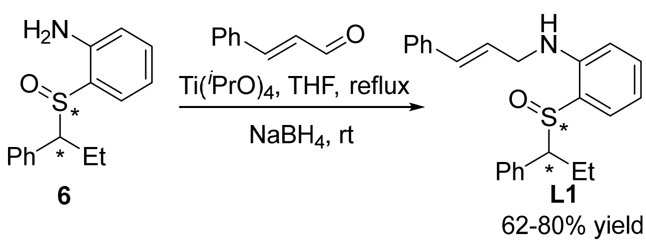
1. General

All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

^1H NMR spectra were obtained at 400 MHz or 600 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent (7.26 ppm for $CDCl_3$, 1.94 ppm for CD_3CN). ^{13}C NMR spectra were obtained at 101 MHz or 151 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.16 ppm, CD_3CN, 1.32 ppm). Data for NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Infrared spectra were recorded on Nicolet FT-IR spectrometers. The accurate masses were measured by ESI-TOF using QTOF Ultima, G2-xs TOF from Waters, and microflex LRF MALDI-TOF. Optical rotations αD were obtained with AUTOPOL VI from rudolph-research-analytical. HPLC using chiral stationary phase columns by comparing the samples with the appropriate racemic samples, column and elution details specified in each entry.

2. Preparation of Ligand L1-L5

1) Procedure for the synthesis of chiral ligands **L1**

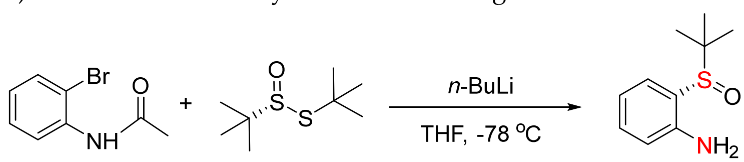


An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with **6**[1] (0.5 mmol), α, β-unsaturated aldehyde (0.6 mmol, 1.2 equiv.), Ti(iPrO)$_4$ (1.0 mmol, 2.0 equiv.) and anhydrous tetrahydrofuran (5.0 mL) under argon atmosphere. The solution was refluxed in an oil bath for 2h and successively cooled down to room temperature. Then $NaBH_4$ (2.0 mmol, 4.0 equiv.) was added into the mixture. After stirring for 2h, the reaction was quenched with MeOH and H_2O. The organic layer was extracted by ethyl acetate, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (PE/EA = 10/1) to provide **L1** in 75% yield (140.7 mg).

***N*-Cinnamyl-2-((*S*)-((*S*)-1-phenylpropyl)sulfinyl)aniline** (**L1**): White solid; m.p. 105.0 – 105.6 °C; 75% yield (140.7 mg); 99% *ee*. **$[\alpha]_D^{20}$** = -97.7° (c 1.0, $CHCl_3$). **HPLC**: [Daicel

CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.2 mL/min; detection wavelength = 214 nm; t_R = 11.286 (major), 21.328(minor) min]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 5H), 7.26 – 7.21 (m, 2H), 7.18 – 7.12 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.66 – 6.57 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.30 (s, 1H), 6.15 (dt, *J* = 15.8, 5.4 Hz, 1H), 4.10 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.79 – 3.66 (m, 2H), 2.09 – 1.95 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 136.9, 133.9, 132.5, 131.2, 129.7, 128.6, 128.4, 128.3, 127.8, 127.6, 126.5, 126.4, 119.7, 115.6, 111.9, 69.6, 45.2, 22.5, 11.9. **IR** (KBr): ν_{max} (cm^{-1}) = 3260, 3062, 3006, 2992, 2969, 2882, 1590, 1489, 1293, 1120, 1045, 745, 650. **HRMS** (ESI+) calcd for $C_{24}H_{25}NNaOS$ $[M+Na]^+$: 398.1549, Found: 398.1554.

2) Procedure for the synthesis of chiral ligands **L2**[2]



L2

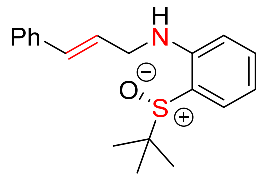
A stirred solution of 2'-bromoacetanilide (428mg, 2 mmol, 1 equiv.) in 3 mL of anhydrous THF was cooled to −78 °C. To this solution was added *n*-BuLi (2.8 mL, 2.2 mmol, 1.55 M in hexane, 2.2 equiv.) dropwise while maintaining the temperature below −70 °C. The resulting yellow mixture was stirred at −78 °C during 2 h, before slow addition of a solution of 2-{[(*R*)-tert-butylsulfinyl]sulfanyl}-2-methylpropane (426 mg, 1.1 mmol, 1.1 equiv.) in 1 mL of anhydrous THF. The resulting strong yellow mixture was further stirred 1h at −78 °C. MeOH (few drops) was added. The mixture was allowed to warm to 0 °C and sat. NH_4Cl saturated solution (3 mL) was added. The mixture was extracted with diethyl ether (5 mL), washed with brine (3 mL), dried (Na_2SO_4), filtered off and evaporated under reduced pressure. The crude material was dissolved in 3 mL of EtOH. KOH (solution in water) (560 mg, 5 mmol, 5 equiv.) was added and the mixture was stirred in a sealed vial overnight at 85 °C. The orange solution was cooled to room temperature and ethanol was evaporated under reduced pressure. Diethyl ether (5 mL) and water (5 mL) were added. The organic layer was extracted, washed with brine (5 mL), dried (Na_2SO_4), filtered off and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel with Petroleum/EtOAc (10/1) to afford **L2** (224 mg, 59 % yield).

(*S*)-2-(tert-Butylsulfinyl) aniline (**L2**):

Yellow solid; 59% yield; *ee*: 99%. **$[\alpha]_D^{20}$** = +58.9 (c 1.0, $CHCl_3$). **HPLC:** [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 11.39 (major), 13.28 (minor) min]. **^{1}H NMR (600 MHz,** $CDCl_3$**)** δ 7.19 (t, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 5.15 (s, 2H), 1.29 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$**)** δ 149.4, 131.8, 128.9, 117.8, 117.6, 116.4, 58.8, 23.5. **IR** (KBr): ν_{max} (cm^{-1}) = 3411, 3143, 3005, 2986, 1642, 1614, 1401, 1281, 1263, 767, 752. **HRMS** (ESI^+) calcd for $C_{10}H_{15}NNaOS$ $[M+Na]^+$: 220.0767, Found: 220.0772.

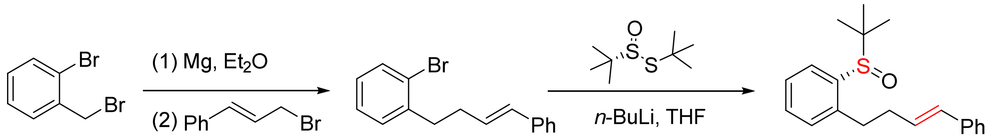
3) Procedure for the synthesis of chiral ligands **L3**

L3 was similarly prepared from the general procedure for preparing **L1**.



(*S*)-2-(tert-Butylsulfinyl)-*N*-cinnamylaniline (**L3**): Pale yellow wax; 36% yield (22.5 mg); *ee*: 97%. **[α]**$_D^{20}$ = -28.8 (c 1.0, $CHCl_3$). **HPLC:** [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 11.42 (minor), 13.94 (major) min]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.29 – 7.21 (m, 2H), 7.18 – 7.11 (m, 1H), 7.08 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.71 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.69 – 6.58 (m, 2H), 6.33 – 6.23 (m, 1H), 3.95 (t, *J* = 5.4 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 136.8, 132.3, 131.2, 129.1, 128.5, 127.4, 126.5, 126.3, 116.6, 114.9, 112.1, 58.8, 45.2, 23.7. **IR** (KBr): ν_{max} (cm^{-1}) = 3410, 3122, 3001, 2917, 1634, 1621, 1411, 1271, 1253, 759, 747. **HRMS** (ESI^+) calcd for $C_{19}H_{23}NNaOS$ $[M+Na]^+$: 336.1393, Found: 336.1380.

4) Procedure for the synthesis of chiral ligands **L4**[3]



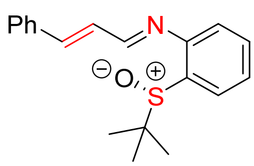
In a three necked flask equipped with a condenser and a dropping funnel are introduced: magnesium (0.389 g; 15.8 mmol), Et_2O (12 mL) and one crystal of I_2. From the dropping funnel was added slowly (a small part and when the reaction started all the solution) 2-bromobenzyl bromide (2.988 g; 11.7 mmol) dissolved in Et_2O (12 mL). The mixture was refluxed for 1h 15 min. Under nitrogen, the Grignard reagent was transferred with a canula to a solution of cinnamyl bromide (2.400 g; 11.8 mmol) in THF (12 mL). After refluxing 2 h 45 min, the reaction mixture was hydrolyzed (HCl 10%), and extracted with Et_2O. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated. The crude residue was purified by flash column chromatography (hexane) to provide (*E*)-1-bromo-2-(4-phenylbut-3-en-1-yl) benzene. The (*E*)-1-bromo-2-(4-phenylbut-3-en-1-yl) benzene (1.1 mmol) is then dissolved in anhydrous tetrahydrofuran (1.5 mL) and the reaction mixture is placed in a low-temperature stirring reactor and cooled to -78 °C. Then, n-butyllithium (2.2 mmol, 1.55 M in hexane) was slowly added to the reaction mixture, and after stirring for 30 minutes, (*R*) -*tert*-butylsulfothiobutyl (1 mmol) dissolved I n 1mL anhydrous tetrahydrofuran was slowly added to the reaction mixture. Continue stirring at -78 °C for 1h. After the reaction, the temperature was slowly raised to 0 °C, the saturated ammonium chloride solution was added, the aqueous phase was extracted by ethyl acetate, the saturated sodium chloride aqueous solution was washed, the organic phase was separated, the anhydrous sodium sulfate was dried, the concentration was reduced pressure, and the crude product was purified by silica gel column chromatography (pure petroleum ether) to obtain compounds **L4** (84.2 mg, 27 %).

(*S*)-1-(tert-Butylsulfinyl)-2-(4-phenylbut-3-en-1-yl) benzene (**L4**): Chromatography (PE/EA = 20/1). Color-free wax; 30% yield (18.7 mg); *ee*: 96%. **[α]**$_D^{20}$ = +118.2 (c 1.0, $CHCl_3$). **HPLC**: [Daicel CHIRALPAK AD-H (0.46 cm × 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 8.64 (minor), 10.98 (major) min]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.89 – 7.82 (m, 1H), 7.43 – 7.39 (m, 2H), 7.39 – 7.35 (m, 2H), 7.35 – 7.31 (m, 3H), 7.28 – 7.19 (m, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.26 – 6.19 (m, 1H), 3.15 – 3.08 (m, 1H), 2.76 – 2.69 (m, 1H), 2.66 – 2.59 (m, 1H), 2.57 – 2.47 (m, 1H), 1.24 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.2, 138.5, 137.3, 131.1, 131.0, 129.1, 128.9, 128.5, 127.1, 126.6, 126.5, 126.0, 57.5, 34.4, 32.4, 23.0. **IR** (KBr): ν_{max} (cm^{-1}) = 3428, 3131, 3010, 2911, 1633, 1612, 1422, 1268, 1249, 758, 746. **HRMS** (ESI^+) calcd for $C_{20}H_{25}OS$ $[M+H]^+$: 313.1621, Found: 313.1617.

5) Procedure for the synthesis of chiral ligands **L5**

L5 was prepared from the procedure for preparing **L3** without reduction step**.**

(*1E*, *2E*)-N-(2-((*R*)-tert-butylsulfinyl) phenyl)-3-phenylprop-2-en-1-imine (L5)

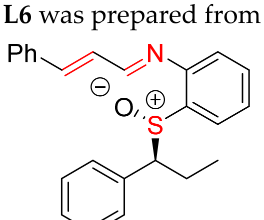


L5

Yellow solid; 87% yield (54.1 mg); **HPLC** *ee*: 99% [Daicel CHIRALCEL OD-H (0.46 cm × 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 15.58 (minor), 22.29 (major) min]. **[α]**$_D^{20}$ = -31.1 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1H), 7.94 (dd, J = 7.8, 1.6 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.50 (td, J = 7.6, 1.6 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.23 – 7.14 (m, 2H), 7.06 (dd, J = 7.8, 1.2 Hz, 1H), 1.20 (s, 9H). ^{13}C **NMR** (151 MHz, $CDCl_3$) δ 162.6, 150.3, 145.4, 135.3, 135.2, 131.8, 130.0, 128.9, 128.1, 127.7, 127.0, 126.2, 117.4, 58.3, 23.4. **IR** (KBr): ν_{max} (cm^{-1}) = 3543, 3111, 3012, 2912, 1643, 1611, 1421, 1235, 1224, 752, 741. **HRMS** (ESI^+) calcd for $C_{19}H_{21}NNaOS$ $[M+Na]^+$: 334.1236, Found: 334.1238.

6) Procedure for the synthesis of chiral ligands **L6**

L6 was prepared from the procedure for preparing **L1** without reduction step**.**

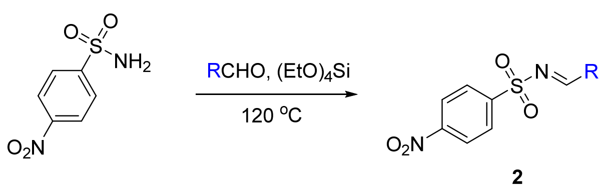


L6

(2*E*)-3-Phenyl-N-(2-((*R*)-((*R*)-1-phenylpropyl) sulfinyl) phenyl) prop-2-en-1-imine (**L6**): Yellow wax; 47% yield (35.1 mg); **[α]**$_D^{20}$ = +0.19 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz,

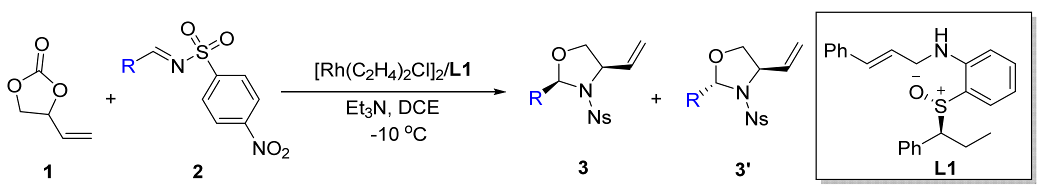
$CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.30 (td, *J* = 7.5, 1.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 (dd, *J* = 15.6, 8.4 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.04 – 6.96 (m, 3H), 6.80 (d, *J* = 7.2 Hz, 2H), 4.06 (t, *J* = 7.8 Hz, 1H), 2.46 (dt, *J* = 14.4, 7.3 Hz, 1H), 2.24 – 2.13 (m, 1H), 1.15 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.8, 147.2, 145.6, 136.7, 135.2, 133.4, 130.9, 130.1, 129.0, 128.9, 128.1, 127.7, 127.5, 127.3, 126.3, 125.6, 116.2, 67.5, 23.3, 12.3. **IR** (KBr): ν_{max} (cm^{-1}) = 747, 757, 1226, 1233, 1471 1615, 1698, 2915, 3113, 3233, 3578. **HRMS** (ESI^+) calcd for $C_{24}H_{23}NNaOS$ $[M+Na]^+$: 396.1393, Found: 396.1384.

3. General procedures for the synthesis of N-nosylimine 2[4]



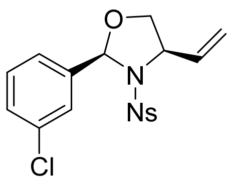
Amixture of 4-nitrobezenesulfonamide (5 mmol), aldehyde (5.5 mmol) and tetraethyl orthosilicate (5.5 mmol) was heated in flask equipped with Dean-Star at 120 ºC for 12h. After cooling at room temperature, the product was crystallized in EtOAc/heptane mixture. The crystals were collected by filtration, washed with pentane and dried under vacuum.

4. General procedure for the synthesis of 3



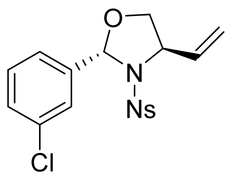
In a screw-cap Schlenk tube filled with argon, $[Rh(C_2H_4)_2Cl]_2$ (0.004 mmol, 2 mol%), Sulfoxide ligand **L1** (0.008 mmol, 4 mol%), N-nosylimine **2** (0.20 mmol) were added. After that, 4-Vinyl-1,3-dioxolan-2-one **1** (0.40 mmol) and 1,2-Dichloroethane (DCE) (2.0 mL) were added. Finally, add Triethylamine (0.3 mmol). After 24 h stirring at -10 °C, the reaction mixture was filtered over silica (CH_2Cl_2) and concentrated under reduced pressure to afford the crude product. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **3**.

(2*R*,4*R*)-2-(3-chlorophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3g)



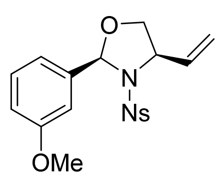
White solid; **m.p.**: 149 - 150 °C; 34% yield (26.7 mg); **HPLC** *ee*: 81% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =20.36 (major), 23.67 (minor) min]. **[α]$^{20}_D$** = + 29.1 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 6.18 (s, 1H), 5.77 – 5.68 (m, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 1H), 4.08 (dd, *J* = 9.1, 7.1 Hz, 1H), 3.78 (dd, *J* = 9.1, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 144.3, 139.0, 135.1, 134.7, 130.0, 129.6, 129.0, 127.5, 125.7, 124.3, 119.6, 91.6, 71.2, 62.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3104, 3061, 2960, 2922, 2871, 2299, 1759, 1600, 1532, 1351, 1266, 1174, 1120, 850, 755, 692, 631, 574. **HRMS** (ESI^+) calcd for $C_{17}H_{15}ClN_2NaO_5S$ $[M+Na]^+$: 417.0282, Found: 417.0294.

(2*S*,4*R*)-2-(3-chlorophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3g′)



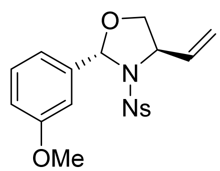
White solid; **m.p.**: 149 - 150 °C; 25% yield (19.7 mg); **HPLC** *ee*: 70% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =17.26 (major), 25.36 (minor) min]. **[α]$^{20}_D$** = - 10.9 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.14 – 7.10 (m, 1H), 6.14 (s, 1H), 5.92 (ddd, *J* = 17.0, 10.1, 8.6 Hz, 1H), 5.46 (d, *J* = 17.0 Hz, 1H), 5.35 (d, *J* = 10.1 Hz, 1H), 4.48 (dt, *J* = 8.6, 5.6 Hz, 1H), 4.30 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.88 (dd, *J* = 8.8, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 146.0, 138.7, 134.5, 134.1, 129.8, 129.7, 128.4, 128.0, 126.7, 123.9, 119.6, 91.5, 71.8, 62.7. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3113, 3067, 2961, 2928, 2873, 2300, 1763, 1607, 1531, 1355, 1268, 1177, 1121, 858, 759, 691, 638, 579. **HRMS** (ESI^+) calcd for $C_{17}H_{15}ClN_2NaO_5S$ $[M+Na]^+$: 417.0282, Found: 417.0294.

(2*R*,4*R*)-2-(3-methoxyphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3h)



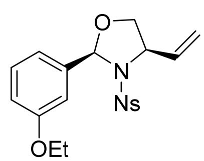
Pale yellow solid; **m.p.**: 108 - 110 °C; 40% yield (31.2 mg); **HPLC** *ee*: 85% [Daicel CHIRALPAK IA-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =23.56 (major), 29.08 (minor) min]. **[α]$^{20}_D$** = + 77.2 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.68 (t, *J* = 2.1 Hz, 1H), 6.12 (s, 1H), 5.92 (ddd, *J* = 17.0, 10.1, 8.6 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.1 Hz, 1H), 4.45 (dt, *J* = 8.6, 5.7 Hz, 1H), 4.30 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.86 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 149.7, 146.1, 138.1, 134.5, 129.4, 128.4, 123.7, 120.7, 119.3, 114.8, 113.9, 92.2, 71.8, 62.6, 55.3. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3109, 3066, 2972, 2916, 2855, 2271, 1739, 1626, 1531, 1327, 1244, 1176, 871, 786, 698, 643. **HRMS** (ESI^+) calcd for $C_{18}H_{18}N_2NaO_6S$ $[M+Na]^+$: 413.0778, Found: 413.0782.

(2*S*,4*R*)-2-(3-methoxyphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3h′)



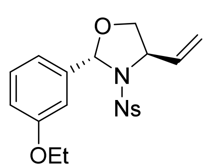
Pale yellow solid; **m.p.**: 108 - 110 °C; 21% yield (16.3 mg); **HPLC** *ee*: 57% [Daicel CHIRALPAK IA-H (0.46 cm × 25cm); n-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =23.43 (major), 26.60 (minor) min]. **$[\alpha]^{20}_D$** = - 26.5 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.12 (s, 1H), 5.92 (dt, *J* = 17.4, 9.3 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.32 (d, *J* = 10.1 Hz, 1H), 4.45 (dt, *J* = 8.6, 5.8 Hz, 1H), 4.30 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.86 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.71 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 149.7, 146.0, 138.0, 134.4, 129.4, 128.4, 123.7, 120.7, 119.3, 114.8, 113.8, 92.2, 71.8, 62.6, 55.3. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3103, 3059, 2962, 2909, 2851, 2274, 1733, 1624, 1537, 1322, 1241, 1175, 866, 781, 671, 649. **HRMS** (ESI$^+$) calcd for $C_{18}H_{18}N_2NaO_6S$ $[M+Na]^+$: 413.0778, Found: 413.0782.

(2*R*,4*R*)-2-(3-ethoxyphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3i)



Yellow solid; **m.p.**: 100 - 102 °C; 32% yield (25.8 mg); **HPLC** *ee*: 73% [Daicel CHIRALPAK IC-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =48.18 (major), 51.53 (minor) min]. **$[\alpha]^{20}_D$** = + 15.9 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.17 (s, 1H), 5.80 – 5.73 (m, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.51 – 4.46 (m, 1H), 4.09 (dd, *J* = 9.1, 7.0 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.81 (dd, *J* = 9.1, 5.2 Hz, 1H), 1.39 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.1, 150.1, 144.6, 138.1, 135.4, 129.7, 128.9, 124.1, 119.6, 119.3, 115.4, 113.5, 92.3, 71.1, 63.6, 62.0, 14.8. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3058, 2960, 2928, 2869, 2307, 1771, 1603, 1539, 1353, 1268, 1174, 857, 756, 703, 620. **HRMS** (ESI$^+$) calcd for $C_{19}H_{20}N_2NaO_6S$ $[M+Na]^+$: 427.0934, Found: 427.0928.

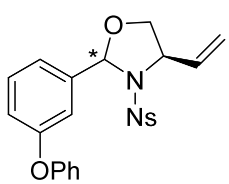
(2*S*,4*R*)-2-(3-ethoxyphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3i′)



Yellow solid; **m.p.**: 100 - 102 °C; 26% yield (21.0 mg); **HPLC** *ee*: 81% [Daicel CHIRALPAK IC-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =63.56 (minor), 70.99 (major) min]. **$[\alpha]^{20}_D$** = - 9.2 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.93 – 6.83 (m, 2H), 6.66 (t, *J* = 2.1 Hz, 1H), 6.12 (s, 1H), 5.96 (ddd, *J* = 17.1, 10.1, 8.5 Hz, 1H), 5.45 (d, *J* = 17.0 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 4.47 (dt, *J* = 8.5, 5.7 Hz, 1H), 4.32 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.91 – 3.83 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 149.7, 146.1, 137.9, 134.5, 129.4, 128.4, 123.7, 120.6, 119.2, 115.3, 114.4, 92.2, 71.8, 63.6, 62.7, 14.8. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3055, 2962, 2930, 2869, 2307, 1773, 1601, 1537, 1352, 1269, 1177, 860, 755, 701, 621. **HRMS** (ESI$^+$) calcd for $C_{19}H_{20}N_2NaO_6S$ $[M+Na]^+$: 427.0934, Found: 427.0928.

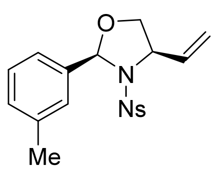
(2,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(3-phenoxyphenyl)-4-vinyloxazolidine (3j/3j′)

(*: representative signals for the minor diastereoisomer)



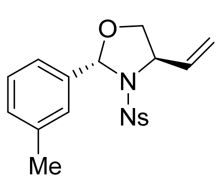
White solid; **m.p.**: 118 - 120 °C; 54% yield (48.7 mg); **HPLC** *ee*: 70% /77% [Daicel CHIRALCEL OD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =42.89 (major), 56.432 (minor) min, t_R =48.41 (major), 67.63 (minor) min,]. $[\alpha]^{20}_D$ = + 75.8 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.9 Hz, 2H), 8.17* (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.59* (d, *J* = 8.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.15 – 7.10 (m, 2H), 7.08 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.03 (t, *J* = 2.1 Hz, 1H), 6.98 (dd, *J* = 2.5, 1.1 Hz, 1H), 6.97 – 6.92 (m, 4H), 6.86 (t, *J* = 2.0 Hz, 1H), 6.20 (s, 1H), 6.13 * (s, 1H), 5.88* (ddd, *J* = 17.1, 10.1, 8.6 Hz, 1H), 5.68 (ddd, *J* = 17.1, 10.2, 7.8 Hz, 1H), 5.45 – 5.35 * (m, 1H), 5.31 (s, 1H), 5.28* (d, *J* = 6.5 Hz, 1H), 5.19 (dt, *J* = 10.1, 1.0 Hz, 1H), 4.51 – 4.44 (m, 1H), 4.44 – 4.39 * (m, 1H), 4.27* (dd, *J* = 8.8, 6.0 Hz, 1H), 4.07 (dd, *J* = 9.1, 7.0 Hz, 1H), 3.84* (dd, *J* = 8.8, 5.1 Hz, 1H), 3.78 (dd, *J* = 9.1, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 157.4*, 156.7, 156.57* , 150.3, 149.8*, 146.1*, 144.6, 138.9, 138.8*, 135.1, 134.3*, 130.0, 129.9, 129.7, 128.9, 128.5*, 124.2, 123.8, 123.8, 122.9*, 122.3, 119.6*, 119.5, 119.3, 119.2, 119.1*, 118.1*, 117.4, 92.0, 91.9*, 71.7*, 71.1, 62.6*, 61.9. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3107, 3055, 2985, 2927, 2830, 2281, 1726, 1616, 1522, 1344, 1267, 1182, 878, 789, 690, 621. **HRMS** (ESI$^+$) calcd for $C_{23}H_{20}N_2NaO_6S$ $[M+Na]^+$: 475.0934, Found: 475.0927.

(2*R*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(m-tolyl)-4-vinyloxazolidine (3k)



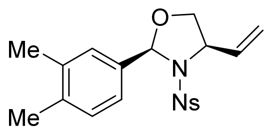
Pale yellow solid; **m.p.**: 105 - 107 °C; 44% yield (32.8 mg); **HPLC** *ee*: 73% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =15.36 (major), 18.38 (minor) min]. $[\alpha]^{20}_D$ = +31.2 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.16 (d, *J* = 6.6 Hz, 1H), 6.16 (s, 1H), 5.82 – 5.74 (m, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.54 – 4.46 (m, 1H), 4.09 (dd, *J* = 9.1, 7.0 Hz, 1H), 3.82 (dd, *J* = 9.2, 4.9 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 144.8, 138.3, 136.5, 135.5, 130.2, 128.9, 128.5, 128.1, 124.7, 124.1, 119.2, 92.6, 71.2, 62.0, 21.4. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3109, 3058, 2981, 2923, 2830, 2289, 1724, 1613, 1516, 1342, 1261, 1177, 880, 781, 686, 621. **HRMS** (ESI$^+$) calcd for $C_{18}H_{18}N_2NaO_5S$ $[M+Na]^+$: 397.0829, Found: 397.0842.

(2*S*,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(m-tolyl)-4-vinyloxazolidine (3k')



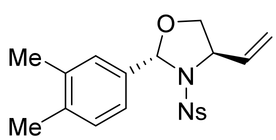
Pale yellow solid; **m.p.**: 105 - 107 °C; 23% yield (17.2 mg); **HPLC** *ee*: 65% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =14.15 (major), 19.33 (minor) min]. $[\alpha]^{20}_D$ = - 16.1 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 6.8 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.96 (s, 1H), 6.11 (s, 1H), 5.97 – 5.90 (m, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.32 (d, *J* = 10.1 Hz, 1H), 4.45 (dt, *J* = 8.7, 5.8 Hz, 1H), 4.30 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.86 (dd, *J* = 8.8, 5.5 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 146.1, 138.1, 136.5, 134.5, 130.5, 128.6, 128.5, 128.3, 125.6, 123.6, 119.2, 92.5, 71.8, 62.7, 21.3. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3109, 3058, 2981, 2923, 2830, 2289, 1724, 1613, 1516, 1342, 1261, 1177, 880, 781, 686, 621. **HRMS** (ESI+) calcd for $C_{18}H_{18}N_2NaO_5S$ $[M+Na]^+$: 397.0829, Found: 397.0842.

(2*R*,4*R*)-2-(3,4-dimethylphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3l)



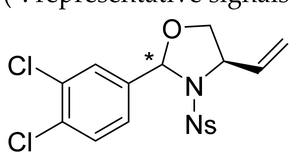
White solid; **m.p.**: 110 - 113 °C; 34% yield (26.3 mg); **HPLC** *ee*: 87% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =39.19 (major), 54.61 (minor) min]. $[\alpha]^{20}_D$ = +32.9 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.12 (s, 1H), 5.79 (ddd, *J* = 17.7, 10.1, 8.1 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.49 (q, *J* = 7.3 Hz, 1H), 4.08 (dd, *J* = 8.9, 7.1 Hz, 1H), 3.82 (dd, *J* = 9.1, 4.8 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.0, 144.8, 138.2, 136.9, 135.5, 133.8, 129.7, 128.9, 128.6, 125.1, 124.0, 119.3, 92.5, 71.1, 61.9, 19.9, 19.7. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3110, 3059, 2979, 2928, 2830, 2280, 1725, 1613, 1517, 1341, 1269, 1181, 873, 788, 682, 675, 620. **HRMS** (ESI+) calcd for $C_{19}H_{20}N_2NaO_5S$ $[M+Na]^+$: 411.0985, Found: 411.09931.

(2*S*,4*R*)-2-(3,4-dimethylphenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3l′)



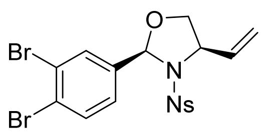
White solid; **m.p.**: 110 - 113 °C; 21% yield (16.2 mg); **HPLC** *ee*: 81% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =44.27 (minor), 45.44 (major) min]. $[\alpha]^{20}_D$ = - 88.6 (c 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 2H), 6.87 (s, 1H), 6.07 (s, 1H), 5.94 (dt, *J* = 17.5, 9.4 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.1 Hz, 1H), 4.49 – 4.45 (m, 1H), 4.33 – 4.28 (m, 1H), 3.85 (dd, *J* = 8.6, 5.6 Hz, 1H), 2.24 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.5, 146.1, 138.5, 136.6, 134.6, 133.9, 129.4, 129.0, 128.5, 126.0, 123.5, 119.1, 92.3, 71.7, 62.7, 19.7, 19.7. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3112, 3058, 2980, 2928, 2831, 2284, 1722, 1617, 1520, 1340, 1266, 1180, 872, 789, 684, 677, 622. **HRMS** (ESI+) calcd for $C_{19}H_{20}N_2NaO_5S$ $[M+Na]^+$: 411.0985, Found: 411.09931.

(2,4*R*)-2-(3,4-dichlorophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3m/3m′)
(*: representative signals for the minor diastereoisomer)



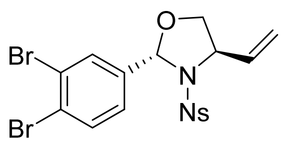
White solid; **m.p.**: 150 - 153 °C; 53% yield (45.3 mg); **HPLC** *ee*: 86%/70% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.3 mL/min; detection wavelength = 214 nm; t_R =38.50 (major), 48.60 (minor) min, t_R =41.85 (major), 50.46 (minor) min]. $[\alpha]^{20}_D$ = + 4.8 (c 1.0, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.7 Hz, 2H), 8.22* (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.64* (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.41* (d, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.17 (s, 1H), 6.10* (s, 1H), 5.85 – 5.78 * (m, 1H), 5.70 (ddd, *J* = 17.4, 10.2, 7.6 Hz, 1H), 5.44 * (d, *J* = 17.0 Hz, 1H), 5.36 – 5.30 (m, 2H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.50 – 4.44* (m, 1H), 4.38 (q, *J* = 6.9 Hz, 1H), 4.25* (dd, *J* = 8.9, 6.1 Hz, 1H), 4.05 (dd, *J* = 9.2, 7.1 Hz, 1H), 3.84* (dd, *J* = 9.0, 5.1 Hz, 1H), 3.73 (dd, *J* = 9.2, 5.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5, 150.0*, 145.9, 143.7*, 137.4, 137.0*, 134.7, 134.08* , 133.80 , 133.73* , 133.01 , 132.80*, 130.74 , 130.40* , 129.75* , 129.25 , 129.10* , 128.5, 127.6, 126.7*, 124.5, 124.0*, 120.0, 119.7*, 91.0, 90.8*, 71.6, 71.0*, 62.6, 62.0*. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3120, 3051, 2977, 2927, 2833, 2273, 1731, 1621, 1516, 1342, 1266, 1180, 876, 792, 690, 626. **HRMS** (ESI^+) calcd for $C_{17}H_{15}Cl_2N_2O_5S$ $[M+H]^+$: 429.0073, Found: 429.0081.

(2*R*,4*R*)-2-(3,4-dibromophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3n)



White solid; **m.p.**: 127 - 129 °C; 34% yield (35.0 mg); **HPLC** *ee*: 81% [Daicel CHIRALPAK IG-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =28.22 (major), 34.21 (minor) min]. $[\alpha]^{20}_D$ = + 22.8 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.97 – 7.88 (m, 2H), 7.68 – 7.59 (m, 2H), 7.31 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.14 (s, 1H), 5.76 – 5.64 (m, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.40 (q, *J* = 6.8 Hz, 1H), 4.06 (dd, *J* = 9.2, 7.0 Hz, 1H), 3.74 (dd, *J* = 9.2, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 143.9, 138.1, 134.8, 133.9, 132.4, 129.0, 127.6, 126.1, 125.2, 124.5, 119.7, 91.0, 71.1, 62.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3125, 3063, 2981, 2933, 2828, 2271, 1737, 1629, 1513, 1345, 1275, 1181, 870, 793, 688, 616. **HRMS** (ESI^+) calcd for $C_{17}H_{15}Br_2N_2O_5S$ $[M+H]^+$: 516.9063, Found: 516.90651.

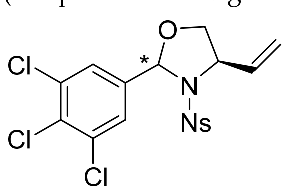
(2*R*,4*R*)-2-(3,4-dibromophenyl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3n′)



White solid; **m.p.**: 127 - 129 °C; 16% yield (16.4 mg); **HPLC** *ee*: 73% [Daicel CHIRALPAK IG-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R =31.97 (major), 39.71 (minor) min]. $[\alpha]^{20}_D$ = - 17.9 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.68 – 7.55 (m, 3H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.09 (s, 1H), 5.92 – 5.82 (m, 1H), 5.46 (d, *J* = 17.0 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 4.55 – 4.45 (m, 1H), 4.28 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.87 (dd, *J* = 8.9, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 145.9, 137.6, 133.9, 133.6, 132.9, 128.5, 128.4, 126.4, 125.0, 124.0, 119.9, 90.8, 71.7, 62.7. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3127, 3066, 2988, 2931, 2822, 2284, 1732, 1630, 1515, 1349, 1277, 1187, 875, 799, 681, 620. **HRMS** (ESI^+) calcd for $C_{17}H_{15}Br_2N_2O_5S$ $[M+Na]^+$: 516.9063, Found: 516.90651.

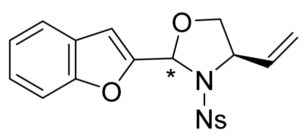
(2,4*R*)-3-((4-nitrophenyl)sulfonyl)-2-(3,4,5-trichlorophenyl)-4-vinyloxazolidine (3o/3o′)

(*: representative signals for the minor diastereoisomer)



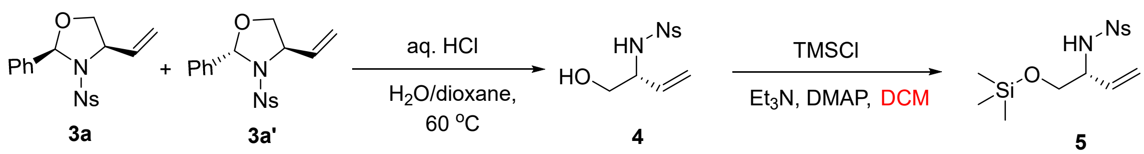
Pale yellow solid; **m.p.**: 133 - 135 °C; 51% yield (46.9 mg); **HPLC** *ee*: 85%/ 53% [Daicel CHIRALPAK IG-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =19.88 (major), 24.49 (minor) min, t_R =16.50 (minor), 20.95 (major) min]. $[\alpha]^{20}_D$ = +10.2 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 2H), 8.25* (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.71* (d, J = 8.5 Hz, 2H), 7.50 (s, 2H), 7.32* (s, 2H), 6.14 (s, 1H), 6.07* (s, 1H), 5.84 – 5.74 (m, 1H), 5.74 – 5.63* (m, 1H), 5.44 (d, J = 17.1 Hz, 1H), 5.34 (d, J = 11.1 Hz, 1H), 5.32 – 5.25* (m, 2H), 4.54 – 4.46 (m, 1H), 4.36* (q, J = 7.3 Hz, 1H), 4.24 (dd, J = 9.0, 6.0 Hz, 1H), 4.04* (dd, J = 9.2, 7.1 Hz, 1H), 3.84 (dd, J = 9.0, 4.9 Hz, 1H), 3.71* (dd, J = 9.2, 6.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.6, 150.1*, 145.9, 143.4*, 137.8, 137.3*, 134.7, 134.5*, 134.4, 133.5*, 132.8, 132.5*, 129.1, 128.6*, 128.0, 127.4*, 124.6, 124.0*, 120.3, 119.9*, 90.5, 90.3*, 71.7, 71.1*, 62.7, 62.0*. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3125, 3063, 2981, 2933, 2828, 2271, 1737, 1629, 1513, 1345, 1275, 1181, 870, 793, 688, 616. **HRMS** (ESI^+) calcd for $C_{17}H_{14}Cl_3N_2O_5S$ $[M+H]^+$: 462.9684, Found: 462.9671.

