Supporting information

Pd-Catalyzed Regio- and Enantioselective Allylic Substitution with 2-Pyridones

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General experimental details

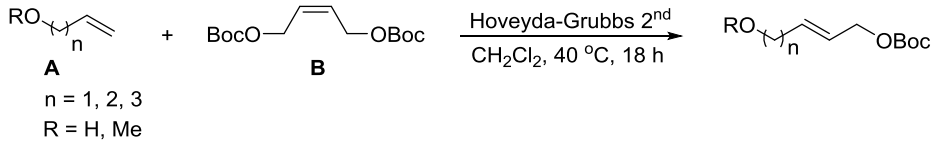
Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University using ESI method. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker AVANCE III HD 500 (500 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or deuterated water and ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform, or ppm relative to the center of the quintet at 3.34 ppm for deuteriomethanol. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Bruker AVANCE III HD 500 (125 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 ppm relative to the center of the septet at 49.54 ppm for deuteriomethanol. ^{13}C NMR spectra were routinely run with broadband decoupling. High performance liquid chromatography (HPLC) was performed with Thermofisher spectrometers using chiral columns. Optical rotations were measured on a SGW®-1polarimeter. All of the palladium sources and phosphine ligands were purchased from Sinocompound Co. and used as received.

General procedure for the synthesis of allylic carbonates (1b-1d)

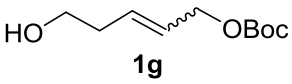
Mono protection of 1,4-butene diol was carried out with di-*tert*-butyl dicarbonate, acetyl chloride and benzoyl chloride according to reported procedures,[1] all characterization data are in accordance with literature.

General procedure for the synthesis of allylic carbonates (1g-1i)

Allylic carbonates **1g-1i** were synthesized according to reported procedure.[2] To an oven dried 100 mL round bottom flask equipped with a stir bar, was added protected alcohol **B** (1.09 g, 3.78 mmol), but-3-en-1-ol (0.272 g, 3.78 mmol), Hoveyda-Grubbs 2nd generation (3 mol %) and DCM (8.0 mL). The mixture was stirred at 40 ℃ for 18 hours. Then the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel to afford desired product **1g**.



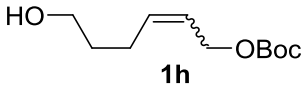
tert-butyl (5-hydroxypent-2-en-1-yl) carbonate



1g

Yield: 84 %; colorless oil; (*E*:*Z* = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83–5.68 (m, 2H), 4.52 (d, *J* = 6.2 Hz, 2H), 3.70-3.65 (m, 2H), 2.36–2.32 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 132.4, 126.4, 82.0, 67.2, 61.5, 35.5, 27.7; HRMS (ESI-MS): Calcd. for $C_{10}H_{18}O_4$ (M+Na): 225.1103, Found: 225.1094.

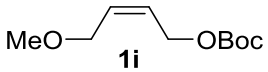
tert-butyl (6-hydroxyhex-2-en-1-yl) carbonate



1h

Yield: 79 %; yellow oil; (*E*:*Z* = 1.2:1); ^{1}H NMR (500 MHz, $CDCl_3$) for *E* isomer: δ 5.84–5.78 (m, 1H), 5.65–5.59 (m, 1H), 4.50 (d, *J* = 6.5 Hz, 2H), 3.69–3.62 (m, 2H), 2.18–3.13 (m, 2H), 1.69–1.64 (m, 2H), 1.48 (s, 9H); ^{1}H NMR (500 MHz, $CDCl_3$) for *Z* isomer: 5.57–5.49 (m, 2H), 4.10–4.06 (m, 2H), 3.69–3.62 (m, 2H), 2.46–2.35 (m, 2H), 2.34–2.25 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) for *E* isomer: δ 153.4, 135.9, 129.2, 81.8, 66.2, 61.6, 35.8, 32.0, 27.6; ^{13}C NMR (125 MHz, $CDCl_3$) for *Z* isomer: 153.2, 128.6, 128.0, 123.9, 67.4, 31.5, 30.9, 28.4, 26.8; HRMS (ESI-MS): Calcd. for $C_{11}H_{20}O_4$ (M+Na): 239.1259, Found: 239.1252.

(*Z*)-*tert*-butyl (4-methoxybut-2-en-1-yl) carbonate



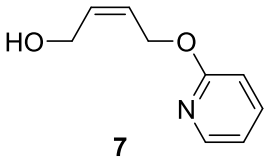
1i

Yield: 77 %; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79–5.70 (m, 2H), 4.65 (d, *J* = 5.8 Hz, 2H), 4.04 (d, *J* = 5.3 Hz, 2H), 3.34 (m, 3H), 1.49 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 130.7, 126.3, 82.0, 67.9, 62.4, 58.0, 27.6; HRMS (ESI-MS): Calcd. for $C_{10}H_{18}O_4$ (M+Na): 225.1103, Found: 225.1093.

General procedure for the synthesis of compound 7

Substrate **7** was synthesized according to reported procedure.[3]

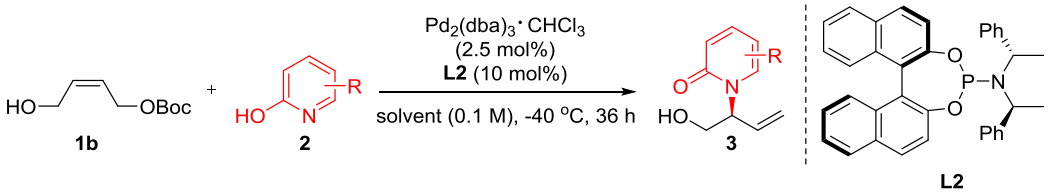
(*Z*)-4-(pyridin-2-yloxy)but-2-en-1-ol



7

Yield: 60 %; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.6 Hz, 1H), 7.56 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.86 (dd, *J* = 7.1, 5.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.89–5.84 (m, 1H), 5.78–5.73 (m, 1H), 4.96 (d, *J* = 6.9 Hz, 2H), 4.31 (d, *J* = 6.4 Hz, 2H), 4.18 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 146.1, 138.8, 132.4, 126.8, 116.7, 111.5, 61.6, 58.6; HRMS (ESI-MS): Calcd. for $C_9H_{11}NO_2$ (M+Na): 174.0531, Found: 174.0528.

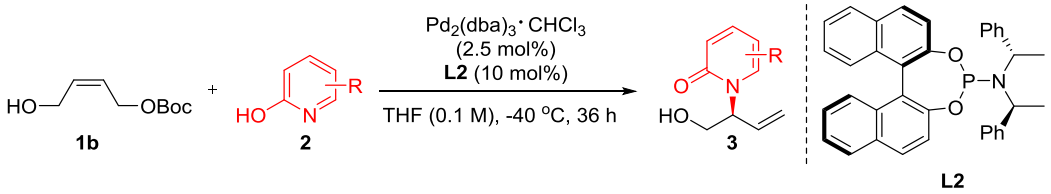
Table S1. Solvent Screening for the Pd-catalyzed allylic substitution of 1b with 2-pyridones 2



entry	solvent	yield (%)[b]	ee (%)[c]
1	THF	87	95: 5
2	Toluene	90	92.5:7.5
3	CH_2Cl_2	92	80.5:19.5
4	Et_2O	58	84:16
5	MTBE	41	82.5:17.5
6	CH_3CN	30	75:25
7[d]	MeOH	59	80.5:19.5

[a] Reaction conditions: $Pd_2(dba)_3$·$CHCl_3$ (2.5 mol %), ligand (10 mol %), **1** (0.2 mmol), **2a** (0.2 mmol), solvent (2.0 mL), 36 h. [b] Isolated yields. [c] Determined by HPLC using a chiral stationary phase. The absolute configuration was assigned by comparing the sign of the optical rotation with that reported.[3a] [d] The ratio of branch to linear selectivity for entry 7 is 3.7:1.

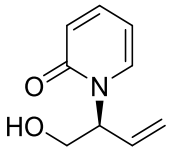
General procedure for the Pd-catalyzed allylic substitution of 1b with various substituted 2-pyridones 2



To an oven dry 10 mL Schlenck flask equipped with a stir bar, was added $Pd_2(dba)_3$.$CHCl_3$ (5.2 mg,

2.5 mol %), phosphoramidite ligand **L2** (10.8 mg, 10 mol %), allylic carbonate **1b** (37.6 mg, 0.2 mmol) and 2-hydroxypyridine (19.0 mg, 0.2 mmol). The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times) and anhydrous THF (2 mL) was added sequentially via syringe. The mixture was stirred at -40 ℃ for 36 hours. Then the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel to afford product **3a**.

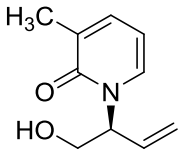
(*S*)-1-(1-hydroxybut-3-en-2-yl)pyridin-2(*1H*)-one



3a

Yield: 87%; white solid; 88-90 ℃; $[\alpha]_D^{25}$ = -23.80 (*c* = 0.28, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.36–7.31 (m, 1H), 6.56 (dd, *J* = 9.8, 8.3 Hz, 1H), 6.24 (dd, *J* = 6.8, 6.8 Hz, 1H), 6.00 (ddd, *J* = 17.2, 10.6, 5.4 Hz, 1H), 5.61–5.55 (m, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 4.10 (bs, 1H), 4.01 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.92 (dd, *J* = 11.6, 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 139.5 135.6, 133.1, 120.4, 119.5, 106.5, 63.2, 59.3; HRMS (ESI-MS): Calcd. for $C_9H_{11}NO_2$ (M+H): 166.0868, Found: 166.0868; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 12.99 min, t_{minor} = 16.71 min; 95:5 *er*.

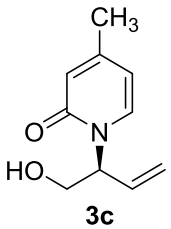
(*S*)-1-(1-hydroxybut-3-en-2-yl)-3-methylpyridin-2(1*H*)-one



3b

Yield: 91%; yellow oil; $[\alpha]_D^{25}$ = -38.54 (*c* = 1.16, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.9 Hz, 1H), 7.21 (d, *J* = 6.1 Hz, 1H), 6.17 (dd, *J* = 6.8, 6.8 Hz, 1H), 6.01 (ddd, *J* = 17.4, 10.7, 5.6 Hz, 1H), 5.66–5.58 (m, 1H), 5.38 (d, *J* = 10.6 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 4.02 (dd, *J* = 11.1, 5.0 Hz 1H), 3.94–3.90 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 136.9, 133.3, 132.8, 129.5, 119.3, 106.2, 63.7, 59.8, 17.4; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M+H): 180.1025, Found: 180.1026; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 3/7, t_{major} = 9.71 min, t_{minor} = 11.89 min; 92:8 *er*.

(*S*)-1-(1-hydroxybut-3-en-2-yl)-4-methylpyridin-2(1*H*)-one

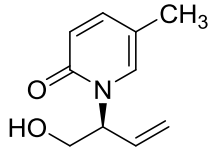


3c

Yield: 83%; yellow oil; $[\alpha]_D^{25}$ = -13.90 (*c* = 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 7.1, 2.4 Hz, 1H), 6.38 (s, 1H), 6.09 (d, *J* = 7.2 Hz, 1H), 5.98 (ddd, *J* = 16.4, 10.7, 5.4 Hz, 1H), 5.54–5.50 (m, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 5.26 (d, *J* = 17.4 Hz, 1H), 4.00–3.94 (m, 2H), 3.89 (dd, *J* = 7.2, 3.4 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 151.3, 134.5, 133.2, 119.4, 118.9,

109.2, 63.5, 59.2, 21.1; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M+H): 180.1025, Found: 180.1025; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/13, t_{minor} = 12.74 min, t_{major} = 14.76 min; 91.5:8.5 *er*.

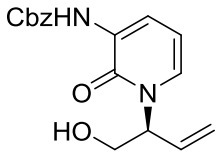
(*S*)-1-(1-hydroxybut-3-en-2-yl)-5-methylpyridin-2(1*H*)-one



3d

Yield: 86%; yellow oil; $[\alpha]_D^{25}$ = -14.11 (*c* = 0.60, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.12 (s, 1H), 6.54 (d, *J* = 9.2 Hz, 1H), 6.00 (ddd, *J* = 17.3, 10.7, 5.5 Hz, 1H), 5.55–5.50 (m, 1H), 5.39 (d, *J* = 10.6 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 4.03 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.91 (dd, *J* = 11.8, 7.2 Hz, 1H), 3.66 (bs, 1H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 142.1, 133.1, 132.9, 120.2, 119.5, 115.7, 63.7, 59.9, 17.3; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M+H): 180.1025, Found: 180.1024; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/9, t_{major} = 7.33 min, t_{minor} = 9.37 min; 90:10 *er*.

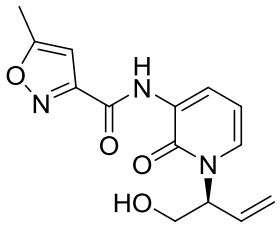
benzyl (*S*)-(1-(1-hydroxybut-3-en-2-yl)-2-oxo-1,2-dihydropyridin-3-yl)carbamate



3e

Yield: 87%; light yellow oil; $[\alpha]_D^{25}$ = -44.08 (c = 1.44, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 (s, 1H), 7.39–7.30 (m, 5H), 7.02 (dd, *J* = 7.0, 1.8 Hz, 1H), 6.25 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.95 (ddd, *J* = 16.3, 10.6, 5.6 Hz, 1H), 5.56–5.52 (m, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.18 (s, 2H), 3.97 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.90 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.40 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 153.3, 135.8, 132.6, 129.1, 128.5, 128.2, 128.0, 127,0, 120.2, 119.7, 106.8, 67.0, 63.3, 60.2; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}N_2O_4$ (M+H): 315.1345, Found: 315.1340; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 10.10 min, t_{minor} = 21.68 min; 89:11 *er*.

(*S*)-*N*-(1-(1-hydroxybut-3-en-2-yl)-2-oxo-1,2-dihydropyridin-3-yl)-5-methylisoxazole-3-carboxamide

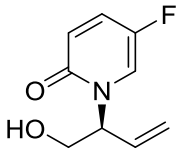


3f

Yield: 83%; white solid; 150-152 ℃; $[\alpha]_D^{25}$ = -14.39 (c = 0.88, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.42 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.18 (dd, *J* = 7.0, 1.8 Hz, 1H), 6.48 (s, 1H), 6.31 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.02 (ddd, *J* = 16.6, 10.7, 5.7 Hz, 1H), 5.60–5.57 (m, 1H), 5.41 (d, *J* = 10.7 Hz, 1H), 5.31 (d, *J* = 17.4 Hz, 1H), 4.09–3.97 (m, 2H), 3.34 (dd, *J* = 5.9, 5.8 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 158.6, 157.6, 132.5, 128.9, 128.3, 123.0, 119.9, 106.6, 101.1, 63.3, 60.6,

30.9, 12.3; HRMS (ESI-MS): Calcd. for $C_{14}H_{15}N_3O_4$ (M+H): 290.1141, Found: 290.1138; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{minor} = 10.60 min, t_{major} = 12.32 min; 92.5:7.5 *er*.

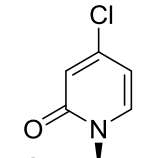
_(S)_- 5-fluoro-1-(1-hydroxybut-3-en-2-yl)pyridin-2(1*H*)-one



3g

Yield: 81%; yellow oil; $[\alpha]_D^{25}$ = -3.67 (c = 1.24, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 4.4, 3.4 Hz 1H), 7.30–7.26 (m, 1H), 6.54 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.96 (ddd, *J* = 17.4, 10.7, 5.5 Hz, 1H), 5.83–5.55 (m, 1H), 5.42 (d, *J* = 10.7 Hz, 1H), 5.32 (d, *J* = 17.4 Hz, 1H), 4.01–3.88 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 148.4, 146.6, 132.6, 131.3, 131.1, 121.3, 121.0, 120.9, 120.8, 120.2, 62.9, 59.1; HRMS (ESI-MS): Calcd. for $C_9H_{10}FNO_2$ (M+H): 184.0774, Found: 184.0771; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/6, t_{major} = 5.76 min, t_{minor} = 8.44 min; 93.5:6.5 *er*.

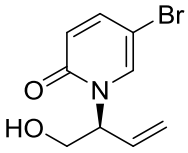
_(S)_- 5-fluoro-1-(1-hydroxybut-3-en-2-yl)pyridin-2(1*H*)-one



3h

Yield: 85%; colorless oil; $[\alpha]_D^{25}$ = -80.29 (c = 0.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 6.27 (dd, *J* = 7.4, 2.4 Hz, 1H), 5.96 (ddd, *J* = 16.5, 10.6, 5.5 Hz, 1H), 5.53–5.49 (m, 1H), 5.41 (d, *J* = 10.7 Hz, 1H), 5.30 (d, *J* = 17.4 Hz, 1H), 3.99–3.89 (m, 2H), 3.73 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 146.8, 136.1, 132.7, 120.0, 118.8, 108.2, 62.8, 58.9; HRMS (ESI-MS): Calcd. for $C_9H_{10}ClNO_2$ (M+H): 200.0478, Found: 200.0478; HPLC conditions: Chiralcel AD-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/3, t_{minor} = 4.85 min, t_{major} = 6.76 min; 92.5:7.5 *er*.

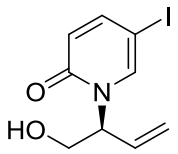
_(S)_- 5-bromo-1-(1-hydroxybut-3-en-2-yl)pyridin-2(1*H*)-one



3i

Yield: 87%; light yellow solid; 76-79 ℃; $[\alpha]_D^{25}$ = -45.06 (c = 0.68, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.7 Hz, 1H), 7.35 (dd, *J* = 9.6, 2.6 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 5.97 (ddd, *J* = 16.2, 10.7, 5.6 Hz, 1H), 5.54–5.50 (m, 1H), 5.42 (d, *J* = 10.6 Hz, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 4.16–4.09 (m, 1H), 3.98–3.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 142.4, 135.8, 132.6, 121.4, 120.2, 98.4, 62.6, 59.2; HRMS (ESI-MS): Calcd. for $C_9H_{10}BrNO_2$ (M+H): 243.9973, Found: 243.9977; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/3, t_{major} = 12.66 min, t_{minor} = 14.56 min; 94:6 *er*.

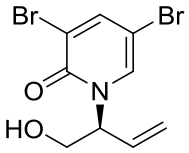
(*S*)-1-(1-hydroxybut-3-en-2-yl)-5-iodopyridin-2(1*H*)-one



3j

Yield: 85%; yellow solid; 70-72 ℃; $[\alpha]_D^{25}$ = -120.19 (c = 2.32, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.37 (d, *J* = 9.5 Hz, 1H), 5.96 (ddd, *J* = 16.2, 10.6, 5.6 Hz, 1H), 5.51–5.47 (m, 1H), 5.42 (d, *J* = 10.7 Hz, 1H), 5.32 (d, *J* = 17.4 Hz, 1H), 4.15 (dd, *J* = 5.8, 5.8 Hz, 1H), 3.98–3.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 146.9, 140.7, 132.7, 122.0, 120.2, 65.0, 62.6, 59.2; HRMS (ESI-MS): Calcd. for $C_9H_{10}INO_2$ (M+H): 291.9834, Found: 291.9833; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 18.57 min, t_{minor} = 21.82 min; 94:6 *er*.

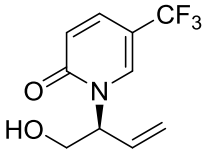
(*S*)- 3,5-dibromo-1-(1-hydroxybut-3-en-2-yl)pyridin-2(1*H*)-one



3k

Yield: 88%; brown solid; 110-112 ℃; $[\alpha]_D^{25}$ = -118.46 (c = 2.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.5 Hz, 1H), 7.58 (d, *J* = 2.6 Hz, 1H), 5.97 (ddd, *J* = 16.6, 10.6, 5.8 Hz, 1H), 5.58–5.54 (m, 1H), 5.44 (d, *J* = 10.6 Hz, 1H), 5.37 (d, *J* = 17.4 Hz, 1H), 4.03–3.92 (m, 2H), 3.72 (dd, *J* = 6.2, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 143.8, 135.3, 132.2, 120.8, 116.8, 97.3, 62.5, 60.8; HRMS (ESI-MS): Calcd. for $C_9H_9Br_2NO_2$ (M+H): 321.9078, Found: 321.9077; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/6, t_{major} = 52.21 min, t_{minor} = 57.60 min; 96:4 *er*.

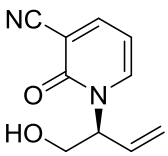
(*S*)-1-(1-hydroxybut-3-en-2-yl)-5-(trifluoromethyl)pyridin-2(1*H*)-one



3l

Yield: 85%; light yellow oil; $[\alpha]_D^{25}$ =-12.70 (c = 0.56, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.46 (dd, *J* = 9.6, 2.6 Hz, 1H), 6.61 (d, *J* = 9.6 Hz, 1H), 5.99 (ddd, *J* = 16.6, 10.7, 5.6 Hz, 1H), 5.59–5.55 (m, 1H), 5.47 (d, *J* = 10.6 Hz, 1H), 5.37 (d, *J* = 17.4 Hz, 1H), 4.02–3.94 (m, 2H), 3.46 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 135.6, 135.5, 135.10, 135.0, 132.2, 126.5, 124.3, 122.2, 120.9, 120.8, 110.4, 110.1, 109.8, 109.6, 62.6, 62.6, 59.2; HRMS (ESI-MS): Calcd. for $C_{10}H_{10}F_3NO_2$ (M+H): 234.0742, Found: 234.0743; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 8.28, t_{minor} = 9.90 min; 94:6 *er*.

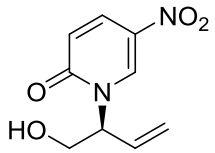
(*S*)-1-(1-hydroxybut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-3-carbonitrile



3m

Yield: 82%; light yellow oil; $[\alpha]_D^{25}$ = -10.29 (c = 0.52, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.78 (dd, *J* = 6.9, 2.0 Hz, 1H), 6.38 (dd, *J* = 7.0, 7.0 Hz, 1H), 5.99 (ddd, *J* = 16.6, 10.6, 5.8 Hz, 1H), 5.61–5.57 (m, 1H), 5.45 (d, *J* = 10.6 Hz, 1H), 5.36 (d, *J* = 17.4 Hz, 1H), 4.04–3.96 (m, 2H), 3.52 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 147.0, 141.8, 132.0, 120.9, 115.7, 105.8, 104.7, 62.3, 59.9; HRMS (ESI-MS): Calcd. for $C_{10}H_{10}N_2O_2$ (M+Na): 213.0640, Found: 213.0637; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 10.32 min, t_{major} = 13.92 min; 90:10 *er*.

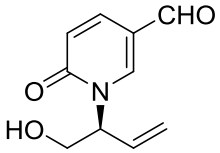
(*S*)-1-(1-hydroxybut-3-en-2-yl)-5-nitropyridin-2(1*H*)-one



3n

Yield: 86%; brown solid; 109-111 ℃; $[\alpha]_D^{25}$ = -4.33 (c = 0.84, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 3.2 Hz, 1H), 8.10 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.56 (d, *J* = 10.0 Hz, 1H), 6.04 (ddd, *J* = 16.7, 10.6, 5.9 Hz, 1H), 5.60–5.57 (m, 1H), 5.54 (d, *J* = 10.6 Hz, 1H), 5.45 (d, *J* = 17.4 Hz, 1H), 4.06–4.00 (m, 2H), 2.99 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 138.2, 133.1, 131.6, 130.9, 121.7, 119.0, 62.4, 59.5; HRMS (ESI-MS): Calcd. for $C_9H_{10}N_2O_4$ (M+H): 211.0719, Found: 211.0718; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 7.23 min, t_{minor} = 8.06 min; 93:7 *er*.

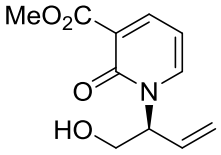
(*S*)-1-(1-hydroxybut-3-en-2-yl)-6-oxo-1,6-dihydropyridine-3-carbaldehyde



3o

Yield: 88%; light yellow solid; 90-92 ℃; $[\alpha]_D^{25}$ = -32.49 (c = 1.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.80 (dd, *J* = 9.5, 2.4 Hz, 1H), 6.58 (d, *J* = 9.4 Hz, 1H), 6.04 (ddd, *J* = 16.4, 10.6, 5.6 Hz, 1H), 5.62–5.58 (m, 1H), 5.50 (d, *J* = 10.6 Hz, 1H), 5.40 (d, *J* = 17.6 Hz, 1H), 4.05 (dd, *J* = 12.0, 4.9 Hz, 1H), 4.05 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.33 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.5, 162.9, 145.6, 135.6, 132.2, 121.0, 120.5, 118.3, 62.5, 59.0; HRMS (ESI-MS): Calcd. for $C_{10}H_{11}NO_3$ (M+H): 194.0817, Found: 194.0816; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/2, t_{major} = 30.13 min, t_{minor} = 33.28 min; 91.5:8.5 *er*.

methyl (*S*)-1-(1-hydroxybut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-3-carboxylate

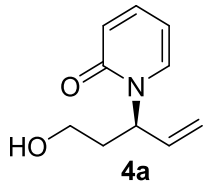


3p

Yield: 83%; white solid; 85-87 ℃; $[\alpha]_D^{25}$ = -33.96 (c = 1.28, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.13 (m, 1H), 7.70 (dd, *J* = 6.8, 2.2 Hz, 1H), 6.30 (dd, *J* = 6.9, 7.0 Hz, 1H), 6.00 (ddd, *J* = 16.5, 10.7, 5.6 Hz, 1H), 5.70 (q, *J* = 6.4 Hz, 1H), 5.40 (d, *J* = 10.6 Hz, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 4.04–3.93 (m, 2H), 3.86 (s, 3H), 3.82 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 159.8, 144.7, 141.2,

133.0, 120.0, 119.8, 104.9, 62.6, 59.2, 52.2; HRMS (ESI-MS): Calcd. for $C_{11}H_{13}NO_4$ (M+Na): 246.0742, Found: 246.0741; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 7.90 min, t_{major} = 10.80 min; 90:10 *er*.

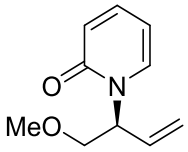
(*R*)-1-(5-hydroxypent-1-en-3-yl)pyridin-2(1H)-one



4a

Yield: 76%; light yellow liquid; $[\alpha]_D^{25}$ = -14.09 (*c* = 0.36, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 11.0, 8.2, 2.6 Hz, 1H), 7.27 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (d, *J* = 11.4 Hz, 1H), 6.30 (dd, *J* = 8.4, 8.4 Hz, 1H), 6.00 (ddd, *J* = 19.4, 13.4, 6.0 Hz, 1H), 5.83–5.77 (m, 1H), 5.42 (d, *J* = 5.3 Hz, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 4.10 (dd, *J* = 12.4, 5.2 Hz, 1H), 3.68–3.60 (m, 1H), 3.30–3.23 (m, 1H), 2.32–2.23 (m, 1H), 1.74–1.66 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 139.5, 136.3, 134.2, 120.2, 118.6, 107.4, 57.4, 52.4, 35.8; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M+H): 180.1025, Found: 180.1024; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 2/8, t_{major} = 11.83 min, t_{minor} = 16.57 min; 95:5 *er*.

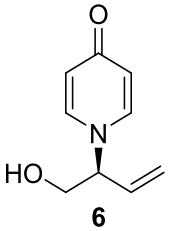
(*S*)-1-(1-methoxybut-3-en-2-yl)pyridin-2(1*H*)-one



4c

Yield: 39%; colorless oil; $[\alpha]_D^{25}$ = -12.56 (c = 0.28, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.31 (ddd, *J* = 8.9, 6.5, 2.0 Hz, 1H), 6.58 (d, *J* = 9.2 Hz, 1H), 6.17 (dd, *J* = 6.7, 6.8 Hz, 1H), 6.00 (ddd, *J* = 16.2, 10.6, 5.4 Hz, 1H), 5.79–5.75 (m, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 3.79 (dd, *J* = 10.4, 5.4 Hz, 1H), 3.69 (dd, *J* = 10.4, 4.2 Hz, 1H), 3.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 139.0, 135.8, 133.5, 120.4, 119.1, 105.6, 72.7, 59.0, 55.6; HRMS (ESI-MS): Calcd. for $C_{10}H_{13}NO_2$ (M+H): 180.1025, Found: 180.1021; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 1/9, t_{major} = 20.67 min, t_{minor} = 23.11 min; 64:36 *er*.

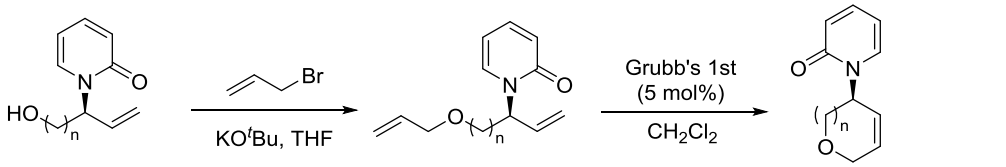
(*S*)-1-(1-hydroxybut-3-en-2-yl)pyridin-4(1*H*)-one



6

Yield: 40%; white solid; 64-66 ℃; $[\alpha]_D^{25}$ = -17.36 (c = 0.52, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_3OD) δ 7.88 (d, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 7.6 Hz, 2H), 6.08 (ddd, *J* = 17.0, 10.7, 6.0 Hz, 1H), 5.44 (d, *J* = 10.6 Hz, 1H), 5.32 (d, *J* = 17.3 Hz, 1H), 4.72–4.68 (m, 1H), 3.95–3.88 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 181.6, 142.9, 134.4, 121.3, 118.8, 71.9, 64.4; HRMS (ESI-MS): Calcd. for $C_9H_{11}NO_2$ (M+H): 166.0868, Found: 166.0866; HPLC conditions: Chiralcel AS-H column, 220 nm, flow rate: 1.0 mL/min, *i*-PrOH/hexanes = 3/7, t_{minor} = 27.90 min, t_{major} = 34.44 min; 83.5:16.5 *er*.

General procedure for ring-closing metathesis of 3a and 4a to 9a and 9b

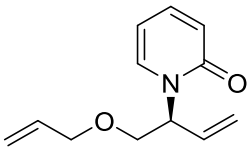


n = 1, **3a**
n = 2, **4a**

n = 1, **8a** = 96% yield
n = 2, **8b** = 87% yield

n = 1, **9a** = 94% yield
n = 2, **9b** = 89% yield

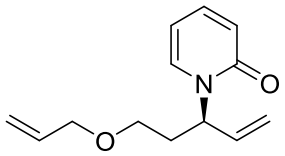
(*S*)-1-(1-(allyloxy)but-3-en-2-yl)pyridin-2(1*H*)-one



8a

To the solution of **3a** in THF (50.0 mg, 0.303 mmol), *t*BuOK (68.0 mg, 0.606 mmol) was added at 0^{o}C and the solution was stirred at room temperature for 30 minutes. Then allyl bromide (29 μL, 0.333 mmol) was added dropwise and the solution was further stirred at room temperature for 2 hours. After filtration, the mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and the solvent was removed in vacuum. The crude product was purified by flash column chromatography on silica gel to afford **8a** as colorless oil in 96% yield (59.8 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.31 (ddd, *J* = 9.4, 6.6, 2.2 Hz, 1H), 6.58 (d, *J* = 9.2 Hz, 1H), 6.17 (dd, *J* = 6.8, 1.5 Hz, 1H), 6.03 (ddd, *J* = 16.2, 10.7, 5.5 Hz, 1H), 5.82 (ddd, *J* = 16.0, 10.7, 5.6 Hz, 1H), 5.78–5.75 (m, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.24–5.14 (m, 2H), 4.00–3.93 (m, 2H), 3.84 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.75 (dd, *J* = 10.4, 4.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 139.1, 136.0, 134.0, 133.6, 120.4, 119.3, 117.2, 105.6, 72.0, 70.0, 55.9; HRMS (ESI-MS): Calcd. for $C_{12}H_{15}NO_2$ (M+H): 206.1121, Found: 206.1121.

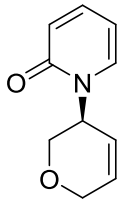
(*R*)-1-(5-(allyloxy)pent-1-en-3-yl)pyridin-2(1*H*)-one



8b

Yield: 87%; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 9.2 Hz, 1H), 6.19 (dd, *J* = 6.7, 6.7 Hz, 1H), 6.01 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.89–5.80 (m, 1H), 5.66–5.62 (m, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 3.94–3.86 (m, 2H), 3.46–3.38 (m, 2H), 2.23–2.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 138.7, 136.4, 134.6, 134.4, 120.7, 117.6, 116.8, 106.0, 71.8, 66.5, 54.6, 33.0; HRMS (ESI-MS): Calcd. for $C_{13}H_{17}NO_2$ (M+H): 220.1338, Found: 220.1334.

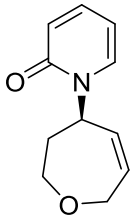
(*S*)-1-(3,6-dihydro-2*H*-pyran-3-yl)pyridin-2(1*H*)-one



9a

According to the reported procedure,[4] under nitrogen atmosphere compound **8a** (46.0 mg, 0.224 mmol), Grubbs 1st generation catalyst (9.23 mg, 0.011 mmol, 5 mol%), and anhydrous degassed CH_2Cl_2 (2.0 mL) were added into a Schlenk flask in order and the mixture was refluxed at 40 ^oC 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 = 2/8 to give the desired product **9a** as colorless oil (37.3 mg, 94%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.62 (m, 1H), 7.35–7.31 (m, 1H), 6.58 (d, *J* = 9.2 Hz, 1H), 6.30 (d, *J* = 10.2 Hz, 1H), 6.19 (dd, *J* = 6.8, 6.7 Hz, 1H), 5.87–5.84 (m, 1H), 5.50–5.47 (m, 1H), 4.33–4.28 (m, 1H), 4.19 (dd, *J* = 17.0, 2.4 Hz, 1H), 3.97–3.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 139.4, 135.6, 133.3, 122.4, 120.0, 105.7, 68.9, 65.2, 47.7; HRMS (ESI-MS): Calcd. for $C_{10}H_{11}NO_2$ (M+H): 178.0868, Found: 178.0866.

