

Supplementary Information

A User's Guide to the Thiol-Thioester Exchange in Organic Media: Scope, Limitation, and Applications in Material Science

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1. General Information

All reactions were carried out under an argon atmosphere with dry solvents using anhydrous conditions unless otherwise stated. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded in C_6D_6 (internal standard: 7.15 ppm, ^1H ; 128.26 ppm, ^{13}C), in THF-d_8 (internal standard: 3.58 ppm, ^1H ; 67.57 ppm, ^{13}C), in CDCl_3 (internal standard: 7.26 ppm, ^1H ; 77.00 ppm, ^{13}C), in MeCN-d_3 (internal standard: 1.94 ppm, ^1H ; 118.3 ppm, ^{13}C), in DMSO-d_6 (internal standard: 2.50 ppm, ^1H ; 39.52 ppm, ^{13}C), in MeOD-d_3 (internal standard: 3.31 ppm, ^1H ; 49.15 ppm, ^{13}C), on a Bruker DRX-400MHz spectrometer. Chemical shifts (δ) were reported as parts per million (ppm) and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, b = broad and all combinations thereof can be explained by their integral parts. Column chromatography was carried out employing EMD (Merck) Geduran Silica Gel 60 (40-63 μm) with the indicated solvent mixtures. Infrared spectra were recorded using a Perkin Elmer Spectrum 100-FTIR spectrometer. Melting points were determined using a Thomas-Hoover capillary melting apparatus and are uncorrected. The following chemicals: 2-mercaptopyridine (99%), thiophenol (97%), s-phenyl thioacetate (98%), 1-octanethiol (98.5%), methyl 3-mercaptopropionate (98%), cysteamine (~95%), acetyl chloride (98%), pyridine (anhydrous, 98.8%), 1-heptanol (98%), diethylene glycol methyl ether (>99%), and 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (>98%) were purchased from Sigma-Aldrich and used as received. The following chemicals: di-tert-butyl dicarbonate, triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene were purchased from Chem-Impex and used as received. 2-(boc-amino)ethanethiol was prepared using published procedures.¹³ All deuterated solvents utilized in this study (C_6D_6 , THF-d_8 , CDCl_3 , MeCN-d_3 , DMSO-d_6 , and MeOD-d_3) were obtained from Cambridge Isotope Laboratories, Inc. and were used as received.

2. General Experimental Procedures

a. General procedures for the preparation of calibration curves of various thioesters

The preparation of various stock solutions required (utilizing thioester **1a** as a representative compound):

- i)* Thioester stock solution (**SS-CC1**): To a 1-dram screw top vial was added 54.7 mgs (48.7 μL , 0.36 mmol) of *s*-phenyl thioacetate and this was diluted with 1.20 mL (0.30 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , CDCl_3 , MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 4 samples with the excess (~200 μL) being discarded.
- ii)* Internal standard (IS) stock solution (**SS-CC2**): To a 1-dram screw top vial was added 20.2 mgs (0.12 mmol) of 1,3,5-trimethoxybenzene and diluted with 1.00 mL (0.12 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , CDCl_3 , MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 4 samples with the excess (~200 μL) being discarded.

To a standard NMR tube, utilizing a calibrated autopipette, the designated amount (see table provided below, **Table S1**) of the thioester stock solution (**SS-CC1**) was added, followed by 200 μL of the internal standard stock solution (**SS-CC2**), and finally was diluted with a designated amount (see table provided below, **Table S1**) of the deuterated solvent (pipette tips were discarded and changed between each addition). This NMR tube was capped and vortexed until fully homogeneous; $^1\text{H-NMR}$ of this series was immediately acquisitioned.

sample #	thioester (SS-CC1)	IS (SS-CC2)	solvent	total
1 (100%)	400 μL	200 μL	0 μL	600 μL
2 (75%)	300 μL	200 μL	100 μL	600 μL
3 (50%)	200 μL	200 μL	200 μL	600 μL
4 (25%)	100 μL	200 μL	300 μL	600 μL

Table S1: Amounts of stock solutions and solvent used to prepare samples which corresponds to 100%, 75%, 50%, and 25% yield of a given thioester in comparison to a constant concentration of the internal standard.

The calibration curves provided in the accompany portion of this Supplemental Information (separate document – Microsoft Excel, titled: Supplementary Information, Part 2) were formed by integrating the aromatic peak of the internal standard (see **Table S2** for chemical shifts in each solvent), normalizing to 1.00, then integrating the acyl peak of the thioester (see **Table S3** for chemical shifts in each solvent), and recording the resultant value for the thioester integral. This procedure was also performed for the aliphatic peak ($-\text{OCH}_3$) of the internal standard (see **Table S2** for chemical shifts in each solvent) and compared to the thioester integral. The two separate ratios (acyl thioester integral/internal standard integral) obtained from this operation were plotted against the respective ideal

yield they represent (25%, 50%, 75%, and 100%) and fitted to a linear function. This operation was performed for each thioester in each solvent (5 thioesters x 6 solvents = 30 total calibration curves). Equations obtained from this procedure were used to calibrate experimental values obtained from the subsequent exchange experiments.

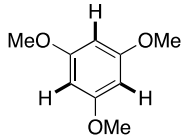
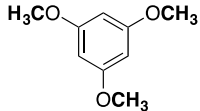
deuterated solvent	aromatic peak of IS 	aliphatic peak of IS 
C ₆ D ₆	6.24	3.32
THF-d ₈	6.05	3.70
CDCl ₃	6.08	3.76
MeCN-d ₃	6.10	3.74
DMSO-d ₆	6.09	3.70
MeOD-d ₃	6.07	3.73

Table S2: Location of the aromatic and aliphatic peaks of the internal standard, 1,3,5-trimethoxybenzene in the deuterated solvents utilized in this study (values given in ppm).

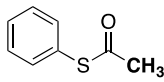
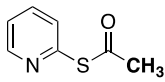
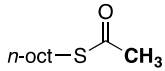
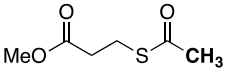
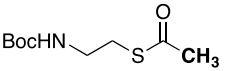
deuterated solvent	thioester 1a 	thioester 1b 	thioester 1c 	thioester 1d 	thioester 1e 
C ₆ D ₆	1.84	1.80	1.90	1.90	1.78
THF-d ₈	2.36	2.40	2.26	2.27	2.27
CDCl ₃	2.42	2.46	2.31	2.31	2.34
MeCN-d ₃	2.39	2.43	2.28	2.29	2.30
DMSO-d ₆	2.43	2.46	2.31	2.32	2.32
MeOD-d ₃	2.39	2.30	2.31	2.31	2.31

Table S3: Location of the aromatic and aliphatic peaks of the internal standard, 1,3,5-trimethoxybenzene in the deuterated solvents utilized in this study (values given in ppm).

b. General procedure for determining the extent of exchange between various thioesters, thiols, and bases/nucleophiles in organic solvent

The preparation of various stock solutions required (utilizing thioester **1a** as the representative thioester and thiol **2c** as the representative thiol):

- i)* Thioester stock solution (**SS-EX1**): To a 1-dram vial was added 152 mgs (135 μ L, 1.00 mmol) of *s*-phenyl thioacetate and diluted with 750 μ L (1.33 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , $CDCl_3$, MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 4 samples with the excess being discarded.
- ii)* Thiol stock solution (**SS-EX2**): To a 1-dram vial was added 146 mgs (174 μ L, 1.00 mmol) of 1-octanethiol and diluted with 750 μ L (1.33 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , $CDCl_3$, MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 4 samples with the excess being discarded.
- iii)* Triethylamine stock solution (**SS-EX3**): To a 20 mL scintillation vial was added 61.3 μ L (44.5 mgs, 0.44 mmol) of triethylamine and diluted with 3.30 mLs (0.13 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , $CDCl_3$, MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 20 samples with the excess being discarded.
- iv)* Internal standard stock solution (**SS-EX4**): To a 20 mL scintillation vial was added 148 mgs (0.88 mmol) of 1,3,5-trimethoxybenzene and diluted with 3.30 mLs (0.27 M) of a deuterated solvent (either C_6D_6 , THF- d_8 , $CDCl_3$, MeCN- d_3 , DMSO- d_6 , or MeOD- d_3), capped, and vortexed until fully homogeneous. These stock solutions were used directly after mixing and made fresh if required after 24 hours. This stock solution was prepared with enough material for 20 samples with the excess being discarded.

To a standard NMR tube, utilizing a calibrated autopipette, 150 μ L of the thioester stock solution (**SS-EX1**) was added, followed by 150 μ L of the thiol stock solution (**SS-EX2**), followed by 150 μ L of the internal standard stock solution (**SS-EX3**), and finally 150 μ L of the triethylamine stock solution (**SS-EX4**) to initiate the exchange reaction (pipette tips were discarded and changed between each addition). This NMR tube was capped and vortexed until fully homogeneous; 1H -NMR of this series was acquisitioned after 12 hours using a timed autosampler.

sample #	thioester (SS-EX1)	thiol (SS-EX2)	IS (SS-EX3)	triethylamine (SS-EX4)	total
1	150 μ L	150 μ L	150 μ L	150 μ L	600 μ L

Table S4: Amounts of the various stock solutions added to prepare a standard exchange experiment.

The exchange values provided in the manuscript were calculated by integrating the aromatic peak of the internal standard (see **Table S2** for the chemical shifts in each solvent), normalizing to 1.00, then integrating the acyl peak of both the acyl thioester (if applicable) and the exchanged acyl peak of the exchanged thioester (if applicable; see **Table S3** for the chemical shifts of each of the thioester acyl peak locations), and recording the resultant value for the thioester integral(s). This procedure was also performed for the aliphatic peak (-OCH₃) of the internal standard (see **Table S2** for the chemical shifts in each solvent) and compared to the thioester integral. The two ratios (acyl thioester integral/aromatic SI and acyl thioester integral/aliphatic SI) obtained from each of these treatments were placed into the equations obtained from each calibration curve ([yield] = slope*[experimental ratio]+y) to account for error and to give an experimental exchange yield. These two experimental values were then averaged and used directly to identify the extent of exchange or lack thereof.

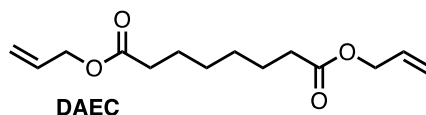
Note: When other formulations were employed, such as other bases (those found in **Table 1** – pyridine, DBU, or BEMP) or nucleophiles (those found in **Table 3** – DMAP, DABCO, or quinuclidine), a similar procedure as above was employed. In these cases, the stock solution **SS-EX4** was mixed using only small quantities of the base (0.08 mmol, enough for 3 samples) to minimize the amount of the somewhat costly deuterated solvents utilized. In the case of experiments where the effect of temperature was explored, the same procedure as above was utilized to prepare the samples. The NMR vials were directly placed into an equilibrated oil bath and allowed to sit undisturbed for the requisite time. Samples that were kept at the designated temperature (25°C, 50°C, and 75°C) for only 5 minutes were quenched with 2 drops of TFA and vortexed to ensure the complete quenching of the exchange; the NMR was acquisitioned after this quenching procedure. Those kept at the designated temperature for 12 hours were not quenched with TFA and the NMRs were acquisitioned directly following this period.

c. General procedure to determine the requirement for free thiol in the nucleophile catalyzed thiol-thioester exchange

+ **free thiol + thioester + nucleophile** formulation: To a 10.0 mL speed mixer vial was added 250 mgs (0.87 mmol, 1.00 equiv) of **TEDAE**, 427 mgs (0.87 mmol, 1.00 equiv, “100% excess thiol”) of pentaerythritol tetra(3-mercaptopropionate) (**PETMP**), and 4.83 mgs (0.04 mmol, 0.05 equiv, 5.00 mol%). This clear resin was then manually mixed with a pipette tip for ~2 minutes to make a homogenous mixture. Following this, approximately 8.91 mgs (3.48×10^{-2} mmol, 0.04 equiv, 4.00 mol%) of 2,2-dimethoxy-2-phenylacetophenone (**DMPA**), which had been crushed with the flat side of a spatula to form a fine powder, was added and the resin was further manually mixed with a pipette tip for an additional ~2 minutes to form a homogeneous mixture. At this time the clear resin was poured between two glass slides treated with Rain-X (ITW Global Brands, Houston, TX) using 250 μm thick spacers (Small Parts Inc., Logansport, IN). The material was irradiated (365 nm, 5.00 $\mu\text{W}/\text{cm}^2$, room temperature) for ~10 minutes to yield the thioester-containing crosslinked network polymer. The conversion was found to be essentially quantitative by FT-IR, revealing complete consumption of the “ene” species. These fully-formed polymers were used directly for all subsequent studies.

–**free SH + thioester + nucleophile** formulation: The representative procedure outlined above was modified to a 2:1 ene:thiol ratio (as opposed to 1:2 ene:thiol) to ensure that all free thiol was consumed and a similar crosslinking density was preserved (**Fig. 9**, green line)

+ **free SH – thioester + nucleophile** formulation: The representative procedure outlined above was utilized, however, **DAEC** (**DiAllylEster Control**, see below for structure), which contained no thioester linkage, was employed in the stead of **TEDAE**; relative stoichiometry of ene:thiol (1:2) was maintained (**Fig. 9**, red line).



+ **free SH + thioester – nucleophile** formulation: The representative procedure outlined above was utilized, however, quinuclidine was not added to the resin (**Fig. 9**, blue line).

3. Additional Figures

Below is a time course ¹H-NMR of the exchange between thioester **1a** (0.20 mmol, 1.00 equiv), thiol **2c** (0.20 mmol, 1.00 equiv), catalyzed by triethylamine (0.02 mmol, 10.0 mol%) in DMSO-d₆ (0.20 M) at room temperature over the course of 12 hours. As can be noted, the reaction has fully equilibrated by 5000 seconds (~1.4 hours). The slight dip in the relative ratios is likely due to the slow hydrolysis of the thioester products under these basic conditions.

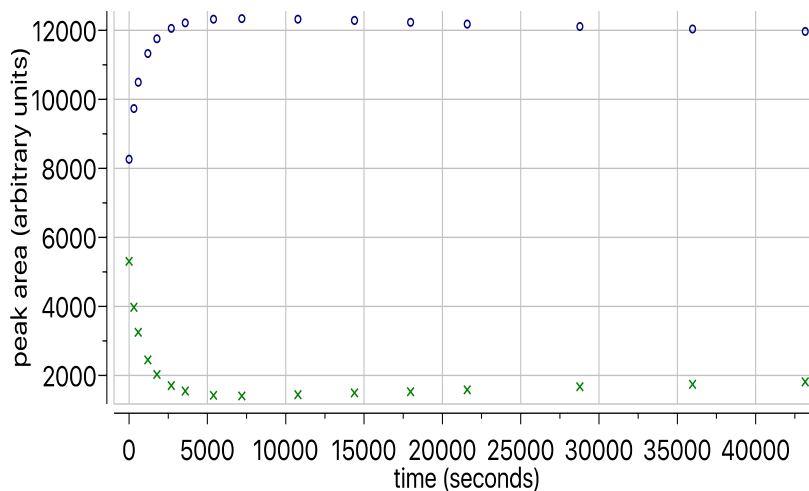


Figure S1: Time course of the exchange of thioester **1a** (1.00 equiv) with thiol **2c** (1.00 equiv) as catalyzed by TEA (10.0 mol%) in DMSO-d₆ (0.20 M) at room temperature.

Legend: blue circles (acyl peak of the thioester corresponding to thioester **1c**), green crosses (acyl peak of the thioester corresponding to thioester **1a**).