(2,4*R*)-2-(benzofuran-2-yl)-3-((4-nitrophenyl)sulfonyl)-4-vinyloxazolidine (3p/3p′)



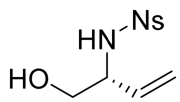
(*: representative signals for the minor diastereoisomer) White solid; **m.p.**: 134 - 137 °C; 68% yield (54.3 mg); **HPLC** *ee*: 11%/91% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =22.88 (minor), 25.91 (major) min, t_R =29.92 (major), 35.63 (minor) min]. $[\alpha]^{20}_D$ = +42.46 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.56 (dt, *J* = 7.5, 1.7 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.16 (m, 2H), 6.96* (d, *J* = 8.2 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.38 (s, 1H), 6.27 * (s, 1H), 6.11 – 6.01* (m, 1H), 5.90 (ddd, *J* = 17.1, 10.1, 8.3 Hz, 1H), 5.49* (d, *J* = 17.1 Hz, 1H), 5.46 – 5.34 (m, 2H), 5.31 (dd, *J* = 10.1, 0.9 Hz, 1H), 4.60 – 4.50 (m, 3H), 4.29 – 4.21 (m, 1H), 4.03 – 3.97 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.3, 154.5*, 151.7, 151.7*, 150.1, 149.5*, 144.5, 144.2*, 135.4, 134.6*, 128.9*, 128.2, 127.1*, 126.6, 125.8*, 125.6, 124.0*, 123.7, 123.5*, 123.4, 122.0, 121.8*, 120.2, 118.7*, 111.5, 111.1*, 108.8, 107.9*, 86.1, 85.2*, 73.1, 71.9*, 62.1, 61.8*. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3123, 3058, 2980, 2921, 2829, 2279, 1731, 1610, 1520, 1344, 1266, 1181, 876, 798, 690, 622. **HRMS** (ESI^+) calcd for $C_{19}H_{16}N_2NaO_6S$ $[M+Na]^+$: 423.0621, Found: 423.0614.

5. General procedure for the synthesis of 4 and 5



To a solution of (2, 4*R*)-3-((4-nitrophenyl)sulfonyl)-2-phenyl-4-vinyloxazolidine (**3a**/**3a′**) (36 mg, 0.1 mmol) in 1,4-dioxane/water (2:1, 1.5 mL) was added hydrochloric acid (20 μL of 6 N solution, 0.1 mmol) at room temperature. The reaction mixture was stirred at 60 ºC for 12 h. The mixture was then cooled, neutralized with aqueous sodium bicarbonate and extracted with ethyl acetate, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (eluent: petroleum ether / ethyl acetate = 2/1) on silica to afford the product **4** (22 mg, 81%) as a white solid.

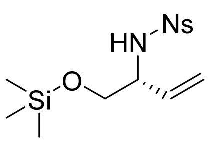
A round bottom flask equipped with a magnetic stir bar was charged with (*R*)-N-(1-hydroxybut-3-en-2-yl)-4-nitrobenzenesulfonamide **4** (27.2 mg, 0.1 mmol), and then CH_2Cl_2 (2 mL) was added via a glass syringe and followed by the addition of Et_3N (28 μL, 0.2 mmol), DMAP (5.0 mg) and chlorotrimethylsilane (14 μL, 0.11 mmol). The resulting reaction mixture was stirred for 12 h at room temperature. Then quenched with water (10.0 mL) and extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (eluent: petroleum ether / ethyl acetate = 5/1) as eluent to afford the pure product **5** in 76% yield as a yellow oil.



(*R*)-N-(1-hydroxybut-3-en-2-yl)-4-nitrobenzenesulfonamide (4)

White solid; **m.p.**: 102 - 104 °C; 81% yield (22.0 mg); **HPLC** *ee*: 95% [Daicel CHIRALCEL OJ-H (0.46 cm × 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =60.15 (minor), 62.01 (major) min]. **$[\alpha]^{20}_D$** = + 11.89 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, CD_3CN) δ 8.32 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 6.06 (d, *J* = 8.0 Hz, 1H), 5.61 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.10 – 4.94 (m, 2H), 3.91 – 3.80 (m, 1H), 3.46 – 3.35 (m, *J* = 5.7 Hz, 2H), 2.91 (t, *J* = 5.9 Hz, 1H) **^{13}C NMR** (151 MHz, CD_3CN) δ 151.0, 148.1, 136.0, 129.2, 125.1, 117.7, 65.0, 59.4. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3441, 3203, 3018, 2780, 2621, 2229, , 1730, 1601, 1511, 1321, 1209, 1129, 870, 766. **HRMS** (ESI^+) calcd for $C_{10}H_{12}N_2NaO_5S$ $[M+Na]^+$: 295.0359, Found: 295.03551.

(*R*)-4-nitro-N-(1-((trimethylsilyl)oxy)but-3-en-2-yl)benzenesulfonamide (5)



Yellow oil; 76% yield (26.0 mg); **HPLC** *ee*: 95% [Daicel CHIRALPAK AD-H (0.46 cm × 25cm); *n*-hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R =8.23 (minor), 9.81 (major) min]. **$[\alpha]^{20}_D$** = + 12.51 (c 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 2H), 8.05 (d, *J* = 8.7 Hz, 2H), 5.60 (ddd, *J* = 17.1, 10.1, 6.8 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.91 – 3.85 (m, 1H), 3.59 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.49 (dd, *J* = 10.1, 5.6 Hz, 1H), 0.06 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.1, 146.9, 134.7, 128.6, 124.2, 118.2, 64.8, 58.0. **IR** (CH_2Cl_2): ν_{max} (cm^{-1}) = 3113, 3057, 2983, 2920, 2810, 2226, 1730, 1609, 1511, 1320, 1268, 1181, 876, 790, 687. **HRMS** (ESI^+) calcd for $C_{13}H_{21}N_2O_5SSi$ $[M+H]^+$: 345.0935, Found: 345.0939.

6. X-ray crystallographic information of 3b

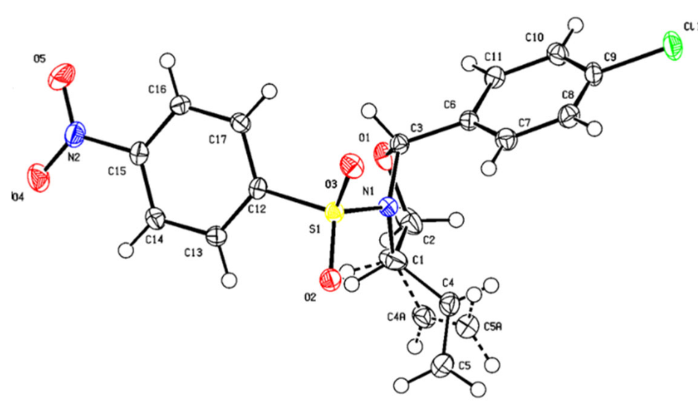
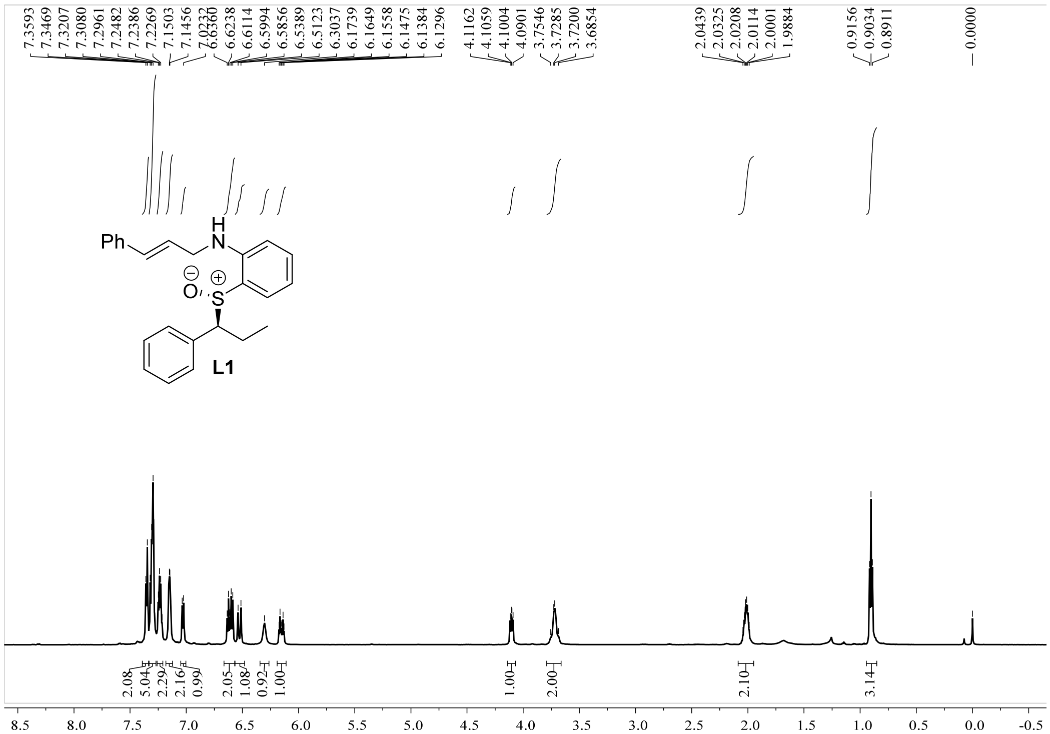


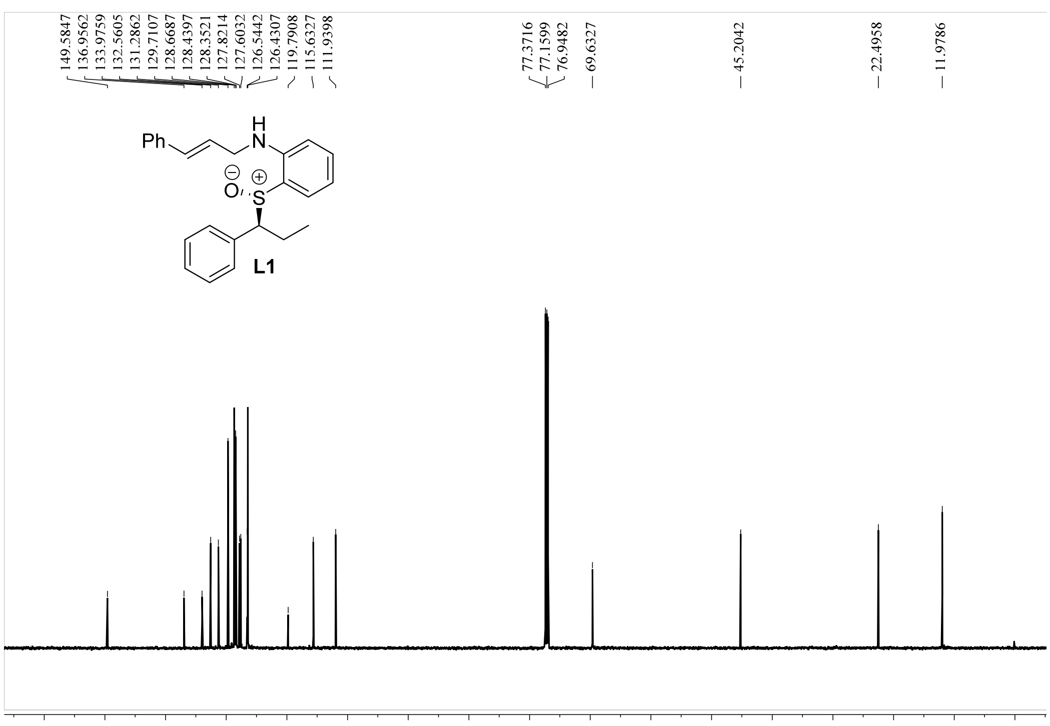
Table S1. Crystal data and structure refinement for compound 3b. (CCDC: 2265381)

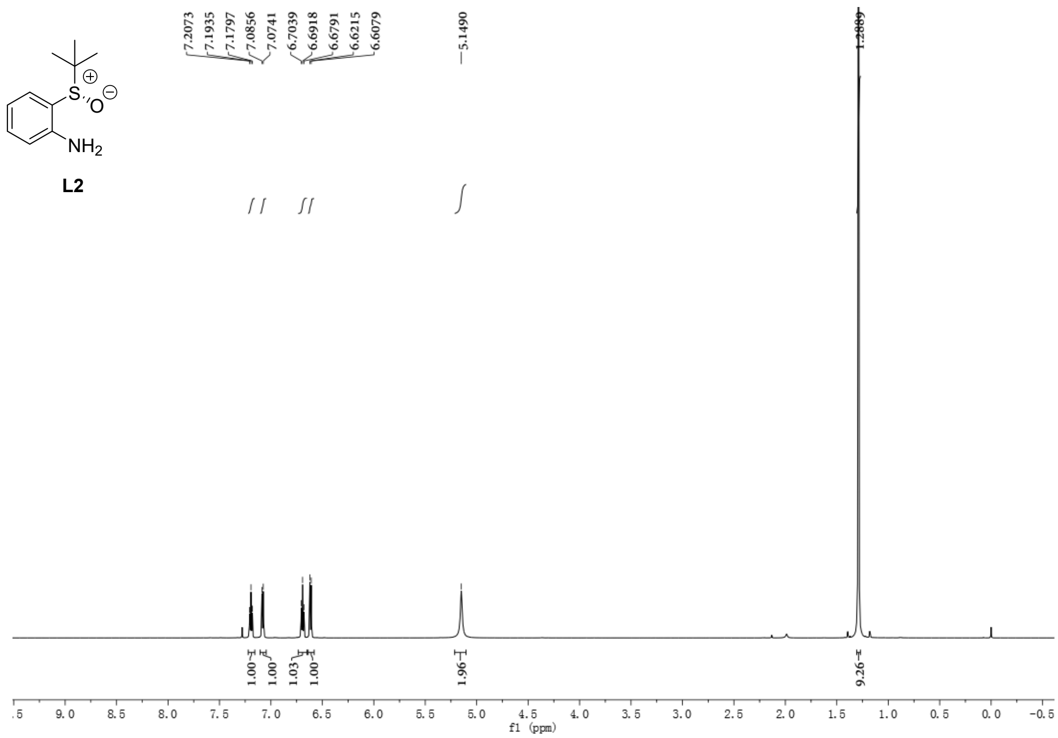
CCDC 2265381 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Empirical formula	$C_{17}H_{15}ClN_2O_5S$
Formula weight	394.82
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.3445(4)
b/Å	10.0239(4)
c/Å	23.4723(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1728.04(15)
Z	4
ρ_{calc}g/cm^3	1.518
μ/mm^{-1}	0.374
F(000)	816.0
Crystal size/mm^3	0.26 × 0.17 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.344 to 55.046
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 13$, $-30 \leq l \leq 30$
Reflections collected	34022
Independent reflections	3960 [R_{int} = 0.0631, R_{sigma} = 0.0330]
Data/restraints/parameters	3960/57/254
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0681
Final R indexes [all data]	R_1 = 0.0368, wR_2 = 0.0711
Largest diff. peak/hole / e Å^{-3}	0.31/-0.32
Flack parameter	-0.01(3)

7. Copies of NMR spectra of compounds L1-L6, 3 / 3′, 4 and 5






L2
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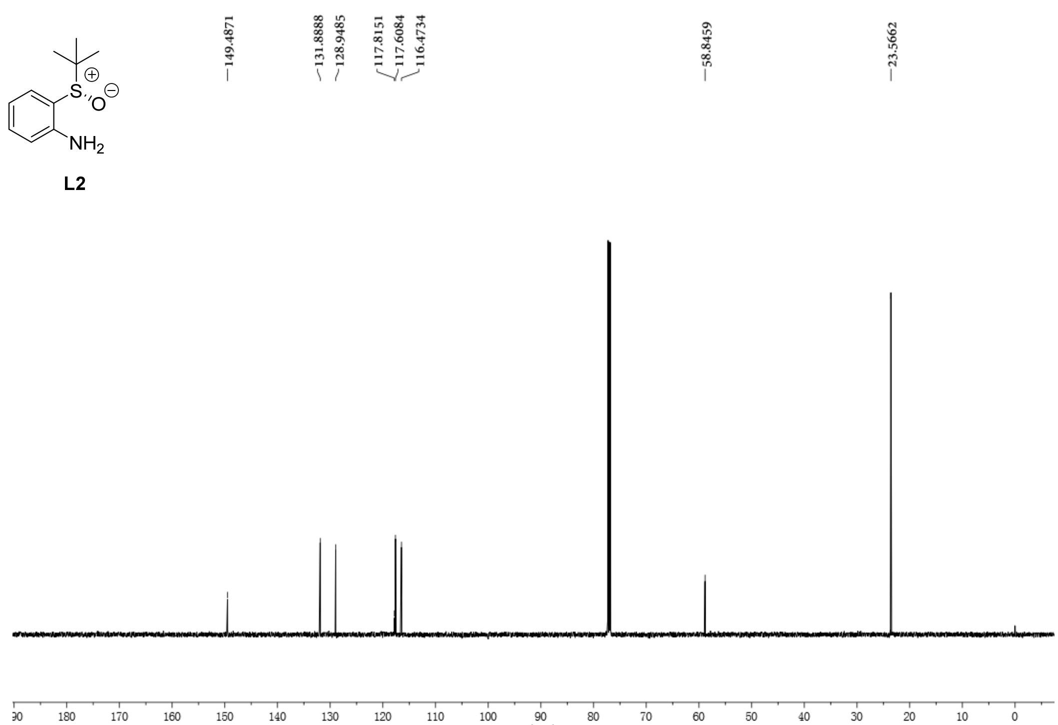
7.1797
7.0856
7.0741
6.7039
6.6918
6.6791
6.6215
6.6079
5.1490
1.2889
1.00
1.00
1.03
1.00
1.96
9.26
f1 (ppm)


L2
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128.9485
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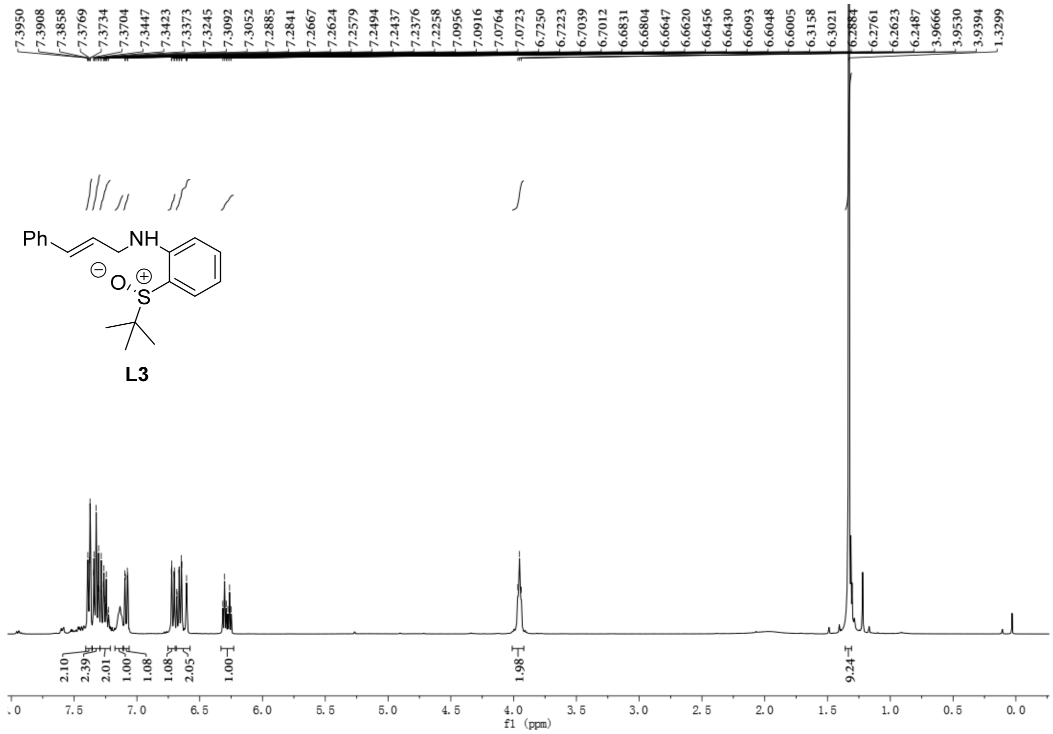
117.6084
116.4734
58.8459
23.5662
f1 (ppm)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7.3052
7.2885
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7.2624
7.2579
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6.6430
6.6093
6.6048
6.6005
6.3158
6.3021
6.2884
6.2761
6.2623
6.2487
3.9666
3.9530
3.9394
1.3299
Ph
NH
O
S
L3
2.10
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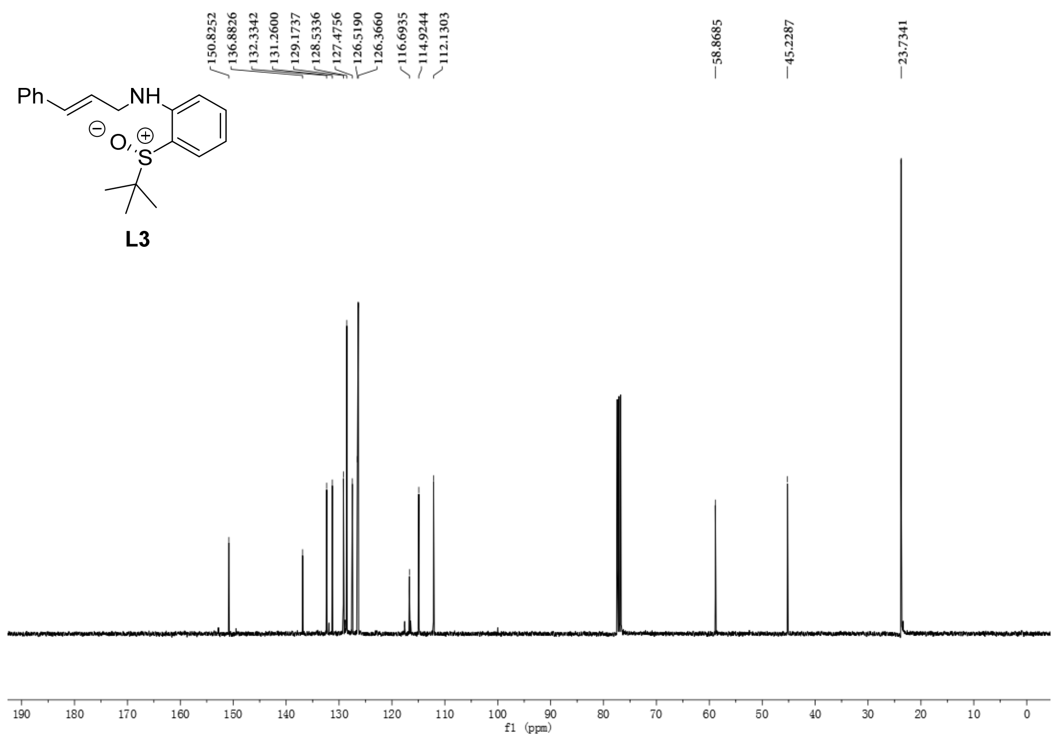
2.01
1.00
1.08
1.08
2.05
1.00
1.98
9.24
f1 (ppm)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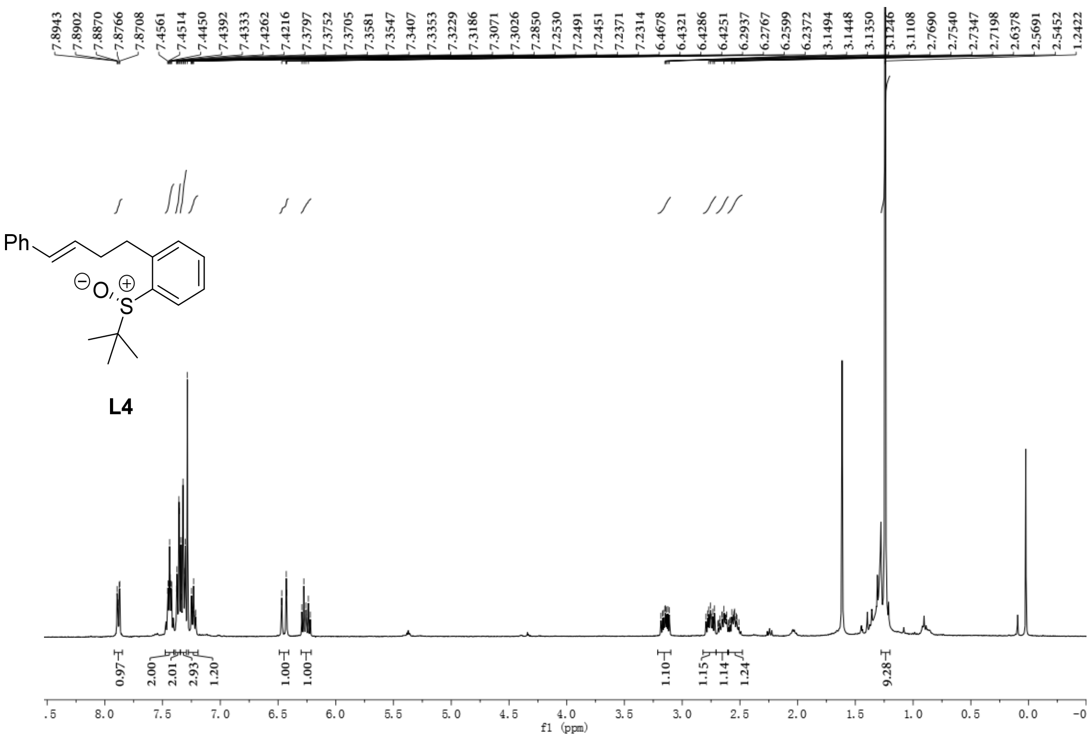
112.1303
58.8685
45.2287
23.7341
Ph
NH
O
S
L3
f1 (ppm)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7.4216
7.3797
7.3752
7.3705
7.3581
7.3547
7.3407
7.3353
7.3229
7.3186
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7.3026
7.2850
7.2530
7.2491
7.2451
7.2371
7.2314
6.4678
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2.6378
2.5691
2.5452
1.2422
Ph
O
S
L4
0.97
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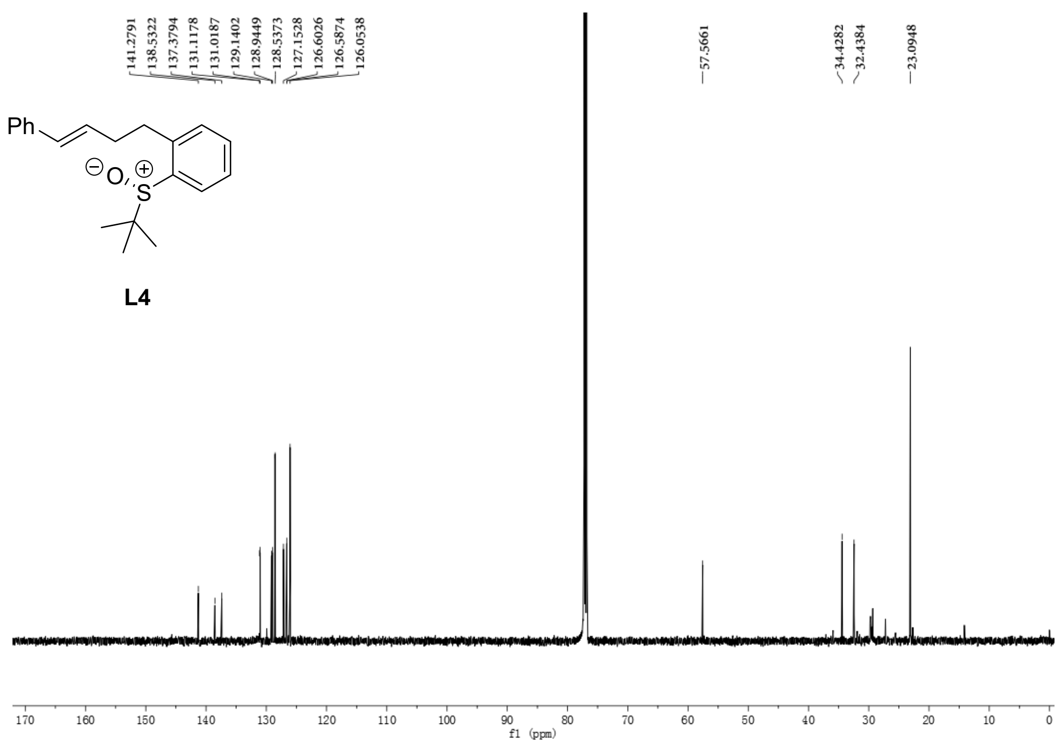
1.20
1.00
1.00
1.10
1.15
1.14
1.24
9.28
f1 (ppm)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57.5661
34.4282
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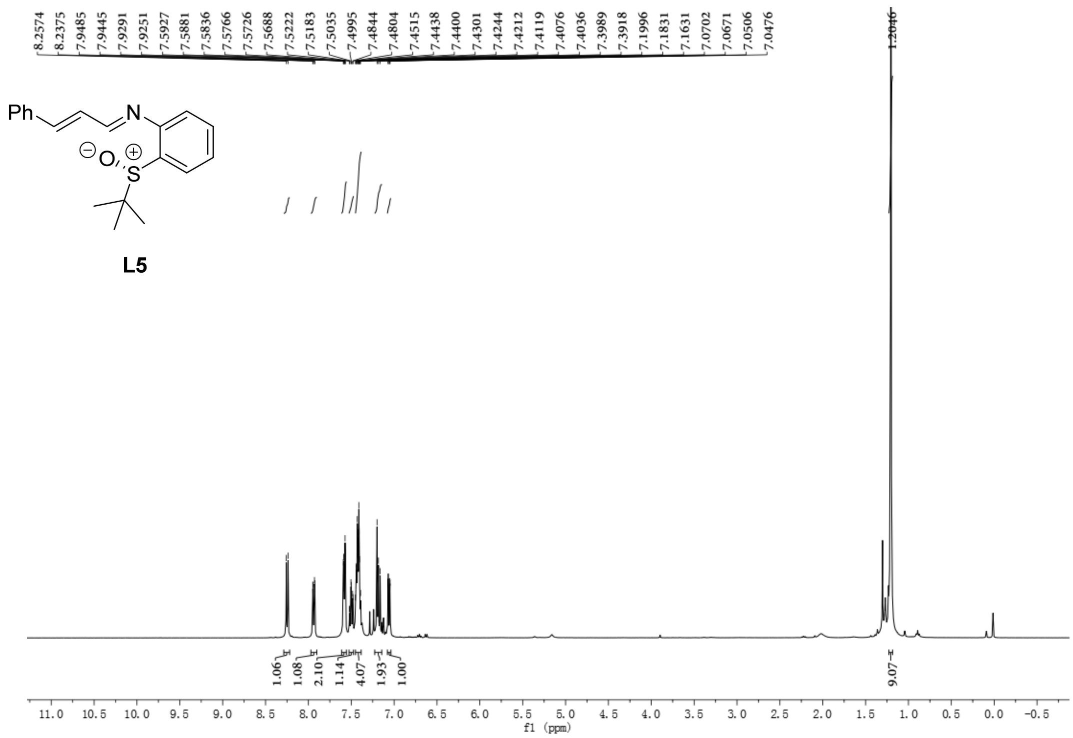
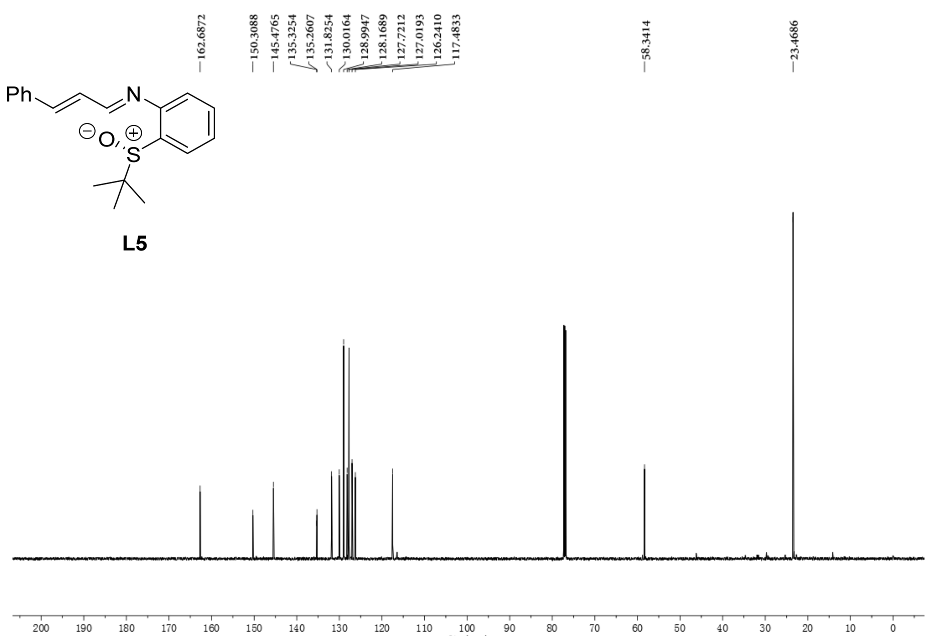
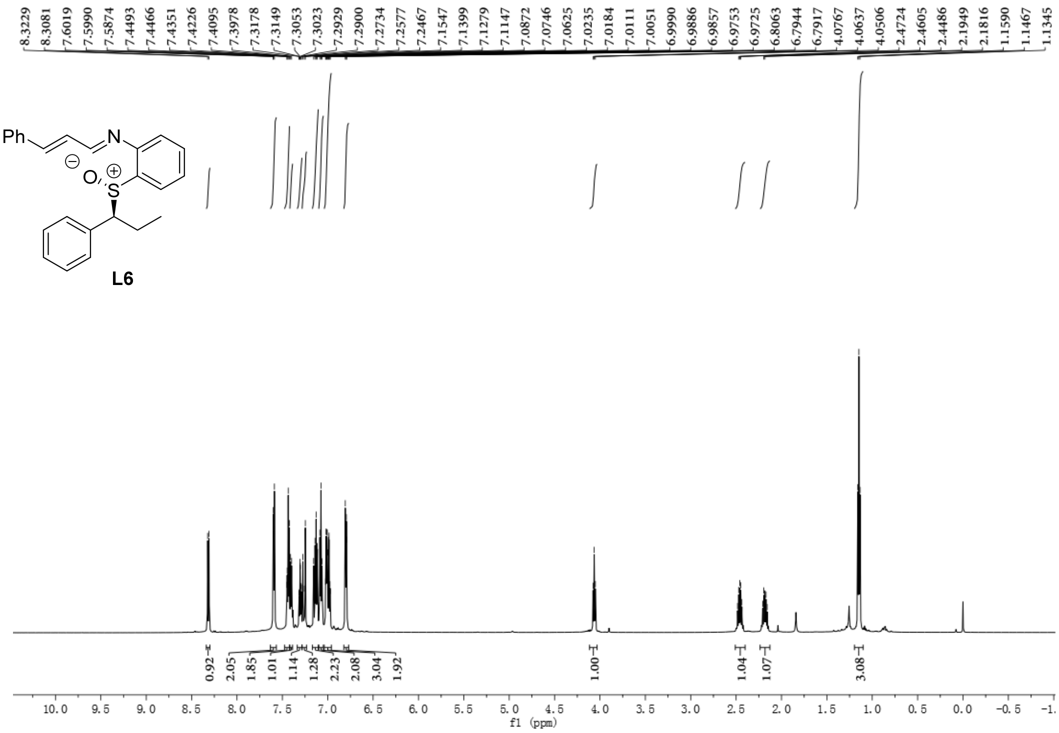
23.0948
Ph
O
S
L4
f1 (ppm)



