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Supporting Information

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Supporting Information

Electro-Initiated Cation Chain Reaction. Intramolecular Carbon-Carbon Bond Formation between Thioacetal and Olefin

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General Remarks.

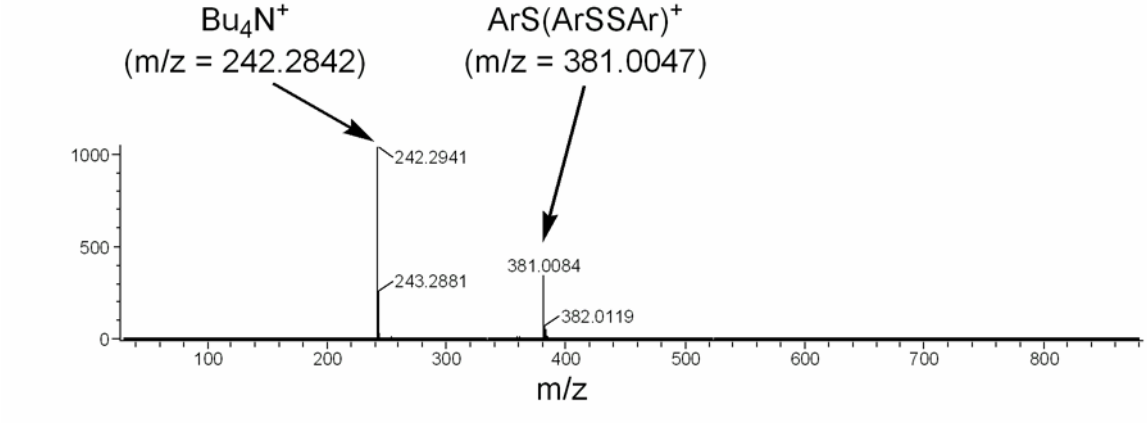
GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (column, CBP1; 0.25 mm x 25 m; initial oven temperature, 100 °C; rate of temperature increase, 10 °C/min). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 2000 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), or JEOL ECA-600P (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer with Me_4Si as an internal standard unless otherwise noted. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMX-HX110A spectrometer. CSI (cold-spray ionization) mass spectrum was recorded on a JEOL JMS-T100CSK spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm). Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluent. All reactions were carried out under Ar atmosphere unless otherwise noted.

Materials.

Bu_4NBF_4 was purchased from TCI and dried at 50 °C/1 mmHg overnight. $Bu_4NB(C_6F_5)_4$ was prepared from Bu_4NBr (35.1 g, 109 mmol) and aqueous solution of $NaB(C_6F_5)_4$ (10 wt%, 499 g, 71.1 mmol) in water (100 mL). The mixture was diluted with EtOAc and was washed with water. After dring over $MgSO_4$ and removal of solvent, the precipitate was recrystallized from $CHCl_3$/hexane and dried at 50 °C/1 mmHg overnight to give $Bu_4NB(C_6F_5)_4$ (65.1 g, 70.6 mmol, 99%). Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Dry THF was used as obtained (Kanto Chemical Co., Inc.). ArSSAr (Ar = *p*-FC_6H_4) was prepared according to the procedure in the literature,[1] and identified by the comparison of its spectral data with that of authentic sample. [2]

Electrochemical Generation and Accumulation of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Ar = *p*-FC_6H_4). Typical Procedure and CSI-MS Analysis.

The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (103 mg, 0.405 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (44.2 mg, 0.295 mmol). The constant current electrolysis (8 mA) was carried out at -78 °C with magnetic stirring until 0.67 F/mol of electricity was consumed. The anodic solution thus obtained was analyzed by CSI-MS (spray temperature; 0 °C): HRMS (CSI) calcd for $C_{18}H_{12}F_3S_3^+$ ($ArS(ArSSAr)^+$ (Ar = *p*-FC_6H_4), M^+): 381.0047, found: 381.0084.

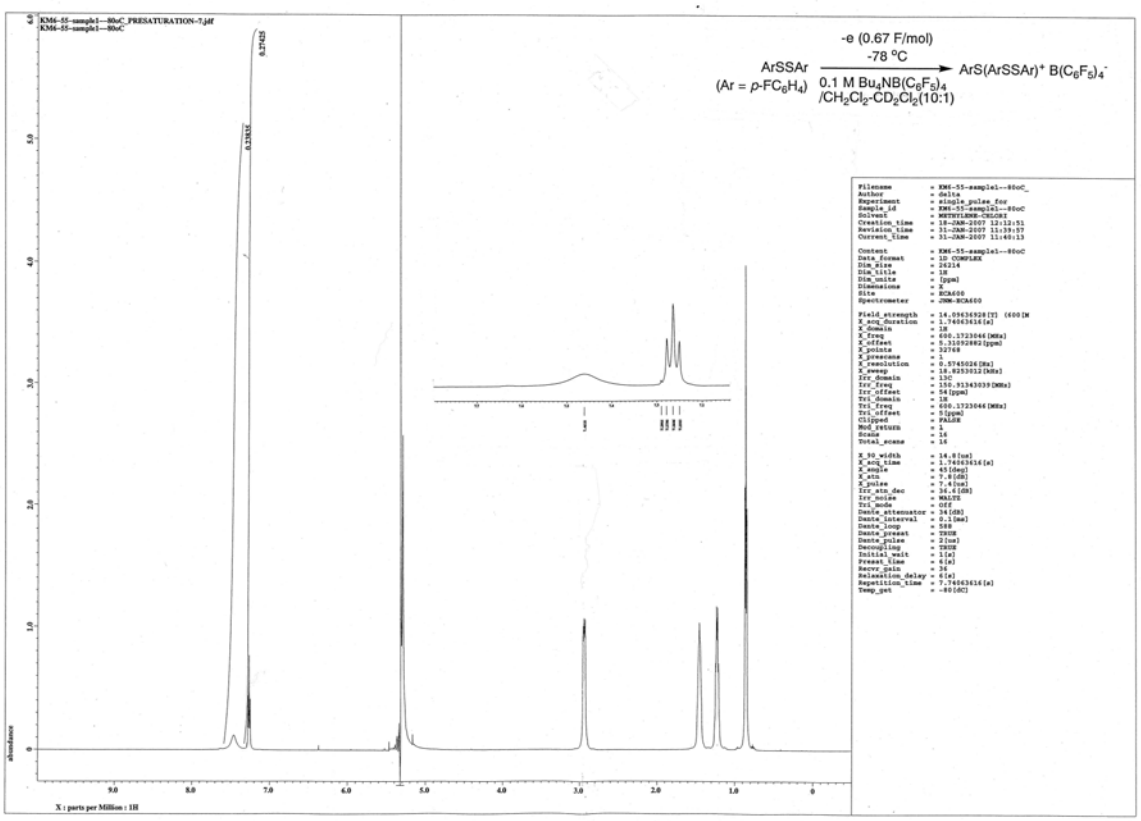


CSI-MS of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Ar = *p*-FC_6H_4) (spray temperature; 0 °C).

NMR Analysis of Electrochemically Generated $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Ar = *p*-FC_6H_4).

The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (51.4 mg, 0.202 mmol) in 4.0 mL of 0.1 M

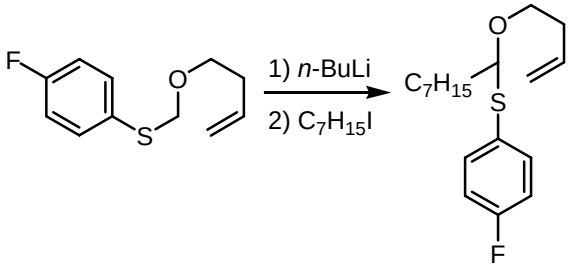
$Bu_4NB(C_6F_5)_4$ in CH_2Cl_2/CD_2Cl_2 (10:1). In the cathodic chamber were placed trifluoromethanesulfonic acid (23.5 mg, 0.157 mmol) and 0.1 M $Bu_4NB(C_6F_5)_4$ in CH_2Cl_2/CD_2Cl_2 (10:1) (4.0 mL). The constant current electrolysis (4.0 mA) was carried out at -78 °C with magnetic stirring. After 0.67 F/mol of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm ϕ NMR tube equipped with a septum cap under Ar atmosphere at -78 °C. The NMR measurement was carried out at -80 °C. Chemical shifts are reported using the methylene signal of CH_2Cl_2 at δ 5.32 (^{1}H NMR) as a standard. The huge signal coming from CH_2Cl_2 is reduced by usual pulse techniques: [3] ^{1}H NMR (600 MHz, CH_2Cl_2/CD_2Cl_2 (10:1)) δ 7.22-7.30 (t, *J* = 8.6 Hz, 6H), 7.35-7.60 (br s, 6H). Thus obtained ^{1}H NMR spectrum was very similar to that of $ArS(ArSSAr)^+BF_4^-$ [4].



^{1}H NMR spectrum of electrochemically generated $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Ar = *p*-FC_6H_4) (-80 °C).

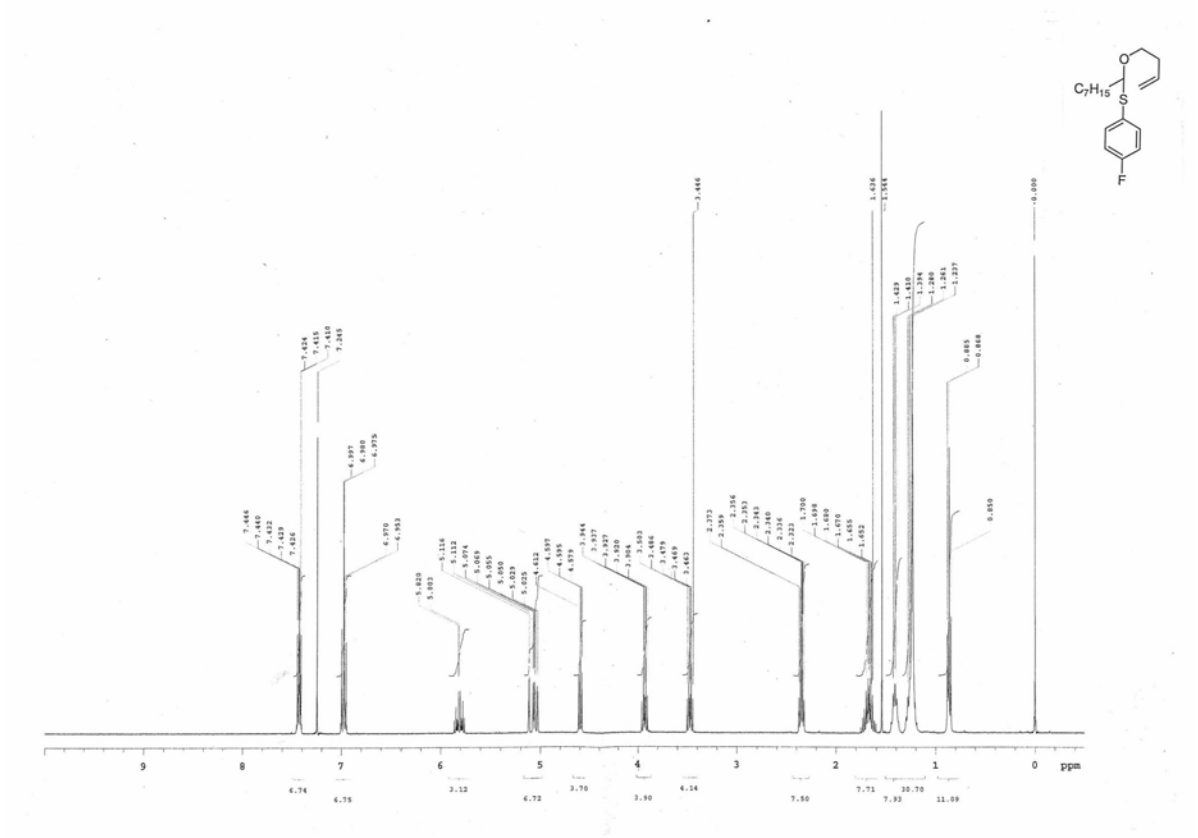
Synthesis of Thioacetals Having a Carbon-Carbon Double Bond.

3-Butenyl 1-(4-fluorophenylthio)octyl ether (6a).

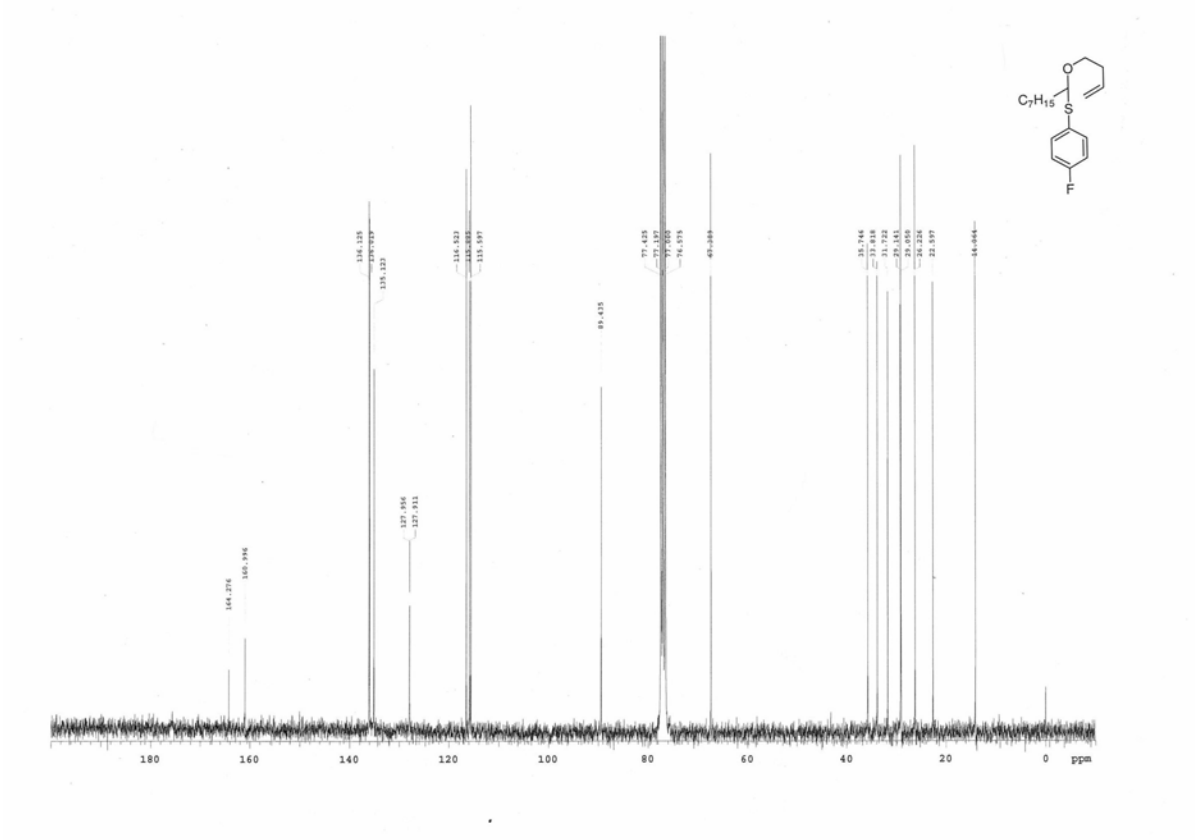


To a solution of 3-butenyl 4-fluorophenylthiomethyl ether (**6g**) (*vide infra*) (5.30 g, 25.0 mmol) in THF (50 mL) was added *n*-BuLi (1.40 M in hexane, 20.0 mL, 28.0 mmol) at -78 °C. The mixture was stirred at -48 °C for 1.5 h and then cooled to -78 °C. 1-Iodoheptane (7.40 g, 32.7 mmol) was added, and the mixture was stirred at -78 °C for 3 h and then at room temperature overnight. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 20:1) to give the title compound (**6a**) (1.31 g, 4.22 mmol, 17 %): TLC R_f 0.46 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.16-1.32 (m, 8H), 1.34-1.46 (m, 2H), 1.58-1.76 (m, 2H), 2.35 (tddd, *J* = 6.8, 6.8, 1.2, 1.2 Hz, 2H), 3.47 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.93 (dt, *J* = 9.6, 6.8 Hz, 1H), 4.60 (t, *J* = 6.0 Hz, 1H), 5.04 (ddt, *J* = 10.2, 1.2, 1.2 Hz, 1H), 5.09 (ddt, *J* = 17.0, 1.2, 1.2 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 6.94-7.02 (m, 2H), 7.40-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 26.2, 29.05, 29.14, 31.7, 33.8, 35.7, 67.4, 89.4, 115.7 (d, *J* = 21.6 Hz), 116.5, 127.9 (d, *J* = 3.4 Hz), 135.1, 136.1 (d, *J* = 8.0 Hz), 162.6 (d, *J* = 246.0

Hz); IR (neat) 2928, 1590, 1489, 830 cm^{-1}; LRMS (CI) m/z 309 (M^+-H), 239 (M^+-$OCH_2CH_2CH{=}CH_2$), 183 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{18}H_{26}FOS$ (M^+-H) 309.1688, found 309.1681.

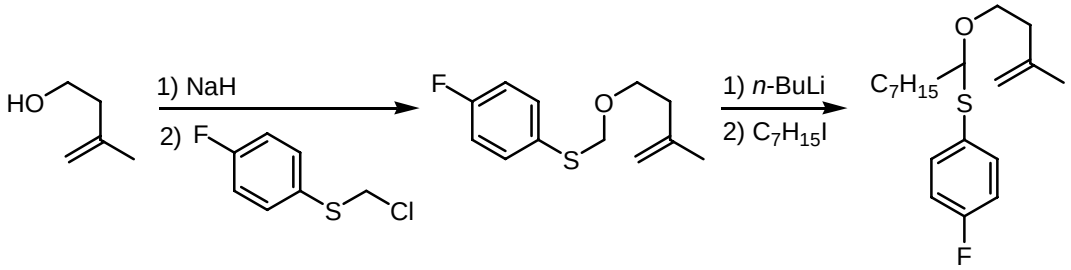


^{1}H NMR spectrum of 3-butenyl 1-(4-fluorophenylthio)octyl ether (**6a**).

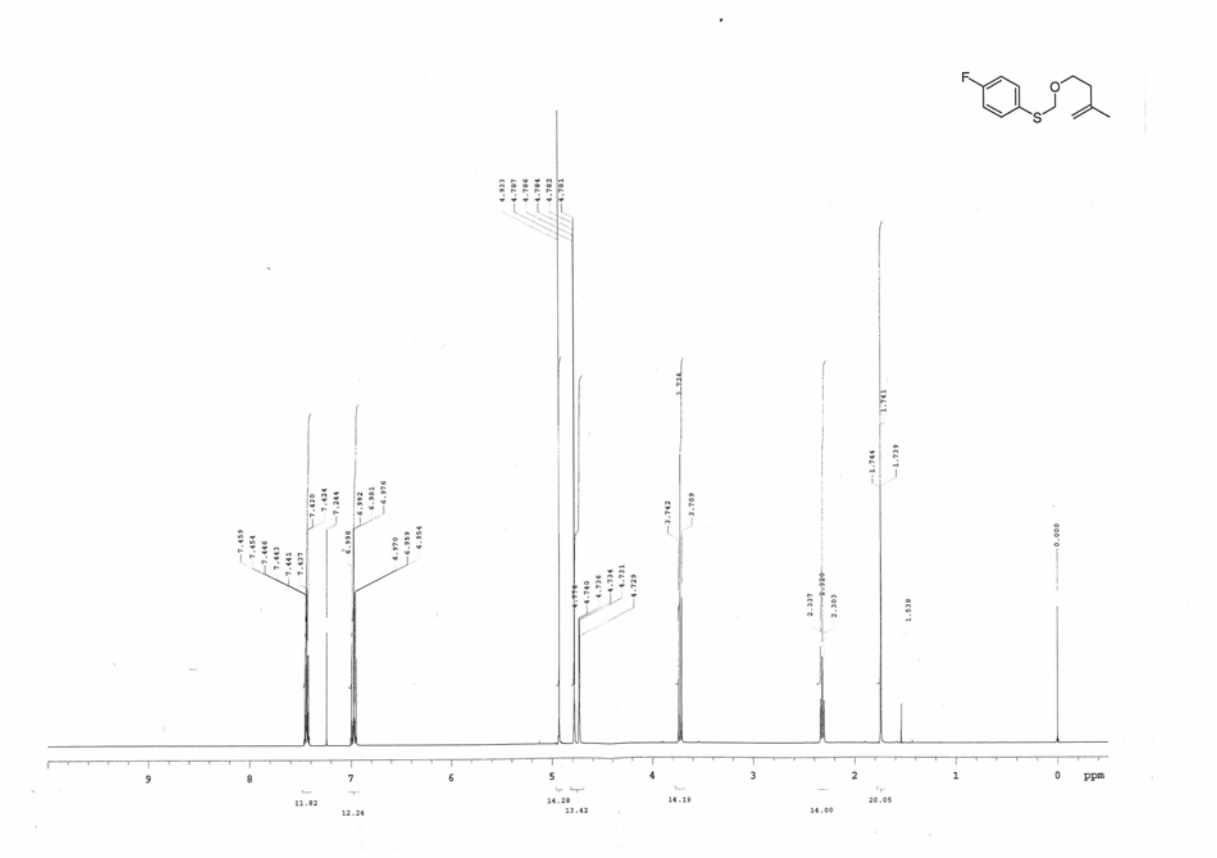


^{13}C NMR spectrum of 3-butenyl 1-(4-fluorophenylthio)octyl ether (**6a**).

