Electronic Supplementary Material for

Ligand regulating for manganese-catalyzed enantioselective epoxidation of olefins without acid

Daqian Xu,[+,a,b] Qiangsheng Sun,[+,a] Jin Lin[a] and Wei Sun[a,*]
[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Excellence in Molecular Synthesis, and Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, China.
Email: wsun@licp.cas.cn
[b] School of Chemistry and Chemical Engineering, Lanzhou City University, Lanzhou 730070, China
[+] These authors contributed equally to this work.

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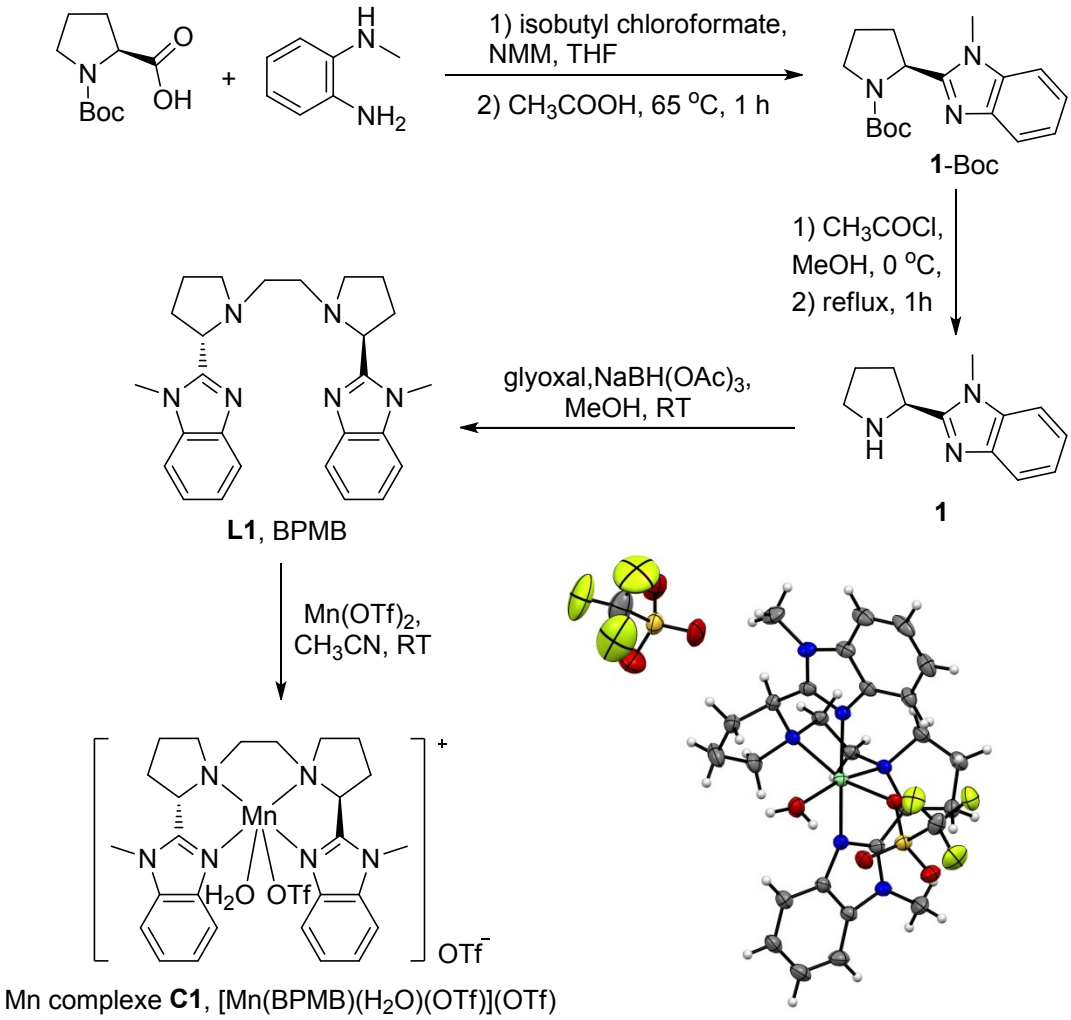
1. General Information

All the solvents and reagents were obtained from commercial sources and used without purification unless stated otherwise. $H_2{}^{18}O$ (> 97% ^{18}O) was obtained from Shanghai Research Institute of Chemical Industry Co. Ltd. *tert*-Butyl hydroperoxide (TBHP, 70% in water) was purchased from TCI company. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were on silica gel GF_{254} plates. Cinnamamides were prepared according to the reported procedures.[1]

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 MHz spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR in deuterated solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were performed on a Bruker micro TOF-Q^{II} spectrometer (ESI). Cryospray ionization mass spectrometry (CSI-MS) was carried out with a Bruker compact Q-TOF spectrometer and the temperature of the nebulizing and drying gases was set at -25 °C. X-ray crystallographic data were collected on a Bruker SMART CCD1000 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296(2)K. GC-MS was recorded by an Agilent 7890A/5975C. High pressure liquid chromatography (HPLC) analysis was performed on a Waters-Breeze instrument (2487 Dual *λ* Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak OD-H, AD-H, OJ, AS, OB, IC columns were purchased from Daicel Chemical Industries, LTD. Gas chromatography (GC) analysis was performed on a Agilent 7890 GC with a CP-Chirasil-Dex CB column.

2. Synthesis of (*S,S*)-BPMB N4 Ligand and (*S,S*)-BPMB-Mn Complexes



Compound **1**-Boc and **1** were prepared according to the reported method from *L*-Boc-proline.[2]

Compound **1** (1.0 equiv) was dissolved in methanol (20 mL) under Argon atmosphere at RT, glyoxal (55% in water, 0.55 equiv) was added and stirred for 2 h until the solvent change to purple, $NaBH(OAc)_3$ (3 equiv) was added in two portions, then the mixture was stirred at RT for 10 h until the raw materials was consumed. At this point, solvent was evaporated and the reaction was quenched with NH_4Cl. Afterwards, the mixture was extracted with $CHCl_3$ (3×10 mL) and the combined organic phases was washed with $NaHCO_3$ and brine, and dried over Na_2SO_4. After the solvent was evaporated, the residue was purified using column chromatography (Methanol/ Ethyl acetate 1:3) to give the target product (*S,S*)-BPMB as a white solid.

[α]20 D= -141 (c 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.33 – 7.16 (m, 6H), 3.76 (m, 2H), 3.72 (s, 6H), 3.12 (m, 2H), 2.62 (m, 2H), 2.36 (s, 2H), 2.28 – 2.08 (m, 4H), 2.03 – 1.71 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 142.2, 136.7, 122.2, 121.8, 119.4, 109.0, 64.3, 53.5, 53.2, 30.1, 30.1, 23.1. HRMS (ESI-MS) m/z Calcd for $[C_{26}H_{33}N_6, M+H]^+$: 429.2761; Found: 429.2777.

[Mn(*S*,*S*-BPMB)(H_2O)(OTf)](OTf) complex **C1** was synthesized according to the reported method from (*S*,*S*)-BPMB and $Mn(OTf)_2$ in MeCN. HRMS (ESI-MS) m/z Calcd for $[C_{26}H_{32}N_6Mn]^{2+}$: 241.6033; Found: 241.6025.

[Mn(*S*,*S*-BPMB)(H_2O)(ClO_4)](ClO_4) complex **C2** was synthesized according to the reported method from (*S*,*S*)-BPMB and $Mn(ClO_4)_2 \cdot 6H_2O$ in MeCN. HRMS (ESI-MS) m/z Calcd for $[C_{26}H_{33}N_6Mn]^{2+}$: 241.6033; Found: 241.6031.

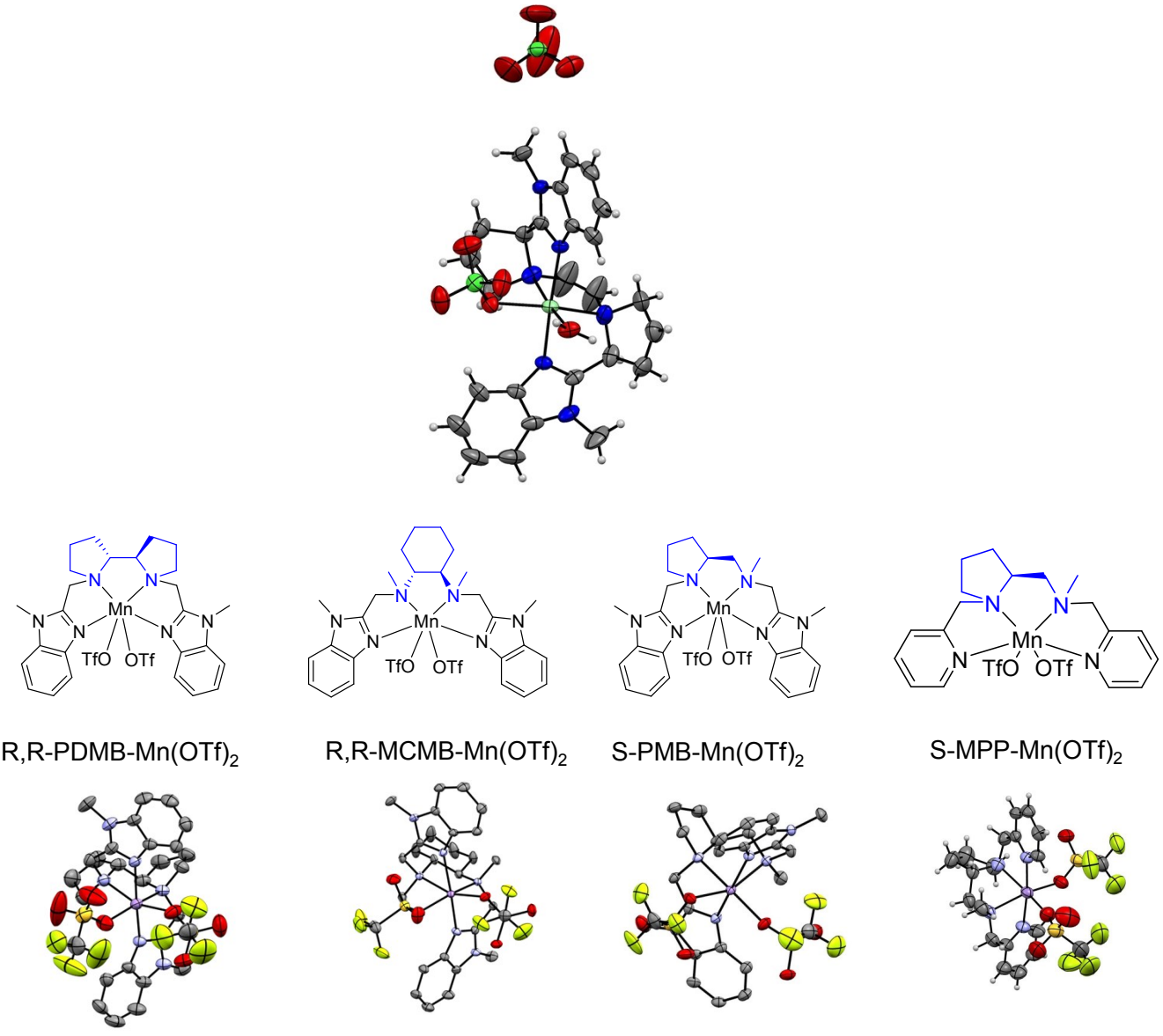
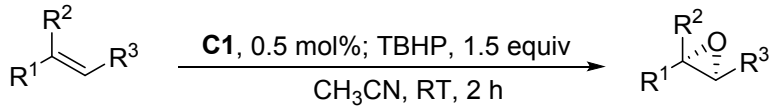


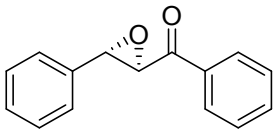
Fig. S1 The crystal structures of manganese complexes with different N4 ligands.

3. General Procedure for Asymmetric Epoxidation of Olefin



Olefin substrate (0.25 mmol), Mn catalyst (0.5 mol %) and MeCN (1.0 mL) were added to a 10 mL flask containing a small stir bar. Then TBHP (1.5 equiv, 70% in water, diluted in 0.5 mL of MeCN) was added via a syringe pump over 1 h with stirring at room temperature, and the mixture was stirred for additional 1h (for chalcones) or 3h (for cinnamamides) respectively. After the reaction, products were purified by column chromatography with silica gel to get pure products.

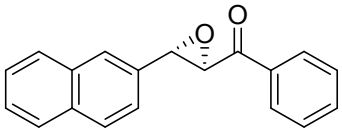
2a. *trans*-(2*R*, 3*S*)-Epoxy-1, 3-diphenyl-propan-1-one[3]



White solid, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.92 (m, 2H), 7.67 – 7.57 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.34 (m, 5H), 4.31 (d, *J* = 1.9 Hz, 1H), 4.08 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 135.5, 135.4, 134.0, 129.0, 128.9, 128.8, 128.3, 125.8, 61.03, 59.4.

HPLC: Chiralcel OD-H column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 8.7 min, t_R(major) = 9.6 min, 93% ee.

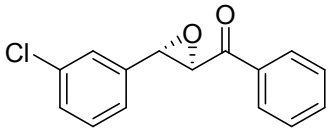
2b. ((2R,3S)-3-(naphthalen-2-yl)oxiran-2-yl)(phenyl)methanone[3]



White solid, 90% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 – 7.82 (m, 3H), 7.59 (m, 2H), 7.48 – 7.38 (m, 5H), 4.44 (d, *J* = 1.9 Hz, 1H), 4.16 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 135.9, 135.6, 132.8, 132.4, 130.4, 129.7, 129.0, 129.0, 128.8, 128.8, 127.8, 127.0, 125.8, 123.6, 61.0, 59.5.

HPLC: Chiralcel AD-H column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 15.4 min, t_R(major) = 17.4 min, 95% ee.

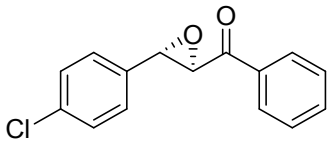
2c. ((2R,3S)-3-(3-chlorophenyl)oxiran-2-yl)(phenyl)methanone[3]



White solid, 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.57 – 7.54 (m, 1H), 7.44 – 7.40 (m, 2H), 7.28 – 7.24 (m, 3H), 7.20 – 7.18 (m, 1H), 4.19 (d, *J* = 1.8 Hz, 1H), 3.98 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 137.6, 135.3, 134.9, 134.1, 130.1, 129.2, 128.9, 128.3, 125.7, 124.1, 60.7, 58.5.

HPLC: Chiralcel OJ column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 10.8 min, t_R(major) = 11.5 min, 97% ee.

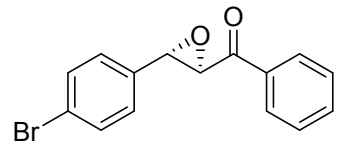
2d. ((2R,3S)-3-(4-chlorophenyl)oxiran-2-yl)(phenyl)methanone[3]



White solid, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.64 – 7.62 (m, 1H), 7.50 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.40 – 7.38 (m, 2H), 7.32 – 7.30 (m, 2H), 4.26 (d, *J* = 1.9 Hz, 1H), 4.06 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 135.3, 134.9, 134.1, 134.0, 129.0, 128.9, 128.3, 127.1, 60.9, 58.7.

HPLC: Chiralcel IC column; hexanes: isopropanol 85/15, 1.0 mL/min, 254 nm, t_R(minor) = 16.5 min, t_R(major) = 17.4 min), 84% ee.

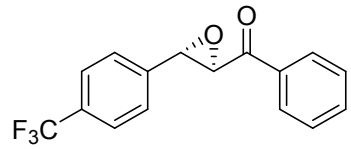
2e. ((2R,3S)-3-(4-bromophenyl)oxiran-2-yl)(phenyl)methanone[3]



White solid, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.65 – 7.57 (m, 1H), 7.56 - 7.50 (m, 4H), 7.28 – 7.26 (m, 2H), 4.26 (d, *J* = 1.9 Hz, 1H), 4.07 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 135.3, 134.9, 134.1, 134.0, 129.0, 128.9, 128.3, 127.1, 60.9, 58.7.

HPLC: Chiralcel AD-H column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 13.3 min, t_R(major) = 15.0 min, 95% ee.

2f. phenyl((2R,3S)-3-(4-(trifluoromethyl)phenyl)oxiran-2-yl)methanone[3]

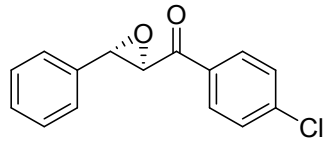


White solid, 46% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.32 (m, 5H), 4.27 (d, *J* = 1.8 Hz, 1H), 4.09 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

192.6, 138.0, 135.3, 135.0, 129.3, 128.9, 128.8, 127.5, 125.9 (q, $J_{C\text{-}F}$ = 4 Hz), 123.4 (d, $J_{C\text{-}F}$ = 271 Hz), 61.3, 59.5.

HPLC, Chiralcel IC column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 12.2 min, t_R(major) = 11.1 min, 88% ee.

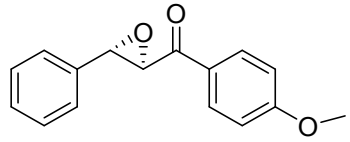
2g. (4-chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)methanone[3]



White solid, 90% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.46 – 7.41 (m, 2H), 7.40 – 7.36 (m, 5H), 4.24 (d, *J* = 1.9 Hz, 1H), 4.07 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 140.6, 135.3, 133.7, 129.8, 129.3, 129.2, 128.8, 125.8, 61.0, 59.4.

HPLC: Chiralcel OJ column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 15.2 min, t_R(major) = 12.7 min, 95% ee.

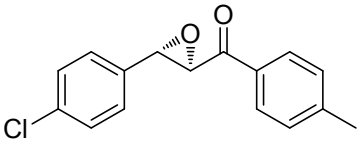
2h. (4-methoxyphenyl)((2R,3S)-3-phenyloxiran-2-yl)methanone[3]



White solid, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.2 Hz, 2H), 7.39-7.38 (m, 5H), 6.97 – 6.94 (m, 2H), 4.26 (d, *J* = 1.9 Hz, 1H), 4.07 (d, *J* = 1.9 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 164.2, 135.7, 130.7, 128.9, 128.7, 128.6, 125.8, 114.1, 60.8, 59.1, 55.5.

HPLC: Chiralcel IC column; hexanes: isopropanol 80/20, 1.0 mL/min, 254 nm, t_R(minor) = 24.6 min, t_R(major) = 25.9 min, 90% ee.

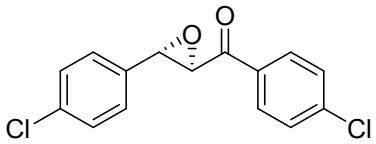
2i. (4-chlorophenyl)((2R,3S)-3-(p-tolyl)oxiran-2-yl)methanone[4]



White solid, 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.27 (m, 4H), 4.23 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 145.2, 134.8, 134.1, 132.9, 129.6, 129.0, 128.4, 127.1, 60.8, 58.6, 21.8.

HPLC: Chiralcel AD-H column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 15.2 min, t_R(major) = 18.6 min, 94% ee.

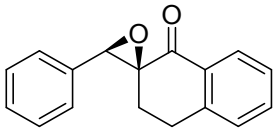
2j. (4-chlorophenyl)((2R,3S)-3-(4-chlorophenyl)oxiran-2-yl)methanone[3]



White solid, 65% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.38 – 7.30 (m, 2H), 4.19 (d, *J* = 1.8 Hz, 1H), 4.06 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 140.7, 135.0, 133.7, 133.5, 129.8, 129.3, 129.0, 127.0, 60.9, 58.7.

HPLC: Chiralcel OJ column; hexanes: isopropanol 95/5, 1.0 mL/min, 254 nm, t_R(minor) = 25.6 min, t_R(major) = 28.6 min, 93% ee.

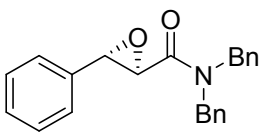
2k (2R,3'S)-3'-phenyl-3,4-dihydro-1H-spiro[naphthalene-2,2'-oxiran]-1-one[3]



White solid, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.18 (m, 6H), 7.18 – 7.01 (m, 1H), 4.24 (s, 1H), 2.70 (dd, *J* = 8.4, 4.0 Hz, 2H), 2.44 – 2.23 (m, 1H), 1.73 (dt, *J* = 13.5, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 134.2, 134.0, 132.6, 128.7, 128.3, 128.3, 127.6, 126.9, 126.6, 64.3, 64.0, 27.3, 25.2.

HPLC: Chiralcel AD-H column; hexanes: isopropanol 90/10, 1.0 mL/min, 254 nm, t_R(minor) = 12.6 min, t_R(major) = 10.8 min, 96% ee.

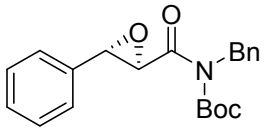
4a. (2S,3R)-N,N-dibenzyl-3-phenyloxirane-2-carboxamide[1]



White solid, 87% yield, [α]20 D = -54 (c 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 –7.25 (m, 11H), 7.24 –7.13 (m, 4H), 4.70 – 4.60 (m, 2H), 4.53 (s, 2H), 4.12 (s, 1H), 3.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 136.5, 135.8, 135.3, 129.0, 128.7, 128.6, 128.5, 127.9, 127.7, 126.6, 125.6, 58.0, 57.4, 49.3, 48.7. HRMS (ESI-MS) m/z Calcd for $C_{23}H_{21}NO_2Na$ $[M+Na]^+$: 366.1465, found: 366.1467.

HPLC: Chiralcel AS-H column; hexanes: isopropanol 75/25, 0.8 mL/min, 210 nm, t_R(minor) = 52.8 min, t_R(major) = 49.6 min, 99.7% ee.

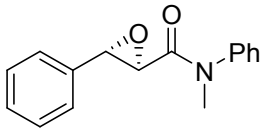
4b tert-butyl benzyl((2S,3R)-3-phenyloxirane-2-carbonyl)carbamate[3]



White solid, 80% yield, [α]20 D = +190 (c 0.35, $CHCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 10H), 4.89 (q, *J* = 14.6 Hz, 2H), 4.33 (d, *J* = 1.9 Hz, 1H), 4.02 (d, *J* = 1.9 Hz, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 152.5, 137.4, 135.6, 128.7, 128.5, 128.4, 128.0, 127.5, 126.1, 84.4, 59.6, 58.9, 47.9, 27.7. HRMS (ESI-MS) m/z Calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 376.1525, found: 376.1527.

HPLC: Chiralcel AS-H column; hexanes: isopropanol 75/25, 1.0 mL/min, 203 nm, t_R(minor) = 13.2 min, t_R(major) = 21.5 min, 91% ee.

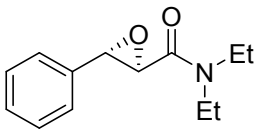
4c (2S,3R)-N-methyl-N,3-diphenyloxirane-2-carboxamide[1]



White solid, 90% yield, [α]20 D = +39.4 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 8H), 7.15 – 7.12 (m, 2H), 4.16 (d, *J* = 1.8 Hz, 1H), 3.38 (s, 3H), 3.24 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.1, 135.4, 129.8, 128.6, 128.4, 128.1, 126.8, 125.7, 58.2, 56.7, 37.7. HRMS (ESI-MS) m/z Calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 276.0999, found: 276.0995.

HPLC: Chiralcel AS-H column; hexanes: isopropanol 90/10, 0.8 mL/min, 220 nm, t_R(minor) = 18.8 min, t_R(major) = 30.3 min, 99% ee.

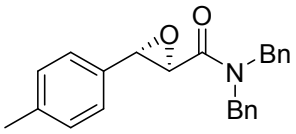
4d (2S,3R)-N,N-diethyl-3-phenyloxirane-2-carboxamide



White solid, 80% yield, [α]20 D = -82 (c 0.9, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 5H), 4.08 (d, *J* = 1.8 Hz, 1H), 3.59 (d, *J* = 2.0 Hz, 1H), 3.50 – 3.39 (m, 4H), 1.22 – 1.15 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 135.8, 128.7, 128.6, 125.7, 57.6, 57.2, 41.5, 40.9, 14.9, 12.9. HRMS (ESI-MS) calcd for $C_{13}H_{17}NO_2Na$ $[M+Na]^+$: 242.1157, found: 242.1159

HPLC: Chiralcel AS-H column; hexanes: isopropanol 70/30, 0.7 mL/min, 203 nm, 35 °C, t_R(minor) = 18.5 min, t_R(major) = 22.9 min, 99.5% ee.

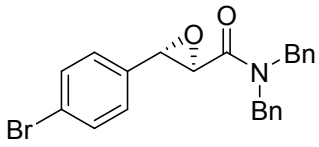
4e (2S,3R)-N,N-dibenzyl-3-(p-tolyl)oxirane-2-carboxamide[1]

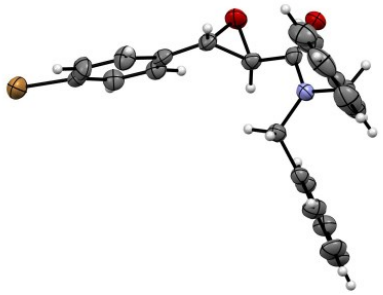


White solid, 83% yield, [α]20 D= -59 (c 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 8H), 7.16 – 7.07 (m, 6H), 4.64 (s, 2H), 4.53 (s, 2H), 4.10 (d, *J* = 1.8 Hz, 1H), 3.68 (d, *J* = 1.9 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 138.6, 136.5, 135.8, 132.3, 129.2, 129.0, 128.7, 128.6, 127.9, 127.7, 126.6, 125.6, 58.1, 57.4, 49.2, 48.6, 21.2. HRMS (ESI-MS) m/z Calcd for $C_{24}H_{23}NO_2Na$ $[M+Na]^+$: 380.1621, found: 380.1624.

HPLC: Chiralcel IC column; hexanes: isopropanol 90/10, 1.5 mL/min, 220 nm, t_R(minor) = 34.3 min, t_R(major) = 22.9 min, 99.5% ee.

4f (2S,3R)-N,N-dibenzyl-3-(4-bromophenyl)oxirane-2-carboxamide[1]

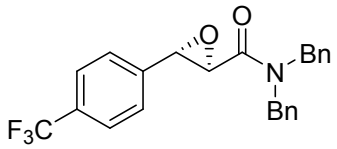




White solid, 86% yield, [α]20 D = -42 (c 0.4, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 7.36 – 7.23 (m, 8H), 7.12 (d, *J* = 6.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.72 (d, *J* = 14.6 Hz, 1H), 4.58 (d, *J* = 14.6 Hz, 1H), 4.53 (d, *J* = 4.1 Hz, 2H), 4.06 (d, *J* = 1.8 Hz, 1H), 3.62 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 136.4, 135.9, 134.5, 131.7, 129.1, 128.8, 128.6, 128.0, 127.8, 127.3, 126.5, 122.7, 57.5, 49.4, 49.0. HRMS (ESI-MS) m/z Calcd for $C_{23}H_{20}BrNO_2Na$ $[M+Na]^+$: 444.0572, found: 444.0570.

HPLC: Chiralcel IC column; hexanes: isopropanol 90/10, 1.5 mL/min, 220 nm, t_R(minor) = 32.9 min, t_R(major) = 36.7 min, 94% ee.

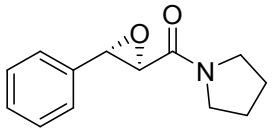
4g (2S,3R)-N,N-dibenzyl-3-(4-(trifluoromethyl)phenyl)oxirane-2-carboxamide[1]



White solid, 42% yield, [α]20 D = -12 (c 0.18, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.26 (m, 10H), 7.13 (d, *J* = 6.8 Hz, 2H), 4.76 (d, *J* = 14.6 Hz, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 2H), 4.16 (d, *J* = 1.5 Hz, 1H), 3.64 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 139.5, 136.4, 135.9, 130.9 (q, J_{C-F} = 33 Hz), 129.1, 128.8, 128.6, 128.0, 127.8, 126.5, 125.6 (q, J_{C-F} = 3.6 Hz), 124.0 (d, J_{C-F} = 293.0 Hz), 57.6, 57.3, 50.1, 49.1. HRMS (ESI-MS) m/z Calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 434.1344, found: 434.1340.

HPLC: Chiralcel IC column; hexanes: isopropanol 90/10, 0.8 mL/min, 220 nm, t_R(minor) = 36.6 min, t_R(major) = 38.8 min, 98% ee.

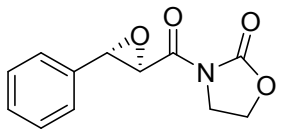
4h ((2S,3R)-3-phenyloxiran-2-yl)(pyrrolidin-1-yl)methanone



White solid, 60% yield, [α]20 D = -71 (c 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 5H), 4.13 (d, *J* = 1.8 Hz, 1H), 3.70 – 3.58 (m, 1H), 3.60 – 3.37 (m, 5H), 2.11 – 1.72 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 135.8, 128.7, 128.6, 125.7, 57.5, 57.5, 46.4, 46.0, 26.1, 23.9. HRMS (ESI-MS) m/z Calcd for $C_{13}H_{15}NO_2Na$ [M+Na]: 240.0995, found: 240.0984.

HPLC: Chiralcel AS-H column; hexanes: isopropanol 70/30, 0.7 mL/min, 203 nm, 35 °C, t_R(minor) = 30.9 min, t_R(major) = 54.3 min, 98% ee.