L5



L5


8.3229 8.3081 7.6019 7.5990 7.5874 7.4493 7.4466 7.4351 7.4226 7.4095 7.3978 7.3178 7.3149 7.3053 7.3023 7.2929 7.2900 7.2734 7.2577 7.2467 7.1547 7.1399 7.1279 7.1147 7.0872 7.0746 7.0625 7.0235 7.0184 7.0111 7.0051 6.9990 6.9886 6.9857 6.9753 6.9725 6.8063 6.7944 6.7917 4.0767 4.0637 4.0506 2.4724 2.4605 2.4486 2.1949 2.1816 1.1590 1.1467 1.1345
Ph
N
O
S
L6
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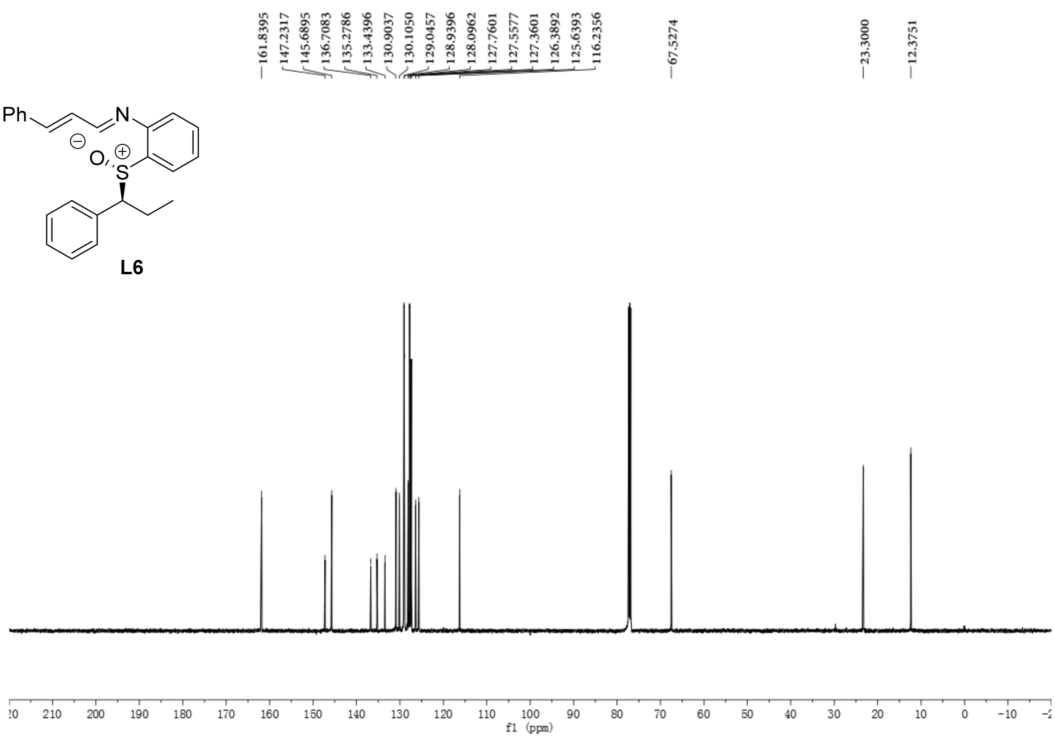
f1 (ppm)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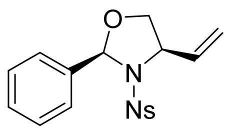
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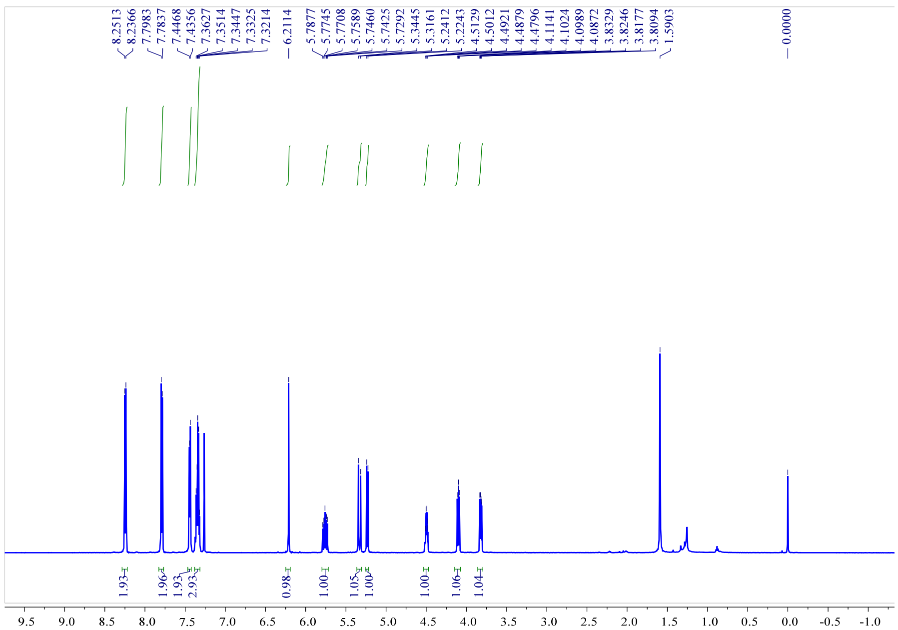
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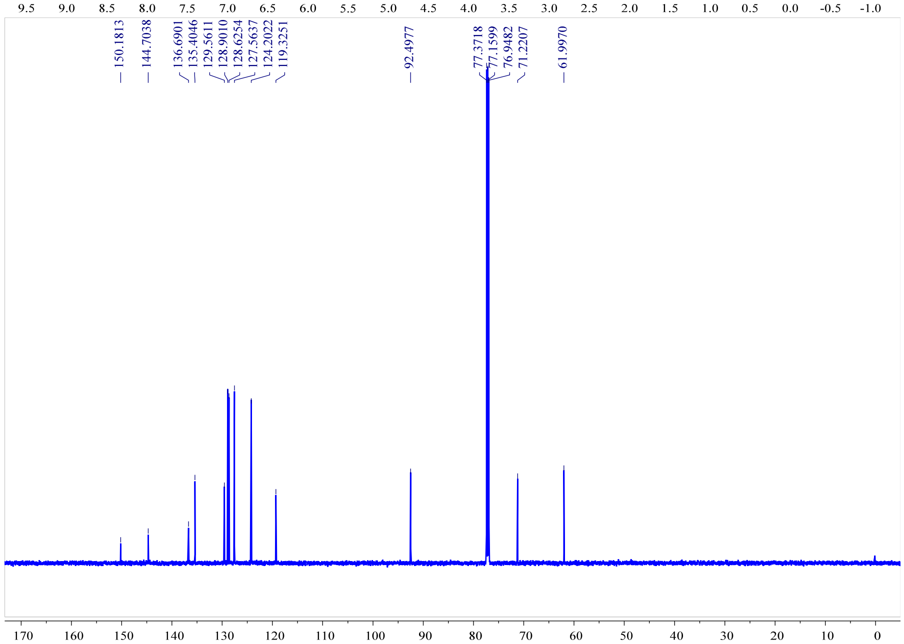
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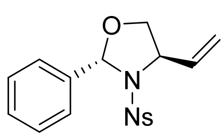
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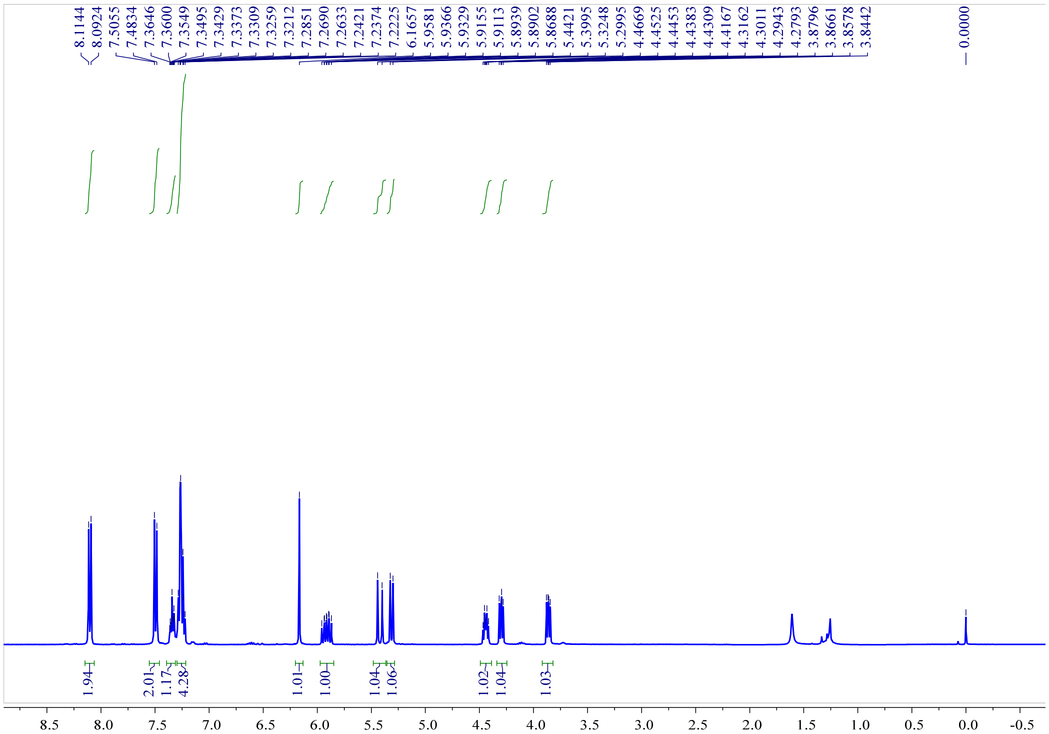
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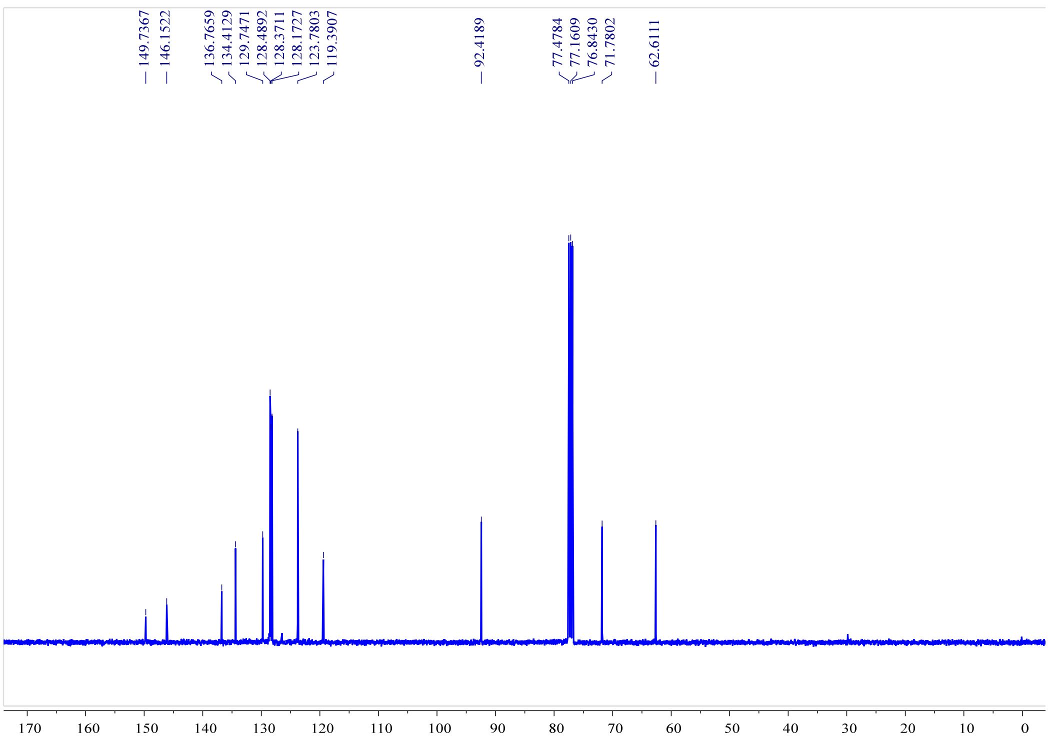
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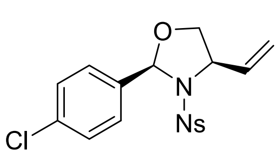
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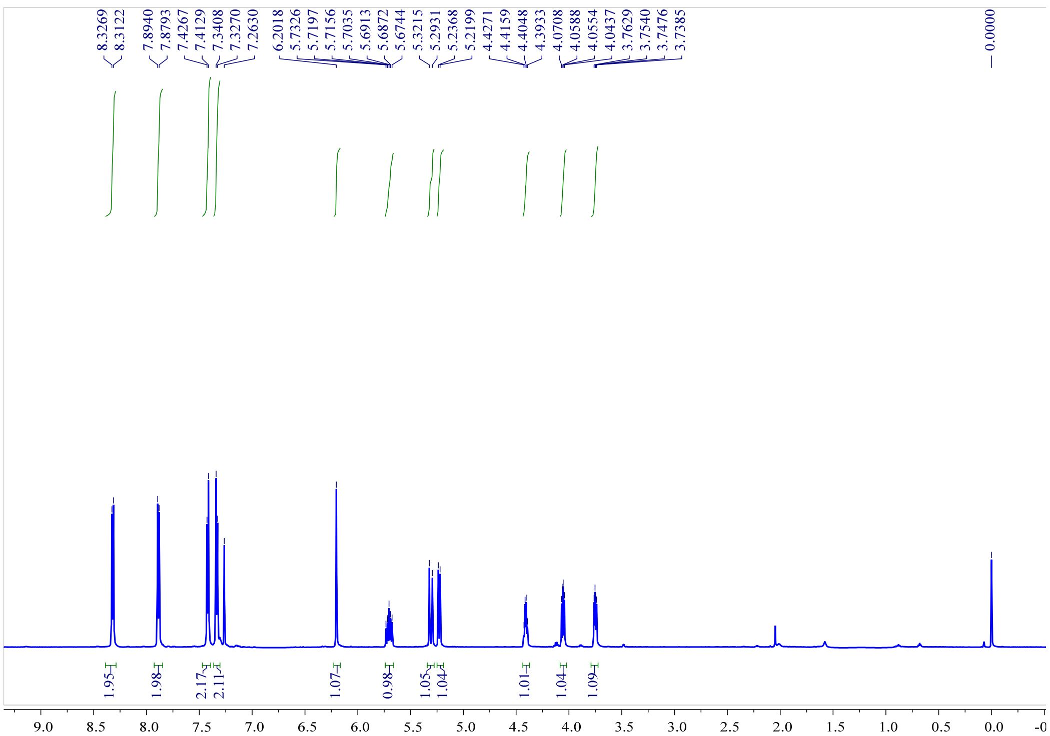
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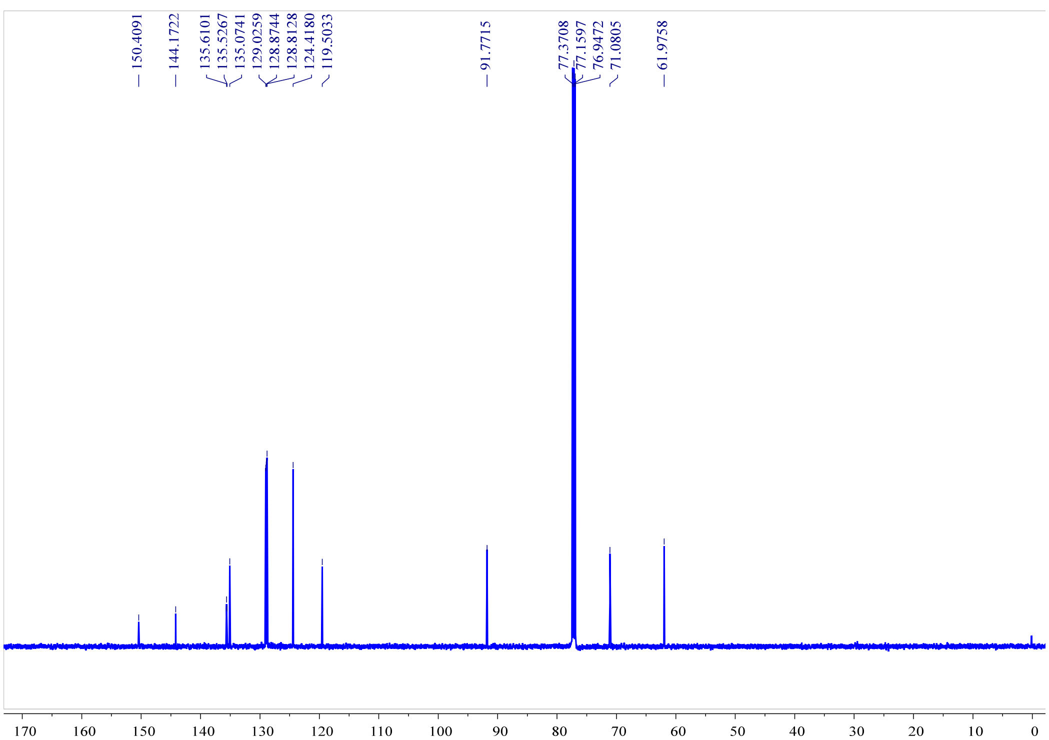
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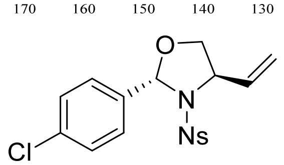
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Ns
Cl

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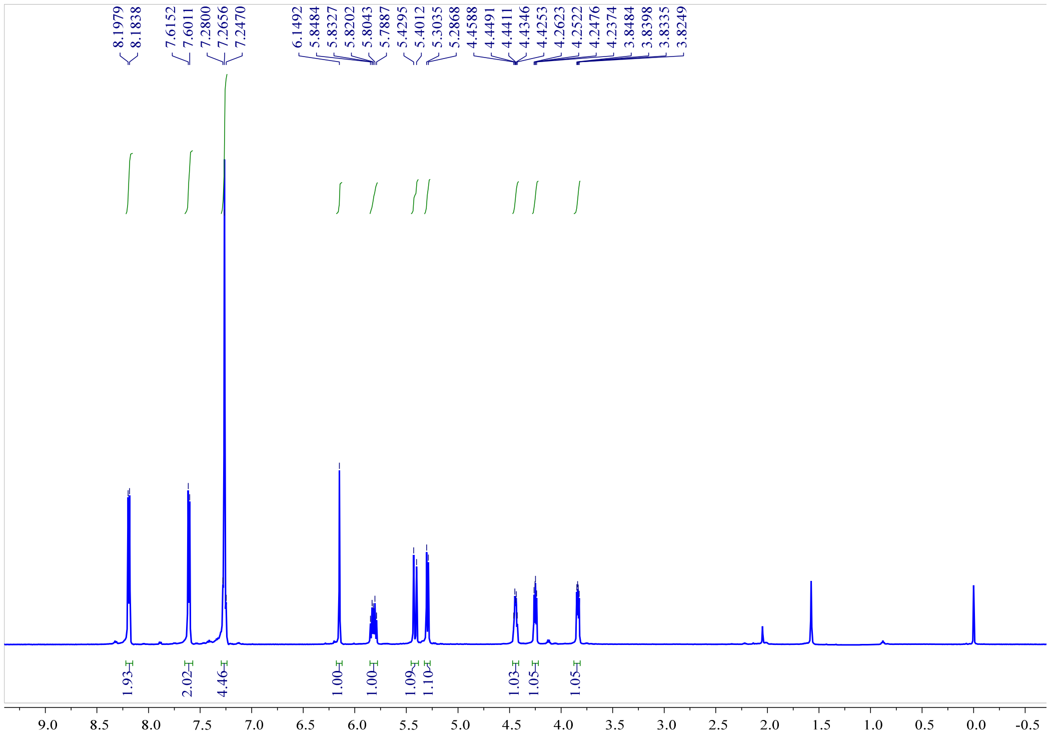
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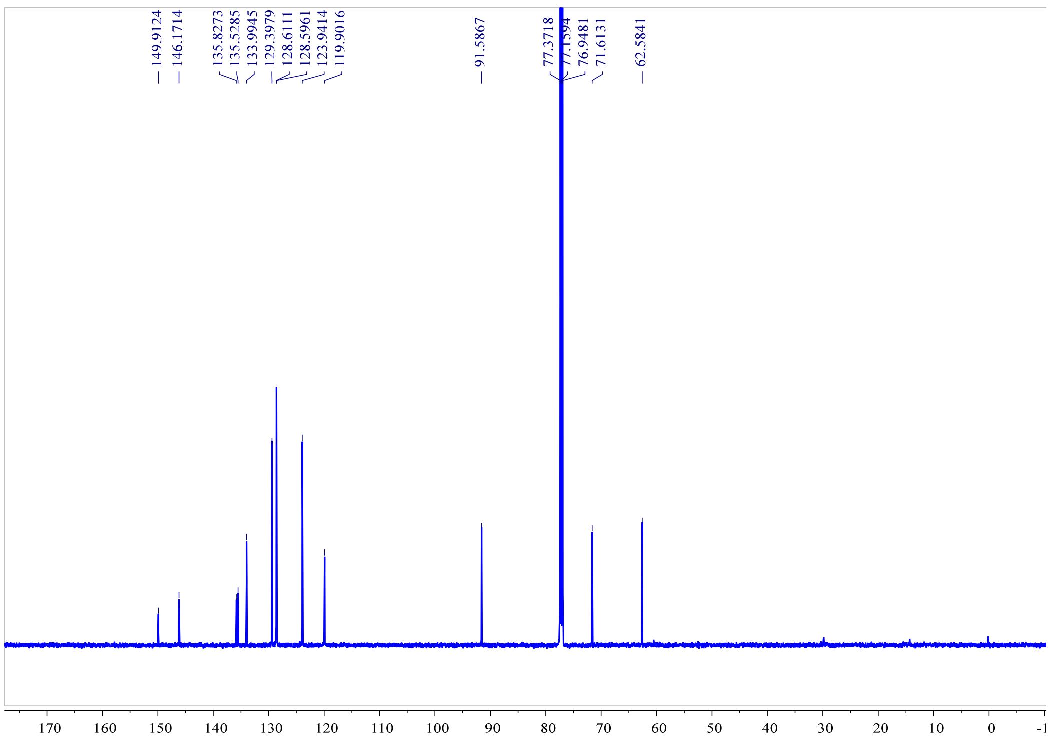
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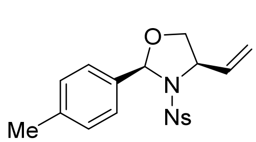
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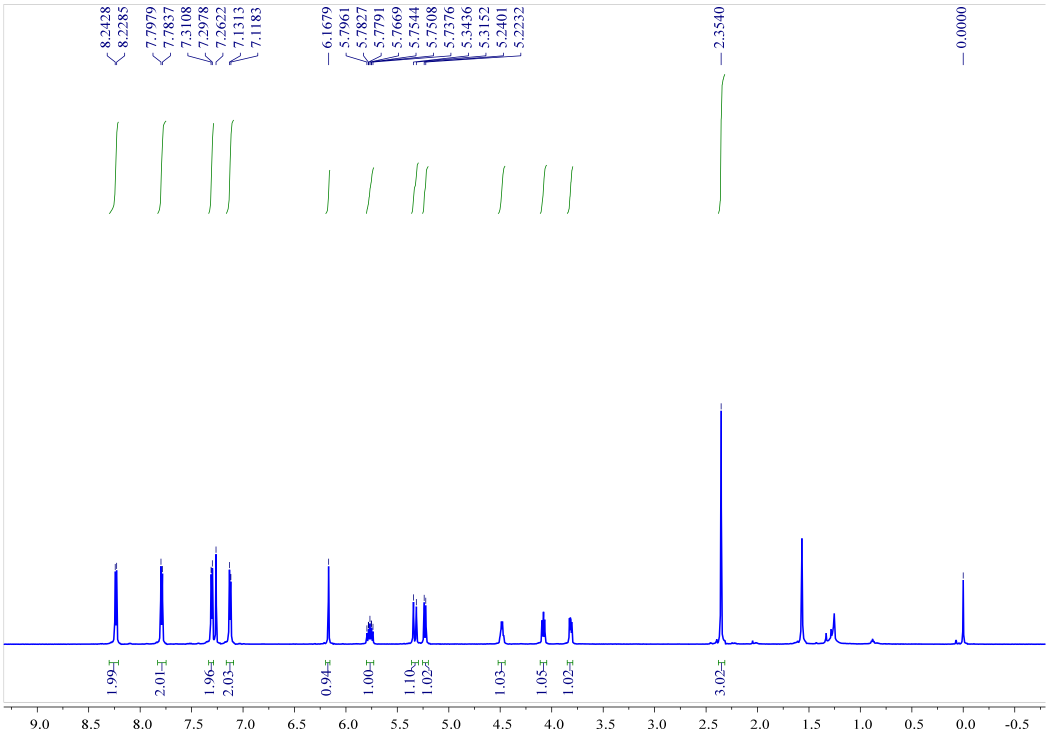
3c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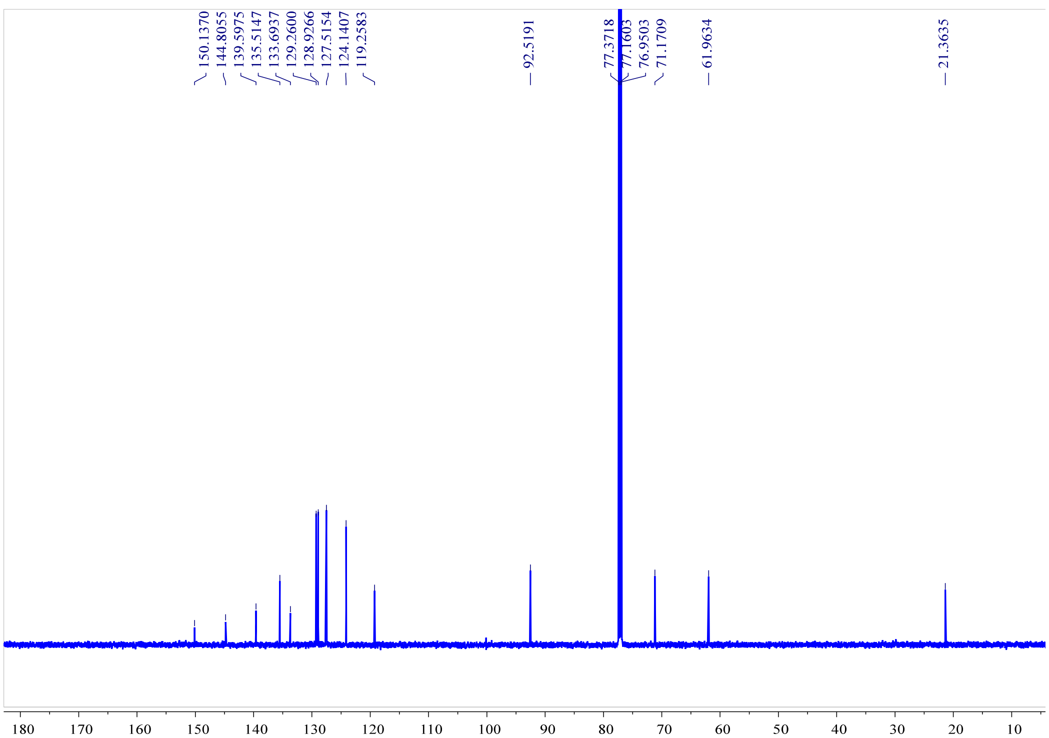
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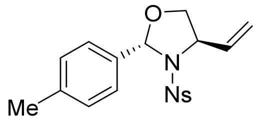
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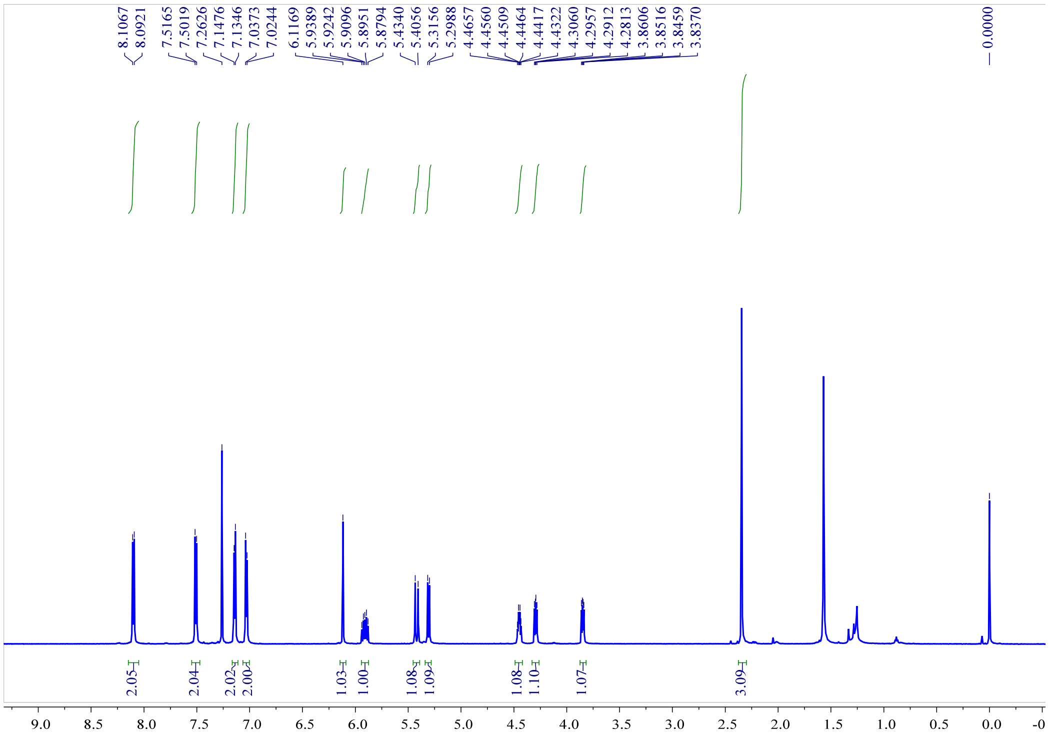
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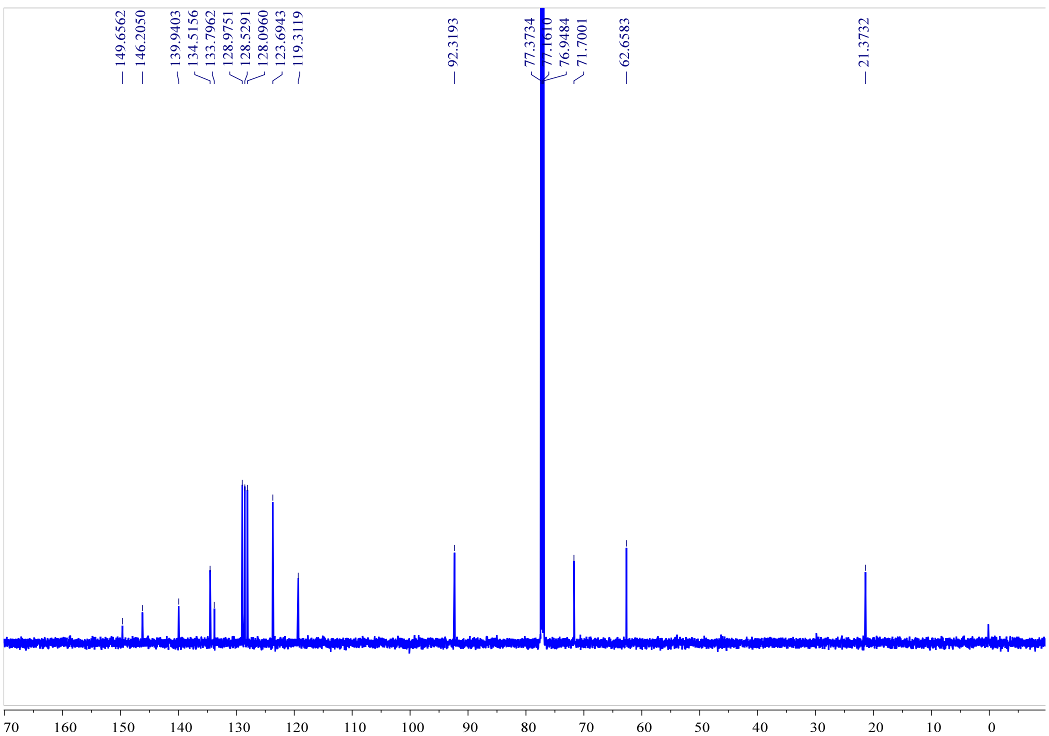
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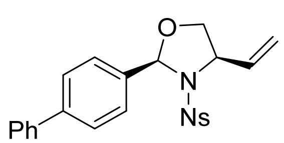
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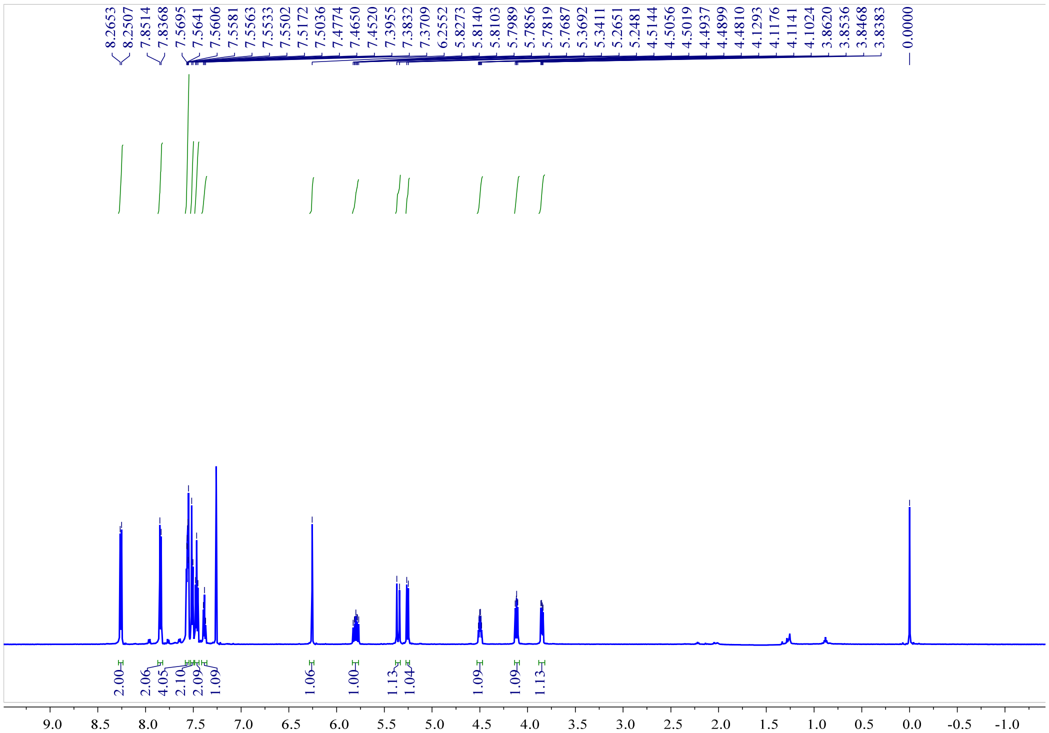
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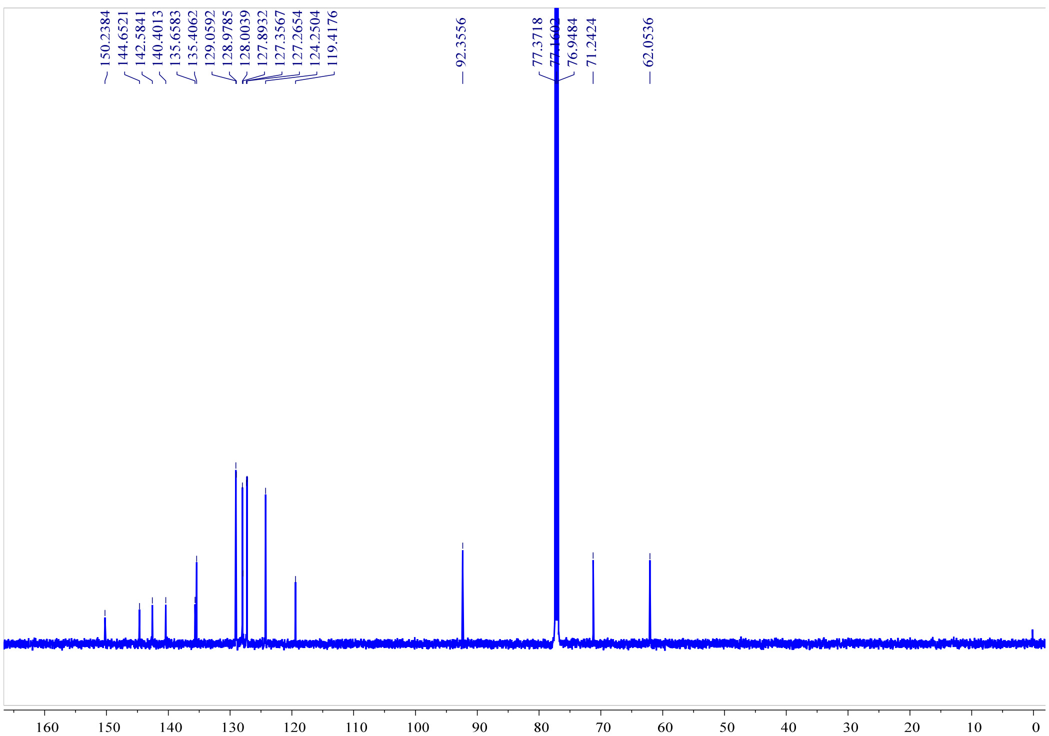
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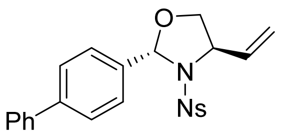
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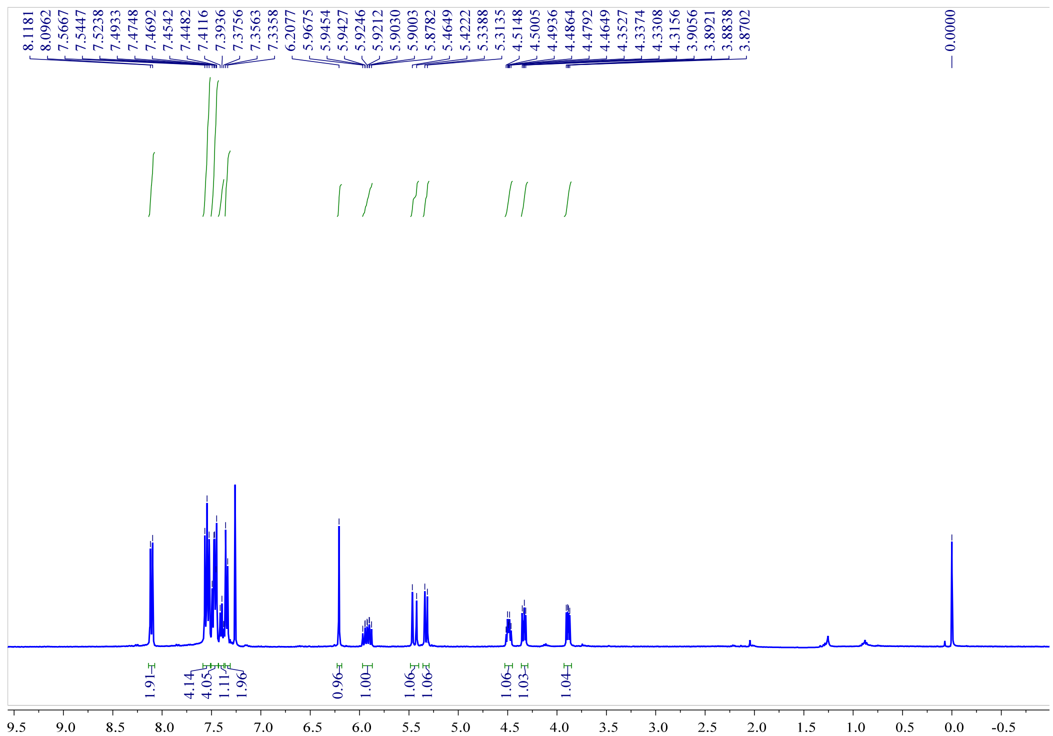