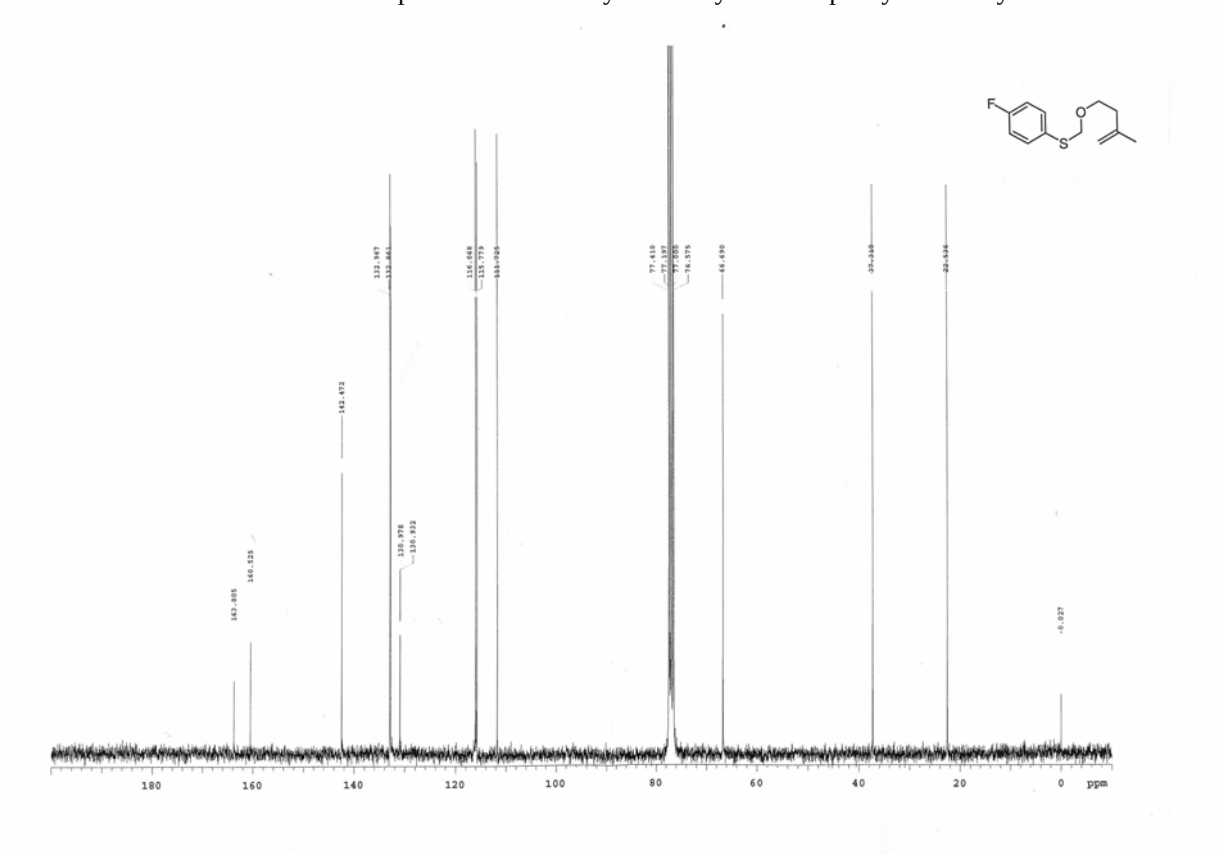
3-Methyl-3-butenyl 1-(4-fluorophenylthio)octyl ether (6b).



To a solution of NaH (55 % in oil, 2.10 g, 48.1 mmol) in THF (20 mL) was added 3-methyl-3-buten-1-ol (3.86 g, 44.8 mmol) at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 1 h and chloromethyl 4-fluorophenyl sulfide (*vide infra, see the synthesis of* ***6g***) (10.0 g, 47.1 mmol) and tetrabutylammonium iodide (638 mg, 1.73 mmol) was added to the mixture, and was stirred at room temperature overnight. Methanol (3.0 mL) was added, and the reaction mixture was partitioned between ether and saturated brine. The organic phase was separated, washed with saturated brine, and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by distillation (108 ^{o}C, 1.79 mmHg) to give 3-methyl-3-butenyl 4-fluorophenylthiomethyl ether (4.13 g, 18.2 mmol, 41 %): TLC R_f 0.36 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 2.32 (t, *J* = 6.8 Hz, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 4.70-4.80 (m, 2H), 4.93 (s, 2H), 6.92-7.02 (m, 2H), 7.40-7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5, 37.3, 66.7, 111.7, 115.9 (d, *J* = 21.7 Hz), 131.0 (d, *J* = 3.5 Hz), 132.9 (d, *J* = 8.0 Hz), 142.5, 162.2 (d, *J* = 246.0 Hz). One signal could not be assigned due to the signal overlap. In order to assign all the signals, CD_2Cl_2 was used as solvent; ^{13}C NMR (150 MHz, CD_2Cl_2) δ 22.6, 37.7, 67.1, 77.2, 111.7, 116.2 (d, *J* = 21.5 Hz), 131.6 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 7.2 Hz), 143.2, 162.4 (d, *J* = 244.2 Hz); IR (neat) 1590, 1491, 828 cm^{-1}; LRMS (EI) m/z 226 (M^+), 141 (M^+-$OCH_2CH_2C(CH_3)CH_2$); HRMS (EI) calcd for $C_{12}H_{15}FOS$ (M^+) 226.0828, found 226.0828.



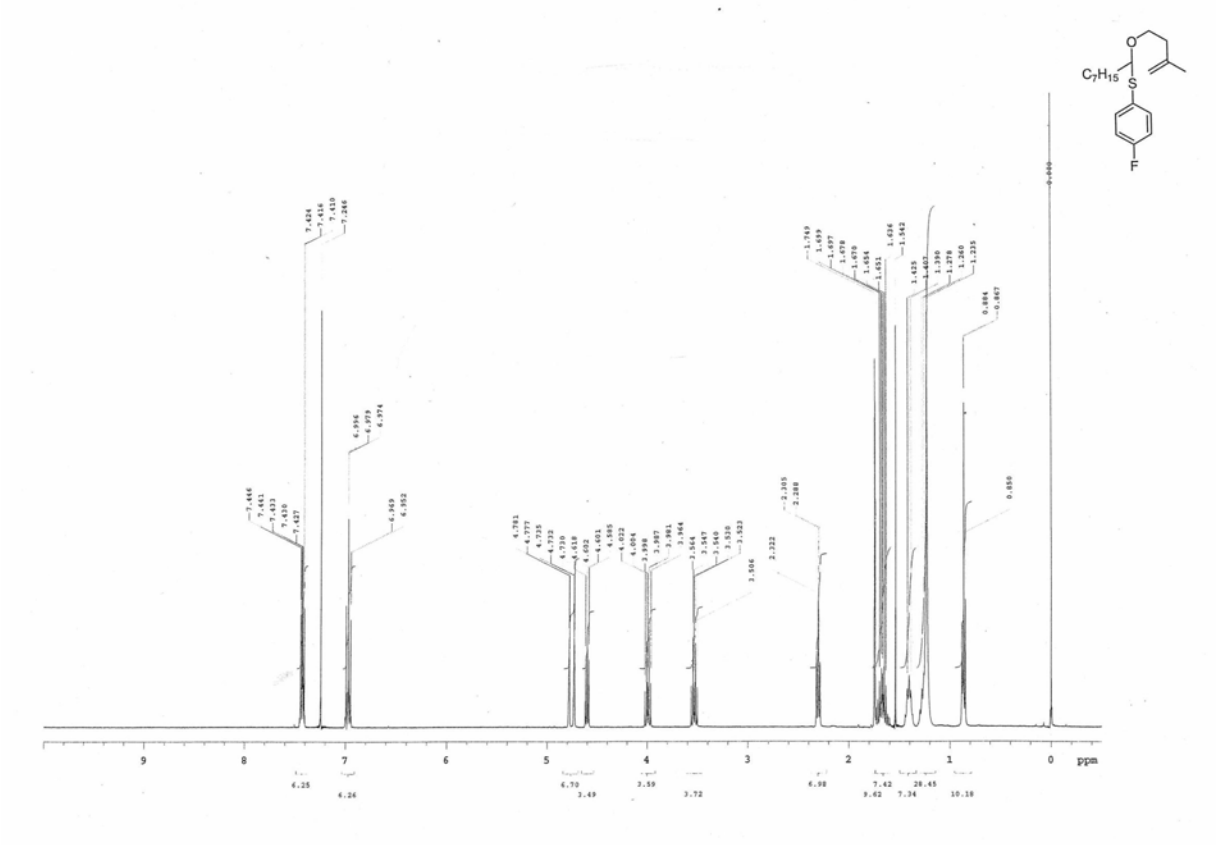
^{1}H NMR spectrum of 3-methyl-3-butenyl 4-fluorophenylthiomethyl ether.



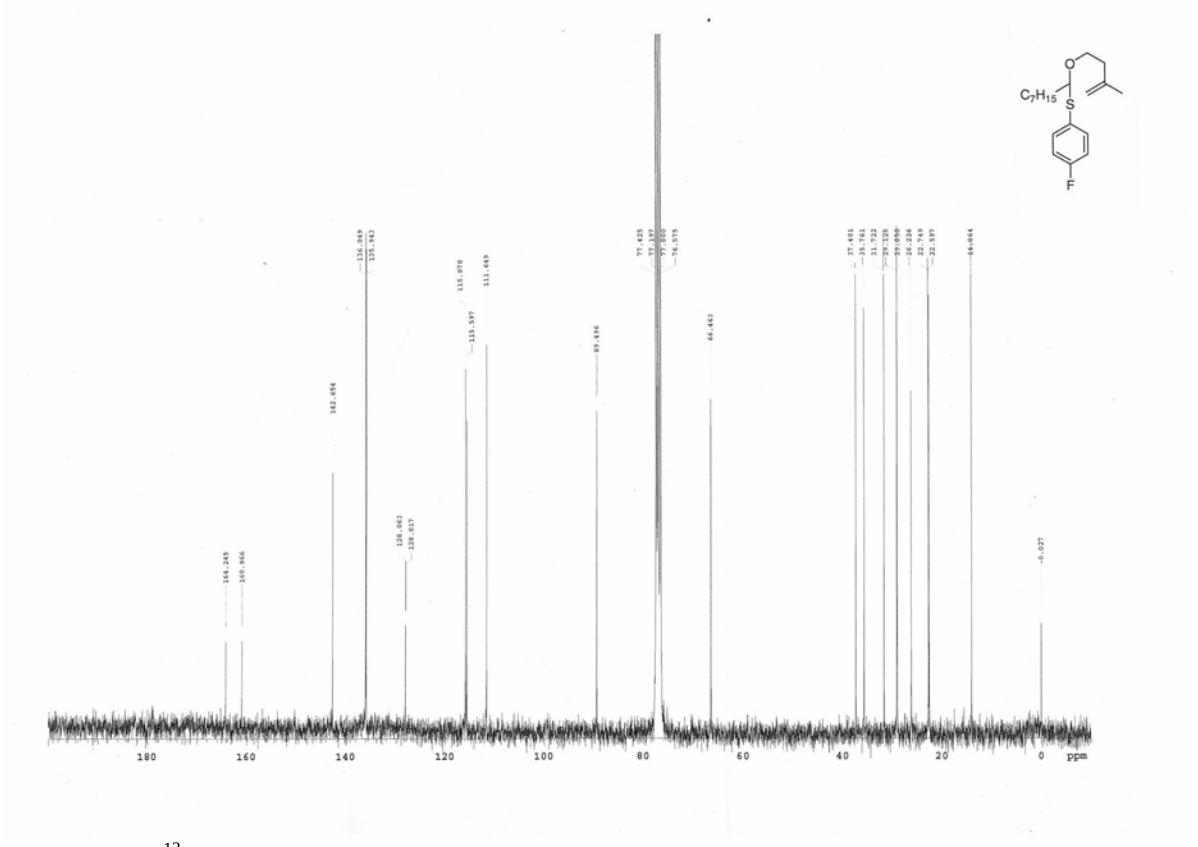
^{13}C NMR spectrum of 3-methyl-3-butenyl 4-fluorophenylthiomethyl ether.

To a solution of 3-methyl-3-butenyl 4-fluorophenylthiomethyl ether (1.47 g, 6.50 mmol) in THF (10 mL) was added *n*-BuLi (1.58 M in hexane, 5.1 mL, 8.06 mmol) at -78 ^{o}C. The mixture was stirred at -48 °C for 1 h and then cooled to -78 °C. 1-Iodoheptane (1.93 g, 8.54 mmol) was added and the mixture was stirred at -78 ^{o}C for 3 h and at room temperature overnight. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and

washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 20:1) to give the title compound (**6b**) (800 mg, 2.47 mmol, 38 %): TLC R_f 0.38 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.16-1.32 (m, 8H), 1.34-1.46 (m, 2H), 1.60-1.74 (m, 2H), 1.75 (s, 3H), 2.31 (t, *J* = 6.8 Hz, 2H), 3.54 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.99 (dt, *J* = 9.6, 6.8 Hz, 1H), 4.60 (t, *J* = 6.6 Hz, 1H), 4.70-4.80 (m, 2H), 6.94-7.02 (m, 2H), 7.40-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 22.7, 26.2, 29.05, 29.13, 31.7, 35.8, 37.4, 66.5, 89.5, 111.6, 115.7 (d, *J* = 20.5 Hz), 128.0 (d, *J* = 3.5 Hz), 136.0 (d, *J* = 8.0 Hz), 142.7, 162.6 (d, *J* = 245.9 Hz); IR (neat) 2926, 1489, 830 cm^{-1}; LRMS (CI) m/z 323 (M^+-H), 239 (M^+-$OCH_2CH_2C(CH_3)=CH_2$), 197 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{19}H_{28}FOS$ (M^+-H) 323.1845, found 323.1855.

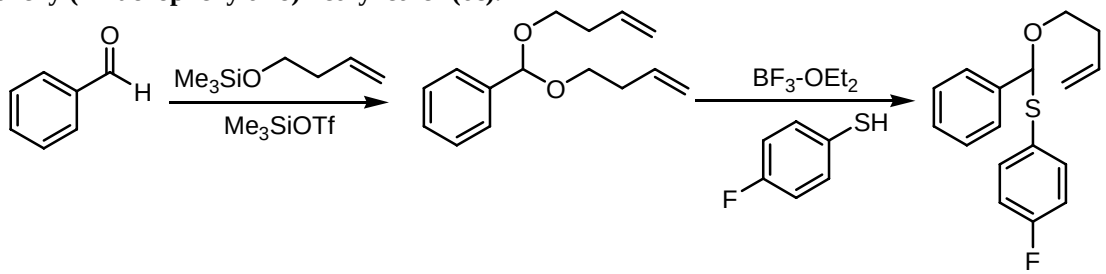


^{1}H NMR spectrum of 3-methyl-3-butenyl 1-(4-fluorophenylthio)octyl ether (**6b**).



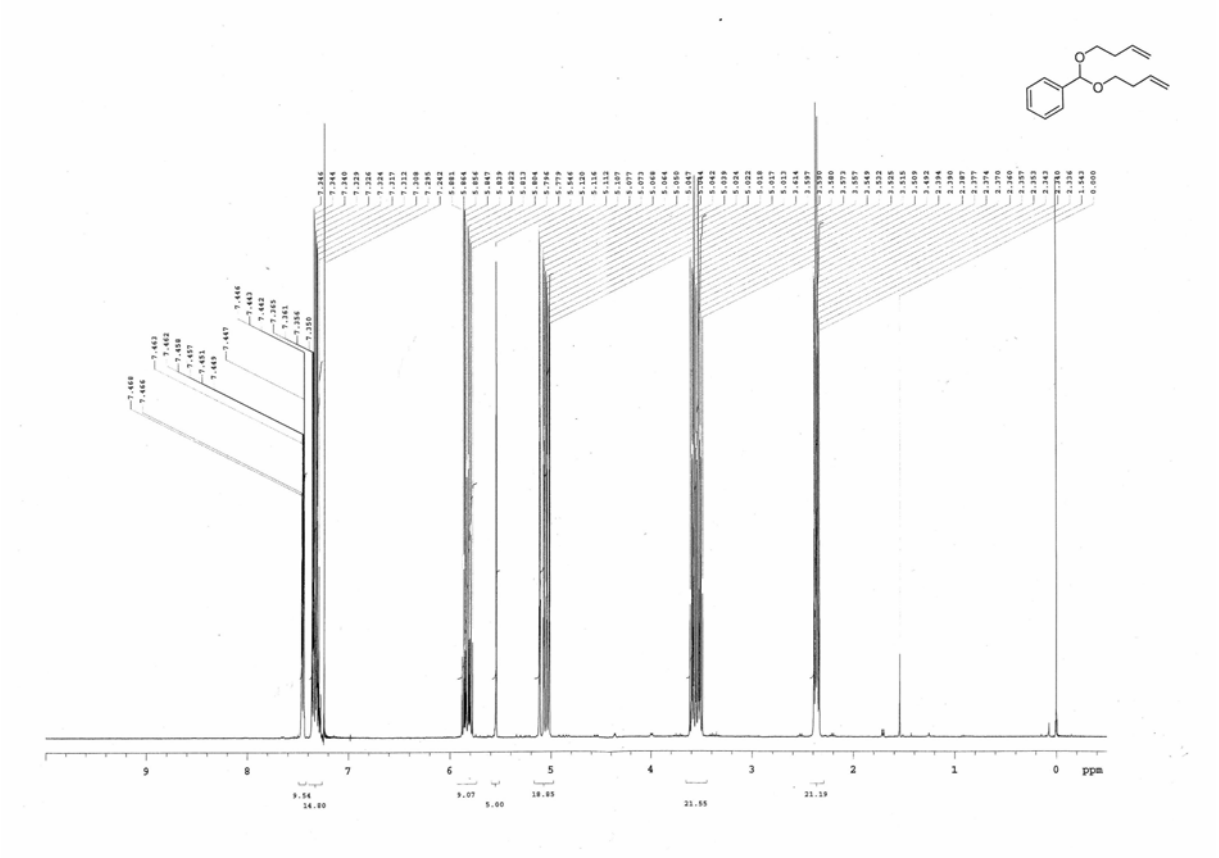
^{13}C NMR spectrum of 3-methyl-3-butenyl 1-(4-fluorophenylthio)octyl ether (**6b**).

3-Butenyl phenyl(4-fluorophenylthio)methyl ether (6c).

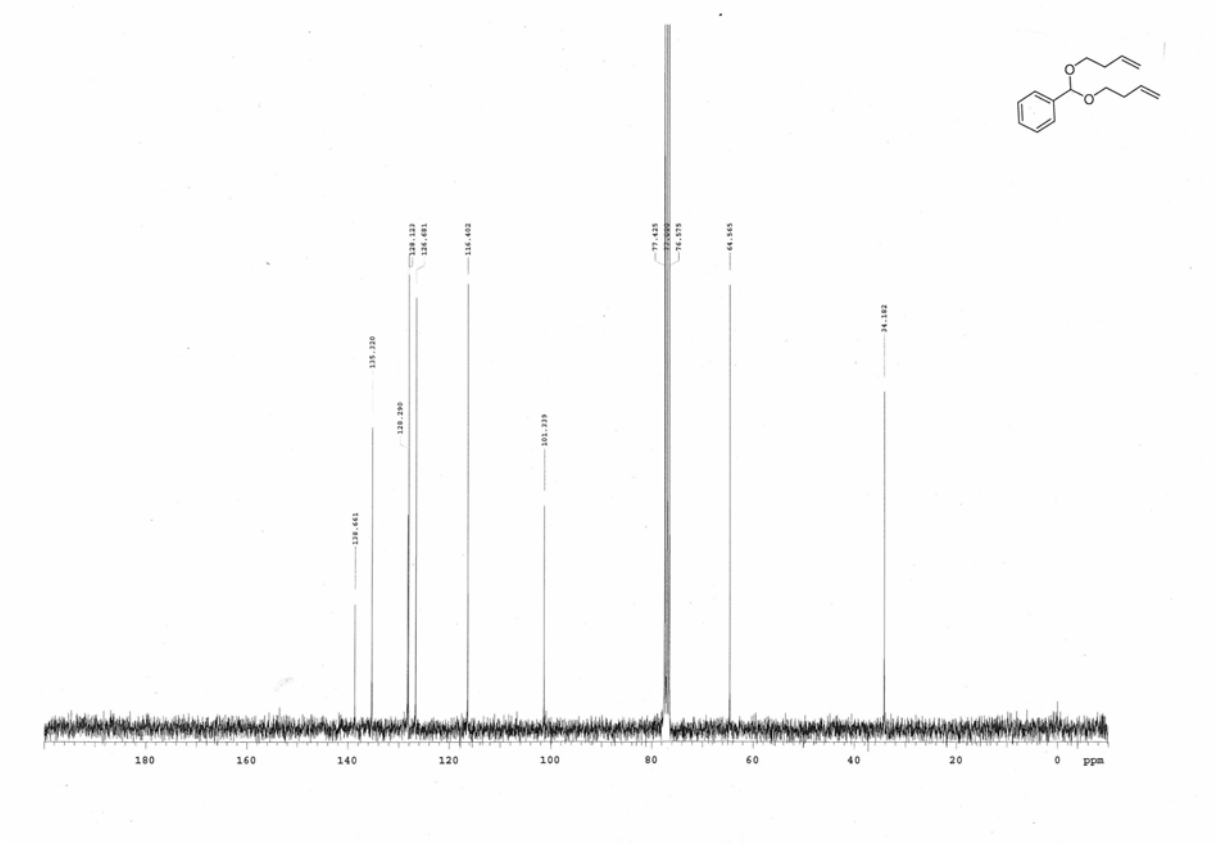


To a solution of *N*,*N*-dimethylaniline (47.0 g, 386 mmol) in Et_2O (160 mL) was added Me_3SiCl (41.7 g, 384 mmol) at 0 ^oC. Then, 3-buten-1-ol (27.7 g, 384 mmol) was added with vigorous stirring at the same temperature. The mixture was then refluxed for 3 h. The hydrochloride formed was filterd off, and the filtrate was distilled (105 ^oC, 760 mmHg) to give 3-butenyloxytrimethylsilane (23.8 g, 165 mmol, 43 %).[5]

To a solution of benzaldehyde (1.60 g, 15.1 mmol) and 3-butenyloxytrimethylsilane (4.40 g, 30.5 mmol) in CH_2Cl_2 (30 mL) was added Me_3SiOTf (368 mg, 1.66 mmol) at -78 ^oC. Then, the mixture was stirred at -25 ^oC overnight. The reaction mixture was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 50:1) to give the (bis(3-butenyloxy))phenylmethane (2.37 g, 10.2 mmol, 68 %): TLC R_f 0.29 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (tddd, *J* = 6.4, 6.4, 1.6, 1.6 Hz, 4H), 3.52 (dt, *J* = 9.2, 6.4 Hz, 2H), 3.59 (dt, *J* = 9.2, 6.4 Hz, 2H), 5.03 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 2H), 5.09 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 2H), 5.55 (s, 1H), 5.83 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 2H), 7.27-7.37 (m, 3H), 7.43-7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.2, 64.6, 101.3, 116.4, 126.7, 128.1, 128.3, 135.3, 138.7; IR (neat) 2928, 1642, 704 cm^{-1}; LRMS (EI) m/z 231 (M^+-H), 161 (M^+-$OCH_2CH_2CH{=}CH_2$); HRMS (FAB) calcd for $C_{15}H_{19}O_2$ (M^+-H) 231.1385, found 231.1396.