(*R*)-1-(2,3,4,7-tetrahydrooxepin-4-yl)pyridin-2(1*H*)-one



9b

Yield: 89%; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.34–7.30 (m, 1H), 6.57 (d, *J* = 9.1 Hz, 1H), 6.21 (dd, *J* = 6.8, 6.6 Hz, 1H), 6.03–5.99 (m, 1H), 5.91–5.88 (m, 1H), 5.66 (d, *J* = 11.6 Hz, 1H), 4.35–4.22 (m, 2H), 3.88–3.75 (m, 2H), 2.26–2.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 139.2, 135.4, 134.0, 130.7, 120.5, 106.0, 67.3, 67.0, 54.6, 34.8; HRMS (ESI-MS): Calcd. for $C_{11}H_{13}NO_2$ (M+H): 192.1025, Found: 192.1024.

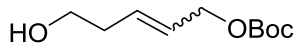
References:

(1) M. Guangning, A. Samson, D. Luca, P. Carlos, L. Leifeng, S. Junliang, I. Ismail and C. Armando, *Angew. Chem., Int. Ed.*, 2013, **52**, 6054.

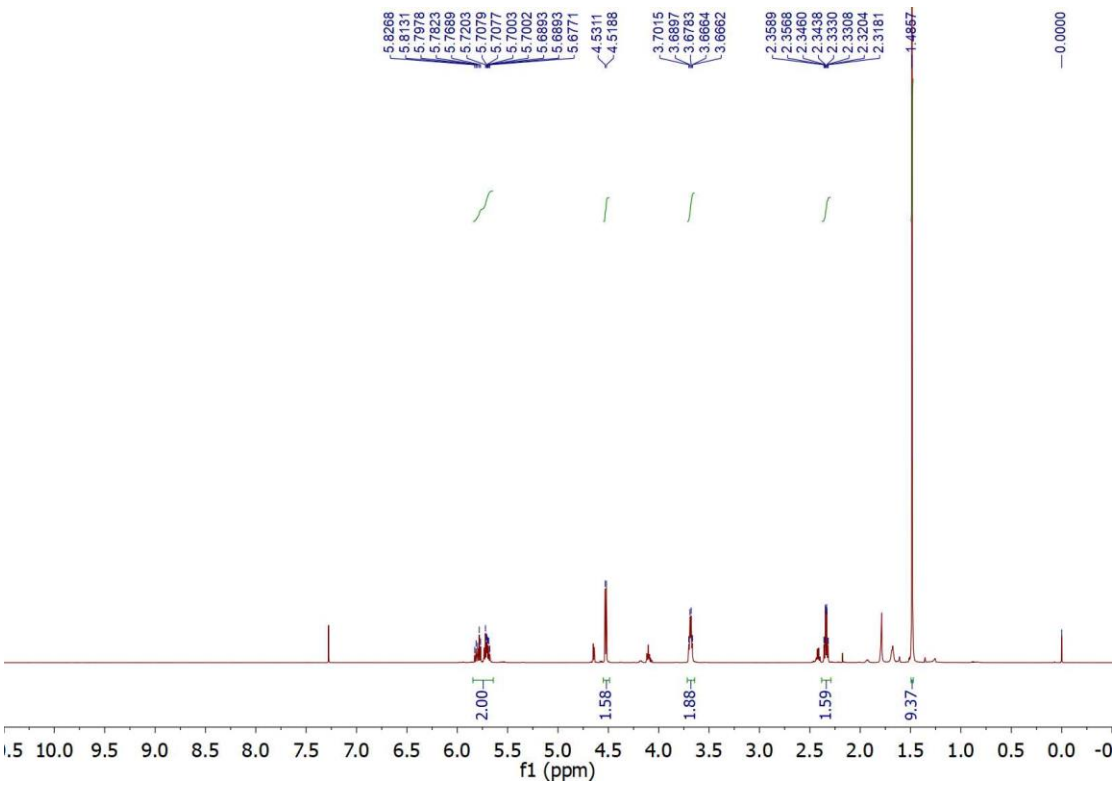
(2) I. K. Kavrakova and M. J. Lyapova, *Collect. Czech. Chem. Commun.*, 2000, **65**, 1586.

(3) R. Alessandro, E. L. Ernest and A. B. Robert, *Org. Lett.*, 2010, **12**, 2637.

(4) B. M. Trost, B. S. Brown, E.-J. McEachern and O. Kuhn, *Chem. - Eur. J.*, 2003, **9**, 4451.


HO
OBoc

1g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5.6893
5.6893
5.6771
4.5311
4.5188
3.7015
3.6897
3.6783
3.6664
3.6662
2.3589
2.3568
2.3460
2.3438
2.3330
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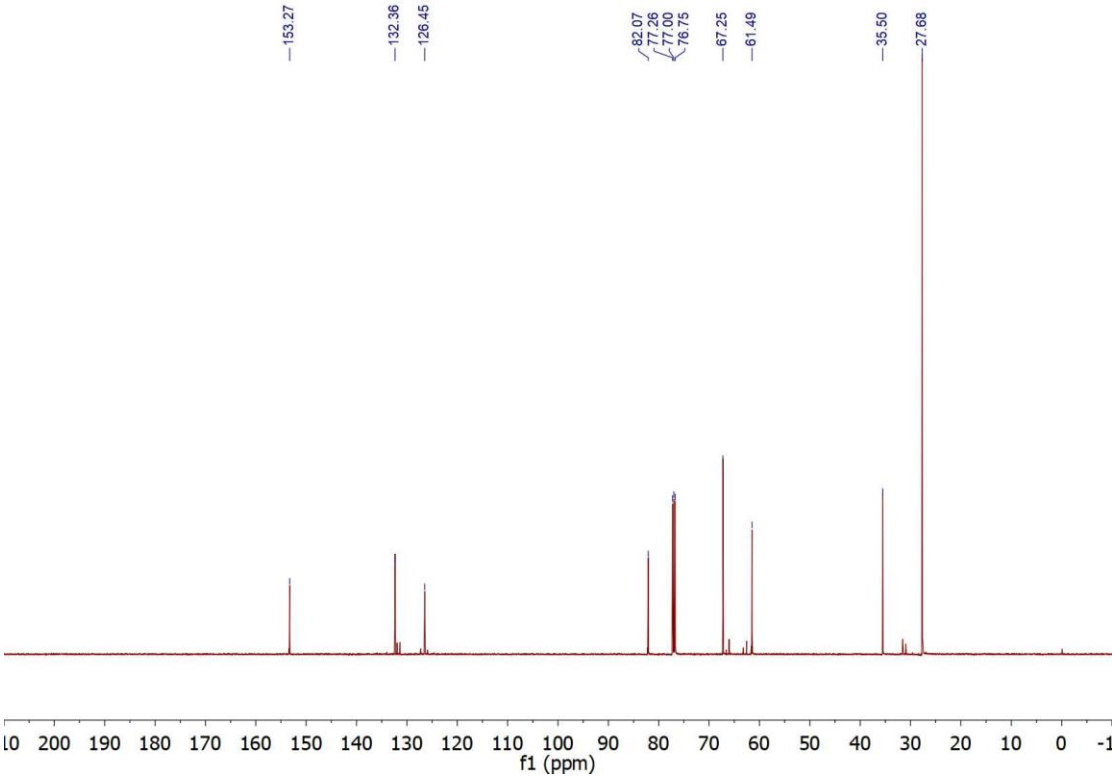
2.00
1.58
1.88
1.59
9.37
f1 (ppm)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82.07
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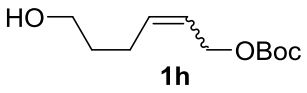
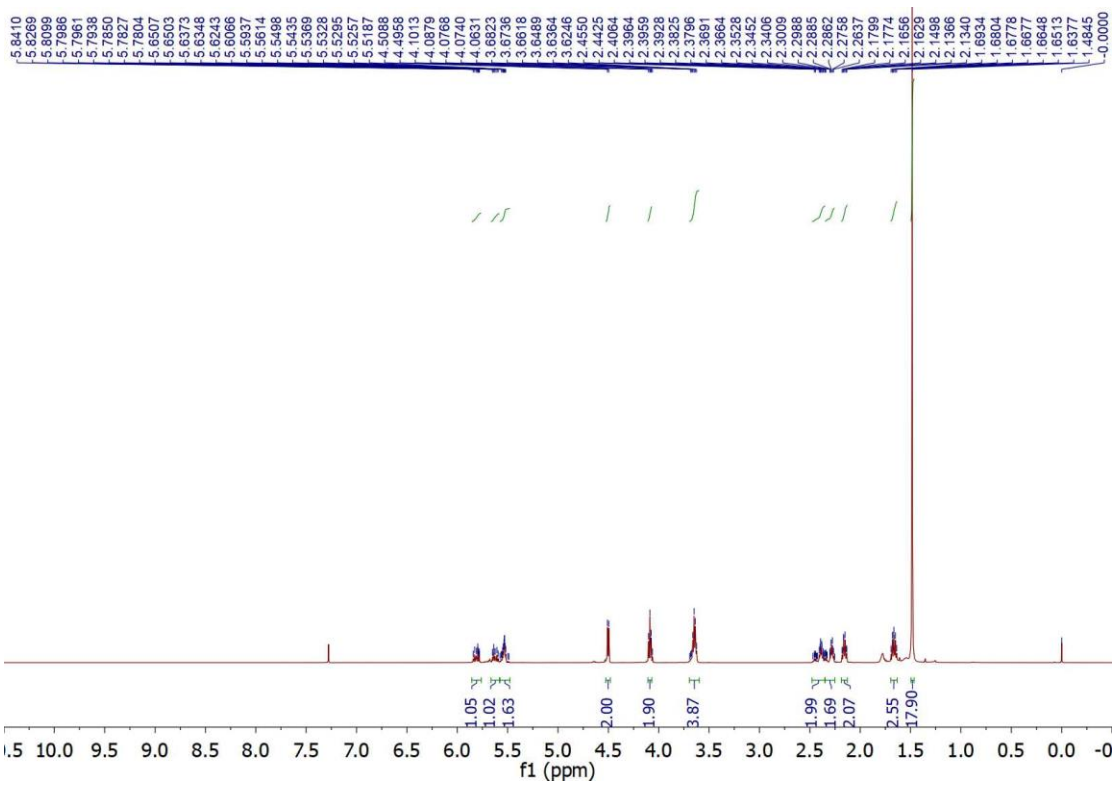
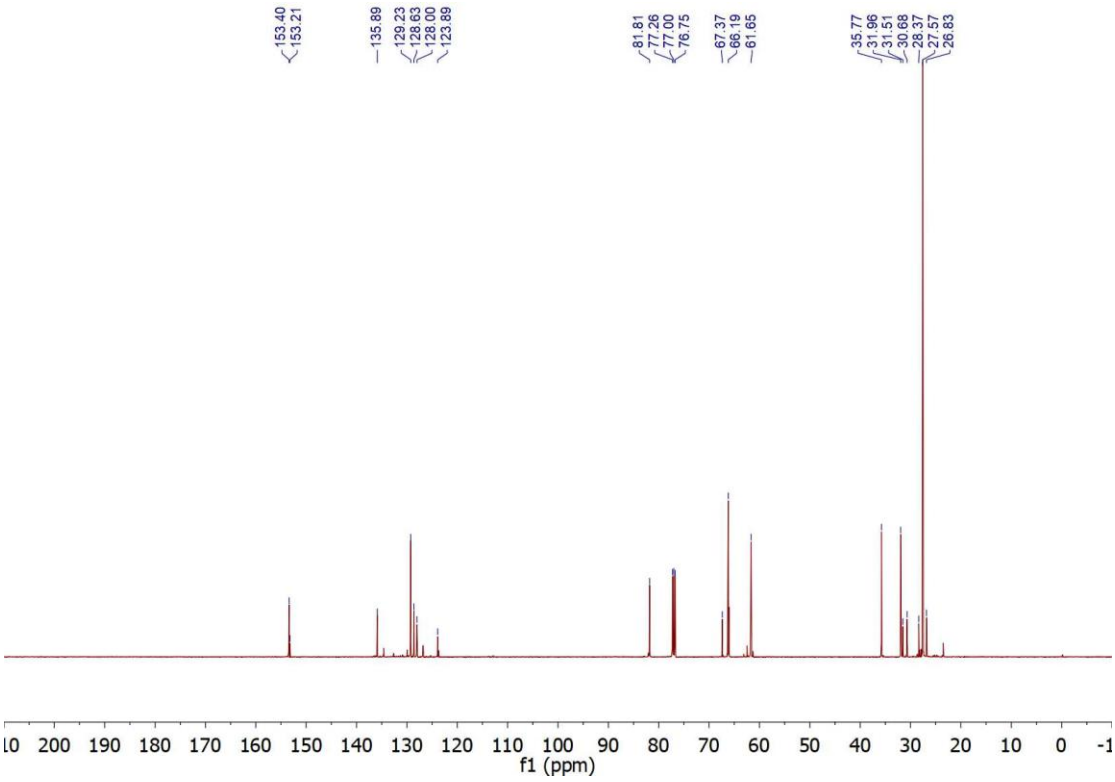
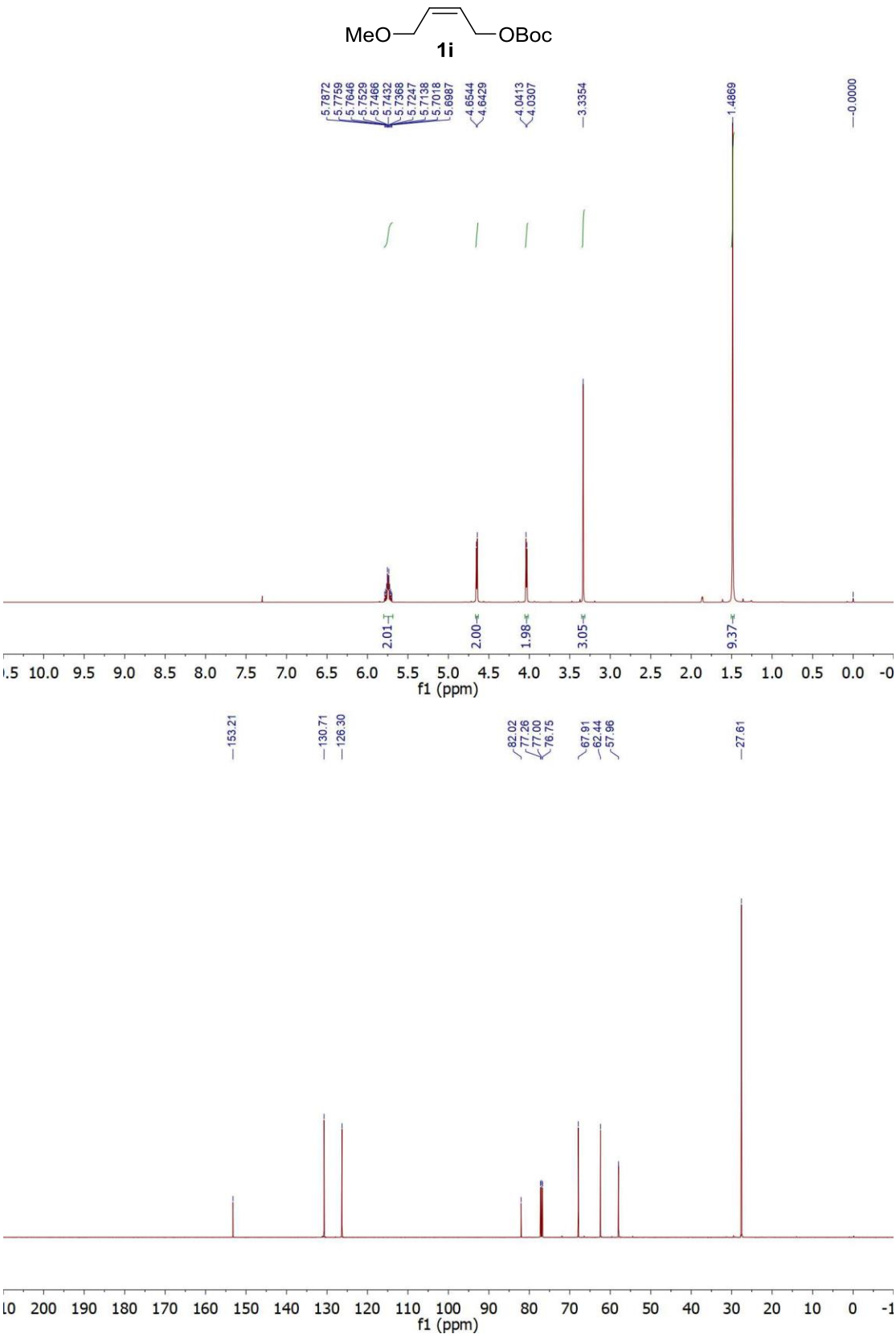
77.00
76.75
67.25
61.49
35.50
27.68
f1 (ppm)



1h



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5.7018
5.6987
4.6544
4.6429
4.0413
4.0307
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2.00
1.98
3.05
9.37
f1 (ppm)
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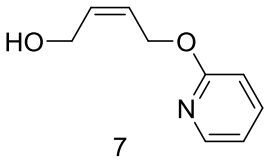
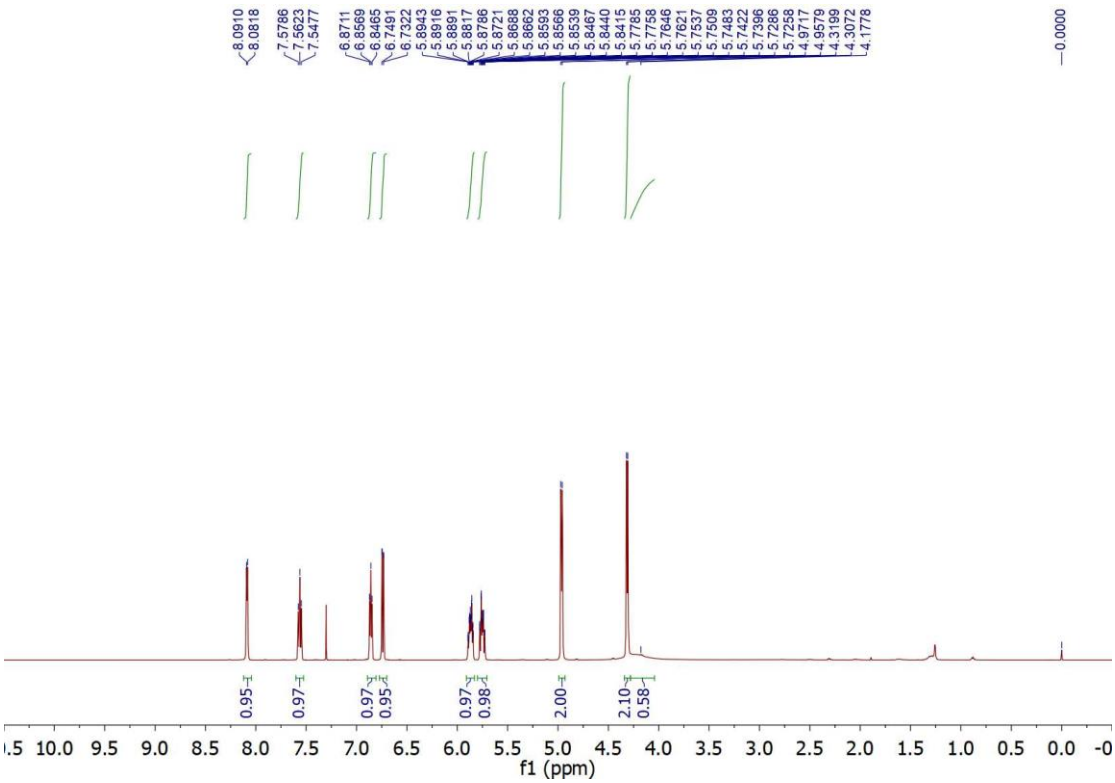
f1 (ppm)


HO
O
N

7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5.8817
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5.8721
5.8688
5.8662
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5.8566
5.8539
5.8467
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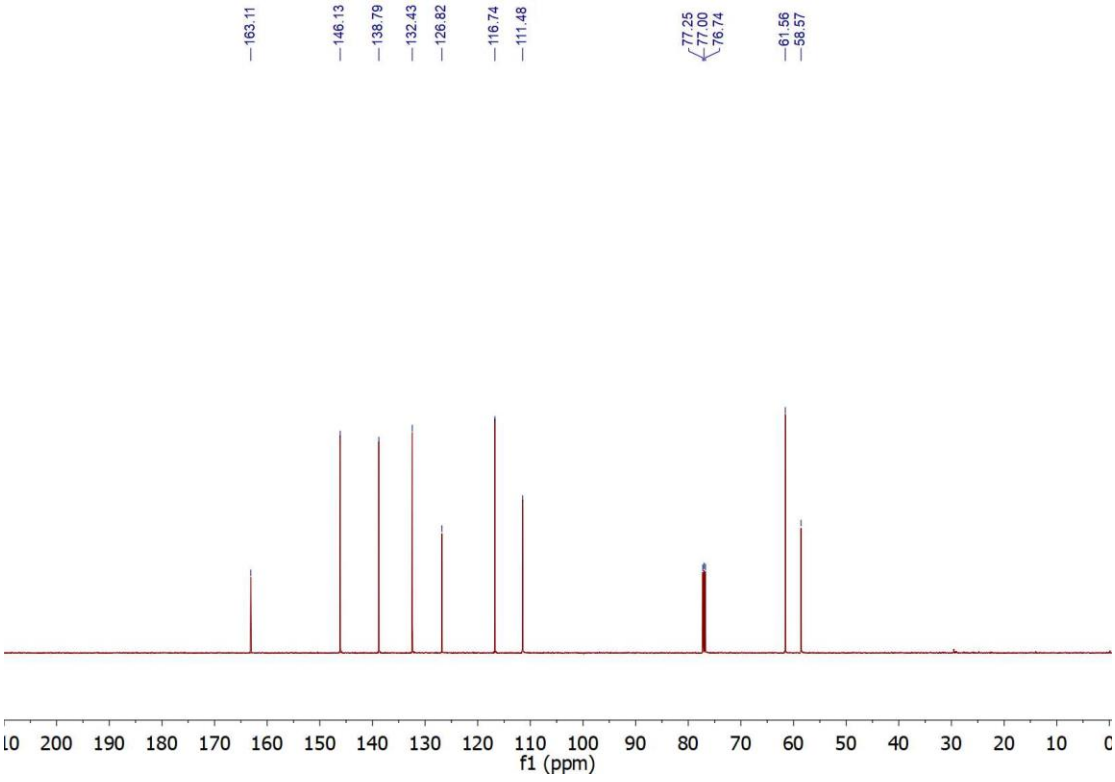
f1 (ppm)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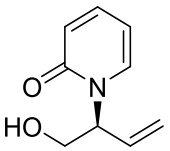
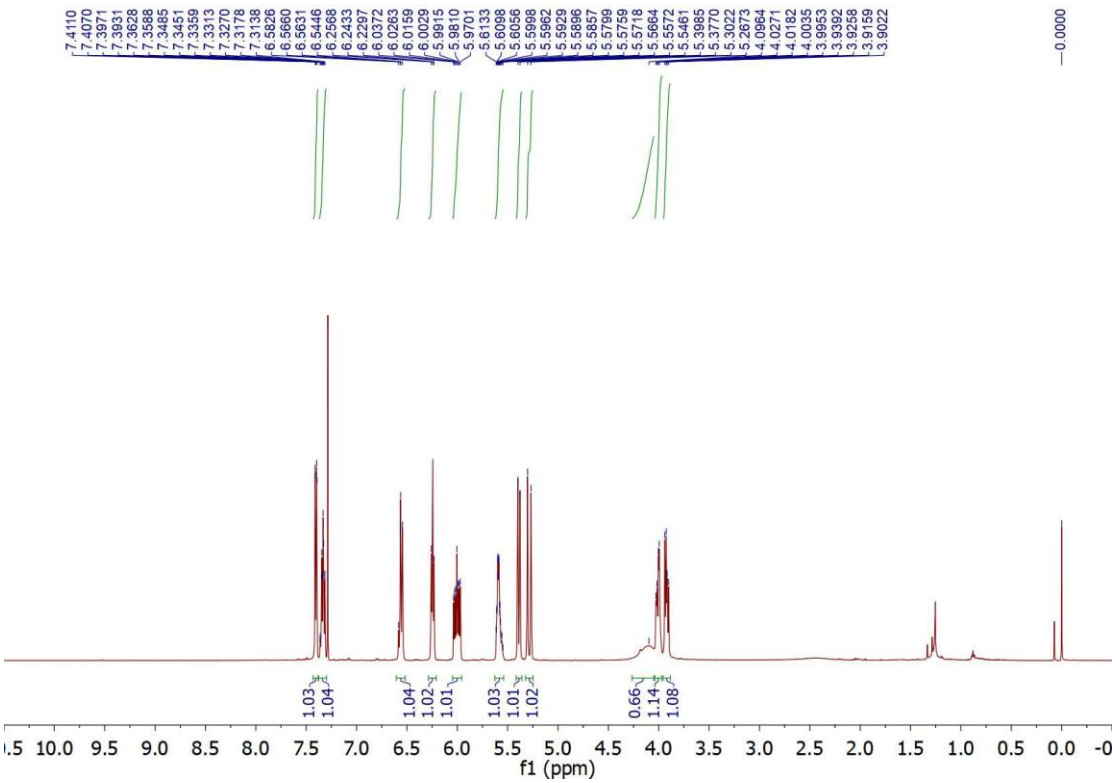
f1 (ppm)


O
N
HO

3a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7.3138
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6.5631
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6.2433
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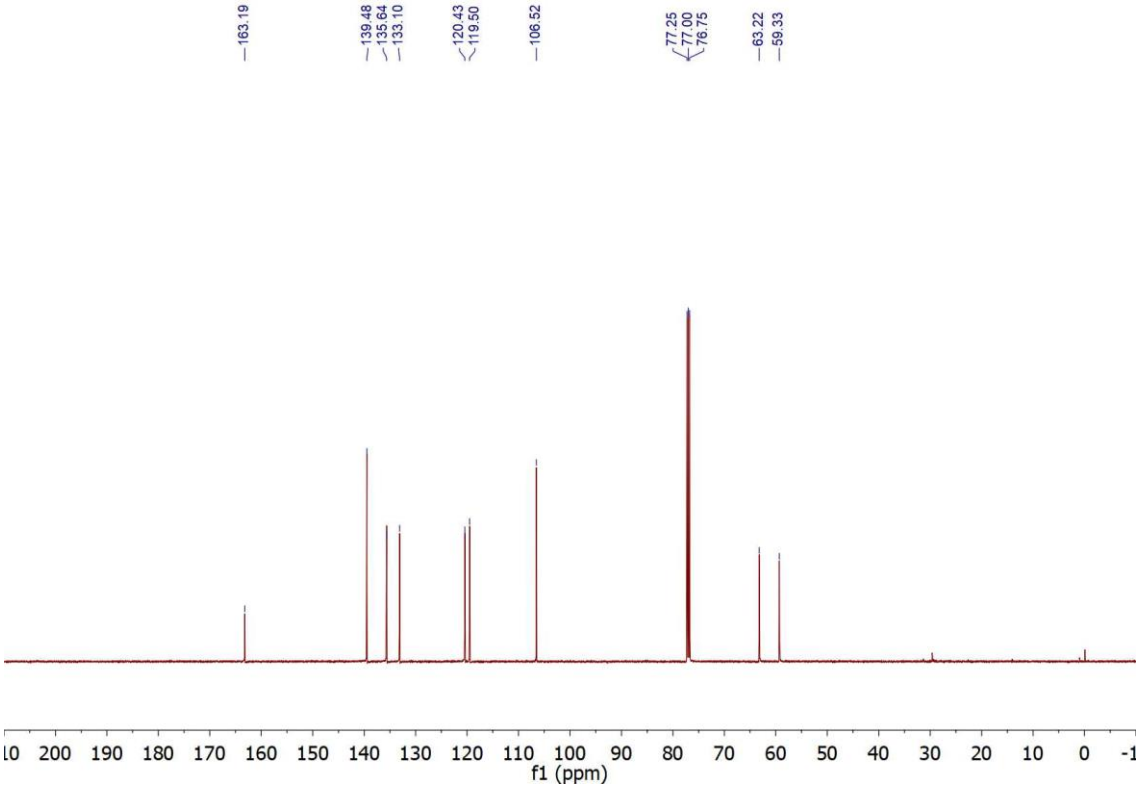
f1 (ppm)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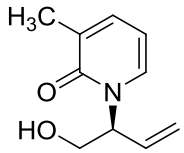
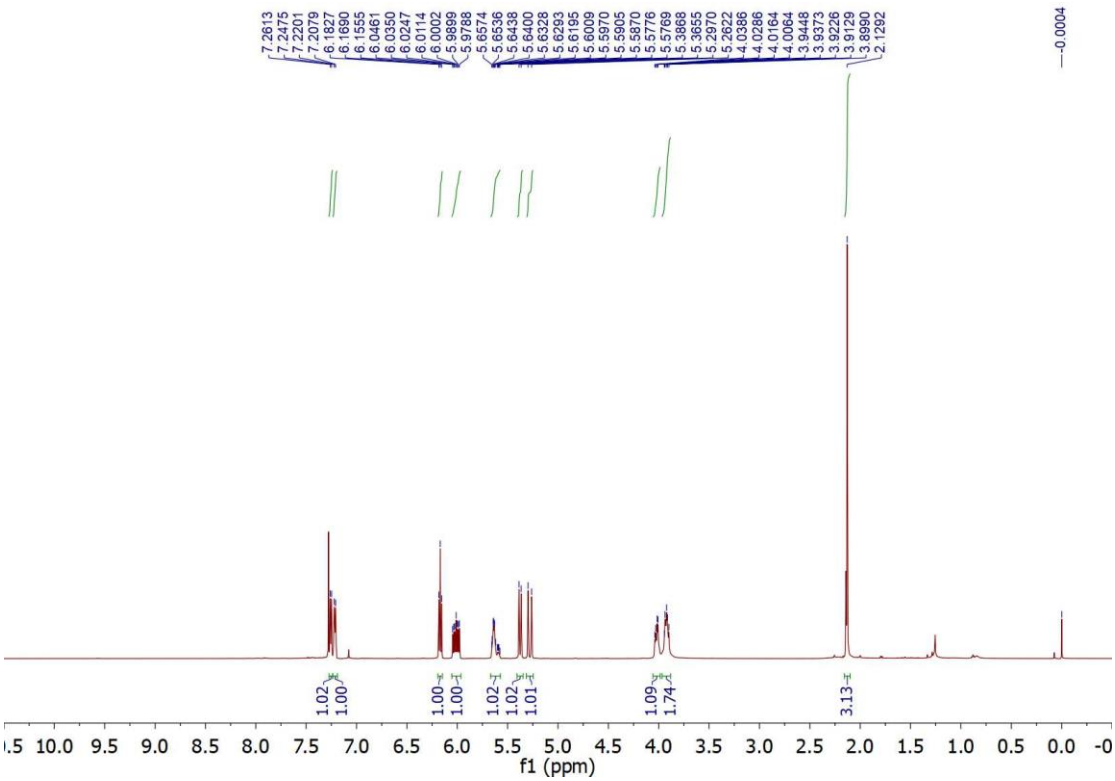
f1 (ppm)