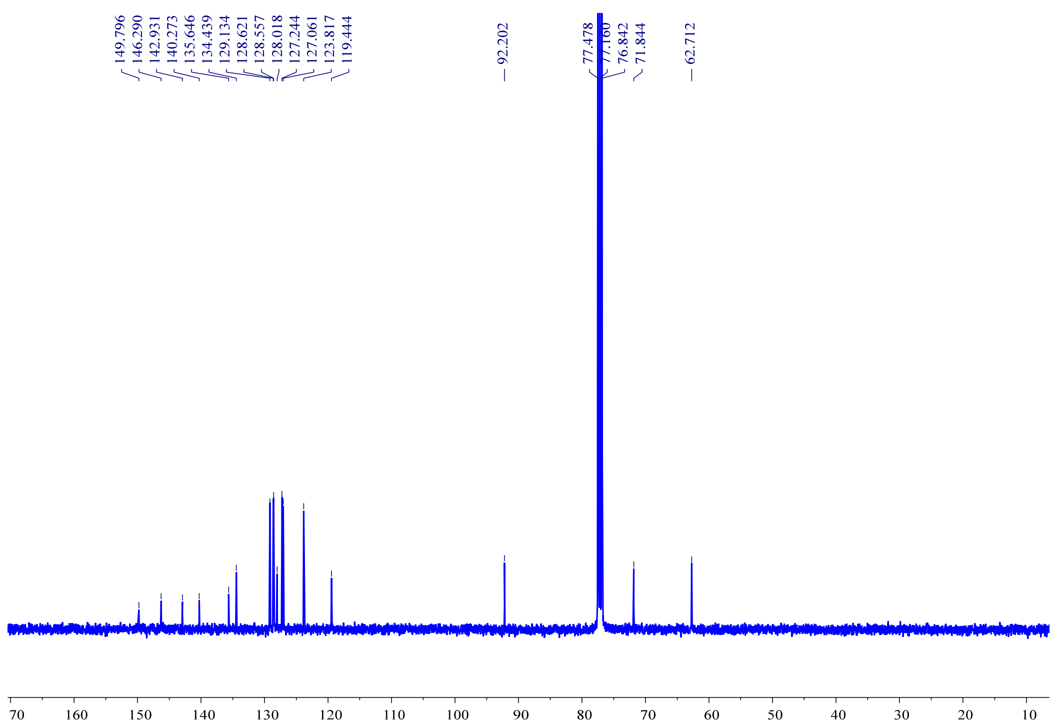

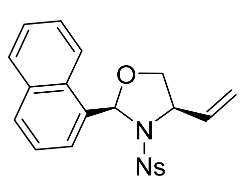

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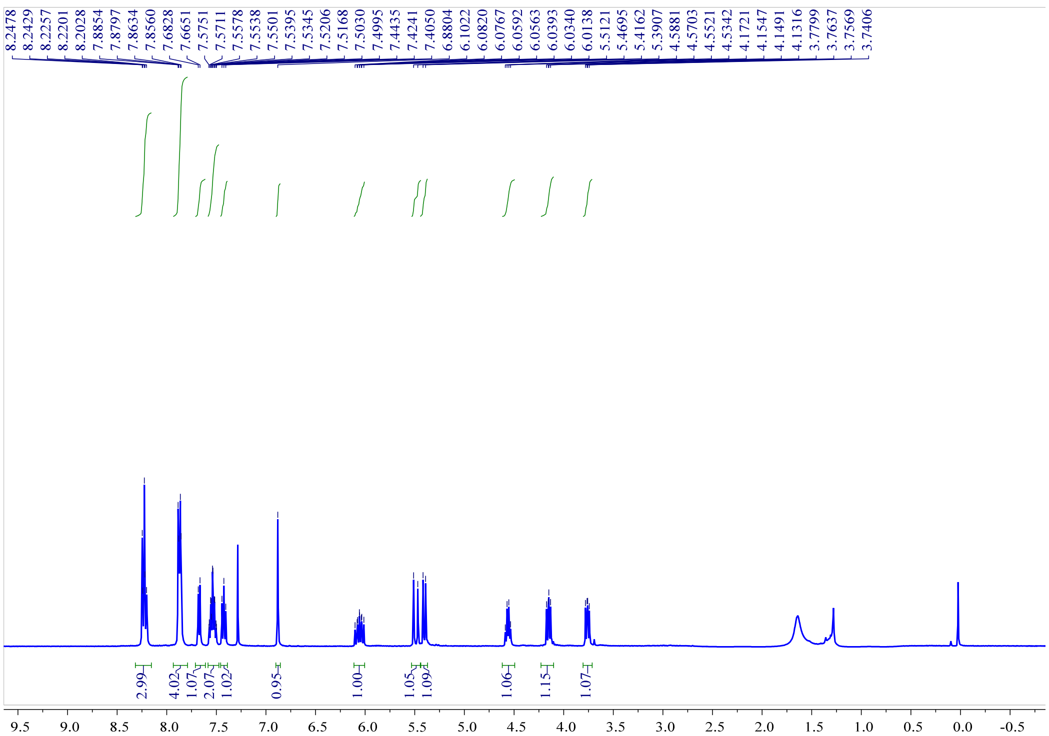
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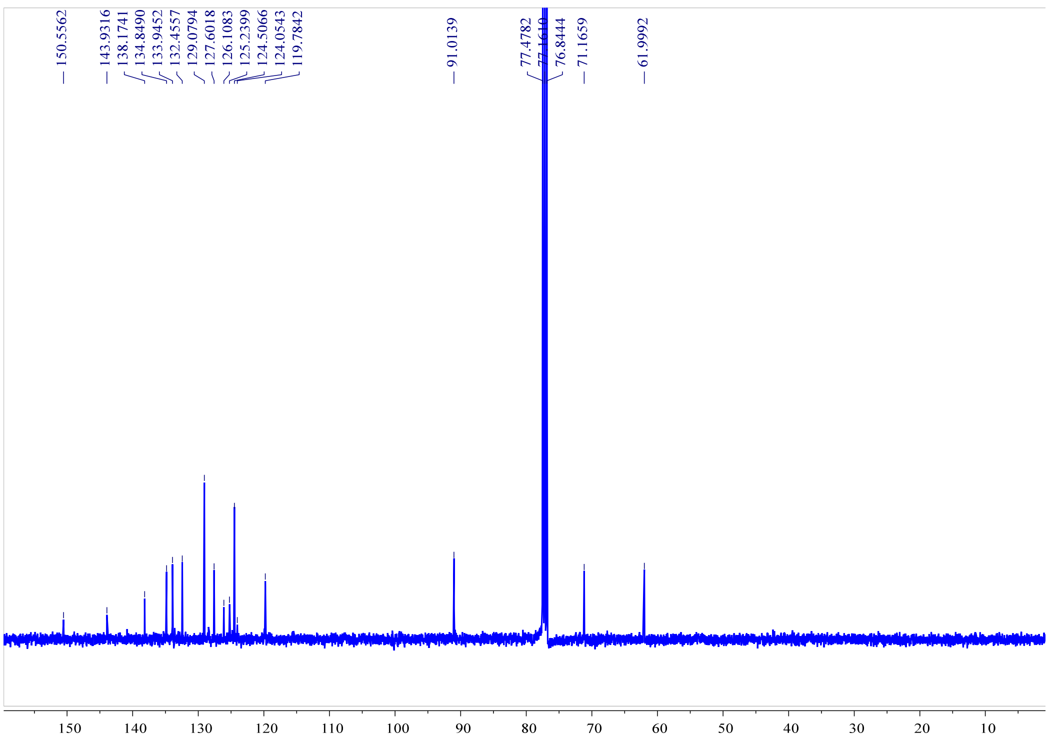
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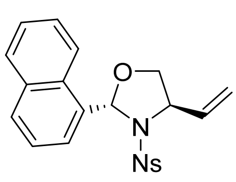
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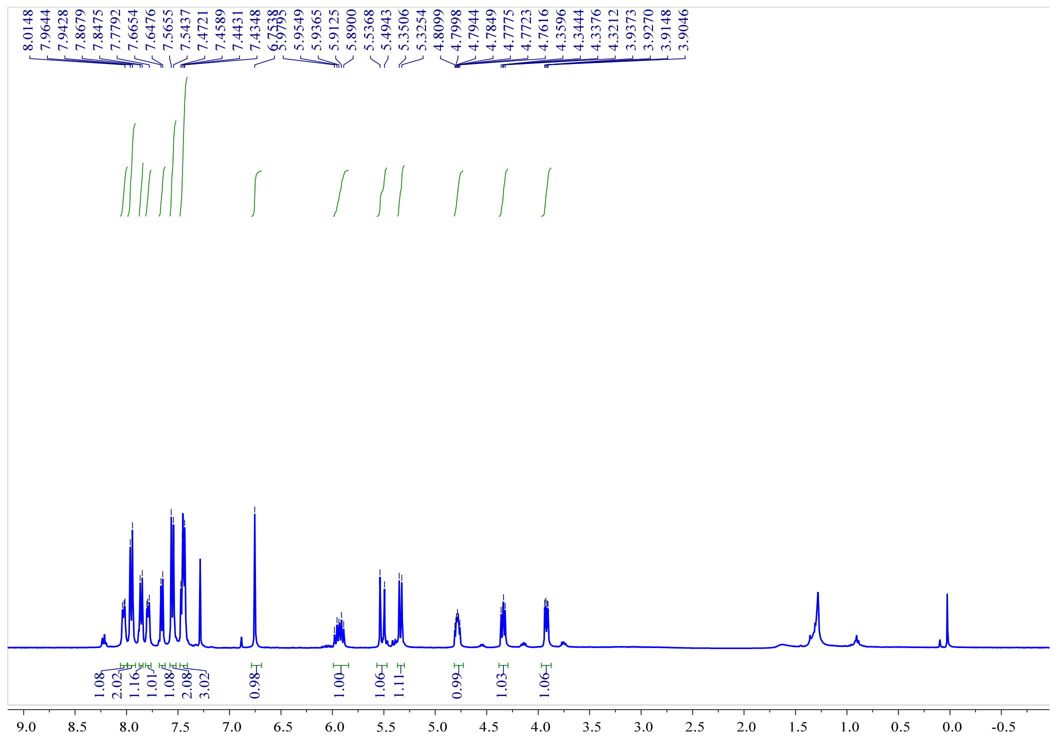

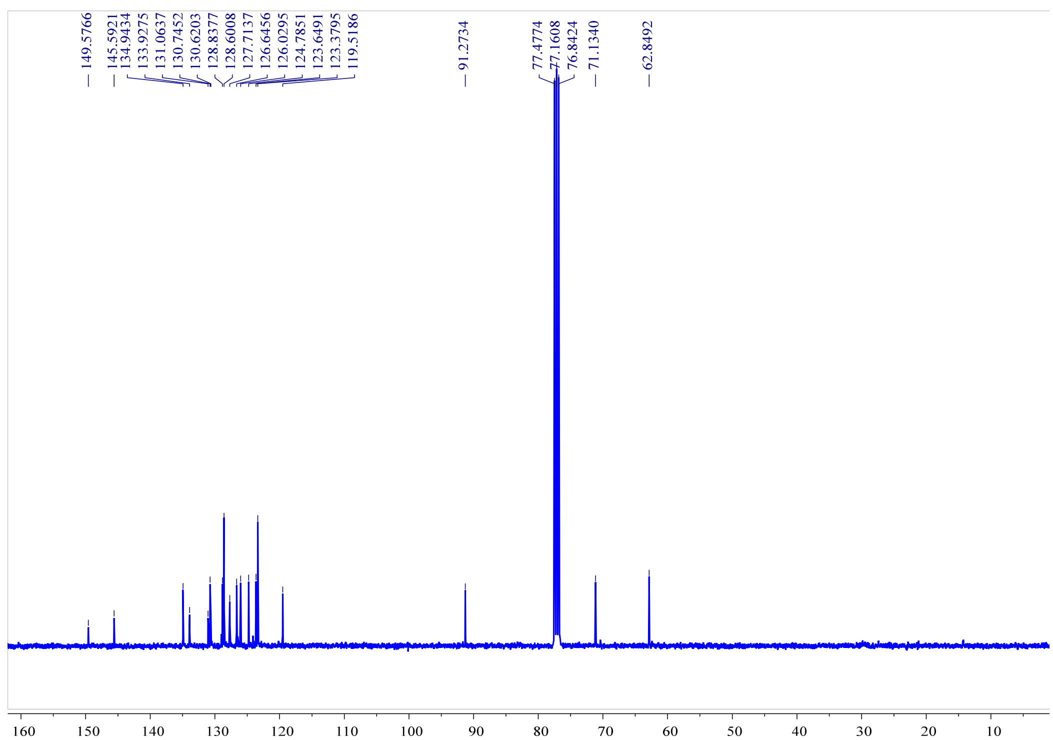

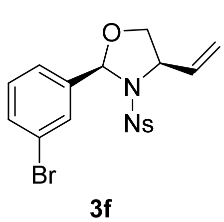

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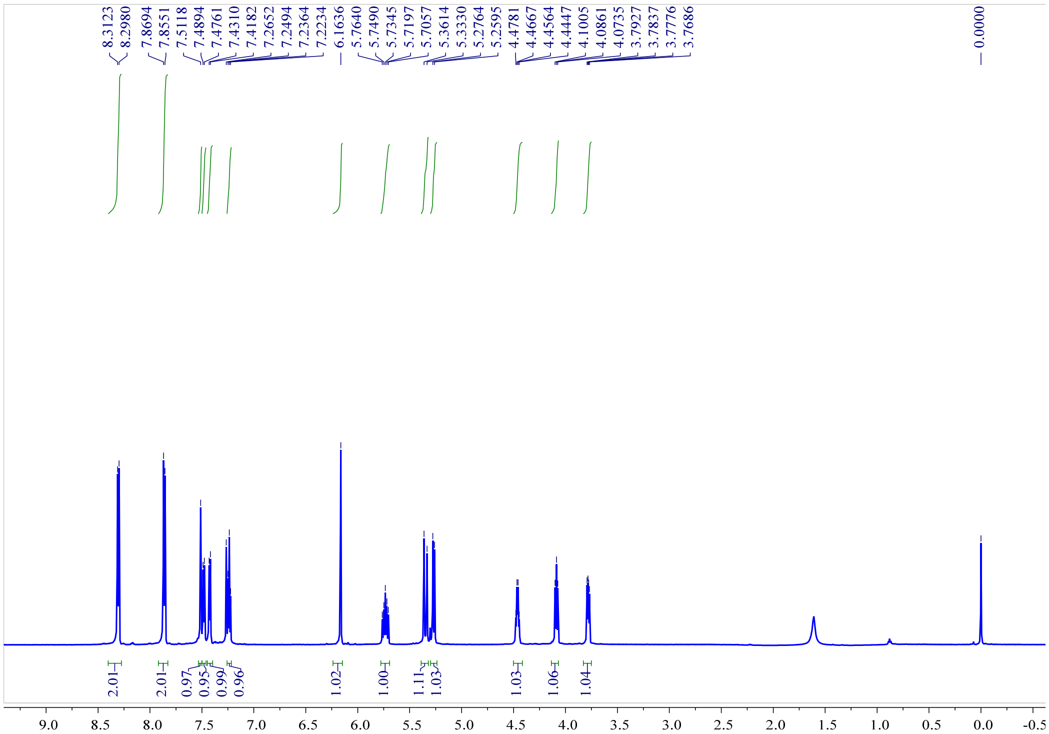
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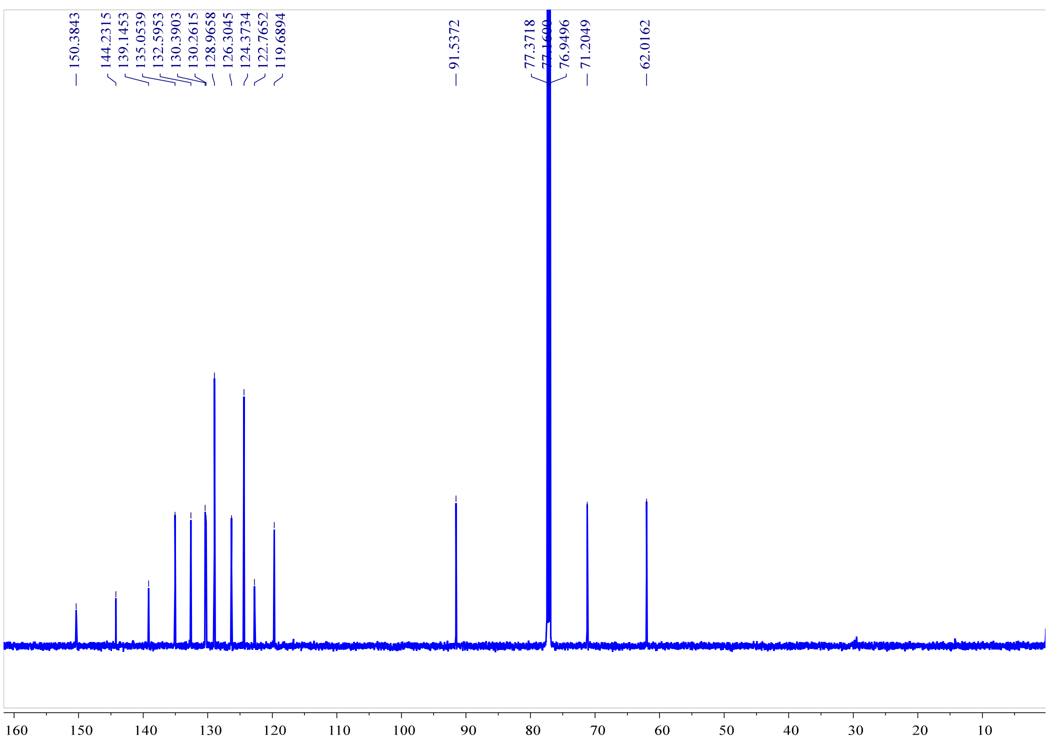
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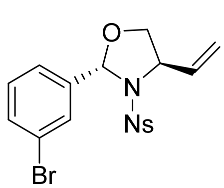
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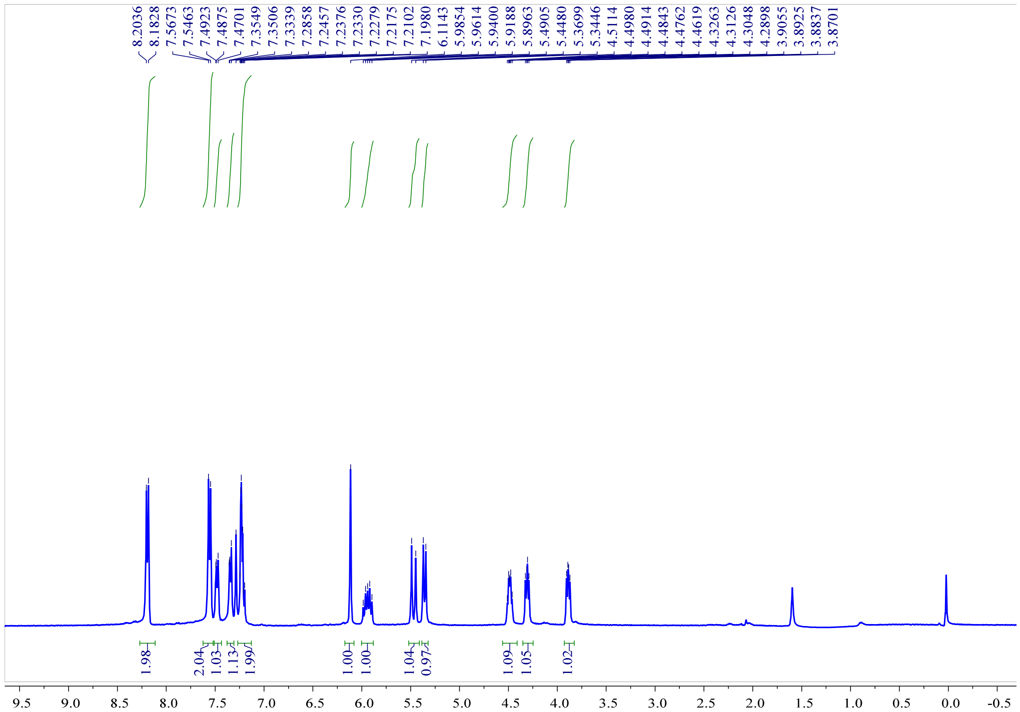
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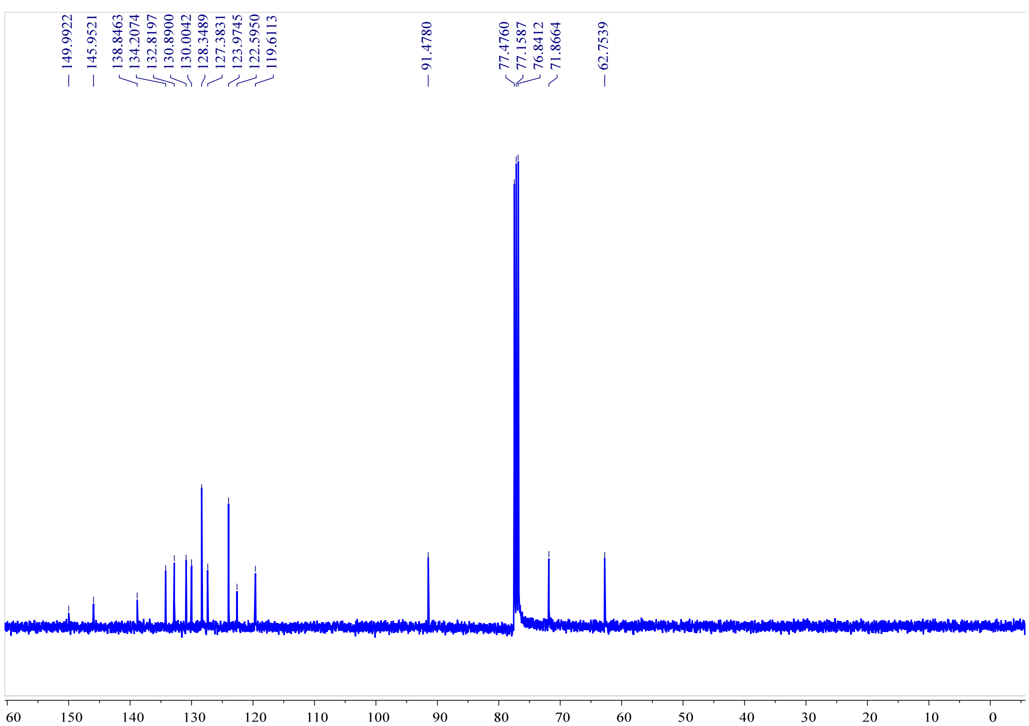
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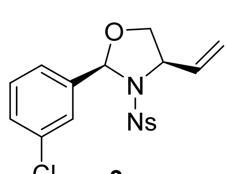
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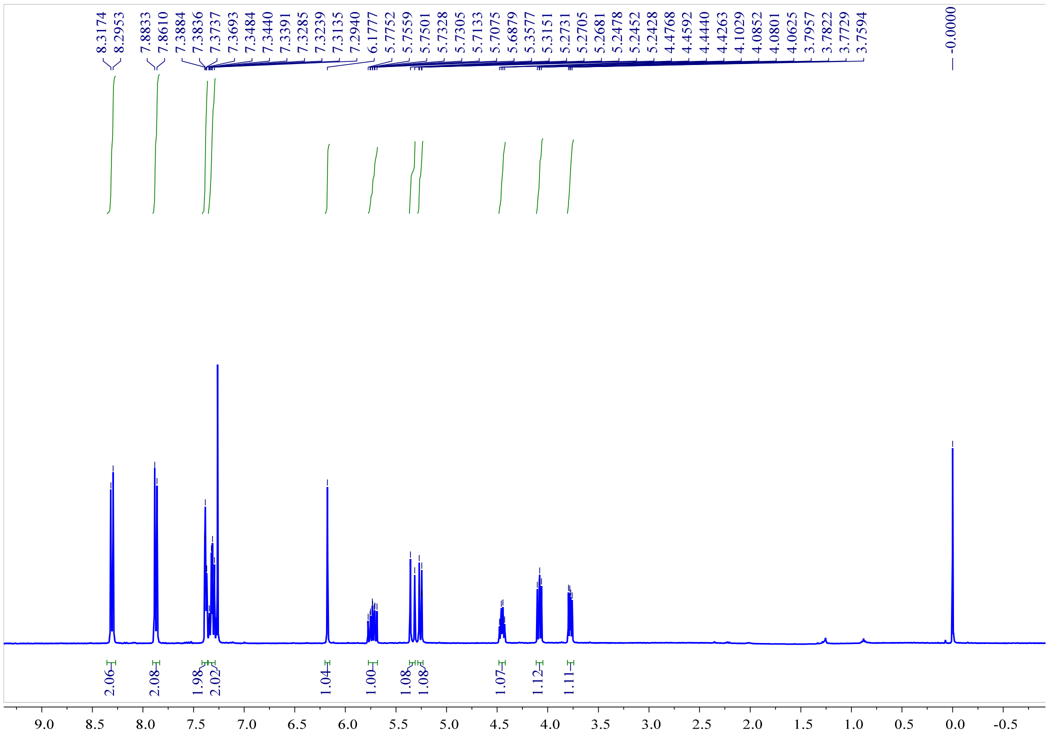
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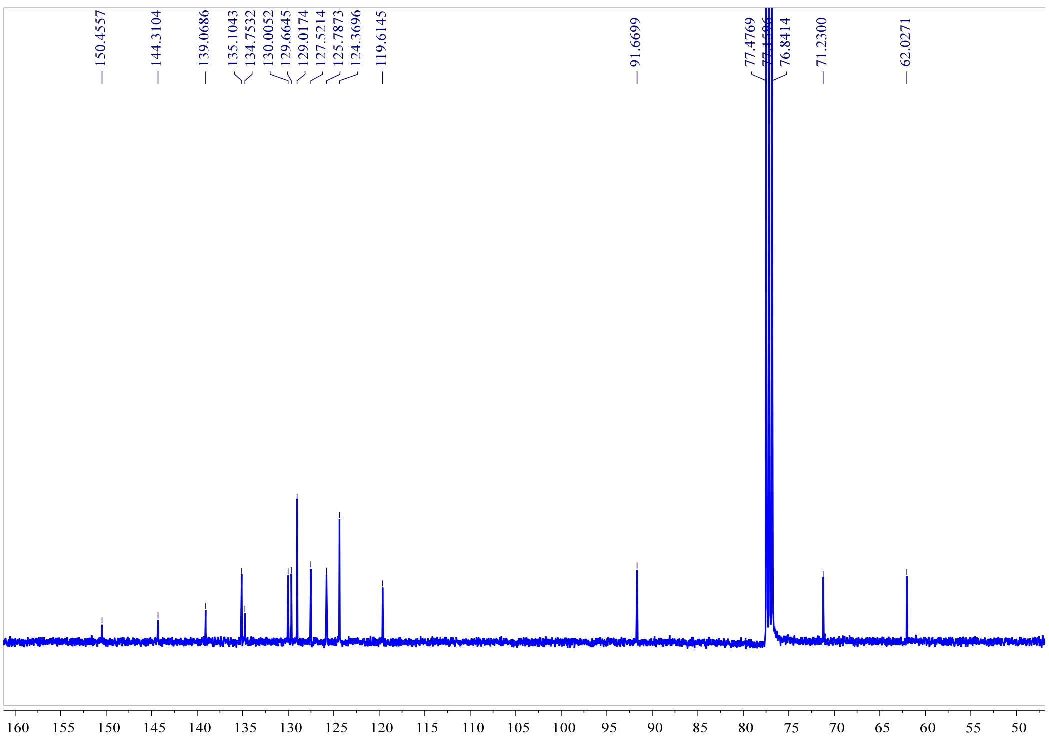
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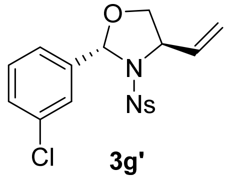
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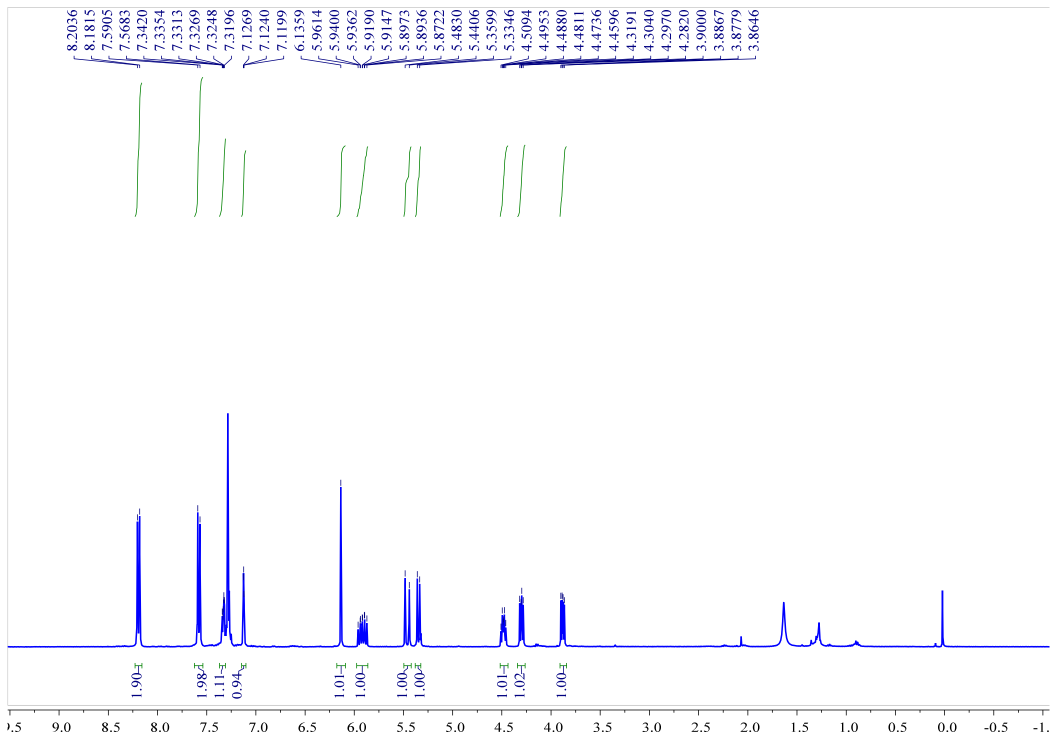

