

Enantioselective Construction of Tertiary C-O Bond via Allylic Substitution of Vinylethylene Carbonates with Water and Alcohols

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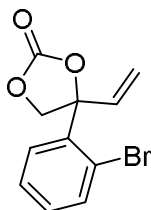
General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University using ESI method. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian Mercuryplus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Mercuryplus 400 (100 MHz) (or AVANCE III HD 400 (100 MHz)) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform and to the center of the heptet at 29.92 ppm for acetone- d_6 . ^{13}C NMR spectra were routinely run with broadband decoupling. ^{11}B NMR spectra were recorded on a Bruker AVANCE III HD 400 (128 MHz) spectrometer. Chemical shifts of ^{11}B NMR spectra were externally referenced to $\text{BF}_3 \cdot \text{OEt}_2$ ($\delta = 0$ ppm). High performance liquid chromatography (HPLC) was performed with Thermo Fisher spectrometers using chiral column as noted for each compound. Optical rotations were measured on a SGW[®]-1 polarimeter. THF was purified by distillation with Na-benzophenone. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ was purchased from Sinocompound Co. and used as received. Substituted vinyl ethylene carbonates (VECs) were synthesized according to our previous reported procedure.¹ Phosphoramidite ligands were synthesized according to the reported literature.²⁻⁴ All other chemicals were used as received from commercial resources.

Characterization vinylethylene carbonates (VECs, 1)

VECs **1** were synthesized according to our previous reported procedures,^[1] All characterization data are in accordance with the literature. New VECs have been fully characterized.

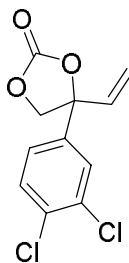
4-(2-bromophenyl)-4-vinyl-1,3-dioxolan-2-one (**1h**)



1h

Obtained as light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.50 (m, 2H), 7.34–7.27 (m, 2H), 6.13 (dd, *J* = 10.8, 17.2 Hz, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 4.66 (d, *J* = 8.8 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 140.6, 135.9, 132.0, 130.6, 128.0, 123.4, 123.1, 118.1, 84.7, 74.3; HRMS (ESI-MS): Calcd. for C₁₁H₉O₃Br (M + Na): 290.9600, Found: 290.9622.

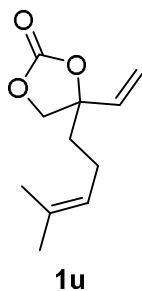
4-(3,4-dichlorophenyl)-4-vinyl-1,3-dioxolan-2-one (**1l**)



1l

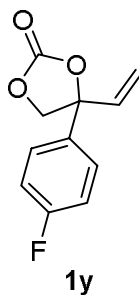
Obtained as a light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.46 (m, 2H), 7.27–7.19 (m, 1H), 6.14 (dd, *J* = 10.8, 17.2 Hz, 1H), 5.47 (d, *J* = 10.8 Hz, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 4.69 (d, *J* = 8.8 Hz, 1H), 4.56 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 138.5, 135.4, 133.1, 133.0, 130.9, 127.0, 124.3, 118.3, 84.4, 74.0; HRMS (ESI-MS): Calcd. for C₁₁H₈O₃Cl₂ (M + Na): 280.9700, Found: 280.9732.

4-(4-methylpent-3-en-1-yl)-4-vinyl-1,3-dioxolan-2-one (**1u**)



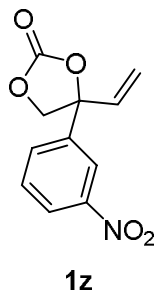
Obtained as a light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 5.88 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.44 (d, $J = 17.2$ Hz, 1H), 5.35 (d, $J = 10.8$ Hz, 1H), 4.27 (d, $J = 8.4$ Hz, 1H), 4.24 (d, $J = 8.4$ Hz, 1H), 2.13–2.04 (m, 2H), 1.87–1.81 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 136.0, 133.0, 122.1, 116.3, 84.8, 73.2, 37.8, 25.5, 21.7, 17.6; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_3$ ($\text{M} + \text{H}$): 197.1200, Found: 197.1250.

4-(4-fluorophenyl)-4-vinyl-1,3-dioxolan-2-one (1y)



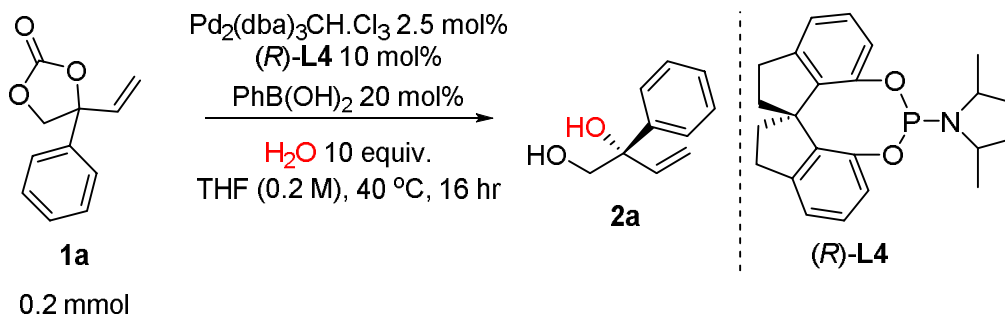
Light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.34 (m, 2H), 7.15–7.10 (m, 2H), 6.17 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.45 (d, $J = 10.8$ Hz, 1H), 5.40 (d, $J = 17.2$ Hz, 1H), 4.66 (d, $J = 8.4$ Hz, 1H), 4.57 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 161.5, 153.8, 136.2, 134.1, 127.0, 126.9, 117.8, 116.0, 115.8, 85.1, 74.4; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_9\text{O}_3\text{F}$ ($\text{M} + \text{Na}$): 231.0443, Found: 231.0433.

4-(3-nitrophenyl)-4-vinyl-1,3-dioxolan-2-one (1z)

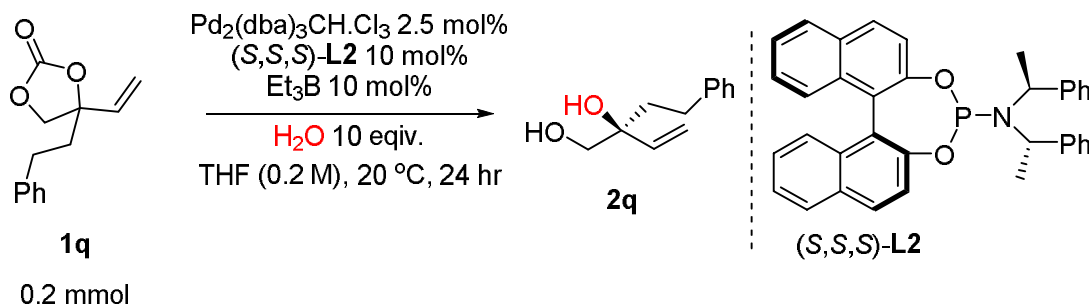


Obtained as a light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.28–8.25 (m, 2H), 7.80–7.77 (m, 1H), 7.71–7.67 (m, 1H), 6.21 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.54 (d, $J = 10.8$ Hz, 1H), 5.48 (d, $J = 17.2$ Hz, 1H), 4.79 (d, $J = 8.8$ Hz, 1H), 4.64 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 148.3, 140.5, 135.4, 131.0, 130.3, 123.8, 120.1, 118.7, 84.6, 74.1; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_9\text{NO}_5$ ($M + \text{Na}$): 258.0400, Found: 258.0432.

General procedures for the allylic substitution of VECs **1** with water

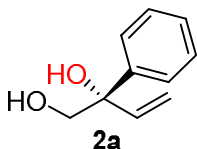


General Procedure A: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Pd}_2(\text{dba})_3\text{CH}_2\text{Cl}_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), Zhou's ligand $(R)\text{-L4}$ (7.6 mg, 0.02 mmol, 10 mol%), $\text{PhB}(\text{OH})_2$ (4.9 mg, 0.04 mmol, 20 mol%), and VEC **1a** (38.0 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Distilled H_2O (36 μL , 2.0 mmol), and anhydrous THF (1 mL) were added sequentially via syringe. The resulting mixture was stirred at 40 °C for 16 hours. The reaction mixture was cool to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography on silica gel to afford the corresponding diol **2a**. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.

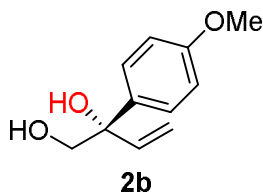


General Procedure B: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Pd}_2(\text{dba})_3\text{CH}_2\text{Cl}_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), Feringa's ligand $(S,S,S)\text{-L2}$ (10.8 mg, 0.02 mmol, 10 mol%), and VEC **1q** (43.7 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum,

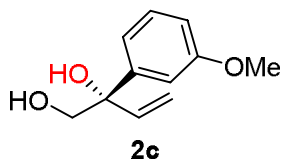
then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et3B (20 μ L of 1 M solution in THF, 0.02 mmol, 10 mol%), distilled H2O (36 μ L, 2.0 mmol), and anhydrous THF (1 mL) were added sequentially via syringe. The resulting mixture was stirred at 20 $^{\circ}$ C for 24 h. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo with the aid of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the corresponding diol **2q**. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.



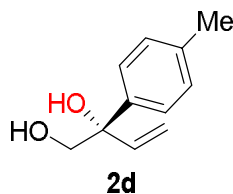
(S)-2-phenylbut-3-ene-1,2-diol (2a) was prepared according to the general procedure **A** from **1a**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 96% yield (31.5 mg). $[\alpha]_D^{25} = -42.8$ ($c = 0.36$, CHCl_3); Lit.⁵ $[\alpha]_D^{20} = -43.4$ ($c = 0.20$, EtOH). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43–7.40 (m, 2H), 7.35–7.31 (m, 2H), 7.27–7.23 (m, 1H), 6.10 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.34 (d, $J = 17.2$ Hz, 1H), 5.24 (d, $J = 10.8$ Hz, 1H), 3.75 (d, $J = 11.6$ Hz, 1H), 3.70 (d, $J = 11.6$ Hz, 1H), 3.05 (br, 1H), 2.24 (br, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.4, 140.5, 128.3, 127.3, 125.8, 115.4, 77.4, 69.1; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$ (M-H₂O+H): 147.0800, Found: 147.0808; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/9, $t_{\text{major}} = 9.70$ min, $t_{\text{minor}} = 10.80$ min; 95% ee.



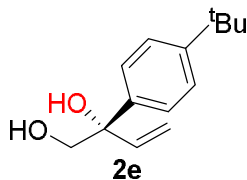
(S)-2-(4-methoxyphenyl)but-3-ene-1,2-diol (2b) was prepared according to the general procedure **A** from **1b**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 97% yield (37.7 mg). $[\alpha]_D^{25} = -47.4$ ($c = 0.15$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39–7.35 (m, 2H), 6.91–6.87 (m, 2H), 6.13 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.37 (d, $J = 17.2$ Hz, 1H), 5.29 (d, $J = 10.4$ Hz, 1H), 3.80 (s, 3H), 3.77 (d, $J = 11.2$ Hz, 1H), 3.73 (d, $J = 11.2$ Hz, 1H), 2.91 (br, 1H), 2.11 (br, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.8, 140.7, 134.4, 126.9, 115.3, 113.8, 77.3, 69.4, 55.2; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$ (M-H): 193.0900, Found: 193.0865; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/9, $t_{\text{minor}} = 11.14$ min, $t_{\text{major}} = 12.68$ min; 93% ee.



(S)-2-(3-methoxyphenyl)but-3-ene-1,2-diol (2c) was prepared according to the general procedure **A** from **1c**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 96% yield (37.3 mg). $[\alpha]_D^{25} = -21.2$ ($c = 0.33$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26–7.22 (m, 1H), 7.03–6.95 (m, 2H), 6.80–6.77 (m, 1H), 6.08 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.33 (d, $J = 17.2$ Hz, 1H), 5.22 (d, $J = 10.8$ Hz, 1H), 3.77 (s, 3H), 3.74 (d, $J = 11.2$ Hz, 1H), 3.69 (d, $J = 11.2$ Hz, 1H), 3.01 (br, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.4, 144.2, 140.4, 129.2, 117.9, 115.2, 112.4, 111.9, 77.3, 69.1, 55.1; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$ (M-H): 193.0900, Found: 193.0865; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 14.60$ min, $t_{\text{minor}} = 17.42$ min; 96% ee.

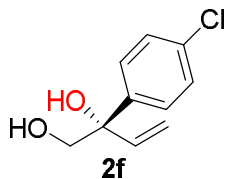


(S)-2-(4-methylphenyl)but-3-ene-1,2-diol (2d) was prepared according to the general procedure **A** from **1d**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 96% yield (33.5 mg). $[\alpha]_D^{25} = -17.90$ ($c = 0.13$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36–7.33 (m, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.15 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.38 (d, $J = 17.2$ Hz, 1H), 5.29 (d, $J = 10.8$ Hz, 1H), 3.79 (d, $J = 11.2$, Hz, 1H), 3.75 (d, $J = 11.2$, Hz, 1H), 2.81 (bs, 1H) 2.34 (s, 3H), 1.97 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.7, 139.4, 137.1, 129.1, 125.5, 115.3, 77.3, 69.4, 21.0; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$ (M-H): 177.0900, Found: 177.0916; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 9.67$ min, $t_{\text{minor}} = 10.95$ min; 98% ee.

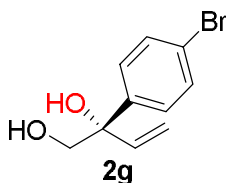


(S)-2-(4-(tert-butyl)phenyl)but-3-ene-1,2-diol (2e) was prepared according to the general procedure **A** from **1e**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether)

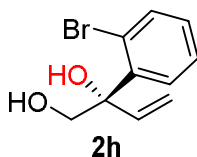
on silica gel to provide the title compound as a colorless oil in 92% yield (42.7 mg). $[\alpha]_D^{25} = +19.17$ ($c = 0.18$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41–7.34 (m, 4H), 6.14 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.39 (d, $J = 17.6$ Hz, 1H), 5.27 (d, $J = 10.8$ Hz, 1H), 3.78 (d, $J = 11.2$, Hz, 1H), 3.73 (d, $J = 11.2$, Hz, 1H), 3.08 (br, 1H) 2.30 (br, 1H), 1.31 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.2, 140.7, 139.3, 125.3, 125.2, 115.3, 77.2, 69.3, 34.4, 31.3; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$ (M-H): 219.1400, Found: 219.1416; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/9$, $t_{\text{major}} = 6.16$ min, $t_{\text{minor}} = 6.79$ min; 93% ee.



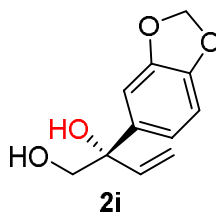
(S)-2-(4-chlorophenyl)but-3-ene-1,2-diol (2f) was prepared according to the general procedure **A** from **1f**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 96% yield (38.1 mg). $[\alpha]_D^{25} = -11.61$ ($c = 1.35$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40–7.30 (m, 4H), 6.10 (dd, $J = 10.4, 17.2$ Hz, 1H), 5.36 (d, $J = 17.6$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H), 3.73 (s, 2H), 3.19 (bs, 1H) 2.42 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.9, 140.1, 133.2, 128.4, 127.2, 115.9, 77.3, 69.1; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Cl}$ (M-H): 197.0400, Found: 197.0370; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/9$, $t_{\text{major}} = 10.57$ min, $t_{\text{minor}} = 13.45$ min; 95% ee.



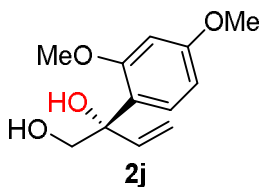
(S)-2-(4-bromophenyl)but-3-ene-1,2-diol (2g) was prepared according to the general procedure **A** from **1g**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 92% yield (44.7 mg). $[\alpha]_D^{25} = -17.78$ ($c = 0.59$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51–7.47 (m, 2H), 7.36–7.32 (m, 2H), 6.12 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.38 (d, $J = 17.2$ Hz, 1H), 5.31 (d, $J = 10.8$ Hz, 1H), 3.78 (d, $J = 11.2$ Hz, 1H), 3.74 (d, $J = 11.2$ Hz, 1H), 2.96 (bs, 1H) 2.04 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.4, 140.0, 131.5, 127.5, 121.5, 116.0, 77.0, 69.2; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ (M-H): 240.9900, Found: 240.9916; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/9$, $t_{\text{major}} = 9.70$ min, $t_{\text{minor}} = 10.45$ min; 94% ee.



(*S*)-2-(2-bromophenyl)but-3-ene-1,2-diol (**2h**) was prepared according to the general procedure **A** from **1h**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 94% yield (45.7 mg). $[\alpha]_D^{25} = -10.02$ ($c = 0.98$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67–7.57 (m, 1H), 7.41–7.32 (m, 2H), 7.23–7.17 (m, 1H), 6.06 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.35 (d, $J = 17.2$ Hz, 1H), 5.27 (d, $J = 10.8$ Hz, 1H), 3.73 (d, $J = 11.2$ Hz, 1H), 3.70 (d, $J = 11.2$ Hz, 1H), 3.02 (br, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.9, 140.0, 130.4, 129.9, 128.9, 124.3, 122.6, 116.0, 76.7, 69.0; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ (M-H): 240.9900, Found: 240.9864; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 9.29$ min, $t_{\text{minor}} = 10.34$ min; 90% ee.

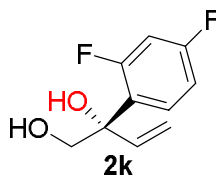


(*S*)-2-(benzo[d][1,3]dioxol-5-yl)but-3-ene-1,2-diol (**2i**) was prepared according to the general procedure **A** from **1i**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 90% yield (37.5 mg). $[\alpha]_D^{25} = -21.24$ ($c = 1.34$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.36–6.97 (m, 1H), 6.92–6.90 (m, 1H), 6.80–6.78 (m, 1H), 6.10 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.95 (s, 2H), 5.39 (d, $J = 17.2$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H), 3.74 (s, 2H), 2.92 (bs, 1H) 2.06 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.8, 146.8, 140.5, 136.4, 118.9, 115.5, 108.0, 106.6, 101.1, 77.2, 69.4; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_4$ (M-H): 207.0700, Found: 207.0650; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 19.17$ min, $t_{\text{minor}} = 22.94$ min; 95% ee.

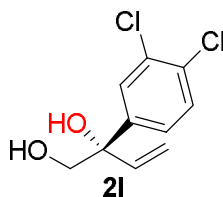


(*S*)-2-(2,4-dimethoxyphenyl)but-3-ene-1,2-diol (**2j**) was prepared according to the general procedure **A** from **1j**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether)

on silica gel to provide the title compound as a colorless oil in 82% yield (36.8 mg). $[\alpha]_D^{25} = +27.64$ ($c = 0.12$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 (dd, $J = 3.2, 6.0$ Hz, 1H), 6.49–6.46 (m, 2H), 6.20 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.27 (dd, $J = 1.2, 17.2$ Hz, 1H), 5.16 (dd, $J = 1.6, 10.8$ Hz, 1H), 4.19 (bs, 1H), 3.93 (d, $J = 11.2$ Hz, 2H), 3.79 (s, 3H) 3.77 (s, 3H), 2.65 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.1, 157.7, 140.5, 128.1, 122.5, 114.3, 104.2, 99.4, 77.3, 67.4, 55.2, 55.1; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_4$ (M-H): 223.1000, Found: 223.0970; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/9, $t_{\text{major}} = 17.71$ min, $t_{\text{minor}} = 19.24$ min; 92% ee.

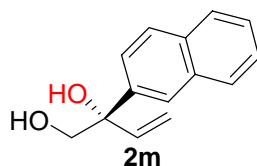


(*S*)-2-(2,4-difluorophenyl)but-3-ene-1,2-diol (**2k**) was prepared according to the general procedure **A** from **1k**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 94% yield (37.6 mg). $[\alpha]_D^{25} = -26.4$ ($c = 1.18$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64–7.58 (m, 1H), 6.89–6.84 (m, 1H), 6.80–6.74 (m, 1H), 6.22 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.34 (d, $J = 17.2$ Hz, 1H), 5.24 (d, $J = 10.8$ Hz, 1H), 3.84 (s, 2H), 3.57 (br, 1H) 2.88 (br, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.7, 163.6, 161.2, 161.1, 160.7, 160.6, 158.2, 158.1, 138.8, 129.1, 129.0, 125.4, 125.4, 125.3, 115.8, 111.3, 111.2, 111.1, 111.0, 104.5, 104.2, 104.0, 76.3, 67.8, 67.7; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{F}_2$ (M-H): 199.0600, Found: 199.0561; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/19, $t_{\text{major}} = 14.56$ min, $t_{\text{minor}} = 24.74$ min; 97% ee.

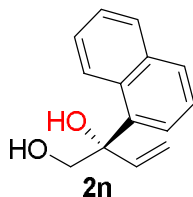


(*S*)-2-(3,4-dichlorophenyl)but-3-ene-1,2-diol (**2l**) was prepared according to the general procedure **A** from **1l**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 98% yield (45.8 mg). $[\alpha]_D^{25} = -28.5$ ($c = 1.34$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 2.0$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.23–7.19 (m, 1H), 6.04 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.37 (dd, $J = 0.8, 17.2$ Hz, 1H), 5.28 (dd, $J = 0.8, 10.8$ Hz, 1H), 3.69 (d, $J = 11.6$ Hz, 1H), 3.66 (d, $J = 11.6$ Hz, 1H), 3.05 (br, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.7, 139.5, 132.4, 131.4, 130.2, 128.0, 125.2, 116.3, 76.8, 69.8; HRMS (ESI-APCI): Calcd. for

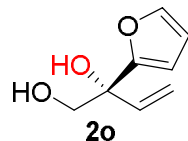
C₁₀H₁₀O₂Cl₂(M+Na): 255.0000, Found: 254.9952; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, t_{major} = 8.13 min, t_{minor} = 8.68 min; 92% ee.



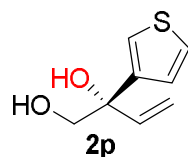
(S)-2-(naphthalen-2-yl)but-3-ene-1,2-diol (2m) was prepared according to the general procedure **A** from **1m**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 90% yield (38.6 mg). $[\alpha]_{\text{D}}^{25} = +82.9$ ($c = 0.18$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.84–7.81 (m, 3H), 7.54–7.45 (m, 3H), 6.23 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.43 (d, $J = 17.2$ Hz, 1H), 5.33 (d, $J = 10.8$ Hz, 1H), 3.90 (d, $J = 11.2$ Hz, 1H), 3.86 (d, $J = 11.2$ Hz, 1H), 3.08 (br, 1H) 2.15 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4, 139.6, 133.1, 132.6, 128.1, 127.5, 126.2, 126.0, 124.6, 123.7, 115.8, 77.5, 69.3; HRMS (ESI-MS): Calcd. for C₁₄H₁₄O₂ (M-H₂O+H): 197.1000, Found: 197.0966; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, t_{major} = 11.47 min, t_{minor} = 16.89 min; 92% ee.



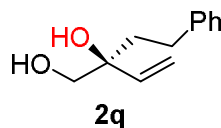
(S)-2-(naphthalen-1-yl)but-3-ene-1,2-diol (2n) was prepared according to the general procedure **A** from **1n**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 83% yield (35.6 mg). $[\alpha]_{\text{D}}^{25} = +32.5$ ($c = 0.49$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.40–8.36 (m, 1H), 7.81–7.73 (m, 2H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.42–7.34 (m, 3H), 6.22 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.21 (d, $J = 10.8$ Hz, 1H), 5.18 (d, $J = 17.6$ Hz, 1H), 4.05 (d, $J = 11.2$ Hz, 1H), 3.83 (d, $J = 11.6$ Hz, 1H), 3.52 (br, 1H) 2.86 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 137.5, 134.7, 130.9, 129.0, 128.8, 127.2, 125.2, 124.7, 124.5, 116.7, 78.1, 68.2; HRMS (ESI-MS): Calcd. for C₁₄H₁₄O₂ (M-H₂O+H): 197.1000, Found: 197.0965; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, t_{minor} = 7.99 min, t_{major} = 10.81 min; 97% ee.



(R)-2-(furan-2-yl)but-3-ene-1,2-diol (2o) was prepared according to the general procedure **A** from **1o**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 93% yield (28.7 mg). $[\alpha]_D^{25} = -10.2$ ($c = 0.49$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (s, 1H), 6.37–6.33 (m, 2H), 6.11 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.46 (dd, $J = 0.8, 17.2$ Hz, 1H), 5.35 (dd, $J = 0.8, 10.8$ Hz, 1H), 3.76 (d, $J = 11.2$ Hz, 1H), 3.72 (d, $J = 11.6$ Hz, 1H), 1.80 (br, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 155.0, 142.4, 137.7, 116.4, 110.4, 107.2, 74.7, 67.8; HRMS (ESI-MS): Calcd. for $\text{C}_8\text{H}_{10}\text{O}_3$ (M-H): 153.0600, Found: 153.0562; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 9.53$ min, $t_{\text{minor}} = 10.52$ min; 80% ee.

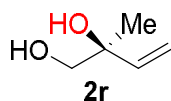


(S)-2-(thiophen-3-yl)but-3-ene-1,2-diol (2p) was prepared according to the general procedure **A** from **1p**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 95% yield (32.3 mg). $[\alpha]_D^{25} = -12.3$ ($c = 1.09$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32–7.29 (m, 1H), 6.26–6.24 (m, 1H), 6.07–6.05 (m, 1H), 6.12 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.38 (d, $J = 17.2$ Hz, 1H), 5.28 (d, $J = 10.8$ Hz, 1H), 3.77 (d, $J = 11.2$, Hz, 1H), 3.70 (d, $J = 11.2$, Hz, 1H), 3.18 (bs, 1H), 2.43 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.9, 139.9, 126.2, 125.8, 121.5, 115.5, 76.3, 69.2; HRMS (ESI-MS): Calcd. for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$ (M-H): 169.0300, Found: 169.0323; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, $t_{\text{major}} = 10.89$ min, $t_{\text{minor}} = 11.73$ min; 90% ee.



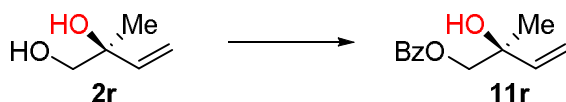
(S)-2-phenethylbut-3-ene-1,2-diol (2q) was prepared according to the general procedure **B** from **1q**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 63% yield (24.2 mg). $[\alpha]_D^{25} = -17.5$ ($c = 0.16$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29–7.24 (m, 2H), 7.19–7.16 (m, 3H), 5.86 (dd, $J = 10.8, 17.2$ Hz, 1H),

5.42 (d, $J = 17.6$ Hz, 1H), 5.33 (d, $J = 10.8$ Hz, 1H), 3.55 (d, $J = 11.2$, Hz, 1H), 3.51 (d, $J = 11.2$, Hz, 1H), 2.74–2.99 (m, 2H), 2.48 (bs, 1H), 2.11 (bs, 1H), 1.95–1.87 (m, 1H), 1.81–1.73 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.1, 140.4, 128.4, 128.3, 125.8, 115.7, 76.0, 68.9, 38.7, 29.5; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_2$ (M-H): 191.1100, Found: 191.1072; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 14.62$ min; >99% ee.

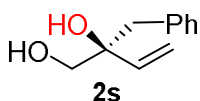


(*S*)-2-methylbut-3-ene-1,2-diol (**2r**)¹ was prepared according to the general procedure **B** from **1r**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 78% yield (16.0 mg). $[\alpha]_{\text{D}}^{25} = -4.2$ ($c = 0.34$, CHCl_3); Lit.⁶ $[\alpha]_{\text{D}} = +4.78$ ($c = 2.50$, CHCl_3) for R isomer. ^1H NMR (400 MHz, CDCl_3) δ 5.88 (dd, $J = 10.8$, 17.6 Hz, 1H), 5.31 (dd, $J = 1.2$, 17.2 Hz, 1H), 5.16 (dd, $J = 1.2$, 10.8 Hz, 1H), 3.54 (br, 2H), 3.48 (d, $J = 11.2$ Hz, 1H), 3.42 (d, $J = 11.2$ Hz, 1H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 113.9, 73.7, 69.4, 23.7; Calcd. for $\text{C}_5\text{H}_{10}\text{O}_2$ (M-H): 101.0600, Found: 101.0603;

For the determination of enantiomeric excess of **2r**, the compound **2r** was converted to corresponding diol monobenzoate **11r**. The ee value of **11r** was determined by chiral HPLC.

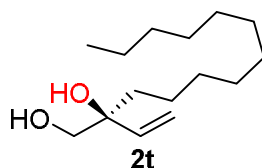


(*S*)-2-hydroxy-2-methylbut-3-en-1-yl benzoate (**11r**)¹ was obtained as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.06–8.02 (m, 2H), 7.57–7.52 (m, 1H), 7.44–7.40 (m, 2H), 6.00 (dd, $J = 10.8$, 17.2 Hz, 1H), 5.40 (dd, $J = 1.2$, 17.6 Hz, 1H), 5.18 (dd, $J = 1.2$, 10.8 Hz, 1H), 4.31 (d, $J = 10.8$ Hz, 1H), 4.23 (d, $J = 11.2$ Hz, 1H), 2.80 (br, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 141.3, 133.0, 129.7, 129.5, 128.3, 114.1, 72.4, 71.0, 24.5; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_3$ (M-H₂O+H): 189.0900, Found: 189.0916; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 7.73$ min, $t_{\text{minor}} = 9.86$ min; 83% ee.



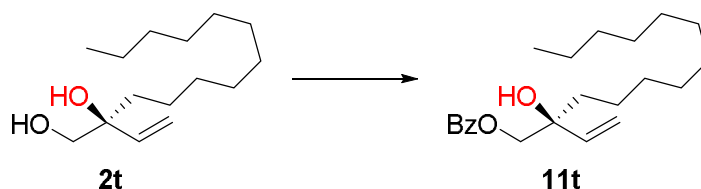
(*S*)-2-benzylbut-3-ene-1,2-diol (**2s**) was prepared according to the general procedure **B** from **1s**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 87% yield (31.0 mg). $[\alpha]_{\text{D}}^{25} = -19.4$ ($c = 0.27$, CHCl_3). ^1H

NMR (400 MHz, CDCl₃) δ 7.27–7.17 (m, 5H), 5.81 (dd, J = 10.8, 17.6 Hz, 1H), 5.20 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.8 Hz, 1H), 3.49 (s, 2H), 2.95 (br, 1H), 2.85 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4, 136.0, 130.6, 128.0, 126.5, 115.1, 75.9, 67.7, 43.6; HRMS (ESI-MS): Calcd. for C₁₁H₁₄O₂ (M-H): 177.0900, Found: 177.0916; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/9, t_{major} = 6.40 min, t_{minor} = 9.11 min; 80% ee.

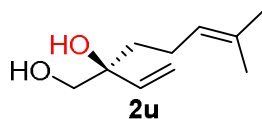


(*S*)-2-vinyltridecane-1,2-diol (**2t**)¹ was prepared according to the general procedure **B** from **1t**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 62% yield (30.1 mg). $[\alpha]_{\text{D}}^{25}$ = -7.36 (c = 0.63, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 5.80 (dd, J = 10.8, 17.6 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 5.23 (d, J = 17.2 Hz, 1H), 3.51 (d, J = 11.2 Hz, 1H), 3.47 (d, J = 11.2 Hz, 1H), 2.62 (br, 2H), 1.57–1.43 (m, 2H), 1.36–1.20 (m, 18H), 0.88 (t, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 114.9, 76.1, 68.7, 37.1, 31.9, 30.1, 29.6, 29.5, 29.3, 23.1, 22.6, 11.1; HRMS (ESI-MS): Calcd. for C₁₅H₃₀O₂ (M-H): 241.2200, Found: 241.2168;

For the determination of enantiomeric excess of **2t**, the compound **2t** was converted to corresponding diol monobenzoate **11t**. The ee value of **11t** was determined by chiral HPLC.

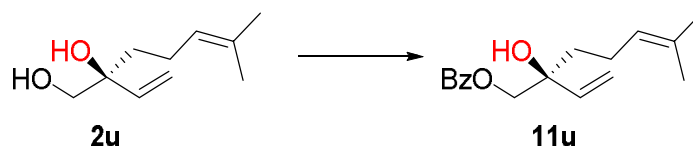


(*S*)-2-hydroxy-2-vinyltridecyl benzoate (**8t**)¹ was obtained as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.05–8.02 (m, 2H), 7.59–7.54 (m, 1H), 7.46–7.42 (m, 2H), 5.91 (dd, J = 10.8, 17.2 Hz, 1H), 5.39 (dd, J = 1.2, 17.6 Hz, 1H), 5.24 (dd, J = 1.2, 11.2 Hz, 1H), 4.34 (d, J = 11.2 Hz, 1H), 4.26 (d, J = 11.2 Hz, 1H), 2.37 (br, 1H), 1.72–1.56 (m, 2H), 1.40–1.27 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 140.3, 133.1, 129.9, 129.8, 128.4, 114.8, 74.9, 70.5, 37.6, 31.9, 30.0, 29.6, 29.5, 29.3, 23.1, 22.7, 14.1; HRMS (ESI-MS): Calcd. for C₂₂H₃₄O₃ (M-H₂O+H): 329.2500, Found: 329.2481; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 2/98, t_{minor} = 10.21 min, t_{major} = 12.05 min; 95% ee.

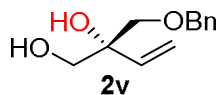


(S)-6-methyl-2-vinylhept-5-ene-1,2-diol (2u) was prepared according to the general procedure **B** from **1u**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a yellow oil in 61% yield (20.8 mg). $[\alpha]_D^{25} = -14.37$ ($c = 0.23$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.80 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.34 (dd, $J = 1.6, 17.6$ Hz, 1H), 5.25 (dd, $J = 1.6, 10.8$ Hz, 1H), 5.13–5.06 (m, 1H), 3.50 (d, $J = 11.2$ Hz, 1H), 3.46 (d, $J = 11.2$ Hz, 1H), 2.92 (br, 2H), 2.11–1.94 (m, 2H), 1.67 (s, 3H), 1.64–1.61 (m, 1H), 1.59 (s, 3H), 1.53–1.47 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.6, 132.0, 124.1, 115.0, 76.2, 68.7, 36.7, 25.6, 21.9, 17.6; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2$ (M-H): 169.1200, Found: 169.1229;

For the determination of enantiomeric excess of **2u**, the compound **2u** was converted to corresponding diol monobenzoyleate **11u**. The ee value of **11u** was determined by chiral HPLC.

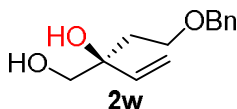


(S)-2-hydroxy-6-methyl-2-vinylhept-5-en-1-yl benzoate (11u) was obtained as a colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05–8.02 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.42 (m, 2H), 5.92 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.42 (dd, $J = 1.2, 17.2$ Hz, 1H), 5.27 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.15–5.11 (m, 1H), 4.34 (d, $J = 11.2$ Hz, 1H), 4.26 (d, $J = 11.2$ Hz, 1H), 2.29 (br, 1H), 2.14–2.05 (m, 2H), 1.78–1.71 (m, 1H), 1.68 (s, 3H), 1.66–1.63 (m, 1H), 1.60 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.5, 140.1, 113.1, 112.4, 129.9, 129.6, 128.4, 123.9, 115.1, 75.0, 70.5, 37.3, 25.7, 22.0, 17.7; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_3$ (M-H₂O+H): 257.1500, Found: 257.1542; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/9$, $t_{\text{major}} = 5.73$ min, $t_{\text{minor}} = 6.12$ min; 85% ee.



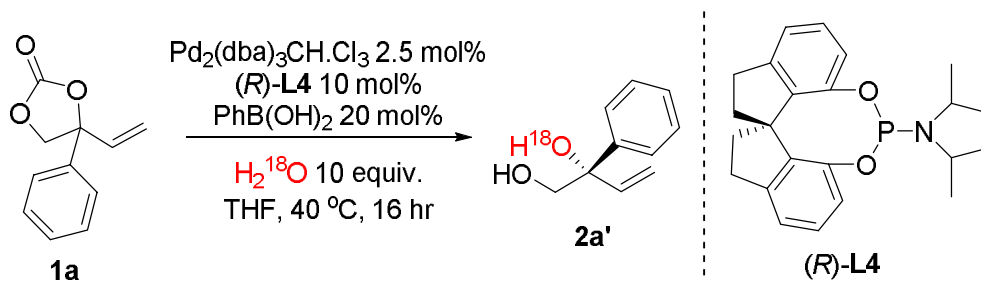
(R)-2-((benzyloxy)methyl)but-3-ene-1,2-diol (2v)⁷ was prepared according to the general procedure **A** from **1v**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 82% yield (34.2 mg). $[\alpha]_D^{25} = -30.1$ ($c = 0.77$, CHCl_3); Lit.⁷ $[\alpha]_D^{23} = +24.0$ ($c = 0.65$, CH_2Cl_2) for *S* isomer. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35–7.24 (m, 5H), 5.83 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.40 (dd, $J = 1.6, 10.8$ Hz, 1H), 5.22 (dd, $J = 1.6, 17.2$ Hz,

1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 12.4$ Hz, 1H), 3.63 (d, $J = 11.6$ Hz, 1H), 3.53 (d, $J = 9.6$ Hz, 1H), 3.48 (d, $J = 9.6$ Hz, 1H), 3.46 (d, $J = 7.6$ Hz, 1H), 3.07 (br, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.2, 137.6, 128.3, 127.7, 127.6, 115.8, 75.0, 74.2, 73.6, 66.9; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (M-H): 207.1000, Found: 207.1021; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 21.00$ min, $t_{\text{minor}} = 22.53$ min; 98% ee.



(*S*)-2-(2-(benzyloxy)ethyl)but-3-ene-1,2-diol (**2w**) was prepared according to the general procedure **B** from **1w**. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 73% yield (32.5 mg). $[\alpha]_{\text{D}}^{25} = +13.1$ ($c = 0.28$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.27 (m, 5H), 5.80 (dd, $J = 10.8, 17.2$ Hz, 1H), 5.39 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.23 (dd, $J = 1.6, 10.8$ Hz, 1H), 4.48 (s, 2H), 3.81 (bs, 1H), 3.75–3.62 (m, 2H), 3.44 (s, 2H), 2.51 (bs, 1H), 2.19–2.12 (m, 1H), 1.69–1.63 (m, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 137.4, 128.7, 128.0, 127.8, 115.3, 76.1, 73.4, 69.1, 67.0, 35.5; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3$ (M-H): 221.1200, Found: 221.1178; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 12.39$ min, $t_{\text{minor}} = 13.24$ min; 90% ee.

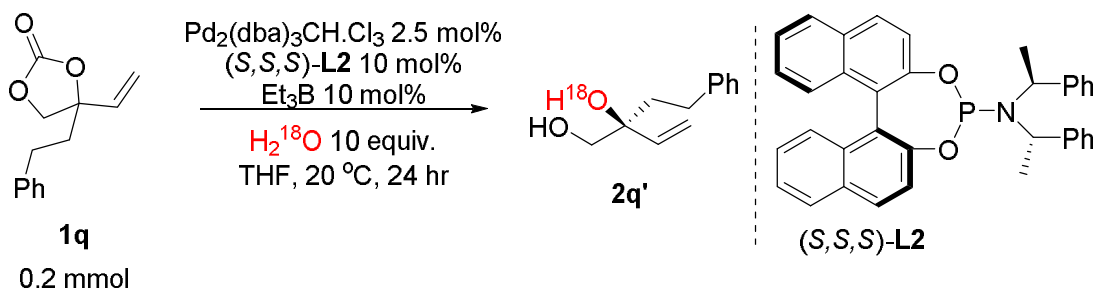
Isotopic labeling experiments



For 1a: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), Zhou's ligand (*R*)-**L4** (7.6 mg, 0.02 mmol, 10 mol%), $\text{PhB}(\text{OH})_2$ (4.9 mg, 0.04 mmol, 20 mol%), and VEC **1a** (38.0 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). ^{18}O -labelled water (97% H_2^{18}O) (36 μL , 2.0 mmol), and anhydrous THF (1 mL) were added sequentially via syringe. The resulting mixture was stirred at 40 °C for 16 hours. The reaction mixture was cool to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator.

The obtained residue was purified by flash column chromatography on silica gel to afford the title compound **2a'** in 93% yield with 84 ¹⁸O%.

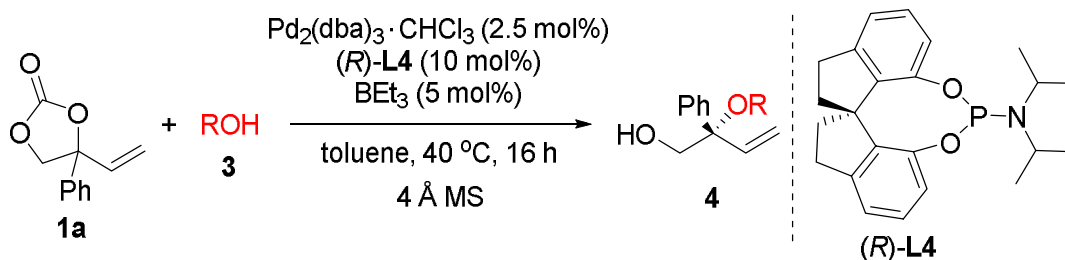
The ¹⁸O% of **2a** was determined by MS spectrum. According to the theoretical calculations, the ratio of C₁₀H₁₁¹⁶O: C₁₀H₁₁O¹⁸ = 100:0.2. Thus the intensity of M-H₂O+H+2 (C₁₀H₁₁¹⁸O) peak will be 0.2% of the intensity of the molecular peak M-H₂O+H (C₁₀H₁₁¹⁶O). The relative abundances of [M(¹⁸O)-H₂O+H] (149.1074) and [M(¹⁶O)-H₂O+H] (147.0805) of **2a'** are 100 and 18.76, respectively (Page S82). The ¹⁸O% of **2a'** can be calculated as follow: $(100-18.76*0.2\%)/(100-18.76*0.2\%+18.76) = 84\%$.⁸



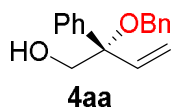
For 1q: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol, 2.5 mol%), Feringa's ligand (S,S,S)-L2 (10.8 mg, 0.02 mmol, 10 mol%), and VEC **1q** (43.7 mg, 0.2 mmol) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et₃B (20 μL of 1 M solution in THF, 0.02 mmol, 10 mol%), ¹⁸O-labelled water (97% H₂¹⁸O) (36 μL, 2.0 mmol), and anhydrous THF (1 mL) were added sequentially via syringe. The resulting mixture was stirred at 20 °C for 24 h. After completion, the reaction mixture was cool to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography on silica gel to afford the title compound **2q'** in 57% yield with 82 ¹⁸O%.

The ¹⁸O% of **2q'** was determined by MS spectrum. According to the theoretical calculations, the ratio of C₁₂H₁₆¹⁶O₂: C₁₂H₁₆O¹⁶O¹⁸ = 100:0.4. Thus the intensity of M+2 (C₁₂H₁₆O¹⁶O¹⁸) peak will be 0.4% of the intensity of the molecular peak M (C₁₂H₁₆¹⁶O₂). The relative abundances of [M(¹⁸O)+Na] (217.1093) and [M(¹⁶O)+Na] (215.1056) of **2q'** are 100 and 21.87, respectively (Page S82). The ¹⁸O% of **2q'** can be calculated as follow: $(100-21.87*0.4\%)/(100-21.87*0.4\%+21.87) = 82\%$.⁸

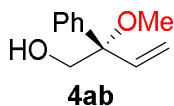
General procedure C for the asymmetric allylic etherification of VEC 1a with various alcohols 3.



To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), Zhou's ligand $(R)\text{-L4}$ (7.6 mg, 0.02 mmol, 10 mol%), BnOH (22.8 μL , 0.22 mmol), VEC **1a** (38.0 mg, 0.2 mmol) and 4 Å molecular sieves (100 mg) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et_3B (10 μL of 1 M solution in THF, 0.01 mmol, 5 mol%), and anhydrous toluene (2 mL) were added sequentially via syringe. The resulting mixture was stirred at 40 °C for 16 h. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the corresponding ether **4aa**. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.

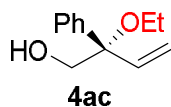


$(S)\text{-2-(benzyloxy)-2-phenylbut-3-en-1-ol}$ (**4aa**) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (47.8 mg). $[\alpha]_D^{25} = -23.6$ ($c = 0.74$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49–7.46 (m, 2H), 7.40–7.35 (m, 6H), 7.33–7.28 (m, 2H), 6.10 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.72 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.49 (dd, $J = 1.2, 17.6$ Hz, 1H), 4.43 (d, $J = 11.2$ Hz, 1H), 4.39 (d, $J = 11.2$ Hz, 1H), 3.98–3.89 (m, 2H), 2.04 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 138.9, 137.3, 128.4, 128.3, 127.7, 127.4, 127.3, 127.0, 118.3, 82.4, 67.6, 65.3; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ (M+Na): 277.1200, Found: 277.1198; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 12.66$ min, $t_{\text{major}} = 16.37$ min; 93% ee.

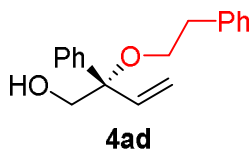


$(S)\text{-2-methoxy-2-phenylbut-3-en-1-ol}$ (**4ab**) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel

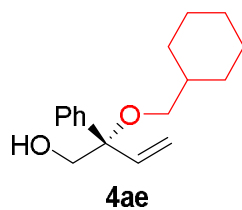
to provide the title compound as a colorless liquid in 91% yield (32.4 mg). $[\alpha]_D^{25} = -3.6$ ($c = 0.40$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42–7.29 (m, 5H), 6.09 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.49 (dd, $J = 1.2$, 11.2 Hz, 1H), 5.41 (dd, $J = 1.2$, 17.6 Hz, 1H), 3.89–3.81 (m, 2H), 3.21 (s, 3H), 1.91 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.9, 137.0, 128.4, 127.6, 127.1, 118.2, 82.2, 67.3, 51.3; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$ ($\text{M}+\text{Na}$): 201.0900, Found: 201.0895; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/20$, $t_{\text{minor}} = 13.98$ min, $t_{\text{major}} = 15.04$ min; 85% ee.



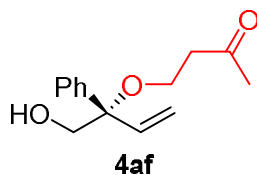
(S)-2-ethoxy-2-phenylbut-3-en-1-ol (4ac) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 90% yield (34.6 mg). $[\alpha]_D^{25} = -4.7$ ($c = 0.58$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42–7.27 (m, 5H), 6.10 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.46 (dd, $J = 1.2$, 11.2 Hz, 1H), 5.39 (dd, $J = 1.2$, 17.6 Hz, 1H), 3.85 (d, $J = 2.0$, Hz 1H), 3.83 (d, $J = 2.8$ Hz, 1H), 3.44–3.31 (m, 2H), 2.02 (brt, 1H), 1.23 (t, $J = 5.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.5, 137.6, 128.3, 127.6, 126.9, 117.8, 81.9, 67.6, 58.7, 15.6; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$ ($\text{M}+\text{Na}$): 215.1000, Found: 215.1041; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/10$, $t_{\text{minor}} = 7.86$ min, $t_{\text{major}} = 8.40$ min; 87% ee.



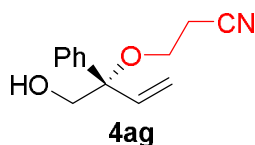
(S)-2-phenethoxy-2-phenylbut-3-en-1-ol (4ad) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 90% yield (48.3 mg). $[\alpha]_D^{25} = -7.8$ ($c = 0.56$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33–7.20 (m, 10H), 6.03 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.42 (dd, $J = 0.8$, 11.2 Hz, 1H), 5.34 (dd, $J = 0.8$, 17.6 Hz, 1H), 3.87–3.78 (m, 2H), 3.58–3.49 (m, 2H), 2.91 (t, $J = 6.8$ Hz, 2H), 1.82 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.2, 139.1, 137.6, 129.0, 128.4, 128.3, 127.6, 126.9, 126.3, 117.8, 81.8, 67.1, 64.2, 36.8; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$ ($\text{M}+\text{Na}$): 291.1400, Found: 291.1358; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/20$, $t_{\text{minor}} = 15.09$ min, $t_{\text{major}} = 18.25$ min; 82% ee.



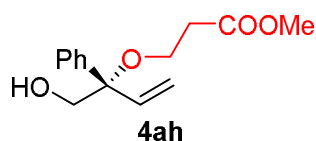
(S)-2-(cyclohexylmethoxy)-2-phenylbut-3-en-1-ol (4ae) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 85% yield (44.3 mg). $[\alpha]_D^{25} = -12.7$ ($c = 0.74$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41–7.28 (m, 5H), 6.04 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.42 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.39 (dd, $J = 1.2, 17.6$ Hz, 1H), 3.90 (d, $J = 6.0$ Hz, 1H), 3.86 (d, $J = 6.0$ Hz, 1H), 3.14 (d, $J = 8.8$ Hz, 1H), 3.10 (d, $J = 8.8$ Hz, 1H), 1.97 (bt, 1H), 1.82–1.861 (m, 5H), 1.31–1.14 (m, 4H), 1.00–0.93 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.0, 138.1, 128.2, 127.5, 126.9, 117.5, 81.1, 68.4, 66.7, 38.5, 30.2, 26.6, 25.9; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_2$ (M+Na): 283.1700, Found: 283.1678; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/20, $t_{\text{minor}} = 6.47$ min, $t_{\text{major}} = 6.68$ min; 82% ee.



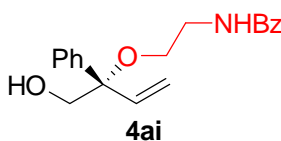
(S)-4-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)butan-2-one (4af) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (40.8 mg). $[\alpha]_D^{25} = -2.2$ ($c = 0.28$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38–7.27 (m, 5H), 6.03 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.38 (d, $J = 11.2$ Hz, 1H), 5.30 (d, $J = 17.6$ Hz, 1H), 3.99 (s, 2H), 3.62–3.54 (m, 2H), 2.86 (brs, 1H), 2.77–2.74 (m, 2H), 2.20 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 208.0, 140.4, 138.5, 128.2, 127.5, 126.7, 117.2, 81.4, 65.5, 57.3, 43.5, 30.4; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (M+Na): 257.1200, Found: 257.1153; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/10, $t_{\text{minor}} = 12.62$ min, $t_{\text{major}} = 13.32$ min; 92% ee.



(S)-3-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)propanenitrile (4ag) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 91% yield (39.5 mg). $[\alpha]_{\text{D}}^{25} = -9.7$ ($c = 1.2$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44–7.29 (m, 5H), 6.12 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.53 (d, $J = 11.2$ Hz, 1H), 5.46 (d, $J = 17.6$ Hz, 1H), 3.91 (d, $J = 11.6$ Hz, 1H), 3.84 (d, $J = 11.6$ Hz, 1H), 3.62–3.51 (m, 2H), 2.61 (t, $J = 6.0$ Hz, 2H), 1.99 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.1, 136.5, 128.5, 128.0, 126.9, 118.8, 117.9, 82.6, 67.4, 58.1, 19.2; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ (M+Na): 240.1000, Found: 240.1006; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 8.63$ min, $t_{\text{major}} = 12.16$ min; 85% ee.

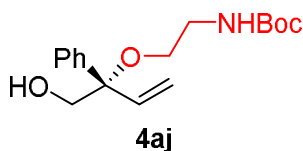


methyl (S)-3-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)propanoate (4ah) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 91% yield (45.2 mg). $[\alpha]_{\text{D}}^{25} = 32.5$ ($c = 1.88$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39–7.33 (m, 4H), 7.29–7.27 (m, 1H), 6.05 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.40 (d, $J = 11.2$ Hz, 1H), 5.33 (d, $J = 17.6$ Hz, 1H), 3.97 (s, 2H), 3.72 (s, 3H), 3.60 (t, $J = 6.0$ Hz, 2H), 2.74 (brs, 1H), 2.63 (t, $J = 6.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.7, 140.3, 138.2, 128.2, 127.5, 126.7, 117.4, 81.8, 65.9, 58.1, 51.8, 34.7; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{NO}_4$ (M+Na): 273.1100, Found: 273.1112; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 23.61$ min, $t_{\text{major}} = 28.22$ min; 86% ee.

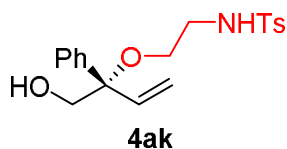


(S)-N-(2-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)ethyl)benzamide (4ai) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:5 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 85% yield (52.9 mg). $[\alpha]_{\text{D}}^{25} = -8.0$ ($c = 1.02$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82–7.79 (m, 2H), 7.48–7.28 (m, 8H), 6.99 (brs, 1H), 6.04 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.45 (d, $J = 11.2$ Hz, 1H), 5.40 (d, $J = 17.6$ Hz, 1H), 3.95 (d, $J = 12.0$ Hz, 1H), 3.92 (d, $J = 12.0$ Hz, 1H), 3.68–3.64 (m, 2H), 3.55–3.53 (m, 2H), 2.19 (bst, $J = 6.0$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.7, 139.9, 137.7, 134.5, 131.4, 128.5, 128.4, 127.8, 127.0, 126.8, 118.0, 81.8, 66.1, 62.1, 40.4; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{21}\text{NNaO}_3$ (M+Na): 334.1400,

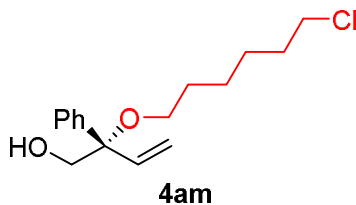
Found: 334.1424; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/10, $t_{\text{major}} = 24.22$ min, $t_{\text{minor}} = 30.29$ min; 57% ee.



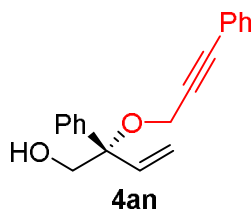
tert-butyl(S)-2-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)ethylcarbamate (4aj) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 82% yield (50.4mg). $[\alpha]_{\text{D}}^{25} = 3.0$ ($c = 1.61$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40–7.27 (m, 5H), 6.06 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.47 (d, $J = 11.2$ Hz, 1H), 5.38 (d, $J = 17.6$ Hz, 1H), 5.05 (brs, 1H), 3.89 (d, $J = 11.6$ Hz, 1H), 3.85 (d, $J = 11.6$ Hz, 1H), 3.43–3.37 (m, 2H), 3.36–3.28 (m, 2H), 2.26 (brs, 1H), 1.45 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.1, 139.9, 137.4, 128.3, 127.8, 126.9, 118.1, 81.9, 69.4, 67.0, 62.4, 40.9, 28.4; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{25}\text{NNaO}_4$ ($\text{M}+\text{Na}$): 330.1700, Found: 330.1686; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/10, $t_{\text{minor}} = 15.55$ min, $t_{\text{major}} = 31.92$ min; 88% ee.



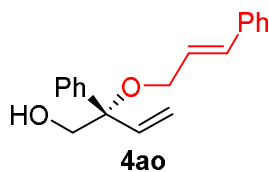
(S)-N-(2-((1-hydroxy-2-phenylbut-3-en-2-yl)oxy)ethyl)-4-methylbenzenesulfonamide (4ak) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 56% yield (40.0 mg). $[\alpha]_{\text{D}}^{25} = -3.3$ ($c = 1.15$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.75 (s, 1H), 7.36–7.27 (m, 7H), 5.97 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.49 (bst, 1H), 5.42 (d, $J = 11.2$ Hz, 1H), 5.32 (d, $J = 17.6$ Hz, 1H), 3.87 (d, $J = 11.6$ Hz, 1H), 3.83 (d, $J = 11.6$ Hz, 1H), 3.42–3.32 (m, 2H), 3.17–3.13 (m, 2H), 2.42 (s, 3), 1.72 (bs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.4, 139.5, 137.2, 137.0, 129.7, 128.4, 127.8, 127.1, 126.8, 118.2, 81.9, 66.4, 61.6, 43.4, 21.5; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{23}\text{NNaO}_4\text{S}$ ($\text{M}+\text{Na}$): 384.1200, Found: 384.1243; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/4, $t_{\text{minor}} = 18.33$ min, $t_{\text{major}} = 20.71$ min; 67% ee.



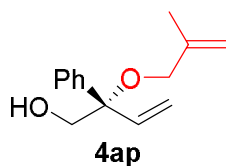
(S)-2-((6-chlorohexyl)oxy)-2-phenylbut-3-en-1-ol (4am) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 83% yield (46.9 mg). $[\alpha]_D^{25} = -5.7$ ($c = 0.71$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43–7.28 (m, 5H), 6.07 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.44 (d, $J = 11.2$ Hz, 1H), 5.39 (d, $J = 17.6$ Hz, 1H), 3.90–3.82 (m, 2H), 3.53 (t, $J = 6.8$ Hz, 2H), 3.36–3.27 (m, 2H), 1.98 (brt, 1H), 1.81–1.74 (m, 2H), 1.66–1.56 (m, 2H), 1.49–1.36 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.4, 137.7, 128.2, 127.5, 126.9, 117.7, 81.5, 67.1, 62.8, 45.0, 32.5, 30.0, 26.7, 25.5; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{23}\text{ClO}_2$ ($\text{M}+\text{Na}$): 305.1300, Found: 305.1289; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/19$, $t_{\text{minor}} = 22.57$ min, $t_{\text{major}} = 25.22$ min; 90% ee.



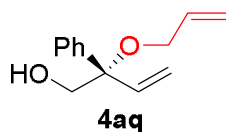
(S)-2-phenyl-2-((3-phenylprop-2-yn-1-yl)oxy)but-3-en-1-ol (4an) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 90% yield (50.1 mg). $[\alpha]_D^{25} = -46.3$ ($c = 0.62$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50–7.29 (m, 10H), 6.18 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.53 (d, $J = 11.2$ Hz, 1H), 5.48 (d, $J = 17.6$ Hz, 1H), 4.30 (d, $J = 11.6$ Hz, 1H), 4.21 (d, $J = 11.6$ Hz, 1H), 3.97–3.87 (m, 2H), 2.20 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.4, 136.6, 131.7, 128.4, 128.2, 127.9, 127.1, 122.5, 118.9, 85.9, 85.7, 83.4, 67.9, 53.0; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}$): 301.1200, Found: 301.1199; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/19$, $t_{\text{minor}} = 10.51$ min, $t_{\text{major}} = 11.57$ min; 93% ee.



(S)-2-(cinnamyloxy)-2-phenylbut-3-en-1-ol (4ao) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 86% yield (48.2 mg). $[\alpha]_D^{25} = -18.5$ ($c = 0.78$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47–7.22 (m, 10H), 6.64 (d, $J = 16.0$ Hz, 1H), 6.35–6.28 (m, 1H), 6.16 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.51 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.47 (dd, $J = 1.2, 17.6$ Hz, 1H), 4.09–3.98 (m, 2H), 3.94–3.85 (m, 2H), 2.02 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 137.2, 136.8, 131.5, 128.5, 128.4, 127.8, 127.6, 127.0, 126.4, 126.3, 118.4, 82.5, 67.9, 64.3; HRMS (ESI-MS): Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$ (M+Na): 303.1400, Found: 303.1364; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 8.89$ min, $t_{\text{major}} = 10.77$ min; 93% ee.

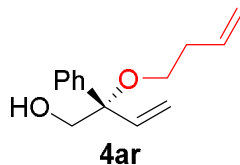


(S)-2-((2-methylallyl)oxy)-2-phenylbut-3-en-1-ol (4ap) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 92% yield (40.2 mg). $[\alpha]_D^{25} = -8.7$ ($c = 0.61$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43–7.27 (m, 5H), 6.12 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.46 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.43 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.09 (s, 1H), 4.90 (s, 1H), 3.90 (d, $J = 4.0$, Hz 1H), 3.88 (d, $J = 5.2$ Hz, 1H), 3.78 (d, $J = 14.0$ Hz, 1H), 3.74 (d, $J = 14.0$ Hz, 1H), 2.03 (brt, 1H), 1.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.5, 140.1, 137.5, 128.3, 127.6, 126.9, 111.9, 110.8, 82.0, 67.4, 66.8, 19.8; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ (M+Na): 241.1200, Found: 241.1209; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 7.32$ min, $t_{\text{major}} = 9.53$ min; 89% ee.

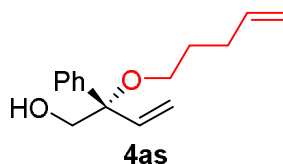


(S)-2-(allyloxy)-2-phenylbut-3-en-1-ol (4aq) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 89% yield (36.3 mg). $[\alpha]_D^{25} = -3.8$ ($c = 0.56$, CHCl_3); Lit. $^9[\alpha]_D^{24} = -10.4$ ($c = 1.49$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44–7.28 (m, 5H), 6.13 (dd, $J = 11.2, 17.6$ Hz, 1H), 6.01–5.91 (m, 1H), 5.48 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.43 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.34 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.18 (dd, $J = 1.6, 17.2$ Hz, 1H), 3.82–3.82 (m, 4H), 2.03 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 137.1, 135.0, 128.4, 127.7, 127.0, 118.2, 116.1, 82.3, 67.8, 64.5;

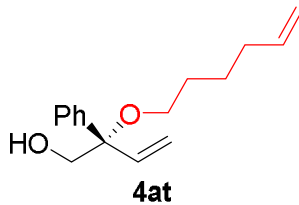
HRMS (ESI-MS): Calcd. for C₁₃H₁₆O₂ (M+Na): 227.1000, Found: 227.1042; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/25, *t*_{major} = 15.03 min, *t*_{minor} = 17.27 min; 95% ee.



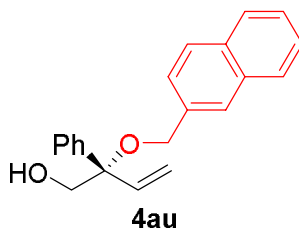
(S)-2-(but-3-en-1-yloxy)-2-phenylbut-3-en-1-ol (4ar) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 93% yield (40.5 mg). [α]_D²⁵ = -5.8 (*c* = 0.29, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.27 (m, 5H), 6.07 (dd, *J* = 11.2, 17.6 Hz, 1H), 5.87–5.79 (m, 1H), 5.45 (dd, *J* = 1.2, 11.2 Hz, 1H), 5.39 (dd, *J* = 1.2, 17.6 Hz, 1H), 5.11 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.05 (dd, *J* = 1.6, 17.2 Hz, 1H), 3.90–3.82 (m, 2H), 3.42–3.33 (m, 2H), 2.40–2.34 (m, 2H), 2.03 (brt, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 137.6, 135.3, 128.3, 127.6, 126.9, 117.8, 116.6, 81.7, 67.1, 62.4, 34.6; HRMS (ESI-MS): Calcd. for C₁₄H₁₈O₂ (M+Na): 241.1200, Found: 241.1200; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/10, *t*_{minor} = 7.44 min, *t*_{major} = 7.96 min; 91% ee.



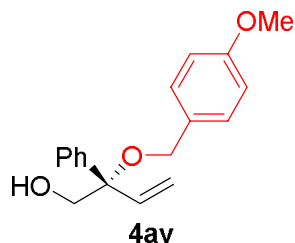
(S)-2-(pent-4-en-1-yloxy)-2-phenylbut-3-en-1-ol (4as) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 78% yield (36.2 mg). [α]_D²⁵ = -3.1 (*c* = 0.16, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.27 (m, 5H), 6.07 (dd, *J* = 11.2, 17.6 Hz, 1H), 5.87–5.77 (m, 1H), 5.45 (dd, *J* = 1.2, 11.2 Hz, 1H), 5.39 (dd, *J* = 1.2, 17.6 Hz, 1H), 5.03 (dd, *J* = 1.6, 12.8 Hz, 1H), 4.97 (dd, *J* = 1.6, 10.8 Hz, 1H), 3.89 (d, *J* = 16.8 Hz, 1H), 3.84 (d, *J* = 16.2 Hz, 1H), 3.37–3.29 (m, 2H), 2.19–2.13 (m, 2H), 1.99 (brt, 1H), 1.76–1.69 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4, 138.4, 137.7, 128.3, 127.6, 126.9, 117.7, 114.7, 81.5, 67.1, 62.3, 30.4, 29.3, ; HRMS (ESI-MS): Calcd. for C₁₅H₂₀O₂ (M+Na): 255.1400, Found: 255.1362; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/20, *t*_{minor} = 7.53 min, *t*_{major} = 7.65 min; 86% ee.



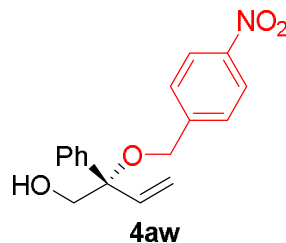
(S)-2-(hex-5-en-1-yloxy)-2-phenylbut-3-en-1-ol (4at) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 92% yield (45.3 mg). $[\alpha]_D^{25} = -2.6$ ($c = 0.14$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41–7.29 (m, 5H), 6.08 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.86–5.76 (m, 1H), 5.45 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.40 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.00 (dd, $J = 1.6, 17.6$ Hz, 1H), 4.95 (dd, $J = 1.6, 12.0$ Hz, 1H), 3.91–3.82 (m, 2H), 3.36–3.27 (m, 2H), 2.10–2.04 (m, 2H), 1.98 (brt, 1H), 1.67–1.60 (m, 2H), 1.51–1.41 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.4, 138.7, 137.7, 128.3, 127.5, 126.9, 117.7, 114.6, 81.5, 67.2, 62.8, 33.6, 29.6, 25.5; HRMS (ESI-MS): Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2$ (M+Na): 269.1500, Found: 269.1522; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/20, $t_{\text{minor}} = 7.35$ min, $t_{\text{major}} = 8.43$ min; 85% ee.



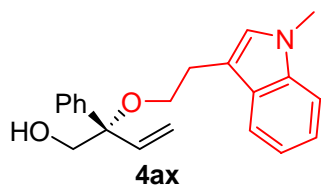
(S)-2-(naphthalen-2-ylmethoxy)-2-phenylbut-3-en-1-ol (4au) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (56.0 mg). $[\alpha]_D^{25} = -42.4$ ($c = 0.47$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85–7.82 (m, 4H), 7.53–7.45 (m, 5H), 7.43–7.38 (m, 2H), 7.35–7.30 (m, 1H), 6.21 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.56 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.52 (dd, $J = 1.2, 17.6$ Hz, 1H), 4.60 (d, $J = 11.6$ Hz, 1H), 4.55 (d, $J = 11.6$ Hz, 1H), 4.00 (d, $J = 11.6$ Hz, 1H), 3.97 (d, $J = 11.6$ Hz, 1H), 2.02 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 137.3, 136.2, 133.3, 132.8, 128.5, 128.1, 127.8, 127.7, 127.6, 127.1, 126.1, 125.8, 125.7, 125.6, 118.5, 82.6, 67.7, 65.5; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_2$ (M+Na): 327.1400, Found: 327.1367; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/10, $t_{\text{major}} = 8.5$ min, $t_{\text{minor}} = 9.3$ min; 86% ee.



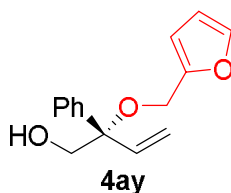
(S)-2-((4-methoxybenzyl)oxy)-2-phenylbut-3-en-1-ol (4av) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 95% yield (54.0 mg). $[\alpha]_D^{25} = -19.0$ ($c = 0.52$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49–7.46 (m, 2H), 7.41–7.37 (m, 2H), 7.33–7.28 (m, 3H), 6.91–6.87 (m, 2H), 6.18 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.52 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.48 (dd, $J = 1.2, 17.6$ Hz, 1H), 4.37 (d, $J = 11.2$ Hz, 1H), 3.31 (d, $J = 11.2$ Hz, 1H), 3.94 (d, $J = 11.2$ Hz, 1H), 3.91 (d, $J = 11.2$ Hz, 1H), 3.81 (s, 3H), 2.03 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.0, 140.1, 137.4, 130.7, 129.0, 128.4, 127.7, 127.1, 118.3, 113.8, 82.3, 67.6, 65.0, 55.3; HRMS (ESI-MS): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_3$ (M+Na): 307.1300, Found: 307.1318; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 3/20, $t_{\text{minor}} = 16.3$ min, $t_{\text{major}} = 31.8$ min; 91% ee.



(S)-2-((4-nitrobenzyl)oxy)-2-phenylbut-3-en-1-ol (4aw) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (52.1 mg). $[\alpha]_D^{25} = -17.5$ ($c = 0.64$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.47–7.34 (m, 5H), 6.17 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.55 (dd, $J = 0.8, 11.2$ Hz, 1H), 5.51 (dd, $J = 0.8, 17.6$ Hz, 1H), 4.55 (d, $J = 13.2$ Hz, 1H), 4.50 (d, $J = 13.2$ Hz, 1H), 4.03–3.93 (m, 2H), 1.90 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.1, 146.4, 139.4, 136.9, 128.6, 128.1, 127.4, 126.9, 123.6, 118.7, 82.8, 67.5, 64.2; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_4$ (M+Na): 322.1100, Found: 322.1078; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 21.8$ min, $t_{\text{major}} = 32.0$ min; 83% ee.

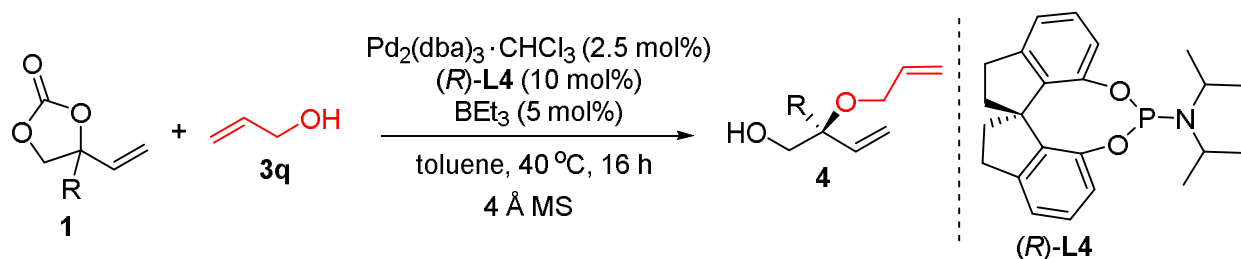


(S)-2-(2-(1-methyl-1H-indol-3-yl)ethoxy)-2-phenylbut-3-en-1-ol (4ax) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 86% yield (50.0 mg). $[\alpha]_D^{25} = -2.3$ ($c = 1.5$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.8$ Hz, 1H), 7.38–7.18 (m, 7H), 7.10–7.06 (m, 1H), 6.87 (s, 1H), 6.07 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.42 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.37 (dd, $J = 1.2, 17.6$ Hz, 1H), 3.86–3.78 (m, 2H), 3.72 (s, 3H), 3.63–3.53 (m, 2H), 3.06 (t, $J = 7.2$ Hz, 2H), 1.96 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.3, 137.6, 136.9, 128.2, 128.0, 127.5, 127.0, 126.8, 121.5, 118.9, 118.7, 117.8, 111.4, 109.2, 81.9, 67.3, 63.9, 32.6, 26.2; HRMS (ESI-MS): Calcd. for $\text{C}_{21}\text{H}_{23}\text{NaNO}_2$ (M+Na): 344.1600, Found: 344.1627; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 3/7, $t_{\text{minor}} = 15.57$ min, $t_{\text{major}} = 18.25$ min; 89% ee.

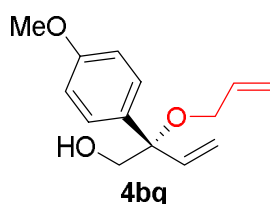


(S)-2-(furan-2-ylmethoxy)-2-phenylbut-3-en-1-ol (4ay) was prepared according to the general procedure C. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (45.9 mg). $[\alpha]_D^{25} = -18.6$ ($c = 1.44$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50–7.47 (m, 2H), 7.41–7.37 (m, 3H), 7.33–7.29 (m, 1H), 6.34 (dd, $J = 1.6, 3.2$ Hz, 1H), 6.28 (d, $J = 3.2$ Hz, 1H), 6.19 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.53 (dd, $J = 1.2, 11.6$ Hz, 1H), 5.48 (dd, $J = 1.2, 17.6$ Hz, 1H), 4.37 (d, $J = 12.0$ Hz, 1H), 4.29 (d, $J = 12.0$ Hz, 1H), 3.92–3.83 (m, 2H), 2.15 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.0, 142.6, 139.8, 136.8, 128.4, 127.7, 127.2, 118.7, 110.3, 108.9, 82.7, 68.0, 58.3; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{16}\text{NaO}_3$ (M+Na): 267.1000, Found: 267.1007; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, i -PrOH/hexanes = 1/10, $t_{\text{minor}} = 15.73$ min, $t_{\text{major}} = 17.98$ min; 88% ee.

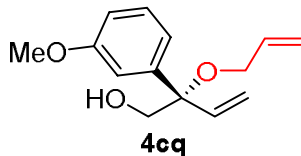
General procedure D for the asymmetric allylic etherification of VECs 1 with allyl alcohol 3q.



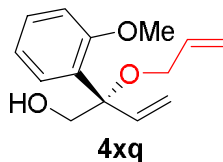
To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), Zhou's ligand $(R)\text{-L4}$ (7.6 mg, 0.02 mmol, 10 mol%), allyl alcohol **3q** (15.0 μL , 0.22 mmol), VEC **1b** (44.0 mg, 0.2 mmol) and 4 \AA molecular sieves (100 mg) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et_3B (10 μL of 1 M solution in THF, 0.01 mmol, 5 mol%), and anhydrous toluene (2 mL) were added sequentially via syringe. The resulting mixture was stirred at 40 °C for 16 h. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel to afford the corresponding ether **4bq**. The enantiomeric excesses of the products were determined by HPLC analysis using chiral stationary phases as indicated for each case.



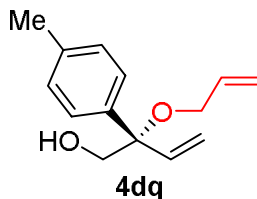
$(S)\text{-2-(allyloxy)-2-(3-methoxyphenyl)but-3-en-1-ol}$ (**4bq**) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (44.5 mg). $[\alpha]_D^{25} = -9.8$ ($c = 0.09$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36–7.31 (m, 2H), 6.91–6.88 (m, 2H), 6.10 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.99–5.89 (m, 1H), 5.46 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.42 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.32 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.16 (dd, $J = 1.2, 17.2$ Hz, 1H), 3.87–3.82 (m, 4H), 3.81 (s, 3H), 2.01 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.0, 137.3, 135.0, 131.8, 128.3, 117.9, 116.0, 113.9, 82.0, 67.8, 64.4, 55.2; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ ($\text{M}+\text{Na}$): 257.1200, Found: 257.1156; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 9.48$ min, $t_{\text{major}} = 10.93$ min; 95% ee.



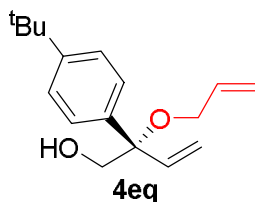
(S)-2-(allyloxy)-2-(3-methoxyphenyl)but-3-en-1-ol (4cq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 96% yield (45.0 mg). $[\alpha]_D^{25} = -11.6$ ($c = 0.76$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31–7.27 (m, 1H), 6.99–6.97 (m, 2H), 6.85–6.82 (m, 1H), 6.11 (dd, $J = 10.8, 17.6$ Hz, 1H), 6.01–5.91 (m, 1H), 5.48 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.44 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.34 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.17 (dd, $J = 1.2, 10.4$ Hz, 1H), 3.90–3.86 (m, 4H), 3.81 (s, 3H), 2.01 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.7, 141.8, 137.1, 135.0, 129.4, 119.3, 118.2, 116.0, 113.0, 112.9, 82.3, 67.8, 64.5, 35.2; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (M+Na): 257.1200, Found: 257.1175; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{minor}} = 9.38$ min, $t_{\text{major}} = 10.29$ min; 93% ee.



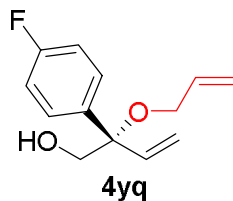
(S)-2-(allyloxy)-2-(2-methoxyphenyl)but-3-en-1-ol (4xq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (44.0 mg). $[\alpha]_D^{25} = -2.2$ ($c = 0.58$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (dd, $J = 1.6, 7.6$ Hz, 1H), 7.31–7.27 (m, 1H), 7.01–7.97 (m, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.13 (dd, $J = 10.8, 17.6$ Hz, 1H), 6.05–5.96 (m, 1H), 5.38 (dd, $J = 2.0, 17.2$ Hz, 1H), 5.30 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.23 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.19 (dd, $J = 1.6, 17.6$ Hz, 1H), 4.14–3.98 (m, 4H), 3.78 (s, 3H), 2.05 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.7, 137.2, 135.2, 128.9, 128.5, 128.4, 120.7, 116.5, 115.8, 111.7, 82.2, 66.5, 64.3, 55.2; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (M+Na): 257.1200, Found: 257.1158; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{major}} = 10.06$ min, $t_{\text{minor}} = 13.91$ min; 99% ee.



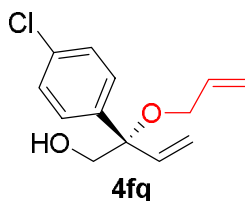
(*S*)-2-(allyloxy)-2-(*p*-tolyl)but-3-en-1-ol (**4dq**) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 95% yield (41.5 mg). $[\alpha]_D^{25} = -12.6$ ($c = 1.10$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31–7.27 (m, 2H), 7.19–7.14 (m, 2H), 6.11 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.99–5.90 (m, 1H), 5.46 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.42 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.32 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.16 (dd, $J = 1.6, 10.8$ Hz, 1H), 3.90–3.79 (m, 4H), 2.35 (s, 3H), 2.02 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.4, 137.3, 136.9, 135.1, 129.1, 126.9, 117.9, 116.0, 82.2, 67.8, 64.4, 21.0; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}$): 241.1200, Found: 241.1202; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 11.60$ min, $t_{\text{major}} = 12.74$ min; 92% ee.



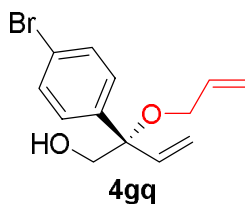
(*S*)-2-(allyloxy)-2-(4-(*tert*-butyl)phenyl)but-3-en-1-ol (**4eq**) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 95% yield (49.5 mg). $[\alpha]_D^{25} = -12.1$ ($c = 0.82$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39–7.32 (m, 4H), 6.12 (dd, $J = 10.8, 17.6$ Hz, 1H), 6.00–5.91 (m, 1H), 5.47 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.43 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.34 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.16 (dd, $J = 1.6, 17.2$ Hz, 1H), 3.91–3.80 (m, 4H), 2.02 (brt, 1H), 1.32 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.5, 137.3, 136.8, 135.1, 126.6, 125.3, 117.9, 115.9, 82.2, 67.8, 64.4, 34.5, 31.3; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$): 283.1700, Found: 283.1669; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 0.5 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{major}} = 11.63$ min, $t_{\text{minor}} = 12.56$ min; 96% ee.



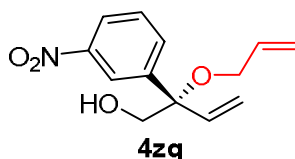
(S)-2-(allyloxy)-2-(4-fluorophenyl)but-3-en-1-ol (4yq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (38.7 mg). $[\alpha]_D^{25} = +6.3$ ($c = 0.53$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41–7.38 (m, 2H), 7.08–7.03 (m, 2H), 6.09 (dd, $J = 10.8$, 17.6 Hz, 1H), 5.99–5.90 (m, 1H), 5.48 (dd, $J = 1.2$, 10.8 Hz, 1H), 5.41 (dd, $J = 1.2$, 17.6 Hz, 1H), 5.33 (dd, $J = 1.6$, 17.2 Hz, 1H), 5.18 (dd, $J = 1.6$, 10.8 Hz, 1H), 3.92–3.80 (m, 4H), 1.98 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.0, 137.1, 134.8, 128.8, 128.7, 118.4, 116.2, 115.1, 81.9, 67.7, 64.5; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{15}\text{FO}_2$ (M+Na): 245.1000, Found: 245.0980; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/49$, $t_{\text{minor}} = 12.21$ min, $t_{\text{major}} = 18.45$ min; 90% ee.



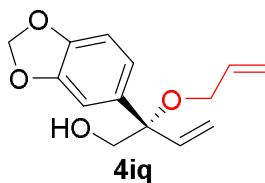
(S)-2-(allyloxy)-2-(4-chlorophenyl)but-3-en-1-ol (4fq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 90% yield (43.0 mg). $[\alpha]_D^{25} = -5.5$ ($c = 0.65$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37–7.32 (m, 4H), 6.08 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.99–5.90 (m, 1H), 5.49 (dd, $J = 1.2$, 11.2 Hz, 1H), 5.40 (dd, $J = 1.2$, 17.6 Hz, 1H), 5.34 (dd, $J = 1.6$, 17.2 Hz, 1H), 5.19 (dd, $J = 1.6$, 10.8 Hz, 1H), 3.92–3.80 (m, 4H), 2.01 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.7, 136.8, 134.7, 133.6, 128.5, 128.4, 118.9, 116.2, 82.0, 67.7, 64.5; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{15}\text{ClO}_2$ (M+Na): 261.0700, Found: 261.0675; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/19$, $t_{\text{minor}} = 11.72$ min, $t_{\text{major}} = 13.34$ min; 92% ee.



(S)-2-(allyloxy)-2-(4-bromophenyl)but-3-en-1-ol (4gq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (49.3 mg). $[\alpha]_{\text{D}}^{25} = +5.1$ ($c = 0.17$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51–7.48 (m, 2H), 7.31–7.28 (m, 2H), 6.08 (dd, $J = 11.2$, 17.6 Hz, 1H), 5.99–5.90 (m, 1H), 5.50 (dd, $J = 1.2$, 11.2 Hz, 1H), 5.40 (dd, $J = 1.2$, 17.6 Hz, 1H), 5.33 (dd, $J = 1.6$, 17.2 Hz, 1H), 5.18 (dd, $J = 1.6$, 10.8 Hz, 1H), 3.92–3.80 (m, 4H), 2.01 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.3, 136.7, 134.7, 131.4, 128.8, 121.8, 118.7, 116.3, 82.0, 67.6, 64.5; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{15}\text{BrO}_2$ ($\text{M}+\text{Na}$): 305.0200, Found: 305.0174; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/49$, $t_{\text{minor}} = 12.27$ min, $t_{\text{major}} = 15.08$ min; 94% ee.

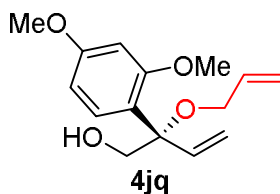


(S)-2-(allyloxy)-2-(3-nitrophenyl)but-3-en-1-ol (4zq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 91% yield (45.4 mg). $[\alpha]_{\text{D}}^{25} = +9.8$ ($c = 0.38$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (t, $J = 2.0$ Hz, 1H), 8.18–8.15 (m, 1H), 7.79–7.77 (m, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 6.10 (dd, $J = 10.8$, 17.6 Hz, 1H), 6.03–5.94 (m, 1H), 5.57 (dd, $J = 1.2$, 10.8 Hz, 1H), 5.42 (dd, $J = 1.2$, 17.6 Hz, 1H), 5.38 (dd, $J = 1.6$, 17.2 Hz, 1H), 5.23 (dd, $J = 1.6$, 10.4 Hz, 1H), 4.00–3.84 (m, 4H), 2.06 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.3, 143.1, 136.3, 134.4, 133.1, 129.2, 122.9, 122.1, 119.6, 116.7, 81.9, 67.4, 64.8; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_4$ ($\text{M}+\text{Na}$): 272.0900, Found: 272.0895; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, $i\text{-PrOH/hexanes} = 1/49$, $t_{\text{minor}} = 27.68$ min, $t_{\text{major}} = 32.21$ min; 94% ee.

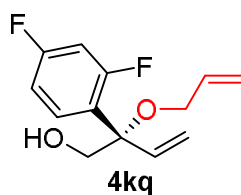


(S)-2-(allyloxy)-2-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (4iq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 92% yield (45.7 mg). $[\alpha]_{\text{D}}^{25} = -8.9$ ($c = 0.56$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.93 (d, $J = 1.6$ Hz, 1H), 6.87 (dd, $J = 1.6$, 8.0 Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.07 (dd, $J = 10.8$, 17.6 Hz, 1H), 5.99–5.89 (m, 3H), 5.47 (dd, $J = 1.2$, 10.8

Hz, 1H), 5.42 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.33 (dd, $J = 2.0, 17.2$ Hz, 1H), 5.17 (dd, $J = 1.6, 10.4$ Hz, 1H), 3.92–3.78 (m, 4H), 1.99 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 147.0, 137.2, 134.9, 133.0, 120.4, 118.0, 116.1, 108.0, 107.7, 101.1, 82.1, 67.7, 64.4; HRMS (ESI-MS): Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_4$ ($\text{M}+\text{Na}$): 271.0900, Found: 271.0922; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{minor}} = 24.55$ min, $t_{\text{major}} = 30.26$ min; 90% ee.

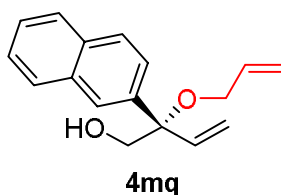


(S)-2-(allyloxy)-2-(2,4-dimethoxyphenyl)but-3-en-1-ol (4jq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 92% yield (48.6 mg). $[\alpha]_{\text{D}}^{25} = +6.3$ ($c = 0.53$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.4$ Hz, 1H), 8.52–6.47 (m, 2H), 6.11 (dd, $J = 10.8, 17.6$ Hz, 1H), 6.00–5.94 (m, 1H), 5.36 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.29 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.26 (dd, $J = 1.6, 17.6$ Hz, 1H), 5.18 (dd, $J = 1.6, 10.4$ Hz, 1H), 4.11–3.94 (m, 4H), 3.81 (s, 3H), 3.76 (s, 3H), 2.02 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 157.9, 137.6, 135.3, 129.4, 120.7, 116.2, 115.8, 104.1, 99.5, 82.0, 66.6, 64.3, 55.3, 55.2; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_4$ ($\text{M}+\text{Na}$): 287.1300, Found: 287.1267; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{major}} = 19.11$ min, $t_{\text{minor}} = 22.31$ min; 98% ee.

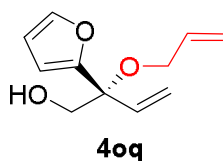


(S)-2-(allyloxy)-2-(2,4-difluorophenyl)but-3-en-1-ol (4kq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 84% yield (40.4 mg). $[\alpha]_{\text{D}}^{25} = -3.1$ ($c = 0.44$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.48 (m, 1H), 6.93–6.87 (m, 1H), 6.83–6.77 (m, 1H), 6.08 (dd, $J = 11.2, 17.6$ Hz, 1H), 6.00–5.93 (m, 1H), 5.43 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.37 (dd, $J = 1.6, 9.6$ Hz, 1H), 5.29 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.22 (dd, $J = 1.6, 10.2$ Hz, 1H), 4.00–3.92 (m, 4H), 1.99 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 163.7, 161.4, 161.3, 161.1, 161.0, 158.8, 158.7, 135.9, 135.8, 134.6, 130.2, 130.1, 130.0, 123.5, 123.3, 118.4, 116.4, 111.3, 111.2, 111.1, 111.0, 104.9, 104.7, 104.6, 104.4, 81.2, 65.9, 65.8, 64.6; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{14}\text{F}_2\text{O}_2$ ($\text{M}+\text{Na}$): 263.0900,

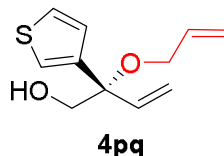
Found: 263.0865; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{minor}} = 17.21$ min, $t_{\text{major}} = 18.45$ min; 90% ee.



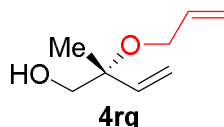
(S)-2-(allyloxy)-2-(naphthalen-2-yl)but-3-en-1-ol (4mq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (47.8 mg). $[\alpha]_{\text{D}}^{25} = -11.4$ ($c = 0.46$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87–8.82 (m, 4H), 7.55–7.47 (m, 3H), 6.20 (dd, $J = 10.8, 17.6$ Hz, 1H), 6.03–5.94 (m, 1H), 5.52 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.48 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.36 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.19 (dd, $J = 1.6, 10.4$ Hz, 1H), 4.03–3.87 (m, 4H), 2.05 (bt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.5, 137.3, 135.0, 133.0, 132.8, 128.2, 128.1, 127.5, 126.2, 126.1, 126.0, 124.9, 118.3, 116.2, 82.4, 67.5, 64.6; HRMS (ESI-MS): Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}$): 277.1200, Found: 277.1204; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{major}} = 9.95$ min, $t_{\text{minor}} = 10.74$ min; 92% ee.



(S)-2-(allyloxy)-2-(furan-2-yl)but-3-en-1-ol (4oq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 93% yield (36.1 mg). $[\alpha]_{\text{D}}^{25} = -5.2$ ($c = 0.53$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, $J = 2.0$ Hz, 1H), 6.42 (dd, $J = 0.8, 3.2$ Hz, 1H), 6.38 (dd, $J = 1.6, 3.2$ Hz, 1H), 6.07 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.91–5.82 (m, 1H), 5.49 (dd, $J = 1.2, 2.4$ Hz, 1H), 5.46 (dd, $J = 1.2, 4.4$ Hz, 1H), 5.24 (dd, $J = 1.2, 17.2$ Hz, 1H), 5.12 (dd, $J = 1.2, 10.8$ Hz, 1H), 3.99 (dd, $J = 5.6, 11.2$ Hz, 1H), 3.94–3.88 (m, 1H), 3.78 (dd, $J = 5.6, 11.2$ Hz, 1H), 3.74–3.68 (m, 1H), 2.08 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.8, 142.7, 135.3, 134.8, 118.3, 116.2, 110.2, 109.8, 79.1, 67.2, 65.3; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$ ($\text{M}+\text{Na}$): 217.0800, Found: 217.0823; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 13.00$ min, $t_{\text{major}} = 20.04$ min; 90% ee.

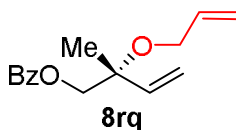


(S)-2-(allyloxy)-2-(thiophen-3-yl)but-3-en-1-ol (4pq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 91% yield (38.1 mg). $[\alpha]_D^{25} = -12.5$ ($c = 0.66$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (dd, $J = 3.2, 5.2$ Hz, 1H), 7.26 (dd, $J = 1.2, 3.2$ Hz, 1H), 7.10 (dd, $J = 1.6, 5.2$ Hz, 1H), 6.12 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.96–5.86 (m, 1H), 5.45 (dd, $J = 1.2, 5.6$ Hz, 1H), 5.43 (dd, $J = 1.2, 12.0$ Hz, 1H), 5.30 (dd, $J = 1.2, 17.2$ Hz, 1H), 5.15 (dd, $J = 1.2, 10.8$ Hz, 1H), 3.92–3.84 (m, 2H), 3.81–3.75 (m, 2H), 2.05 (brt, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.4, 137.1, 135.0, 126.9, 125.9, 123.1, 117.8, 116.1, 80.8, 68.0, 64.7; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ ($\text{M}+\text{Na}$): 233.0600, Found: 233.0617; HPLC conditions: Chiralcel OJ-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 12.15$ min, $t_{\text{major}} = 13.16$ min; 87% ee.



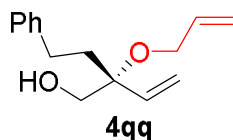
(R)-2-(allyloxy)-2-methylbut-3-en-1-ol (4rq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 87% yield (27.4 mg). $[\alpha]_D^{25} = -2.5$ ($c = 0.16$, CHCl_3). Lit. $^9[\alpha]_D^{24} = -7.9$ ($c = 1.4$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.96–5.87 (m, 1H), 5.83 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.30–5.24 (m, 3H), 5.14 (dd, $J = 1.6, 10.8$ Hz, 1H), 3.89 (dd, $J = 1.2, 5.6$ Hz, 2H), 3.50 (d, $J = 6.0$ Hz, 1H), 3.46 (d, $J = 6.0$ Hz, 1H), 2.09 (brt, 1H), 1.31 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.8, 135.5, 116.9, 116.0, 78.2, 69.4, 63.8, 18.6; HRMS (ESI-MS): Calcd. for $\text{C}_8\text{H}_{14}\text{O}_2$ ($\text{M}+\text{Na}$): 165.0900, Found: 165.0894;

For the determination of enantiomeric excess of **4rq**, the compound **4rq** was converted to corresponding diol monobenzoyle **8rq**. The ee value of **8rq** was determined by chiral HPLC.

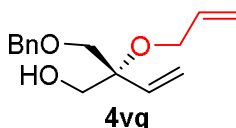


(R)-2-(allyloxy)-2-methylbut-3-en-1-yl benzoate (8rq)¹ was obtained as a colorless liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07–8.04 (m, 2H), 7.59–7.52 (m, 1H), 7.47–7.43 (m, 2H), 5.97–5.86 (m, 2H), 5.35–5.27

(m, 3H), 5.13 (dd, $J = 1.6, 10.4$ Hz, 1H), 4.35 (d, $J = 11.2$ Hz, 1H), 4.31 (d, $J = 11.2$ Hz, 1H), 3.97 (d, $J = 9.2$ Hz, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 139.4, 135.5, 133.0, 130.1, 129.6, 128.4, 116.9, 115.9, 76.8, 69.2, 64.0, 20.4; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3$ (M+Na): 269.1200, Found: 269.1198; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/19, $t_{\text{minor}} = 7.58$ min, $t_{\text{major}} = 8.11$ min; 37% ee.

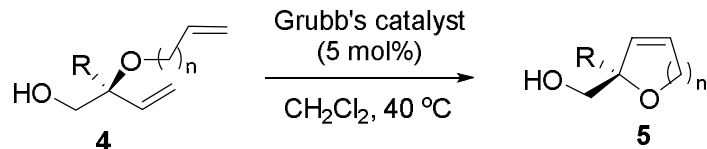


(R)-2-(allyloxy)-2-phenethylbut-3-en-1-ol (4qq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 97% yield (45.1 mg). $[\alpha]_{\text{D}}^{25} = -1.2$ ($c = 2.6$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.27 (m, 2H), 7.22–7.17 (m, 3H), 6.00–5.90 (m, 1H), 5.83 (dd, $J = 10.8, 17.6$ Hz, 1H), 5.38 (dd, $J = 1.2, 10.8$ Hz, 1H), 5.32 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.33 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.17 (dd, $J = 1.6, 10.4$ Hz, 1H), 3.99–3.91 (m, 2H), 3.73–3.61 (m, 2H), 2.71–2.61 (m, 2H), 2.03–1.89 (m, 2H), 1.87 (brt, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 138.7, 135.2, 128.4, 128.3, 125.8, 117.4, 116.1, 79.8, 65.1, 63.3, 35.0, 29.6; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ (M+Na): 255.1400, Found: 215.1361; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{major}} = 19.97$ min, $t_{\text{minor}} = 27.53$ min; 61% ee.

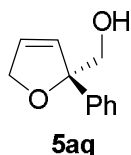


(R)-2-(allyloxy)-2-((benzyloxy)methyl)but-3-en-1-ol (4vq) was prepared according to the general procedure D. The crude product was purified by flash column chromatography (1:40 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless liquid in 94% yield (46.8 mg). $[\alpha]_{\text{D}}^{25} = -5.2$ ($c = 0.63$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.27 (m, 5H), 5.97–5.87 (m, 1H), 5.77 (dd, $J = 11.2, 17.6$ Hz, 1H), 5.34 (dd, $J = 1.2, 11.2$ Hz, 1H), 5.32 (dd, $J = 1.2, 17.6$ Hz, 1H), 5.28 (dd, $J = 1.6, 17.2$ Hz, 1H), 5.14 (dd, $J = 1.6, 10.4$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.05–3.94 (m, 2H), 3.78 (d, $J = 11.6$ Hz, 1H), 3.70 (d, $J = 11.6$ Hz, 1H), 3.66 (d, $J = 9.4$ Hz, 1H), 3.59 (d, $J = 9.4$ Hz, 1H), 2.39 (brs, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 136.1, 135.3, 128.4, 127.7, 127.6, 117.9, 116.1, 79.3, 73.7, 72.5, 65.3, 64.2; HRMS (ESI-MS): Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3$ (M+Na): 271.1300, Found: 271.1308; HPLC conditions: Chiralcel OD-H column, 220 nm, flow rate: 1 ml/min, *i*-PrOH/hexanes = 1/49, $t_{\text{major}} = 10.79$ min, $t_{\text{minor}} = 11.73$ min; 83% ee.

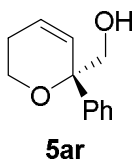
General procedure E for Ring-closing Metathesis of **4** to tertiary cyclic ethers **5**.



According to the reported literature procedure,⁹ under nitrogen atmosphere acyclic homo-allyl ether **4aq** (30.0 mg, 0.15 mmol), Grubbs 1st generation catalyst (6.2 mg, 0.007 mmol, 5 mol%), and anhydrous degassed CH₂Cl₂ (2.0 mL) were added into a Schlenk flask in order and the mixture was refluxed at 40 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated under reduce pressure and the resulting residue was chromatographed on silica gel (EA/PE = 1/10) to give the desired product **5aq** as a tan oil (23.8 mg, 92%).

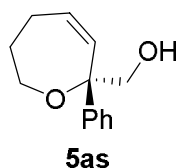


(*S*)-(2-phenyl-2,5-dihydrofuran-2-yl)methanol (**5aq**) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a tan oil in 92% yield (23.8 mg). $[\alpha]_{\text{D}}^{25} = -79.8$ ($c = 0.32$, CHCl₃); Lit.⁹ $[\alpha]_{\text{D}}^{24} = -102.8$ ($c = 1.0$, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.27 (m, 5H), 6.08–6.03 (m, 2H), 4.85 (d, $J = 13.6$ Hz, 1H), 4.75 (d, $J = 13.6$ Hz, 1H), 3.84–3.76 (m, 2H), 1.99 (brt, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 129.7, 128.5, 128.0, 127.4, 125.0, 94.3, 75.6, 68.6; HRMS (ESI-MS): Calcd. for C₁₁H₁₂O₂ (M+Na): 199.0700, Found: 199.0736;

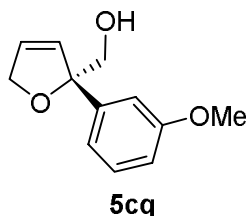


(*S*)-(2-phenyl-5,6-dihydro-2H-pyran-2-yl)methanol (**5ar**) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 89% yield (24.6 mg). $[\alpha]_{\text{D}}^{25} = -42.7$ ($c = 0.13$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.27 (m, 5H), 6.22–6.12 (m, 2H), 3.91 (dd, $J = 10.4, 11.2$ Hz, 1H), 3.70 (d, $J = 11.2$ Hz, 1H), 3.63 (dd, $J = 10.0, 11.2$ Hz, 1H), 3.57 (d, $J = 11.2$ Hz, 1H), 2.46–2.36 (m, 1H), 2.11 (brt, 1H), 1.93–1.86 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 129.2, 128.4,

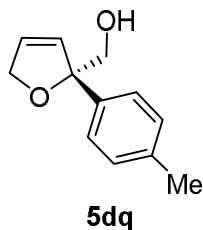
127.6, 127.5, 126.5, 78.7, 70.4, 60.3, 25.0; HRMS (ESI-MS): Calcd. for C₁₂H₁₄O₂ (M+Na): 213.0900, Found: 213.0889;



(S)-(2-phenyl-2,5,6,7-tetrahydrooxepin-2-yl)methanol (5as) was prepared according to the general procedure E by using Grubbs 2st generation catalyst. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a colorless oil in 84% yield (18.5 mg). $[\alpha]_D^{25} = -13.8$ ($c = 0.75$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.28 (m, 5H), 6.23–6.12 (m, 2H), 3.94–3.89 (m, 1H), 3.72–3.55 (m, 3H), 2.46–2.36 (m, 1H), 2.08 (brt, 1H), 1.93–1.86 (m, 1H), 0.90–0.83 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 129.2, 128.4, 127.7, 127.5, 126.5, 78.7, 70.4, 60.3, 29.7, 25.0; HRMS (ESI-MS): Calcd. for C₁₃H₁₆O₂ (M+Na): 227.1000, Found: 227.1051;

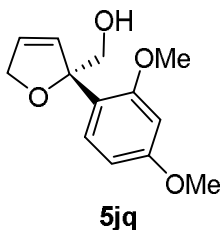


(S)-(2-(3-methoxyphenyl)-2,5-dihydrofuran-2-yl)methanol (5cq) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a tan oil in 83% yield (29.2 mg). $[\alpha]_D^{25} = -74.2$ ($c = 0.74$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.25 (m, 1H), 6.98–6.91 (m, 2H), 6.82–6.79 (m, 1H), 6.03 (s, 2H), 4.84 (d, $J = 12.8$ Hz, 1H), 4.75 (d, $J = 12.8$ Hz, 1H), 3.81 (s, 3H), 3.78 (s, 2H), 2.05 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 143.9, 129.6, 129.5, 128.0, 117.3, 112.5, 111.0, 94.3, 75.6, 68.5, 55.2; HRMS (ESI-MS): Calcd. for C₁₂H₁₄O₃ (M+Na): 229.0800, Found: 229.0823;

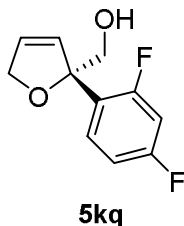


(S)-(2-(p-tolyl)-2,5-dihydrofuran-2-yl)methanol (5dq) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on

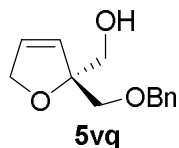
silica gel to provide the title compound as a tan oil in 94% yield (24.6 mg). $[\alpha]_D^{25} = -87.8$ ($c = 0.96$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29–7.15 (m, 4H), 6.05–6.01 (m, 2H), 4.83 (d, $J = 12.8$ Hz, 1H), 4.73 (dd, $J = 1.2, 13.2$ Hz, 1H), 3.80 (d, $J = 12.4$ Hz, 1H), 3.77 (d, $J = 12.4$ Hz, 1H), 2.33 (s, 3H), 2.08 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.3, 137.0, 129.8, 129.1, 127.8, 125.0, 94.2, 75.5, 68.5, 21.0; HRMS (ESI-MS): Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_2$ ($\text{M}+\text{Na}$): 213.0900, Found: 213.0895;



(S)-2-(3-methoxyphenyl)-2,5-dihydrofuran-2-ylmethanol (5jq) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a tan oil in 87% yield (23.3 mg). $[\alpha]_D^{25} = -106.4$ ($c = 0.55$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.4$ Hz, 1H), 6.50–6.45 (m, 2H), 6.37–6.34 (m, 1H), 5.92 (d, $J = 6.0$ Hz, 1H), 4.80 (d, $J = 12.8$ Hz, 1H), 4.70 (d, $J = 12.8$ Hz, 1H), 4.03 (d, $J = 11.6$ Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.70 (d, $J = 11.6$ Hz, 1H), 1.98 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.4, 136.2, 129.8, 127.2, 126.8, 122.6, 104.0, 99.0, 93.8, 74.6, 66.9, 55.3, 55.1; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$ ($\text{M}+\text{Na}$): 259.0900, Found: 259.0946;

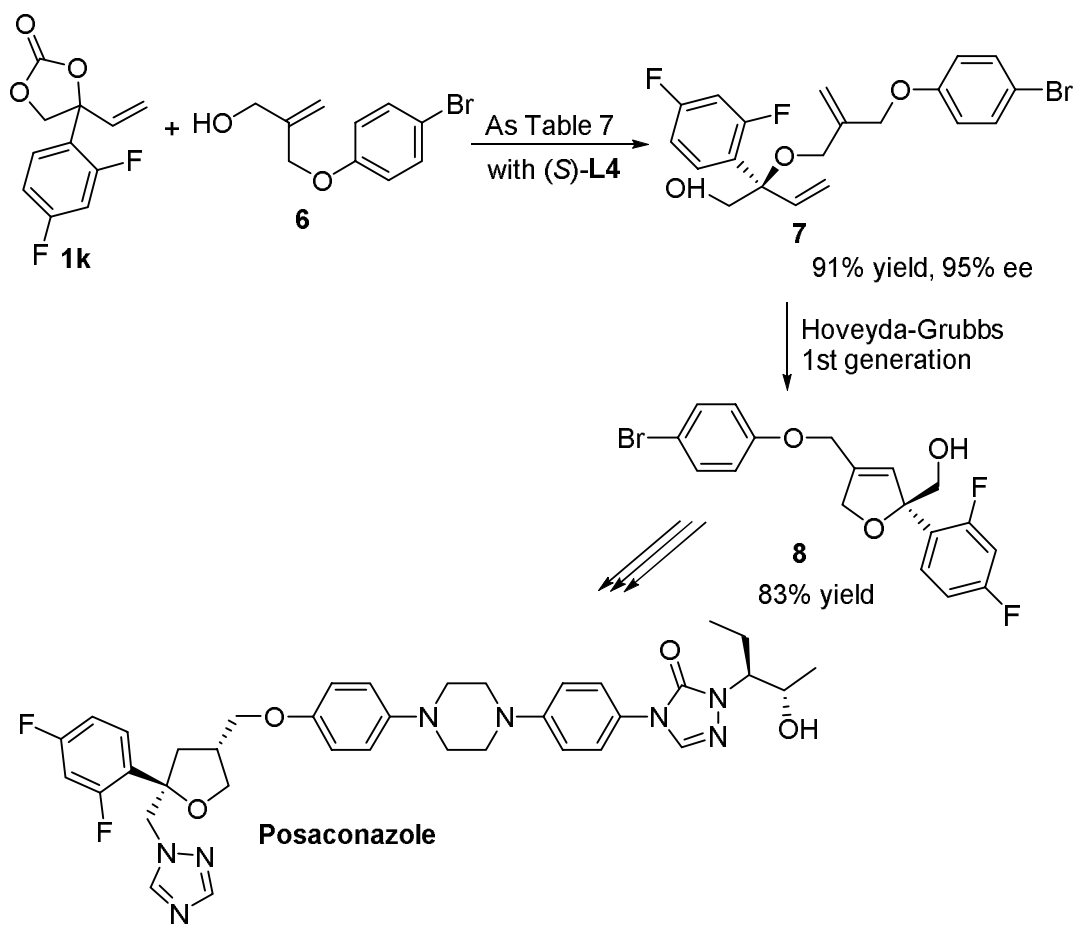


(S)-2-(2,4-difluorophenyl)-2,5-dihydrofuran-2-ylmethanol (5kq) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a tan oil in 96% yield (32.2 mg). $[\alpha]_D^{25} = -74.3$ ($c = 0.68$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60–7.54 (m, 1H), 6.90–6.85 (m, 1H), 6.81–6.76 (m, 1H), 6.20–6.17 (m, 1H), 6.03 (d, $J = 6.4$ Hz, 1H), 4.84 (d, $J = 13.2$ Hz, 1H), 4.72 (d, $J = 13.2$ Hz, 1H), 3.91 (d, $J = 11.6$ Hz, 1H), 3.73 (d, $J = 11.6$ Hz, 1H), 2.01 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.7, 163.6, 161.2, 161.1, 159.9, 159.8, 157.4, 157.3, 128.5, 128.4, 128.2, 125.1, 125.0, 111.4, 111.3, 111.2, 111.1, 104.4, 104.1, 123.9, 92.6, 75.2, 67.3, 67.2; HRMS (ESI-MS): Calcd. for $\text{C}_{11}\text{H}_{10}\text{F}_2\text{O}_2$ ($\text{M}+\text{Na}$): 235.0500, Found: 235.0553;



(R)-2-((benzyloxy)methyl)-2,5-dihydrofuran-2-yl)methanol (5vq) was prepared according to the general procedure E. The crude product was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound as a tan oil in 87% yield (21.1 mg). $[\alpha]_D^{25} = -17.4$ ($c = 0.55$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37–7.27 (m, 5H), 6.05 (d, $J = 6.4$ Hz, 1H), 5.83–5.80 (m, 1H), 4.71 (s, 2H), 4.58 (d, $J = 12.4$ Hz, 1H), 4.54 (d, $J = 12.4$ Hz, 1H), 3.75–3.65 (m, 2H), 3.59 (d, $J = 9.6$ Hz, 1H), 3.51 (d, $J = 9.6$ Hz, 1H), 1.98 (brs, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.1, 129.1, 128.4, 127.6, 127.5, 92.4, 75.7, 73.6, 72.9, 65.7; HRMS (ESI-MS): Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_3$ ($\text{M}+\text{Na}$): 243.1000, Found: 243.0998;

Procedure for the Synthesis of key intermediate Posaconazole.



2-((4-bromophenoxy)methyl)prop-2-en-1-ol (6) was prepared according to the reported literature.¹⁰ To a Schlenk test tube charged with a mixture of 1,4-dibromobenzene (1.0 mmol, 236 mg) and potassium carbonate (3.0 mmol, 415 mg) was added copper chloride (6.7 mg, 0.05 mmol) and 2-methylenepropane-1,3-diol (1.0 mL) under Nitrogen atmosphere. The resulting mixture was stirred for 24 h at 130 °C. The reaction mixture was then acidified to pH=3 with 1N HCl solution. The aqueous phase was extracted three times with EtOAc and the combined organic layers was washed with H₂O, dried over MgSO₄, and concentrated in vacuo. Purification of the crude product by column chromatography afforded the desired product (**6**) in 42% yield (97.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.34 (m, 2H), 7.83–7.78 (m, 2H), 5.29 (s, 1H), 5.26 (s, 1H), 4.55 (s, 2H), 4.24 (s, 2H), 2.07 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 143.65, 132.2, 116.5, 114.0, 113.2, 69.1, 63.8; HRMS (ESI-MS): Calcd. for C₁₀H₁₁BrO₂ (M+Na): 264.9800, Found: 264.9769;

(R)-2-((2-((4-bromophenoxy)methyl)allyl)oxy)-2-(2,4-difluorophenyl)but-3-en-1-ol (7):

Following general procedure B, using Pd₂(dba)₃·CHCl₃ (10.4 mg, 0.01 mmol, 2.5 mol%), Zhou's ligand (*S*)-**L4** (15.2 mg, 0.04 mmol, 10 mol%), allyl alcohol **6** (97.2 mg, 0.4 mmol), VEC **1k** (90.5 mg, 0.4 mmol) and 4 Å molecular sieves (100 mg) were added to a 10 mL flask. The flask was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et₃B (20 µL of 1 M solution in THF, 0.02 mmol, 5 mol%), and anhydrous toluene (4 mL) were added sequentially via syringe. The resulting mixture was stirred at 40 °C for 16 h. After completion, the reaction mixture was cooled to room temperature and the solvent was removed *in vacuo* with the aid of a rotary evaporator. The obtained residue was purified by flash column chromatography (1:20 EtOAc: Petroleum ether) on silica gel to provide the title compound **7** as a colorless oil in 91% yield (155 mg) and 95% ee. [α]_D²⁵ = +17.4 (*c* = 0.68, CHCl₃).

