Supporting Information

Modular Assembling of Chiral Multisubstituted Tetrahydropyrans through the Cascade Asymmetric Aldehyde Allylboration/oxa-Cyclization by a Chiral Phosphoric Acid

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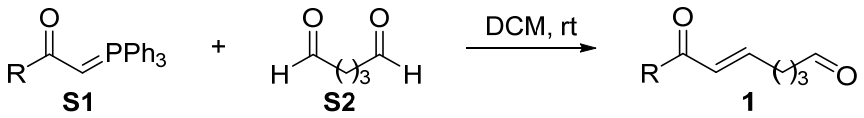
Content

General methods

All purchased chemicals from commercial suppliers were used without further purification. Anhydrous tetrahydrofuran, diethyl ether and toluene were distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2 was distilled from CaH_2 under an atmosphere of nitrogen. Unless indicated otherwise, all reactions were conducted under an atmosphere of nitrogen using oven-dried (110 °C) glassware. Chiral phosphoric acid catalyst was prepared from chiral BINOL according to the known literature procedure[1]. All reactions were monitored by TLC. TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the S2 stationary phase. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.2 ppm). ^{19}F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. High resolution MS (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer.

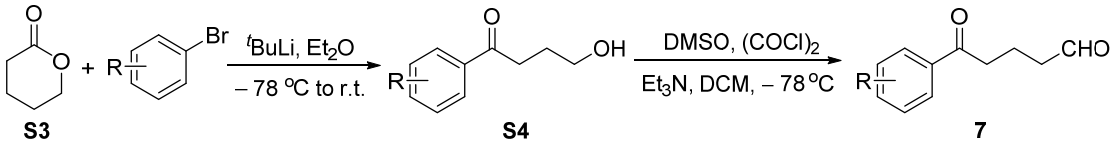
Synthesis of aldehydes 1 and 7

General procedure for the synthesis of aldehydes 1[2]:



Phosphorus ylides **S1** were firstly synthesized according to the literature method.[3] Then, to the solution of compound **S2** (1.0 equiv., 2.0 mmol) in DCM (15.0 mL), the commercially purchased glutaraldehyde (25% aqueous solution, 3.0 equiv., 6.0 mmol) was added dropwise at room temperature. After stirring at room temperature for 48 h, H_2O (30 mL) was added and the reaction mixture was extracted with DCM (3 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and the solvent was removed by evaporation. The stuff was purified by silica gel chromatography to afford the pure product **1**. The analytical data were in agreement with those reported in literature.

General procedure for the synthesis of 5-oxo-5-phenylpentanal 7[4]

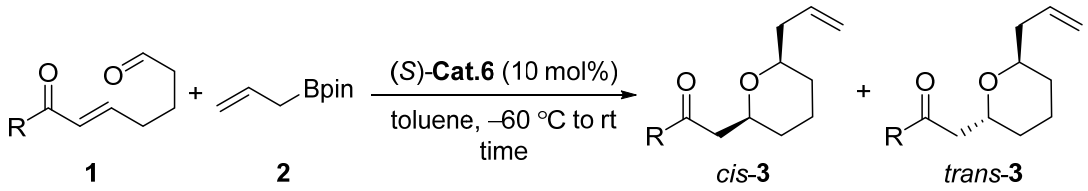


To a stirred solution of aryl bromide (10.0 mmol) in 30 mL of anhydrous Et_2O was added 7.5 mL of ^{t}BuLi (1.6 M in pentane, 12.0 mmol) at –78 °C over 45 min. The obtained reaction mixture was stirred at the same temperature for 30 min, and then a solution of δ-valerolactone **S3** (10.0 mmol) in 10 mL of anhydrous Et_2O was added. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for another 2 h. The reaction mixture was quenched with 15 mL of brine, extracted with EtOAc (100 mL × 3), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by a column chromatography on silica gel with EtOAc/petroleum ether as eluent to offer the δ-hydroxy aryl ketone **S4**.

To a stirred solution of DMSO (30.0 mmol, 6.0 equiv) in CH_2Cl_2 (25.0 mL) at −78 °C under N_2 atmosphere was added oxalyl chloride (20.0 mmol, 4.0 equiv). After stirring at −78 °C for 10 min, a solution of **S4** (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added. The reaction mixture was stirred for 30 min at the same temperature. After that a solution of triethylamine (20.0 mmol, 4.0 equiv) in 20.0 mL of anhydrous CH_2Cl_2 was added slowly over a period of 30 min. After stirring at − 78 °C for 1h, the reaction mixture was allowed to warm to room temperature slowly and stirred for another 2 h. $NaHCO_3$ (aq) was added, and extracted with CH_2Cl_2 twice (20 mL × 2). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The yellowish oil product **7** was obtained by the column chromatography on silica gel using ethyl acetate/petroleum ether = 1/10 to 1/5 as eluent.

Synthesis and characterization data of products 3

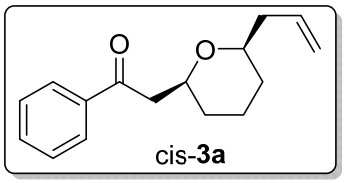
General procedure for the asymmetric allyboration/oxa-Michael tandem reaction of 1 and 2:



To an oven dried 5 mL test tube with a stir bar was added aldehyde **1** (0.1 mmol) and catalyst (10 mol%). At nitrogen atmosphere, anhydrous toluene (0.4 mL) was added at rt. The reaction mixture was then cooled to –60 °C followed by the addition of a solution of allylboronate pinacol ester **2** (0.12 mmol) in 0.1 mL toluene over 10 minutes. The mixture was kept stirring at –60 °C until aldehyde **1** was disappeared. Then the mixture was allowed to warm to rt and kept stirring for 24 h. The mixture was directly purified by PTLC to afford the desired products **3**.

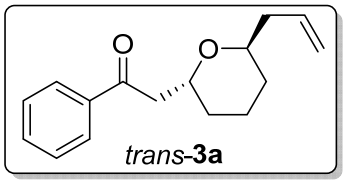
Analytical data of products *cis*-3

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-phenylethan-1-one (*cis*-3a)



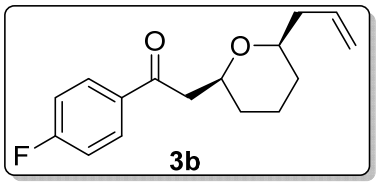
According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 79% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **cis-3a** as colorless oil (R_f = 0.65); **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, t_{major} = 10.94 min, t_{minor} = 12.67 min), *ee* = 90%. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.98–7.95 (m, 2H), 7.56–7.52 (m, 1H), 7.46–7.43 (m, 2H), 5.79–5.70 (m, 1H), 5.03–4.95 (m, 2H), 3.98–3.93 (m, 1H), 3.40–3.35 (m, 1H), 3.30 (dd, J^1 = 15.8, J^2 = 6.4 Hz, 1H), 2.93 (dd, J^1 = 15.8, J^2 = 6.2 Hz, 1H), 2.27–2.22 (m, 1H), 2.13–2.10 (m, 1H), 1.85–1.81 (m, 1H), 1.75–1.72 (m, 1H), 1.59–1.52 (m, 2H), 1.31–1.27 (m, 1H), 1.23–1.15 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 198.9, 137.6, 135.1, 133.0, 128.6, 128.4, 116.5, 77.7, 74.7, 45.7, 41.0, 31.8, 31.0, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{20}O_2Na$ ($[M+Na]^+$): 267.1361; found: 267.1356.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-phenylethan-1-one (*trans*-3a)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 11% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **trans-3a** as colorless oil (R_f = 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 28.55 min, t_{minor} = 24.27 min), *ee* = 99%. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.96–7.94 (m, 2H), 7.57–7.54 (m, 1H), 7.47–7.44 (m, 2H), 5.79–5.71 (m, 1H), 5.06–4.98 (m, 2H), 4.42–4.38 (m, 1H), 3.85–3.80 (m, 1H), 3.30 (dd, J^1 = 15.6, J^2 = 6.4 Hz, 1H), 3.01 (dd, J^1 = 15.6 J^2 = 6.8 Hz, 1H), 2.46–2.40 (m, 1H), 2.23–2.18 (m, 1H), 1.80–1.76 (m, 1H), 1.74–1.63 (m, 3H), 1.45–1.38 (m, 2H) ppm.

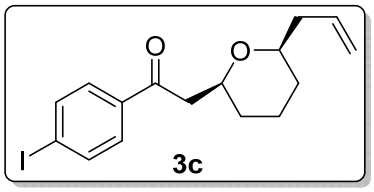
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(4-fluorophenyl)ethan-1-one (3b)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 92% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3b** as colorless oil (R_f (*major*)= 0.60). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 16.61 min, t_{minor} = 19.36 min), *ee* = 89%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.94–3.89, 3.39–3.34 ppm; trans:4.40–4.30, 3.85–3.75 ppm);

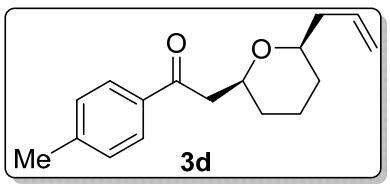
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H), 7.13–7.08 (m, 2H), 5.76–5.68 (m, 1H), 5.01–4.93 (m, 2H), 3.94–3.89 (m, 1H), 3.39–3.34 (m, 1H), 3.27 (dd, J^1 = 15.5, J^2 = 6.7 Hz, 1H), 2.87 (dd, J^1 = 15.5, J^2 = 5.8 Hz, 1H), 2.25–2.20 (m, 1H), 2.13–2.08 (m, 1H), 1.85–1.81 (m, 1H), 1.73–1.70 (m, 1H), 1.60–1.50 (m, 2H), 1.31–1.14 (m, 2H) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): δ −105.7 (m, 1F) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 197.5, 165.8 (d, J = 254.9) , 135.1, 134.1 (d, J = 2.9), 131.2, 131.1, 116.5, 115.7, 115.5, 77.7, 74.8, 45.6, 41.0, 31.8, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{20}O_2FNa$ ([M+Na]$^+$): 285.1266; found: 285.1261.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(4-iodophenyl)ethan-1-one (3c)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 93% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3c** as colorless oil (R_f (*major*)= 0.60). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 22.65 min, t_{minor} = 31.18 min), *ee* = 90%. *dr* = 9:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.93–3.88, 3.38–3.33 ppm; trans:4.42–4.35, 3.85–3.80 ppm); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.80 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 5.76–5.67 (m, 1H), 5.01–4.94 (m, 2H), 3.93–3.88 (m, 1H), 3.38–3.33 (m, 1H), 3.24 (dd, J^1 = 15.6, J^2 = 6.7 Hz, 1H), 2.85 (dd, J^1 = 15.6, J^2 = 5.8 Hz, 1H), 2.25–2.19 (m, 1H), 2.13–2.07 (m, 1H), 1.86–1.81 (m, 1H), 1.72–1.69 (m, 1H), 1.59–1.50 (m, 2H), 1.30–1.15 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$):** δ 198.3, 137.9, 136.9, 135.0, 129.9, 116.5, 101.0, 77.7, 74.7, 45.6, 41.0, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{19}O_2INa$ ([M+Na]$^+$): 393.0327; found: 393.0322.

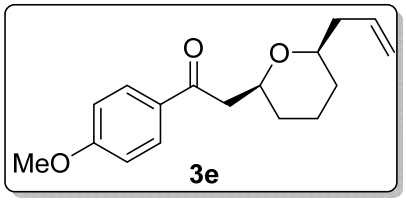
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(p-tolyl)ethan-1-one (3d)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 67% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3d** as colorless oil (R_f (*major*)= 0.65). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.60). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 16.99 min, t_{minor} = 21.88 min), *ee* = 88%. *dr* = 14:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy(cis: 3.96–3.91, 3.39–3.34 ppm; trans:4.40–4.27, 3.80–3.75 ppm); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.86 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 5.79–5.71 (m, 1H), 5.03–4.95 (m, 2H), 3.96–3.91 (m, 1H), 3.39–3.34 (m, 1H), 3.26 (dd, J^1 = 15.7, J^2 = 6.3 Hz, 1H), 2.91 (dd, J^1 = 15.7, J^2 = 6.3 Hz, 1H), 2.39 (s, 3H), 2.27–2.22 (m, 1H), 2.14–2.08 (m, 1H), 1.83–1.79 (m, 1H), 1.74–1.71 (m, 1H), 1.60–1.50 (m, 2H), 1.29–1.15 (m, 2H) ppm; **^{13}C NMR (126 MHz,**

$CDCl_3$): δ 198.4, 143.8, 135.12, 135.11, 129.2, 128.5, 116.4, 77.6, 74.7, 45.5, 41.0, 31.7, 30.9, 23.5, 21.7 ppm; **HRMS (ESI) m/z:** calcd for $C_{17}H_{22}O_2Na$ ($[M+Na]^+$): 281.1517; found: 285.1512.

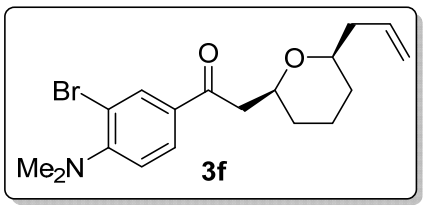
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(4-methoxyphenyl)ethan-1-one (3e)



3e

According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 76%. A purification by column chromatography in PE:EA = 10:1 v/v to give **3e** as colorless oil (R_f (*major*)= 0.55). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.50). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 31.71 min, t_{minor} = 41.62 min), *ee* = 86%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.95–3.90 ppm; trans:4.42–4.38 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.95–7.93 (m, 2H), 6.92–6.90 (m, 2H), 5.79–5.70 (m, 1H), 5.02–4.94 (m, 2H), 3.95–3.90 (m, 1H), 3.85 (s, 3H), 3.39–3.34 (m, 1H), 3.24 (dd, J^1 = 15.6, J^2 = 6.2 Hz, 1H), 2.87 (dd, J^1 = 15.6, J^2 = 6.3 Hz, 1H), 2.27–2.22 (m, 1H), 2.13–2.08 (m, 1H), 1.83–1.78 (m, 1H), 1.73–1.70 (m, 1H), 1.60–1.49 (m, 2H), 1.28–1.14 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 197.3, 163.5, 135.1, 130.74, 130.73, 116.4, 113.7, 77.6, 74.8, 55.5, 45.3, 41.0, 31.8, 31.0, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{17}H_{22}O_3Na$ ($[M+Na]^+$): 297.1466; found: 297.1461.

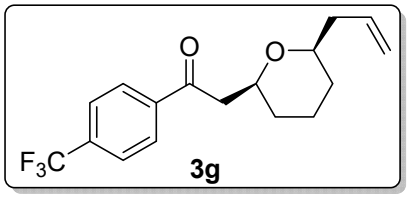
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(3-bromo-4-(dimethylamino)phenyl)ethan-1-one (3f)



3f

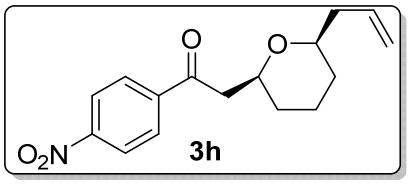
According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 72%. A purification by column chromatography in PE:EA = 8:1 v/v to give **3f** as colorless oil (R_f (*major*)= 0.55). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.45). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, t_{major} = 15.83 min, t_{minor} = 26.55 min), *ee* = 80%. *dr* = 5:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.93–3.88 ppm; trans:4.43–4.37 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.16 (d, J = 2.1 Hz, 1H), 7.85 (dd, J^1 = 8.5, J^2 = 2.1 Hz, 1H), 7.00 (d, J = 8.5 Hz, 1H), 5.78–5.70 (m, 1H), 5.02–4.94 (m, 2H), 3.93–3.88 (m, 1H), 3.39–3.34 (m, 1H), 3.20 (dd, J^1 = 15.5, J^2 = 6.4 Hz, 1H), 2.90 (s, 6H), 2.84 (dd, J^1 = 15.5, J^2 = 6.1 Hz, 1H), 2.27–2.21 (m, 1H), 2.14–2.08 (m, 1H), 1.84–1.80 (m, 1H), 1.72–1.66 (m, 1H), 1.60–1.50 (m, 2H), 1.29–1.14 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 196.5, 155.8, 135.14, 135.05, 132.3, 128.7, 119.2, 116.9, 116.5, 77.6, 74.8, 45.4, 43.7, 41.0, 31.8, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{18}H_{24}O_2NBrNa$ ($[M+Na]^+$): 388.0888; found: 388.0888.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3g)



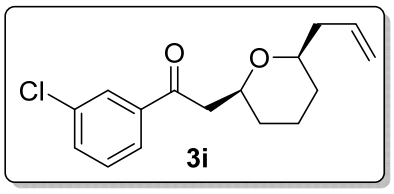
According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 88% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3g** as colorless oil (R_f (*major*)= 0.55). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.50). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 13.16 min, t_{minor} = 15.02 min), *ee* = 89%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.95–3.91 ppm; trans:4.35–4.27 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.07 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 5.74–5.66 (m, 1H), 5.00–4.93 (m, 2H), 3.95–3.91 (m, 1H), 3.38–3.29 (m, 2H), 2.91 (dd, J^1 = 15.6, J^2 = 5.4 Hz, 1H), 2.24–2.08 (m, 2H), 1.86–1.17 (m, 2H), 1.61–1.52 (m, 2H), 1.33–1.16 (m, 2H) ppm; ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.1 (s, 3F) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 198.3, 140.4, 135.0, 134.3(q, J = 32.8 Hz), 128.9, 125.6 (q, J = 3.8 Hz), 123.8 (q, J = 273.2 Hz), 116.5, 77.7, 74.8, 45.9, 41.0, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{17}H_{19}O_2F_3Na$ ([M+Na]$^+$): 335.1234; found: 335.1229.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(4-nitrophenyl)ethan-1-one (3h)



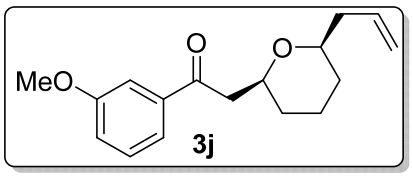
According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 84% yield. A purification by column chromatography in PE:EA = 8:1 v/v to give **3h** as colorless oil (R_f (*major*)= 0.50). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.35). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 31.10 min, t_{minor} = 35.73 min), *ee* = 91%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.95–3.90 ppm; trans:4.45–4.38 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.29–8.28 (m, 2H), 8.13–8.11 (m, 2H), 5.71–5.63 (m, 1H), 4.98–4.92 (m, 2H), 3.95–3.90 (m, 1H), 3.38–3.30 (m, 2H), 2.91 (dd, J^1 = 15.3, J^2 = 5.0 Hz, 1H), 2.22–2.07 (m, 2H), 1.88–1.71 (m, 2H), 1.35–1.16 (m, 4H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 198.0, 150.3, 142.2, 134.9, 129.6, 123.7, 116.6, 77.7, 74.9, 46.1, 40.9, 31.7, 30.8, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{19}O_4NNa$ ([M+Na]$^+$): 312.1212; found: 312.1206.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(3-chlorophenyl)ethan-1-one (3i)



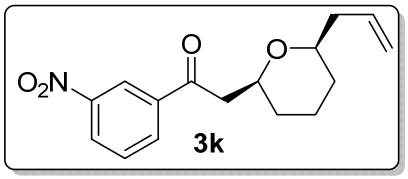
According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 90% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3i** as colorless oil (R_f (*major*)= 0.60). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 16.47 min, t_{minor} = 18.52 min), *ee* = 90%. *dr* = 6:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.94–3.89 ppm; trans:4.45–4.38 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.94–7.93 (m, 1H), 7.84–7.82 (m, 1H), 7.52–7.50 (m, 1H), 7.40–7.37 (m, 1H), 5.76–5.68 (m, 1H), 5.01–4.94 (m, 2H), 3.94–3.89 (m, 1H), 3.39–3.33 (m, 1H), 3.25 (dd, J^1 = 15.6, J^2 = 6.8 Hz, 1H), 2.87 (dd, J^1 = 15.6, J^2 = 5.6 Hz, 1H), 2.25–2.19 (m, 1H), 2.13–2.08 (m, 1H), 1.86–1.81 (m, 1H), 1.73–1.70 (m, 1H), 1.60–1.51 (m, 2H), 1.31–1.15 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 197.8, 139.3, 135.1, 134.9, 132.9, 129.9, 128.7, 126.6, 116.5, 77.7, 74.7, 45.8, 41.0, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{19}O_2ClNa$ ([M+Na]$^+$): 301.0971; found: 301.0966.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(3-methoxyphenyl)ethan-1-one (3j)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 83% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3j** as colorless oil (R_f (*major*)= 0.60). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 24.14 min, t_{minor} = 27.48 min), *ee* = 91%. *dr* = 14:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.97–3.92 ppm; trans:4.45–4.40 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.54–7.53 (m, 1H), 7.49–7.48 (m, 1H), 7.36–7.33 (m, 1H), 7.10–7.08 (m, 1H), 5.79–5.71 (m, 1H), 5.03–4.95 (m, 2H), 3.97–3.92 (m, 1H), 3.84 (s, 3H), 3.40–3.35 (m, 1H), 3.27 (dd, J^1 = 15.8, J^2 = 6.3 Hz, 1H), 2.93 (dd, J^1 = 15.8, J^2 = 6.3 Hz, 1H), 2.28–2.22 (m, 1H), 2.14–2.09 (m, 1H), 1.84–1.80 (m, 1H), 1.74–1.71 (m, 1H), 1.61–1.51 (m, 2H), 1.29–1.15 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 198.6, 159.9, 139.0, 135.1, 129.6, 121.2, 119.7, 116.5, 112.5, 77.7, 74.7, 55.5, 45.8, 41.0, 31.7, 31.0, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{17}H_{22}O_3Na$ ([M+Na]$^+$): 297.1467; found: 297.1461.

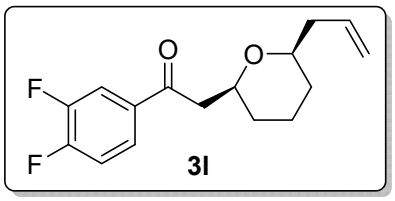
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(3-nitrophenyl)ethan-1-one (3k)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 67% yield. A purification by column

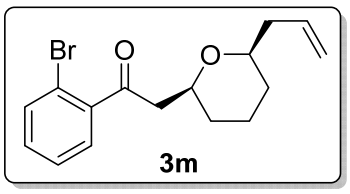
chromatography in PE:EA = 8:1 v/v to give **3k** as colorless oil (R_f (*major*)= 0.50). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.45). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, t_{major} = 47.11 min, t_{minor} = 47.55 min), *ee* = 92%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.94–3.89 ppm; trans:4.42–4.35 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: *δ* 8.80–8.79 (m, 1H), 8.39–8.37 (m, 1H), 8.30–8.28 (m, 1H), 7.66–7.62 (m, 1H), 5.68–5.60 (m, 1H), 4.94–4.87 (m, 2H), 3.94–3.89 (m, 1H), 3.36–3.30 (m, 2H), 2.91 (dd, J^1 = 15.2, J^2 = 5.0 Hz, 1H), 2.20–2.14 (m, 1H), 2.10–2.05 (m, 1H), 1.87–1.82 (m, 1H), 1.73–1.71 (m, 1H), 1.60–1.50 (m, 2H), 1.36–1.27 (m, 1H), 1.24–1.14 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: *δ* 197.3, 148.4, 139.0, 134.9, 134.1, 129.7, 127.2, 123.7, 116.4, 77.6, 74.9, 45.8, 40.8, 31.7, 30.8, 23.5 ppm; HRMS (ESI) m/z: calcd for $C_{16}H_{19}O_4NNa$ ($[M+Na]^+$): 312.1212; found: 312.1206.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(3,4-difluorophenyl)ethan-1-one (3l)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 91% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3l** as colorless oil (R_f (*major*)= 0.55). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.45). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 17.57 min, t_{minor} = 20.43 min), *ee* = 90%. *dr* = 4:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.92–3.87 ppm; trans:4.35–4.30 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: *δ* 7.84–7.80 (m, 1H), 7.77–7.74 (m, 1H), 7.25–7.19 (m, 1H), 5.75–5.66 (m, 1H), 5.01–4.93 (m, 2H), 3.92–3.87 (m, 1H), 3.38–3.33 (m, 1H), 3.23 (dd, J^1 = 15.3, J^2 = 7.0 Hz, 1H), 2.83 (dd, J^1 = 15.3, J^2 = 5.4 Hz, 1H), 2.24–2.08 (m, 2H), 1.86–1.69 (m, 2H), 1.60–1.51 (m, 2H), 1.32–1.16 (m, 2H) ppm; **^{19}F NMR (471 MHz, $CDCl_3$)**: *δ* −130.2– −130.3 (m, 1F), −136.0– −136.1 (m, 1F) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: *δ* 196.6, 153.7 (dd, J^1 = 257.0, J^2 = 13.0 Hz), 150.4 (dd, J^1 = 250.7, J^2 = 13.0 Hz), 135.0, 134.9 (dd, J = 3.8 Hz), 125.6 (dd, J^1 = 7.6, J^2 = 3.8 Hz), 117.9 (dd, J^1 = 18.0, J^2 = 1.5 Hz), 117.4 (d, J^1 = J^2 = 17.6 Hz), 116.6, 77.7, 74.8, 45.6, 40.9, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{18}O_2F_2Na$ ($[M+Na]^+$): 303.1173; found: 303.1167.

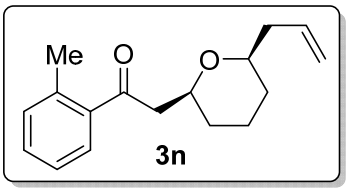
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(2-bromophenyl)ethan-1-one (3m)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 89% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3m** as colorless oil (R_f (*major*)= 0.50). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.40). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-

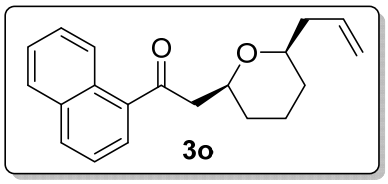
PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 19.38 min, t_{minor} = 21.41 min), *ee* = 89%. *dr* = 9:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.89–3.84 ppm; trans:4.40–4.38 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.57 (dd, J^1 = 8.0, J^2 = 0.9 Hz, 1H), 7.44 (dd, J^1 = 7.6, J^2 = 1.7 Hz, 1H), 7.35–7.32 (m, 1H), 7.28–7.24 (m, 1H), 5.80–5.72 (m, 1H), 5.04–4.97 (m, 2H), 3.89–3.84 (m, 1H), 3.34–3.29 (m, 1H), 3.13 (dd, J^1 = 15.5, J^2 = 8.1 Hz, 1H), 2.96 (dd, J^1 = 15.5, J^2 = 4.9 Hz, 1H), 2.25–2.20 (m, 1H), 2.14–2.08 (m, 1H), 1.84–1.80 (m, 1H), 1.70–1.67 (m, 1H), 1.58–1.48 (m, 2H), 1.31–1.12 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 203.0, 142.2, 135.2, 133.5, 131.5, 129.0, 127.4, 118.6, 116.5, 77.6, 74.9, 49.6, 41.0, 31.4, 30.8, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{16}H_{19}O_2BrNa$ ($[M+Na]^+$): 345.0465; found: 345.0461.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(o-tolyl)ethan-1-one (3n)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 92% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3n** as colorless oil (R_f (*major*)= 0.65). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.2 mL/min, λ = 254 nm, t_{major} = 36.73 min, t_{minor} = 40.23 min), *ee* = 91%. *dr* = 6:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.95–3.89 ppm; trans:4.35–4.28 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.66–7.64 (m, 1H), 7.35–7.32 (m, 1H), 7.25–7.21 (m, 2H), 5.80–5.72 (m, 1H), 5.04–4.96 (m, 2H), 3.95–3.89 (m, 1H), 3.38–3.33 (m, 1H), 3.17 (dd, J^1 = 15.6, J^2 = 7.4 Hz, 1H), 2.84 (dd, J^1 = 15.6, J^2 = 5.4 Hz, 1H), 2.48 (s, 3H), 2.27–2.21 (m, 1H), 2.15–2.09 (m, 1H), 1.84–1.80 (m, 1H), 1.72–1.67 (m, 1H), 1.60–1.50 (m, 2H), 1.31–1.15 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 203.2, 138.8, 137.9, 135.2, 131.8, 131.1, 128.7, 125.6, 116.5, 77.6, 74.9, 48.7, 41.0, 31.6, 30.9, 23.5, 21.1 ppm; **HRMS (ESI) m/z**: calcd for $C_{17}H_{22}O_2Na$ ($[M+Na]^+$): 281.1517; found: 281.1512.

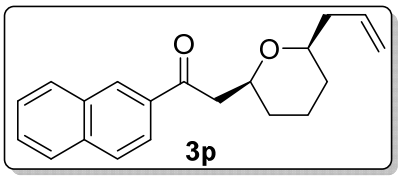
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(naphthalen-1-yl)ethan-1-one (3o)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 76% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3b** as colorless oil (R_f (*major*)= 0.6). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 25.71 min, t_{minor} = 27.78 min), *ee* = 88%. *dr* = 13:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 4.03–3.98 ppm; trans:4.48–4.42, 3.80–3.85 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.56 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.90–7.86 (m, 2H), 7.59–7.56 (m, 1H), 7.54–7.47 (m, 2H), 5.78–5.70 (m,

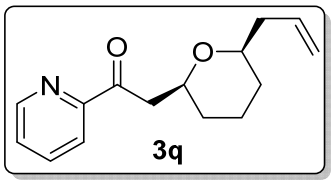
1H), 5.03–4.93 (m, 2H), 4.03–3.98 (m, 1H), 3.38–3.32 (m, 2H), 3.00 (dd, J^1 = 15.3, J^2 = 5.0 Hz, 1H), 2.27–2.21 (m, 1H), 2.15–2.09 (m, 1H), 1.87–1.82 (m, 1H), 1.75–1.72 (m, 1H), 1.60–1.51 (m, 2H), 1.37–1.27 (m, 1H), 1.24–1.16 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 203.4, 137.0, 135.2, 134.0, 132.3, 130.2, 128.4, 127.74, 127.66, 126.4, 126.0, 124.5, 116.4, 77.6, 75.2, 49.3, 41.0, 31.6, 30.9, 23.6 ppm; **HRMS (ESI) m/z**: calcd for $C_{20}H_{22}O_2Na$ ([M+Na]$^+$): 317.1517; found: 317.1512.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(naphthalen-2-yl)ethan-1-one (3p)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 69% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3p** as colorless oil (R_f (*major*)= 0.6). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.55). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 21.55 min, t_{minor} = 26.55 min), *ee* = 88%. *dr* = 7:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 4.04–3.99 ppm; trans:4.51–4.48 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.50 (s, 1H), 8.04 (dd, J^1 = 8.6, J^2 = 1.8 Hz, 1H), 7.96–7.95 (m, 1H), 7.89–7.86 (m, 2H), 7.61–7.53 (m, 2H), 5.80–5.72 (m, 1H), 5.03–4.94 (m, 2H), 4.04–3.99 (m, 1H), 3.47–3.38 (m, 2H), 3.07 (dd, J^1 = 15.7, J^2 = 6.2 Hz, 1H), 2.29–2.23 (m, 1H), 2.16–2.11 (m, 1H), 1.88–1.77 (m, 2H), 1.63–1.53 (m, 2H), 1.36–1.17 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 198.81, 135.7, 135.1, 135.0, 132.6, 130.3, 129.7, 128.5, 128.4, 127.9, 126.8, 124.2, 116.5, 77.7, 74.9, 45.8, 41.0, 31.8, 31.0, 23.6 ppm; **HRMS (ESI) m/z**: calcd for $C_{20}H_{22}O_2Na$ ([M+Na]$^+$): 317.1517; found: 317.1512.

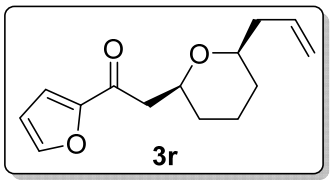
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(pyridin-2-yl)ethan-1-one (3q)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 87% yield. A purification by column chromatography in PE:EA = 8:1 v/v to give **3q** as colorless oil (R_f (*major*)= 0.55). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.50). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 22.78 min, t_{minor} = 23.84 min), *ee* = 76%. *dr* = 6:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 4.02–3.97 ppm; trans:4.55–4.49 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.66–8.65 (m, 1H), 8.02–7.99 (m, 1H), 7.82–7.78 (m, 1H), 7.45–7.42 (m, 1H), 5.75–5.66 (m, 1H), 4.98–4.89 (m, 2H), 4.02–3.97 (m, 1H), 3.52 (dd, J^1 = 16.1, J^2 = 7.5 Hz, 1H), 3.35–3.31 (m, 1H), 3.20 (dd, J^1 = 16.1, J^2 = 5.4 Hz, 1H), 2.24–2.18 (m, 1H), 2.10–2.04 (m, 1H), 1.84–1.79 (m, 1H), 1.69–1.66 (m, 1H), 1.58–1.49 (m, 2H), 1.35–1.13 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 200.1, 153.9, 149.0, 136.9, 135.3, 127.0, 121.9, 116.3, 77.5, 74.5, 44.6, 41.0, 31.6, 30.9, 23.6 ppm; **HRMS (ESI)**

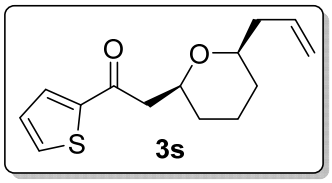
m/z: calcd for $C_{15}H_{19}O_2NNa$ ([M+Na]$^+$): 268.1313; found: 268.1308.

2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(furan-2-yl)ethan-1-one (3r)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 47% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3r** as colorless oil (R_f (*major*)= 0.50). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.40). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 26.06 min, t_{minor} = 31.10 min), *ee* = 90%. *dr* = 6:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.93–3.88 ppm; trans:4.42–4.39 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.58–7.57 (m, J^1 = 1.7, J^2 = 0.5 Hz, 1H), 7.19 (dd, J^1 = 3.5, J^2 = 0.5 Hz, 1H), 6.51 (dd, J^1 = 3.5, J^2 = 1.7 Hz, 1H), 5.77–5.68 (m, 1H), 5.00–4.93 (m, 2H), 3.93–3.88 (m, 1H), 3.38–3.32 (m, 1H), 3.12 (dd, J^1 = 15.0, J^2 = 7.0 Hz, 1H), 2.77 (dd, J^1 = 15.0, J^2 = 5.8 Hz, 1H), 2.25–2.19 (m, 1H), 2.12–2.07 (m, 1H), 1.83–1.79 (m, 1H), 1.71–1.66 (m,1H), 1.59–1.49 (m, 2H), 1.30–1.14 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 187.5, 153.2, 146.6, 135.1, 117.9, 116.4, 112.3, 77.6, 74.5, 45.6, 41.0, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{14}H_{18}O_3Na$ ([M+Na]$^+$): 257.1153; found: 257.1148.

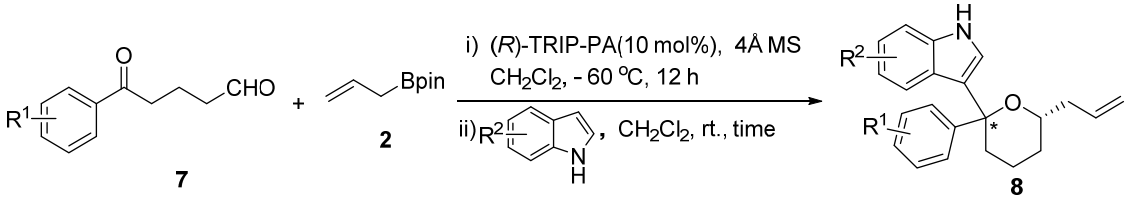
2-(6-allyltetrahydro-2H-pyran-2-yl)-1-(thiophen-2-yl)ethan-1-one (3s)



According to the general procedure for the asymmetric allyboration/oxa-Michael tandem reaction of aldehydes, the title compound was obtained in 83% yield. A purification by column chromatography in PE:EA = 10:1 v/v to give **3s** as colorless oil (R_f (*major*)= 0.50). The *trans* isomer was observed as minor product (R_f (*minor*)= 0.40). **HPLC Condition**: The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 22.07 min, t_{minor} = 24.86 min), *ee* = 88%. *dr* = 13:1, determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy (cis: 3.39–3.34 ppm; trans:4.40–4.37 ppm); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.73 (d, J = 3.7 Hz, 1H), 7.61 (d, J = 4.9 Hz, 1H), 7.10 (dd, J^1 = 3.9 J^2 = 4.8 Hz, 1H), 5.77–5.69 (m, 1H), 5.01–4.94 (m, 2H), 3.94–3.89 (m, 1H), 3.39–3.34 (m, 1H), 3.20 (dd, J^1 = 15.0, J^2 = 6.6 Hz, 1H), 2.87 (dd, J^1 = 15.1, J^2 = 6.1 Hz, 1H), 2.26–2.20 (m, 1H), 2.13–2.08 (m, 1H), 1.84–1.80 (m, 1H), 1.72–1.69 (m, 1H), 1.60–1.52 (m, 2H), 1.30–1.14 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 191.5, 145.1, 135.1, 133.8, 132.7, 128.1, 116.5, 77.6, 74.7, 46.5, 41.0, 31.7, 30.9, 23.5 ppm; **HRMS (ESI) m/z**: calcd for $C_{14}H_{18}O_2NaS$ ([M+Na]$^+$): 273.0924; found: 273.0920.

Synthesis and Characterization Data of Products 8

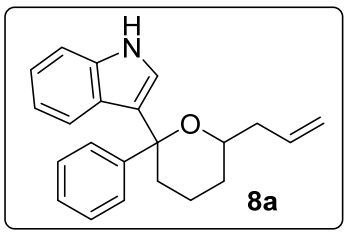
General procedure for the tandem process of Antilla allylboration/oxa−Pictet−Spengler reaction of 5-oxo-5-phenylpentanal 7:



To a 5 mL reaction flask containing a magnetic stirrer was added 5-oxo-5-phenylpentanal **7** (0.10 mmol), (*R*)-TRIP-PA (10 mol%) and activated 4 Å MS (20 mg). The vessel was placed under vacuum and the atmosphere exchanged with N_2 three times before the addition of anhydrous CH_2Cl_2 (0.5 mL). The mixture was allowed to cooled to −60 °C, before allylboronate **2** (0.15 mmol) was added. After stirring for 12 h at −60 °C, the reaction was allowed to warm to room temperature gradually followed by the addition of indole (0.20 mmol). Then the mixture was stirred at room temperature and monitored by TLC. After the complete consumption of the ketone, the mixture was concentrated under reduced pressure and directly purified by PTLC to afford desired products **8**.

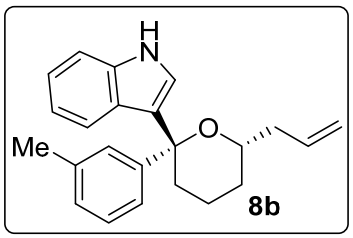
Analytical data of products 8

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-1H-indole (8a)



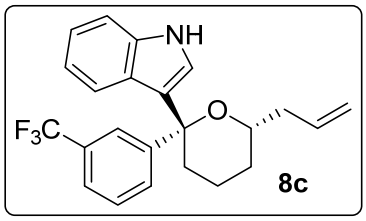
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8a** as colorless liquid (14.3 mg, 45%, R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.05 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.47 (m, 2H), 7.32 (d, J = 8.1 Hz, 1H), 7.24–7.21 (m, 3H), 7.13 (m, 2H), 6.97 (m, 1H), 5.92–5.84 (m, 1H), 5.08–5.02 (m, 2H), 3.55–3.50 (m, 1H), 2.51–2.47 (m, 1H), 2.44–2.38 (m, 1H), 2.35–2.30 (m, 1H), 2.07–1.95 (m, 1H), 1.84–1.76 (m, 2H), 1.53–1.34 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 149.4, 136.9, 135.8, 127.8, 126.4, 126.2, 125.2, 123.2, 122.4, 122.2, 119.6, 118.6, 116.5, 110.8, 78.4, 70.8, 41.6, 37.3, 30.6, 21.5 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel OJ-H, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 36.00 min, t_2 = 45.27 min, ee = 98%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +89.93 (c = 0.3, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}ON$ ($[M-H]^+$): 316.1707, found: 316.1711

3-(6-allyl-2-(m-tolyl)tetrahydro-2H-pyran-2-yl)-1H-indole (8b)



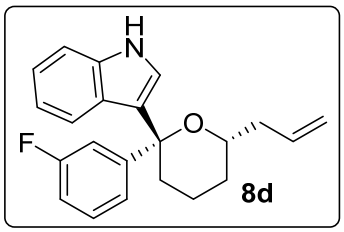
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8b** as colorless liquid (16.2 mg, 49%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.05 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.28 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 7.16–7.04 (m, 2H), 6.98–6.95 (m, 1H), 6.93–6.92 (m, 1H), 5.91–5.82 (m, 1H), 5.07–5.00 (m, 2H), 3.53–3.48 (m, 1H), 2.49–2.45 (m, 1H), 2.43–2.38 (m, 1H), 2.34–2.30 (m, 1H), 2.28 (s, 3H), 2.03–1.93 (m, 1H), 1.82–1.73 (m, 2H), 1.44–1.32 (m, 2H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 150.0, 137.3, 136.7, 135.9, 127.8, 126.8, 126.1, 125.7, 124.6, 122.2, 121.4, 121.3, 118.6, 117.0, 116.8, 111.6, 78.3, 70.5, 41.5, 36.9, 30.6, 25.4, 21.8, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 12.43 min, t_2 = 13.49 min, ee = 97%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +117.61 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{24}NO$ ($[M-H]^+$): 330.1863, found: 330.1867.

3-(6-allyl-2-(3-(trifluoromethyl)phenyl)tetrahydro-2H-pyran-2-yl)-1H-indole (8c)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8c** as yellow liquid (23.1 mg, 60%, R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.09 (s, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.8, 7.8 Hz, 1H), 7.26–7.25 (m, 1H), 7.17–7.14 (m, 1H), 7.01– 6.98 (m, 1H), 5.91–5.82 (m, 1H), 5.11–5.04 (m, 2H), 3.56–3.51 (m, 1H), 2.51–2.47 (m, 1H), 2.45–2.49 (m, 1H), 2.37–2.31 (m, 1H), 2.04–1.98 (m, 1H), 1.86–1.82 (m, 1H), 1.77–1.71 (m, 1H), 1.58–1.54 (m, 1H), 1.43–1.35 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 150.2, 136.9, 135.3, 130.1(q, *J* = 31.9, 31.9 Hz), 128.5, 128.1, 125.9, 125.6, 124.5(q, *J* = 272.8, 272.8 Hz), 123.4, 123.1, 122.9(q, *J* = 3.6, 3.6 Hz), 122.3, 121.9, 121.9(q, *J* = 4.0, *J* = 4.0 Hz), 119.6, 117.7, 116.5, 110.7, 77.9, 70.7, 41.3, 37.0, 30.3, 21.3 ppm; **^{19}F NMR (471 MHz, $CDCl_3$)**: δ -62.29 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel OJ-H, Hexanes/IPA = 97/3, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 38.34 min, t_2 = 45.97 min, ee = 98%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +20.16 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{21}F_3ON$ ($[M-H]^+$): 384.1581, found: 384.1584

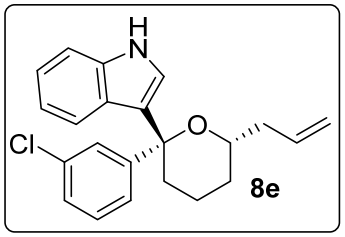
3-(6-allyl-2-(3-fluorophenyl)tetrahydro-2H-pyran-2-yl)-1H-indole (8d)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8d** as colorless liquid (18.4 mg, 55%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.08 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.26–7.23 (m, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.20–7.12 (m, 3H), 7.00–6.97 (t, *J* = 7.5 Hz, 1H), 6.82–6.76 (m, 1H), 5.90–5.81 (m, 1H), 5.07–5.02 (m, 2H), 3.53–3.48 (m, 1H), 2.48–2.43 (m, 1H), 2.43–2.36 (m, 1H), 2.35–2.28 (m, 1H), 2.04–1.95 (m, 1H), 1.84–1.79 (m, 1H), 1.75 (td,

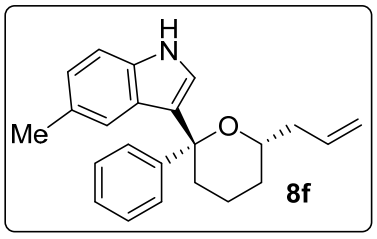
J = 13.7, 4.3 Hz, 1H), 1.44–1.30 (m, 2H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 163.3, 161.4, 153.1(d, *J* = 6.5Hz), 137.3, 135.9, 129.9(d, *J* = 8.2 Hz), 125.9, 124.9, 121.5, 121.3(d, *J* = 2.3 Hz), 121.1, 118.9, 117.1, 116.2, 112.9, 112.8, 111.9, 111.7, 78.1, 78.1, 70.6, 41.4, 36.5, 30.5, 25.4, 21.3 ppm; **^{19}F NMR (471 MHz, $(CD_3)_2SO$)**: δ -113.93 (m, 1F) ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 93/7, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 17.17 min, t_2 = 18.74 min, ee = 98%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +58.52 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}NOF$ ($[M-H]^+$): 334.1613, found: 334.1618.

3-(6-allyl-2-(3-chlorophenyl)tetrahydro-2H-pyran-2-yl)-1H-indole (8e)



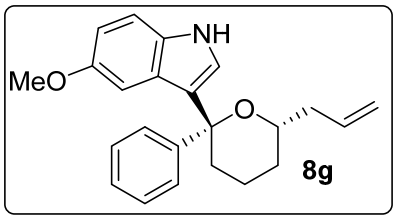
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8e** as colorless liquid (20.4 mg, 58%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.08 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51–7.50 (m, 1H), 7.34–7.32 (m, 1H), 7.30 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.17–7.10 (m, 2H), 7.10–7.08 (m, 1H), 7.01–6.97 (m, 1H), 5.89–5.81 (m, 1H), 5.08–5.01 (m, 2H), 3.52–3.47 (m, 1H), 2.46–2.42 (m, 1H), 2.41–2.37 (m, 1H), 2.34–2.28 (m, 1H), 2.03–1.94 (m, 1H), 1.84–1.79 (m, 1H), 1.73 (td, *J* = 13.7, 4.2 Hz, 1H), 1.44–1.30 (m, 2H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 152.5, 137.3, 135.8, 132.8, 129.9, 126.2, 125.8, 125.0, 124.9, 123.9, 121.5, 121.1, 118.9, 117.1, 116.0, 111.8, 78.1, 70.6, 41.3, 36.5, 30.5, 25.4, 21.3 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 13.86 min, t_2 = 14.85 min, ee = 98%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +63.52 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}NOCl$ ($[M-H]^+$): 350.1317, found: 350.1322.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-5-methyl-1H-indole (8f)



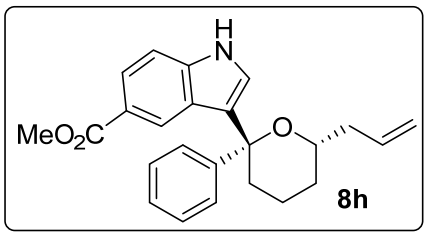
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8f** as yellow liquid (21.1 mg, 64%, R_f = 0.50); **^{1}H NMR (500 MHz, $(CD_3)_2SO$)**: δ 10.89 (s, 1H), 7.42–7.40 (m, 3H), 7.36 (s, 1H), 7.22–7.18 (m, 3H), 7.10–7.08 (m, 1H), 6.82 (dd, J^1 = 8.2 Hz, J^2 = 1.6 Hz, 1H), 5.90–5.81 (m, 1H), 5.07–5.014 (m, 2H), 2.58 (m, 1H), 2.34–2.31 (m, 1H), 2.25 (s,3H), 1.95– 1.86 (m, 1H), 1.76–1.70 (m, 1H), 1.58–1.47 (m, 2H), 1.29–1.21 (m, 1H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 150.0, 136.3, 135.6, 127.9, 126.9, 126.3, 126.1, 125.1, 124.7, 122.9, 121.1, 116.7, 116.0, 111.3, 78.5, 70.5, 41.6, 36.9, 30.8, 21.7, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 93/7, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 14.58 min, t_2 = 15.83 min, ee = 96%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +78.60 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{24}NO$ ($[M-H]^+$): 330.1863, found: 330.1866.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-5-methoxy-1H-indole (8g)



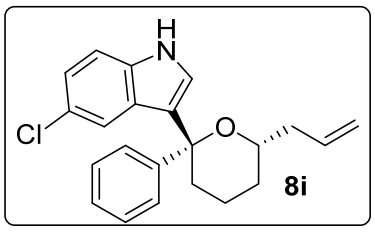
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8g** as colorless liquid (16.0 mg, 46%,R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.94(s, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 7.5 Hz, 2H), 7.14–7.08 (m, 2H), 6.80 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 5.92–5.81 (m, 1H), 5.10–4.96 (m, 2H), 3.79 (s, 3H), 3.55–3.47 (m, 1H), 2.47–2.34 (m, 2H), 2.34–2.24 (m, 1H), 2.07–1.92 (m, 1H), 1.83–1.70 (m, 2H), 1.56–1.50 (m, 1H), 1.40–1.30 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 156.5, 149.4, 137.7, 135.7, 127.8, 126.2, 125.2, 123.0, 122.0, 120.7, 118.6, 116.4, 109.4, 94.3, 78.4, 70.8, 55.7, 41.6, 37.2, 30.7, 21.5 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 14.87 min, t_2 = 17.77 min, ee = 94%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +132.53 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: **$C_{23}H_{24}O_2N$ ($[M-H]^+$)**: 346.1818, found: 346.1855.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-1H-indol-5-yl acetate (8h)



A purification by column chromatography in CH_2Cl_2 to give **8h** as yellow liquid (15.8 mg, 42%, R_f = 0.50); **^{1}H NMR (500 MHz, $(CD_3)_2SO$)**: δ 11.47 (s, 1H), 8.32 (s, 1H), 7.67–7.64 (m, 2H), 7.42–7.39 (m,3H), 7.23–7.20 (dd, J^1 = 7.7 Hz, J^2 = 7.6 Hz, 2H), 7.11–7.08 (m, 1H), 5.89–5.83 (m, 1H), 5.04–4.97 (m, 1H), 3.78 (s, 3H), 2.61–2.58 (m, 1H), 2.34–2.30 (m, 1H), 2.27–2.23 (m, 1H), 1.91–1.88 (m, 1H), 1.76–1.73 (m, 1H), 1.61–1.56 (m, 1H), 1.50–1.48 (m, 1H), 1.29–1.25 (m, 1H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 167.7, 149.6, 139.9, 135.9, 128.1, 126.6, 126.4, 125.6, 125.1, 124.4, 122.5, 120.3, 118.2, 116.9, 111.6, 78.5, 70.9, 52.0, 41.5, 36.9, 30.7, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 21.60 min, t_2 = 23.64 min, ee = 96%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +58.67 (c = 0.3, $CHCl_3$); **HRMS (ESI) m/z**: $C_{24}H_{24}NO_3$ ($[M-H]^+$): 374.1762, found: 374.1763.

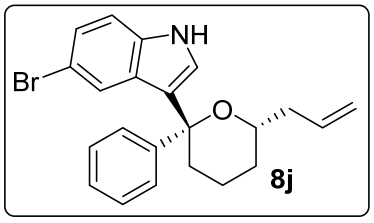
3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-5-chloro-1H-indole (8i)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8i** as colorless liquid (20.7 mg, 59%, R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.12 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.49–7.74 (m, 2H), 7.29–7.22 (m, 4H), 7.18-7.13 (m, 1H), 7.10 (dd, J^1 = 8.6 Hz, J^2 = 2.0 Hz, 1H), 5.95–5.85 (m, 1H), 5.15–5.07 (m, 2H), 3.52–3.43 (m, 1H), 2.50–2.38 (m, 2H), 2.36–2.27 (m, 1H), 2.03–1.91 (m, 1H), 1.87–1.74 (m, 2H), 1.58–1.52 (m, 1H), 1.47–1.34 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 148.9, 135.8, 135.3, 127.9, 127.3, 126.3, 125.3, 125.1, 124.3, 122.7, 121.9, 118.5, 116.7, 111.7, 78.2, 71.0, 41.6, 37.2, 30.8, 21.5 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3,

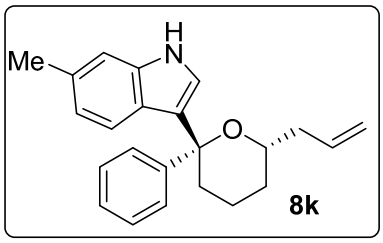
Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 15.18 min, t_2 = 16.86 min, ee = 95%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +71.42 (c = 0.7, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}ClON$ ($[M-H]^+$): 350.1347, found: 350.1320.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-5-bromo-1H-indole (8j)



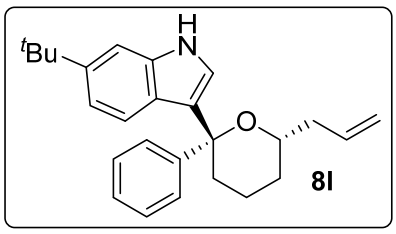
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8j** as yellow liquid (22.2mg, 56%, R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.06 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 1.1 Hz, 1H), 7.44–7.42 (m, 2H), 7.22 (dd, $J^1 = J^2$ = 7.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.15–7.06 (m, 1H), 7.05 (dd, J^1 = 8.6 Hz, J^2 = 1.4 Hz, 1H), 5.90–5.78 (m, 1H), 5.10–4.98 (m, 2H), 3.49–3.40 (m, 1H), 2.47–2.33 (m, 2H), 2.33–2.25 (m, 1H), 2.03–1.90 (m, 1H), 1.57–1.51 (m, 1H), 1.44–1.32 (m, 1H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 149.0, 137.7, 135.1, 127.9, 126.3, 125.3, 125.1, 123.7, 123.7, 122.9, 118.9, 116.6, 116.0, 113.8, 78.2, 70.9, 41.5, 37.1, 30.6, 21.5 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3 , Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 15.44 min, t_2 = 16.97 min, ee = 94%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +82.60 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{22}BrON$ ($[M-H]^+$): 394.0843, found: 394.0891.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-methyl-1H-indole (8k)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8k** as colorless liquid (22.2 mg, 67%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.95 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52–7.40 (m, 2H), 7.25–7.21 (m, 2H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.14–7.11 (m, 2H), 6.83 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.95–5.86 (m, 1H), 5.10–5.02 (m, 2H), 3.58–3.53 (m, 1H), 2.49–2.46 (m, 1H), 2.43 (s, 3H), 2.41–2.31 (m, 2H), 2.04–1.97 (m, 1H), 1.84–1.76 (m, 2H), 1.46–1.32 (m, 2H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 150.0, 137.7, 135.9, 130.3, 127.9, 126.1, 125.1, 124.0, 123.9, 121.1, 120.5, 117.0, 116.6, 111.4, 78.4, 70.4, 41.5, 36.8, 30.6, 25.4, 21.7, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 93/7, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 14.43 min, t_2 = 17.40 min, ee = 96%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +100.25 (c = 0.8, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{24}NO$ ($[M-H]^+$): 330.1863, found: 330.1865.

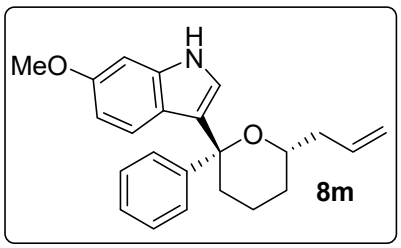
3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-(tert-butyl)-1H-indole (8l)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8l** as yellow liquid (17.2 mg, 46%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.97 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.51–7.42 (m, 2H), 7.31 (d, J = 1.7 Hz, 1H), 7.23–7.20 (m, 2H), 7.16 (d, J = 2.5 Hz, 1H), 7.13–7.08 (m, 1H), 7.05 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.94–5.86 (m, 1H), 5.08–5.02 (m, 2H), 3.59–3.54 (m, 1H), 2.51–2.46

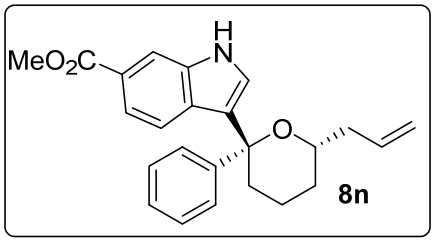
(m, 1H), 2.45–2.37 (m, 1H), 2.37–2.29 (m, 1H), 2.02–1.90 (m, 1H), 1.83–1.71 (m, 2H), 1.34 (s, 9H), 1.29–1.24 (m, 2H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 150.1, 144.0, 137.5, 135.9, 127.9, 126.1, 125.1, 124.2, 123. 8, 120.8, 117.1, 116.9, 116.5, 107.6, 78.4, 70.4, 41.4, 36.7, 34.7, 32.1, 30.6, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 93/7, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 11.61 min, t_2 = 12.53 min, ee = 96%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +65.75 (c = 0.8, $CHCl_3$); **HRMS (ESI) m/z**: $C_{26}H_{30}NO$ ($[M-H]^+$): 372.2333, found: 372.2336.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-methoxy-1H-indole (8m)



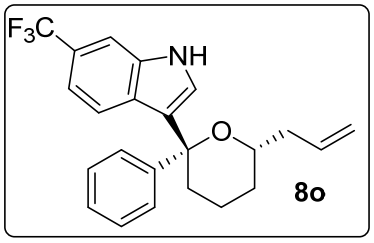
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8m** as colorless liquid (13.9 mg, 46%, R_f = 0.30); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.97 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.28–7.15 (m, 5H), 7.14–7.08 (m, 1H), 6.82–6.74 (m, 1H), 5.94–5.82 (m, 1H), 5.10–4.96 (m, 2H), 3.72 (s, 1H), 3.56–3.48 (m, 1H), 2.48–2.35 (m, 2H), 2.35–2.28 (m, 1H), 2.06–1.94 (m, 1H), 1.84–1.70 (m, 2H), 1.48–1.30 (m, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 153.8, 149.2, 135.8, 132.1, 127.8, 126.9, 126.1, 125.2, 123.8, 118.2, 116.4, 112.7, 111.4, 103.9, 78.4, 70.6, 55.8, 41.7, 37.2, 30.7, 21.5 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 16.53 min, t_2 = 21.99 min, ee = 91%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +62.86 (c = 0.7, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{24}O_2N$ ($[M-H]^+$): 346.1852, found: 346.1830.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-1H-indol-6-yl acetate (8n)



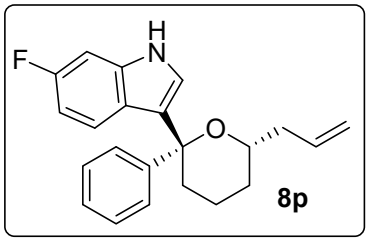
A purification by column chromatography in CH_2Cl_2 to give **8n** as yellow liquid (13.1 mg, 35%, R_f = 0.50); **^{1}H NMR (500 MHz, $(CD_3)_2SO$)**: δ 11.49 (s, 1H), 8.00 (s, 1H), 7.77 (d, *J* = 2.5 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, J^1 = 8.5, J^2 = 1.5 Hz, 1H), 7.41–7.39 (m, 2H), 7.21 (dd, $J^1 = J^2$ = 7.8 Hz, 1H), 711–7.07 (m, 1H), 5.85–5.76 (m, 1H), 5.06–5.00 (m, 2H), 3.82 (s, 3H), 2.63 (m, 1H), 2.35–2.23 (m, 2H), 1.91–1.85 (m, 1H), 1.77–1.73 (m, 1H), 1.61–1.55 (m, 1H), 1.51–1.48 (m, 1H), 1.30–1.22 (m, 1H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 167.7, 149.6, 136.5, 135.9, 129.7, 128.7, 128.0, 126.3, 125.1, 122.5, 121.1, 119.4, 117.5, 117.1, 113.7, 78.2, 70.7, 52.2, 41.4, 36.7, 30.6, 21.3 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 17.24 min, t_2 = 19.85 min, ee = 94%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +70.50 (c = 0.4, $CHCl_3$); **HRMS (ESI) m/z**: $C_{24}H_{24}NO_3$ ($[M-H]^+$): 374.1762, found: 374.1763.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-(trifluoromethyl)-1H-indole (8o)



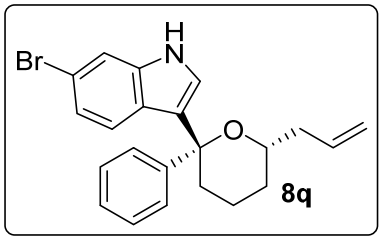
A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8o** as yellow liquid (8.1 mg, 21%, R_f = 0.30); **^{1}H NMR (500 MHz, CD Cl$_3$)**: δ 8.30 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.45–7.41 (m, 2H), 7.38–7.35 (m, 2H), 7.27–7.16 (m, 3H), 7.16–7.10 (m, 1H), 5.90–5.78 (m, 1H) 5.10–5.10 (m, 2H), 3.50–3.50 (m, 1H), 2.50–2.44 (m, 2H), 2.43–2.35 (m, 1H), 2.34–2.27 (m, 1H), 2.02–1.91 (m, 1H), 1.87–1.75 (m, 1H), 1.58–1.50 (m, 1H) ppm; **^{13}C NMR (126 MHz, CDCl$_3$)**: δ 148.9, 135.8, 135.5, 128.7, 127.9, 126.4, 125.6, 125.3 (q, *J* = 32.0 Hz), 125.1, 124.4 (q, *J* = 126.0 Hz), 122.8, 119.1, 116.7, 116.3 (q, *J* = 3.5 Hz), 118.4 (q, *J* = 4.4 Hz), 78.1, 71.0, 41.5, 37.1, 30.6, 21.5 ppm; **^{19}F NMR (471 MHz, CDCl$_3$)**: δ -60.71 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 17.82 min, t_2 = 19.31 min, ee = 98%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +99.10 (c = 0.6, $CHCl_3$); **HRMS (ESI) m/z**: $C_{23}H_{22}F_3ON$ ($[M-H]^+$): 384.1573, found: 384.1589.

3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-fluoro-1H-indole (8p) –



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8p** as colorless liquid (15.4 mg, 45%, R_f = 0.45); **^{1}H NMR (500 MHz, CDCl$_3$)**: *δ* 8.02 (s, 1H), 7.61 (dd, *J* = 8.9, 5.6 Hz, 1H), 7.45–7.43 (m, 2H), 7.25–7.21 (m, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.15–7.11 (m, 1H), 6.98 (dd, *J* = 9.6, *J* = 2.3 Hz, 1H), 5.89–5.80 (m, 1H), 5.08–5.00 (m, 2H), 3.49–3.45 (m, 1H), 2.46–2.41 (m, 1H), 2.40–2.36 (m, 1H), 2.33–2.27 (m, 1H), 2.03–1.94 (m, 1H), 1.83–1.73 (m, 2H), 1.54–1.53 (m, 1H), 1.41–1.33 (m, 1H) ppm; **^{13}C NMR (126 MHz, CDCl$_3$)**: *δ* 160.9, 159.1, 149.0, 136.77 (d, *J* = 12.3 Hz), 135.5, 127.7, 126.1, 125.0, 123.22 (d, *J* = 3.3 Hz), 123.14 (d, *J* = 10.0 Hz), 122.7, 118.7, 116.4, 108.3, 108.1, 97.0, 96.8, 78.1, 70.8, 41.4, 37.0, 30.6, 29.7, 21.4 ppm; **^{19}F NMR (471 MHz, CDCl$_3$)**: *δ* -121.1 (m, 1F) ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 93/7, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 16.35 min, t_2 = 18.85 min, ee = 96%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +68.2 (c = 1.0, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}NOF$ ($[M-H]^-$): 334.1685, found: 334.1611

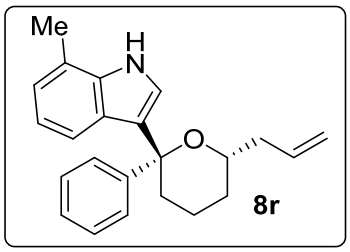
3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-6-bromo-1H-indole (8q)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8q** as colorless liquid (15.8 mg, 40%, R_f = 0.35); **^{1}H NMR (500 MHz, CDCl$_3$)**: δ 8.12 (s, 1H), 7.92 (d, *J* = 1.4 Hz, 1H), 7.48 (m, 2H)., 7.30–7.26 (m, 2H), 7.25–7.21 (m, 2H), 7.20–7.15 (m, 2H), 5.97–5.87 (m, 1H), 5.20–5.10 (m, 2H), 3.52–3.46 (m, 1H) 2.50–2.40 (m, 2H), 2.36–2.29 (m, 1H), 2.02–1.92 (m, 1H), 1.87–1.76 (m 2H), 1.60–1.53 (m, 1H), 1.48–1.34 (m, 1H) ppm; **^{13}C NMR (126 MHz, CDCl$_3$)**: δ 148.9,

135.8, 135.5, 127.9, 126.3, 125.2, 125.1, 124.9, 124.1, 118.4, 116.7, 112.9, 112.2, 78.2, 71.0, 41.6, 37.2, 30.8, 21.4 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 13.28 min, t_2 = 14.51 min, ee = 94%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +20.5 (c = 0.8, $CHCl_3$); **HRMS (ESI) m/z**: $C_{22}H_{21}BrON$ ($[M-H]^+$): 394.0812, found: 394.0816.

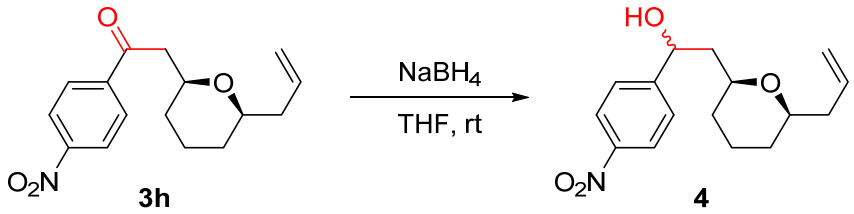
3-(6-allyl-2-phenyltetrahydro-2H-pyran-2-yl)-7-methyl-1H-indole (8r)



A purification by column chromatography in PE:CH_2Cl_2 = 2:1 v/v to give **8r** as colorless liquid (13.2 mg, 40%, R_f = 0.50); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.00 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49–7.43 (m, 2H), 7.25–7.18 (m, 3H), 7.12–7.08 (m, 1H), 6.94–6.88 (m, 2H), 5.92–5.84 (m, 1H), 5.07–5.00 (m, 2H), 3.56–3.50 (m, 1H), 2.51–2.49 (m, 1H), 2.48 (s, 3H), 2.42–2.37 (m, 1H), 2.35–2.29 (m, 1H), 2.04–1.95 (m, 1H), 1.85–1.73 (m, 2H), 1.41–1.33 (m, 1H) ppm; **^{13}C NMR (126 MHz, $(CD_3)_2SO$)**: δ 145.0, 136.8, 135.9, 127.9, 126.1, 125.8, 125.1, 124.4, 121.9, 120.7, 119.0, 118.9, 117.1, 117.0, 78.4, 70.5, 41.5, 36.8, 30.6, 25.4, 21.5, 17.2 ppm; **HPLC Condition**: The enantiomeric excess was determined by Daicel Chiralcel IB-N3, Hexanes/IPA = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, t_1 = 16.45 min, t_2 = 18.11 min, ee = 94%; **Optical Rotation**: $[\alpha]_{25}^{D}$ = +100.50 (c = 0.4, $CHCl_3$); **HRMS (ESI) m/z**: $C_{26}H_{30}NO$ ($[M-H]^+$): 330.1863, found: 330.1865.