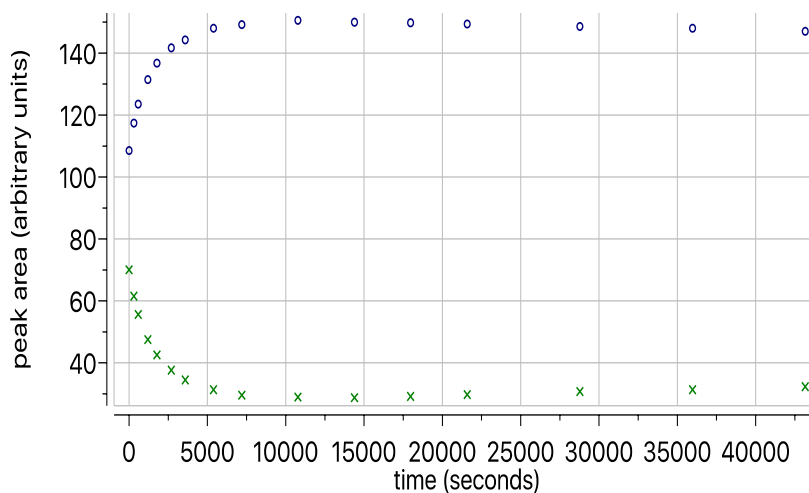
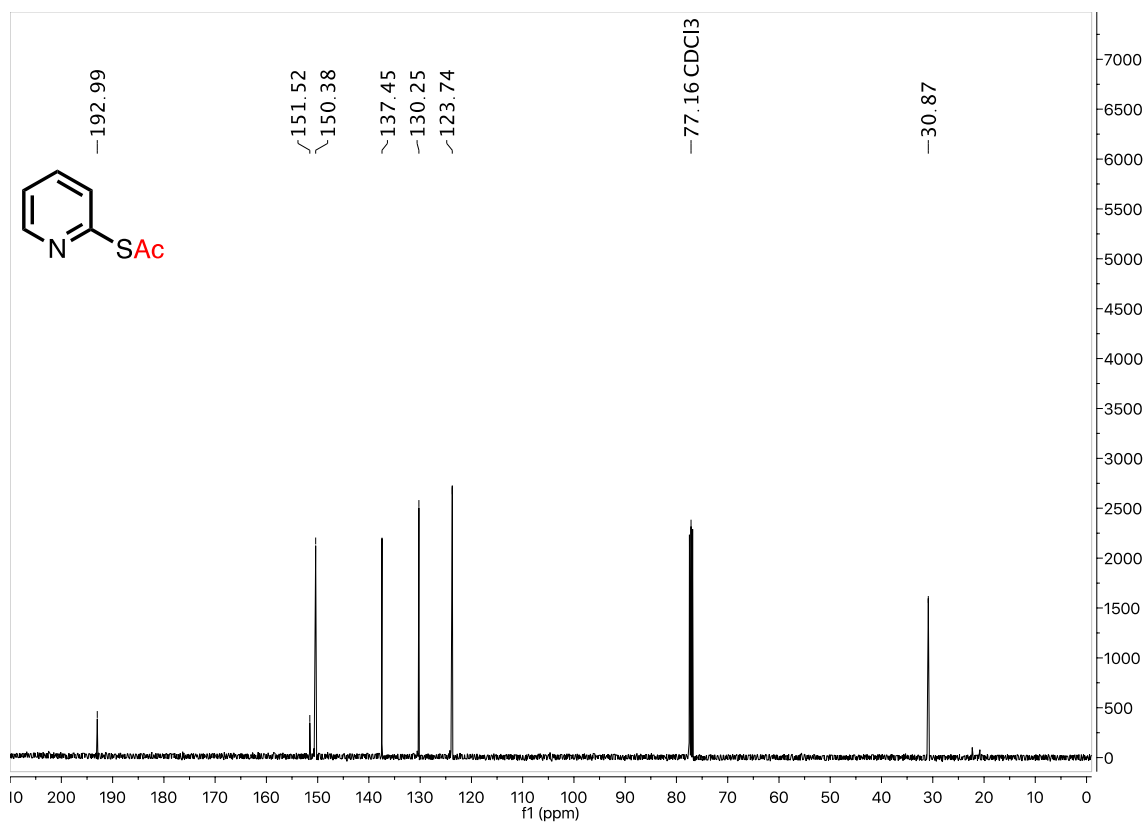
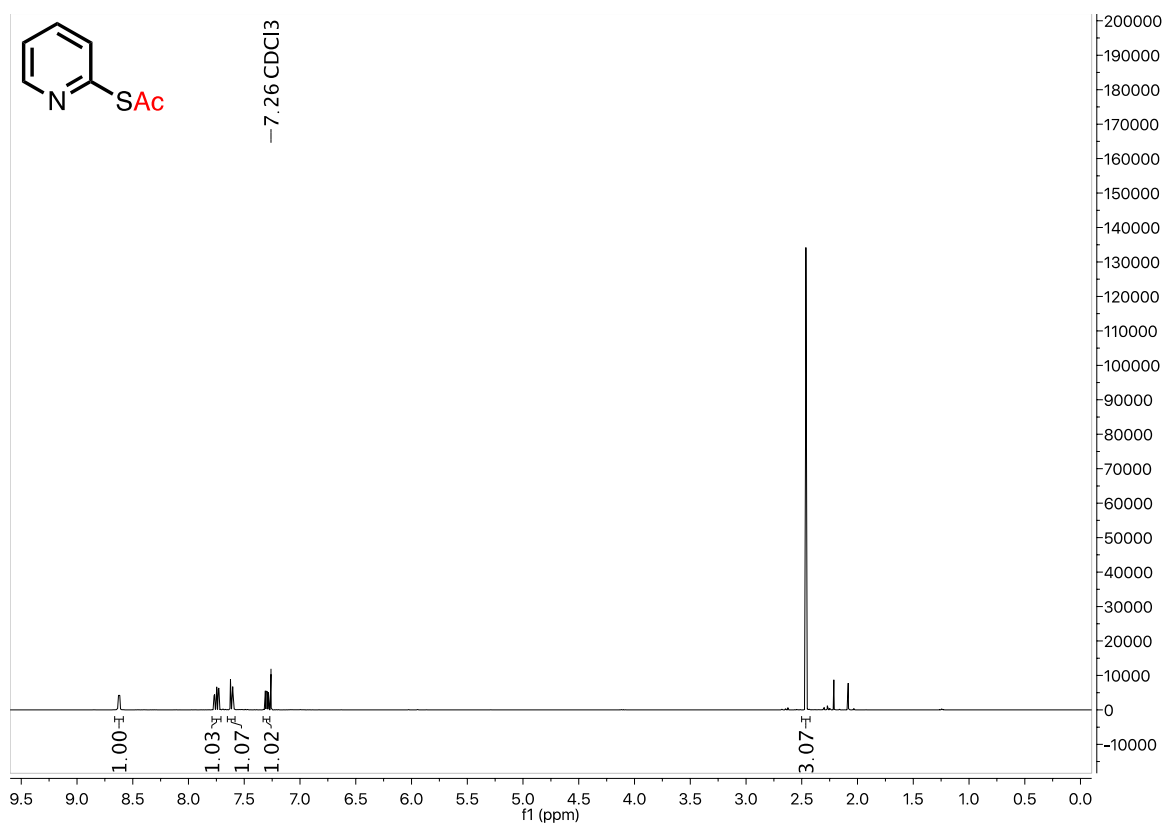
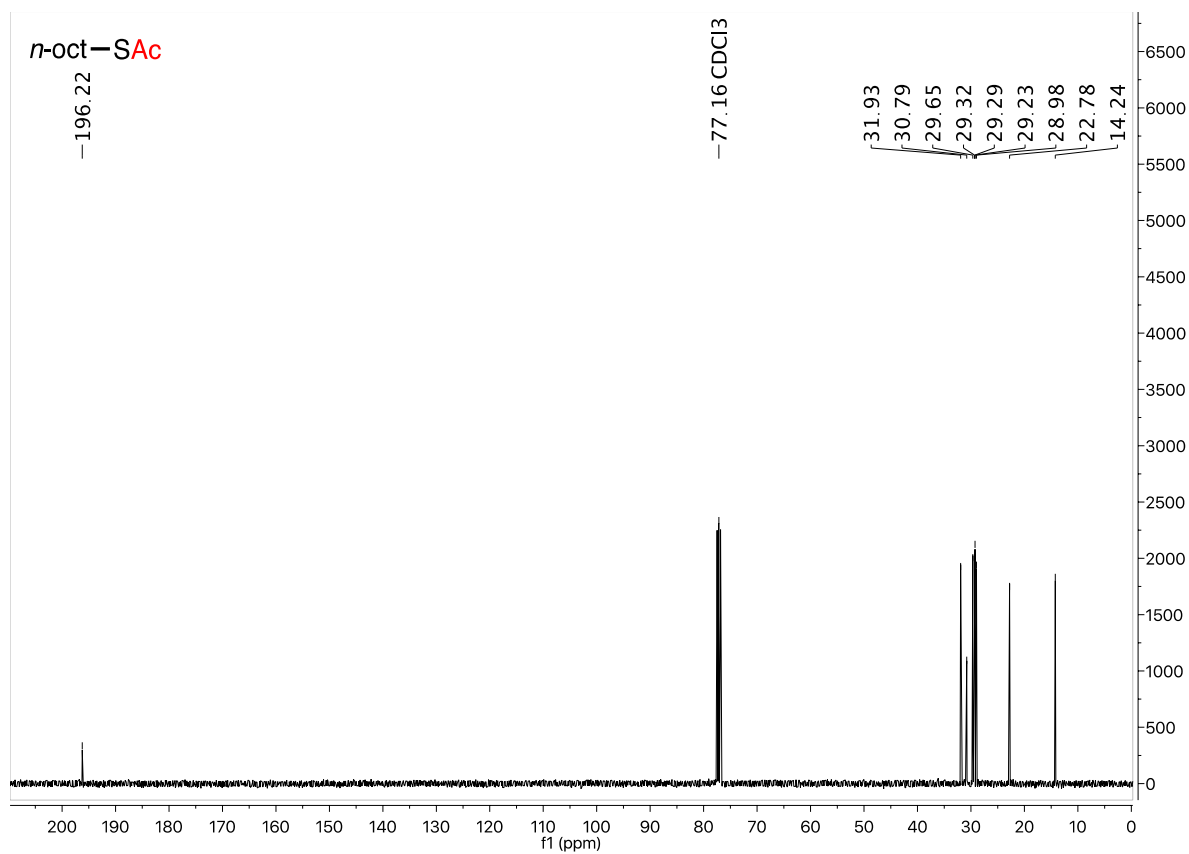
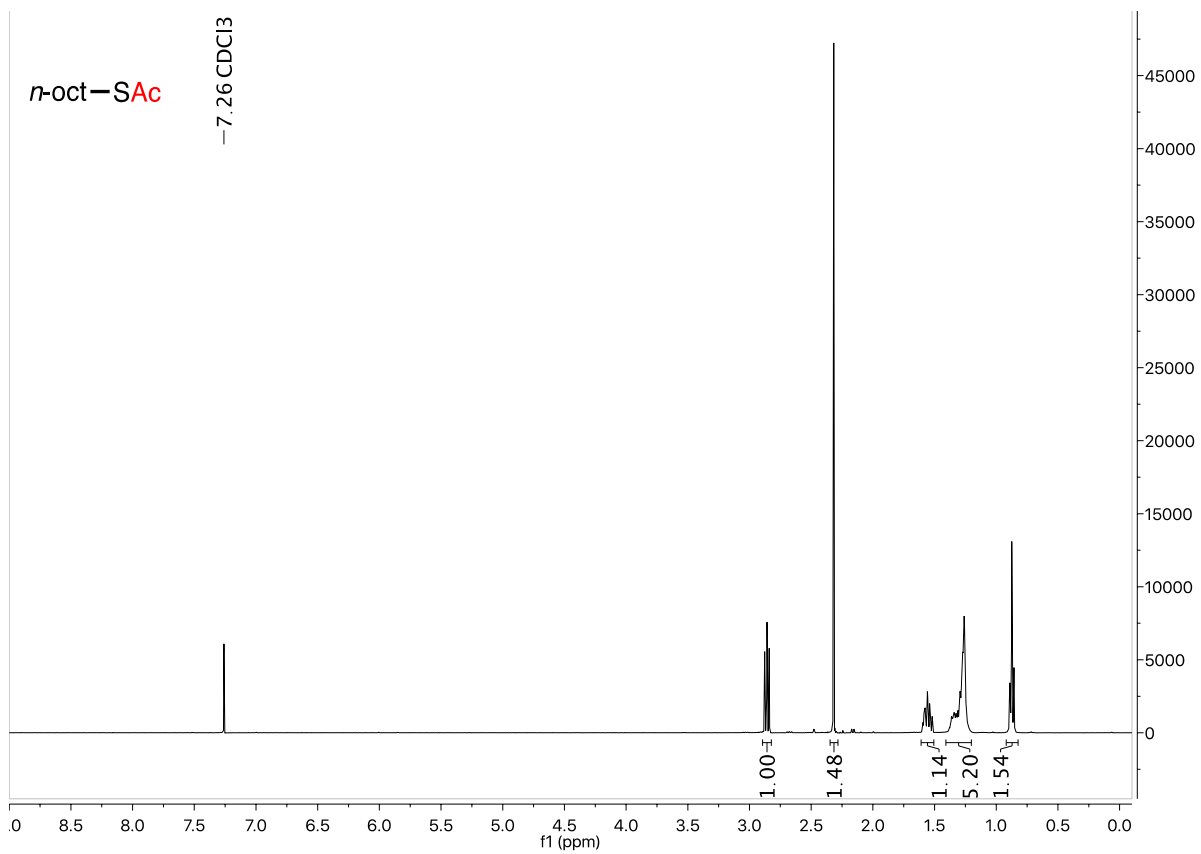


