

**FUNCTIONAL GROUP TOLERANT NICKEL-CATALYZED CROSS-COUPLING  
REACTION FOR ENANTIOSELECTIVE CONSTRUCTION OF 3<sup>0</sup> METHYL-BEARING  
STEREOCENTERS**

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## **I. GENERAL PROCEDURES**

All reactions were set up under an atmosphere of  $\text{N}_2$ . All glassware was either oven or flame-dried prior to use. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrahydrofuran (THF) and toluene (PhMe) were degassed with argon and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 h) to remove  $\text{H}_2\text{O}$ . All other solvents were purchased “anhydrous” commercially, or purified as

described (vide infra). Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific or silver-impregnated silica gel.<sup>1</sup> Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with *p*-anisaldehyde (PAA), cerium-ammonium-molybdate (CAM), or potassium permanganate (KMnO<sub>4</sub>) solutions. Melting points (mp) were obtained using a Mel-Temp melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on Bruker GN-500 (500 MHz <sup>1</sup>H, 125.7 MHz <sup>13</sup>C), CRYO-500 (500 MHz <sup>1</sup>H, 125.7 MHz <sup>13</sup>C), DRX-400 (400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C, 376.5 MHz <sup>19</sup>F) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data is reported as follows: chemical shift, multiplicity [singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), pentet (p), doublet of doublets (dd), broad doublet of doublets (br dd), doublet of triplets (dt), doublet of quartets (dq), doublet of pentets (dp), doublet of doublet of doublets (ddd), doublet of triplet of doublets (dtd), doublet of doublet of doublets of doublets (dddd), triplet of doublets (td), triplet of triplets (tt), quartet of doublets (qd), apparent triplet (at), apparent pentet (ap), apparent sextet (as), apparent doublet of doublets (add), apparent pentet of doublets (apd), multiplet (m)], coupling constants [Hz], integration. Carbon chemical shifts are reported in ppm (δ) relative to the respective solvent resonance as the internal standard (CDCl<sub>3</sub>, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 °C. Infrared spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm<sup>-1</sup>). High-resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Optical rotations were measured with a Rudolph Research Analytical Autopol III Automatic Polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (AS-H, AD-H, OD-H, or OJ-H; 100 psi, 215 nm, 50 °C).

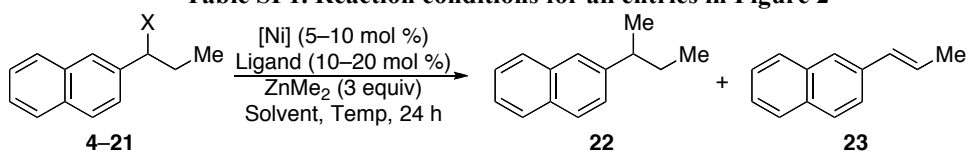
All Grignard and zinc reagents were titrated with iodine prior to use.<sup>2</sup> Activated manganese oxide was prepared according to a procedure reported by Attenburrow.<sup>3</sup> [{(R)-H<sub>8</sub>-BINOLate}Ti(O*i*-Pr)<sub>2</sub>]<sub>n</sub> **SI 24** (0.13 g, 0.28 mmol, 0.10 equiv) was prepared according to a procedure reported by Walsh.<sup>4</sup> 2-naphthyltitanium triisopropoxide **SI 25** was prepared according to a procedure reported by Gau.<sup>5</sup> 2-(Methylthio)acetic acid **SI 51** was prepared according to a procedure reported by Pan.<sup>6</sup> 2-(Methylthio)acetic acid is also commercially available. Grignard reagent **SI 35** was prepared according to a procedure reported by Normant.<sup>7</sup> 4-Hydroxybutyl benzoate **SI 42** was prepared according to a procedure reported by Carotti.<sup>8</sup> 3-Morpholinopropyl chloride **SI 44** was prepared according to Tung.<sup>9</sup> 1-Tosyl-1*H*-indole-3-carboxaldehyde **SI 50** was prepared according to a procedure reported by Carreira.<sup>10</sup> (*S*)-(1-tritylaziridin-2-yl)diphenylmethanol **49** was prepared according to a procedure by Braga.<sup>11</sup> 2-(benzoylthio)acetic acid **SI 58** and 2-(benzoylthio)-2-methylpropanoic acid **SI 59** were prepared according to a procedure reported by Eisenhut.<sup>12</sup> Methyl 6-formyl-2-naphthoate **47** was prepared according to a procedure reported by Diaz.<sup>13</sup> Benzo[b]thiophen-2-yl lithium **54** was prepared according to a procedure reported by Denis.<sup>14</sup> All other reagents were purchased commercially and used as received.

## II. EXPERIMENTAL

### A. A COMPLETE LIST OF CONDITIONS FOR FIGURE 2

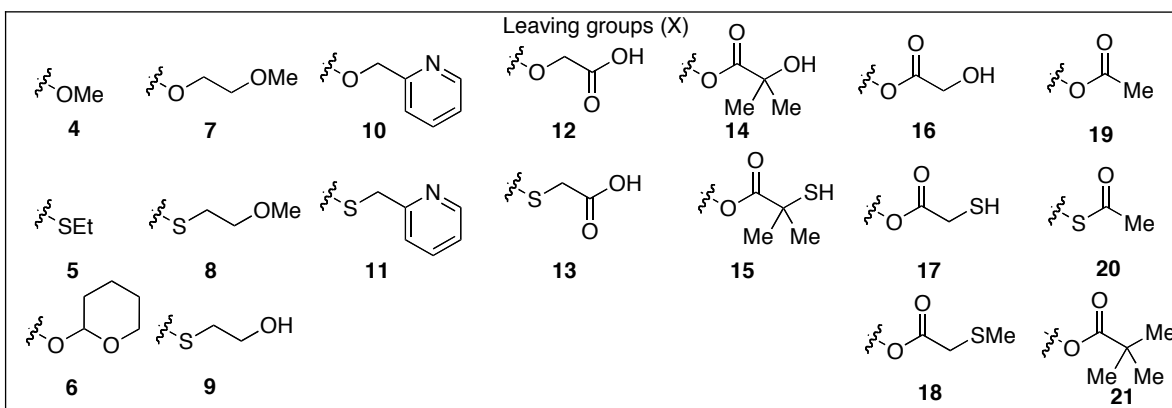
Many experiments were performed with each activating group presented in the paper. The results in Figure 2 of the main document represent the optimal results for each directing group. Table SI 1 comprises the exact conditions for each reaction.

Table SI 1. Reaction conditions for all entries in Figure 2



Entry	Starting Material	Yield <b>22</b> (%) <sup>a</sup>	es <sup>b</sup>	Yield <b>23</b> (%) <sup>a</sup>	Ni source (x equiv)	Ligand (2x)	Solvent	Temp (°C)
1 <sup>c</sup>	<b>4</b>	0	ND	0	Ni(cod) <sub>2</sub> (0.05)	DPEphos	PhMe	100
2	<b>5</b>	13	ND	41	Ni(cod) <sub>2</sub> (0.05)	Xantphos	PhMe	50
3	<b>6</b>	0	ND	0	Ni(cod) <sub>2</sub> (0.05)	rac-BINAP	PhMe	rt
4	<b>7</b>	0	ND	0	Ni(cod) <sub>2</sub> (0.05)	DPEphos	PhMe	rt
5	<b>8</b>	6	ND	7	Ni(cod) <sub>2</sub> (0.05)	DPEphos	PhMe	50
6	<b>9</b>	58	58	38	Ni(cod) <sub>2</sub> (0.05)	DPEphos	PhMe	50
7	<b>10</b>	51	86	7	NiCl <sub>2</sub> ·DME (0.10)	rac-BINAP	PhMe	rt
8	<b>11</b>	41	27	44	NiCl <sub>2</sub> ·DME (0.10)	rac-BINAP	PhMe	rt
9	<b>12</b>	70	27	13	NiCl <sub>2</sub> ·DME (0.10)	rac-BINAP	PhMe	rt
10	<b>13</b>	60	67	21	Ni(cod) <sub>2</sub> (0.05)	DPEphos	PhMe	rt
11	<b>14</b>	59	97	18	Ni(acac) <sub>2</sub> (0.10)	DPEphos	THF	rt
12	<b>15</b>	67	98	18	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	Et <sub>2</sub> O	rt
13	<b>16</b>	71	79	27	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	PhMe	rt
14	<b>17</b>	62	99	13	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	THF	rt
15	<b>18</b>	75	99	20	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	PhMe	rt
16	<b>19</b>	79	61	13	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	PhMe	rt
17	<b>19</b>	62	98	28	NiCl <sub>2</sub> ·DME (0.10)	Xantphos	PhMe	rt
18	<b>20</b>	48	ND	8	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	PhMe	rt
19	<b>21</b>	84	87	15	NiCl <sub>2</sub> ·DME (0.10)	DPEphos	PhMe	rt
20	<b>21</b>	45	99	28	NiCl <sub>2</sub> ·DME (0.10)	Xantphos	PhMe	rt

<sup>a</sup>Yields determined by <sup>1</sup>H NMR with PhTMS as internal standard or by GC analysis with dodecane as the internal standard; <sup>b</sup>enantiospecificity (es) = (ee of the product)/(ee of the starting material); <sup>c</sup>Reaction run with 1.0 equiv of MgBr<sub>2</sub>

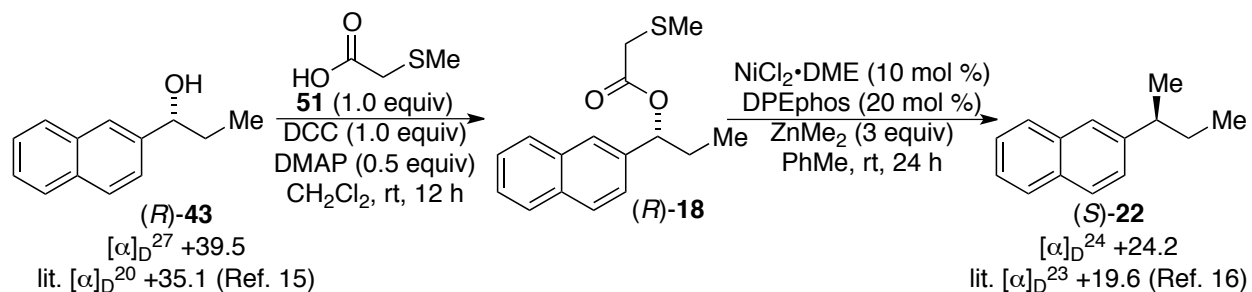


## B. STEREOCHEMICAL PROOFS

The absolute configurations of the products of cross-coupling reactions were assigned for five examples. Those experiments are summarized below. In all five examples, we confirm that the cross-coupling reaction proceeds with inversion. For full experimental details of synthesis of starting materials, cross-coupling reactions, and derivatization of products, including full characterization for all of these compounds, please see subsequent sections of this document.

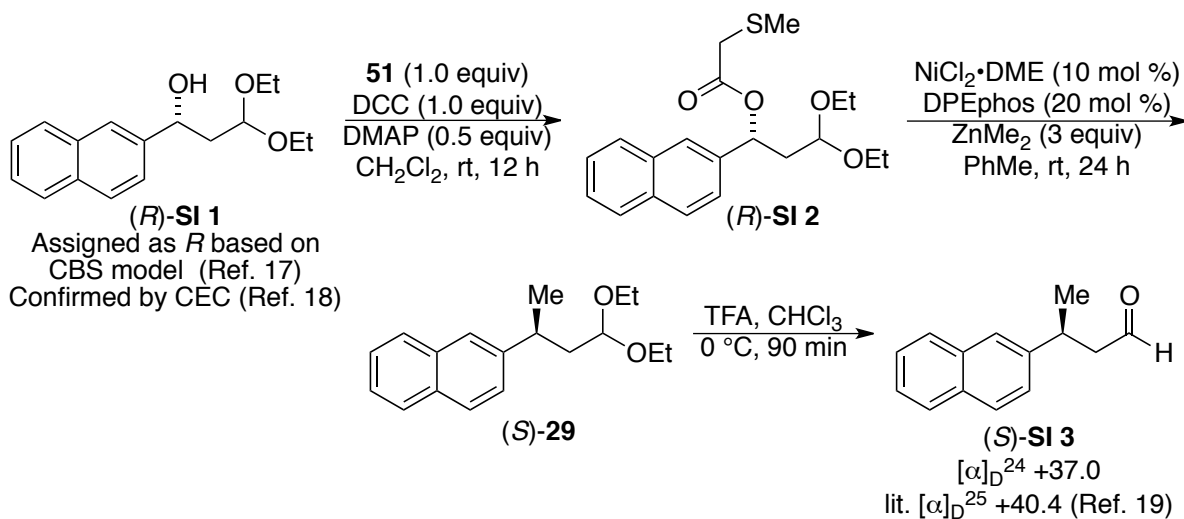
The absolute configurations of all other products were assigned based on the assumption that the cross-coupling reaction proceeds with inversion. These assignments are summarized in Table SI 2. Table SI 2 also summarizes how the absolute configuration of each alcohol was assigned; full experimental details, including characterization data, are provided in Section F.

Scheme SI 1. Stereochemical Course of the Cross-Coupling Reaction



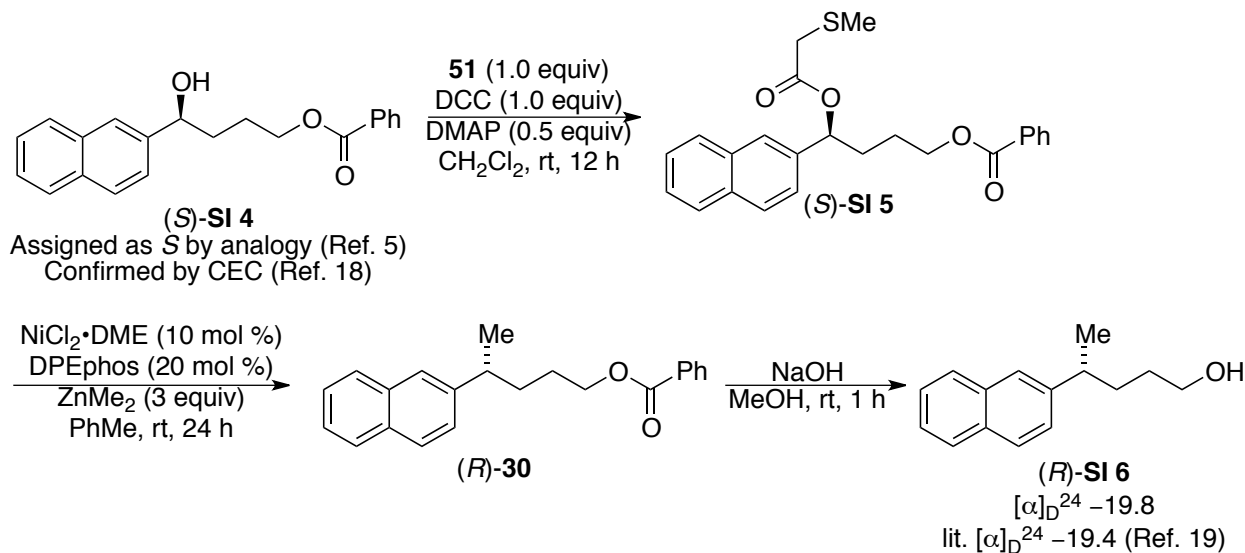
Enantioenriched alcohol (*R*)-**43** was prepared by enantioselective alkylation (vide infra) and the stereochemistry was verified by comparison of the optical rotation to the literature value.<sup>15</sup> Conversion to ester (*R*)-**18**, followed by stereospecific cross-coupling produced (*S*)-**22**, the stereochemistry of which was determined by comparison of the optical rotation to the literature value.<sup>16</sup> This product corresponds to net inversion in the cross-coupling reaction.

Scheme SI 2. Stereochemical Course of the Cross-Coupling Reaction



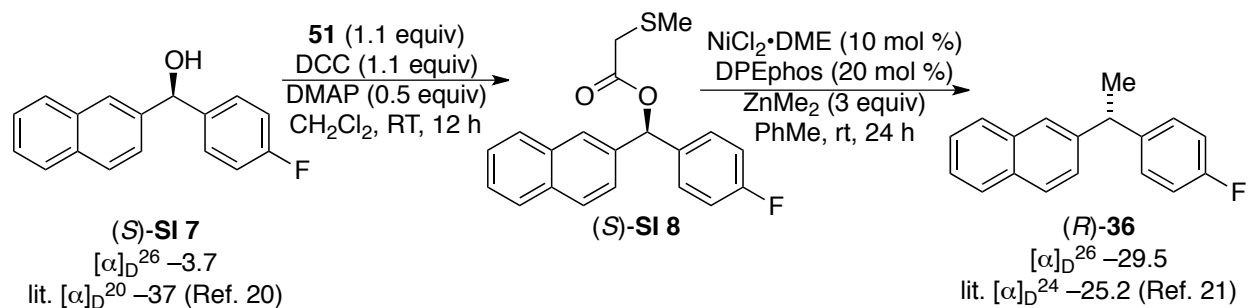
Enantioenriched alcohol (*R*)-**SI 1** was prepared by enantioselective CBS reduction (*vide infra*). Absolute configuration was assigned based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> Conversion to ester (*R*)-**SI 2**, followed by stereospecific cross-coupling produced (*S*)-**29**. The acetal was then removed to reveal aldehyde (*S*)-**SI 3**, the stereochemistry of which was determined by comparison of the optical rotation to the literature value.<sup>19</sup> This product corresponds to net inversion in the cross-coupling reaction.

### Scheme SI 3. Stereochemical Course of the Cross-Coupling Reaction



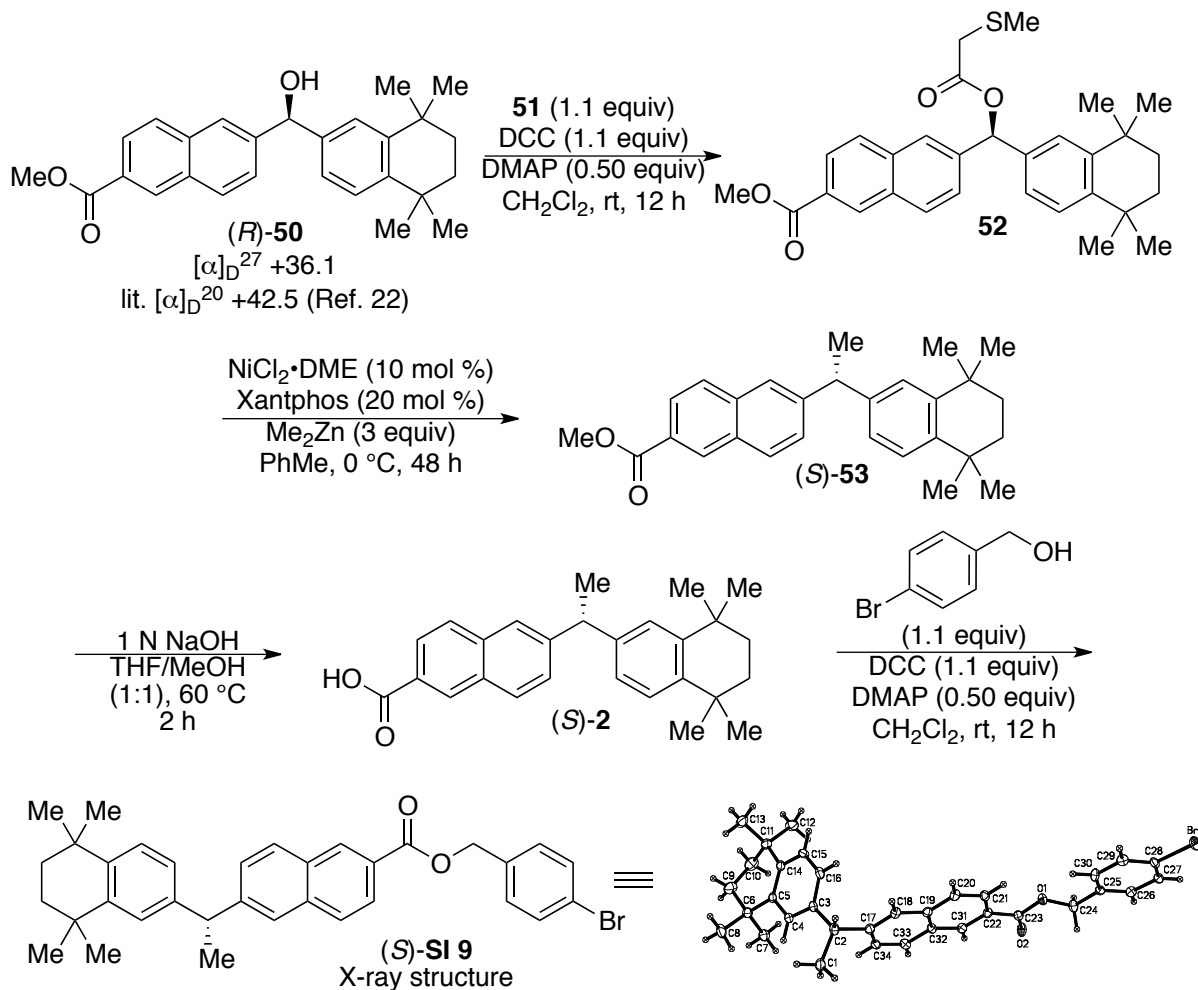
Enantioenriched alcohol (*S*)-**SI 4** was prepared by enantioselective titanium-catalyzed arylation (*vide infra*). Absolute configuration assigned as *S* by analogy to similar compounds synthesized by Gau<sup>5</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> Conversion to ester (*S*)-**SI 5**, followed by stereospecific cross-coupling produced (*R*)-**30**. The benzoyl protecting group was then removed to reveal alcohol (*S*)-**SI 6**, the stereochemistry of which was determined by comparison of the optical rotation to the literature value.<sup>19</sup> This product corresponds to net inversion in the cross-coupling reaction.

### Scheme SI 4. Stereochemical Course of the Cross-Coupling Reaction



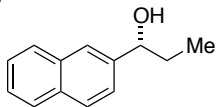
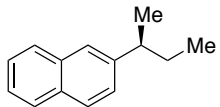
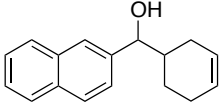
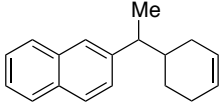
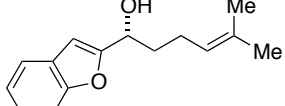
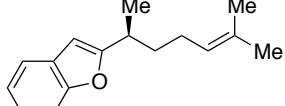
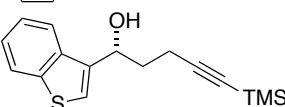
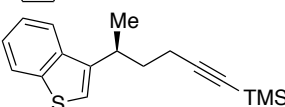
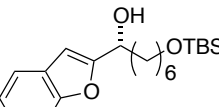
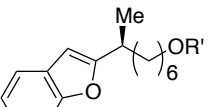
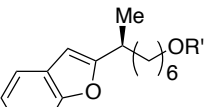
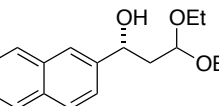
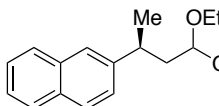
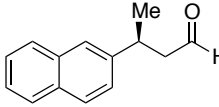
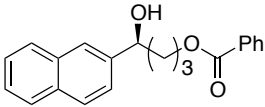
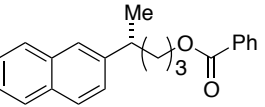
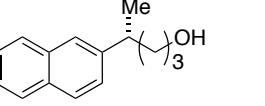
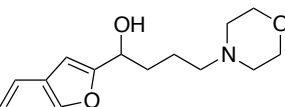
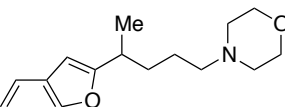
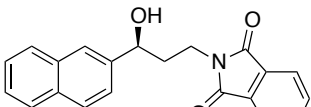
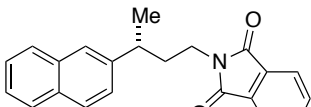
Enantioenriched alcohol (*S*)-**SI 7** was prepared by enantioselective arylation (vida infra) and the stereochemistry was verified by comparison of the optical rotation to the literature value.<sup>20</sup> Conversion to ester (*S*)-**SI 8**, followed by stereospecific cross-coupling produced (*R*)-**36**, the stereochemistry of which was determined by comparison of the optical rotation to the literature value.<sup>21</sup> This product corresponds to net inversion in the cross-coupling reaction.

Scheme SI 5. Stereochemical Course of the Cross-Coupling Reaction



Enantioenriched alcohol (*R*)-**50** was prepared by enantioselective arylation (vida infra) and the stereochemistry was verified by comparison of the optical rotation to the literature value.<sup>22</sup> Conversion to ester (*R*)-**52**, followed by stereospecific cross-coupling produced (*S*)-**53**. Transesterification over two steps afforded (*S*)-**SI 9**, the absolute configuration of which was determined by X-ray crystallography. See Section IV for crystallographic data. This product corresponds to net inversion in the cross-coupling reaction.

**Table SI 2. Configuration of Starting Materials and Products**

Alcohol	Configuration <sup>a</sup> Assigned by:	Product	Configuration <sup>b</sup> Assigned by:
	( <i>R</i> )-43 <i>R</i> (+) lit [ $\alpha$ ] <sub>D</sub>		( <i>S</i> )-22 <i>S</i> (+) lit [ $\alpha$ ] <sub>D</sub>
	SI 10 <i>racemic</i>		24 <i>racemic</i>
	( <i>R</i> )-SI 11 <i>R</i> (-) CBS model CEC confirm		25 <i>S</i> (+) by analogy
	( <i>R</i> )-SI 12 <i>R</i> (-) CBS model CEC confirm		26 <i>S</i> (+) by analogy
	( <i>R</i> )-SI 13 <i>R</i> (+) CBS model CEC confirm		R' = TBS 27 <i>S</i> (+) by analogy
			R' = H 28 <i>S</i> (+) by analogy
	( <i>R</i> )-SI 1 <i>R</i> (+) CBS model CEC confirm		( <i>S</i> )-29 <i>S</i> (+) lit [ $\alpha$ ] <sub>D</sub> of derivative
			( <i>S</i> )-SI 3 <i>S</i> (+) lit [ $\alpha$ ] <sub>D</sub>
	( <i>S</i> )-SI 4 <i>S</i> (-) analogy to Ti arylation CEC confirm		( <i>R</i> )-30 <i>R</i> (-) lit [ $\alpha$ ] <sub>D</sub> of derivative
			( <i>R</i> )-SI 6 <i>R</i> (-) lit [ $\alpha$ ] <sub>D</sub>
	SI 14 <i>racemic</i>		31 <i>racemic</i>
	( <i>S</i> )-SI 15 <i>S</i> (-) analogy to Ti arylation CEC confirm		32 <i>R</i> (-) by analogy

<sup>a</sup>For optical rotation for each compound, see the characterization data. For CBS model, see Ref. 17. For Competing Enantioselective Conversion (CEC), see Ref. 18. For Ti-catalyzed arylation of alkyl aldehydes, see Ref. 5. For Zn-mediated arylation of aryl aldehydes, see Ref. 11.

<sup>b</sup>For optical rotation for each compound, see the characterization data. In the absence of known optical rotations, the absolute configurations of products were assigned based on the assumption that the cross-coupling reaction proceeds with inversion. This is by analogy to the compounds in the stereochemical proof section (Schemes SI 1-5).



Table SI 2 Continued

Alcohol	Configuration <sup>a</sup> Assigned by:	Product	Configuration <sup>a</sup> Assigned by:
<b>Scheme 3</b>			
	( <i>R</i> )-SI 16 <i>R</i> CBS model		34 <i>S</i> (+) by analogy
			SI 17 <i>S</i> (-) by analogy
<hr/>			
<b>Table 2</b>			
	R = H ( <i>S</i> )-SI 18 R = F ( <i>S</i> )-SI 7 R = CF <sub>3</sub> ( <i>S</i> )-SI 19 R = OMe ( <i>S</i> )-SI 20		R = H 35 R = F ( <i>R</i> )-36 R = CF <sub>3</sub> 37 R = OMe 38
	<i>S</i> (-) lit [ $\alpha$ ] <sub>D</sub> <i>S</i> (-) lit [ $\alpha$ ] <sub>D</sub> <i>S</i> (-) lit [ $\alpha$ ] <sub>D</sub> <i>S</i> (+) analogy to Zn arylation		<i>R</i> (-) lit [ $\alpha$ ] <sub>D</sub> <i>R</i> (-) lit [ $\alpha$ ] <sub>D</sub> <i>R</i> (-) by analogy <i>R</i> (-) by analogy
	( <i>R</i> )-SI 21		39 <i>S</i> (+) by analogy
	( <i>R</i> )-SI 22		40 <i>R</i> (+) by analogy
	<i>R</i> (-) analogy to Zn arylation		<i>S</i> (-) analogy to Zn arylation
<hr/>			
<b>Eq 1</b>			
	( <i>R</i> )-SI 23		45 <i>S</i> (+) by analogy
	<i>R</i> (+) CBS model CEC confirm		
<hr/>			
<b>Scheme 4</b>			
	( <i>R</i> )-50		( <i>S</i> )-53 <i>S</i> (-) X-Ray of derivative
	<i>R</i> (+) lit [ $\alpha$ ] <sub>D</sub>		
			( <i>S</i> )-SI 9 <i>S</i> (-) X-Ray
<hr/>			
<b>Scheme 5</b>			
	( <i>R</i> )-56		58 <i>S</i> (+) by analogy
	<i>R</i> (-) CBS model CEC confirm		

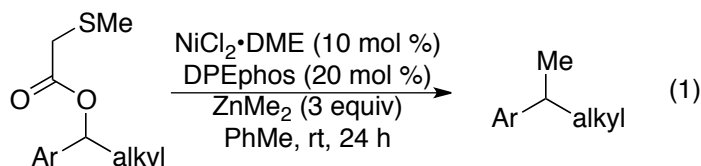
<sup>a</sup>For optical rotation for each compound, see the characterization data. For CBS model, see Ref. 17. For Competing Enantioselective Conversion (CEC), see Ref. 18. For Ti-catalyzed arylation of alkyl aldehydes, see Ref. 5. For Zn-mediated arylation of aryl aldehydes, see Ref. 11.

<sup>b</sup>For optical rotation for each compound, see the characterization data. In the absence of known optical rotations, the absolute configurations of products were assigned based on the assumption that the cross-coupling reaction proceeds with inversion. This is by analogy to the compounds in the stereochemical proof section (Schemes SI 1-5).

### C. GENERAL CROSS-COUPLING PROCEDURES

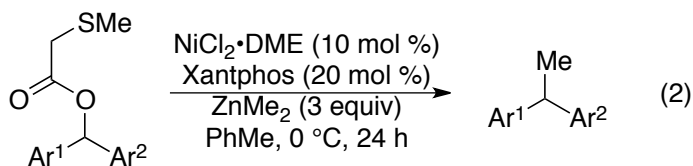
The general cross-coupling procedures will be used throughout the SI. Method A was used to couple singly benzylic substrates (Table 1). Method B was used to couple benzhydryl substrates (Table 2). Method C was used to couple diethylzinc (Scheme 3). In each instance the general method is used, it is specified by letter (A, B, or C) and the exact amounts of reagents used for each reaction are listed for the specific compounds synthesized.

#### METHOD A: CROSS-COUPLING OF SINGLY BENZYLIC ELECTROPHILES (TABLE 1)



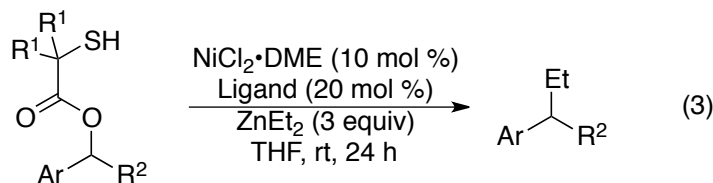
In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with NiCl<sub>2</sub>·DME (0.10 equiv) and DPEphos (0.20 equiv). The reaction vial was capped with a screw-cap fitted with a septum and PhMe was added. After a 5 min pre-stir, substrate (1.0 equiv) was added and the reaction was removed from the glovebox. The reaction vial was equipped with a nitrogen line and allowed to stir for approximately 5 min. ZnMe<sub>2</sub> (3.0 equiv) was then added resulting in an immediate color change from slightly pink to dark orange. After 24 h, the reaction was quenched with isopropyl alcohol and filtered through a plug of silica gel (100% Et<sub>2</sub>O).

#### METHOD B: CROSS-COUPLING OF BENZHYDRYL ELECTROPHILES (TABLE 2)



In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with NiCl<sub>2</sub>·DME (0.10 equiv) and Xantphos (0.20 equiv). The reaction vial was capped with a screw-cap fitted with a septum and PhMe was added. After a 5 min pre-stir, substrate (1.0 equiv) was added and the reaction was removed from the glovebox. The reaction vial was equipped with a nitrogen line and cooled to 0 °C. ZnMe<sub>2</sub> (3.0 equiv) was added resulting in an immediate color change from colorless to orange. After 48 h at 0 °C, the reaction was quenched with isopropyl alcohol, and filtered through a plug of silica gel (100% Et<sub>2</sub>O).

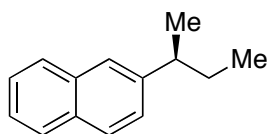
METHOD C: CROSS-COUPLING WITH DIETHYLZINC (TABLE 3)



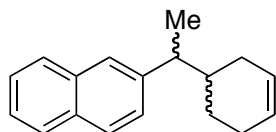
In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with  $\text{NiCl}_2 \cdot \text{DME}$  (0.10 equiv) and DPEphos (0.20 equiv). The reaction vial was capped with a screw-cap fitted with a septum and THF was added. After a 5 min pre-stir, substrate (1.0 equiv) was added and the reaction was removed from the glovebox. The reaction vial was equipped with a nitrogen line and allowed to stir for approximately 5 min. A freshly prepared solution of  $\text{ZnEt}_2$  (3.0 equiv) was then added resulting in an immediate color change from purple to dark orange. After 24 h, the reaction was quenched with isopropyl alcohol and filtered through a plug of silica gel (100%  $\text{Et}_2\text{O}$ ).

**PREPARATION OF  $\text{ZnEt}_2$  SOLUTION:** In a glovebox,  $\text{ZnEt}_2$  (0.60 mL, 5.9 mmol) and PhMe (2.4 mL) were combined in a flame-dried 7 mL vial equipped with a stir bar and equipped with a screw-cap fitted with a septum, resulting in a 1.6 M solution.

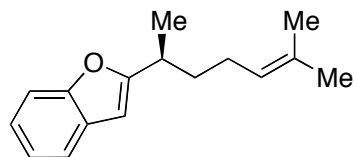
#### D. CHARACTERIZATION DATA FOR PRODUCTS 22–32 (TABLE 1)



**(S)-2-(sec-butyl)naphthalene (S)-22** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-**18** (0.80 mL, 0.20 mmol, 1.0 equiv, 0.25 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.4 mL). Purification by flash chromatography with silver impregnated silica gel (100% pentane) afforded the title compound as a colorless oil (30 mg, 81%). Analytical data are consistent with literature values.<sup>23</sup> **TLC** *R<sub>f</sub>* = 0.5 (pentane, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.82–7.42 (m, 3H), 7.60 (s, 1H), 7.42 (apd, *J* = 7.31, 1.40, 2H), 7.34 (dd, *J* = 8.5, 1.6, 1H), 2.76 (sextet, *J* = 7.0, 1H), 1.77–1.61 (m, 2H), 1.32 (d, *J* = 6.9, 3H), 0.85 (t, *J* = 7.4, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 145.3, 133.8, 132.3, 128.0, 127.71, 127.67, 126.0, 125.9, 125.3, 125.2, 42.0, 31.2, 22.0, 12.5; [ $\alpha$ ]<sub>D</sub><sup>24</sup> +24.2 (*c* 1.0, CHCl<sub>3</sub>), lit.<sup>16</sup> [ $\alpha$ ]<sub>D</sub><sup>23</sup> +19.6 (neat, 65% ee (*S*)-enantiomer); **SFC** analysis (OD-H, 1.0% hexanes, 2.5 mL/min, 215 nm) indicated 98% ee: *t<sub>R</sub>* (major) = 5.9 min, *t<sub>R</sub>* (minor) = 6.3 min.

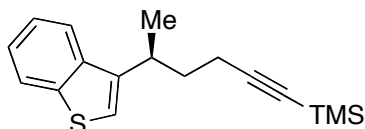


**2-(1-(cyclohex-3-en-1-yl)ethyl)naphthalene 24** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate **SI 27** (0.40 mL, 0.20 mmol, 1.0 equiv, 0.5 M in PhMe), and ZnMe<sub>2</sub> (0.32 mL, 0.60 mmol, 3.0 equiv, 1.9 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (100% pentane) afforded the title compound as 5:1 mixture with the elimination byproduct (41 mg, calculated as 34 mg, 71%, dr 1:1 by <sup>1</sup>H NMR integration). Compound **24** was re-purified by silica gel chromatography to obtain a sample of analytically pure material. **TLC** *R<sub>f</sub>* = 0.9 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.81–7.76 (m, 3H), 7.59 (d, *J* = 2.4, 1H), 7.46–7.32 (m, 3H), 5.71–5.52 (m, 2H), 2.71–2.66 (m, 1H), 2.28–1.51 (m, 6H), 1.39–1.12 (m, 4H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 144.6, 144.4, 133.64, 133.62, 132.3, 127.88, 127.85, 127.71, 127.66, 127.3, 126.9, 126.8, 126.6, 126.42, 126.38, 126.1, 126.0, 125.9, 125.2, 45.8, 45.2, 40.20, 40.15, 30.7, 29.9, 27.4, 26.6, 25.8, 25.7, 19.4, 19.2; **IR** (neat, cm<sup>-1</sup>) 3019, 2963, 2910, 1506, 1434, 908; **HRMS** (TOF MS EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> calculated for C<sub>18</sub>H<sub>20</sub> 236.1565, found 236.1555.

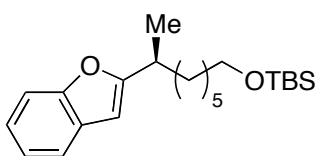


**2-((S)-6-methyl-5-hepten-2-yl)benzofuran 25** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-**SI 30** (0.80 mL, 0.20 mmol, 1.0 equiv, 0.25 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.4 mL). Purification by flash chromatography (100% pentane) afforded the title compound as 12:1 mixture with the elimination byproduct (42 mg, calculated as 39 mg, 86% desired product). Compound **25** was re-purified by silica gel chromatography to obtain a sample of analytically pure material. **TLC** *R<sub>f</sub>* = 0.5 (100% pentane, UV active, stain with CAM); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.48 (dd, *J* = 6.9, 1.8, 1H), 7.41 (d, *J* = 7.8, 1H), 7.18 (apd, *J* = 7.1, 1.4, 2H), 6.36 (s, 1H), 5.11 (tt, *J* = 7.1, 1.3, 1H), 2.94 (sextet, *J* = 6.9, 1H), 2.01 (q, *J* = 7.4, 2H), 1.84 (as, *J* = 7.2, 1H), 1.67 (s, 3H), 1.67–1.54 (m, 1H), 1.57 (s, 3H), 1.33 (d, *J* = 6.9, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.0, 154.7, 132.1, 129.0, 124.2,

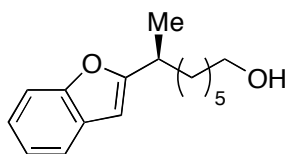
123.1, 122.4, 120.4, 110.9, 100.8, 35.6, 33.3, 25.9, 25.8, 19.2, 17.9; **IR** (neat,  $\text{cm}^{-1}$ ) 2967, 2925, 1254, 1253, 795, 738; **HRMS** (TOF MS EI+)  $m/z$ :  $[\text{M}]^+$  calculated for  $\text{C}_{16}\text{H}_{20}\text{O}$  228.1514, found 228.1508;  $[\alpha]_{\text{D}}^{25} + 61.0$  ( $c$  0.86,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 1.0% hexanes, 3.0 mL/min, 215 nm) indicated 93% ee:  $t_{\text{R}}$  (major) = 4.3 min,  $t_{\text{R}}$  (minor) = 5.0 min.



**(S)-((5-(benzo[b]thiophen-3-yl)hex-1-yn-1-yl)trimethylsilane) 26** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-**SI 34** (0.80 mL, 0.20 mmol, 1.0 equiv, 0.25 M in PhMe), and  $\text{ZnMe}_2$  (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.4 mL). Purification by flash chromatography (0–5%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a colorless oil (46 mg, 81%). **TLC**  $R_{\text{f}}$  = 0.3 (pentane, UV active, stain with CAM);  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.85 (add,  $J = 7.5, 2.3$ , 2H), 7.35 (apd,  $J = 7.2, 1.0$ , 2H), 7.09 (s, 1H), 3.37 (sextet,  $J = 6.9$ , 1H), 2.34–2.18 (m, 2H), 2.03 (as,  $J = 6.9$ , 1H), 1.80 (as,  $J = 6.9$ , 1H), 1.38 (d,  $J = 6.9$ , 3H), 0.17 (s, 9H);  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  141.8, 140.8, 138.8, 124.3, 123.9, 123.0, 122.1, 120.0, 107.3, 85.1, 36.1, 31.9, 20.3, 18.2, 0.3; **IR** (neat,  $\text{cm}^{-1}$ ) 2959, 2173, 1427, 1248, 871, 759; **HRMS** (TOF MS EI+)  $m/z$ :  $[\text{M}]^+$  calculated for  $\text{C}_{17}\text{H}_{22}\text{SSi}$  286.1212, found 286.1212;  $[\alpha]_{\text{D}}^{29} + 57.6$  ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 1.0% hexanes, 3.0 mL/min, 215 nm) indicated 96% ee:  $t_{\text{R}}$  (major) = 3.4 min,  $t_{\text{R}}$  (minor) = 3.9 min.

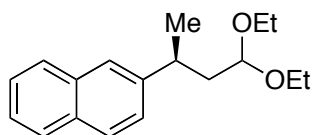


**(S)-((7-(benzofuran-2-yl)octyl)oxy)(tert-butyl)dimethylsilane) 27** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (2.2 mg, 0.010 mmol, 0.10 equiv), DPEphos (11 mg, 0.020 mmol, 0.20 equiv), substrate (*R*)-**SI 38** (0.40 mL, 0.10 mmol, 1.0 equiv 0.25 M in PhMe), and  $\text{ZnMe}_2$  (0.17 mL, 0.30 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (1.2 mL). Purification by flash chromatography with silver impregnated silica gel (2%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a colorless oil (27 mg, 75%). **TLC**  $R_{\text{f}}$  = 0.3 (2%  $\text{Et}_2\text{O}$  in pentane, UV active, stains with CAM);  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.48 (dd,  $J = 7.1, 1.3$ , 1H), 7.41 (d,  $J = 7.8$ , 1H), 7.18 (apd,  $J = 7.6, 1.3$ , 2H), 6.35 (s, 1H), 3.58 (t,  $J = 6.6$ , 2H), 2.92 (sextet,  $J = 6.9$ , 1H), 1.83–1.73 (m, 1H), 1.62–1.53 (m, 1H), 1.53–1.44 (m, 2H), 1.38–1.26 (m, 9H), 0.88 (s, 9H), 0.04 (s, 6H);  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  164.1, 154.6, 129.0, 123.1, 122.4, 120.4, 110.9, 100.7, 63.4, 35.5, 33.7, 33.0, 29.6, 27.3, 26.1, 25.9, 19.2, 18.5, -5.1; **IR** (neat,  $\text{cm}^{-1}$ ) 2928, 2856, 1455, 1253, 1096, 834; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{22}\text{H}_{37}\text{O}_2\text{Si}$  361.2563, found 361.2561;  $[\alpha]_{\text{D}}^{28} + 18.7$  ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 1.0% hexanes, 3.0 mL/min, 215 nm) indicated 88% ee:  $t_{\text{R}}$  (major) = 3.2 min,  $t_{\text{R}}$  (minor) = 3.6 min.

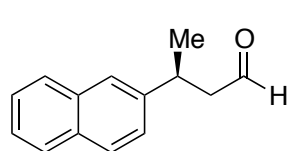
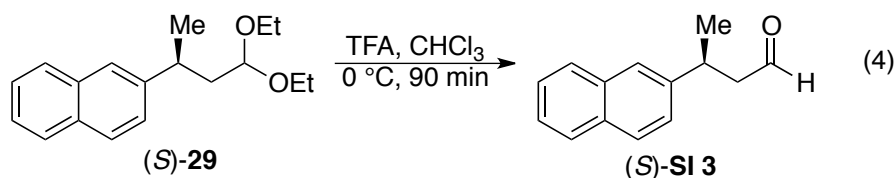


**(S)-7-(benzofuran-2-yl)octan-1-ol) 28** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (2.2 mg, 0.010 mmol, 0.10 equiv), DPEphos (11 mg, 0.020 mmol, 0.20 equiv), substrate (*R*)-**SI 39** (0.40 mL, 0.10 mmol, 1.0 equiv 0.25 M in PhMe), and  $\text{ZnMe}_2$  (0.17 mL, 0.30 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (1.2 mL). Purification by flash chromatography with silver impregnated silica gel (10–40%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a colorless oil (19 mg, 77%). **TLC**  $R_{\text{f}}$  = 0.5 (1:1  $\text{Et}_2\text{O}$ /pentane, UV active, stains with CAM);  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.48 (dd,  $J$

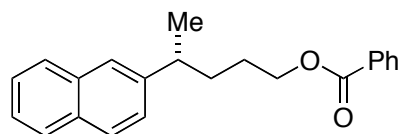
= 6.9, 1.5, 1H), 7.41 (d,  $J = 7.7$ , 1H), 7.18 (apd,  $J = 7.1$ , 1.2, 2H), 6.36 (s, 1H), 3.62 (br dd,  $J = 9.4$ , 6.2, 2H), 2.92 (sextet,  $J = 6.9$ , 1H), 1.85–1.72 (m, 1H), 1.66–1.48 (m, 3H), 1.40–1.27 (m, 9H), 1.20 (br s, 1H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  164.0, 154.6, 129.0, 123.1, 122.4, 120.4, 110.9, 100.7, 63.1, 35.5, 33.7, 32.9, 29.5, 27.2, 25.8, 19.1; IR (neat, cm<sup>-1</sup>) 3326, 2930, 1454, 1253, 795, 739; HRMS (TOF MS EI+)  $m/z$ : [M]<sup>+</sup> calculated for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub> 246.1620, found 246.1616;  $[\alpha]_{\text{D}}^{29}$  +44.1 ( $c$  0.97, CHCl<sub>3</sub>); SFC analysis (OJ-H, 10.0% IPA, 3.0 mL/min, 215 nm) indicated 90% ee:  $t_{\text{R}}$  (major) = 4.7 min,  $t_{\text{R}}$  (minor) = 5.4 min.



