Highly Enantioselective Organocatalytic Sulfa-Michael Addition to α, β-Unsaturated Ketones

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Supporting information

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General Methods

Unless stated otherwise, all reactions were carried out in flamedried glassware. All solvents were purified and dried according to standard methods prior to use. Catalyst **1a-i** were prepared according to literature known procedure. All the thiols and enone **8a-d** were commercially available and used without further purification. Enone **8e** and **8f** were prepared according to literature known procedures. ^{1}H spectra were recorded on 500 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 125 MHz in $CDCl_3$ using TMS or residual protio solvent signals as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}. Highresolution mass spectra (HRMS) were obtained by the ESI ionization sources. Melting point was measured using commercial melting point apparatus. The enantioselectivity was determined by chiral HPLC analysis using chiracel OD-H, OB-H, OJ-H and chiralpak AD, AD-H, AS-H columns with a 200 UV-detector. Optical rotations were measured on a commercial automatic polarimeter and reported as follows: $[\alpha]\ ^{T}_{D}$ (c = g/100 mL, solvent).

Experimental section

Preparation of chiral catalysts

Catalysts **1a**,[1] **1b**,[2] **1c**,[1] **1d**,[2] **1e**,[3] **1f**,[3] **1g**[4], **1h**,[4] and **1i**[5] were prepared according to literature known procedure.

1,1,1-trifluoro-*N*-((1S)-(6-methoxyquinolin-4-yl)((2S)-5-vinylquinuclidin-2-yl)methyl)methanesulfonamide (1g)[4]: This compound was synthesized according to literature known procedure. Yield: 46%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24-1.25 (m, 1H), 1.39-1.42 (m, 1H), 1.93-1.97 (m, 3H), 2.65 (bs, 1H), 3.17-3.64 (m, 5H), 3.98 (s, 3H), 5.04-5.11 (m, 2H), 5.30-5.35 (m, 1H), 5.60-5.64 (m, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 7.39-7.48 (m, 1H), 8.03-8.18 (m, 2H), 8.79 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ 24.0, 25.3, 28.2, 38.2, 41.7, 54.3, 55.8, 56.2, 65.3, 102.5, 117.3, 121.8, 123.3, 123.4, 124.3, 129.5, 131.1, 131.4, 138.9, 144.8, 147.5 , 148.2, 148.3, 159.9 (excess peaks due to C-F coupling); $[\alpha]_D^{23}$ = +22.0 (*c* 0.25, $CHCl_3$)]; HRMS (ES+) calc. for $C_{21}H_{25}F_3N_3O_3S$ $[M+H]^+$:456.1569, found: 456.1566.

***N*-((1S)-(6-methoxyquinolin-4-yl)((2S)-5-vinylquinuclidin-2-yl)methyl)-3,5-bis(trifluoromethyl)benzenesulfonamide (1h)[4]:** Yield: 55%; ^{1}H NMR (500 MHz, CD_3OD): δ 1.25-1.32 (m, 2H), 1.49-1.52 (m, 1H), 1.72-1.78 (m, 3H), 2.52 (bs, 1H), 2.94-2.97 (m, 2H), 3.37-3.49 (m, 2H), 4.00 (s, 3H), 5.02-5,10 (m, 2H), 5.22 (d, *J* = 11.0 Hz, 1H), 5.82 (dd, *J* = 17.0, 7.5 Hz, 1H), 7.35-7.43 (m, 3H), 7.65-7.79 (m, 4H), 8.45(d, *J* = 4.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ 25.8, 27.1, 28.6, 39.7, 41.7, 54.5, 55.7, 56.2, 61.9, 101.8, 115.7, 121.0, 122.7, 123.7, 124.9, 125.4, 127.5, 127.7, 129.4, 131.3, 132.1, 132.4, 141.1, 144.6, 145.7, 147.0, 147.0, 147.9, 160.0 (excess peaks due to C-F coupling); $[\alpha]_D^{25}$

= +17.5 (*c* 1.0, $CHCl_3$)]; HRMS (ES+) calc. for $C_{28}H_{28}F_6N_3O_3S$ $[M+H]^+$: 600.1756, found: 600.1752.

2,3,4,5,6-pentafluoro-*N*-((1S)-(6-methoxyquinolin-4-yl)((2S)-5-vinylquinuclidin-2-yl)methyl)benzamide (1i)[5]: This compound was synthesized according to literature known procedure. Yield: 89%; ^1H NMR (500 MHz, $CDCl_3$): δ 1.02-1.06 (m, 1H), 1.24-1.43-1.48 (m, 1H), 1.61-1.70 (m, 3H), 2.30 (bs, 1H), 2.65-2.78 (m, 2H), 2.94-3.15 (m, 3H), 3.24 (dd, *J* = 14.0, 10.5 Hz, 1H), 3.97 (s, 3H), 4.93-4.98 (m, 2H), 5.67-5.70 (m, 1H), 7.39-7.41 (m, 2H), 7.59 (bs, 1H), 8.04 (d, *J* = 9.5 Hz, 1H), 8.76 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ 25.8, 27.3, 28.6, 39.7, 41.7, 54.5, 55.7, 56.2, 61.9, 101.8, 115.9, 121.0, 122.7, 123.7, 124.9, 125.4, 127.5, 127.7, 129.4, 131.3, 132.1, 132.4, 141.1, 144.6, 145.7, 147.0, 147.9, 160.0, 172.0 (excess peaks due to C-F coupling); $[\alpha]_D^{23}$ = -50.6 (*c* 0.5, $CHCl_3$)]; HRMS (ES+) calc. for $C_{27}H_{25}F_5N_3O_2$ $[M+H]^+$: 518.1868, found: 518.1863.

Synthesis of (*E*)-4,4-dimethyl-1-phenylpent-2-en-1-one (8e)[6]

1M Potassium hydroxide (0.7 mmol) was added to a solution of acetophenone (3.65 mmol) and pivalaldehyde (7.3 mmol) in methanol (17 mL) at 0 ºC. The reaction mixture was warmed to room temperature and stirred at this temperature until completion of the reaction (TLC). Methanol was evaporated and the residue was suspended in water (15 mL). The mixture was neutralized with 2M HCl (0.35 mL, 0.7 mmol) and extracted with CH_2Cl_2 thrice. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product was isolated by column chromatography.

Yield: 84%; ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 9H), 6.77 (d, *J* = 16.0 Hz, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 7.44-7.47 (m, 2H), 7.53-7.54 (m, 1H), 7.90-7.92 (m, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 28.8, 34.3, 121.0, 128.4, 128.6, 132.6, 138.3, 159.7, 191.7; HRMS (ES+) calc. for $C_{13}H_{17}O$ $[M+H]^+$: 189.1279, found: 189.1284.

Synthesis of (*E*)-1,5-diphenylpent-2-en-1-one (8f)[7]

To a solution of dihydro cinnamaldehyde (10 mmol) in dichloromethane at -78 C, was added $BF_3.OEt_2$ (6 mmol) dropwise. After 10 minutes Trimethyl-(1-phenyl-vinyloxy)-silane (11 mmol) in dichloromethane was added dropwise. The reaction mixture was stirred and allowed to warm to room temperature. The reaction was quenched by addition of 1N HCl. The organic layer was separated, washed with saturated brine and dried over anhydrous Na_2SO_4. The organic layer was evaporated and filtered through silicagel. It gave the mixture of alkene and β-hydroxyketone. A mixture of this aldol (10 mmol), *p*-toluenesulfonic acid hydrate (12 mmol), and toluene (40 mL) was heated to 40 °C for 4 hours. After completion (judged by TLC), sodium sulfate was added to the reaction mixture, filtered, and the solid residue was washed with toluene (50 mL). The solvent was removed from the filtrate *in vacuo* and the crude product was purified by column chromatography to give α, β-unsaturated ketone as crude yellow oil.

Yield: 65%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.62-2.66 (m, 2H), 2.85 (t, J = 7.5 Hz, 2H), 6.84-6.88 (m, 1H), 7.07 (td, J = 15.5, 7.0 Hz, 1H), 7.20-7.22 (m, 3H), 7.27-7.32 (m, 2H), 7.43-7.46 (m, 2H), 7.52-7.56 (m, 1H), 7.86-7.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 34.5, 34.6, 126.3, 126.6, 127.9, 128.3, 128.5, 128.6, 132.7, 137.9, 140.9, 148.5, 190.9; HRMS (ES+) calc. for $C_{17}H_{17}O$ $[M+H]^+$: 237.1279, found: 237.1286.

General Procedure for the enantioselective organocatalytic Michael addition of thiols with α, β-unsaturated ketones.

The thiol (0.6 mmol) was added to a mixture of enone (0.5 mmol) and the catalyst **1e** (50 µl 0.01 M stock solution in dry toluene, 0.0289 mg, 0.0005 mmol) in toluene (1.0 mL) at the required temperature. The reaction mixture was stirred and the progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated in vacuum and the crude product was purified over silica gel by column chromatography. The enantiomeric excess of the Michael adduct was determined by chiral HPLC analysis.

(*S*)-3-(phenylthio)cyclohexanone (2a)[8]: This compound was obtained in >99% yield and 94% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 98:2]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 13.85 min (*S*), t_R(minor) = 17.98 min (*R*); $[\alpha]_D^{25}$ = –85.2 (*c* 1.0, $CHCl_3$) [lit.[8] (*S*) ee = 78%; $[\alpha]_D^{23}$ = –68.7 (*c* 1. 1, $CHCl_3$)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66-1.77 (m, 2H), 2.11-2.16 (m, 2H), 2.26-2.39 (m, 3H), 2.66-2.69 (m, 1H), 3.39-3.42 (m, 1H), 7.26-7.35 (m, 3H), 7.41-7.42(m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.0, 31.2, 40.8, 46.1, 46.7, 127.7, 129.0, 132.9, 133.2, 208.7; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2943, 1712. HRMS (ES+) calc. for $C_{12}H_{15}OS$ $[M+H]^+$: 207.0844, found: 207.0845.

(*S*)-3-(*o*-tolylthio)cyclohexanone (2b)[8]: This compound was obtained in >99% yield and 95% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 8.14 min (*S*), t_R(minor) = 11.46 min (*R*); $[\alpha]_D^{25}$ = –102.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68-1.77 (m, 2H), 2.12-2.14 (m, 2H), 2.28-2.41 (m, 6H), 2.66 (d, *J* = 13.0 Hz, 1H),

3.38-3.40 (m, 1H), 7.12-7.27 (m, 3H), 7.35-7.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.9, 24.2, 31.4, 41.0, 45.6, 47.8, 126.5, 127.8, 130.6, 132.7, 133.3, 140.6, 208.9; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2941, 1713. HRMS (ES+) calc. for $C_{13}H_{17}OS$ $[M+H]^+$: 221.1000, found: 221.1005.

(*S*)-3-(*p*-tolylthio)cyclohexanone (2c)[8]: This compound was obtained in >99% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 95:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 8.62 min (*S*), t_R(minor) = 10.64 min (*R*); $[\alpha]_D^{25}$ = –79.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.64-1.72 (m, 2H), 2.08-2.13 (m, 2H), 2.14 (s, 3H), 2.25-2.35 (m, 3H), 2.61-2.65 (m, 1H), 3.28-3.34 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 23.9, 31.1, 40.7, 46.3, 47.7, 129.0, 129.7, 133.8, 138.0, 208.8; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2941, 1713. HRMS (ES+) calc. for $C_{13}H_{17}OS$ $[M+H]^+$: 221.1000, found: 221.1009.

(*S*)-3-(2,4-dimethylphenylthio)cyclohexanone (2d): This compound was obtained in >99% yield and 88% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 7.40 min (*S*), t_R(minor) = 13.77 min (*R*); $[\alpha]_D^{25}$ = –72.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66-1.77 (m, 2H), 2.09-2.14 (m, 2H), 2.29-2.39 (m, 9H), 2.61-2.65 (m, 1H), 3.28-3.34 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.9, 21.1, 24.2, 31.4, 41.0, 46.1, 47.8, 127.3, 128.8, 131.5, 134.5, 138.2, 141.1, 209.1; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2959, 1714. HRMS (ES+) calc. for $C_{14}H_{19}OS$ $[M+H]^+$: 235.1157, found: 235.1158.

(*S*)-3-(2,6-dimethylphenylthio)cyclohexanone (2e)[8]: This compound was obtained in >99% yield and 99% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 6.81 min (*R*), t_R(major) = 8.30 min (*S*); $[\alpha]_D^{25}$ = –103.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.62-1.67 (m, 1H), 1.74-1.81 (m, 1H), 2.04-2.14 (m, 2H), 2.29-2.41 (m, 3H), 2.55 (s, 6H), 2.55-2.59 (m, 1H), 3.15-3.20 (m, 1H), 7.09-7.14 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.2, 24.3, 31.7, 40.9, 46.3, 47.9, 128.2, 128.5, 131.5, 143.3, 208.9; IR(KBr pellet, cm^{-1}) 2958, 1715; m.p = 80 °C. HRMS (ES+) calc. for $C_{14}H_{19}OS$ $[M+H]^+$: 235.1157, found: 235.1159.

(*S*)-3-(2-ethylphenylthio)cyclohexanone (2f): This compound was obtained in >99% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 7.55 min (*S*), t_R(minor) = 11.47 min (*R*); $[\alpha]_D^{25}$ = –76.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.5 Hz, 3H), 1.58-1.80 (m, 2H), 2.11-2.16 (m, 2H), 2.28-2.41 (m, 3H), 2.66 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.82 (q, *J* = 7.5, 2H), 3.38-3.43 (m, 1H), 7.12-7.16 (m, 1H), 7.19-7.25 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.4, 24.2, 27.3, 31.4, 41.0, 46.2, 47.8, 126.5, 128.0, 129.1, 132.1, 133.5, 146.5, 208.9; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2962, 1714. HRMS (ES+) calc. for $C_{14}H_{19}OS$ $[M+H]^+$: 235.1157, found: 235.1155.

(*S*)-3-(naphthalen-2-ylthio)cyclohexanone (2g)[9]: This compound was obtained in 97% yield and 93% ee. The optical purity was determined by HPLC on chiralpak AD-H column [*n*-hexane/2-propanol 99:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 21.40 min (*S*), t_R(minor) = 29.34 min (*R*); $[\alpha]_D^{25}$ = –78.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz,

$CDCl_3$): δ 1.68-1.81 (m, 2H), 2.11-2.20 (m, 2H), 2.29-2.44 (m, 3H), 2.70-2.74 (m, 1H), 3.50-3.56 (m, 1H), 7.46-7.50 (m, 3H), 7.76-7.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 31.3, 40.8, 46.1, 47.7, 126.4, 126.6, 127.4, 127.6, 128.6, 130.2, 130.4, 132.1, 132.5, 133.6, 208.4; IR (KBr pellet, cm^{-1}): 2933, 1704; m.p = 58 °C. HRMS (ES+) calc. for $C_{16}H_{17}OS$ $[M+H]^+$: 257.1000, found: 257.1004.

(*S*)-3-(4-tert-butylphenylthio)cyclohexanone (2h)[8]: This compound was obtained in >99% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 98:2]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 9.55 min (*S*), t_R(minor) = 12.83 min (*R*); $[\alpha]_D^{25}$ = –59.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 9H), 1.67-1.75 (m, 2H), 2.11-2.14 (m, 2H), 2.27-2.38 (m, 3H), 2.64-2.67 (m, 1H), 2.32-2.35 (m, 1H), 7.31-7.36 (m, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.2, 31.3, 31.4, 34.5, 40.9, 46.4, 47.9, 126.2, 129.3, 133.6, 151.3, 209.1; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2959, 1713. HRMS (ES+) calc. for $C_{16}H_{23}OS$ $[M+H]^+$: 263.1470, found: 263.1472.

(*S*)-3-(2-methoxyphenylthio)cyclohexanone(2i)[9]: This compound was obtained in >99% yield and 97% ee. The optical purity was determined by HPLC on chiralcel OB-H column [*n*-hexane/2-propanol 99:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 61.60 min (*S*), t_R(minor) = 71.50 min (*R*); $[\alpha]_D^{25}$ = –99.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.57-1.74 (m, 2H), 2.10-2.15 (m, 2H), 2.27-2.38 (m, 3H), 2.63 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.52-3.57 (m, 1H), 3.88 (s, 3H), 6.87-6.91 (m, 2H), 7.25-7.29 (m, 1H), 7.36-7.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1, 31.1, 40.9, 43.9, 47.7, 55.7, 110.9, 120.7, 120.9, 129.4, 134.6, 159.1, 209.1; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2921, 1710. HRMS (ES+) calc. for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0949, found: 237.0948.

(*S*)-3-(4-methoxyphenylthio)cyclohexanone (2j)[9]: This compound was obtained in >99% yield and >99% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 18.39 min (*S*), t_R(minor) = 37.94 min (*R*); $[\alpha]_D^{25}$ = –61.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.64-1.67 (m, 2H), 2.09-2.11 (m, 2H), 2.26-2.32 (m, 3H), 2.59- 2.62 (m, 1H), 3.22-3.24 (m, 1H), 3.79 (s, 3H), 6.82-6.85 (m, 2H), 6.36-6.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.2, 31.3, 40.9, 47.1, 47.9, 55.4, 114.7, 122.9, 136.6, 160.1, 209.2; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2941, 1712. HRMS (ES+) calc. for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0949, found: 237.0947.

(*S*)-3-(2-fluorophenylthio)cyclohexanone (2k): This compound was obtained in >99% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 9.98 min (*S*), t_R(minor) = 16.53 min (*R*); $[\alpha]_D^{25}$ = –68.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58-1.73 (m, 2H), 2.10-2.14 (m, 2H), 2.29-2.38 (m, 3H), 2.64 (dd, *J* = 15.0, 5.0 Hz, 1H), 3.46-3.51 (m, 1H), 7.06-7.11 (m, 2H), 7.28-7.31 (m, 1H), 7.41-7.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.0, 31.3, 40.9, 45.4, 47.9, 116.1 (d, *J* = 22.5 Hz), 119.7 (d, *J* = 17.5 Hz) ,124.6 (d, *J* = 7.8 Hz), 130.4 (d, *J* = 8.8 Hz), 136.2, 162.8 (d, *J* = 246.2 Hz), 208.6 (excess peaks due to C-F coupling); IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2944, 1713. HRMS (ES+) calc. for $C_{12}H_{14}FOS$ $[M+H]^+$: 225.0749, found: 225.0745.

(*S*)-3-(4-fluorophenylthio)cyclohexanone (2l): This compound was obtained in >99% yield and 91% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 11 mL/min; λ = 254 nm; t_R(major) = 9.64 min (*S*), t_R(minor) = 24.54 min (*R*); $[\alpha]_D^{25}$ = –65.6 (*c* 1.0, $CHCl_3$);^{1}H NMR (500 MHz,

$CDCl_3$): δ 1.66-1.71 (m, 2H), 2.10-2.15 (m, 2H), 2.28-2.35 (m, 3H), 2.62 (dd, *J* = 14.0, 4.0 Hz, 1H), 3.31 (m, 1H), 6.99-7.03 (m, 2H), 7.40-7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1, 31.2, 40.9, 46.9, 47.8, 116.2 (d, *J* = 21.3 Hz), 127.9, 136.2 (d, *J* = 8.8 Hz), 162.9 (d, *J* = 246.3 Hz), 208.7 (excess peaks due to C-F coupling); IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2923, 1713. HRMS (ES+) calc. for $C_{12}H_{14}FOS$ $[M+H]^+$: 225.0749, found: 225.0747.

(*S*)-3-(2,4-difluorophenylthio)cyclohexanone (2m): This compound was obtained in >99% yield and 85% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 8.82 min (*S*), t_R(minor) = 19.60 min (*R*); $[\alpha]_D^{25}$ = –68.4 (*c* 1.0, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$): δ 1.63-1.72 (m, 2H), 2.06-2.14 (m, 2H), 2.24-2.35 (m, 3H), 2.58-2.62 (m, 1H), 3.35-3.41 (m, 1H), 6.82-6.87 (m, 2H), 7.40-7.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 31.1, 40.7, 45.8, 47.6, 104.4, 104.7, 104.9, 111.8, 111.9, 112.0, 112.0, 114.8, 115.0, 137.8, 137.9, 162.2, 162.3, 162.4, 162.5, 164.2, 164.3, 164.4, 164.8, 208.3 (excess peaks due to C-F coupling); IR (NaCl cell, CH_2Cl^2, cm^{-1}): 2929, 1713. HRMS (ES+) calc. for $C_{12}H_{13}F_2OS$ $[M+H]^+$: 243.0655, found: 243.0659.

(*S*)-3-(2-chlorophenylthio)cyclohexanone (2n): This compound was obtained in >99% yield and 91% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 99:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 17.64 min (*S*), t_R(minor) = 24.95 min (*R*); $[\alpha]_D^{25}$ = –70.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58-1.81 (m, 2H), 2.12-2.17 (m, 2H), 2.30-2.44 (m, 3H), 2.68 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.55-3.59 (m, 1H), 7.19-7.22 (m, 2H), 7.40-7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.2, 31.1, 40.9, 44.9, 47.6, 127.3, 128.8, 130.3, 132.6, 133.8, 137.0,

208.4; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2943, 1713. HRMS (ES+) calc. for $C_{12}H_{14}ClOS$ $[M+H]^+$: 241.0454, found: 241.0456.

(*S*)-3-(4-chlorophenylthio)cyclohexanone (2o)[8]: This compound was obtained in >99% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 99:1]; flow rate 0.5 mL/min; λ = 254 nm; t_R(major) = 43.20 min (*S*), t_R(minor) = 51.99 min (*R*); $[\alpha]_D^{25}$ = –79.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65-1.73 (m, 2H), 2.07-2.14(m, 2H), 2.25-2.35 (m, 3H), 2.62-2.66 (m, 1H), 3.35-3.40 (m, 1H), 7.26 (d, *J* = 13.4 Hz, 2H), 7.32 (d, *J* = 13.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 31.1, 40.7, 46.2, 47.5, 129.1, 131.5, 134.0, 134.4, 208.1; IR (KBr pellet, cm^{-1}): 2954, 1704; m.p = 76 °C. HRMS (ES+) calc. for $C_{12}H_{14}ClOS$ $[M+H]^+$: 241.0454, found: 241.0457.

(*S*)-3-(2-bromophenylthio)cyclohexanone (2p): This compound was obtained in 95% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 99:1]; flow rate 0.5 mL/min; λ = 254 nm; t_R(minor) = 45.28 min (*R*), t_R(major) = 49.57 min (*S*); $[\alpha]_D^{25}$ = –117.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68-1.83 (m, 2H), 2.12-2.19 (m, 2H), 2.31-2.45 (m, 3H), 2.68-2.72 (m, 1H), 3.54-3.60 (m, 1H), 7.09-7.12 (m, 1H), 7.24-7.27 (m, 1H), 7.40-7.42 (m, 1H), 7.58-7.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1, 30.9, 40.8, 45.1, 47.4, 127.3, 127.8, 128.6, 133.2, 133.4, 133.6, 208.3; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2940, 1712. HRMS (ES+) calc. for $C_{12}H_{14}BrOS$ $[M+H]^+$: 284.9949, found: 284.9946.

(*S*)-3-(4-bromophenylthio)cyclohexanone (2q): This compound was obtained in 97% yield and 89% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 11.01

min (*S*), t_R(minor) = 18.37 min (*R*); $[\alpha]_D^{25}$ = –67.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68-1.73 (m, 2H), 2.11-2.14 (m, 2H), 2.27-2.37 (m, 3H), 2.65 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.37-3.41(m, 1H), 7.25-7.28 (m, 2H), 7.42-7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.0, 31.2, 40.9, 46.3, 47.7, 122.2, 132.3, 134.8, 137.0, 208.5; IR (KBr pellet, cm^{-1}): 2953, 1704; m.p = 90 °C. HRMS (ES+) calc. for $C_{12}H_{14}BrOS$ $[M+H]^+$: 284.9949, found: 284.9948.

(*R*)-4,4-dimethyl-3-(phenylthio)cyclohexanone (3a)[10]: This compound was obtained in >99% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 23.34 min (*S*), t_R(major) = 28.41 min (*R*); $[\alpha]_D^{25}$ = –108.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (s, 3H), 1.24 (s, 3H), 1.60-1.66 (m, 1H), 1.86-1.90 (m, 1H), 2.27-2.31 (m, 1H), 2.41-2.48 (m, 1H), 2.54-2.64 (m, 2H), 3.15-3.18 (m, 1H), 7.21-7.23 (m, 4H), 7.38-7.40 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 29.1, 34.7, 37.9, 38.7, 45.5, 57.7, 127.5, 129.2, 132.8, 134.6, 209.1; IR (KBr pellet, cm^{-1}): 2953, 2925, 1706; m.p = 78 °C. HRMS (ES+) calc. for $C_{14}H_{19}OS$ $[M+H]^+$: 235.1157, found: 235.1159.

(*R*)-4,4-dimethyl-3-(naphthalen-2-ylthio)cyclohexanone (3b)[9]: This compound was obtained in 96% yield and 91% ee. The optical purity was determined by HPLC on chiralpak AD-H column [*n*-hexane/2-propanol 99:1]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 13.44 min (*S*), t_R(major) = 15.77 min (*R*); $[\alpha]_D^{25}$ = –81.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 3H), 1.30 (s, 3H), 1.63-1.69 (m, 1H), 1.89-1.93 (m, 1H), 2.29-2.32 (m, 1H), 2.43-2.50 (m, 1H), 2.56-2.68 (m 2H), 3.29 (dd, *J* = 11.0, 5.0 Hz, 1H), 7.44-7.49 (m, 3H), 7.74-7.87 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 29.1, 34.7, 37.8, 38.6, 45.3, 57.4, 126.2, 126.5, 127.3, 127.6, 128.7, 129.7, 131.3, 131.8, 132.3,

133.6, 208.9; IR (KBr pellet, cm^{-1}) 2962, 2922, 1706. HRMS (ES+) calc. for $C_{18}H_{21}OS$ $[M+H]^+$: 285.1313, found: 285.1316.

(*R*)-4,4-dimethyl-3-(*o*-tolylthio)cyclohexanone (3c): This compound was obtained in 96% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 8.64 min (*S*), t_R(major) = 9.36 min (*R*); $[\alpha]_D^{25}$ = –108.3 (*c* 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 3H), 1.28 (s, 3H), 1.64 (dt, *J* = 10.0, 5.0 Hz, 1H), 1.86-1.93 (m, 1H), 2.30 (td, *J* = 15.3, 5.0 Hz, 1H), 2.38-2.51 (m, 4H), 2.53-2.60 (m, 2H), 3.13 (dd, *J* = 10.5, 5.5 Hz, 1H), 7.11-7.25 (m, 3H), 7.37 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 21.3, 29.0, 34.7, 37.9, 38.7, 45.3, 56.7, 126.7, 127.7, 130.6, 133.4, 133.5, 140.6, 209.2; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 3009, 2958, 1704. HRMS (ES+) calc. for $C_{15}H_{21}OS$ $[M+H]^+$: 249.1313, found: 249.1315.

(*R*)-4,4-dimethyl-3-(*p*-tolylthio)cyclohexanone (3d): This compound was obtained in >99% yield and >99% ee. The optical purity was determined by HPLC on chiralcel OB-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 6.11 min (*R*), t_R(minor) = 10.08 min (*S*); $[\alpha]_D^{25}$ = –99.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (s, 3H), 1.26 (s, 3H), 1.61 (dt, *J* = 12.5, 5.0 Hz, 1H), 1.85-1.90 (m, 1H), 2.25-2.30 (m, 1H), 2.31 (s, 3H), 2.40-2.61 (m, 3H), 3.08 (dd, *J* = 15.0, 5.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 21.2, 29.1, 34.7, 37.9, 38.7, 45.4, 58.2, 129.9, 131.8, 133.5, 137.7, 209.3; IR (KBr pellet, cm^{-1}): 3020, 2949, 1705; m.p = 76 °C. HRMS (ES+) calc. for $C_{15}H_{21}OS$ $[M+H]^+$: 249.1313, found: 249.1317.

(*R*)-3-(2-methoxyphenylthio)-4,4-dimethylcyclohexanone (3e): This compound was obtained in 94% yield and 97% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 11.76 min (*S*), t_R(major) = 14.95 min (*R*); $[\alpha]_D^{25}$ = –143.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (s, 3H), 1.25 (s, 3H), 1.59-1.65 (m, 1H), 1.85-1.89 (m, 1H), 226-2.29 (m,1H), 2.40-2.60 (m, 3H), 3.23 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.86 (s, 3H), 6.83-6.89 (m, 2H), 7.22-7.24 (m, 1H), 7.34-7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6, 28.9, 34.6, 37.9, 38.8, 45.3, 54.8, 55.7, 110.9, 121.0, 121.9, 129.2, 134.3, 158.9, 209.6; IR (KBr pellet, cm^{-1}) 3071, 3007, 1707; m.p = 95 °C.; HRMS (ES+) calc. for $C_{15}H_{21}O_2S$ $[M+H]^+$: 265.1262, found: 265.1262.

(*R*)-3-(4-methoxyphenylthio)-4,4-dimethylcyclohexanone (3f): This compound was obtained in 98% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 11.47 min (*S*), t_R(major) = 16.04 min (*R*); $[\alpha]_D^{25}$ = –65.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 3H), 1.26 (s, 3H), 1.59 (dt, *J* = 13.0, 5.0 Hz, 1H), 1.84-1.89 (m, 1H), 2.25-2.29 (m, 1H), 2.39-2.57 (m, 3H), 2.98 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.81 (s, 3H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 29.2, 31.3, 34.6, 37.9, 38.8, 45.6, 57.9, 126.2, 130.9, 133.0, 150.9, 209.4; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2923, 1591; HRMS (ES+) calc. for $C_{15}H_{21}O_2S$ $[M+H]^+$: 265.1262, found: 265.1267.

(*R*)-3-(4-chlorophenylthio)-4,4-dimethylcyclohexanone (3g): This compound was obtained in >99% yield and 91% ee. The optical purity was determined by HPLC on chiralcel OB-H column [*n*-hexane/2-propanol 98:2]; flow rate 1 mL/min; λ = 254 nm;

t_R(major) = 11.89 min (*R*), t_R(minor) = 15.10 min (*S*); $[\alpha]_D^{25}$ = –78.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (s, 3H), 1.25 (s, 3H), 1.63 (dt, *J* = 15.0, 4.5 Hz, 1H), 1.86-1.96 (m, 1H), 2.27-2.32 (m, 1H), 2.41-2.49 (m, 1H), 2.52-2.61 (m, 2H), 312 (ddd, *J* = 10.0, 5.0, 1.5 Hz, 1H), 7.25 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.32 (dd, *J* = 8.5, 2.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 29.1, 34.8, 37.9, 38.6, 45.3, 58.0, 129.4, 133.2, 133.8, 134.1, 208.8; IR (KBr pellet, cm^{-1}): 2972, 2859, 1706; m.p = 98 °C.; HRMS (ES+) calc. for $C_{14}H_{17}ClOSNa$ $[M+Na]^+$: 291.0586, found: 291.0587.

(*R*)-3-(4-tert-butylphenylthio)-4,4-dimethylcyclohexanone (3h): This compound was obtained in 92% yield and 91% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 90:10]; flow rate 0.7 mL/min; λ = 220 nm; t_R(minor) = 7.12 min (*S*), t_R(major) = 12.84 min (*R*); $[\alpha]_D^{25}$ = –57.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (s, 3H), 1.29 (bs, 12H), 1.59-1.66 (m, 1H), 1.87-1.91 (m, 1H), 2.27-2.32 (m, 1H), 2.42-2.43 (m, 1H), 2.52-2.64 (m, 2H), 3.10 (dd, *J* = 10.5, 4.5 Hz, 1H), 7.29-7.34 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 27.8, 29.2, 31.3, 34.5, 37.9, 38.8, 45.6, 57.9, 126.2, 133.1, 150.9, 169.9, 209.4; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2961, 1715. HRMS (ES+) calc. for $C_{18}H_{26}OSNa$ $[M+Na]^+$: 313.1602, found: 313.1600.

(*S*)-3-(phenylthio)cyclopentanone (4a)[10]: This compound was obtained in >99% yield and 80% ee. The optical purity was determined by HPLC on chiralcel OB-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 20.15 min (*S*), t_R(minor) = 25.77 min (*R*); $[\alpha]_D^{25}$ = +7.4 (*c* 1.0, $CHCl_3$); [lit.[8] (*S*) ee = 21%; $[\alpha]_D^{23}$ = +1.8 (*c* 1. 3, $CHCl_3$)] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.97-2.04 (m, 1H), 2.18-2.27 (m, 2H), 2.30-2.37 (m, 1H), 2.43-2.50 (m, 1H), 2.59 (dd, *J* = 18.5, 7.0 Hz, 1H), 3.86-3.91 (m, 1H), 7.19-7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.4, 36.9, 43.5, 45.3, 127.5, 129.2,

132.1, 134.3, 216.5; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2923, 1742. HRMS (ES+) calc. for $C_{11}H_{13}OS$ $[M+H]^+$: 193.0687, found: 193.0689.

(*S*)-3-(*o*-tolylthio)cyclopentanone (4b): This compound was obtained in 98% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 8.64 min (*R*), t_R(major) = 9.36 min (*S*); $[\alpha]_D^{25}$ = +16.9 (*c* 1.0, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$): δ 2.00-2.06 (m, 1H), 2.19-2.27 (m, 2H), 2.30-2.37 (m, 1H), 2.39 (s, 3H), 2.47-2.53 (m, 1H), 2.60 (dd, *J* = 18.5, 7.0 Hz, 1H), 3.86-3.91 (m, 1H), 7.15-7.21 (m, 3H), 7.33-7.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 29.3, 36.7, 42.6, 45.3, 126.6, 127.3, 130.6, 131.6, 133.5, 139.6, 216.7; IR (NaCl cell, CH2Cl2, cm^{-1}): 2919, 1743.; HRMS (ES+) calc. for $C_{12}H_{14}OSNa$ $[M+Na]^+$: 229.0663, found: 229.0667.

(*S*)-3-(2-methoxyphenylthio)cyclopentanone (4c): This compound was obtained in 98% yield and 88% ee. The optical purity was determined by HPLC on chiralcel OB-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 33.25 min (*S*), t_R(minor) = 41.07 min (*R*); $[\alpha]_D^{25}$ = +18.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98-2.01 (m, 1H), 2.18-2.30 (m, 3H), 2.46-2.50 (m, 1H), 2.56 (dd, *J* = 19.0, 7.5 Hz, 1H), 3.87 (s, 3H), 3.98-4.00 (m, 1H), 6.86-6.92 (m, 2H), 7.24-7.28 (m, 1H), 7.33-7.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.3, 36.8, 41.6, 45.3, 55.9, 110.9, 121.1, 122.2, 129.2, 133.4, 158.8, 216.9; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2932, 1742.; HRMS (ES+) calc. for $C_{12}H_{14}O_2SNa$ $[M+Na]^+$: 245.0612, found: 245.0613.

(*S*)-3-(phenylthio)cycloheptanone (5a)[8]: This compound was obtained in 98% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 98:2]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 10.08 min (*R*),

t_R(major) = 12.45 min (*S*); $[\alpha]_D^{25}$ = –35.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47-1.54 (m, 1H), 1.62-1.74 (m, 2H), 1.82-1.84 (m, 1H), 1.94- 1.96 (m, 1H), 2.11-2.14 (m, 1H), 2.44-2.57 (m, 2H), 2.68-2.79 (m, 2H), 3.37-3.41 (m, 1H), 7.23-7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9, 28.2, 36.9, 44.1, 44.2, 49.5, 127.5, 129.2, 132.5, 134.1, 211.6; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2928, 1700. HRMS (ES+) calc. for $C_{13}H_{17}OS$ $[M+H]^+$: 221.1000, found: 221.1005.

(*S*)-3-(*o*-tolylthio)cycloheptanone (5b): This compound was obtained in 98% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 98:2]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 9.92 min (*R*), t_R(major) = 12.89 min (*S*); $[\alpha]_D^{25}$ = –39.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47-1.55 (m, 1H), 1.63-1.73 (m, 2H), 1.83-1.87 (m, 1H), 1.97-2.01 (m, 1H), 2.10-2.14 (m, 1H), 2.45-2.51 (m, 1H), 2.56-2.61 (m, 1H), 2.67-2.71 (m, 2H), 3.51-3.56 (m, 1H), 3.88 (s, 3H), 6.87-6.93 (m, 2H), 7.25-7.28 (m, 1H), 7.36 (dd, *J* = 7.5, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9, 28.3, 36.7, 41.9, 44.0, 49.4, 55.7, 110.9, 121.0, 121.8, 129.1, 133.7, 158.8, 211.8; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2927, 1700.; HRMS (ES+) calc. for $C_{14}H_{19}OS$ $[M+H]^+$: 235.1157, found: 235.1150.

(*S*)-3-(2-methoxyphenylthio)cycloheptanone (5c): This compound was obtained in 95% yield and 92% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 90:10]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 9.28 min (*R*), t_R(major) = 17.33 min (*S*); $[\alpha]_D^{25}$ = –61.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50-1.56 (m, 1H), 1.67-1.76 (m, 2H), 1.84-1.86 (m, 1H), 1.97- 2.00 (m, 1H), 2.11-2.15 (m, 1H), 2.40 (s, 3H), 2.46-2.52 (m, 1H), 2.65-2.60 (m, 1H), 2.72-2.75 (m, 2H), 3.35-3.39 (m, 1H), 7.14-7.17 (m, 2H), 7.19-7.21 (m, 1H), 7.357.38 (m, 1H); ^{13}C

NMR (125 MHz, $CDCl_3$): δ 20.7, 23.9, 28.2, 36.8, 43.4, 44.0, 49.4, 126.5, 127.3, 130.5, 132.2, 133.4, 139.9, 211.6; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2929, 1698.; HRMS (ES+) calc. for $C_{14}H_{18}O_2SNa$ $[M+Na]^+$: 273.0925, found: 273.0926.

(*S*)-3-(2,6-dimethylphenylthio)cycloheptanone (5d): This compound was obtained in 93% yield and 91% ee. The optical purity was determined by HPLC on chiralpak AS-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 5.29 min (*R*), t_R(major) = 7.89 min (*S*); $[\alpha]_D^{25}$ = –43.9 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.43-1.47 (m, 1H), 1.60- 1.73 (m, 2H), 1.80-1.84 (m, 1H), 1.95-2.00 (m, 2H), 2.40-2.47 (m, 1H), 2.50 (s, 6H), 2.53-2.60 (m, 2H), 2.68-2.74 (m, 1H), 3.12-3.17 (m, 1H),7.00-7.11 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.2, 23.9, 28.3, 37.0, 44.1, 44.2, 49.5, 128.2, 128.5, 132.2, 143.5, 211.7; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2927, 1700.; HRMS (ES+) calc. for $C_{15}H_{21}OS$ $[M+H]^+$: 249.1313, found: 249.1317.

(*R*)-4,4-dimethyl-3-(naphthalen-2-ylthio)-1-phenylpentan-1-one (6a): This compound was obtained in 95% yield and 82% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(minor) = 8.40 min (*S*), t_R(major) = 9.54 min (*R*); $[\alpha]_D^{25}$ = –125.4 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.08 (s, 9H), 3.34-3.36 (m, 2H), 4.01 (dd, *J* = 7.5, 5.5 Hz, 1H), 7.37-7.42 (m, 4H), 7.49-7.55 (m, 2H), 7.67-7.73 (m, 3H), 7.83-7.89 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.9, 36.3, 41.2, 55.5, 125.7, 126.4, 127.4, 127.7, 128.2, 128.4, 128.6, 128.7, 128.9, 132.0, 133.1, 133.8, 134.8, 137.3, 198.8; IR (KBr pellet, cm^{-1}): 2923, 1590; m.p = 65 °C.; HRMS (ES+) calc. for $C_{23}H_{25}OS$ $[M+H]^+$: 349.1626, found: 349.1626.

(*R*)-4,4-dimethyl-1-phenyl-3-(*o*-tolylthio)pentan-1-one (6b): This compound was btained in 98% yield and 90% ee. The optical purity was determined by HPLC on chiralpak AD column [*n*-hexane/2-propanol 99:1]; flow rate 0.5 mL/min; λ = 254 nm; t_R(major) = 13.88 min (*R*), t_R(minor) = 16.04 min (*S*); $[\alpha]_D^{25}$ = –59.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.03 (s, 9H), 2.35 (s, 3H), 3.18-3.45 (m, 2H), 3.97-3.98 (m, 1H), 7.00-7.08 (m, 3H), 7.36-7.54 (m, 4H), 7.85-7.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 27.8, 36.0, 41.5, 54.1, 126.0, 126.6, 128.1, 128.6, 130.1, 130.2, 133.1, 136.2, 137.2, 138.2, 198.7; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2961, 1685.; HRMS (ES+) calc. for $C_{20}H_{25}OS$ $[M+H]^+$: 313.1626, found: 313.1622.

(*R*)-3-(4-chlorophenylthio)-4,4-dimethyl-1-phenylpentan-1-one (6c): This compound was obtained in 97% yield and 87% ee. The optical purity was determined by HPLC on chiralcel OD-H column [*n*-hexane/2-propanol 99:1]; flow rate 0.5 mL/min; λ = 254 nm; t_R(major) = 10.30 min (*R*), t_R(minor) = 12.64 min (*S*); $[\alpha]_D^{25}$ = –114.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 9H), 3.30-3.41 (m, 2H), 3.86 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.21-7.24 (m, 2H), 7.43-7.45 (m, 2H), 7.49-7.52 (m, 2H), 7.59 -7.62 (m, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.8, 36.3, 41.1, 56.4, 128.2, 128.7, 129.0, 132.3, 132.4, 133.2, 136.1, 137.2, 198.6; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2959, 2921, 2851, 1685.; HRMS (ES+) calc. for $C_{19}H_{22}ClOS$ $[M+H]^+$: 333.1080, found: 333.1086.

(*R*)-3-(4-fluorophenylthio)-4,4-dimethyl-1-phenylpentan-1-one (6d): This compound was obtained in 92% yield and 86% ee. The optical purity was determined by HPLC on chiralcel OD-H column [*n*-hexane/2-propanol 99:1]; flow rate 0.5 mL/min; λ = 254 nm; t_R(major) = 8.83 min (*R*), t_R(minor) = 10.63 min (*S*); $[\alpha]_D^{25}$ = –68.2 (*c* 1.0, $CHCl_3$);^1H NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 9H), 3.23 (dd, *J* = 17.5, 4.0 Hz, 1H), 3.34 (dd, *J* =

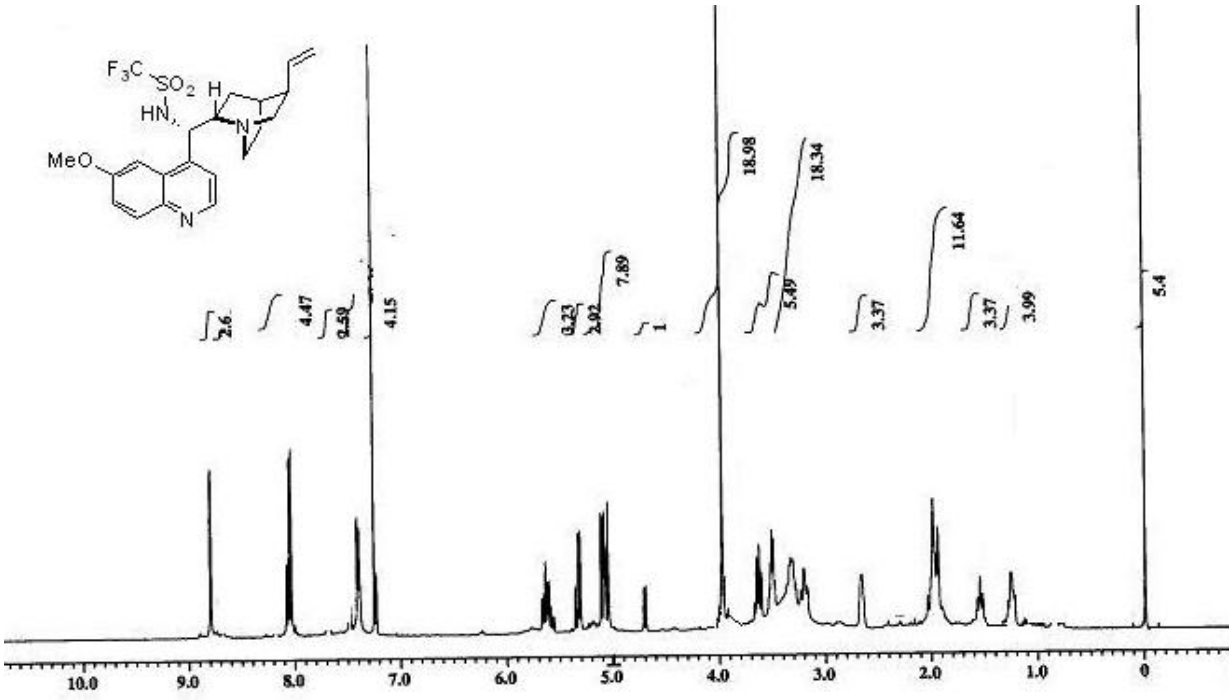
17.5, 9.0 Hz, 1H), 3.75 (dd, *J* = 8.5, 4.5 Hz, 1H), 6.88-6.92 (m, 2H), 7.42-7.46 (m, 4H), 7.53-7.56 (m, 1H), 7.89-7.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.2, 36.3, 41.2, 57.3, 115.6, 115.7, 115.8, 116.2, 127.5, 127.8, 128.0, 128.1, 128.6, 132.3, 132.4, 133.1, 133.7, 133.8, 137.3, 138.6, 138.7, 160.9, 162.9, 198.7 (excess peaks due to C-F coupling); IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2960, 2918, 2850, 1684.; HRMS (ES+) calc. for $C_{19}H_{22}FOS$ $[M+H]^+$: 317.1375, found: 317.1372.

(*S*)-1,5-diphenyl-3-(*o*-tolylthio)pentan-1-one (7a): This compound was obtained in 97% yield and 94% ee. The optical purity was determined by HPLC on chiralcel OJ-H column [*n*-hexane/2-propanol 95:5]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 10.22 min (*S*), t_R(minor) = 12.51 min (*R*); $[\alpha]_D^{25}$ = –27.3 (*c* 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30-2.49 (m, 5H), 2.80-3.05 (m, 2H), 3.19-3.33 (m, 2H), 3.84-3.88 (m, 1H), 7.11-7.24 (m, 9H), 7.35-7.414 (m, 2H), 7.58-7.61 (m, 1H), 7.85-7.92 (m, 2H); ^{13}C NMR (125MHz, $CDCl_3$): δ 20.8, 33.1, 36.4, 42.9, 44.1, 125.9, 126.9, 127.8, 128.0, 128.3, 128.4, 128.6, 130.4, 131.6, 133.2, 126.5, 127.0, 129.6, 141.4, 198.2; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2919, 2850, 1587.; HRMS (ES+) calc. for $C_{24}H_{25}OS$ $[M+H]^+$: 361.1626, found: 361.1620.