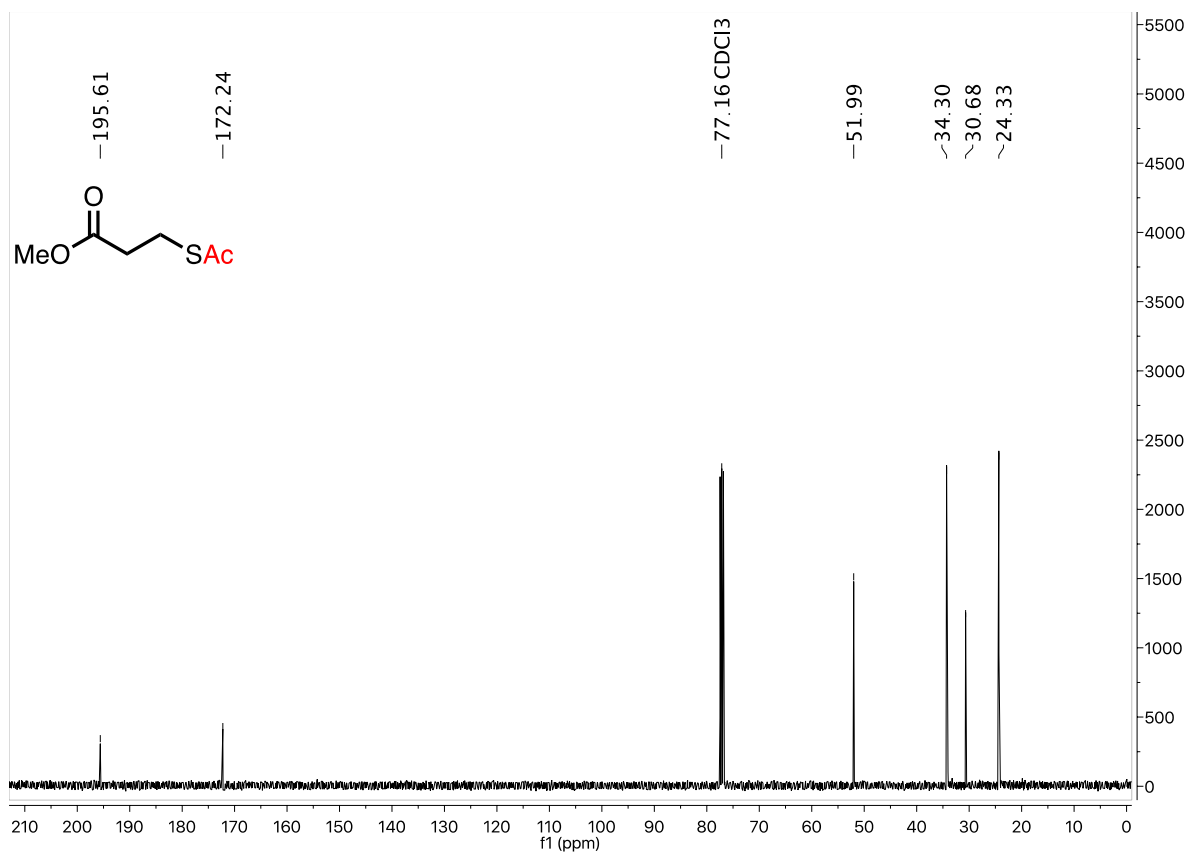
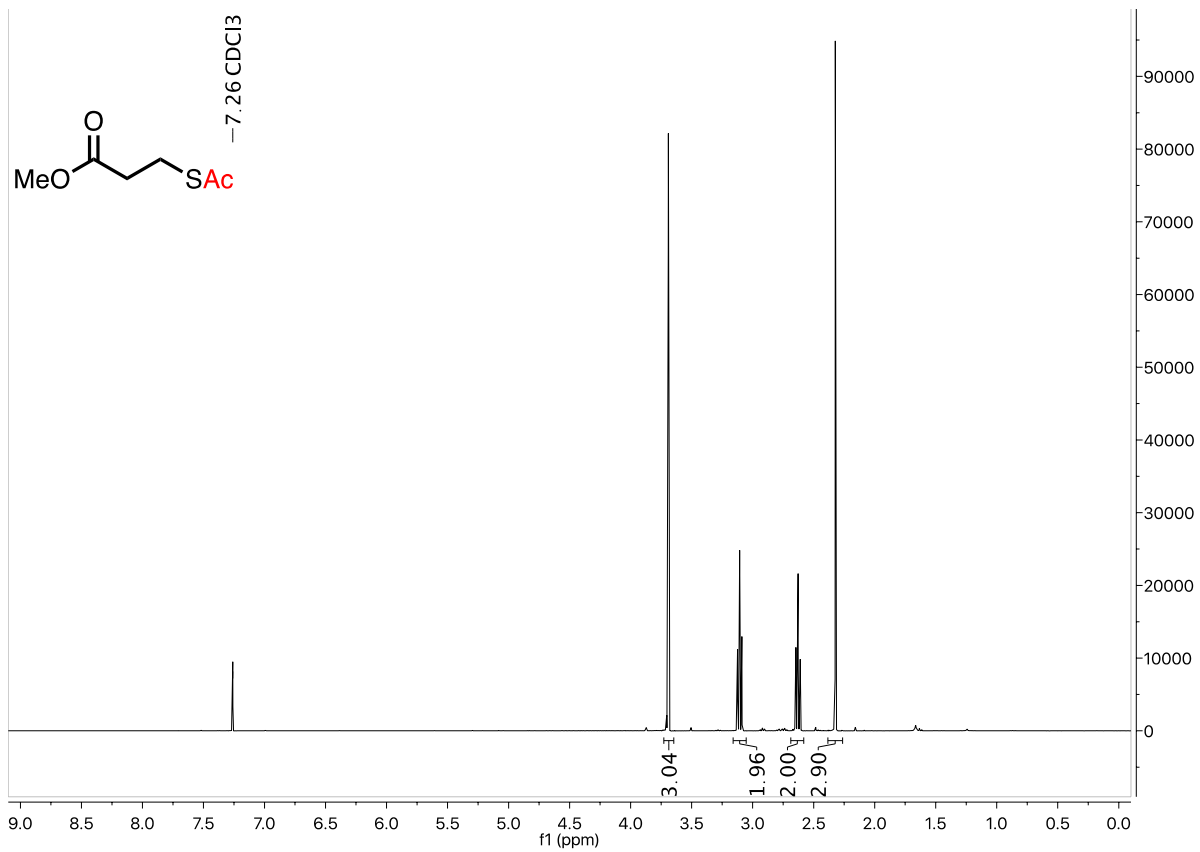
Figure S2: Time course of the exchange of thioester **1a** (1.00 equiv) with thiol **2c** (1.00 equiv) as catalyzed by TEA (5.00 mol%) in DMSO-d₆ (0.20 M) at room temperature. With less of the basic catalyst the exchange had slightly slower kinetics, however, a similar trend was observed as above.

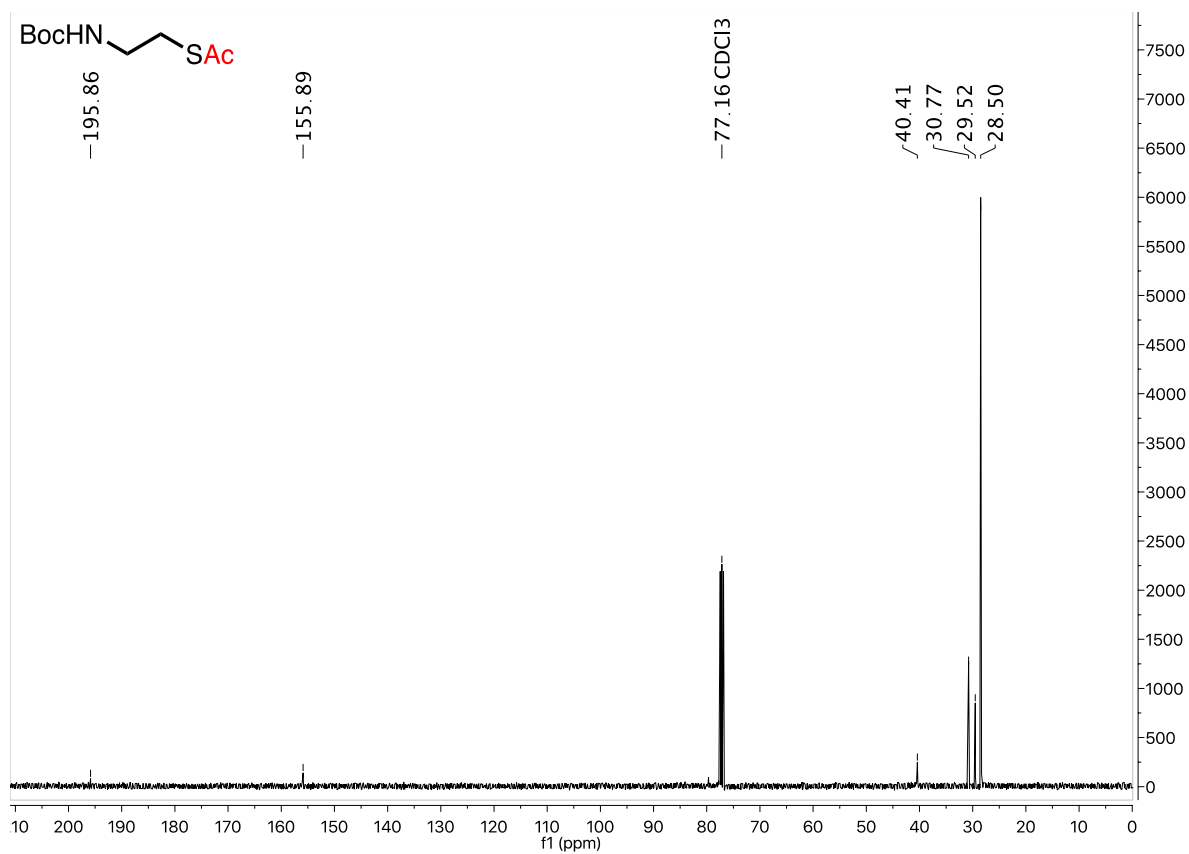
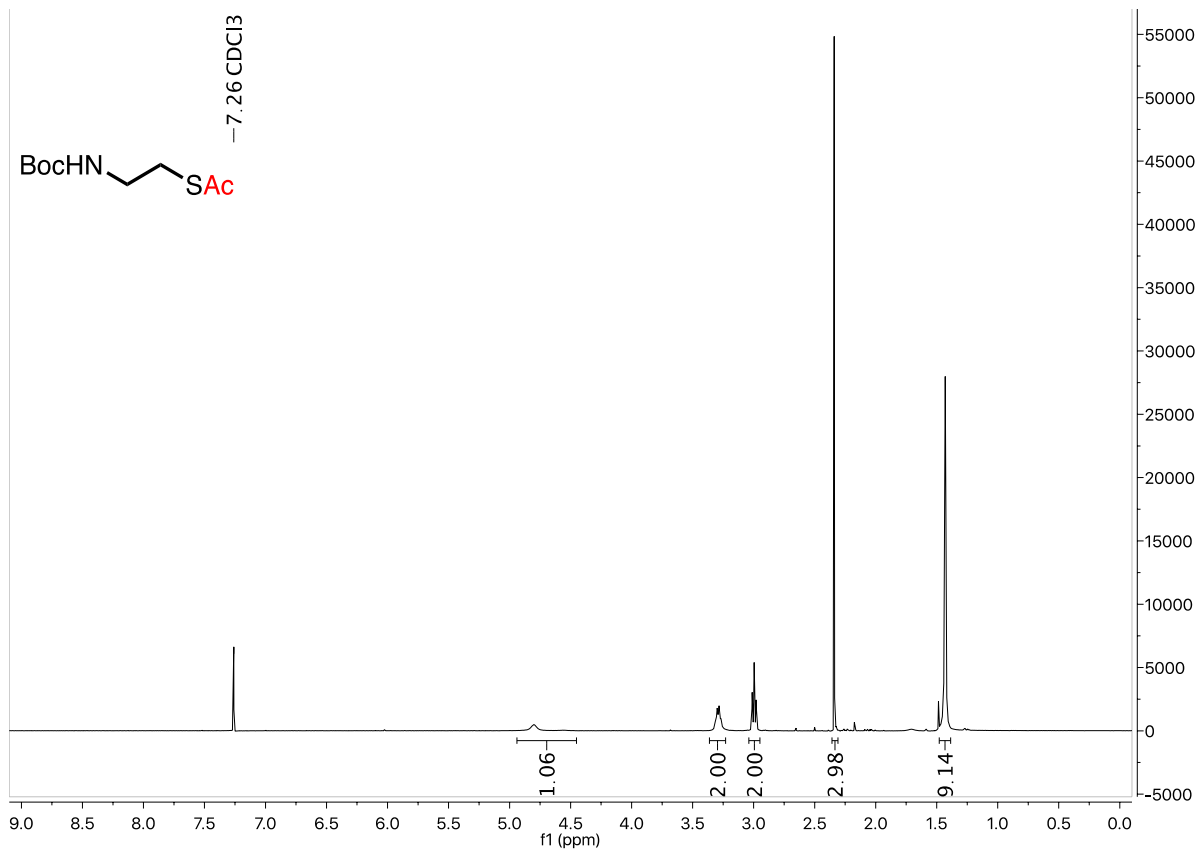
Legend: blue circles (acyl peak of the thioester corresponding to thioester **1c**), green crosses (acyl peak of the thioester corresponding to thioester **1a**).

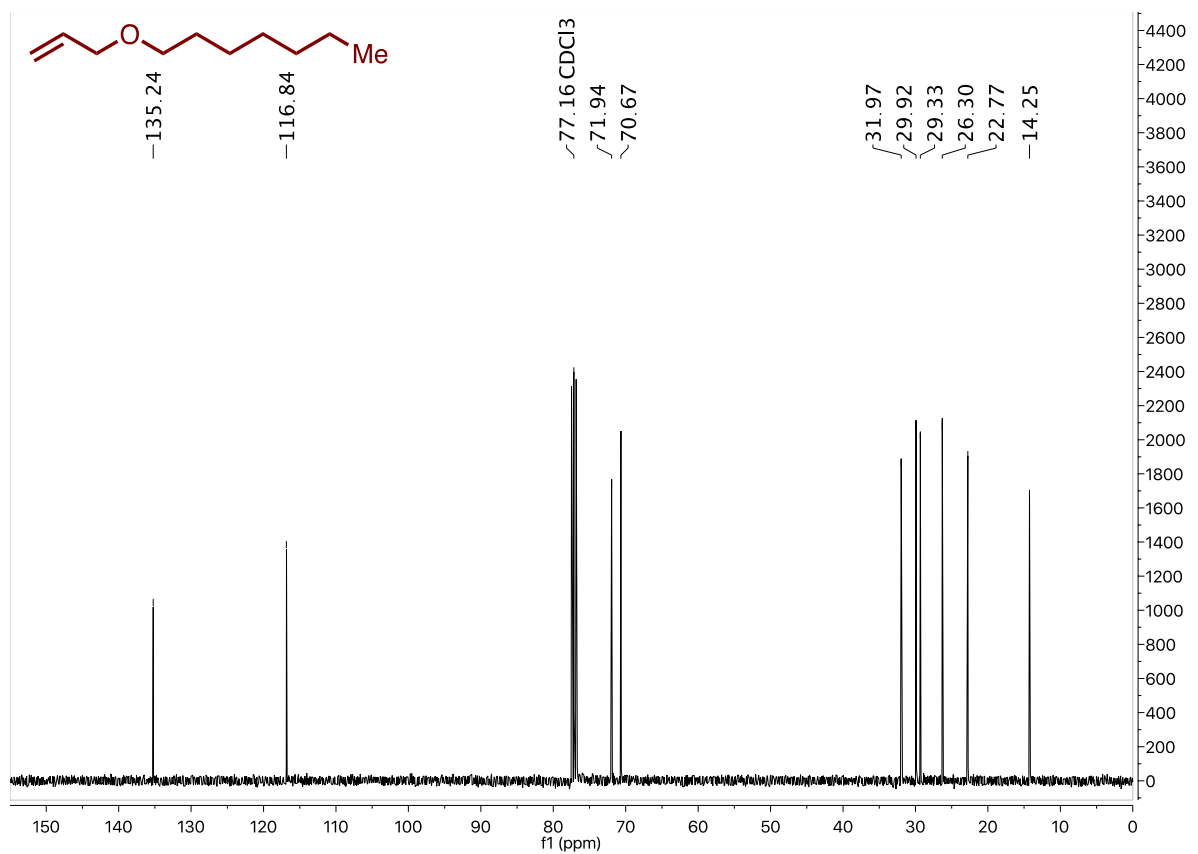
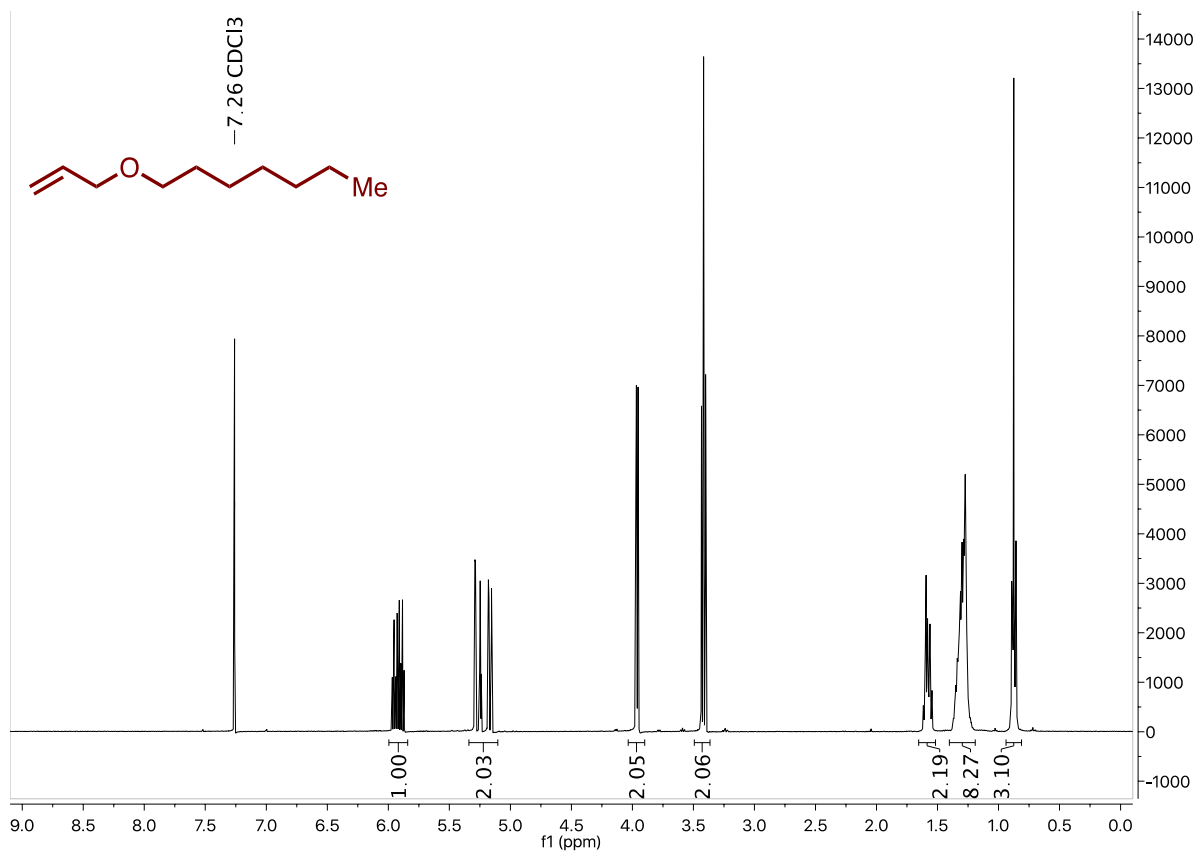
4. Relevant Spectra