H3C
O
N
HO

3b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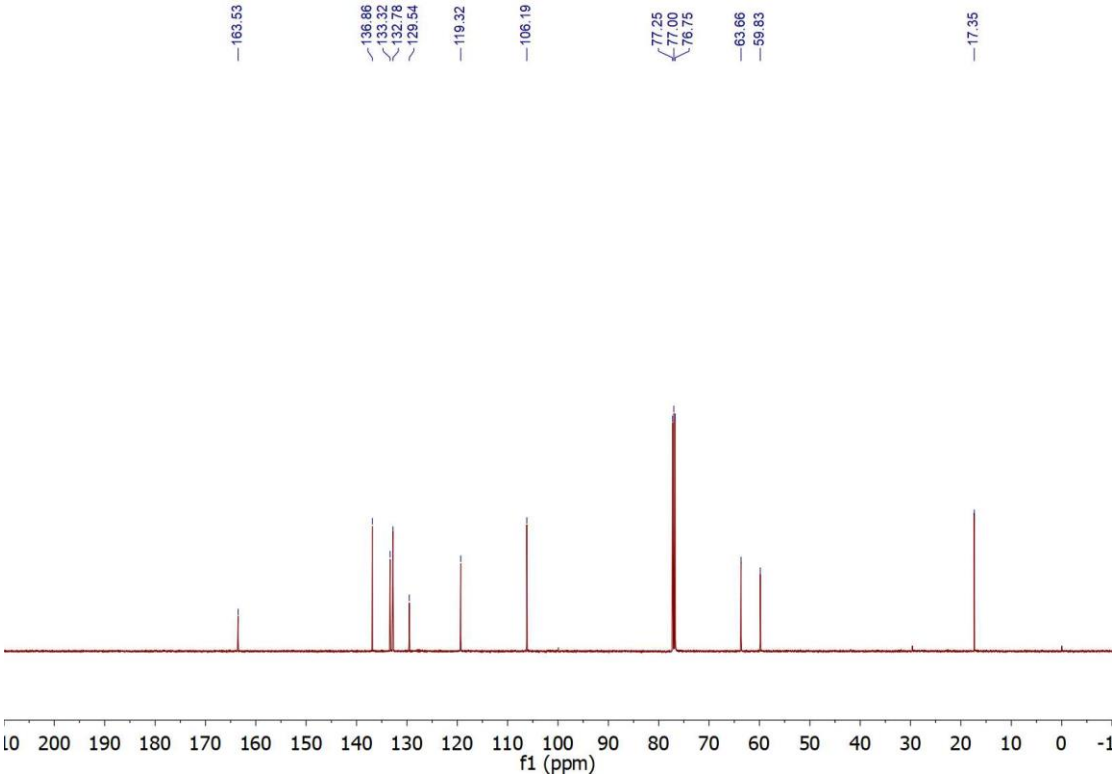
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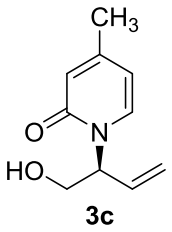
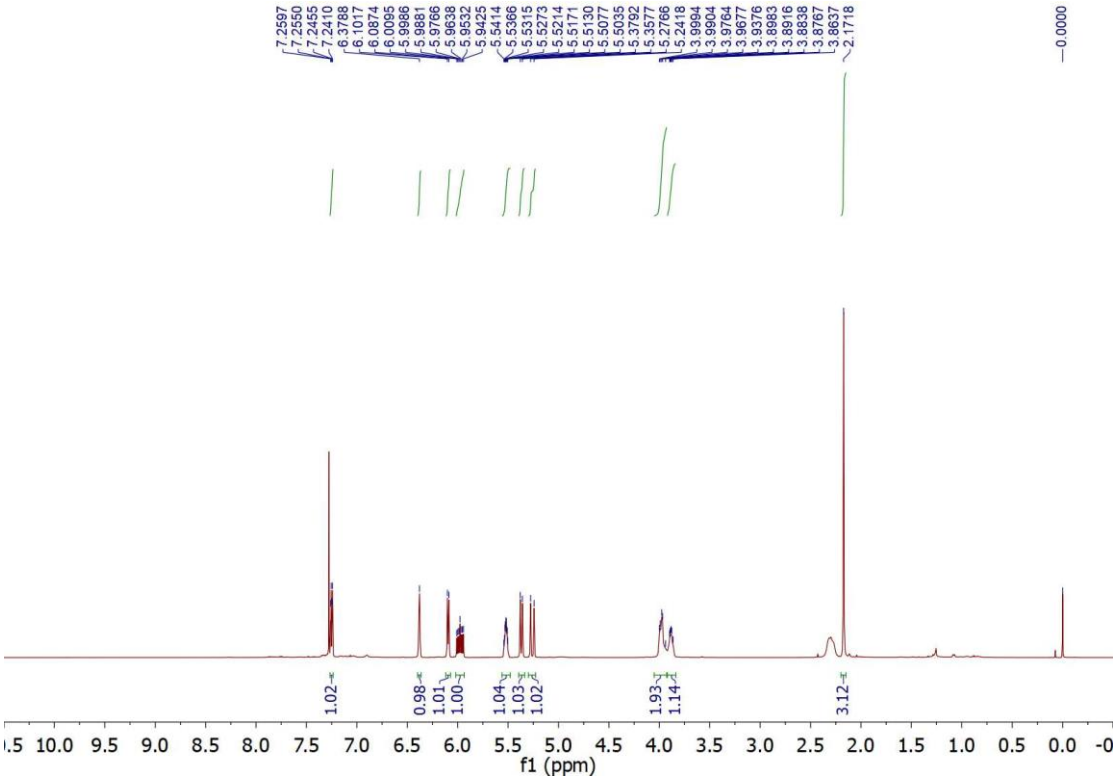
f1 (ppm)


CH3
O
N
HO

3c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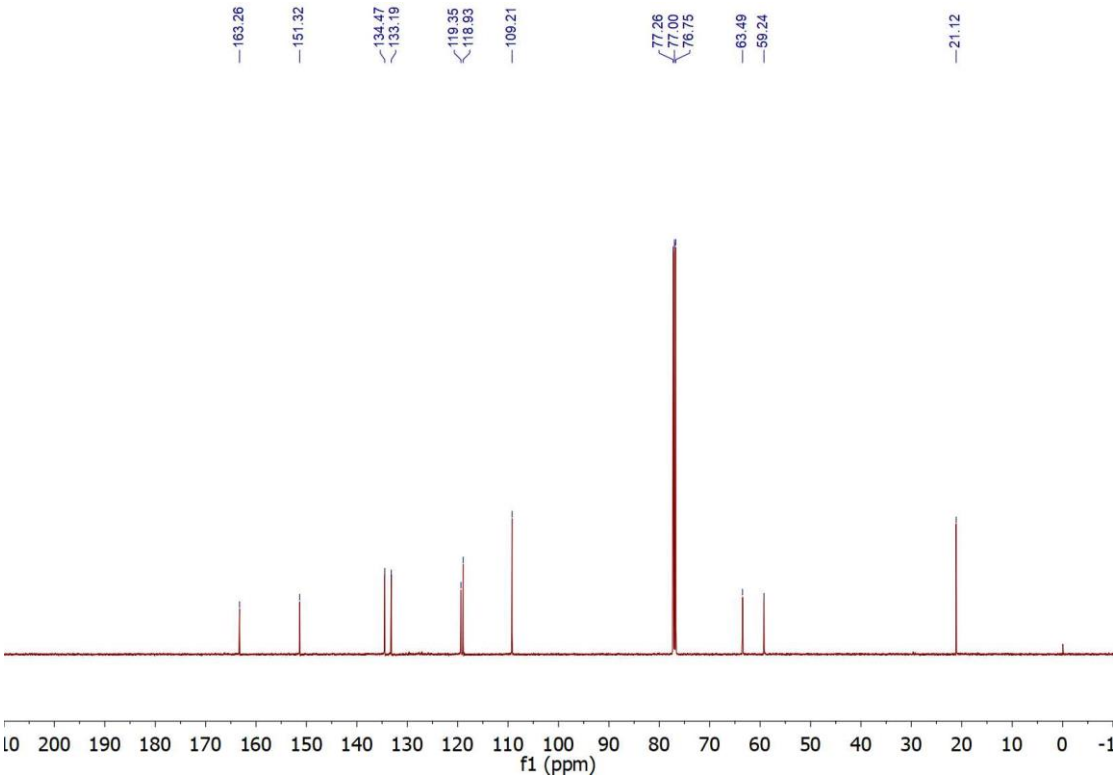
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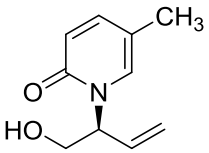
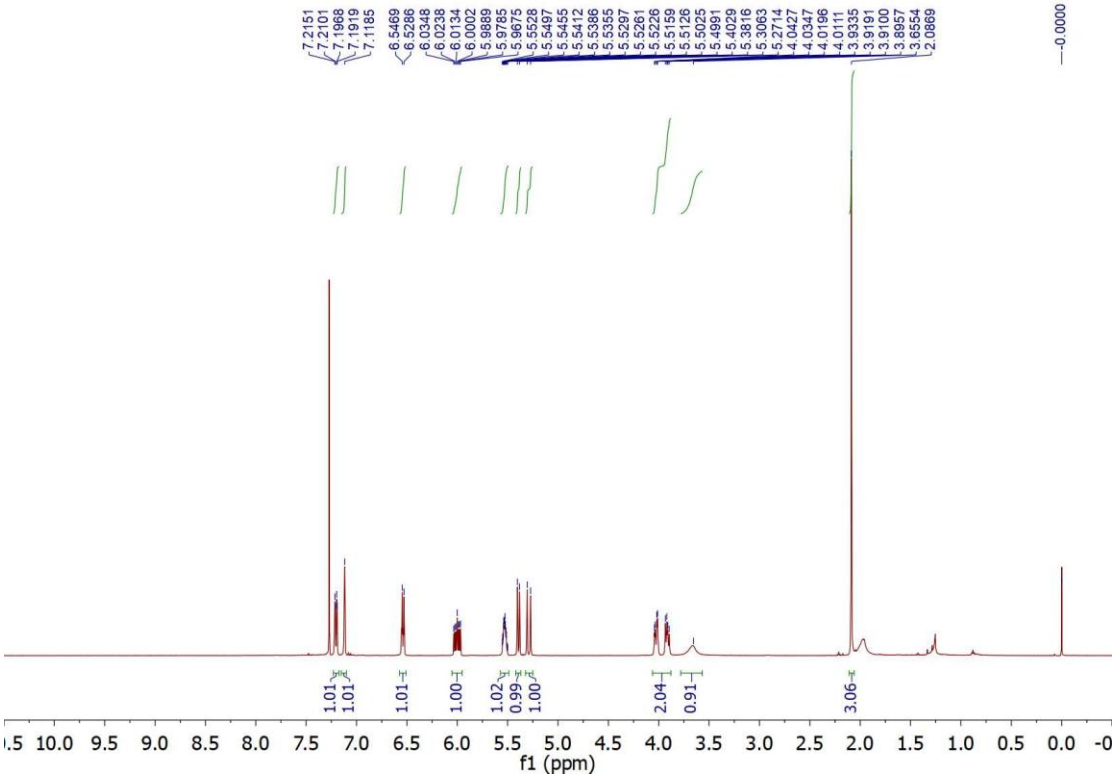
f1 (ppm)


CH3
O
N
HO

3d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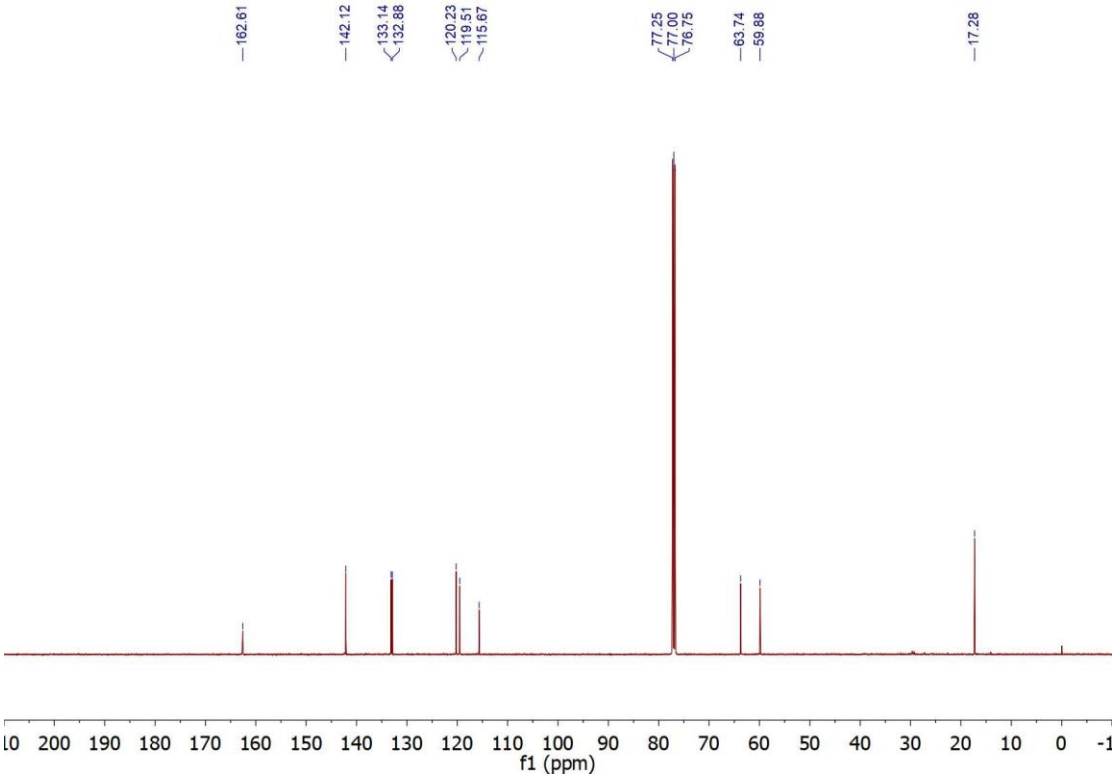
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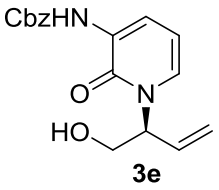

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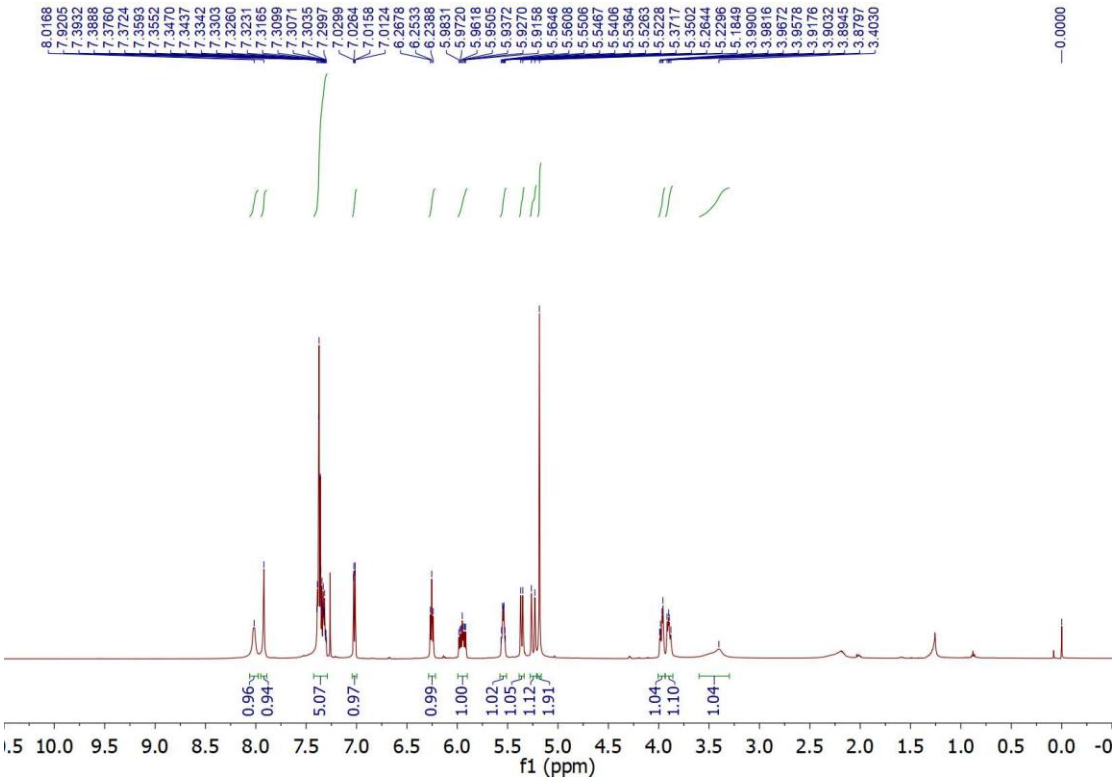

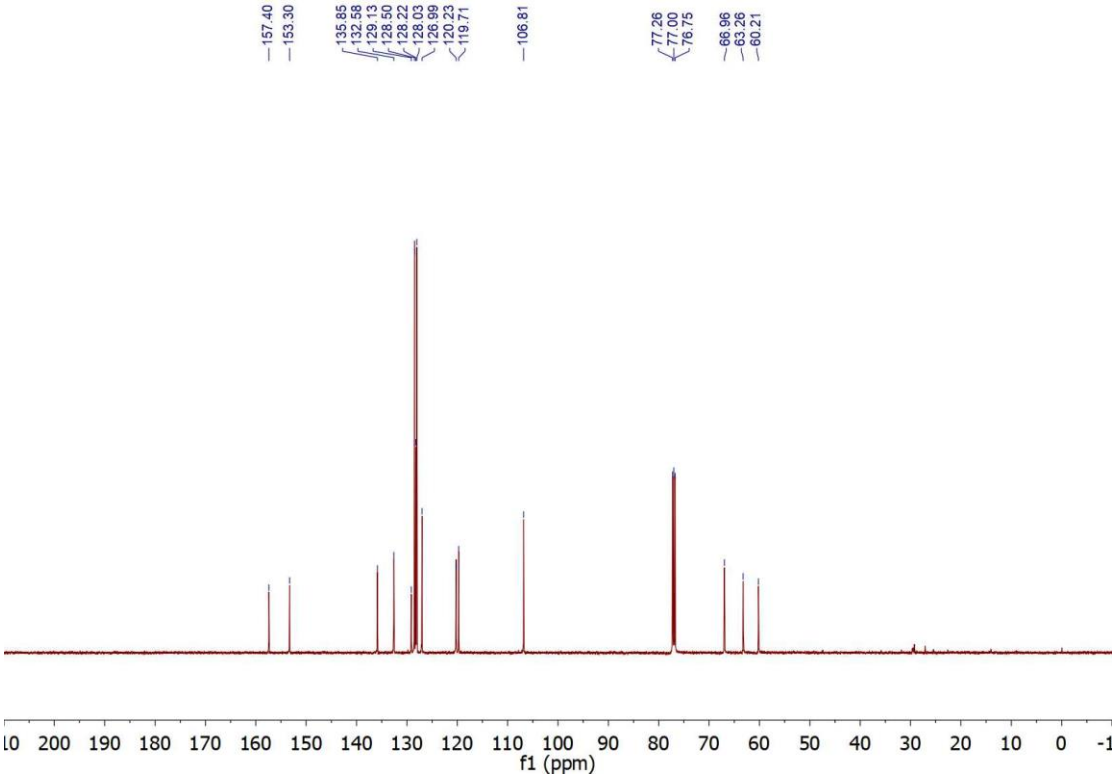

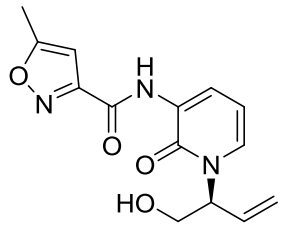

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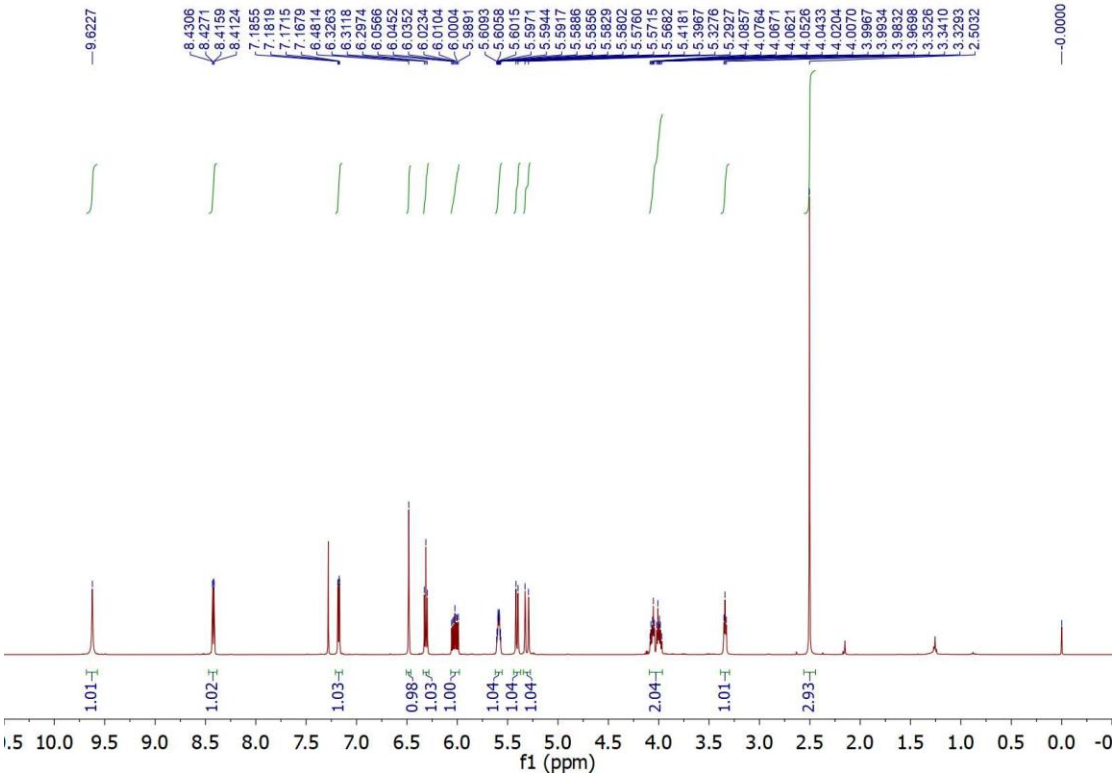
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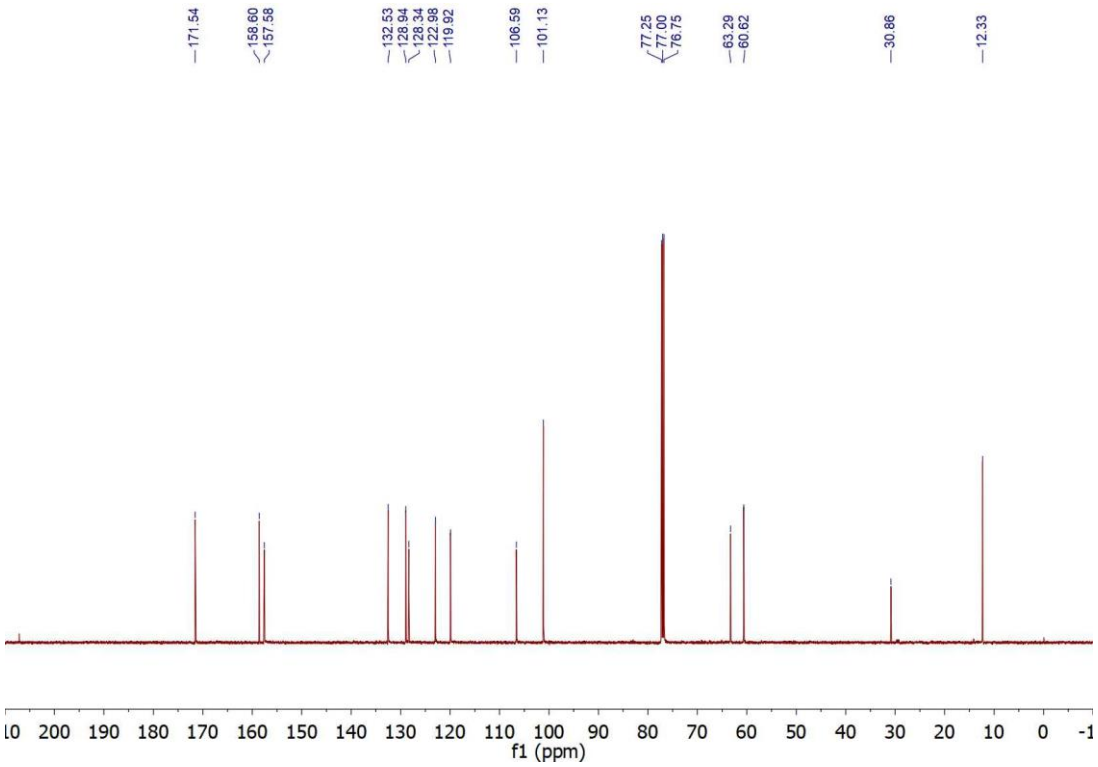
f1 (ppm)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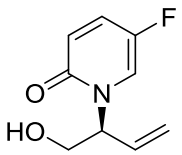
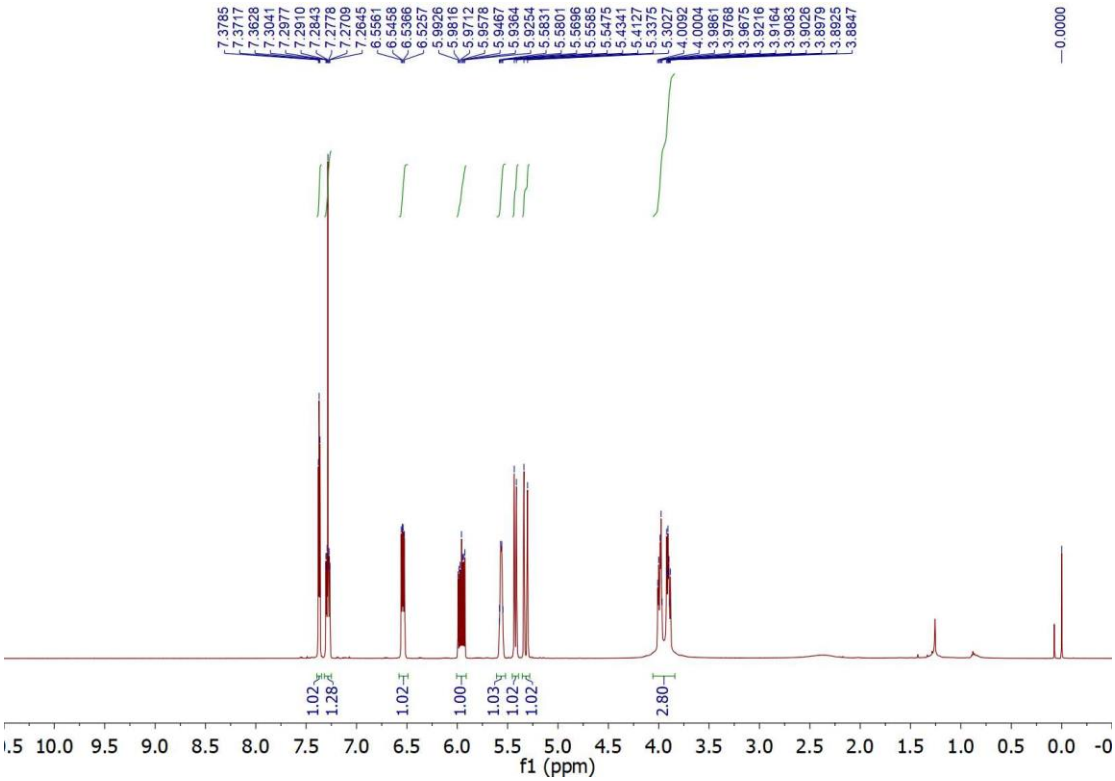
f1 (ppm)


F
O
N
HO

3g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7.2977
7.2910
7.2843
7.2778
7.2709
7.2645
6.5561
6.5458
6.5366
6.5257
5.9926
5.9816
5.9712
5.9578
5.9467
5.9364
5.9254
5.5831
5.5801
5.5696
5.5585
5.5475
5.4341
5.4127
5.3375
5.3027
4.0092
4.0004
3.9861
3.9768
3.9675
3.9216
3.9164
3.9083
3.9026
3.8979
3.8925
3.8847
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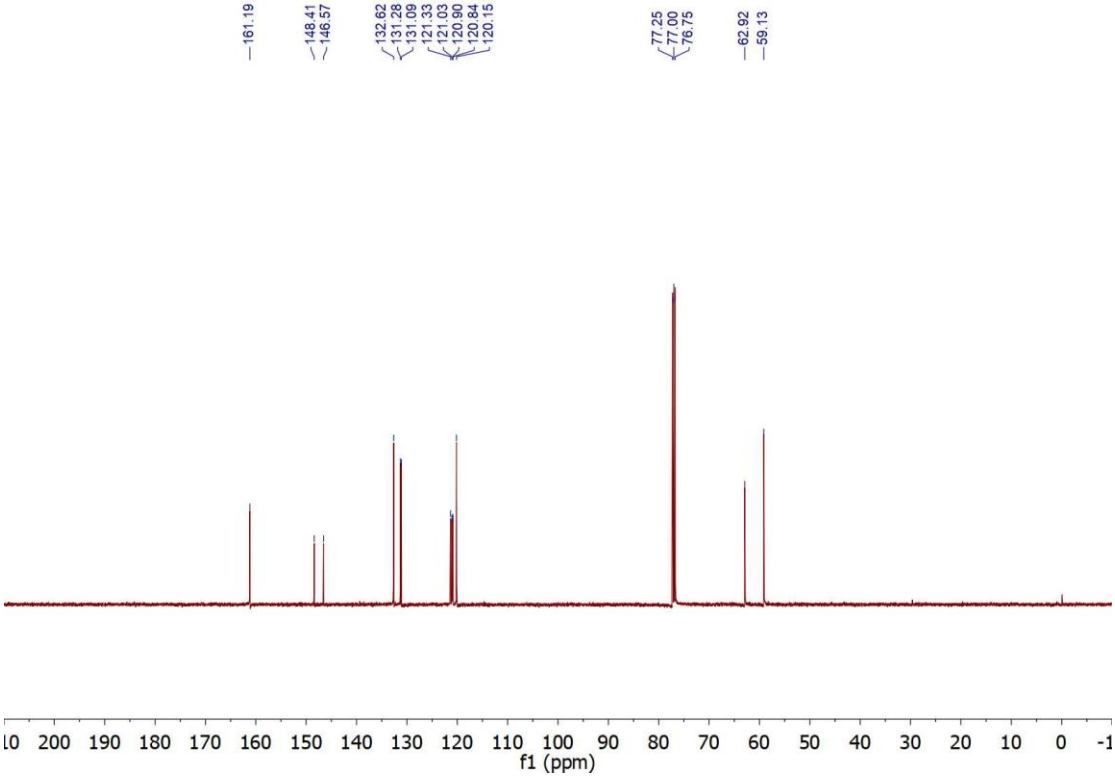
1.02
1.28
1.02
1.00
1.03
1.02
1.02
2.80
f1 (ppm)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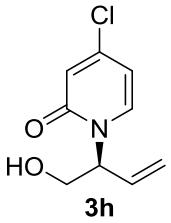
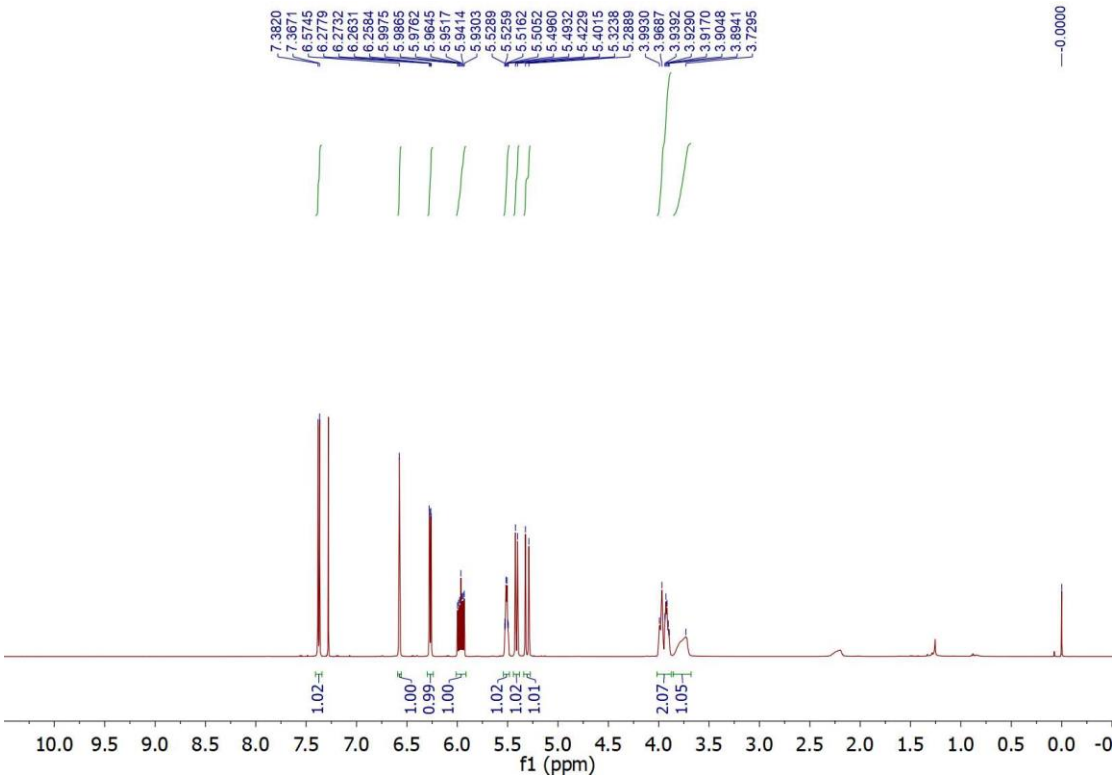
146.57
132.62
131.28
131.09
121.33
121.03
120.90
120.84
120.15
77.25
77.00
76.75
62.92
59.13
f1 (ppm)