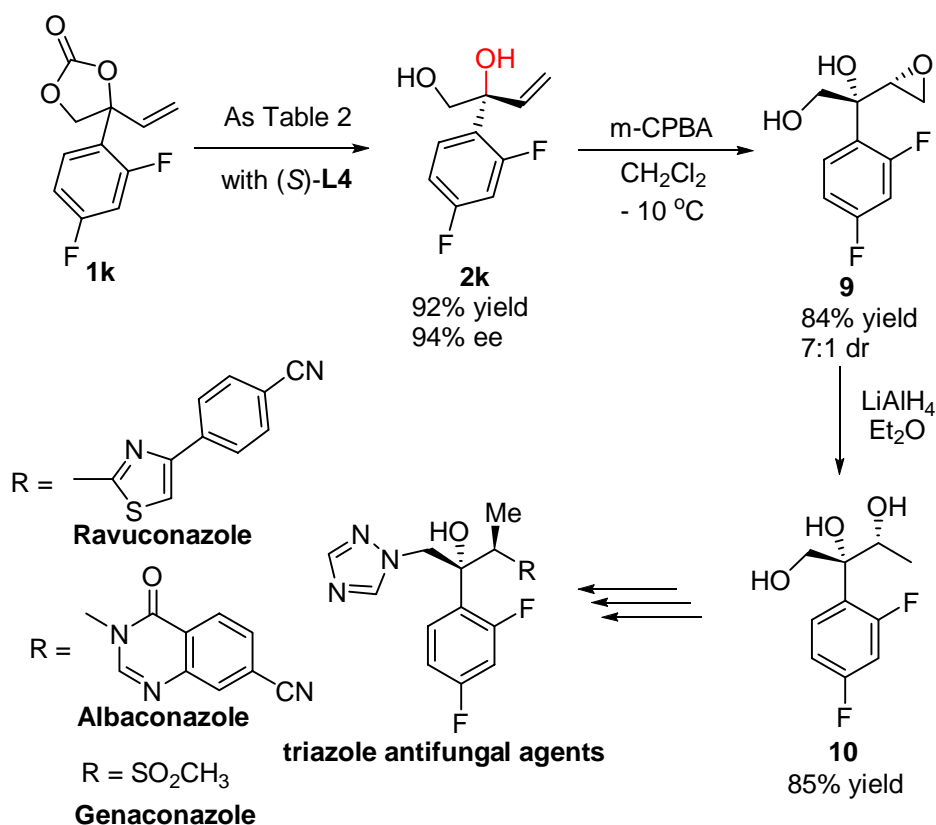
Under nitrogen atmosphere acyclic ether **7** (50.0 mg, 0.12 mmol), Hovryda-Grubbs 1st catalyst (7.2 mg, 0.01 mmol, 10 mol%), and anhydrous degassed CH₂Cl₂ (2.0 mL) were added into a Schlenk flask in order and the mixture was refluxed at 40°C for overnight. After cooling to room temperature, the reaction mixture was concentrated under reduce pressure and the resulting residue was chromatographed on silica gel (EA/PE = 1/10) to give the desired product **8** as a tan oil (38.8 mg, 83%).

(R)-2-((2-((4-bromophenoxy)methyl)allyl)oxy)-2-(2,4-difluorophenyl)but-3-en-1-ol (7) was obtained as a colorless oil in 91% yield (155 mg). [α]_D²⁵ = +17.4 (*c* = 0.68, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.45 (m, 1H), 7.38–7.34 (m, 2H), 6.87–6.74 (m, 4H), 6.04 (d, *J* = 10.8, 17.6 Hz, 1H), 5.41 (d, *J* = 10.8 Hz, 1H), 5.37 (s, 1H), 5.32 (s, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 4.62 (d, *J* = 13.2 Hz, 1H), 4.58 (d, *J* = 13.2 Hz, 1H), 4.09–4.01 (m, 4H), 2.18 (brt, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 163.7, 161.3,

161.2, 161.1, 158.7, 158.6, 157.4, 141.3, 136.1, 132.2, 130.0, 129.9, 123.5, 118.2, 116.5, 115.4, 113.2, 111.2, 111.0, 104.9, 104.6, 104.4, 81.0, 69.1, 65.0, 64.9, 63.8; HRMS (ESI-MS): Calcd. for $C_{20}H_{19}BrF_2O_3$ (M+Na): 447.0400, Found: 447.0389;

(R)-4-((4-bromophenoxy)methyl)-2-(2,4-difluorophenyl)-2,5-dihydrofuran-2-yl)methanol (**8**) was obtained as a tan oil in 83% yield (38.8 mg). $[\alpha]_D^{25} = +74.4$ ($c = 1.2$, $CHCl_3$). 1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 1H), 7.37–7.35 (m, 2H), 6.91–6.75 (m, 4H), 6.20 (s, 1H), 4.87 (d, $J = 12.8$ Hz, 1H), 4.77 (d, $J = 12.8$ Hz, 1H), 4.64 (d, $J = 14.0$ Hz, 1H), 4.61 (d, $J = 14.0$ Hz, 1H), 3.92 (d, $J = 11.6$ Hz, 1H), 3.73 (d, $J = 11.6$ Hz, 1H), 2.04 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.6, 161.3, 161.2, 159.9, 159.8, 157.3, 138.1, 132.3, 128.5, 128.4, 128.3, 125.5, 125.4, 116.3, 113.5, 111.4, 111.2, 104.4, 104.2, 103.9, 93.1, 74.8, 67.3, 61.9; HRMS (ESI-MS): Calcd. for $C_{18}H_{15}BrF_2O_3$ (M+Na): 419.0100, Found: 419.0075;

Synthesis of key intermediate for triazole antifungal agents



(R)-2-(2,4-difluorophenyl)but-3-ene-1,2-diol (**2k**): Following General Procedure A, using $Pd_2(dba)_3 \cdot CHCl_3$ (77.6 mg, 0.075 mmol, 1.25 mol%), Zhou's ligand **(S)-L4** (114.4 mg, 0.3 mmol, 5 mol%), $PhB(OH)_2$ (146.3 mg, 1.2 mmol, 20 mol%), and VEC **1k** (1.36 g, 6 mmol), and distilled H_2O (1.1 mL, 60.0 mmol) in THF (20 mL), the reaction mixture was stirred at $40\text{ }^\circ\text{C}$ for 48 hours. After completion, the

reaction mixture was cooled to room temperature followed by addition of water and EtOAc (10 mL). The phases were separated and the aqueous layer was extracted with EtOAc and then concentrated in vacuo. The obtained residue was purified by flash column chromatography (1:10 EtOAc: Petroleum ether) on silica gel to provide the title compound **2k** as a colorless oil in 92% yield (1.1 g) and 94% ee. $[\alpha]_{\text{D}}^{25} = +29.1$ ($c = 0.36$, CHCl_3).

According to the reported literature¹¹ with some modifications, *m*-chloroperbenzoic acid (1.2 g, 6.87 mmol) was added to a solution of diol **2k** (550 mg, 2.75 mmol) in CH_2Cl_2 (10 mL) at $-10\text{ }^\circ\text{C}$. After overnight stirring at the same temperature, the reaction mixture was poured into water, and extracted with CH_2Cl_2 . The organic layer was dried on anhydrous sodium sulfate and concentrated in vacuo. The diastereomeric ratio is a 7:1, which was determined by ^1H NMR analysis of the crude mixture. The obtained residue was purified by flash column chromatography (1:5 EtOAc: Petroleum ether) on silica gel column to afford **9** (497 mg, 84% yield) as a single diastereomer.

(R)-1-(2,4-difluorophenyl)-1-((R)-oxiran-2-yl)ethane-1,2-diol (9) was obtained as a white solid in 84% yield (497 mg); mp. 77-79 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.61 (m, 1H), 6.93–6.88 (m, 1H), 6.84–6.78 (m, 1H), 4.14 (dd, $J = 2.0, 11.6$ Hz, 1H), 3.84 (d, $J = 11.6$ Hz, 1H), 3.65 (dd, $J = 4.0, 7.2$ Hz, 1H), 3.26 (br, 2H), 2.69–2.65 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 163.8, 161.4, 161.3, 160.6, 160.5, 158.1, 158.0, 129.4, 129.3, 129.3, 129.2, 123.2, 123.1, 123.0, 123.0, 111.6, 111.6, 111.4, 111.4, 104.4, 104.1, 104.1, 103.9, 72.6, 72.5, 68.3, 68.3, 54.4, 54.3, 42.5; HRMS (APCI-MS): Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_3\text{F}_2$ (M+H): 217.0700, Found: 217.0674;

The epoxide **6** (250 mg, 1.16 mmol) was added to a suspension of LiAlH_4 (132 mg, 3.47 mmol) in Et_2O (10 mL) at $0\text{ }^\circ\text{C}$. The mixture was stirred at room temperature for 5 hours. The mixture was then quenched with saturated aqueous solution of sodium sulfate at $0\text{ }^\circ\text{C}$, and the white solid was filtered out and washed with ether. The obtained filtrate was dried on anhydrous sodium sulfate and concentrated in vacuo. The residue was purified with column chromatography on silica gel (1:3 EtOAc: Petroleum ether) to afford the triol **10** (215 mg, 85% yield).

(2R,3R)-2-(2,4-difluorophenyl)butane-1,2,3-triol (10)¹² was obtained as a viscous oil in 85% yield; mp. 81-83 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} = +12.03$ ($c = 1.02$, CHCl_3); Lit. $^{11}[\alpha]_{\text{D}} = +5.74$ ($c = 1.11$, CHCl_3), Lit. $^{13}[\alpha]_{\text{D}}^{25} = +11.4$ ($c = 1.11$, CHCl_3). ^1H NMR (400 MHz, acetone- d_6) δ 7.81–7.75 (m, 1H), 7.02–6.90 (m, 2H), 4.34–4.28 (m, 1H), 4.20 (s, 1H), 4.13–4.01 (m, 3H), 3.83 (dd, $J = 6.8, 10.8$ Hz, 1H); 0.87 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 164.2, 161.9, 161.8, 161.3, 161.2, 158.9, 158.7, 131.6, 131.6, 131.5, 127.0, 126.9, 111.8, 111.6, 104.6, 104.4, 104.1, 78.6, 78.5, 70.6, 70.6, 68.5, 68.5, 18.3; HRMS (ESI-MS): Calcd. for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{F}_2$ (M+H): 219.0900, Found: 219.0916; The ^1H NMR is same as the reported one.^{10,12}

Determination of the absolute configuration of products **2**

The absolute configuration of **2a** and **2r** (prepared from **1a** and **1r** using general procedures A and B respectively) was determined to be *S* in both cases. The *S* configuration of compound **2a** and **2r** were deduced by comparing the signs of the optical rotations with that reported previously in literatures. For **2a**, $[\alpha]_{\text{D}}^{25} = -42.8$ ($c = 0.36$, CHCl_3), {Lit.⁵ $[\alpha]_{\text{D}}^{20} = -43.4$ ($c = 0.20$, EtOH) for *S* isomer and Lit.¹⁴ $[\alpha]_{\text{D}}^{24} = +35.5$ ($c = 0.2$, EtOH) for *R* isomer}. For **2r**, $[\alpha]_{\text{D}}^{25} = -4.2$ ($c = 0.34$, CHCl_3), {for *S* isomer, Lit.¹ $[\alpha]_{\text{D}}^{25} = -3.2$ ($c = 0.24$, CHCl_3), for *R* isomer, Lit.⁶ $[\alpha]_{\text{D}} = +4.78$ ($c = 2.50$, CHCl_3)}. The absolute configurations of the other products **2** as shown in Table 2 and 3 were assigned by analogy.

Determination of the absolute configuration of products **4**

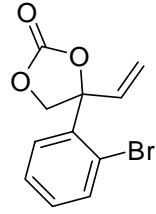
The absolute configuration of **4aq** and **4rq** (prepared from **1a** and **1r** using general procedures C and D respectively) was determined to be *S* and *R*. The *S* configuration of compound **4aq** and *R* configuration of compound **4rq** was deduced by comparing the signs of the optical rotations with that reported previously in literature. For **4aq** $[\alpha]_{\text{D}}^{25} = -3.8$ ($c = 0.56$, CHCl_3); Lit.⁹ $[\alpha]_{\text{D}}^{24} = -10.4$ ($c = 1.49$, CH_2Cl_2). For **4rq**, $[\alpha]_{\text{D}}^{25} = -2.5$ ($c = 0.16$, CHCl_3). Lit.⁹ $[\alpha]_{\text{D}}^{24} = -7.9$ ($c = 1.4$, CHCl_3). The absolute configurations of the other products **3** as shown in Table 2 and 3 were assigned by analogy.

The absolute configuration of cyclic ether **5aq** (prepared from acyclic ether **4aq**) was determined to be *S*. The *S* configuration of compound **5aq** was deduced by comparing the sign of optical rotation with that reported in the literature. $[\alpha]_{\text{D}}^{25} = -79.8$ ($c = 0.32$, CHCl_3); Lit.⁹ $[\alpha]_{\text{D}}^{24} = -102.8$ ($c = 1.0$, CH_2Cl_2). The absolute configurations of other products **5** as shown in Table 8 and Scheme 3 were assigned by analogy.

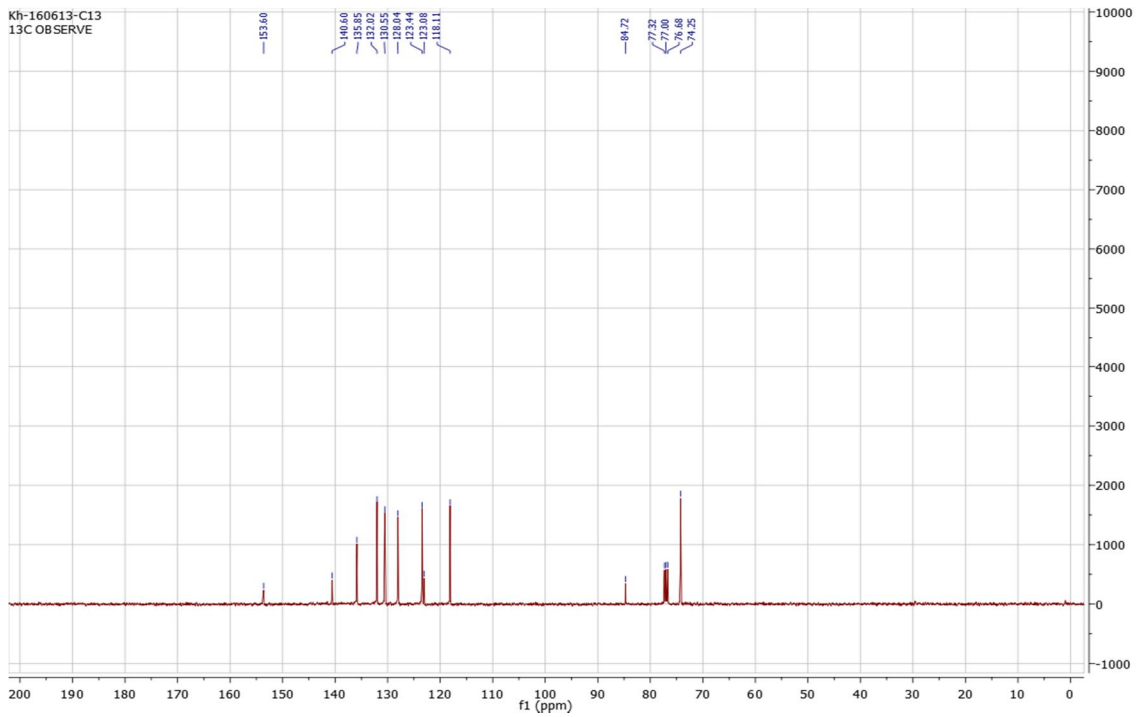
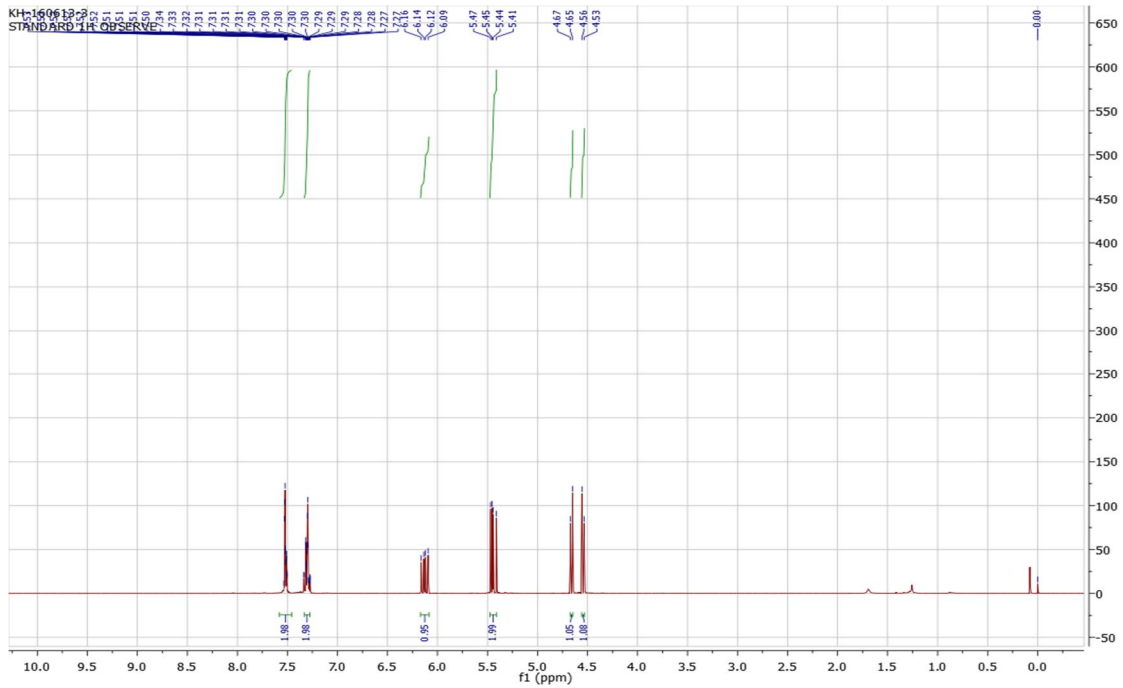
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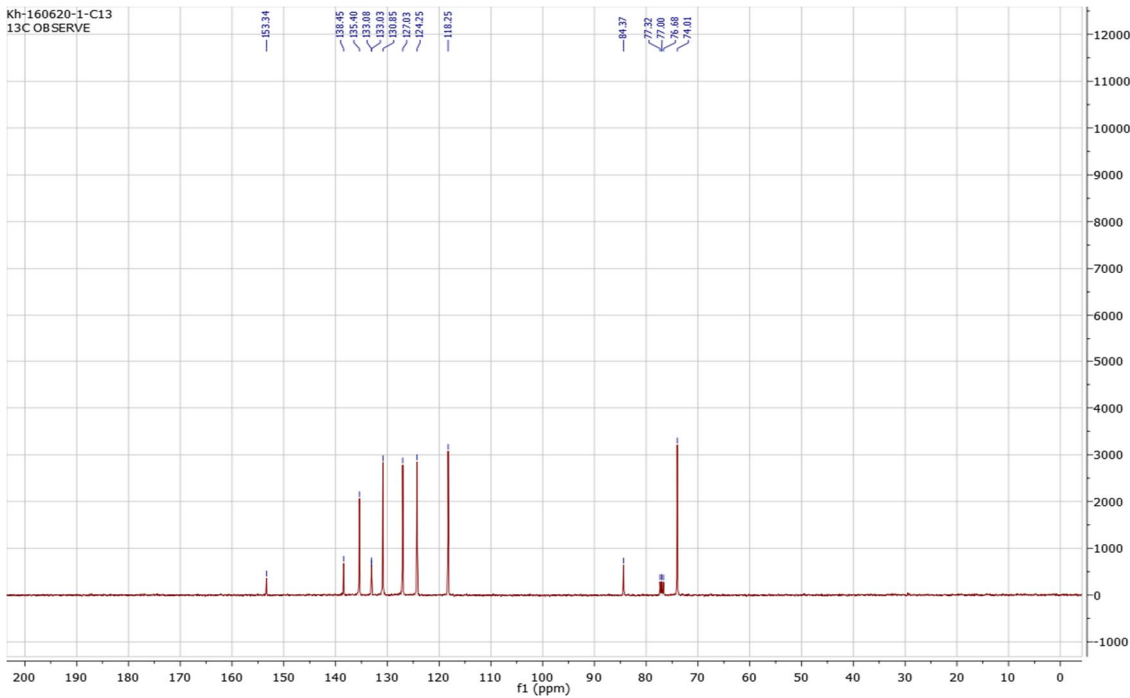
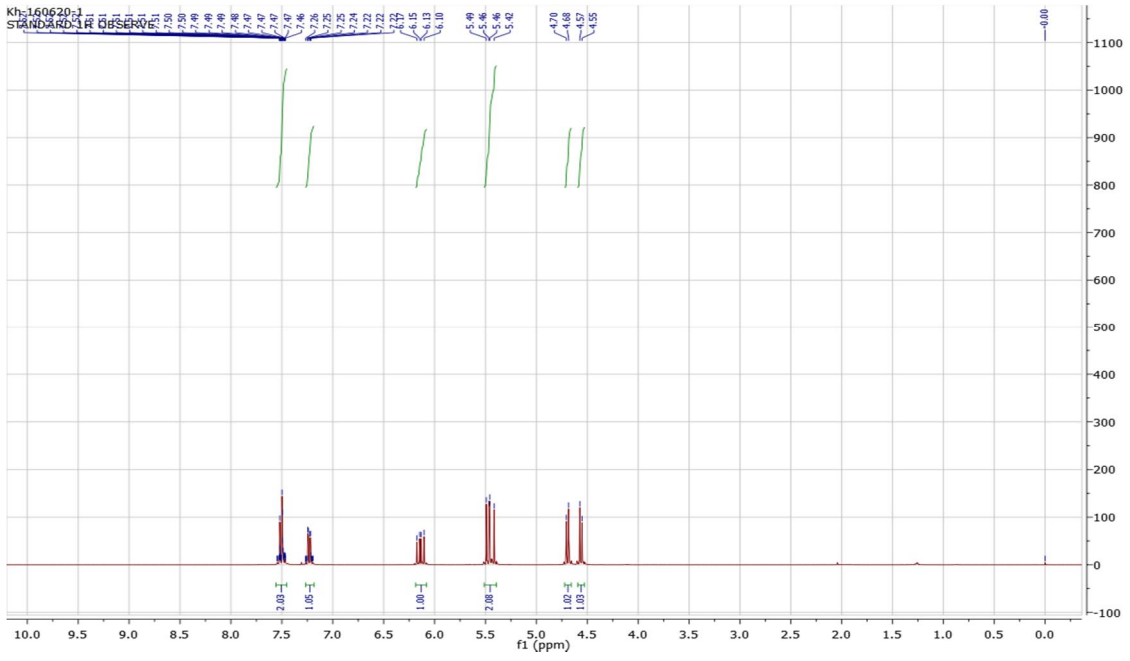
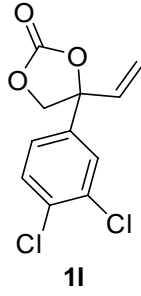
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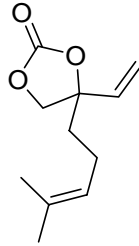
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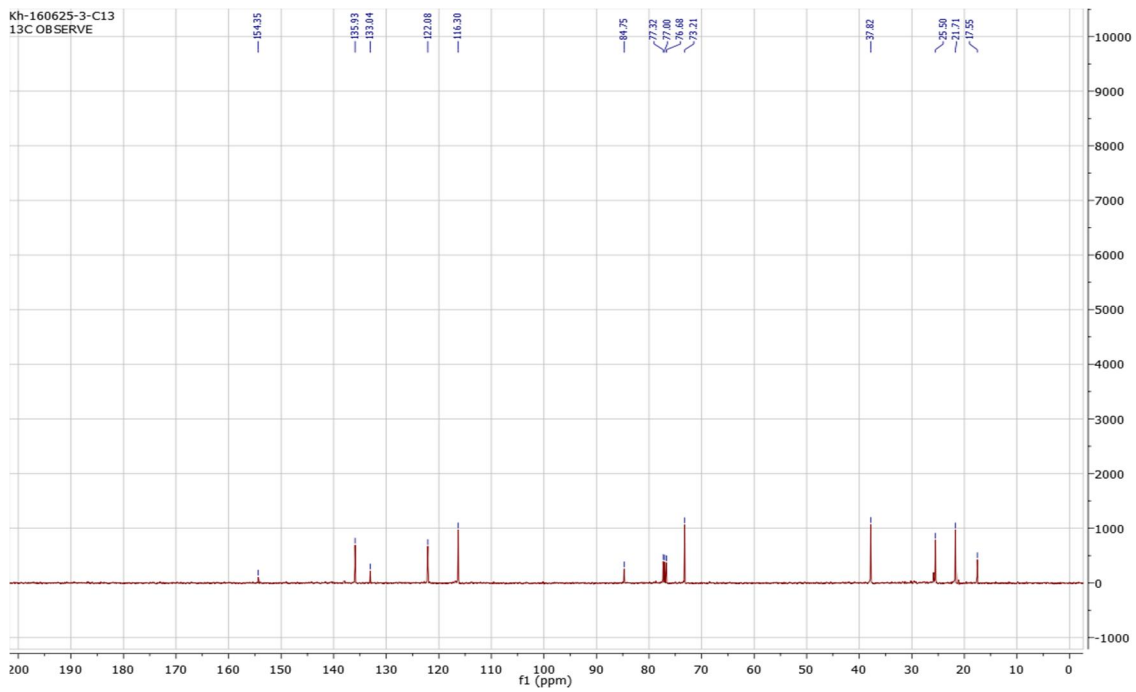
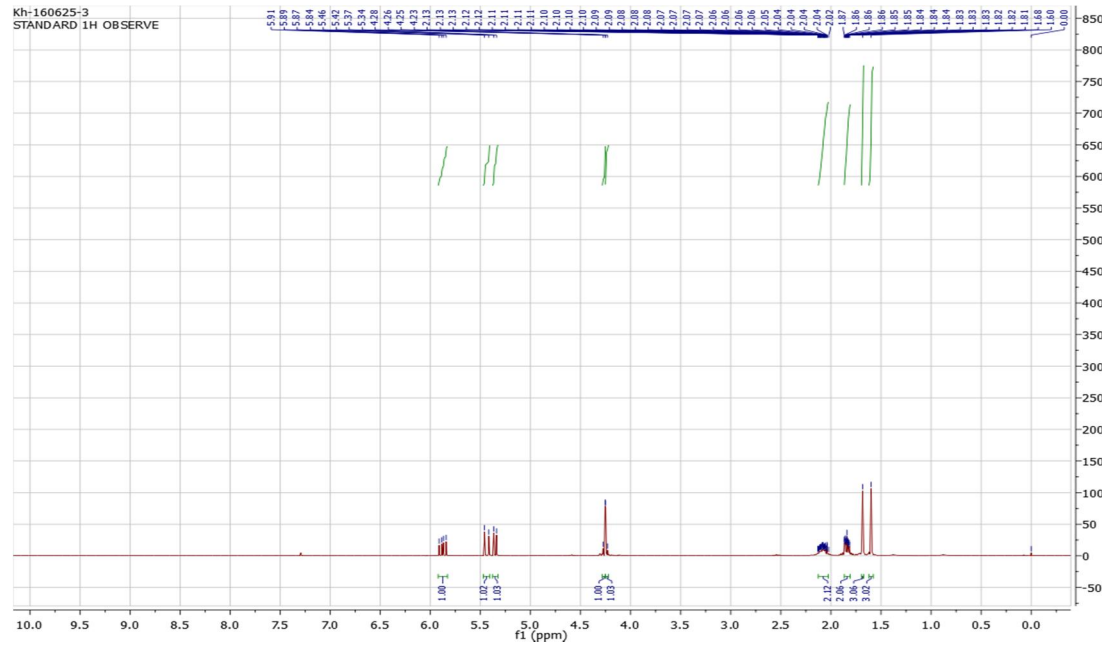
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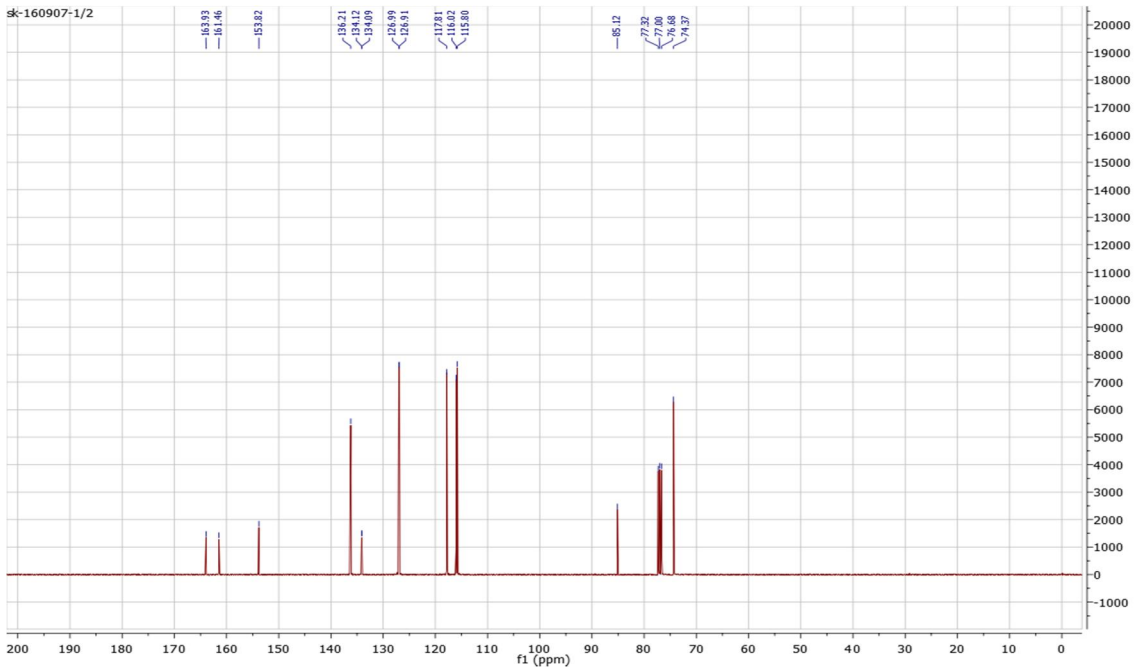
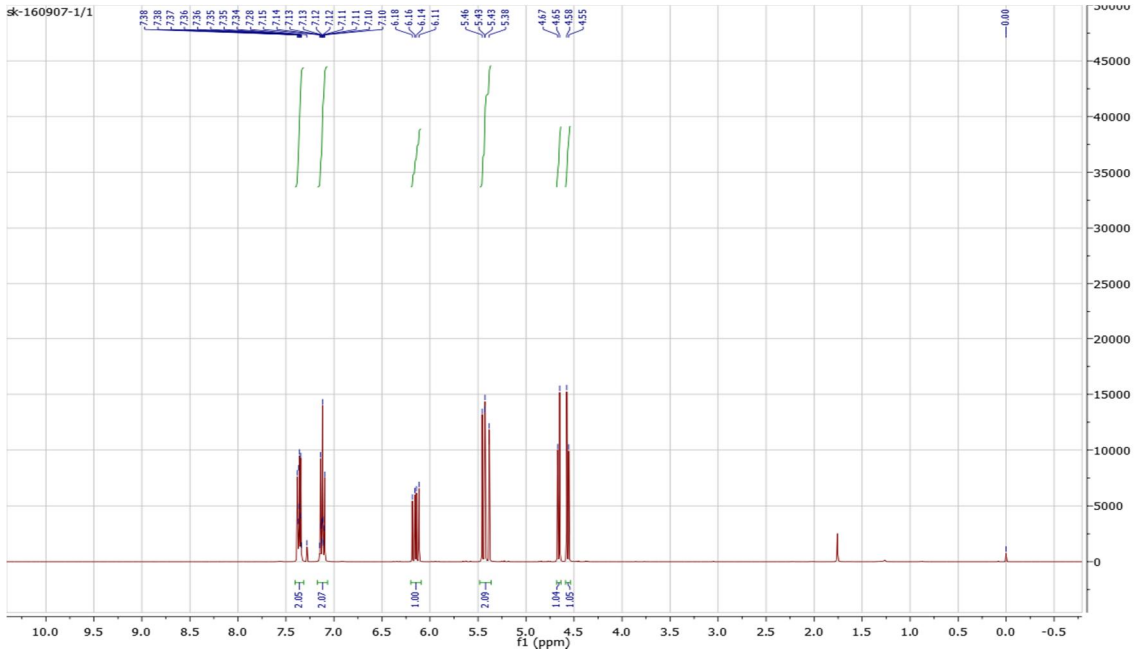
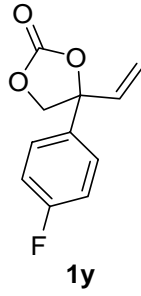


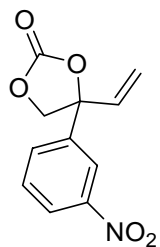




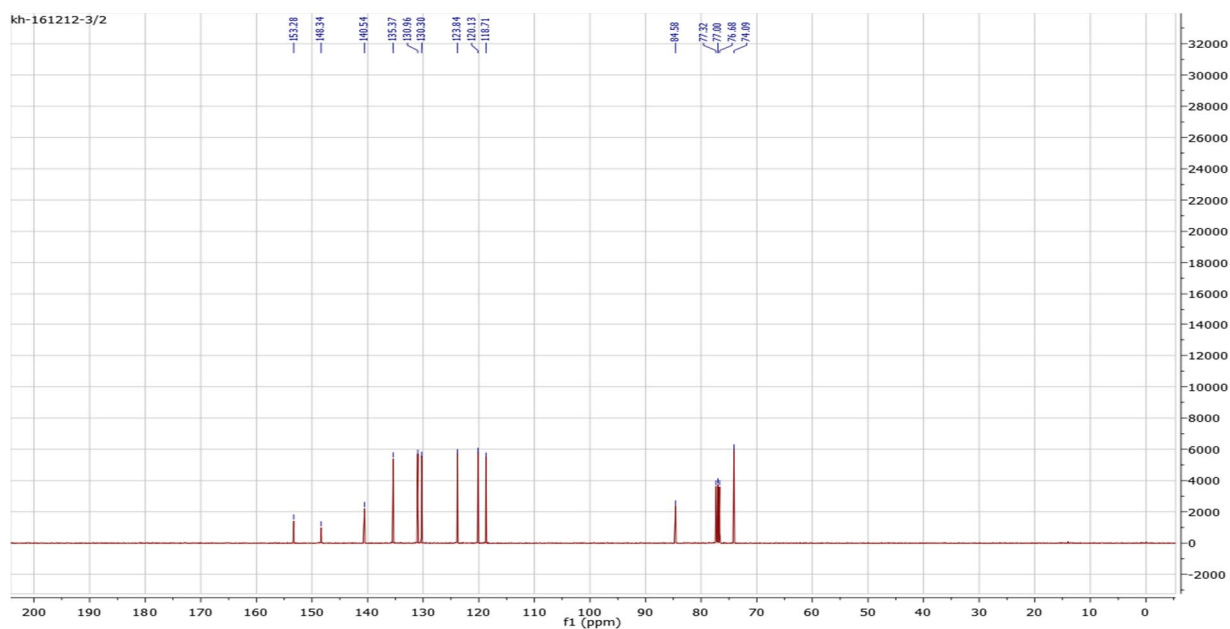
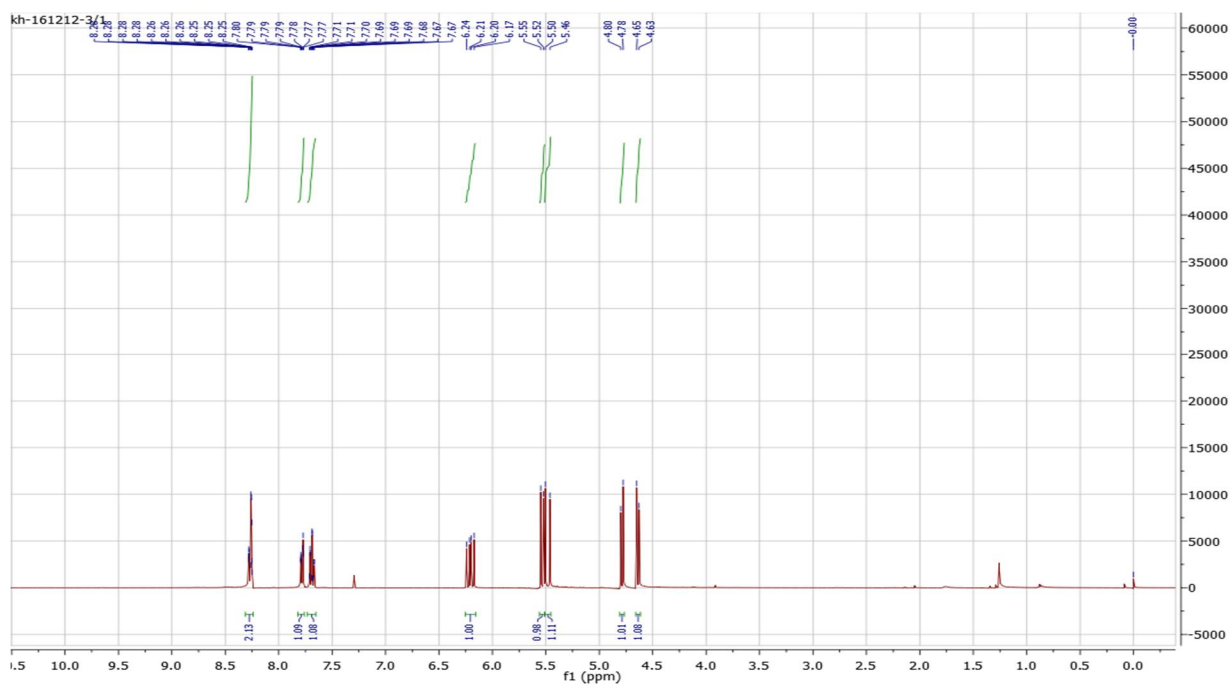
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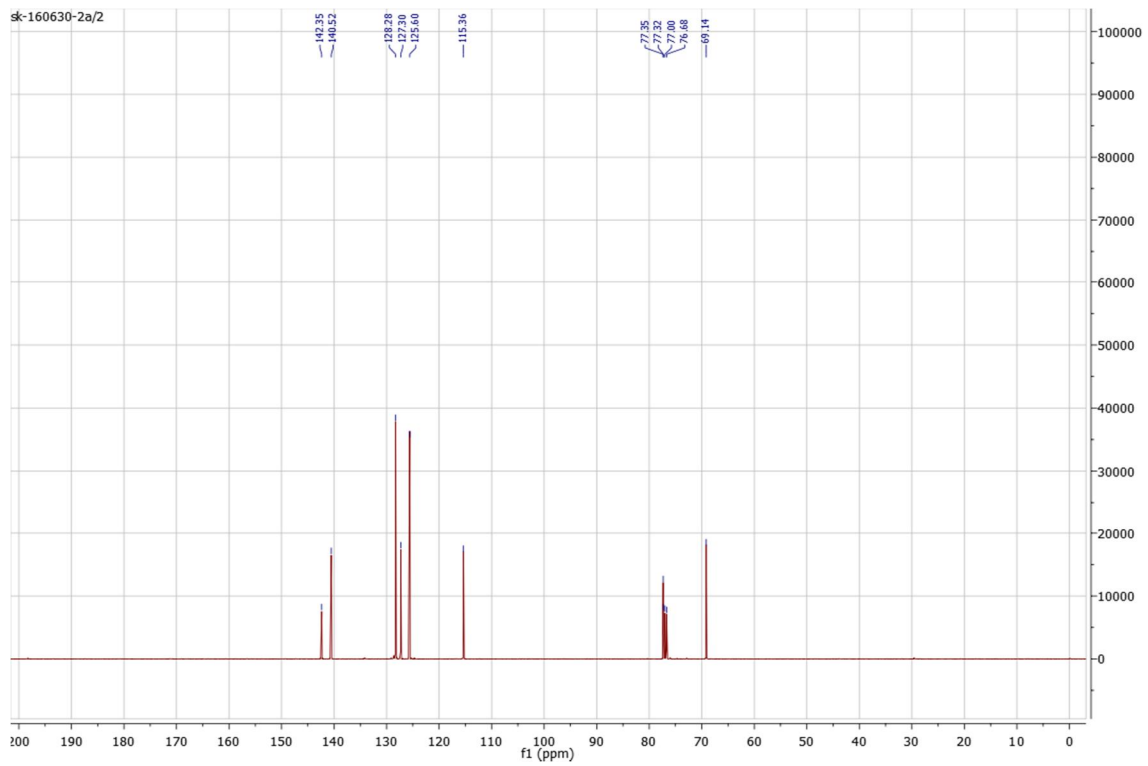
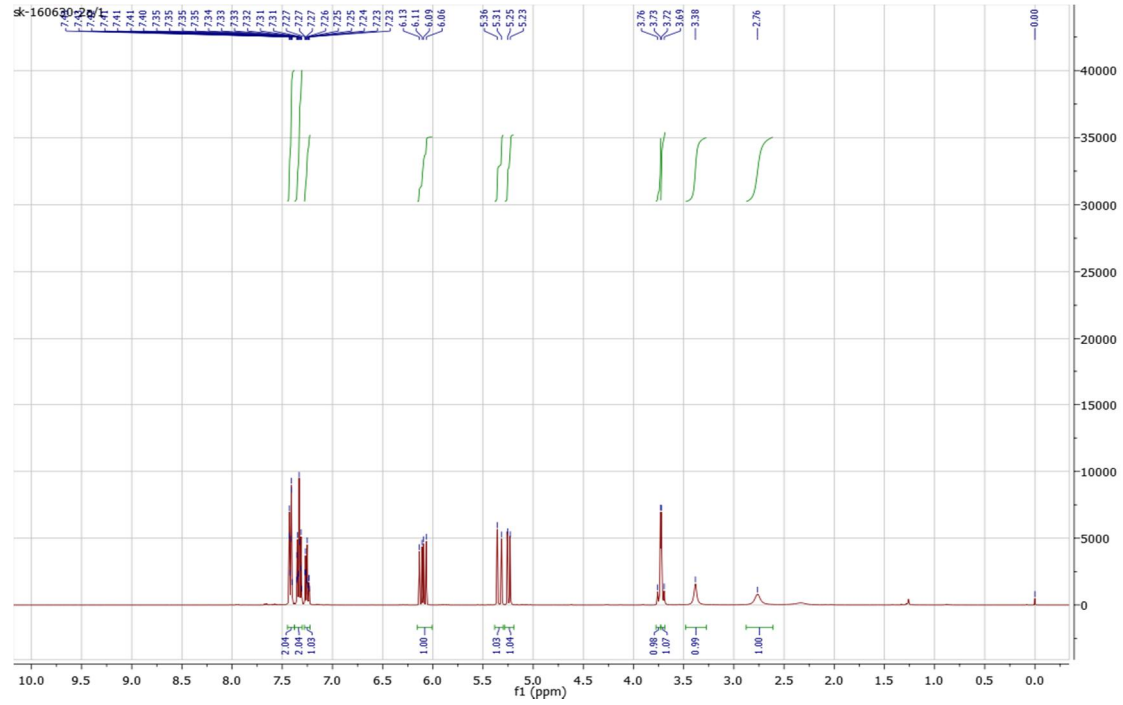
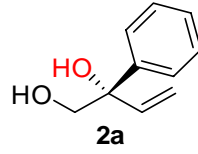


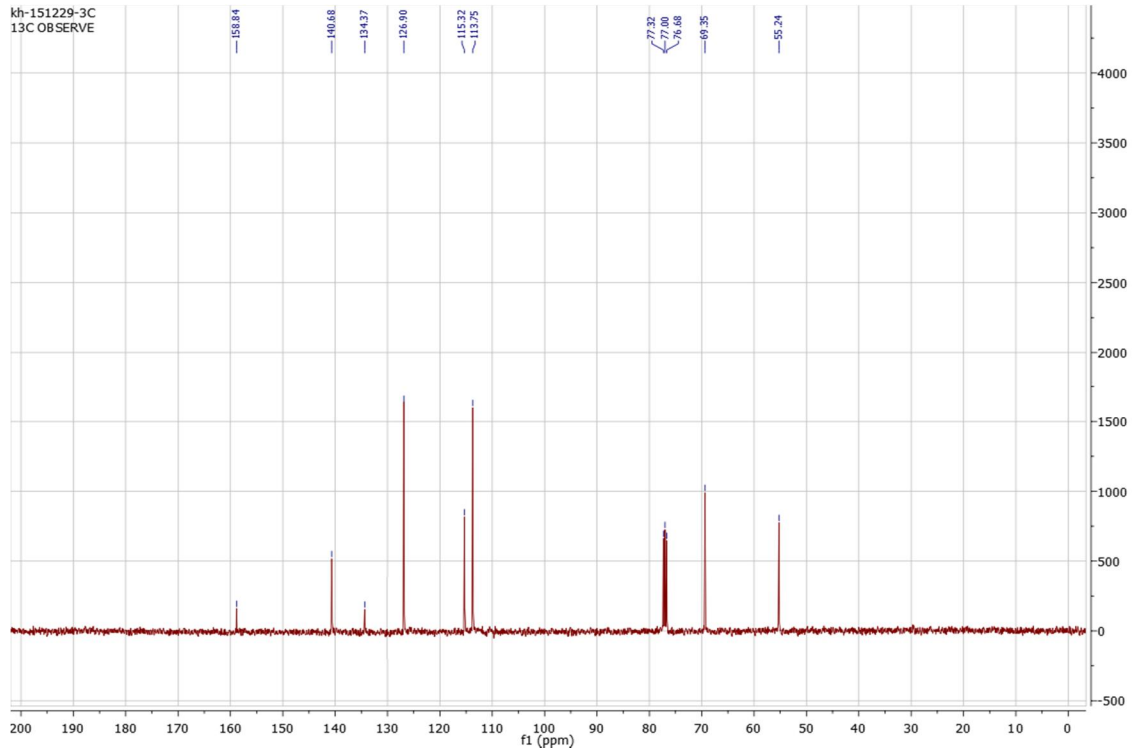
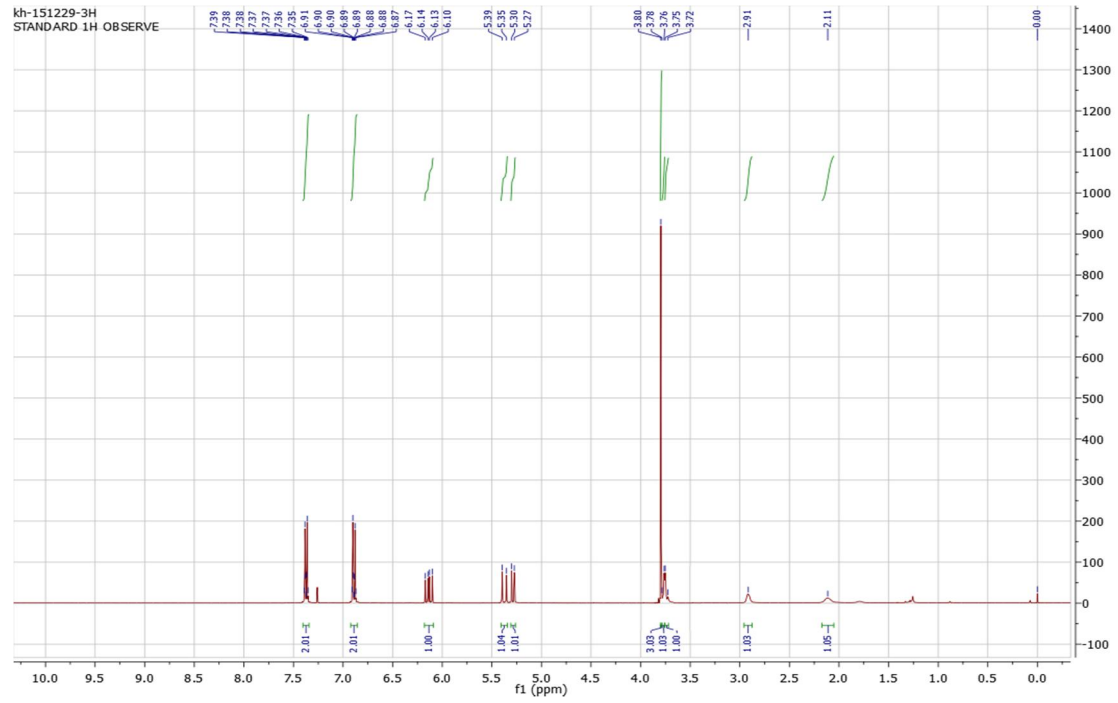
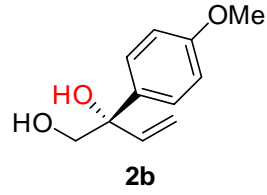


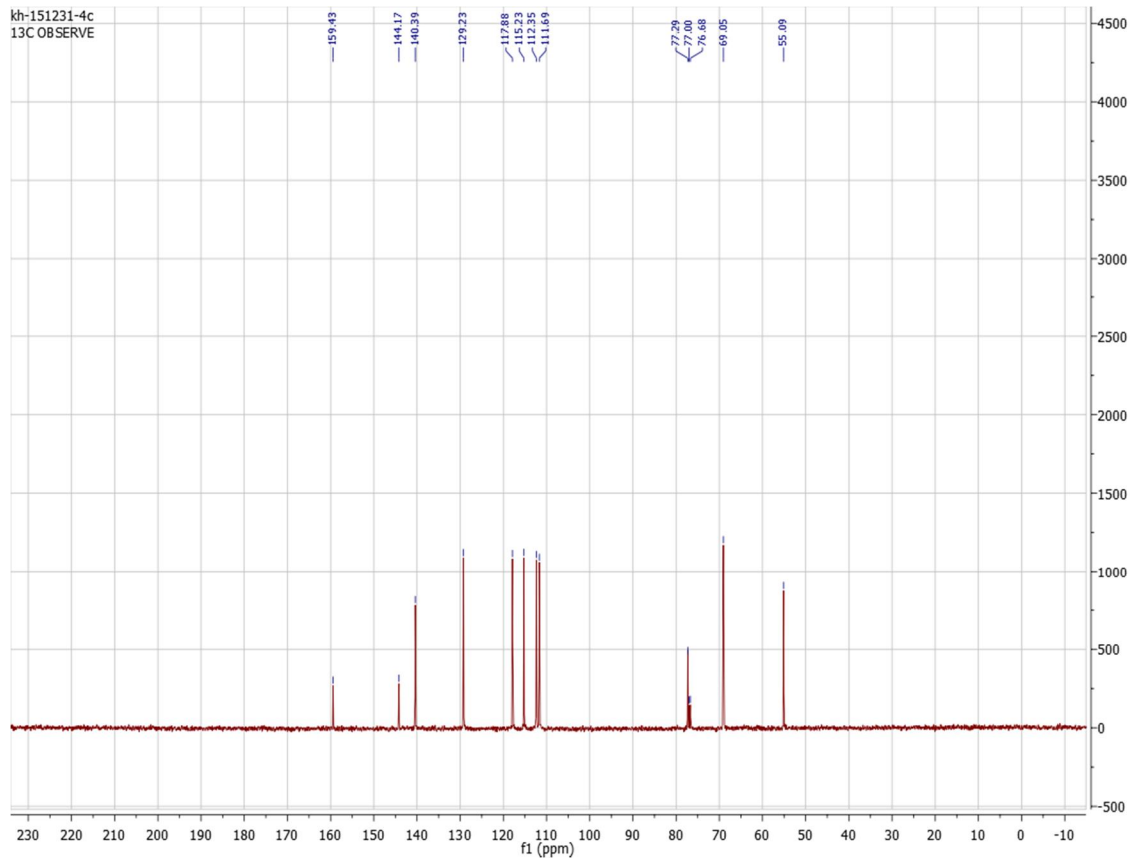
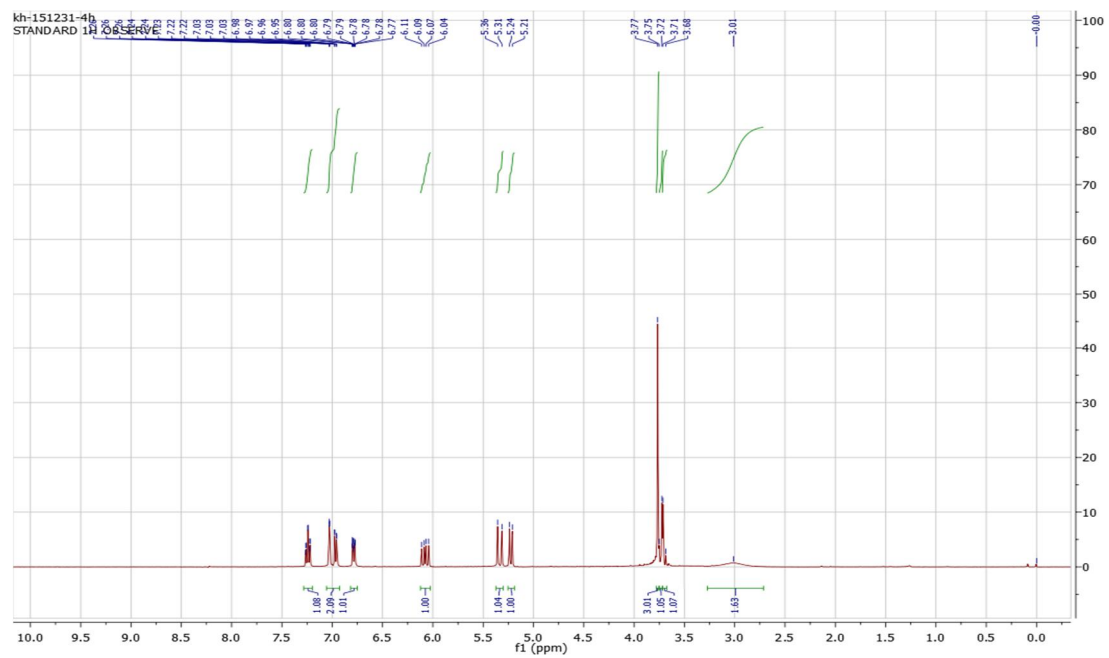
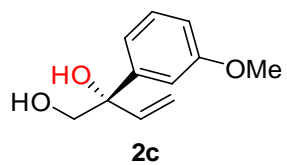


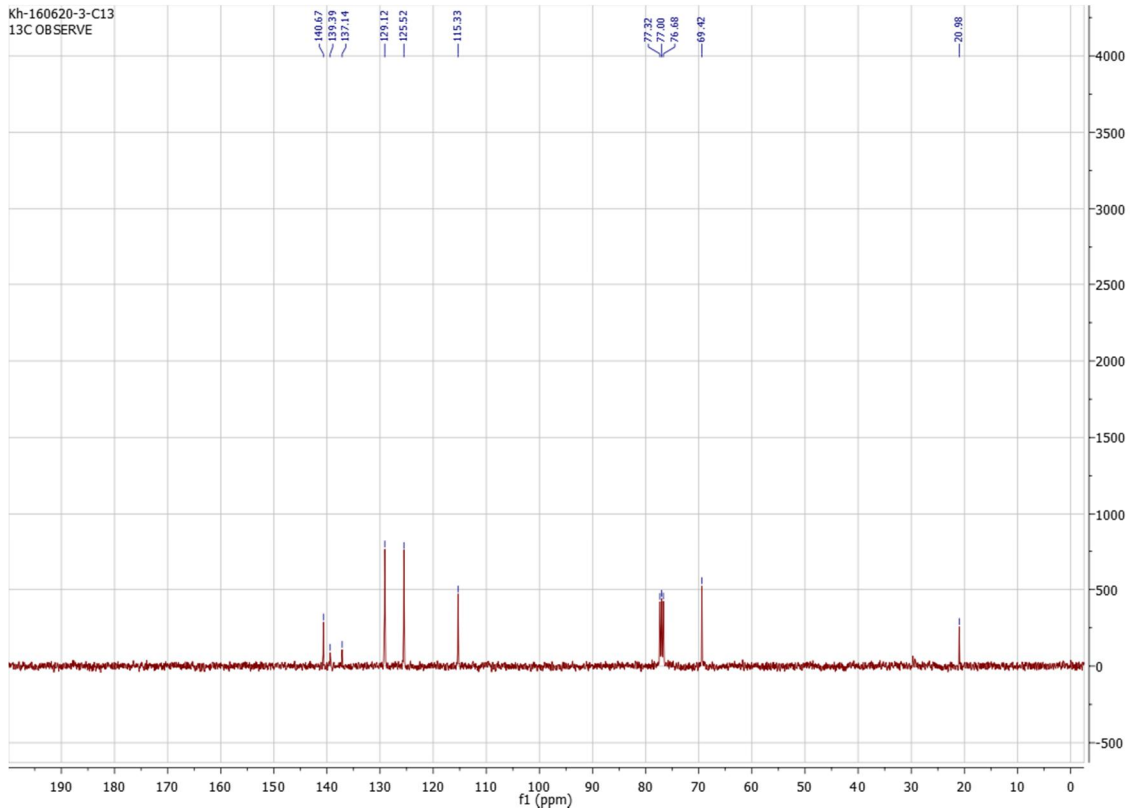
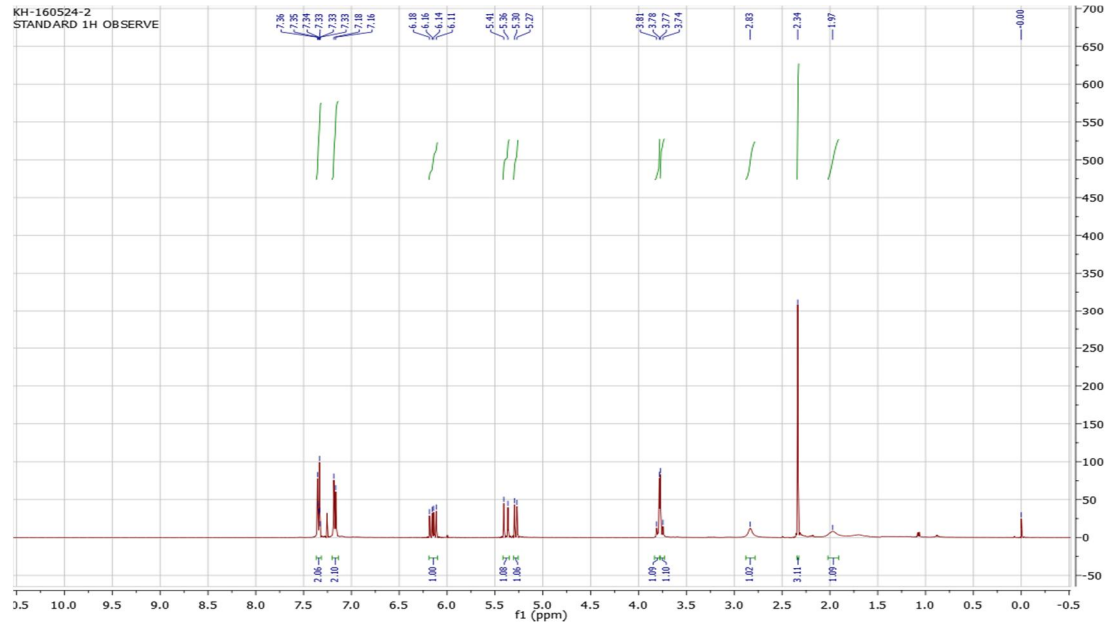
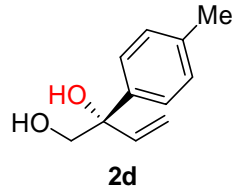
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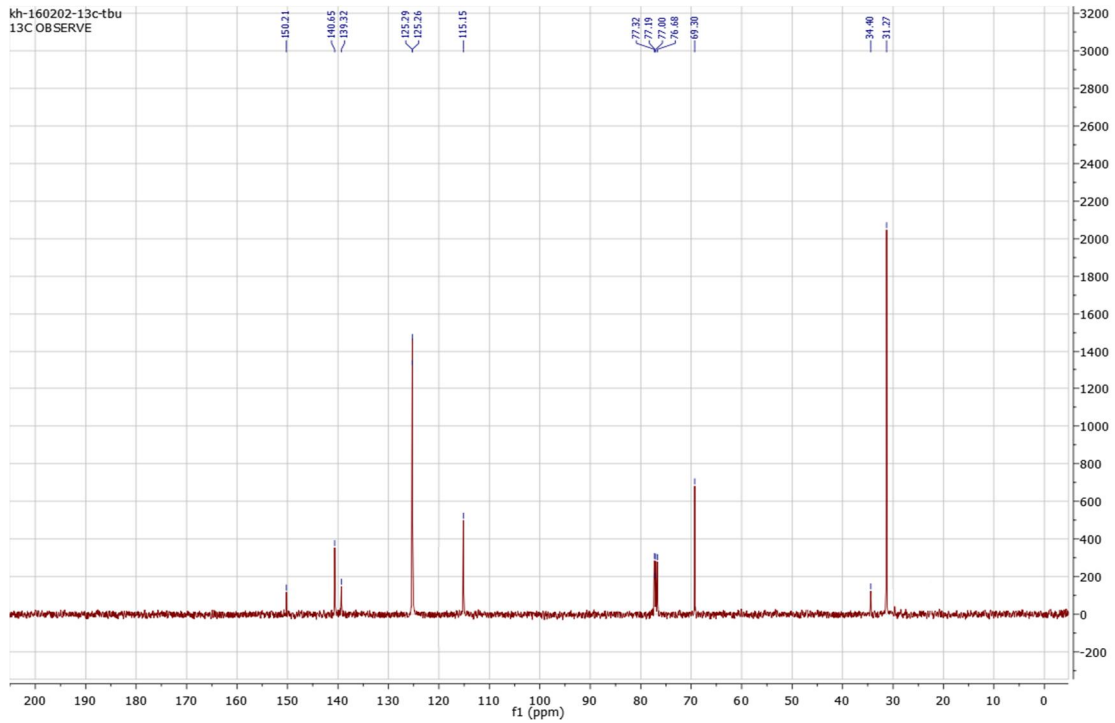
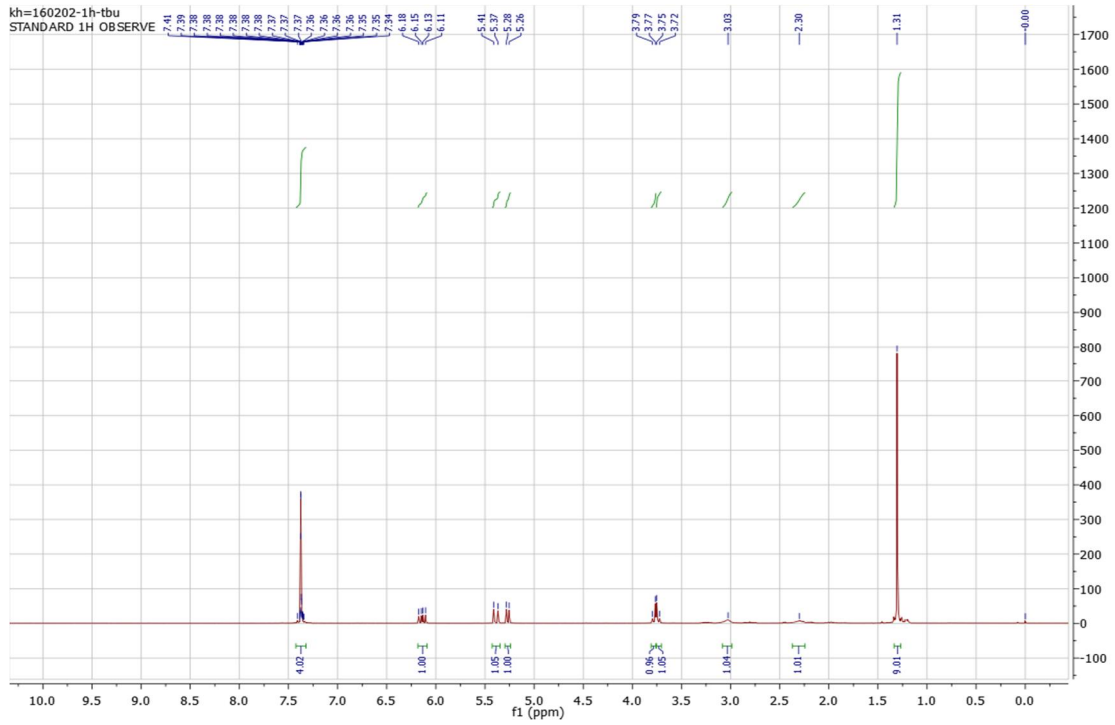
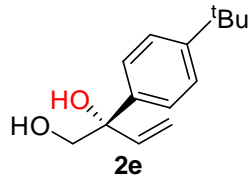


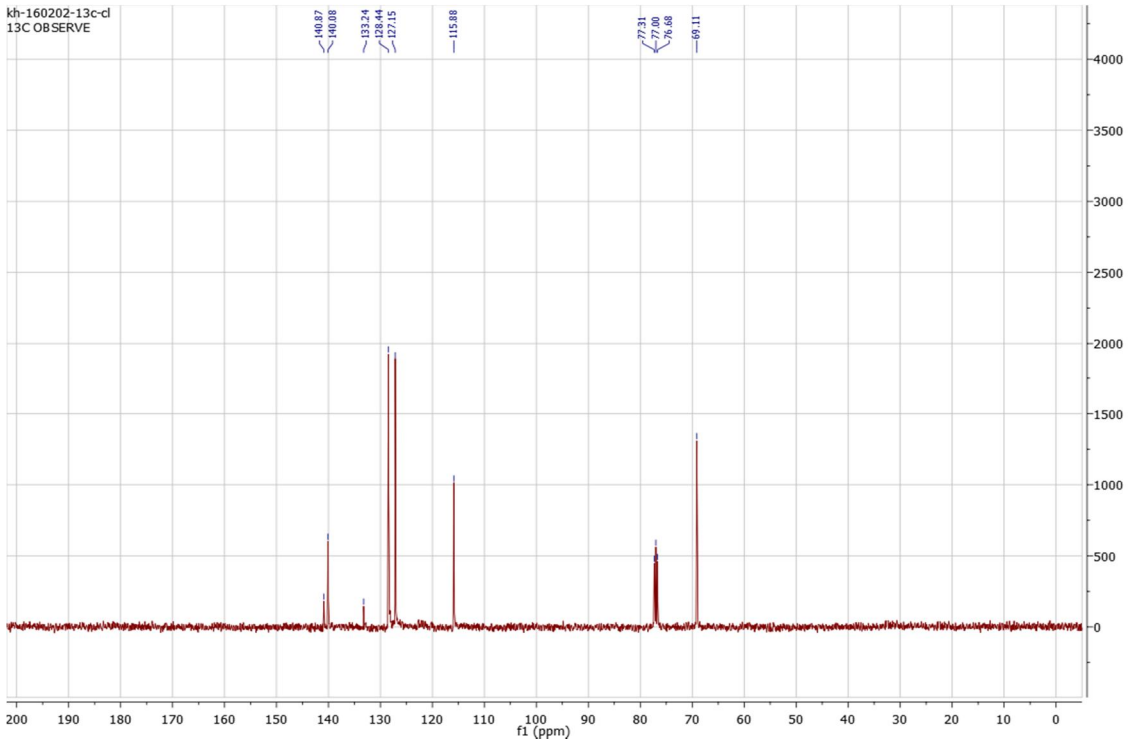
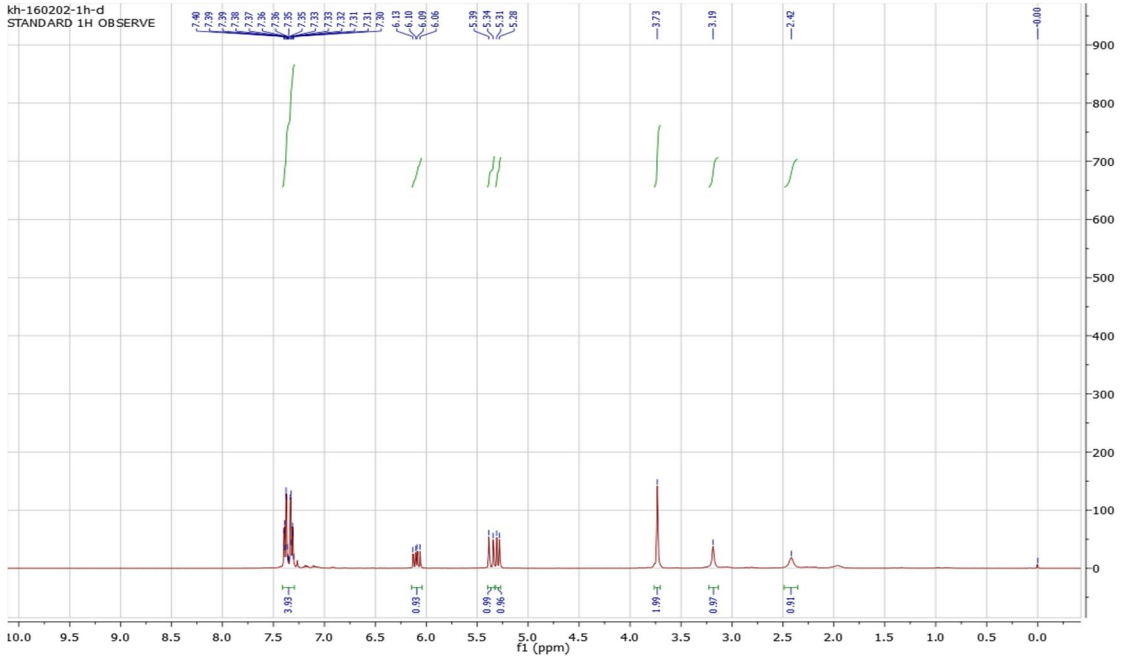
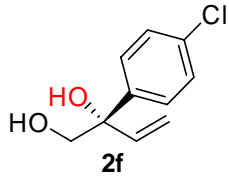


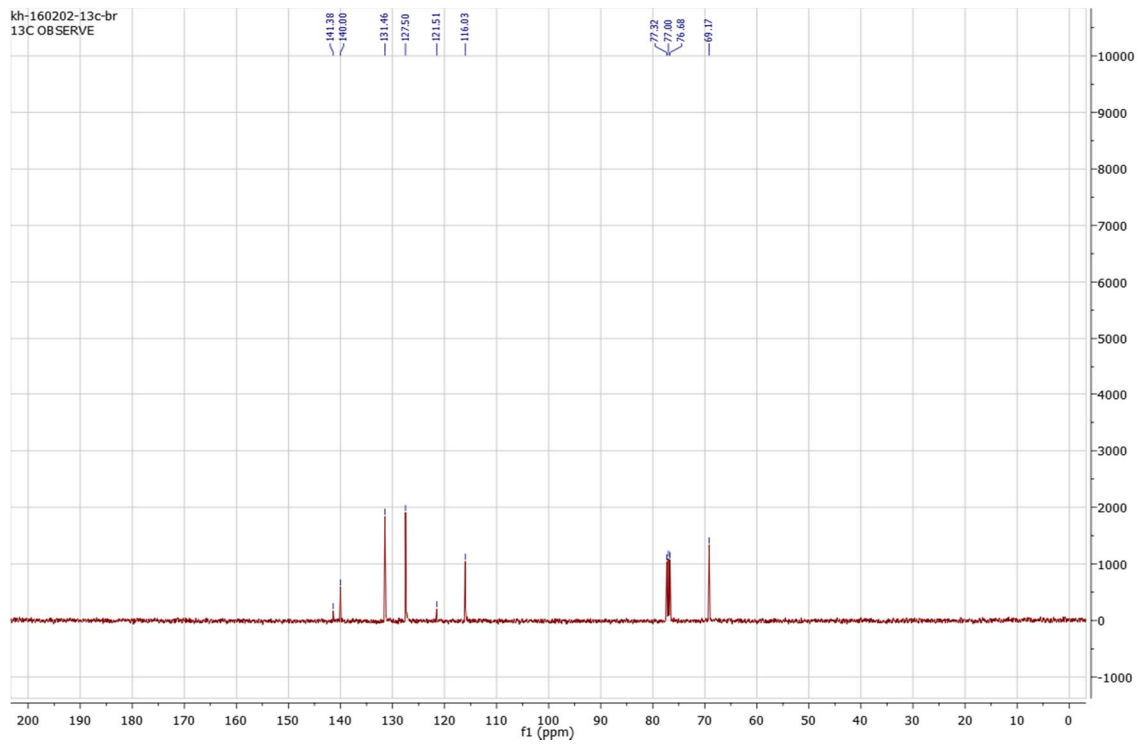
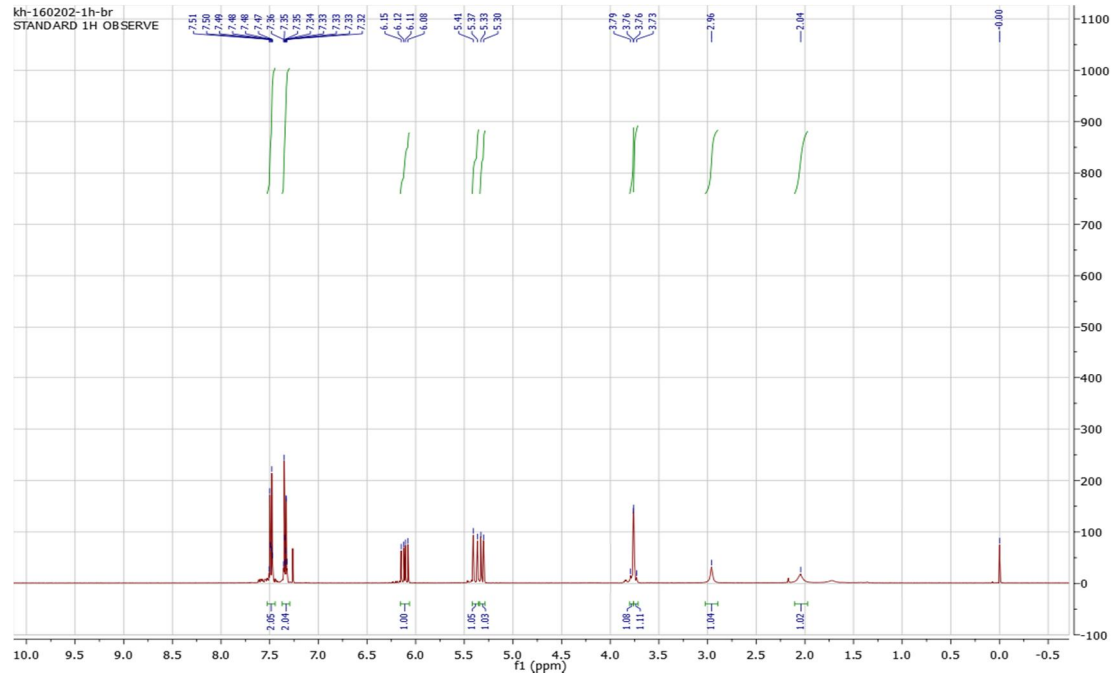
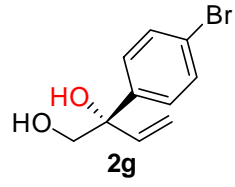


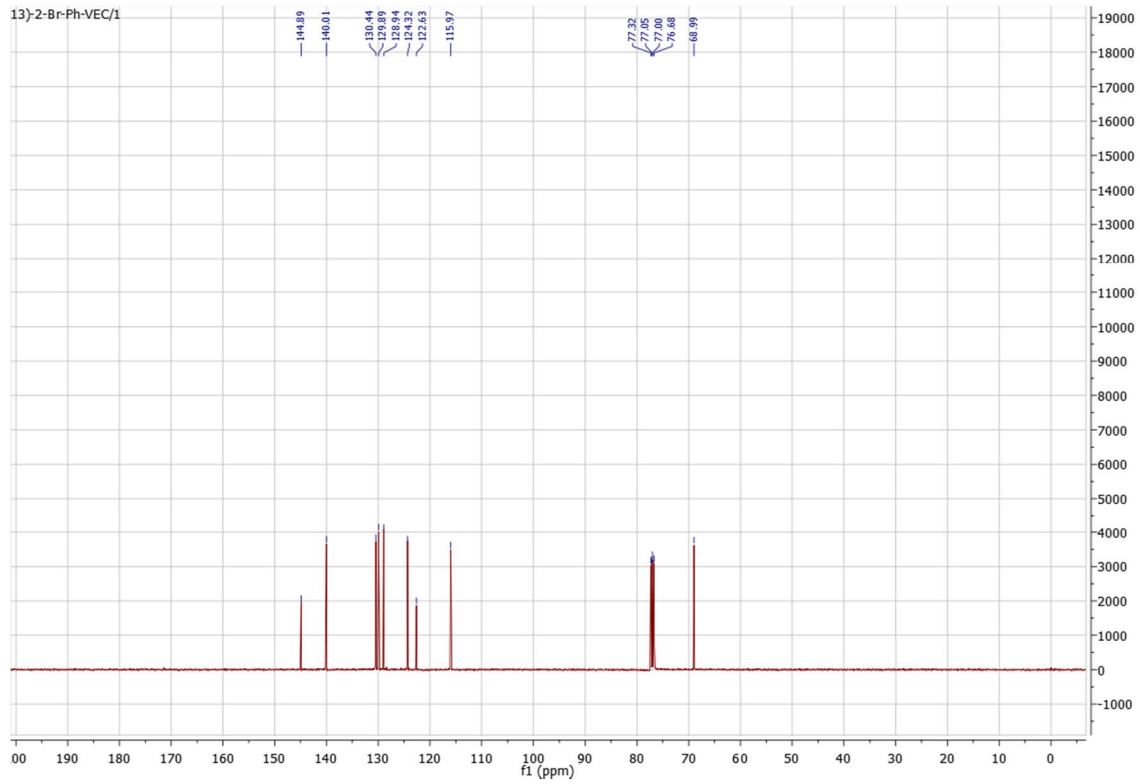
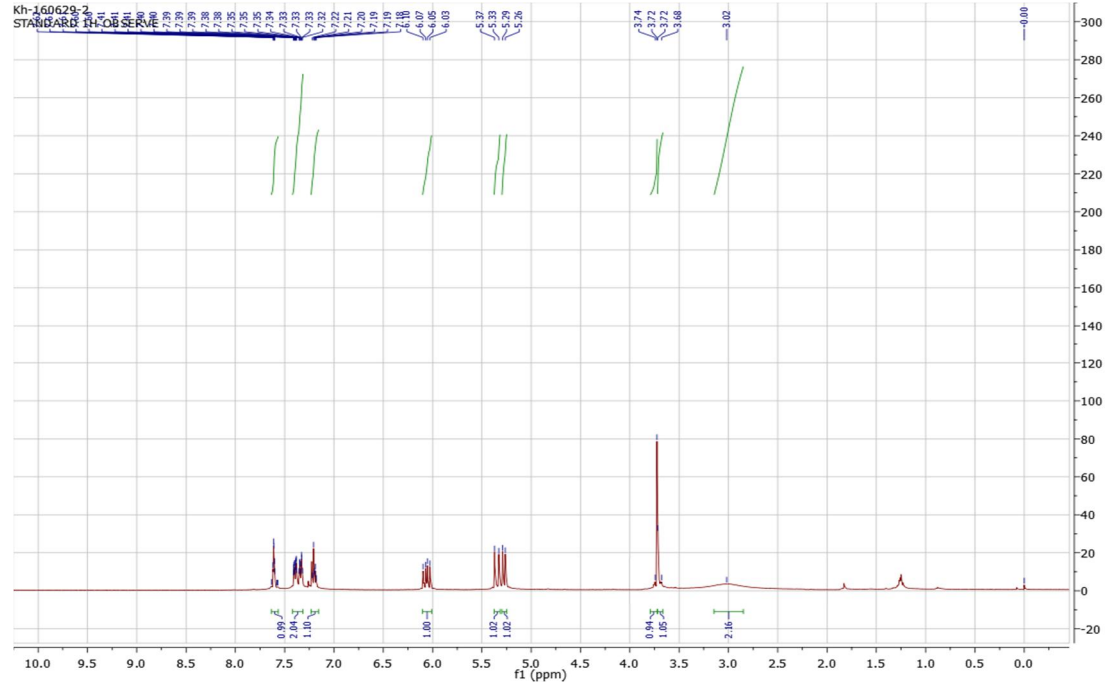
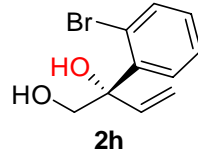


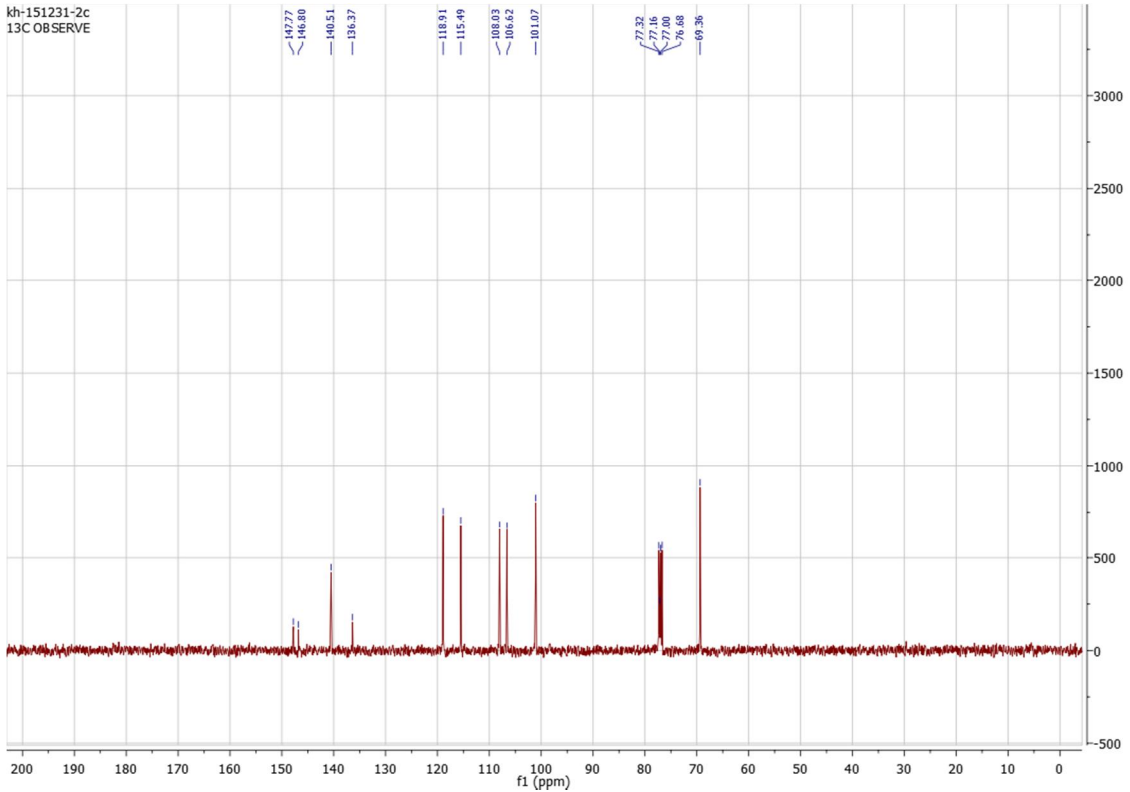
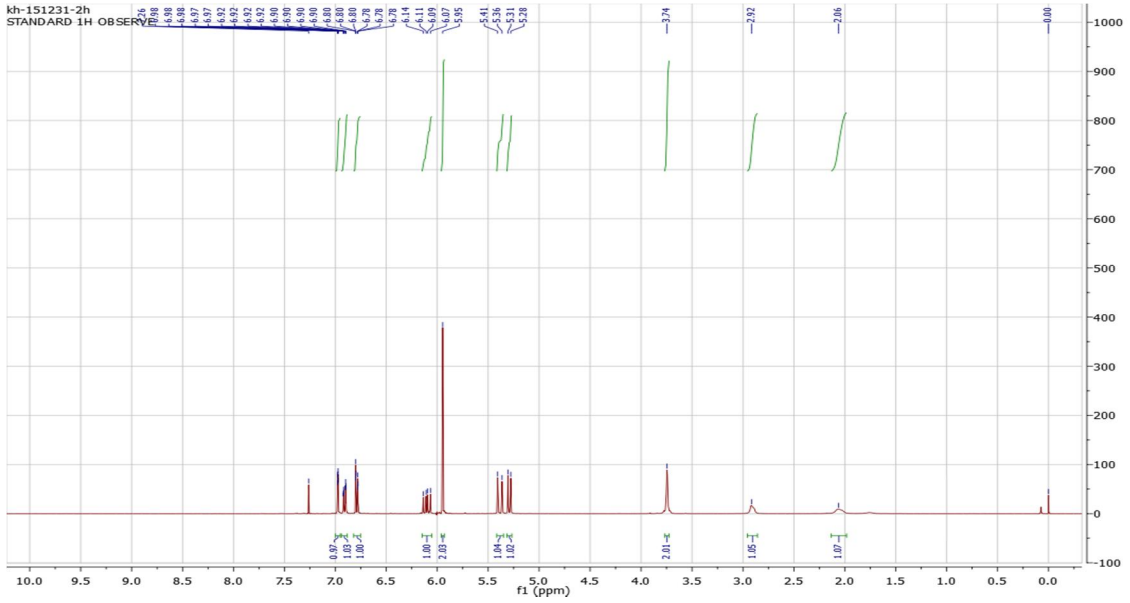
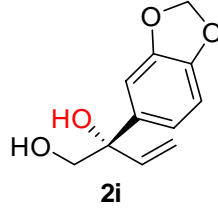


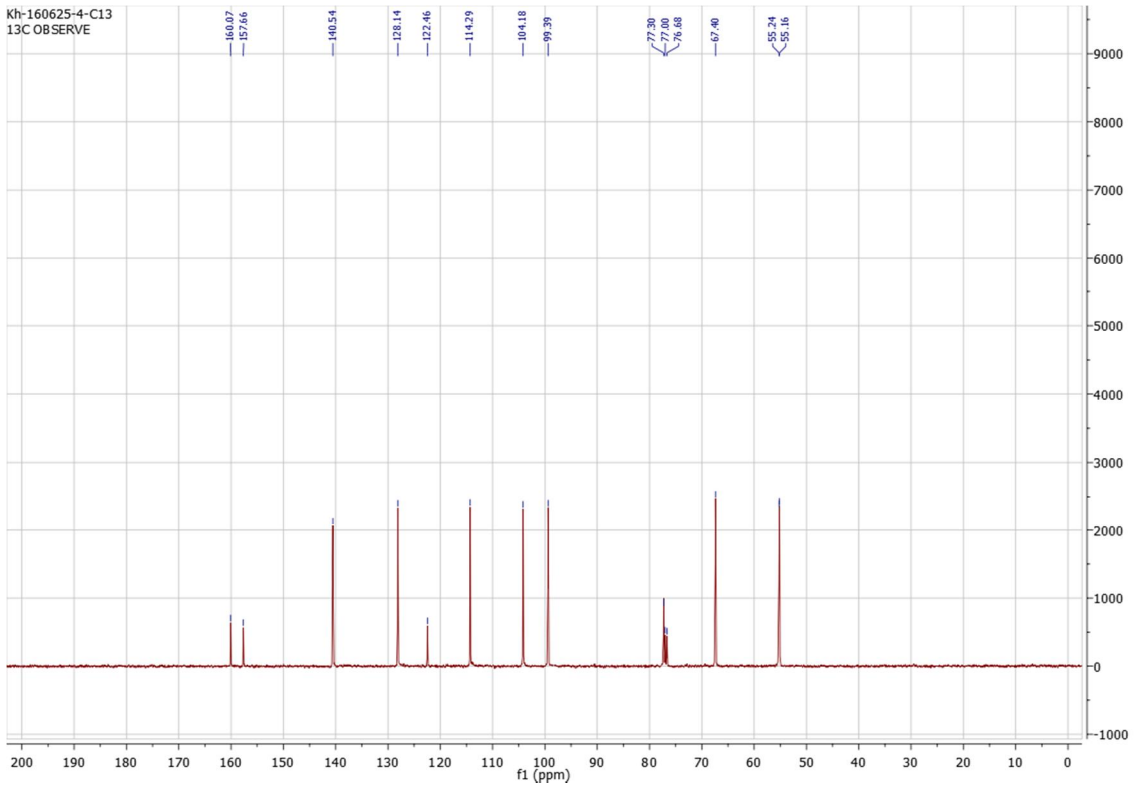
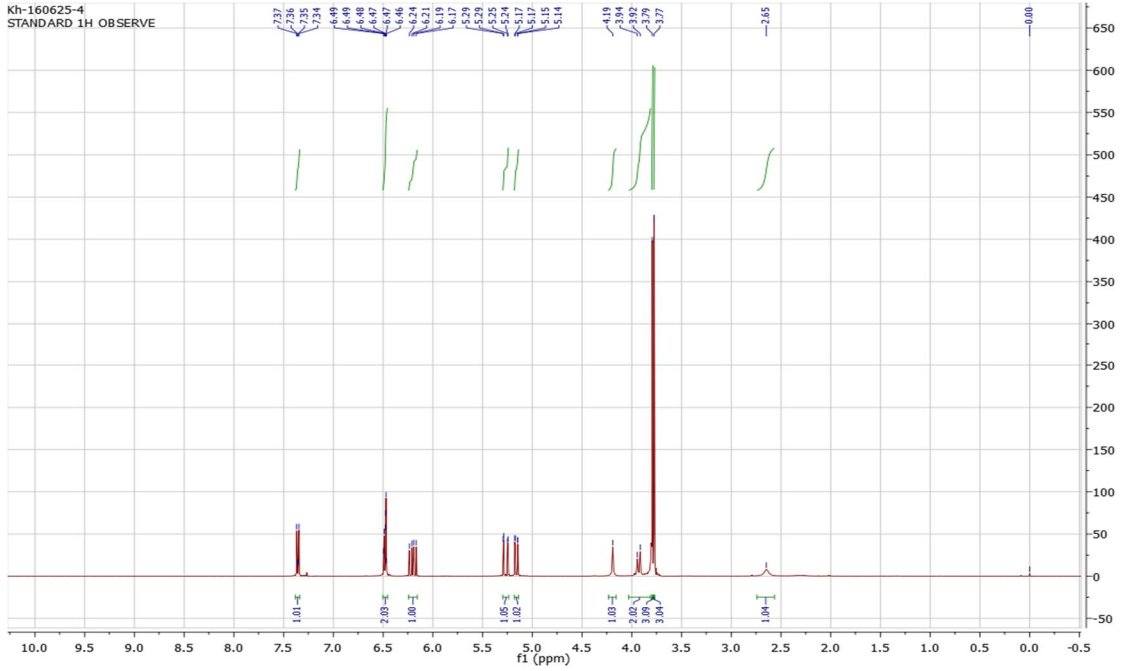
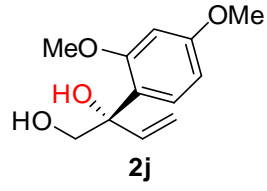


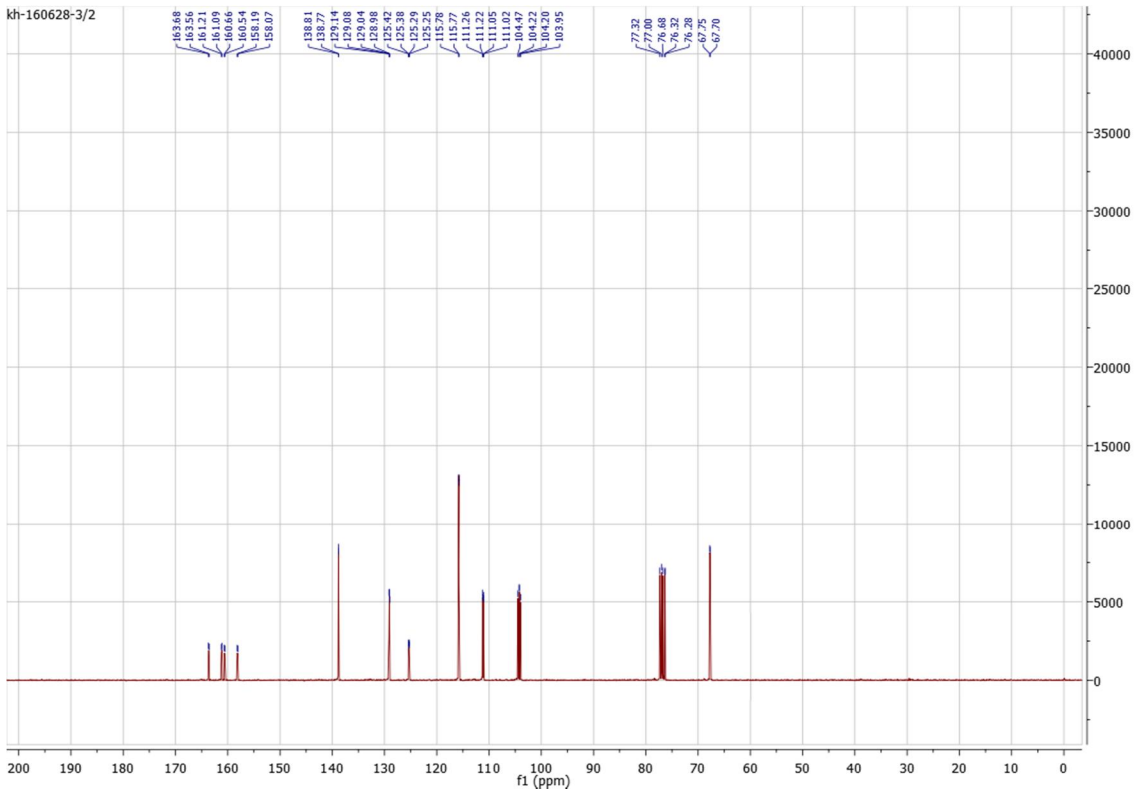
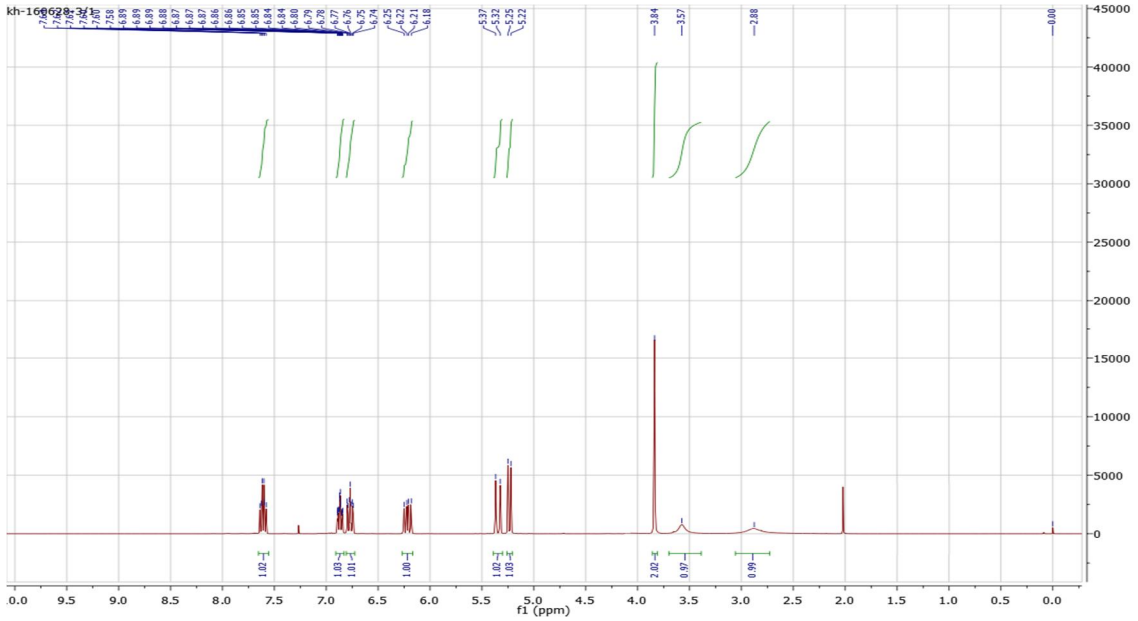
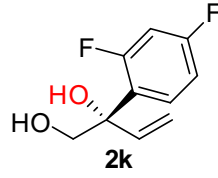


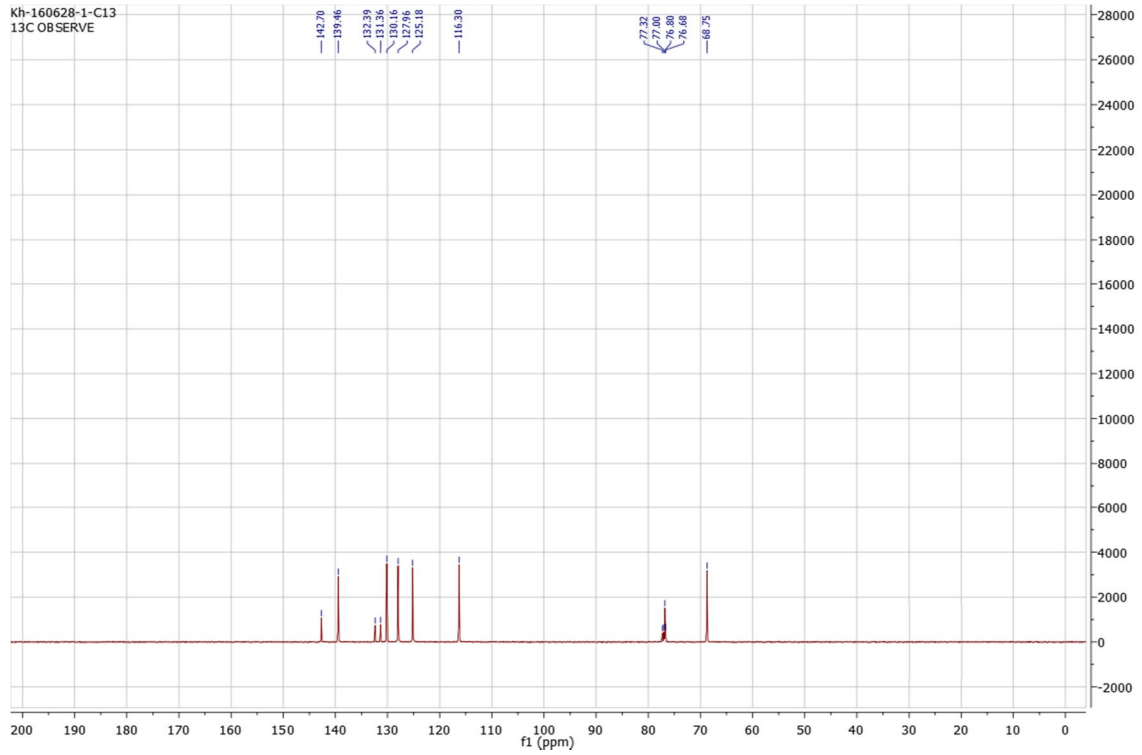
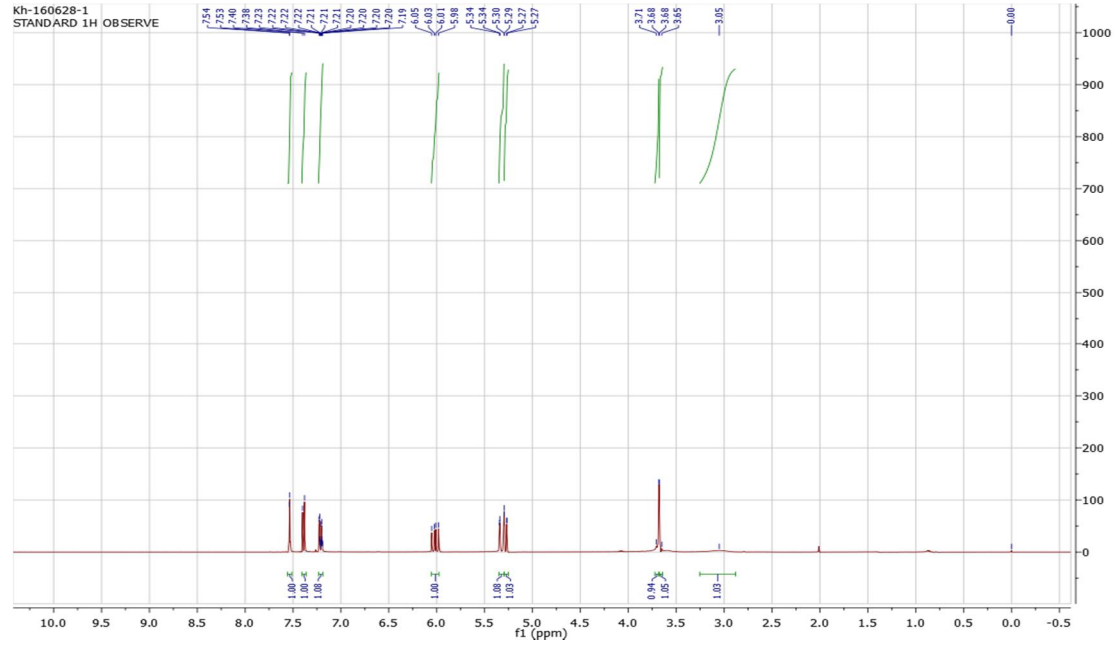
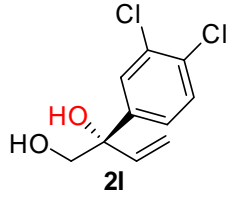


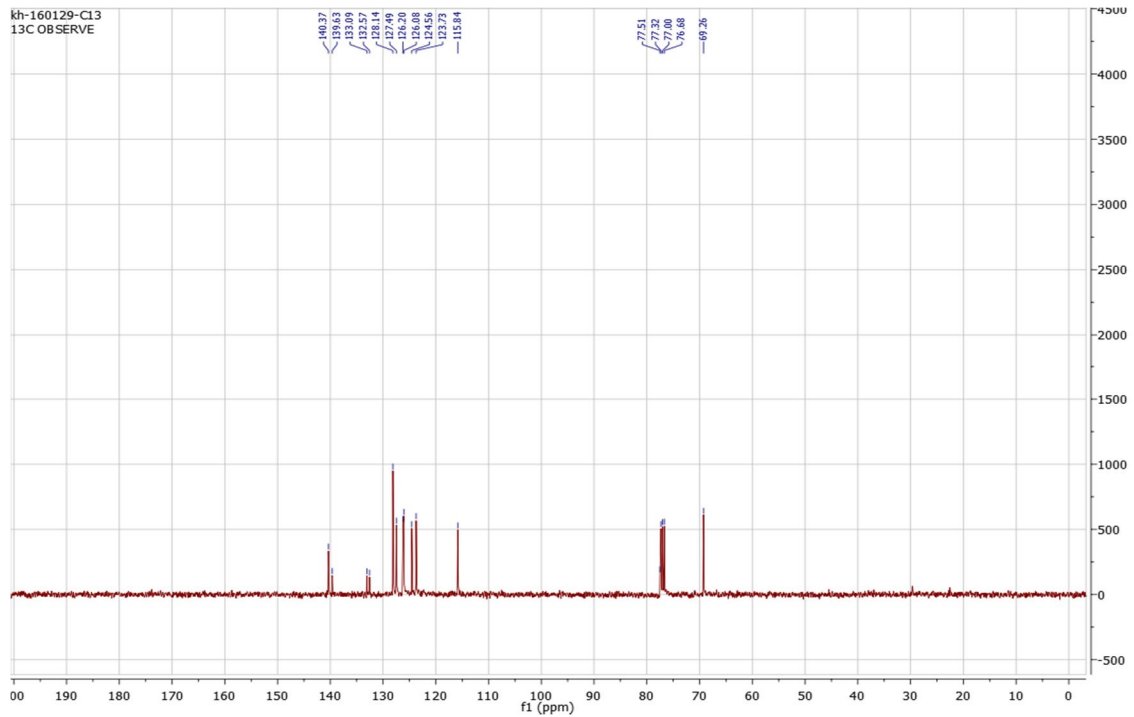
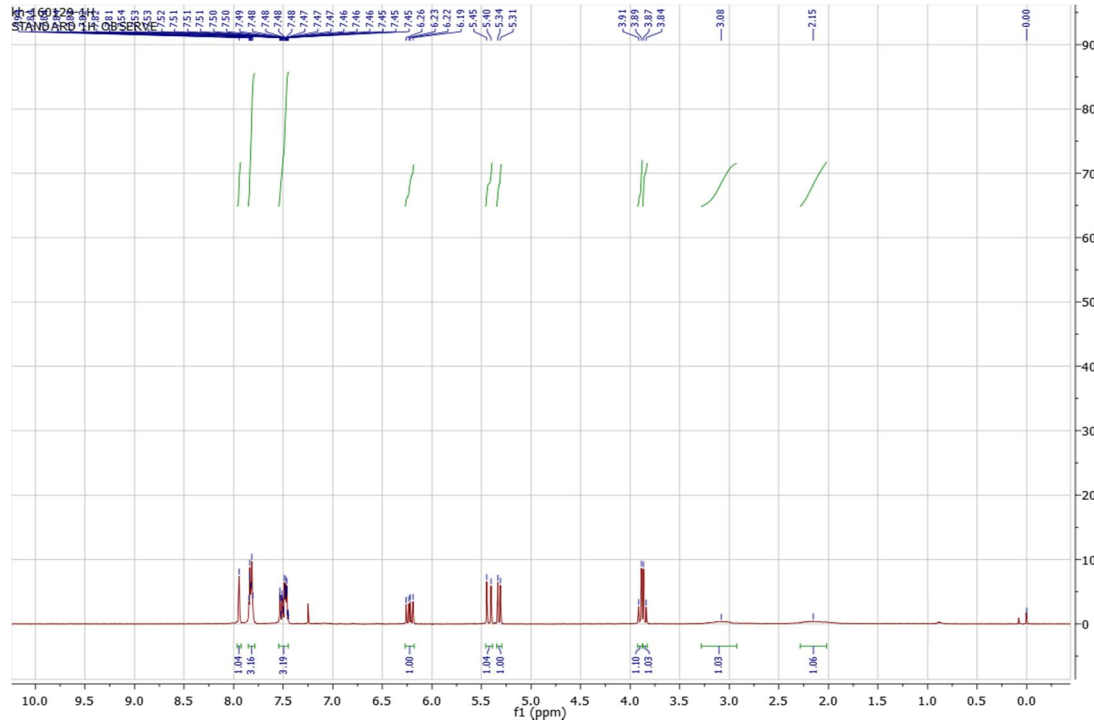
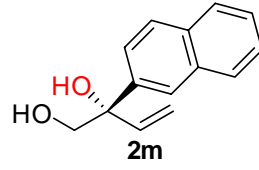


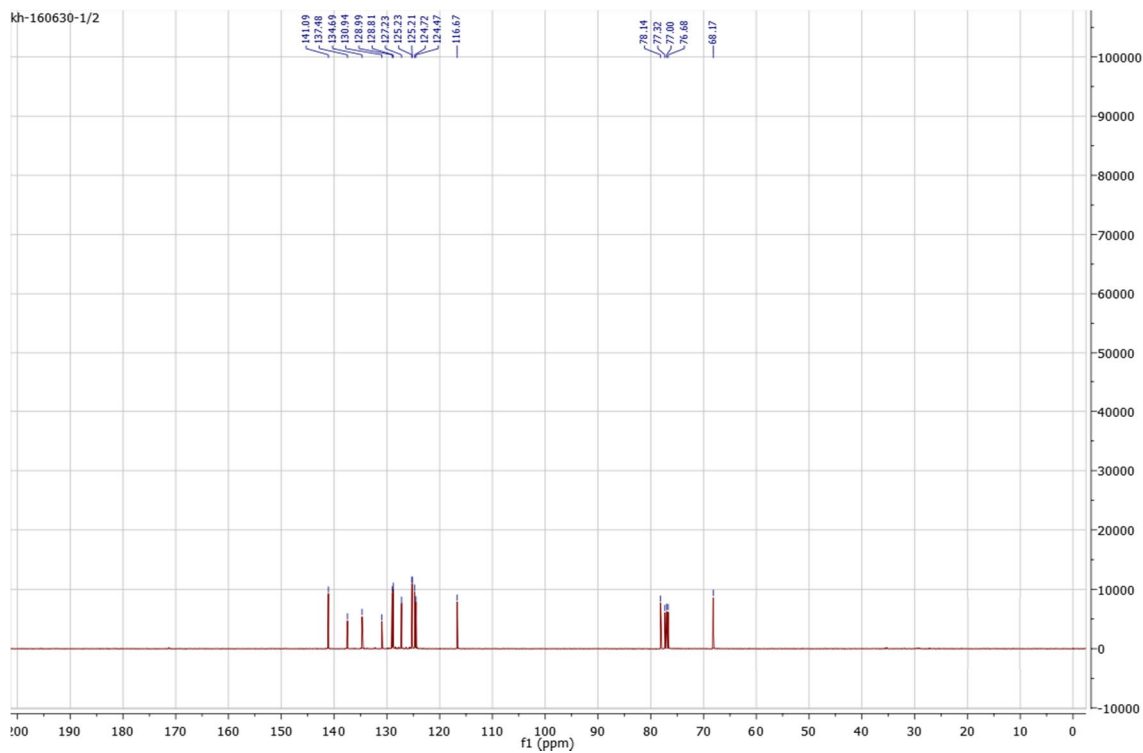
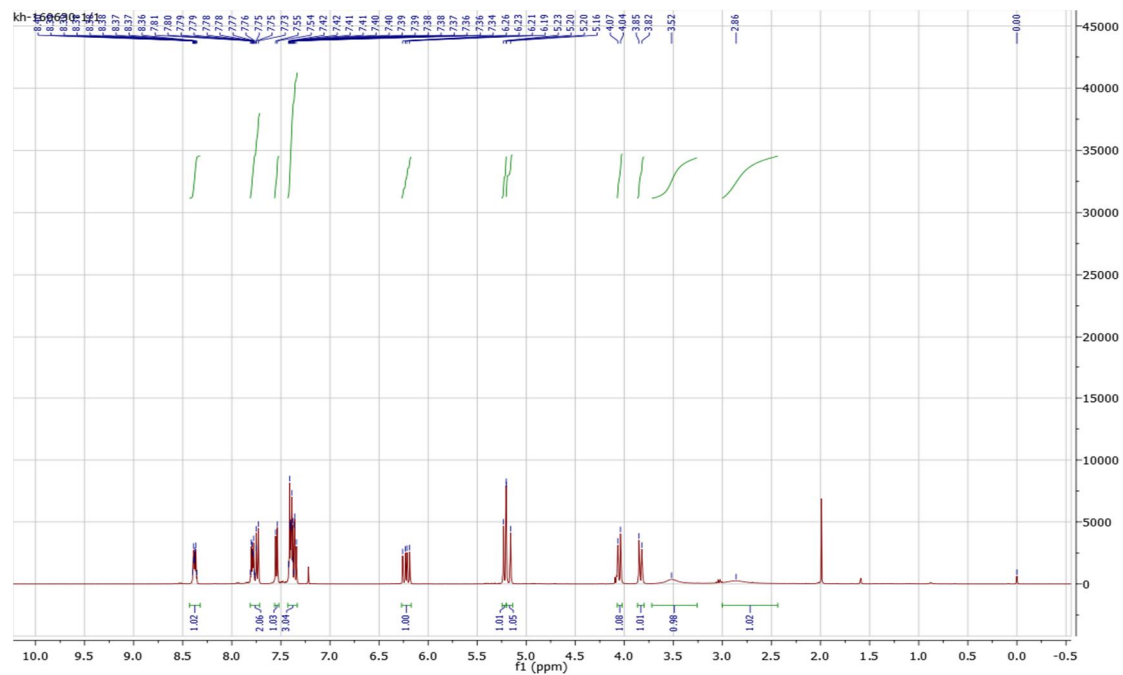
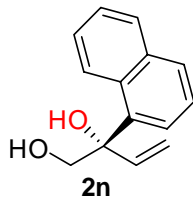