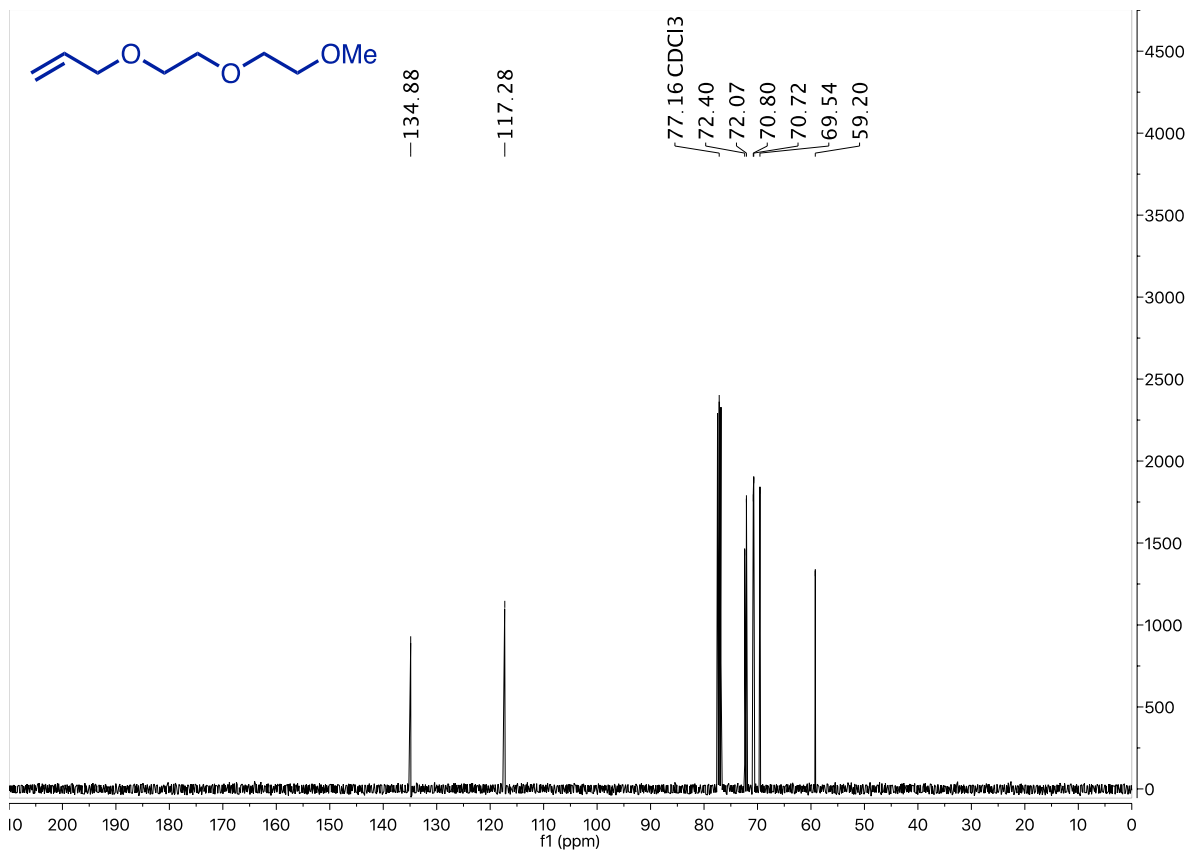
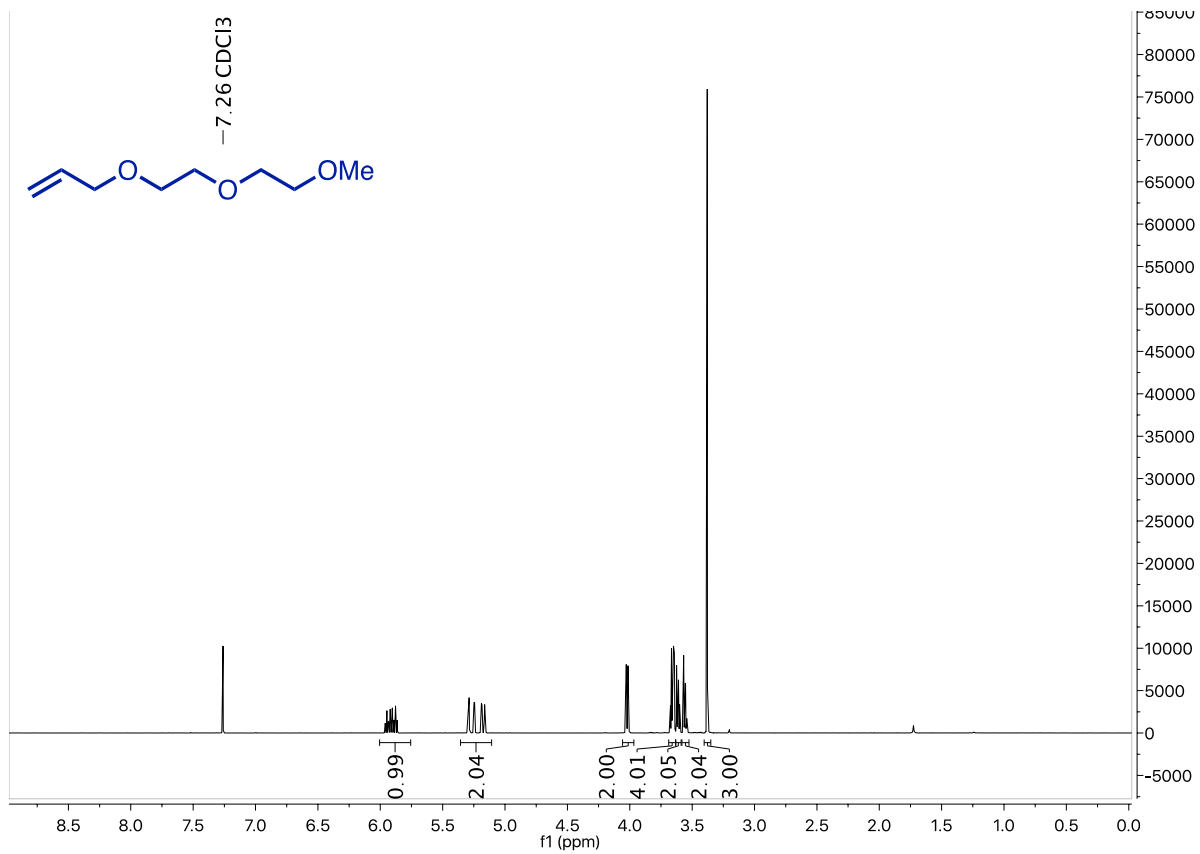








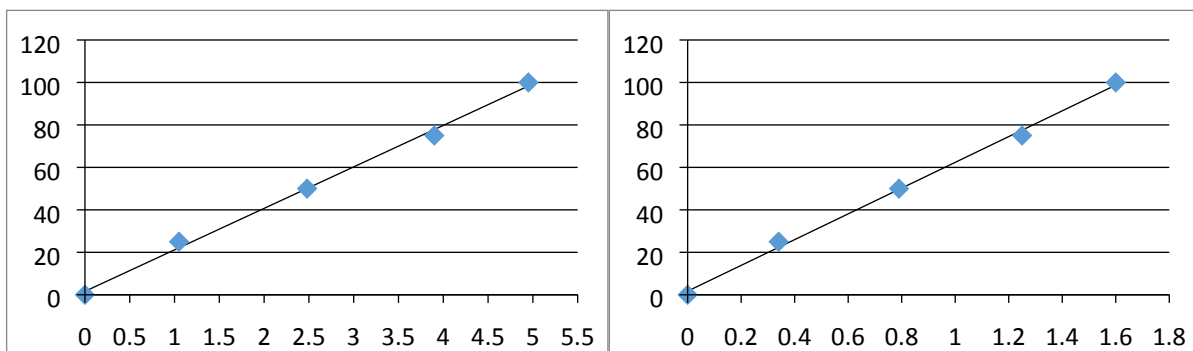




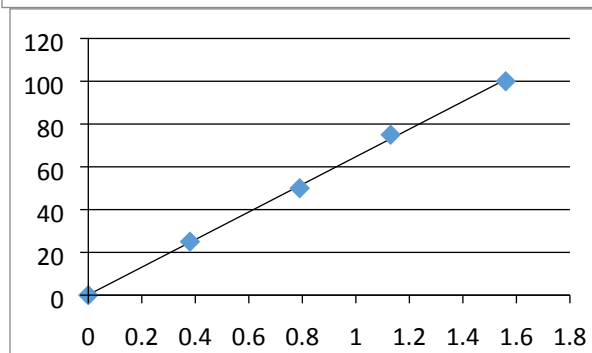
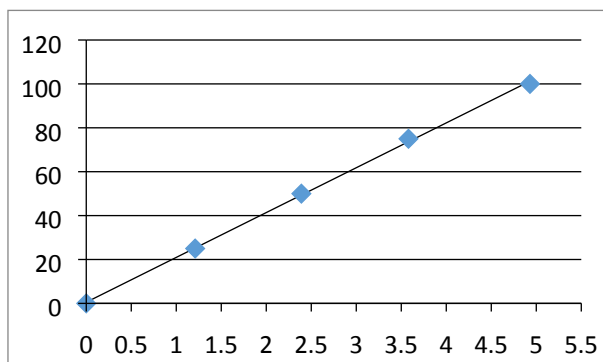
5. Calibration Curves

Shown below are calibration curves taken with different thioesters in deuterated solvents. *Ratio to aromatic* = aromatic peak of internal standard; *ratio to aliphatic* = aliphatic peak of internal standard; *thioester* = mole percentage of thioester used. For further experimental details on how this data was generated, see above (page 3 of this document). Both the thioester and solvent used are defined in the table above the calibration curves. Calibration curves with respect to the two characteristic peaks of the internal standard were generated (left – w.r.t. aromatic, right – w.r.t. aliphatic).

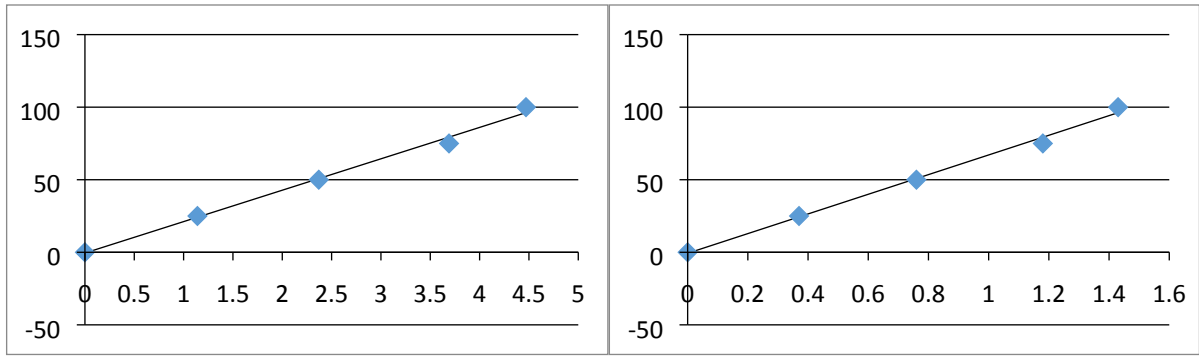
thiophenol (1a) in D ₆ -Benzene		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.05	0.34	25
2.48	0.79	50
3.9	1.25	75
4.95	1.6	100



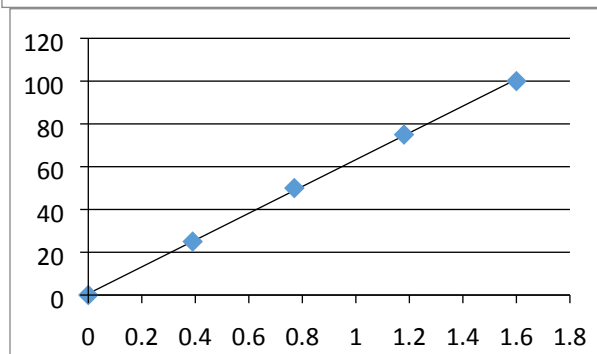
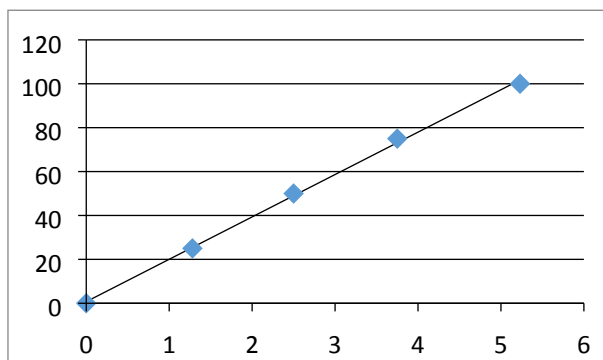
thiophenol (1a) in D₈-THF		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.21	0.38	25
2.39	0.79	50
3.58	1.13	75
4.93	1.56	100