4i 3-((2S,3R)-3-phenyloxirane-2-carbonyl)oxazolidin-2-one



White solid, 70% yield, [α]20 D = -19 (c 0.6, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 5.39 (d, *J* = 2.8 Hz, 1H), 5.05 (d, *J* = 2.7 Hz, 1H),

4.48 – 4.42 (m, 1H), 4.34 (dd, *J* = 17.0, 8.7 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.92 –3.86 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 174.3, 155.5, 142.6, 128.9, 128.4, 127.5, 75.8, 75.1, 64.5, 43.9. HRMS (ESI-MS) m/z Calcd for $C_{12}H_{11}NO_4Na$ $[M+Na]^+$: 256.0587, found: 256.0580.

HPLC: Chiralcel IC column; hexanes: isopropanol 75/25, 0.8 mL/min, 210 nm, t_R(minor) = 37.0 min, t_R(major) = 44.7 min, 87% ee.

4. CSI-MS Studies

4.1 CSI-MS Experiment for $[Mn(IV)(O)(S,S\text{-BPMB})]^{2+}$ and $[Mn(IV)(O)(S,S\text{-BPMB})(OTf)]^{+}$

The solution of TBHP (70% in water, diluted to 0.5mM, 1.0 mL) was added to a solution of [Mn(*S*,*S*-BPMB)(H_2O)(OTf)](OTf) complex (**C1)** (0.05 mM, 1mL), and the mixture was stirred at room temperature for 5 min. The solution was injected directly into the Q-TOF spectrometer (CSI-MS at -25°C).

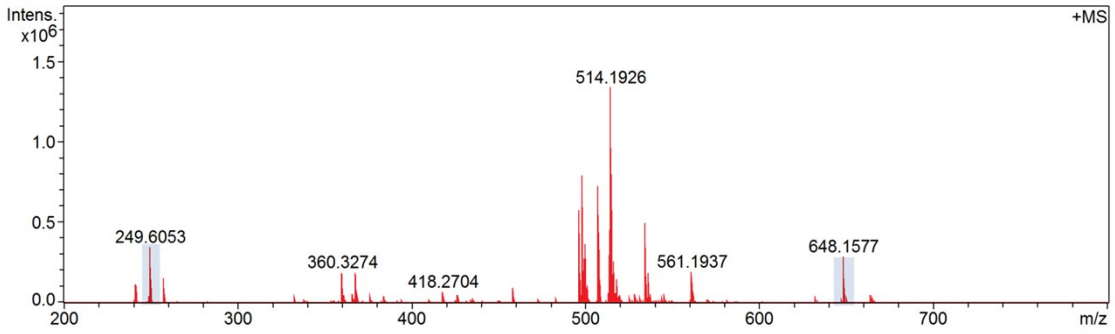


Fig. S2 Full CSI-MS spectrum of the reaction mixture ([Mn(*S*,*S*-BPMB)(H_2O)(OTf)](OTf) complex **(C1**) and 10 equiv of TBHP in MeCN at –25 °C.

4.2 CSI-MS Experiment for ^{18}O-labelled water experiment

H_2O^{18} (10 µl, 0.55 mmol) was added to a solution of [Mn(*S*,*S*-BPMB)(H_2O)(OTf)](OTf) complex (**C1)** (0.05 mM, 1 mL), then TBHP (10 equiv) was added, and the mixture was stirred at room temperature for 5 min. Afterwards, the solution was injected directly into the Q-TOF spectrometer (CSI-MS at -25°C).

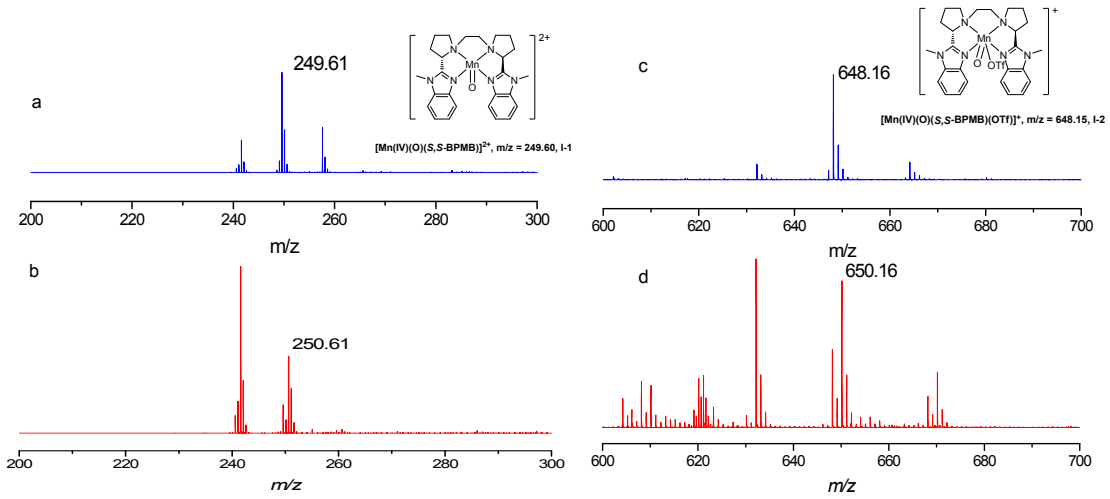


Fig. S3 (a) CSI-MS spectrum of the solution showing the signal of [Mn(IV)(O)(*S*,*S*-BPMB)]$^{2+}$, **I-1** at m/z 249.10. (b) CSI-MS spectrum of [Mn(IV)(O)(*S*,*S*-BPMB)]$^{2+}$ partial exchanged by $H_2{}^{18}O$. (c) CSI-MS spectrum of the solution showing the signal of [Mn(IV)(O)(*S*,*S*-BPMB)(OTf)]$^{+}$, **I-2** at m/z 648.15. (d) CSI-MS spectrum of [Mn(IV)(O)(*S*,*S*-BPMB)(OTf)]$^{+}$ partial exchanged by $H_2{}^{18}O$.

4.3 CSI-MS Experiment for the Asymmetric Epoxidation of Styrene

The solution of TBHP (70% in water, diluted to 0.5 mM, 1.0 mL) was added to a solution of [Mn(*S*,*S*-BPMB)(H_2O)(OTf)](OTf) complex (**C1)** (0.05 mM, 1mL). After the mixture was stirred at room temperature for 5 min, styrene (100 µl, about 10000 equiv) was added to the system. The solution was monitored every 5 min by using Q-TOF spectrometer (CSI-MS at -25°C).

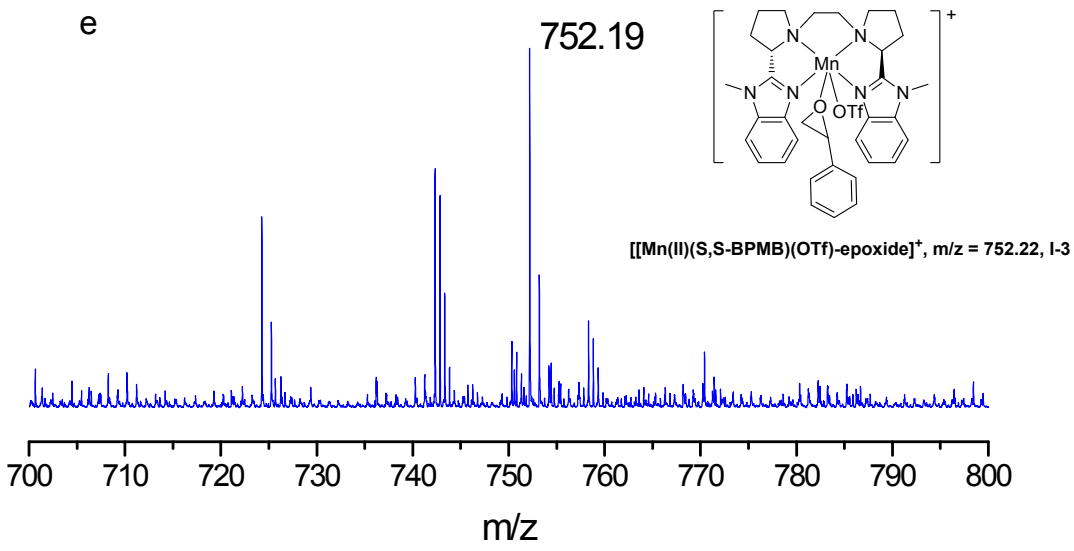


Fig. S4 CSI-MS spectrum of the solution showing the signal of [Mn(IV)(O)(*S*,*S*-BPMB)(OTf)-(styrene oxide)]$^{+}$, **I-3** at m/z 752.19.

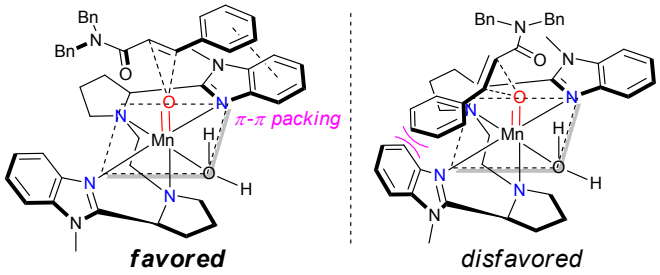
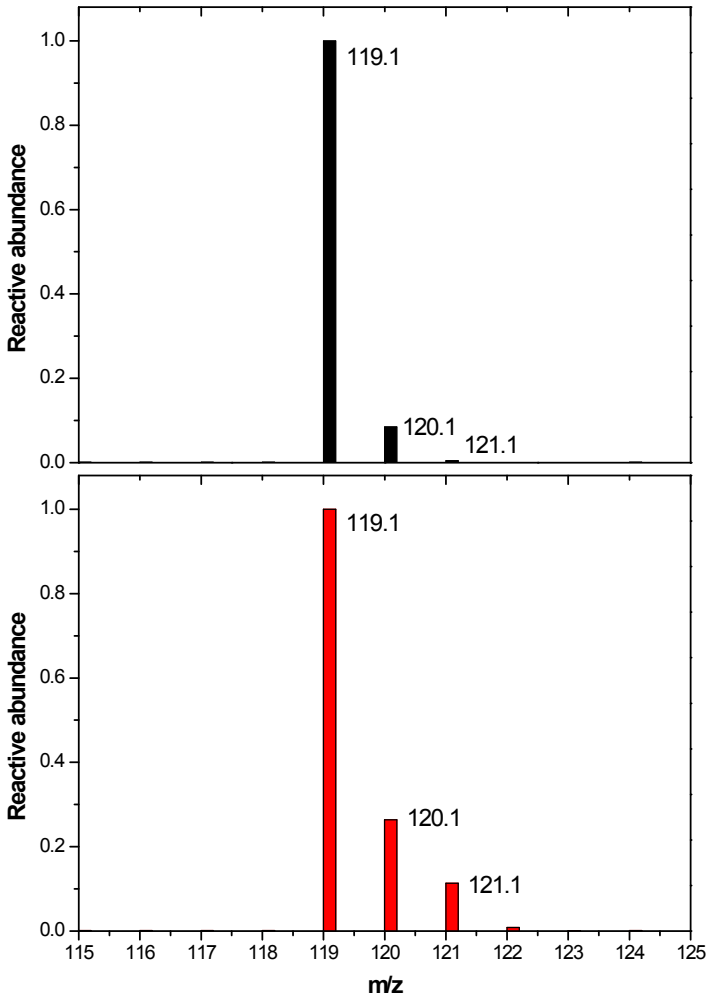


Fig. S5 Enantioselective epoxidation induced by the manganese complex without acid.

5. O^{18} labeling Experiment in the Asymmetric Epoxidation of Styrene

Styrene (0.2 mmol), Mn catalyst (0.5 mol %), H_2O^{18} (5 equiv, 20 mg) and MeCN (1.0 mL) were added to a 10 mL flask containing a small stir bar. Then TBHP (1.5 equiv, 70% in water, diluted in 0.5 mL of MeCN) was added via a syringe pump over 1 h with stirring at room temperature, and the mixture was stirred for an additional 1h. The product was detected by GC-MS, 10.2% ^{18}O-labeled epoxide was observed on the basis of the MS spectrum.

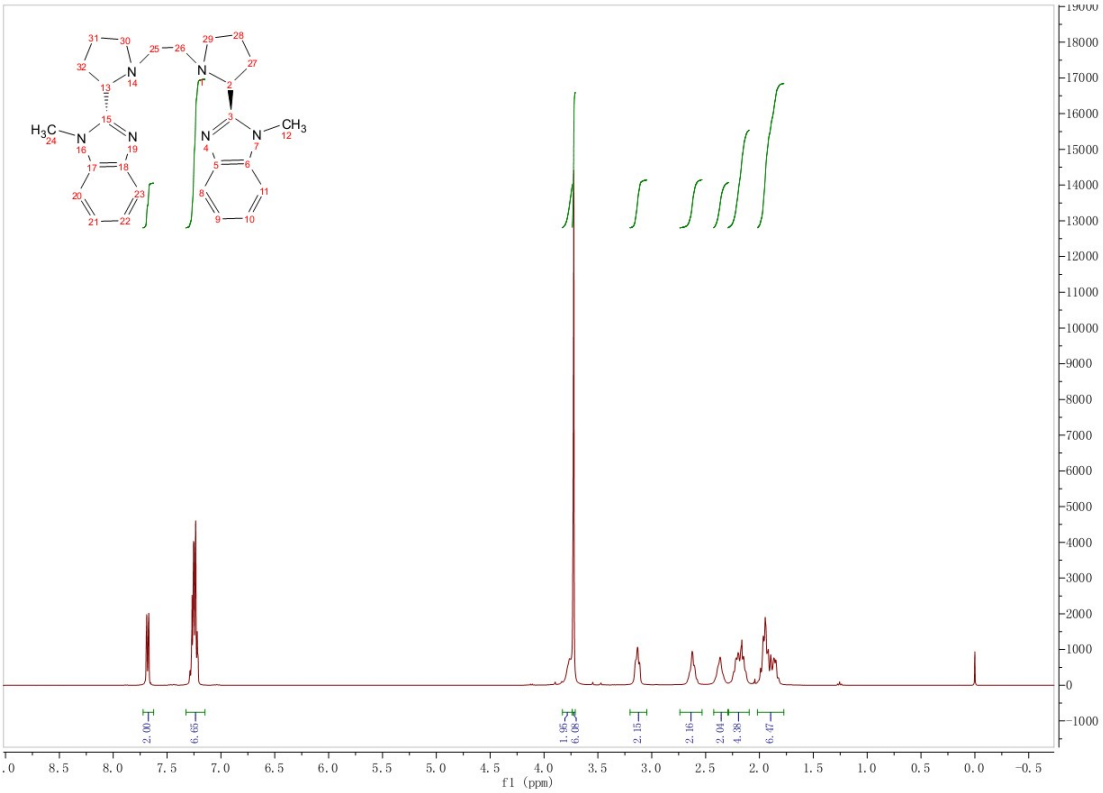


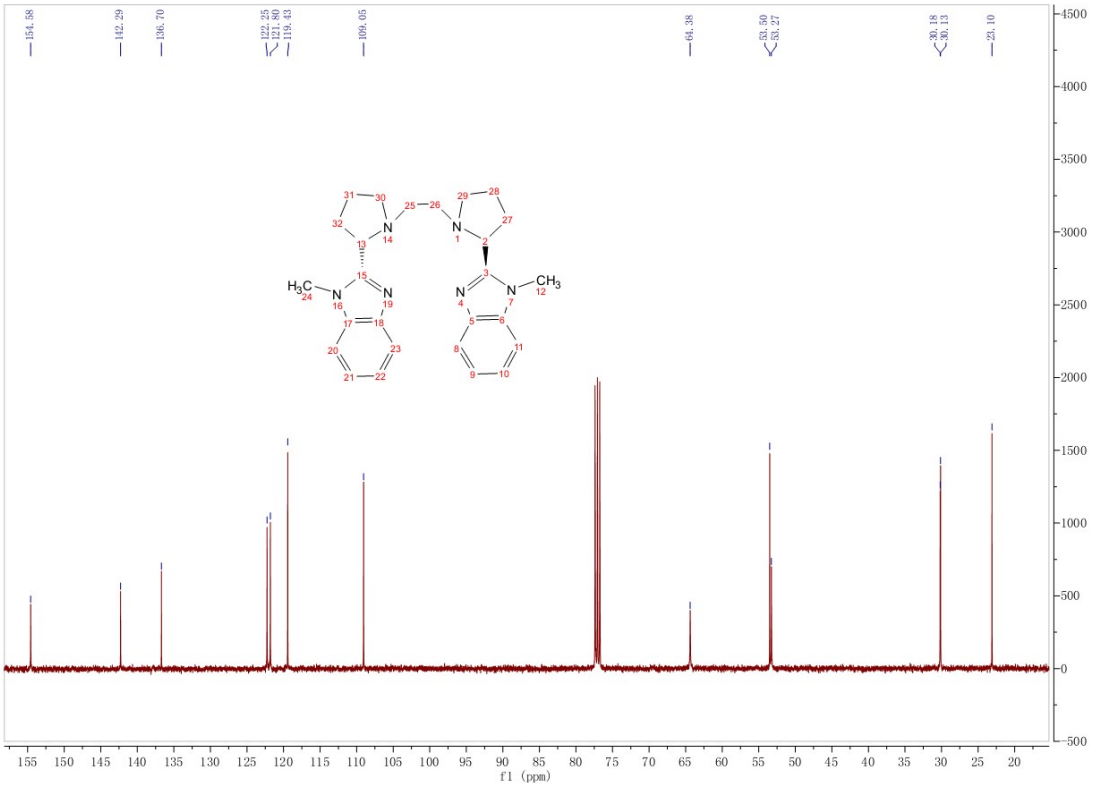
References

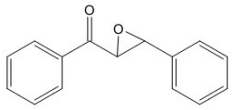
1 (a) X. N. Chen, B. Gao, Y. J. Su and H. M. Huang, *Adv. Syn. Catal.,* 2017, **359**, 2535–2541; (b) W. F. Wang, Q. S. Sun, C. G. Xia and W. Sun, *Chin. J. Catal.,* 2018, **39**, 1463–1469.

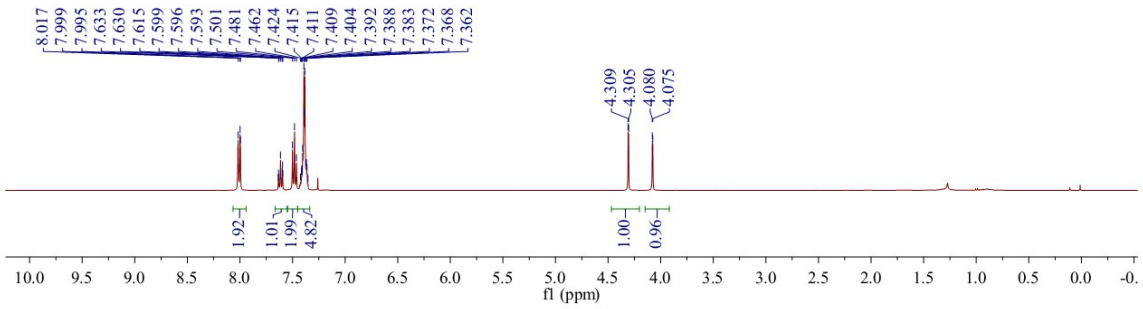
2 G. Balboni, R. Guerrini, S. Salvadori, C. Bianchi, D. Rizzi, S. D. Bryant, and L. H. Lazarus, *J. Med. Chem.,* 2002, **45**, 713–720.

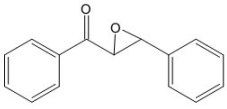
7. Copies of NMR for BPMB ligand, epoxides 2a-2k and 4a-4i

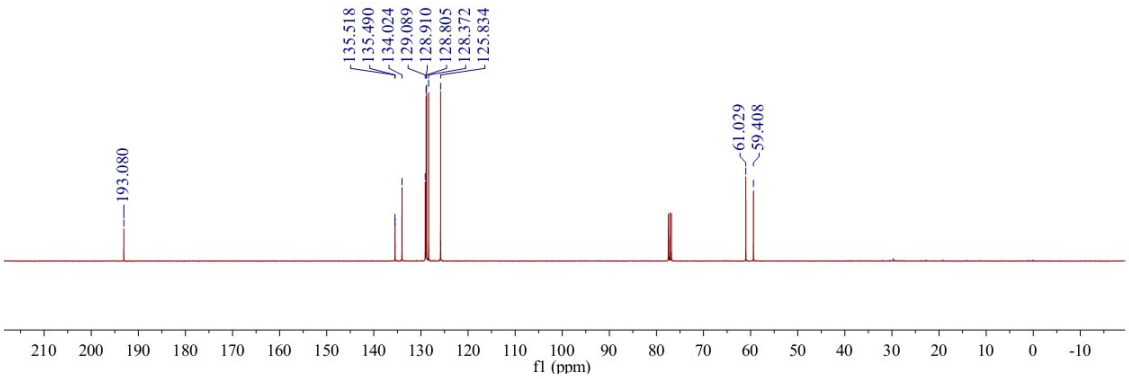







8.017
7.999
7.995
7.633
7.630
7.615
7.599
7.596
7.593
7.501
7.481
7.462
7.424
7.415
7.411
7.409
7.404
7.392
7.388
7.383
7.372
7.368
7.362
4.309
4.305
4.080
4.075
1.92
1.01
1.99
4.82
1.00
0.96
f1 (ppm)

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135.490
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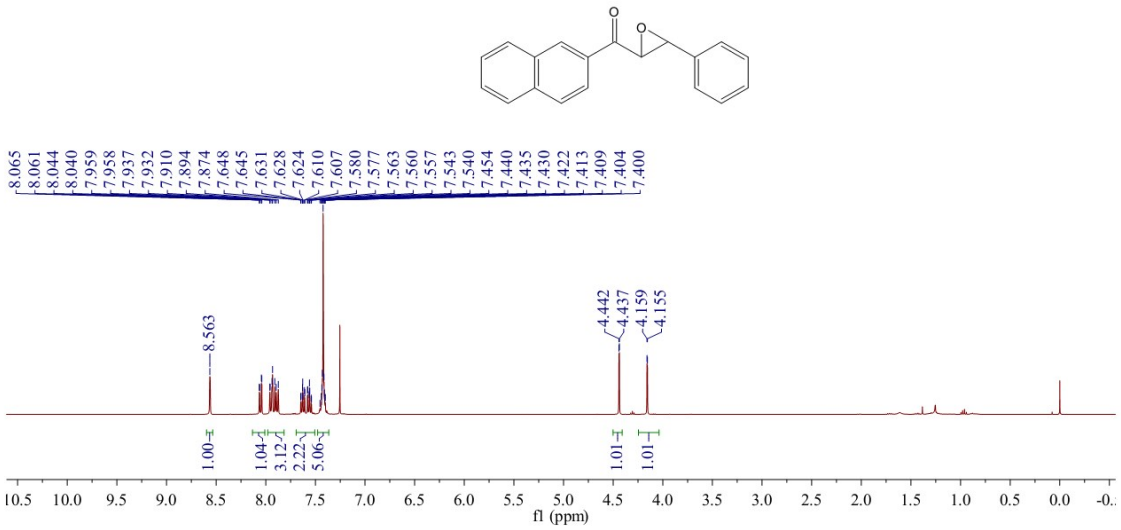
129.089
128.910
128.805
128.372
125.834
193.080
61.029
59.408
f1 (ppm)


8.065
8.061
8.044
8.040
7.959
7.958
7.937
7.932
7.910
7.894
7.874
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7.631
7.628
7.624
7.610
7.607
7.580
7.577
7.563
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7.557
7.543
7.540
7.454
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7.435
7.430
7.422
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7.409
7.404
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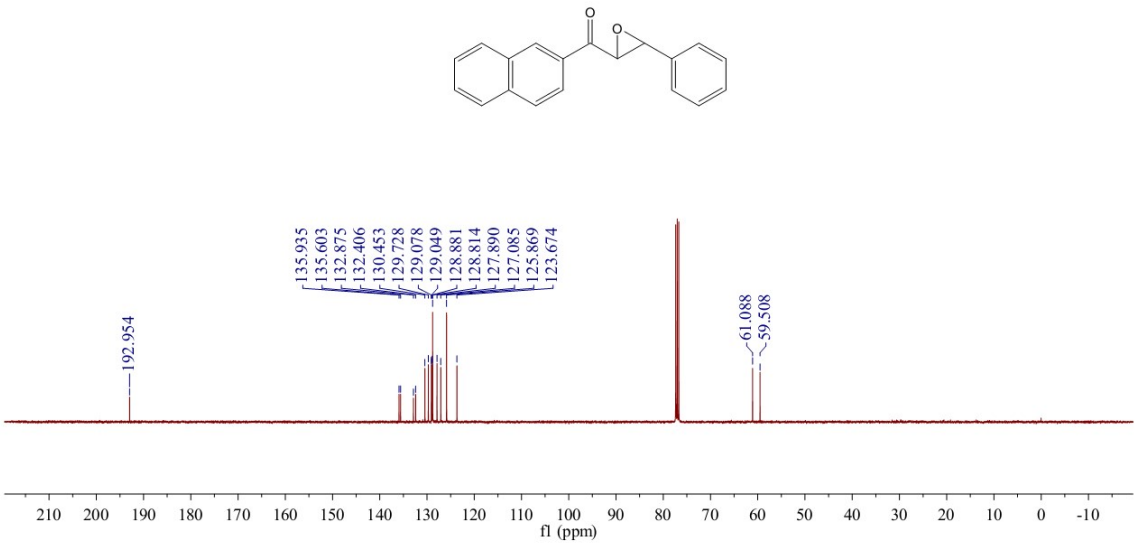
2.22
5.06
1.01
1.01
fl (ppm)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135.603
132.875
132.406
130.453
129.728
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129.049
128.881
128.814
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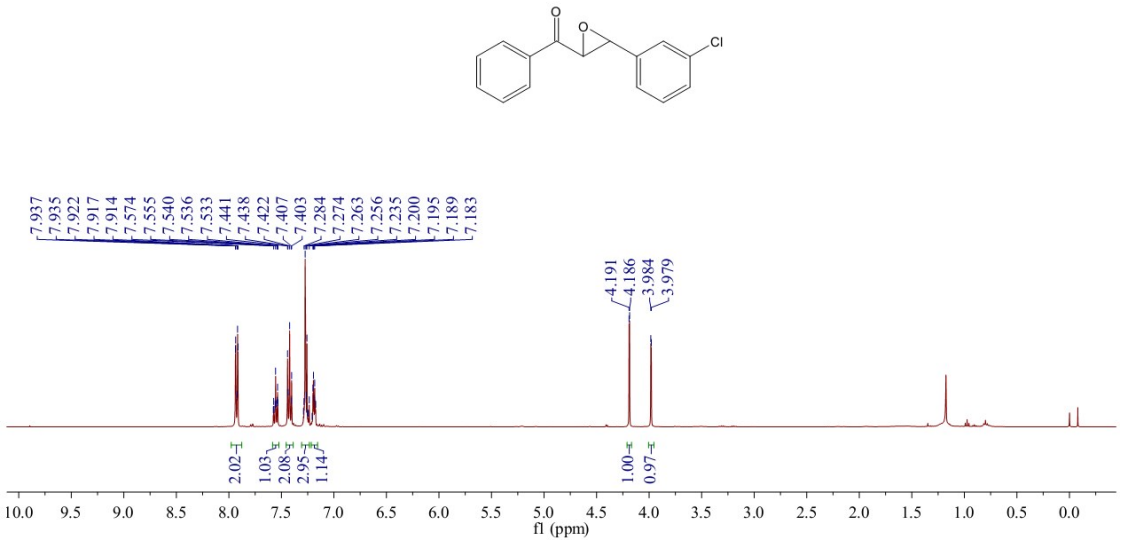
123.674
192.954
61.088
59.508
fl (ppm)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O
Cl
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7.922
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7.540
7.536
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7.441
7.438
7.422
7.407
7.403
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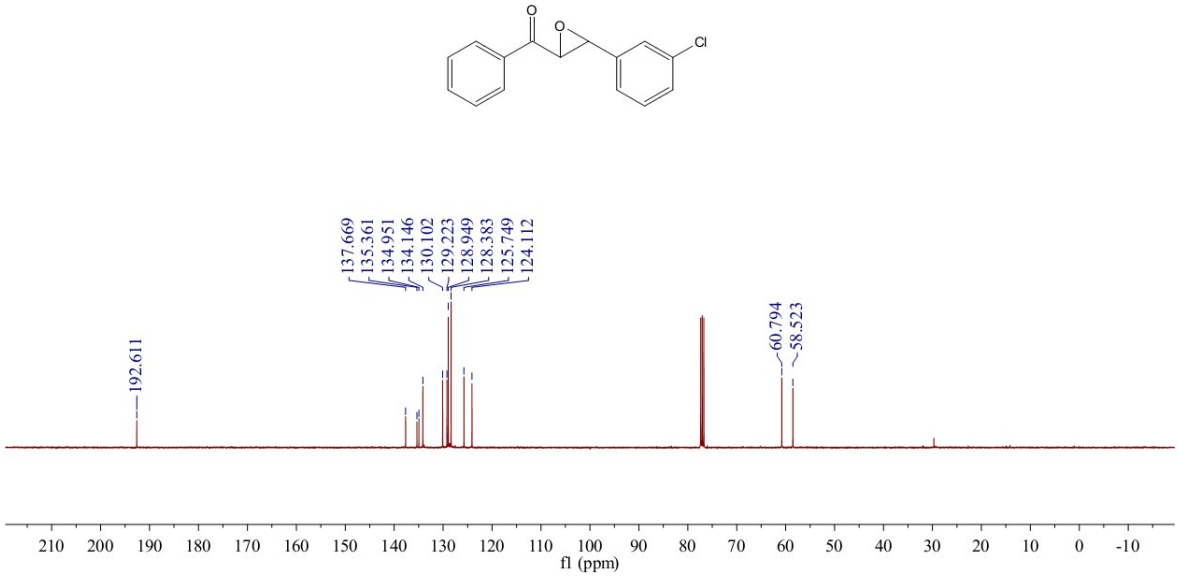
7.274
7.263
7.256
7.235
7.200
7.195
7.189
7.183
4.191
4.186
3.984
3.979
2.02
1.03
2.08
2.95
1.14
1.00
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
Cl
137.669
135.361
134.951
134.146
130.102
129.223
128.949
128.383
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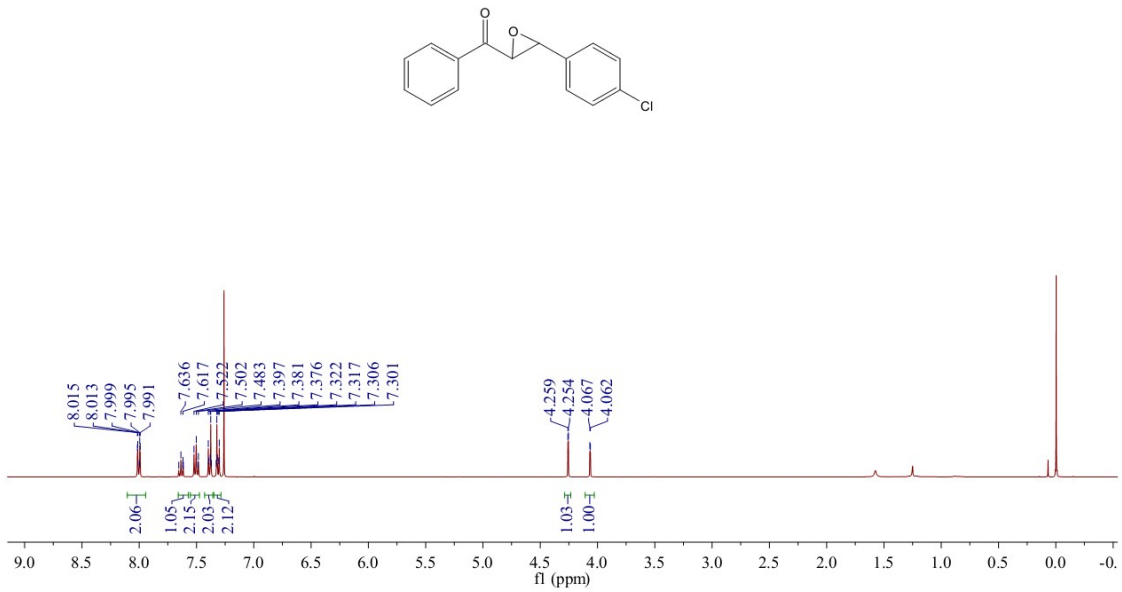
60.794
58.523
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
Cl
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8.013
7.999
7.995
7.991
7.636
7.617
7.622
7.502
7.483
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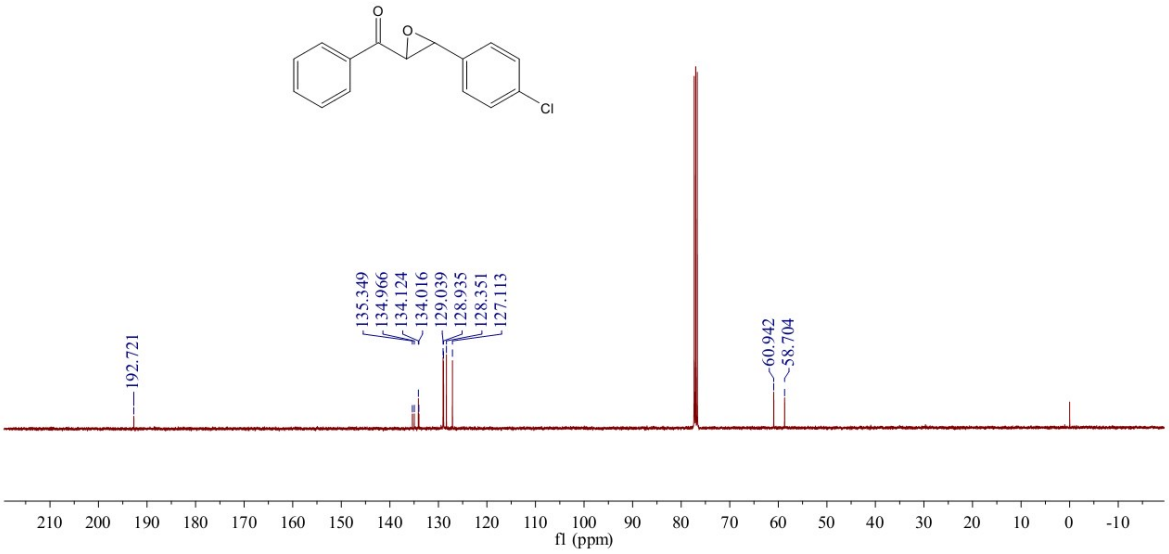
7.381
7.376
7.322
7.317
7.306
7.301
4.259
4.254
4.067
4.062
2.06
1.05
2.15
2.03
2.12
1.03
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