Cl
O
N
HO

3h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6.2779
6.2732
6.2631
6.2584
5.9975
5.9865
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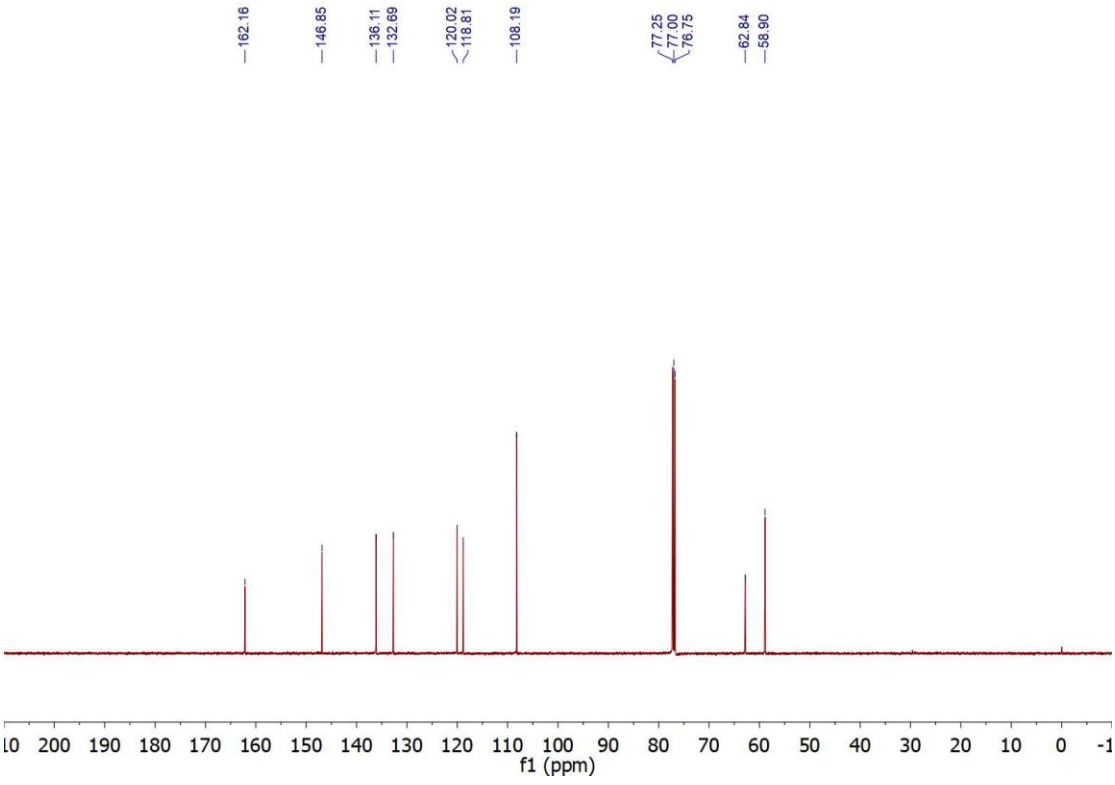
5.9645
5.9517
5.9414
5.9303
5.5289
5.5259
5.5162
5.5052
5.4960
5.4932
5.4229
5.4015
5.3238
5.2889
3.9930
3.9687
3.9392
3.9290
3.9170
3.9048
3.8941
3.7295
-0.0000
1.02
1.00
0.99
1.00
1.02
1.02
1.01
2.07
1.05
f1 (ppm)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132.69
120.02
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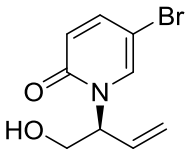
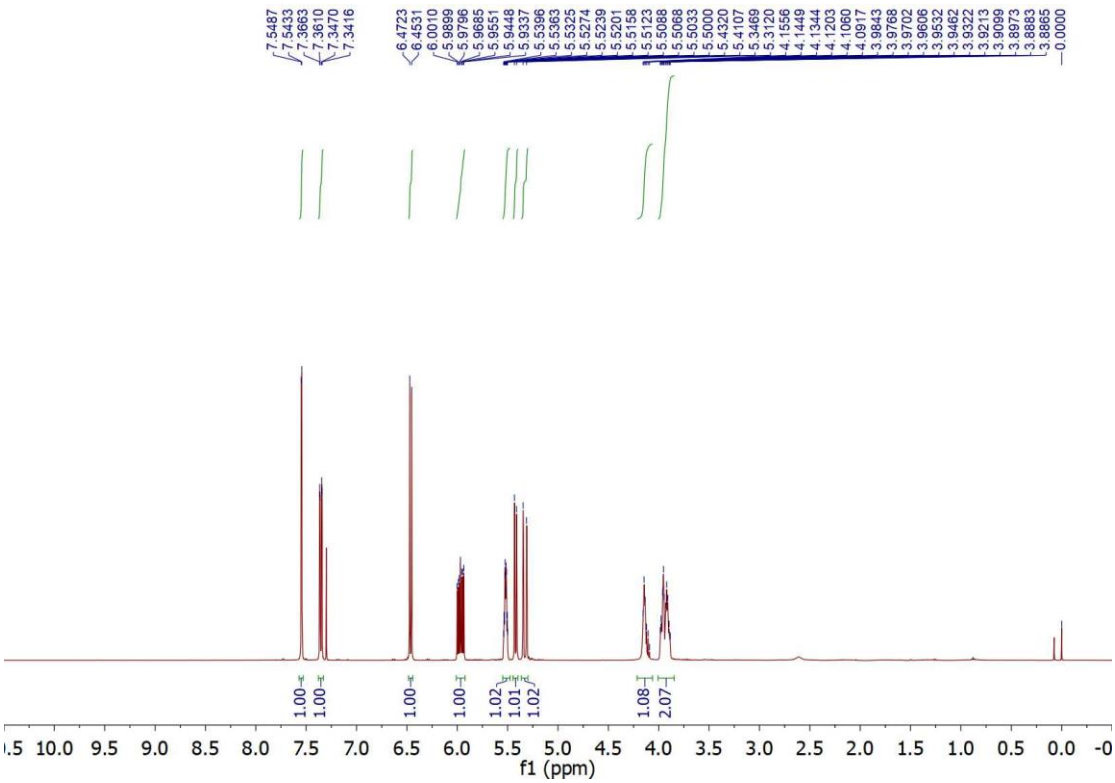
108.19
77.25
77.00
76.75
62.84
58.90
f1 (ppm)


Br
O
N
HO

3i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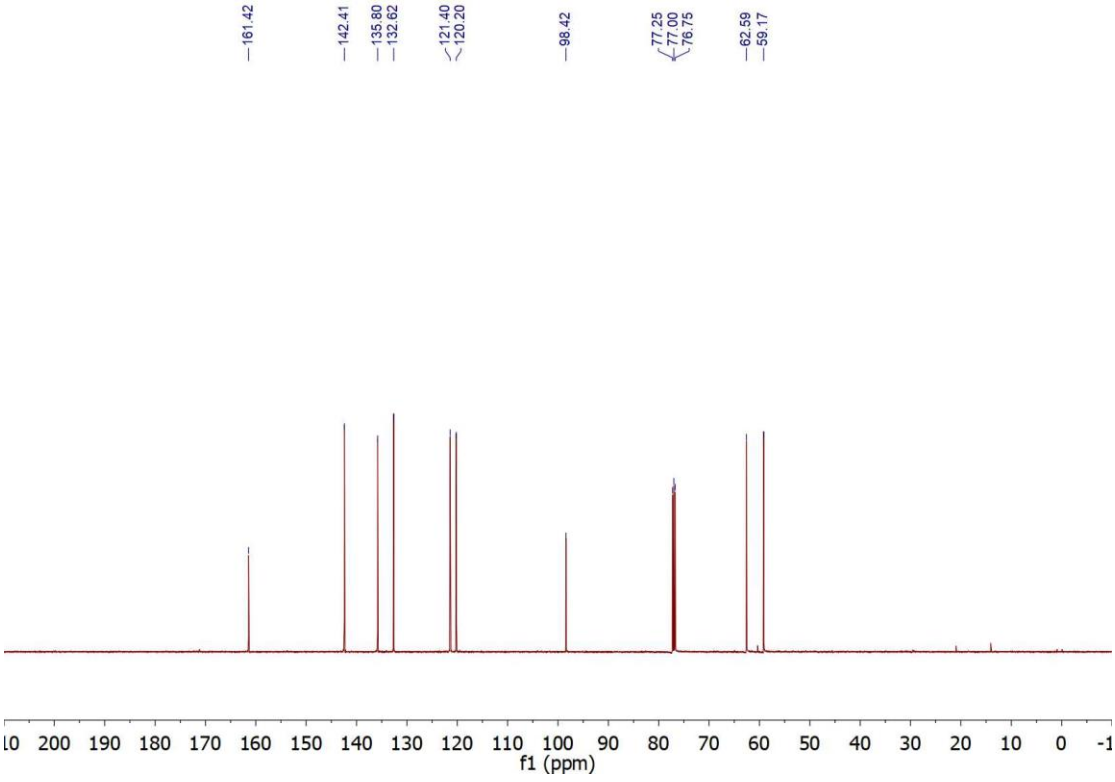
7.3610
7.3470
7.3416
6.4723
6.4531
6.0010
5.9899
5.9796
5.9685
5.9551
5.9448
5.9337
5.5396
5.5363
5.5325
5.5274
5.5239
5.5201
5.5158
5.5123
5.5088
5.5068
5.5033
5.5000
5.4320
5.4107
5.3469
5.3120
4.1556
4.1449
4.1344
4.1203
4.1060
4.0917
3.9843
3.9768
3.9702
3.9606
3.9532
3.9462
3.9322
3.9213
3.9099
3.8973
3.8883
3.8865
0.0000
1.00
1.00
1.00
1.00
1.02
1.01
1.02
1.08
2.07
f1 (ppm)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135.80
132.62
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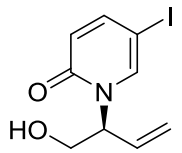
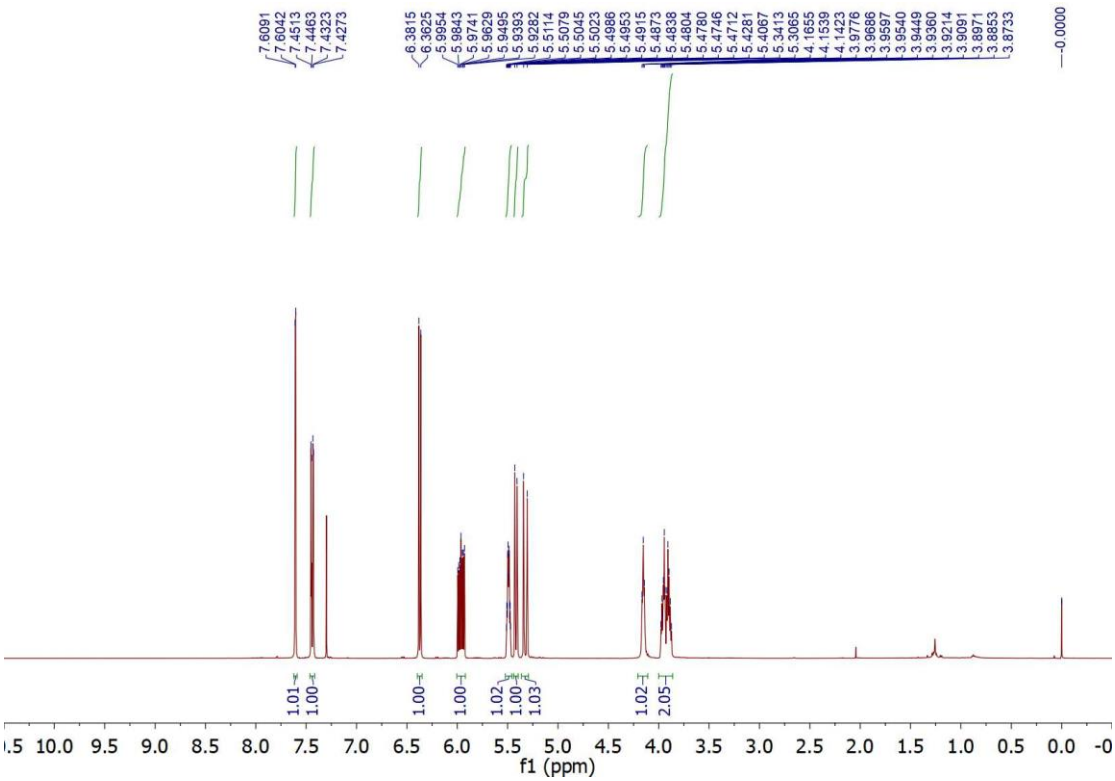
120.20
98.42
77.25
77.00
76.75
62.59
59.17
f1 (ppm)


I
O
N
HO

3j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7.4513
7.4463
7.4323
7.4273
6.3815
6.3625
5.9954
5.9843
5.9741
5.9629
5.9495
5.9393
5.9282
5.5114
5.5079
5.5045
5.5023
5.4986
5.4953
5.4915
5.4873
5.4838
5.4804
5.4780
5.4746
5.4712
5.4281
5.4067
5.3413
5.3065
4.1655
4.1539
4.1423
3.9776
3.9686
3.9597
3.9540
3.9449
3.9360
3.9214
3.9091
3.8971
3.8853
3.8733
0.0000
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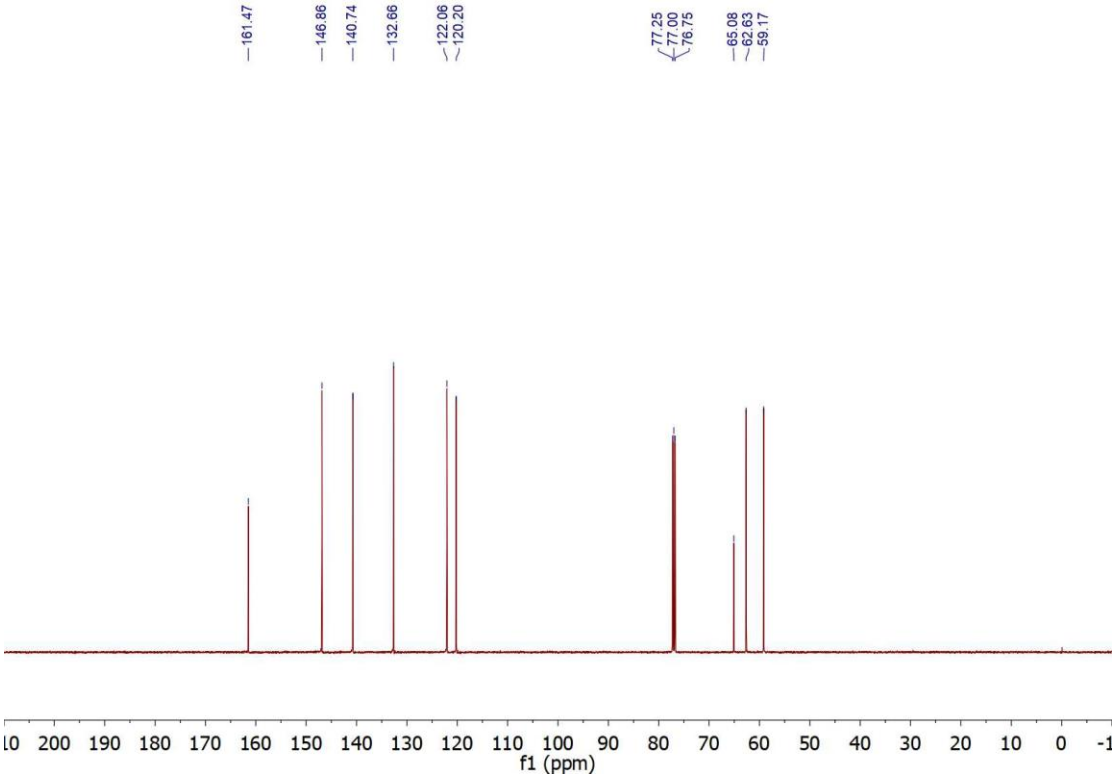
1.00
1.00
1.00
1.02
1.00
1.03
1.02
2.05
f1 (ppm)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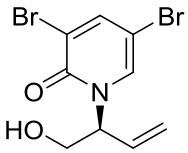
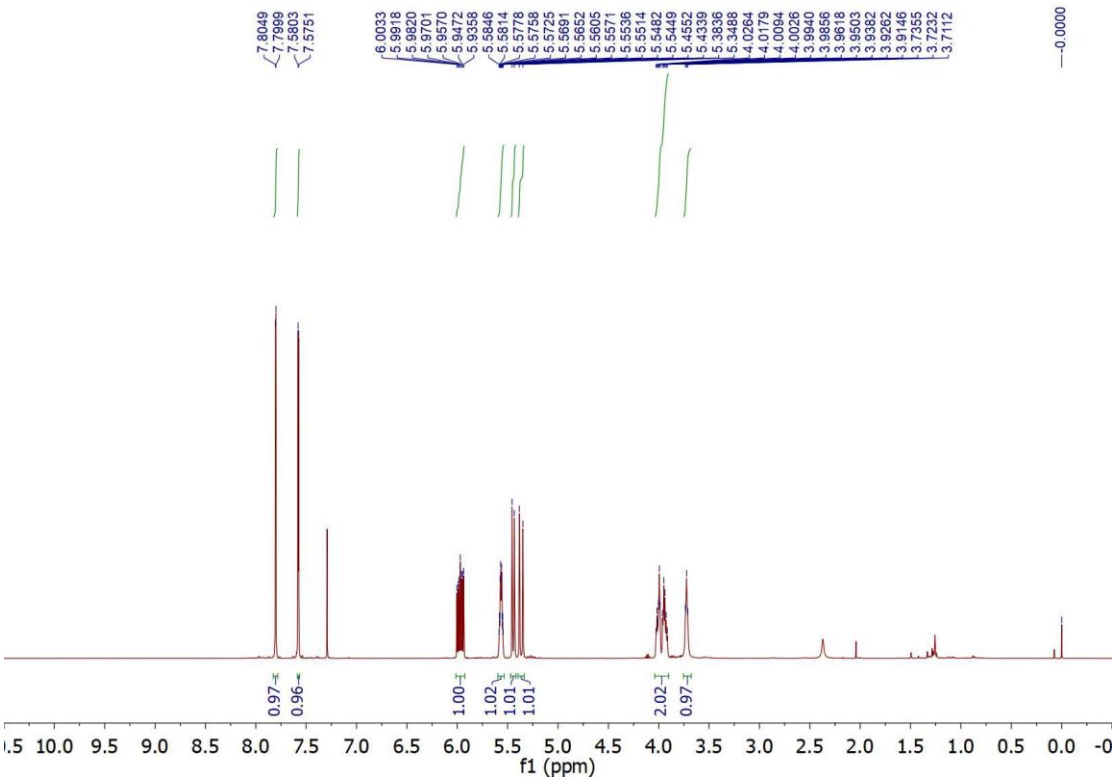
140.74
132.66
122.06
120.20
77.25
77.00
76.75
65.08
62.63
59.17
f1 (ppm)


Br
Br
O
N
HO

3k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7.7999
7.5803
7.5751
6.0033
5.9918
5.9820
5.9701
5.9570
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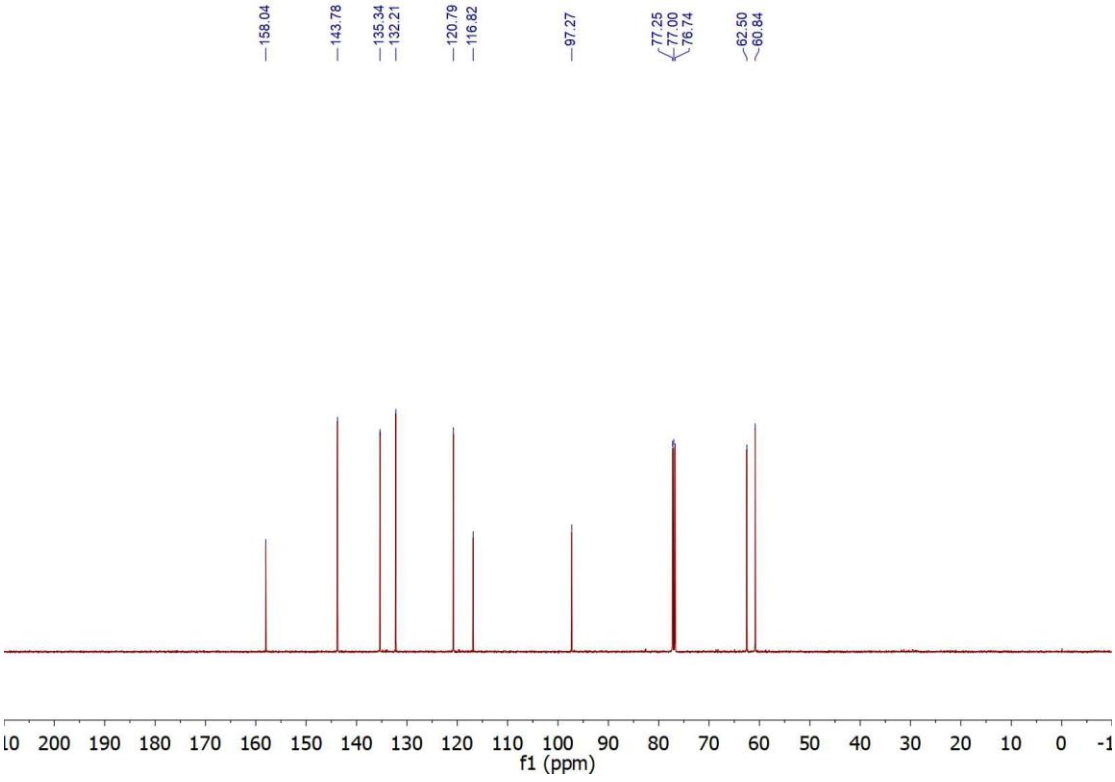
5.5758
5.5725
5.5691
5.5652
5.5605
5.5571
5.5536
5.5514
5.5482
5.5449
5.4552
5.4439
5.3836
5.3488
4.0264
4.0179
4.0094
4.0026
3.9940
3.9856
3.9618
3.9503
3.9382
3.9262
3.9146
3.7355
3.7232
3.7112
-0.0000
0.97
0.96
1.00
1.02
1.01
1.01
2.02
0.97
f1 (ppm)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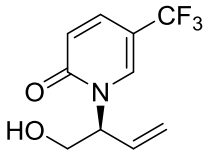
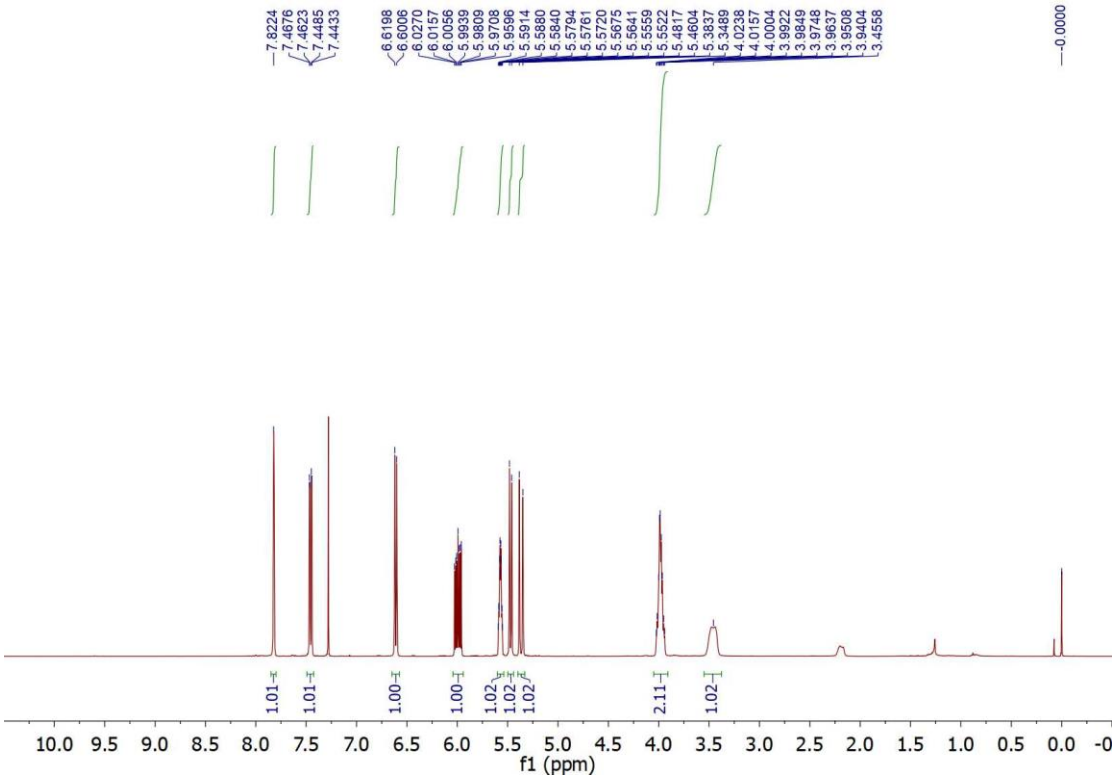
143.78
135.34
132.21
120.79
116.82
97.27
77.25
77.00
76.74
62.50
60.84
f1 (ppm)


CF3
O
N
HO

3l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7.4433
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6.6006
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6.0157
6.0056
5.9939
5.9809
5.9708
5.9596
5.9514
5.5880
5.5840
5.5794
5.5761
5.5720
5.5675
5.5641
5.5559
5.5522
5.4817
5.4604
5.3837
5.3489
4.0238
4.0157
4.0004
3.9922
3.9849
3.9748
3.9637
3.9508
3.9404
3.4558
-0.0000
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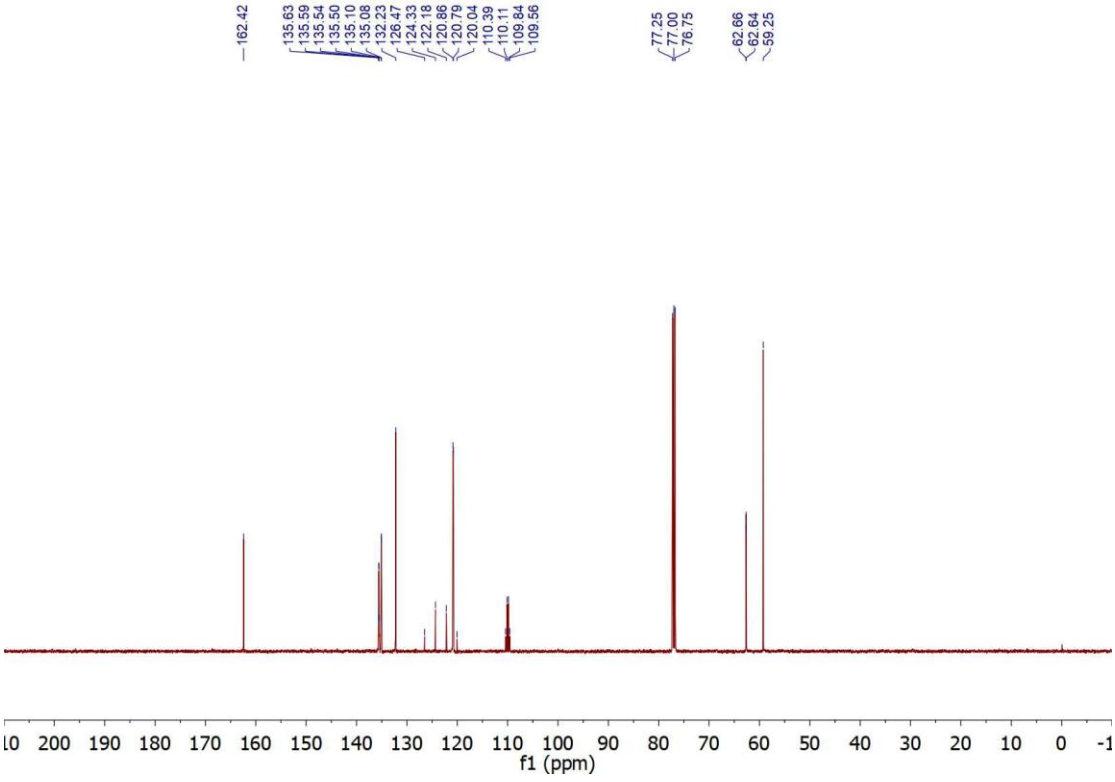
1.01
1.00
1.00
1.02
1.02
1.02
2.11
1.02
f1 (ppm)


162.42
135.63
135.59
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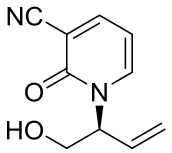
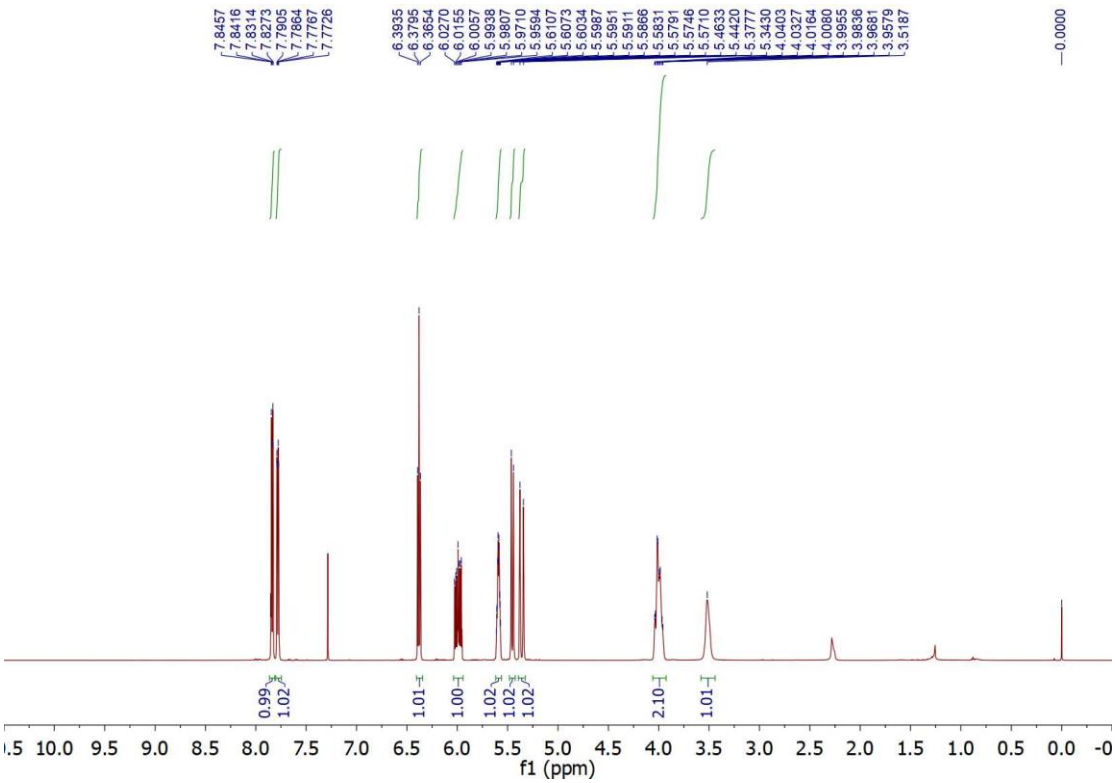
135.50
135.10
135.08
132.23
126.47
124.33
122.18
120.86
120.79
120.04
110.39
110.11
109.84
109.56
77.25
77.00
76.75
62.66
62.64
59.25
f1 (ppm)


NC
O
N
HO

3m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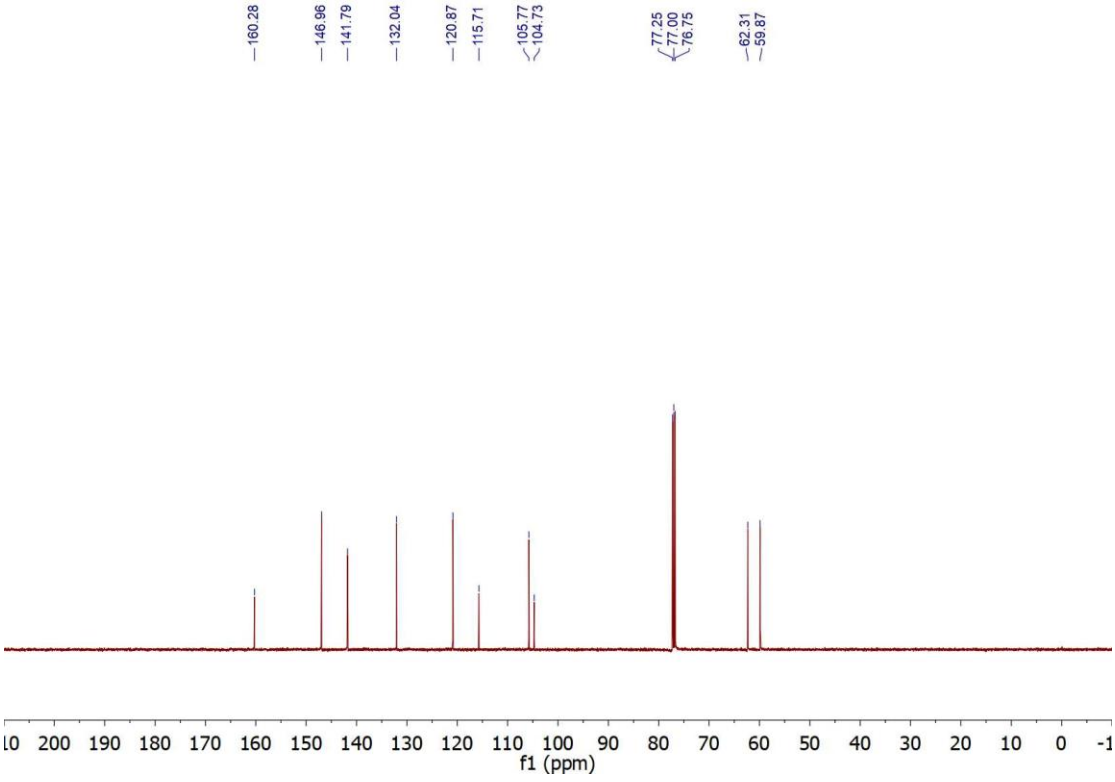
7.8314
7.8273
7.7905
7.7864
7.7767
7.7726
6.3935
6.3795
6.3654
6.0270
6.0155
6.0057
5.9938
5.9807
5.9710
5.9594
5.6107
5.6073
5.6034
5.5987
5.5951
5.5911
5.5866
5.5831
5.5791
5.5746
5.5710
5.4633
5.4420
5.3777
5.3430
4.0403
4.0327
4.0164
4.0080
3.9955
3.9836
3.9681
3.9579
3.5187
0.0000
0.99
1.02
1.01
1.00
1.02
1.02
1.02
2.10
1.01
f1 (ppm)


