Novel Reaction Course of Thiiranes to Vinyl Epoxides: Reaction of Benzyne with Thiiranes and Aldehydes

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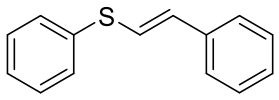
Experimental Section
^{1}H NMR and ^{13}C NMR chart

Experimental

General: All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica gel (Merck, 70-230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 101 MHz) were recorded in $CDCl_3$, and chemical shifts are expressed in ppm relative to internal TMS for ^{1}H- and ^{13}C-NMR. ^{19}F NMR (376 MHz) spectra were recorded on a Bruker AVANCE spectrometer and referenced against the external standard $CFCl_3$. EI and ESI-TOF mass spectra were recorded on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively.

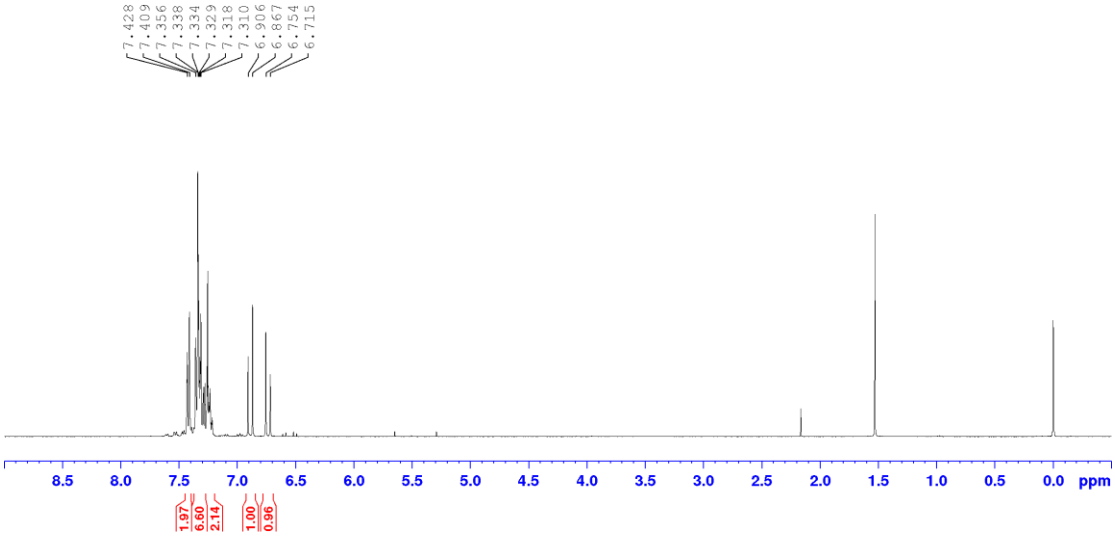
Reaction of 2-trimethylsilylphenyl triflate with 2-phenylthiirane 2a in the presence of chloroform

To a suspension of 2-trimethylsilylphenyl triflate **1a** (90 g, 0.3 mmol) and CsF (137 mg, 0.9 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane **2a** (41 mg, 0.3 mmol) in chloroform (2 mL). After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale brown oily crystals, which were chromatographed over silica gel by elution with hexane to afford (*E*)-but-1-enylphenyl sulfide **3a** (54 mg, 0.26 mmol).



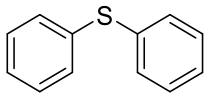
(*E*)-but-1-enylphenyl sulfide **3a**. Colorless oil (lit.[1] Colorless oil);^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.74 (d, 1H, *J* = 16 Hz, CH), 6.89 (d, 1H, *J* = 16 Hz, CH), 7.27 - 7.21 (m, 2H), 7.37 - 7.27 (m, 6H), 7.44 - 7.40 (m, 2H).

^{1}H NMR (400 MHz, $CDCl_3$) **3a**



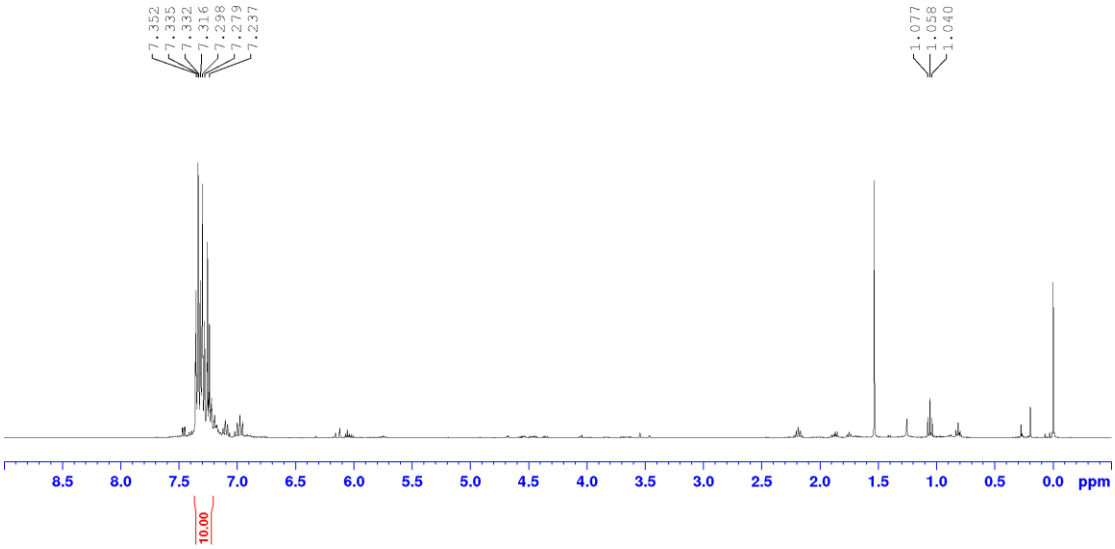
Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-phenylthiirane 2a in the presence of chloroform

To a suspension of 2-trimethylsilylphenyl triflate **1a** (208 mg, 0.7 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane **2a** (41 mg, 0.3 mmol) in chloroform (2 mL). After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane to afford diphenyl sulfide **4** (46 mg, 0.25 mmol).



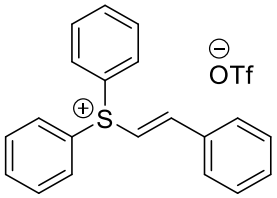
diphenyl sulfide **4**. Colorless oil (lit.[2] Colorless oil);^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 - 7.22 (m, 10H).