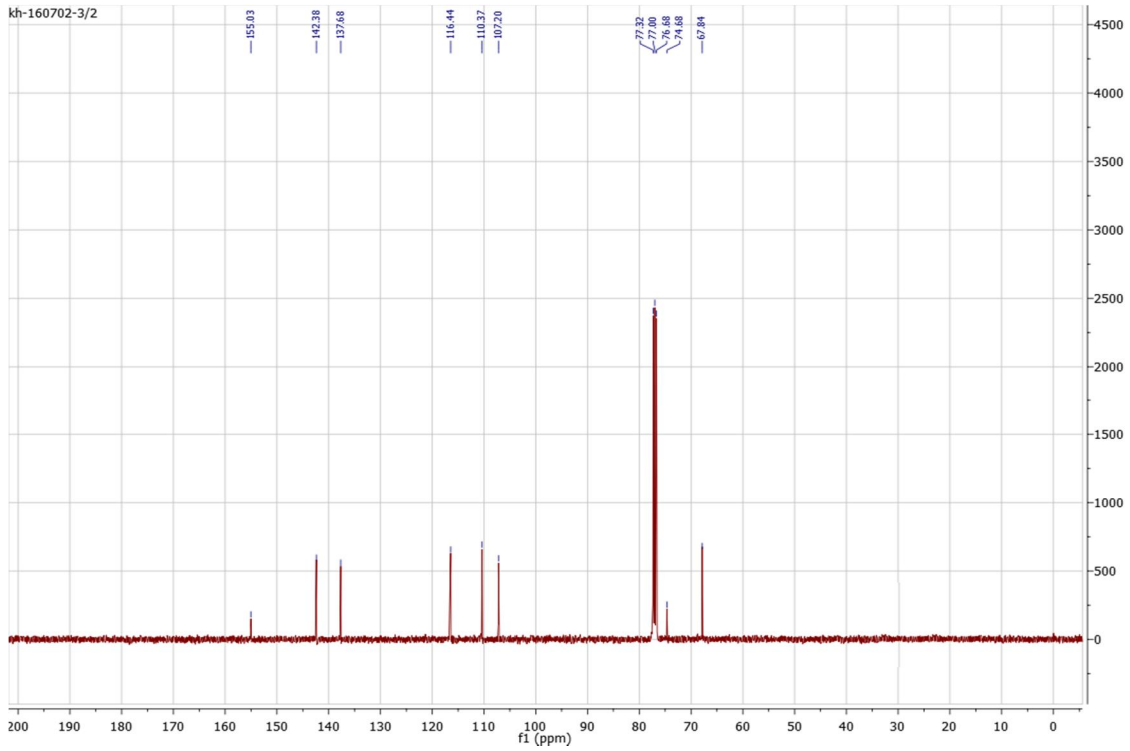
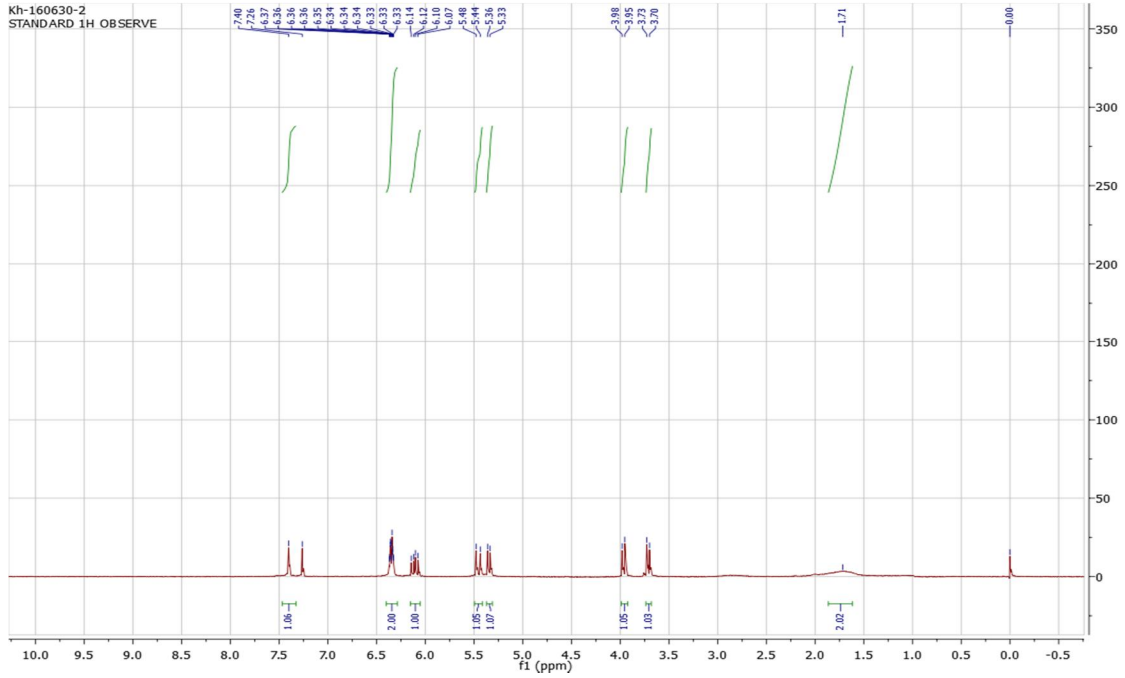
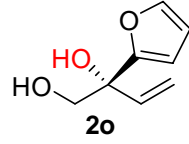


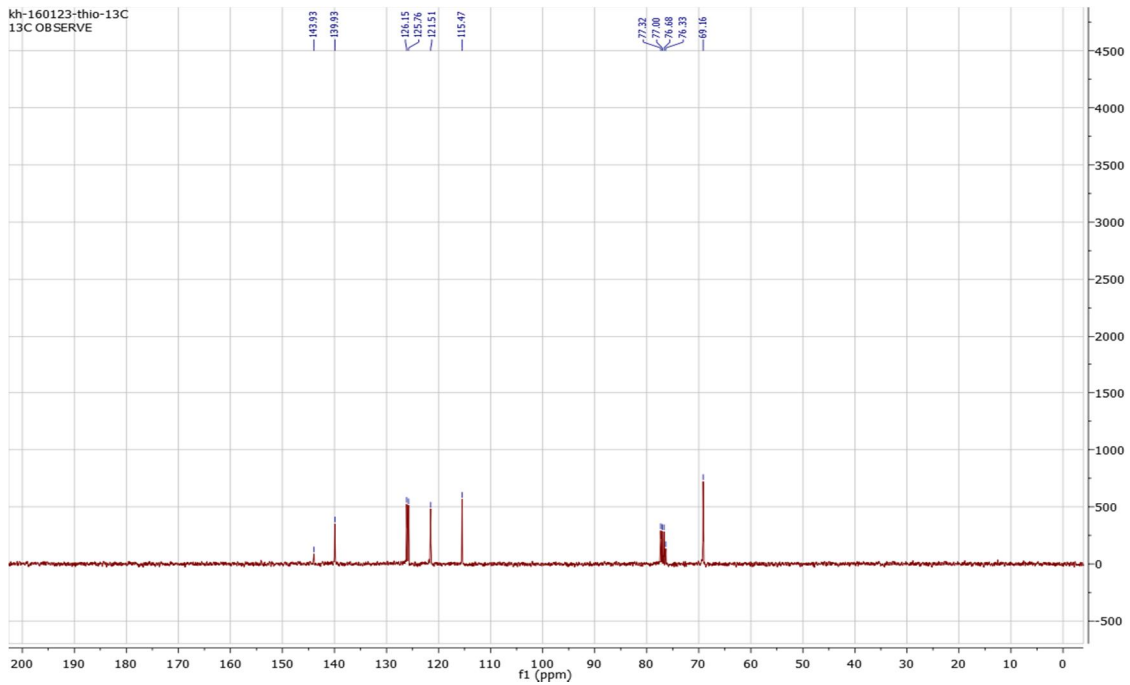
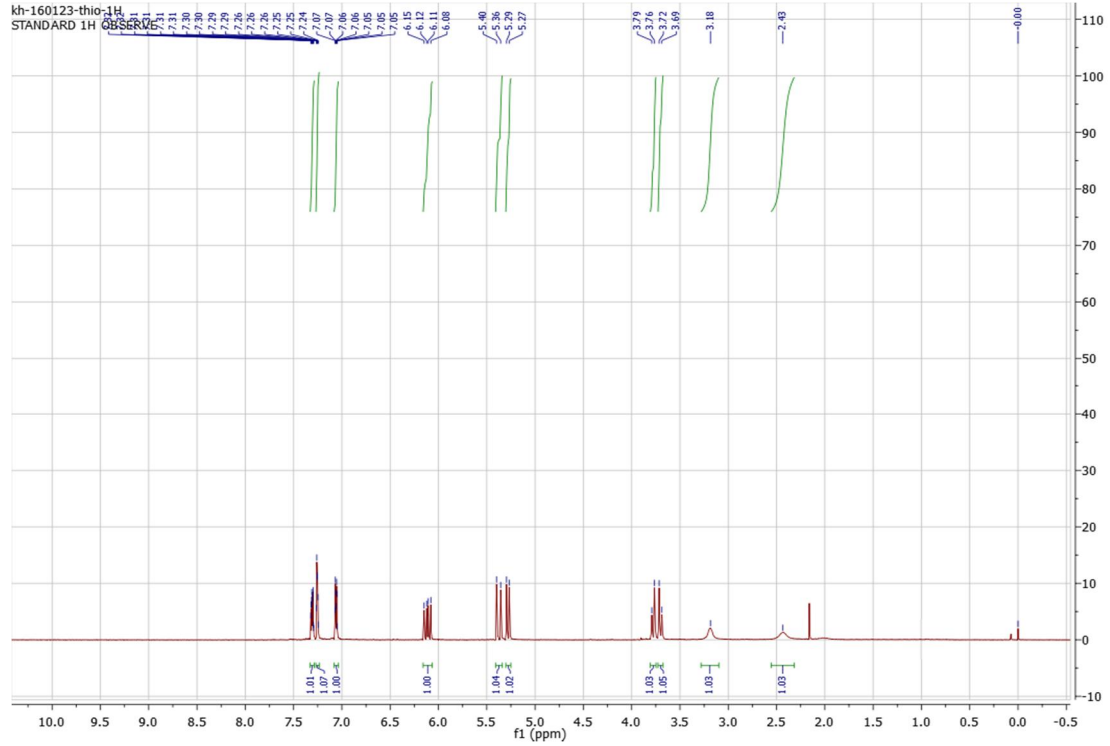
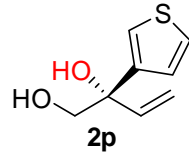


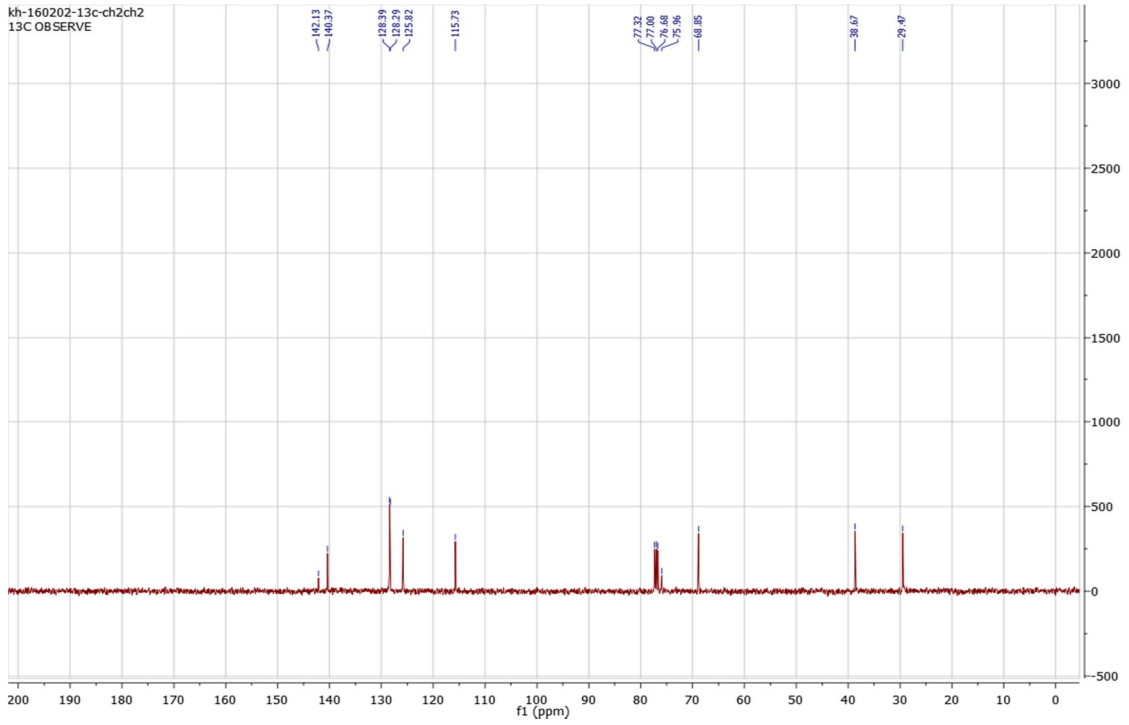
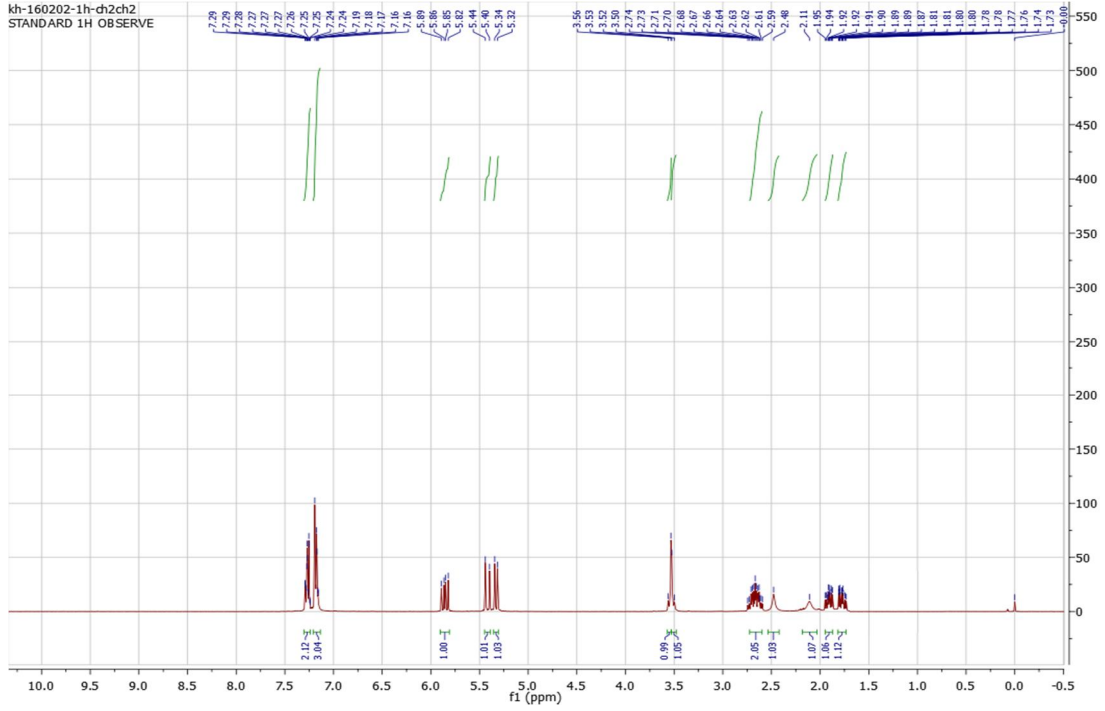
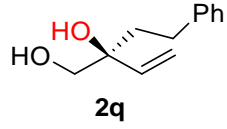


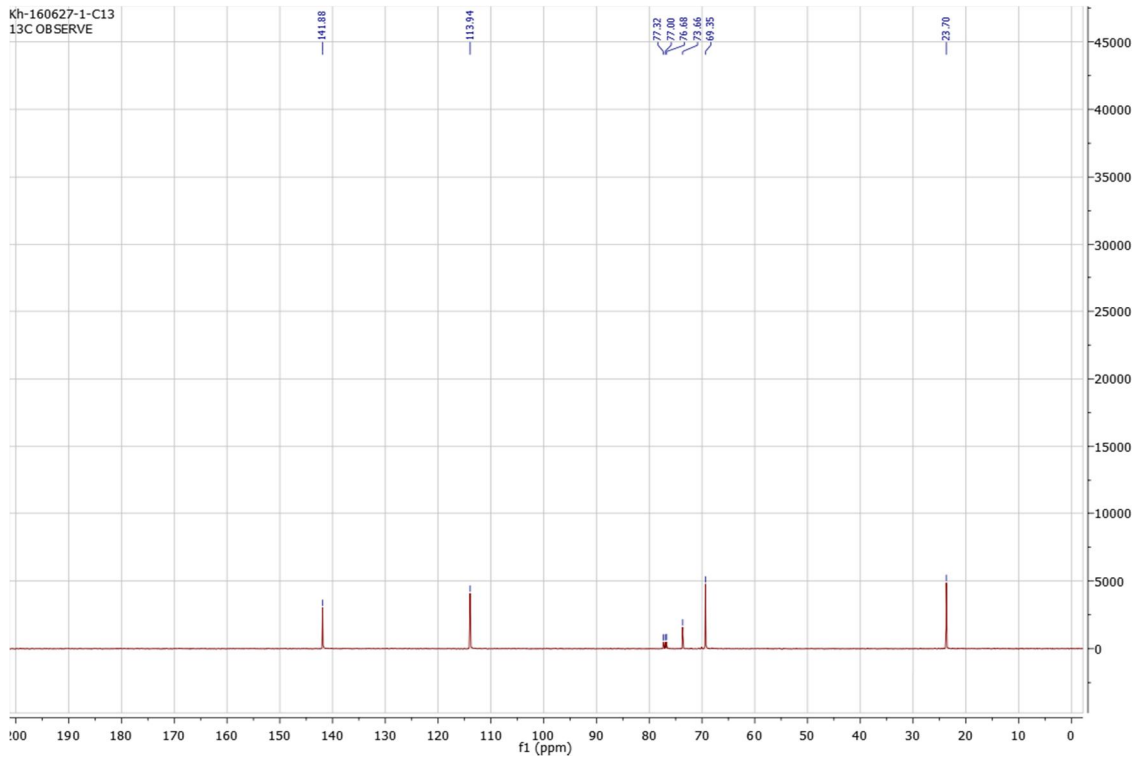
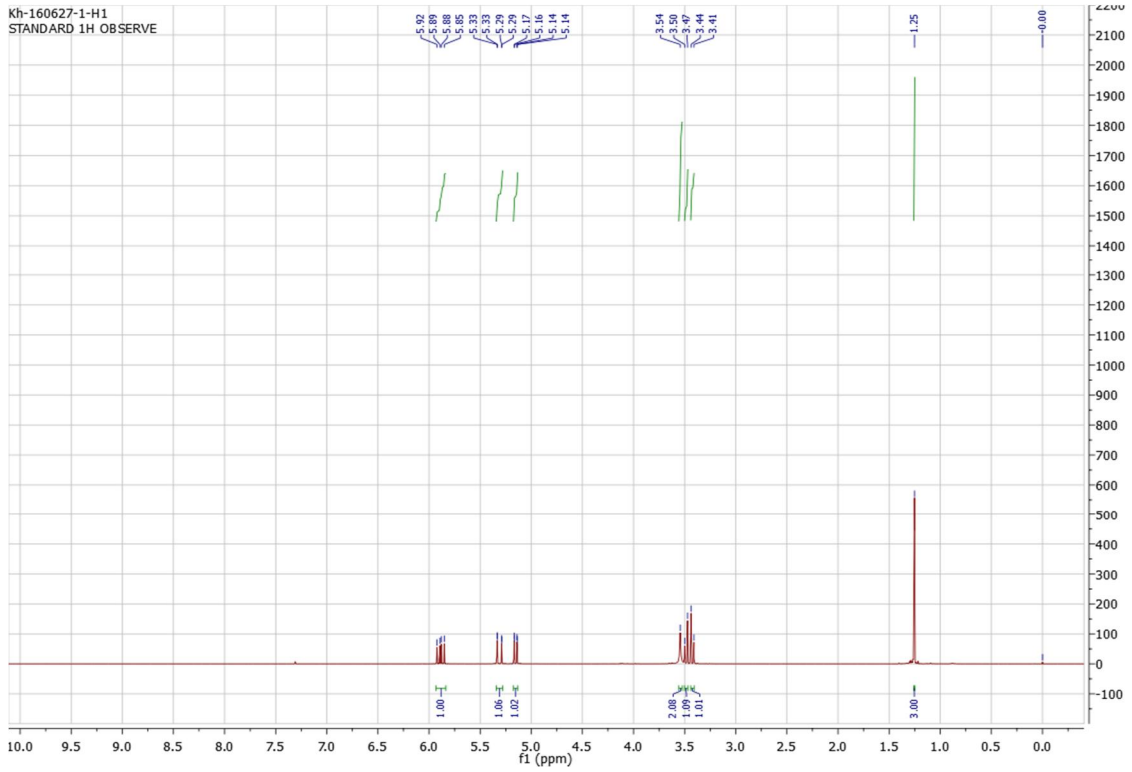
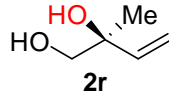


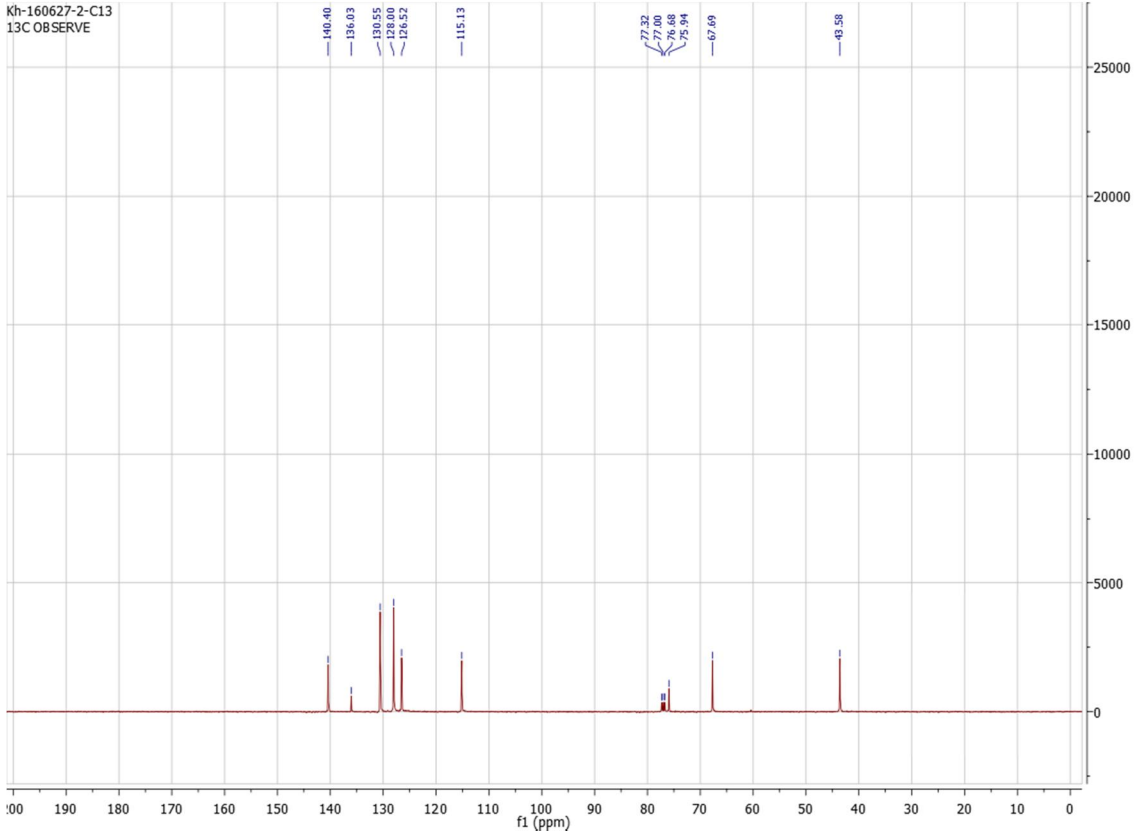
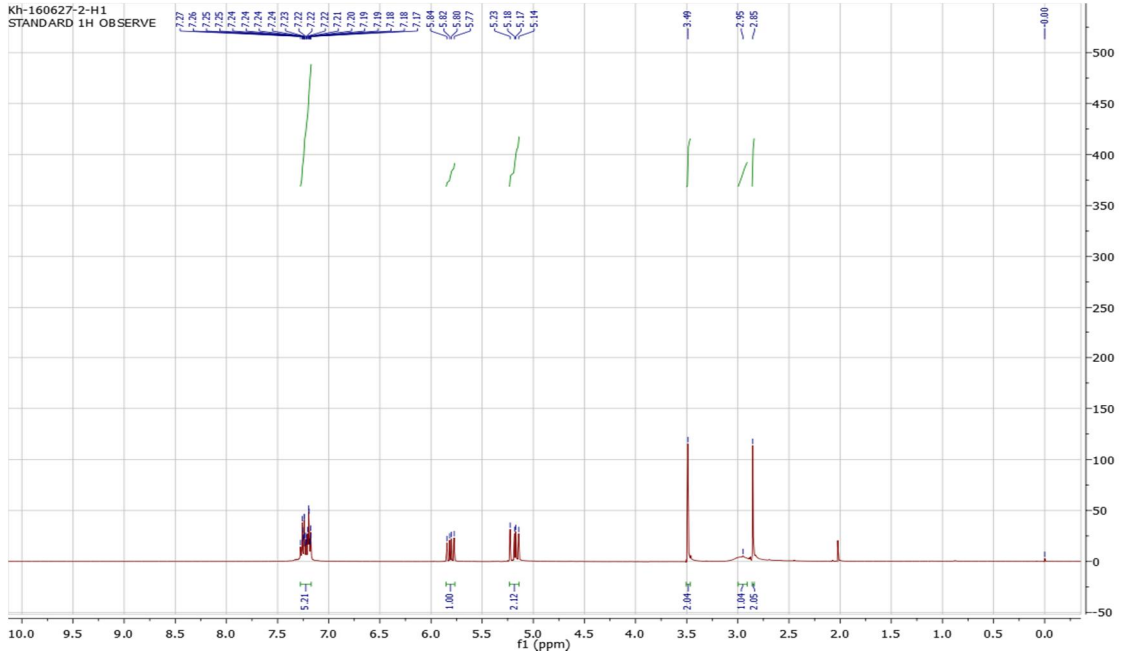
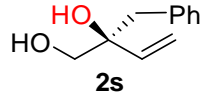


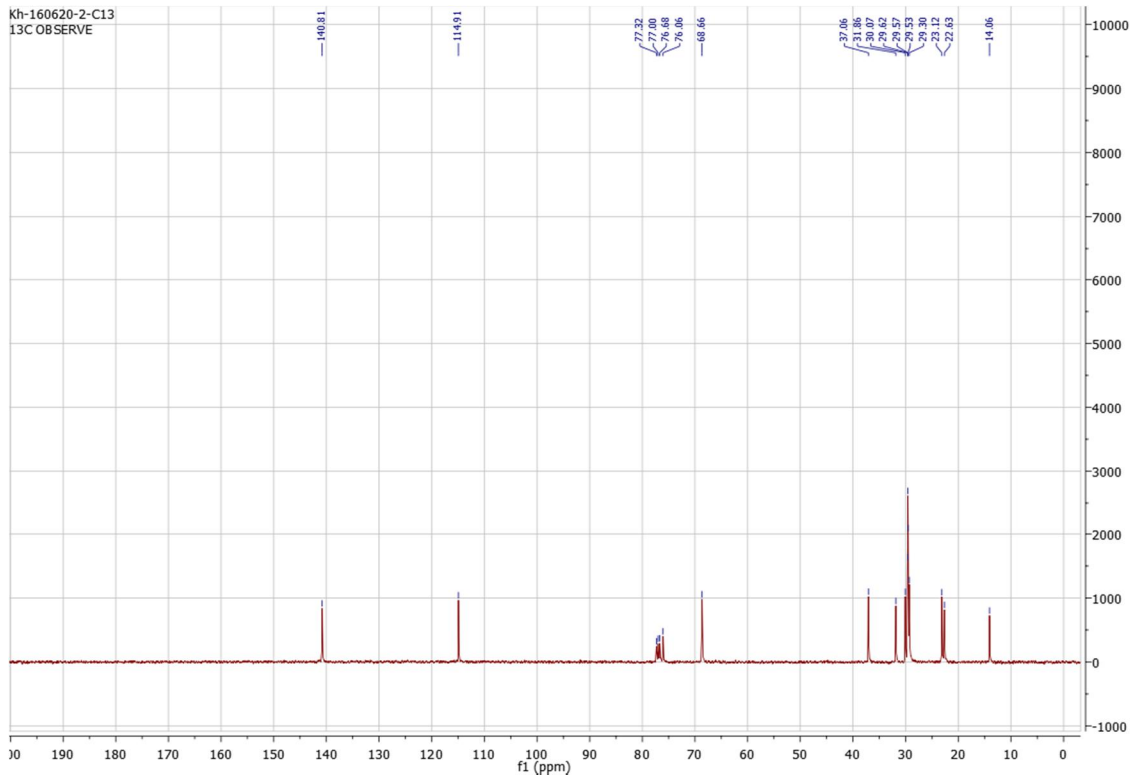
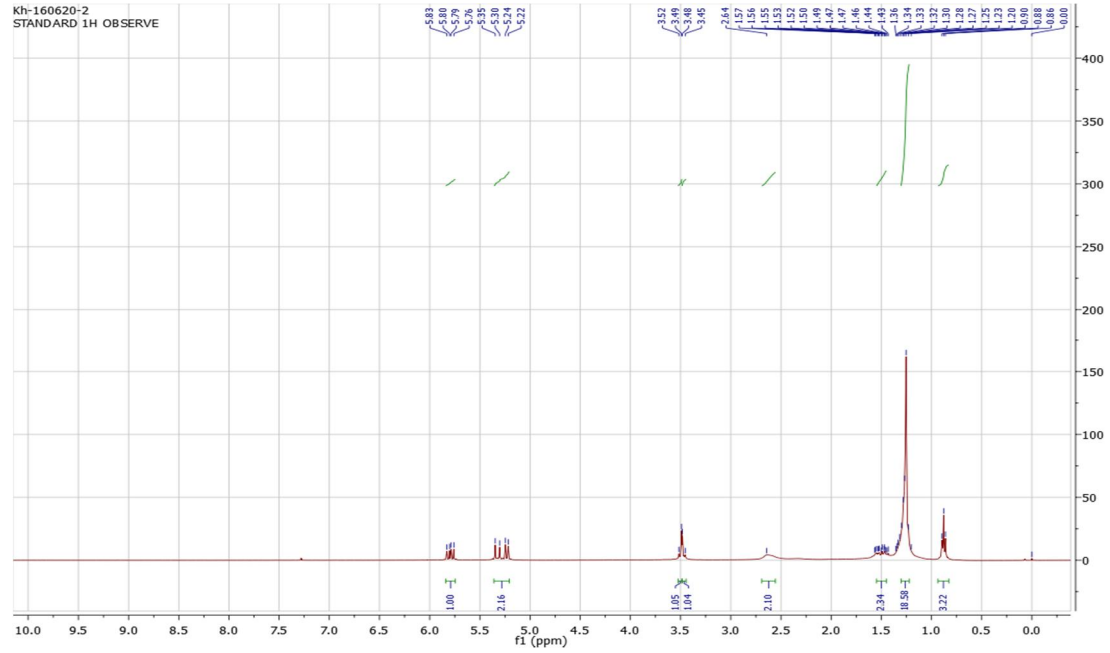
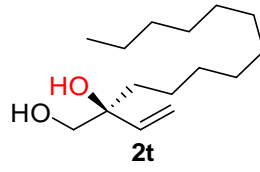


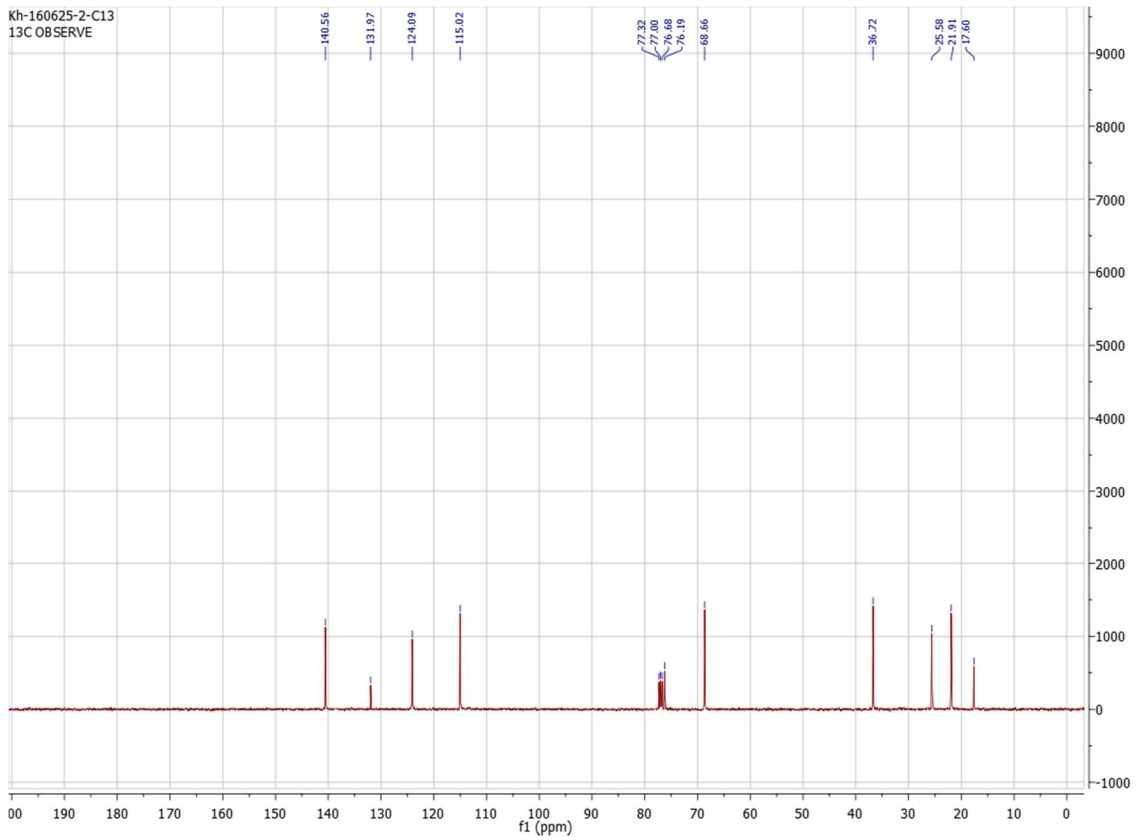
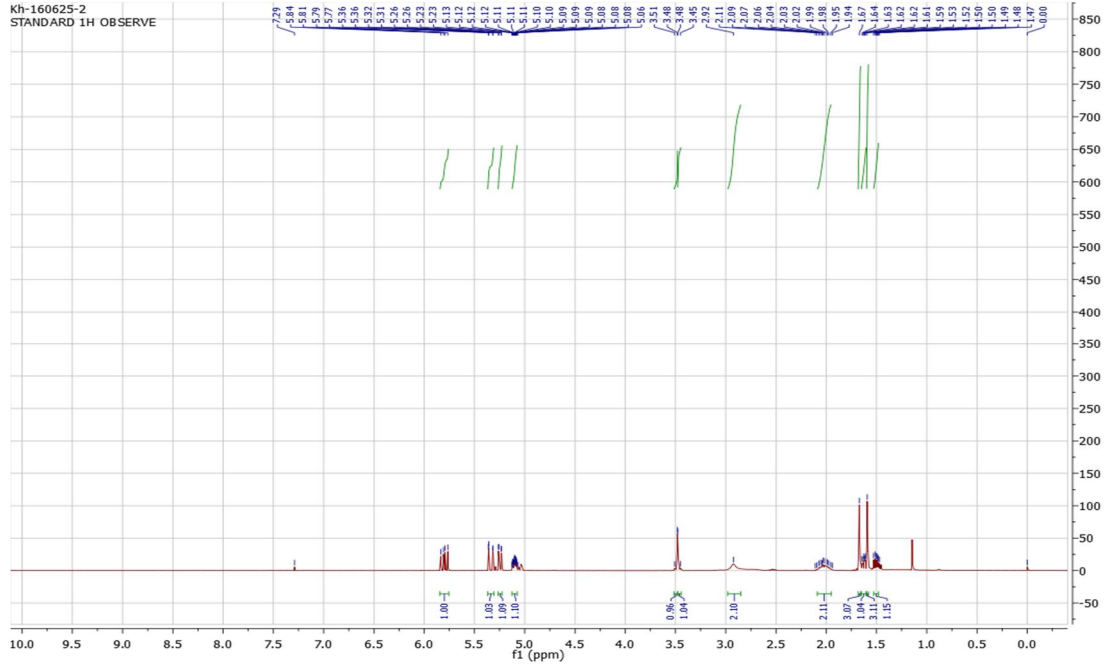
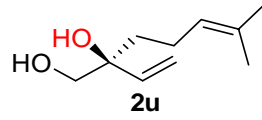


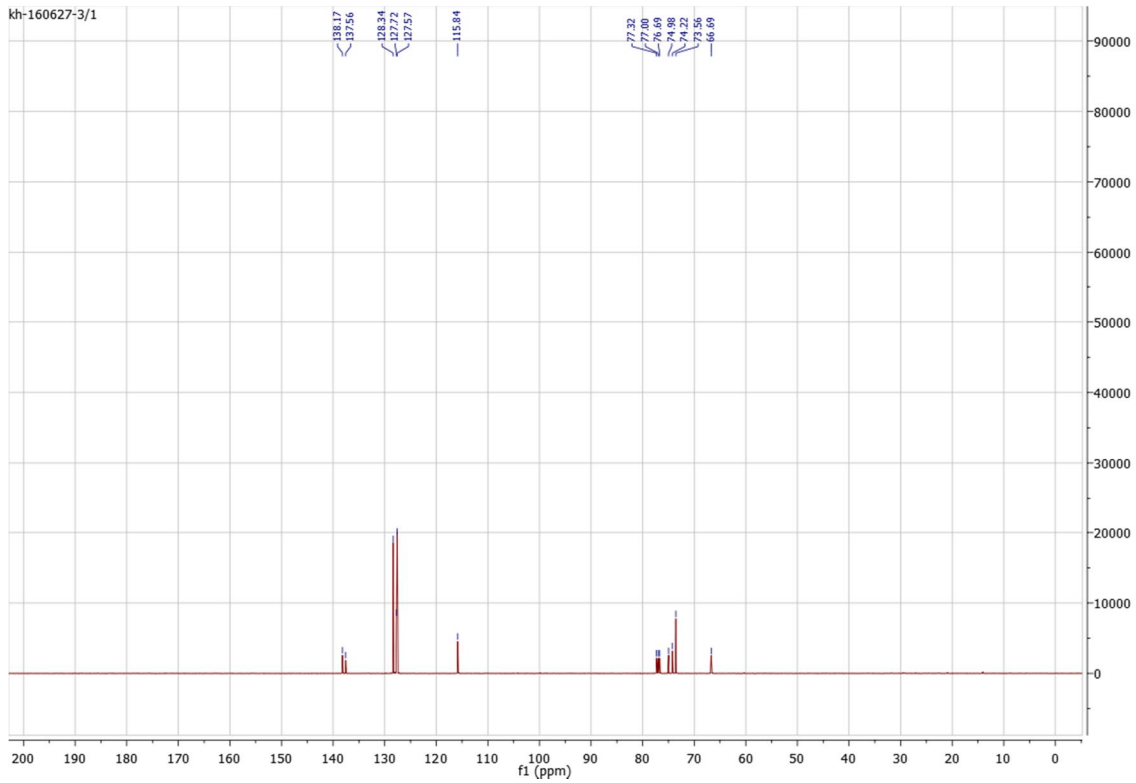
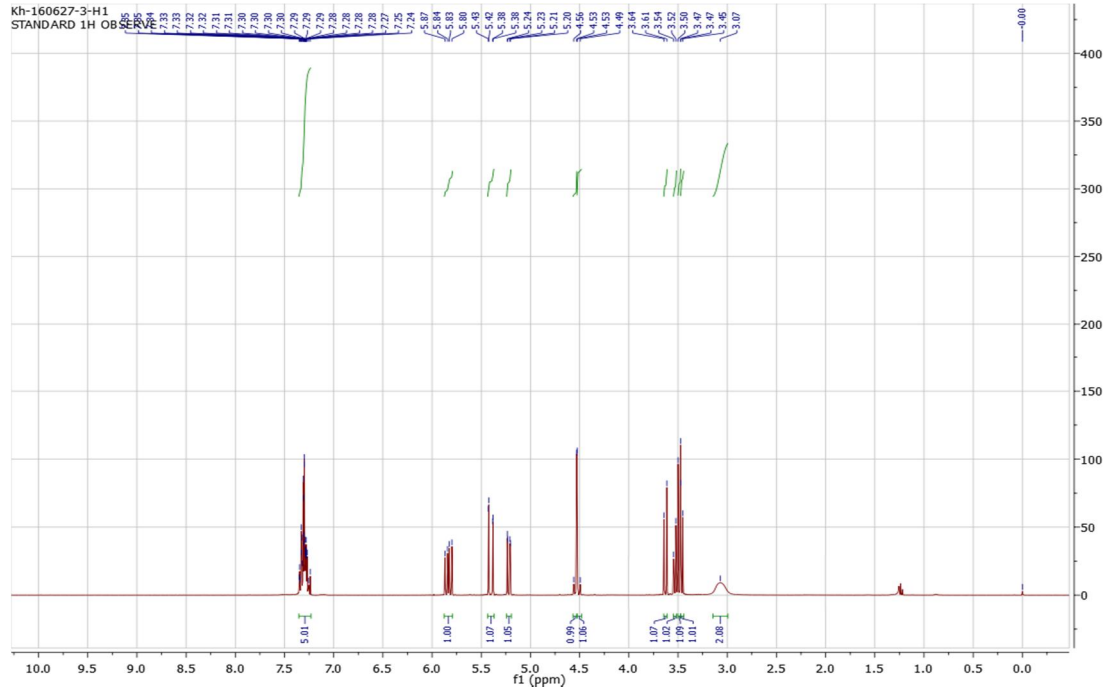
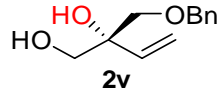


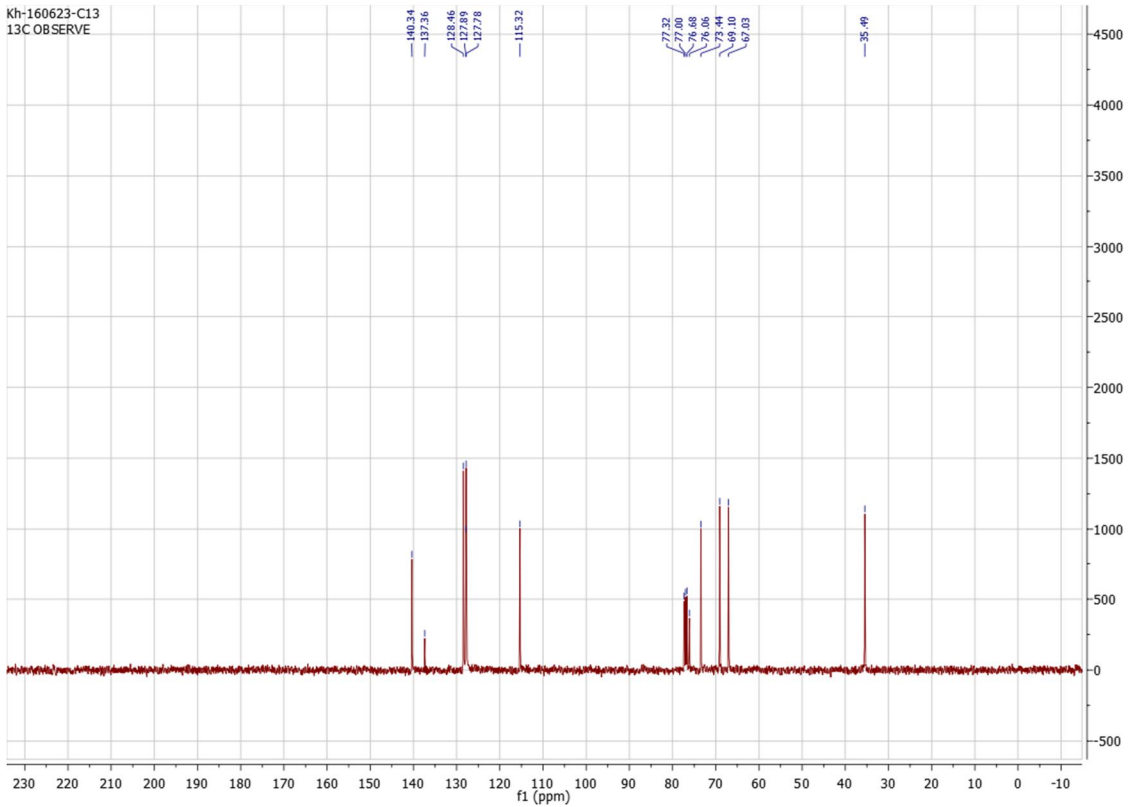
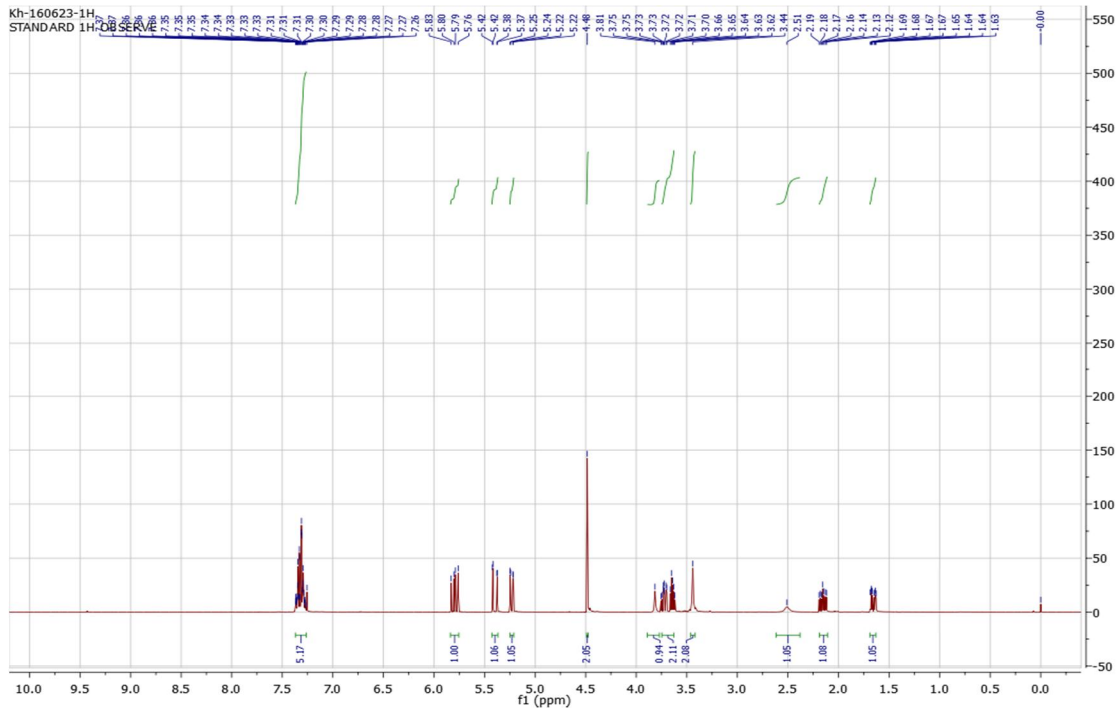
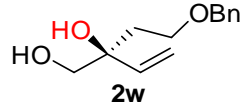


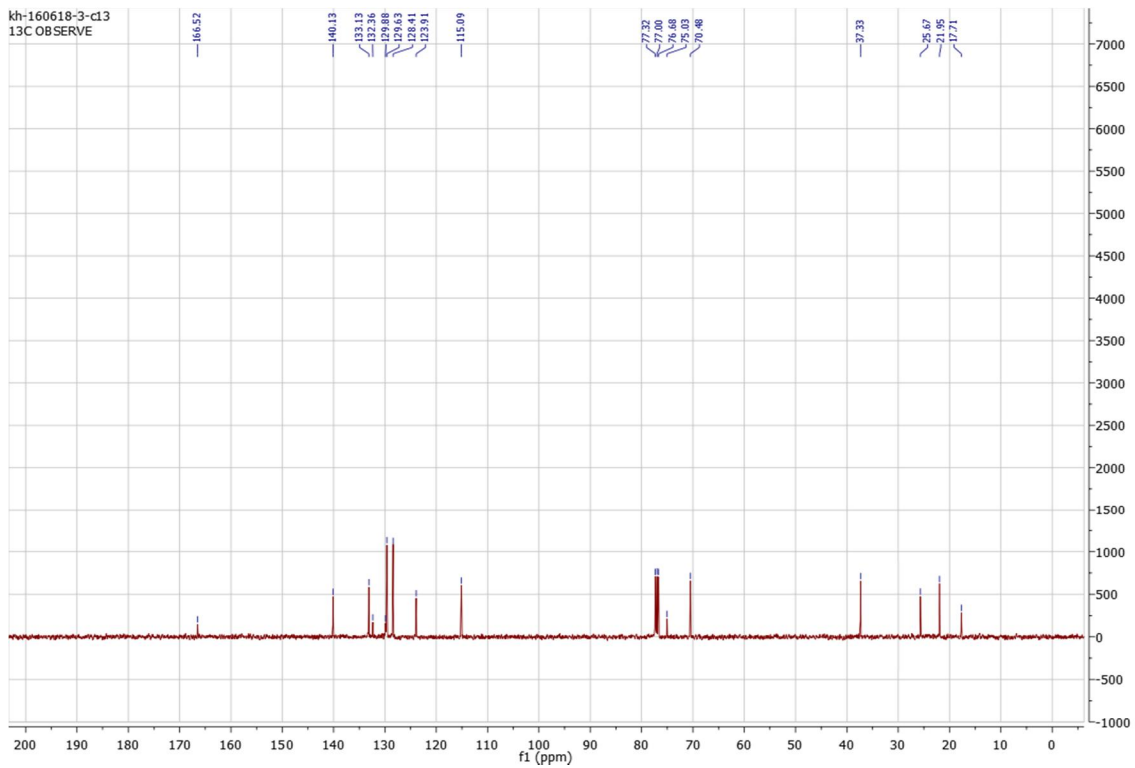
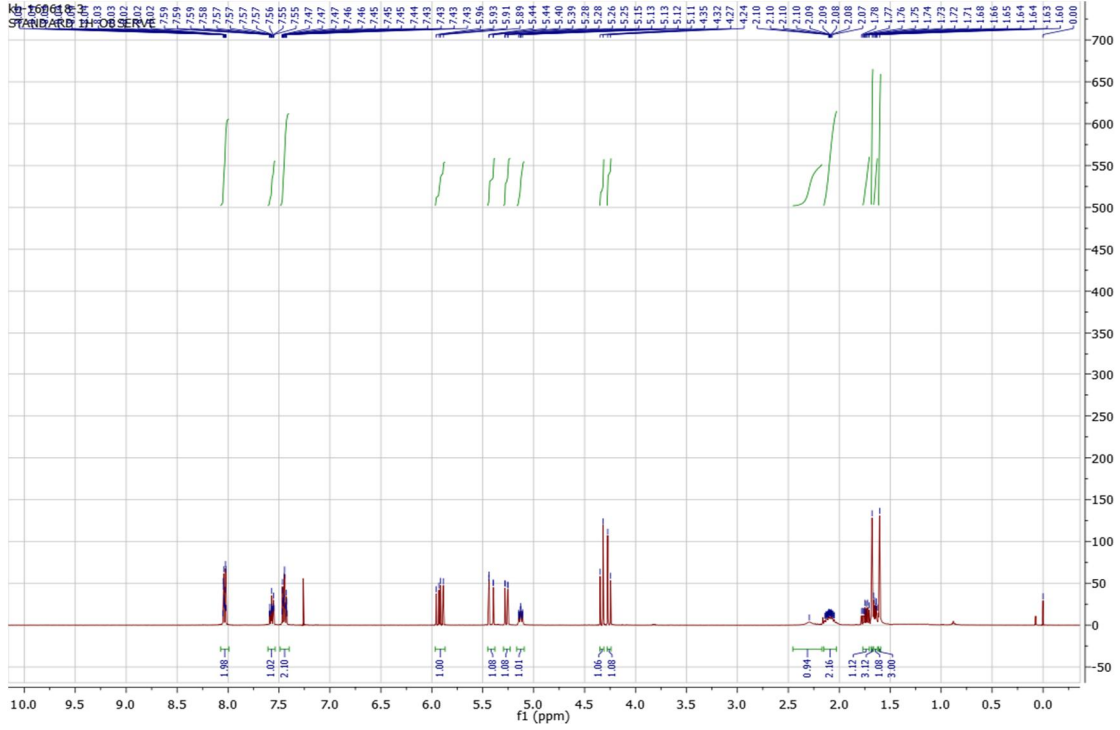
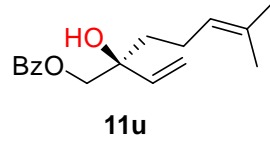


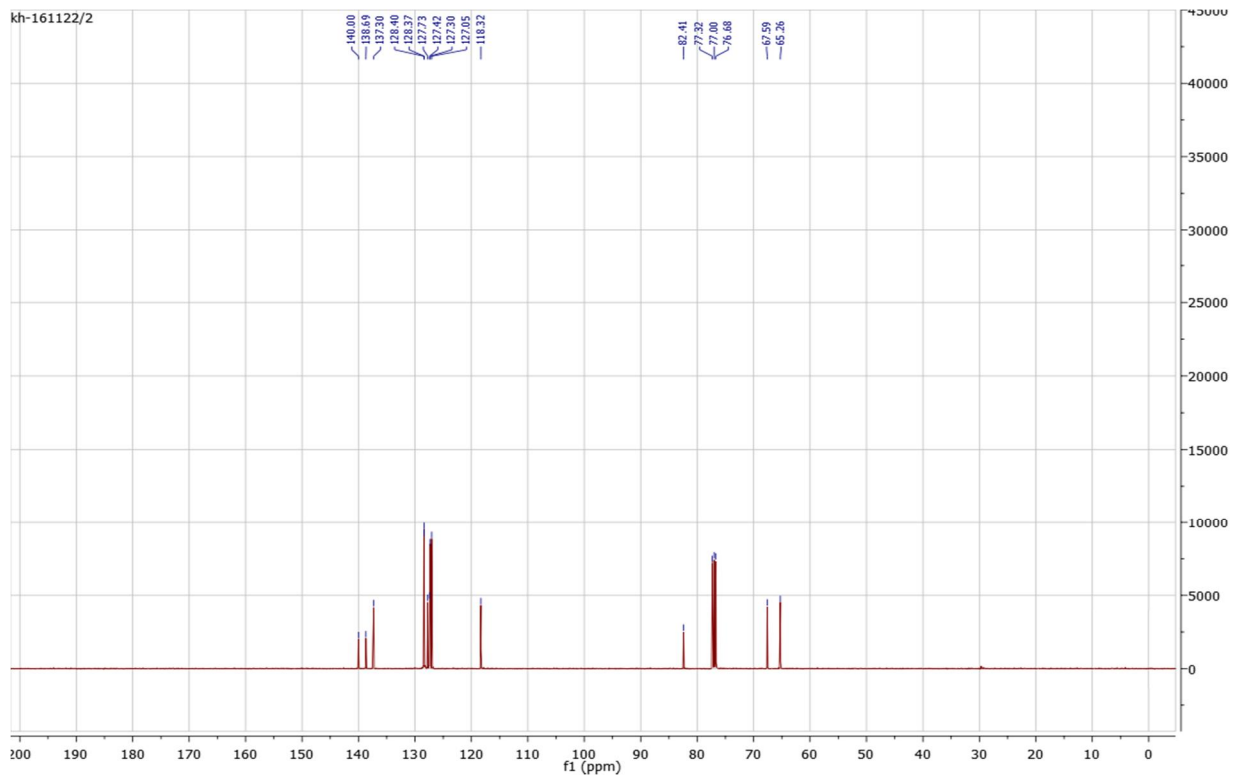
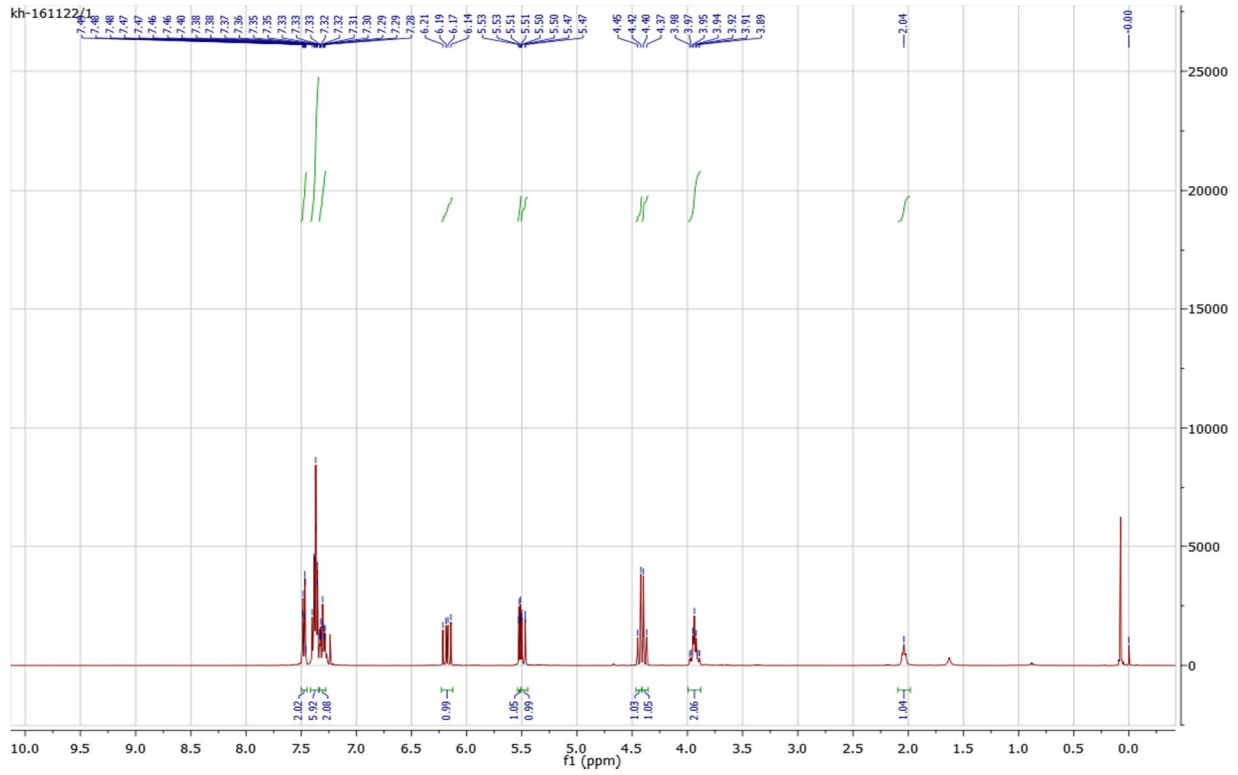
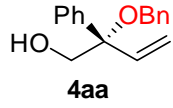


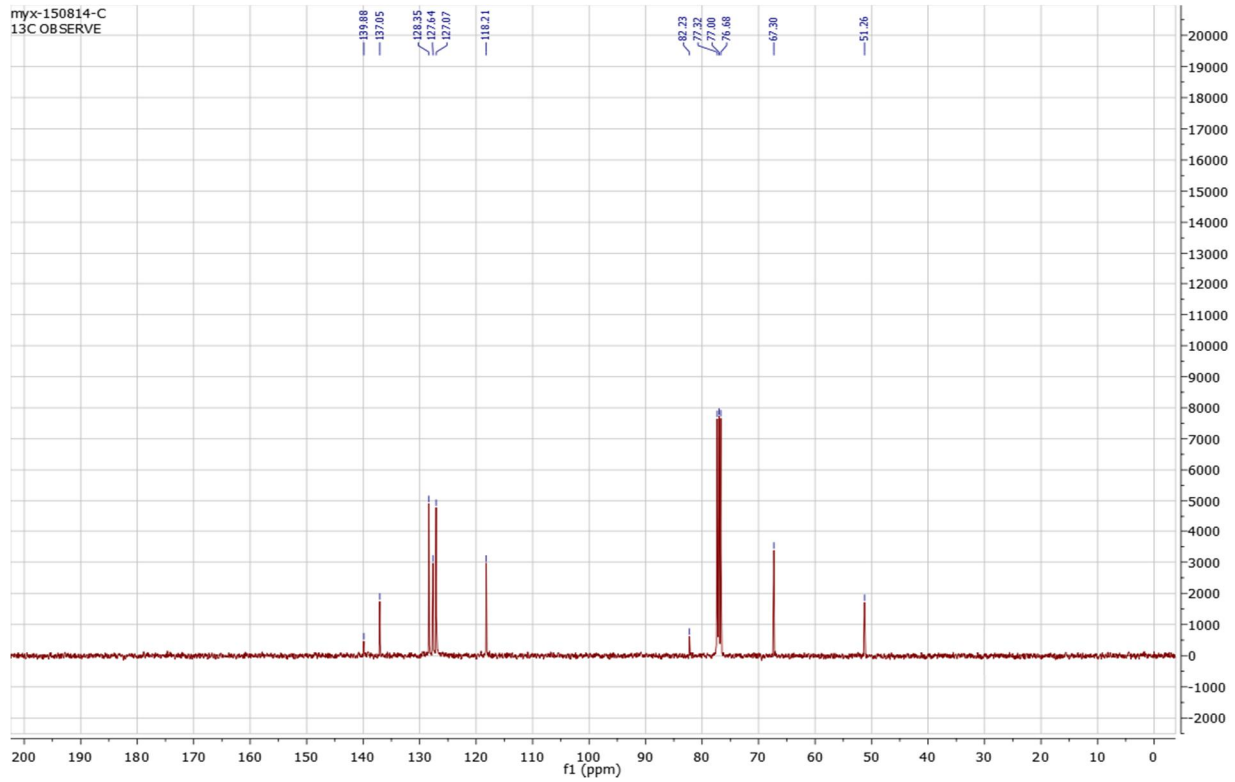
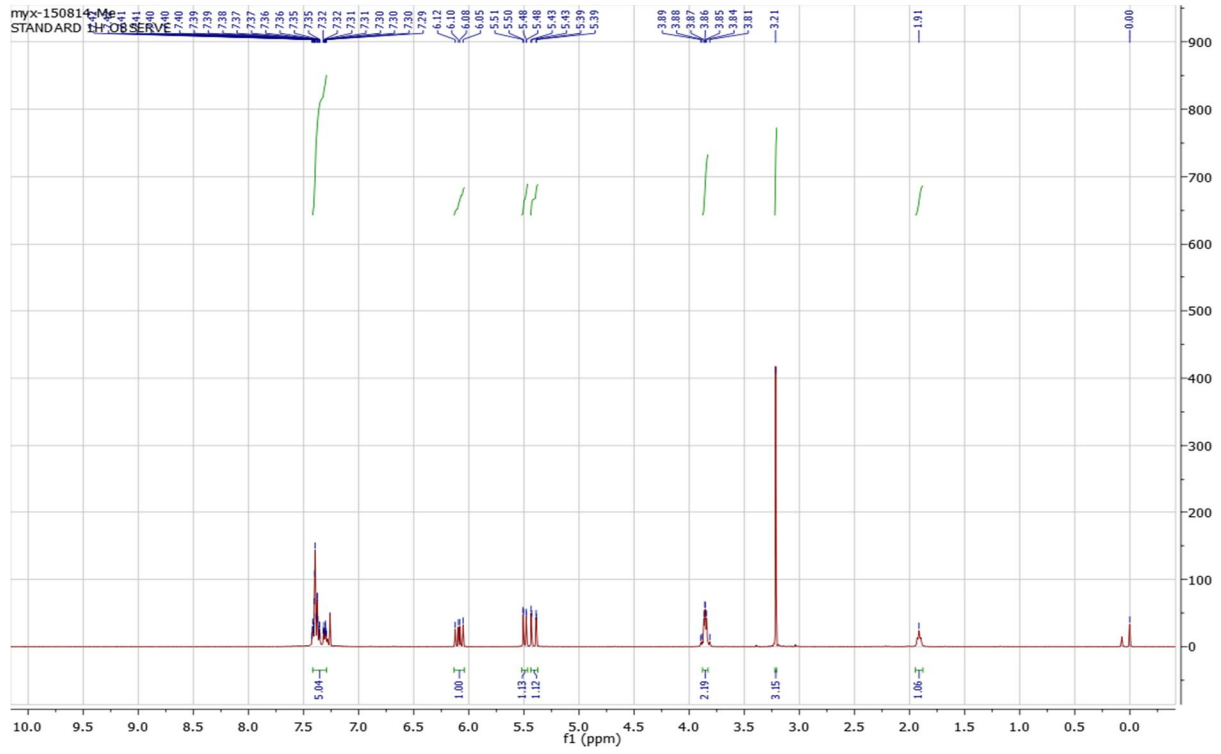
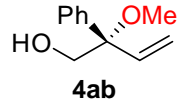


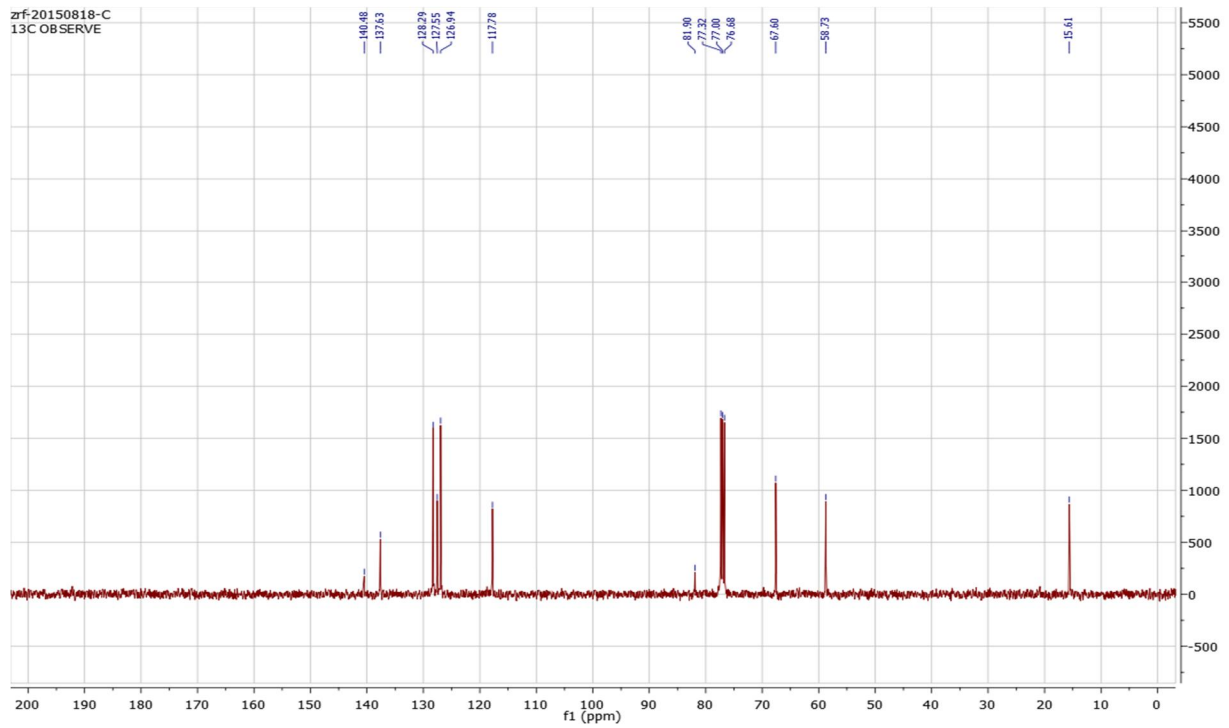
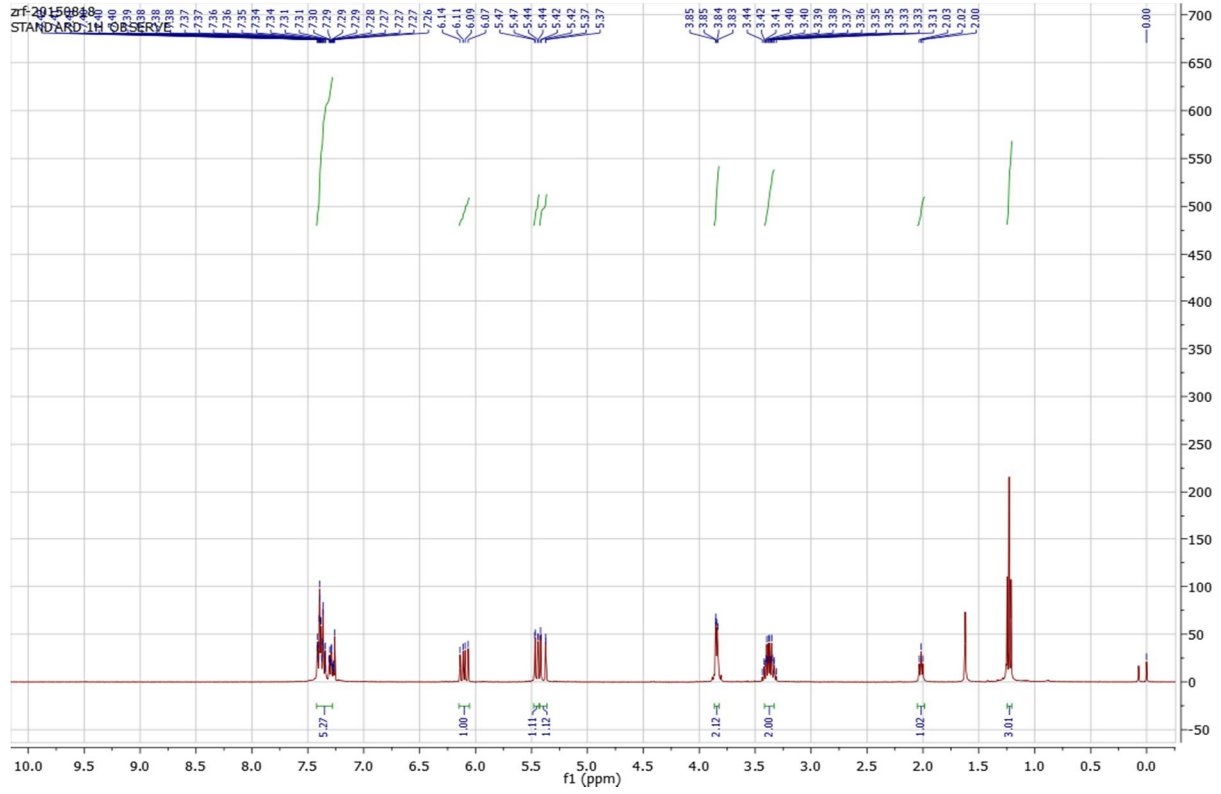
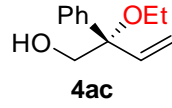


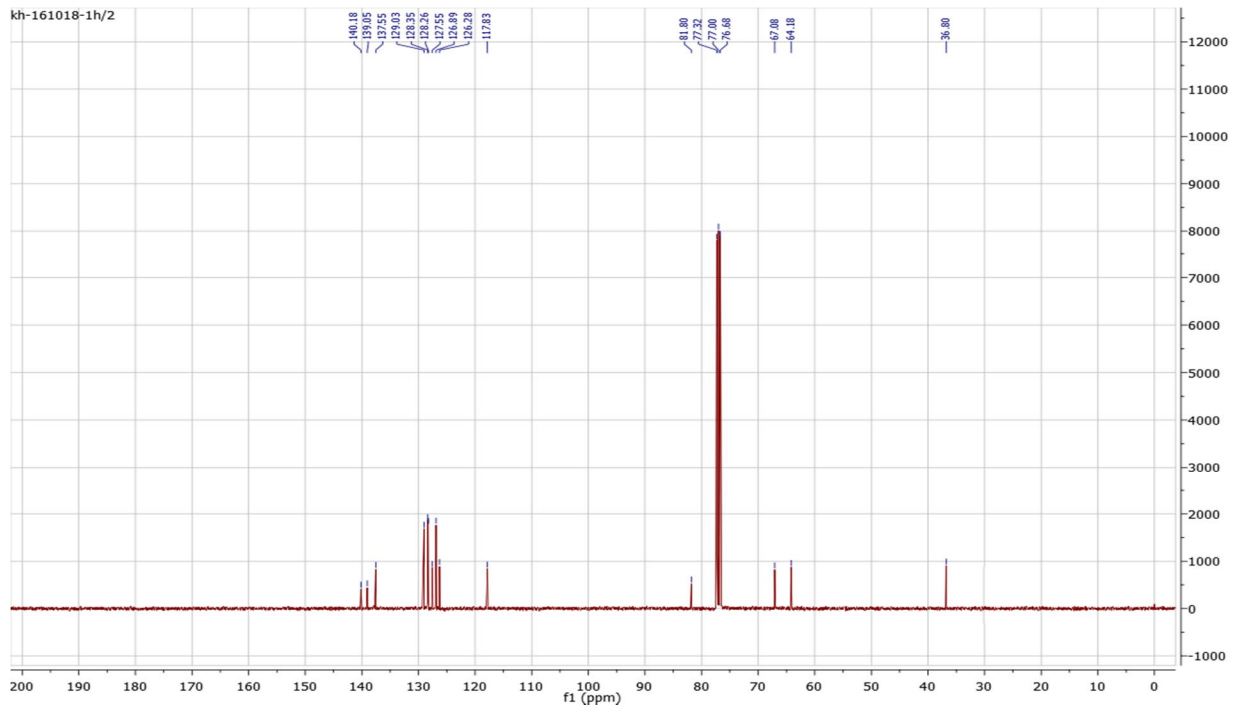
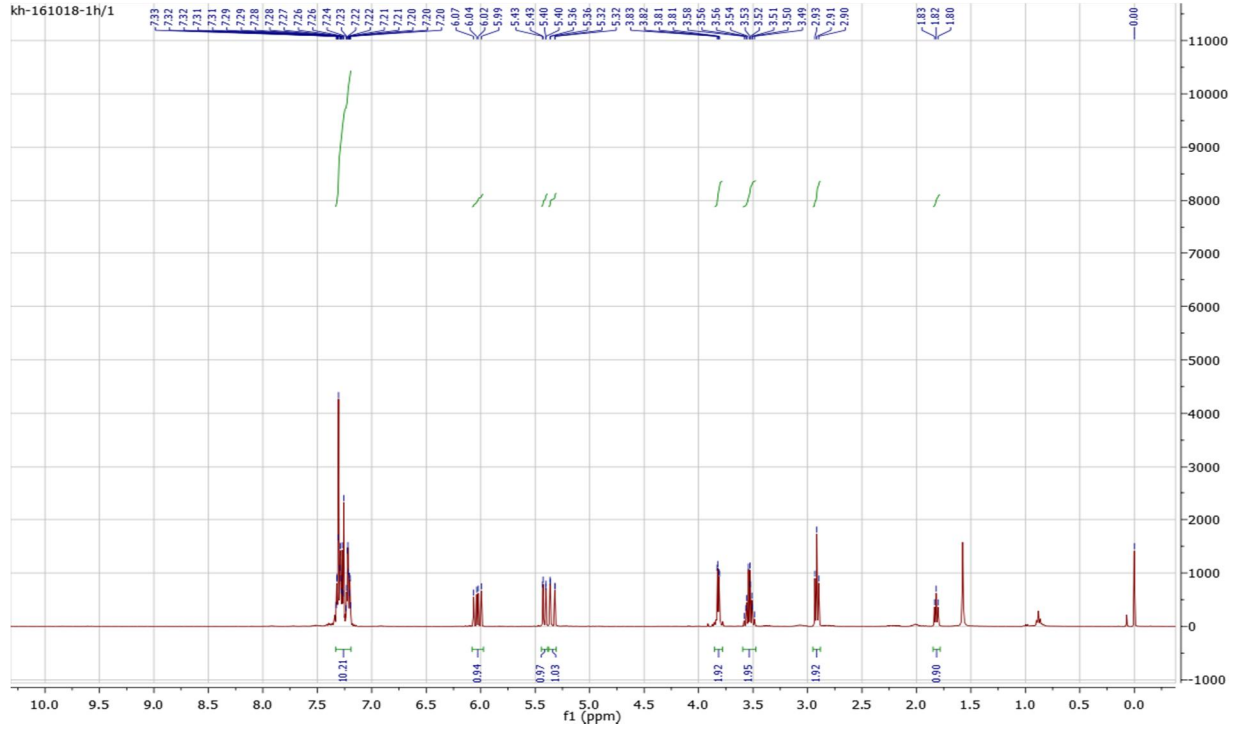
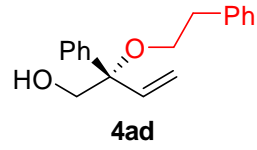


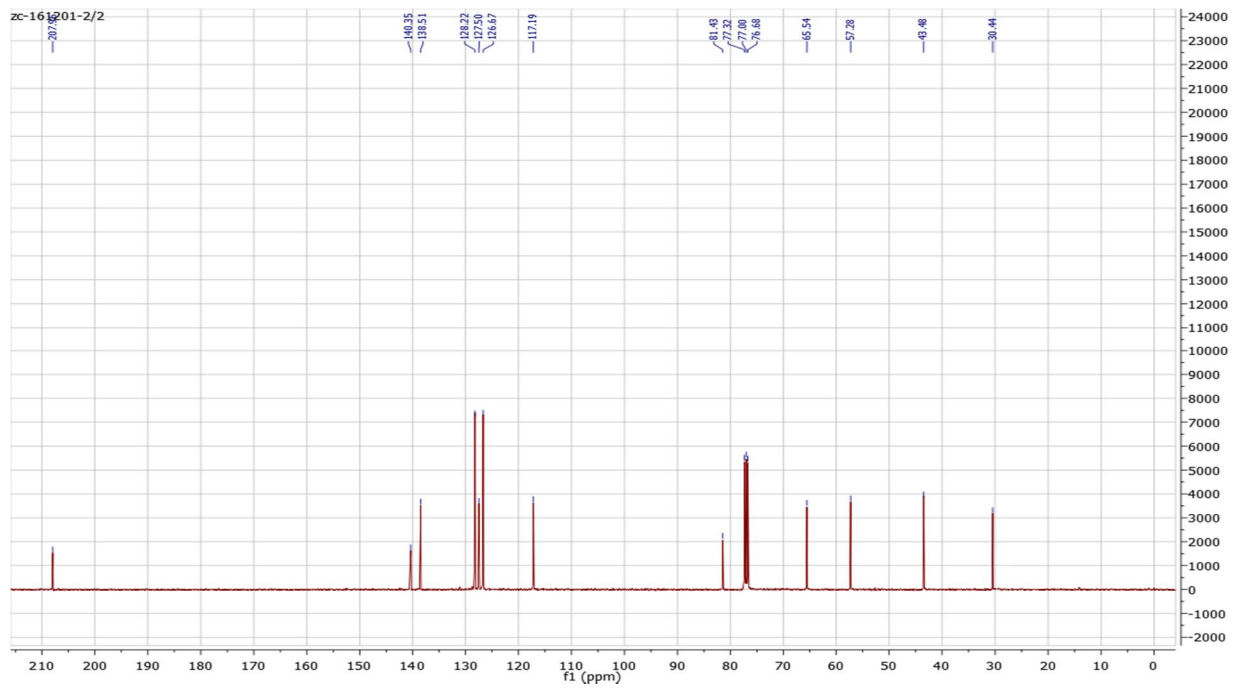
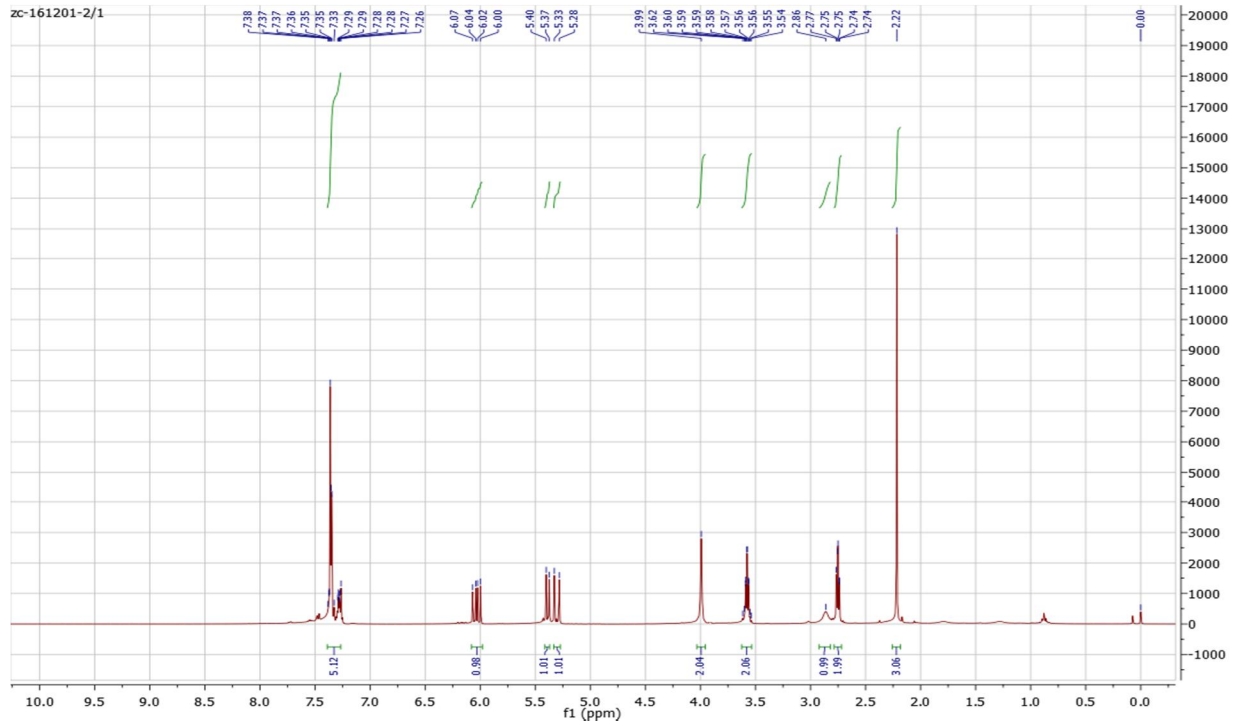
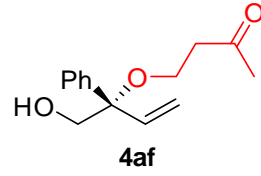


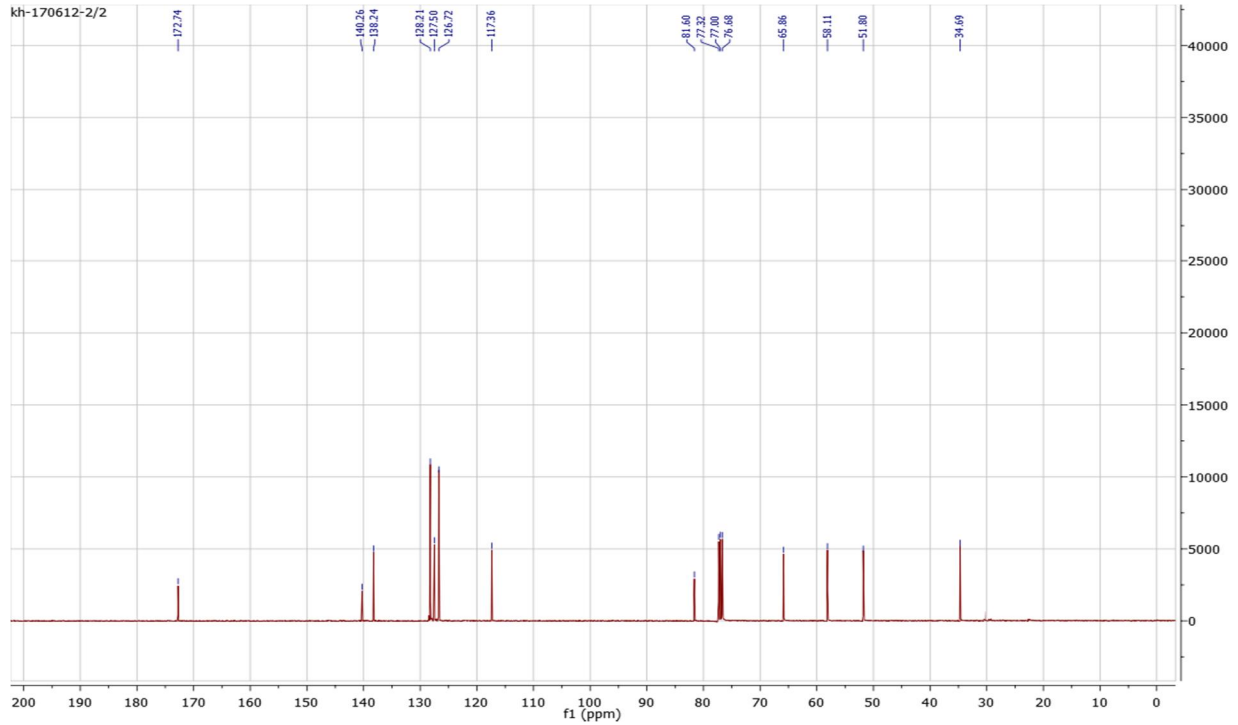
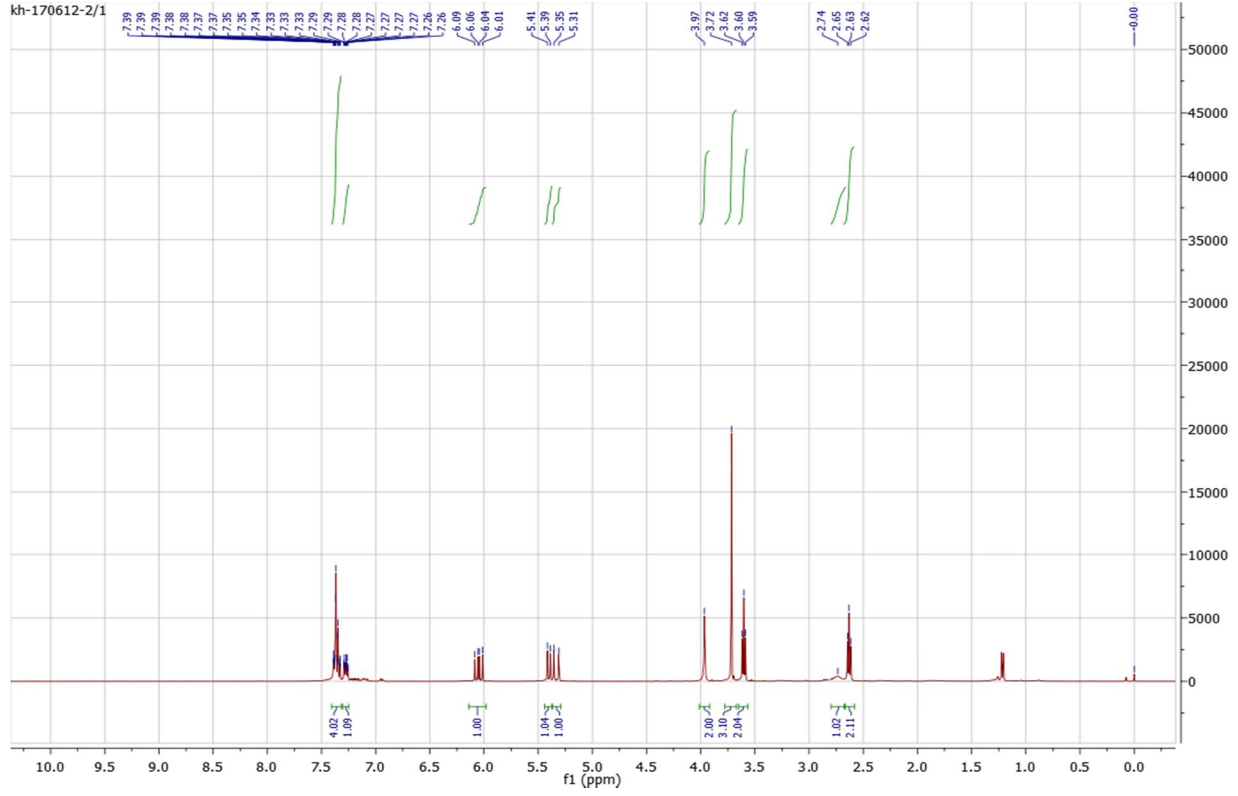
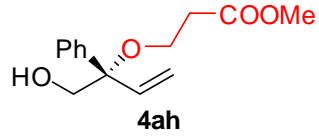


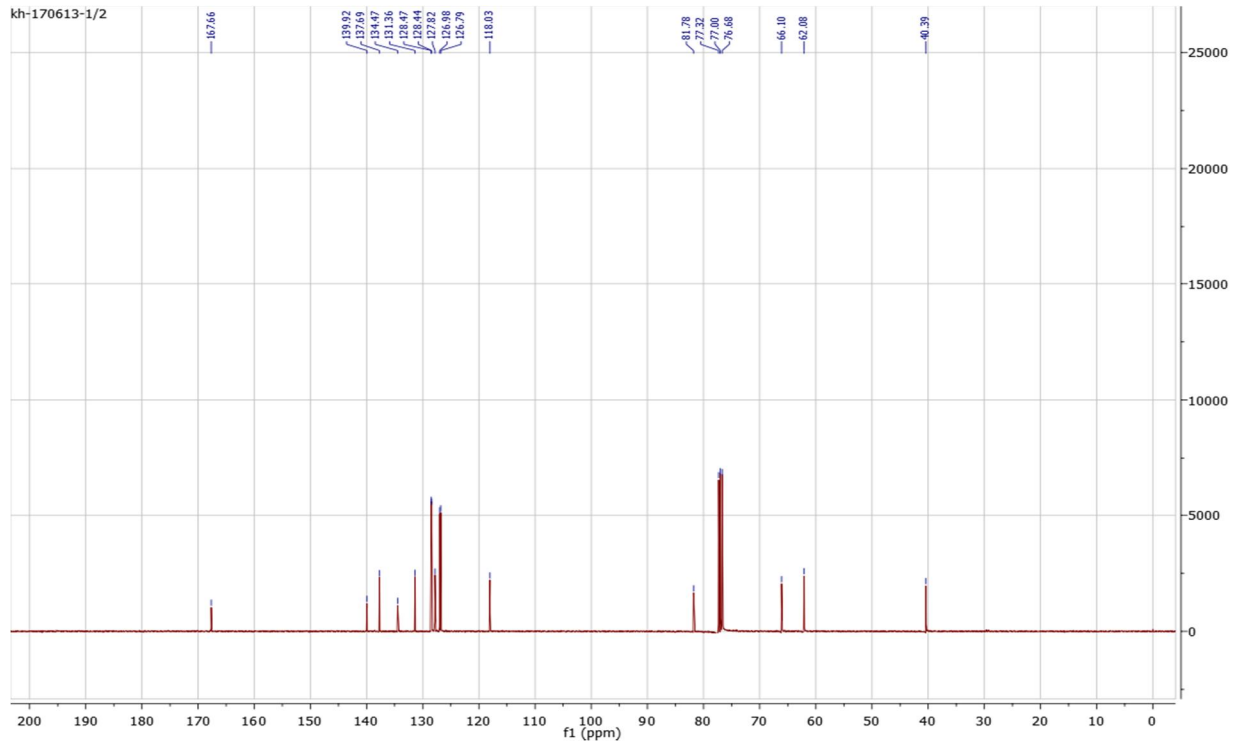
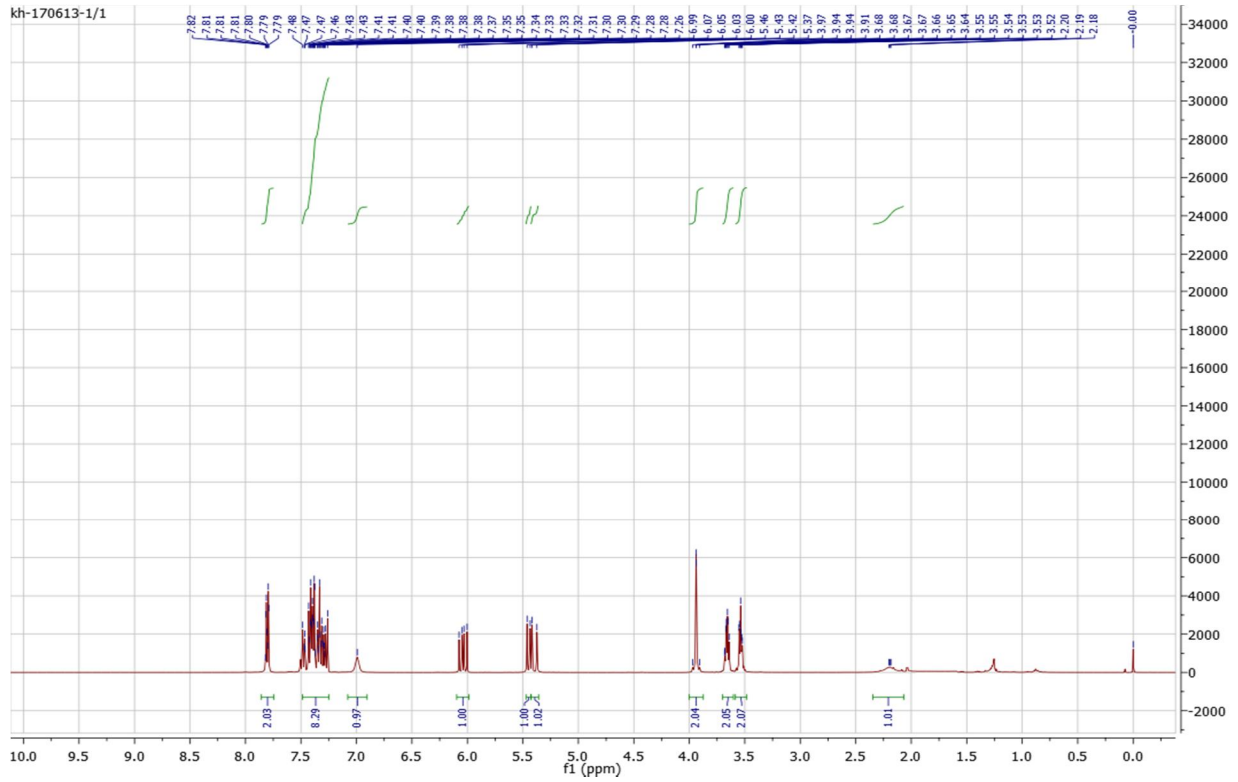
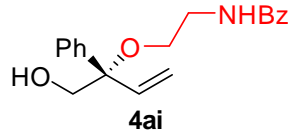


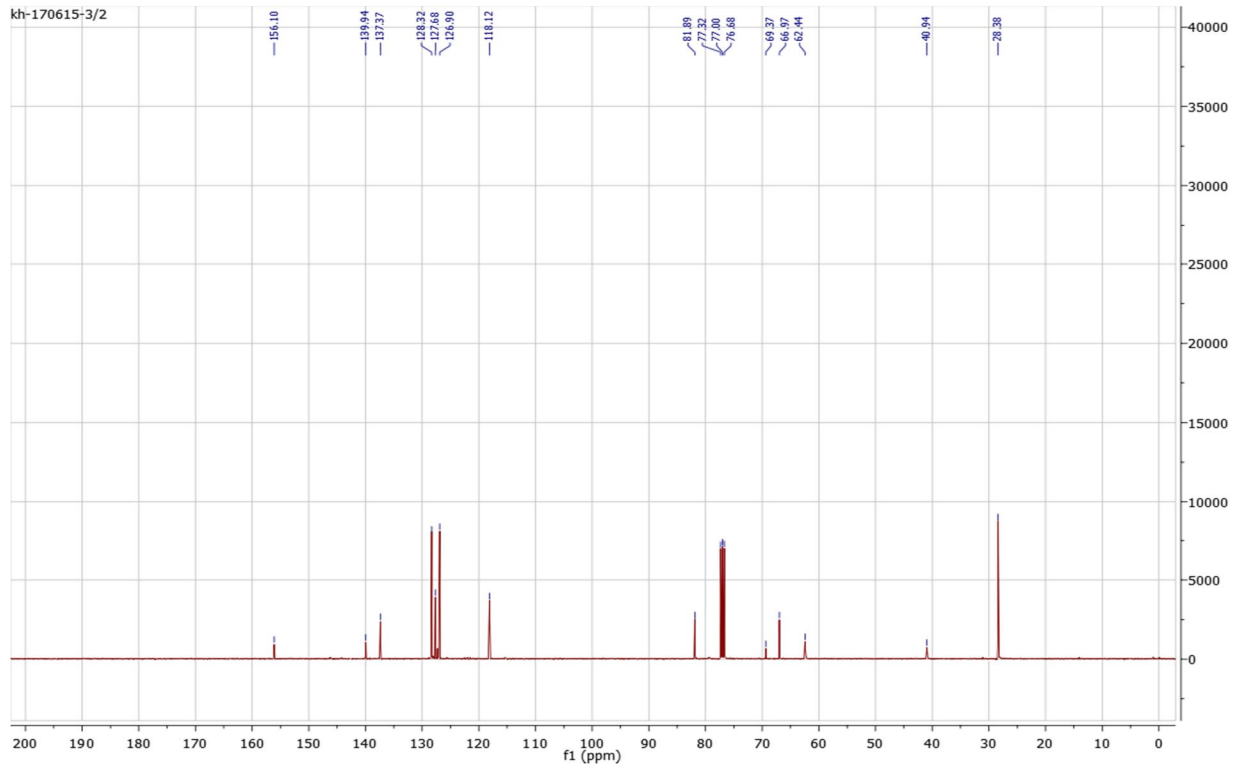
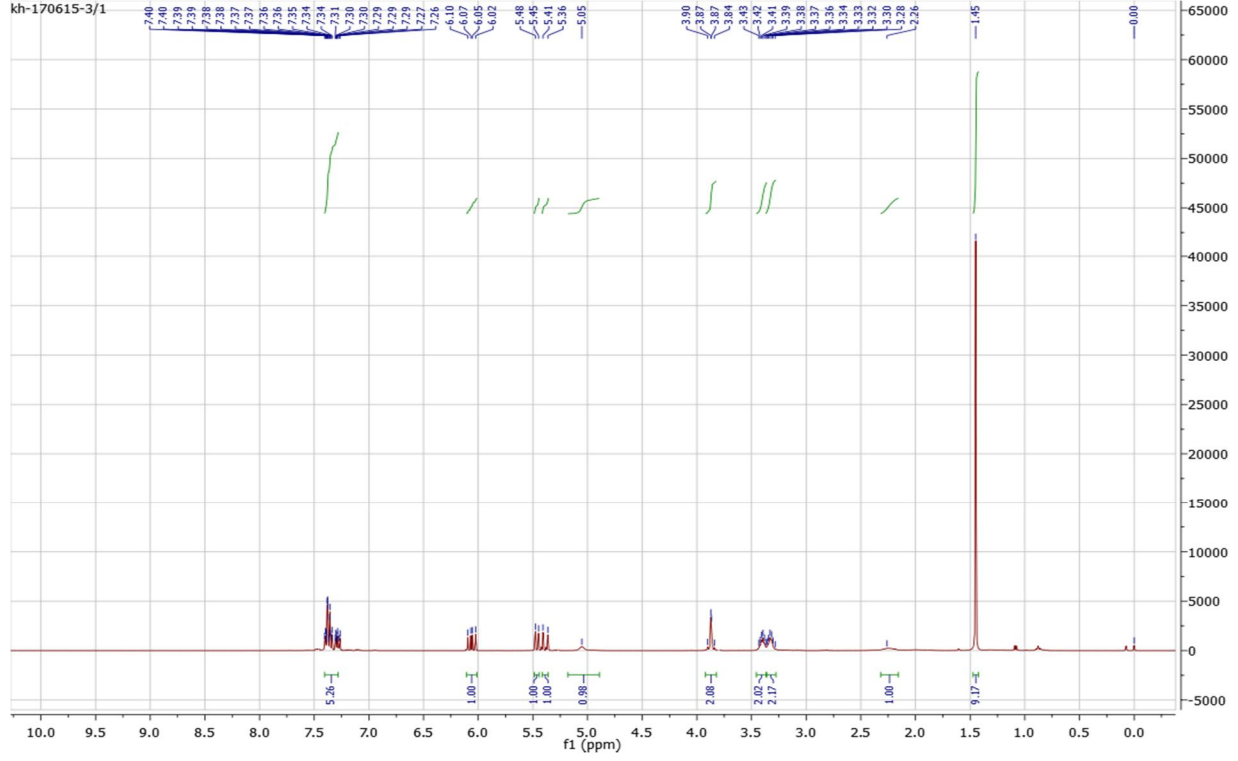
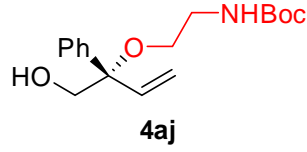


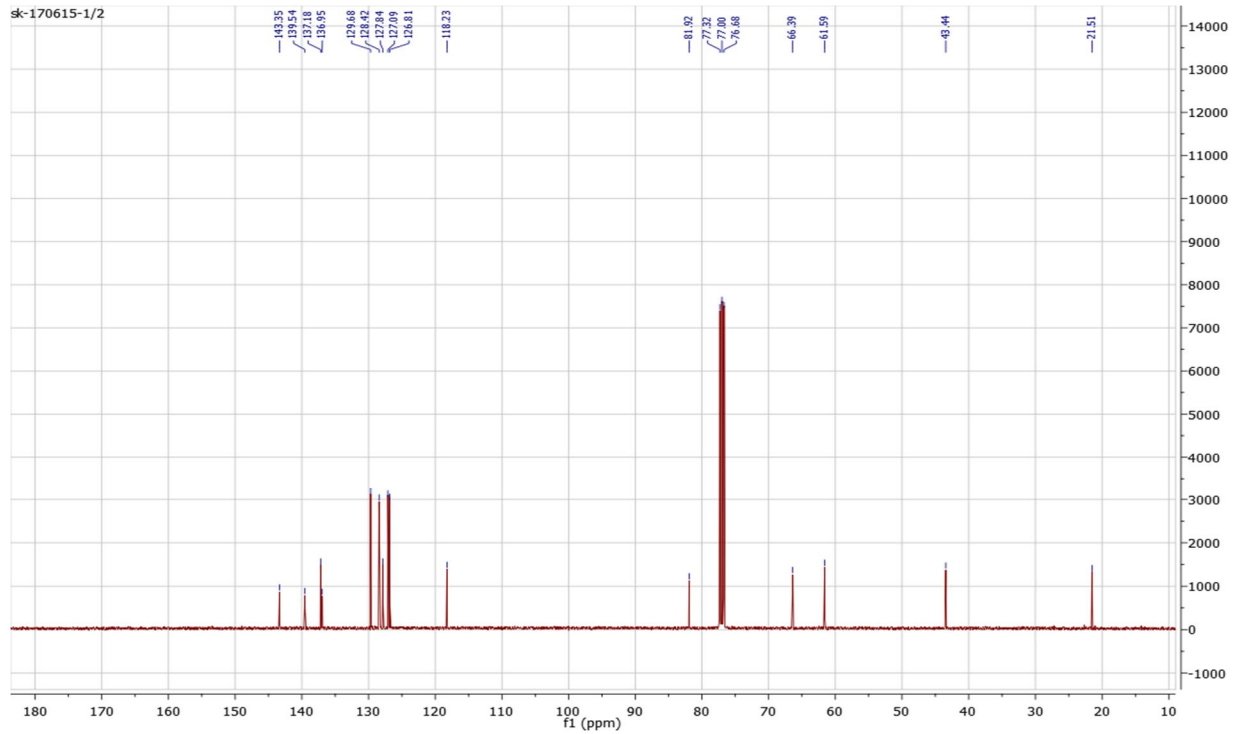
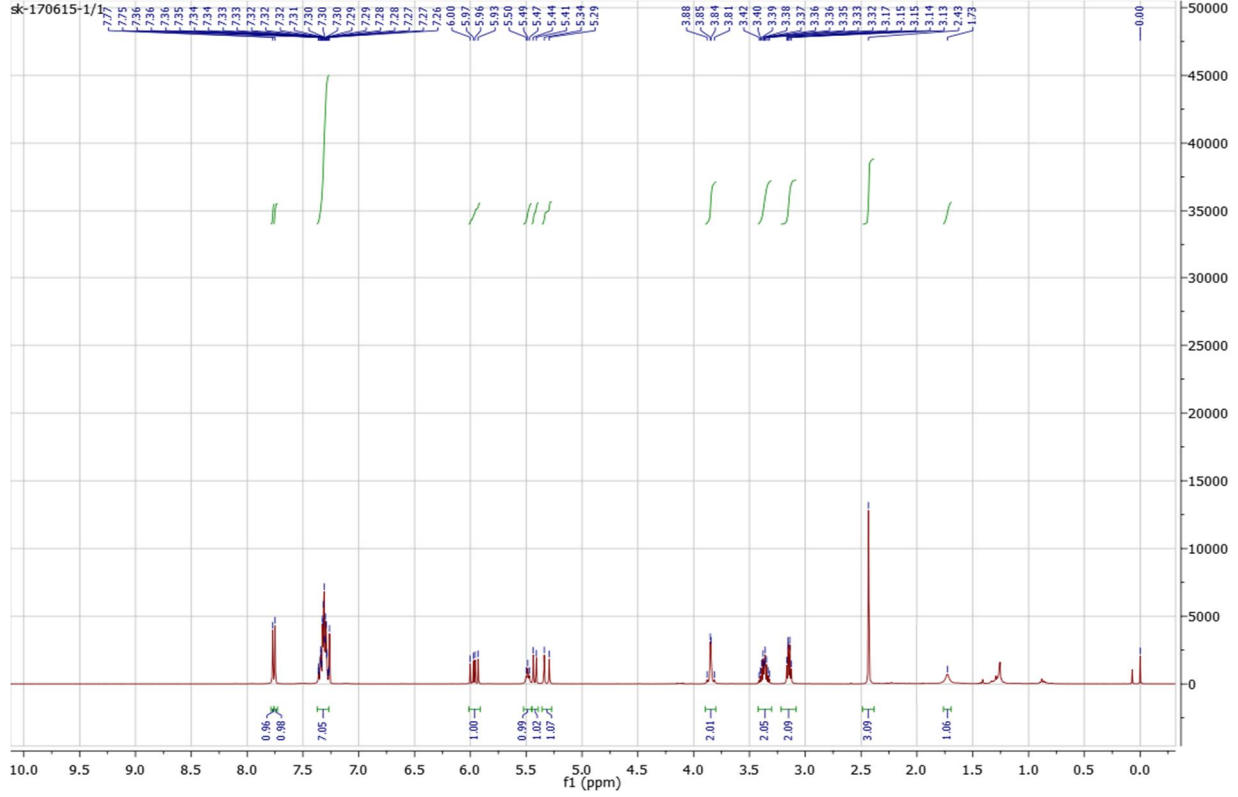
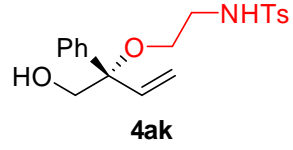


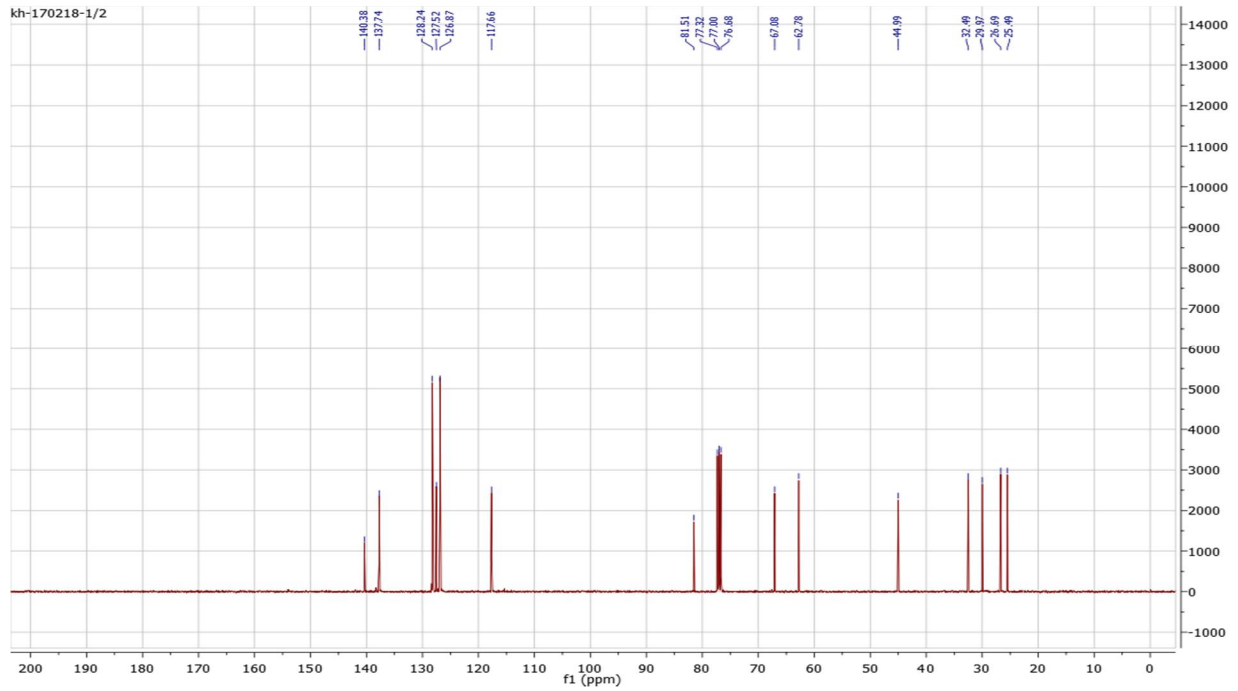
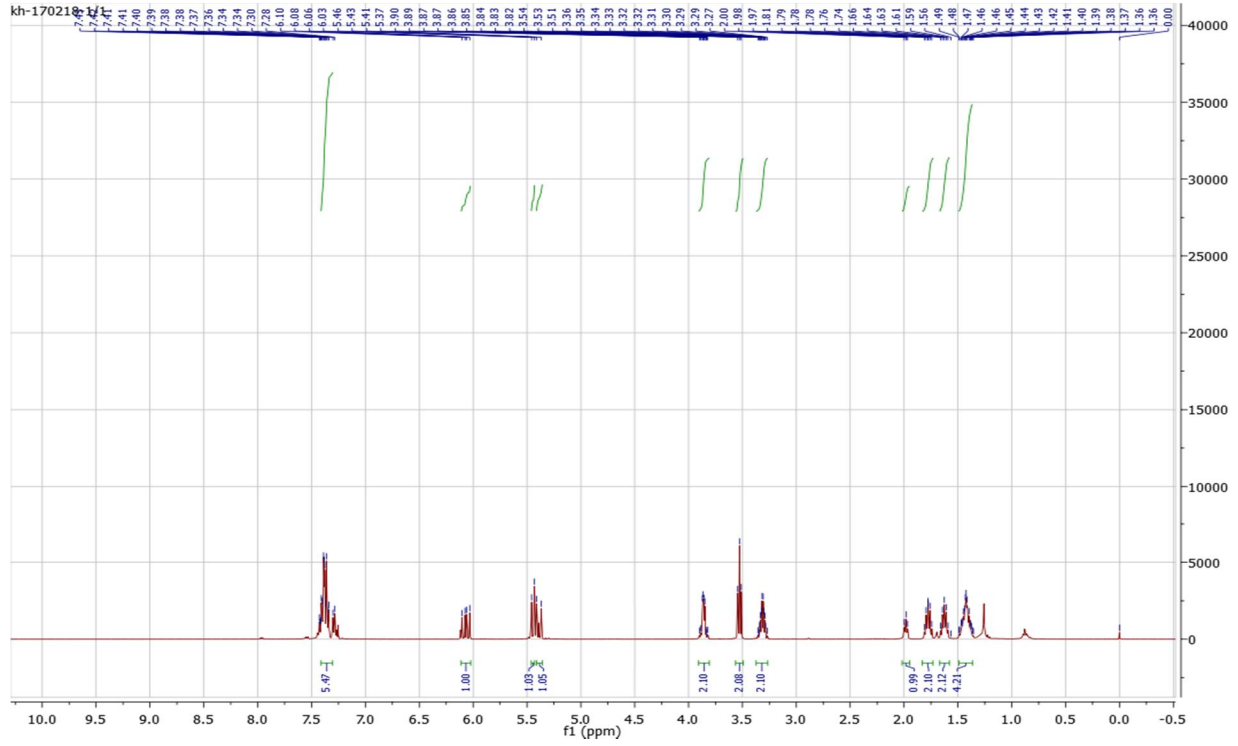
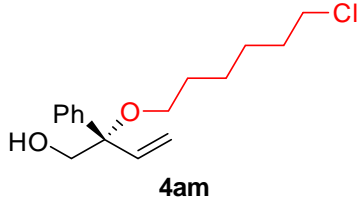