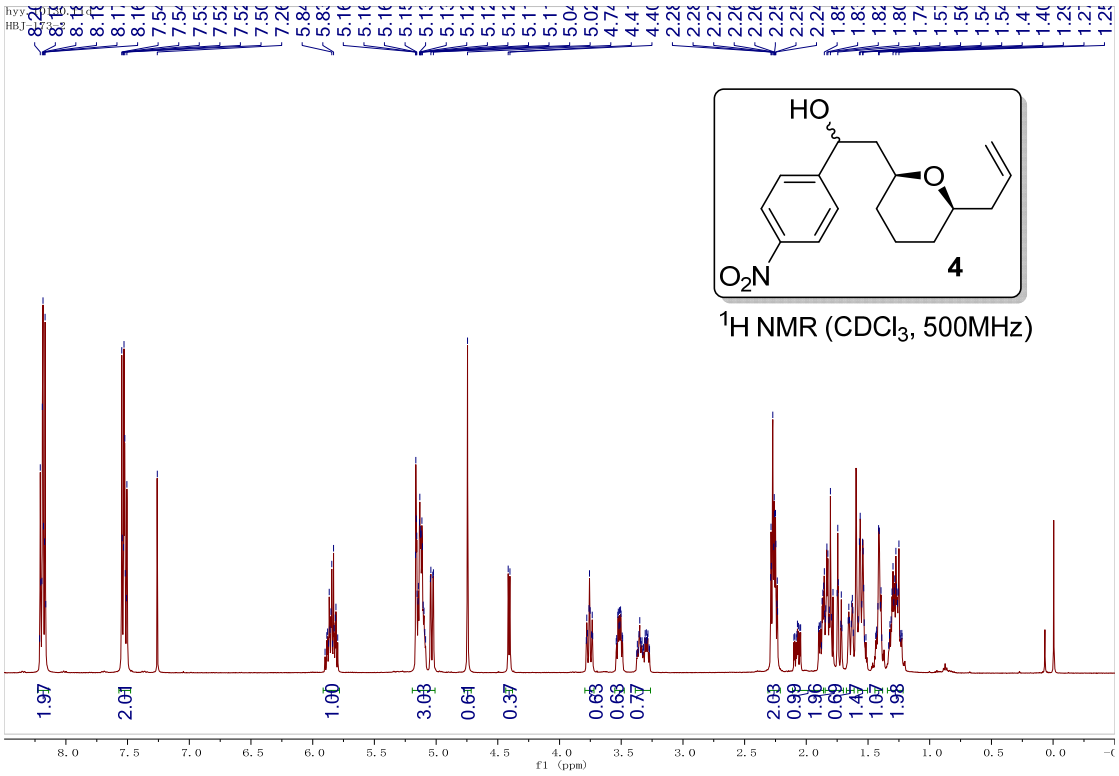
Synthetic applications

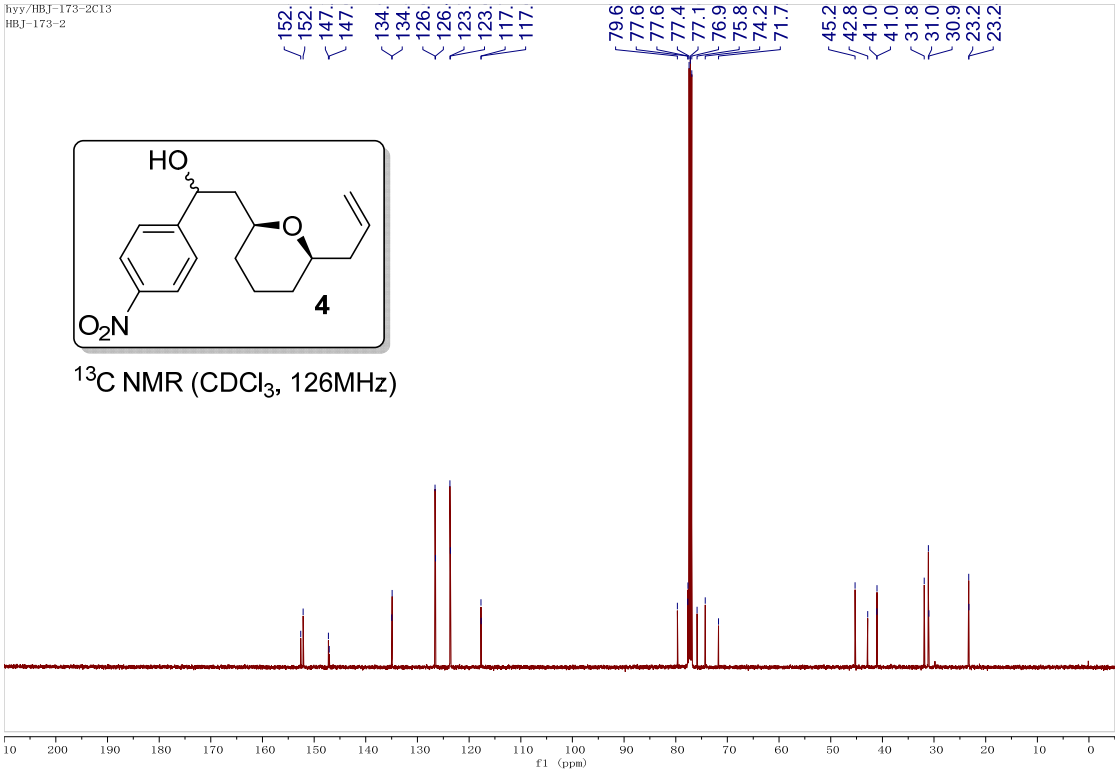
2-((2*S*,6*R*)-6-allyltetrahydro-2H-pyran-2-yl)-1-(4-nitrophenyl)ethan-1-ol (4)



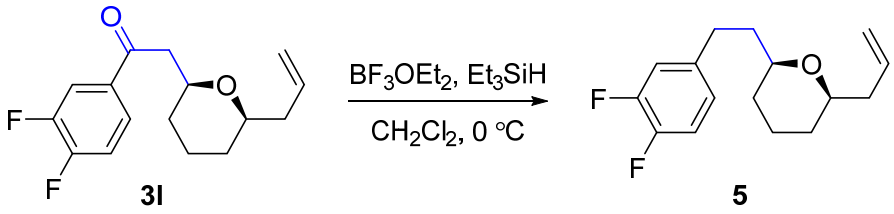
In a Schlenk tube, $NaBH_4$ (0.12 mmol, 1.2 equiv) was added to a mixture of **3h** (29.1 mg, 0.1 mmol) and THF (1 mL). The mixture was stirred at room temperature for 12 h before purification by PTLC (PE/EA = 3:1), providing product **4** as a yellowish oil (23.8 mg, 82% yield), R_f = 0.50 (PE/EA = 3:1), *dr* = 2:1, ee_{major} = 90%, ee_{minor} = 89%. The enantiomeric purity was determined by HPLC (Chiralcel IE-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm, t_1 = 50.59 min, t_2 = 53.31 min, t_3 = 61.35 min, t_4 = 78.03 min). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.21–8.16 (m, 2H), 7.55–7.51 (m, 2H), 5.90–5.80 (m, 1H), 5.17–5.02 (m, 3H), 4.75–4.40 (m, 1H), 3.78–3.27 (m, 2H), 2.29–2.23 (m, 2H), 2.10–1.86 (m, 1H), 1.85–1.71 (m, 2H), 1.67–1.53 (m, 2H), 1.42–1.40 (m, 1H), 1.33–1.23 (m, 2H) ppm; ^{13}C NMR (126 MHz,

$CDCl_3$): δ 152.6(152.1), 147.2(147.1), 134.9(135.0), 126.6(126.5), 123.7(123.6), 117.70(117.67), 77.7(79.7), 74.3(75.9), 77.6(71.7), 45.3(42.9), 41.0(41.1), 31.9(31.0), 31.1, 23.3(23.2) ppm; HRMS (ESI) m/z: calcd for $C_{16}H_{20}NO_4$ ([M]$^+$): 290.1403; found: 290.1398.

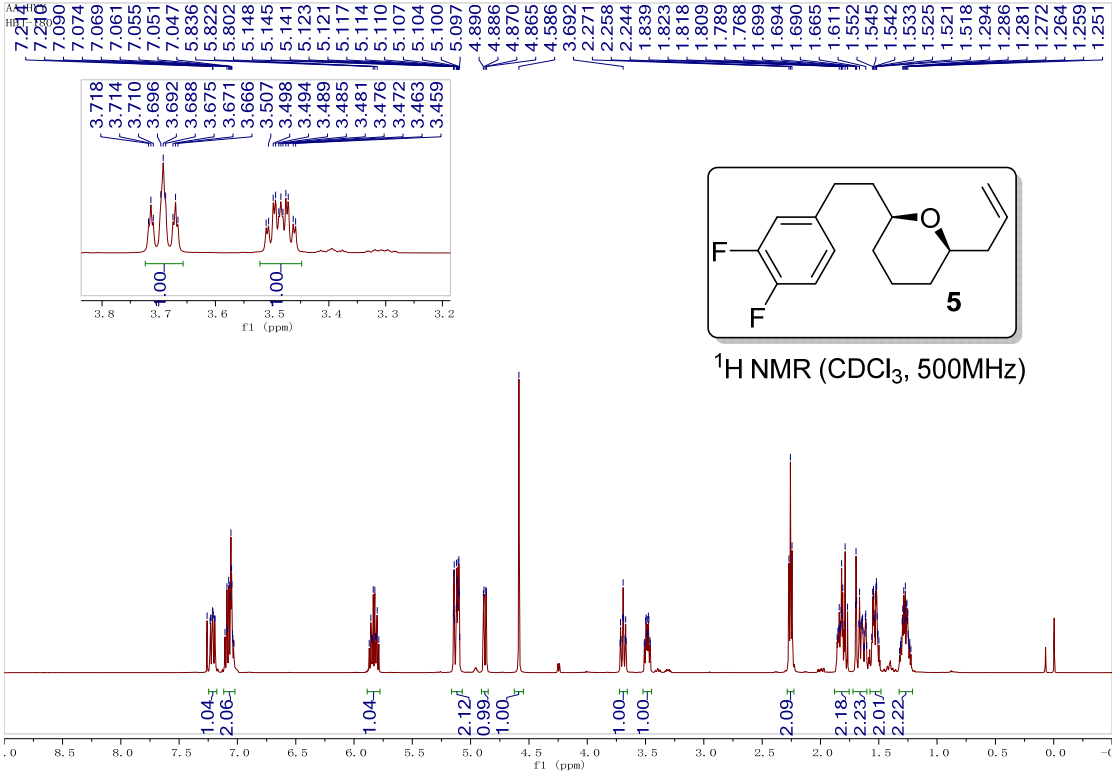


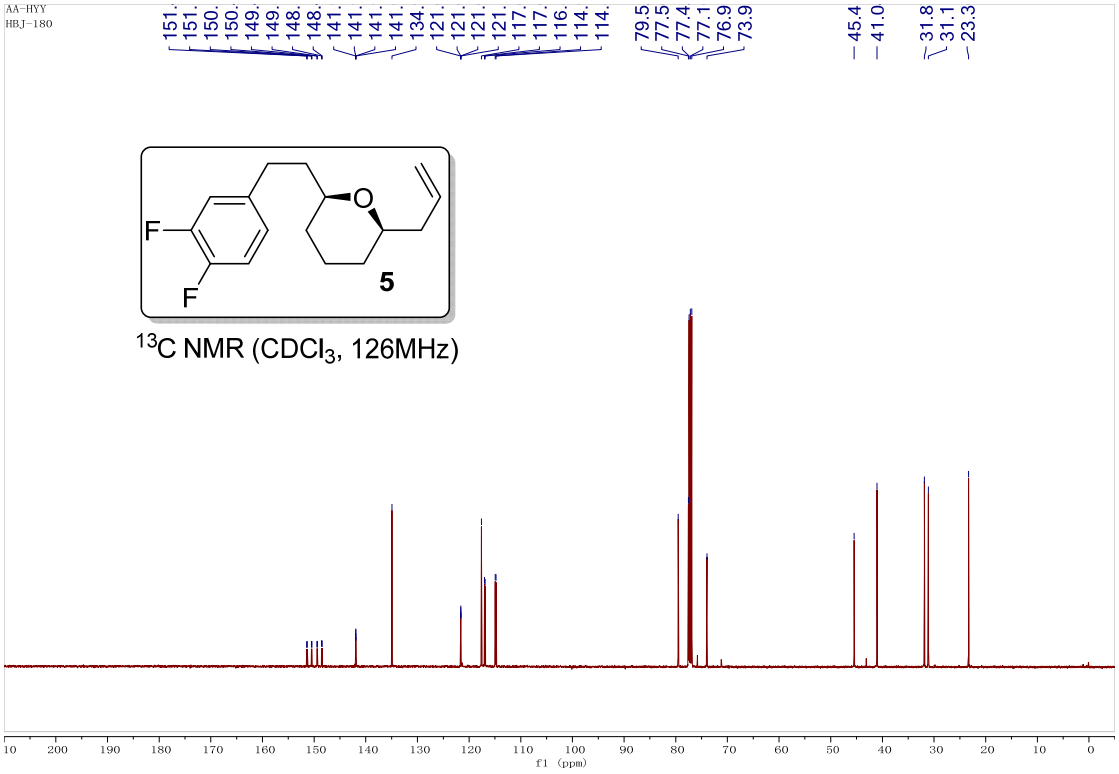


(2R,6S)-2-allyl-6-(3,4-difluorophenethyl)tetrahydro-2H-pyran (5)



In a Schlenk tube, Et_3SiH (0.12 mmol, 1.2 equiv) was added to a mixture of **3l** (28.0 mg, 0.1 mmol) and $BF_3 \cdot Et_2O$ (0.15 mmol, 1.5 equiv) in CH_2Cl_2 (1.0 mL). The mixture was stirred at 0 ℃ for 12 h before purification by PTLC (PE/EA = 5:1), providing product **5** as a colorless oil (26.8 mg, 96% yield), R_f = 0.60 (PE/EA = 5:1), *ee* = 93%. The enantiomeric purity was determined by HPLC (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm, t_{major} = 21.56 min, t_{minor} = 27.11 min). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.19 (m, 1H), 7.11–7.03 (m, 2H), 5.87–5.79 (m, 1H), 5.15–5.09 (m, 2H), 4.88 (dd, J = 10.2, 2.3 Hz, 1H), 4.59 (s, 1H), 3.72–3.67 (m, 1H), 3.51–3.46 (m, 1H), 2.26 (t, J = 6.7 Hz, 2H), 1.86–1.77 (m, 2H), 1.70–1.60 (m, 2H), 1.56–1.50 (m, 2H), 1.32–1.23 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.9(dd, J = 117.2, 12.6 Hz), 148.9(dd, J = 115.9, 12.6 Hz), 141.9(dd, J = 5.0, 3.7 Hz), 134.9, 121.6(dd, J = 6.3, 3.6 Hz), 117.6, 117.0(d, J = 17.2 Hz), 114.9(d, J = 17.7 Hz), 79.5, 77.6, 74.0, 45.5, 41.0, 31.9, 31.1, 23.3 ppm; HRMS (ESI) m/z: calcd for $C_{16}H_{19}OF_2$ ($[M]^+$): 265.1405; found: 265.1399; ^{19}F NMR (471 MHz, $CDCl_3$): δ –138.2 (m, 1F), –140.6 (m, 1F) ppm.




AA-HYY
HBJ-180
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151.
150.
150.
149.
149.
148.
148.
141.
141.
141.
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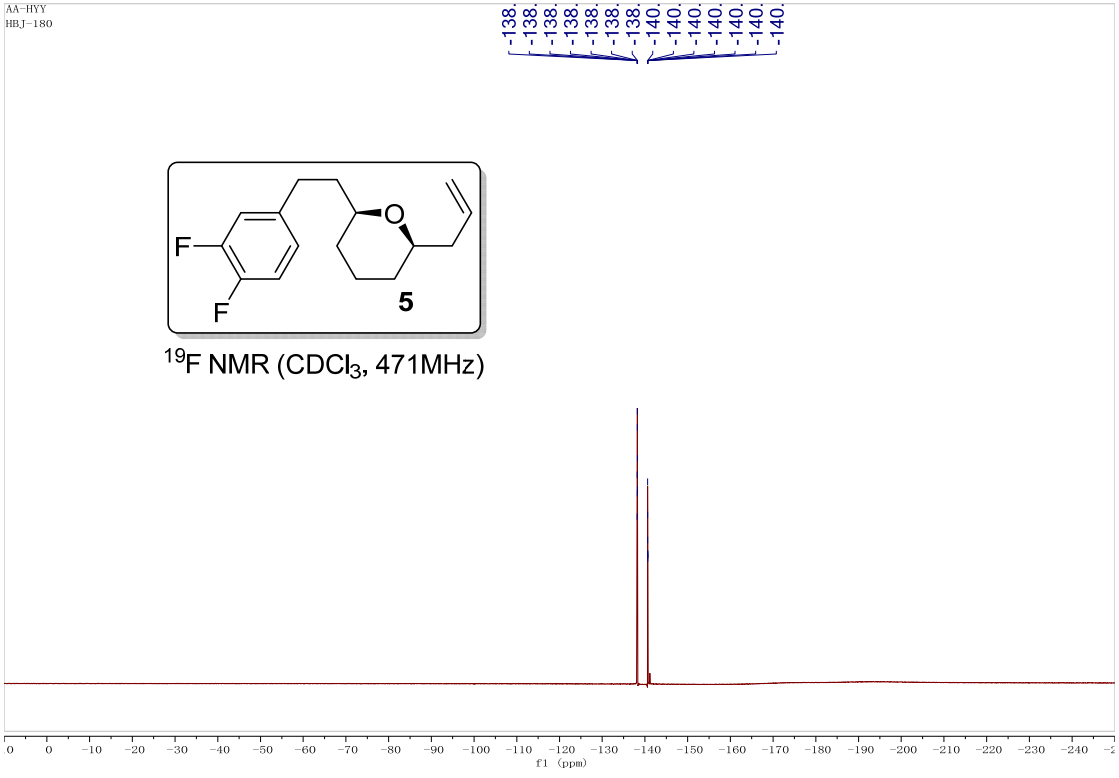
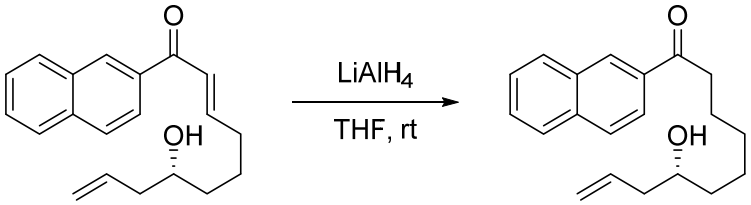
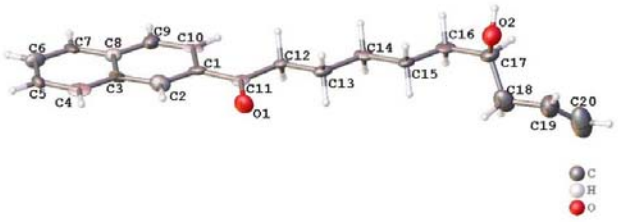
134.
121.
121.
121.
121.
117.
117.
116.
114.
114.
79.5
77.5
77.4
77.1
76.9
73.9
45.4
41.0
31.8
31.1
23.3
F
F
O
5
13C NMR (CDCl3, 126MHz)
f1 (ppm)


AA-HYY
HBJ-180
-138.
-138.
-138.
-138.
-138.
-138.
-138.
-140.
-140.
-140.
-140.
-140.
-140.
-140.
F
F
O
5
19F NMR (CDCl3, 471MHz)
f1 (ppm)

(*R*)-7-hydroxy-1-(naphthalen-2-yl)dec-9-en-1-one (6)

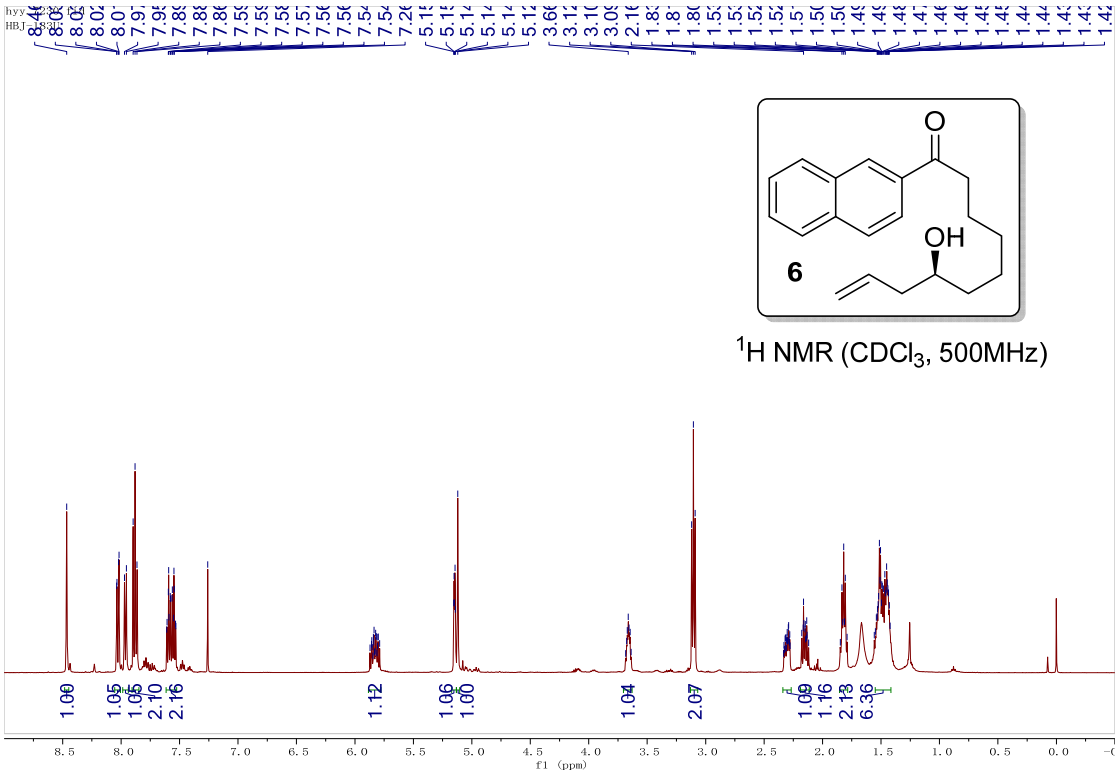


6

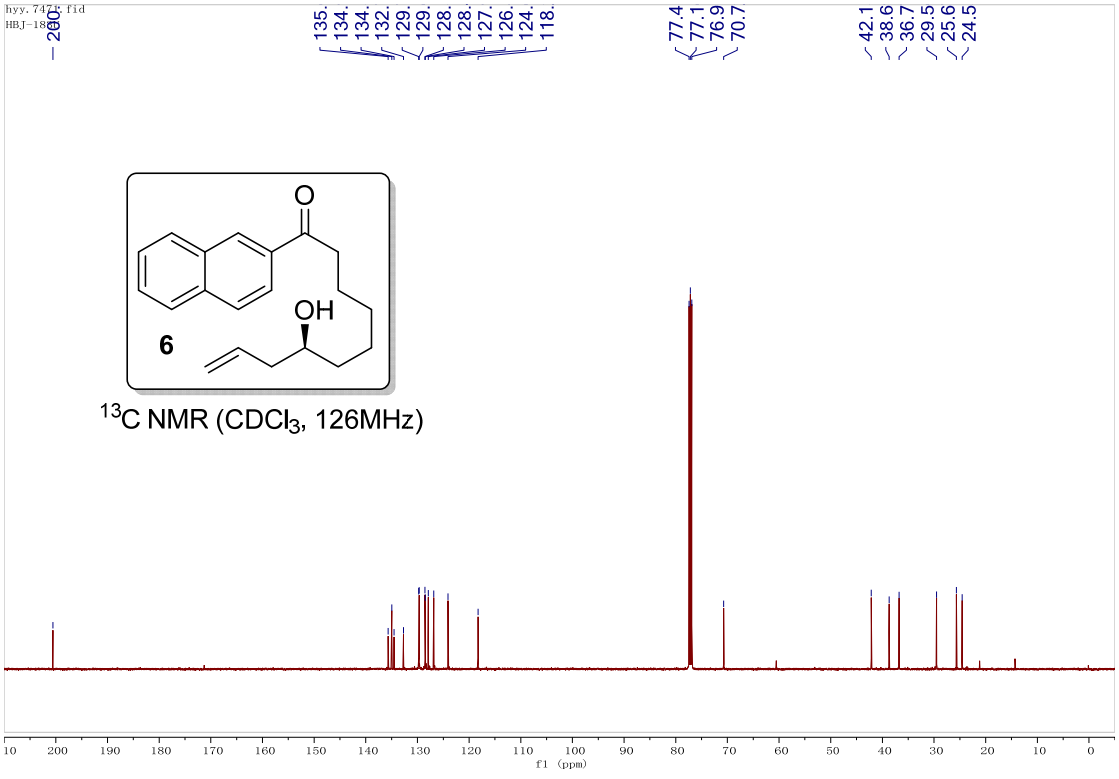


(Deposition Number: CCDC 2295936)

In a Schlenk tube, the THF (0.5 mL) solution of (*E*,*R*)-7-hydroxy-1-(naphthalen-2-yl)deca-2,9-dien-1-one (58.8 mg, 0.2 mmol, 91% *ee*) was solwly added to a mixture of $LiAlH_4$ (0.2 mmol, 1.0 equiv) and THF (2 mL). The mixture was stirred at room temperature for 12 h before purification by PTLC (PE/EA = 5:1) to give product **6** as a white solide (16.2 mg, 27% yield), R_f = 0.56 (PE/EA = 5:1), *ee* = 88%. The enantiomeric purity was determined by HPLC (Chiralcel OD-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 41.97 min, t_{major} = 48.54 min). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.03 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (dd, *J* = 8.5, 8.5, 2H), 7.61–7.53 (m, 2H), 5.87–5.79 (m, 1H), 5.16–5.14 (m, 1H), 5.12 (s, 1H), 3.69–3.64 (m, 1H), 3.10 (t, *J* = 7.4 Hz, 2H), 2.33–2.28 (m, 1H), 2.18–2.12 (m, 1H), 1.85–1.79 (m, 2H), 1.56–1.42 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.6, 135.7, 135.0, 134.5, 132.7, 129.8, 129.7, 128.54, 128.48, 127.9, 126.9, 124.1, 118.3, 70.7, 42.2, 38.7, 36.8, 29.5, 25.7, 24.6 ppm; mp = 48.8–50.2 ℃; HRMS (ESI) m/z: calcd for $C_{20}H_{24}O_2Na$ ($[M+Na]^+$): 319.1672; found: 319.1669.



^{1}H NMR ($CDCl_3$, 500MHz)



^{13}C NMR ($CDCl_3$, 126MHz)

Crystal data and structure refinement

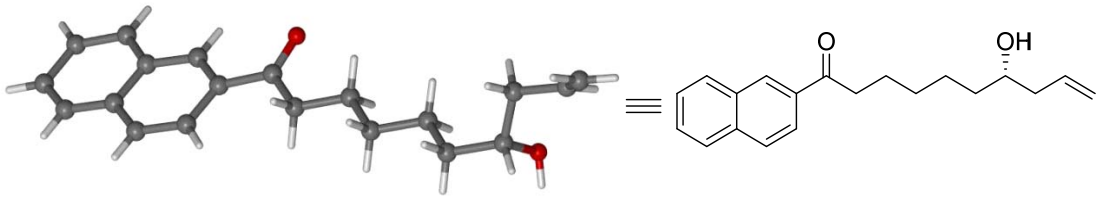


Fig S1: View of the X-ray crystal structure of **6** (CCDC: **2295936**) determined at 100 K.

Crystallization: Crystals of compound **6** was grown from the solvent dichloromethane/hexane (20:80) by a slow evaporation method.

X-Ray Data Collection and Structure Refinement Details: A suitable crystal of **6** was selected and detected on a ' Bruker D8 Venture Photon III' diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2[5], the structure was solved with the XM[2] structure solution program Dual Space and refined with the XL[6] refinement package using Least Squares minimisation.

Crystal data and structure refinement for **6 (CCDC: 2295936)**.

Identification code	**6**	
Empirical formula	C20 H24 O2	
Formula weight	296.39	
Temperature	100(1) K	
Wavelength	1.34139 ?	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 41.348(17) Å	a= 90?
	b = 5.454(2) Å	b= 90?
	c = 14.665(6) Å	g = 90?
Volume	3307(2) $Å^3$	
Z	8	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.373 mm^{-1}	
F(000)	1280	
Crystal size	0.1 x 0.06 x 0.02 mm^3	

Theta range for data collection	1.859 to 38.377?
Index ranges	-38<=h<=38, -5<=k<=4, -13<=l<=13
Reflections collected	10500
Independent reflections	2645 [R(int) = 0.1013]
Completeness to theta = 38.377?	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7490 and 0.5350
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2645 / 36 / 400
Goodness-of-fit on F^2	1.170
Final R indices [I>2sigma(I)]	R1 = 0.1120, wR2 = 0.2755
R indices (all data)	R1 = 0.1282, wR2 = 0.2911
Absolute structure parameter	0.1(6)
Extinction coefficient	0.0029(12)
Largest diff. peak and hole	0.520 and -0.405 e. $Å^{-3}$

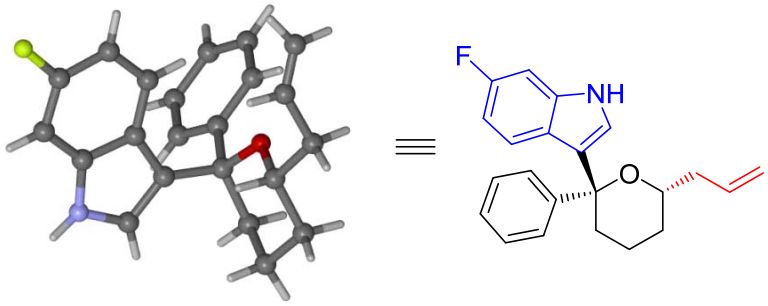


Fig S2: View of the X-Ray Crystal Structure of **8p** (CCDC: 2339828) determined at 289 K.

Crystallization: Crystals of compound **8p** was grown from the solvent dichloromethane/hexane (20:80) by a slow evaporation method.

X-Ray Data Collection and Structure Refinement Details: A suitable crystal of **8p** was selected and detected on a 'Rigaku XtaLAB Synergy Custom' single crystal X-ray diffractometer equipped with a HyPix-Arc 150 detector and .Cu-Kα X-ray source (1.54184 Å). The crystal was kept at 289 K during data collection. Data collection and reduction were undertaken with SHELXL-2018/3.

Crystal data and structure refinement for **8p**

Deposition No. CCDC: 2339828

Identification code	**8p**	
Empirical formula	C22 H21 F N O	
Formula weight	334.40	
Temperature	289(2) K	
Wavelength	1.54184	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.9351(5) Å	a= 90°.
	b = 11.0138(6) Å	b=90°.
	c = 21.9872(13) Å	g = 90°.
Volume	1921.6(2) $Å^3$	
Z	4	
Density (calculated)	1.156 Mg/m^3	
Absorption coefficient	0.618 mm-1	
F(000)	708	
Crystal size	0.1 x 0.05 x 0.03 mm^3	
Theta range for data collection	4.021 to70.062°.	
Index ranges	-9<=h<=9, -13<=k<=12, -24<=l<=26	
Reflections collected	11171	
Independent reflections	3640 [R(int) = 0.0311]	
Completeness to θmax (%)	1.000	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.941 and 0.982	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3640 / 1 / 231	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1212	
R indices (all data)	R1 = 0.0602, wR2 = 0.1357	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.134 and -0.117 $e.Å^{-3}$	

Computational information

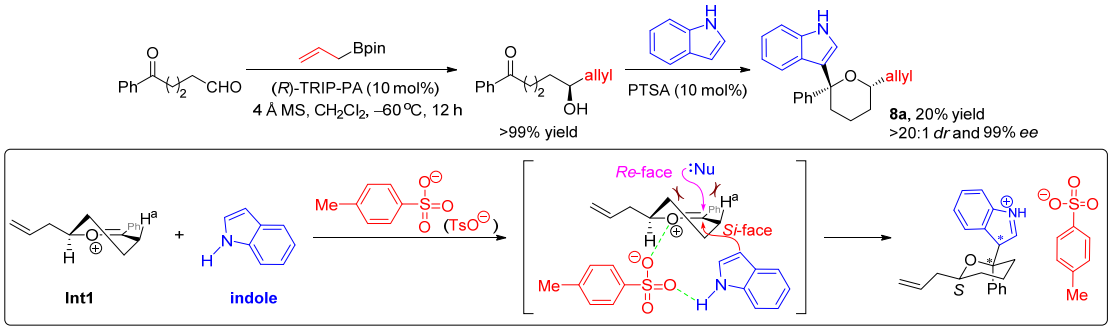


Figure S3. Control experiment

To a 5 mL reaction flask containing a magnetic stirrer was added 5-oxo-5-phenylpentanal **7a** (0.10 mmol), (*R*)-TRIP-PA (10 mol%) and activated 4 Å MS (20 mg). The vessel was placed under vacuum and the atmosphere exchanged with N_2 three times before the addition of anhydrous CH_2Cl_2 (0.5 mL). The mixture was allowed to cooled to − 60 °C,and stirred for 15 h. the desired chiral homoallyl alcohol intermediate was isolated with 99% yield. After that, to a 5 mL reaction flask containing a magnetic stirrer was added the chiral homoallyl alcohol intermediate (0.10 mmol), TsOH (10 mol%) and indole (0.20 mmol). The vessel was placed under vacuum and the atmosphere exchanged with N_2 three times before the addition of anhydrous CH_2Cl_2 (0.5 mL). Then the mixture was stirred at room temperature and monitored by TLC. After 24 h of reaction, the mixture was concentrated under reduced pressure and directly purified by PTLC to afford desired products **8a** with 20% yield, >20:1 *dr* and 99% *ee*.

(1) Computational details

All the DFT calculations have been performed with the Gaussian 16 suite of program. [7] The geometric optimization and vibration analysis of the reactants, intermediates and transition states were performed using B3LYP functional corrected with the empirical dispersion Grimme-D3, and 6-31G(d,p) basis set. Single point calculations for all the optimized structures were further performed using the def2-TZVP basis set. The solvation effects in CH_2Cl_2 have been calculated with the SMD solvation model. [8] For transition states, the intrinsic reaction coordinate (IRC) analysis was performed to confirm that they connect the correct reactants and products on the potential energy surface.

(2) Cartesian coordinates of computed structures

Name	Electronic energy (Hartree)	Thermal correction to Gibbs Free Energy (Hartree)	Imaginary Frequencies
Int1	-618.721865	0.236642	
TsO⁻	-894.974655	0.092930	
indole	-363.815643	0.099652	
Int-Si-Re	-1877.547985	0.475996	

Int-Re-Re	-1877.551018	0.473502	
Int-Si-Si	-1877.552042	0.473306	
Int-Re-Si	-1877.548430	0.470608	
Ts-Si-Re	-1877.542024	0.477831	-128.5496
TS-Re-Re	-1877.532975	0.476652	-70.3736
TS-Si-Si	-1877.542733	0.475903	-276.4750
TS-Re-Si	-1877.526363	0.474586	-125.9649
Int-S-R	-1877.559122	0.477240	
Int-R-R	-1877.561373	0.478546	
Int-S-S	-1877.556169	0.478721	
Int-R-S	-1877.559636	0.477757	
P	-982.134721	0.349722	
dia-P	-982.131881	0.349852	

Int1

O	1.51280879	1.12769603	0.35160646	C	5.20831979	2.83198303	0.50832946
C	2.47073179	0.29254503	0.54181646	H	5.32898079	3.90529603	0.41409246
C	3.78959979	0.86753703	0.58390846	C	-0.21436121	-0.54284497	0.96008246
C	4.93097779	0.05100903	0.75956646	H	-0.11976221	-0.47108897	2.05045846
H	4.83449379	-1.02365497	0.85703146	H	-1.25018921	-0.81932497	0.74437446
C	0.04964079	0.80951103	0.33139846	C	0.76098379	-1.57883597	0.40167746
H	-0.17668721	0.79684703	-0.73964654	H	0.63889979	-1.66025197	-0.68392654
C	2.19862079	-1.16918497	0.73422446	H	0.56363879	-2.56813397	0.81915446
H	2.92576379	-1.73935297	0.14950546	C	-0.61696321	2.00064803	1.00977746
H	2.42890579	-1.38535997	1.78764846	H	-1.69632521	1.79795003	0.98723546
C	6.33079379	2.01250703	0.68137246	H	-0.31827321	2.02526903	2.06346546
H	7.32006879	2.45713303	0.71797146	C	-0.31663021	3.31389503	0.33991246
C	3.94321179	2.27098703	0.46081146	H	-0.64724021	3.41250103	-0.69354454
H	3.06479579	2.89398603	0.33740446	C	0.30301279	4.33148703	0.93570546
C	6.19133179	0.62577403	0.80895446	H	0.63073279	4.27262003	1.97073946
H	7.06683579	0.00082103	0.94321346	H	0.47812779	5.26997803	0.42019246

TsO^-

O	-2.06622524	2.90728472	0.00000000	C	2.17281076	4.11487172	-1.45490100
S	-1.74235824	2.91296572	-1.45178000	H	0.21468476	5.04366872	-1.51242500
O	-2.11241124	4.16965872	-2.15761700	C	2.89229176	2.91357172	-1.44008700
O	-2.11154824	1.66141472	-2.16708100	H	2.71513776	0.76756272	-1.44812600
C	0.07495076	2.91348572	-1.49205700	H	2.71524576	5.05903372	-1.44820400
C	0.77926376	1.70908772	-1.48270200	C	4.40259876	2.91269572	-1.44811700
C	0.77889676	4.11760272	-1.48266800	H	4.80593176	2.05056972	-0.90586400
C	2.17274476	1.71180072	-1.45489700	H	4.80382376	2.86618872	-2.46977300
H	0.21517276	0.78294372	-1.51265200	H	4.80553776	3.81969072	-0.98510500

Indole

C	-1.27152322	1.98723247	0.15639859	C	-1.26920922	0.56311347	0.15634759

C	-0.08715422	-0.18294053	0.15622359	H	2.04965178	-0.03083153	0.15594759
C	1.11282178	0.51762847	0.15608159	H	2.09211778	2.44109747	0.15579559
C	1.13586078	1.92716247	0.15599759	H	-0.01276522	3.75002147	0.15620259
C	-0.04042122	2.66434547	0.15614259	H	-4.48631422	1.14983247	0.15513159
C	-2.64753222	2.40225847	0.15612959	N	-2.58776822	0.15441647	0.15590859
C	-3.41239122	1.26581647	0.15608359	H	-3.01855022	3.41670447	0.15669959
H	-0.10479922	-1.26884653	0.15634359	H	-2.90060822	-0.80178753	0.15699759

Int-Si-Re

O	1.17975400	2.02401700	-0.66877600	C	1.98166000	-1.95895300	1.19532600
C	1.97760500	1.05967800	-1.04842400	C	1.79970000	-3.29547000	0.84623700
C	1.33789200	-0.17937500	-1.37563800	C	2.86655600	-3.95081300	0.23495600
C	2.02313100	-1.17826200	-2.10861200	C	4.07957300	-3.28688800	-0.02138400
H	3.04035800	-1.01920800	-2.44151900	C	4.26270700	-1.95306900	0.33976200
C	1.66960600	3.27939300	-0.08905500	C	3.00415100	0.07603400	1.42762300
H	1.86362700	3.02825900	0.96064600	C	1.70662700	0.13091600	1.93075200
C	3.40511900	1.35084900	-1.42267000	H	0.85794800	-3.79652700	1.04114300
H	4.01357800	0.47129400	-1.20817400	H	2.75970900	-4.99291100	-0.04934800
H	3.39873700	1.46869600	-2.51755600	H	4.89181300	-3.82895600	-0.49602300
C	0.07774200	-2.59393400	-1.96534800	H	5.21460600	-1.45999200	0.15954400
H	-0.40728000	-3.53933200	-2.18862800	H	3.75221800	0.84760300	1.52803200
C	0.01509000	-0.41653800	-0.93523600	H	1.14248200	0.94939700	2.35233000
H	-0.48423100	0.32349100	-0.32116300	N	1.09991900	-1.06914400	1.77849700
C	1.38964700	-2.37013500	-2.40515600	H	0.08971600	-1.24056200	2.01104000
H	1.91760700	-3.13914700	-2.95758900	O	-1.50555500	-1.35538300	2.28235200
C	-0.60772300	-1.62077800	-1.23744900	S	-2.17326900	-0.01417300	2.09956300
H	-1.61457900	-1.80145900	-0.88128900	O	-1.18261400	1.02995500	1.67905300
C	2.94619700	3.73146800	-0.77986000	O	-3.05879600	0.37457300	3.20743200
H	2.70577300	4.03251500	-1.80716200	C	-3.20825700	-0.27522700	0.64933300
H	3.32408400	4.61931600	-0.26382400	C	-3.25350900	0.67206800	-0.37020300
C	3.98532300	2.61312200	-0.78150400	C	-3.94786200	-1.45581300	0.54355500
H	4.29045000	2.39715000	0.24605700	C	-4.03568500	0.43332800	-1.50041700
H	4.88475700	2.91618000	-1.32430000	H	-2.65637800	1.57179900	-0.28581700
C	0.53600000	4.29158400	-0.18963800	C	-4.72577900	-1.68189800	-0.58810100
H	0.88024800	5.16925300	0.37748000	H	-3.88561700	-2.19500200	1.33448700
H	0.43147600	4.61749200	-1.23142800	C	-4.78380400	-0.74147900	-1.62765900
C	-0.79005800	3.82239700	0.34777900	H	-4.05886000	1.16984500	-2.29969800
H	-0.78284600	3.16702600	1.21581300	H	-5.29399900	-2.60487800	-0.67268600
C	-1.95577700	4.17021600	-0.19507000	C	-5.64855600	-0.98635900	-2.83920700
H	-2.01668200	4.79623400	-1.08308000	H	-5.63344100	-2.03972300	-3.13604900
H	-2.89411600	3.84422700	0.24110300	H	-6.69401800	-0.72293600	-2.63727800
C	3.20817100	-1.26878500	0.96280000	H	-5.31949000	-0.38732500	-3.69299300

Int-Re-Re

O	-2.95945000	-0.87247200	-1.25430500	C	-0.64706500	1.50083300	1.85465400
C	-1.67247600	-0.98425800	-1.07744800	C	-0.01285200	2.73990900	1.75108400
C	-0.93265700	0.23344400	-1.20527800	C	-0.80864000	3.85410300	1.50309100
C	0.47199000	0.22577000	-1.04546700	C	-2.20617000	3.73878100	1.36122100
H	0.98890300	-0.68500300	-0.76716200	C	-2.83861500	2.50598500	1.46801300
C	-3.91142000	-1.97441900	-1.05937300	C	-2.34646600	-0.03358100	1.89008200
H	-4.09022000	-2.37297800	-2.06554200	C	-1.13312000	-0.66198100	2.11301100
C	-1.01693100	-2.31140900	-0.89474200	H	1.06338100	2.82330200	1.85879400
H	-0.34786400	-2.44998400	-1.75315500	H	-0.34480700	4.83233400	1.42129400
H	-0.32185300	-2.23830300	-0.04870700	H	-2.79617800	4.63087600	1.17402500
C	0.51456200	2.59410300	-1.48729900	H	-3.91911500	2.43211900	1.37900500
H	1.07708400	3.51664100	-1.59281800	H	-3.32001000	-0.50018300	1.91247200
C	-1.60460100	1.44909700	-1.48661700	H	-0.90175600	-1.70066200	2.29865200
H	-2.68287500	1.45033200	-1.58155800	N	-0.12003200	0.25088900	2.08592800
C	1.18729000	1.40491900	-1.19752100	H	0.87681600	-0.01672500	2.22839400
H	2.26255000	1.39668600	-1.06797500	O	2.34387200	-0.75239900	2.47968000
C	-0.87863600	2.61505400	-1.63513300	S	2.71372600	-1.75681500	1.42426300
H	-1.39049900	3.54942800	-1.83368700	O	3.61059800	-2.82576400	1.88598400
C	-3.31435000	-3.04860000	-0.16941600	O	1.51112300	-2.24141900	0.66631800
H	-3.18034000	-2.65061000	0.84159700	C	3.62336400	-0.78326000	0.20952200
H	-4.02206400	-3.88076800	-0.10723600	C	3.72767000	-1.23214800	-1.10807800
C	-1.97691500	-3.50043100	-0.75319700	C	4.22320300	0.41676100	0.58730000
H	-2.15491700	-3.96506700	-1.72993100	C	4.41993200	-0.47087200	-2.04571300
H	-1.51057200	-4.25933900	-0.12108400	H	3.24466700	-2.16112700	-1.39150500
C	-5.17854200	-1.31074000	-0.52261900	C	4.92039300	1.16918500	-0.35829100
H	-5.91087000	-2.11140900	-0.35593300	H	4.11699800	0.75501700	1.61164000
H	-4.95327500	-0.86607900	0.45104400	C	5.02978900	0.73976200	-1.68665100
C	-5.73962700	-0.27124600	-1.45287500	H	4.48814500	-0.81673900	-3.07404100
H	-6.14443900	-0.63834900	-2.39600600	H	5.38193800	2.10779500	-0.06228900
C	-5.74887300	1.03578700	-1.19733800	C	5.80267600	1.54385100	-2.70236000
H	-5.34347500	1.43518800	-0.27162300	H	5.33189300	1.50116700	-3.68939400
H	-6.16169000	1.75184200	-1.90071900	H	5.88005500	2.59386900	-2.40658700
C	-2.06423800	1.36001300	1.72126700	H	6.82381300	1.15950100	-2.81404300

Int-Si-Si

O	3.15446400	1.48274600	0.49064900	H	0.70787400	2.44099700	1.79999200
C	1.91950200	1.12714900	0.75127300	C	1.46033800	-2.79171700	2.23033800
C	1.77439500	-0.19310900	1.27742700	H	1.34119600	-3.80999100	2.58834500
C	0.49775700	-0.66372100	1.65145300	C	2.90145200	-1.04592500	1.39531800
H	-0.38283900	-0.04308700	1.56922200	H	3.87588200	-0.68569400	1.09296400
C	3.51130100	2.71901400	-0.20234100	C	0.34488900	-1.96010500	2.12224600
H	3.43478500	2.46844800	-1.26692100	H	-0.65375900	-2.29782300	2.37411600
C	0.81416500	2.13636300	0.74615400	C	2.73766000	-2.32965700	1.87799400
H	-0.13905400	1.67047300	0.47505400	H	3.59321700	-2.99124500	1.95241400

C	2.54456100	3.84214000	0.12711700	H	4.73399900	-3.45506000	-1.47671300
H	2.67998000	4.14918300	1.17185200	H	4.45777900	-1.05825100	-2.05180900
H	2.79129500	4.70431000	-0.50074100	H	2.30175200	1.05819900	-2.43086200
C	1.11073600	3.36593500	-0.11059000	H	-0.36867300	0.87729300	-1.87426500
H	0.97572800	3.11382100	-1.16822000	N	0.06486100	-1.13727200	-1.44144000
H	0.38946200	4.15215600	0.12428500	H	-0.89540400	-1.39241400	-1.13319700
C	4.96956800	2.97548700	0.16621300	O	-2.48113900	-1.46216200	-0.54312300
H	5.26378100	3.91142400	-0.32717600	S	-2.75069400	-0.29834200	0.36964300
H	5.04019600	3.14093800	1.24683800	O	-2.61177000	-0.63421400	1.80897700
C	5.87897900	1.85513100	-0.25746600	O	-1.97915700	0.91966400	-0.04579500
H	5.93407900	1.66695900	-1.32988200	C	-4.47454900	0.12230700	0.11693700
C	6.58439800	1.09568200	0.57830900	C	-4.83761900	0.95844900	-0.93769700
H	6.55016000	1.25129500	1.65355600	C	-5.44539300	-0.42047800	0.95594300
H	7.22523800	0.29685500	0.21934000	C	-6.18304800	1.24424200	-1.15351500
C	2.30729900	-1.10199700	-1.78065200	H	-4.06489500	1.39115900	-1.56286900
C	1.19945900	-1.92250300	-1.40854700	C	-6.78825200	-0.12696800	0.72900900
C	1.34809000	-3.27088700	-1.08521500	H	-5.13670700	-1.04799400	1.78414600
C	2.63404600	-3.80294100	-1.12250100	C	-7.17842000	0.70246600	-0.32957800
C	3.74459300	-3.00788900	-1.46459300	H	-6.46766300	1.90221100	-1.97064100
C	3.59409300	-1.66373500	-1.79128500	H	-7.54654400	-0.54359700	1.38692700
C	1.77166400	0.20402500	-2.03574600	C	-8.63651700	0.98914200	-0.58995900
C	0.40276500	0.12433600	-1.81924000	H	-9.22243800	0.95173800	0.33301300
H	0.49005600	-3.87455000	-0.81006800	H	-8.77598900	1.97548800	-1.04219500
H	2.78434100	-4.85001900	-0.87829100	H	-9.06640100	0.25145400	-1.27891000

Int-Re-Si

O	3.05607200	0.78976500	1.30430800	C	2.62659200	-1.53775700	2.05618100
C	1.80203600	0.98604200	1.05815900	H	2.57912800	-2.01002100	1.07144300
C	1.51876400	2.18461600	0.30170700	H	3.01048600	-2.28502900	2.75803700
C	0.18611900	2.58888700	0.08967800	C	1.24431300	-1.03753500	2.47013900
H	-0.64708000	2.04980800	0.52425000	H	1.27617200	-0.63046900	3.48806200
C	3.61031000	-0.38533700	2.02438500	H	0.51618000	-1.85100300	2.46962000
H	3.78895100	0.00926900	3.03125800	C	4.92914100	-0.69569800	1.32385100
C	0.76499200	0.02861300	1.48900600	H	5.38979000	-1.51604800	1.89115600
H	-0.13551600	0.55074600	1.83336200	H	4.70716700	-1.08307600	0.32579800
H	0.41126400	-0.44904000	0.56288000	C	5.86548100	0.47693000	1.24762200
C	0.97828000	4.40893800	-1.28358200	H	6.20540700	0.89133700	2.19716100
H	0.76914600	5.26867500	-1.91310100	C	6.28410900	1.02166000	0.10607000
C	2.58351200	2.91700800	-0.27358800	H	5.96165300	0.63270900	-0.85644100
H	3.60364900	2.58746800	-0.11470100	H	6.96930100	1.86340700	0.09150600
C	-0.07395500	3.69545300	-0.71118400	C	2.41070800	-1.43031700	-1.85767200
H	-1.10402600	3.97911200	-0.89339900	C	1.23148600	-2.08295500	-1.38060700
C	2.30827400	4.02261400	-1.05884200	C	1.26296800	-3.36276300	-0.81685500
H	3.12029800	4.58214400	-1.51125300	C	2.49495200	-4.00506800	-0.74115300

C	3.66928500	-3.38894500	-1.22241300	O	-2.19482600	0.90936600	-1.04667100
C	3.63677300	-2.11548600	-1.78121900	C	-4.31766600	-0.04054900	0.18792600
C	1.99724500	-0.13746900	-2.32628700	C	-4.99813100	-0.21270600	1.39243500
C	0.63677000	-0.05609200	-2.13194800	C	-5.00418300	-0.06595100	-1.02437300
H	0.35362400	-3.83093600	-0.45367200	C	-6.37531700	-0.41681700	1.37637200
H	2.55315100	-4.99983000	-0.31040600	H	-4.44670700	-0.17222900	2.32491200
H	4.61227100	-3.92403300	-1.16142400	C	-6.38200200	-0.27128200	-1.02600600
H	4.54631600	-1.65938000	-2.16394000	H	-4.45563200	0.08641900	-1.94691500
H	2.62401800	0.62924000	-2.75835300	C	-7.08778600	-0.44952900	0.17033600
H	-0.06108700	0.74792400	-2.30889300	H	-6.90872200	-0.55048200	2.31398700
N	0.17153200	-1.22674900	-1.57755600	H	-6.92002600	-0.29105200	-1.97022000
H	-0.75877300	-1.32927800	-1.14837900	C	-8.58465800	-0.63742600	0.16375900
O	-1.96334000	-1.23614600	0.18621900	H	-8.92409900	-1.10772600	-0.76360600
S	-2.53668400	0.15541500	0.19202100	H	-8.91286600	-1.25997700	1.00131600
O	-2.21585800	0.89207100	1.45345900	H	-9.10404600	0.32503900	0.25060200

TS-Si-Re

O	-1.44805800	1.91730300	0.63824800	C	0.30538200	3.85551500	-0.46893800
C	-2.18076100	0.80234900	0.82974200	H	0.28497600	3.29164200	-1.39831100
C	-1.35890200	-0.31300100	1.33109700	C	1.48664700	4.19260300	0.04484000
C	-1.93628300	-1.36964800	2.05846600	H	1.57326300	4.73800400	0.98214800
H	-2.99169900	-1.36144900	2.29765400	H	2.40849400	3.93607200	-0.46595900
C	-2.06356200	3.11057000	0.09351000	C	-2.99913400	-1.32705400	-0.93486400
H	-2.29678200	2.88976200	-0.95784700	C	-1.79150500	-1.99039500	-1.26087800
C	-3.57609500	1.00330700	1.39628300	C	-1.60238400	-3.35285700	-1.07077000
H	-4.17307300	0.10388200	1.24179400	C	-2.67889500	-4.07548600	-0.55451500
H	-3.43643800	1.10711900	2.48179700	C	-3.89451100	-3.44621200	-0.24879100
C	0.20133200	-2.48664300	2.14839300	C	-4.06675100	-2.07184500	-0.43312800
H	0.80410100	-3.33561500	2.45629700	C	-2.74811900	0.09955400	-1.13471200
C	0.01426600	-0.35569500	1.02895700	C	-1.45504800	0.16134500	-1.74075600
H	0.46102500	0.44232000	0.44895300	H	-0.65605500	-3.82440100	-1.31053600
C	-1.15992000	-2.44802700	2.46141000	H	-2.57561900	-5.14342000	-0.39288000
H	-1.61804500	-3.26294800	3.01229600	H	-4.71786600	-4.03991000	0.13562200
C	0.78790200	-1.43761700	1.44126000	H	-5.01605400	-1.60079700	-0.19516000
H	1.84138500	-1.46313200	1.19230800	H	-3.51853900	0.82743400	-1.34786400
C	-3.34286900	3.44537900	0.85038100	H	-0.86505100	1.01363300	-2.04789400
H	-3.07644000	3.72574800	1.87688700	N	-0.89198200	-1.03526900	-1.75049800
H	-3.81587300	4.31717400	0.38719700	H	0.15227300	-1.18472700	-2.00251900
C	-4.29270000	2.24702600	0.86343900	O	1.62244400	-1.25859000	-2.27383600
H	-4.67012000	2.06507300	-0.14895000	S	2.30176200	0.09207900	-2.12065700
H	-5.16857000	2.45365700	1.48562700	O	1.30467100	1.15558500	-1.78892800
C	-1.01358800	4.21482800	0.15980700	O	3.22877500	0.40238000	-3.21713500
H	-1.45222800	5.08313300	-0.35365600	C	3.27695900	-0.11226700	-0.62537700
H	-0.86520600	4.50952500	1.20522300	C	3.25487300	0.86483300	0.36636900

C	4.03763800	-1.27120500	-0.45669700	H	3.96082600	1.43216200	2.31509000
C	3.99129700	0.67526800	1.53565300	H	5.35352200	-2.35419600	0.84966600
H	2.63788400	1.74467400	0.22952300	C	5.57300800	-0.66931400	2.98358900
C	4.76942200	-1.44754500	0.71384300	H	5.59163400	-1.71887000	3.29283200
H	4.02853600	-2.03318000	-1.22807500	H	6.61370800	-0.35897900	2.82928800
C	4.75904000	-0.47813600	1.72815300	H	5.17462500	-0.07696800	3.81206800

TS-Re-Re

O	3.04673000	-1.09163400	0.13308400	C	0.78342900	2.30049300	-1.12342400
C	1.71525700	-1.04753000	-0.07154700	C	0.45140700	3.44580600	-0.40724200
C	0.98393500	-0.16870700	0.79264200	C	1.48511700	4.10444600	0.25892100
C	-0.42369600	-0.05899700	0.70692300	C	2.80459500	3.62332900	0.21726700
H	-0.97140400	-0.63415600	-0.02922600	C	3.13006800	2.46993400	-0.49446400
C	3.64588100	-2.32819900	0.63551300	C	2.04700900	0.57015200	-1.92955700
H	3.36765100	-2.37785700	1.69858500	C	0.71334900	0.43205700	-2.34561300
C	1.12718300	-2.21149900	-0.81779600	H	-0.57146600	3.80334000	-0.36531100
H	0.04569300	-2.12694300	-0.91596800	H	1.26398400	5.00419000	0.82426600
H	1.54199600	-2.21978300	-1.83034600	H	3.58190200	4.15875600	0.75349800
C	-0.39378000	1.60543500	2.45216600	H	4.14688100	2.09017800	-0.50452200
H	-0.92770500	2.29922800	3.09467000	H	2.87880600	-0.03343200	-2.25767700
C	1.69019100	0.63345900	1.72557200	H	0.22572100	-0.35795300	-2.89712100
H	2.76799800	0.55453800	1.77446500	N	-0.02993700	1.43241700	-1.84510600
C	-1.10326600	0.81386100	1.54780700	H	-1.08068600	1.42609800	-1.93872100
H	-2.18206000	0.88683200	1.47694300	O	-2.62121000	1.05710800	-2.19133500
C	1.00157600	1.50997900	2.54309500	S	-2.98815100	-0.39910400	-2.03546700
H	1.54430800	2.13395900	3.24502400	O	-3.97658000	-0.87267900	-3.01393800
C	3.10143500	-3.55553100	-0.08150000	O	-1.77027700	-1.26446000	-1.89755000
H	3.50042700	-3.58815200	-1.10296100	C	-3.75726700	-0.45773200	-0.40817600
H	3.46402100	-4.44825100	0.43969900	C	-3.63591800	-1.59969900	0.38249600
C	1.57143000	-3.51534900	-0.12499700	C	-4.46951100	0.64636100	0.06102100
H	1.15973900	-3.56235100	0.89062300	C	-4.21676600	-1.62863000	1.64842800
H	1.17169800	-4.37104400	-0.67572900	H	-3.06539400	-2.44254300	0.00860000
C	5.15204700	-2.12758300	0.50339000	C	-5.05040800	0.60487000	1.32708300
H	5.63558700	-3.04823800	0.85659200	H	-4.53496100	1.53350100	-0.55855100
H	5.39754500	-2.01566500	-0.55841000	C	-4.93376400	-0.53058000	2.14019300
C	5.65262800	-0.94495100	1.28478400	H	-4.10873800	-2.51488400	2.26849100
H	5.53443100	-1.00458500	2.36704600	H	-5.59751700	1.46927000	1.69470400
C	6.20061800	0.14226900	0.74519100	C	-5.58486900	-0.57845800	3.50003600
H	6.33249400	0.23683900	-0.32970100	H	-5.02418900	-1.21576700	4.19018900
H	6.54481900	0.97138000	1.35514000	H	-5.66175500	0.41896200	3.94260800
C	2.11417600	1.79955400	-1.18669800	H	-6.60166300	-0.98475500	3.43513100

TS-Si-Si

O	3.35900800	1.25901900	0.45797500	C	2.02893000	0.98952400	0.51744500

C	1.77671600	-0.28672600	1.21732000	C	1.29876300	-3.08878500	-1.43915700
C	0.47357300	-0.63933600	1.60013700	C	2.60570300	-3.56825200	-1.53863700
H	-0.36076000	0.03012700	1.43904700	C	3.69199500	-2.69261400	-1.67909500
C	3.84184600	2.48104600	-0.14075600	C	3.50955400	-1.30817100	-1.71413600
H	3.72262900	2.38189500	-1.22945200	C	1.64863000	0.53463200	-1.48085600
C	1.12408600	2.17086000	0.83309300	C	0.23257400	0.33559900	-1.46585600
H	0.07819600	1.92452600	0.64525300	H	0.45276400	-3.75518700	-1.31427000
H	1.21803100	2.31677100	1.91854700	H	2.78363200	-4.63801100	-1.50189100
C	1.26778500	-2.77788100	2.38347000	H	4.69560600	-3.10003200	-1.75037700
H	1.07182500	-3.75155900	2.82280900	H	4.36044900	-0.63893900	-1.77676000
C	2.83211800	-1.18797500	1.45046600	H	2.08394700	1.41851200	-1.92697000
H	3.83791900	-0.91417700	1.16101500	H	-0.57256500	1.05062200	-1.36355400
C	0.22040300	-1.88187500	2.17694200	N	-0.04943200	-0.95517700	-1.40628400
H	-0.80492700	-2.12498200	2.43179400	H	-1.04360400	-1.26672900	-1.17243300
C	2.57403400	-2.42306300	2.02968600	O	-2.54686300	-1.27772200	-0.72403000
H	3.39127200	-3.11783500	2.19681300	S	-2.87010200	-0.26491600	0.35504100
C	3.04886200	3.69054300	0.33846800	O	-2.76864100	-0.81880900	1.72253900
H	3.25533600	3.85433700	1.40355900	O	-2.11512000	1.01242500	0.14289700
H	3.39621600	4.57708800	-0.20251700	C	-4.59442800	0.14199800	0.09440500
C	1.55042000	3.45759600	0.12658900	C	-4.94344400	1.14636800	-0.80644000
H	1.32964400	3.39762000	-0.94610500	C	-5.57769400	-0.57374000	0.77456700
H	0.96858700	4.29726700	0.51669000	C	-6.28874700	1.42714400	-1.03068700
C	5.33264000	2.53064600	0.19459200	H	-4.16191400	1.70981300	-1.30314900
H	5.71778900	3.49562700	-0.15988400	C	-6.91958300	-0.28333600	0.54035100
H	5.44306800	2.51256200	1.28407200	H	-5.28110700	-1.33193000	1.49022700
C	6.10612600	1.40439500	-0.43230600	C	-7.29612700	0.71437900	-0.36764000
H	6.17399500	1.42276400	-1.52077400	H	-6.56359900	2.21589900	-1.72620400
C	6.68095700	0.40895900	0.24050900	H	-7.68833200	-0.83489800	1.07518100
H	6.63134000	0.35496700	1.32488200	C	-8.75197900	1.00110800	-0.63970100
H	7.22340700	-0.38360800	-0.26519200	H	-9.37023300	0.79979700	0.23995100
C	2.21159800	-0.81016100	-1.62577700	H	-8.90642200	2.04344100	-0.93335300
C	1.12966600	-1.71171700	-1.49592700	H	-9.13145800	0.37285800	-1.45510200

TS-Re-Si

O	3.27686600	0.64533800	0.43383700	C	0.67837200	4.63576400	-0.97831200
C	1.93483300	0.76506900	0.33128100	H	0.36463400	5.61969100	-1.31336600
C	1.48471800	2.09487000	-0.12255000	C	2.44052600	3.04781900	-0.52319700
C	0.11821900	2.42857600	-0.16027300	H	3.49075700	2.78213200	-0.49949000
H	-0.64699000	1.71400000	0.11752800	C	-0.27412000	3.69223600	-0.58844100
C	3.92593600	0.43238400	1.72697800	H	-1.33239400	3.92705500	-0.62500200
H	3.97398500	1.43009300	2.18797600	C	2.03694600	4.31005500	-0.94318700
C	1.09618900	-0.07422500	1.25418000	H	2.78061900	5.04077400	-1.24565100
H	0.04862000	0.22360300	1.23953800	C	3.12987600	-0.49534700	2.62868700
H	1.13489600	-1.11542700	0.92178400	H	3.18890600	-1.51951000	2.24054500

H	3.59241300	-0.48860800	3.62185200	H	4.51114400	-1.50282500	-1.26832200
C	1.67308200	-0.04045200	2.67930600	H	2.39864000	0.49162500	-2.09985700
H	1.60255500	0.97110600	3.09774900	H	-0.34250500	0.28218400	-1.87844200
H	1.07261100	-0.69489500	3.31619400	N	0.08331600	-1.68439900	-1.32130200
C	5.33687400	-0.05570100	1.42141000	H	-0.91878500	-1.89230500	-1.05160200
H	5.85337700	-0.14231800	2.38780800	O	-2.42037300	-1.71056300	-0.47161400
H	5.28208200	-1.06071100	0.99203700	S	-2.70820600	-0.26416200	-0.14189500
C	6.10178200	0.86535100	0.51403200	O	-2.10053100	0.16068000	1.15012300
H	6.14152100	1.91137600	0.82005800	O	-2.39183100	0.64353400	-1.28183600
C	6.71896900	0.48927700	-0.60445800	C	-4.48134200	-0.18559100	0.08643100
H	6.70732800	-0.54473200	-0.94007200	C	-5.02581200	-0.42050400	1.34753100
H	7.26770700	1.19471500	-1.22010700	C	-5.30538500	0.07452400	-1.00691700
C	2.35722000	-1.61467000	-1.29529200	C	-6.40902800	-0.40130900	1.50816100
C	1.23102000	-2.44347700	-1.05912300	H	-4.36380000	-0.60375200	2.18615600
C	1.34984300	-3.75811200	-0.61745900	C	-6.68683400	0.09116700	-0.83157400
C	2.64130400	-4.24523300	-0.41478200	H	-4.85706100	0.27059800	-1.97418400
C	3.77105200	-3.44170100	-0.64819200	C	-7.25937500	-0.14596900	0.42469000
C	3.64167900	-2.12420400	-1.08690800	H	-6.83746100	-0.58451700	2.49012200
C	1.84335200	-0.30149400	-1.62324600	H	-7.33277900	0.29372400	-1.68191600
C	0.43408700	-0.44950700	-1.68898600	C	-8.75521400	-0.09305300	0.61330700
H	0.47453000	-4.37182000	-0.43448800	H	-9.28337900	-0.39258800	-0.29657500
H	2.77576100	-5.26656000	-0.07358700	H	-9.07875700	-0.74908900	1.42661900
H	4.76034400	-3.85961200	-0.48921400	H	-9.08610100	0.92279400	0.86268700