160.28
146.96
141.79
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115.71
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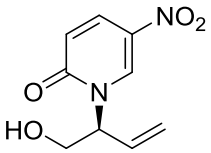
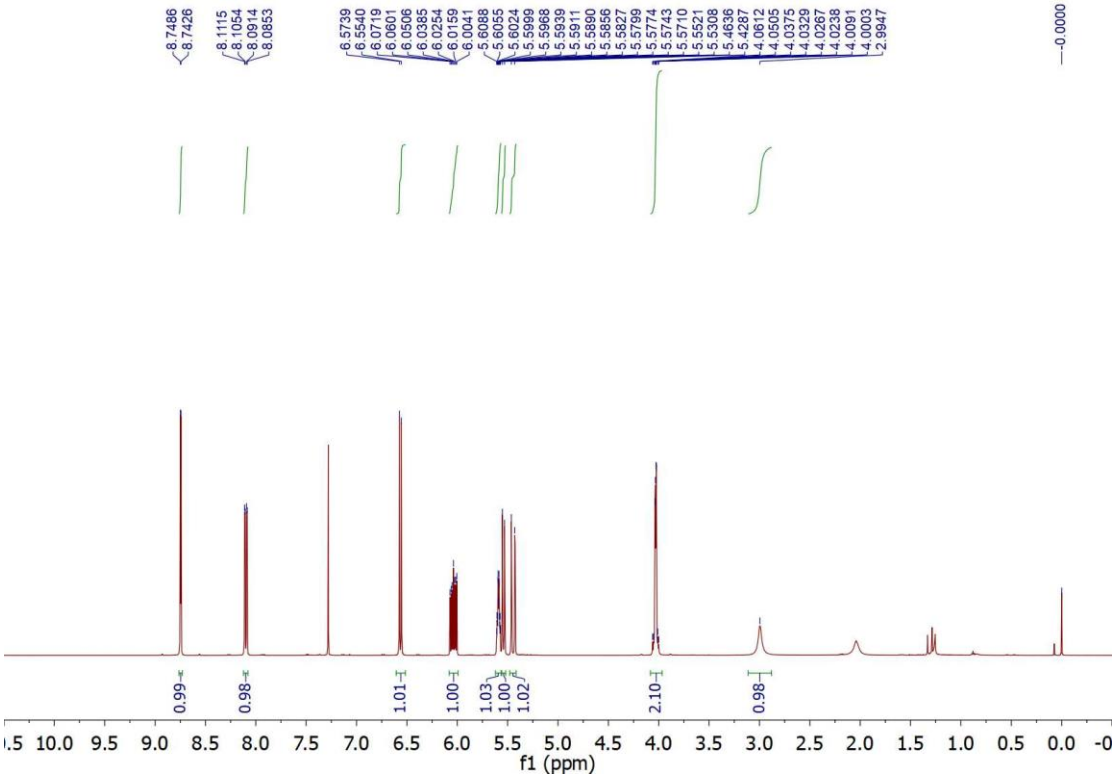
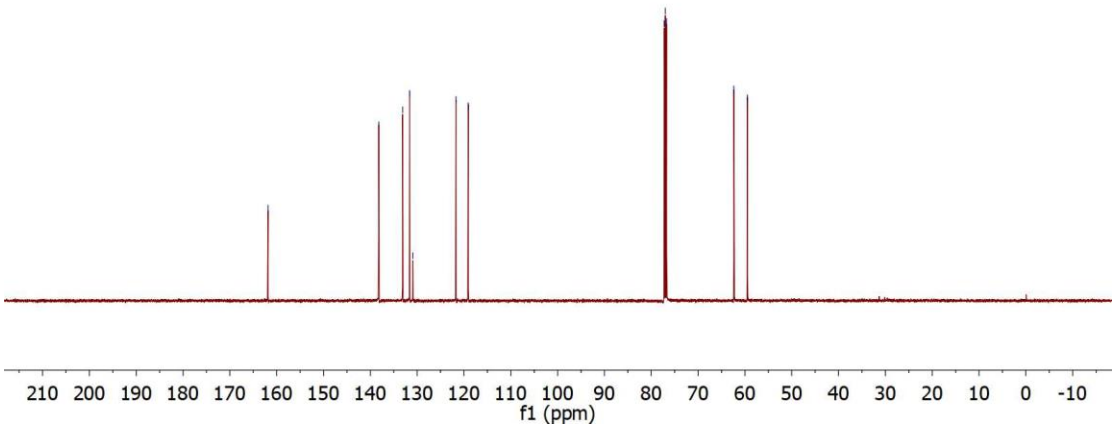
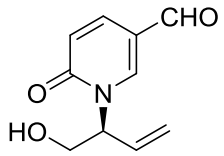
104.73
77.25
77.00
76.75
62.31
59.87
f1 (ppm)



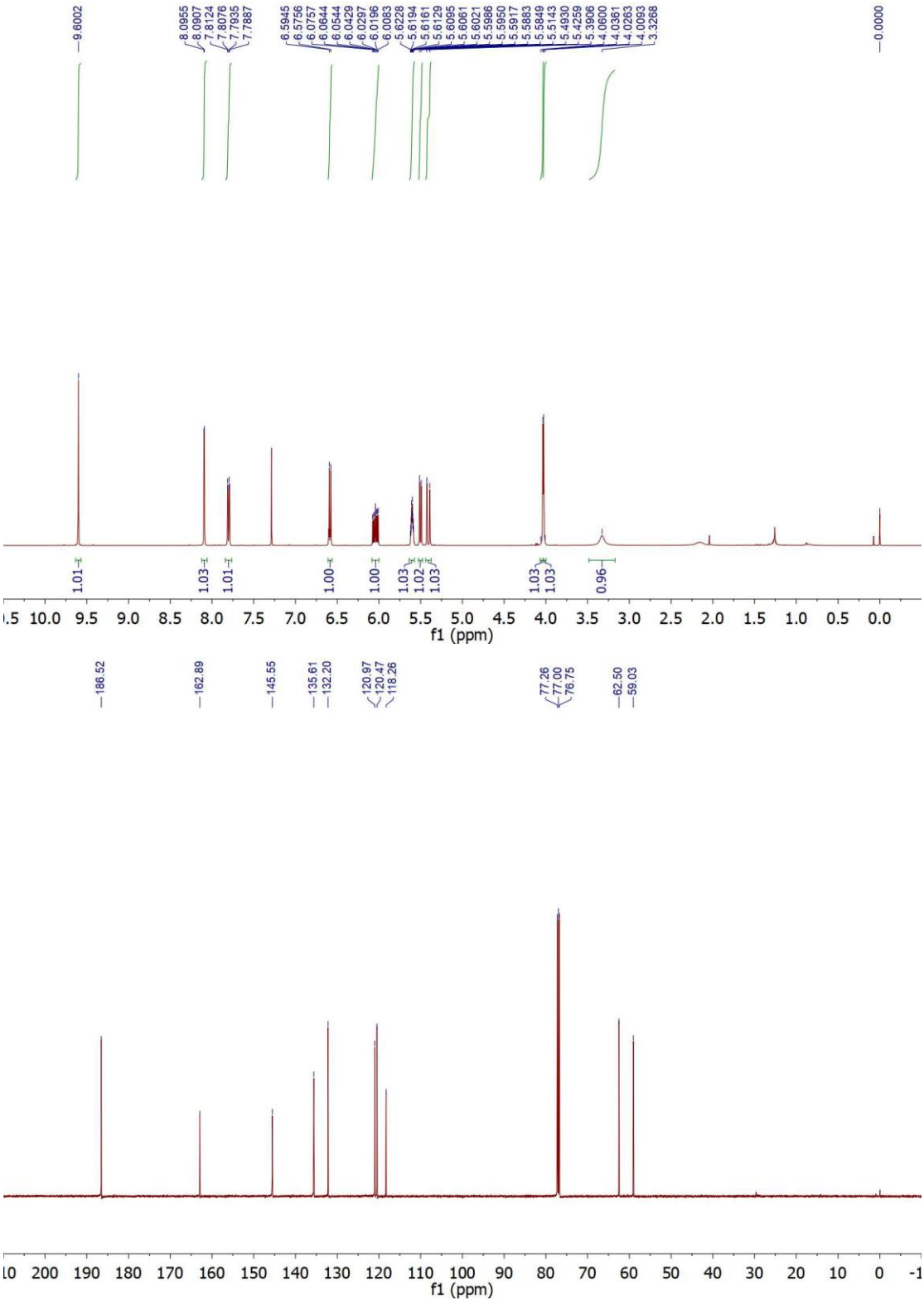
3n






CHO
O
N
HO

3o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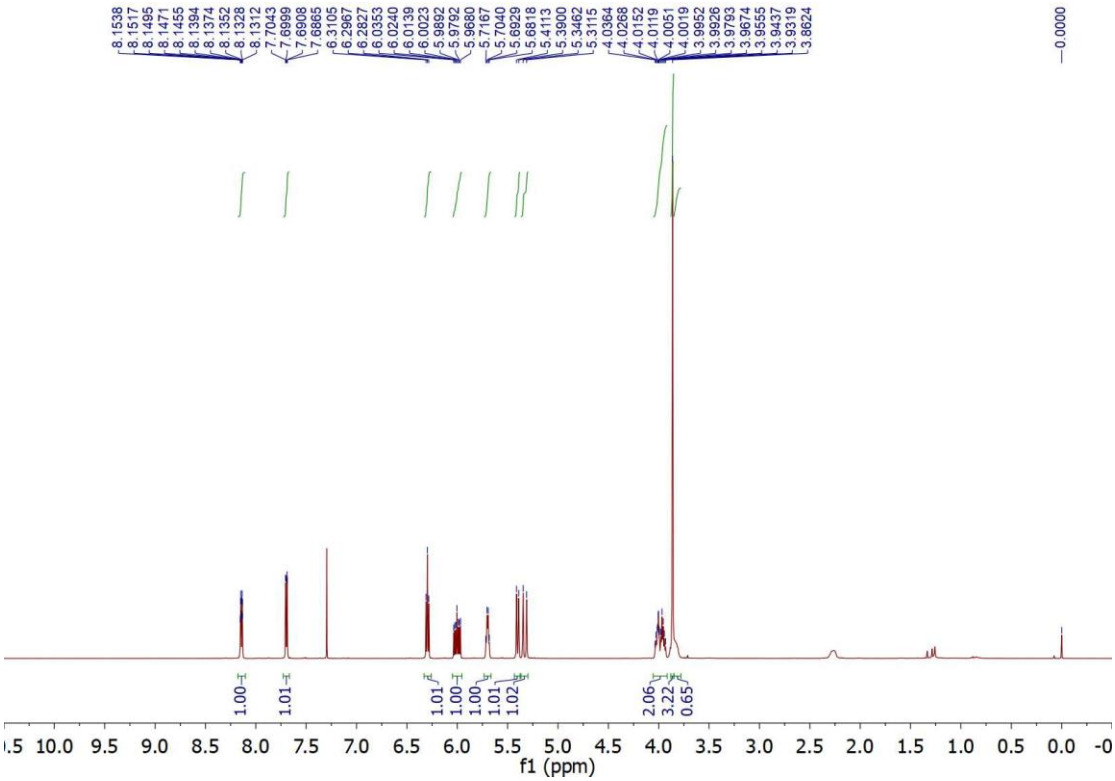
7.8076
7.7935
7.7887
6.5945
6.5756
6.0757
6.0644
6.0544
6.0429
6.0297
6.0196
6.0083
5.6228
5.6194
5.6161
5.6129
5.6095
5.6061
5.6021
5.5986
5.5950
5.5917
5.5883
5.5849
5.5143
5.4930
5.4259
5.3906
4.0600
4.0361
4.0263
4.0093
3.3268
0.0000
1.01
1.03
1.01
1.00
1.00
1.03
1.02
1.03
1.03
1.03
0.96
f1 (ppm)
186.52
162.89
145.55
135.61
132.20
120.97
120.47
118.26
77.26
77.00
76.75
62.50
59.03
f1 (ppm)


MeO2C
O
N
HO

3p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8.1328
8.1312
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7.6999
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7.6865
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6.2967
6.2827
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6.0240
6.0139
6.0023
5.9892
5.9792
5.9680
5.7167
5.7040
5.6929
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5.3900
5.3462
5.3115
4.0364
4.0268
4.0152
4.0119
4.0051
4.0019
3.9952
3.9926
3.9793
3.9674
3.9555
3.9437
3.9319
3.8624
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1.01
1.00
1.00
1.01
1.02
2.06
3.22
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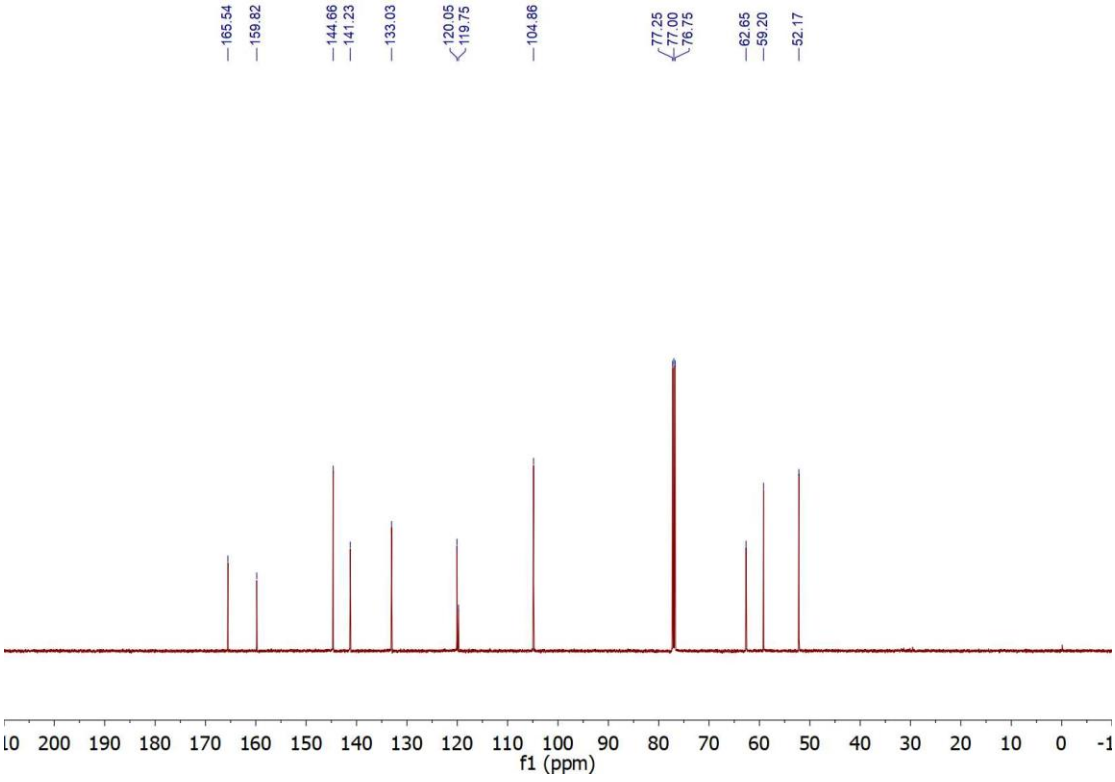
f1 (ppm)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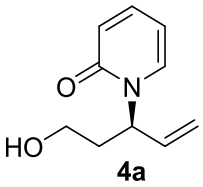
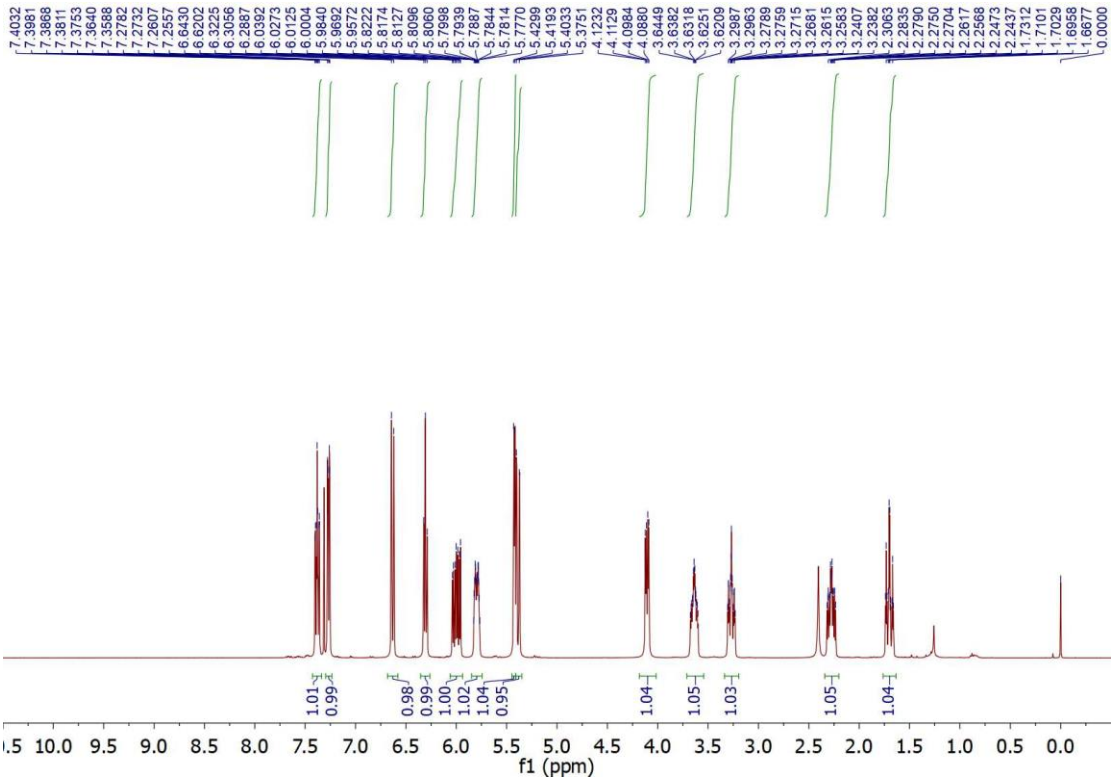
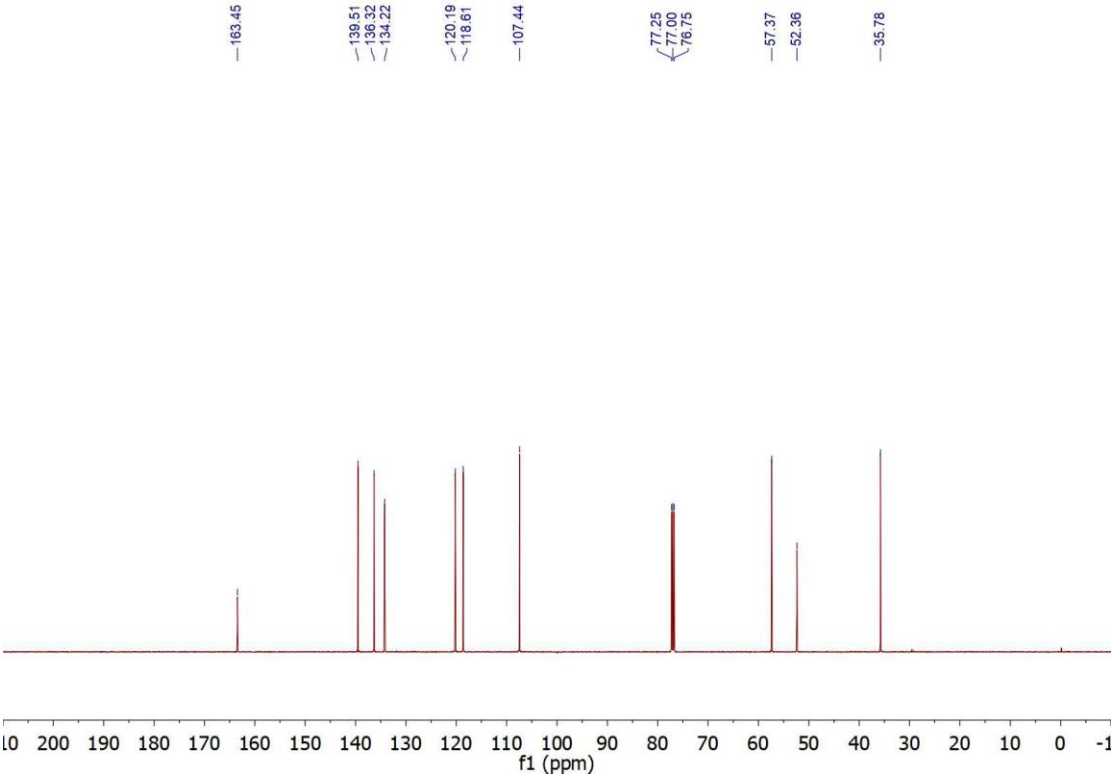
159.82
144.66
141.23
133.03
120.05
119.75
104.86
77.25
77.00
76.75
62.65
59.20
52.17
f1 (ppm)


O
N
HO

4a


1.01
0.99
0.98
0.99
1.00
1.02
1.04
0.95
1.04
1.05
1.03
1.05
1.04
f1 (ppm)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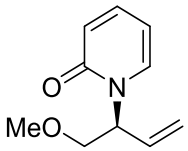
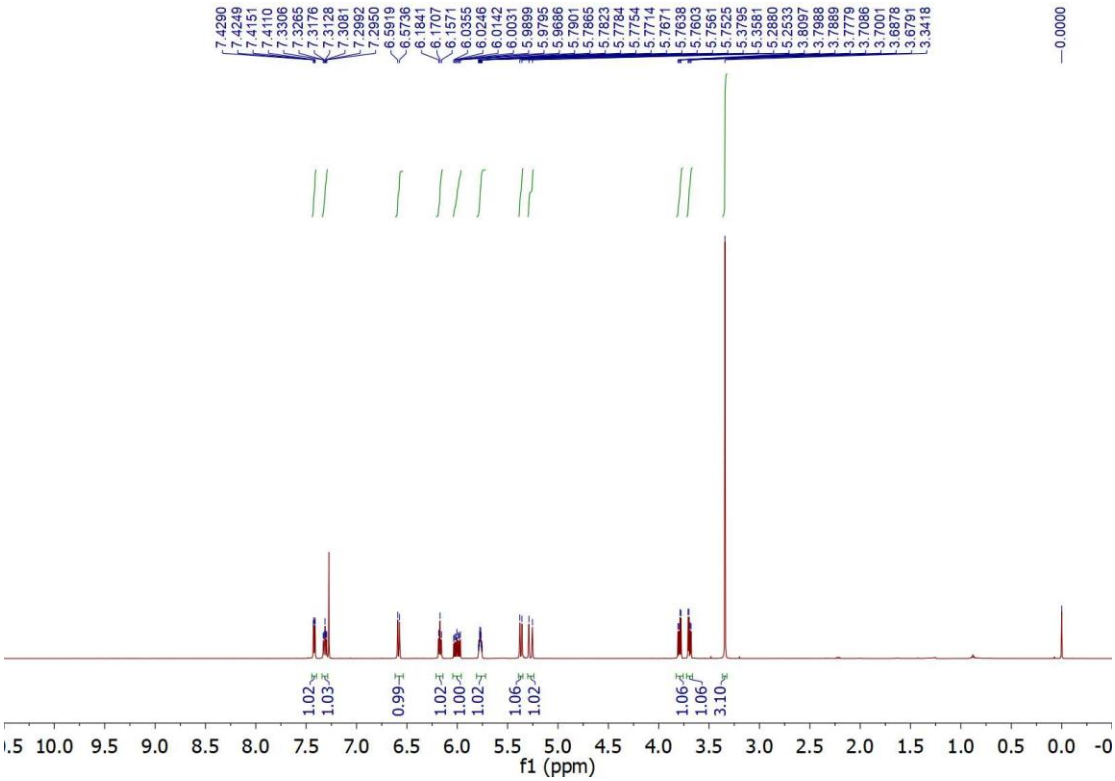
139.51
136.32
134.22
120.19
118.61
107.44
77.25
77.00
76.75
57.37
52.36
35.78
f1 (ppm)


O
N
MeO

4c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7.3265
7.3176
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7.3081
7.2992
7.2950
6.5919
6.5736
6.1841
6.1707
6.1571
6.0355
6.0246
6.0142
6.0031
5.9899
5.9795
5.9686
5.7901
5.7865
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5.7525
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5.2880
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3.6791
3.3418
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1.03
0.99
1.02
1.00
1.02
1.06
1.02
1.06
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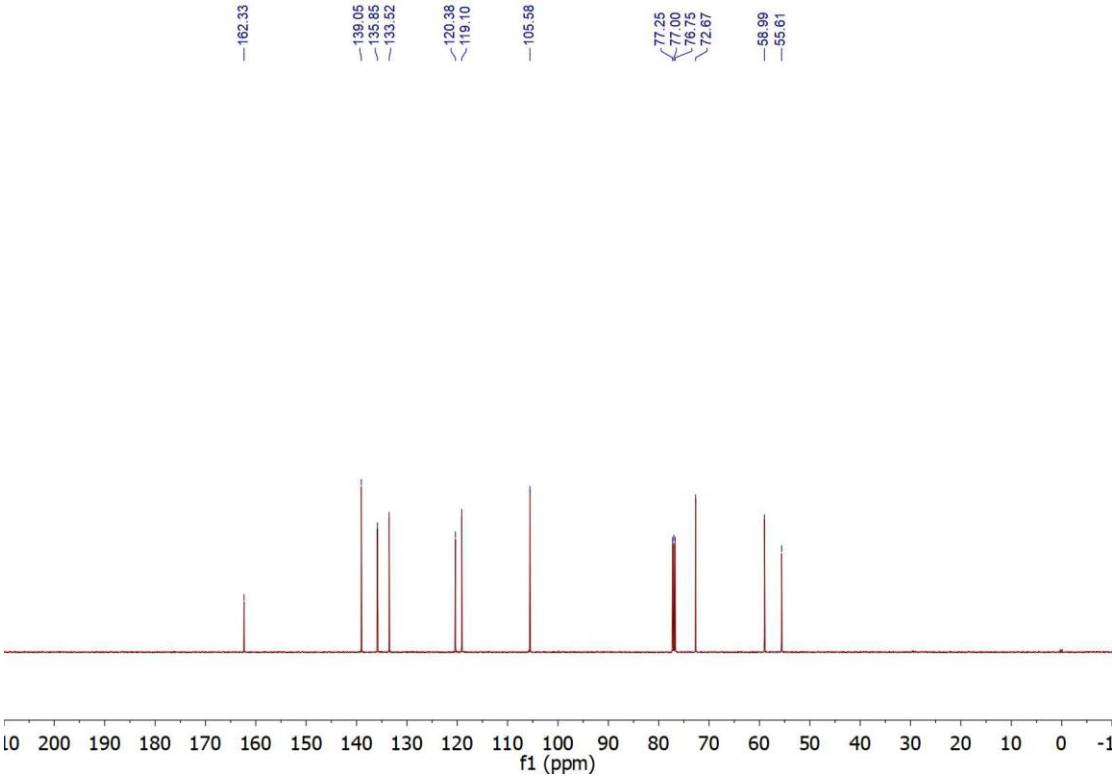
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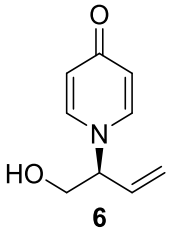
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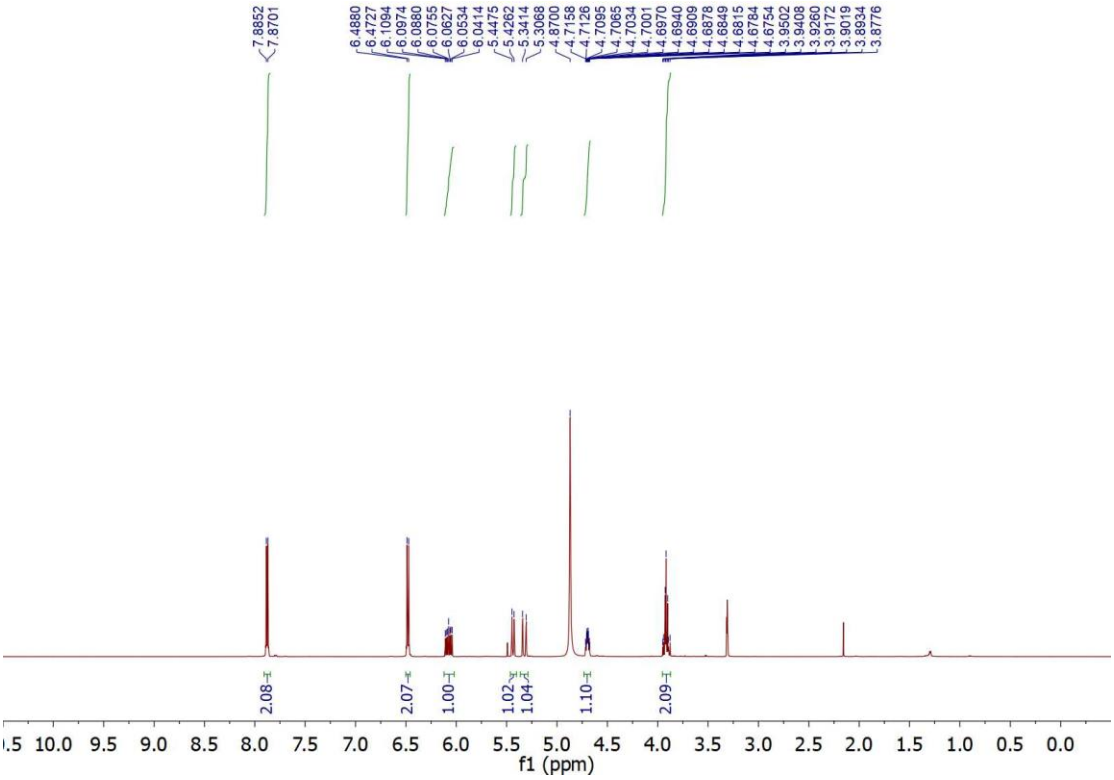
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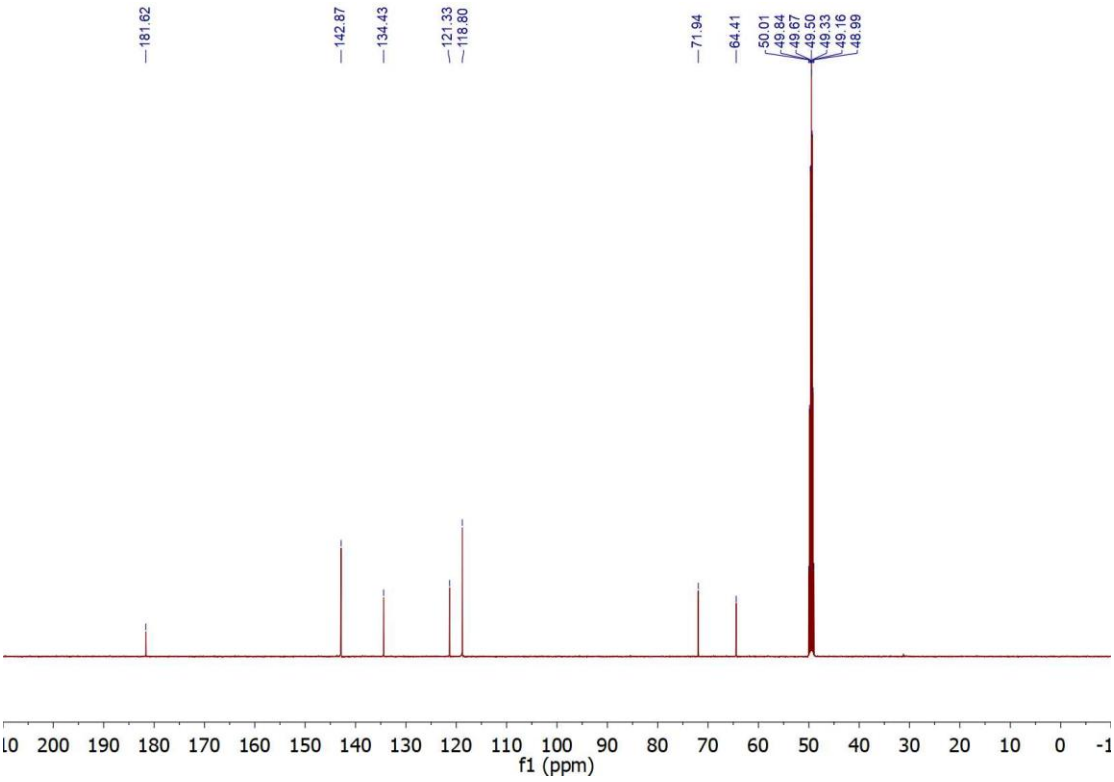
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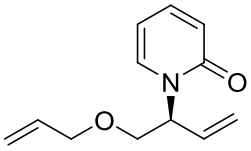