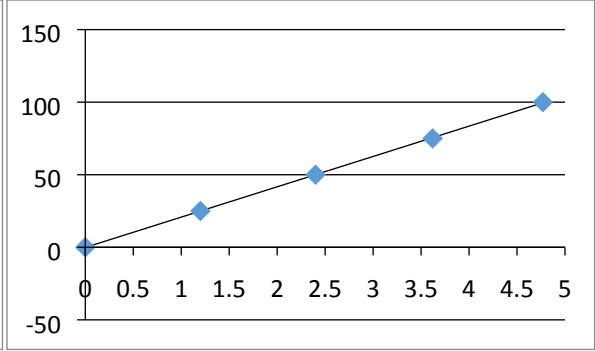
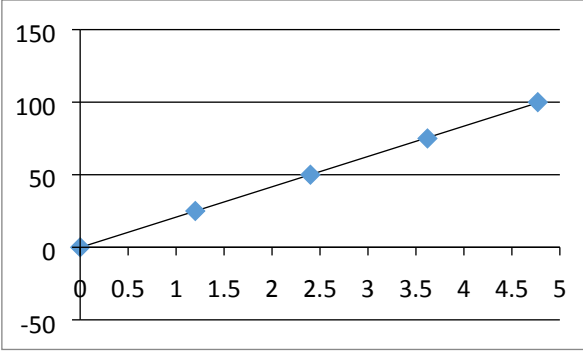
thiophenol (1a) in CDCl₃		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.14	0.37	25
2.37	0.76	50
3.69	1.18	75
4.47	1.43	100



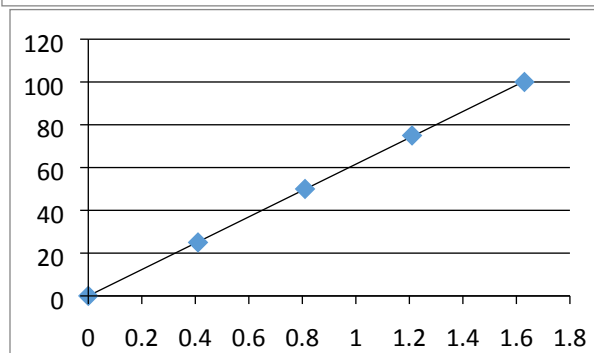
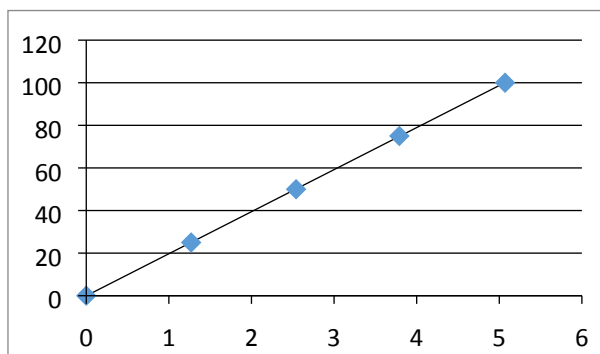
thiophenol (1a) in D₃-MeCN		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.28	0.39	25
2.5	0.77	50
3.75	1.18	75
5.23	1.6	100



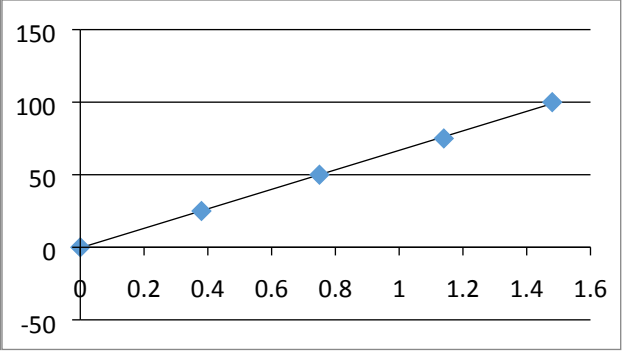
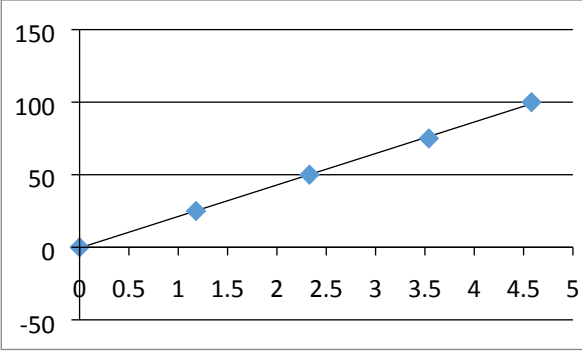
thiophenol (1a) in D₆-DMSO		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.2	0.4	25
2.4	0.78	50
3.62	1.18	75
4.77	1.56	100



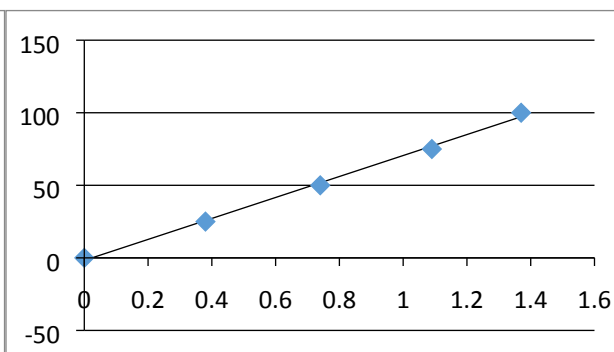
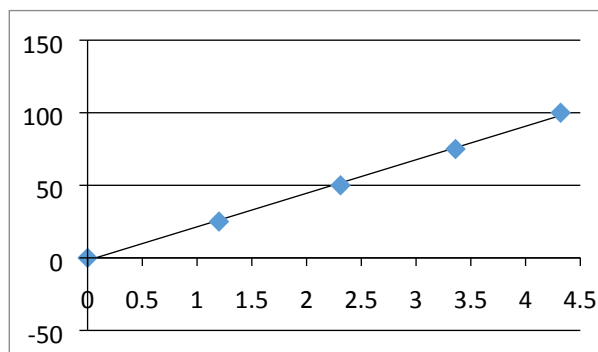
thiophenol (1a) in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.27	0.41	25
2.54	0.81	50
3.79	1.21	75
5.07	1.63	100



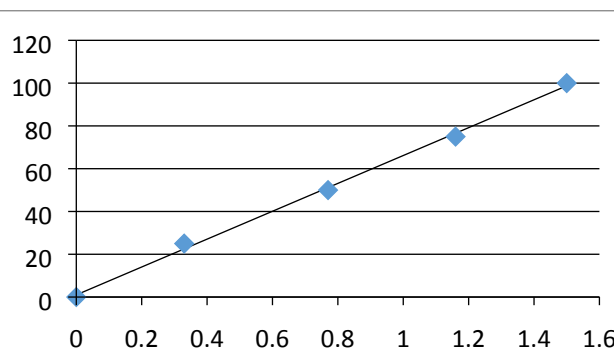
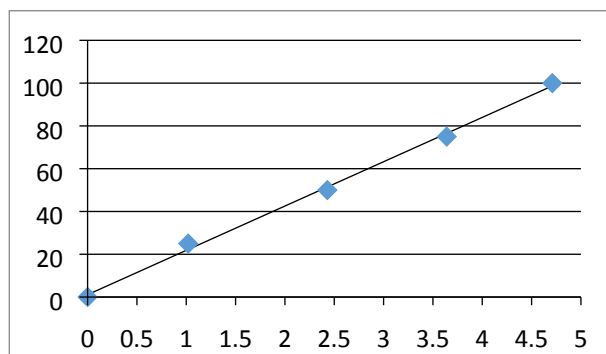
2-mercaptopyridine (1b) in D₆-Benzene		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.18	0.38	25
2.33	0.75	50
3.54	1.14	75
4.58	1.48	100



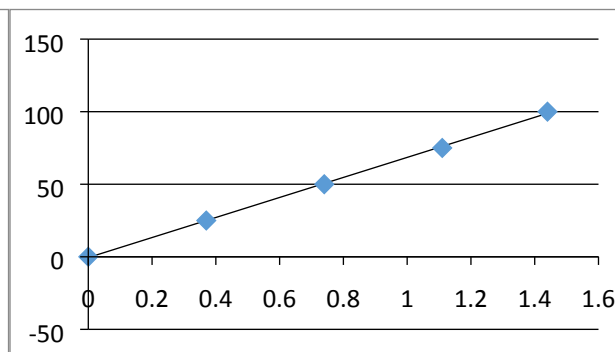
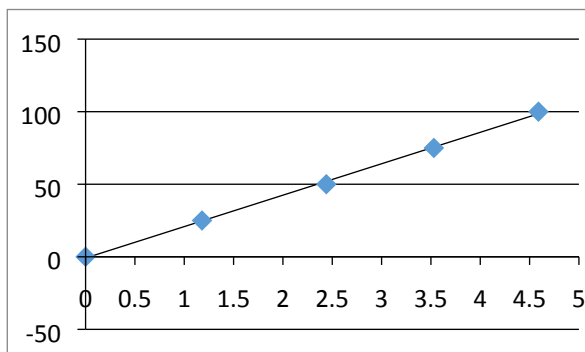
2-mercaptopyridine (1b) in D₈-THF		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.2	0.38	25
2.31	0.74	50
3.36	1.09	75
4.32	1.37	100



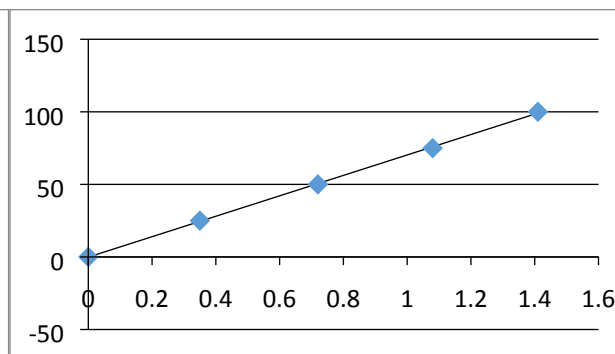
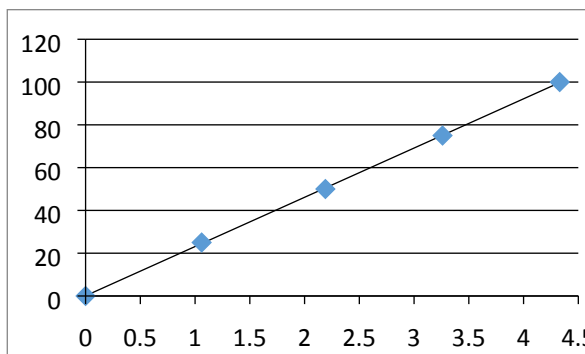
2-mercaptopyridine (1b) in CDCl₃		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.02	0.33	25
2.43	0.77	50
3.64	1.16	75
4.71	1.5	100



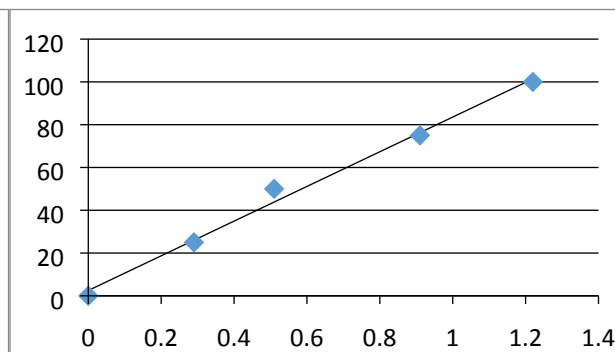
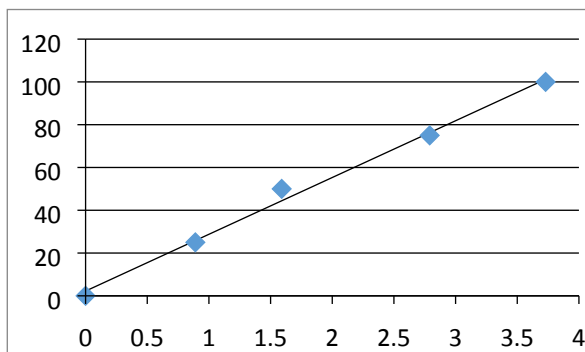
2-mercaptopyridine (1b) in D₃-MeCN		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.18	0.37	25
2.44	0.74	50
3.53	1.11	75
4.59	1.44	100



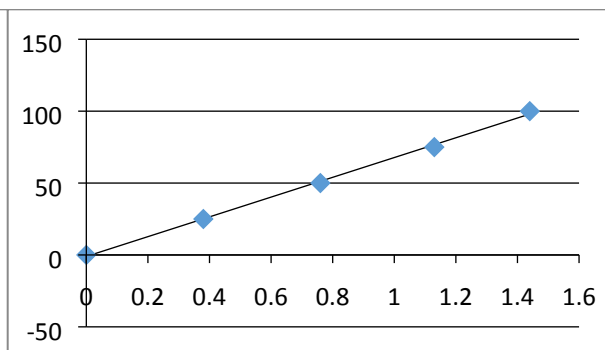
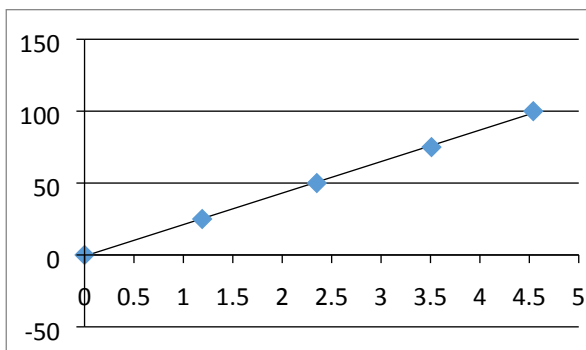
2-mercaptopyridine (1b) in D₆-DMSO		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.06	0.35	25
2.19	0.72	50
3.26	1.08	75
4.33	1.41	100



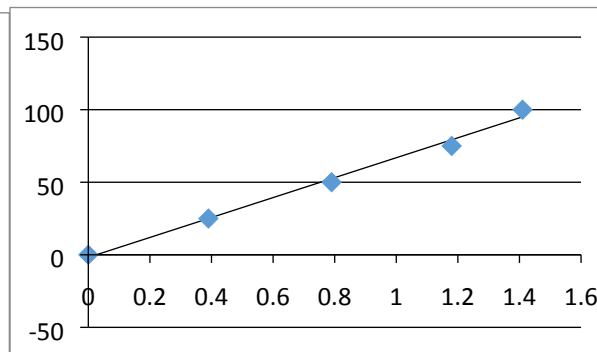
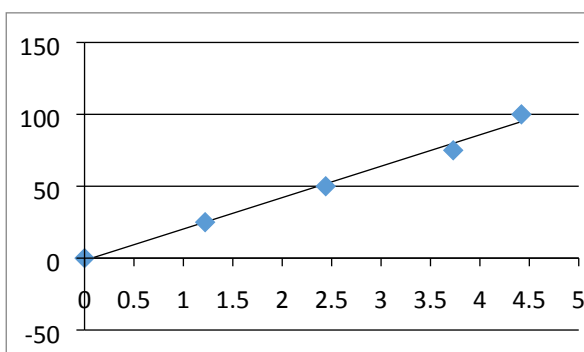
2-mercaptopyridine (1b) in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
0.89	0.29	25
1.59	0.51	50
2.79	0.91	75
3.73	1.22	100