Int-S-R

O	2.09271530	2.03311255	0.00000000	H	-0.33330170	0.91174155	0.39656200
C	2.97141030	0.90417955	-0.01875300	H	-0.74738670	0.79583355	-1.32050800
C	3.96644330	1.14532355	1.11506400	C	0.92291530	-0.46618145	-0.71030000
C	4.67206630	0.08564555	1.69841900	H	1.23337630	-0.62214645	-1.75217500
H	4.53699330	-0.92668245	1.33670200	H	0.32338930	-1.34041945	-0.43662300
C	0.97470030	2.02591355	-0.88931300	C	0.29032830	3.38020855	-0.68412600
H	1.32459130	1.97129455	-1.93352600	H	-0.65906070	3.37195755	-1.23446700
C	2.14927630	-0.38008845	0.20510000	H	0.05779930	3.48448255	0.38106300
H	2.77983330	-1.26356945	0.08449700	C	1.15590630	4.51923955	-1.14966200
H	1.82008430	-0.36482145	1.24953600	H	1.25060230	4.63454855	-2.23019200
C	5.75591130	1.61155355	3.23088200	C	1.82728330	5.34387955	-0.34652800
H	6.44829030	1.79183055	4.04710600	H	1.76327630	5.25511155	0.73482200
C	4.18876130	2.44435355	1.58712600	H	2.46215830	6.13353155	-0.73553400
H	3.66165430	3.27301055	1.13389100	C	4.89387230	-0.01633745	-1.60610100
C	5.55480530	0.31610955	2.75307400	C	5.98326130	0.79365955	-1.97623100
H	6.08297030	-0.51977445	3.20224300	C	7.23706330	0.27235955	-2.26384300
C	5.07731630	2.67523955	2.63679900	C	7.39315730	-1.11305945	-2.17541300
H	5.25193330	3.69205655	2.97098400	C	6.31771630	-1.93494045	-1.82390600
C	0.08802630	0.81571155	-0.61191900	C	5.05522830	-1.39457545	-1.54505500

C	3.71643730	0.90691155	-1.39814800	C	8.53777530	2.98784355	-0.27382900
C	4.36572230	2.24531755	-1.66861000	C	9.78686030	2.74246855	-0.84402900
H	8.06315430	0.92448555	-2.52242100	C	7.91286230	2.03592155	0.52778800
H	8.36160430	-1.55569145	-2.38514600	C	10.40308430	1.51400155	-0.61568300
H	6.46045730	-3.00962345	-1.76962500	H	10.26300730	3.50432655	-1.45123700
H	4.22935530	-2.05153645	-1.29263100	C	8.54728130	0.81899655	0.75375500
H	2.96940130	0.72419855	-2.18262900	H	6.94238030	2.24689855	0.95384300
H	3.85751830	3.19857655	-1.57424800	C	9.79095430	0.53401955	0.17799300
N	5.60861630	2.16390555	-2.00098300	H	11.37395830	1.31185555	-1.05922500
H	6.58112530	3.46886255	-2.17549000	H	8.05194030	0.07396055	1.36831900
O	7.23176430	4.25664355	-2.17069300	C	10.43557030	-0.81186845	0.39146100
S	7.68412330	4.51167255	-0.65297100	H	9.82594930	-1.60653145	-0.05437100
O	6.49703330	4.58630655	0.20517700	H	11.43081930	-0.85815145	-0.05764500
O	8.65110930	5.60318255	-0.68718900	H	10.53375130	-1.04200245	1.45759300

Int-R-R

O	3.52317893	2.23178805	0.00000000	H	6.28330693	1.84180905	1.92810600
C	2.11701793	2.27042005	0.27165400	C	6.83782493	3.33391105	0.56850500
C	1.84076193	2.12983105	1.77203900	H	6.86266193	3.68862205	-0.45876200
C	0.57489893	1.78262405	2.25618100	H	7.28691493	3.97660805	1.31946500
H	-0.23772207	1.56289505	1.57567500	C	2.20023893	4.82719805	0.66996500
C	4.17267793	0.96870205	0.20190900	C	1.06087593	5.49140105	1.15324200
H	4.05758893	0.66788005	1.25383600	C	1.14588493	6.56180005	2.03349800
C	1.40510193	1.20910405	-0.59000100	C	2.42537693	6.96577405	2.42774300
H	0.33753293	1.17707105	-0.36276600	C	3.56667993	6.31482305	1.94668900
H	1.50165393	1.51543605	-1.63869900	C	3.46708893	5.23495305	1.05988600
C	1.34203793	2.02224805	4.53916500	C	1.71563593	3.70304805	-0.21028500
H	1.14817793	1.98045305	5.60659500	C	0.22641193	3.94195205	-0.16390300
C	2.84883793	2.43615105	2.69596400	H	0.25303893	7.06101805	2.39403100
H	3.82252793	2.73624105	2.33104900	H	2.53394193	7.79933405	3.11440000
C	0.32866693	1.72960405	3.62902400	H	4.54741393	6.65140805	2.26842800
H	-0.66364407	1.46696005	3.97789300	H	4.34966993	4.71524405	0.70410400
C	2.60469593	2.37887505	4.06566200	H	2.08599293	3.78586705	-1.23984500
H	3.40086793	2.62181905	4.76289000	H	-0.52124907	3.38454605	-0.71494300
C	3.53951893	-0.10625895	-0.67762000	N	-0.12132507	4.91723905	0.60647500
H	3.72110793	0.14110205	-1.73156800	H	-1.68993207	5.13126005	0.86580300
H	4.01876693	-1.07119895	-0.47763400	O	-2.70944707	5.12713205	1.03564000
C	2.03334993	-0.17482195	-0.40766000	S	-3.43250007	4.10900605	0.04565400
H	1.85794693	-0.52183795	0.61809700	O	-4.86318507	4.36952505	0.13519100
H	1.55108093	-0.89533095	-1.07651300	O	-2.75440507	4.10971605	-1.25797500
C	5.65345493	1.21265505	-0.09045900	C	-3.07472707	2.52417005	0.79792800
H	6.16527093	0.24138305	-0.05122000	C	-3.27972307	2.33653505	2.16487300
H	5.75095093	1.59485905	-1.11266200	C	-2.63238707	1.47635905	-0.00791400
C	6.28957593	2.16146705	0.88522900	C	-3.01313707	1.09167205	2.72572200

H	-3.62999207	3.15942905	2.77759900	H	-2.00502607	-0.57837595	-0.05183500
C	-2.36150107	0.23713405	0.57103300	C	-2.15763707	-1.28189095	2.58371200
H	-2.50019707	1.64257305	-1.07092700	H	-1.14015607	-1.22716795	2.99026000
C	-2.53321807	0.02965205	1.94508400	H	-2.82737607	-1.53189995	3.41136800
H	-3.17003907	0.94110905	3.79020400	H	-2.18184007	-2.10227395	1.86182600

Int-S-S

O	3.00612974	2.74785144	0.07532804	C	6.09561574	0.72346344	2.37970204
C	3.61143074	1.46673244	-0.13098496	C	6.47300274	0.62089844	3.71283904
C	2.78610674	0.46220644	0.66390004	C	5.89495574	1.51876544	4.61441604
C	3.09030874	-0.90246356	0.59564304	C	4.96926374	2.47570944	4.18169904
H	3.89986374	-1.25273656	-0.03640096	C	4.59757574	2.57088944	2.83458204
C	3.53497174	3.85150144	-0.66255096	C	5.05789774	1.52066544	0.44348604
H	4.57775774	4.03296344	-0.35388196	C	5.97344574	0.34382444	0.22209804
C	3.59582174	1.13016544	-1.63604596	H	7.19167974	-0.12641156	4.03161204
H	4.10392574	0.17947844	-1.81764096	H	6.16302174	1.46945844	5.66516404
H	2.54691774	0.98722744	-1.91745396	H	4.52541374	3.15279644	4.90535504
C	1.32466774	-1.40589456	2.16634404	H	3.87080774	3.30293044	2.50430504
H	0.76091974	-2.12749856	2.74947904	H	5.58142874	2.35253744	-0.04751796
C	1.73960774	0.88122244	1.49027904	H	6.23657774	-0.06352556	-0.74740196
H	1.50602874	1.93603844	1.54760404	N	6.57347074	-0.06135256	1.29438704
C	2.36737374	-1.83034656	1.34276904	H	8.22434674	-0.33361056	1.17911704
H	2.62050974	-2.88414656	1.28006104	O	9.22187574	-0.15435356	1.11658504
C	1.01404874	-0.04854056	2.23490204	S	9.48046374	1.00142044	0.03111204
H	0.20511874	0.29227644	2.87429404	O	10.92332074	1.19220144	-0.02518196
C	3.50686374	3.57602544	-2.16542796	O	8.72205974	0.71523844	-1.19345596
H	2.46028274	3.53001944	-2.49264696	C	8.69614074	2.41817744	0.79388704
H	3.98077774	4.40901444	-2.69662496	C	8.77306474	2.61447244	2.17313304
C	4.20395174	2.25028344	-2.48501996	C	8.01880774	3.32535444	-0.01924996
H	5.28103974	2.33662144	-2.29230096	C	8.13045974	3.70860644	2.74079004
H	4.10163974	2.00911444	-3.54776096	H	9.29813874	1.89712044	2.79228004
C	2.69453574	5.06643444	-0.26138896	C	7.38759174	4.42263144	0.56512804
H	2.98574274	5.90072244	-0.91391496	H	7.97579374	3.15537844	-1.08921796
H	1.64230274	4.84085544	-0.46559296	C	7.41660974	4.61925744	1.95092504
C	2.87801874	5.46053244	1.17569304	H	8.15736274	3.84243444	3.81745504
H	3.88197674	5.78211744	1.45360004	H	6.85747774	5.13229744	-0.06409596
C	1.92403174	5.43403244	2.10535104	C	6.66454974	5.75564044	2.59226604
H	0.91186274	5.11527944	1.87025604	H	5.75212274	5.38052144	3.07025704
H	2.11736774	5.73219844	3.13127404	H	7.26088374	6.24360044	3.36901904
C	5.17728674	1.68781244	1.93501504	H	6.37619074	6.51322644	1.85863004

Int-R-S

O	2.87417229	2.52317877	0.00000000	C	2.83191329	4.95402277	-0.17466600
C	2.00986029	3.66384877	-0.08697400	C	2.32888129	6.19147077	0.24665500

H	1.33721829	6.26799677	0.67902800	C	-1.83358371	0.57951077	-1.80588800
C	3.60498229	2.39606877	1.22786100	C	-0.58250771	0.07162177	-1.43946100
H	4.24203629	3.28458677	1.35492100	C	0.52998029	0.91348977	-1.30451000
C	1.00677829	3.64157677	1.07620800	C	1.29312129	3.45055677	-1.45651300
H	0.35831129	4.51784477	1.03571800	C	0.34704929	4.57148477	-1.81422900
H	0.36690129	2.76575977	0.93576200	H	-2.98067971	2.35311277	-2.31387200
C	4.35573429	7.29395977	-0.48841300	H	-2.67785471	-0.09534323	-1.90670000
H	4.94468829	8.19826777	-0.60664800	H	-0.47160571	-0.99279823	-1.25670900
C	4.10161729	4.90591177	-0.76546300	H	1.49873229	0.52942277	-1.00801200
H	4.49003729	3.94749077	-1.09406200	H	2.09578029	3.38550977	-2.20316800
C	3.08810929	7.35243477	0.08910100	H	0.61562229	5.62132977	-1.83319400
H	2.68166929	8.30338377	0.41924100	N	-0.85943471	4.18353477	-2.05789500
C	4.85964929	6.06520477	-0.91734600	H	-2.01986571	5.29910777	-1.86975100
H	5.84417029	6.00879277	-1.37226600	O	-2.68374171	6.01340677	-1.54836500
C	2.65078129	2.30955477	2.41660500	S	-2.68319871	6.02754077	0.05131300
H	2.06202529	1.38662677	2.33234400	O	-1.30330971	6.12482877	0.55221800
H	3.23009129	2.24872577	3.34490700	O	-3.67514571	7.01233177	0.46221700
C	1.71863129	3.52577877	2.42605000	C	-3.26197171	4.37485077	0.41190200
H	2.30072329	4.43435377	2.62161800	C	-2.54754071	3.57409477	1.29963600
H	0.98105629	3.44261977	3.23146600	C	-4.41237471	3.89772177	-0.21666200
C	4.49451129	1.16371677	1.05838600	C	-2.96900071	2.26790477	1.52821400
H	4.98923129	0.97347777	2.02025000	H	-1.66910371	3.97306377	1.78855000
H	3.85665229	0.29907277	0.84160200	C	-4.82305671	2.58993677	0.02611200
C	5.52329729	1.33912777	-0.02205300	H	-4.96279571	4.53600477	-0.89879400
H	6.27717829	2.10542877	0.16211300	C	-4.10044271	1.75139977	0.88552300
C	5.55563829	0.65545877	-1.16440800	H	-2.40349871	1.63514277	2.20627600
H	4.81636929	-0.10972523	-1.38736400	H	-5.71209371	2.20862577	-0.46803500
H	6.31919729	0.83103977	-1.91591000	C	-4.50276171	0.31357377	1.08711600
C	0.35710529	2.26990577	-1.53958000	H	-3.84786171	-0.34925823	0.50886200
C	-0.90609971	2.76851277	-1.90089000	H	-4.41798371	0.01739977	2.13695000
C	-2.01383971	1.94517077	-2.04600000	H	-5.53067371	0.13340677	0.76250300

P

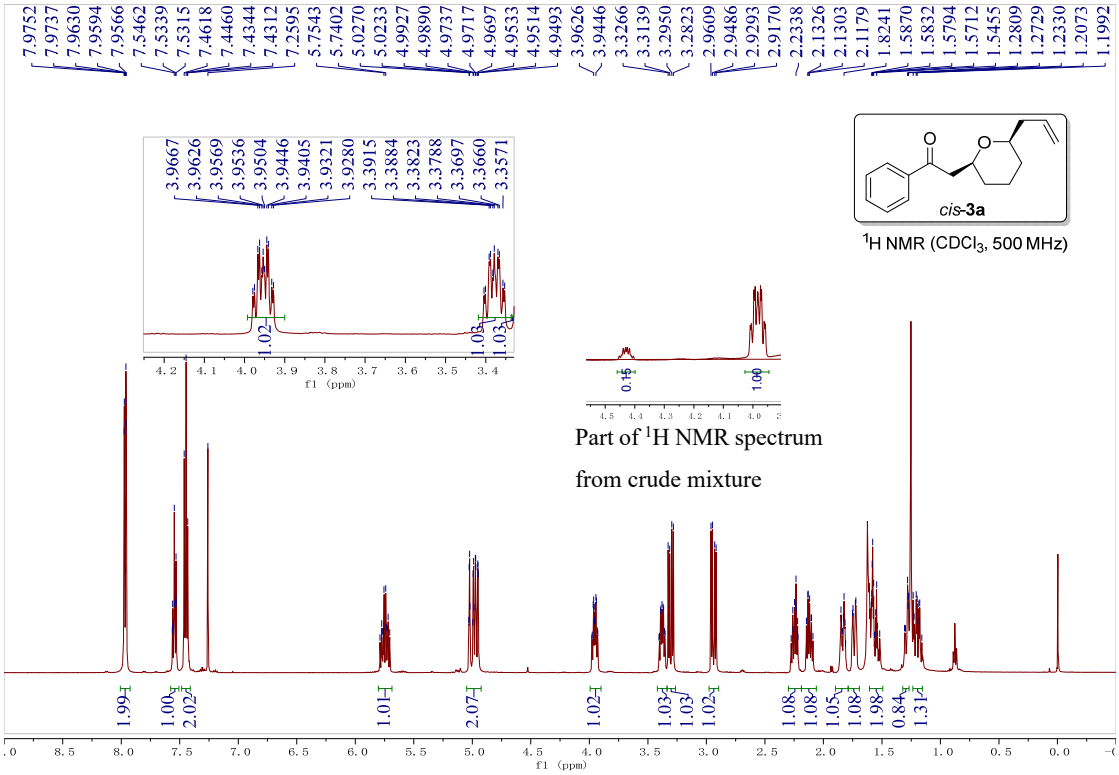
O	2.99337759	1.84768209	0.00000000	C	-1.15098241	-1.46846791	-1.14648800
N	0.50861359	-1.30490091	2.17757200	C	1.69666659	-0.61368491	2.34375300
C	1.08828859	-0.44416491	0.17519100	H	2.17054859	-0.57221891	3.31296000
C	2.09093559	-0.07004491	1.14563600	C	-0.18717541	-0.71144291	-1.84342300
C	0.10754659	-1.21281591	0.85837400	H	-0.32358041	-0.52890491	-2.90491500
C	3.33805459	0.72256609	0.82861800	C	-1.01867141	-1.73076991	0.21192700
C	4.30862059	-0.12231791	0.00045500	H	-1.76053141	-2.31493691	0.74833200
C	4.60328859	-1.43214291	0.39269100	C	2.15396459	2.82391909	0.61654400
H	4.09011959	-1.85951391	1.24837600	H	1.22437159	2.33614909	0.94950100
C	0.93040559	-0.19783791	-1.19878300	C	4.06640459	1.24305609	2.08968900
H	1.66456159	0.39566309	-1.72854700	H	4.29806759	0.40507909	2.75532500

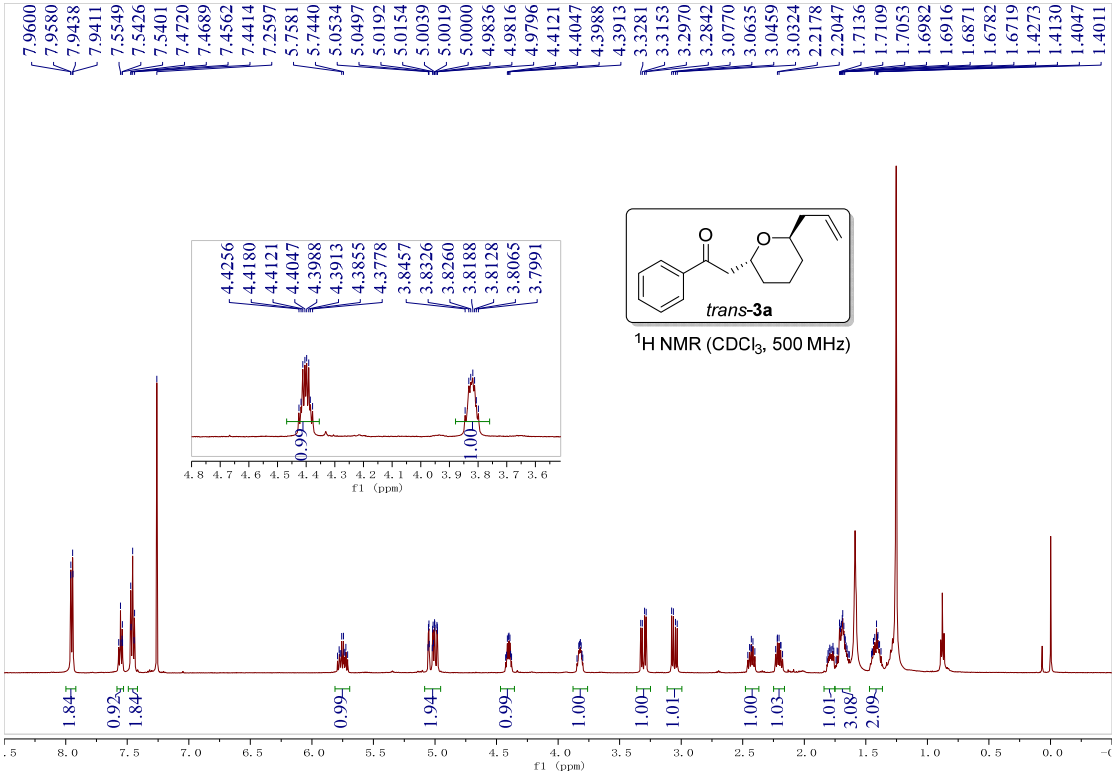
H	5.02508859	1.65261209	1.75410500	H	2.36795159	1.90408809	3.26517800
C	6.16540659	-1.65899591	-1.43758500	H	3.86665059	2.75289109	3.63100500
H	6.88050859	-2.25477091	-1.99688400	C	1.81948759	3.85032909	-0.46602000
C	4.95187059	0.41178409	-1.11967600	H	1.21387959	4.63815009	0.00425800
H	4.71545859	1.42222309	-1.42738400	H	2.74836959	4.31791209	-0.81276900
C	5.52776959	-2.19496291	-0.31765600	C	1.07249559	3.25743309	-1.62608300
H	5.74312559	-3.21160791	-0.00204300	H	0.15272659	2.72810409	-1.37851200
C	5.87148159	-0.35556991	-1.83600200	C	1.46412259	3.32152309	-2.89727900
H	6.35757359	0.06835409	-2.71000000	H	2.38474259	3.82383209	-3.18395200
C	2.85848359	3.43422009	1.82805800	H	0.88219959	2.87313709	-3.69672800
H	3.74815859	3.97336109	1.47744900	H	-2.01367941	-1.85508891	-1.68039900
H	2.19982959	4.16484809	2.31175700	H	0.00880059	-1.78354791	2.90781200
C	3.26866359	2.33457909	2.81377900				

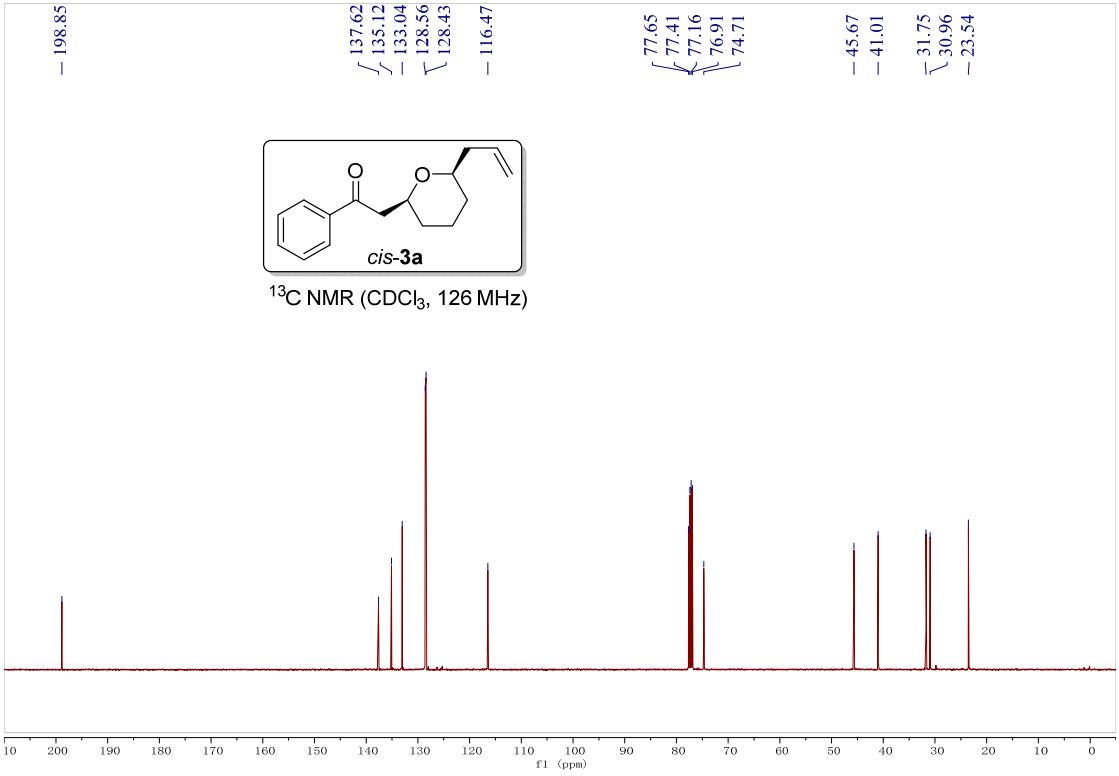
dia-P

O	2.10596034	1.31788078	0.00000000	C	1.57016534	4.32475778	1.90011700
C	2.03986134	-0.11412722	-0.12529400	H	0.95067834	4.70441878	1.09171300
C	2.62238134	-0.77298622	1.13920600	H	1.22188434	4.50913678	2.91182100
C	3.27128534	-2.01126222	1.11367700	C	-0.53023866	0.24243378	0.43751100
H	3.42186434	-2.53029222	0.17343100	C	-1.70692366	-0.51455222	0.17324500
C	3.42583634	1.86890278	0.03342100	C	-2.96933866	-0.12903322	0.63390100
H	3.98355434	1.42377878	0.87203700	C	-3.04952966	1.04081478	1.37825300
C	2.76022734	-0.51758322	-1.42881500	C	-1.89985066	1.81017678	1.64773900
H	2.75814034	-1.60390422	-1.55504200	C	-0.64836666	1.42885078	1.18400800
H	2.16720634	-0.10324522	-2.25029100	C	0.56754034	-0.45359122	-0.19626200
C	3.54857634	-1.96449922	3.51641100	C	0.03294134	-1.56644522	-0.79746900
H	3.90760334	-2.42334522	4.43255600	H	-3.85294366	-0.72250122	0.41781400
C	2.43887234	-0.14205122	2.37710100	H	-4.01412166	1.36882278	1.75358900
H	1.93376634	0.81579378	2.40810900	H	-1.99737166	2.72481078	2.22500100
C	3.73193034	-2.60268022	2.29118900	H	0.22449434	2.04018278	1.37032900
H	4.23650334	-3.56345022	2.24682500	H	0.51906734	-2.35168122	-1.35651600
C	2.89765134	-0.73022922	3.55305800	N	-1.33142866	-1.61035022	-0.57661900
H	2.74431234	-0.22360022	4.50146500	H	-1.95420666	-2.31745122	-0.92877000
C	4.16802034	1.55175678	-1.26327100				
H	3.65622634	2.05209278	-2.09553700				
H	5.18721334	1.95202778	-1.21272600				
C	4.18601234	0.03666278	-1.49292200				
H	4.80583434	-0.44087322	-0.72454900				
H	4.63790134	-0.20270622	-2.46162100				
C	3.25400834	3.36590478	0.29217300				
H	4.24108734	3.83746178	0.18633000				
H	2.60398234	3.78547178	-0.48357000				
C	2.69952934	3.66105378	1.65665500				
H	3.28714534	3.28529978	2.49528900				

Copies of ^{1}H, ^{13}C, and ^{19}F spectra charts of compounds 3 and 8



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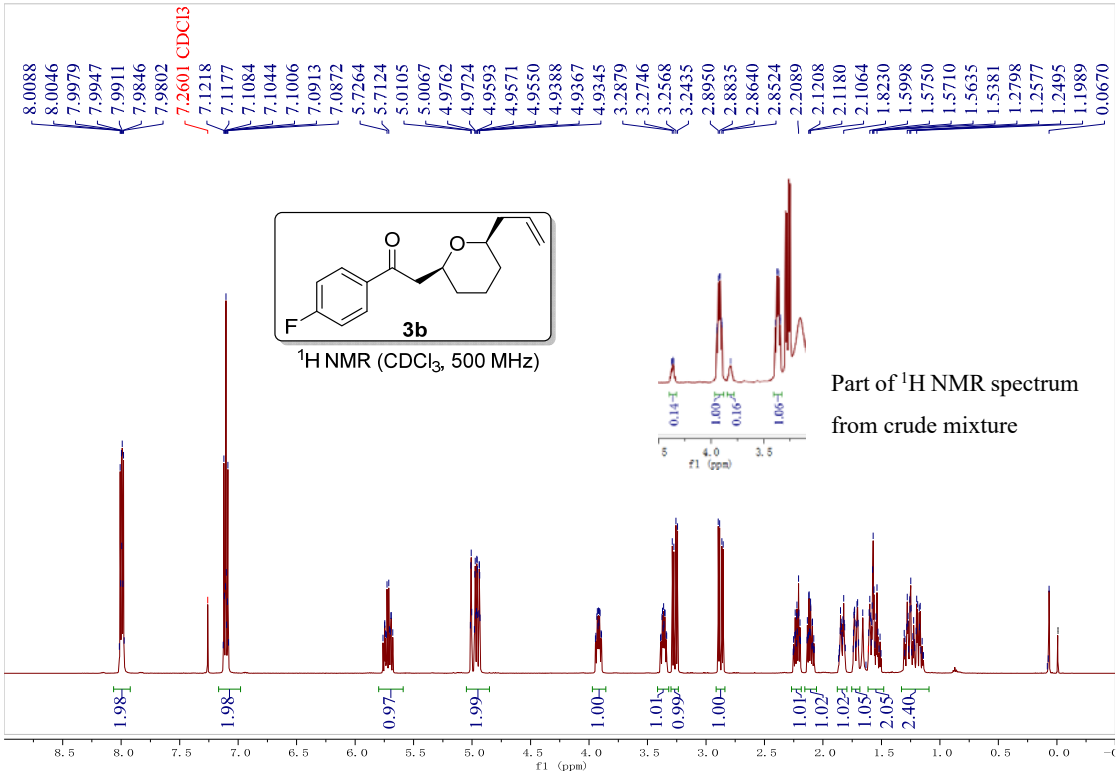
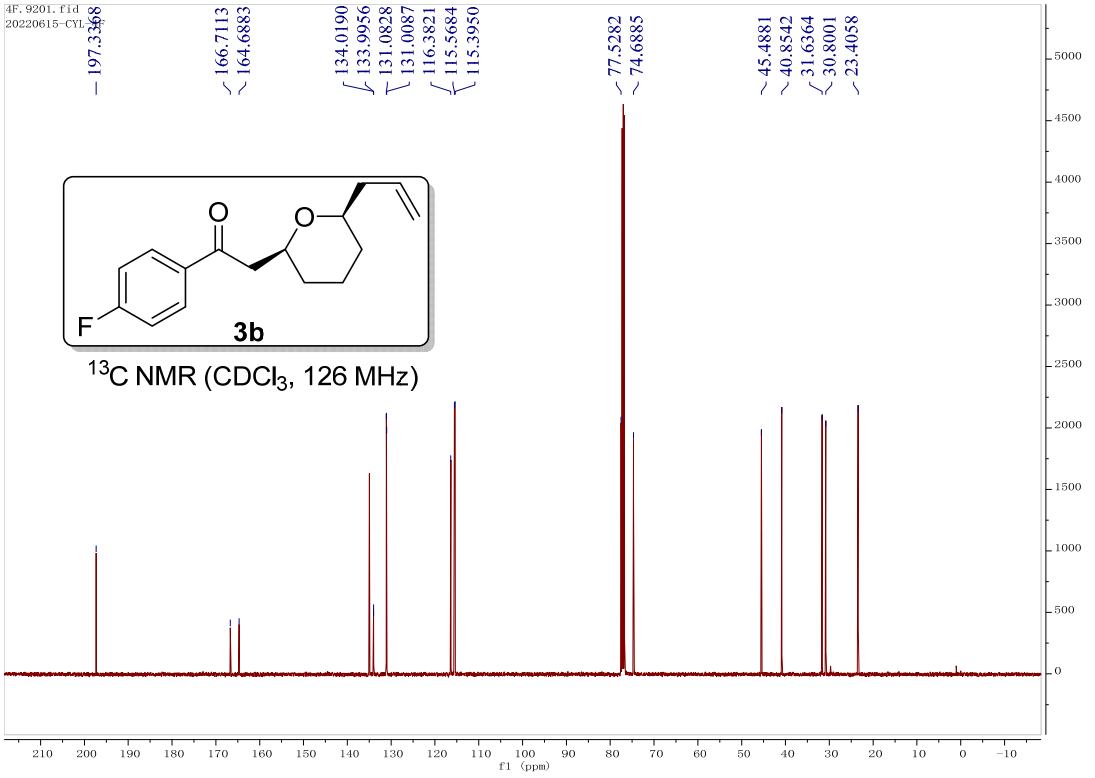
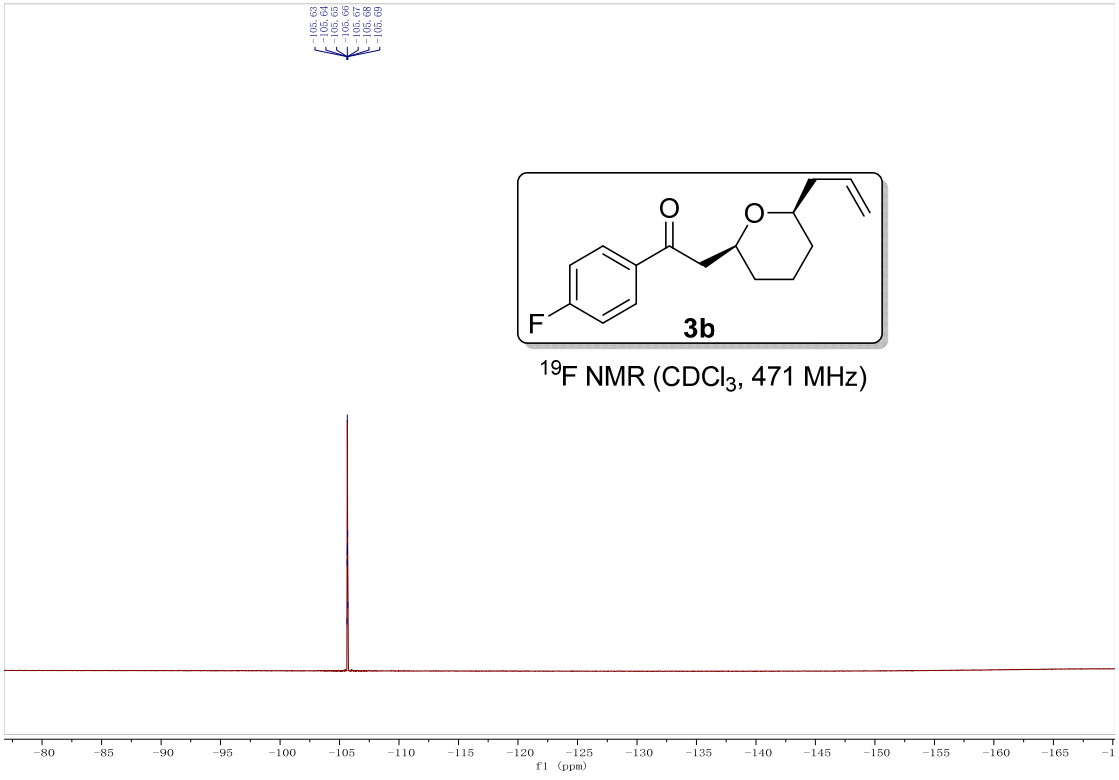
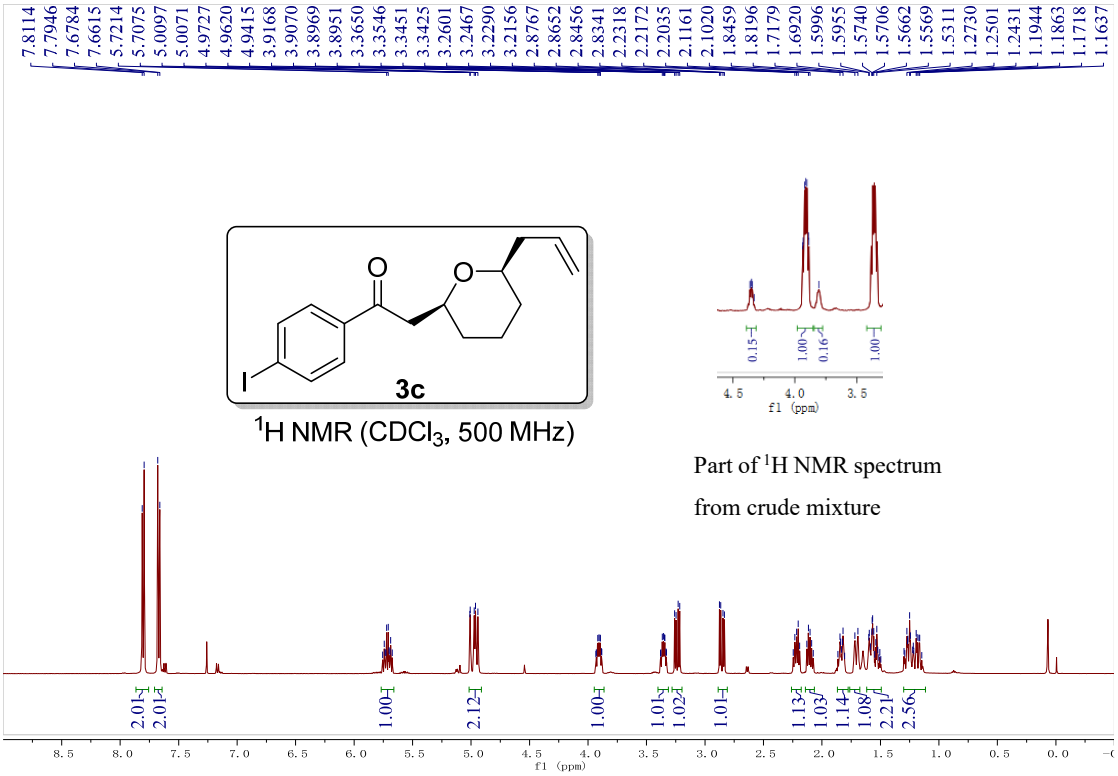
135.12
133.04
128.56
128.43
116.47
77.65
77.41
77.16
76.91
74.71
45.67
41.01
31.75
30.96
23.54
cis-3a
13C NMR (CDCl3, 126 MHz)
f1 (ppm)


8.0088
8.0046
7.9979
7.9947
7.9911
7.9846
7.9802
7.2601 CDCl3
7.1218
7.1177
7.1084
7.1044
7.1006
7.0913
7.0872
5.7264
5.7124
5.0105
5.0067
4.9762
4.9724
4.9593
4.9571
4.9550
4.9388
4.9367
4.9345
3.2879
3.2746
3.2568
3.2435
2.8950
2.8835
2.8640
2.8524
2.2089
2.1208
2.1180
2.1064
1.8230
1.5998
1.5750
1.5710
1.5635
1.5381
1.2798
1.2577
1.2495
1.1989
0.0670
3b
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
1.98
1.98
0.97
1.99
1.00
1.01
0.99
1.00
1.01
1.02
1.02
1.05
2.05
2.40
f1 (ppm)

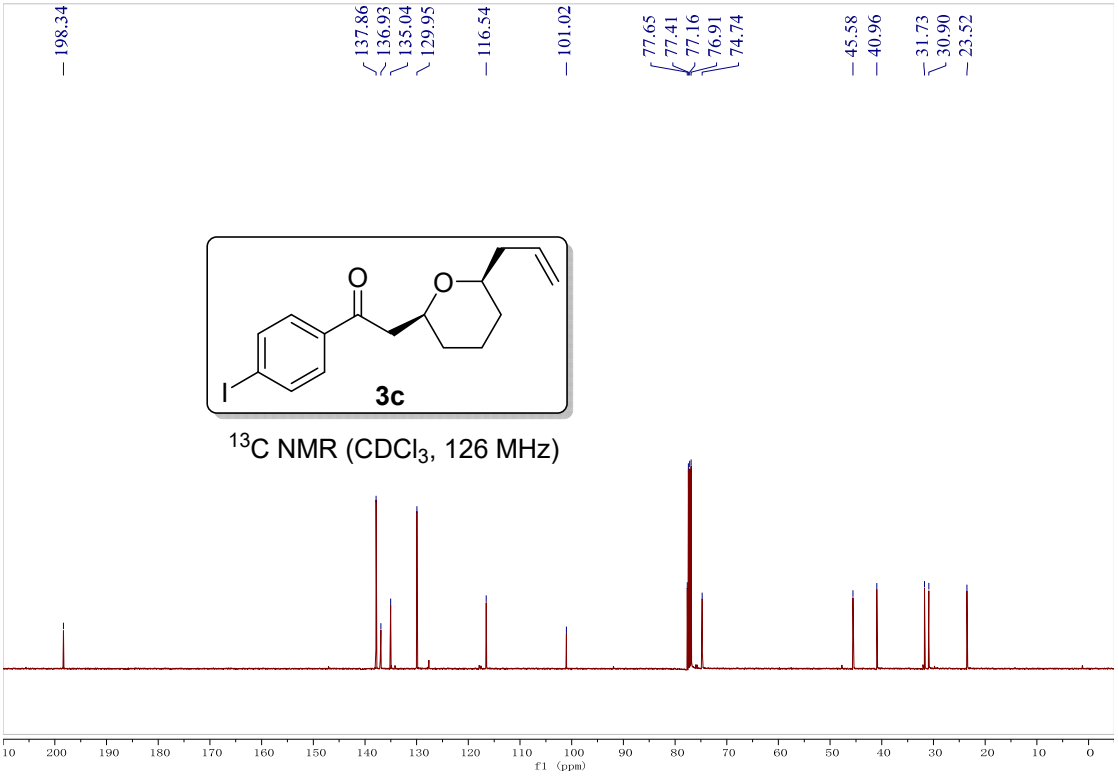

4F.9201.fid
20220615-CYL-4F
197.3368
166.7113
164.6883
134.0190
133.9956
131.0828
131.0087
116.3821
115.5684
115.3950
77.5282
74.6885
45.4881
40.8542
31.6364
30.8001
23.4058
O
O
F
3b
13C NMR (CDCl3, 126 MHz)
f1 (ppm)


-105.63
-105.64
-105.65
-105.66
-105.67
-105.68
-105.69
O
O
F
3b
19F NMR (CDCl3, 471 MHz)
f1 (ppm)

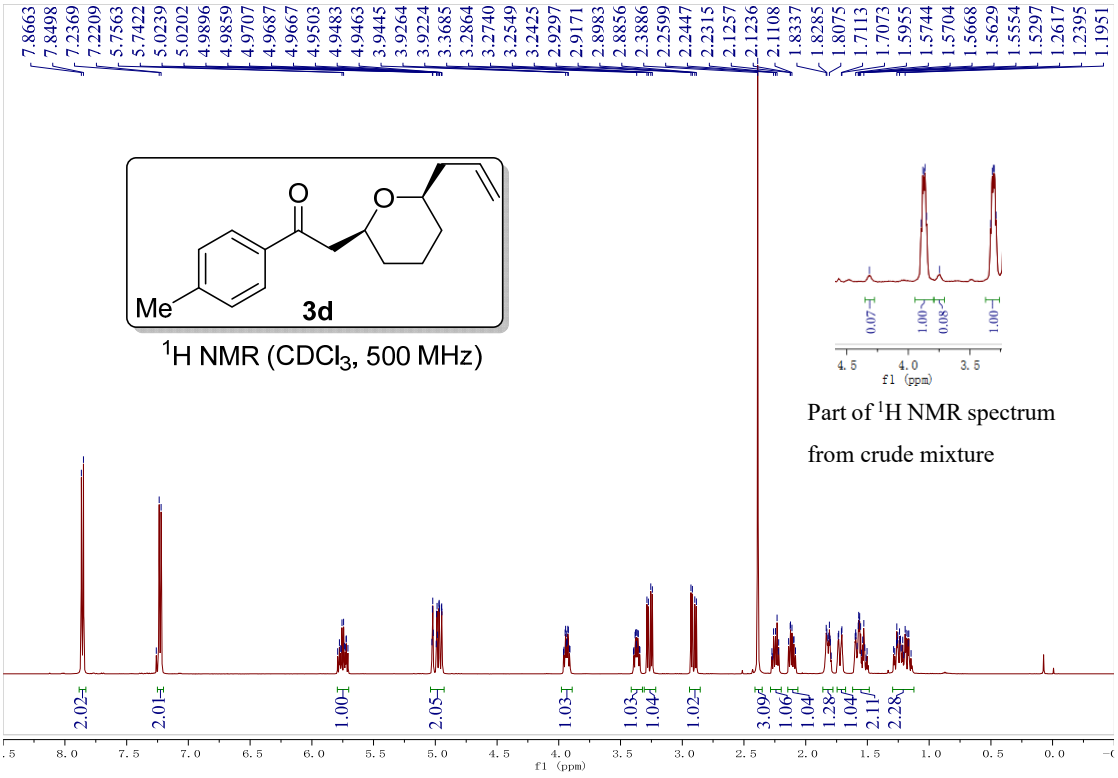


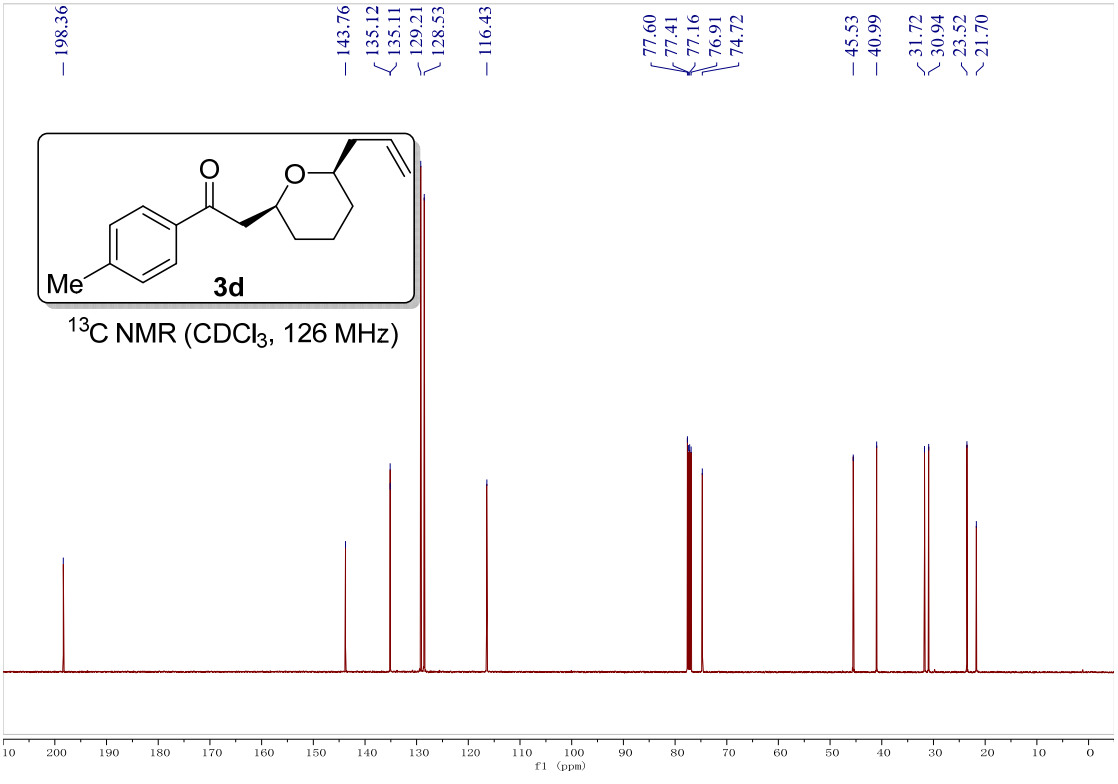
^{1}H NMR ($CDCl_3$, 500 MHz)

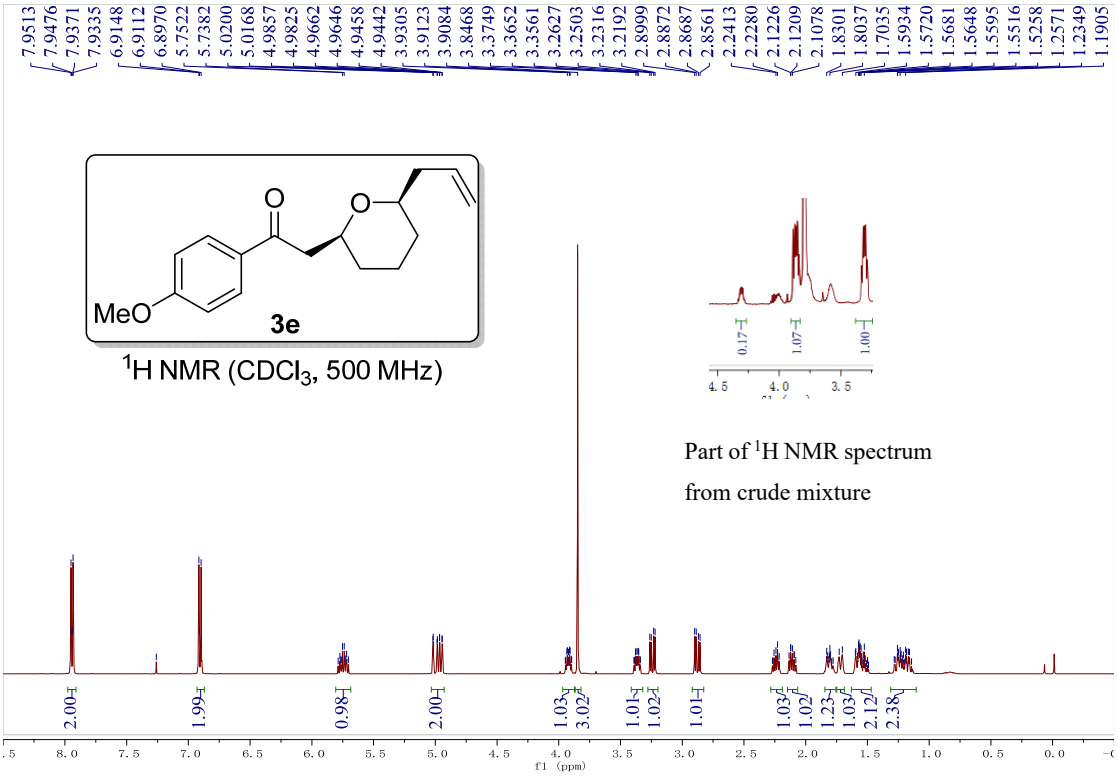
Part of ^{1}H NMR spectrum from crude mixture



^{13}C NMR ($CDCl_3$, 126 MHz)


Me
3d
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
f1 (ppm)


Me
3d
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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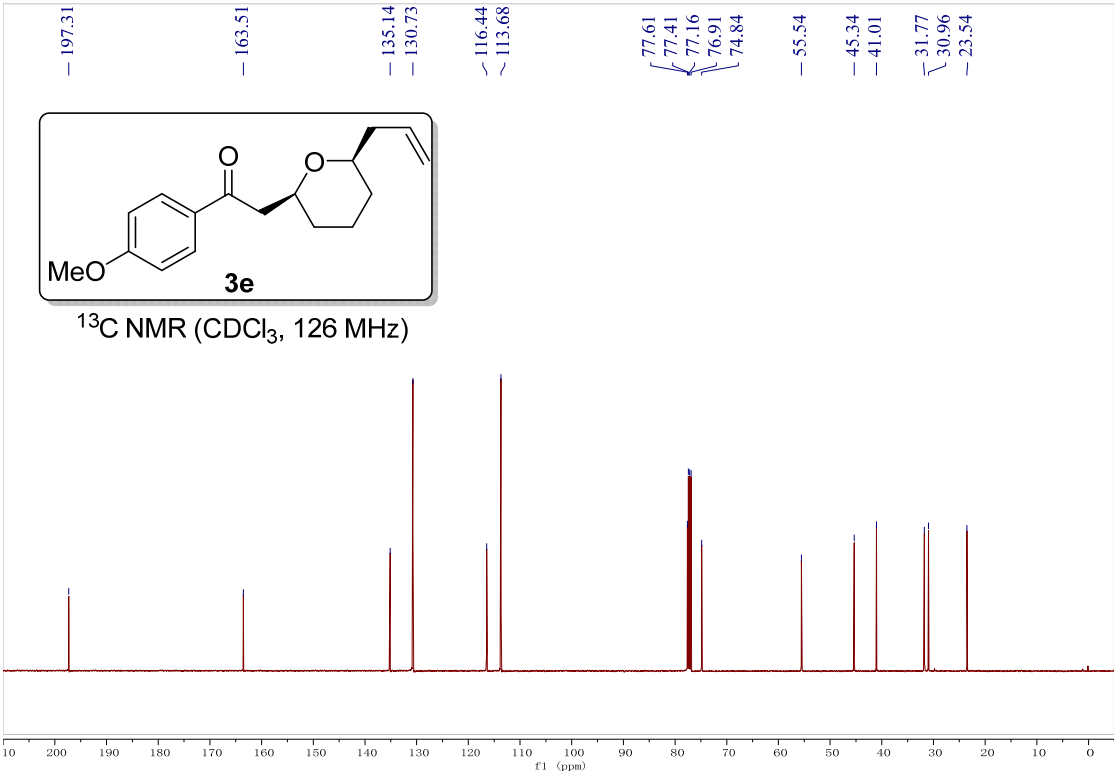
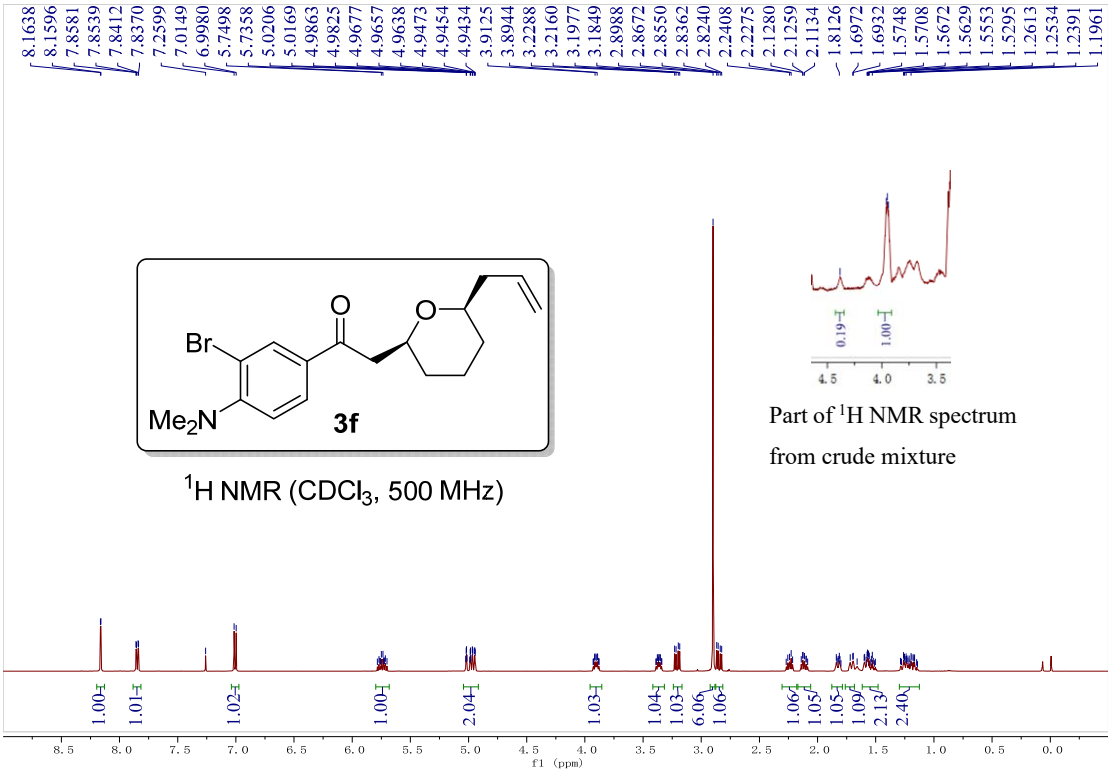
7.9476
7.9371
7.9335
6.9148
6.9112
6.8970
5.7522
5.7382
5.0200
5.0168
4.9857
4.9825
4.9662
4.9646
4.9458
4.9442
3.9305
3.9123
3.9084
3.8468
3.3749
3.3652
3.3561
3.2627
3.2503
3.2316
3.2192
2.8999
2.8872
2.8687
2.8561
2.2413
2.2280
2.1226
2.1209
2.1078
1.8301
1.8037
1.7035
1.5934
1.5720
1.5681
1.5648
1.5595
1.5516
1.5258
1.2571
1.2349
1.1905
MeO
3e
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
f1 (ppm)


197.31
163.51
135.14
130.73
116.44
113.68
77.61
77.41
77.16
76.91
74.84
55.54
45.34
41.01
31.77
30.96
23.54
MeO
3e
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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7.8581
7.8539
7.8412
7.8370
7.2599
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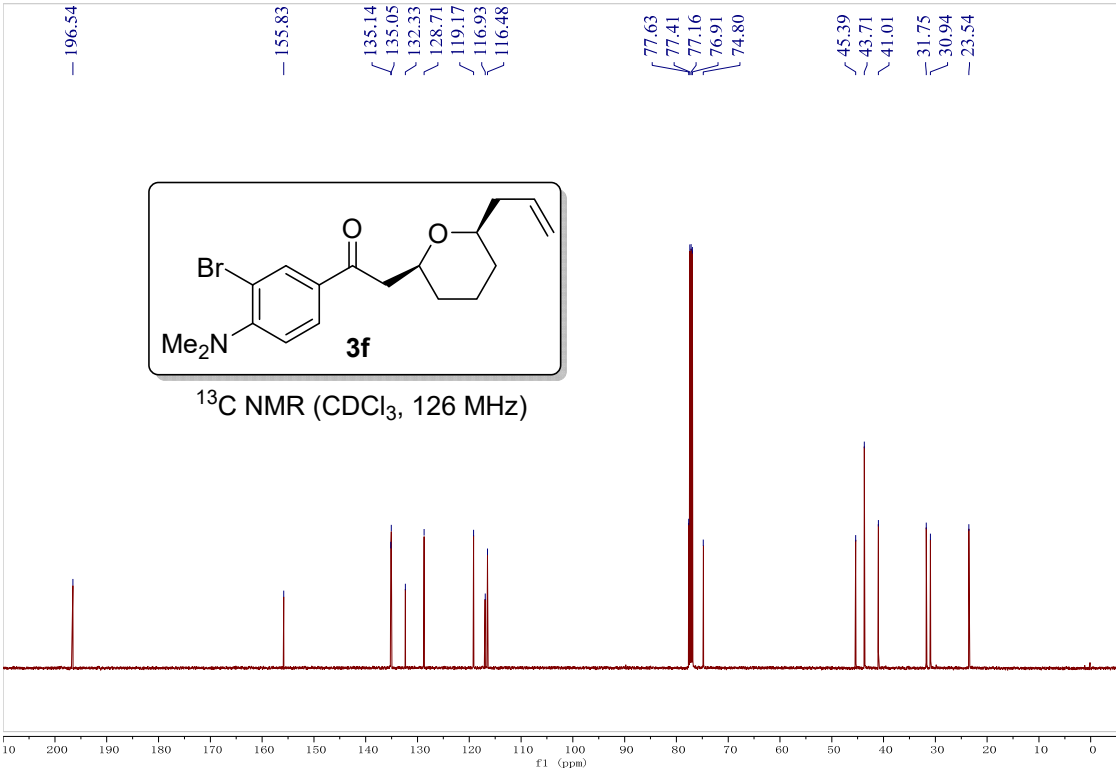
6.9980
5.7498
5.7358
5.0206
5.0169
4.9863
4.9825
4.9677
4.9657
4.9638
4.9473
4.9454
4.9434
3.9125
3.8944
3.2288
3.2160
3.1977
3.1849
2.8988
2.8672
2.8550
2.8362
2.8240
2.2408
2.2275
2.1280
2.1259
2.1134
1.8126
1.6972
1.6932
1.5748
1.5708
1.5672
1.5629
1.5553
1.5295
1.2613
1.2534
1.2391
1.1961
Br
O
O
Me2N
3f
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
1.00
1.01
1.02
1.00
2.04
1.03
1.04
1.03
6.06
1.06
1.06
1.05
1.05
1.09
2.13
2.40
f1 (ppm)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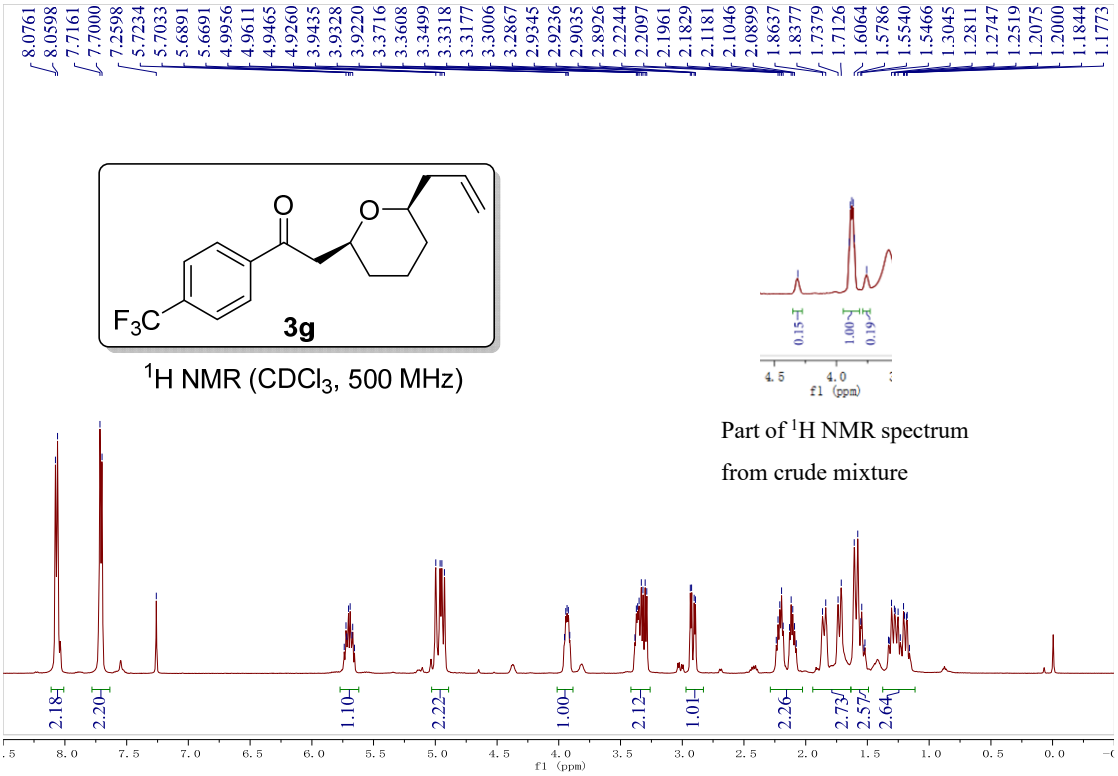
155.83
135.14
135.05
132.33
128.71
119.17
116.93
116.48
77.63
77.41
77.16
76.91
74.80
45.39
43.71
41.01
31.75
30.94
23.54
Br
O
O
Me2N
3f
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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7.2598
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5.6691
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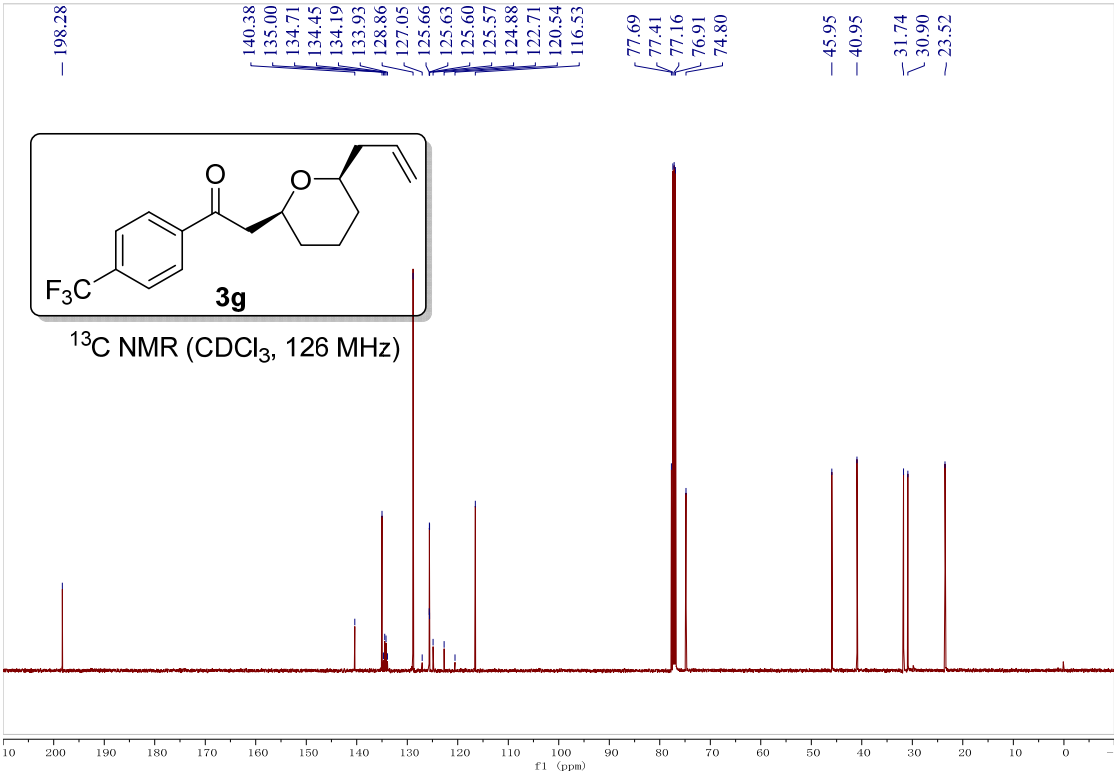
4.9611
4.9465
4.9260
3.9435
3.9328
3.9220
3.3716
3.3608
3.3499
3.3318
3.3177
3.3006
3.2867
2.9345
2.9236
2.9035
2.8926
2.2244
2.2097
2.1961
2.1829
2.1181
2.1046
2.0899
1.8637
1.8377
1.7379
1.7126
1.6064
1.5786
1.5540
1.5466
1.3045
1.2811
1.2747
1.2519
1.2075
1.2000
1.1844
1.1773
O
O
F3C
3g
1H NMR (CDCl3, 500 MHz)
0.15
1.00
0.19
4.5
4.0
f1 (ppm)
Part of 1H NMR spectrum
from crude mixture
2.18
2.20
1.10
2.22
1.00
2.12
1.01
2.26
2.73
2.57
2.64
f1 (ppm)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140.38
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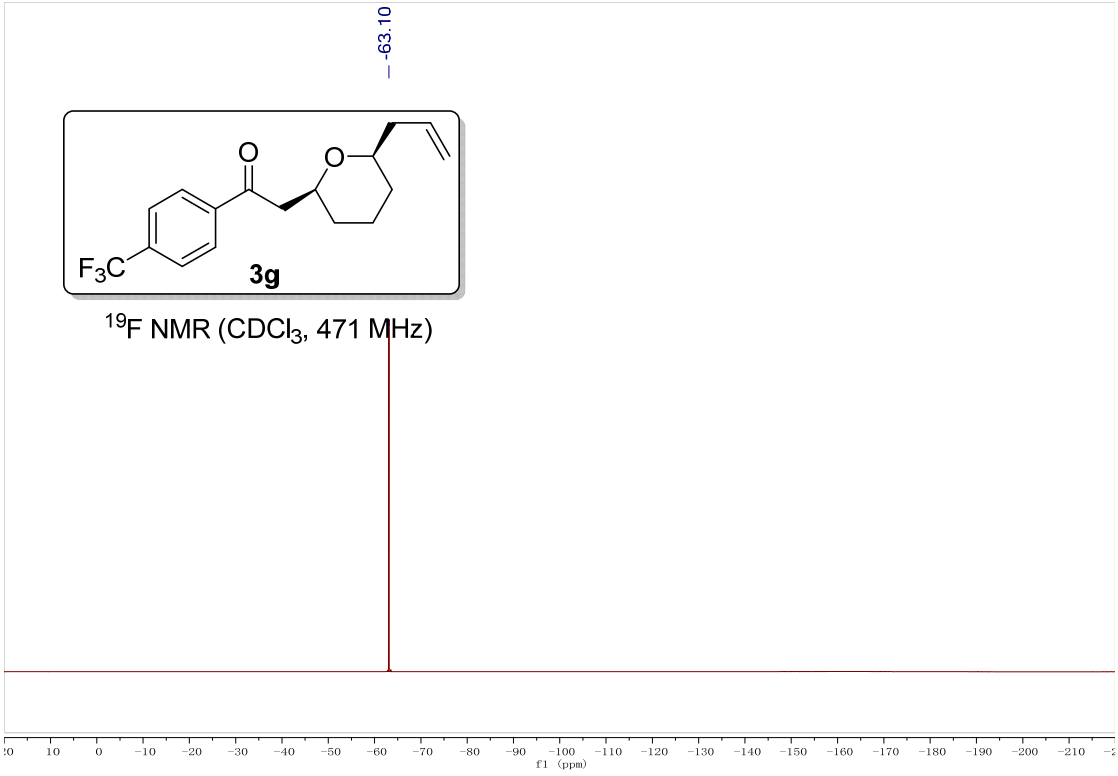
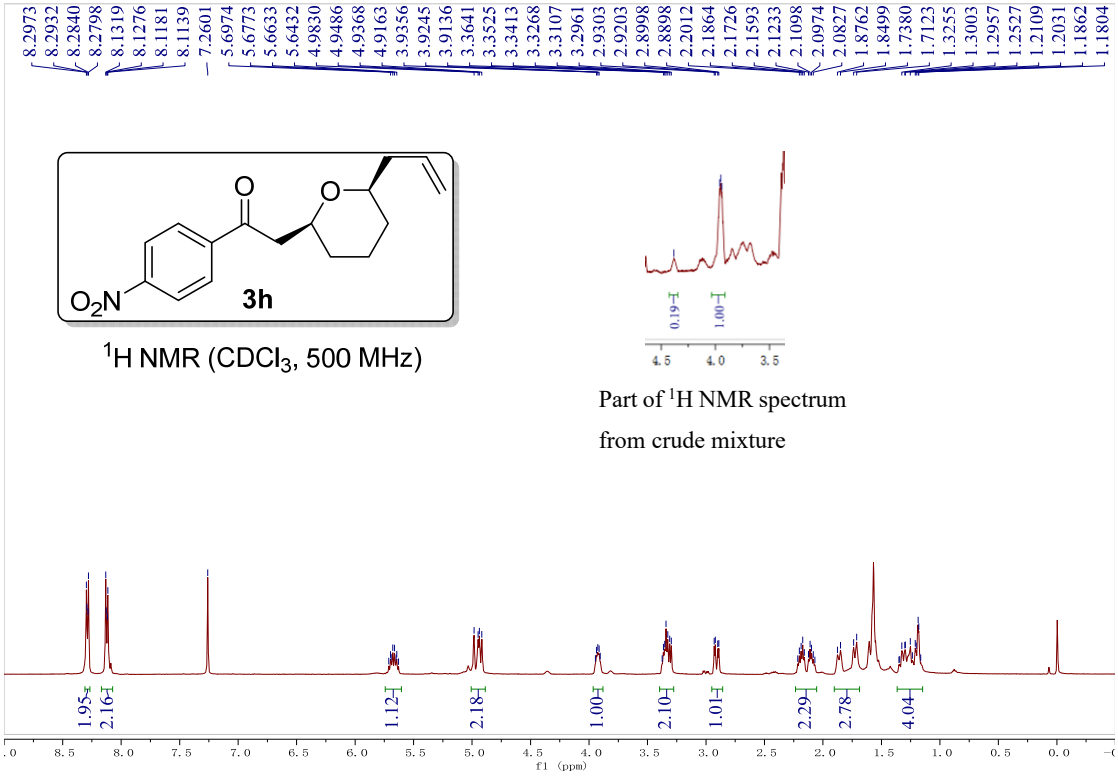
134.71
134.45
134.19
133.93
128.86
127.05
125.66
125.63
125.60
125.57
124.88
122.71
120.54
116.53
77.69
77.41
77.16
76.91
74.80
45.95
40.95
31.74
30.90
23.52
O
O
F3C
3g
13C NMR (CDCl3, 126 MHz)
f1 (ppm)