O
O
Cl
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134.966
134.124
134.016
129.039
128.935
128.351
127.113
60.942
58.704
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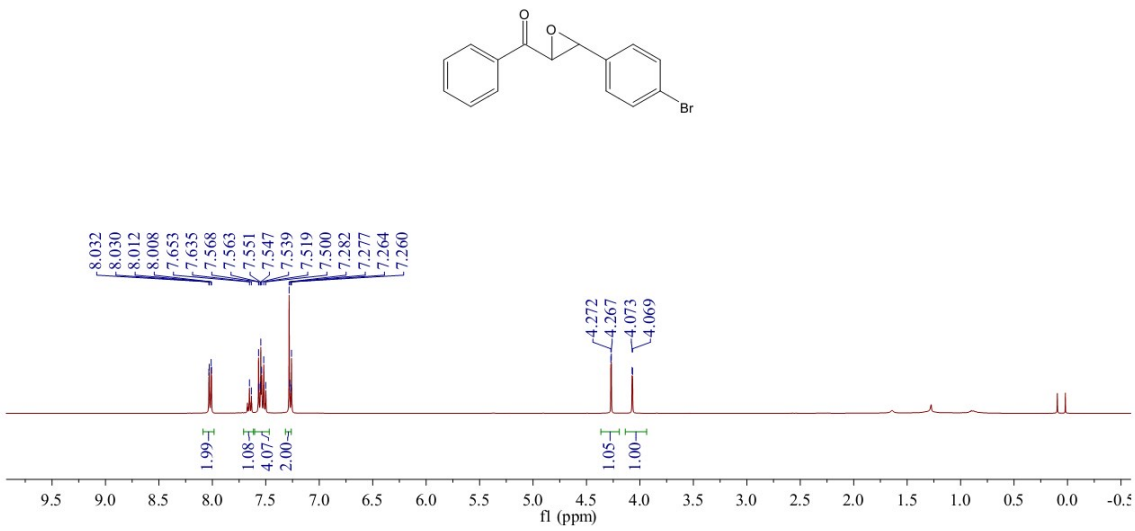
f1 (ppm)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O
Br
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7.635
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7.563
7.551
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7.519
7.500
7.282
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7.264
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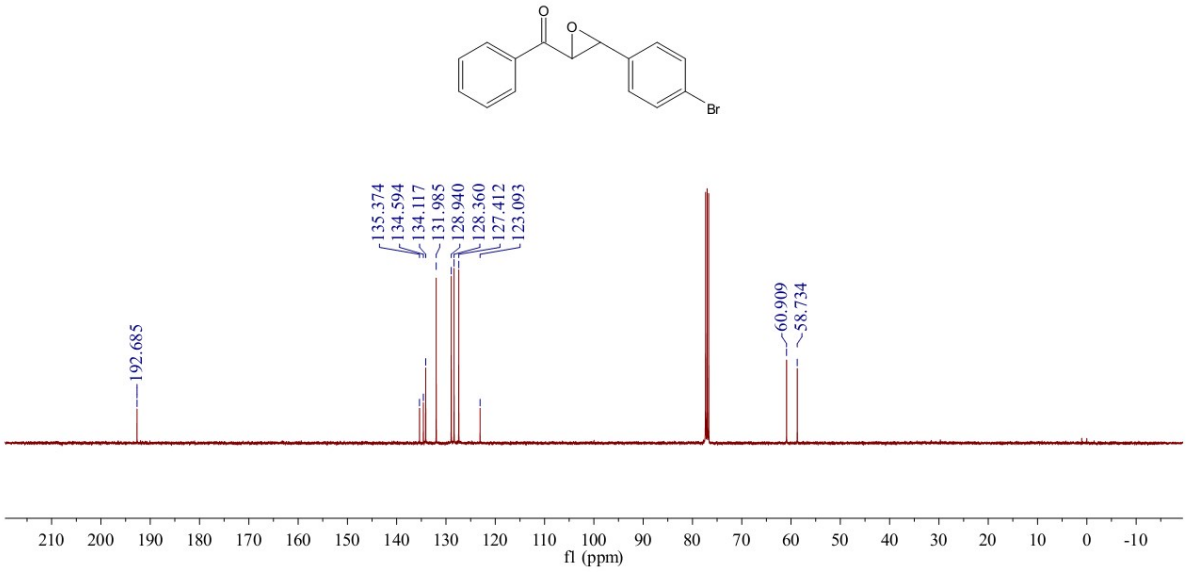
4.07
2.00
1.05
1.00
f1 (ppm)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O
Br
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123.093
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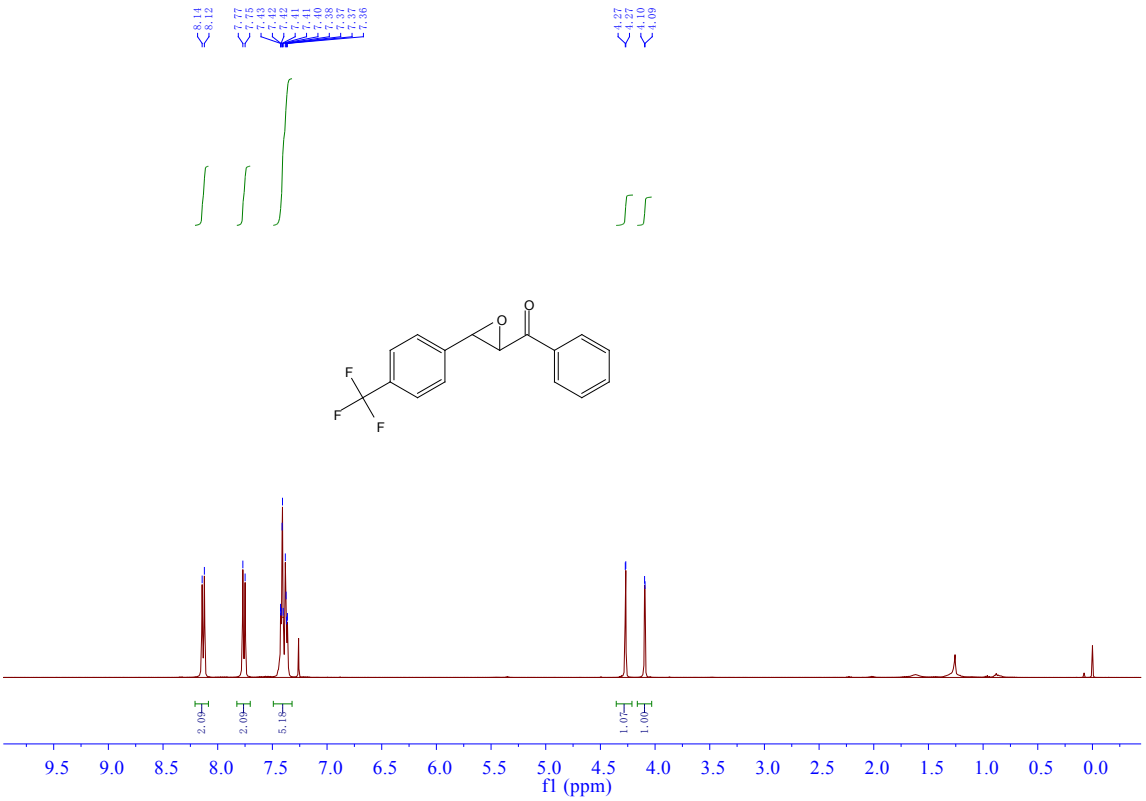
58.734
f1 (ppm)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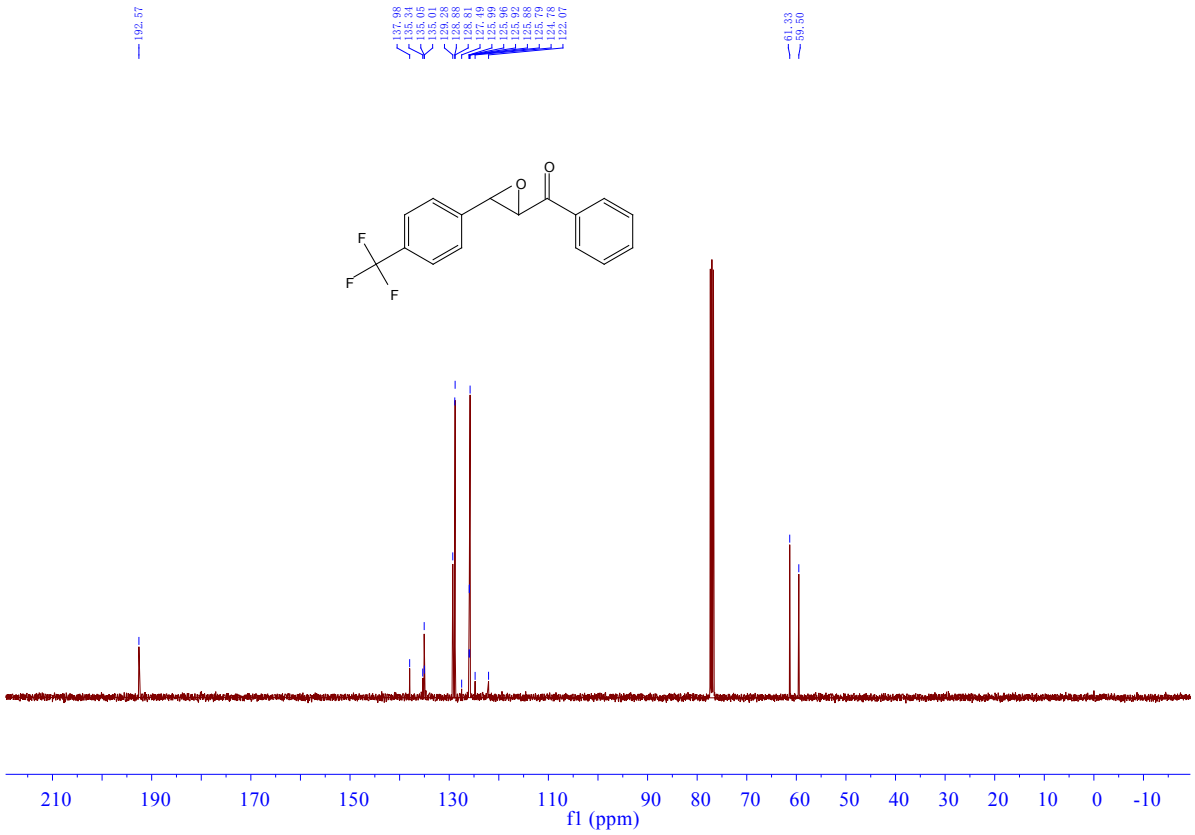
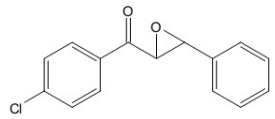
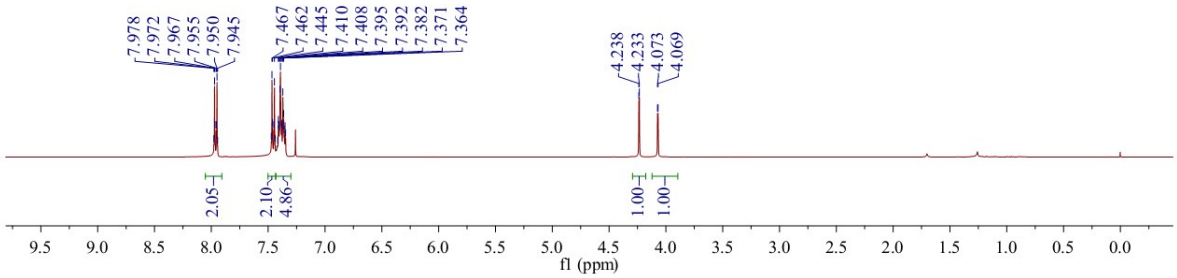
8.12
7.77
7.75
7.43
7.42
7.42
7.41
7.41
7.40
7.38
7.37
7.37
7.36
4.27
4.27
4.10
4.09
O
O
F
F
F
2.09
2.09
5.18
1.07
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


192.57
137.98
135.34
135.05
135.01
129.28
128.88
128.81
127.49
125.99
125.96
125.92
125.88
125.79
124.75
122.07
61.33
59.50
O
O
F
F
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
Cl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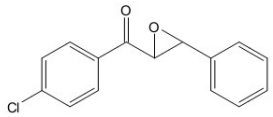
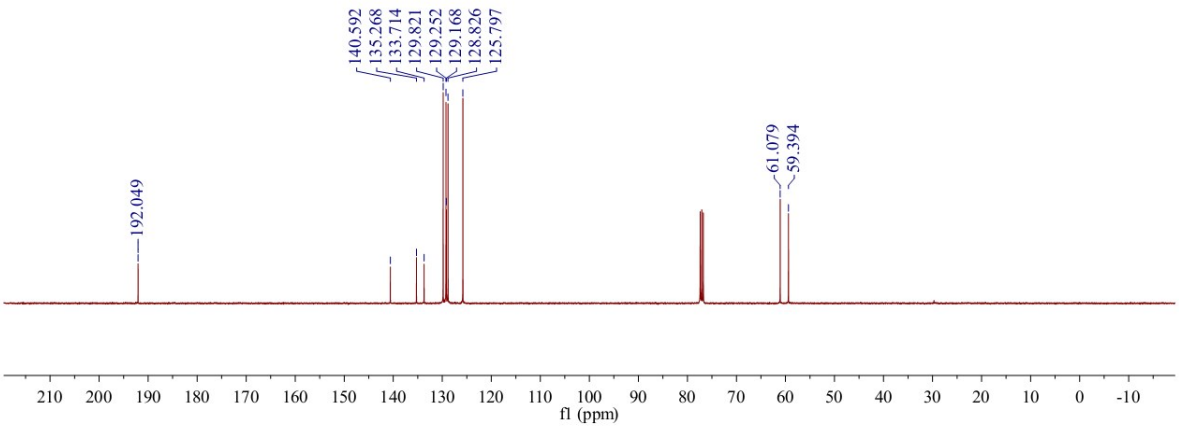
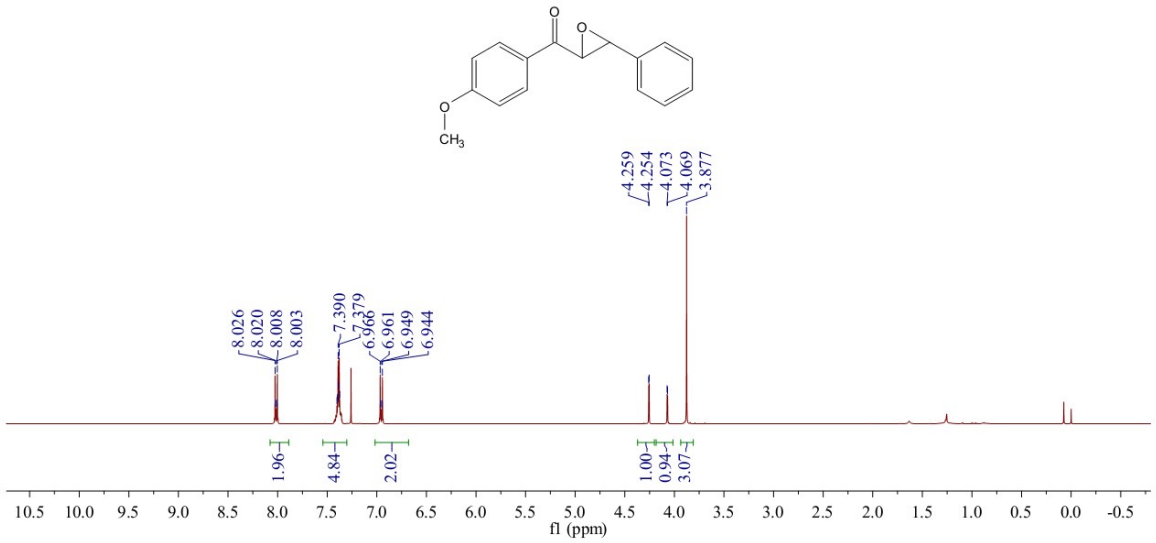
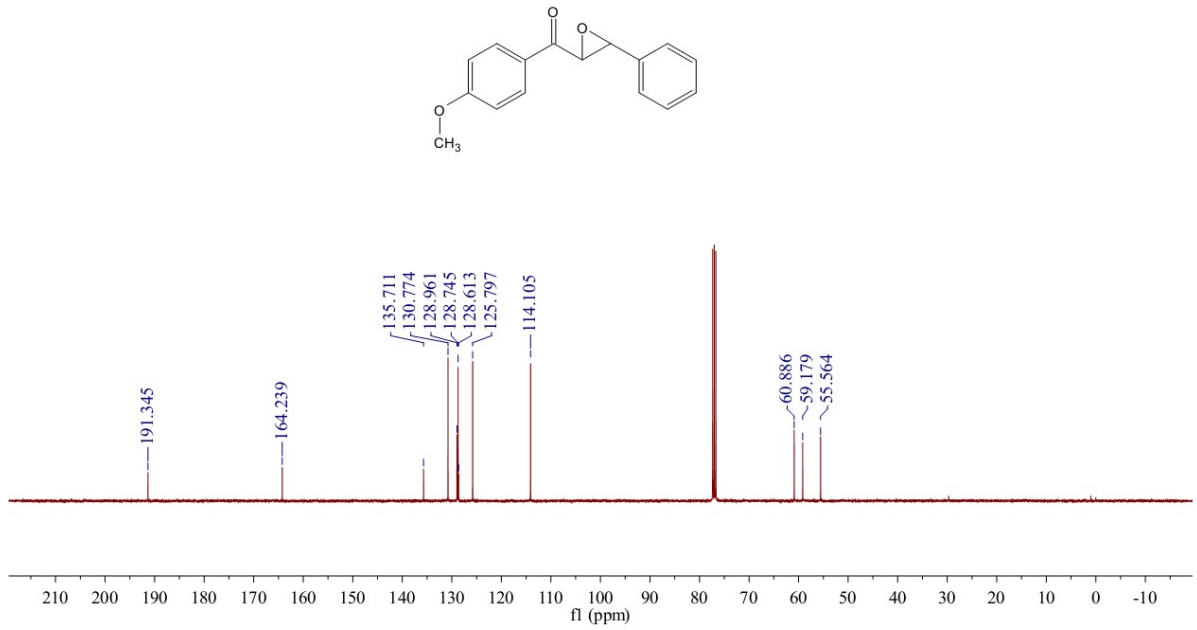
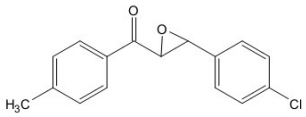
7.950
7.945
7.467
7.462
7.445
7.410
7.408
7.395
7.392
7.382
7.371
7.364
4.238
4.233
4.073
4.069
2.05
2.10
4.86
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

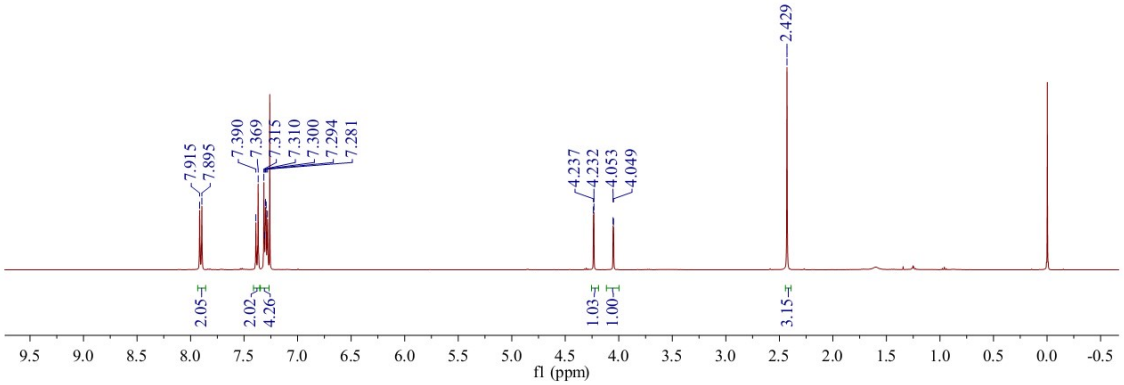

O
O
Cl

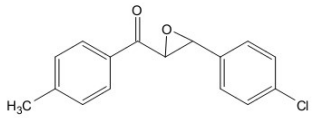

140.592
135.268
133.714
129.821
129.252
129.168
128.826
125.797
192.049
61.079
59.394
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
O
CH3
4.259
4.254
4.073
4.069
3.877
8.026
8.020
8.008
8.003
7.390
7.379
6.966
6.961
6.949
6.944
1.96
4.84
2.02
1.00
0.94
3.07
10.5 10.0 9.5 9.0 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 -0.5
f1 (ppm)

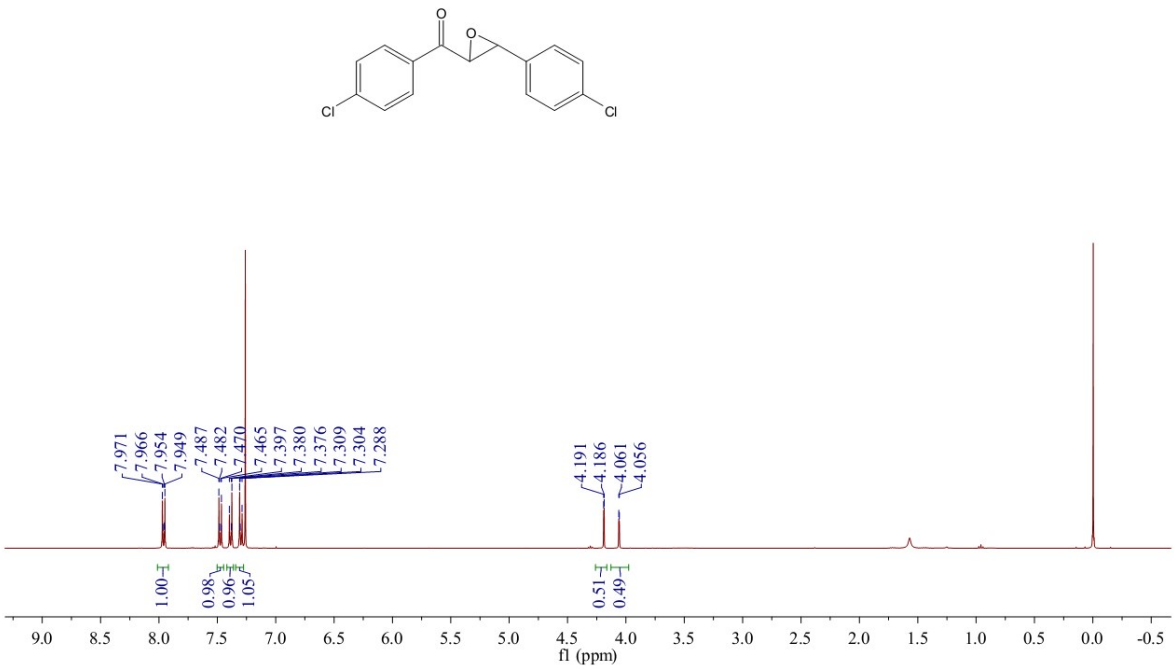

O
O
O
CH3
191.345
164.239
135.711
130.774
128.961
128.745
128.613
125.797
114.105
60.886
59.179
55.564
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