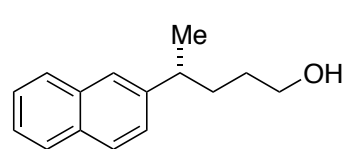
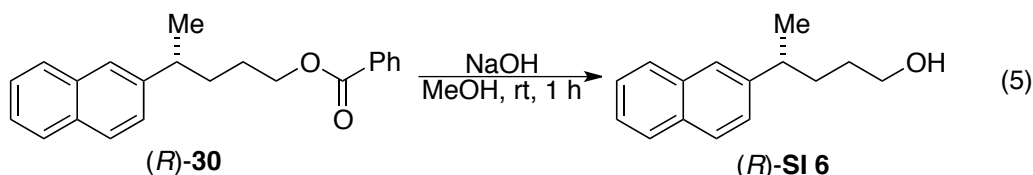
**(S)-2-(4,4-diethoxybutan-2-yl)naphthalene (S)-29** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (2.2 mg, 0.010 mmol, 0.10 equiv), DPEphos (11 mg, 0.020 mmol, 0.20 equiv), substrate (*R*)-SI 2 (1.0 mL, 0.10 mmol, 1.0 equiv 0.10 M in PhMe), and ZnMe<sub>2</sub> (0.17 mL, 0.30 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (0.60 mL). Purification by flash chromatography (2–5% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (22 mg, 81%). TLC  $R_{\text{f}}$  = 0.3 (5% Et<sub>2</sub>O in pentane, UV active, stain with CAM);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.84–7.75 (m, 3H), 7.63 (s, 1H), 7.43 (ap,  $J = 7.6$ , 2H), 7.37 (dd,  $J = 8.4$ , 1.1, 1H), 4.30 (t,  $J = 6.0$ , 1H), 3.64 (dq,  $J = 9.2$ , 7.1, 1H), 3.54 (dq,  $J = 9.3$ , 7.1, 1H), 3.45–3.36 (m, 2H), 3.06 (sextet,  $J = 7.2$ , 1H), 2.05–1.94 (m, 2H), 1.34 (d,  $J = 7.1$ , 3H), 1.22 (t,  $J = 7.0$ , 3H), 1.13 (t,  $J = 7.0$ , 3H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  144.4, 133.8, 132.4, 128.2, 127.71, 127.70, 126.0, 125.8, 125.4, 125.3, 101.6, 61.5, 60.9, 41.9, 36.3, 22.8; IR (neat, cm<sup>-1</sup>) 2971, 1372, 1124, 1055, 745; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>Na 295.1674, found 295.1668;  $[\alpha]_{\text{D}}^{28}$  +29.6 ( $c$  1.0, CHCl<sub>3</sub>); SFC analysis (OJ-H, 1.0% IPA, 3.0 mL/min, 215 nm) indicated 89% ee:  $t_{\text{R}}$  (minor) = 5.7 min,  $t_{\text{R}}$  (major) = 6.2 min.



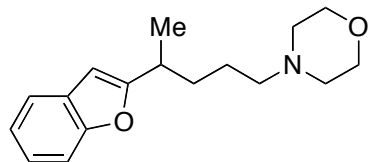
**(S)-3-(naphthalene-2-yl)butanal (S)-SI 3** was prepared according to a modified Ellison.<sup>24</sup> Acetal (*S*)-29 (34 mg, 0.12 mmol, 1.0 equiv) was dissolved in wet CHCl<sub>3</sub> (2 mL) and cooled to 0 °C. The reaction mixture was treated with TFA (50% aq. solution, 1 mL) and stirred at the same temperature for 90 min. The reaction was quenched with sat. NaHCO<sub>3</sub> (2 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 1 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (5–10% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (17 mg, 71%). Analytical data are consistent with literature values.<sup>19</sup> TLC  $R_{\text{f}}$  = 0.1 (5% Et<sub>2</sub>O in pentane, UV active, stain with KMnO<sub>4</sub>);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.74 (t,  $J = 1.7$ , 1H), 7.79 (at,  $J = 7.0$ , 3H), 7.65 (s, 1H), 7.45 (apd  $J = 6.8$ , 1.1, 2H), 7.37 (dd,  $J = 8.5$ , 1.2, 1H), 3.53 (sextet,  $J = 7.1$ , 1H), 2.86 (ddd,  $J = 16.7$ , 6.8, 1.4, 1H), 2.74 (ddd,  $J = 16.7$ , 7.7, 1.8, 1H), 2.41 (d,  $J = 6.9$ , 3H);  $[\alpha]_{\text{D}}^{24}$  +37.0 ( $c$  0.9, Et<sub>2</sub>O), lit.<sup>19</sup>  $[\alpha]_{\text{D}}^{25}$  +40.4 ( $c$  0.2, Et<sub>2</sub>O, >95% ee (*S*)-enantiomer); SFC analysis (OJ-H, 5.0% IPA, 3.0 mL/min, 215 nm) indicated 84% ee:  $t_{\text{R}}$  (major) = 6.5 min,  $t_{\text{R}}$  (minor) = 7.2 min.



**(R)-4-(naphthalen-2-yl)pentyl benzoate (R)-30** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*S*)-**SI 5** (82 mg, 0.20 mmol, 1.0 equiv), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (3.2 mL). Purification by flash chromatography with silver impregnated silica gel (5% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (52 mg, 81%). **TLC** R<sub>f</sub> = 0.3 (5% Et<sub>2</sub>O in pentane, UV active, stain with CAM); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 8.01 (d, *J* = 7.3, 2H), 7.82 (m, 3H), 7.62 (s, 1H), 7.52 (t, *J* = 7.3, 1H), 7.47–7.38 (m, 4H), 7.35 (d, *J* = 8.6, 1H), 4.28 (t, *J* = 6.4, 2H), 2.92 (sextet, *J* = 6.9, 1H), 1.90–1.56 (m, 4H), 1.36 (d, *J* = 6.9, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 166.7, 144.5, 133.7, 132.9, 132.4, 130.5, 129.7, 128.4, 128.2, 127.72, 127.66, 126.0, 125.7, 125.4, 125.3, 65.1, 39.9, 34.5, 27.1, 22.6; **IR** (neat, cm<sup>-1</sup>) 2957, 1714, 1270, 1110, 709; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>Na 341.1518, found 341.1515; [α]<sub>D</sub><sup>26</sup> -6.8 (*c* 1.0, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 5.0% MeOH, 3.0 mL/min, 215 nm) indicated 97% ee: t<sub>R</sub> (minor) = 6.7 min, t<sub>R</sub> (major) = 7.3 min.

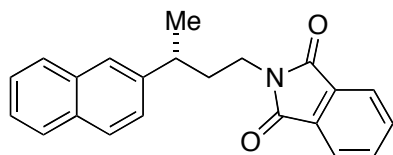


**(R)-4-(naphthalen-2-yl)pentan-1-ol (R)-SI 6** was prepared according to a modified procedure by Sato.<sup>25</sup> Ester (*R*)-**30** (37 mg, 0.12 mmol, 1.0 equiv) was treated with a solution of NaOH in MeOH (1%, 5 ml). The reaction was stirred at rt for 1 h and then MeOH was removed in vacuo. The solid residue was taken up in H<sub>2</sub>O (2 mL) the mixture was extracted with EtOAc (3 x 1 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (40% Et<sub>2</sub>O in pentane) to afford the title compound as a viscous colorless oil (19 mg, 72%). Analytical data are consistent with literature values.<sup>19</sup> **TLC** R<sub>f</sub> = 0.3 (40% Et<sub>2</sub>O in pentane, UV active, stain with KMnO<sub>4</sub>); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.79 (at, *J* = 7.0, 3H), 7.60 (s, 1H), 7.43 (ap, *J* = 7.2, 2H), 7.34 (d, *J* = 8.6, 1H), 3.59 (t, *J* = 6.5, 2H), 2.88 (sextet, *J* = 7.0, 1H), 1.74 (q, *J* = 7.7, 2H), 1.61–1.50 (m, 1H), 1.50–1.38 (m, 1H), 1.34 (d, *J* = 6.9, 3H), 1.21 (br s, 1H); [α]<sub>D</sub><sup>24</sup> -19.8 (*c* 0.9, CHCl<sub>3</sub>), lit.<sup>19</sup> [α]<sub>D</sub><sup>24</sup> -19.4 (*c* 0.3, CHCl<sub>3</sub>, >95% ee, (*R*)-enantiomer); **SFC** analysis (OJ-H, 5.0% MeOH, 3.0 mL/min, 215 nm) indicated 96% ee: t<sub>R</sub> (minor) = 13.6 min, t<sub>R</sub> (major) = 14.5 min.

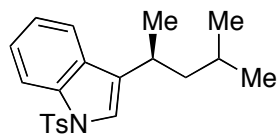


**4-(4-(benzofuran-2-yl)pentyl)morpholine 31** was prepared according to Method A. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), DPEphos (22 mg, 0.040 mmol, 0.20 equiv), substrate **SI 46** (0.40 mL, 0.20 mmol, 1.0 equiv, 0.5 M in PhMe), and ZnMe<sub>2</sub> (0.32 mL, 0.60 mmol, 3.0 equiv, 1.9M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (100% Et<sub>2</sub>O) afforded the title compound as 16:1 mixture with the elimination byproduct (39 mg, calculated as 37 mg, 68%). Compound **31** was re-purified by silica gel chromatography to obtain a sample of analytically pure material. **TLC** R<sub>f</sub> = 0.4 (100% Et<sub>2</sub>O, UV active); **mp** 48–49

°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.48 (d,  $J = 6.9$ , 1H), 7.40, (d,  $J = 7.5$ , 1H), 7.20–7.17 (m, 2H), 6.37 (s, 1H), 3.69 (t,  $J = 4.6$ , 4H), 2.99–2.91 (m, 1H), 2.40 (br s, 4H), 2.33 (t,  $J = 7.6$ , 2H), 1.84–1.76 (m, 1H), 1.64–1.59 (m, 3H), 1.34 (d,  $J = 7.0$ , 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  163.5, 154.7, 128.9, 123.3, 122.5, 120.4, 110.9, 101.0, 67.1, 59.1, 53.9, 33.7, 33.4, 24.3, 19.2; **IR** (neat,  $\text{cm}^{-1}$ ) 2934, 2853, 1454, 1298, 1253, 1166, 1137; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{17}\text{H}_{24}\text{O}_2\text{N}$  274.1807, found 274.1813.

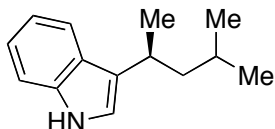
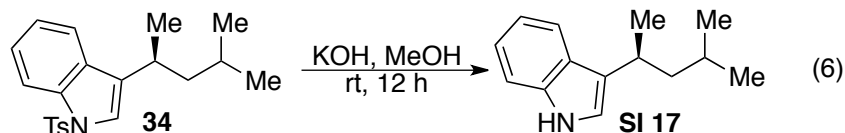


**(R)-2-(3-(naphthalen-2-yl)butyl)isoindoline-1,3-dione 32** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (2.2 mg, 0.010 mmol, 0.13 equiv), DPEphos (11 mg, 0.020 mmol, 0.25 equiv), substrate (**S-SI 48**) (0.20 mL, 0.080 mmol, 1.0 equiv, 0.50 M in PhMe), and  $\text{ZnMe}_2$  (0.17 mL, 0.30 mmol, 3.8 equiv, 1.8 M in PhMe) in PhMe (1.4 mL). Purification by flash chromatography (5–15%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a white solid (21 mg, 80%). **TLC**  $R_f = 0.5$  (4:1 hexane/ $\text{EtOAc}$ , UV active, stain with CAM); **mp** 73–76 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.76 (d,  $J = 8.2$ , 1H), 7.73–7.64 (m, 4H), 7.61 (s, 1H), 7.60–7.54 (m, 2H), 7.41 (t,  $J = 7.3$ , 1H), 7.35 (t,  $J = 7.5$ , 2H), 3.67 (t,  $J = 7.2$ , 2H), 2.96 (as,  $J = 7.0$ , 1H), 2.24 (dq,  $J = 13.7, 8.3$ , 1H), 2.00 (as,  $J = 6.5$ , 1H), 1.37 (d,  $J = 6.9$ , 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  168.5, 143.6, 133.8, 133.6, 133.3, 132.0, 128.3, 127.7, 127.6, 126.0, 125.44, 125.41, 125.2, 123.0, 38.4, 37.0, 35.8, 23.1; **IR** (neat,  $\text{cm}^{-1}$ ) 2960, 1705, 1396, 747, 715; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{Na}$  352.1313, found 352.1314;  $[\alpha]_D^{25} -3.1$  ( $c$  0.72,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 10.0% MeOH, 3.0 mL/min, 215 nm) indicated 94% ee:  $t_R$  (major) = 6.9 min,  $t_R$  (minor) = 7.6 min.



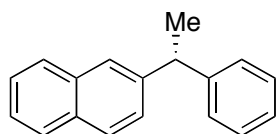
**(S)-3-(4-methylpentan-2-yl)-1-tosyl-1H-indole 34** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (3.3 mg, 0.015 mmol, 0.10 equiv), DPEphos (16 mg, 0.030 mmol, 0.20 equiv), substrate **33** (0.30 mL, 0.15 mmol, 1.0 equiv, 0.5 M in PhMe), and  $\text{ZnMe}_2$  (0.23 mL, 0.45 mmol, 3.0 equiv, 1.9 M in PhMe) in PhMe (2.1 mL). Purification by flash chromatography (2–5%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a colorless oil (49 mg, 91%). **TLC**  $R_f = 0.7$  (4:1 Hexane/ $\text{EtOAc}$ , UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.97 (d,  $J = 8.3$ , 1H), 7.71 (d,  $J = 8.3$ , 2H), 7.51 (d,  $J = 7.9$ , 1H), 7.30–7.18 (m, 5H), 2.99 (sextet,  $J = 7.1$ , 1H), 2.32 (s, 3H), 1.65–1.50 (m, 2H), 1.44–1.37 (m, 1H), 1.27 (d  $J = 6.9$ , 3H), 0.88 (at,  $J = 6.8$ , 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  144.6, 135.7, 135.4, 130.7, 129.9, 129.5, 126.8, 124.6, 123.0, 121.8, 120.0, 114.0, 46.3, 28.5, 25.8, 23.1, 22.6, 21.7, 21.1; **IR** (neat,  $\text{cm}^{-1}$ ) 2956, 1446, 1365, 1279, 1172, 1120, 1090; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{25}\text{O}_2\text{NSNa}$  378.1504, found 378.1501;  $[\alpha]_D^{27} +0.94$  ( $c$  1.5,  $\text{CHCl}_3$ ). Enantiomeric excess determined after deprotection, see **SI 1**.



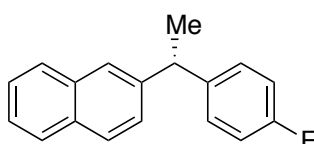


**(S)-3-(4-methylpentan-2-yl)-1H-indole SI 17** was prepared according to a modified procedure by Kozikowski.<sup>26</sup> To a stirred solution of **34** (10 mg, 0.030 mmol, 1.0 equiv) in wet MeOH (2 mL) was added powdered KOH (0.50 g, 10 mmol, 33 equiv). The reaction was stirred at ambient temperature overnight, after which the reaction was acidified with 3N HCl until pH < 7. The crude product was extracted with Et<sub>2</sub>O (3 x 5 mL) and the combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a yellow oil (5.0 mg, 88%). Analytical data are consistent with literature values.<sup>27</sup> **TLC**  $R_f$  = 0.7 (4:1 Hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.88 (br s, 1H), 7.66 (d,  $J$  = 7.8, 1H), 7.35 (d,  $J$  = 8.1, 1H), 7.17 (t,  $J$  = 7.5, 1H), 7.09 (t,  $J$  = 7.4, 1H), 6.95 (d,  $J$  = 2.2, 1H), 3.11 (sextet,  $J$  = 7.2, 1H), 1.75–1.58 (m, 2H), 1.48–1.41 (m, 1H), 1.32 (d,  $J$  = 7.0, 3H), 0.92 (d,  $J$  = 4.8, 3H), 0.90 (d,  $J$  = 5.0, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  136.6, 127.0, 123.2, 121.9, 119.9, 119.5, 119.1, 111.3, 47.3, 28.6, 25.9, 23.1, 22.8, 22.0;  $[\alpha]_D^{26}$  –1.6 ( $c$  0.24, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 5.0% IPA, 1.0 mL/min, 215 nm) indicated 96% ee:  $t_R$  (minor) = 36.3 min,  $t_R$  (major) = 38.1 min.

## E. CHARACTERIZATION DATA FOR PRODUCTS 35–40 (TABLE 2)

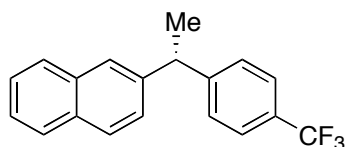


**(R)-2-(1-phenylethyl)naphthalene 35** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*S*-**SI 52**) (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (43 mg, 87%). Analytical data are consistent with literature values.<sup>28</sup> **TLC**  $R_f$  = 0.8 (4:1 Hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.80–7.69 (m, 4H), 7.43 (apd,  $J$  = 7.0, 1.8, 2H), 7.31–7.26 (m, 5H), 7.20–7.16 (m, 1H), 4.31 (q,  $J$  = 7.2, 1H), 1.71 (d,  $J$  = 7.2, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  146.4, 143.9, 133.7, 132.2, 128.5, 128.1, 127.89, 127.86, 127.7, 127.0, 126.2, 126.1, 125.50, 125.48, 45.0, 21.9;  $[\alpha]_D^{26}$  –42.5 ( $c$  0.78, CHCl<sub>3</sub>), lit.<sup>23</sup>  $[\alpha]_D^{23}$  –46.2 ( $c$  1.0, CHCl<sub>3</sub>, 99% ee); **SFC** analysis (OD-H, 2.0% IPA, 2.5 mL/min, 215 nm) indicated 98% ee:  $t_R$  (minor) = 12.2 min,  $t_R$  (major) = 12.8 min.

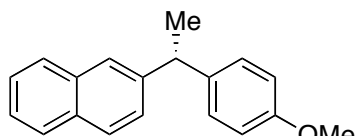


**(R)-2-(1-(4-fluorophenyl)ethyl)naphthalene (R)-36** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*S*-**SI 8**) (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (2–10% Et<sub>2</sub>O in pentane) afforded the title compound as a white solid (45 mg, 89%). Analytical data are consistent with literature values.<sup>21</sup> **TLC**  $R_f$  = 0.8 (4:1 Hexane/EtOAc, UV active); **mp**

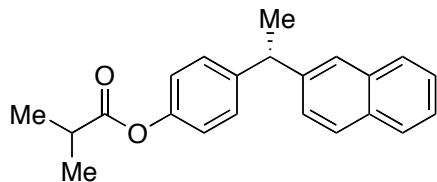
52–55 °C; lit.<sup>21</sup> mp 54–58 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.79–7.73 (m, 3H), 7.66 (s, 1H), 7.43 (ap, *J* = 7.0, 2H), 7.27–7.18 (m, 3H), 6.98–6.94 (m, 2H), 4.28 (q, *J* = 7.2, 1H), 1.71 (d, *J* = 7.2, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 161.4 (d, *J*<sub>(C-F)</sub> = 244.1 Hz), 143.7, 142.0 (d, *J*<sub>(C-F)</sub> = 3.2 Hz), 133.6, 132.2, 129.3 (d, *J*<sub>(C-F)</sub> = 7.4 Hz), 128.2, 127.8, 127.7, 126.8, 126.2, 125.6, 125.4, 115.2 (d, *J*<sub>(C-F)</sub> = 21.3 Hz), 44.2, 22.0; [α]<sub>D</sub><sup>26</sup> –29.5 (*c* 1.57, CHCl<sub>3</sub>), lit.<sup>21</sup> [α]<sub>D</sub><sup>24</sup> –25.2 (*c* 1.88, CHCl<sub>3</sub>, 95% ee, (*R*)-enantiomer); SFC analysis (OD-H, 2.0% IPA, 2.5 mL/min, 215 nm) indicated 93% ee: t<sub>R</sub> (minor) = 11.11 min, t<sub>R</sub> (major) = 12.14 min.



**(*R*)-2-(1-(4-(trifluoromethyl)phenyl)ethyl)naphthalene 37** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*S*)-SI 53 (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (47 mg, 78%). TLC R<sub>f</sub> = 0.8 (4:1 hexane/EtOAc, UV active); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.80–7.68 (m, 4H), 7.52 (d, *J* = 8.1, 2H), 7.44 (ap, *J* = 6.2, 2H), 7.34 (d, *J* = 7.9, 2H), 7.25 (d, *J* = 8.4, 1H), 4.34 (q, *J* = 7.1, 1H), 1.73 (d, *J* = 7.2, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 150.4, 142.8, 133.6, 132.3, 128.6 (q, *J*<sub>C-F</sub> = 32.4, 1C), 128.4, 128.2, 127.9, 127.8, 126.7, 126.3, 125.8, 125.6, 125.5 (q, *J*<sub>C-F</sub> = 3.7, 2C), 124.4 (q, *J*<sub>C-F</sub> = 271.8, 1C), 44.9, 21.7; IR (neat, cm<sup>-1</sup>) 2970, 1739, 1322, 1112, 1069, 840; HRMS (TOF MS Cl<sup>+</sup>) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>15</sub>F<sub>3</sub>Na 300.1126, found 300.1123; [α]<sub>D</sub><sup>28</sup> –34.2 (*c* 0.71, CHCl<sub>3</sub>); SFC analysis (OD-H, 2.0% IPA, 2.5 mL/min, 215 nm) indicated 91% ee: t<sub>R</sub> (minor) = 11.2 min, t<sub>R</sub> (major) = 12.5 min.

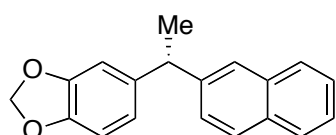


**(*R*)-2-(1-(4-methoxyphenyl)ethyl)naphthalene 38** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-SI 54 (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (49 mg, 93%). Analytical data are consistent with literature values.<sup>29</sup> TLC R<sub>f</sub> = 0.6 (4:1 hexane/EtOAc, UV active); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.78–7.66 (m, 4H), 7.41 (apd, *J* = 7.2, 1.8, 2H), 7.28 (dd, *J* = 8.4, 1.6, 1H), 7.16 (d, *J* = 8.7, 2H), 6.82 (d, *J* = 8.6, 2H), 4.25 (q, *J* = 7.2, 1H), 3.75 (s, 3H), 1.69 (d, *J* = 7.1, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 158.0, 144.3, 138.5, 133.7, 132.1, 128.8, 128.1, 127.8, 127.7, 126.9, 125.5, 125.3, 113.9, 55.4, 44.1, 30.5, 22.1; [α]<sub>D</sub><sup>28</sup> –32.1 (*c* 0.83, CHCl<sub>3</sub>); SFC analysis (OJ-H, 5.0% IPA, 3.0 mL/min, 215 nm) indicated 95% ee: t<sub>R</sub> (major) = 20.8 min, t<sub>R</sub> (minor) = 23.0 min.



**(*S*)-4-(1-(naphthalen-2-yl)ethyl)phenyl isobutyrate 39** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-SI 56 (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (30% benzene in pentane) afforded the title compound as a colorless oil (46 mg, 76%). TLC R<sub>f</sub> = 0.7 (4:1 hexane/EtOAc, UV active);

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.78–7.68 (m, 4H), 7.43 (ap, *J* = 7.1, 2H), 7.30–7.23 (m, 3H), 6.98 (d, *J* = 8.4, 2H), 4.31 (q, *J* = 7.1, 3H), 2.77 (septet, *J* = 7.0, 1H), 1.71 (d, *J* = 7.1, 1H), 1.29 (d, *J* = 7.0, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 175.9, 149.2, 143.67, 143.65, 133.6, 132.3, 128.8, 128.1, 127.9, 127.7, 126.9, 126.1, 125.6, 125.5, 121.4, 44.4, 34.3, 22.0, 19.1; IR (neat, cm<sup>-1</sup>) 2969, 1753, 1505, 1203, 1165, 1129, 1094; HRMS (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>Na 341.1518, found 341.1526 [ $\alpha$ ]<sub>D</sub><sup>28</sup> +28.5 (*c* 0.82, CHCl<sub>3</sub>); SFC analysis (OD-H, 3.0% IPA, 3 mL/min, 215 nm) indicated 97% ee: *t*<sub>R</sub> (major) = 13.7 min, *t*<sub>R</sub> (minor) = 14.7 min.

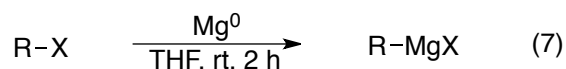


**(*R*)-5-(1-(naphthalen-2-yl)ethyl)benzo[*d*][1,3]dioxole 40** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (4.4 mg, 0.020 mmol, 0.10 equiv), Xantphos (22 mg, 0.040 mmol, 0.20 equiv), substrate (*R*)-SI 57 (0.40 mL, 0.20 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.33 mL, 0.60 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.8 mL). Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a colorless oil (54 mg, 98%). TLC *R*<sub>f</sub> = 0.6 (4:1 hexane/EtOAc, UV active); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.80–7.67 (m, 4H), 7.43 (apd, *J* = 7.3, 1.8, 2H), 7.29 (dd, *J* = 8.5, 1.7, 1H), 6.73 (s, 1H), 6.72 (d, *J* = 7.4, 2H), 5.89 (s, 2H), 4.22 (q, *J* = 7.2, 1H), 1.68 (d, *J* = 7.2, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 147.8, 145.9, 143.9, 140.5, 133.6, 132.2, 128.1, 127.9, 127.7, 126.8, 126.1, 125.5, 125.3, 120.7, 108.5, 108.2, 101.0, 44.7, 22.1; IR (neat, cm<sup>-1</sup>) 2966, 2892, 1598, 1484, 1223, 1034, 937; HRMS (TOF MS ES+) *m/z*: [M]<sup>+</sup> calculated for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> 276.1150, found 276.1152; [ $\alpha$ ]<sub>D</sub><sup>28</sup> +29.7 (*c* 0.80, CHCl<sub>3</sub>); SFC analysis (OD-H, 3.0% IPA, 3.0 mL/min, 215 nm) indicated 90% ee: *t*<sub>R</sub> (major) = 15.3 min, *t*<sub>R</sub> (minor) = 16.9 min.

## F. GENERAL PROCEDURES FOR STARTING MATERIAL SYNTHESIS

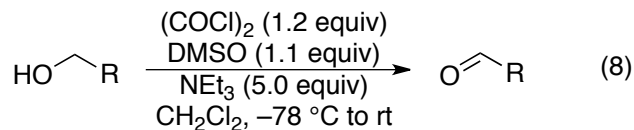
The general procedures for starting material synthesis will be used throughout the rest of the SI. In each instance a general method is used, it is specified by letter (D, E etc.) and the exact amounts of reagents used for each reaction are listed for the specific compounds synthesized.

### METHOD D: GRIGNARD PREPARATION



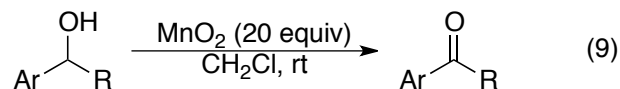
Magnesium turnings (1.5 equiv) were added to a two-neck round-bottom flask equipped with a stir bar and condenser. The reaction apparatus was flame-dried under vacuum and cooled under N<sub>2</sub>. THF was added to the reaction apparatus, followed by a single crystal of I<sub>2</sub> (ca. 2 mg). The organohalide (1.0 equiv) was added portion-wise over 1 h. The reaction was stirred at ambient temperature for an additional hour and then titrated.<sup>2</sup>

#### METHOD E: SWERN OXIDATION



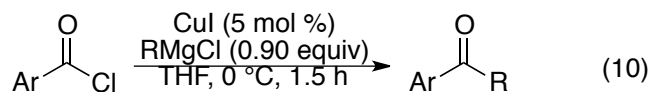
Modified from a procedure reported by Cossy.<sup>30</sup> A solution of DMSO (1.1 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added drop-wise to a stirred solution of oxalyl chloride (1.2 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> at -78 °C, under a positive pressure of N<sub>2</sub>. After 15 min, a solution of alcohol (1.0 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added drop-wise to the reaction mixture. The reaction was then stirred for an additional 30 min at -78 °C followed by the addition of triethylamine (5.0 equiv). After an additional 10 min of stirring at -78 °C, the reaction was allowed to warm to ambient temperature. The reaction mixture was then diluted with additional CH<sub>2</sub>Cl<sub>2</sub> and washed with sat. NH<sub>4</sub>Cl and then brine (x 2). The organic layer was then dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo.

#### METHOD F: OXIDATION OF BENZYLIC ALCOHOLS



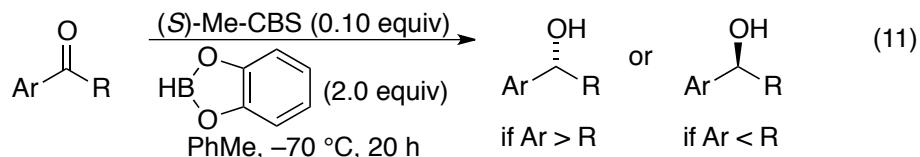
Modified from a procedure reported by Wipf.<sup>31</sup> Activated MnO<sub>2</sub> (20 equiv) was added to a solution of alcohol (1.0 equiv) in wet CH<sub>2</sub>Cl<sub>2</sub> and the reaction was stirred vigorously at ambient temperature until complete by TLC (typically 24 h). The heterogeneous mixture was then passed through a plug of celite with additional CH<sub>2</sub>Cl<sub>2</sub> and concentrated in vacuo.

#### METHOD G: COPPER-CATALYZED ADDITION OF GRIGNARD REAGENTS TO ACID CHLORIDES



Modified from a procedure reported by Hultzsch.<sup>32</sup> In a glovebox, CuI (0.050 equiv) was added to a flame-dried round-bottom flask equipped with a stirbar. The flask was capped with a septum and removed from the glovebox. Anhydrous THF and acid chloride (0.90 equiv) were added to the flask resulting in a suspension. The reaction mixture was cooled to 0 °C and the Grignard reagent (0.90 equiv) was added drop-wise over 30 min. After an additional hour of stirring at 0 °C, the reaction mixture was concentrated in vacuo. The crude residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with 1 M HCl resulting in precipitate formation. The layers were separated and the organic layer was filtered through a plug of celite to remove the copper salts. The filtrate was then washed with NaHCO<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo.

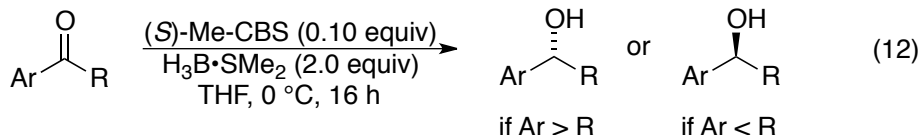
#### METHOD H: CBS REDUCTION WITH CATECHOLBORANE



Modified from a procedure reported by Okamura.<sup>33</sup> In a glovebox, (*S*)-Me-CBS-oxazaborolidine (0.10 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar. The flask was capped with a septum and taken out of the glovebox. Anhydrous PhMe and ketone (1.0 equiv) were added and the reaction mixture was stirred at ambient temperature until complete dissolution. The reaction was then cooled to  $-70\text{ }^\circ\text{C}$  and catecholborane (1.5–2.0 equiv) was added drop-wise via syringe. After stirring for 20 h at  $-70\text{ }^\circ\text{C}$ , wet methanol was added to quench the excess borane and the reaction was allowed to warm to ambient temperature. Sat.  $\text{NH}_4\text{Cl}$  was added to the reaction flask and the mixture was extracted with  $\text{Et}_2\text{O}$  (x 3). The combined organics were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo.

The above model for stereoselectivity is described by Corey.<sup>17</sup>

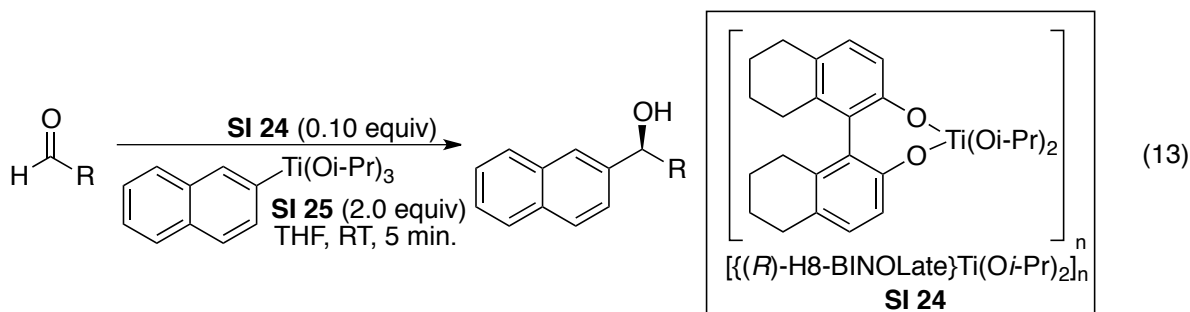
#### METHOD I: CBS REDUCTION WITH $\text{SMe}_2\cdot\text{BH}_3$



Modified from a procedure reported by Panek.<sup>34</sup> In the glovebox, (*S*)-Me-CBS-oxazaborolidine (0.10 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar. The flask was capped with a septum and taken out of the box. Anhydrous THF was added to the flask followed by  $\text{H}_3\text{B}\cdot\text{SMe}_2$  (2.0 equiv). The reaction flask was cooled to  $-20\text{ }^\circ\text{C}$  and ketone (1.0 equiv) as a solution in THF was added drop-wise over 15 min. After 16 h, methanol (0.5 mL) was slowly added to quench the excess borane. The reaction mixture was then partitioned between sat.  $\text{NH}_4\text{Cl}$  and EtOAc and the aqueous layer was extracted with EtOAc (x 2). The combined organics were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo.

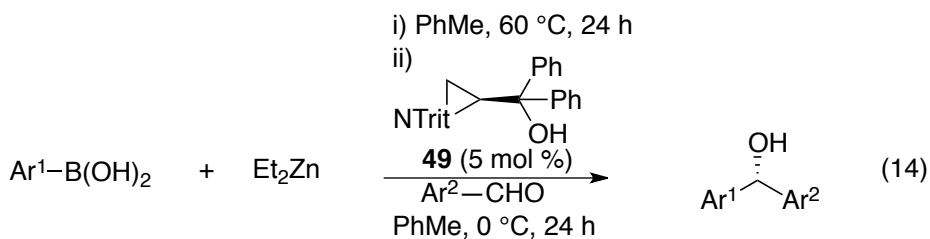
The above model for stereoselectivity is described by Corey.<sup>17</sup>

METHOD J: ENANTIOSELECTIVE ARYLATION OF ALKYL ALDEHYDES



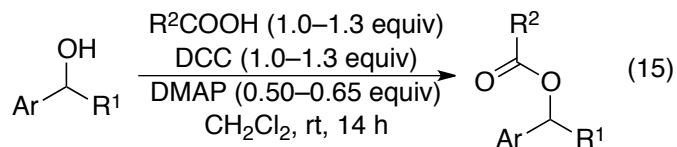
Modified from a procedure reported by Gau.<sup>5</sup> In the glovebox, [ $\{(R)\text{-H}_8\text{-BINOLate}\}\text{Ti}(\text{O}i\text{-Pr})_2$ ]<sub>n</sub> **SI 24** (0.10 equiv) and 2-naphthyltitanium triisopropoxide **SI 25** (2.0 equiv) were added to a dry 50 mL round bottom flask equipped with a stir bar. The flask was capped with a septum and taken out of the glovebox. Anhydrous THF followed by alkyl aldehyde (1.0 equiv) were then added to flask. After stirring for 5 min at ambient temperature, the reaction was quenched with 2 M NaOH and extracted with ethyl acetate (x 3). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo.

METHOD K: ENANTIOSELECTIVE ARYLATION OF ARYL ALDEHYDES



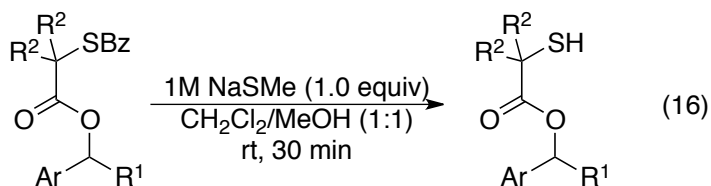
Modified from a procedure reported by Braga.<sup>11</sup> To a solution of boronic acid (2.4 equiv) in toluene was added diethylzinc (7.2 equiv, 1.0 M in toluene), and the solution was heated and stirred at 65 °C for 24 h. Upon cooling to 0 °C, (*S*)-1-(tritylaziridin-2-yl)diphenylmethanol **49** (0.050 equiv) was added as a solution in toluene. After stirring for 10 min, aldehyde (1.0 equiv) was added, also as a solution in toluene. The reaction was stirred at 0 °C for 20 h before quenching with 1 N hydrochloric acid. The product was extracted with EtOAc (x 3) and the combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo.

#### METHOD L: DCC COUPLING



Modified from a procedure reported by Meyer.<sup>35</sup> To a stirred solution of carboxylic acid (1.0–1.3 equiv) and alcohol (1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  were added 4-dimethylaminopyridine (0.50–0.65 equiv) and *N,N*-dicyclohexylcarbodiimide (1.0–1.3 equiv). After stirring at ambient temperature for 20 h, the resulting opaque white mixture was filtered through Celite and concentrated in vacuo.

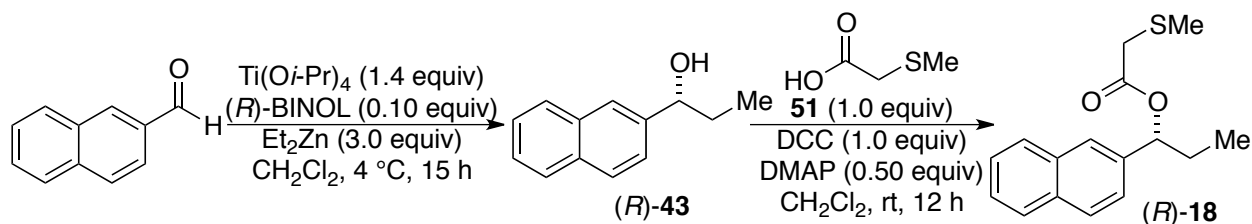
#### METHOD M: DEPROTECTION OF BENZOYL THIOLS



Modified from a procedure reported by Wallace and Springer.<sup>36</sup> NaSMe (1.0 equiv) was added to a stirred solution of ester (1.0 equiv) in a 1:1 mixture of wet MeOH and  $\text{CH}_2\text{Cl}_2$ . After 15 min, the reaction was quenched with 0.1 M HCl (2.0 equiv) and extracted with  $\text{CH}_2\text{Cl}_2$  (x 3). The combined organics were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo.

## G. STARTING MATERIALS FOR TABLE 1

Scheme SI 6. Synthesis of substrate for Table 1, entry 1

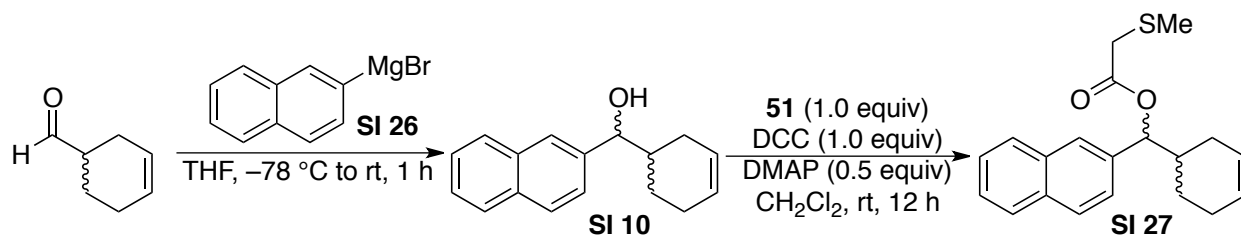


**(R)-1-(2-naphthalenyl)-1-propanol (R)-43** was prepared according to a modified procedure reported by Chan.<sup>37</sup> To a solution of (*R*)-binaphthol (0.82 g, 2.9 mmol, 0.10 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (220 mL) was added titanium isopropoxide (12 mL, 40 mmol, 1.4 equiv), and the solution was stirred at ambient temperature for 10 min. Diethylzinc (43 mL, 86 mmol, 3.0 equiv, 2.0 M in hexane) was added and the mixture was stirred for an additional 10 min at ambient temperature. The reaction mixture was cooled to 0 °C and a solution of 2-naphthaldehyde (4.5 g, 29 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added drop-wise. After stirring overnight at 4 °C, the reaction was quenched by the addition of 1 M HCl (200 mL). The reaction mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL) and the combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The resultant solid co-crystallized with (*R*)-BINOL from hexane/EtOAc and then was purified by flash chromatography (5–10% acetone in hexane) to afford the title compound as a white solid (3.50 g, 66%). Absolute configuration was assigned as *R* by comparison of optical rotation with literature values. Analytical data are consistent with literature values.<sup>38</sup> **TLC** *R<sub>f</sub>* = 0.3 (4:1 hexane/EtOAc, UV active); **mp** 39–42 °C, lit.<sup>23</sup> mp 37–38 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.88–7.80 (m, 3H), 7.78 (s, 1H), 7.52–7.43 (m, 3H), 4.78 (dt, *J* = 6.5, 3.3, 1H), 1.98–1.78 (m, 2H), 1.92 (d, *J* = 3.3, 1H), 0.95 (t, *J* = 7.4, 3H); **[α]<sub>D</sub><sup>27</sup>** +39.5 (*c* 1.0, CHCl<sub>3</sub>), lit.<sup>15</sup> **[α]<sub>D</sub><sup>20</sup>** +35.1 (*c* 2.4, CHCl<sub>3</sub>, 92% ee, (*R*)-enantiomer); **SFC** analysis (OD-H, 10.0% IPA, 2.5 mL/min, 215 nm) indicated 98% ee: *t<sub>R</sub>* (minor) = 9.1 min, *t<sub>R</sub>* (major) = 9.7 min.

**(R)-1-(2-naphthalenyl)propyl 2-(methylthio)acetate (R)-18** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (0.21 g, 2.0 mmol, 1.0 equiv), alcohol (*R*)-**43** (0.37 g, 2.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (0.12 g, 1.0 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.41 g, 2.0 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (11 mL). The crude residue was purified by flash chromatography (2.5–5% Et<sub>2</sub>O in pentane) to afford to the title compound as a colorless oil (0.48 g, 87%) **TLC** *R<sub>f</sub>* = 0.7 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 7.86–7.72 (m, 4H), 7.51–7.39 (m, 3H), 5.87 (t, *J* = 6.8, 1H), 3.23 (s, 2H), 2.14 (s, 3H), 2.09–1.99 (m, 1H), 1.99–1.88 (m, 1H), 0.93 (t, *J* = 7.4, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.7, 137.6, 133.23, 133.20, 128.4, 128.1, 127.8, 126.3, 126.2, 125.9, 124.4, 78.6, 36.1, 29.3, 16.3, 10.1; **IR** (neat, cm<sup>-1</sup>) 2969, 1726, 1267, 1125, 817, 747; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>SNa 297.0925, found 297.0928; **[α]<sub>D</sub><sup>27</sup>** + 95.1 (*c* 0.99, CHCl<sub>3</sub>); **SFC** analysis (OD-H, 5.0% IPA, 3.0 mL/min, 215 nm) indicated 98% ee: *t<sub>R</sub>* (major) = 5.1 min, *t<sub>R</sub>* (minor) = 6.0 min.