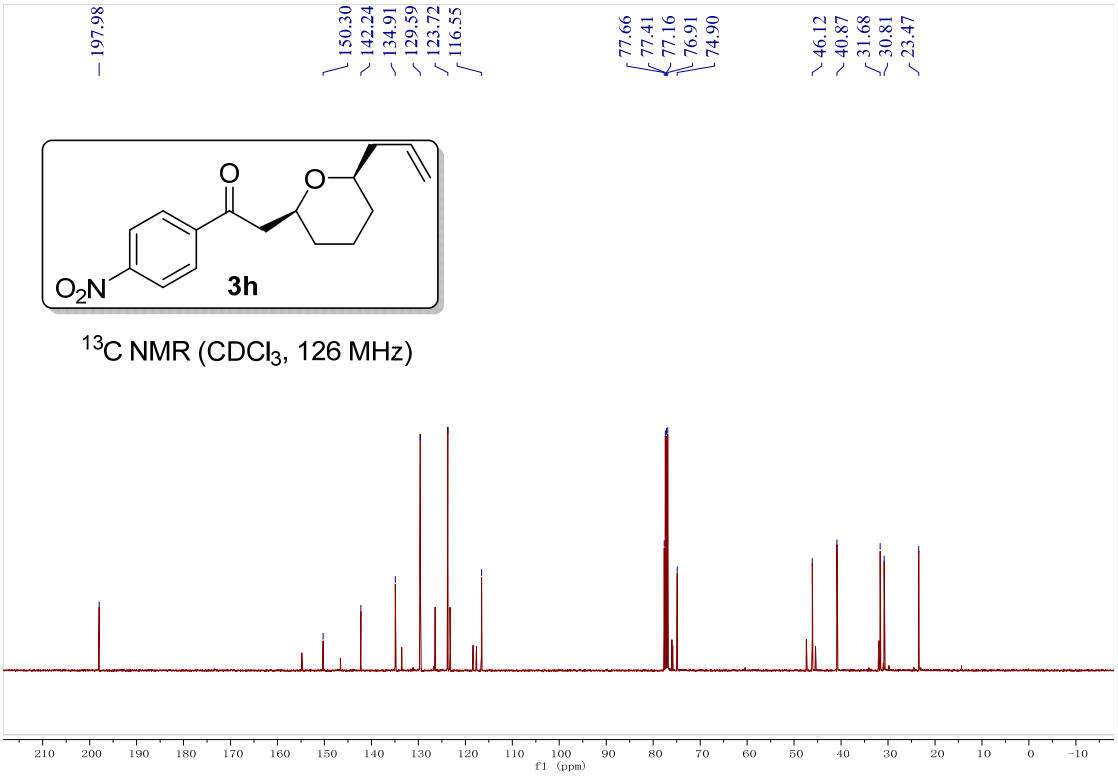


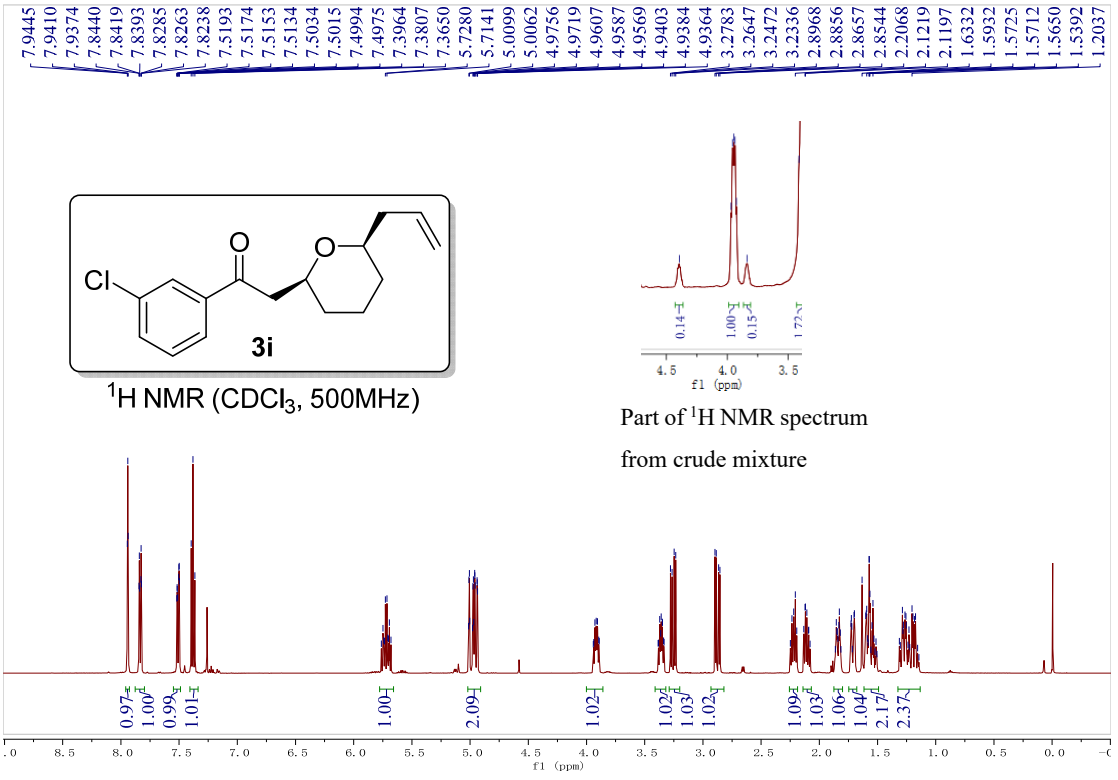
^{19}F NMR ($CDCl_3$, 471 MHz)

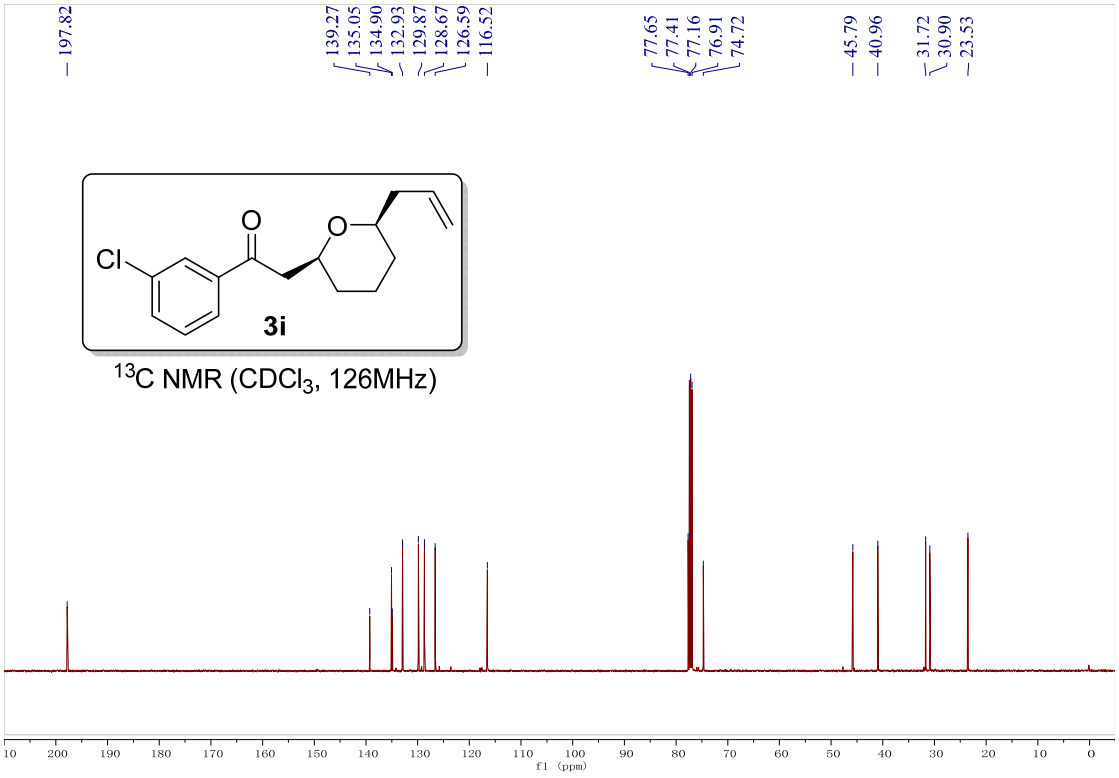


^{1}H NMR ($CDCl_3$, 500 MHz)

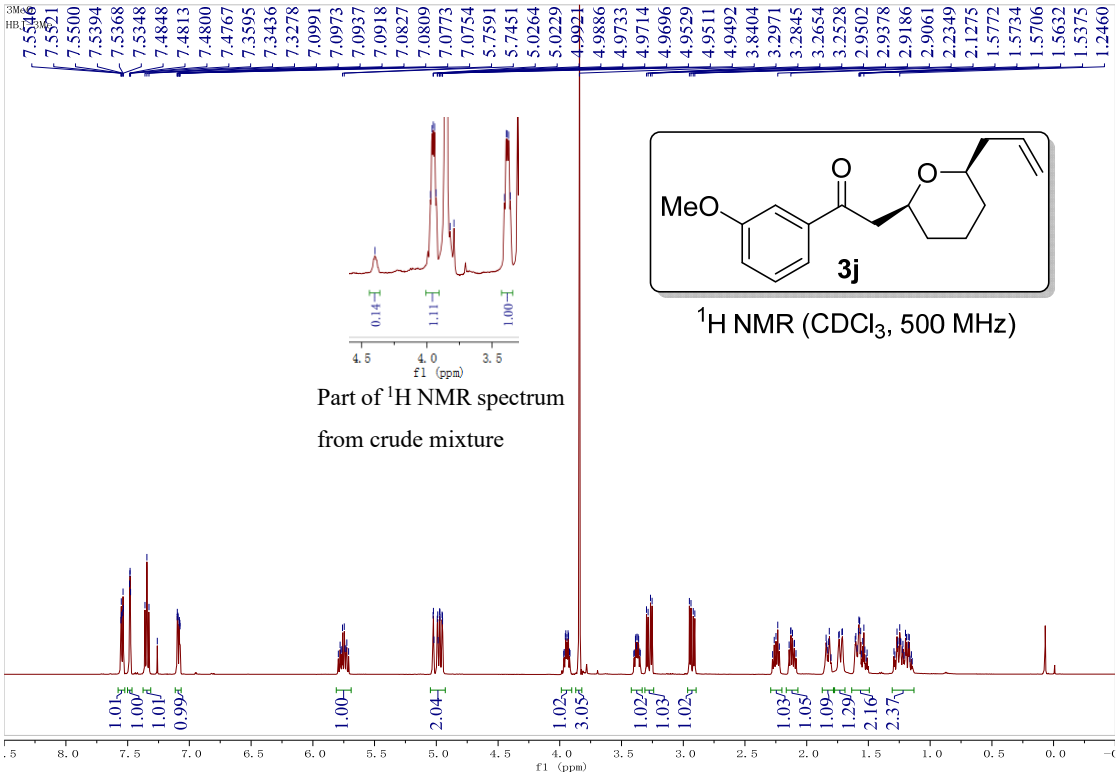
Part of ^{1}H NMR spectrum from crude mixture


197.98
150.30
142.24
134.91
129.59
123.72
116.55
77.66
77.41
77.16
76.91
74.90
46.12
40.87
31.68
30.81
23.47
O
O
O2N
3h
13C NMR (CDCl3, 126 MHz)
f1 (ppm)


7.9445
7.9410
7.9374
7.8440
7.8419
7.8393
7.8285
7.8263
7.8238
7.5193
7.5174
7.5153
7.5134
7.5034
7.5015
7.4994
7.4975
7.3964
7.3807
7.3650
5.7280
5.7141
5.0099
5.0062
4.9756
4.9719
4.9607
4.9587
4.9569
4.9403
4.9384
4.9364
3.2783
3.2647
3.2472
3.2336
2.8968
2.8856
2.8657
2.8544
2.2068
2.1219
2.1197
1.6332
1.5932
1.5725
1.5712
1.5650
1.5392
1.2037
O
O
Cl
3i
1H NMR (CDCl3, 500MHz)
0.14
1.00
0.15
1.72
f1 (ppm)
Part of 1H NMR spectrum
from crude mixture
0.97
1.00
0.99
1.01
1.00
2.09
1.02
1.02
1.03
1.02
1.09
1.03
1.06
1.04
2.17
2.37
f1 (ppm)

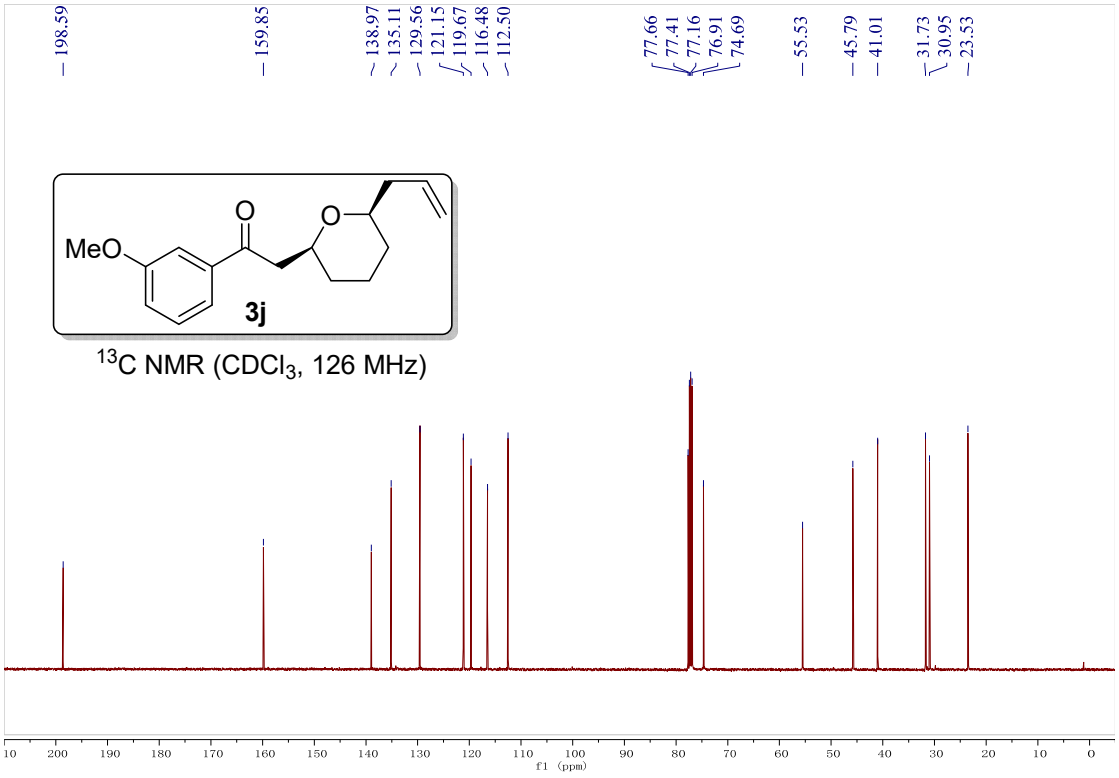


^{13}C NMR ($CDCl_3$, 126MHz)

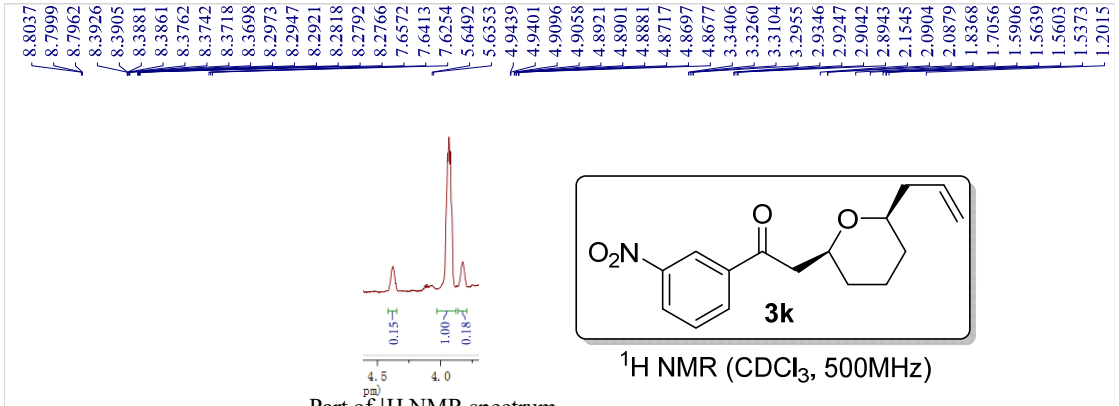


^{1}H NMR ($CDCl_3$, 500 MHz)

Part of ^{1}H NMR spectrum from crude mixture

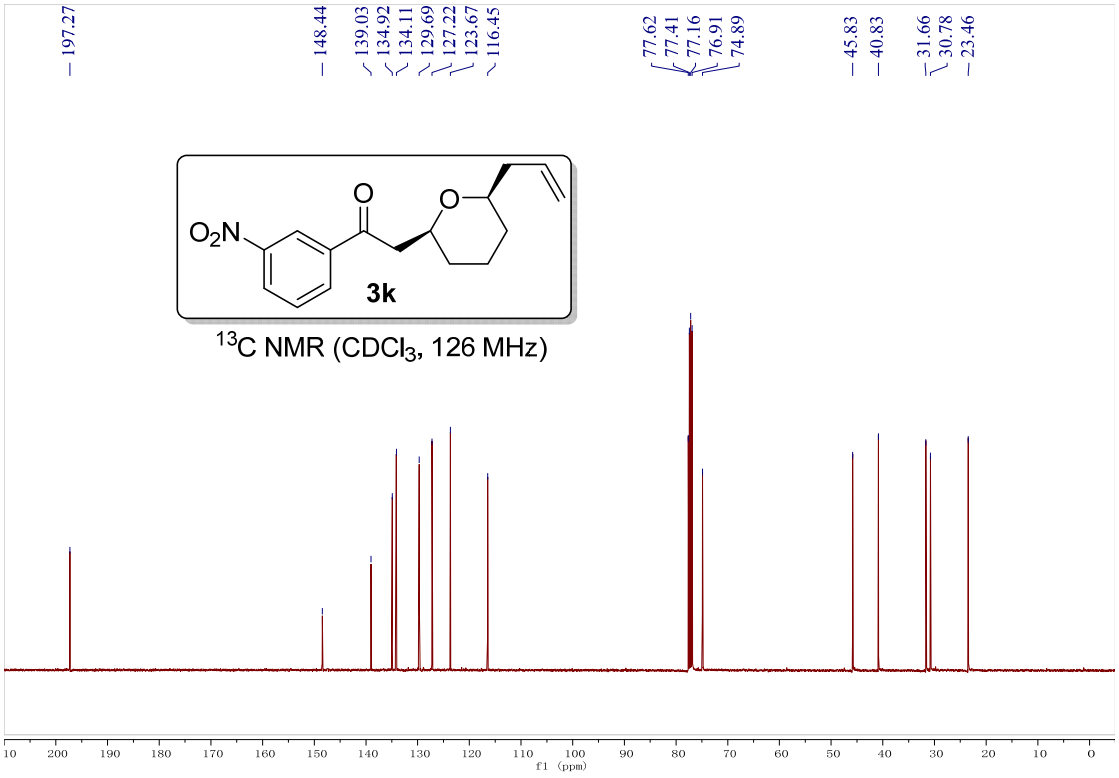


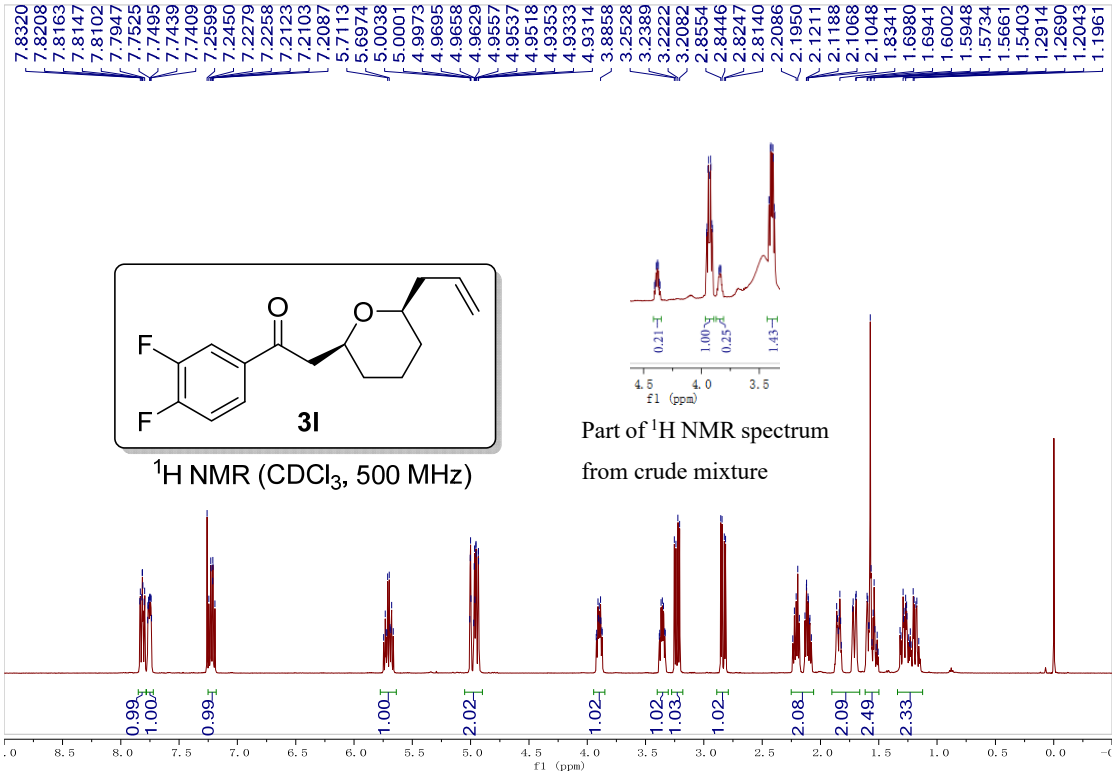
^{13}C NMR ($CDCl_3$, 126 MHz)

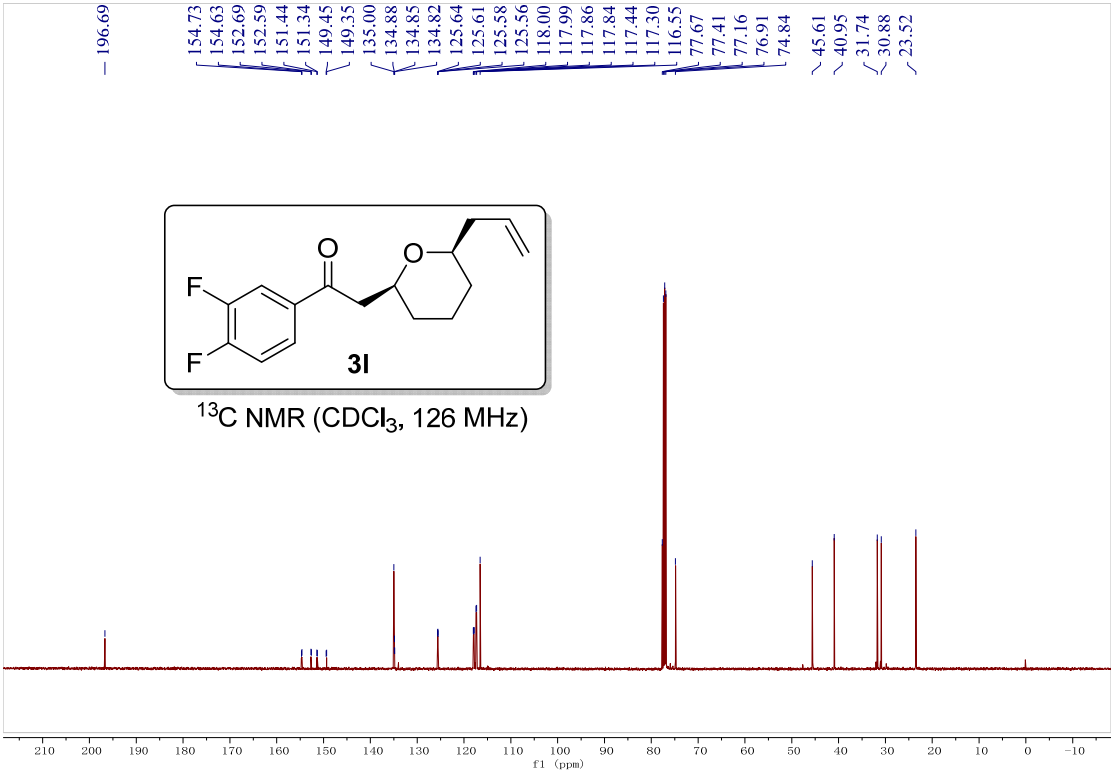


^{1}H NMR ($CDCl_3$, 500MHz)

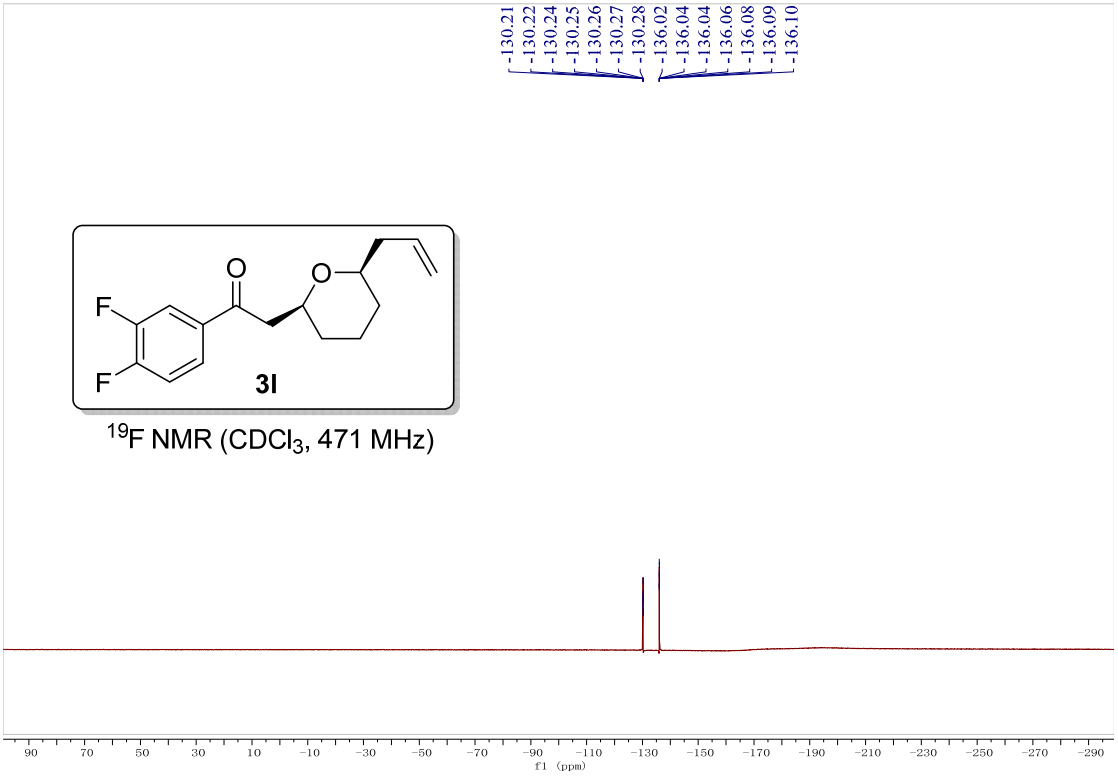
Part of ^{1}H NMR spectrum from crude mixture


197.27
148.44
139.03
134.92
134.11
129.69
127.22
123.67
116.45
77.62
77.41
77.16
76.91
74.89
45.83
40.83
31.66
30.78
23.46
O2N
O
O
3k
13C NMR (CDCl3, 126 MHz)
f1 (ppm)

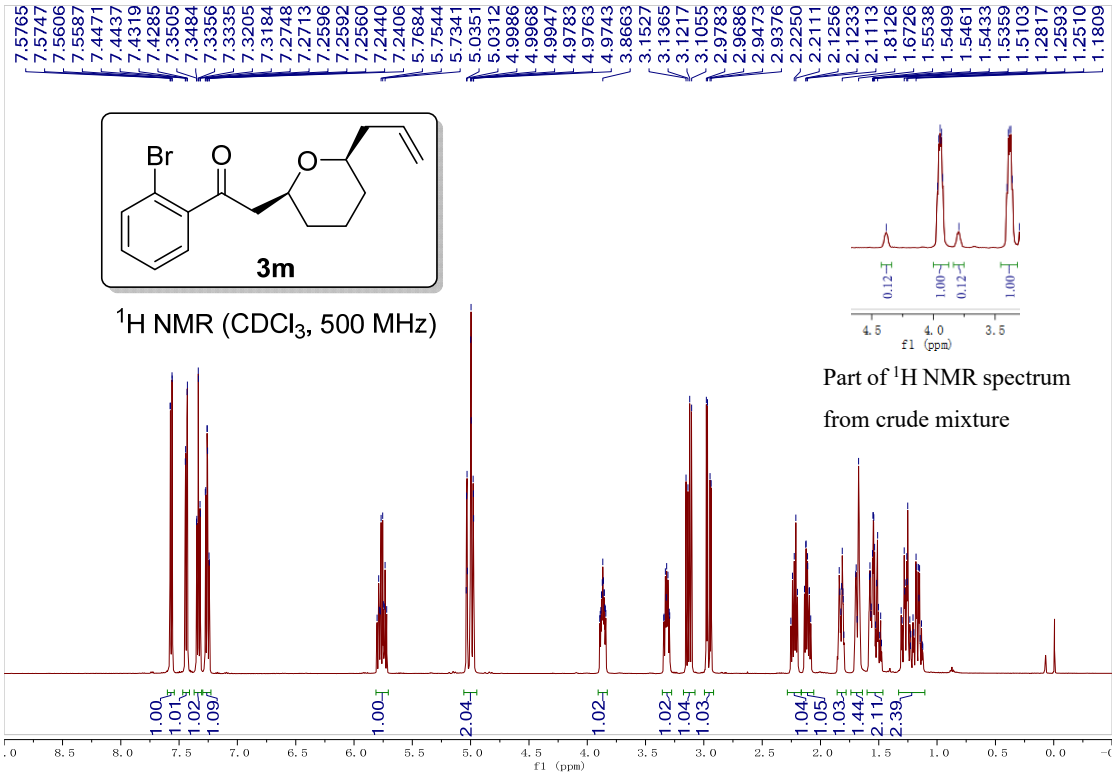

7.8320
7.8208
7.8163
7.8147
7.8102
7.7947
7.7525
7.7495
7.7439
7.7409
7.2599
7.2450
7.2279
7.2258
7.2123
7.2103
7.2087
5.7113
5.6974
5.0038
5.0001
4.9973
4.9695
4.9658
4.9629
4.9557
4.9537
4.9518
4.9353
4.9333
4.9314
3.8858
3.2528
3.2389
3.2222
3.2082
2.8554
2.8446
2.8247
2.8140
2.2086
2.1950
2.1211
2.1188
2.1068
2.1048
1.8341
1.6980
1.6941
1.6002
1.5948
1.5734
1.5661
1.5403
1.2914
1.2690
1.2043
1.1961
F
F
O
O
3l
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
0.21
1.00
0.25
1.43
4.5
4.0
3.5
f1 (ppm)
0.99
1.00
0.99
1.00
2.02
1.02
1.02
1.03
1.02
2.08
2.09
2.49
2.33
f1 (ppm)

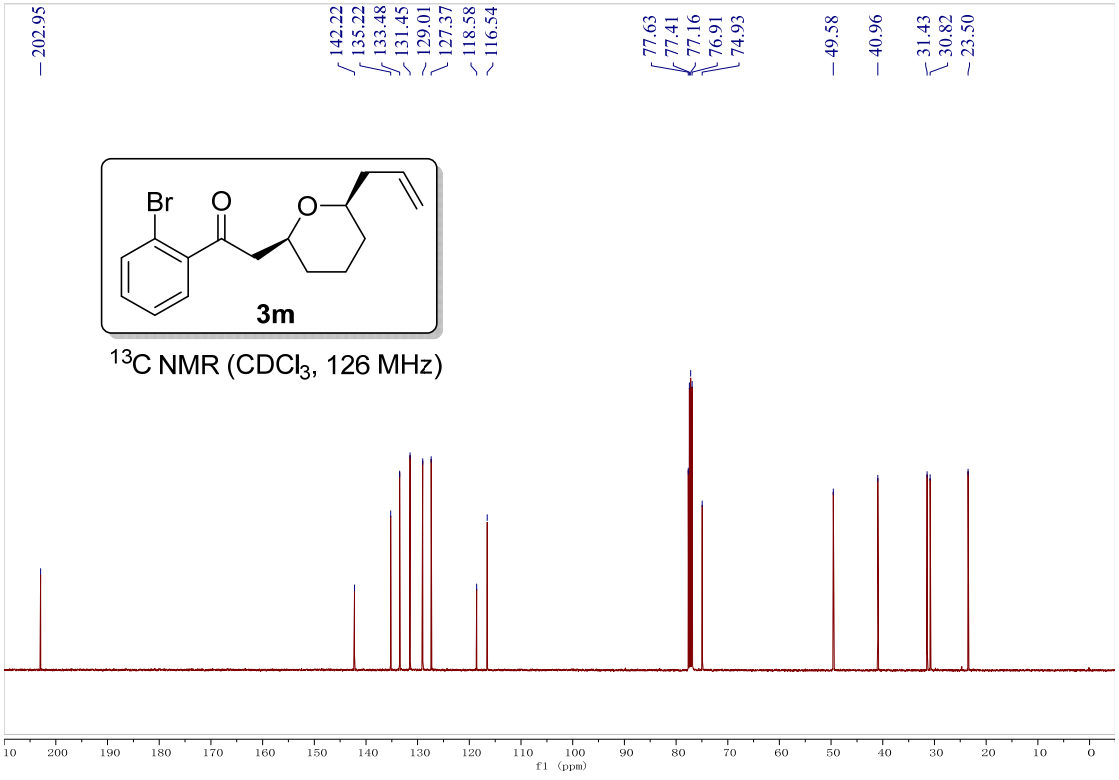


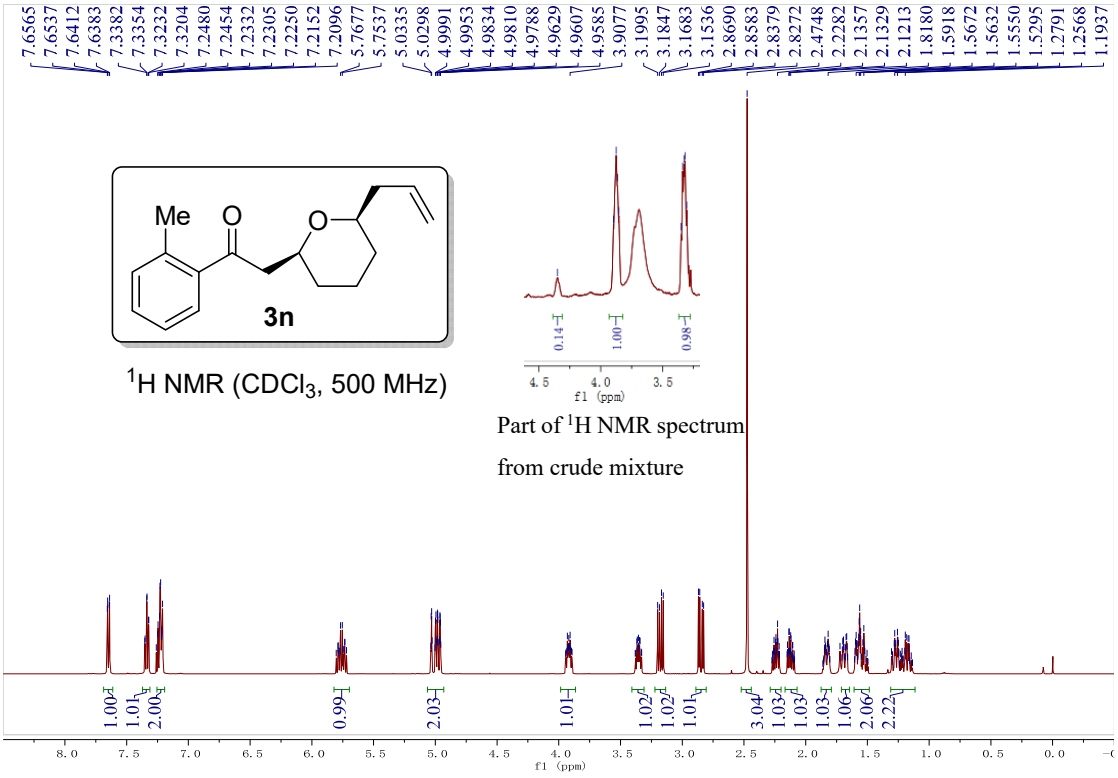
^{13}C NMR ($CDCl_3$, 126 MHz)



^{19}F NMR ($CDCl_3$, 471 MHz)

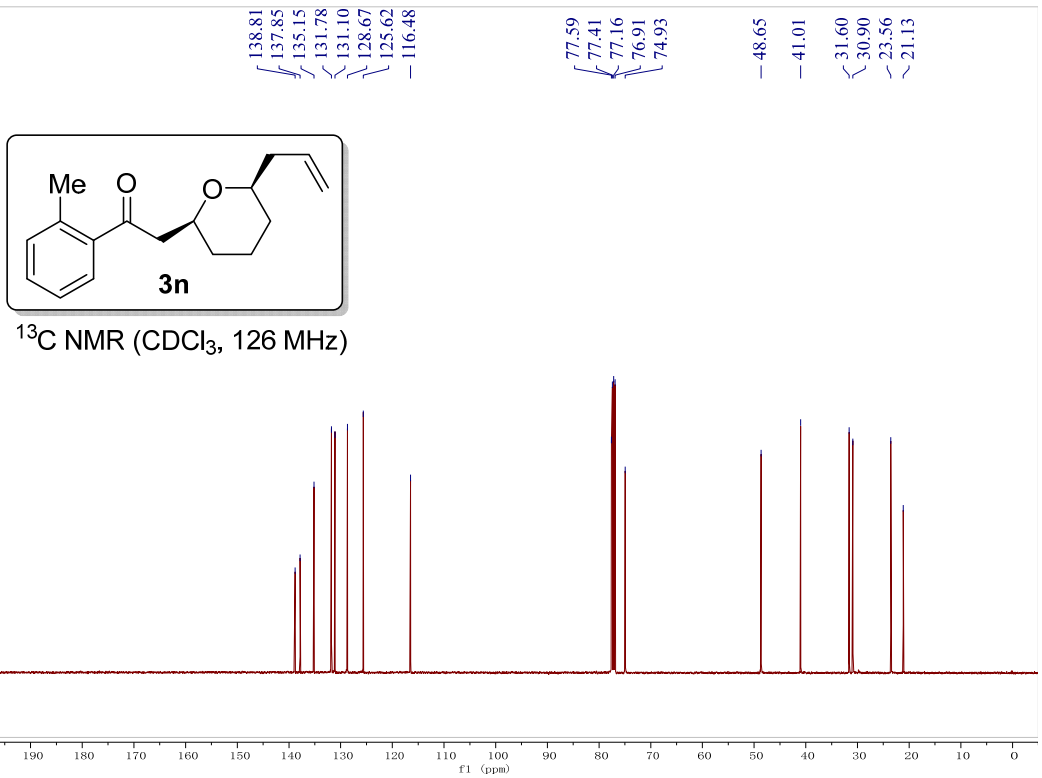

Br
O
O
3m
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
f1 (ppm)


Br
O
O
3m
13C NMR (CDCl3, 126 MHz)
f1 (ppm)

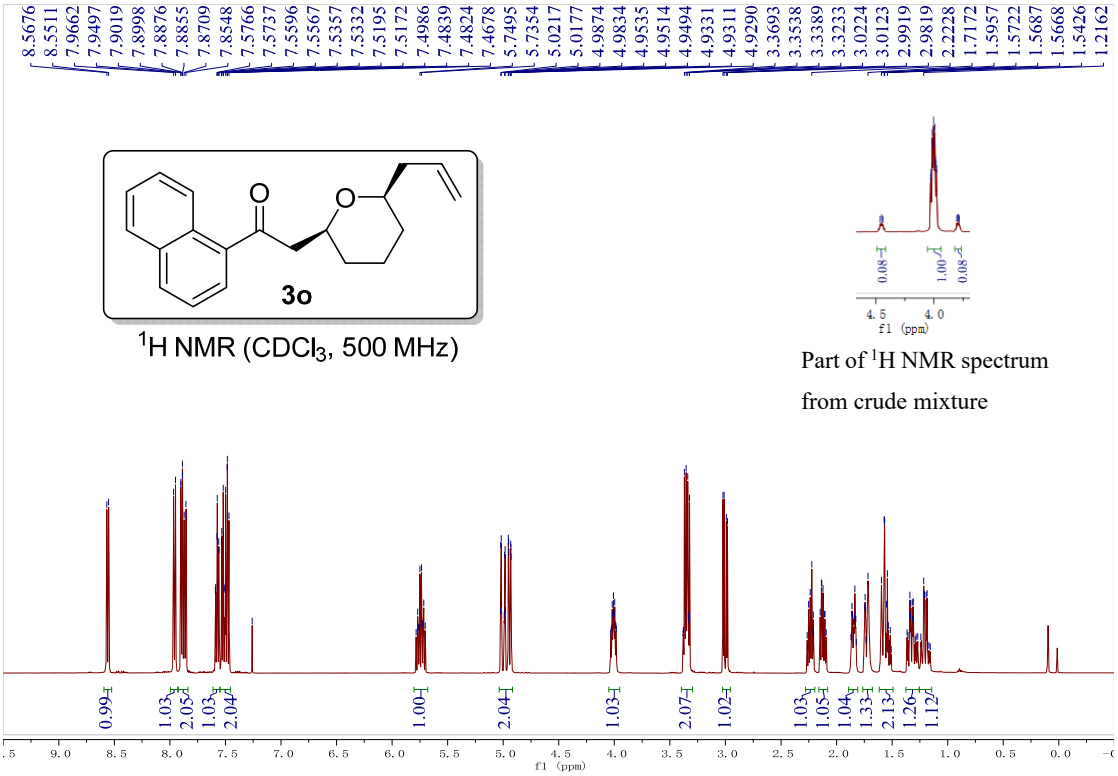


^{1}H NMR ($CDCl_3$, 500 MHz)

Part of ^{1}H NMR spectrum from crude mixture

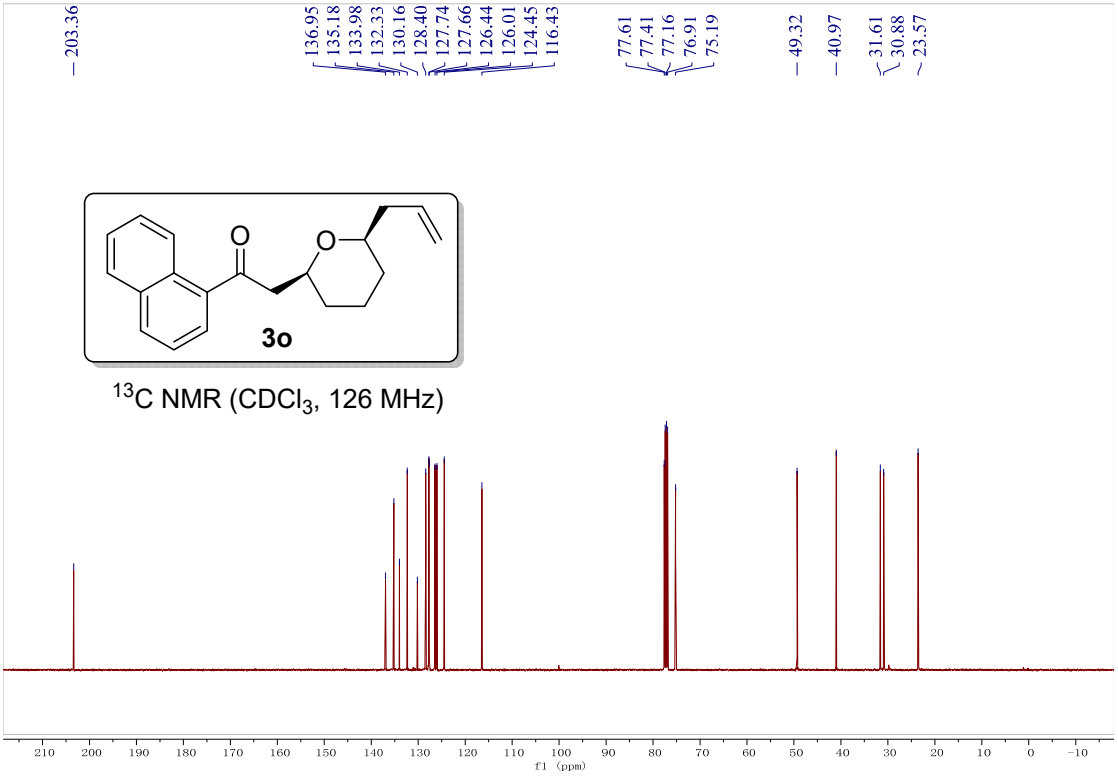


^{13}C NMR ($CDCl_3$, 126 MHz)

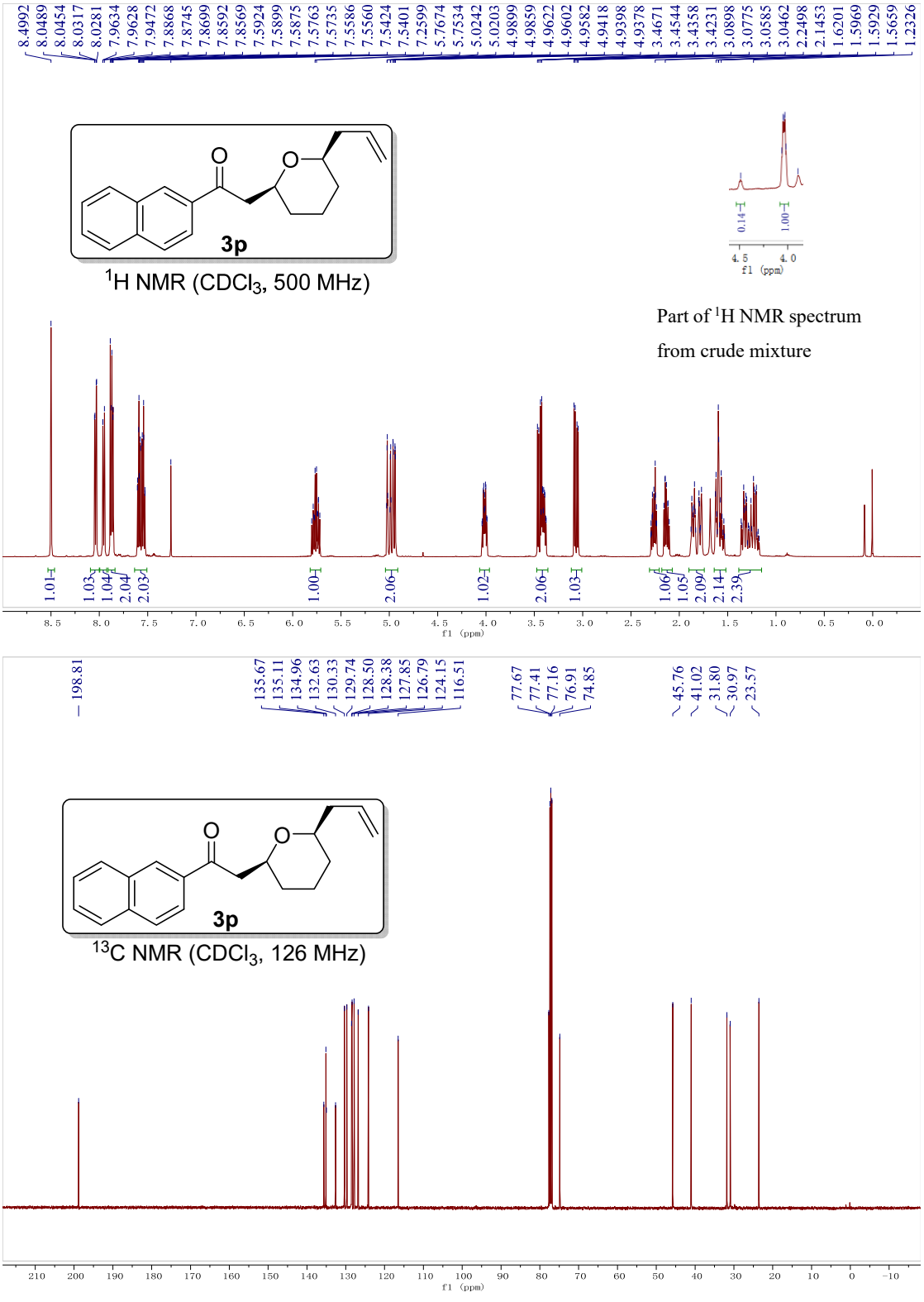


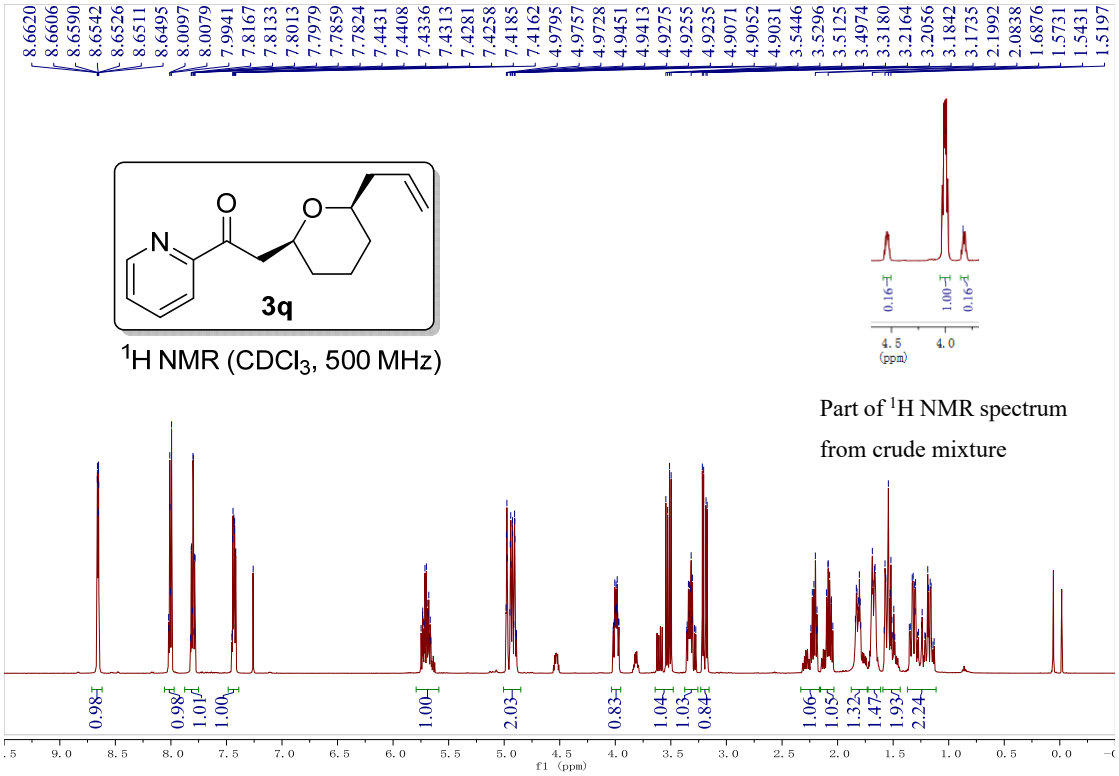
^{1}H NMR ($CDCl_3$, 500 MHz)

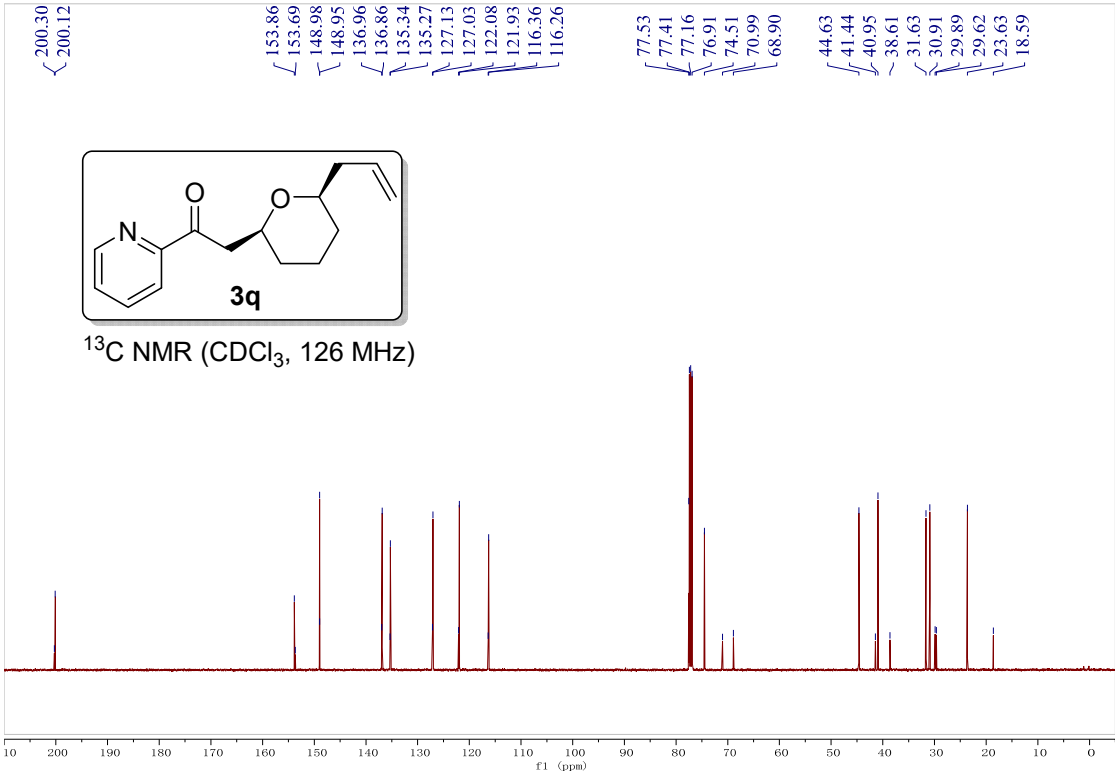
Part of ^{1}H NMR spectrum from crude mixture

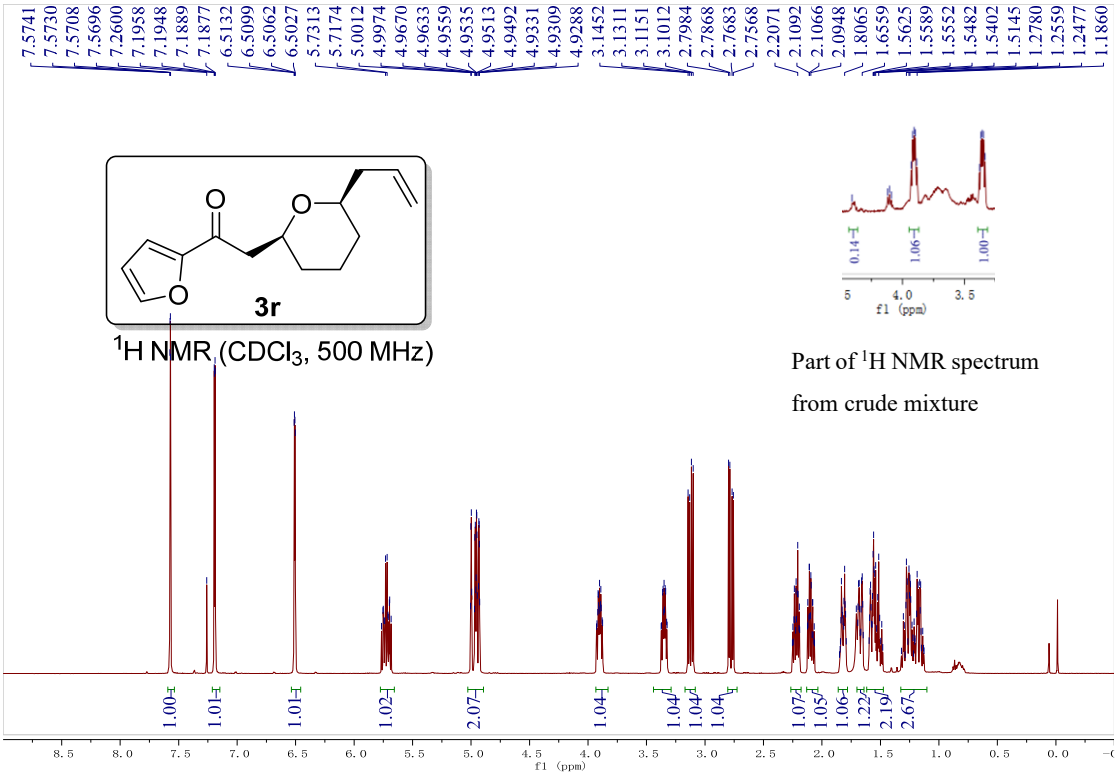


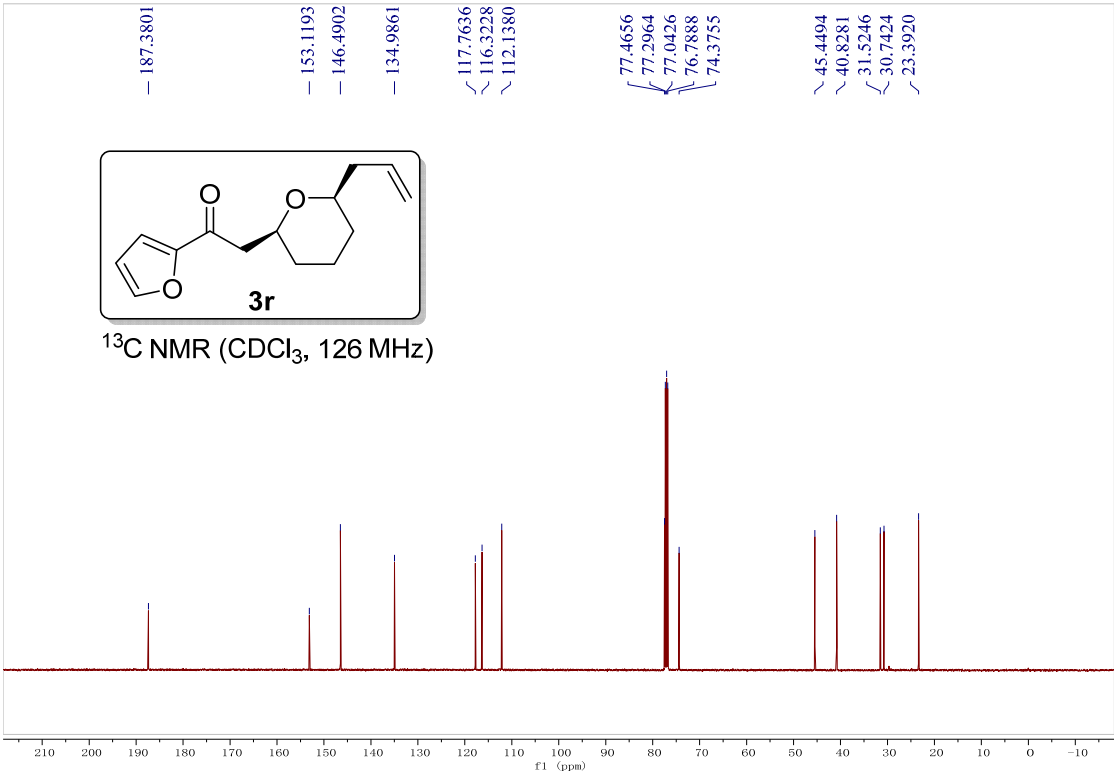
^{13}C NMR ($CDCl_3$, 126 MHz)

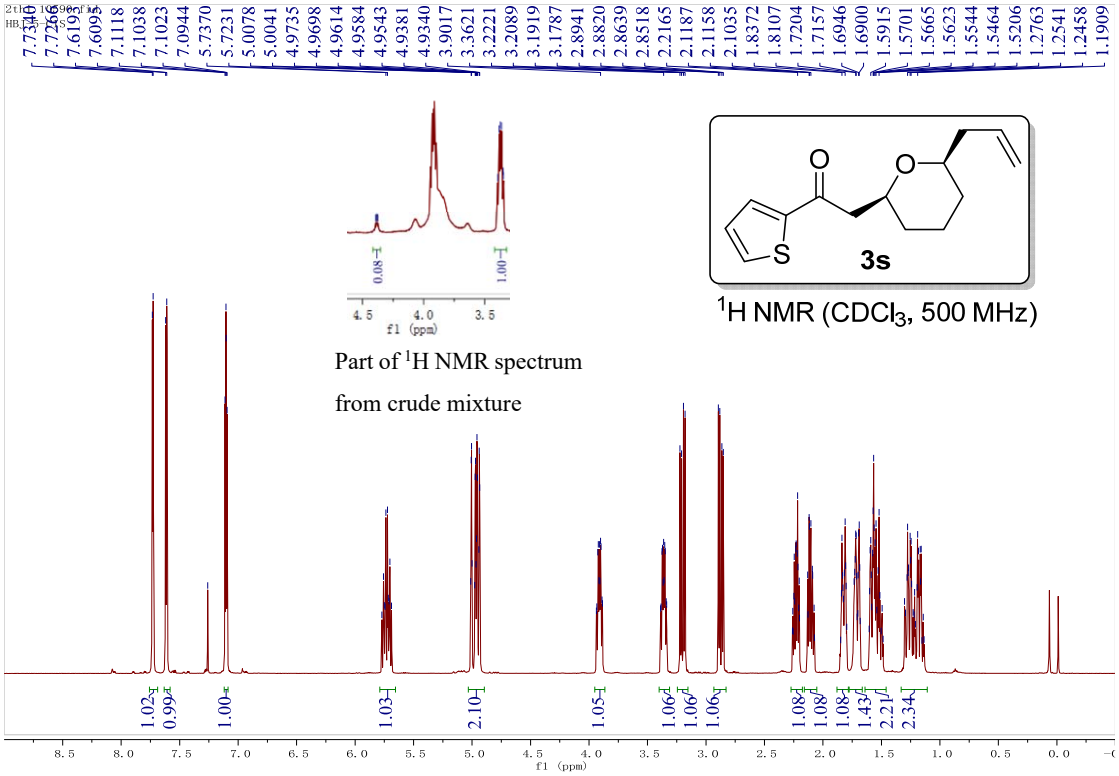

3p
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
3p
13C NMR (CDCl3, 126 MHz)