^{1}H NMR (400 MHz, $CDCl_3$) **4**



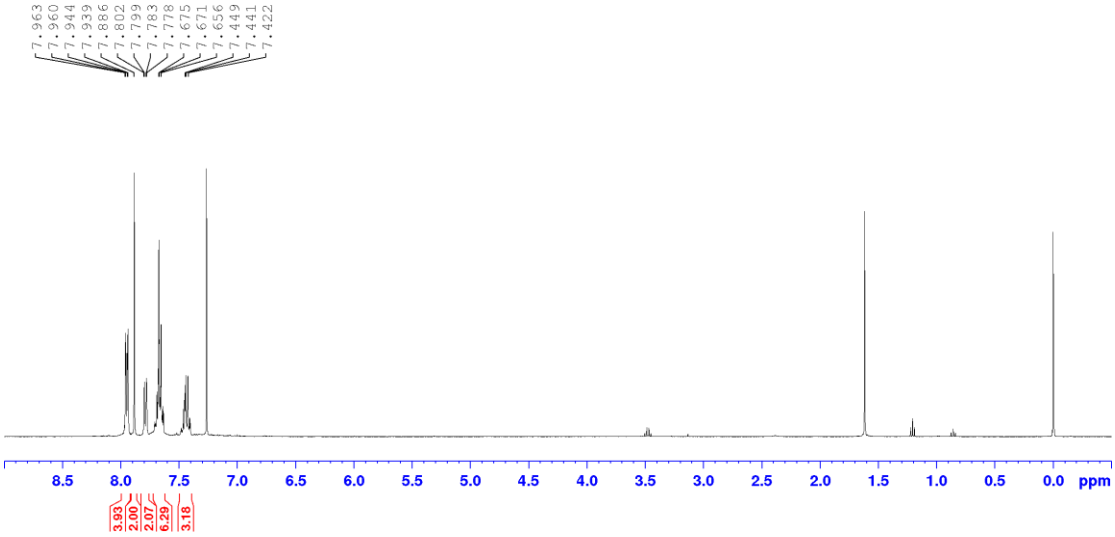
Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-phenylthiirane 2a

To a suspension of 2-trimethylsilylphenyl triflate **1a** (208 mg, 0.7 mmol), and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-phenylthiirane **2a** (76 mg, 0.3 mmol) in acetonitrile (2 mL). After being stirred for 12 h, the reaction mixture was added TfOH (45 mg, 0.3 mmol) with dichloromethane (5 mL). After being stirred for 12 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale yellow oil. Diethyl ether (10 mL) was added to the dichloromethane solution to afford diphenyl(styryl)sulfonium triflate **5a** (79 mg 0.18 mmol).

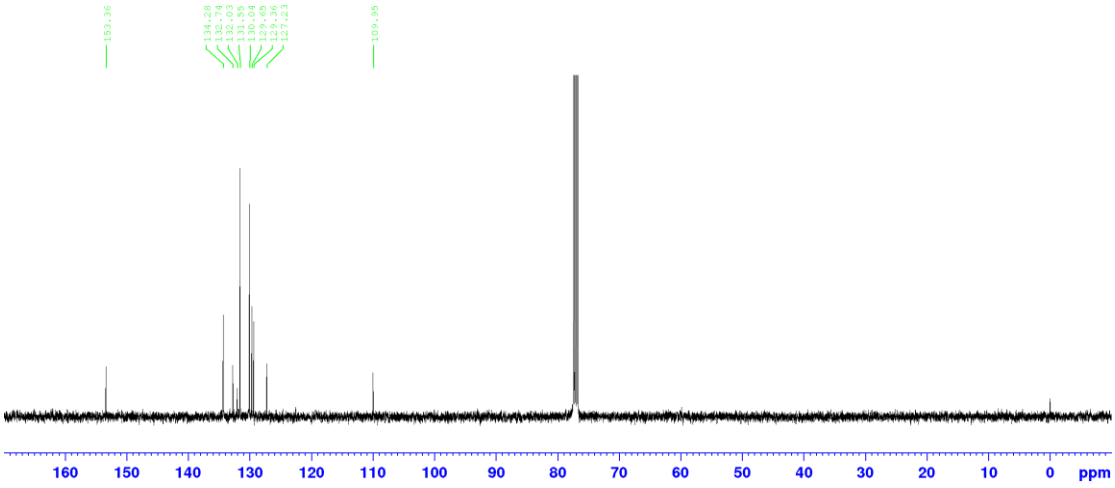


diphenyl(styryl)sulfonium triflate **5a**: Colorless oil (lit.[3] white solid); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 - 7.39 (m, 3H), 7.71 - 7.62 (m, 6H), 7.82 - 7.77 (m, 2H), 7.89 (s, 2H, CH), 7.98 - 7.93 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 109.9, 127.2, 129.3, 129.6, 130.0, 121.5, 132.0, 132.7, 134.3, 153.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -78.1; MS (ESI): Calcd for $C_{20}H_{17}S$ m/z = 289.10, Found; m/z = 289.15 $[M]^+$.