Scheme SI 7. Synthesis of substrate for Table 1, entry 2

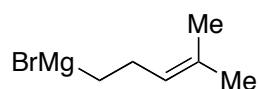
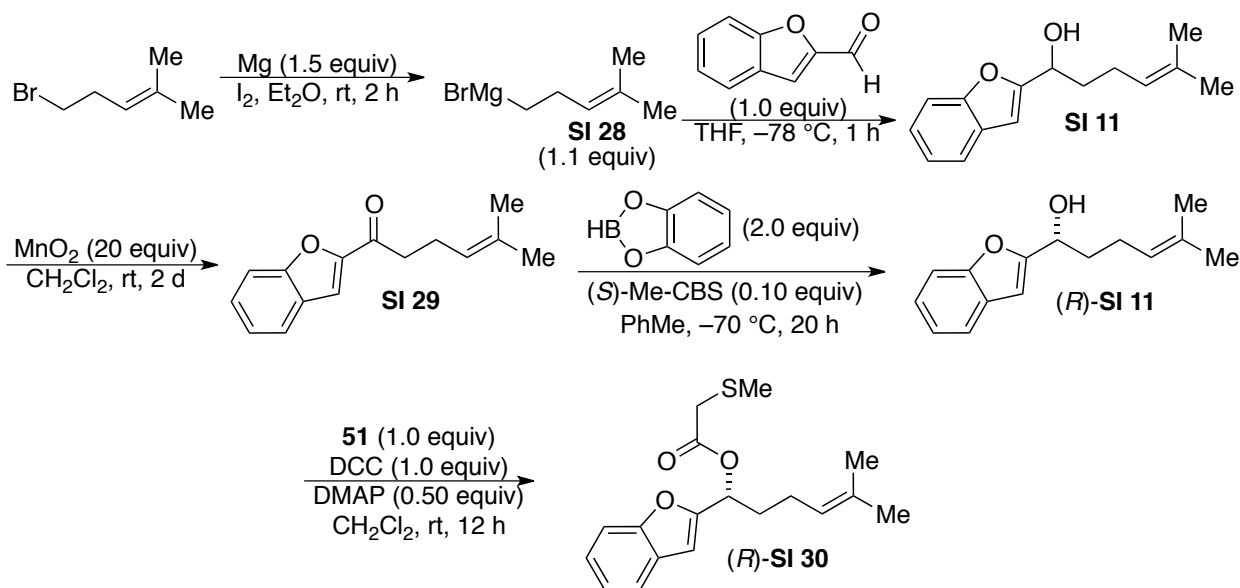


**2-naphthylmagnesium bromide SI 26** was prepared according to Method D. The following amounts of reagents were used: 2-bromonaphthlene (4.1 g, 20 mmol, 1.0 equiv), magnesium (0.96 g, 40 mmol, 2.0 equiv), THF (18 mL). Grignard titrated to 0.49 M.<sup>2</sup>

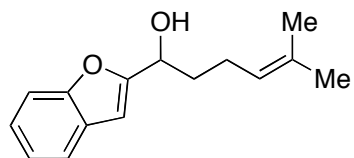
**Cyclohex-3-enyl(naphthalen-2-yl)methanol SI 10.** To a cooled (0 °C) solution of *rac*-cyclohex-3-enecarbaldehyde (0.23 mL, 2.0 mmol, 1.0 equiv) in THF (10 mL) was added Grignard **SI 26** (4.9 mL, 2.4 mmol, 1.2 equiv, 0.49 M in THF). The reaction was stirred and allowed to warm to ambient temperature. After 2 h, the remaining Grignard was quenched with sat. NH<sub>4</sub>Cl, and the aqueous was extracted with EtOAc (2 x 20 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The product was purified by flash chromatography (5–20% EtOAc in hexanes) to afford the title compound as a white solid (0.35 g, 72%, dr = 52:48 by NMR integration). **TLC**  $R_f$  = 0.4 (4:1 hexane/EtOAc, UV active); **mp** 83–86 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.82 (d,  $J$  = 8.6, 3H), 7.45 (d,  $J$  = 5.5, 1H), 7.49–7.44 (m, 3H), 5.71–5.54 (m, 2H), 4.64 (d,  $J$  = 6.5, 0.52H), 4.57 (d,  $J$  = 7.8, 0.48H), 2.26–1.98 (m, 6H), 1.76–1.24 (m, 2H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  141.0, 140.9, 133.3, 133.2, 133.1, 128.33, 128.25, 128.05, 128.04, 127.8, 127.3, 127.0, 126.33, 126.27, 126.1, 125.98, 125.96, 125.74, 125.66, 124.7, 79.0, 78.8, 40.99, 40.94, 28.4, 27.7, 25.4, 25.2, 24.9; **IR** (neat, cm<sup>-1</sup>) 3419, 3021, 2916, 2888, 2834, 1435, 1301; **HRMS** (TOF MS EI+)  $m/z$ : [M]<sup>+</sup> calculated for C<sub>17</sub>H<sub>18</sub>O 238.1358, found 238.1396.

**Cyclohex-3-enyl(naphthalen-2-yl)methyl 2-(methylthio)acetate SI 27** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (0.11 g, 1.0 mmol, 1.0 equiv), alcohol **SI 10** (0.24 g, 1.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (61 mg, 0.50 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.21 mg, 1.0 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (6 mL). The crude residue was purified by flash chromatography (10–20% EtOAc in hexanes) to afford the title compound as a colorless oil (0.31 g, 95%, dr = 53:47 by <sup>1</sup>H NMR integration). **TLC**  $R_f$  = 0.5 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.83–7.81 (m, 4H), 7.48–7.45 (m, 3H), 5.78 (d,  $J$  = 7.9, 0.53H), 5.73 (d,  $J$  = 8.9, 0.47H), 5.69–5.53 (m, 2H), 3.23 (s, 2H), 2.27–1.97 (m, 7H), 1.73–1.71 (m, 1H), 1.59–1.22 (m, 2H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  169.8, 169.7, 136.7, 136.5, 133.24, 133.22, 122.1, 128.33, 128.31, 128.2, 127.8, 127.3, 127.1, 126.8, 126.7, 126.4, 126.26, 126.25, 125.8, 125.6, 124.78, 124.75, 81.1, 80.6, 39.2, 39.0, 36.12, 36.10, 28.1, 27.9, 25.0, 24.91, 24.89, 16.38, 16.37; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>SNa 349.1238, found 349.1244.

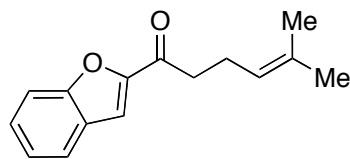
Scheme SI 8. Synthesis of substrate for Table 1, entry 3



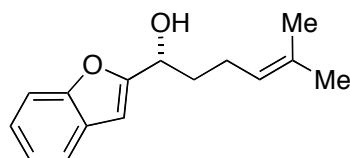
**(4-methylpent-3-en-1-yl)magnesium bromide SI 28.** Magnesium turnings (0.18 g, 7.5 mmol, 1.5 equiv) were added to a 2-neck round-bottom flask equipped with a stir bar, a condenser and septa tops. The reaction apparatus was flame-dried under vacuum and cooled under N<sub>2</sub>. Et<sub>2</sub>O (1 mL) was added to the reaction flask. 5-bromo-2-methyl-2-pentene (0.67 mL, 5.0 mmol, 1.0 equiv), as a solution in Et<sub>2</sub>O (3 mL), was then added to the reaction flask portion-wise over 1 h. The reaction was stirred at ambient temperature for an additional hour and then titrated to 0.71 M.<sup>2</sup>



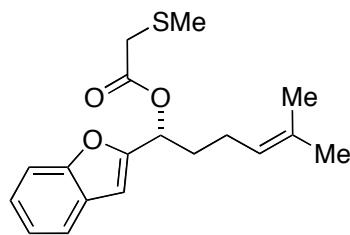
**1-(2-benzofuryl)-5-methyl-4-hexen-1-ol SI 11.** Benzofuran-2-carbaldehyde (0.47 g, 3.2 mmol, 1.0 equiv) and anhydrous THF (5 mL) were added to a flame-dried 50 mL round-bottom flask equipped with a stir bar and a septum. The homogeneous solution was cooled to -78 °C and Grignard SI 28 (4.8 mL, 3.4 mmol, 1.1 equiv, 0.71 M in Et<sub>2</sub>O) was added drop-wise over 15 min. The reaction mixture was allowed to warm to ambient temperature over 1 h. The reaction was then quenched with sat. NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (2–10% EtOAc in hexanes) to afford the title compound as a colorless oil (0.49 g, 66%). **TLC** R<sub>f</sub> = 0.3 (4:1 hexane/EtOAc, UV active, stains blue with PAA); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 7.52 (d, *J* = 7.2, 1H), 7.44 (d, *J* = 7.9, 1H), 7.25 (td, *J* = 7.2, 1.1, 1H), 7.20 (td, *J* = 7.2, 0.9, 1H), 6.59 (s, 1H), 5.15 (tt, *J* = 7.2, 1.2, 1H), 4.81 (dd, *J* = 12.7, 5.7, 1H), 2.20 (d, *J* = 5.3, 1H), 2.14 (q, *J* = 7.3, 2H), 1.97 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 159.6, 154.9, 132.9, 128.3, 124.2, 123.5, 122.8, 121.1, 111.3, 102.6, 68.0, 35.6, 25.9, 24.1, 17.9; **IR** (neat, cm<sup>-1</sup>) 3358, 2919, 1454, 1253, 740; **HRMS** (TOF MS ES<sup>+</sup>) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>Na 253.1205, found 253.1208.



**1-(2-benzofuryl)-5-methyl-4-hexen-1-one SI 29** was prepared according to Method F. The following amounts of reagents were used: MnO<sub>2</sub> (2.3 g, 26 mmol, 20 equiv), alcohol **SI 11** (0.30 g, 1.3 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The crude residue was purified by flash chromatography (5% Et<sub>2</sub>O in hexanes) to afford **SI 29** as a slightly yellow solid (0.27 g, 92%). **TLC** R<sub>f</sub> = 0.7 (4:1 hexane/EtOAc, UV active, stains turquoise with PAA); **mp** 48–49 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.70 (d, *J* = 7.9, 1H), 7.58 (d, *J* = 8.4, 1H), 7.49 (s, 1H), 7.47 (t, *J* = 7.9, 1H), 7.31 (t, *J* = 7.6, 1H), 5.18 (tt, *J* = 7.2, 1.2, 1H), 2.99 (t, *J* = 7.5, 2H), 2.46 (q, *J* = 7.4, 2H), 1.69 (s, 3H), 1.65 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 191.3, 155.7, 152.8, 133.3, 128.3, 127.2, 124.0, 123.4, 122.6, 112.7, 112.6, 39.3, 25.8, 23.0, 17.8; **IR** (neat, cm<sup>-1</sup>) 2907, 1681, 1560, 1153, 841, 751; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>Na 251.1048, found 251.1057.

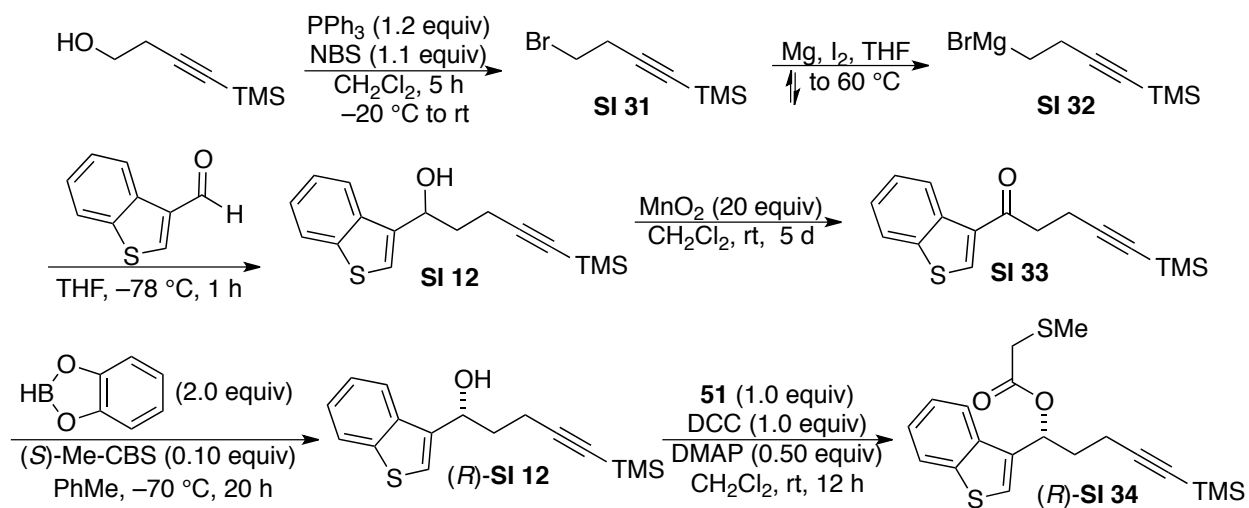


**(R)-1-(2-benzofuryl)-5-methyl-4-hexen-1-ol ((R)-SI 11)** was prepared according to Method H. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (21 mg, 0.076 mmol, 0.10 equiv), ketone **SI 29** (0.17 g, 0.76 mmol, 1.0 equiv), catecholborane (0.12 mL, 1.1 mmol, 1.5 equiv), and PhMe (7 mL). The crude residue was purified by flash chromatography (2–10% EtOAc in hexane) to afford the title compound as a colorless oil (0.15 g, 68%). Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> For analytical data see *rac*-alcohol **SI 11**. [α]<sub>D</sub><sup>26</sup> -19.1 (*c* 1.0, CHCl<sub>3</sub>); **SFC** analysis (OJ-H, 10.0% MeOH, 3.0 mL/min, 215 nm) indicated 93% ee: t<sub>R</sub> (major) = 3.8 min, t<sub>R</sub> (minor) = 4.4 min.



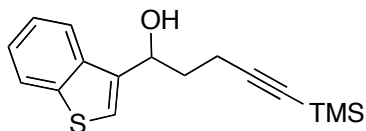
**(R)-1-(2-benzofuryl)-5-methyl-4-hexen-2-(methylthio)acetate ((R)-SI 30)** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (61 mg, 0.58 mmol, 1.0 equiv), alcohol (*R*)-**SI 11** (0.13 g, 0.58 mmol, 1.0 equiv), 4-dimethylaminopyridine (35 mg, 0.29 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.12 g, 0.58 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The crude residue was purified by flash chromatography (5% Et<sub>2</sub>O in pentane) to afford to the title compound as a colorless oil (0.48 g, 87%). **TLC** R<sub>f</sub> = 0.7 (4:1 hexane/EtOAc, UV active); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.54 (d, *J* = 7.6, 1H), 7.46 (d, *J* = 8.2, 1H), 7.28 (td, *J* = 7.7, 1.2, 1H), 7.21 (td, *J* = 7.3, 0.8, 1H), 6.72 (s, 1H), 5.99 (at, *J* = 6.5, 1H), 5.11 (br s, 1H), 3.24 (d, *J* = 14.6, 1H), 3.20 (d, *J* = 15.3, 1H), 2.18 (s, 3H), 2.15–2.03 (m, 4H), 1.67 (s, 3H), 1.60 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 169.6, 154.9, 154.8, 133.1, 127.9, 124.7, 123.0, 122.7, 121.4, 111.5, 105.4, 69.8, 35.9, 32.7, 25.8, 23.9, 17.8, 16.4; **IR** (neat, cm<sup>-1</sup>) 2920, 1732, 1454, 1252, 1126, 958; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>SNa 341.1187, found 341.1178; [α]<sub>D</sub><sup>26</sup> +150.9 (*c* 0.69, CHCl<sub>3</sub>); **SFC** analysis (OJ-H, 10.0% MeOH, 3.0 mL/min, 215 nm) indicated 93% ee: t<sub>R</sub> (minor) = 2.1 min, t<sub>R</sub> (major) = 2.4 min.

Scheme SI 9. Synthesis of substrate for Table 1, entry 4



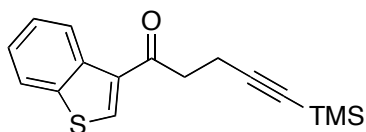
(4-bromobut-1-yn-1-yl)trimethylsilane **SI 31** was prepared according to a modified procedure by Steliou.<sup>39</sup> A flame-dried 250 mL round-bottom flask equipped with a stir bar and a septum was charged with 4-trimethylsilyl-3-butyn-1-ol (3.0 g, 21 mmol, 1.0 equiv). The flask was placed under reduced pressure and back-filled with nitrogen (x 3). CH<sub>2</sub>Cl<sub>2</sub> (35 mL) was then added and the flask cooled to -20 °C. Triphenylphosphine (6.6 g, 25 mmol, 1.2 equiv) was added followed by recrystallized NBS (4.1 g, 23 mmol, 1.1 equiv). The reaction mixture was allowed to warm to ambient temperature and the progress of the reaction was followed by TLC. Once complete (5 h), Et<sub>2</sub>O (150 mL) was added and the organics were successively washed with sat. NaHCO<sub>3</sub> (30 mL x 2) and brine (30 mL). The organics were then dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The resultant solid was then suspended in hexanes (300 mL) and stirred vigorously for 15 min. The suspension was then filtered through a plug of celite and the filtrate was concentrated in vacuo. The crude was purified by flash chromatography (100% petroleum ether) to afford the title compound as a colorless oil (3.2 g, 75%). Analytical data are consistent with literature values.<sup>40</sup> TLC R<sub>f</sub> = 0.5 (100 % petroleum ether, stain with KMnO<sub>4</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.43 (t, *J* = 7.5, 2H), 2.77 (t, *J* = 7.5, 2H), 0.16 (s, 9H).

4-trimethylsilyl-3-butynyl-1-magnesium bromide **SI 32** was prepared according to a modified procedure reported by Waldman.<sup>41</sup> A 100 mL 3-neck round-bottom flask, equipped with a reflux condenser, an addition funnel, and a stir bar was charged with magnesium turnings (0.57 g, 24 mmol, 1.5 equiv), flame-dried under reduced pressure and cooled under nitrogen. Anhydrous THF (3 mL) was added to the reaction flask followed by iodine to activate the magnesium. Substrate **SI 31** (3.2 g, 16 mmol, 1.0 equiv), as a solution in THF (19 mL), was transferred to the addition funnel. The solution of alkyl bromide **SI 31** was added drop-wise to the activated magnesium turnings. Gentle heating with a heat gun was necessary to initiate the reaction after which the reaction continued at a reflux for the remainder of the addition. Upon completion, the addition funnel was rinsed with an additional 1 mL of anhydrous THF and the reaction was stirred at 60 °C for an additional 30 min. The resultant Grignard reagent was cooled to ambient temperature and titrated to 0.44 M.<sup>2</sup>



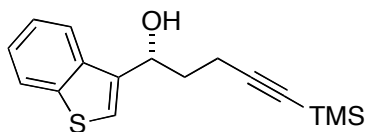
### 1-(3-benzothiophenyl)-5-(trimethylsilyl)-4-pentyn-1-ol SI 12.

Benzothiophene-3-carbaldehyde (0.60 g, 3.7 mmol, 1.0 equiv) was added to a flame-dried 50 mL round-bottom flask equipped with a stir bar and a septum. The flask was then evacuated and back-filled with nitrogen three times. Anhydrous THF (4 mL) was added to the flask and the homogeneous solution was cooled to  $-78\text{ }^{\circ}\text{C}$ . Grignard **SI 32** (10 mL, 4.5 mmol, 1.2 equiv, 0.44 M in THF) was added via syringe and the reaction mixture was allowed to stir at  $-78\text{ }^{\circ}\text{C}$  until complete by TLC (1 h). The reaction was then quenched with sat.  $\text{NH}_4\text{Cl}$  (10 mL) and extracted with  $\text{Et}_2\text{O}$  (3 x 10 mL). The combined organics were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (2–10% EtOAc in hexanes) to afford the title compound as a yellow oil (1.1 g, 95%). **TLC**  $R_f$  = 0.5 (4:1 hexane/EtOAc, UV active);  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.92–7.83 (m, 2H), 7.40 (s, 1H), 7.40–7.33 (m, 2H), 5.30 (dt,  $J$  = 8.1, 3.8, 1H), 2.49 (ddd,  $J$  = 17.1, 7.8, 7.0, 1H), 2.38 (dt,  $J$  = 17.1, 6.4, 1H), 2.27 (d,  $J$  = 3.7, 1H), 2.19–2.02 (m, 2H), 0.18 (s, 9H);  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  141.1, 139.4, 137.2, 124.6, 124.2, 123.1, 122.3, 122.2, 106.8, 85.9, 69.1, 36.1, 16.9, 0.3; **IR** (neat,  $\text{cm}^{-1}$ ) 3385, 1739, 1248, 837, 758; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{16}\text{H}_{20}\text{OSSiNa}$  311.0902, found 311.0904.



### 1-(3-benzothiophenyl)-5-(trimethylsilyl)-4-pentyn-1-one SI 33

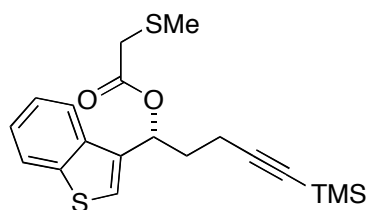
was prepared according to Method F. The following amounts of reagents were used:  $\text{MnO}_2$  (5.0 g, 58 mmol, 16 equiv), alcohol **SI 12** (0.75 g, 2.6 mmol, 1.0 equiv), and  $\text{CH}_2\text{Cl}_2$  (30 mL). The crude residue was recrystallized from hexanes/EtOAc to afford **SI 4** as a white crystalline solid (0.51 g, 68%). **TLC**  $R_f$  = 0.7 (4:1 hexane/EtOAc, UV active); **mp** 96–99  $^{\circ}\text{C}$ ;  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.75 (d,  $J$  = 8.2, 1H), 8.31 (s, 1H), 7.86 (d,  $J$  = 8.2, 1H), 7.49 (t,  $J$  = 7.7, 1H), 7.41 (t,  $J$  = 7.6, 1H), 3.24 (t,  $J$  = 7.6, 2H), 2.70 (t,  $J$  = 7.5, 2H), 0.14 (s, 9H);  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  193.2, 139.9, 137.1, 136.6, 134.9, 126.0, 125.7, 125.6, 122.4, 105.9, 85.5, 39.2, 15.1, 0.2; **IR** (neat,  $\text{cm}^{-1}$ ) 3087, 2180, 1667, 842, 762; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{16}\text{H}_{18}\text{OSSiNa}$  309.0745, found 309.0742.



### (*R*)-1-(3-benzothiophenyl)-5-(trimethylsilyl)-4-pentyn-1-ol

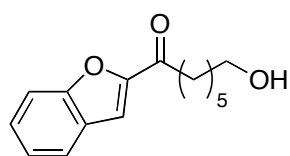
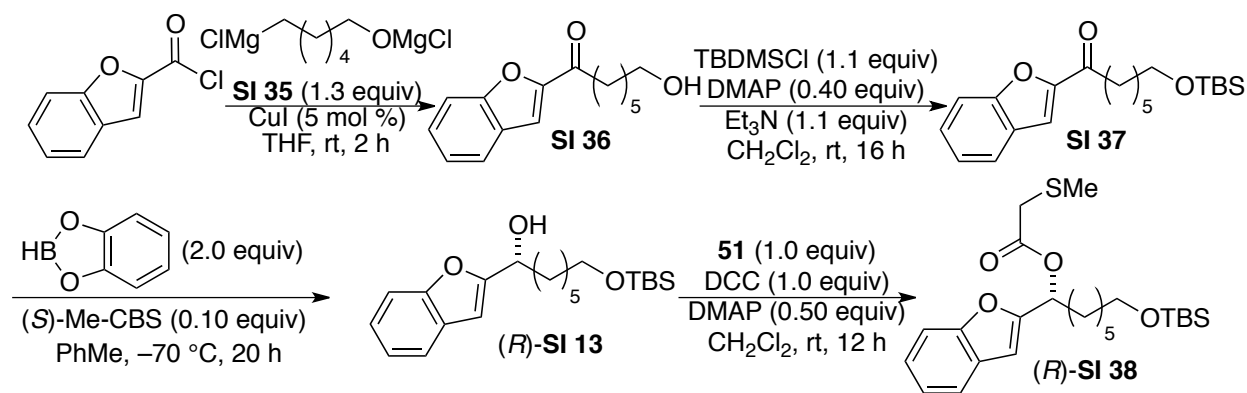
#### (*R*)-SI 12

was prepared according to Method H. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (18 mg, 0.066 mmol, 0.10 equiv), ketone **SI 33** (0.19 g, 0.66 mmol, 1.0 equiv), catecholborane (0.11 mL, 1.0 mmol, 1.5 equiv), and PhMe (7 mL). The crude residue was purified by flash chromatography (2–10% EtOAc in hexanes) to afford the title compound as a colorless oil (0.15 g, 80%). Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> For analytical data see *rac*-alcohol **SI 12**.  $[\alpha]_D^{28}$   $-16.3$  ( $c$  1.2,  $\text{CHCl}_3$ ); **SFC** analysis (AD-H, 3.0% MeOH, 3.0 mL/min, 215 nm) indicated 96% ee:  $t_R$  (minor) = 6.7 min,  $t_R$  (major) = 8.1 min.

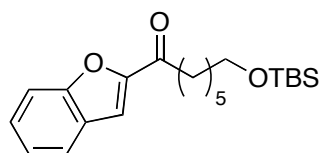


**(R)-1-(benzo[b]thiophen-3-yl)-5-(trimethylsilyl)pent-4-yn-1-yl 2-(methylthio)acetate (R)-SI 34** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (54 mg, 0.51 mmol, 1.0 equiv), alcohol (*R*)-**SI 12** (0.15 g, 0.51 mmol, 1.0 equiv), 4-dimethylaminopyridine (31 mg, 0.29 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.11 g, 0.51 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The crude residue was purified by flash chromatography (2–5% Et<sub>2</sub>O in pentane) to afford to the title compound as a colorless oil (0.18 g, 89%). **TLC** *R<sub>f</sub>* = 0.7 (4:1 hexane/EtOAc, UV active); <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.93 (dd, *J* = 7.1, 1.1, 1H), 7.85 (dd, *J* = 7.3, 1.1, 1H), 7.45 (s, 1H), 7.37 (apd, *J* = 7.5, 1.2, 2H), 6.36 (dd, *J* = 7.1, 5.5, 1H), 3.22 (s, 2H), 2.45–2.17 (m, 4H), 2.14 (s, 3H), 0.17 (s, 9H); <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.3, 140.8, 137.0, 134.7, 124.7, 124.4, 123.8, 123.1, 122.3, 105.6, 86.0, 71.2, 35.9, 34.0, 16.6, 16.3, 0.2; **IR** (neat, cm<sup>-1</sup>) 2958, 2174, 1731, 1249, 1128, 839; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>SiNa 399.0885, found 399.0879; [α]<sub>D</sub><sup>26</sup> +9.7 (*c* 1.0, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 15.0% IPA, 1.0 mL/min, 215 nm) indicated 97% ee: *t<sub>R</sub>* (major) = 6.8 min, *t<sub>R</sub>* (minor) = 7.8 min.

**Scheme SI 10. Synthesis of substrate for Table 1, entry 5**

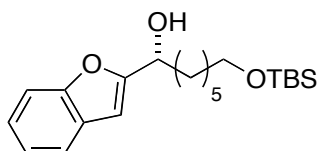


**1-(benzofuran-2-yl)-3-hydroxypropan-1-one SI 36** was prepared according to Method G. The following amounts of reagents were used: CuI (32 mg, 0.17 mmol, 0.050 equiv), benzofuran-2-carbonyl chloride (0.60 g, 3.3 mmol, 1.0 equiv) Grignard reagent **SI 35** (5.0 mL, 3.2 mmol, 0.95 equiv, 0.63 M in THF), and THF (3.5 mL). The crude material was carried to the next step without purification (0.42 g).



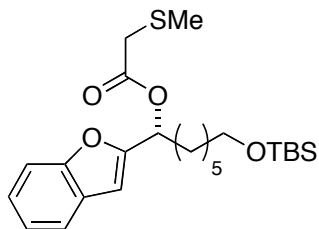
**1-(2-benzofuryl)-7-[(*tert*-butyldimethylsilyl)oxy]-1-heptanone SI 37** was prepared according to a modified procedure reported by Hernandez.<sup>42</sup> *tert*-Butyldimethylsilyl chloride (0.28 g, 1.9 mmol, 1.1 equiv) was added to a stirred solution of crude alcohol **SI 36** (0.42 g, 1.7 mmol, 1.0 equiv), dimethylaminopyridine (84 mg, 0.69 mmol, 0.40 equiv), and triethylamine (0.26 mL, 1.9 mmol, 1.1 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (17 mL) under N<sub>2</sub>. The reaction was allowed to stir overnight (14 h) and subsequently quenched with sat. NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL). The combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography

(2–10% Et<sub>2</sub>O in pentane) to afford the title compound as a slightly yellow oil (0.22 g, 53%). **TLC**  $R_f$  = 0.7 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.70 (d,  $J$  = 7.9, 1H), 7.58 (d,  $J$  = 8.4, 1H), 7.49 (s, 1H), 7.47 (t,  $J$  = 8.1, 1H), 7.30 (t,  $J$  = 7.5, 1H), 3.61 (t,  $J$  = 6.5, 2H), 2.95 (t,  $J$  = 7.5, 2H), 1.79 (p, 7.3, 2H), 1.54 (p,  $J$  = 6.7, 2H), 1.48–1.34 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  191.7, 155.7, 152.8, 128.2, 127.2, 124.0, 123.4, 112.7, 112.6, 63.3, 39.0, 32.8, 29.2, 26.1, 25.7, 24.4, 18.5, –5.2; **IR** (neat, cm<sup>-1</sup>) 2928, 2856, 1683, 1558, 1096, 833; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>SiNa 383.2018, found 383.2015.



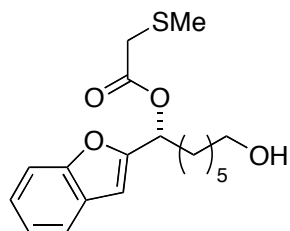
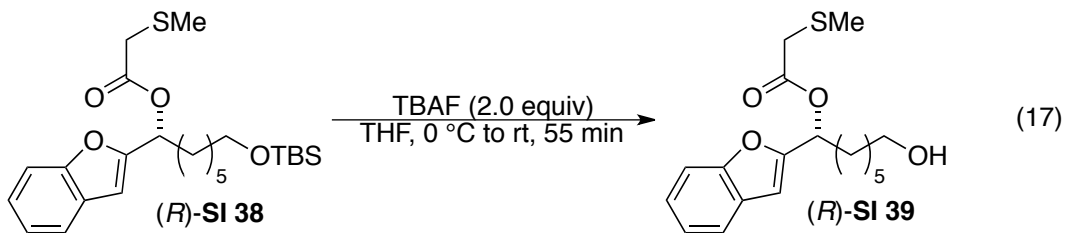
**(R)-1-(2-benzofuryl)-7-[(tert-butyldimethylsilyl)oxy]-1-heptanol**

**(R)-SI 13** was prepared according to Method H. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (21 mg, 0.077 mmol, 0.10 equiv), ketone **SI 37** (0.28 g, 0.77 mmol, 1.0 equiv), catecholborane (0.12 mL, 1.2 mmol, 1.5 equiv), and PhMe (7 mL). The crude residue was purified by flash chromatography (2–10% EtOAc in hexanes) to afford the title compound as a colorless oil (0.28 g, 91%). Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> **TLC**  $R_f$  = 0.4 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.52 (d,  $J$  = 7.4, 1H), 7.44 (d,  $J$  = 7.9, 1H), 7.25 (td,  $J$  = 7.7, 1.3, 1H), 7.20 (t,  $J$  = 7.3, 1H), 6.59 (s, 1H), 4.79 (dd,  $J$  = 10.2, 6.3, 1H), 3.58 (t,  $J$  = 6.6, 2H), 2.20 (d,  $J$  = 4.4, 1H) 2.01–1.84 (m, 2H), 1.56–1.42 (m, 3H), 1.42–1.26 (m, 5H), 0.89 (s, 9H), 0.04 (s, 6H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  159.6, 154.9, 128.3, 124.2, 122.9, 121.1, 111.3, 102.6, 68.4, 63.4, 35.7, 32.9, 29.3, 26.1, 25.8, 25.5, 18.5, –5.1; **IR** (neat, cm<sup>-1</sup>) 3362, 2929, 2856, 1253, 1097, 881; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>34</sub>O<sub>3</sub>SiNa 385.2175, found 385.2177; **[ $\alpha$ ]<sub>D</sub><sup>27</sup>** +3.8 (*c* 0.99, CHCl<sub>3</sub>); **SFC** analysis (OD-H, 5.0% MeOH, 3.0 mL/min, 215 nm) indicated 88% ee:  $t_R$  (major) = 11.1 min,  $t_R$  (minor) = 12.1 min.



**(R)-1-(benzofuran-2-yl)-7-[(tert-butyldimethylsilyl)oxy]heptyl 2-(methylthio)acetate**

**(R)-SI 38** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (59 mg, 0.65 mmol, 1.0 equiv), alcohol **(R)-SI 13** (0.24 g, 0.65 mmol, 1.0 equiv), 4-dimethylaminopyridine (40 mg, 0.32 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.13 g, 0.65 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The crude residue was purified by flash chromatography (2–5% Et<sub>2</sub>O in pentane) to afford to the title compound as a colorless oil (0.27 g, 92%). **TLC**  $R_f$  = 0.7 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.55 (d,  $J$  = 7.5, 1H), 7.47 (d,  $J$  = 8.2, 1H), 7.28 (td,  $J$  = 7.7, 1.2, 1H), 7.22 (t,  $J$  = 7.4, 1H), 6.72 (s, 1H), 5.99 (t,  $J$  = 7.1, 1H), 3.60 (t,  $J$  = 6.5, 2H), 3.24 (d,  $J$  = 14.9, 1H), 3.20 (d,  $J$  = 15.0, 1H), 2.18 (s, 3H), 2.06 (q,  $J$  = 7.0, 2H), 1.49 (p,  $J$  = 6.7, 2H), 1.45–1.24 (m, 6H), 0.88 (s, 9H), 0.03 (s, 6H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  169.7, 154.93, 154.91, 127.9, 124.7, 123.0, 121.4, 111.5, 105.3, 70.2, 63.3, 35.9, 32.8, 32.6, 29.1, 26.1, 25.7, 25.3, 18.5, 16.4, –5.1; **IR** (neat, cm<sup>-1</sup>) 2928, 1733, 1252, 1096, 836; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>SSiNa 473.2158, found 473.2154; **[ $\alpha$ ]<sub>D</sub><sup>26</sup>** –26.8 (*c* 1.2, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 15.0% IPA, 1.0 mL/min, 215 nm) indicated 90% ee:  $t_R$  (minor) = 7.0 min,  $t_R$  (major) = 7.4 min.

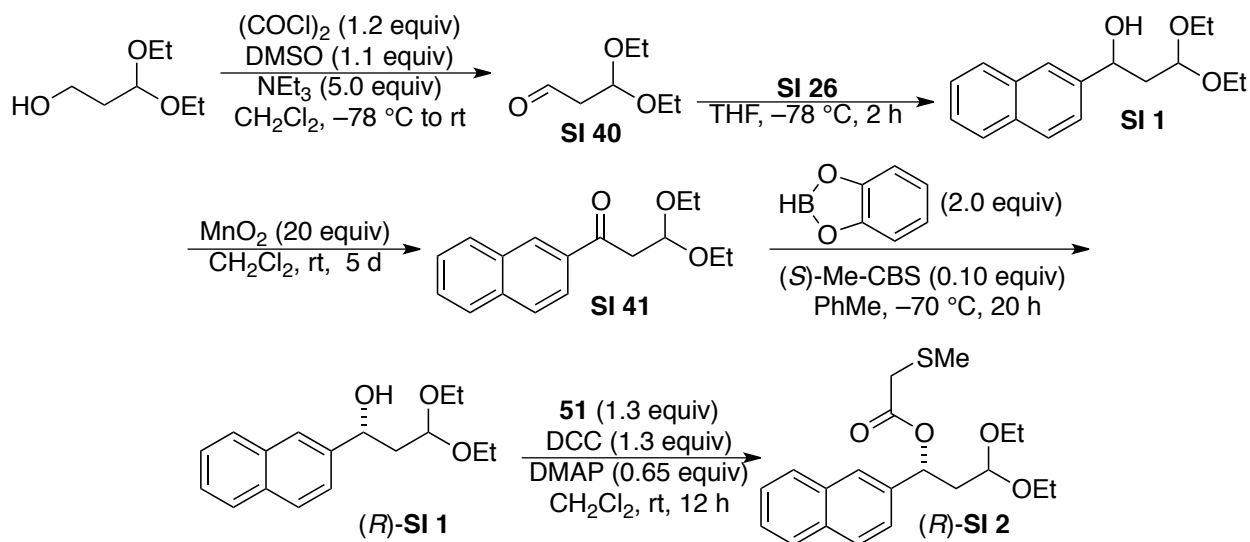


**(R)-1-(benzofuran-2-yl)-7-hydroxyheptyl 2-(methylthio)acetate (R)-SI 39** was prepared according to a modified procedure reported by Corey.<sup>43</sup> Tetrabutylammonium fluoride (0.44 mL, 0.44 mmol, 2.0 equiv, 1.0 M in THF) was added to a stirred solution of substrate **(R)-SI 38** (0.10 g, 0.22 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) at 5 °C. After 5 min, the reaction was warmed to ambient temperature and stirred for an additional 50 min before quenching with sat. NH<sub>4</sub>Cl. The

reaction mixture was then extracted with Et<sub>2</sub>O (3x 3mL). The combined organics were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (20–40% EtOAc in hexanes to afford the title compound as a colorless oil (49 mg, 66%). **TLC** *R<sub>f</sub>* = 0.5 (1:1 hexane/EtOAc, UV active, stain with CAM); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.55 (d, *J* = 7.6, 1H), 7.50 (d, *J* = 8.2, 1H), 7.29 (td, *J* = 7.7, 1.2, 1H), 7.22 (td, *J* = 7.5, 0.6, 1H), 6.72 (s, 1H), 5.99 (t, *J* = 7.1, 1H), 3.62 (t *J* = 6.2, 2H), 3.24 (d, *J* = 15.2, 1H), 3.20 (d, *J* = 14.8, 1H), 2.18 (s, 3H), 2.07 (q, *J* = 7.2, 2H), 1.60–1.50 (m, 2H), 1.49–1.28 (m, 6H), 1.22 (br s, 1H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.7, 154.9, 154.8, 127.9, 124.7, 123.0, 121.4, 111.5, 105.3, 70.2, 63.0, 35.9, 32.7, 32.5, 29.1, 25.7, 25.3, 16.4; **IR** (neat, cm<sup>-1</sup>) 3335, 2927, 1730, 1253, 1127, 751; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>24</sub>O<sub>4</sub>SNa 359.1293, found 359.1306; **[α]<sub>D</sub><sup>27</sup>** +95.5 (*c* 0.53, CHCl<sub>3</sub>); **SFC** analysis (OJ-H, 10.0% IPA, 3.0 mL/min, 215 nm) indicated 92% ee: *t<sub>R</sub>* (minor) = 6.5 min, *t<sub>R</sub>* (major) = 11.4 min.

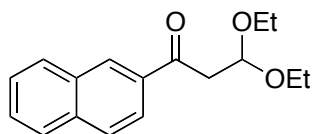


Scheme SI 11. Synthesis of substrate for Table 1, entry 7

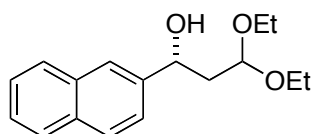


**3,3-diethoxy-1-propanal SI 40** was prepared according Method E. The following amounts of reagents were used: DMSO (0.78 mL, 11 mmol, 1.1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (17 mL), oxalyl chloride (1.0 mL, 12 mmol, 1.2 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) 3,3-diethoxy propanol (1.5 g, 10 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and triethylamine (7.7 mL, 50 mmol, 5.0 equiv). The crude yellow oil was used without further purification. Analytical data was consistent with literature values.<sup>44</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.76 (t, *J* = 1.9, 1H), 4.96 (t, *J* = 5.5, 1H), 3.69 (dq, *J* = 9.1, 7.2, 2H), 3.56 (dq, *J* = 9.1, 7.2, 2H), 2.73 (dd, *J* = 5.4, 2.0, 2H), 1.22 (t, *J* = 7.0, 6H)

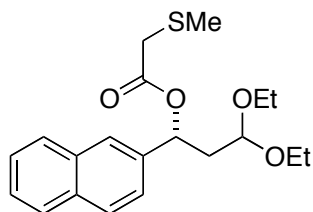
**3,3-diethoxy-1-(2-naphthalenyl)-1-propanol SI 1.** Grignard **SI 26** (9.0 mL, 4.4 mmol, 1.1 equiv, 0.5 M in THF) was added to a solution of aldehyde **SI 40** (0.59 g, 4.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) at -78 °C. The reaction was stirred for 2 h at -78 °C. Subsequently, the reaction was quenched with sat. NH<sub>4</sub>Cl and warmed to ambient temperature. The crude reaction mixture was extracted with Et<sub>2</sub>O (3 x 20 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (5–20% EtOAc in hexane with 1% TEA) to afford the title compound as a slightly yellow oil (0.27 g, 25%). TLC R<sub>f</sub> = 0.2 (4:1 hexane/EtOAc, stain with CAM); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.88–7.75 (m, 4H), 7.50–7.38 (m, 3H), 5.05 (dd, *J* = 9.0, 2.6, 1H), 4.69 (t, *J* = 5.4, 1H), 3.77 (br s, 1H), 3.72 (dq, *J* = 9.3, 7.1, 1H) 3.65 (dq, *J* = 9.3, 7.1, 1H), 3.56–3.47 (m, 2H), 2.15 (ddd, *J* = 14.3, 8.9, 5.9, 1H), 2.07 (ddd, *J* = 14.3, 4.9, 3.3, 1H), 1.23 (t, *J* = 7.2, 3H), 1.21 (t, *J* = 7.0, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 141.7, 133.4, 132.9, 128.2, 128.0, 127.7, 126.1, 125.8, 124.3, 124.1, 102.0, 71.0, 62.4, 61.7, 42.5, 15.5, 15.4; IR (neat, cm<sup>-1</sup>) 3446, 2972, 1739, 1123, 1050, 818; HRMS (TOF MS ES<sup>+</sup>) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>Na 297.1467, found 297.1476.



**3,3-diethoxy-1-(2-naphthalenyl)-1-propanone SI 41** was prepared according to Method F. The following amounts of reagents were used: alcohol **SI 1** (0.44 g, 1.6 mmol, 1.0 equiv), manganese oxide (4.8 g, 55 mmol, 34 equiv) in  $\text{CH}_2\text{Cl}_2$  (20 mL). The crude residue was purified by flash chromatography (5–10% EtOAc in hexanes) to afford the title compound as a yellow oil (0.38 g, 88%). **TLC**  $R_f$  = 0.4 (4:1 hexane/EtOAc, stains orange with CAM);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.49 (s, 1H), 8.03 (dd,  $J$  = 8.6, 1.7, 1H), 7.96 (d,  $J$  = 8.3, 1H), 7.88 (t,  $J$  = 8.7, 2H), 7.60 (td,  $J$  = 7.5, 1.2, 1H), 7.55 (td,  $J$  = 7.5, 1.1, 1H), 5.17 (t,  $J$  = 5.6, 1H), 3.76 (dq,  $J$  = 9.3, 7.1, 2H), 3.62 (dq,  $J$  = 9.2, 7.1, 2H), 3.43 (d,  $J$  = 5.5, 2H), 1.2 (t,  $J$  = 7.1, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  197.3, 135.7, 134.7, 132.6, 130.4, 129.8, 128.6, 128.5, 127.9, 126.9, 124.0, 100.1, 62.9, 43.9, 15.4. **IR** (neat,  $\text{cm}^{-1}$ ) 2972, 1739, 1680, 1376, 1112, 1055, 745; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$  295.1310, found 295.1308.

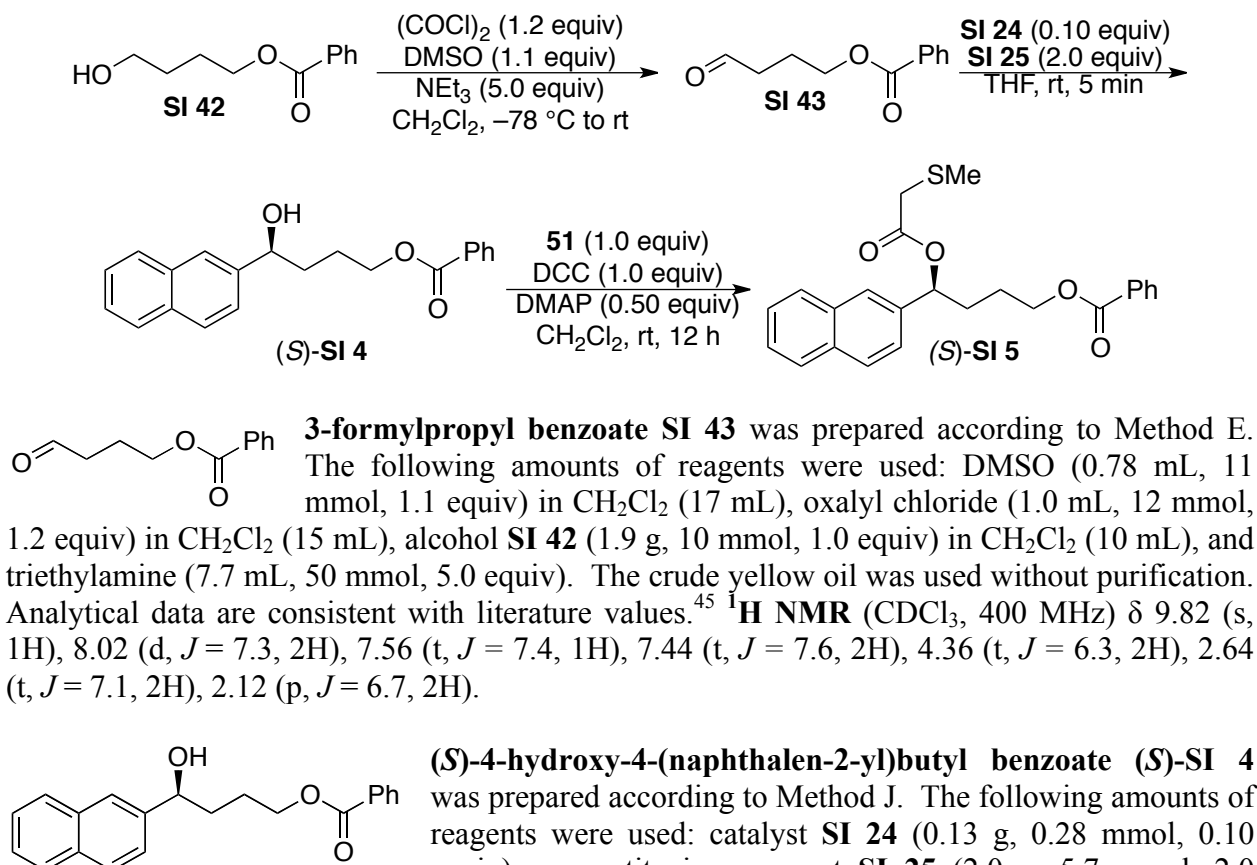


**(R)-3,3-diethoxy-1-(2-naphthalenyl)-1-propanol ((R)-SI 1)** was prepared according to Method H. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (20 mg, 0.073 mmol, 0.10 equiv), ketone **SI 41** (0.20 g, 0.73 mmol, 1.0 equiv), catecholborane (0.12 mL, 1.1 mmol, 1.5 equiv), and PhMe (7 mL). The crude compound was carried to the next step without purification (70 mg). Optical rotation and absolute configuration assignment was performed on a sample obtained using Method I which resulted in clean material but with lower ee.  $[\alpha]_D^{27}$  +16.8 ( $c$  0.99,  $\text{CHCl}_3$ , 86% ee). Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> For analytical data see *rac*-alcohol **SI 1**.