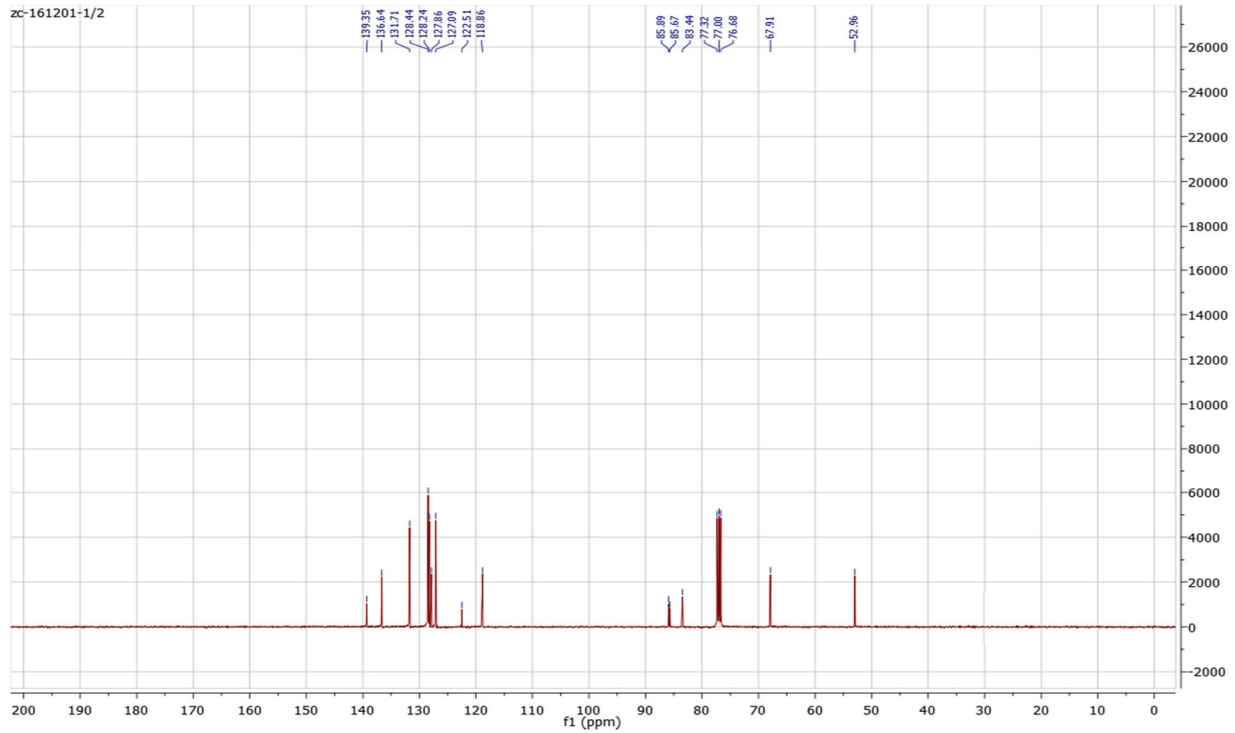
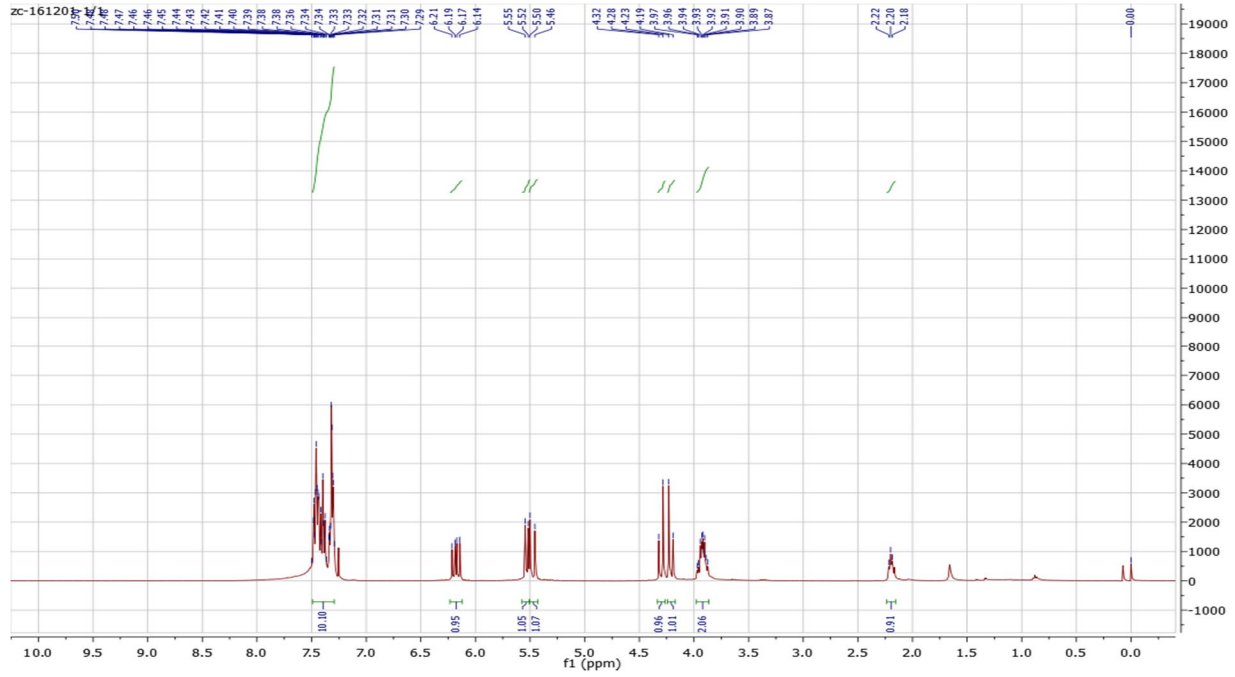
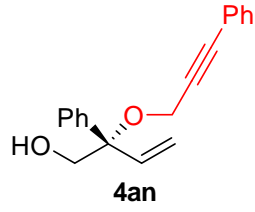


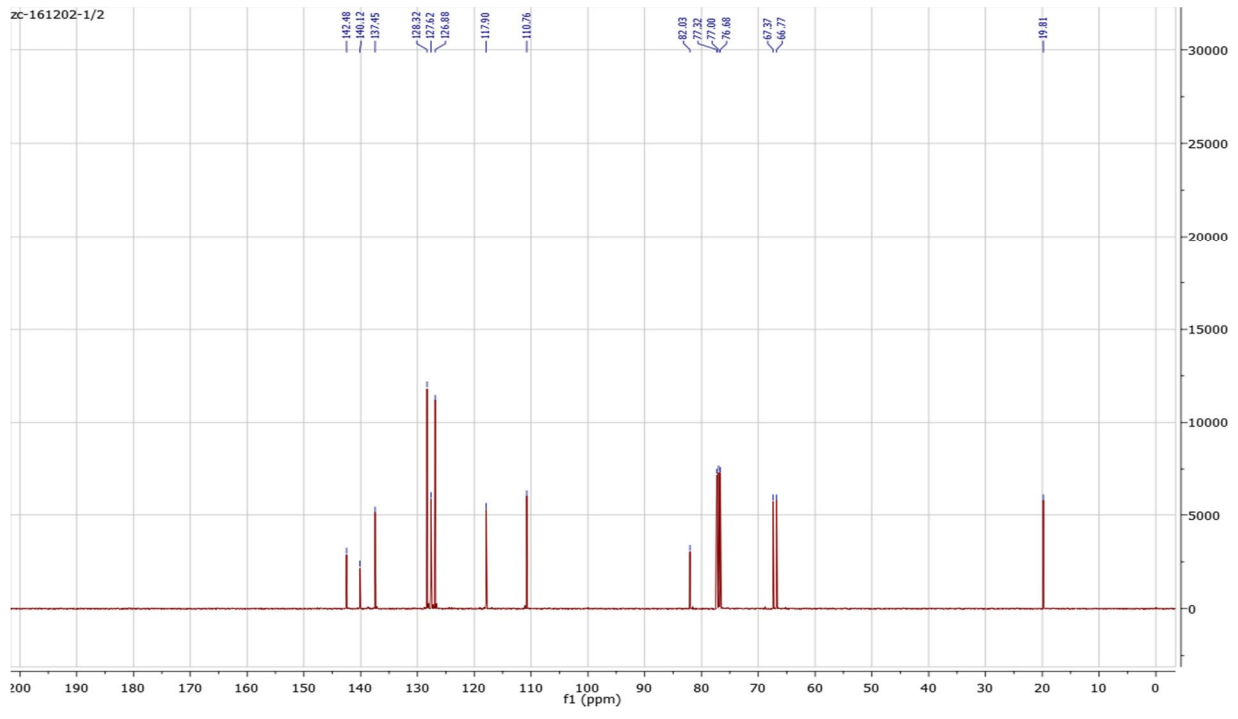
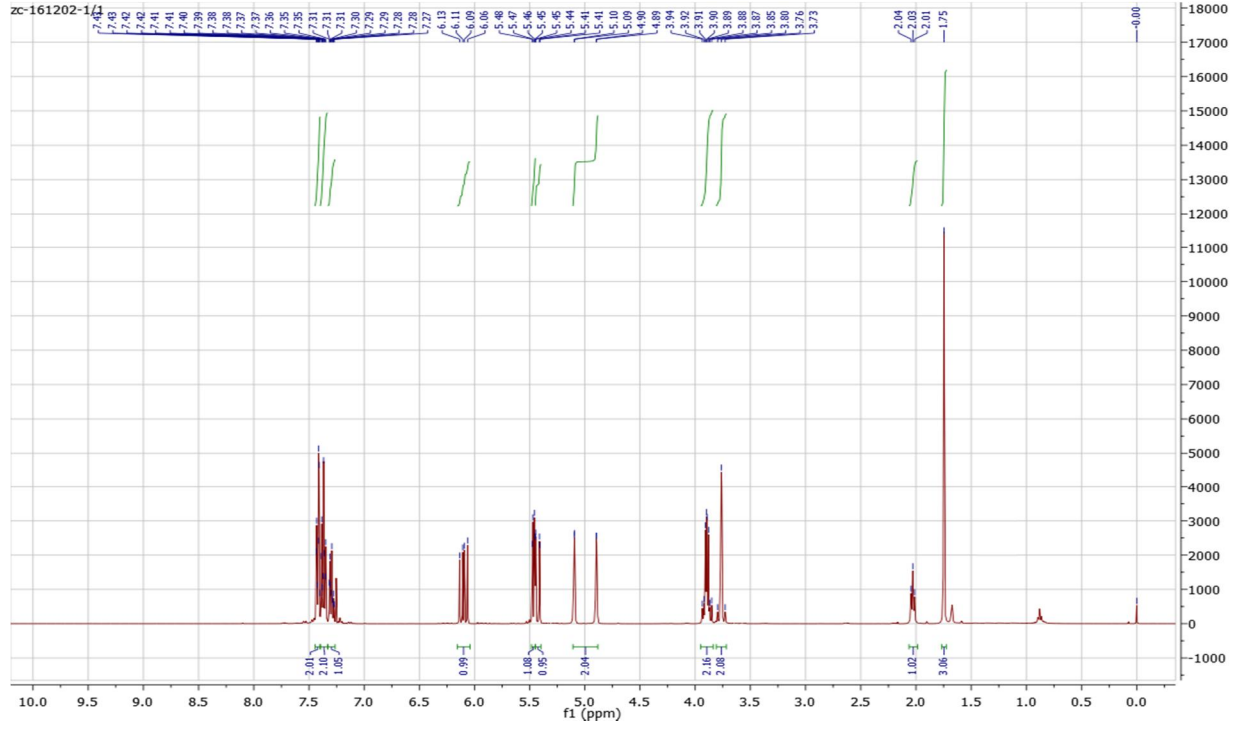
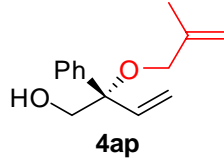


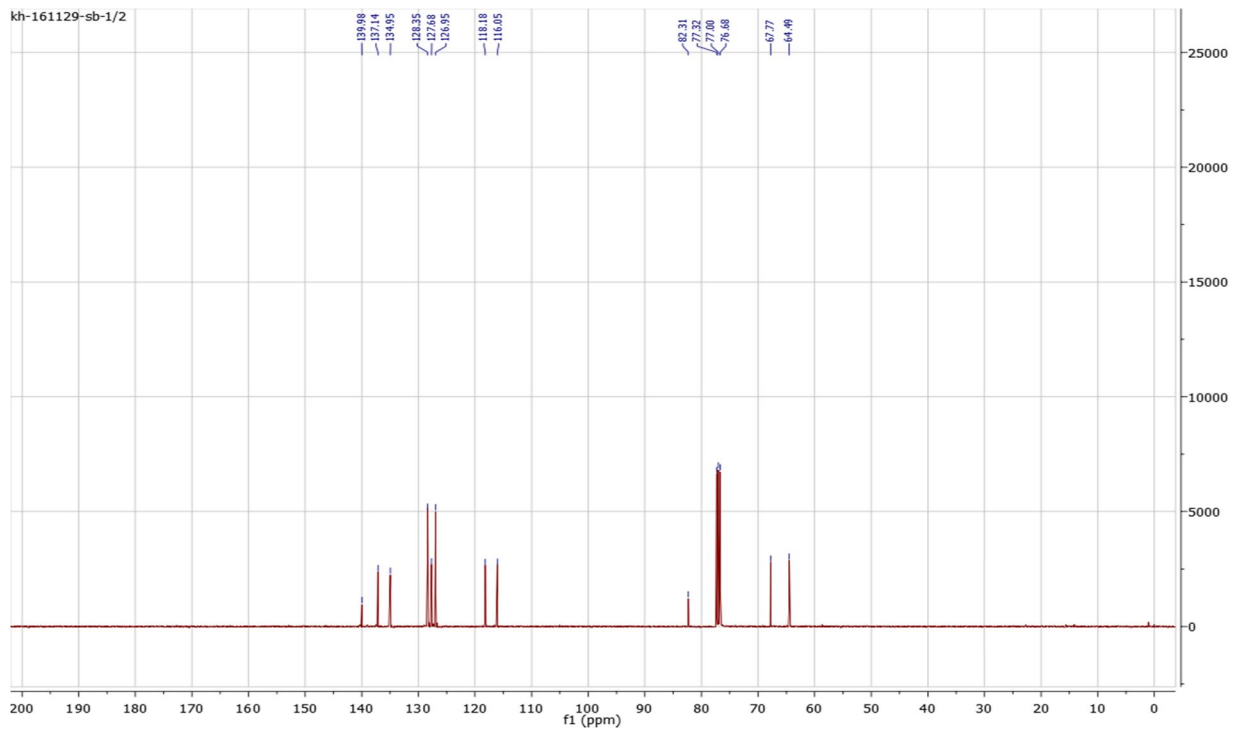
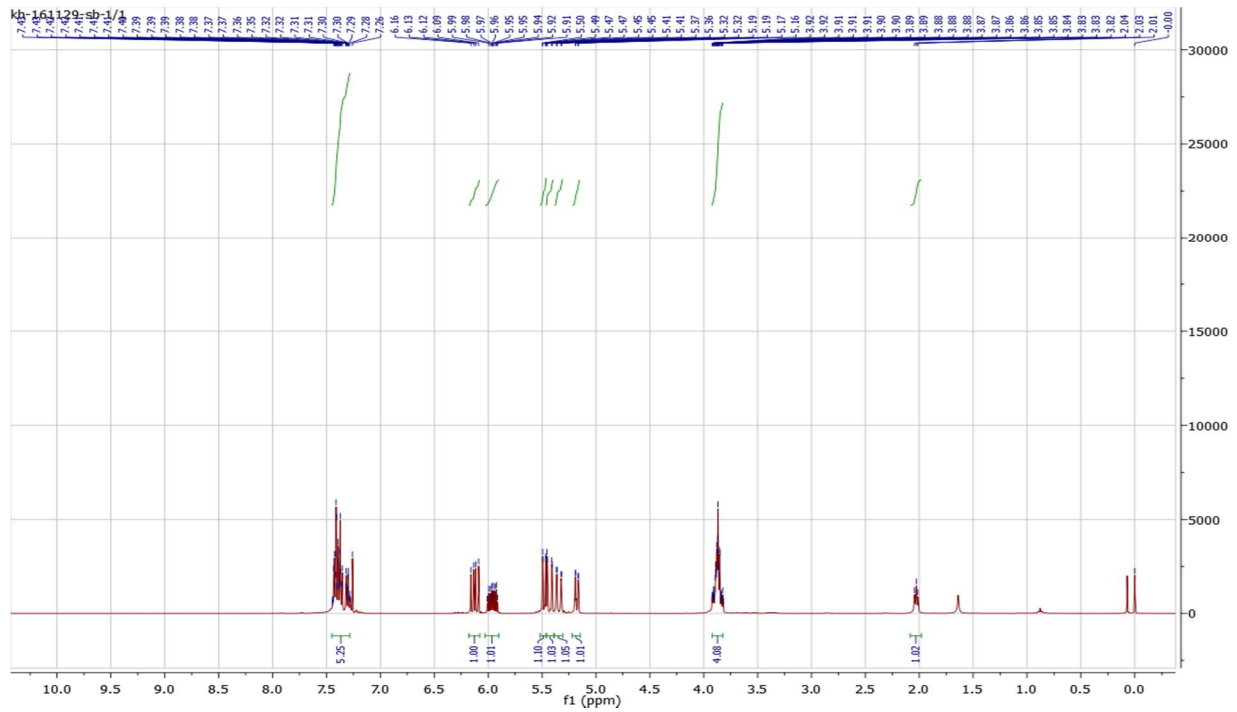
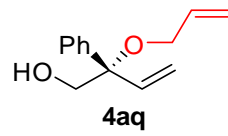


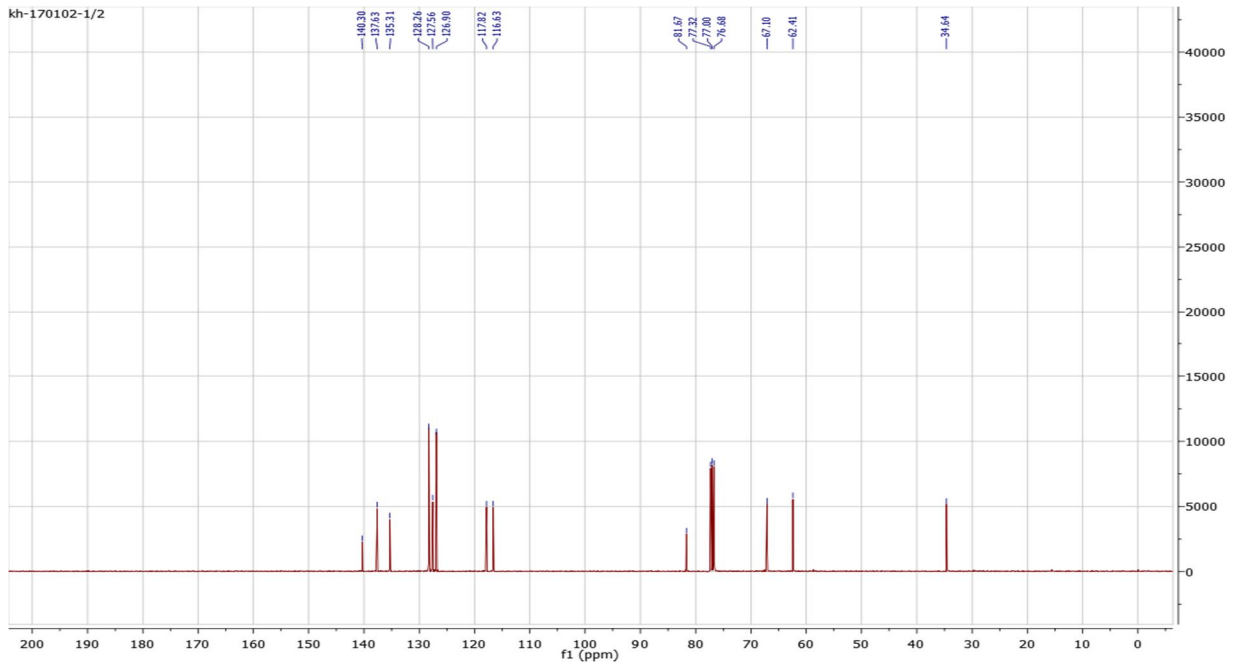
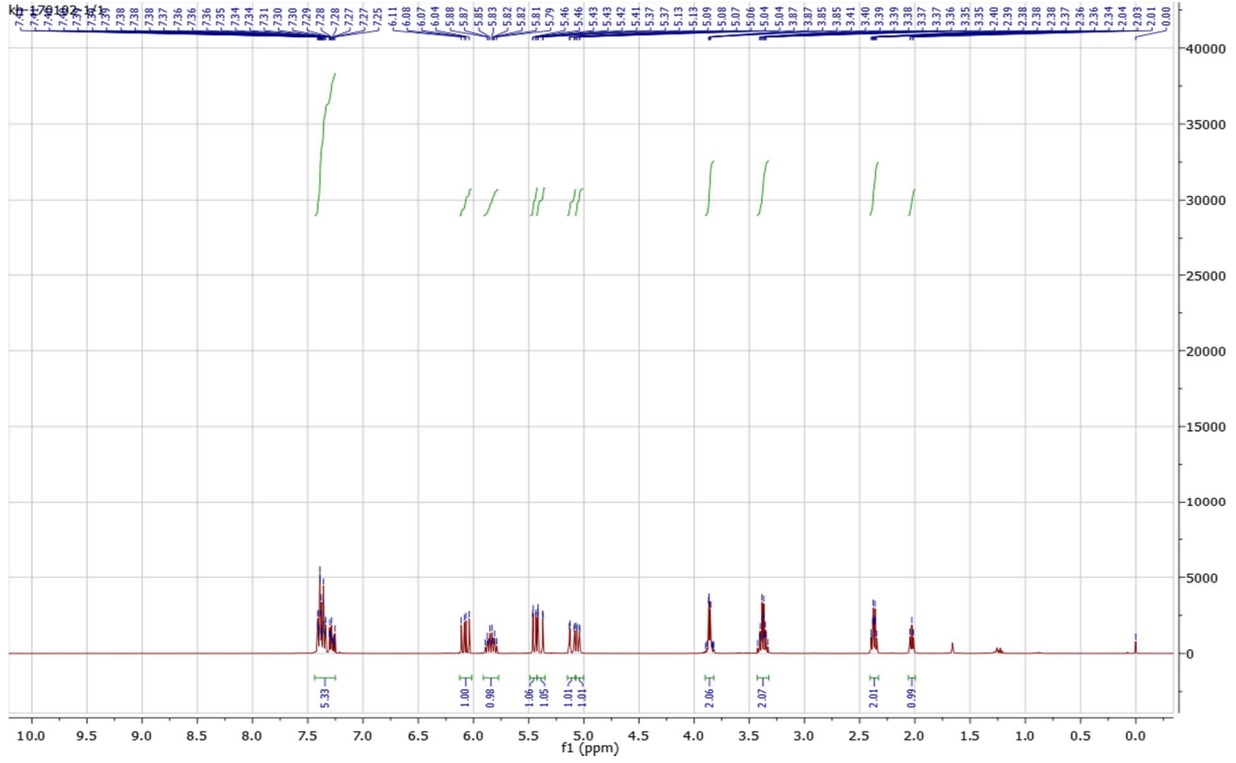
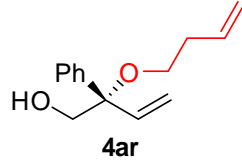


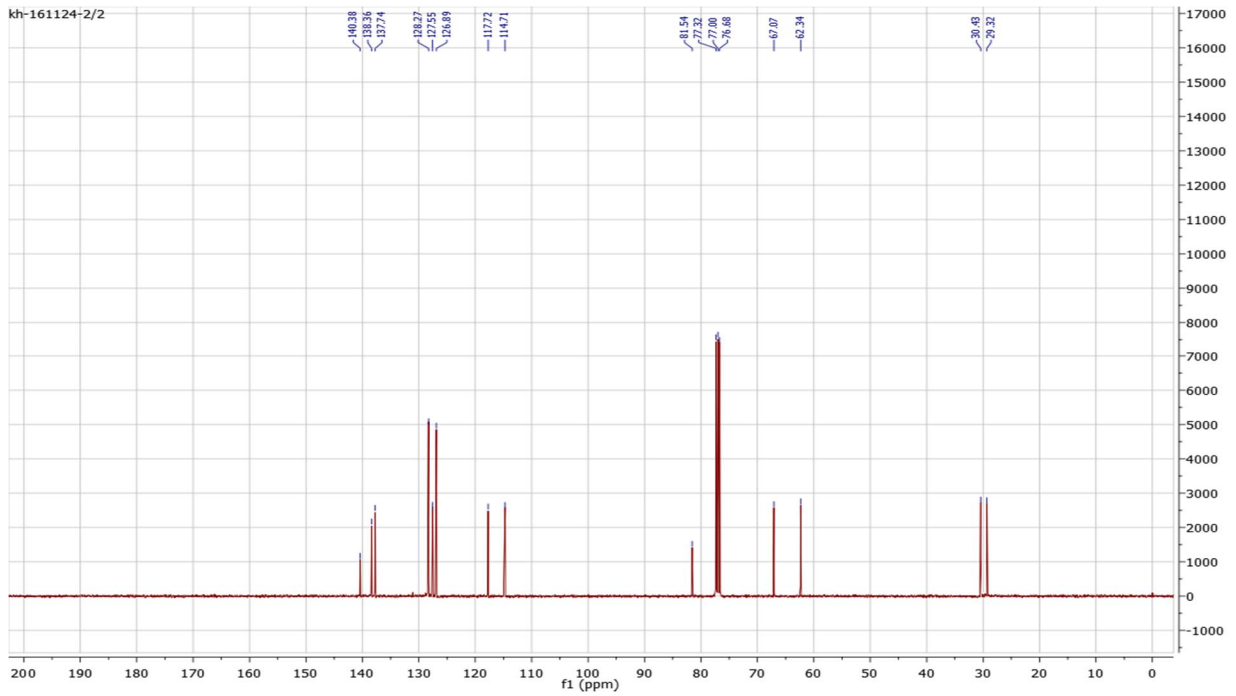
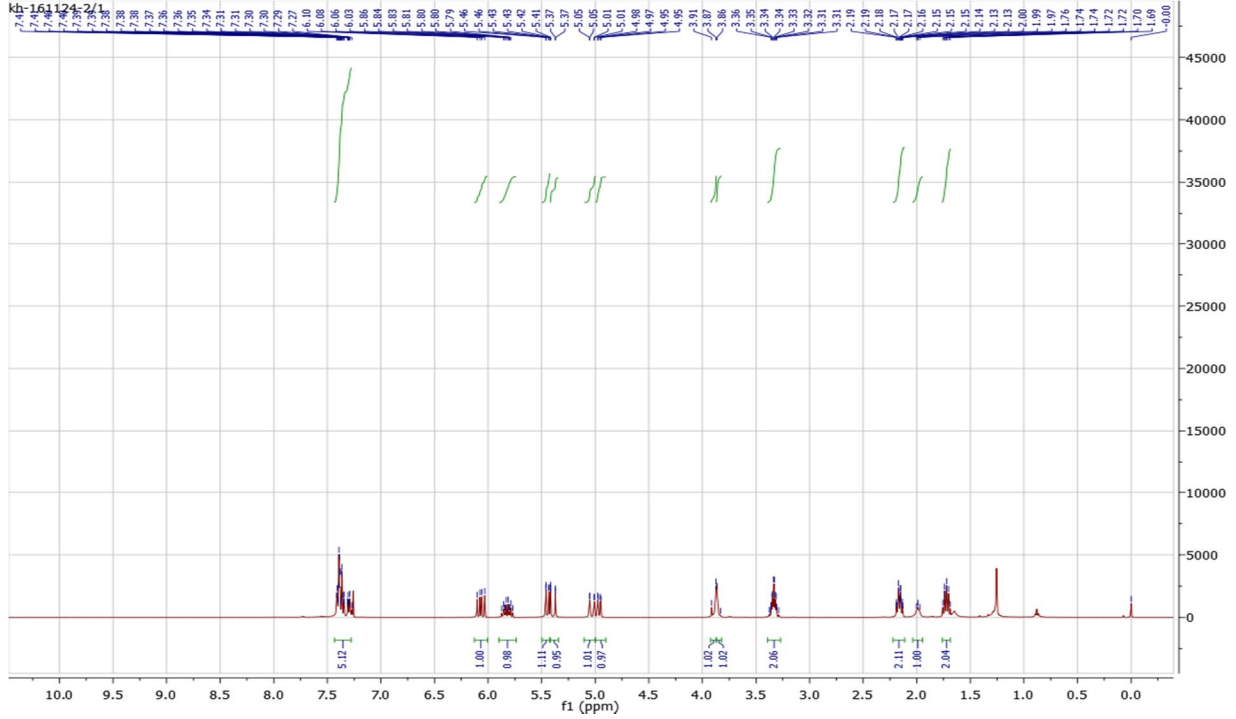
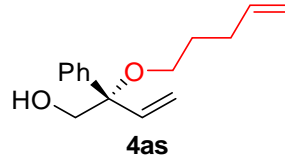


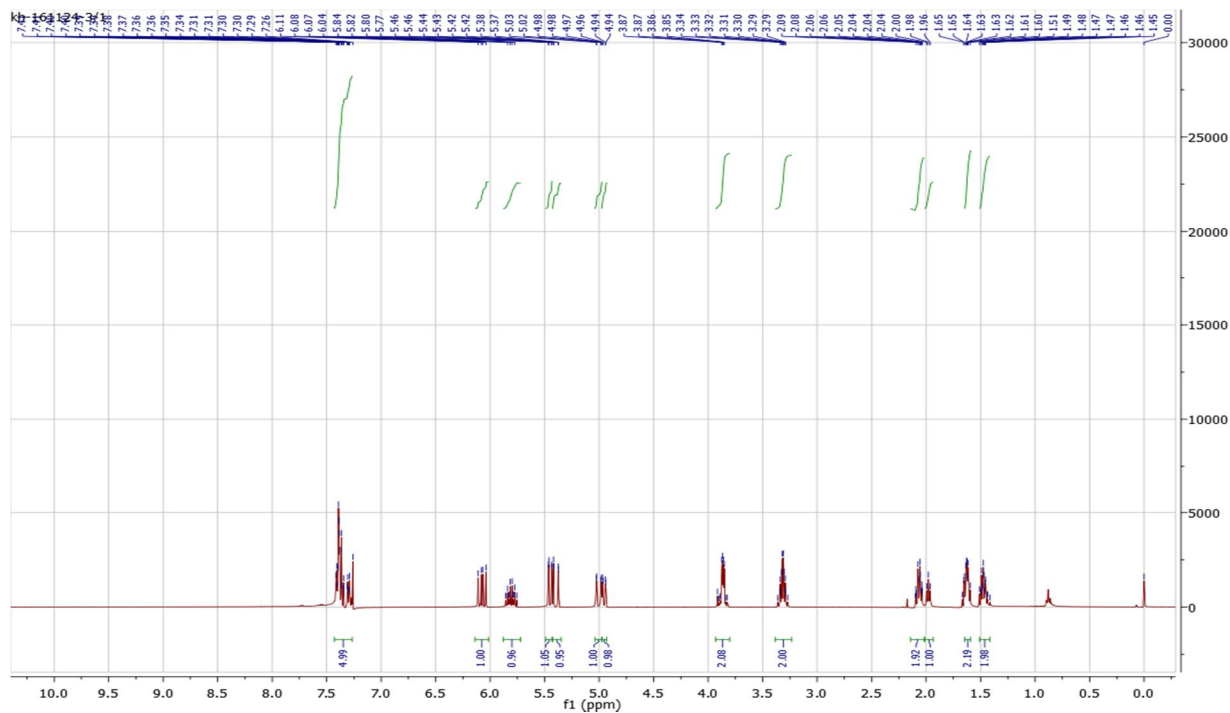
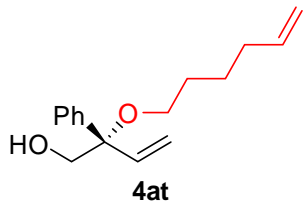


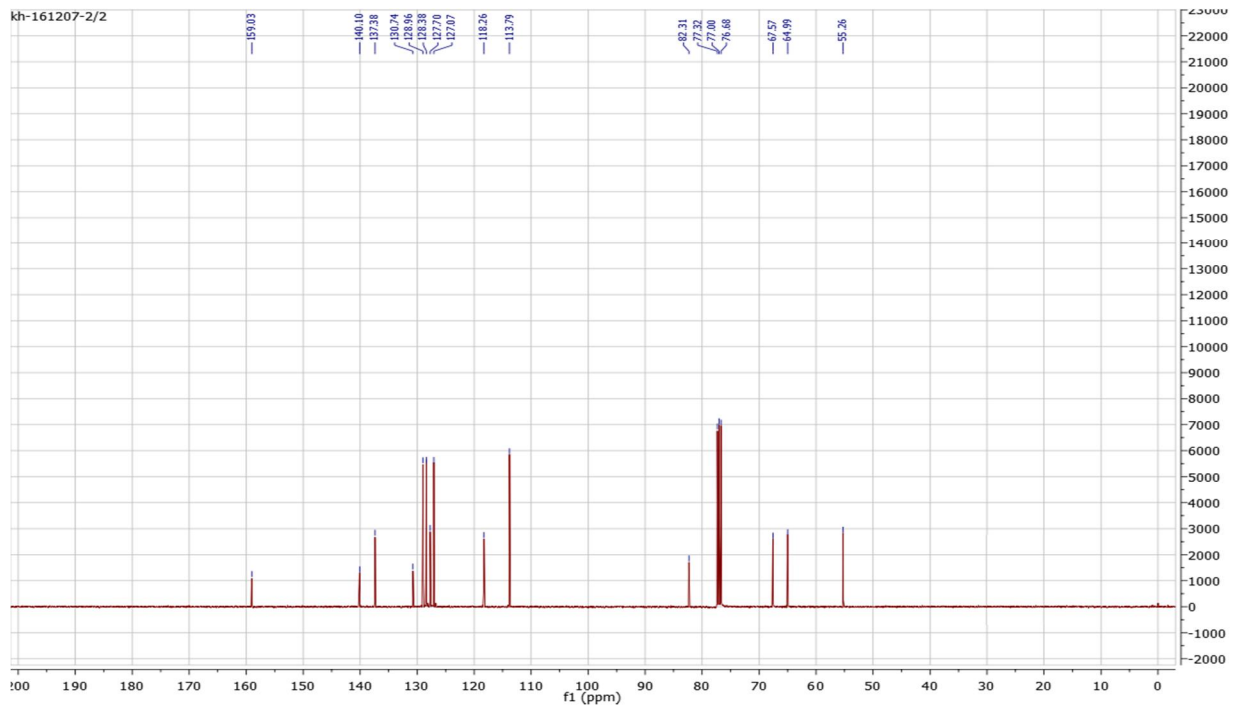
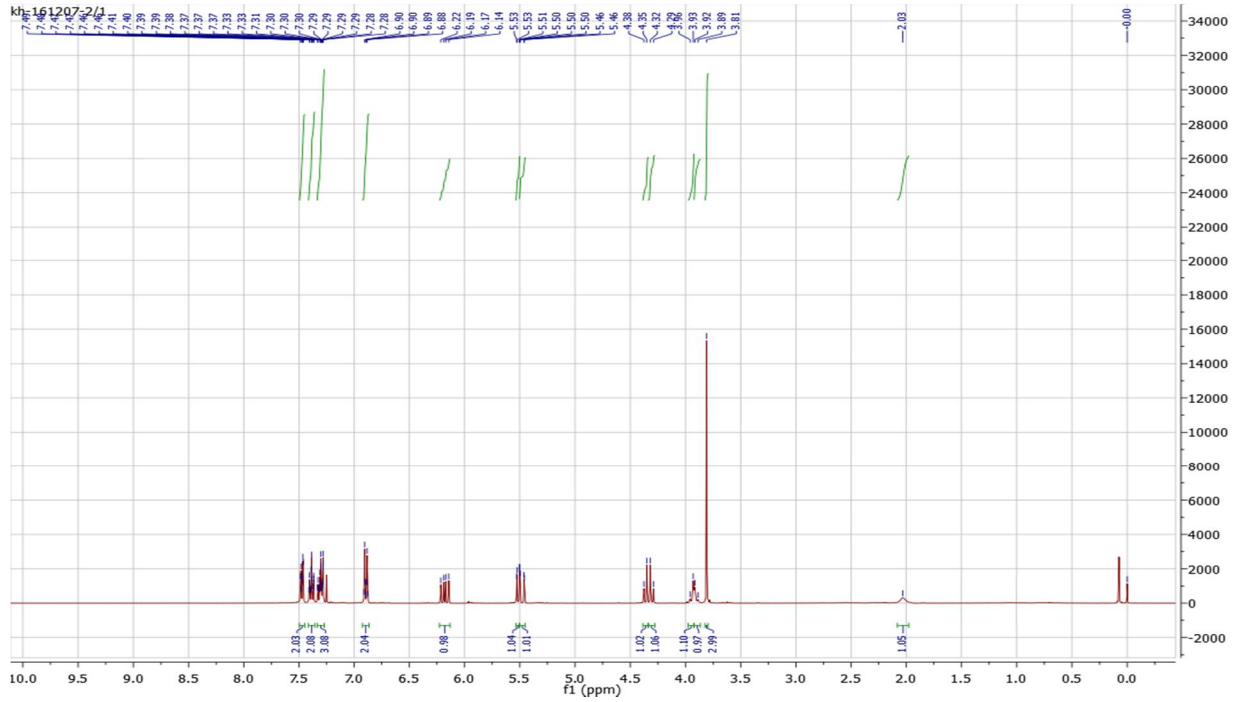
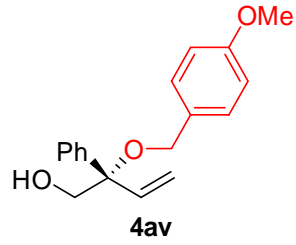


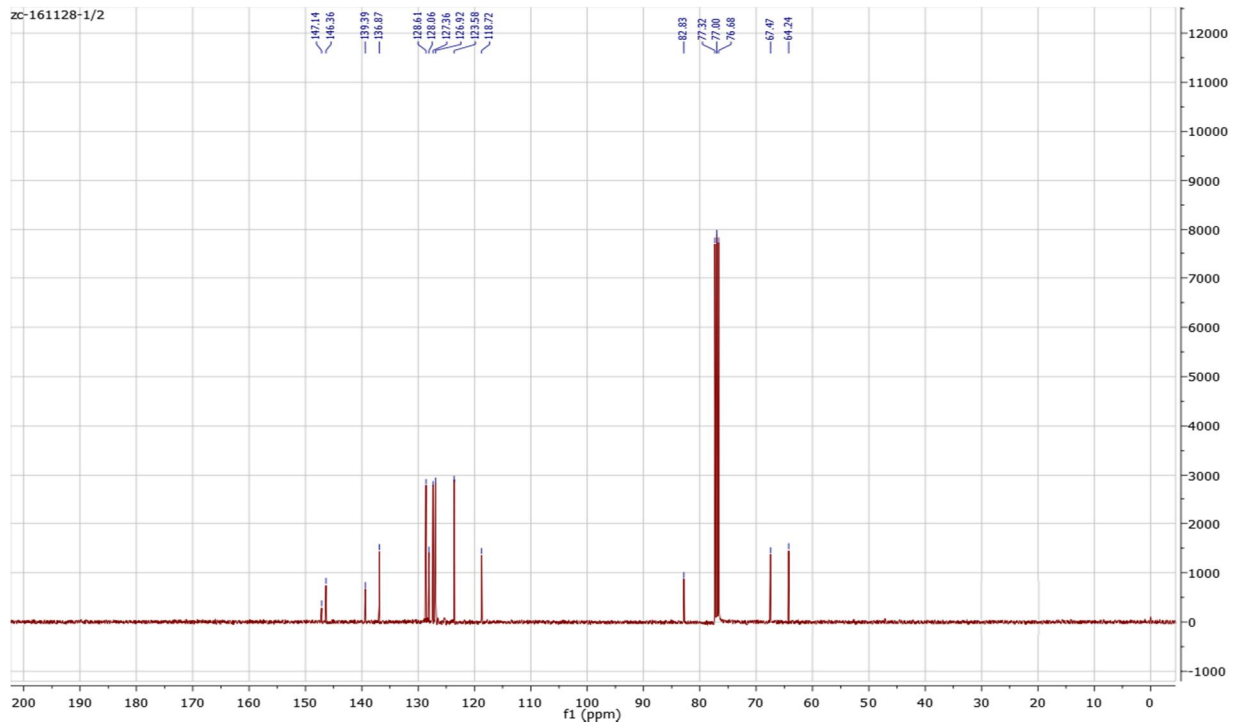
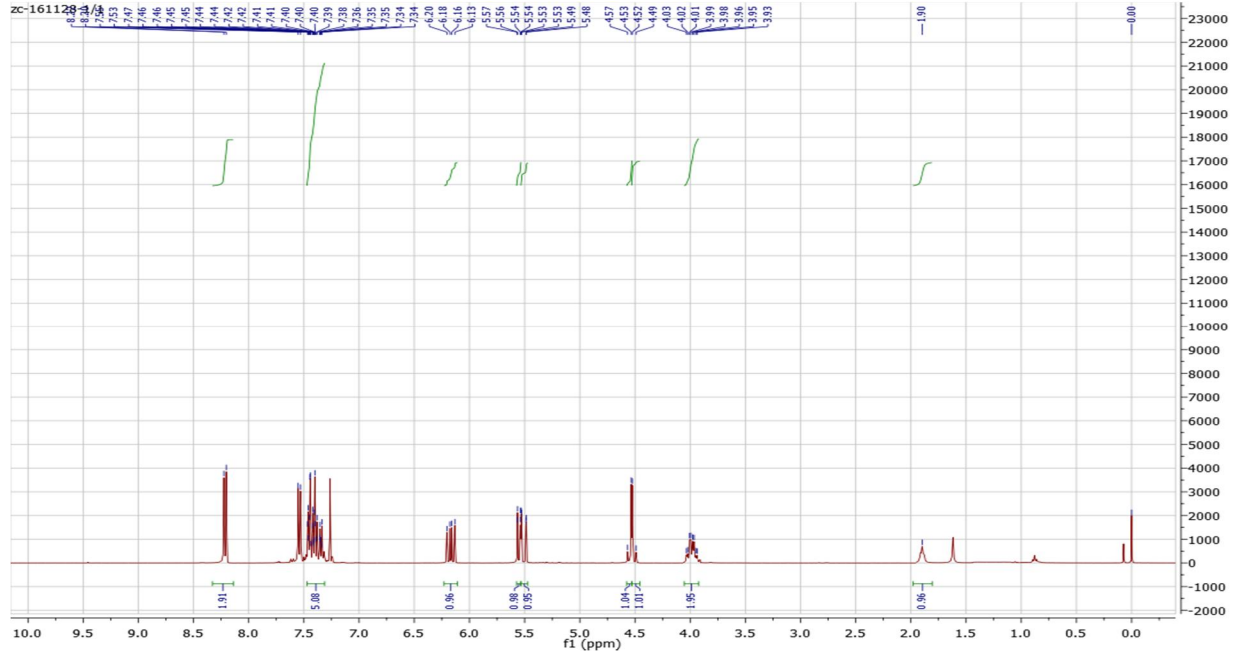
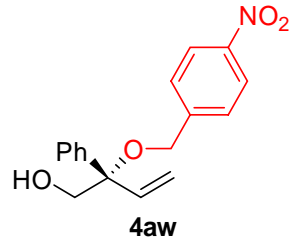


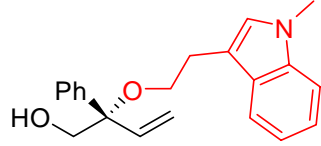




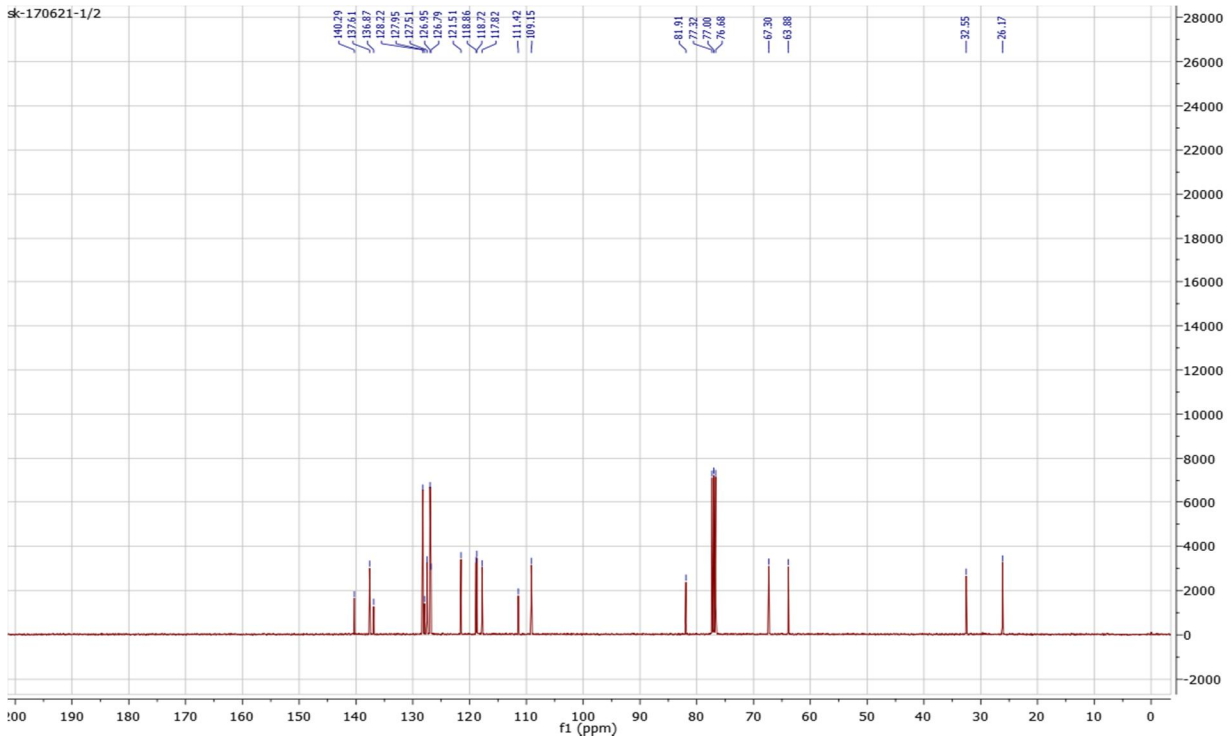
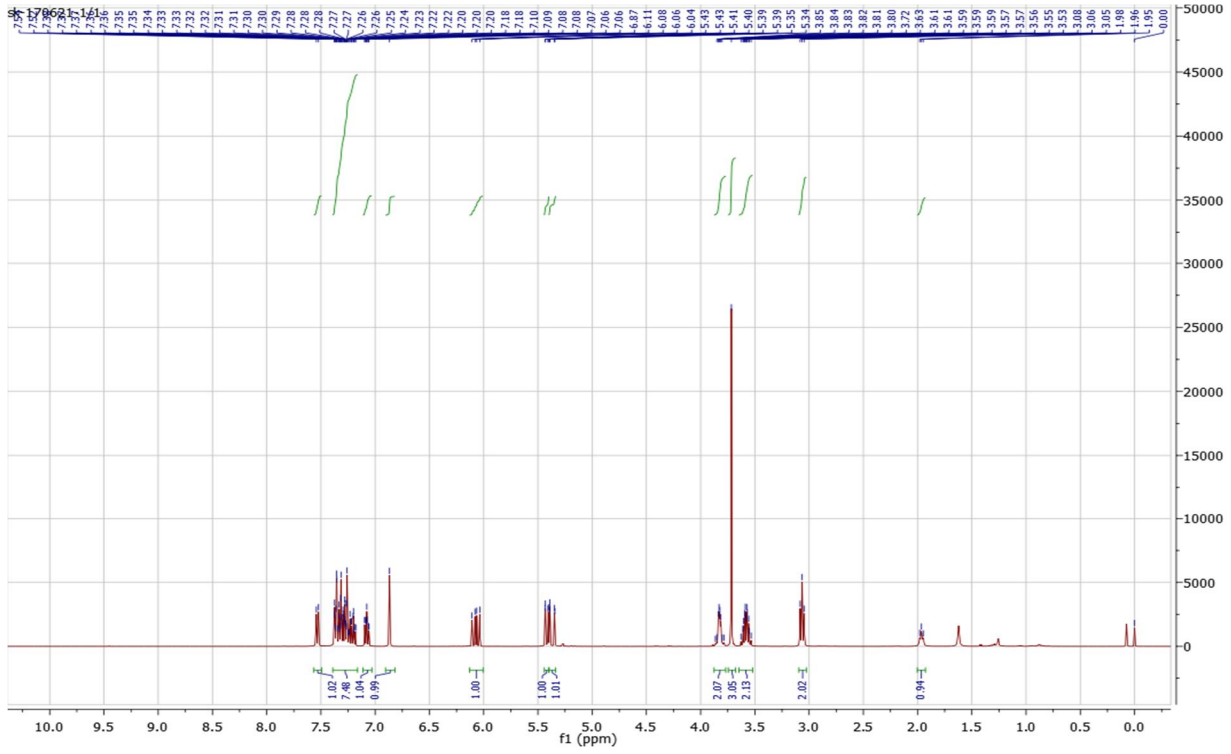


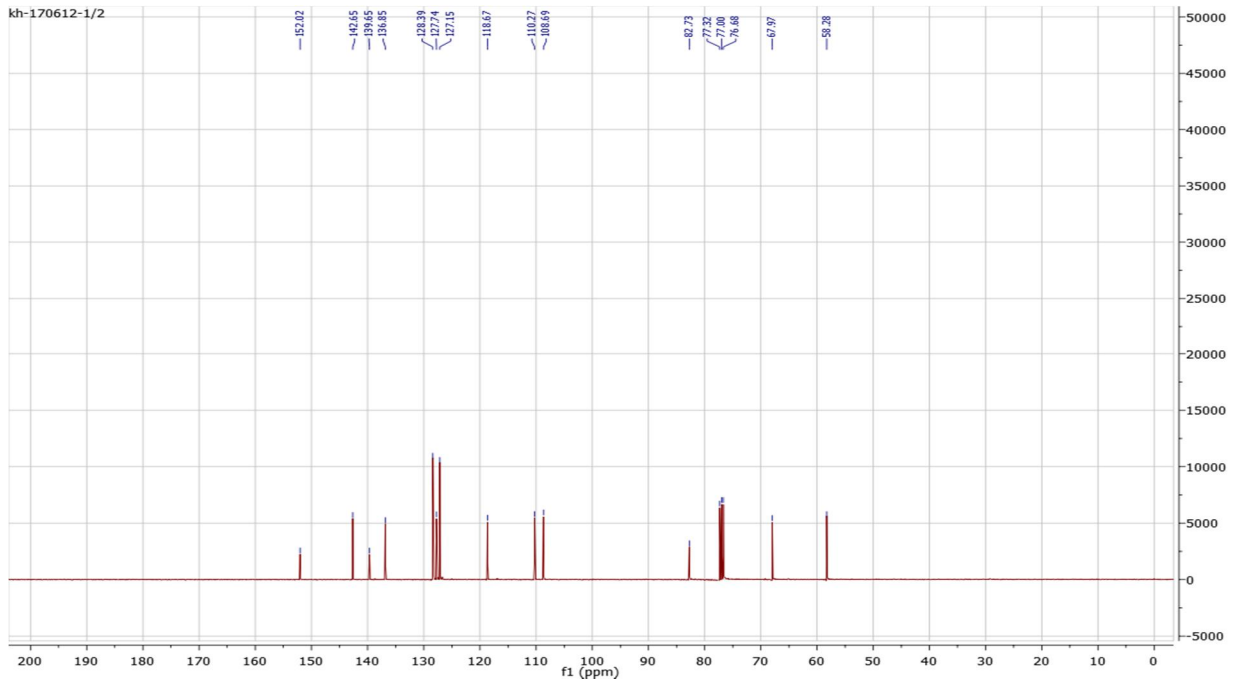
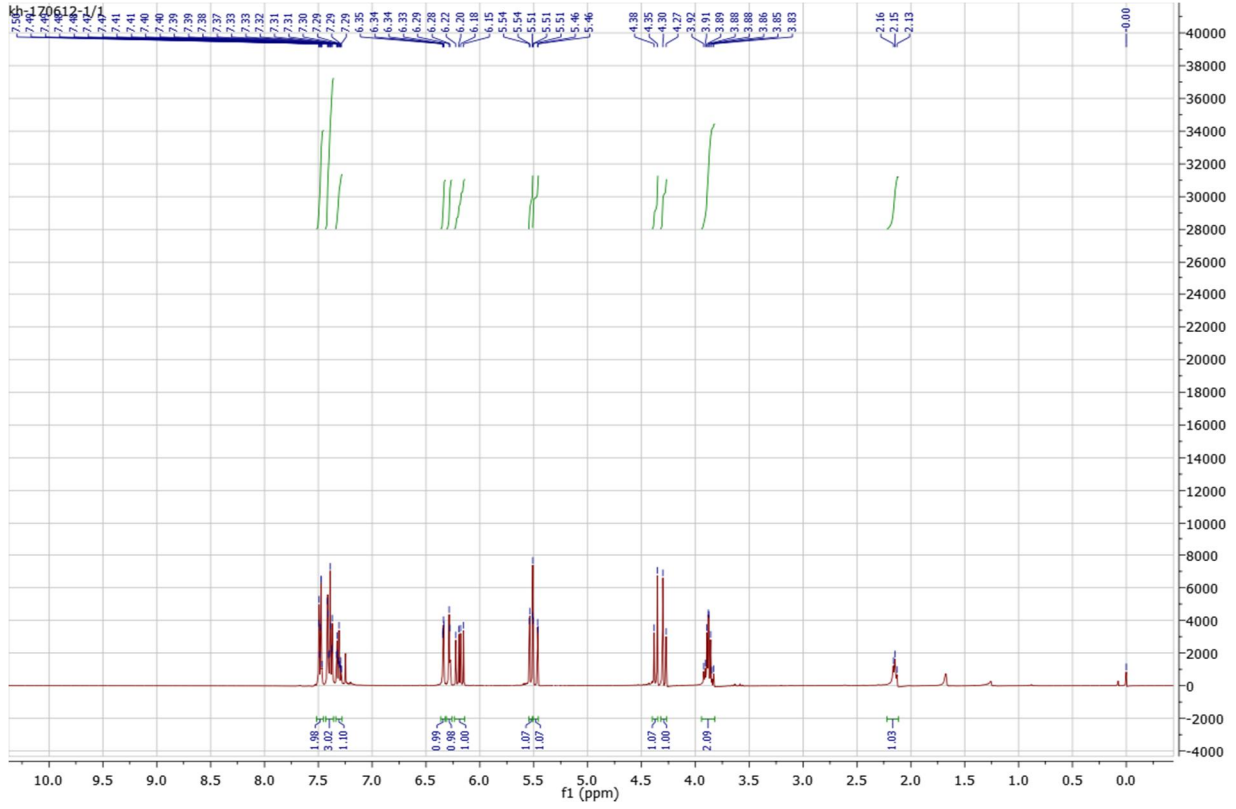
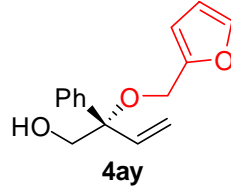


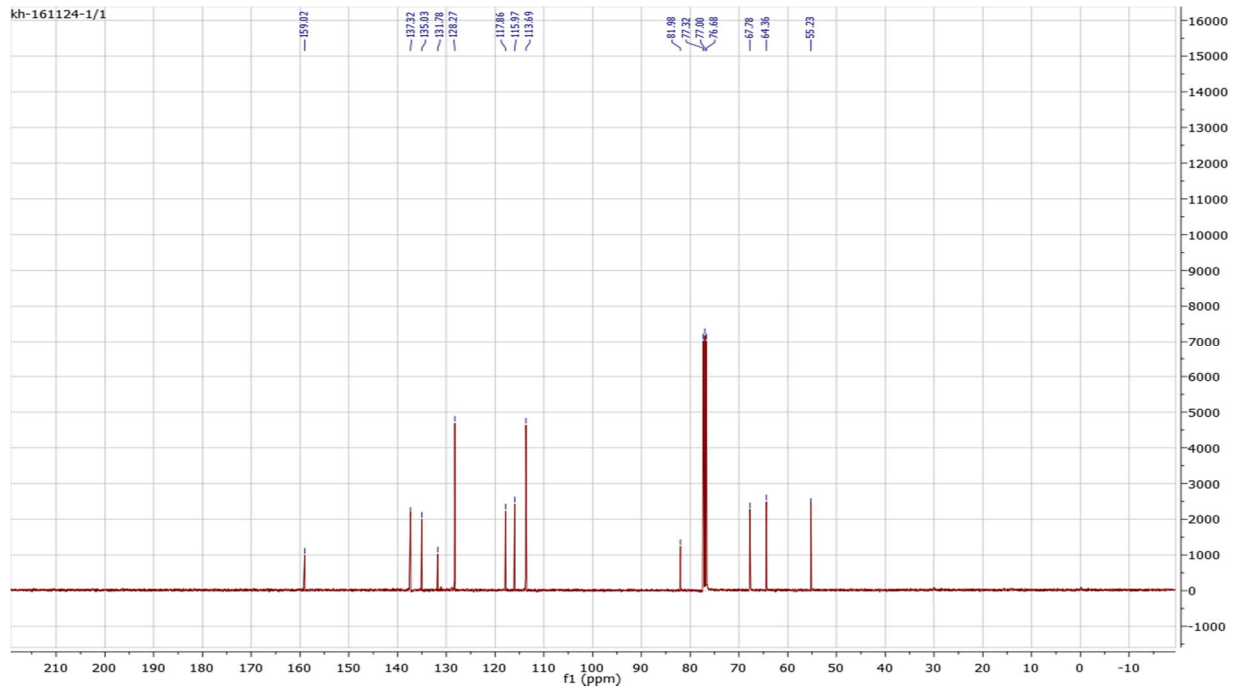
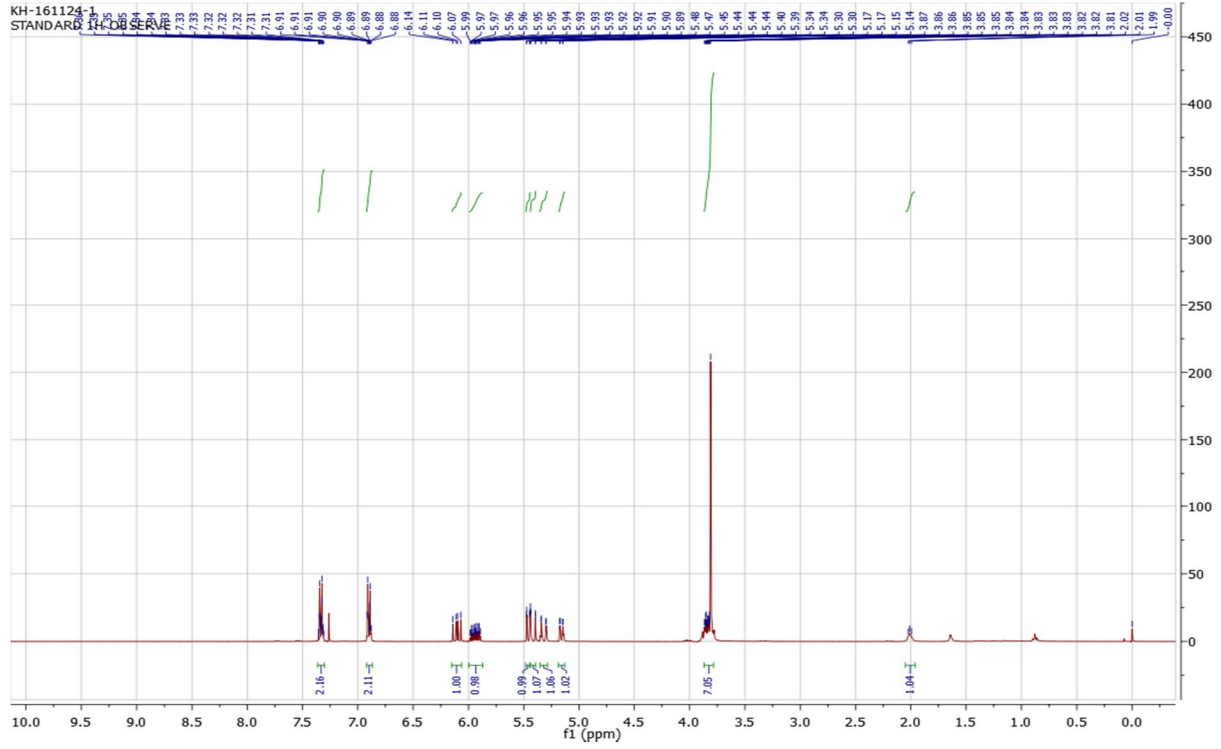
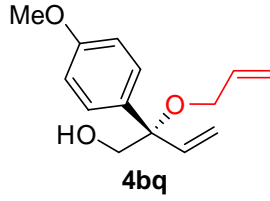


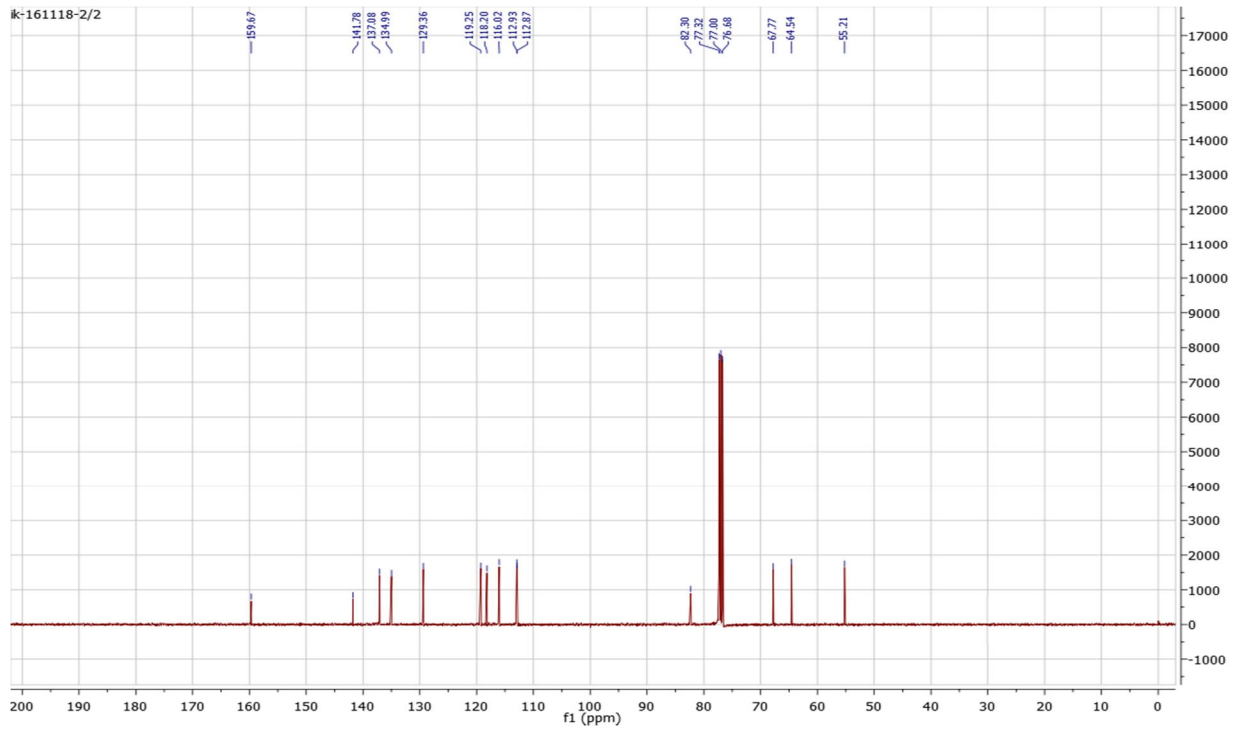
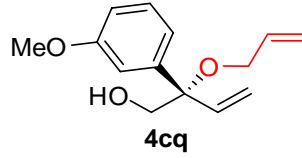


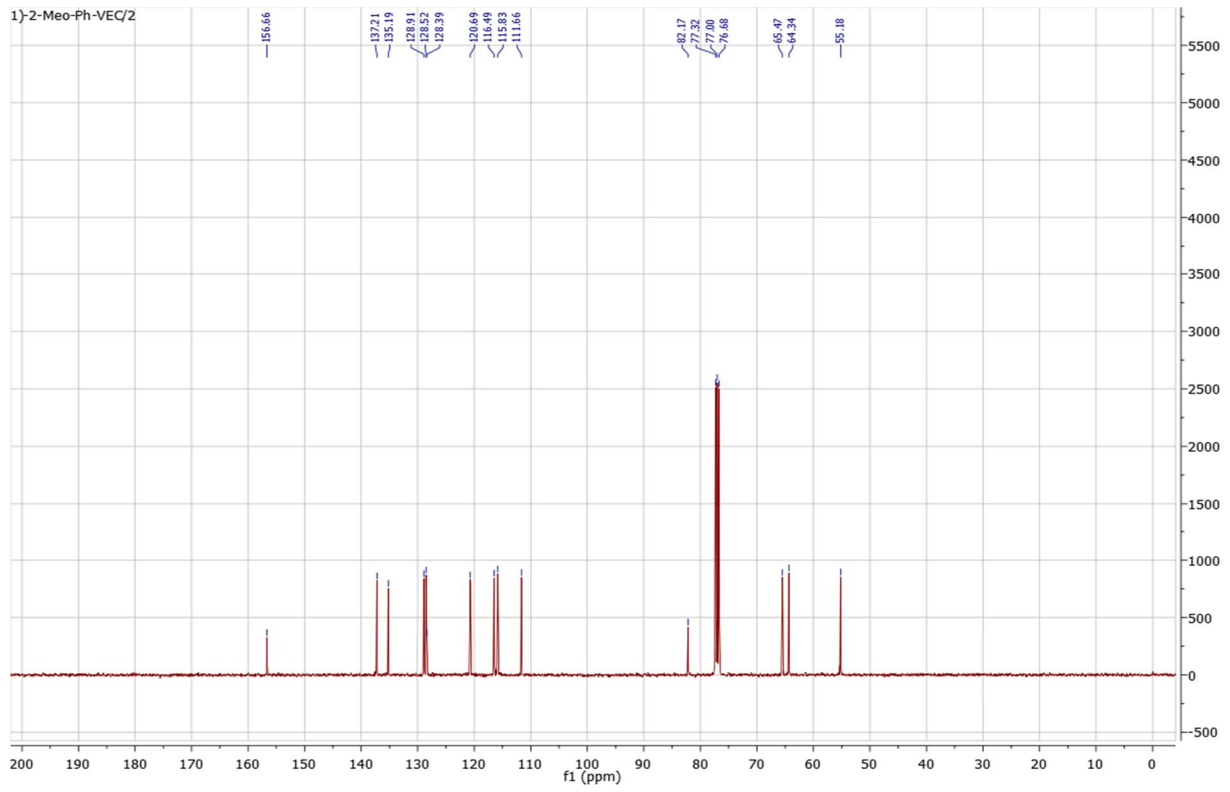
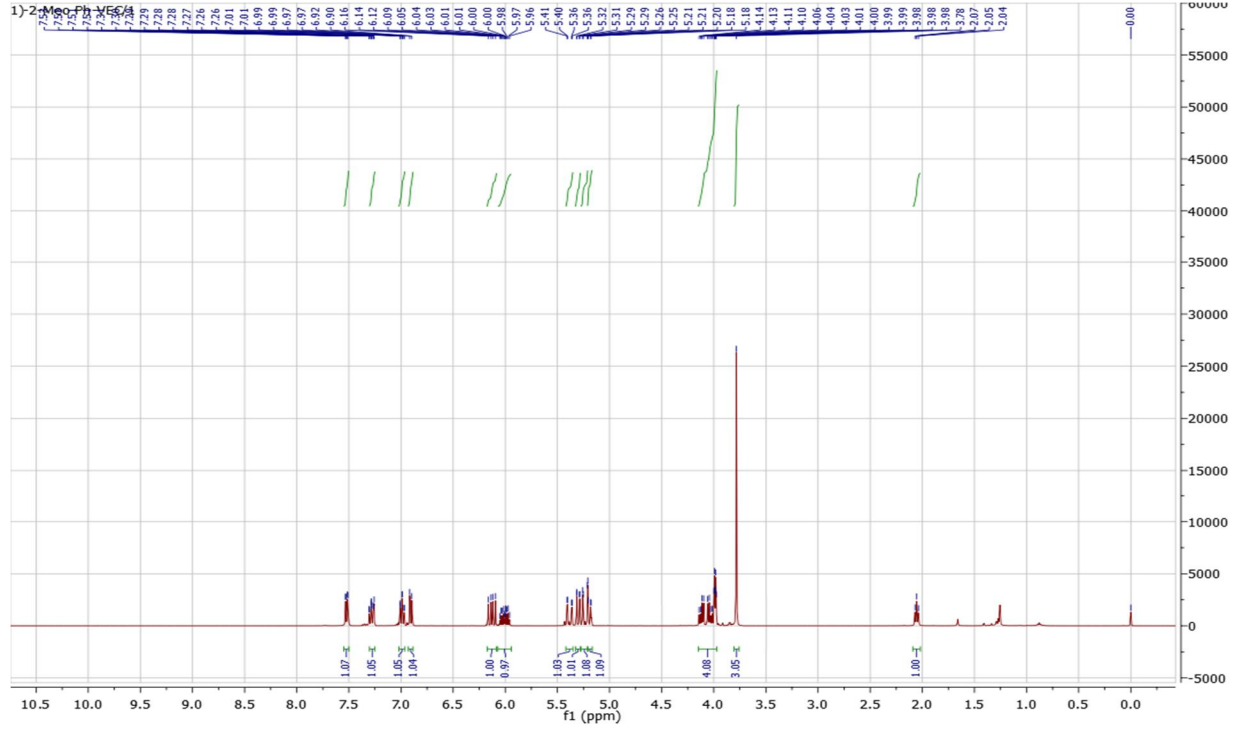
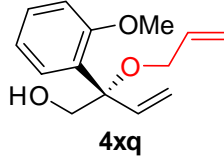
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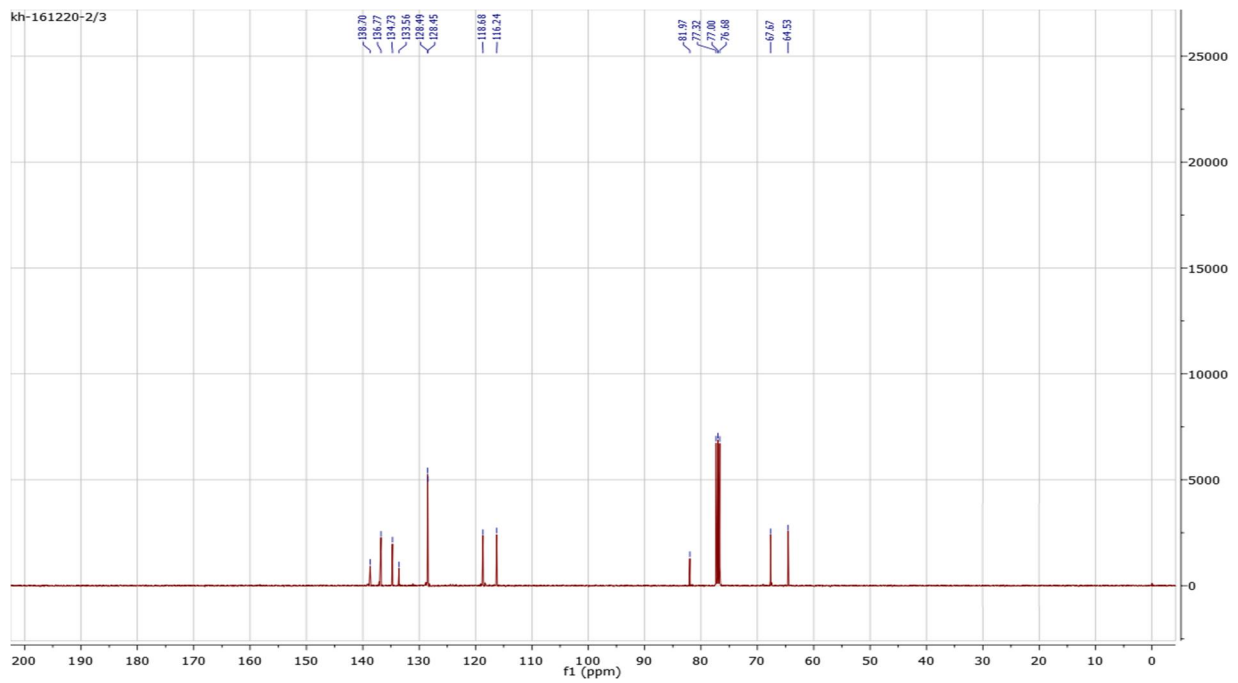
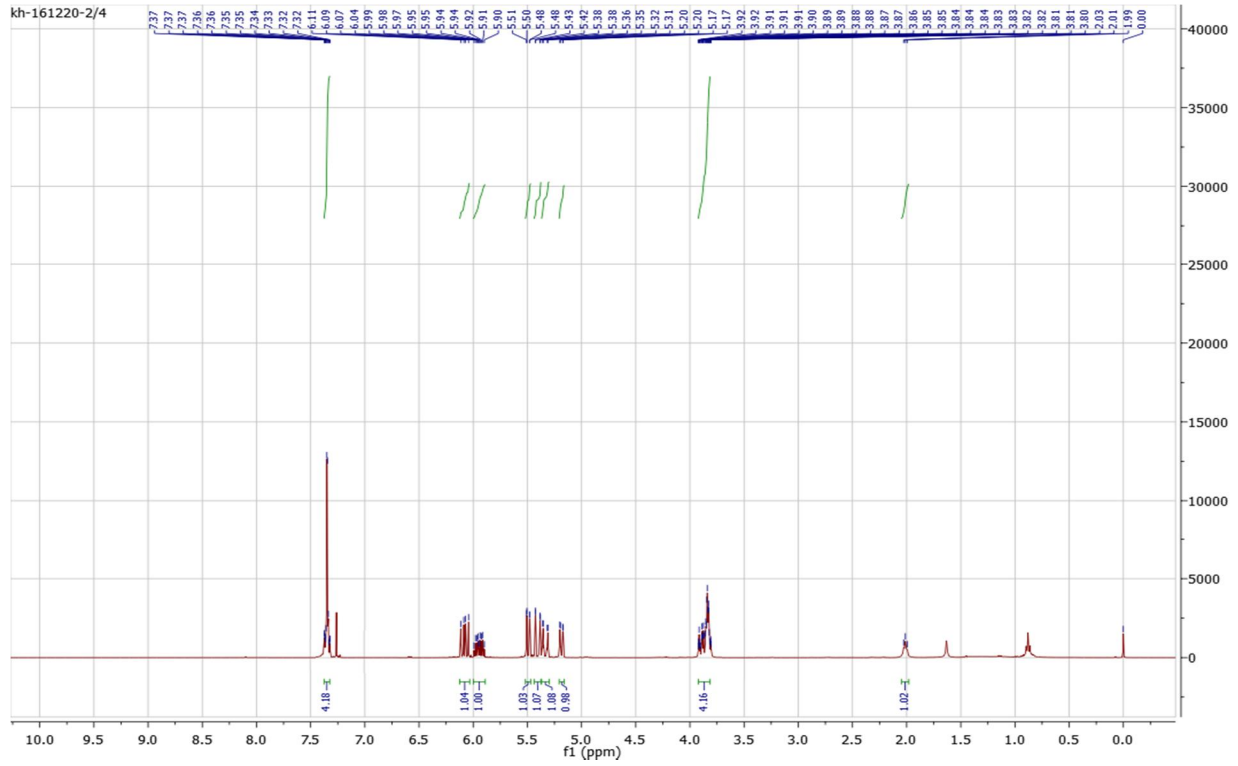
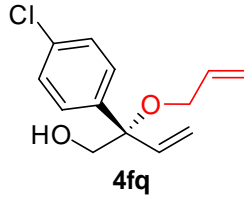


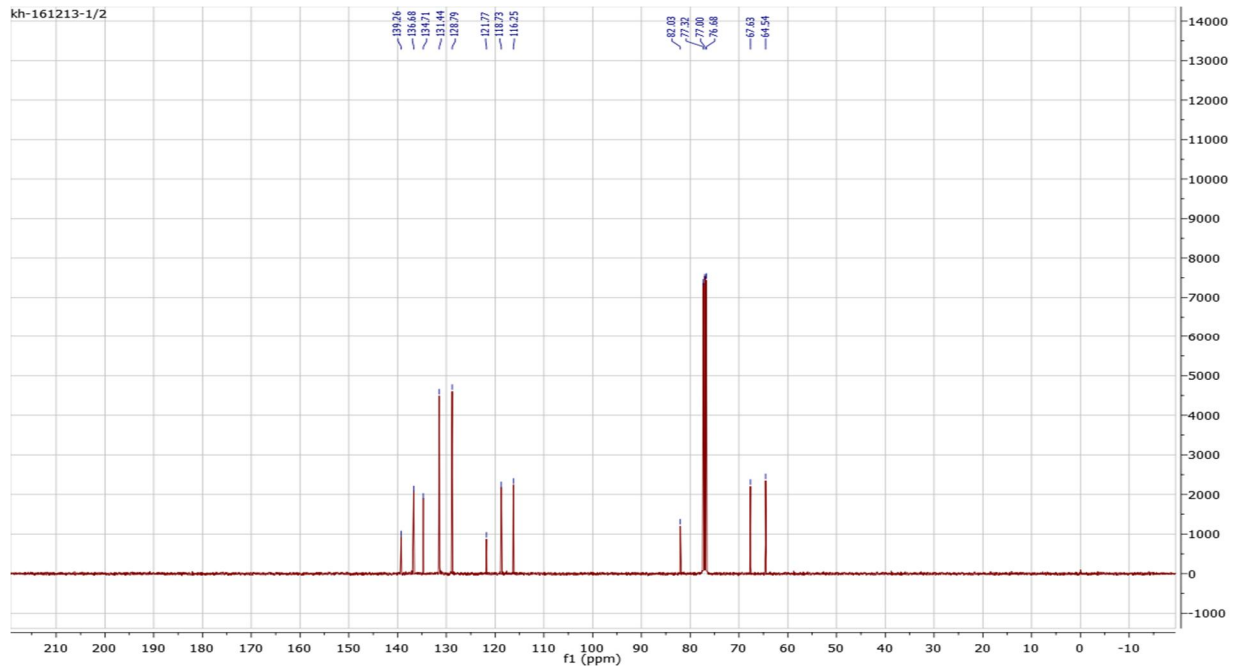
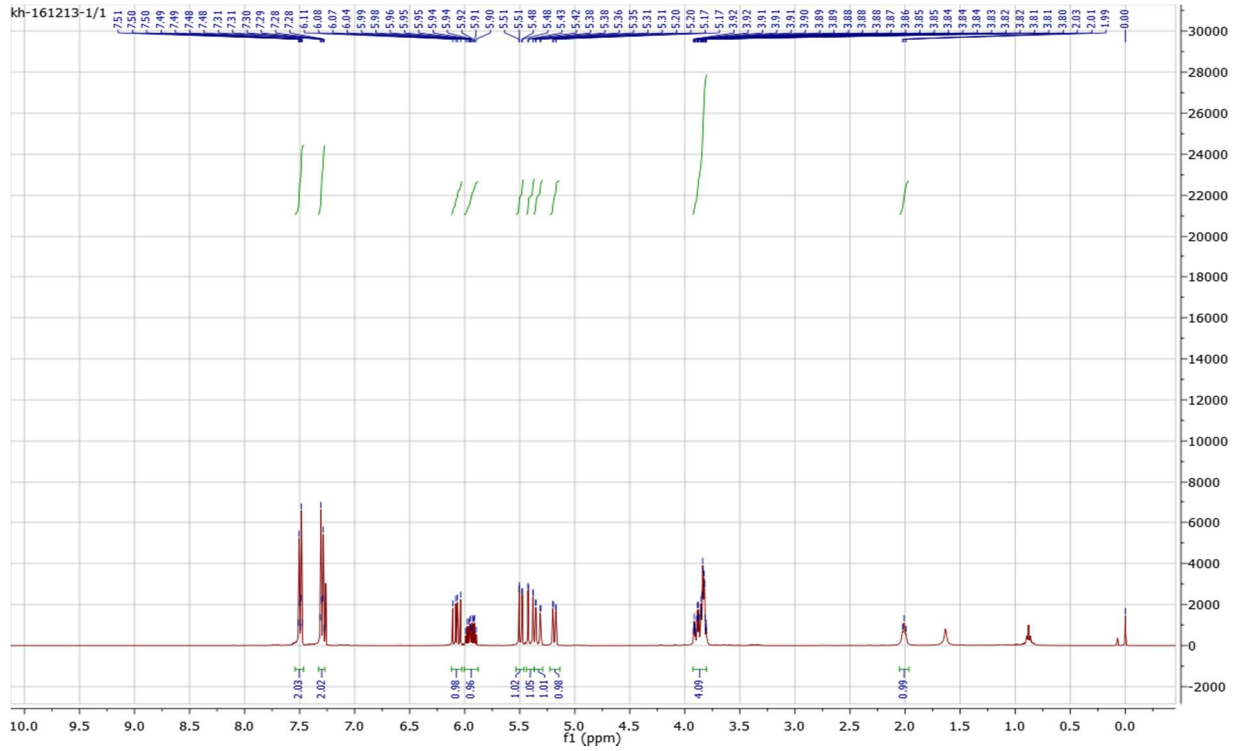
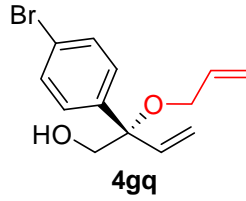


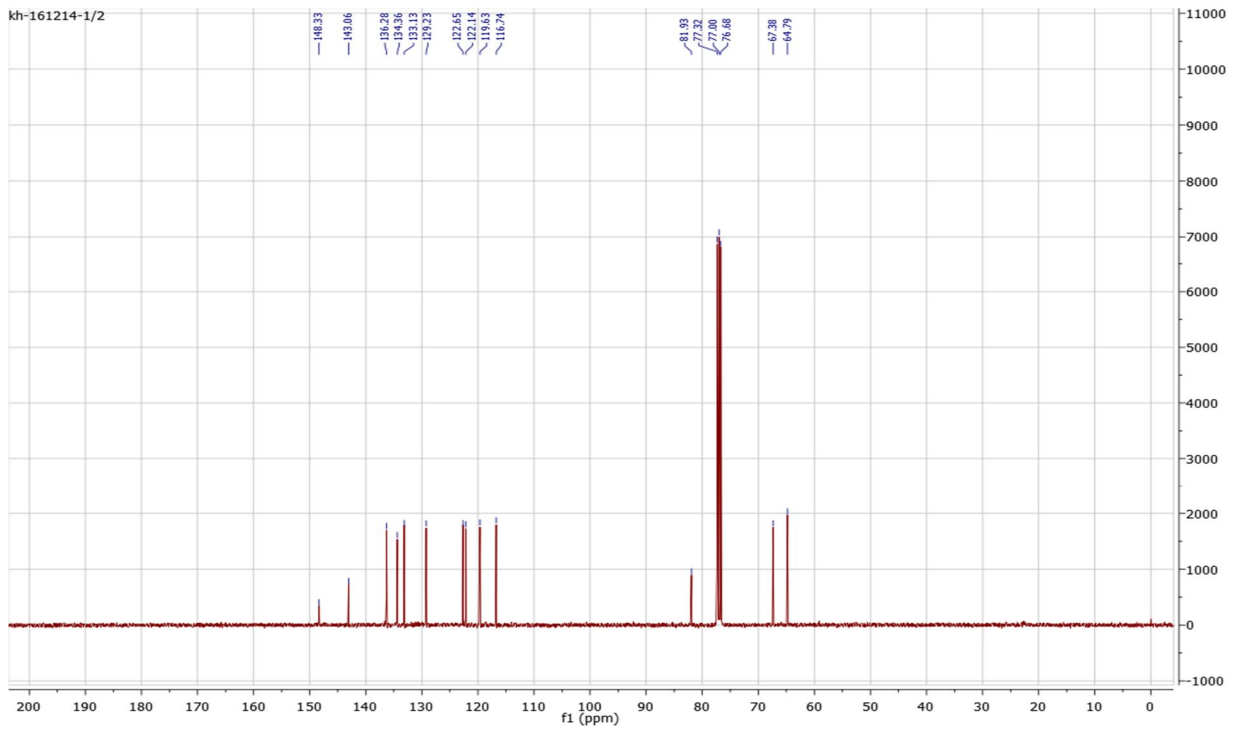
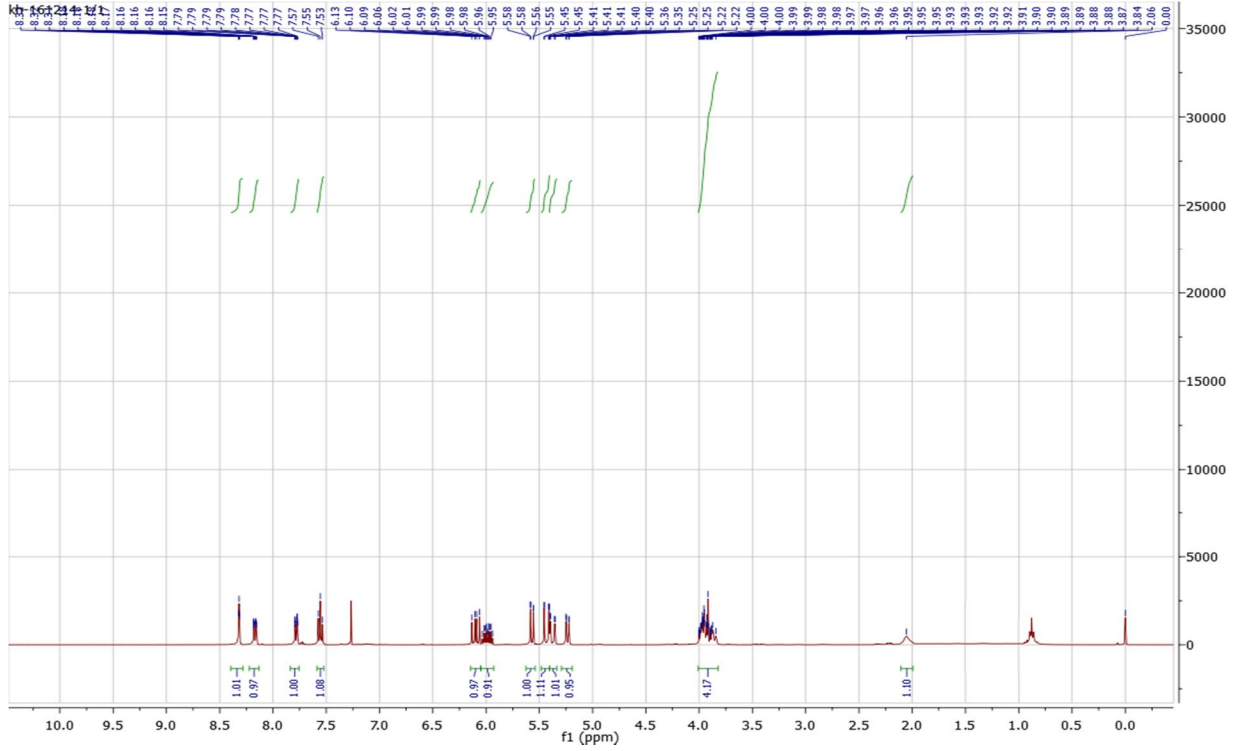
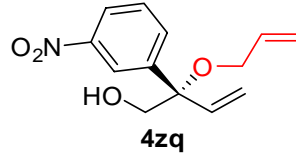


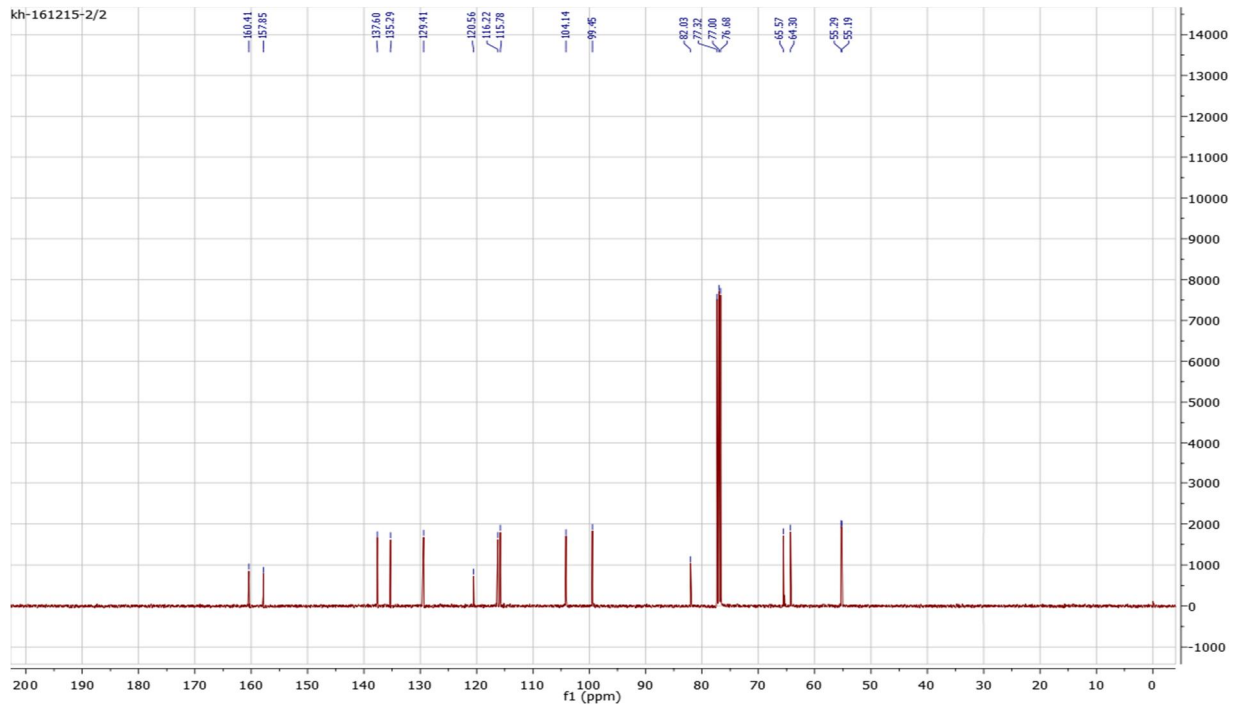
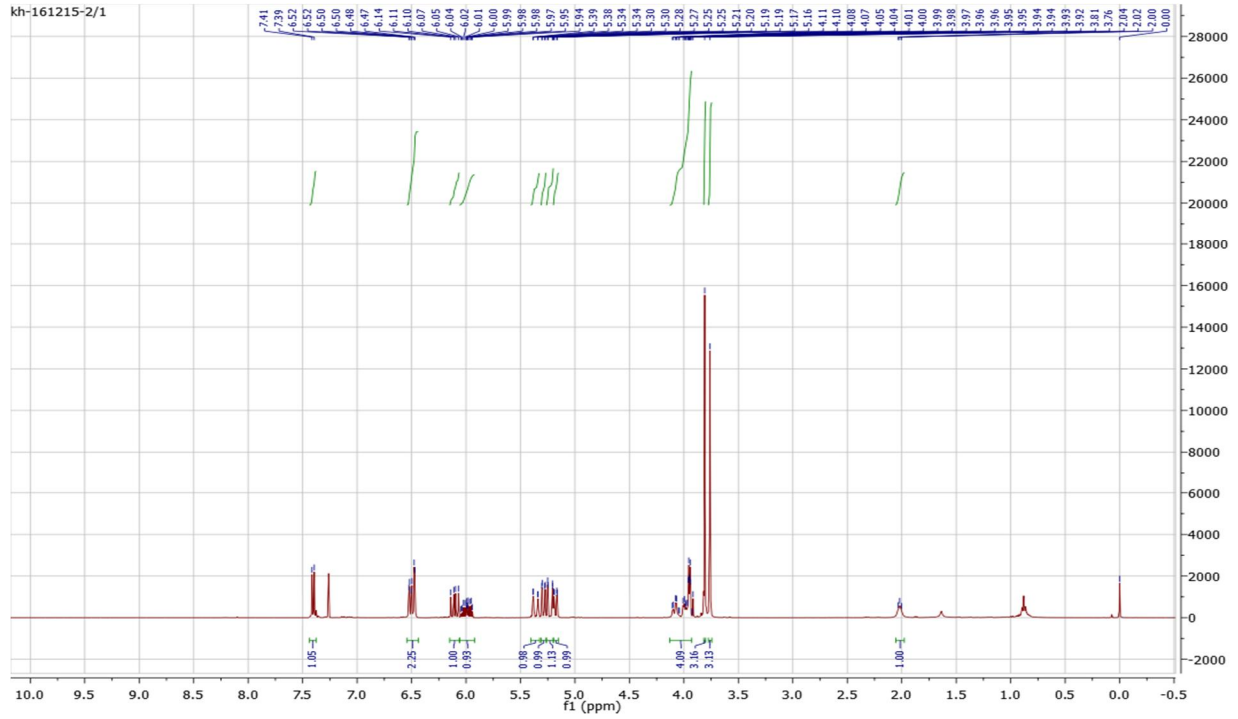
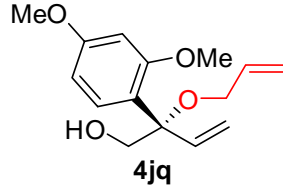


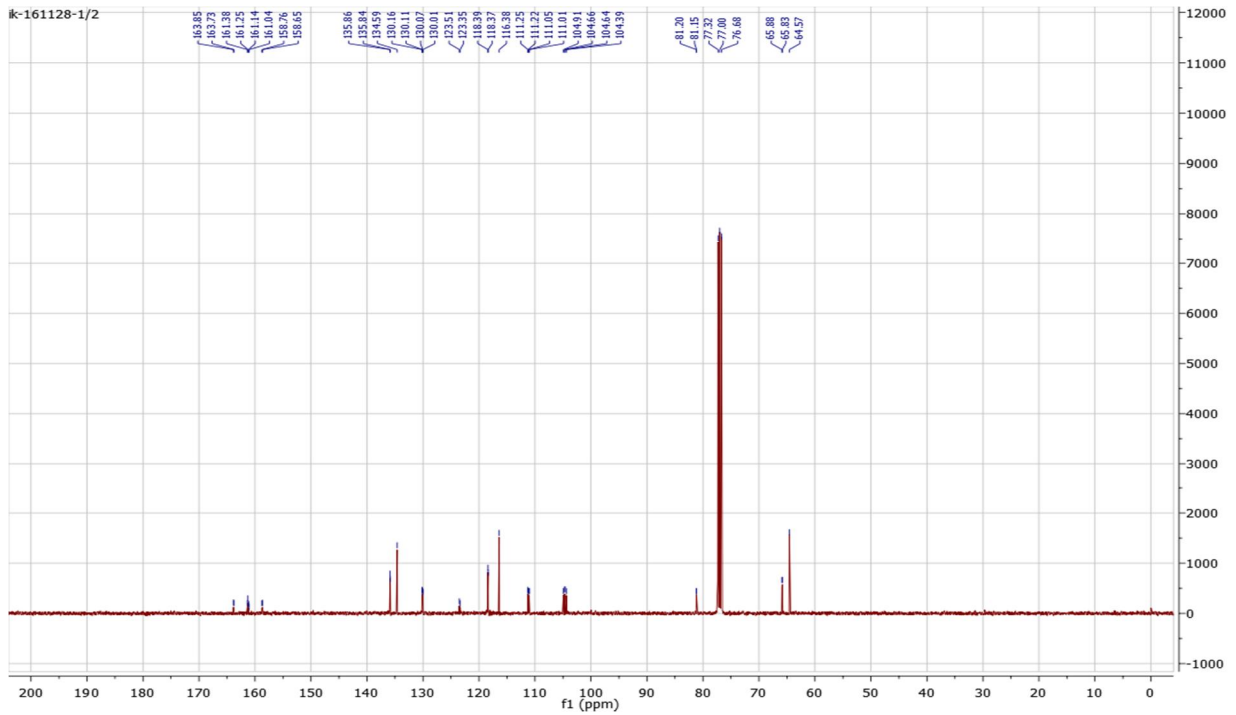
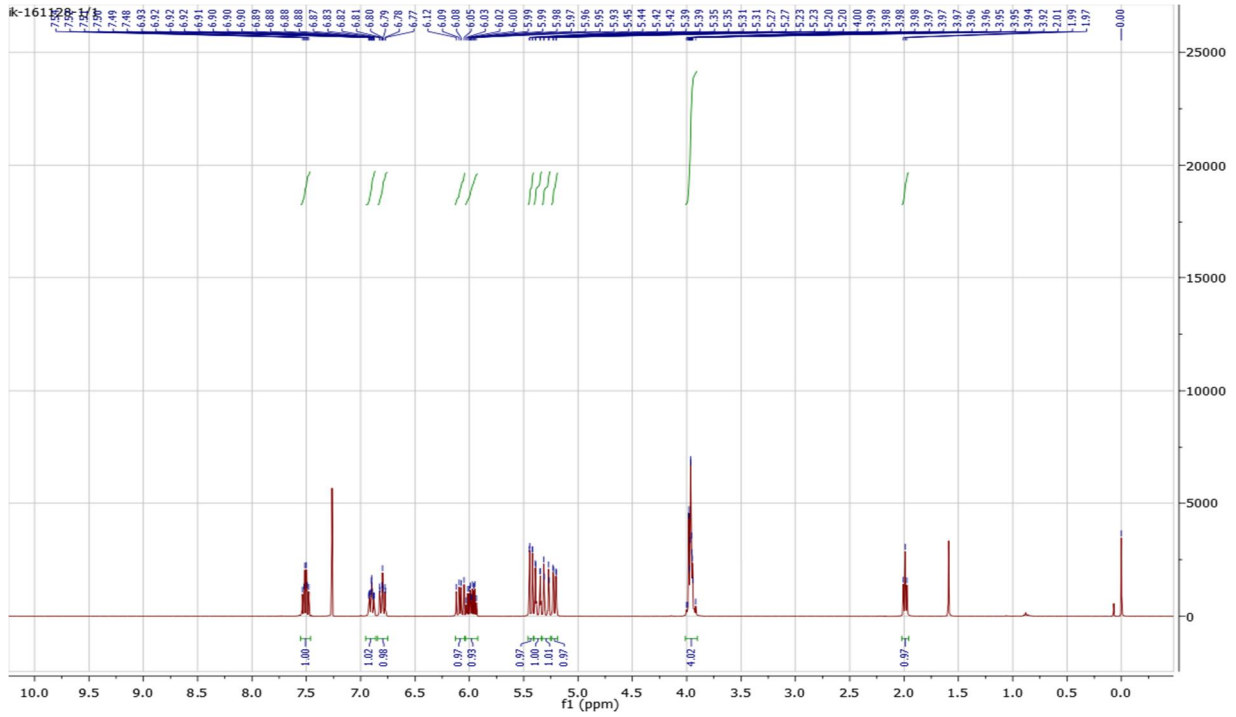
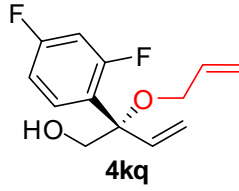


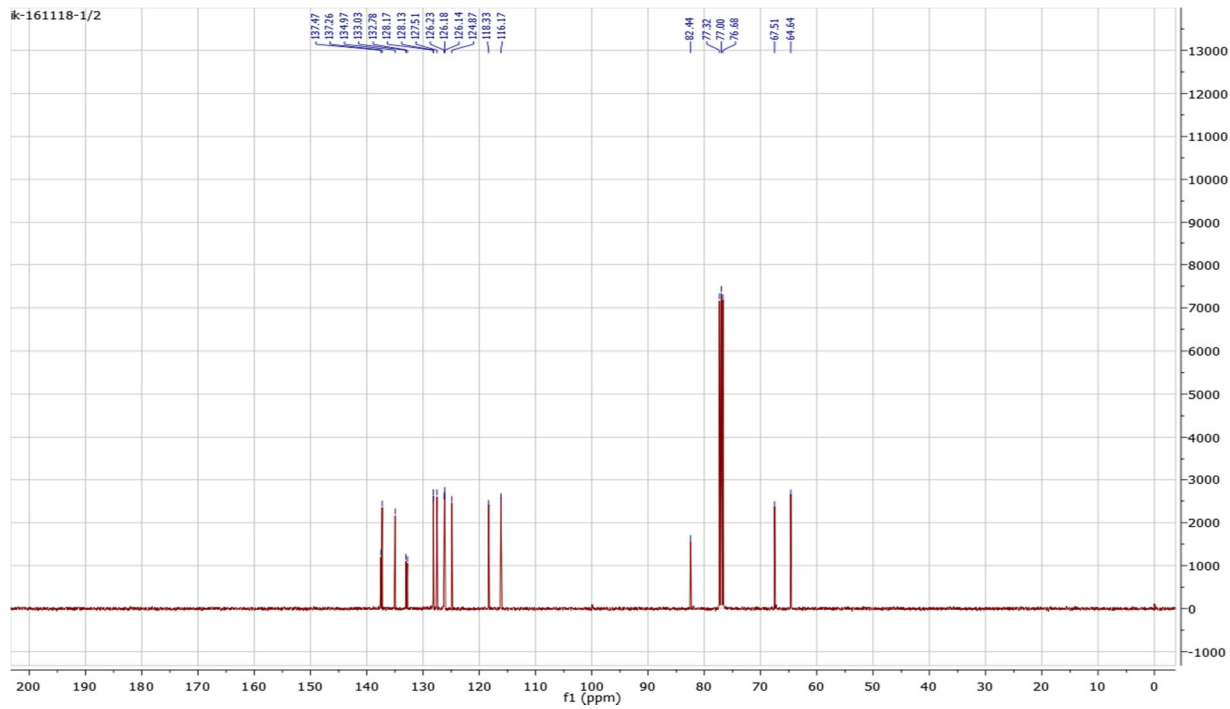
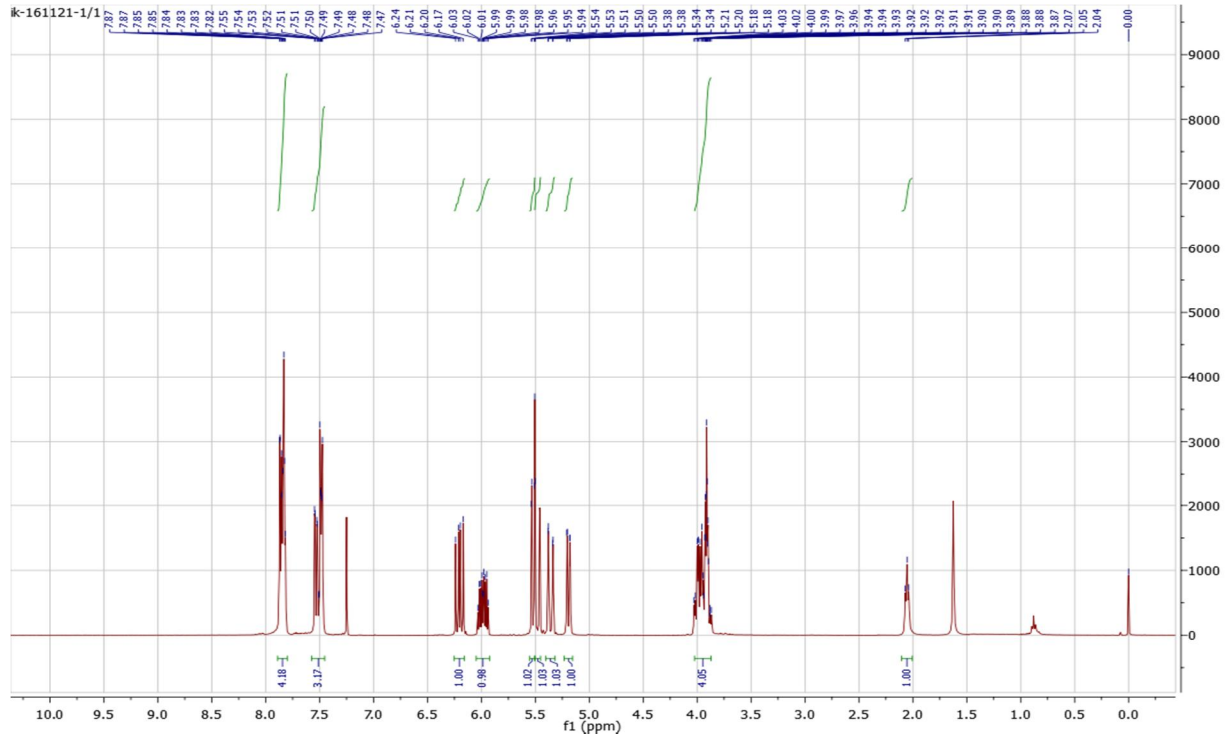
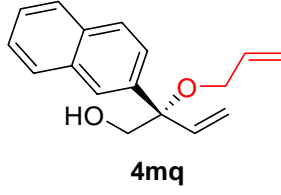


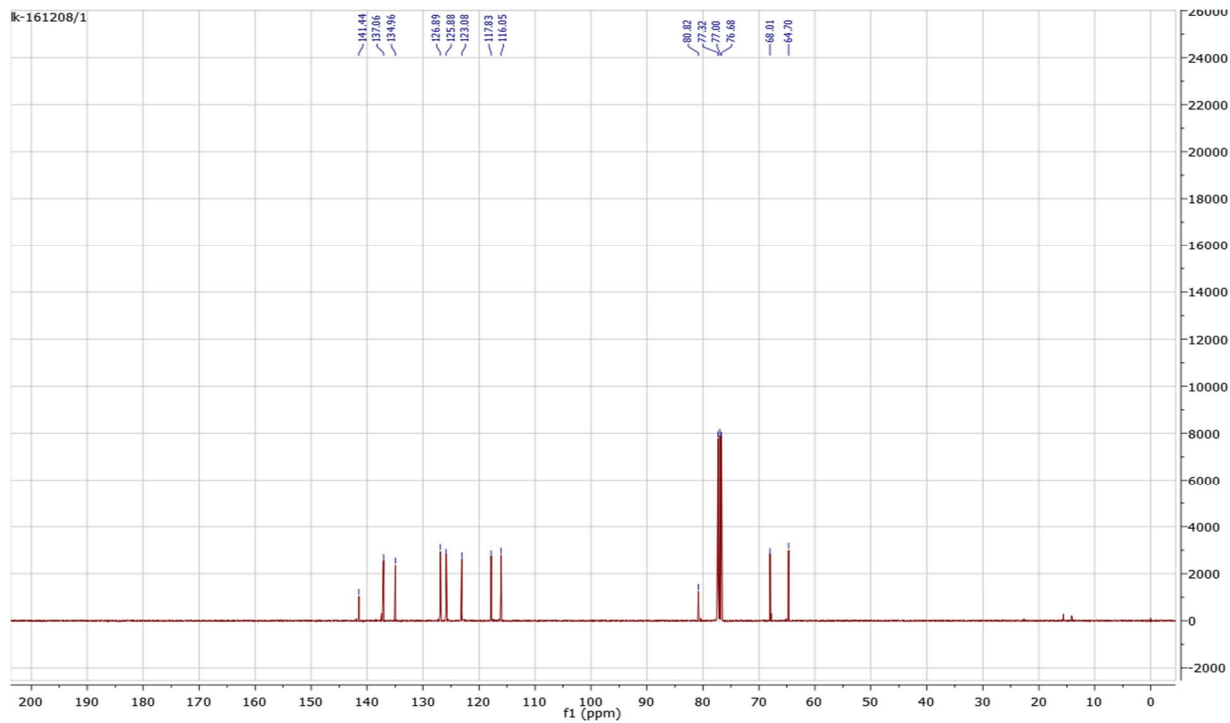
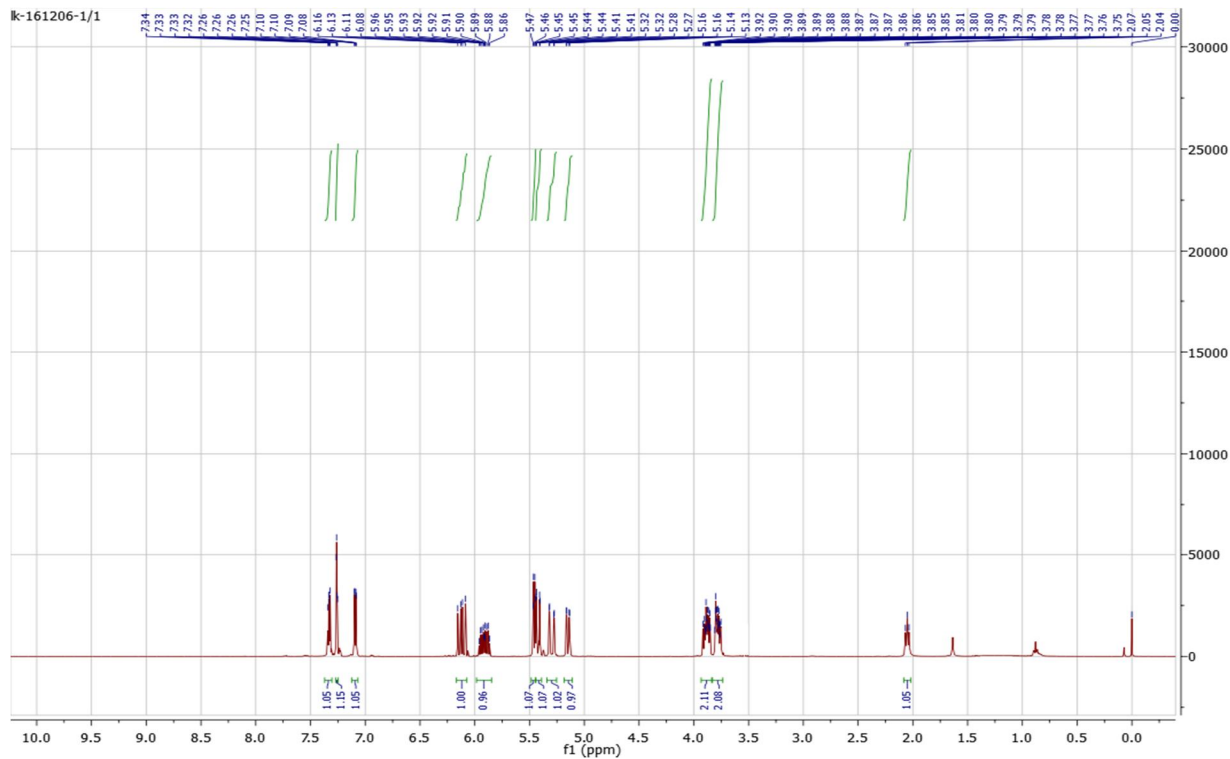
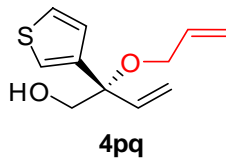