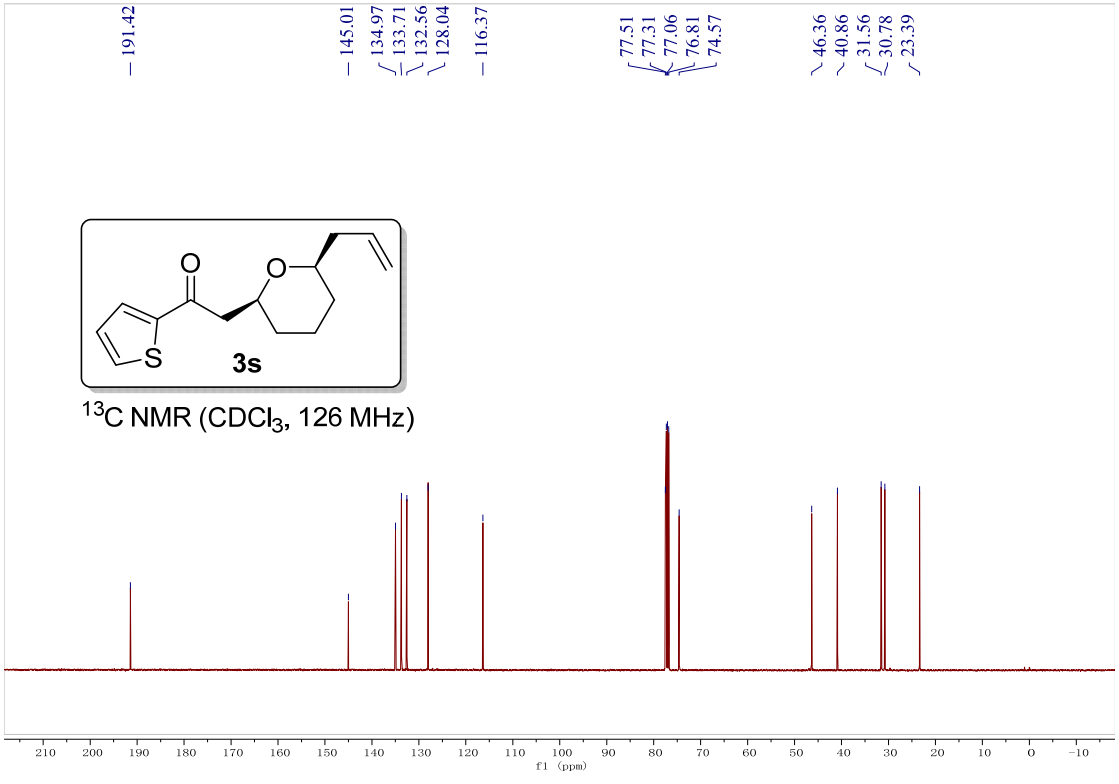

3q
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture

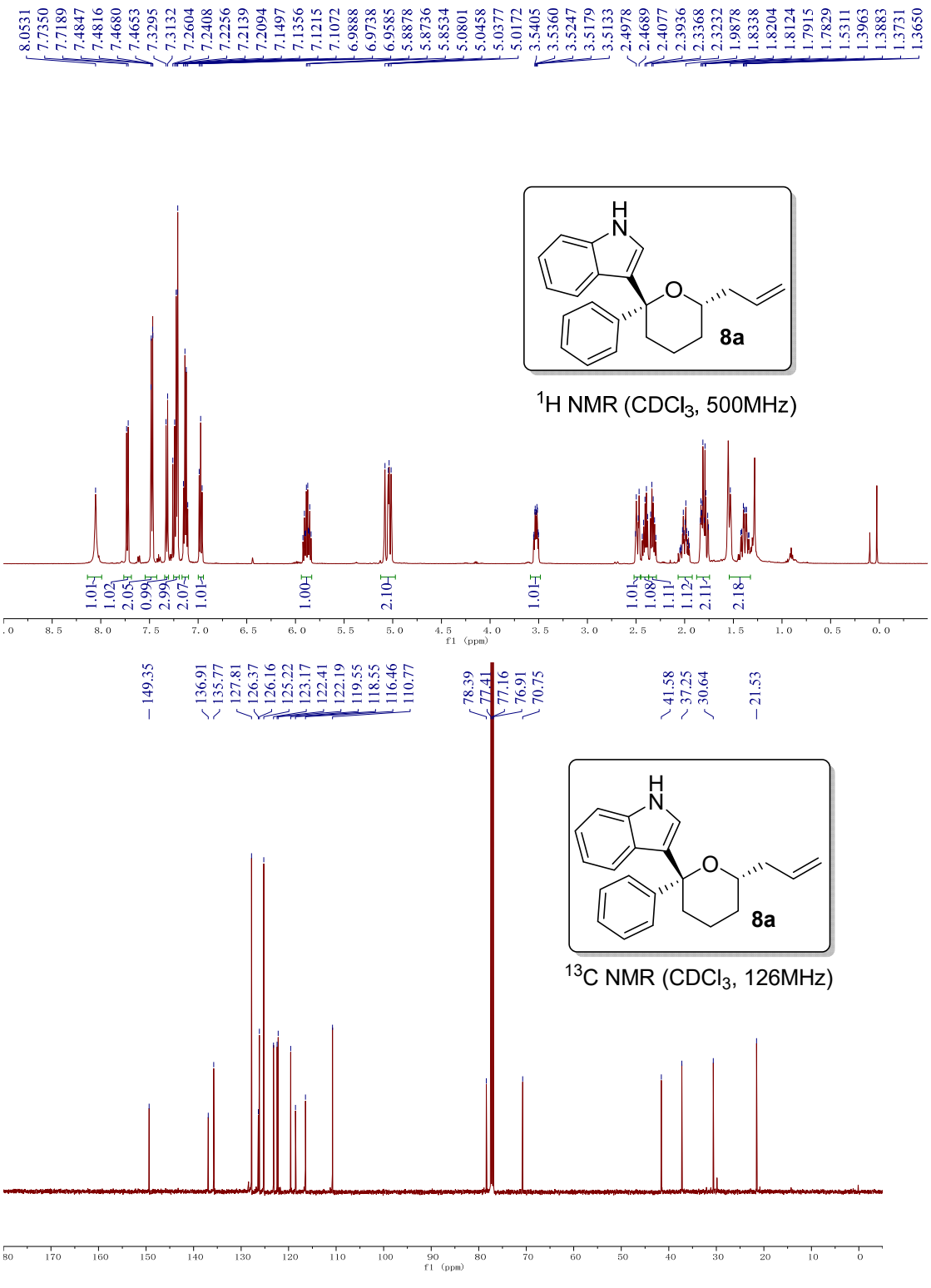

3q
13C NMR (CDCl3, 126 MHz)

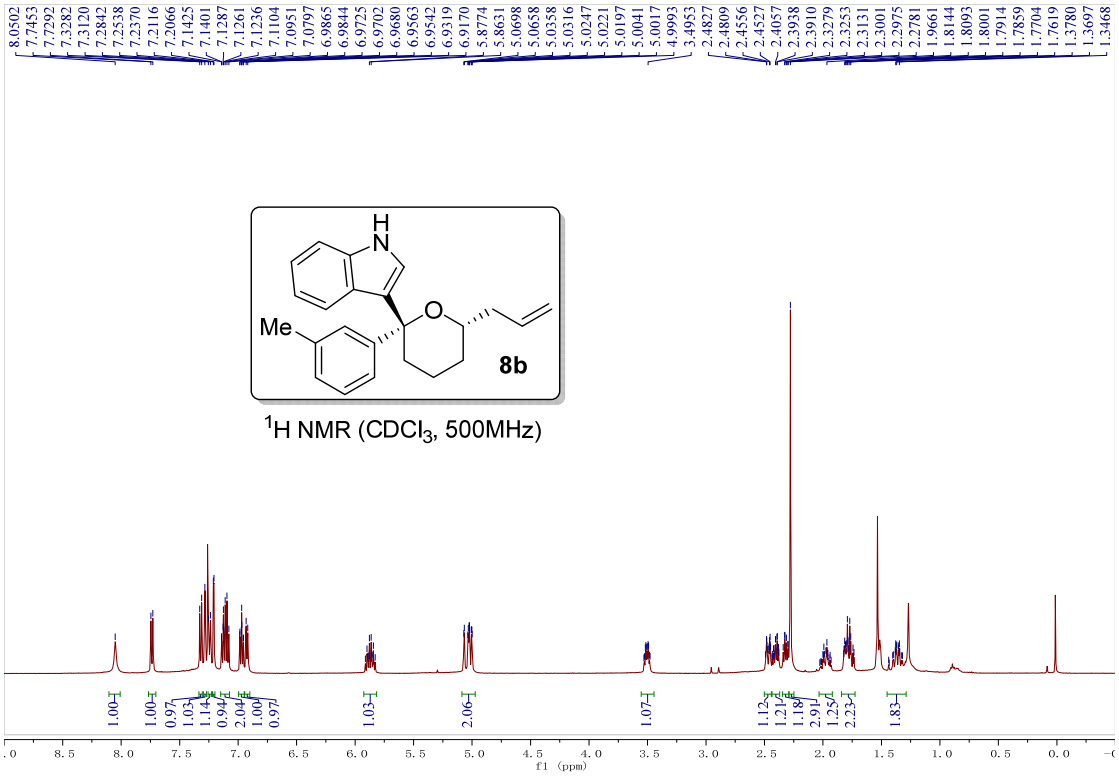

7.5741
7.5730
7.5708
7.5696
7.2600
7.1958
7.1948
7.1889
7.1877
6.5132
6.5099
6.5062
6.5027
5.7313
5.7174
5.0012
4.9974
4.9670
4.9633
4.9559
4.9535
4.9513
4.9492
4.9331
4.9309
4.9288
3.1452
3.1311
3.1151
3.1012
2.7984
2.7868
2.7683
2.7568
2.2071
2.1092
2.1066
2.0948
1.8065
1.6559
1.5625
1.5589
1.5552
1.5482
1.5402
1.5145
1.2780
1.2559
1.2477
1.1860
O
O
O
3r
1H NMR (CDCl3, 500 MHz)
0.14
1.06
1.00
5
4.0
3.5
f1 (ppm)
Part of 1H NMR spectrum
from crude mixture
1.00
1.01
1.01
1.02
2.07
1.04
1.04
1.04
1.04
1.07
1.05
1.06
1.22
2.19
2.67
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

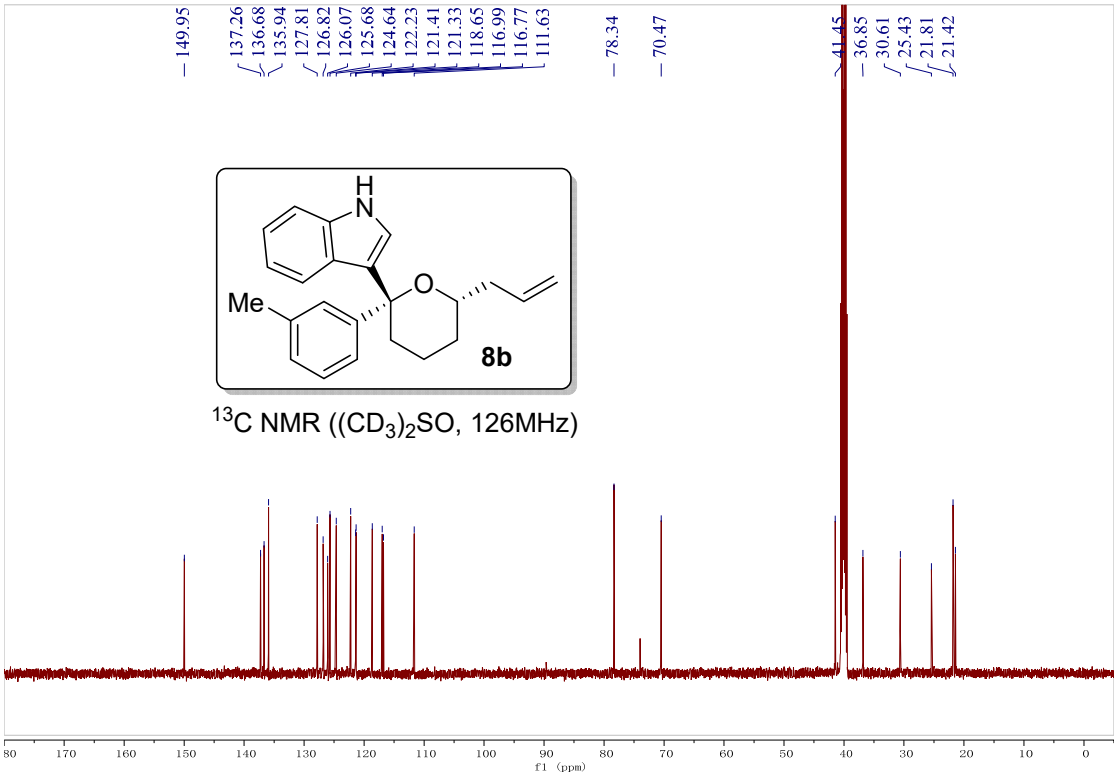

187.3801
153.1193
146.4902
134.9861
117.7636
116.3228
112.1380
77.4656
77.2964
77.0426
76.7888
74.3755
45.4494
40.8281
31.5246
30.7424
23.3920
O
O
O
3r
13C NMR (CDCl3, 126 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

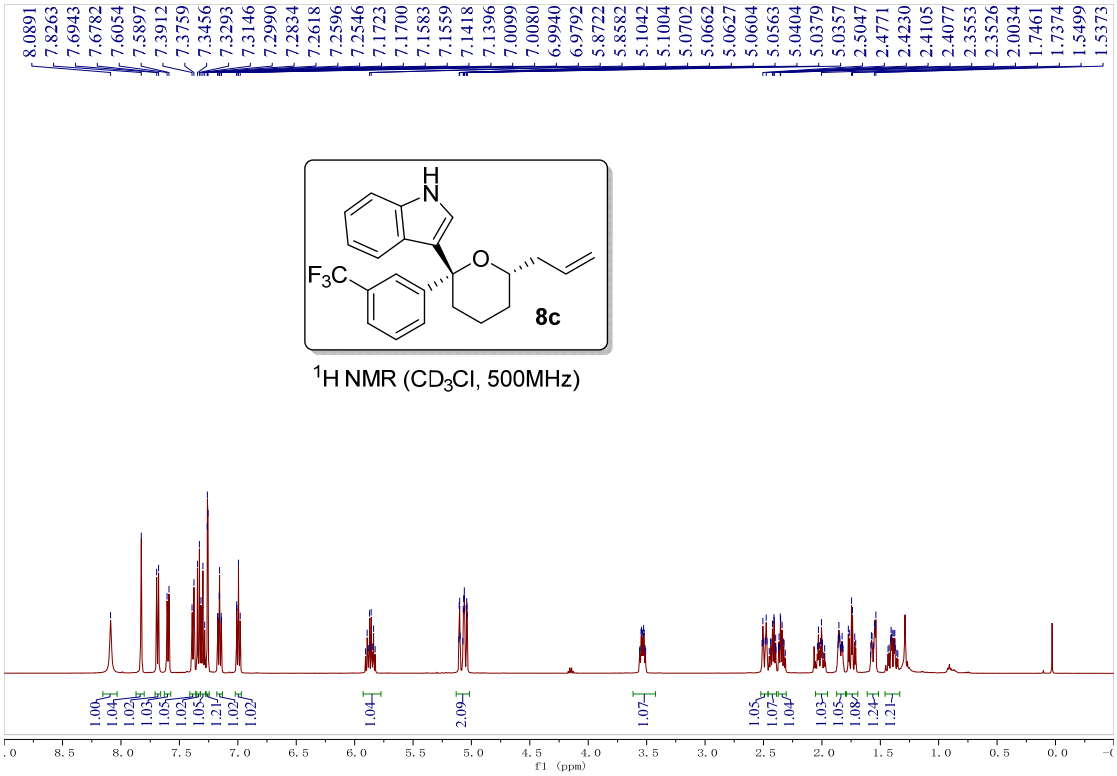

3s
1H NMR (CDCl3, 500 MHz)
Part of 1H NMR spectrum
from crude mixture
f1 (ppm)

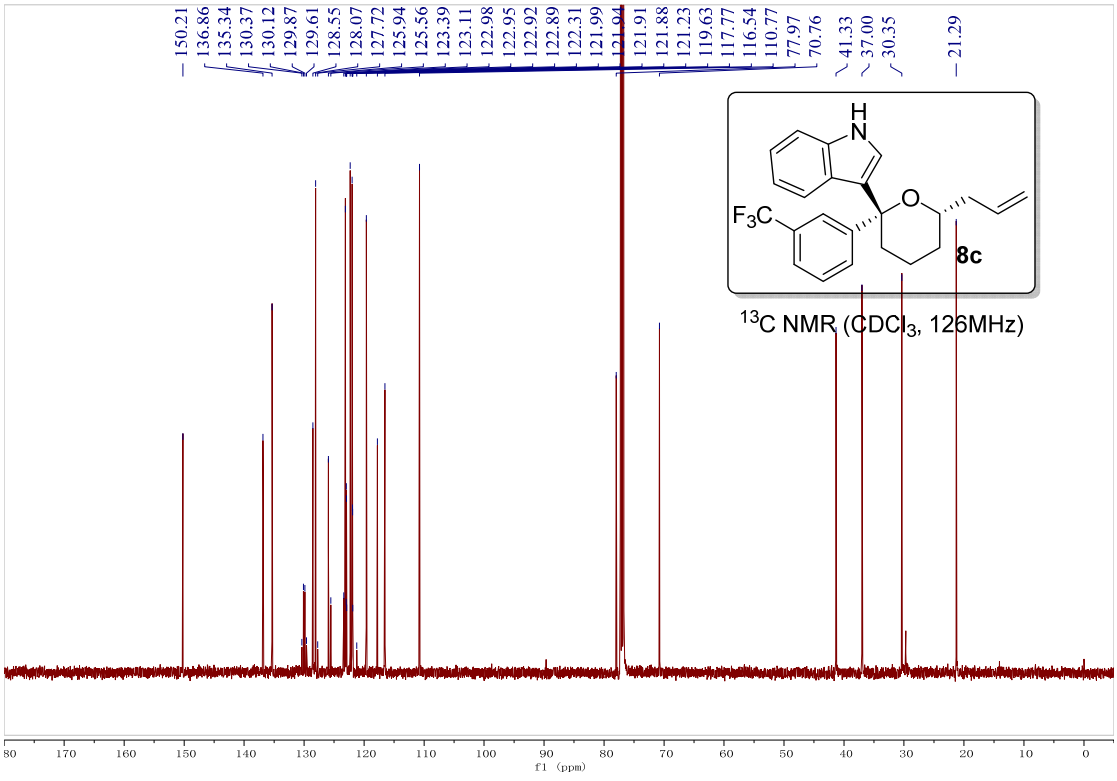

3s
13C NMR (CDCl3, 126 MHz)
f1 (ppm)

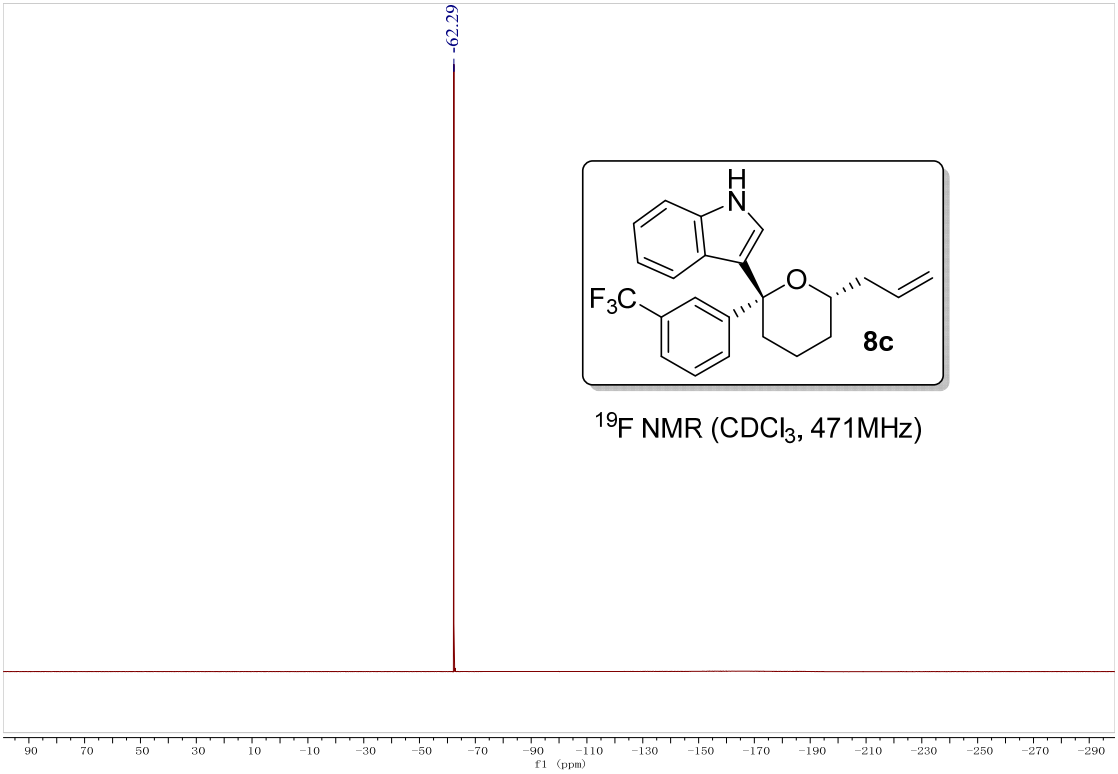

8.0531
7.7350
7.7189
7.4847
7.4816
7.4680
7.4653
7.3295
7.3132
7.2604
7.2408
7.2256
7.2139
7.2094
7.1497
7.1356
7.1215
7.1072
6.9888
6.9738
6.9585
5.8878
5.8736
5.8534
5.0801
5.0458
5.0377
5.0172
3.5405
3.5360
3.5247
3.5179
3.5133
2.4978
2.4689
2.4077
2.3936
2.3368
2.3232
1.9878
1.8338
1.8204
1.8124
1.7915
1.7829
1.5311
1.3963
1.3883
1.3731
1.3650
8a
1H NMR (CDCl3, 500MHz)
1.01
1.02
2.05
0.99
2.99
2.07
1.01
1.00
2.10
1.01
1.01
1.08
1.11
1.12
2.11
2.18
f1 (ppm)
149.35
136.91
135.77
127.81
126.37
126.16
125.22
123.17
122.41
122.19
119.55
118.55
116.46
110.77
78.39
77.41
77.16
76.91
70.75
41.58
37.25
30.64
21.53
8a
13C NMR (CDCl3, 126MHz)
f1 (ppm)

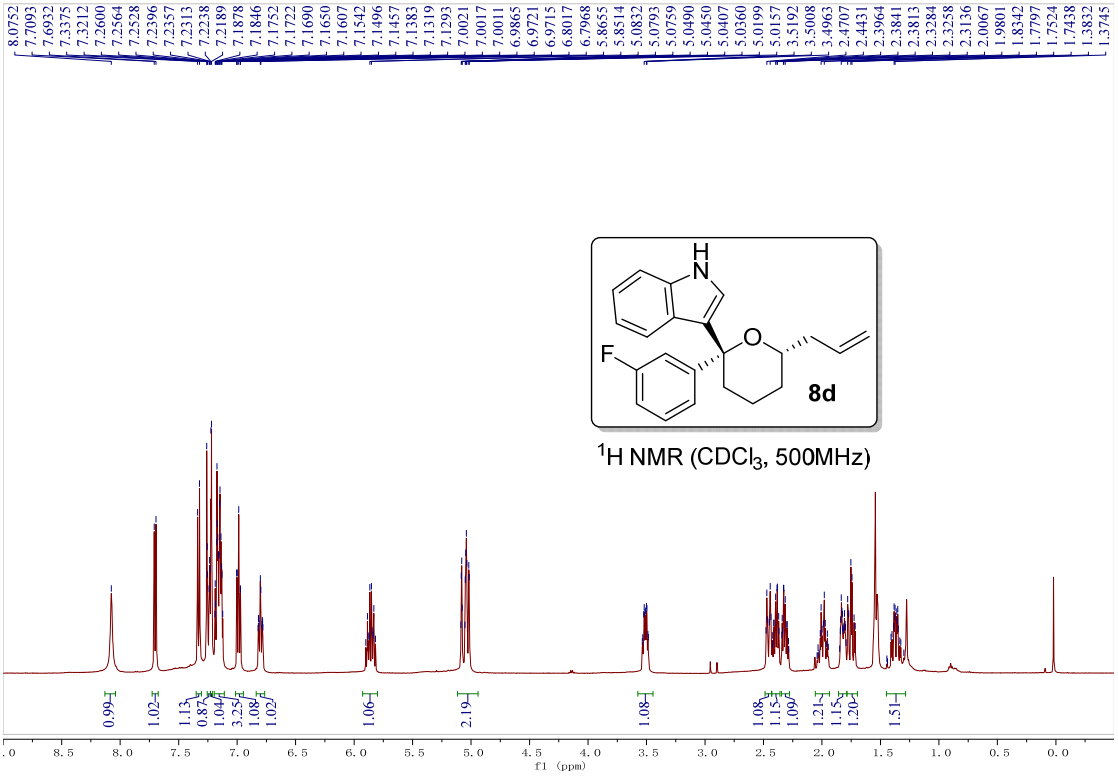

8b
^{1}H NMR (CDCl$_3$, 500MHz)
f1 (ppm)

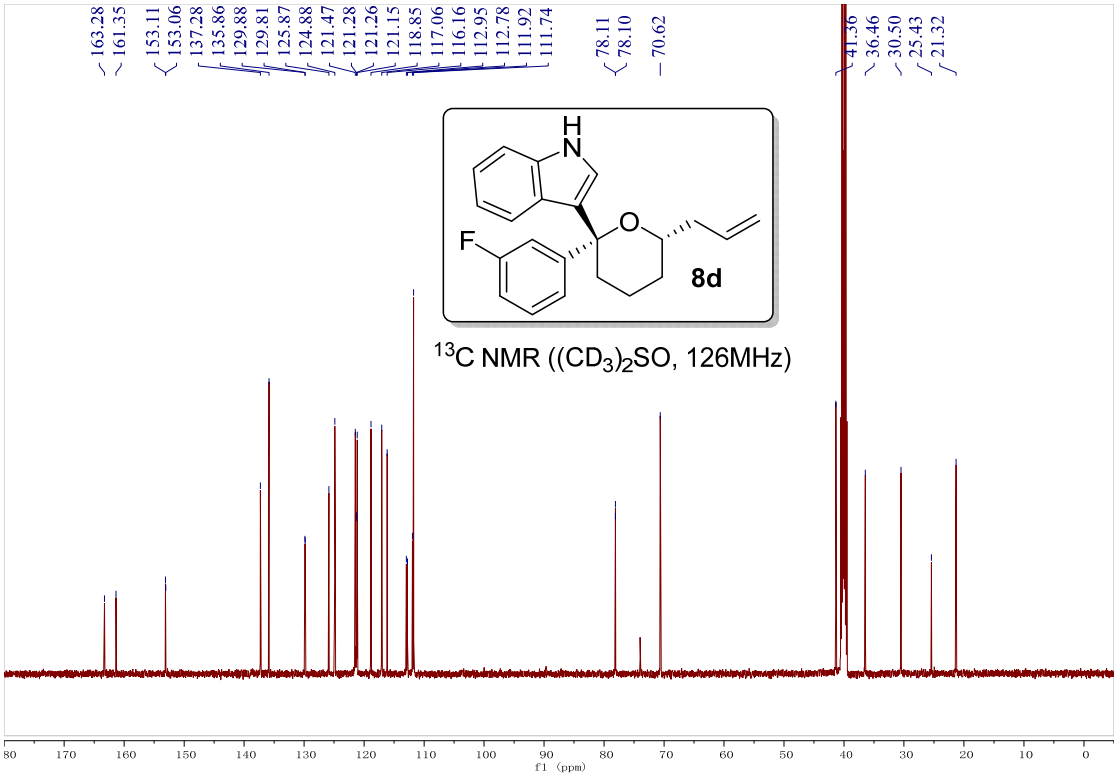

8b
^{13}C NMR ((CD$_3$)$_2$SO, 126MHz)
f1 (ppm)


8.0891
7.8263
7.6943
7.6782
7.6054
7.5897
7.3912
7.3759
7.3456
7.3293
7.3146
7.2990
7.2834
7.2618
7.2596
7.2546
7.1723
7.1700
7.1583
7.1559
7.1418
7.1396
7.0099
7.0080
6.9940
6.9792
5.8722
5.8582
5.1042
5.1004
5.0702
5.0662
5.0627
5.0604
5.0563
5.0404
5.0379
5.0357
2.5047
2.4771
2.4230
2.4105
2.4077
2.3553
2.3526
2.0034
1.7461
1.7374
1.5499
1.5373
H
N
O
F3C
8c
1H NMR (CD3Cl, 500MHz)
1.00
1.04
1.02
1.03
1.05
1.02
1.05
1.21
1.02
1.02
1.04
2.09
1.07
1.05
1.07
1.04
1.03
1.05
1.08
1.24
1.21
f1 (ppm)

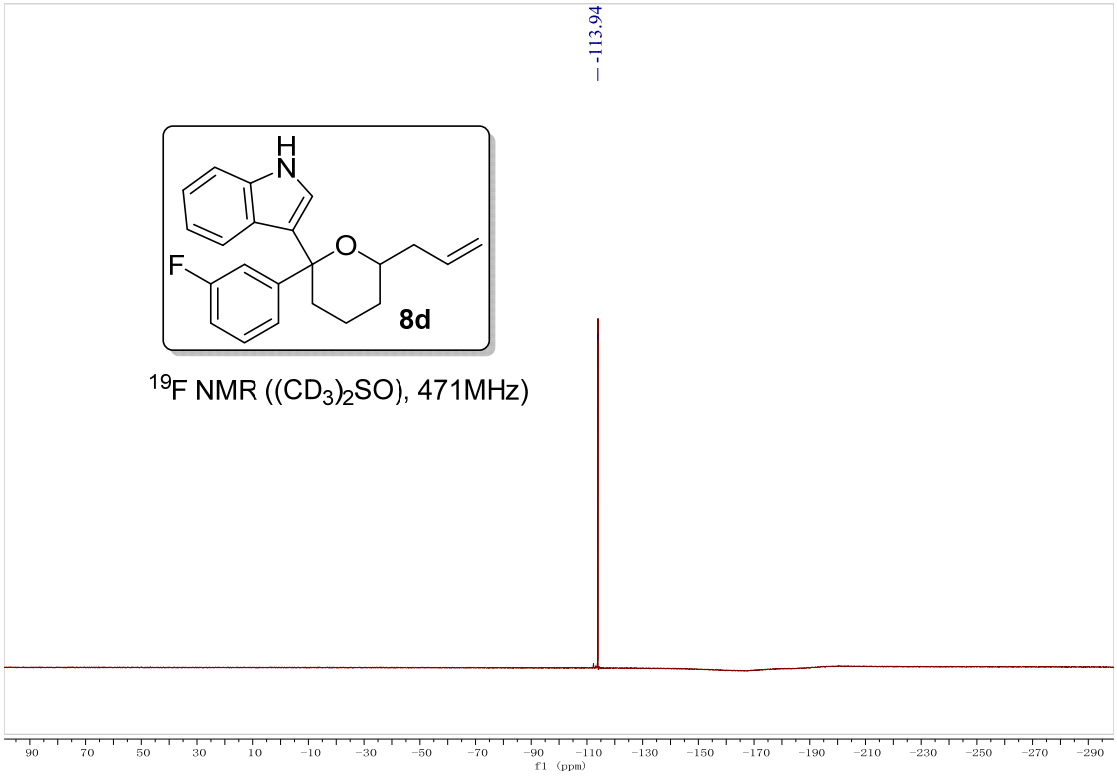

150.21
136.86
135.34
130.37
130.12
129.87
129.61
128.55
128.07
127.72
125.94
125.56
123.39
123.11
122.98
122.95
122.92
122.89
122.31
121.99
121.94
121.91
121.88
121.23
119.63
117.77
116.54
110.77
77.97
70.76
41.33
37.00
30.35
21.29
H
N
O
F3C
8c
13C NMR (CDCl3, 126MHz)
f1 (ppm)


-62.29
H
N
O
F3C
8c
19F NMR (CDCl3, 471MHz)
f1 (ppm)

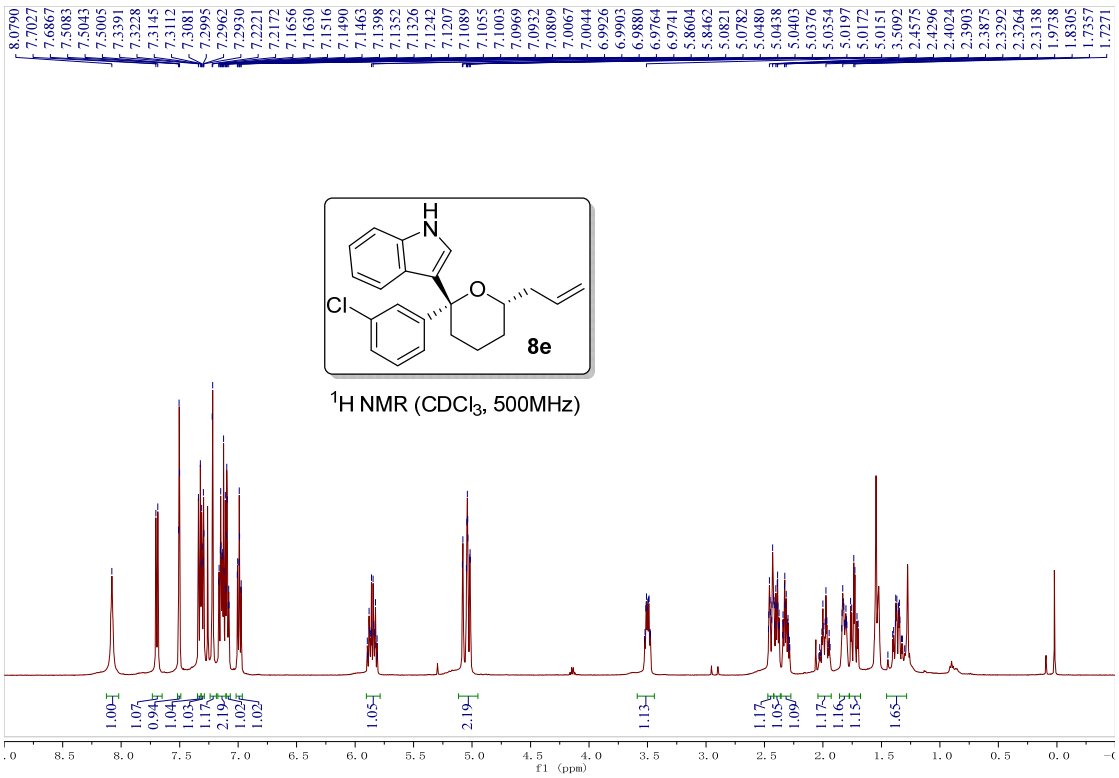

H
N
O
F
8d
1H NMR (CDCl3, 500MHz)
f1 (ppm)

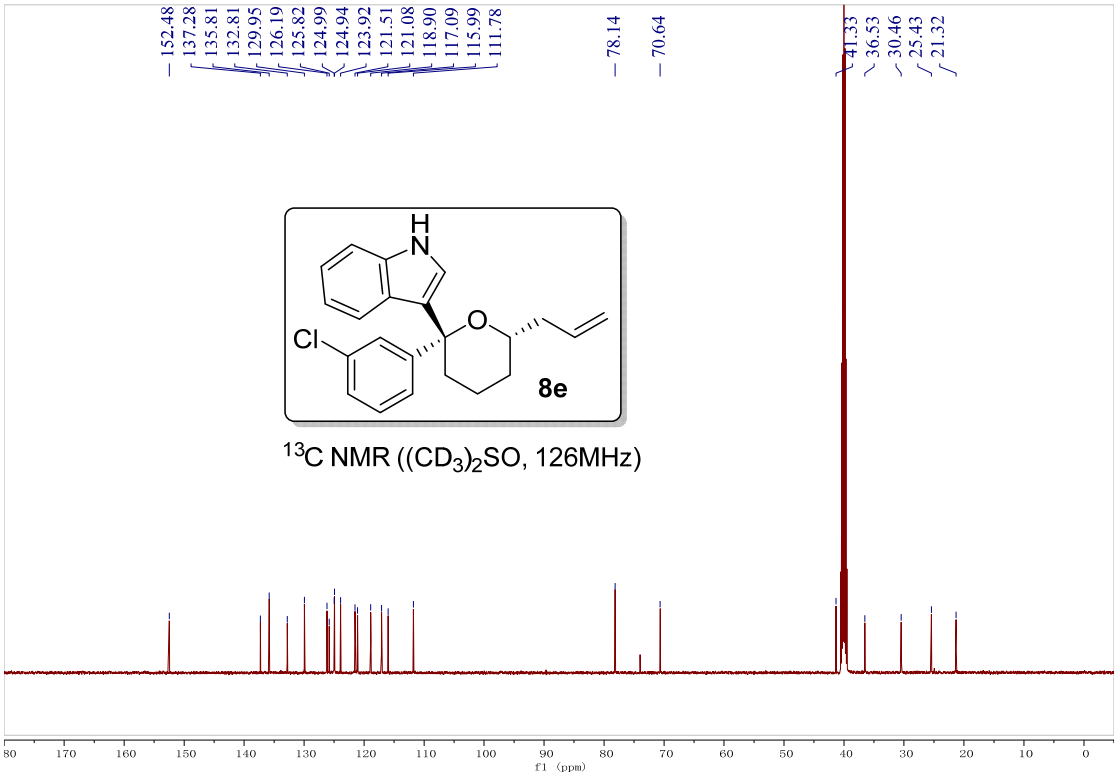


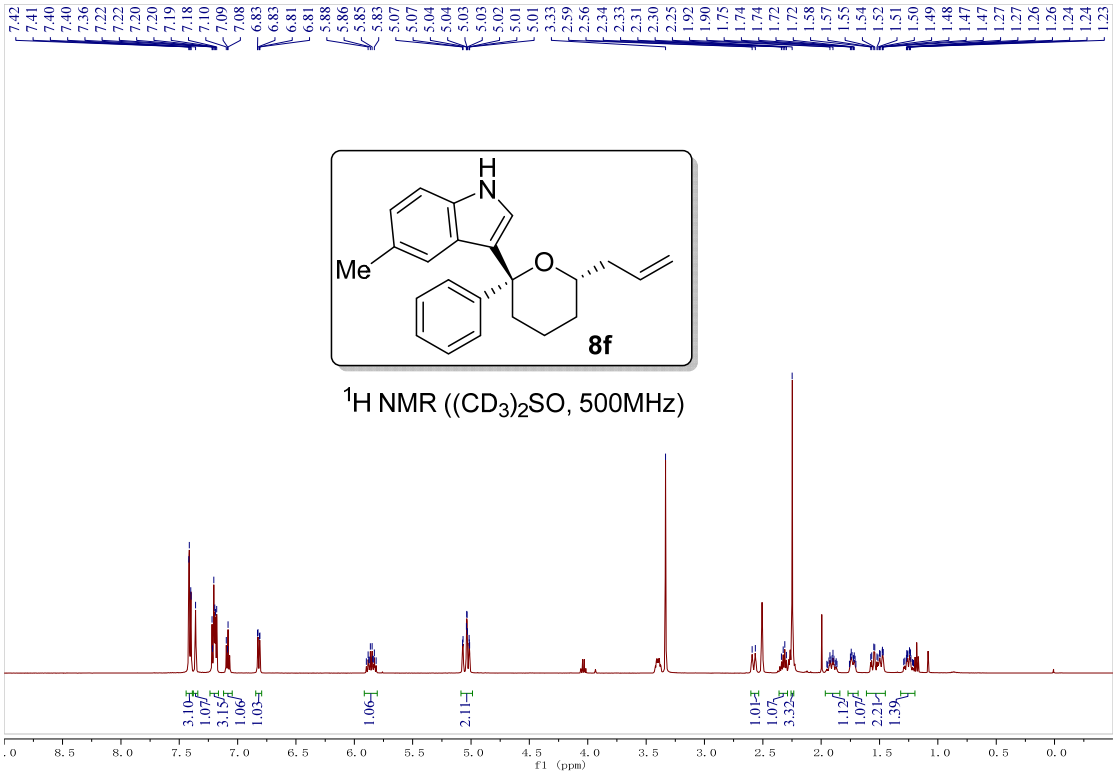
^{13}C NMR ((CD$_3$)$_2$SO, 126MHz)

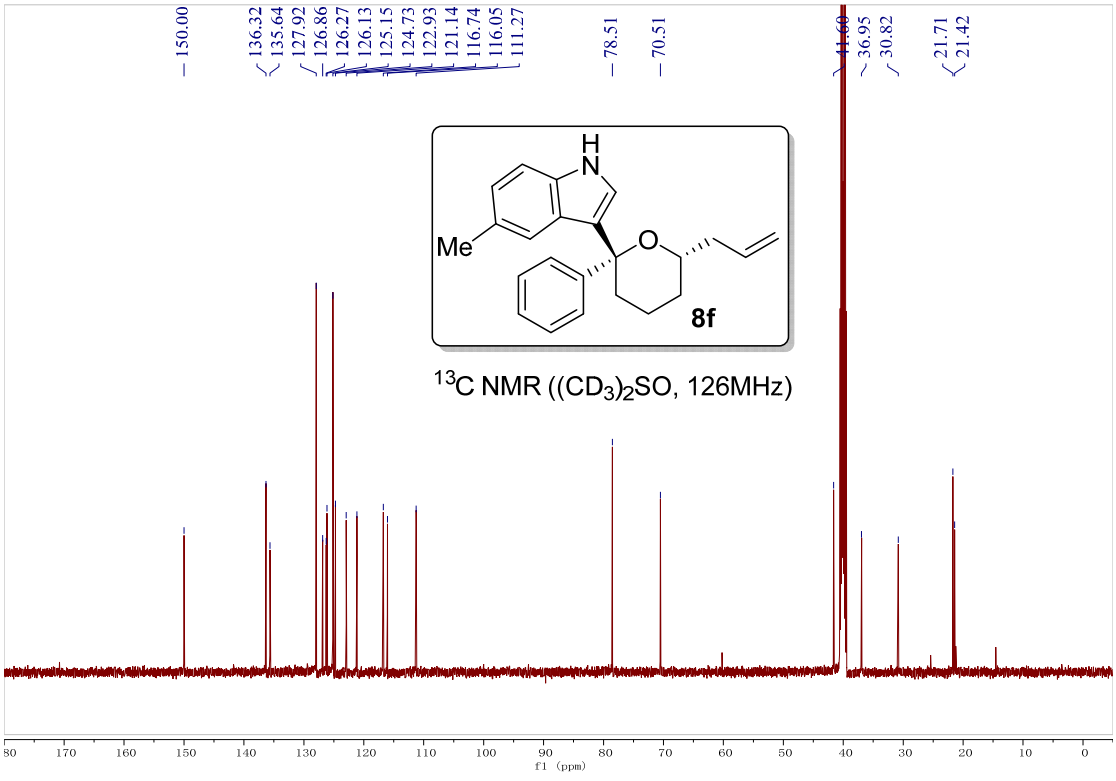


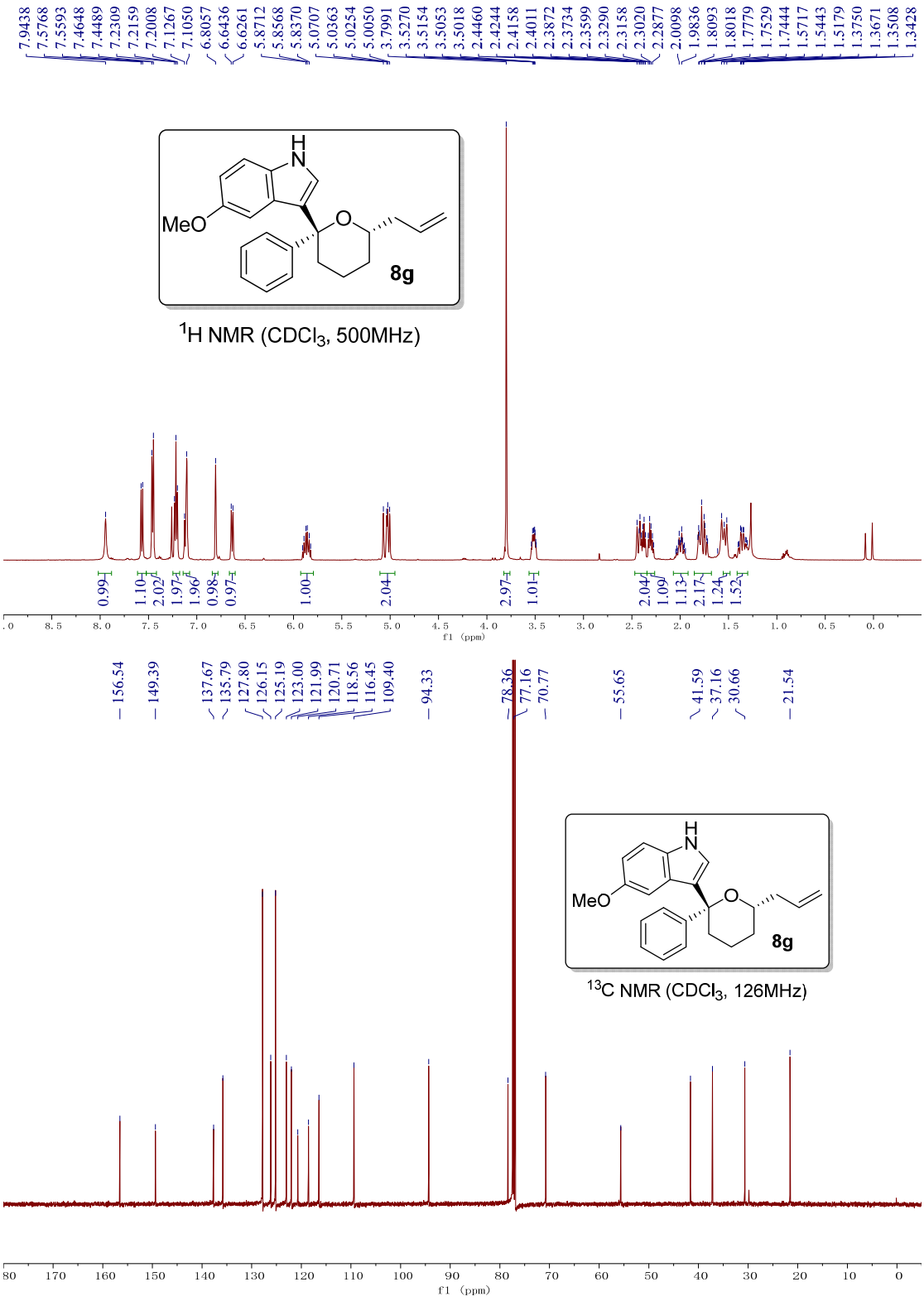
^{19}F NMR ((CD$_3$)$_2$SO), 471MHz)


8e
1H NMR (CDCl3, 500MHz)
f1 (ppm)


8e
13C NMR ((CD3)2SO, 126MHz)
f1 (ppm)


Me
O
H
N
8f
1H NMR ((CD3)2SO, 500MHz)
f1 (ppm)


Me
O
H
N
8f
13C NMR ((CD3)2SO, 126MHz)
f1 (ppm)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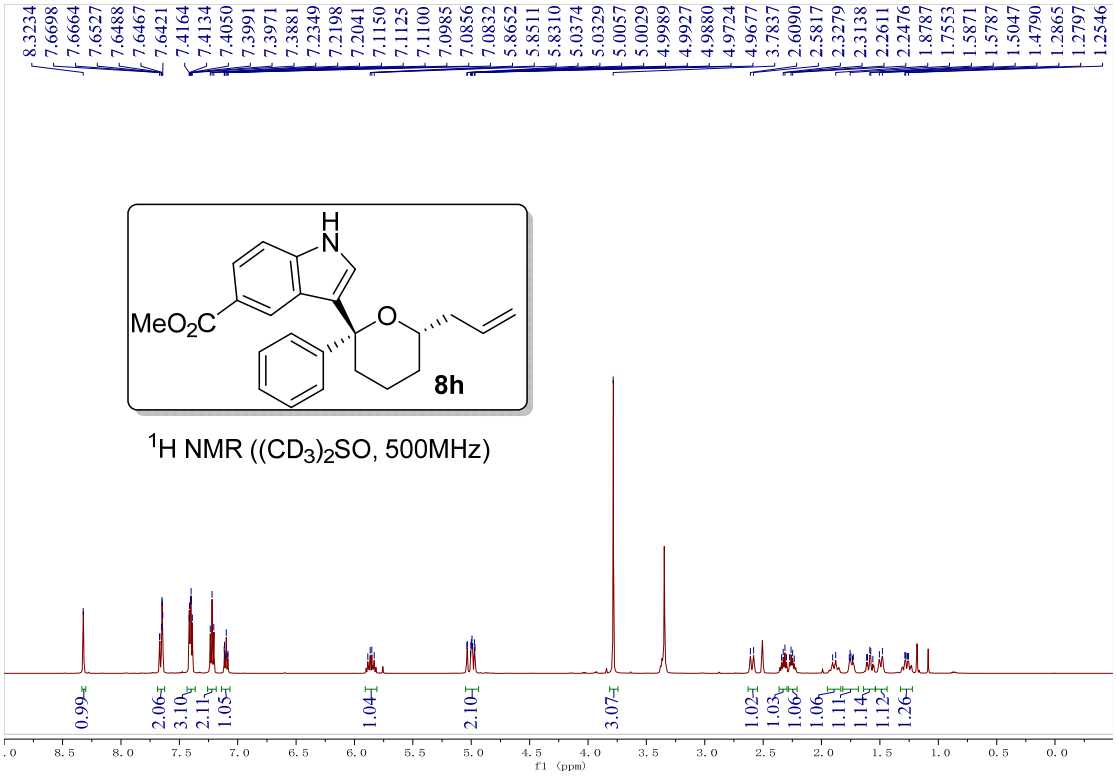
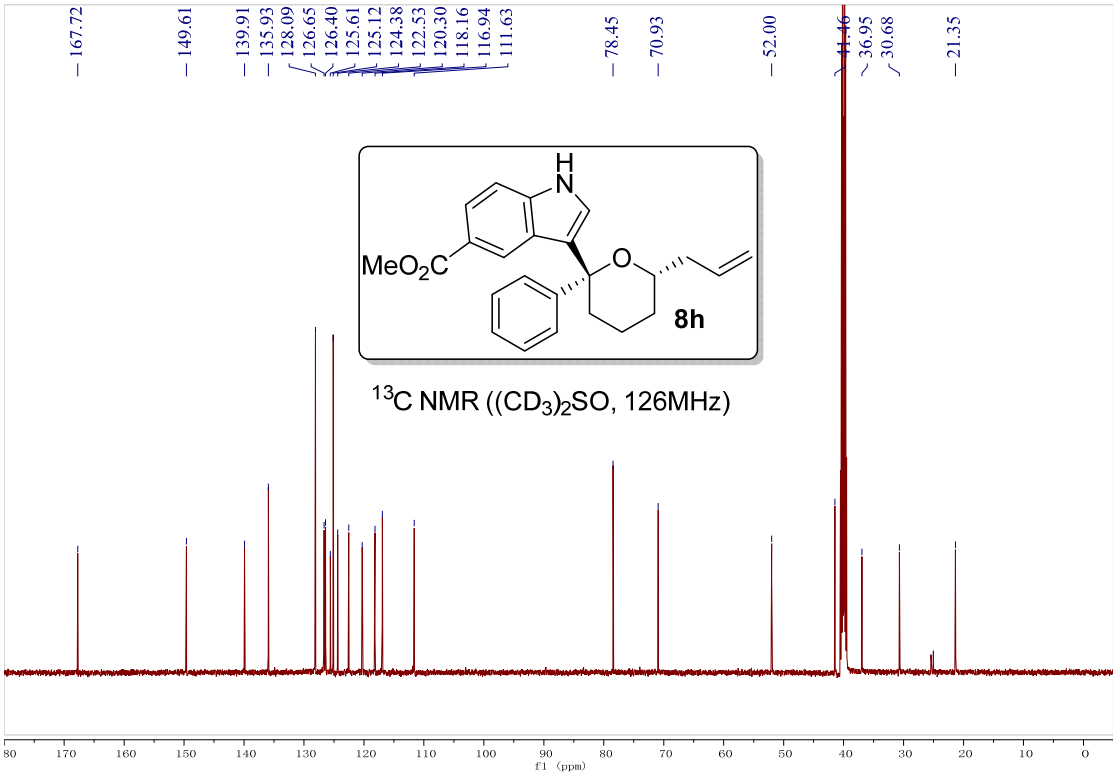
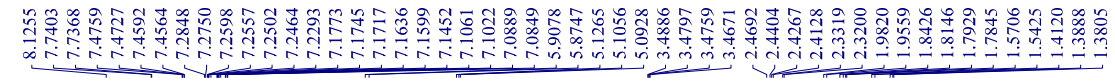
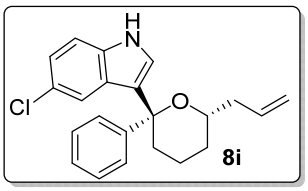
7.5768
7.5593
7.4648
7.4489
7.2309
7.2159
7.2008
7.1267
7.1050
6.8057
6.6436
6.6261
5.8712
5.8568
5.8370
5.0707
5.0363
5.0254
5.0050
3.7991
3.5270
3.5154
3.5053
3.5018
2.4460
2.4244
2.4158
2.4011
2.3872
2.3734
2.3599
2.3290
2.3158
2.3020
2.2877
2.0098
1.9836
1.8093
1.8018
1.7779
1.7529
1.7444
1.5717
1.5443
1.5179
1.3750
1.3671
1.3508
1.3428
MeO
H
N
O
8g
1H NMR (CDCl3, 500MHz)
0.99
1.10
2.02
1.97
1.96
0.98
0.97
1.00
2.04
2.97
1.01
2.04
1.09
1.13
2.17
1.24
1.52
f1 (ppm)
156.54
149.39
137.67
135.79
127.80
126.15
125.19
123.00
121.99
120.71
118.56
116.45
109.40
94.33
78.36
77.16
70.77
55.65
41.59
37.16
30.66
21.54
MeO
H
N
O
8g
13C NMR (CDCl3, 126MHz)
f1 (ppm)

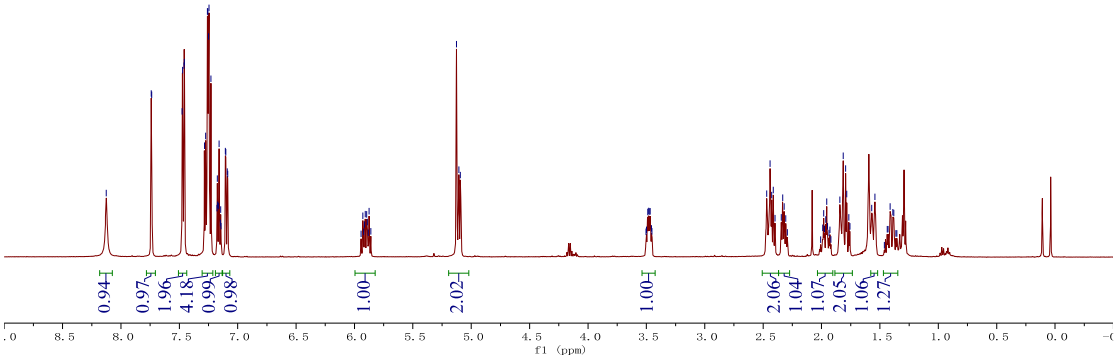

8.3234
7.6698
7.6664
7.6527
7.6488
7.6467
7.6421
7.4164
7.4134
7.4050
7.3991
7.3971
7.3881
7.2349
7.2198
7.2041
7.1150
7.1125
7.1100
7.0985
7.0856
7.0832
5.8652
5.8511
5.8310
5.0374
5.0329
5.0057
5.0029
4.9989
4.9927
4.9880
4.9724
4.9677
3.7837
2.6090
2.5817
2.3279
2.3138
2.2611
2.2476
1.8787
1.7553
1.5871
1.5787
1.5047
1.4790
1.2865
1.2797
1.2546
MeO2C
H
N
O
8h
1H NMR ((CD3)2SO, 500MHz)
0.99
2.06
3.10
2.11
1.05
1.04
2.10
3.07
1.02
1.03
1.06
1.06
1.11
1.14
1.12
1.26
f1 (ppm)

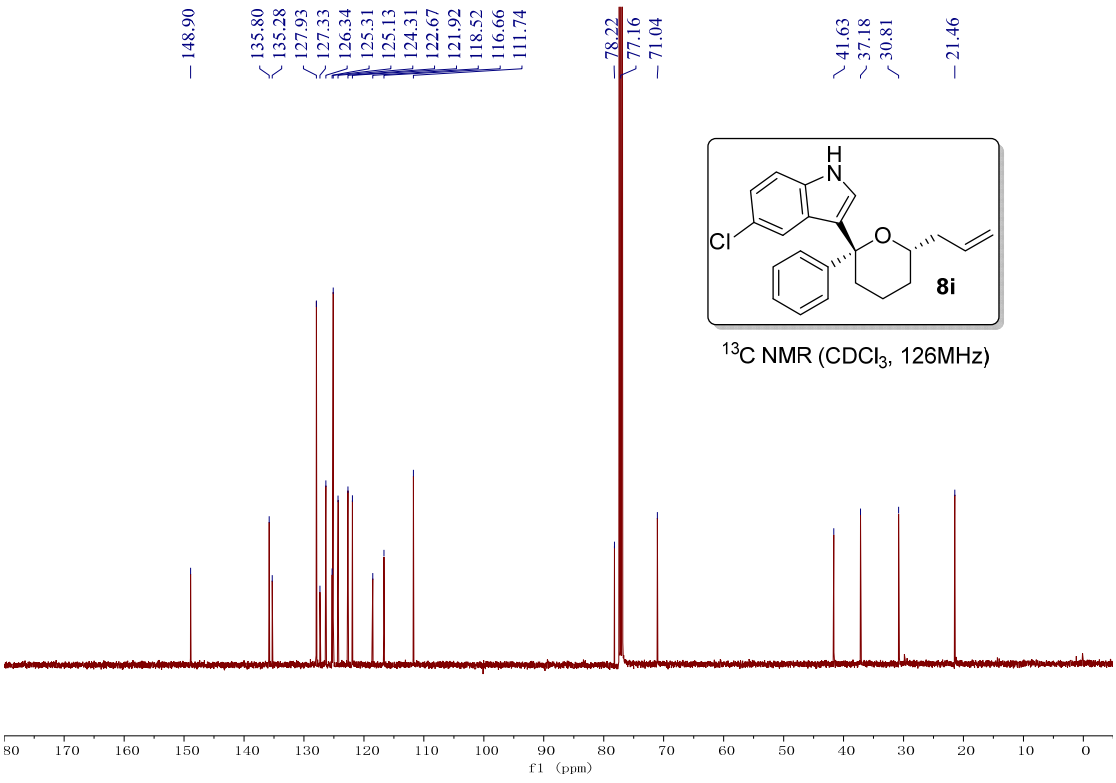

167.72
149.61
139.91
135.93
128.09
126.65
126.40
125.61
125.12
124.38
122.53
120.30
118.16
116.94
111.63
78.45
70.93
52.00
41.46
36.95
30.68
21.35
MeO2C
H
N
O
8h
13C NMR ((CD3)2SO, 126MHz)
f1 (ppm)



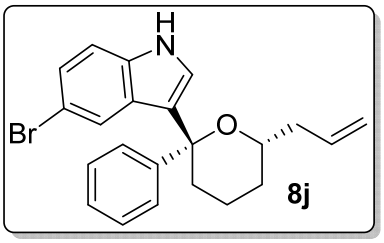


^{1}H NMR ($CDCl_3$, 500MHz)

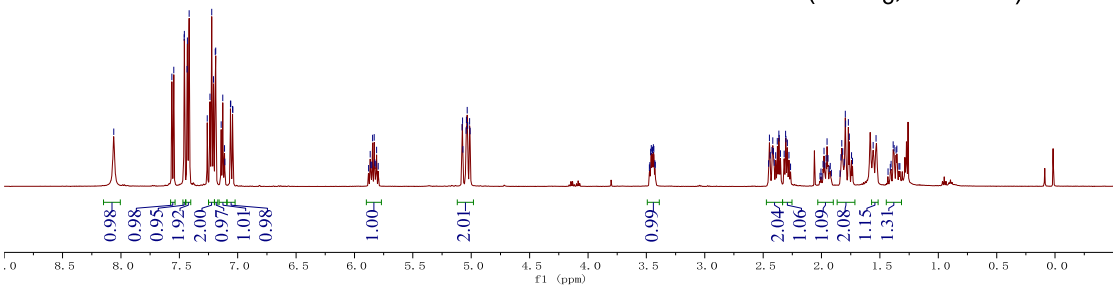


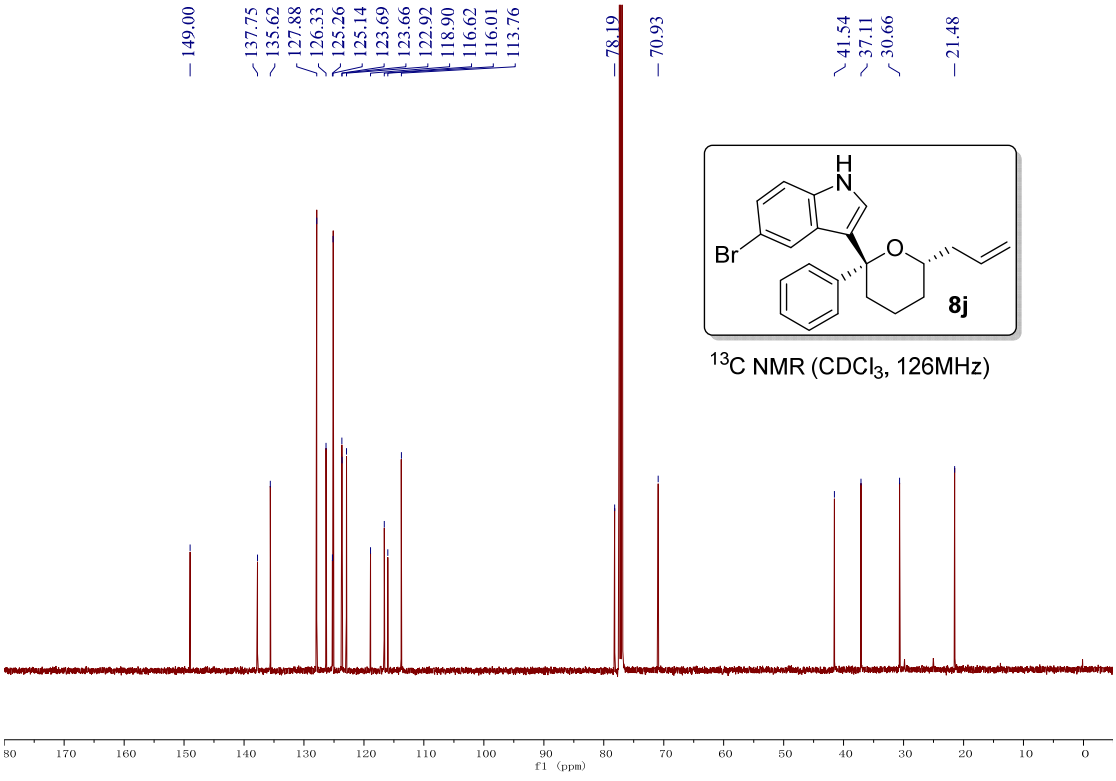


^{13}C NMR ($CDCl_3$, 126MHz)

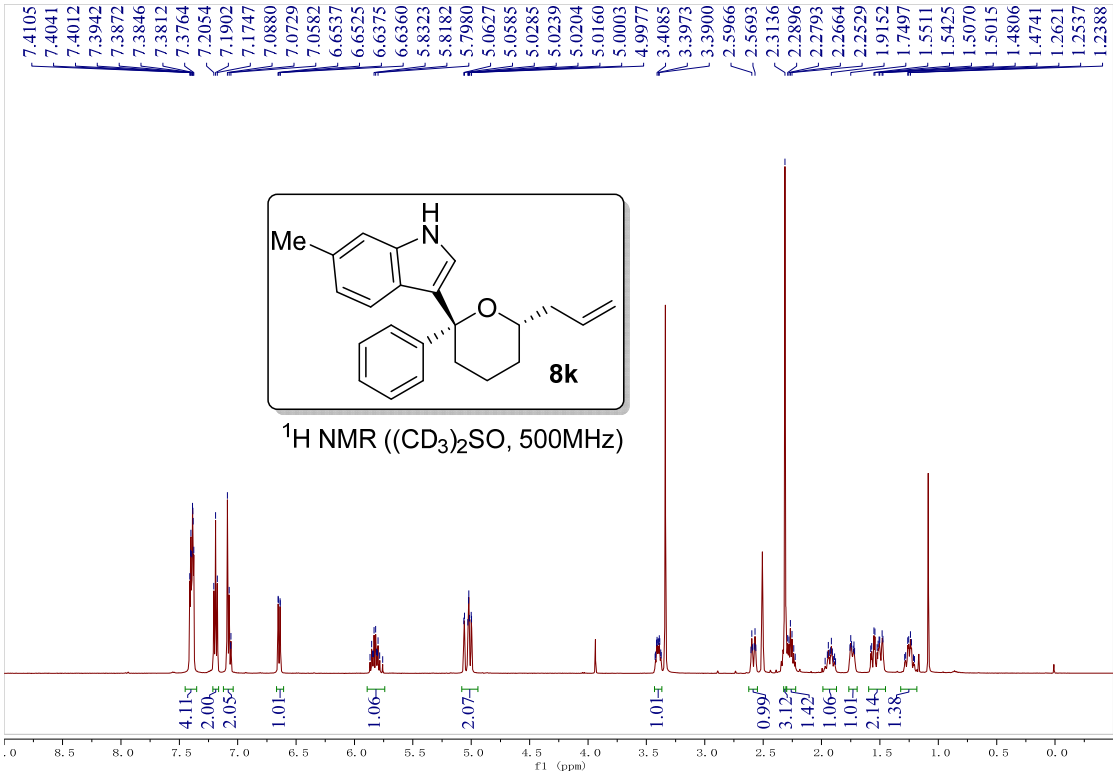


^{1}H NMR ($CDCl_3$, 500MHz)