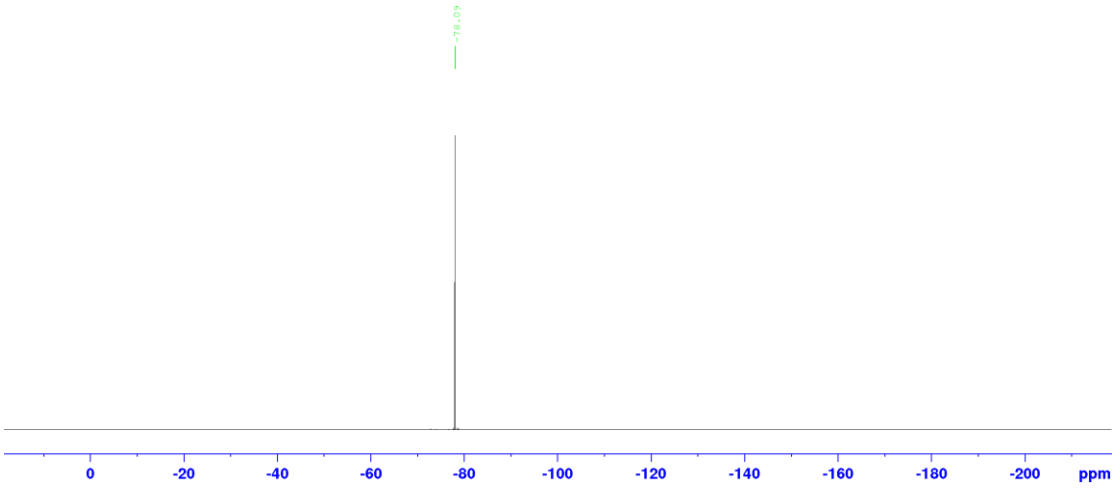
^{1}H NMR (400 MHz, $CDCl_3$) **5a**



^{13}C NMR (101 MHz, $CDCl_3$) **5a**

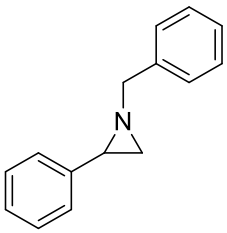


^{19}F NMR (376 MHz, $CDCl_3$) **5a**



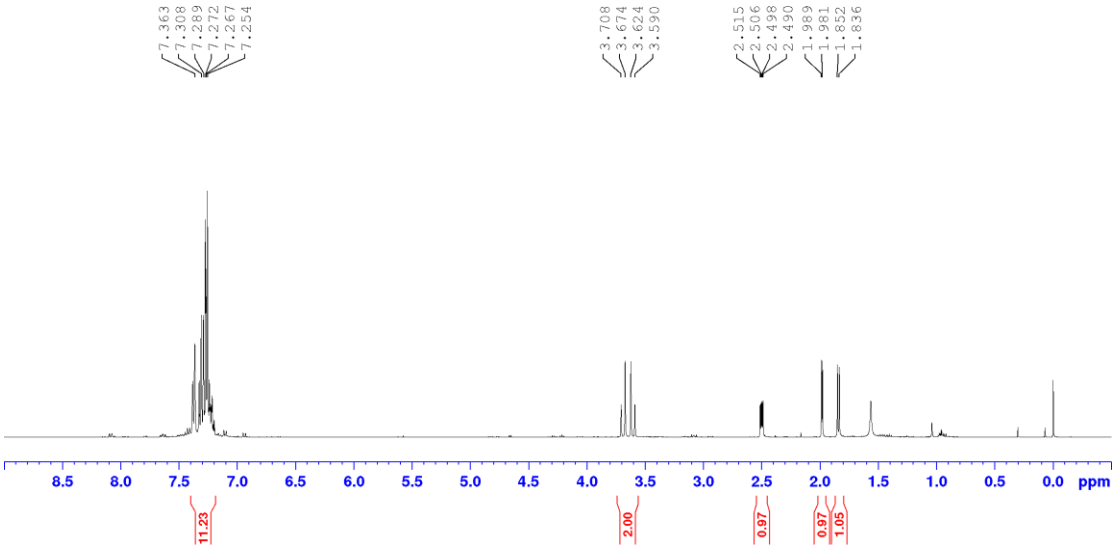
Reaction of triflate 1 with 2-phenylthiirane 2a followed by the addition of benzylamine in the presence of CsF.

To a suspension of triflate **1** (208 mg, 0.7 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added a solution of 2-phenylthiirane **2a** (76 mg, 0.3mmol) in acetonitrile (2 mL). After being stirred for 12h, benzylamine (48 mg, 0.45 mmol) in acetonitrile (1 mL) was added to the reaction mixture at rt. After being stirred for 6 h, the reaction mixture was washed with water and extracted with dichloromethane (5mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was subjected to alumina chromatography by elution with hexane:dichlrometane (1:1) to afford diphenyl sulfide **4** and 1-benzyl-2-phenylaziridine **6** (177 mg, 0.26 mmol).

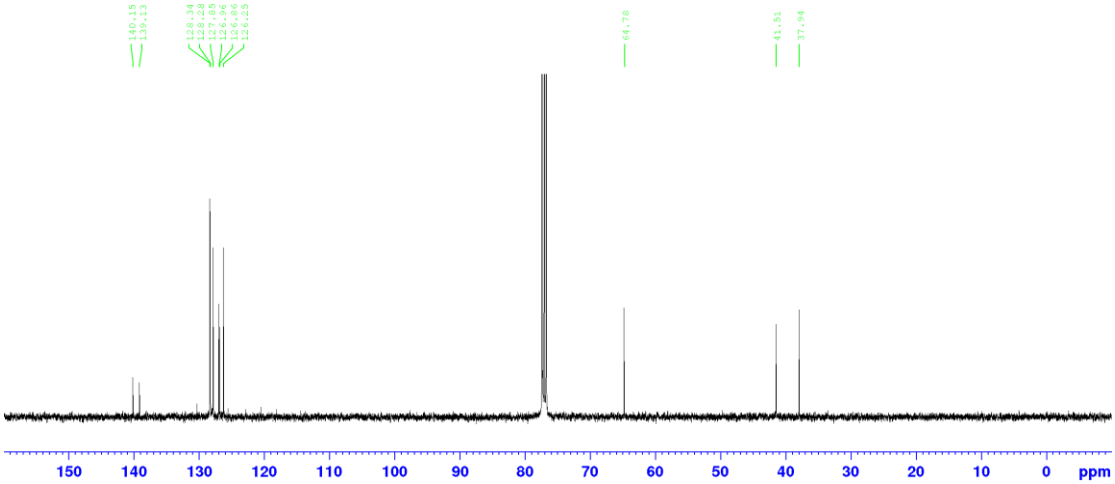


1-benzyl-2-phenylaziridine **6**: pale yellow oil (lit.[4] colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.84 (d, 1H, J = 7 Hz, C<u>H</u>H), 1.99 (d, 1H, J = 3 Hz, CH<u>H</u>), 2.50 (dd, 1H, J = 3, 7 Hz, CH), 3.61 (d, 1H, J = 14 Hz, C<u>H</u>H), 3.69 (d, 1H, J = 14 Hz, CH<u>H</u>), 7.40 - 7.19 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 37.9, 41.5, 64.7, 126.3, 126.8, 126.9, 127.8, 128.3, 128.3, 139.1, 140.1; MS (ESI): Calcd for $C_{15}H_{15}N$ m/z = 209.12, Found; m/z = 209.09 $[M+H]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) **6**

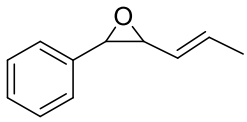


^{13}C NMR (101 MHz, $CDCl_3$) **6**



Reaction of 2-trimethylsilylphenyl triflate (2 eq) with 2-ethylthiirane 2b and benzaldehyde

To a suspension of 2-trimethylsilylphenyl triflate **1a** (208 g, 0.7 mmol), benzaldehyde (0.35 mg, 0.33 mmol) and CsF (320 mg, 2.1 mmol) in acetonitrile (2 mL) was added 2-ethylthiirane **2b** (27 mg, 0.3 mmol) in acetonitrile (2 mL). After being stirred for 12 h, the reaction mixture was washed with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with dichloromethane: hexane (1:3) to afford isomer's mixture of 2-phenyl-3-(prop-1-en-1-yl)oxirane **8aa** (25 mg, 0.15 mmol).



2-phenyl-3-(prop-1-en-1-yl)oxirane **8aa**: (1E, 3Z): (1Z, 3Z): (1E, 3E): (1E, 3Z) = 32:51:3:8; colorless oil (lit.[5] colorless oil); MS (ESI): Calcd for $C_{11}H_{12}O$ m/z = 160.09, Found: m/z = 161.03 $[M+H]^+$.

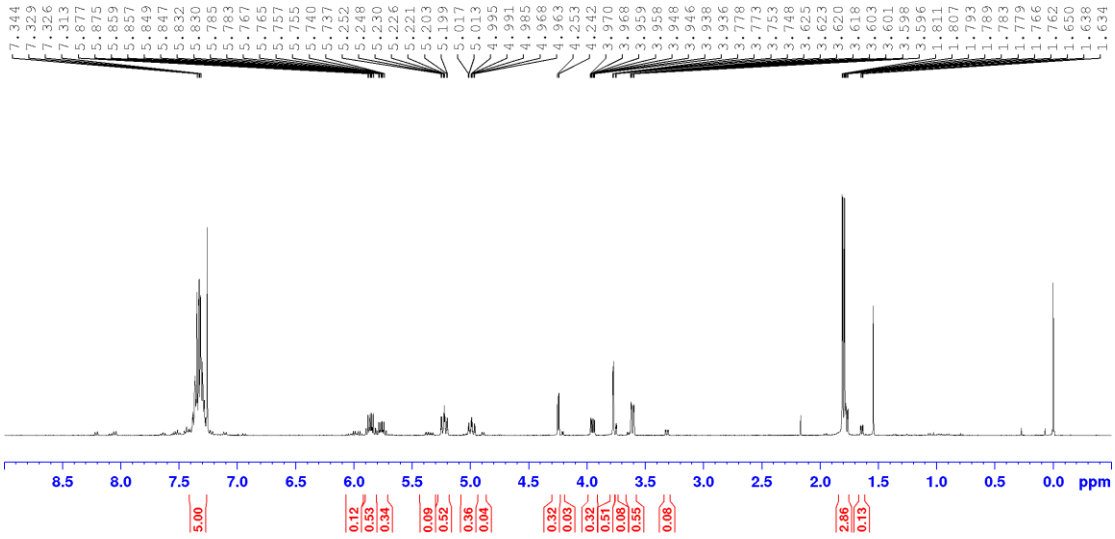
(1E, 3Z) isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.79 - 1.75 (m, 3H), 3.95 (dd, 1H, J = 4, 9 Hz, CH), 4.25 (d, 1H, J = 4 Hz, CH), 4.99 (dd, 1H, J = 9, 10 Hz, CH), 5.76 (m, 1H), 7.40 - 7.27 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 13.4, 54.8, 58.7, 125.4, 127.3, 128.0, 128.5, 131.4, 137.4.