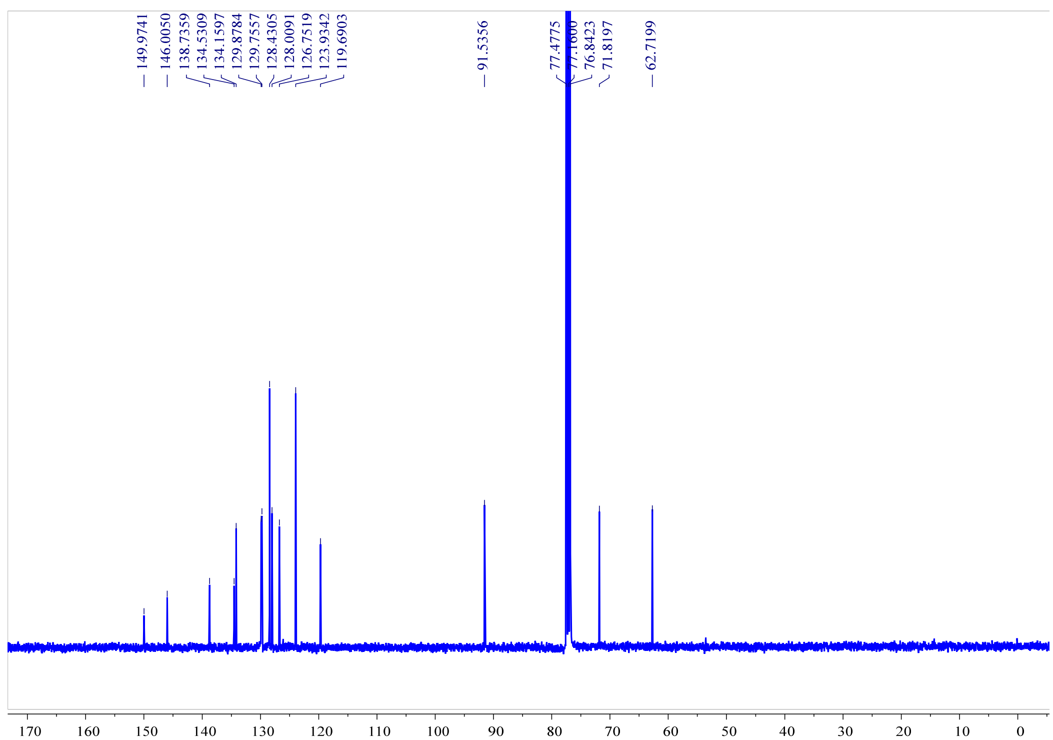

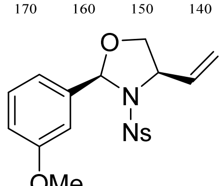

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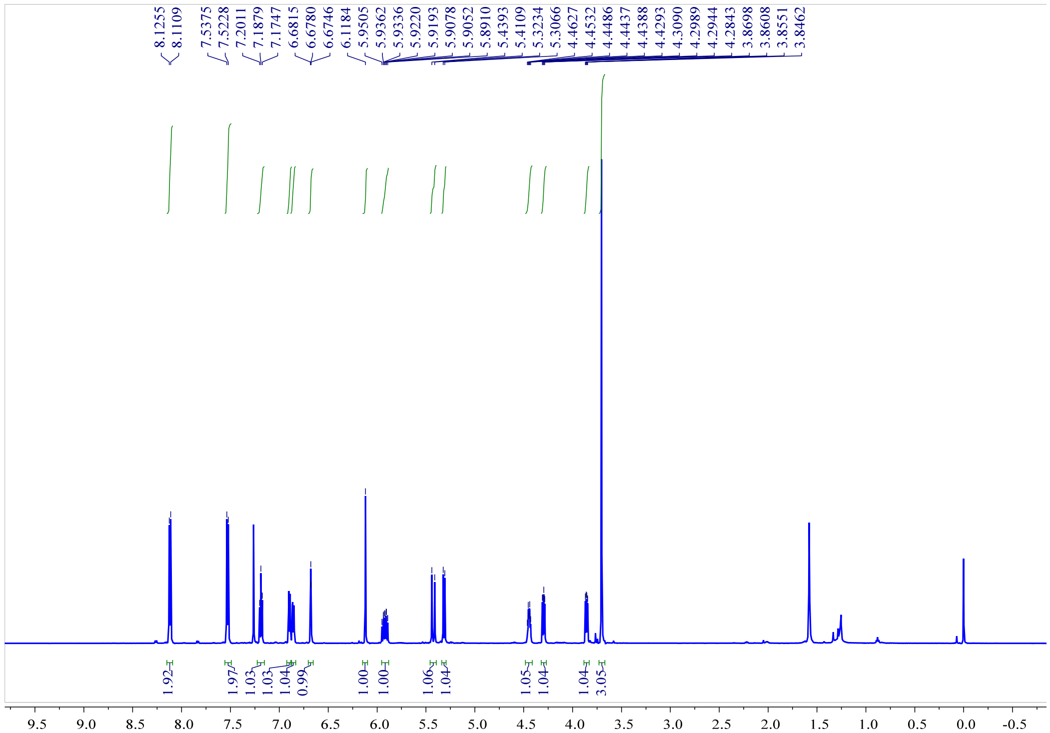
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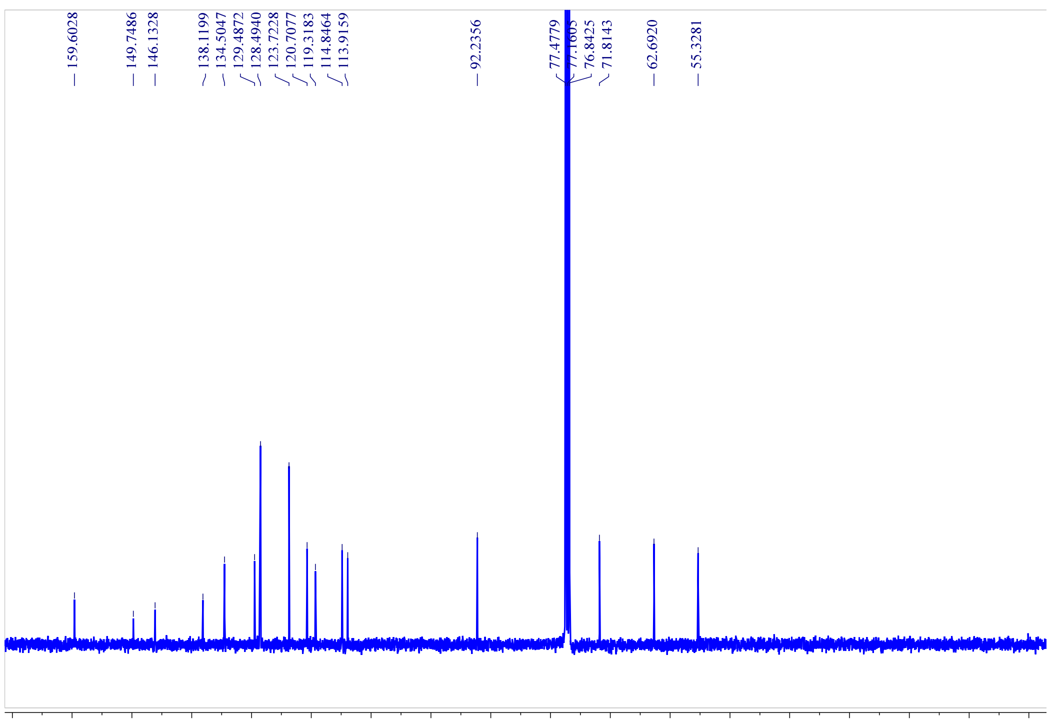
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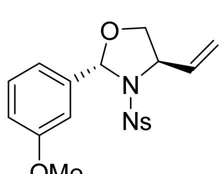
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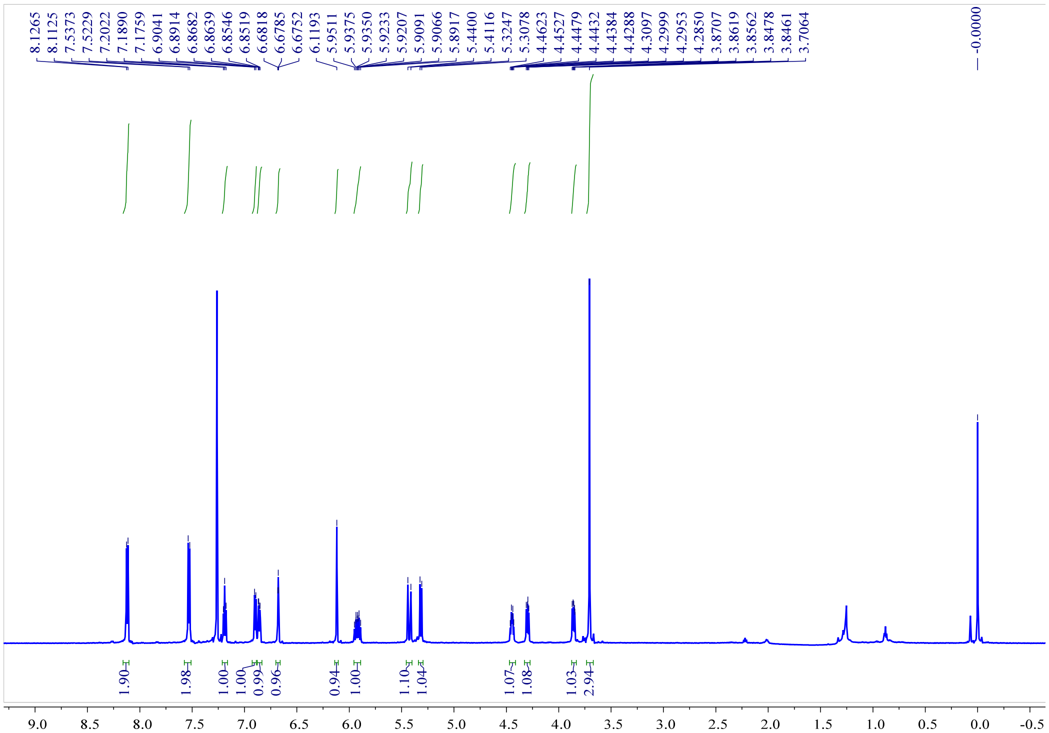
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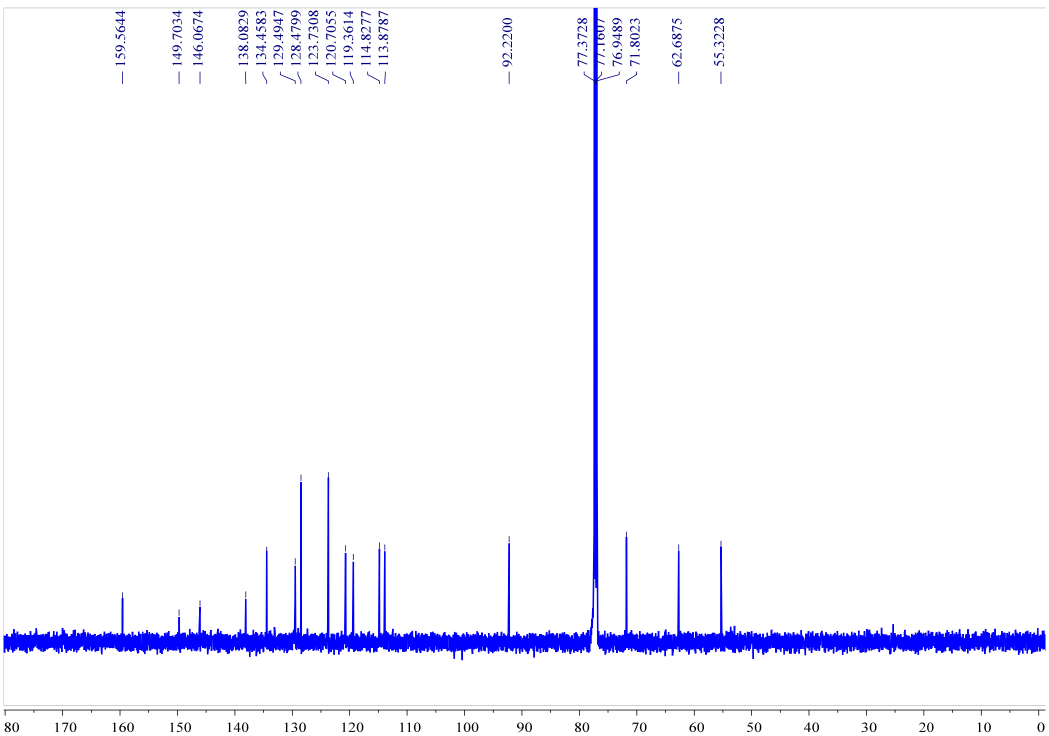
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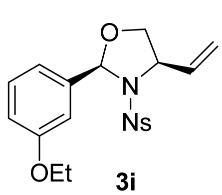
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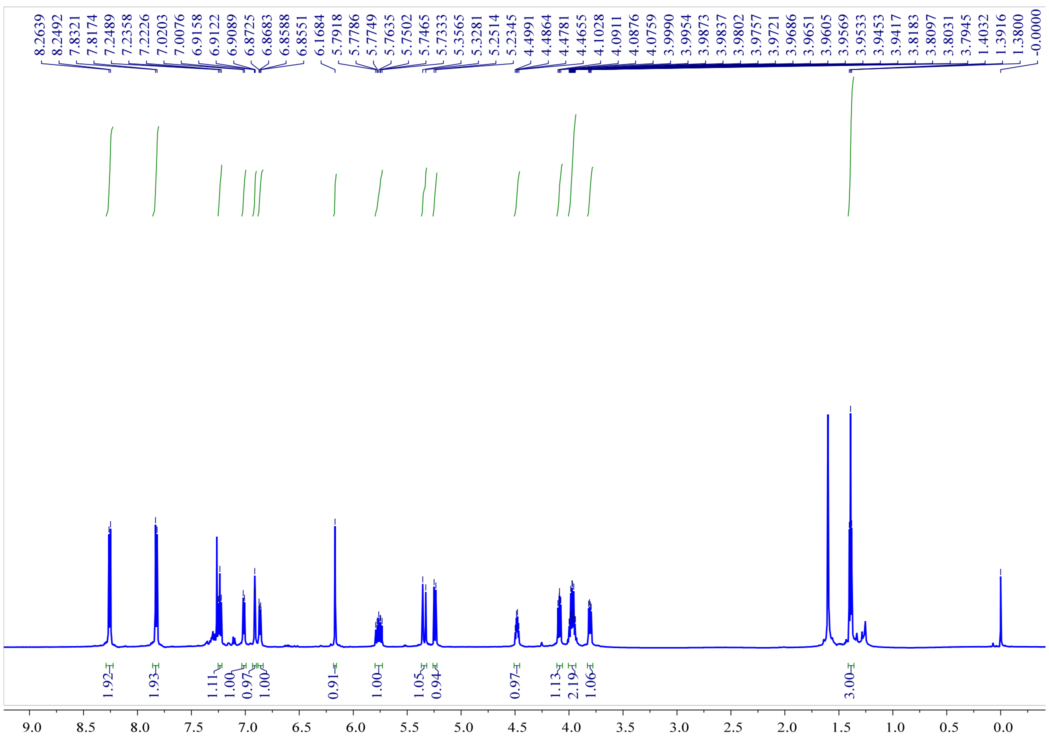
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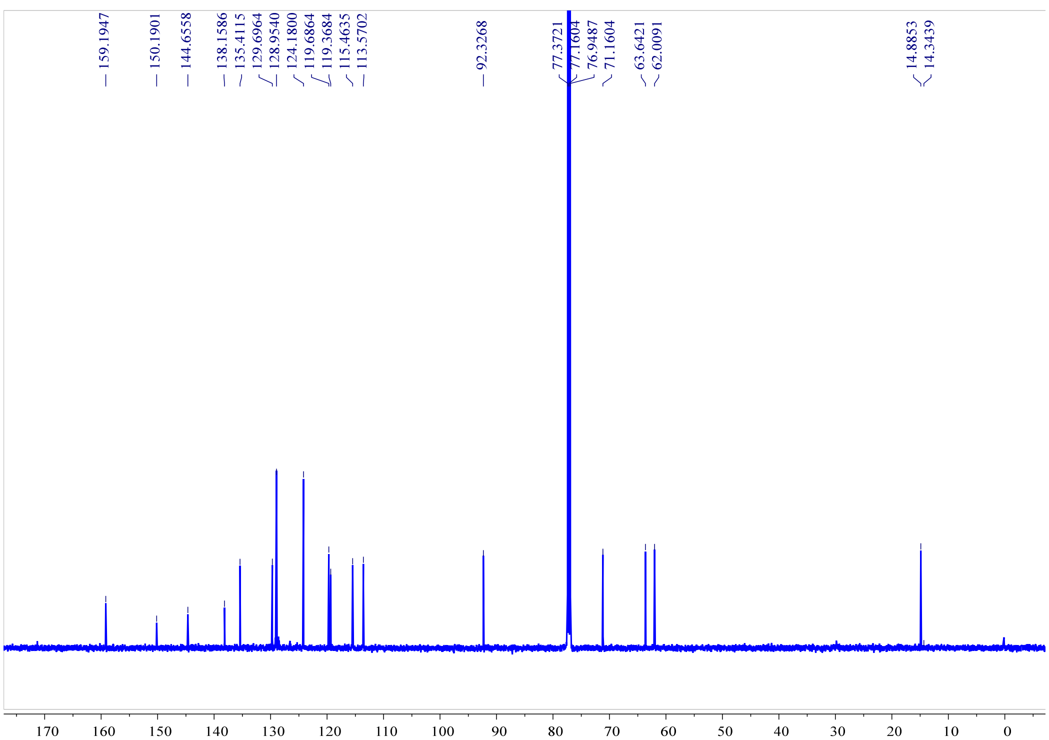
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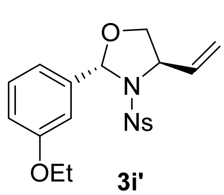
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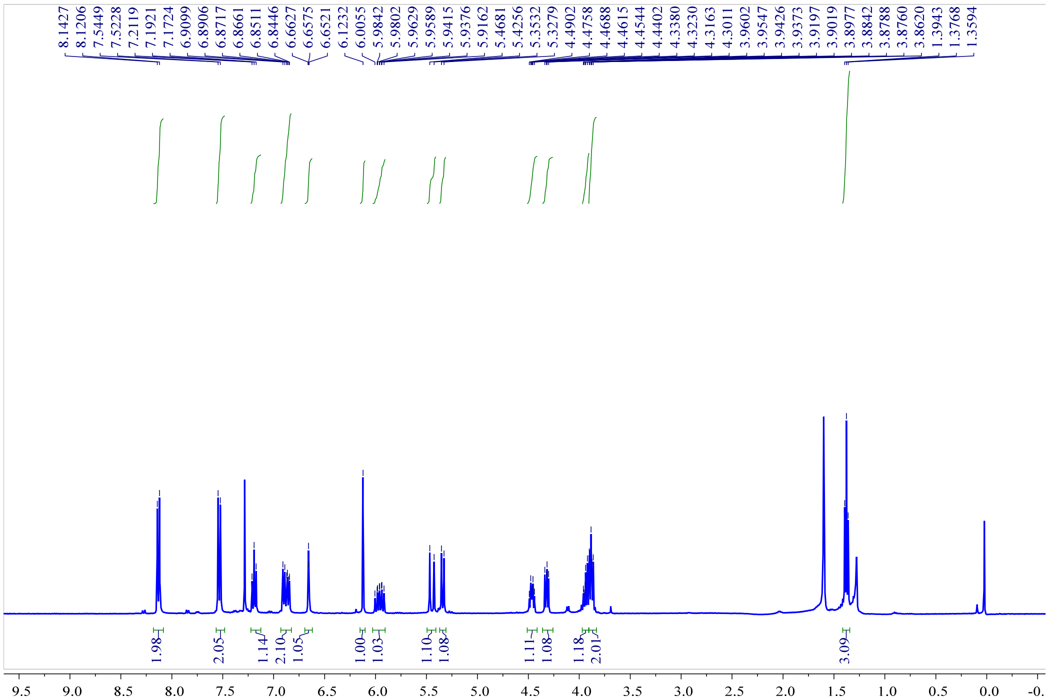
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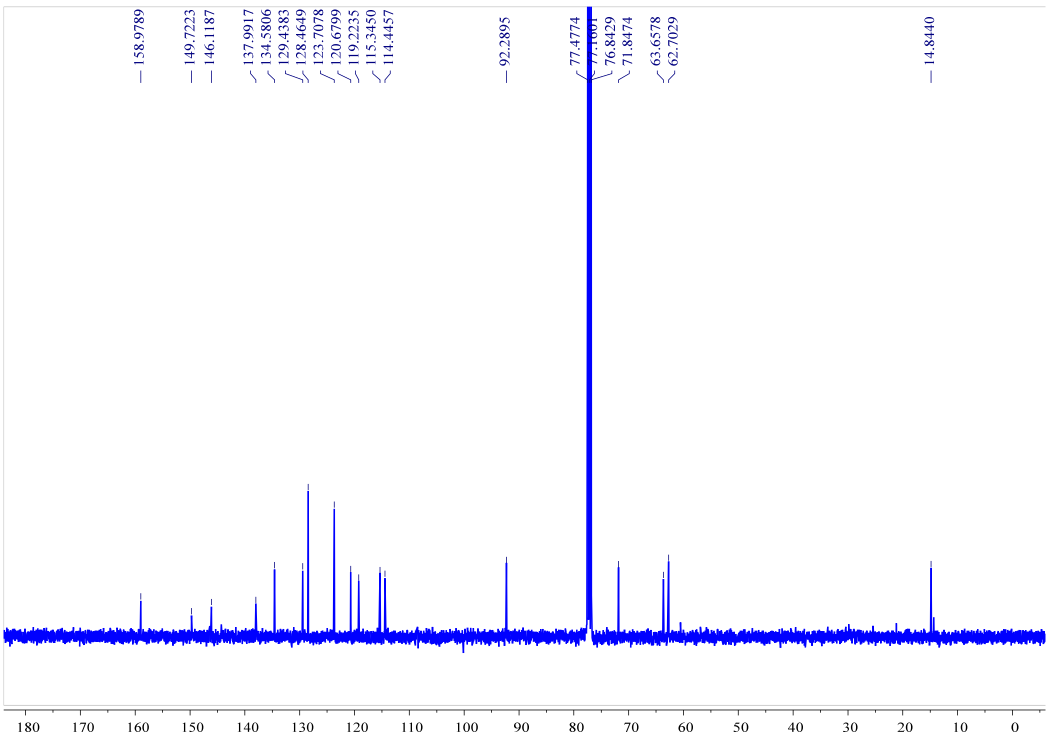
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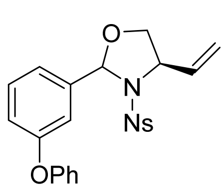
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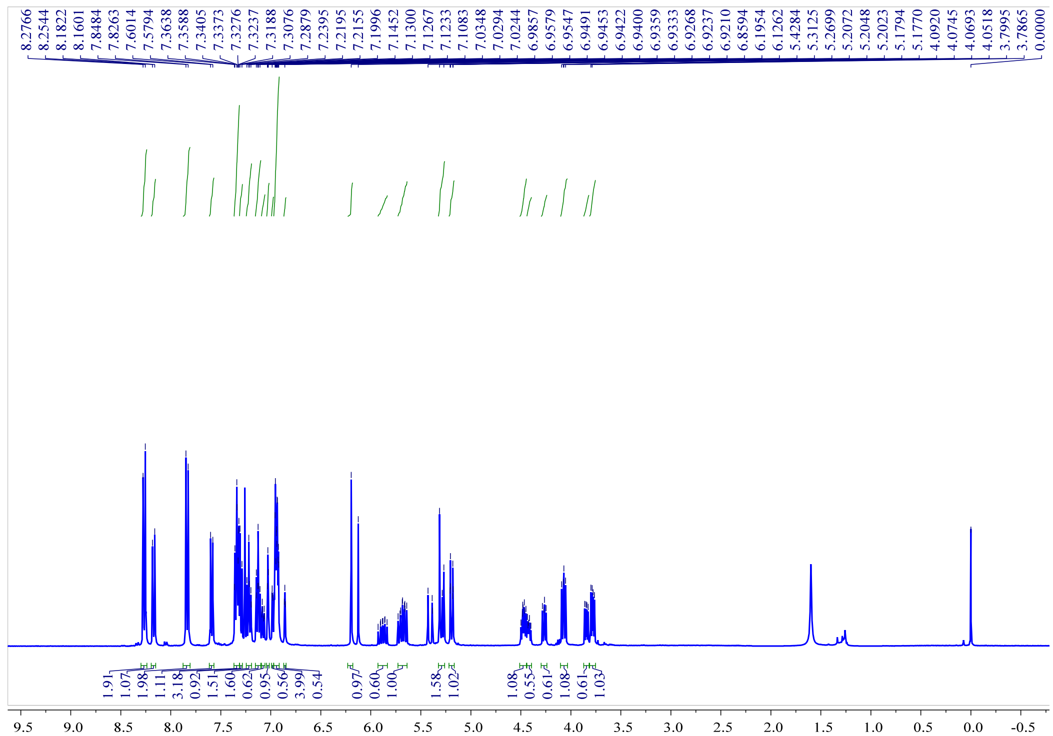
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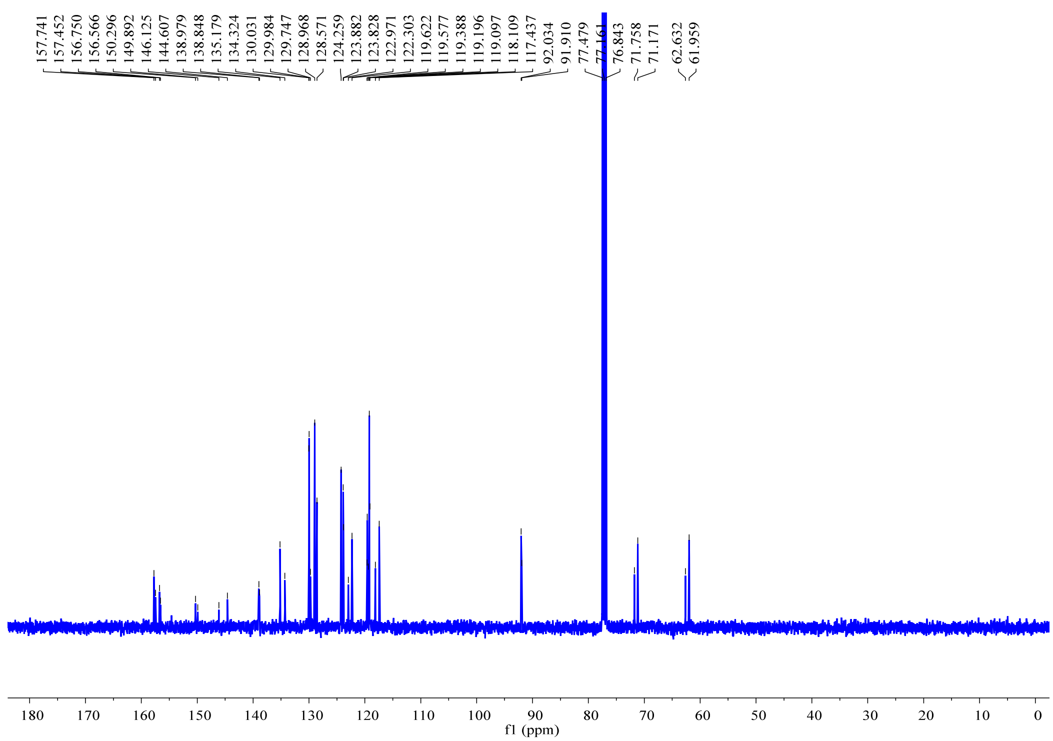
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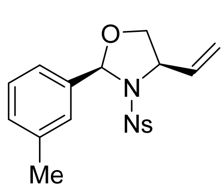
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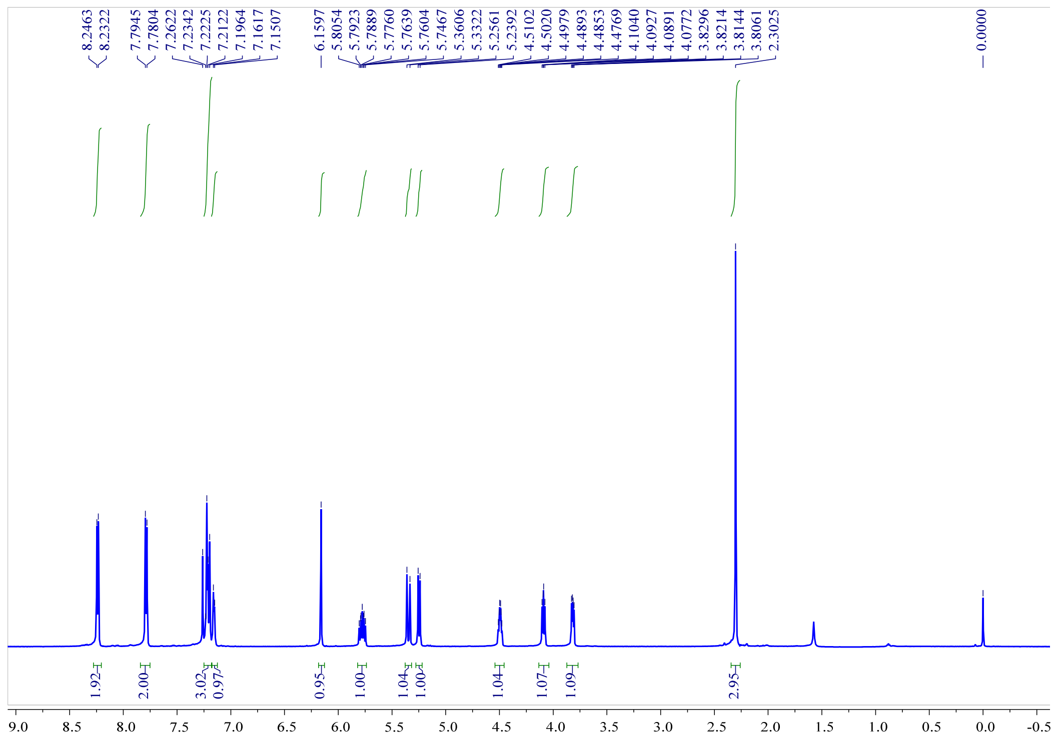
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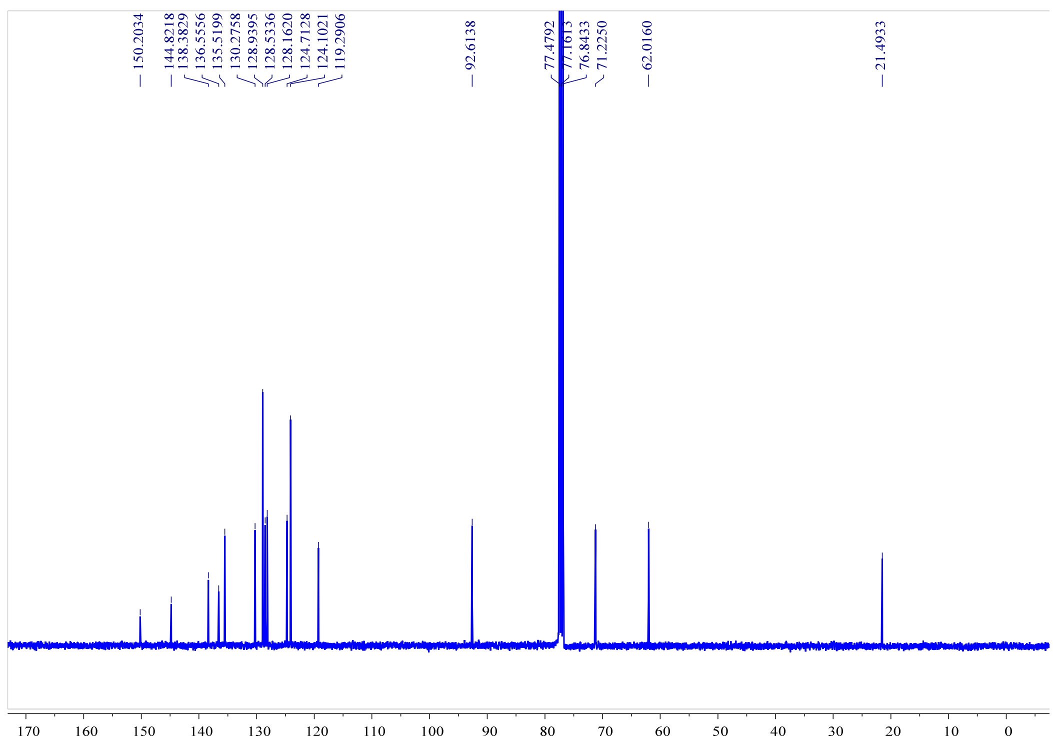
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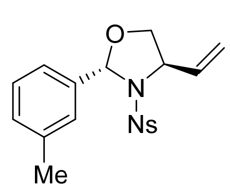
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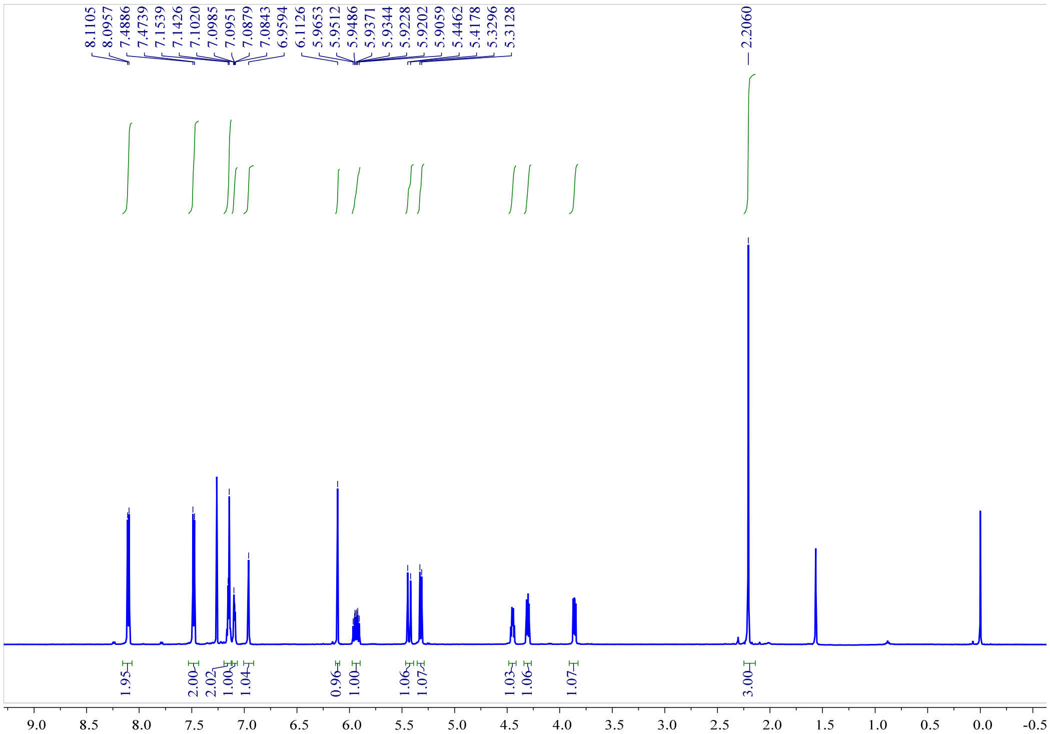
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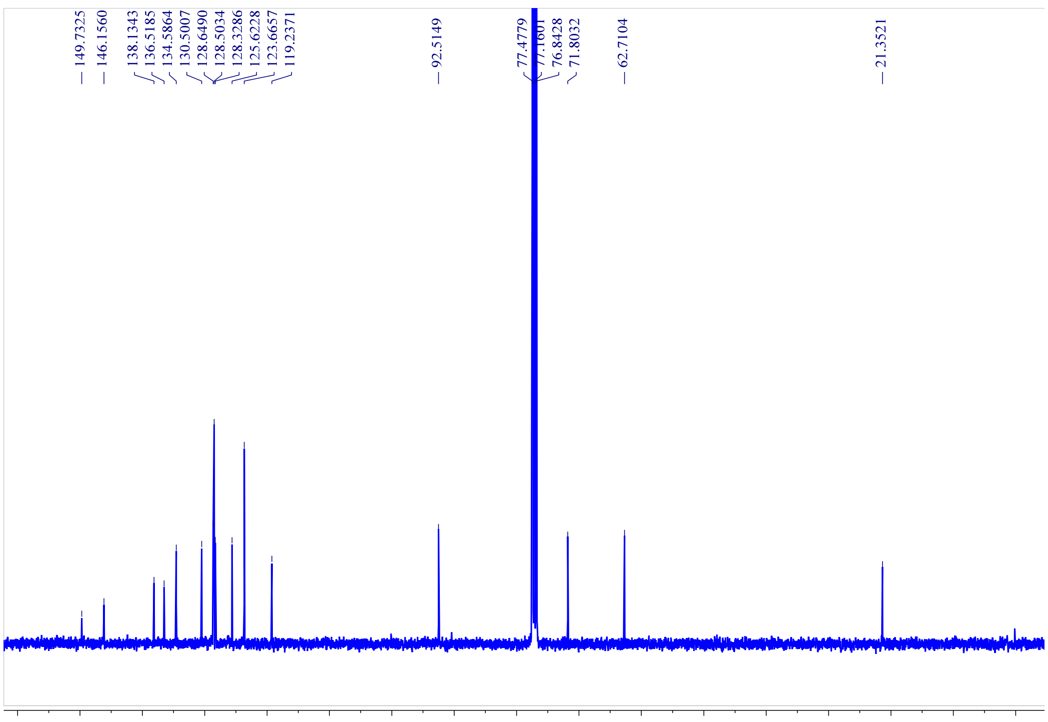
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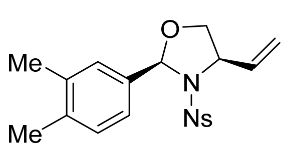
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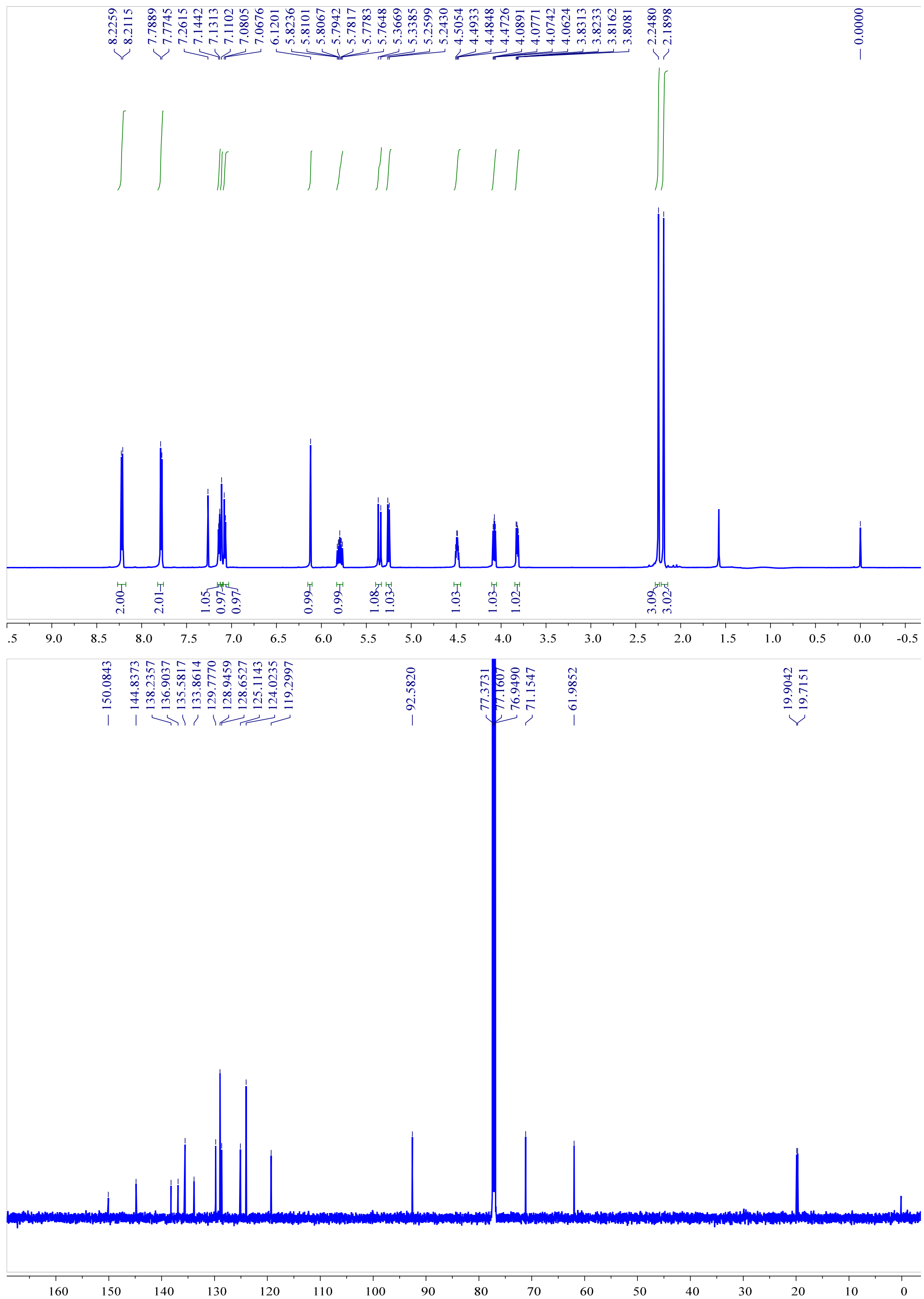
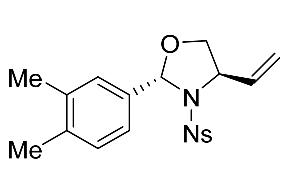
Ns

3l





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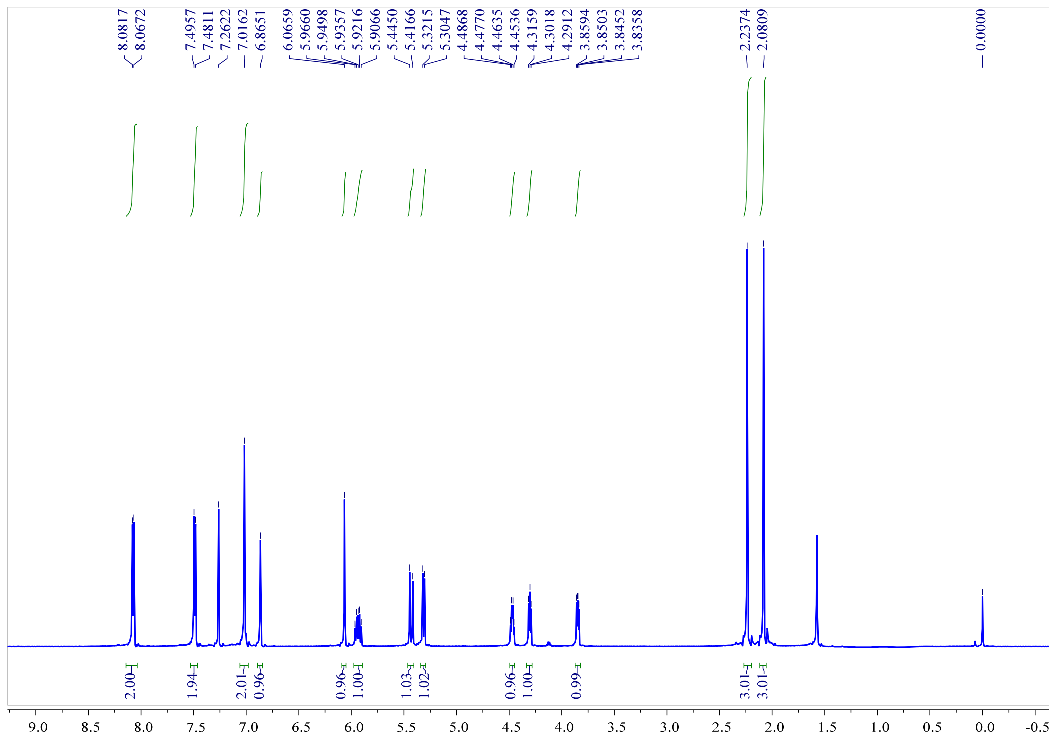
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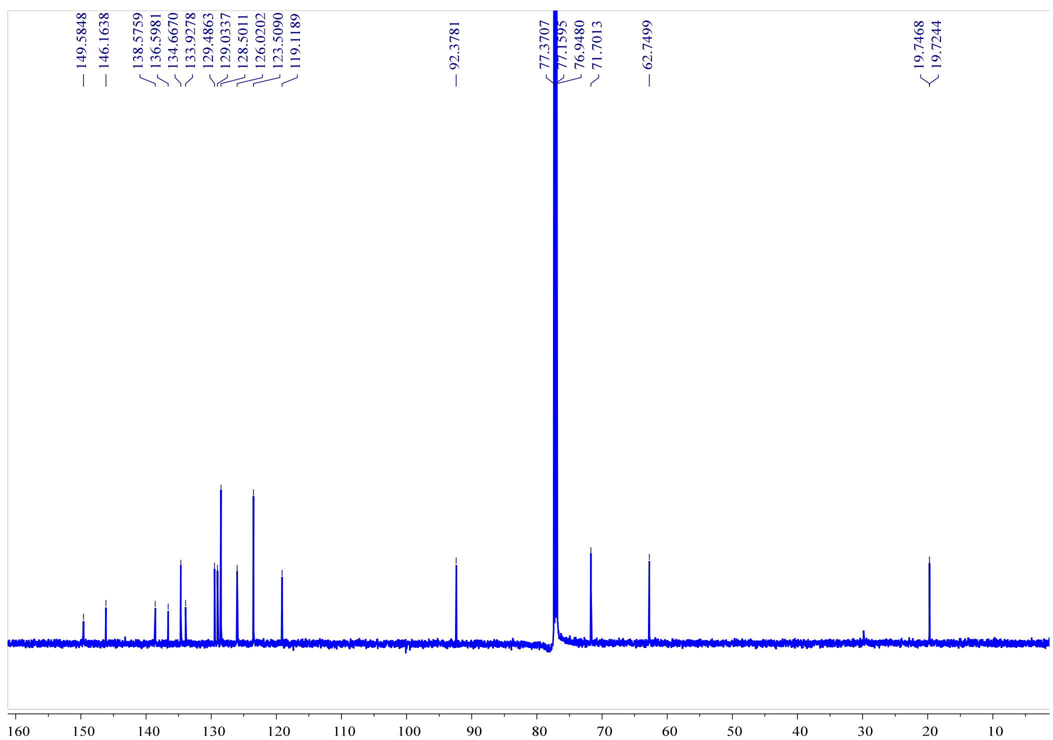
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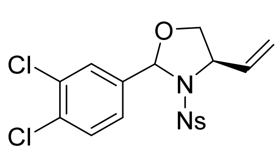
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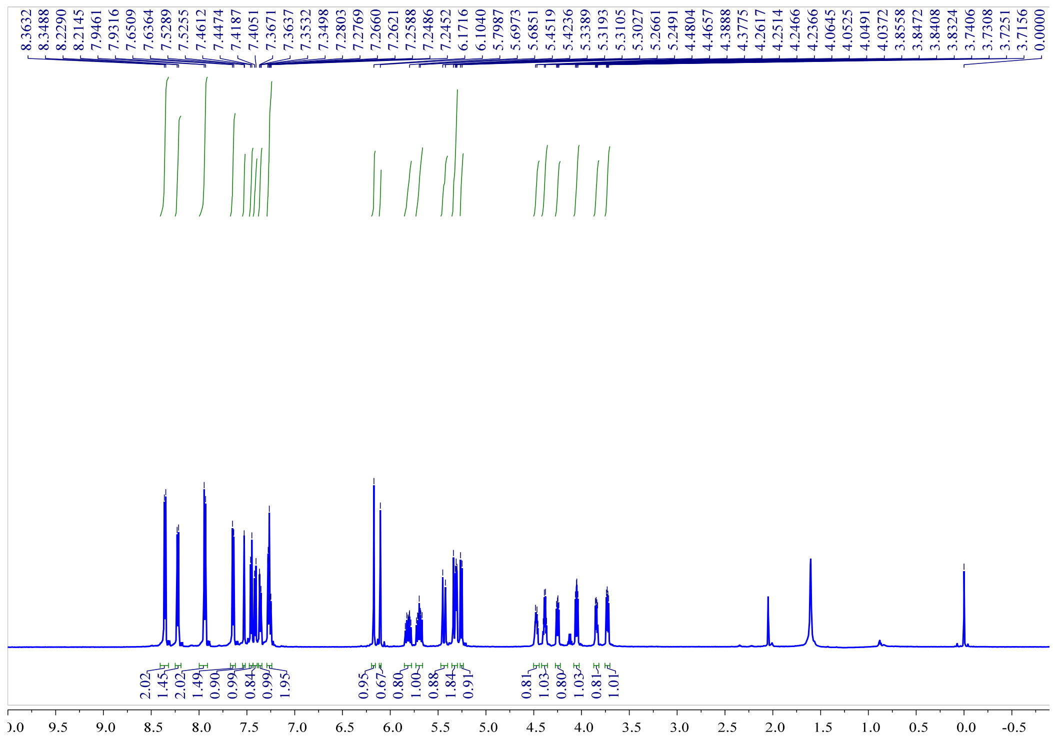