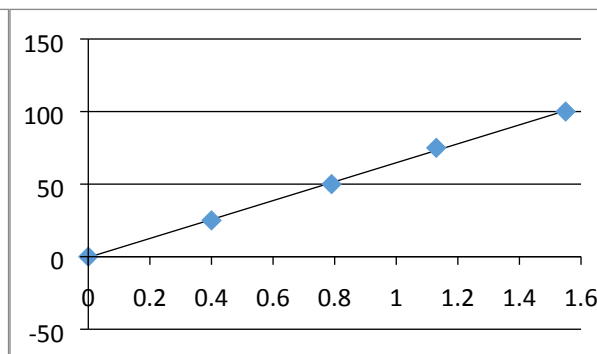
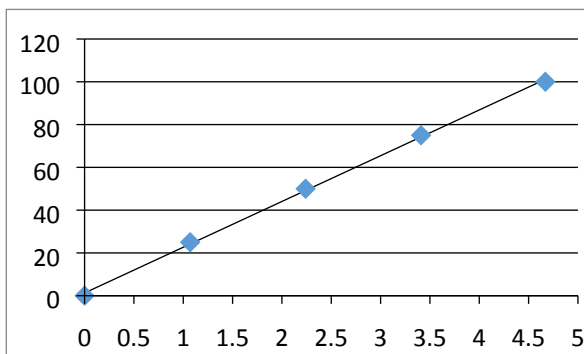
n-octanthiol (1c) in D₆-Benzene		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.19	0.38	25
2.35	0.76	50
3.51	1.13	75
4.54	1.44	100



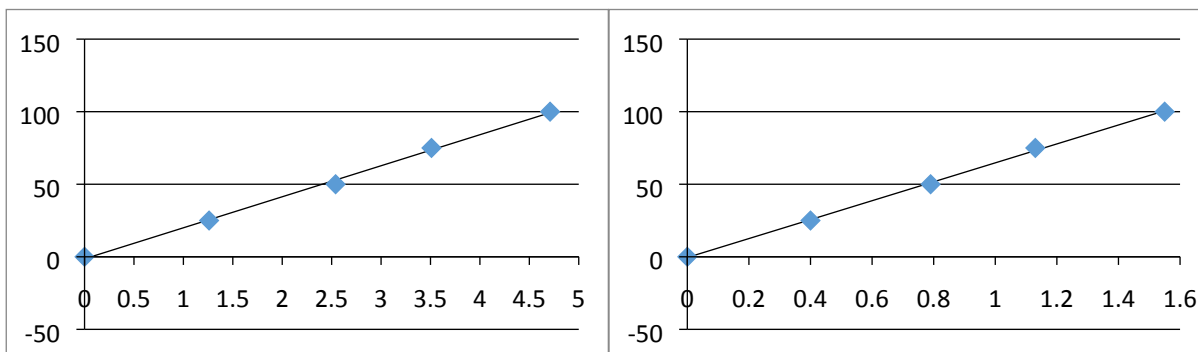
n-octanethiol (1c) in D₈-THF		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.22	0.39	25
2.44	0.79	50
3.73	1.18	75
4.42	1.41	100



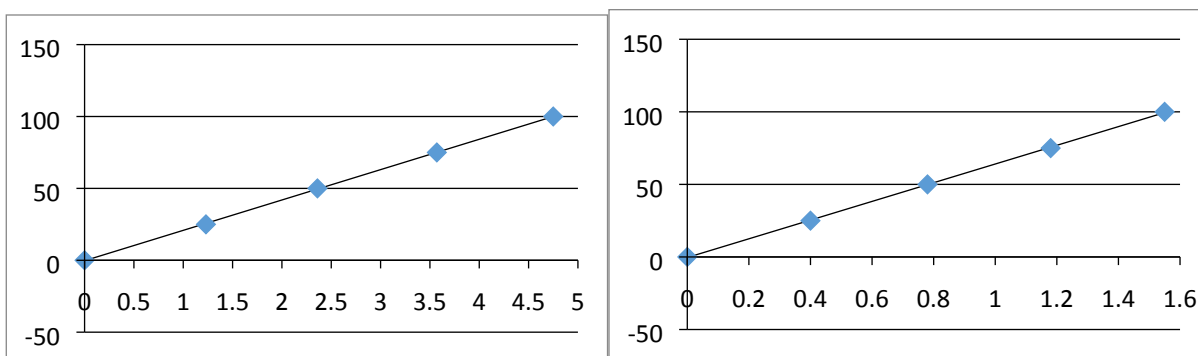
n-octanethiol (1c) in CDCl₃		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.07	0.4	25
2.24	0.79	50
3.41	1.13	75
4.67	1.55	100



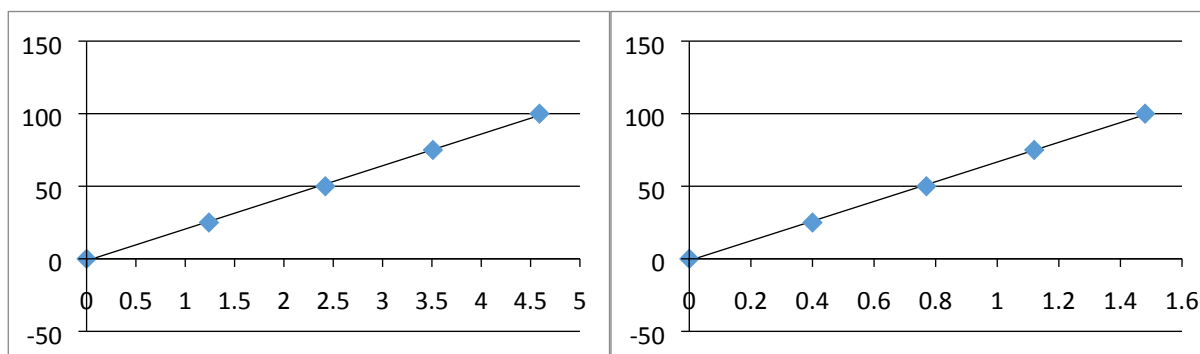
n-octanethiol (1c) in D₃-MeCN		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.26	0.4	25
2.54	0.79	50
3.51	1.13	75
4.71	1.55	100



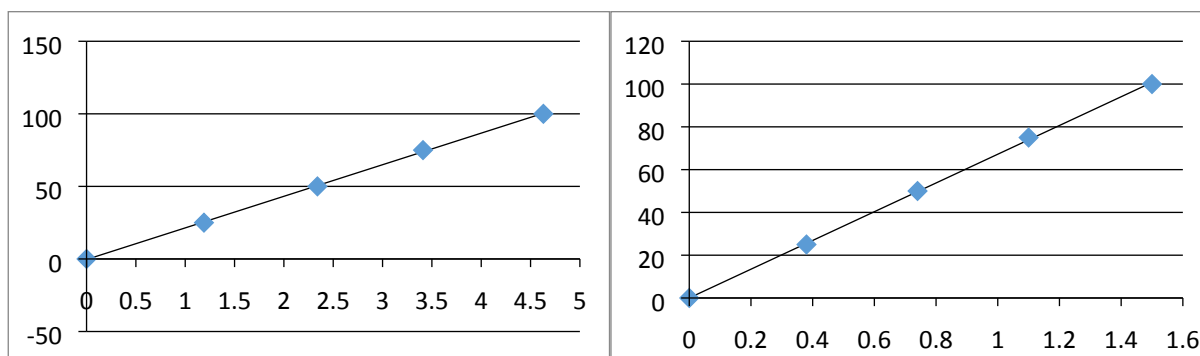
n-octanethiol (1c) in D₆-DMSO		
<i>ratio to aliphatic</i>	<i>ratio to aromatic</i>	<i>thioester</i>
0	0	0
1.23	0.4	25
2.36	0.78	50
3.57	1.18	75
4.75	1.55	100



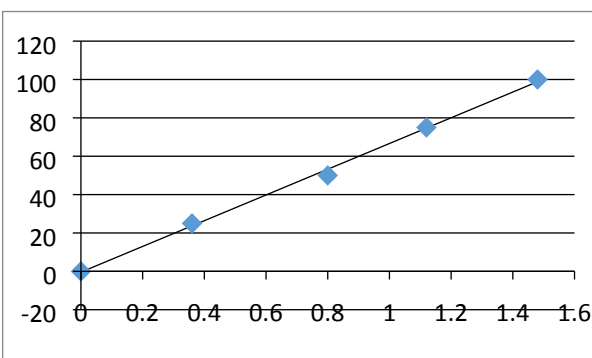
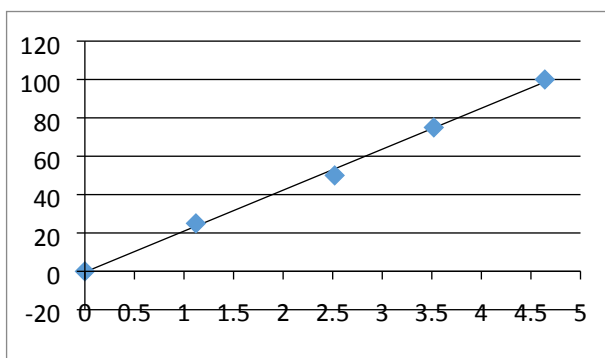
n-octanethiol (1c) in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.24	0.4	25
2.42	0.77	50
3.51	1.12	75
4.59	1.48	100



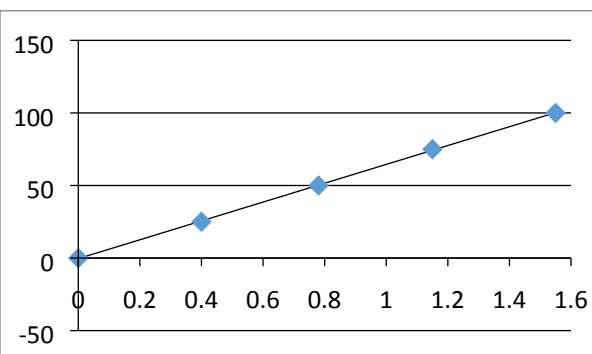
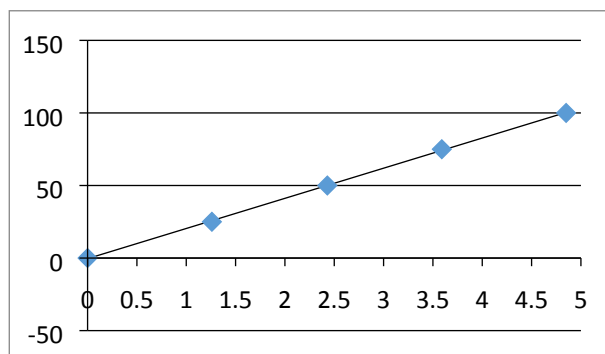
methyl-mercaptopropionate (1d) in D₆-benzene		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.19	0.38	25
2.34	0.74	50
3.41	1.1	75
4.63	1.5	100



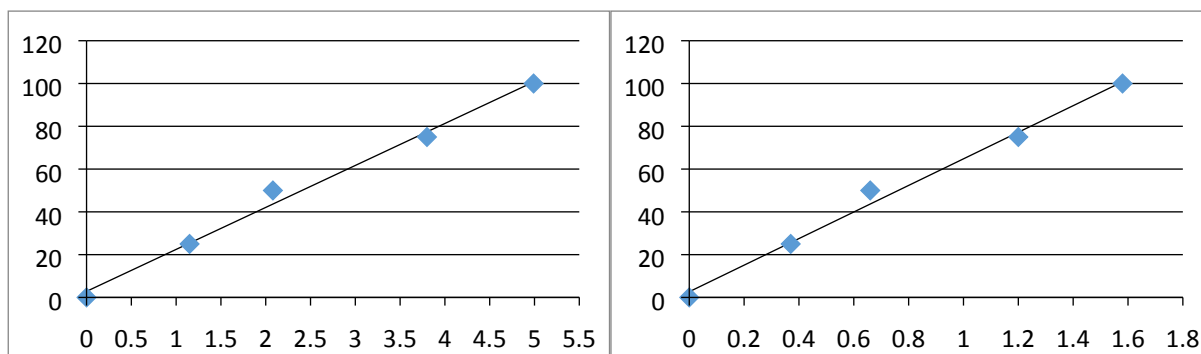
methyl-mercaptopropionate (1d) in D ₈ -THF		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.12	0.36	25
2.52	0.8	50
3.52	1.12	75
4.64	1.48	100



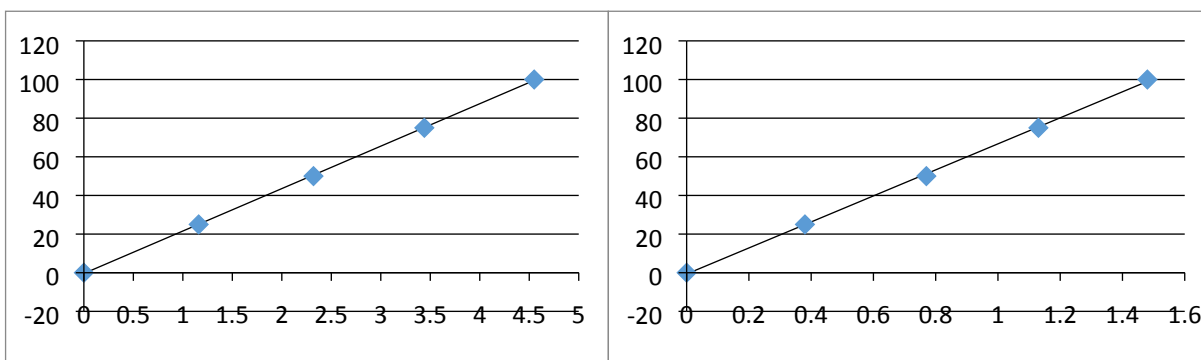
methyl-mercaptopropionate (1d) in CDCl ₃		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.26	0.4	25
2.43	0.78	50
3.59	1.15	75
4.85	1.55	100



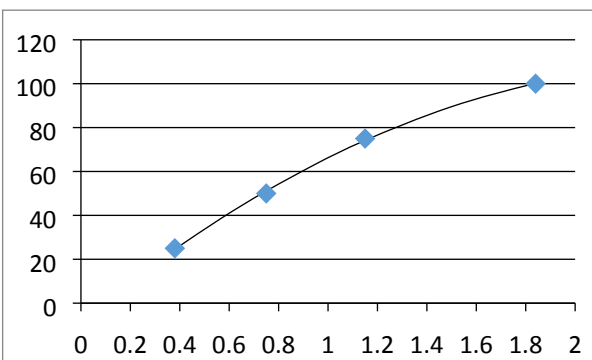
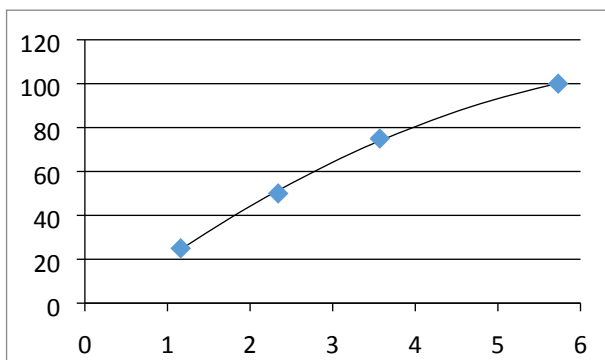
methyl-mercaptopropionate (1d) in D₃-MeCN		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.15	0.37	25
2.08	0.66	50
3.8	1.2	75
4.99	1.58	100