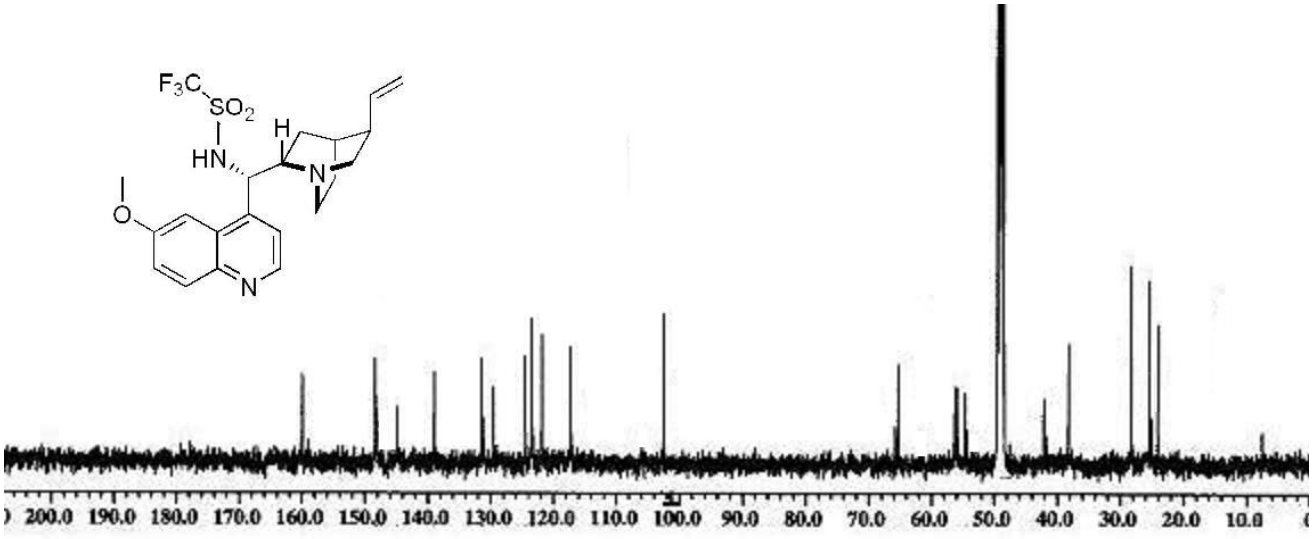
(*S*)-3-(2,6-dimethylphenylthio)-1,5-diphenylpentan-1-one (7b): This compound was obtained in 96% yield and 99% ee. The optical purity was determined by HPLC on chiralpak AD-H column [*n*-hexane/2-propanol 99:1]; flow rate 1 mL/min; λ = 254 nm; t_R(major) = 7.91 min (*S*), t_R(minor) = 10.12 min (*R*); $[\alpha]_D^{25}$ = –60.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.89-1.91 (m, 1H), 2.02-2.07 (m, 1H), 2.51 (s, 6H), 2.76-2.81 (m, 1H), 2.84-2.89 (m, 1H), 3.06-3.16 (m, 2H), 3.60-3.63 (m, 1H), 7.06-7.15 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz 2H), 7.51 (t, J = 7.0 Hz, 1H), 7.72 (d, J =

7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.3, 32.9, 36.3, 43.7, 43.9, 125.8, 126.7, 127.9, 128.2, 128.3, 128.4, 128.5, 132.2, 133.1, 136.7, 141.4, 143.5, 198.3; IR (NaCl cell, CH_2Cl_2, cm^{-1}): 2918, 2851, 1589.; HRMS (ES+) calc. for $C_{25}H_{27}OS$ $[M+H]^+$: 375.1783, found: 375.1784.

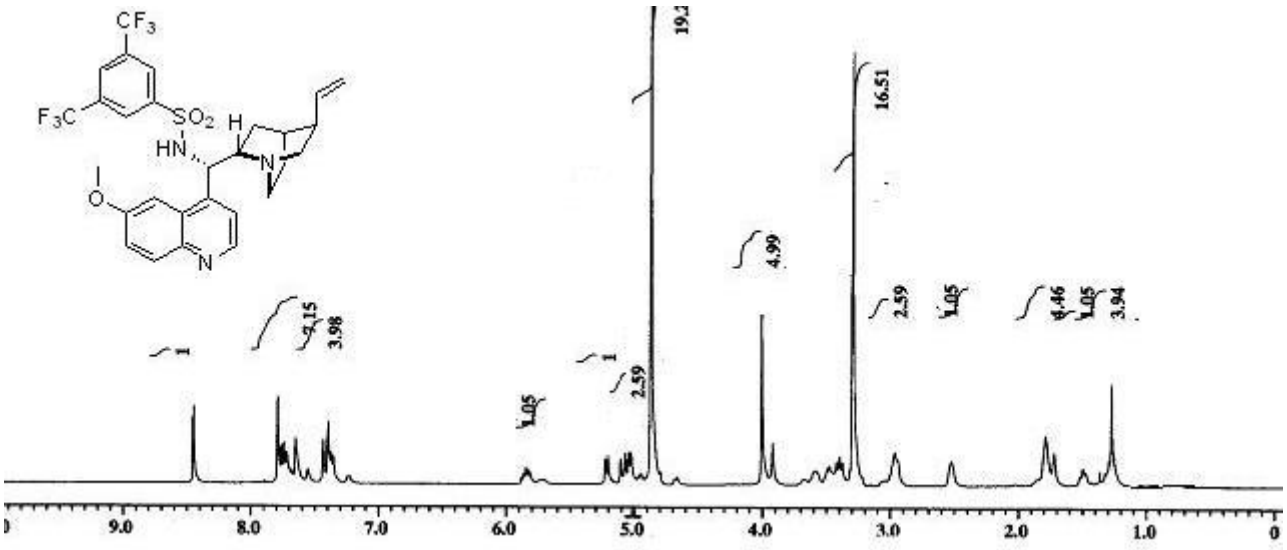
Spectra:



500 MHz ^{1}H NMR spectra of **1g** in $CDCl_3$

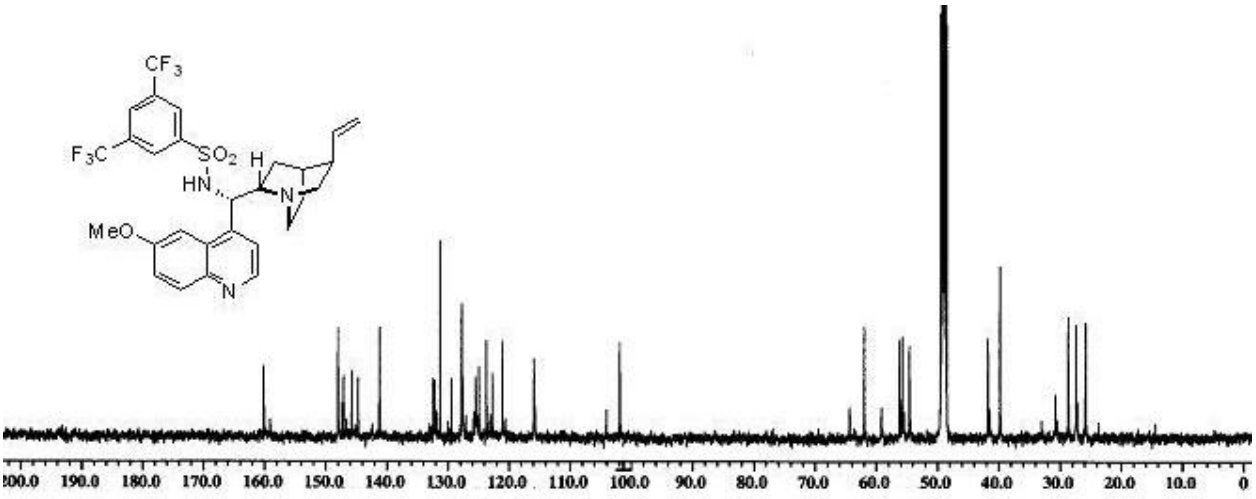


125 MHz ^{13}C NMR spectra of **1g** in CD_3OD

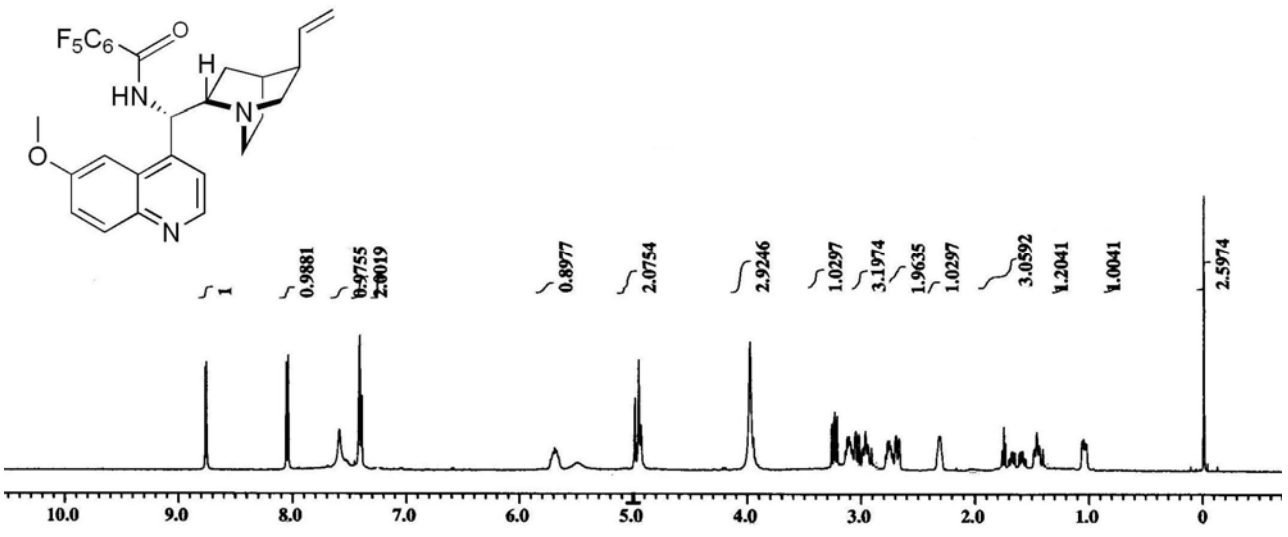


s

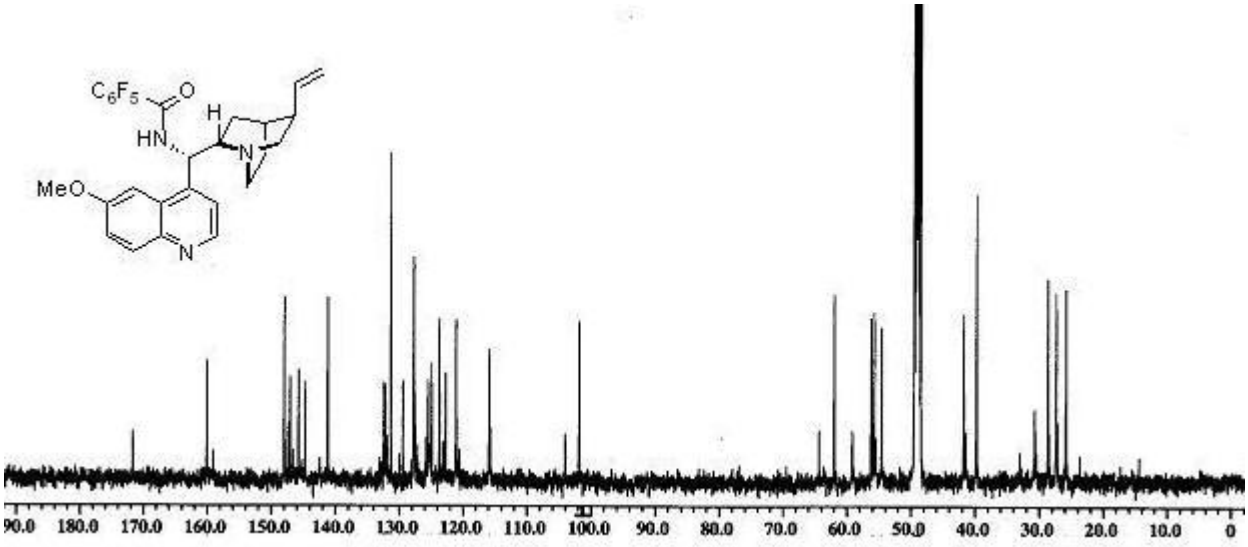
500 MHz ^{1}H NMR spectra of **1h** in CD_3OD



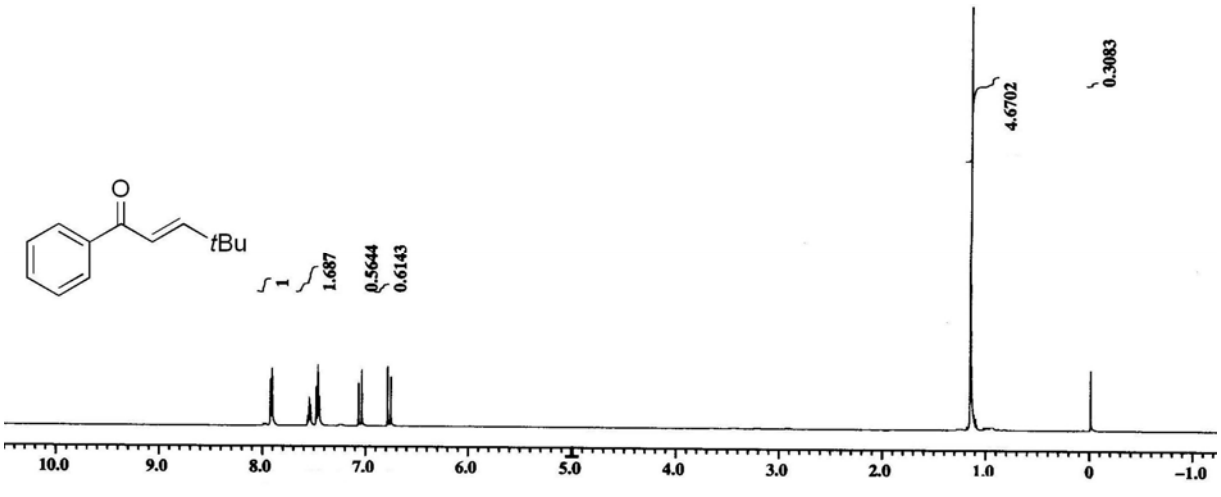
125 MHz ^{13}C NMR spectra of **1h** in CD_3OD



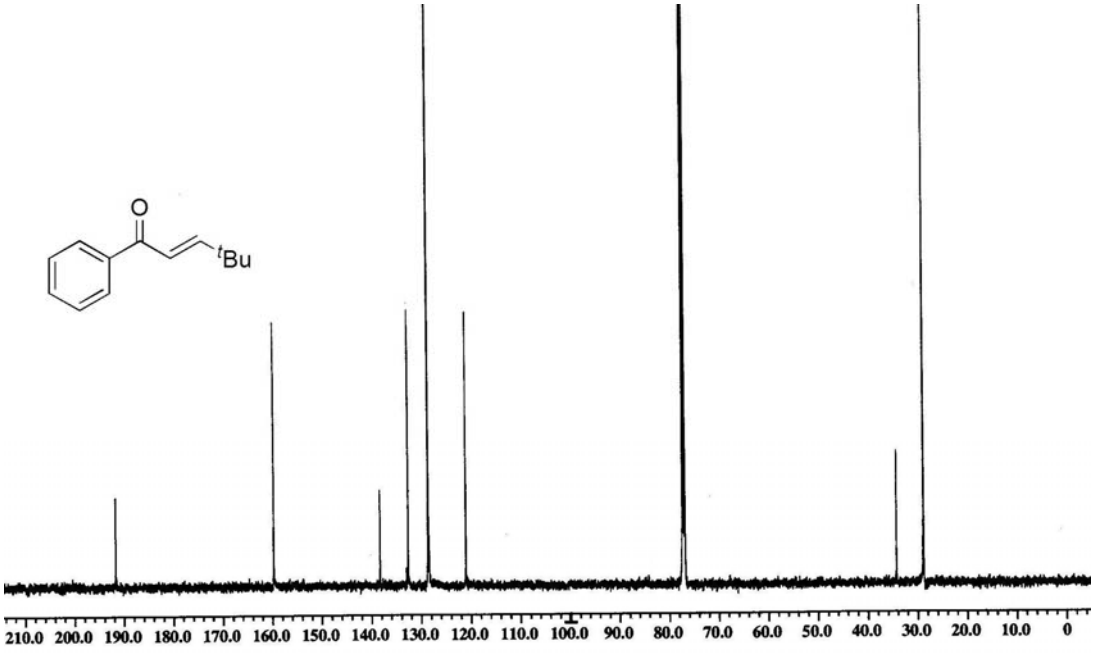
500 MHz ^{1}H NMR spectra of **1i** in $CDCl_3$



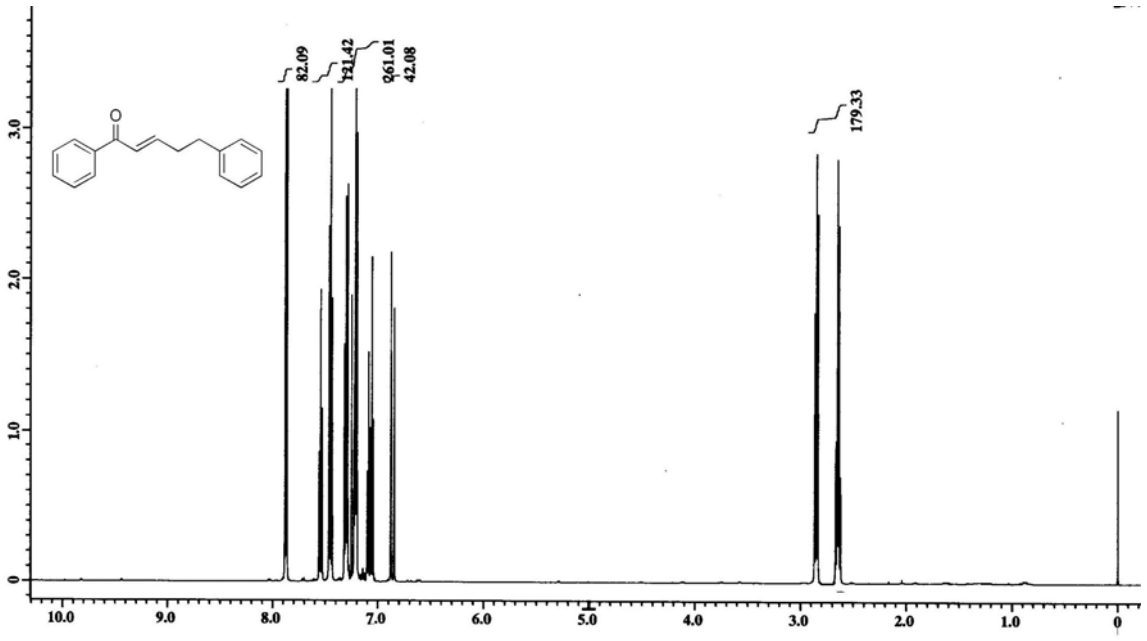
125 MHz ^{13}C NMR spectra of **1i** in CD_3OD



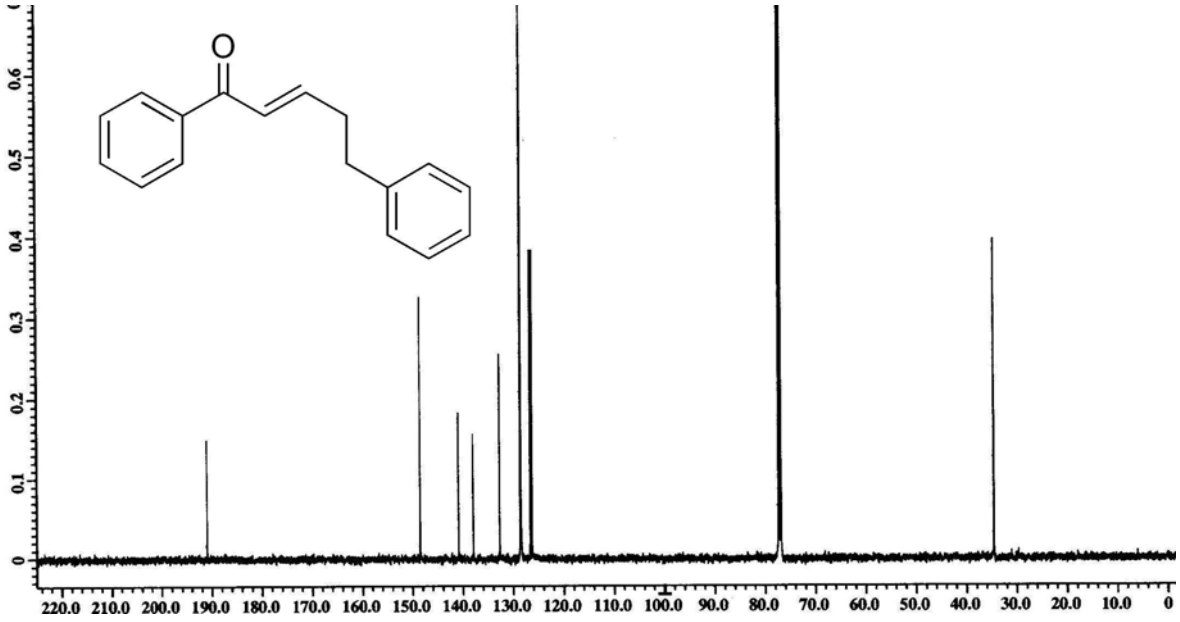
500 MHz ^{1}H NMR spectra of **8e** in $CDCl_3$



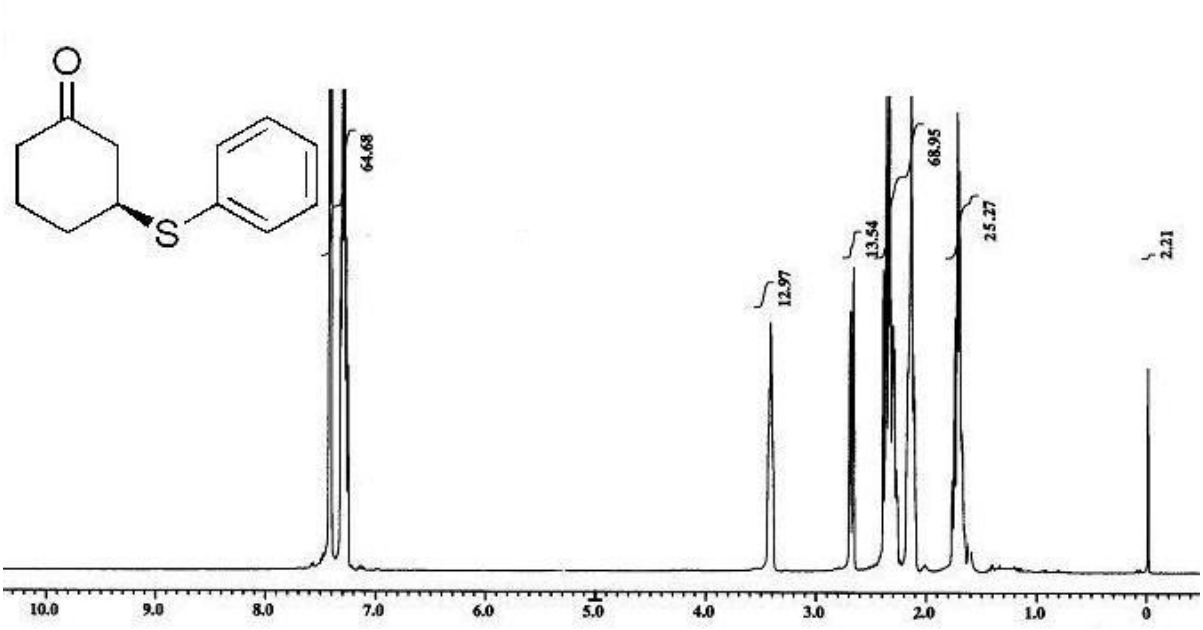
125 MHz ^{13}C NMR spectra of **8e** in $CDCl_3$



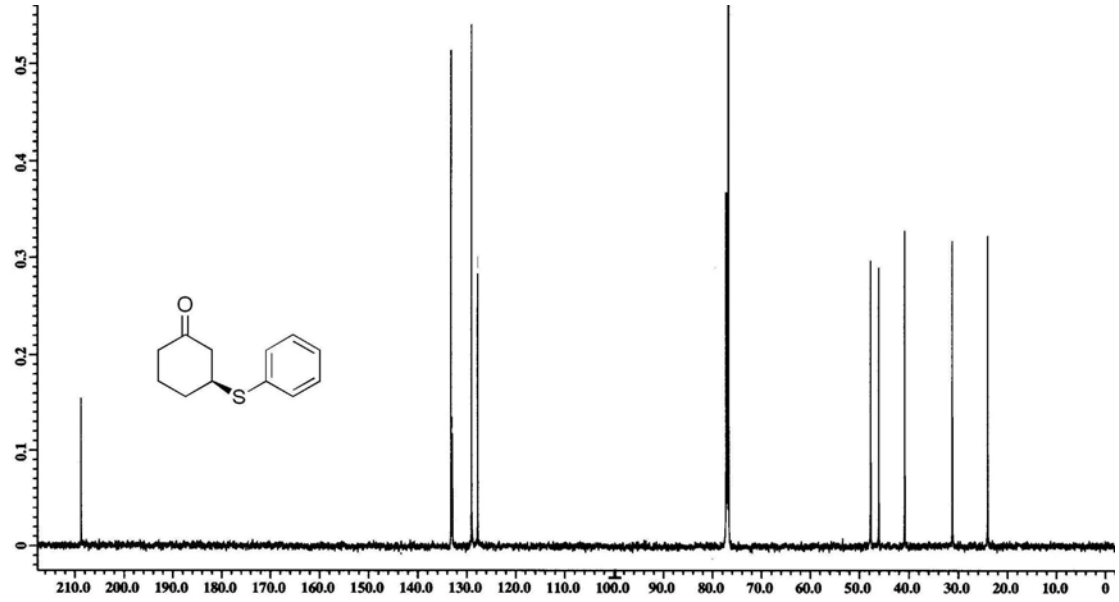
500 MHz ^{1}H NMR spectra of **8f** in $CDCl_3$



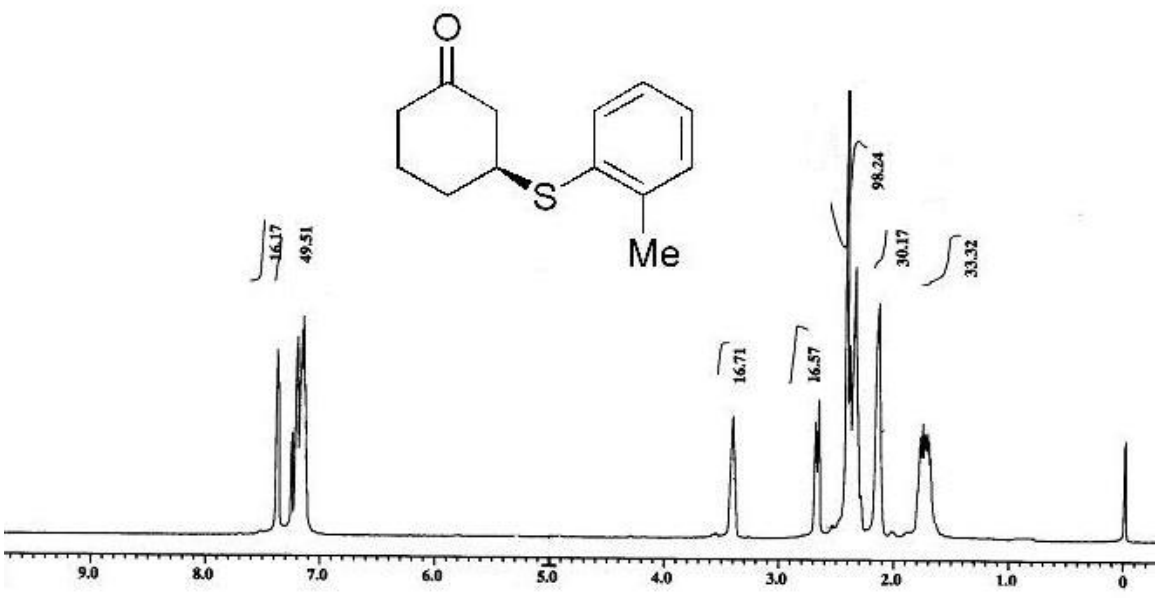
125 MHz ^{13}C NMR spectra of **8f** in $CDCl_3$



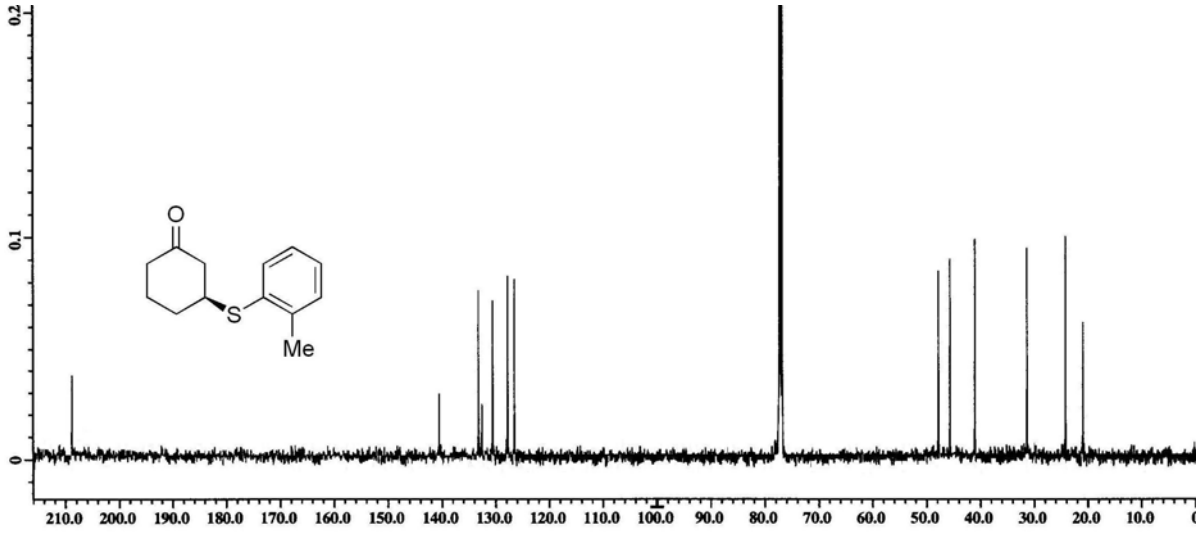
500 MHz ^{1}H NMR spectra of **2a** in $CDCl_3$



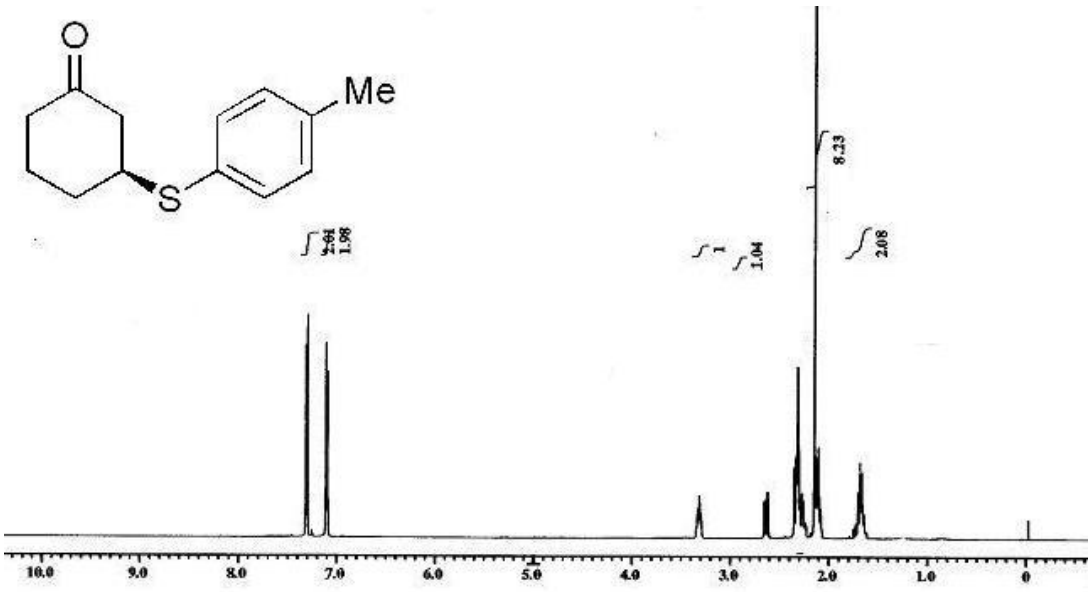
125 MHz ^{13}C NMR spectra of **2a** in $CDCl_3$



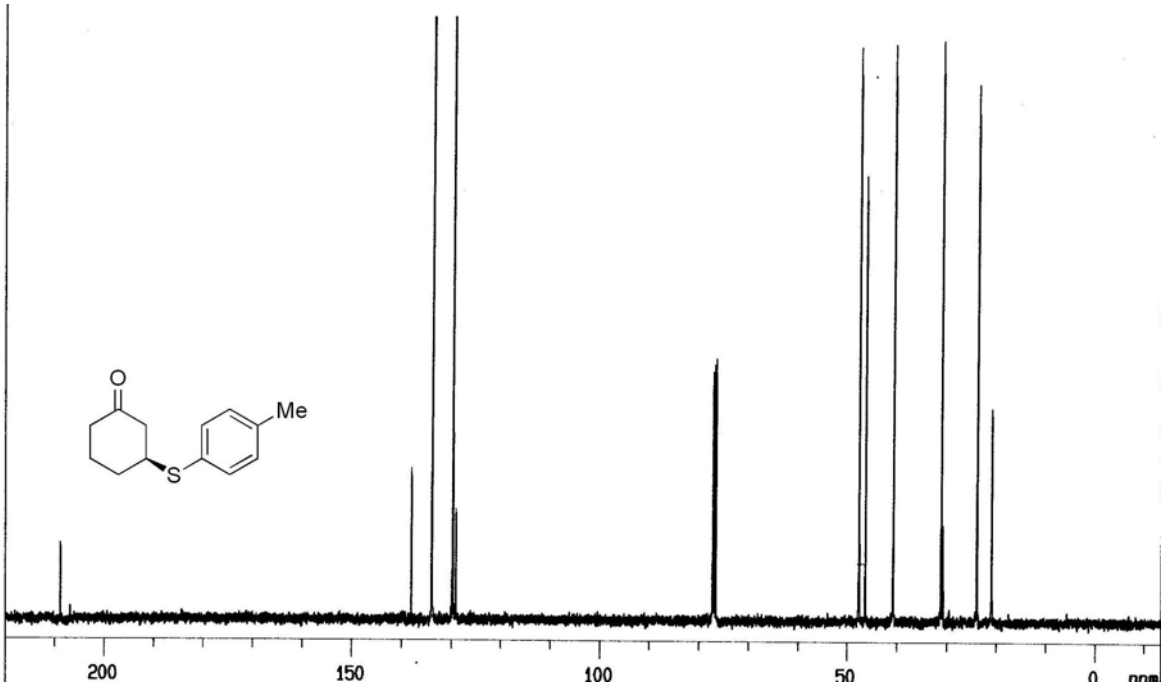
500 MHz ^{1}H NMR spectra of **2b** in $CDCl_3$



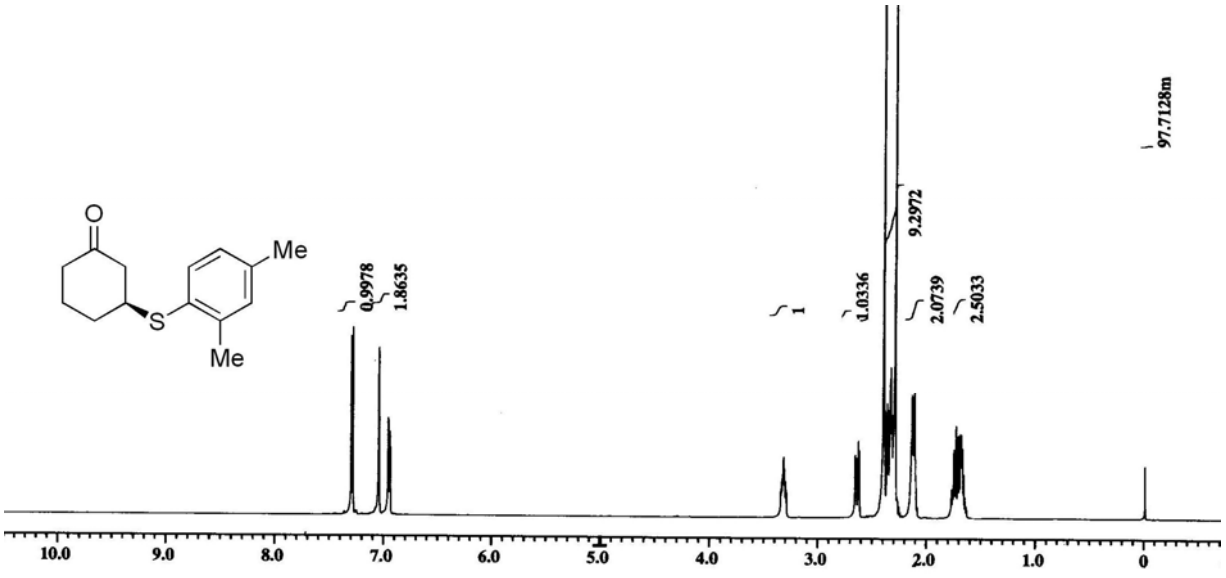
125 MHz ^{13}C NMR spectra of **2b** in $CDCl_3$



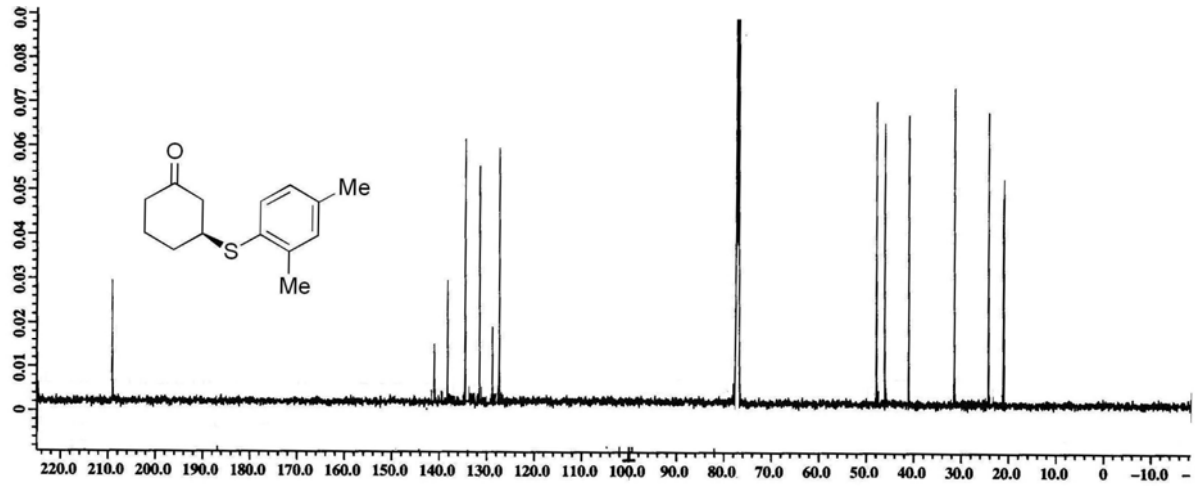
500 MHz ^{1}H NMR spectra of **2c** in $CDCl_3$



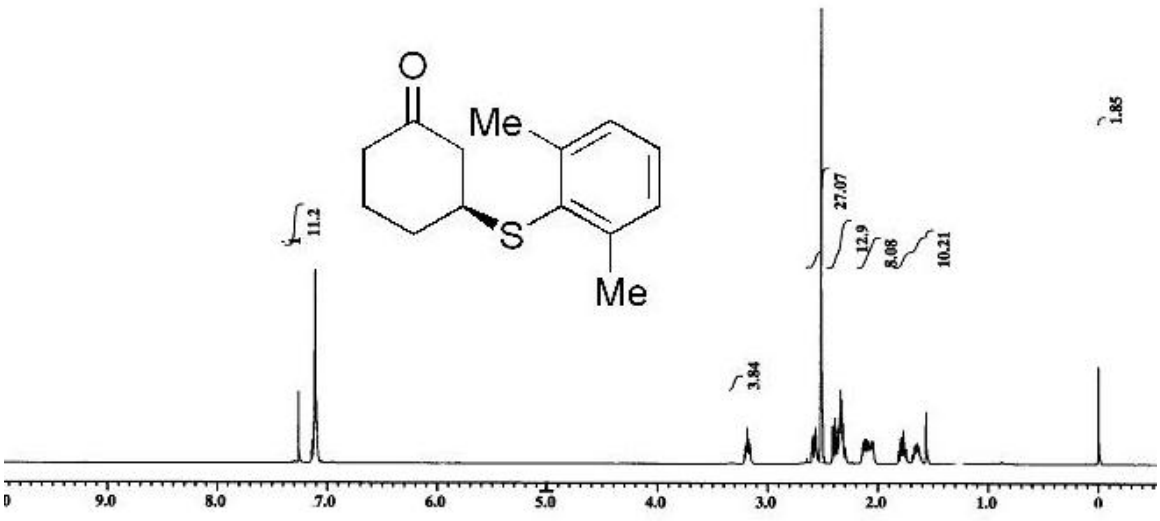
100 MHz ^{13}C NMR spectra of **2c** in $CDCl_3$



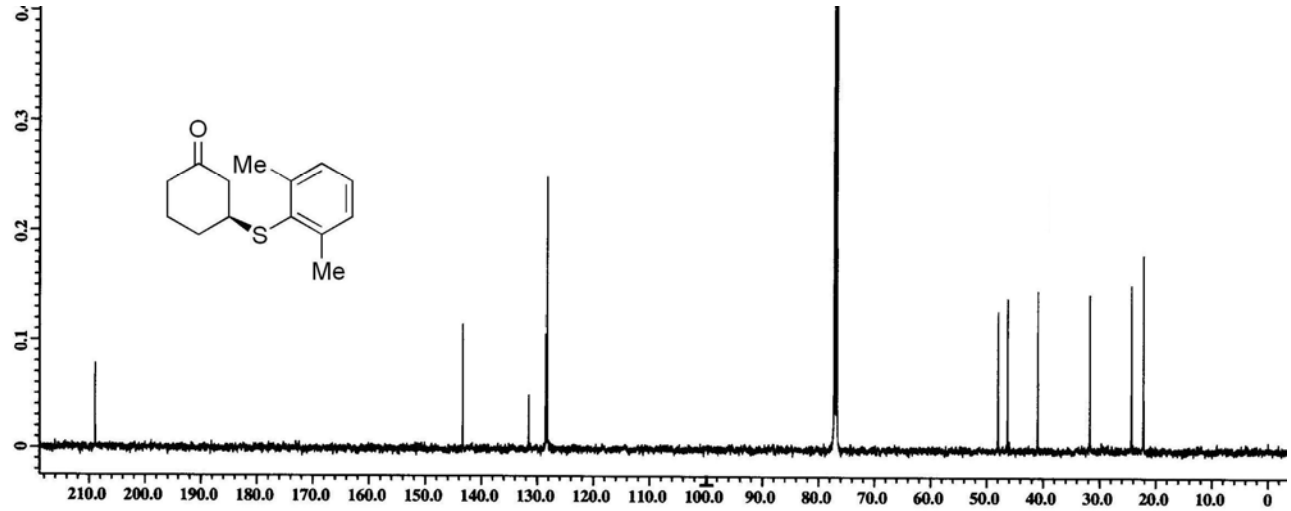
500 MHz ^{1}H NMR spectra of **2d** in $CDCl_3$



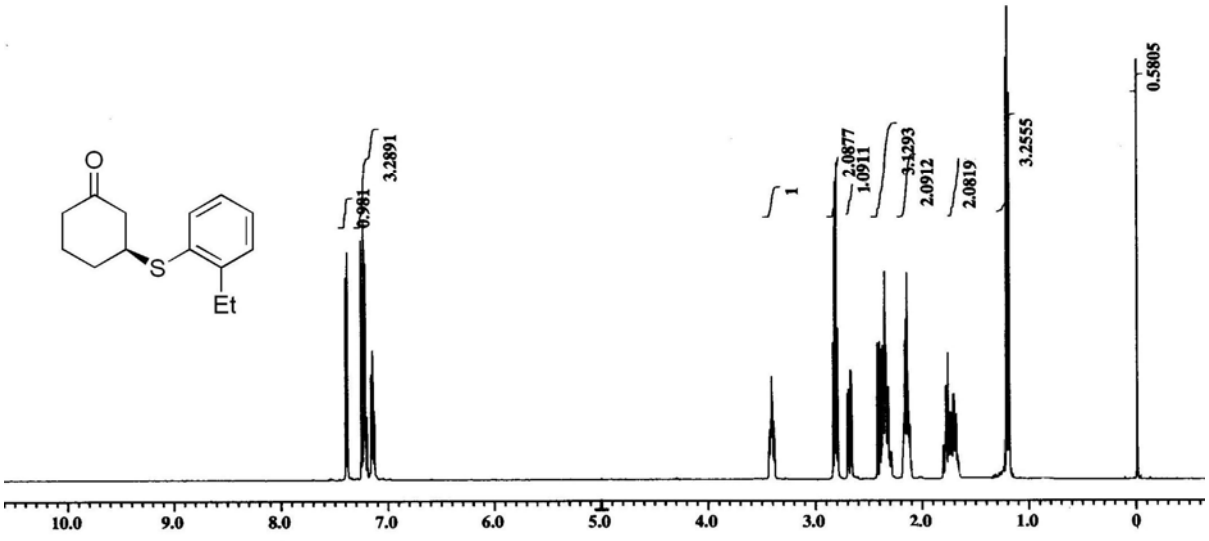
125 MHz ^{13}C NMR spectra of **2d** in $CDCl_3$



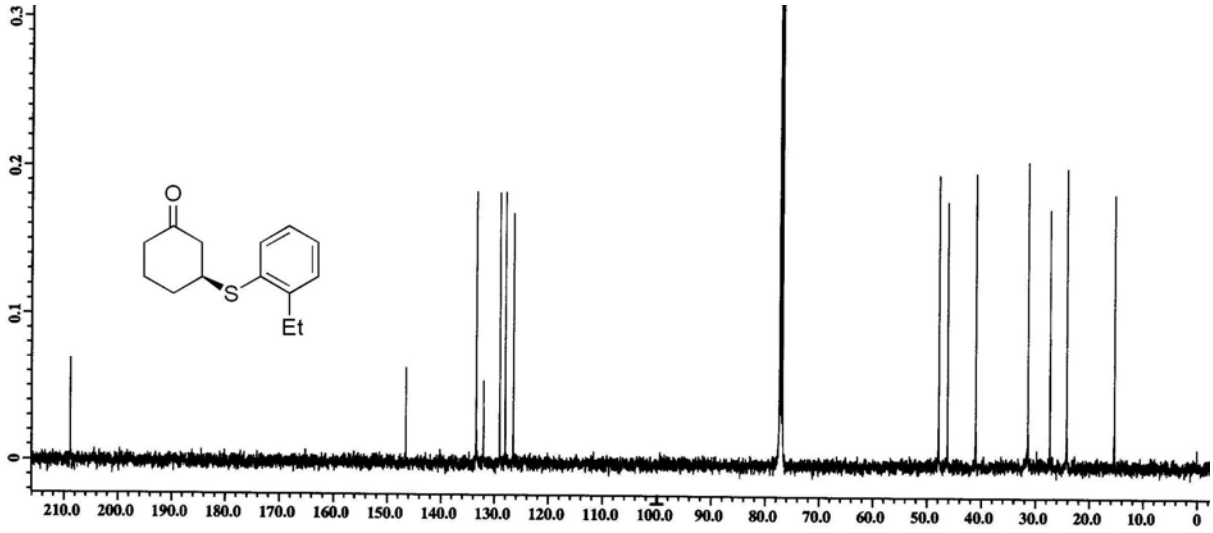
500 MHz ^{1}H NMR spectra of **2e** in $CDCl_3$