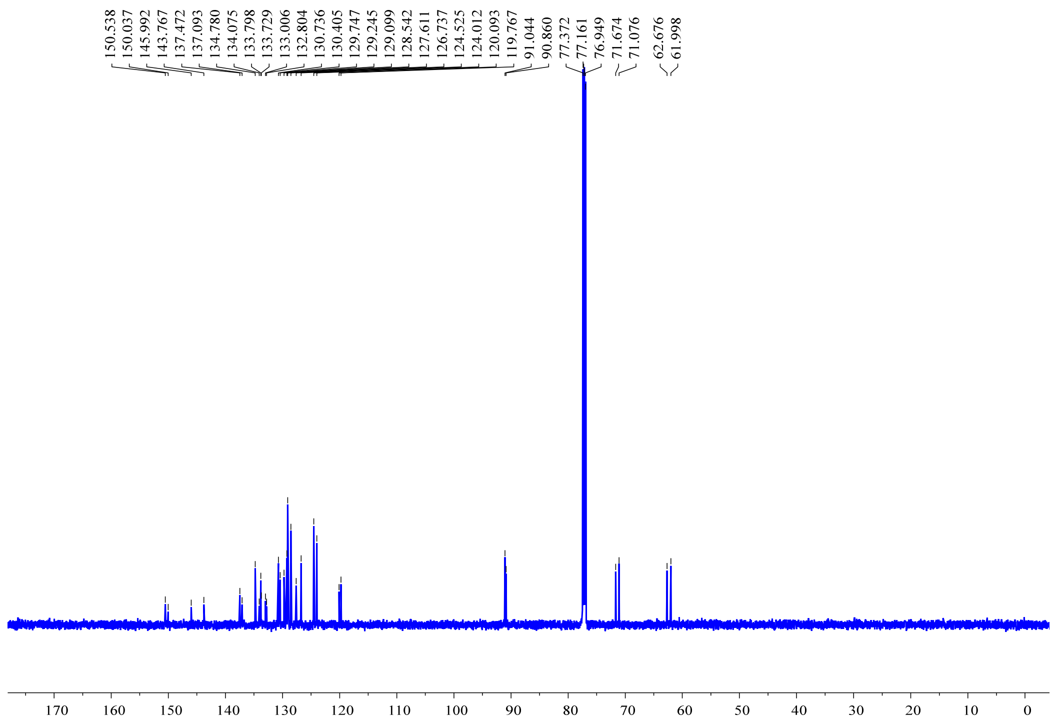

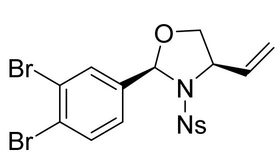

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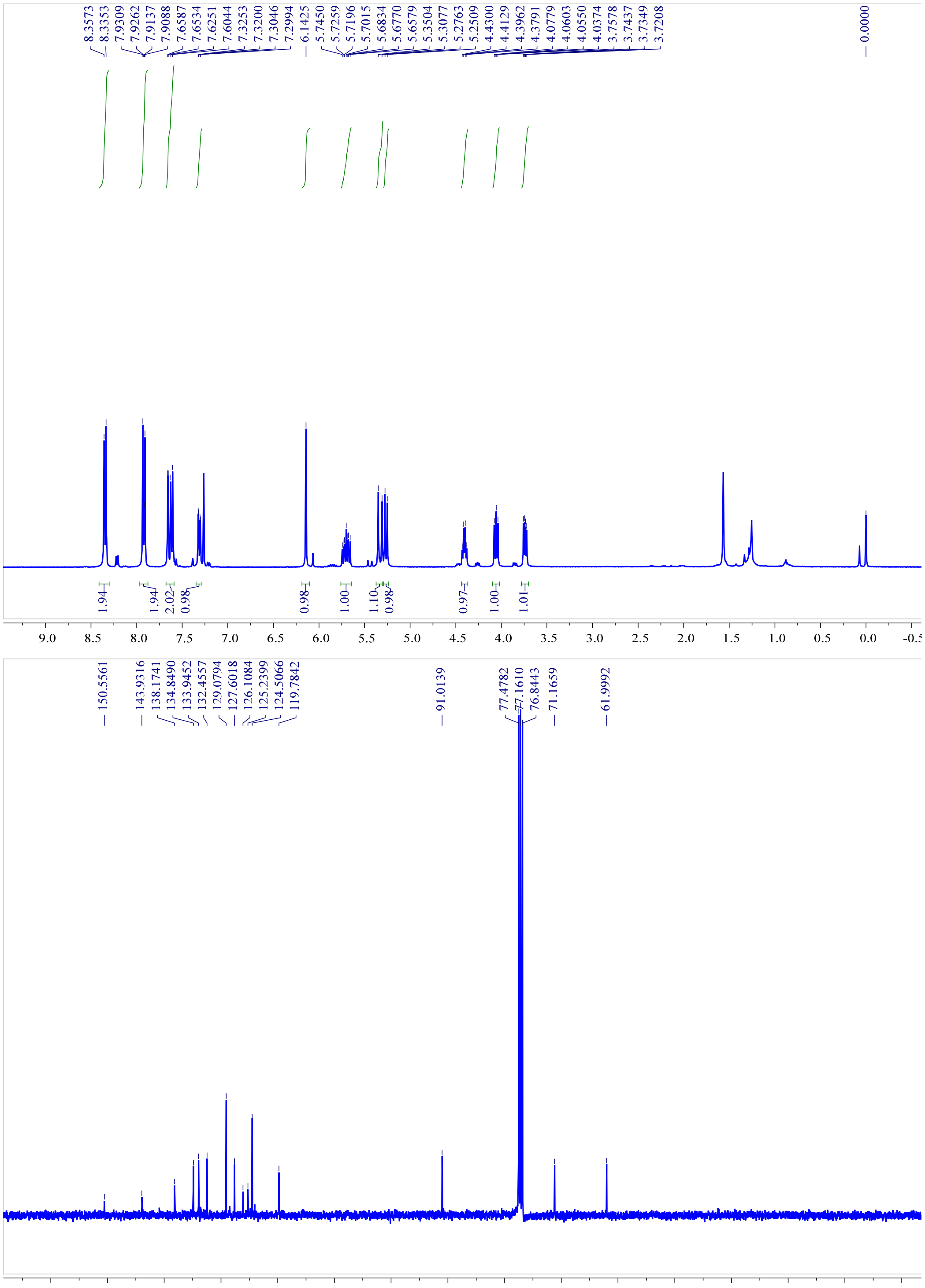
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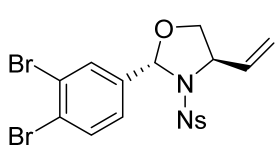
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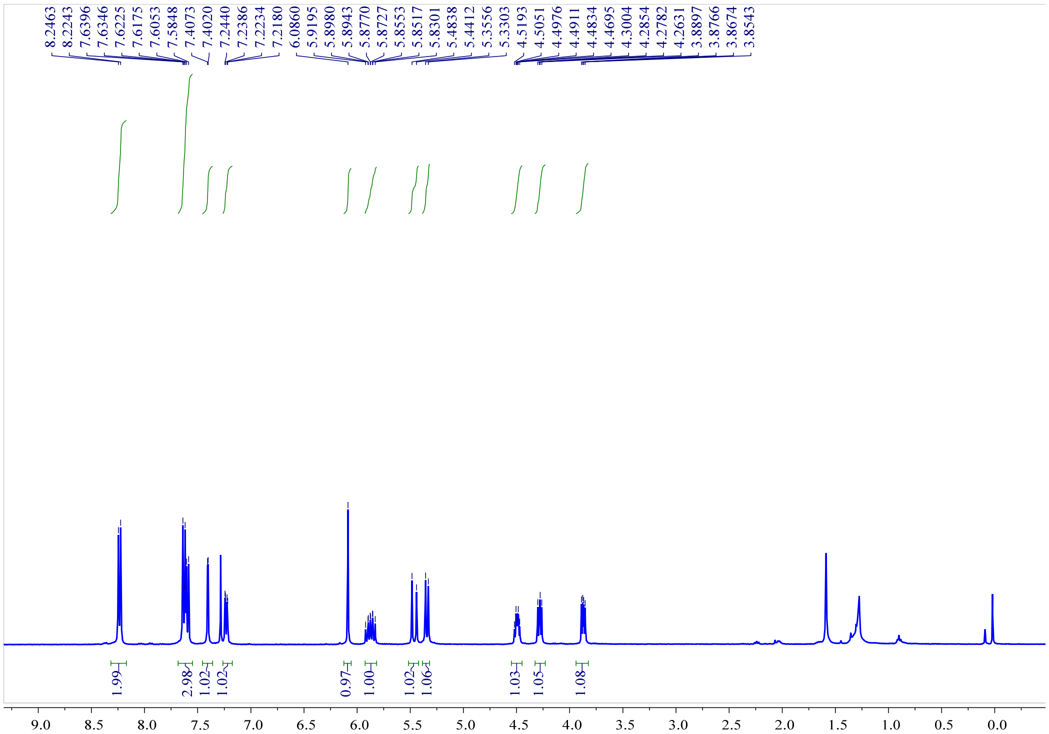
N
Ns

3m'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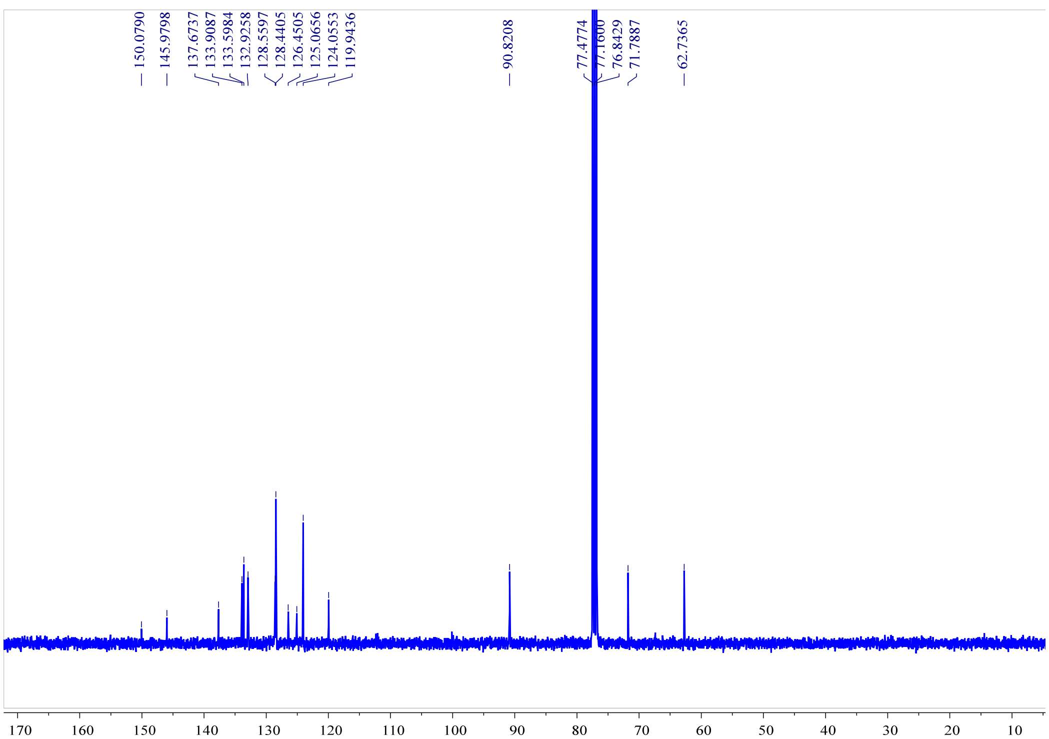
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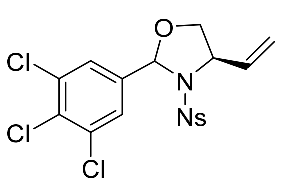
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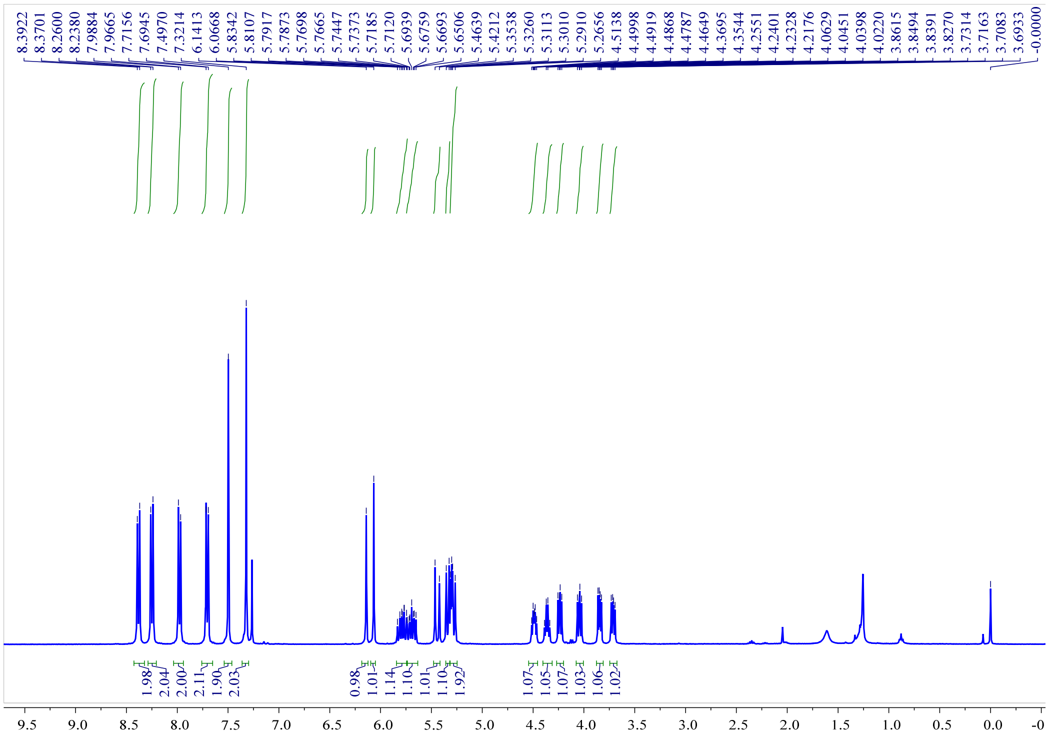
3n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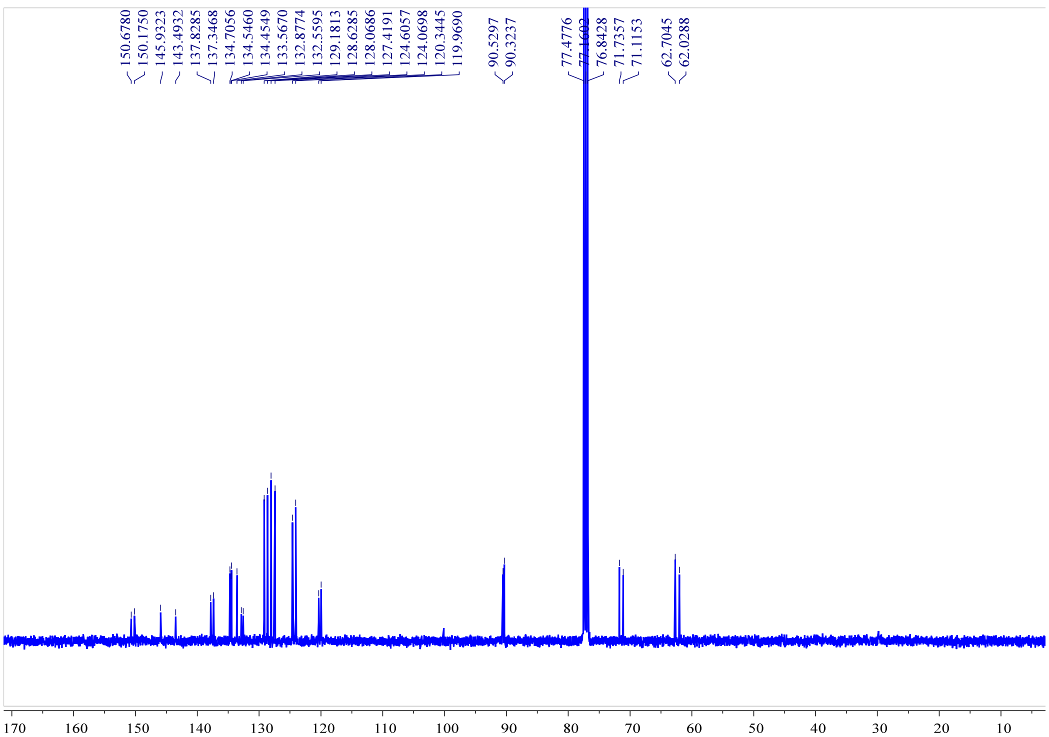
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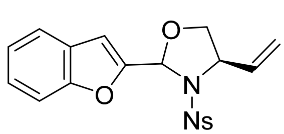
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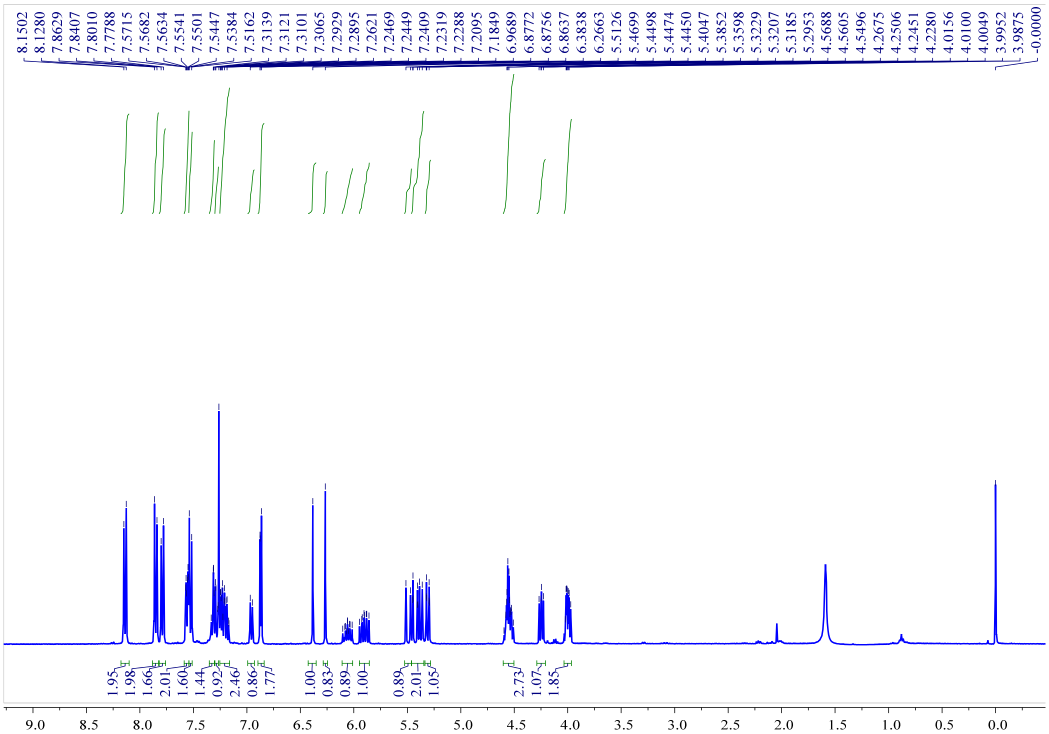
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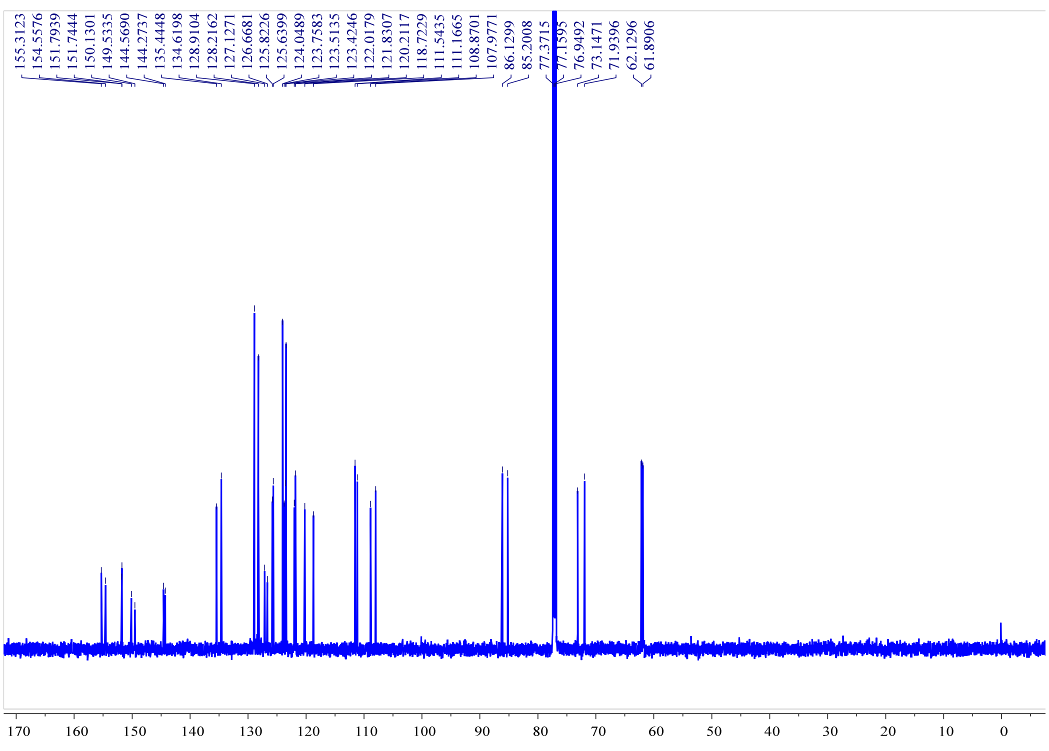
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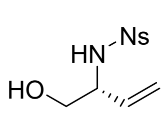
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HO

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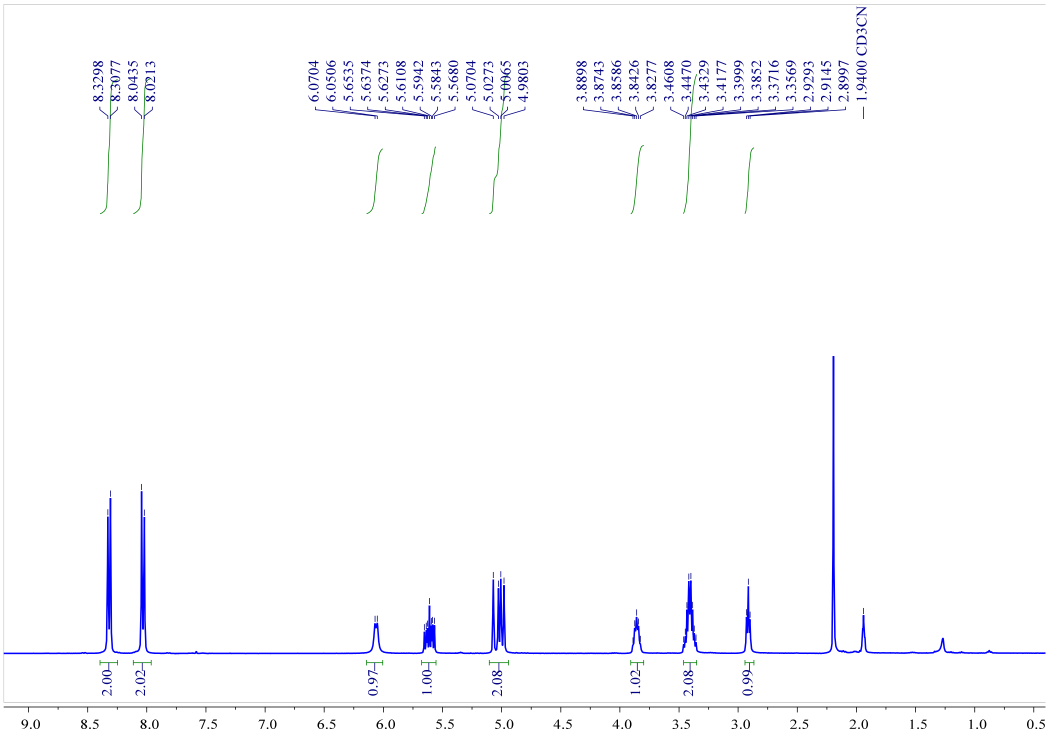
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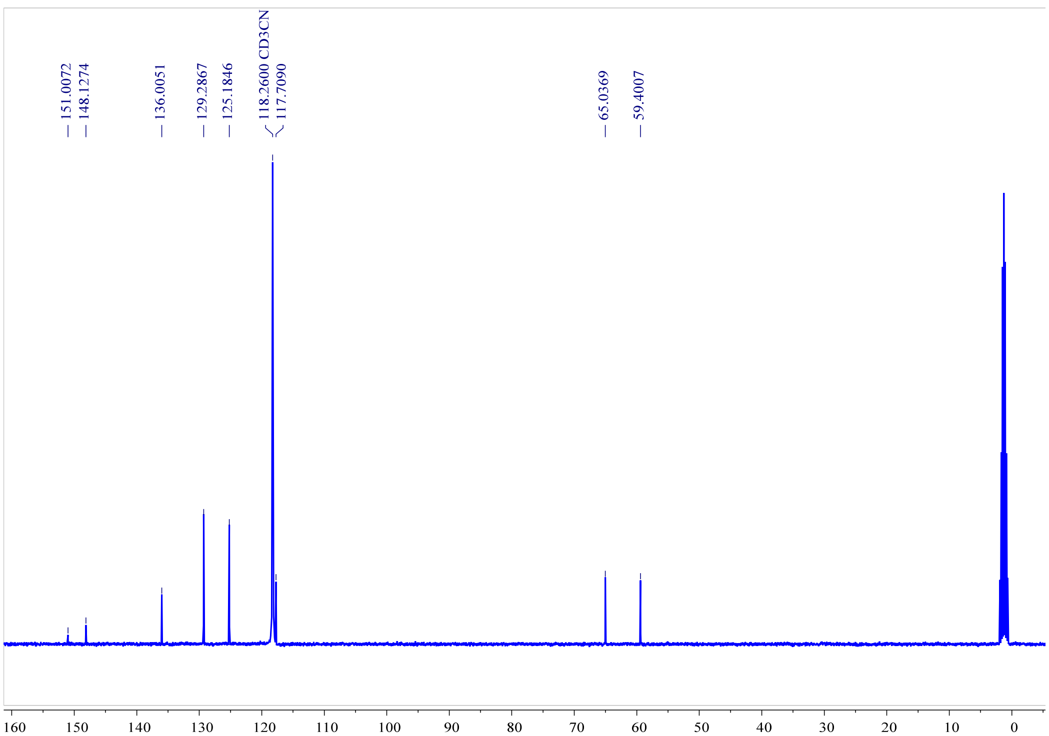
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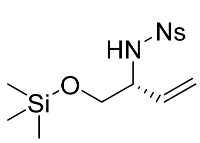
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Ns
O
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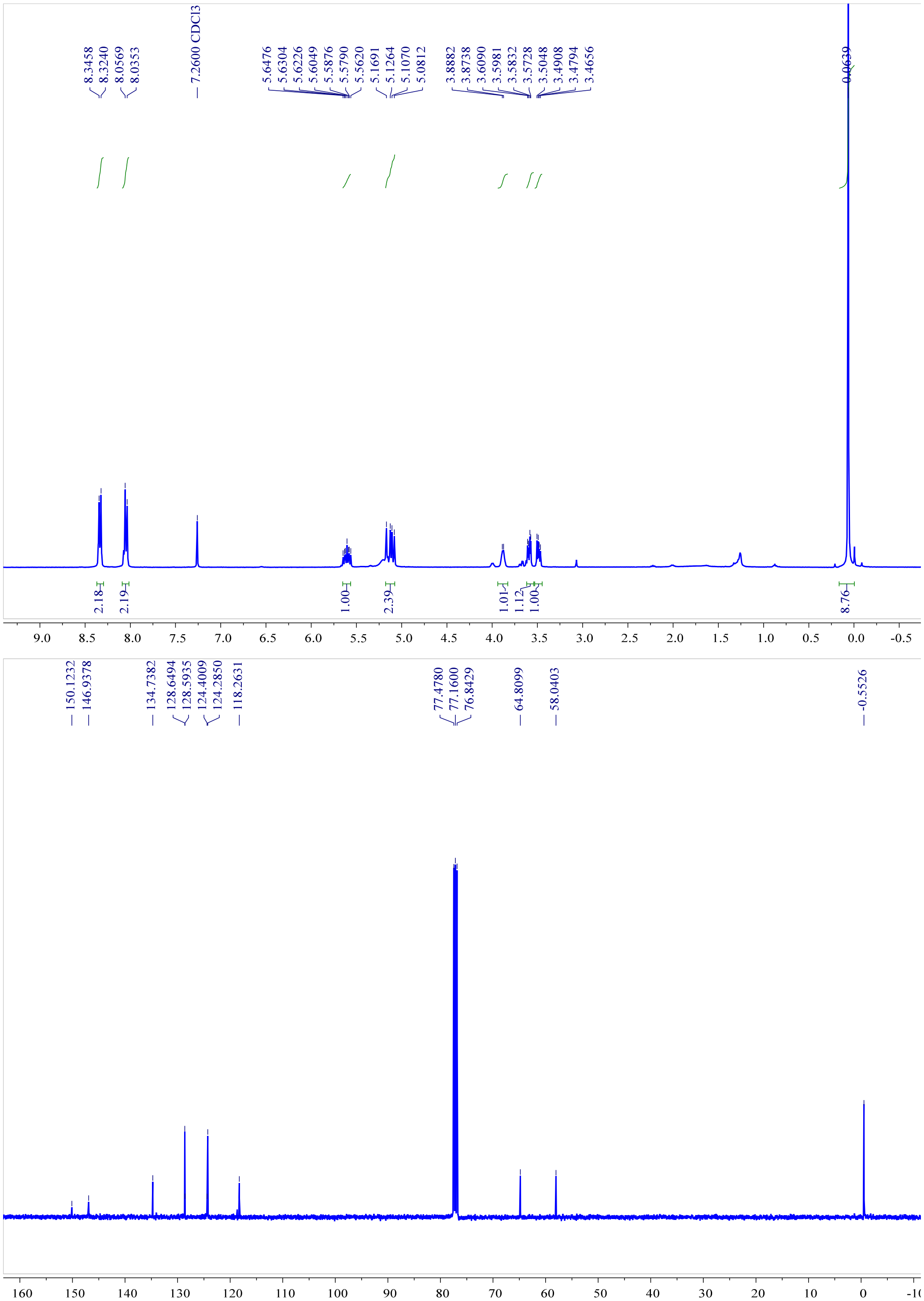
5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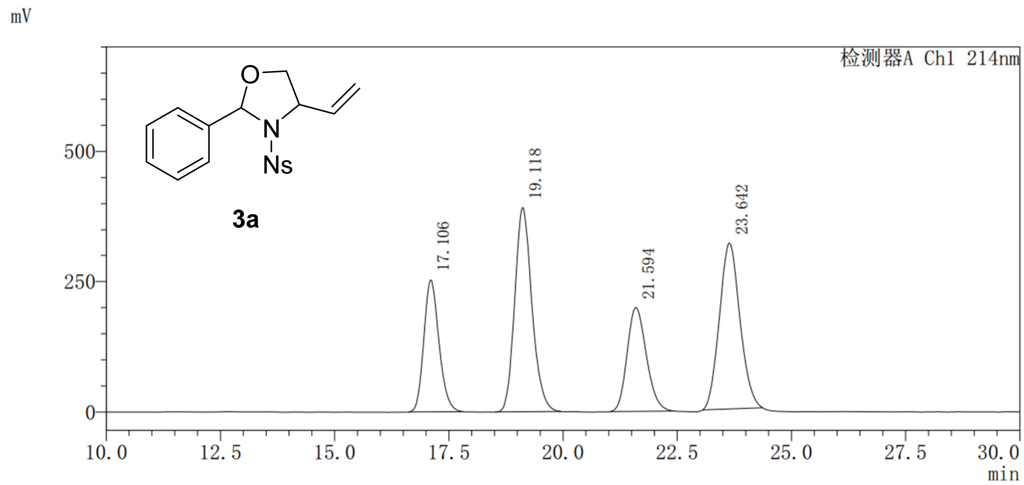
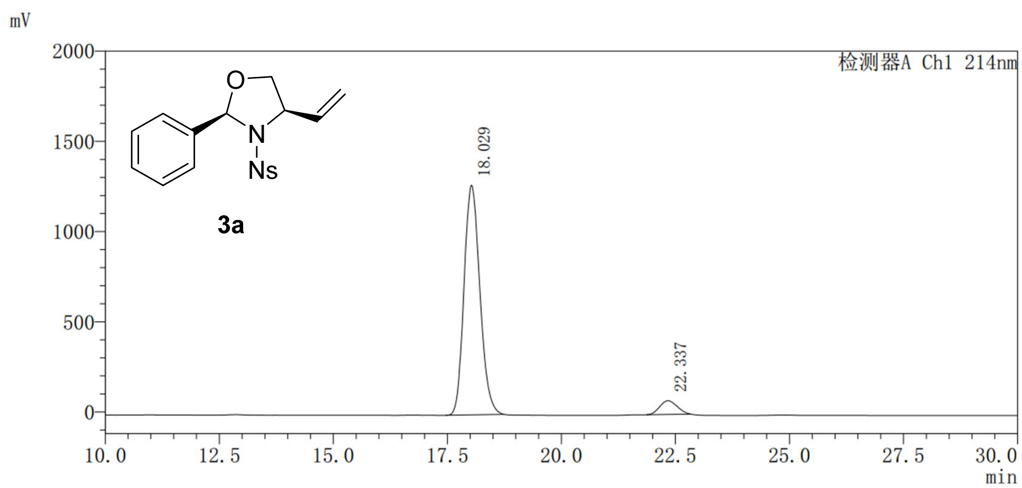
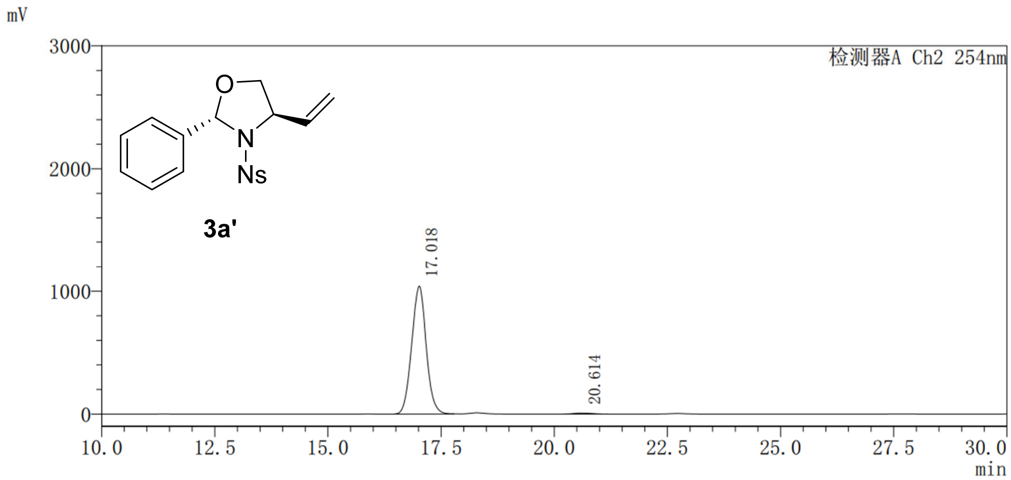
8. HPLC Spectra of compounds 3 / 3′, 4 and 5



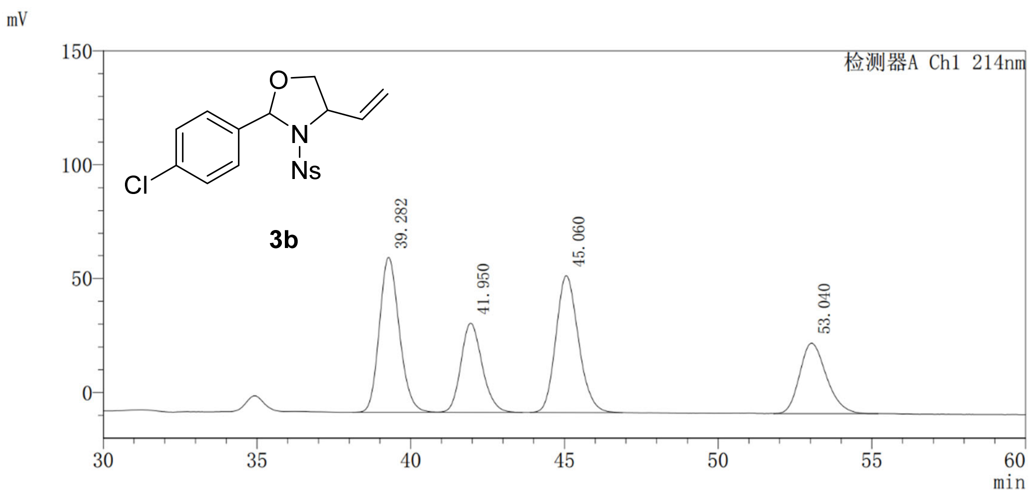
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	17.106	5836701	18.343
2	19.118	10267306	32.267
3	21.594	5807382	18.251
4	23.642	9908455	31.139
Total		31819844	100.000