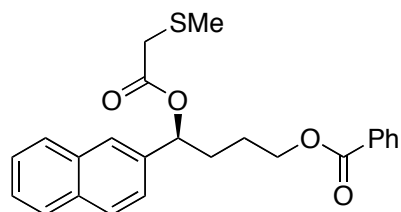
**(R)-3,3-diethoxy-1-(2-naphthalenyl)propyl-2-(methylthio)acetate ((R)-SI 2)** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (34 mg, 0.32 mmol, 1.3 equiv), alcohol **(R)-SI 1** (70 mg, 0.29 mmol, 1.0 equiv), 4-dimethylaminopyridine (20 mg, 0.16 mmol, 0.65 equiv), *N,N'*-dicyclohexylcarbodiimide (66 mg, 0.32 mmol, 1.3 equiv), and  $\text{CH}_2\text{Cl}_2$  (2 mL). The crude residue was purified by flash chromatography (5–15%  $\text{Et}_2\text{O}$  in pentane) to afford to the title compound as a colorless oil (48 mg, 52%). **TLC**  $R_f$  = 0.5 (4:1 hexane/EtOAc, UV active, stains with CAM);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.90–7.78 (m, 4H), 7.53–7.44 (m, 3H), 6.06 (dd,  $J$  = 8.6, 5.7, 1H), 4.54 (t,  $J$  = 5.8, 1H), 3.66 (ap,  $J$  = 7.6, 2H), 3.49 (dq,  $J$  = 9.2, 7.1, 2H), 3.20 (t,  $J$  = 14.7, 2H), 2.41 (ddd,  $J$  = 14.1, 8.7, 5.2, 1H), 2.18 (dt,  $J$  = 14.2, 6.1, 1H), 2.12 (s, 3H), 1.22 (t,  $J$  = 7.1, 3H), 1.20 (t,  $J$  = 7.0, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.3, 137.3, 133.24, 133.23, 128.6, 128.2, 127.8, 126.4, 126.3, 126.0, 124.3, 99.9, 74.2, 62.1, 61.1, 40.5, 36.0, 16.3, 15.5, 15.4; **IR** (neat,  $\text{cm}^{-1}$ ) 2974, 1731, 1269, 1122 1057; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{SNa}$  385.1450, found 385.1448;  $[\alpha]_D^{28}$  +58.6 ( $c$  0.99,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 5.0% MeOH, 3.0 mL/min, 215 nm) indicated 89% ee:  $t_R$  (major) = 3.2 min,  $t_R$  (minor) = 3.6 min.

Scheme SI 12. Synthesis of substrate for Table 1, entry 8



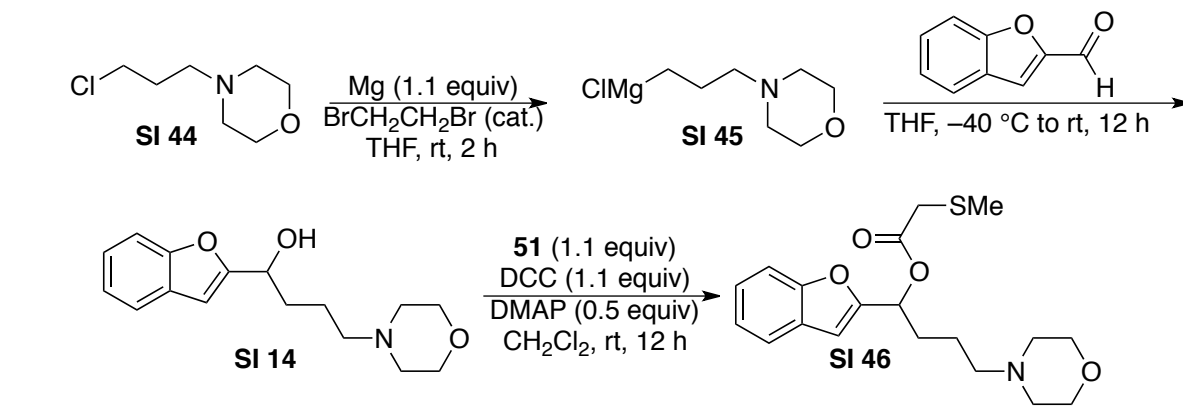
**3-formylpropyl benzoate SI 43** was prepared according to Method E. The following amounts of reagents were used: DMSO (0.78 mL, 11 mmol, 1.1 equiv) in  $\text{CH}_2\text{Cl}_2$  (17 mL), oxalyl chloride (1.0 mL, 12 mmol, 1.2 equiv) in  $\text{CH}_2\text{Cl}_2$  (15 mL), alcohol **SI 42** (1.9 g, 10 mmol, 1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (10 mL), and triethylamine (7.7 mL, 50 mmol, 5.0 equiv). The crude yellow oil was used without purification. Analytical data are consistent with literature values.<sup>45</sup>  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.82 (s, 1H), 8.02 (d,  $J = 7.3$ , 2H), 7.56 (t,  $J = 7.4$ , 1H), 7.44 (t,  $J = 7.6$ , 2H), 4.36 (t,  $J = 6.3$ , 2H), 2.64 (t,  $J = 7.1$ , 2H), 2.12 (p,  $J = 6.7$ , 2H).

**(S)-4-hydroxy-4-(naphthalen-2-yl)butyl benzoate (S)-SI 4** was prepared according to Method J. The following amounts of reagents were used: catalyst **SI 24** (0.13 g, 0.28 mmol, 0.10 equiv), organotitanium reagent **SI 25** (2.0 g, 5.7 mmol, 2.0 equiv), in THF (16 mL), and aldehyde **SI 43** (0.55 g, 2.8 mmol, 1.0 equiv) in THF (6 mL). The crude residue was purified by flash chromatography (5–20% EtOAc in hexane) to afford the title compound as a slightly yellow solid (0.78 g, 86%, 62% ee). The solid was then successively recrystallized to improve the ee: first from hexane/EtOAc to afford a white solid (82% ee), then from hexane/ $\text{CH}_2\text{Cl}_2$  (92% ee), and once again from hexane/ $\text{CH}_2\text{Cl}_2$  (97% ee). Absolute configuration assigned as *S* by analogy to similar compounds synthesized by Gau<sup>5</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> **TLC**  $R_f = 0.3$  (4:1 hexane/EtOAc, UV active); **mp** 51–54 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.01 (d,  $J = 7.2$ , 2H), 7.87–7.78 (m, 4H), 7.54 (t,  $J = 7.3$ , 1H), 7.52–7.45 (m, 3H), 7.42 (t,  $J = 7.7$ , 2H), 4.96–4.89 (m, 1H), 4.35 (at,  $J = 7.7$ , 2H), 2.07 (d,  $J = 3.2$ , 1H), 2.06–1.89 (m, 3H), 1.88–1.75 (m, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  166.8, 141.8, 133.4, 133.2, 133.0, 130.4, 129.7, 128.6, 128.5, 128.1, 127.8, 126.4, 126.1, 124.8, 124.1, 74.4, 64.9, 35.4, 25.3; **IR** (neat,  $\text{cm}^{-1}$ ) 3272, 1716, 1270, 1094, 707; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{Na}$  343.1310, found 343.1310;  $[\alpha]_D^{28} -25.7$  ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (AD-H, 20.0% IPA, 3.0 mL/min, 215 nm) indicated 97% ee:  $t_R$  (major) = 7.2 min,  $t_R$  (minor) = 8.4 min.

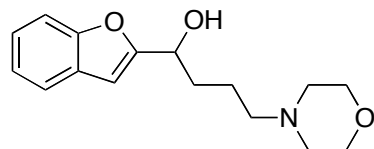


**(S)-4-(2-(methylthio)acetoxy)-4-(naphthalen-2-yl)butyl benzoate (S)-SI 5** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (68 mg, 0.49 mmol, 1.0 equiv), alcohol (S)-**SI 4** (0.21 g, 0.64 mmol, 1.0 equiv), 4-dimethylaminopyridine (39 mg, 0.32 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.13 g, 0.64 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The crude residue was purified by flash chromatography (5% Et<sub>2</sub>O in pentane) to afford to the title compound as a white solid (0.23 g, 87%). **TLC** *R<sub>f</sub>* = 0.7 (4:1 hexane/EtOAc, UV active); **mp** 61–62 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 8.01 (d, *J* = 7.6, 2H), 7.87–7.80 (m, 4H), 7.55 (t, *J* = 7.4, 1H), 7.51–7.45 (m, 3H), 7.42 (t, *J* = 7.6, 2H), 6.01 (t, *J* = 6.9, 1H), 4.39–4.30 (m, 2H), 3.23 (s, 2H), 2.25–2.15 (m, 1H), 2.15–2.04 (m, 1H), 2.13 (s, 3H), 1.95–1.84 (m, 1H), 1.84–1.73 (m, 1H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.6, 166.6, 137.3, 133.3, 133.2, 133.1, 130.3, 129.7, 128.6, 128.5, 128.2, 127.8, 126.5, 126.4, 125.9, 124.1, 76.7, 64.5, 36.0, 32.9, 25.1, 16.4; **IR** (neat, cm<sup>-1</sup>) 2916, 1711, 1275, 1136, 705; **HRMS** (TOF MS ES<sup>+</sup>) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>SNa 431.1293, found 431.1274; **[α]<sub>D</sub><sup>28</sup>** –67.2 (*c* 1.0, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 20.0% MeOH, 3.0 mL/min, 215 nm) indicated 97% ee: *t<sub>R</sub>* (minor) = 3.9 min, *t<sub>R</sub>* (minor) = 4.4 min.

Scheme SI 13. Synthesis of substrate for Table 1, entry 9

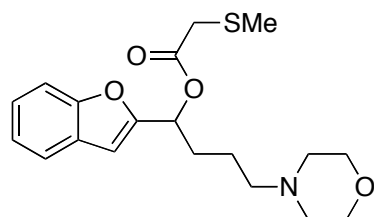


**(3-morpholinopropyl)magnesium chloride SI 45** was prepared according to Method D with the following exception: dibromoethane (0.01 mL) was added dropwise with the first portion of the alkyl chloride to promote Grignard initiation and the reaction was heated to reflux for 4 h. The following amounts of reagents were used: 3-morpholinopropyl chloride **SI 44** (0.82 g, 5.0 mmol, 1.0 equiv), magnesium (0.14 g, 5.5 mmol, 1.1 equiv), THF (5 mL). Grignard was titrated to 0.65 M.<sup>2</sup>



**1-(benzofuran-2-yl)-4-morpholinobutan-1-ol SI 14.** To a cooled (–40 °C) solution of benzofuran-2-carboxaldehyde (0.11 mL, 0.87 mmol, 1.0 equiv) in THF (9 mL) was added Grignard **SI 45** (2.0 mL, 0.65 M, 1.3 mmol, 1.5 equiv). The reaction was stirred and allowed to warm to ambient temperature overnight. The remaining Grignard was quenched with sat. NH<sub>4</sub>Cl, and the aqueous layer was extracted with Et<sub>2</sub>O (2 x 10 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The product was purified by flash chromatography (50–

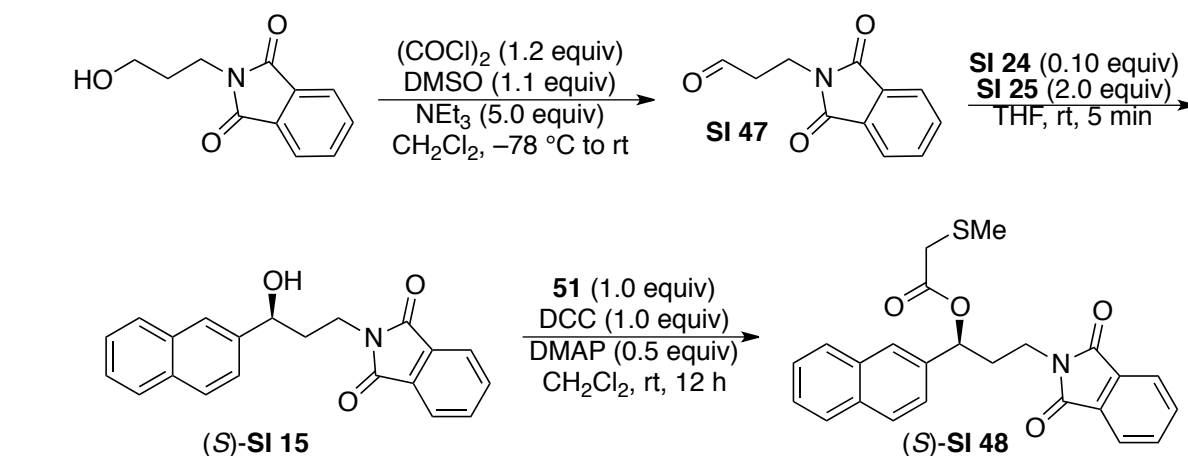
100% EtOAc in hexanes with 1% NEt<sub>3</sub>) to afford the title compound as white solid (0.15 g, 62%). **TLC** R<sub>f</sub> = 0.1 (100% EtOAc, UV active); **mp** 67–70 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.52 (dd, *J* = 7.1, 1.3, 1H), 7.43 (d, *J* = 7.8, 1H), 7.24–7.17 (m, 2H), 6.62 (s, 1H), 4.84 (t, *J* = 4.7, 1H), 3.82–3.76 (m, 4H), 2.53 (br s, 4H), 2.44 (t, *J* = 5.6, 2H), 2.15–2.10 (m, 2H), 1.74–1.68 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 161.1, 154.9, 125.6, 123.7, 122.6, 120.8, 111.2, 102.0, 68.1, 66.5, 59.3, 53.5, 36.3, 22.9; **IR** (neat, cm<sup>-1</sup>) 3088, 2817, 1252, 1113, 1066, 1044; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>Na 298.1419, found 298.1422.



**1-(benzofuran-2-yl)-4-morpholinobutyl 2-(methylthio)acetate SI 46** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **SI 1** (0.10 g, 0.93 mmol, 1.1 equiv), alcohol **SI 14** (0.23 g, 0.85 mmol, 1.0 equiv), 4-dimethylaminopyridine (52 mg, 0.42 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.19 mg, 0.93 mmol, 1.1 equiv), and

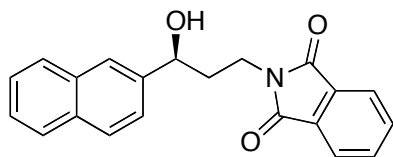
CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The crude residue was purified by flash chromatography (50–100% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (0.17 g, 54%). **TLC** R<sub>f</sub> = 0.2 (100% EtOAc, UV active); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.54 (d, *J* = 7.1, 1H), 7.46 (d, *J* = 8.0, 1H), 7.29 (td, *J* = 8.5, 1.2, 1H), 7.22 (td, *J* = 7.6, 0.9, 1H), 6.73 (s, 1H), 6.02 (t, *J* = 7.0, 1H), 3.69 (t, *J* = 4.6, 4H), 3.22 (s, 2H), 2.39 (m, 6H), 2.18 (s, 3H), 2.15–2.08 (m, 2H), 1.61–1.52 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 169.6, 154.9, 154.6, 127.9, 124.8, 133.1, 121.4, 111.5, 105.4, 70.0, 67.1, 58.4, 53.8, 35.9, 30.5, 22.4, 16.4; **IR** (neat, cm<sup>-1</sup>) 2953, 2853, 2808, 1731, 1453, 1252, 1116; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>25</sub>NO<sub>4</sub>SNa 386.1402, found 386.1409.

Scheme SI 14. Synthesis of substrate for Table 1, entry 10

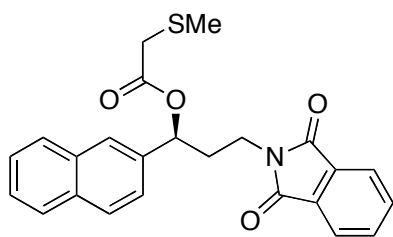


**3-Phthalimidopropanal SI 47** was prepared according to a modified procedure reported by Timmerman.<sup>46</sup> Oxalyl chloride (1.07 mL, 1.59 g, 12.5 mmol, 1.25 equiv) was combined with anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL) in a flame-dried 100 mL round-bottom flask equipped with a stir bar and an N<sub>2</sub> line. The reaction flask was cooled to –78 °C and a solution of DMSO (1.88 mL, 2.07 g, 26.5 mmol, 2.65 equiv) in 5 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added drop-wise. After completion of the addition, the reaction was allowed to stir for 15 min. Subsequently, a solution

of 3-phthalimidopropanol (2.05 g, 10.0 mmol, 1.00 equiv) in 10 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added drop-wise to the reaction mixture. The reaction was stirred for an additional 30 min at -78 °C followed by the addition of triethylamine (7.67 mL, 5.57 g, 55.0 mmol, 5.5 equiv). The reaction was allowed to warm to ambient temperature before the addition of water (25 mL). After stirring for 30 min, the organic and aqueous layers were separated and the organic layer was washed with H<sub>2</sub>O (3 x 15 mL). The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo to yield crude **SI 47** (1.49 g, 72%). The resultant white solid was used without further purification. Analytical data was consistent with literature values.<sup>47</sup> **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 9.83 (t, *J* = 1.3, 1H), 7.85 (add, *J* = 5.3, 3.2, 2H), 7.23 (add, *J* = 5.5, 3.0, 2H), 4.04 (t, *J* = 7.0, 2H), 2.88 (td, *J* = 7.0, 1.3, 2H).



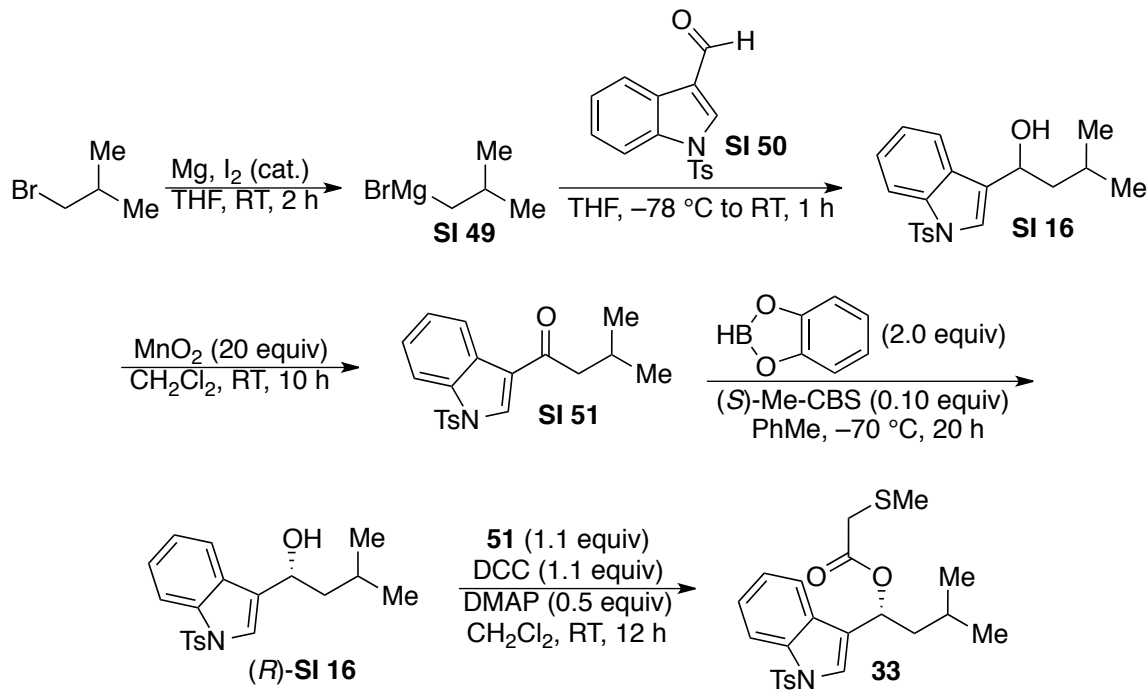
**(S)-3-phthalimido-1-(2-naphthalenyl)-1-propanol (S)-SI 15** was prepared according to Method J. The following amounts of reagents were used: catalyst **SI 24** (0.13 g, 0.28 mmol, 0.10 equiv), organotitanium reagent **SI 25** (2.0 g, 5.7 mmol, 2.0 equiv) in THF (16 mL), and aldehyde **SI 47** (0.58 g, 2.8 mmol, 1.0 equiv) in THF (6 mL). The crude residue was purified by flash chromatography (10–40% EtOAc in hexanes with 1% TEA) to afford the title compound as a slightly yellow solid (0.55 g, 59%, 63% ee). The solid was then recrystallized first from hexane/CH<sub>2</sub>Cl<sub>2</sub> to afford a white crystalline solid (63% ee) and subsequently twice from Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> (96% ee). Absolute configuration assigned as *S* by analogy to similar compounds synthesized by Gau<sup>5</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> **TLC** *R<sub>f</sub>* = 0.2 (4:1 hexane/EtOAc, UV active); **mp** 124–127 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 7.80–7.71 (m, 6H), 7.63 (add, *J* = 5.3, 3.1, 2H), 7.46–7.37 (m, 3H), 4.85 (br s, 1H), 3.91 (t, *J* = 6.5, 2H), 3.08 (s, 1H), 2.24–2.11 (m, 2H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 168.7, 141.0, 134.0, 133.3, 132.9, 132.0, 128.4, 128.0, 127.7, 126.2, 125.9, 124.5, 123.9, 123.3, 71.5, 37.4, 34.9; **IR** (neat, cm<sup>-1</sup>) 3482, 1697, 1396, 1372, 1346, 1072, 720; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub>Na 354.1106, found 354.1105; **[α]<sub>D</sub><sup>27</sup>** -16.1 (*c* 1.0, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 30.0% IPA, 3.0 mL/min, 215 nm) indicated 95% ee: *t<sub>R</sub>* (major) = 17.7 min, *t<sub>R</sub>* (minor) = 20.9 min.



**(S)-3-(1,3-dioxisoindolin-2-yl)-1-(naphthalen-2-yl)propyl 2-(methylthio)acetate (S)-SI 48** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (52 mg, 0.49 mmol, 1.0 equiv), alcohol (**S**)-**SI 15** (0.16 g, 0.49 mmol, 1.0 equiv), 4-dimethylaminopyridine (30 mg, 0.25 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.10 g, 0.49 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The crude residue was purified by flash chromatography (5–30% EtOAc in hexanes) to afford to the title compound as a colorless, thick oil which was then triturated with pentane to a sticky solid (0.11 g, 52%). **TLC** *R<sub>f</sub>* = 0.8 (1:1 hexane/EtOAc, UV active, stain with KMnO<sub>4</sub>); **mp** 62–65 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.84–7.70 (m, 6H), 7.66–7.59 (m, 2H), 7.48–7.38 (m, 3H), 5.96 (t, *J* = 6.8, 1H), 3.93–3.75 (m, 2H), 3.24 (s, 2H), 2.48–2.33 (m, 2H), 2.13 (s, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.5, 168.3, 136.7, 134.0, 133.13, 133.10, 131.9, 128.6, 128.1, 127.7, 126.4, 126.3, 125.9, 123.9, 123.2, 74.7, 35.9, 34.7, 34.4, 16.3; **IR** (neat, cm<sup>-1</sup>) 2923, 1705, 1395, 1262, 1123, 717; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub>SNa 442.1089, found

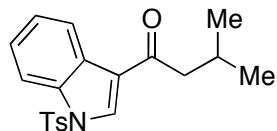
442.1074;  $[\alpha]_D^{28}$   $-41.8$  ( $c$  0.80,  $\text{CHCl}_3$ ); SFC analysis (OJ-H, 30.0% MeOH, 3.0 mL/min, 215 nm) indicated 94% ee:  $t_R$  (minor) = 3.8 min,  $t_R$  (major) = 5.1 min.

Scheme SI 15. Synthesis of substrate for Table 1, entry 11

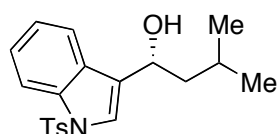


**iso-butylmagnesium bromide SI 49** was prepared according to Method D, with the following exception: dibromoethane (0.01 mL) was added dropwise with the first portion of the alkyl bromide to promote Grignard initiation. The following amounts of reagents were used: 1-bromo-2-methylpropane (1.1 mL, 10.0 mmol, 1.0 equiv), magnesium (0.36 g, 15 mmol, 1.5 equiv), THF (8 mL). Grignard titrated to 0.87 M.<sup>2</sup>

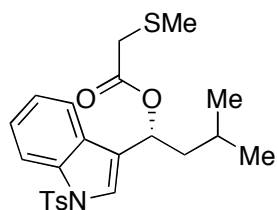
**3-methyl-1-(1-tosyl-1H-indol-3-yl)butan-1-ol SI 16.** To a cooled ( $-78$  °C) solution of aldehyde **SI 50** (1.5 g, 5.0 mmol, 1.0 equiv) in THF (25 mL) was added Grignard reagent **SI 49** (6.3 mL, 5.5 mmol, 1.1 equiv, 0.87 M in THF). The reaction was let stir and warm to ambient temperature. After 2 h, the remaining Grignard was quenched with sat.  $\text{NH}_4\text{Cl}$ , and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organics were washed with brine, dried with  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The product was purified by flash chromatography (10% EtOAc in hexanes) to afford the title compound as gummy oil (1.5 g, 82%). TLC  $R_f$  = 0.3 (4:1 hexane/EtOAc, UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.98 (d,  $J$  = 8.3, 1H), 7.76 (d,  $J$  = 8.3, 2H), 7.65 (d,  $J$  = 7.8, 1H), 7.50 (s, 1H), 7.32 (t,  $J$  = 8.3, 1H), 7.25 – 7.19 (m, 3H), 5.00 (dt,  $J$  = 8.4, 4.3, 1H), 2.34 (s, 3H), 1.86–1.66 (m, 4H), 0.96 (d,  $J$  = 6.1, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  145.1, 135.7, 135.4, 130.0, 129.1, 127.0, 126.5, 125.0, 123.3, 122.7, 120.6, 113.9, 66.3, 46.3, 25.0, 23.3, 22.3, 21.7; IR (neat,  $\text{cm}^{-1}$ ) 2954, 1596, 1364, 1170, 118, 1093; HRMS (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{SNa}$  380.1296, found 380.1300.



**3-methyl-1-(1-tosyl-1H-indol-3-yl)butan-1-one SI 51** was prepared according to Method F. The following amounts of reagents were used:  $\text{MnO}_2$  (5.8 g, 67 mmol, 20 equiv), alcohol **SI 16** (1.2 g, 3.4 mmol, 1.0 equiv), and  $\text{CH}_2\text{Cl}_2$  (40 mL). The product was purified by flash chromatography (10% EtOAc in hexanes) to afford the title compound a white solid (1.1 g, 90%). **TLC**  $R_f = 0.5$  (4:1 hexane/EtOAc, UV active); **mp** 98–99 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.35 (d,  $J = 7.2$ , 1H), 8.20 (s, 1H), 7.92 (d,  $J = 7.2$ , 1H), 7.83 (d,  $J = 8.4$ , 2H), 7.35 (apd,  $J = 7.4$ , 1.6, 2H), 7.28 (d,  $J = 8.2$ , 2H), 2.75 (d,  $J = 7.0$ , 2H), 2.37 (s, 3H), 2.32 (septet,  $J = 6.7$ , 1H), 1.02 (d,  $J = 6.7$ , 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  196.3, 146.0, 135.0, 134.7, 131.8, 130.4, 127.8, 127.3, 125.8, 124.9, 123.4, 121.9, 113.2, 49.2, 25.7, 22.9, 21.8; **IR** (neat,  $\text{cm}^{-1}$ ) 3140, 2953, 1672, 1597, 1365, 1167, 1145, 1087, 1105; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{SNa}$  378.1140, found 378.1127.



**(R)-3-methyl-1-(1-tosyl-1H-indol-3-yl)butan-1-ol (R-SI 16)** was prepared according to Method H. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (55 mg, 0.20 mmol, 0.10 equiv), ketone **SI 51** (0.71 g, 2.0 mmol, 1.0 equiv), catecholborane (0.26 mL, 2.4 mmol, 1.2 equiv), and PhMe (20 mL). The crude residue was used without purification. See *rac*-alcohol **SI 16** for analytical data. Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions.<sup>17</sup>

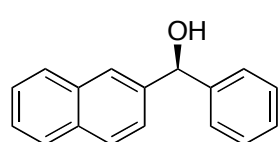
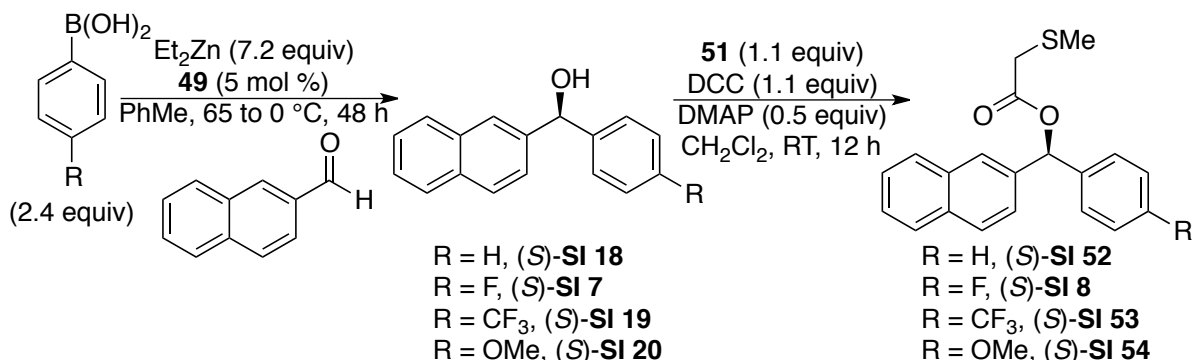


**(R)-3-methyl-1-(1-tosyl-1H-indol-3-yl)butyl 2-(methylthio)acetate 33** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (0.25 g, 2.4 mmol, 1.2 equiv), crude alcohol (*R*)-**SI 16** (0.72 g, 2.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (0.12 g, 1.0 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.49 mg, 2.4 mmol, 1.2 equiv), and  $\text{CH}_2\text{Cl}_2$  (8 mL). The crude residue was purified by flash chromatography (5–10%  $\text{Et}_2\text{O}$  in pentane with 0.5%  $\text{Et}_3\text{N}$ ) to afford to the title compound as a yellow oil (84 mg, 9% over 2 steps). **TLC**  $R_f = 0.5$  (4:1 hexane/EtOAc, UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.96 (d,  $J = 8.2$ , 1H), 7.74 (d,  $J = 8.3$ , 2H), 7.64 (d,  $J = 7.7$ , 1H), 7.59 (s, 1H), 7.33–7.21 (m, 4H), 6.17 (dd,  $J = 8.5$ , 5.6, 1H), 3.16 (s, 2H), 2.33 (s, 3H), 2.06 (s, 3H), 2.00 (ddd,  $J = 13.7$ , 8.6, 6.3, 1H), 1.79 (ddd,  $J = 14.0$ , 7.6, 5.7, 1H), 1.61 (septet,  $J = 6.7$ , 1H), 0.96 (d,  $J = 4.3$ , 3H), 0.94 (d,  $J = 4.3$ , 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.7, 145.2, 135.4, 135.2, 130.0, 128.9, 127.0, 125.1, 124.2, 123.4, 122.0, 120.5, 113.9, 68.8, 43.5, 36.0, 24.9, 22.9, 22.4, 21.7, 16.3; **IR** (neat,  $\text{cm}^{-1}$ ) 2956, 1727, 1446, 1328, 1173, 1120; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{27}\text{NO}_4\text{S}_2\text{Na}$  468.1279, found 468.1266;  $[\alpha]_D^{30} +41.1$  ( $c$  0.97,  $\text{CHCl}_3$ ); **SFC** analysis (AD-H, 5.0 % IPA, 3.0 mL/min, 215 nm) indicated 95% ee:  $t_R$  (major) = 12.0 min,  $t_R$  (minor) = 15.7 min.

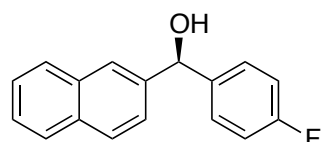


## H. STARTING MATERIALS FOR TABLE 2

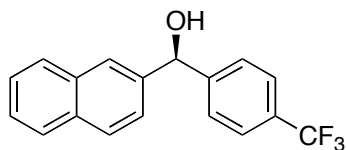
Scheme SI 16. Synthesis of substrates for Table 2, entry 1–3



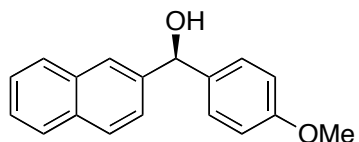
**(S)-naphthalen-2-yl(phenyl)methanol (S)-SI 18** was prepared according to Method K. The following amounts of reagents were used: phenylboronic acid (0.73 g, 6.0 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 7.2 equiv, 1.0 M in PhMe), aminoalcohol **49** (59 mg, 0.13 mmol, 0.050 equiv), 2-naphthaldehyde (0.39 g, 2.5 mmol, 1.0 equiv), and PhMe (38 mL). Purification by flash chromatography (25% EtOAc in hexane) afforded the title compound as a white solid (0.55 g, 94%). The product was recrystallized (100% hexane) to yield higher enantiopurity (99% ee). Absolute configuration was assigned as *S* by comparison of optical rotation with literature values. Analytical data are consistent with literature values.<sup>48</sup> **TLC**  $R_f$  = 0.3 (4:1 hexane/EtOAc, UV active); **mp** 79–80 °C, lit.<sup>48</sup> mp 82–83 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86–7.75 (m, 4H), 7.47–7.22 (m, 8H), 5.96 (s, 1H), 2.36 (s, 1H);  $[\alpha]_D^{26}$  –4.1 (*c* 1.2, benzene), lit.<sup>48</sup>  $[\alpha]_D$  +7.4 (*c* 0.77, benzene, 98% ee, (*R*)-enantiomer); **SFC** analysis (OD-H, 20% IPA, 3.0 mL/min, 215 nm) indicated 99% ee:  $t_R$  (major) = 6.8 minutes,  $t_R$  (minor) = 7.9 minutes.



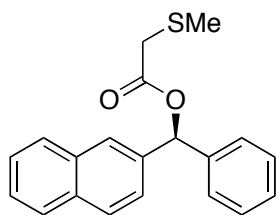
**(S)-naphthalen-2-yl(4-(fluoro)phenyl)methanol (S)-SI 7** was prepared according to the Method K. The following amounts of reagents were used: 4-fluorophenylboronic acid (0.84 g, 6.0 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 7.2 equiv, 1.0 M in PhMe), aminoalcohol **49** (75 mg, 0.15 mmol, 0.060 equiv), 2-naphthaldehyde (0.39 g, 2.5 mmol, 1.0 equiv), and PhMe (38 mL). Purification by flash chromatography (25% EtOAc/hexane) afforded the title compound as a white solid (0.62 g, 98%). Absolute configuration was assigned as *S* by comparison of optical rotation with literature values. Analytical data are consistent with literature values.<sup>49</sup> **TLC**  $R_f$  = 0.3 (4:1 hexane/EtOAc, UV active); **mp** 61–63 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86–7.78 (m, 4H), 7.50–7.45 (m, 2H), 7.30–7.35 (m, 3H), 7.04–7.6.98 (m, 2H), 5.98 (s, 1H), 2.36 (s, 1H);  $[\alpha]_D^{26}$  –3.7 (*c* 3.06, EtOH); lit.<sup>20</sup>  $[\alpha]_D^{20}$  –37 (*c* 30.9, EtOH, 98% ee, (*S*)-enantiomer); **SFC** analysis (OD-H, 15% IPA, 3 mL/min, 215 nm) indicated 95% ee:  $t_R$  (major) = 7.97 minutes,  $t_R$  (minor) = 9.34 minutes.



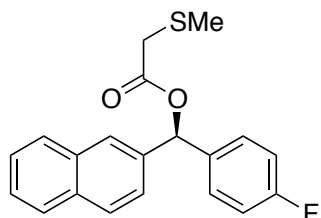
**(S)-naphthalen-2-yl(4-(trifluoromethyl)phenyl)methanol (S)-SI 19** was prepared according to the Method K. The following amounts of reagents were used: 4-(trifluoromethyl)phenylboronic acid (1.1 g, 6.0 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 7.2 equiv, 1.0 M in PhMe), aminoalcohol **49** (59 mg, 0.13 mmol, 0.050 equiv), 2-naphthaldehyde (0.39 g, 2.5 mmol, 1.0 equiv), and PhMe (38 mL). The product was purified by flash chromatography (25% EtOAc in hexane) to afford the title compound as a white solid (0.64 g, 85%). The product was then recrystallized from hexanes to yield higher enantiopurity (96% ee). Absolute configuration was assigned as *S* by comparison of optical rotation with literature values. Analytical data are consistent with literature values.<sup>50</sup> **TLC**  $R_f$  = 0.2 (4:1 hexane/EtOAc, UV active); **mp** 101–103 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.87–7.80 (m, 4H), 7.58 (q,  $J$  = 8.4, 4H), 7.49 (at,  $J$  = 3.8, 2H), 7.40 (dd,  $J$  = 8.5, 1.7, 1H), 6.05 (s, 1H), 2.39 (s, 1H);  $[\alpha]_D^{26}$  –44.4 ( $c$  1.0, CHCl<sub>3</sub>), lit.<sup>50</sup>  $[\alpha]_D$  –45.3 ( $c$  2.2, CHCl<sub>3</sub>, 90% ee, (*S*)-enantiomer); **SFC** analysis (OD-H, 20.0% IPA, 3.0 mL/min, 215 nm) indicated 96% ee:  $t_R$  (major) = 4.7 min,  $t_R$  (minor) = 5.1 min.



**(S)-(4-methoxyphenyl)(naphthalen-2-yl)methanol (S)-SI 20** was prepared according to Method K. The following amounts of reagents were used: 4-methoxyphenylboronic acid (0.91 g, 6.0 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 7.2 equiv, 1.0 M in PhMe), aminoalcohol **49** (59 mg, 0.13 mmol, 0.050 equiv), 2-naphthaldehyde (0.39 g, 2.5 mmol, 1.0 equiv), and PhMe (38 mL). The product was purified by flash chromatography (25% EtOAc in hexane) to afford the title compound as a white solid (0.63 g, 96%). The product was then recrystallized from hexanes/EtOAc to yield higher enantiopurity (99% ee). Absolute configuration assigned as *S* by analogy to (*S*)-**SI 18** made by the same method. Analytical data are consistent with literature values.<sup>51</sup> **TLC**  $R_f$  = 0.2 (4:1 hexane/EtOAc, UV active); **mp** 88–90 °C, lit.<sup>51</sup> **mp** 84 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.90 (s, 1H), 7.85–7.78 (m, 3H), 7.49–7.44 (m, 2H), 7.41 (dd,  $J$  = 8.8, 1.7, 1H), 7.33 (dt,  $J$  = 8.7, 2.5, 2H), 6.87 (dt,  $J$  = 8.7, 2.5, 2H), 5.98 (d,  $J$  = 3.2, 1H), 3.79 (s, 3H), 2.24 (d,  $J$  = 3.4, 1H);  $[\alpha]_D^{29}$  +22.6 ( $c$  0.56, THF), lit.<sup>51</sup>  $[\alpha]_D^{20}$  –31.4 ( $c$  0.26, THF, 91% ee); **SFC** analysis (OD-H, 20.0% IPA, 3.0 mL/min, 215 nm) indicated 95% ee:  $t_R$  (major) = 8.3 min,  $t_R$  (minor) = 9.5 min.



**(S)-naphthalen-2-yl(phenyl)methyl 2-(methylthio)acetate (S)-SI 52**. Prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (0.15 g, 1.4 mmol, 1.1 equiv), alcohol (*S*)-**SI 18** (0.30 g, 1.3 mmol, 1.0 equiv), 4-dimethylaminopyridine (78 mg, 0.64 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.29 g, 1.4 mmol, 1.1 equiv), and dichloromethane (7 mL). The crude residue was purified by flash chromatography (10% Et<sub>2</sub>O in pentane) to afford the title compound as a slightly yellow oil (0.27 g, 84%). **TLC**  $R_f$  = 0.6 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.87 (s, 1H), 7.84–7.80 (m, 3H), 7.50–7.40 (m, 5H), 7.36–7.28 (m, 3H), 7.07 (s, 1H), 3.32 (s, 2H), 2.15 (s, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  169.4, 139.9, 137.3, 133.2, 133.1, 128.7, 128.6, 128.28, 128.25, 127.8, 127.4, 126.49, 126.46, 126.2, 125.0, 77.9, 36.1, 16.4; **IR** (neat, cm<sup>-1</sup>) 3028, 2918, 1729, 1258, 1120; **HRMS** (TOF MS ES+)  $m/z$ :  $[M + Na]^+$  calculated for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>SNa 345.0925, found 345.0937;  $[\alpha]_D^{26}$  –26.8 ( $c$  1.2, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 10.0% IPA, 3.0 mL/min, 215 nm) indicated >99% ee:  $t_R$  (minor) = 11.6 min,  $t_R$  (major) = 12.7 min.

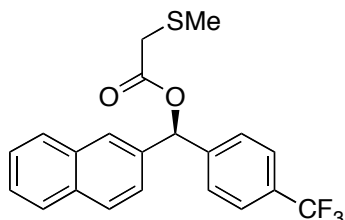


**(S)-(4-fluorophenyl)(naphthalen-2-yl)methyl**

**2-**

**(methylthio)acetate (S)-SI 8** was prepared according to Method L.

The following amounts of reagents were used: carboxylic acid **51** (63 mg, 0.60 mmol, 1.2 equiv), alcohol (**S**)-**SI 7** (0.13 g, 0.50 mmol, 1.0 equiv), 4-dimethylaminopyridine (31 mg, 0.25 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.14 g, 0.6 mmol, 1.2 equiv), and dichloromethane (3 mL). The crude residue was purified by silica gel chromatography (25% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (0.15 g, 90%). **TLC** *R<sub>f</sub>* = 0.5 (4:1 hexane/EtOAc, UV active); <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.85–7.80 (m, 4H), 7.50–7.48 (m, 2H), 7.40–7.36 (m, 3H), 7.05–7.01 (m, 3H), 3.31 (s, 2H), 2.14 (s, 3H); <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.3, 162.6 (d, *J*<sub>(C-F)</sub> = 246.9 Hz), 137.5, 135.7 (d, *J*<sub>(C-F)</sub> = 3.2 Hz), 133.2, 133.1, 129.3 (d, *J*<sub>(C-F)</sub> = 8.3 Hz), 128.7, 128.3, 128.3, 127.8, 126.59, 126.56, 126.1, 124.8, 115.6 (d, *J*<sub>(C-F)</sub> = 21.3 Hz), 77.2, 36.0, 16.4; **IR** (film, cm<sup>-1</sup>) 3056, 2919, 1729, 1603, 1508, 1258; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>20</sub>H<sub>17</sub>FO<sub>2</sub>SNa 363.0831, found 363.0834; [α]<sub>D</sub><sup>26</sup> -11.9 (*c* 1.08, CHCl<sub>3</sub>); **SFC** analysis (OD-H, 5.0% IPA, 2.5 mL/min, 215 nm) indicated 96% ee: *t<sub>R</sub>* (minor) = 14.02 min, *t<sub>R</sub>* (major) = 15.09 min.

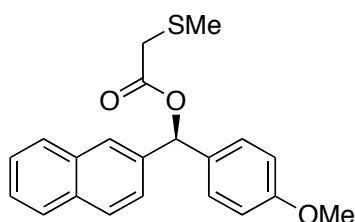


**(S)-naphthalen-2-yl(4-(trifluoromethyl)phenyl)methyl**

**2-**

**(methylthio)acetate (S)-SI 53** was prepared according to Method L.

The following amounts of reagents were used: carboxylic acid **51** (74.0 mg, 0.703 mmol, 1.10 equiv), alcohol (**S**)-**SI 19** (193 mg, 0.640 mmol, 1.00 equiv), 4-dimethylaminopyridine (39 mg, 0.32 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (144 mg, 0.703 mmol, 1.10 equiv), and dichloromethane (2 mL). The crude residue was purified by flash chromatography (25% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (0.24 g, 94%). **TLC** *R<sub>f</sub>* = 0.5 (4:1 hexane/EtOAc, UV active); <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.87 (s, 1H), 7.85–7.80 (m, 3H), 7.62 (d, *J* = 8.5, 2H), 7.55 (d, *J* = 8.2, 2H), 7.51–7.49 (m, 2H), 7.40 (dd, *J* = 8.7, 1.8, 1H), 7.09 (s, 1H), 3.32 (s, 2H), 2.16 (s, 3H); <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 169.2, 143.8, 136.4, 133.21, 133.16, 130.3 (q, *J*<sub>C-F</sub> = 32.8, 1C), 128.9, 128.3, 127.8, 127.4, 126.72, 126.68, 126.6, 125.7 (q, *J*<sub>C-F</sub> = 3.7, 2C), 124.7, 124.1 (q, *J*<sub>C-F</sub> = 271.8, 1C), 77.2, 36.0, 16.4; **IR** (neat, cm<sup>-1</sup>) 2920, 1734, 1323, 1163, 1118, 1065; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>17</sub>F<sub>3</sub>O<sub>2</sub>S 413.0799, found 413.0811; [α]<sub>D</sub><sup>26</sup> -46.3 (*c* 1.1, CHCl<sub>3</sub>); **SFC** analysis (OD-H, 5.0% IPA, 2.5 mL/min, 215 nm) indicated 97% ee: *t<sub>R</sub>* (minor) = 11.4 min, *t<sub>R</sub>* (major) = 12.2 min.