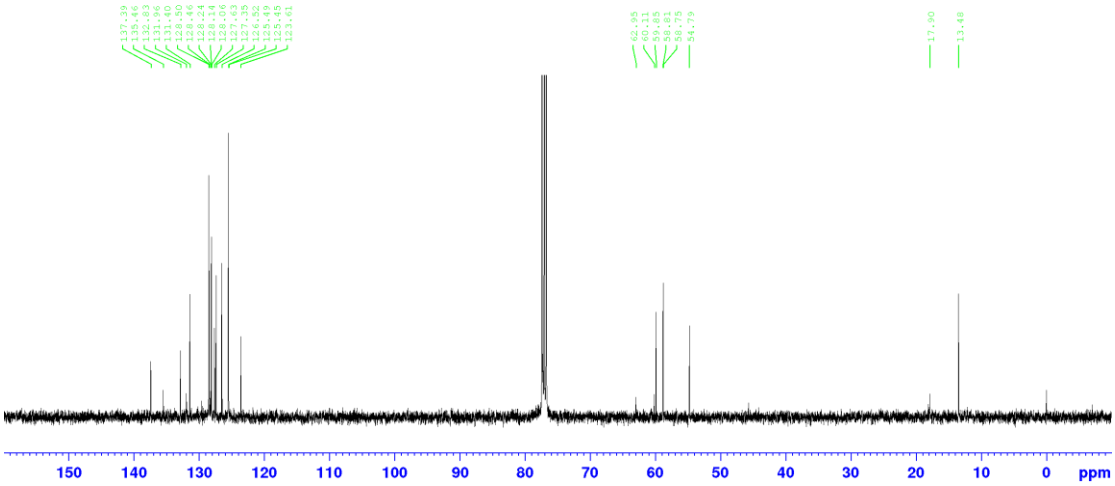
(1Z, 3Z) isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.79 - 1.75 (m, 3H), 3.61 (d, 1H, J = 9 Hz, CH), 3.78 (d, 1H, J = 2 Hz, CH), 5.23 (dd, 1H, J = 9, 10 Hz, CH), 5.90 - 5.81 (m, 1H), 7.40 - 7.27 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 13.4, 58.8, 59.8, 123.6, 126.5, 127.6, 128.1, 132.8, 135.5.

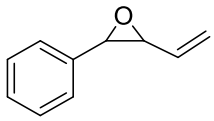
^{1}H NMR (400 MHz, $CDCl_3$) **8aa**



^{13}C NMR (101 MHz, $CDCl_3$) **8aa**



Other oxiranes were synthesized in a similar manner.



2-phenyl-3-vinyloxirane **8ba**: E/Z = 40/60; colorless oil (lit.[6]); MS (ESI): Calcd for $C_{10}H_{10}O$ m/z = 146.07, Found: m/z = 147.07 $[M+H]^+$.

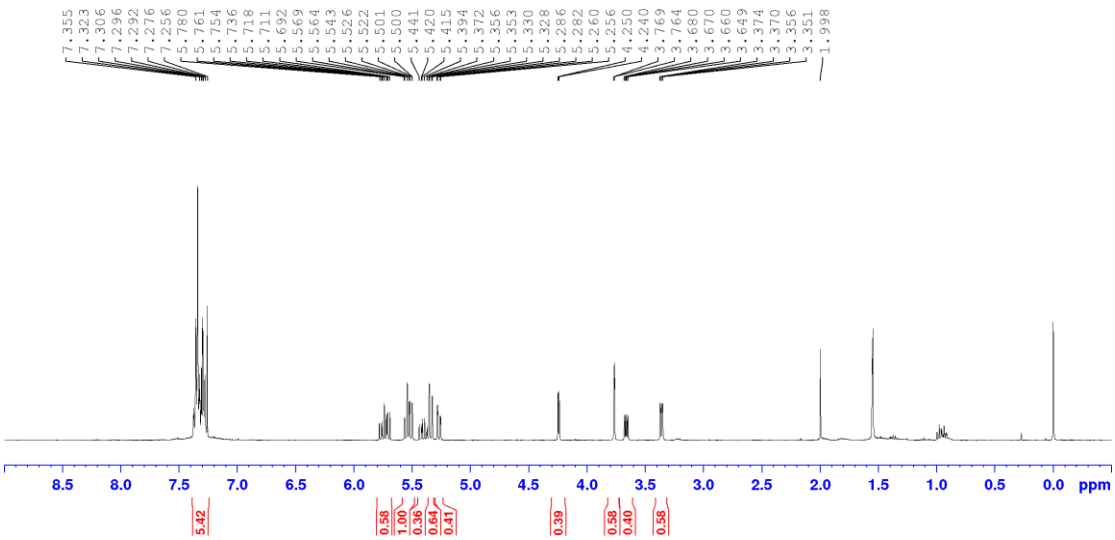
E isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.66 (dd, 1H, J = 4, 8 Hz, CH), 4.24 (d, 1H, J = 4 Hz, CH), 5.28 (dd, 1H, J = 2, 11 Hz, CH), 5.41 (ddd, 1H, J = 11, 11, 7 Hz, CH), 5.55 (dd, 1H, J = 2, 17 Hz, CH), 7.39 - 7.26 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.8, 59.7, 121.8, 126.4, 127.4, 128.2, 132.0, 135.1.