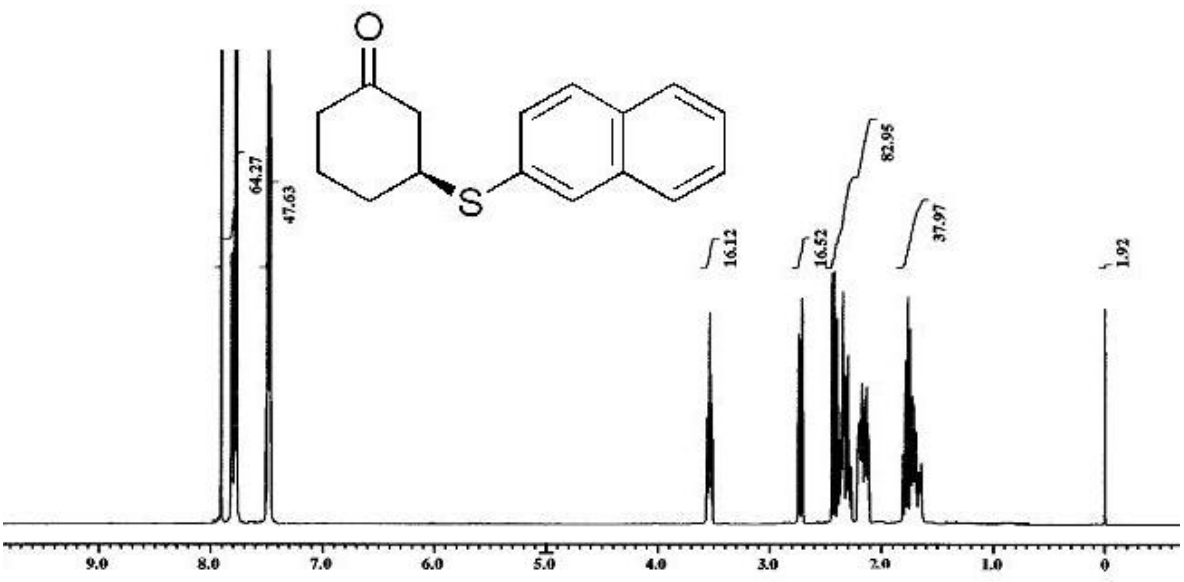
125 MHz ^{13}C NMR spectra of **2e** in $CDCl_3$



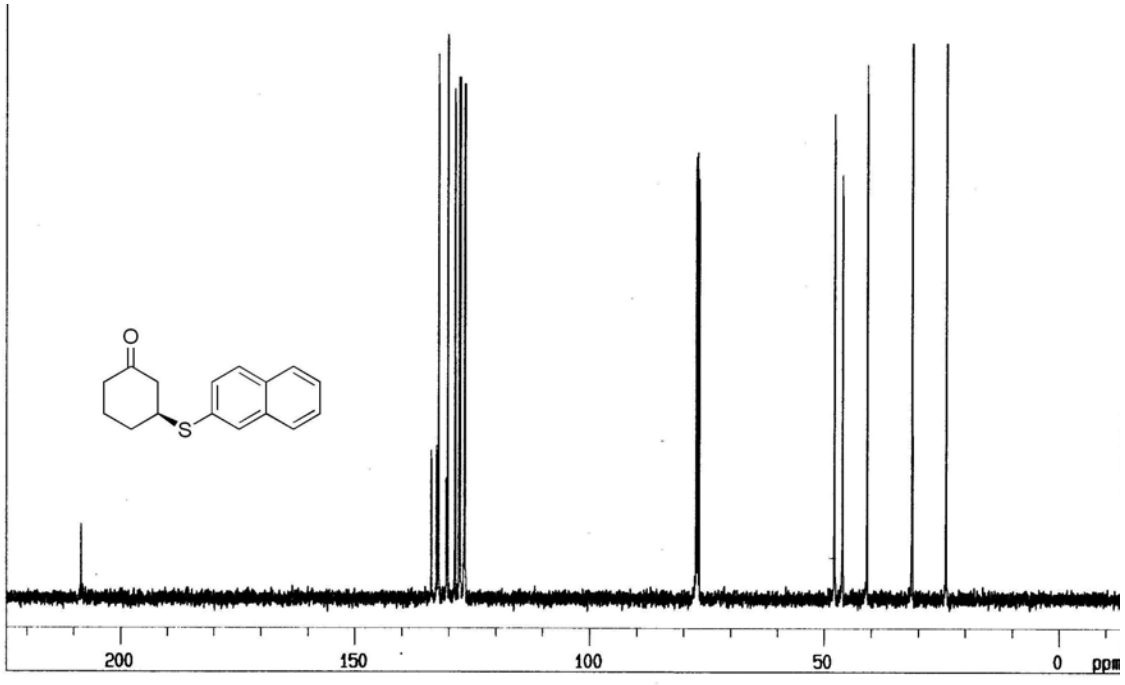
500 MHz ^{1}H NMR spectra of **2f** in $CDCl_3$



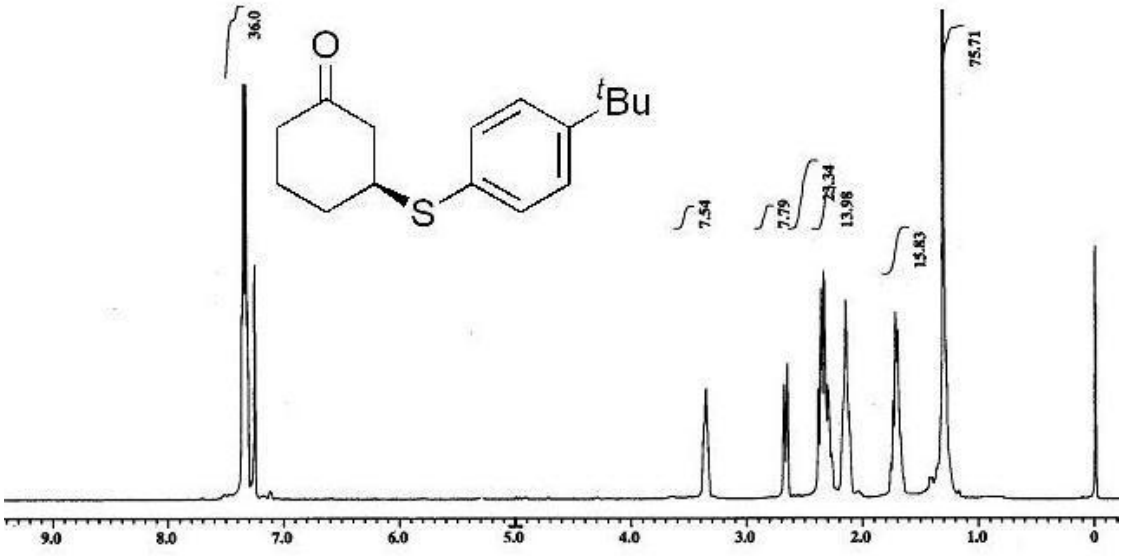
125 MHz ^{13}C NMR spectra of **2f** in $CDCl_3$



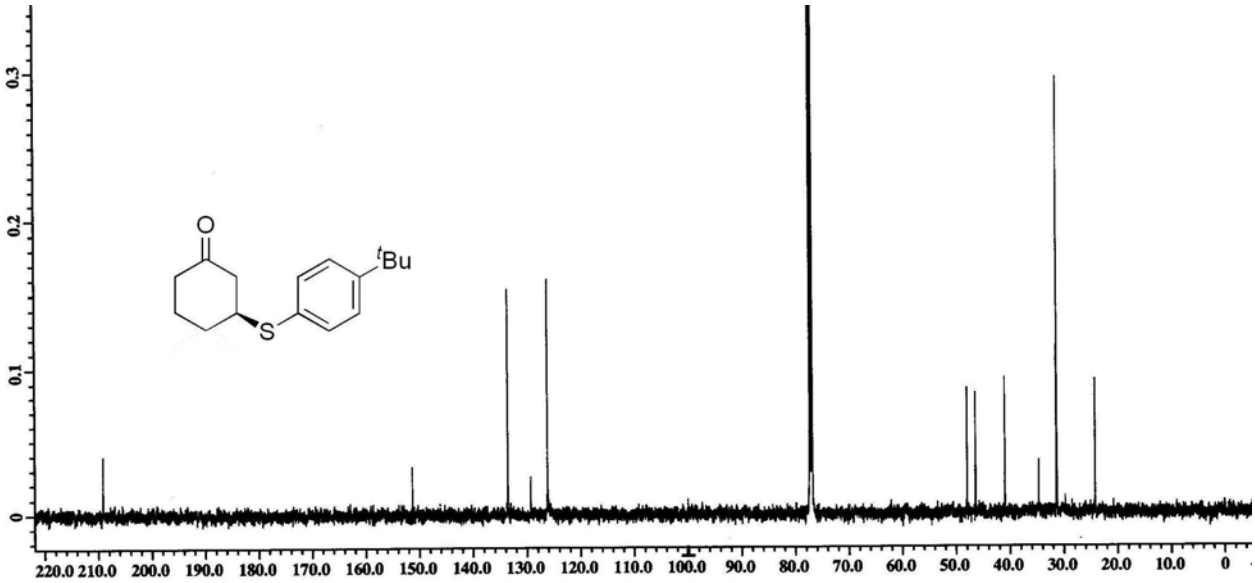
500 MHz ^{1}H NMR spectra of **2g** in $CDCl_3$



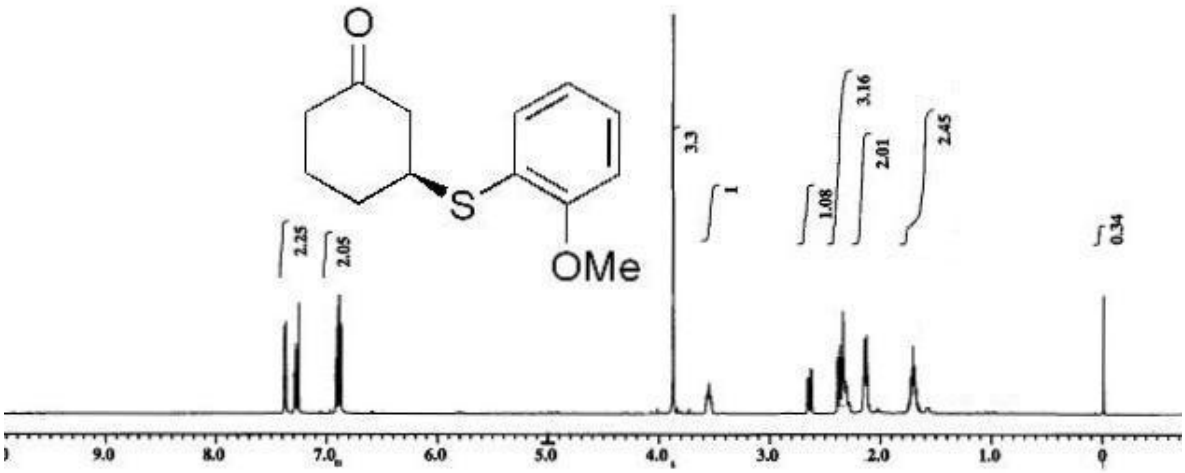
100 MHz ^{13}C NMR spectra of **2g** in $CDCl_3$



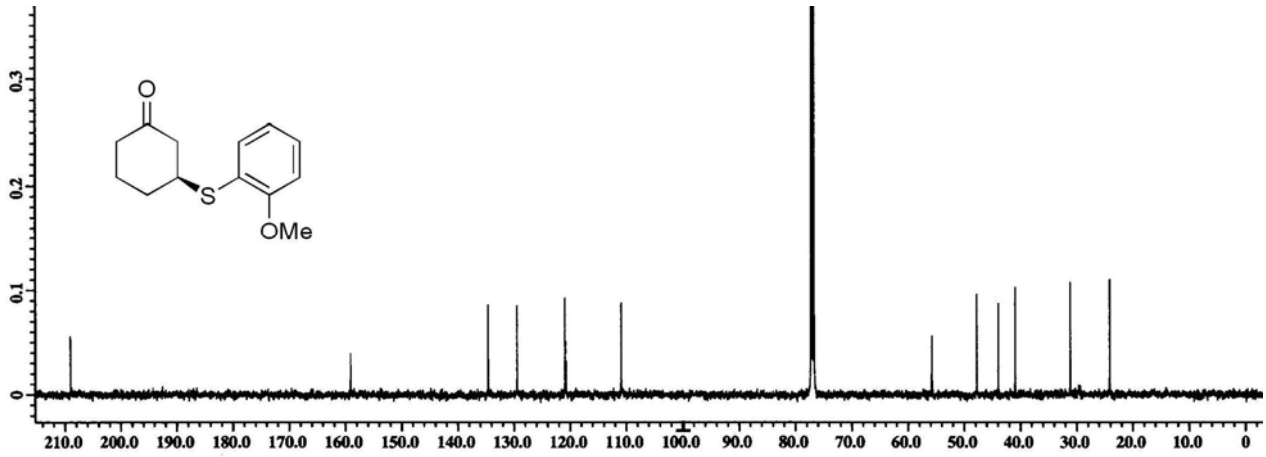
500 MHz ^{1}H NMR spectra of **2h** in $CDCl_3$



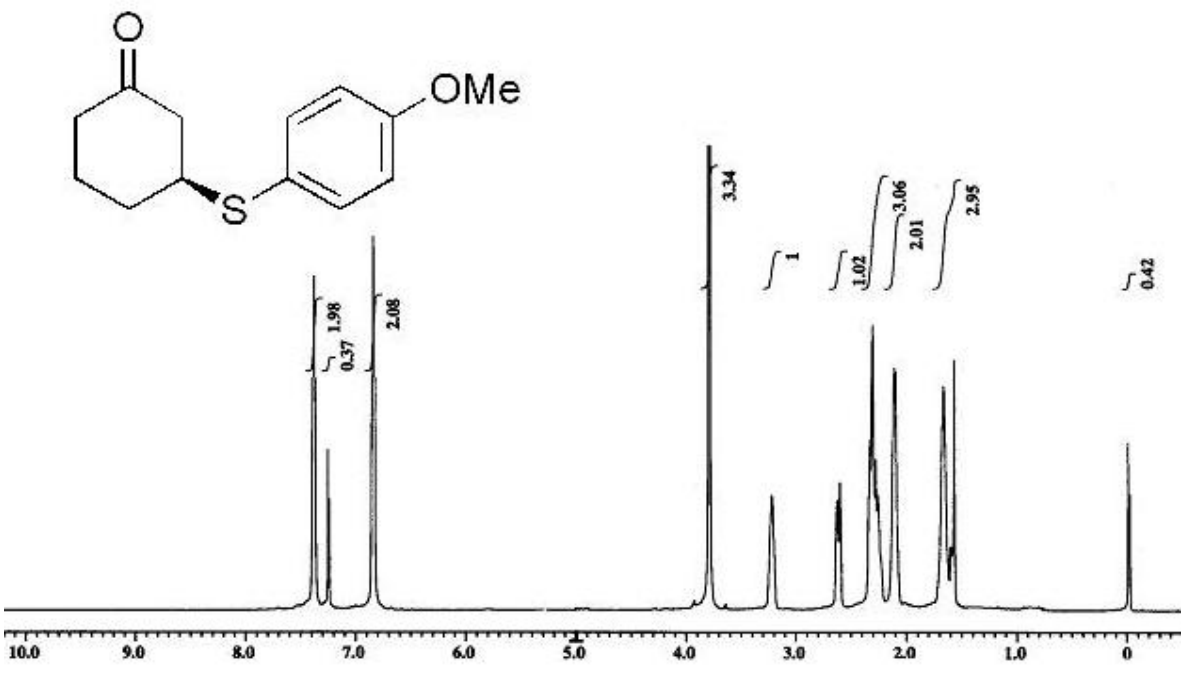
125 MHz ^{13}C NMR spectra of **2h** in $CDCl_3$



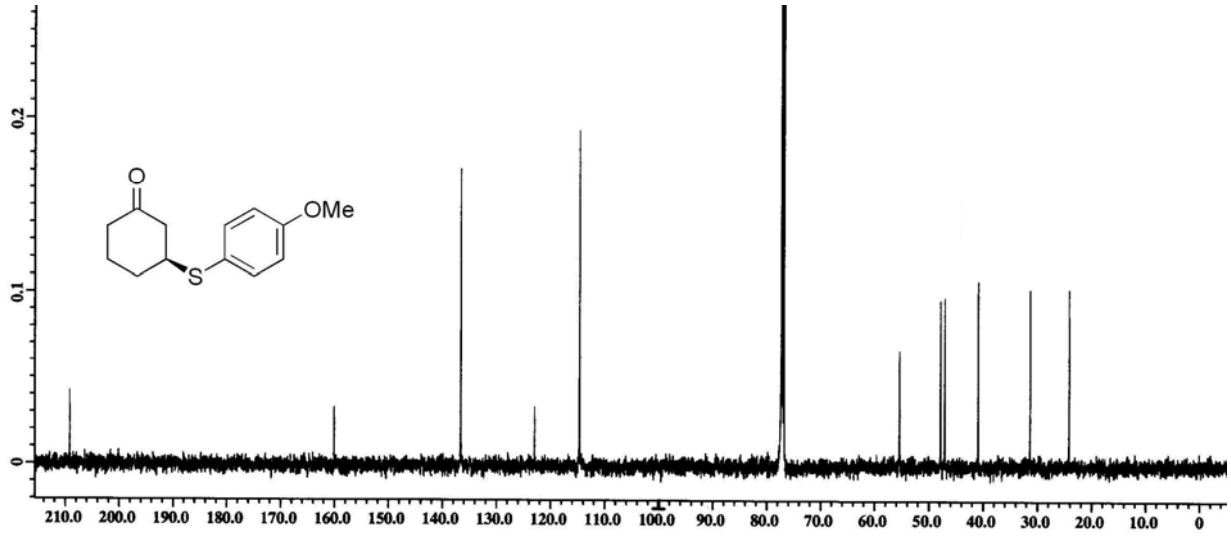
500 MHz ^{1}H NMR spectra of **2i** in $CDCl_3$



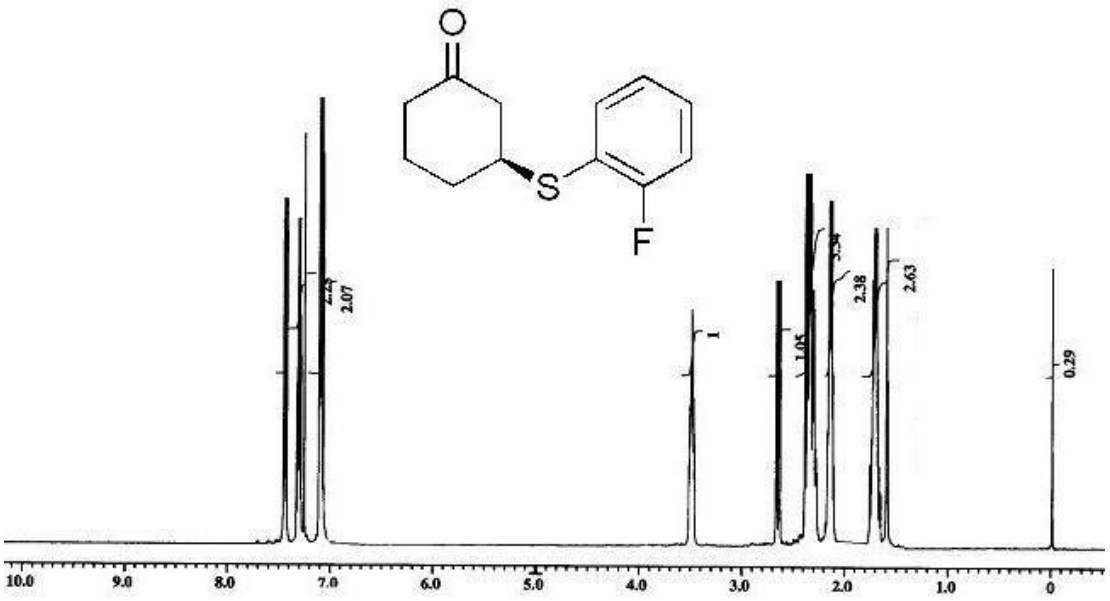
125 MHz ^{13}C NMR spectra of **2i** in $CDCl_3$



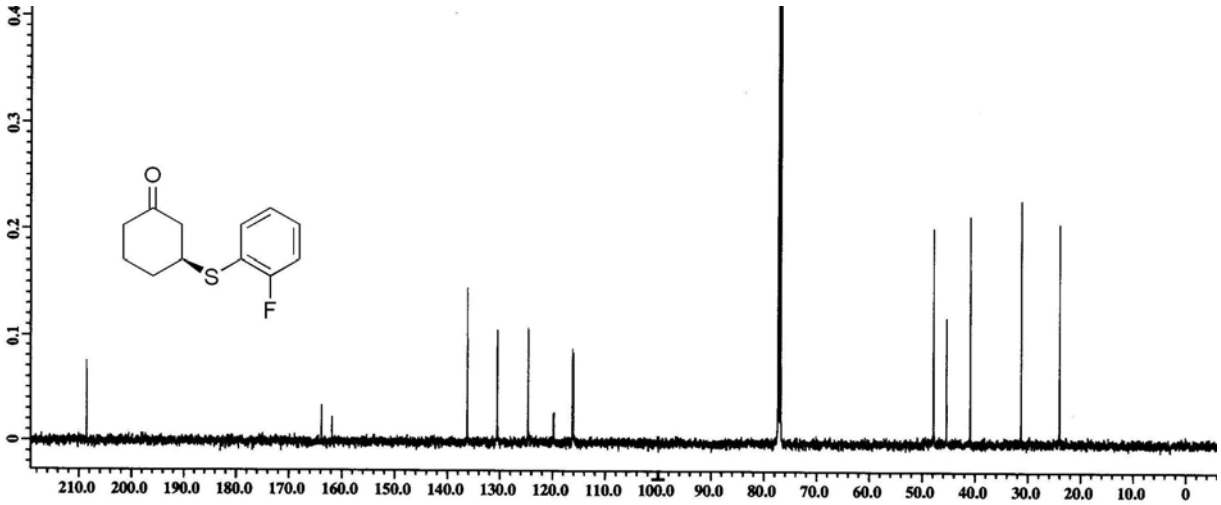
500 MHz ^{1}H NMR spectra of **2j** in $CDCl_3$



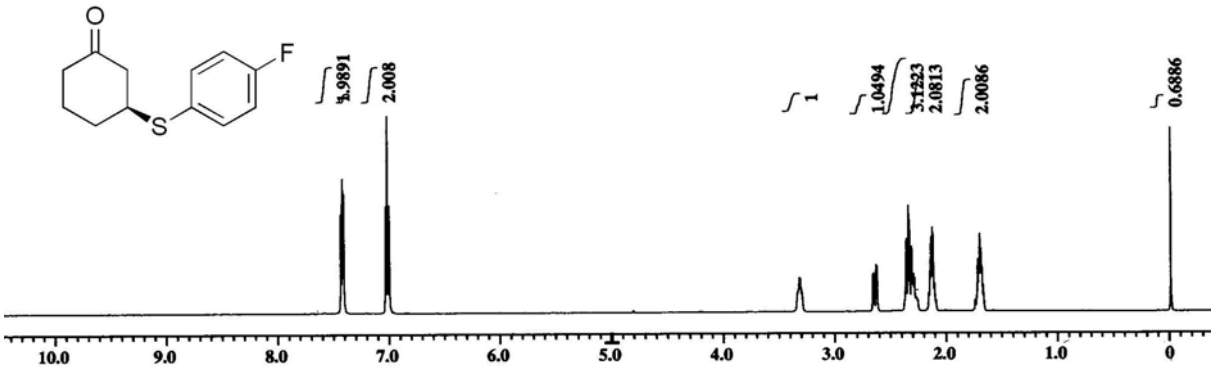
125 MHz ^{13}C NMR spectra of **2j** in $CDCl_3$



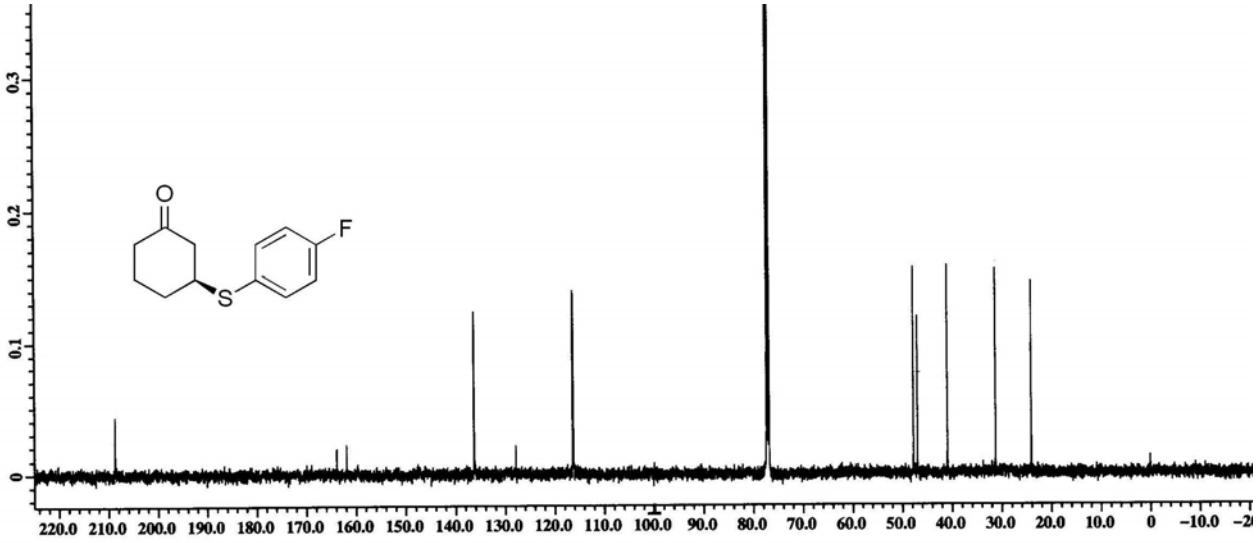
500 MHz ^{1}H NMR spectra of **2k** in $CDCl_3$



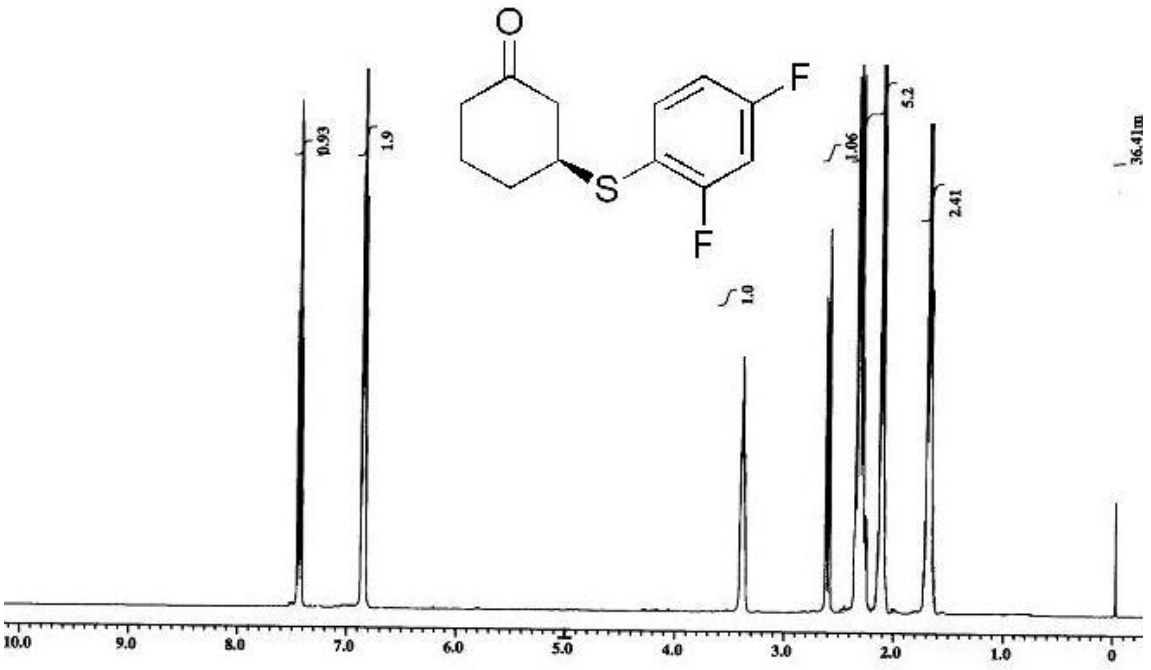
125 MHz ^{13}C NMR spectra of **2k** in $CDCl_3$



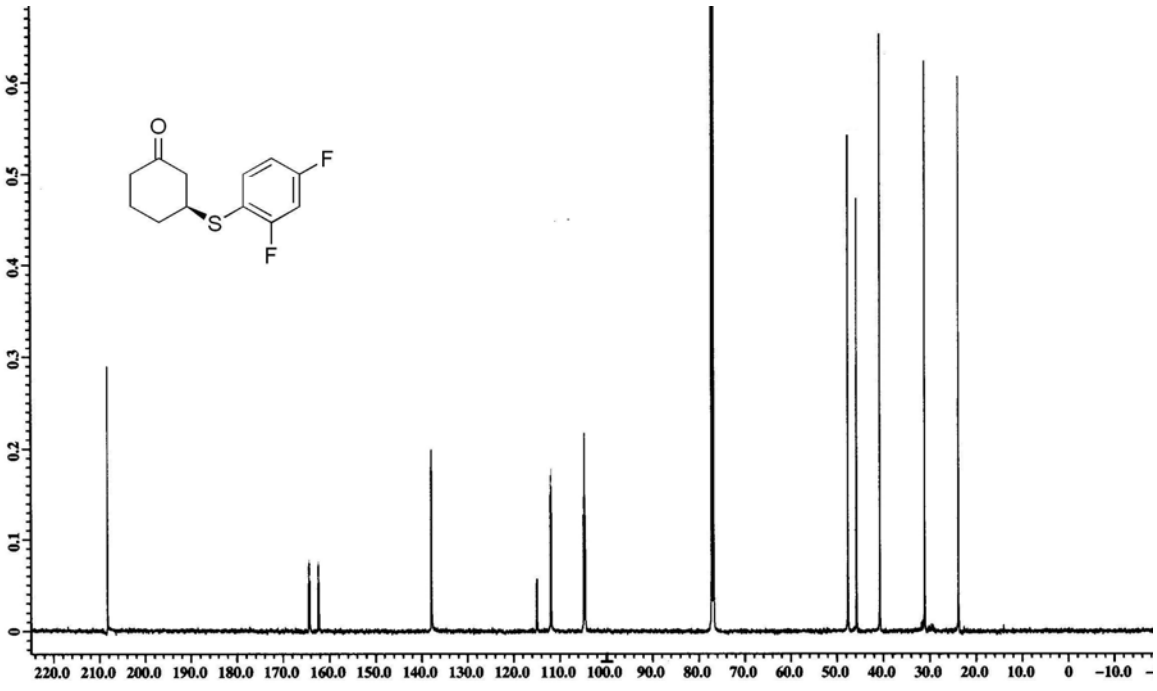
500 MHz ^{1}H NMR spectra of **2l** in $CDCl_3$



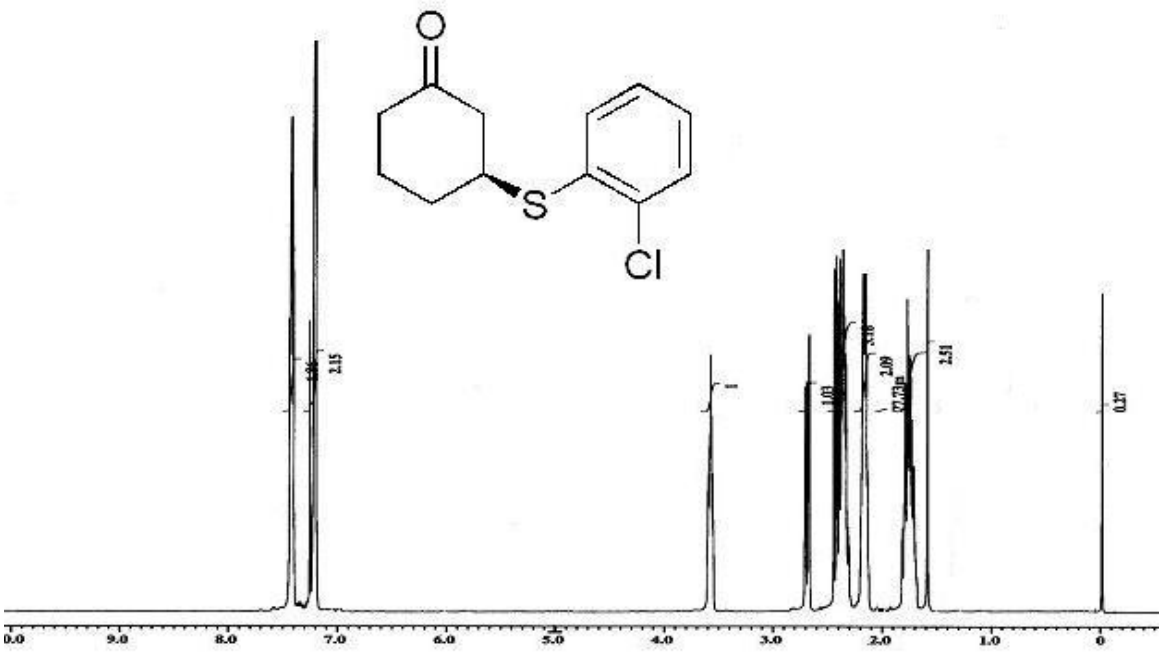
125 MHz ^{13}C NMR spectra of **2l** in $CDCl_3$



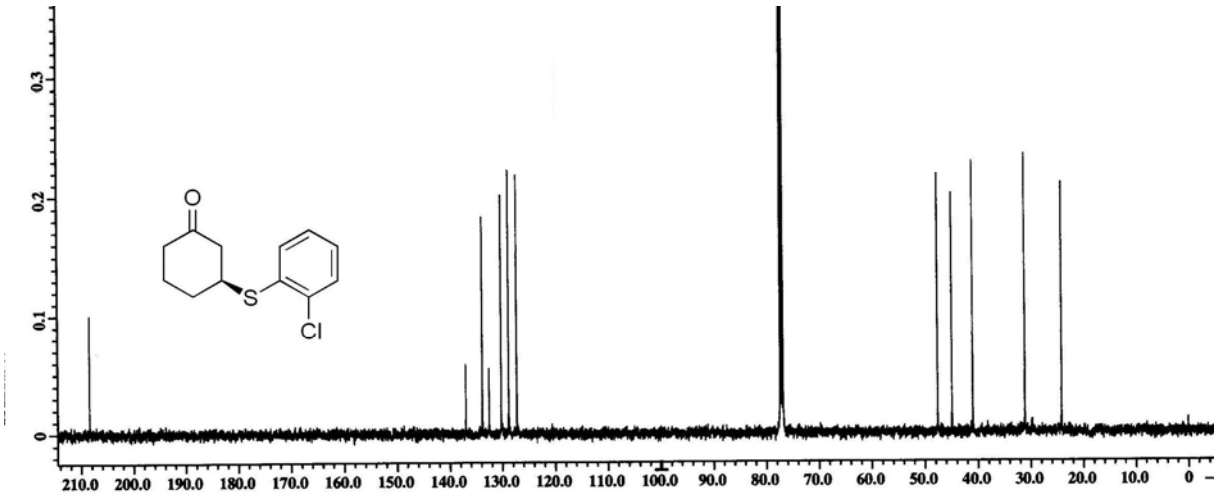
500 MHz ^{1}H NMR spectra of **2m** in $CDCl_3$



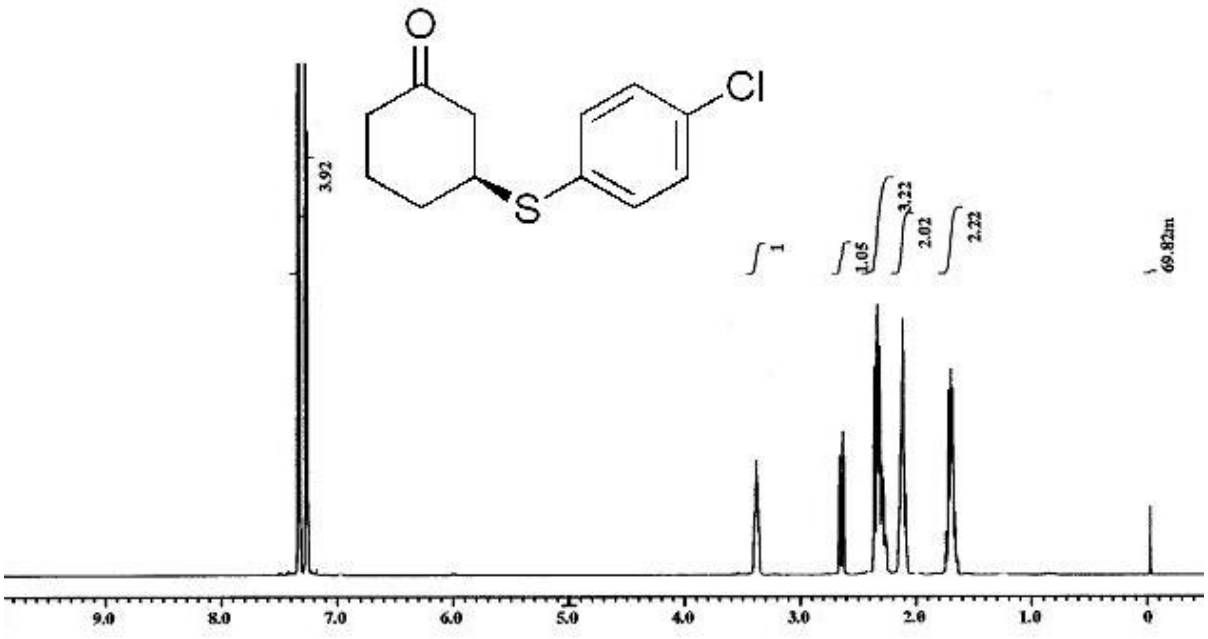
125 MHz ^{13}C NMR spectra of **2m** in $CDCl_3$



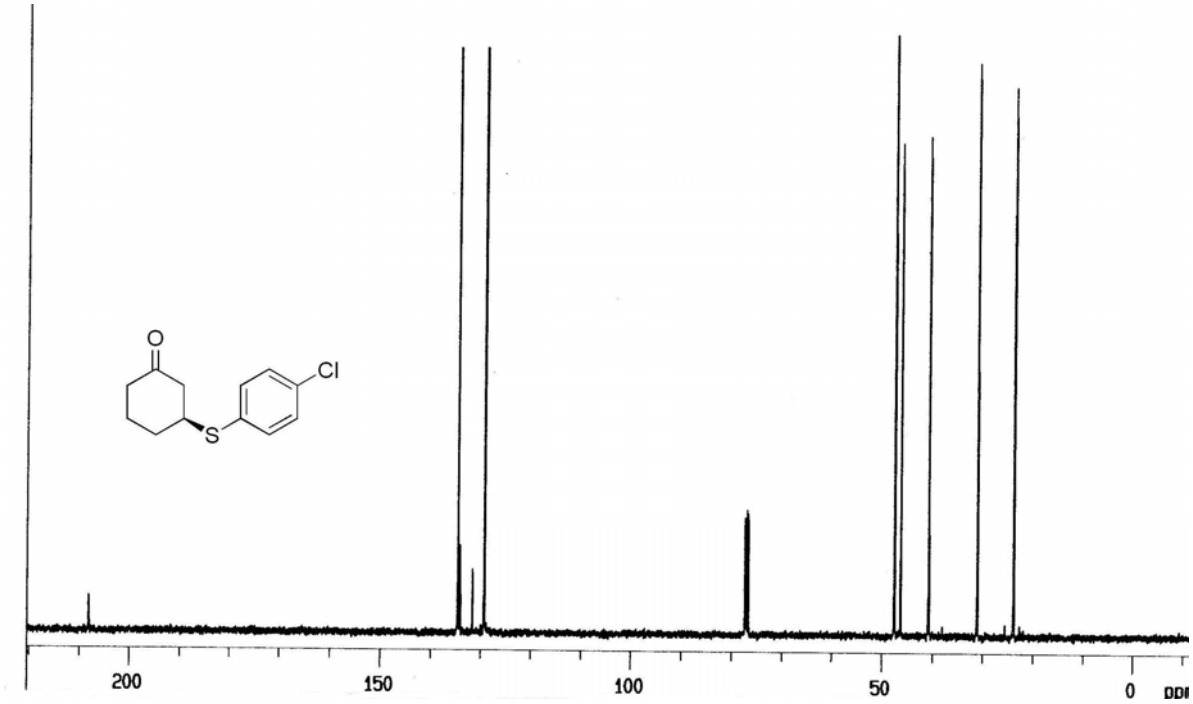
500 MHz ^{1}H NMR spectra of **2n** in $CDCl_3$



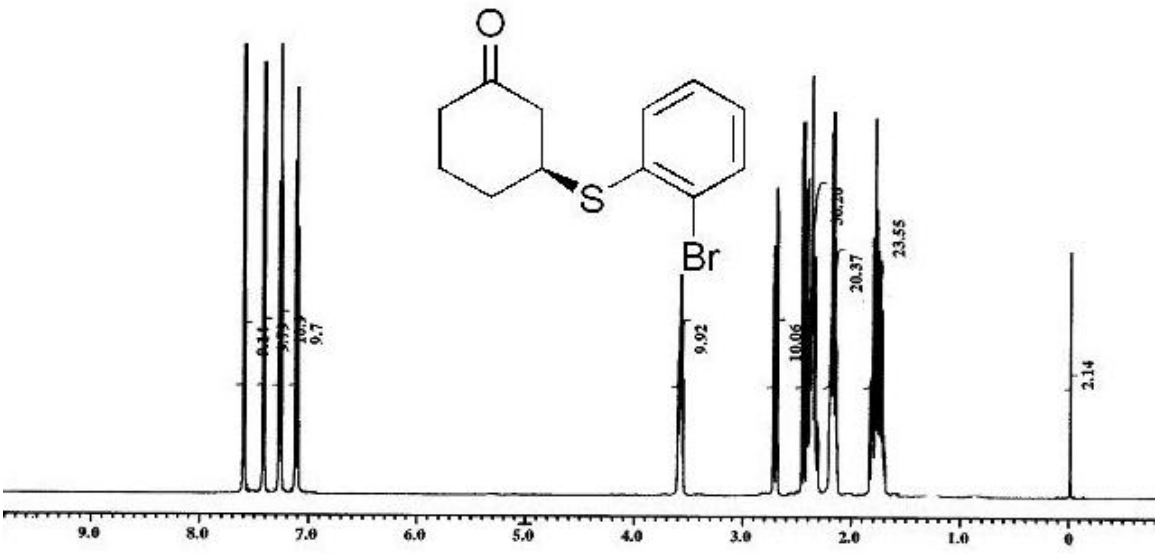
125 MHz ^{13}C NMR spectra of **2n** in $CDCl_3$



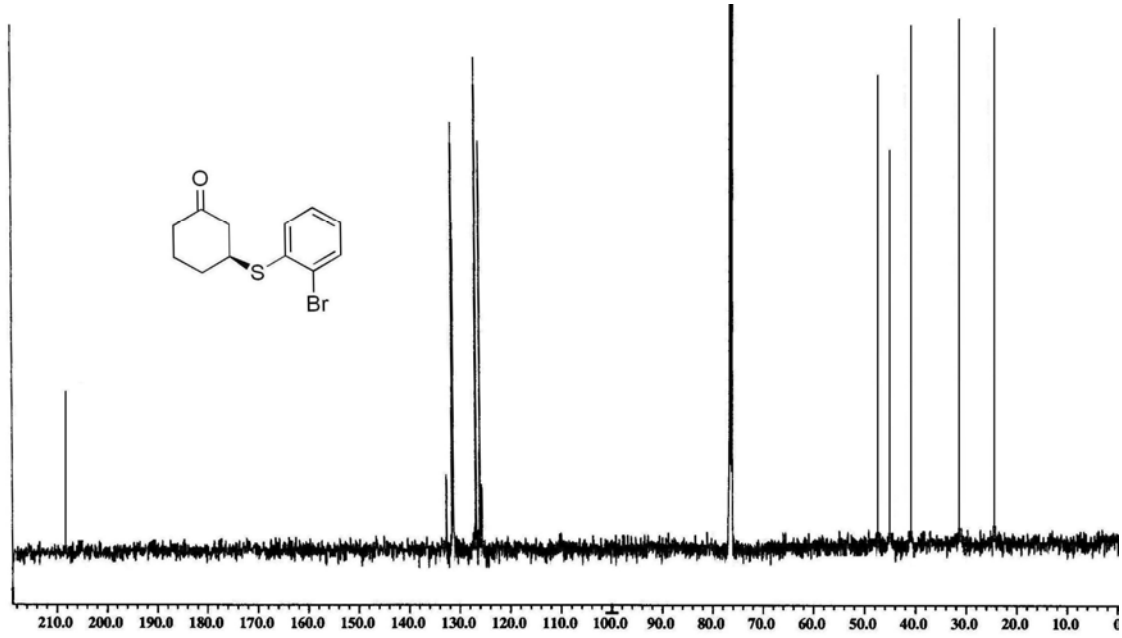
500 MHz ^{1}H NMR spectra of **2o** in $CDCl_3$



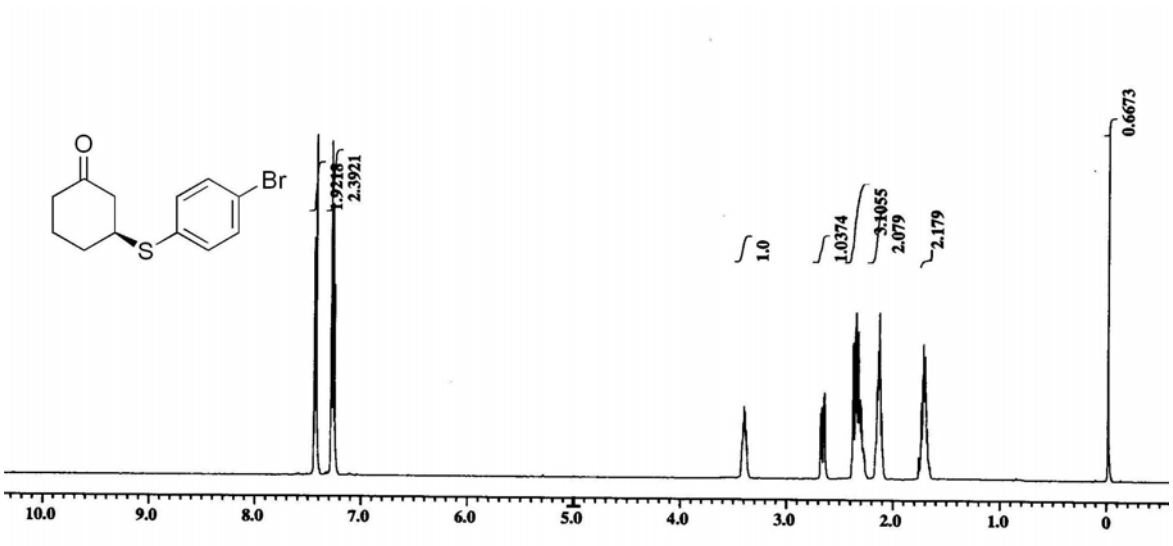
100 MHz ^{13}C NMR spectra of **2o** in $CDCl_3$



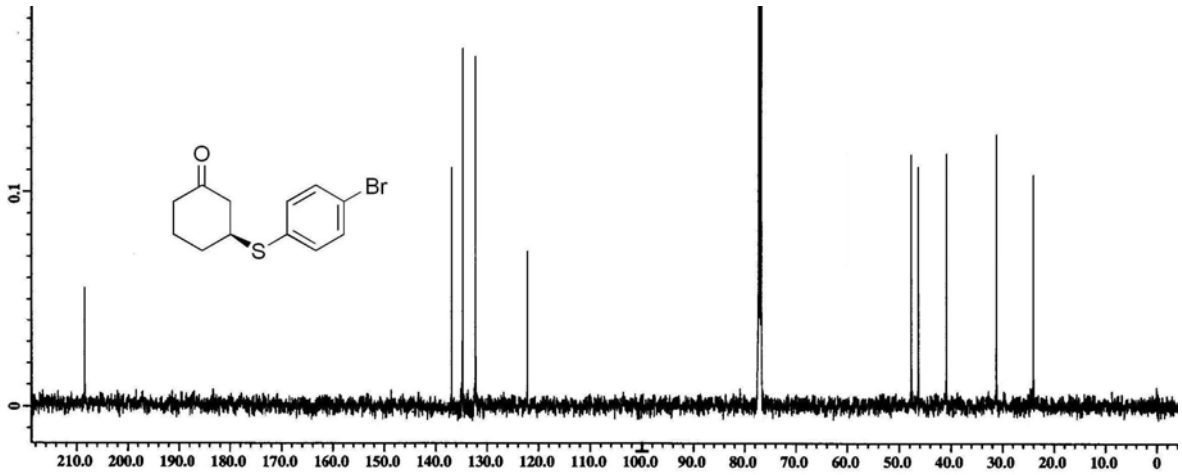
500 MHz ^{1}H NMR spectra of **2p** in $CDCl_3$