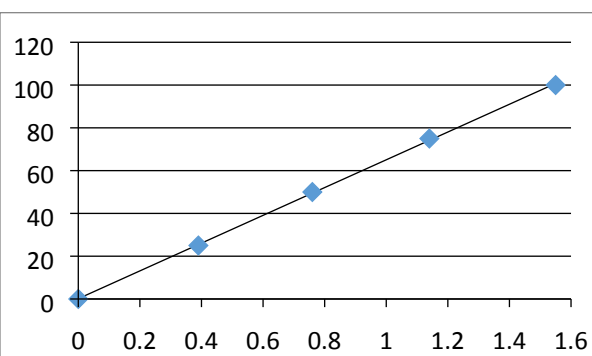
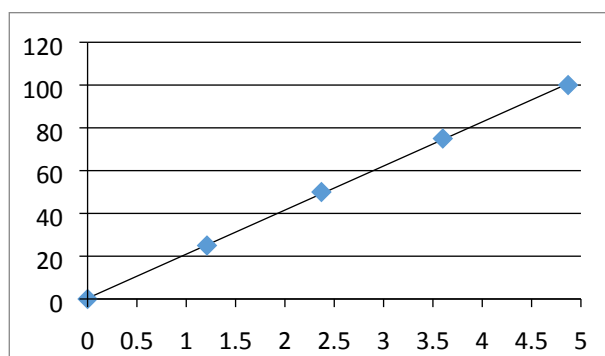
methyl-mercaptopropionate (1d) in D₆-DMSO		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.16	0.38	25
2.32	0.77	50
3.44	1.13	75
4.55	1.48	100



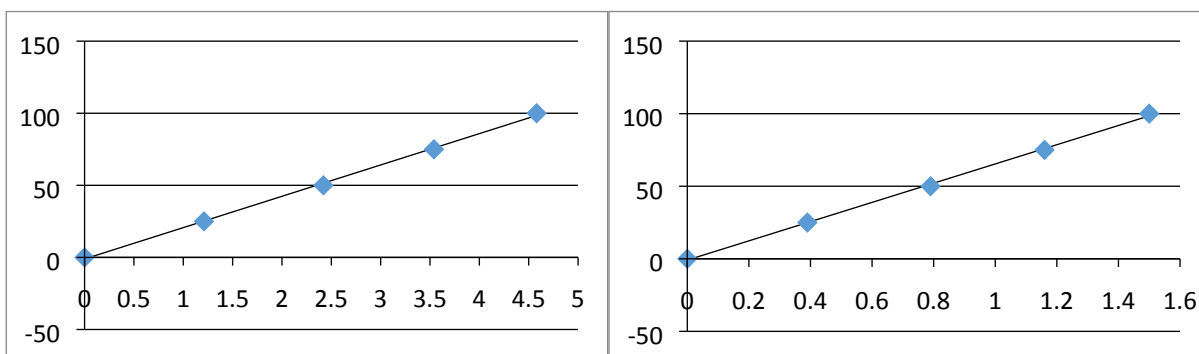
methyl-mercaptopropionate (1d) in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
1.16	0.38	25
2.34	0.75	50
3.57	1.15	75
5.73	1.84	100



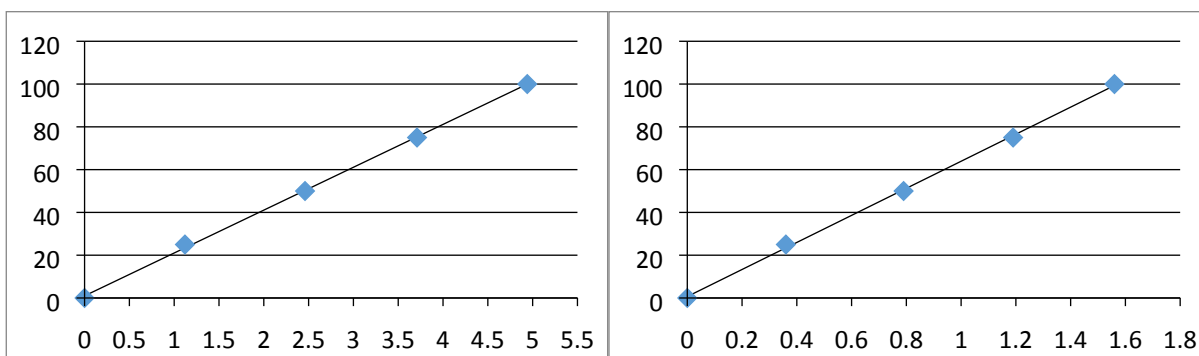
boc-cystemine (1e) in D₆-Benzene		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.21	0.39	25
2.37	0.76	50
3.6	1.14	75
4.87	1.55	100



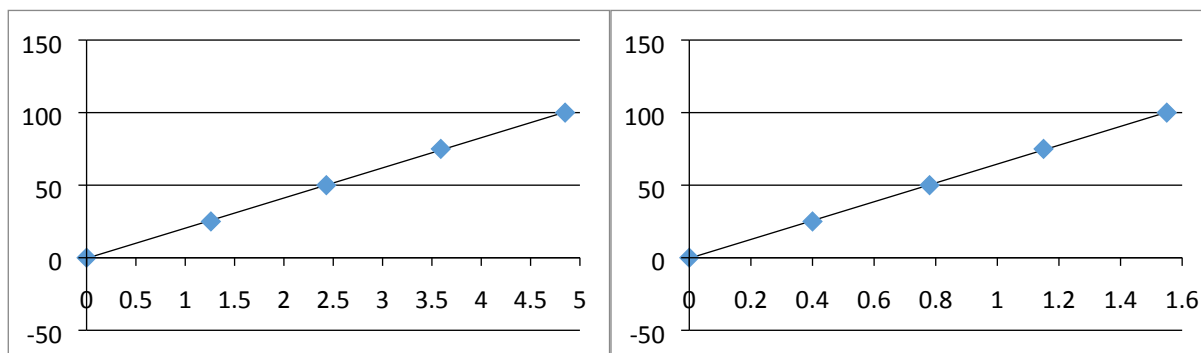
boc-cystemine (1e) in D₈-THF		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.21	0.39	25
2.42	0.79	50
3.54	1.16	75
4.58	1.5	100



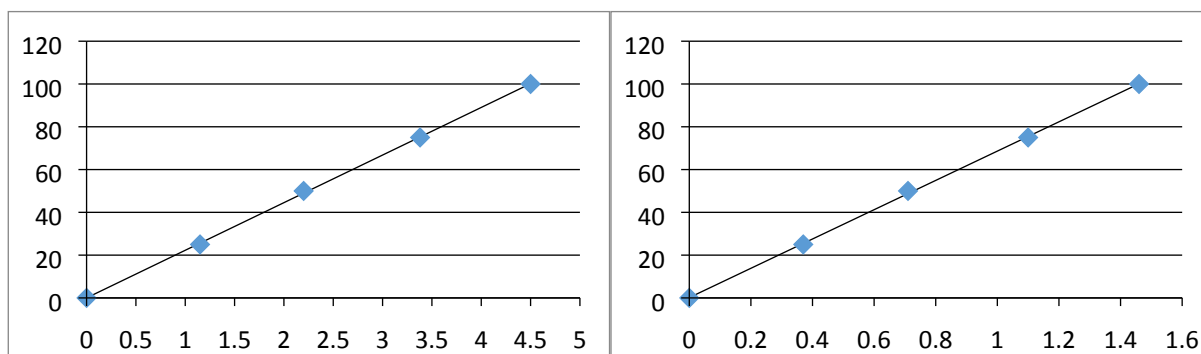
boc-cystemine (1e) in CDCl₃		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.12	0.36	25
2.46	0.79	50
3.71	1.19	75
4.94	1.56	100



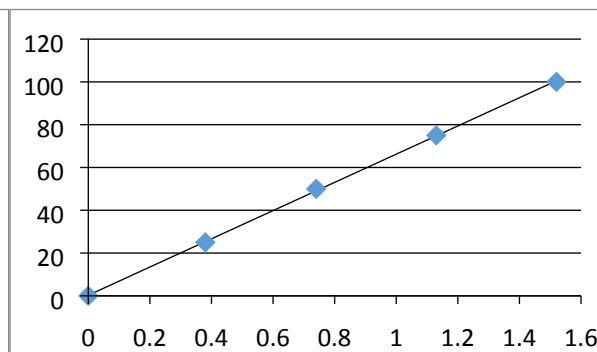
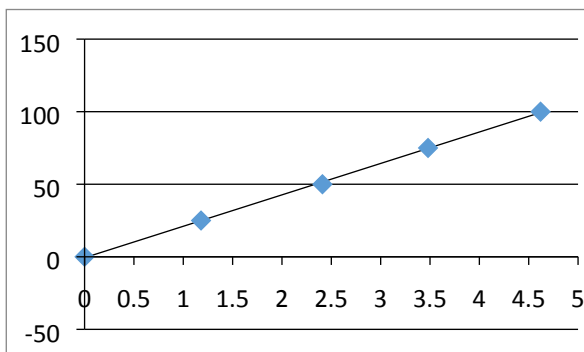
boc-cystemine (1e) in D₃-MeCN		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.26	0.4	25
2.43	0.78	50
3.59	1.15	75
4.85	1.55	100



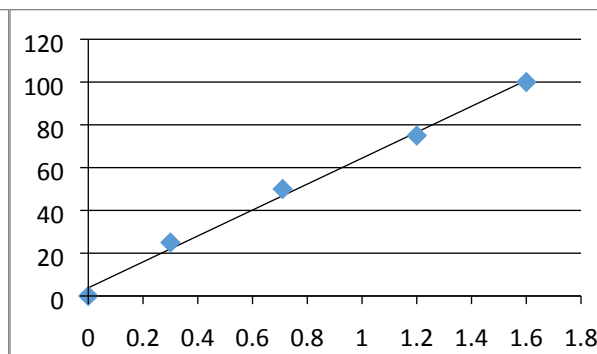
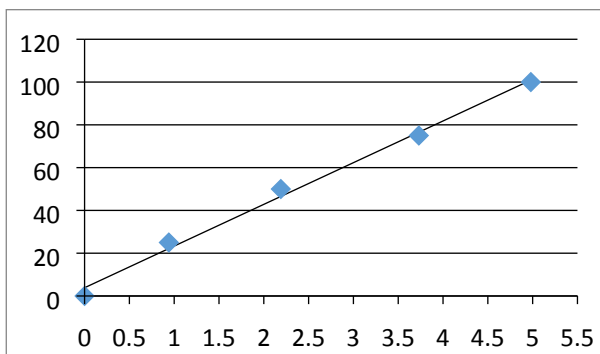
boc-cystemine (1e) in D₆-DMSO		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.15	0.37	25
2.2	0.71	50
3.38	1.1	75
4.5	1.46	100



boc-cystemine (1e) in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
1.18	0.38	25
2.41	0.74	50
3.48	1.13	75
4.62	1.52	100



methyl acetate in D₃-MeOD		
<i>ratio to aromatic</i>	<i>ratio to aliphatic</i>	<i>thioester</i>
0	0	0
0.94	0.3	25
2.19	0.71	50
3.73	1.2	75
4.98	1.6	100



6. Raw and Processed Exchange Data

Below are charts of the processed exchange data, the solvent employed as well as the thioester (**1**) and thiol (**2**) exchanged are labeled within the table in context of their use. For further experimental details on how this data was generated and the workflow for generating percentages, see above (page 5 of this document).

Below are the raw and processed data which generated **Fig. 3** of the main manuscript:

THF		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K _{eq}
1a/2b	IS-Aro	4.55		93.4704		93			
	IS-Ali	1.44		93.113		93	93	-	-
1a/2c	IS-Aro	4.52		92.85756		93			
	IS-Ali	1.44		93.113		93	93	-	-
1a/2d	IS-Aro	4.56		93.67468		94			
	IS-Ali	1.46		94.4038		94	94	-	-
1a/2e	IS-Aro	4.51		92.65328		93			
	IS-Ali	1.46		94.4038		94	94	-	-
1b/2a	IS-Aro	2.24	2.38	50.04668	53.28166	103			
	IS-Ali	0.73	0.77	51.01149	53.90161	105	104	TE/SH	1.06
1b/2c	IS-Aro	3.12	1.27	70.38084	27.63289	98			
	IS-Ali	1.02	0.42	71.96486	28.61306	101	99	TE	0.40
1b/2d	IS-Aro	2.75	1.57	61.83125	34.56499	96			
	IS-Ali	0.9	0.51	63.2945	35.11583	98	97	TE	0.55
1b/2e	IS-Aro	2.58	1.83	57.90306	40.57281	98			
	IS-Ali	0.85	0.6	59.68185	41.6186	101	100	TE	0.70
1c/2a	IS-Aro					0			
	IS-Ali					0	0		
1c/2b	IS-Aro	4.33		92.97052		93			
	IS-Ali	1.33		89.55781		90	91	-	-
1c/2d	IS-Aro	4.22		90.56878		91			
	IS-Ali	1.36		91.61812		92	91	-	-
1c/2e	IS-Aro	4.3		92.3155		92			

THF Contd.		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
	IS-Ali	1.37		92.30489		92	92	-	-
1d/2a	IS-Aro	4.35		92.4864		92			
	IS-Ali	1.37		91.44119		91	92	-	-
1d/2b	IS-Aro	4.22		89.7109		90			
	IS-Ali	1.32		88.08834		88	89	-	-
1d/2c	IS-Aro	4.23		89.9244		90			
	IS-Ali	1.34		89.42948		89	90	-	-
1d/2e	IS-Aro	4.17		88.6434		89			
	IS-Ali	1.31		87.41777		87	88	-	-
1e/2a	IS-Aro	4.22		90.6444		91			
	IS-Ali	1.34		87.89372		88	89	-	-
1e/2b	IS-Aro	3.99		85.64535		86			
	IS-Ali	1.33		87.23124		87	86	-	-
1e/2c	IS-Aro	4.2		90.2097		90			
	IS-Ali	1.39		91.20612		91	91	-	-
1e/2d	IS-Aro	4.06		87.1668		87			
	IS-Ali	1.33		87.23124		87	87	-	-

CDCl₃		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K _{eq}
1a/2b	IS-Aro	5.39		116.12213		116			
	IS-Ali	1.64		110.43112		110	113	-	-
1a/2c	IS-Aro	4.9		105.52		106			
	IS-Ali	1.57		105.68876		106	106	-	-
1a/2d	IS-Aro	4.79	0.18	103.13993	3.39336	107			
	IS-Ali	1.54	0.06	103.65632	3.38928	107	107	TE (above 90)	0.03
1a/2e	IS-Aro	4.71	0.28	101.40897	5.55706	107			
	IS-Ali	1.51	0.09	101.62388	5.42172	107	107	TE (above 90)	0.05
1b/2a	IS-Aro	0.19	4.36	5.04986	91.42724	96			
	IS-Ali	0.06	1.39	4.92216	91.55969	96	96	SH (above 90)	18.6 0
1b/2c	IS-Aro	3.92	0.58	82.31308	13.12832	95			
	IS-Ali	1.26	0.19	83.09136	13.39049	96	96	TE	0.16
1b/2d	IS-Aro	2.76	1.65	58.28484	35.2923	94			
	IS-Ali	0.88	0.52	58.33778	34.88702	93	93	TE	0.60
1b/2e	IS-Aro	2.62	1.89	55.38488	40.26366	96			
	IS-Ali	0.83	0.6	55.08073	40.0983	95	95	TE	0.73
1c/2a	IS-Aro	4.63		100.30201		100			
	IS-Ali	1.4		90.8267		91	96	-	-
1c/2b	IS-Aro	4.61		99.87427		100			
	IS-Ali	1.39		90.17451		90	95	-	-
1c/2d	IS-Aro	4.53		98.16331		98			
	IS-Ali	1.41		91.47889		91	95	-	-
1c/2e	IS-Aro	4.54		98.37718		98			
	IS-Ali	1.43		92.78327		93	96	-	-
1d/2a	IS-Aro	3.78		78.13028		78			
	IS-Ali	1.18		76.22874		76	77	-	-
CDCl₃		ratio	ratio	percent	percent	total	avg	towards	K _{eq}

contd.		(remaining)	(exchanged)	(remaining)	(exchanged)				
1d/2b	IS-Aro	4.68		96.82868		97			
	IS-Ali	1.39		89.86257		90	93	-	-
1d/2c	IS-Aro	4.63		95.78988		96			
	IS-Ali	1.46		94.40718		94	95	-	-
1d/2e	IS-Aro	4.64		95.99764		96			
	IS-Ali	1.46		94.40718		94	95	-	-
1e/2a	IS-Aro	4.22		85.54272		86			
	IS-Ali	1.34		85.4176		85	85	-	-
1e/2b	IS-Aro	4.58		92.75568		93			
	IS-Ali	1.39		88.57985		89	91	-	-
1e/2c	IS-Aro	4.55		92.1546		92			
	IS-Ali	1.45		92.37455		92	92	-	-
1e/2d	IS-Aro	4.45		90.151		90			
	IS-Ali	1.42		90.4772		90	90	-	-