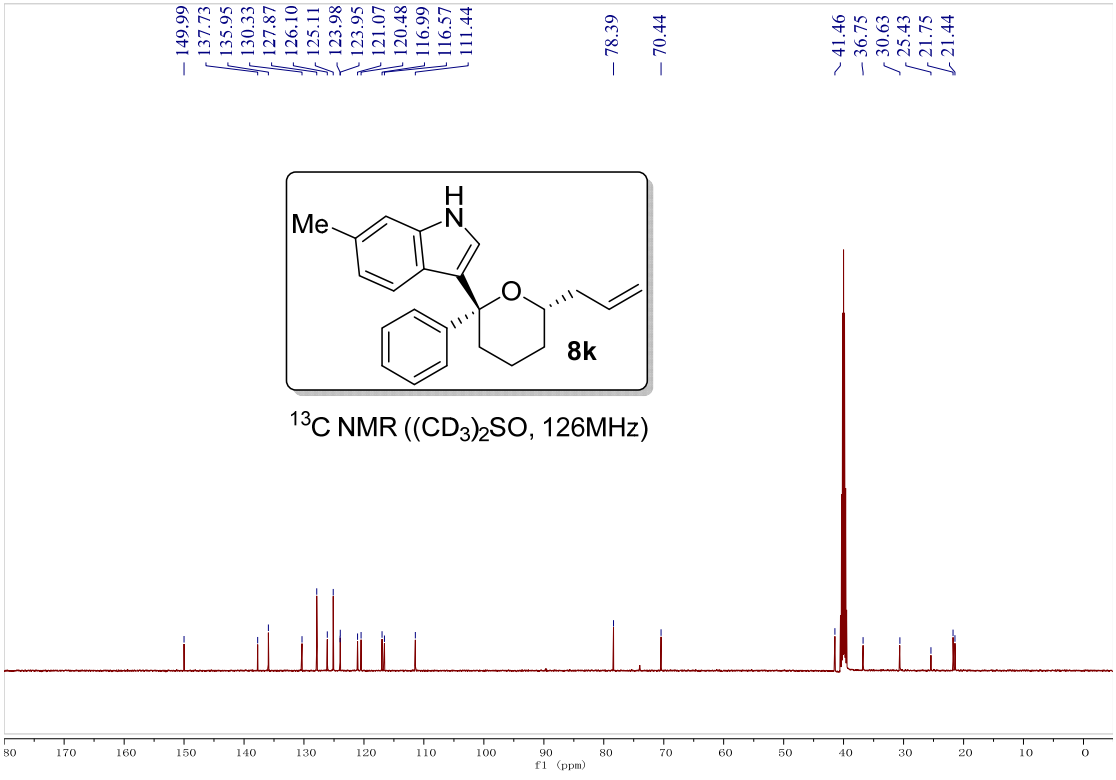




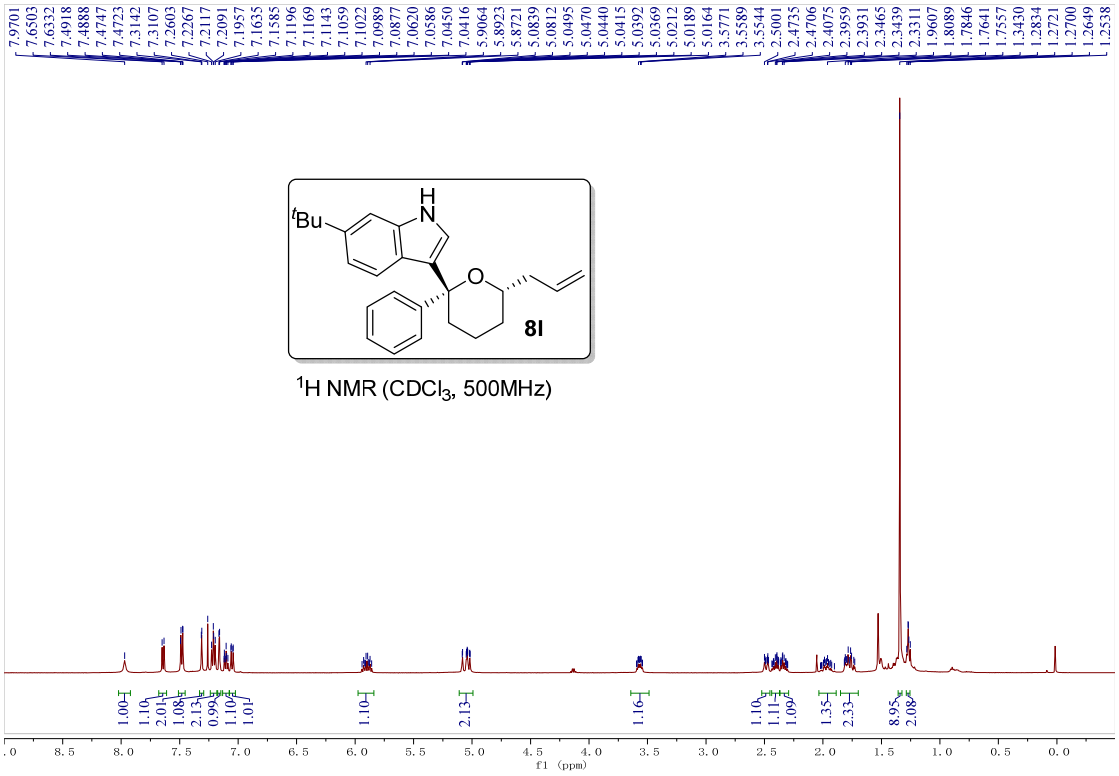
^{13}C NMR ($CDCl_3$, 126MHz)



^{1}H NMR ((CD$_3$)$_2$SO, 500MHz)



^{13}C NMR ((CD$_3$)$_2$SO, 126MHz)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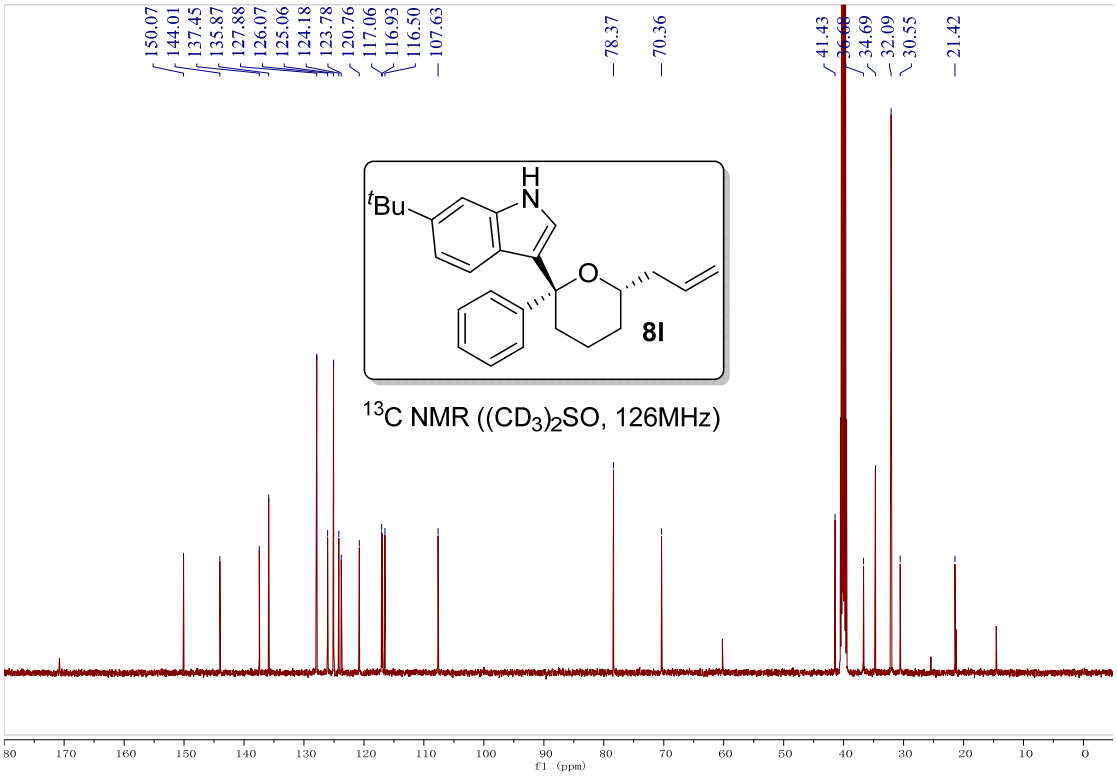
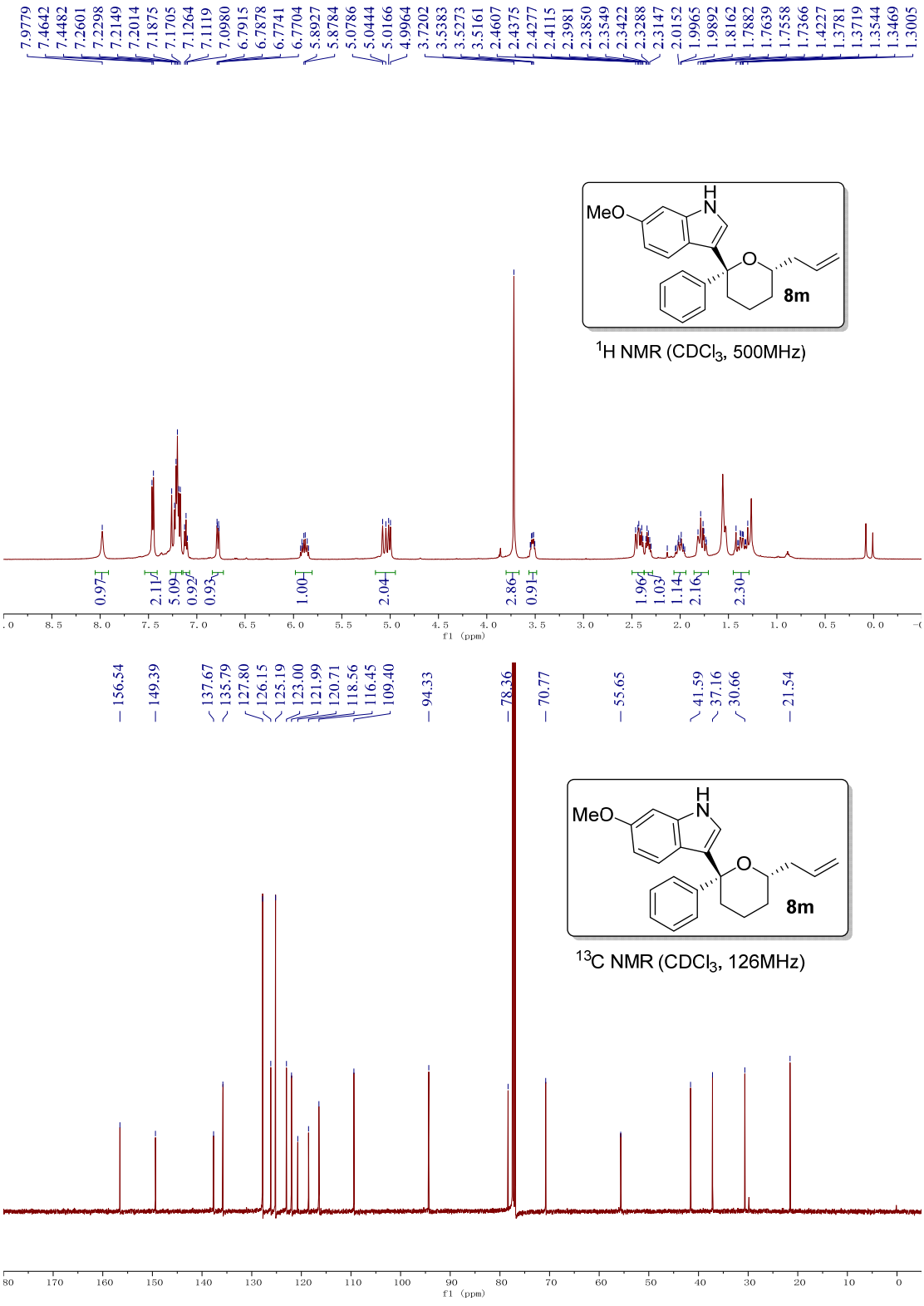
7.6503
7.6332
7.4918
7.4888
7.4747
7.4723
7.3142
7.3107
7.2603
7.2267
7.2117
7.2091
7.1957
7.1635
7.1585
7.1196
7.1169
7.1143
7.1059
7.1022
7.0989
7.0877
7.0620
7.0586
7.0450
7.0416
5.9064
5.8923
5.8721
5.0839
5.0812
5.0495
5.0470
5.0440
5.0415
5.0392
5.0369
5.0212
5.0189
5.0164
3.5771
3.5589
3.5544
2.5001
2.4735
2.4706
2.4075
2.3959
2.3931
2.3465
2.3439
2.3311
1.9607
1.8089
1.7846
1.7641
1.7557
1.3430
1.2834
1.2721
1.2700
1.2649
1.2538
tBu
H
N
O
8l
1H NMR (CDCl3, 500MHz)
1.00
1.10
2.01
1.08
2.13
0.99
1.10
1.01
1.10
2.13
1.16
1.10
1.11
1.09
1.35
2.33
8.95
2.08
f1 (ppm)


150.07
144.01
137.45
135.87
127.88
126.07
125.06
124.18
123.78
120.76
117.06
116.93
116.50
107.63
78.37
70.36
41.43
36.68
34.69
32.09
30.55
21.42
tBu
H
N
O
8l
13C NMR ((CD3)2SO, 126MHz)
f1 (ppm)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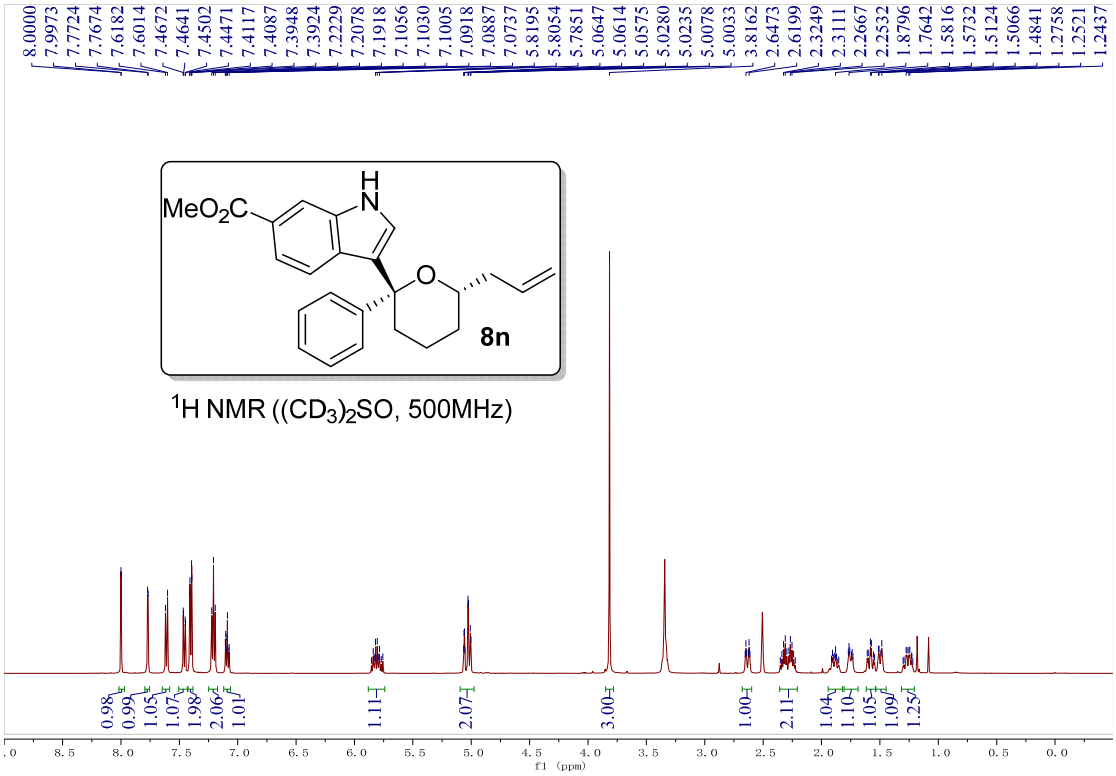
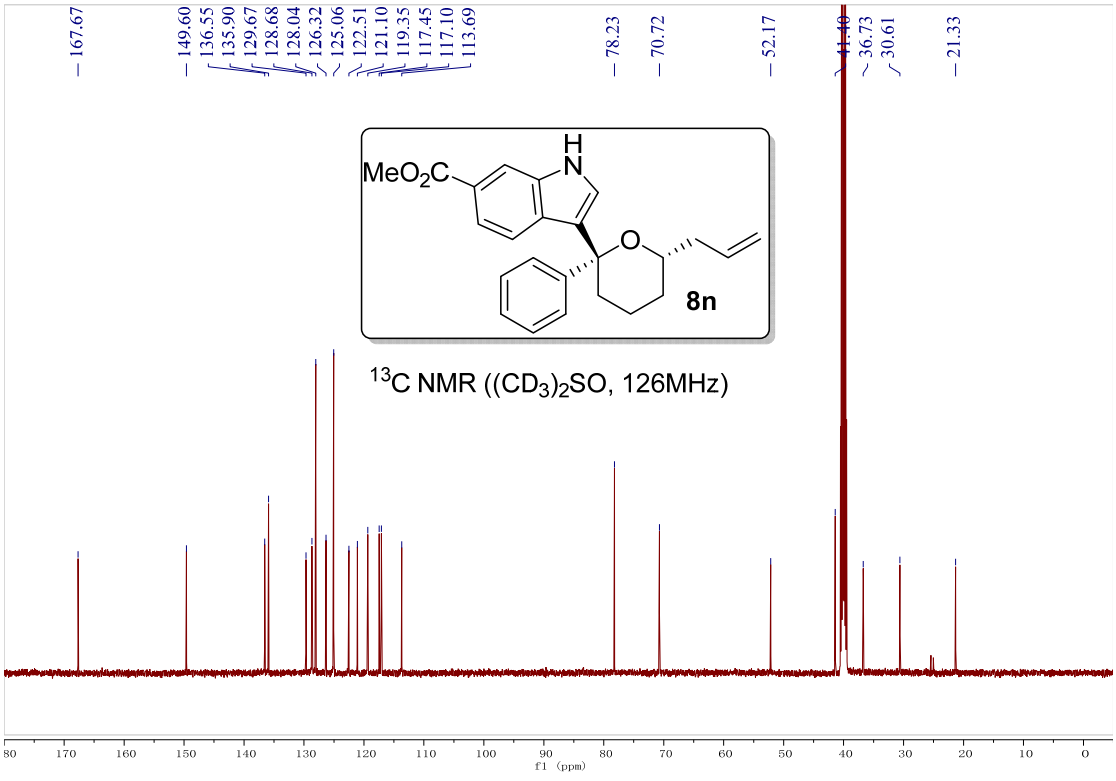
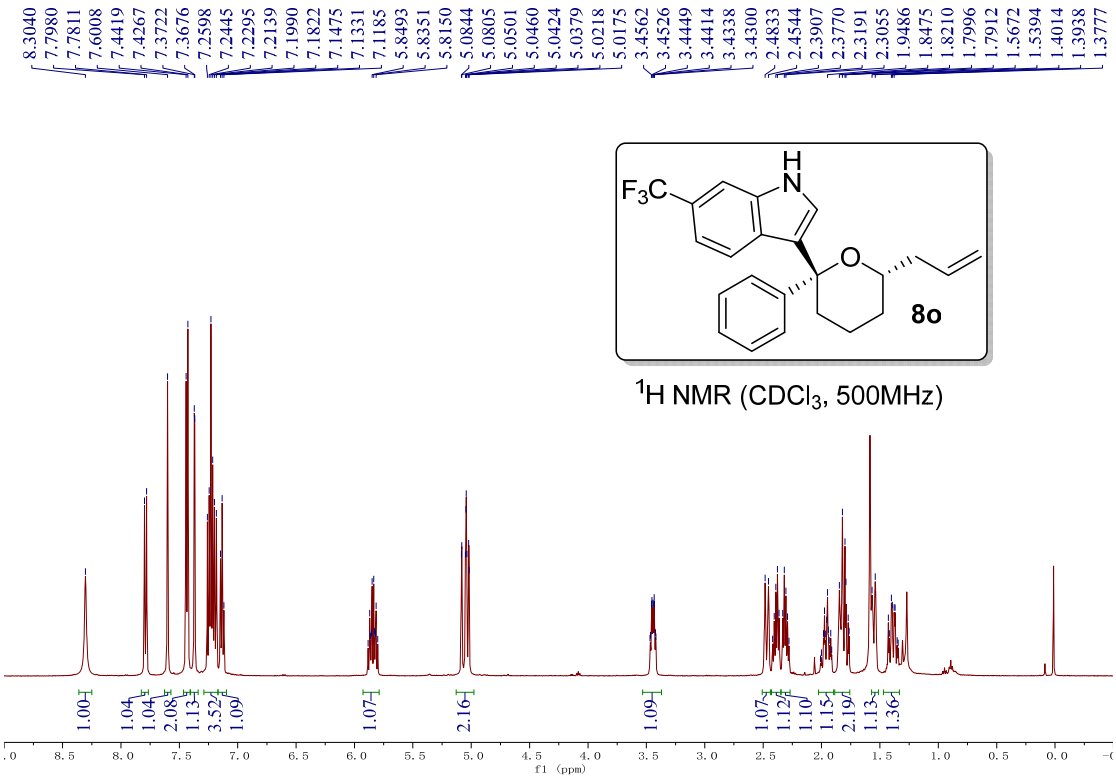
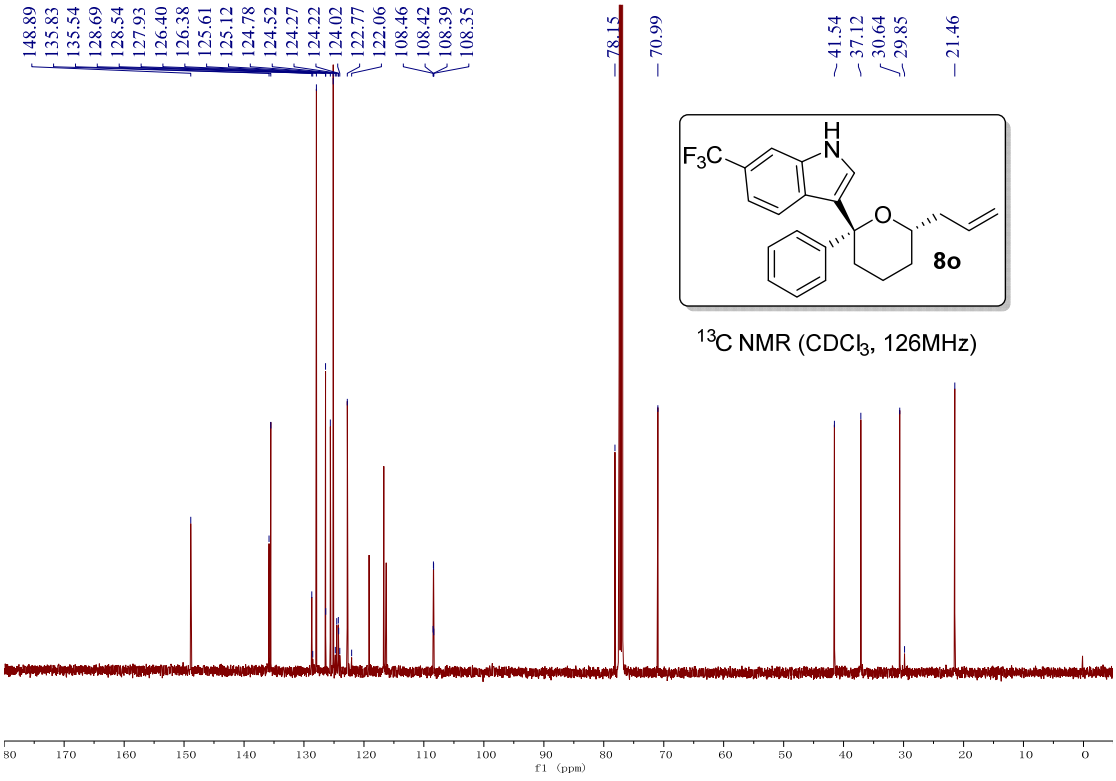
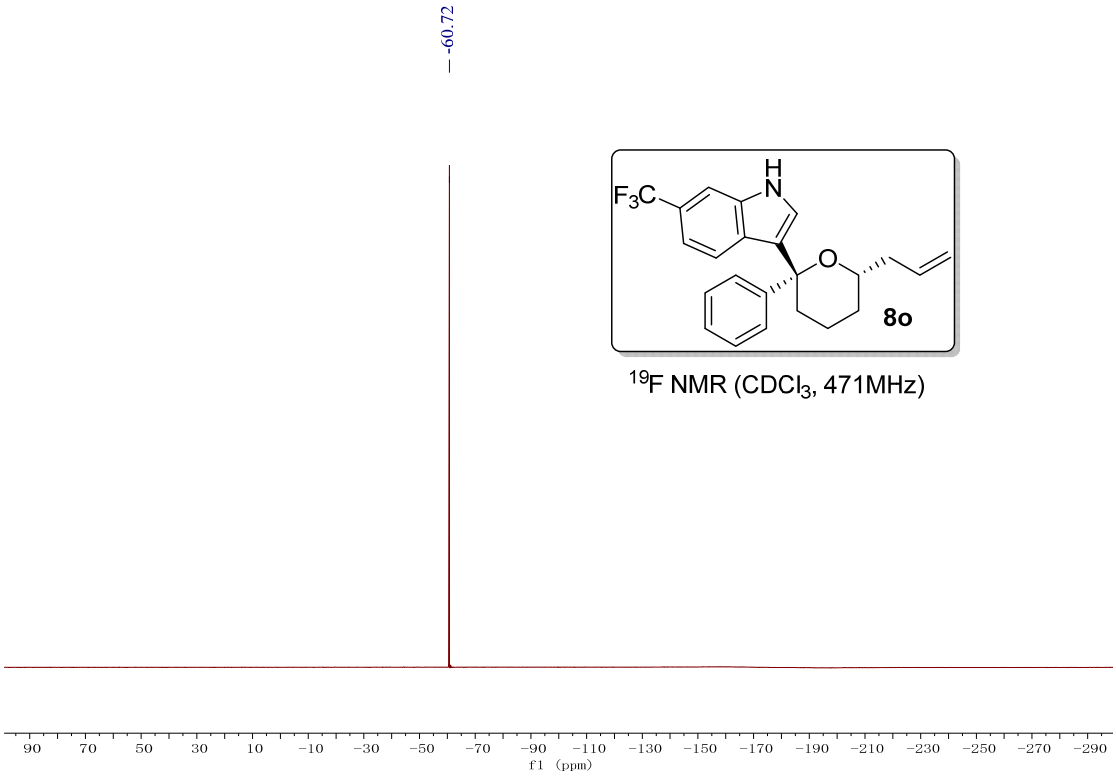
7.4642
7.4482
7.2601
7.2298
7.2149
7.2014
7.1875
7.1705
7.1264
7.1119
7.0980
6.7915
6.7878
6.7741
6.7704
5.8927
5.8784
5.0786
5.0444
5.0166
4.9964
3.7202
3.5383
3.5273
3.5161
2.4607
2.4375
2.4277
2.4115
2.3981
2.3850
2.3549
2.3422
2.3288
2.3147
2.0152
1.9965
1.9892
1.8162
1.7882
1.7639
1.7558
1.7366
1.4227
1.3781
1.3719
1.3544
1.3469
1.3005
MeO
H
N
O
8m
1H NMR (CDCl3, 500MHz)
0.97
2.11
5.09
0.92
0.93
1.00
2.04
2.86
0.91
1.96
1.03
1.14
2.16
2.30
f1 (ppm)
156.54
149.39
137.67
135.79
127.80
126.15
125.19
123.00
121.99
120.71
118.56
116.45
109.40
94.33
78.36
70.77
55.65
41.59
37.16
30.66
21.54
MeO
H
N
O
8m
13C NMR (CDCl3, 126MHz)
f1 (ppm)


8.0000
7.9973
7.7724
7.7674
7.6182
7.6014
7.4672
7.4641
7.4502
7.4471
7.4117
7.4087
7.3948
7.3924
7.2229
7.2078
7.1918
7.1056
7.1030
7.1005
7.0918
7.0887
7.0737
5.8195
5.8054
5.7851
5.0647
5.0614
5.0575
5.0280
5.0235
5.0078
5.0033
3.8162
2.6473
2.6199
2.3249
2.3111
2.2667
2.2532
1.8796
1.7642
1.5816
1.5732
1.5124
1.5066
1.4841
1.2758
1.2521
1.2437
MeO2C
H
N
O
8n
1H NMR ((CD3)2SO, 500MHz)
0.98
0.99
1.05
1.07
1.98
2.06
1.01
1.11
2.07
3.00
1.00
2.11
1.04
1.10
1.05
1.09
1.25
f1 (ppm)

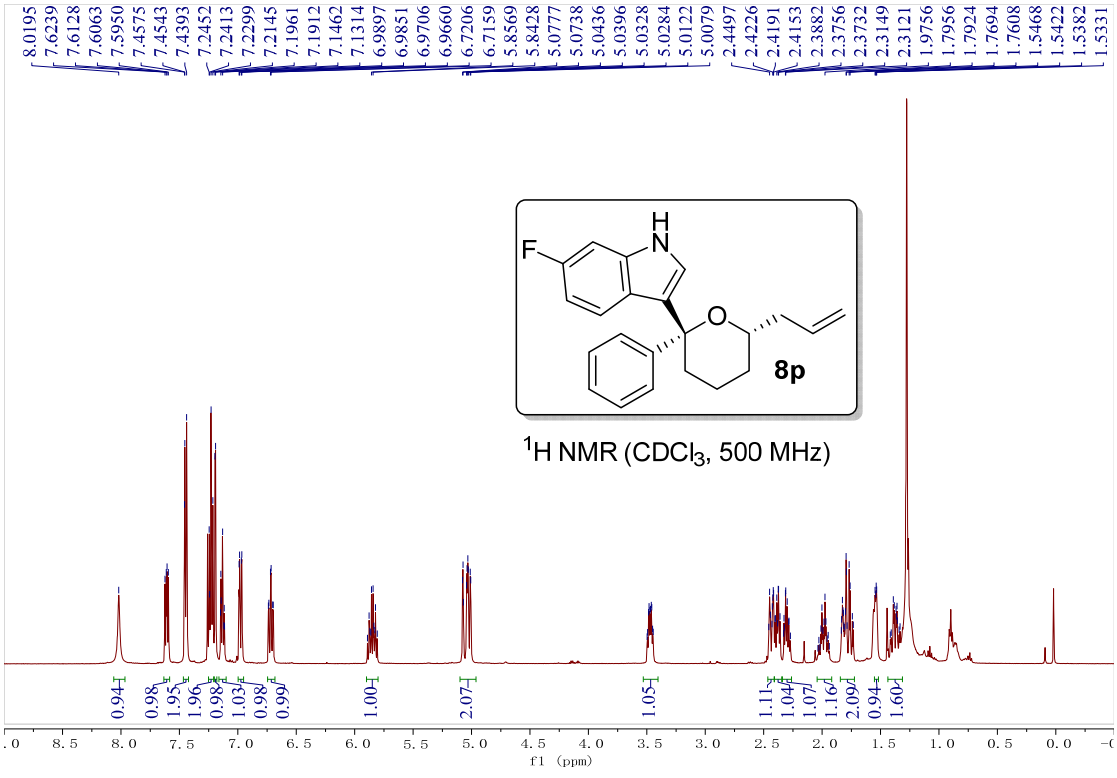

167.67
149.60
136.55
135.90
129.67
128.68
128.04
126.32
125.06
122.51
121.10
119.35
117.45
117.10
113.69
78.23
70.72
52.17
41.40
36.73
30.61
21.33
MeO2C
H
N
O
8n
13C NMR ((CD3)2SO, 126MHz)
f1 (ppm)


8.3040
7.7980
7.7811
7.6008
7.4419
7.4267
7.3722
7.3676
7.2598
7.2445
7.2295
7.2139
7.1990
7.1822
7.1475
7.1331
7.1185
5.8493
5.8351
5.8150
5.0844
5.0805
5.0501
5.0460
5.0424
5.0379
5.0218
5.0175
3.4562
3.4526
3.4449
3.4414
3.4338
3.4300
2.4833
2.4544
2.3907
2.3770
2.3191
2.3055
1.9486
1.8475
1.8210
1.7996
1.7912
1.5672
1.5394
1.4014
1.3938
1.3777
F3C
H
N
O
8o
1H NMR (CDCl3, 500MHz)
1.00
1.04
1.04
2.08
1.13
3.52
1.09
1.07
2.16
1.09
1.07
1.12
1.10
1.15
2.19
1.13
1.36
f1 (ppm)

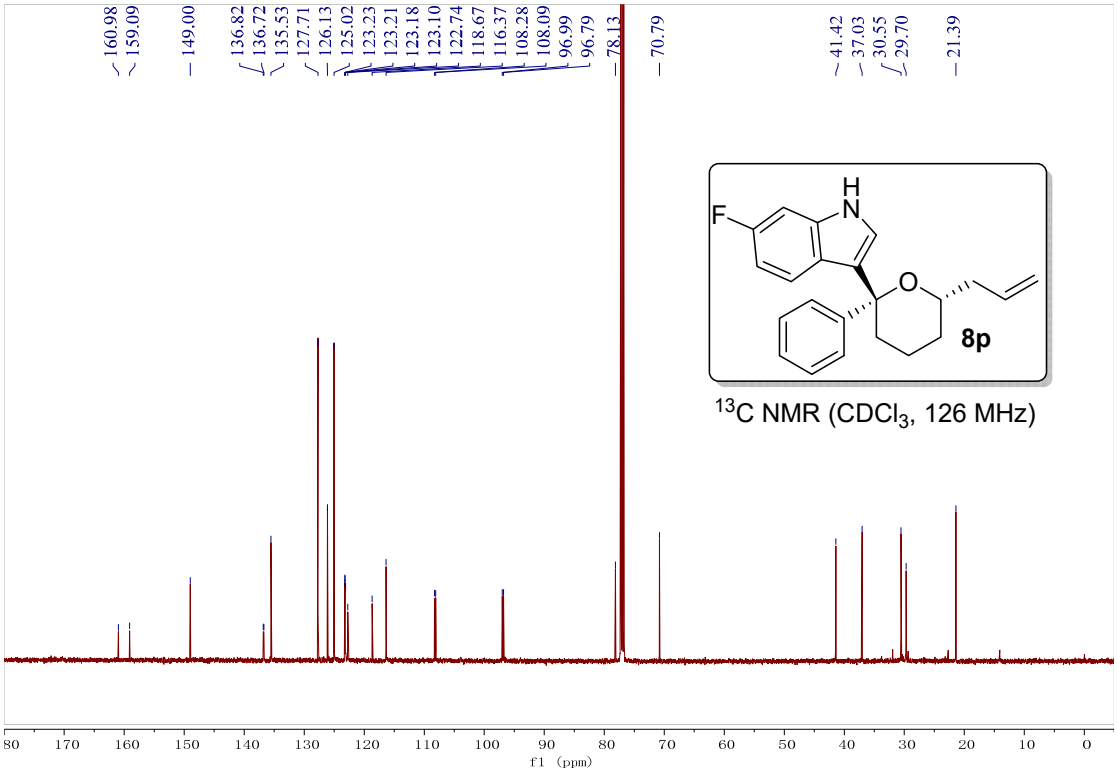

148.89
135.83
135.54
128.69
128.54
127.93
126.40
126.38
125.61
125.12
124.78
124.52
124.27
124.22
124.02
122.77
122.06
108.46
108.42
108.39
108.35
78.15
70.99
41.54
37.12
30.64
29.85
21.46
F3C
H
N
O
8o
13C NMR (CDCl3, 126MHz)
f1 (ppm)



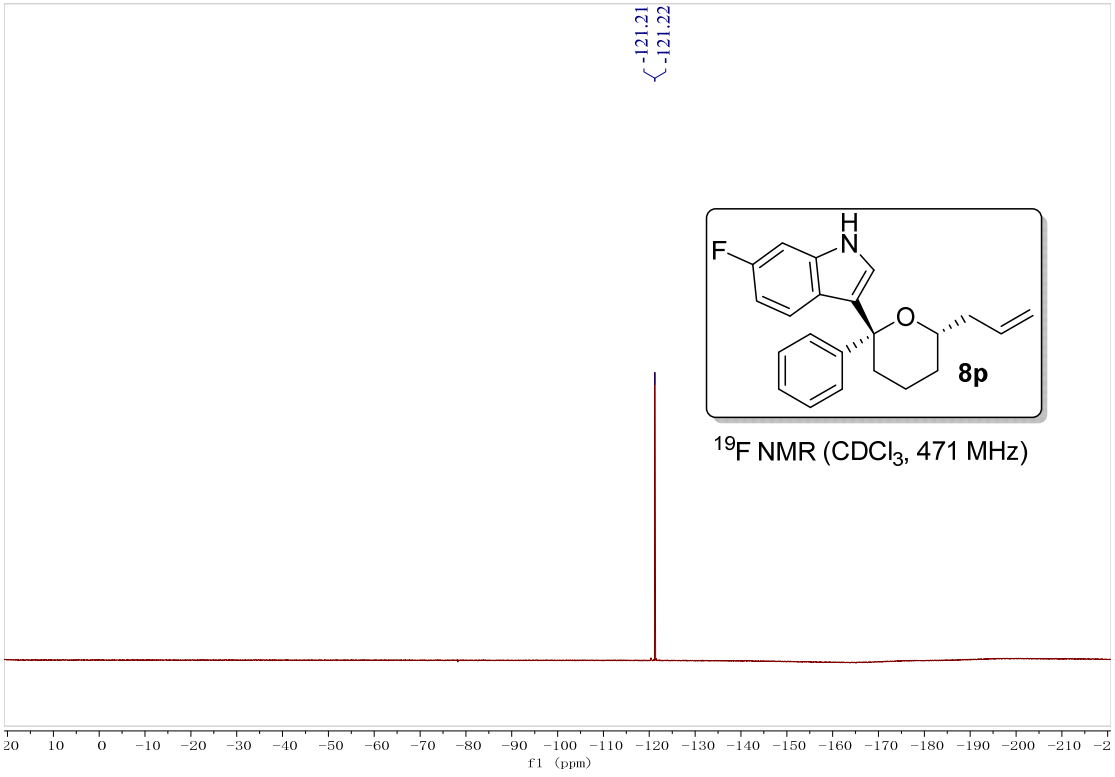
^{19}F NMR ($CDCl_3$, 471MHz)



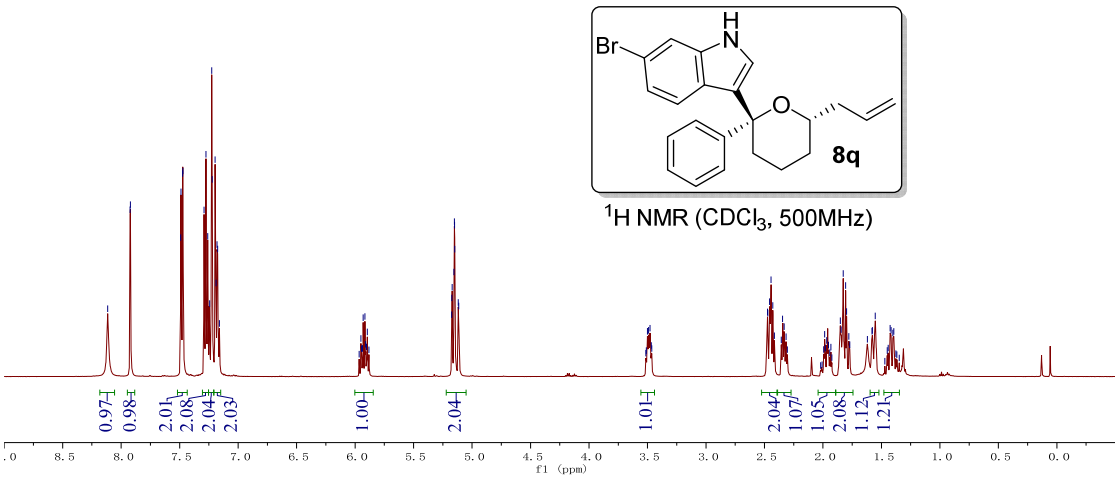
^{1}H NMR ($CDCl_3$, 500 MHz)



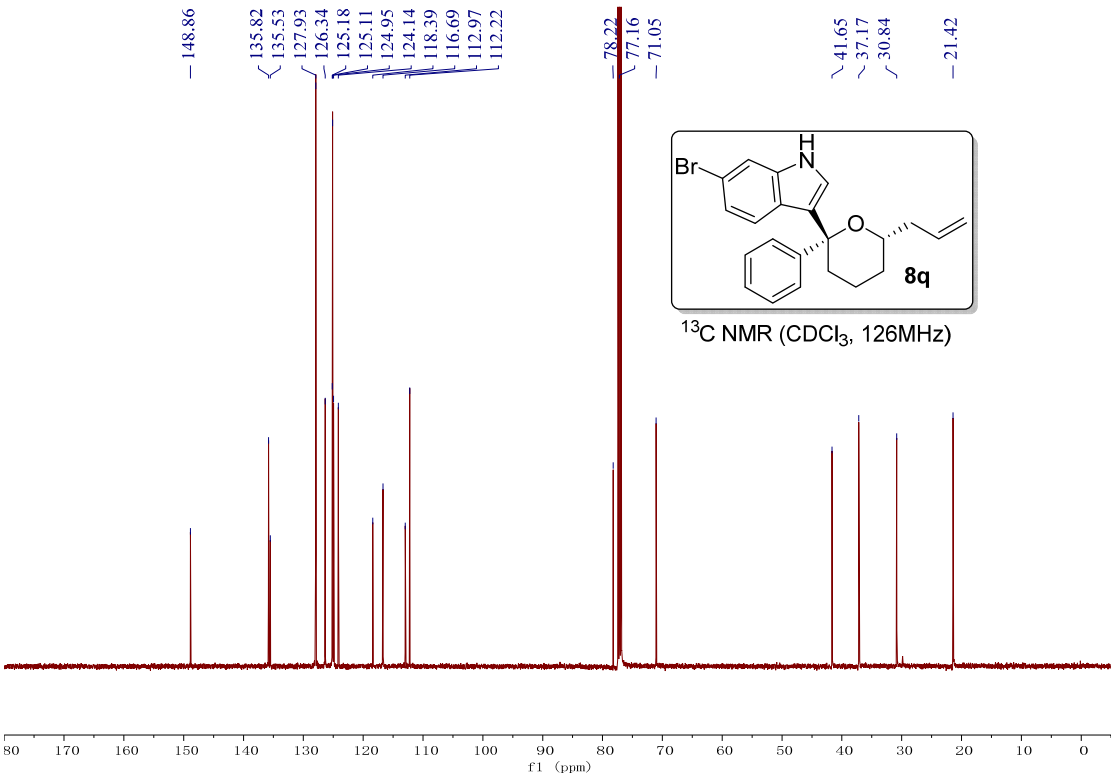
^{13}C NMR ($CDCl_3$, 126 MHz)



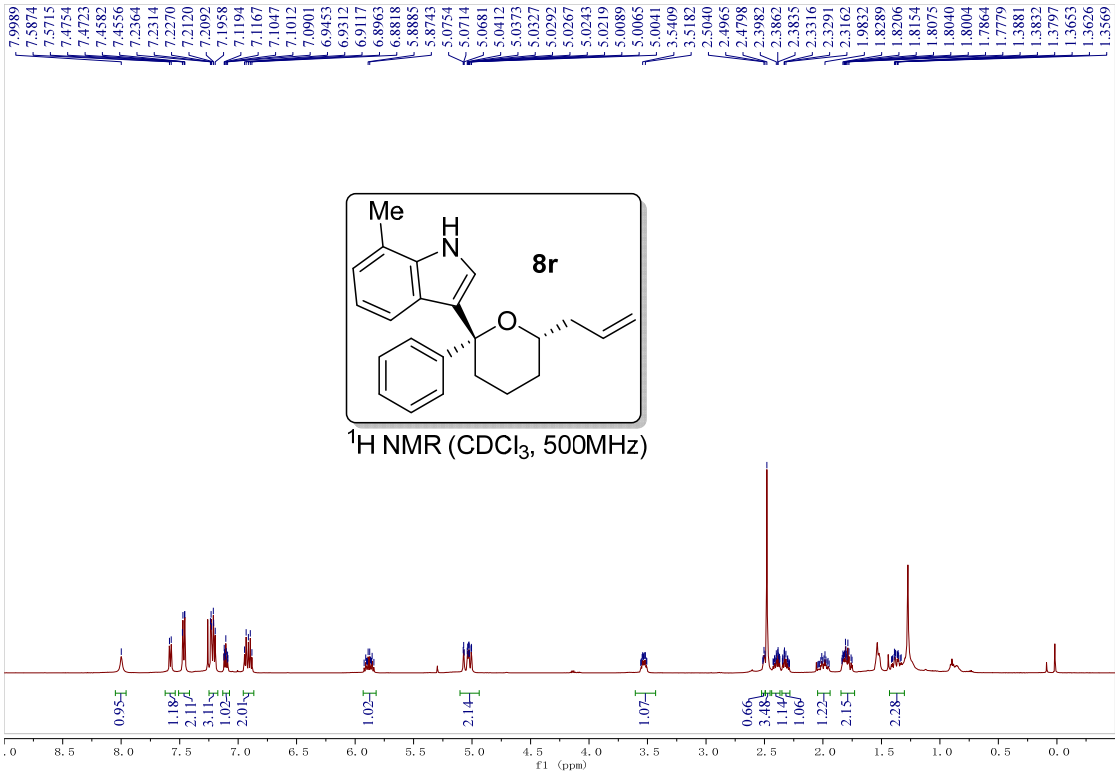
^{19}F NMR ($CDCl_3$, 471 MHz)

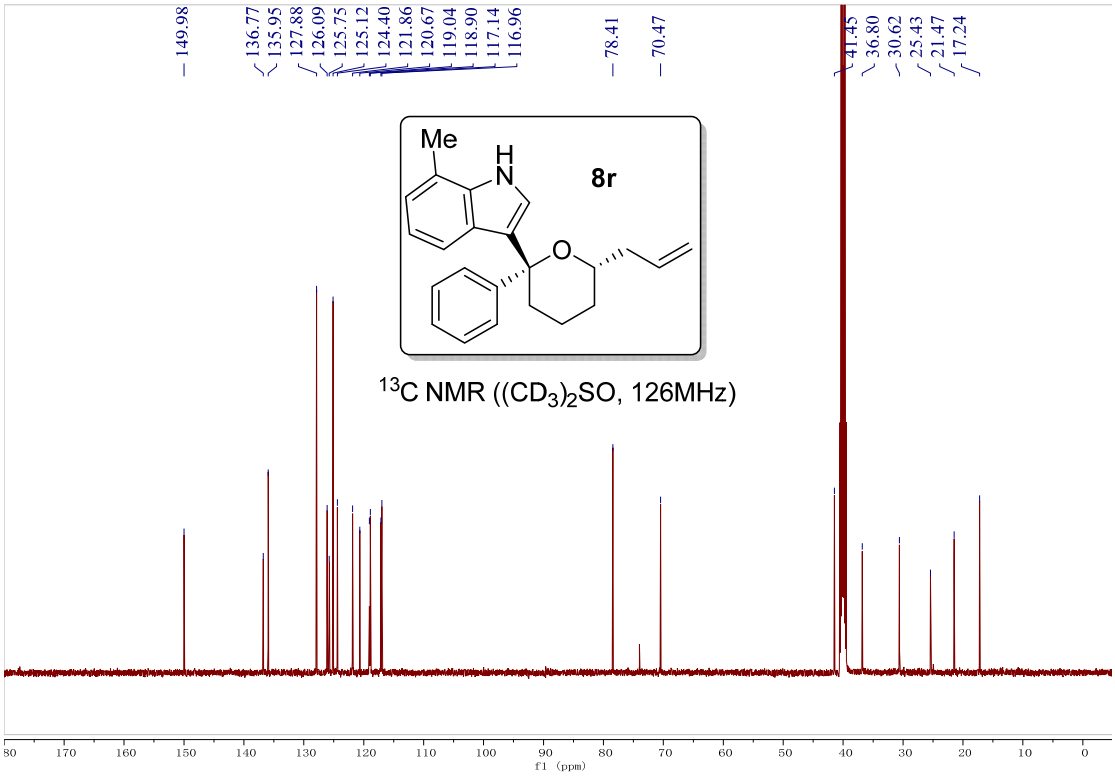


^{1}H NMR ($CDCl_3$, 500MHz)



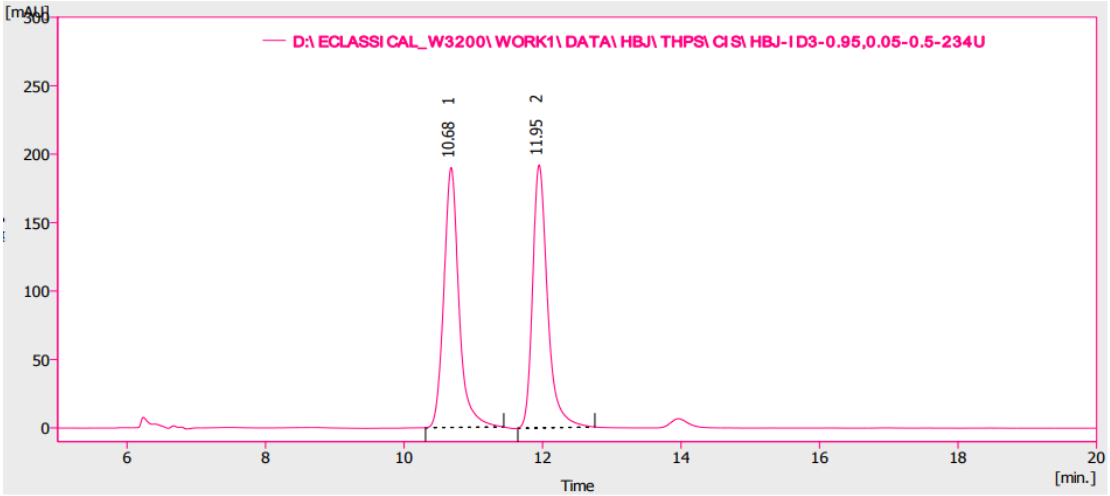
^{13}C NMR ($CDCl_3$, 126MHz)

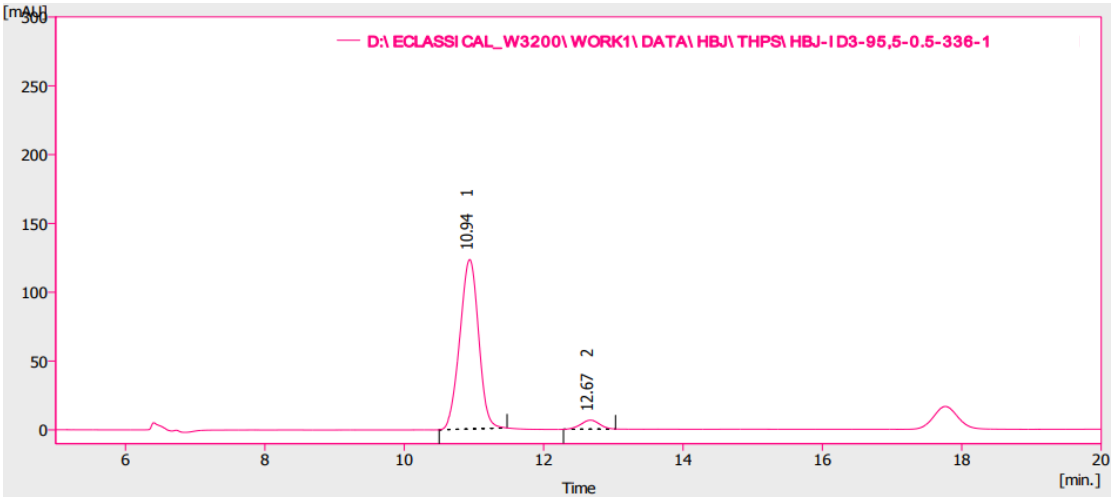

Me
H
N
8r
O
^{1}H NMR ($CDCl_3$, 500MHz)
f1 (ppm)


Me
H
N
8r
O
^{13}C NMR ($(CD_3)_2SO$, 126MHz)
f1 (ppm)

Copies of HPLC charts

cis-**3a**, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm)

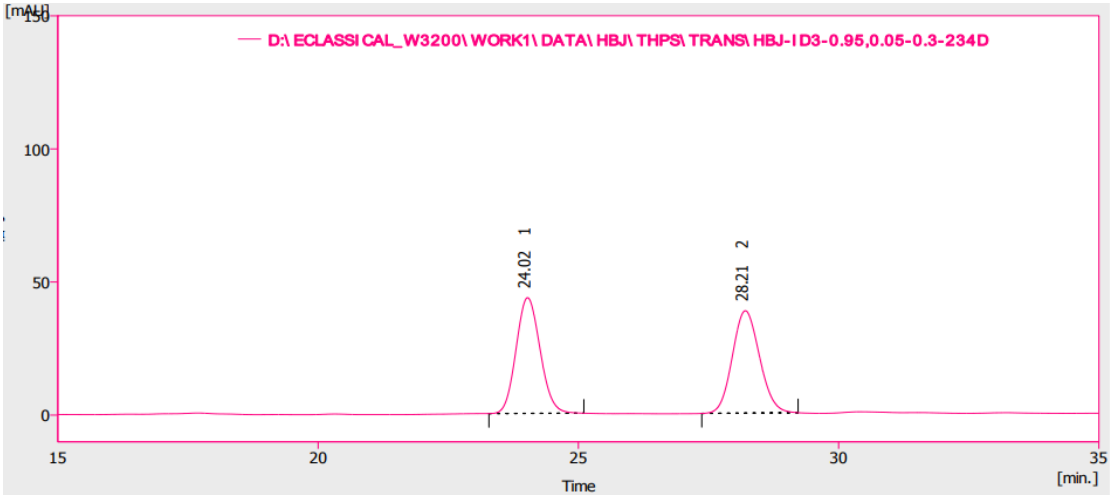


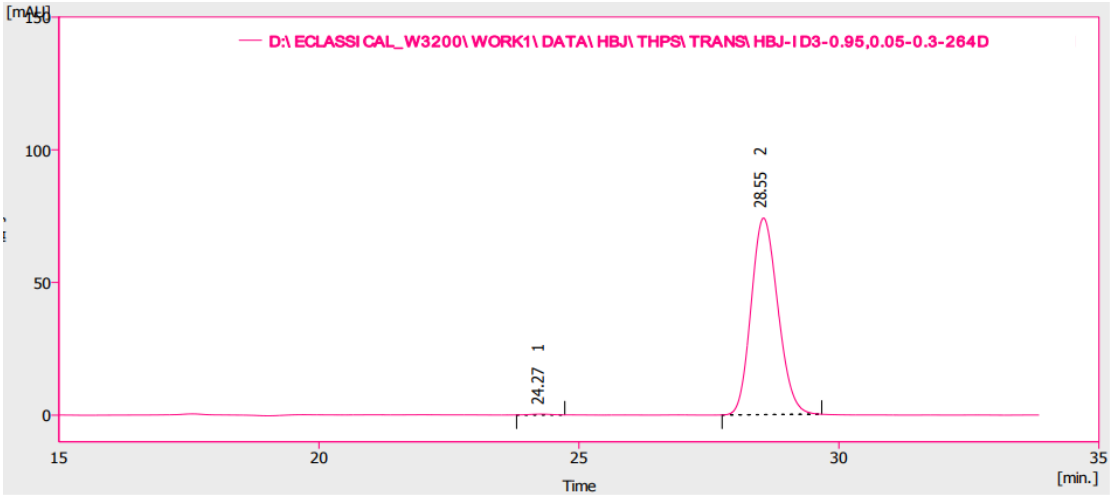


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	10.68	316.51	4817.25	50.0
2	11.95	320.29	4809.97	50.0
Total		636.80	9627.22	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	10.94	205.21	3840.06	95.0
2	12.67	10.87	201.21	5.0
Total		216.08	4041.28	100.0

trans-**3a**, 99% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

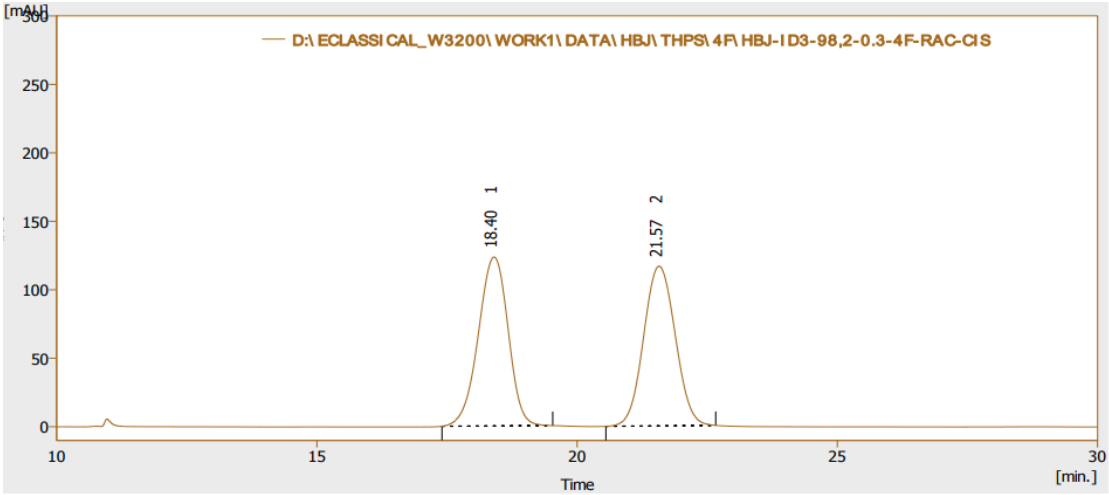


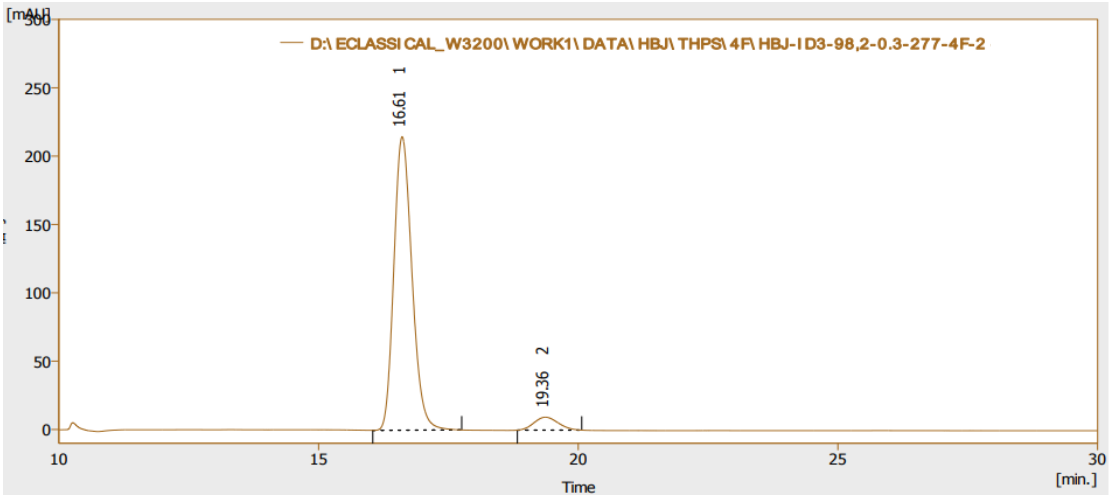


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	24.02	72.48	2326.14	50.0
2	28.21	64.11	2330.59	50.0
Total		216.08	4656.73	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	24.27	0.52	14.04	0.3
2	28.55	123.47	4414.42	99.7
Total		123.99	4428.47	100.0

3b, 89% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm)

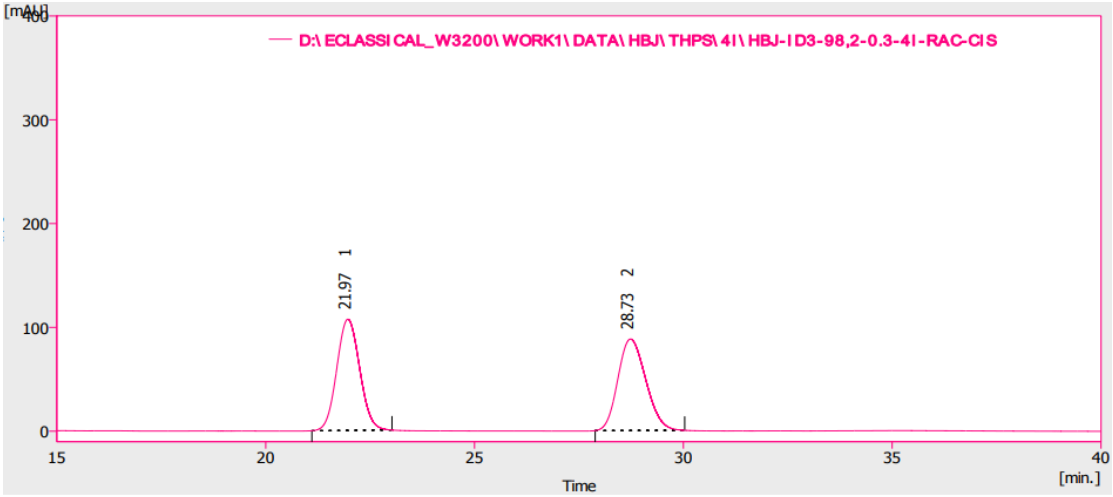


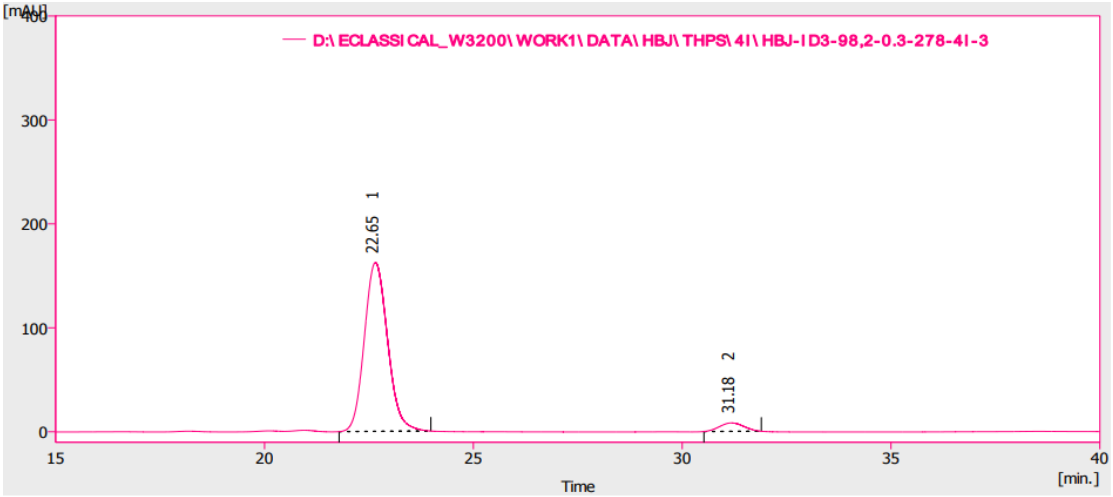


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	18.40	205.63	8203.12	50.0
2	21.57	194.41	8213.68	50.0
Total		400.04	16416.80	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.61	357.92	8676.57	94.5
2	19.36	15.81	509.57	5.5
Total		373.73	9186.14	100.0

3c, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm)

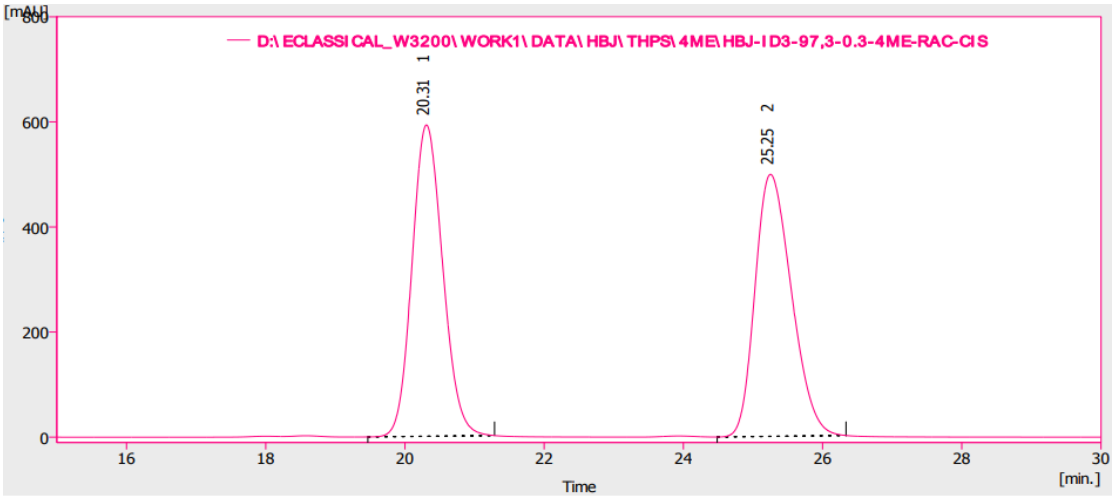


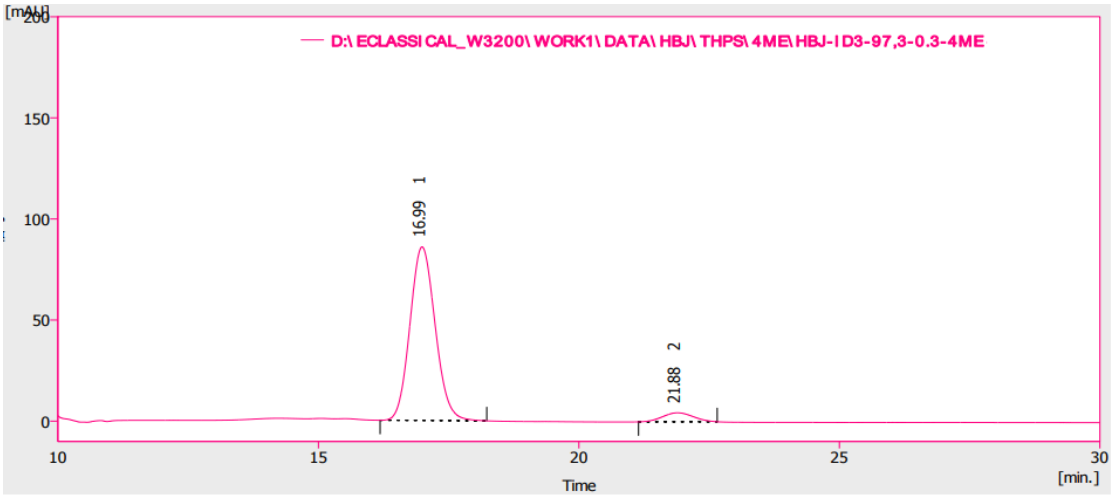


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.97	178.62	6808.83	50.0
2	28.73	146.85	6801.76	50.0
Total		325.47	13610.59	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	22.65	270.93	10479.51	95.1
2	31.18	13.59	544.89	4.9
Total		284.52	11024.40	100.0