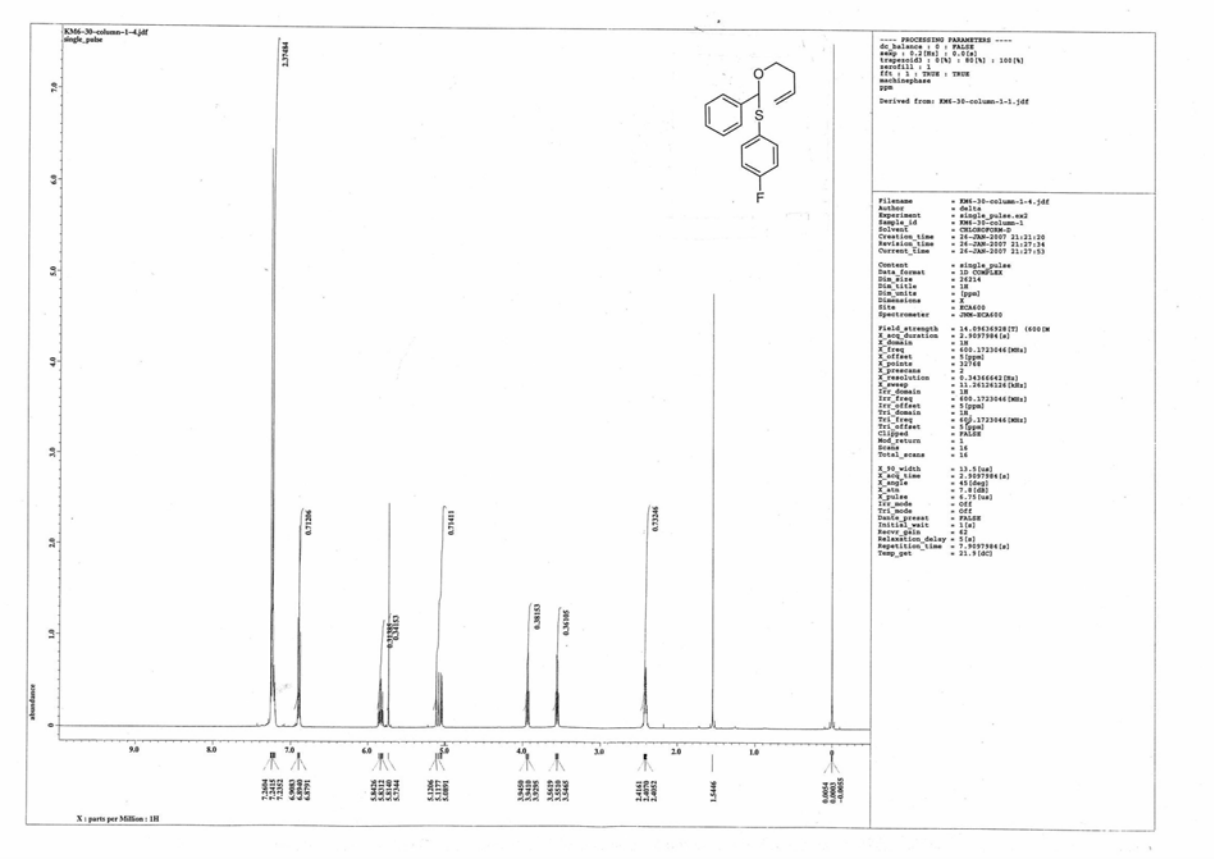
^{1}H NMR spectrum of (bis(3-butenyloxy))phenylmethane.



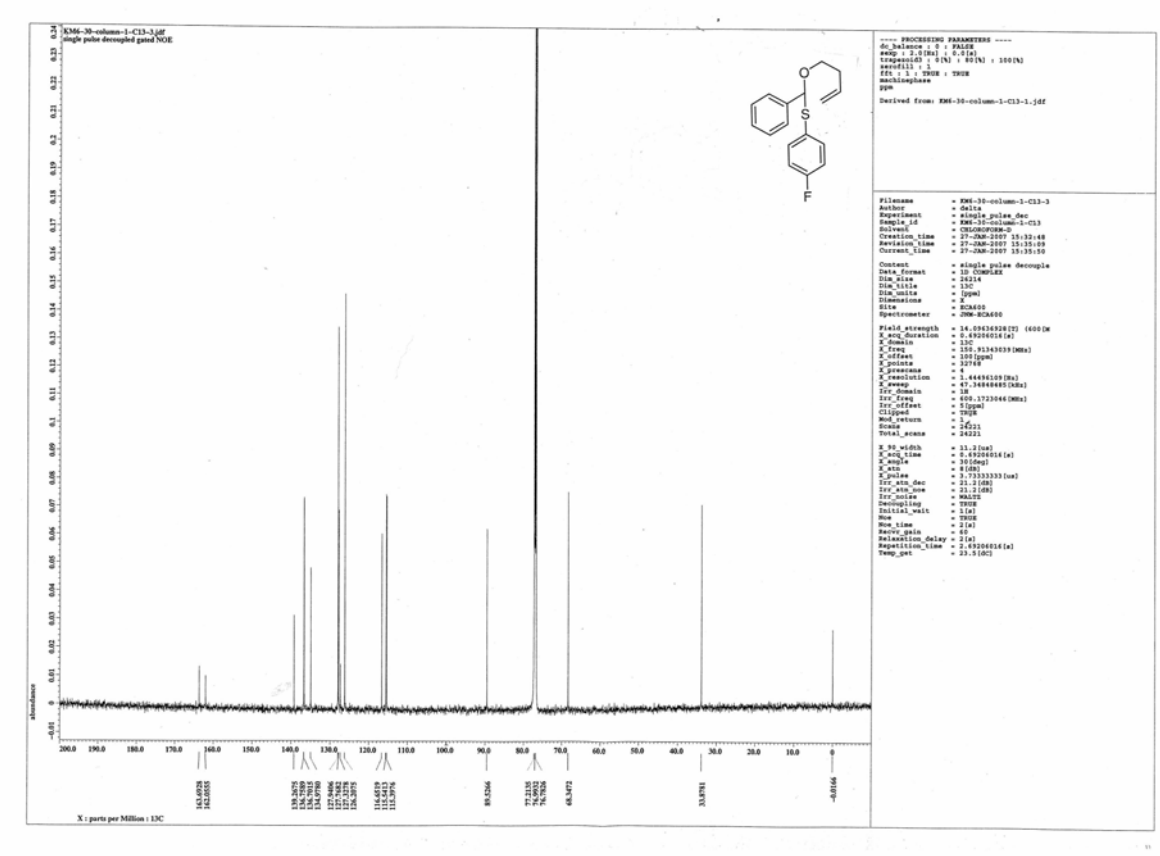
^{13}C NMR spectrum of (bis(3-butenyloxy))phenylmethane.

To a solution of (bis(3-butenyloxy))phenylmethane (881 mg, 3.79 mmol) and *p*-fluorothiophenol (541 mg, 4.22 mmol) in toluene (50 mL) was added BF_3-OEt_2 (694 mg, 4.89 mmol) at -78 ^{o}C. The solution was stirred for 2 h and Et_3N (2.0 mL) was added. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the crude product

was purified via flash chromatography (hexane/EtOAc 20:1) to give the title compound (**6c**) (823 mg, 2.85 mmol, 75 %): TLC R_f 0.34 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.35-2.47 (m, 2H), 3.55 (dt, *J* = 9.2, 6.5 Hz, 1 H), 3.94 (dt, *J* = 9.2, 6.5 Hz, 1H), 5.03-5.14 (m, 2H), 5.73(s, 1H), 5.84 (ddt, *J* = 17.2, 10.3, 6.5 Hz, 1H), 6.87-6.92 (m, 2H), 7.19-7.27 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.9, 68.3, 89.5, 115.5 (d, *J* = 21.6 Hz), 116.7, 126.2, 127.3, 127.8, 127.9, 135.0, 136.7 (d, *J* = 8.6 Hz), 139.3, 162.9 (d, *J* = 245.6 Hz); IR (neat) 1590, 1489, 698 cm^{-1}; LRMS (CI) m/z 289 (MH^+), 217 (M^+-$OCH_2CH_2CH{=}CH_2$), 161 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{17}H_{18}FOS$ (MH^+) 289.1062, found 289.1064.

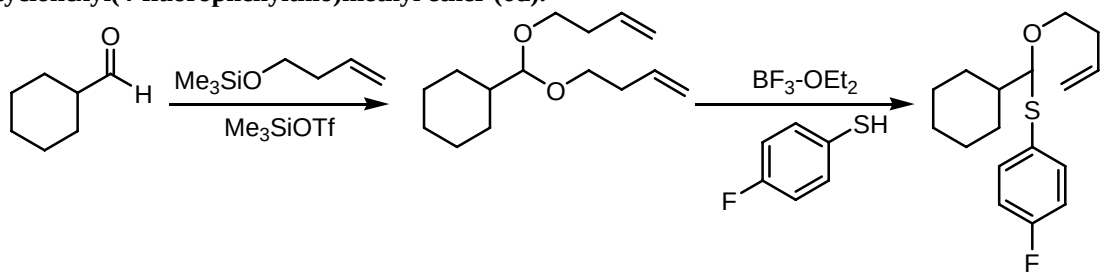


^{1}H NMR spectrum of 3-butenyl phenyl(4-fluorophenylthio)methyl ether (**6c**).

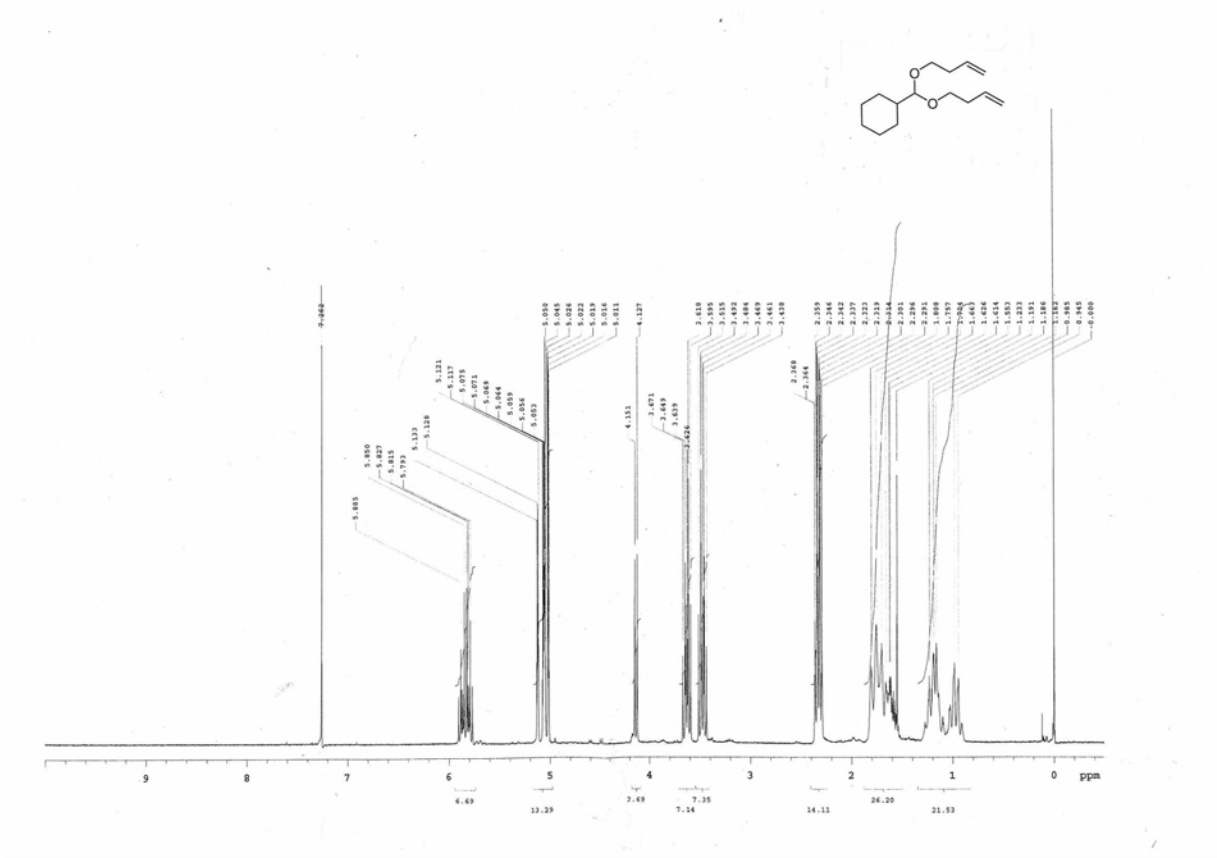


^{13}C NMR spectrum of 3-butenyl phenyl(4-fluorophenylthio)methyl ether (**6c**).

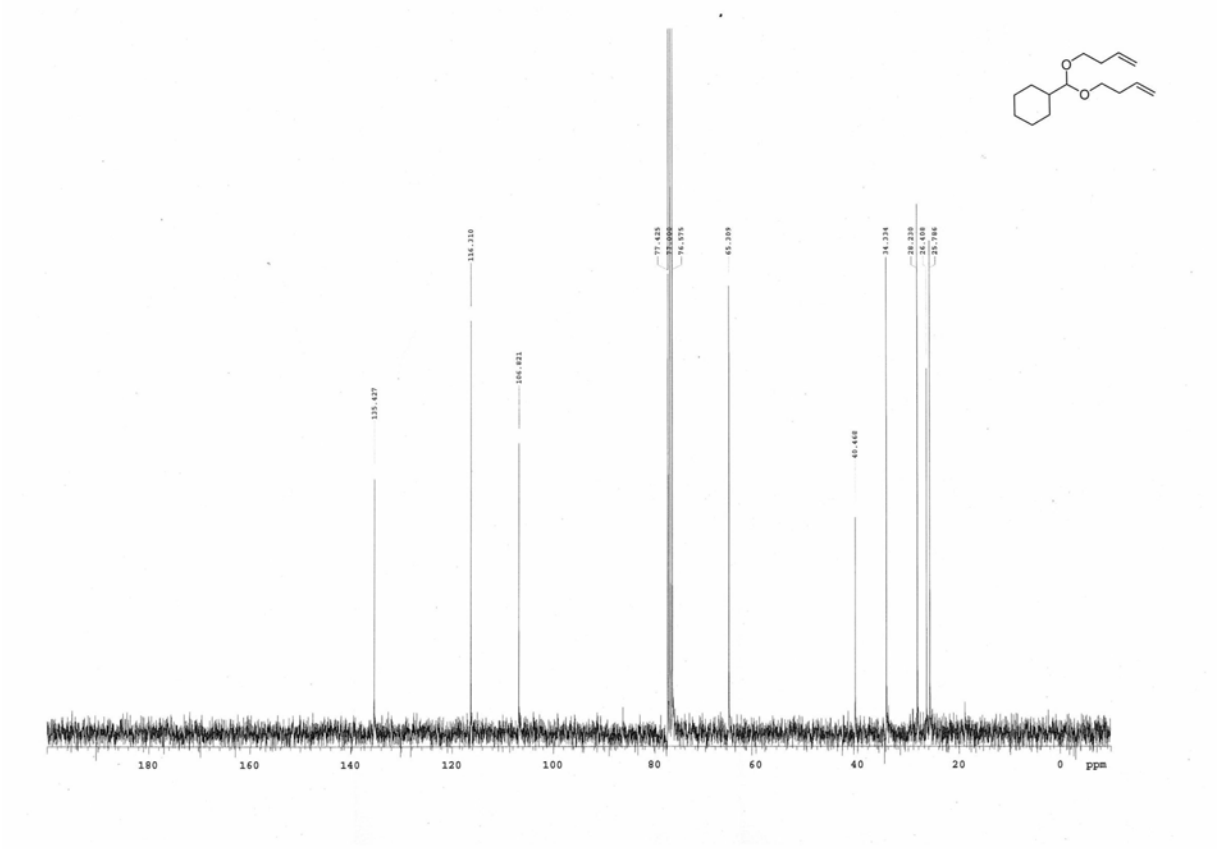
3-Butenyl cyclohexyl(4-fluorophenylthio)methyl ether (6d).



To a solution of cyclohexanecarbaldehyde (1.63 g, 14.5 mmol) and 3-butenyloxytrimethylsilane (4.28 g, 29.7 mmol) in CH_2Cl_2 (35 mL) was added Me_3SiOTf (475 mg, 2.14 mmol) at -78 ^oC. Then the mixture was stirred at -25 ^oC overnight. The reaction mixture was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 50:1) to give the (bis(3-butenyloxy))cyclohexylmethane (2.34 g, 9.82 mmol, 68 %): TLC R_f 0.38 (hexane/EtOAc 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88-1.30 (m, 5H), 1.50-1.84 (m, 6H), 2.33 (tddd, J = 6.9, 6.9, 1.2, 1.2 Hz, 4H), 3.48 (dt, J = 9.3, 6.9 Hz, 2H), 3.63 (dt, J = 9.3, 6.9 Hz, 2H), 4.14 (d, J = 7.2 Hz, 1H), 5.00-5.16 (m, 4H), 5.84 (ddt, J = 17.3, 10.5, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8, 26.4, 28.2, 34.3, 40.5, 65.3, 106.8, 116.3, 135.4; IR (neat) 2924, 1642, 914 cm^{-1}; LRMS (FAB) m/z 237 (M^+-H); HRMS (FAB) calcd for $C_{15}H_{25}O_2$ (M^+-H) 237.1855, found 237.1853.



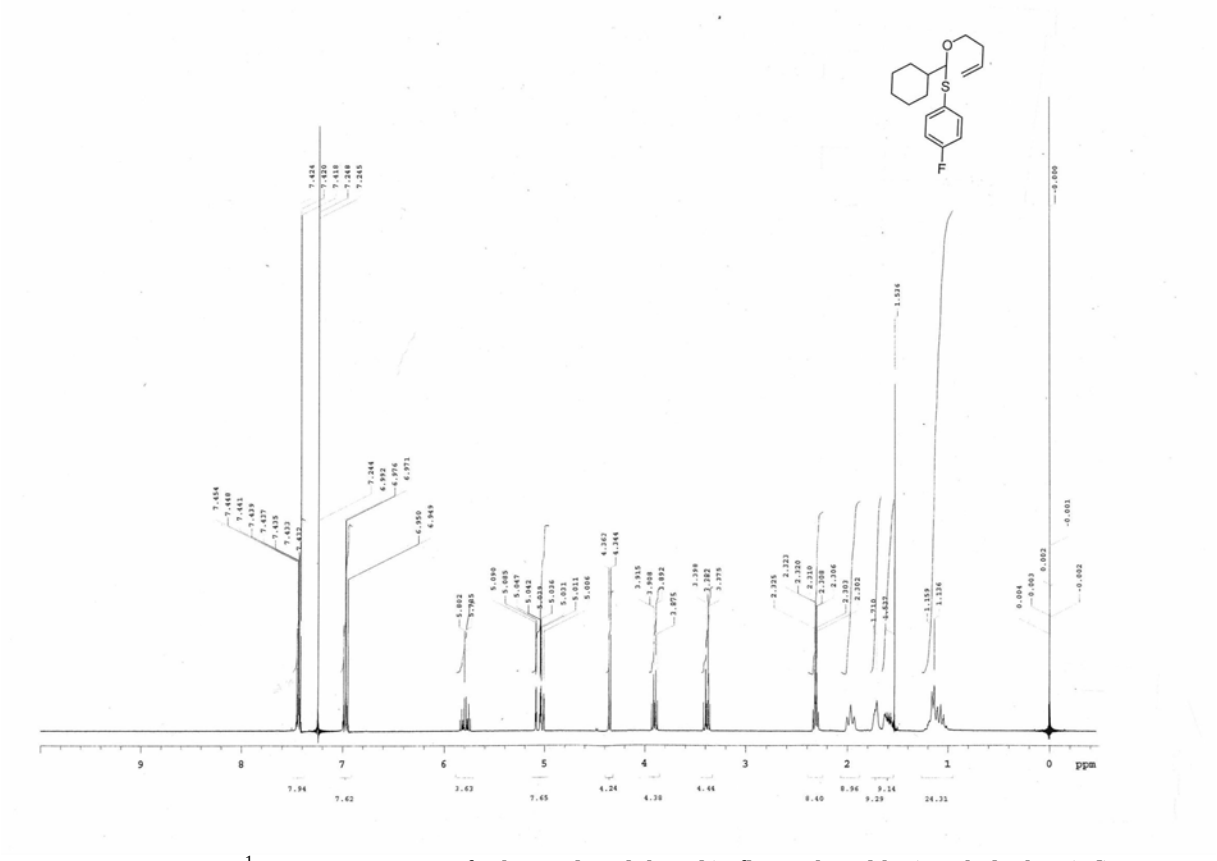
^{1}H NMR spectrum of (bis(3-butenyloxy))cyclohexylmethane.