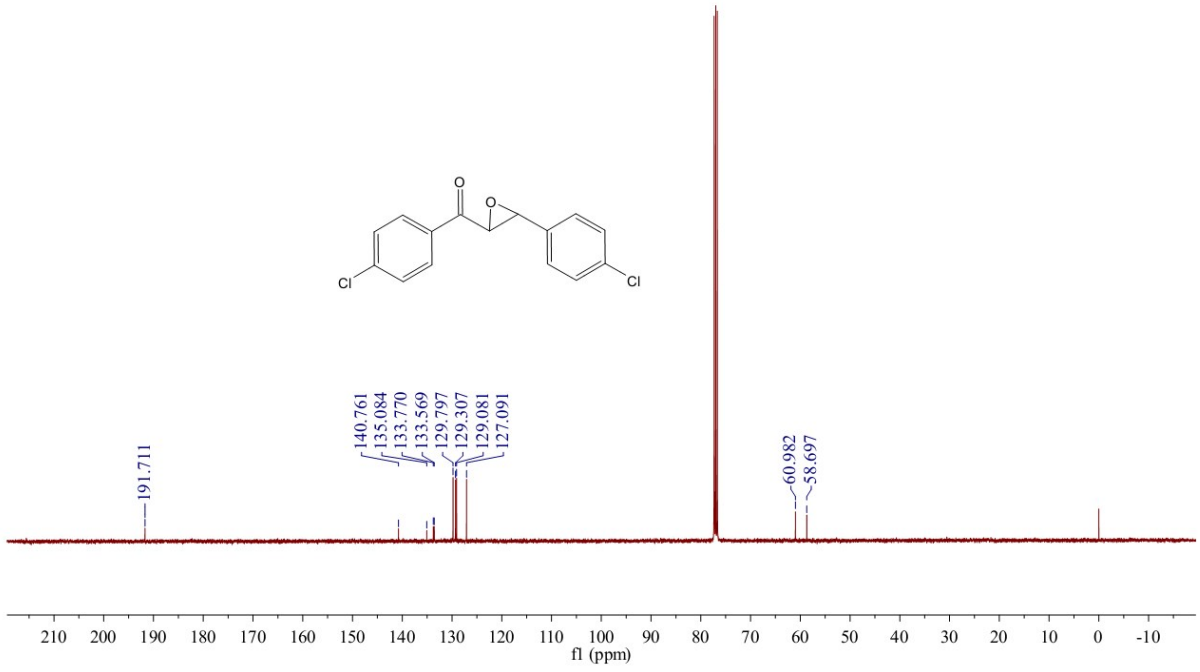

O
O
H3C
Cl

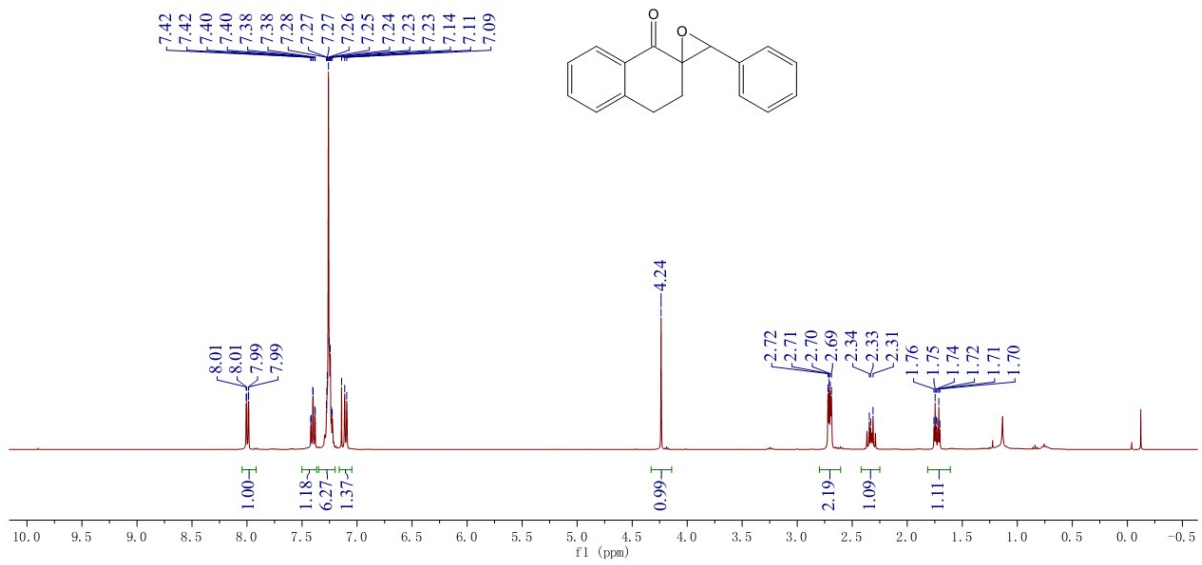

7.915
7.895
7.390
7.369
7.315
7.310
7.300
7.294
7.281
4.237
4.232
4.053
4.049
2.429
2.05
2.02
4.26
1.03
1.00
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O
O
H3C
Cl

192.222
145.235
134.885
134.153
132.920
129.611
129.005
128.467
127.111
60.838
58.625
21.814
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)


O
O
Cl
Cl
7.971
7.966
7.954
7.949
7.487
7.482
7.470
7.465
7.397
7.380
7.376
7.309
7.304
7.288
4.191
4.186
4.061
4.056
1.00
0.98
0.96
1.05
0.51
0.49
9.0 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 -0.5
f1 (ppm)


O
O
Cl
Cl
191.711
140.761
135.084
133.770
133.569
129.797
129.307
129.081
127.091
60.982
58.697
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)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7.40
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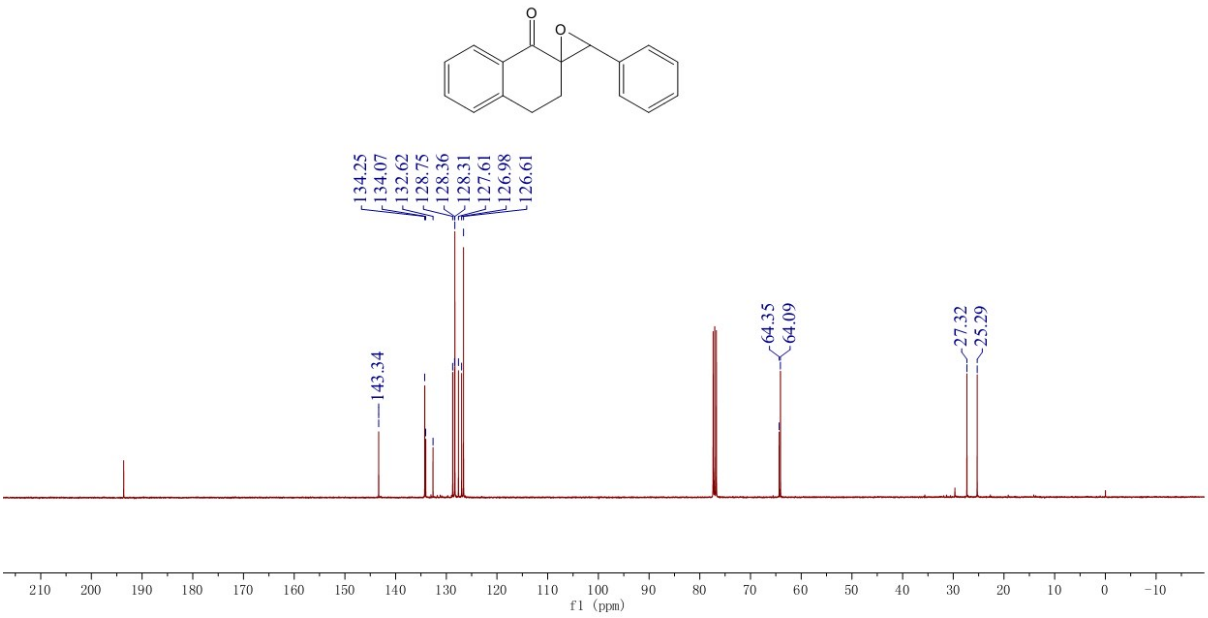
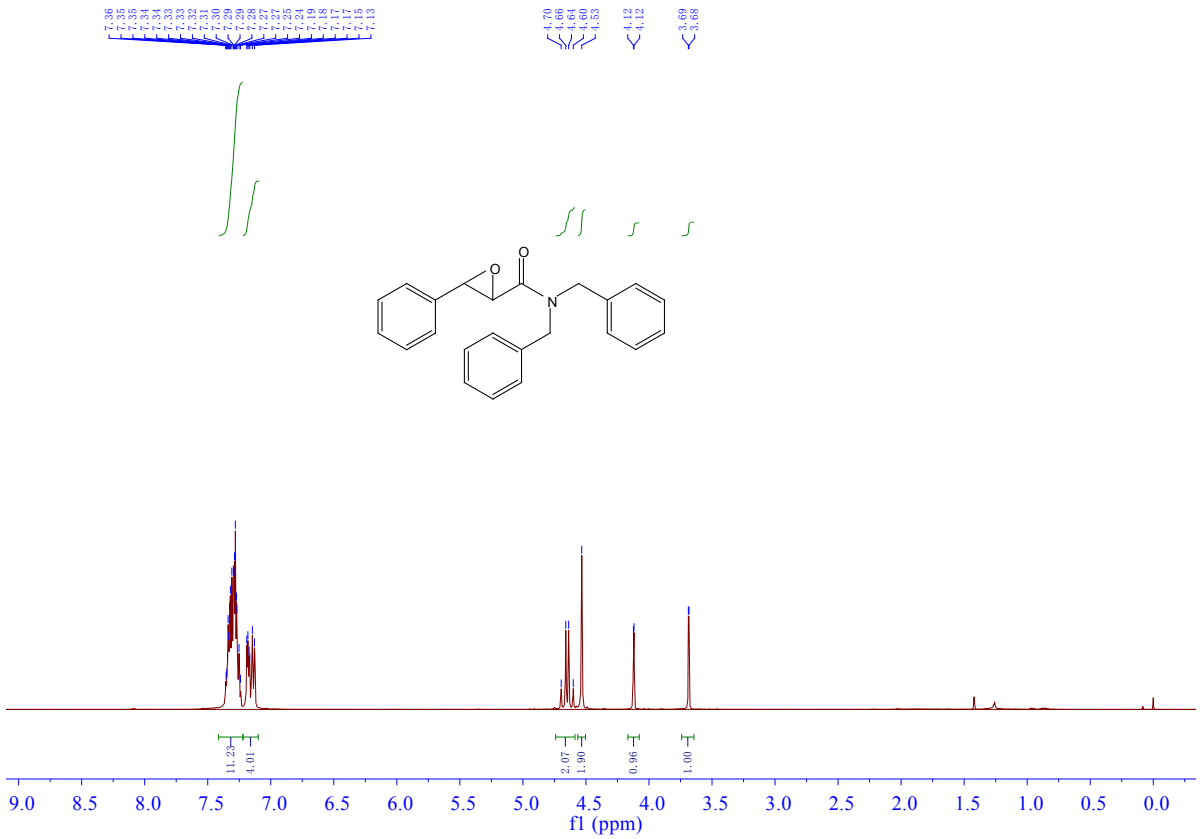
7.38
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.14
7.11
7.09
8.01
8.01
7.99
7.99
4.24
2.72
2.71
2.70
2.69
2.34
2.33
2.31
1.76
1.75
1.74
1.72
1.71
1.70
1.00
1.18
6.27
1.37
0.99
2.19
1.09
1.11
f1 (ppm)


134.25
134.07
132.62
128.75
128.36
128.31
127.61
126.98
126.61
143.34
64.35
64.09
27.32
25.29
f1 (ppm)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7.35
7.35
7.34
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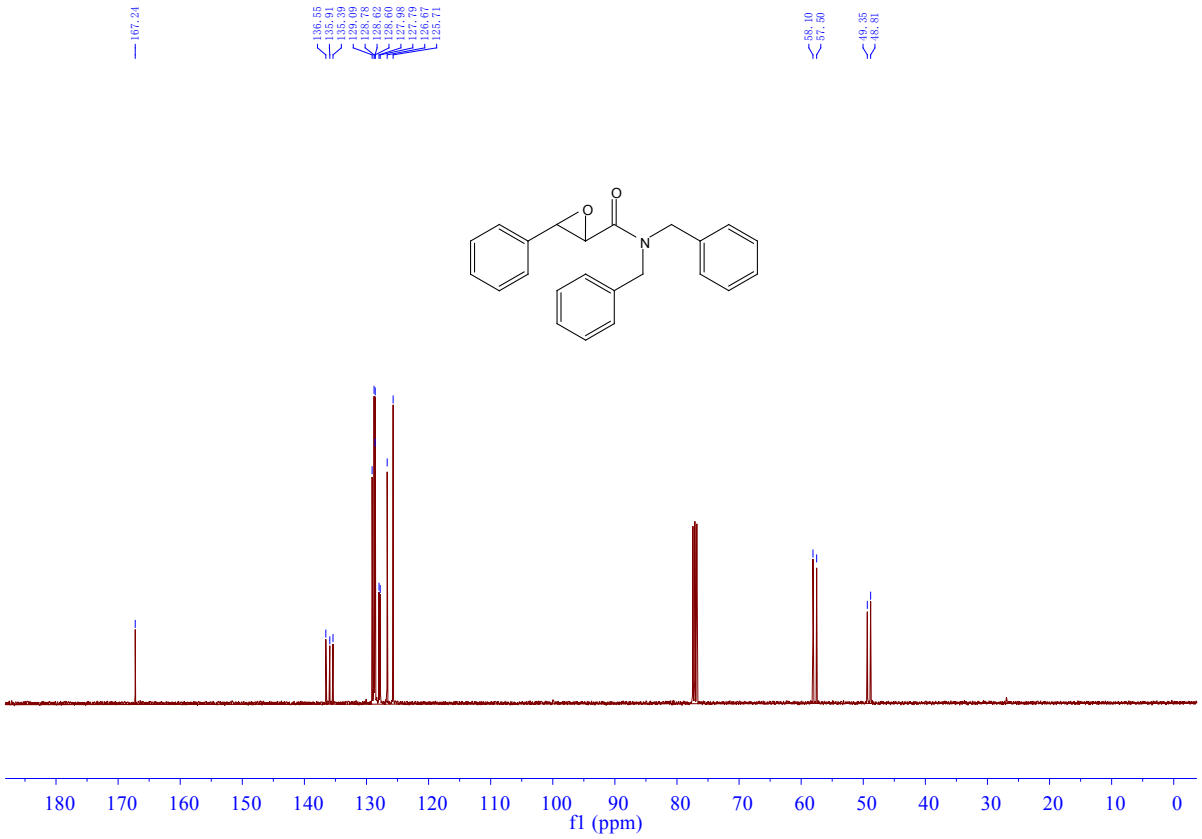
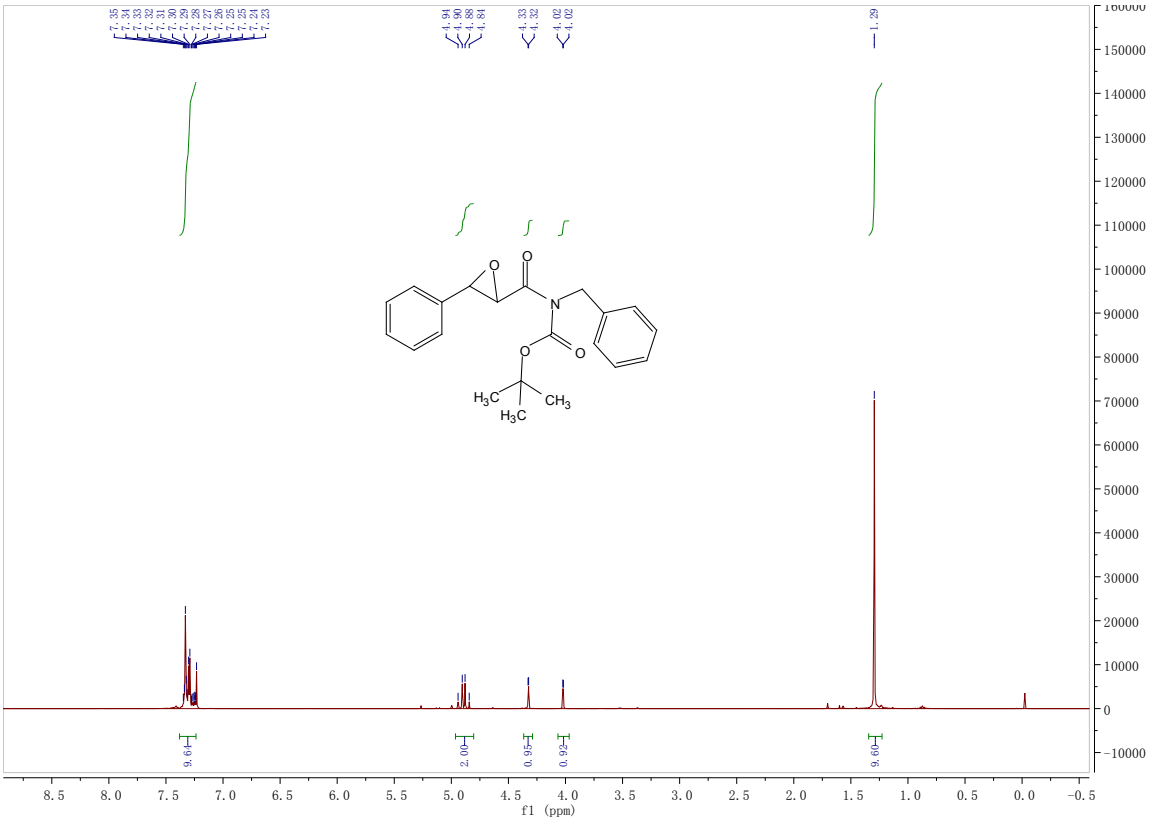
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.25
7.24
7.19
7.18
7.17
7.17
7.15
7.13
4.70
4.66
4.64
4.60
4.53
4.12
4.12
3.69
3.68
O
O
N
11.23
4.01
2.07
1.90
0.96
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.24
136.55
135.91
135.39
129.09
128.78
128.62
128.60
128.08
127.79
126.67
125.71
58.10
57.50
49.35
48.81
O
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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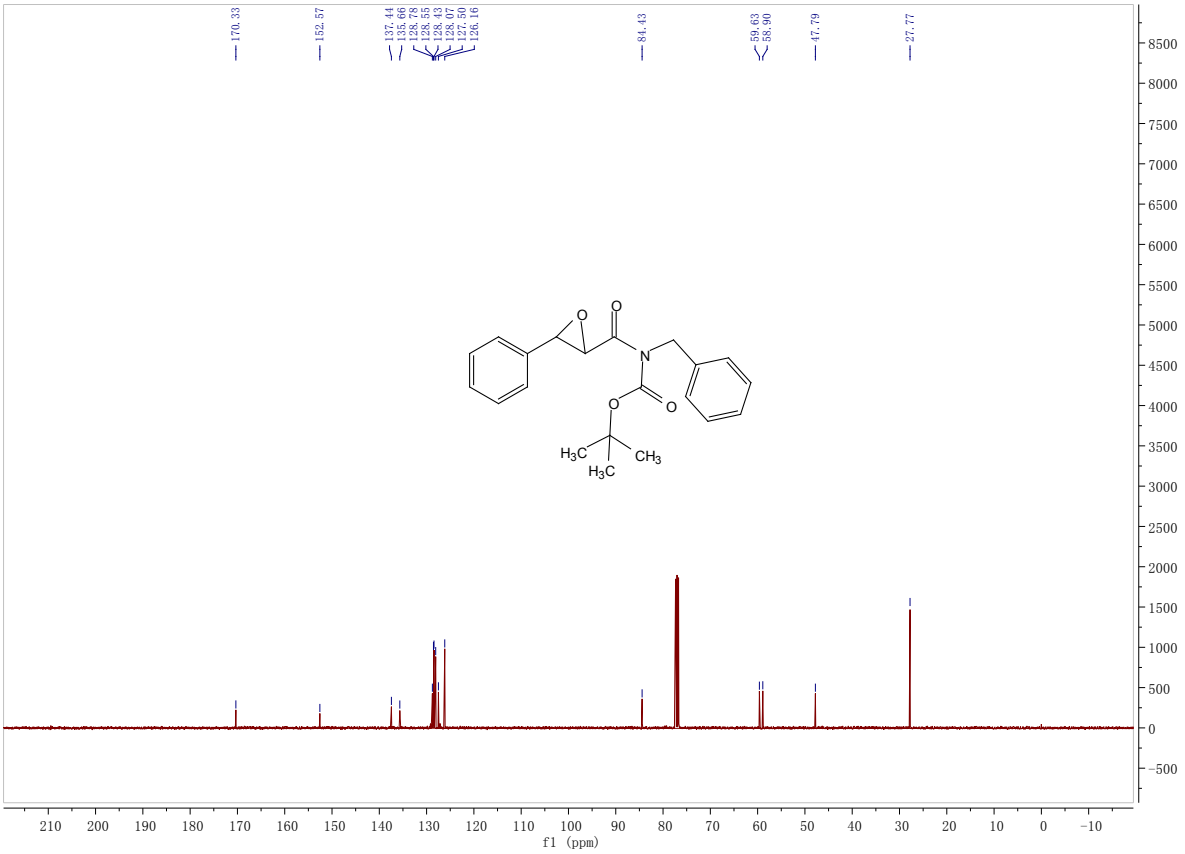
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
4.94
4.90
4.88
4.84
4.33
4.32
4.02
4.02
1.29
9.61
2.00
0.95
0.93
9.60
f1 (ppm)