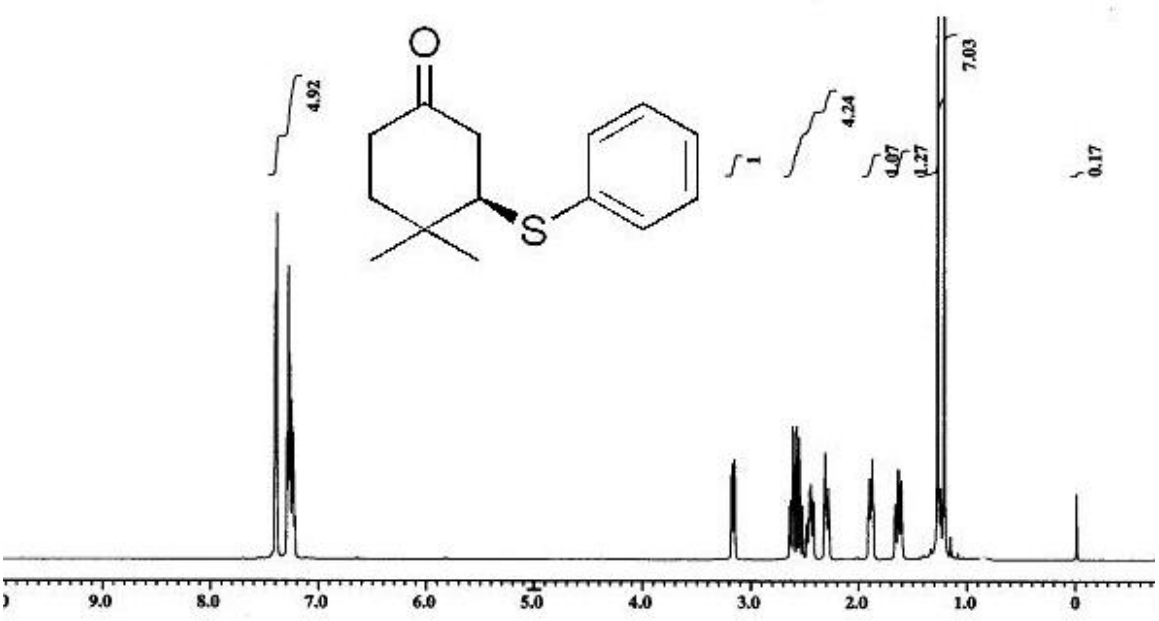
125 MHz ^{13}C NMR spectra of **2p** in $CDCl_3$



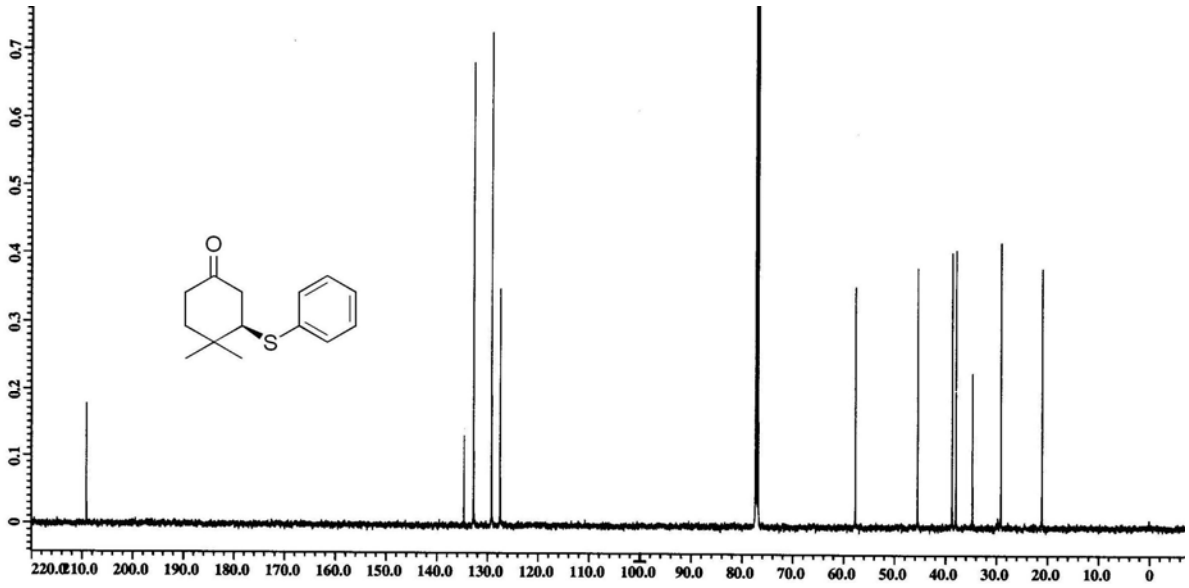
500 MHz ^{1}H NMR spectra of **2q** in $CDCl_3$



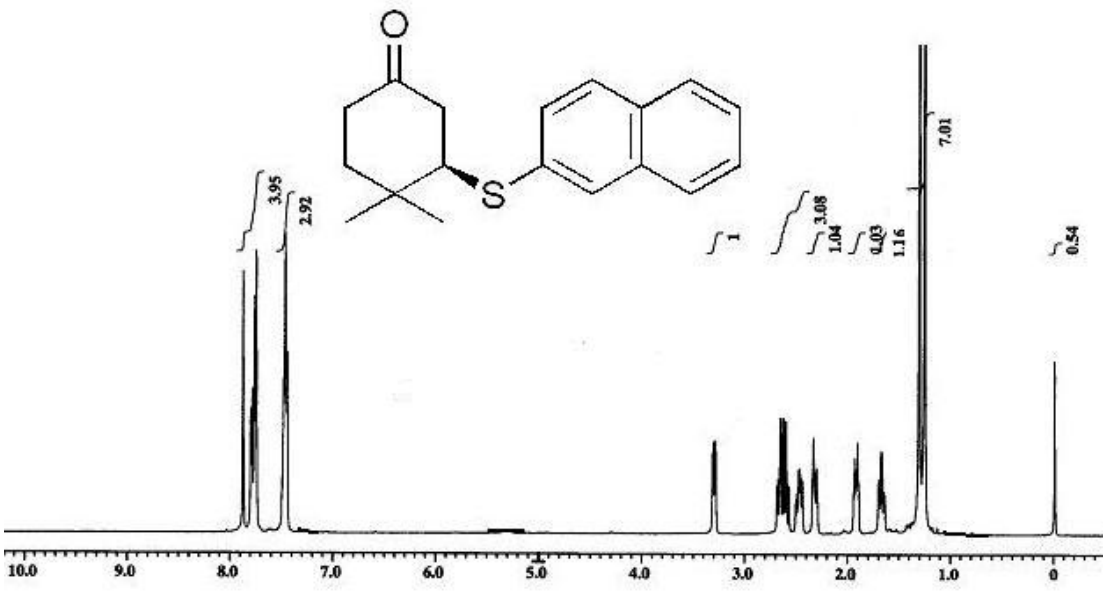
125 MHz ^{13}C NMR spectra of **2q** in $CDCl_3$



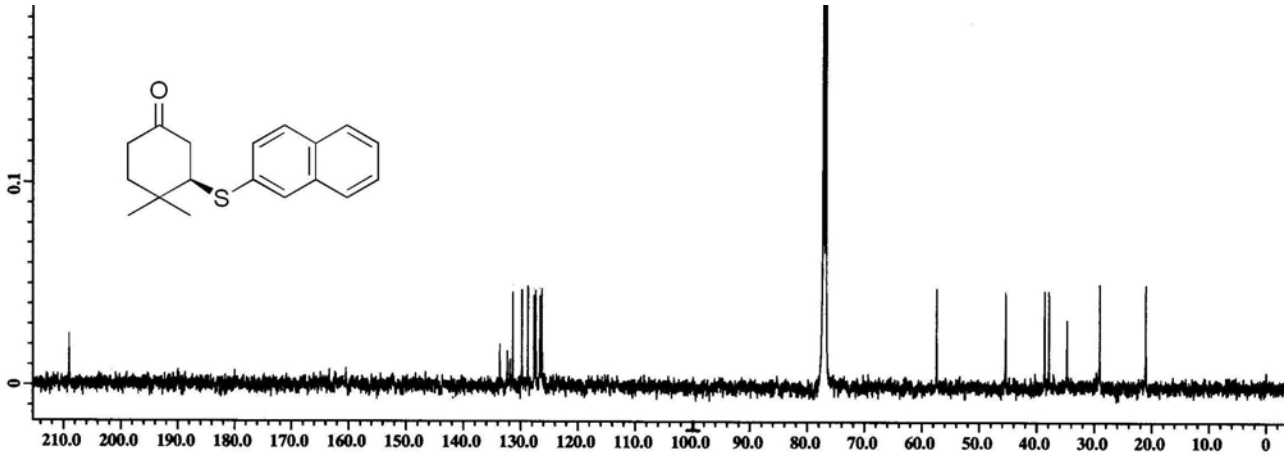
500 MHz ^{1}H NMR spectra of **3a** in $CDCl_3$



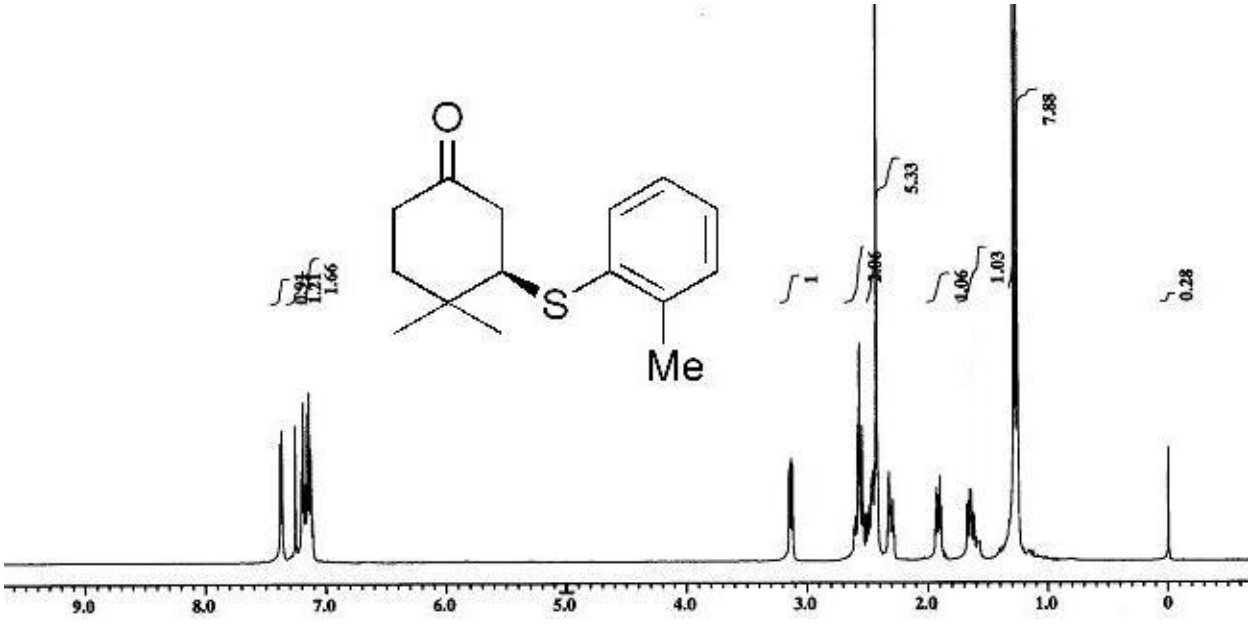
125 MHz ^{13}C NMR spectra of **3a** in $CDCl_3$



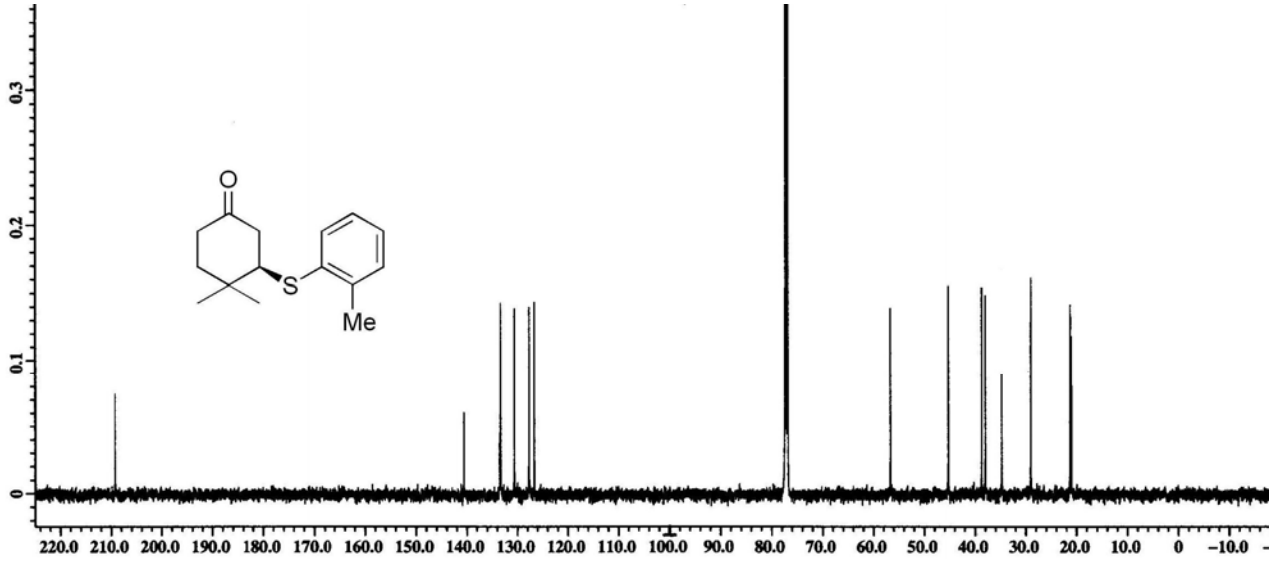
500 MHz ^{1}H NMR spectra of **3b** in $CDCl_3$



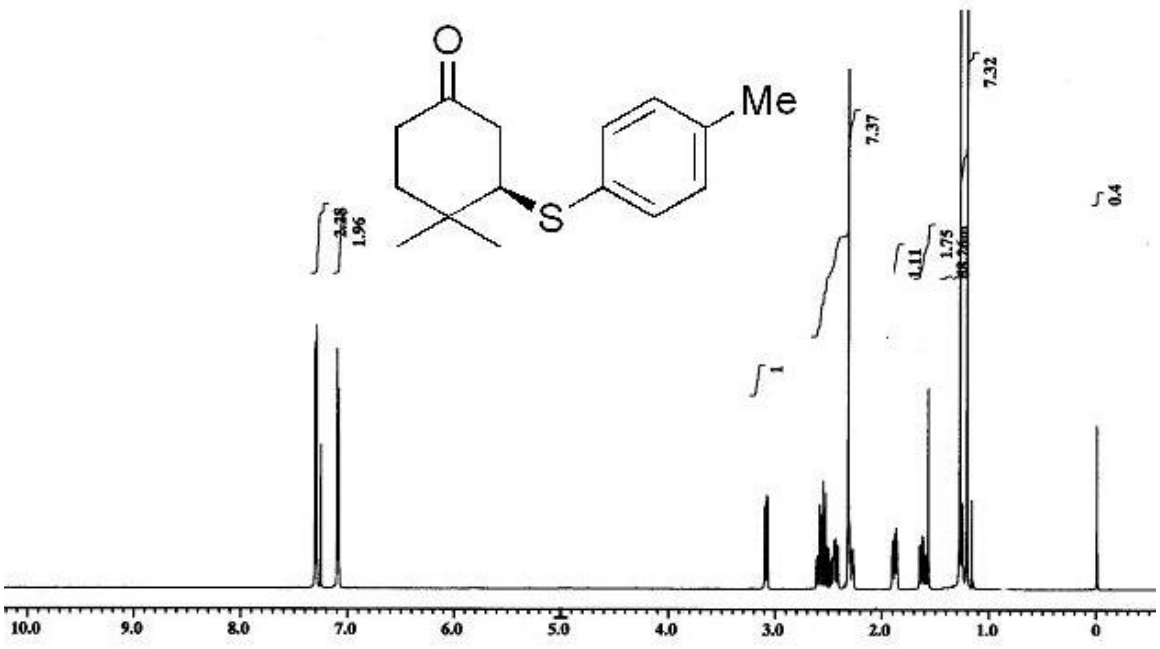
125 MHz ^{13}C NMR spectra of **3b** in $CDCl_3$



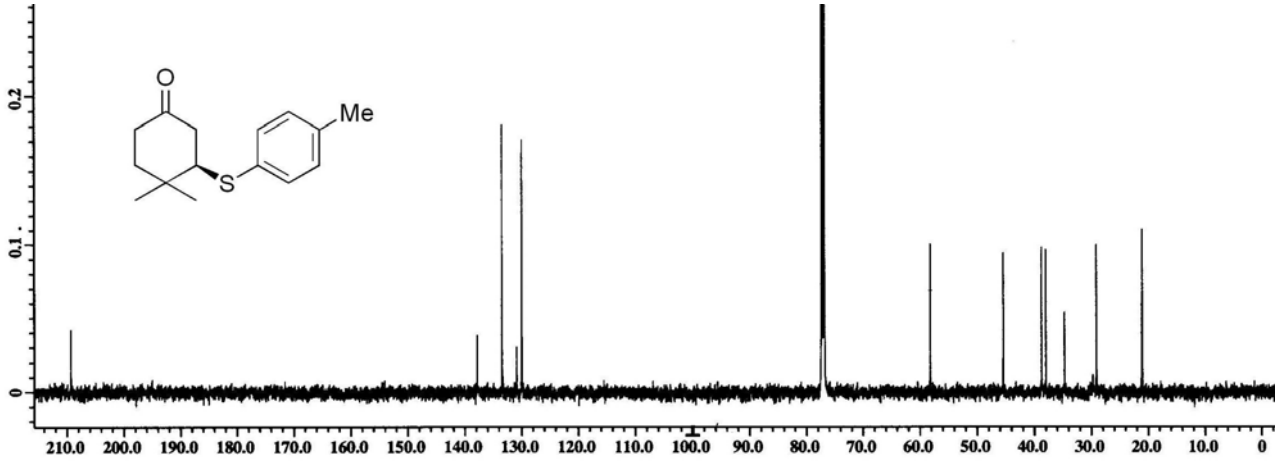
500 MHz ^{1}H NMR spectra of **3c** in $CDCl_3$



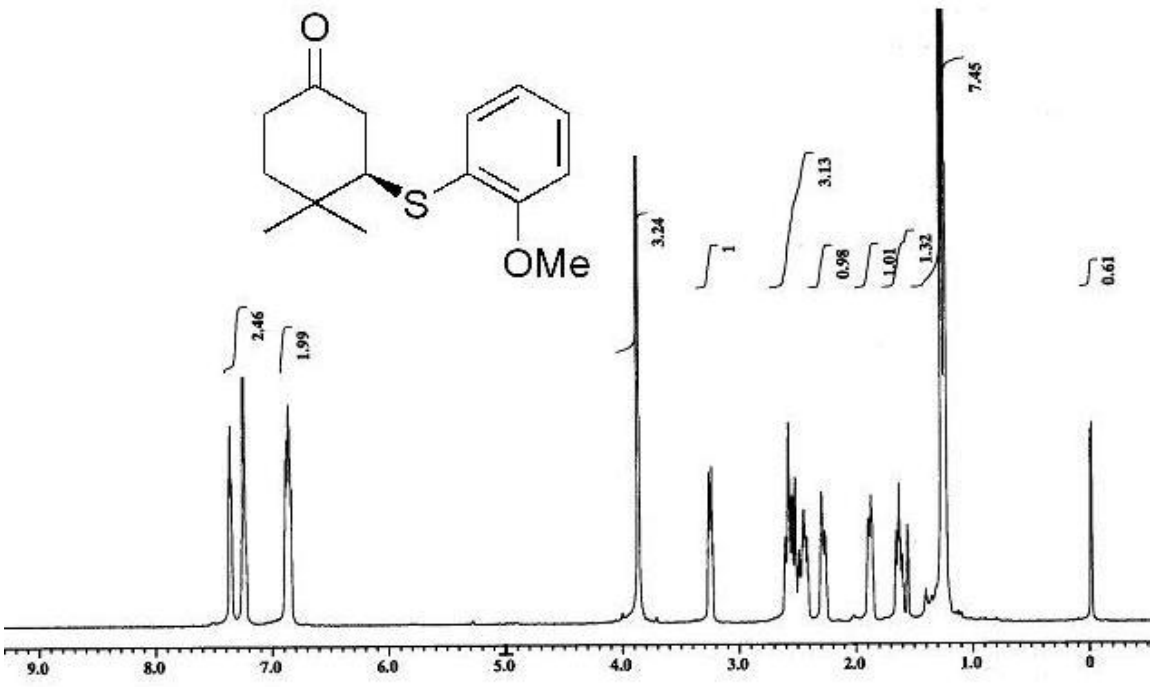
125 MHz ^{13}C NMR spectra of **3c** in $CDCl_3$



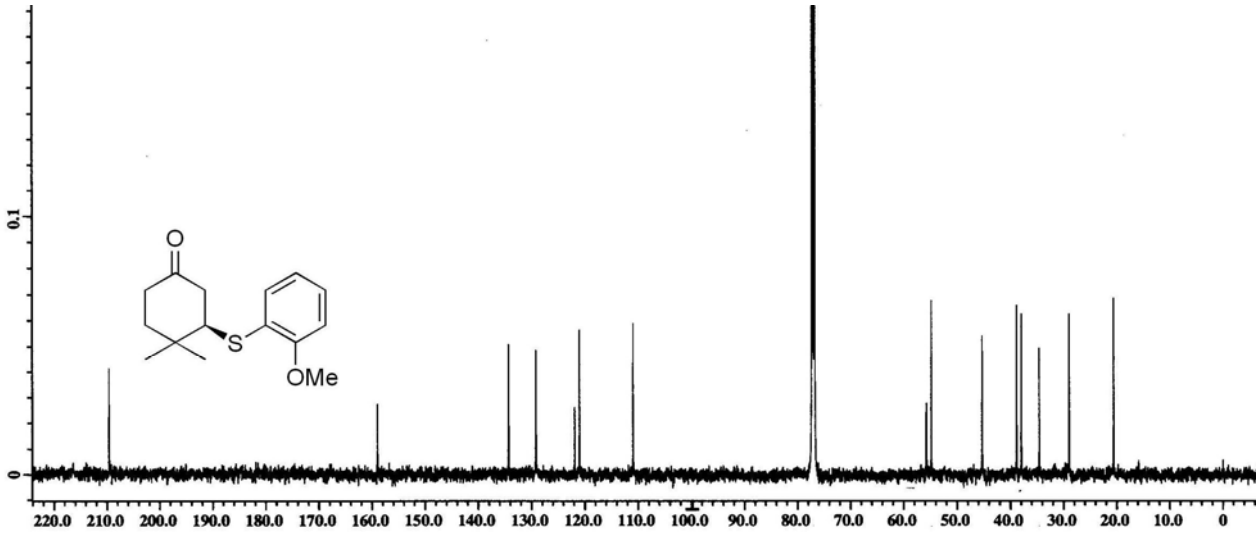
500 MHz ^{1}H NMR spectra of **3d** in $CDCl_3$



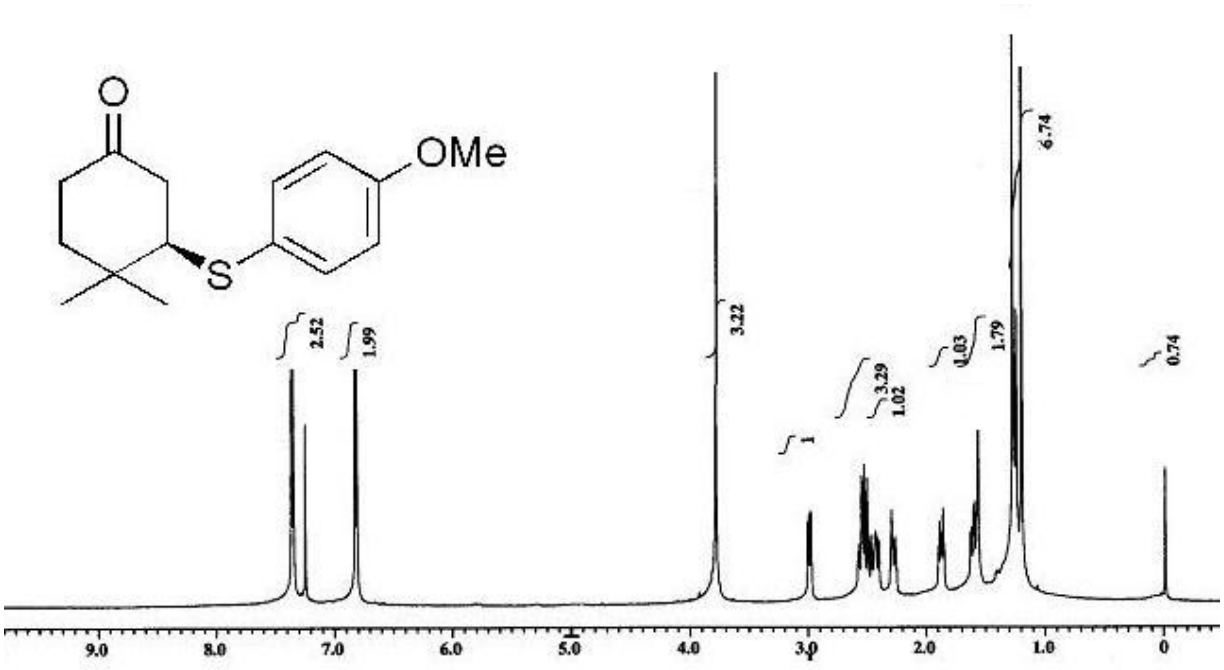
125 MHz ^{13}C NMR spectra of **3d** in $CDCl_3$



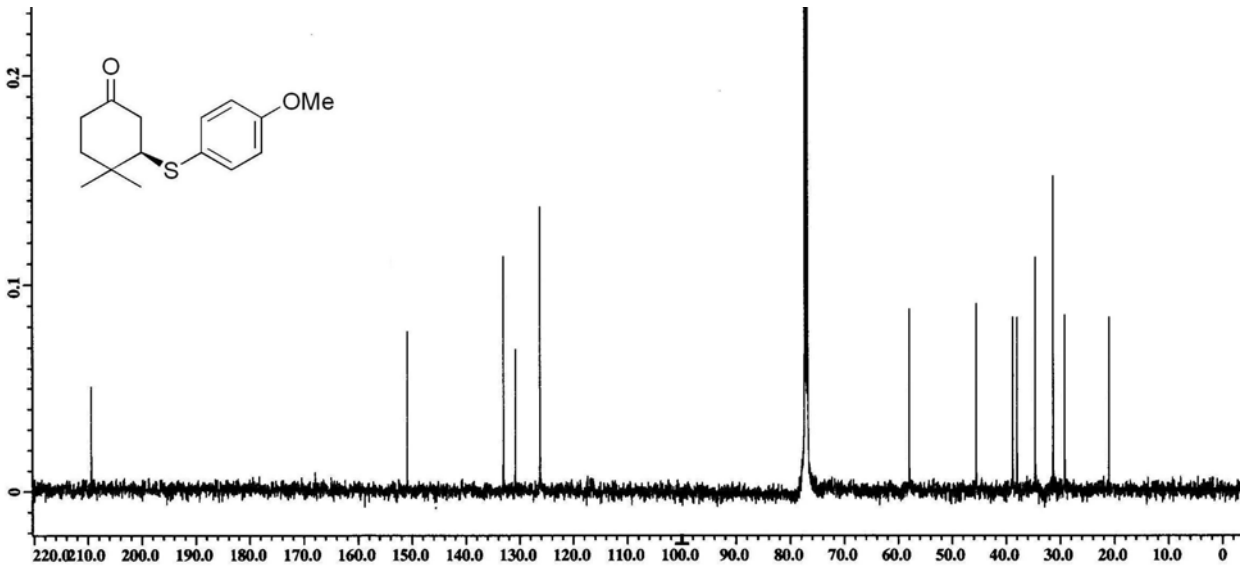
500 MHz ^{1}H NMR spectra of **3e** in $CDCl_3$



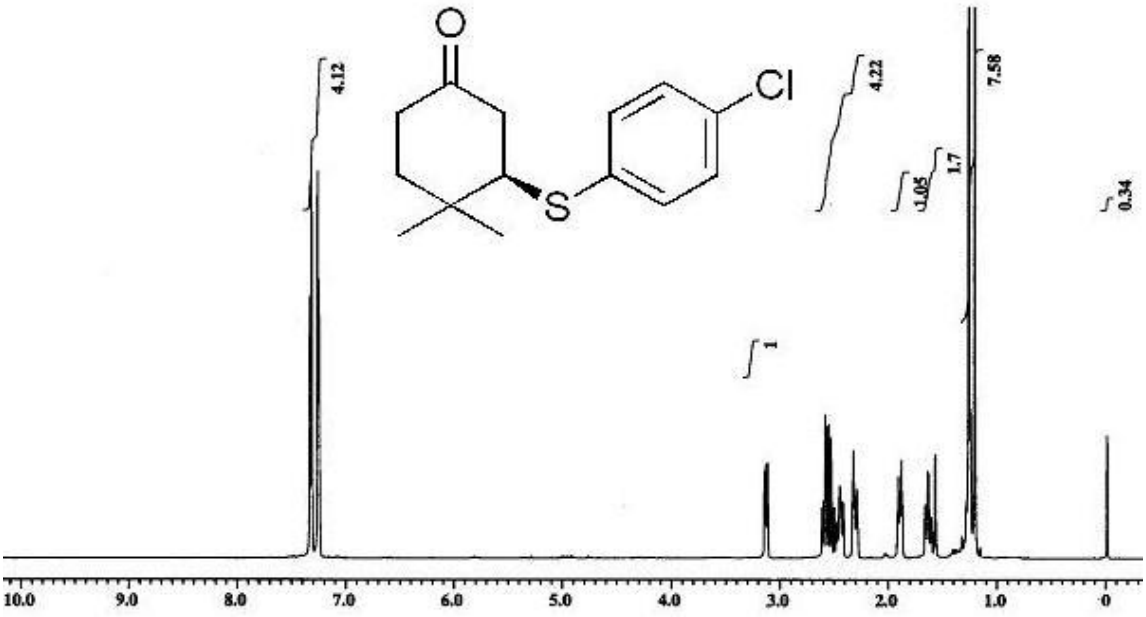
125 MHz ^{13}C NMR spectra of **3e** in $CDCl_3$



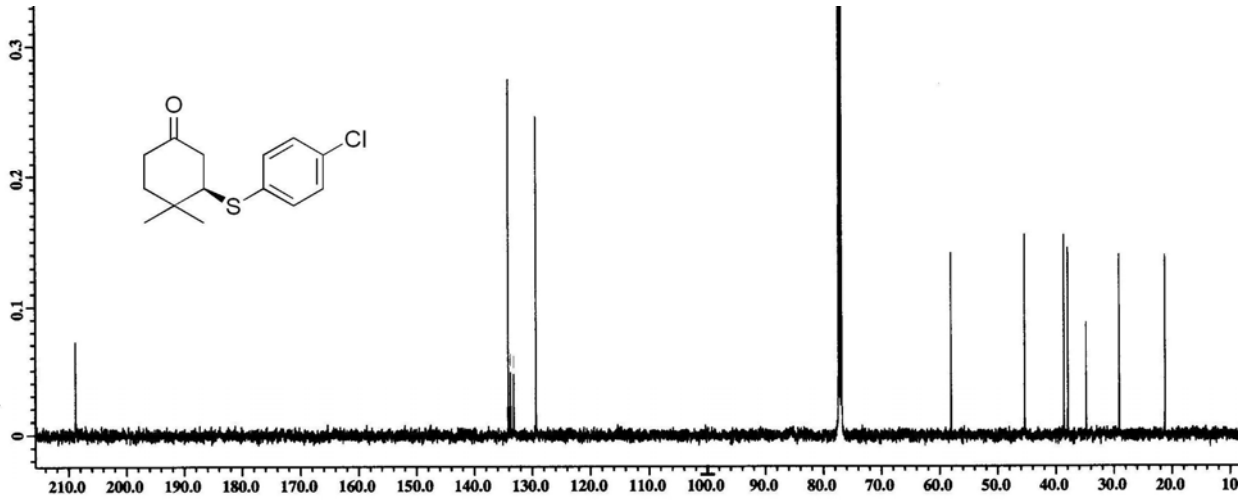
500 MHz ^{1}H NMR spectra of **3f** in $CDCl_3$



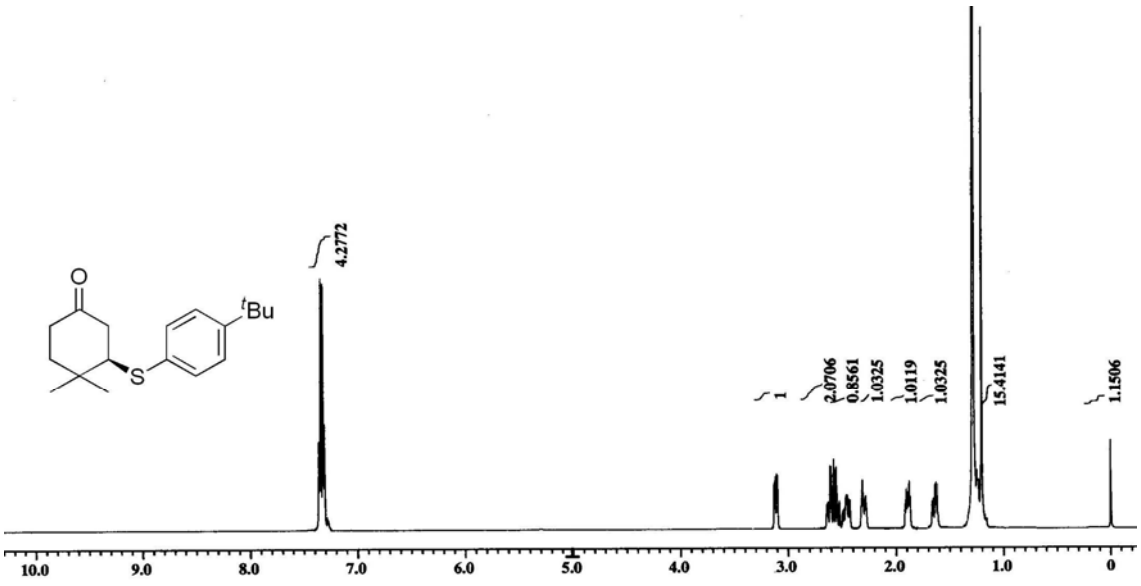
125 MHz ^{13}C NMR spectra of **3f** in $CDCl_3$



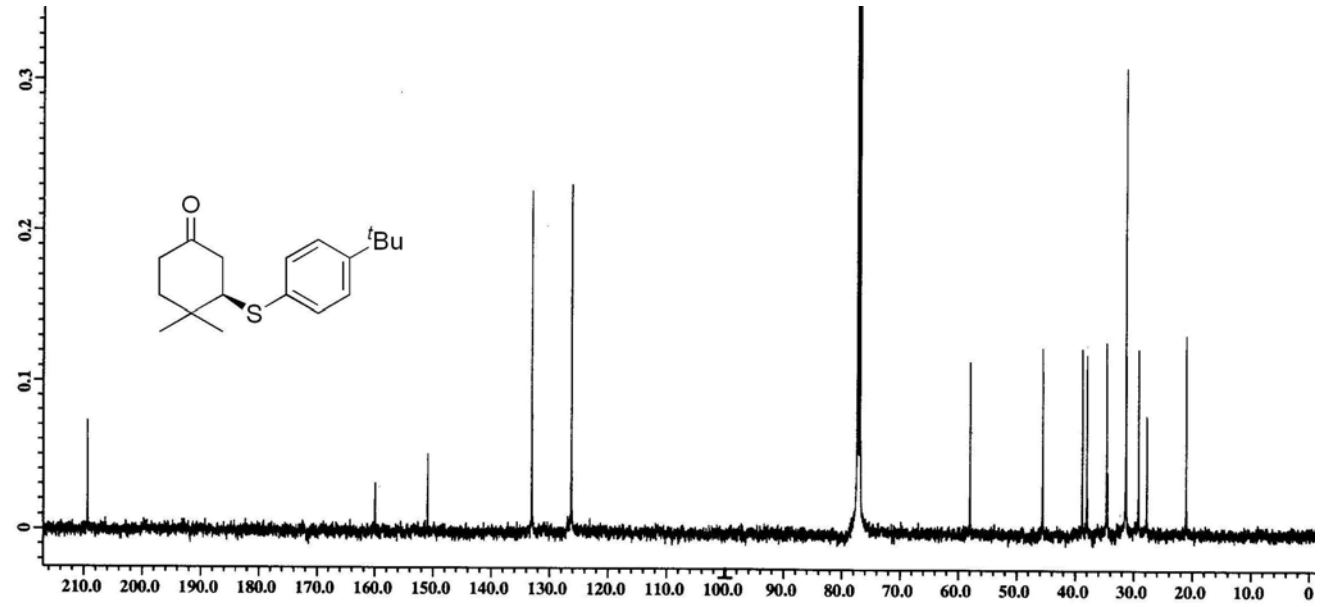
500 MHz ^{1}H NMR spectra of **3g** in $CDCl_3$



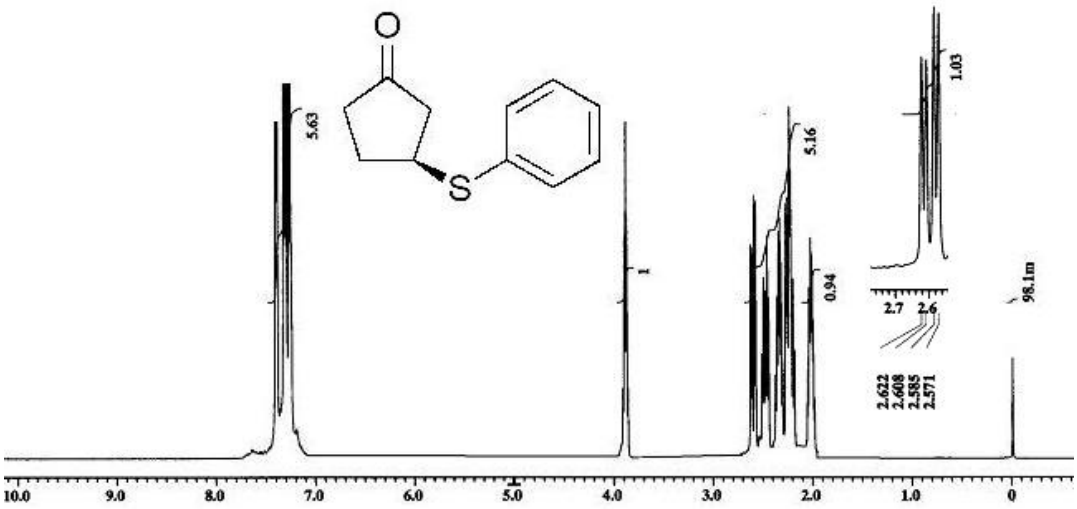
125 MHz ^{13}C NMR spectra of **3g** in $CDCl_3$



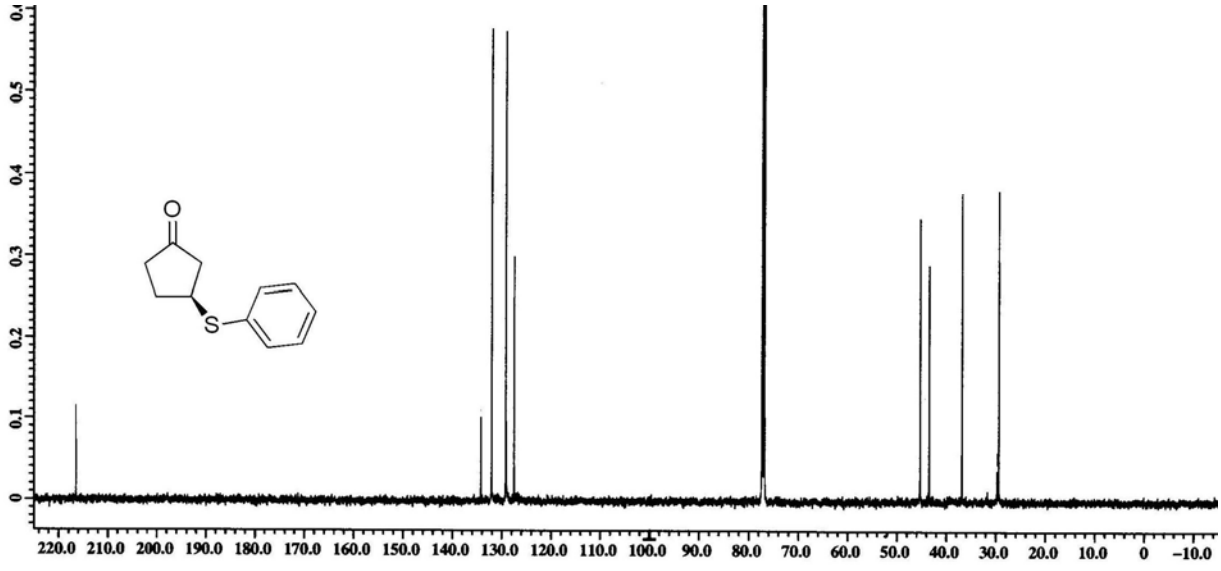
500 MHz ^{1}H NMR spectra of **3h** in $CDCl_3$



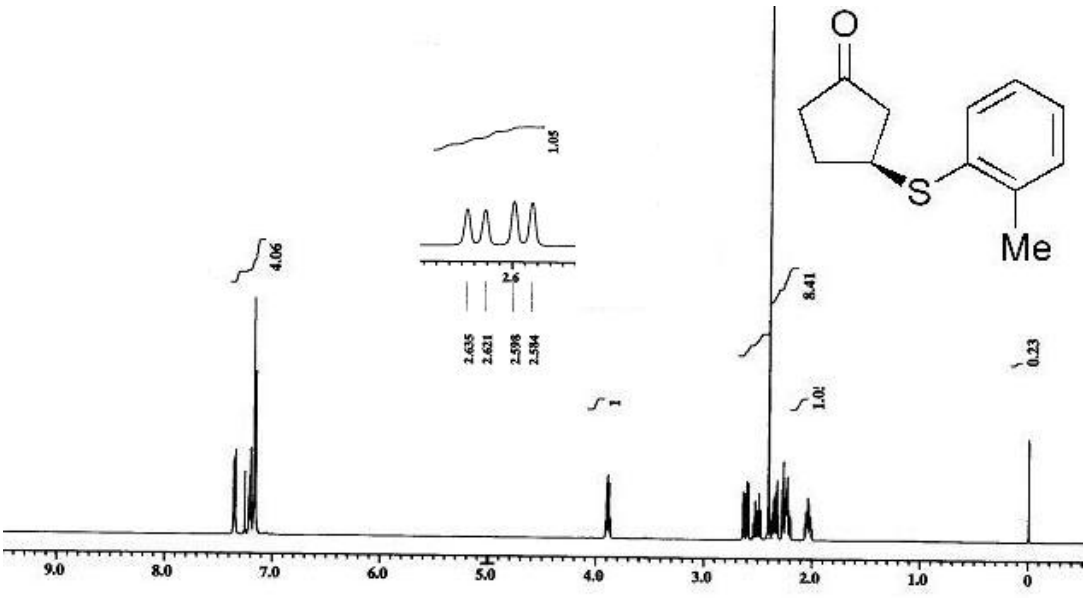
125 MHz ^{13}C NMR spectra of **3h** in $CDCl_3$



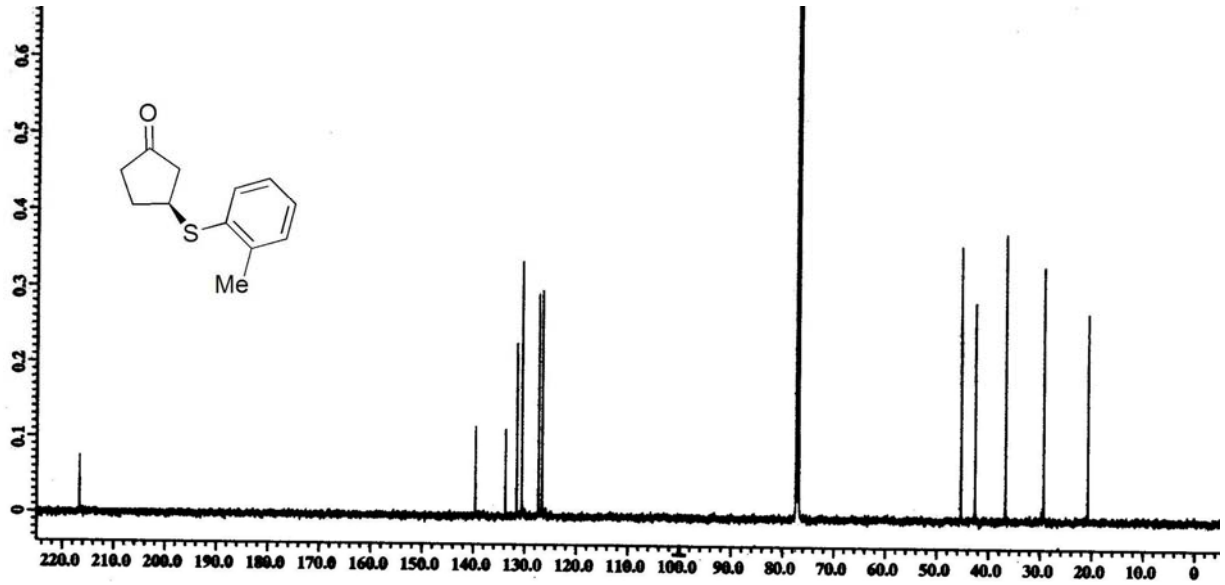
500 MHz ^{1}H NMR spectra of **4a** in $CDCl_3$



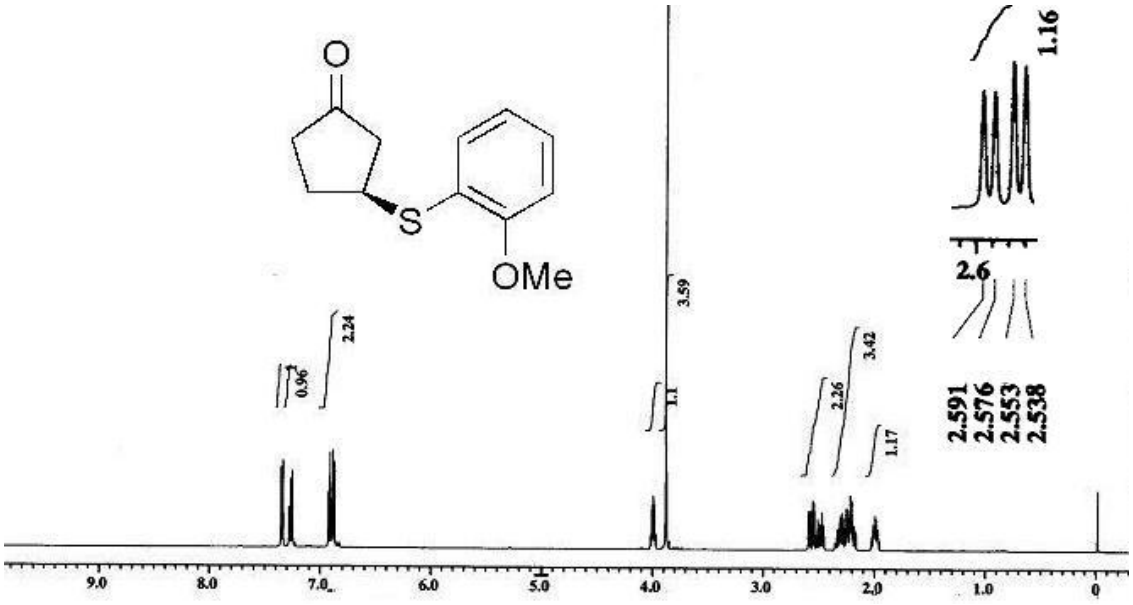
125 MHz ^{13}C NMR spectra of **4a** in $CDCl_3$