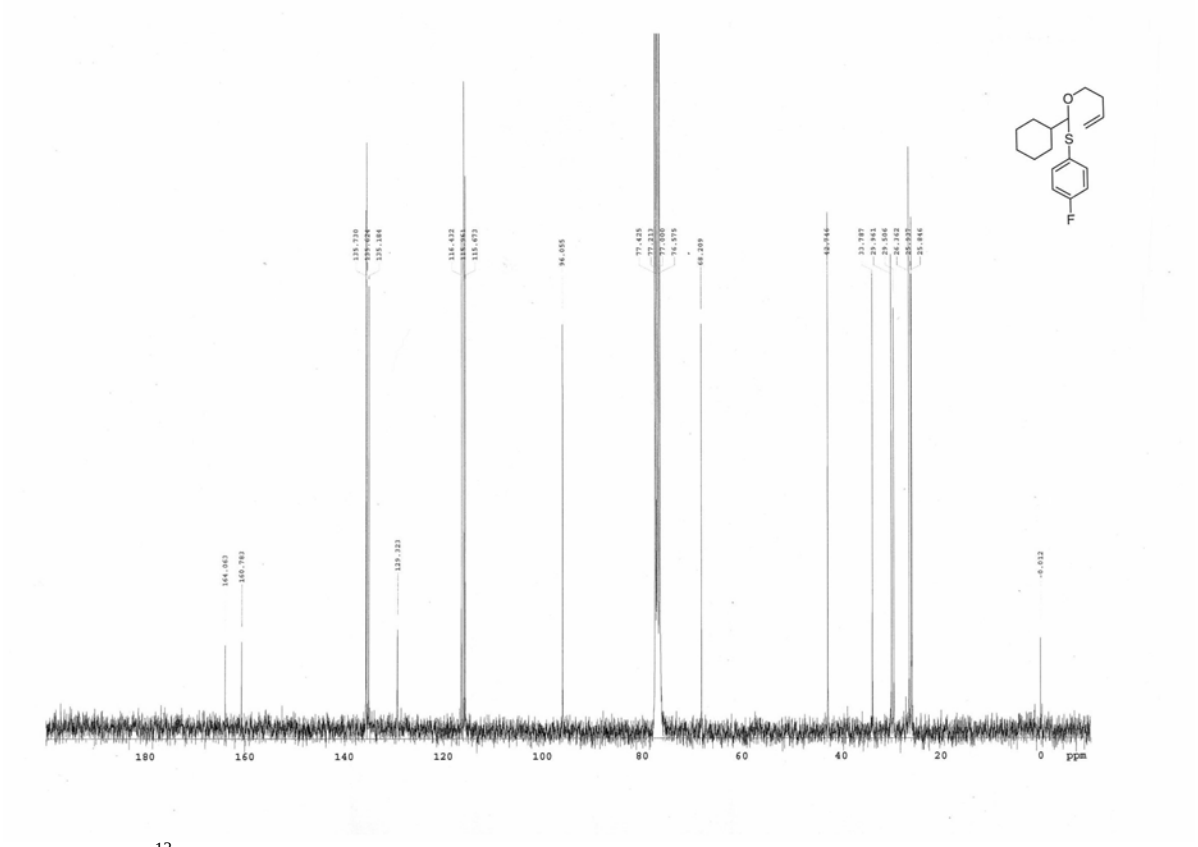
^{13}C NMR spectrum of (bis(3-butenyloxy))cyclohexylmethane.

To a solution of (bis(3-butenyloxy))cyclohexylmethane (959 mg, 4.02 mmol) and *p*-fluorothiophenol (578 mg, 4.51 mmol) in toluene (50 mL) was added BF_3-OEt_2 (683 mg, 4.81 mmol) at -78 ^{o}C. The solution was stirred for 2 h, and Et_3N (2.0 mL) was added. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the crude product

was purified via flash chromatography (hexane/EtOAc 100:1 to 50:1) to give the title compound (**6d**) (697 mg, 2.37 mmol, 59 %): TLC R_f 0.36 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.24 (m, 5H), 1.50-1.66 (m, 2H), 1.67-1.76 (m, 2H), 1.90-2.03 (m, 2H), 2.28-2.35 (m, 2H), 3.39 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.90 (dt, *J* = 9.2, 6.8 Hz, 1H), 4.35 (d, *J* = 7.6 Hz, 1H), 5.00-5.10 (m, 2H), 5.79 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 6.94-7.00 (m, 2H), 7.41-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8, 25.9, 26.4, 30.0, 33.8, 42.7, 68.2, 96.1, 115.8 (d, *J* = 21.6 Hz), 116.4, 129.3, 135.2, 135.7 (d, *J* = 8.0 Hz), 162.4 (d, *J* = 246.0 Hz); IR (neat) 2924, 1489, 830 cm^{-1}; LRMS (CI) m/z 293 (M^+-H), 223 (M^+-$OCH_2CH_2CH{=}CH_2$), 167 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{17}H_{22}FOS$ (M^+-H) 293.1375, found 293.1367.

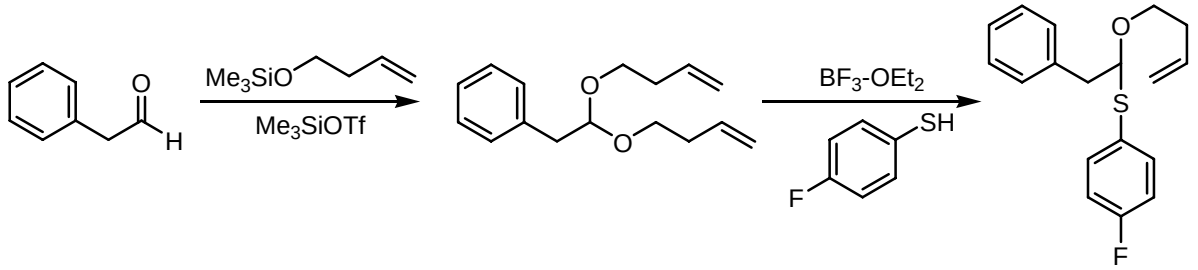


^{1}H NMR spectrum of 3-butenyl cyclohexyl(4-fluorophenylthio)methyl ether (**6d**).

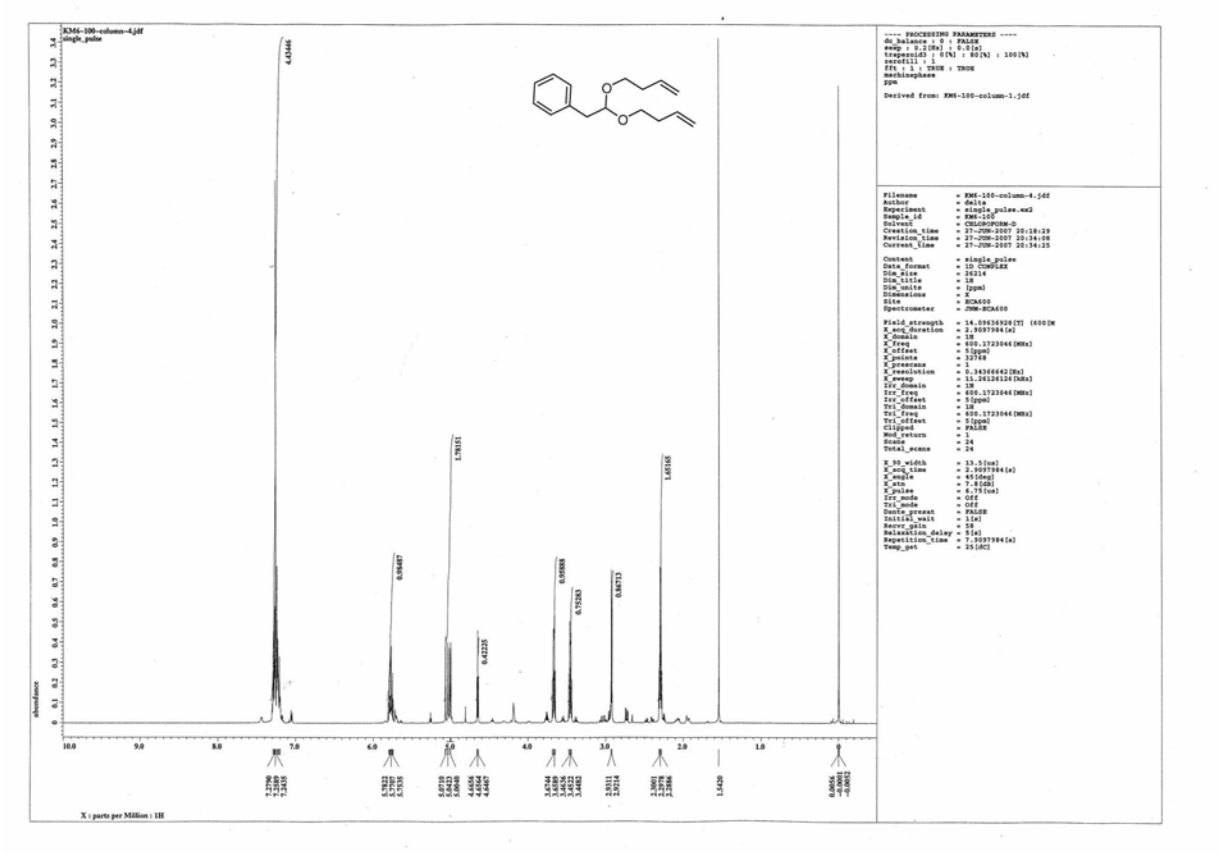


^{13}C NMR spectrum of 3-butenyl cyclohexyl(4-fluorophenylthio)methyl ether (**6d**).

3-Butenyl benzyl(4-fluorophenylthio)methyl ether (6e).

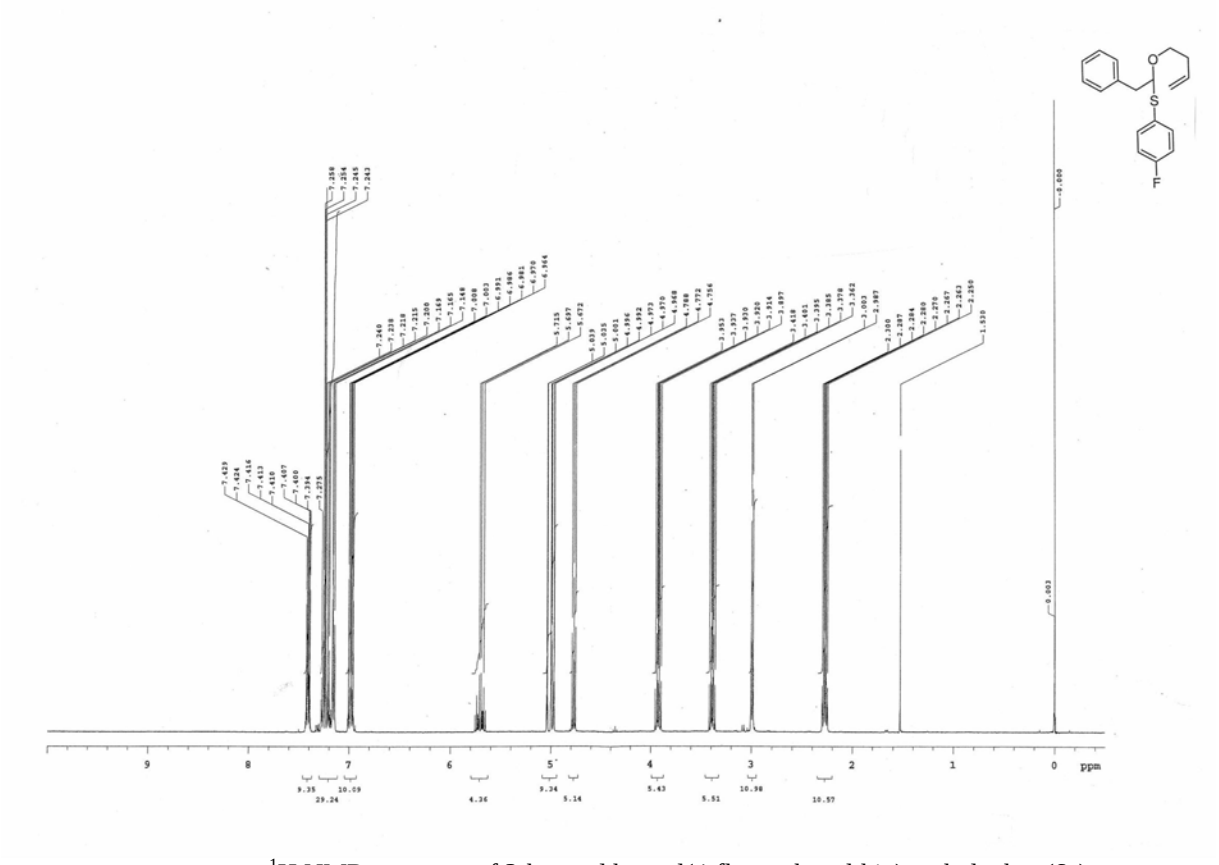


To a solution of 2-phenylacetaldehyde (1.30 g, 10.8 mmol) and 3-butenyloxytrimethylsilane (3.37 g, 23.4 mmol) in CH_2Cl_2 (25 mL) was added Me_3SiOTf (656 mg, 2.90 mmol) at -78 ^{o}C. Then the mixture was warmed slowly to room temperature, and stirred for 26 h. The reaction mixture was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 20:1) to give the (bis(3-butenyloxy))benzylmethane (1.36 g, 5.52 mmol, 51 %, purity ca. 80%): TLC R_f 0.25 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27-2.32 (m, 4H), 2.93 (d, *J* = 5.5 Hz, 2H), 3.46 (dt, *J* = 9.2, 6.5 Hz, 2H), 3.67 (dt, *J* = 9.2, 6.5 Hz, 2H), 4.66 (t, *J* = 5.5 Hz, 1H), 4.99-5.09 (m, 4H), 5.78 (ddt, *J* = 17.2, 10.3, 6.5 Hz, 2H), 7.15-7.31 (m, 5H).

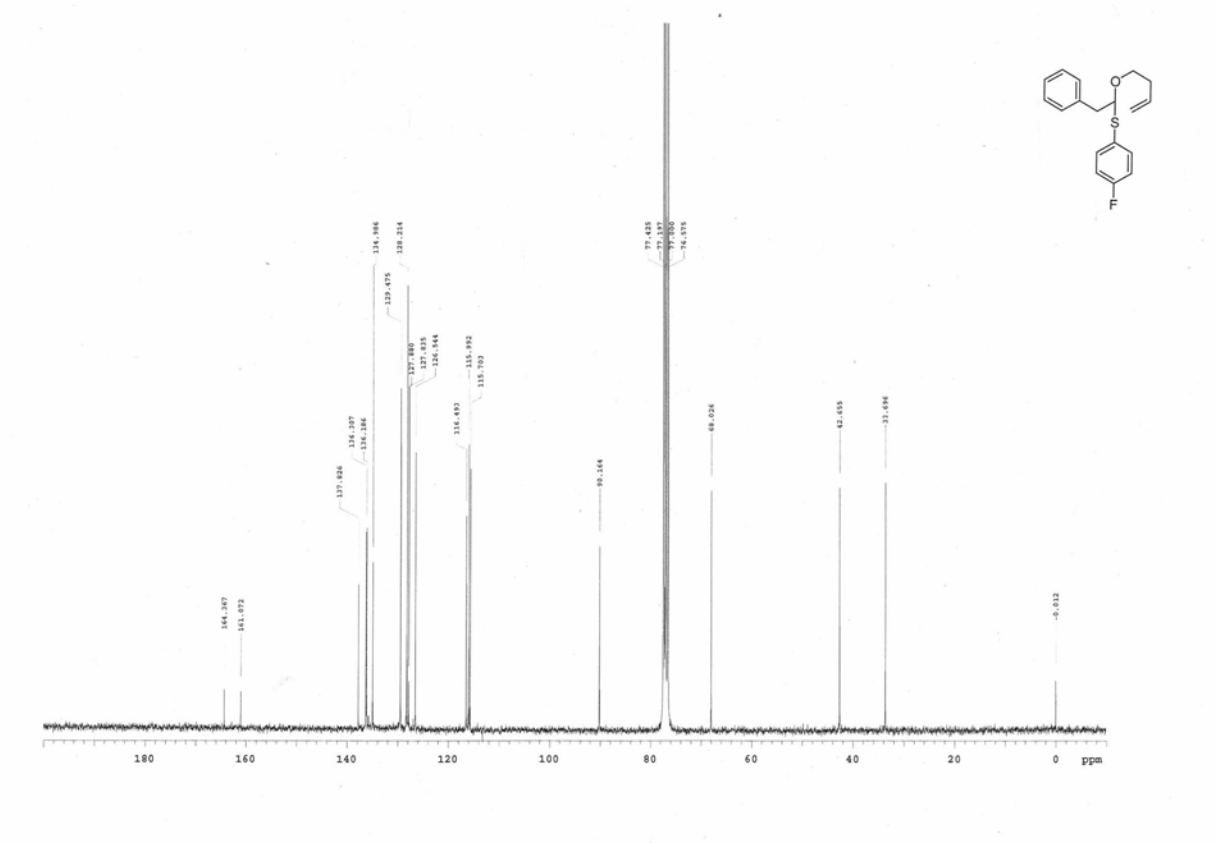


^{1}H NMR spectrum of (bis(3-butenyl))benzylmethane.

To a solution of (bis(3-butenyloxy))benzylmethane (871 mg, 3.54 mmol, purity ca. 80%) and *p*-fluorothiophenol (541 mg, 4.22 mmol) in toluene (48 mL) was added BF_3-OEt_2 (672 mg, 4.73 mmol) at -78 ^{o}C. The solution was stirred for 2 h and Et_3N (3.0 mL) was added. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 40:1) to give the title compound (**6e**) (579 mg, 1.91 mmol, 54 %, purity ca. 95%): TLC R_f 0.34 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (tddd, *J* = 6.8, 6.8, 1.6, 1.6 Hz, 2H), 3.00 (d, *J* = 6.4 Hz, 2H), 3.39 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.93 (dt, *J* = 9.2, 6.8 Hz, 1H), 4.77 (t, *J* = 6.4 Hz, 1H), 4.96-5.05 (m, 2H), 5.71 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 6.92-7.02 (m, 2H), 7.12-7.28 (m, 5H), 7.36-7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.7, 42.7, 68.0, 90.2, 115.8 (d, *J* = 21.7 Hz), 116.5, 126.5, 127.9 (d, *J* = 3.4 Hz), 128.2, 129.5, 135.0, 136.2 (d, *J* = 9.0 Hz), 137.8, 162.7 (d, *J* = 247.1 Hz); IR (neat) 2865, 1489, 1223 cm^{-1}; LRMS (EI) m/z 302 (M^+), 175 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{18}H_{19}FOS$ (M^+) 302.1141, found 302.1145.

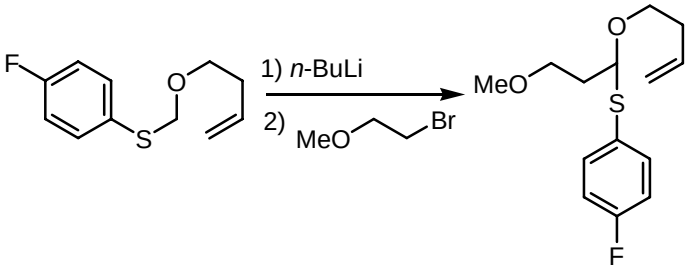


^{1}H NMR spectrum of 3-butenyl benzyl(4-fluorophenylthio)methyl ether (**6e**).

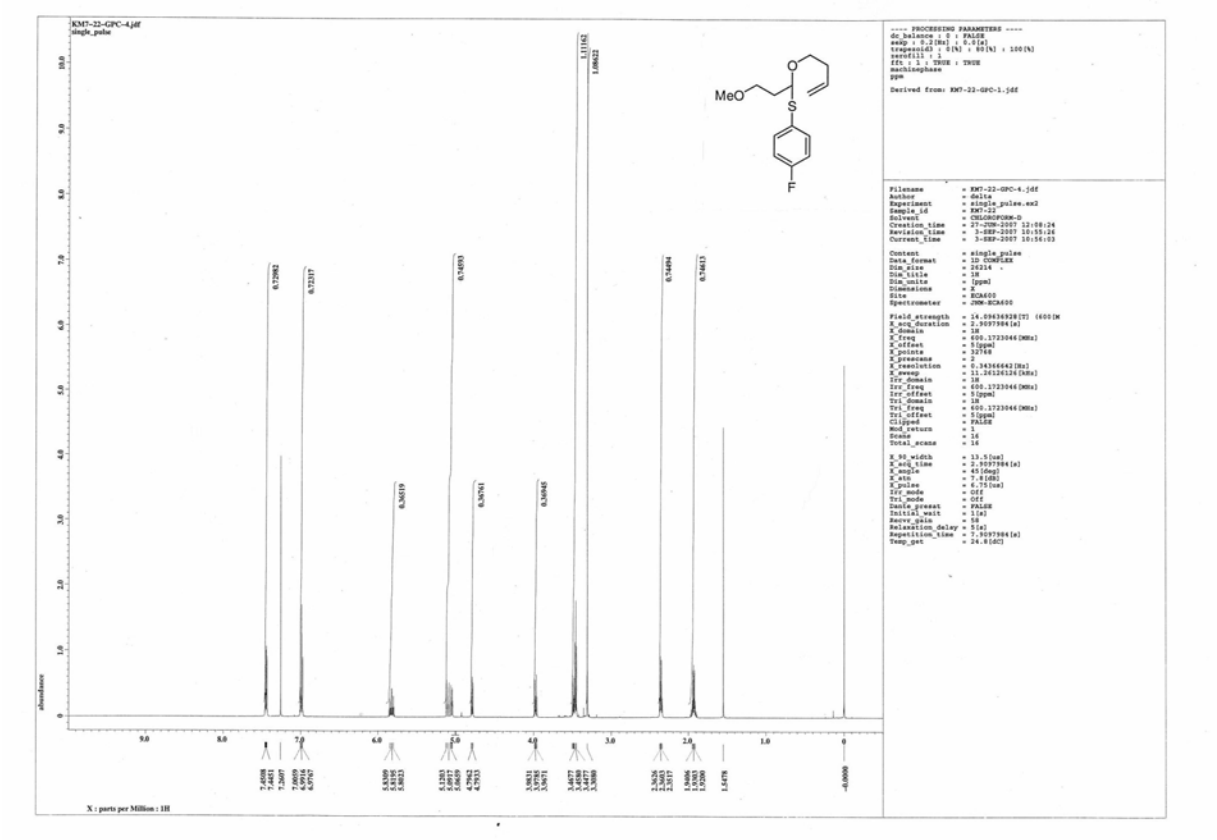


^{13}C NMR spectrum of 3-butenyl benzyl(4-fluorophenylthio)methyl ether (**6e**).