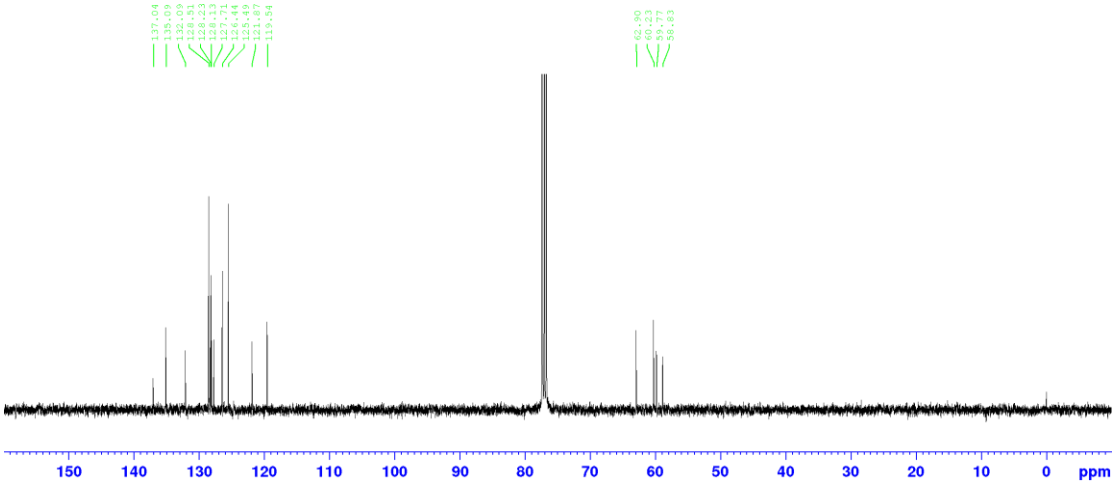
Z isomer:

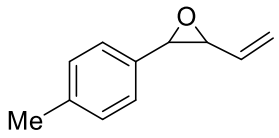
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.37 (dd, 2H, J = 2, 8 Hz), 3.77 (d, 1H, J = 2 Hz), 5.34 (d, 1H, J = 10 Hz), 5.53 (d, 1H, J = 17 Hz), 5.74 (ddd, 1H, J = 7, 10, 17 Hz), 7.39 - 7.26 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 60.2, 62.9, 119.5, 125.5, 128.1, 128.5, 135.1, 137.0.

^{1}H NMR (400 MHz, $CDCl_3$) **8ba**



^{13}C NMR (101 MHz, $CDCl_3$) **8ba**





2-(4-methylphenyl)-3-vinyloxirane **8bb**: E/Z = 40/60; colorless oil (lit.[7] colorless liquid); MS (ESI): Calcd for $C_{11}H_{12}O$ m/z = 160.09, Found: m/z = 161.02 $[M+H]^+$.

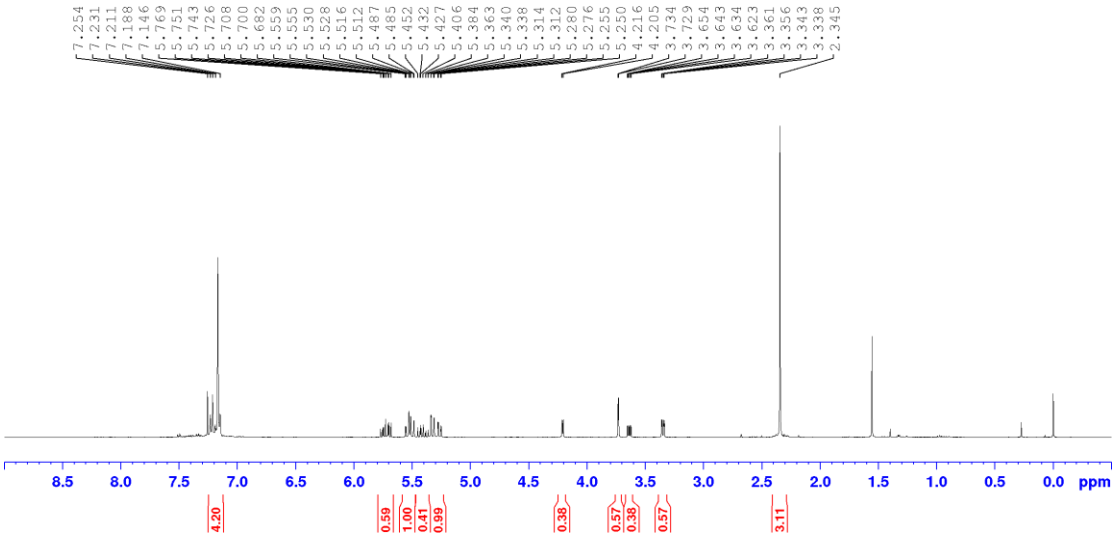
E isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.35 (s, 3H, CH_3), 3.35 (dd, 1H, J = 2, 7 Hz, CH), 3.73 (d, 1H, J = 2 Hz, CH), 5.33 (d, 1H, J = 10 Hz, CH), 5.51 (d, 1H, J = 17 Hz, CH), 5.73 (ddd, 1H, J = 7, 10, 17 Hz, CH), 7.25 - 7.12 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.1, 58.8, 59.8, 121.7, 126.4, 128.8, 132.0, 134.0, 137.4.

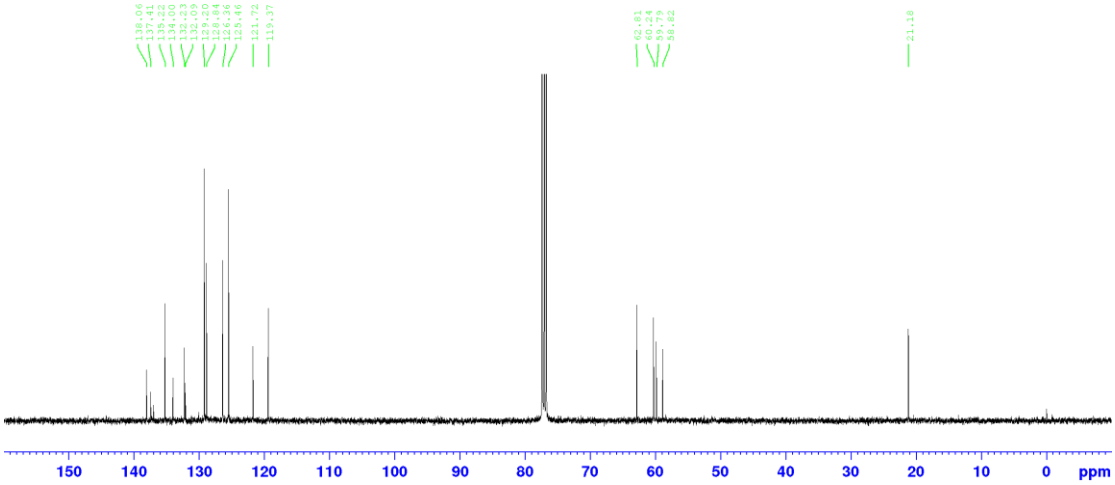
Z isomer:

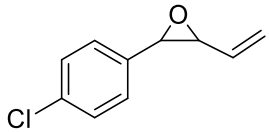
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.35 (s, 3H, CH_3), 3.64 (dd, 1H, J = 4, 8 Hz, CH), 4.21 (d, 1H, J = 5 Hz, CH), 5.27 (dd, 1H, J = 2, 10 Hz, CH), 5.41 (ddd, 1H, J = 8, 10, 17 Hz, CH), 5.54 (dd, 1H, J = 2, 17 Hz, CH), 7.25 - 7.12 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.2, 60.2, 62.8, 119.3, 125.5, 129.2, 132.2, 135.2, 138.0.