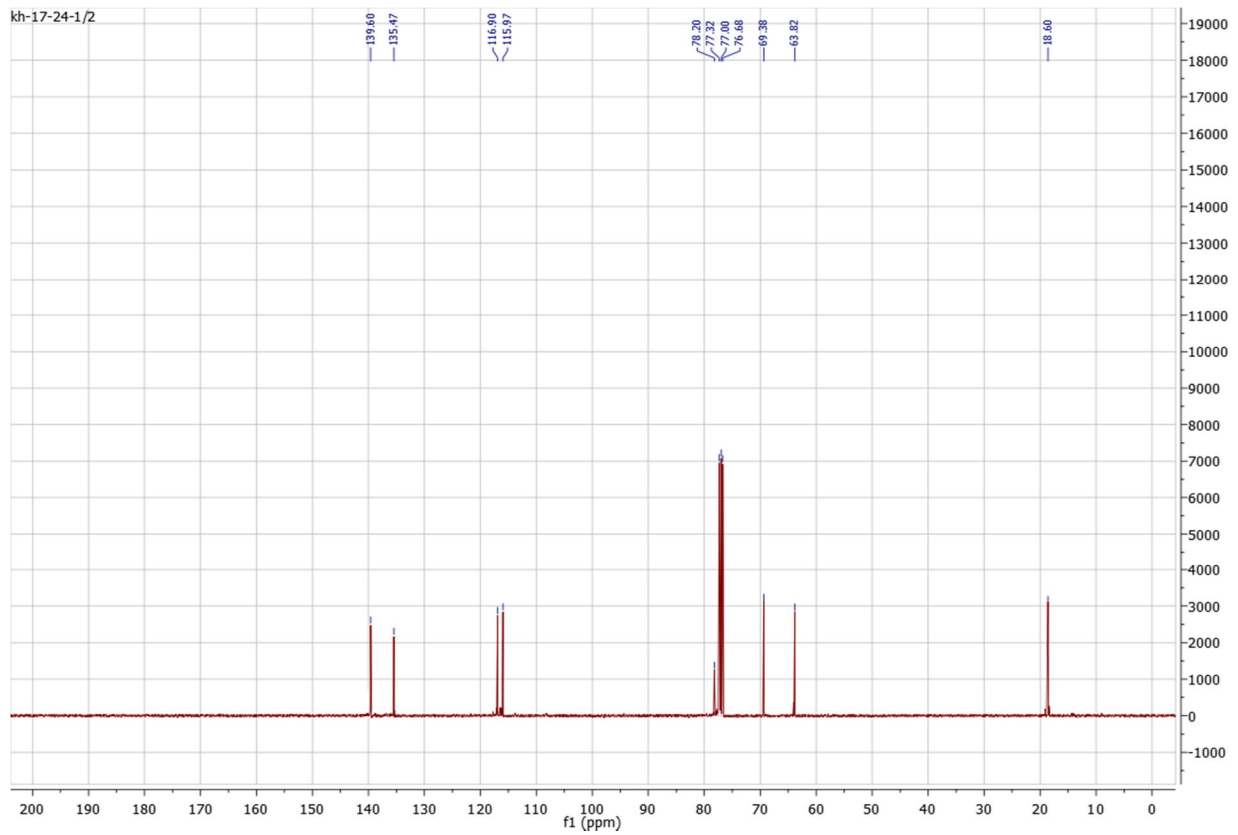
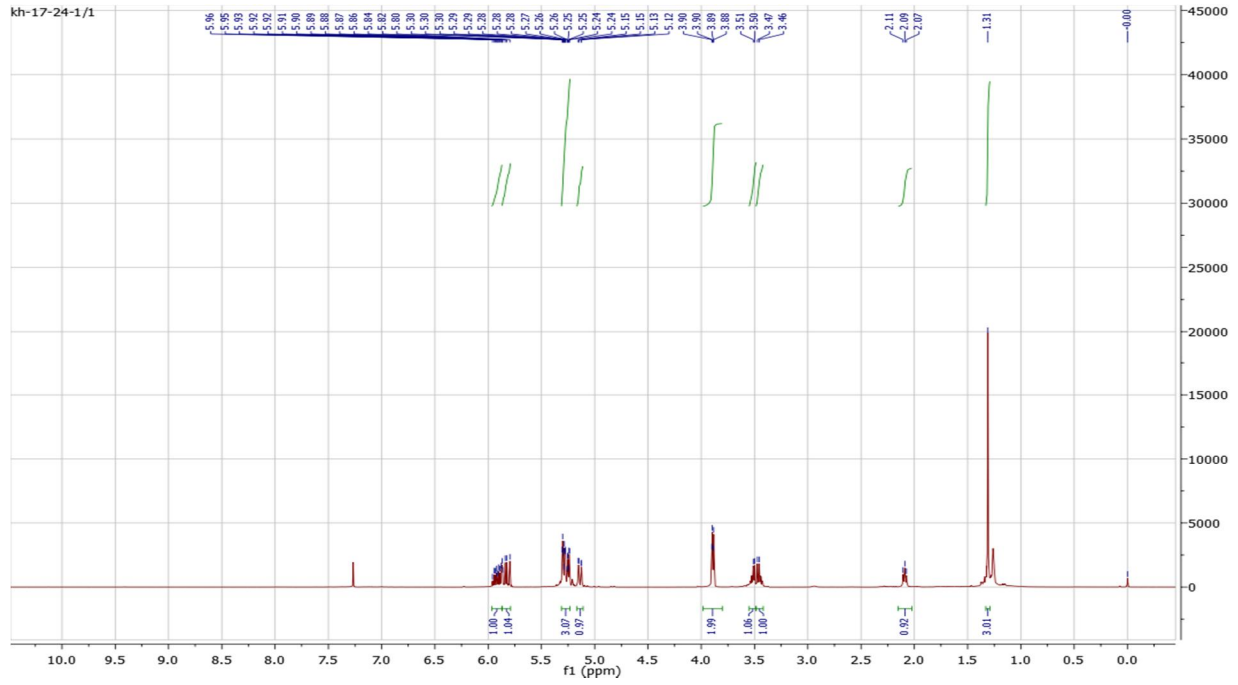
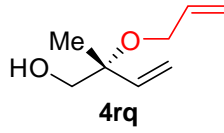


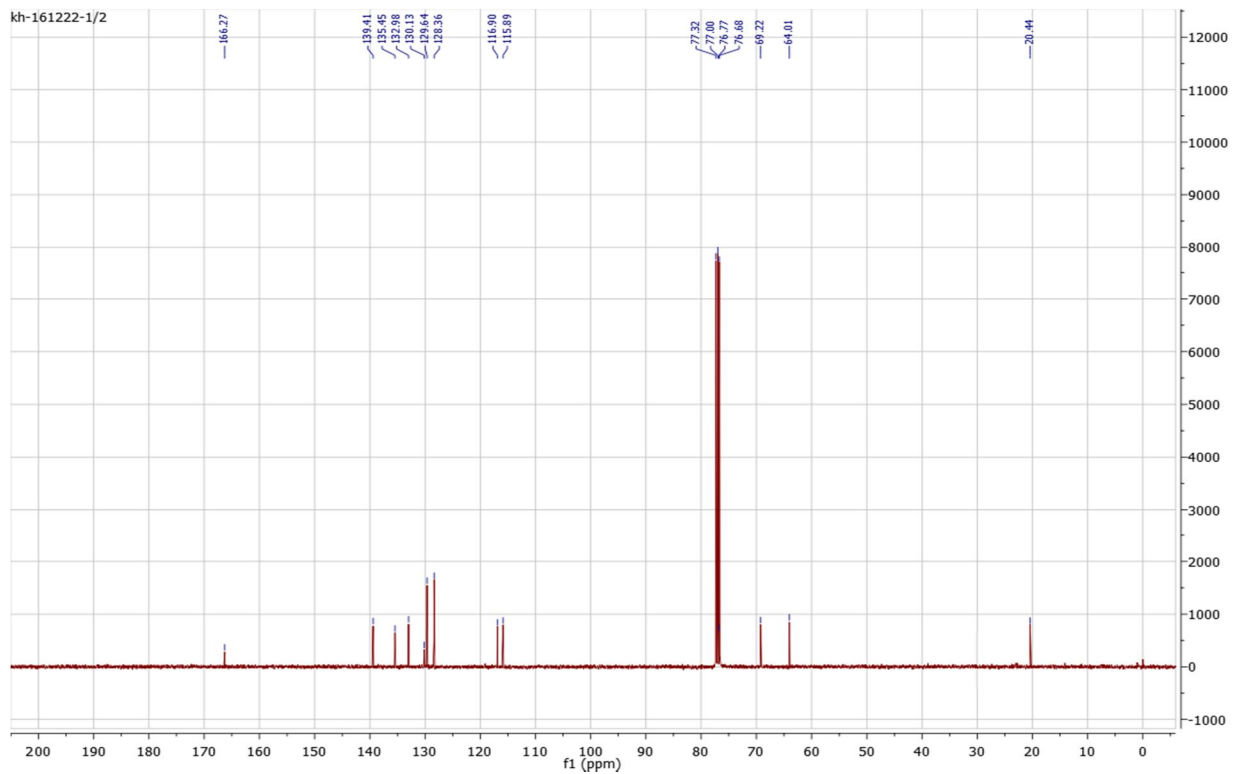
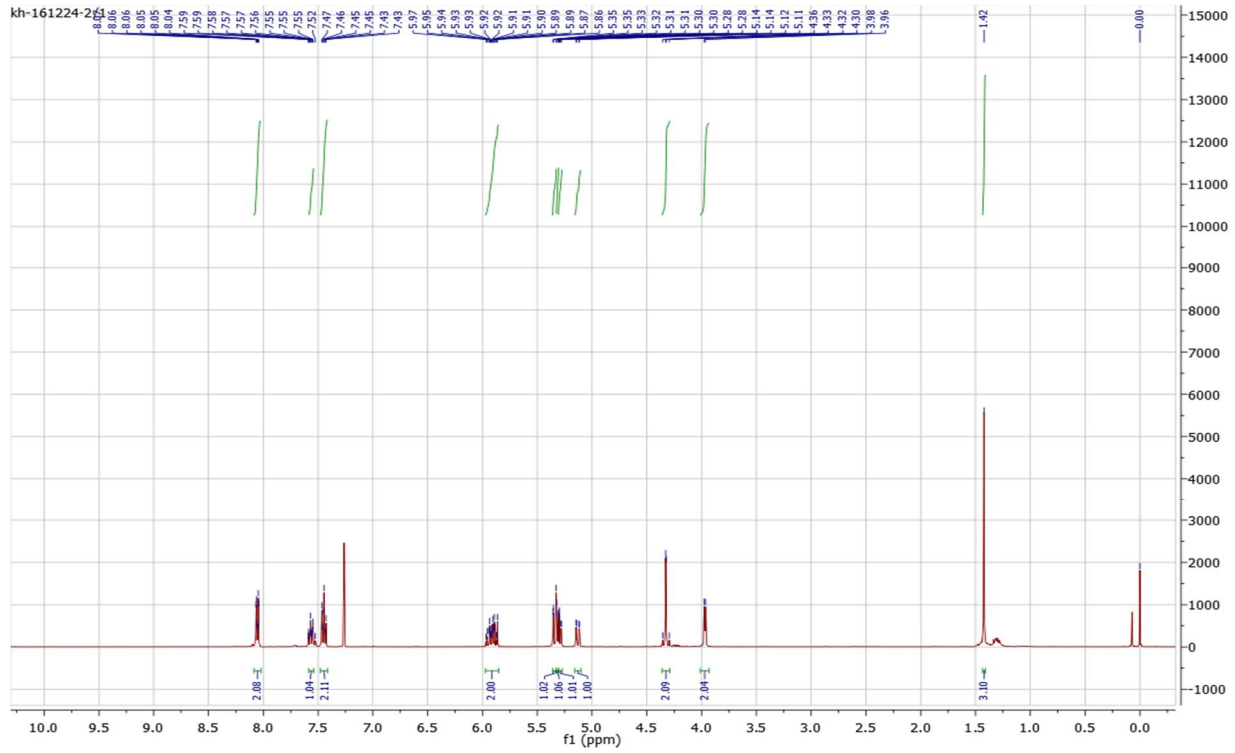
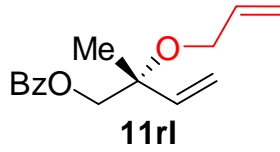


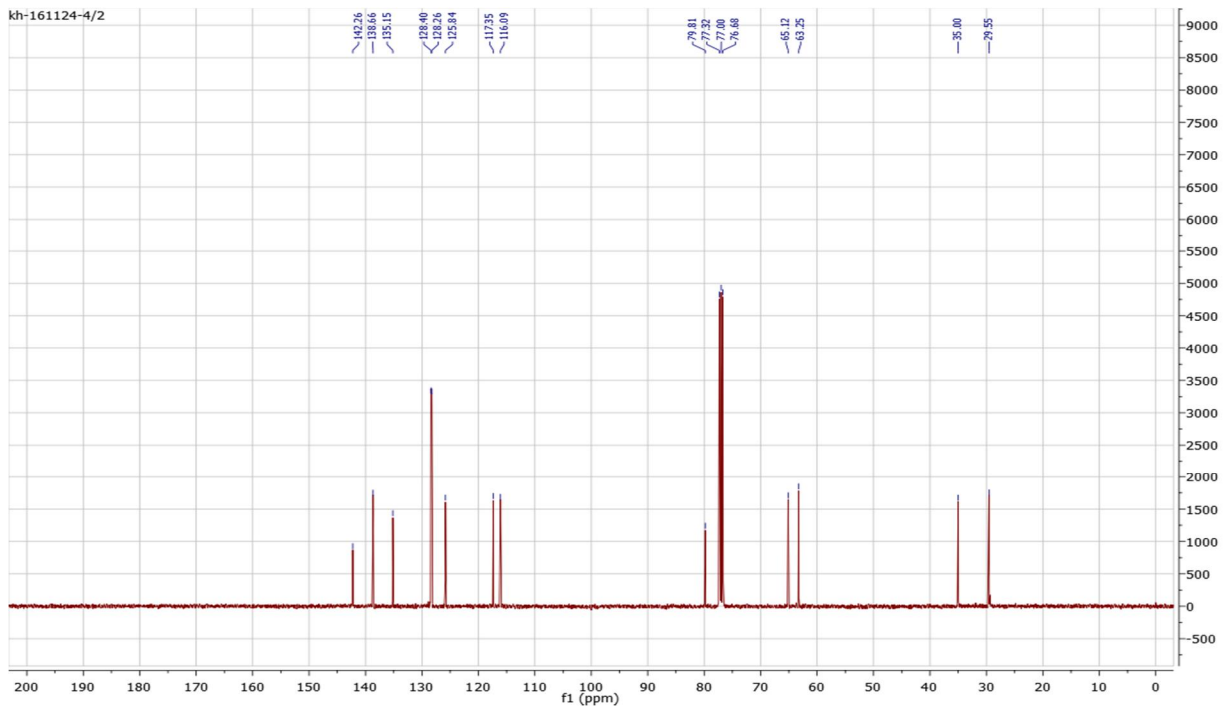
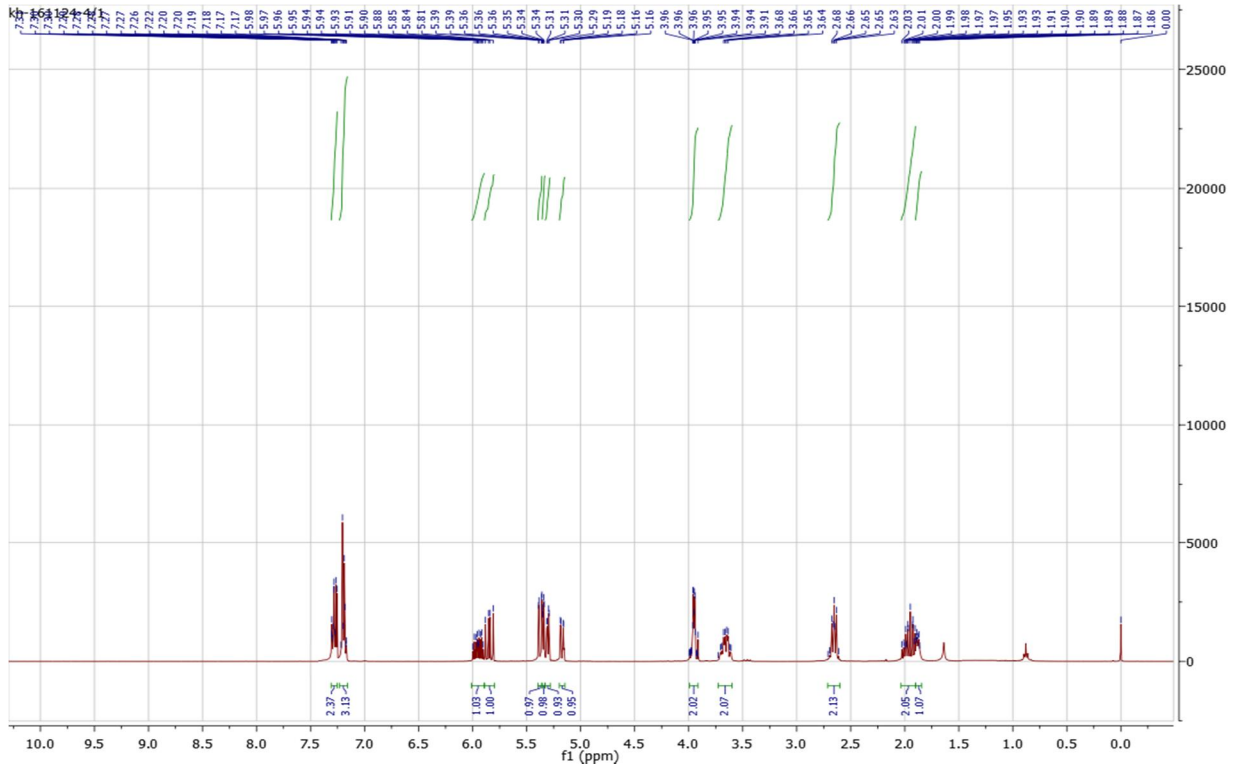
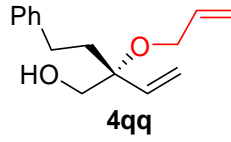


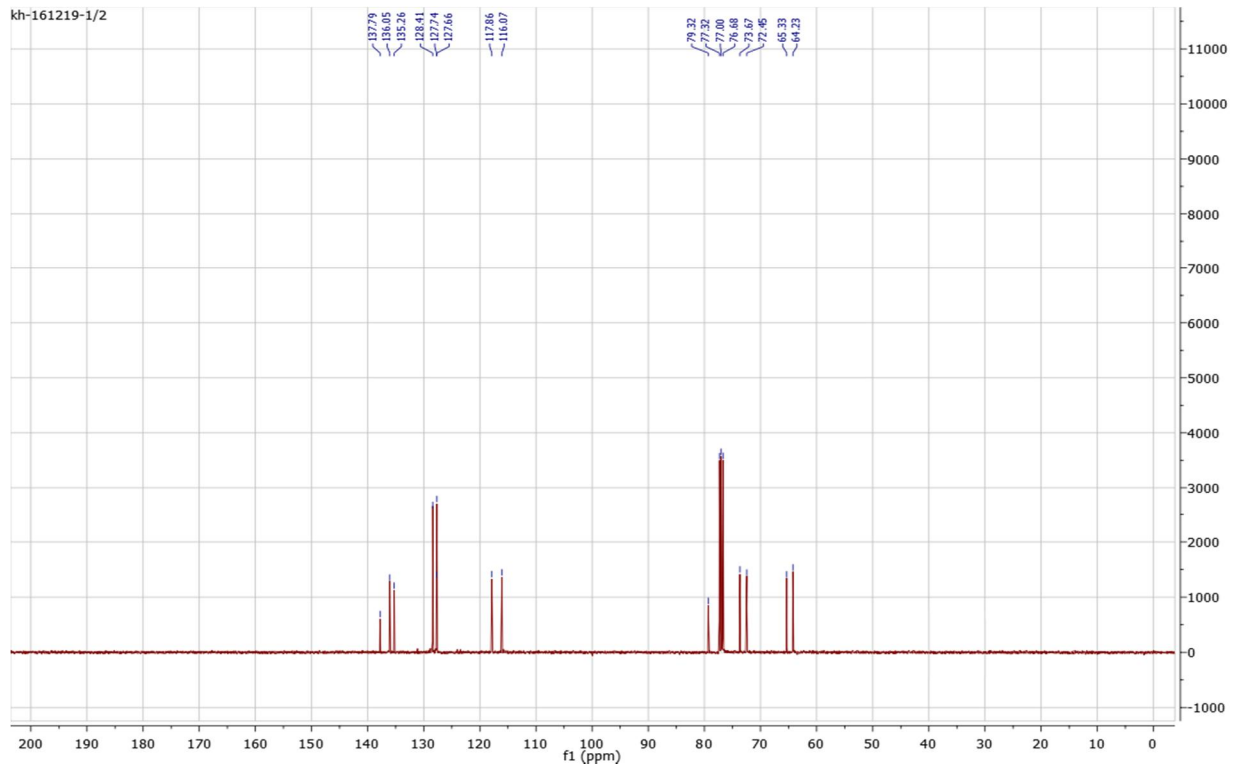
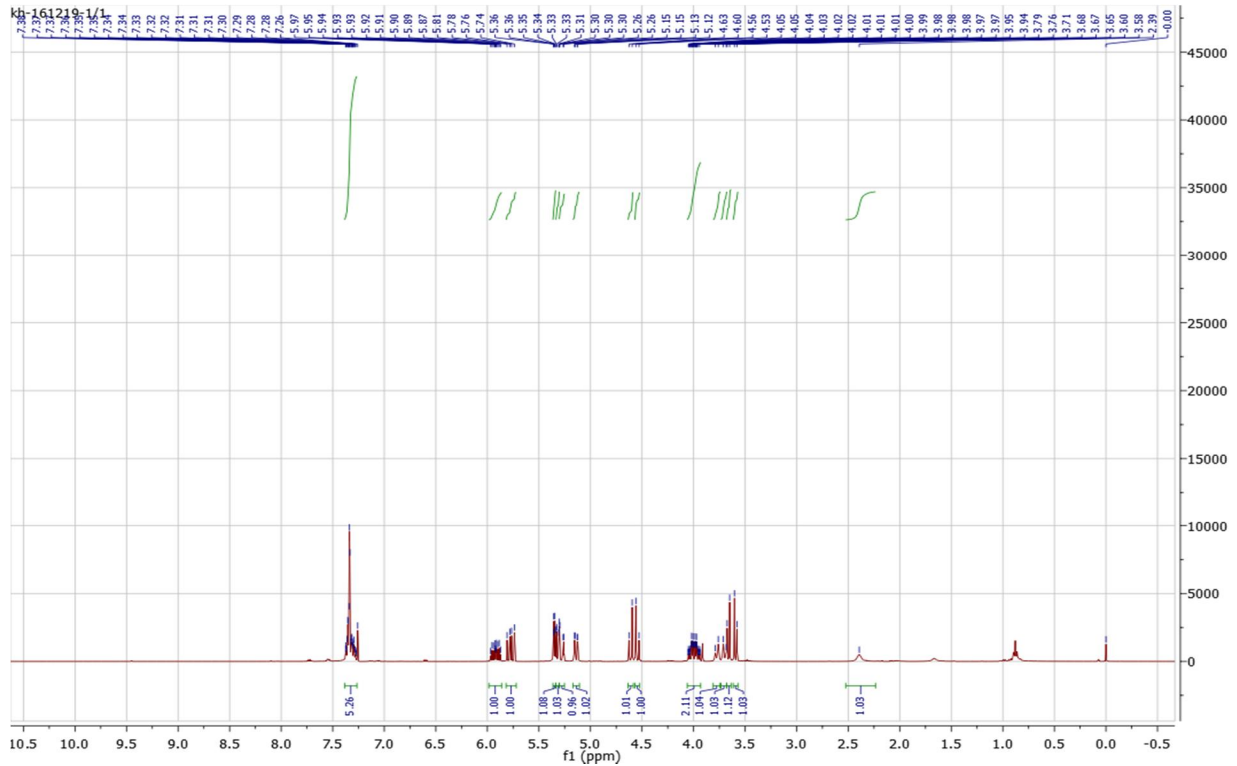
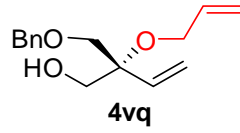


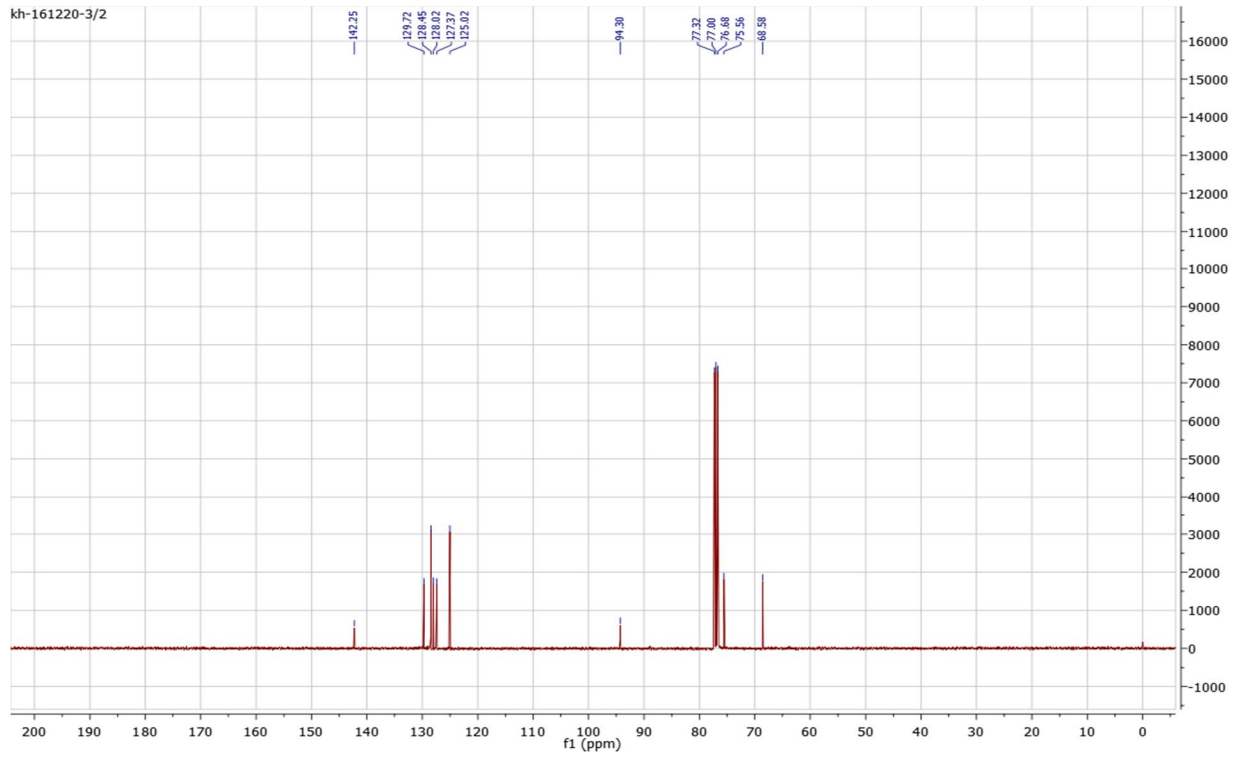
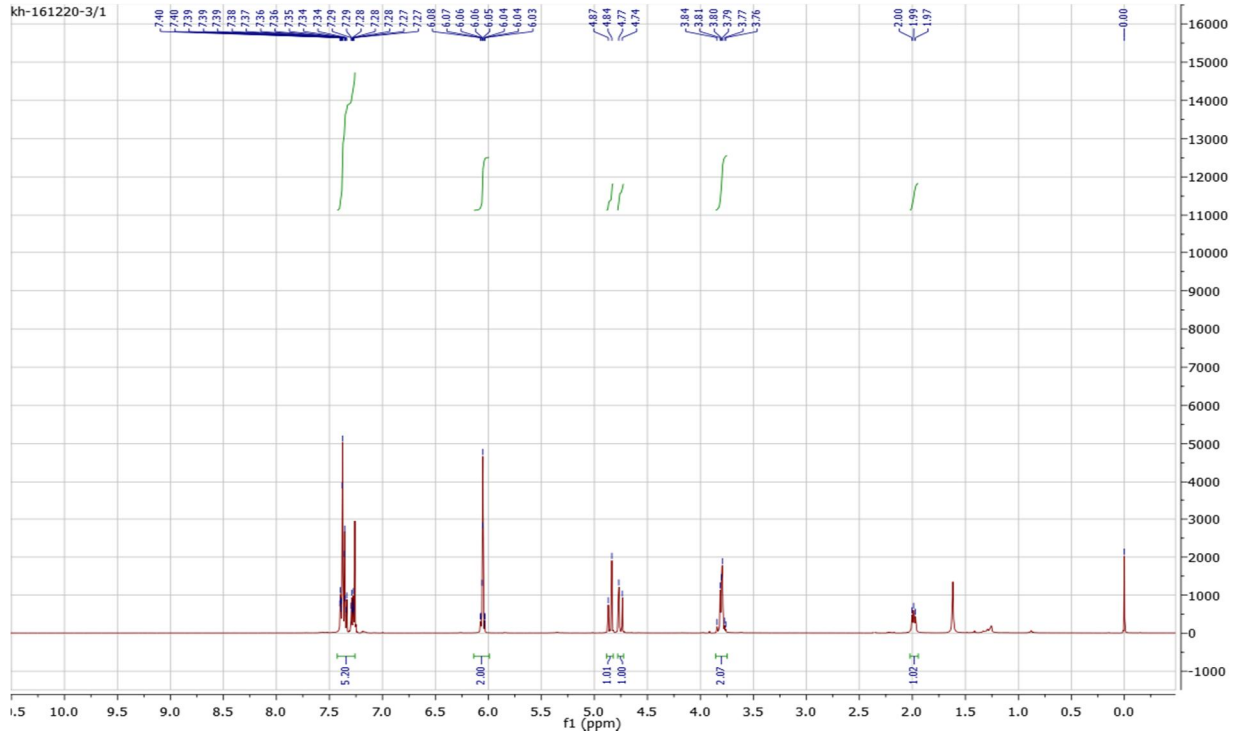
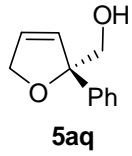


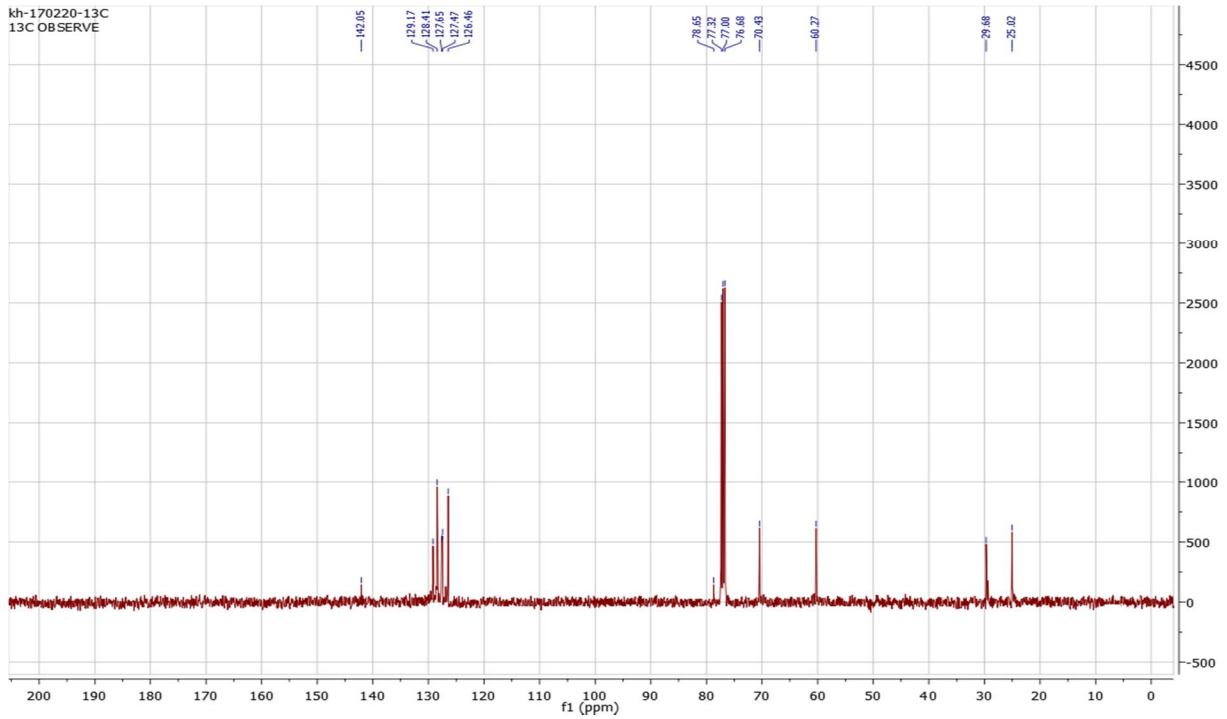
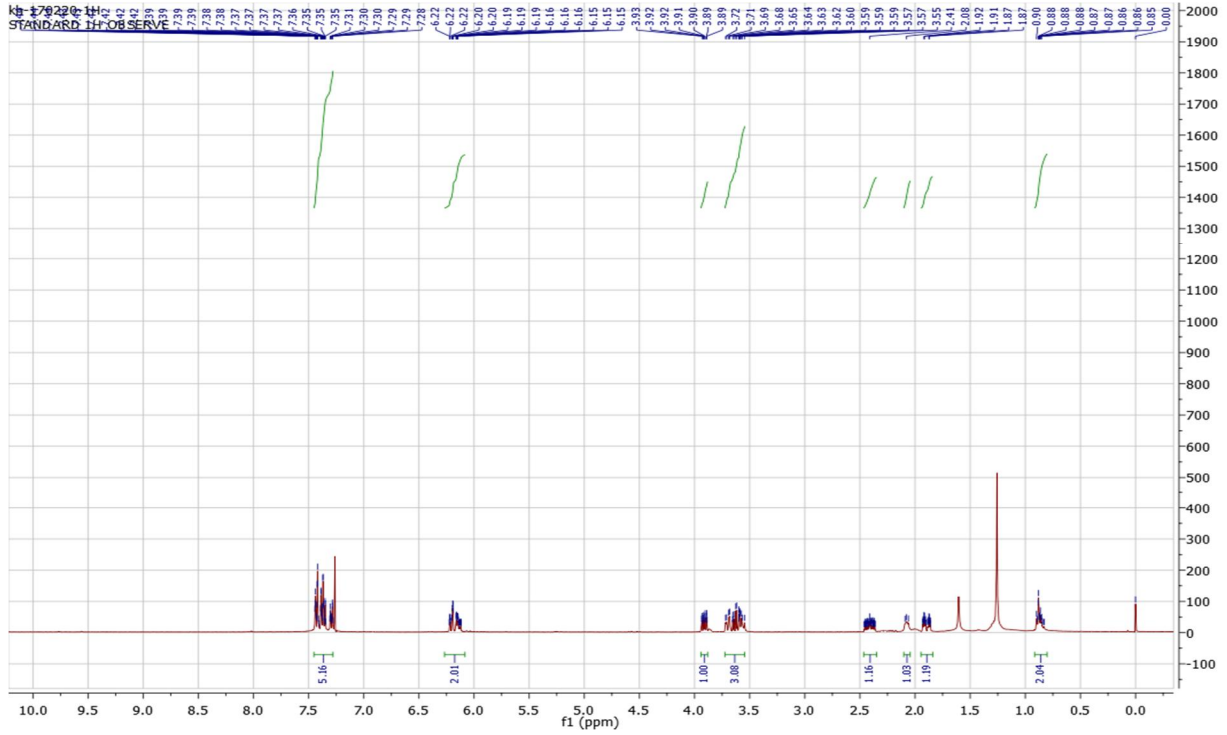
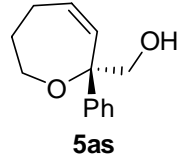


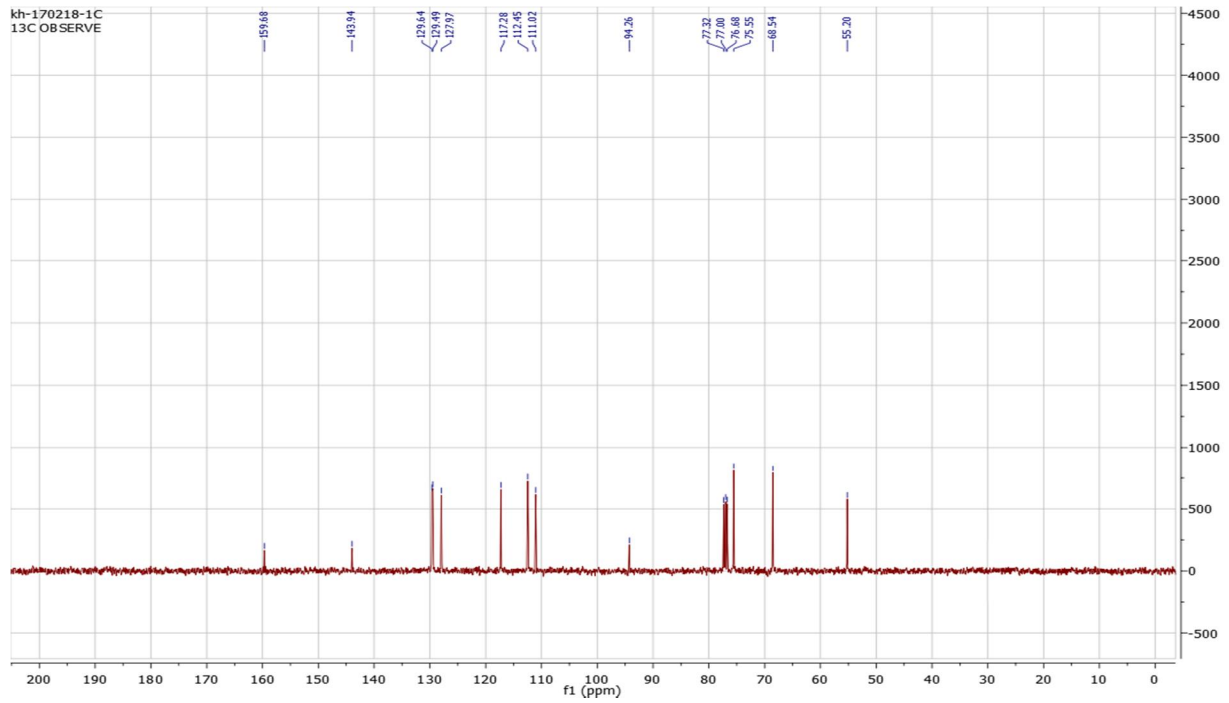
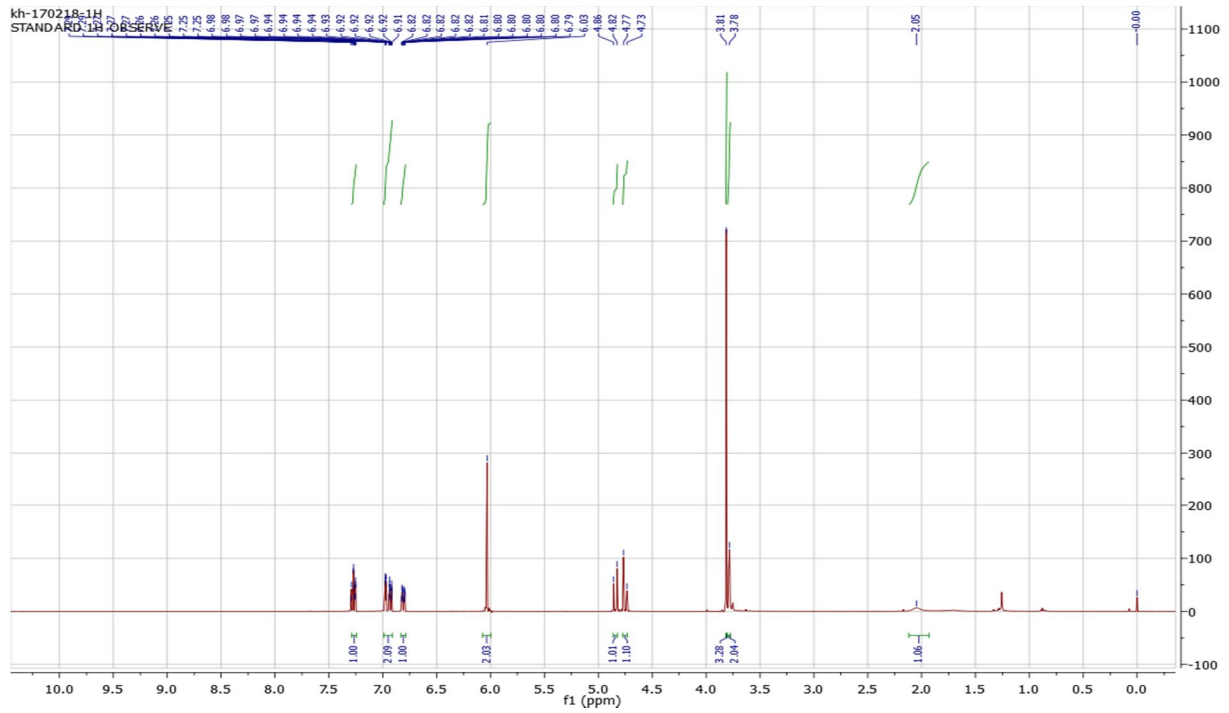
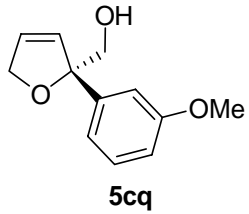


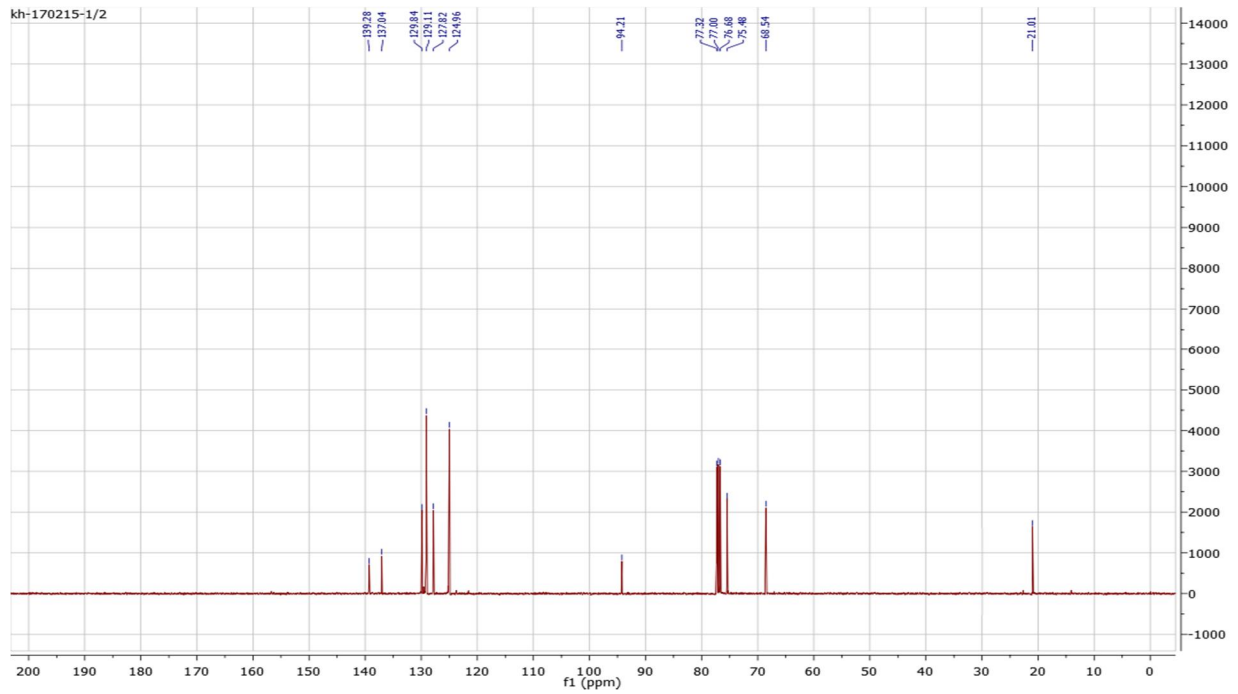
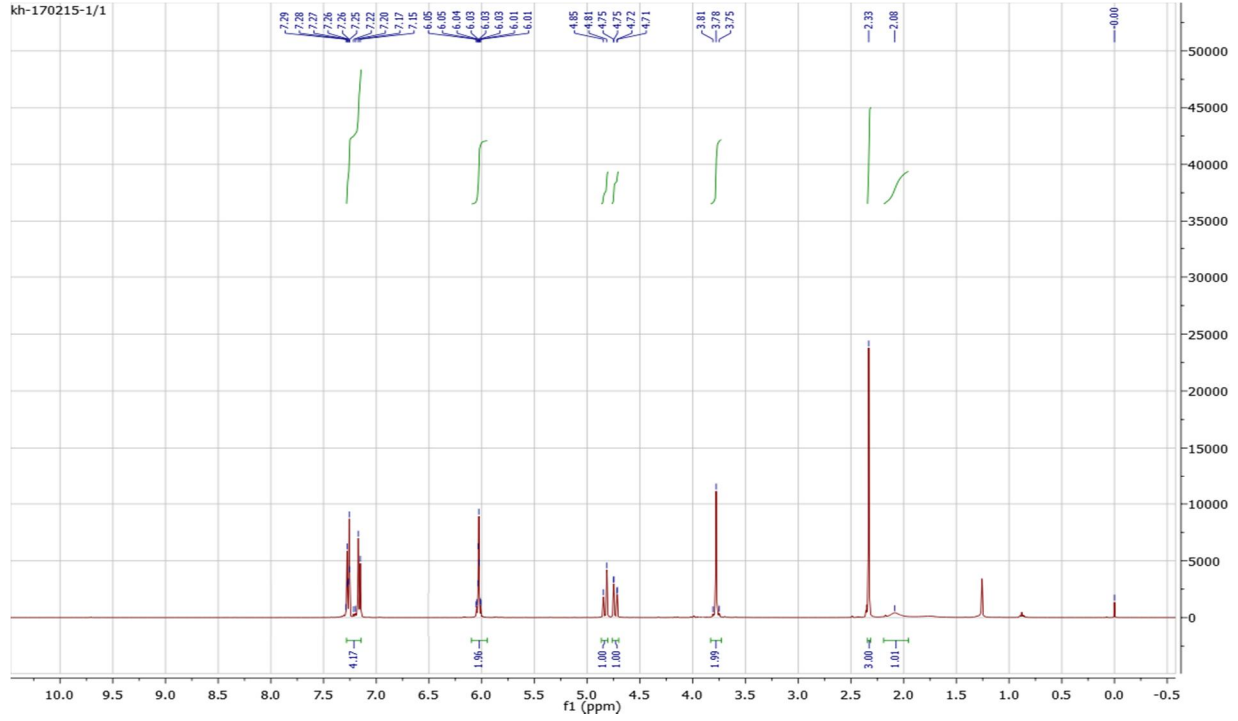
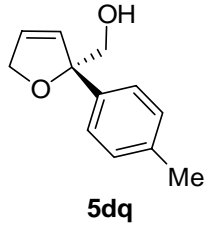


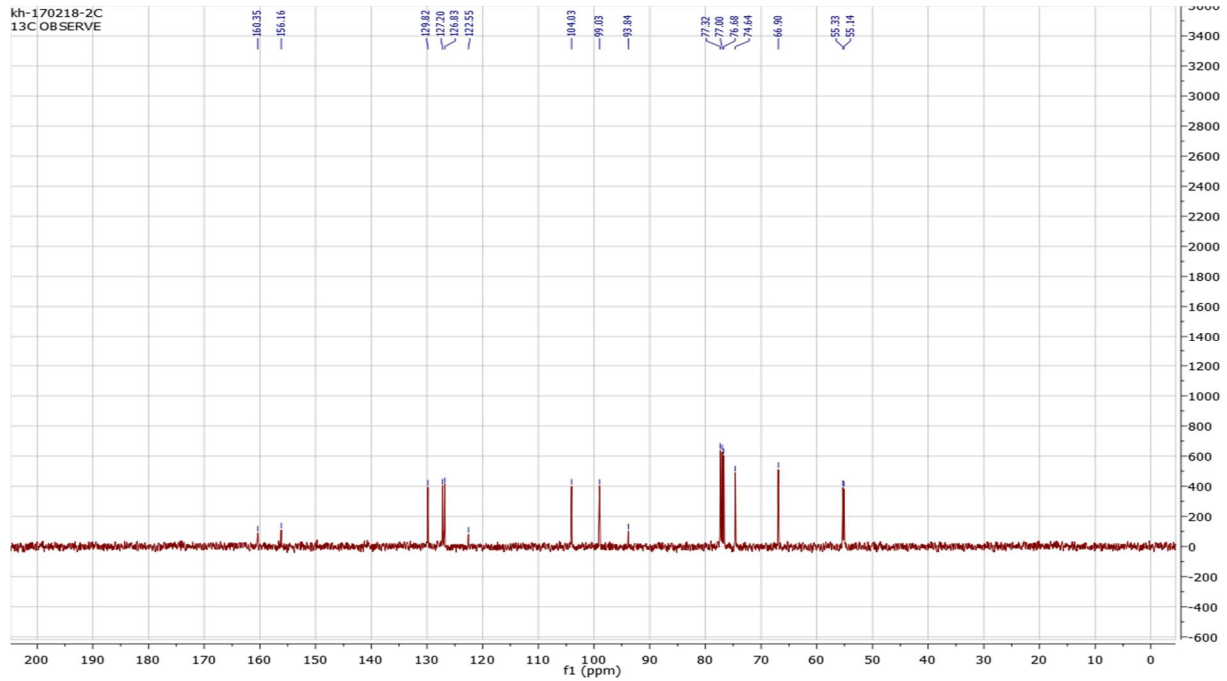
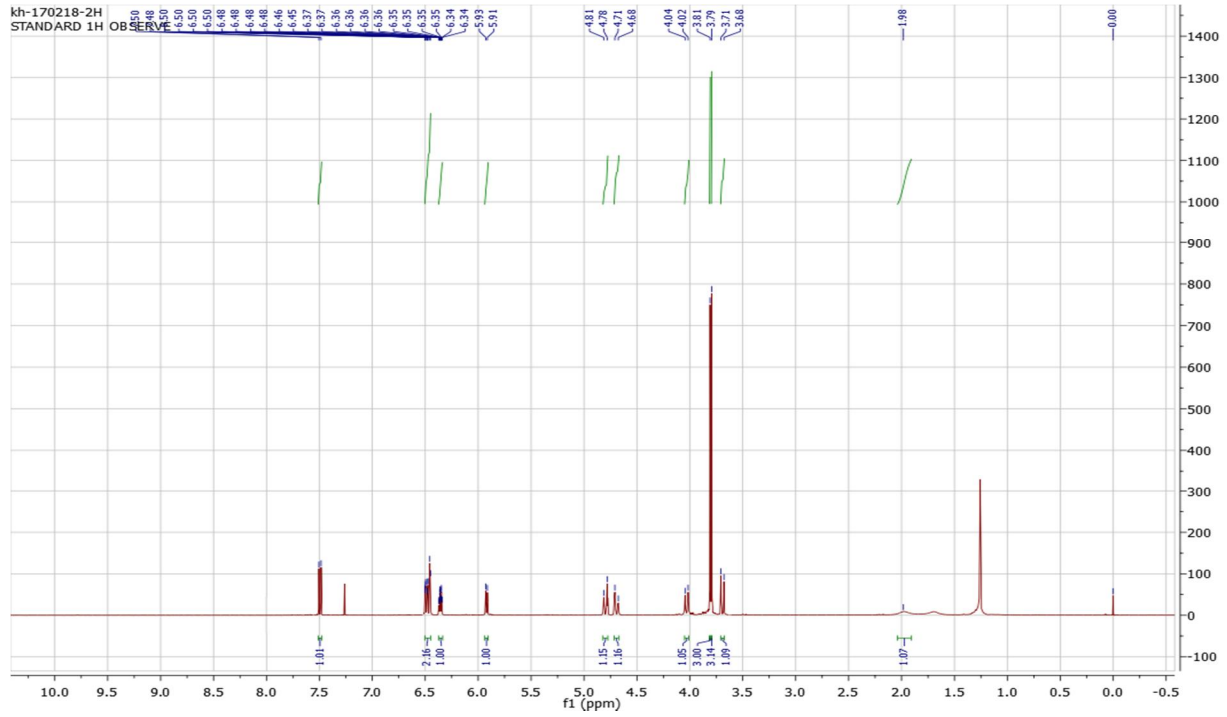
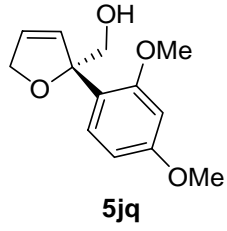


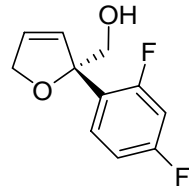




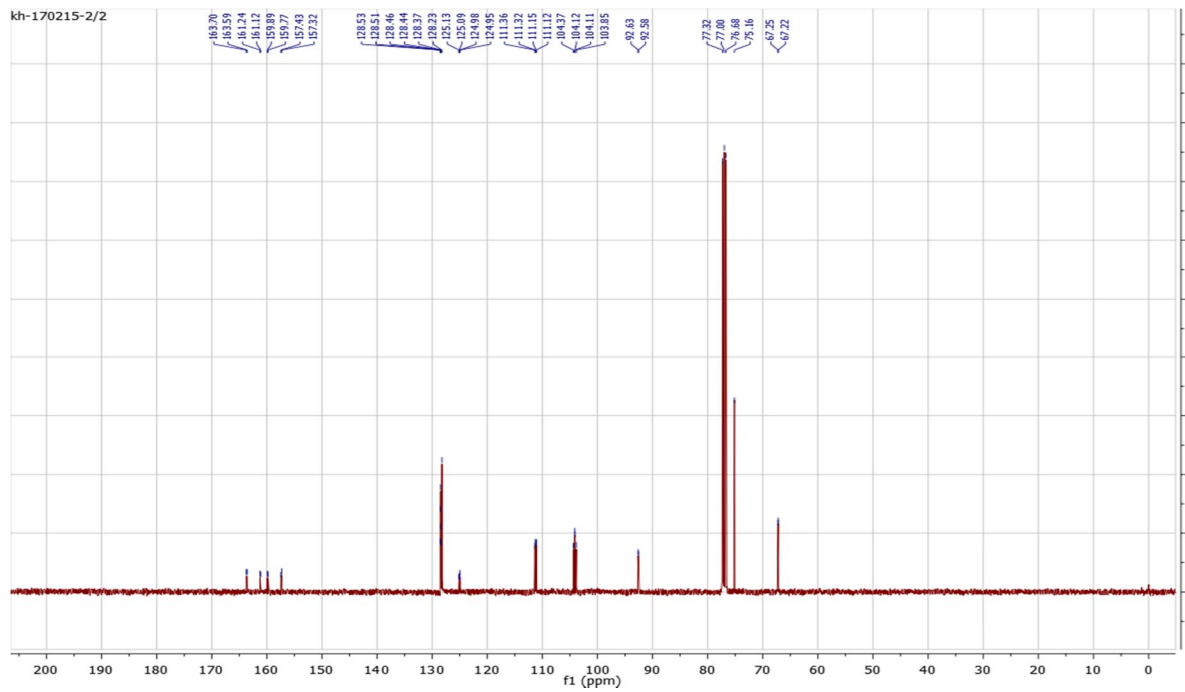
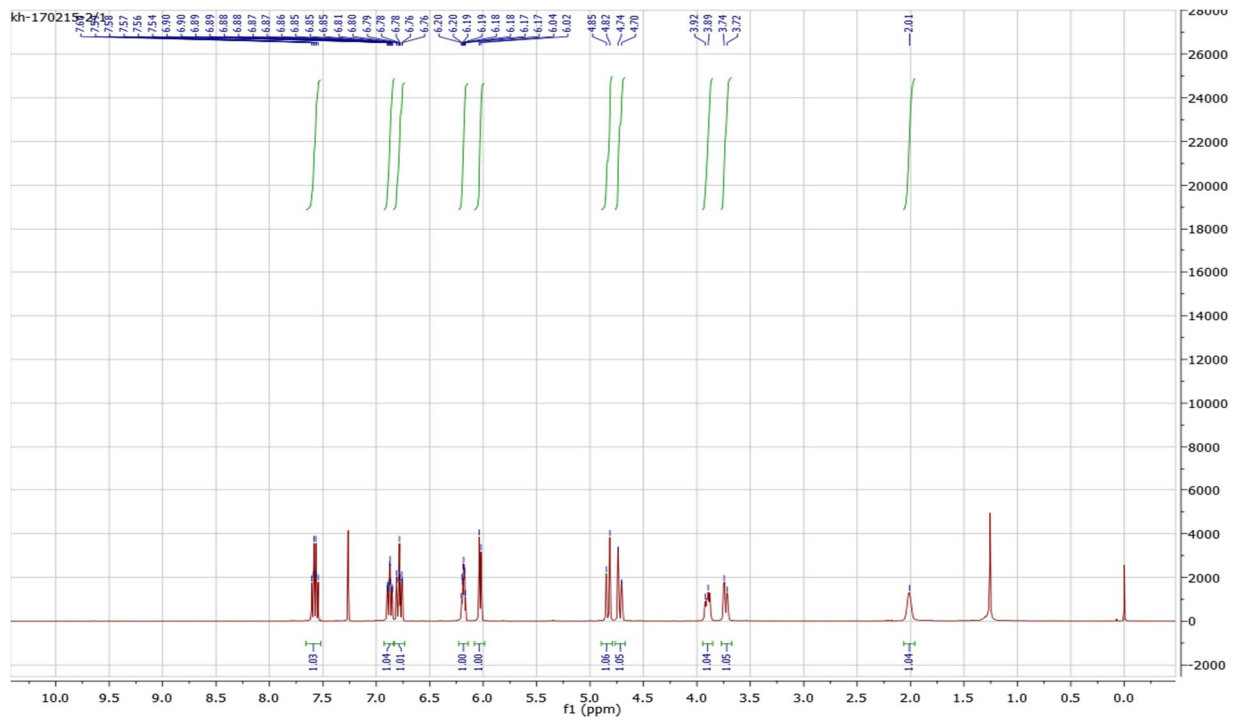


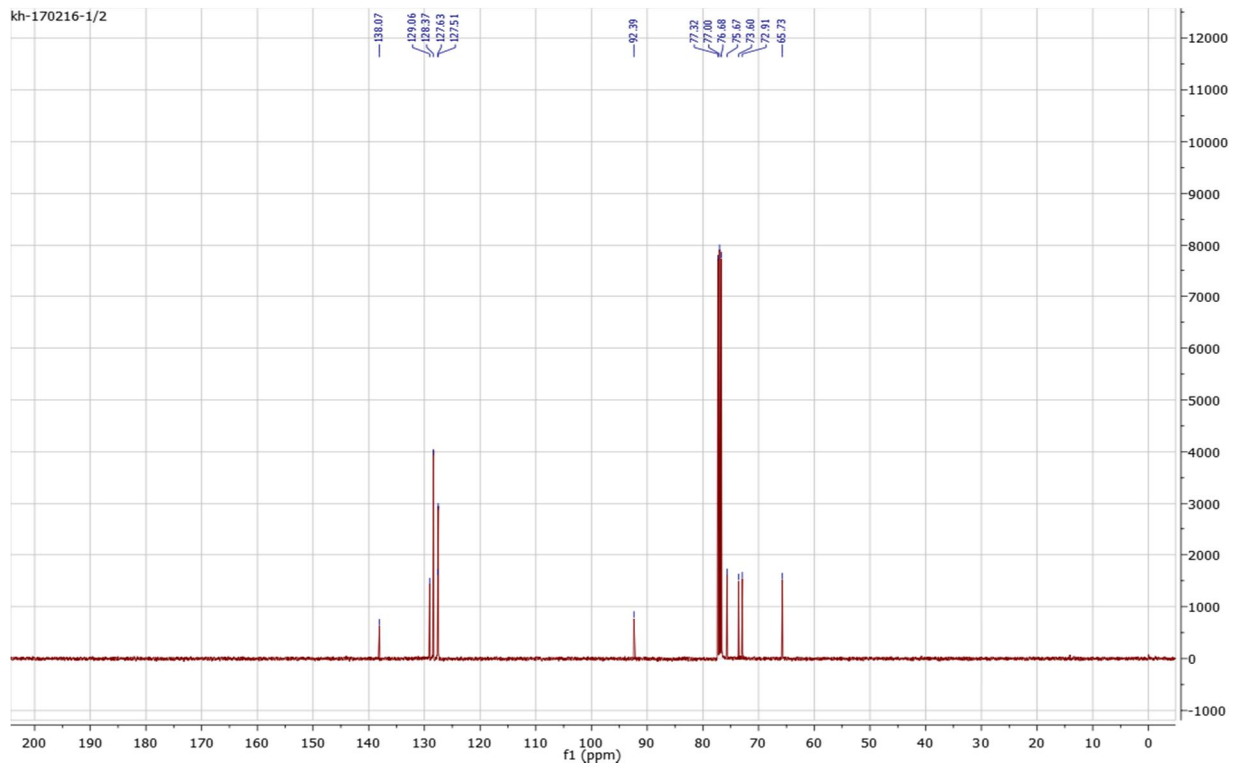
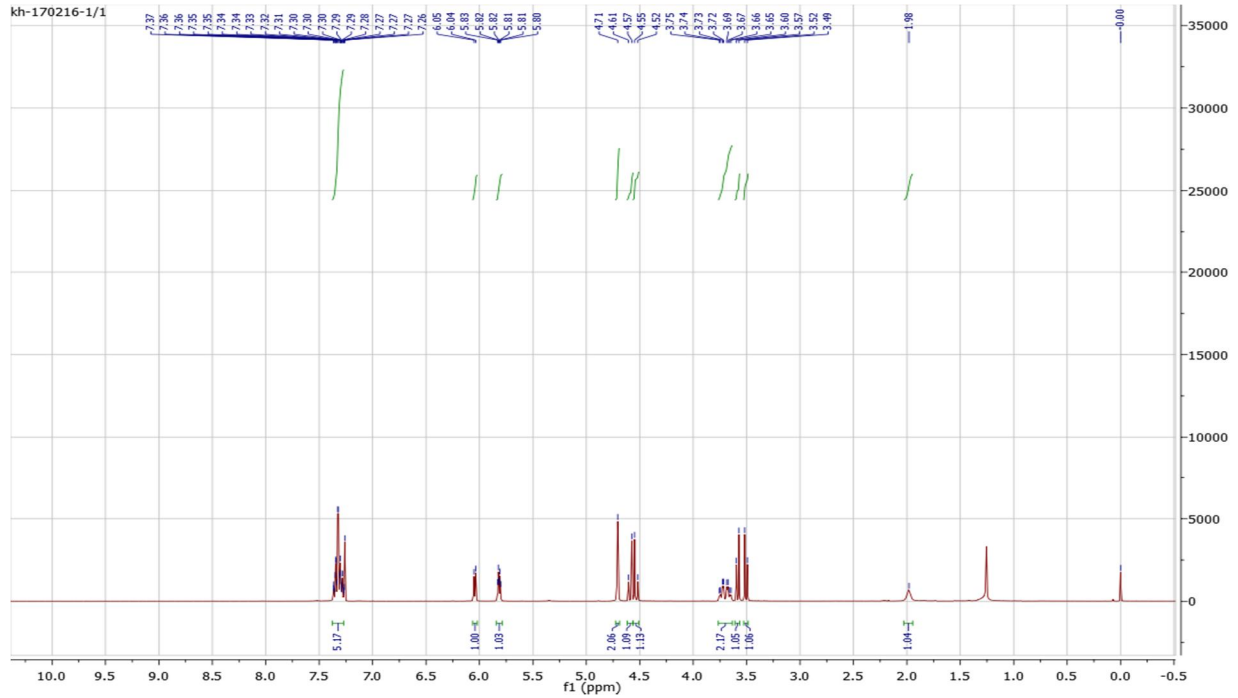
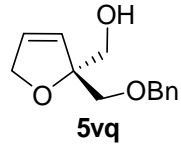


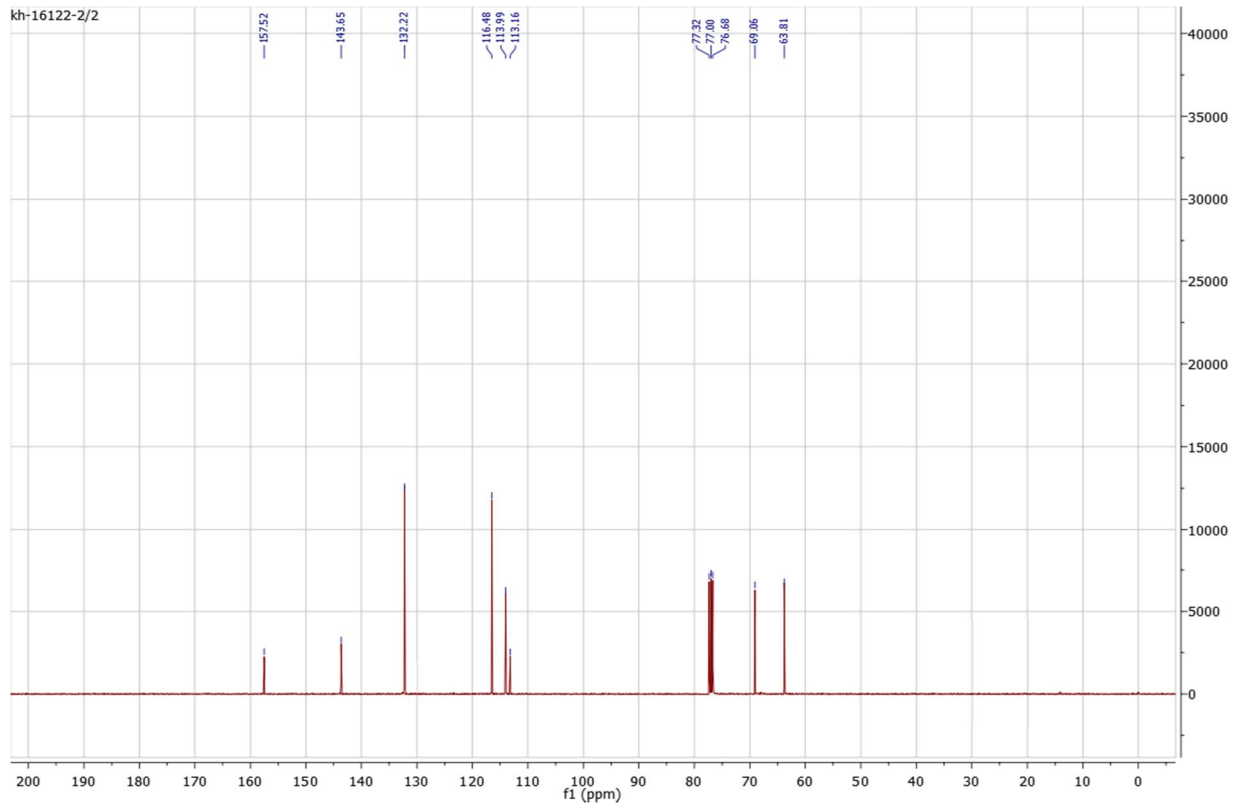
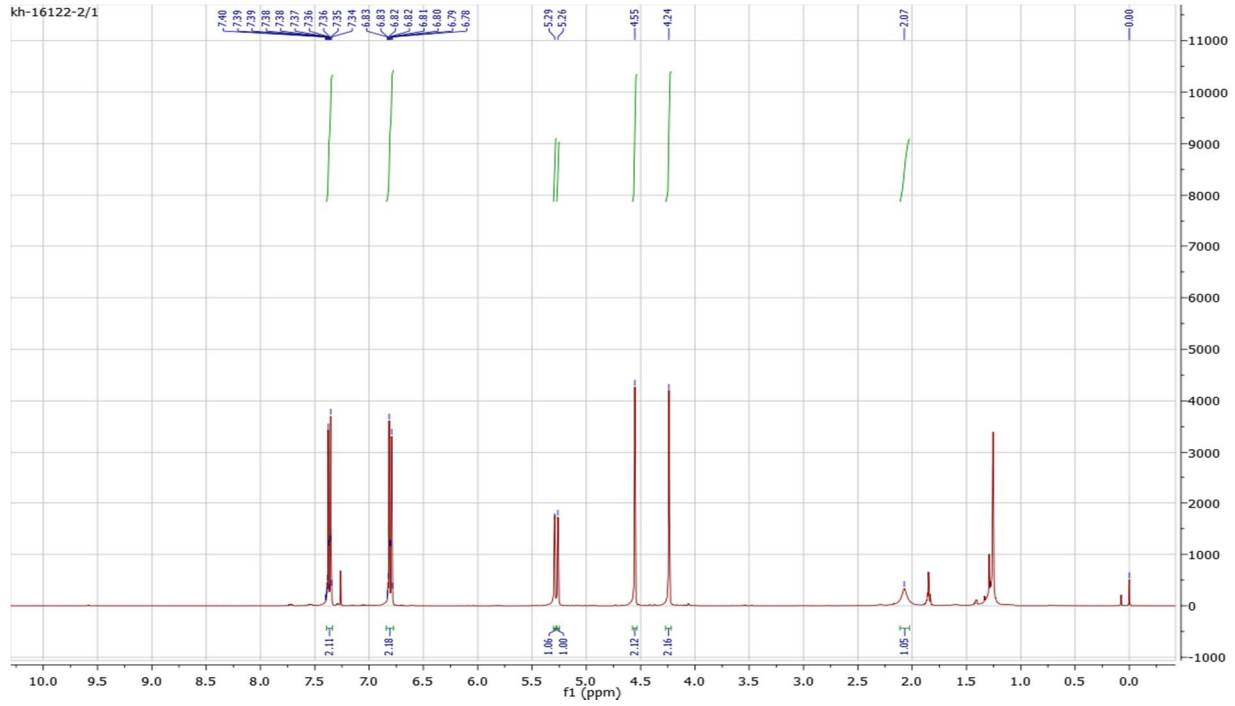
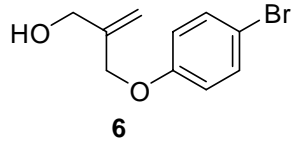


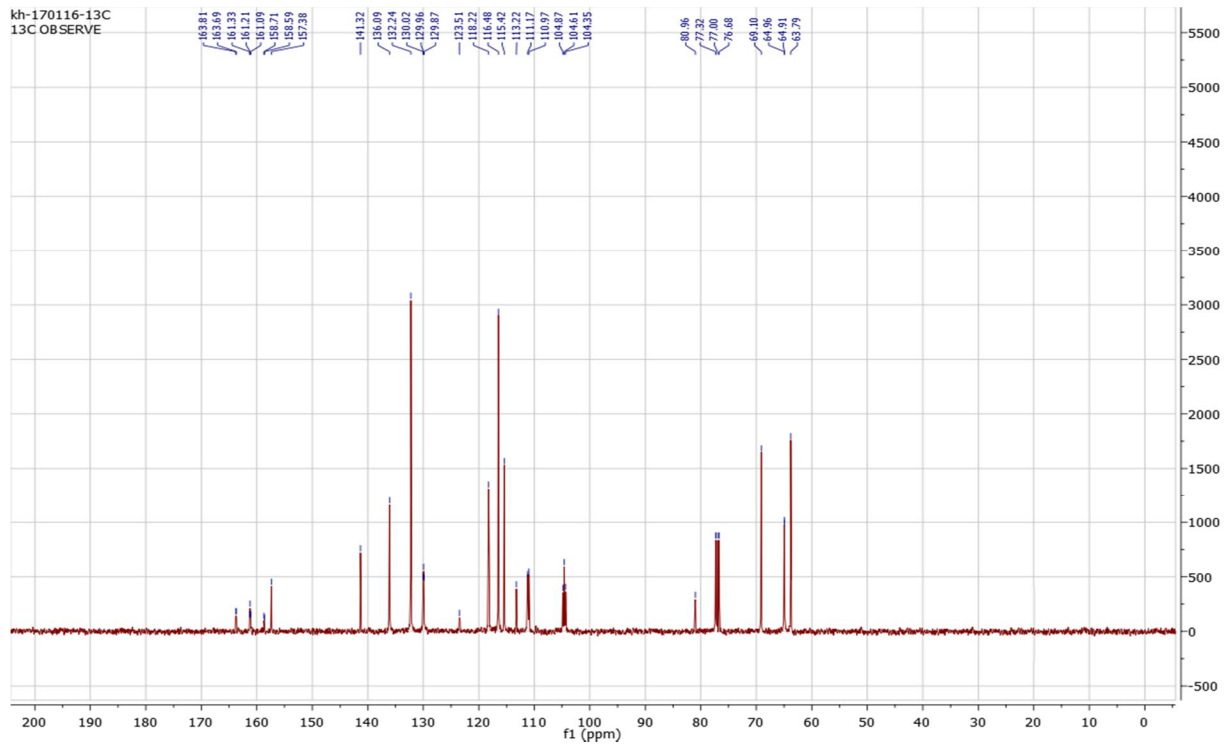
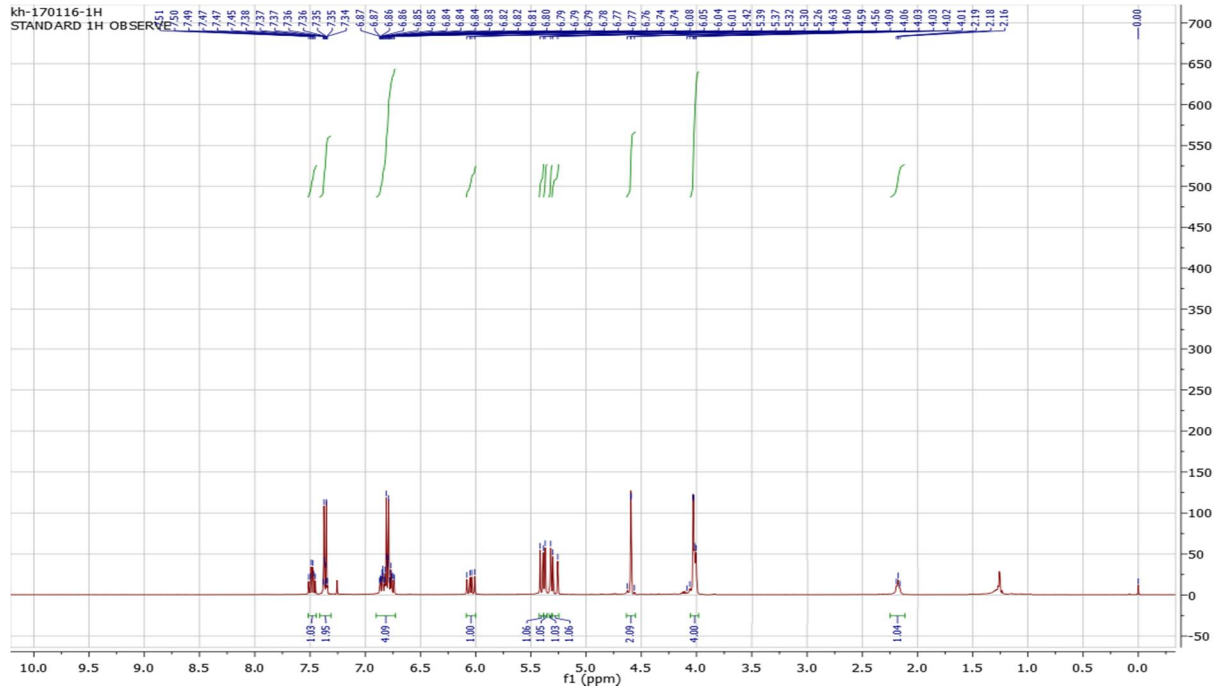
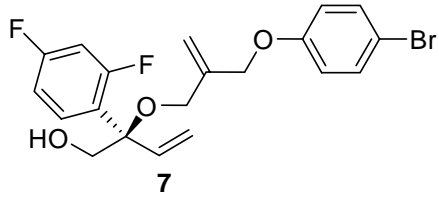


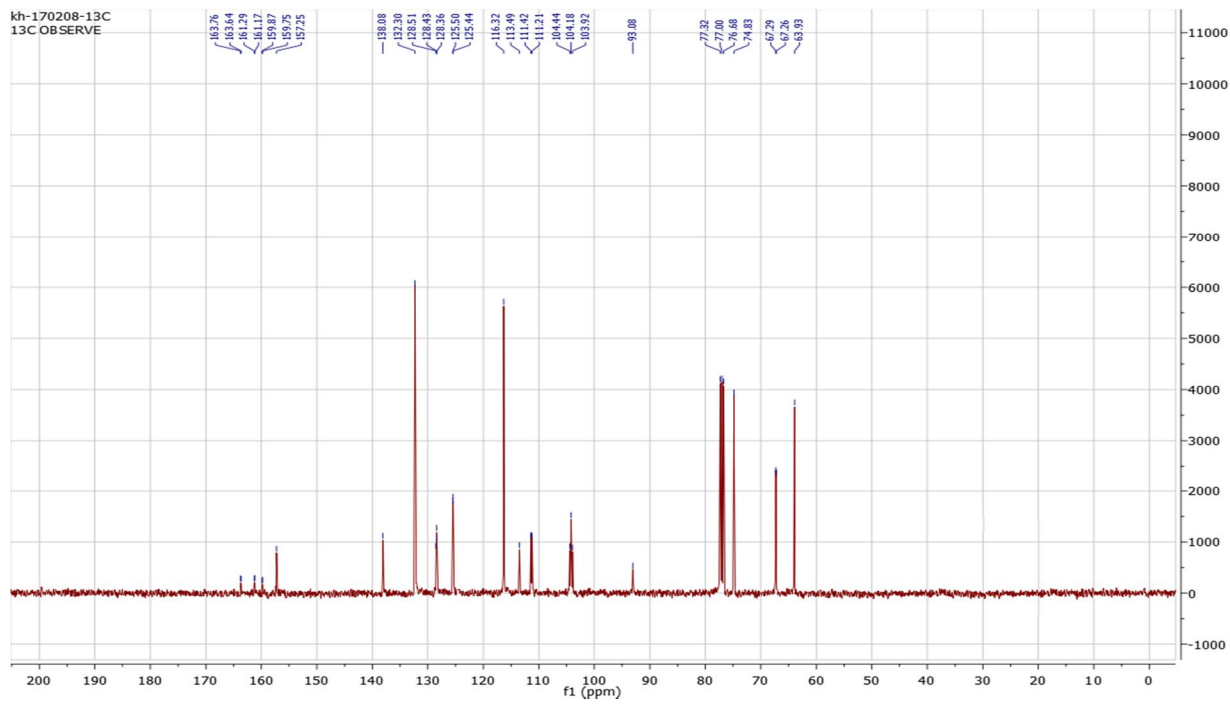
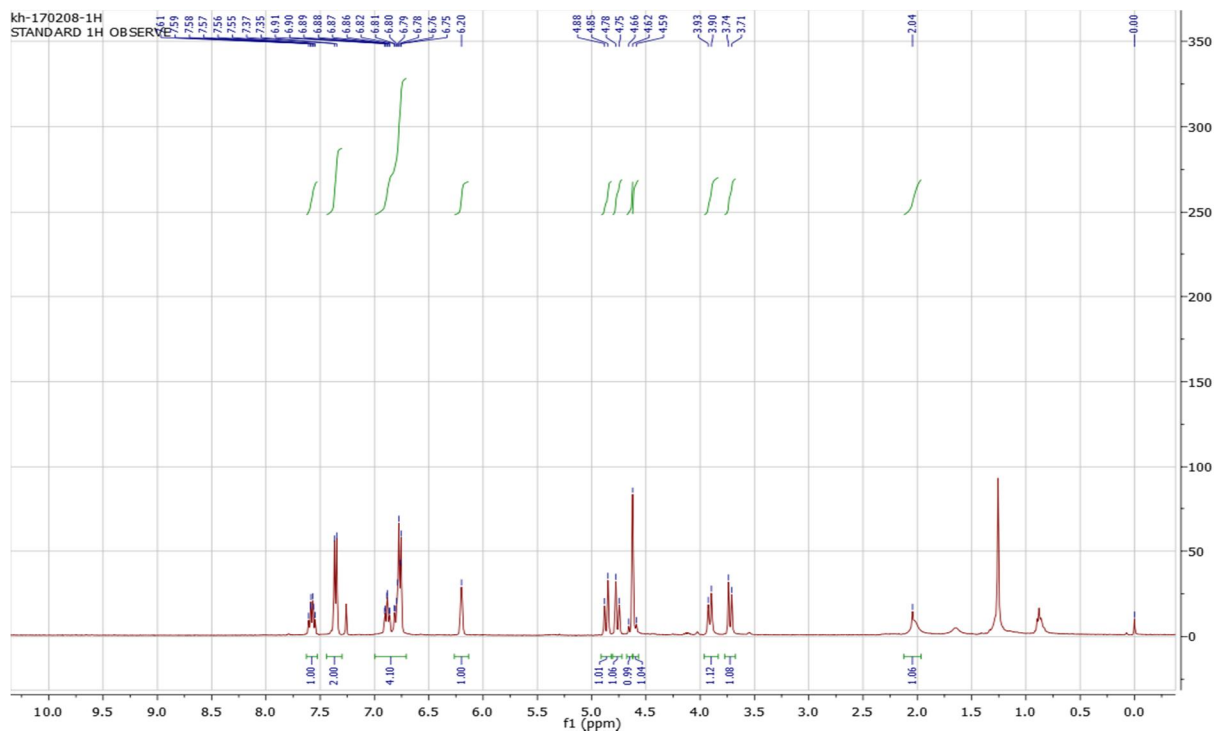
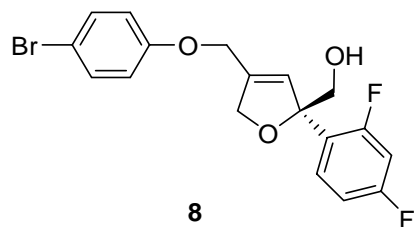
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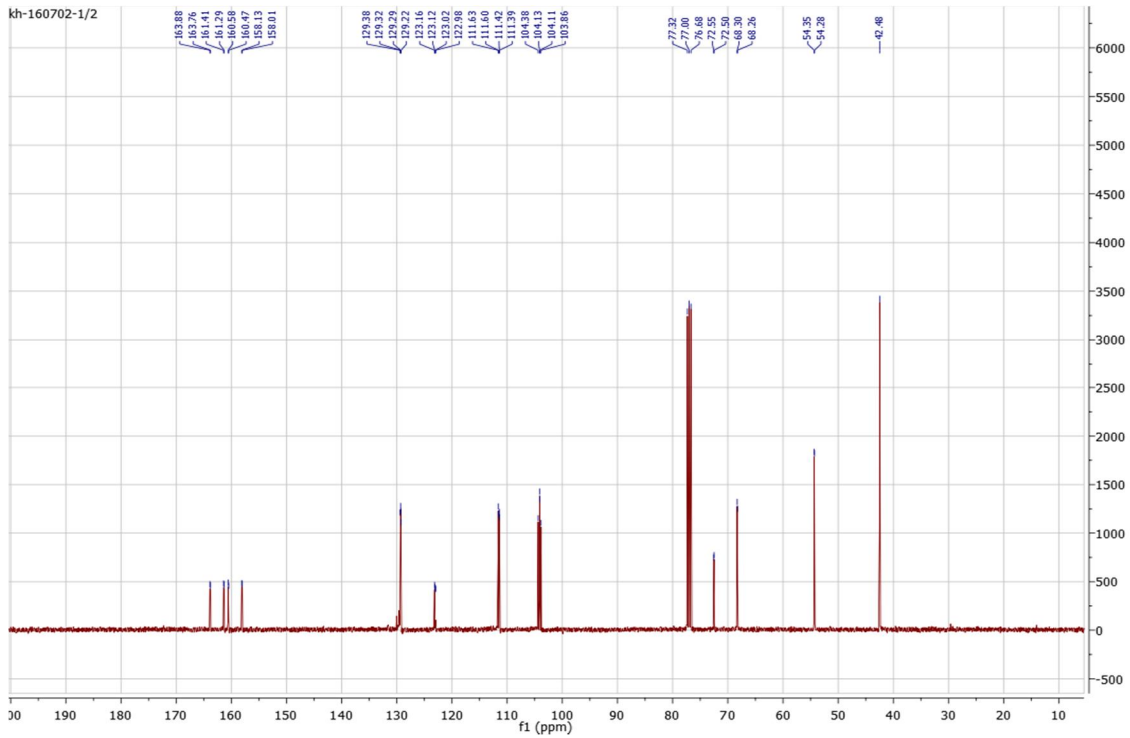
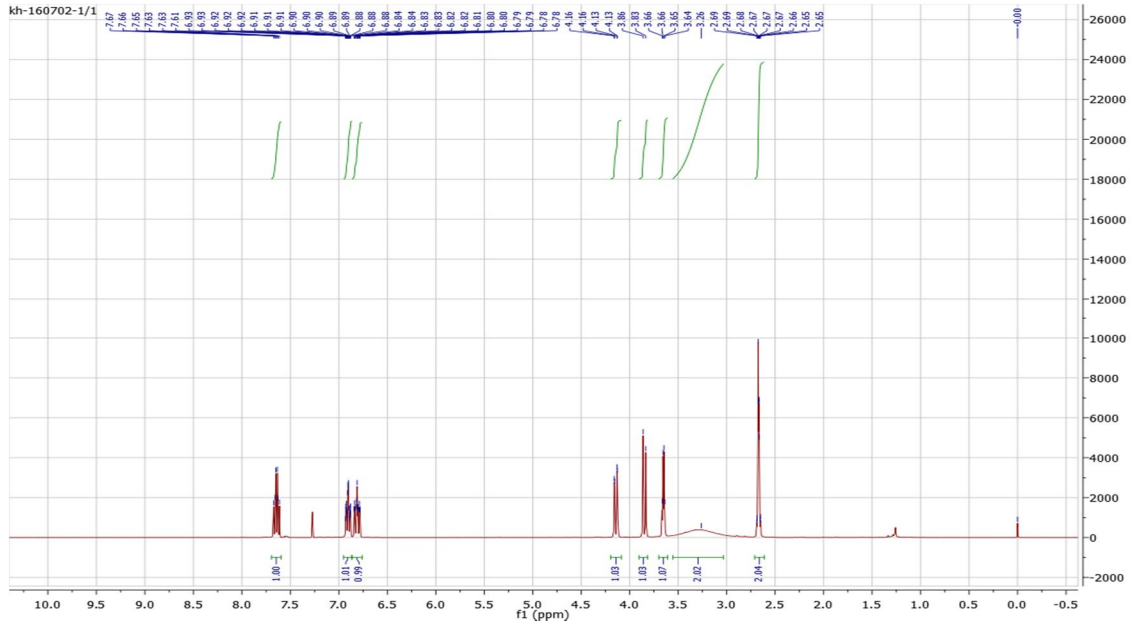
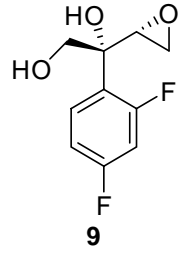


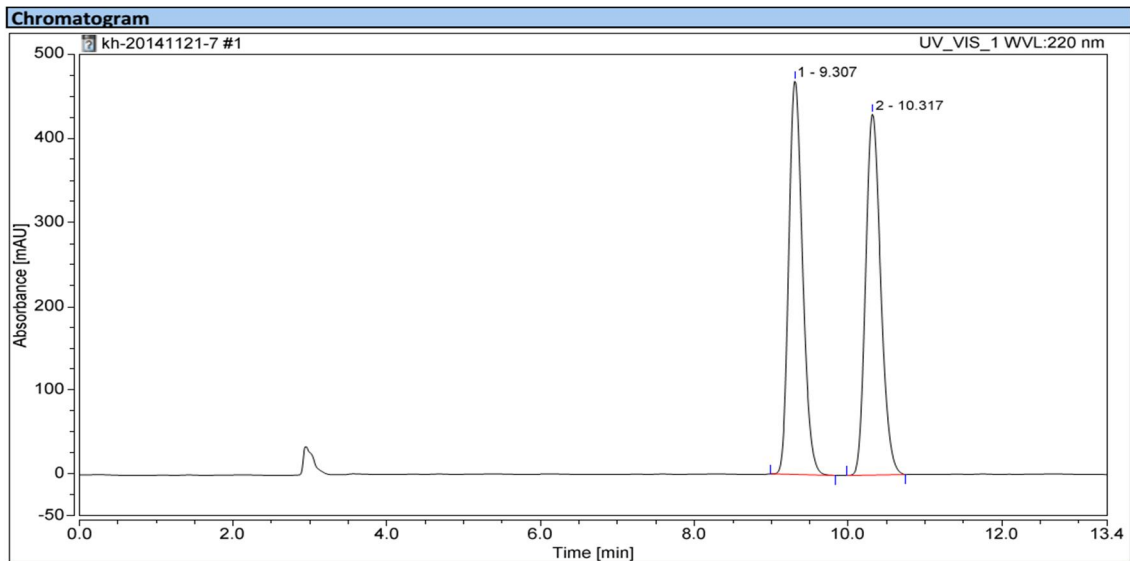
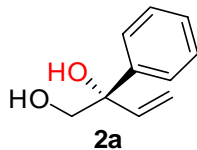






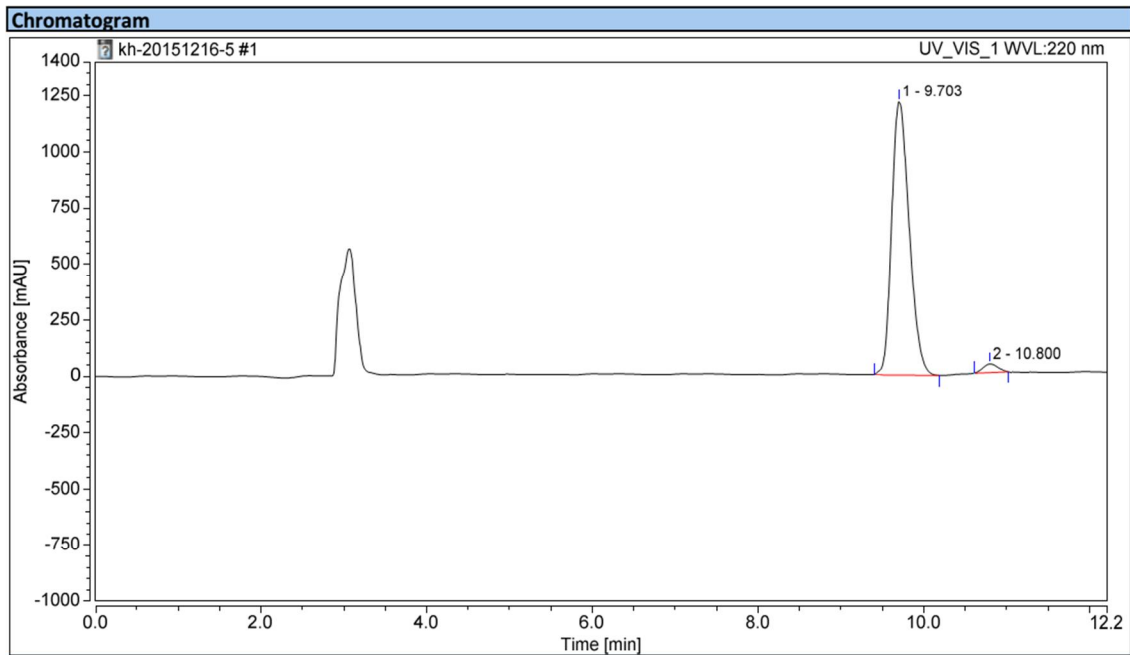






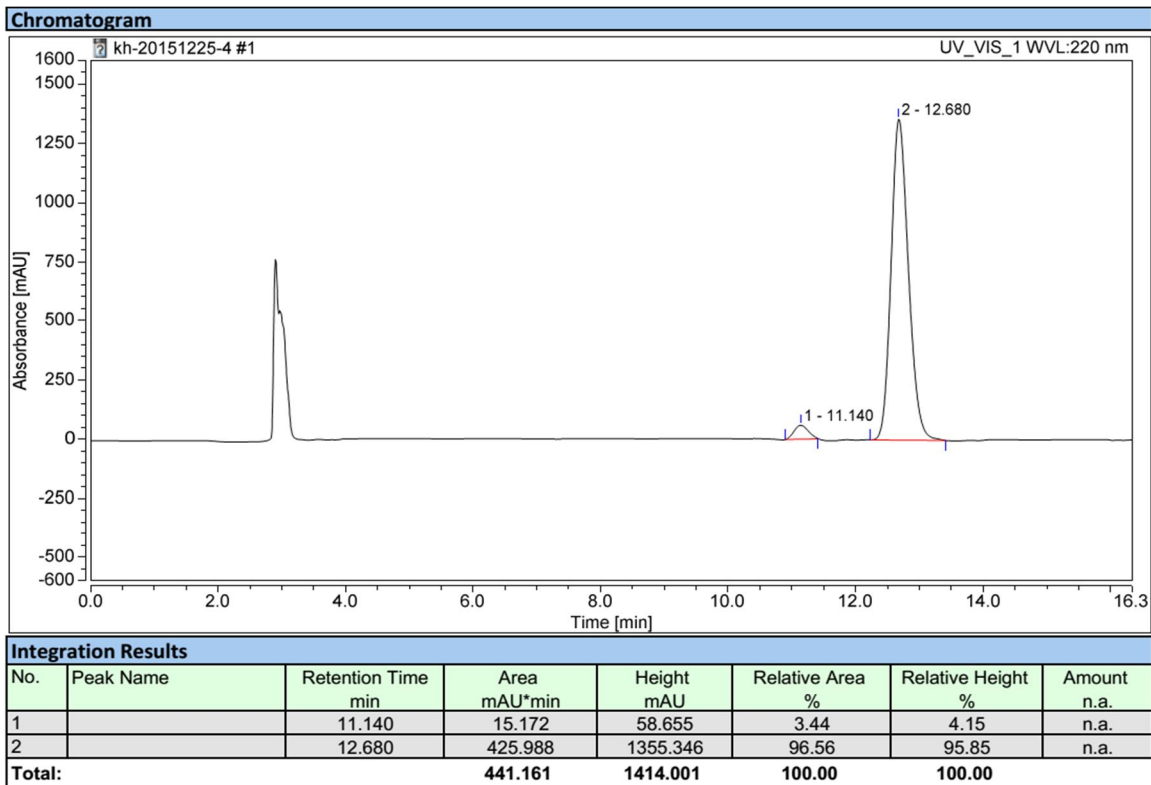
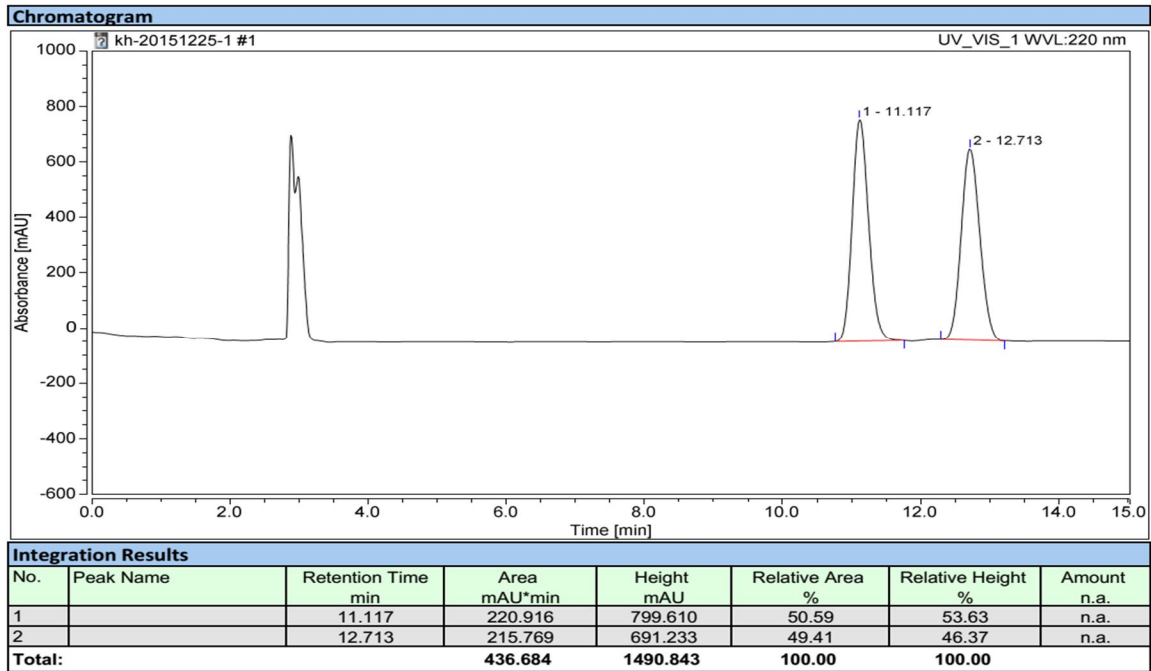
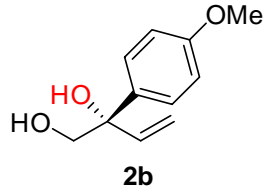
Integration Results

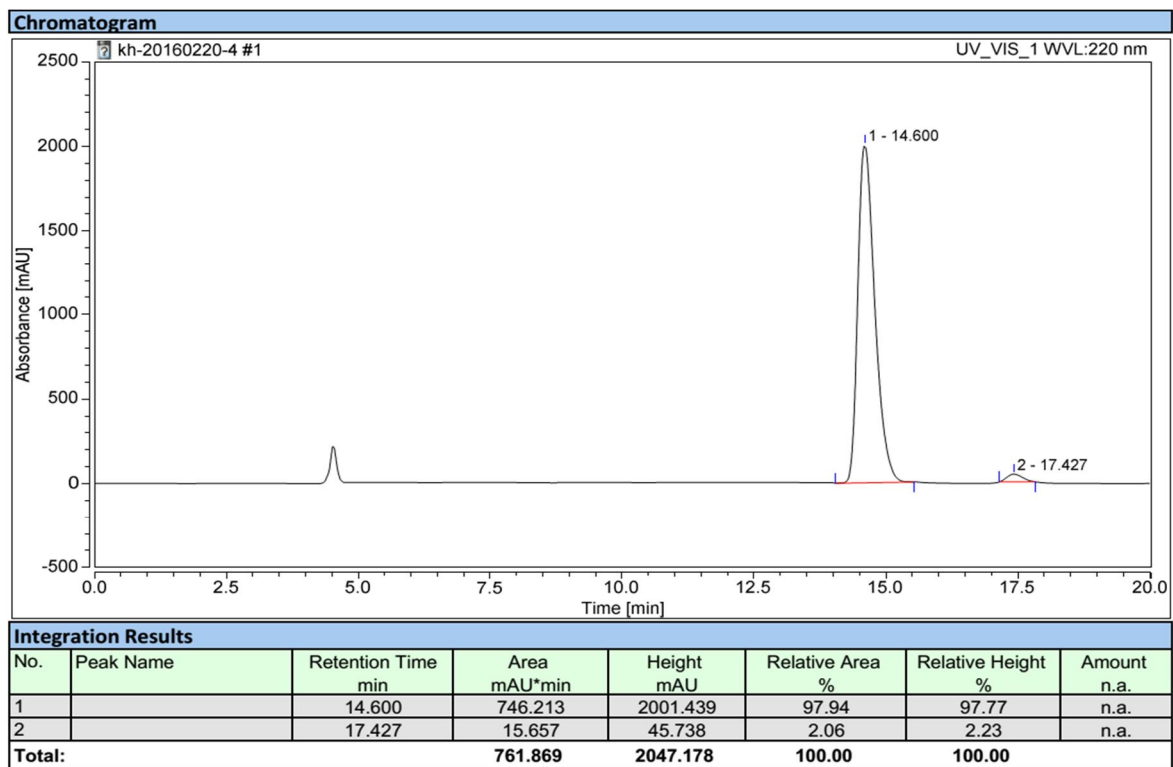
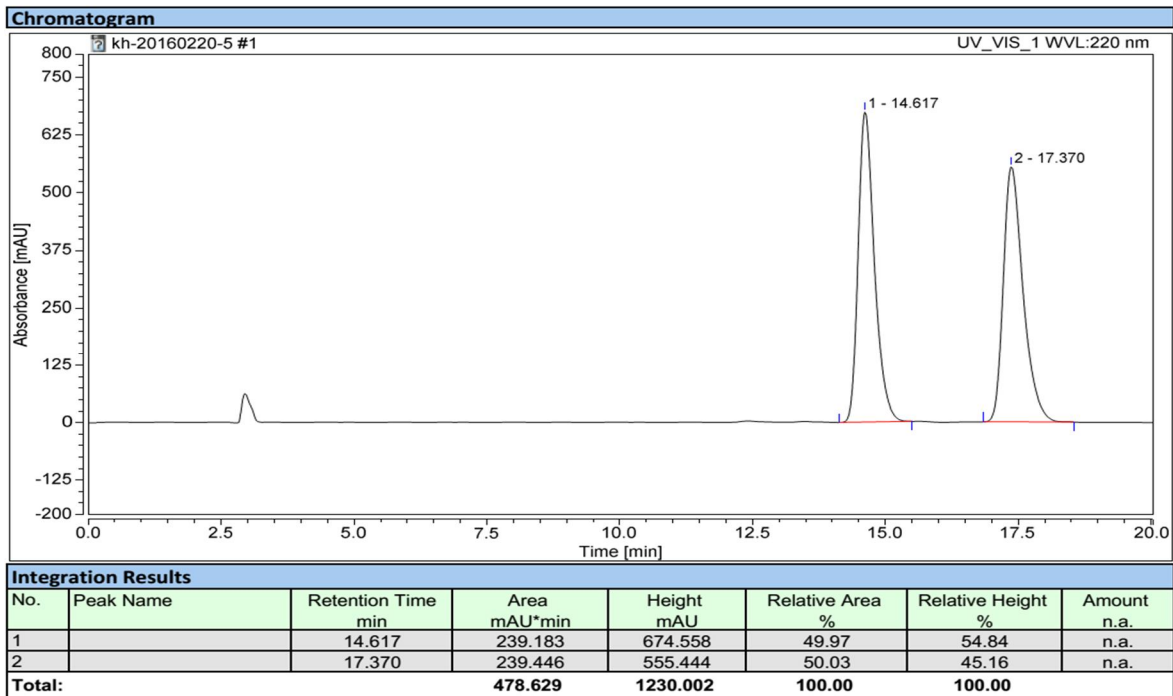
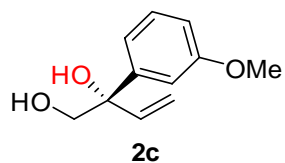
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.307	97.236	469.573	49.82	52.17	n.a.
2		10.317	97.927	430.437	50.18	47.83	n.a.
Total:			195.163	900.010	100.00	100.00	

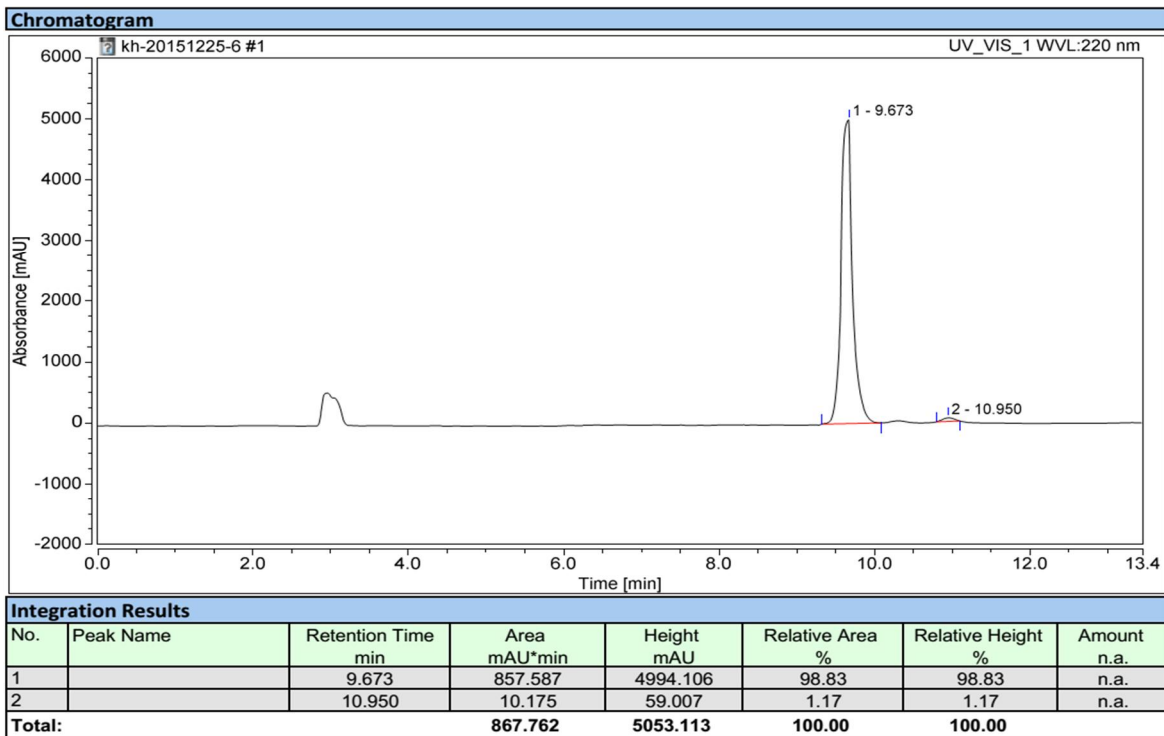
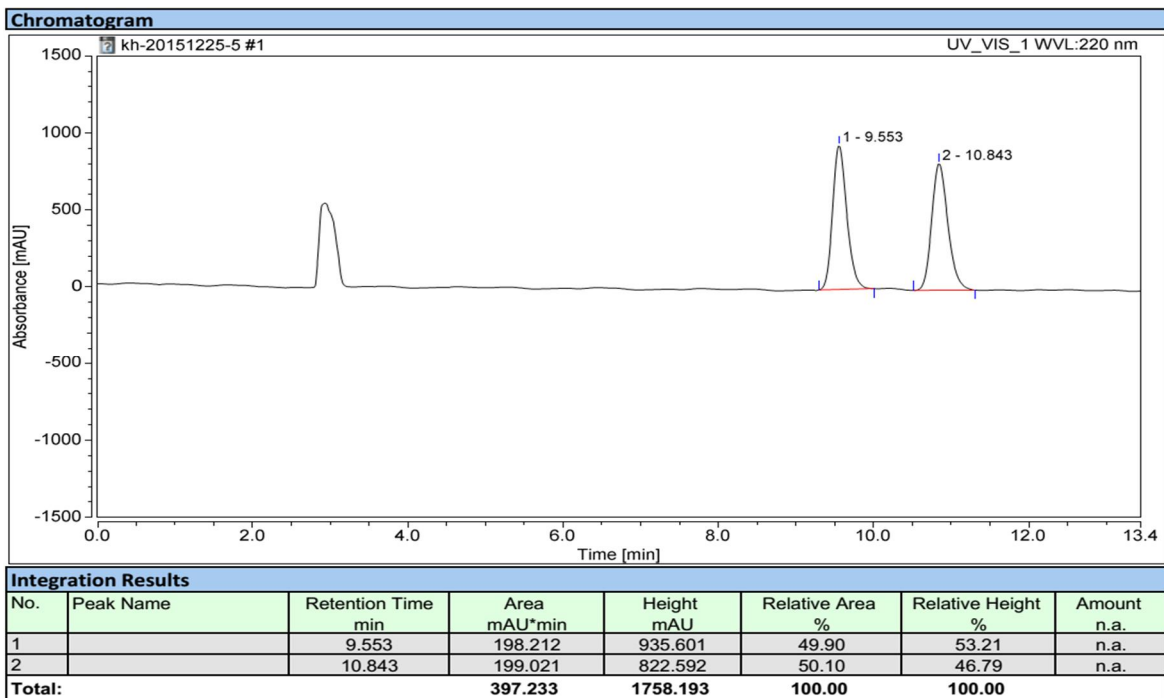
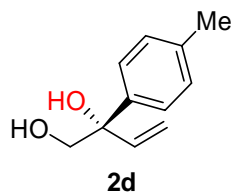