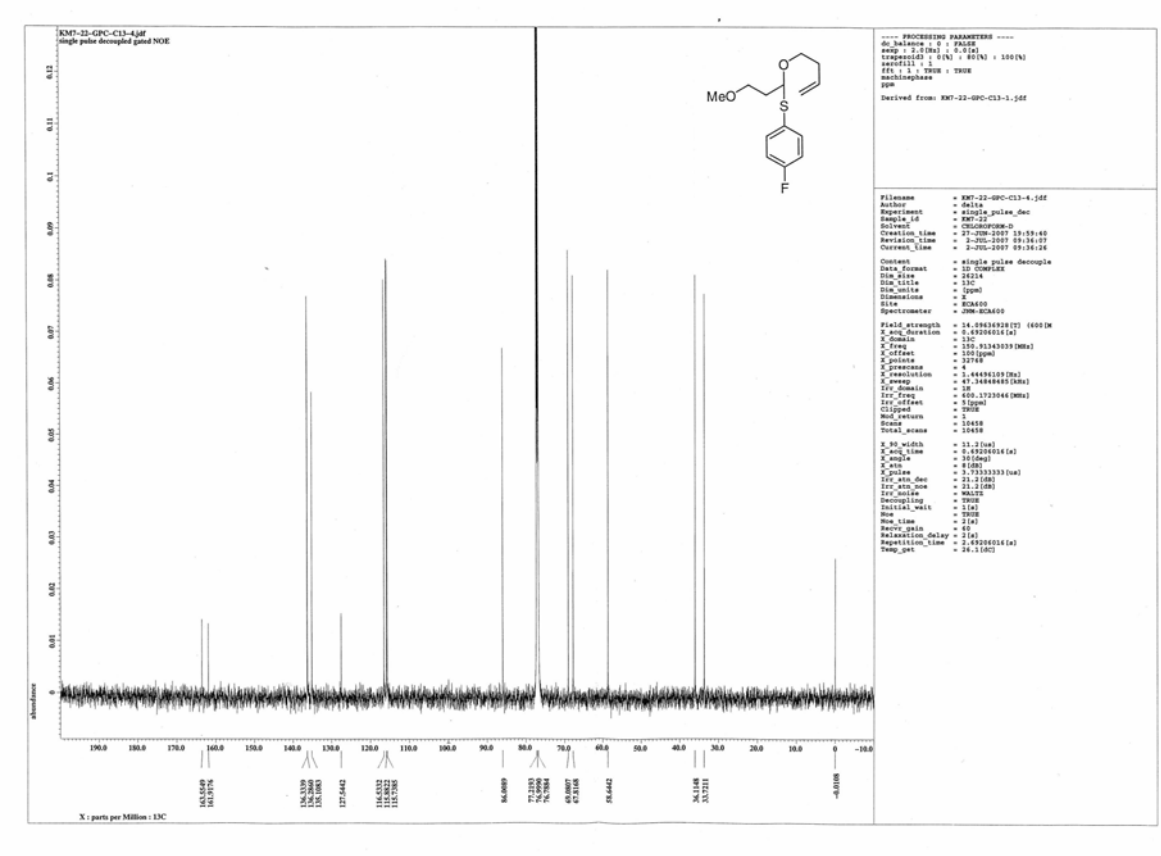
3-Butenyl 2-methoxyethyl(4-fluorophenylthio)methyl ether (6f).



To a solution of 3-butenyl 4-fluorophenylthiomethyl ether (**6g**) (*vide infra*) (1.65 g, 7.80 mmol) in THF (8 mL) was added *n*-BuLi (1.58 M in hexane, 5.5 mL, 8.70 mmol) at -78 °C. The mixture was stirred at -48 °C for 1 h and then cooled to -78 °C. Bromoethyl methyl ether (1.83 g, 13.2 mmol) was added and the mixture was gradually allowed to warm from -78 °C to room temperature, and then stirred for 14 h. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 20:1) and purified via GPC to give the title compound (**6f**) (479 mg, 1.77 mmol, 23 %): TLC R_f 0.21 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.88-1.98 (m, 2H), 2.36 (tddd, *J* = 6.5, 6.5, 1.4, 1.4 Hz, 2H), 3.31 (s, 3H), 3.44-3.51 (m, 3H), 3.98 (dt, *J* = 9.6, 6.5 Hz, 1H), 4.79 (dd, *J* = 7.6, 5.8 Hz, 1H), 5.06 (ddt, *J* = 10.3, 1.4, 1.4 Hz, 1H), 5.11 (ddt, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.3, 6.5 Hz, 1H), 6.97-7.02 (m, 2H), 7.43-7.47 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.7, 36.1, 58.6, 67.8, 69.1, 86.0, 115.8 (d, *J* = 21.5 Hz), 116.5, 127.5, 135.1, 136.3 (d, *J* = 7.2 Hz), 162.7 (d, *J* = 245.6 Hz); IR (neat) 1491, 1223, 831 cm^{-1}; LRMS (EI) m/z 270 (M^+), 199 (M^+-$OCH_2CH_2CH{=}CH_2$), 143 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{14}H_{19}FO_2S$ (M^+) 270.1090, found 270.1088.

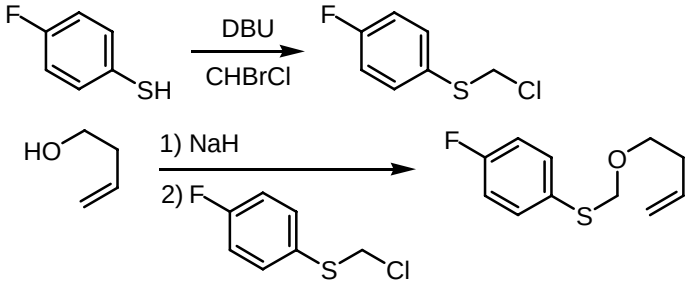


^{1}H NMR spectrum of 3-butenyl 2-methoxyethyl(4-fluorophenylthio)methyl ether (**6f**).

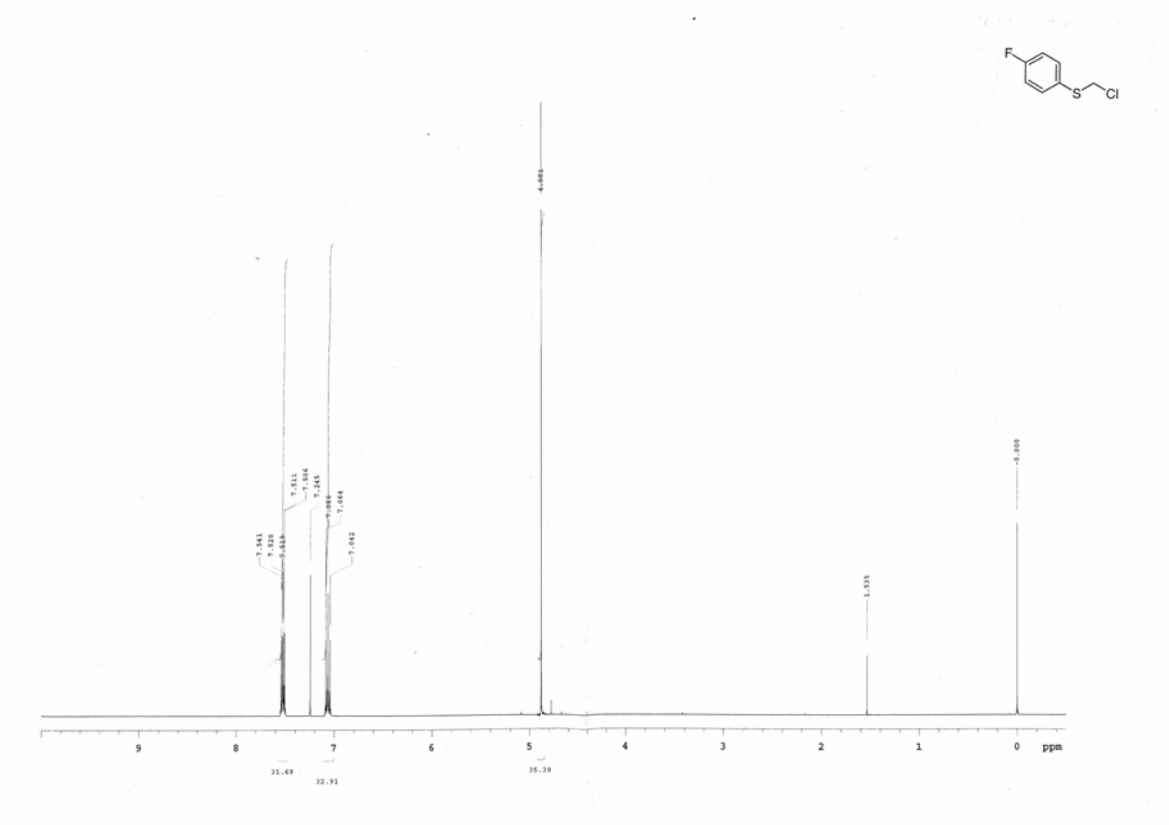


^{13}C NMR spectrum of 3-butenyl 2-methoxyethyl(4-fluorophenylthio)methyl ether (**6f**).

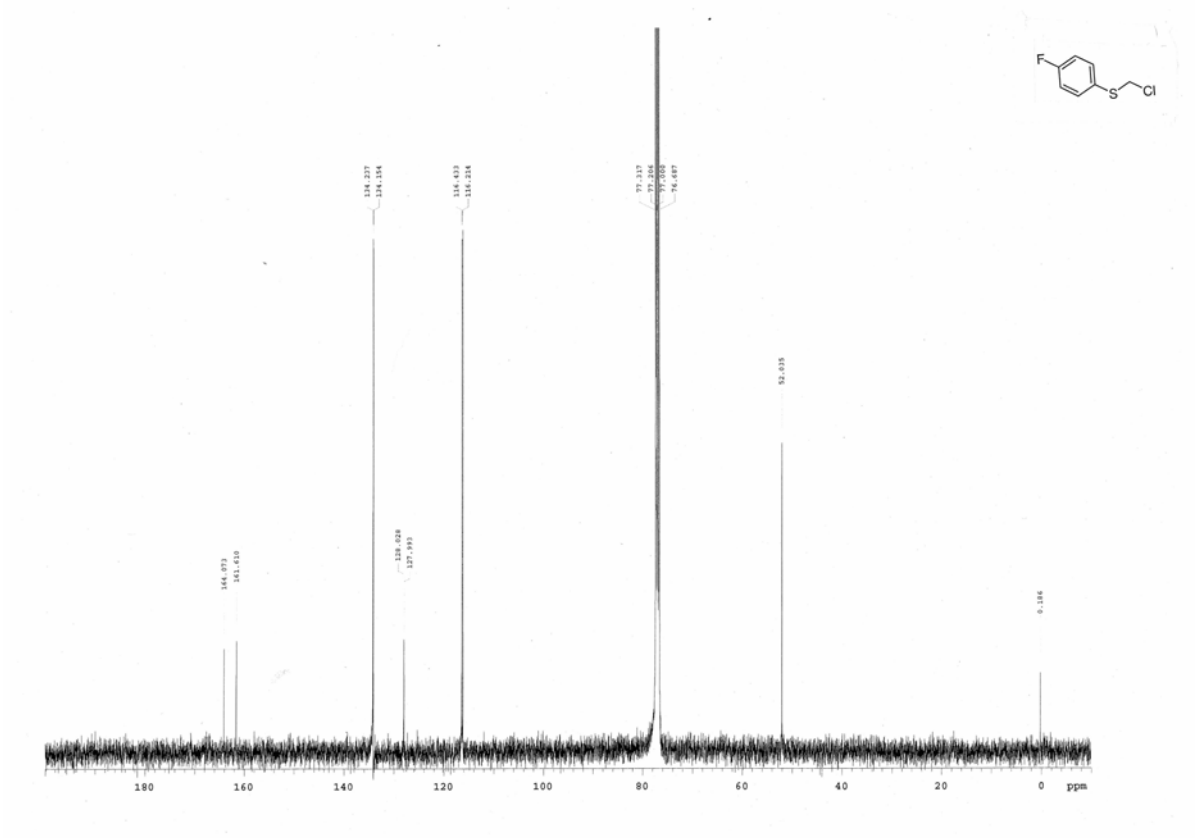
3-Butenyl 4-fluorophenylthiomethyl ether (6g).



A solution of the *p*-fluorothiophenol (19.2g, 150 mmol) and DBU (24.9g, 164 mmol) in CH_3CN (75 mL) was added to CH_2BrCl (200 mL) at 0 ^oC and the mixture was stirred for 1 h at the same temperature. After being warmed up to room temperature, the mixture was stirred for the 4 h and saturated aqueous $NaHCO_3$ was added. The organic materials were extracted with CH_2Cl_2, and the organic phase was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by distillation (108 ^oC, 14.2 mmHg) to give chloromethyl 4-fluorophenyl sulfide (20.6 g, 117 mmol, 78 %): TLC R_f 0.55 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 2H), 7.02-7.10 (m, 2H), 7.48-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 116.3 (d, J = 21.9 Hz), 128.0 (d, J = 3.5 Hz), 134.2 (d, J = 8.3 Hz), 162.8 (d, J = 246.3 Hz); IR (neat) 1592, 1491, 828 cm^{-1}; LRMS (EI) m/z 176 (M^+), 141 (M^+-Cl); HRMS (EI) calcd for C_7H_6ClFS (M^+) 175.9863, found 175.9864.



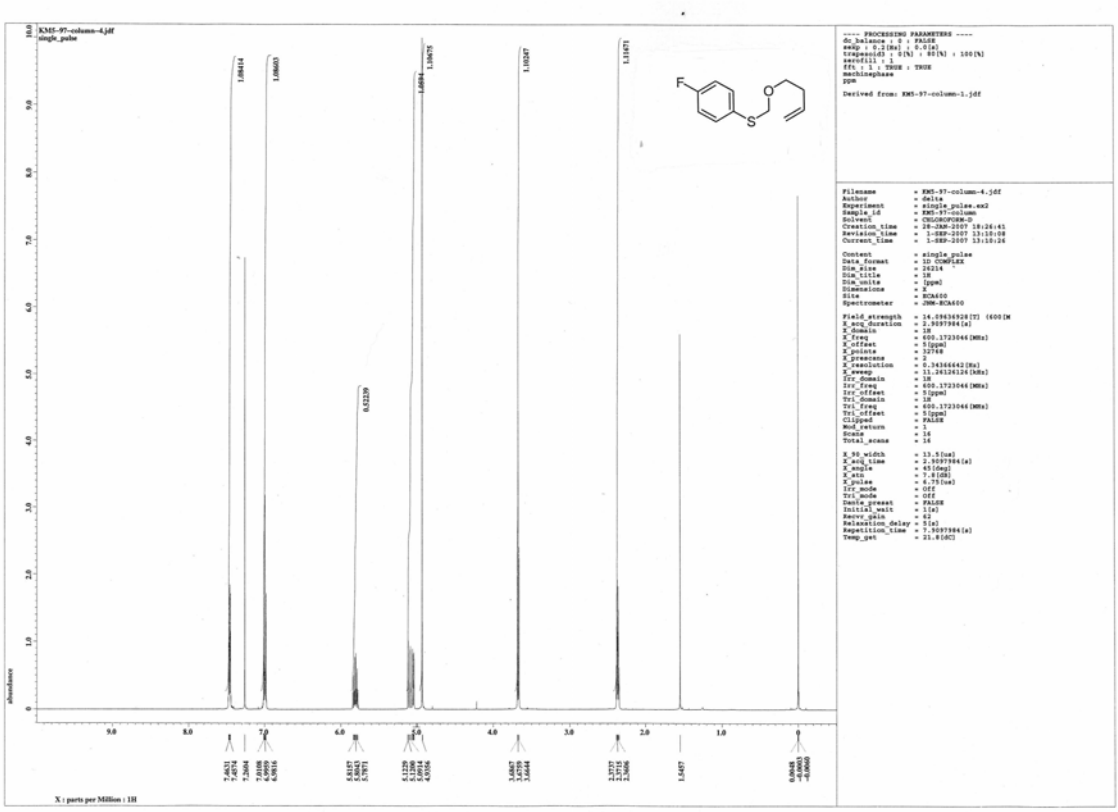
^{1}H NMR spectrum of chloromethyl 4-fluorophenyl sulfide.



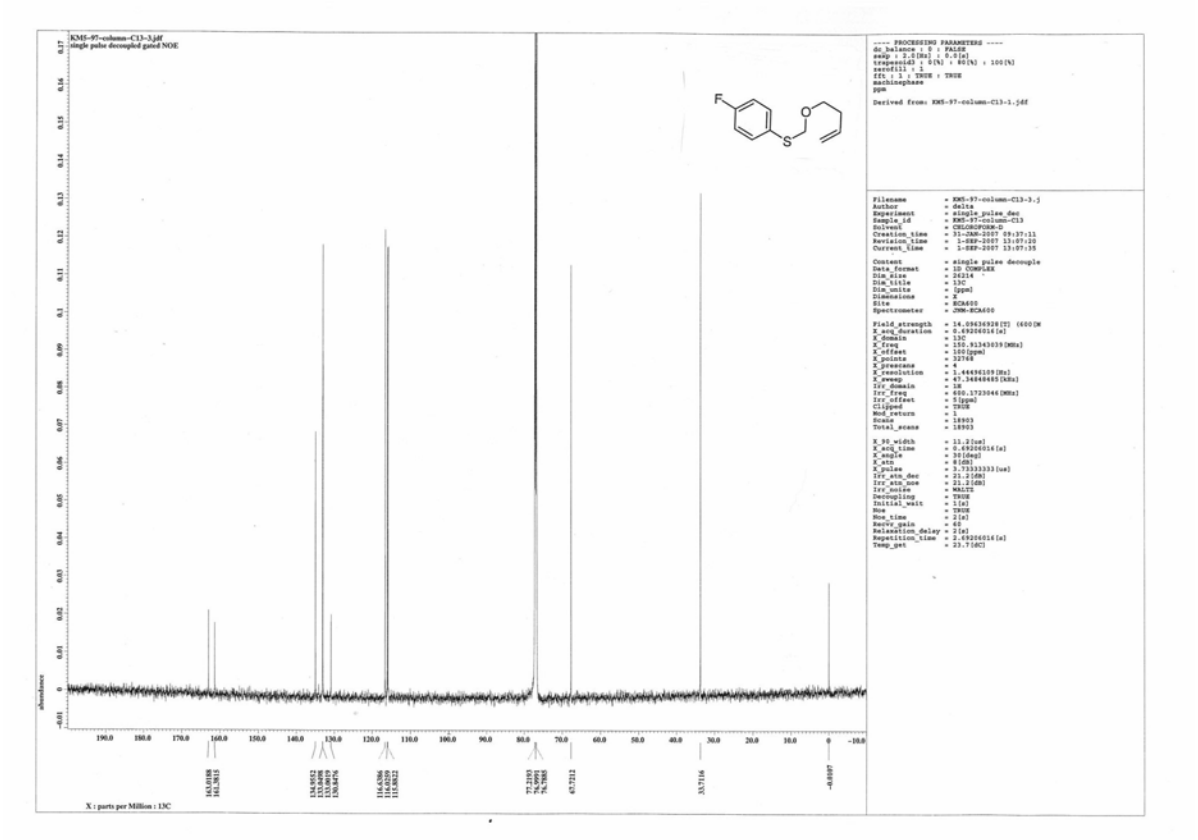
^{13}C NMR spectrum of chloromethyl 4-fluorophenyl sulfide.

To a suspension of NaH (55 % in oil, 2.81 g, 64.4 mmol) in THF (40 mL) was added 3-buten-1-ol (4.63g, 64.2 mmol) at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 1 h and chloromethyl 4-fluorophenyl sulfide (9.81g, 55.5 mmol) and tetrabutylammonium iodide (1.53g, 4.14 mmol) was added to the mixture, and was stirred at room temperature for 3 h. Methanol (1.0 mL) was added, and the reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated, washed with saturated brine, and dried over $MgSO_4$. After removal of the solvent, the crude

product was purified by distillation (100 °C, 1.98 mmHg) to give the title compound (**6g**) (6.35 g, 29.9 mmol, 54 %): TLC R_f 0.33 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.37 (tddd, *J* = 6.5, 6.5, 1.4, 1.4 Hz, 2H), 3.68 (t, *J* = 6.5 Hz, 2H), 4.94 (s, 2H), 5.05 (ddt, *J* = 10.3, 1.4, 1.4 Hz, 1H), 5.11 (ddt, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.81 (ddt, *J* = 17.2, 10.3, 6.5 Hz, 1H), 6.97-7.03 (m, 2H), 7.43-7.48 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.7, 67.7, 116.0 (d, *J* = 21.6 Hz), 116.6, 130.8, 133.0 (d, *J* = 7.2 Hz), 135.0, 162.2 (d, *J* = 245.6 Hz). One signal could not be assigned due to the signal overlap. In order to assign all the signals, CD_2Cl_2 was used as solvent; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 34.1, 68.1, 77.2, 116.2 (d, *J* = 22.7 Hz), 116.6, 131.5, 133.4 (d, *J* = 8.0 Hz), 135.6, 162.5 (d, *J* = 244.9 Hz); IR (neat) 2863, 1491, 830 cm^{-1}; LRMS (CI) m/z 212 (M^+), 141 (M^+-$OCH_2CH_2CH{=}CH_2$), 85 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{11}H_{13}FOS$ (M^+) 212.0671, found 212.0670.



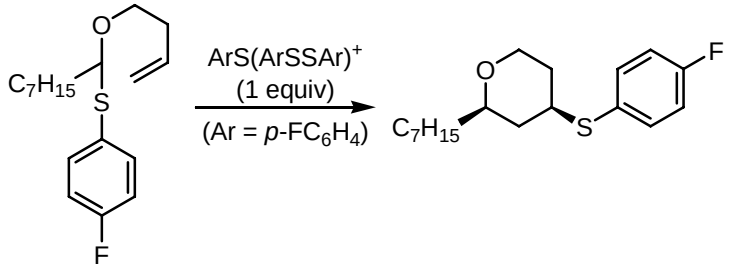
^{1}H NMR spectrum of 3-butenyl 4-fluorophenylthiomethyl ether (**6g**).