**(S)-(4-methoxyphenyl)(naphthalen-2-yl)methyl**

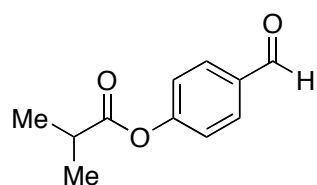
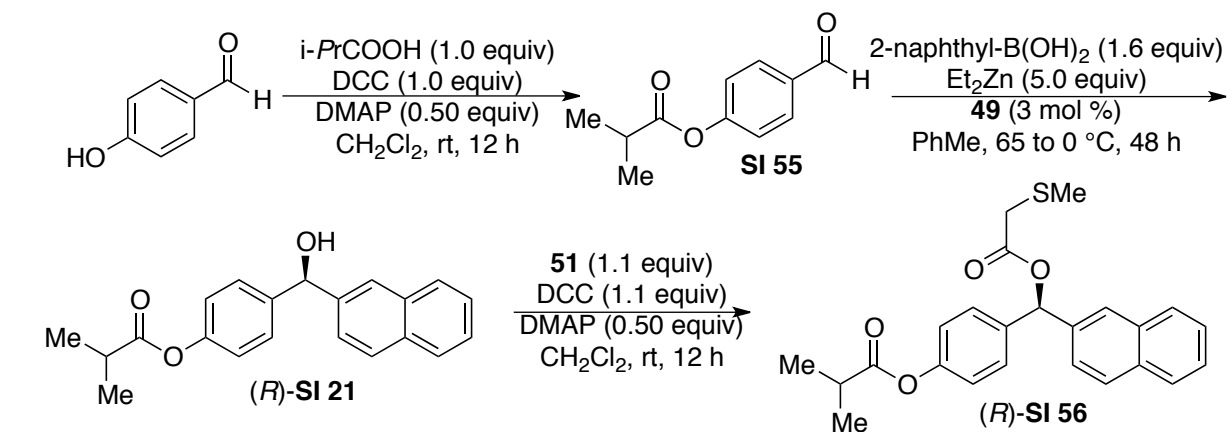
**2-**

**(methylthio)acetate (S)-SI 54** was prepared according to Method L.

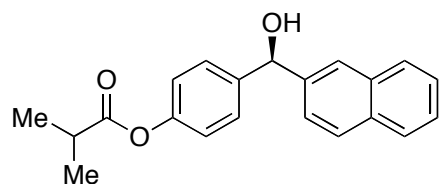
The following amounts of reagents were used: carboxylic acid **51** (35 mg, 0.33 mmol, 1.10 equiv), alcohol (**S**)-**SI 20** (78 mg, 0.30 mmol, 1.00 equiv), 4-dimethylaminopyridine (18 mg, 0.15 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (68 mg, 0.33 mmol, 1.10 equiv), and dichloromethane (2 mL). The crude residue was purified by flash chromatography (25% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (0.10 g, 96%). **TLC** *R<sub>f</sub>* = 0.3 (4:1 hexane/EtOAc, UV active); <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.87 (s, 1H), 7.84–7.80 (m, 3H), 7.50–7.45 (m, 2H), 7.41 (dd, *J* = 8.8, 1.7, 1H), 7.32 (dt, *J* = 8.8, 2.5, 2H), 7.03 (s, 1H), 6.87 (dt, *J* = 8.8, 2.5, 2H), 3.79 (s, 3H), 3.31 (s, 2H), 2.15 (s,

3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.4, 159.6, 137.5, 133.2, 133.0, 132.0, 129.0, 128.5, 128.3, 127.8, 126.5, 126.4, 125.8, 124.9, 114.1, 77.6, 55.4, 36.1, 16.4; **IR** (neat,  $\text{cm}^{-1}$ ) 2918, 1728, 1512, 1246, 1157; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{SNa}$  375.1031, found 375.1023;  $[\alpha]_{\text{D}}^{26}$  +22.2 ( $c$  0.85,  $\text{CHCl}_3$ ); **SFC** analysis (OD-H, 5.0% IPA, 3.0 mL/min, 215 nm) indicated 95% ee:  $t_{\text{R}}$  (minor) = 20.6 min,  $t_{\text{R}}$  (major) = 22.2 min.

Scheme SI 17. Synthesis of substrate for Table 2, entry 4

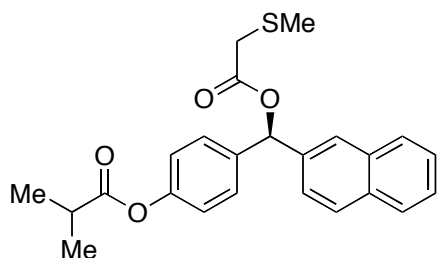


**4-formylphenyl isobutyrate SI 55** was prepared according to Method L. The following amounts of reagents were used: isobutyric acid (0.91 mL, 10 mmol, 1.0 equiv), 4-hydroxybenzaldehyde (1.2 g, 10 mmol, 1.0 equiv), 4-dimethylaminopyridine (0.61 g, 5.0 mmol, 0.50 equiv),  $N,N'$ -dicyclohexylcarbodiimide (2.1 g, 10 mmol, 1.0 equiv), and dichloromethane (50 mL). The crude residue was purified by flash chromatography (10% EtOAc in hexane) to afford the title compound as a colorless semi-solid (1.5 g, 79%). Analytical data are consistent with literature values.<sup>52</sup> **TLC**  $R_{\text{f}}$  = 0.3 (4:1 hexane/EtOAc, UV active)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  10.0 (s, 1H), 7.92 (d,  $J$  = 8.5, 2H), 7.27 (d,  $J$  = 8.5, 2H), 2.84 (septet,  $J$  = 7.0, 1H), 1.34 (d,  $J$  = 6.9, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  191.1, 175.0, 155.8, 134.0, 131.3, 122.4, 116.0, 34.3, 19.1.



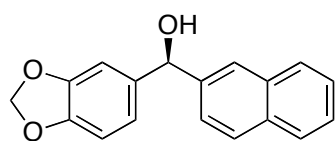
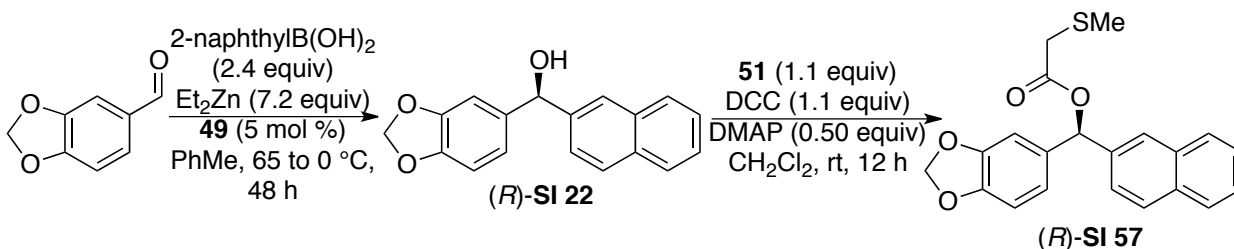
**(R)-4-(hydroxy(naphthalen-2-yl)methyl)phenyl isobutyrate ((R)-SI 21)** was prepared according to Method K. The following amounts of reagents were used: 2-naphthylboronic acid (1.0 g, 6.0 mmol, 1.7 equiv), diethylzinc (18 mL, 18 mmol, 5.0 equiv, 1.0 M in PhMe), aminoalcohol **49** (59 mg, 0.13 mmol, 0.030 equiv), aldehyde **SI 55** (0.70 g, 3.6 mmol, 1.0 equiv), and PhMe (36 mL). Purification by flash chromatography (25% EtOAc in hexane) afforded the title compound as a white solid (0.70 g, 61%). The product was recrystallized from EtOAc/hexanes to yield higher enantiopurity (97% ee). Absolute configuration assigned as *R* based on predictive model described by Braga.<sup>11</sup> **TLC**  $R_{\text{f}}$  = 0.2 (4:1 hexane/EtOAc, UV active); **mp** 124–128 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.88 (s, 1H), 7.84–7.78 (m, 3H), 7.50–7.45 (m, 2H), 7.45–7.40 (m, 3H), 7.05 (d,  $J$  = 8.4, 2H), 6.01 (s, 1H), 2.78 (septet,  $J$  = 7.0, 1H), 2.34 (s, 1H), 1.30 (d,  $J$  = 7.0, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  175.7, 150.4, 141.1, 141.0, 133.3, 133.0, 128.5, 128.2, 127.9, 127.8, 126.4, 126.2, 125.2, 124.9, 121.7, 76.0, 34.3, 19.1; **IR** (neat,

cm<sup>-1</sup>) 3277, 2970, 1746, 1164, 754; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>Na 343.1310, found 343.1304; [α]<sub>D</sub><sup>29</sup> -10.8 (*c* 0.19, CHCl<sub>3</sub>); **SFC** analysis (OJ-H, 15% IPA, 3.0 mL/min, 215 nm) indicated 97% ee: *t*<sub>R</sub> (minor) = 12.8 min, *t*<sub>R</sub> (major) = 13.8 min.



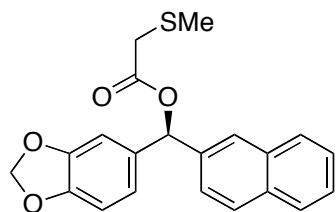
**(R)-4-((2-(methylthio)acetoxy)(naphthalen-2-yl)methyl)phenyl isobutyrate (R)-SI 56** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (93 mg, 0.88 mmol, 1.1 equiv), alcohol **(R)-SI 21** (0.26 g, 0.80 mmol, 1.0 equiv), 4-dimethylaminopyridine (49 mg, 0.40 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.18 g, 0.88 mmol, 1.1 equiv), and dichloromethane (4 mL). The crude residue was purified by flash chromatography (25% Et<sub>2</sub>O in pentane) to afford the title compound as a slightly yellow oil (0.27 g, 81%). **TLC** *R*<sub>f</sub> = 0.4 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.87 (s, 1H), 7.84–7.80 (m, 3H), 7.51–7.48 (m, 2H), 7.41 (d, *J* = 8.5, 3H), 7.07 (s, 1H), 7.06 (d, *J* = 8.5, 2H), 3.31 (s, 2H), 2.79 (septet, *J* = 7.04, 1H), 2.15 (s, 3H), 1.30 (d, *J* = 7.04, 6H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 175.6, 169.3, 150.7, 137.2, 137.0, 133.2, 133.1, 128.64, 128.60, 128.3, 127.8, 126.54, 126.51, 126.2, 125.0, 121.8, 77.3, 36.1, 34.3, 19.0, 16.4; **IR** (neat, cm<sup>-1</sup>) 2974, 1753, 1731, 1506, 1203, 1165; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>SNa 431.1293, found 431.1276; [α]<sub>D</sub><sup>26</sup> +8.6 (*c* 1.1, CHCl<sub>3</sub>); **SFC** analysis (OJ-H, 10% IPA, 3.0 mL/min, 215 nm) indicated 98% ee: *t*<sub>R</sub> (major) = 8.6 min, *t*<sub>R</sub> (minor) = 11.0 min.

Scheme SI 18. Synthesis of substrate for Table 2, entry 5



**(S)-benzo[*d*][1,3]dioxol-5-yl(naphthalen-2-yl)methanol (R)-SI 22** was prepared according to Method K. The following amounts of reagents were used: 2-naphthylboronic acid (1.0 g, 6.0 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 7.2 equiv, 1.0 M in PhMe), aminoalcohol **49** (59 mg, 0.13 mmol, 0.050 equiv), piperonyl aldehyde (0.38 g, 2.5 mmol, 1.0 equiv), and PhMe (38 mL). Purification by flash chromatography (5–25% EtOAc in hexane) afforded the title compound as a white solid (0.62 g, 89%). The product was recrystallized from DCM/pentane to yield higher enantiopurity (93% ee). Absolute configuration assigned as *S* based on predictive model described by Braga.<sup>11</sup> **TLC** *R*<sub>f</sub> = 0.3 (4:1 hexane/EtOAc, UV active); **mp** 64–66 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.86 (s, 1H), 7.83–7.76 (m, 3H), 7.48–7.43 (m, 2H), 7.40 (dd, *J* = 8.5, 1.6, 1H), 6.86 (d, *J* = 6.4, 2H), 6.75 (d, *J* = 8.5, 1H), 5.90–5.88 (m, 3H), 2.35 (br s, 1H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 148.0, 147.2, 141.2, 137.9, 133.3, 133.0, 128.4, 128.2, 127.8, 126.3, 126.1, 124.8, 124.7, 120.4, 108.2, 107.5, 101.2, 76.2; **IR** (neat, cm<sup>-1</sup>) 3363, 2889, 1500, 1485, 1444, 1239, 1035; **HRMS** (TOF MS ES+) *m/z*: [M]<sup>+</sup> calculated for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>

278.0943, found 278.0938;  $[\alpha]_D^{29} -12.0$  ( $c$  0.86,  $\text{CHCl}_3$ ); SFC analysis (OD-H, 15.0% IPA, 3.0 mL/min, 215 nm) indicated 93% ee:  $t_R$  (minor) = 14.0 min,  $t_R$  (major) = 15.8 min.

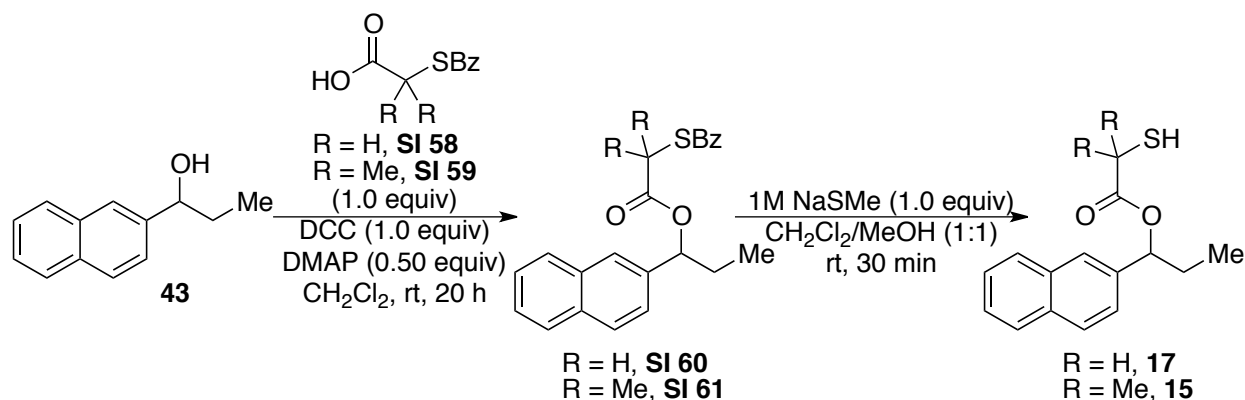


**(S)-benzo[*d*][1,3]dioxol-5-yl(naphthalen-2-yl)methyl 2-(methylthio)acetate (R)-SI 57** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (93 mg, 0.88 mmol, 1.1 equiv), alcohol (R)-**SI 22** (0.22 g, 0.80 mmol, 1.0 equiv), 4-dimethylaminopyridine (49 mg, 0.40 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.18 g, 0.88 mmol, 1.1 equiv), and dichloromethane (4 mL). Purification by flash chromatography (10%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as an off-white oil (0.24 g, 82%). TLC  $R_f$  = 0.3 (4:1 hexane/EtOAc, UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.87–7.78 (m, 4H), 7.51–7.45 (m, 2H), 7.41 (dd,  $J$  = 8.5, 1.6, 1H), 6.98 (s, 1H), 6.88 (td,  $J$  = 8.0, 1.7, 2H), 6.77 (d,  $J$  = 8.0, 1H), 5.93 (d,  $J$  = 1.7, 2H), 3.31 (s, 2H), 2.16 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.3, 148.0, 147.6, 137.3, 133.8, 133.2, 133.1, 128.6, 128.3, 127.8, 126.5, 126.4, 125.8, 124.8, 121.3, 108.3, 108.0, 101.3, 77.7, 36.1, 16.4; IR (neat,  $\text{cm}^{-1}$ ) 2918, 1727, 1487, 1236, 1121; HRMS (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{18}\text{O}_4\text{SNa}$  389.0823, found 389.0826;  $[\alpha]_D^{30} -5.7$  ( $c$  0.87,  $\text{CHCl}_3$ ); SFC analysis (OJ-H, 10.0% IPA, 3.0 mL/min, 215 nm) indicated 95% ee:  $t_R$  (major) = 13.3 min,  $t_R$  (minor) = 15.7 min.

## I. CROSS-COUPLING OF DIETHYLZINC (TABLE 3)

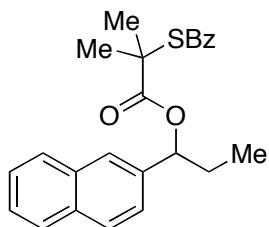
### 1) STARTING MATERIAL SYNTHESIS

Scheme SI 19. Synthetic sequence for starting material synthesis

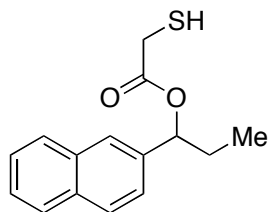


**1-(naphthalen-2-yl)propyl 2-(benzoylthio)acetate SI 60** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **SI 58** (0.53 g, 2.7 mmol, 1.0 equiv), alcohol **43** (0.50 g, 2.7 mmol, 1.0 equiv), 4-dimethylaminopyridine (0.16 g, 1.3 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.55 g, 2.7 mmol, 1.0 equiv), and  $\text{CH}_2\text{Cl}_2$  (14 mL). The crude residue was purified by flash chromatography (5–10% EtOAc in hexanes) to afford the title compound as a viscous colorless oil (0.92 g, 93%). TLC  $R_f$  = 0.5 (4:1 hexane/EtOAc, UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.95 (d,  $J$  = 7.4, 2H), 7.83–7.45 (m, 4H), 7.55 (t,  $J$  = 7.4, 1H), 7.48–7.38 (m, 5H), 5.89 (t,  $J$  = 7.8, 1H), 3.97 (d,  $J$

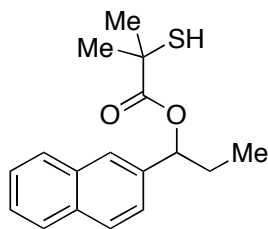
= 16.0, 1H), 3.89 (d,  $J = 16.0$ , 1H), 2.11–1.87 (m, 2H), 0.92 (t,  $J = 7.4$ , 3H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  190.0, 168.2, 137.3, 136.3, 133.8, 133.2 (2C), 128.8, 128.4, 128.1, 127.7, 127.5, 126.3, 126.2, 125.9, 124.3, 79.2, 31.7, 29.2, 10.0; IR (neat, cm<sup>-1</sup>) 1736, 1666, 1152, 909, 686; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>SNa 387.1031, found 387.1030.



**1-(naphthalen-2-yl)propyl 2-(benzoylthio)-2-methylpropanoate SI 61** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **SI 59** (0.36 g, 1.6 mmol, 1.0 equiv), alcohol **43** (0.30 g, 1.6 mmol, 1.0 equiv), 4-dimethylaminopyridine (98 mg, 0.81 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (0.33 g, 1.6 mmol, 1.0 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (9 mL). The crude residue was purified by flash chromatography (5–10% EtOAc in hexanes) to afford the title compound as a viscous yellow oil which solidified upon standing for several days to a white crystalline solid (0.32 g, 58%). TLC  $R_f = 0.6$  (4:1 hexane/EtOAc, UV active); mp 56–60 °C;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.86–7.68 (m, 6H), 7.54 (t,  $J = 7.4$ , 1H), 7.48–7.34 (m, 5H), 5.89 (t,  $J = 6.8$ , 1H), 2.08–1.83 (m, 2H), 1.70 (s, 3H), 1.68 (s, 3H), 0.88 (t,  $J = 7.4$ , 3H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  190.9, 173.2, 137.8, 136.8, 133.5, 133.2, 133.1, 128.7, 128.22, 128.18, 127.7, 127.3, 126.1, 126.0, 125.8, 124.4, 78.8, 51.4, 29.3, 26.2, 26.1, 10.0; IR (neat, cm<sup>-1</sup>) 2970, 1732, 1661, 1157, 904, 689; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>24</sub>O<sub>3</sub>SNa 415.1344, found 415.1337.



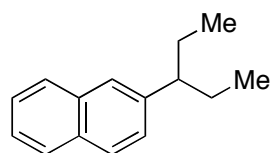
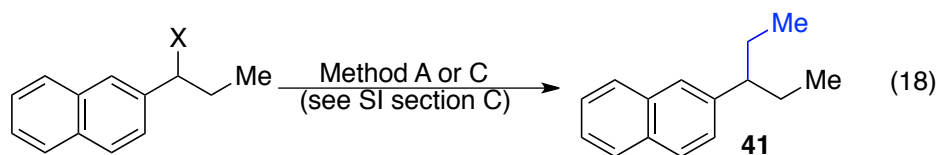
**1-(naphthalen-2-yl)propyl 2-mercaptoacetate 17** was prepared according to Method M. The following amounts of reagents were used: NaSMe (1.6 mL, 1.6 mmol, 1.0 equiv, 1.0 M in MeOH), substrate **SI 60** (0.59 g, 1.6 mmol, 1.0 equiv), wet MeOH (8 mL) and CH<sub>2</sub>Cl<sub>2</sub> (8 mL). The crude residue was purified by flash chromatography (2% Et<sub>2</sub>O in pentane) and then heated to 40 °C under reduced pressure overnight to remove volatile byproducts which coeluted with the product. The title compound was isolated as a colorless oil (0.33 g, 78%). TLC  $R_f = 0.5$  (4:1 hexane/EtOAc, UV active);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.89–7.73 (m, 4H), 7.52–7.39 (m, 3H), 5.85 (t,  $J = 6.9$ , 1H), 3.31 (dd,  $J = 14.9$ , 8.4, 2H), 3.26 (dd,  $J = 15.0$ , 8.2, 1H), 2.12–1.86 (m, 2H), 0.93 (t,  $J = 7.4$ , 3H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.3, 137.3, 133.21, 133.18, 128.5, 128.1, 127.8, 126.4, 126.3, 126.0, 124.3, 79.0, 29.2, 26.9, 10.1; IR (neat, cm<sup>-1</sup>) 2968, 1731, 1143, 817, 746; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>SNa 283.0769, found 283.0767.



**1-(naphthalen-2-yl)propyl 2-mercapto-2-methylpropanoate 15** was prepared according to Method M. The following amounts of reagents were used: NaSMe (0.76 mL, 0.76 mmol, 1.0 equiv, 1.0M in MeOH), substrate **SI 61** (0.30 g, 0.76 mmol, 1.0 equiv) in a mixture of MeOH (4 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4 mL), 30 min. The crude residue was purified by flash chromatography (5% Et<sub>2</sub>O in pentane) and then heated to 40 °C under reduced pressure to remove volatile byproducts that coeluted with the product. The title compound was isolated as a colorless oil (68 mg, 31%). TLC  $R_f = 0.7$  (4:1 hexane/EtOAc, UV active);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.87–7.81 (m, 3H), 7.80 (s, 1H), 7.51–7.43 (m, 3H), 5.82 (t,  $J = 6.8$ , 1.7, 1H), 2.43 (s, 1H), 2.06 (apparent septet,  $J = 7.3$ , 1H), 1.94 (apparent septet  $J = 7.0$ , 1H), 1.62 (s, 3H), 1.61 (s, 3H), 0.96 (t,  $J = 7.4$ , 3H);  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>, 125 MHz)  $\delta$  174.3, 137.7, 133.3, 133.2, 128.4, 128.2, 127.8, 126.3, 126.2, 125.7, 124.2, 78.6, 45.2, 29.5, 29.2, 29.1, 10.1; **IR** (neat, cm<sup>-1</sup>) 2970, 1727, 1462, 1262, 1154, 1125; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>SNa 311.1082, found 311.1087.

## 2) OPTIMIZATION

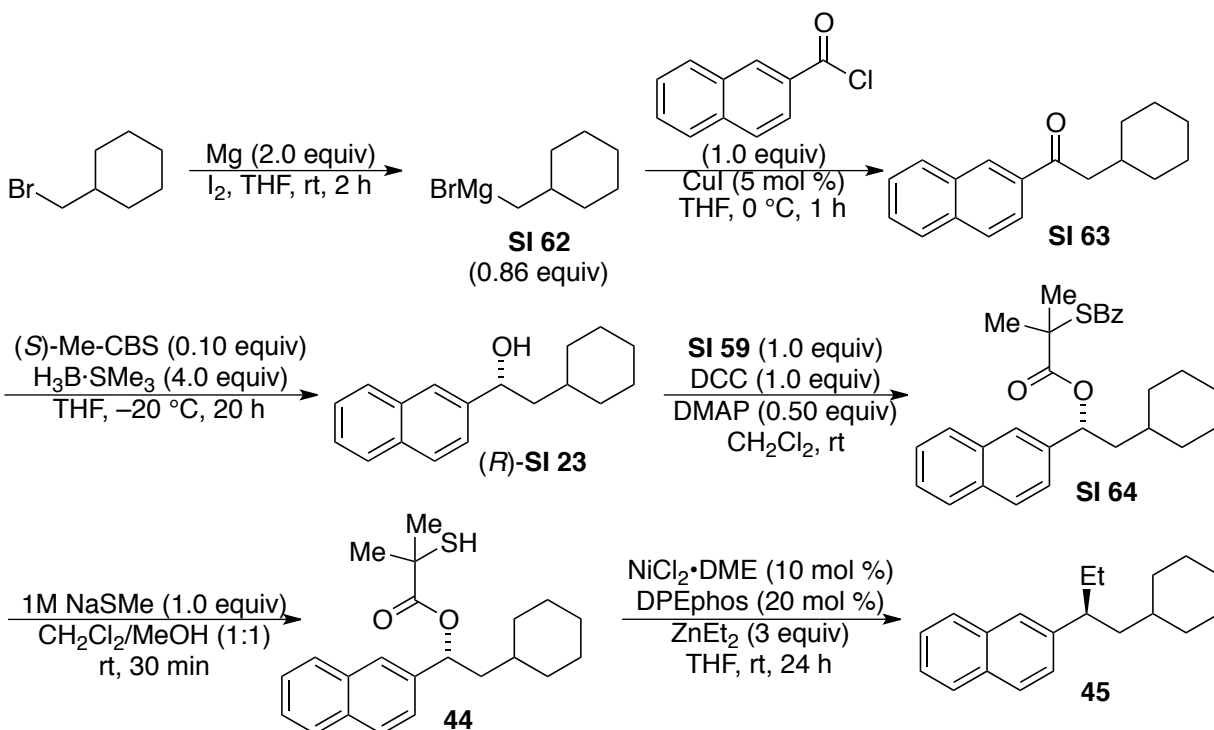


**2-(pentan-3-yl)naphthalene 41** was prepared according to either Method A or C depending on the leaving group. Analytical data was consistent with literature values.<sup>53</sup> **TLC**  $R_f$  = 0.5 (100% pentane, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.83–7.75 (m, 3H), 7.56 (s, 1H), 7.42 (apd,  $J$  = 7.6, 1.5, 2H), 7.31 (dd,  $J$  = 8.5, 1.6, 1H), 2.48 (apparent septet,  $J$  = 4.8, 1H), 1.83–1.71 (m, 2H), 1.71–1.58 (m, 2H), 0.79 (t,  $J$  = 7.4, 6H).



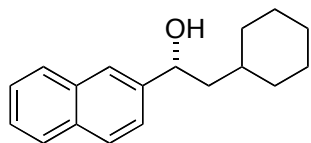
### 3) DETERMINATION OF ENANTIOSPECIFICITY (EQ 1)

Scheme SI 20. Synthesis of 43 from Equation 1



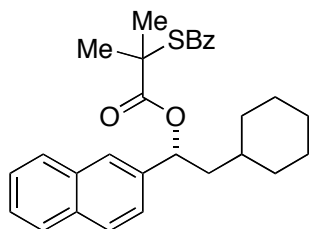
(cyclohexylmethyl)magnesium bromide **SI 62** was prepared according to Method D. The following amounts of reagents were used: magnesium turnings (1.9 g, 80 mmol, 2.0 equiv), I<sub>2</sub> (ca. 2 mg), (bromomethyl)cyclohexane (5.5 mL, 40 mmol, 1.0 equiv), and anhydrous THF (40 mL). The Grignard titrated to 0.56 M.<sup>2</sup>

**2-cyclohexyl-1-(naphthalen-2-yl)ethan-1-one SI 63** was prepared according to Method G. The following amounts of reagents were used: CuI (0.25 g, 1.3 mmol, 0.050 equiv), 2-naphthoyl chloride (5.1 g, 27 mmol, 1.0 equiv), Grignard reagent **SI 62** (37 mL, 21 mmol, 0.86 equiv, 0.56 M in THF), and THF (60 mL). The crude residue was recrystallized to afford the title compound as a white crystalline solid (1.6 g, 31%). **TLC** R<sub>f</sub> = 0.4 (5% EtOAc in hexanes, UV active); **mp** 74–76 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz) δ 8.45 (s, 1H), 8.03 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91–7.85 (m, 2H), 7.59 (td, *J* = 7.5, 1.3, 1H), 7.54 (td, *J* = 7.4, 1.5, 1H), 2.95 (d, *J* = 6.9 Hz, 2H), 2.10–1.98 (m, 1H), 1.81 (d, *J* = 12.3, 2H), 1.76–1.62 (m, 3H), 1.38–1.24 (m, 2H), 1.24–1.14 (m, 1H), 1.14–0.99 (qd, *J* = 12.1, 2.8, 2H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 200.4, 135.7, 135.0, 132.7, 129.9, 129.7, 128.51, 128.46, 127.9, 126.8, 124.2, 46.4, 34.9, 33.7, 26.4, 26.3; **IR** (neat, cm<sup>-1</sup>) 2918, 2849, 1684, 815, 744; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>20</sub>ONa 275.1412, found 275.1413.



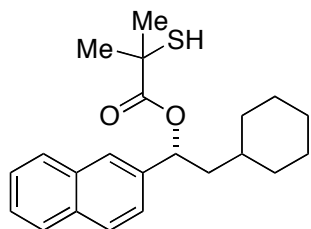
**(R)-2-cyclohexyl-1-(naphthalen-2-yl)ethan-1-ol (R)-SI 23** was prepared according to Method I. The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (0.75 g, 3.0 mmol, 0.10 equiv) and  $\text{H}_3\text{B}\cdot\text{SMe}_2$  (0.64 mL, 6.0 mmol, 2.0 equiv) in THF (15 mL), and ketone **SI 63** (0.75 g, 3.0 mmol, 1.0 equiv) in THF (15 mL).

The crude residue was purified by flash chromatography (5–20% EtOAc in hexanes)<sup>§</sup> to afford the title compound as a white solid (0.42 g, 55%). Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> **TLC**  $R_f$  = 0.3 (9:1 hexane/EtOAc, UV active); **mp** 99–100 °C; **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.84–7.82 (m, 3H), 7.78 (s, 1H), 7.49–7.45 (m, 3H), 4.96 (m, 1H), 1.85–1.77 (m, 4H), 1.71–1.60 (m, 4H), 1.51–1.40 (m, 1H), 1.29–1.13 (m, 3H), 1.04–0.92 (m, 2H); **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  142.8, 133.5, 133.1, 128.4, 128.1, 127.8, 126.3, 125.9, 124.6, 124.3, 72.4, 47.1, 34.4, 34.1, 33.1, 26.7, 26.4, 26.3; **IR** (neat  $\text{cm}^{-1}$ ) 3594, 2926, 2852, 1448; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{22}\text{ONa}$  277.1568, found 277.1567;  **$[\alpha]_D^{28}$**  +23.8 ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (AS-H, 3.0% IPA, 3.0 mL/min, 215 nm) indicated 87% ee:  $t_R$  (minor) = 12.9 min,  $t_R$  (major) = 13.5 min.



**(R)-2-cyclohexyl-1-(naphthalen-2-yl)ethyl 2-(benzoylthio)-2-methylpropanoate (R)-SI 64** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **SI 59** (0.27 g, 1.2 mmol, 1.0 equiv), alcohol (*R*)-**SI 23** (0.30 g, 1.2 mmol, 1.0 equiv) 4-dimethylaminopyridine (45 mg, 0.55 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (0.24 g, 1.2 mmol, 1.0 equiv), and dichloromethane (6 mL). The crude residue was purified by flash

chromatography (5%  $\text{Et}_2\text{O}$  in pentane) to afford the title compound as a white solid (0.30 g, 58%). **TLC**  $R_f$  = 0.6 (4:1 hexane/EtOAc, UV active); **mp** 101–104 °C; **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.86–7.67 (m, 6H), 7.54 (t,  $J$  = 7.4, 1H), 7.48–7.35 (m, 5H), 6.03 (dd,  $J$  = 9.2, 5.3, 1H), 1.95 (ddd,  $J$  = 14.1, 9.3, 5.6, 1H), 1.82 (d,  $J$  = 13.5, 1H), 1.72–1.50 (m, 5H), 1.68 (s, 3H), 1.64 (s, 3H), 1.37–1.24 (m, 1H) 1.16–0.83 (m, 5H); **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  190.7, 173.2, 138.6, 136.7, 133.6, 133.3, 133.1, 128.6, 128.3, 128.2, 127.7, 127.3, 126.1, 126.0, 125.7, 124.4, 75.4, 51.2, 44.2, 34.0, 33.8, 32.8, 26.6, 26.2, 26.11, 26.07, 26.0; **IR** (neat,  $\text{cm}^{-1}$ ) 2921, 1739, 1654, 1156, 910, 691; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{29}\text{H}_{32}\text{O}_3\text{SNa}$  483.1970, found 483.1950;  **$[\alpha]_D^{27}$**  +18.6 ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (OD-H, 15.0% IPA, 3.0 mL/min, 215 nm) indicated 92% ee:  $t_R$  (major) = 5.9 min,  $t_R$  (minor) = 6.5 min.

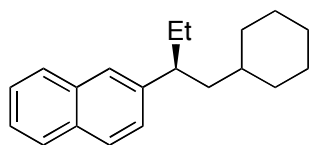


**(R)-2-cyclohexyl-1-(naphthalen-2-yl)ethyl 2-mercapto-2-methylpropanoate 44** was prepared according to Method M. The following amounts of reagents were used: NaSMe (0.54 mL, 0.54 mmol, 1.0 equiv, 1.0 M in MeOH), (*R*)-**SI 64** (0.25 g, 0.54 mmol, 1.0 equiv) in MeOH (5.4 mL), 5 min. The crude residue was purified by flash chromatography (2%  $\text{Et}_2\text{O}$  in pentane) and then heated to 40 °C under reduced pressure overnight to remove volatile byproducts that

coeluted with the desired product. The title compound was isolated as a white solid (96 mg, 50%). **TLC**  $R_f$  = 0.7 (4:1 hexane/EtOAc, UV active); **mp** 82–86 °C; **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.86–7.78 (m, 4H), 7.50–7.43 (m, 3H), 5.89 (dd,  $J$  = 8.8, 5.7, 1H), 2.40 (s, 1H), 1.98

<sup>§</sup> The material must be dry-loaded to avoid isolating the borane adduct.

(ddd,  $J = 14.1, 8.9, 6.2$ , 1H), 1.83–1.56 (m, 6H), 1.59 (s, 6H), 1.42–1.31 (m, 1H), 1.28–1.11 (m, 3H), 1.07–0.90 (m, 2H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  174.3, 138.4, 133.3, 133.2, 128.5, 128.2, 127.8, 126.3, 126.2, 125.6, 124.2, 75.3, 45.1, 44.1, 34.3, 33.7, 33.0, 29.2, 29.1, 26.6, 26.3, 26.2; IR (neat, cm<sup>-1</sup>) 2922, 2851, 1720, 1259, 1153, 743; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for [C<sub>22</sub>H<sub>28</sub>O<sub>2</sub>SNa 379.1708, found 379.1707;  $[\alpha]_{\text{D}}^{28}$  +52.3 ( $c$  1.0, CHCl<sub>3</sub>); SFC analysis (OJ-H, 3.0% IPA, 3.0 mL/min, 215 nm) indicated 92% ee:  $t_{\text{R}}$  (minor) = 8.8 min,  $t_{\text{R}}$  (major) = 9.5 min.

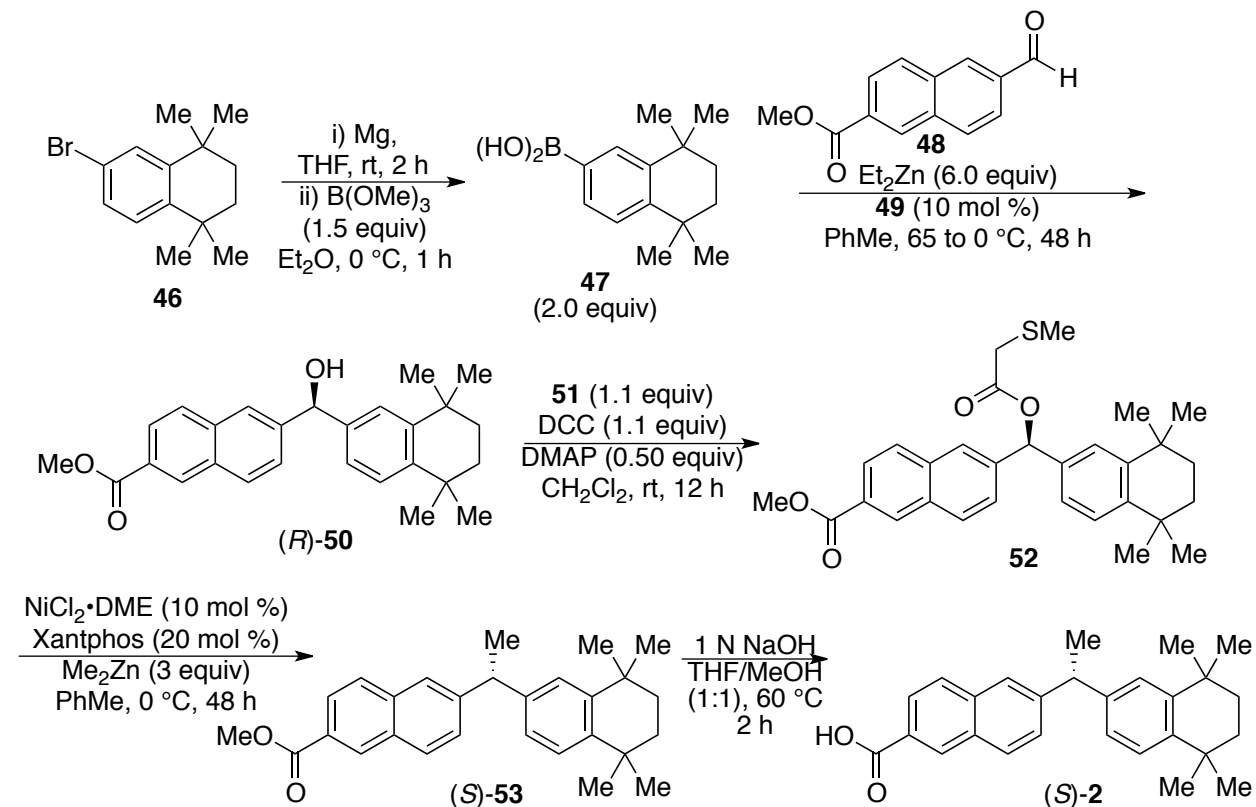


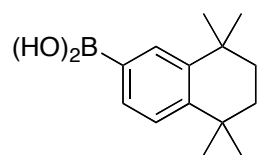
**(S)-2-(1-cyclohexylbutan-2-yl)naphthalene 45** was prepared according to Method C. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (2.2 mg, 0.010 mmol, 0.10 equiv), DPEphos (11 mg, 0.020 mmol, 0.20 equiv), substrate **44** (0.20 mL, 0.10 mmol, 1.0 equiv, 0.50 M in PhMe), ZnEt<sub>2</sub> (0.20 mL, 0.30 mmol, 3.0 equiv, 1.6 M in PhMe) and THF (1.4 mL). The crude residue was purified by flash chromatography with silver impregnated silica gel (100% pentane) to afford the title compound as a 91:1 mixture with the reduction byproduct (16 mg, calculated as 14 mg, 52%). Compound **45** was re-purified by silica gel chromatography to obtain a sample of analytically pure material. TLC  $R_{\text{f}}$  = 0.5 (100% pentane, UV active);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.85–7.73 (m, 3H), 7.56 (s, 1H), 7.43 (apd,  $J = 7.5, 1.3$ , 2H), 7.31 (dd,  $J = 8.5, 1.6$ , 1H), 2.70 (apparent septet,  $J = 4.9$ , 1H), 1.83 (d,  $J = 12.9$ , 1H), 1.75–1.46 (m, 8H), 1.15–0.99 (m, 4H), 0.95–0.79 (m, 2H), 0.76 (t,  $J = 7.3$ , 3H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  143.8, 133.7, 132.2, 127.9, 127.73, 127.67, 126.5, 126.2, 125.8, 125.1, 44.8, 44.6, 35.0, 34.4, 33.0, 30.4, 26.8, 26.4, 26.3, 12.4; IR (neat, cm<sup>-1</sup>) 2991, 2950, 1447, 815, 743; HRMS (TOF MS EI+)  $m/z$ : [M]<sup>+</sup> calculated for C<sub>20</sub>H<sub>26</sub> 266.2035, found 266.2046;  $[\alpha]_{\text{D}}^{25}$  +8.8 ( $c$  0.72, CHCl<sub>3</sub>); SFC analysis (OJ-H, 1.0% IPA, 2.5 mL/min, 215 nm) indicated 90% ee:  $t_{\text{R}}$  (major) = 9.3 min,  $t_{\text{R}}$  (minor) = 10.6 min.

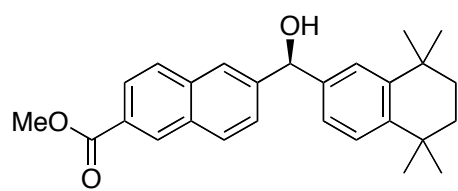
## J. SYNTHESIS OF RETINOIC ACID RECEPTOR LIGAND 2 (SCHEME 4)

### 1) ENANTIOSELECTIVE SYNTHESIS OF 2

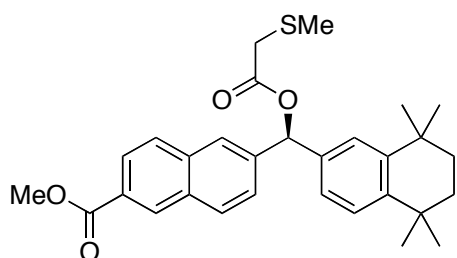
Scheme SI 21. Synthetic sequence for preparation of RAR ligand 2




**5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ylboronic acid 47** was prepared according to a modified procedure by Frohn.<sup>54</sup> Under a nitrogen atmosphere, a flame-dried round-bottom flask was charged with magnesium turnings (0.11 g, 4.7 mmol, 2.5 equiv) and THF (2 mL). 6-bromo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene **46** (0.52 g, 2.0 mmol, 1.0 equiv) was added and the mixture was stirred for 2 h at ambient temperature before being cooled to 0 °C. Meanwhile, trimethyl borate (0.28 g, 2.7 mmol, 1.5 equiv) was dissolved in Et<sub>2</sub>O (1 mL) and cooled to 0 °C. Pre-cooled Grignard solution was added to trimethyl borate solution and the reaction was allowed to stir. After for 1 h at 0 °C, the reaction was quenched with 1 M HCl. The organics were extracted with Et<sub>2</sub>O (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The off-white solid obtained was used without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ 7.46 (d, *J* = 7.8, 1H), 7.29 (dd, *J* = 3.4, 5.9, 1H), 7.11 (dd, *J* = 3.5, 6.1, 1H), 1.74 (s, 2H), 1.68 (s, 2H), 1.40 (s, 6H), 1.34 (s, 6H), 0.87 (br s, 2H).

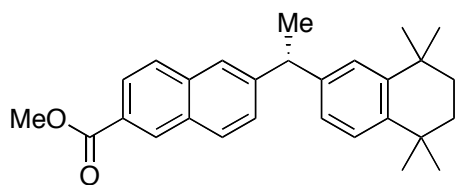

**(R)-methyl 6-(hydroxy(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methyl)-2-naphthoate (R)-50** was prepared according to Method K. The following amounts of reagents were used: boronic acid **47** (0.16 g, 0.70 mmol, 2.0 equiv), diethylzinc (2.1 mL, 2.1 mmol, 6.0

equiv, 1.0 M in toluene), aminoalcohol **49** (24 g, 0.035 mmol, 0.10 equiv), methyl 6-formyl-2-naphthoate **48** (75 mg, 0.35 mmol, 1.0 equiv), PhMe (6 mL). The product was purified by flash chromatography (10% EtOAc in hexane) to afford the title compound as a white solid (0.13 g, 94%). Absolute configuration was assigned as *R* by comparison of optical rotation with literature values. Analytical data are consistent with literature values.<sup>51</sup> **TLC**  $R_f$  = 0.4 (4:1 hexane/EtOAc, UV active); **mp** 159–161 °C, lit.<sup>51</sup> mp 154 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.57 (s, 1H), 8.01 (dd,  $J$  = 8.5, 1.6, 1H), 7.97 (s, 1H), 7.89 (t,  $J$  = 7.6, 2H), 7.52 (dd,  $J$  = 8.7, 1.9, 1H), 7.38 (d,  $J$  = 2.0, 1H), 7.27–7.25 (m, 1H), 7.09 (dd,  $J$  = 8.0, 2.0, 1H), 5.97 (d,  $J$  = 3.3, 1H), 3.98 (s, 3H), 2.26 (d,  $J$  = 3.5, 1H), 1.67 (s, 4H), 1.27–1.24 (m, 12H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  167.4, 145.4, 144.8, 144.0, 140.5, 135.6, 132.0, 130.9, 129.7, 128.5, 127.5, 127.1, 125.8, 125.7, 125.1, 124.7, 124.1, 76.5, 52.4, 35.2, 35.1, 34.5, 34.3, 32.01, 32.00, 31.96, 31.95; **IR** (neat, cm<sup>-1</sup>) 3525, 2956, 1697, 1430, 1297, 1123, 757; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>27</sub>H<sub>30</sub>O<sub>3</sub>Na 425.2093, found 425.2093; [ $\alpha$ ]<sub>D</sub><sup>29</sup> +36.1 ( $c$  0.58, THF), lit.<sup>22</sup> [ $\alpha$ ]<sub>D</sub><sup>20</sup> +45.2 ( $c$  0.31, THF, >99.8% ee, (*R*)-enantiomer); **SFC** analysis (OD-H, 15.0% IPA, 3.0 mL/min, 215 nm) indicated 94% ee:  $t_R$  (major) = 9.8 min,  $t_R$  (minor) = 12.6 min.