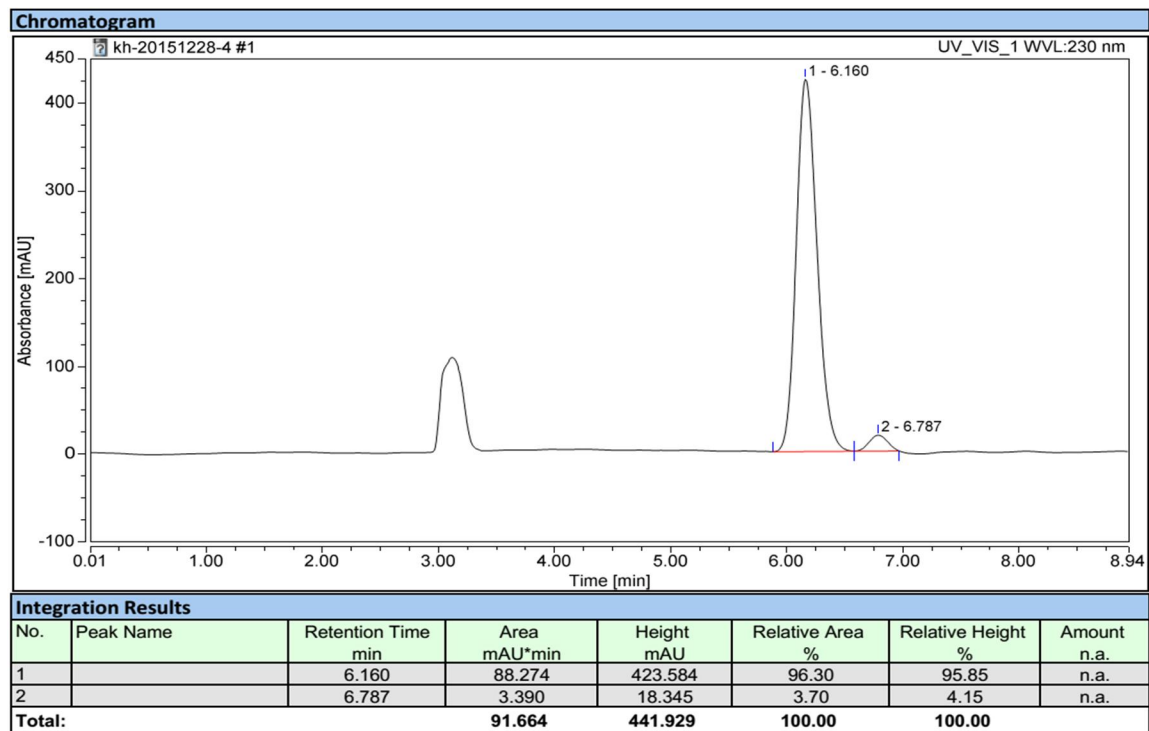
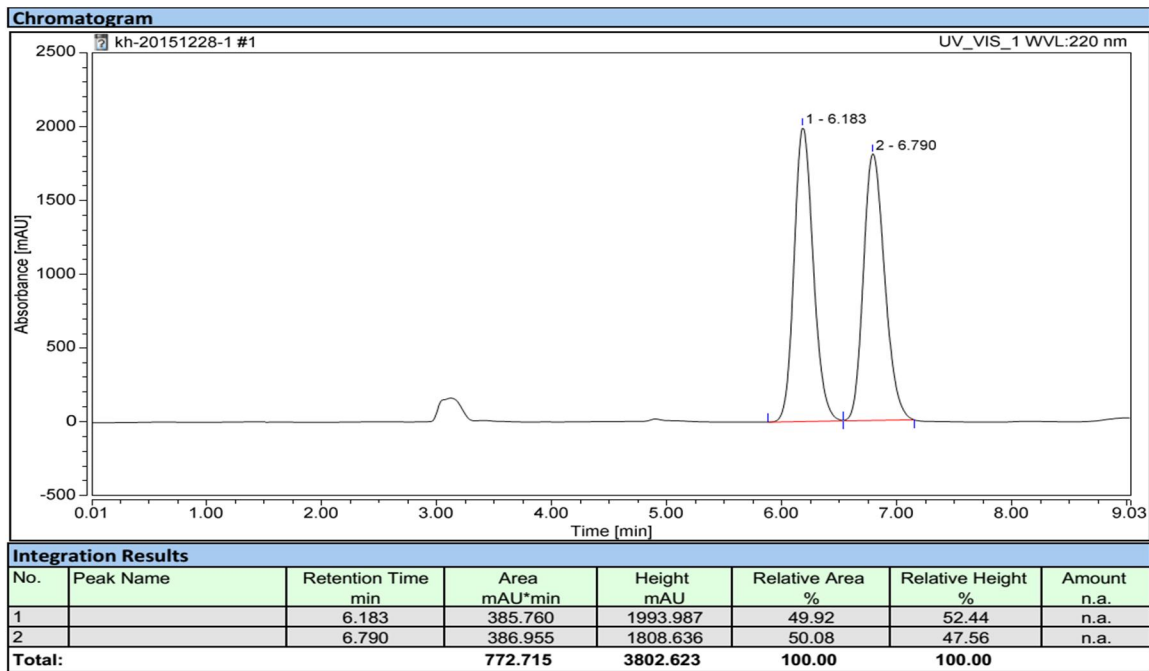
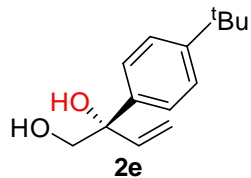
Integration Results

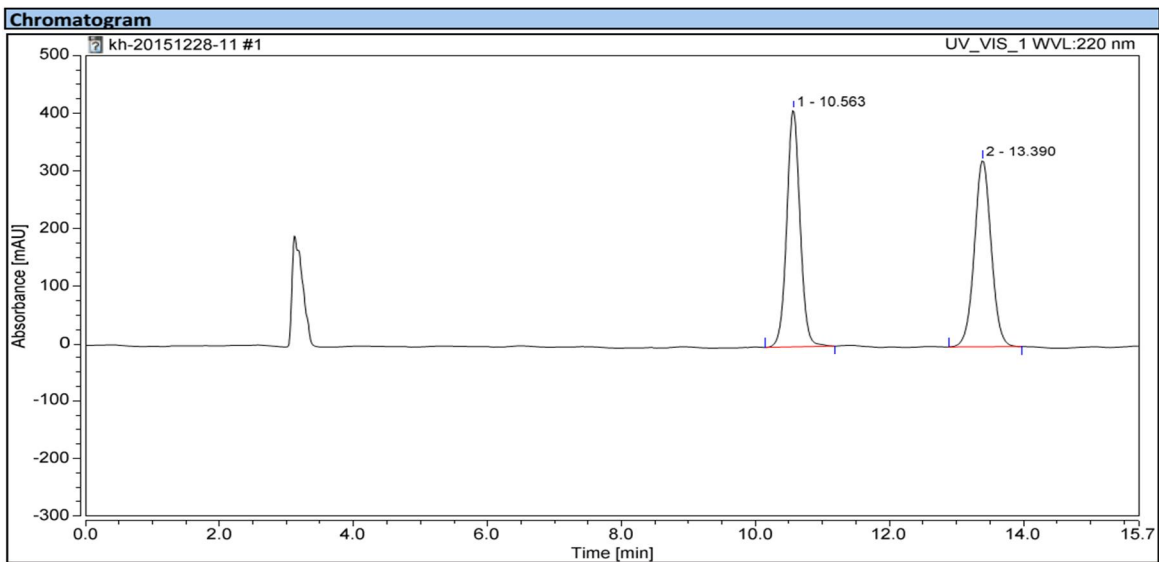
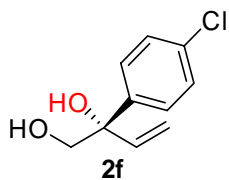
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.703	299.356	1221.307	97.46	96.98	n.a.
2		10.800	7.816	37.992	2.54	3.02	n.a.
Total:			307.172	1259.298	100.00	100.00	





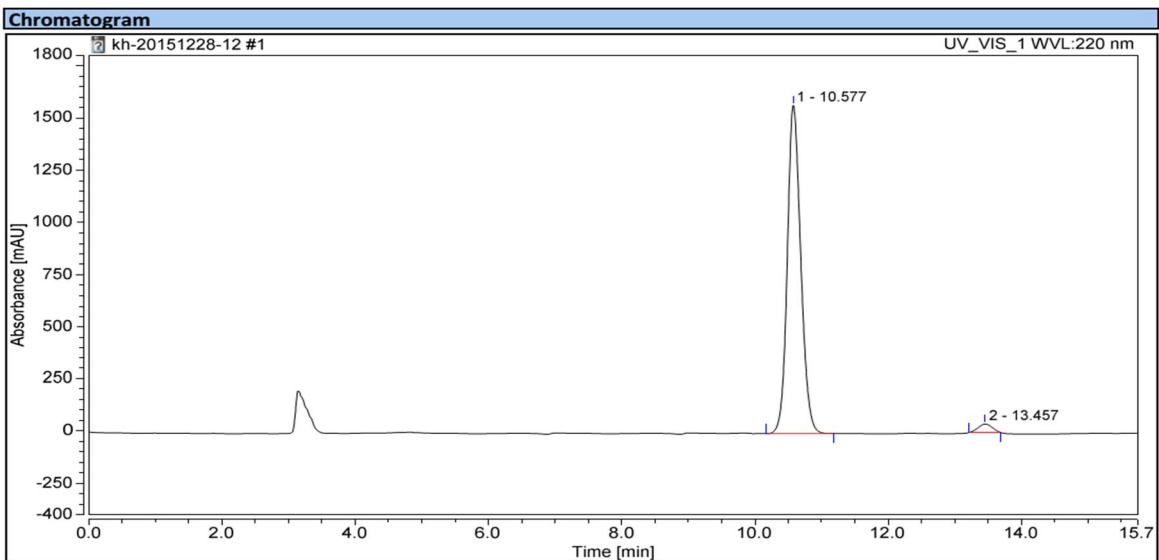






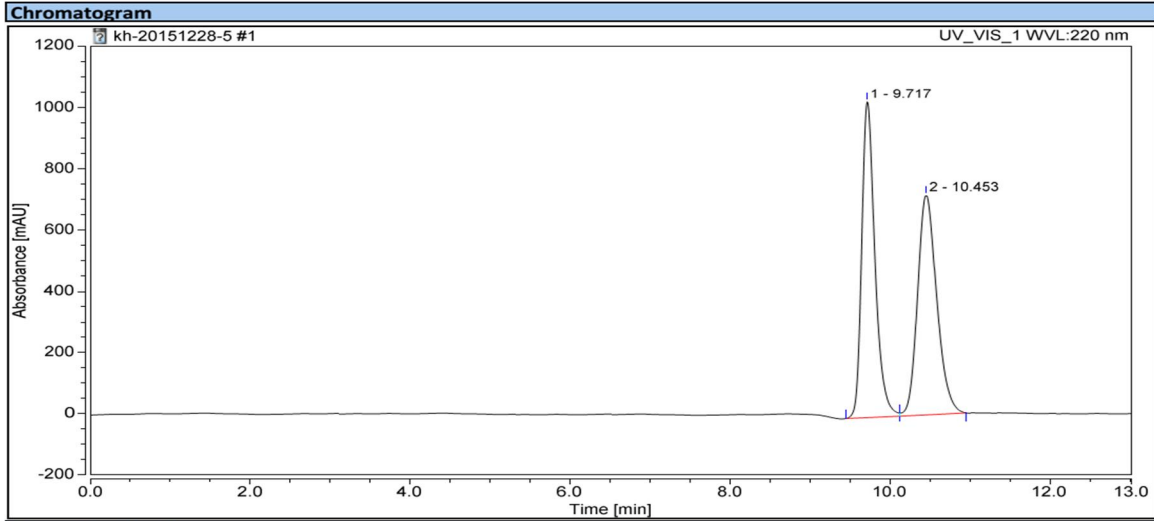
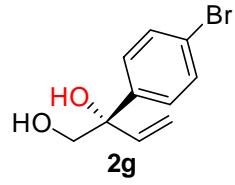
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.563	94.254	410.166	50.07	55.95	n.a.
2		13.390	94.002	322.974	49.93	44.05	n.a.
Total:			188.256	733.140	100.00	100.00	



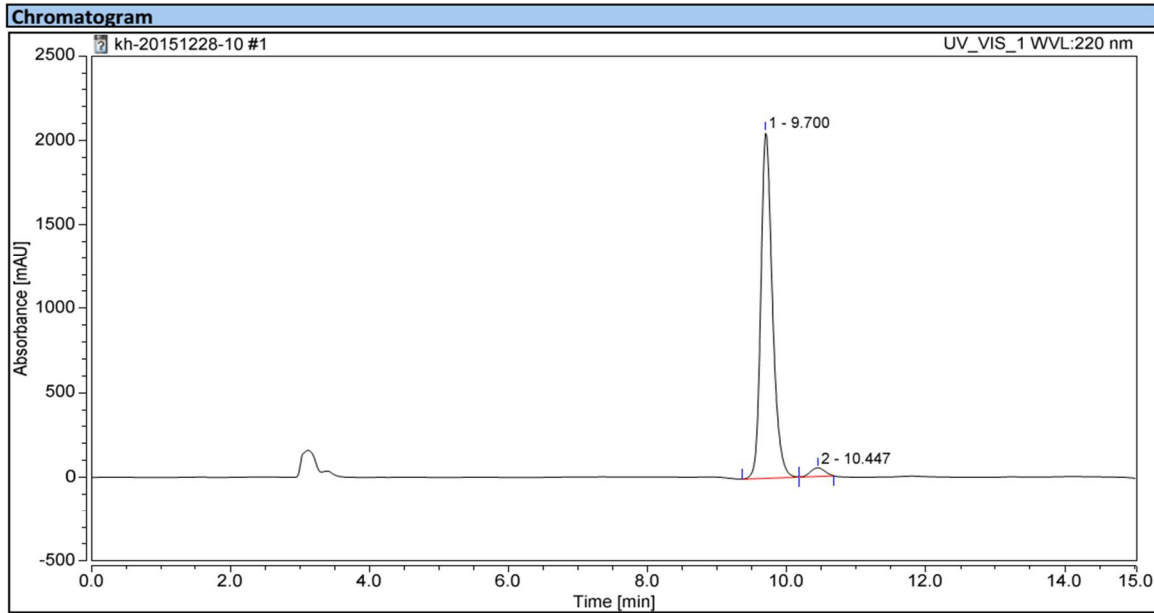
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.577	368.261	1573.874	97.37	97.50	n.a.
2		13.457	9.931	40.418	2.63	2.50	n.a.
Total:			378.192	1614.292	100.00	100.00	



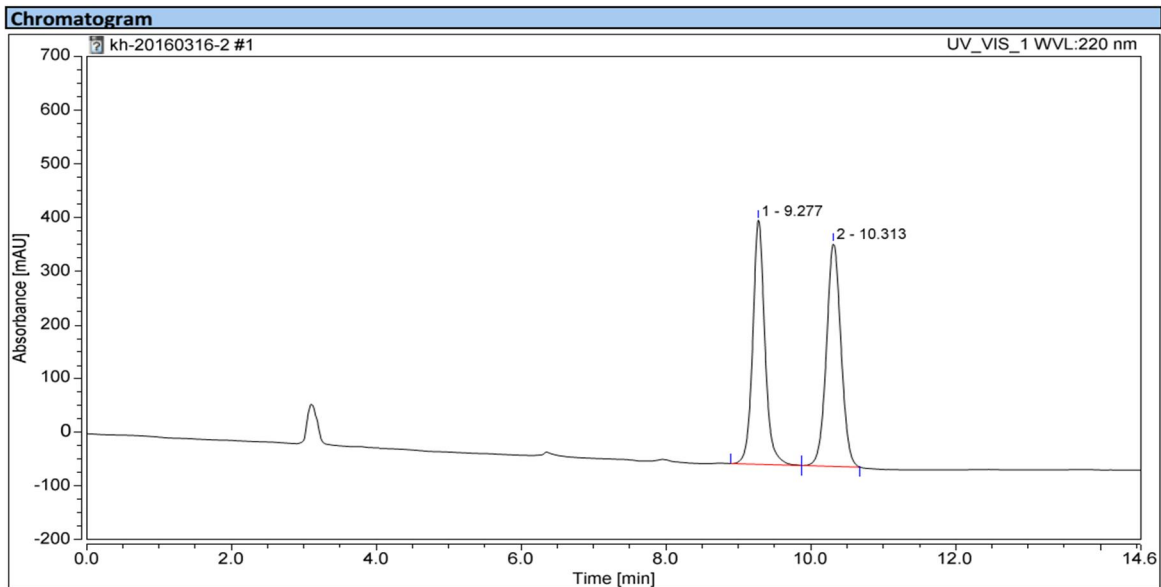
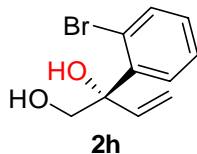
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.717	198.815	1032.340	49.94	58.93	n.a.
2		10.453	199.302	719.564	50.06	41.07	n.a.
Total:			398.117	1751.904	100.00	100.00	



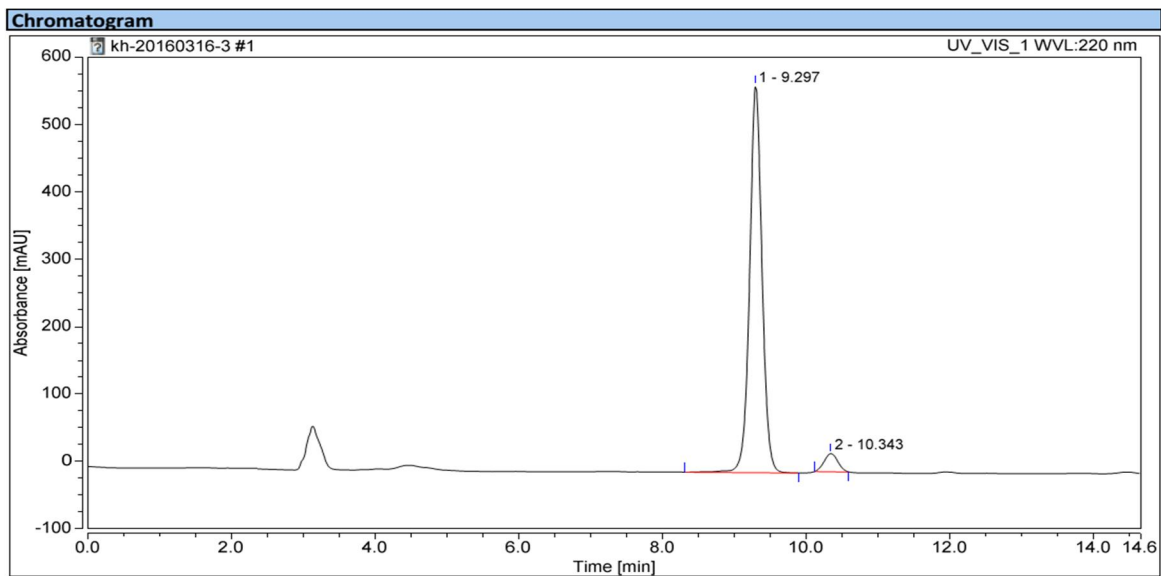
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.700	395.859	2053.104	97.04	97.56	n.a.
2		10.447	12.085	51.250	2.96	2.44	n.a.
Total:			407.944	2104.354	100.00	100.00	



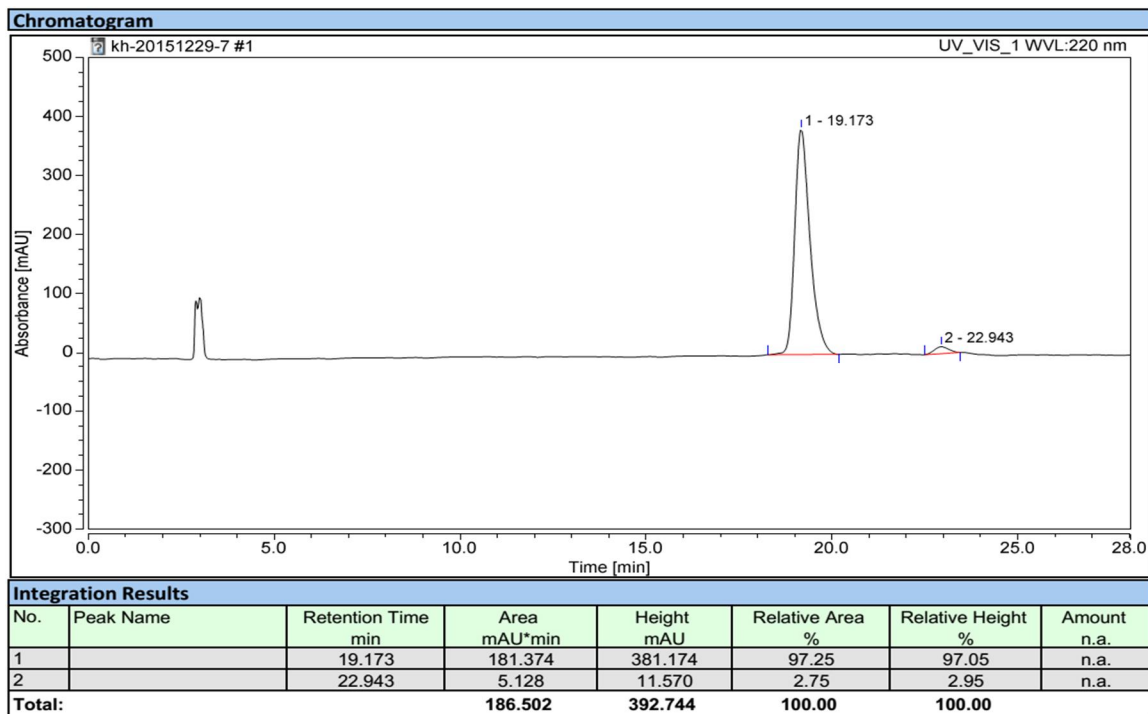
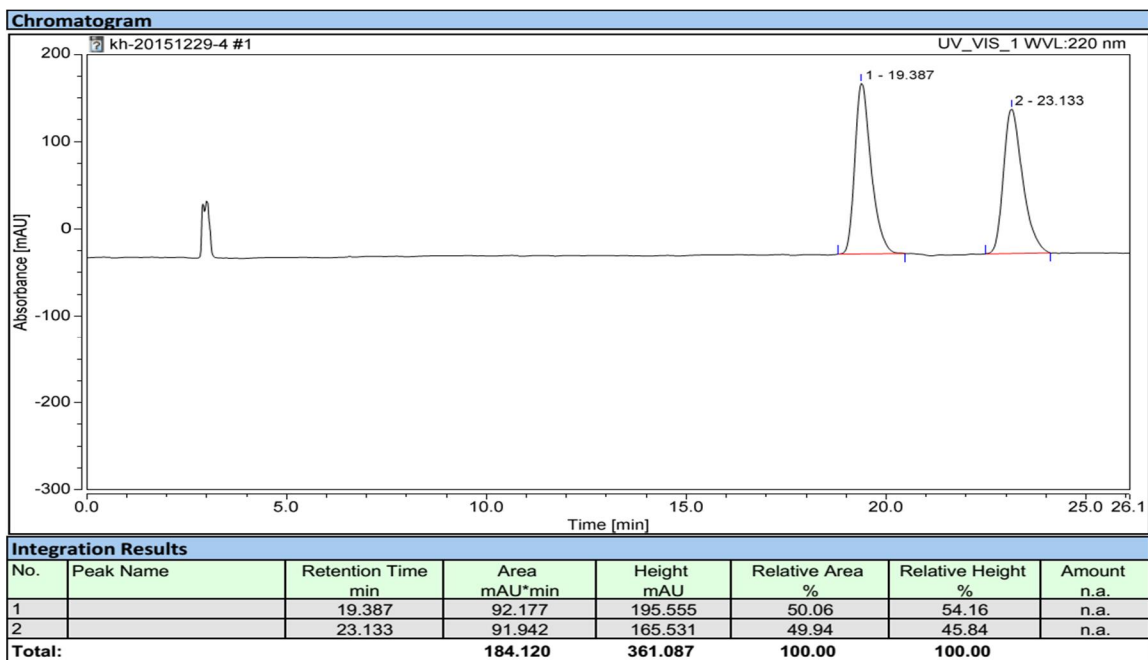
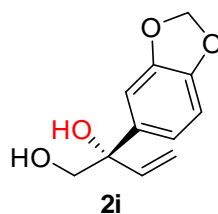
Integration Results

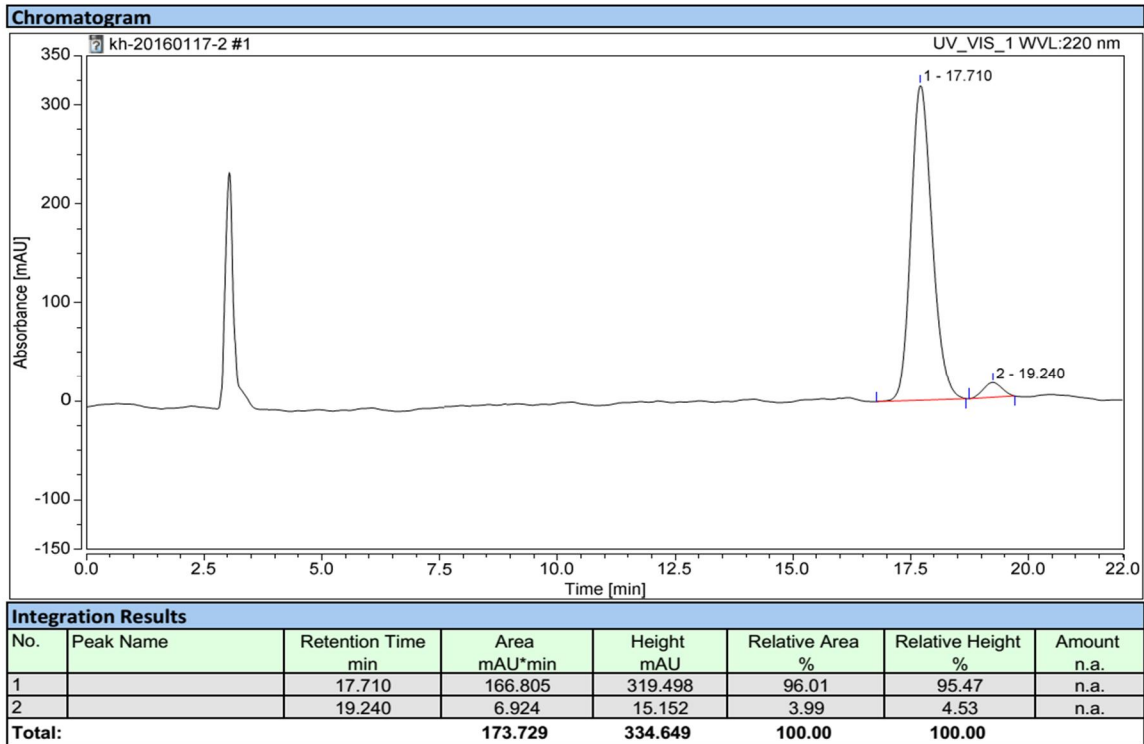
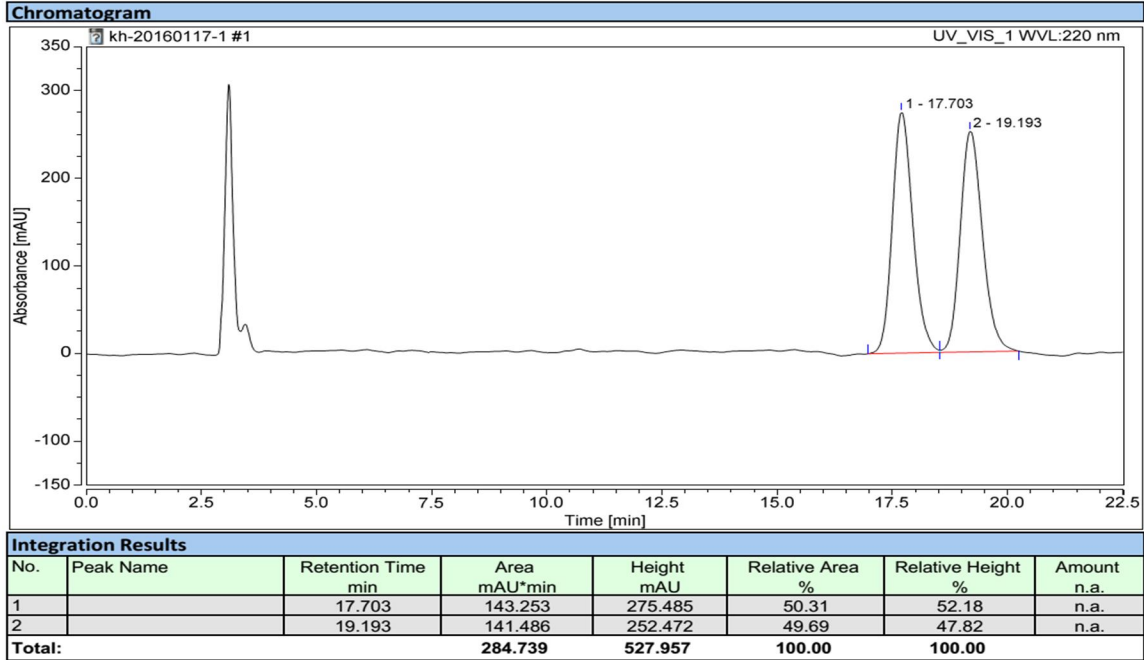
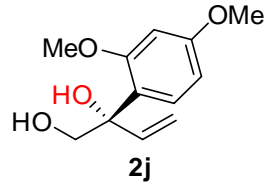
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.277	88.615	455.719	47.75	52.26	n.a.
2		10.313	96.978	416.330	52.25	47.74	n.a.
Total:			185.593	872.049	100.00	100.00	

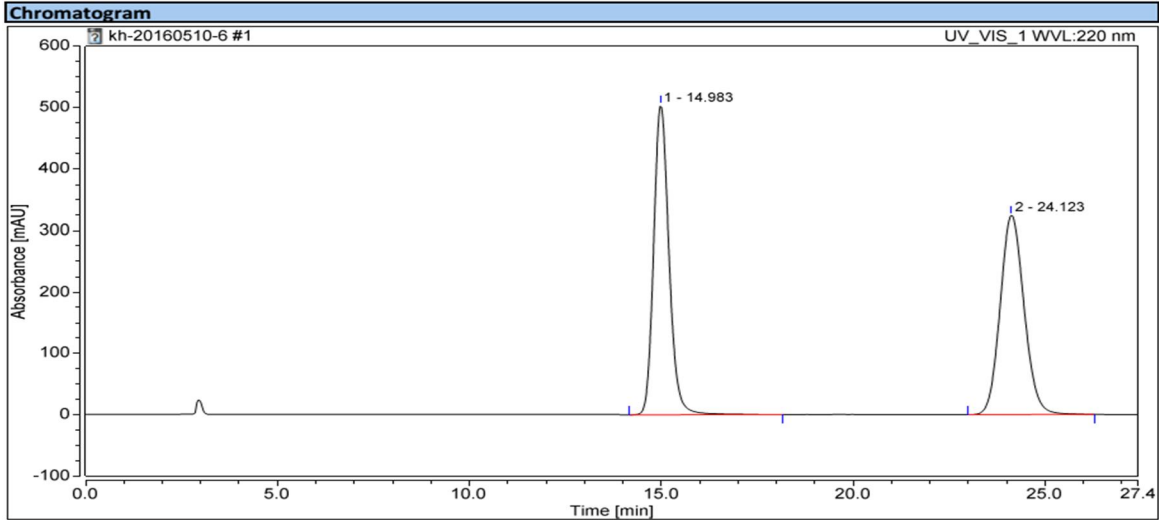
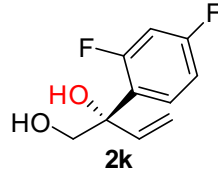


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.297	114.910	574.903	95.08	95.51	n.a.
2		10.343	5.942	27.031	4.92	4.49	n.a.
Total:			120.852	601.934	100.00	100.00	

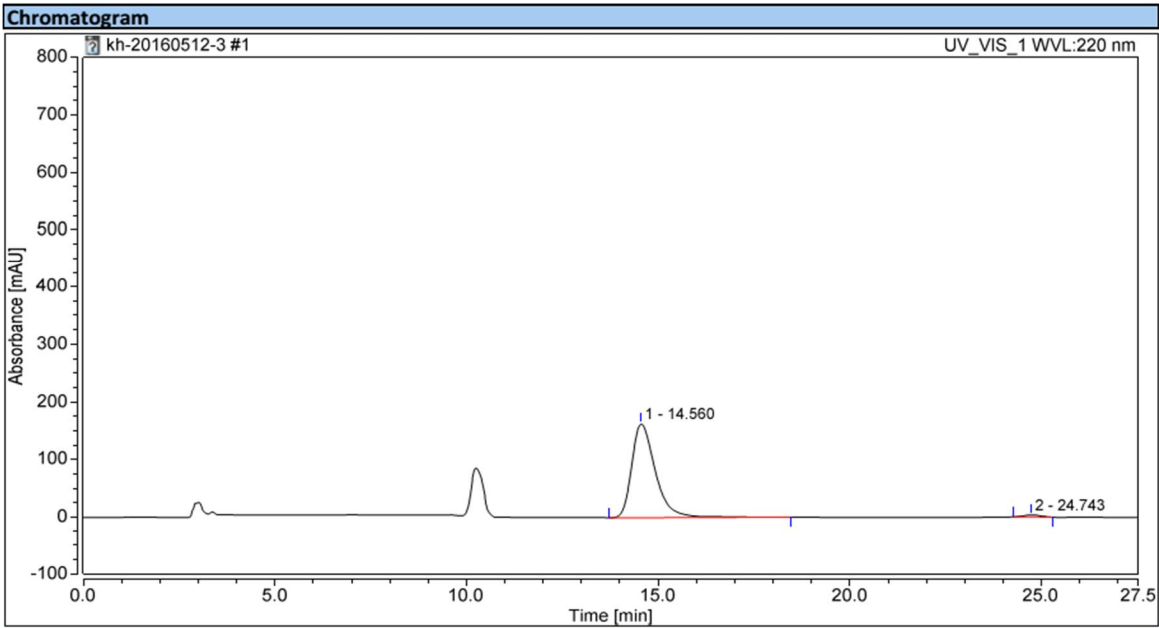






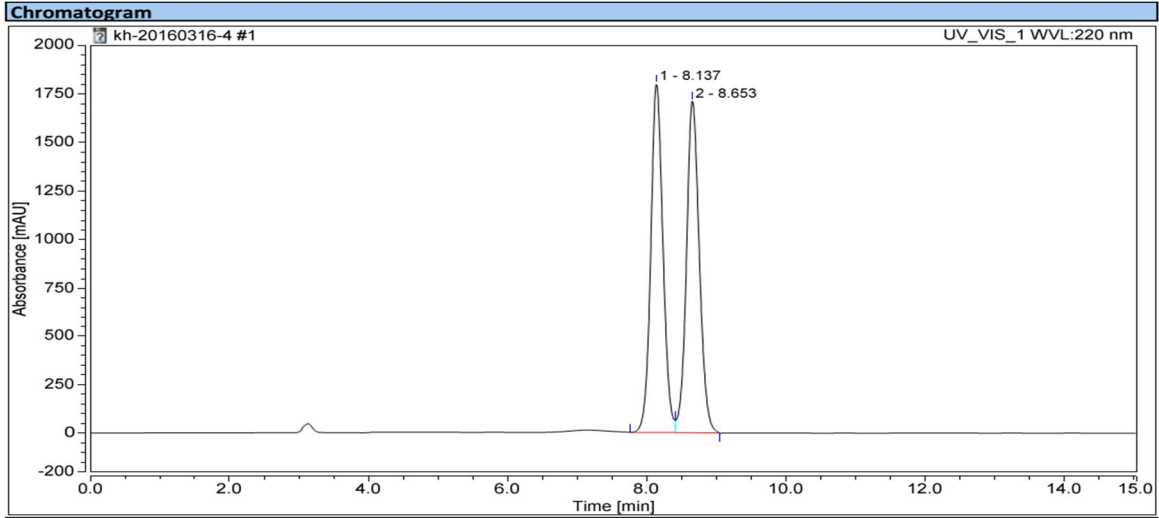
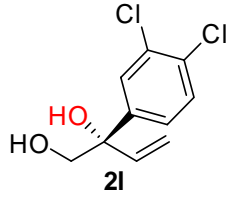
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.983	233.998	504.768	49.97	60.79	n.a.
2		24.123	234.241	325.511	50.03	39.21	n.a.
Total:			468.239	830.279	100.00	100.00	



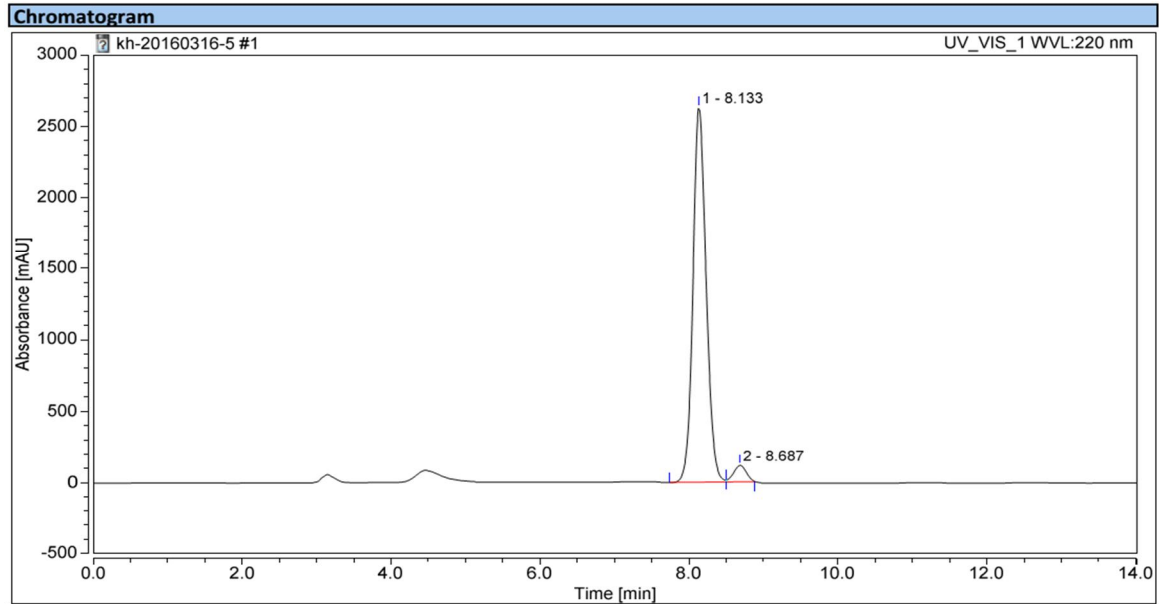
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.560	116.354	162.677	98.46	97.87	n.a.
2		24.743	1.817	3.539	1.54	2.13	n.a.
Total:			118.171	166.216	100.00	100.00	



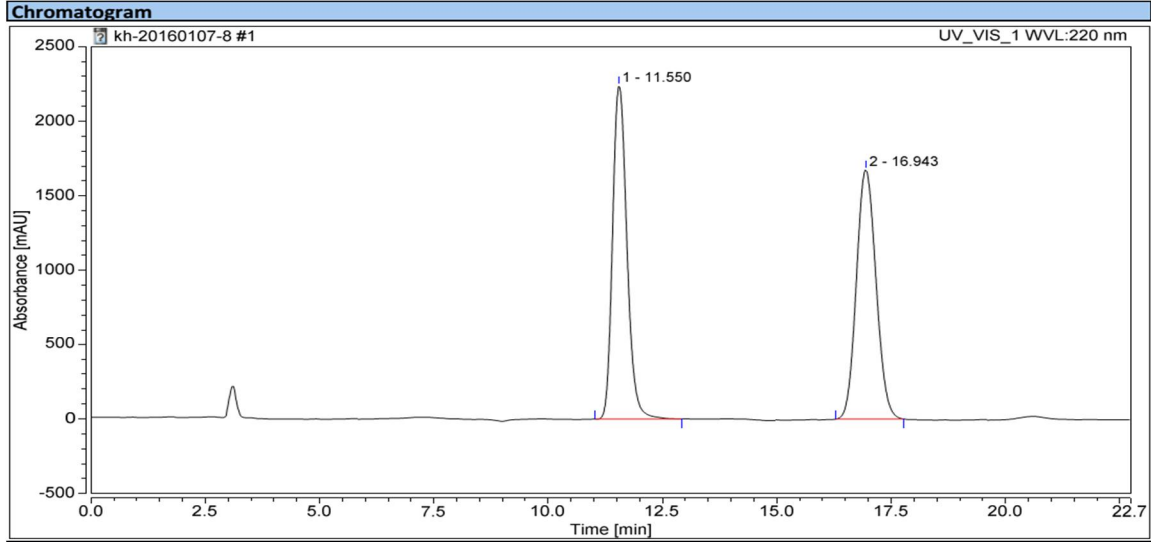
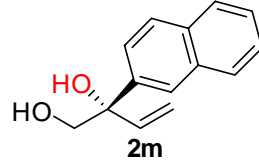
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		8.137	364.815	1799.574	49.89	51.25	n.a.
2		8.653	366.394	1711.668	50.11	48.75	n.a.
Total:			731.209	3511.242	100.00	100.00	



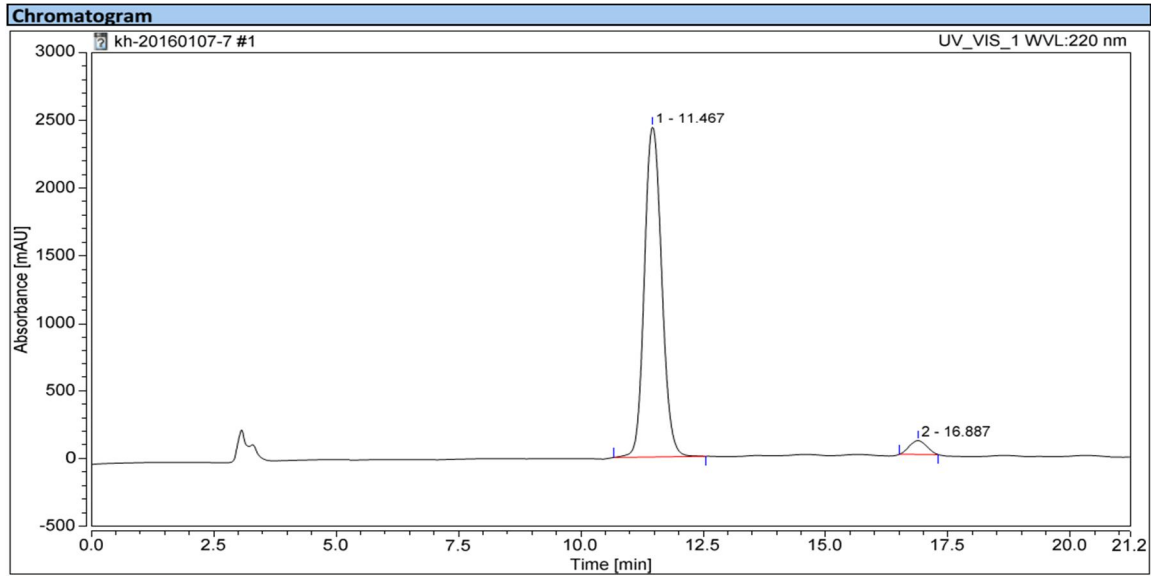
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		8.133	538.174	2629.487	95.97	95.81	n.a.
2		8.687	22.607	115.059	4.03	4.19	n.a.
Total:			560.780	2744.545	100.00	100.00	



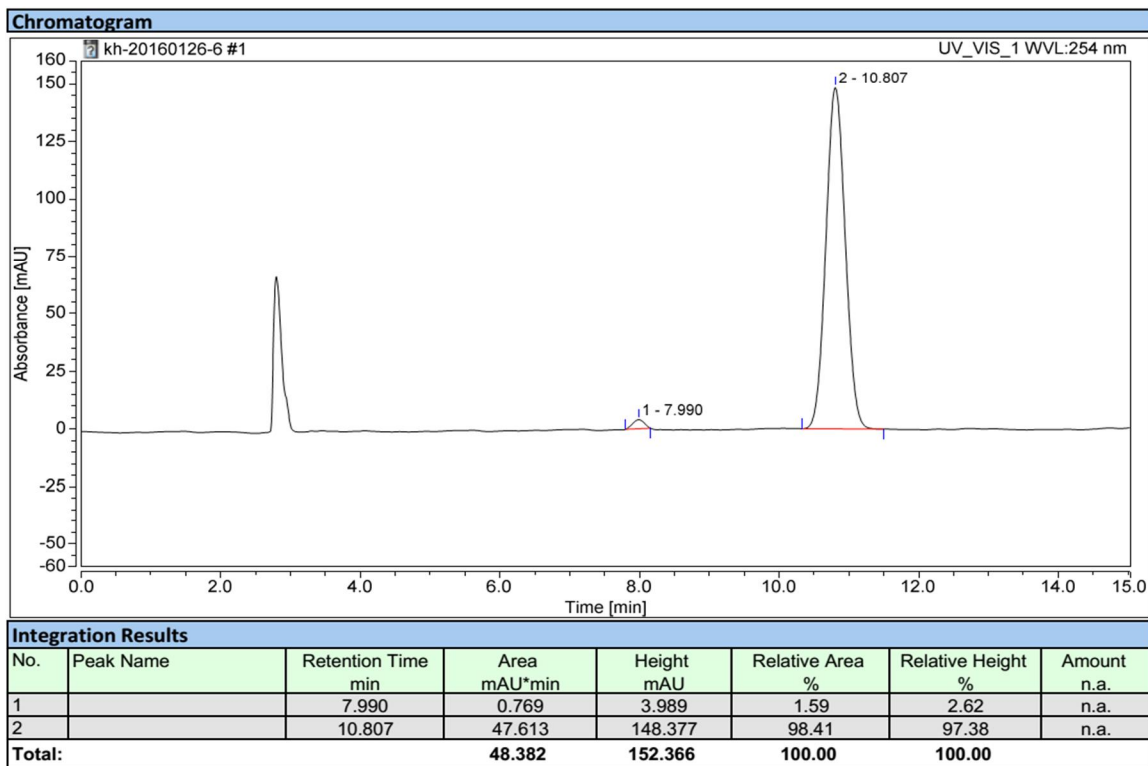
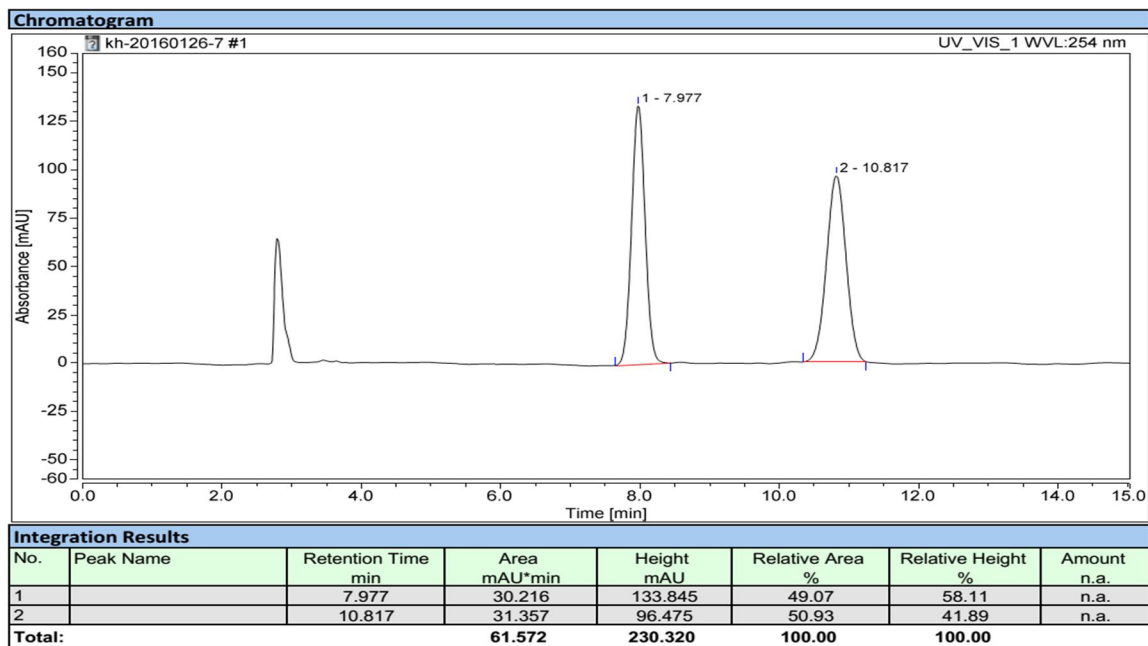
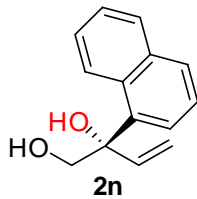
Integration Results

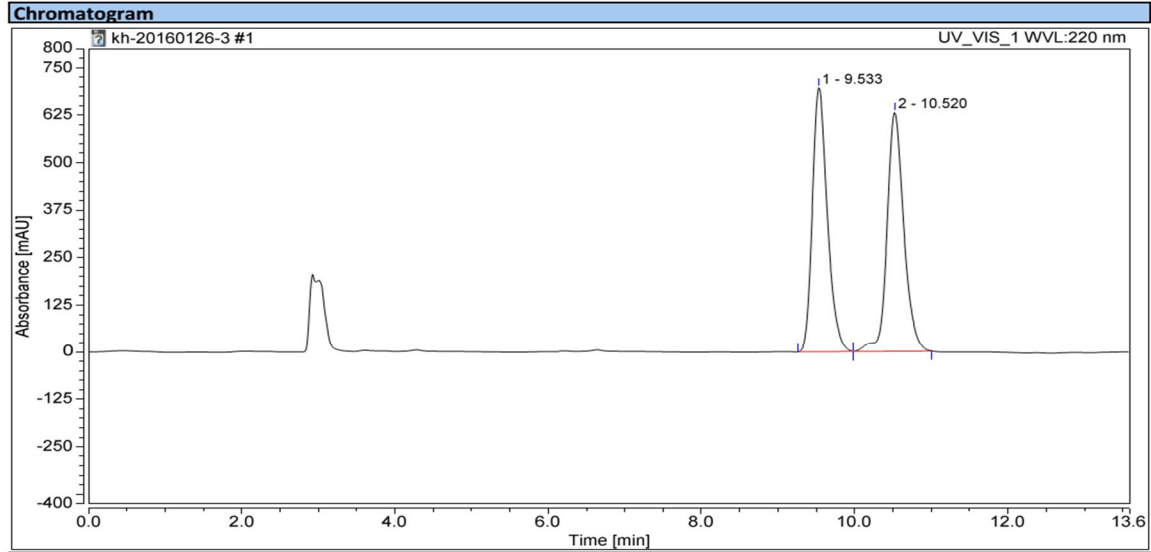
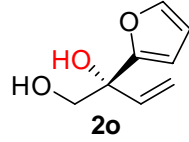
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.550	817.854	2239.847	49.45	57.19	n.a.
2		16.943	835.900	1676.711	50.55	42.81	n.a.
Total:			1653.754	3916.557	100.00	100.00	



Integration Results

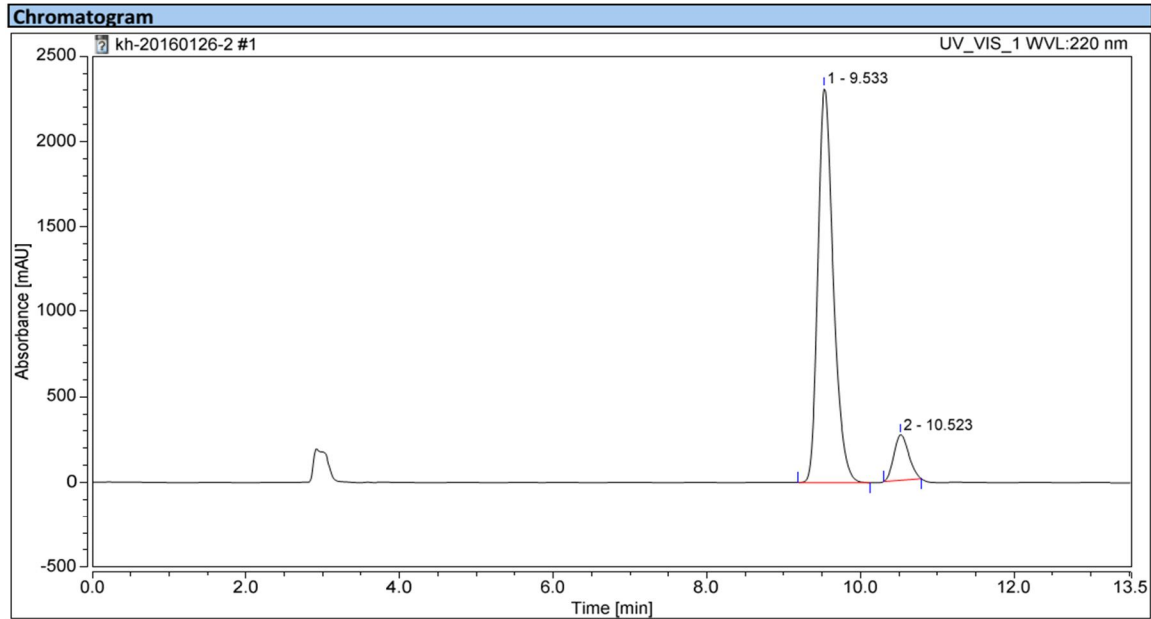
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.467	1000.683	2437.800	96.02	96.03	n.a.
2		16.887	41.428	100.703	3.98	3.97	n.a.
Total:			1042.111	2538.503	100.00	100.00	





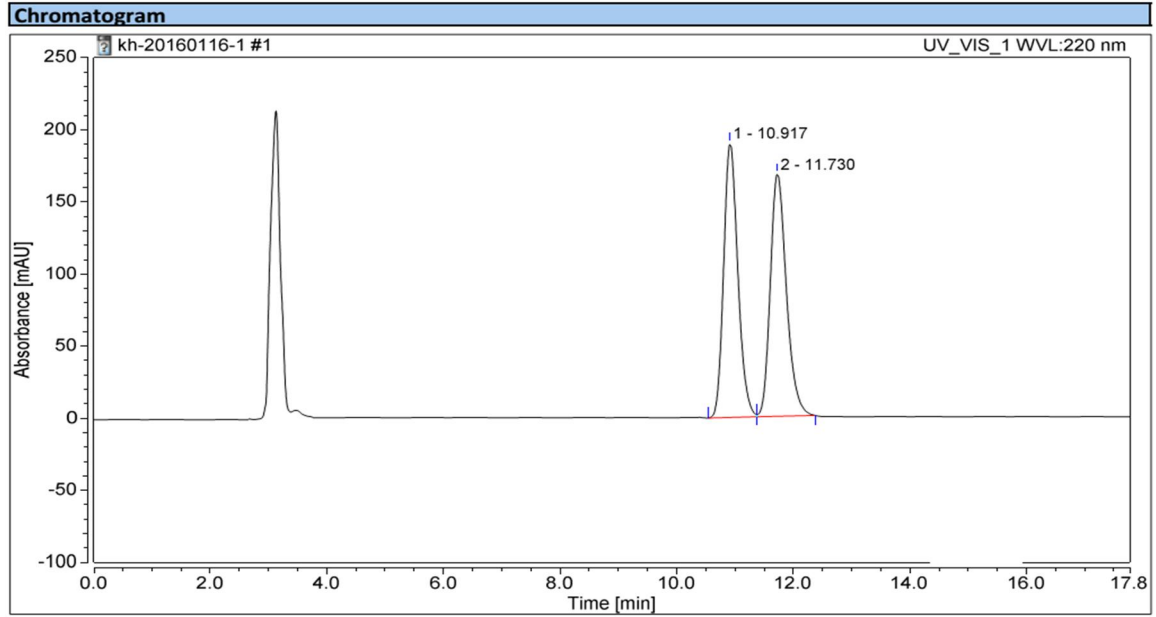
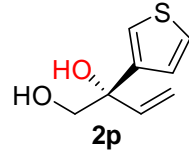
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.533	158.036	697.151	49.57	52.46	n.a.
2		10.520	160.785	631.660	50.43	47.54	n.a.
Total:			318.821	1328.811	100.00	100.00	



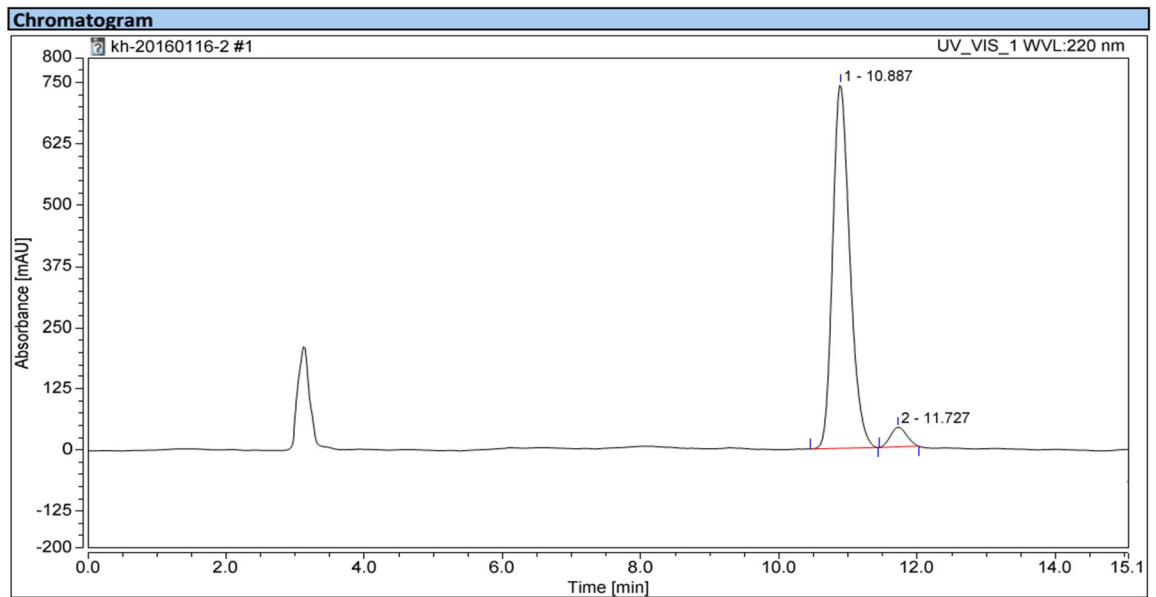
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.533	536.845	2315.665	90.04	89.68	n.a.
2		10.523	59.397	266.543	9.96	10.32	n.a.
Total:			596.242	2582.208	100.00	100.00	



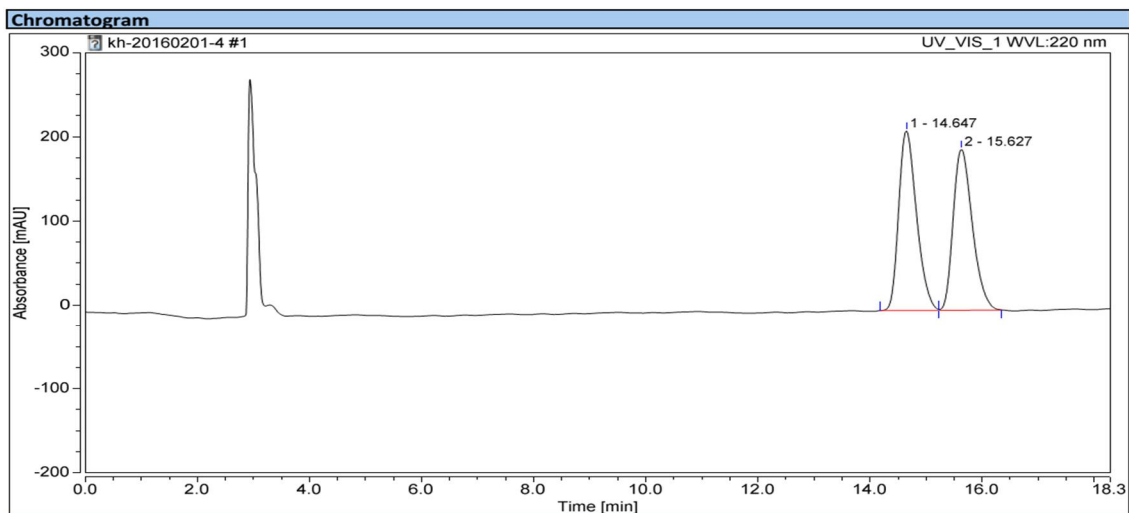
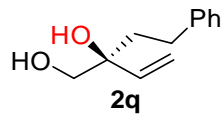
SST Results

No.	Name	Inj.Condition	Peak	Test Result	Injection
Number of executed test cases: n.a.			Total Result:	Passed	



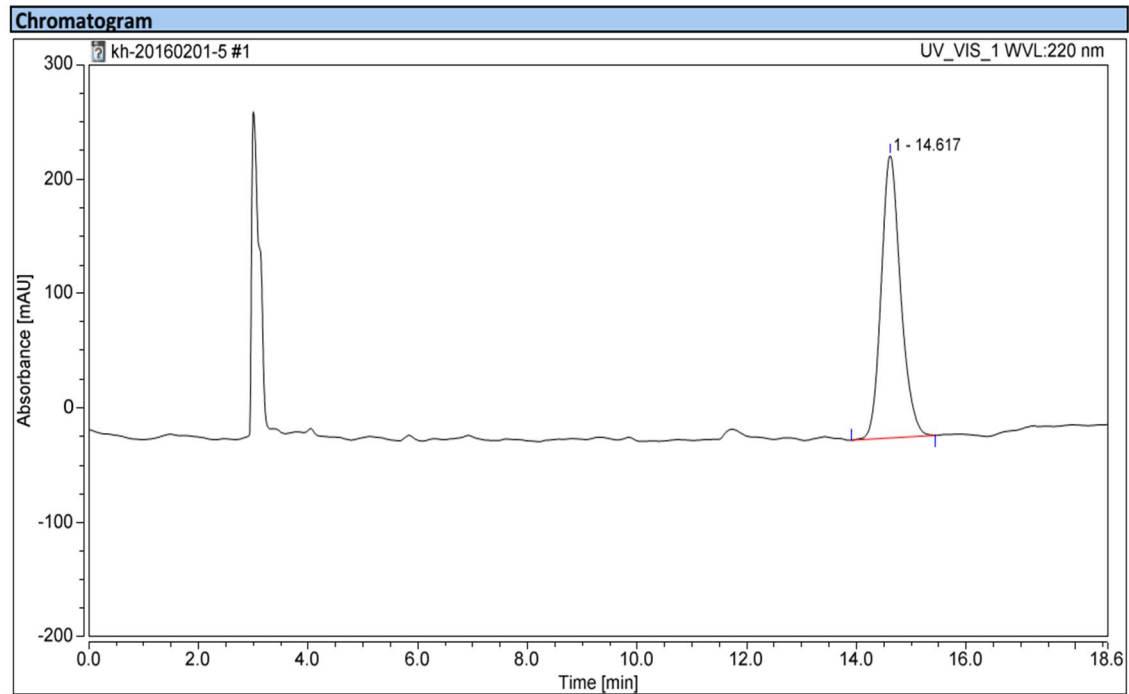
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.887	213.996	742.366	95.17	94.91	n.a.
2		11.727	10.856	39.782	4.83	5.09	n.a.
Total:			224.852	782.148	100.00	100.00	



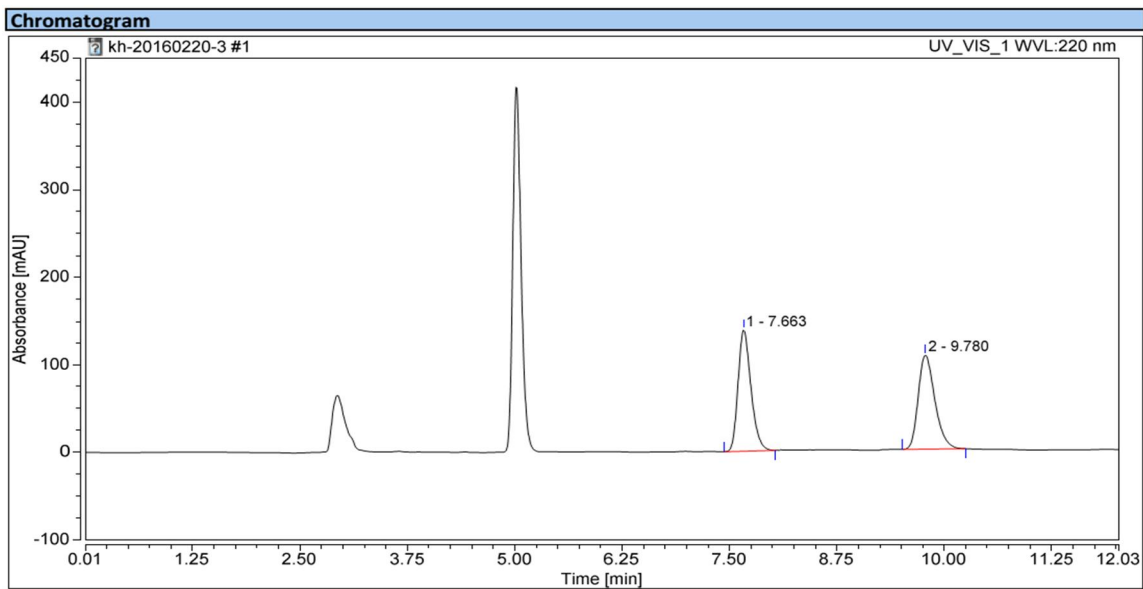
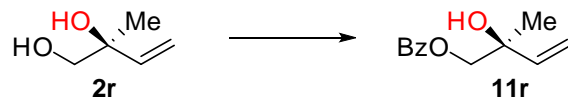
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.647	78.577	213.107	50.94	52.73	n.a.
2		15.627	75.666	191.047	49.06	47.27	n.a.
Total:			154.242	404.153	100.00	100.00	



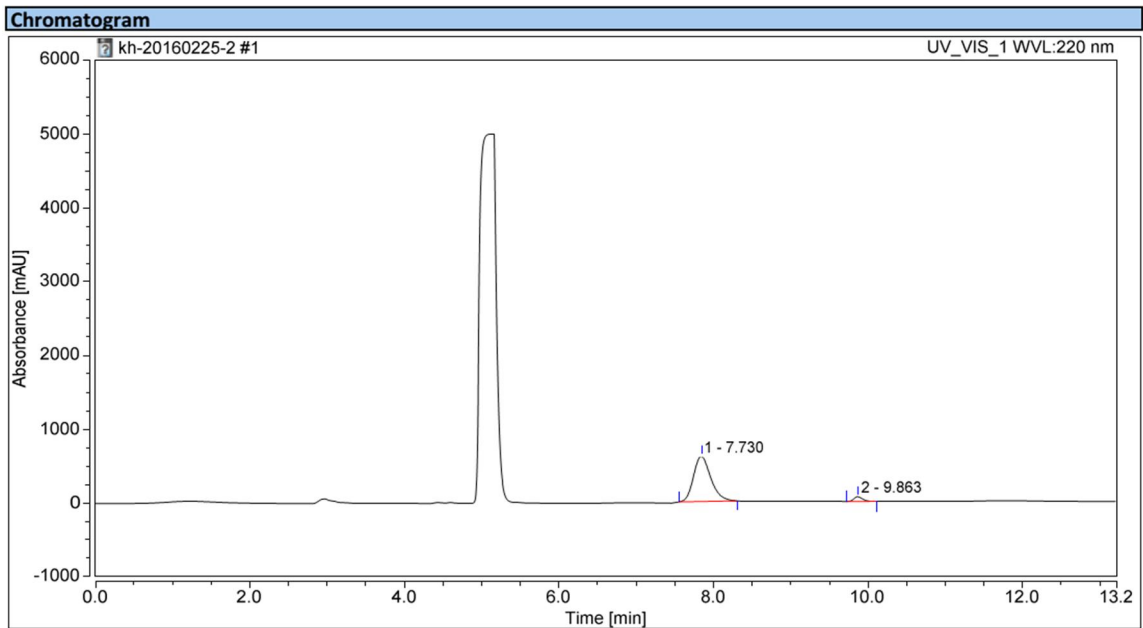
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.617	101.318	247.088	100.00	100.00	n.a.
Total:			101.318	247.088	100.00	100.00	



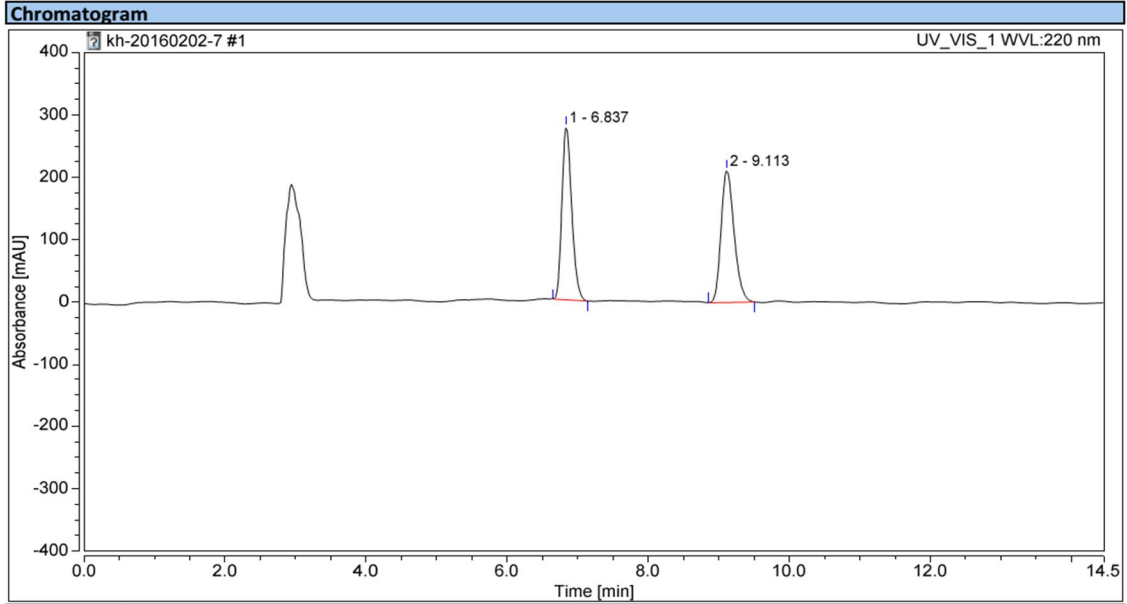
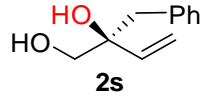
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.663	24.212	139.193	50.00	56.21	n.a.
2		9.780	24.210	108.430	50.00	43.79	n.a.
Total:			48.422	247.623	100.00	100.00	



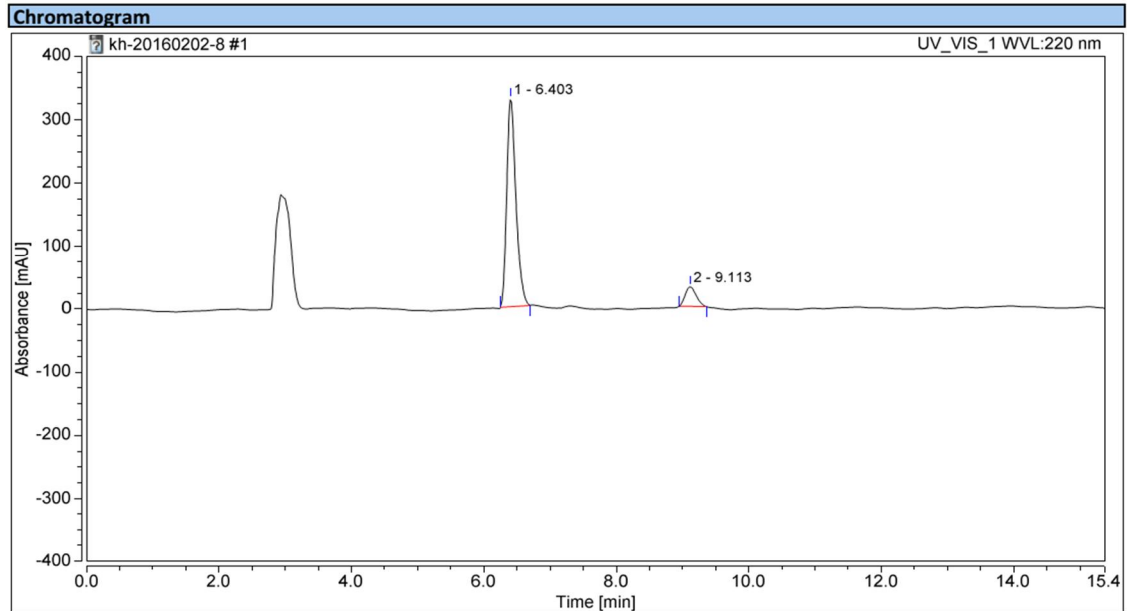
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.730	9.882	56.354	91.61	86.77	n.a.
2		9.863	0.905	8.596	8.39	13.23	n.a.
Total:			10.787	64.950	100.00	100.00	



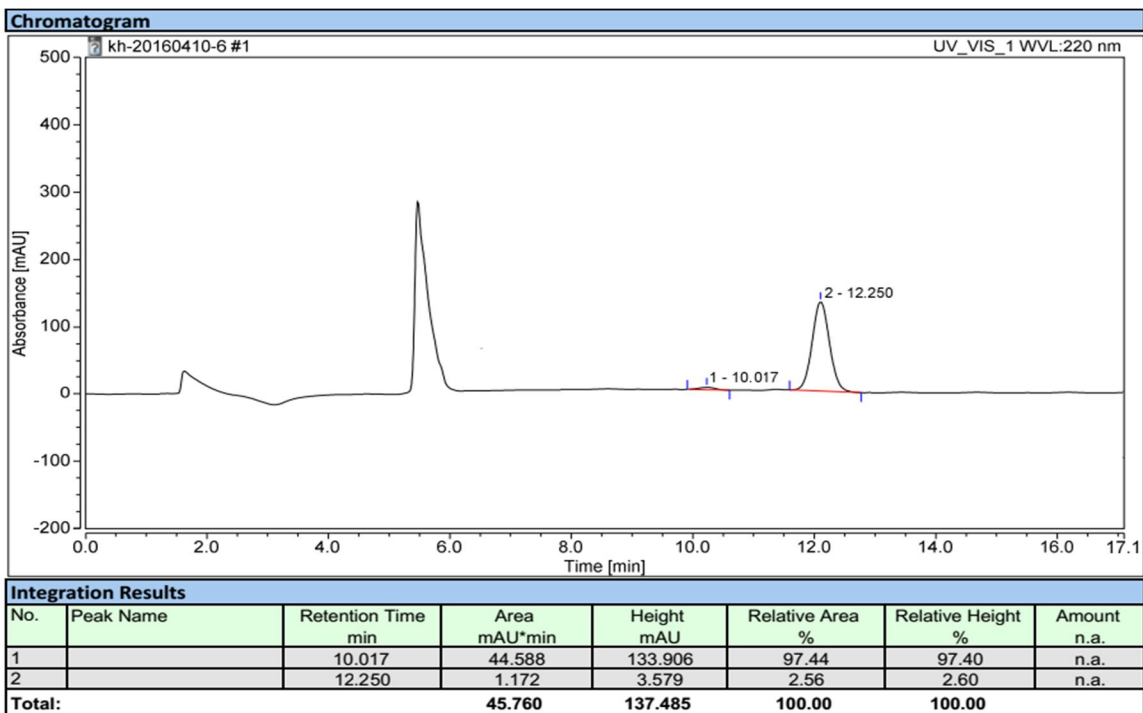
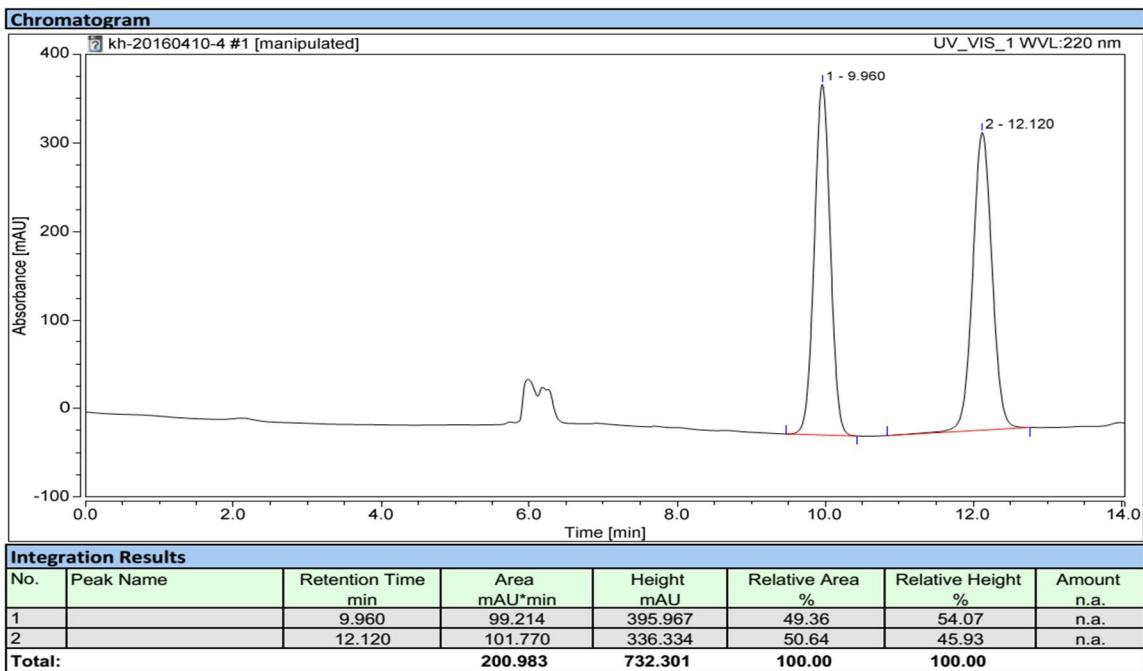
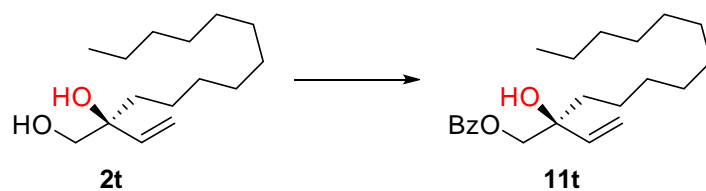
Integration Results

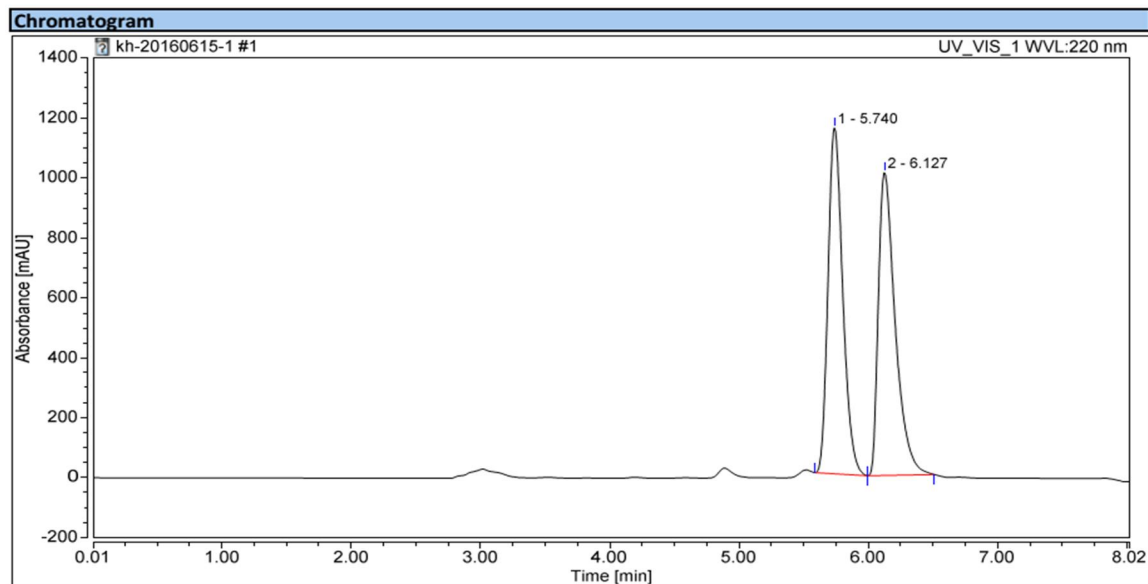
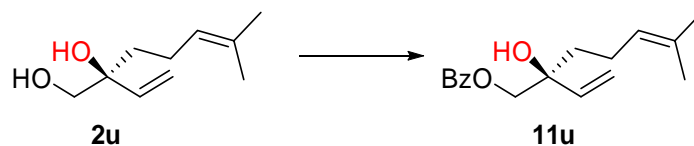
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.837	44.538	277.234	49.62	56.75	n.a.
2		9.113	45.225	211.280	50.38	43.25	n.a.
Total:			89.763	488.515	100.00	100.00	



Integration Results

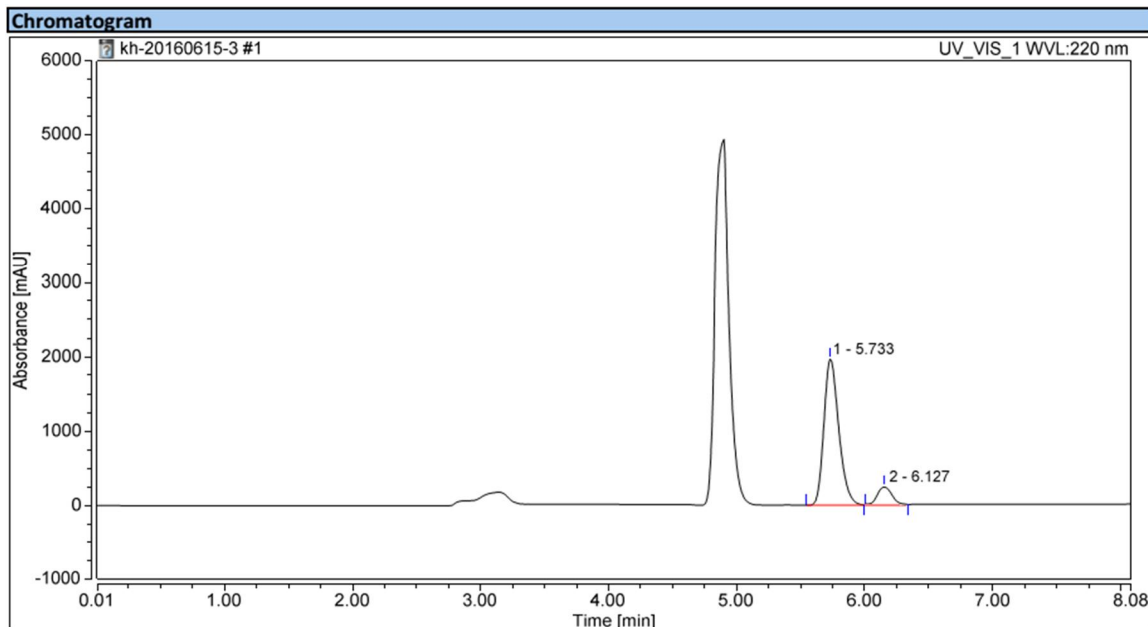
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.403	53.033	329.148	89.83	91.32	n.a.
2		9.113	6.001	31.301	10.17	8.68	n.a.
Total:			59.034	360.449	100.00	100.00	





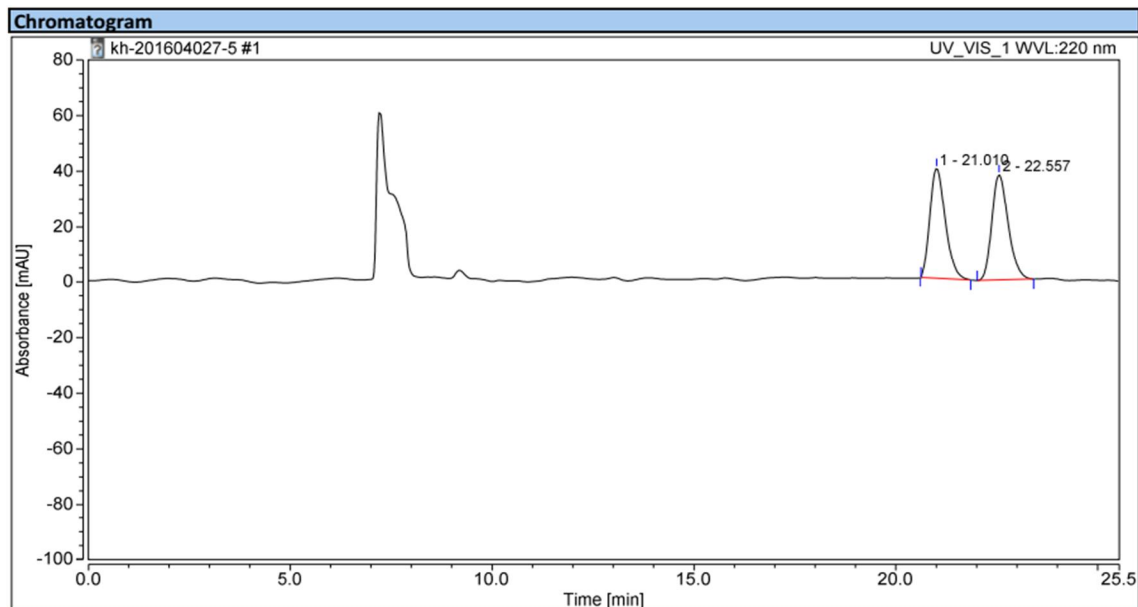
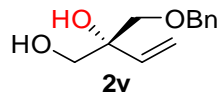
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.740	152.537	1156.872	49.96	53.31	n.a.
2		6.127	152.809	1013.222	50.04	46.69	n.a.
Total:			305.345	2170.094	100.00	100.00	



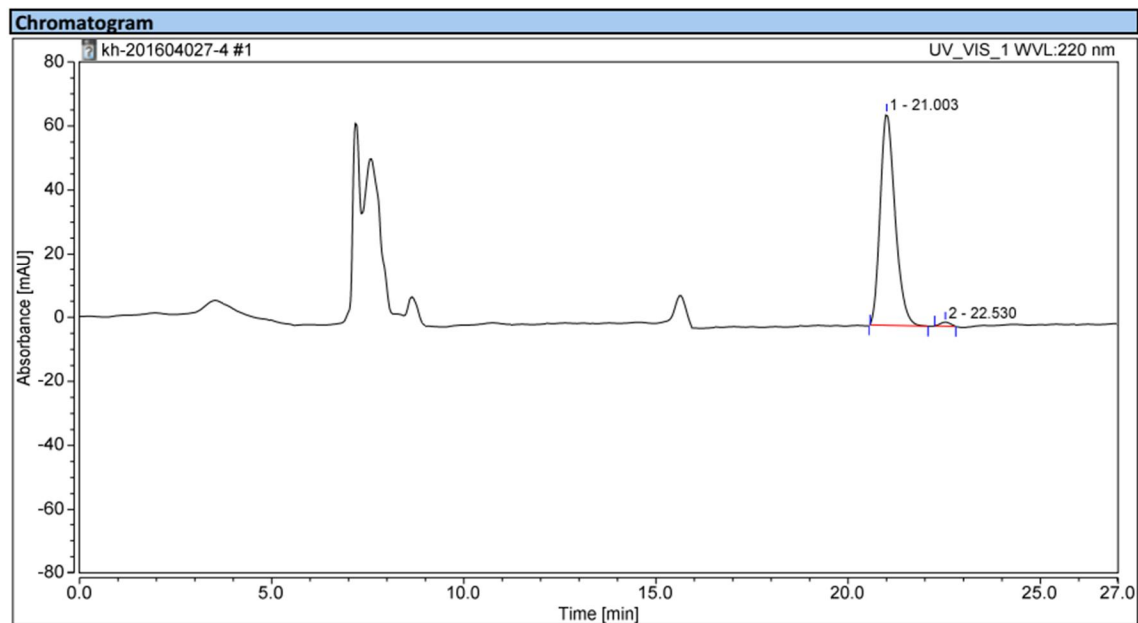
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.733	175.108	727.592	92.61	90.23	n.a.
2		6.127	13.975	78.759	7.39	9.77	n.a.
Total:			385.772	2748.487	100.00	100.00	



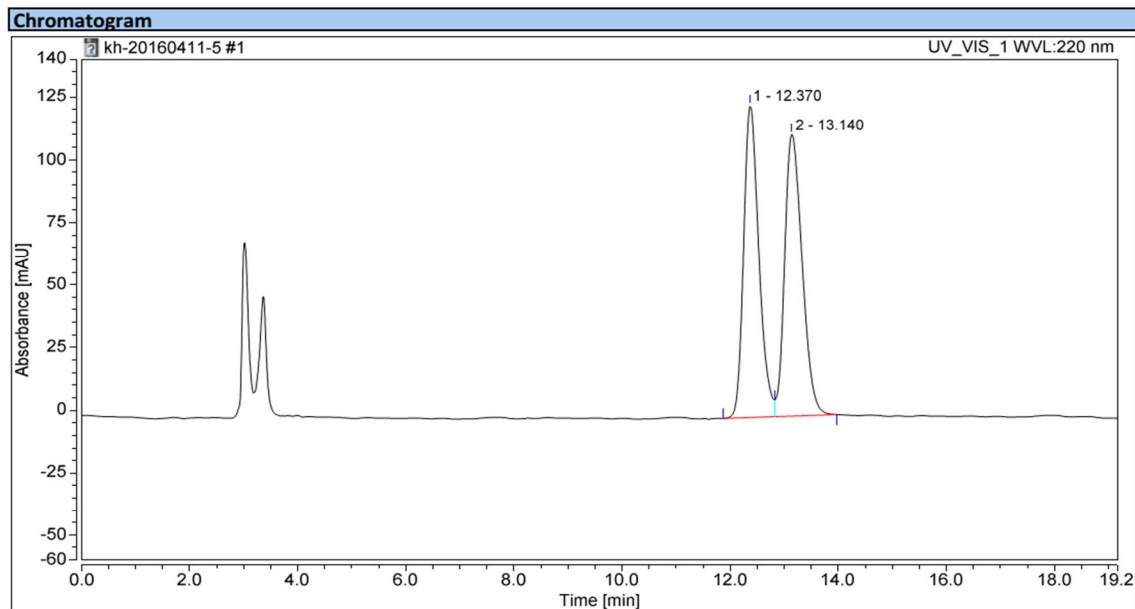
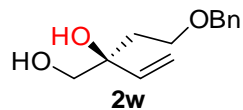
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.010	17.698	39.692	49.57	51.05	n.a.
2		22.557	18.003	38.064	50.43	48.95	n.a.
Total:			35.701	77.756	100.00	100.00	



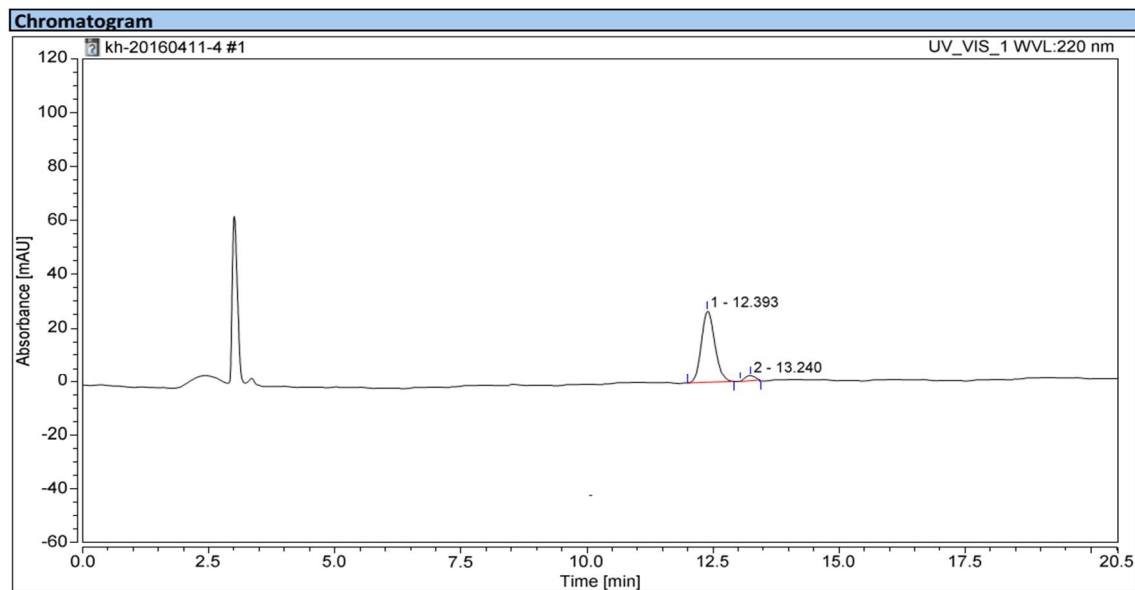
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.003	29.856	66.196	98.75	98.17	n.a.
2		22.530	0.378	1.231	1.25	1.83	n.a.
Total:			30.233	67.427	100.00	100.00	



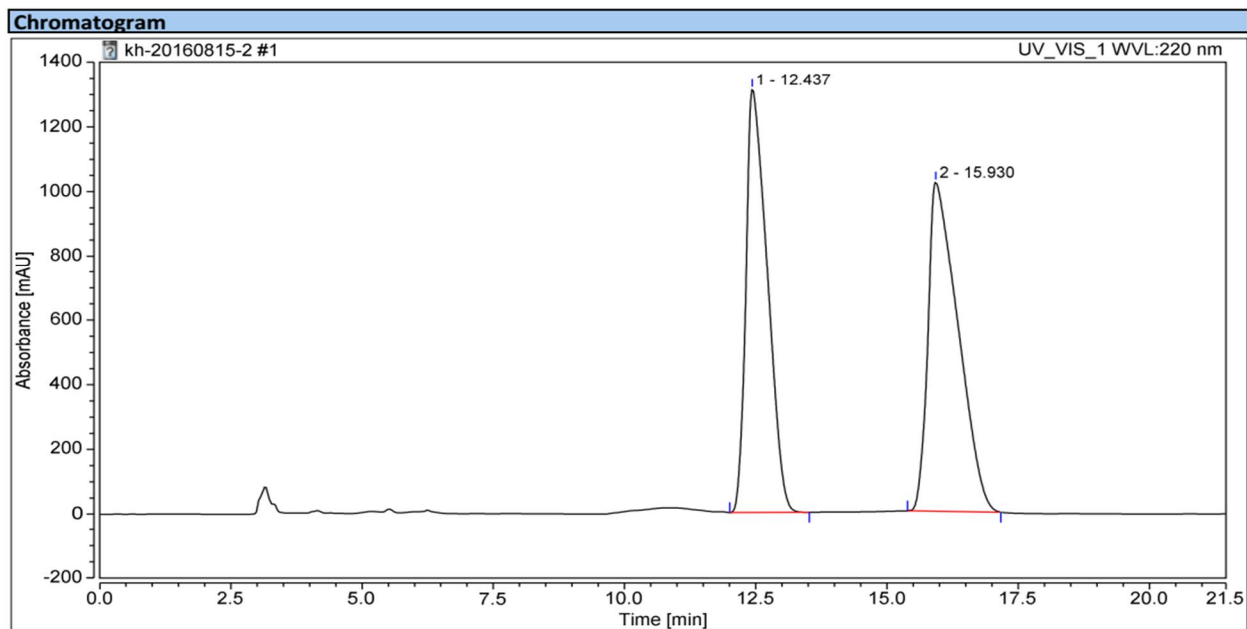
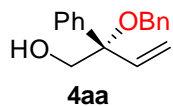
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.370	40.582	124.529	49.11	52.54	n.a.
2		13.140	42.056	112.479	50.89	47.46	n.a.
Total:			82.639	237.008	100.00	100.00	



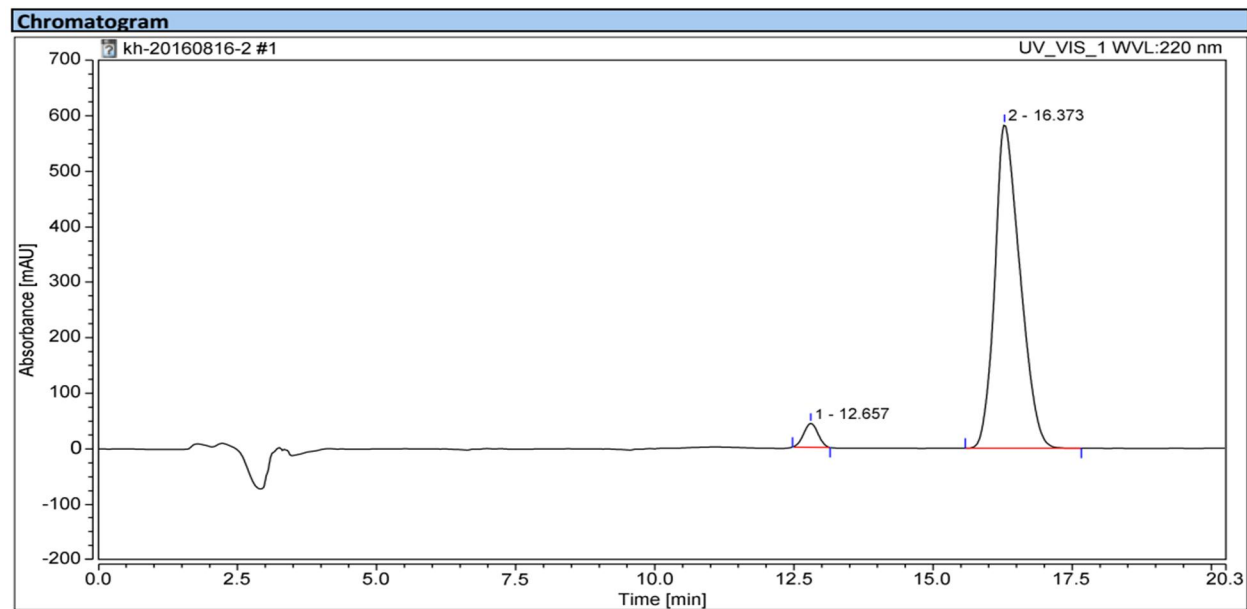
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.393	8.382	26.736	95.01	93.25	n.a.
2		13.240	0.440	1.937	4.99	6.75	n.a.
Total:			8.822	28.673	100.00	100.00	



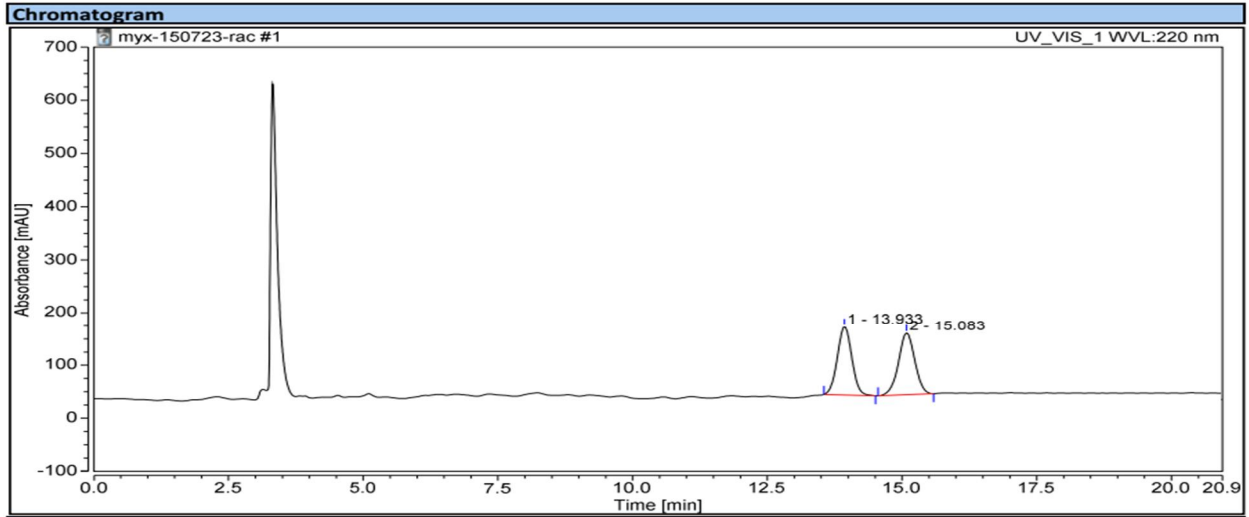
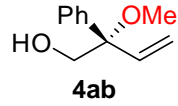
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.437	618.069	1310.908	49.78	56.24	n.a.
2		15.930	676.419	1020.179	50.22	43.76	n.a.
Total:			1294.488	2331.087	100.00	100.00	



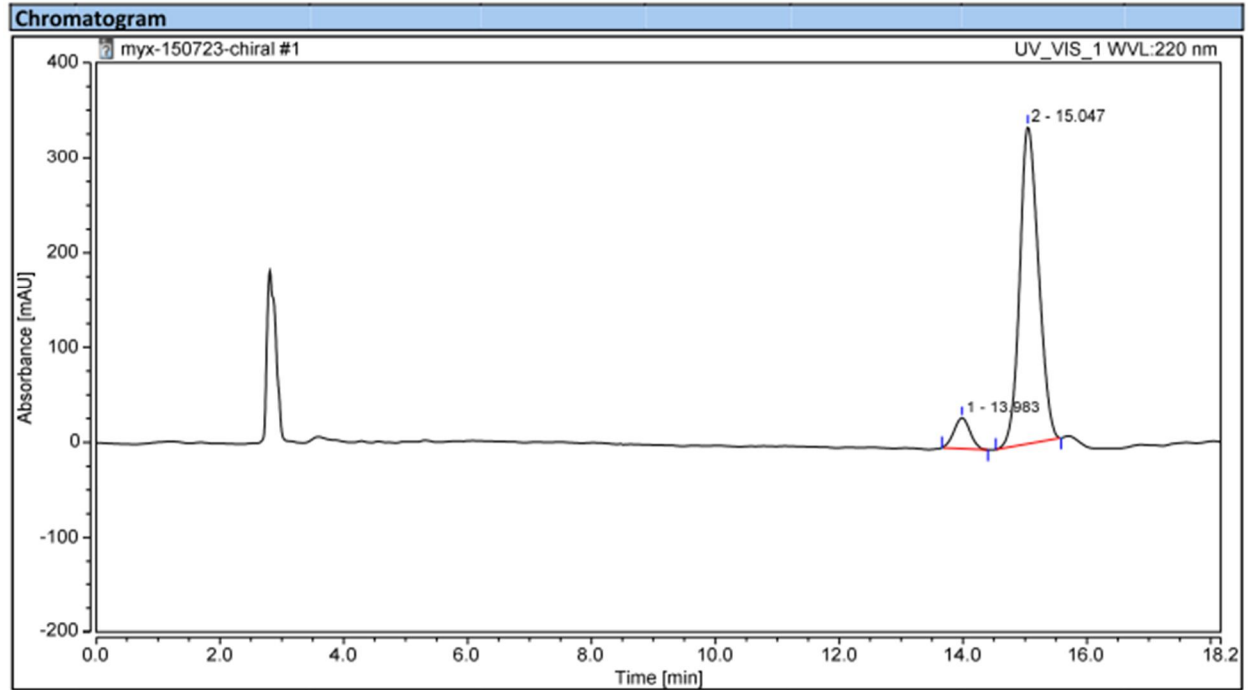
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.657	11.154	40.233	3.43	6.14	n.a.
2		16.373	313.650	615.207	96.57	93.86	n.a.
Total:			324.804	655.439	100.00	100.00	



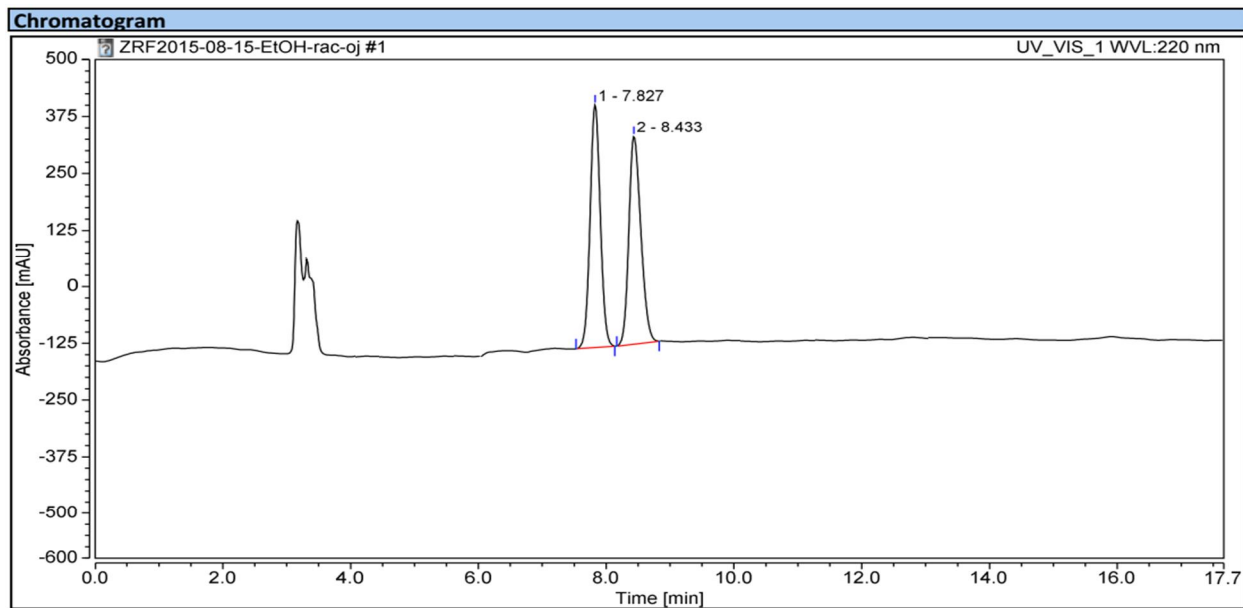
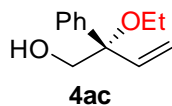
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.933	40.249	129.210	49.65	52.57	n.a.
2		15.083	40.819	116.592	50.35	47.43	n.a.
Total:			81.068	245.802	100.00	100.00	



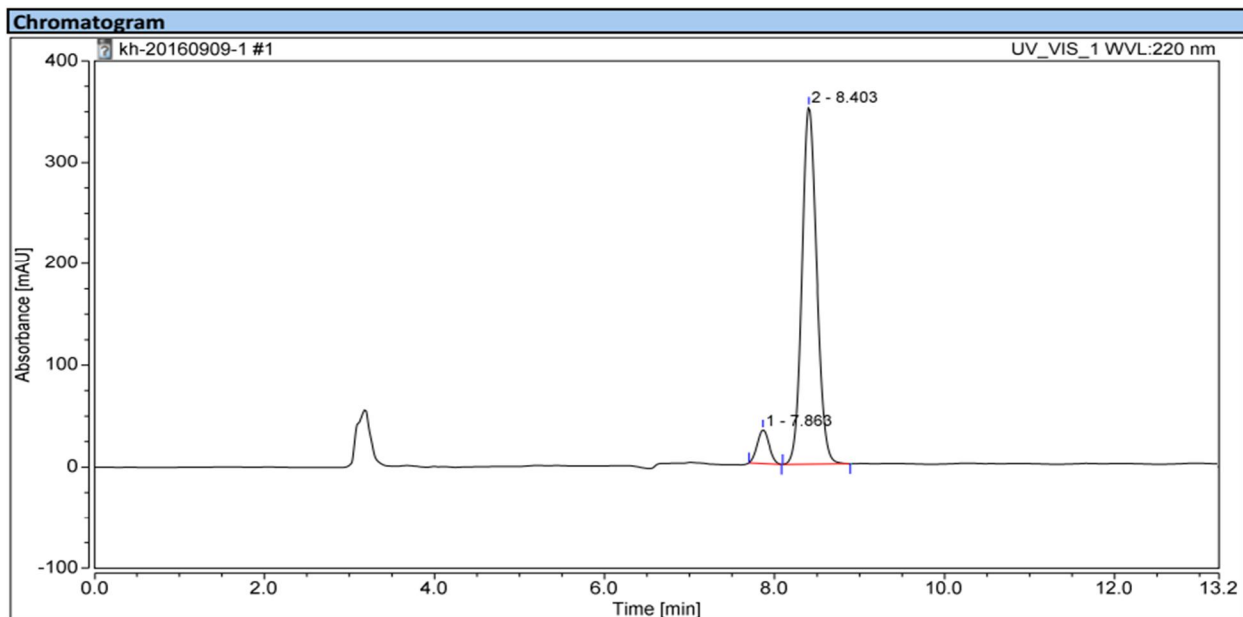
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.983	9.822	32.373	7.73	8.82	n.a.
2		15.047	117.275	334.525	92.27	91.18	n.a.
Total:			127.097	366.897	100.00	100.00	



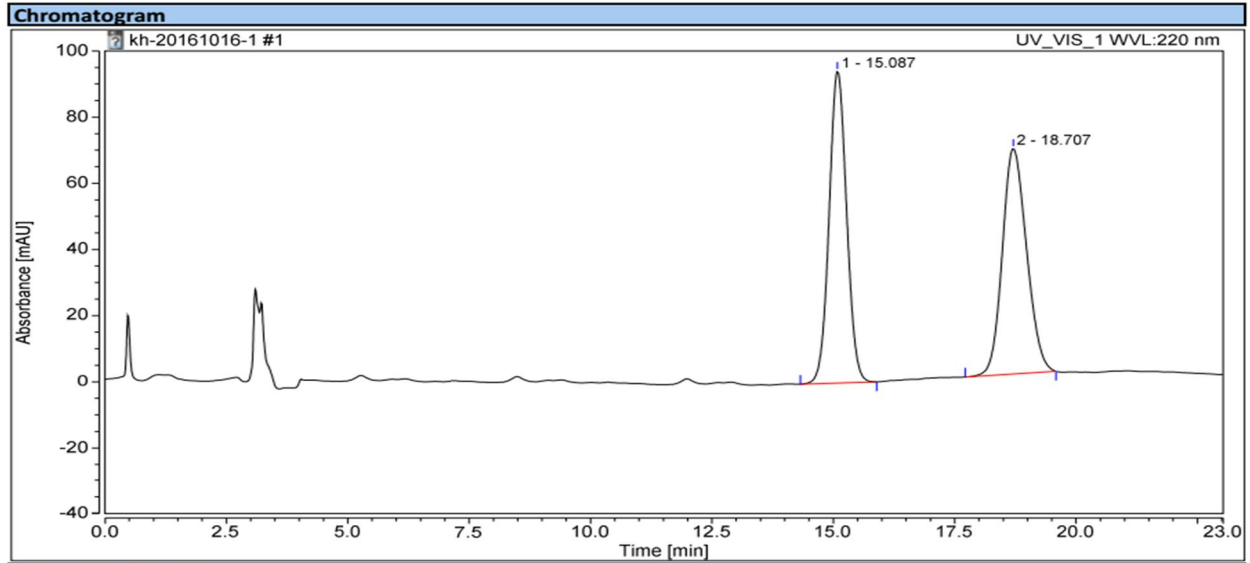
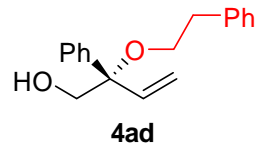
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.827	99.124	534.631	49.78	53.83	n.a.
2		8.433	100.014	458.492	50.22	46.17	n.a.
Total:			199.139	993.123	100.00	100.00	



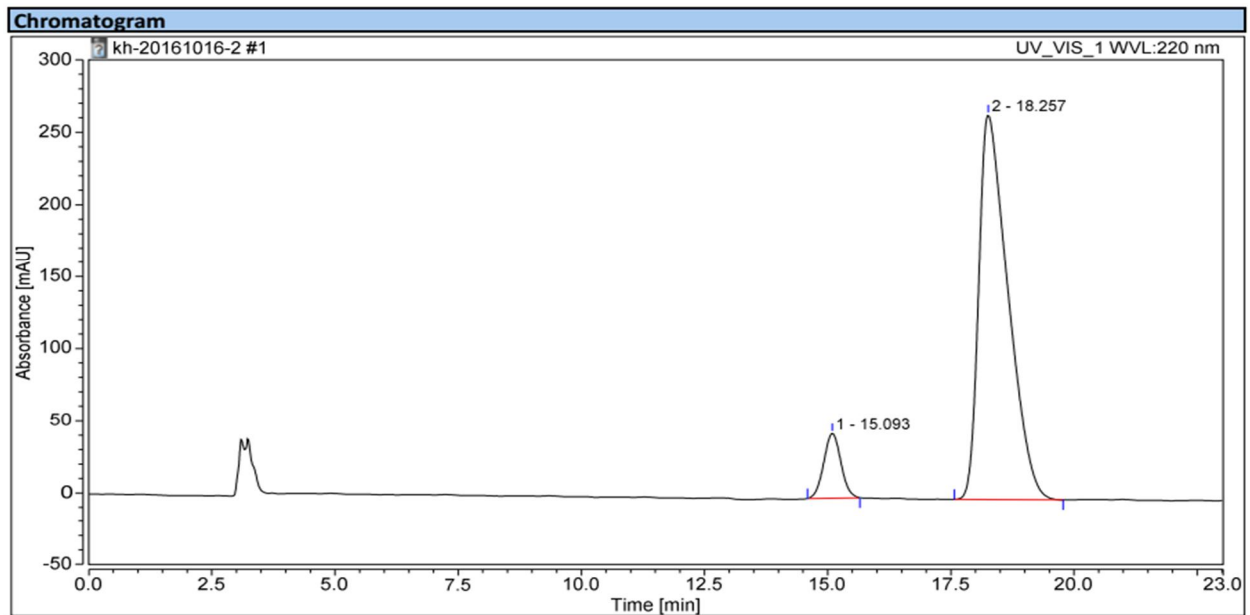
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.863	5.346	32.977	6.76	8.57	n.a.
2		8.403	70.841	351.728	93.24	91.43	n.a.
Total:			76.187	384.705	100.00	100.00	