^{13}C NMR spectrum of 3-butenyl 4-fluorophenylthiomethyl ether (**6g**).

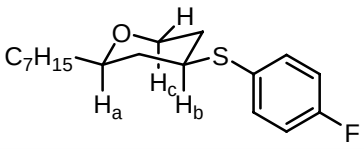
Cyclization of Thioacetals Having a Carbon-Carbon Double Bond.

***cis*-4-(4-Fluorophenylthio)-2-heptyltetrahydropyran (8a): A Typical Procedure.**

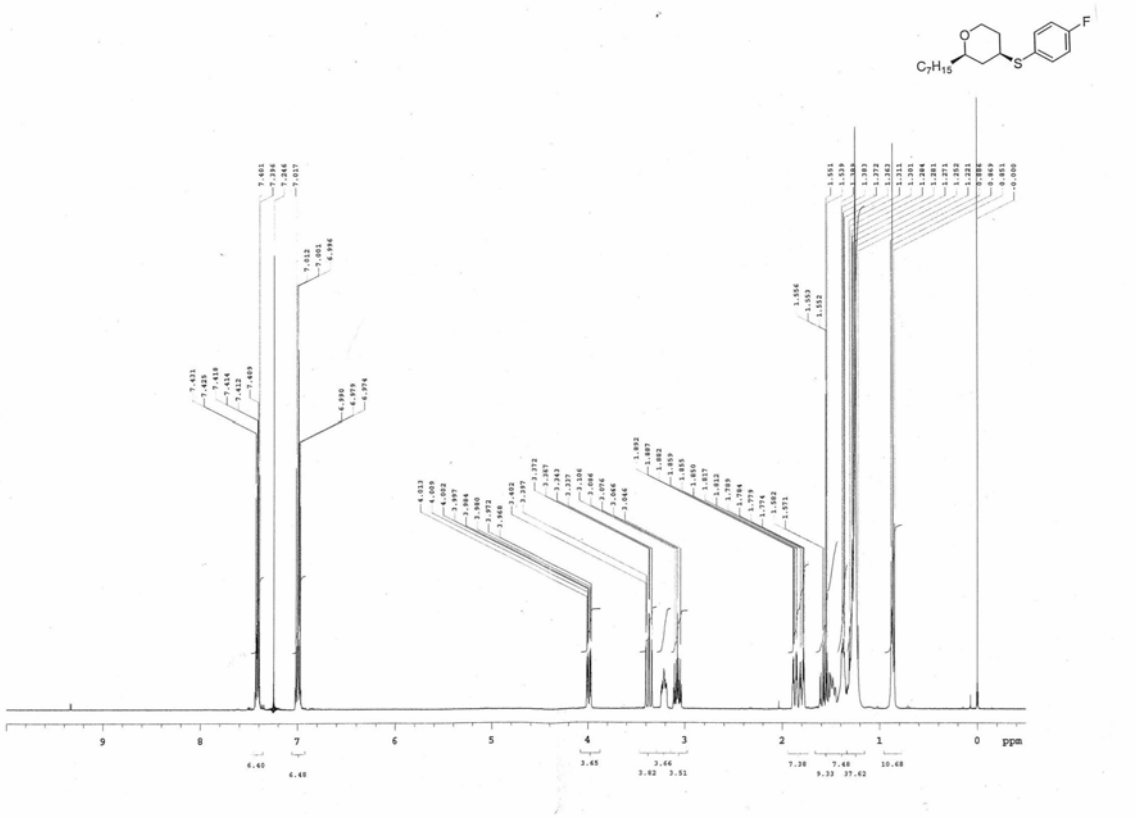


The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (103 mg, 0.405 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (46.5 mg, 0.310 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^oC with magnetic stirring until 0.67 F/mol of electricity was consumed. To the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$, was added 3-butenyl 1-(4-fluorophenylthio)octyl ether (**6a**) (83.4 mg, 0.269 mmol) and the mixture was stirred for 5 min at -78 ^oC. The reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The GC analysis of the combined filtrate indicated that the title compound (**8a**) was formed in 72 % yield (GC ^tR 17.6 min, column, CBP-1; 0.22 mm ϕ x 0.25 μm x 25 m; initial oven temperature, 100 ^oC; rate of temperature increase, 10 ^oC/min). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.21 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.18-1.62 (m, 14H), 1.76-1.90 (m, 2H), 3.08 (dddd, *J* = 12.0, 12.0, 4.0, 4.0 Hz, 1H), 3.16-3.25 (m, 1H), 3.37 (ddd, *J* = 12.0, 12.0, 2.0 Hz, 1H), 3.99 (ddd, *J* = 12.0, 6.4, 1.6 Hz, 1H), 6.96-7.03 (m, 2H), 7.38-7.44 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.6, 25.4, 29.2, 29.6, 31.8, 33.3, 36.2, 38.8, 44.7, 67.6, 77.6, 116.0 (d, *J* = 21.5 Hz), 128.3, 135.8 (d, *J* = 8.6 Hz), 162.6 (d, *J* = 245.6 Hz); LRMS (EI) m/z 310 (M^+), 183 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{18}H_{27}FOS$ (M^+) 310.1767, found 310.1767.

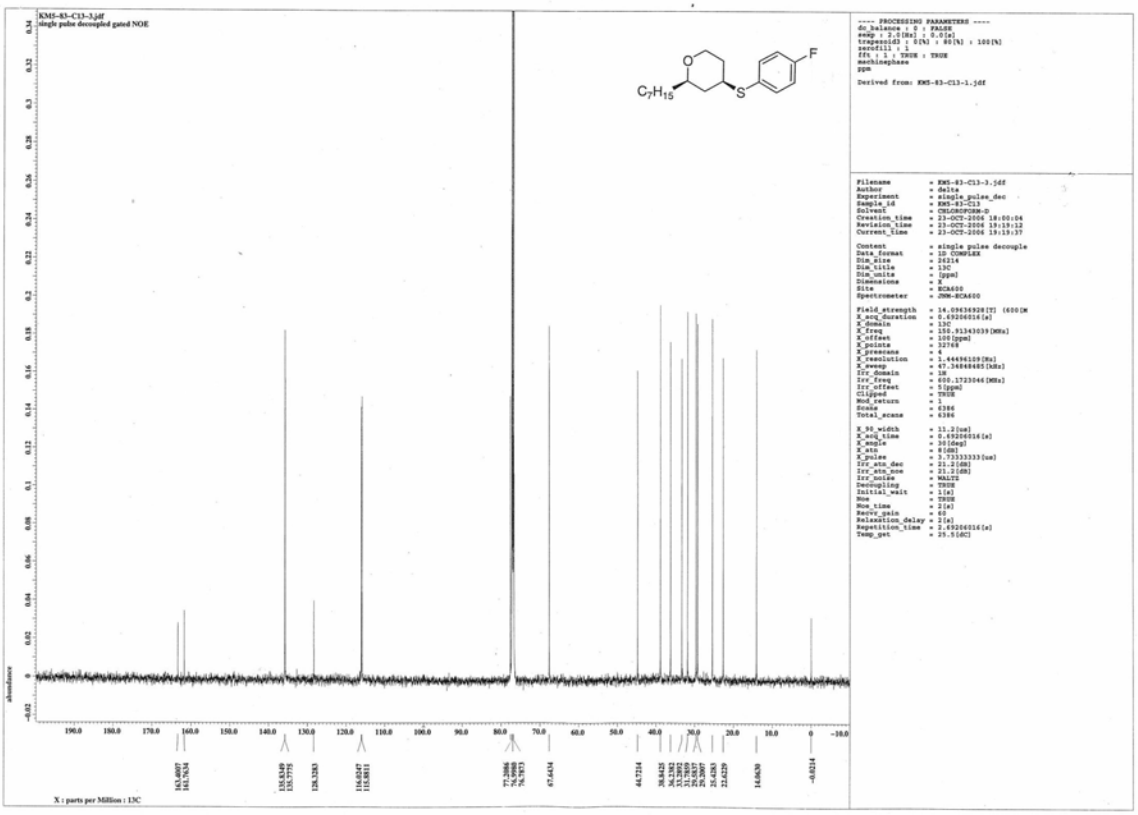
NOE Data for **8a**:



Signal Irradiated	NOE's observed
H_a	H_b (8.2 %), H_c (5.5 %)
H_b	H_a (7.0 %), H_c (2.7 %)

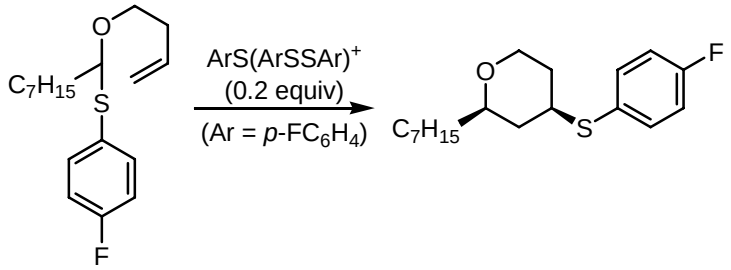


^{1}H NMR spectrum of *cis*-4-(4-fluorophenylthio)-2-heptyltetrahydropyran (**8a**).



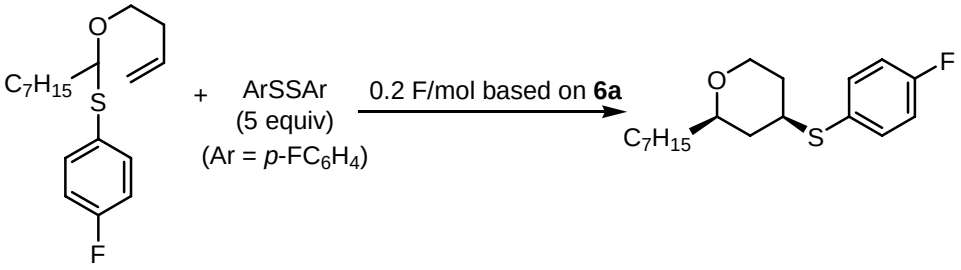
^{13}C NMR spectrum of *cis*-4-(4-fluorophenylthio)-2-heptyltetrahydropyran (**8a**).

A Typical Procedure for Cyclization Using a Catalytic Amount of $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (Initiation Method A).



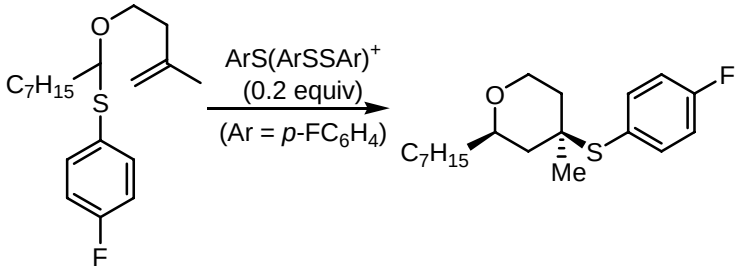
The anodic oxidation was carried out in an H-type divided cell as described above. In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (254 mg, 1.00 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (6.8 mg, 0.0453 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^oC with magnetic stirring until 0.04 F/mol of electricity was consumed. To the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$ was added 3-butenyl 1-(4-fluorophenylthio)octyl ether (**6a**) (60.5 mg, 0.195 mmol) and the mixture was stirred for 20 min at -78 ^oC. The reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The GC analysis of the combined filtrate indicated that the title compound was formed in 82 % yield (GC ^tR 17.5 min, column, CBP-1; 0.22 mm ϕ x 0.25 μm x 25 m; initial oven temperature, 100 ^oC; rate of temperature increase, 10 ^oC/min).

A Typical Procedure for Cyclization Using a Catalytic Amount of Electricity (Initiation Method B, *In-Cell Electrolysis*).



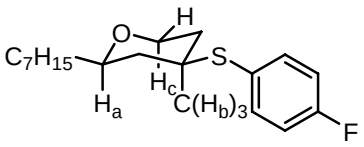
The anodic oxidation was carried out in an H-type divided cell as described above. In the anodic chamber was placed a solution of 3-butenyl 1-(4-fluorophenylthio)octyl ether (**6a**) (62.0 mg, 0.200 mmol) and ArSSAr (Ar = *p*-FC_6H_4) (254.1 mg, 1.00 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (10.2 mg, 0.0680 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^oC with magnetic stirring until 0.20 F/mol of electricity (based on **6a**) was consumed. The mixture was stirred for 20 min at -78 ^oC, and then the reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The GC analysis of the combined filtrate indicated that the title compound (**8a**) was formed in 63 % yield.

4-(4-Fluorophenylthio)-4-methyl-2-heptyltetrahydropyran (8b).

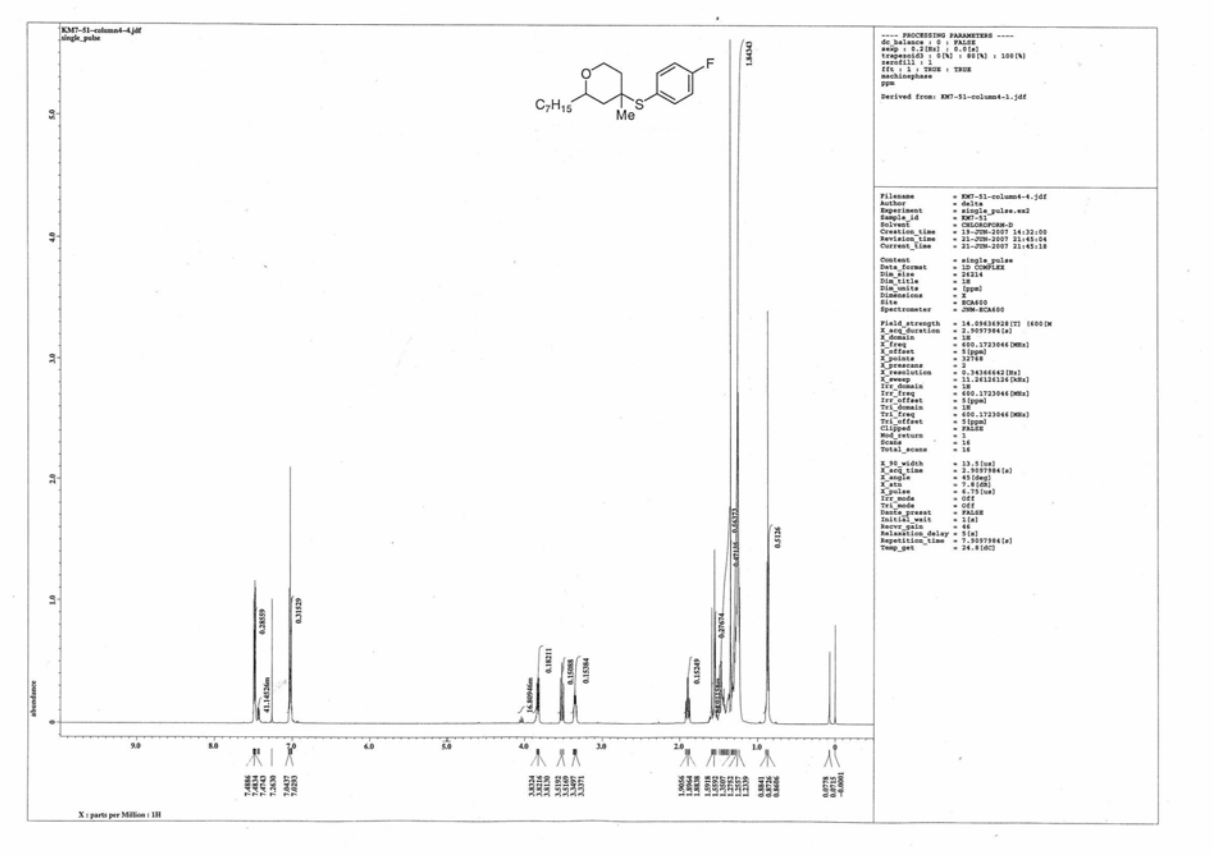


Prepared from ArSSAr (Ar = *p*-FC_6H_4) (154 mg, 0.605 mmol) and 3-methyl-3-butenyl 1-(4-fluorophenylthio)octyl ether (**6b**) (65.3 mg, 0.201 mmol) with 0.067 F/mol of electricity (initiation method A) and purified with flash chromatography (hexane/ EtOAc 100:1) (55.0 mg, 84%). This compound was characterized as a mixture of two diasteromers (ca 9.9:1 by GC analysis): TLC R_f 0.29 (hexane/EtOAc 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 0.83-0.91 (m, 3H), 1.20-1.63 (m, 18H), 1.90 (ddd, *J* = 12.4, 12.4, 5.2 Hz, 1H), 3.31-3.40 (m, 1H), 3.52 (ddd, *J* = 12.4, 12.4, 2.0 Hz, 1H), 3.78-3.88 (m, 1H), 4.01-4.07 (m, 1H, minor diasteromer), 6.98-7.06 (m, 2H), 7.41-7.51 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.6, 23.5, 25.46 and 25.52, 29.2 and 29.3, 29.6 and 29.7, 31.8 and 32.1, 36.2 and 36.4, 37.0 and 38.2, 43.1 and 44.1, 46.6 and 48.3, 64.0 and 64.2, 72.9 and 73.7, 115.7 (d, *J* = 21.5 Hz) and 115.8, 125.9 and 126.8, 139.6 (d, *J* = 8.6 Hz) and 139.5, 163.5 (d, *J* = 247.0 Hz); IR (neat) 2928, 1489, 1223 cm^{-1}; LRMS (EI) m/z 324 (M^+), 197 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{19}H_{29}FOS$ (M^+) 324.1923, found 324.1924.

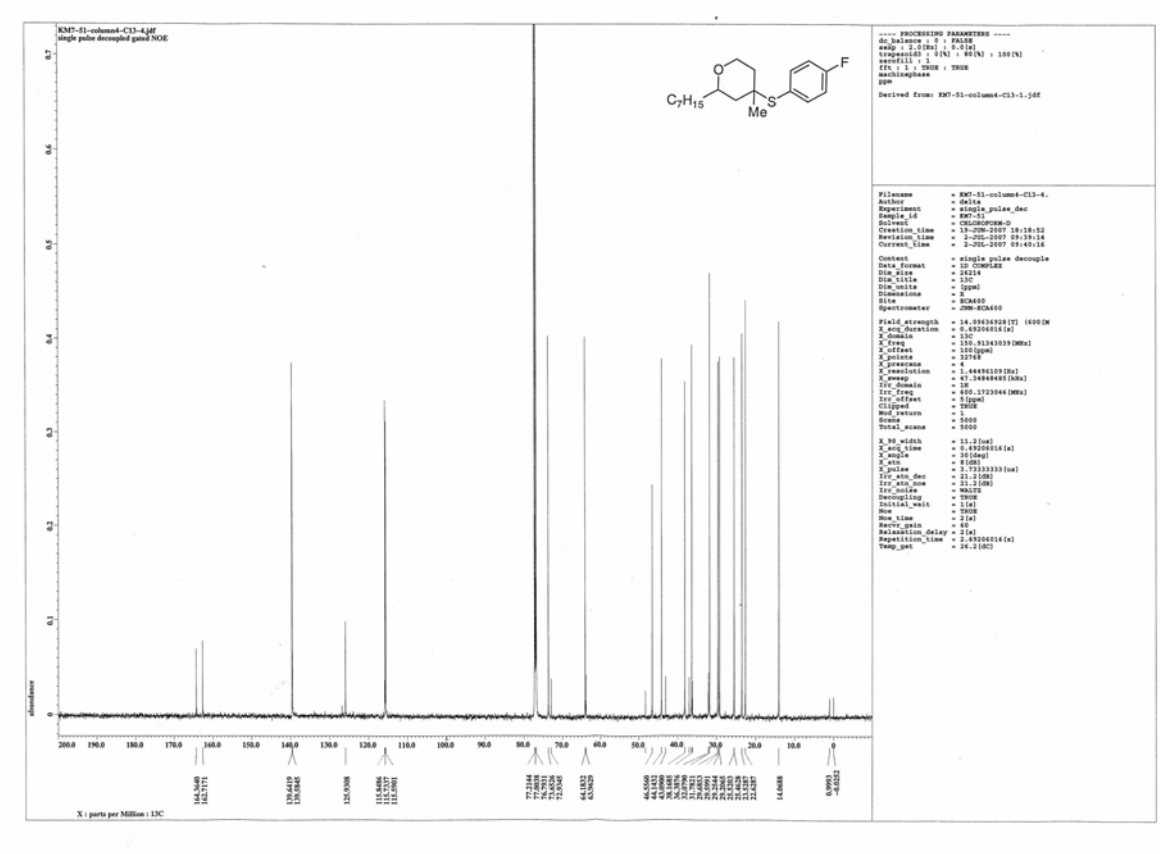
NOE Data for major product of **8b**:



Signal Irradiated	NOE's observed
H_b	H_a (9.6 %), H_c (3.9 %)

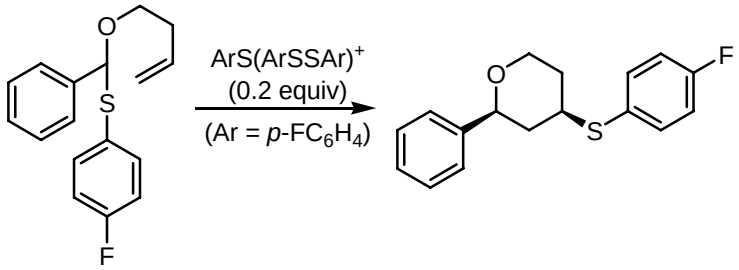


^{1}H NMR spectrum of 4-(4-fluorophenylthio)-4-methyl-2-heptyltetrahydropyran (**8b**).



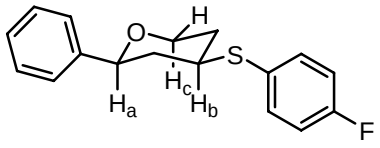
^{13}C NMR spectrum of 4-(4-fluorophenylthio)-4-methyl-2-heptyltetrahydropyran (**8b**).