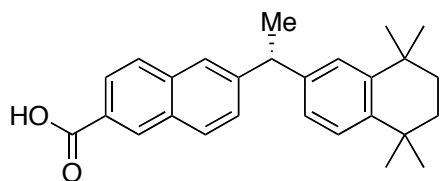
**(*R*)-methyl 6-((2-(methylthio)acetoxy)(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methyl)-2-naphthoate **52**** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (32 mg, 0.30 mmol, 1.2 equiv), alcohol (*R*)-**50** (0.10 g, 0.25 mmol, 1.0 equiv), 4-dimethylaminopyridine (15 mg, 0.13 mmol, 0.50 equiv), *N,N'*-dicyclohexylcarbodiimide (62 mg, 0.30 mmol, 1.2 equiv), and CH<sub>2</sub>Cl<sub>2</sub> (1 mL).

Purification by flash chromatography (10% Et<sub>2</sub>O in pentane) afforded the title compound as a white foam (0.11 g, 90%). **TLC**  $R_f$  = 0.5 (4:1 hexane/EtOAc, UV active); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.58 (s, 1H), 8.07 (dd,  $J$  = 8.4, 1.7, 1H), 7.93–7.87 (m, 3H), 7.52 (dd,  $J$  = 8.7, 1.7, 1H), 7.36 (d,  $J$  = 2.0, 1H), 7.25 (s, 1H), 7.08 (dd,  $J$  = 8.0, 2.2, 1H), 7.03 (s, 1H), 3.98 (s, 3H), 3.32 (s, 2H), 2.16 (s, 3H), 1.67 (s, 4H), 1.25 (s, 12H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz)  $\delta$  169.4, 167.3, 145.3, 145.1, 140.1, 136.2, 135.4, 132.1, 130.9, 129.8, 128.5, 127.8, 127.0, 125.84, 125.80, 127.7, 125.6, 124.6, 77.8, 52.4, 36.1, 35.10, 35.05, 34.5, 34.3, 32.0, 31.9, 16.4; **IR** (neat, cm<sup>-1</sup>) 2956, 2922, 1719, 1278, 1195; **HRMS** (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>30</sub>H<sub>34</sub>O<sub>4</sub>SNa 513.2076, found 513.2061; [ $\alpha$ ]<sub>D</sub><sup>29</sup> +3.2 ( $c$  0.92, CHCl<sub>3</sub>); **SFC** analysis (OD-H, 10.0% IPA, 3.0 mL/min, 215 nm) indicated 93% ee:  $t_R$  (major) = 10.3 min,  $t_R$  (minor) = 12.3 min.



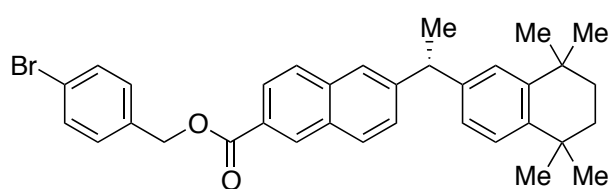
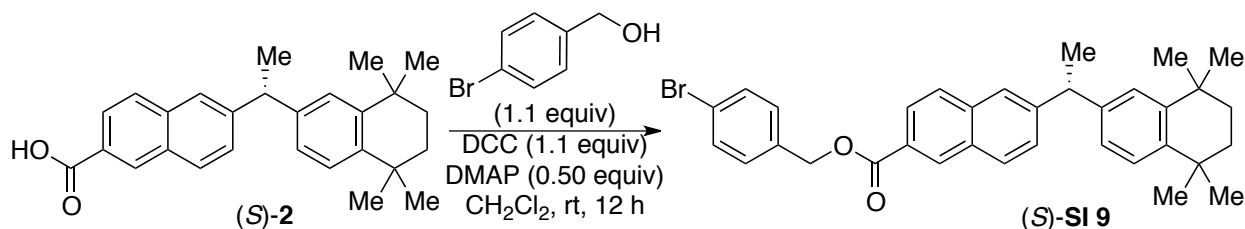
**(*S*)-methyl 6-(1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)-2-naphthoate (*S*)-**53**** was prepared according to Method B. The following amounts of reagents were used: NiCl<sub>2</sub>•DME (3.3 mg, 0.015 mmol, 0.10 equiv), Xantphos (17 mg, 0.03 mmol, 0.20 equiv), substrate (*R*)-**52** (0.30 mL, 0.15 mmol, 1.0 equiv, 0.50 M in PhMe), and ZnMe<sub>2</sub> (0.25 mL, 0.45 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2.1 mL). Purification by flash chromatography (2–5% Et<sub>2</sub>O in pentane) afforded the title compound as a white solid (55 mg, 92%). **TLC**  $R_f$  = 0.6 (4:1 hexane/EtOAc, UV active); **mp** 117–120 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.55 (s, 1H), 8.03 (dd,  $J$  = 8.7, 1.7, 1H), 7.83 (t,  $J$  = 7.7, 2H), 7.72 (s, 1H), 7.40 (dd,  $J$  =

8.8, 1.8, 1H), 7.21 (d,  $J = 2.9$ , 1H), 7.19 (d,  $J = 3.3$ , 1H), 6.97 (dd,  $J = 8.1$ , 1.8, 1H), 4.26 (q,  $J = 7.1$ , 1H), 3.97 (s, 3H), 1.71 (d,  $J = 7.2$ , 3H), 1.66 (s, 4H), 1.25–1.23 (m, 12H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  167.5, 147.1, 144.9, 142.8, 142.4, 135.9, 131.2, 130.9, 129.4, 128.1, 127.9, 126.9, 126.7, 125.8, 125.42, 125.39, 125.0, 52.3, 45.0, 35.3, 35.2, 34.4, 34.1, 32.1, 32.0 (3C), 21.9; IR (neat, cm<sup>-1</sup>) 2955, 1715, 1457, 1434, 1289, 1233, 1186; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>28</sub>H<sub>32</sub>O<sub>2</sub>Na 423.2300, found 423.2303;  $[\alpha]_{\text{D}}^{27}$  -23.0 ( $c$  0.94, CHCl<sub>3</sub>); SFC analysis (OD-H, 3.0% IPA, 3.0 mL/min, 215 nm) indicated 90% ee:  $t_{\text{R}}$  (minor) = 21.7 min,  $t_{\text{R}}$  (major) = 24.2 min.



**(S)-6-(1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)-2-naphthoic acid (S)-2**

was prepared according to a modified procedure by Yu.<sup>22</sup> To a stirred solution of ester (S)-53 (42 mg, 0.12 mmol, 1.0 equiv) in THF (1 mL) and methanol (1 mL) was added 1 N NaOH (2 mL, 2.0 mmol, 20 equiv). The reaction was heated and let stir at 60 °C for 2 hours before acidification with cold 1 N HCl (3 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL), washed with brine (2 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo to afford the title compound as a white solid (38 mg, 92%). Analytical data are consistent with literature values.<sup>22</sup> mp 193–195 °C;  $^1\text{H}$  NMR (DMSO, 400 MHz) 8.55 (s, 1H), 8.03–7.96 (m, 4H), 7.53 (dd,  $J = 8.6$ , 1.4, 1H), 7.32 (d,  $J = 1.5$ , 1H), 7.23 (d,  $J = 8.1$ , 1H), 7.05 (dd,  $J = 8.0$ , 1.5, 1H), 4.31 (q,  $J = 7.2$ , 1H), 1.70 (d,  $J = 7.3$ , 3H), 1.63 (s, 4H), 1.24 (s, 6H), 1.22 (s, 3H), 1.21 (s, 3H);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.65 (s, 1H), 8.08 (dd,  $J = 8.7$ , 1.6, 1H), 7.88 (d,  $J = 6.1$ , 1H), 7.86 (d,  $J = 6.3$ , 1H), 7.75 (s, 1H), 7.42 (dd,  $J = 8.6$ , 1.6, 1H), 7.21 (d,  $J = 3.9$ , 1H), 7.20 (d,  $J = 2.2$ , 1H), 6.97 (dd,  $J = 8.3$ , 1.8, 1H), 4.28 (q,  $J = 7.3$ , 1H), 1.73 (d,  $J = 7.4$ , 3H), 1.66 (s, 4H), 1.25–1.24 (m, 12H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  171.8, 147.6, 144.9, 142.9, 142.4, 136.3, 131.9, 131.2, 129.6, 128.3, 128.0, 126.7, 126.0, 125.8, 125.6, 125.5, 125.0, 45.0, 35.3, 35.2, 34.4, 34.1, 32.1, 32.0 (3C), 21.9; IR (neat, cm<sup>-1</sup>) 2954, 1677, 1628, 1428, 1286;  $[\alpha]_{\text{D}}^{29}$  -23.2 ( $c$  0.73, CHCl<sub>3</sub>).

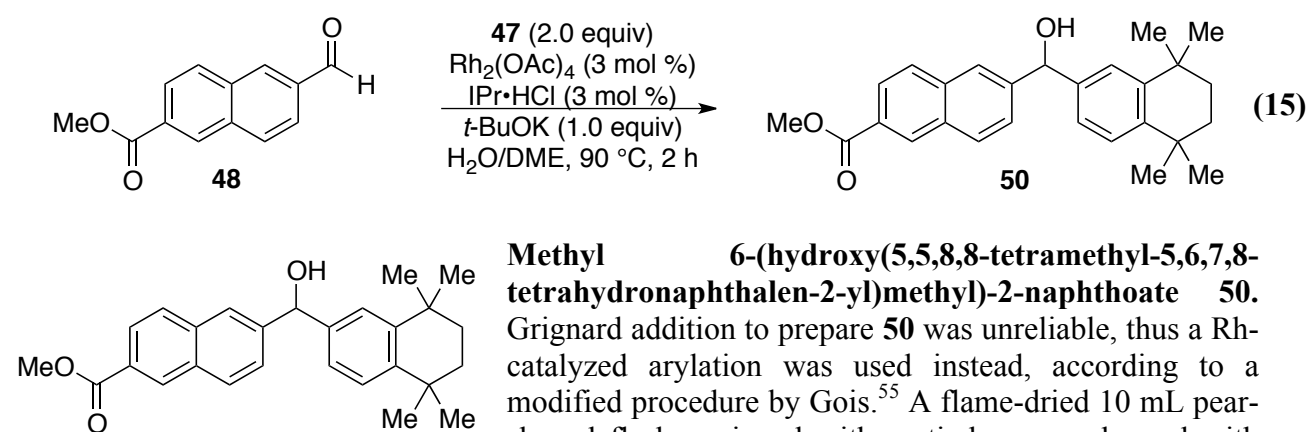


**4-bromobenzyl (S)-6-(1-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)-2-naphthoate (S)-SI 9**

was prepared according to Method L. The following amounts of reagents were used: carboxylic acid (S)-2 (19 mg, 0.050 mmol, 1.0 equiv), (4-bromophenyl)methanol (10 mg, 0.055 mmol, 1.1 equiv), 4-dimethylaminopyridine (3.1 mg, 0.025 mmol, 0.50 equiv), *N,N*-dicyclohexylcarbodiimide (11 mg, 0.055 mmol, 1.1 equiv), and dichloromethane (1 mL). The crude residue was purified by silica gel chromatography (10% Et<sub>2</sub>O in pentane), to afford the title compound as a white solid (0.024 g, 86%). A single crystal

suitable for X-ray crystallographic analysis was grown by slow evaporation from ether-pentanes. For X-ray crystallographic data, see Section IV. **TLC**  $R_f$  = 0.6 (4:1 hexane/EtOAc, UV active); **m.p.** 122–123 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.56 (s, 1H), 8.03 (dd,  $J$  = 8.8, 1.6, 1H), 7.84 (d,  $J$  = 4.6, 1H), 7.82 (d,  $J$  = 4.5, 1H), 7.72 (s, 1H), 7.54–7.51 (m, 2H), 7.41–7.34 (m, 3H), 7.20–7.19 (m, 2H), 6.96 (dd,  $J$  = 8.3, 2.3, 1H), 5.36 (s, 2H), 4.26 (q,  $J$  = 7.3, 1H), 1.71 (d,  $J$  = 7.1, 3H), 1.65 (s, 4H), 1.24 (d,  $J$  = 1.7, 6H), 1.23 (d,  $J$  = 2.6, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  166.6, 147.3, 144.9, 142.8, 142.4, 136.0, 135.3, 131.9, 131.2, 131.1, 130.0, 129.4, 128.2, 128.0, 126.7, 126.6, 125.8, 125.4, 125.0, 122.4, 66.1, 45.0, 35.3, 35.2, 34.4, 34.1, 32.1, 32.0 (3C); **IR** (neat,  $\text{cm}^{-1}$ ) 2922, 1726, 1285, 1239, 1197, 1008; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{34}\text{H}_{35}\text{O}_2\text{BrNa}$  577.1718, found 577.1720;  $[\alpha]_D^{26}$   $-8.4$  ( $c$  0.235,  $\text{CHCl}_3$ ).

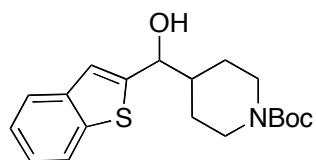
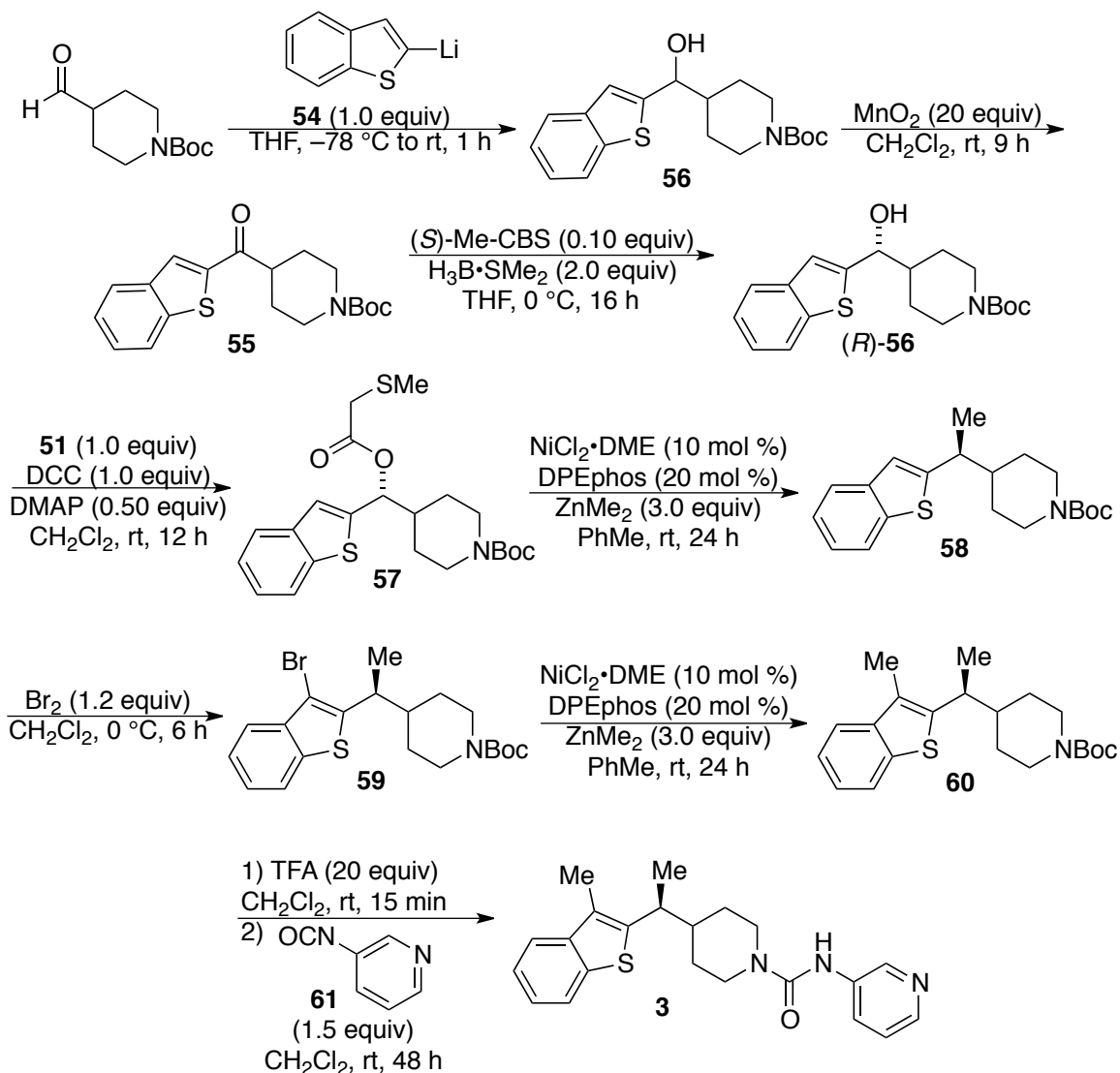
## 2) PREPARATION OF RACEMIC ALCOHOL STANDARD



**Methyl 6-(hydroxy(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methyl)-2-naphthoate 50.** Grignard addition to prepare **50** was unreliable, thus a Rh-catalyzed arylation was used instead, according to a modified procedure by Gois.<sup>55</sup> A flame-dried 10 mL pear-shaped flask equipped with a stir bar was charged with rhodium(II) acetate (1.6 mg, 0.0036 mmol, 0.030 equiv) and dimethoxyethane (0.3 mL). The resulting turquoise solution was let stir 5 min before the addition of boronic acid **47** (55 mg, 0.24 mmol, 2.0 equiv), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (1.5 mg, 0.0036 mmol, 0.030 equiv),  $\text{KO}t\text{-Bu}$  (14 mg, 0.12 mmol, 1.0 equiv), and aldehyde **48** (26 mg, 0.12 mmol, 1.0 equiv). To this brown solution was added  $\text{H}_2\text{O}$  (60  $\mu\text{L}$ ) and the reaction vessel was fitted with a reflux condenser before heating to 90 °C. After 2 h, the reaction was cooled to ambient temperature and partitioned between sat. aqueous  $\text{NaHCO}_3$  (1 mL) and EtOAc (1 mL). The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organics were washed with brine (2 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. Purification of the crude residue by flash chromatography (10% EtOAc in hexanes) afforded the title compound as a pale yellow solid (0.032 g, 66%). For analytic data see (*R*)-**50**.

## K. SYNTHESIS OF FATTY ACID AMIDE HYDROLASE INHIBITOR 3 (SCHEME 5)

Scheme SI 22. Synthetic sequence for preparation of FAAH inhibitor 3

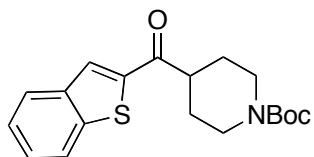


### **tert-butyl 4-(benzo[b]thiophen-2-yl(hydroxy)methyl)piperidine-1-carboxylate 56.**

Lithiate **54** (8.0 mL, 5.0 mmol, 1.0 equiv, 0.63 M in Et<sub>2</sub>O/Hexanes) was added to a stirring solution of 1-Boc-piperidine-4-carboxaldehyde (1.1 g, 5.0 mmol, 1.0 equiv) in THF (4 mL) at  $-78^\circ\text{C}$ . The reaction was allowed to warm to ambient temperature over 1 h and subsequently quenched with sat. NH<sub>4</sub>Cl and extracted with EtOAc (3 x 10 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (20–30% EtOAc in hexanes with 1% TEA) to afford the title compound as a white crystalline solid (1.3 g, 75%) TLC  $R_f = 0.2$  (4:1 hexane/EtOAc, UV active); mp 129–132 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 323 K)  $\delta$  7.76 (d,  $J = 8.1$ , 1H), 7.67 (d,  $J = 7.7$ , 1H), 7.30 (td,  $J = 7.4$ , 1.2, 1H), 7.26 (td,  $J = 7.6$ , 1.4, 1H),

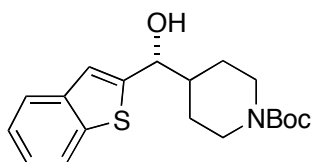


7.11 (s, 1H), 4.66 (dd,  $J = 7.2, 2.6$ , 1H), 4.11 (d,  $J = 12.8$ , 1H), 4.03 (d,  $J = 12.8$ , 1H), 2.71–2.54 (m, 3H), 1.95 (dp,  $J = 13.2, 2.7$ , 1H), 1.81 (dddd,  $J = 14.9, 11.4, 7.4, 3.6$ , 1H), 1.42 (s, 9H), 1.28 (qd,  $J = 12.4, 4.3$ , 1H), 1.20 (qd,  $J = 12.4, 4.5$ , 1H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz, 323 K)  $\delta$  155.0, 148.0, 139.6, 124.4, 124.3, 123.5, 122.6, 121.1, 79.5, 74.8, 43.9, 43.8 (br s, 2C), 28.59, 28.57, 28.2; IR (neat, cm<sup>-1</sup>) 3433, 2938, 1653, 1428, 1168, 744; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>25</sub>NO<sub>3</sub>SNa 370.1453, found 370.1464.



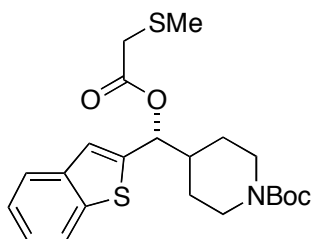
**tert-butyl 4-(benzo[b]thiophen-2-carbonyl)piperidine-1-carboxylate 55** was prepared according to Method F. The following amounts of reagents were used: MnO<sub>2</sub> (2.6 g, 30 mmol, 20 equiv), alcohol **56** (0.53 g, 1.5 mmol, 1.0 equiv), wet CH<sub>2</sub>Cl<sub>2</sub> (20 mL), 9 h.

The crude residue was purified by flash chromatography (20–40% EtOAc in hexanes) to afford the title compound as a white powder (0.38 g, 72%). TLC R<sub>f</sub> = 0.3 (4:1 hexane/EtOAc, UV active, stains with CAM); mp 130–132 °C;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz, 323 K)  $\delta$  7.96 (s, 1H), 7.87 (d,  $J = 7.9$ , 1H), 7.85 (dd,  $J = 8.1, 0.7$ , 1H), 7.45 (td,  $J = 7.6, 1.2$ , 1H), 7.39 (td,  $J = 7.5, 1.1$ , 1H), 4.18 (d,  $J = 13.1$ , 2H), 3.36 (tt,  $J = 11.0, 3.9$ , 1H), 2.93 (td,  $J = 12.7, 2.6$ , 2H), 1.91 (dd,  $J = 13.3, 2.4$ , 2H), 1.79 (dtd,  $J = 13.6, 11.5, 4.3$ , 2H), 1.47 (s, 9H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz, 323 K)  $\delta$  196.3, 154.8, 142.9, 142.7, 139.3, 128.8, 127.6, 126.0, 125.2, 123.1, 79.8, 45.4, 43.4 (br s), 28.8, 28.6; IR (neat, cm<sup>-1</sup>) 2928, 1688, 1651, 1161, 753; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>23</sub>NO<sub>3</sub>SNa 368.1296, found 368.1290.



**tert-butyl (R)-4-(benzo[b]thiophen-2-yl(hydroxy)methyl)piperidine-1-carboxylate (R)-56** was prepared according to Method I with the following exception: The reaction was set up at 0 °C and then transferred to a cold room where it was allowed to stir at 4 °C.

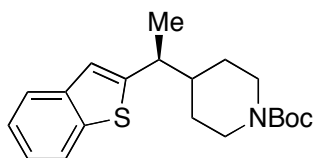
The following amounts of reagents were used: (*S*)-Me-CBS-oxazaborolidine (15 mg, 0.053 mmol, 0.10 equiv) and H<sub>3</sub>B•SMe<sub>2</sub> (0.11 mL, 1.1 mmol, 2.0 equiv) in THF (3 mL), and ketone **55** (0.18 g, 0.53 mmol, 1.0 equiv), as a solution in THF (3 mL). The crude residue was purified by flash chromatography (20–30% EtOAc in hexanes with 1% TEA) to afford the title compound as a white crystalline solid (0.18 g, 99%, 68% ee). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexanes afforded white crystals of reduced ee, therefore, the mother liquor from three successive recrystallizations was pooled together to afford the title compound in 95% ee. Absolute configuration assigned as *R* based on the accepted model for selectivity in CBS reductions<sup>17</sup> and confirmed by Competing Enantioselective Conversion (CEC).<sup>18</sup> See *rac*-alcohol **52** for analytical data. mp 138–140 °C; [ $\alpha$ ]<sub>D</sub><sup>29</sup> -24.2 (*c* 1.0, CHCl<sub>3</sub>); SFC analysis (OJ-H, 15.0% MeOH, 3.0 mL/min, 215 nm) indicated 93% ee: t<sub>R</sub> (minor) = 3.9 min, t<sub>R</sub> (major) = 4.9 min.



**tert-butyl (R)-4-(benzo[b]thiophen-2-yl(2-(methylthio)acetoxy)methyl)piperidine-1-carboxylate 57** was prepared according to Method L. The following amounts of reagents were used: carboxylic acid **51** (24 mg, 0.23 mmol, 1.1 equiv), alcohol (*R*)-**56** (72 mg, 0.21 mmol, 1.0 equiv), 4-dimethylaminopyridine (14 mg, 0.11 mmol, 0.55 equiv), *N,N'*-dicyclohexylcarbodiimide (47 mg, 0.23 mmol, 1.1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (2 mL). The crude residue was purified by flash

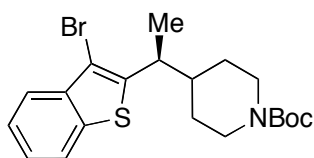
chromatography (20–30% Et<sub>2</sub>O in pentane) to afford the title compound as a viscous oil (75 mg,

83%). **TLC**  $R_f$  = 0.3 (4:1 hexane/EtOAc, UV active);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 323K)  $\delta$  7.76 (d,  $J$  = 7.8, 1H), 7.71 (dd,  $J$  = 7.0, 1.6, 1H), 7.31 (apd,  $J$  = 7.2, 1.5, 2H), 7.25 (s, 1H), 5.91 (d,  $J$  = 7.2, 1H), 4.15 (d,  $J$  = 12.8, 1H), 4.08 (d,  $J$  = 13.0, 1H), 3.22 (d,  $J$  = 14.3, 1H), 3.18 (d,  $J$  = 14.4, 1H), 2.71 (td,  $J$  = 12.7, 1.9, 1H), 2.66 (td,  $J$  = 12.6, 1.9, 1H), 2.15 (s, 3H), 2.11–2.01 (m, 1H), 1.92 (dp,  $J$  = 13.1, 2.7, 1H), 1.52 (dp,  $J$  = 13.0, 2.8, 1H), 1.44 (s, 9H), 1.33 (qd,  $J$  = 12.5, 4.4, 1H), 1.24 (qd,  $J$  = 12.7, 5.5, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz, 323 K)  $\delta$  169.3, 154.8, 142.0, 139.7, 139.2, 124.8, 124.6, 123.9, 123.5, 122.5, 79.6, 76.3, 43.6 (br s, 2C), 42.0, 36.0, 28.6, 28.4, 28.3, 16.4; **IR** (neat,  $\text{cm}^{-1}$ ) 2921, 1733, 1686, 1422, 1129; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{S}_2\text{Na}$  458.1436, found 458.1422;  $[\alpha]_D^{26}$  +24.3 ( $c$  1.0,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 15.0% MeOH, 3 mL/min, 215 nm) indicated 94% ee:  $t_R$  (minor) = 3.6 min,  $t_R$  (major) = 4.0 min.



**tert-butyl (S)-4-(1-(benzo[b]thiophen-2-yl)ethyl)piperidine-1-carboxylate 58** was prepared according to Method A. The following amounts of reagents were used:  $\text{NiCl}_2 \cdot \text{DME}$  (3.1 mg, 0.014 mmol, 0.10 equiv), DPEphos (15 mg, 0.028 mmol, 0.20 equiv), substrate **57** (0.56 mL, 0.14 mmol, 1.0 equiv, 0.25 M in PhMe), and  $\text{ZnMe}_2$  (0.23

mL, 0.42 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (1.7 mL). Purification by flash chromatography (15%  $\text{Et}_2\text{O}$  in pentane) afforded the title compound as a 94:6 mixture of desired product and  $\beta$ -H elimination byproduct (44 mg, calculated as 42 mg, 87%). Compound **58** was re-purified by silica gel chromatography to obtain a sample of analytically pure material. **TLC**  $R_f$  = 0.6 (4:1 hexane/EtOAc, UV active, stain with CAM);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.77 (d,  $J$  = 7.9, 1H), 7.67 (d,  $J$  = 7.7, 1H), 7.31 (td,  $J$  = 7.5, 0.9, 1H), 7.25 (td,  $J$  = 7.5, 1.1, 1H), 6.99 (s, 1H), 4.14 (br s, 1H), 4.06 (br s, 1H), 2.89 (p,  $J$  = 7.1, 1H), 2.64 (t,  $J$  = 12.3, 1H), 2.61 (t,  $J$  = 12.3, 1H), 1.81 (d,  $J$  = 13.2, 1H), 1.68–1.51 (m, 2H), 1.44 (s, 9H), 1.37 (d,  $J$  = 7.0, 3H), 1.29–1.08 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz, 323 K)  $\delta$  154.9, 150.9, 140.0, 139.1, 124.2, 123.7, 122.7, 122.3, 120.3, 79.4, 44.3 (br s, 2C), 43.4, 41.6, 30.6, 29.6, 28.6, 19.4; **IR** (neat,  $\text{cm}^{-1}$ ) 2975, 1680, 1424, 1169, 748; **HRMS** (TOF MS ES+)  $m/z$ :  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{SNa}$  338.1660, found 368.1666;  $[\alpha]_D^{25}$  +58.3 ( $c$  0.93,  $\text{CHCl}_3$ ); **SFC** analysis (OJ-H, 10.0% MeOH, 3.0 mL/min, 215 nm) indicated 93% ee:  $t_R$  (major) = 4.4 min,  $t_R$  (minor) = 5.0 min.

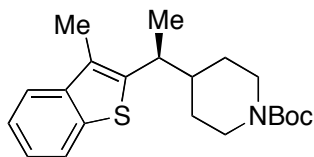


**tert-butyl (S)-4-(1-(3-bromobenzo[b]thiophen-2-yl)ethyl)piperidine-1-carboxylate 59** was prepared according to a modified procedure reported by Kose.<sup>56</sup> Bromine (33  $\mu\text{L}$ , 0.63 mmol, 1.3 equiv) was added to a stirring solution of **58**\*\* (77% ee, 0.17 g, 0.49 mmol, 1.0 equiv) in anhydrous THF (3.5 mL) at 0 °C. The reaction

was then transferred to a cold room and stirred at 4 °C. After 6 h, the reaction was quenched by the successive addition of aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL, 10% by wt.) and  $\text{NaHCO}_3$  (5 mL, 10% by wt.) The reaction mixture was extracted with EtOAc (3 x 5 mL) and the combined organics were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (100%  $\text{CH}_2\text{Cl}_2$ ) to afford the title compound as a colorless oil (50 mg, 24%). **TLC**  $R_f$  = 0.7 (4:1 hexane/EtOAc, UV active, stain with CAM);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 323 K)  $\delta$  7.76 (d,  $J$  = 8.0, 1H), 7.73 (d,  $J$  = 8.1, 1H), 7.40 (td,  $J$  = 7.5, 1.0, 1H), 7.32 (td,  $J$  = 7.6, 1.2, 1H), 4.15 (d,  $J$  = 12.8, 1H), 4.03 (d,  $J$  = 12.8, 1H), 3.27 (dq,  $J$  = 8.6, 7.0, 1H), 2.69 (td,  $J$  = 12.9, 2.6, 1H), 2.60 (td,  $J$  = 12.8, 2.6, 1H), 1.95–1.87 (m, 1H), 1.73–1.65

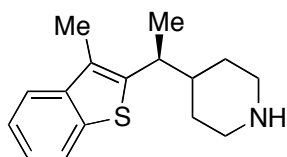
\*\* Starting material for this reaction was pooled from several experiments. The combined ee = 77%

(m, 1H), 1.55–1.47 (m, 1H), 1.44 (s, 9H), 1.34 (d,  $J = 7.0$ , 3H), 1.30–1.18 (m, 2H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  155.0, 145.6, 138.3, 137.1, 125.12, 125.08, 123.1, 122.5, 106.0, 79.5, 44.2, 44.1, 43.3, 40.7, 30.5, 30.0, 28.7, 19.3; IR (neat, cm<sup>-1</sup>) 2974, 1687, 1422, 1166, 727; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>20</sub>H<sub>26</sub>BrNO<sub>2</sub>SNa 446.0765, found 446.0750;  $[\alpha]_{\text{D}}^{28} +36.6$  ( $c$  1.2, CHCl<sub>3</sub>); SFC analysis (OJ-H, 4.0% MeOH, 2.5 mL/min, 215 nm) indicated 76% ee:  $t_{\text{R}}$  (major) = 9.3 min,  $t_{\text{R}}$  (minor) = 10.3 min.



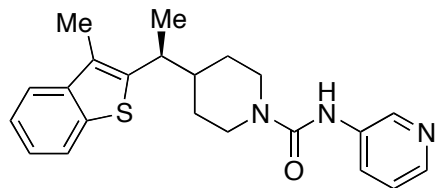
**tert-butyl-(S)-4-[1-(3-methylbenzo[b]thiophen-2-yl)ethyl]piperidine-1-carboxylate 60** was prepared according to Method A.

The following amounts of reagents were used: NiCl<sub>2</sub>•DME (2.6 mg, 0.012 mmol, 0.10 equiv), DPEphos (13 mg, 0.024 mmol, 0.20 equiv), substrate **59** (50 mg, 0.12 mmol, 1.0 equiv), and ZnMe<sub>2</sub> (0.20 mL, 0.36 mmol, 3.0 equiv, 1.8 M in PhMe) in PhMe (2 mL). The crude residue was purified by flash chromatography (15% Et<sub>2</sub>O in pentane) to afford the title compound as a colorless oil (32 mg, 75%). TLC  $R_{\text{f}} = 0.6$  (4:1 hexane/EtOAc, UV active);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz, 323 K)  $\delta$  7.74 (d,  $J = 8.0$ , 1H), 7.60 (d,  $J = 8.1$ , 1H), 7.33 (td,  $J = 7.6$ , 1.1, 1H), 7.25 (td,  $J = 7.6$ , 1.1, 1H), 4.15 (d,  $J = 12.8$ , 1H), 4.00 (d,  $J = 12.6$ , 1H), 3.00 (dq,  $J = 8.8$ , 6.9, 1H), 2.68 (td,  $J = 12.8$ , 2.5, 1H), 2.57 (td,  $J = 12.8$ , 2.4, 1H), 2.30 (s, 3H), 1.93 (dp,  $J = 12.7$ , 2.6, 1H), 1.65–1.54 (m, 1H), 1.54–1.47 (m, 1H), 1.44 (s, 9H), 1.33 (d,  $J = 7.0$ , 3H), 1.21 (qd,  $J = 12.3$ , 4.4, 1H), 1.09 (qd,  $J = 12.4$ , 4.4, 1H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz, 323 K)  $\delta$  155.0, 145.0, 141.0, 138.4, 126.6, 124.0, 123.8, 122.4, 121.5, 79.4, 44.3 (br s, 2C), 43.9, 39.2, 30.9, 30.4, 28.7, 20.1, 12.1; IR (neat, cm<sup>-1</sup>) 2973, 1688, 1422, 1170, 728; HRMS (TOF MS ES+)  $m/z$ : [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>29</sub>NO<sub>2</sub>SNa 382.1817, found 382.1812;  $[\alpha]_{\text{D}}^{25} +59.1$  ( $c$  0.82, CHCl<sub>3</sub>); SFC analysis (OD-H, 5.0% MeOH, 3.0 mL/min, 215 nm) indicated 72% ee:  $t_{\text{R}}$  (major) = 4.4 min,  $t_{\text{R}}$  (minor) = 4.9 min.



**(S)-4-(1-(3-methylbenzo[b]thiophen-2-yl)ethyl)piperidine 65** was prepared according to a modified procedure by Davis.<sup>57</sup> TFA (0.12 mL, 1.6 mmol, 20 equiv) was added to a stirred solution of **60** (28 mg, 0.078 mmol, 1.0 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0 °C under an atmosphere of nitrogen. The reaction was then warmed to ambient

temperature and stirred until complete by TLC (30 min) and then quenched with sat. NaHCO<sub>3</sub> (5 mL). The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 3 mL) and the combined organics were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The resultant yellow oil was carried on without further purification (20 mg, 99%). TLC  $R_{\text{f}} = 0$  (4:1 hexane/EtOAc, UV active);  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.76 (d,  $J = 7.8$ , 1H), 7.61 (d,  $J = 7.9$ , 1H), 7.34 (td,  $J = 7.6$ , 1.0, 1H), 7.26 (td,  $J = 7.5$ , 1.1, 1H), 3.16 (d,  $J = 12.0$ , 1H), 3.06–2.96 (m, 2H), 2.91 (td,  $J = 12.2$ , 2.2, 1H), 2.49 (td,  $J = 12.2$ , 2.1, 1H), 2.45 (br s, 1H), 2.32 (s, 3H), 1.98 (d,  $J = 12.8$ , 1H), 1.62–1.46 (m, 2H), 1.39–1.18 (m, 1H), 1.32 (d,  $J = 6.9$ , 3H), 1.12 (qd,  $J = 12.2$ , 3.4, 1H).



**(S)-4-(1-(3-methylbenzo[b]thiophen-2-yl)ethyl)-N-(pyridin-3-yl)piperidine-1-carboxamide 3** was prepared according to a modified procedure reported by Carruthers.<sup>58</sup> Crude amine **SI 65** (20 mg, 0.078 mmol, 1.0 equiv), pyridine-3-isocyanate **61** (14 mg, 0.12 mmol, 1.5 equiv), anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and anhydrous DMF (1 mL) were

combined in a 7 mL vial equipped with a stir bar and an N<sub>2</sub> line. After 48 h of stirring at ambient temperature, the reaction was quenched with sat. NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude residue was purified by flash chromatography (2–5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> with 1% TEA) to afford the title compound as a white solid (20 mg, 68% over 2 steps). **TLC** R<sub>f</sub> = 0.5 (10% MeOH and 1% TEA in CH<sub>2</sub>Cl<sub>2</sub>); **mp** 145–148 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 8.40 (d, *J* = 2.0, 1H), 8.23 (d, *J* = 4.5, 1H), 7.96 (dq *J* = 8.4, 1.2, 1H), 7.78 (d, *J* = 8.0, 1H), 7.62 (d, *J* = 7.9, 1H), 7.36 (t, *J* = 7.4, 1H), 7.28 (d, *J* = 7.4, 1H), 7.20 (dd, *J* = 8.4, 4.8, 1H), 6.62 (s, 1H), 4.19 (d, *J* = 13.3, 1H), 3.98 (d, *J* = 13.4, 1H), 3.03 (dq, *J* = 8.5, 7.0, 1H), 2.88 (td, *J* = 12.9, 2.5, 1H), 2.78 (td, *J* = 12.9, 2.3, 1H), 2.31 (s, 3H), 2.05 (d, *J* = 13.2, 1H), 1.78–1.56 (m, 2H), 1.42–1.13 (m, 2H), 1.36 (d, *J* = 6.9, 3H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz) δ 154.6, 144.4, 144.1, 141.2, 140.8, 138.1, 136.3, 127.3, 126.8, 124.0, 123.9, 123.7, 122.4, 121.6, 44.9, 44.7, 43.7, 39.0, 30.6, 30.3, 20.2, 12.2; **IR** (neat, cm<sup>-1</sup>) 3307, 2921, 1641, 1524, 1266, 754; **HRMS** (TOF MS ES+) *m/z*: [M + Na]<sup>+</sup> calculated for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>OSNa 402.1616, found 402.1614; [α]<sub>D</sub><sup>26</sup> +85.2 (*c* 0.75, CHCl<sub>3</sub>).

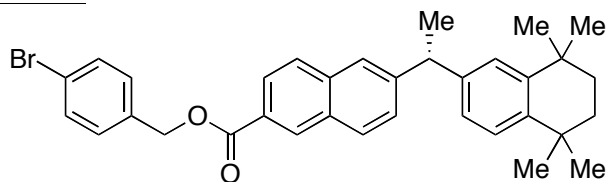
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#### IV. CRYSTALLOGRAPHIC DATA



(*S*)-SI 9  
Scheme SI 6.

X-ray Data Collection, Structure Solution and Refinement for (*S*)-SI 9. CCDC 940966 contains the supplementary crystallographic data for this structure. These data can be obtained via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html). The crystal was obtained by slow evaporation from ether over pentane.

A colorless crystal of approximate dimensions 0.321 x 0.153 x 0.050 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. The diffraction symmetry was  $2/m$  and the systematic absences were consistent with the monoclinic space groups  $P2_1$  and  $P2_1/m$ . It was later determined that space group  $P2_1$  was correct.

The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques.<sup>5</sup> The analytical scattering factors<sup>6</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

At convergence,  $wR2 = 0.0902$  and  $Goof = 1.071$  for 339 variables refined against 6467 data (0.74 Å),  $R1 = 0.0401$  for those 5869 data with  $I > 2.0\sigma(I)$ . The absolute structure was assigned by refinement of the Flack<sup>7</sup> parameter.

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## Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S =  $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$  where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.



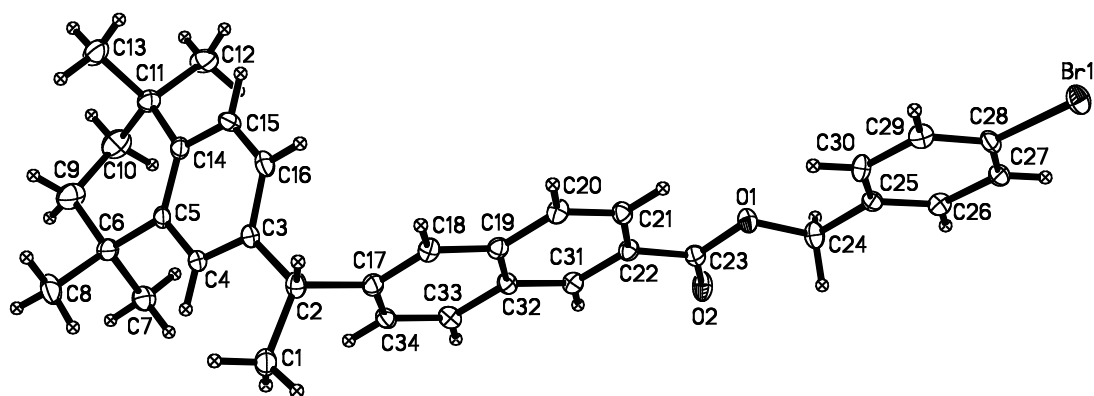


Table 1. Crystal data and structure refinement for erj13.