^{1}H NMR (400 MHz, $CDCl_3$) **8bb**



^{13}C NMR (101 MHz, $CDCl_3$) **8bb**





2-(4-chlorophenyl)-3-vinyloxirane **8bc**: E/Z = 35/65; colorless oil (lit.[6]); MS (ESI): Calcd for $C_{10}H_9ClO$ m/z = 180.03, Found: m/z = 181.10 $[M+H]^+$.

E isomer:

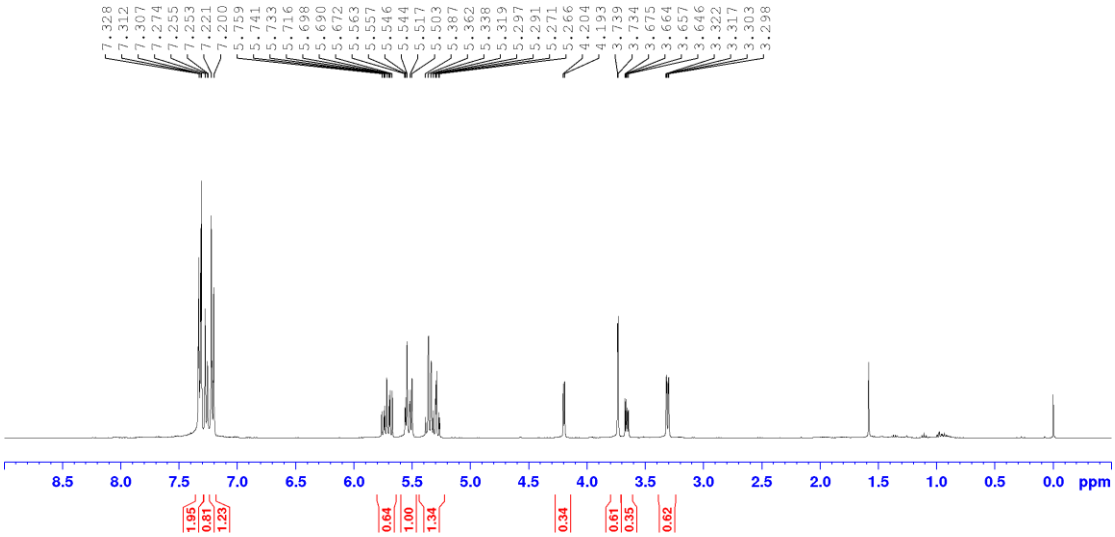
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.66 (dd, 1H, J = 4, 7 Hz, CH), 4.20 (d, 1H, J = 4 Hz, CH), 5.40 - 5.25 (m, 2H, CH), 5.59 - 5.48 (m, 1H), 7.27 (d, 2H, J = 8 Hz, CH), 7.38 - 7.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.2, 59.7, 122.1, 127.8, 128.3, 133.5, 134.0, 135.6.

Z isomer:

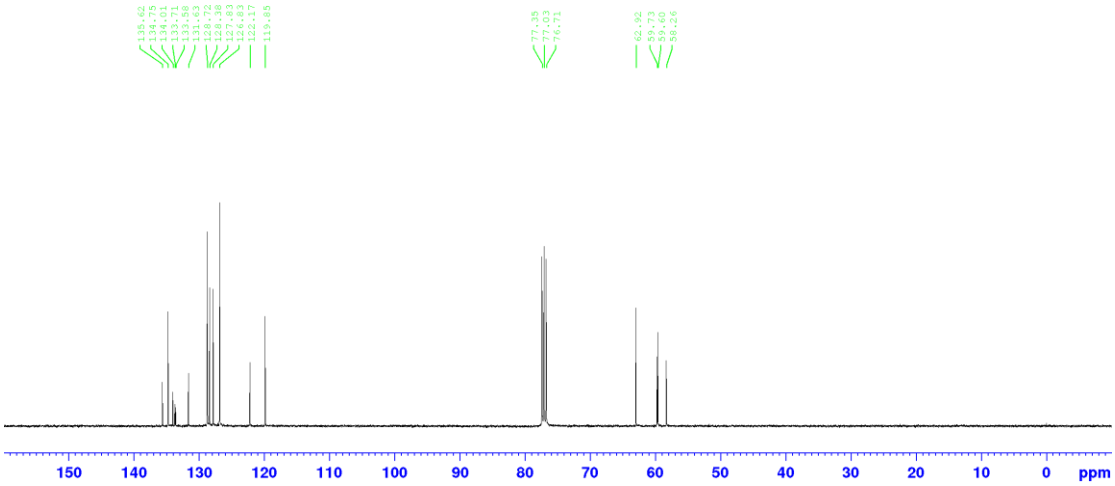
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.31 (dd, 1H, J = 2, 8 Hz, CH), 3.74 (d, 1H, J = 2 Hz, CH), 5.40 - 5.25 (m, 1H), 5.59 - 5.48 (m, 1H), 5.72 (ddd, 1H, J = 7, 10, 17 Hz,

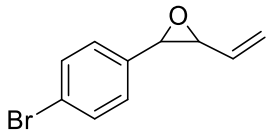
CH), 7.21 (d, 2H, J = 8 Hz, CH), 7.38 - 7.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ= 59.5, 62.9, 119.8, 126.8, 128.7, 131.6, 133.7, 134.7.

^{1}H NMR (400 MHz, $CDCl_3$) **8bc**



^{13}C NMR (101 MHz, $CDCl_3$) **8bc**





2-(4-bromophenyl)-3-vinyloxirane **8bd**: E/Z = 40/60; colorless oil (lit.[8]); MS (ESI): Calcd for $C_{10}H_9BrO$ m/z = 223.98, Found: m/z = 224.87 $[M+H]^+$.

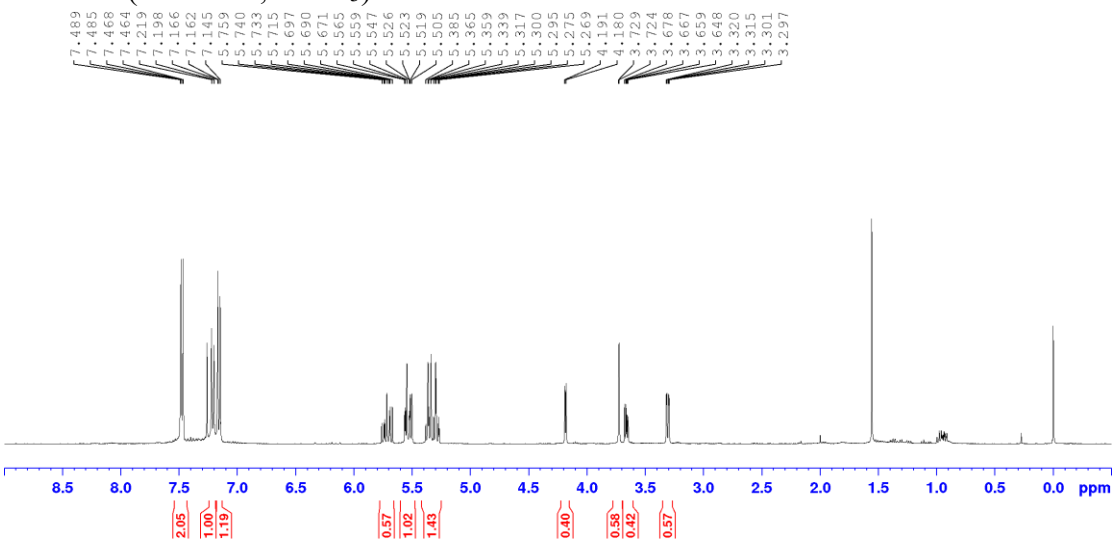
E isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.66 (dd, 1H, J = 4, 7 Hz, CH), 4.19 (d, 1H, J = 4 Hz, CH), 5.40 - 5.26 (m, 2H, CH), 5.58 - 5.48 (m, 1H), 7.21 (d, 2H, J = 8 Hz, ArH), 7.51 - 7.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ= 58.3, 59.6, 121.7, 122.1, 128.2, 131.6, 134.2, 136.1.