3d, 88% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm)

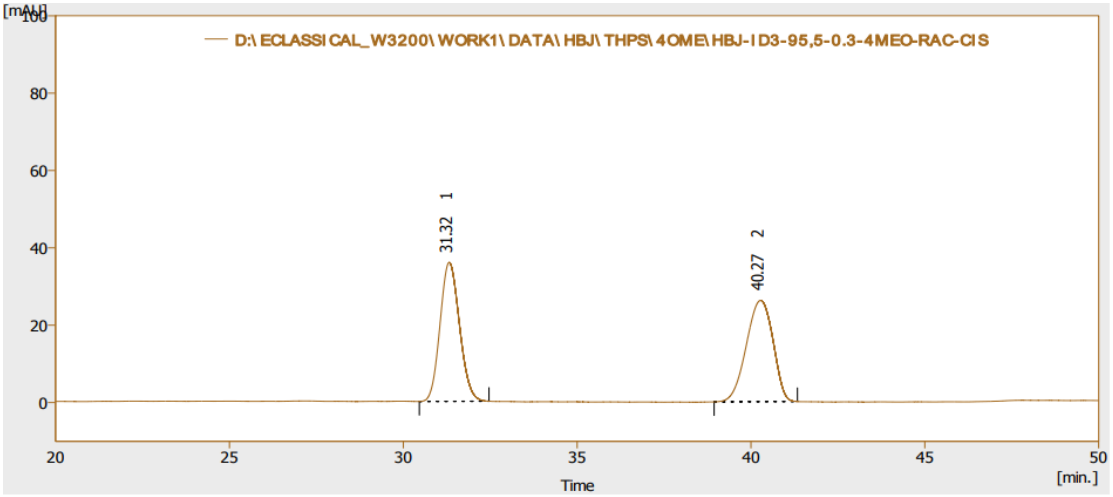


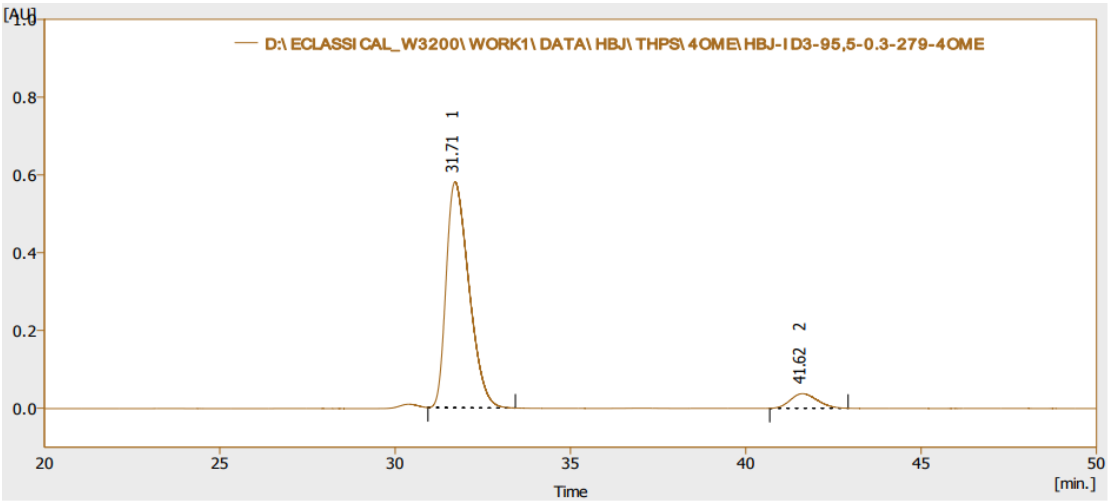


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	20.31	987.73	30243.96	50.0
2	25.25	831.30	30240.97	50.0
Total		1819.04	60484.93	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.99	143.10	4830.50	94.1
2	21.88	7.42	301.39	5.9
Total		150.52	5131.89	100.0

3e, 86% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

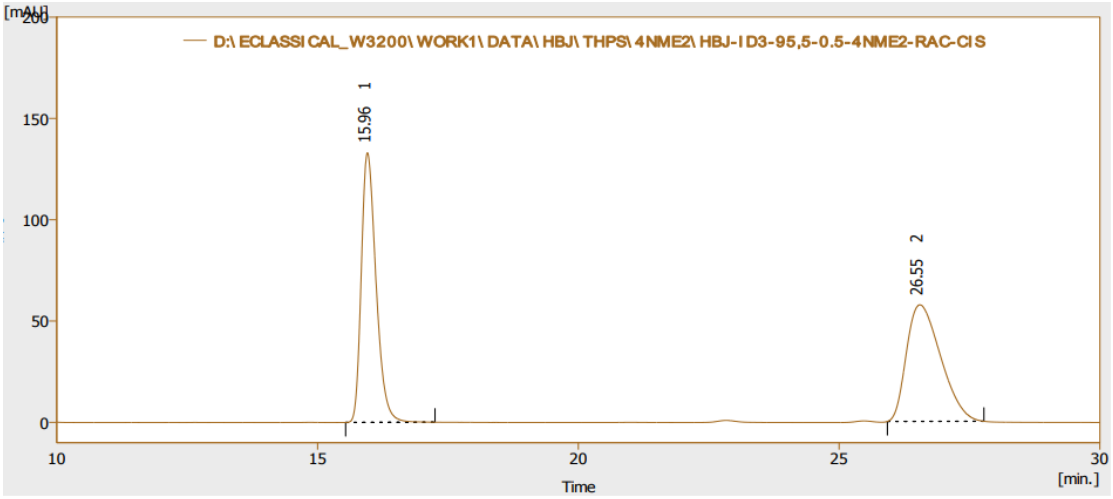


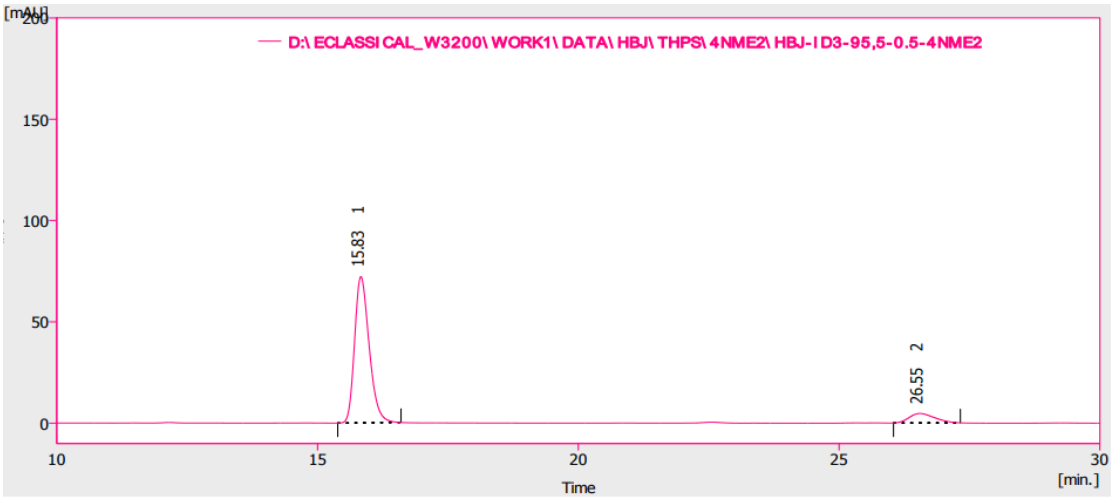


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	31.32	59.90	2323.88	50.0
2	40.27	43.64	2326.30	50.0
Total		103.54	4653.18	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	31.71	967.95	43674.64	92.9
2	41.62	62.74	3345.28	7.1
Total		1030.68	47019.91	100.0

3f, 80% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm)

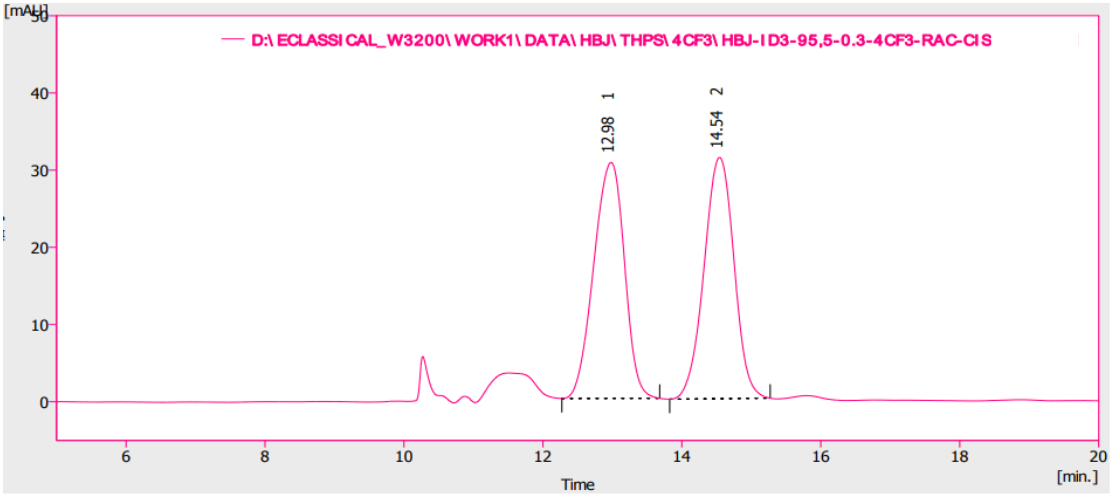


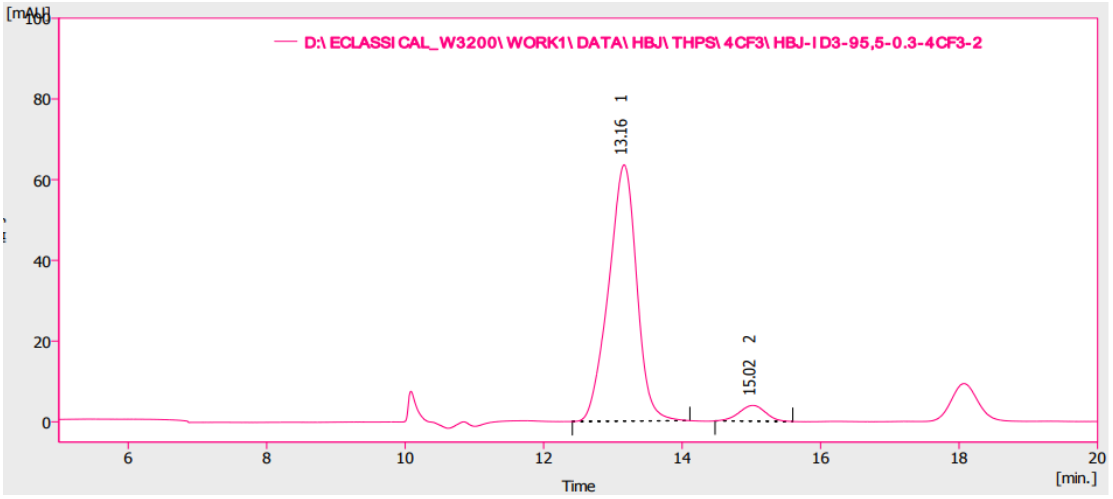


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.96	221.82	4367.61	50.0
2	26.55	95.93	4370.19	50.0
Total		317.75	8737.80	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.83	120.29	2339.79	90.0
2	26.55	7.77	260.70	10.0
Total		128.06	2600.49	100.0

3g, 89% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

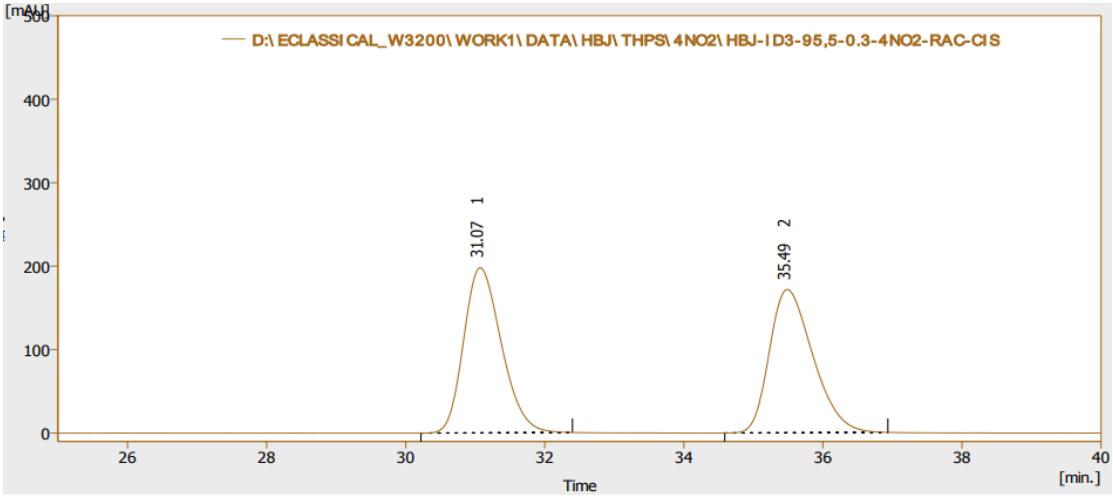


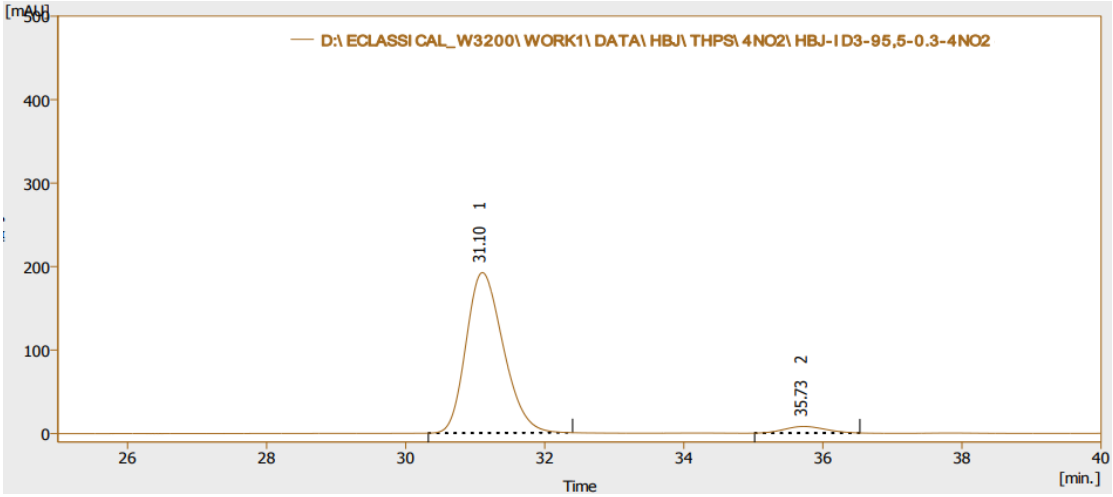


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	12.98	50.95	1564.84	50.0
2	14.54	52.08	1561.83	50.0
Total		103.03	3126.67	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	13.16	105.85	2988.36	94.6
2	15.02	6.50	172.00	5.4
Total		112.35	3160.37	100.0

3h, 91% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

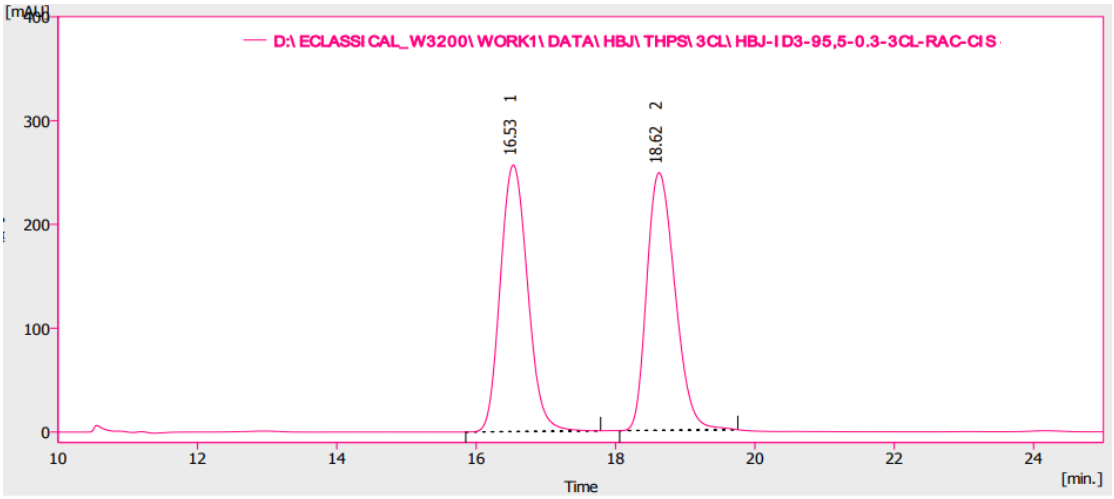


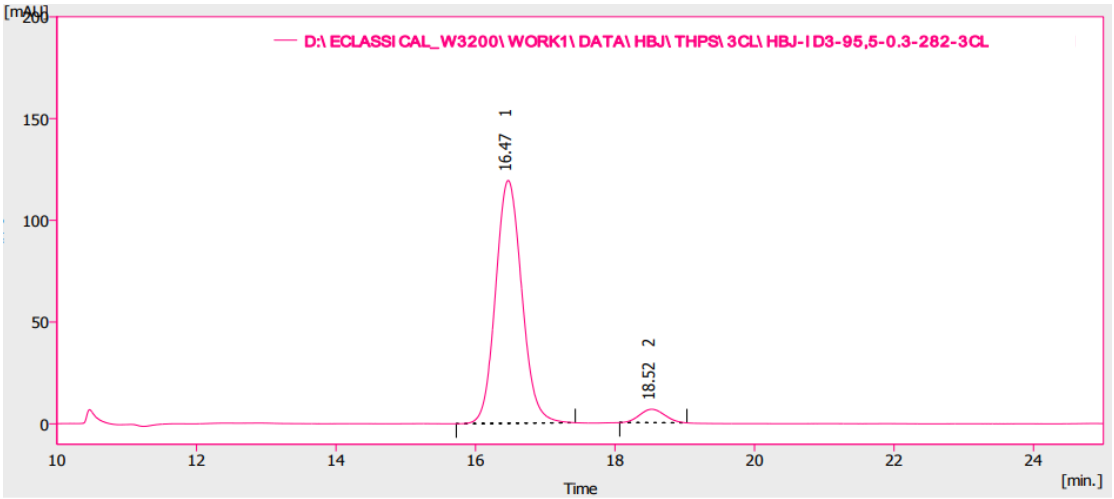


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	31.07	329.96	12437.57	50.0
2	35.49	286.05	12439.32	50.0
Total		616.01	24876.89	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	31.10	320.31	11918.54	95.7
2	35.73	13.12	535.30	4.3
Total		333.43	12453.84	100.0

3i, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

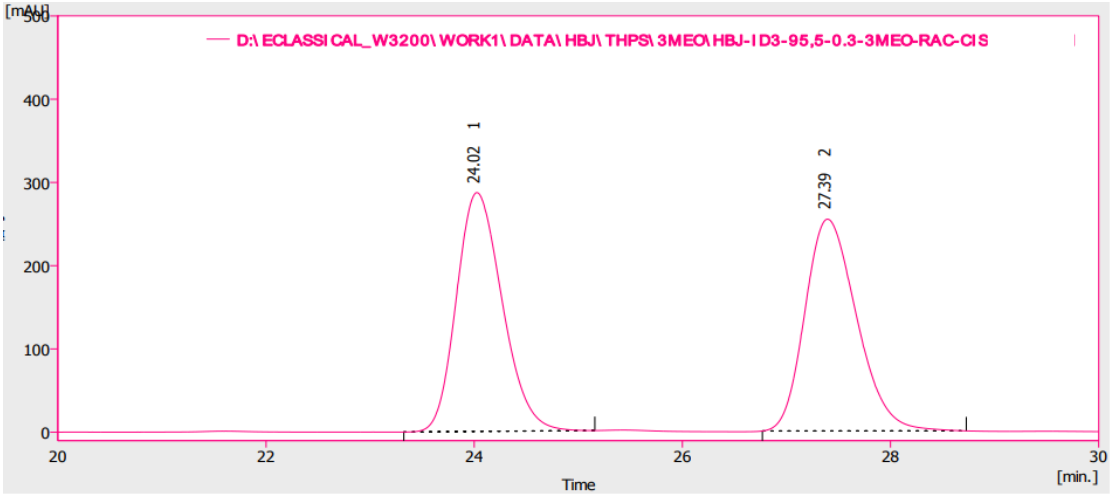


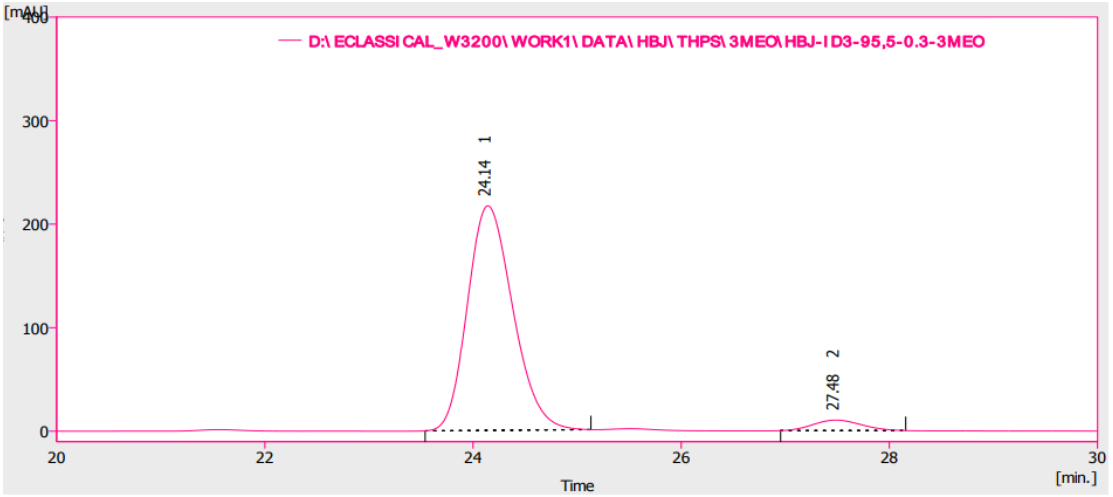


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.53	428.01	11640.71	50.0
2	18.62	413.72	11647.51	50.0
Total		841.73	23288.22	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.47	198.94	5191.72	95.0
2	18.52	11.02	276.01	5.0
Total		209.96	5467.73	100.0

3j, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

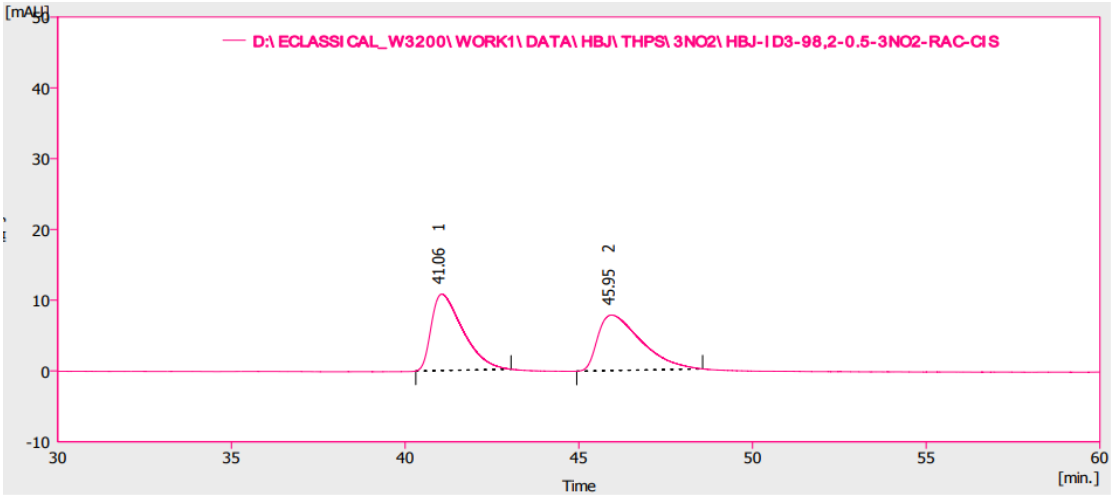


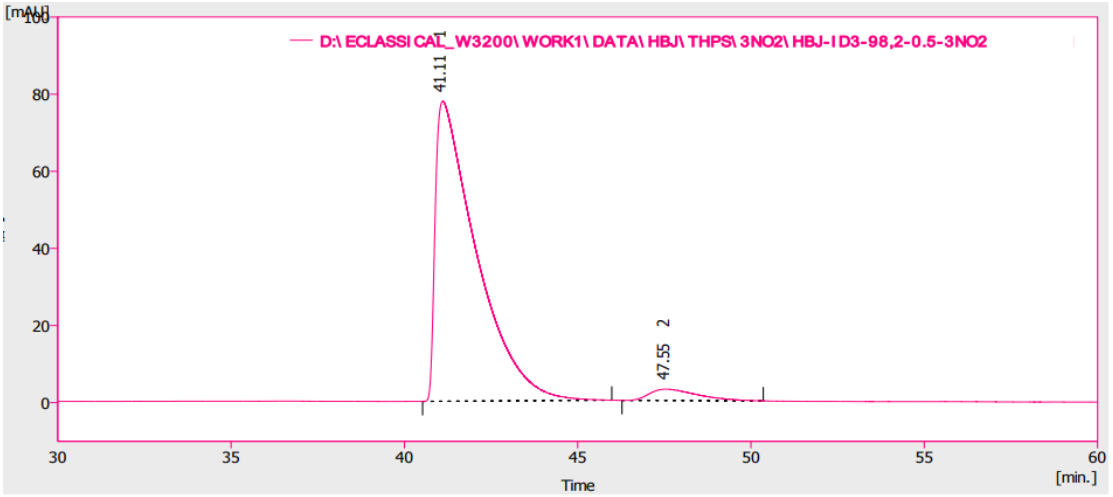


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	24.02	478.21	14632.88	50.0
2	27.39	424.02	14647.22	50.0
Total		902.23	29280.10	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	24.14	361.58	10962.84	95.3
2	27.48	16.87	540.20	4.7
Total		378.45	11503.04	100.0

3k, 91% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm)

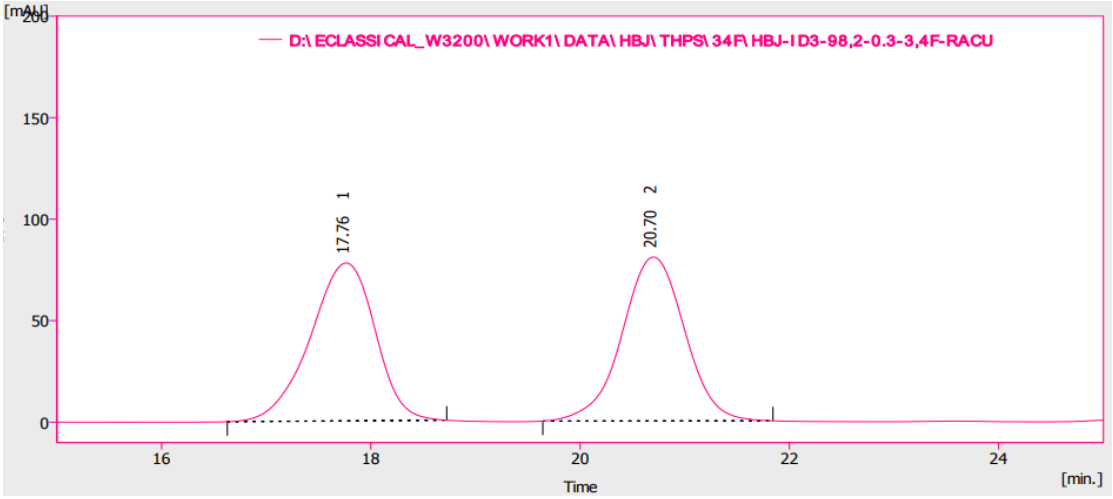


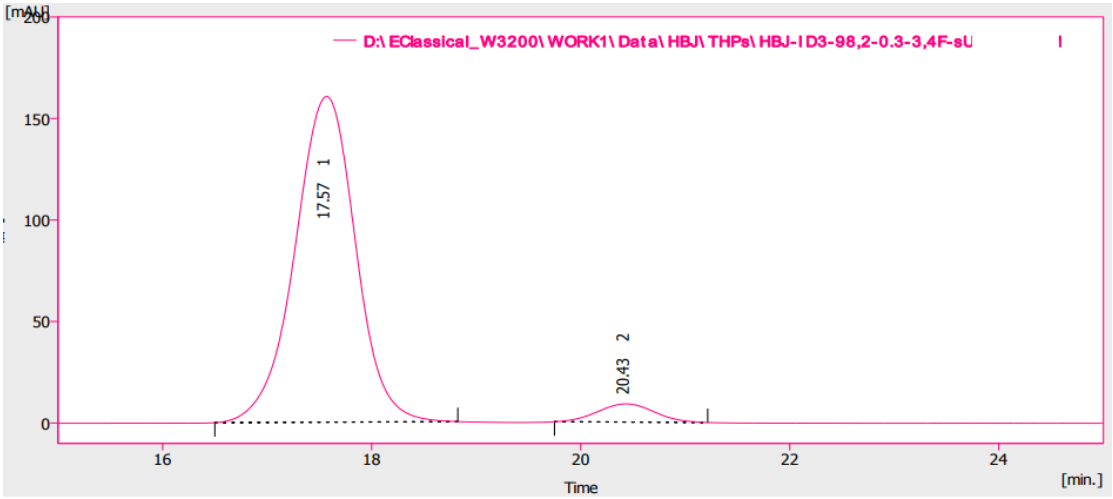


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	41.06	18.00	1134.44	50.0
2	45.95	13.07	1132.36	50.0
Total		31.07	2266.80	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	47.11	129.72	10664.76	95.8
2	47.55	4.92	470.21	4.2
Total		134.64	11134.97	100.0

3l, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.3 mL/min, λ = 254 nm)

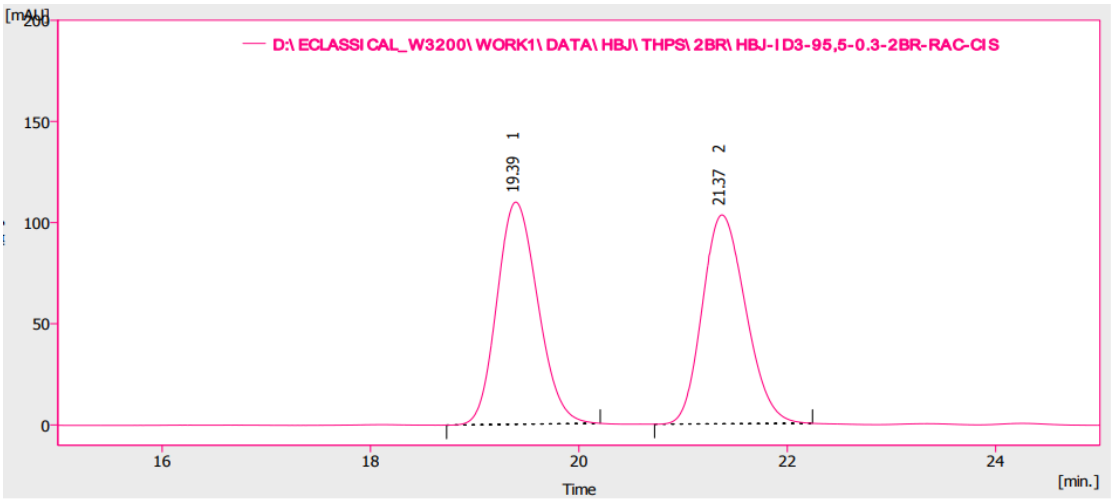


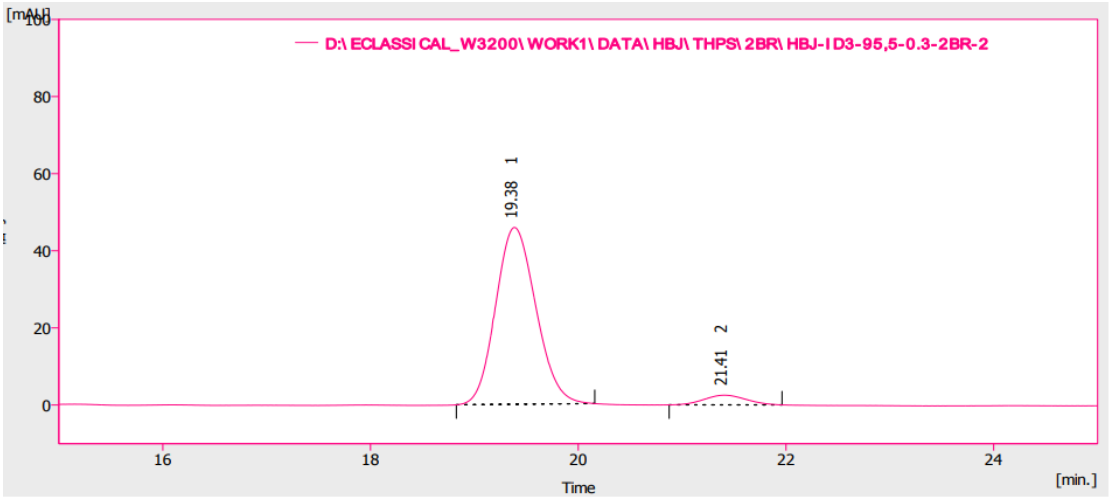


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	25.62	56.92	2490.19	50.0
2	30.54	54.67	2492.65	50.0
Total		111.59	4982.84	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.57	267.40	10798.78	95.0
2	20.43	14.97	562.96	5.0
Total		282.37	11361.74	100.0

3m, 89% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

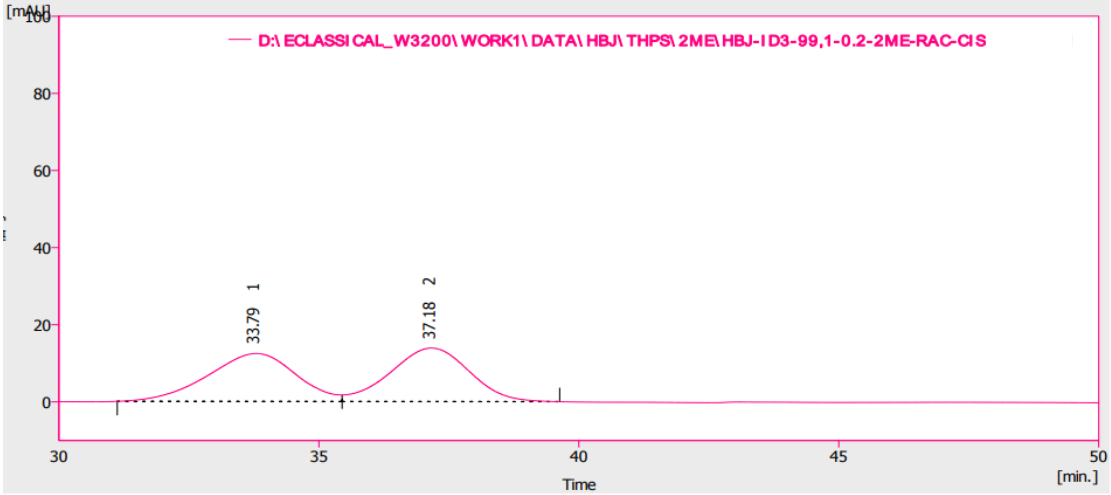


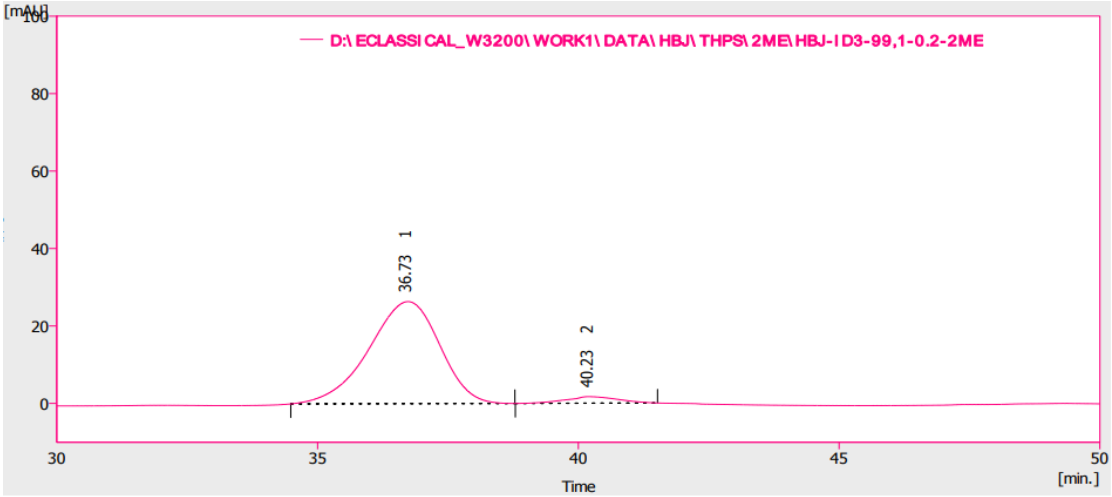


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	19.39	183.06	4993.69	50.0
2	21.37	172.10	4987.61	50.0
Total		355.16	9981.30	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	19.38	76.43	2058.00	94.6
2	21.41	4.19	117.17	5.4
Total		80.62	2175.17	100.0

3n, 91% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.2 mL/min, λ = 254 nm)

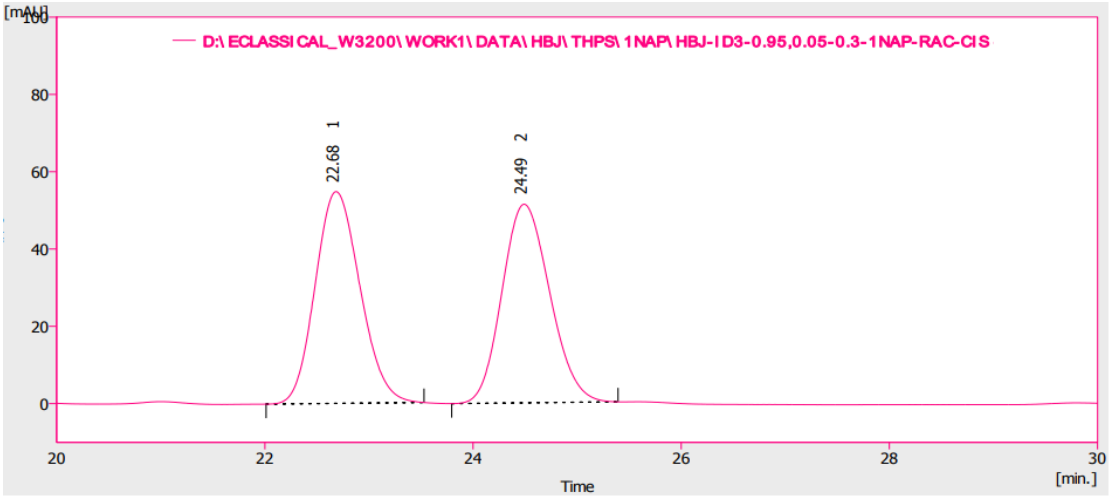


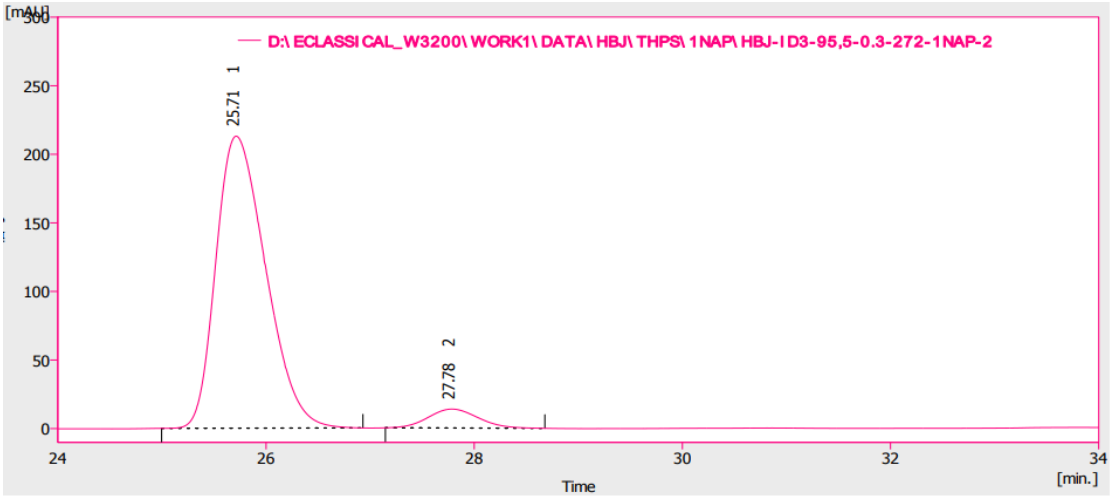


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	33.79	20.76	2445.10	50.0
2	37.18	23.14	2445.38	50.0
Total		43.90	4889.48	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	36.73	43.93	4150.79	95.5
2	40.23	2.84	195.95	4.5
Total		46.77	4346.74	100.0

3o, 88% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

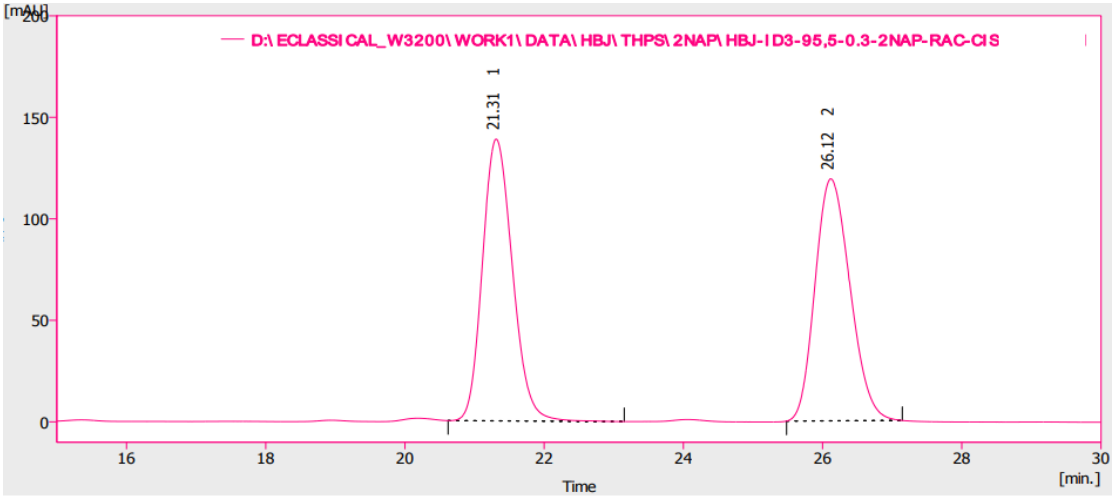


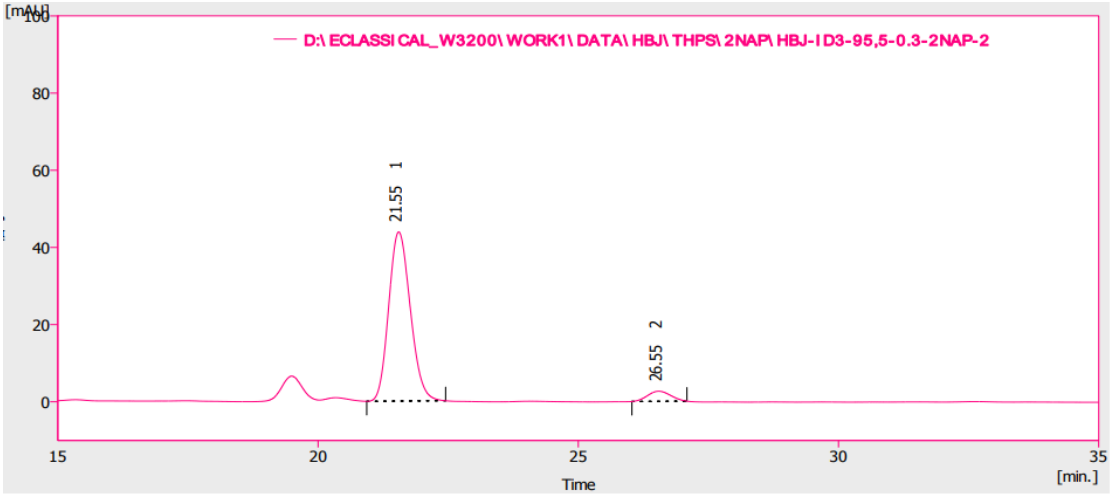


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	22.68	91.36	2734.06	50.0
2	24.49	85.65	2730.86	50.0
Total		177.01	5464.92	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	25.71	354.89	11791.45	93.9
2	27.78	23.04	768.56	6.1
Total		377.93	12560.01	100.0

3p, 88% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

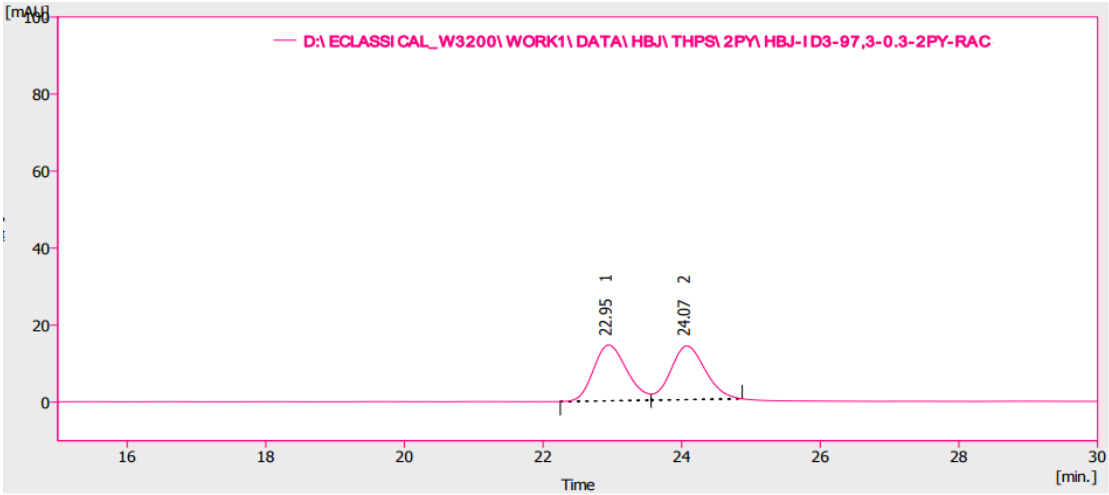


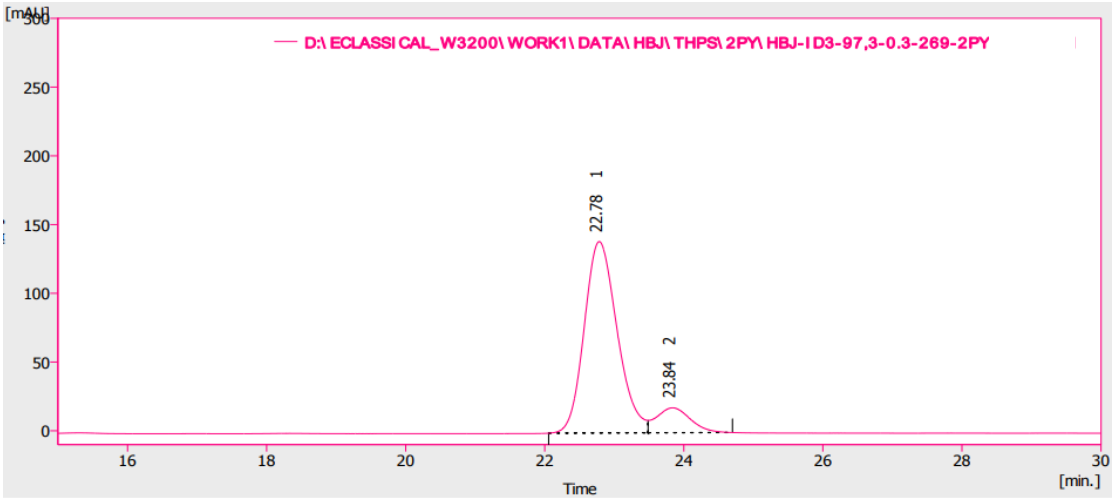


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.31	231.31	6942.70	50.0
2	26.12	198.66	6939.46	50.0
Total		429.97	13882.16	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.55	73.10	2109.76	94.1
2	26.55	4.37	133.28	5.9
Total		77.47	2243.04	100.0

3q, 76% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ = 254 nm)

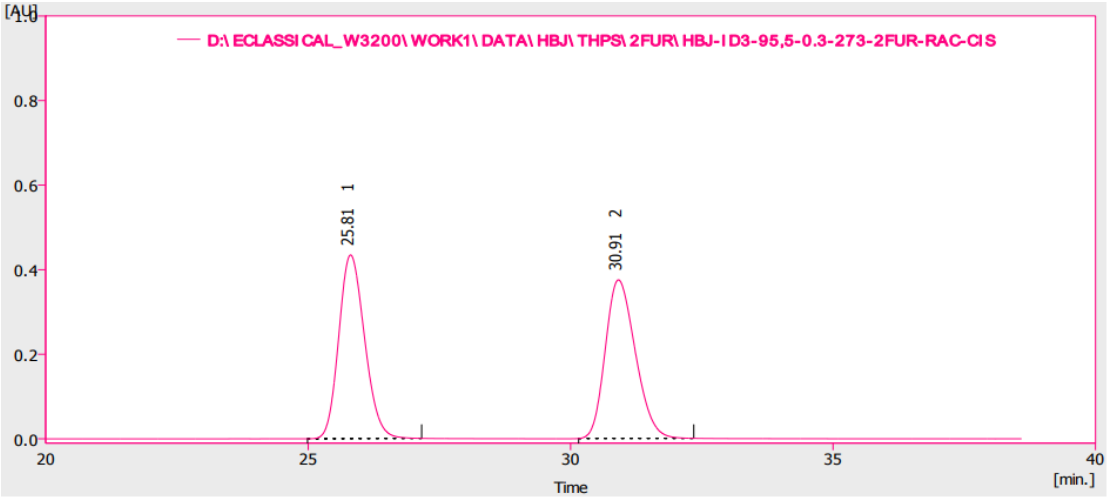


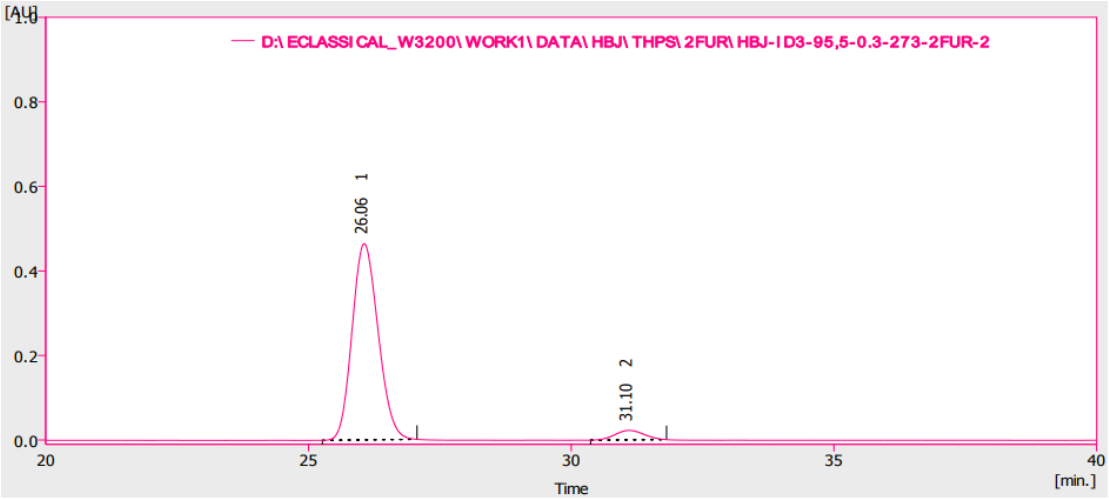


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	22.95	24.15	805.81	50.0
2	24.07	23.23	804.60	50.0
Total		47.38	1610.41	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	22.78	232.12	7642.81	88.2
2	23.84	30.25	1026.14	11.8
Total		262.37	8668.95	100.0

3r, 90% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

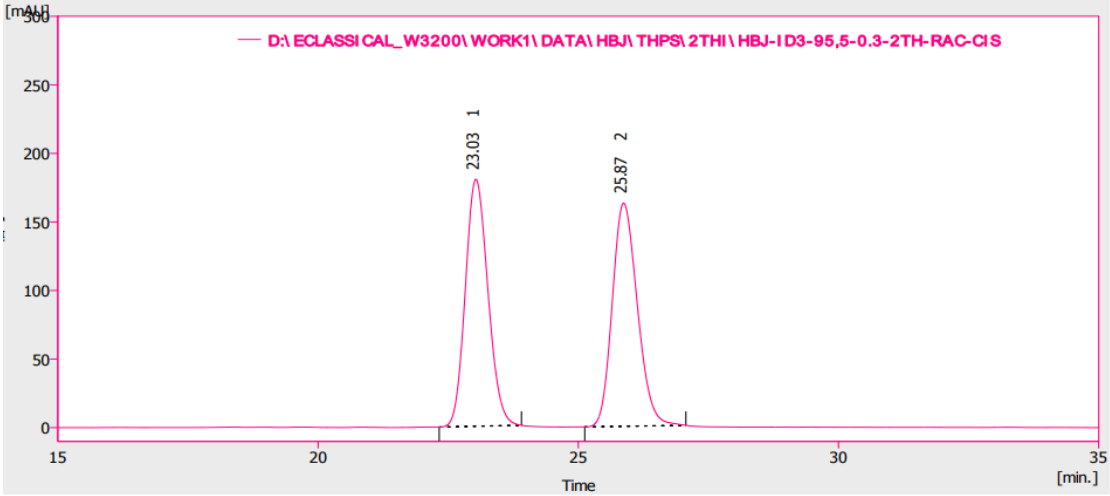


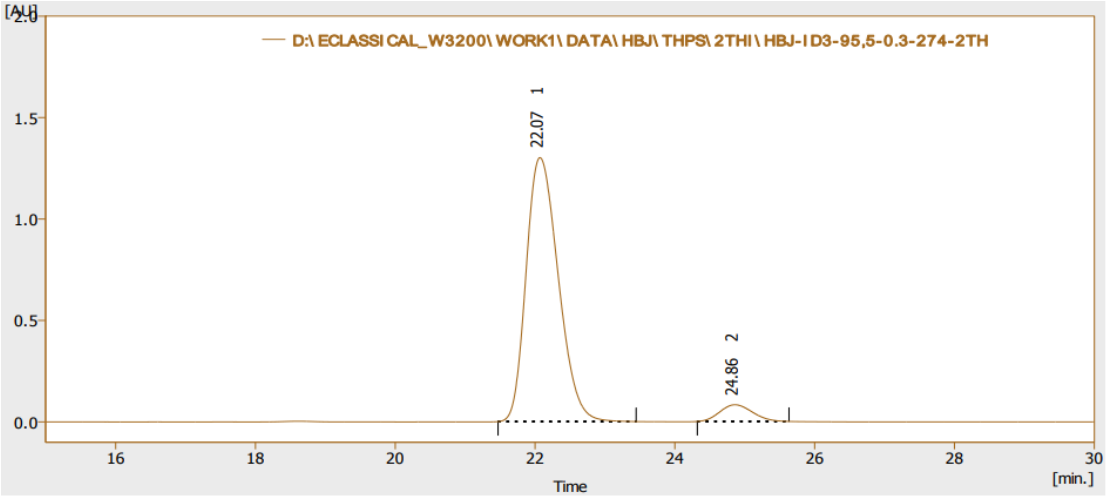


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	25.81	724.24	24826.92	50.0
2	30.91	625.43	24866.72	50.0
Total		1349.67	49693.64	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	26.06	773.82	26650.40	94.9
2	31.10	37.50	1423.55	5.1
Total		811.32	28073.95	100.0

3s, 88% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)

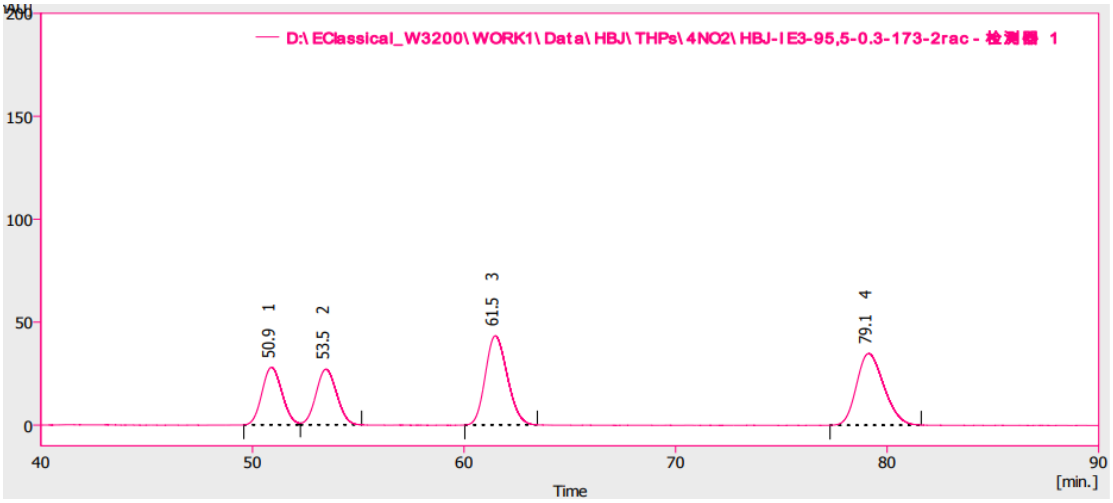




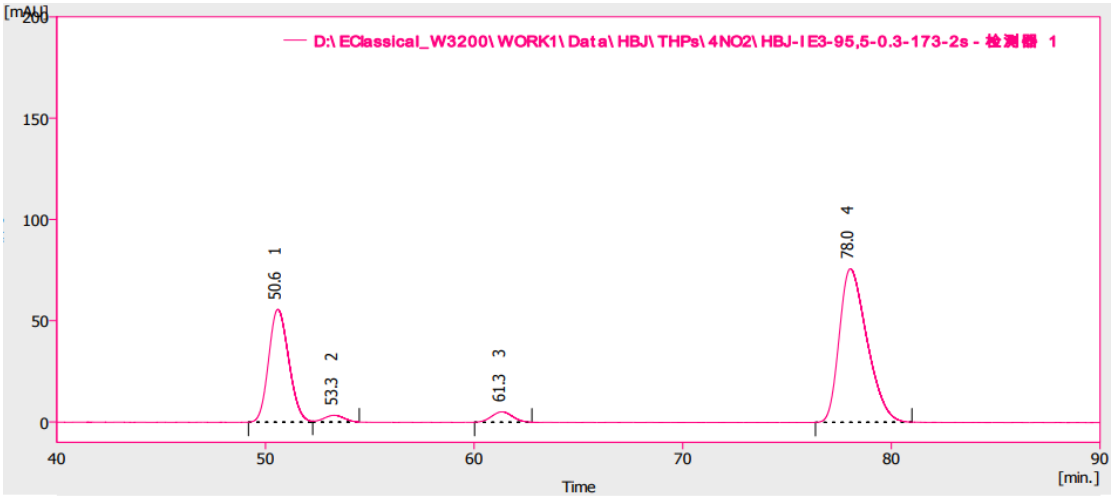
Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	23.03	300.32	9089.29	50.0
2	25.87	271.50	9095.24	50.0
Total		571.82	18184.53	100.0

Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	22.07	2168.55	69321.38	94.0
2	24.86	137.14	4441.75	6.0
Total		2305.69	73763.13	100.0

4, ee_1 = 89%, ee_2 = 90% (Chiralcel IE-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.3 mL/min, λ = 254 nm)



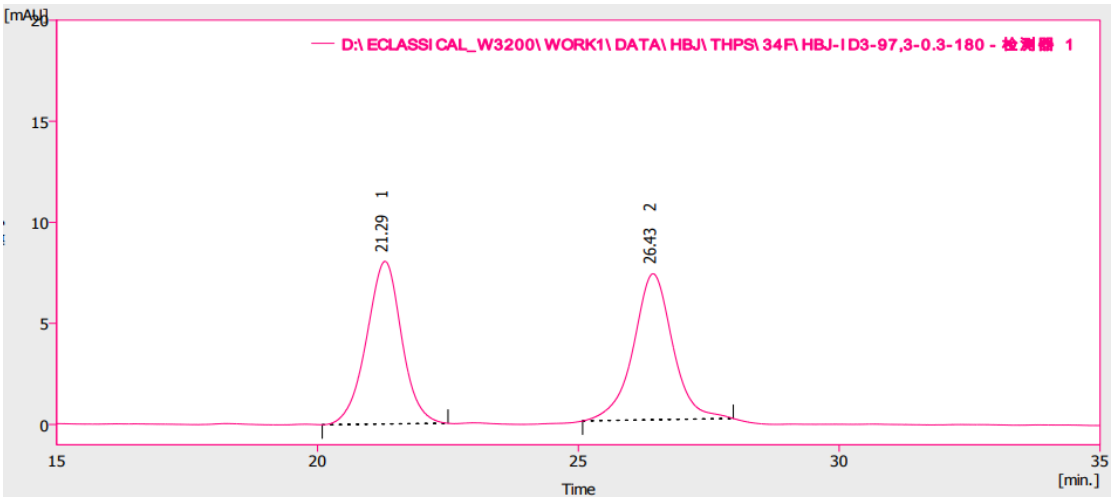
Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	50.90	46.60	3067.06	18.5
2	53.47	45.09	3062.48	18.5
3	61.48	72.18	5207.17	31.5
4	79.12	58.02	5205.05	31.5
Total		221.89	16541.76	100.0



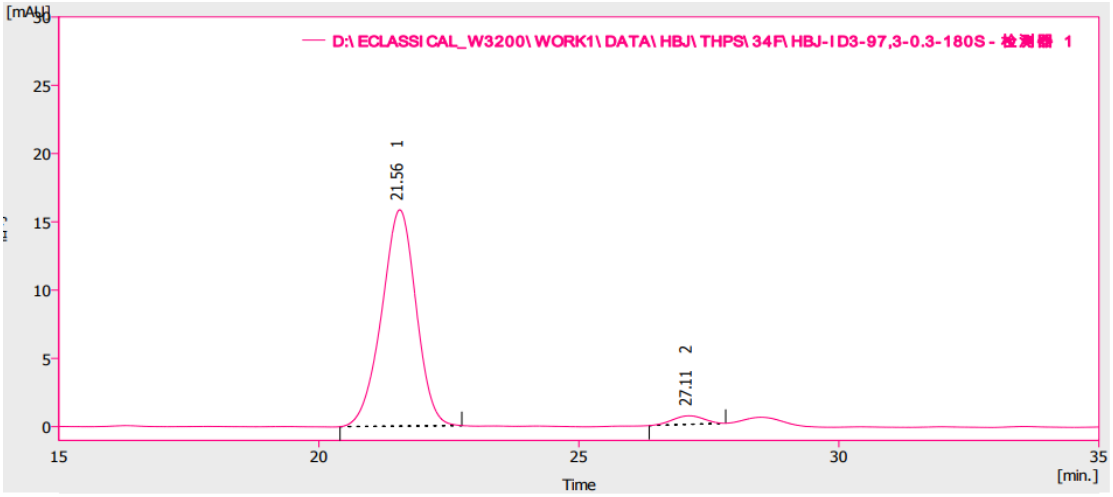
Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	50.59	92.83	6211.89	33.0
2	53.31	5.56	371.40	2.0
3	61.35	8.53	590.92	3.1
4	78.03	126.34	11653.87	61.9
Total		233.26	18828.08	100.0

5, 93% *ee* (Chiralcel ID-3 column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.3 mL/min, λ

= 254 nm)



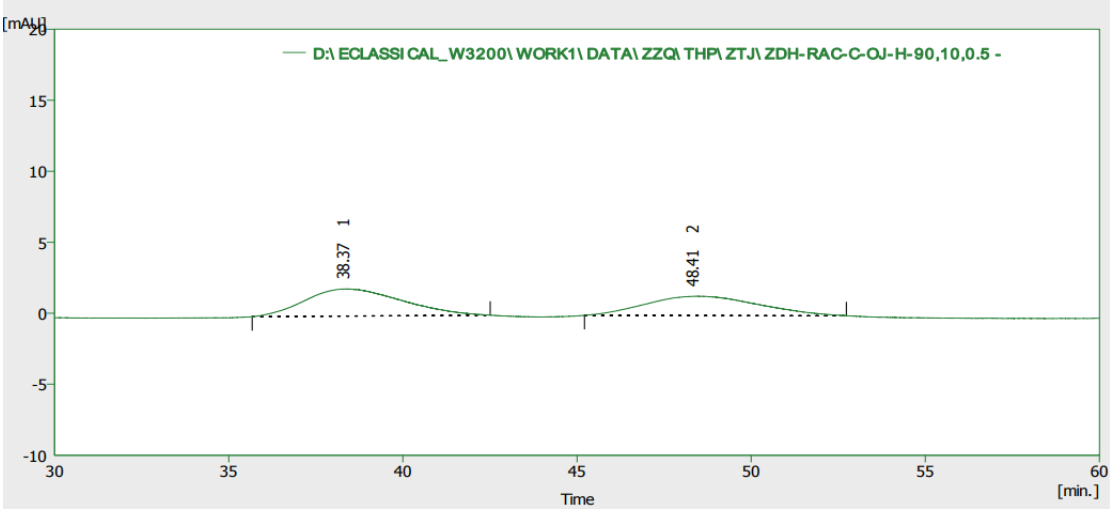
Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.29	13.42	627.54	49.8
2	26.43	12.04	631.65	50.2
Total		25.46	1256.19	100.0



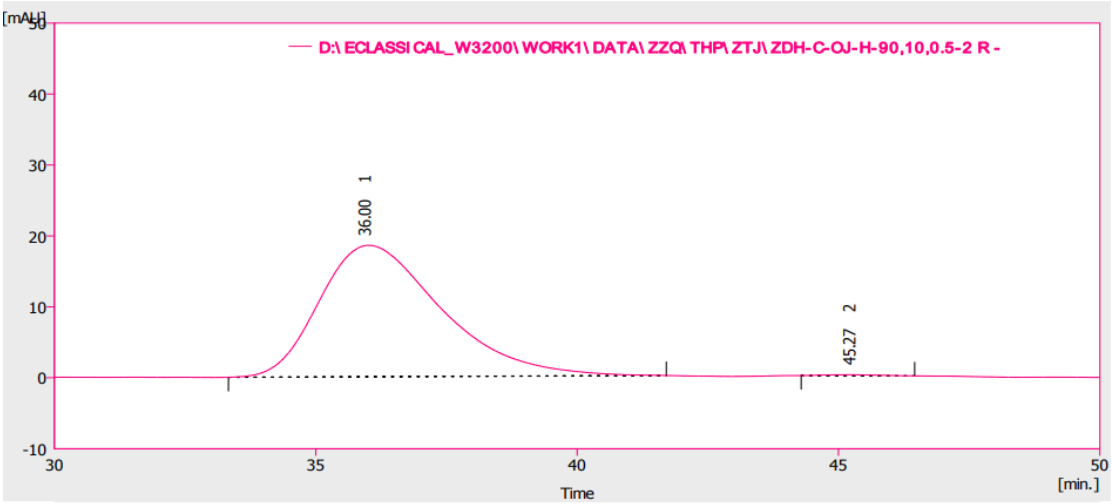
Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.56	26.41	1217.53	96.5
2	27.11	1.05	43.57	3.5
Total		27.46	1261.10	100.0