Identification code	erj13 (Elizabeth Swift)	
Empirical formula	$C_{34} H_{35} Br O_2$	
Formula weight	555.53	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 8.3009(7)$ Å	$\alpha = 90^\circ$ .
	$b = 5.7479(5)$ Å	$\beta = 90.5440(11)^\circ$ .
	$c = 28.630(2)$ Å	$\gamma = 90^\circ$ .
Volume	$1366.0(2)$ Å <sup>3</sup>	
Z	2	
Density (calculated)	1.351 Mg/m <sup>3</sup>	
Absorption coefficient	$1.534$ mm <sup>-1</sup>	
F(000)	580	
Crystal color	colorless	
Crystal size	$0.321 \times 0.153 \times 0.050$ mm <sup>3</sup>	
Theta range for data collection	2.134 to 28.782°	
Index ranges	$-11 \leq h \leq 11, -7 \leq k \leq 7, -38 \leq l \leq 38$	
Reflections collected	14421	
Independent reflections	6467 [R(int) = 0.0303]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6256	

Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6467 / 1 / 339
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indices [I>2sigma(I) = 5869 data]	R1 = 0.0401, wR2 = 0.0885
R indices (all data, 0.74 Å)	R1 = 0.0458, wR2 = 0.0902
Absolute structure parameter	0.042(5)
Largest diff. peak and hole	1.076 and -0.752 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for erj13.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Br(1)	-58(1)	7413(1)	-2215(1)	22(1)
O(1)	2582(3)	2752(6)	-143(1)	18(1)
O(2)	4190(4)	31(5)	185(1)	23(1)
C(1)	5682(5)	8589(8)	2902(1)	23(1)
C(2)	3986(5)	8002(7)	2725(1)	18(1)
C(3)	2923(5)	6761(7)	3081(1)	17(1)
C(4)	3503(5)	5754(8)	3490(1)	18(1)
C(5)	2506(5)	4511(7)	3798(1)	16(1)
C(6)	3285(5)	3493(8)	4241(1)	21(1)
C(7)	4503(5)	1602(8)	4098(1)	23(1)
C(8)	4181(6)	5418(9)	4519(1)	28(1)
C(9)	2013(5)	2468(14)	4566(1)	31(1)
C(10)	730(6)	1189(9)	4311(2)	33(1)
C(11)	-273(5)	2812(9)	3980(1)	23(1)
C(12)	-1292(5)	1213(8)	3668(2)	28(1)
C(13)	-1369(6)	4397(9)	4256(2)	32(1)
C(14)	883(5)	4257(7)	3685(1)	17(1)
C(15)	295(5)	5360(8)	3282(1)	20(1)
C(16)	1281(5)	6598(7)	2987(1)	19(1)
C(17)	4016(5)	6541(7)	2278(1)	18(1)
C(18)	3215(4)	7247(10)	1885(1)	17(1)
C(19)	3192(5)	5904(7)	1471(1)	16(1)
C(20)	2359(5)	6627(7)	1061(1)	17(1)
C(21)	2399(5)	5328(7)	663(1)	17(1)
C(22)	3267(5)	3201(7)	652(1)	16(1)
C(23)	3417(5)	1807(6)	218(1)	16(1)
C(24)	2929(5)	1714(7)	-591(1)	19(1)
C(25)	2129(4)	3143(7)	-972(1)	16(1)
C(26)	2202(4)	2281(11)	-1425(1)	18(1)
C(27)	1537(5)	3550(7)	-1797(1)	18(1)
C(28)	812(5)	5661(7)	-1707(1)	17(1)

C(29)	699(5)	6552(8)	-1257(1)	20(1)
C(30)	1385(5)	5261(7)	-887(1)	19(1)
C(31)	4060(4)	2416(10)	1047(1)	16(1)
C(32)	4042(5)	3756(7)	1464(1)	16(1)
C(33)	4871(5)	3016(6)	1879(1)	17(1)
C(34)	4844(5)	4381(8)	2272(1)	18(1)

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Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for erj13.

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Br(1)-C(28)	1.906(4)
O(1)-C(23)	1.352(4)
O(1)-C(24)	1.446(4)
O(2)-C(23)	1.210(5)
C(1)-C(2)	1.529(6)
C(2)-C(3)	1.531(5)
C(2)-C(17)	1.532(5)
C(3)-C(4)	1.386(5)
C(3)-C(16)	1.390(6)
C(4)-C(5)	1.410(6)
C(5)-C(14)	1.390(6)
C(5)-C(6)	1.534(5)
C(6)-C(9)	1.533(6)
C(6)-C(7)	1.542(6)
C(6)-C(8)	1.549(6)
C(9)-C(10)	1.482(7)
C(10)-C(11)	1.564(7)
C(11)-C(13)	1.516(6)
C(11)-C(14)	1.529(6)
C(11)-C(12)	1.530(6)
C(14)-C(15)	1.399(6)
C(15)-C(16)	1.379(6)
C(17)-C(18)	1.362(5)
C(17)-C(34)	1.420(6)
C(18)-C(19)	1.414(5)
C(19)-C(20)	1.420(5)
C(19)-C(32)	1.422(6)
C(20)-C(21)	1.362(5)
C(21)-C(22)	1.420(6)
C(22)-C(31)	1.379(5)
C(22)-C(23)	1.486(5)
C(24)-C(25)	1.512(5)
C(25)-C(30)	1.387(6)
C(25)-C(26)	1.391(5)

C(26)-C(27)	1.400(6)
C(27)-C(28)	1.380(6)
C(28)-C(29)	1.390(5)
C(29)-C(30)	1.409(6)
C(31)-C(32)	1.421(5)
C(32)-C(33)	1.430(5)
C(33)-C(34)	1.372(5)

C(23)-O(1)-C(24)	114.0(3)
C(1)-C(2)-C(3)	114.6(3)
C(1)-C(2)-C(17)	112.0(3)
C(3)-C(2)-C(17)	108.4(3)
C(4)-C(3)-C(16)	117.8(4)
C(4)-C(3)-C(2)	124.0(3)
C(16)-C(3)-C(2)	118.2(3)
C(3)-C(4)-C(5)	122.6(4)
C(14)-C(5)-C(4)	118.7(4)
C(14)-C(5)-C(6)	123.5(4)
C(4)-C(5)-C(6)	117.8(3)
C(9)-C(6)-C(5)	111.2(3)
C(9)-C(6)-C(7)	110.3(4)
C(5)-C(6)-C(7)	108.8(3)
C(9)-C(6)-C(8)	107.0(4)
C(5)-C(6)-C(8)	110.4(4)
C(7)-C(6)-C(8)	109.1(3)
C(10)-C(9)-C(6)	112.8(3)
C(9)-C(10)-C(11)	112.3(5)
C(13)-C(11)-C(14)	110.2(4)
C(13)-C(11)-C(12)	109.5(3)
C(14)-C(11)-C(12)	110.6(3)
C(13)-C(11)-C(10)	111.1(4)
C(14)-C(11)-C(10)	109.0(3)
C(12)-C(11)-C(10)	106.4(4)
C(5)-C(14)-C(15)	118.3(4)
C(5)-C(14)-C(11)	122.7(4)
C(15)-C(14)-C(11)	119.0(4)

C(16)-C(15)-C(14)	122.2(4)
C(15)-C(16)-C(3)	120.2(4)
C(18)-C(17)-C(34)	118.9(4)
C(18)-C(17)-C(2)	121.0(4)
C(34)-C(17)-C(2)	120.1(3)
C(17)-C(18)-C(19)	122.1(5)
C(18)-C(19)-C(20)	122.4(4)
C(18)-C(19)-C(32)	118.8(4)
C(20)-C(19)-C(32)	118.7(3)
C(21)-C(20)-C(19)	121.1(4)
C(20)-C(21)-C(22)	120.4(4)
C(31)-C(22)-C(21)	120.2(4)
C(31)-C(22)-C(23)	117.8(4)
C(21)-C(22)-C(23)	121.9(3)
O(2)-C(23)-O(1)	123.1(3)
O(2)-C(23)-C(22)	124.7(3)
O(1)-C(23)-C(22)	112.1(3)
O(1)-C(24)-C(25)	109.0(3)
C(30)-C(25)-C(26)	119.9(4)
C(30)-C(25)-C(24)	123.0(3)
C(26)-C(25)-C(24)	117.1(4)
C(25)-C(26)-C(27)	120.3(5)
C(28)-C(27)-C(26)	119.0(4)
C(27)-C(28)-C(29)	122.0(4)
C(27)-C(28)-Br(1)	119.0(3)
C(29)-C(28)-Br(1)	119.0(3)
C(28)-C(29)-C(30)	118.2(4)
C(25)-C(30)-C(29)	120.6(4)
C(22)-C(31)-C(32)	120.2(5)
C(31)-C(32)-C(19)	119.4(4)
C(31)-C(32)-C(33)	121.8(4)
C(19)-C(32)-C(33)	118.8(3)
C(34)-C(33)-C(32)	119.9(4)
C(33)-C(34)-C(17)	121.4(4)

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for erj13. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
Br(1)	28(1)	19(1)	20(1)	3(1)	-5(1)	-1(1)
O(1)	22(1)	18(2)	14(1)	-2(1)	-2(1)	2(1)
O(2)	36(2)	18(2)	16(1)	0(1)	1(1)	6(1)
C(1)	26(2)	27(2)	17(2)	-4(2)	2(2)	-5(2)
C(2)	25(2)	16(2)	14(2)	-1(1)	1(1)	-4(2)
C(3)	18(2)	18(2)	13(2)	-4(1)	-1(1)	-1(1)
C(4)	16(2)	23(2)	14(2)	-5(2)	0(1)	-2(2)
C(5)	18(2)	18(2)	12(2)	-3(2)	-1(1)	1(2)
C(6)	19(2)	29(2)	16(2)	4(2)	1(2)	1(2)
C(7)	25(2)	22(2)	22(2)	2(2)	-1(2)	1(2)
C(8)	35(3)	32(3)	17(2)	-3(2)	-8(2)	6(2)
C(9)	28(2)	42(2)	24(2)	14(3)	5(2)	2(3)
C(10)	35(3)	31(3)	34(3)	7(2)	9(2)	-5(2)
C(11)	19(2)	28(3)	22(2)	-3(2)	4(1)	-6(2)
C(12)	22(2)	24(2)	38(2)	-7(2)	4(2)	-8(2)
C(13)	25(2)	39(3)	33(2)	-15(2)	11(2)	-10(2)
C(14)	19(2)	18(2)	14(2)	-2(2)	0(2)	2(2)
C(15)	14(2)	25(2)	21(2)	-5(2)	-4(2)	1(2)
C(16)	24(2)	20(2)	13(2)	-1(1)	-4(2)	2(2)
C(17)	18(2)	20(2)	15(2)	1(2)	2(1)	-5(2)
C(18)	20(2)	14(2)	16(2)	0(2)	3(1)	-2(2)
C(19)	17(2)	16(2)	16(2)	-1(2)	2(1)	-3(2)
C(20)	21(2)	13(2)	16(2)	1(1)	3(2)	3(2)
C(21)	18(2)	17(2)	14(2)	3(2)	-1(1)	-1(2)
C(22)	17(2)	15(2)	15(2)	0(1)	2(1)	2(1)
C(23)	17(2)	15(2)	16(2)	0(1)	-1(1)	-2(1)
C(24)	28(2)	14(2)	15(2)	-2(1)	-2(2)	0(2)
C(25)	15(2)	17(2)	16(2)	-2(1)	-1(1)	-4(1)
C(26)	19(2)	15(2)	20(2)	0(2)	2(1)	1(2)
C(27)	17(2)	21(2)	16(2)	-3(2)	-2(2)	-4(2)
C(28)	17(2)	19(2)	15(2)	5(2)	-5(1)	-3(2)



C(29)	20(2)	17(2)	22(2)	1(2)	1(2)	-1(2)
C(30)	26(2)	17(2)	12(2)	-2(2)	2(2)	0(2)
C(31)	18(2)	13(2)	18(2)	-1(2)	1(1)	1(2)
C(32)	17(2)	15(2)	14(2)	3(2)	-2(1)	-1(2)
C(33)	19(2)	13(2)	20(2)	2(1)	-3(1)	-1(1)
C(34)	16(2)	25(2)	14(2)	3(2)	-2(2)	-4(2)

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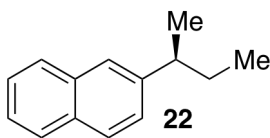
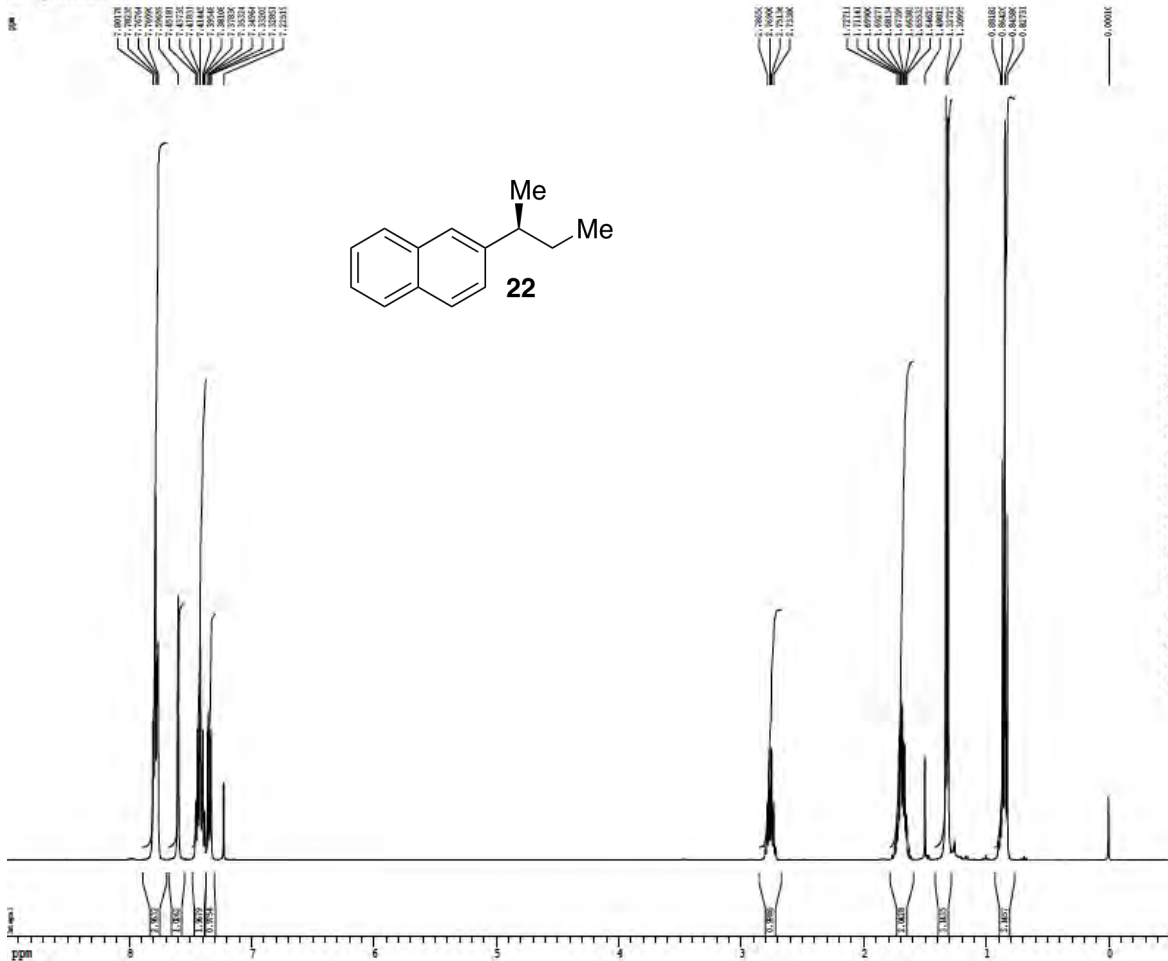
Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for erj13.

	x	y	z	U(eq)
H(1A)	5610	9522	3187	35
H(1B)	6253	9474	2662	35
H(1C)	6269	7146	2969	35
H(2A)	3445	9507	2645	22
H(4A)	4615	5908	3564	21
H(7A)	3930	320	3944	35
H(7B)	5063	1015	4377	35
H(7C)	5289	2268	3883	35
H(8A)	3420	6651	4601	42
H(8B)	5041	6070	4327	42
H(8C)	4649	4750	4805	42
H(9A)	2545	1398	4790	38
H(9B)	1517	3744	4748	38
H(10A)	-1	454	4539	40
H(10B)	1225	-65	4123	40
H(12A)	-2016	2155	3473	42
H(12B)	-1931	170	3864	42
H(12C)	-584	290	3469	42
H(13A)	-2096	5224	4042	48
H(13B)	-716	5526	4432	48
H(13C)	-2003	3465	4475	48
H(15A)	-821	5252	3210	24
H(16A)	837	7341	2719	23
H(18A)	2654	8687	1889	20
H(20A)	1765	8040	1064	20
H(21A)	1842	5849	391	20
H(24A)	2518	98	-601	23
H(24B)	4108	1672	-640	23
H(26A)	2706	826	-1482	22
H(27A)	1584	2965	-2107	22

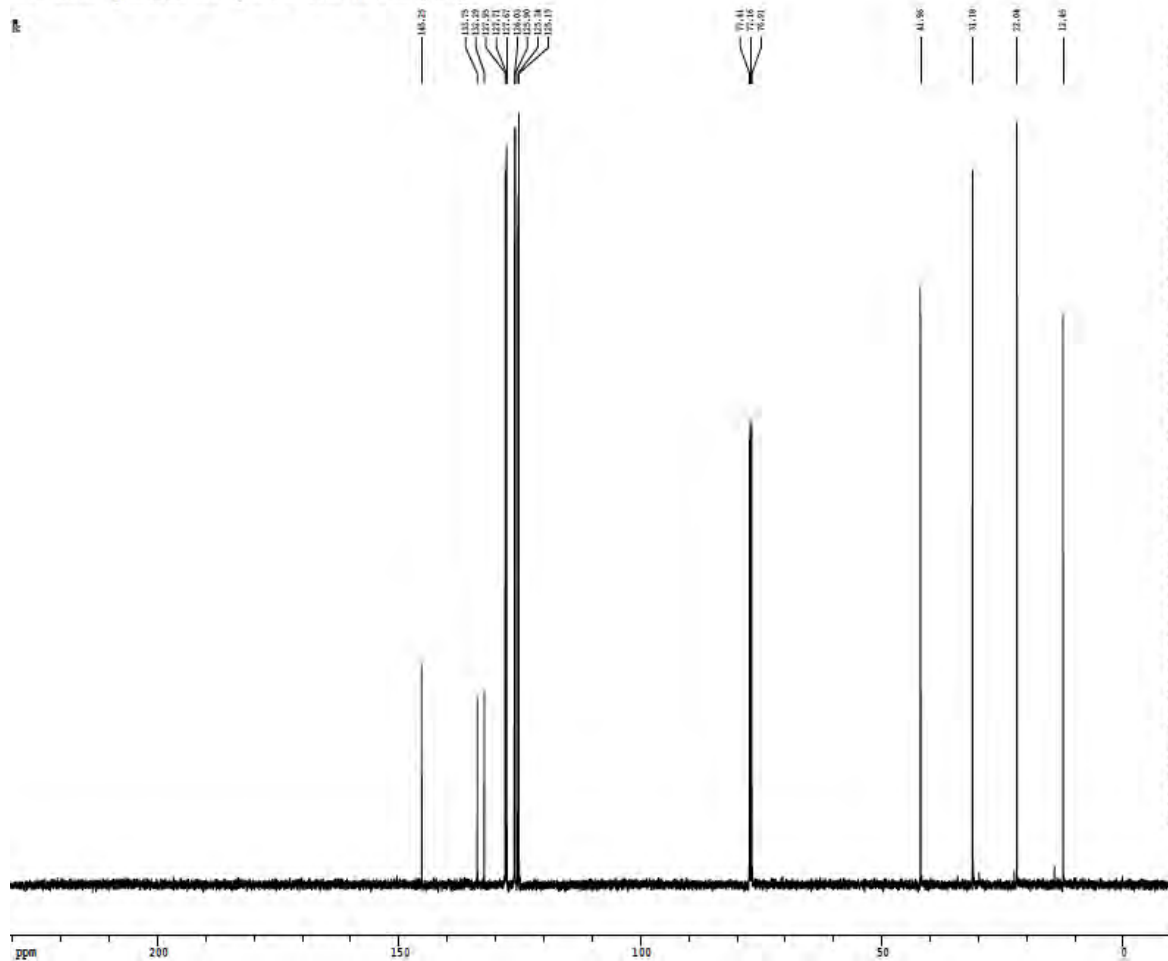
H(29A)	174	7992	-1201	24
H(30A)	1338	5846	-577	22
H(31A)	4621	976	1041	19
H(33A)	5439	1582	1882	21
H(34A)	5392	3869	2546	22

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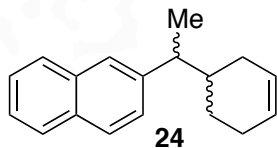
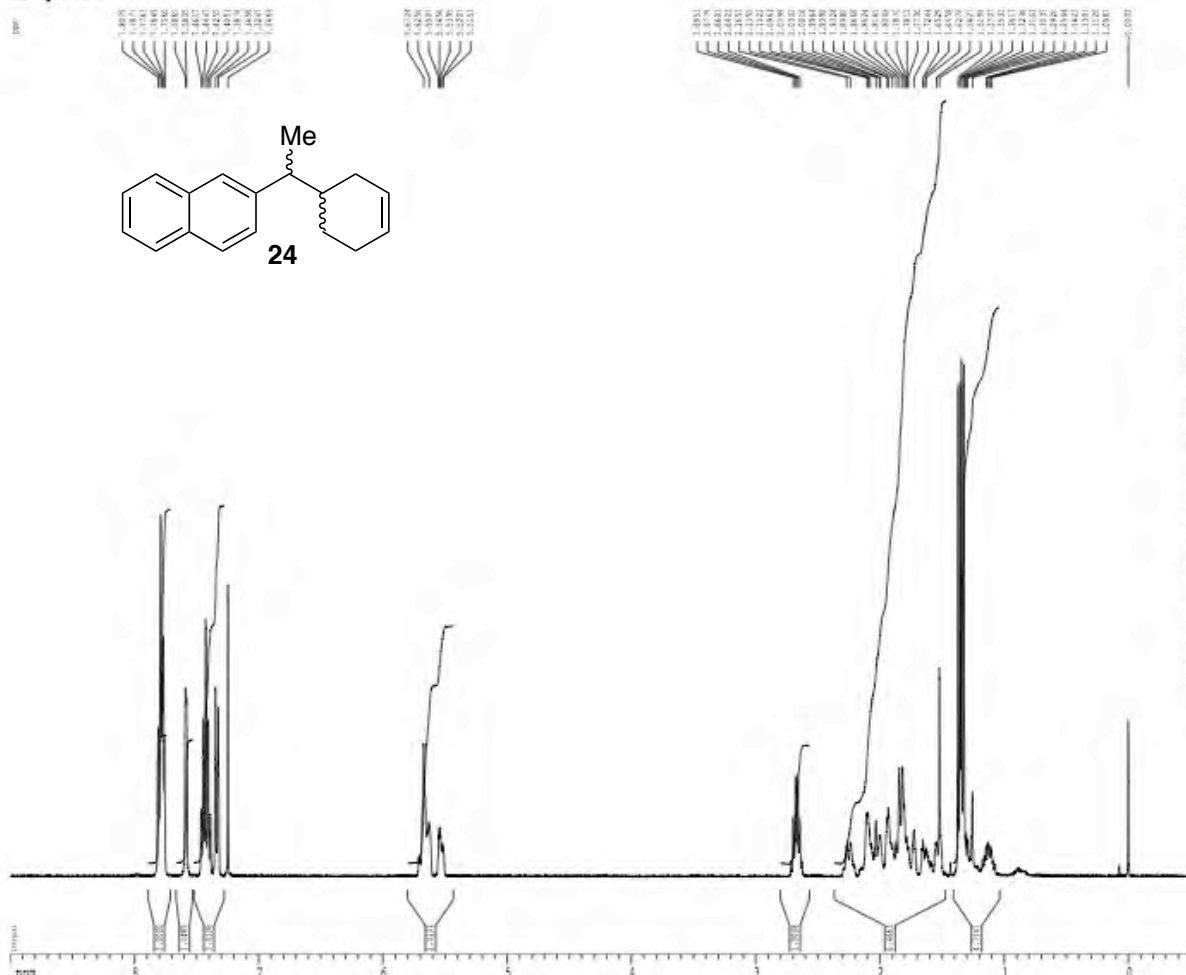
# 1H spectrum



# Z-restored spin-echo 13C spectrum with 1H decoupling

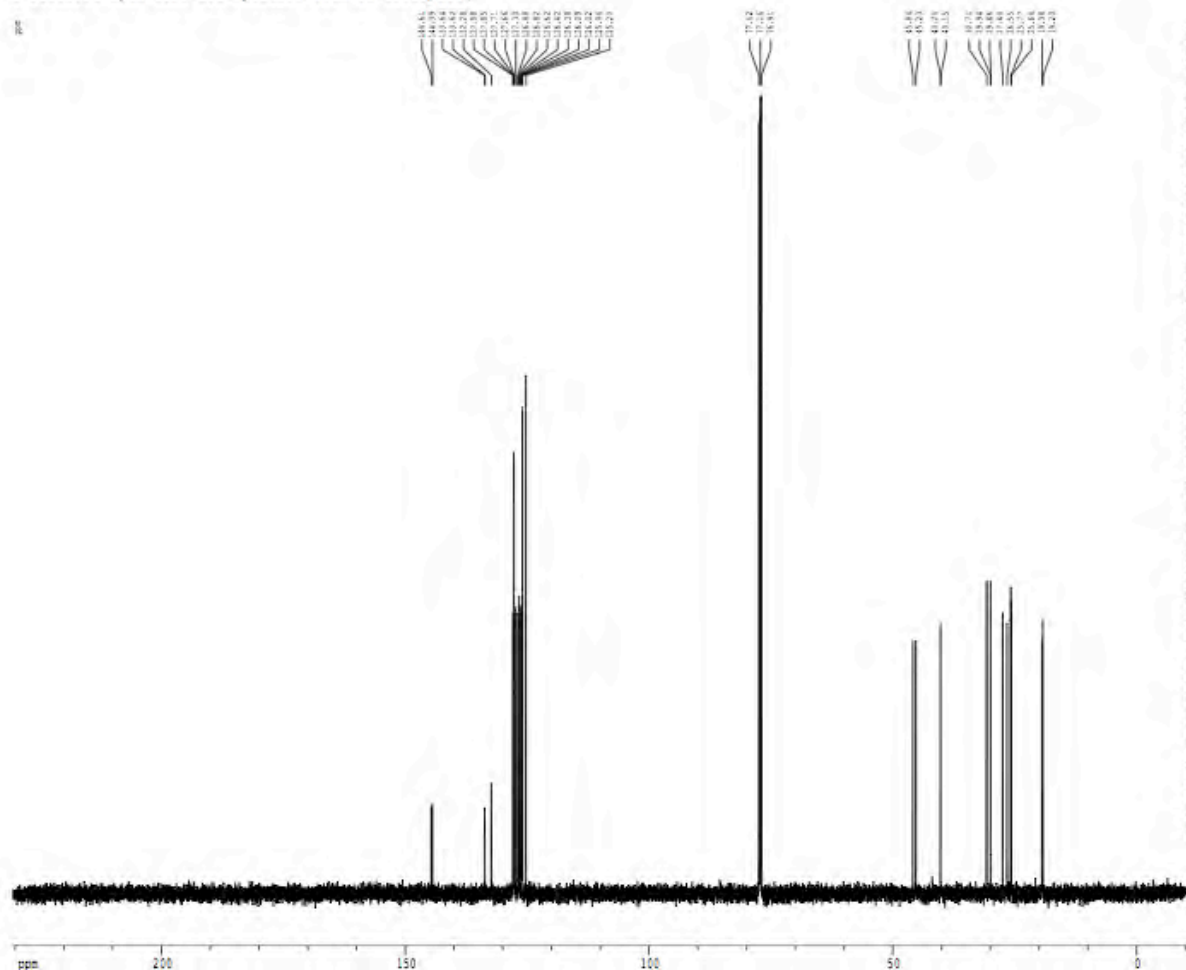


<sup>1</sup>H spectrum



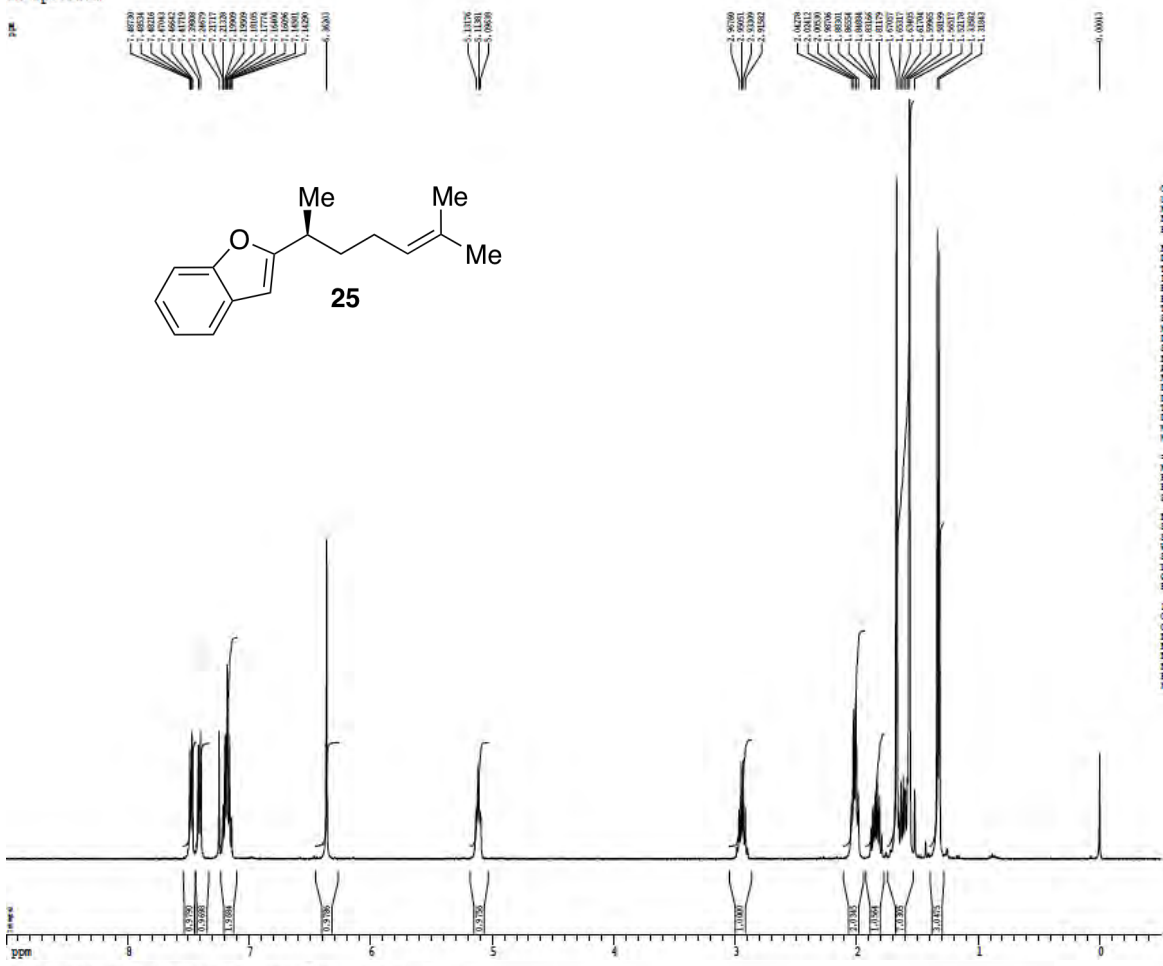
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 Time\_ 15.4711  
 Name\_ 24  
 INSTRUM spect  
 PROBRP 5 mm QNP 1H/1  
 F2PRG2 zgpg30  
 F2 400MHz  
 SOLVENT CDCl3  
 NS 4  
 DS 4  
 SWH 4418.254 Hz  
 FIDRES 0.247811 Hz  
 AQ 5.111911 sec  
 RG 256  
 SW 18.320 kHz  
 F2 400.146 MHz  
 T2 286.17 N  
 D1 0.1000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec  
 ===== CHANNEL f2 =====  
 NUC1 13C  
 P1 12.00 usec  
 PL1 -1.80 dB  
 SFO1 101.253144 MHz  
 F2 - Processing parameters  
 SI 400.146 MHz  
 SF 101.253144 MHz  
 NS 4  
 DS 4  
 SW 18.320 kHz  
 F2 400.146 MHz  
 T2 286.17 N  
 D1 0.1000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 12.00 usec  
 PL1 -1.80 dB  
 SFO1 499.999999 MHz  
 F1 - Processing parameters  
 SI 499.999999 MHz  
 SF 499.999999 MHz  
 NS 4  
 DS 4  
 SW 18.320 kHz  
 F1 499.999999 MHz  
 T1 286.17 N  
 D1 0.1000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec

Z-restored spin-echo 13C spectrum with 1H decoupling



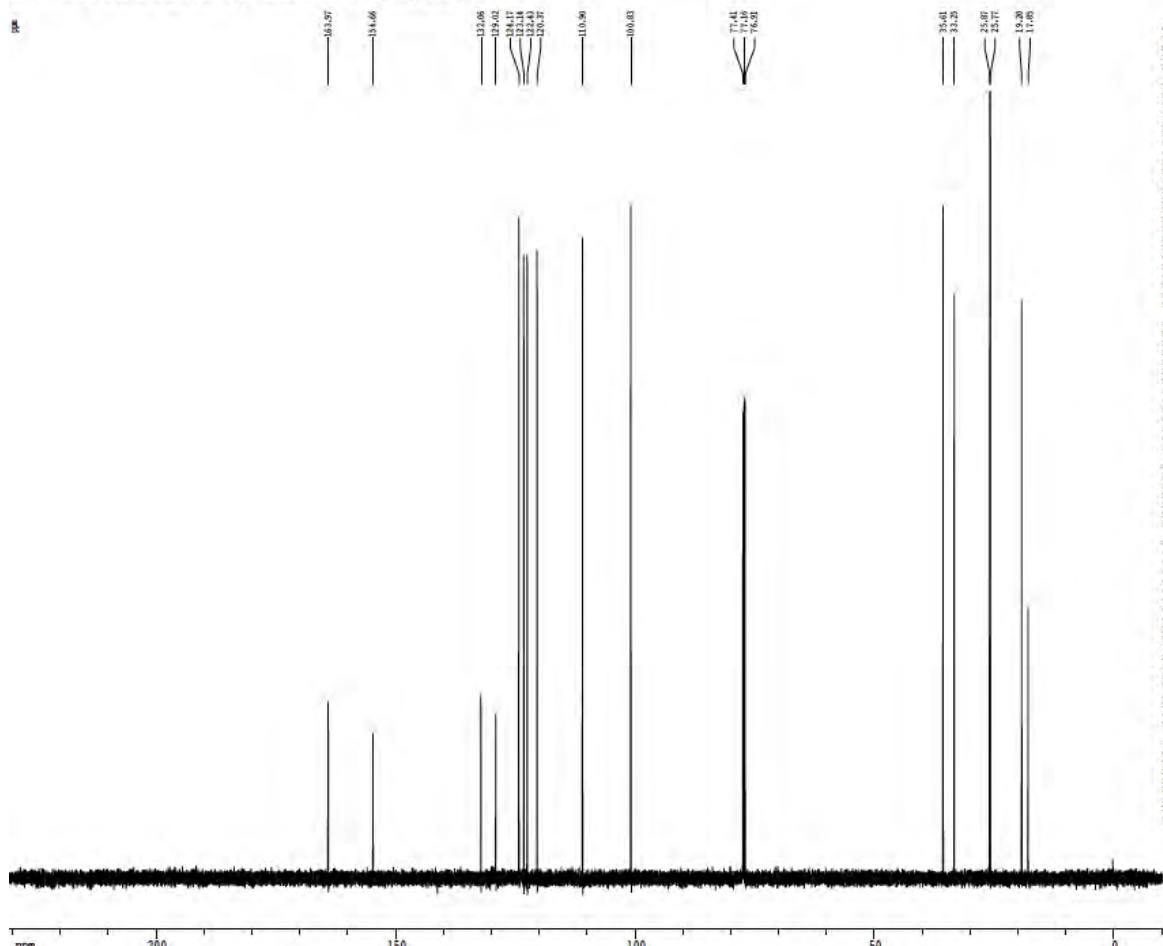
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 F2 400MHz  
 SOLVENT CDCl3  
 NS 4  
 DS 4  
 SWH 18313.451 Hz  
 FIDRES 0.462288 Hz  
 AQ 1.951949 sec  
 RG 256  
 SW 18.320 kHz  
 F2 400.146 MHz  
 T2 286.17 N  
 D1 0.2000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec  
 ===== CHANNEL f2 =====  
 NUC1 13C  
 P1 12.00 usec  
 PL1 -1.80 dB  
 SFO1 101.253144 MHz  
 F2 - Processing parameters  
 SI 400.146 MHz  
 SF 101.253144 MHz  
 NS 4  
 DS 4  
 SW 18.320 kHz  
 F2 400.146 MHz  
 T2 286.17 N  
 D1 0.2000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 12.00 usec  
 PL1 -1.80 dB  
 SFO1 499.999999 MHz  
 F1 - Processing parameters  
 SI 499.999999 MHz  
 SF 499.999999 MHz  
 NS 4  
 DS 4  
 SW 18.320 kHz  
 F1 499.999999 MHz  
 T1 286.17 N  
 D1 0.2000000 sec  
 ACQRES 0.0000000 sec  
 NSCAN 2.0000000 sec

1H spectrum

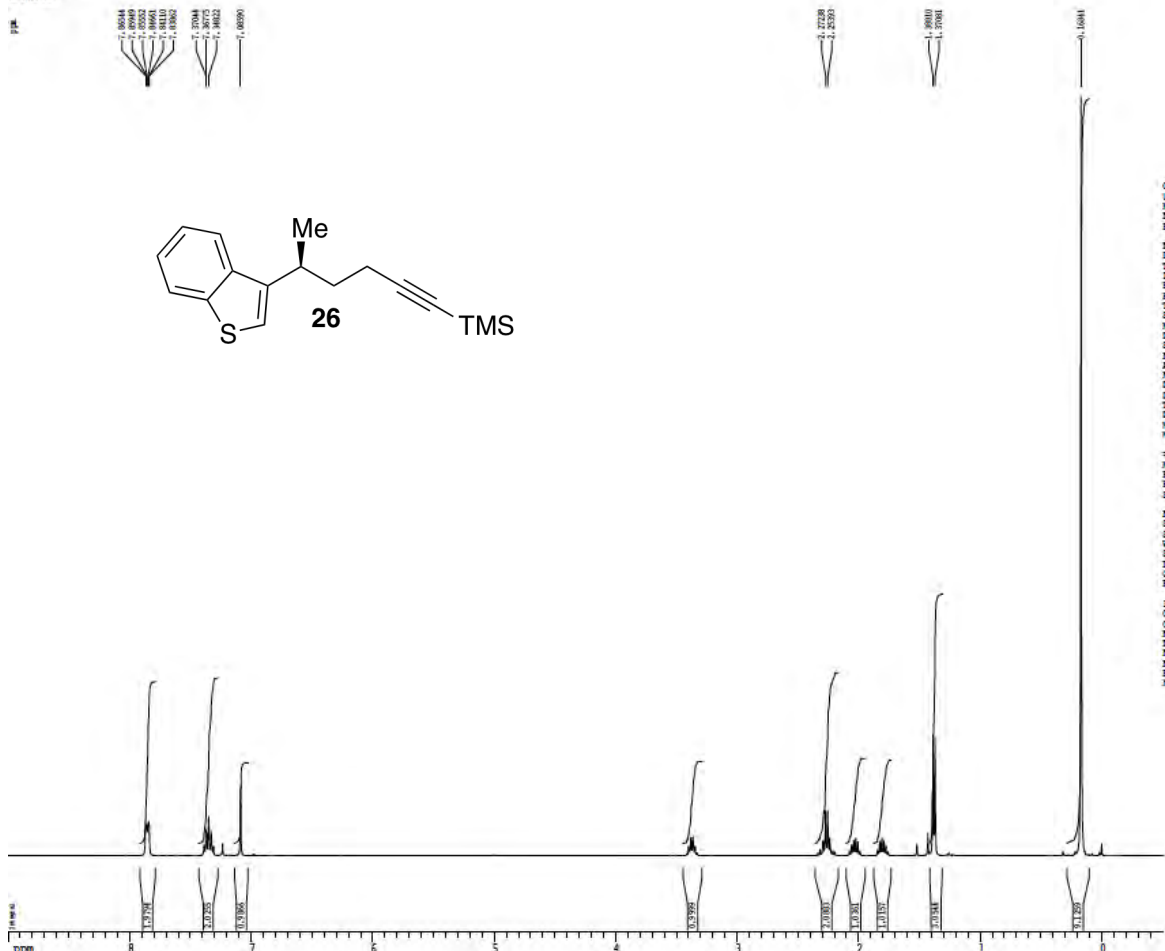


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 DS 4  
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 FIDRES 0.097632 Hz  
 AQ 5.1118079 sec  
 RG 101  
 SW 78.500 USAC  
 SF 400.146 MHz  
 EQ 4.50 USAC  
 ZF 120.0 MHz  
 SFO1 400.146090 MHz  
 F2 - Acquisition Parameters  
 DATE 20130114  
 TIME 15.18  
 INSTRUM spect  
 PULPROG zgpg30  
 SOLVENT CDCl3  
 NS 400  
 DS 4  
 SWH 500.136090 MHz  
 FIDRES 0.097632 Hz  
 AQ 5.1118079 sec  
 RG 101  
 SW 78.500 USAC  
 SF 400.146 MHz  
 EQ 4.50 USAC  
 ZF 120.0 MHz  
 SFO1 400.146090 MHz  
 F2 - Processing Parameters  
 SI 65536  
 SF 400.146090 MHz  
 WF 70  
 GB 0  
 CB 0  
 SC 0.00 Hz  
 PC 2.00  
 IS MR plot parameters  
 CH 22.80 cm  
 CT 15.40 cm  
 ZF 9.800 ppm  
 F2 3651.17 Hz  
 F3 -1.590 ppm  
 F4 -200.00 Hz  
 FREQ 4.4161 ppm/cm  
 SCA 164.72084 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling

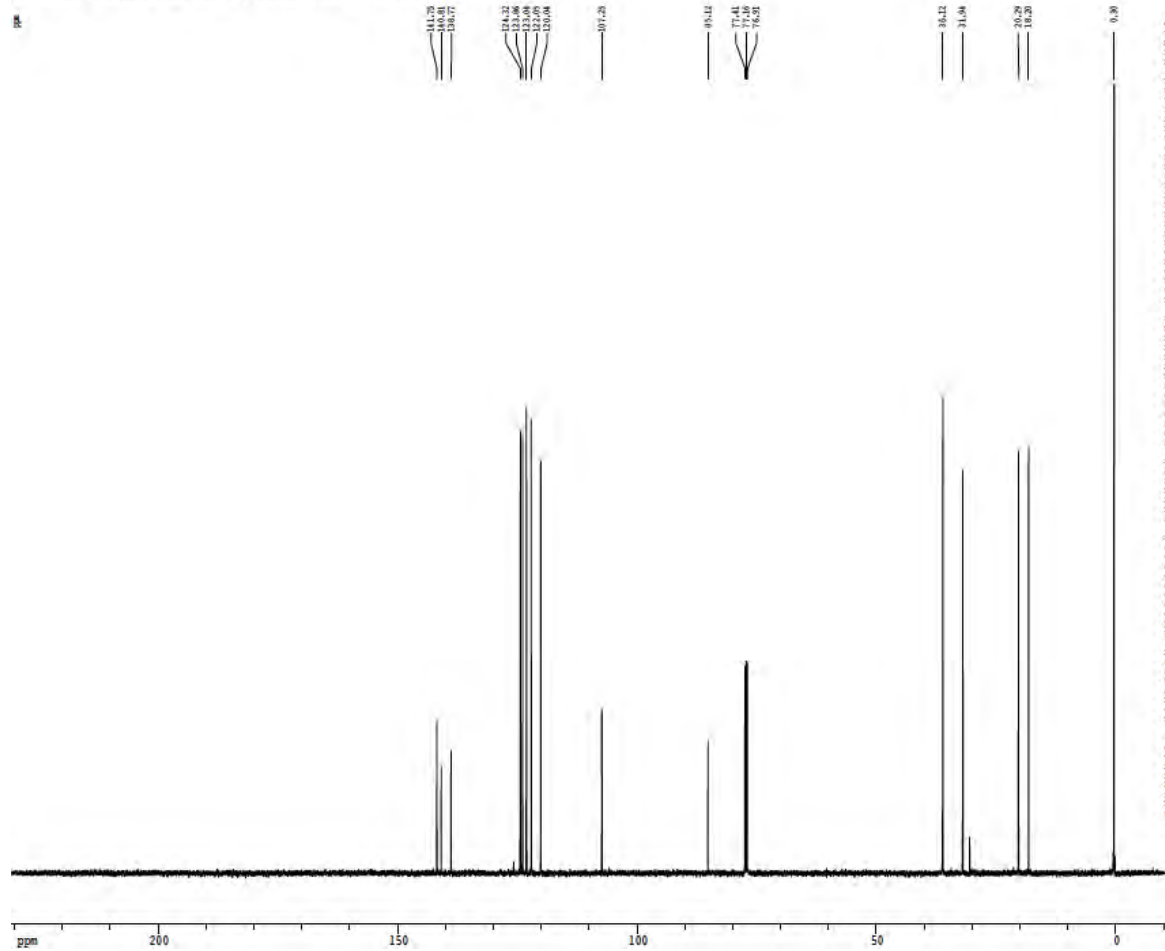


Current Data Parameters  
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 TIME 15.18  
 INSTRUM spect  
 PULPROG zgpg30  
 SOLVENT CDCl3  
 NS 400  
 DS 4  
 SWH 500.136090 MHz  
 FIDRES 0.097632 Hz  
 AQ 5.1118079 sec  
 RG 101  
 SW 78.500 USAC  
 SF 400.146 MHz  
 EQ 4.50 USAC  
 ZF 120.0 MHz  
 SFO1 400.146090 MHz  
 F2 - Acquisition Parameters  
 DATE 20130114  
 TIME 15.18  
 INSTRUM spect  
 PULPROG zgpg30  
 SOLVENT CDCl3  
 NS 400  
 DS 4  
 SWH 500.136090 MHz  
 FIDRES 0.097632 Hz  
 AQ 5.1118079 sec  
 RG 101  
 SW 78.500 USAC  
 SF 400.146 MHz  
 EQ 4.50 USAC  
 ZF 120.0 MHz  
 SFO1 400.146090 MHz  
 F2 - Processing Parameters  
 SI 65536  
 SF 400.146090 MHz  
 WF 70  
 GB 0  
 CB 0  
 SC 0.00 Hz  
 PC 2.00  
 IS MR plot parameters  
 CH 22.80 cm  
 CT 15.40 cm  
 ZF 9.800 ppm  
 F2 3651.17 Hz  
 F3 -1.590 ppm  
 F4 -200.00 Hz  
 FREQ 4.4161 ppm/cm  
 SCA 164.72084 Hz/cm