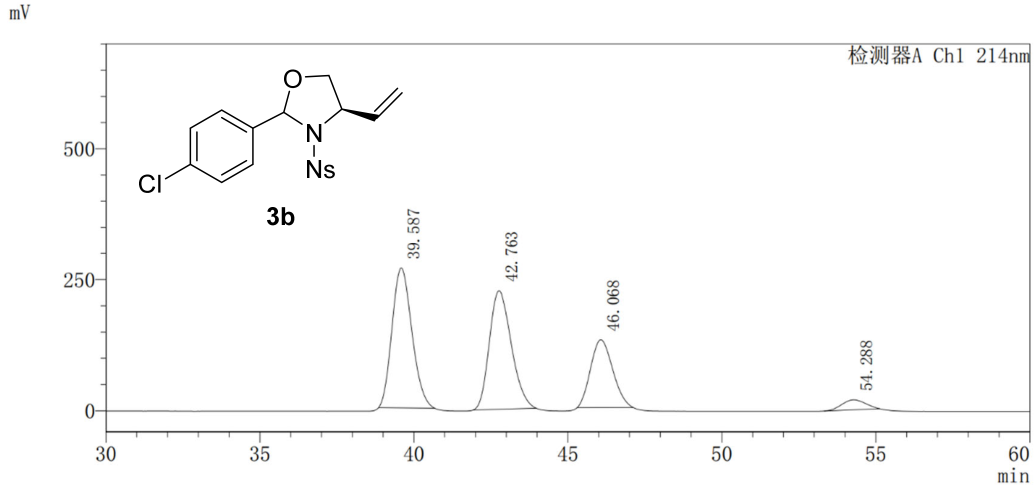
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	18.029	30932429	93.854
2	22.337	2025483	6.146
Total		32957912	100.000



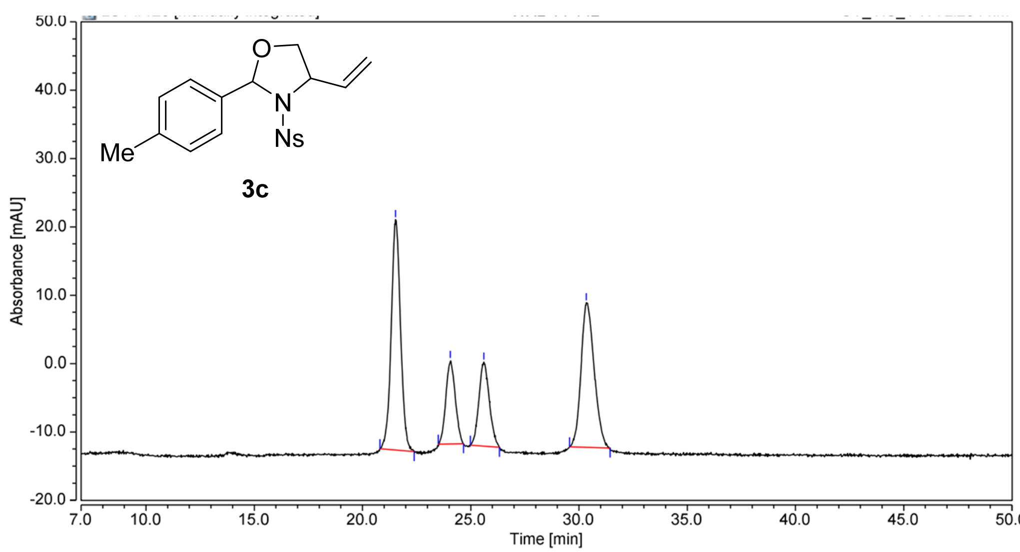
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	17.016	42570141	99.232
2	20.610	329296	0.768
Total		42899437	100.000



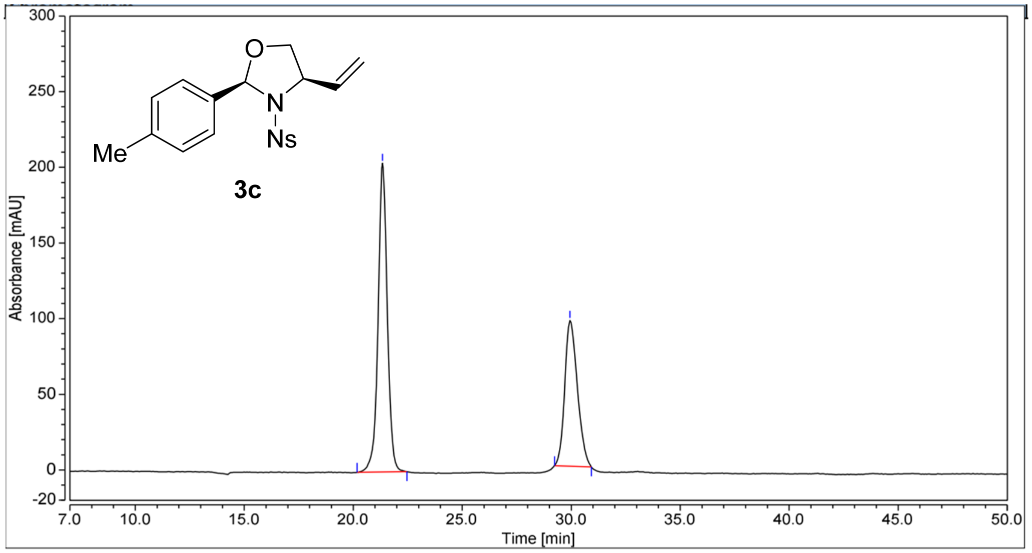
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	39.282	3056421	30.884
2	41.950	1881503	19.012
3	45.060	3075031	31.072
4	53.040	1883632	19.033
Total		9896586	100.000



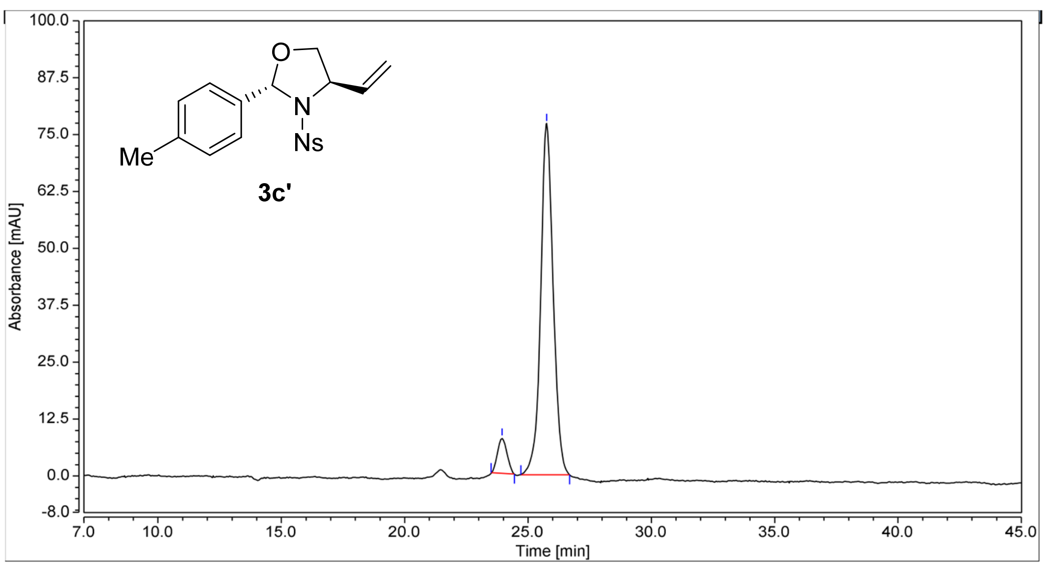
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	39.587	11954001	39.080
2	42.763	11164872	36.500
3	46.068	6459749	21.118
4	54.288	1009853	3.301
Total		30588474	100.000



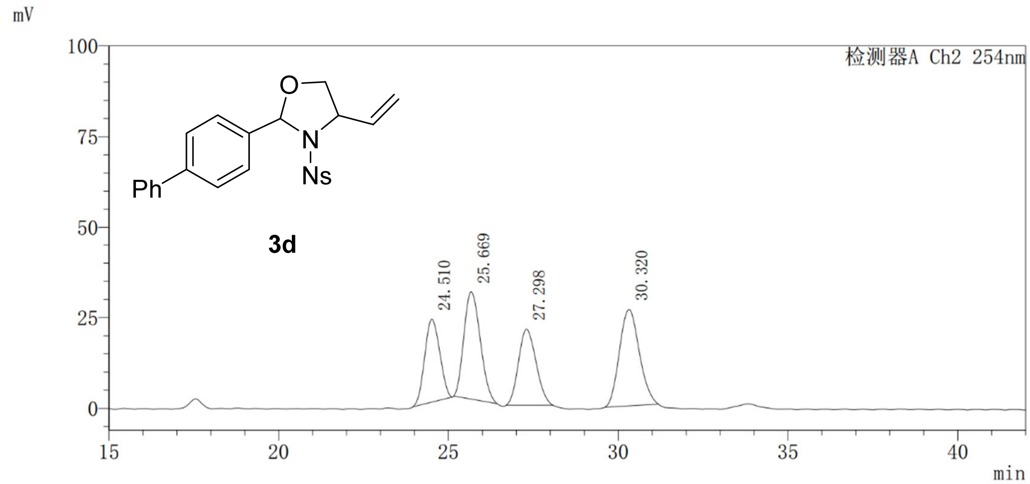
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	21.524	16.755	36.60
2	24.057	6.130	13.75
3	25.607	6.848	15.37
4	30.340	14.834	34.29
Total		44.567	100.000



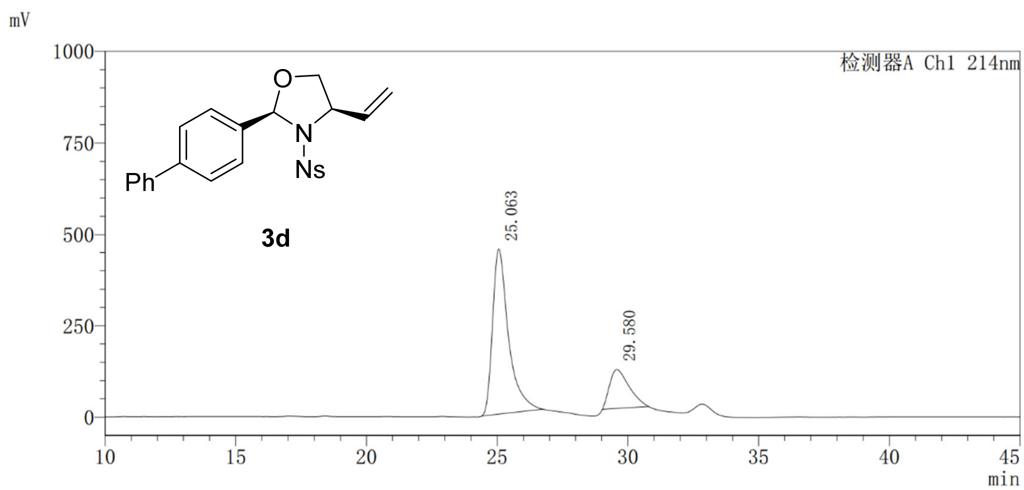
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	21.337	100.227	60.74
2	29.945	64.786	39.26
Total		165.013	100



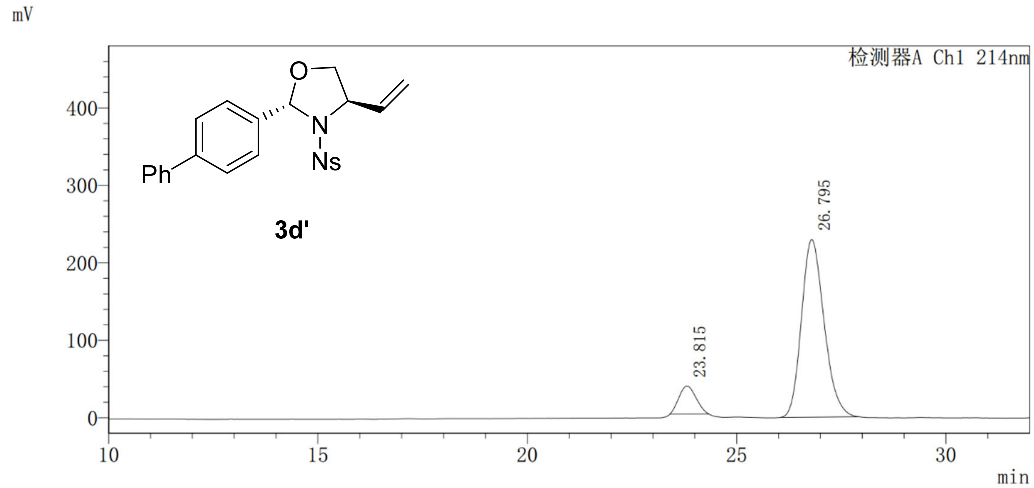
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	23.945	3.478	9.20
2	25.753	45.127	90.80
Total		48.605	100



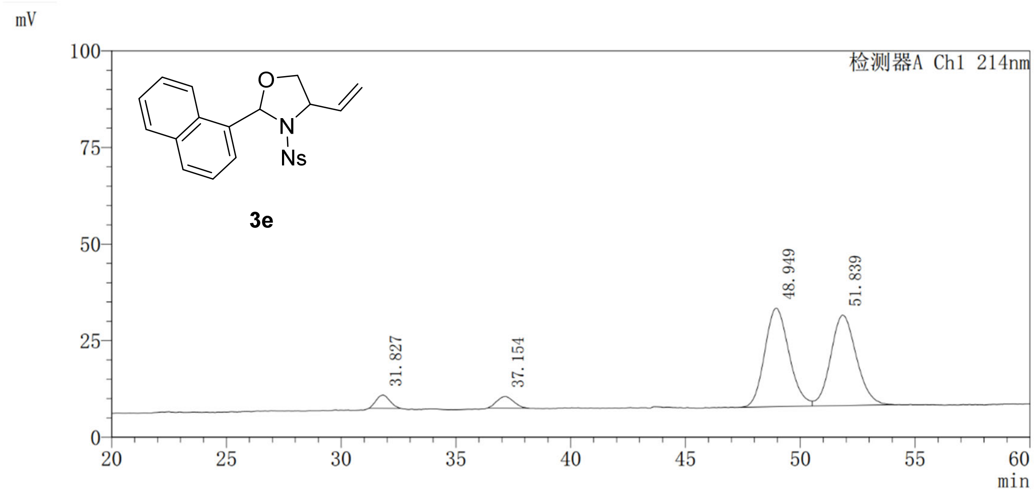
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	24.510	704199	19.900
2	25.669	994826	28.112
3	27.298	755426	21.347
4	30.320	1084290	30.641
Total		3538742	100.000



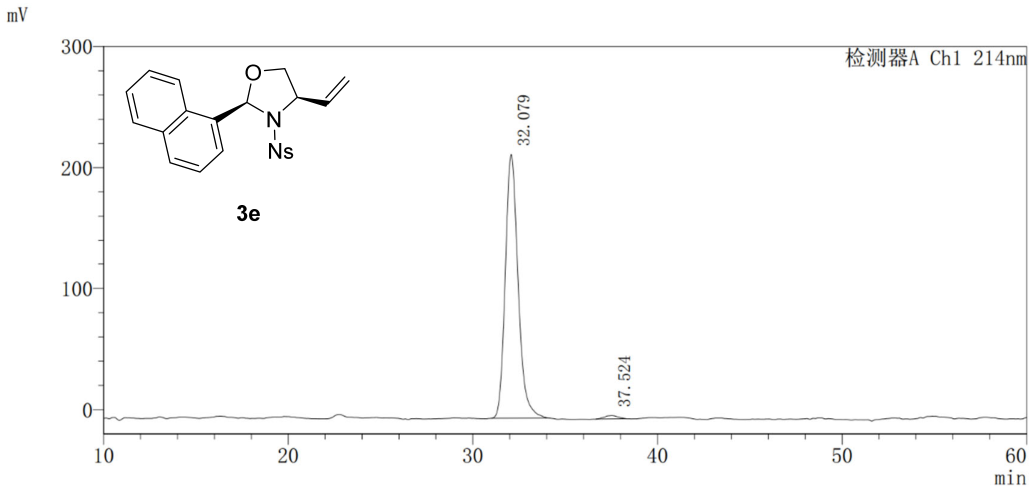
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	25.063	19100735	77.582
2	29.580	5519236	22.418
Total		24619971	100.000



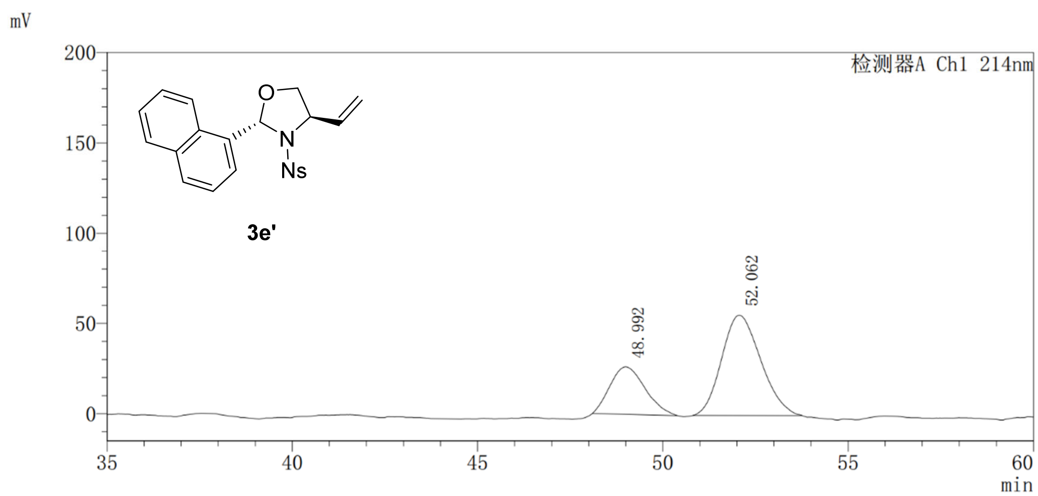
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	23.815	975158	9.981
2	26.795	8794048	90.018
Total		9769206	100.000



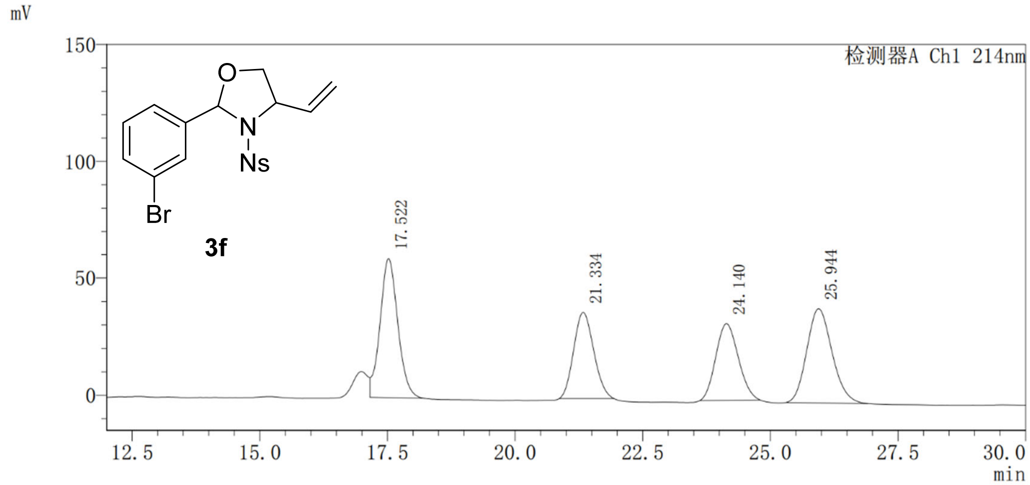
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	31.827	142559	3.561
2	37.154	150352	3.756
3	48.949	1884274	47.074
4	51.839	1825607	45.608
Total		4002792	100.000



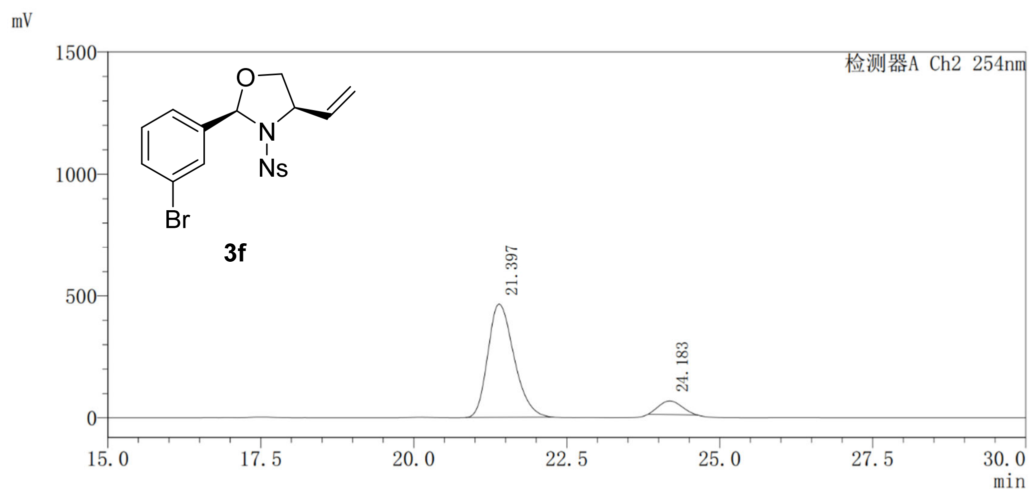
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	32.079	10530438	98.747
2	37.524	133640	1.253
Total		10664077	100.000



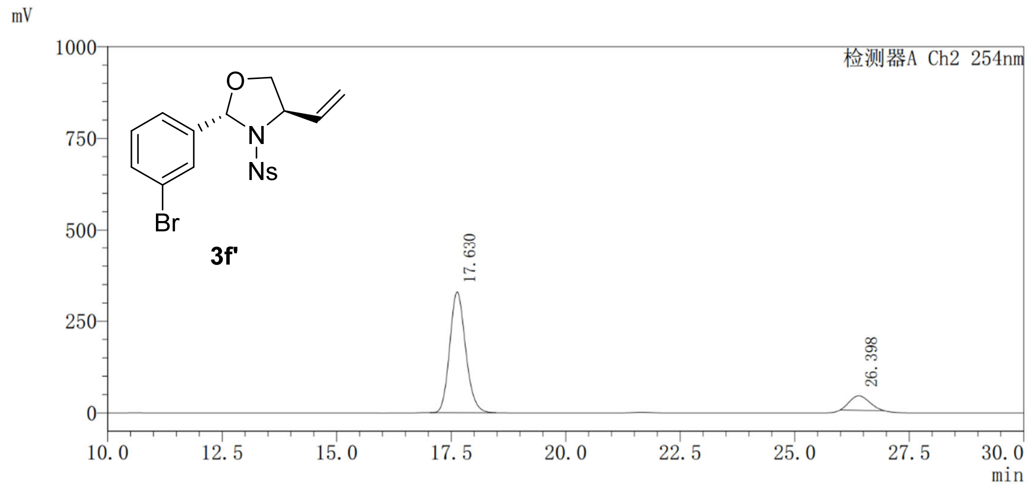
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	48.992	1731676	29.833
2	52.062	4072936	70.167
Total		5804612	100.000



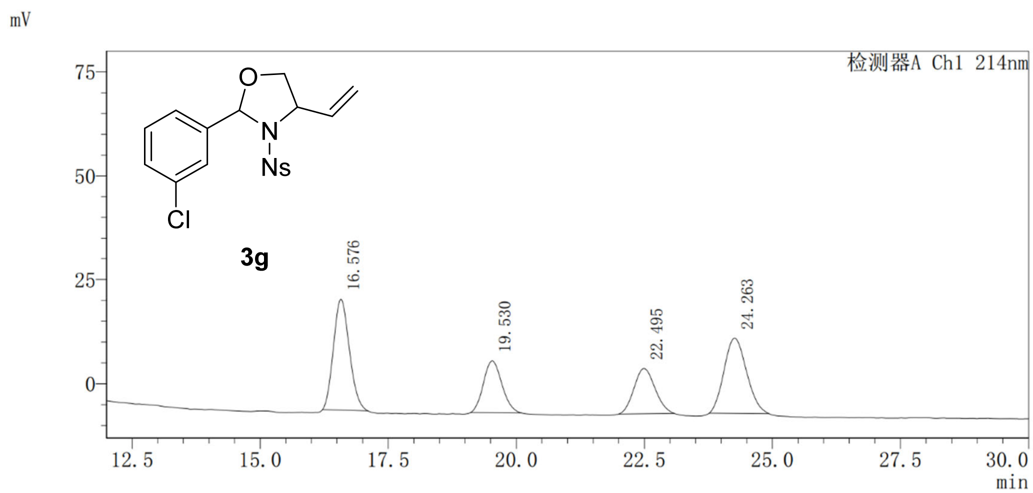
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	**17.522**	1435080	29.716
2	21.334	1004127	20.792
3	24.140	1003009	20.769
4	25.944	1387090	28.722
Total		4829306	100.000



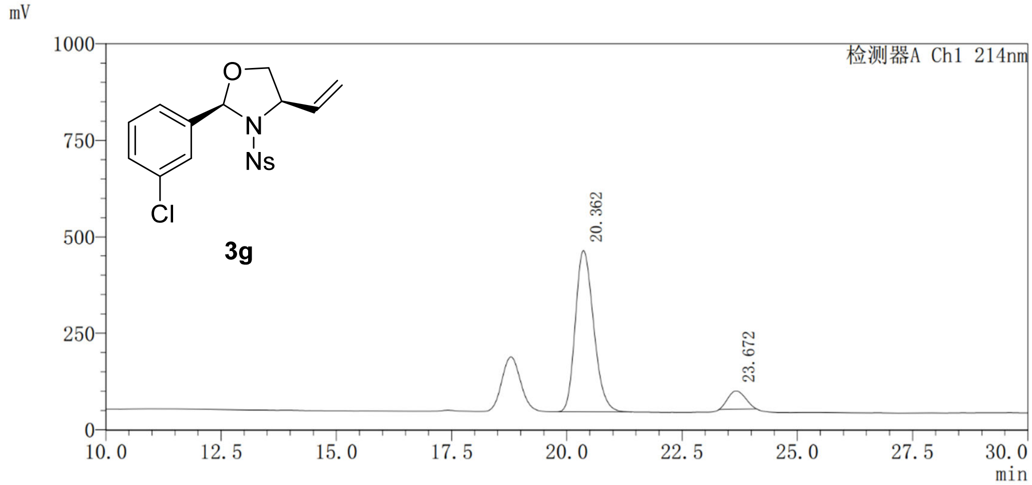
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	21.397	13839602	90.482
2	24.183	1455838	9.518
Total		15295440	100.000



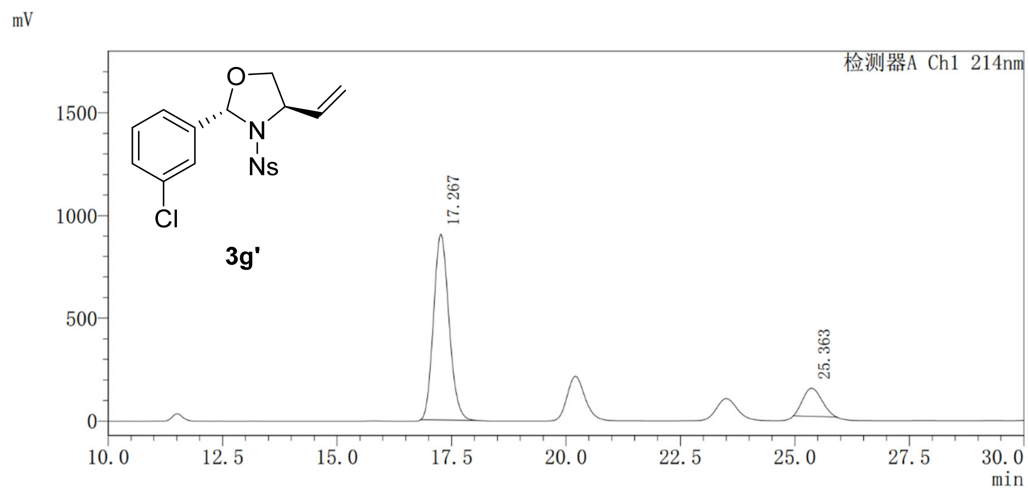
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	17.630	7960221	87.138
2	26.398	1174972	12.862
Total		9135193	100.000



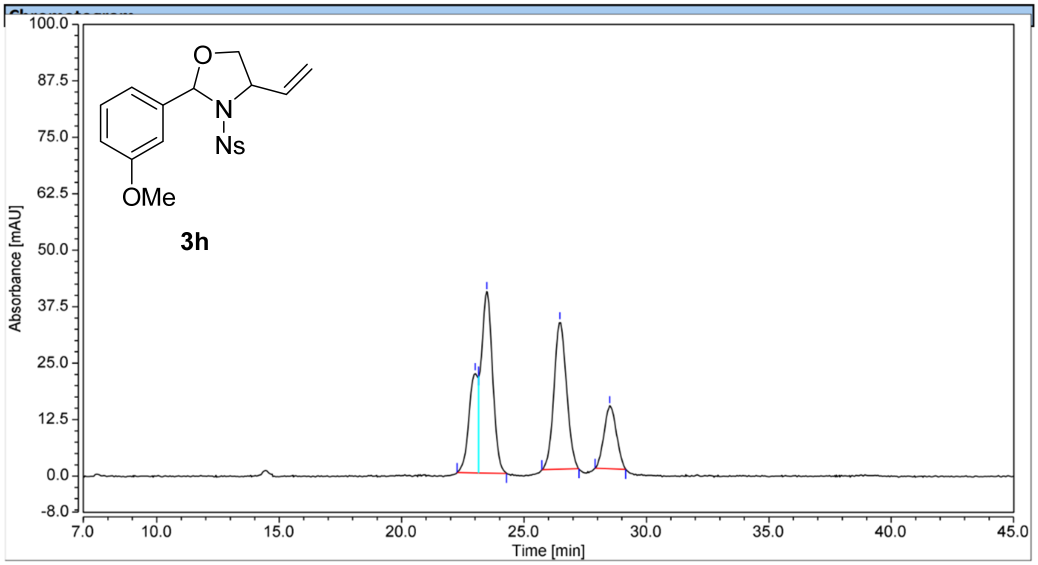
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	16.576	576484	32.894
2	19.530	312817	17.849
3	22.495	310431	17.713
4	24.263	552821	31.544
Total		1752554	100.000



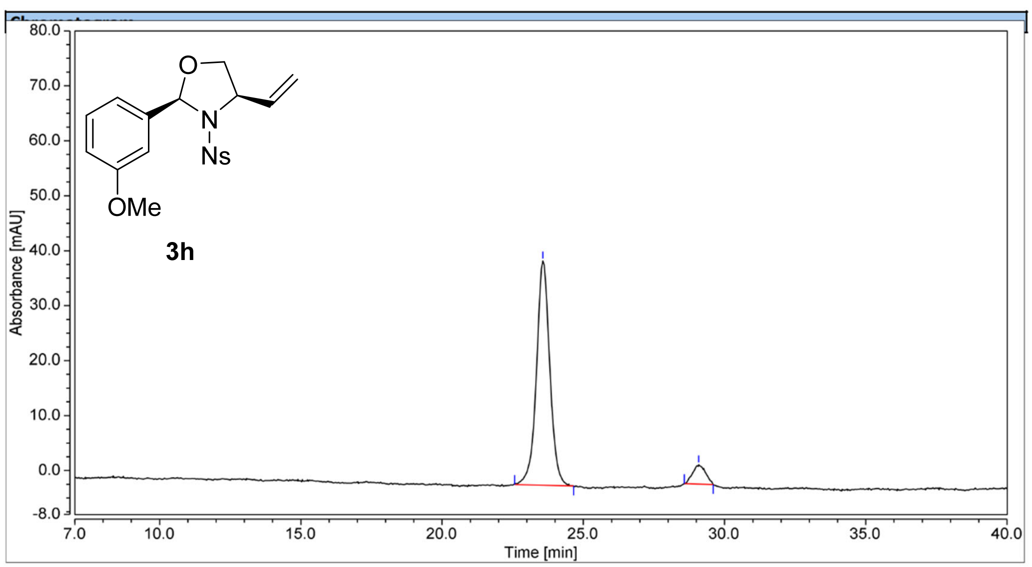
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	20.362	11548122	90.231
2	23.672	1250333	9.769
Total		12798455	100.000



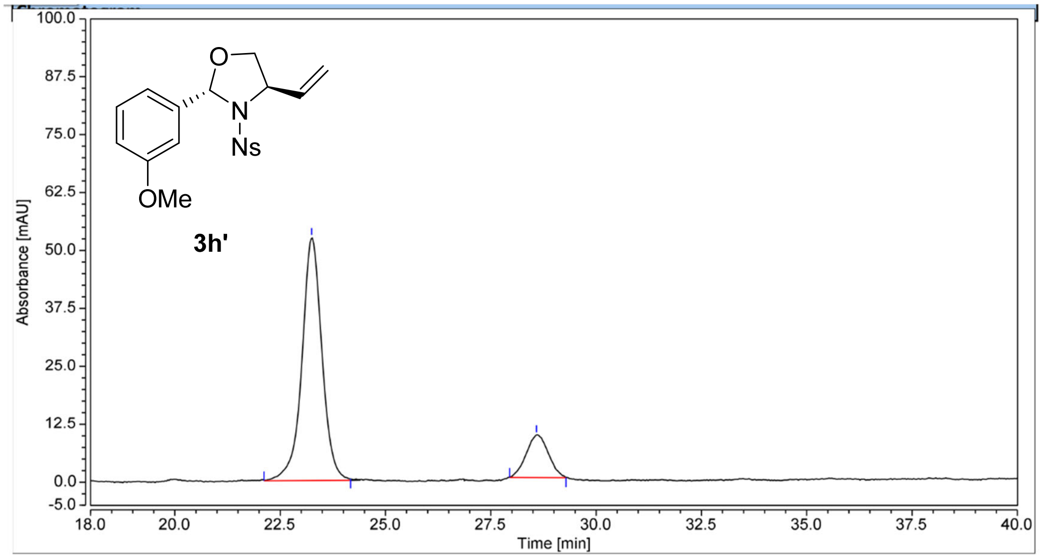
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	17.267	21150588	84.228
2	25.363	3960574	15.772
Total		25111163	100.000



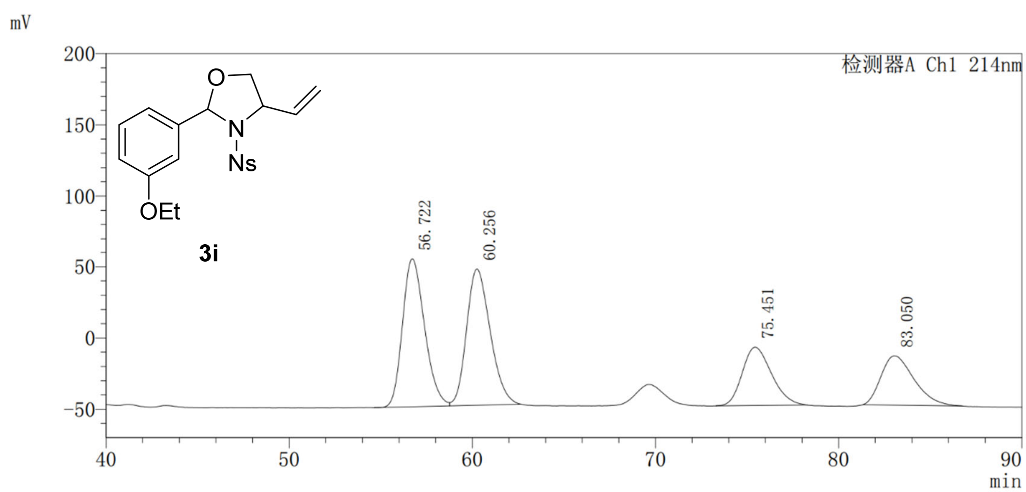
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	23.012	9.484	15.21
2	23.485	21.466	35.68
3	26.465	19.433	34.21
4	28.505	8.139	14.91
Total		58.521	100.000



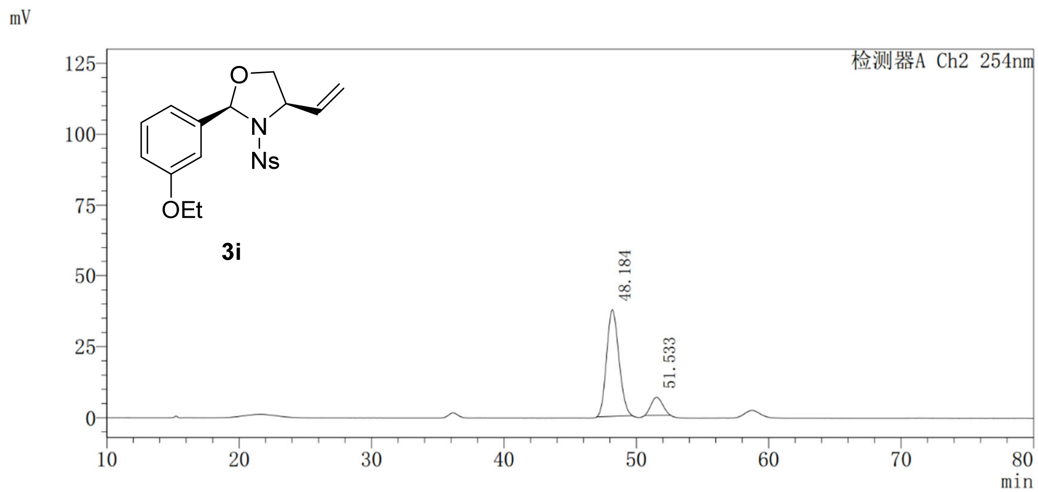
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	23.566	22.356	92.39
2	29.086	1.841	7.61
Total		24.197	100.000