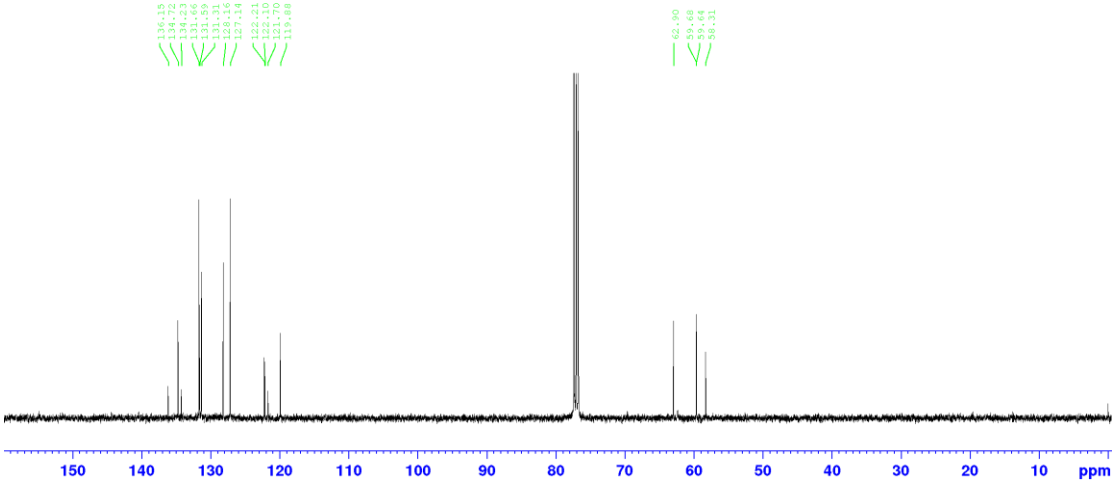
Z isomer:

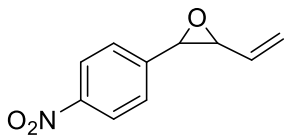
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.31 (dd, 1H, J = 2, 7 Hz, CH), 3.73 (d, 1H, J = 2 Hz, CH), 5.40 - 5.26 (m, 1H), 5.58 - 5.48 (m, 1H), 5.72 (ddd, 1H, J = 7, 10, 17 Hz, CH), 7.16 (d, 2H, J = 8 Hz, ArH), 7.51 - 7.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 59.6, 62.9, 119.9, 122.2, 127.1, 131.5, 131.6, 134.7.

^{1}H NMR (400 MHz, $CDCl_3$) **8bd**



^{13}C NMR (101 MHz, $CDCl_3$) **8bd**





2-(4-nitrophenyl)-3-vinyloxirane **8bf**: E/Z = 35/65; pale yellow oil (lit.[7] mp. 54-56°C); MS (ESI): Calcd for $C_{10}H_9NO_3$ m/z = 191.06, Found: m/z = 191.10 $[M+H]^+$.

E isomer:

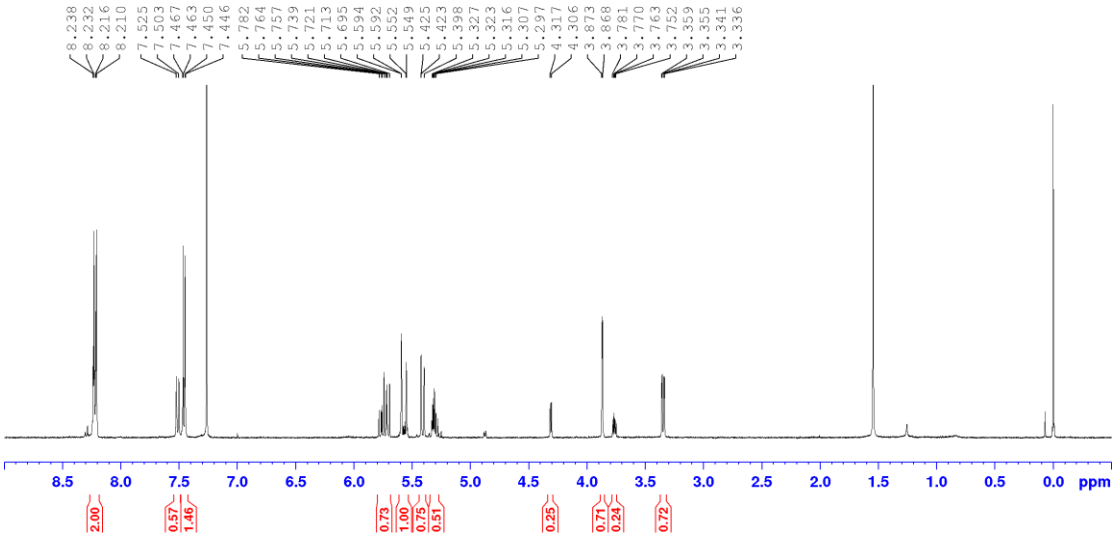
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.77 (dd, 1H, J = 4, 7 Hz, CH), 4.31 (d, 1H, J = 4 Hz, CH), 5.34 - 5.27 (m, 2H), 5.61 - 5.53 (m, 1H), 7.52 (d, 2H, J = 9 Hz, ArH), 8.25 -

8.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.0, 59.9, 122.8, 123.4, 130.8, 134.1, 147.8.