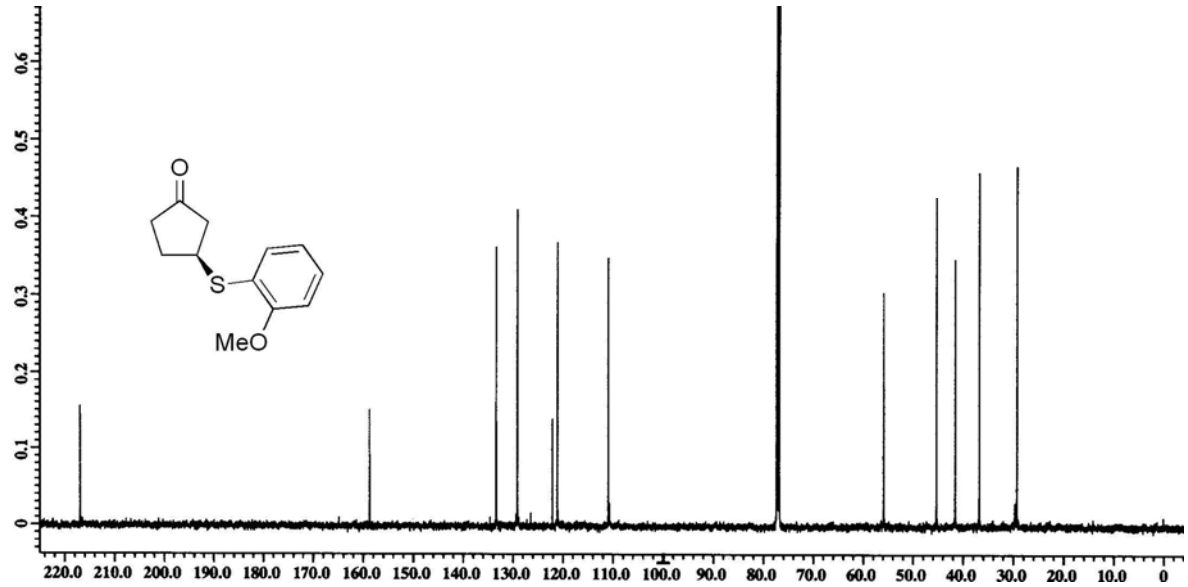
500 MHz ^{1}H NMR spectra of **4b** in $CDCl_3$



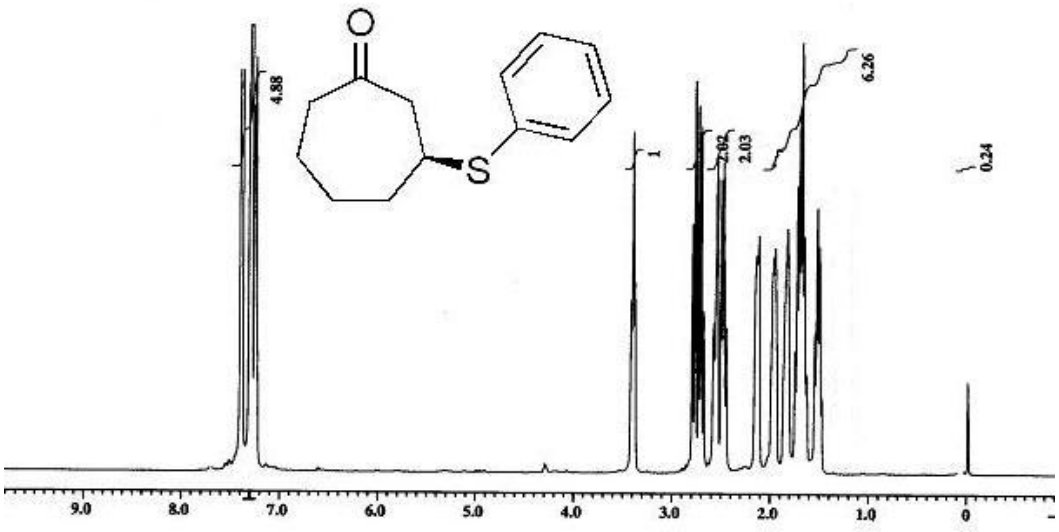
125 MHz ^{13}C NMR spectra of **4b** in $CDCl_3$



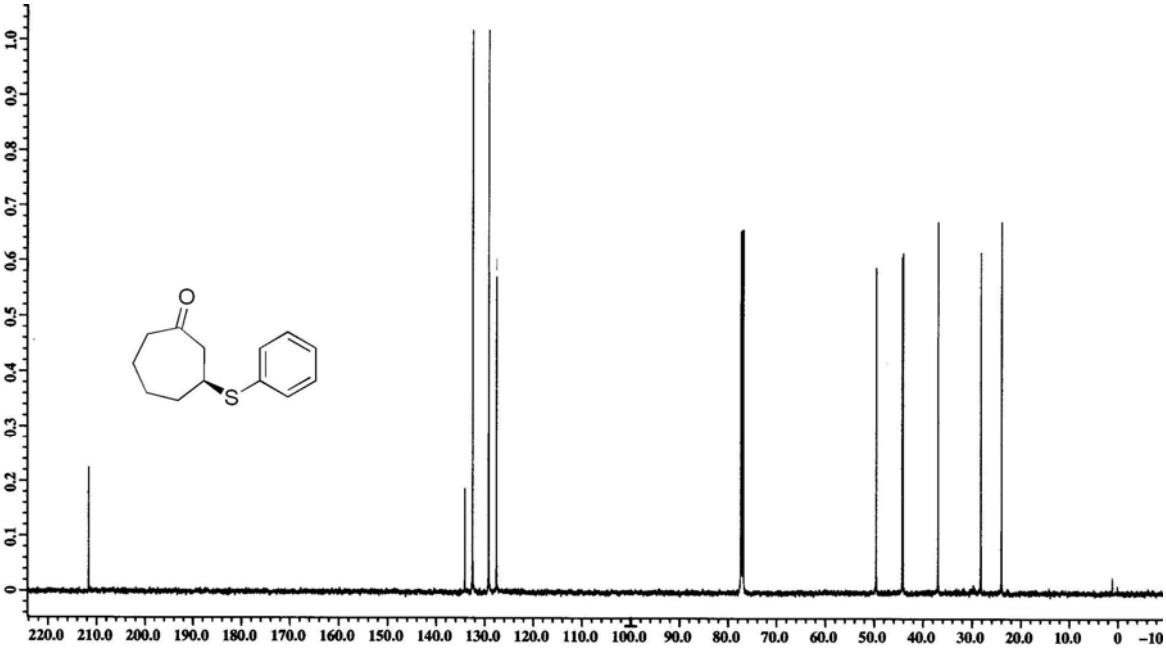
500 MHz ^{1}H NMR spectra of **4c** in $CDCl_3$



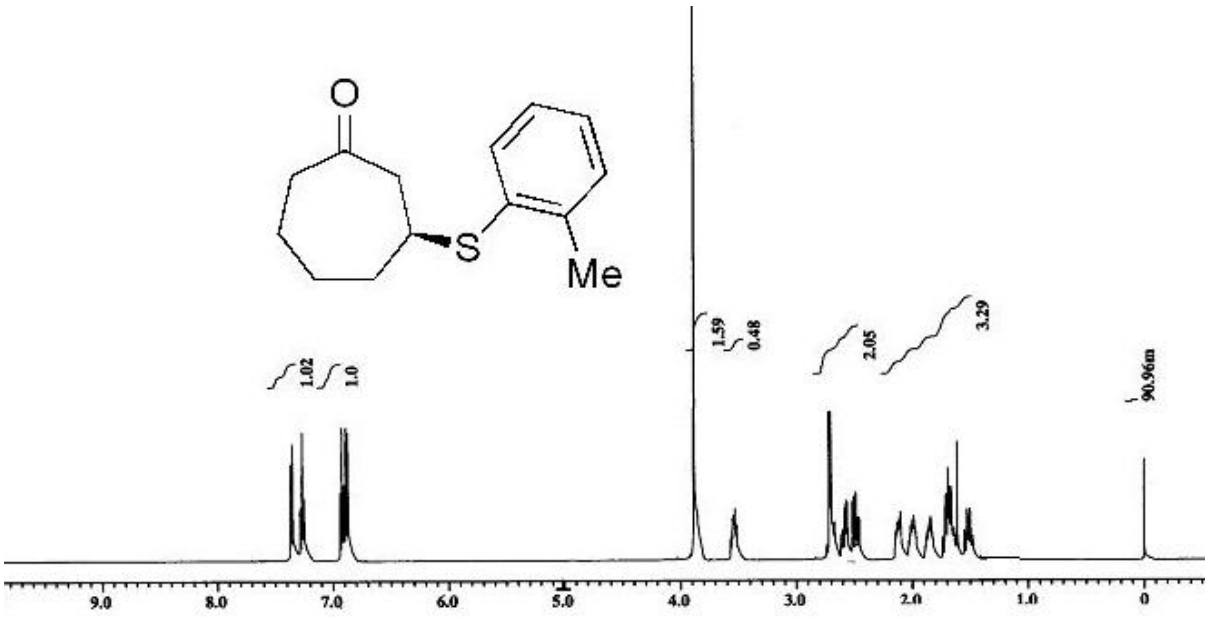
125 MHz ^{13}C NMR spectra of **4c** in $CDCl_3$



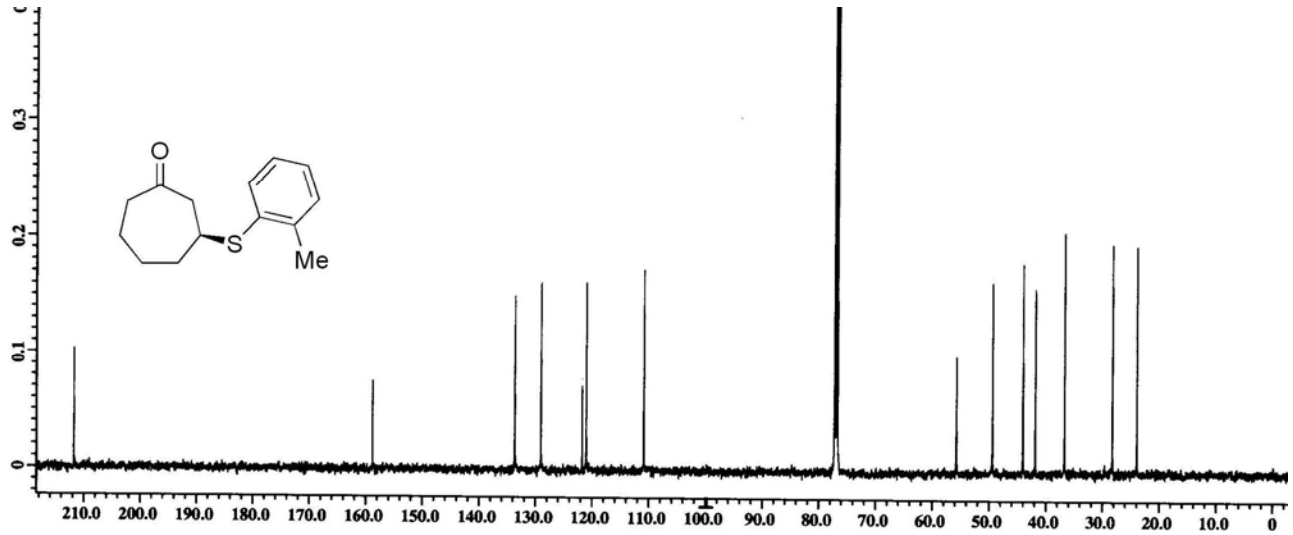
500 MHz ^{1}H NMR spectra of **5a** in $CDCl_3$



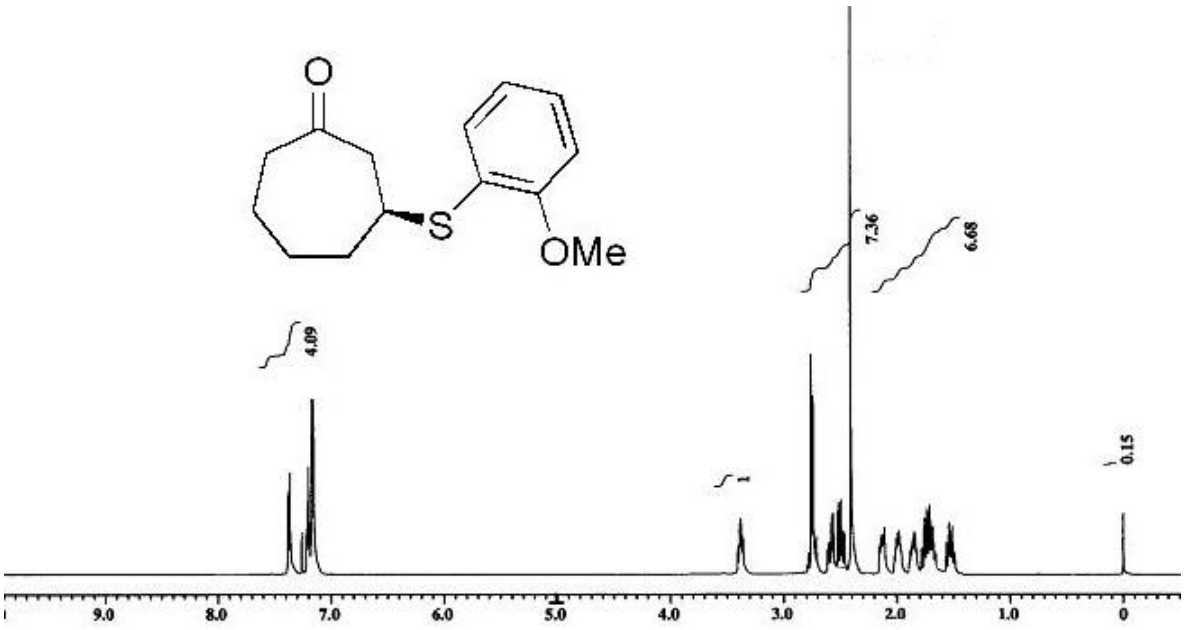
125 MHz ^{13}C NMR spectra of **5a** in $CDCl_3$



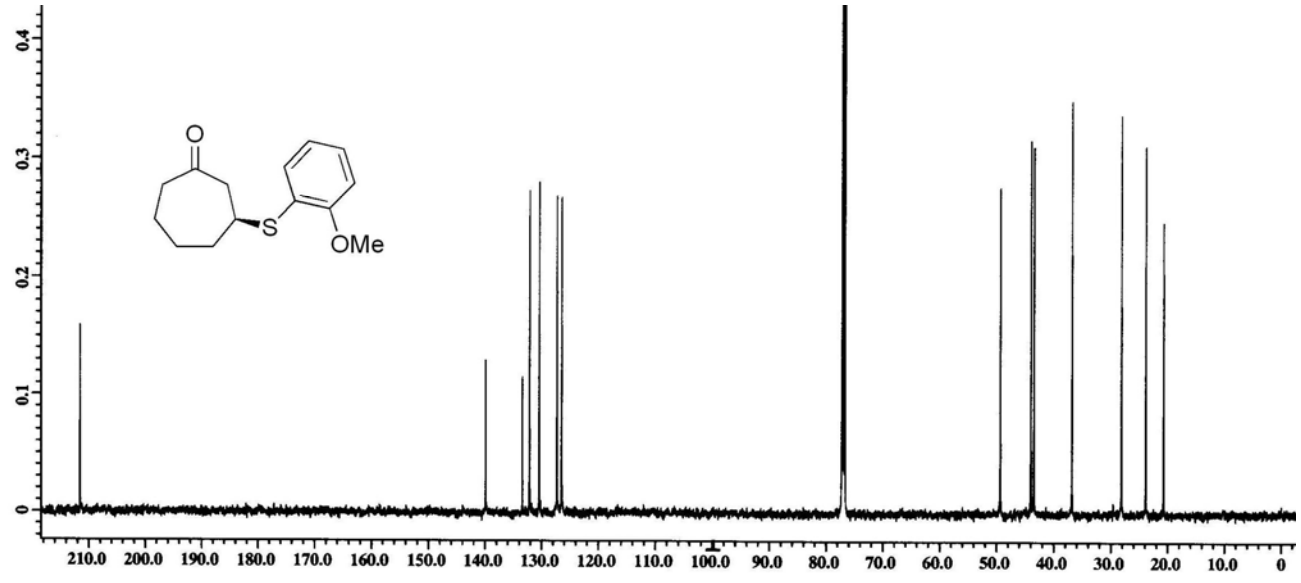
500 MHz ^{1}H NMR spectra of **5b** in $CDCl_3$



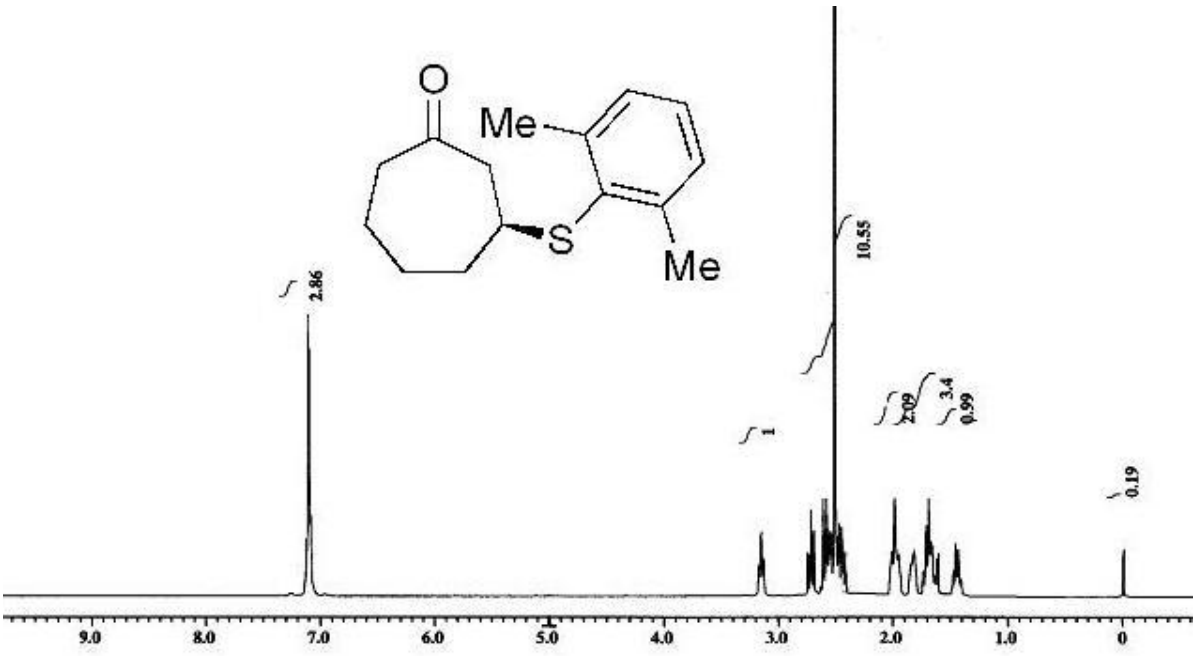
125 MHz ^{13}C NMR spectra of **5b** in $CDCl_3$



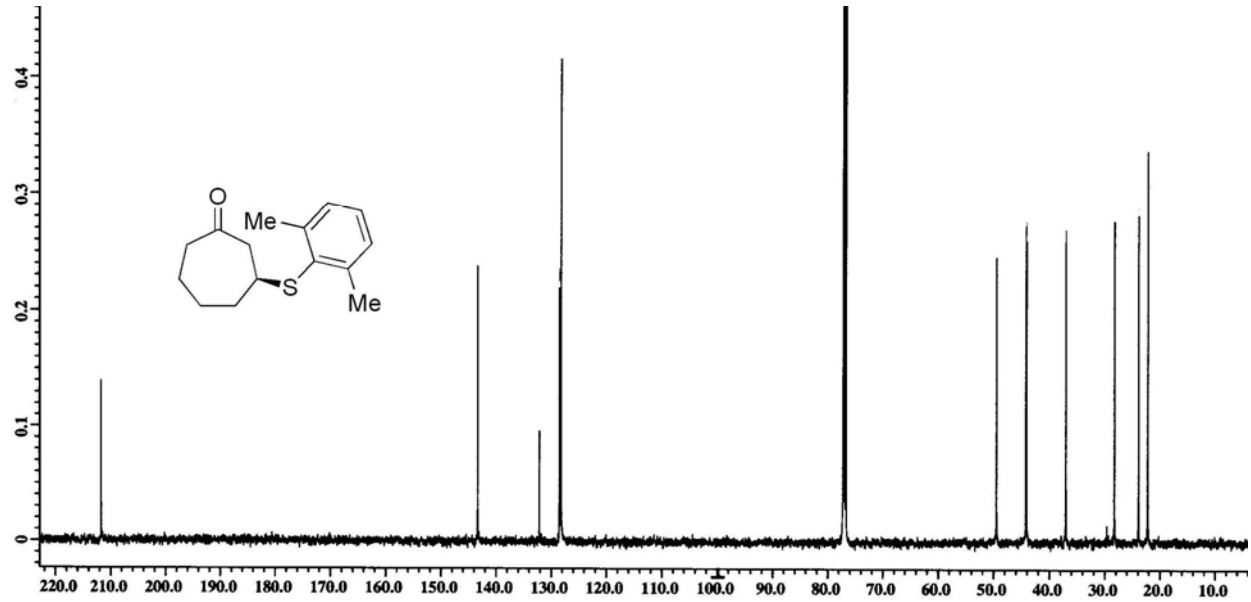
500 MHz ^{1}H NMR spectra of **5c** in $CDCl_3$



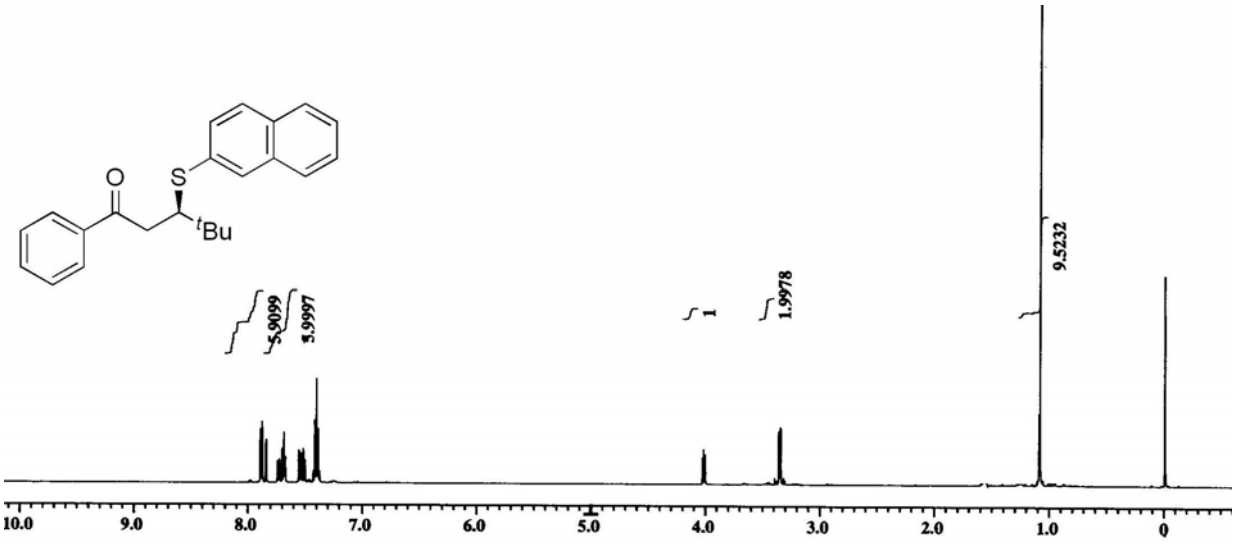
125 MHz ^{13}C NMR spectra of **5c** in $CDCl_3$



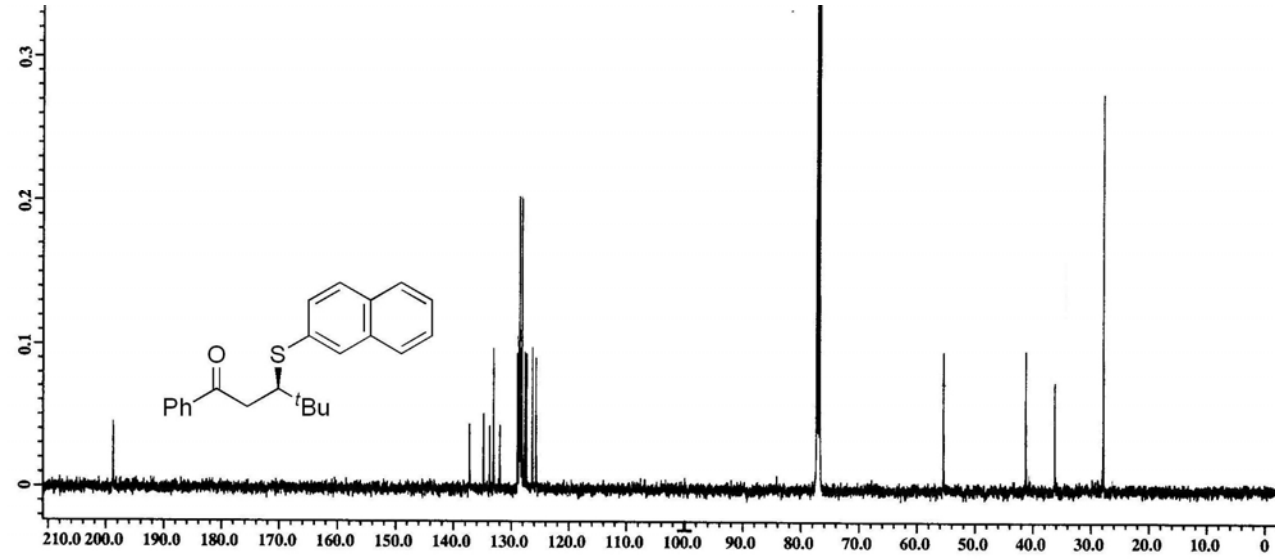
500 MHz ^{1}H NMR spectra of **5d** in $CDCl_3$



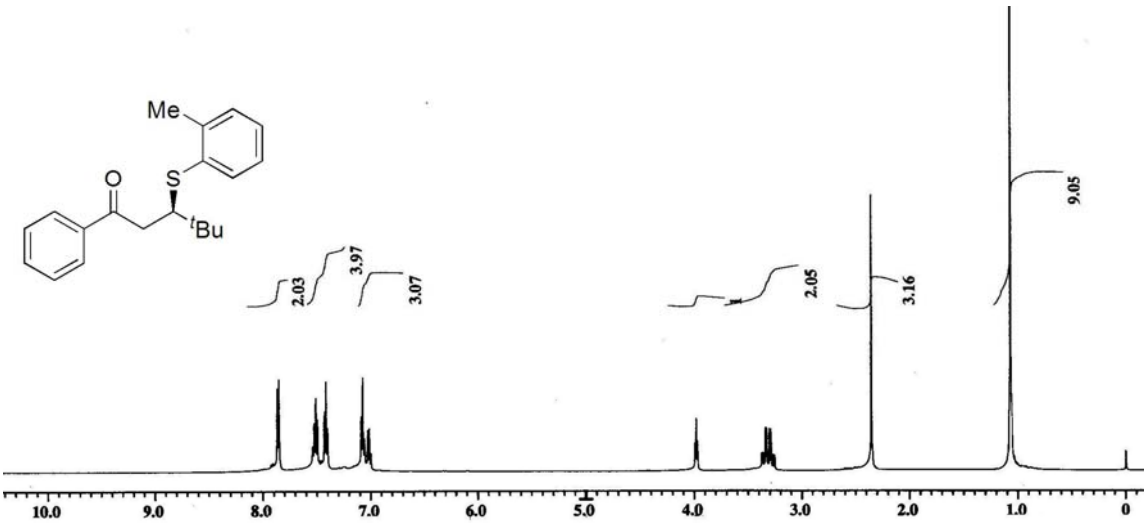
125 MHz ^{13}C NMR spectra of **5d** in $CDCl_3$



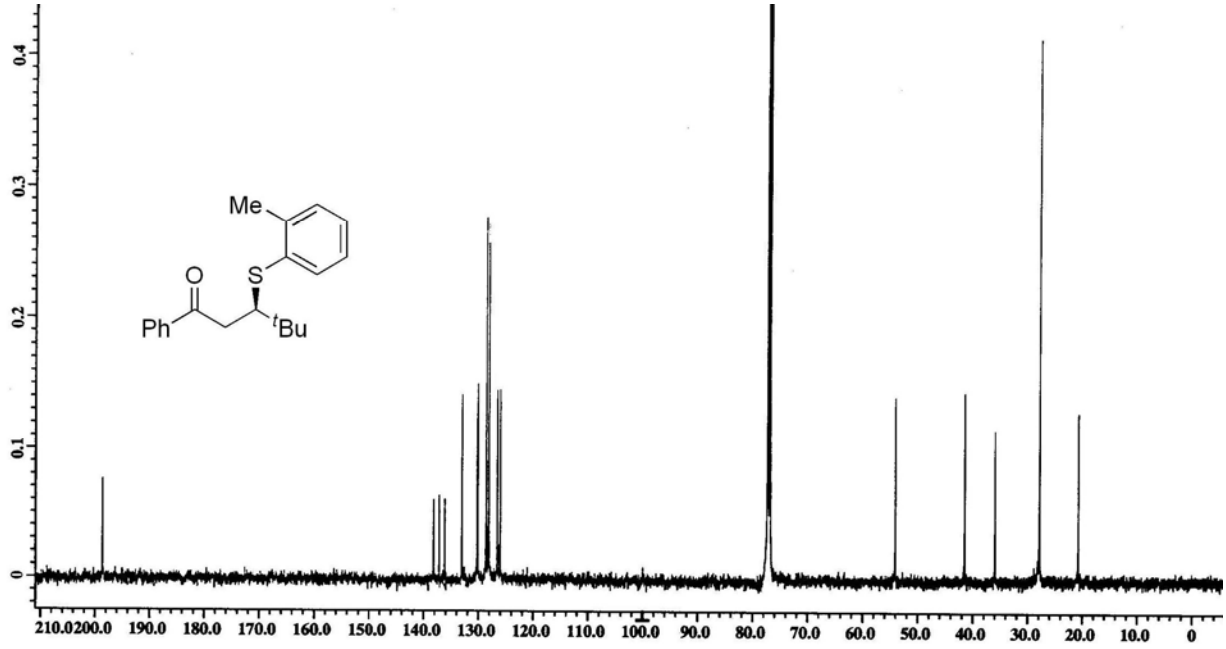
500 MHz ^{1}H NMR spectra of **6a** in $CDCl_3$



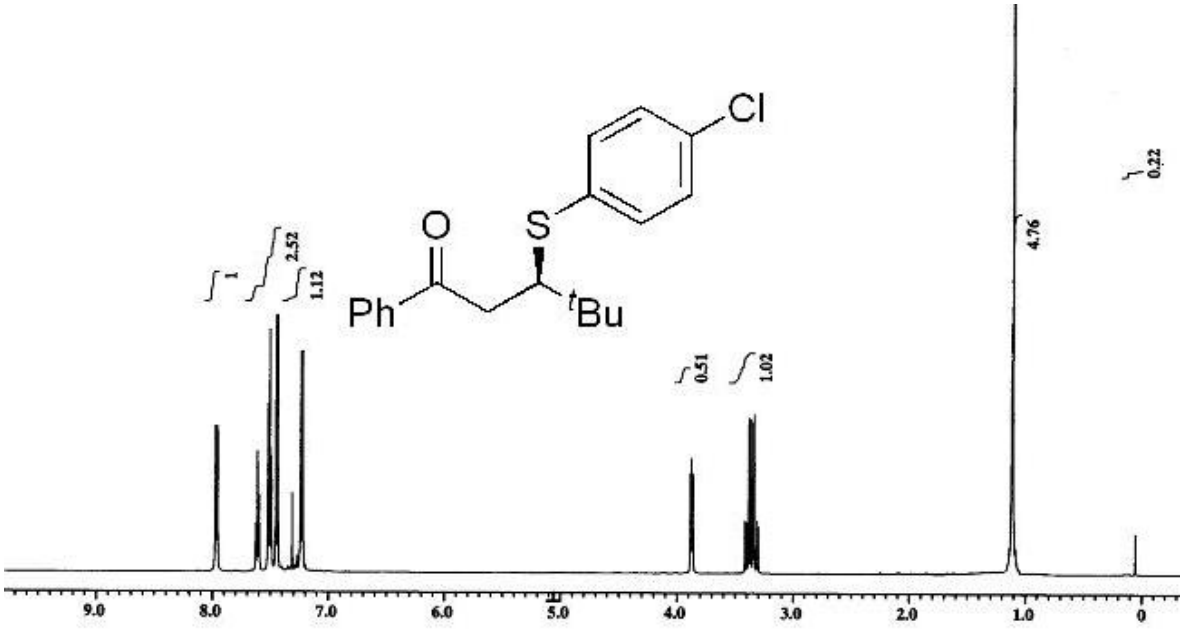
125 MHz ^{13}C NMR spectra of **6a** in $CDCl_3$



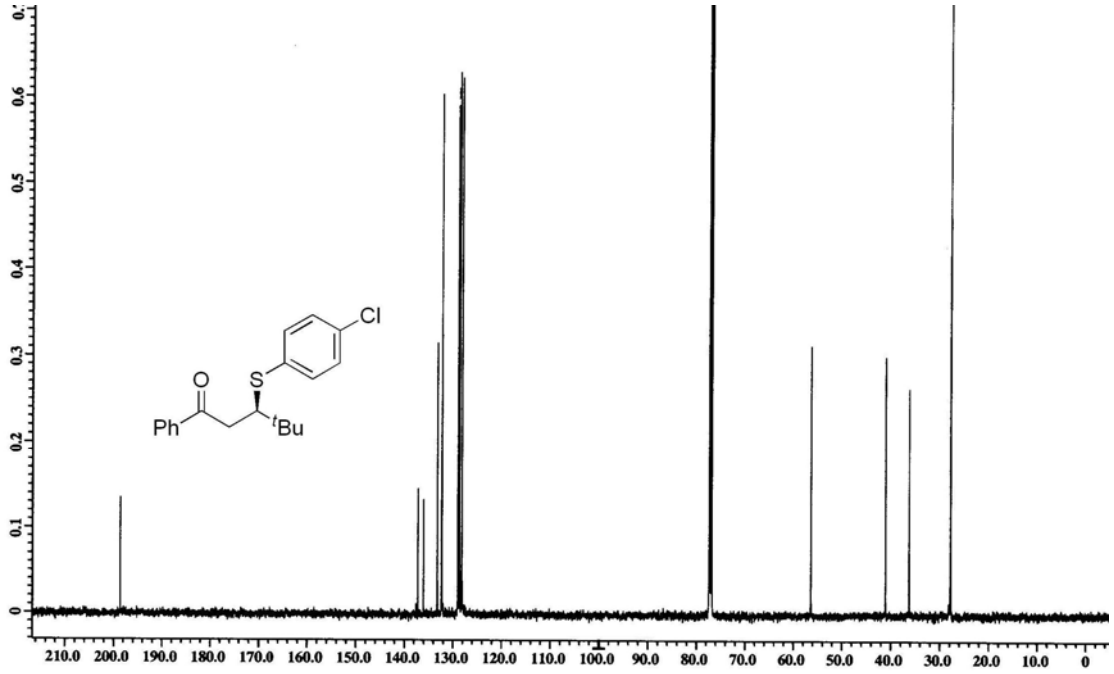
500 MHz ^{1}H NMR spectra of **6b** in $CDCl_3$



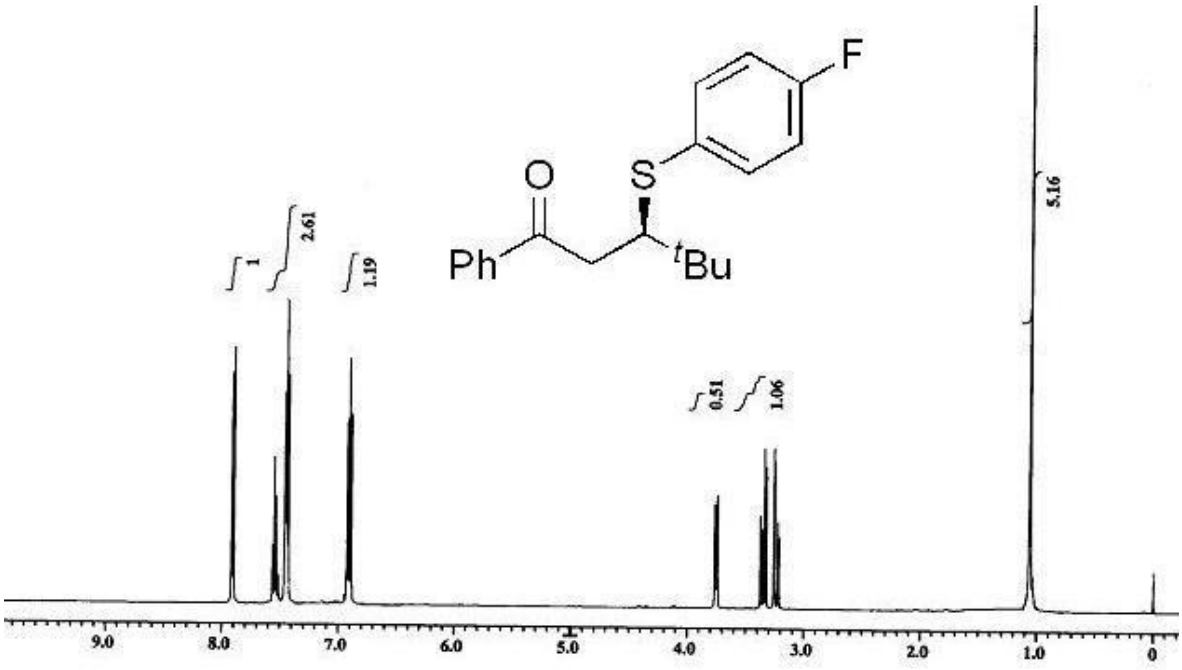
125 MHz ^{13}C NMR spectra of **6b** in $CDCl_3$



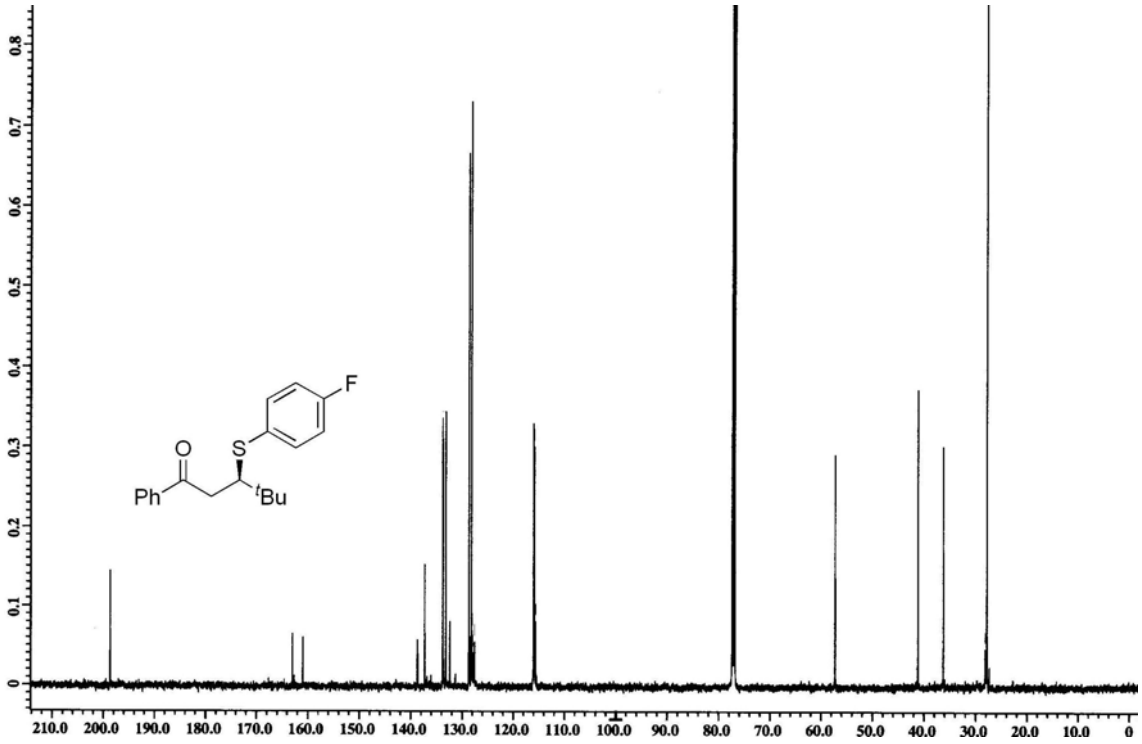
500 MHz ^{1}H NMR spectra of **6c** in $CDCl_3$



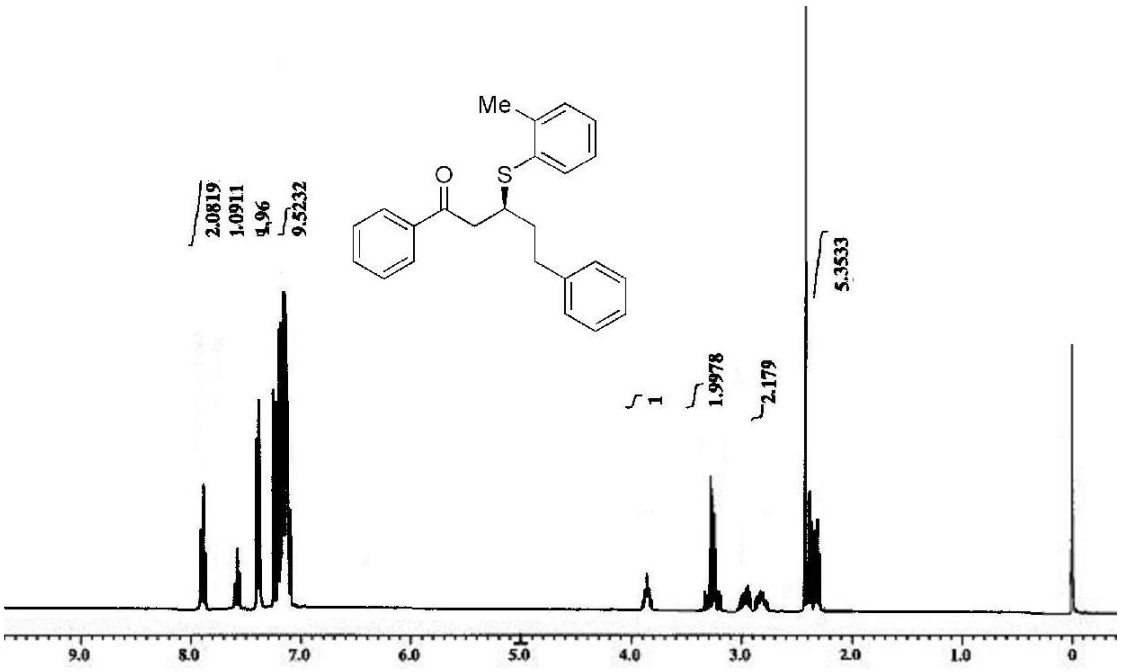
125 MHz ^{13}C NMR spectra of **6c** in $CDCl_3$



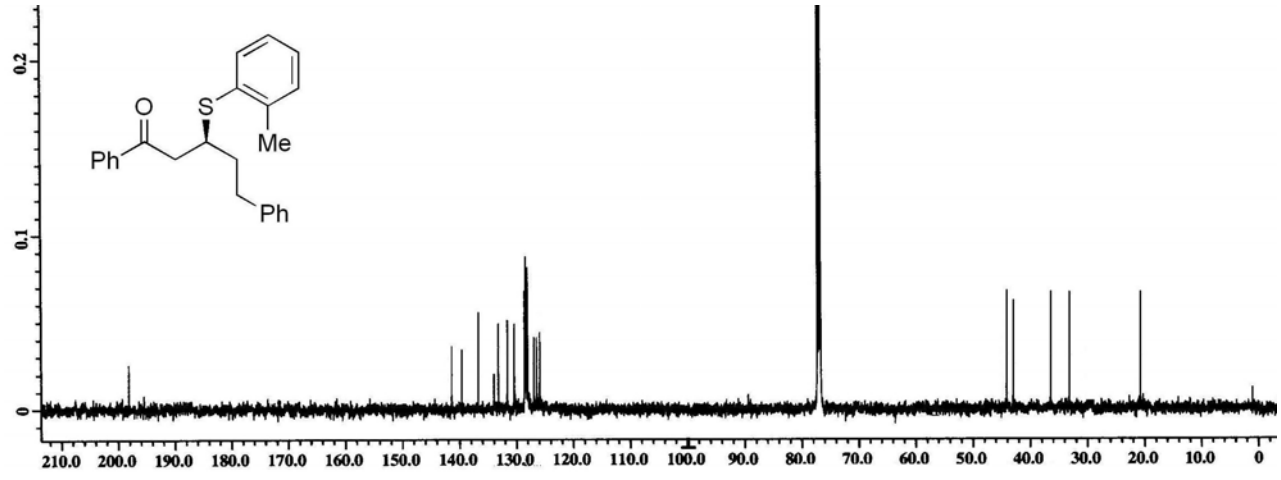
500 MHz ^{1}H NMR spectra of **6d** in $CDCl_3$



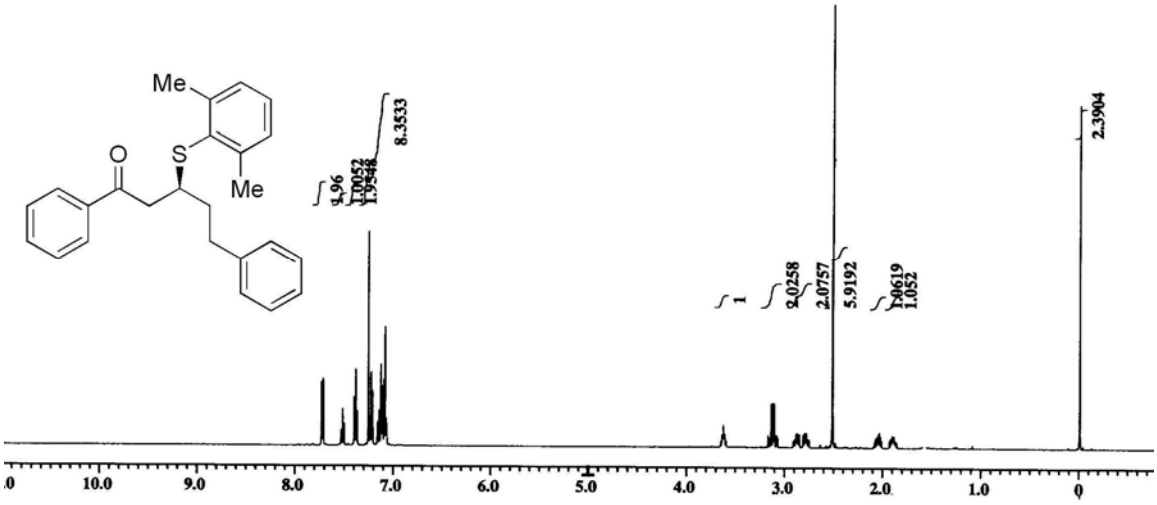
125 MHz ^{13}C NMR spectra of **6d** in $CDCl_3$