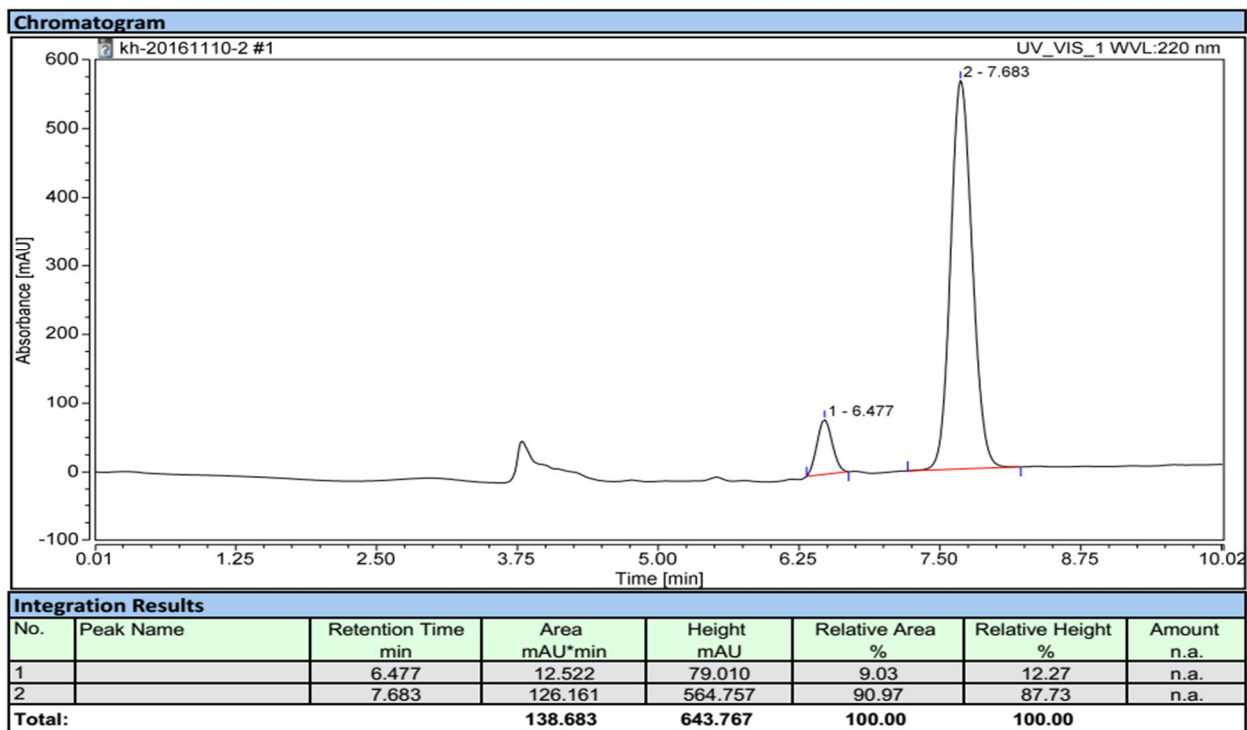
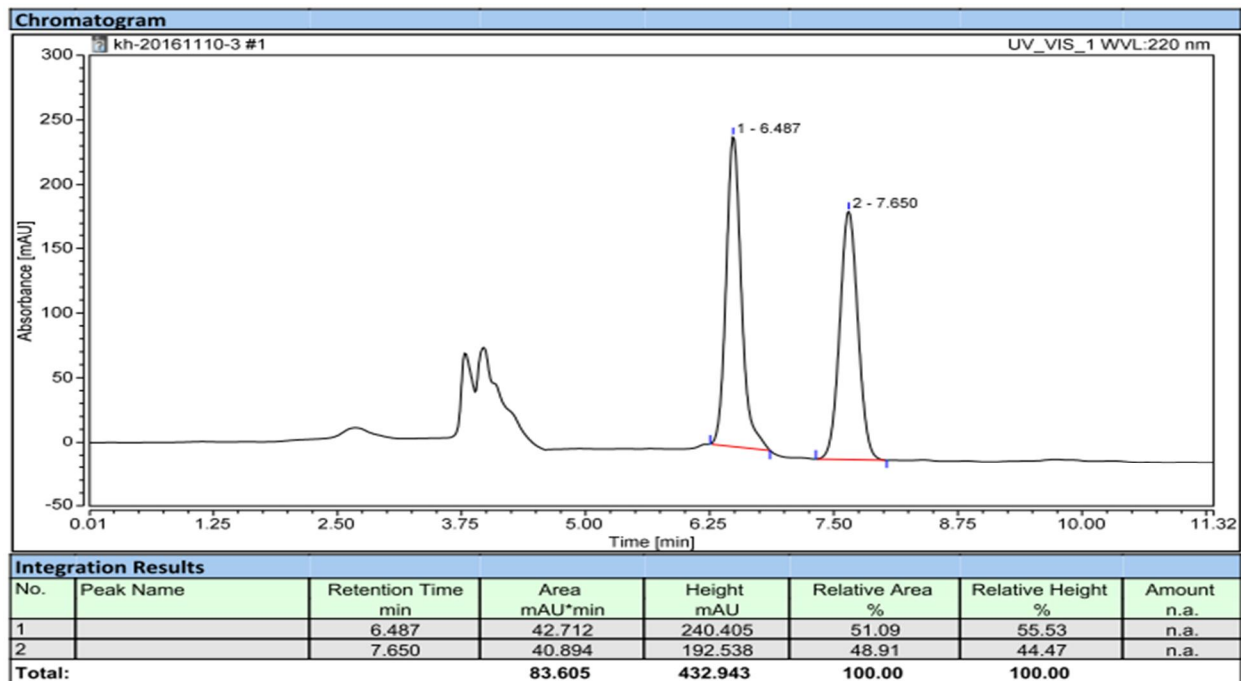
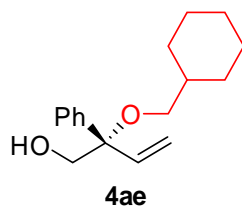
Integration Results

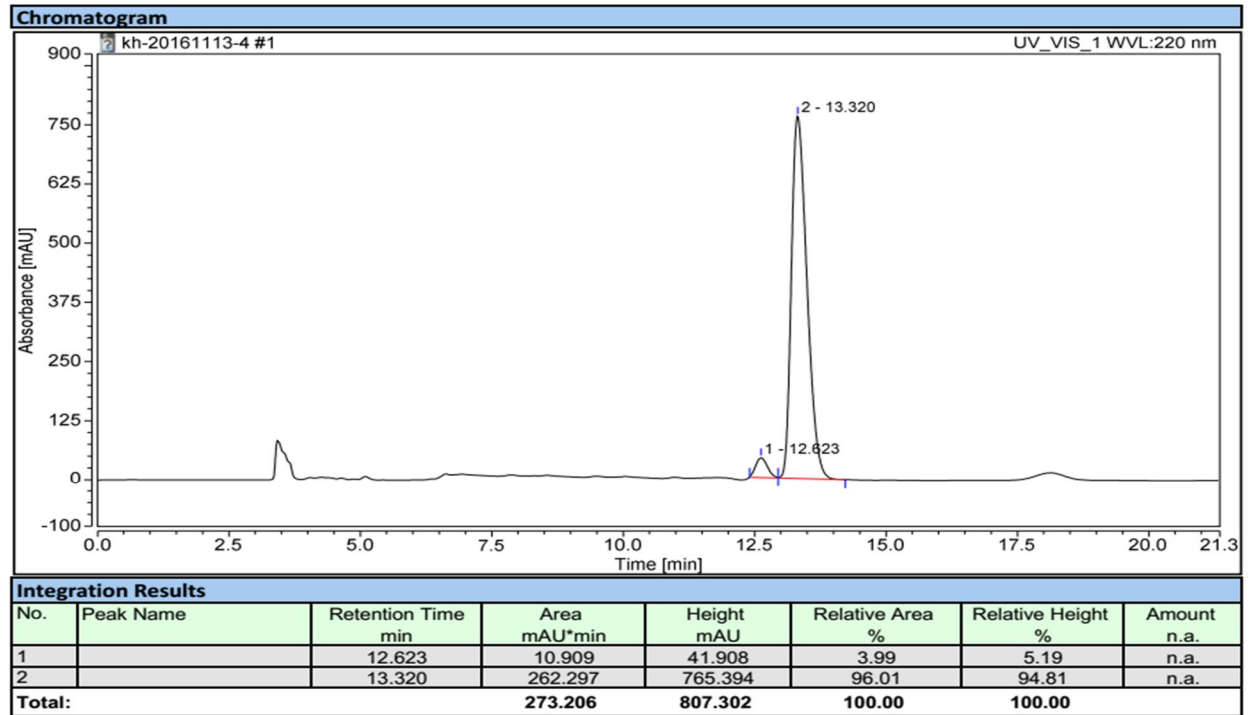
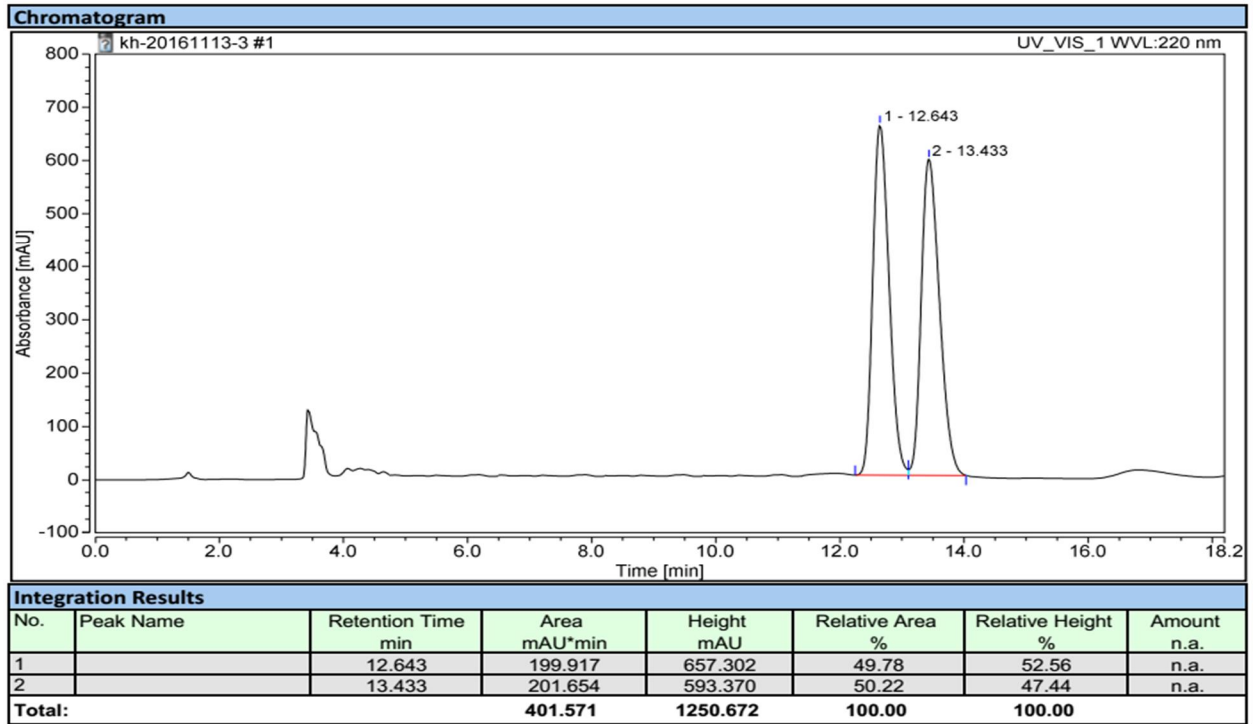
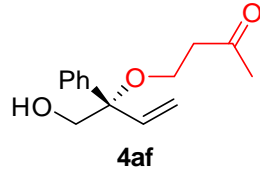
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.087	39.456	94.201	50.00	58.02	n.a.
2		18.707	39.462	68.151	50.00	41.98	n.a.
Total:			78.918	162.352	100.00	100.00	

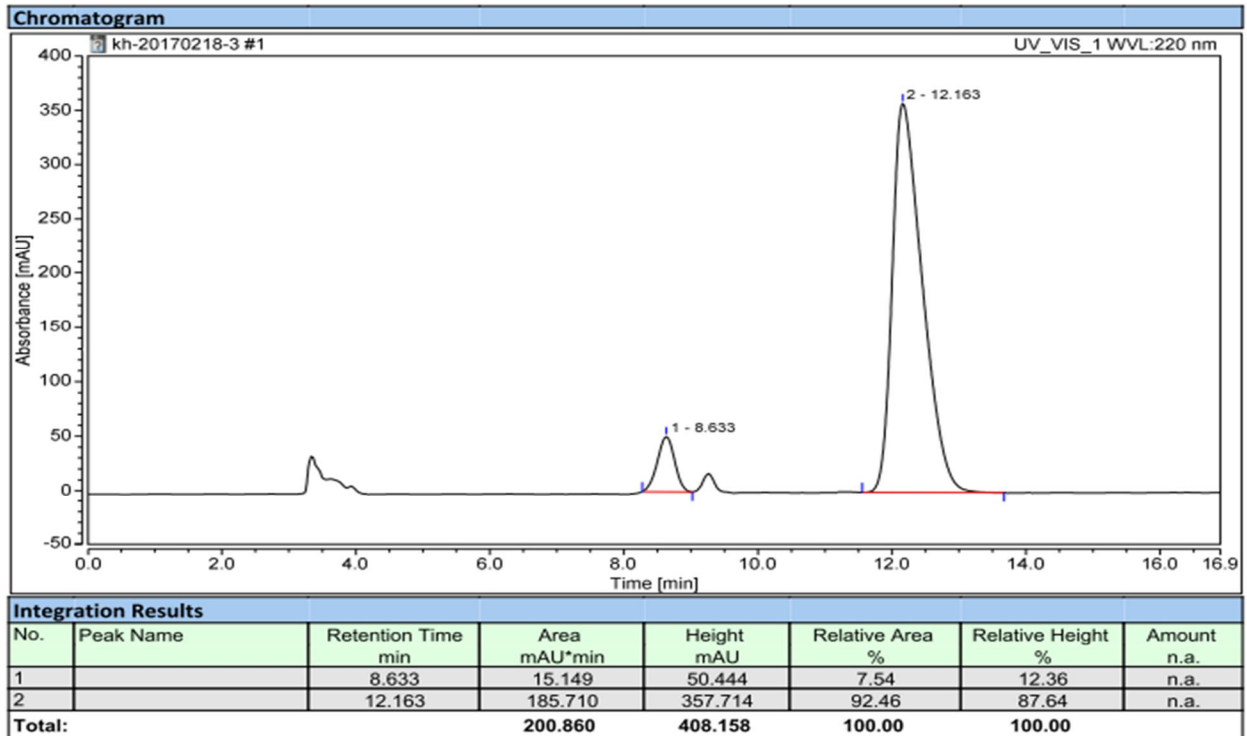
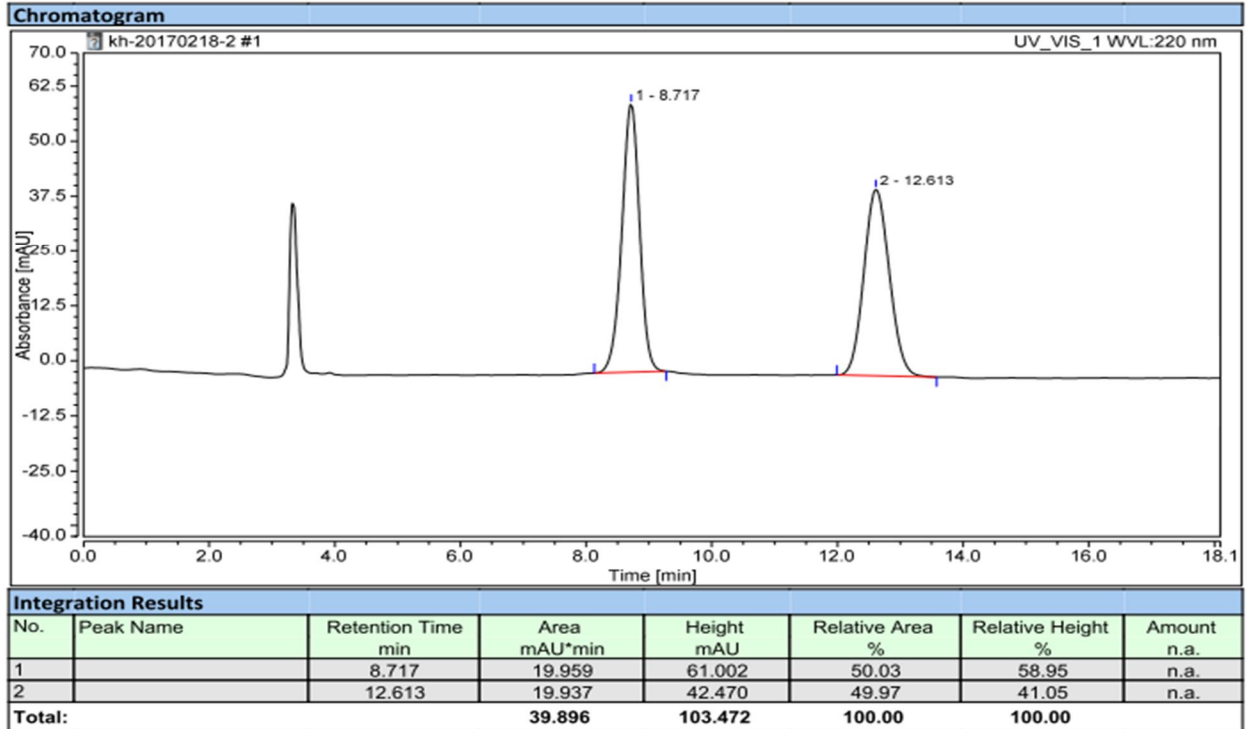
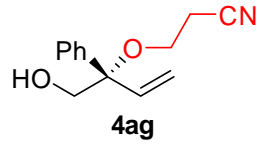


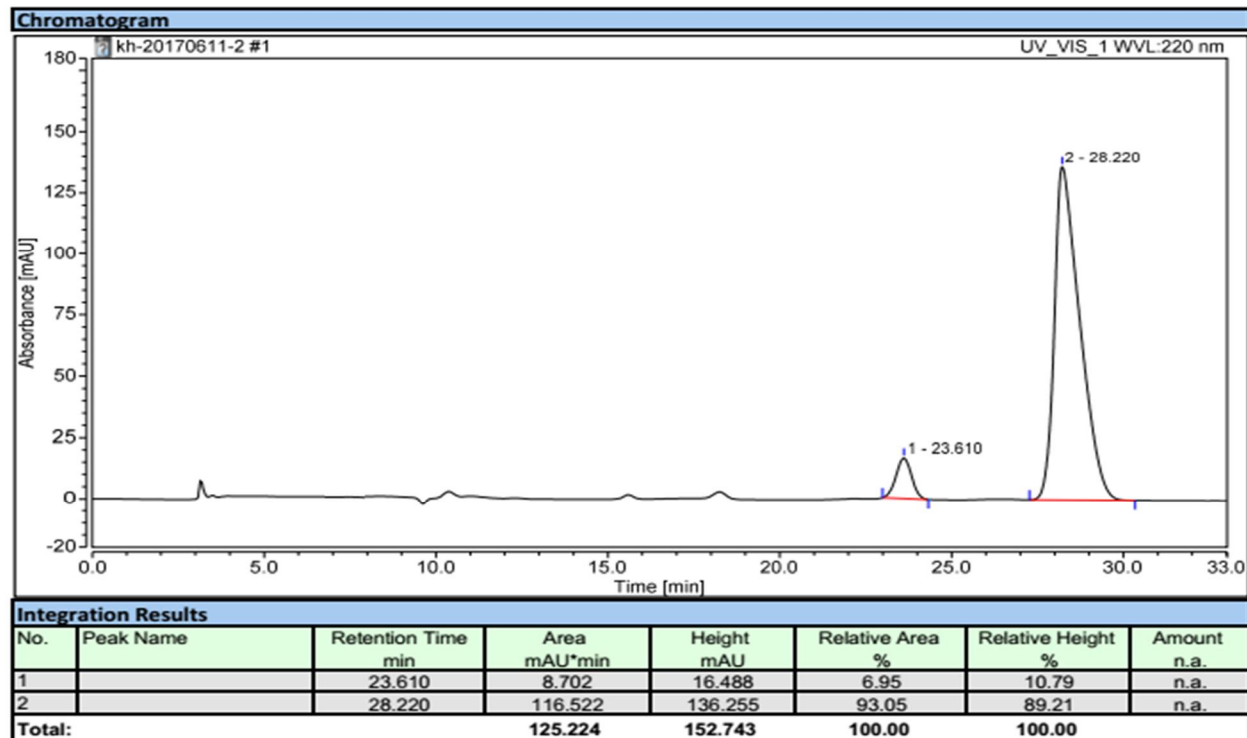
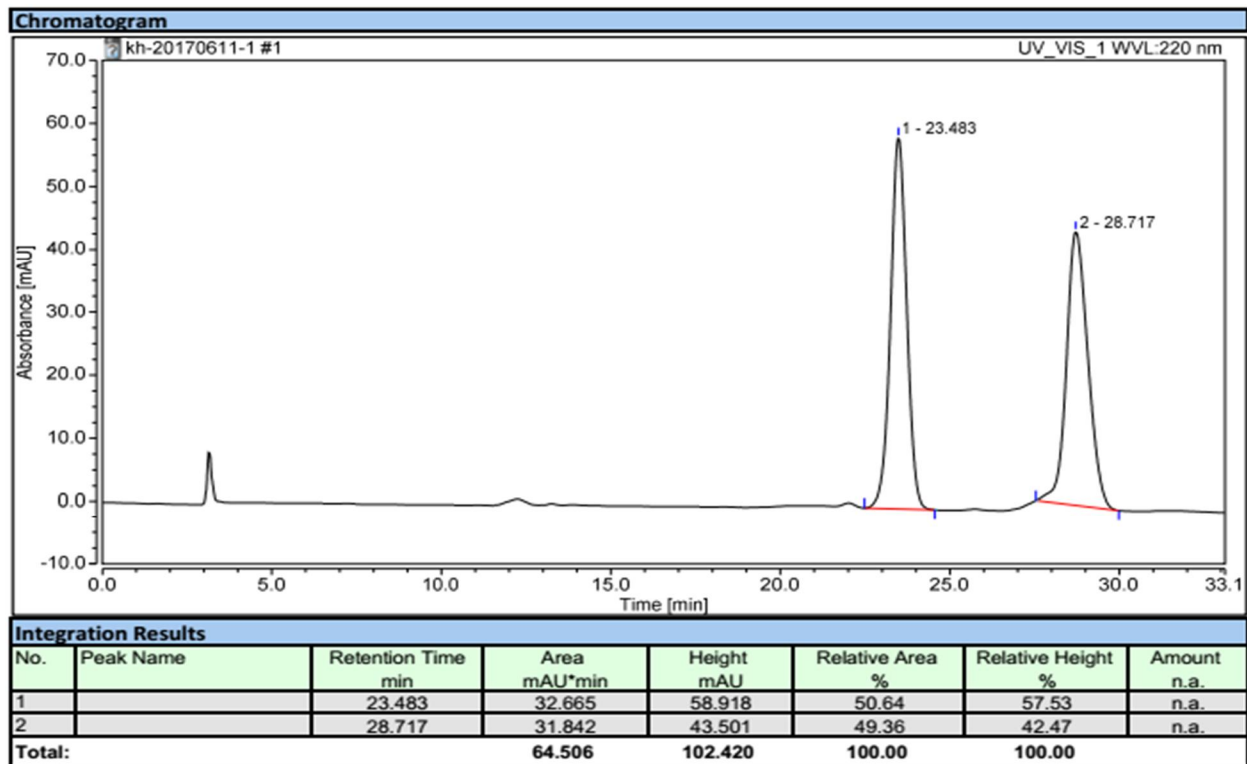
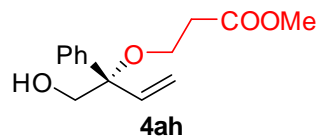
Integration Results

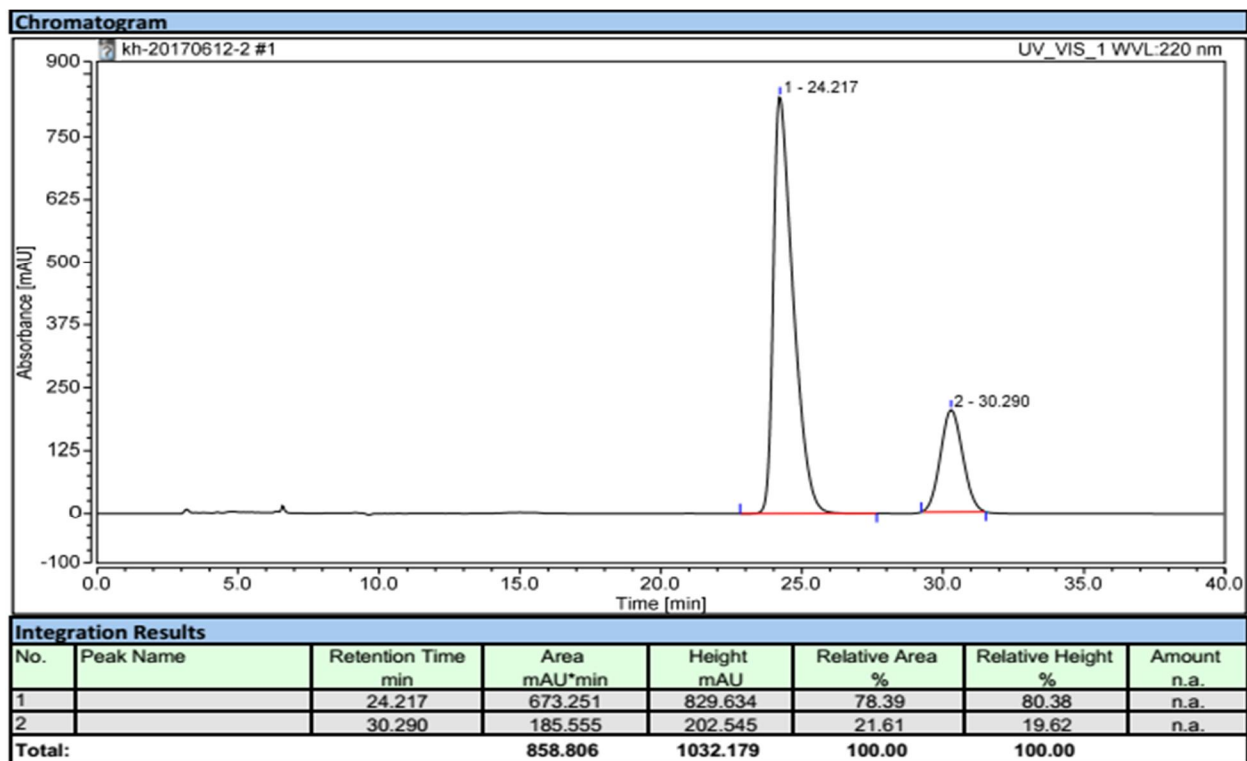
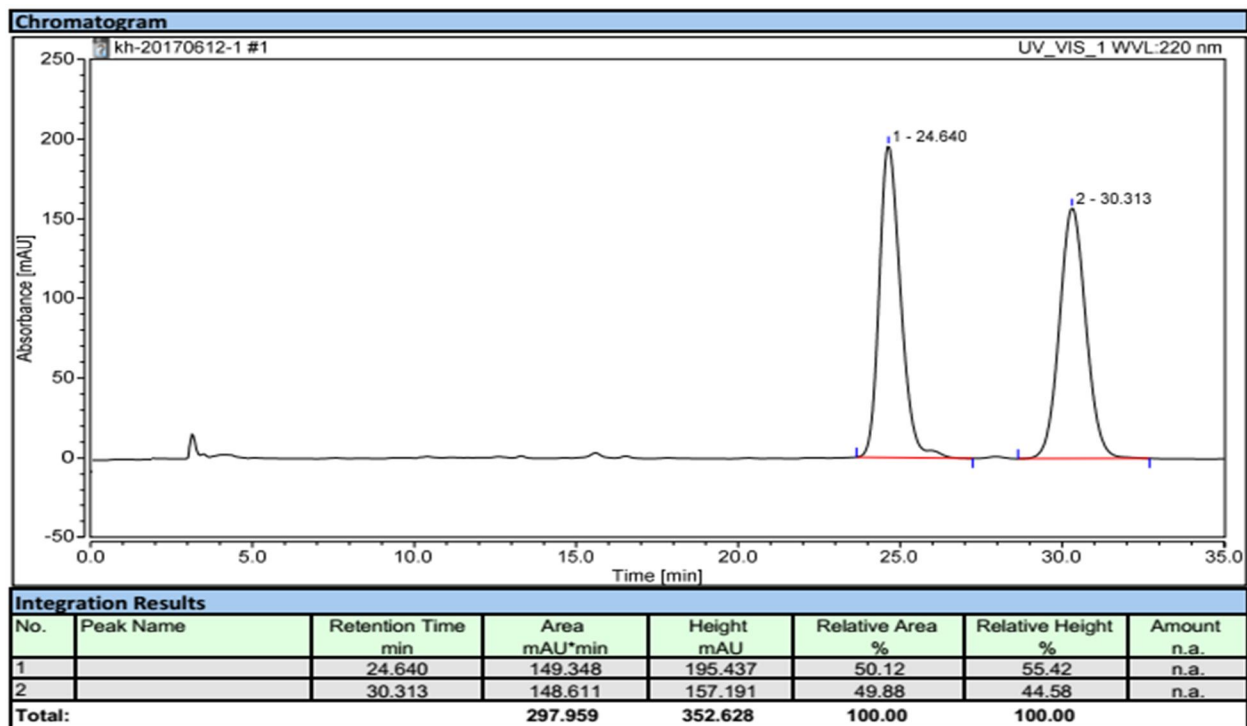
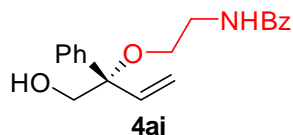
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.093	18.138	44.831	9.01	14.40	n.a.
2		18.257	183.135	266.495	90.99	85.60	n.a.
Total:			201.273	311.325	100.00	100.00	

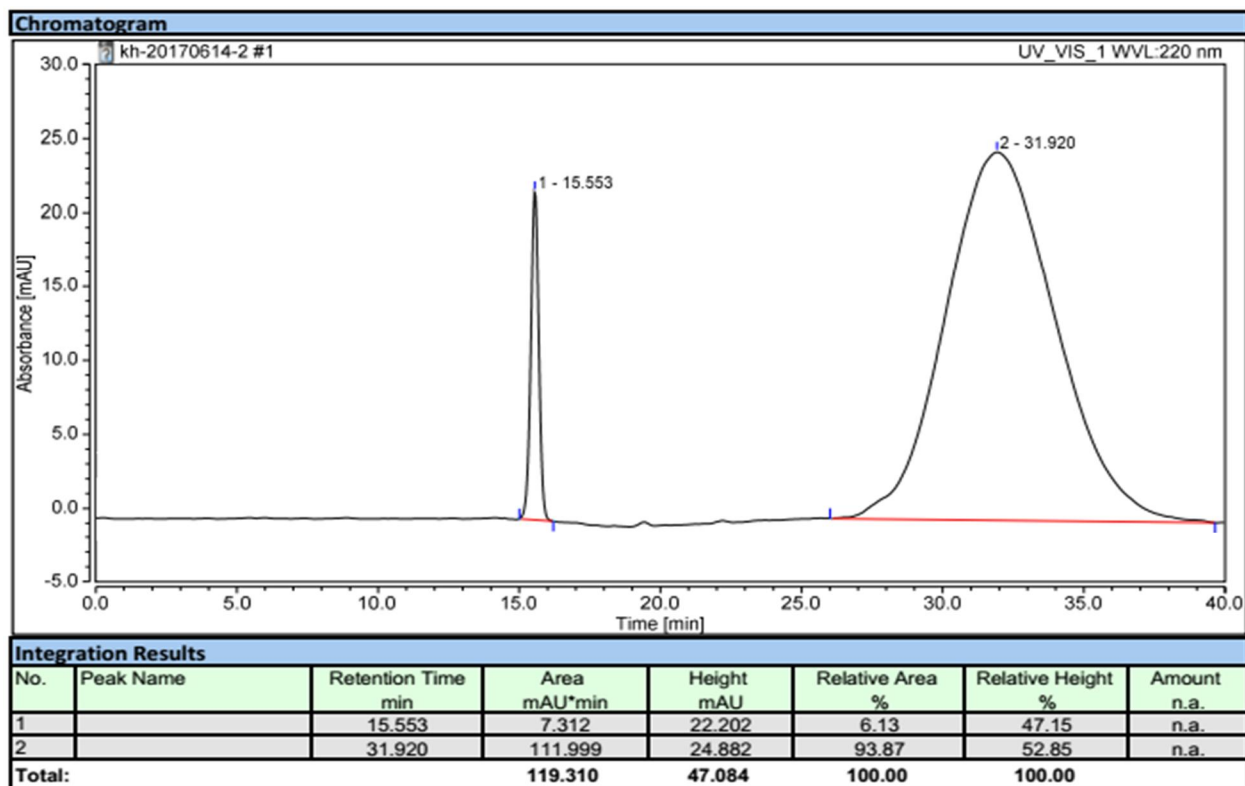
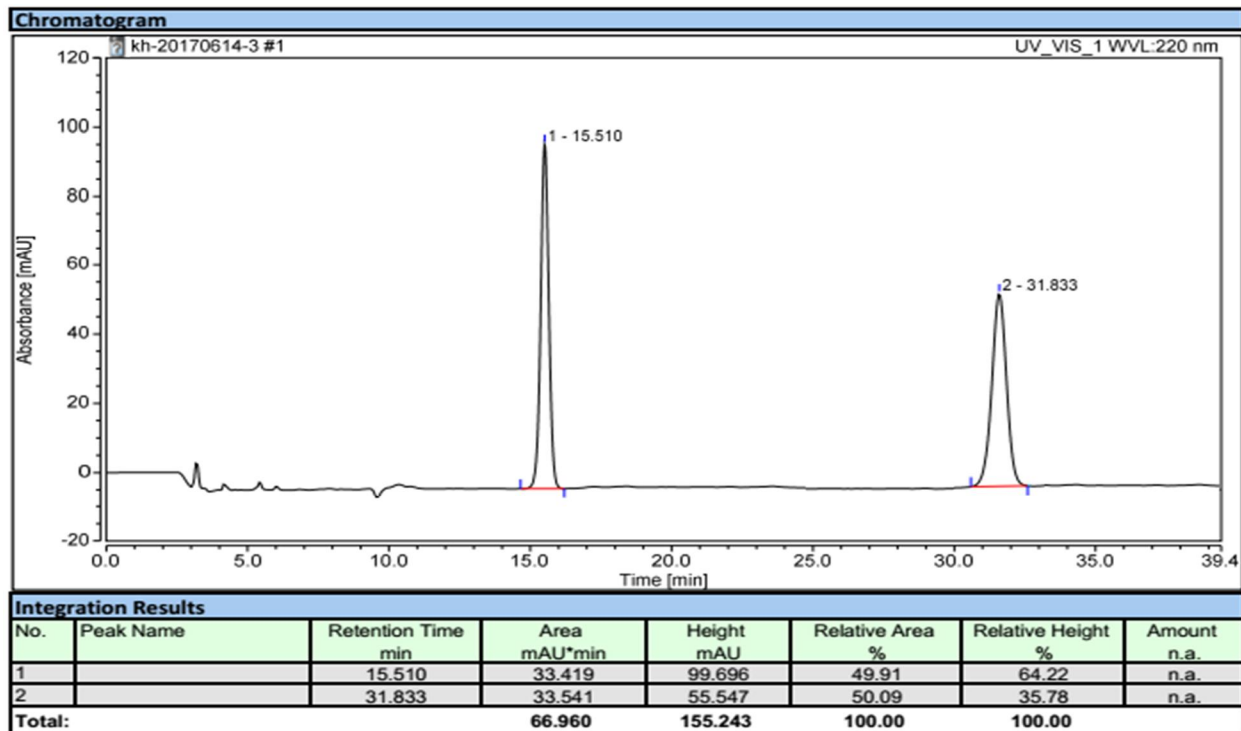
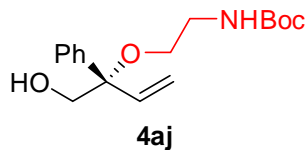


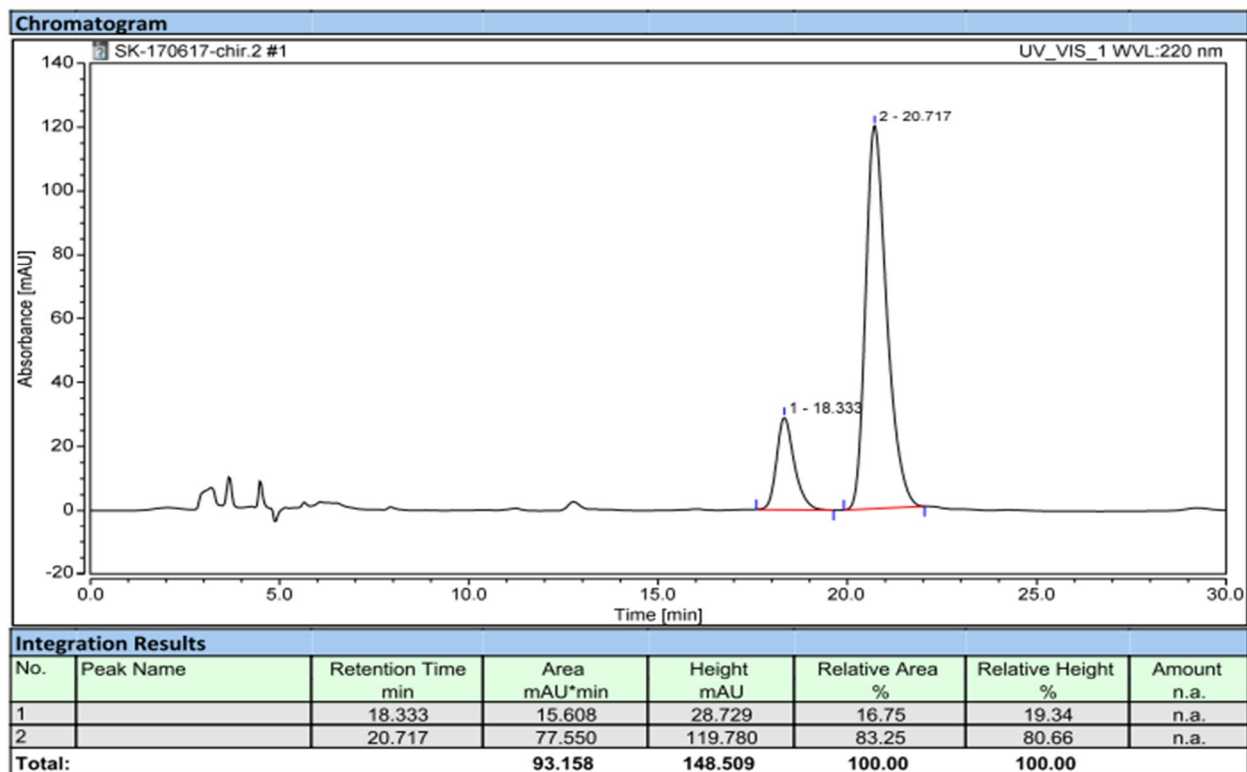
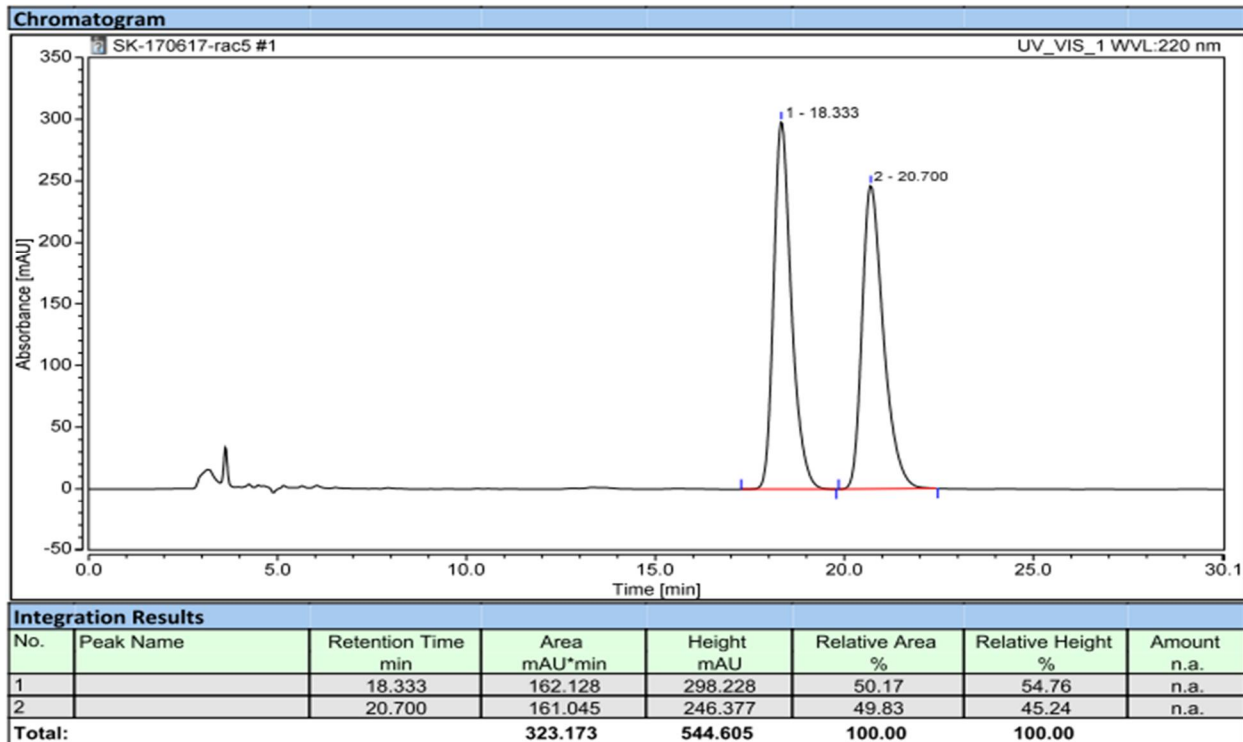
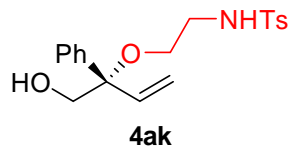


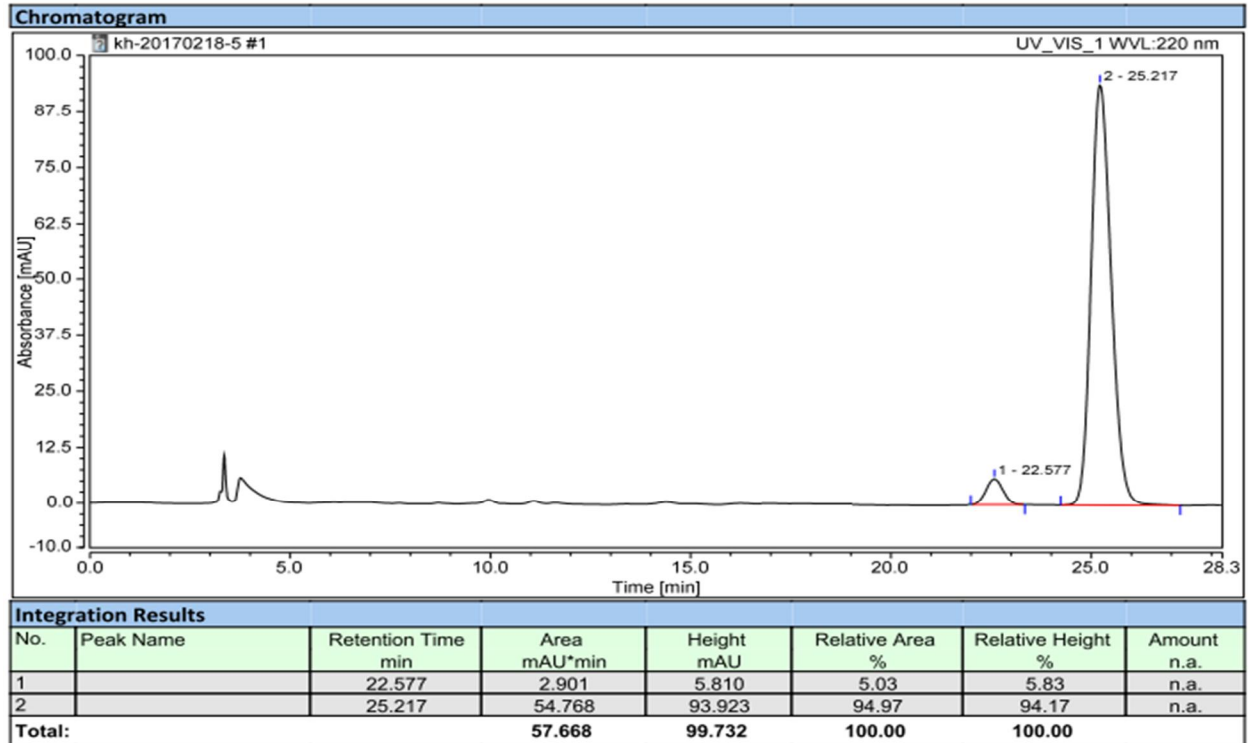
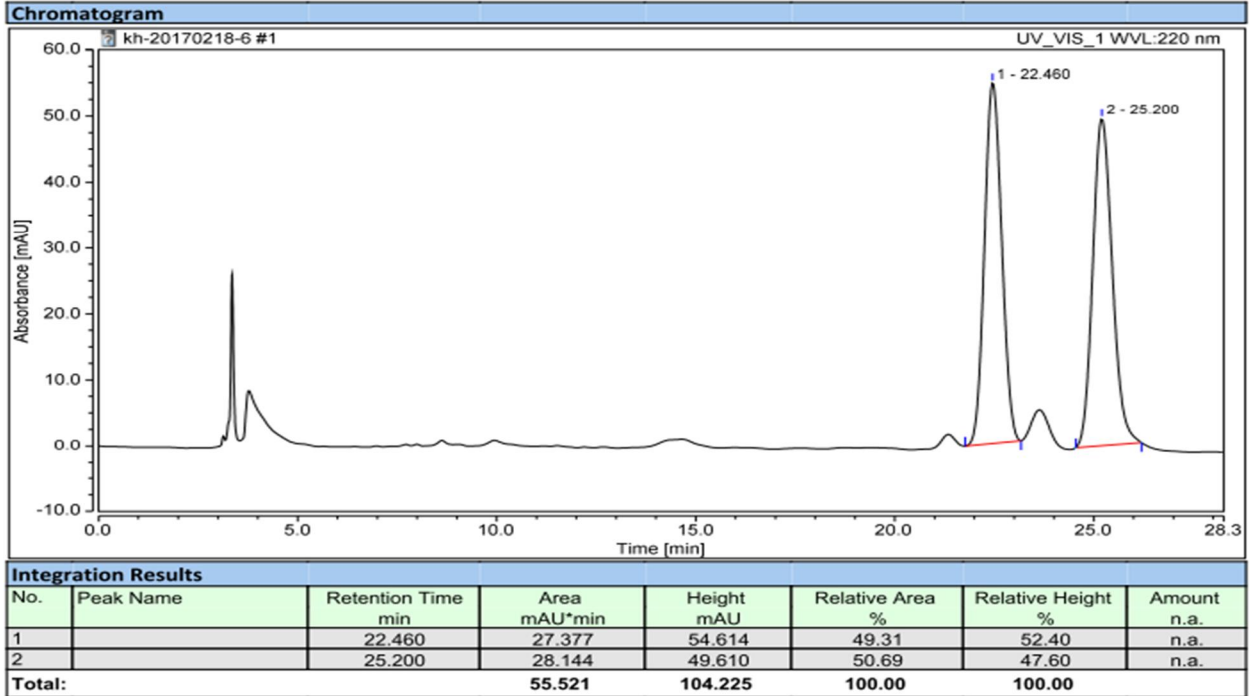
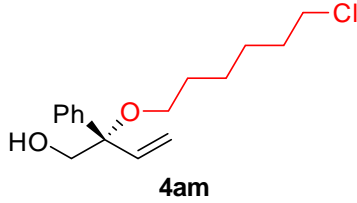


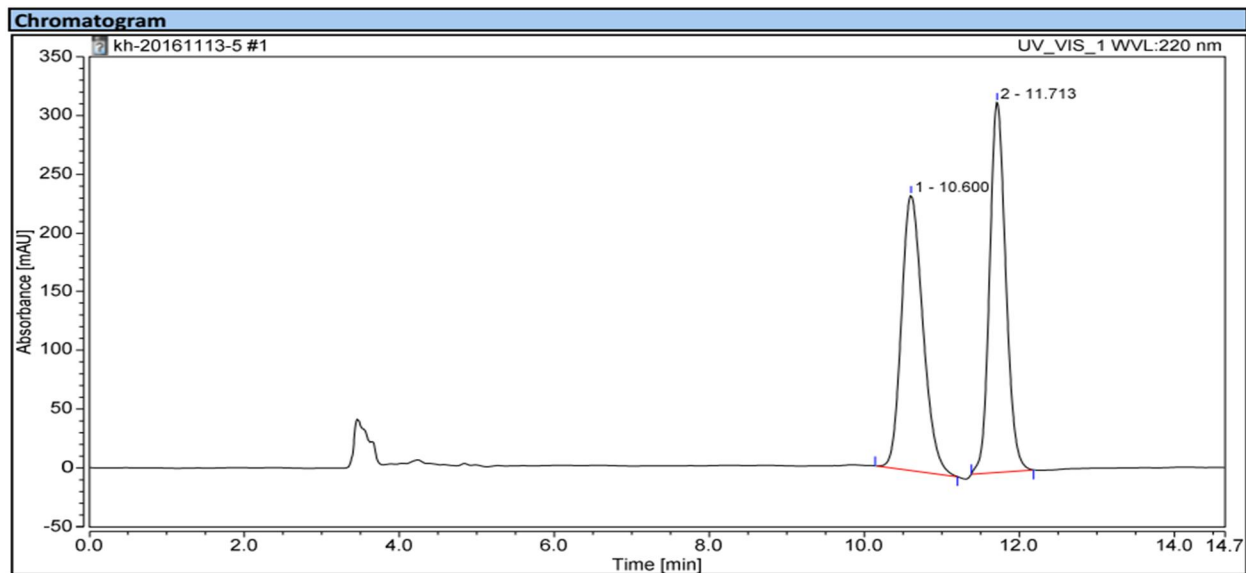
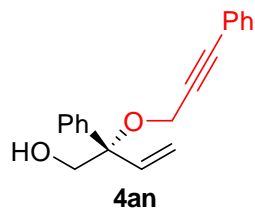






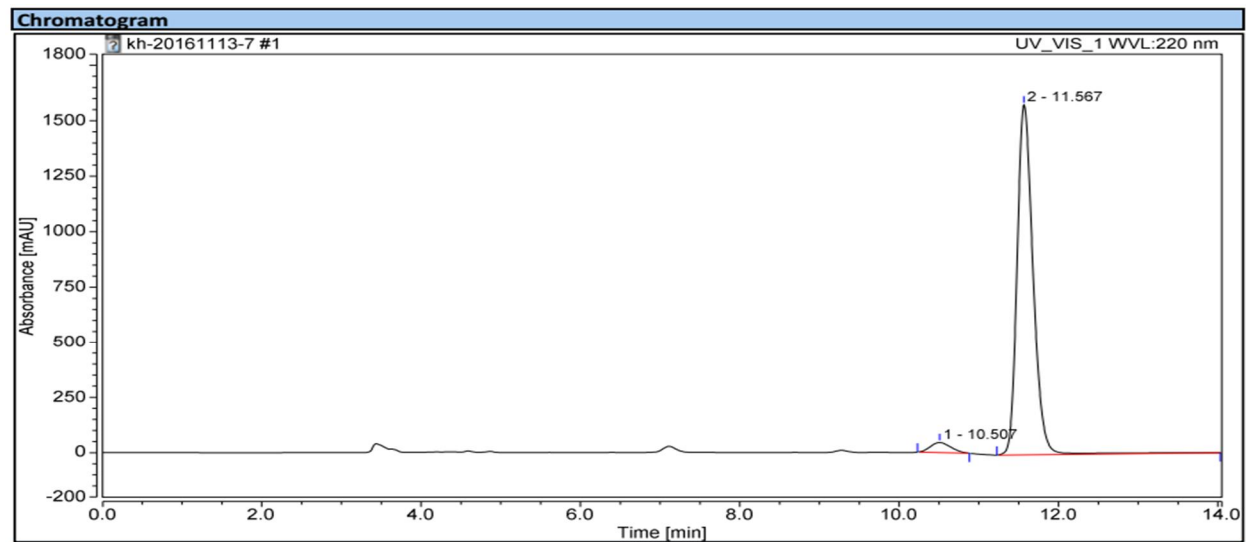






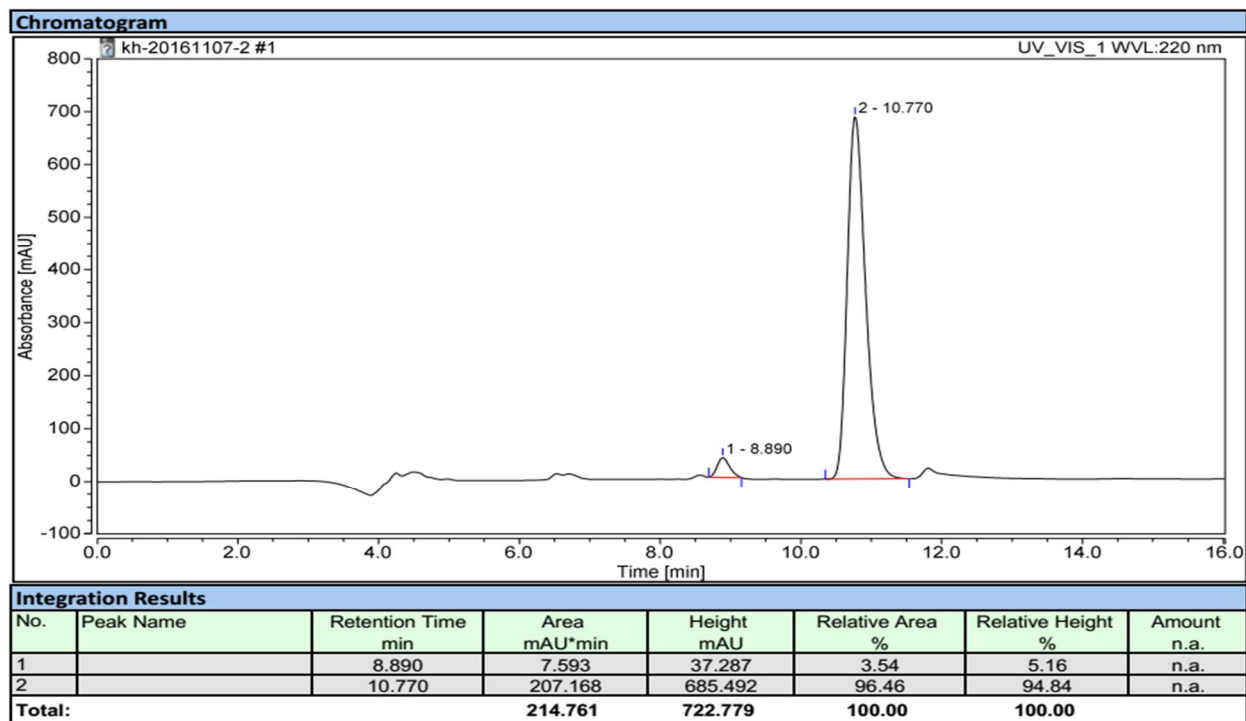
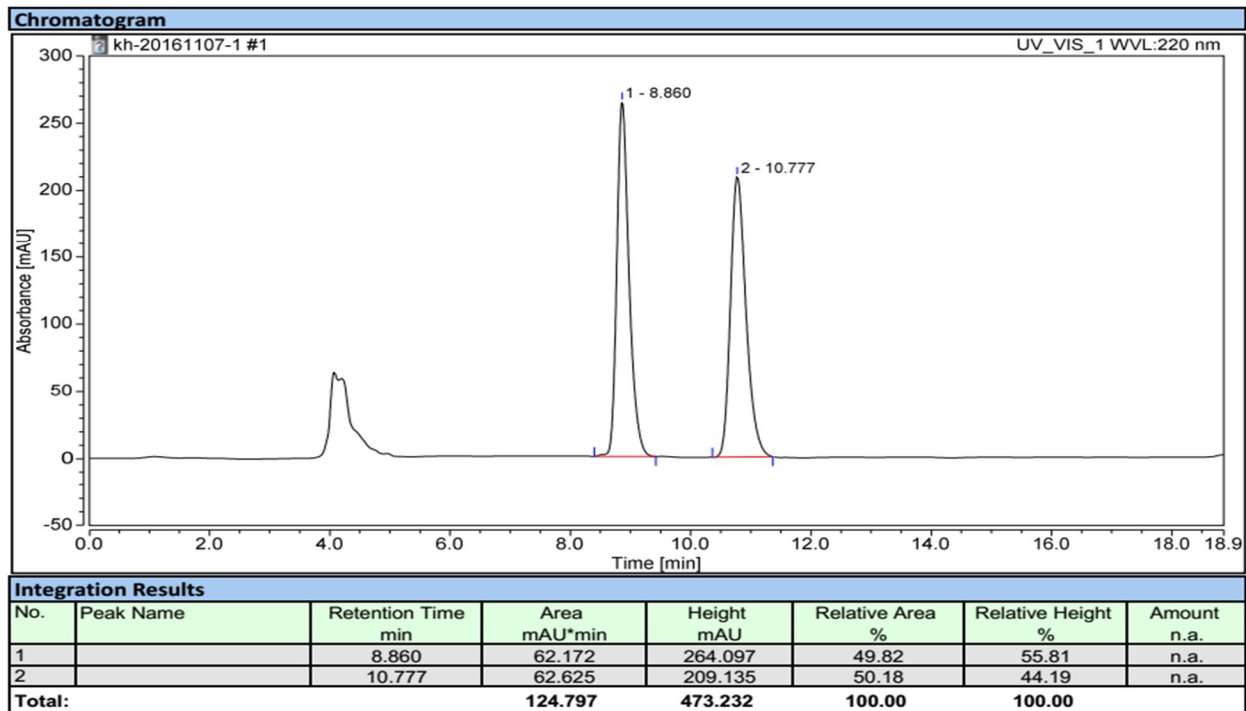
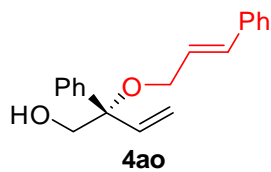
Integration Results

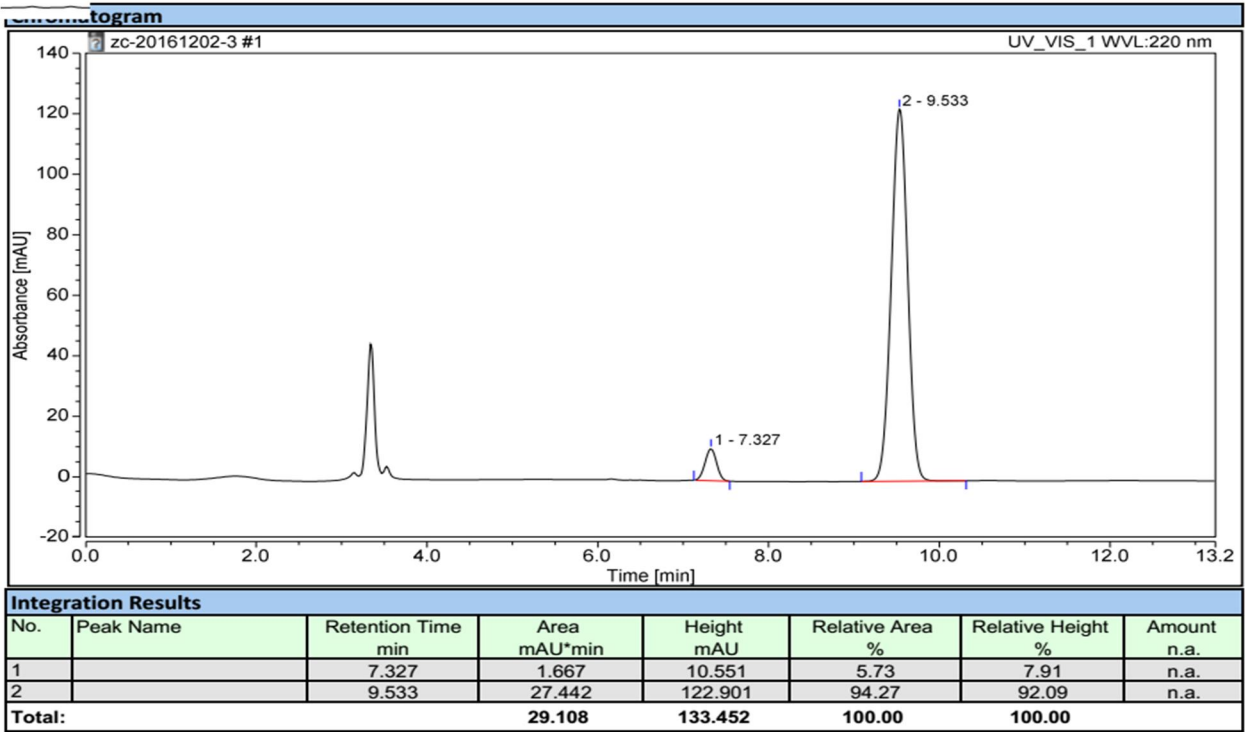
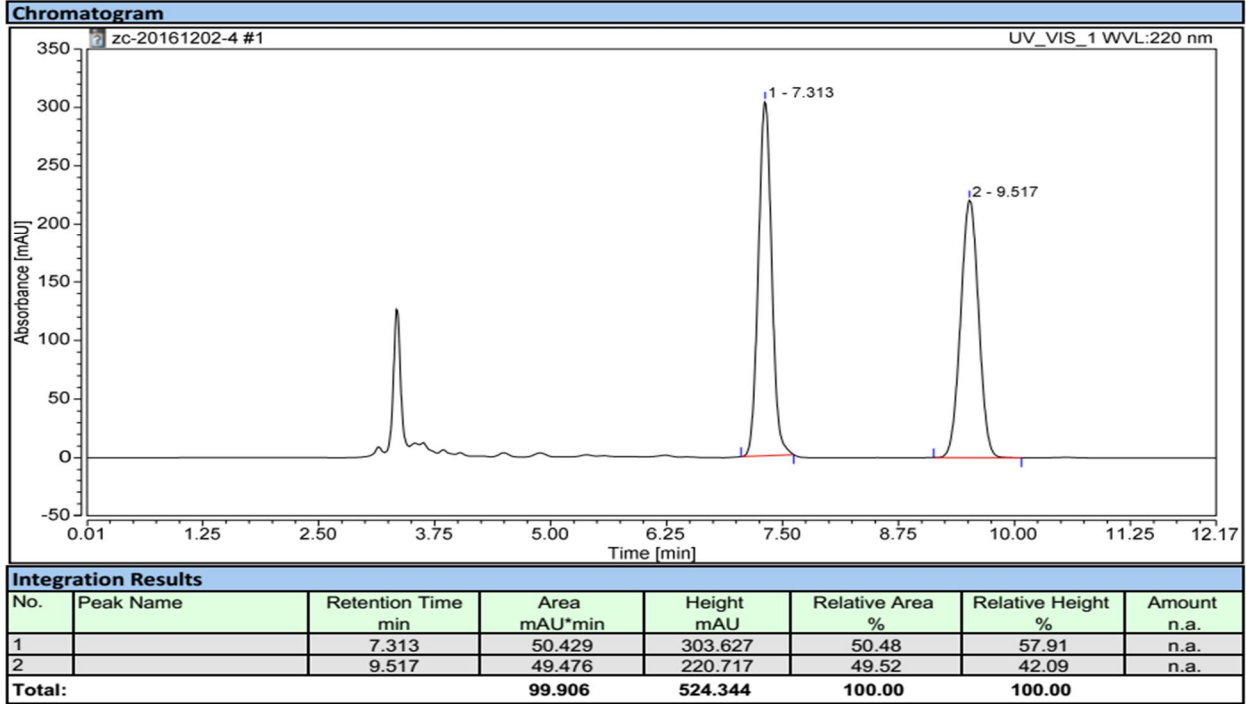
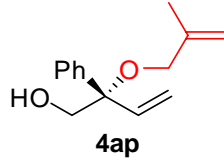
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.600	75.096	234.463	49.66	42.68	n.a.
2		11.713	76.129	314.851	50.34	57.32	n.a.
Total:			151.224	549.314	100.00	100.00	

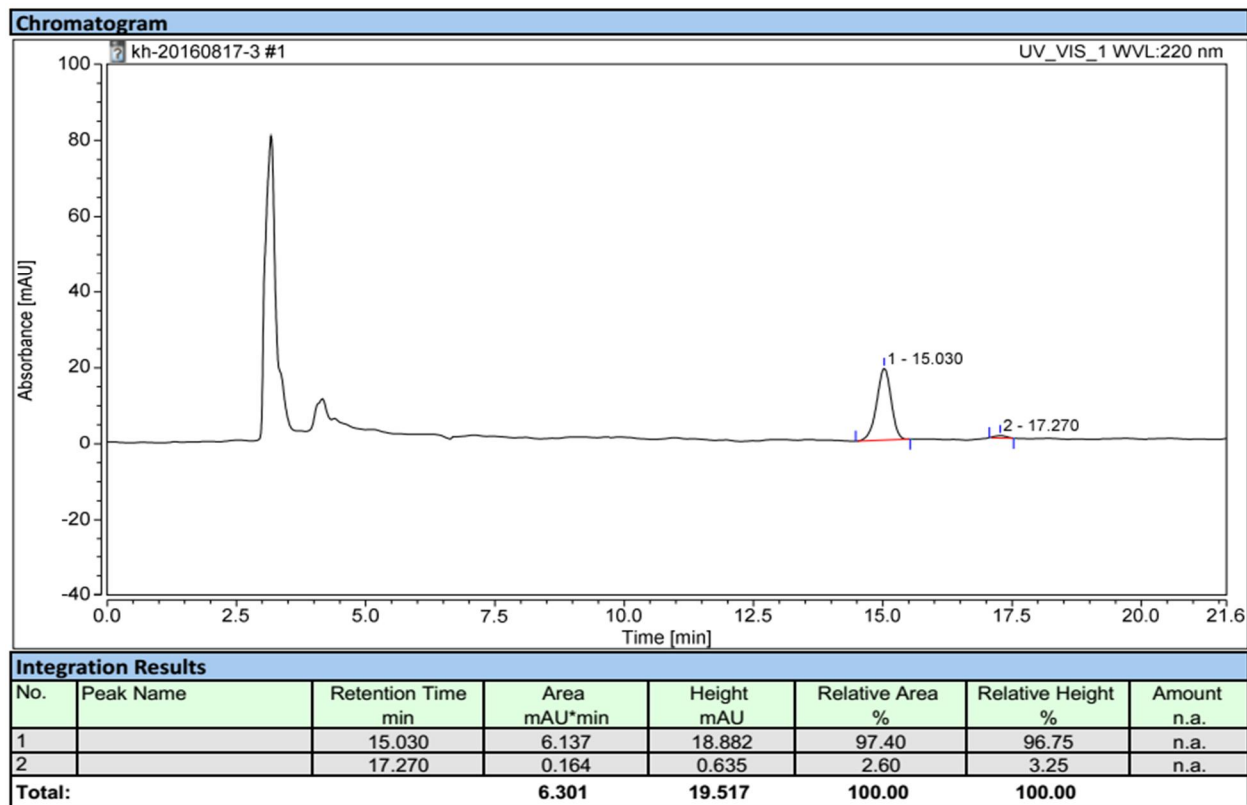
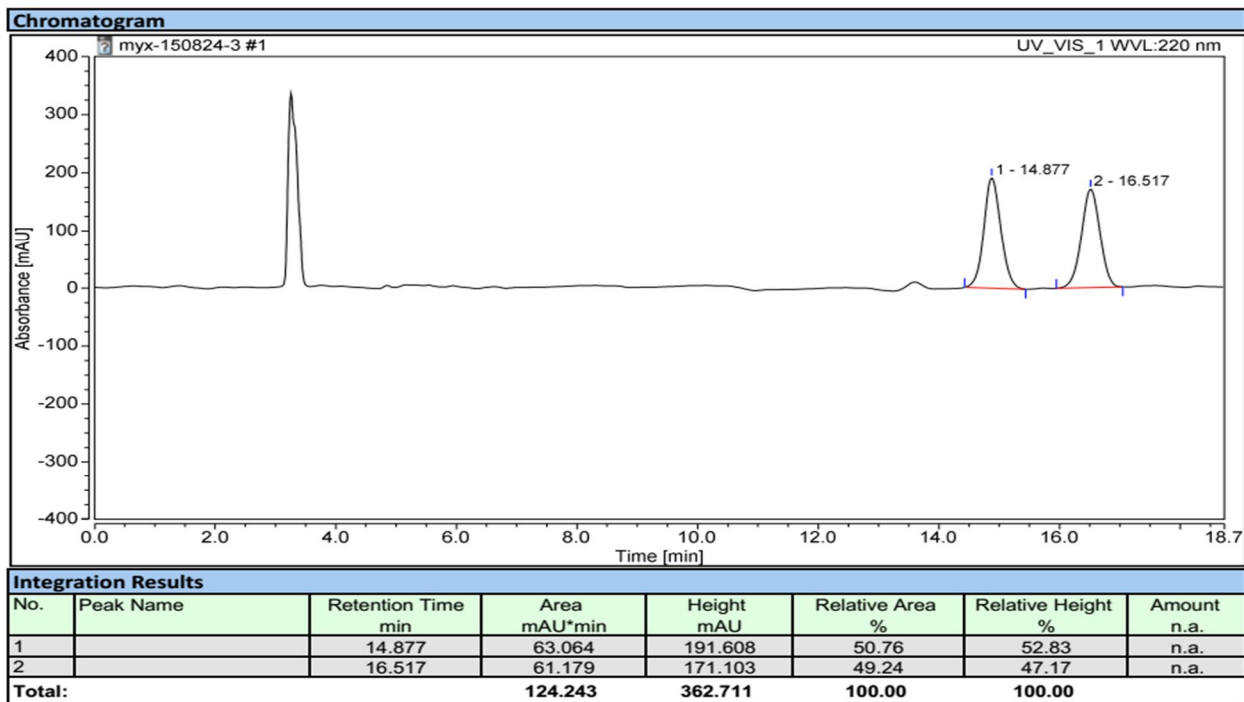
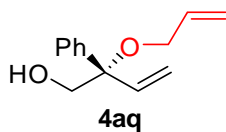


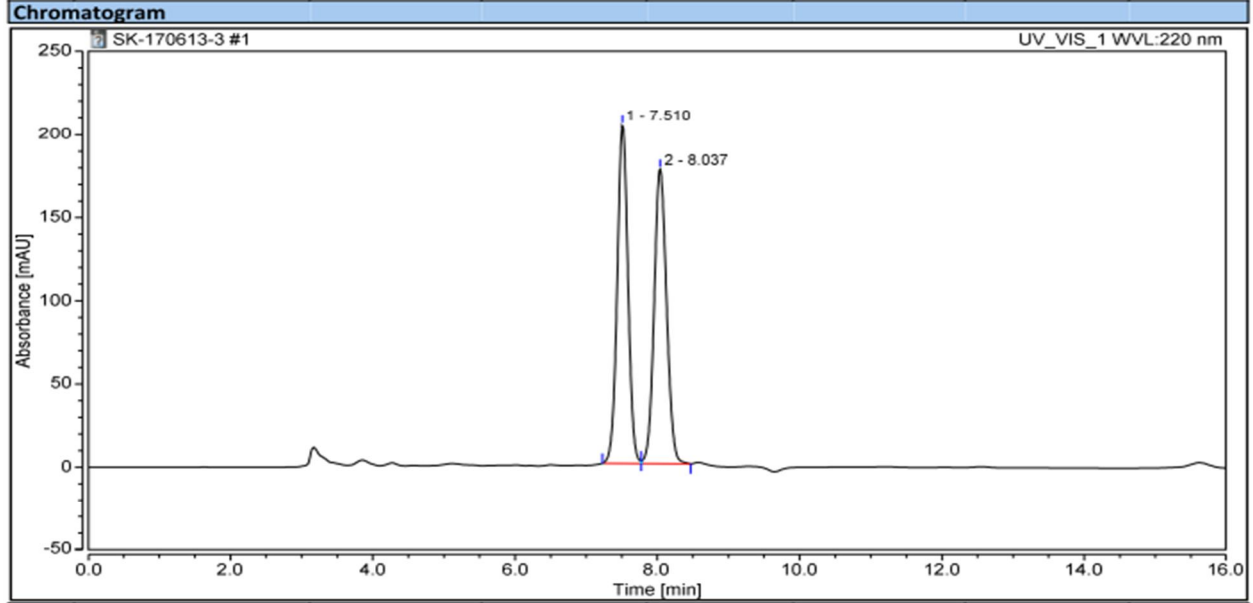
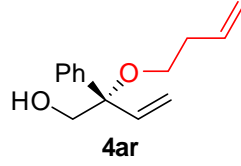
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.507	13.621	45.383	3.56	2.79	n.a.
2		11.567	368.878	1580.937	96.44	97.21	n.a.
Total:			382.499	1626.320	100.00	100.00	



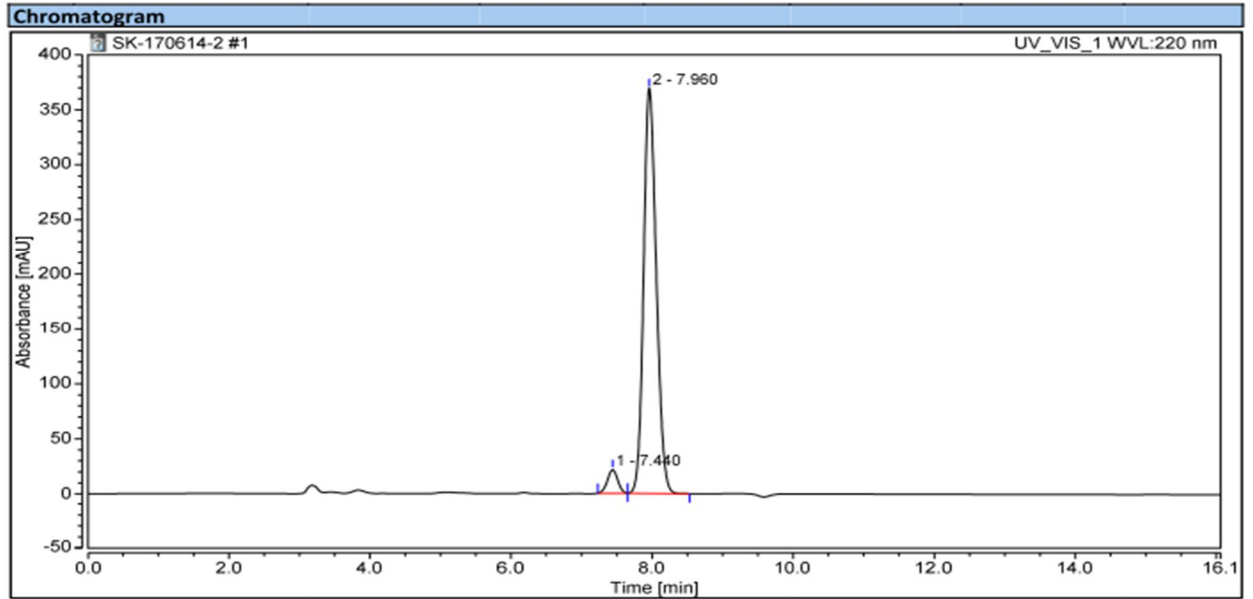






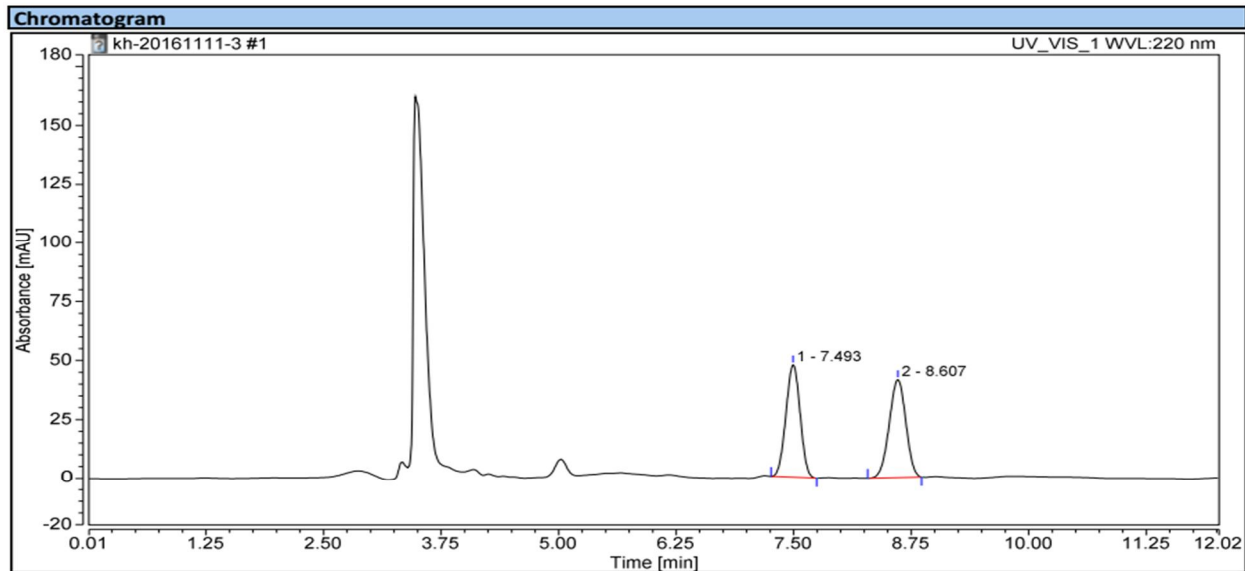
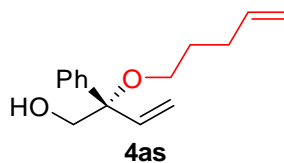
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		7.510	35.649	203.373	49.91	53.48	n.a.
2		8.037	35.782	176.940	50.09	46.52	n.a.
Total:			71.430	380.313	100.00	100.00	



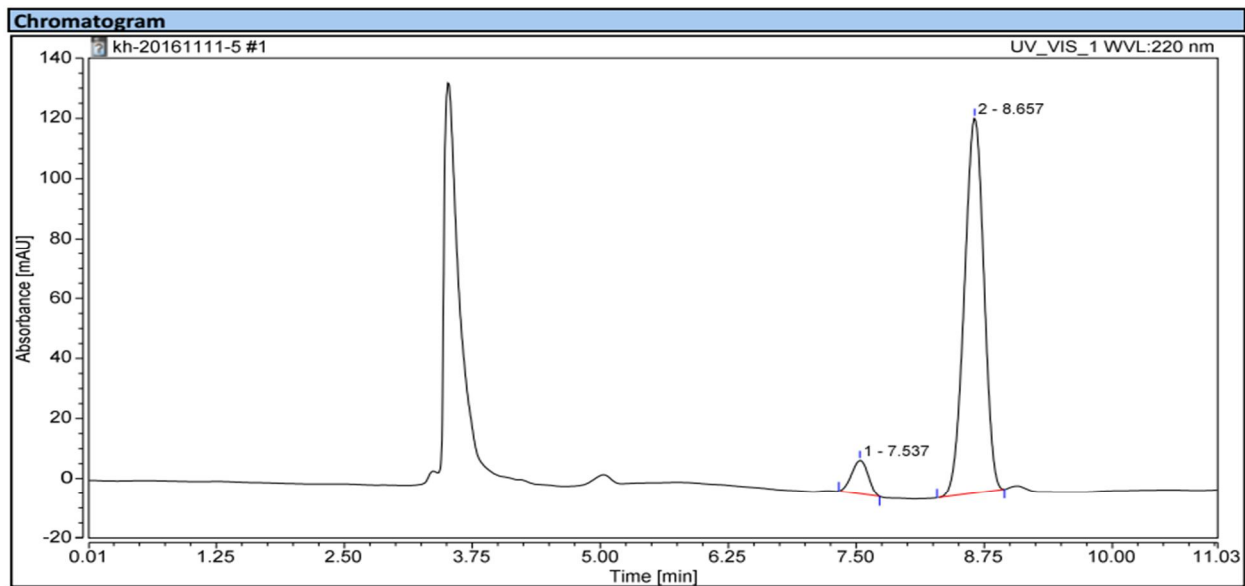
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		7.440	3.656	21.485	4.55	5.50	n.a.
2		7.960	76.761	368.978	95.45	94.50	n.a.
Total:			80.417	390.463	100.00	100.00	



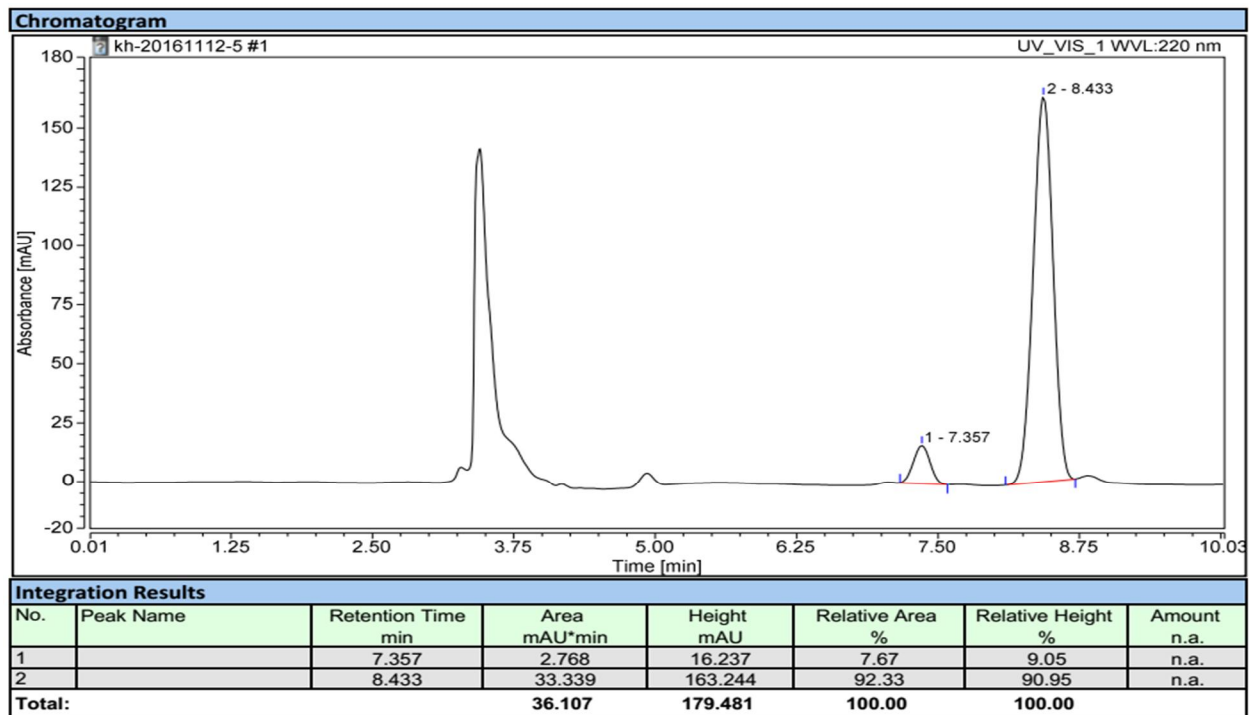
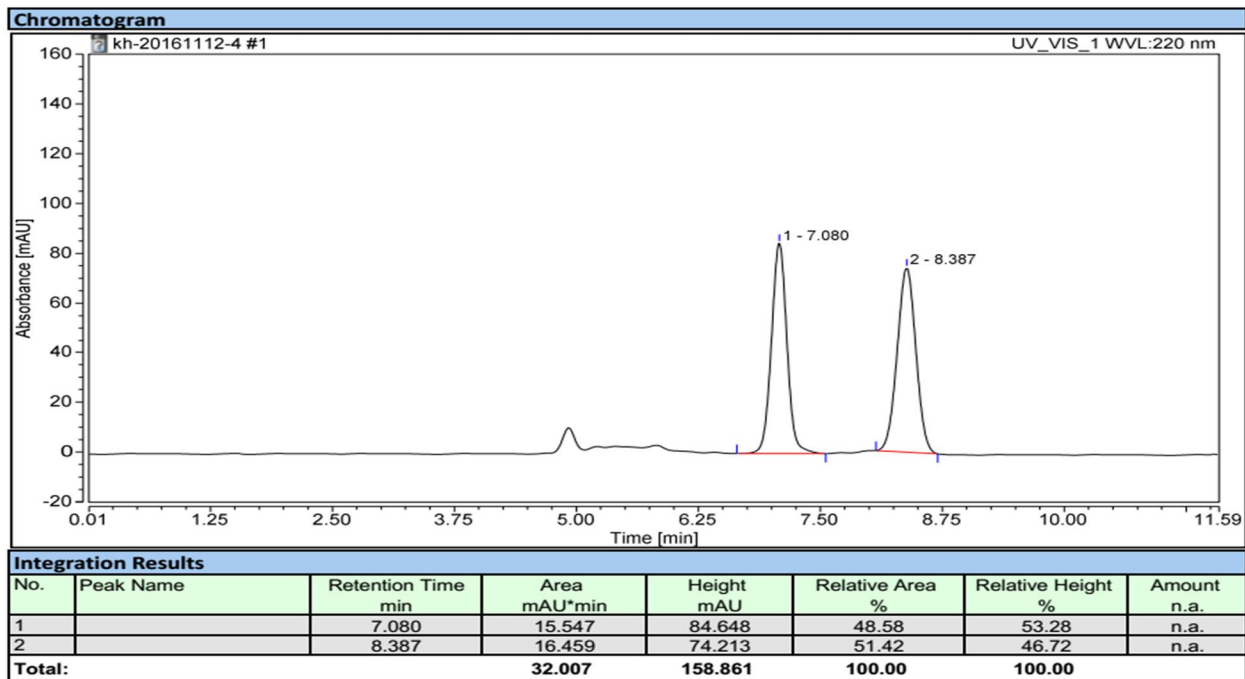
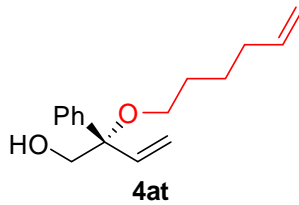
Integration Results

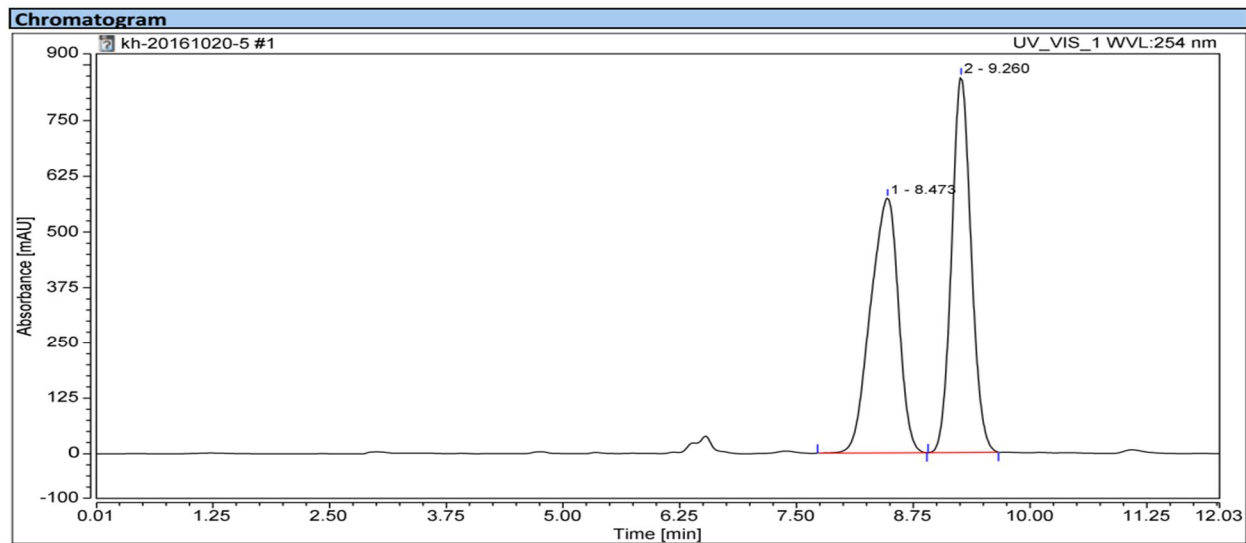
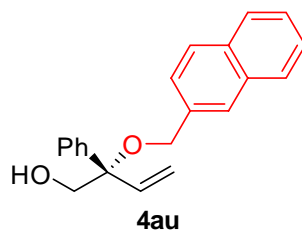
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.493	8.354	47.661	49.55	53.42	n.a.
2		8.607	8.506	41.561	50.45	46.58	n.a.
Total:			16.860	89.222	100.00	100.00	



Integration Results

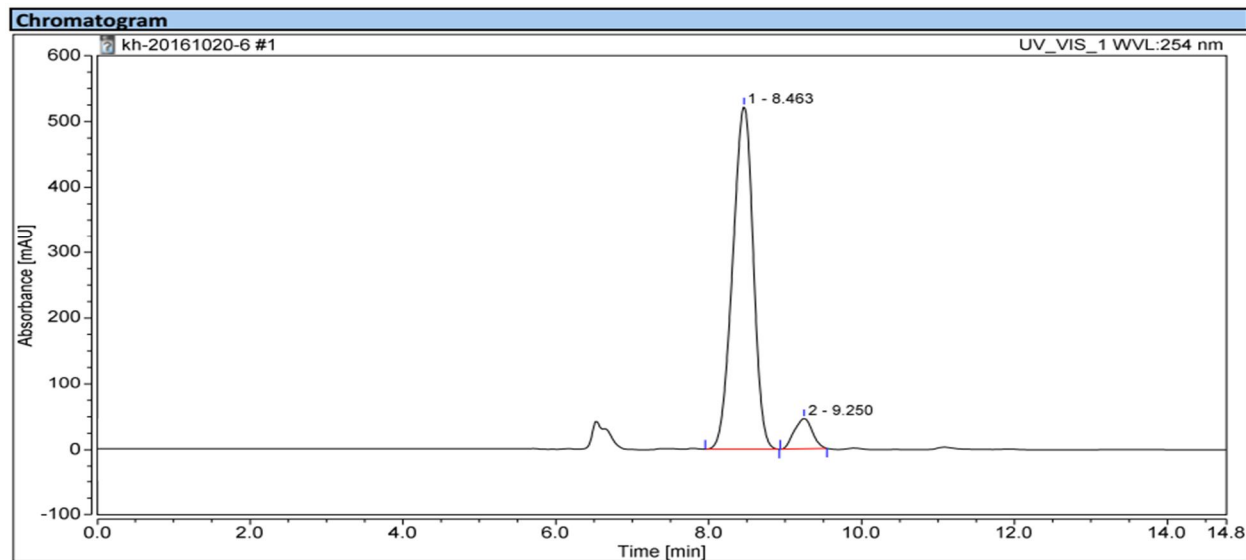
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.537	2.108	11.307	7.09	8.30	n.a.
2		8.657	27.629	124.993	92.91	91.70	n.a.
Total:			29.737	136.300	100.00	100.00	





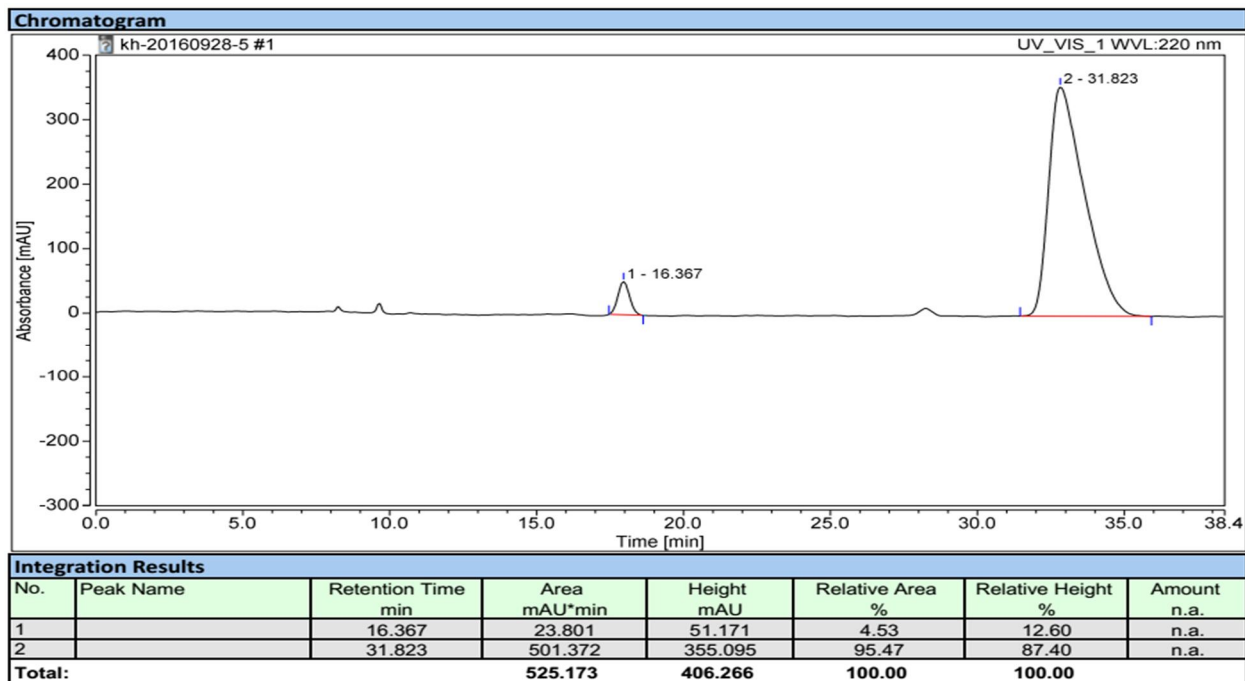
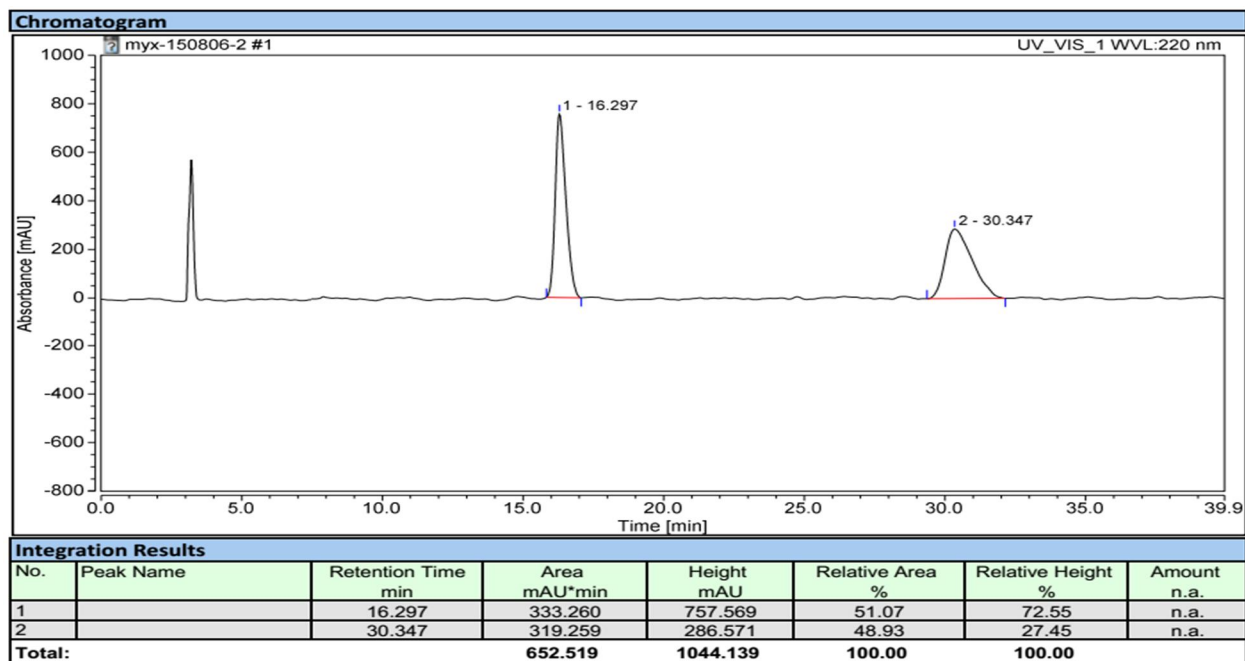
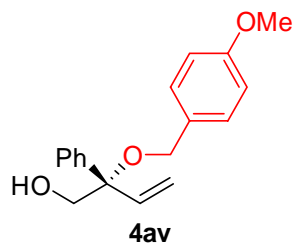
Integration Results

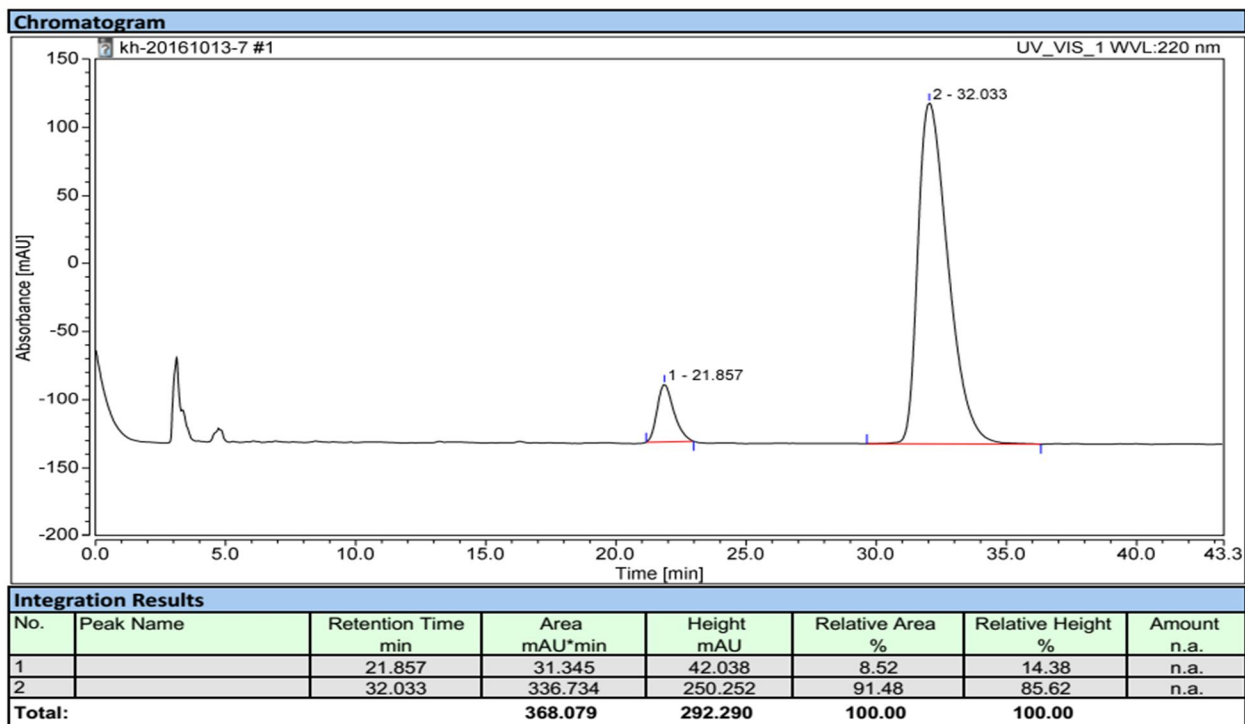
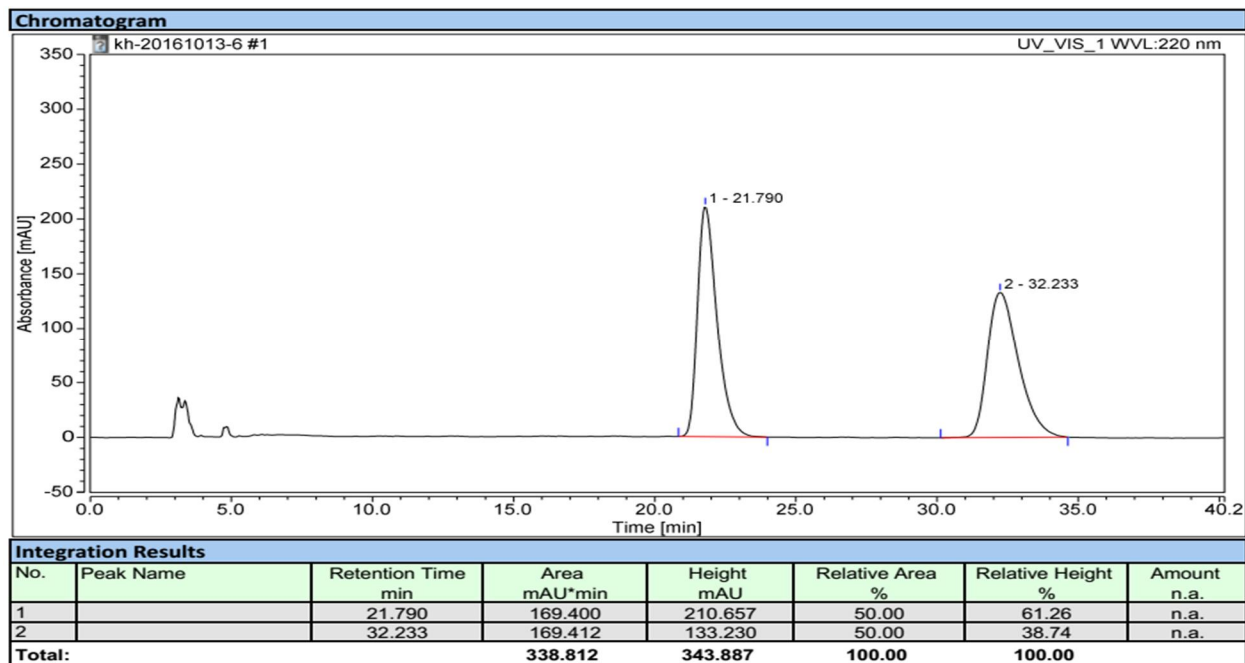
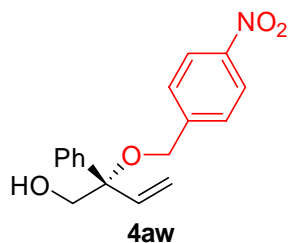
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.473	199.618	574.517	49.32	40.46	n.a.
2		9.260	205.126	845.335	50.68	59.54	n.a.
Total:			404.743	1419.852	100.00	100.00	

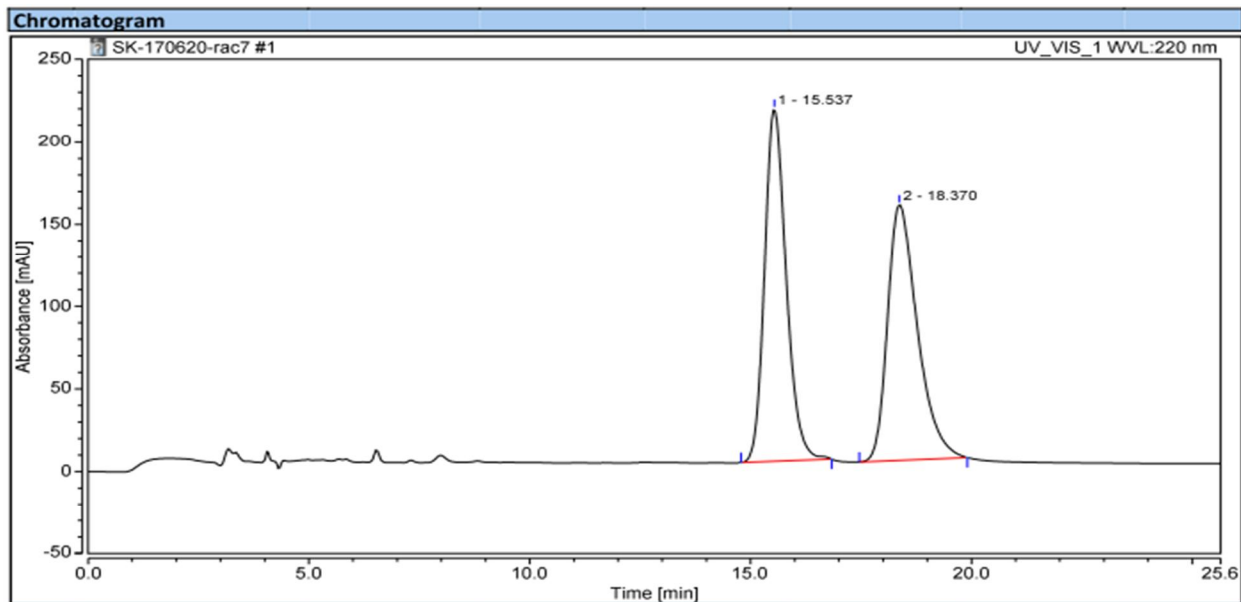
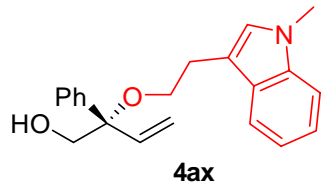


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.463	162.675	521.381	92.84	91.89	n.a.
2		9.250	12.549	46.023	7.16	8.11	n.a.
Total:			175.224	567.405	100.00	100.00	

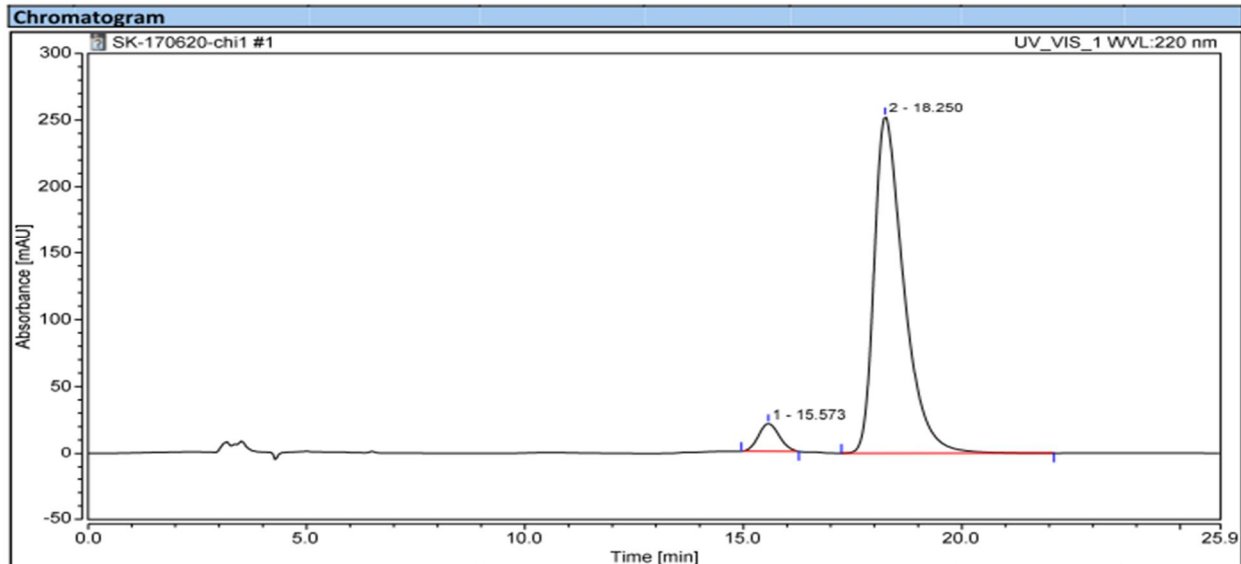






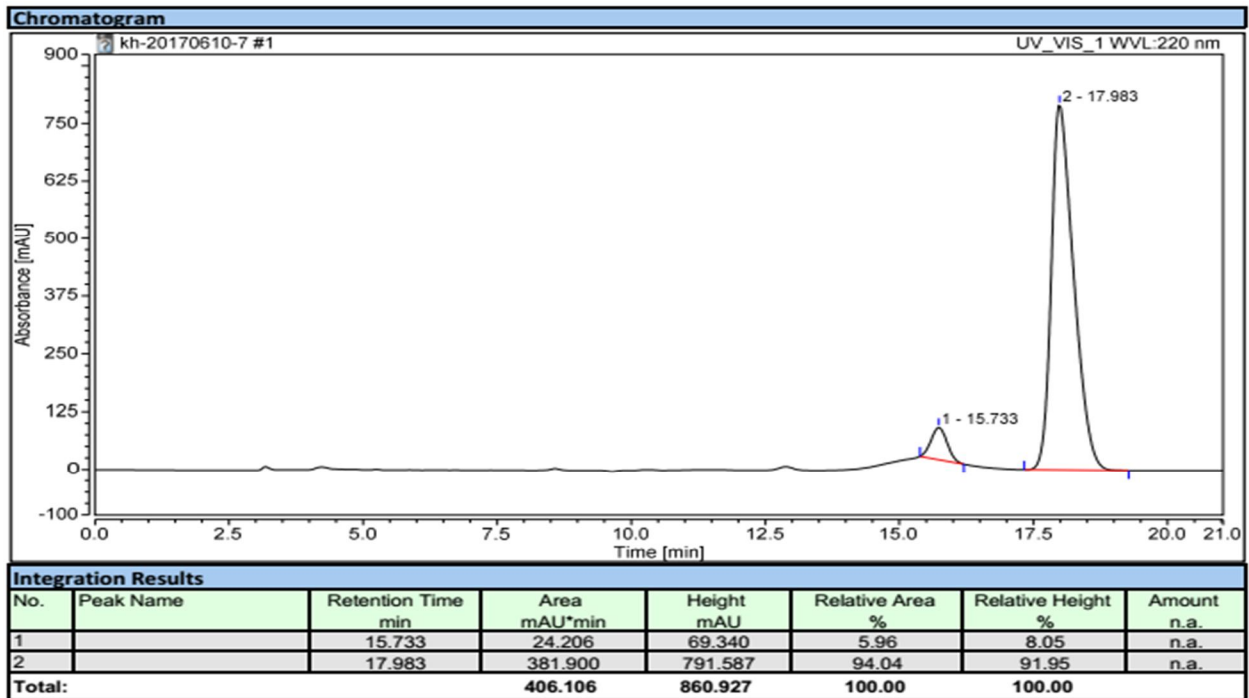
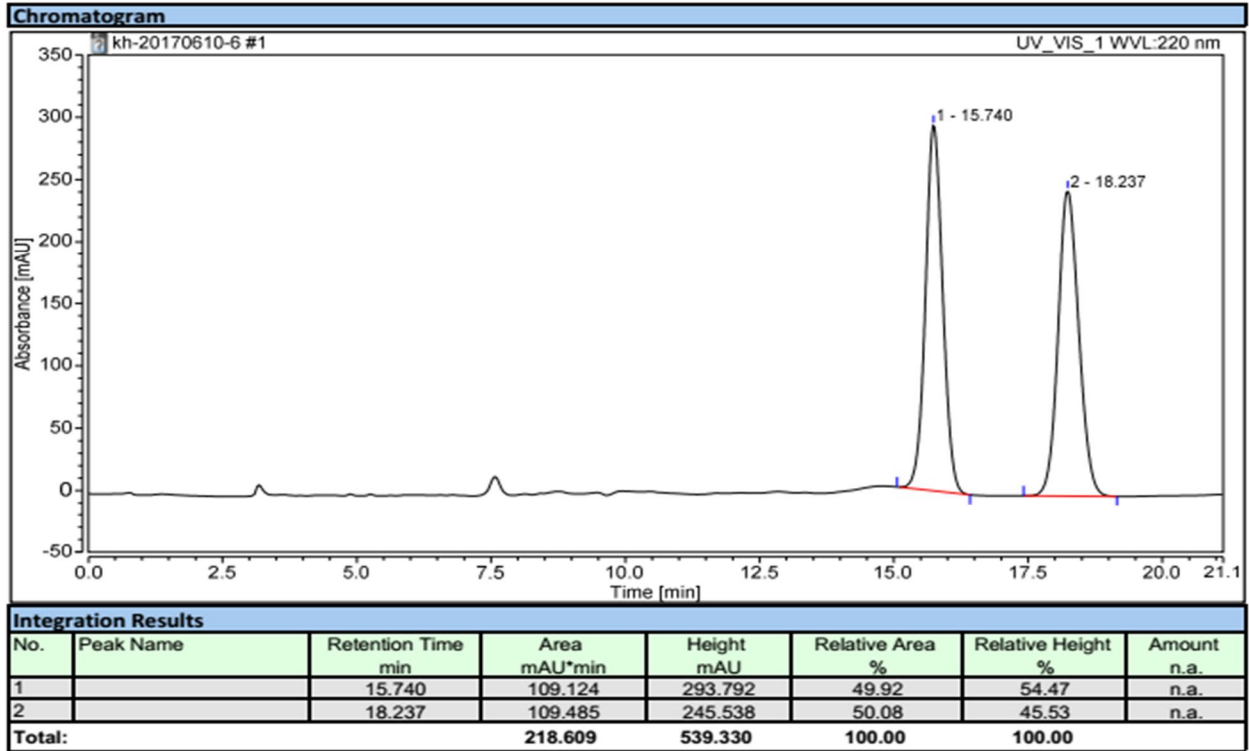
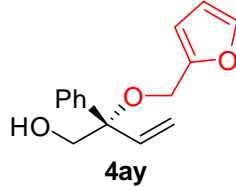
Integration Results