170.33
152.57
137.44
135.66
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128.55
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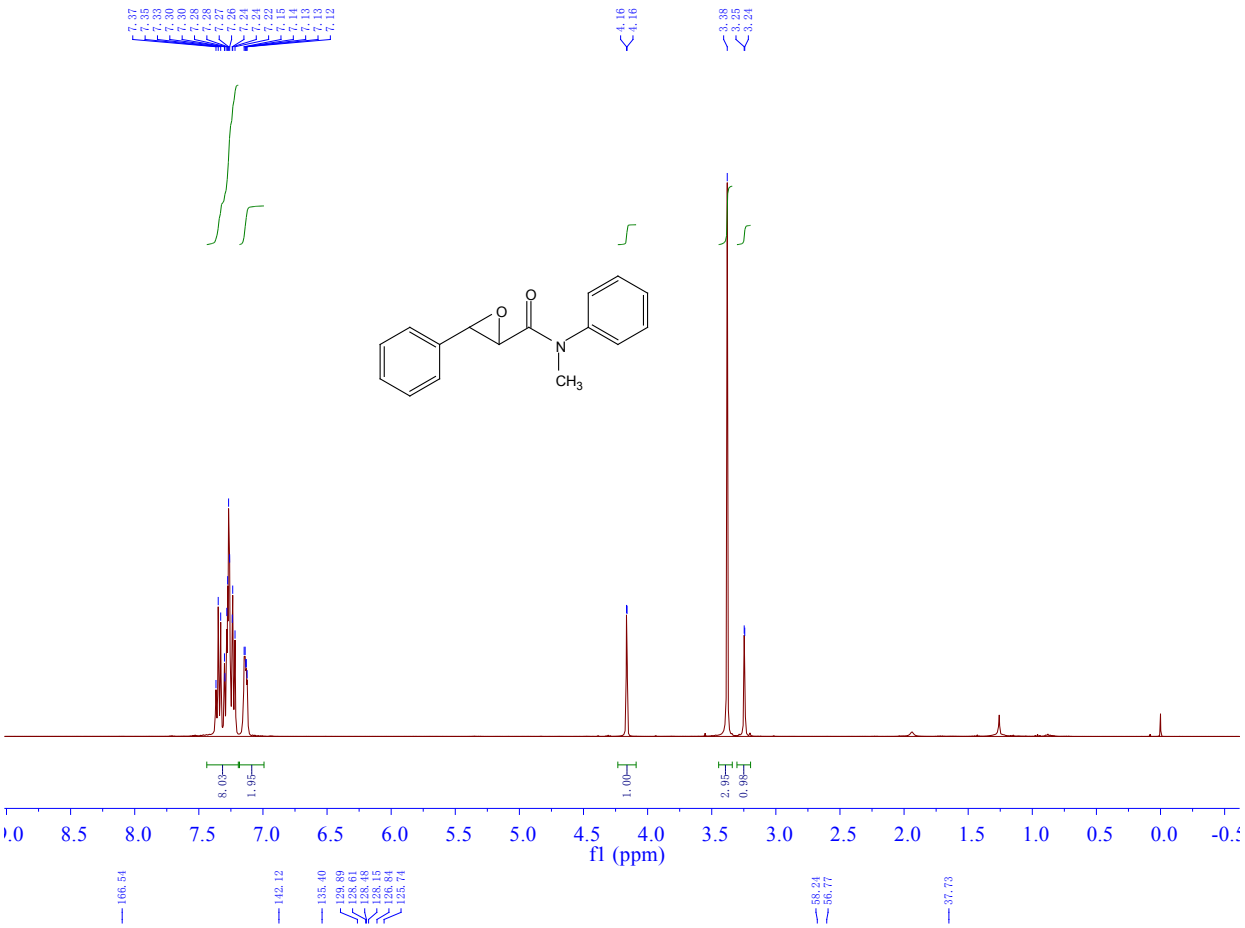
128.07
127.50
126.16
84.43
59.63
58.90
47.79
27.77
f1 (ppm)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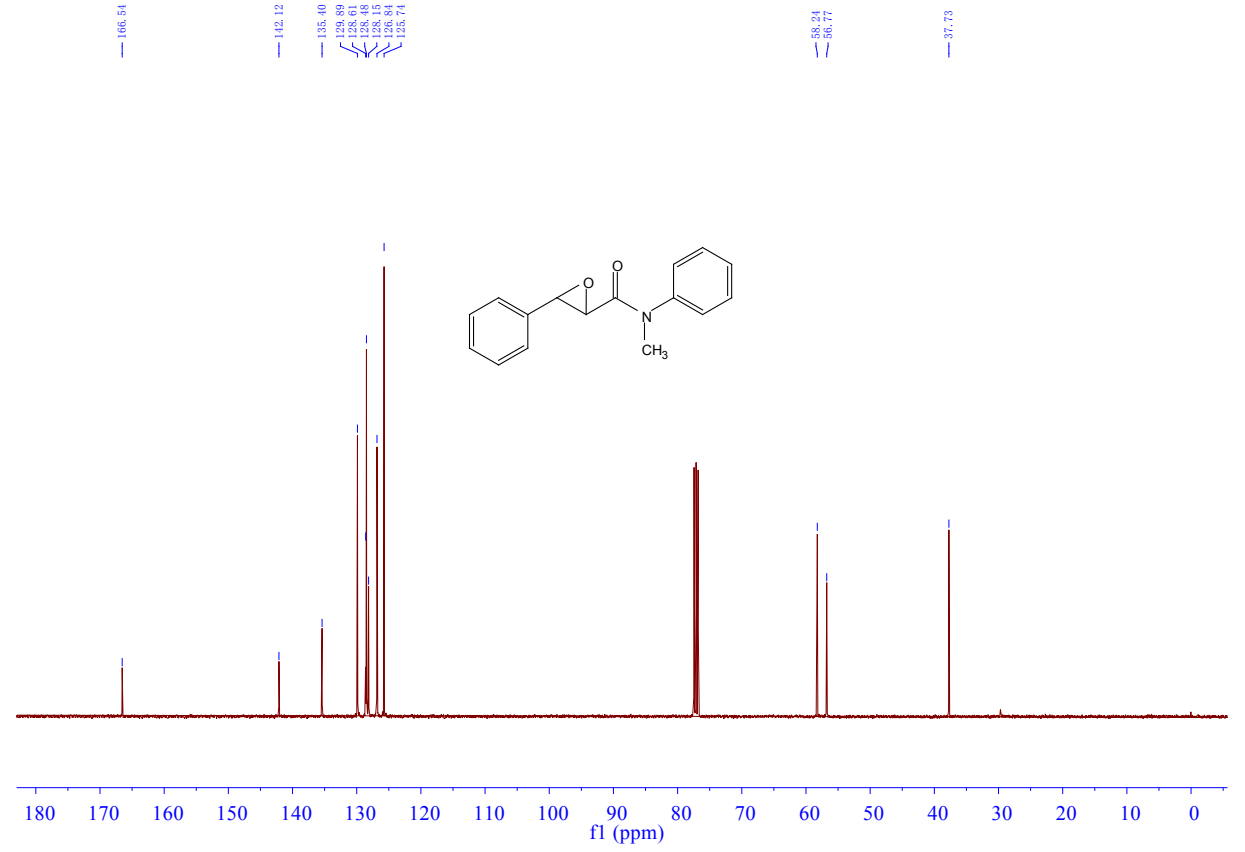
7.28
7.27
7.26
7.24
7.24
7.22
7.15
7.14
7.13
7.13
7.12
4.16
4.16
3.38
3.25
3.24
O
O
N
CH3
8.03
1.95
1.00
2.95
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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135.40
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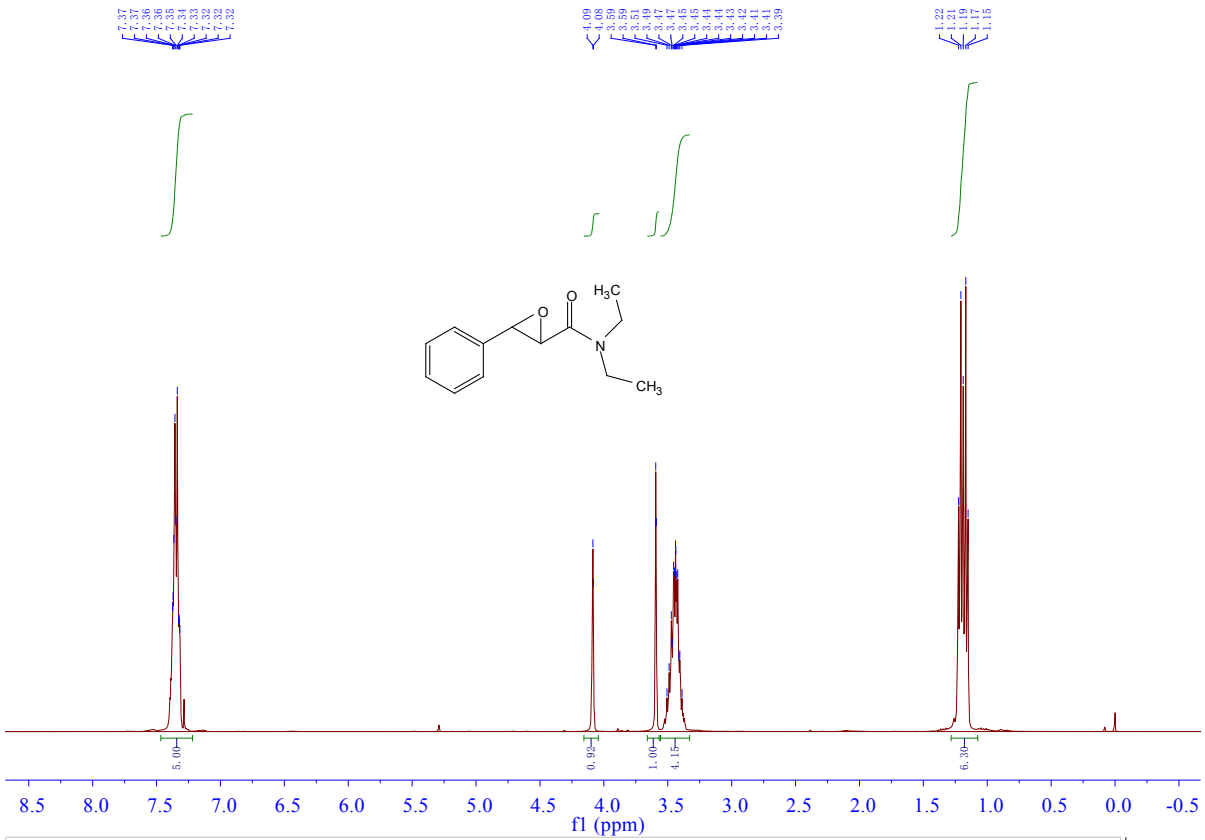
129.61
128.48
128.15
126.84
125.74
58.24
56.77
37.73
O
O
N
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.37
7.36
7.36
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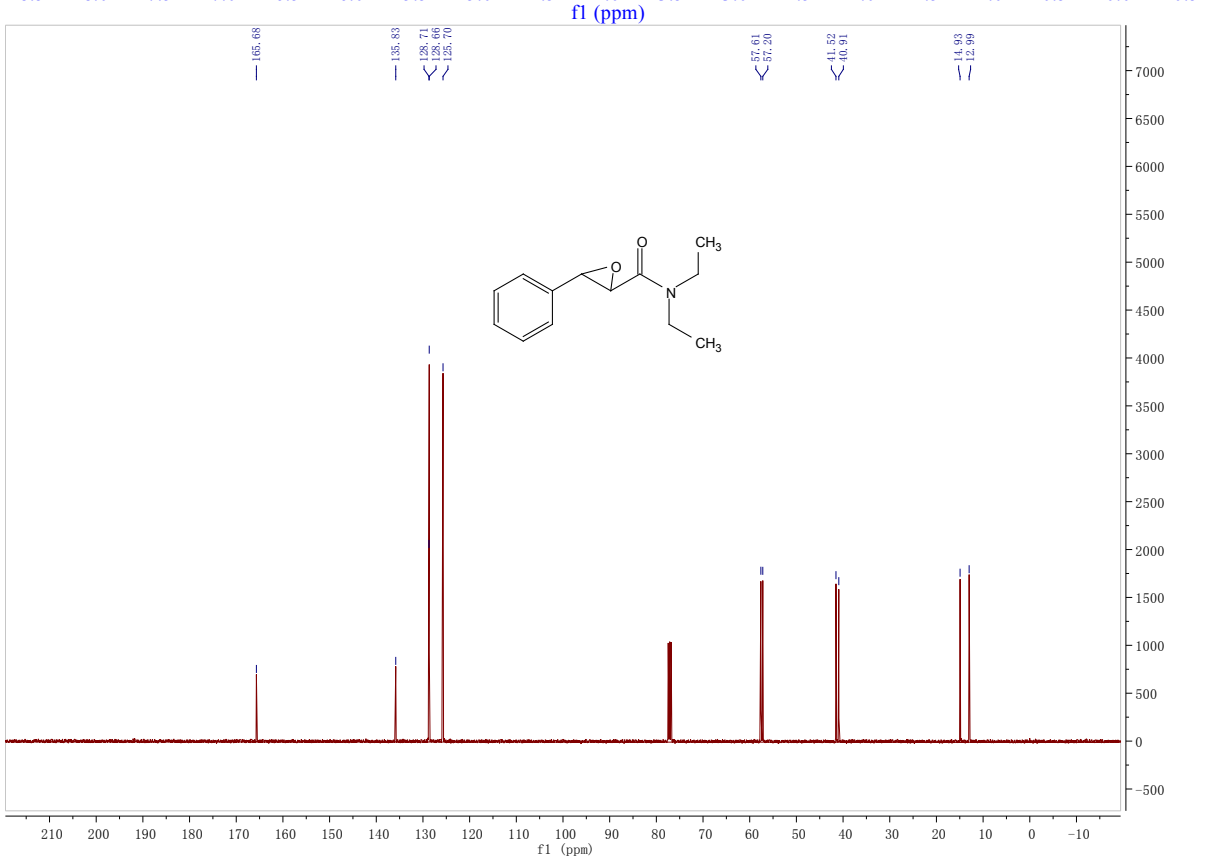
7.34
7.33
7.32
7.32
7.32
4.09
4.08
3.59
3.59
3.51
3.49
3.47
3.45
3.44
3.44
3.43
3.42
3.41
3.41
3.39
1.22
1.21
1.19
1.17
1.17
1.15
O
O
H3C
N
CH3
5.00
0.92
1.00
4.15
6.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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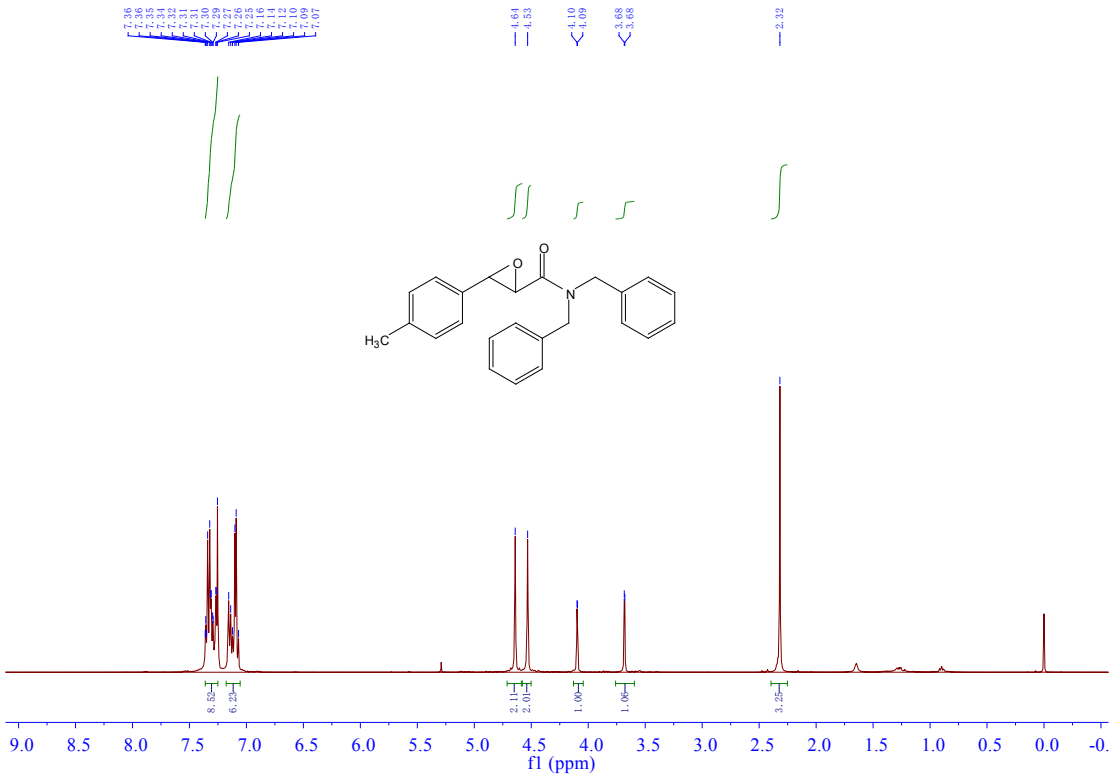
128.71
128.66
125.70
57.61
57.20
41.52
40.91
14.93
12.99
O
O
CH3
N
CH3
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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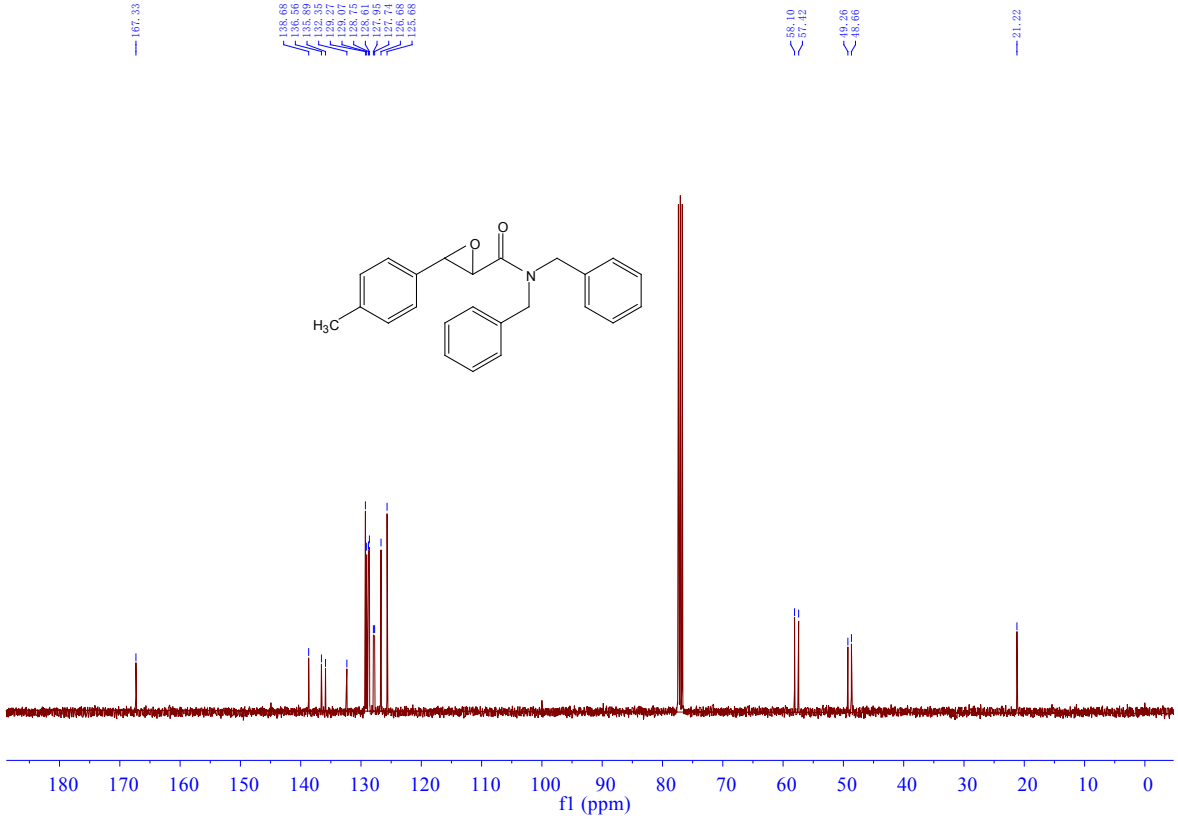
7.27
7.26
7.25
7.16
7.11
7.12
7.10
7.09
7.07
4.64
4.53
4.10
4.09
3.68
3.68
2.32
O
O
N
H3C
8.52
6.22
2.11
2.01
1.00
1.06
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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138.68
136.56
135.89
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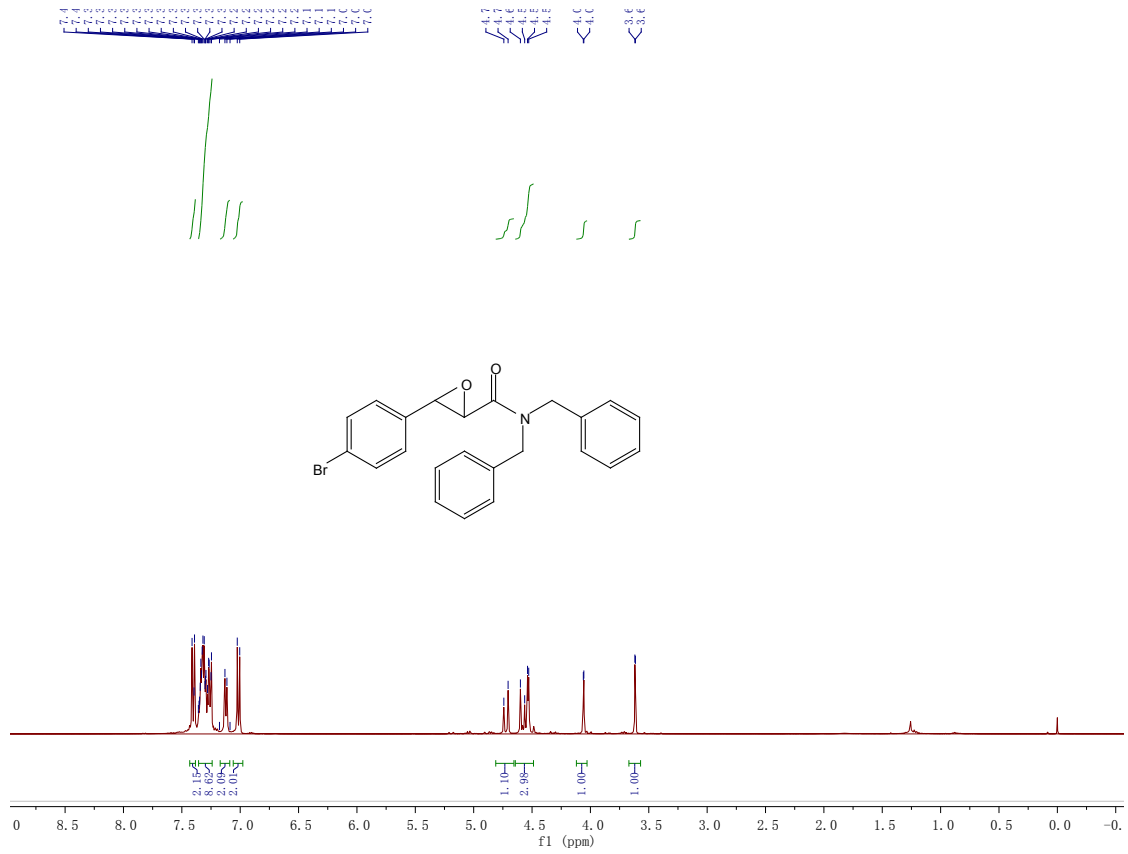
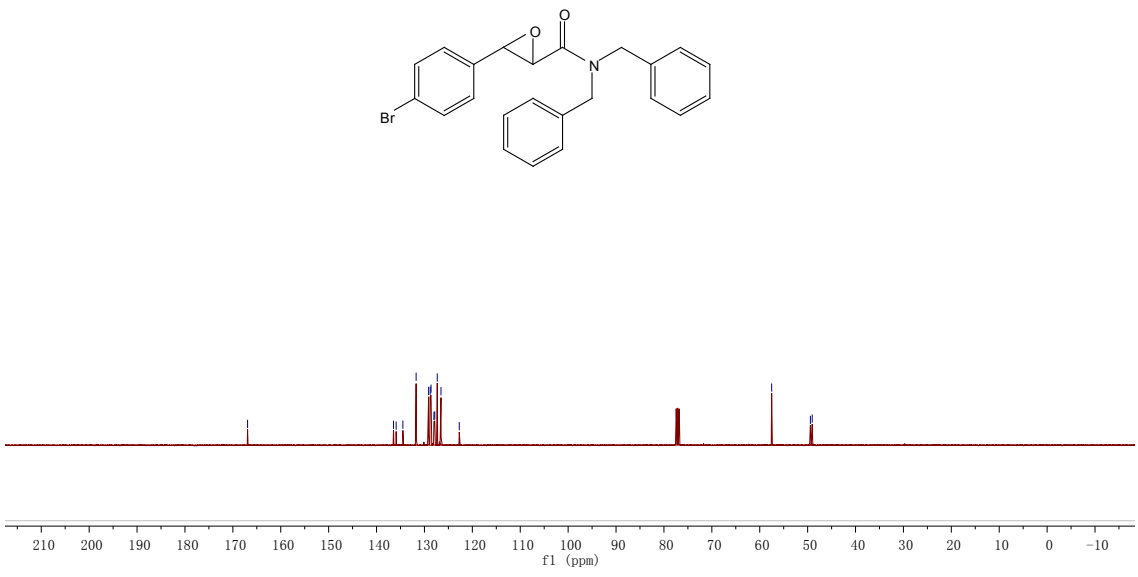
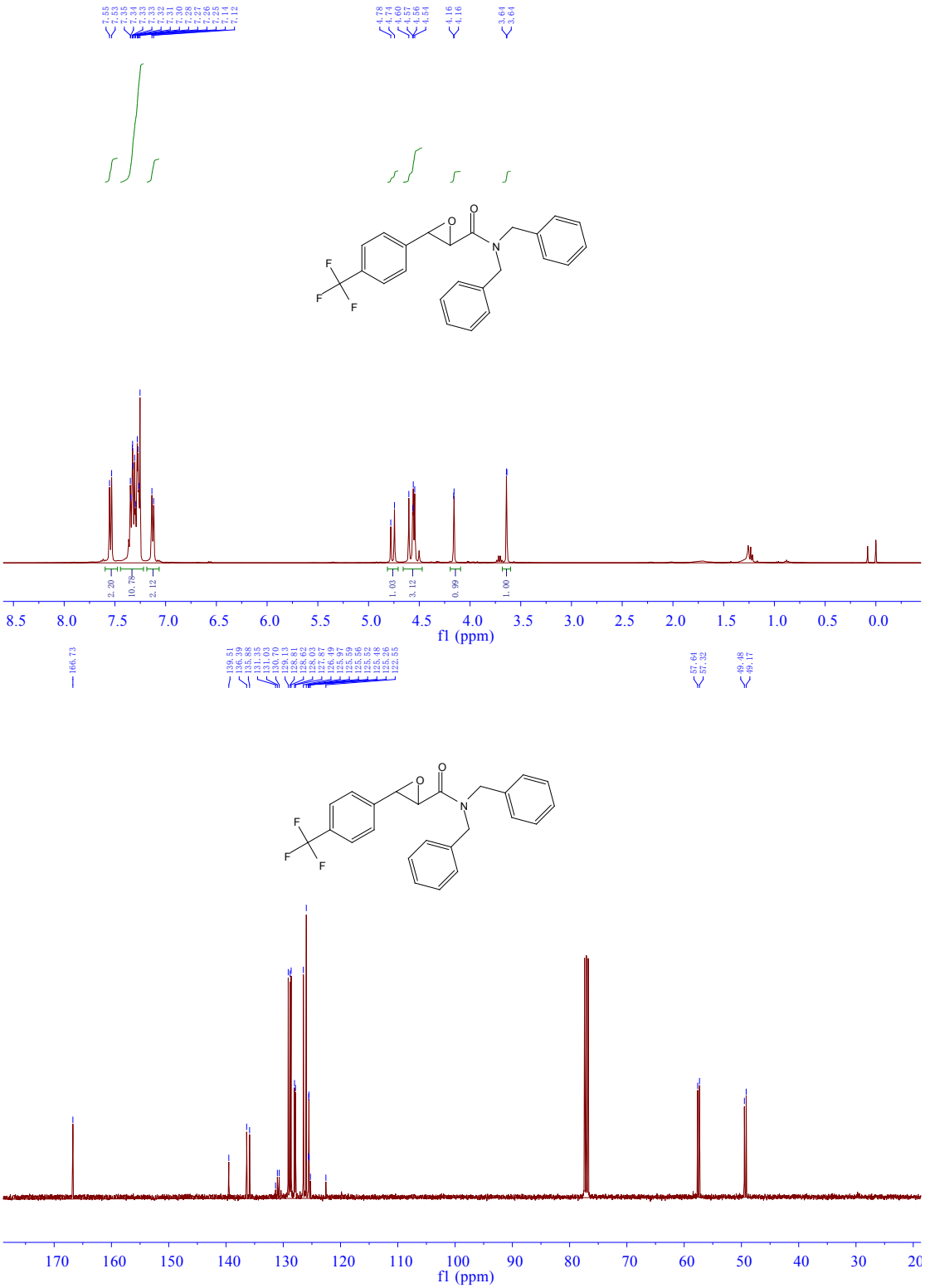
129.27
129.07
128.75
128.61
128.45
127.94
127.74
126.68
125.68
58.10
57.42
19.26
18.66
21.22
O
O
N
H3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
N
Br
f1 (ppm)


O
O
N
Br
f1 (ppm)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7.32
7.31
7.30
7.30
7.28
7.27
7.26
7.15
7.11
7.12
4.78
4.71
4.60
4.57
4.56
4.54
4.16
4.16
3.64
3.64
O
O
N
F
F
F
2.20
10.78
2.12
1.03
3.12
0.99
1.00
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)
166.73
139.51
136.89
135.58
131.35
131.03
130.70
129.13
128.81
128.62
128.03
127.87
126.49
125.97
125.59
125.56
125.52
125.48
125.26
122.55
57.64
57.32
49.48
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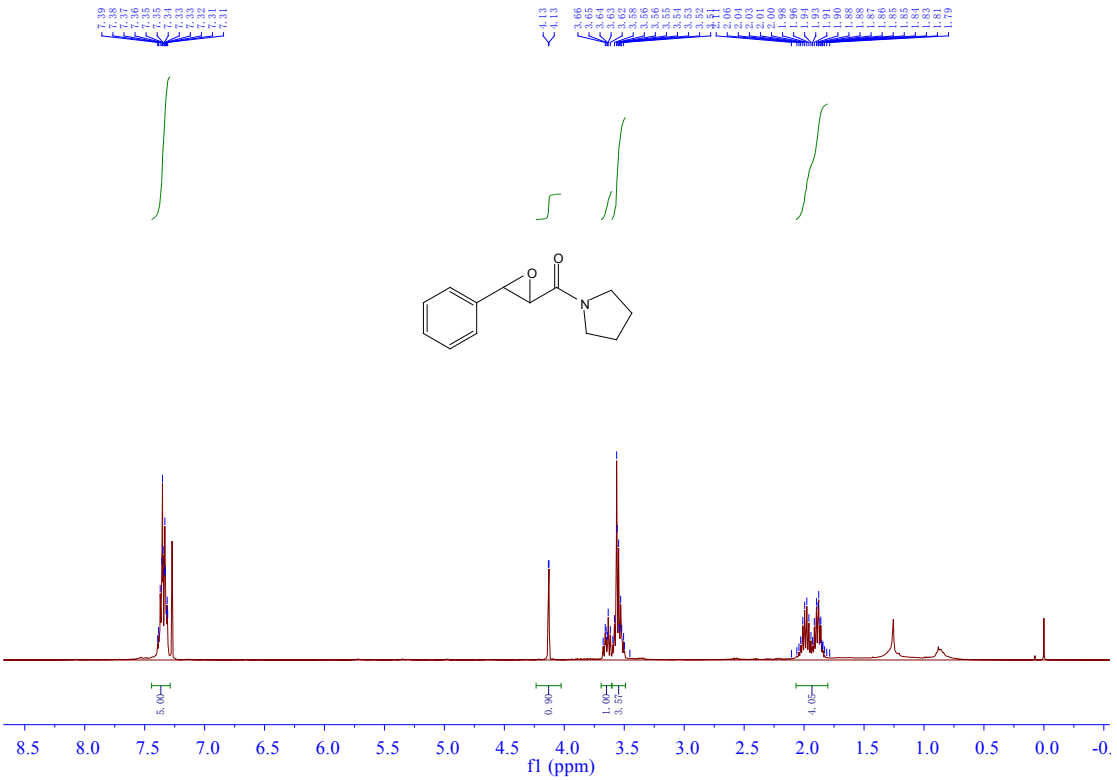
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.34
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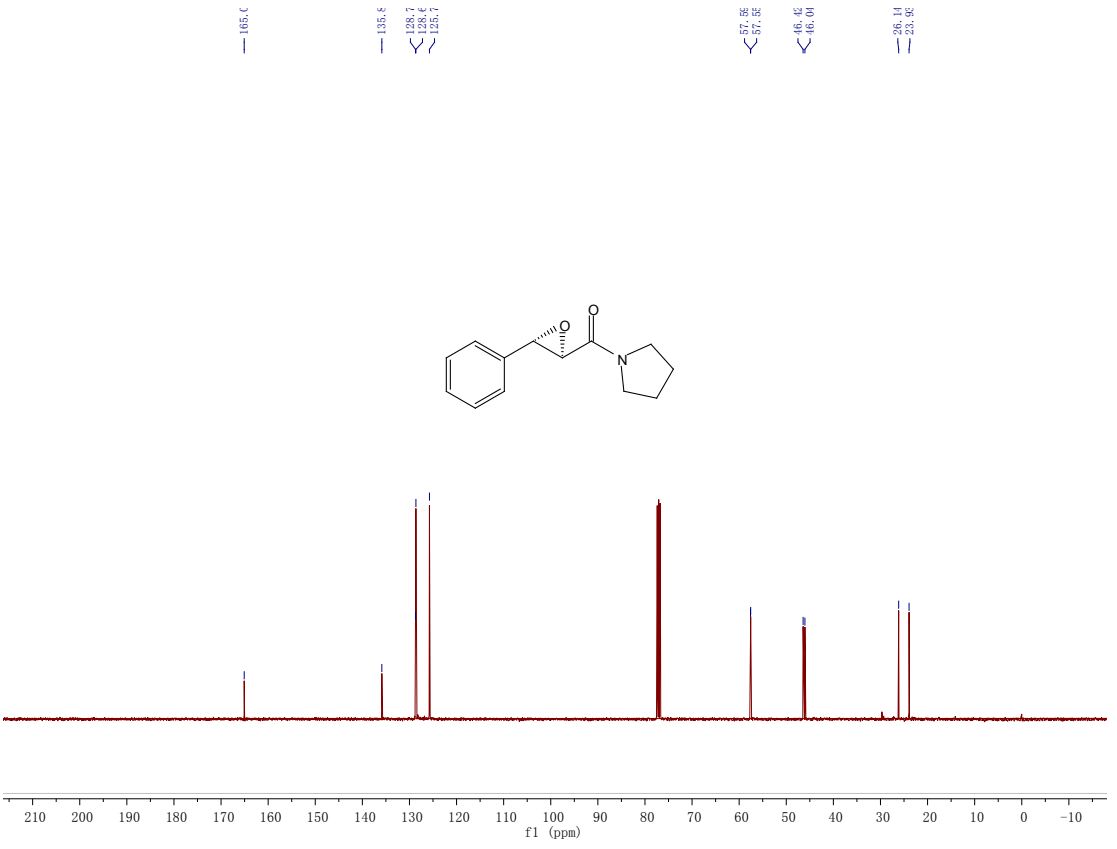
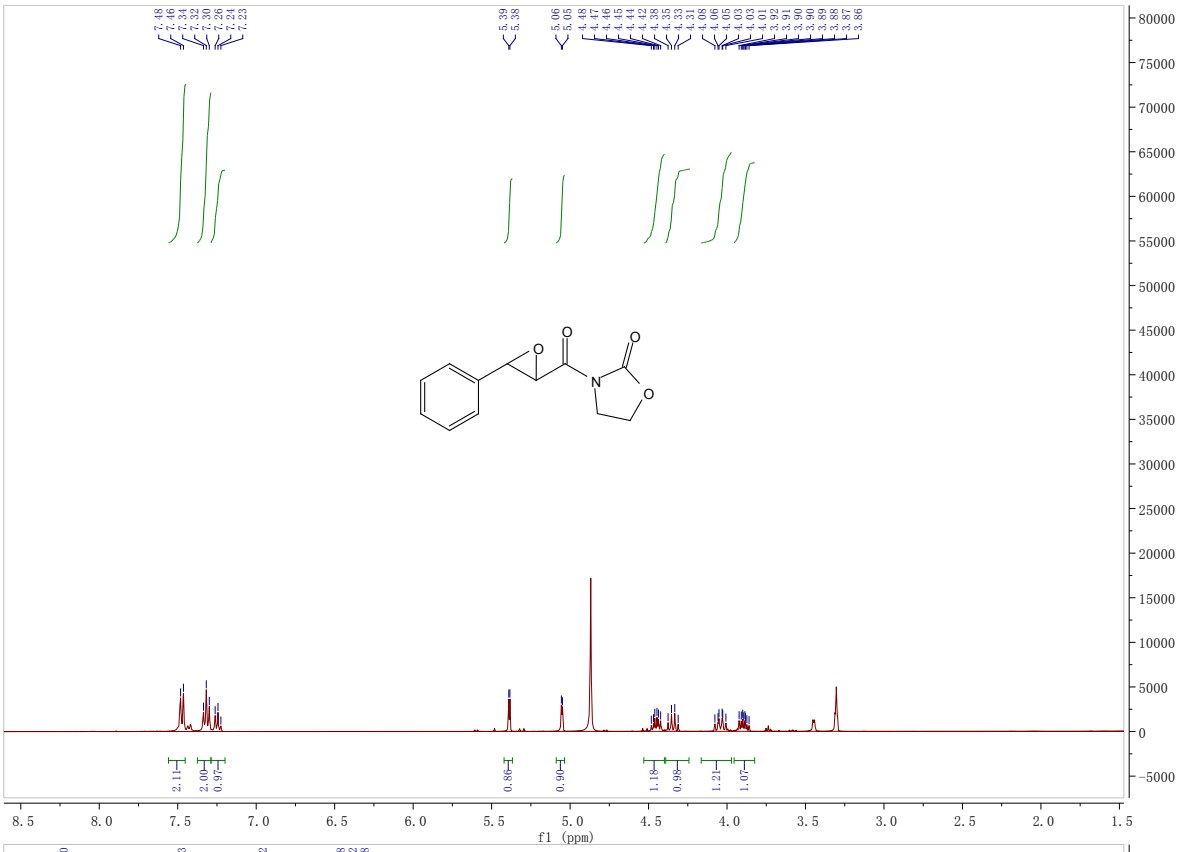
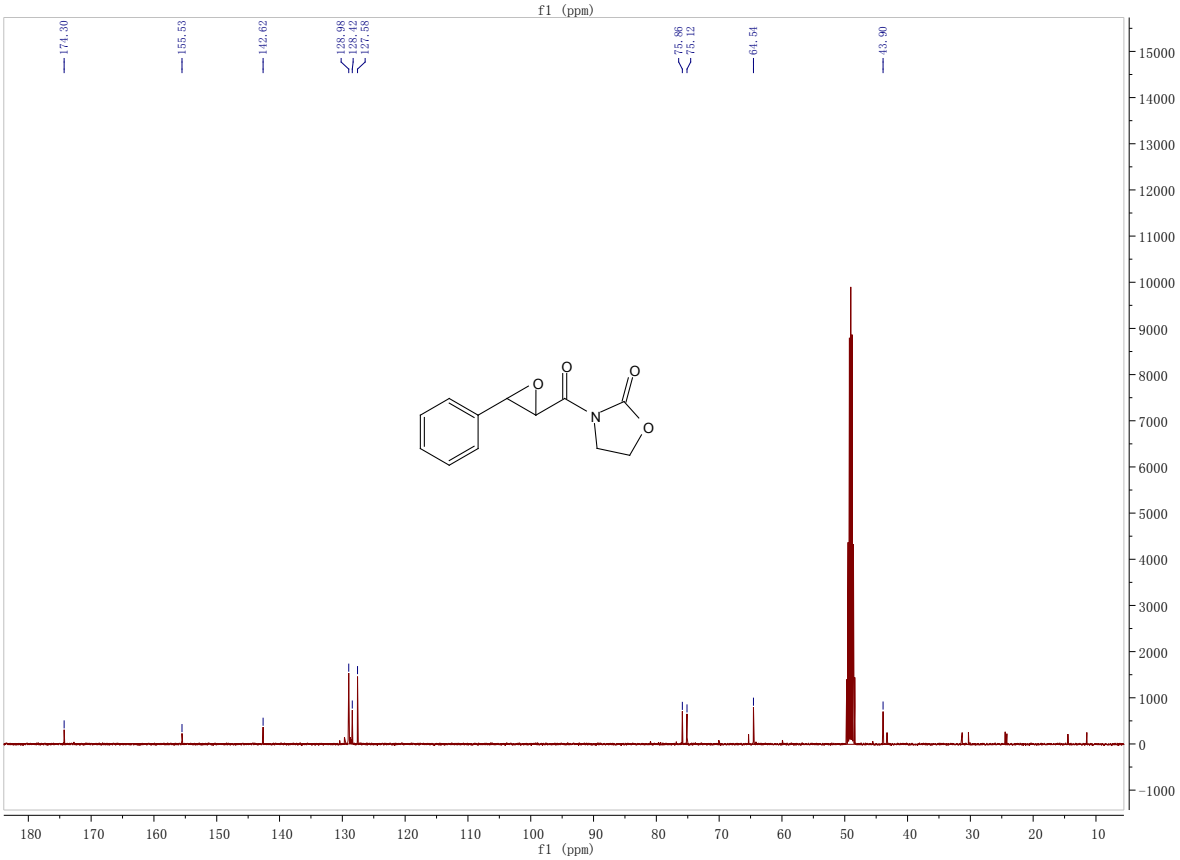
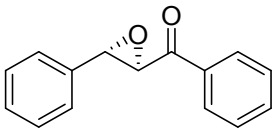
7.32
7.31
4.13
3.66
3.65
3.64
3.63
3.62
3.58
3.56
3.55
3.54
3.53
3.52
2.06
2.04
2.03
2.01
2.00
1.98
1.96
1.94
1.93
1.91
1.90
1.88
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.81
1.79
O
O
N
5.00
0.90
1.00
3.57
4.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