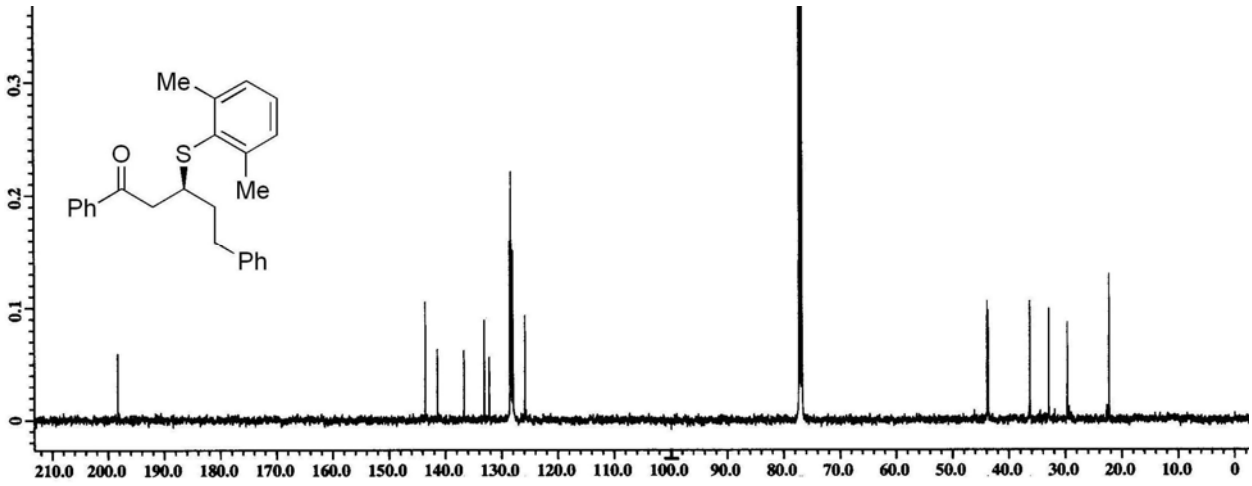
500 MHz ^{1}H NMR spectra of **7a** in $CDCl_3$



125 MHz ^{13}C NMR spectra of **7a** in $CDCl_3$

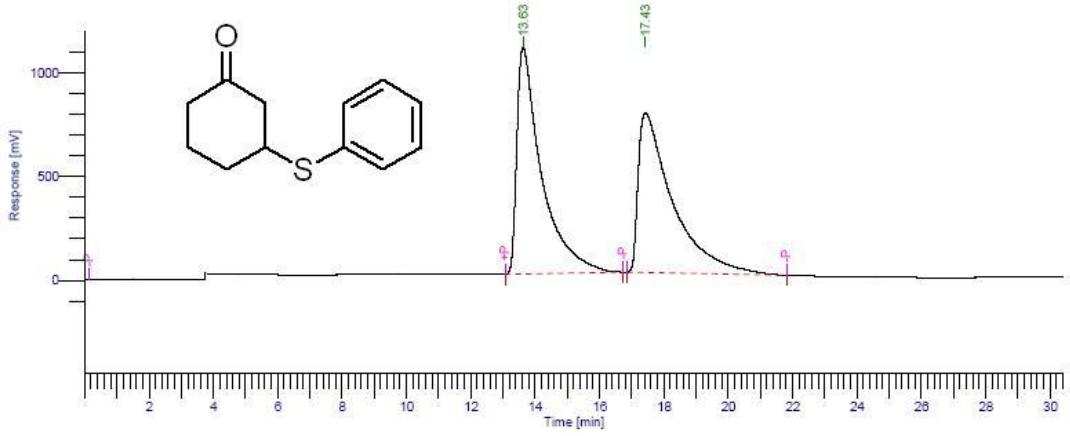


500 MHz ^{1}H NMR spectra of **7b** in $CDCl_3$



125 MHz ^{13}C NMR spectra of **7b** in $CDCl_3$

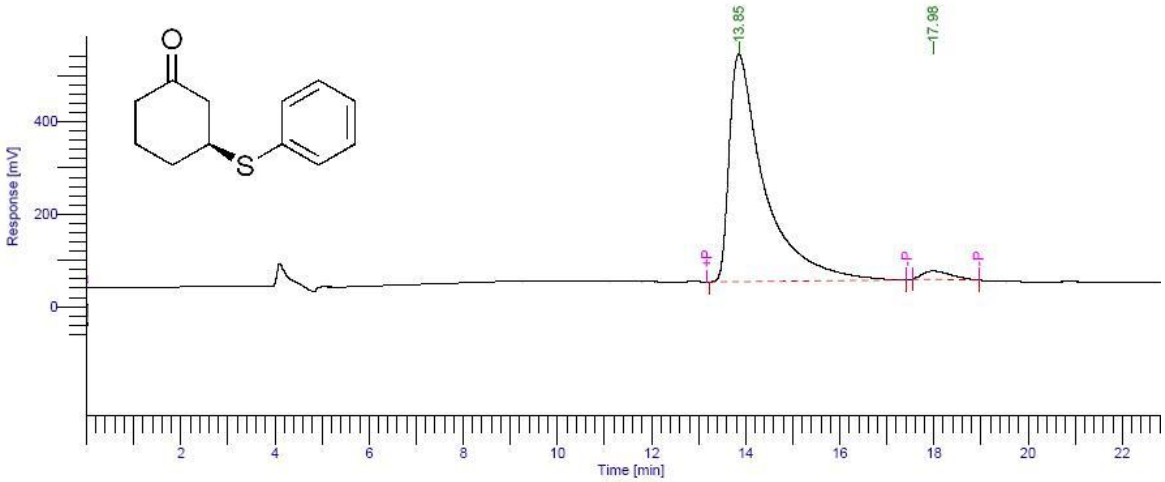
HPLC graph



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		13.628	57821666.76	1.09e+06	50.38	50.38
2		17.429	56947194.43	769111.43	49.62	49.62
			1.15e+08	1.86e+06	100.00	100.00

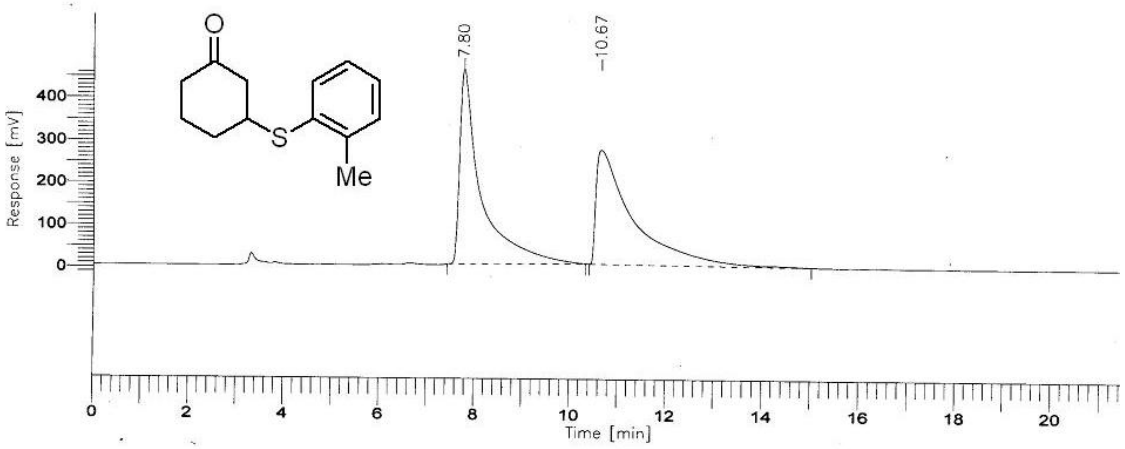
HPLC Graph for racemic **2a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		13.854	25503578.47	492142.60	97.08	97.08
2		17.981	766650.62	18102.56	2.92	2.92
			26270229.09	510245.17	100.00	100.00

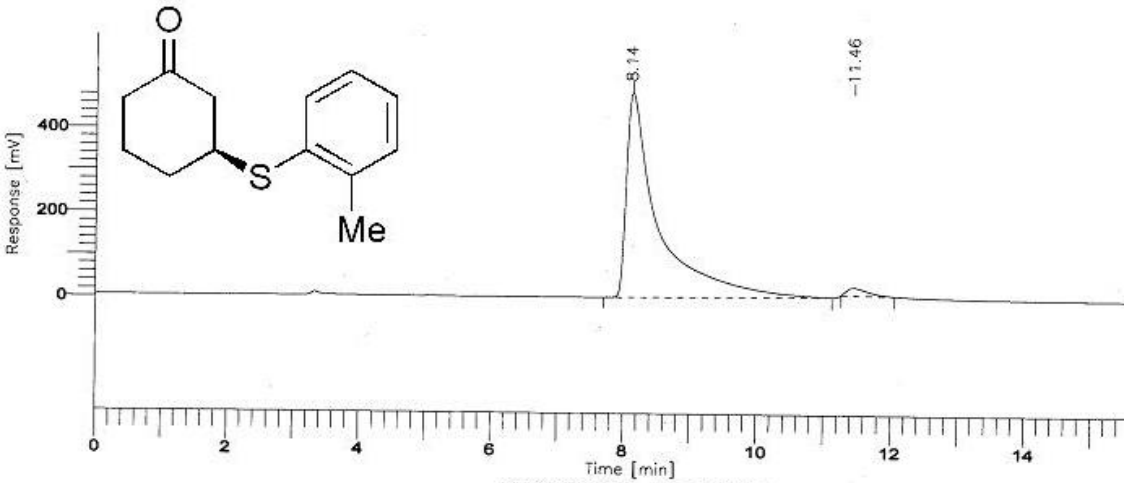
HPLC Graph for enantioenriched **2a**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	7.796	14354602.00	458835.37	49.80	31.28
2	10.671	14469328.00	270066.90	50.20	53.58
		28823930.00	728902.27	100.00	

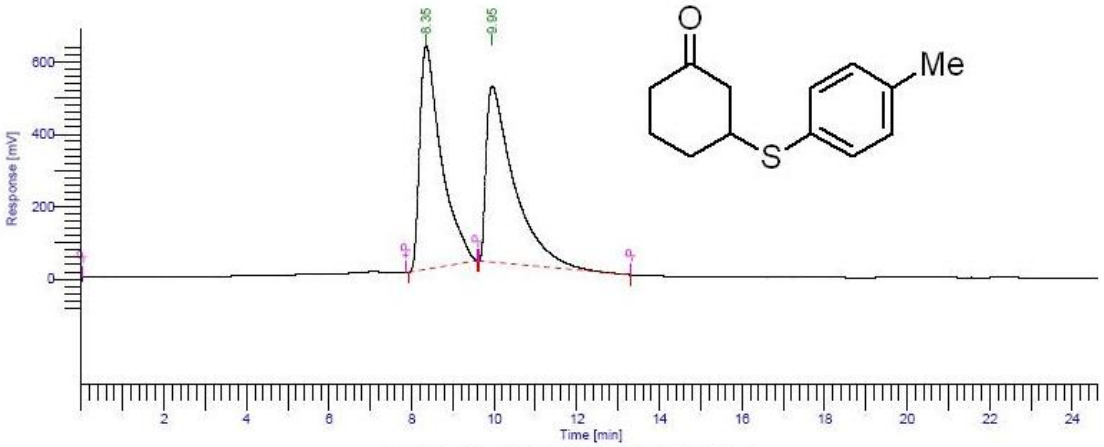
HPLC Graph for racemic **2b**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	8.140	16178242.00	484625.12	97.55	33.38
2	11:455	406645.00	18666.69	2.45	21.78
		16584887.00	503291.81	100.00	

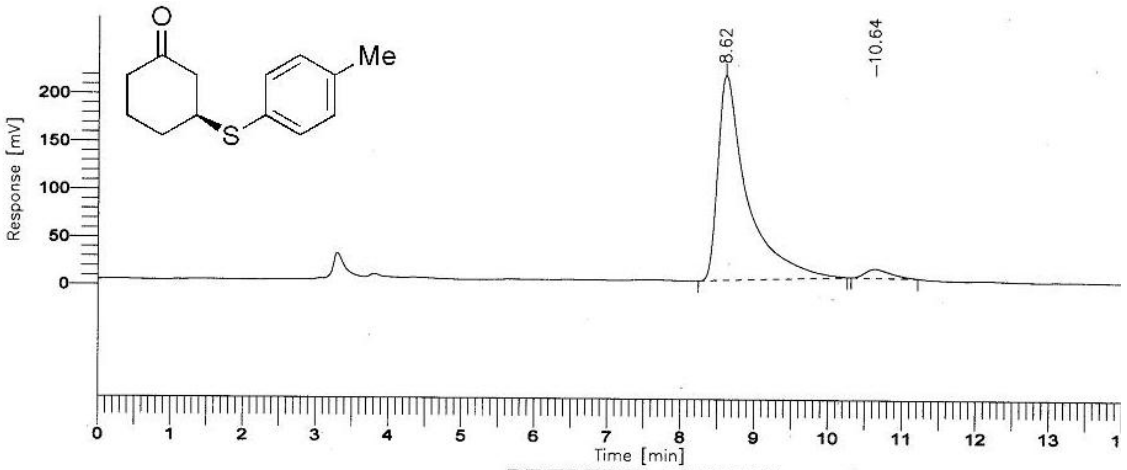
HPLC Graph for enantioenriched **2b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.351	22432012.76	618656.76	49.66	49.66
2		9.953	22735142.90	486302.42	50.34	50.34
			45167155.66	1.10e+06	100.00	100.00

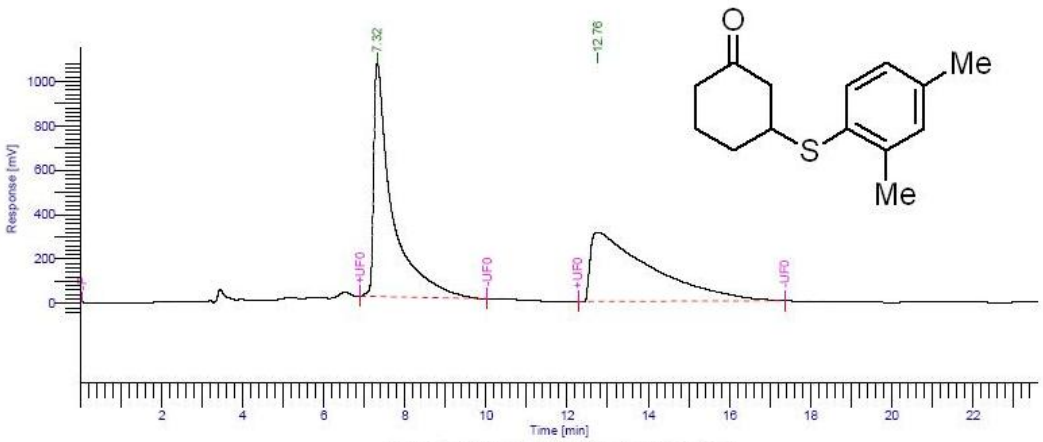
HPLC Graph for racemic **2c**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	8.621	5964180.50	214620.06	96.23	27.79
2	10.640	233697.00	9553.72	3.77	24.46
		6197877.50	224173.78	100.00	

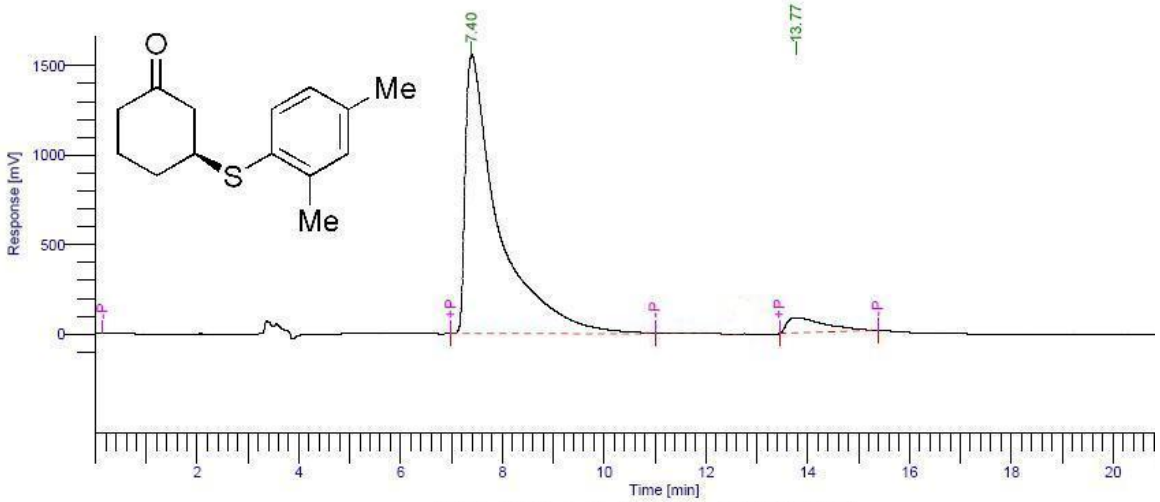
HPLC Graph for enantioenriched **2c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.320	33045636.11	1.05e+06	50.67	50.67
2		12.758	32172106.59	311068.68	49.33	49.33
			65217742.70	1.36e+06	100.00	100.00

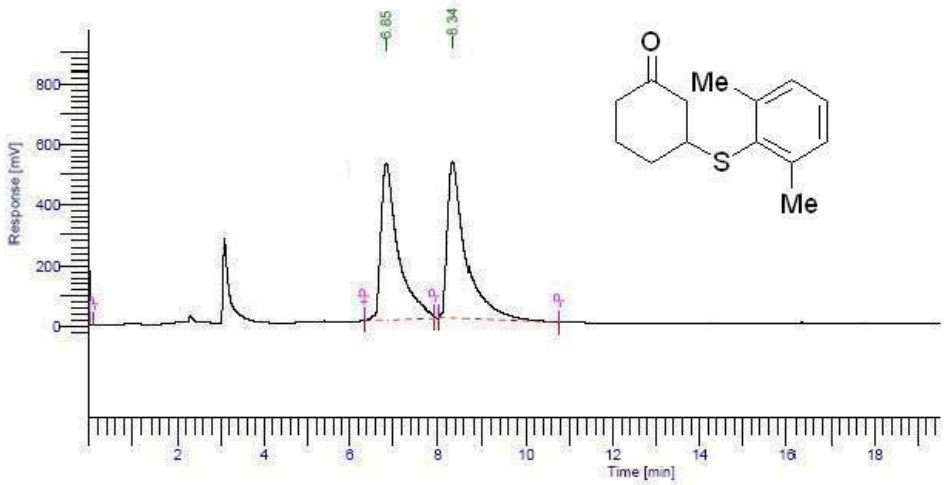
HPLC Graph for racemic **2d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.395	70611841.96	1.56e+06	94.09	94.09
2		13.774	4433125.89	84874.22	5.91	5.91
			75044967.85	1.64e+06	100.00	100.00

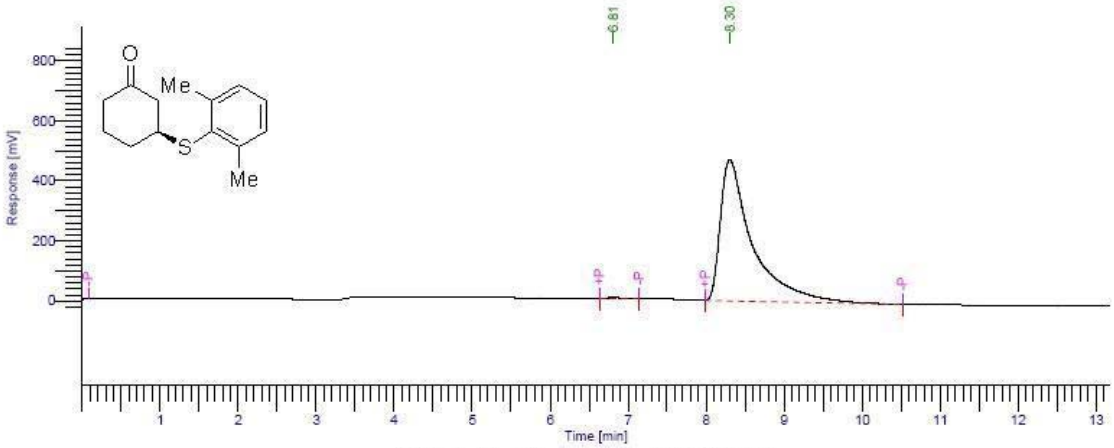
HPLC Graph for enantioenriched **2d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		6.848	14842382.44	512291.10	50.01	50.01
2		8.342	14841039.70	512219.84	49.99	49.99
			29683432.14	1024510.94	100.00	100.00

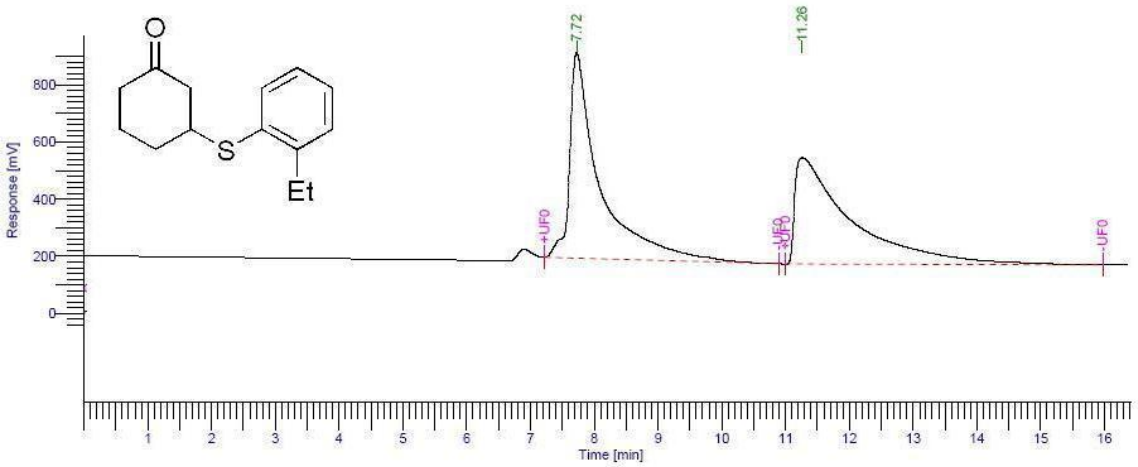
HPLC Graph for racemic **2e**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		6.812	65217.80	4312.26	0.48	0.48
2		8.304	13490630.65	471800.66	99.52	99.52
			13555848.46	476112.91	100.00	100.00

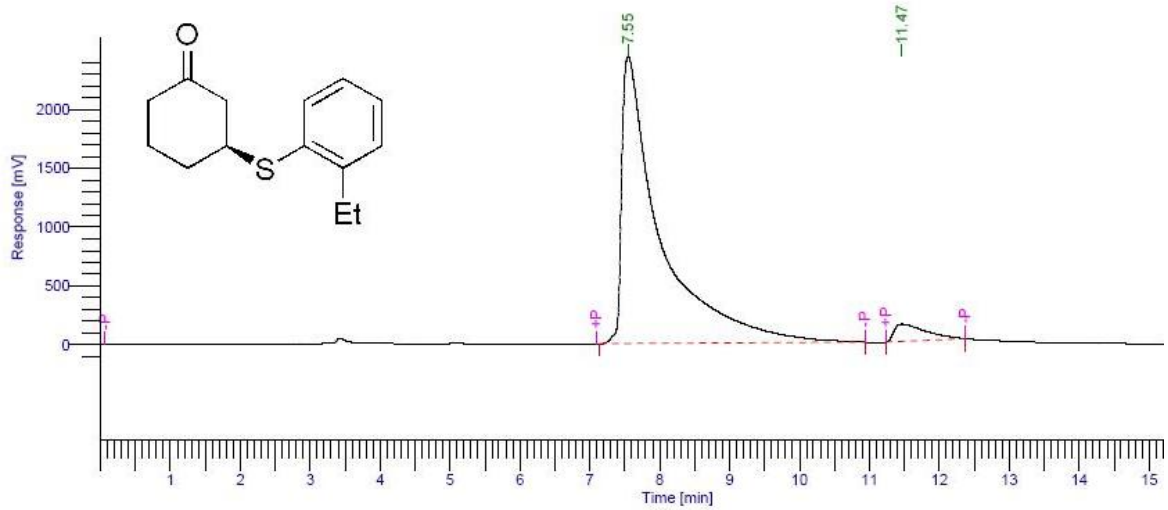
HPLC Graph for enantioenriched **2e**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.723	23722382.44	719220.23	50.99	50.99
2		11.260	22802708.67	371987.88	49.01	49.01
			46525091.10	1.09e+06	100.00	100.00

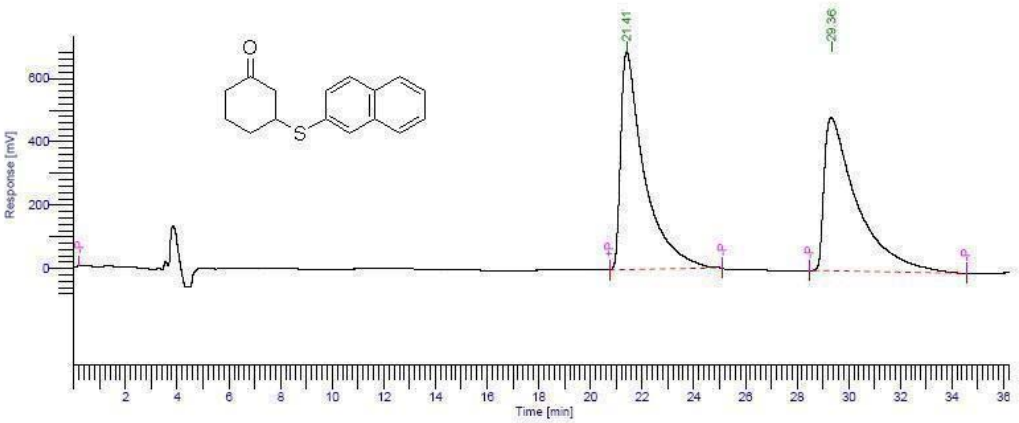
HPLC Graph for racemic **2f**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.547	93004704.98	2.44e+06	95.27	95.27
2		11.466	4612996.68	146550.89	4.73	4.73
			97617701.66	2.59e+06	100.00	100.00

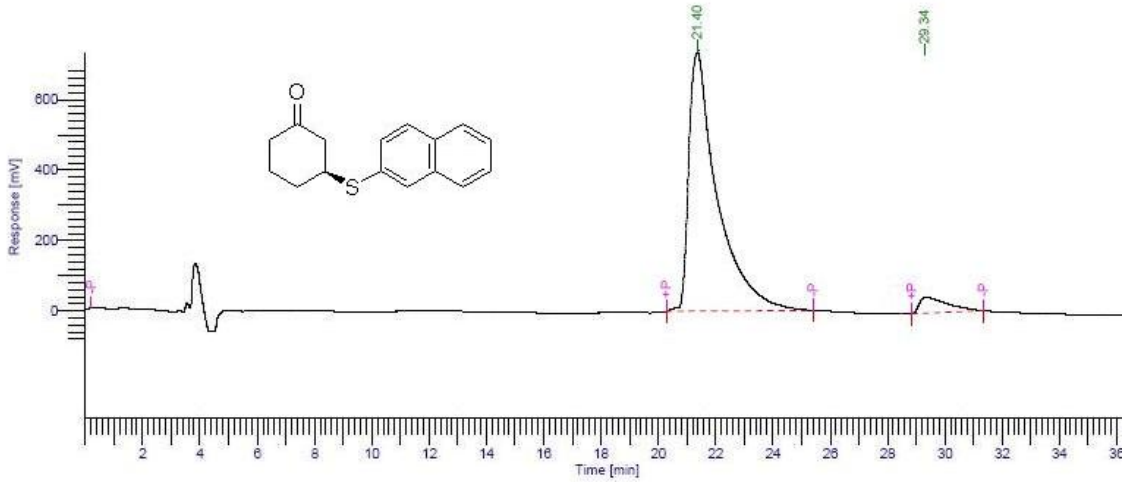
HPLC Graph for enantioenriched **2f**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		21.412	62787319.63	669770.53	50.32	50.32
2		29.360	52803588.77	462977.35	49.68	49.68
			1.16e+08	1.13e+06	100.00	100.00

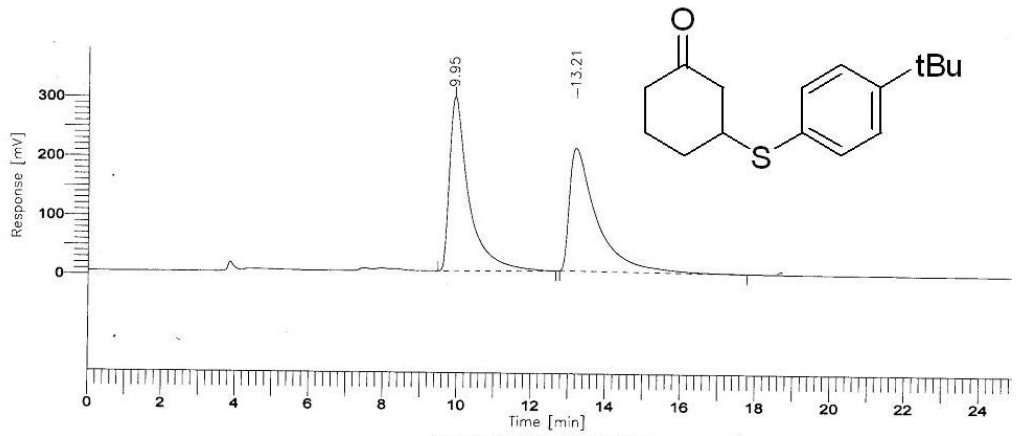
HPLC Graph for racemic **2g**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		21.402	21140147.02	847685.11	96.51	96.51
2		29.340	764786.62	46989.15	3.49	3.49
			21904933.64	894674.26	100.00	100.00

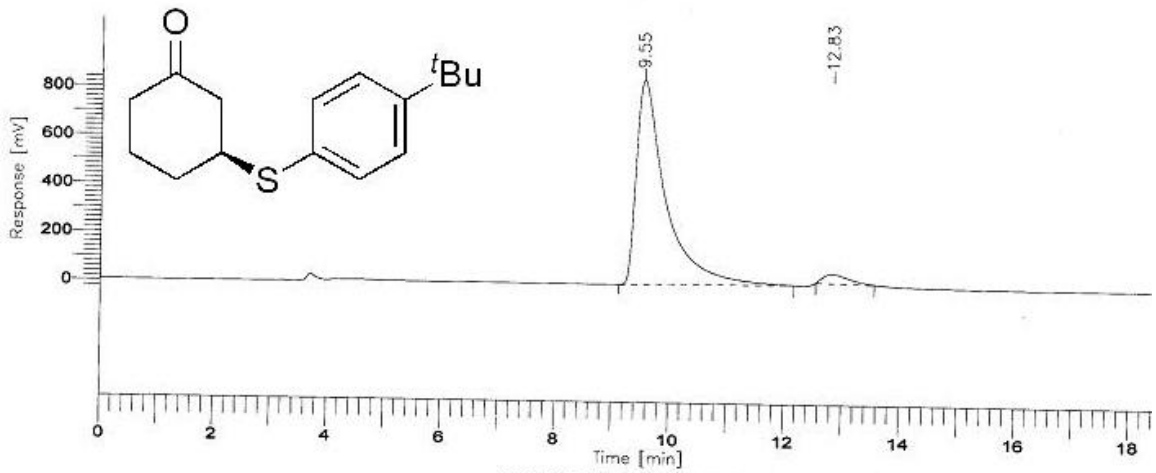
HPLC Graph for enantioenriched **2g**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	9.946	10812914.32	294796.13	50.34	36.68
2	13.209	10665763.00	207997.23	49.66	51.28
		21478677.32	502793.36	100.00	

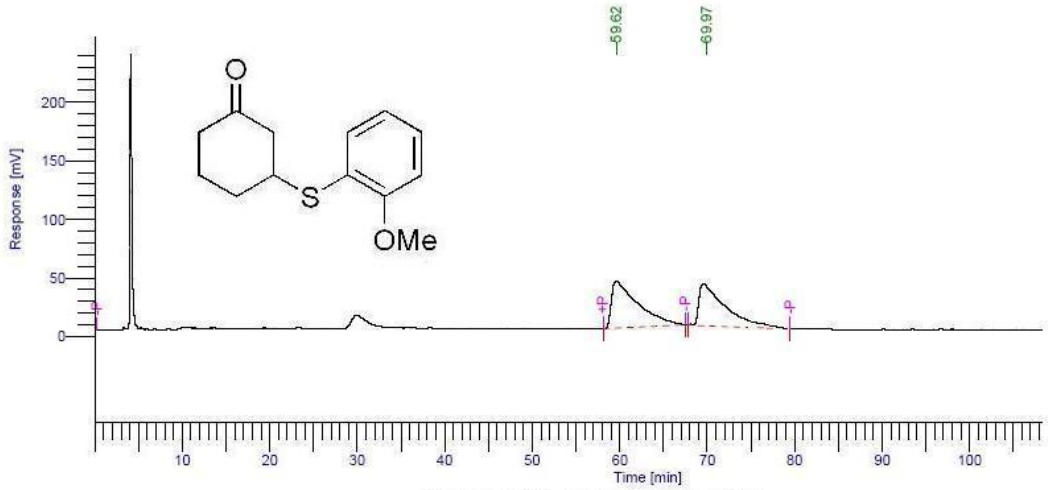
HPLC Graph for racemic **2h**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	9.550	30122496.44	844071.34	96.17	35.69
2	12.833	1200200.50	38840.33	3.83	30.90
		31322696.94	882911.67	100.00	

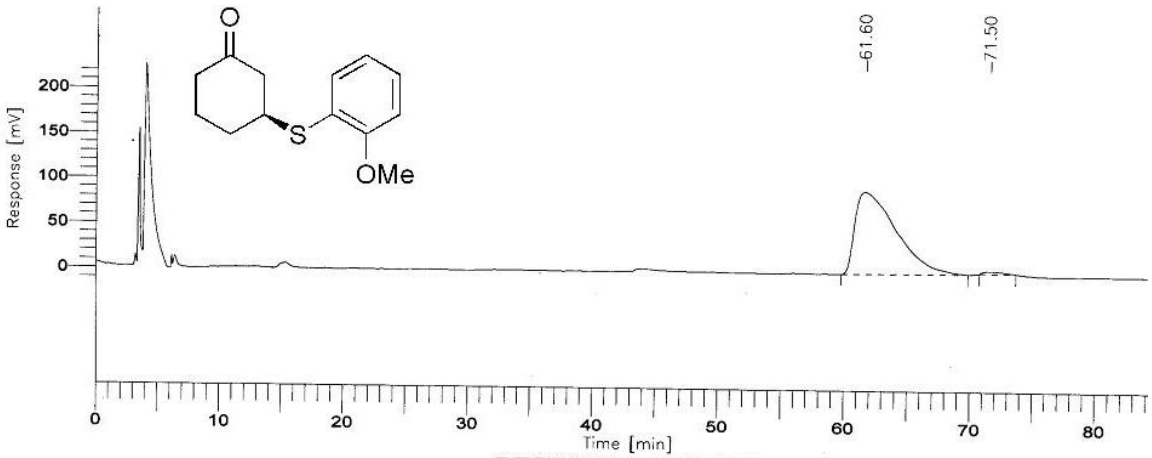
HPLC Graph for enantioenriched **2h**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		59.624	4852064.70	50813.99	50.10	50.10
2		69.968	4832096.95	50315.63	49.90	49.90
			9684161.65	101129.62	100.00	100.00

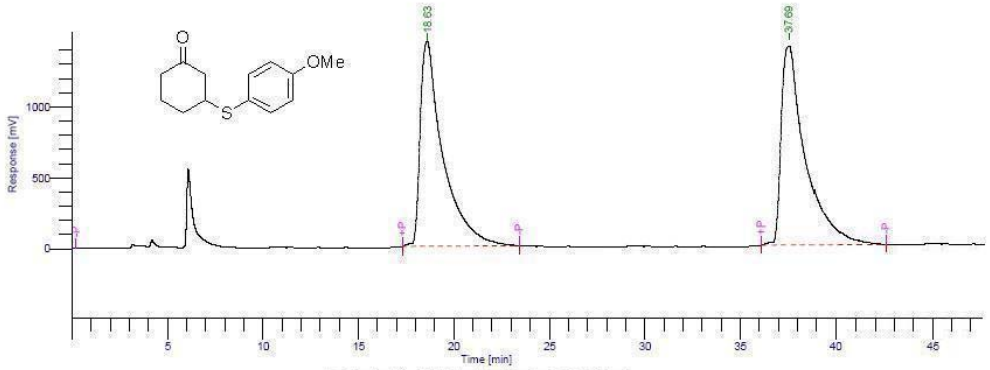
HPLC Graph for racemic **2i**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	61.604	20738337.00	91093.47	98.51	227.66
2	71.502	314323.50	2774.76	1.49	113.28
		21052660.50	93868.22	100.00	

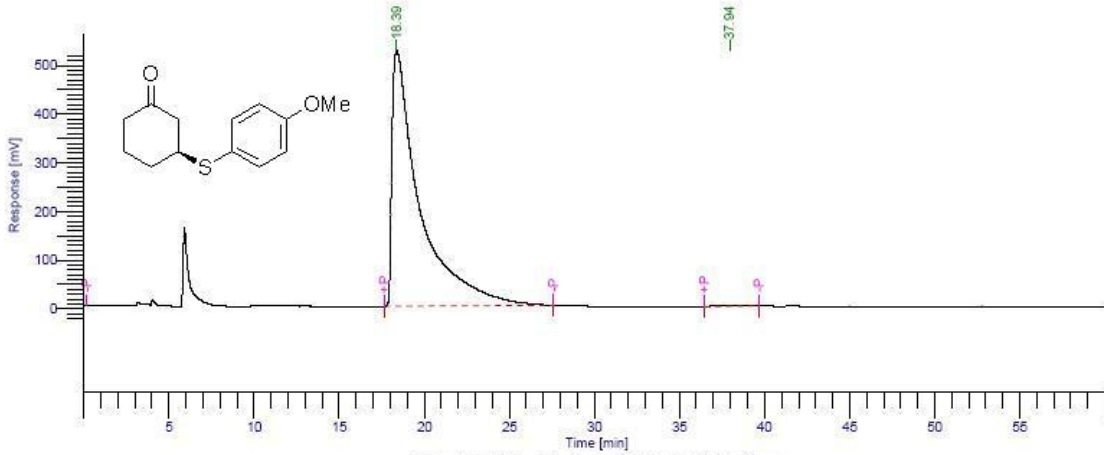
HPLC Graph for enantioenriched **2i**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		18.632	38028106.81	1.43e+06	50.20	50.20
2		37.690	37724553.08	1.41e+06	49.80	49.80
			75752659.89	2.84e+06	100.00	100.00

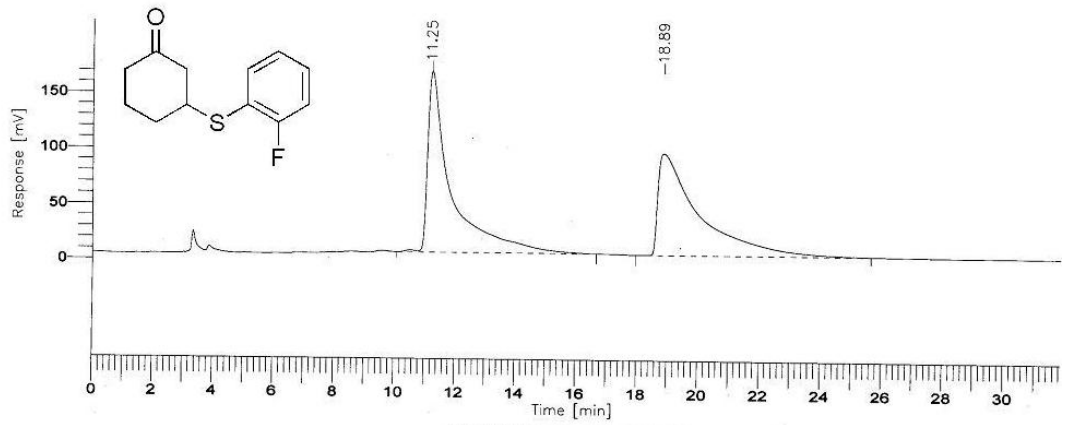
HPLC Graph for racemic **2j**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		18.389	59169383.10	524478.67	99.88	99.88
2		37.943	73828.79	2717.74	0.12	0.12
			59243211.89	527196.41	100.00	100.00

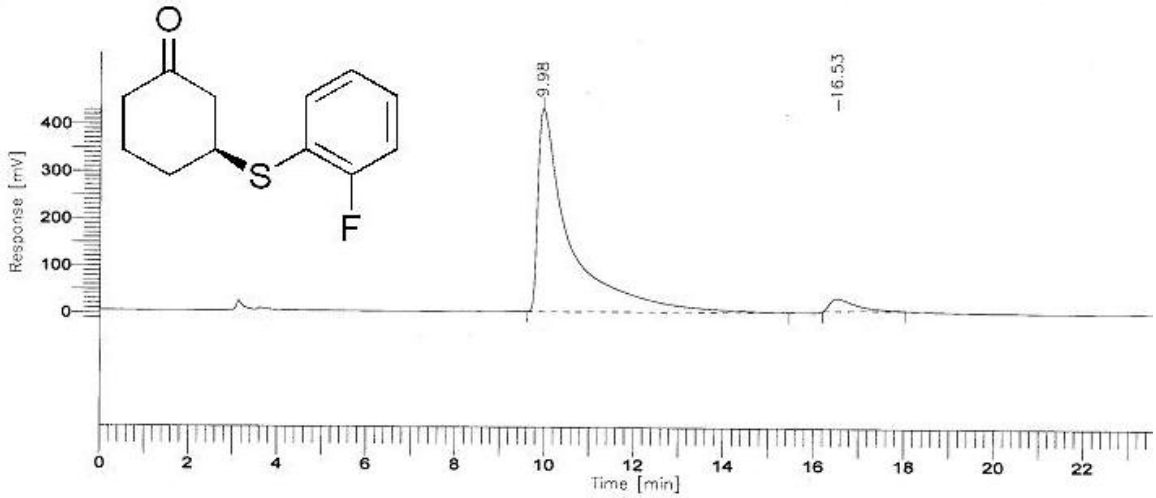
HPLC Graph for enantioenriched **2j**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	11.254	8851955.00	162929.20	50.80	54.33
2	18.891	8574335.00	91501.56	49.20	93.71
		17426290.00	254430.76	100.00	

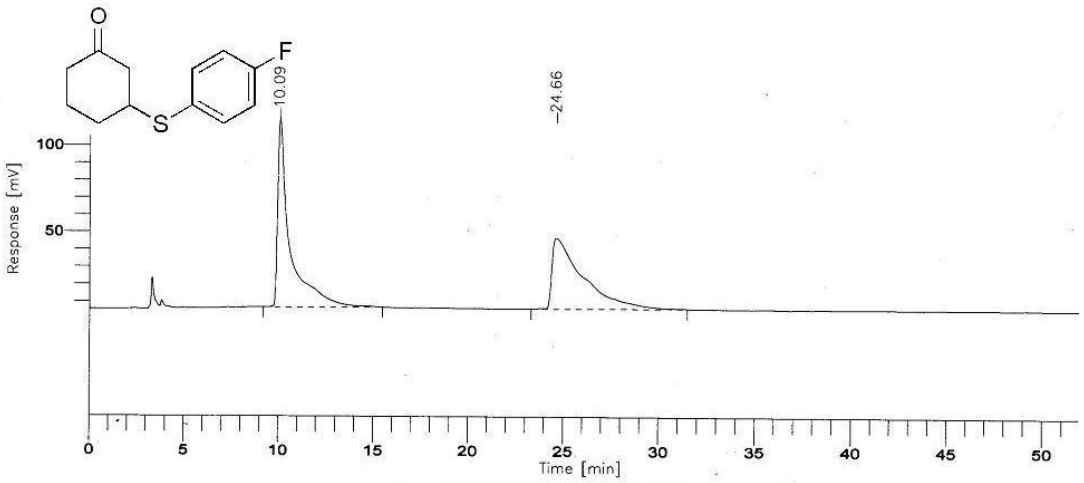
HPLC Graph for racemic **2k**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	9.982	21503908.50	430521.50	95.18	49.95
2	16.530	1088556.00	26420.09	4.82	41.20
		22592464.50	456941.59	100.00	

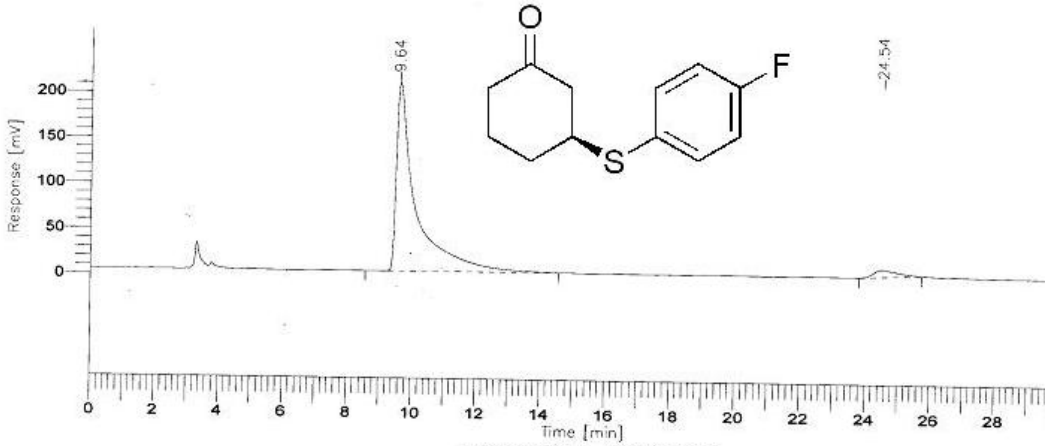
HPLC Graph for enantioenriched **2k**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	10.094	4845723.00	106609.58	50.35	45.45
2	24.658	4777150.00	40513.81	49.65	117.91
		9622873.00	147123.39	100.00	

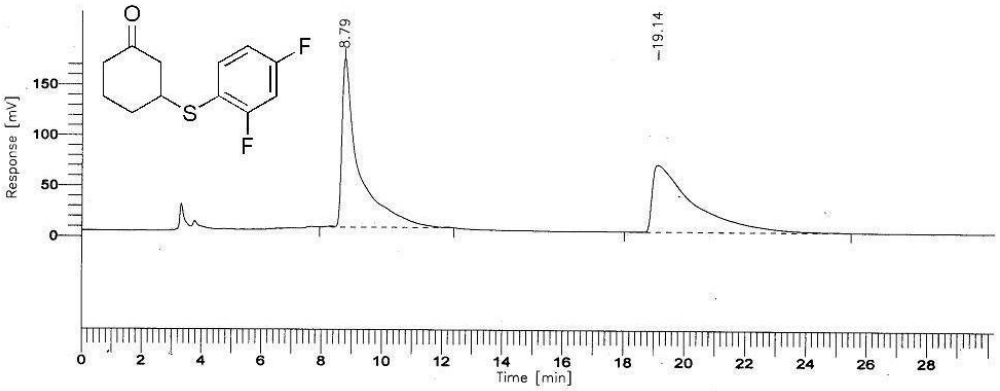
HPLC Graph for racemic **2l**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	9.635	8806625.00	207674.27	95.57	42.41
2	24.536	408219.00	7969.27	4.43	51.22
		9214844.00	215643.55	100.00	