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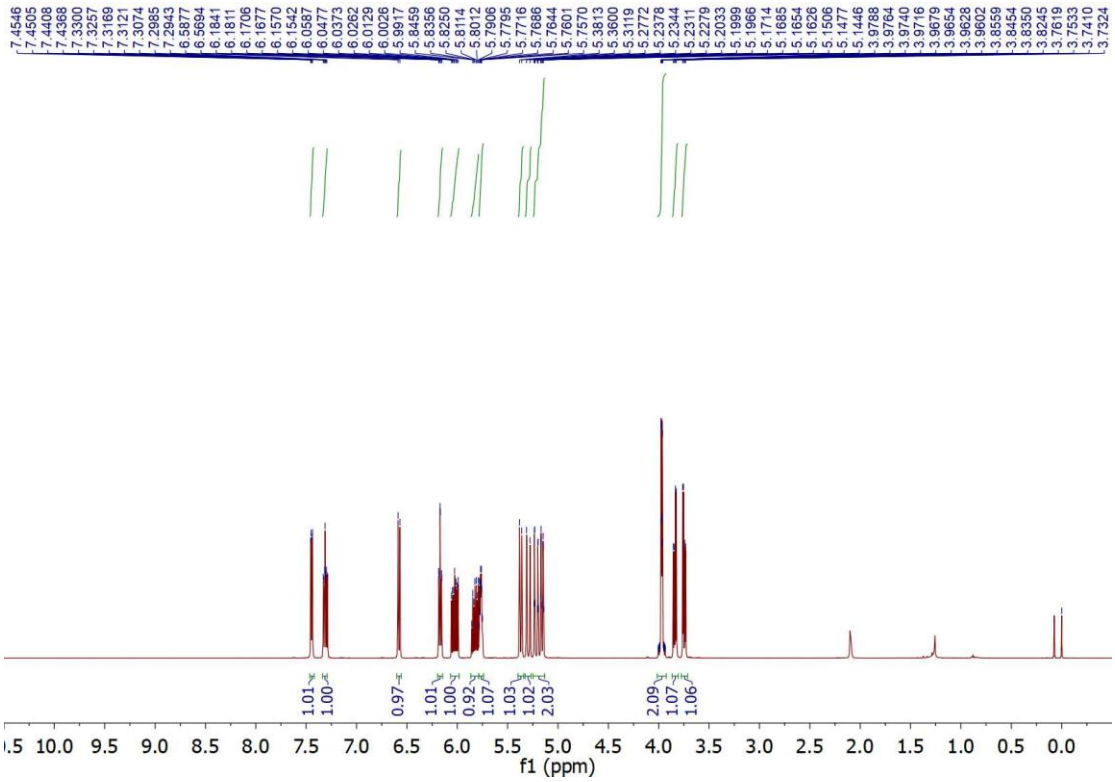
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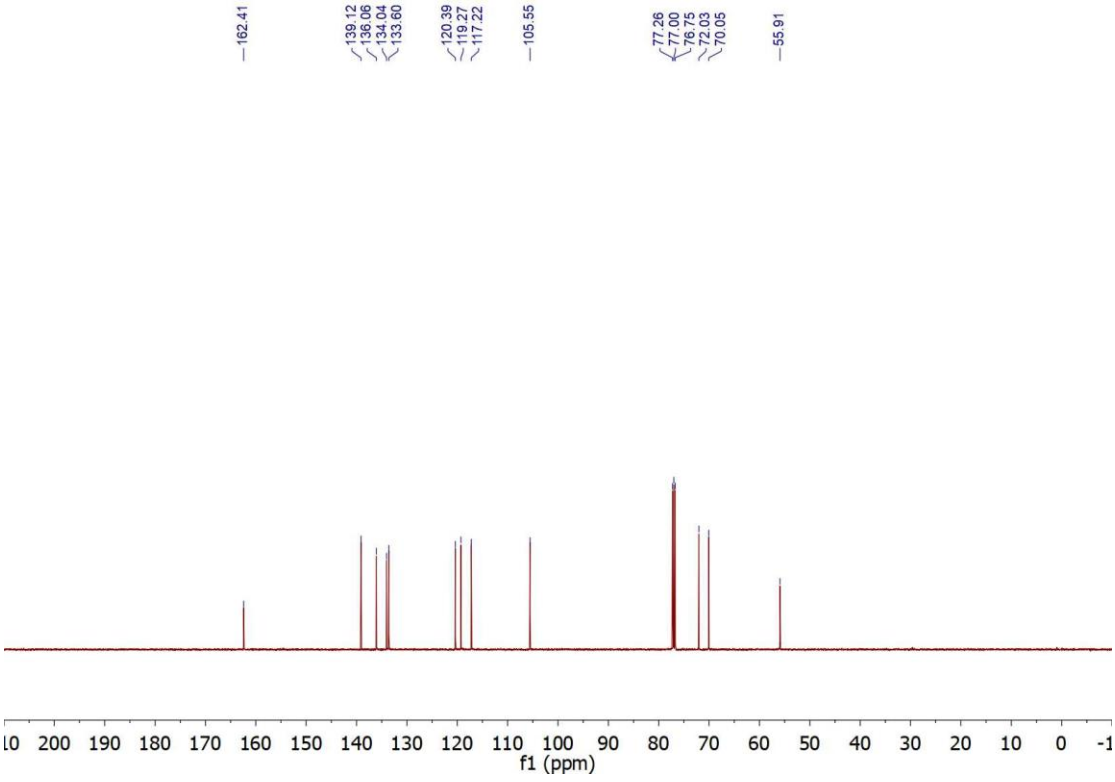
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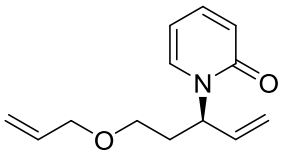

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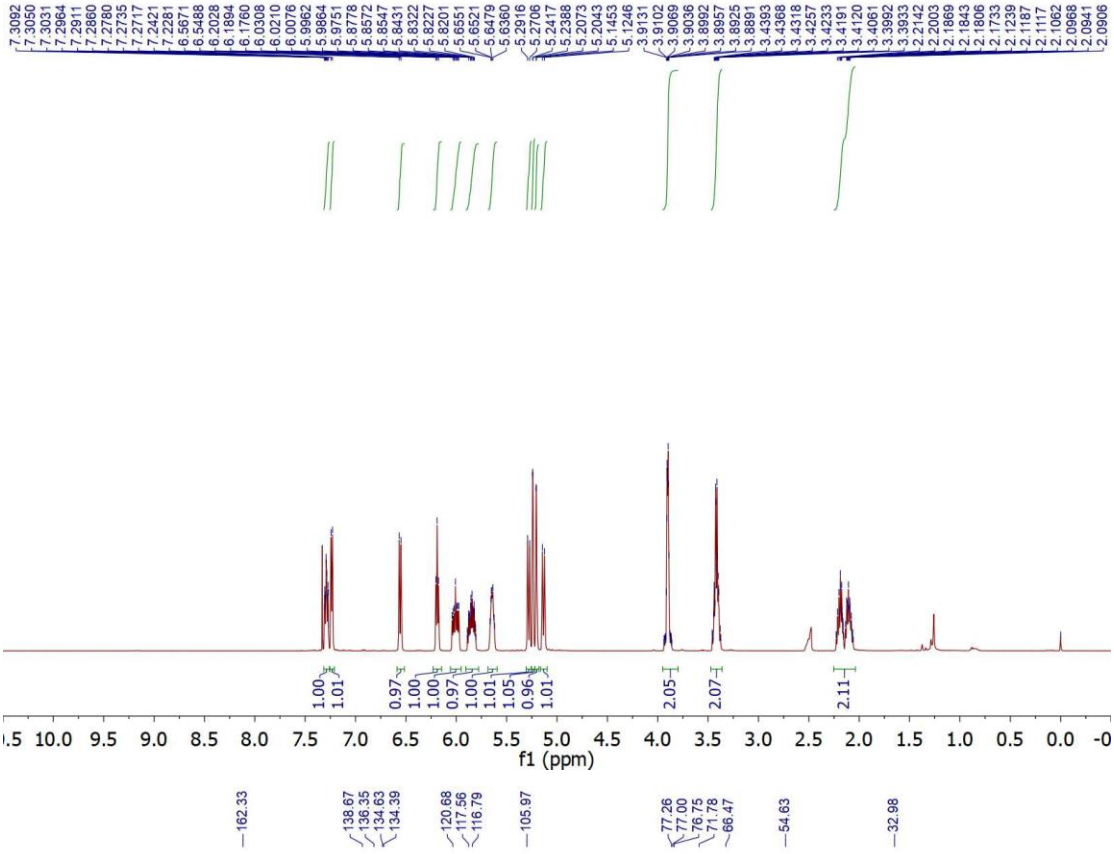

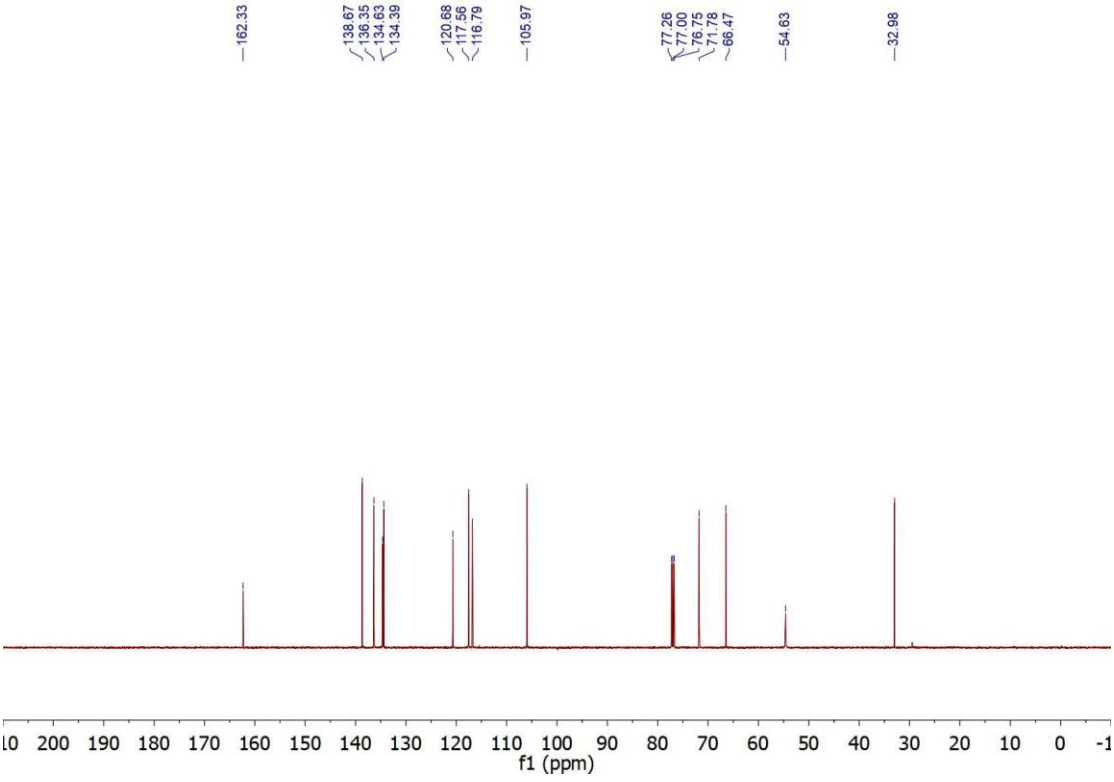

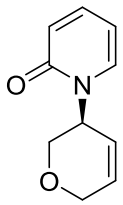
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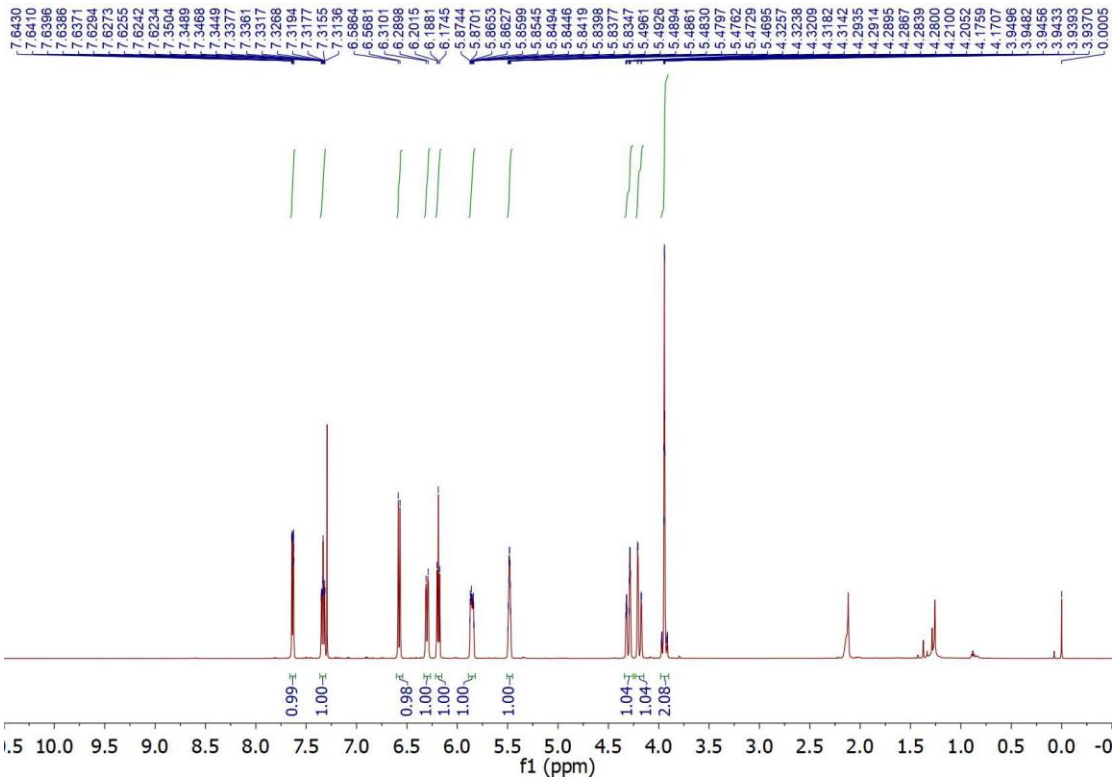
9a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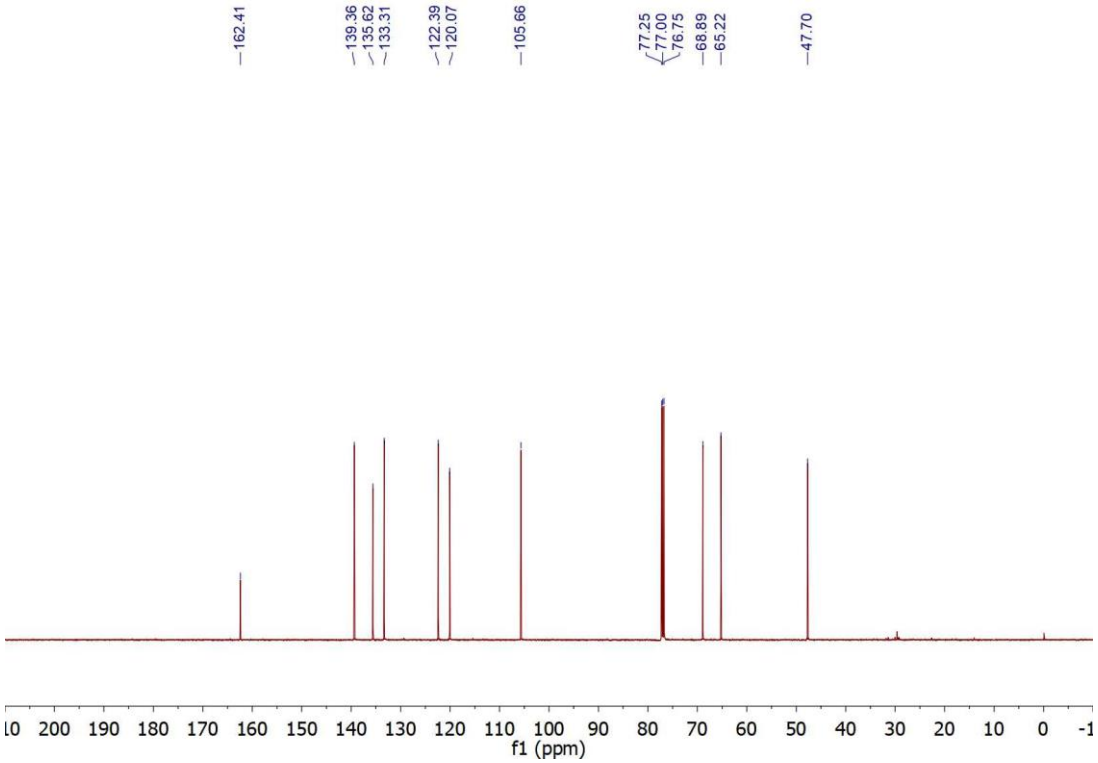
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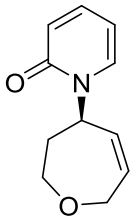

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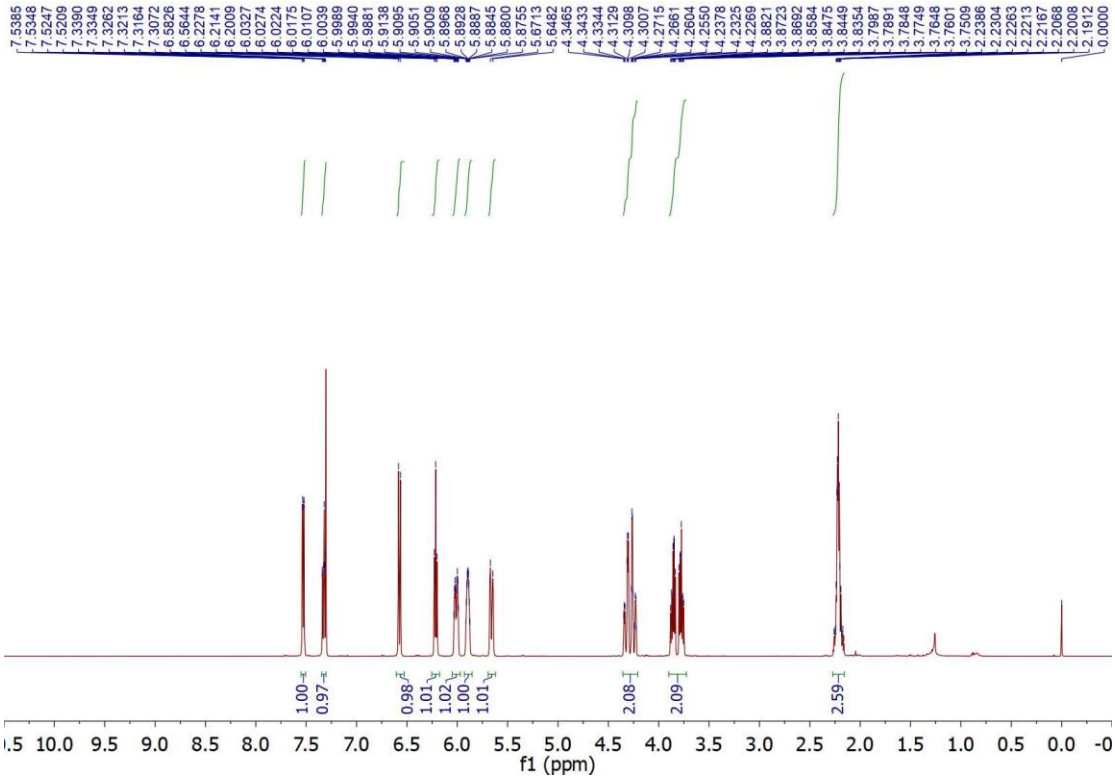
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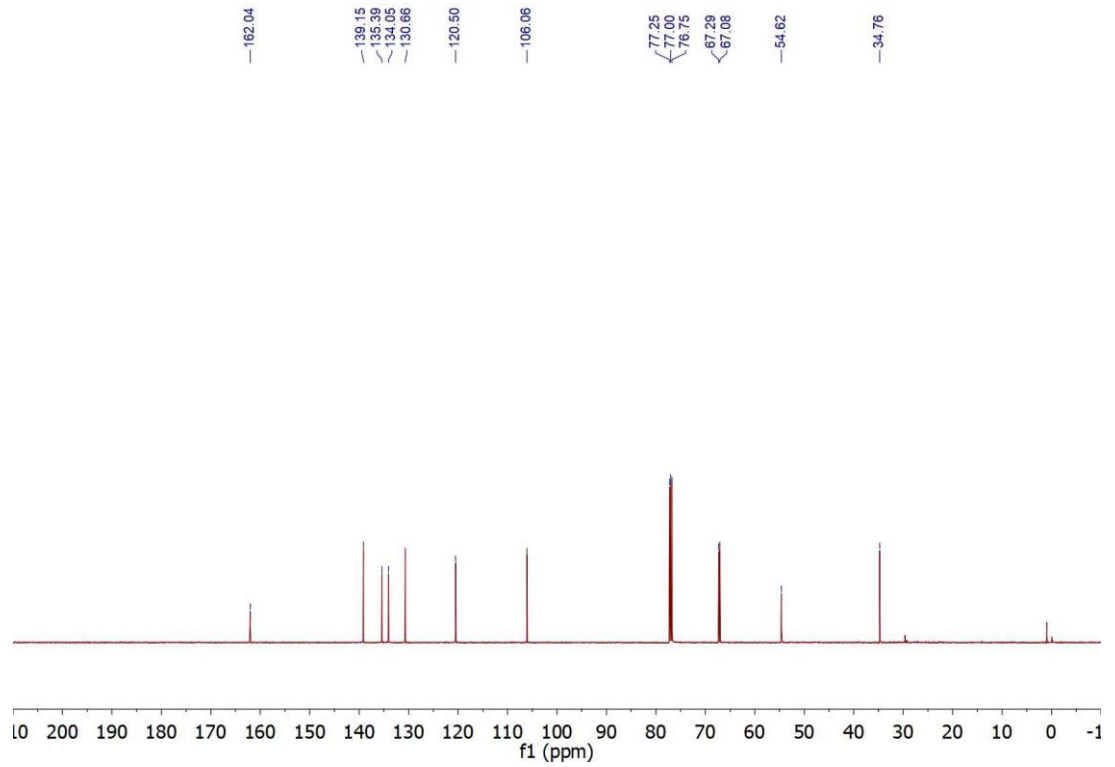
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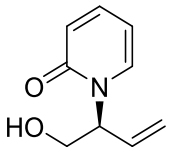
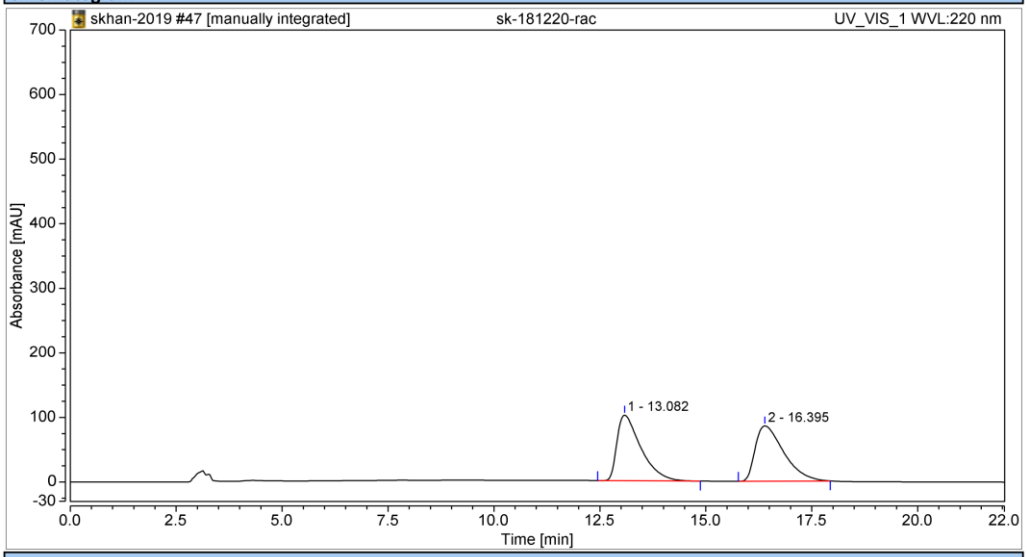


3a

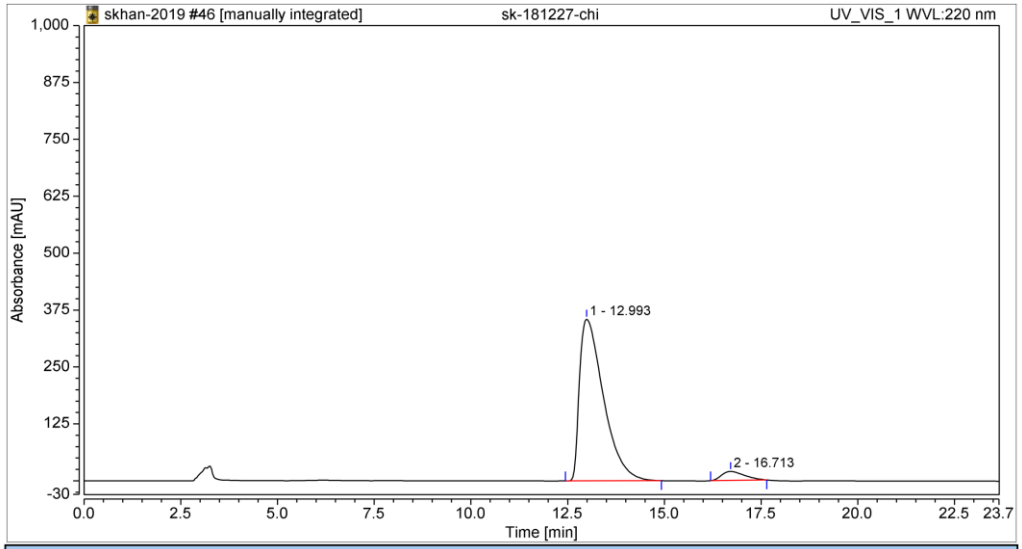
Chromatogram



Integration Results

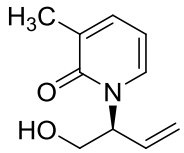
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.082	66.345	101.705	49.77	54.23	n.a.
2		16.395	66.951	85.833	50.23	45.77	n.a.
Total:			**133.295**	**187.538**	**100.00**	**100.00**	

Chromatogram



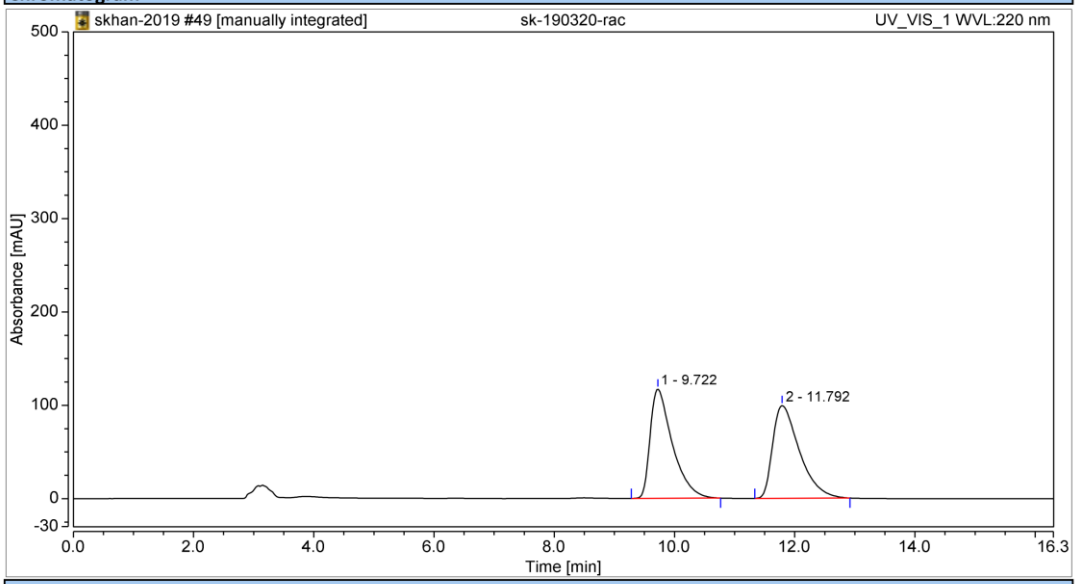
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.993	254.943	355.208	94.96	94.73	n.a.
2		16.713	13.532	19.770	5.04	5.27	n.a.
Total:			**268.475**	**374.978**	**100.00**	**100.00**	



3b

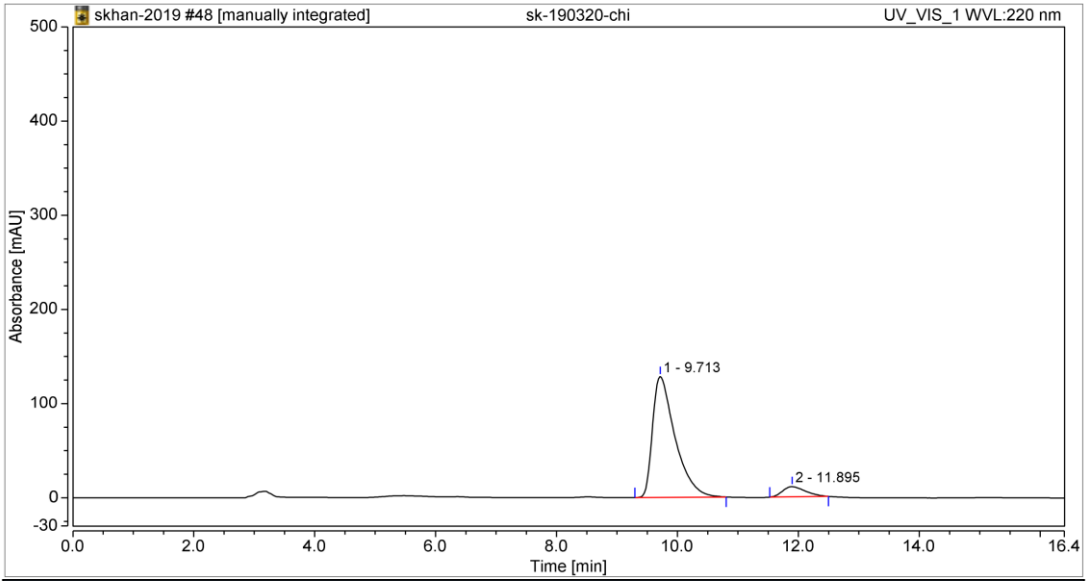
Chromatogram



Integration Results

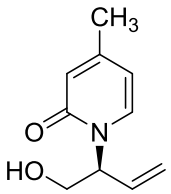
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.722	50.038	117.005	49.48	54.11	n.a.
2		11.792	51.094	99.230	50.52	45.89	n.a.
Total:			**101.132**	**216.234**	**100.00**	**100.00**	

Chromatogram



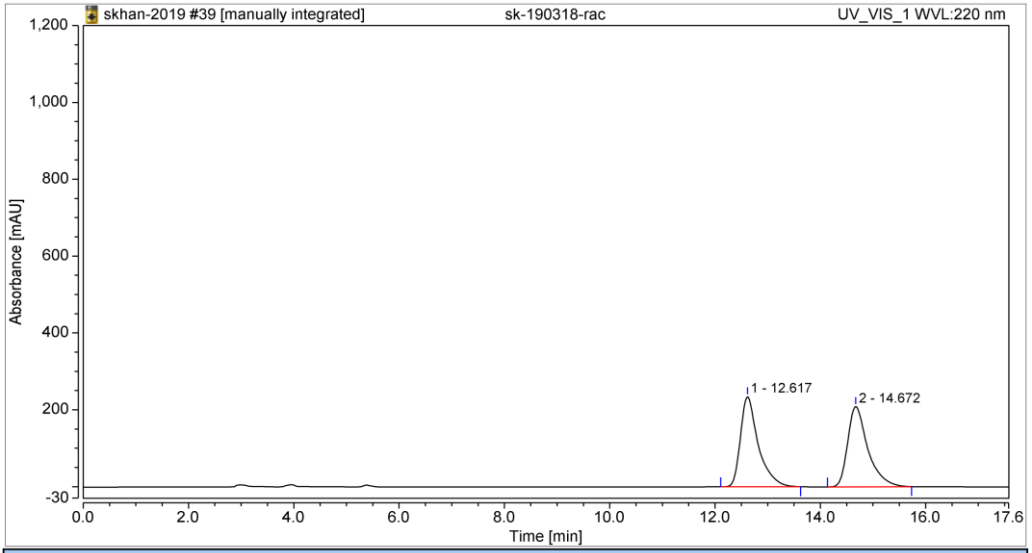
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.713	55.309	128.347	92.09	92.20	n.a.
2		11.895	4.754	10.853	7.91	7.80	n.a.
Total:			**60.063**	**139.200**	**100.00**	**100.00**	



3c

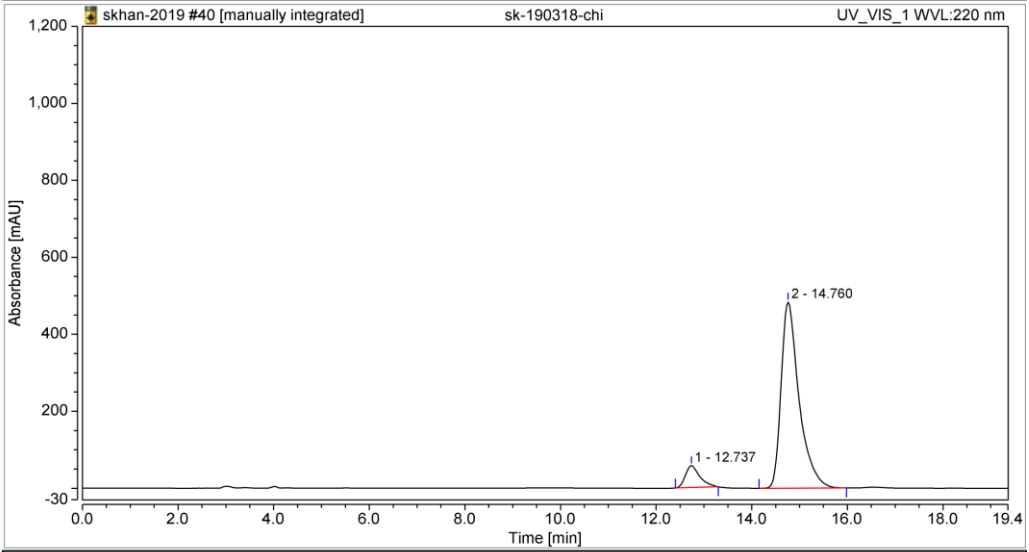
Chromatogram



Integration Results

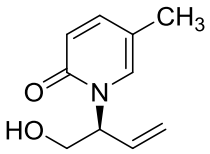
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.617	91.968	234.307	49.91	52.86	n.a.
2		14.672	92.311	208.959	50.09	47.14	n.a.
Total:			**184.279**	**443.267**	**100.00**	**100.00**	