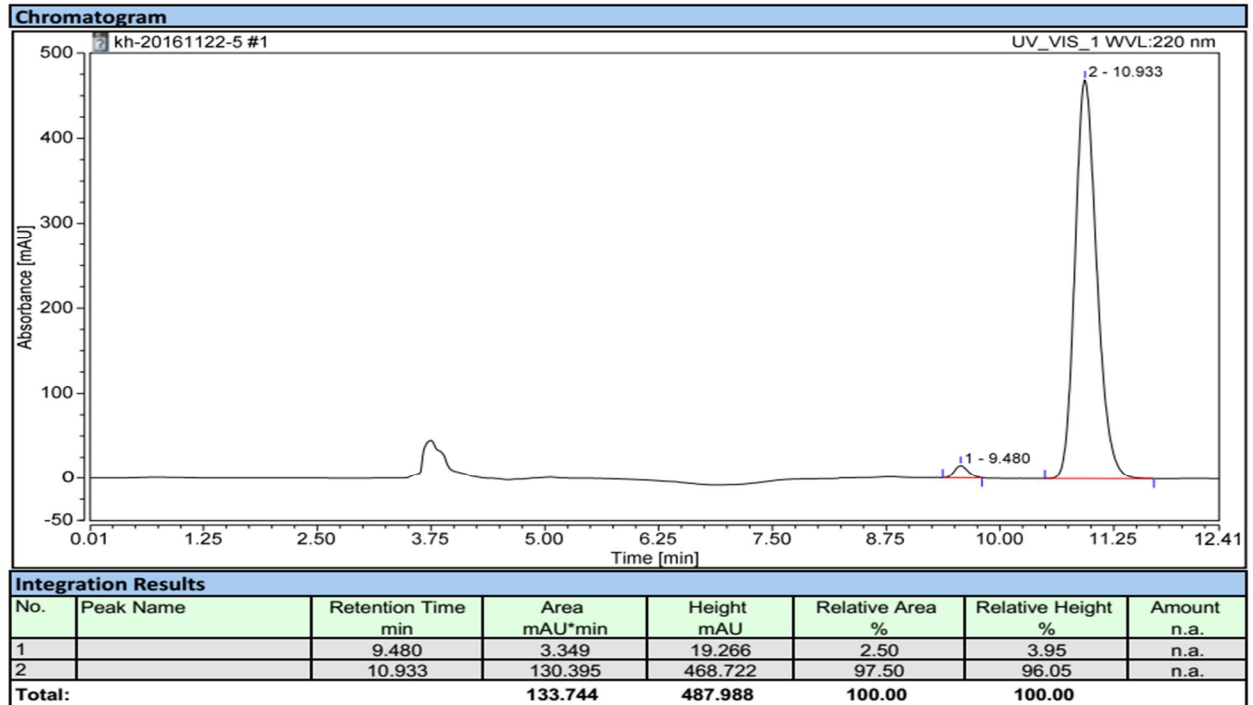
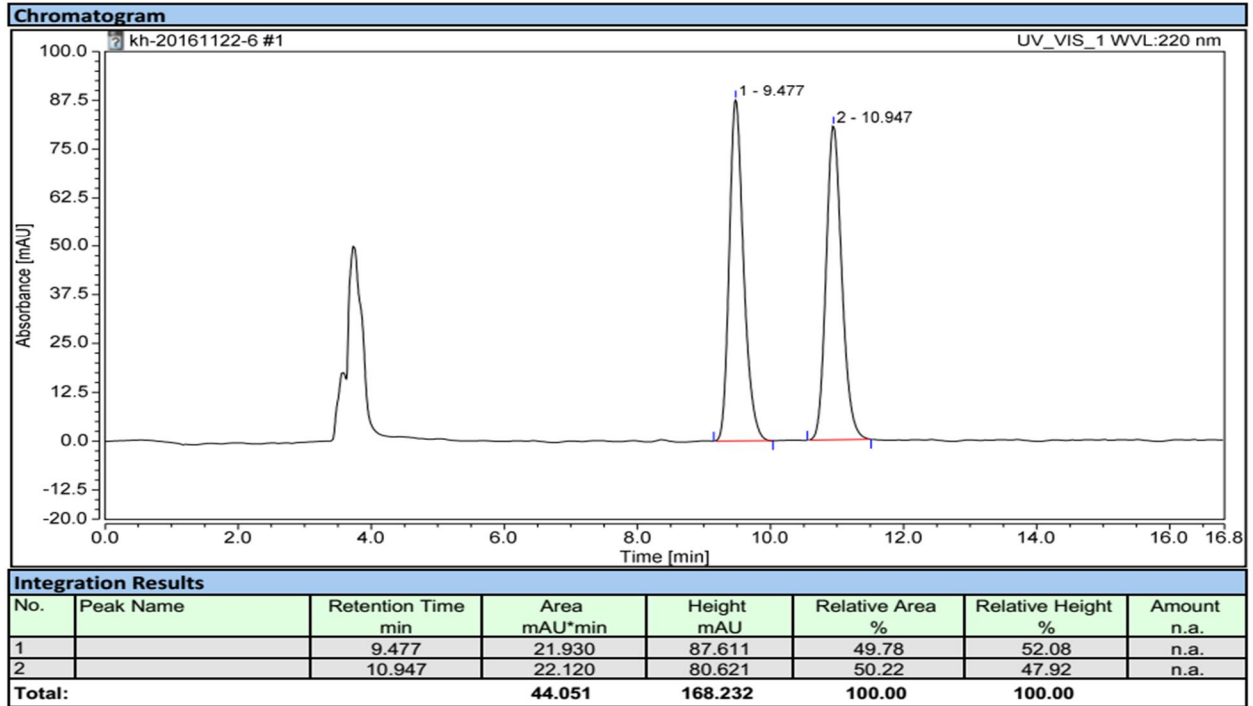
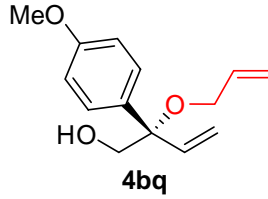
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.537	121.130	213.417	50.01	57.91	n.a.
2		18.370	121.065	155.125	49.99	42.09	n.a.
Total:			242.195	368.542	100.00	100.00	

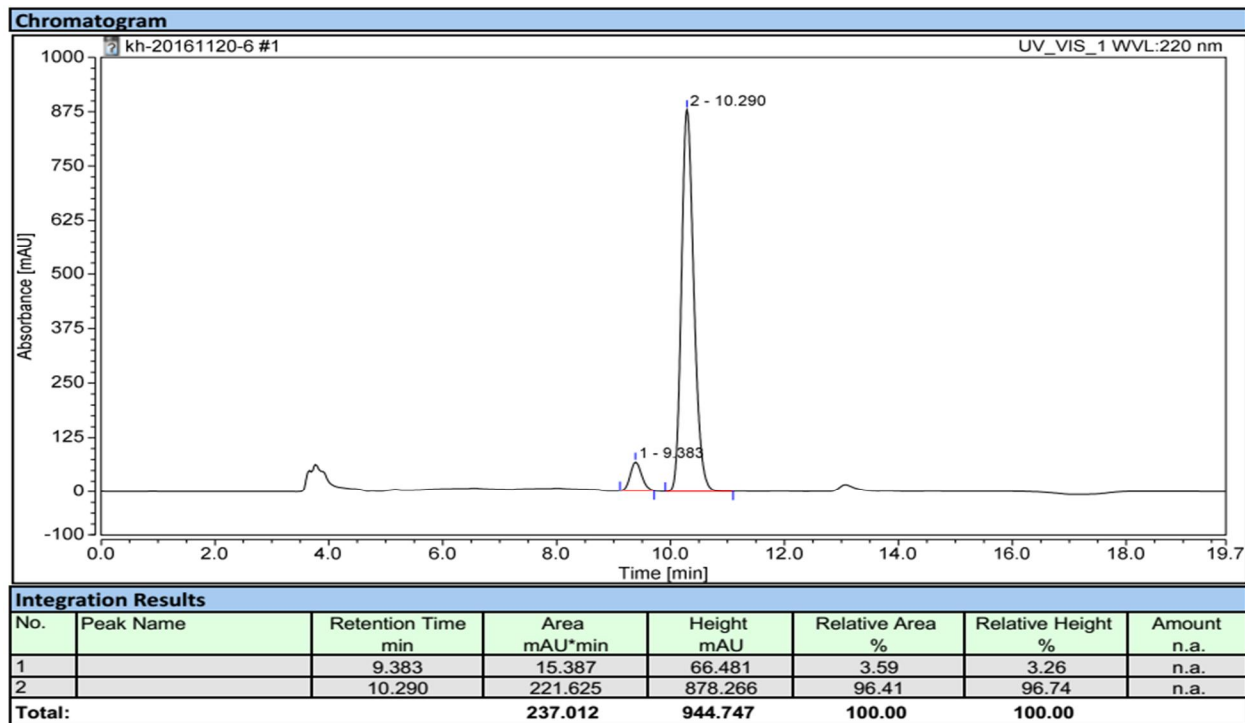
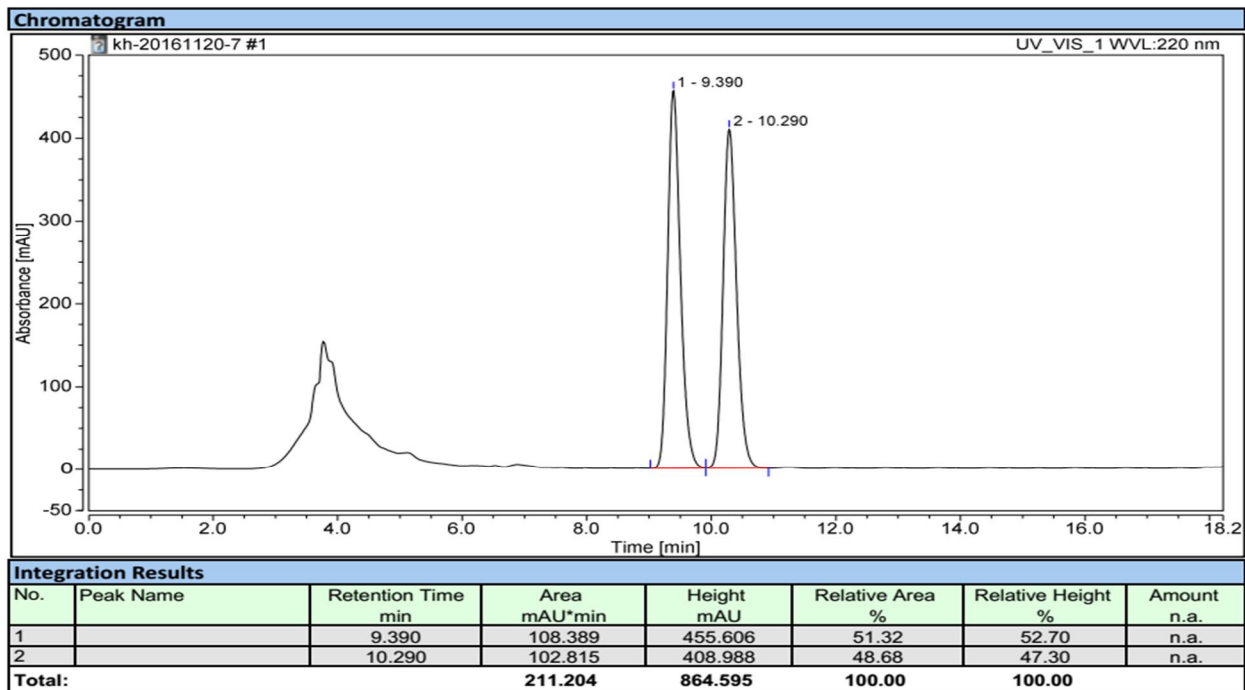
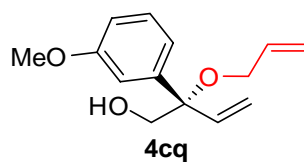


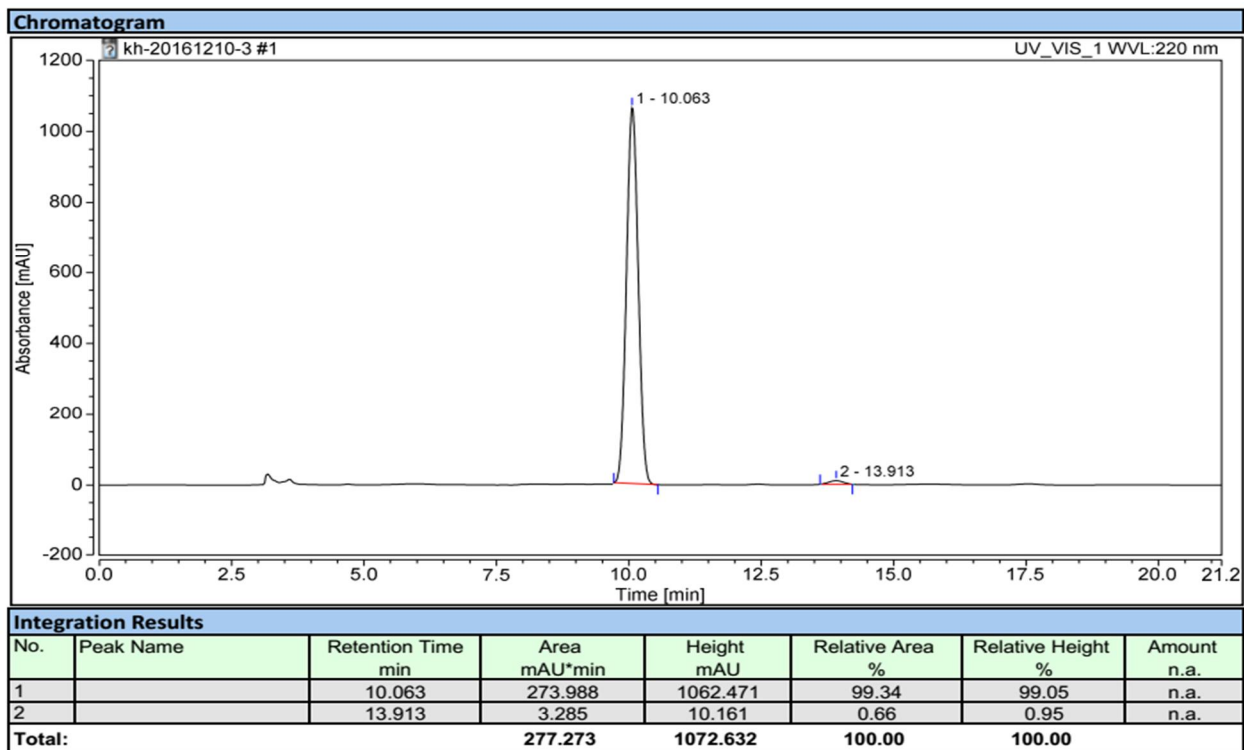
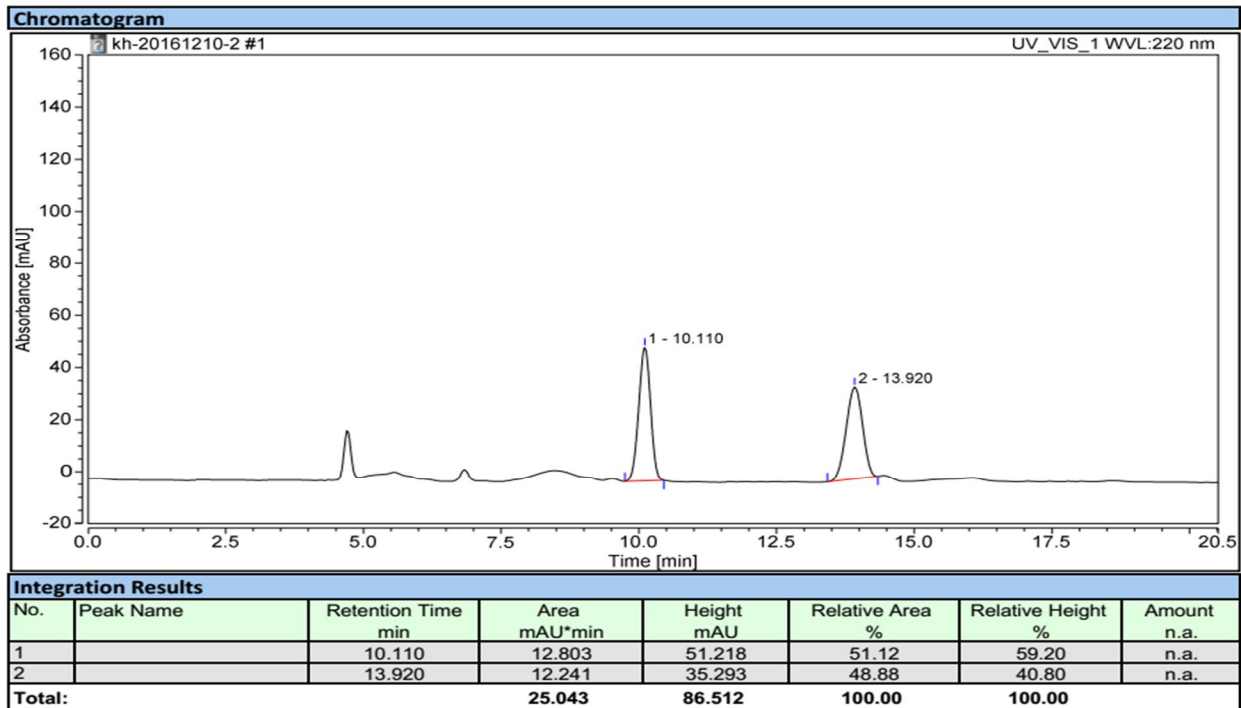
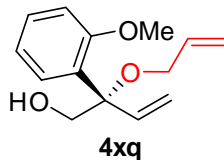
Integration Results

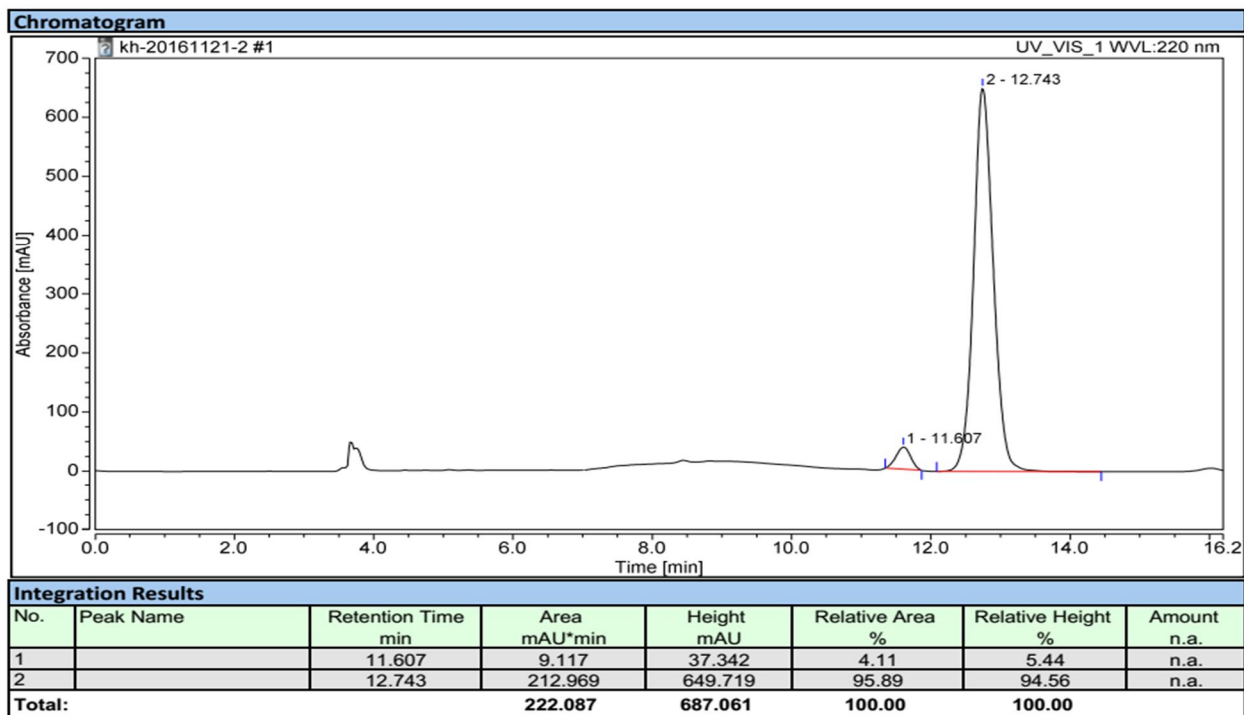
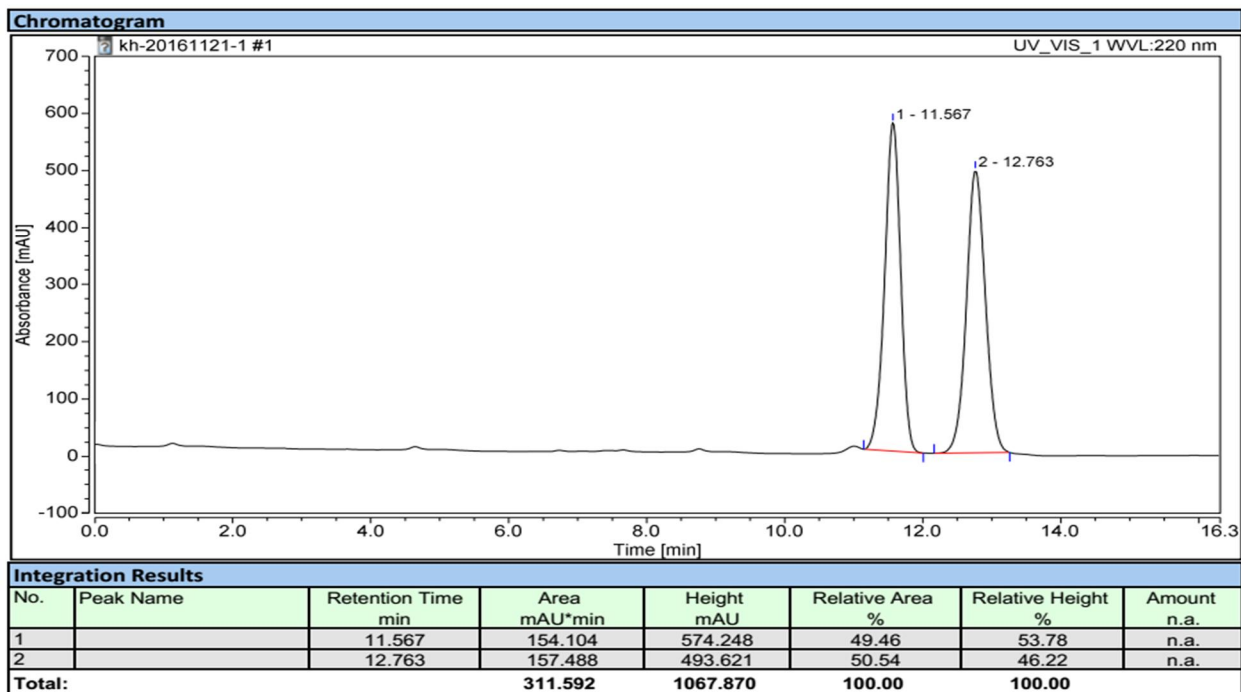
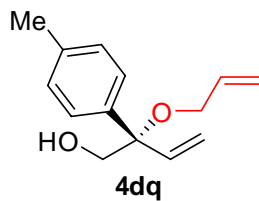
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.573	11.419	20.723	5.46	7.59	n.a.
2		18.250	197.888	252.290	94.54	92.41	n.a.
Total:			209.307	273.013	100.00	100.00	

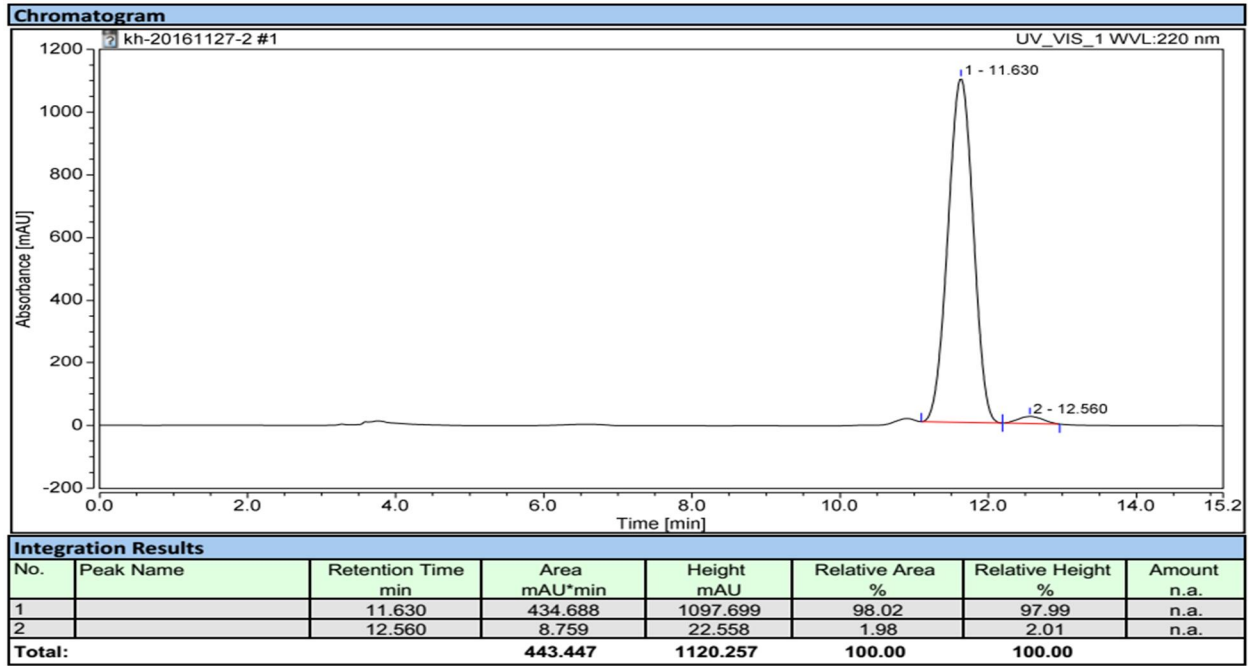
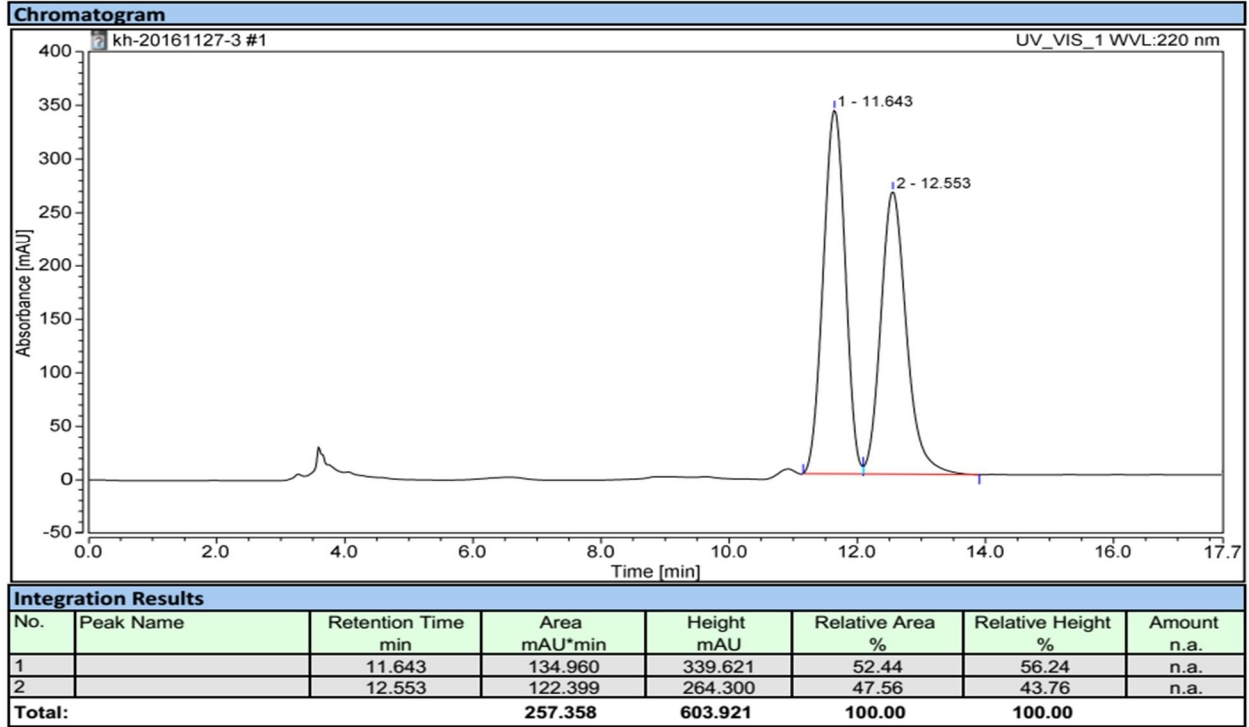
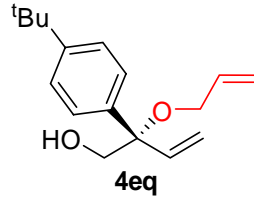


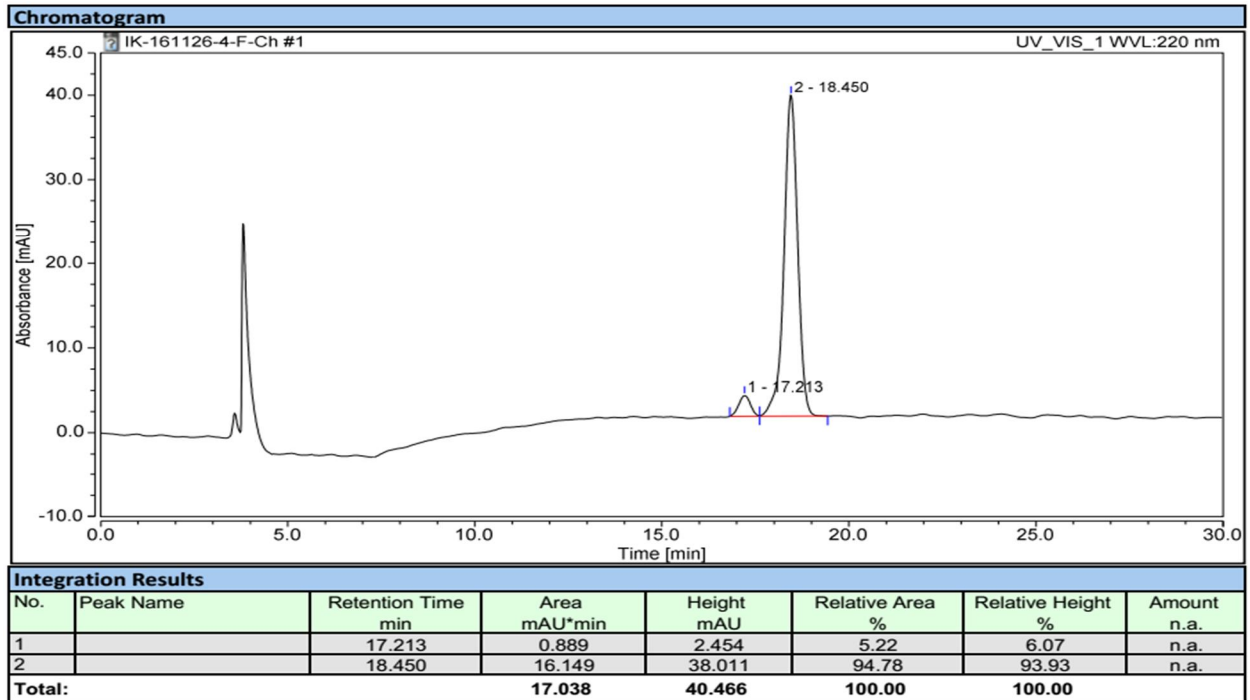
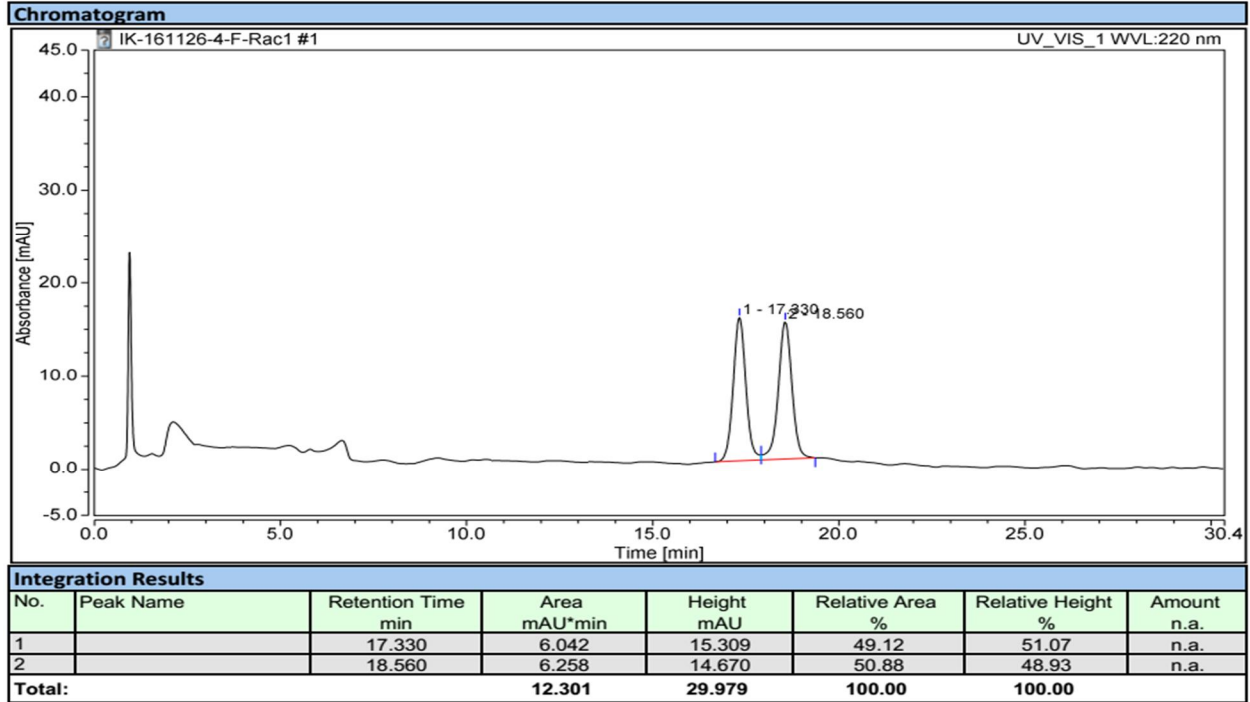
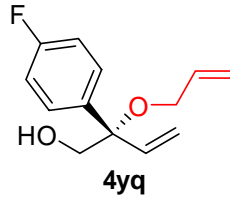


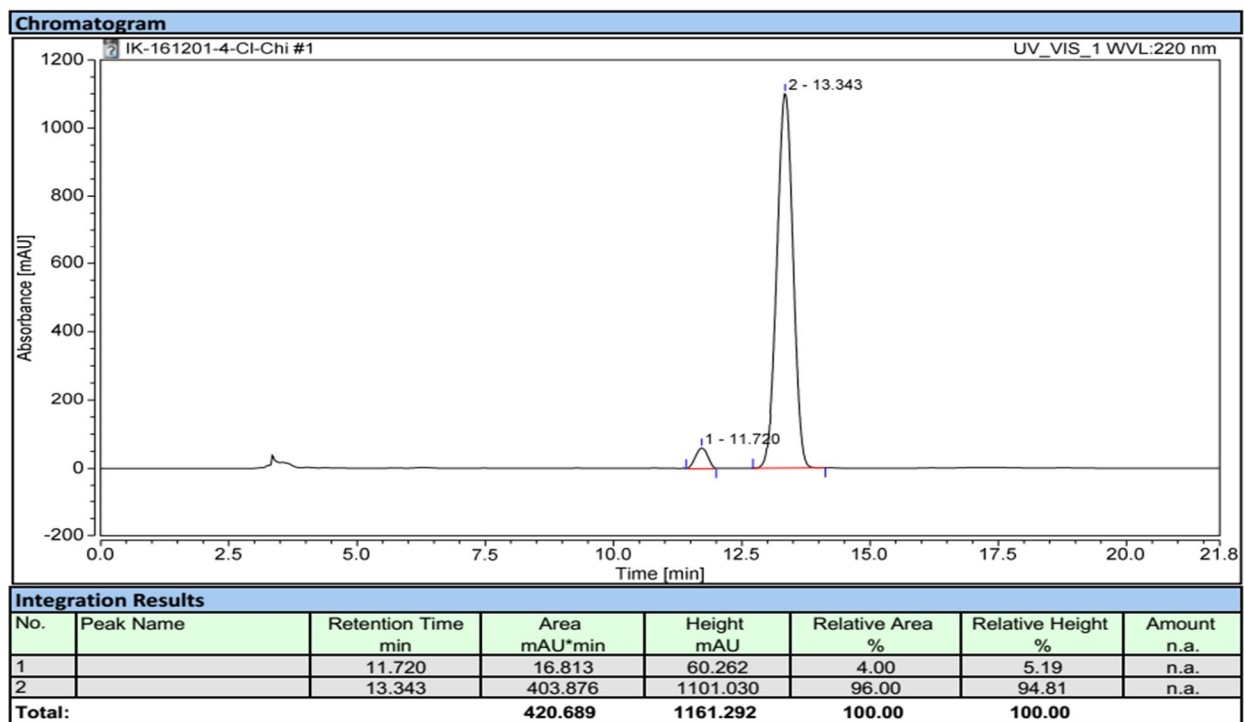
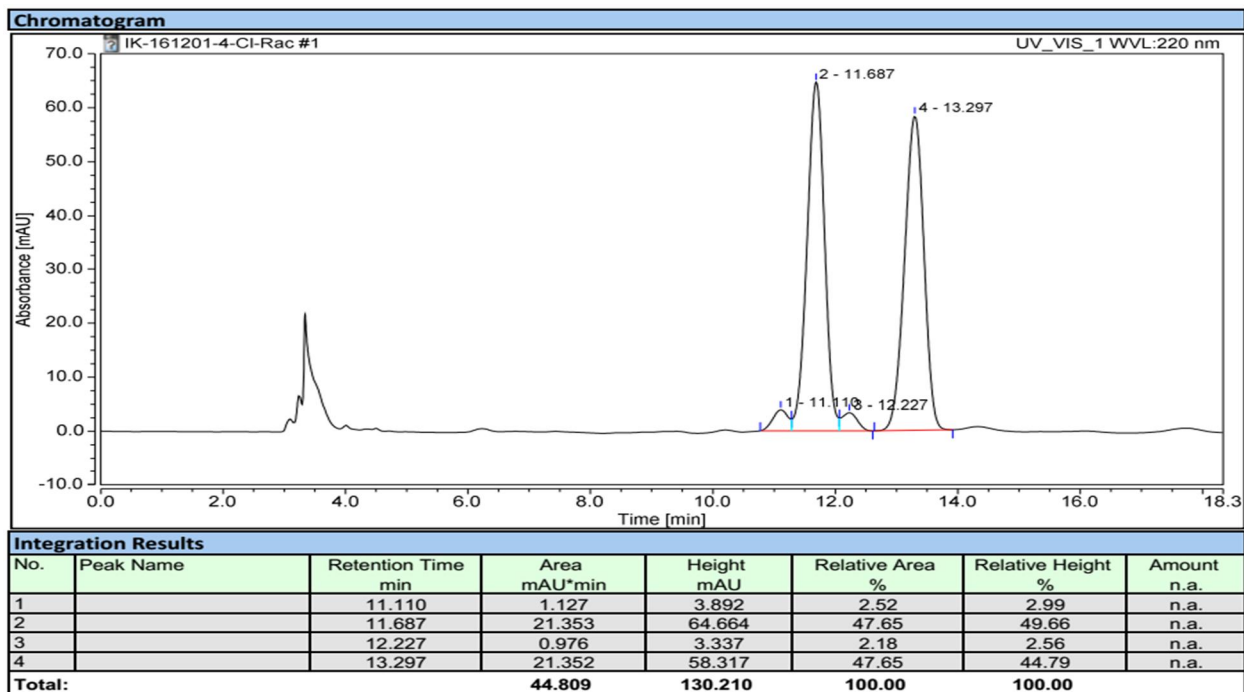
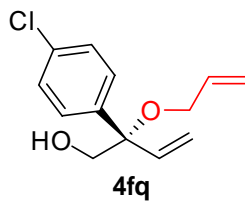


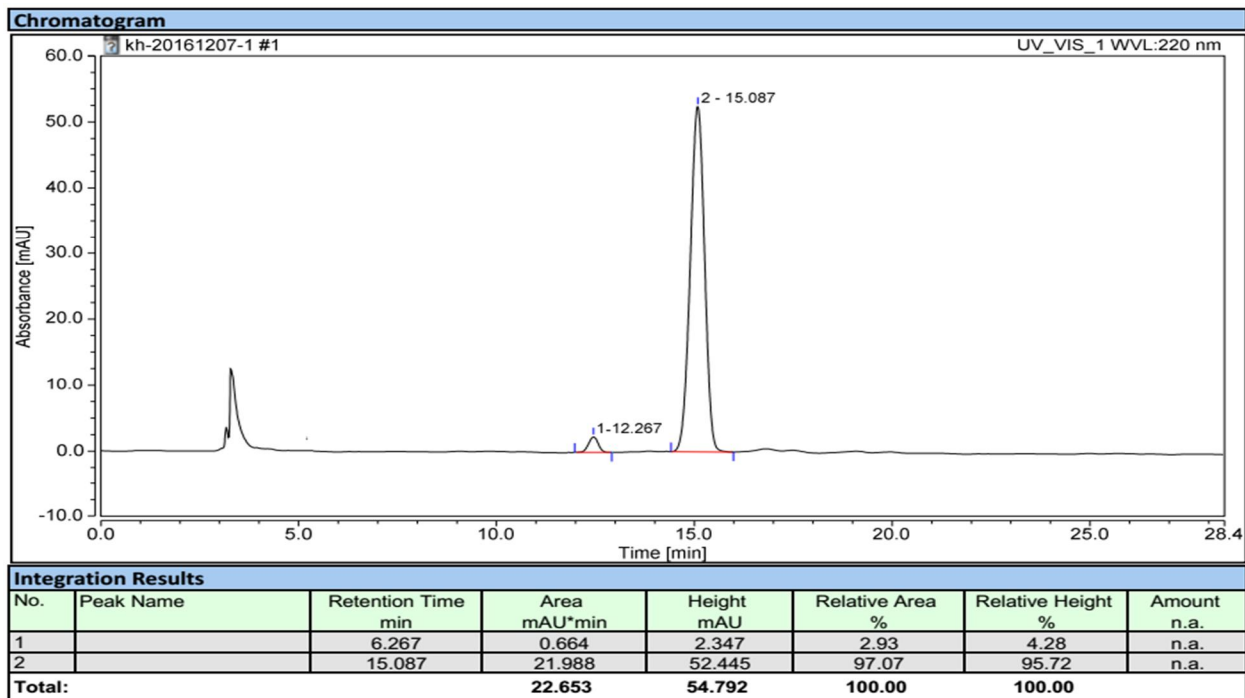
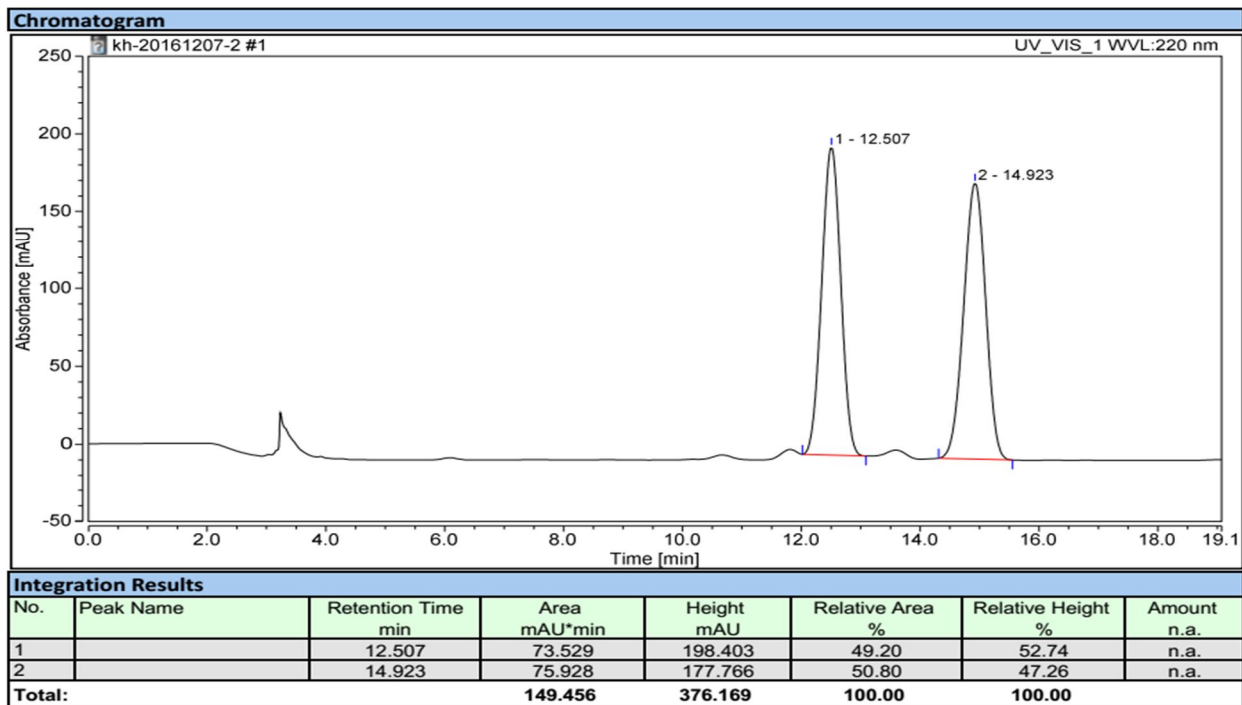
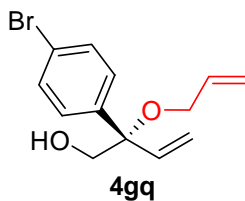


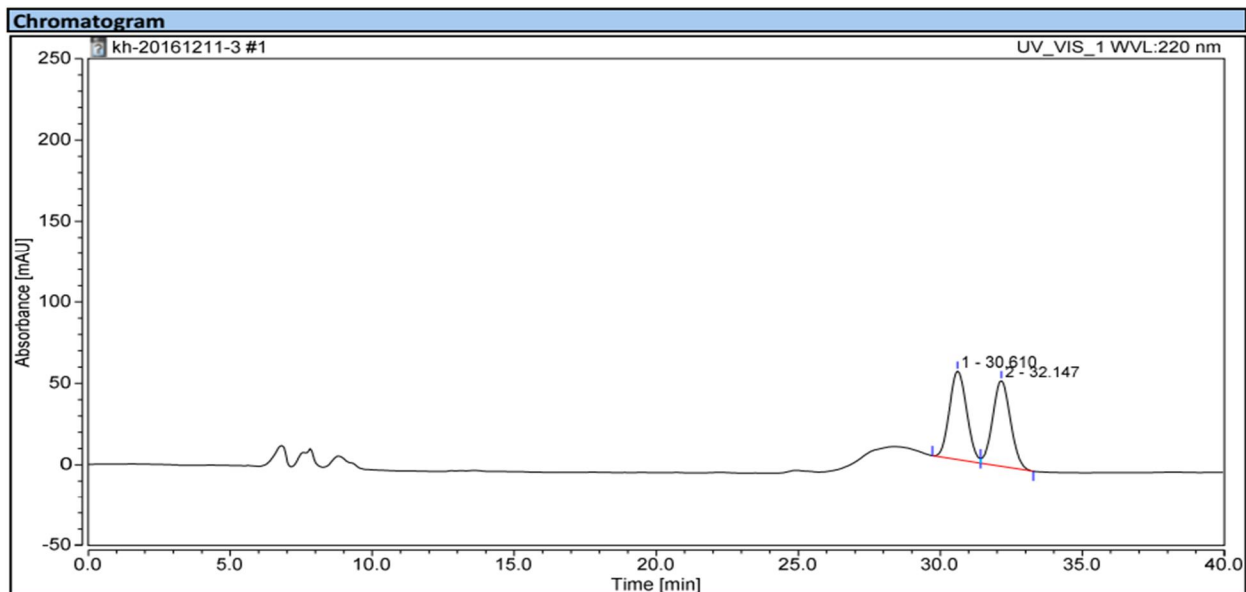
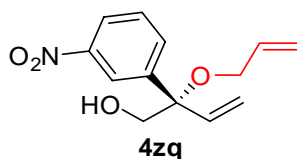






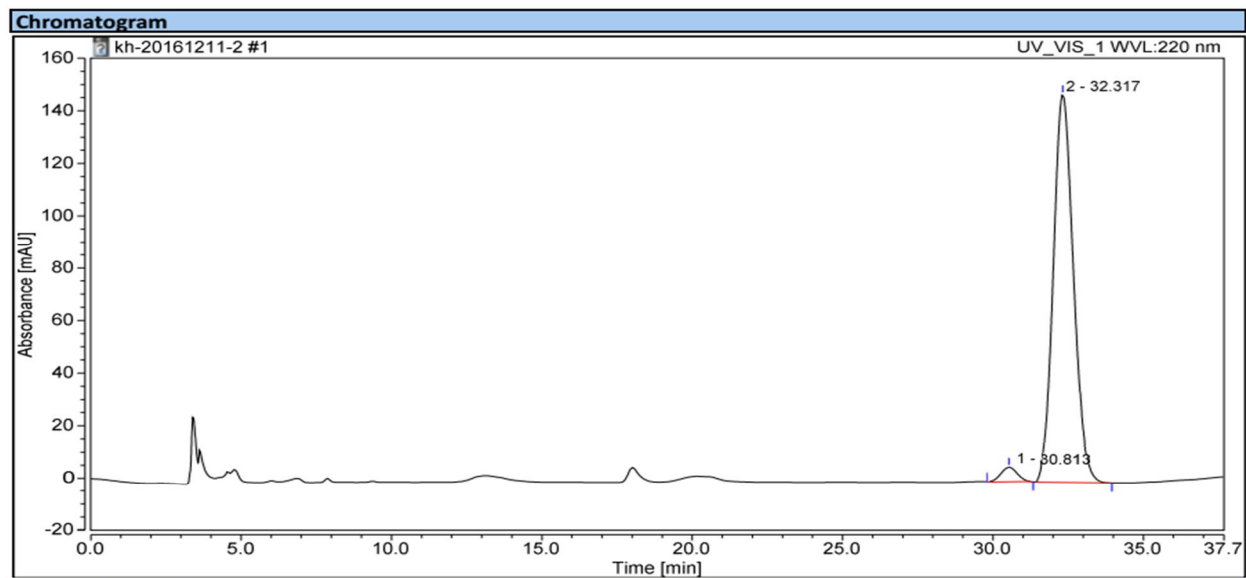






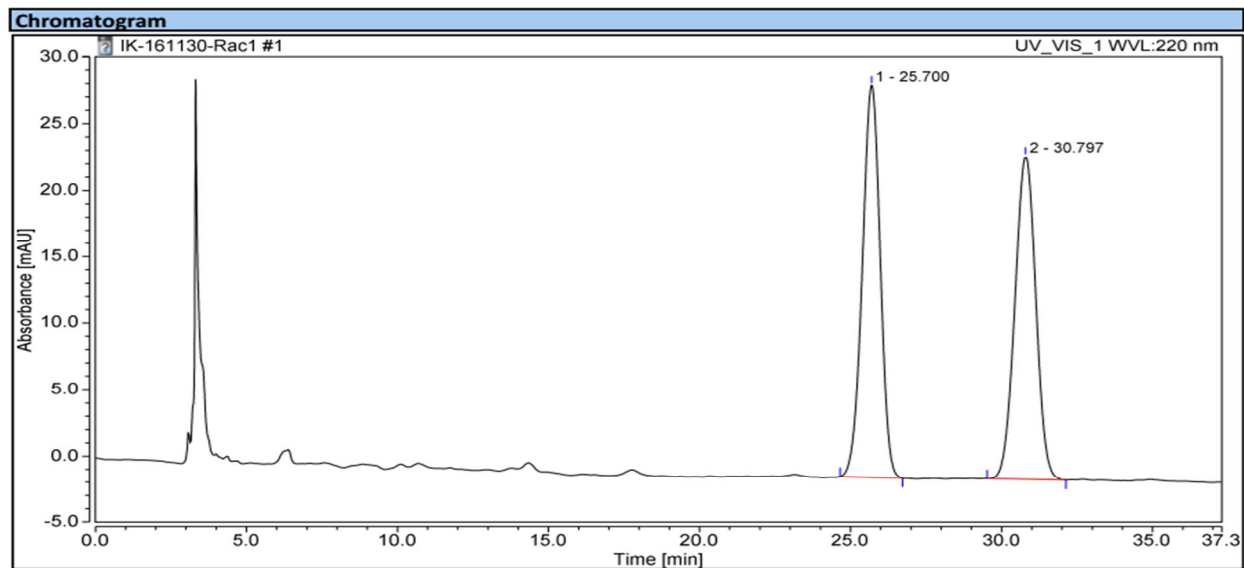
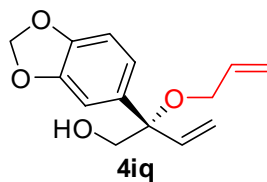
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.610	38.110	54.282	49.80	50.79	n.a.
2		32.147	38.411	52.587	50.20	49.21	n.a.
Total:			76.520	106.869	100.00	100.00	



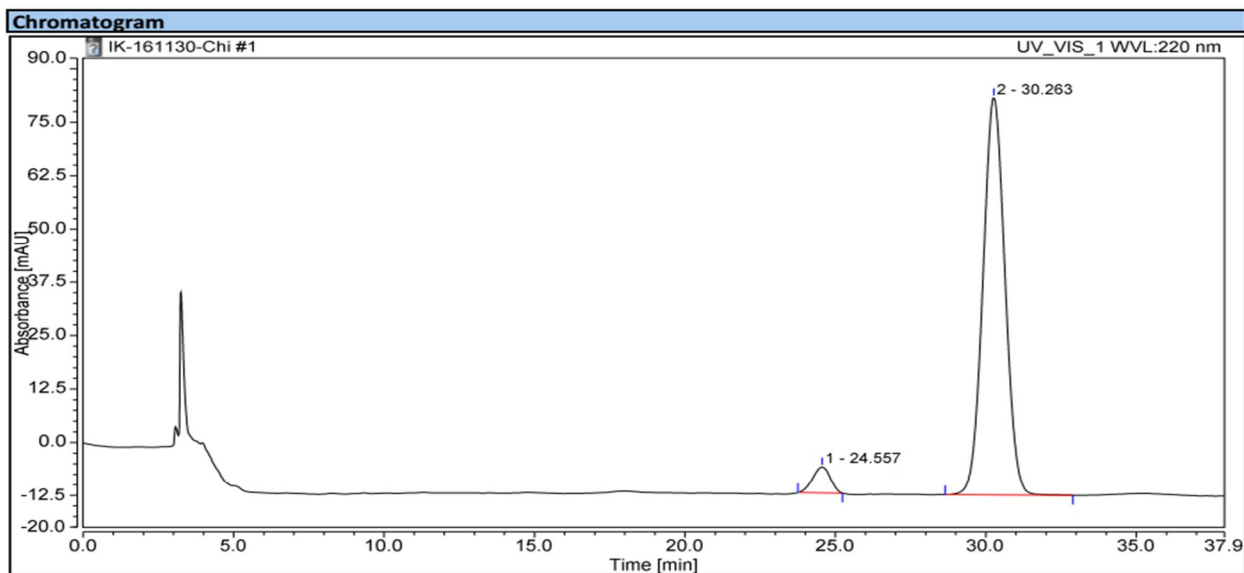
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.687	3.500	5.530	3.11	3.69	n.a.
2		32.317	108.940	144.350	96.89	96.31	n.a.
Total:			112.440	149.880	100.00	100.00	



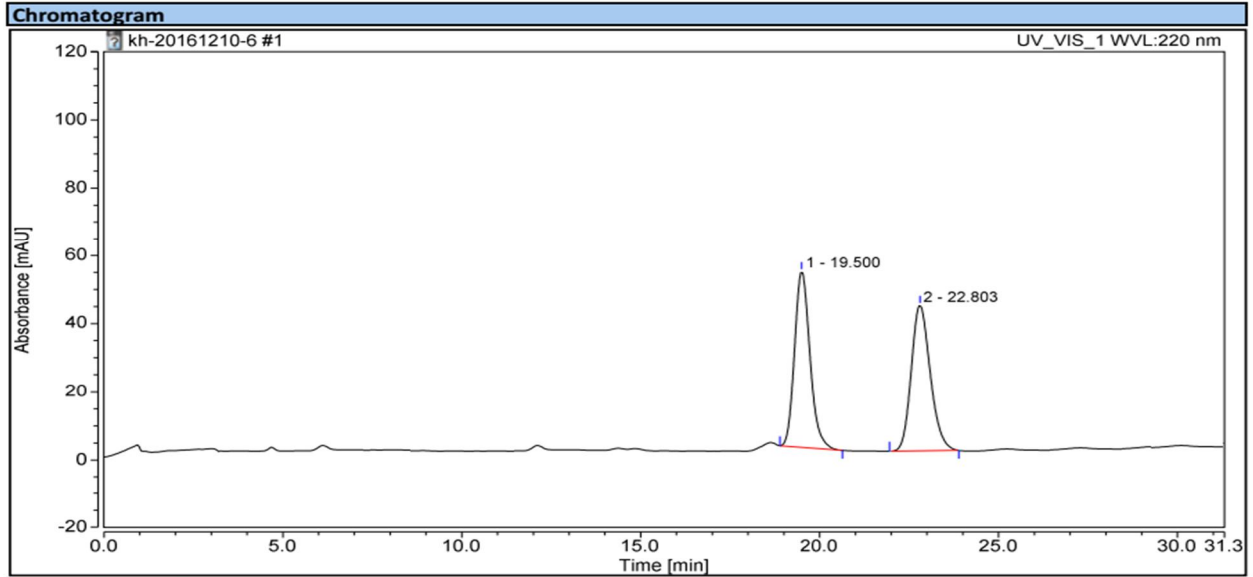
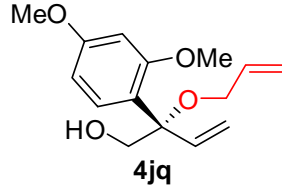
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.700	20.249	29.484	50.93	54.81	n.a.
2		30.797	19.511	24.304	49.07	45.19	n.a.
Total:			39.760	53.788	100.00	100.00	



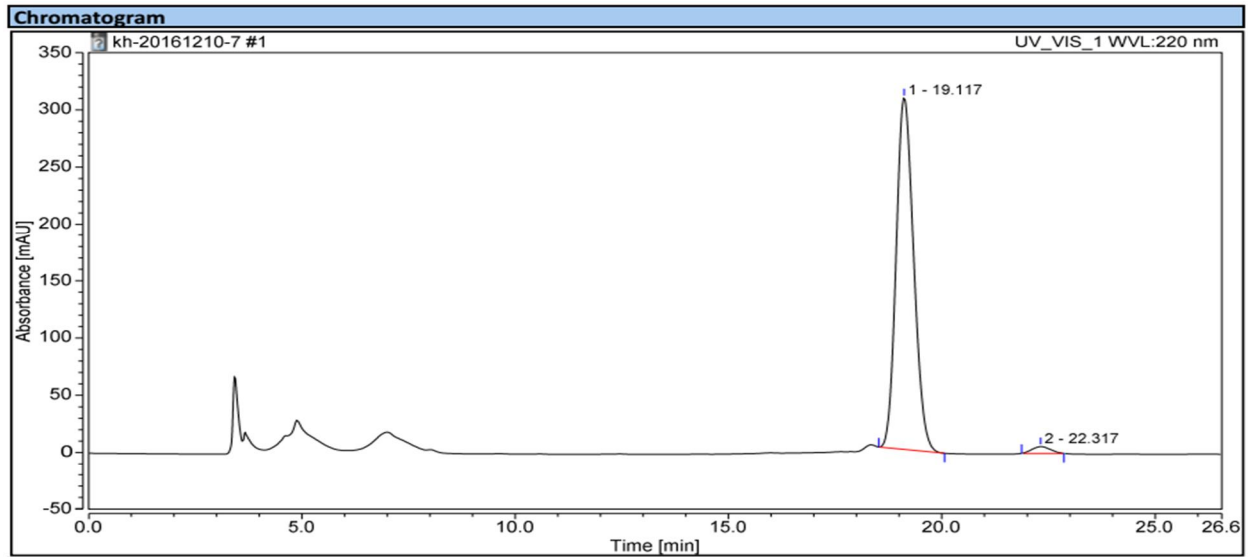
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.557	4.240	6.242	5.09	6.28	n.a.
2		30.263	78.991	93.196	94.91	93.72	n.a.
Total:			83.232	99.438	100.00	100.00	



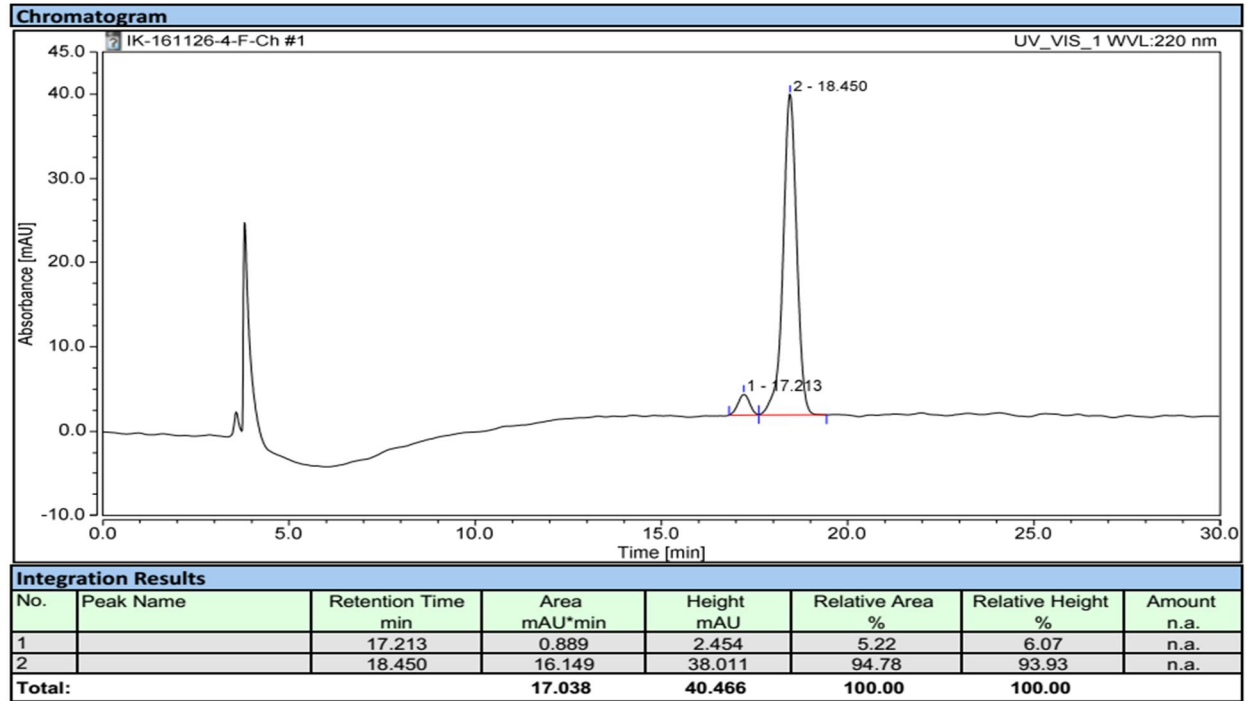
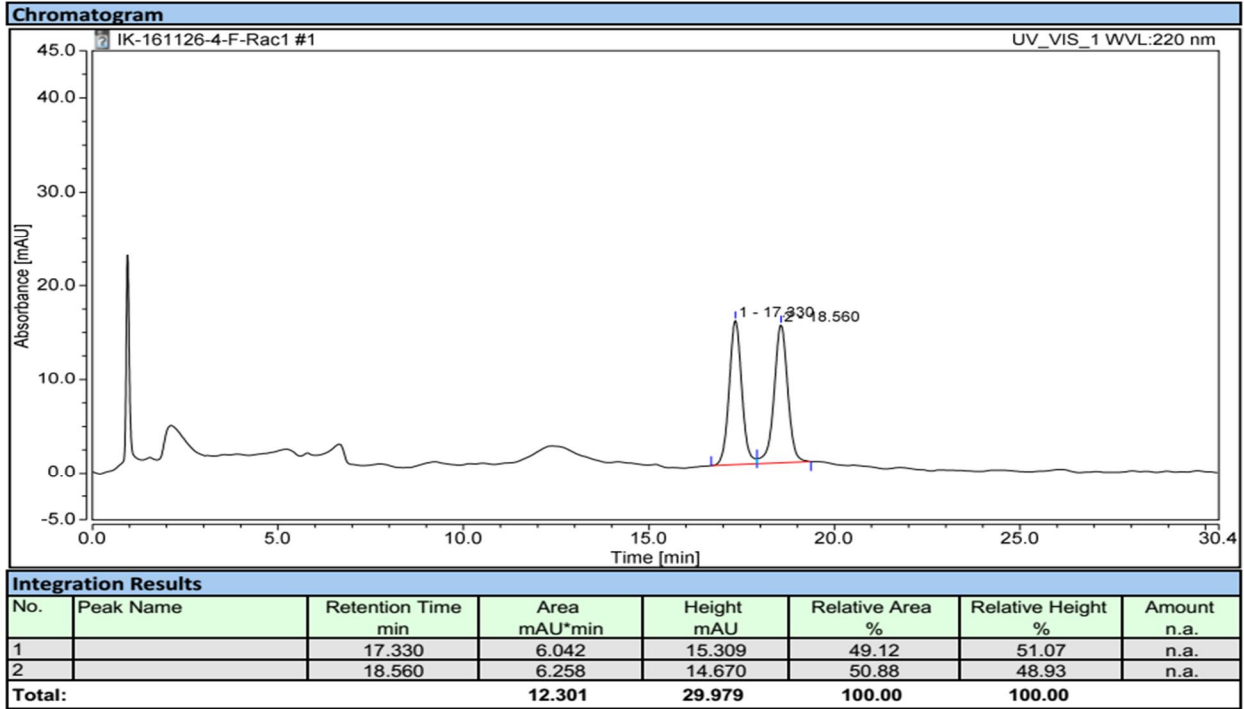
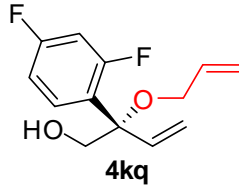
Integration Results

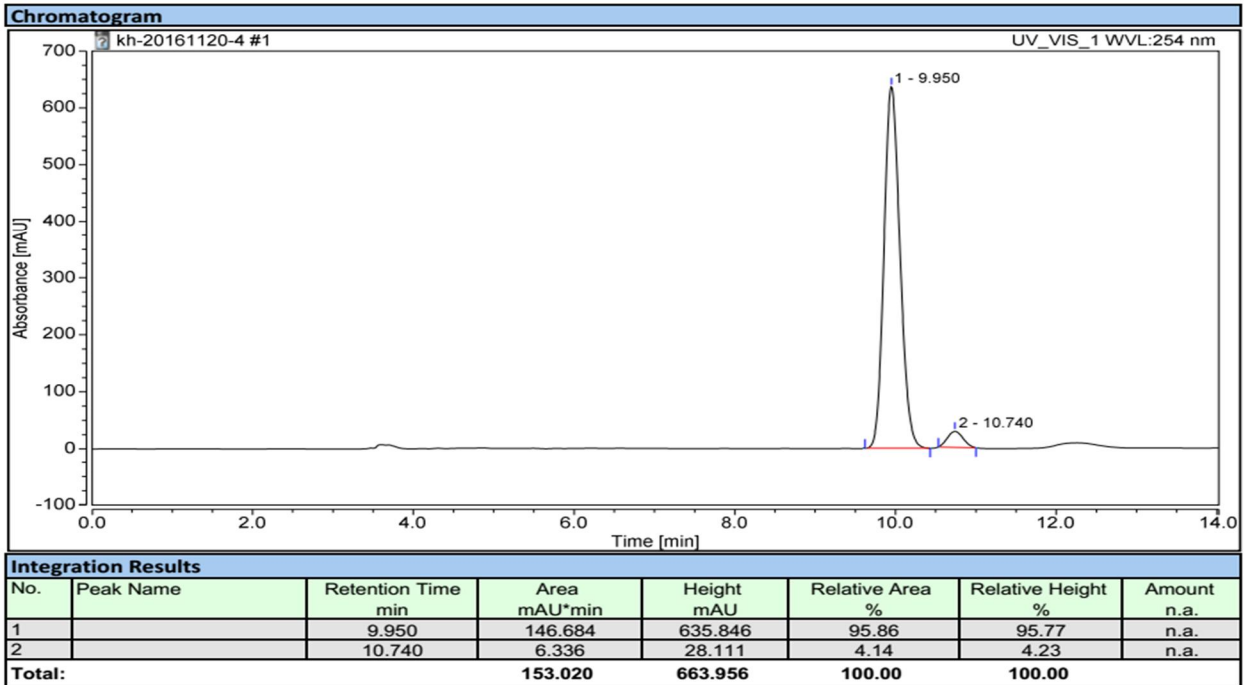
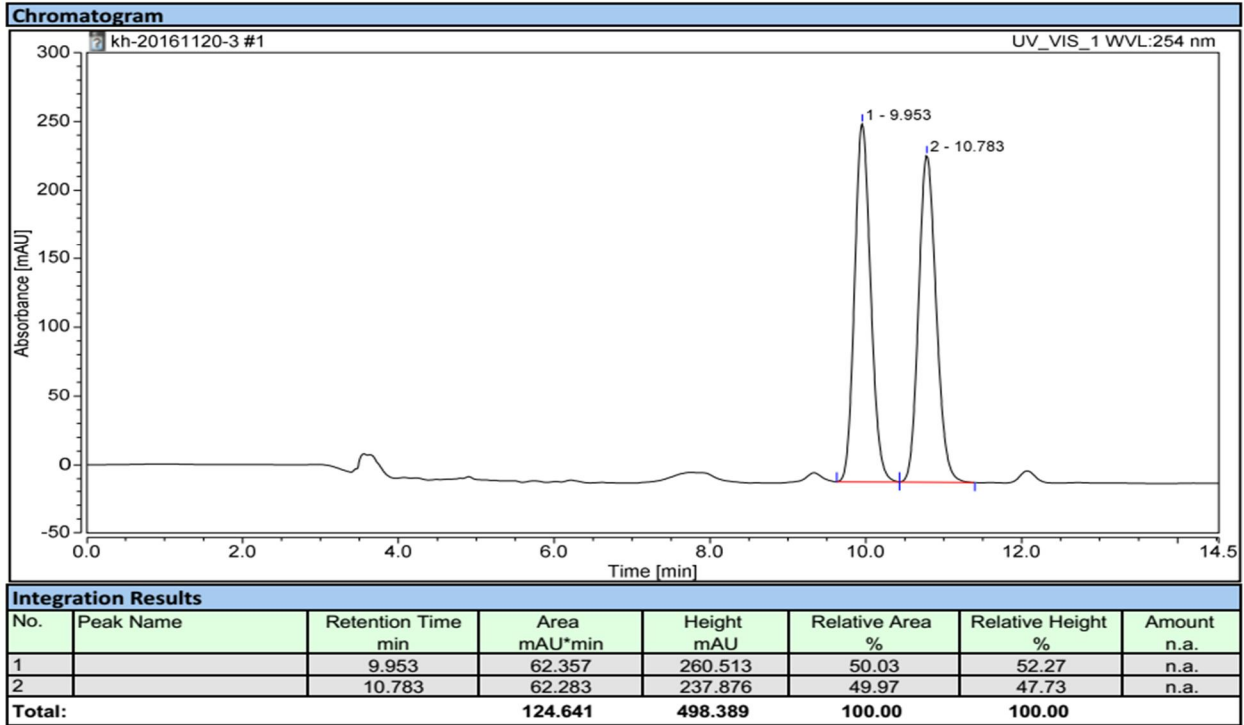
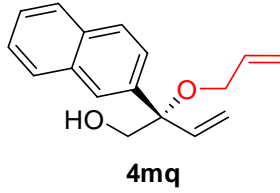
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.500	25.803	51.588	49.47	54.72	n.a.
2		22.803	26.357	42.680	50.53	45.28	n.a.
Total:			52.160	94.269	100.00	100.00	

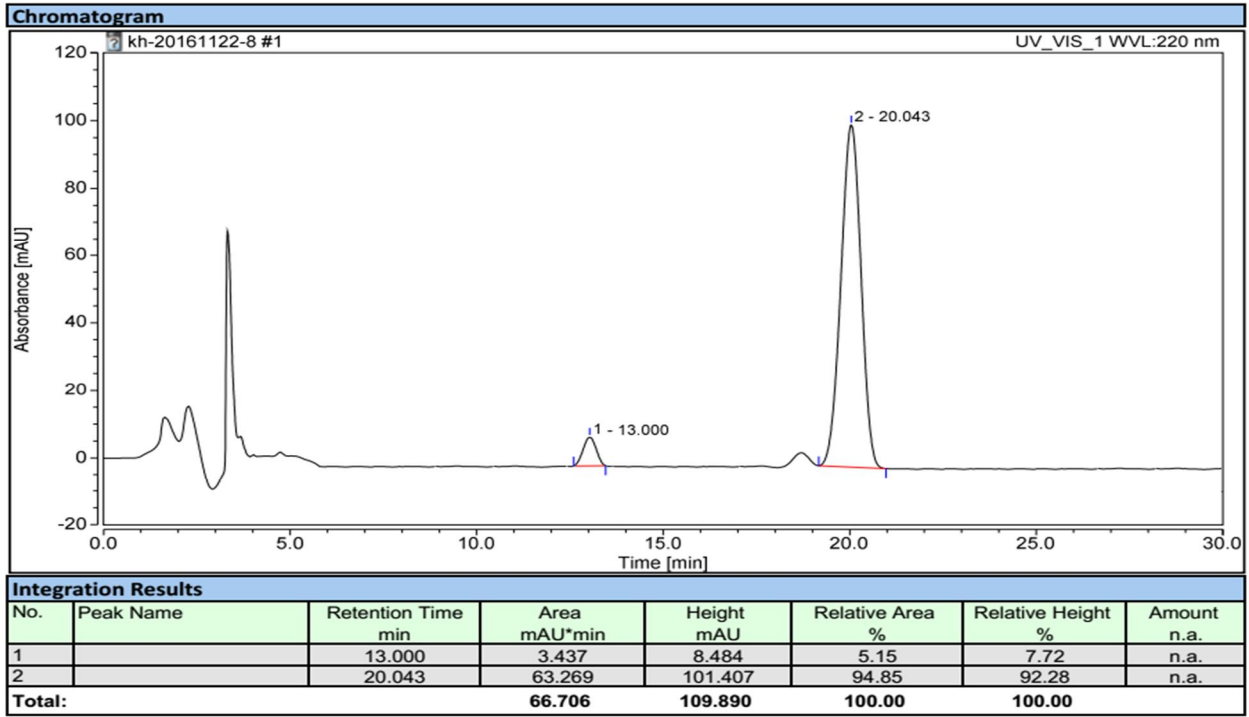
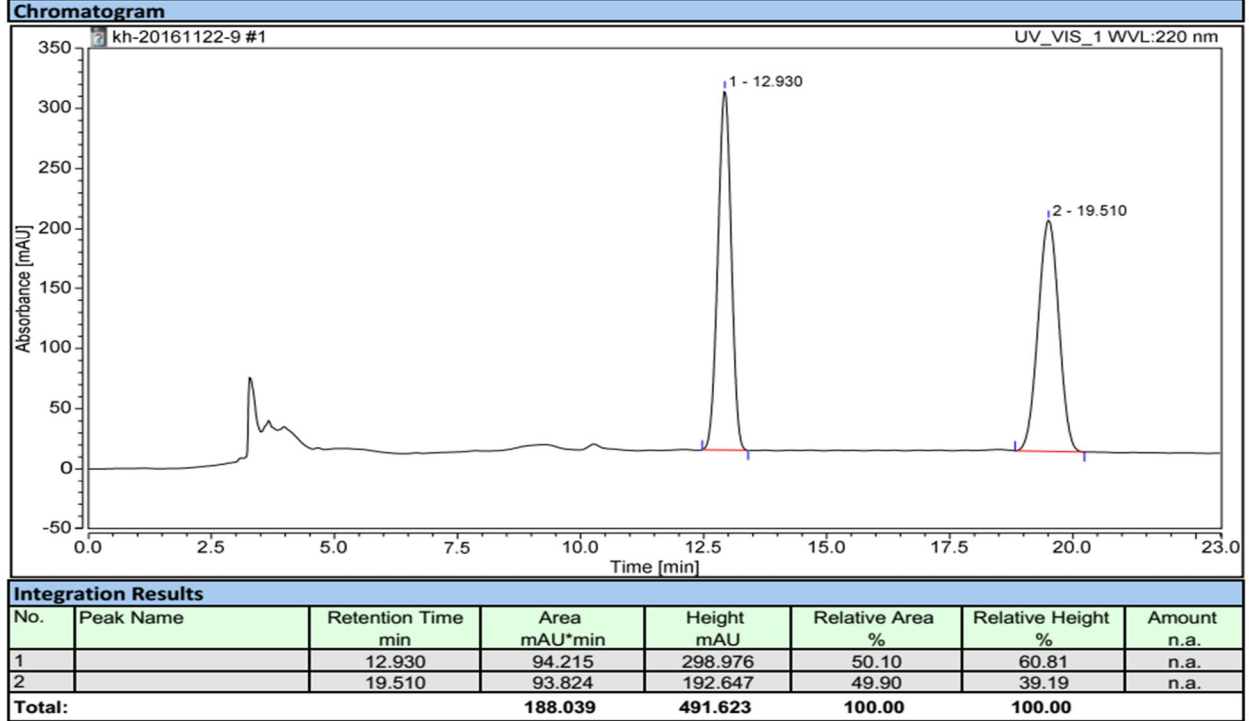
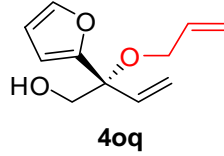


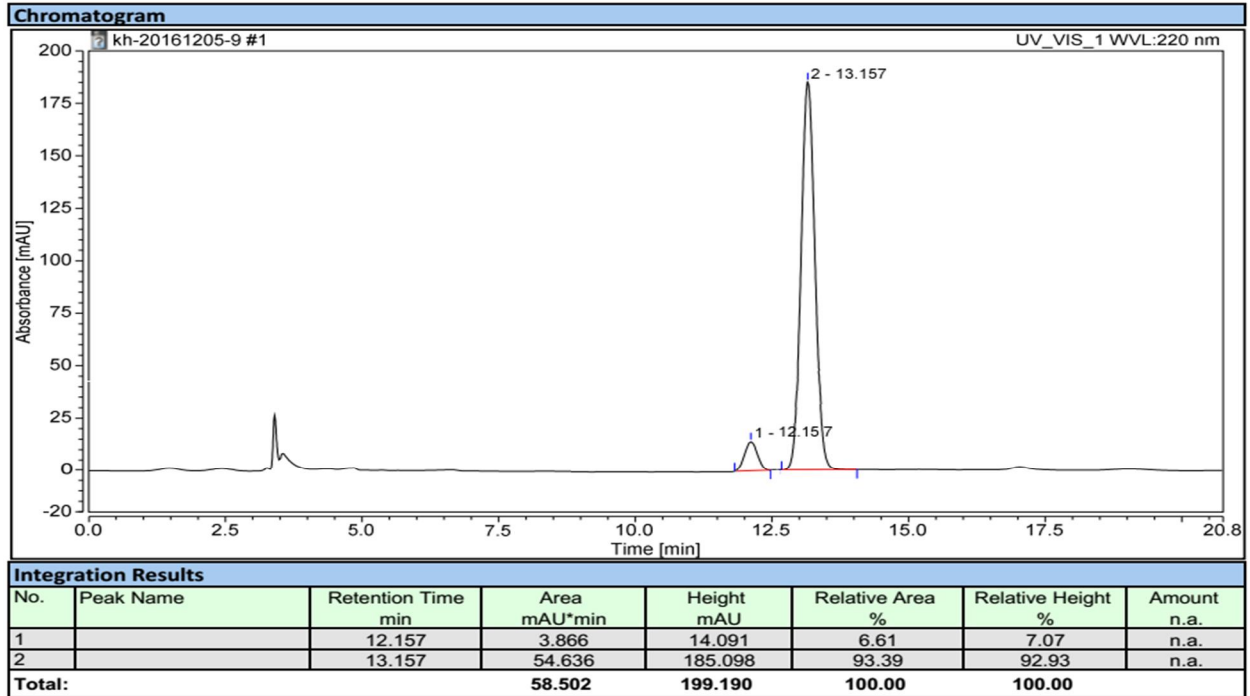
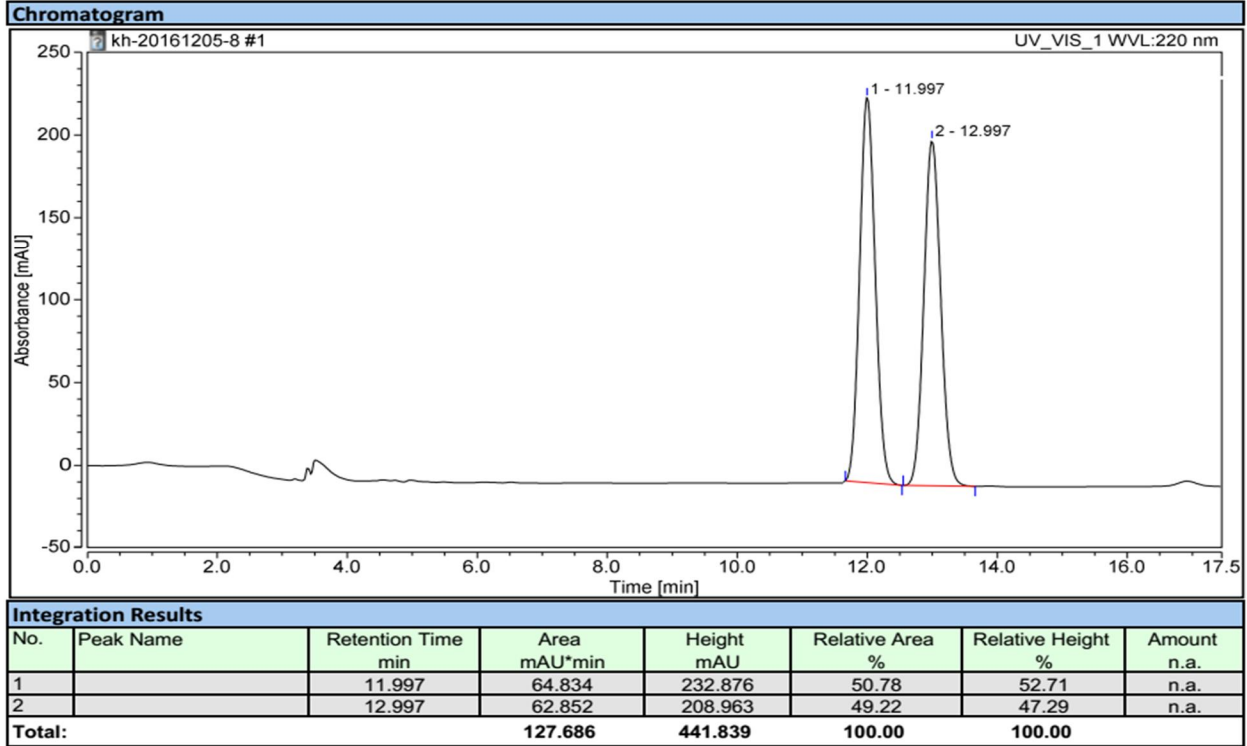
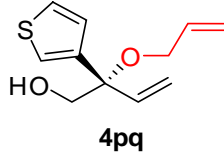
Integration Results

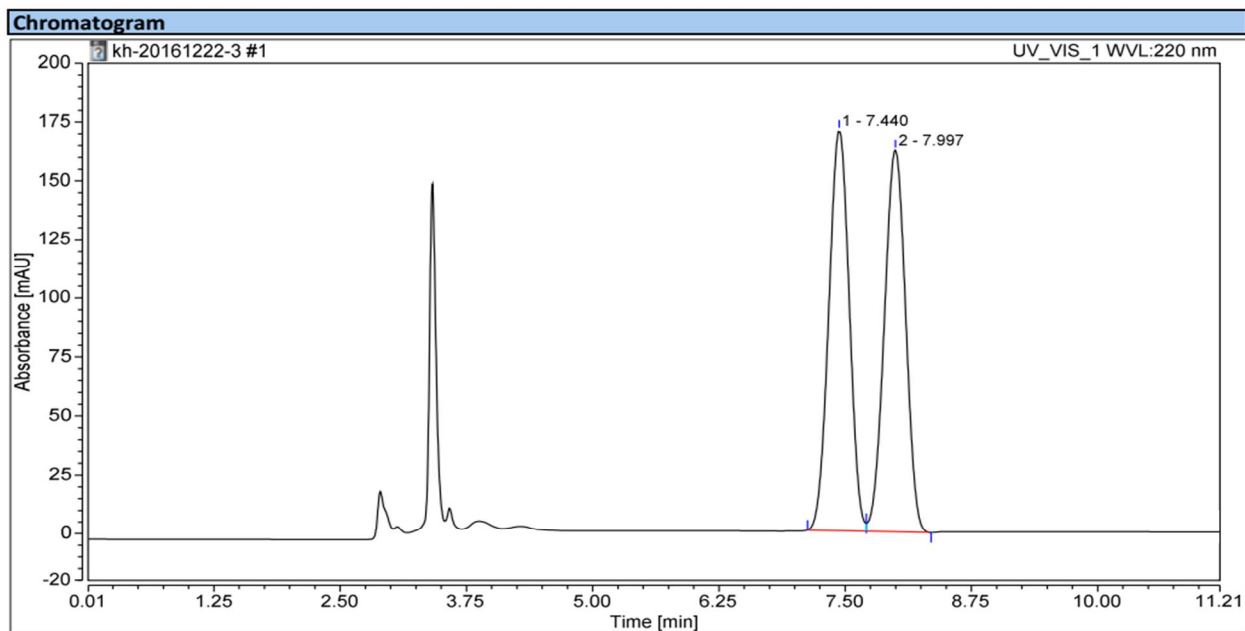
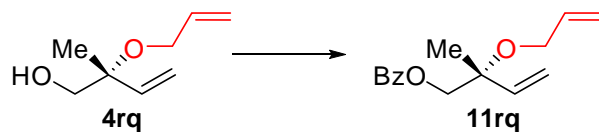
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.117	146.633	307.843	98.90	98.64	n.a.
2		22.317	2.966	5.917	1.10	1.36	n.a.
Total:			149.599	313.760	100.00	100.00	





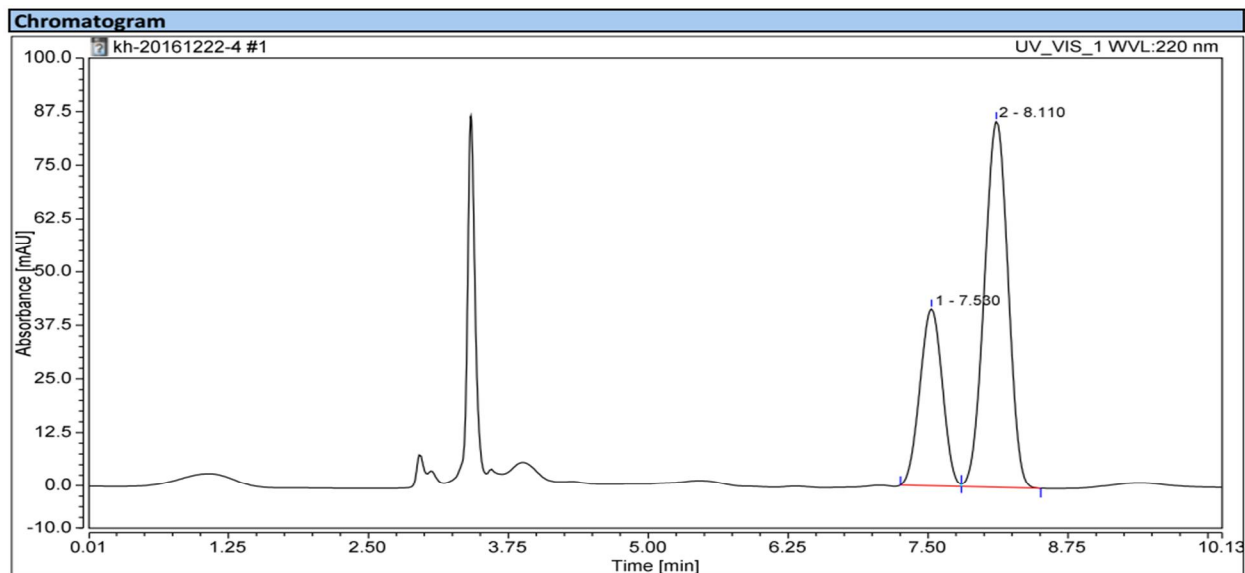






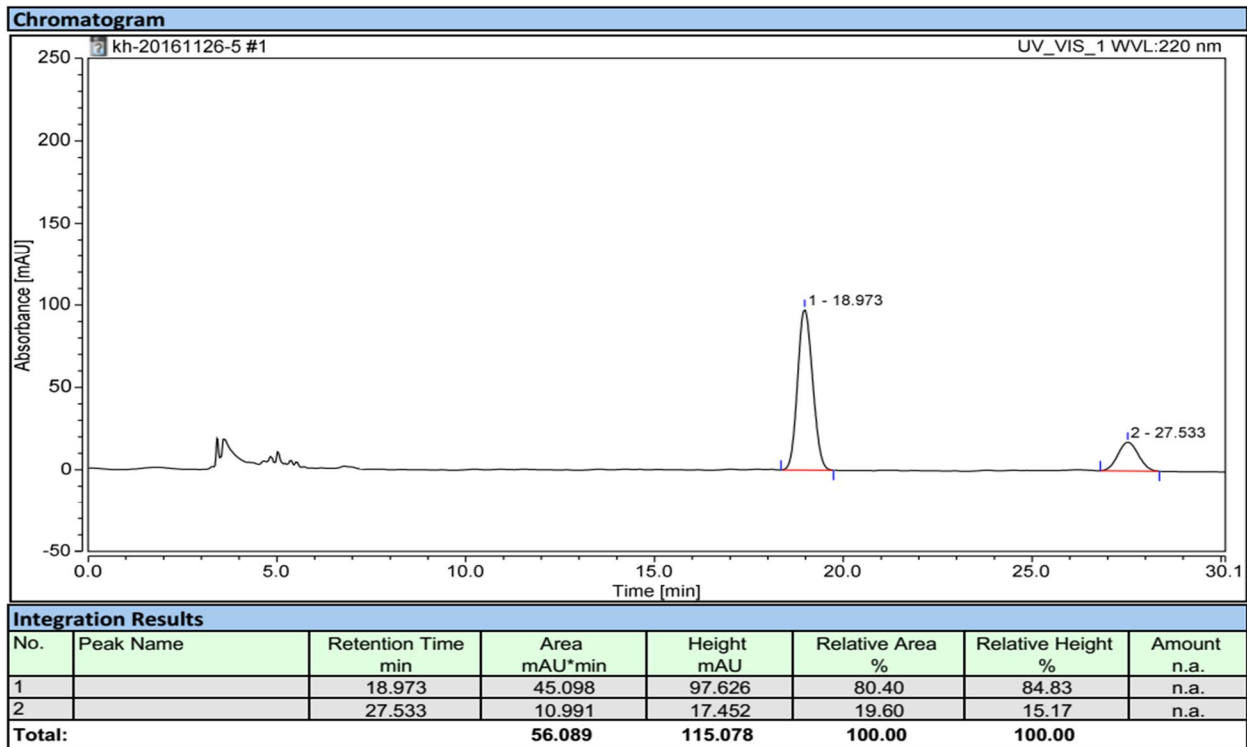
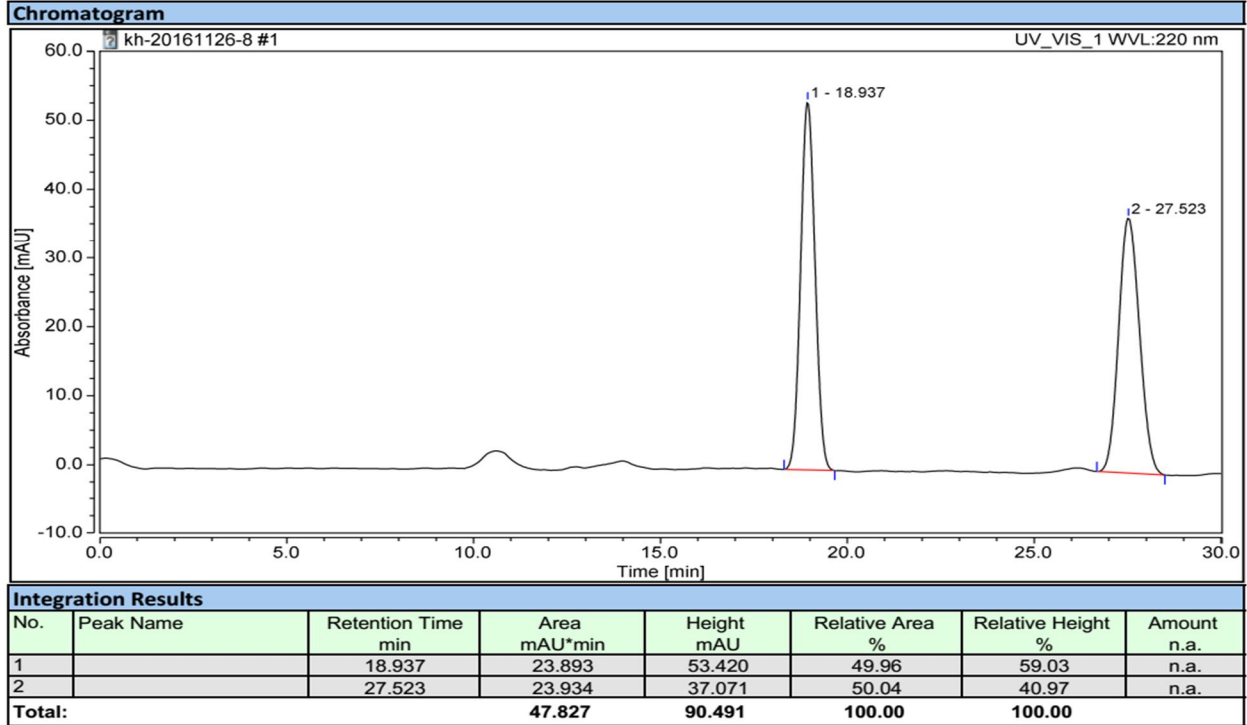
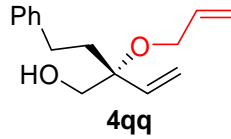
Integration Results

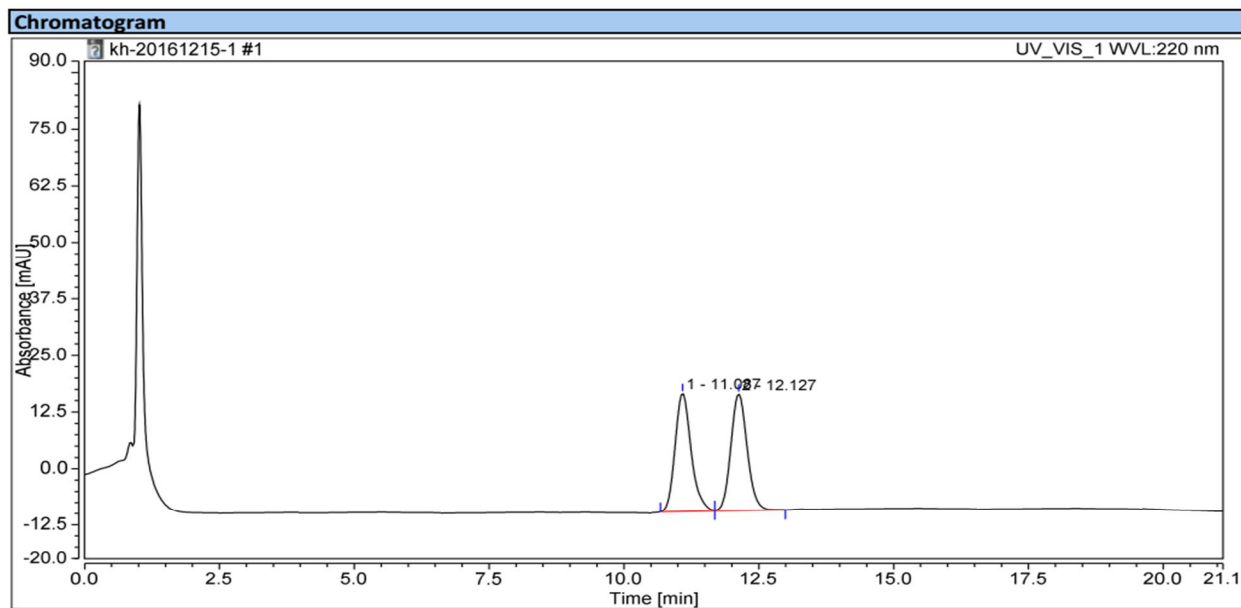
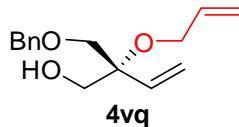
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.440	39.863	170.294	50.18	51.18	n.a.
2		7.997	39.574	162.431	49.82	48.82	n.a.
Total:			79.437	332.725	100.00	100.00	



Integration Results

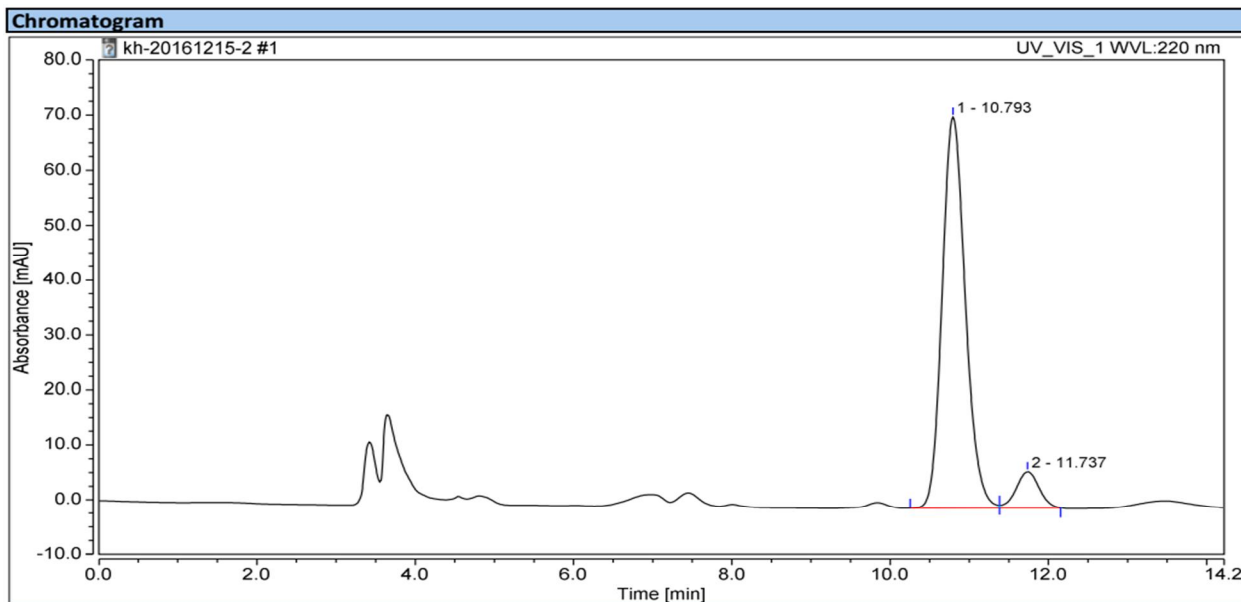
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.530	9.626	41.332	31.44	32.55	n.a.
2		8.110	20.995	85.642	68.56	67.45	n.a.
Total:			30.621	126.974	100.00	100.00	





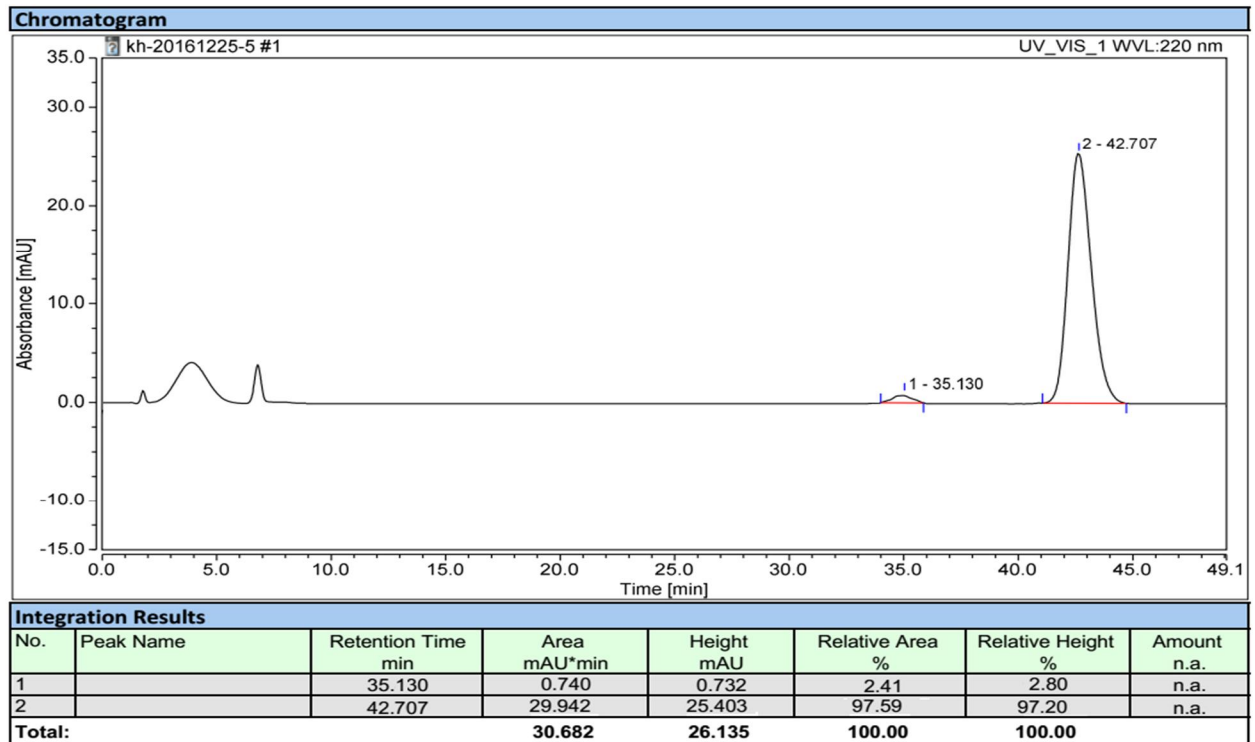
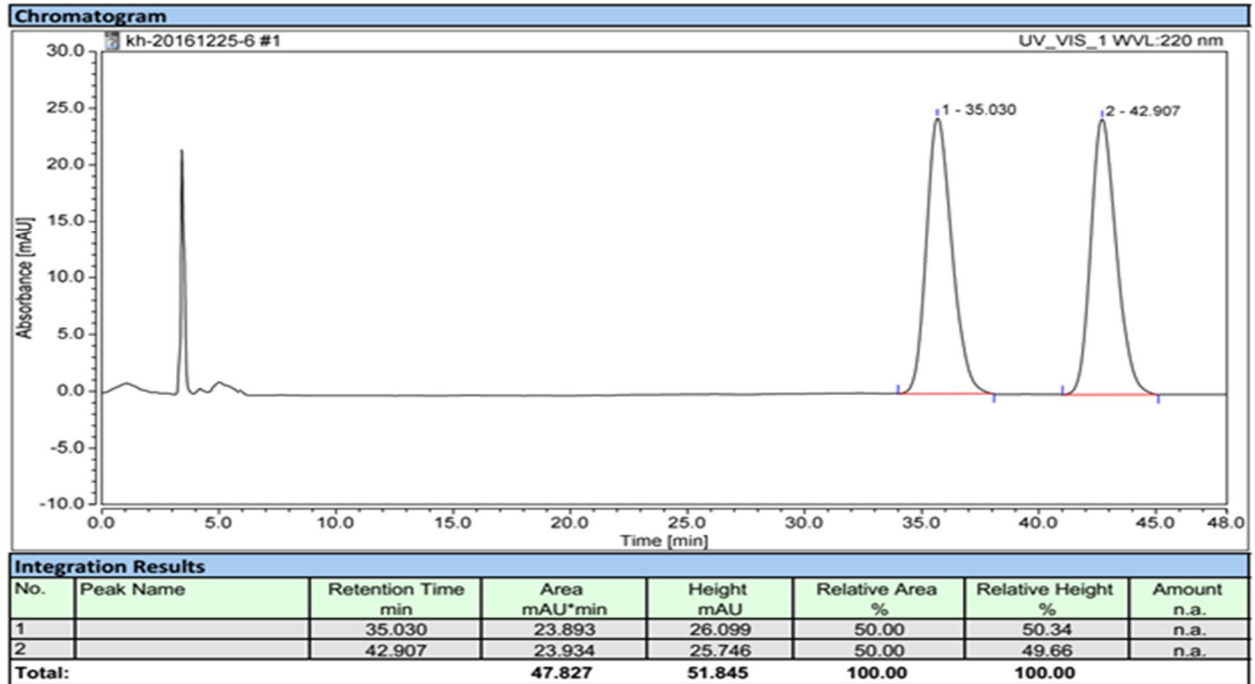
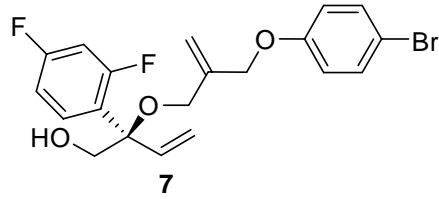
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.087	9.061	26.099	50.00	50.34	n.a.
2		12.127	9.062	25.746	50.00	49.66	n.a.
Total:			18.122	51.845	100.00	100.00	

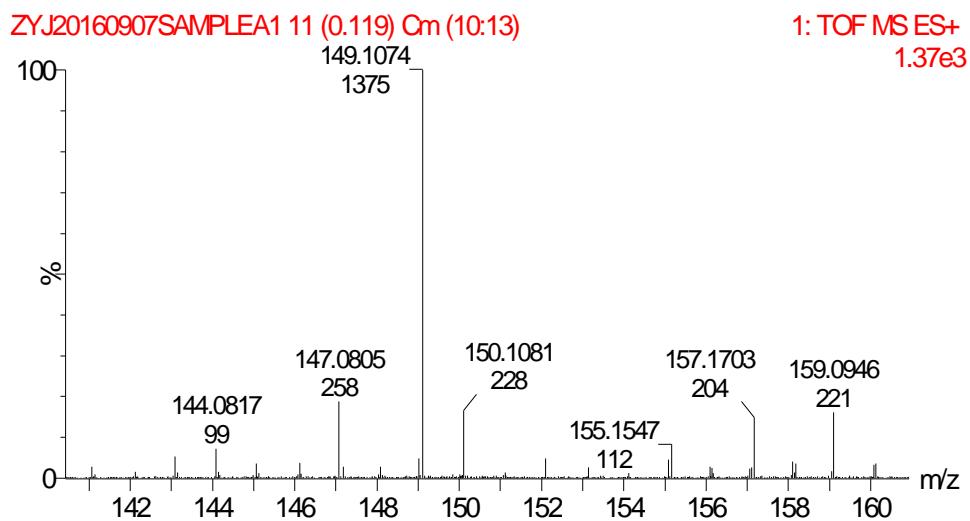


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.793	24.130	71.169	91.52	91.44	n.a.
2		11.737	2.235	6.664	8.48	8.56	n.a.
Total:			26.366	77.832	100.00	100.00	



1. MS Spectra of 2a'-¹⁸O



2. MS Spectra of 2q'-¹⁸O