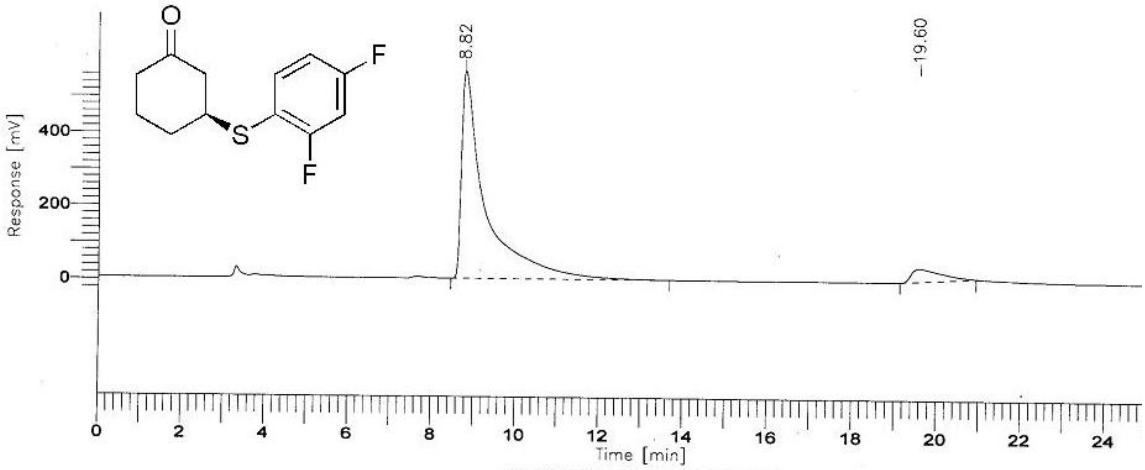
HPLC Graph for enantioenriched **2l**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	8.791	6561814.00	167071.40	50.13	39.28
2	19.140	6526906.00	66014.84	49.87	98.87
		13088720.00	233086.24	100.00	

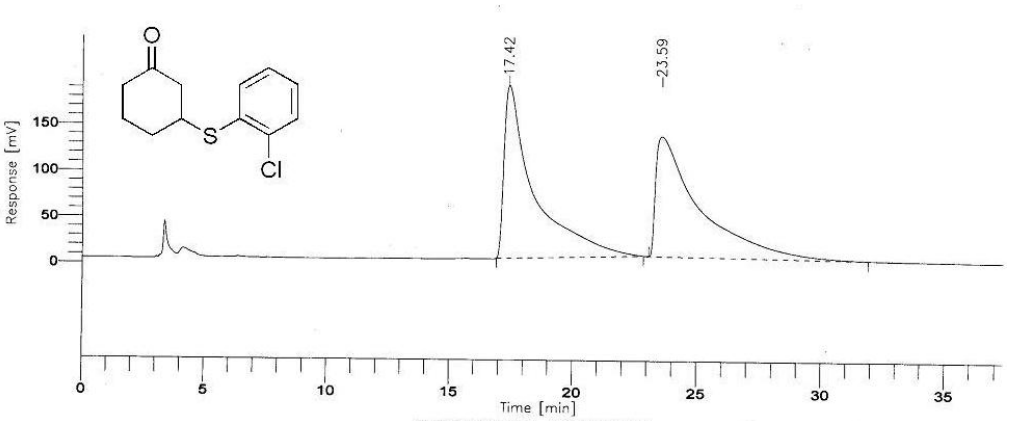
HPLC Graph for racemic **2m**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	8.820	22529824.50	566232.22	92.72	39.79
2	19.599	1768553.00	35363.26	7.28	50.01
		24298377.50	601595.47	100.00	

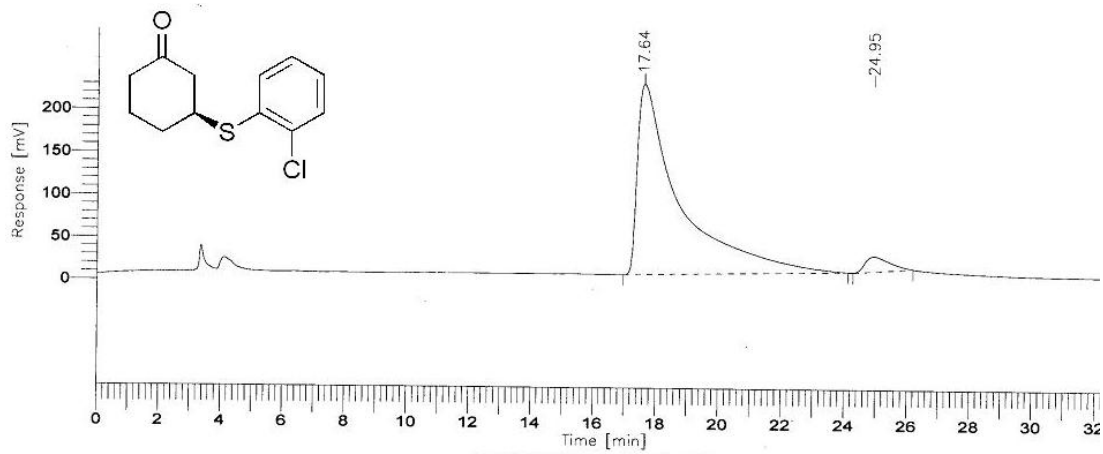
HPLC Graph for enantioenriched **2m**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	17.424	15852696.50	186158.48	49.89	85.16
2	23.591	15925329.68	129686.51	50.11	122.80
		31778026.18	315844.99	100.00	

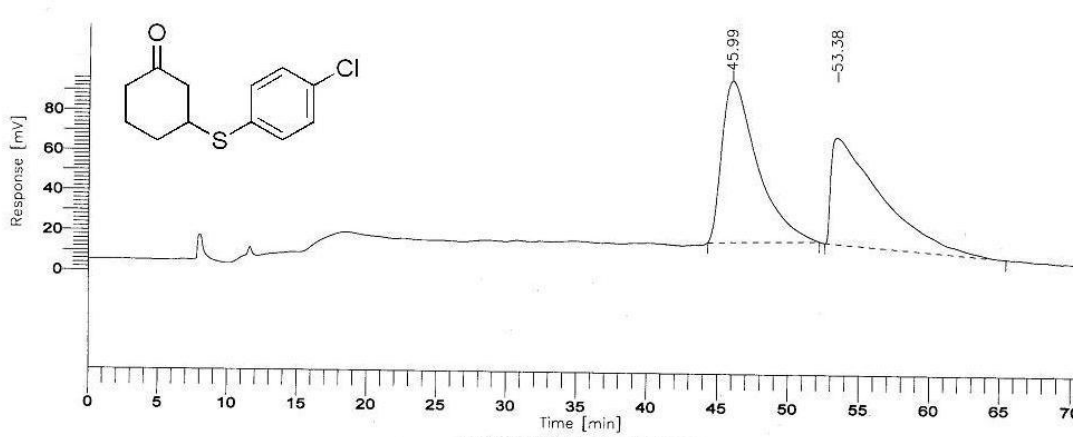
HPLC Graph for racemic **2n**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	17.636	21219542.50	223261.38	95.59	95.04
2	24.949	980095.00	17980.97	4.41	54.51
		22199637.50	241242.35	100.00	

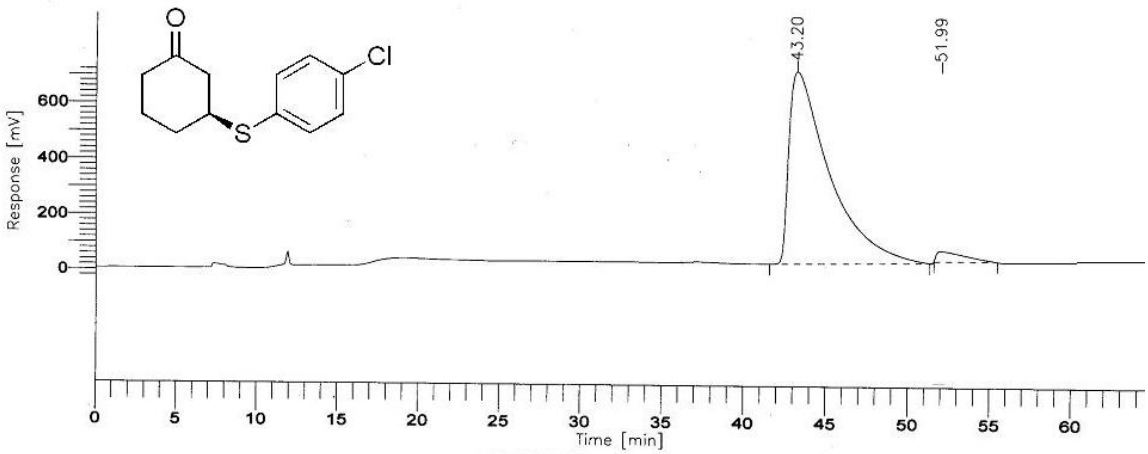
HPLC Graph for enantioenriched **2n**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	45.985	14006838.50	80660.08	50.06	173.65
2	53.375	13972398.05	53172.62	49.94	262.77
		27979236.55	133832.70	100.00	

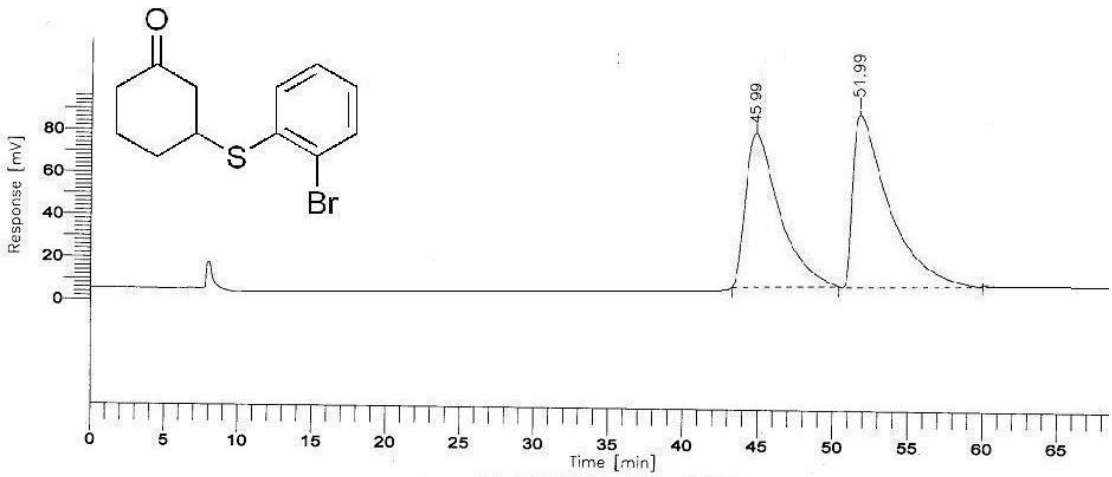
HPLC Graph for racemic **2o**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	43.200	1.19e+08	689810.02	96.20	172.05
2	51.985	4690632.00	38116.73	3.80	123.06
		1.23e+08	727926.75	100.00	

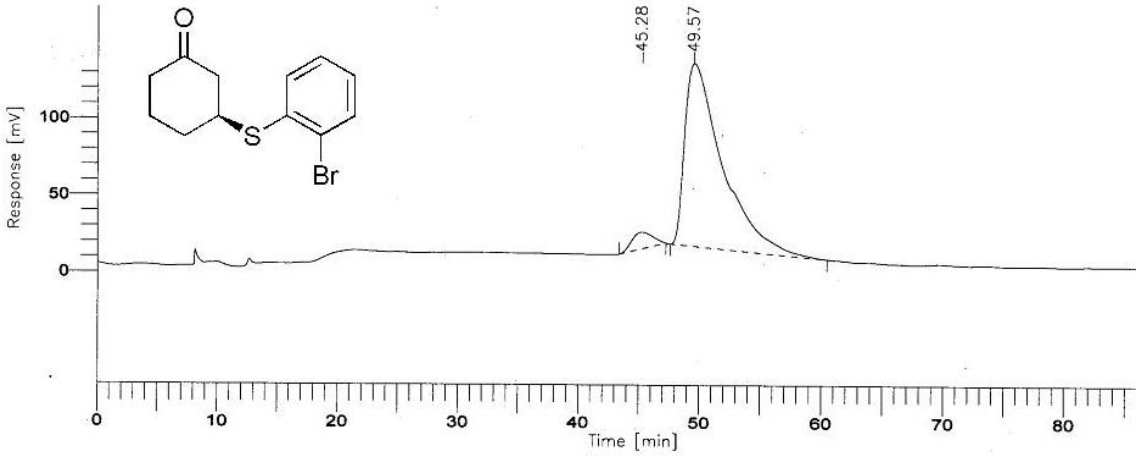
HPLC Graph for enantioenriched **2o**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	45.985	8821681.50	77218.89	49.67	114.24
2	51.987	8937813.00	85546.71	50.33	104.47
		17759494.50	162765.60	100.00	

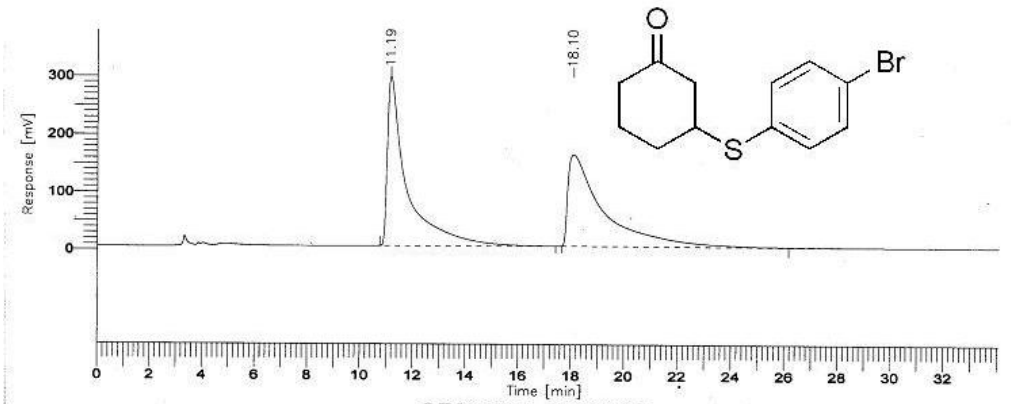
HPLC Graph for racemic **2p**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	45.284	1304860.19	10819.67	4.83	120.60
2	49.574	25736981.65	119409.90	95.17	215.53
		27041841.83	130229.57	100.00	

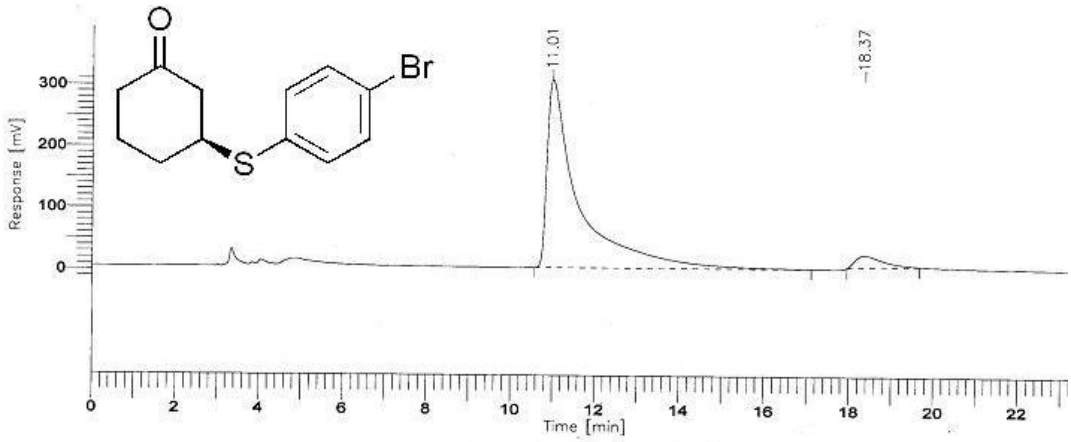
HPLC Graph for enantioenriched **2p**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	11.189	15276303.05	293668.63	50.56	52.02
2	18.104	14938359.83	159248.07	49.44	93.81
		30214662.88	452916.70	100.00	

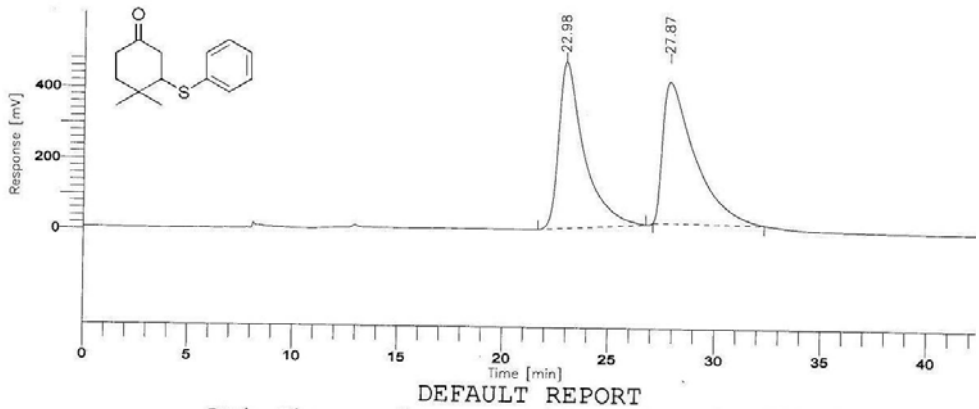
HPLC Graph for racemic **2q**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	11.010	16043624.00	305247.73	94.57	52.56
2	18.368	921368.00	19963.66	5.43	46.15
		16964992.00	325211.39	100.00	

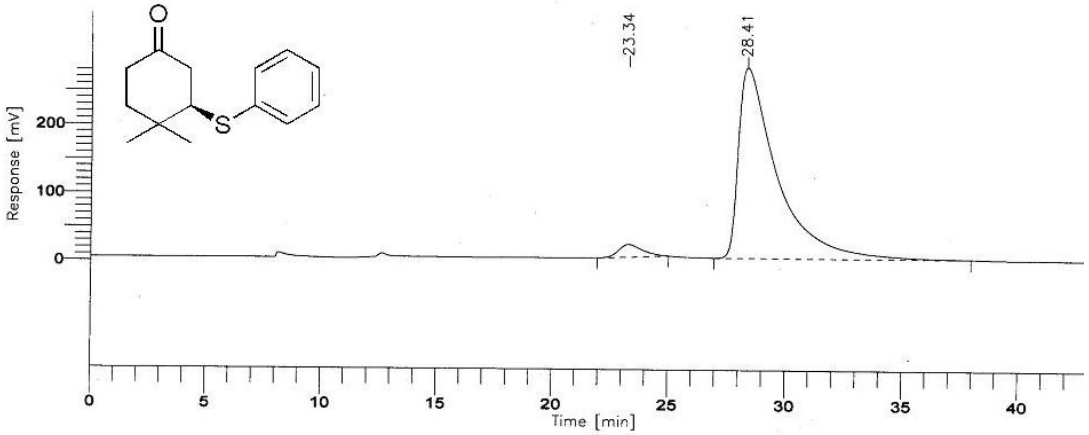
HPLC Graph for enantioenriched **2q**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	22.983	39166993.46	468885.29	49.45	83.53
2	27.868	40042854.50	397855.70	50.55	100.64
		79209847.96	866740.99	100.00	

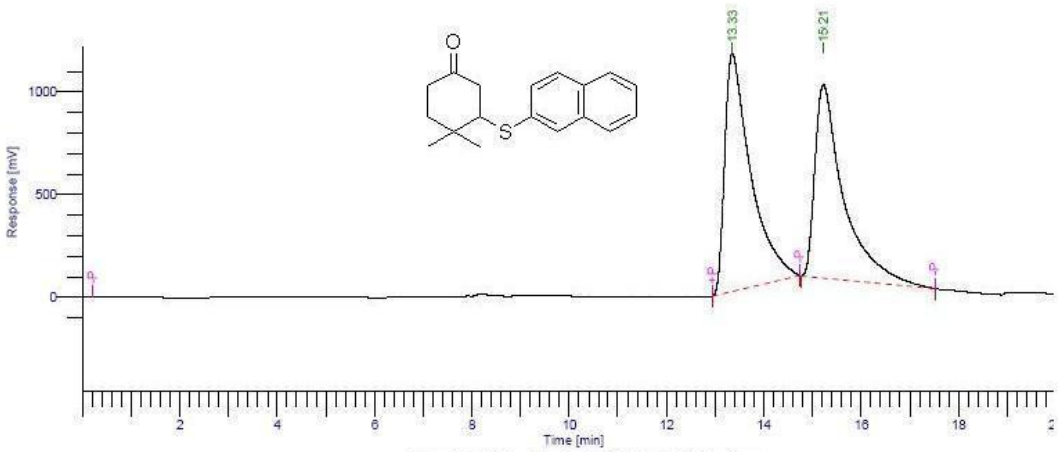
HPLC Graph for racemic **3a**



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Area/Height [s]
1	23.338	1341335.00	18708.65	3.99	71.70
2	28.413	32272737.00	279307.35	96.01	115.55
		33614072.00	298016.01	100.00	

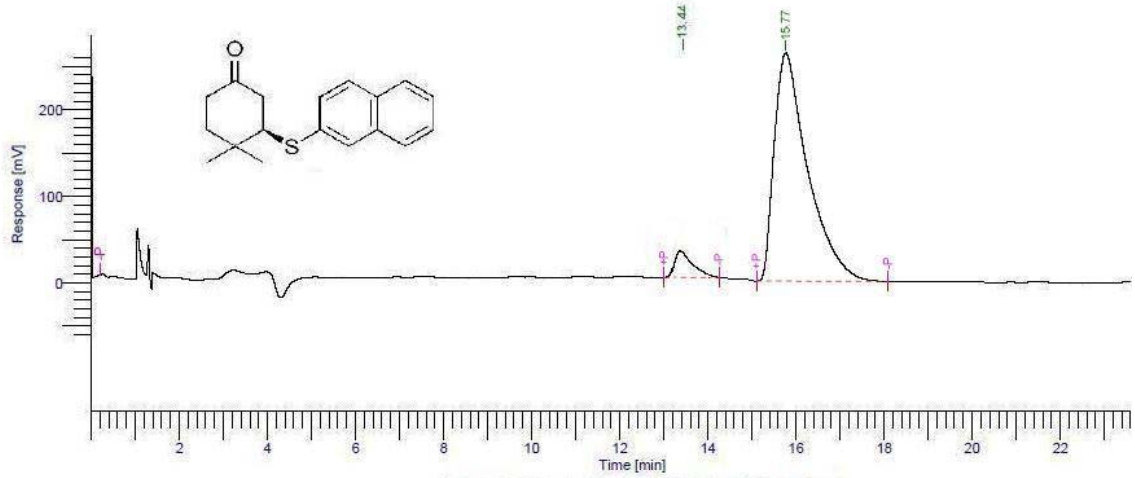
HPLC Graph for enantioenriched **3a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		13.325	33045636.11	1.05e+06	50.67	50.67
2		15.210	32172106.59	1.03e+06	49.33	49.33
			65217742.70	2.08e+06	100.00	100.00

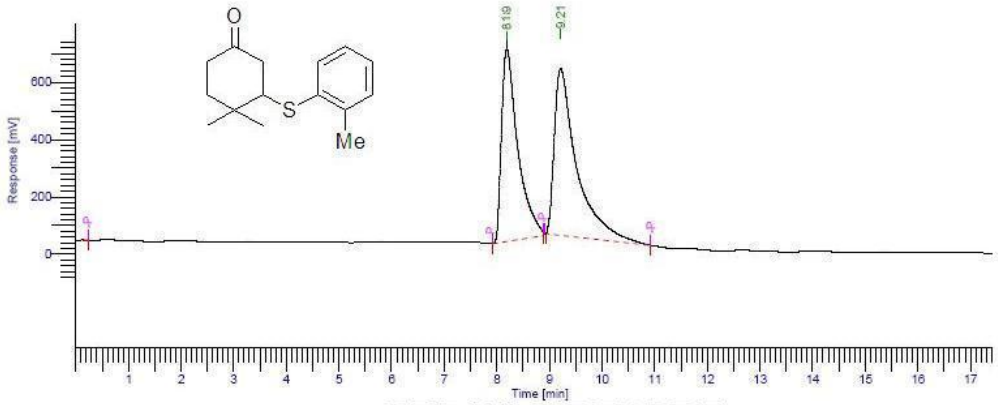
HPLC Graph for racemic **3b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		13.437	357066.94	13333.38	4.17	4.17
2		15.774	8207236.17	123171.90	95.83	95.83
			8564303.10	136505.28	100.00	100.00

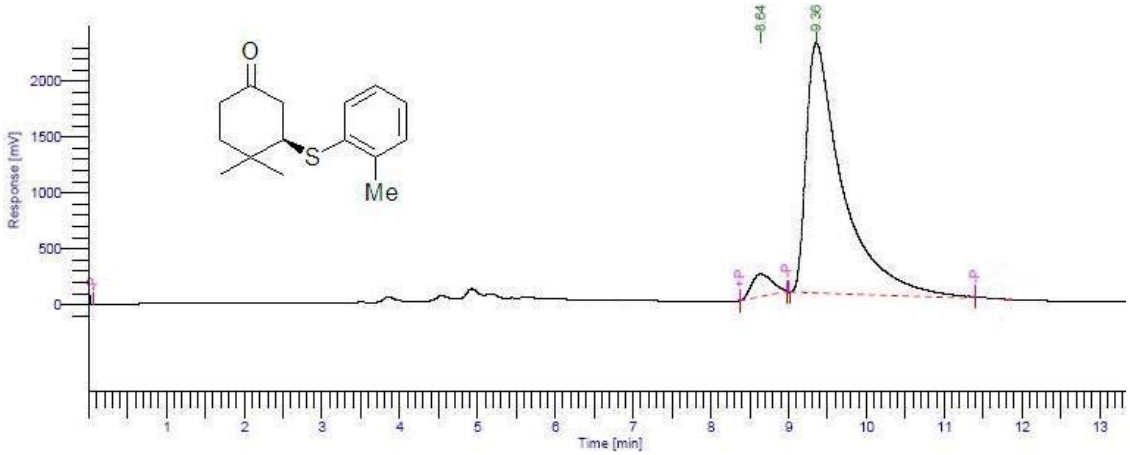
HPLC Graph for enantioenriched **3b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.186	22432012.76	718656.76	49.66	49.66
2		9.214	22735142.90	626302.42	50.34	50.34
			45167155.66	1.44e+06	100.00	100.00

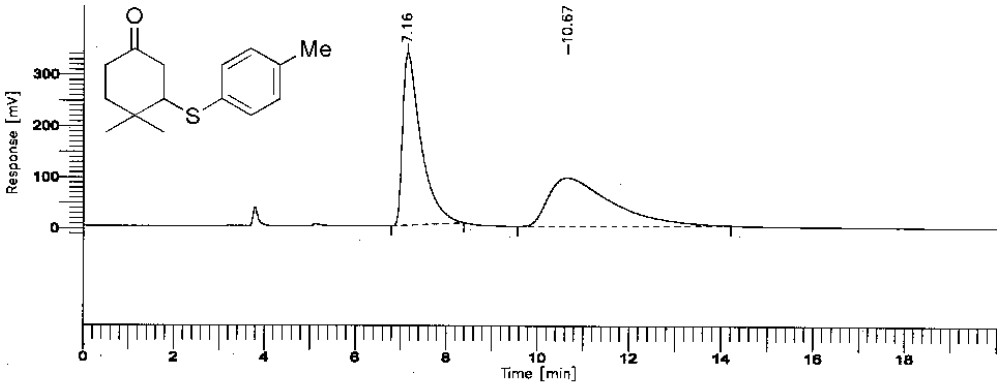
HPLC Graph for racemic **3c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.641	3688141.51	203260.45	4.82	4.82
2		9.355	72780717.63	2.24e+06	95.18	95.18
			76468859.13	2.44e+06	100.00	100.00

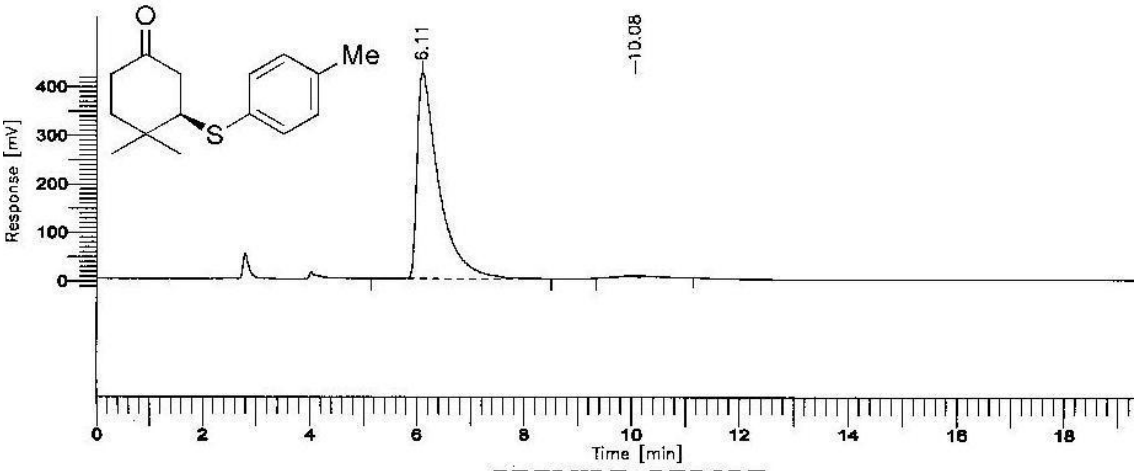
HPLC Graph for enantioenriched **3c**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	7.161	9450949.00	335351.17	50.87	28.18
2	10.670	9129104.00	94580.51	49.13	96.52
		18580053.00	429931.68	100.00	

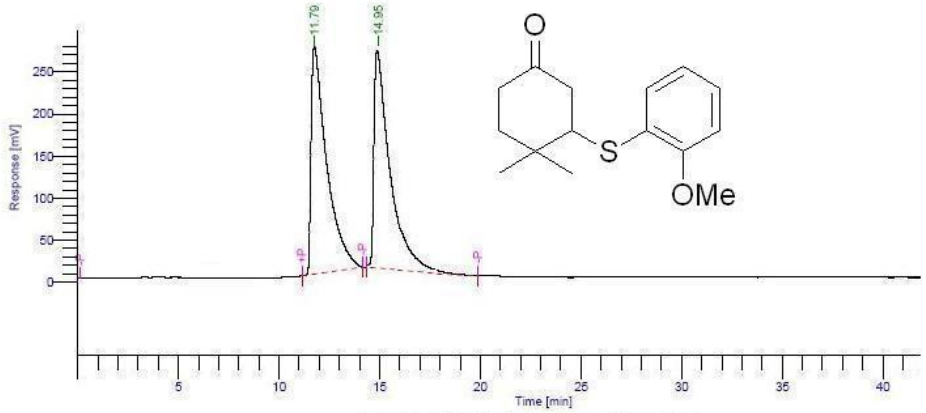
HPLC Graph for racemic **3d**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	6.114	11958154.00	423309.83	99.61	28.25
2	10.083	47031.00	1460.38	0.39	32.20
		12005185.00	424770.21	100.00	

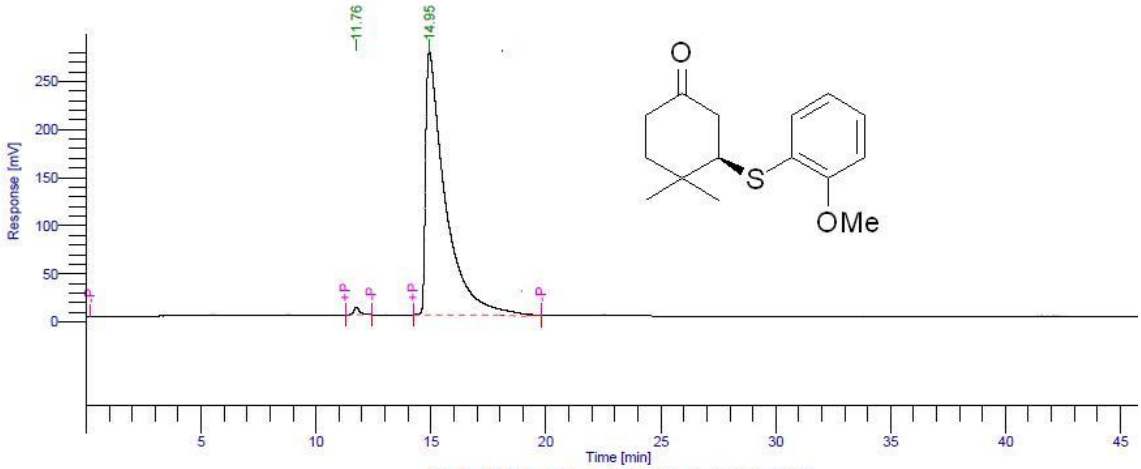
HPLC Graph for enantioenriched **3d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.792	22427918.95	279871.22	49.21	49.21
2		14.952	23145362.89	266573.18	50.79	50.79
			45573281.84	546444.40	100.00	100.00

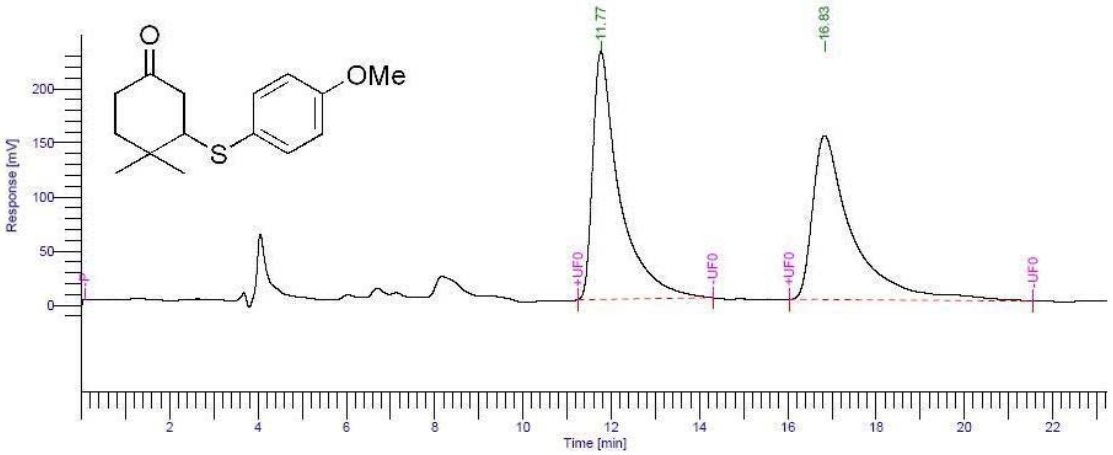
HPLC Graph for racemic **3e**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.759	166824.46	8032.69	1.28	1.28
2		14.954	12824284.50	259327.56	98.72	98.72
			12991108.95	267360.25	100.00	100.00

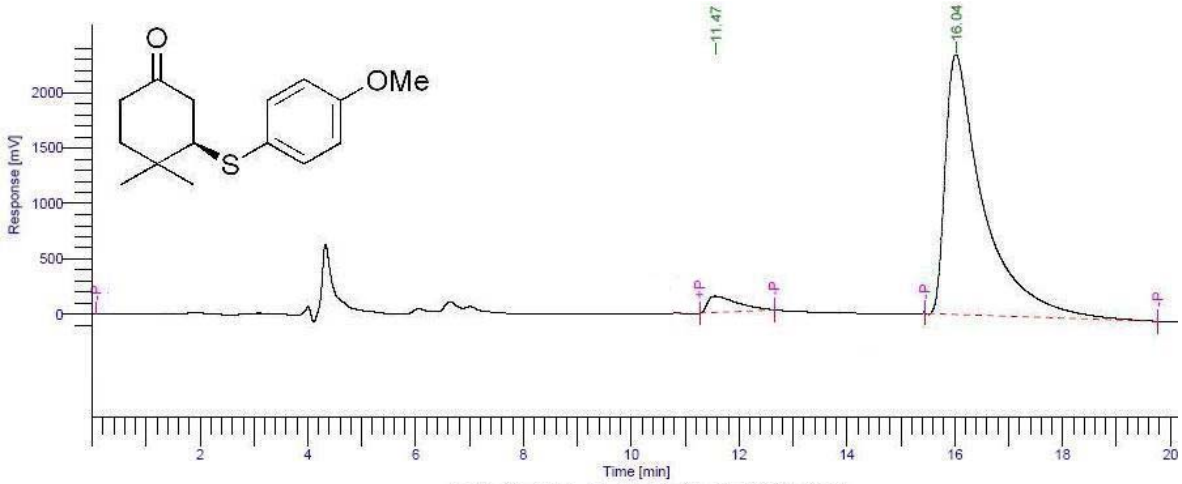
HPLC Graph for enantioenriched **3e**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.768	9640556.50	228804.97	50.47	50.47
2		16.833	9462646.12	151326.94	49.53	49.53
			19103202.61	380131.91	100.00	100.00

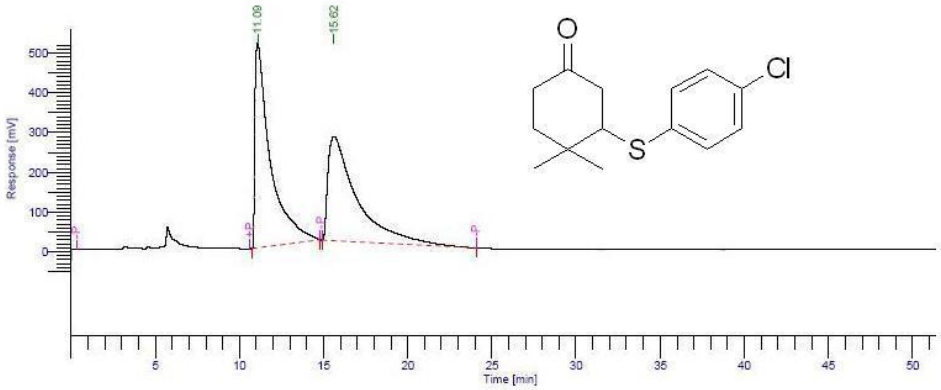
HPLC Graph for racemic **3f**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.466	3688141.51	203260.45	4.82	4.82
2		16.036	72780717.63	2.24e+06	95.18	95.18
			76468859.13	2.44e+06	100.00	100.00

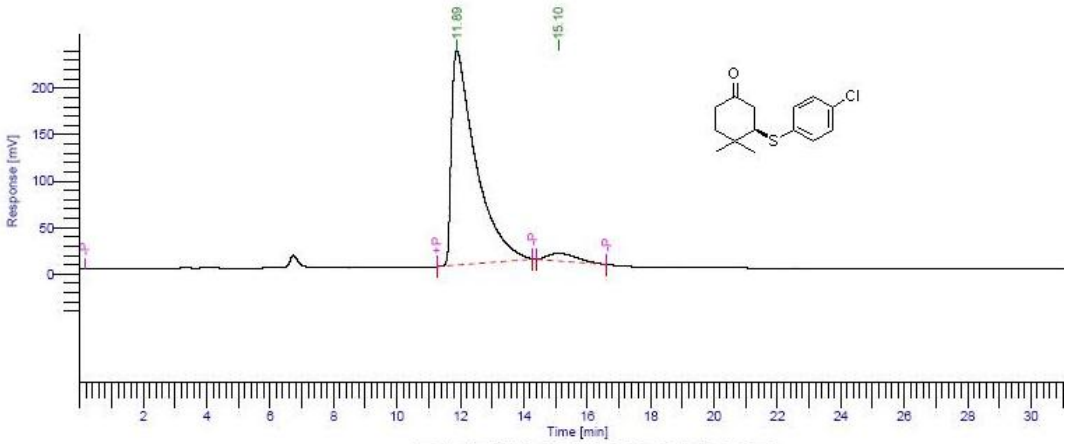
HPLC Graph for enantioenriched **3f**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.092	12107485.99	524079.53	49.17	49.17
2		15.622	12515234.81	282854.57	50.83	50.83
			24622720.80	806934.10	100.00	100.00

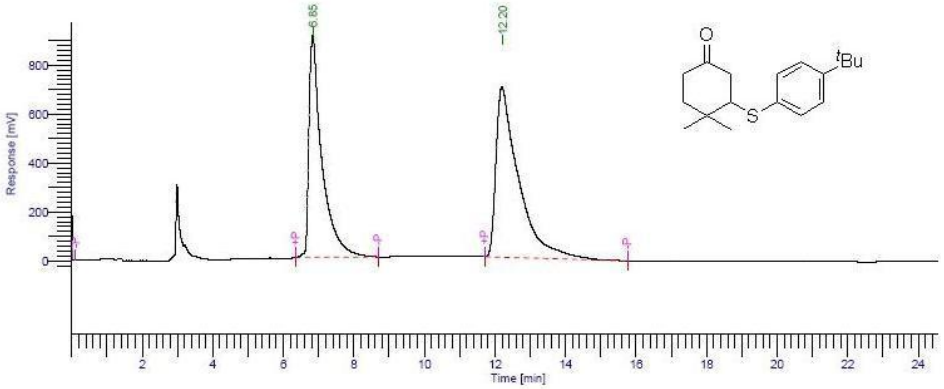
HPLC Graph for racemic **3g**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		11.893	12278501.70	231004.56	95.75	95.75
2		15.097	545209.96	8508.38	4.25	4.25
			12823711.66	239512.94	100.00	100.00

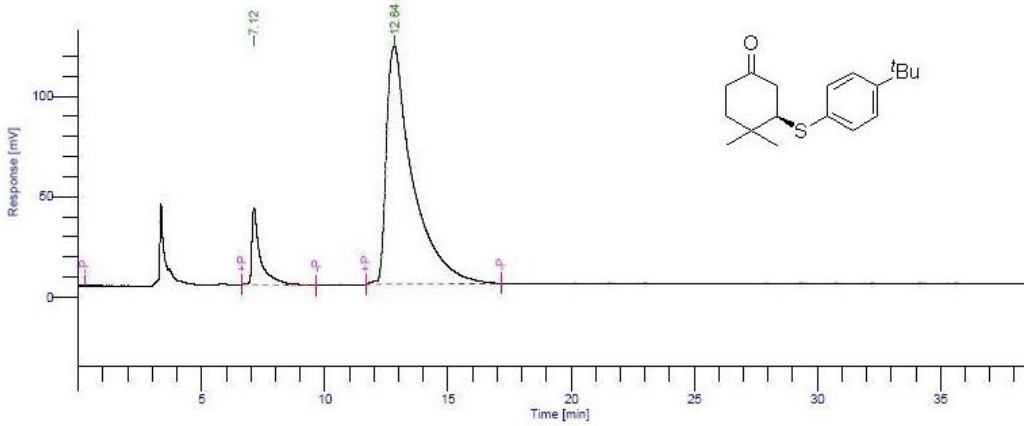
HPLC Graph for enantioenriched **3g**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		6.854	30449442.30	935622.94	49.35	49.35
2		12.201	31247512.56	723052.04	50.65	50.65
			61696954.86	1.65e+06	100.00	100.00

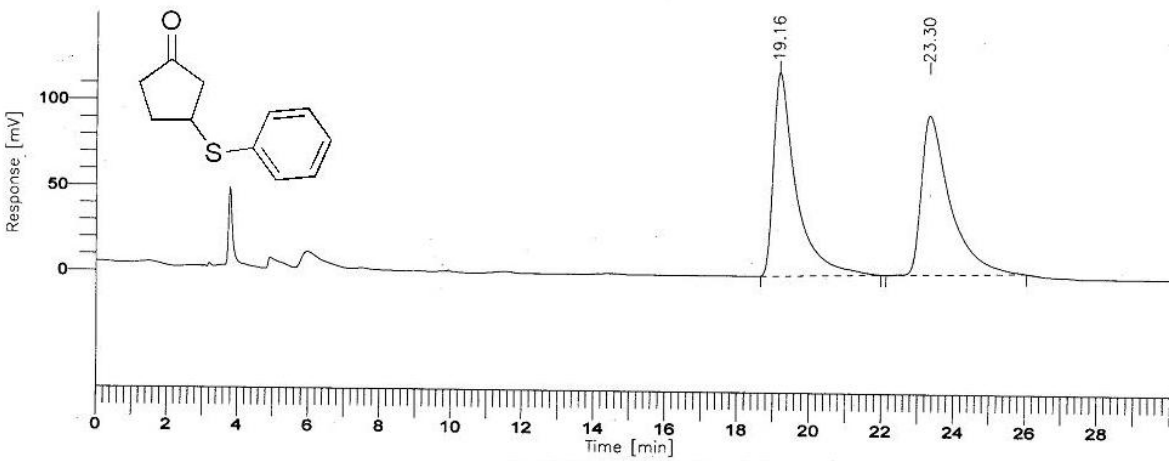
HPLC Graph for racemic **3h**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.120	584971.13	40473.88	4.16	4.16
2		12.840	13479136.20	119308.36	95.84	95.84
			14064107.33	159782.24	100.00	100.00

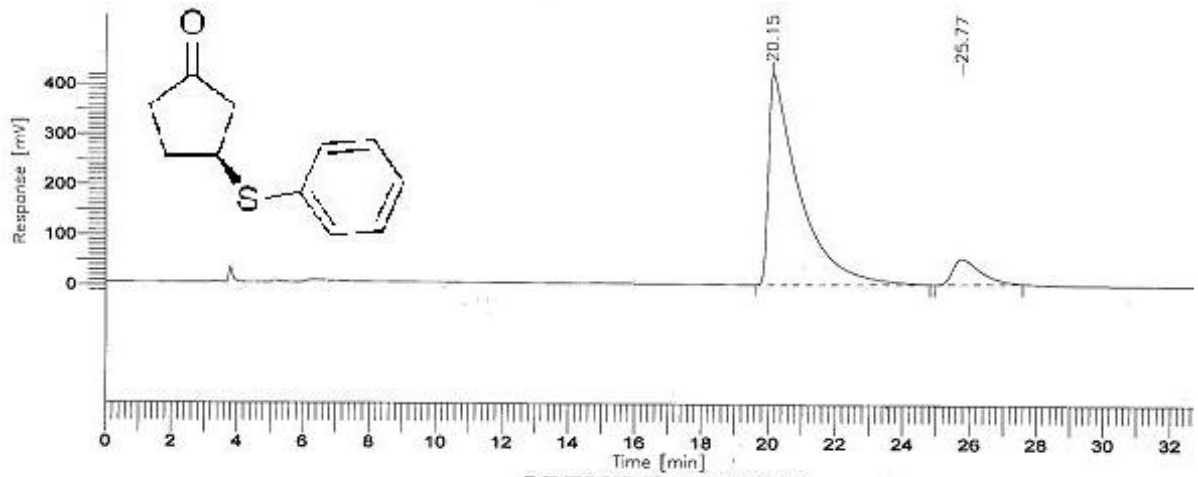
HPLC Graph for enantioenriched **3h**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	19.155	5177606.00	118697.85	50.07	43.62
2	23.304	5162240.00	92901.77	49.93	55.57
		10339846.00	211599.61	100.00	

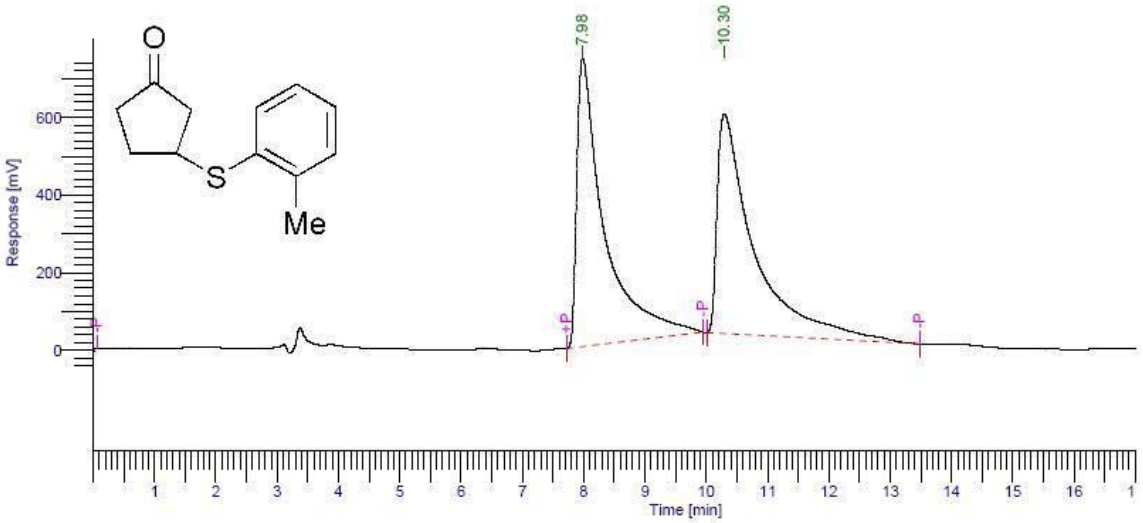
HPLC Graph for racemic **4a**



DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Area/Height [s]
1	20.152	26632830.00	421228.67	90.01	63.23
2	25.772	2956708.00	51387.20	9.99	57.54
		29589538.00	472615.87	100.00	