***cis*-4-(Fluorophenylthio)-2-phenyltetrahydropyran (8c).**

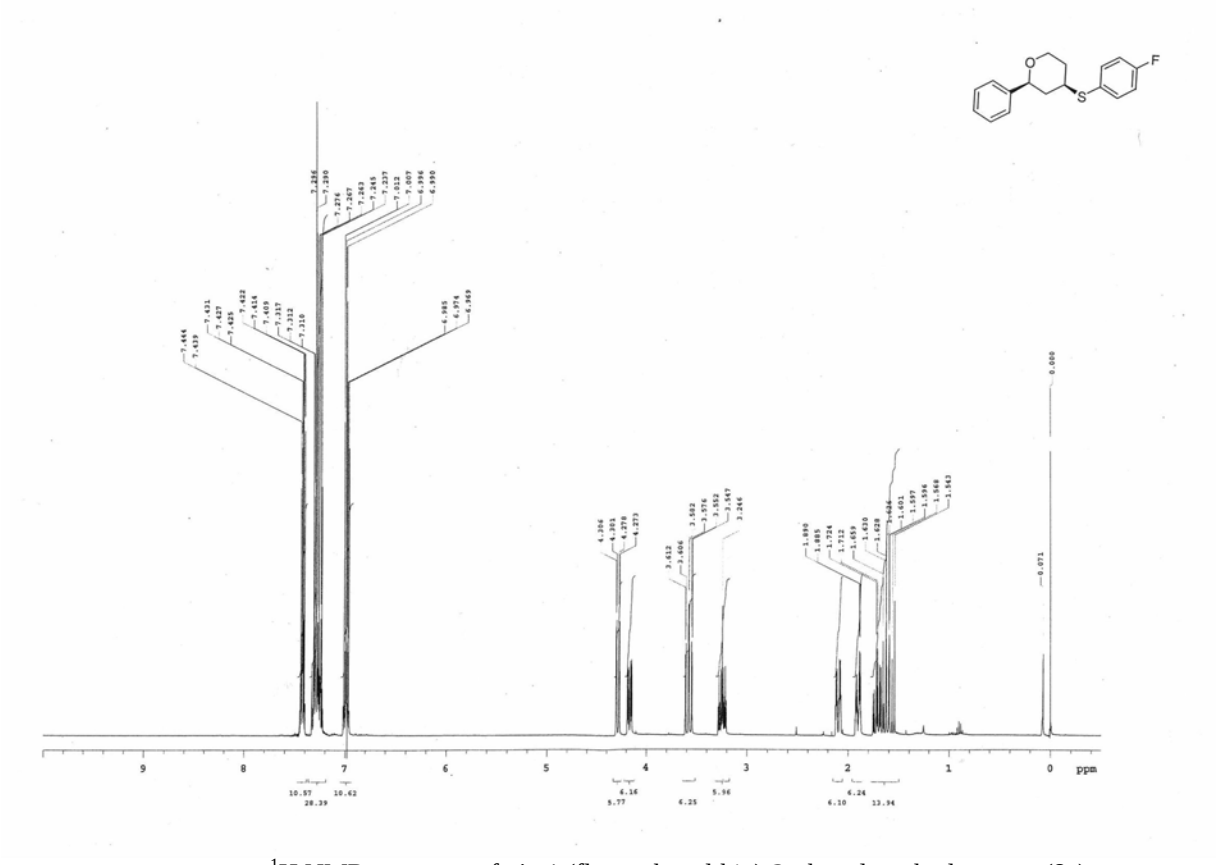


Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255 mg, 1.00 mmol) and 3-butenyl phenyl(4-fluorophenylthio)methyl ether (**6c**) (58.2 mg, 0.202 mmol) with 0.04 F/mol of electricity (initiation method A) and purified with flash chromatography (hexane/ EtOAc 20:1) (37.7 mg, 65%). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.17 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53-1.64 (m, 1H), 1.64-1.76 (m, 1H), 1.86-1.94 (m, 1H), 2.06-2.14 (m, 1H), 3.25 (dddd, *J* = 12.0, 12.0, 3.6, 3.6 Hz, 1H), 3.58 (ddd, *J* = 12.0, 12.0, 2.4 Hz, 1H), 4.17 (ddd, *J* = 12.0, 4.8, 1.6 Hz, 1H), 4.29 (dd, *J* = 11.2, 2.0 Hz, 1H), 6.96-7.02 (m, 2H), 7.22-7.34 (m, 5H), 7.40-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.8, 40.9, 44.9, 68.0, 79.8, 116.0 (d, *J* = 21.7 Hz), 125.8, 127.7, 128.0 (d, *J* = 3.4 Hz), 128.4, 136.1 (d, *J* = 8.0 Hz), 141.9, 162.7 (d, *J* = 247.1 Hz); LRMS (EI) 288 (M^+), 161 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{17}H_{17}FOS$ (M^+) 288.0984, found 288.0987.

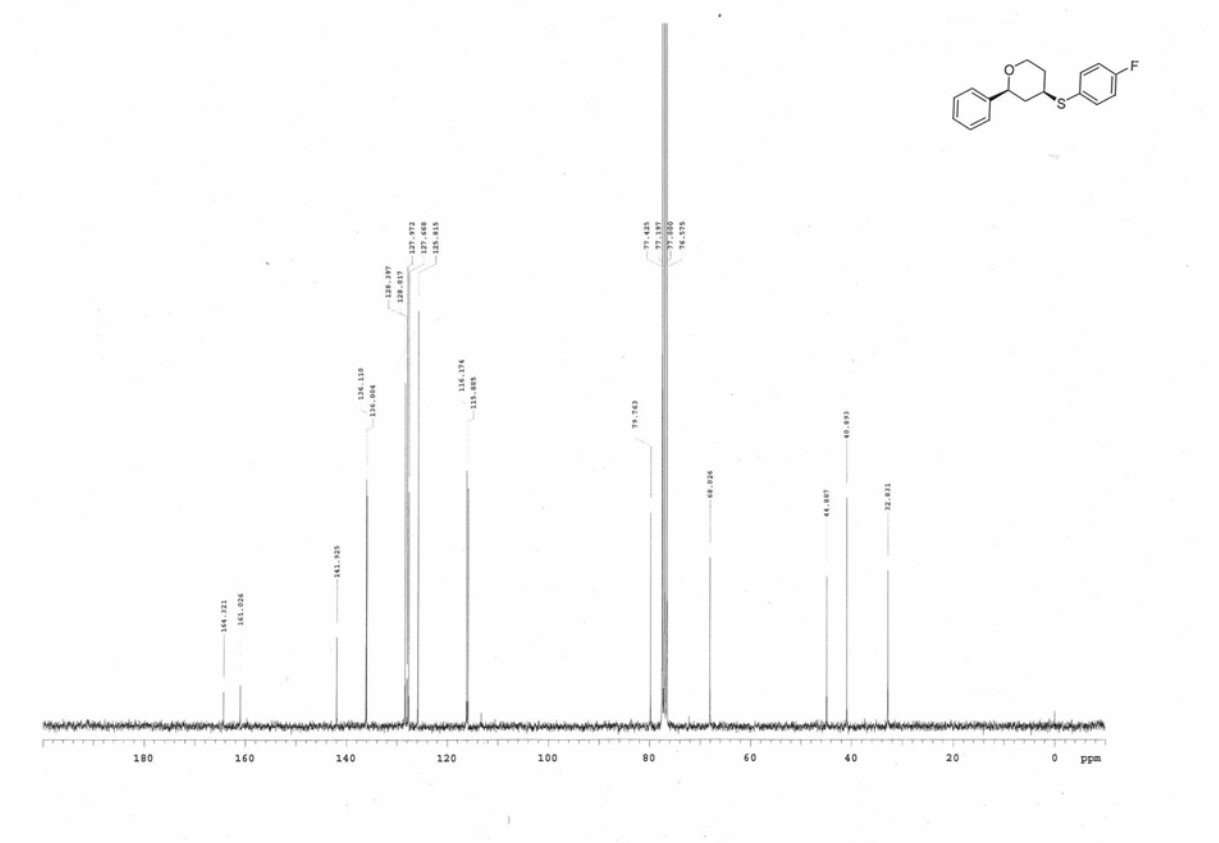
NOE Data for **8c**:



Signal Irradiated	NOE's observed
H_a	H_b (7.4 %), H_c (5.0 %)
H_b	H_a (7.9 %), H_c (2.8 %)

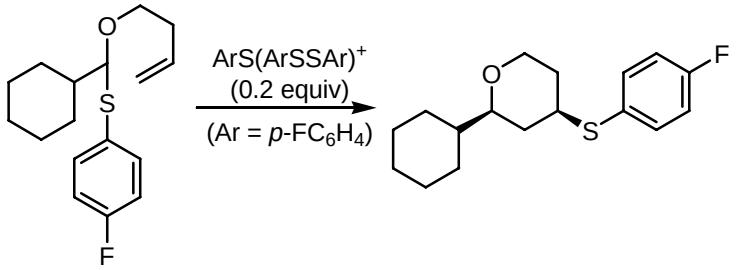


^{1}H NMR spectrum of *cis*-4-(fluorophenylthio)-2-phenyltetrahydropyran (**8c**).



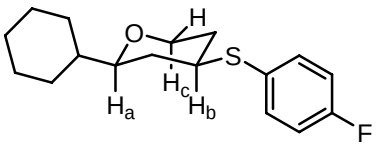
^{13}C NMR spectrum of *cis*-4-(fluorophenylthio)-2-phenyltetrahydropyran (**8c**).

***cis*-2-Cyclohexyl-4-(4-fluorophenylthio)tetrahydropyran (8d).**

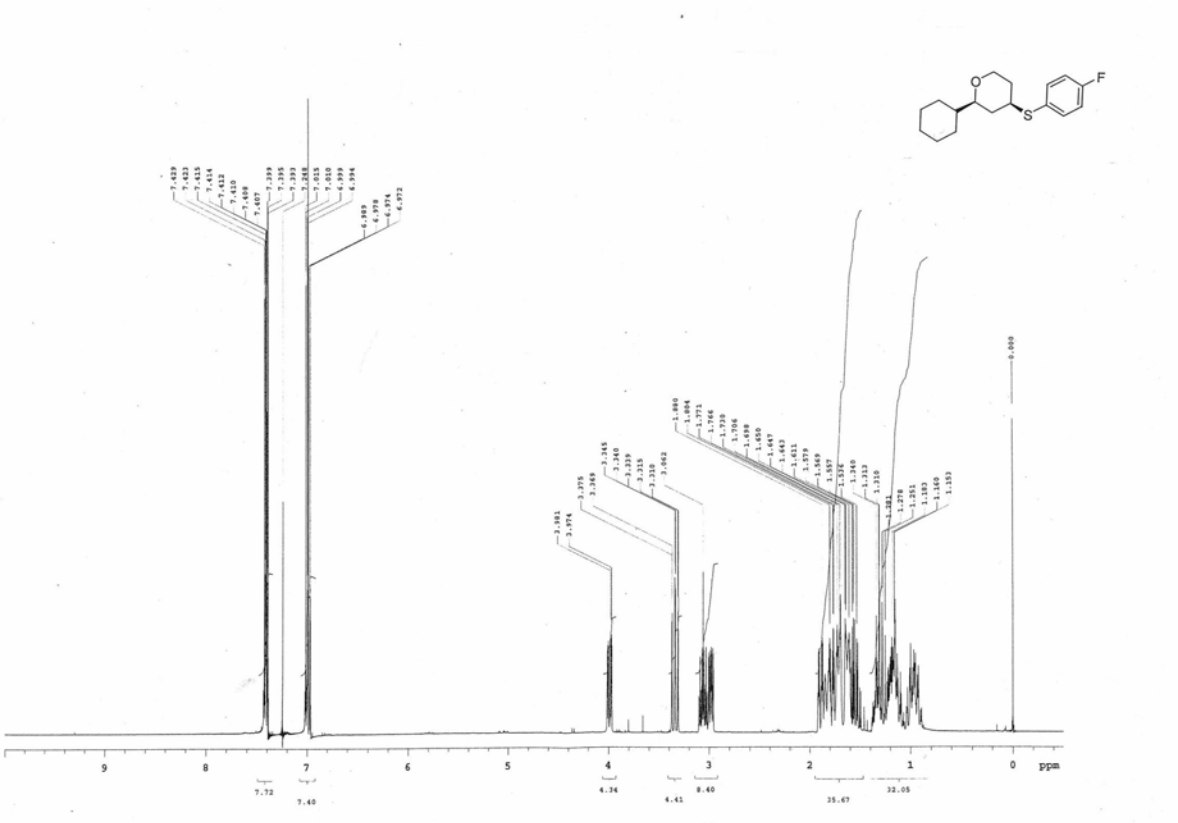


Prepared from ArSSAr (Ar = *p*-FC_6H_4) (254 mg, 0.999 mmol) and 3-butenyl cyclohexyl(4-fluorophenylthio)methyl ether (**6d**) (57.5 mg, 0.195 mmol) with 0.04 F/mol of electricity (initiation method A) and purified with flash chromatography (hexane/ EtOAc 20:1) (50.8 mg, 88%). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.31 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80-1.40 (m, 7H), 1.48-1.94 (m, 8H), 2.98 (ddd, *J* = 11.0, 4.0, 2.0 Hz, 1H), 3.06 (dddd, *J* = 16.0, 16.0, 4.0, 4.0 Hz, 1H), 3.34 (ddd, *J* = 11.9, 11.9, 2.4 Hz, 1H), 3.99 (ddd, *J* = 11.9, 4.6, 2.0 Hz, 1H), 6.96-7.04 (m, 2H), 7.38-7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.10, 26.18, 26.5, 28.7, 28.8, 33.5, 35.7, 43.0, 45.0, 67.8, 82.0, 116.0 (d, *J* = 21.7 Hz), 128.4 (d, *J* = 3.4 Hz), 135.7 (d, *J* = 8.0 Hz), 162.5 (d, *J* = 246.0 Hz); LRMS (EI) m/z 294 (M^+), 211 (M^+-C_6H_{11}), 167 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{17}H_{23}FOS$ (M^+) 294.1454, found 294.1451.

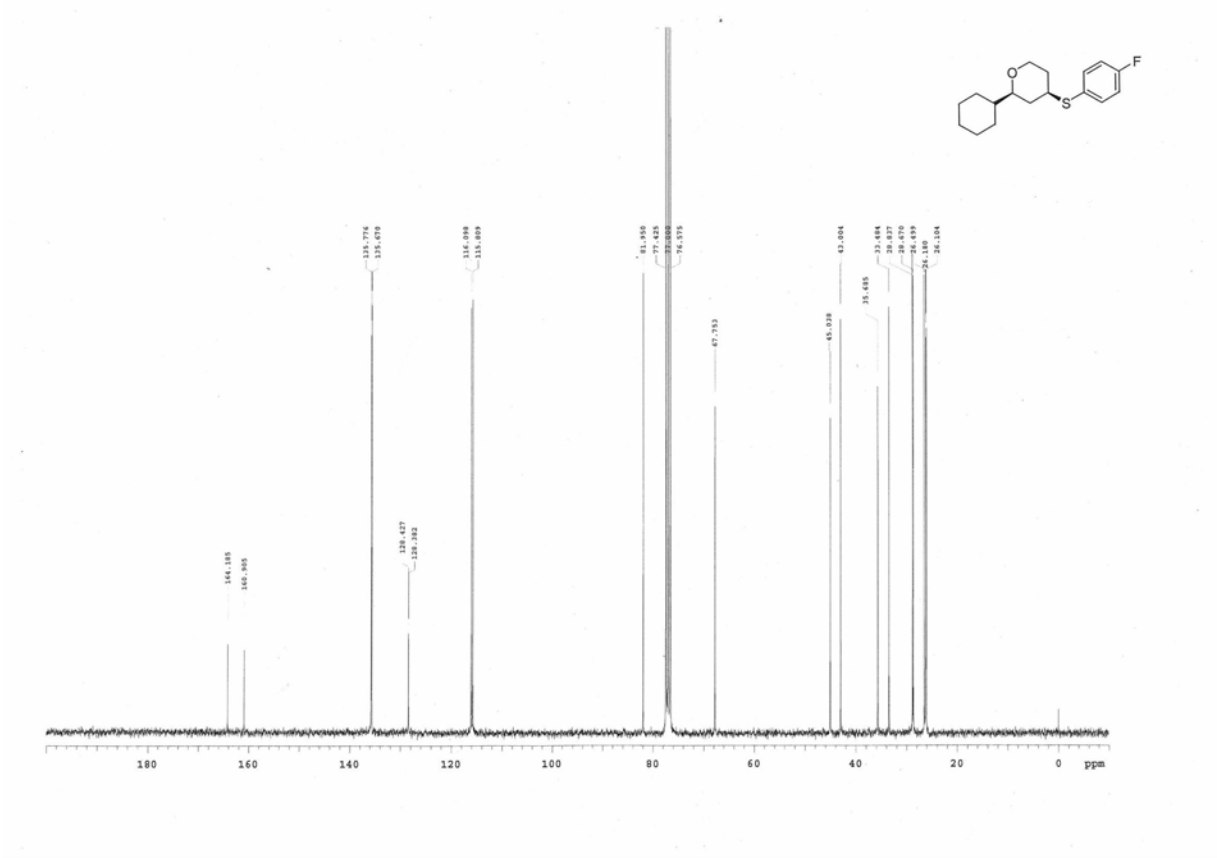
NOE Data for **8d**:



Signal Irradiated	NOE's observed
H_a	H_b (5.9 %), H_c (5.0 %)
H_b	H_a (5.6 %), H_c (3.1 %)

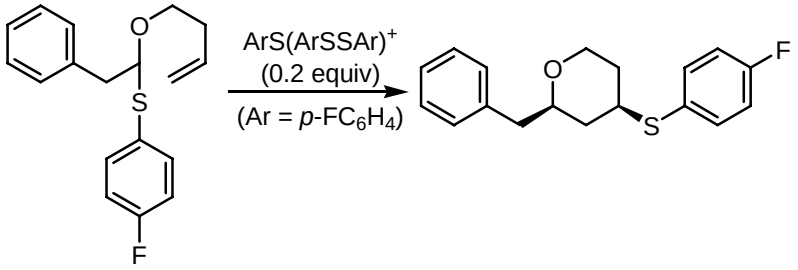


^{1}H NMR spectrum of *cis*-2-cyclohexyl-4-(4-fluorophenylthio)tetrahydropyran (**8d**).



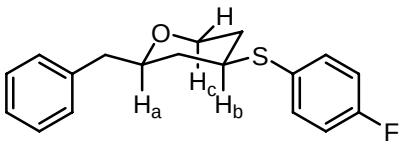
^{13}C NMR spectrum of *cis*-2-cyclohexyl-4-(4-fluorophenylthio)tetrahydropyran (**8d**).

2-Benzyl-4-(4-fluorophenylthio)tetrahydropyran (8e).

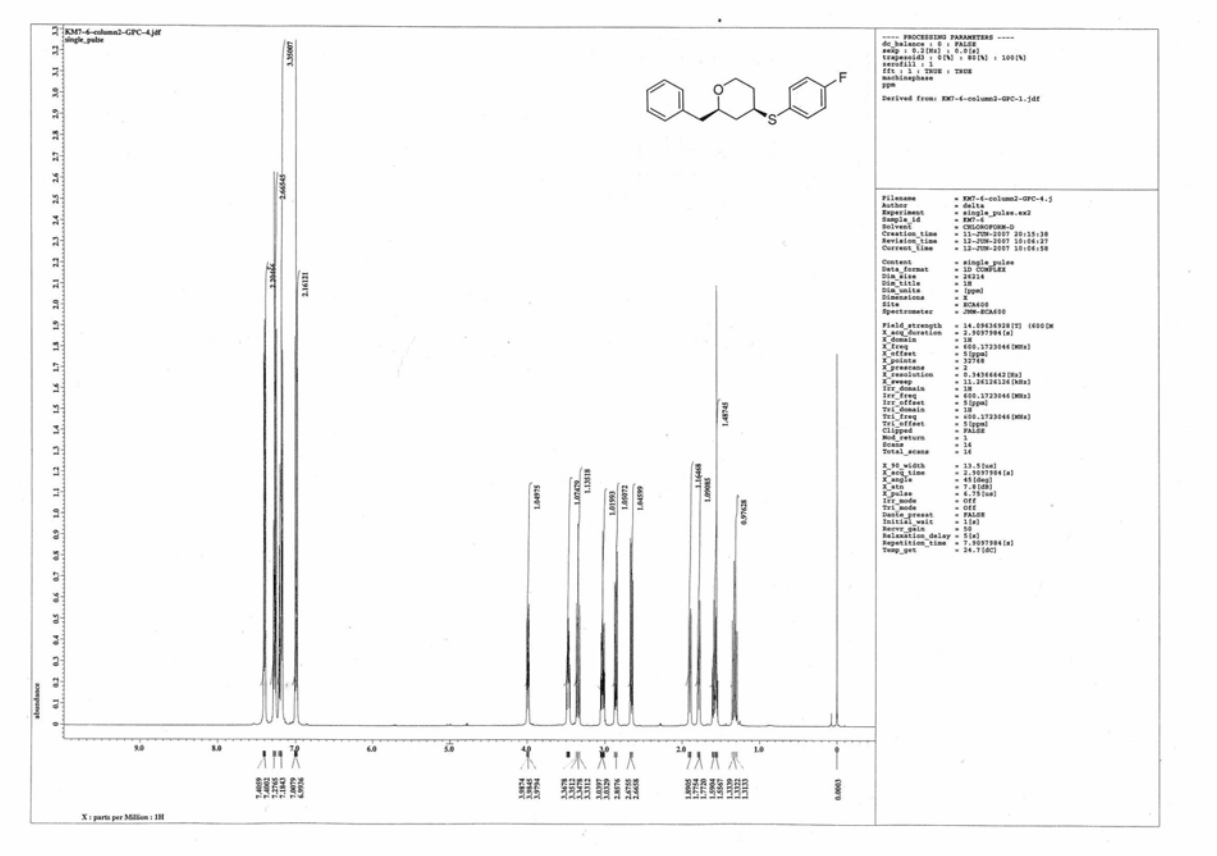


Prepared from ArSSAr (Ar = *p*-FC_6H_4) (254 mg, 0.999 mmol) and 3-butenyl benzyl(4-fluorophenylthio)methyl ether (**6e**) (60.3 mg, 0.199 mmol) with 0.04 F/mol of electricity (initiation method A) and purified with flash chromatography (hexane/ EtOAc 10:1) (45.2 mg, 75%). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.17 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.58 (dddd, *J* = 12.0, 12.0, 12.0, 4.9 Hz, 1H), 1.75-1.81 (m, 1H), 1.87-1.93 (m, 1H), 2.66 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.86 (dd, *J* = 13.7, 7.2 Hz, 1H), 3.03 (dddd, *J* = 12.0, 12.0, 4.1, 4.1 Hz, 1H), 3.35 (ddd, *J* = 12.0, 12.0, 2.1 Hz, 1H), 3.44-3.50 (m, 1H), 3.99 (ddd, *J* = 12.0, 4.9, 1.7 Hz, 1H), 6.95-7.02 (m, 2H), 7.15-7.23 (m, 3H), 7.24-7.31 (m, 2H), 7.37-7.44 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.2, 38.3, 42.7, 44.6, 67.7, 78.4, 116.0 (d, *J* = 21.5 Hz), 126.3, 128.2 (d, *J* = 2.9 Hz), 128.3, 129.3, 135.9 (d, *J* = 7.2 Hz), 138.1, 162.6 (d, *J* = 247.0 Hz); IR (neat) 1588, 1489, 1225 cm^{-1}; LRMS (EI) m/z 302 (M^+), 211 (M^+-CH_2Ph); HRMS (EI) calcd for $C_{18}H_{19}FOS$ (M^+) 302.1141, found 302.1142.