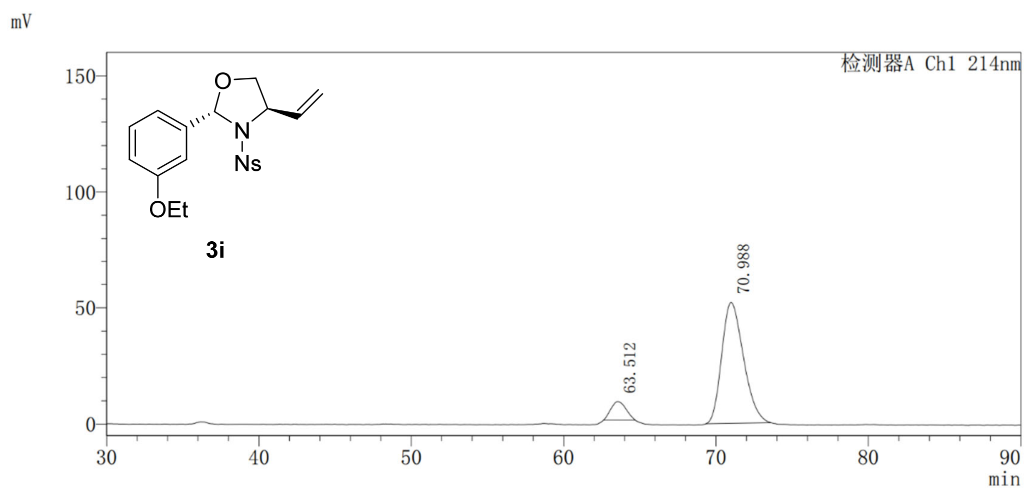
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	23.246	28.958	83.79
2	28.586	5.604	16.21
Total		34.562	100.000



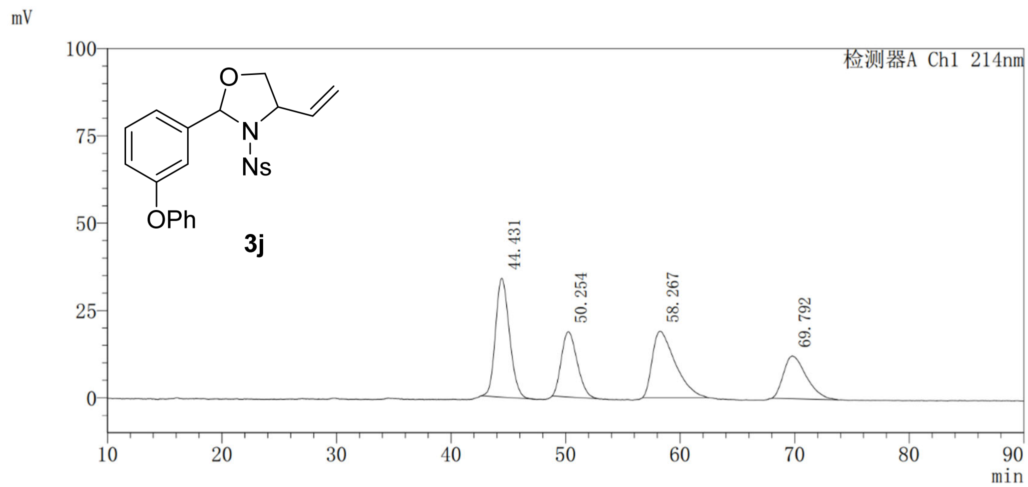
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	56.722	8718047	33.238
2	60.256	8613710	32.840
3	75.451	4553943	17.362
4	83.050	4343843	16.561
Total		26229542	100.000



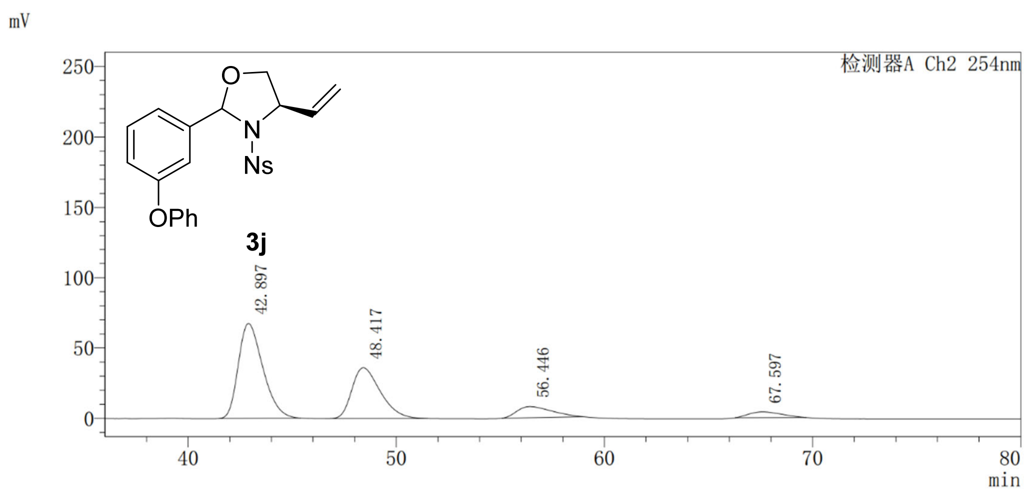
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	48.184	2425553	86.347
2	51.533	383534	13.653
Total		2809087	100.000



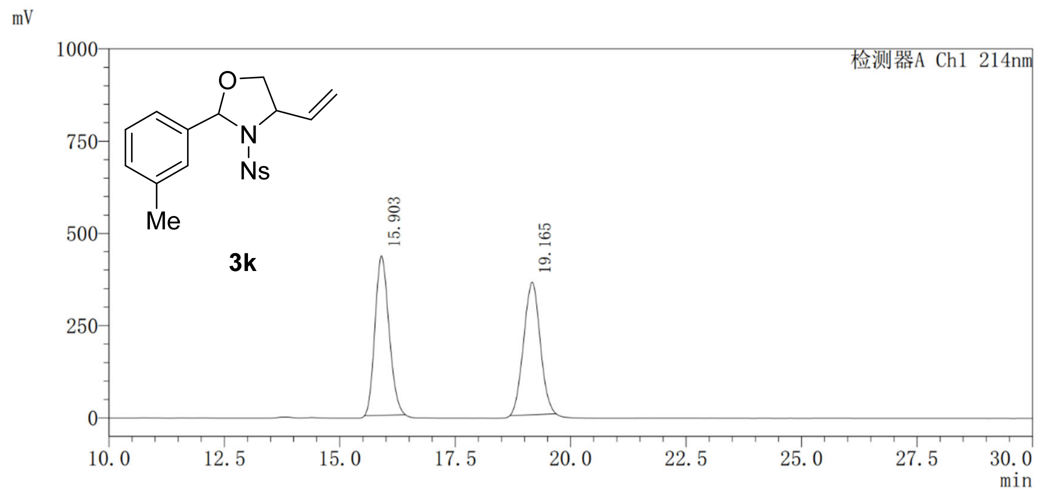
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	63.512	551111	9.653
2	70.988	5158395	90.347
Total		5709507	100.000



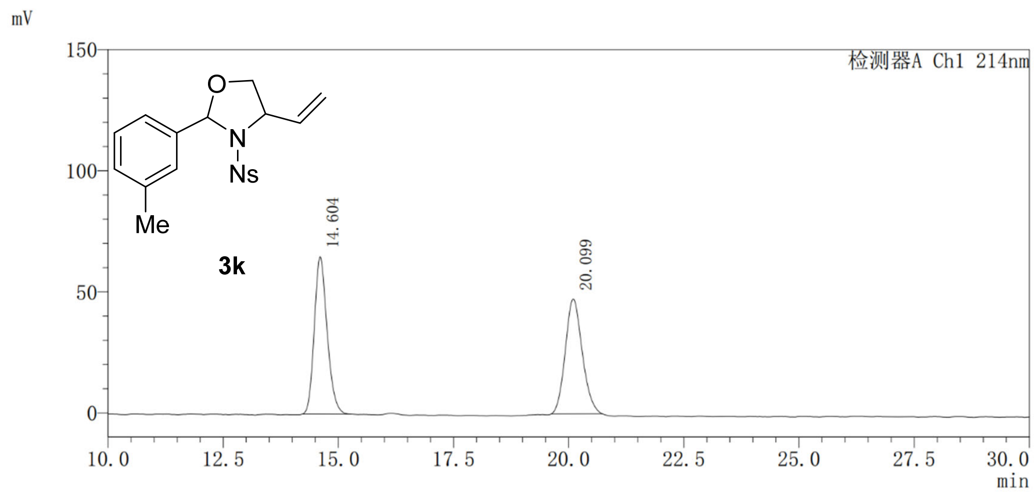
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	44.431	2886227	31.910
2	50.254	1800761	19.909
3	58.267	2655459	29.359
4	69.792	1702331	18.821
Total		9044778	100.000



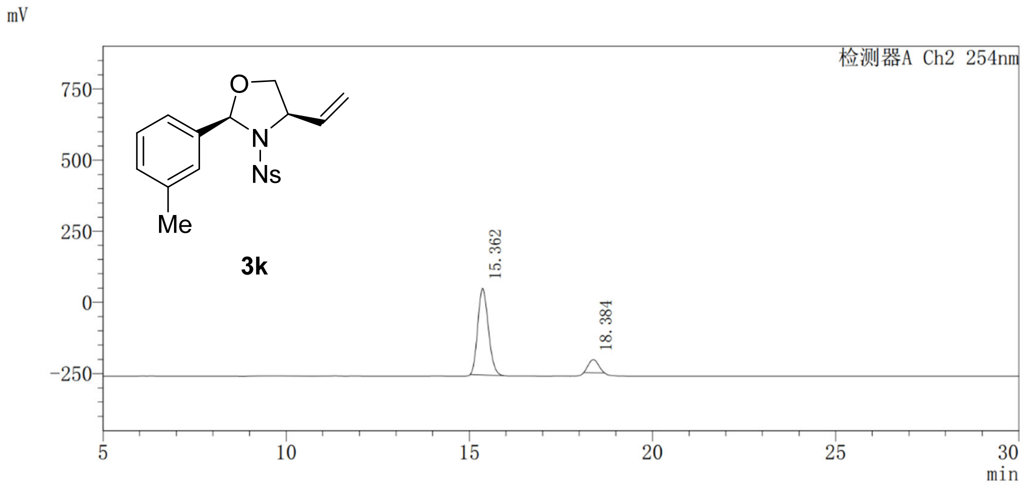
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	42.897	5519302	53.380
2	48.417	3445528	33.324
3	56.446	921351	8.911
4	67.597	453378	4.385
Total		10339559	100.000



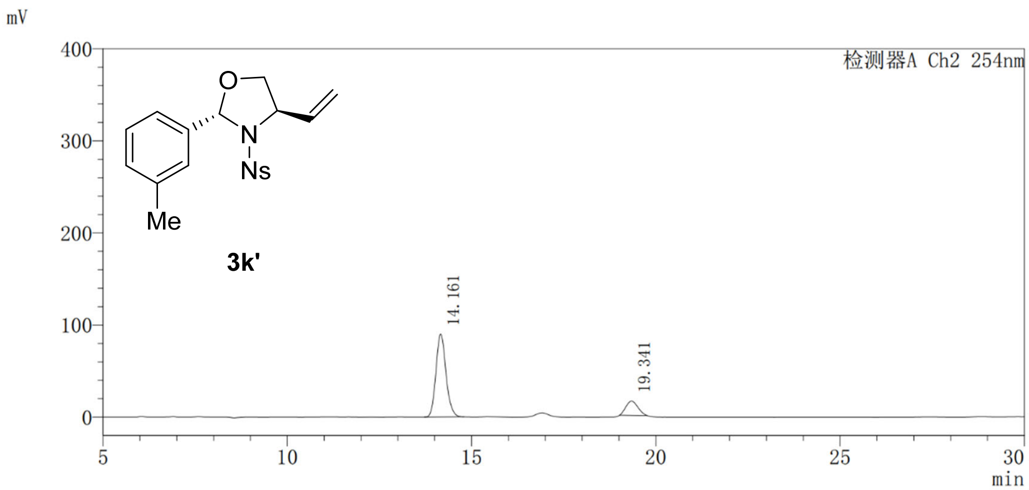
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	15.903	9136961	50.489
2	19.165	8959816	49.511
Total		18096777	100.000



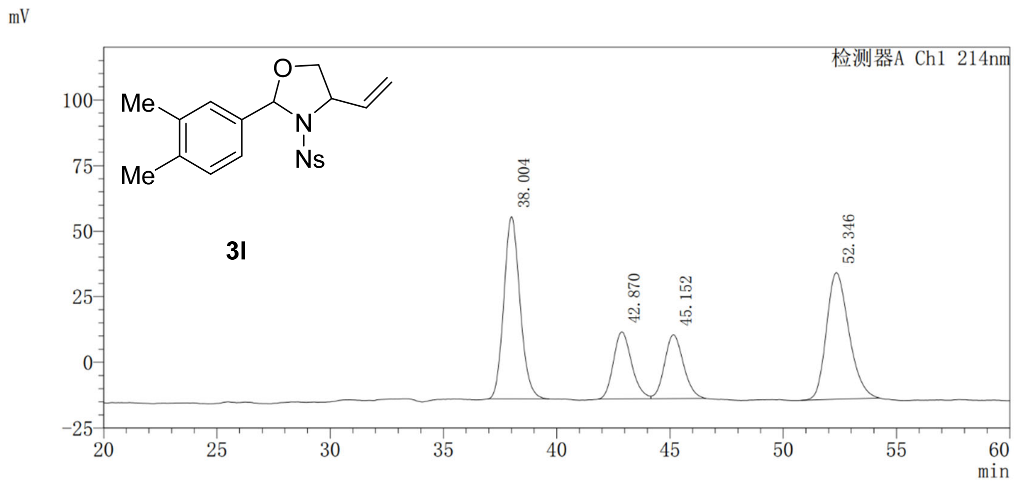
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	14.604	1264614	50.954
2	20.099	1217248	49.046
Total		2481861	100.000



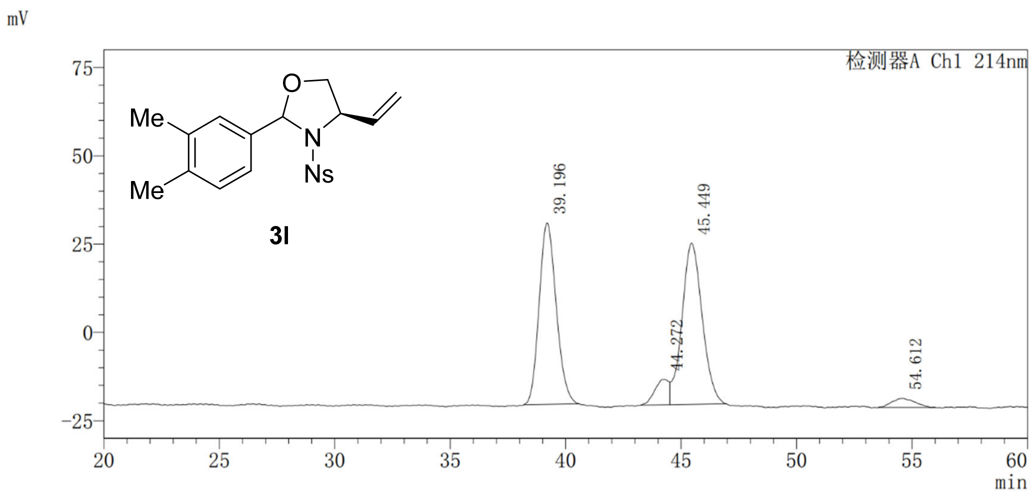
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	15.362	6113905	87.668
2	18.384	860035	12.332
Total		6973940	100.000



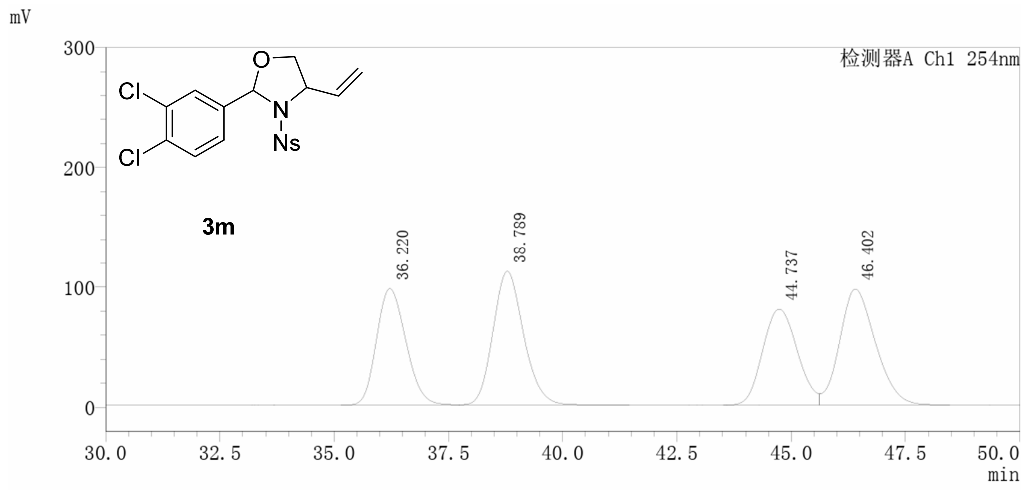
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	14.161	1713244	83.017
2	19.341	350476	16.983
Total		2063720	100.000



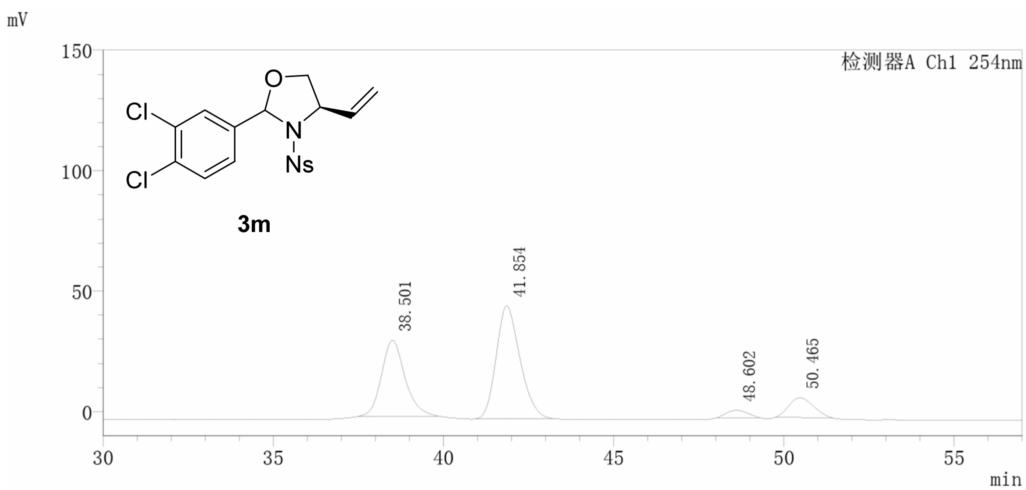
Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	38.004	3449617	35.892
2	42.870	1429065	14.869
3	45.152	1406736	14.636
4	52.346	3325763	34.603
Total		9611181	100.000



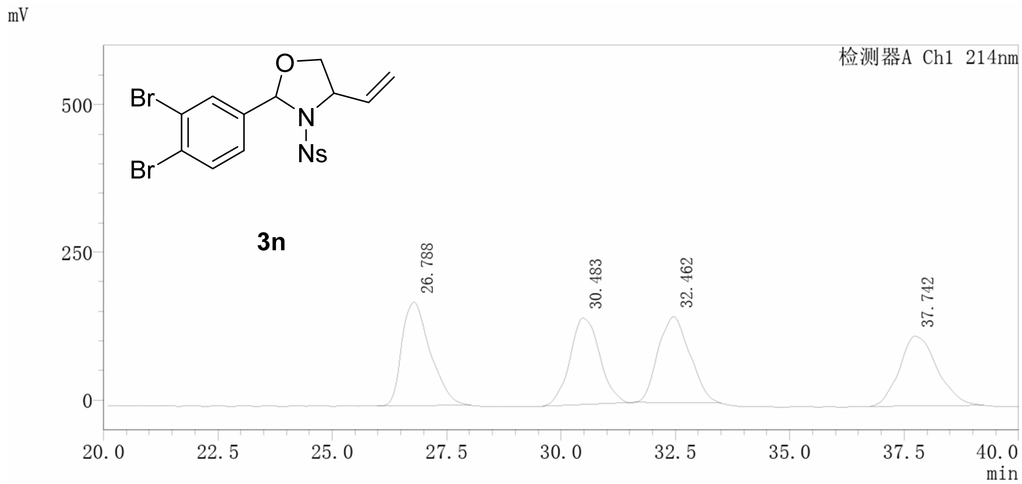
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	39.196	2643867	44.656
2	44.272	306555	5.178
3	45.449	2793066	47.176
4	54.612	177080	2.991
Total		5920568	100.000



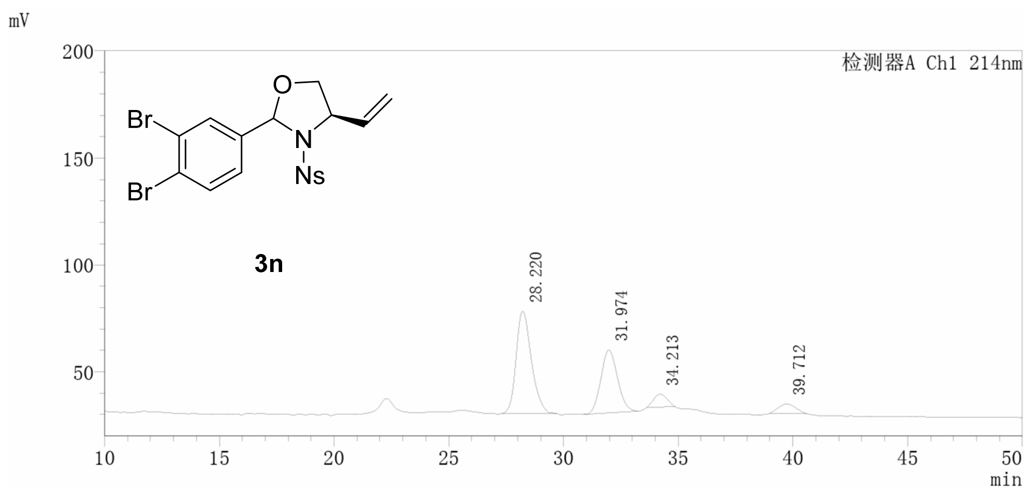
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	36.220	4302473	22.744
2	38.789	5167317	27.316
3	44.737	4199722	22.201
4	46.402	5247190	27.738
Total		18916701	100.000



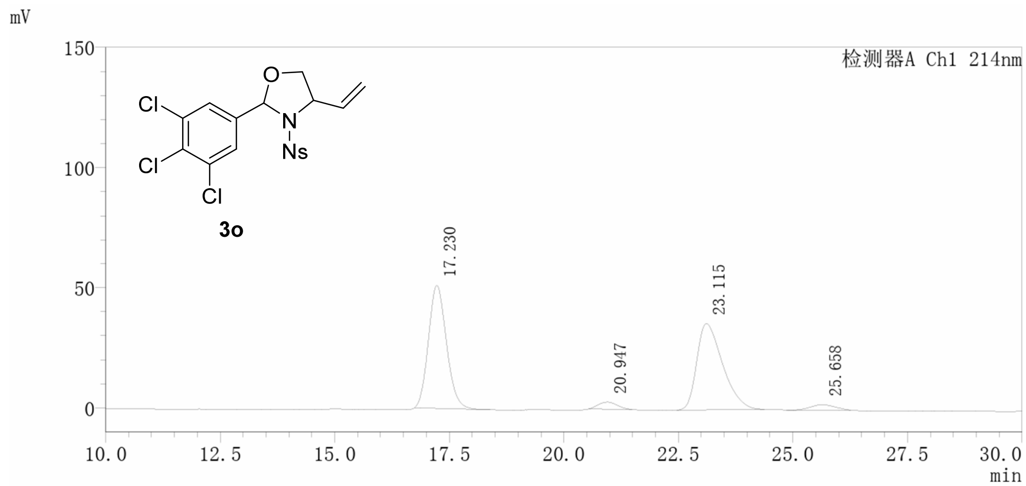
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	38.501	1504615	34.933
2	41.854	2262281	52.523
3	48.602	129457	3.006
4	50.465	410846	9.539
Total		4307200	100.000



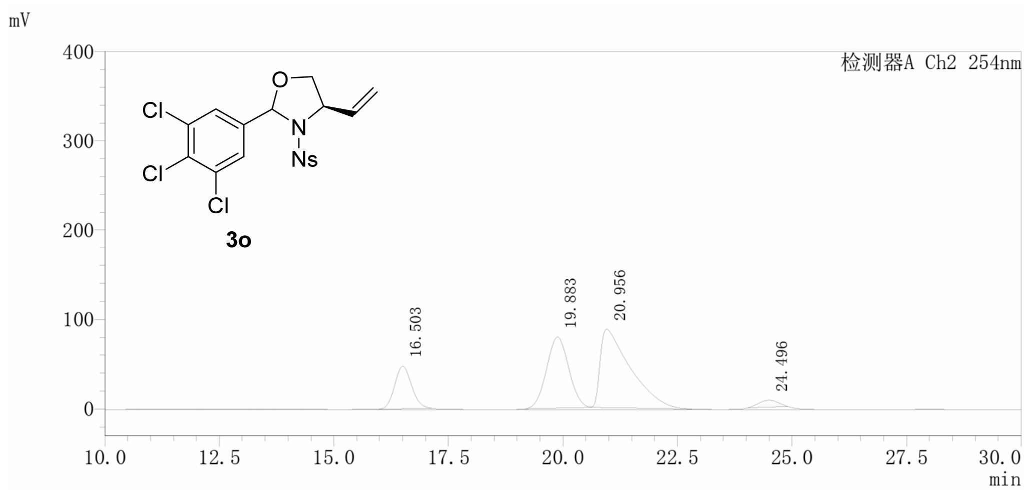
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	26.788	7500028	26.962
2	30.483	6589142	23.688
3	32.462	6990842	25.132
4	37.742	6736615	24.218
Total		27816627	100.000



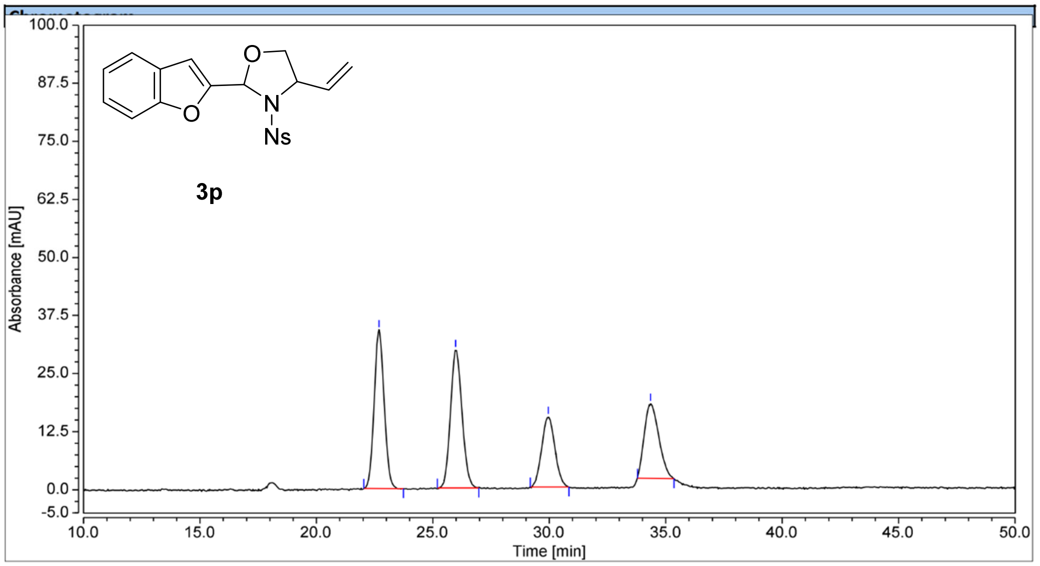
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	28.220	2215831	53.194
2	31.974	1472320	35.345
3	34.213	242395	5.819
4	39.712	234984	5.641
Total		4165530	100.000



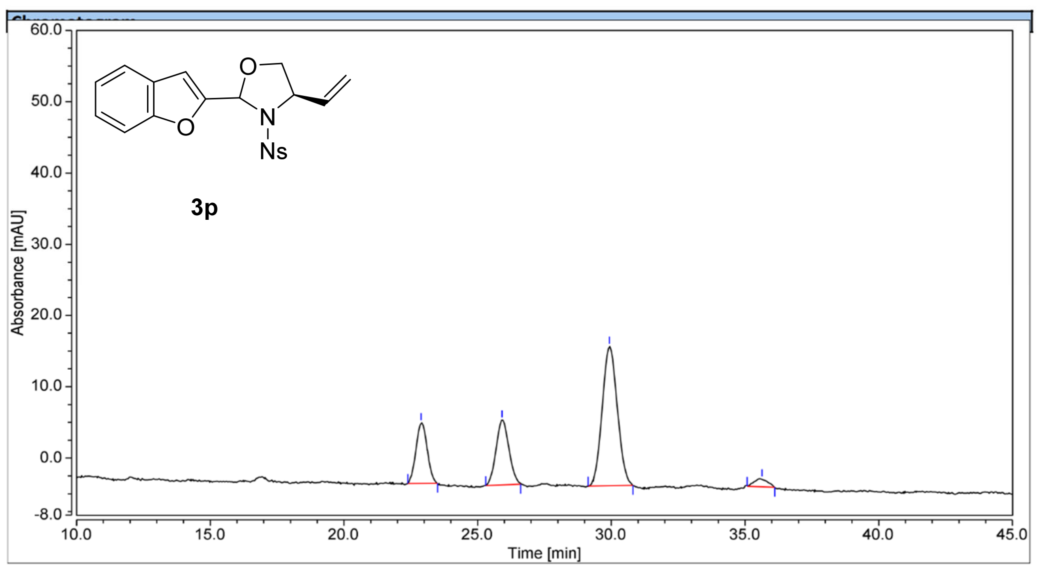
Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	17.230	1392884	47.040
2	20.947	85491	2.887
3	23.115	1403079	47.385
4	25.658	79585	2.688
Total		2961039	100.000



Peak No.	R. Time (min)	Peak Area (mV*min)	Percent (%)
1	16.503	1207558	14.961
2	19.883	2664472	33.011
3	20.956	3976378	49.264
4	24.496	223123	2.764
Total		8071531	100.000

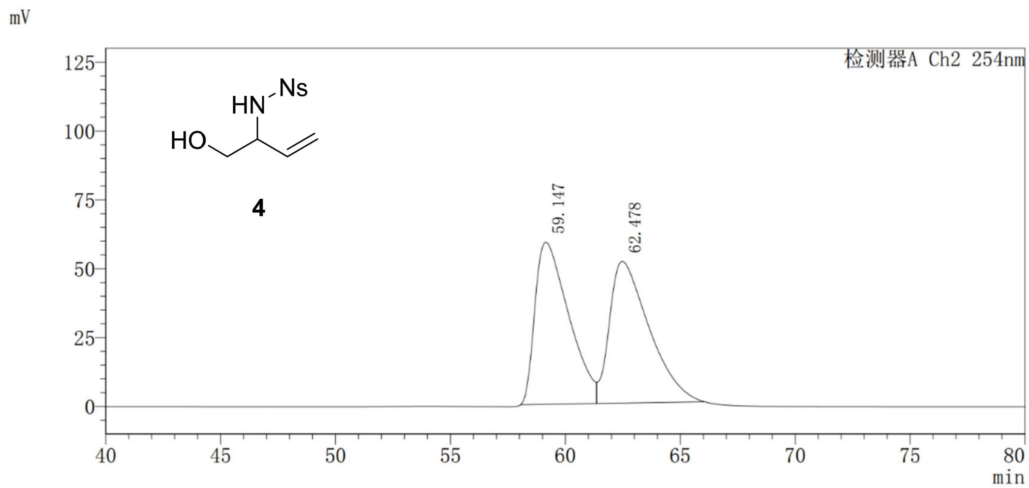


Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	22.685	16.958	30.50
2	25.979	17.106	30.76
3	29.952	9.891	17.79
4	34.345	11.653	20.96
Total		55.608	100.000

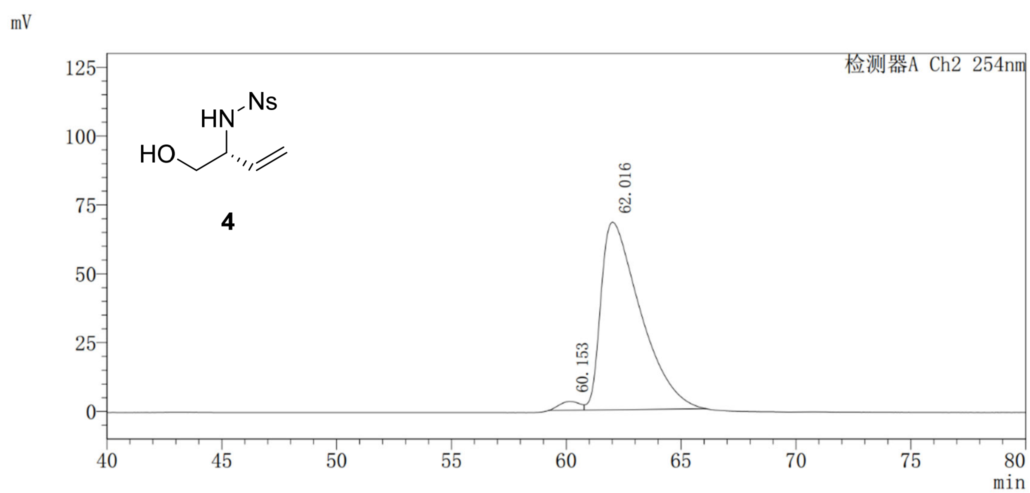


Peak No.	R. Time (min)	Peak Area (mAU*min)	Percent (%)
1	22.886	4.089	18.06
2	25.913	5.111	22.58
3	29.926	12.791	56.51
4	34.639	0.645	2.85

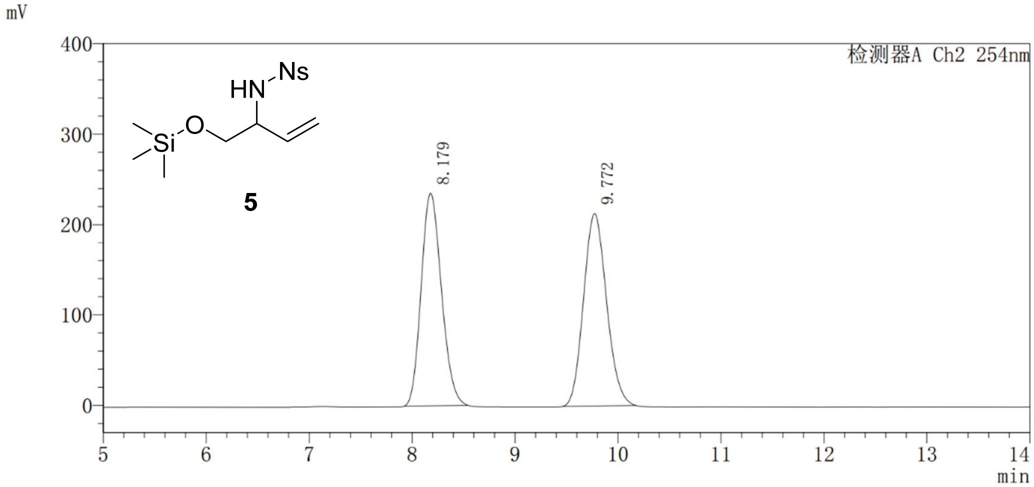
Total		22.635	100.000



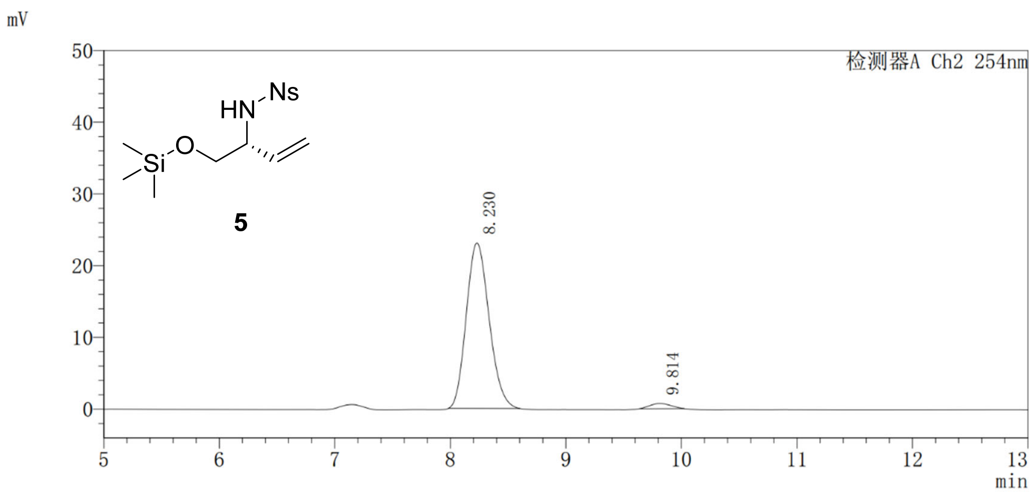
Peak No.	R. Time (min)	Peak Area (mV *min)	Percent (%)
1	59.147	6009579	49.280
2	62.478	6185224	50.720
Total		12194803	100.000



Peak No.	R. Time (min)	Peak Area (mV *min)	Percent (%)
1	60.153	200264	2.386
2	62.016	8193184	97.614
Total		8393448	100.000



Peak No.	R. Time (min)	Peak Area (mV *min)	Percent (%)
1	8.179	3218288	49.307
2	9.772	3308794	50.693
Total		6527082	100.000



Peak No.	R. Time (min)	Peak Area (mV *min)	Percent (%)
1	8.230	8.230	97.144
2	9.814	9.814	2.856
Total		8.230	100.000

9. References

[1] (a) N. Gao, X.-W. Guo, S.-C. Zheng, W.-K. Yang, X.-M. Zhao, *Tetrahedron* **2012**, *68*, 9413. (b) M. Zhang, M. Zhao, P. Zheng, H. Zhang, X. Zhao, *J. Fluorine Chem.* **2016**, *189*, 13.

[2] L. Marin, S. Jerhaoui, E. Kolodziej, R. Guillot, V. Gandon, F. Colobert, E. Schulz, J.

Wencel-Delord, D. Lebœuf, *Adv. Synth. Catal.* **2021**, *363*, 4277.
[3] N. Bodineau, J.-M. Mattali, V. Thimokhin, K. Handoo, J. C. Négrel, M. Chanon, *Org. Lett.* **2000**, *2*, 2303.
[4] F. Tato, V. Reboul, P. Metzner. *J. Org. Chem.* **2008**, *73*, 7837.