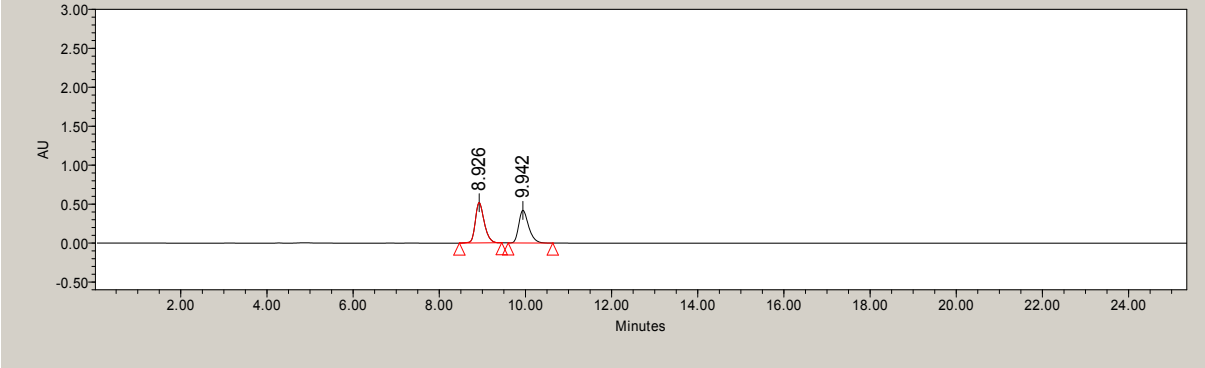

165.6
135.8
128.7
128.6
125.7
57.5
57.5
46.4
46.0
26.1
23.9
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.48
7.46
7.34
7.32
7.30
7.26
7.24
7.23
5.39
5.38
5.06
5.05
4.48
4.47
4.46
4.45
4.44
4.42
4.38
4.35
4.33
4.31
4.08
4.06
4.05
4.03
4.01
3.92
3.91
3.90
3.89
3.88
3.87
3.86
2.11
2.00
0.97
0.86
0.90
1.19
0.99
1.21
1.07
f1 (ppm)

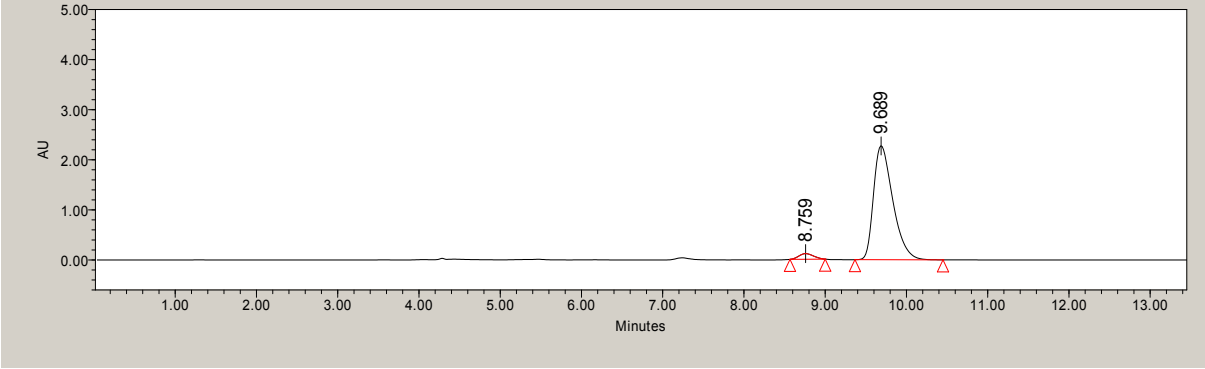

174.30
155.53
142.62
128.98
128.42
127.58
75.86
75.12
64.54
43.90
f1 (ppm)