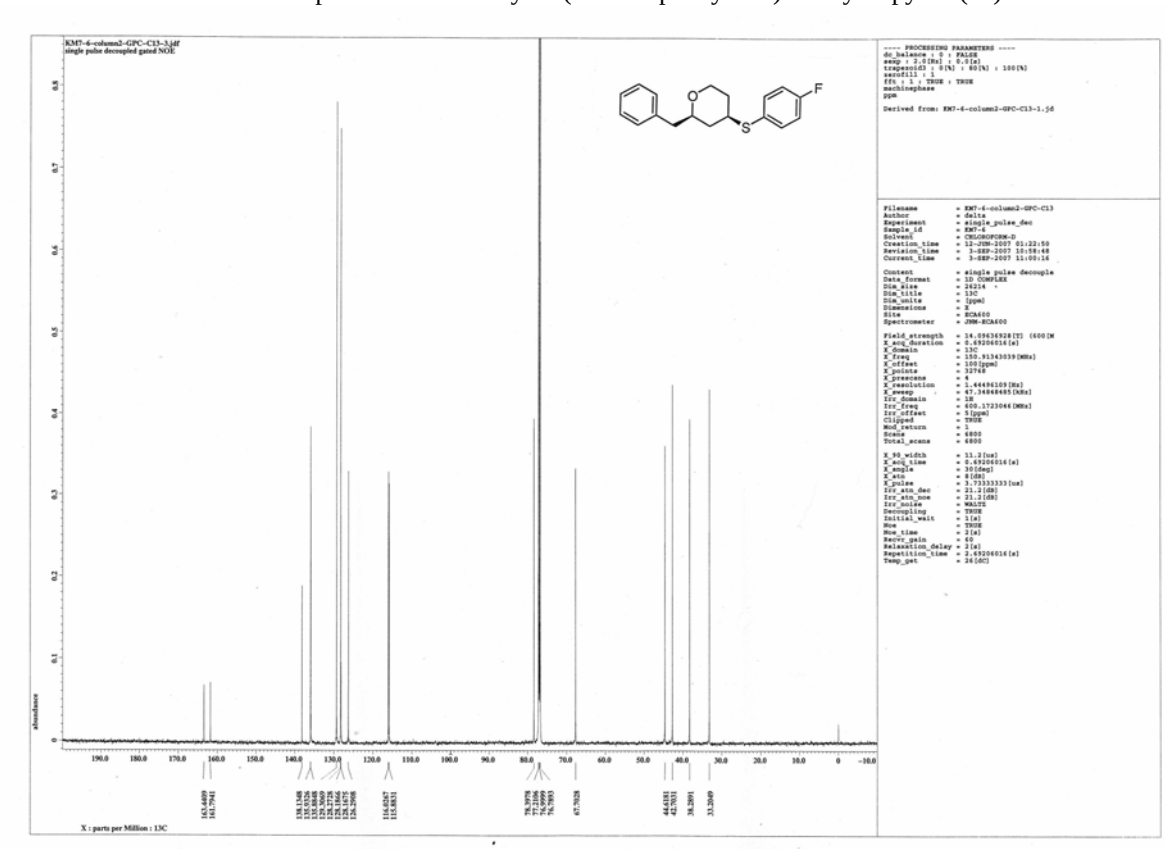
NOE Data for **8e**:



Signal Irradiated	NOE's observed
H_a	H_b (7.0 %), H_c (4.2 %)
H_b	H_a (7.1 %), H_c (2.5 %)

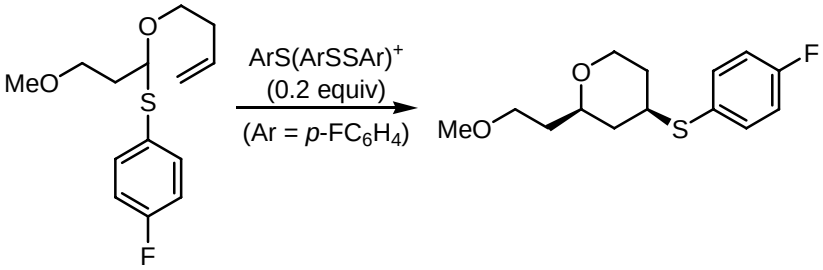


^{1}H NMR spectrum of 2-benzyl-4-(4-fluorophenylthio)tetrahydropyran (**8e**).

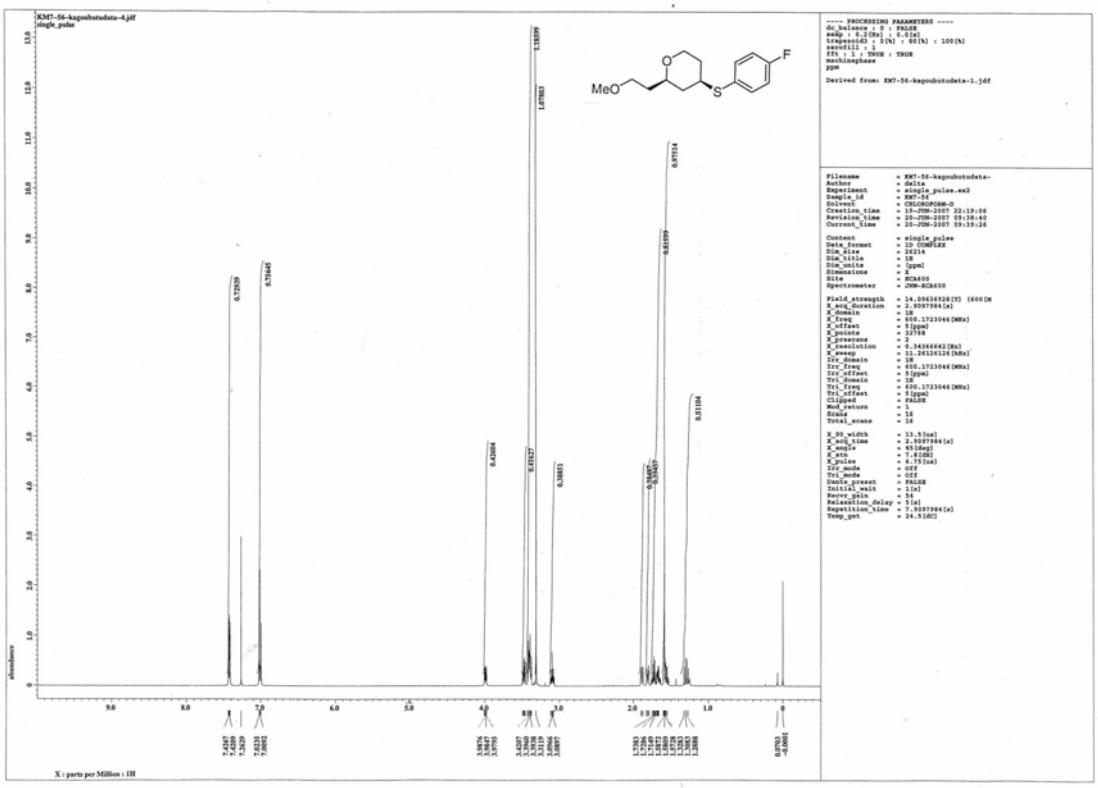


^{13}C NMR spectrum of 2-benzyl-4-(4-fluorophenylthio)tetrahydropyran (**8e**).

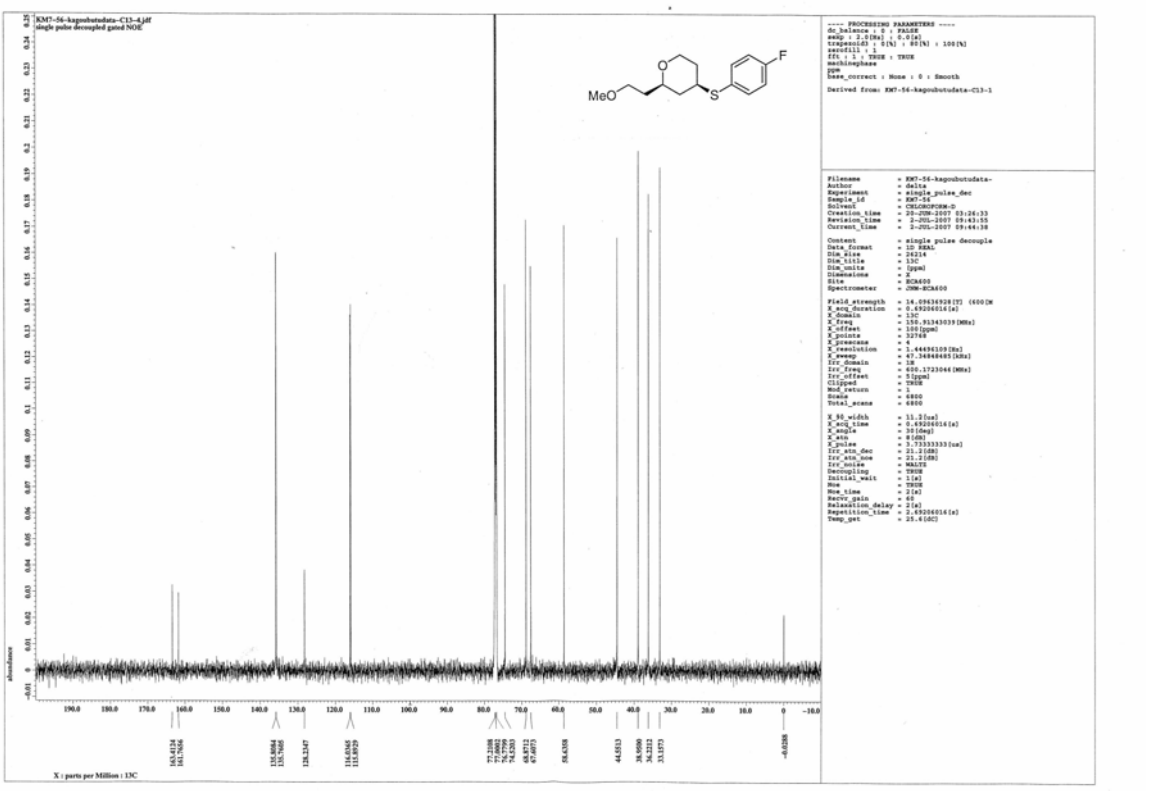
***cis*-4-(4-Fluorophenylthio)-2-(2-methoxyethyl)tetrahydropyran (8f).**



Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255 mg, 1.00 mmol) and 3-butenyl 2-methoxyethyl(4-fluorophenylthio)methyl ether (**6f**) (55.2 mg, 0.204 mmol) with 0.04 F/mol of electricity (initiation method A) and purified with flash chromatography (hexane/ EtOAc 5:1) (34.1 mg, 62%). This compound was obtained as a single diastereomer. The stereochemistry was determined based on the proton-proton coupling constants because proton homonuclear NOE experiments could not provide clear results due to the overlapping of signals: TLC R_f 0.32 (hexane/EtOAc 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.52-1.61 (m, 1H), 1.63-1.77 (m, 2H), 1.78-1.84 (m, 1H), 1.86-1.91 (m, 1H), 3.10(dddd, *J* = 12.0, 12.0, 4.1, 4.1 Hz, 1H), 3.31 (s, 3H), 3.36-3.44 (m, 3H), 3,45-3.50 (m, 1H), 3.99 (ddd, *J* = 10.3, 4.6, 1.7 Hz, 1H), 6.98-7.04 (m, 2H), 7.40-7.45 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.2, 36.2, 39.0, 44.6, 58.6, 67.6, 68.9, 74.5, 116.0 (d, *J* = 21.6 Hz), 128.2, 135.8 (d, *J* = 7.2 Hz), 162.6 (d, *J* = 247.0 Hz); IR (neat) 2849, 1489, 1225 cm^{-1}; LRMS (EI) m/z 270 (M^+), 143 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{14}H_{19}FO_2S$ (M^+) 270.1090, found 270.1091.

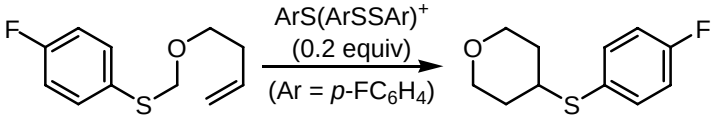


^{1}H NMR spectrum of
cis-4-(4-fluorophenylthio)-2-(2-methoxyethyl)tetrahydropyran (**8f**).

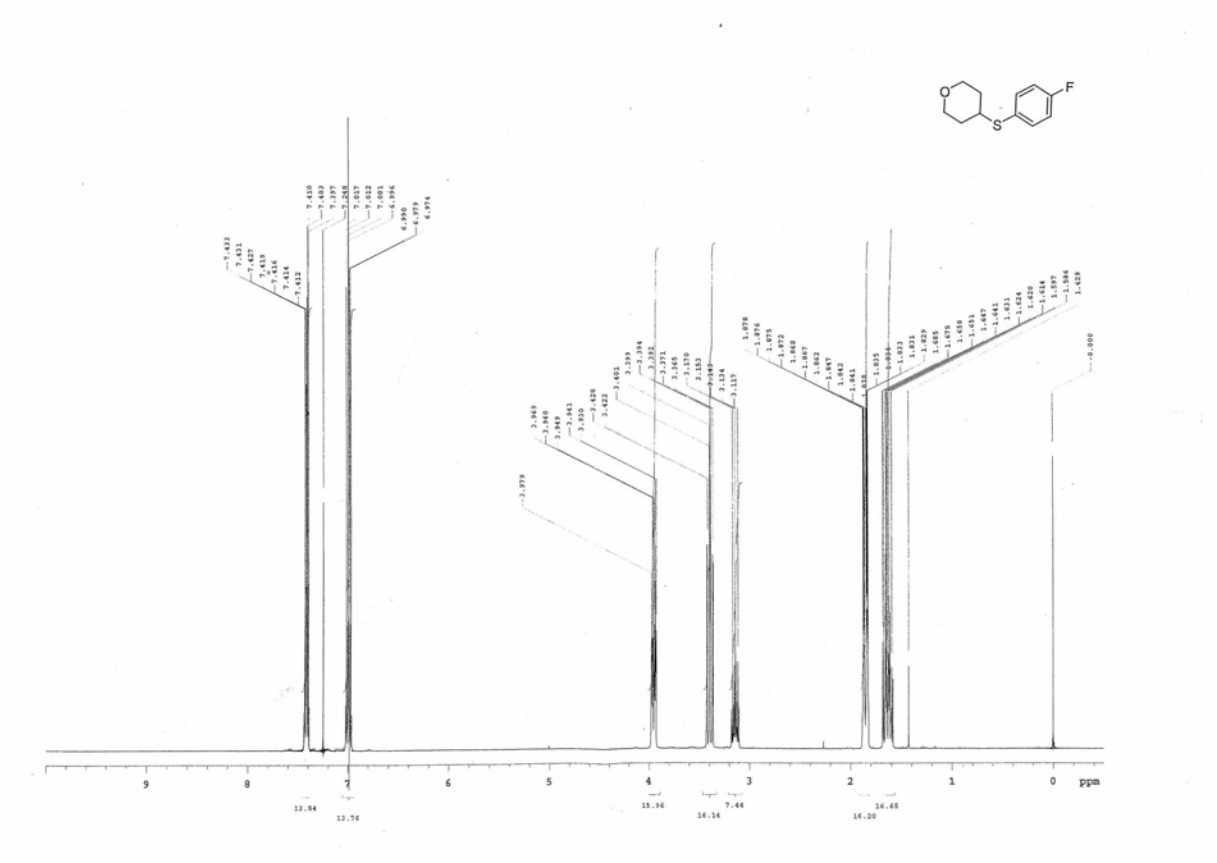


^{13}C NMR spectrum of
cis-4-(4-fluorophenylthio)-2-(2-methoxyethyl)tetrahydropyran (**8f**).

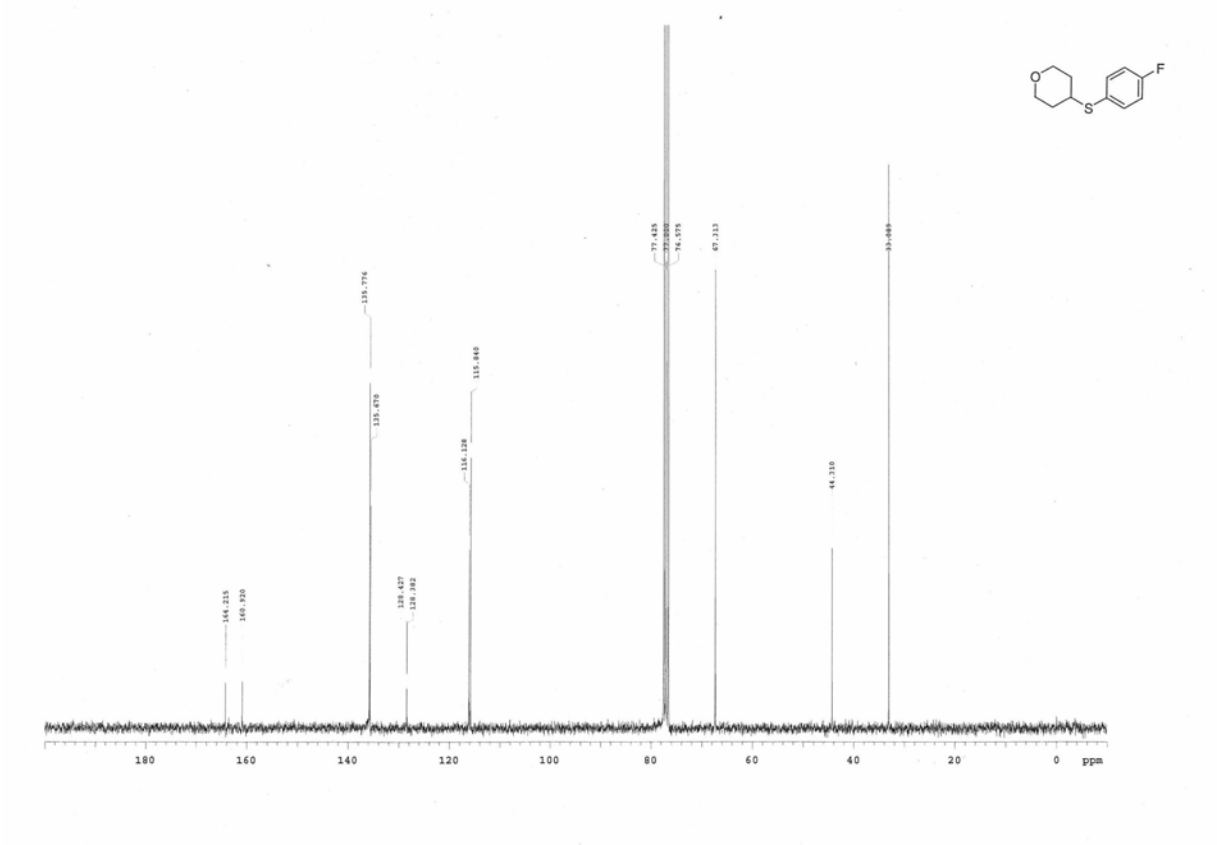
4-(4-Fluorophenylthio)tetrahydropyran (8g).



Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255 mg, 1.00 mmol) and 3-butenyl 4-fluorophenylthiomethyl ether (**6g**) (42.8mg, 0.202 mmol) with 0.04 F/mol of electricity (initiation method A, reaction temperature: -15 ^{o}C), and purified with flash chromatography (hexane/ EtOAc 20:1) (27.1 mg, 63%): TLC R_f 0.11 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.70 (m, 2H), 1.81-1.90 (m, 2H), 3.14 (dddd, *J* = 10.8, 10.8, 4.0, 4.0 Hz, 1H), 3.40 (ddd, *J* = 11.2, 11.2, 2.4 Hz, 2H), 3.95 (ddd, *J* = 11.2, 4.0, 4.0 Hz, 2H), 6.96-7.03 (m, 2H), 7.38-7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.1, 44.3, 67.3, 116.0 (d, *J* = 21.6 Hz), 128.4 (d, *J* = 3.4 Hz), 135.7 (d, *J* = 8.0 Hz), 162.6 (d, *J* = 247.1 Hz); IR (neat) 2845, 1590, 1489, 831 cm^{-1}; LRMS (EI) m/z 212 (M^+), 127 (M^+-C_5H_9O); HRMS (EI) calcd for $C_{11}H_{13}FOS$ (M^+) 212.0671, found 212.0664.



^{1}H NMR spectrum of 4-(4-fluorophenylthio)tetrahydropyran (**8g**).



^{13}C NMR spectrum of 4-(4-fluorophenylthio)tetrahydropyran (**8g**).

Other Products. Compound **7a**[6] (a mixture of two diastereomers; 6.8:1 by ^{1}H NMR analysis) was identified by the comparison of its spectral data with those of authentic samples.

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