Chromatogram



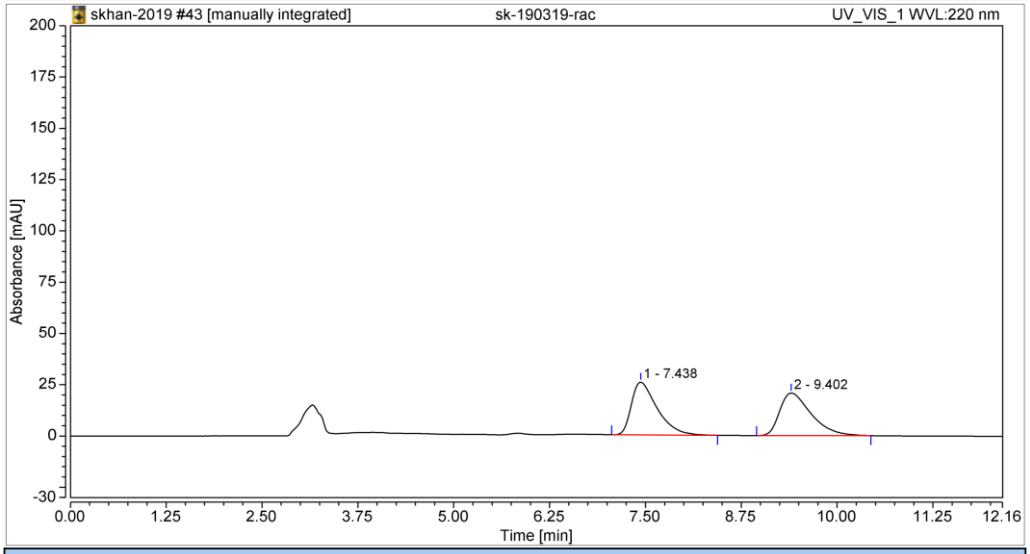
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.737	19.854	56.798	8.64	10.51	n.a.
2		14.760	209.879	483.474	91.36	89.49	n.a.
Total:			**229.733**	**540.272**	**100.00**	**100.00**	



3d

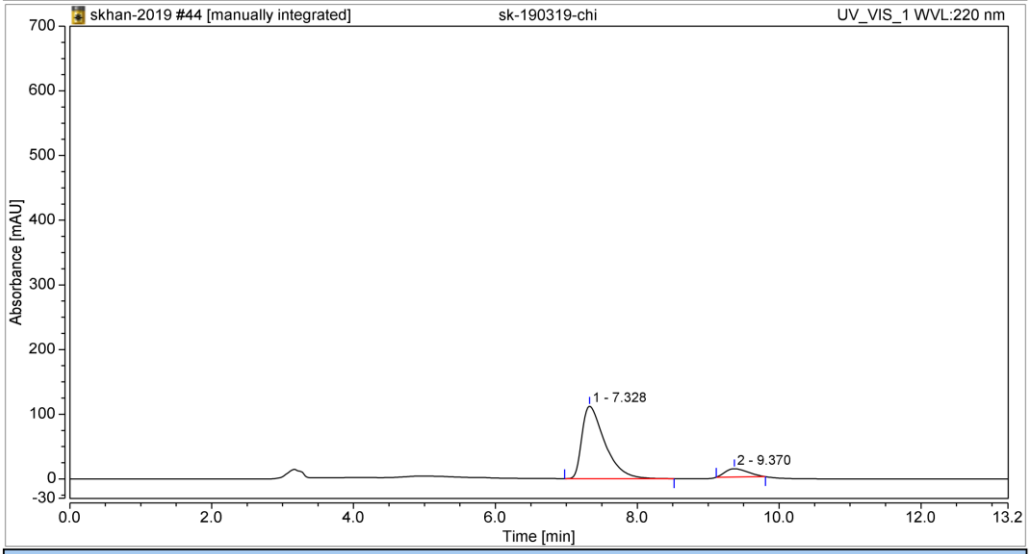
Chromatogram



Integration Results

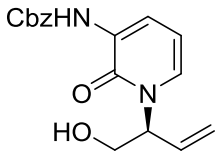
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.438	10.001	25.701	50.38	55.33	n.a.
2		9.402	9.850	20.745	49.62	44.67	n.a.
Total:			**19.851**	**46.446**	**100.00**	**100.00**	

Chromatogram



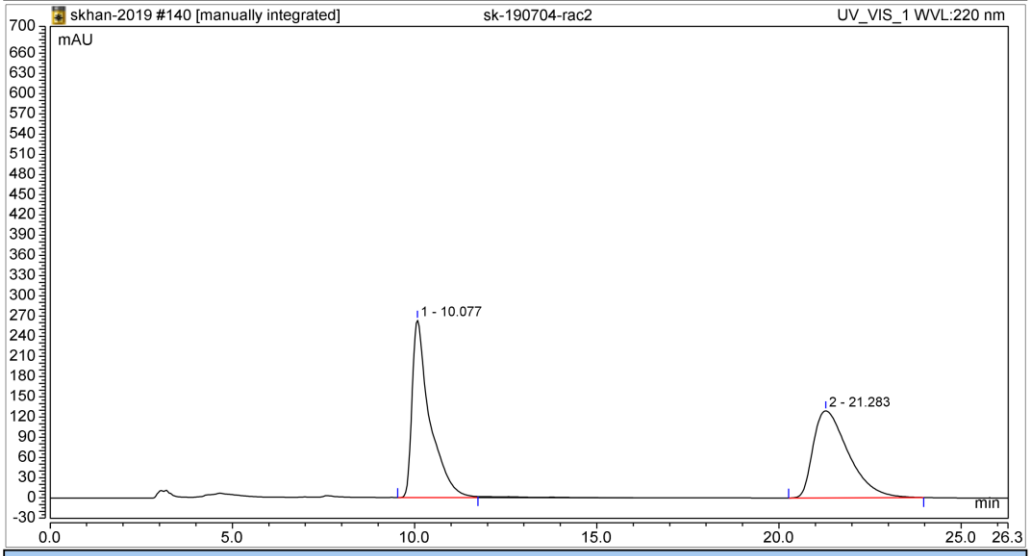
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.328	41.866	111.959	89.81	89.71	n.a.
2		9.370	4.748	12.841	10.19	10.29	n.a.
Total:			**46.614**	**124.800**	**100.00**	**100.00**	



3e

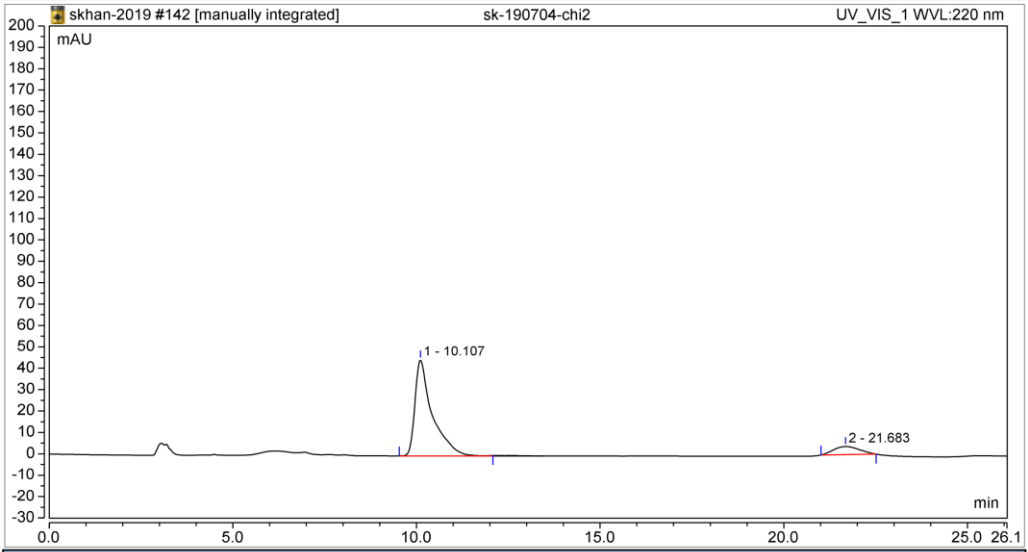
Chromatogram



Integration Results

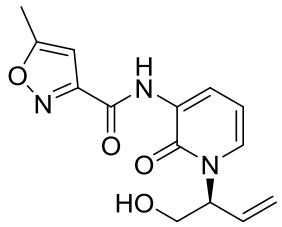
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.077	148.340	263.347	50.65	67.09	n.a.
2		21.283	144.532	129.188	49.35	32.91	n.a.
Total:			**292.873**	**392.535**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.107	24.524	44.865	88.89	92.27	n.a.
2		21.683	3.066	3.757	11.11	7.73	n.a.
Total:			**27.590**	**48.622**	**100.00**	**100.00**	



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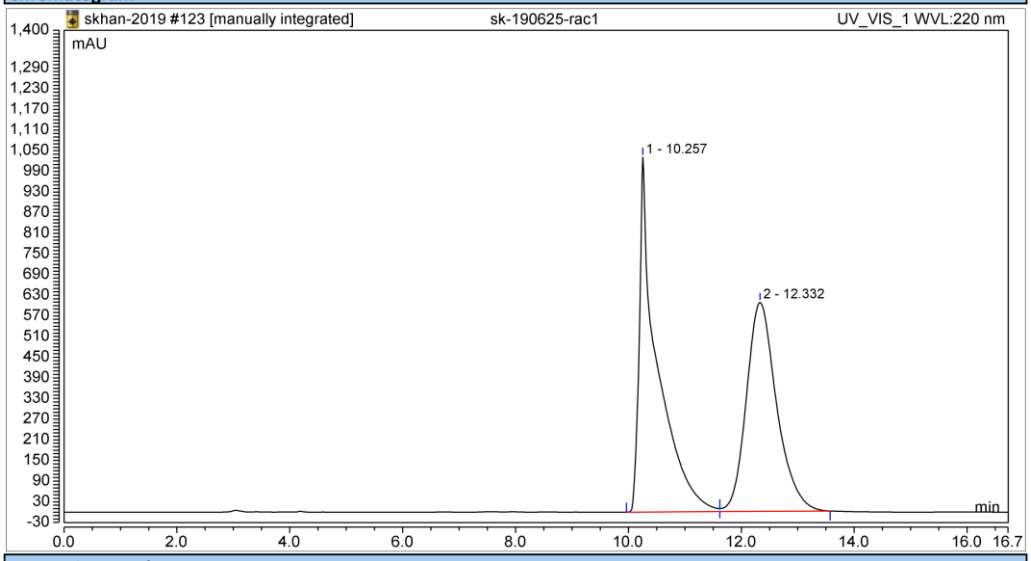
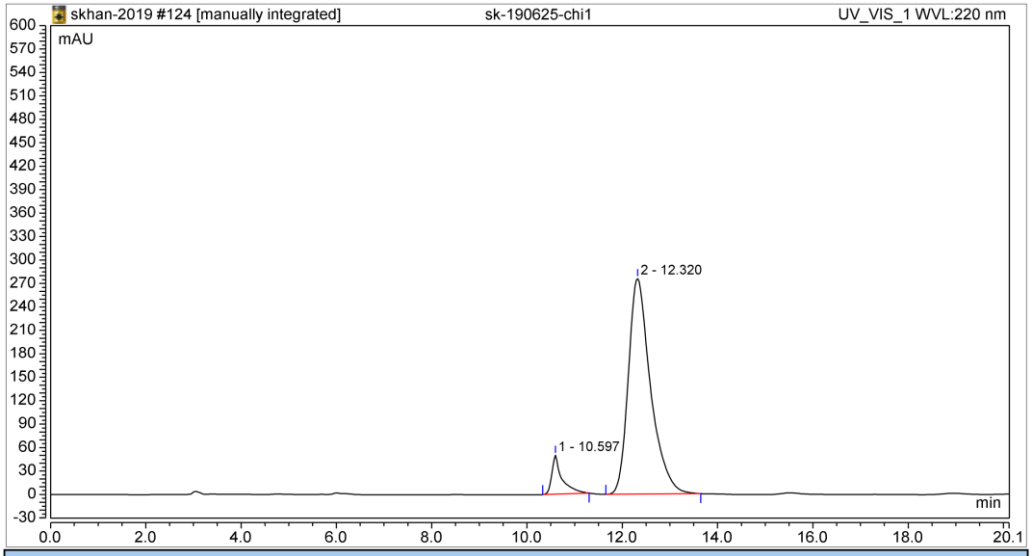
Chromatogram



Integration Results

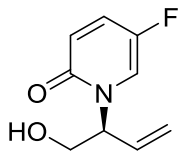
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.257	375.929	1030.649	49.92	62.93	n.a.
2		12.332	377.158	607.198	50.08	37.07	n.a.
Total:			**753.087**	**1637.847**	**100.00**	**100.00**	

Chromatogram



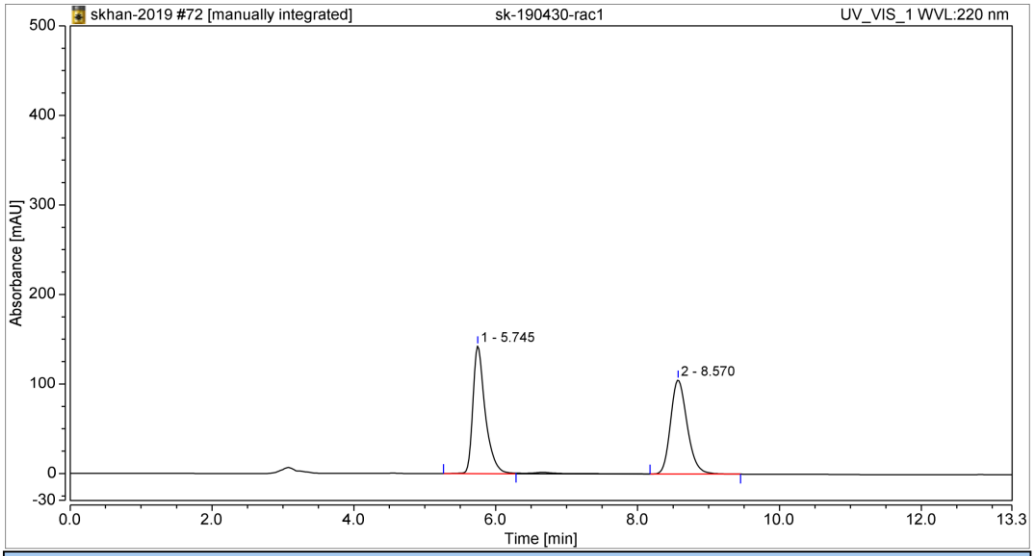
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.597	12.290	49.845	7.62	15.30	n.a.
2		12.320	149.078	275.966	92.38	84.70	n.a.
Total:			**161.367**	**325.812**	**100.00**	**100.00**	



3g

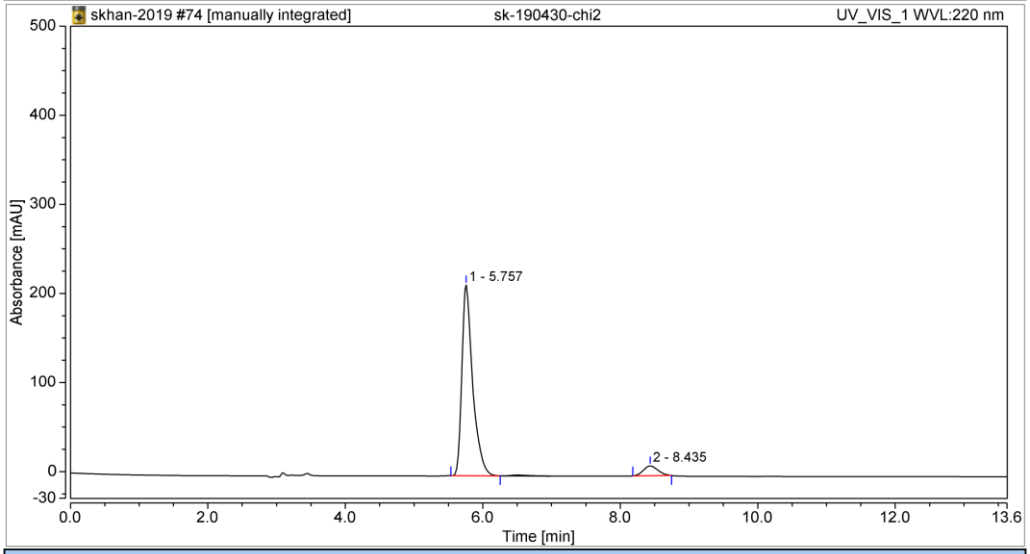
Chromatogram



Integration Results

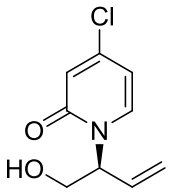
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.745	28.744	142.781	50.17	57.62	n.a.
2		8.570	28.547	104.997	49.83	42.38	n.a.
Total:			**57.291**	**247.778**	**100.00**	**100.00**	

Chromatogram



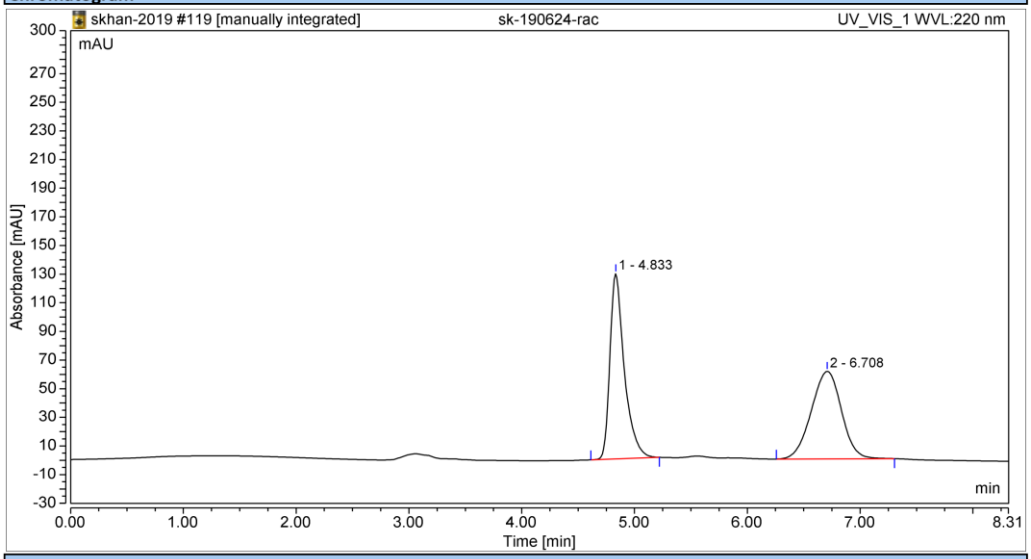
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.757	39.266	214.274	93.51	95.11	n.a.
2		8.435	2.725	11.016	6.49	4.89	n.a.
Total:			**41.991**	**225.290**	**100.00**	**100.00**	



3h

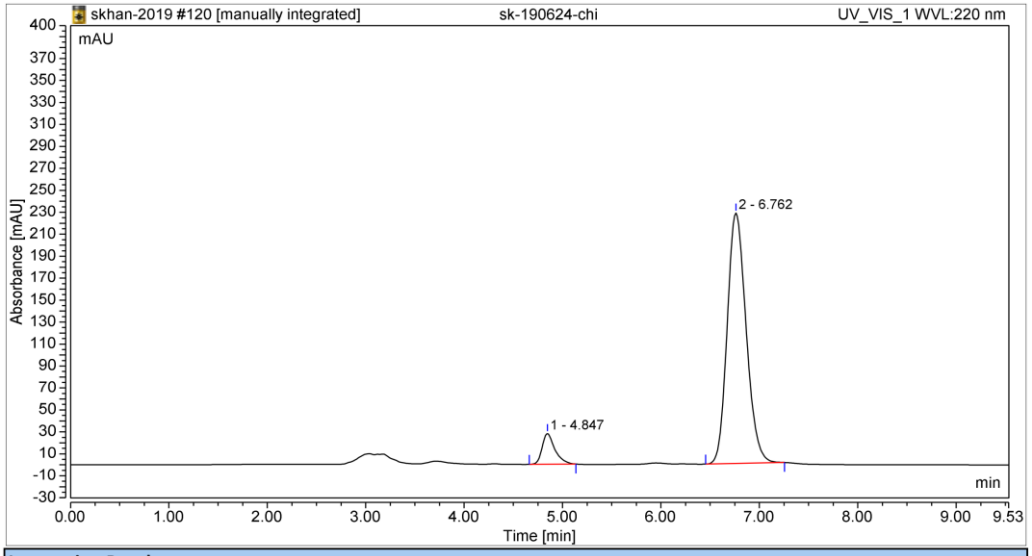
Chromatogram



Integration Results

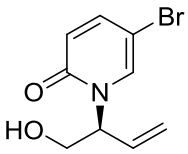
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.833	19.191	129.344	50.32	67.92	n.a.
2		6.708	18.945	61.092	49.68	32.08	n.a.
Total:			**38.136**	**190.436**	**100.00**	**100.00**	

Chromatogram



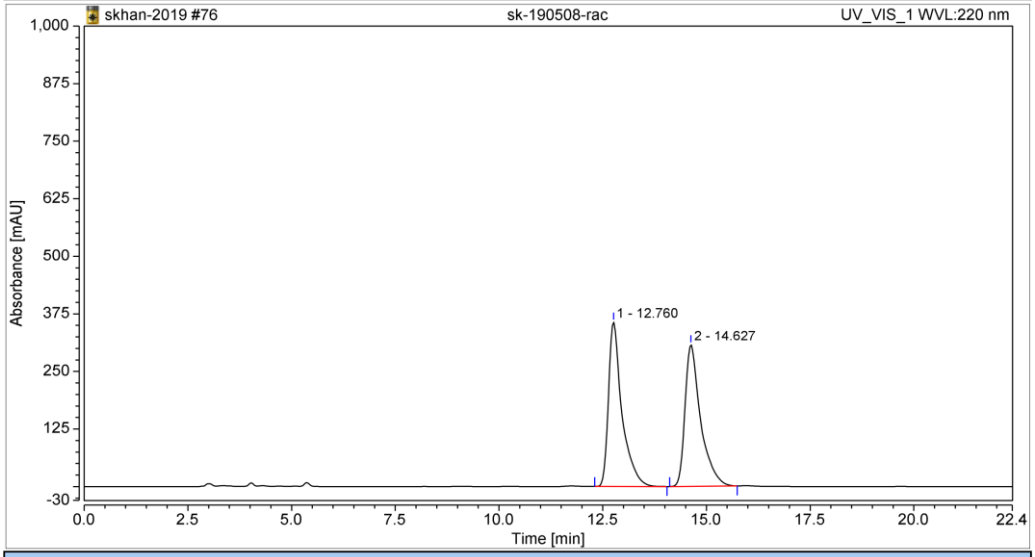
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.847	4.181	27.946	7.60	10.91	n.a.
2		6.762	50.829	228.104	92.40	89.09	n.a.
Total:			**55.009**	**256.050**	**100.00**	**100.00**	



3i

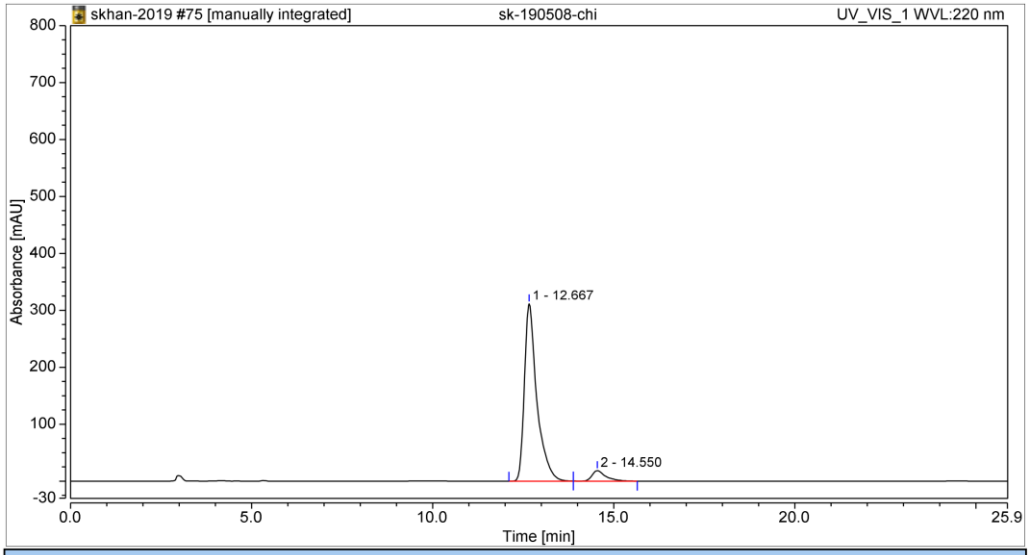
Chromatogram



Integration Results

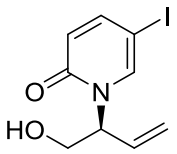
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.760	134.328	357.388	50.12	53.74	n.a.
2		14.627	133.705	307.632	49.88	46.26	n.a.
Total:			**268.033**	**665.020**	**100.00**	**100.00**	

Chromatogram



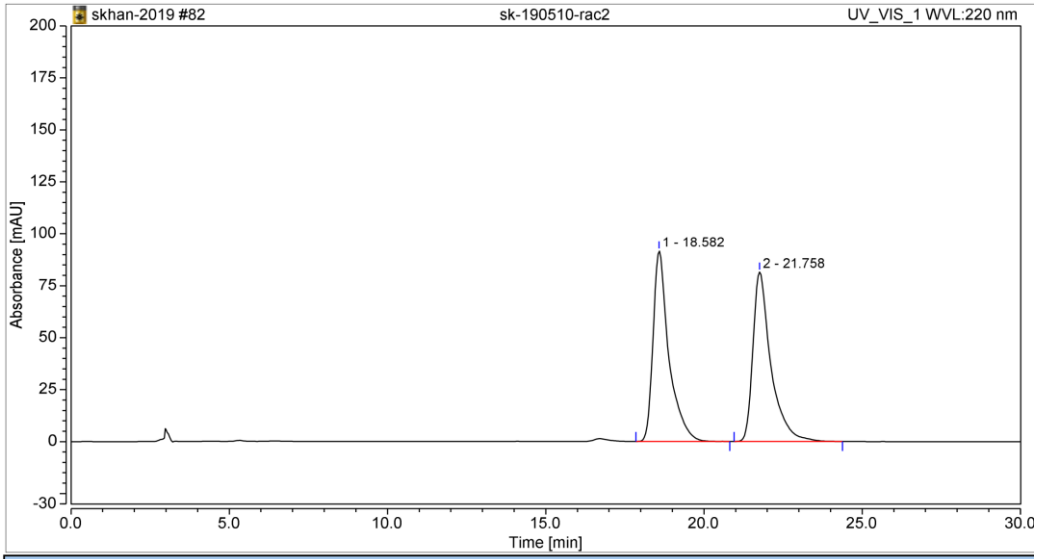
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.667	124.386	311.541	93.79	94.42	n.a.
2		14.550	8.235	18.415	6.21	5.58	n.a.
Total:			**132.620**	**329.956**	**100.00**	**100.00**	



3j

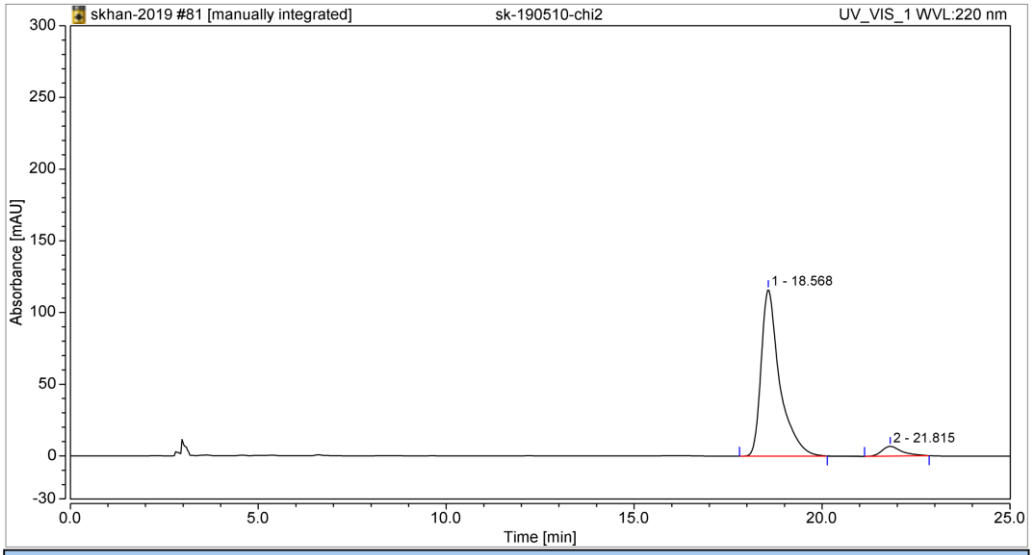
Chromatogram



Integration Results

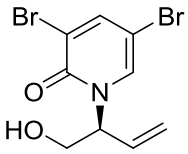
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.582	53.029	91.684	49.72	52.93	n.a.
2		21.758	53.634	81.542	50.28	47.07	n.a.
Total:			**106.662**	**173.226**	**100.00**	**100.00**	

Chromatogram



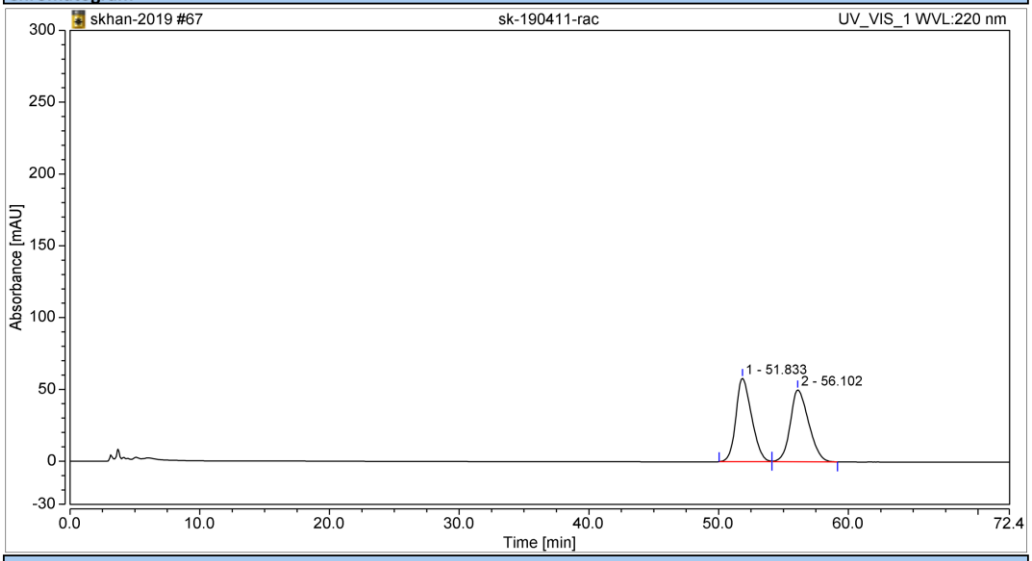
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.568	66.506	116.183	94.17	94.52	n.a.
2		21.815	4.120	6.739	5.83	5.48	n.a.
Total:			**70.626**	**122.923**	**100.00**	**100.00**	



3k

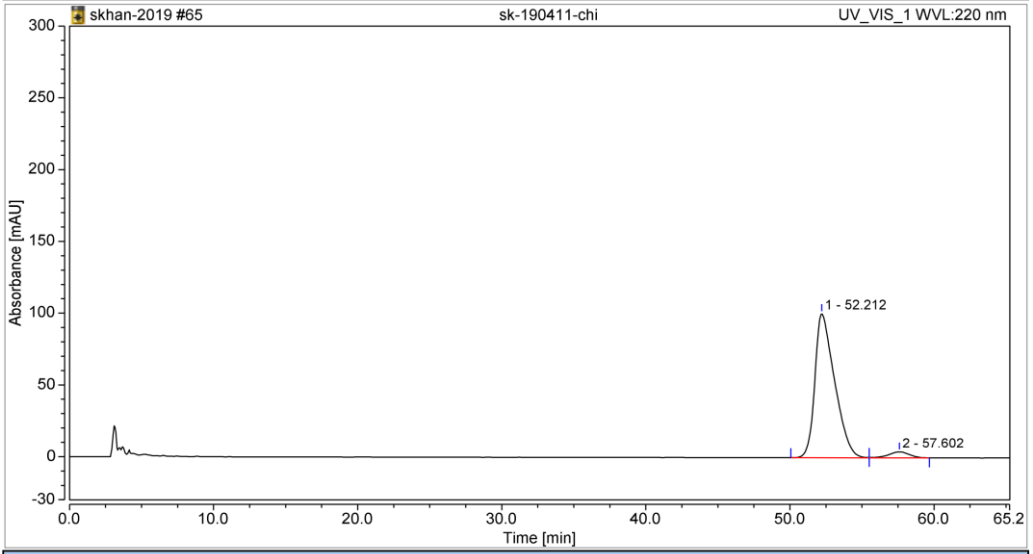
Chromatogram



Integration Results

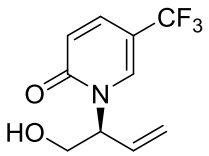
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		51.833	81.862	58.092	49.86	53.72	n.a.
2		56.102	82.315	50.052	50.14	46.28	n.a.
Total:			**164.177**	**108.144**	**100.00**	**100.00**	