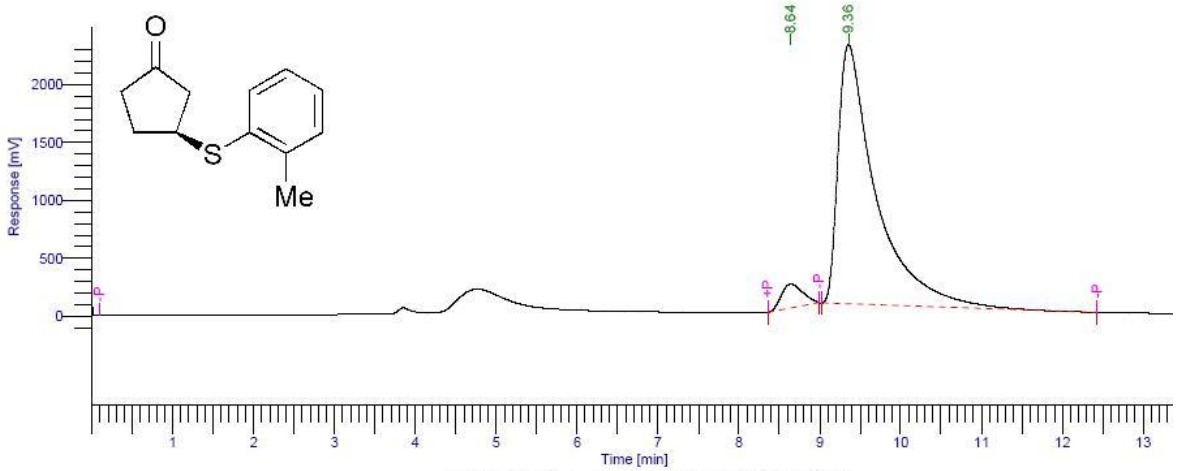
HPLC Graph for enantioenriched **4a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.983	23187727.30	743305.09	49.78	49.78
2		10.295	23396762.55	565030.51	50.22	50.22
			46584489.85	1.31e+06	100.00	100.00

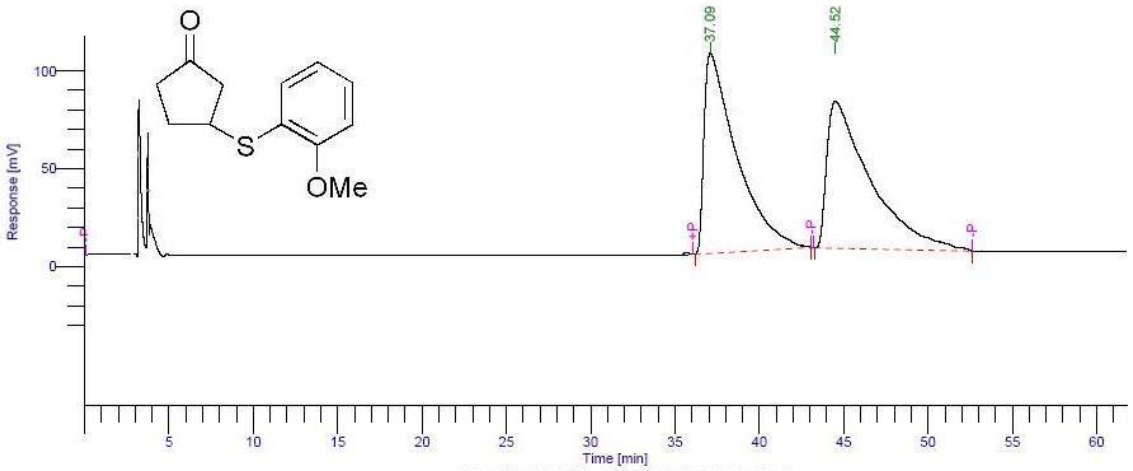
HPLC Graph for racemic **4b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.641	3789182.15	205753.80	4.95	4.95
2		9.355	72724168.34	2.24e+06	95.05	95.05
			76513350.49	2.44e+06	100.00	100.00

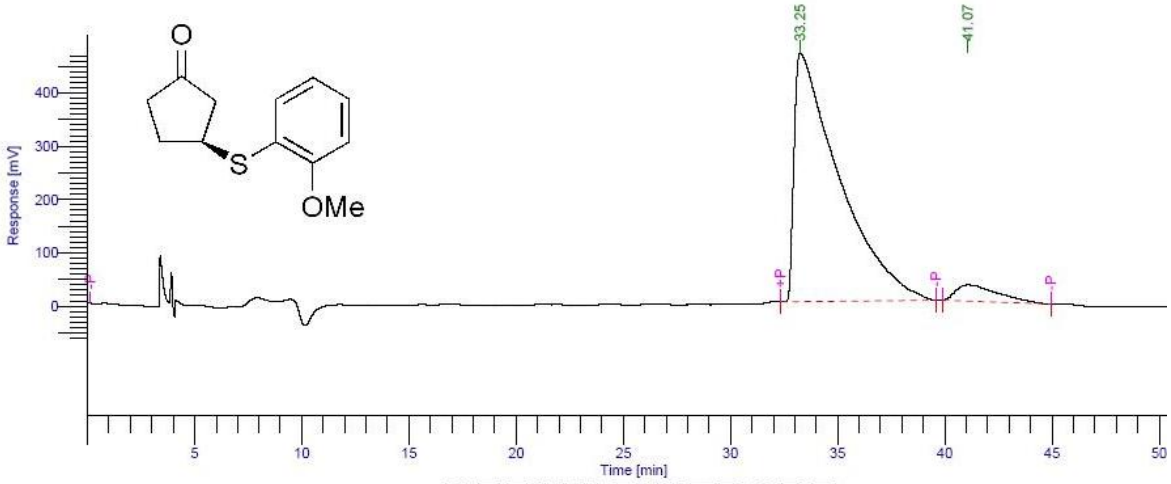
HPLC Graph for enantioenriched **4b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		37.087	13756959.90	102257.15	50.46	50.46
2		44.517	13505004.53	75048.93	49.54	49.54
			27261964.44	177306.08	100.00	100.00

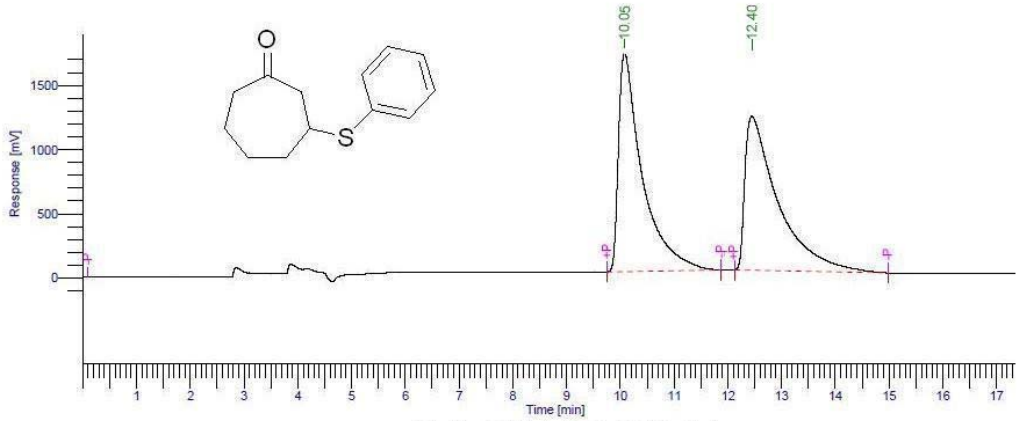
HPLC Graph for racemic **4c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		33.250	68151255.86	467278.85	94.18	94.18
2		41.070	4207936.87	30519.61	5.82	5.82
			72359192.73	497798.46	100.00	100.00

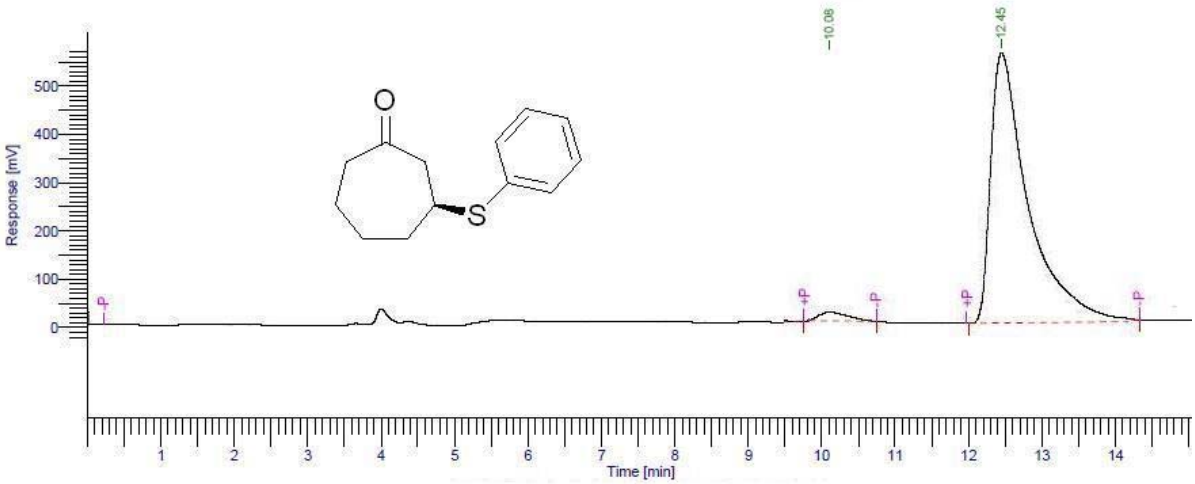
HPLC Graph for enantioenriched **4c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.054	1.29e+08	1.72e+06	49.94	49.94
2		12.401	1.29e+08	1.25e+06	50.06	50.06
			2.58e+08	2.97e+06	100.00	100.00

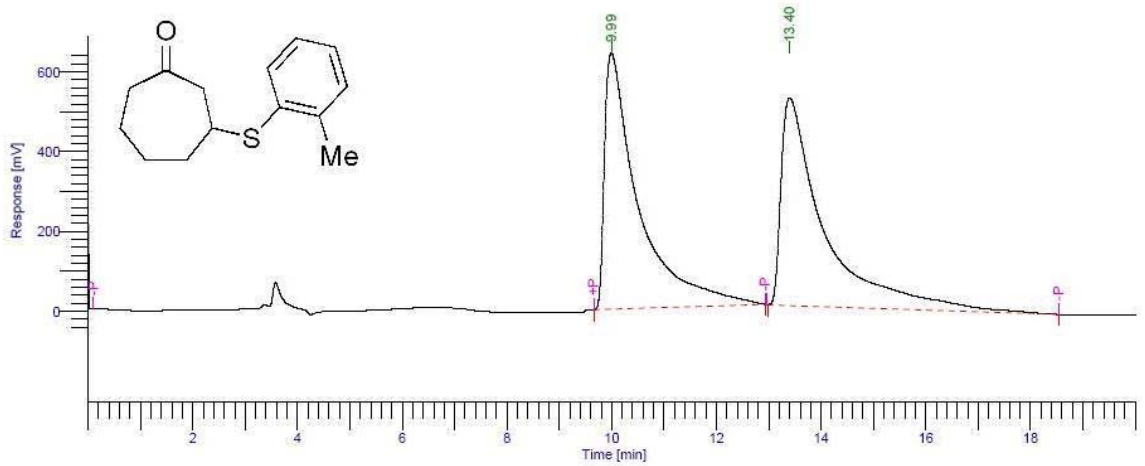
HPLC Graph for racemic **5a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.082	68602542.17	1.75e+06	96.00	96.00
2		12.453	2859307.06	83297.53	4.00	4.00
			71461849.24	1.83e+06	100.00	100.00

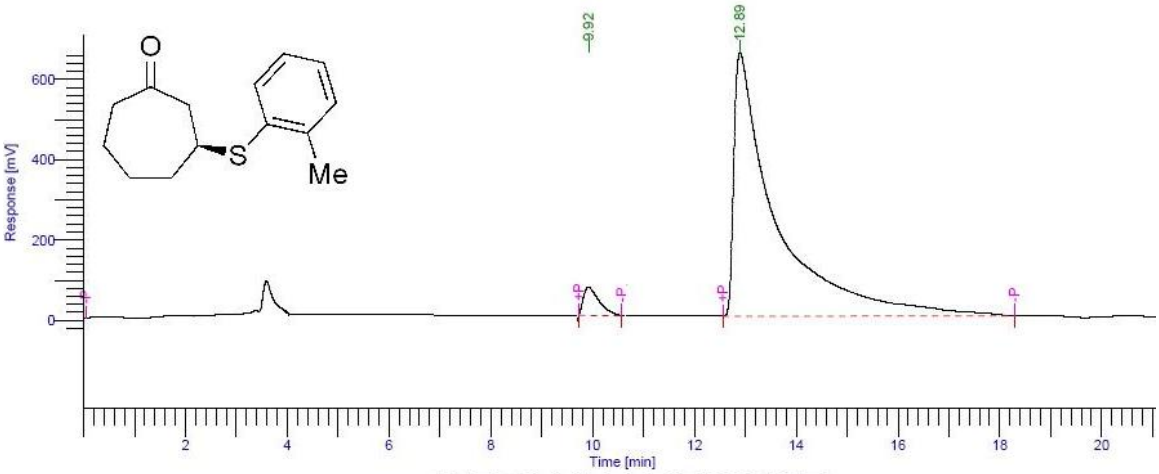
HPLC Graph for enantioenriched **5a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		9.993	28952720.74	641449.24	49.42	49.42
2		13.399	29632479.68	520353.97	50.58	50.58
			58585200.42	1.16e+06	100.00	100.00

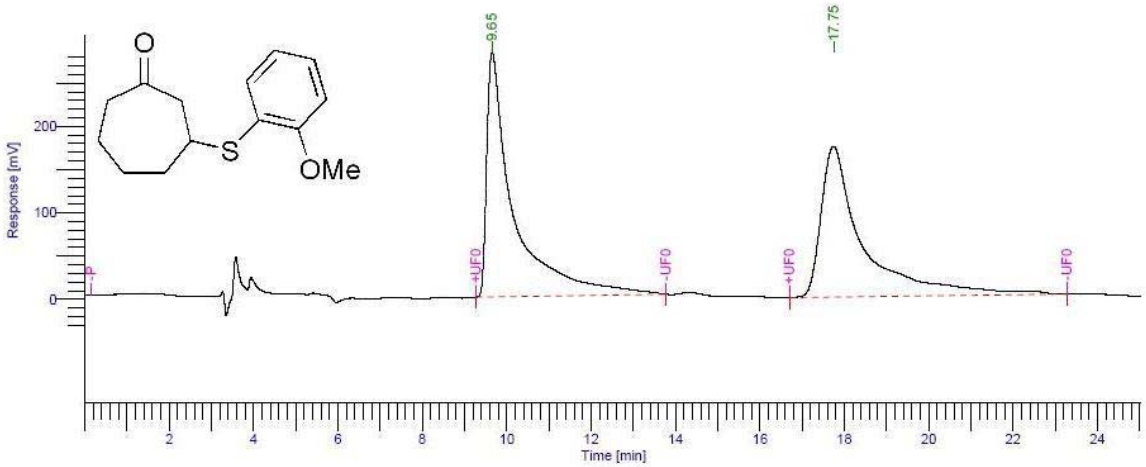
HPLC Graph for racemic **5b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		9.918	1510825.35	69663.63	3.84	3.84
2		12.893	37824144.16	656693.93	96.16	96.16
			39334969.51	726357.57	100.00	100.00

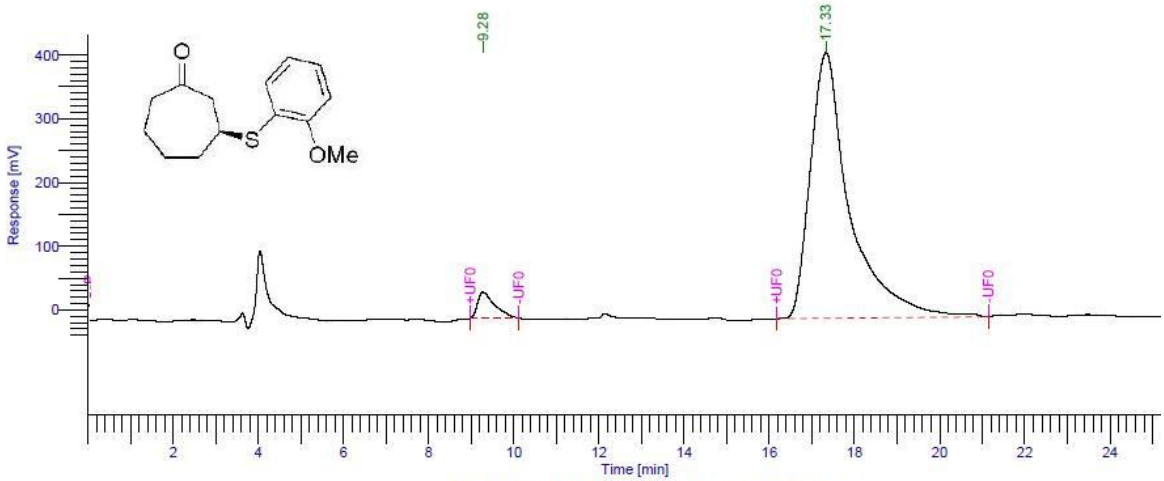
HPLC Graph for enantioenriched **5b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		9.653	12515234.81	282854.57	50.83	50.83
2		17.747	12107485.99	174079.53	49.17	49.17
			24622720.80	456934.10	100.00	100.00

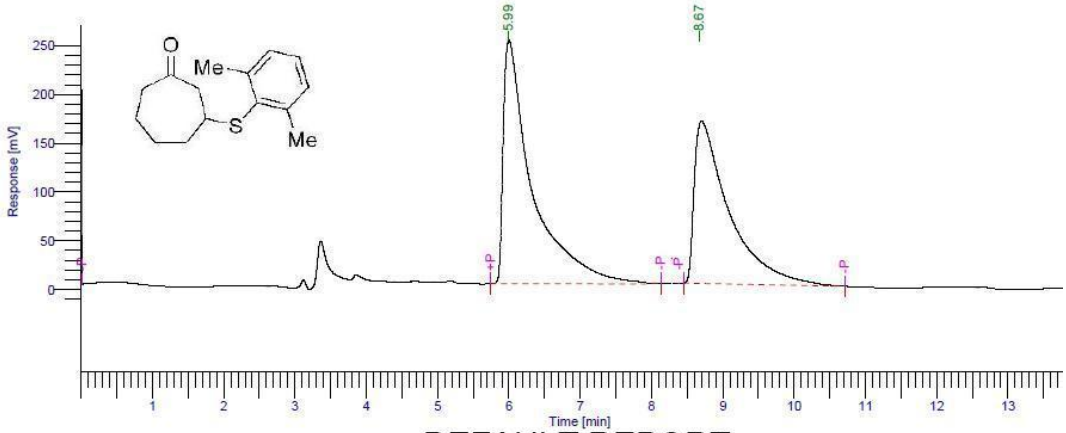
HPLC Graph for racemic **5c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		9.278	1150127.86	40877.59	3.76	3.76
2		17.330	29417636.74	416745.94	96.24	96.24
			30567764.59	457623.54	100.00	100.00

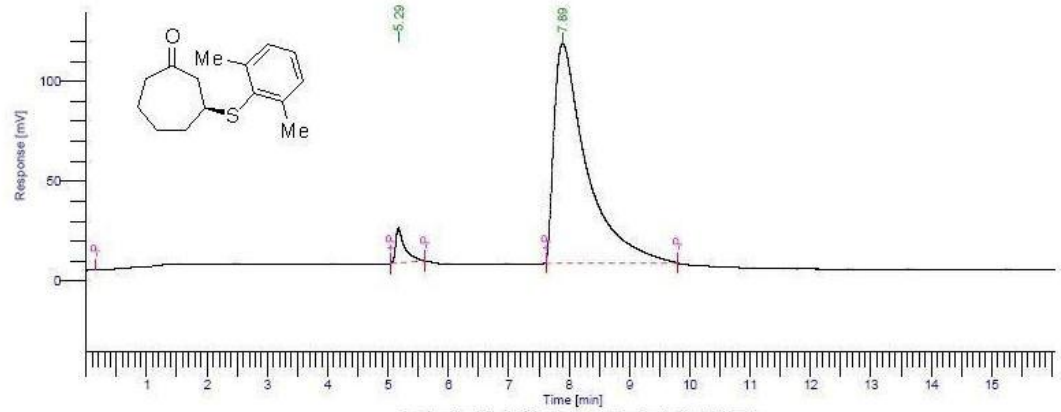
HPLC Graph for enantioenriched **5c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		5.992	5278176.96	255457.61	50.74	50.74
2		8.667	5124426.85	170903.43	49.26	49.26
			10402603.82	426361.04	100.00	100.00

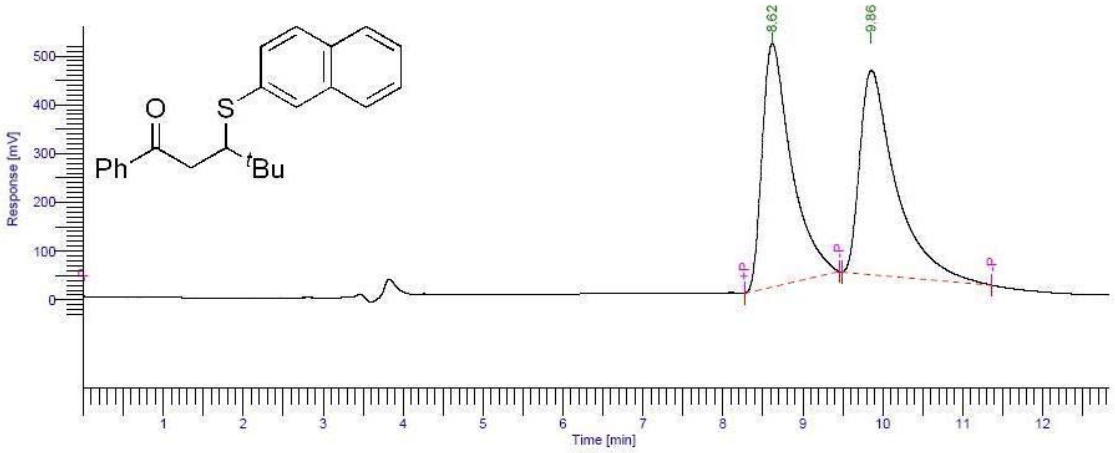
HPLC Graph for racemic **5d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		5.290	181728.04	17408.78	4.22	4.22
2		7.893	4127916.70	110233.81	95.78	95.78
			4309644.74	127642.59	100.00	100.00

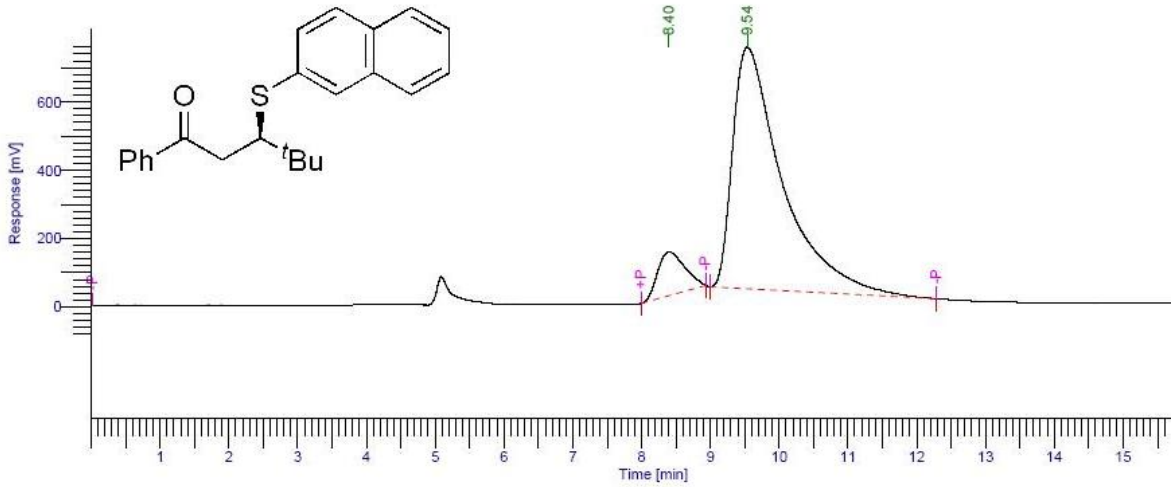
HPLC Graph for enantioenriched **5d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.619	12726222.90	499672.93	49.28	49.28
2		9.858	13097270.70	419324.43	50.72	50.72
			25823493.60	918997.37	100.00	100.00

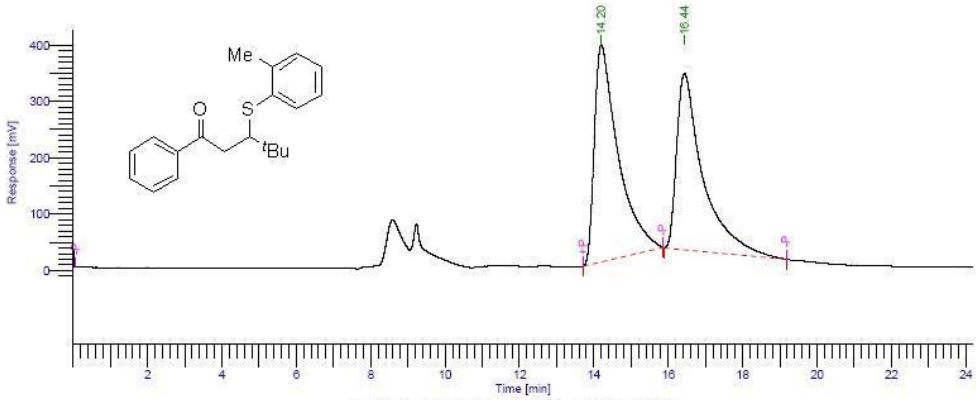
HPLC Graph for racemic **6a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.399	3472054.88	127982.70	8.91	8.91
2		9.537	35484754.19	707154.45	91.09	91.09
			38956809.07	835137.15	100.00	100.00

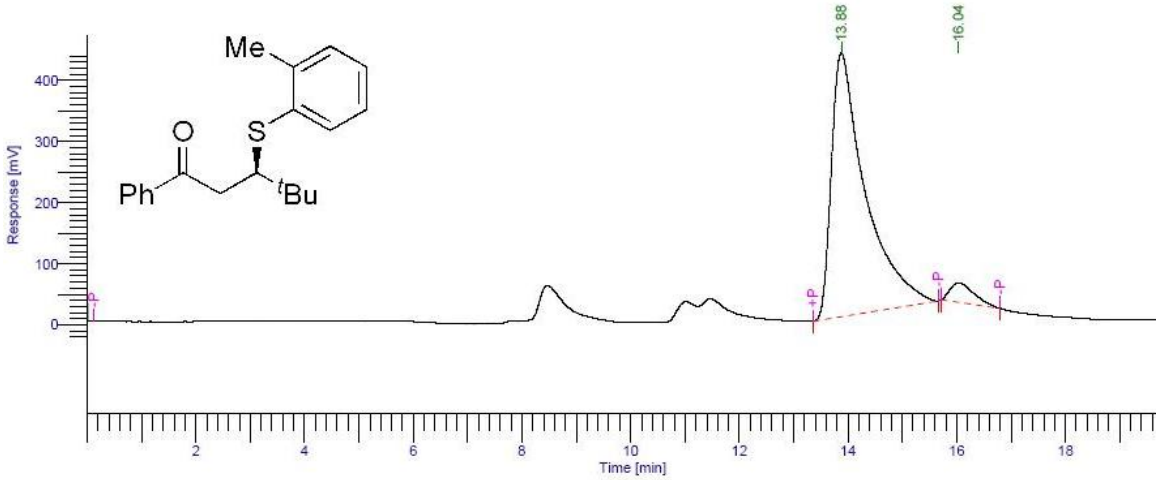
HPLC Graph for enantioenriched **6a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		14.198	17111717.72	385675.82	50.72	50.72
2		16.436	16624063.26	313316.36	49.28	49.28
			33735780.99	698992.18	100.00	100.00

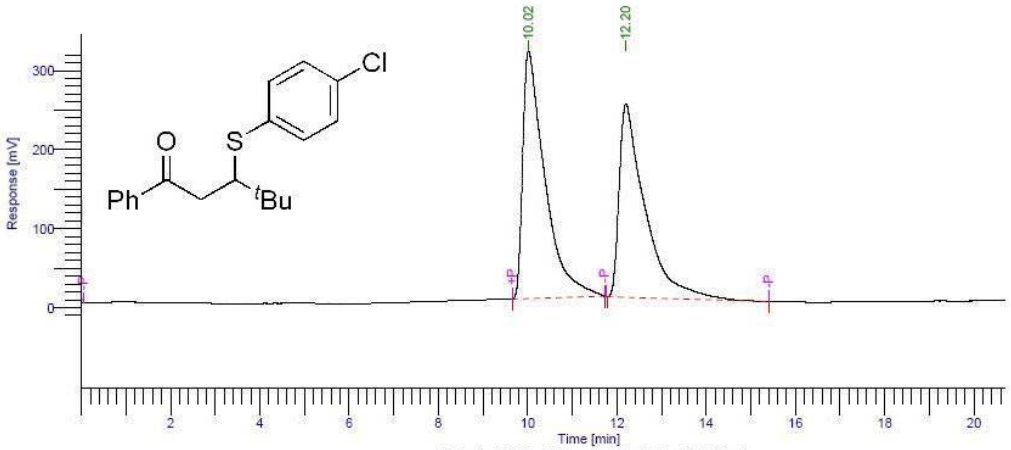
HPLC Graph for racemic **6b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		13.878	18733373.91	431510.71	95.00	95.00
2		16.036	986773.62	31872.44	5.00	5.00
			19720147.53	463383.15	100.00	100.00

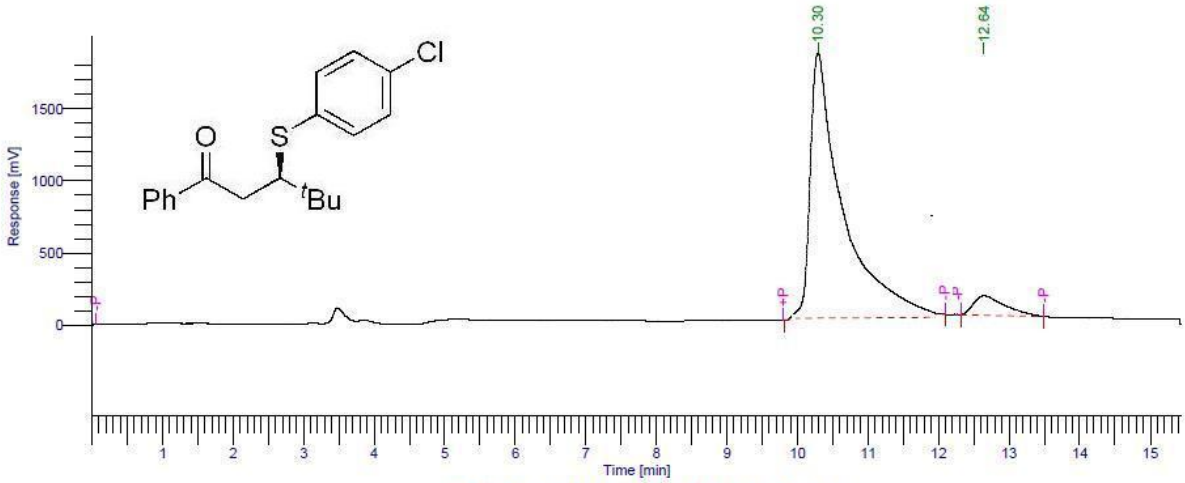
HPLC Graph for enantioenriched **6b**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.019	10817603.07	313339.38	49.93	49.93
2		12.203	10845291.03	245114.87	50.07	50.07
			21662894.10	558454.25	100.00	100.00

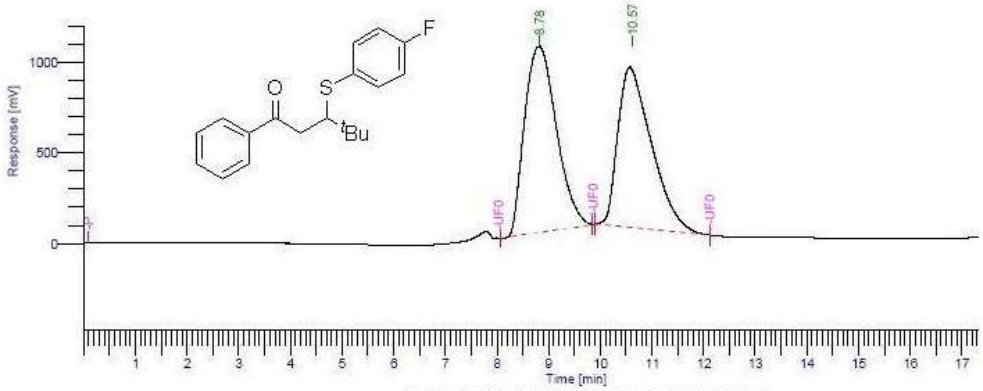
HPLC Graph for racemic **6c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.298	55745532.69	1.84e+06	93.55	93.55
2		12.644	4148892.55	135142.96	6.45	6.45
			59894425.24	1.97e+06	100.00	100.00

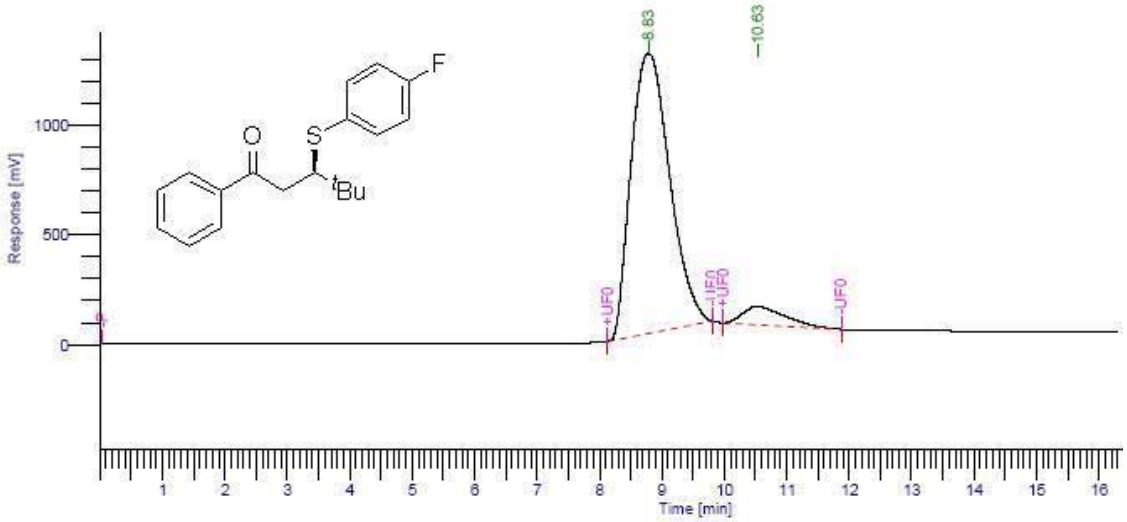
HPLC Graph for enantioenriched **6c**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.781	11669711.08	1.08e+06	50.13	50.13
2		10.574	11609436.31	976075.59	49.87	49.87
			23279147.39	2.05e+06	100.00	100.00

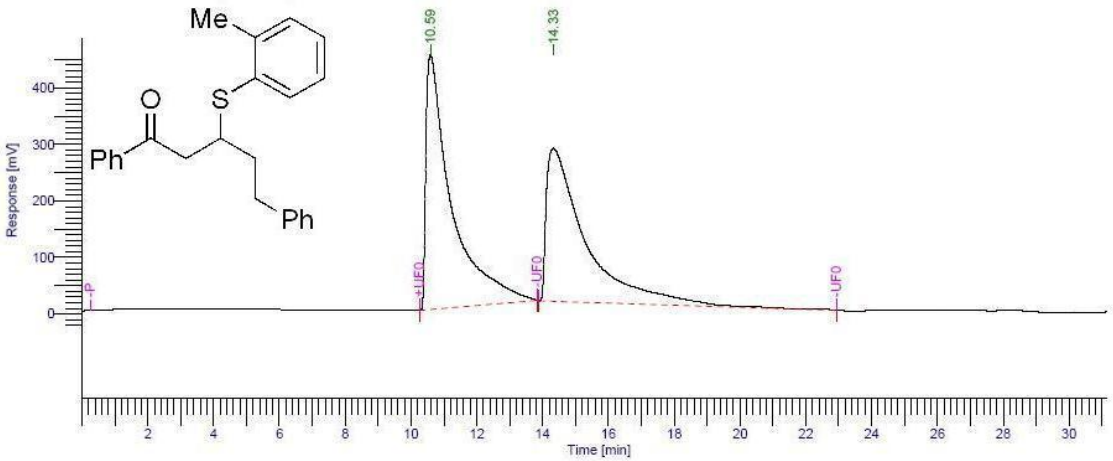
HPLC Graph for racemic **6d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		8.827	54974705.99	1.28e+06	93.32	93.32
2		10.633	3937218.64	83385.45	6.68	6.68
			58911924.63	1.37e+06	100.00	100.00

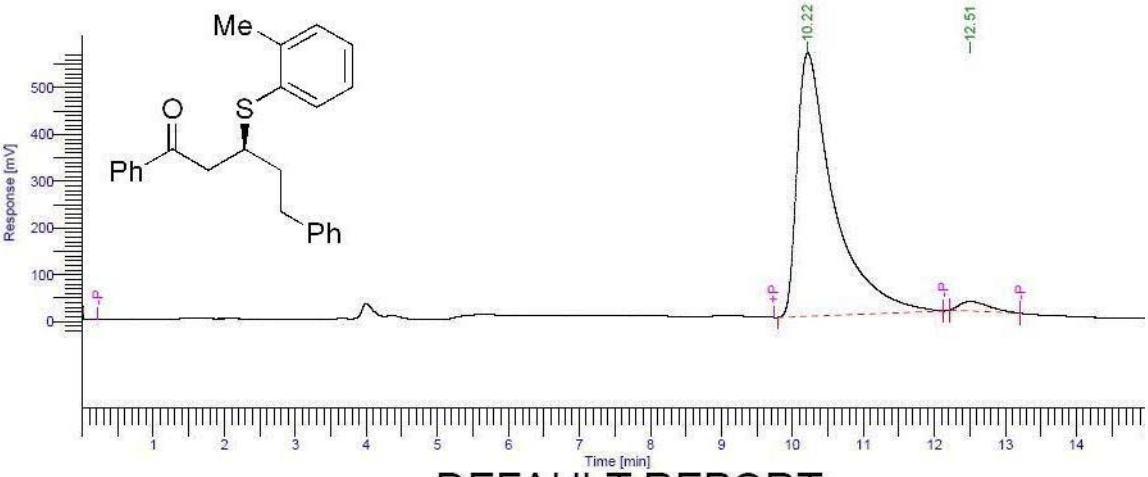
HPLC Graph for enantioenriched **6d**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.589	12726222.90	499672.93	49.28	49.28
2		14.334	13097270.70	289324.43	50.72	50.72
			25823493.60	758997.37	100.00	100.00

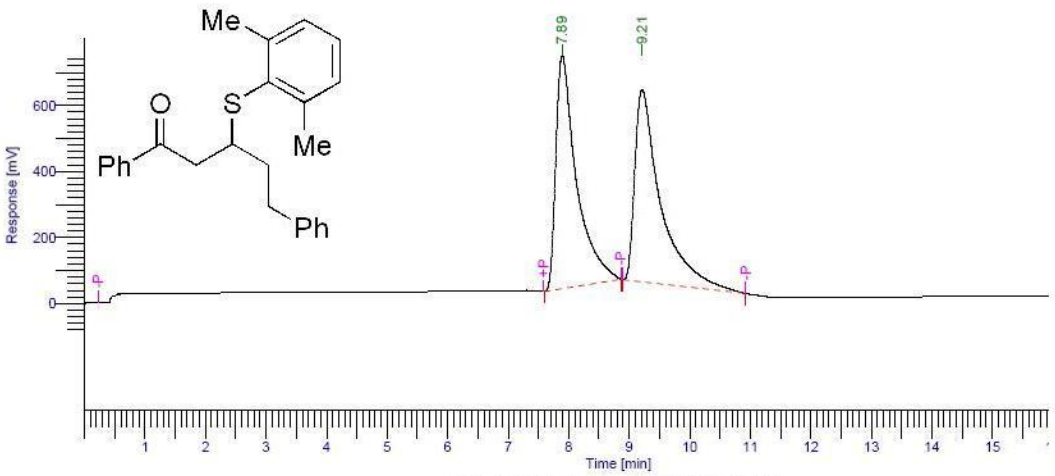
HPLC Graph for racemic **7a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		10.215	20125417.37	563612.96	97.13	97.13
2		12.505	593853.99	20440.45	2.87	2.87
			20719271.36	584053.41	100.00	100.00

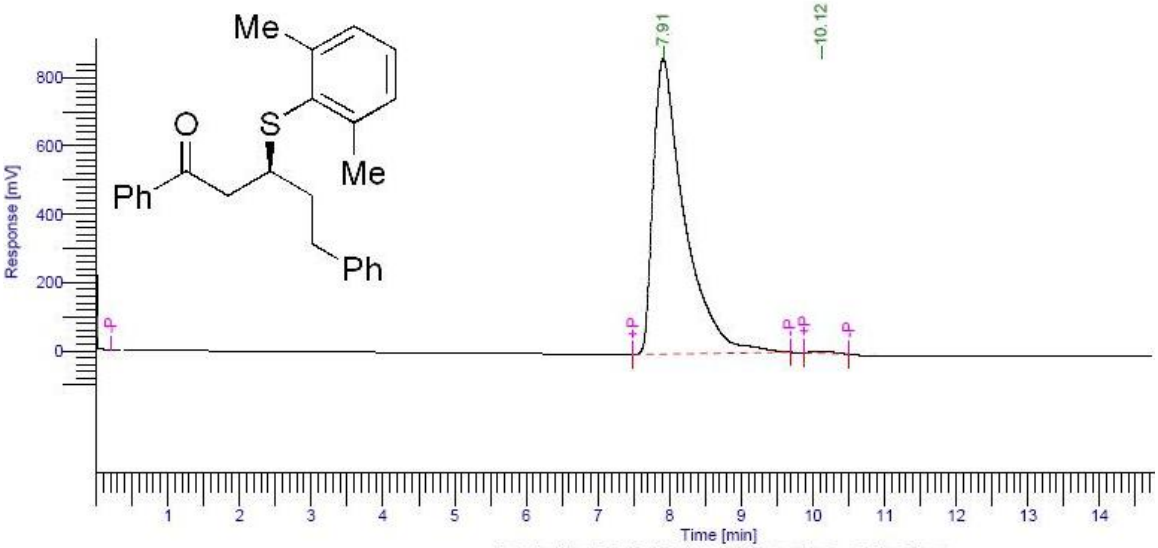
HPLC Graph for enantioenriched **7a**



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.893	16773816.43	705952.10	49.34	49.34
2		9.214	17225701.78	581557.39	50.66	50.66
			33999518.21	1.29e+06	100.00	100.00

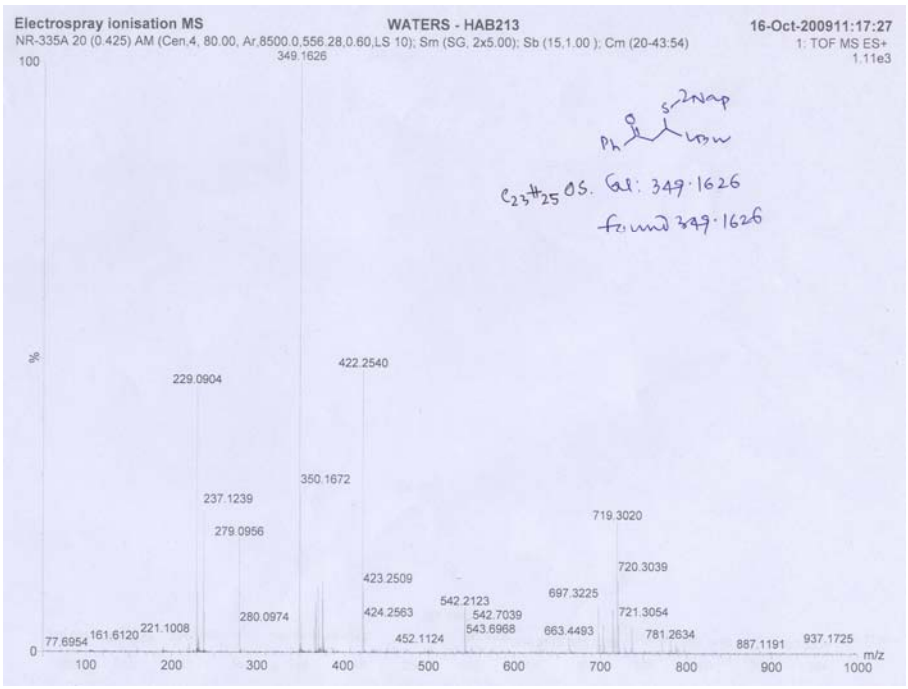
HPLC Graph for racemic **7b**



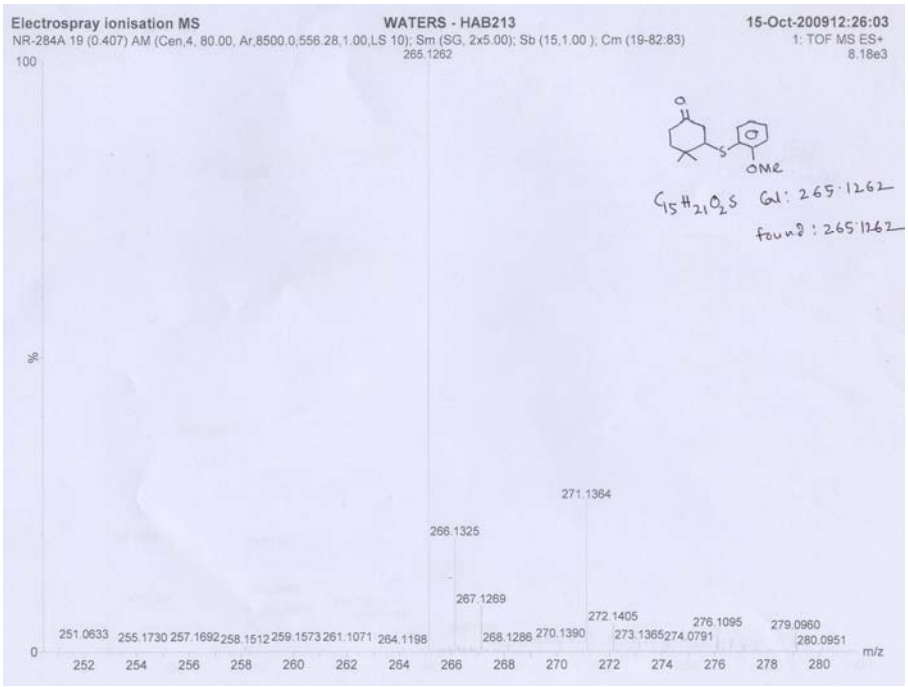
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1		7.911	26214583.30	863774.11	99.56	99.56
2		10.115	116620.33	5384.01	0.44	0.44
			26331203.63	869158.11	100.00	100.00

HPLC Graph for enantioenriched **7b**



Scan copy of HRMS for compound **6a**



Scan copy of HRMS for compound **3e**

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