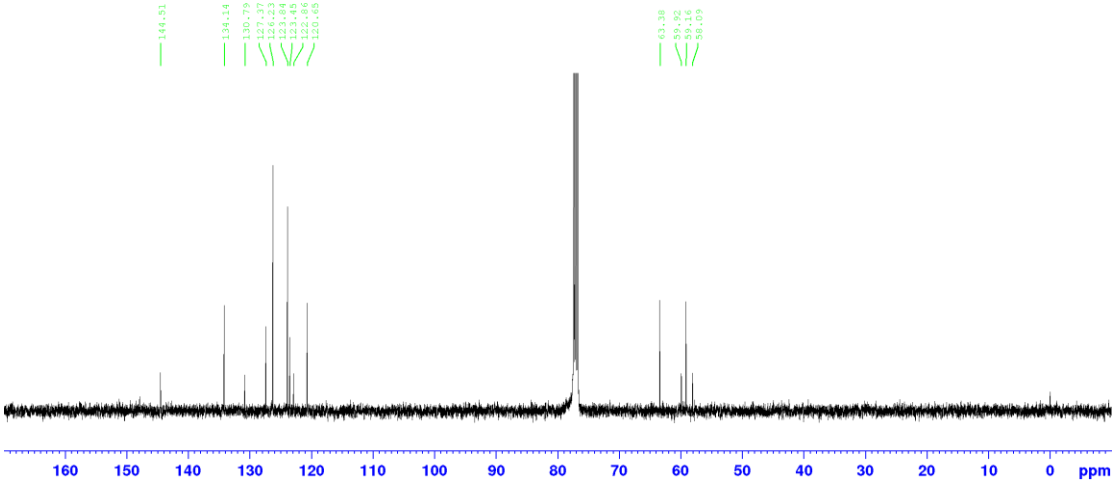
Z isomer:

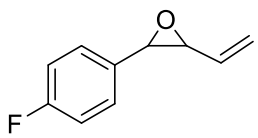
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.35 (dd, 1H, J = 2, 7 Hz, CH), 3.87 (d, 1H, J = 2 Hz, CH), 5.41 (d, 1H, J = 10 Hz, CH), 5.61 - 5.53 (m, 1H), 5.74 (ddd, 1H, J = 7, 10, 17 Hz, CH), 7.46 (d, 2H, J = 9 Hz, ArH), 8.25 - 8.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 59.1, 63.4, 120.6, 123.8, 126.2, 134.1, 144.5.

^{1}H NMR (400 MHz, $CDCl_3$) **8bf**



^{13}C NMR (101 MHz, $CDCl_3$) **8bf**





2-(4-fluorophenyl)-3-vinyloxirane **8bg**: E/Z = 35/65; colorless oil (lit.[8]); MS (ESI): Calcd for $C_{10}H_9FO$ m/z = 164.06, Found: m/z = 164.12 $[M+H]^+$.

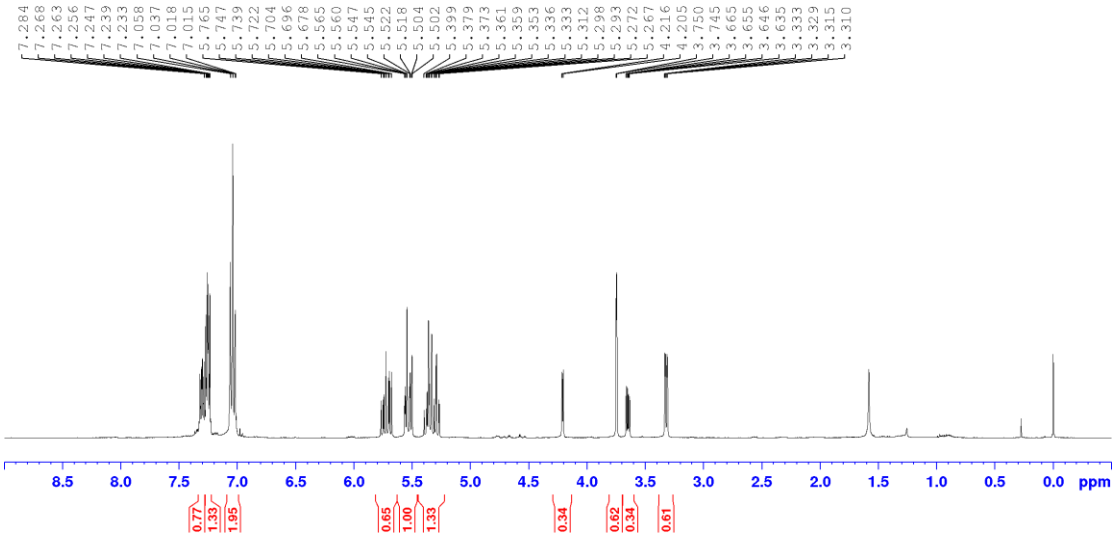
E isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.65 (dd, 1H, J = 4, 8 Hz, CH), 4.21 (d, 1H, J = 4 Hz, CH), 5.41 - 5.25 (m, 2H), 5.59 - 5.49 (m, 1H), 7.04 (m, 2H), 7.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 58.3, 59.7, 115.1 (d, $J_{C\text{-}F}$ = 22 Hz), 122.0, 128.0 (d, $J_{C\text{-}F}$ = 8 Hz), 130.7 (d, $J_{C\text{-}F}$ = 4 Hz), 131.7, 162.3 (d, $J_{C\text{-}F}$ = 246 Hz).

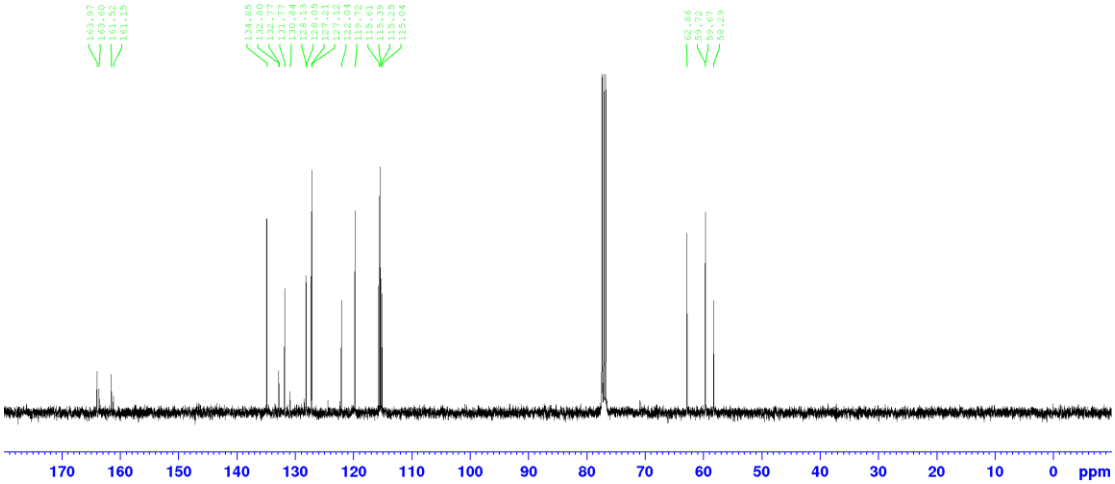
Z isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.32 (dd, 1H, J = 2, 7 Hz, CH), 3.75 (d, 1H, J = 2 Hz, CH), 5.41 - 5.25 (m, 1H), 5.59 - 5.49 (m, 1H), 5.72 (ddd, 1H, J = 7, 10, 17 Hz, CH), 7.08 - 7.00 (m, 2H), 7.27 - 7.23 (m, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ = 59.6, 62.8, 115.5 (d, $J_{C\text{-}F}$ = 22 Hz), 119.7, 127.1 (d, $J_{C\text{-}F}$ = 8 Hz), 133.7 (d, $J_{C\text{-}F}$ = 4 Hz), 134.8, 162.7 (d, $J_{C\text{-}F}$ = 246 Hz).

^{1}H NMR (400 MHz, $CDCl_3$) **8bg**



^{13}C NMR (101 MHz, $CDCl_3$) **8bg**



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