8a, 99% *ee* (Daicel Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5

mL/min, λ = 254 nm)

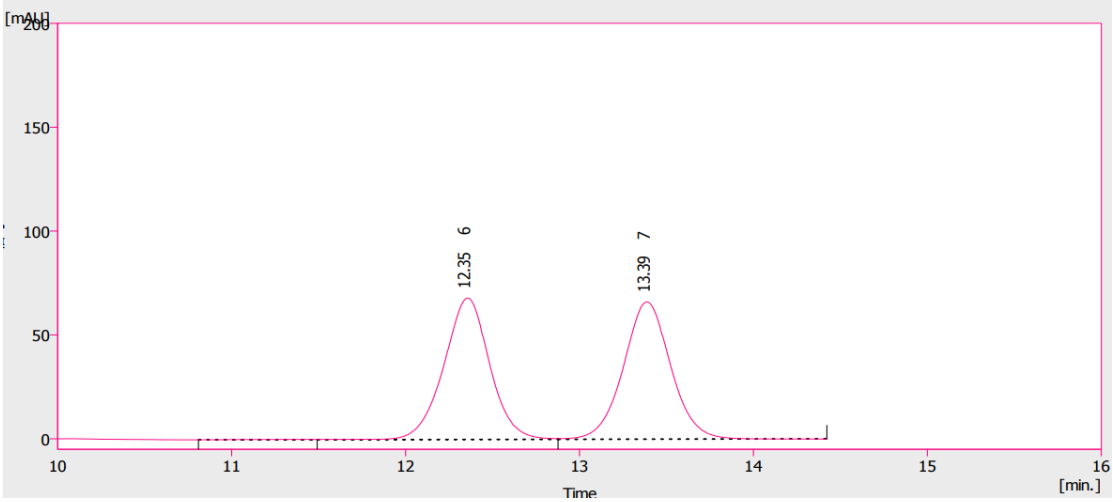


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	38.37	3.19	617.03	54.5
2	48.41	2.27	514.42	45.5
Total			1131.45	100.0

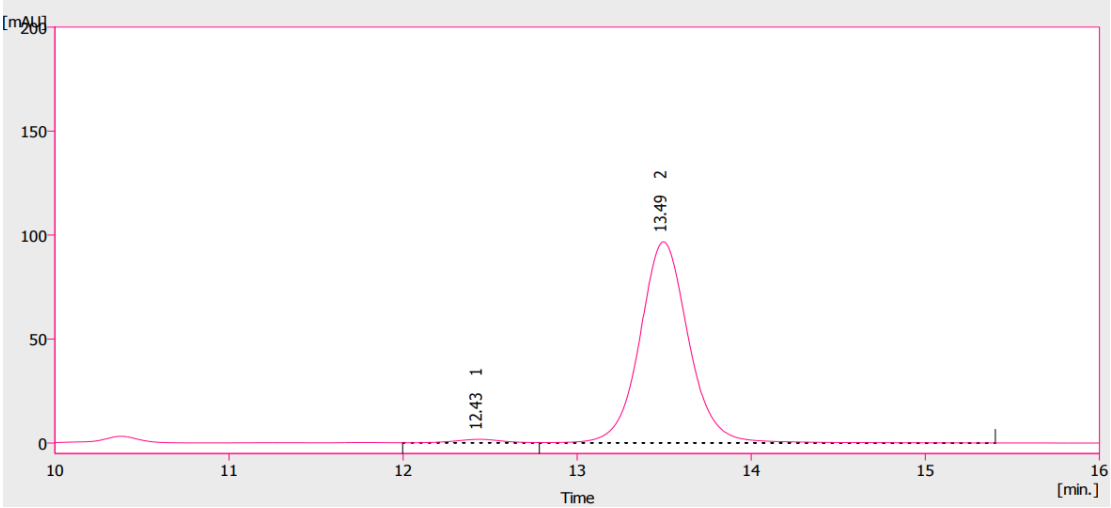


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	36.00	30.92	5019.56	99.6
2	45.27	0.28	19.20	0.4
Total			5038.76	100.0

8b, 97% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

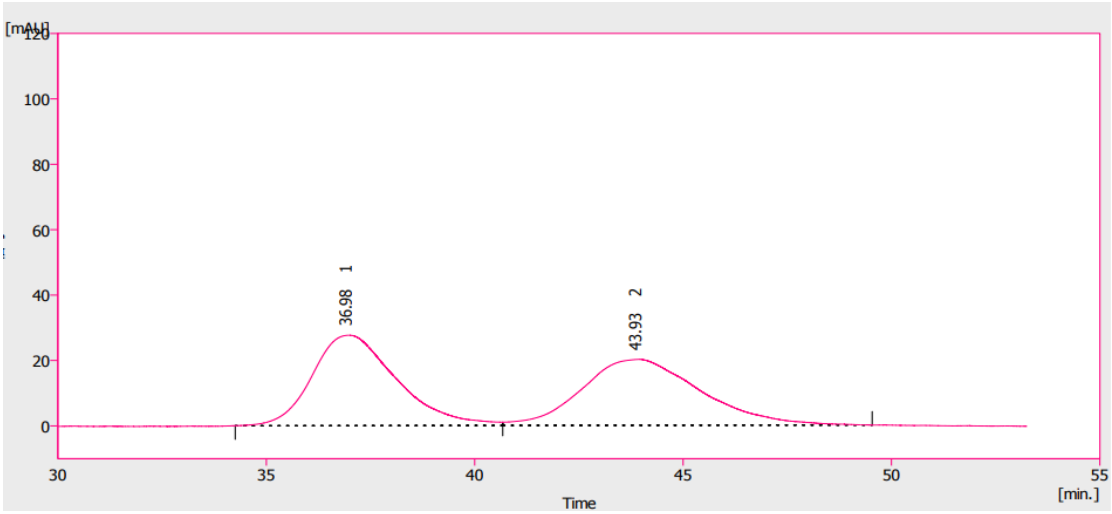


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	12.35	113.43	2082.17	49.8
2	13.39	110.18	2091.44	50.2
Total			4173.61	100.0

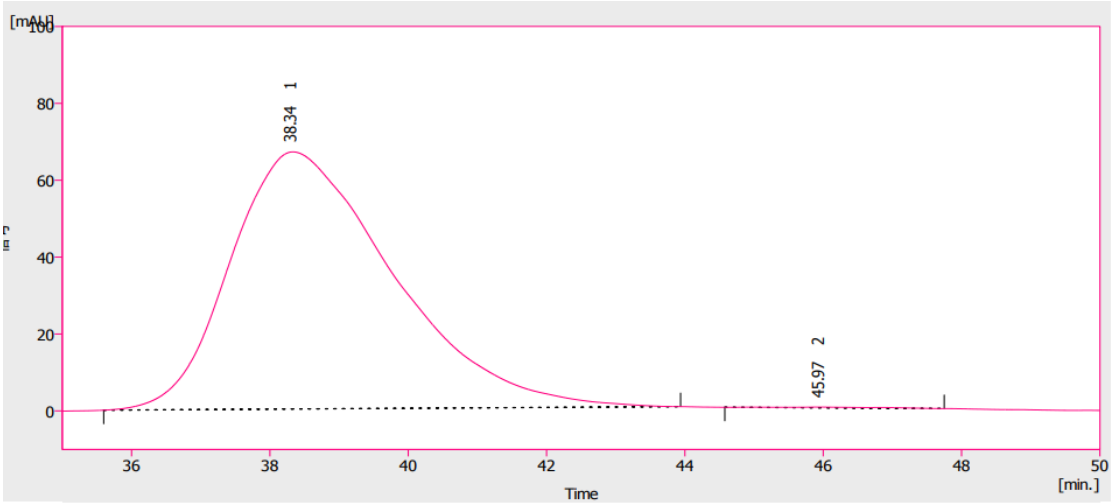


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	12.43	2.79	51.18	1.6
2	13.49	161.13	3141.64	98.4
Total			3192.82	100.0

8c, 99% *ee* (Daicel Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.5 mL/min, λ = 254 nm)

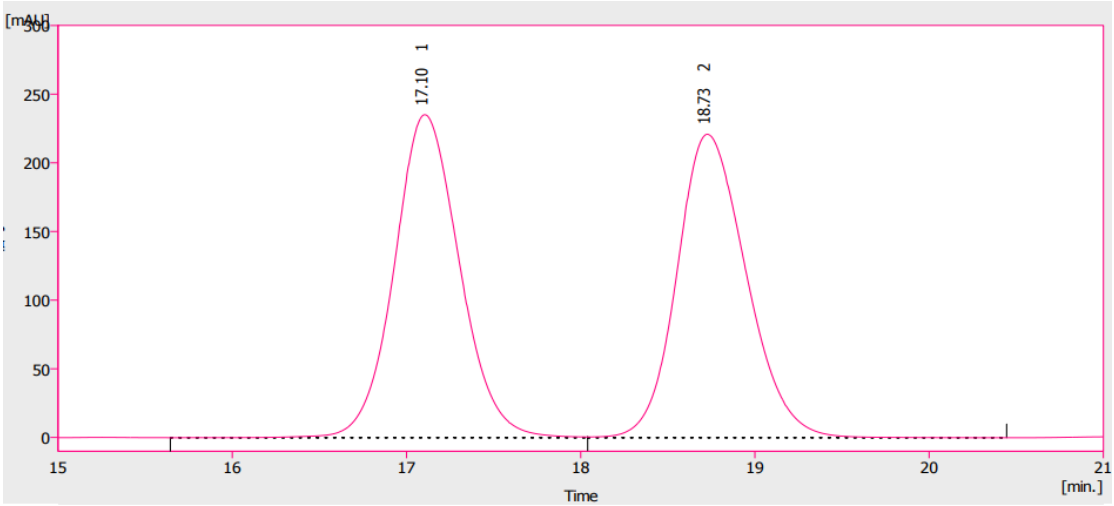


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	36.98	46.09	6479.00	49.4
2	43.93	33.64	6645.59	50.6
Total			13124.59	100.0

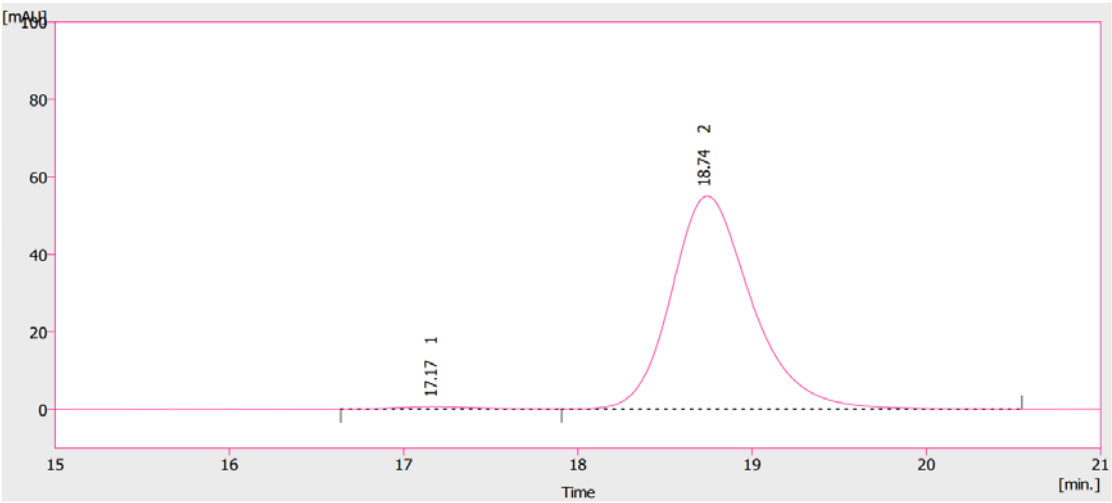


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	38.34	111.48	18235.40	99.8
2	45.97	0.34	36.69	0.2
Total			18272.09	100.0

8d, 98% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 93/7, flow rate = 0.5 mL/min, λ = 254 nm)

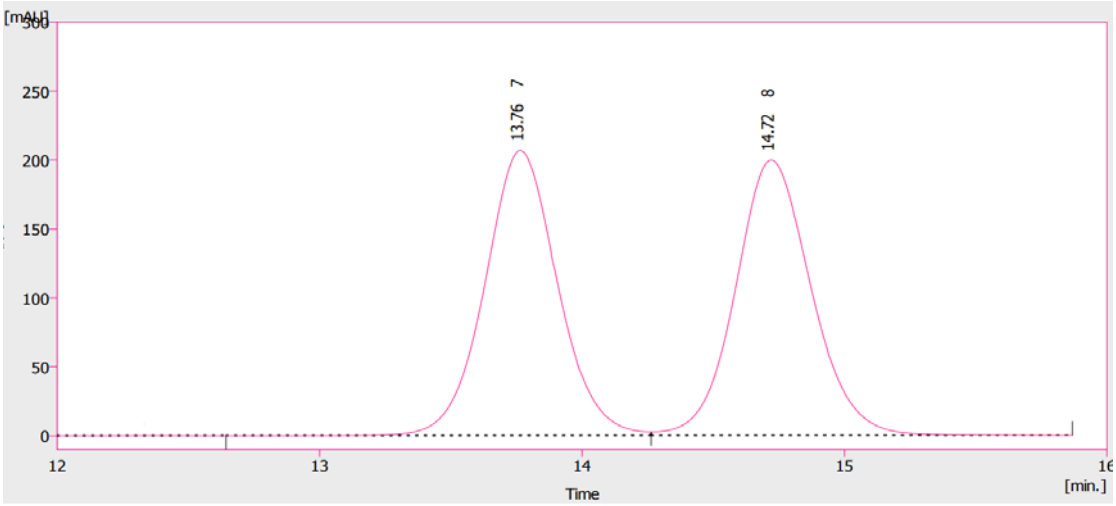


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.10	392.05	10235.93	50.1
2	18.73	368.35	10195.29	49.9
Total			20431.22	100.0

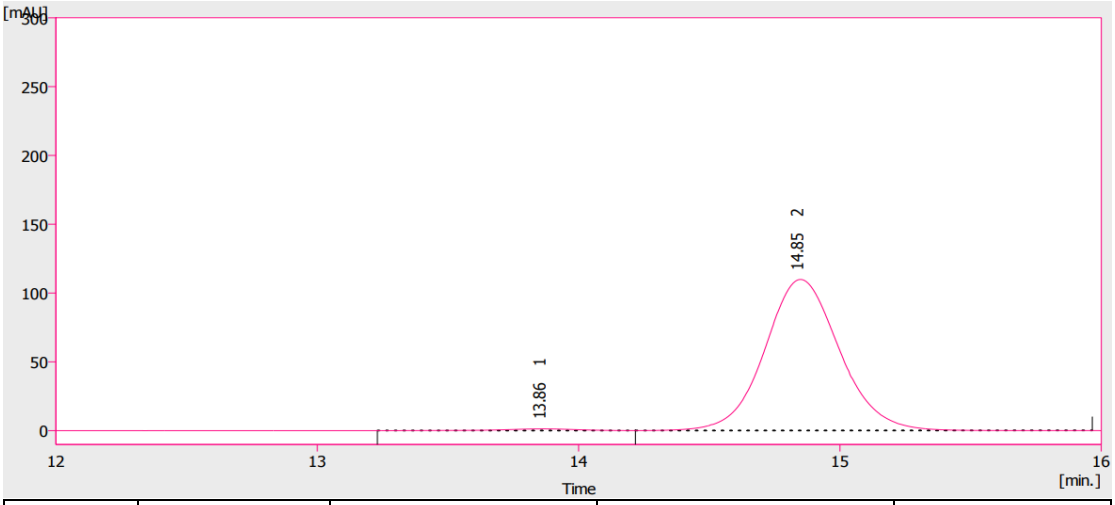


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.17	1.0	31.23	1.1
2	18.74	91.68	2942.32	98.9
Total			2973.55	100.0

8e, 98% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

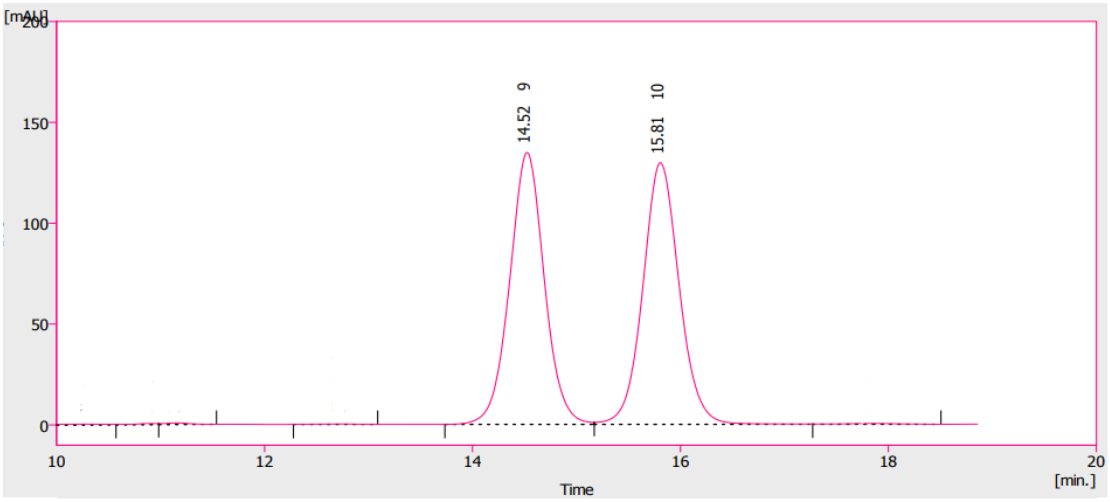


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	13.76	344.41	6644.58	49.8
2	14.72	332.84	6681.16	50.2
Total			13325.74	100.0

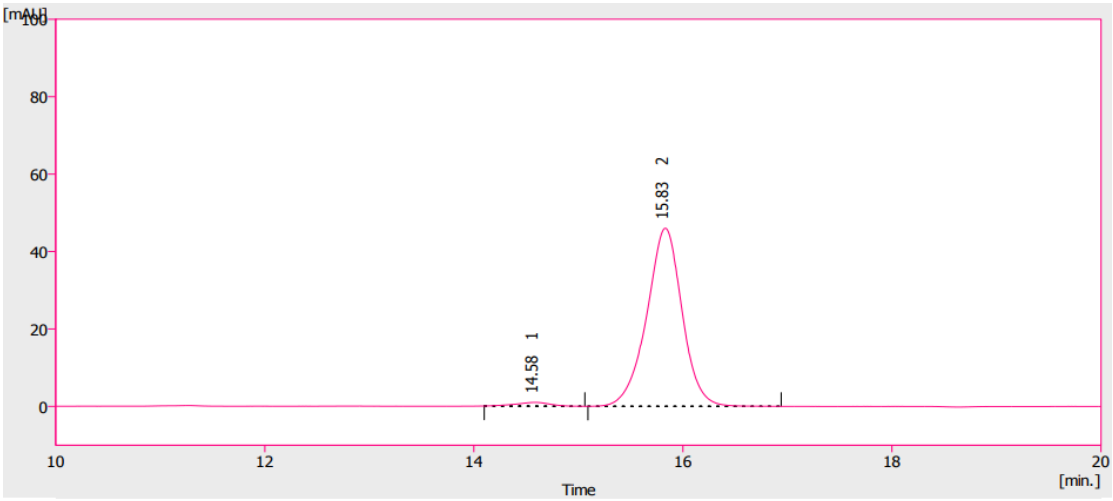


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	13.86	2.13	42.18	1.1
2	14.85	183.06	3652.99	98.9
Total			3695.17	100.0

8f, 96% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 93/7, flow rate = 0.5 mL/min, λ = 254 nm)

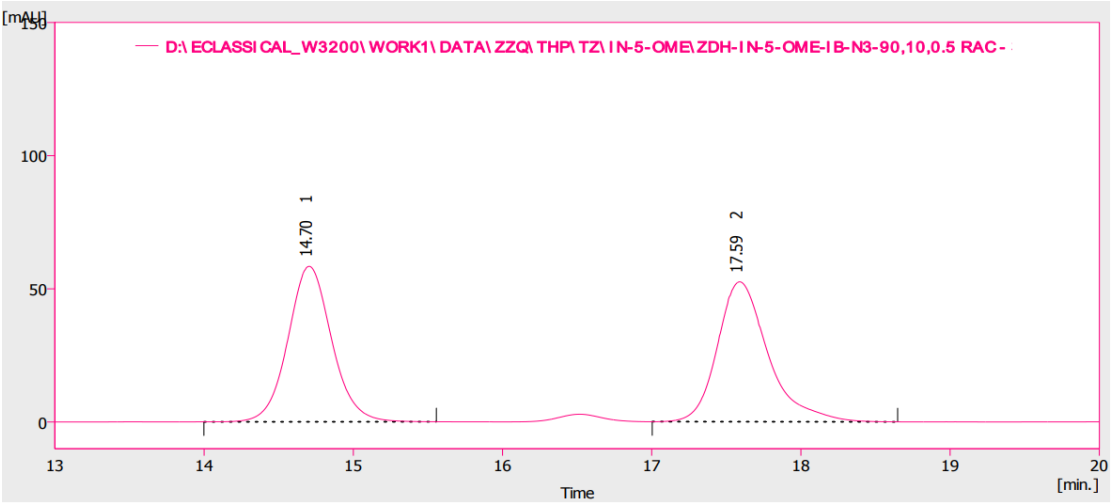


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.52	224.65	5216.50	49.8
2	15.81	216.22	5261.70	50.2
Total			10478.2	100.0

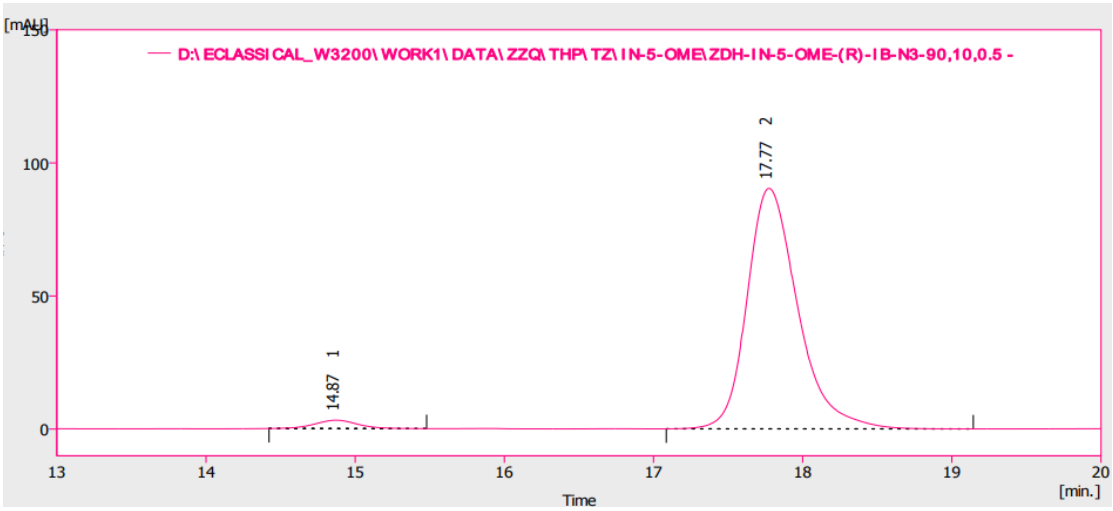


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.58	1.62	36.37	2.0
2	15.83	76.65	1803.36	98.0
Total			1839.73	100.0

8g, 94% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

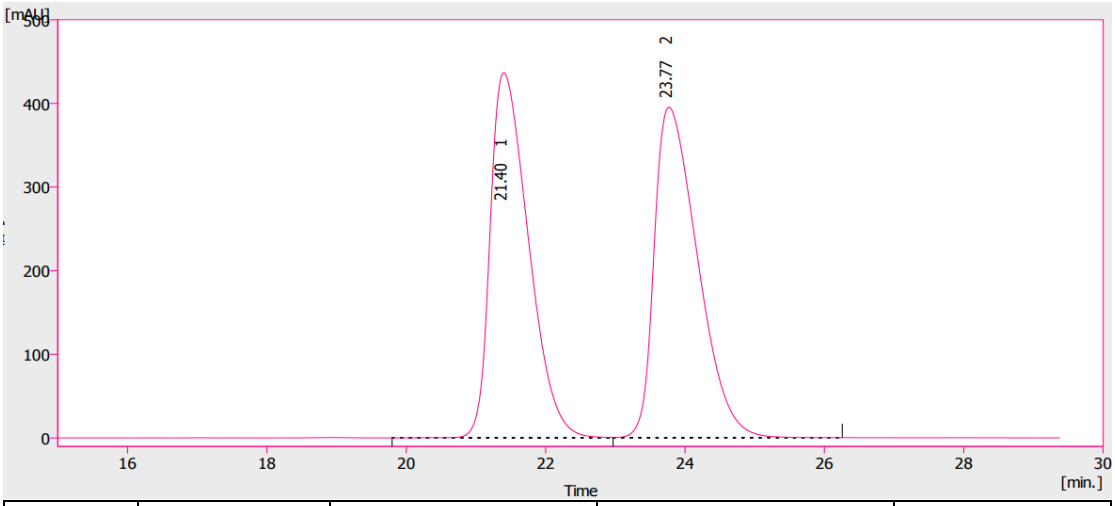


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.70	97.29	1985.89	48.9
2	17.59	87.58	2072.61	51.1
Total			4058.50	100.0

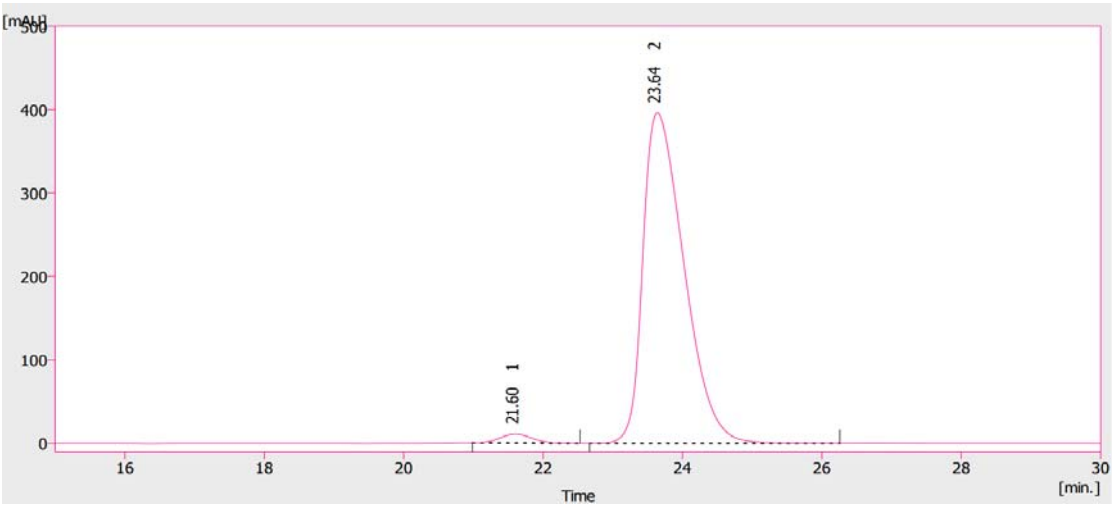


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.87	5.22	104.57	2.9
2	17.77	150.62	3558.46	97.1
Total			3663.03	100.0

8h, 96% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

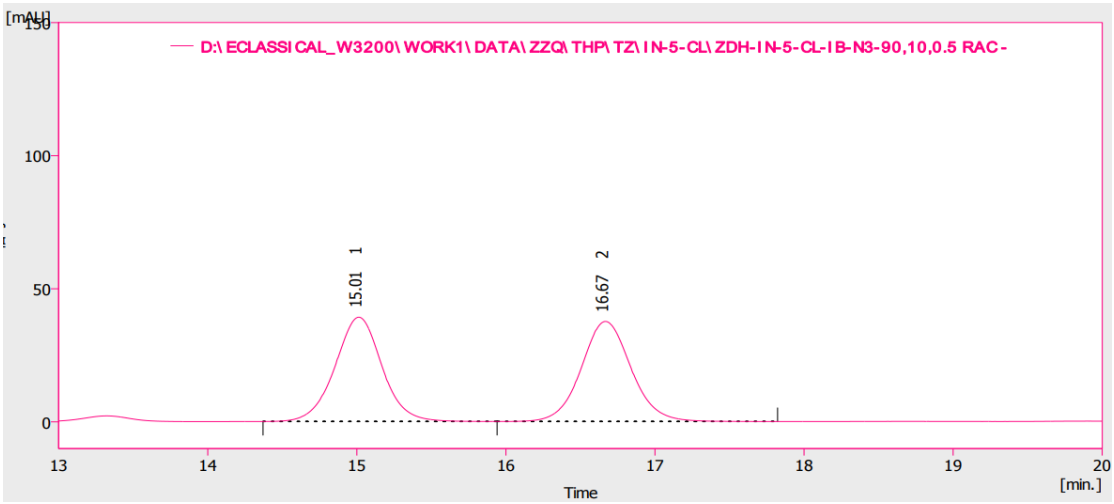


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.40	727.585	27749.08	49.4
2	23.77	658.572	28421.90	50.6
Total			56170.98	100.0

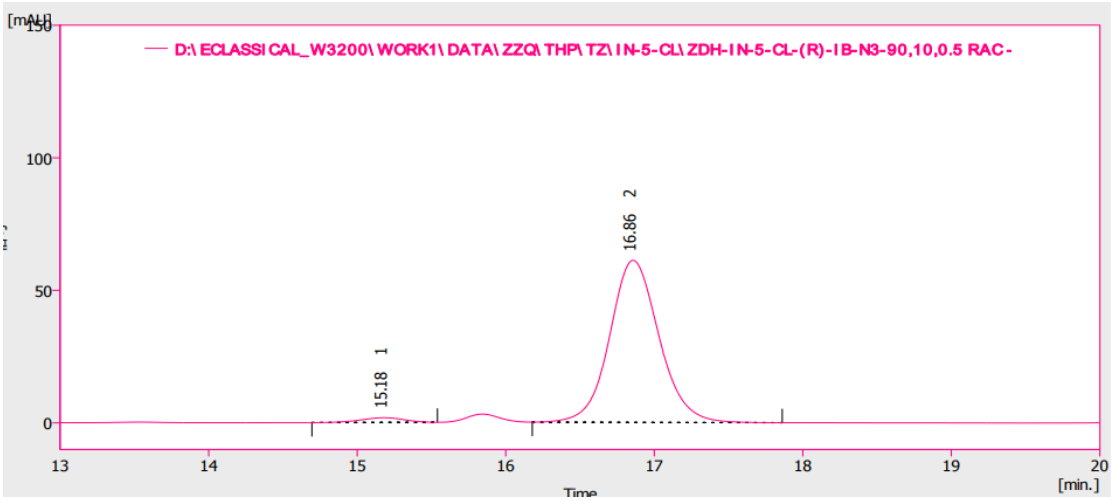


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	21.60	18.50	566.84	2.1
2	23.64	660.51	27054.11	97.9
Total			27620.95	100.0

8i, 95% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

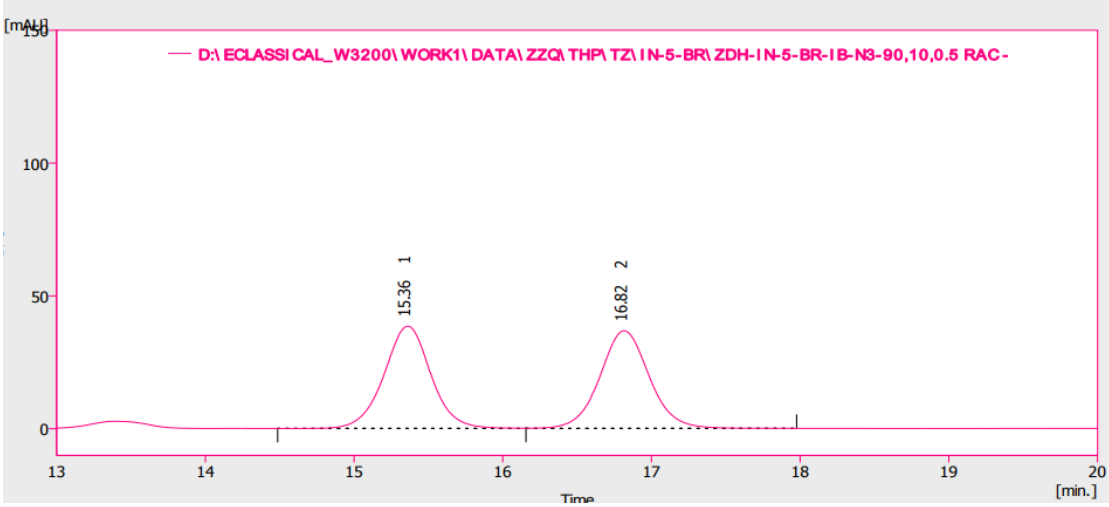


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.01	65.30	1431.83	49.5
2	16.67	62.65	1459.80	50.5
Total			2891.63	100.0

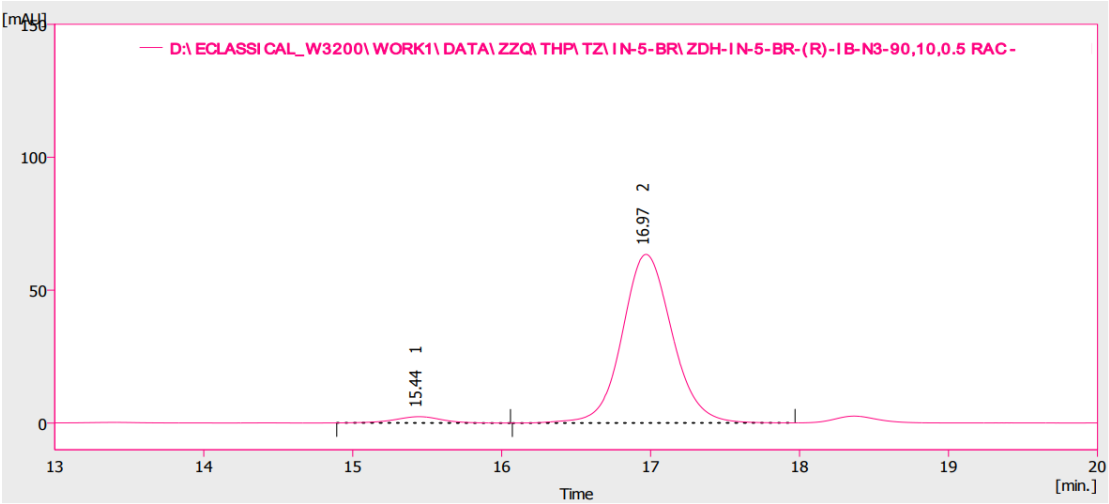


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.18	2.96	59.20	2.4
2	16.86	101.89	2358.60	97.6
Total			2419.80	100.0

8j, 93% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

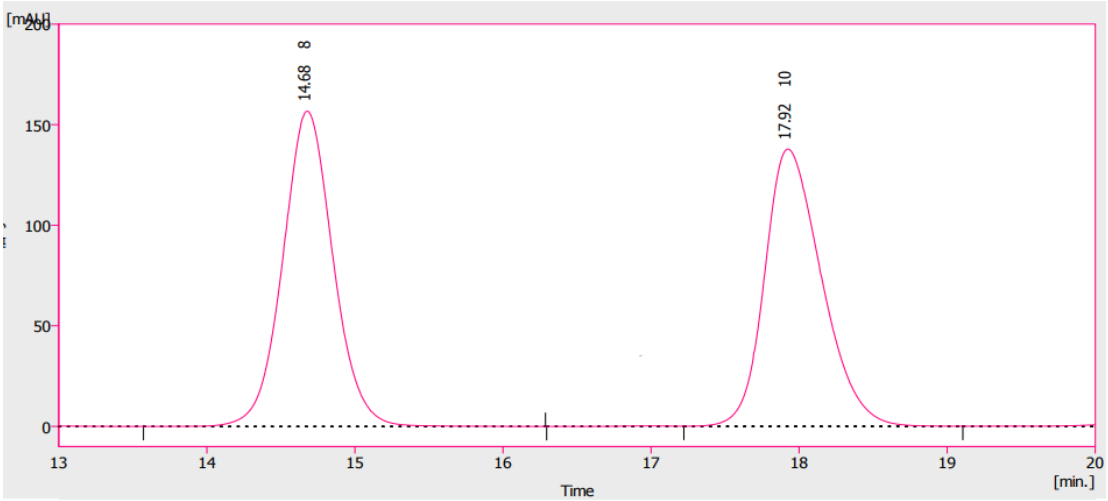


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.36	64.19	1411.97	49.9
2	16.82	61.27	1419.15	50.1
Total			2831.12	100.0

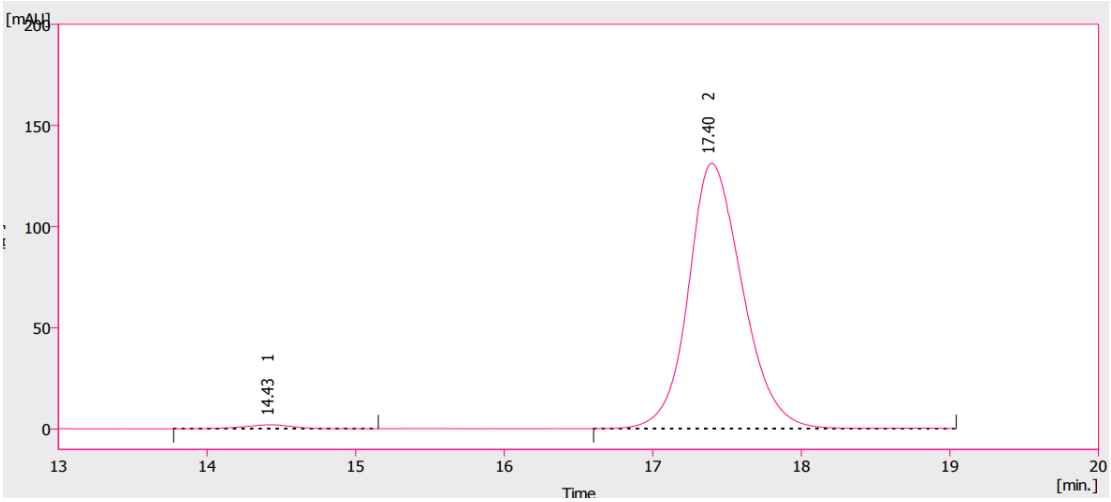


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	15.44	3.95	86.76	3.4
2	16.97	105.68	2466.39	96.6
Total			2553.15	100.0

8k, 96% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 93/7, flow rate = 0.5 mL/min, λ = 254 nm)

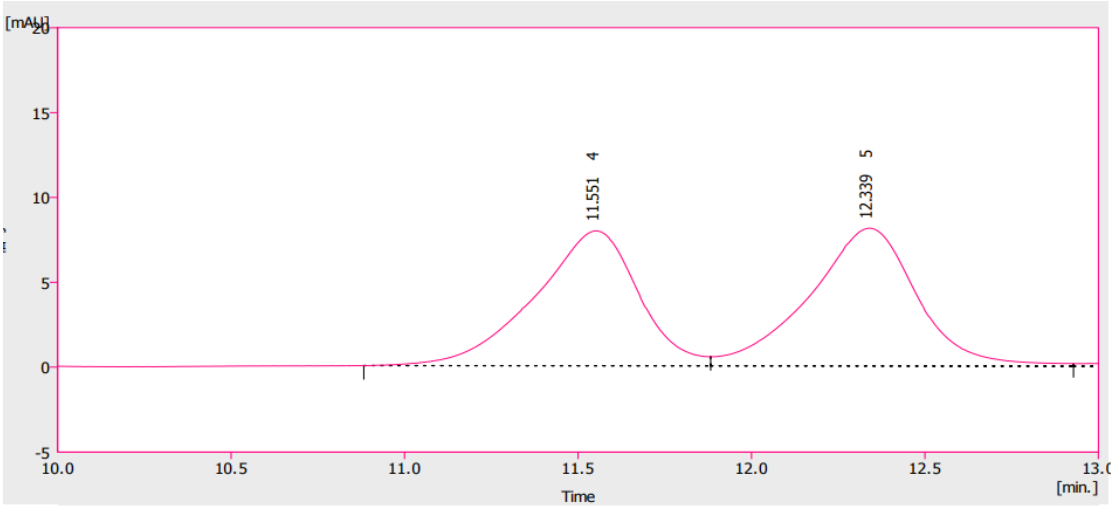


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.68	261.29	6194.51	50.2
2	17.92	229.85	6157.33	49.8
Total			12351.84	100.0

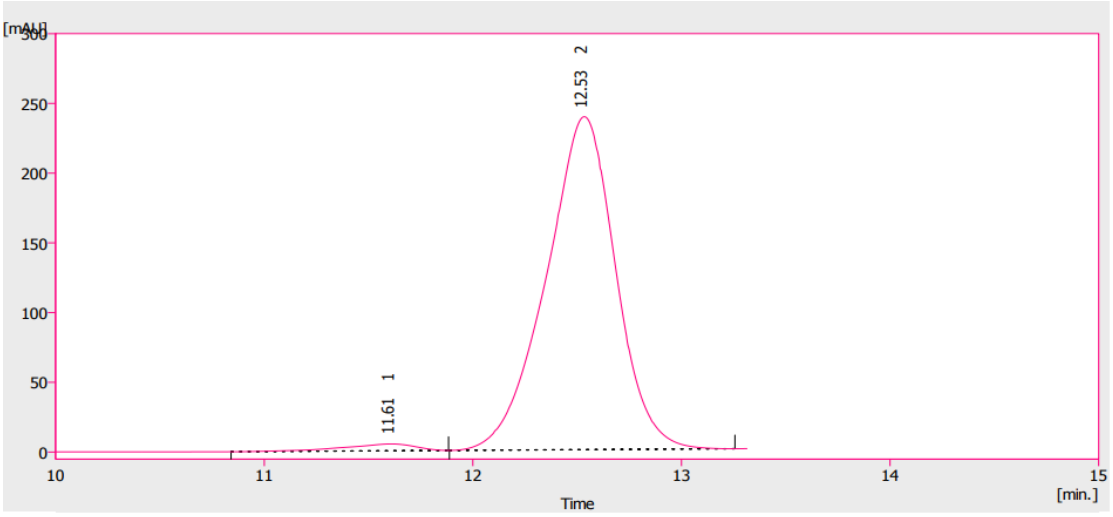


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	14.43	3.25	73.50	1.3
2	17.40	218.48	5538.40	98.7
Total			5611.90	100.0

8l, 96% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 93/7, flow rate = 0.5 mL/min, λ = 254 nm)

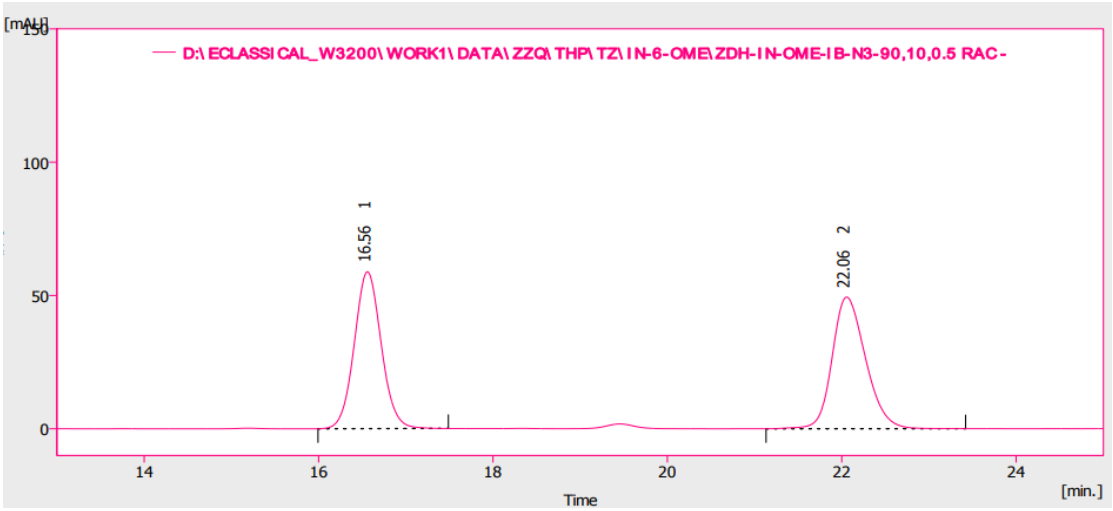


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	11.55	13.25	276.08	48.5
2	12.34	13.54	293.06	51.5
Total			569.14	100.0

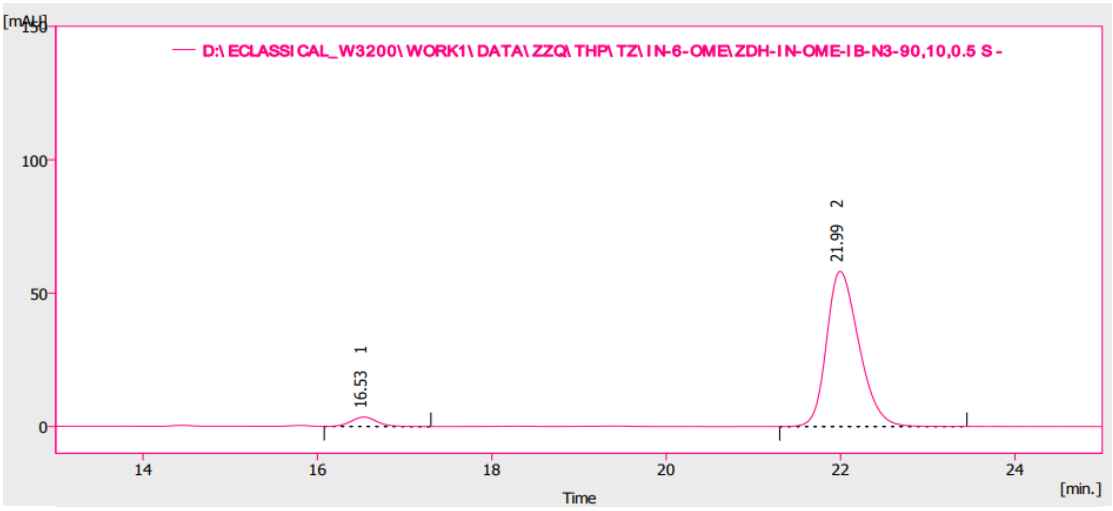


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	11.61	8.18	194.21	2.1
2	12.53	397.88	9201.35	97.9
Total			9395.566	100.0

8m, 91% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

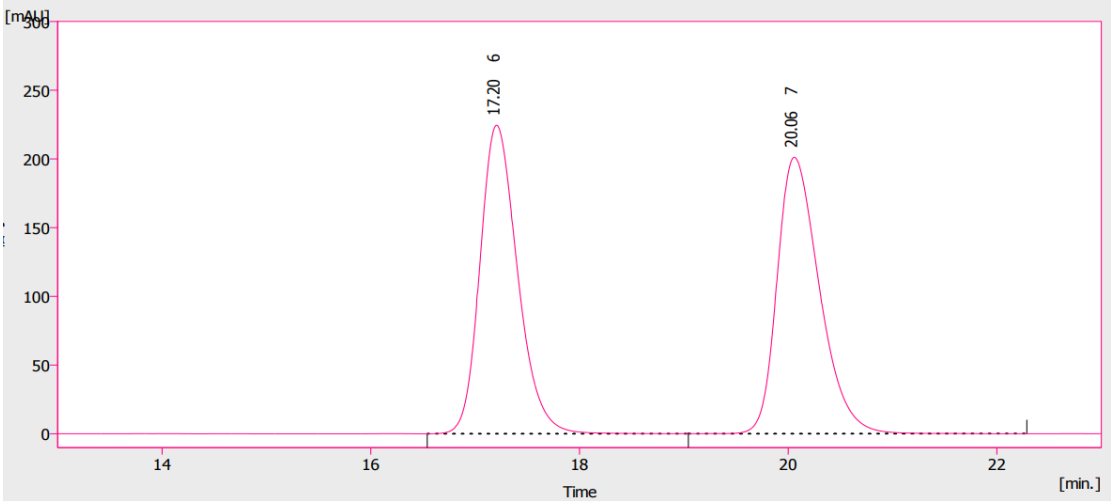


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.56	98.08	2110.28	49.1
2	22.06	82.31	2191.64	50.9
Total			4301.92	100.0

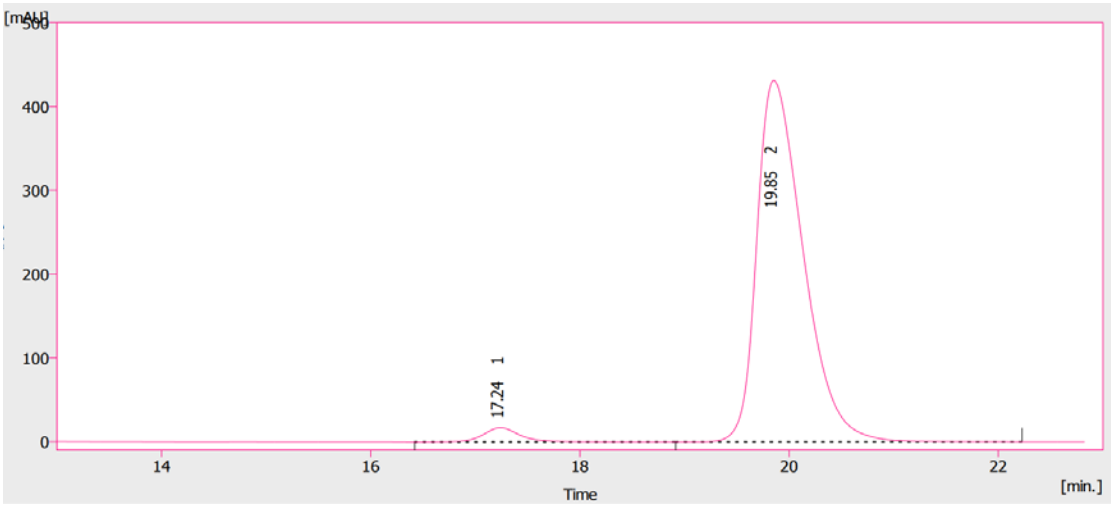


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.53	5.89	122.04	4.6
2	21.99	97.02	2503.96	95.4
Total			2626.00	100.0

8n, 94% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

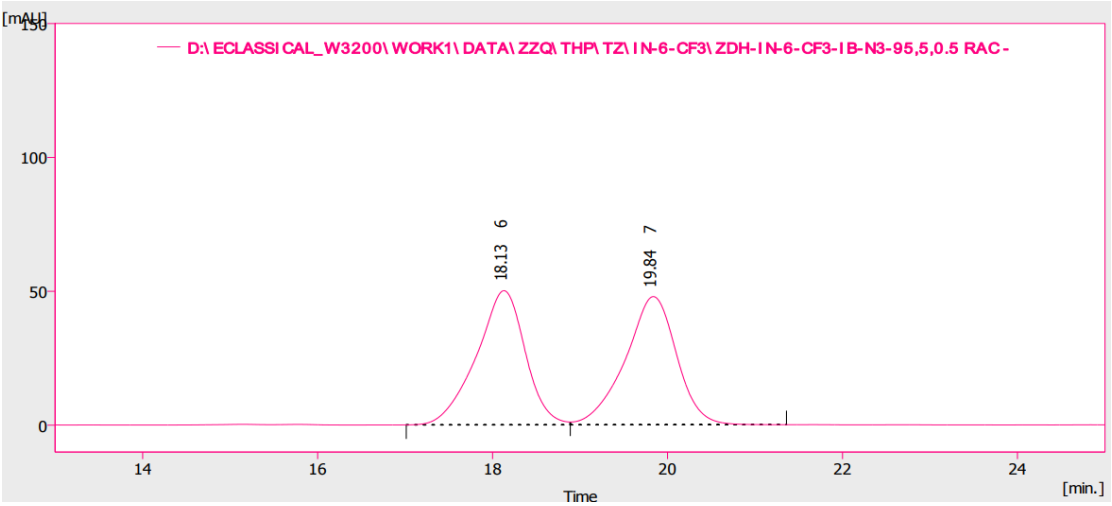


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.20	374.20	9382.41	49.7
2	20.06	335.32	9480.34	50.3
Total			18862.75	100.0

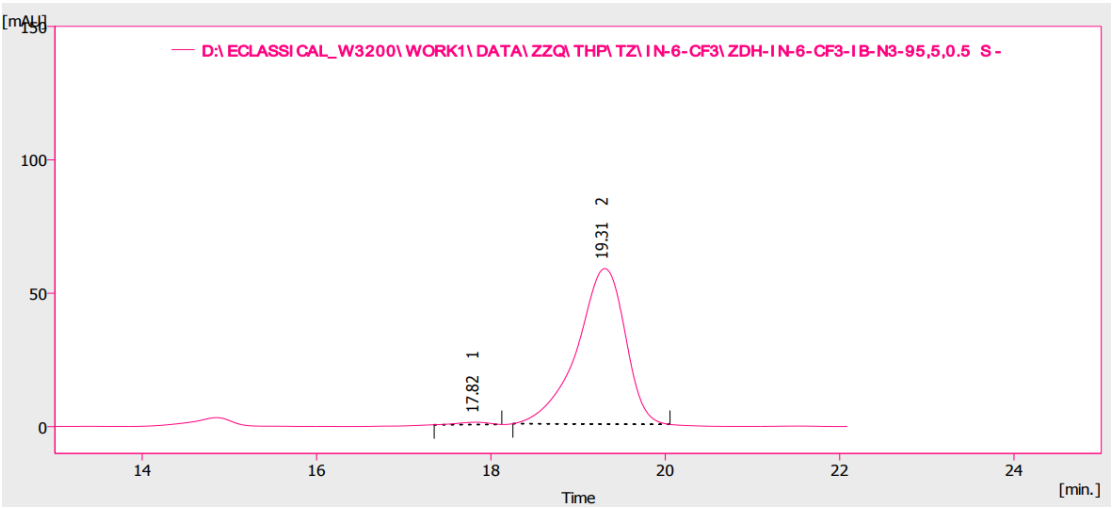


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.24	28.25	690.74	3.0
2	19.85	718.99	22125.10	97.0
Total			22815.84	100.0

8o, 98% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm)

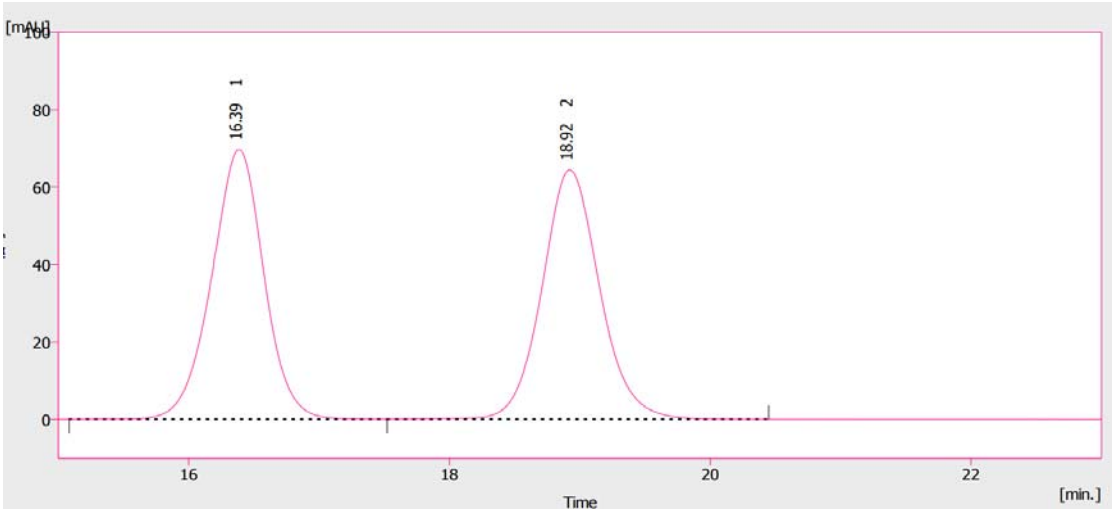


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	18.13	83.51	3245.06	49.8
2	19.84	79.79	3260.46	50.2
Total			7027.52	100.0

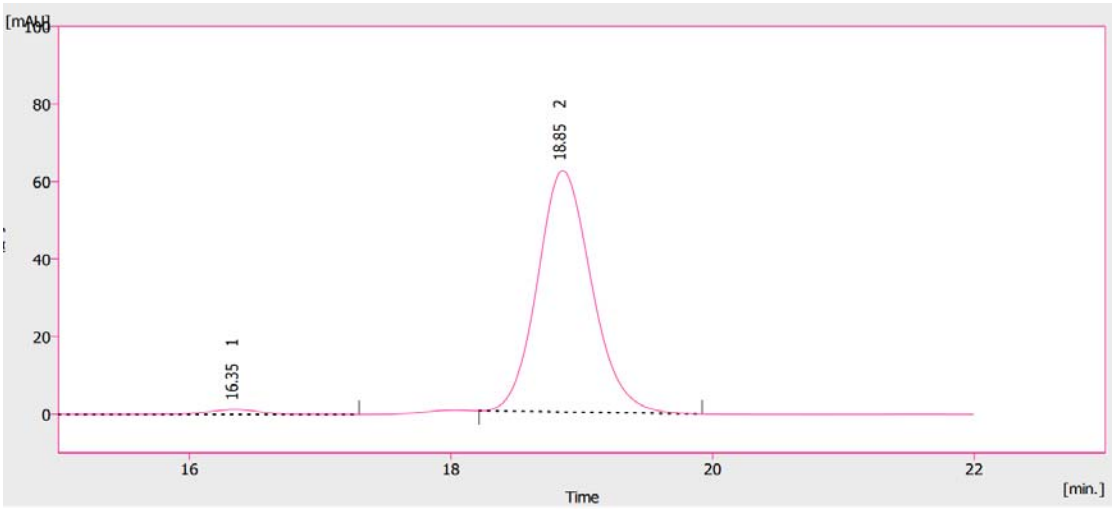


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	17.82	1.46	34.63	0.9
2	19.31	97.17	3724.19	99.1
Total			3758.82	100.0

8p, 96% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 93/7, flow rate = 0.5 mL/min, λ = 254 nm)

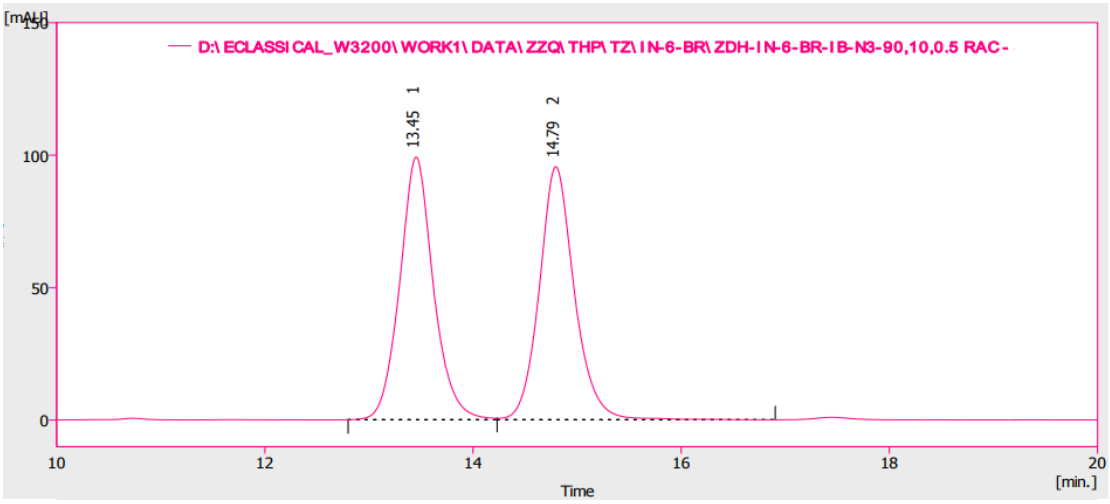


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.39	116.12	3250.54	49.6
2	18.92	1.07.31	3306.73	50.1
Total			6557.27	100.0

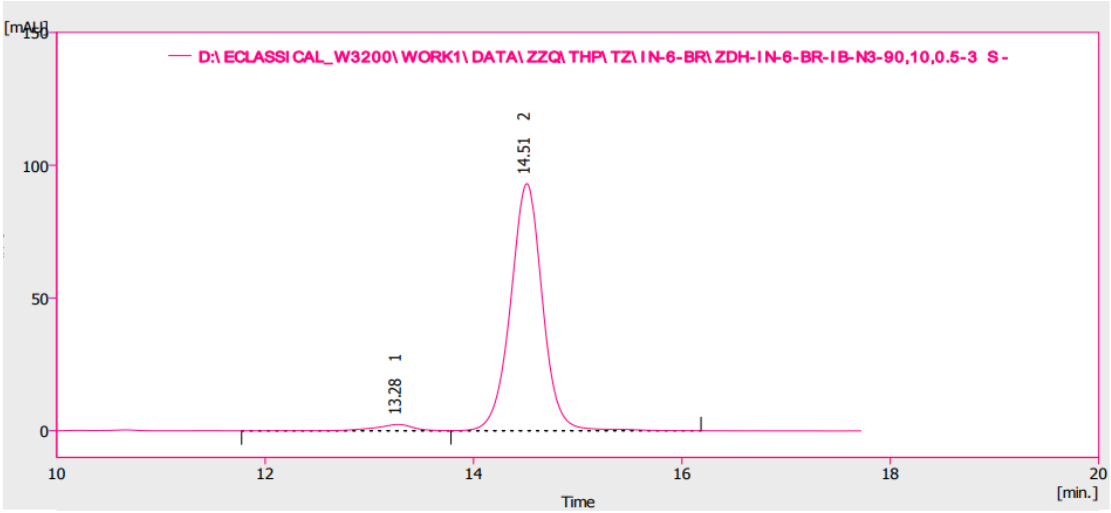


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.35	14.68	59.88	2.0
2	18.85	18.21	2985.22	98.0
Total			3045.10	100.0

8q, 94% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, λ = 254 nm)

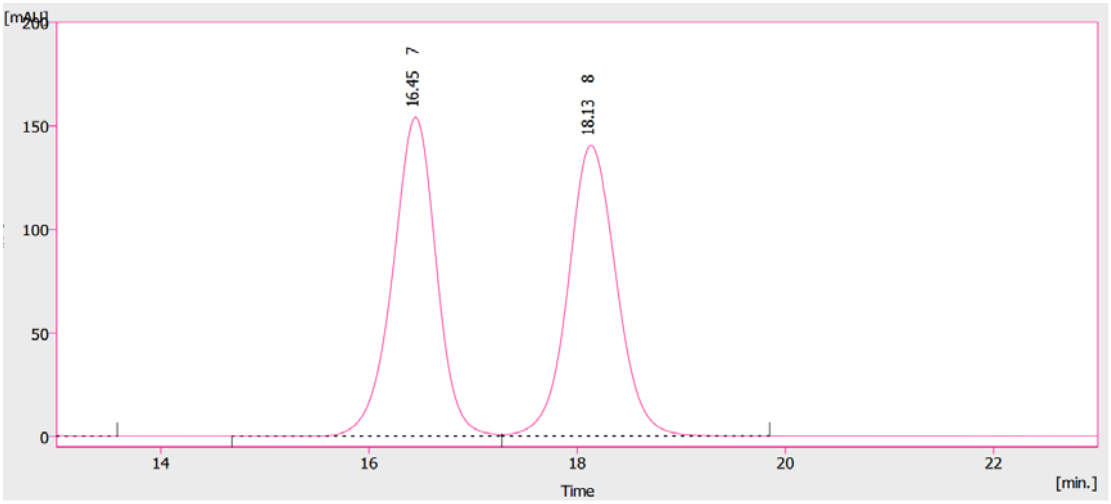


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	13.45	165.22	3728.84	49.9
2	14.79	159.17	3743.64	50.1
Total			7472.48	100.0

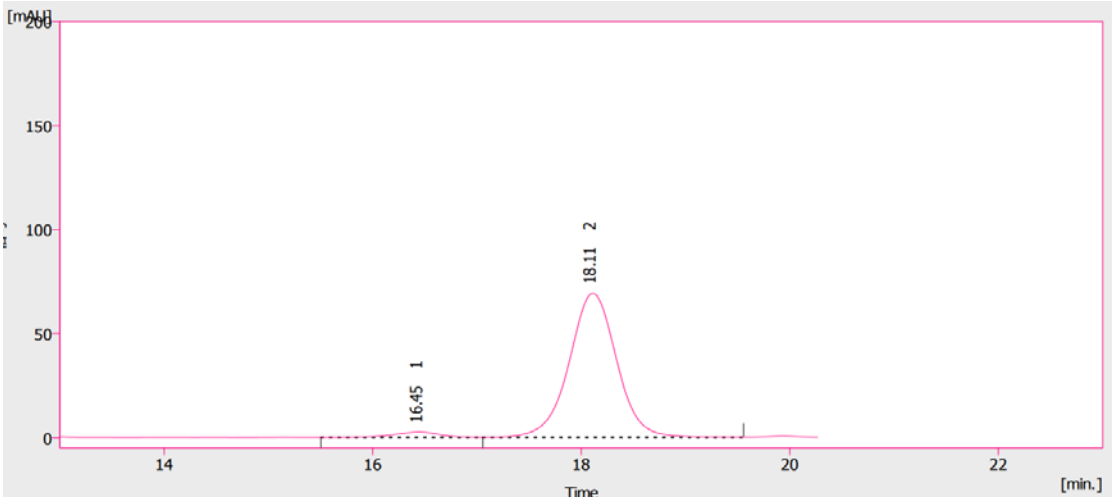


Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	13.28	3.98	102.91	3.0
2	14.51	155.13	3312.13	97.0
Total			3415.04	100.0

8r, 94% *ee* (Daicel Chiralcel IB-N3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm)



Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.45	256.76	7489.08	49.8
2	18.13	234.09	7549.06	50.2
Total			15038.14	100.0



Index	t_R / (min)	Height / (mv)	Area / (mv.sec)	Area / (%)
1	16.45	4.14	117.78	3.1
2	18.11	115.25	3637.65	96.9
Total			3755.43	100.0

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