8. Copies of HPLC or GC spectra of epoxides

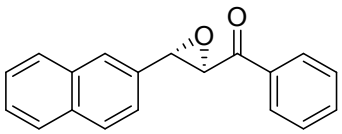


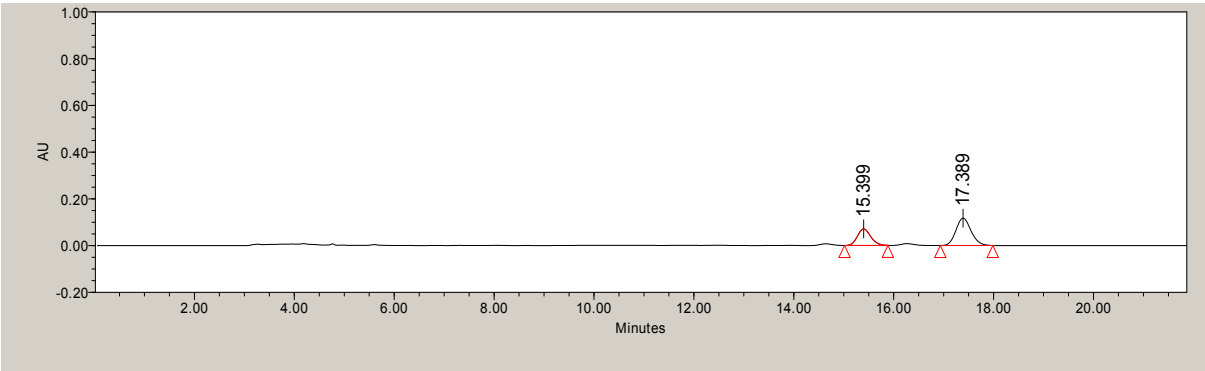


	RT (min)	Area (Pa*s)	% Area
1	8.926	7446503	52.75
2	9.942	6671080	47.25

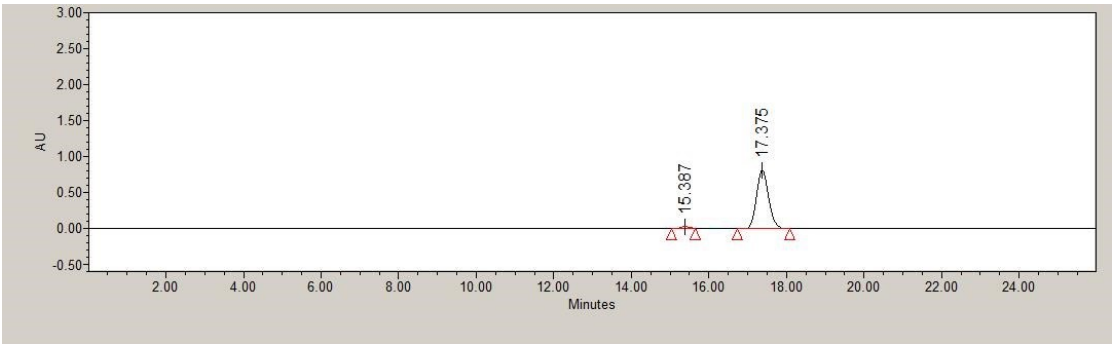


	RT (min)	Area (Pa*s)	% Area
1	8.759	1482252	3.60
2	9.689	37551008	96.40

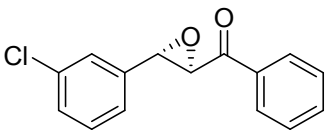


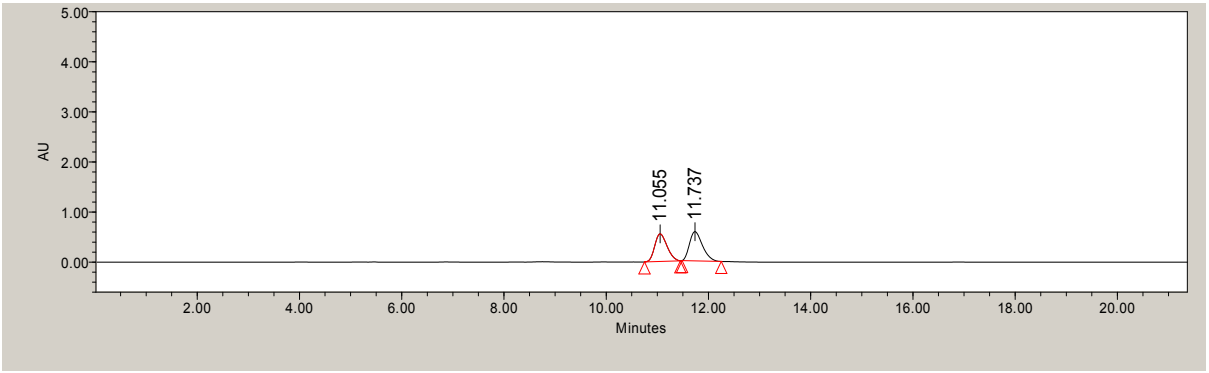


	RT (min)	Area (Pa*s)	% Area
1	15.399	2010022	44.26
2	17.389	2468686	55.74

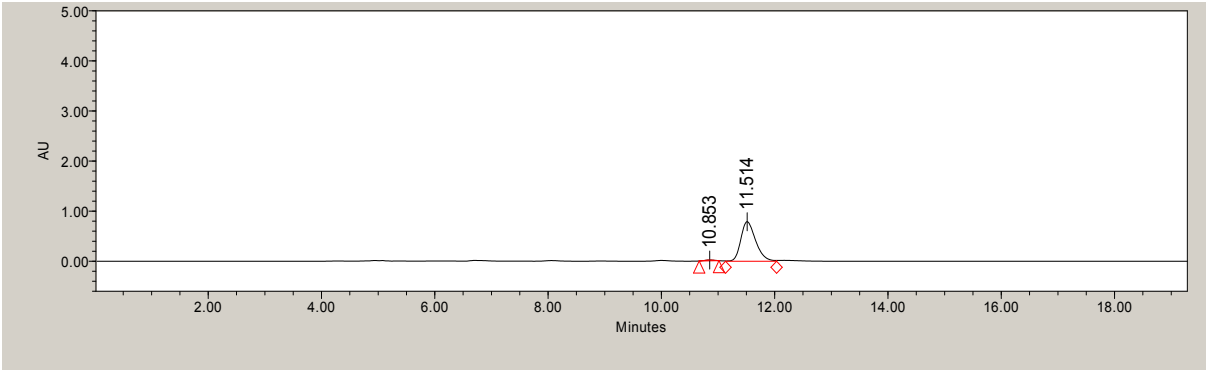


	RT (min)	Area (Pa*s)	% Area
1	15.387	444391	2.46
2	17.375	17591103	97.54

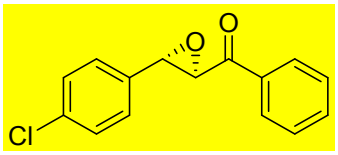


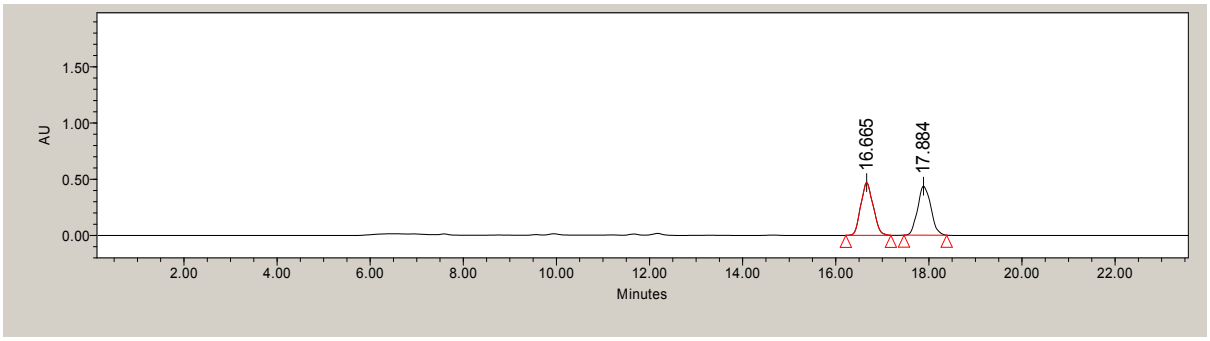


	RT (min)	Area (Pa*s)	% Area
1	11.055	9810830	49.05
2	11.737	10300276	50.95

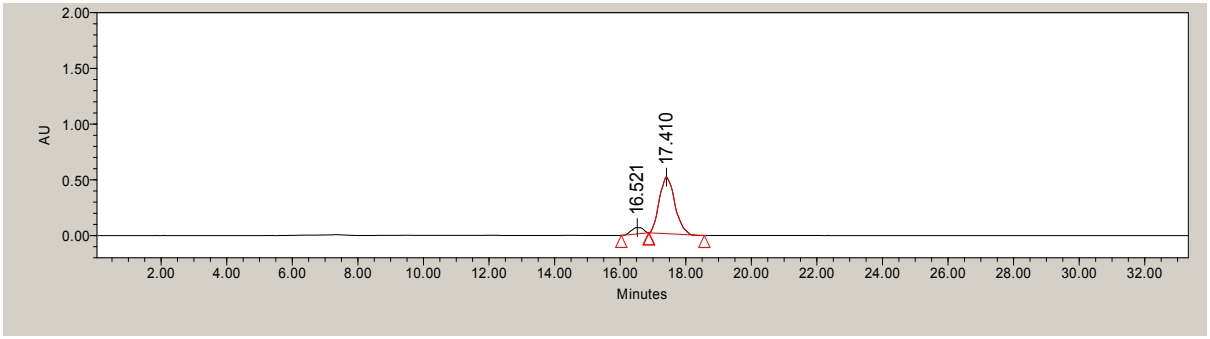


	RT (min)	Area (Pa*s)	% Area
1	10.853	219874	1.46
2	11.514	14365136	98.54

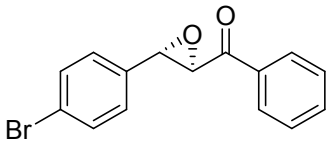


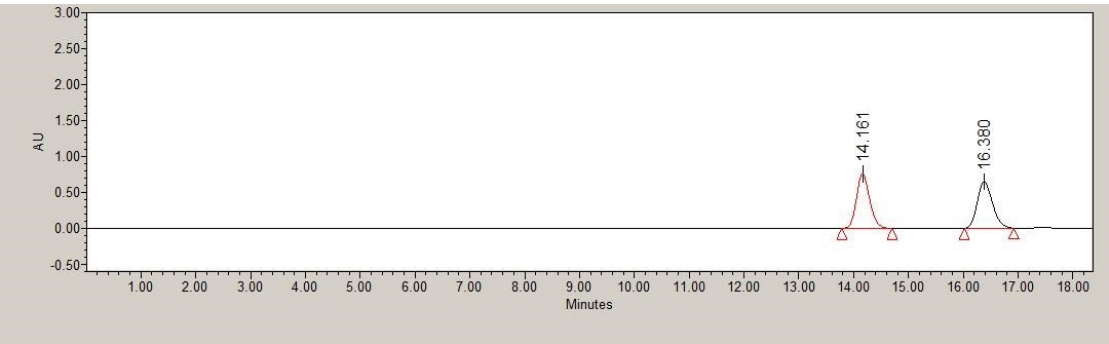


	RT (min)	Area (Pa*s)	% Area
1	16.665	8672020	49.93
2	23.990	8696014	50.07

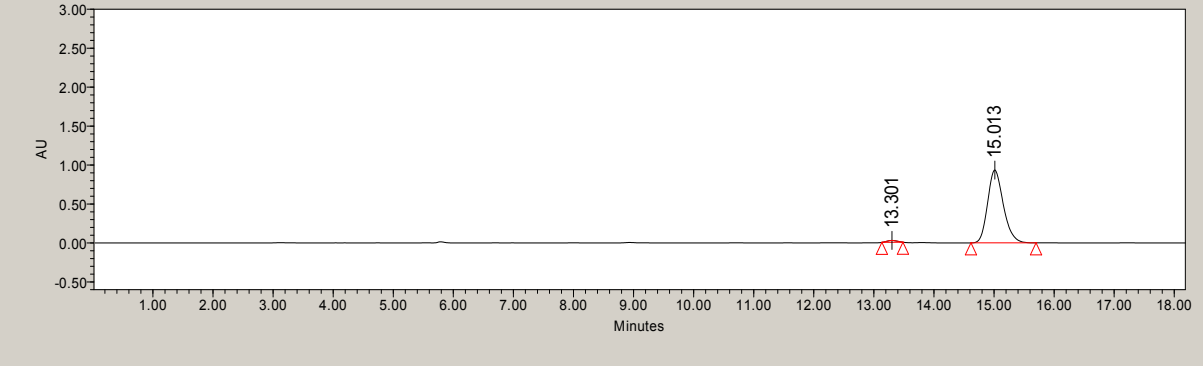


	RT (min)	Area (Pa*s)	% Area
1	16.521	1443117	7.92
2	17.410	16781355	92.08

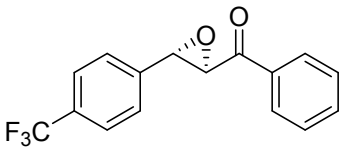


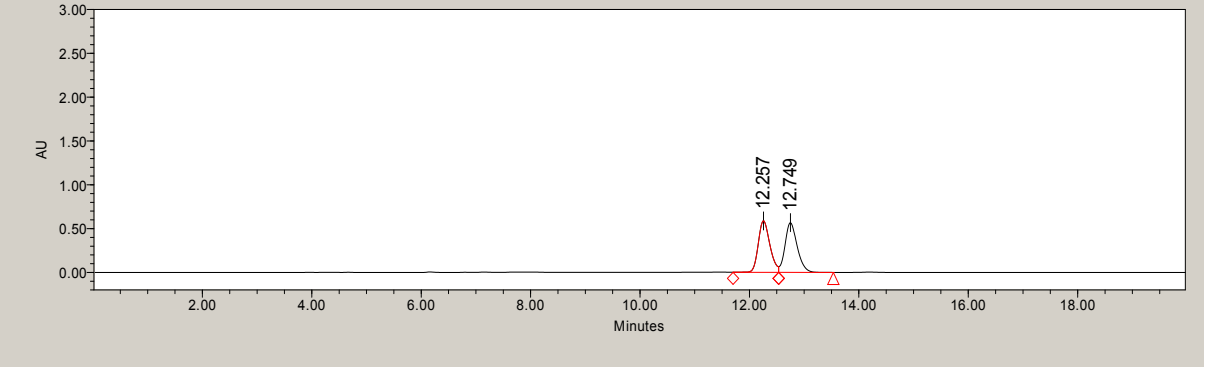


	RT (min)	Area (Pa*s)	% Area
1	14.161	12582216	50.27
2	16.380	12445139	49.73

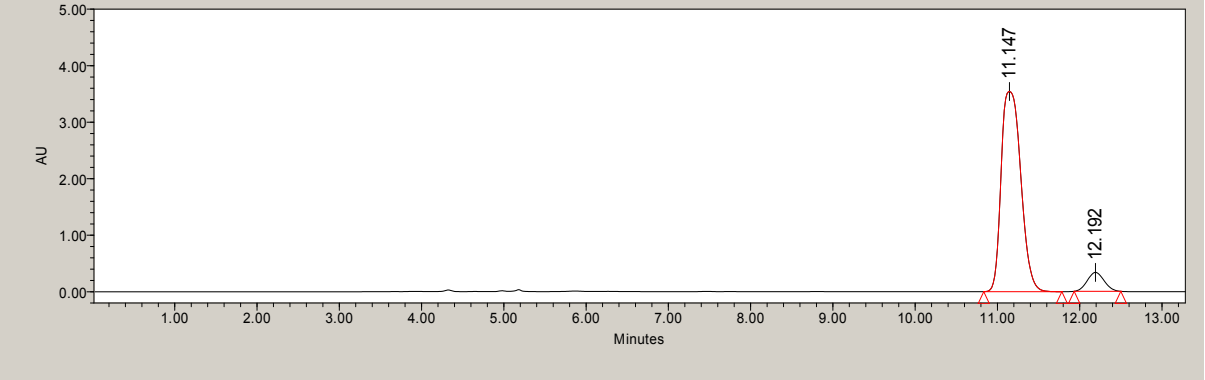


	RT (min)	Area (Pa*s)	% Area
1	13.301	279844	2.48
2	15.031	16988518	97.52

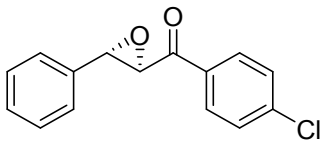


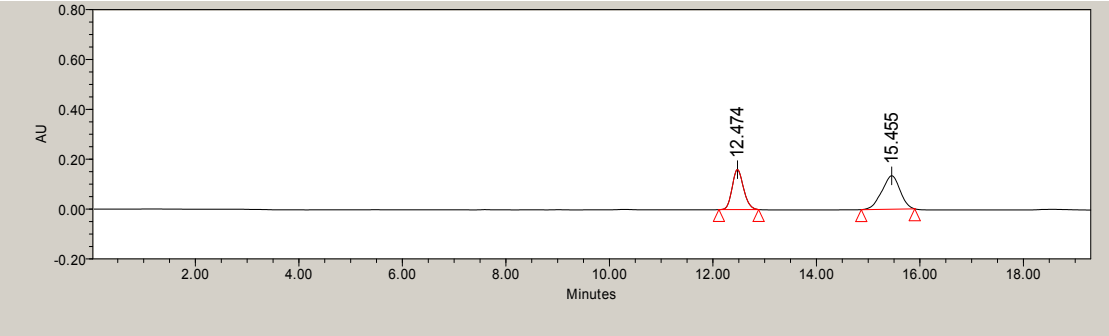


	RT (min)	Area (Pa*s)	% Area
1	12.257	3680056	50.86
2	12.749	3664587	49.14

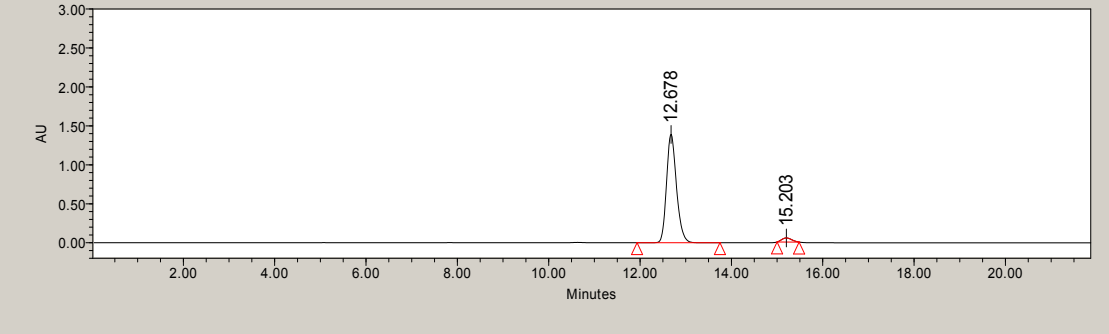


	RT (min)	Area (Pa*s)	% Area
1	11.147	58802605	93.91
2	12.192	4759364	6.08

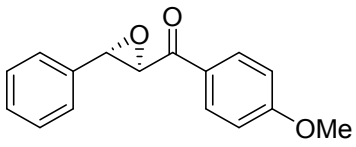


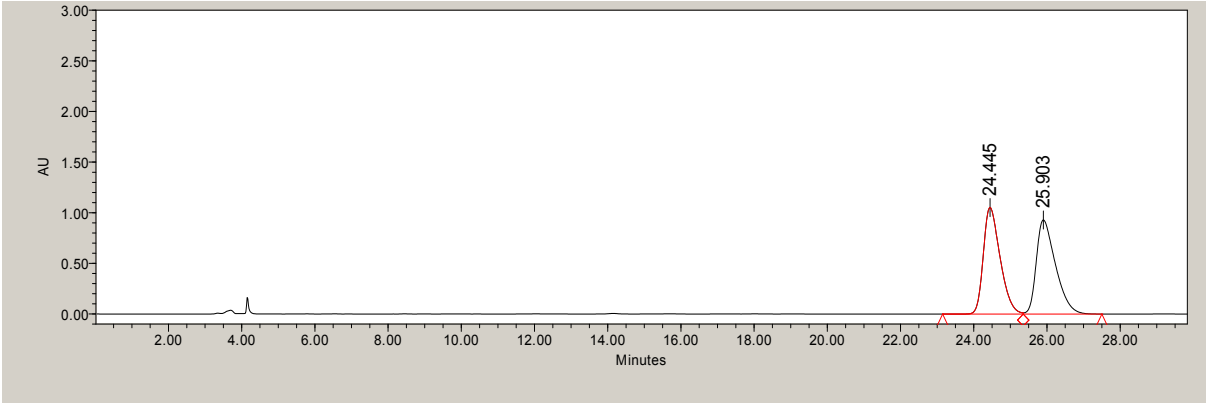


	RT (min)	Area (Pa*s)	% Area
1	12.474	2457653	45.68
2	15.455	2922037	54.32

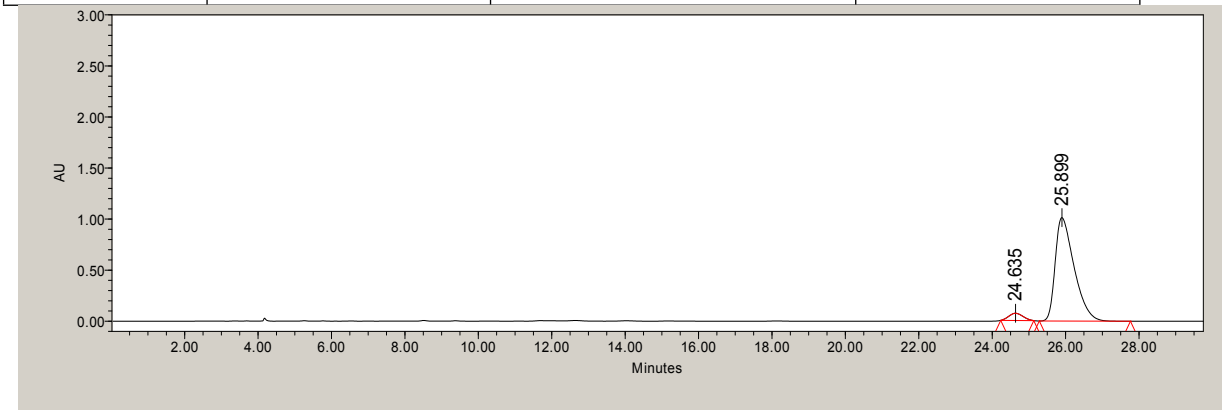


	RT (min)	Area (Pa*s)	% Area
1	12.678	21054968	97.58
2	15.203	791342	2.42

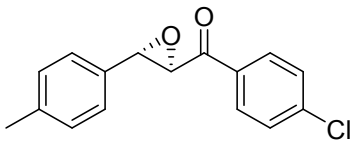


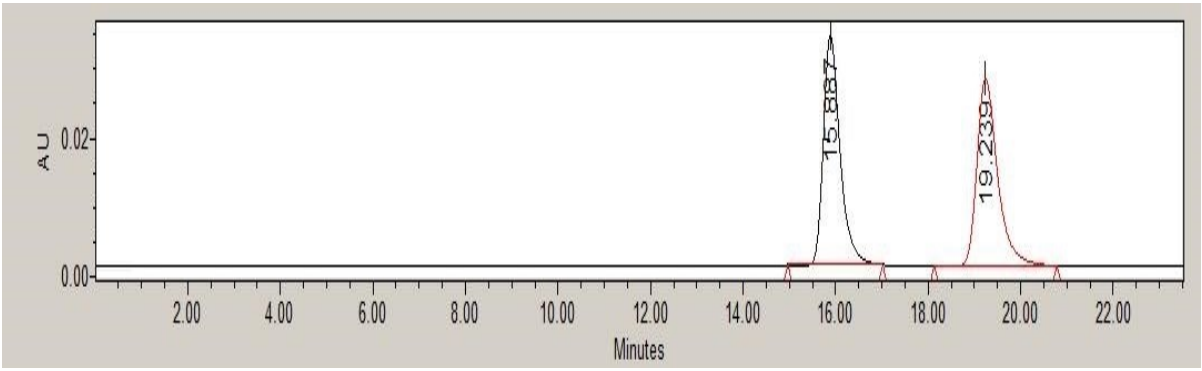


	RT (min)	Area (Pa*s)	% Area
1	24.445	33481947	49.23
2	25.903	22850715	50.27

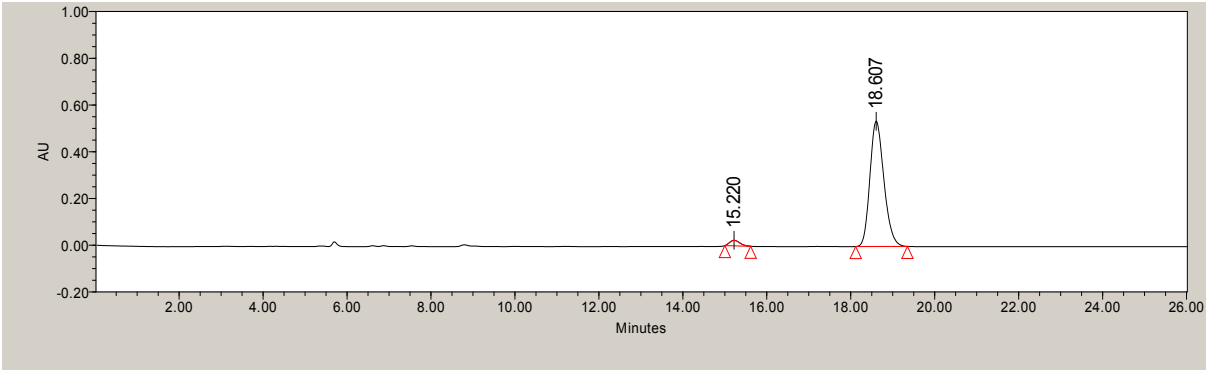


	RT (min)	Area (Pa*s)	% Area
1	24.635	1885952	4.95
2	25.899	36222283	95.05

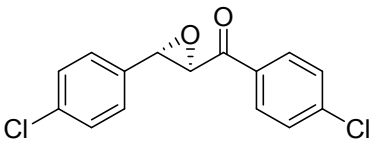


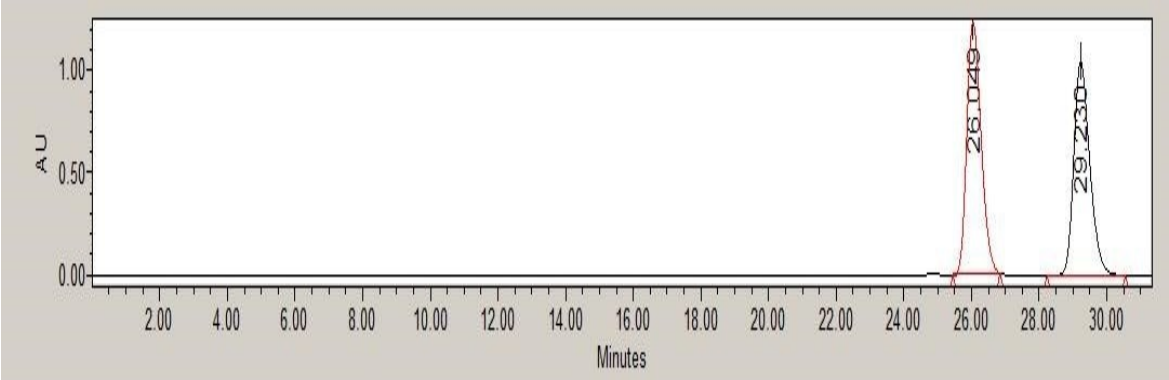


	RT (min)	Area (Pa*s)	% Area
1	15.887	266584	51.14
2	19.230	254668	48.86

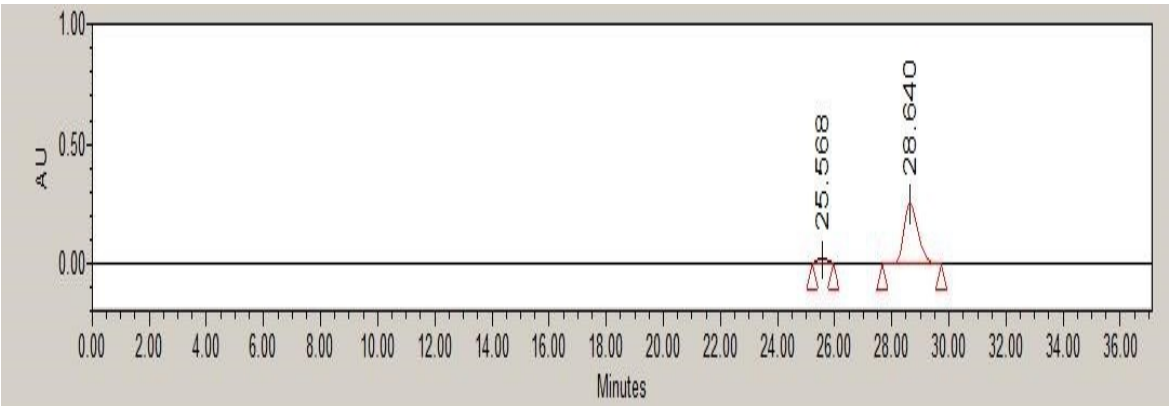


	RT (min)	Area (Pa*s)	% Area
1	15.220	400130	3.12
2	18.607	12428715	96.88

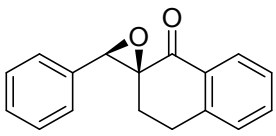


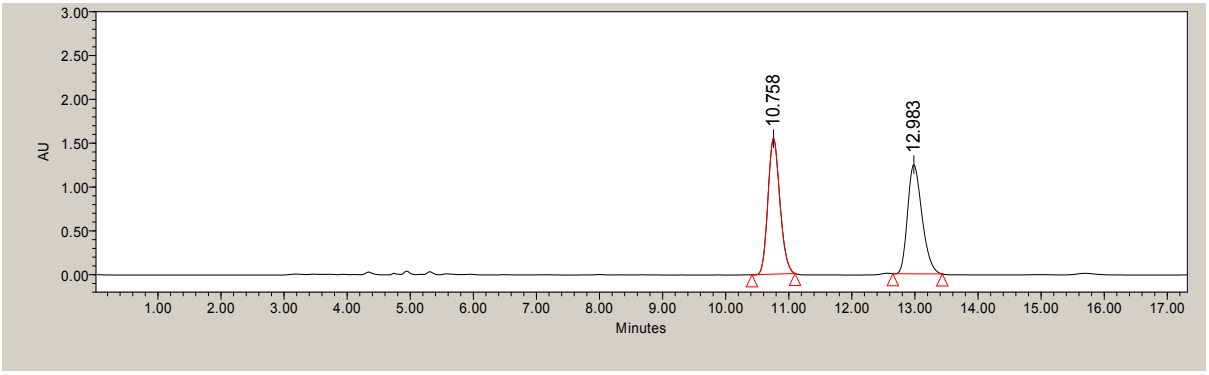


	RT (min)	Area (Pa*s)	% Area
1	26.049	35911357	51.44
2	29.230	33896541	48.56

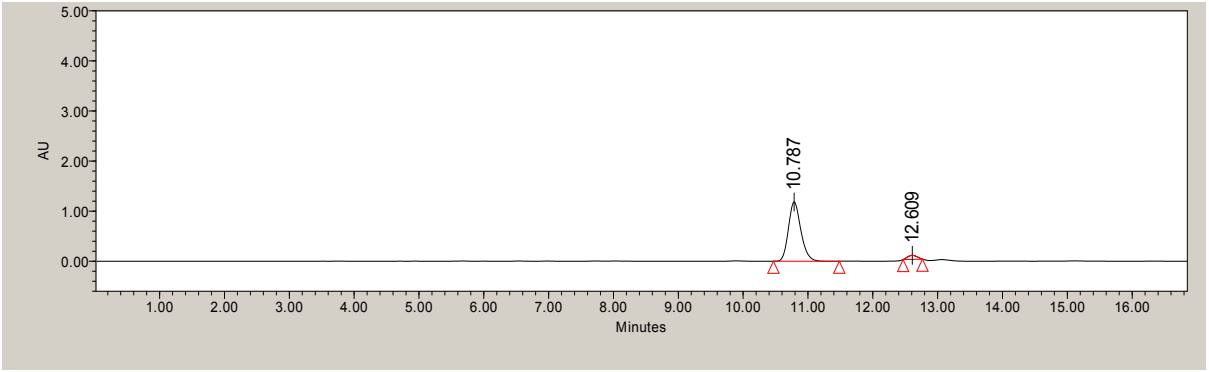


	RT (min)	Area (Pa*s)	% Area
1	25.568	413960	3.65
2	28.640	10921426	96.45

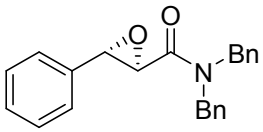


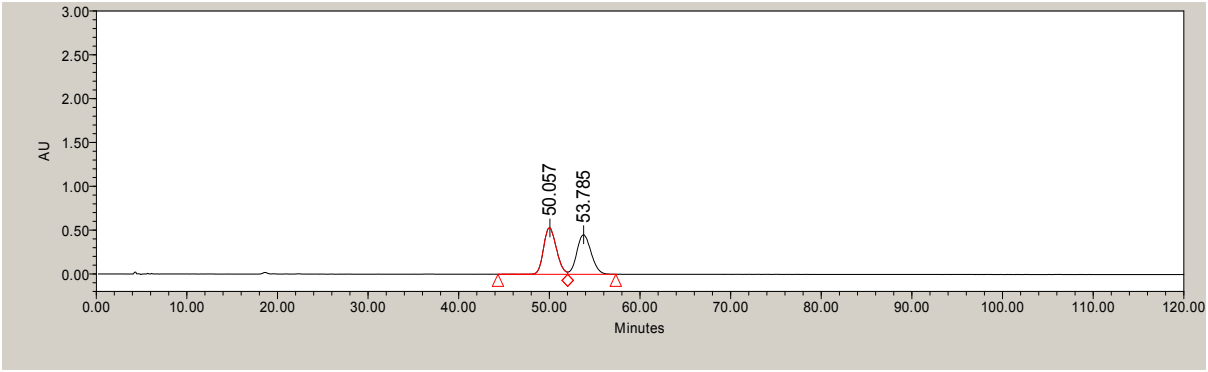


	RT (min)	Area (Pa*s)	% Area
1	10.758	20443472	50.80
2	12.983	19798802	49.20

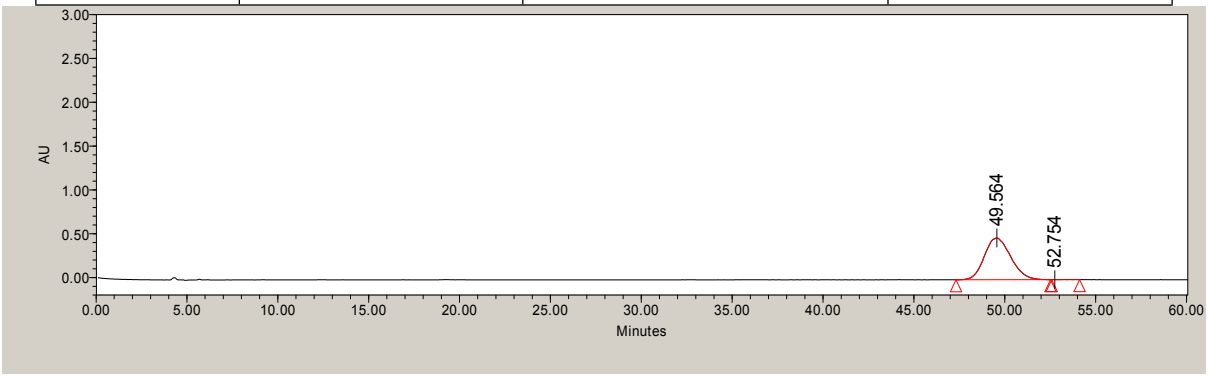


	RT (min)	Area (Pa*s)	% Area
1	10.787	15758323	98.19
2	13.066	290795	1.81

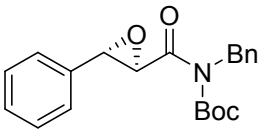


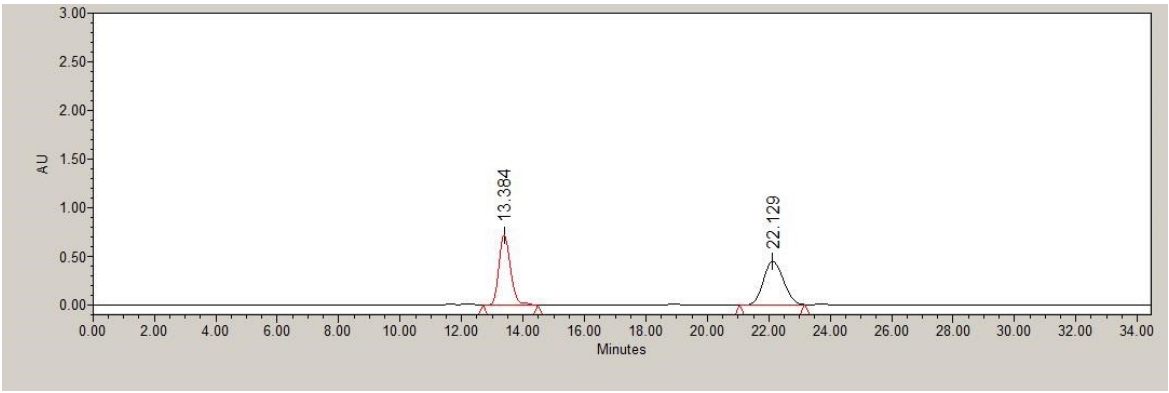


	RT (min)	Area (Pa*s)	% Area
1	50.057	52288271	53.93
2	53.785	49537011	46.07

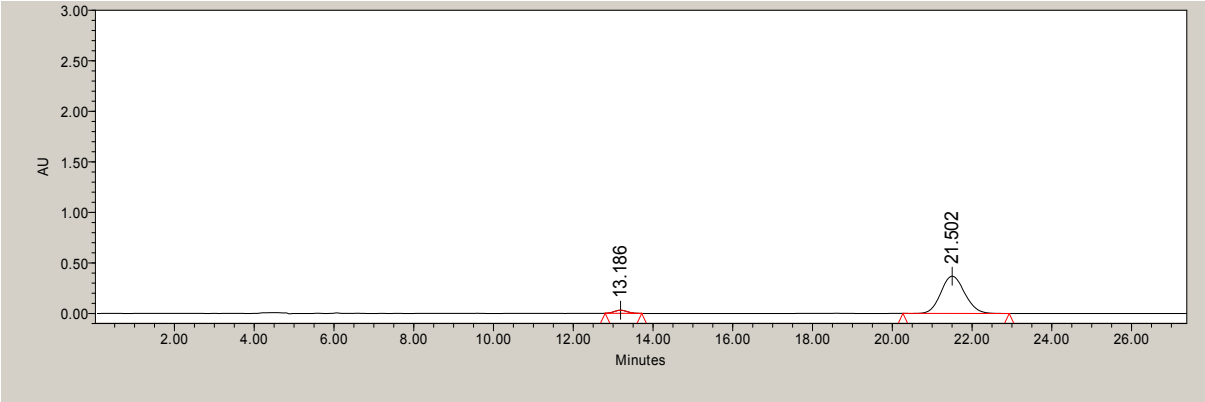


	RT (min)	Area (Pa*s)	% Area
1	49.564	47861179	99.89
2	52.754	51079	0.11

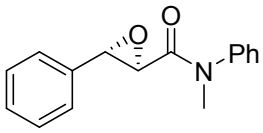


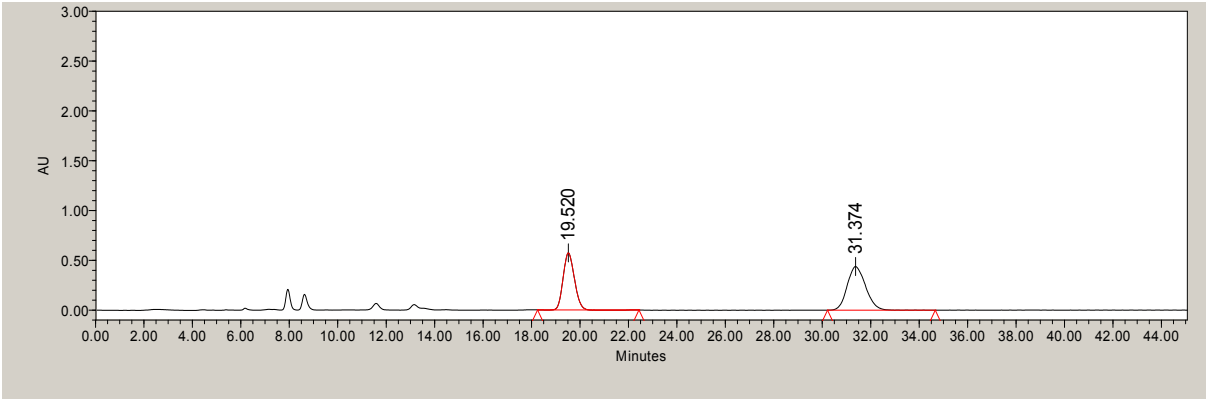


	RT (min)	Area (Pa*s)	% Area
1	13.384	18798519	48.30
2	22.129	20123391	51.70

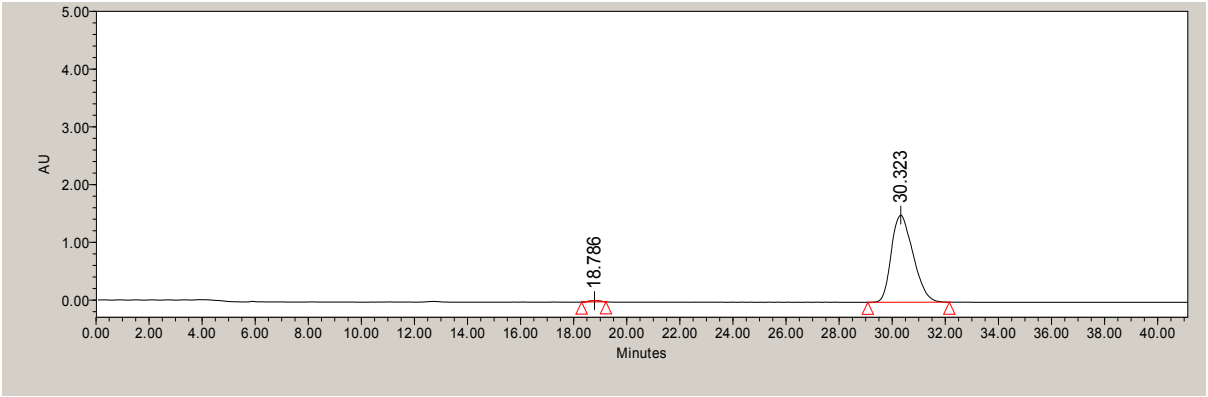


	RT (min)	Area (Pa*s)	% Area
1	13.186	70185	4.36
2	21.502	1532276	95.64

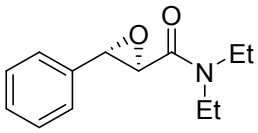


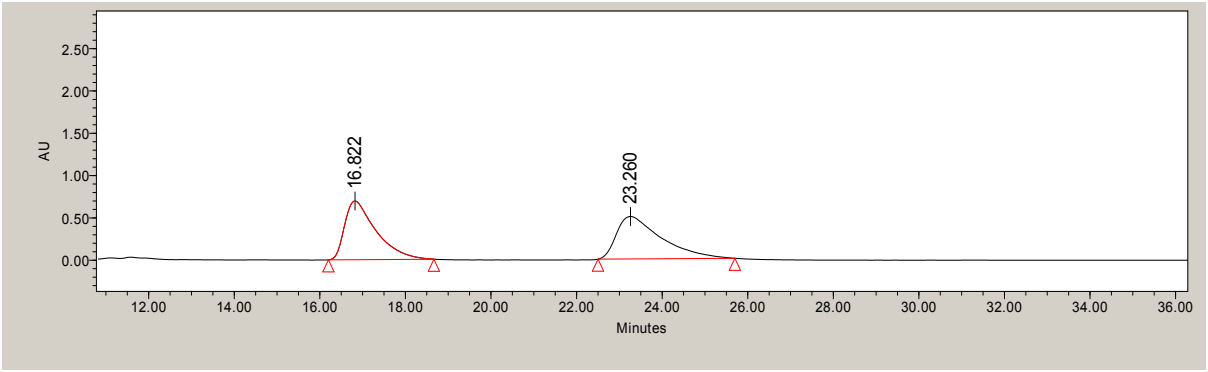


	RT (min)	Area (Pa*s)	% Area
1	19.520	18698724	44.81
2	31.374	23032424	55.19

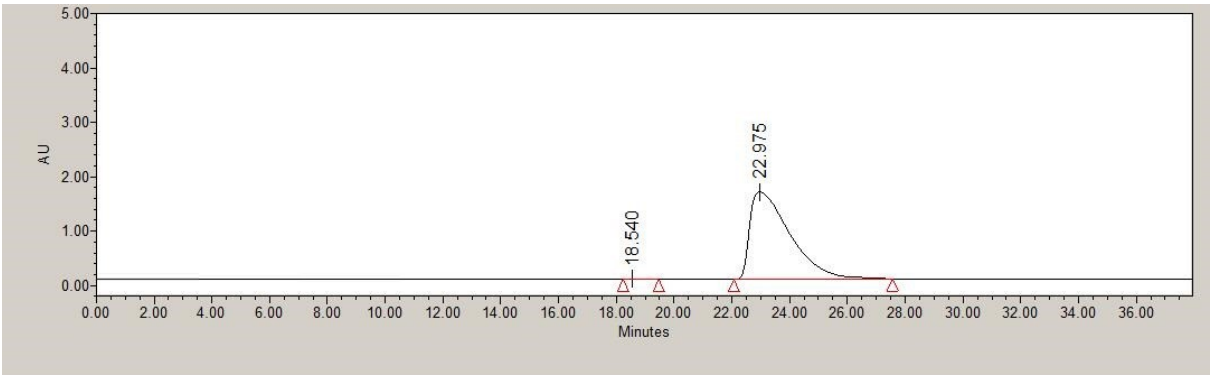


	RT (min)	Area (Pa*s)	% Area
1	18.786	928454	0.58
2	30.323	158563603	99.42

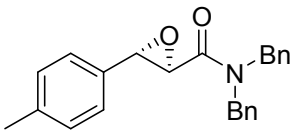


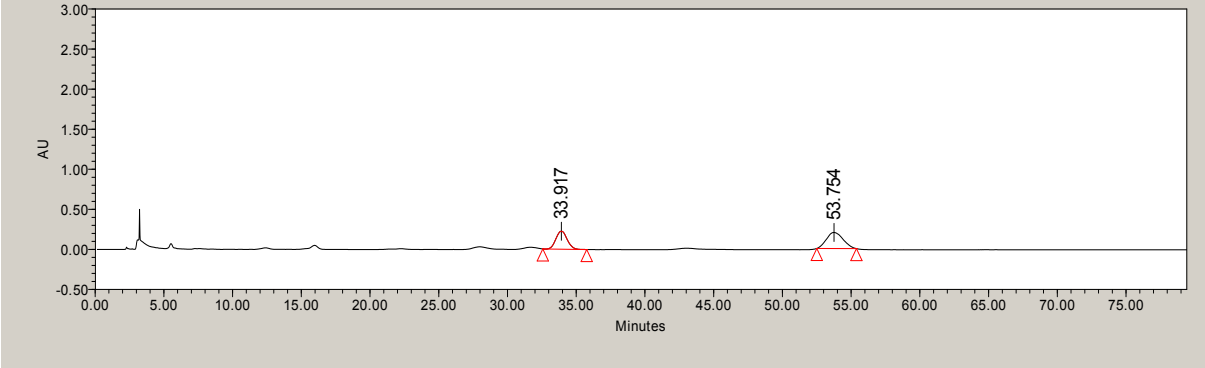


	RT (min)	Area (Pa*s)	% Area
1	16.822	35151960	49.08
2	23.260	36471647	50.92

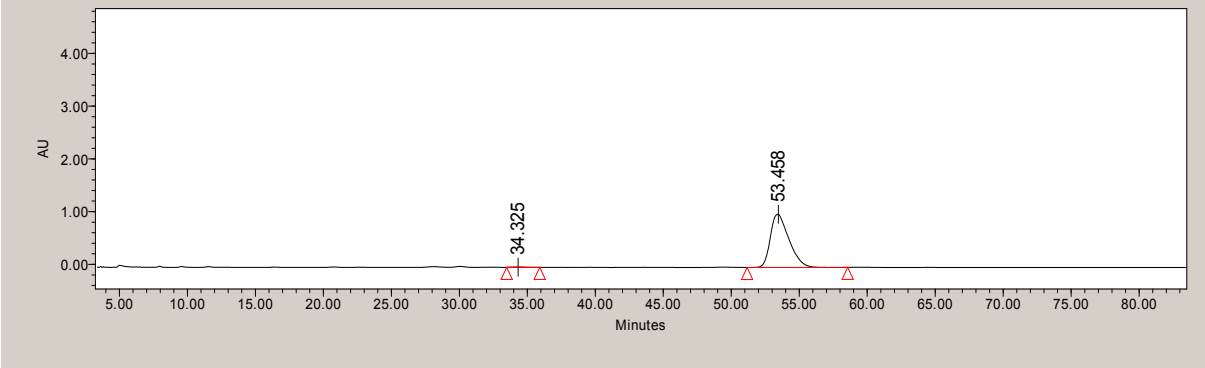


	RT (min)	Area (Pa*s)	% Area
1	18.540	325926	0.21
2	22.975	155956916	99.79

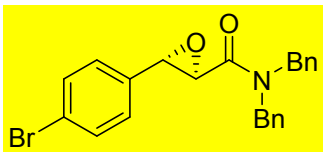


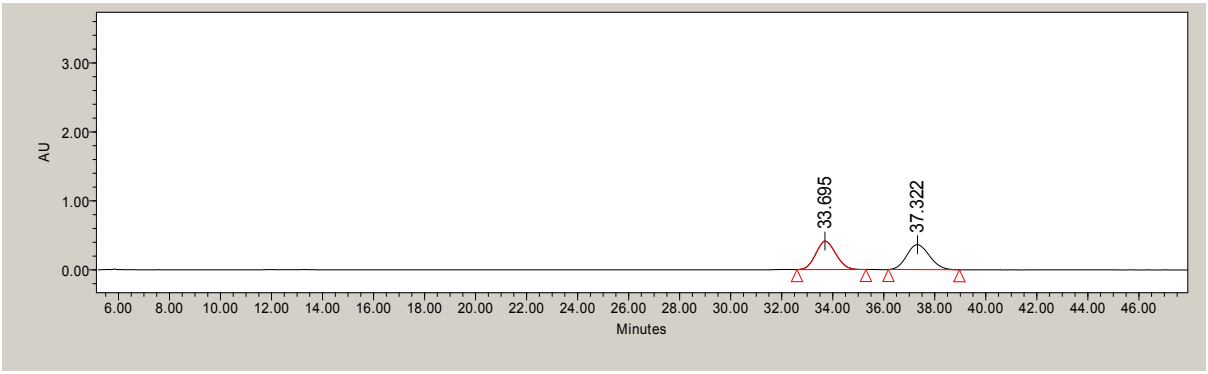


	RT (min)	Area (Pa*s)	% Area
1	33.917	12791372	43.12
2	53.754	16871192	56.88

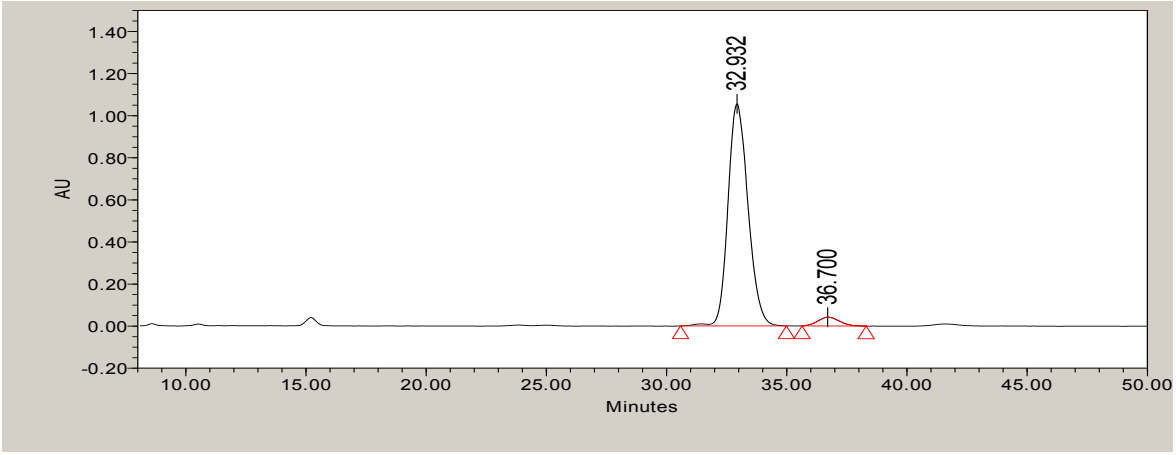


	RT (min)	Area (Pa*s)	% Area
1	34.325	279620	0.29
2	53.458	95471391	99.71

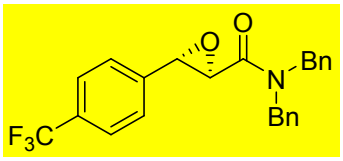


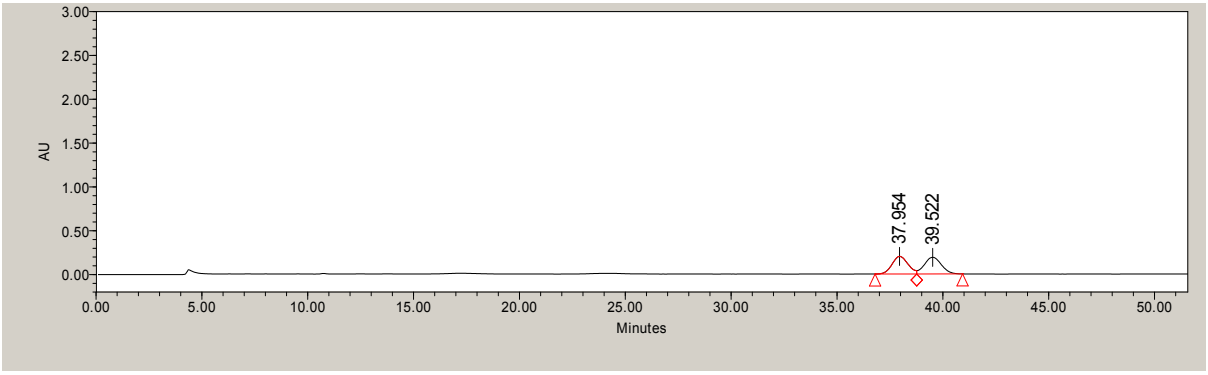


	RT (min)	Area (Pa*s)	% Area
1	33.695	22366453	49.88
2	37.322	22475771	50.12

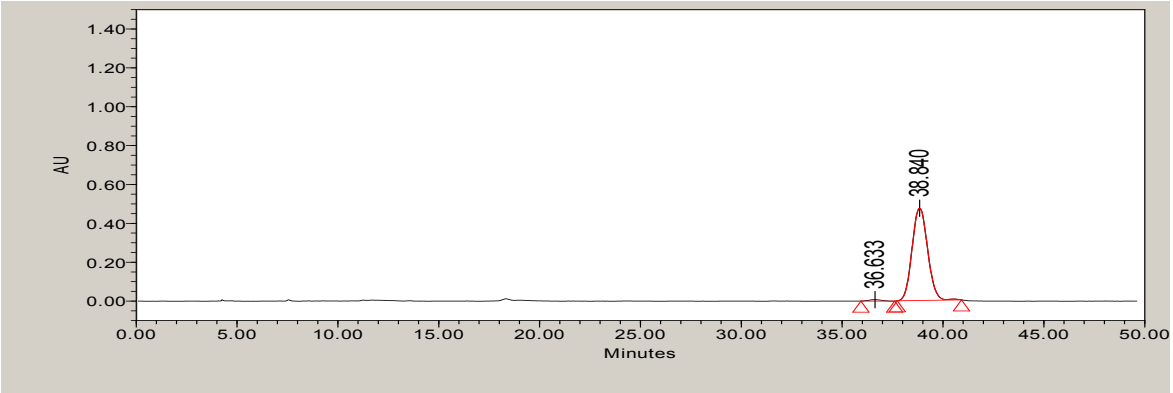


	RT (min)	Area (Pa*s)	% Area
1	32.932	60145523	97.03
2	36.696	1840377	2.97

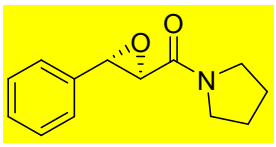


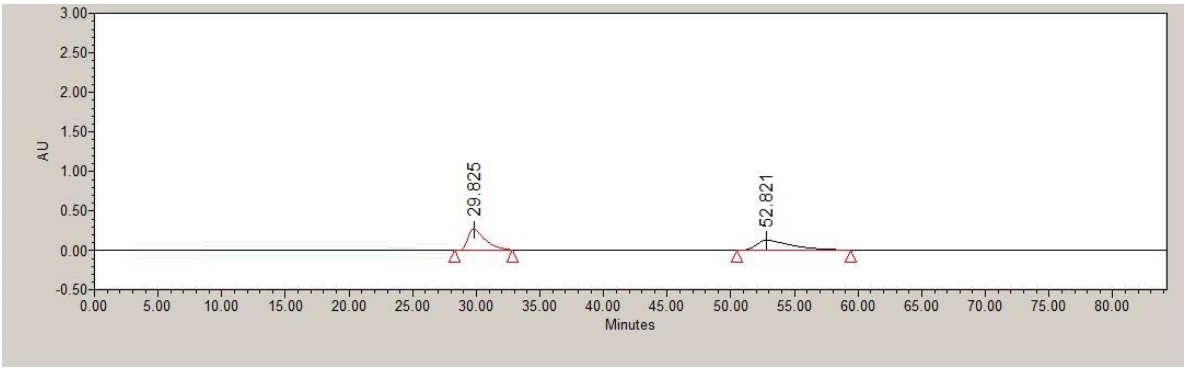


	RT (min)	Area (Pa*s)	% Area
1	37.954	10489162	49.74
2	39.522	10600556	50.26

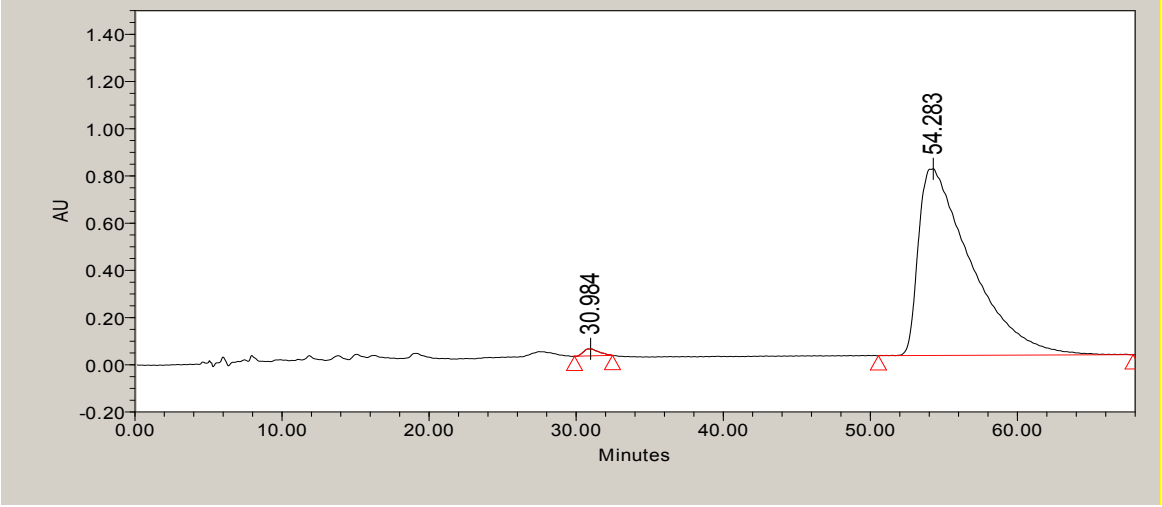


	RT (min)	Area (Pa*s)	% Area
1	36.633	205563	0.81
2	38.840	25274574	99.19

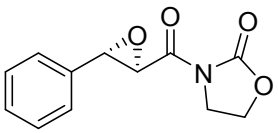


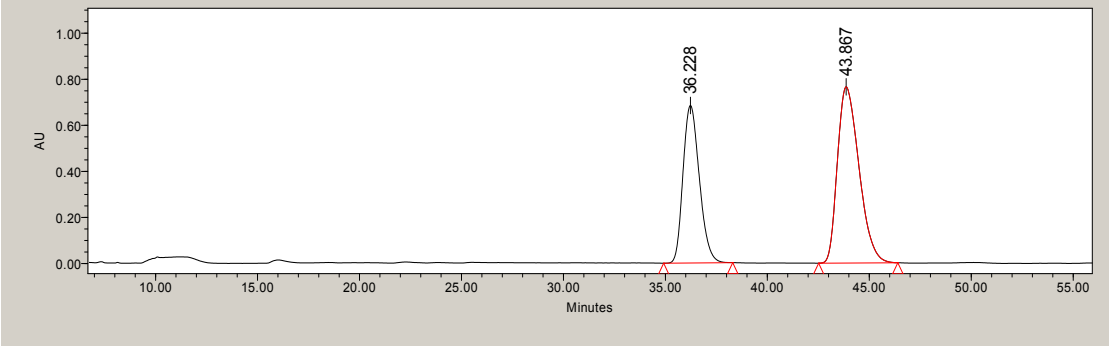


	RT (min)	Area (Pa*s)	% Area
1	29.825	24499128	49.98
2	52.821	24609799	50.11

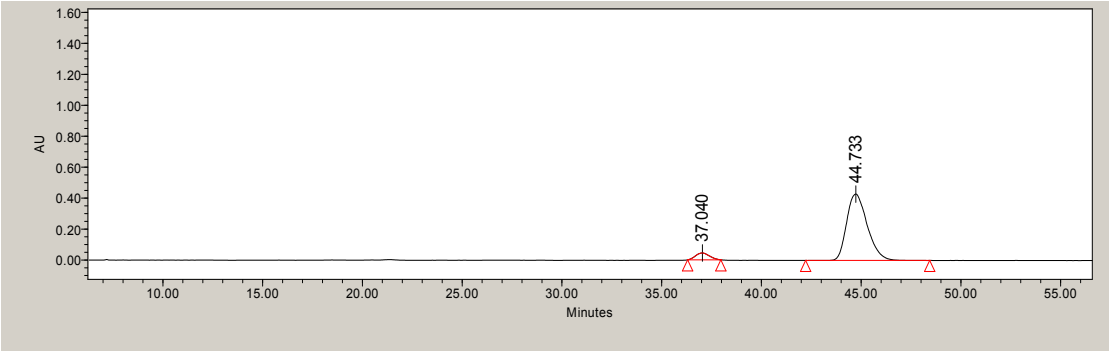