Chromatogram



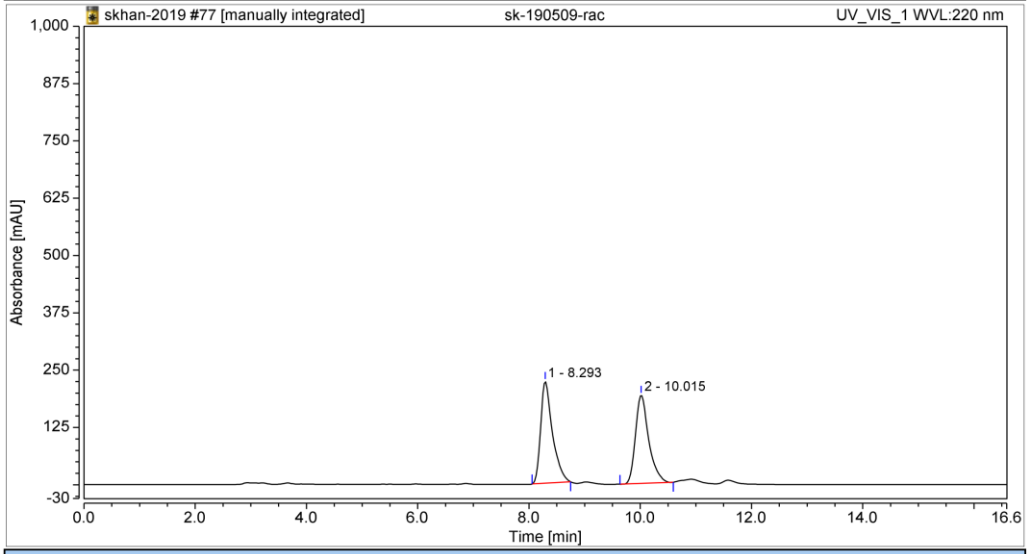
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		52.212	159.123	100.432	95.83	96.01	n.a.
2		57.602	6.922	4.175	4.17	3.99	n.a.
Total:			**166.045**	**104.608**	**100.00**	**100.00**	



3l

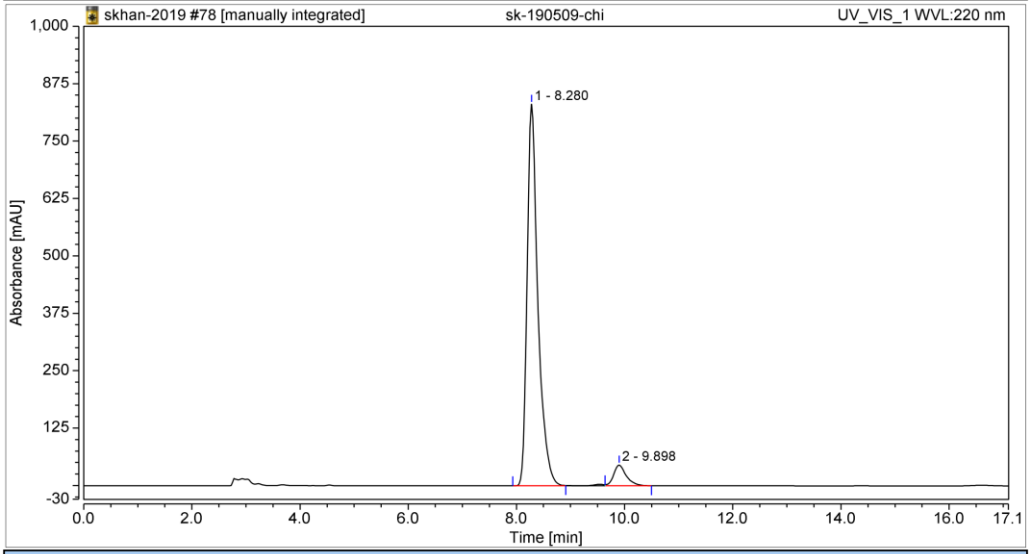
Chromatogram



Integration Results

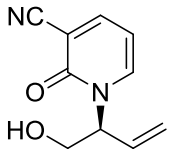
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.293	54.741	221.922	50.66	53.52	n.a.
2		10.015	53.317	192.703	49.34	46.48	n.a.
Total:			**108.058**	**414.625**	**100.00**	**100.00**	

Chromatogram



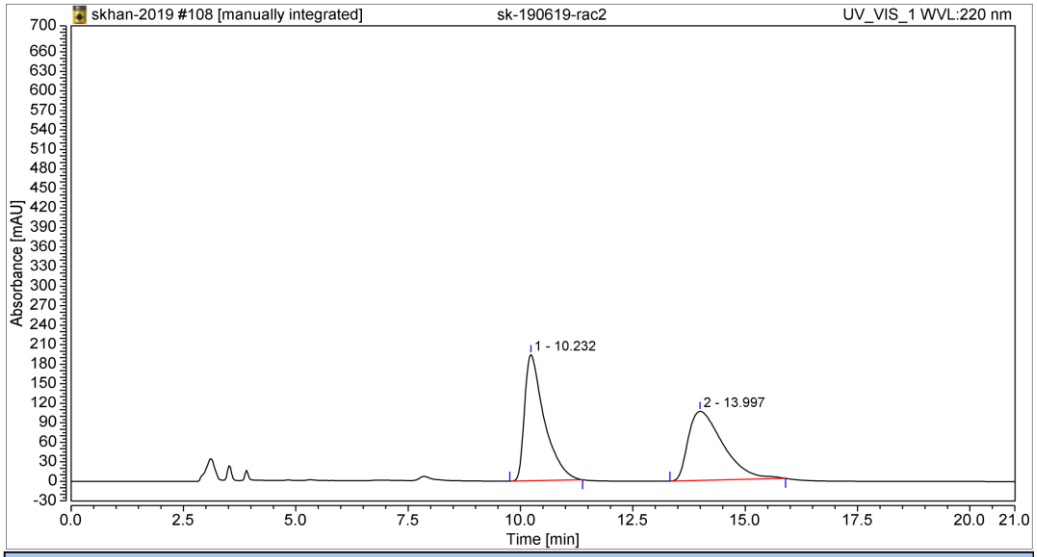
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.280	191.965	830.668	94.06	94.84	n.a.
2		9.898	12.120	45.206	5.94	5.16	n.a.
Total:			**204.085**	**875.874**	**100.00**	**100.00**	



3m

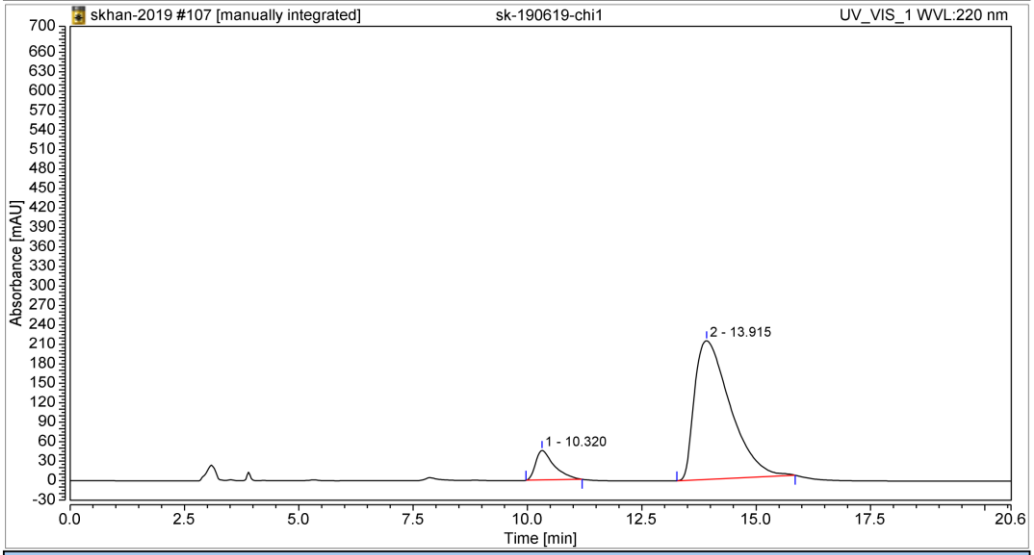
Chromatogram



Integration Results

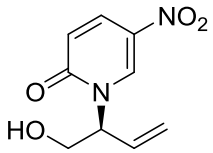
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.232	98.518	193.620	50.84	64.59	n.a.
2		13.997	95.263	106.135	49.16	35.41	n.a.
Total:			**193.781**	**299.755**	**100.00**	**100.00**	

Chromatogram



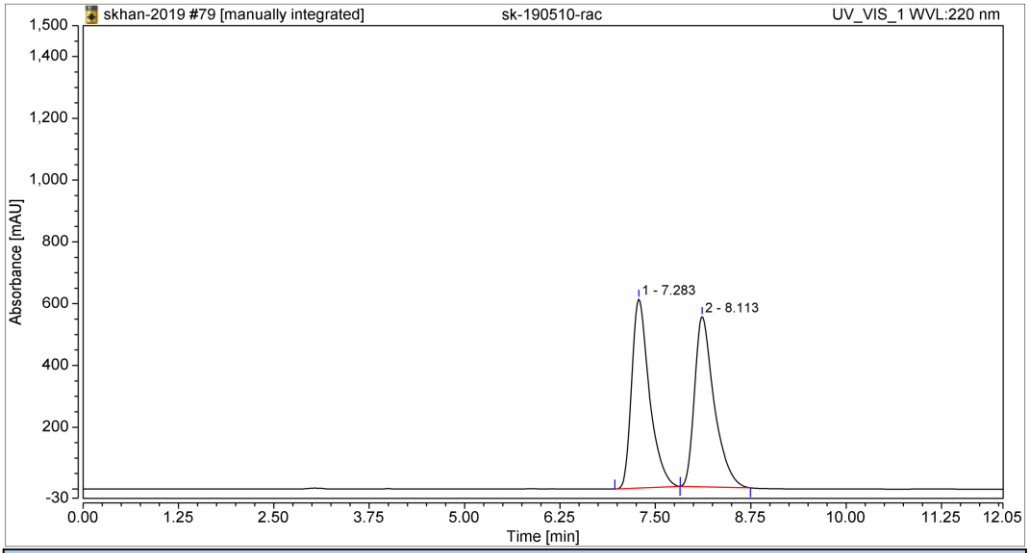
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.320	21.409	45.583	9.94	17.58	n.a.
2		13.915	193.936	213.735	90.06	82.42	n.a.
Total:			**215.345**	**259.318**	**100.00**	**100.00**	



3n

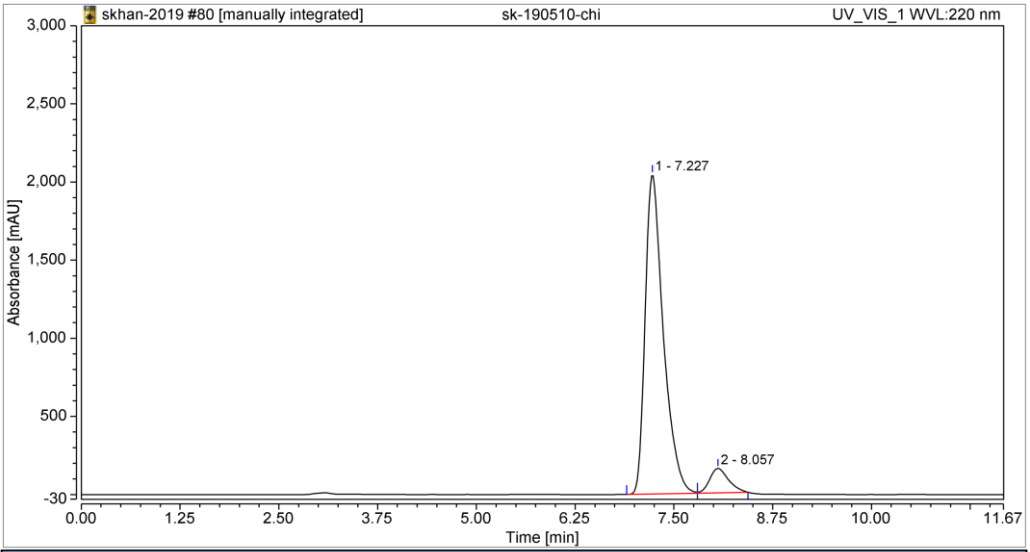
Chromatogram



Integration Results

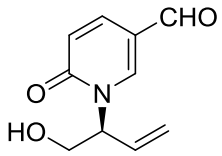
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.283	164.526	611.777	50.02	52.59	n.a.
2		8.113	164.413	551.497	49.98	47.41	n.a.
Total:			**328.939**	**1163.274**	**100.00**	**100.00**	

Chromatogram



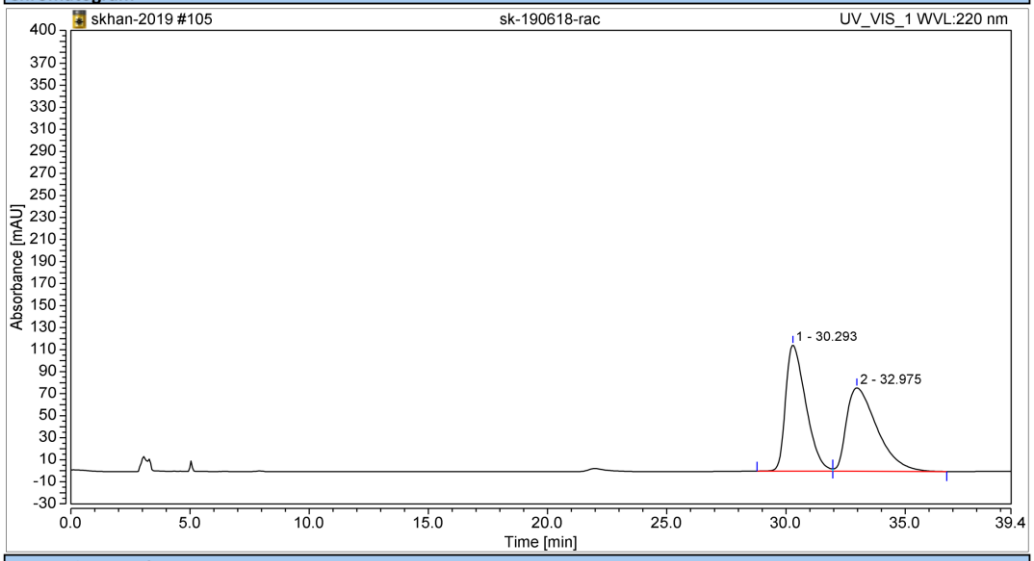
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.227	545.474	2044.071	92.68	92.91	n.a.
2		8.057	43.095	156.051	7.32	7.09	n.a.
Total:			**588.569**	**2200.122**	**100.00**	**100.00**	



3o

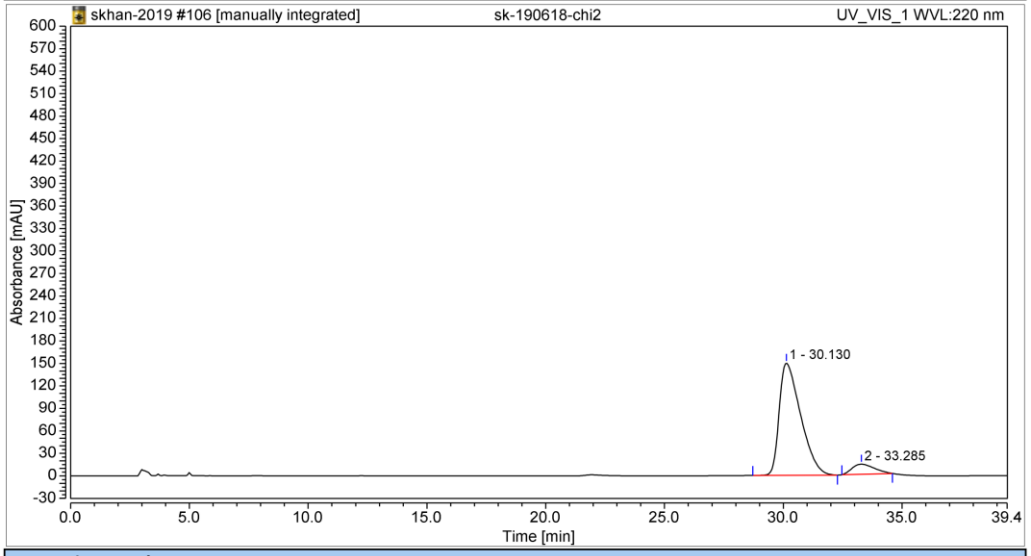
Chromatogram



Integration Results

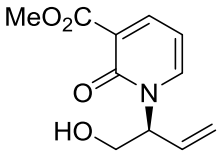
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.293	112.513	114.421	49.90	60.17	n.a.
2		32.975	112.947	75.757	50.10	39.83	n.a.
Total:			**225.459**	**190.178**	**100.00**	**100.00**	

Chromatogram



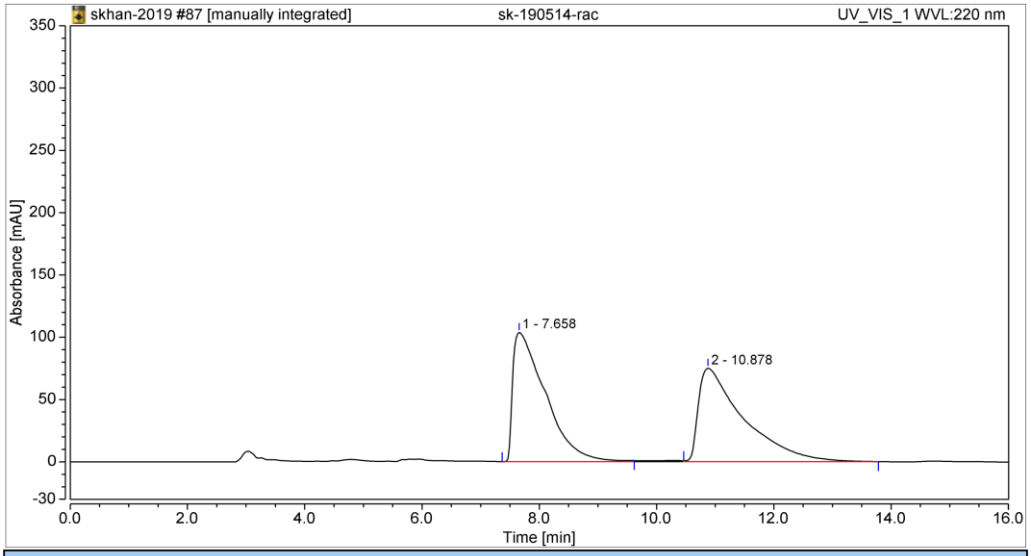
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.130	156.139	149.636	91.51	91.81	n.a.
2		33.285	14.493	13.341	8.49	8.19	n.a.
Total:			**170.632**	**162.977**	**100.00**	**100.00**	



3p

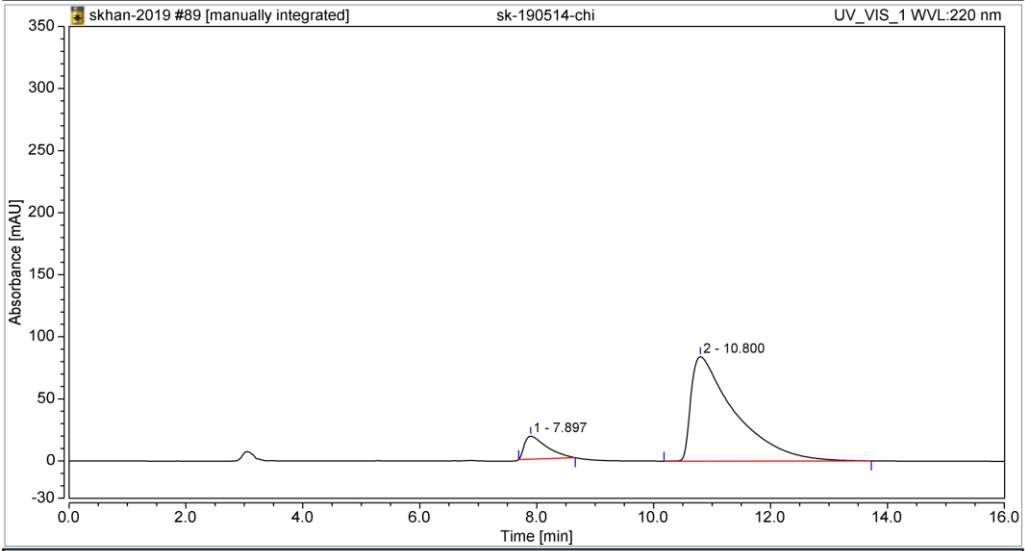
Chromatogram



Integration Results

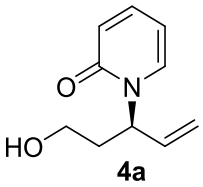
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.658	66.637	103.552	50.09	58.05	n.a.
2		10.878	66.398	74.819	49.91	41.95	n.a.
Total:			**133.035**	**178.372**	**100.00**	**100.00**	

Chromatogram



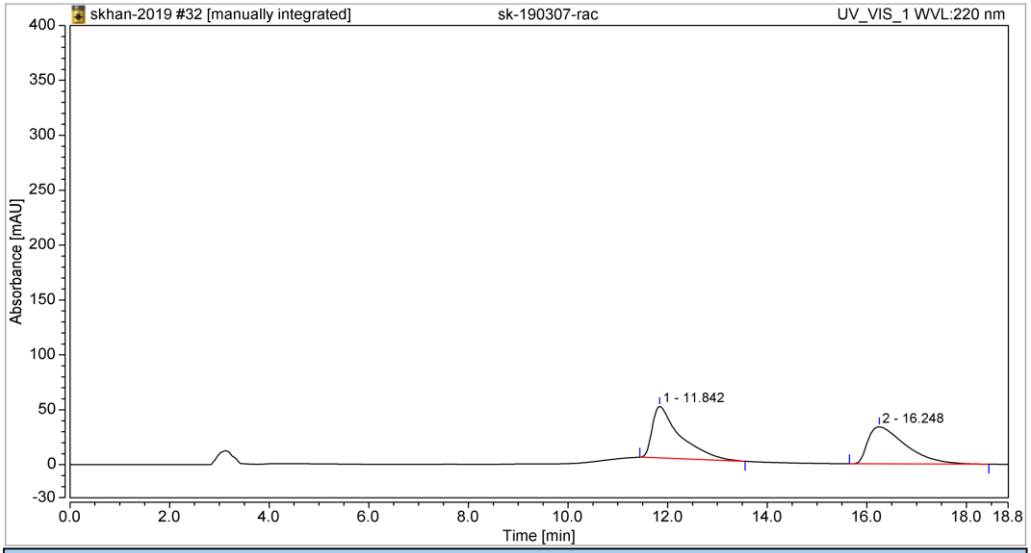
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.897	8.122	18.485	10.04	18.03	n.a.
2		10.800	72.801	84.026	89.96	81.97	n.a.
Total:			**80.922**	**102.511**	**100.00**	**100.00**	



4a

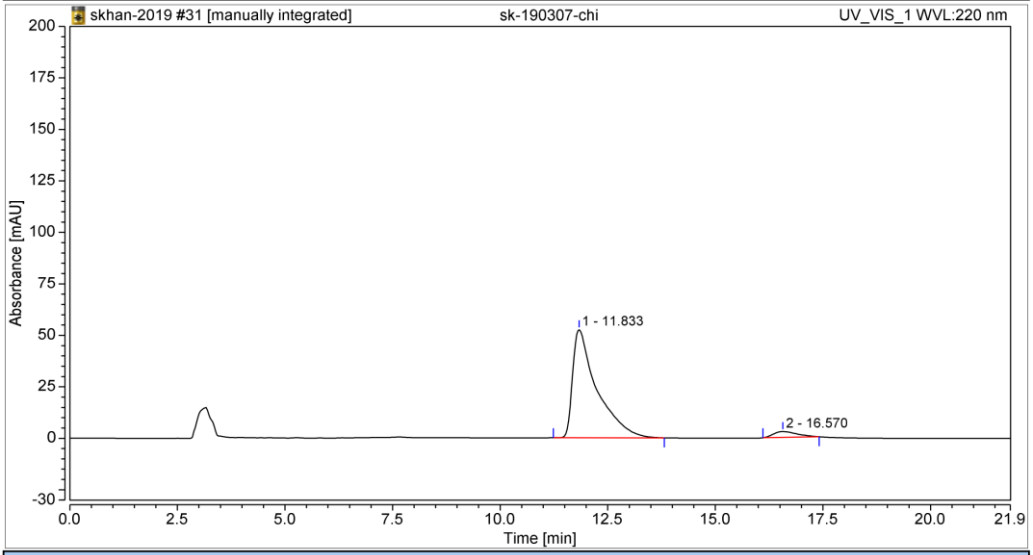
Chromatogram



Integration Results

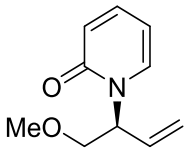
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.842	30.239	46.870	50.53	58.17	n.a.
2		16.248	29.607	33.703	49.47	41.83	n.a.
Total:			**59.847**	**80.573**	**100.00**	**100.00**	

Chromatogram



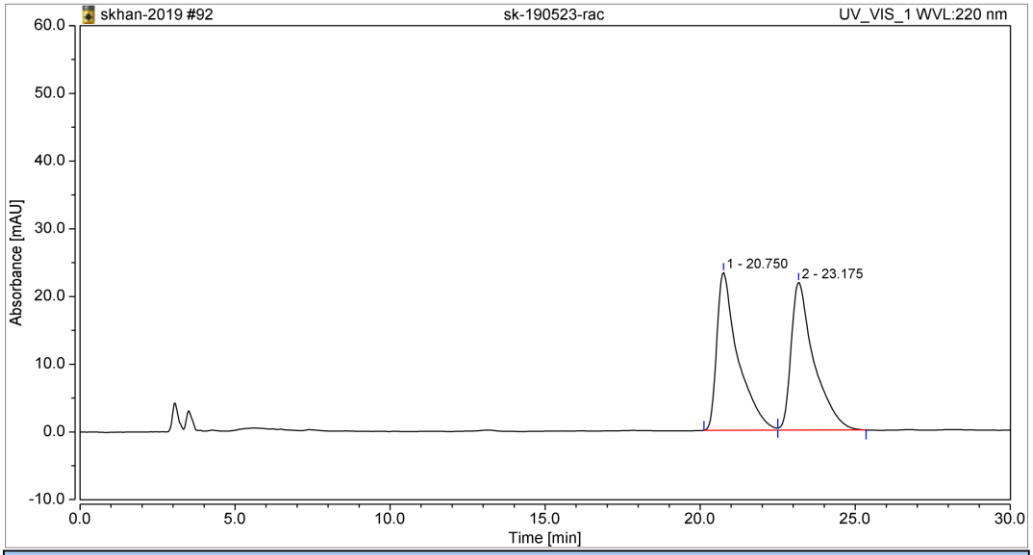
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.833	34.231	52.488	94.98	94.88	n.a.
2		16.570	1.809	2.831	5.02	5.12	n.a.
Total:			**36.040**	**55.319**	**100.00**	**100.00**	



4c

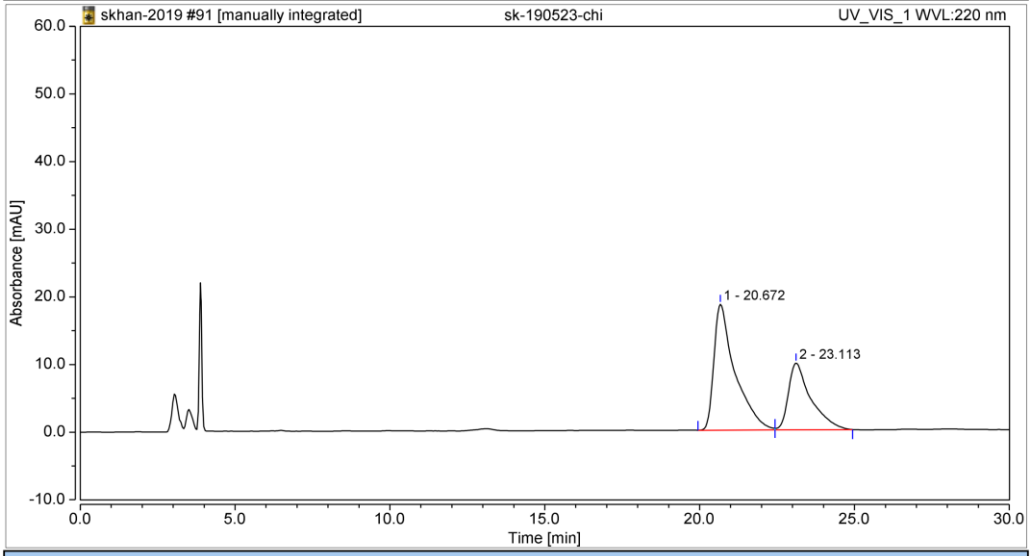
Chromatogram



Integration Results

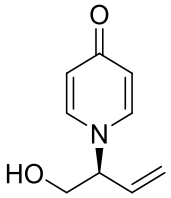
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.750	18.449	23.328	49.80	51.65	n.a.
2		23.175	18.597	21.840	50.20	48.35	n.a.
Total:			**37.047**	**45.168**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.672	14.678	18.628	63.94	65.35	n.a.
2		23.113	8.276	9.878	36.06	34.65	n.a.
Total:			**22.954**	**28.506**	**100.00**	**100.00**	



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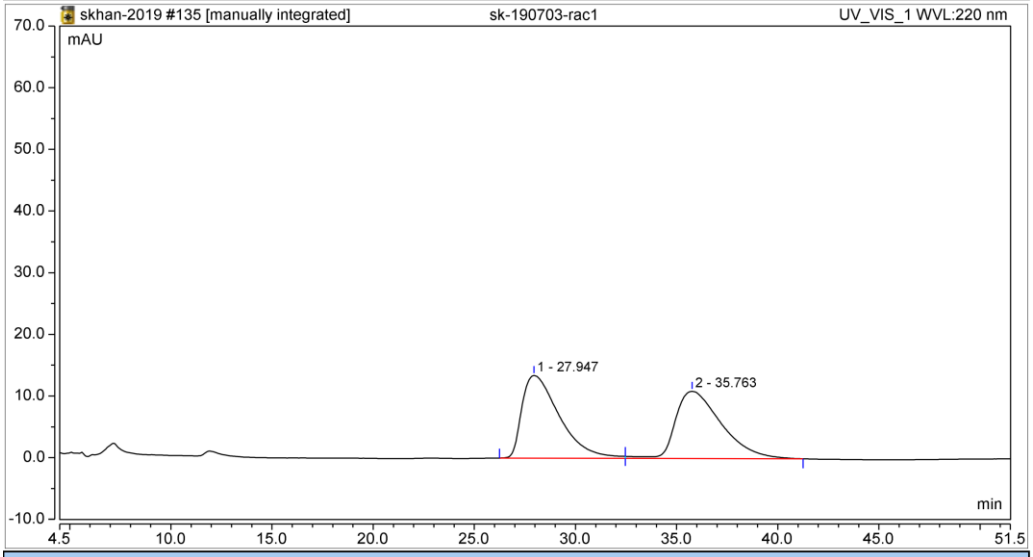
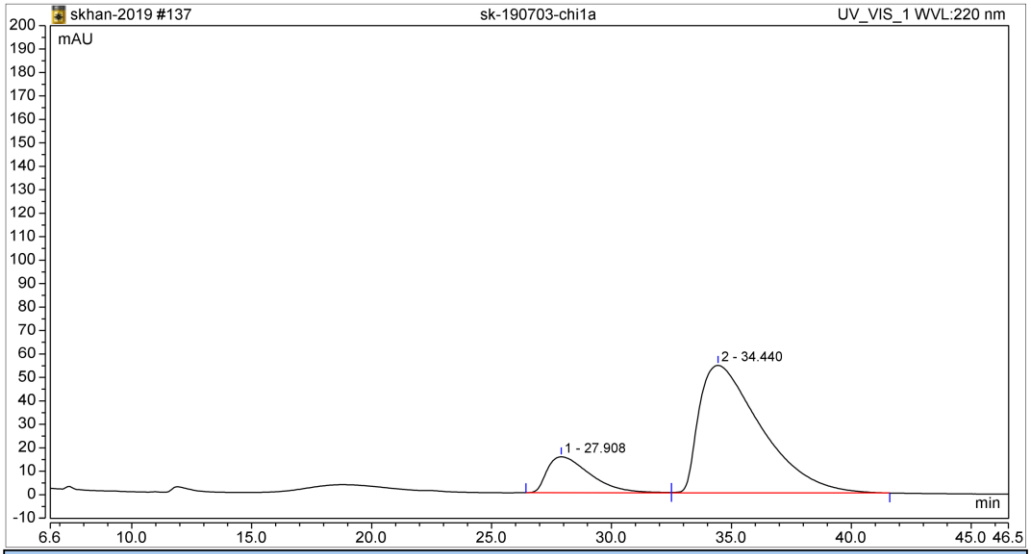
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.947	28.776	13.401	50.12	55.14	n.a.
2		35.763	28.643	10.902	49.88	44.86	n.a.
Total:			**57.419**	**24.303**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.908	31.764	15.307	16.30	21.98	n.a.
2		34.440	163.084	54.350	83.70	78.02	n.a.
Total:			**194.848**	**69.657**	**100.00**	**100.00**	