MeCN		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
1a/2b	IS-Aro	insoluble							
	IS-Ali								
1a/2c	IS-Aro	3.9	0.98	76.0306	19.6454	96			
	IS-Ali	1.14	0.29	72.0455	18.81	91	93	TE	0.26
1a/2d	IS-Aro	1.45	3.41	28.7211	66.5687	95			
	IS-Ali	0.4	0.95	25.6993	60.1458	86	91	SH	2.34
1a/2e	IS-Aro	0.94	3.62	18.873	70.6238	89			
	IS-Ali	0.36	1.07	23.1941	67.6614	91	90	SH	2.92
1b/2a	IS-Aro	0.94	3.62	19.50578	77.54654	97			
	IS-Ali	0.3	1.16	20.1803	79.54352	100	98	SH	3.94
1b/2c	IS-Aro	1.48	3.21	31.20056	68.66717	100			
	IS-Ali	0.47	1.02	31.91489	69.87974	102	101	SH	2.19
1b/2d	IS-Aro	0.24	4.42	4.34588	94.87214	99			
	IS-Ali	0.08	1.41	4.99436	96.80027	102	101	SH (above 90)	
1b/2e	IS-Aro	0.7	3.96	14.3081	84.90992	99			
	IS-Ali	0.22	1.26	14.65814	86.44622	101	100	SH	5.90
1c/2a	IS-Aro	4.54		95.66382		96			
	IS-Ali	1.32		85.60918		86	91	-	-
1c/2b	IS-Aro	insoluble							
	IS-Ali								
1c/2d	IS-Aro	4.58		96.51894		97			
	IS-Ali	1.44		93.43546		93	95	-	-
1c/2e	IS-Aro	4.43		93.31224		93			
	IS-Ali	1.4		90.8267		91	92	-	-
1d/2a	IS-Aro	4.61	0.33	93.2807	9.3071	103			
	IS-Ali	1.32	0.09	84.66446	8.25317	93	98	TE (above 90)	0.07
1d/2b	IS-Aro	insoluble							
MeCN		ratio	ratio	percent	percent	total	avg	towards	K_{eq}

Contd.		(remaining)	(exchanged)	(remaining)	(exchanged)				
	IS-Ali								
1d/2c	IS-Aro	4.7		95.0465		95			
	IS-Ali	1.48		94.60414		95	95	-	-
1d/2e	IS-Aro	3.09	1.62	63.4583	34.6169	98			
	IS-Ali	0.97	0.51	62.92141	34.34483	97	98	TE	0.52
1e/2a	IS-Aro	4.1	0.65	84.7786	13.1014	98			
	IS-Ali	1.19	0.19	76.87797	11.95497	89	93	TE	0.16
1e/2b	IS-Aro	insoluble							
	IS-Ali								
1e/2c	IS-Aro	4.2	0.36	86.8562	7.07636	94			
	IS-Ali	1.32	0.11	85.31796	6.76113	92	93	TE (above 90)	0.09
1e/2d	IS-Aro	2.82	1.72	58.18532	35.33172	94			
	IS-Ali	0.88	0.54	56.75184	34.67802	91	92	TE	0.61

DMSO		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
1a/2b	IS-Aro	4.35		90.79785		91			
	IS-Ali	1.41		90.12578		90	90	-	-
1a/2c	IS-Aro	1.1	3.17	22.8696	66.13467	89			
	IS-Ali	0.36	1.04	22.82288	66.40952	89	89	SH	2.91
1a/2d	IS-Aro	0.93	3.34	19.31643	69.68784	89			
	IS-Ali	0.3	1.09	18.977	69.61442	89	89	SH	3.67
1a/2e	IS-Aro	0.83	3.56	17.22633	74.28606	92			
	IS-Ali	0.27	1.16	17.05406	74.10128	91	91	SH	4.35
1b/2a	IS-Aro	1.51	2.51	34.85398	57.87198	93			
	IS-Ali	0.49	0.82	34.37181	57.60348	92	92	SH	1.68
1b/2c	IS-Aro	0.07	4.07	1.70806	93.78006	95			
	IS-Ali	0.02	1.32	1.28428	92.80298	94	95	SH	72.26
1b/2d	IS-Aro	0.31	3.78	7.23238	87.10484	94			
	IS-Ali	0.1	1.24	6.9162	87.17106	94	94	SH	12.60
1b/2e	IS-Aro	0.36	3.75	8.38328	86.4143	95			
	IS-Ali	0.12	1.23	8.32418	86.46707	95	95	SH	10.39
1c/2a	IS-Aro	4.25		89.4366		89			
	IS-Ali	1.39		89.16937		89	89	-	-
1c/2b	IS-Aro	4.28		90.06996		90			
	IS-Ali	1.38		88.52514		89	89	-	-
1c/2d	IS-Aro	2.51	1.66	52.70172	34.75652	87			
	IS-Ali	0.81	0.54	51.80403	34.40982	86	87	TE	0.66
1c/2e	IS-Aro	2.72	1.9	57.13524	39.8234	97			
	IS-Ali	0.88	0.61	56.31364	38.91943	95	96	TE	0.69
1d/2a	IS-Aro	3.71	0.42	81.10416	8.83602	90			
	IS-Ali	1.21	0.14	80.84793	8.78022	90	90	SH	0.11
DMSO		ratio	ratio	percent	percent	total	avg	towards	K_{eq}

Contd.		(remaining)	(exchanged)	(remaining)	(exchanged)				
1d/2b	IS-Aro	4.21		92.08716		92			
	IS-Ali	1.37		91.62441		92	92	-	-
1d/2c	IS-Aro	2.27	1.93	49.47312	42.00468	91			
	IS-Ali	0.62	0.73	41.10966	48.51849	90	91	equal	1.18
1d/2e	IS-Aro	2.19	2.16	47.71584	47.05686	95			
	IS-Ali	0.71	0.7	47.17143	46.4979	94	94	equal	0.99
1e/2a	IS-Aro	3.73	0.52	83.02688	11.58512	95			
	IS-Ali	1.21	0.17	83.00301	11.79317	95	95	TE	0.14
1e/2b	IS-Aro	4.23		94.15488		94			
	IS-Ali	1.38		94.64308		95	94	-	-
1e/2c	IS-Aro	2.14	2.61	47.63984	58.10016	106			
	IS-Ali	0.69	0.85	47.39809	58.35345	106	106	equal	1.23
1e/2d	IS-Aro	2.1	1.72	46.7496	38.29232	85			
	IS-Ali	0.68	0.56	46.71338	38.49686	85	85	TE	0.82

MeOH		ratio (remaining)	ratio (exchanged)	ratio (hydrolyzed)	percent (remaining)	percent (exchanged)	percent (hydrolyzed)	total	avg	twrds	K _{eq}
1a/2b	IS-Aro	3.66		0.54	72.25		14.38	87			
	IS-Ali	1.04		0.15	64.04		12.90	77	82	-	-
1a/2c	IS-Aro	1.73	2.8	0.04	34.13	55.26	4.63	94			
	IS-Ali	0.53	0.87	0.01	32.64	53.57	4.41	91	92	SH	1.64
1a/2d	IS-Aro	0.72	4.06	0.02	14.19	80.14	4.24	99			
	IS-Ali	0.22	1.24	0	13.55	76.35	3.81	94	96	SH	5.64
1a/2e	IS-Aro	0.95	3.75	0.02	18.73	74.02	4.24	97			
	IS-Ali	0.29	1.14	0.01	17.86	70.20	4.41	92	95	SH	3.93
1b/2a	IS-Aro	n/d	2.93	1.17		79.99	26.65	107			
	IS-Ali	n/d	0.91	0.37		76.26	26.24	103	105	SH	n/d
1b/2c	IS-Aro	n/d	3.69	0.95		100.16	22.37	123			
	IS-Ali	n/d	1.15	0.3		95.72	21.99	118	120	SH	n/d
1b/2d	IS-Aro	n/d	3.84	0.87		104.14	20.81	125			
	IS-Ali	n/d	1.18	0.27		98.15	20.18	118	122	SH	n/d
1b/2e	IS-Aro	n/d	3.58	0.98		97.24	22.95	120			
	IS-Ali	n/d	1.15	0.31		95.72	22.60	118	119	SH	n/d
1c/2a	IS-Aro	4.14	0.09		89.00	4.62		94			
	IS-Ali	1.24	0.03		83.00	4.93		88	91	TE (above 90%)	-
1c/2b	IS-Aro	4.21		0.09	90.53		5.61	96			
	IS-Ali	1.26		0.03	84.35		5.63	90	93	TE (above 90%)	-
1c/2d	IS-Aro	2.39	1.7	0.26	50.83	35.78	8.92	96			
	IS-Ali	0.76	0.54	0.08	50.41	35.47	8.66	95	95	TE	0.70
1c/2e	IS-Aro	2.51	1.64	0.26	53.45	34.47	8.92	97			
MeOH		ratio	ratio	ratio	percent	percent	percent	total	avg	twrds	K_{eq}

contd.		(remaining)	(exchanged)	(hydrolyzed)	(remaining)	(exchanged)	(hydrolyzed)				
	IS-Ali	0.79	0.51	0.08	52.44	33.43	8.66	95	96	TE	0.64
1d/2a	IS-Aro	4	0.45		80.54	5.85		86			
	IS-Ali	1.17	0.13		75.16	3.80		79	83	TE (above 90%)	-
1d/2b	IS-Aro	3.9		0.23	79.07	-6.92	8.33	80			
	IS-Ali	1.22		0.07	77.59	-7.90	8.05	78	79	-	-
1d/2c	IS-Aro	1.64	2.22	0.29	36.03	48.86	9.50	94			
	IS-Ali	0.51	0.69	0.09	34.47	47.14	9.26	91	93	SH	1.37
1d/2e	IS-Aro	2.18	1.69	0.38	48.02	37.19	11.26	96			
	IS-Ali	0.63	0.49	0.11	43.05	32.98	10.48	87	91	TE	0.77
1e/2a	IS-Aro	3.76	0.53		80.79	10.85		92			
	IS-Ali	1.18	0.17		78.09	11.49		90	91	TE	0.15
1e/2b	IS-Aro	4.07	0.29		87.50	5.66		93			
	IS-Ali	1.25	0.09		82.71	6.21		89	91	TE	0.08
1e/2c	IS-Aro	1.62	2.4	0.25	34.45	51.34	8.72	95			
	IS-Ali	0.51	0.76	0.08	33.91	50.40	8.66	93	94	SH	1.49
1e/2d	IS-Aro	1.93	2.01	0.3	41.17	42.90	9.70	94			
	IS-Ali	0.61	0.63	0.09	40.50	41.82	9.26	92	93	equal	1.03

Below is the raw and processed data which generated **Table 1** of the manuscript:

w/ pyridine		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
CDCl₃									
1a/2c	IS-Aro	4.75		102.27445		102			
	IS-Ali	1.51		101.62388		102	102	-	-
THF									
1a/2c	IS-Aro	4.73		97.14744		97			
	IS-Ali	1.49		96.34		96	97	-	-
MeCN									
1a/2c	IS-Aro	4.94		96.113		96			
	IS-Ali	1.53		96.4712		96	96	-	-

w/ DBU		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
CDCl₃									
1a/2c	IS-Aro	1.74	1.9	37.14708	39.0714	76			
	IS-Ali	0.85	0.59	56.9102	37.92417	95	86	TE	0.67
THF									
1a/2c	IS-Aro	1.06	3.66	22.17668	77.7549	100			
	IS-Ali	0.31	1.07	20.1828	71.32409	92	96	SH	3.53
MeCN									
1a/2c	IS-Aro	1.58	3.31	31.2314	67.7672	99			
	IS-Ali	0.47	0.98	30.0834	63.54264	94	96	SH	2.11

w/ BEMP		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K _{eq}
CDCI₃									
1a/2c	IS-Aro	3.27	1.53	70.25169	31.38428	102			
	IS-Ali	0.98	0.46	65.71744	29.48418	95	98	TE	0.45
THF									
1a/2c	IS-Aro	1.32	3.42	27.48796	72.6309	100			
	IS-Ali	0.39	1	25.346	66.6301	92	96	SH	2.63
MeCN									
1a/2c	IS-Aro	1.36	3.63	26.9832	74.0456	101			
	IS-Ali	0.4	1.08	25.6993	69.75494	95	98	SH	2.71

Below is the raw and processed data that generated **Table 3** of the manuscript:

w/ DMAP		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K _{eq}
CDCI₃									
1a/2c	IS-Aro	4.79	0.01	103.13993	-0.19524	103			
	IS-Ali	1.53	0	102.97884	-0.3804	103	103	TE	0.00
THF									
1a/2c	IS-Aro	5.07	0.01	104.09296	-0.1726	104			
	IS-Ali	1.63	0	105.3756	-0.4269	105	104	TE	0.00
MeCN									
1a/2c	IS-Aro	4.4	0.37	85.6856	10.0844	96			
	IS-Ali	1.31	0.11	82.6926	9.49563	92	94	TE	0.11
DMSO									
1a/2c	IS-Aro	1.74	2.64	36.24624	55.44628	92			
	IS-Ali	0.56	0.85	35.64248	54.38095	90	91	TE	1.53

w/ DABCO		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
CDCl₃									
1a/2c	IS-Aro	4.81	0.04	103.57267	0.42804	104			
	IS-Ali	1.53	0.01	102.97884	0.26883	103	104	TE	0.00
THF									
1a/2c	IS-Aro	5.26	0.06	107.97428	0.8949	109			
	IS-Ali	1.53	0.02	98.9216	0.91424	100	104	TE	0.01
MeCN									
1a/2c	IS-Aro	3.77	0.98	73.5203	22.0526	96			
	IS-Ali	1.08	0.28	68.2877	20.05654	88	92	TE	0.29
DMSO									
1a/2c	IS-Aro	1.17	3.2	24.33267	67.269	92			
	IS-Ali	0.36	1	22.82288	64.0444	87	89	SH	2.81

w/ quin.		ratio (remaining)	ratio (exchanged)	percent (remaining)	percent (exchanged)	total	avg	towards	K_{eq}
CDCl₃									
1a/2c	IS-Aro	4.55	0.35	97.94705	6.8686	105			
	IS-Ali	1.43	0.11	96.20404	6.76113	103	104	TE	0.07
THF									
1a/2c	IS-Aro	4.93	0.27	101.23304	5.3784	107			
	IS-Ali	1.55	0.08	100.2124	4.93766	105	106	TE	0.05
MeCN									
1a/2c	IS-Aro	2.51	2.46	49.1897	51.0902	100			
	IS-Ali	0.71	0.69	45.1146	45.52697	91	95	TE/SH	1.01
DMSO									
1a/2c	IS-Aro	1.03	3.29	21.40653	69.16908	91			
	IS-Ali	0.33	1.06	20.89994	67.90978	89	90	SH	3.25