	RT (min)	Area (Pa*s)	% Area
1	30.984	2022594	1.02
2	54.283	195366098	98.98

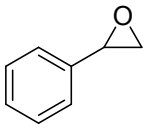


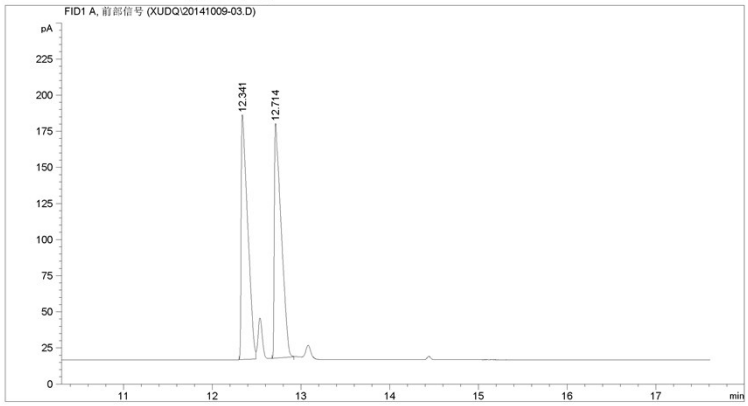


	RT (min)	Area (Pa*s)	% Area
1	36.228	44708235	46.42
2	43.867	51643894	53.58



	RT (min)	Area (Pa*s)	% Area
1	37.040	2160446	6.57
2	44.733	30742842	93.43





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面积百分比报告

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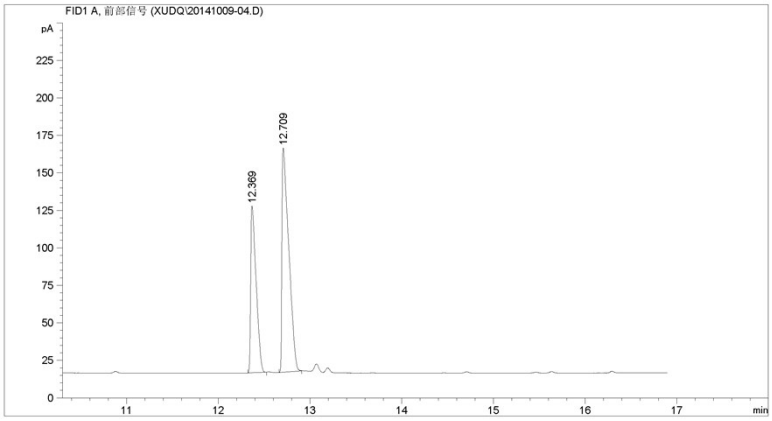
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	12.341	BV	0.0662	858.03998	169.21709	49.67924
2	12.714	BB	0.0695	869.12006	162.30457	50.32076

总量 : 1727.16003 331.52165



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面积百分比报告

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排序 : 信号
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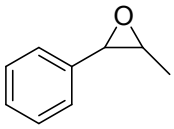
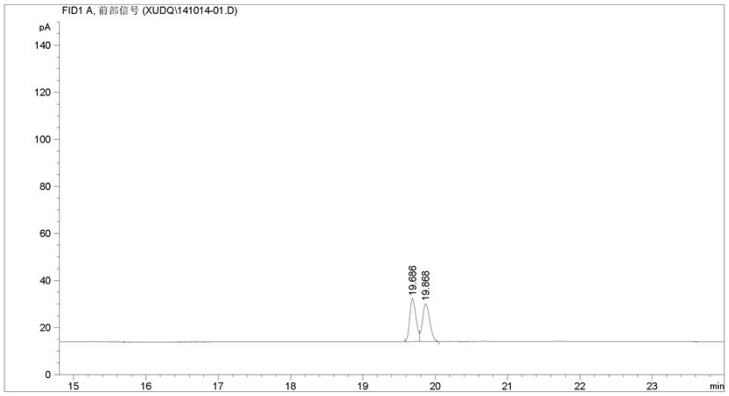
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	12.369	BB	0.0619	457.11514	111.30312	37.29103
2	12.709	BB	0.0720	768.68951	149.44196	62.70897





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面积百分比报告

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排序 : 信号
乘积因子: : 1.0000
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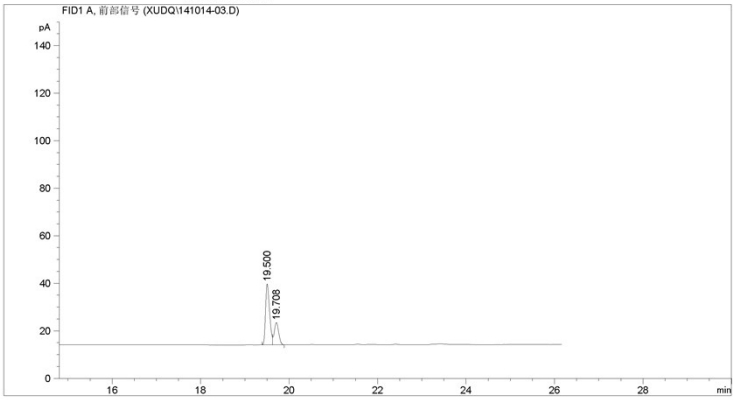
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	4.023	VB S	0.0348	2.81729e4	1.22419e4	82.91734
2	4.149	BB T	0.0410	5555.26270	2024.91589	16.34999
3	7.337	BB	0.0602	26.56840	6.86199	0.07819
4	19.686	BV	0.0932	110.56200	18.37225	0.32540
5	19.868	VB	0.1078	111.80995	16.14630	0.32907



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面积百分比报告

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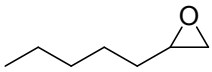
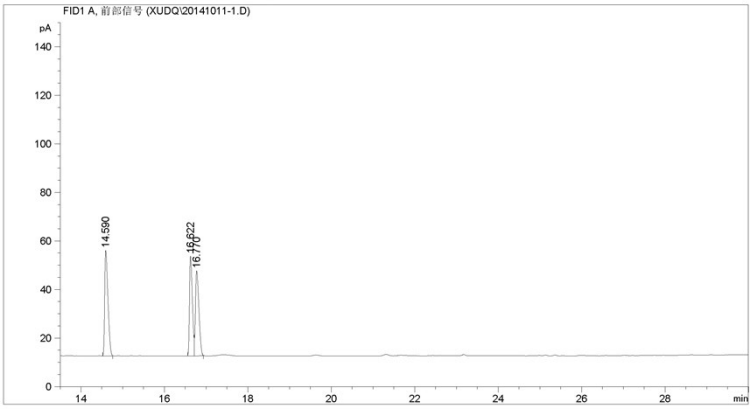
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	19.500	BV	0.0998	163.76114	25.55682	71.60809
2	19.708	VB	0.1046	64.92969	9.28622	28.39191





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面积百分比报告
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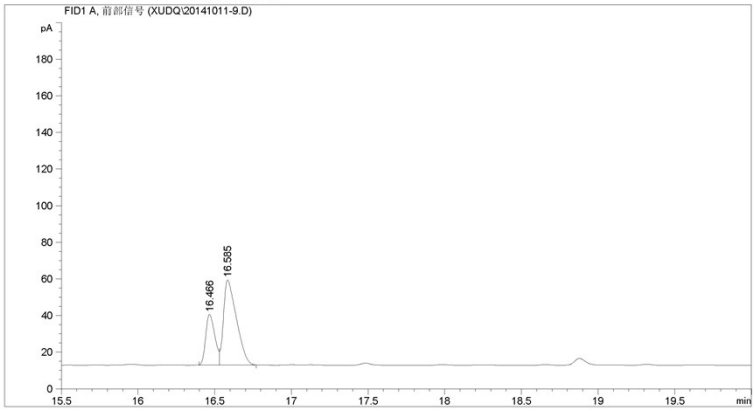
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	4.678	BB S	0.0621	4.47914e4	9309.34766	84.38632
2	4.927	BV T	0.0455	157.79070	53.33381	0.29728
3	5.078	VB T	0.0780	7496.57422	1231.25378	14.12344
4	14.590	BB	0.0791	234.85864	43.40932	0.44247
5	16.622	BV	0.0728	196.74643	41.11325	0.37067
6	16.770	VB	0.0880	201.60826	35.08638	0.37983



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面积百分比报告
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排序 : 信号
乘积因子: : 1.0000
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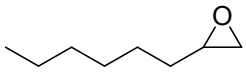
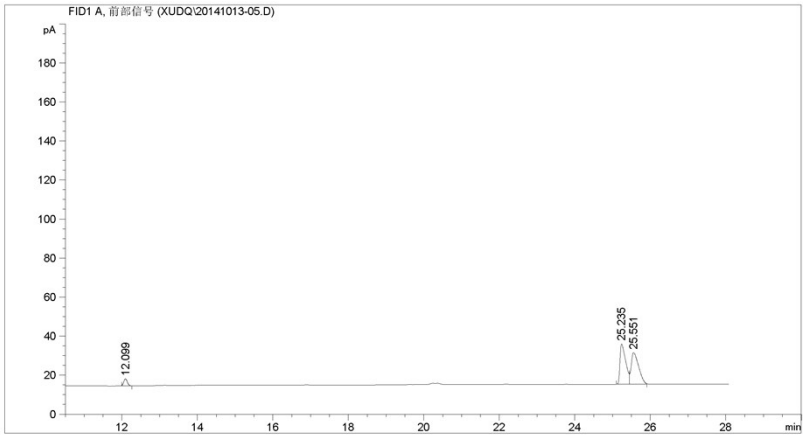
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	16.466	BV	0.0632	114.18850	27.65462	29.49682
2	16.585	VB	0.0825	272.93286	46.50646	70.50318





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面积百分比报告

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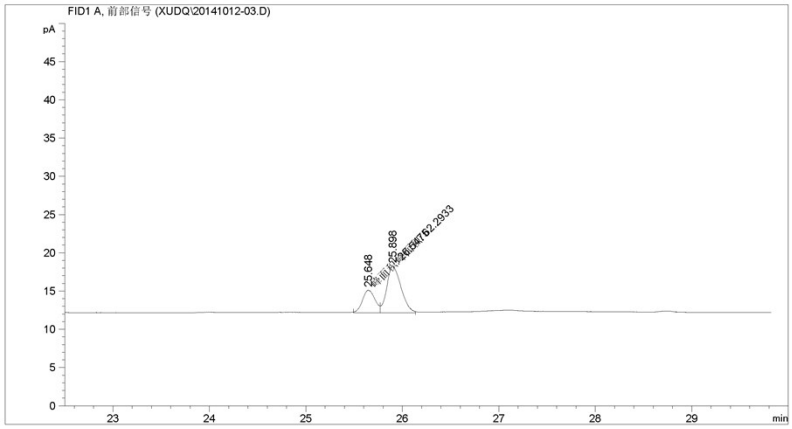
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	4.020	BB	0.0400	21.55063	8.38319	0.03734
2	4.153	BV S	0.0436	4.68786e4	1.45399e4	81.21768
3	4.360	VB S	0.0576	1.03303e4	2382.80811	17.89734
4	4.889	BB	0.0581	28.51650	7.71478	0.04941
5	12.099	BB	0.1011	23.45864	3.55068	0.04064
6	25.235	BV	0.1504	215.21159	20.68316	0.37286
7	25.551	VB	0.1779	222.07162	16.10038	0.38474



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面积百分比报告

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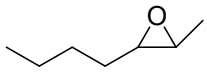
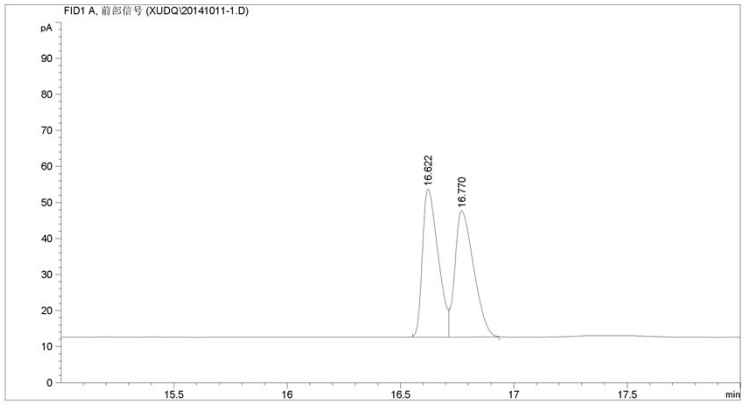
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	25.648	MF	0.1500	26.54750	2.94960	29.88211
2	25.898	FM	0.1708	62.29329	6.07975	70.11789

总量 : 88.84079 9.02936





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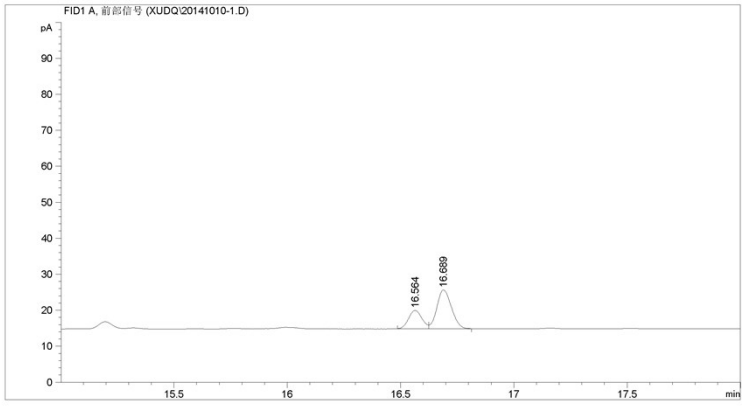
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	4.678	BB S	0.0621	4.47914e4	9309.34766	84.38632
2	4.927	BV T	0.0455	157.79070	53.33381	0.29728
3	5.078	VB T	0.0780	7496.57422	1231.25378	14.12344
4	14.590	BB	0.0791	234.85864	43.40932	0.44247
5	16.622	BV	0.0728	196.74643	41.11325	0.37067
6	16.770	VB	0.0880	201.60826	35.08638	0.37983



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面积百分比报告
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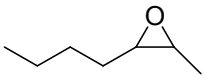
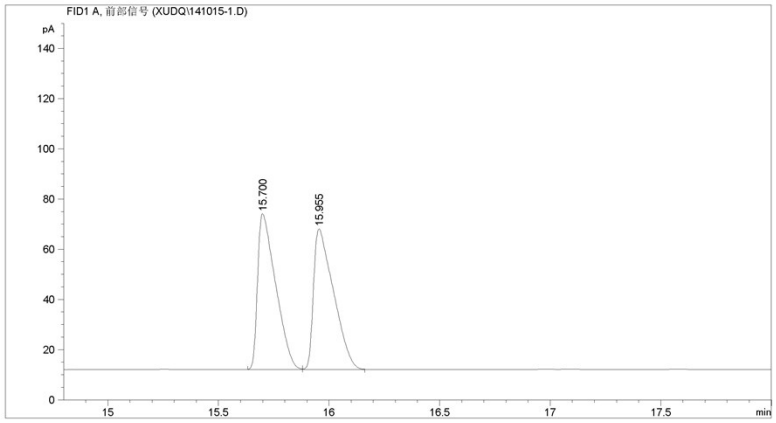
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	16.564	BV	0.0628	20.93639	5.11071	30.25591
2	16.689	VB	0.0702	48.26129	10.79206	69.74409





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面积百分比报告

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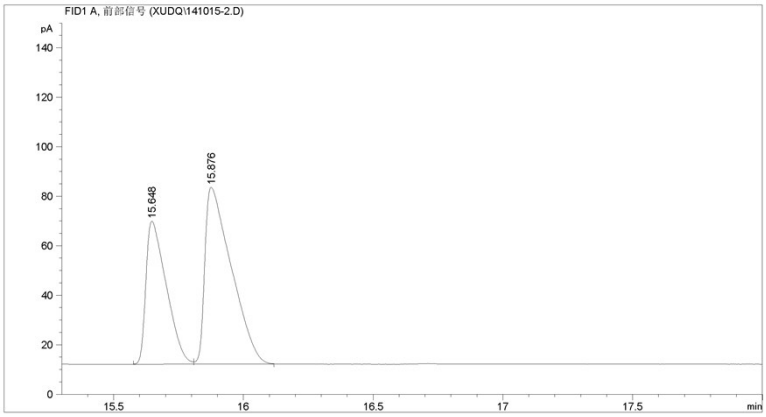
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	4.811	VV	0.0249	15.82051	10.31358	0.04706
2	4.848	VB S	0.1515	3.26475e4	3590.69824	97.12102
3	7.365	BB	0.0642	13.07788	3.23222	0.03890
4	14.531	BB	0.0711	81.83118	17.98641	0.24343
5	15.700	BV	0.0822	351.83694	62.00648	1.04666
6	15.955	VB	0.0873	351.80273	56.01804	1.04655



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面积百分比报告

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排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	15.648	BV	0.0826	314.99573	57.80317	38.39726
2	15.876	VB	0.0986	505.36417	71.39670	61.60274