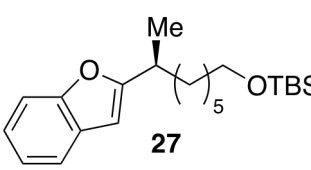
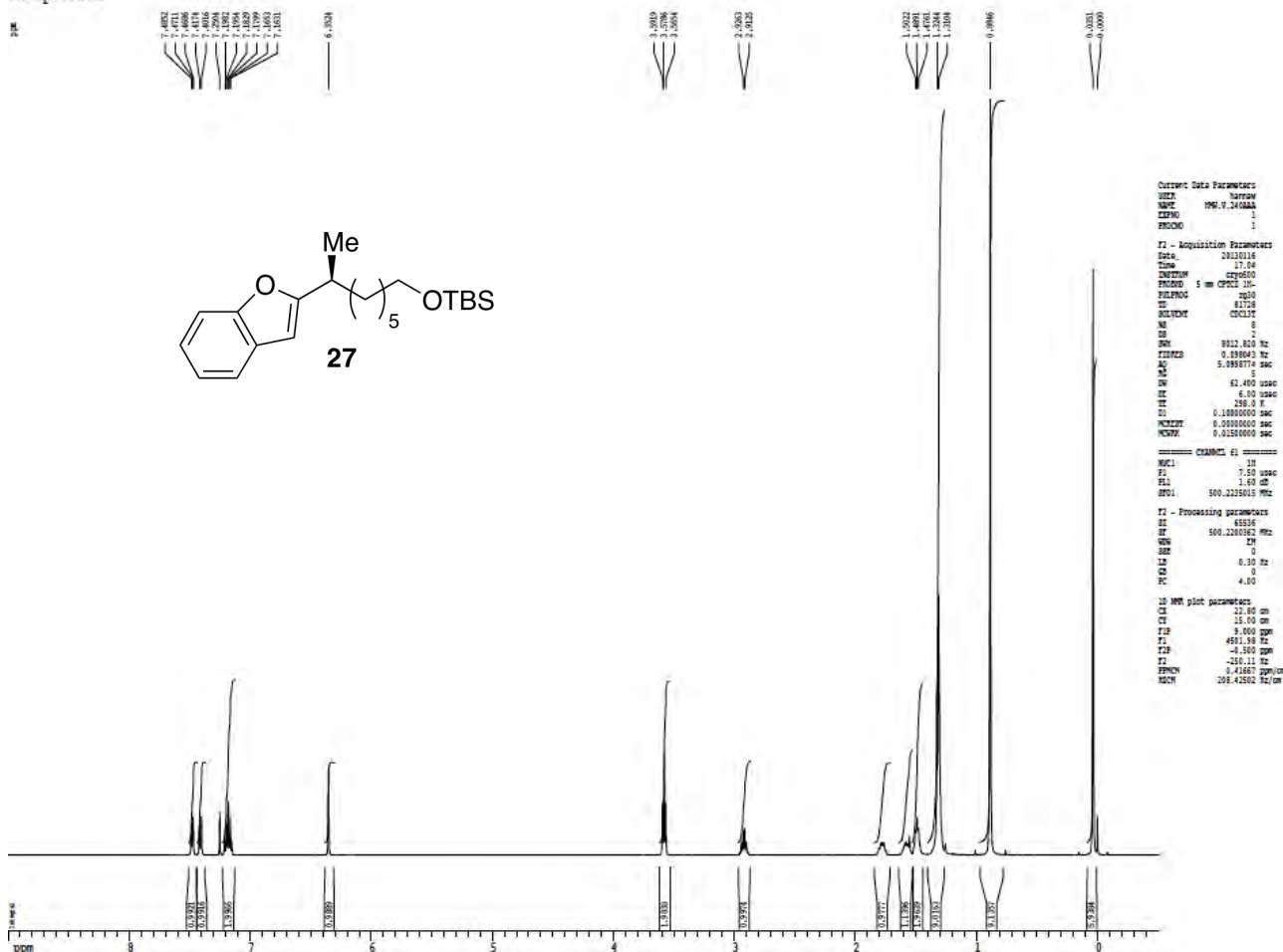
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 Time: 13.10  
 CHANNEL: CPDPR03  
 PROCNO: 5 mm QNP 1H/13  
 PULPROG: zgpg30  
 TD: 65536  
 SOLVENT: CDCl3  
 NS: 2  
 DS: 2  
 SWH: 6410.100 Hz  
 FIDRES: 0.337613 Hz  
 AQ: 5.1118979 sec  
 RG: 71.5  
 DW: 78.000 usec  
 DE: 4.50 usec  
 TE: 300.2 K  
 D1: 0.1000000 sec  
 DELTA: 0.3000000 sec  
 WALTZ16: 0.2000000 sec  
 WALTZ17: 0.2000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13  
 P1: 12.00 usec  
 PL1: -4.60 dB  
 SFO1: 400.1264600 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 400.1264600 MHz  
 WDW: EM  
 SSB: 0  
 GB: 0  
 SC: 0  
 PC: 2.00  
 ===== CHANNEL f2 =====  
 ISH NMR plot parameters  
 SI: 65536  
 SF: 125.7604112 MHz  
 CT: 15.00 cm  
 FIDRES: 0.1000000 ppm  
 P1: 300.00 usec  
 PL1: -4.500 dB  
 SFO1: 125.7604112 MHz  
 SFO2: 500.1364500 MHz  
 F2CN: 0.41667 ppm/cm  
 F2SCN: 166.72666 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling

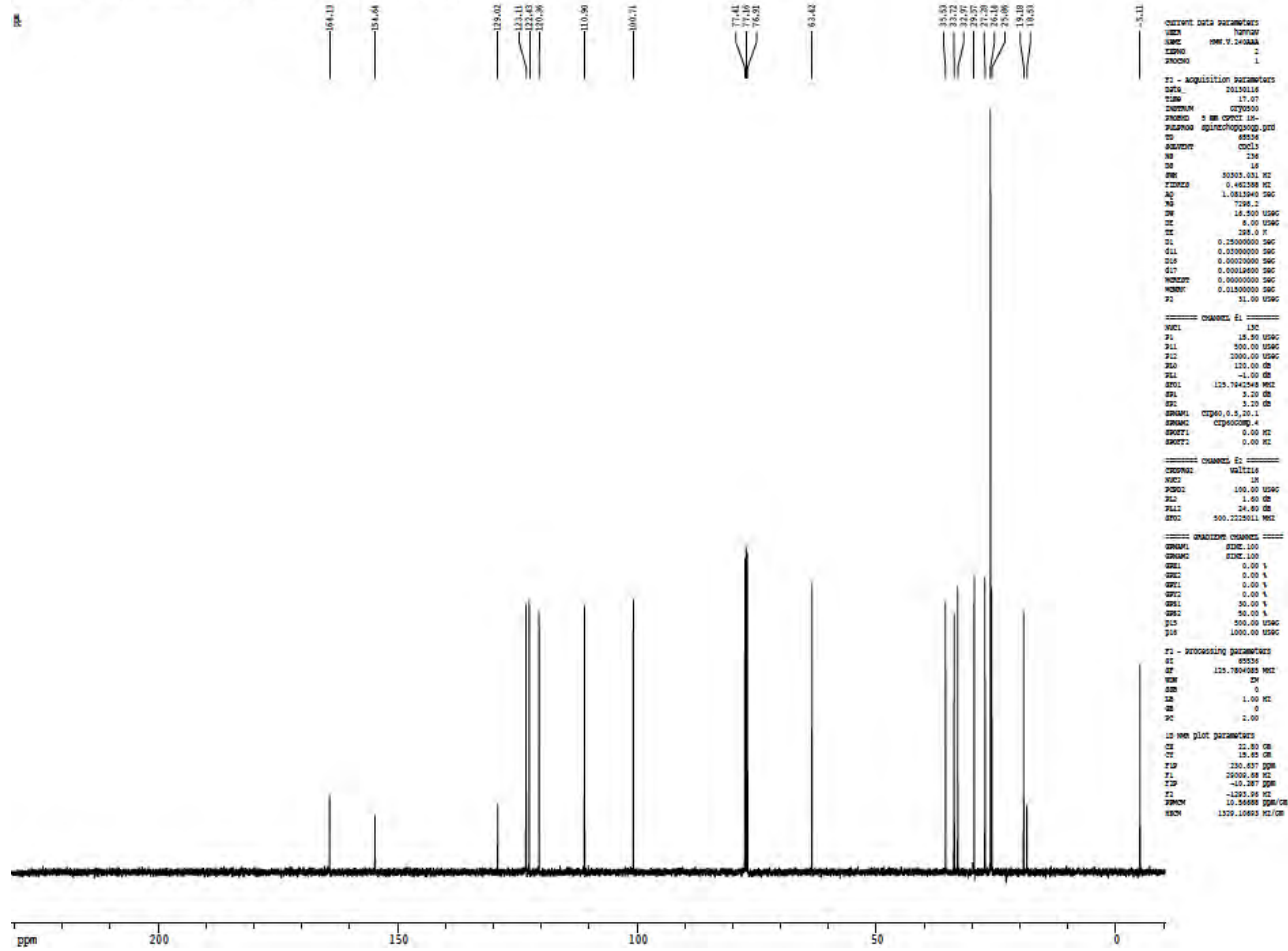


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 PROCNO: 1  
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 Time: 13.10  
 CHANNEL: CPDPR03  
 PROCNO: 5 mm QNP 1H/13  
 PULPROG: zgpg30  
 TD: 65536  
 SOLVENT: CDCl3  
 NS: 2  
 DS: 2  
 SWH: 6410.100 Hz  
 FIDRES: 0.337613 Hz  
 AQ: 5.1118979 sec  
 RG: 71.5  
 DW: 78.000 usec  
 DE: 4.50 usec  
 TE: 300.2 K  
 D1: 0.1000000 sec  
 DELTA: 0.3000000 sec  
 WALTZ16: 0.2000000 sec  
 WALTZ17: 0.2000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13  
 P1: 12.00 usec  
 PL1: -4.60 dB  
 SFO1: 400.1264600 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 400.1264600 MHz  
 WDW: EM  
 SSB: 0  
 GB: 0  
 SC: 0  
 PC: 2.00  
 ===== CHANNEL f2 =====  
 ISH NMR plot parameters  
 SI: 65536  
 SF: 125.7604112 MHz  
 CT: 15.00 cm  
 FIDRES: 0.1000000 ppm  
 P1: 300.00 usec  
 PL1: -4.500 dB  
 SFO1: 125.7604112 MHz  
 SFO2: 500.1364500 MHz  
 F2CN: 0.41667 ppm/cm  
 F2SCN: 166.72666 Hz/cm

1H spectrum



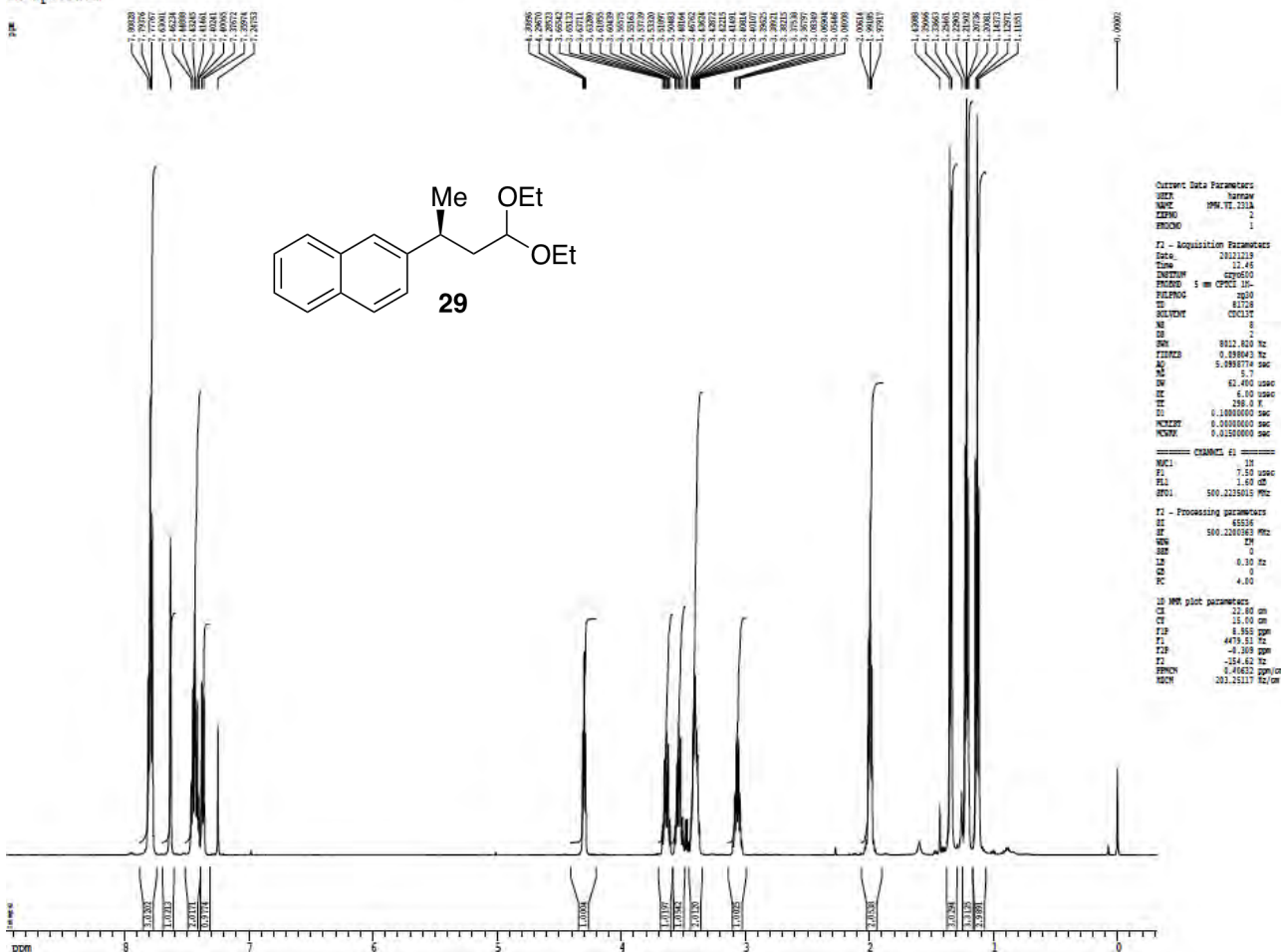
Z-restored spin-echo 13C spectrum with 1H decoupling



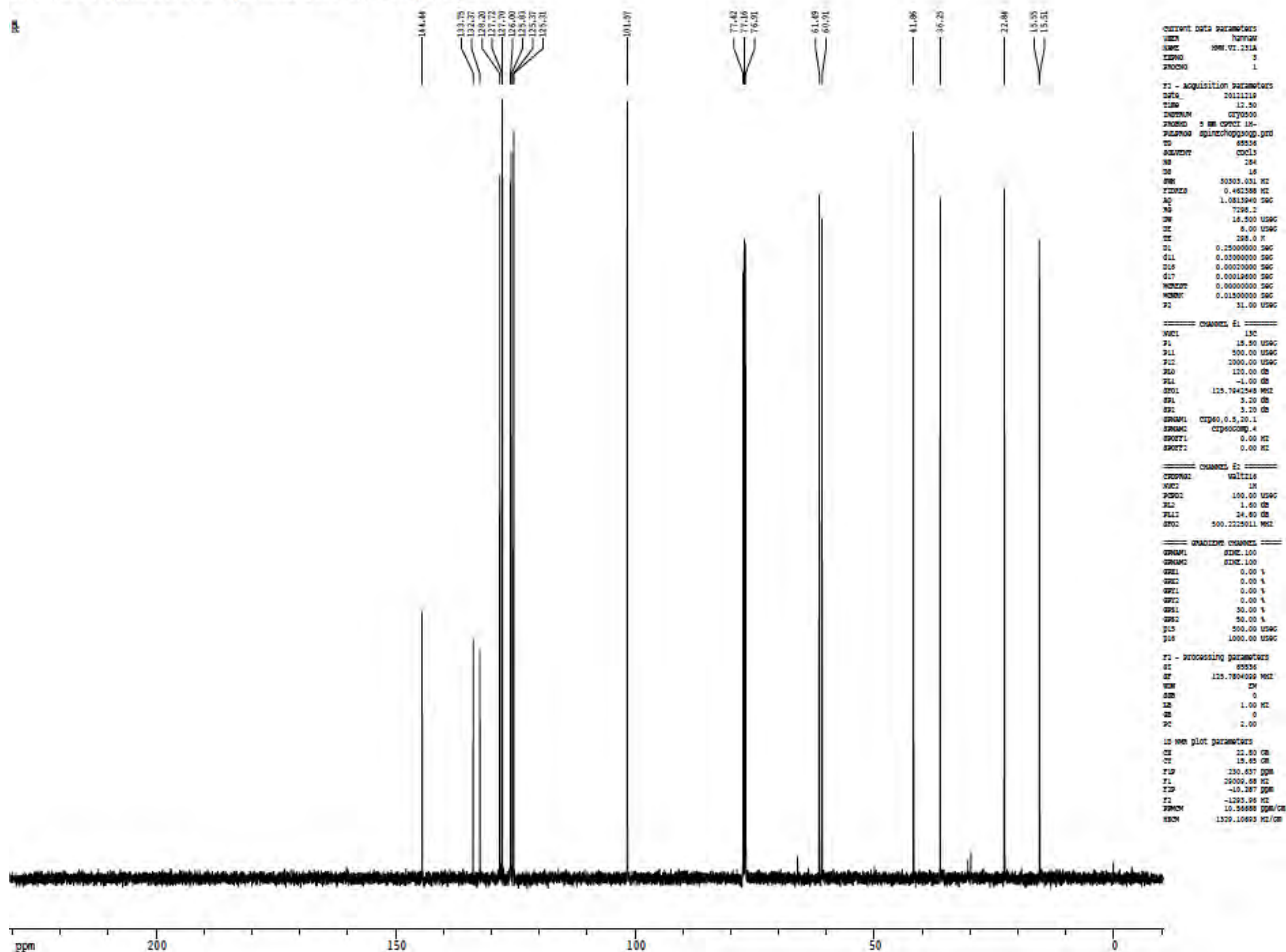




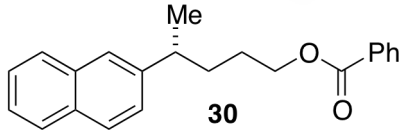
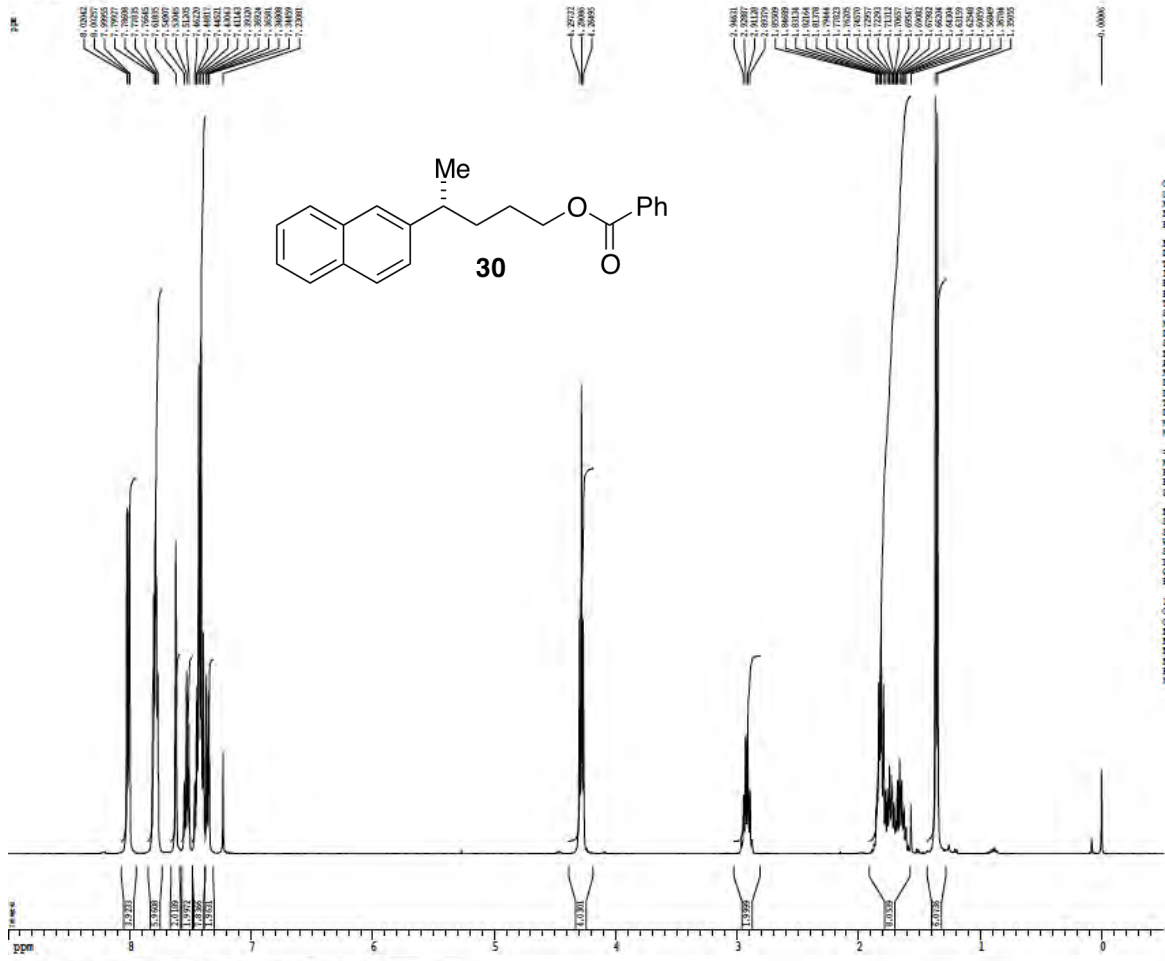
1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling

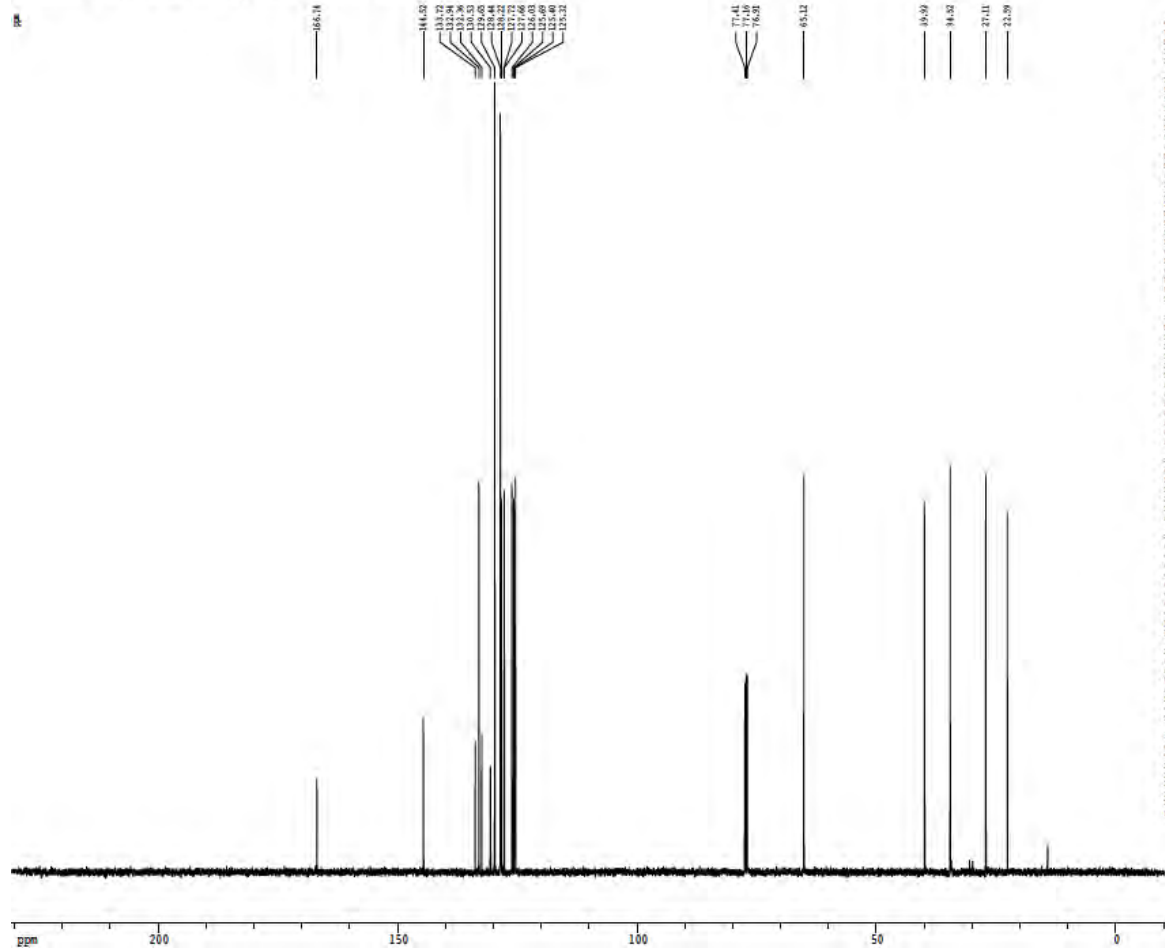


# 1H spectrum



Current Data Parameters  
NAME 140812  
EXPNO 1  
PROCNO 1  
PROCPS 1  
F1 - Acquisition Parameters  
Date\_ 20110115  
Time 1.23  
SOLVENT CDCl3  
PROBHD 5 mm QNP 1H/13  
PULPROG zgpg30  
PC 128.0  
SOLVENT CDCl3  
NUC1 13  
NUC2 1H  
FREQ 400.146400 MHz  
P1 12.00  
PD1 0.00  
P2 1.00  
PD2 0.00  
PC 2.00  
F2 - Processing parameters  
SI 32768  
SF 400.146401 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00  
F3 - Spin echo parameters  
SI 32768  
SF 400.146401 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00  
F4 - Spin echo parameters  
SI 32768  
SF 400.146401 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00

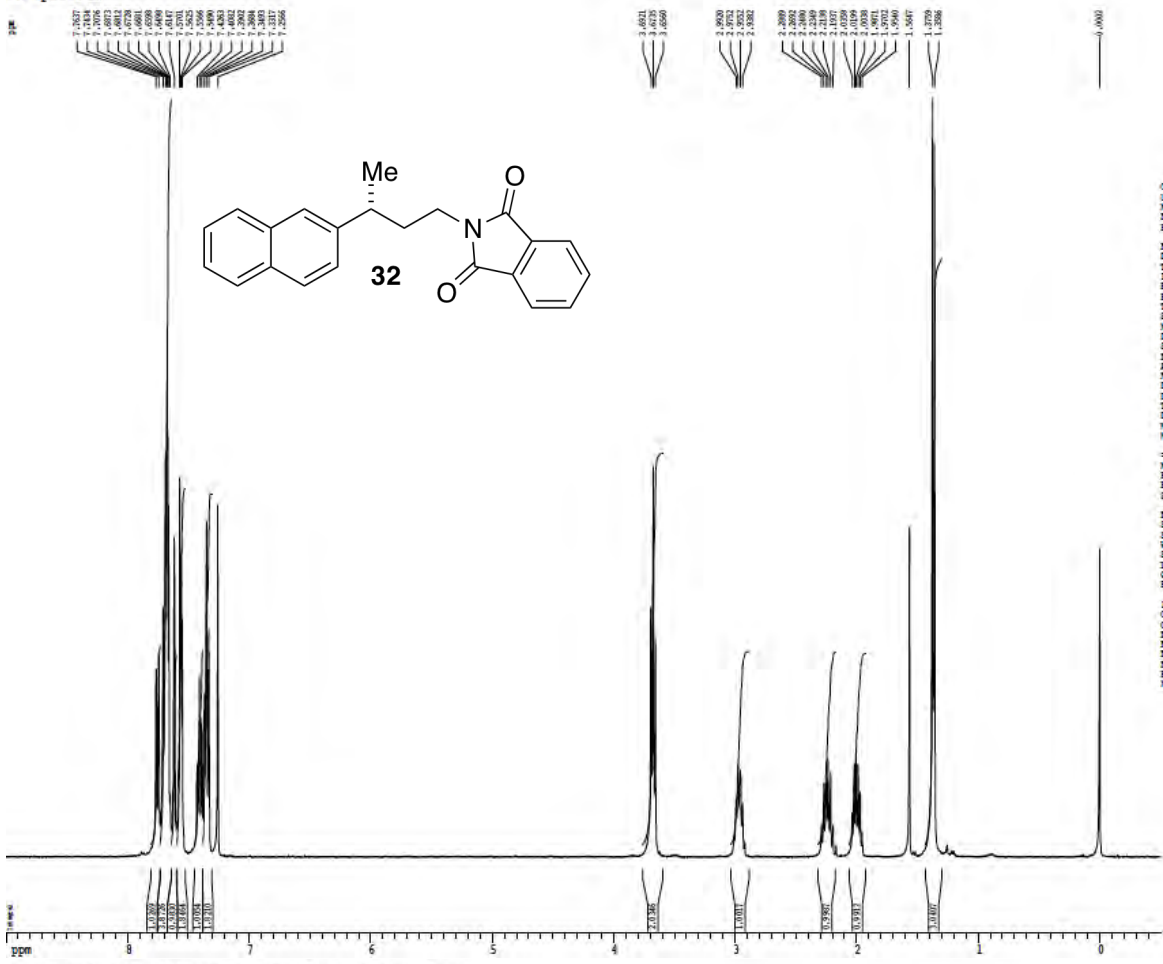
# Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
NAME 140812  
EXPNO 1  
PROCNO 1  
PROCPS 1  
F1 - Acquisition Parameters  
Date\_ 20110115  
Time 20.21  
SOLVENT CDCl3  
PROBHD 5 mm QNP 1H/13  
PULPROG zgpg30  
PC 128.0  
SOLVENT CDCl3  
NUC1 13C  
NUC2 1H  
FREQ 101.625361 MHz  
P1 12.00  
PD1 0.00  
P2 1.00  
PD2 0.00  
PC 2.00  
F2 - Processing parameters  
SI 65536  
SF 125.760424 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00  
F3 - Spin echo parameters  
SI 65536  
SF 125.760424 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00  
F4 - Spin echo parameters  
SI 65536  
SF 125.760424 MHz  
WDW EM  
SSB 0  
GB 0  
PC 2.00

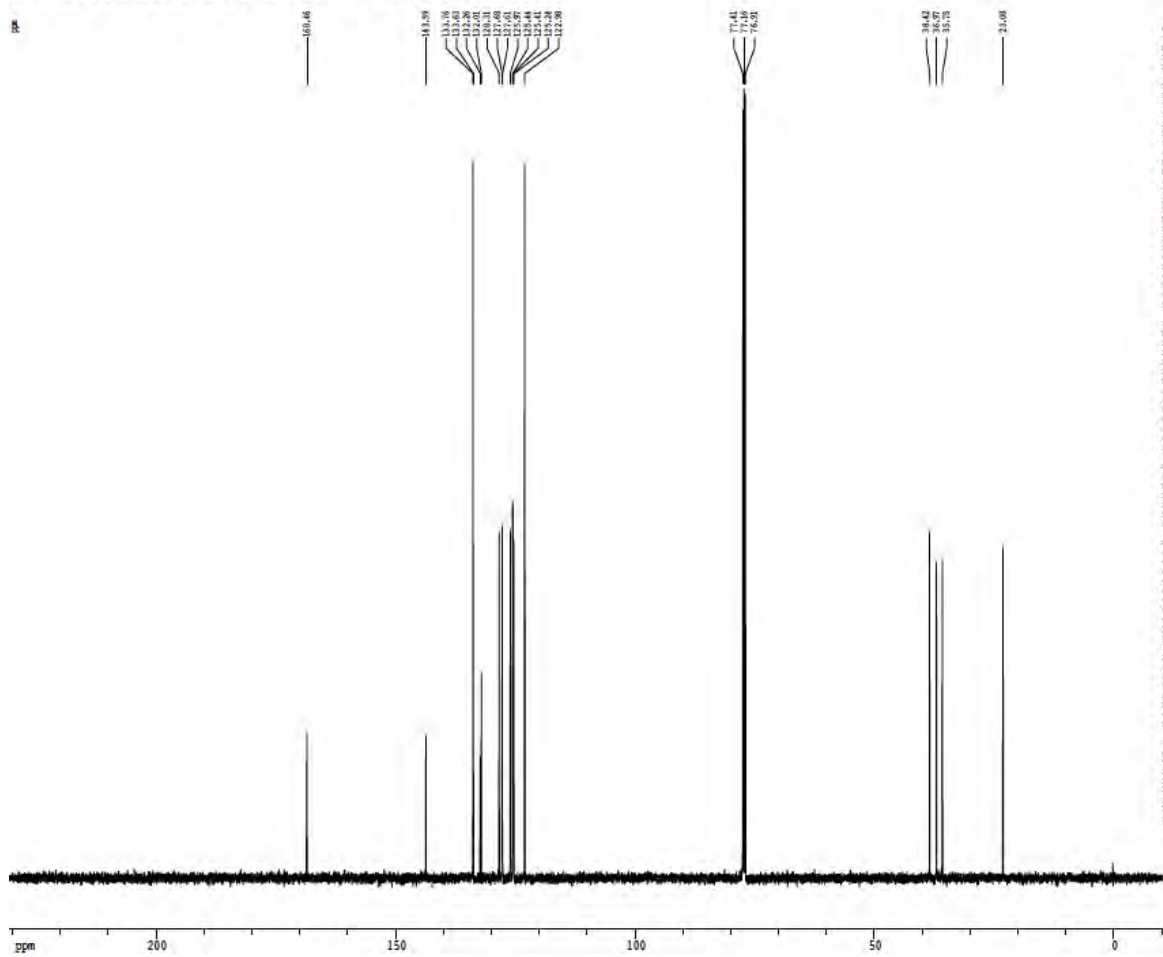


1H spectrum



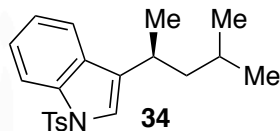
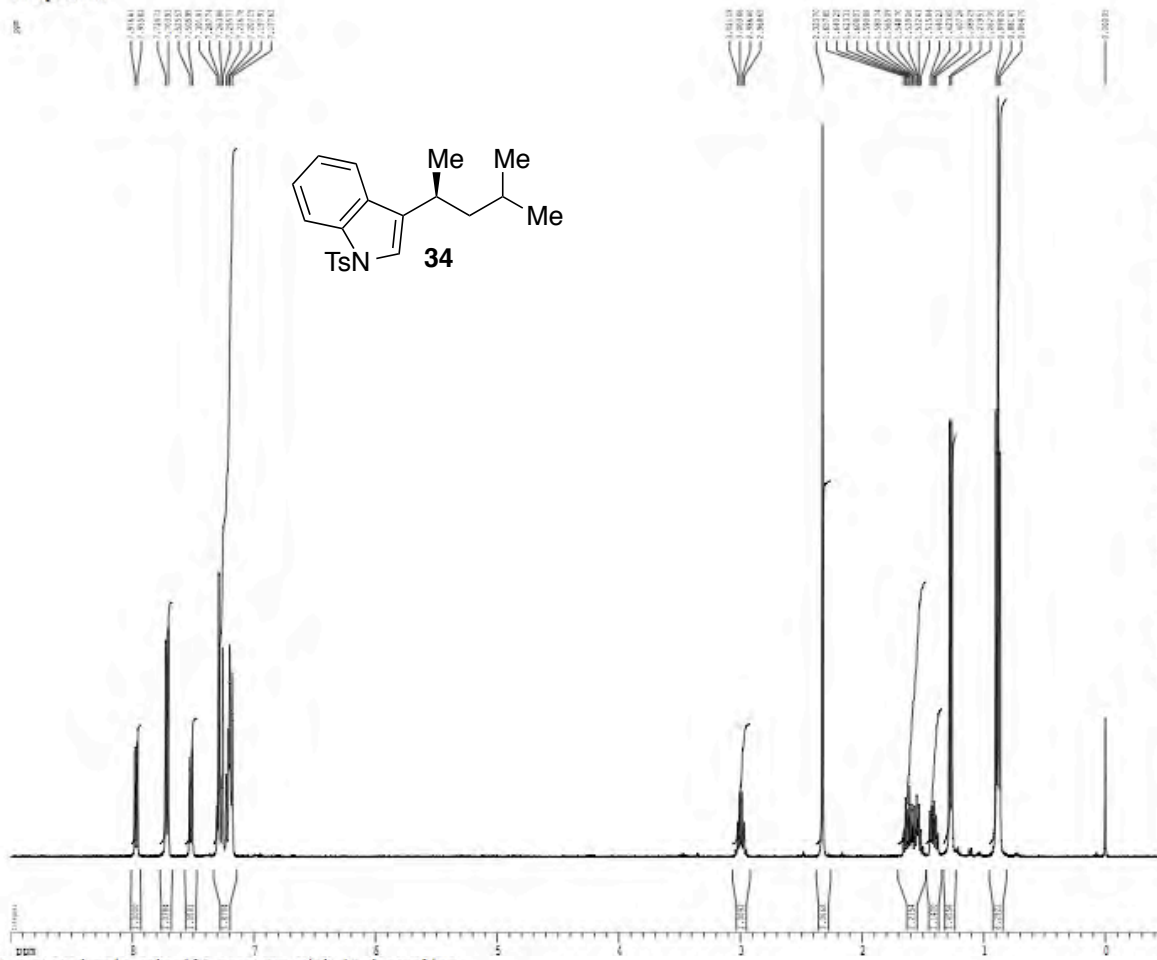
Current Data Parameters  
 EXP: 100000  
 NAME: 100000  
 PROCNO: 1  
 F1 - Acquisition Parameters  
 DATE\_: 20110111  
 TIME: 20.43  
 INSTRUM: spect  
 PULPROG: zgpg30  
 SFO: 500.135063 MHz  
 SOLVENT: CDCl3  
 NS: 8  
 DS: 4  
 SWH: 6420.256 Hz  
 FIDRES: 0.097813 Hz  
 AQ: 5.1118579 sec  
 RG: 406  
 WC: 78.800 USAC  
 WDE: 4.50 USAC  
 WFLD: 128.0 Hz  
 SFO2: 0.10000000 sec  
 WALTZ16: 0.0000000 sec  
 WALTZ2: 0.0000000 sec  
 WALTZ3: 0.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 12.00 USAC  
 PL1: -1.50 dB  
 SFO1: 400.1328063 MHz  
 F1 - Processing parameters  
 SI: 65536  
 SF: 400.1302224 MHz  
 F2: 0  
 SFO2: 0  
 WDE: 0.30 Hz  
 WFLD: 0  
 WALTZ16: 0  
 WALTZ2: 0  
 WALTZ3: 0  
 ===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 12.00 USAC  
 PL2: -1.50 dB  
 SFO2: 400.1464010 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 400.1464010 MHz  
 F2: 0  
 SFO2: 0  
 WDE: 0.30 Hz  
 WFLD: 0  
 WALTZ16: 0  
 WALTZ2: 0  
 WALTZ3: 0

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 EXP: 100000  
 NAME: 100000  
 PROCNO: 2  
 F1 - Acquisition Parameters  
 DATE\_: 20110111  
 TIME: 16.49  
 INSTRUM: spect  
 PULPROG: zgpg30  
 SFO: 500.135063 MHz  
 SOLVENT: CDCl3  
 NS: 8  
 DS: 4  
 SWH: 8203.031 MHz  
 FIDRES: 0.462388 MHz  
 AQ: 1.0812840 sec  
 RG: 500  
 WC: 14.500 USAC  
 WDE: 4.50 USAC  
 WFLD: 128.0 Hz  
 SFO2: 0.10000000 sec  
 WALTZ16: 0.0000000 sec  
 WALTZ2: 0.0000000 sec  
 WALTZ3: 0.0000000 sec  
 WALTZ4: 0.0000000 sec  
 WALTZ5: 0.0000000 sec  
 WALTZ6: 0.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 12.00 USAC  
 PL1: 500.00 USAC  
 SFO1: 500.135063 MHz  
 F1 - Processing parameters  
 SI: 65536  
 SF: 500.135063 MHz  
 F2: 0  
 SFO2: 0  
 WDE: 0.30 Hz  
 WFLD: 0  
 WALTZ16: 0  
 WALTZ2: 0  
 WALTZ3: 0  
 WALTZ4: 0  
 WALTZ5: 0  
 WALTZ6: 0  
 ===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 12.00 USAC  
 PL2: 500.00 USAC  
 SFO2: 500.1464010 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 500.1464010 MHz  
 F2: 0  
 SFO2: 0  
 WDE: 0.30 Hz  
 WFLD: 0  
 WALTZ16: 0  
 WALTZ2: 0  
 WALTZ3: 0  
 WALTZ4: 0  
 WALTZ5: 0  
 WALTZ6: 0

<sup>1</sup>H spectrum



```

===== CHANNEL F1 =====
NUC1 13C
P1 12.00 sec
PL1 -1.00 dB
SFO1 400.1510000 MHz

F2 - Processing parameters
SI 6554
SF 400.1510000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

===== CHANNEL F2 =====
NUC2 1H
P2 12.00 sec
PL2 -1.00 dB
SFO2 400.1510000 MHz

===== CHANNEL F3 =====
NUC3 13C
P3 12.00 sec
PL3 -1.00 dB
SFO3 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

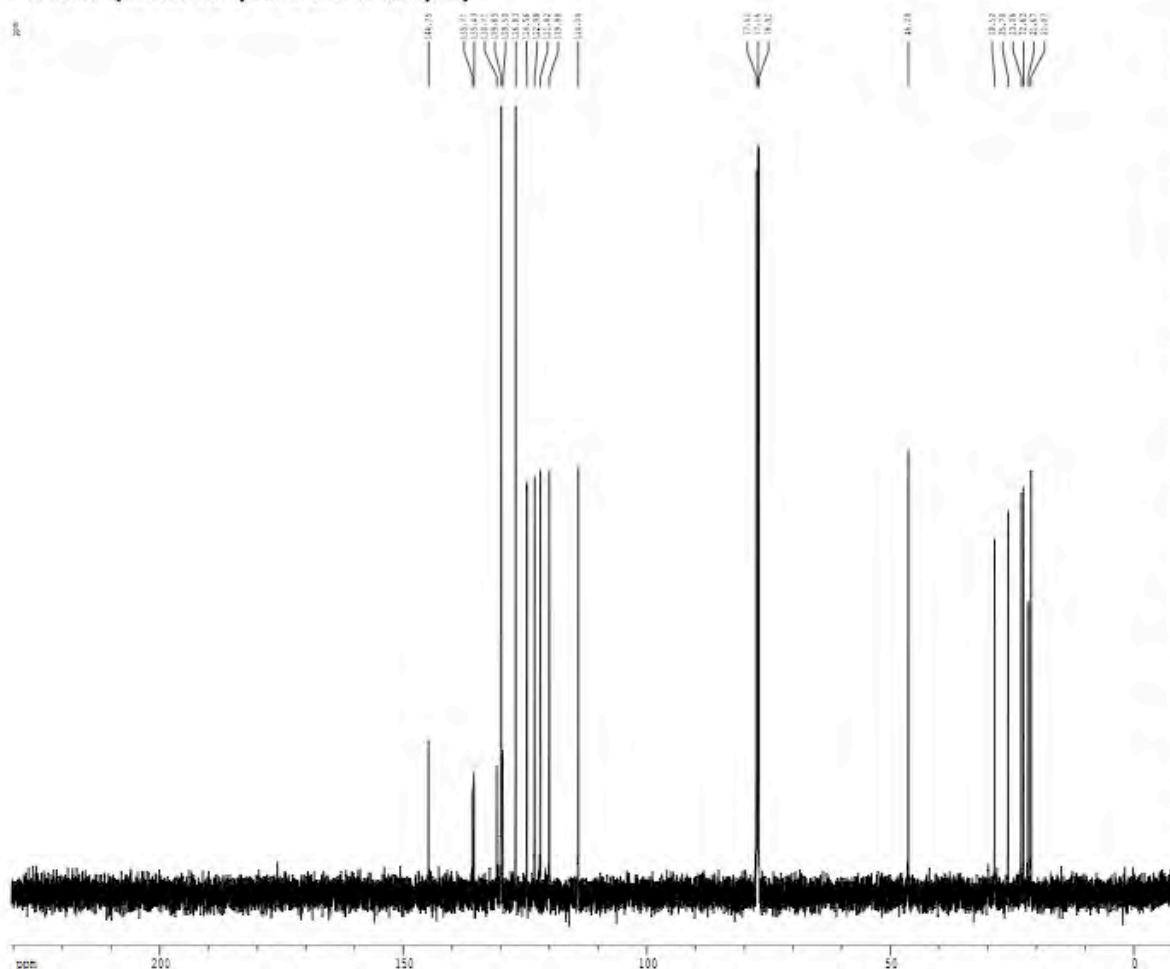
===== CHANNEL F4 =====
NUC4 1H
P4 12.00 sec
PL4 -1.00 dB
SFO4 400.1510000 MHz

===== CHANNEL F5 =====
NUC5 13C
P5 12.00 sec
PL5 -1.00 dB
SFO5 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

===== CHANNEL F6 =====
NUC6 1H
P6 12.00 sec
PL6 -1.00 dB
SFO6 400.1510000 MHz

===== CHANNEL F7 =====
NUC7 13C
P7 12.00 sec
PL7 -1.00 dB
SFO7 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00
    
```

Z-restored spin-echo <sup>13</sup>C spectrum with <sup>1</sup>H decoupling



```

===== CHANNEL F1 =====
NUC1 13C
P1 12.00 sec
PL1 -1.00 dB
SFO1 100.6275000 MHz

F2 - Processing parameters
SI 6554
SF 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

===== CHANNEL F2 =====
NUC2 1H
P2 12.00 sec
PL2 -1.00 dB
SFO2 400.1510000 MHz

===== CHANNEL F3 =====
NUC3 13C
P3 12.00 sec
PL3 -1.00 dB
SFO3 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

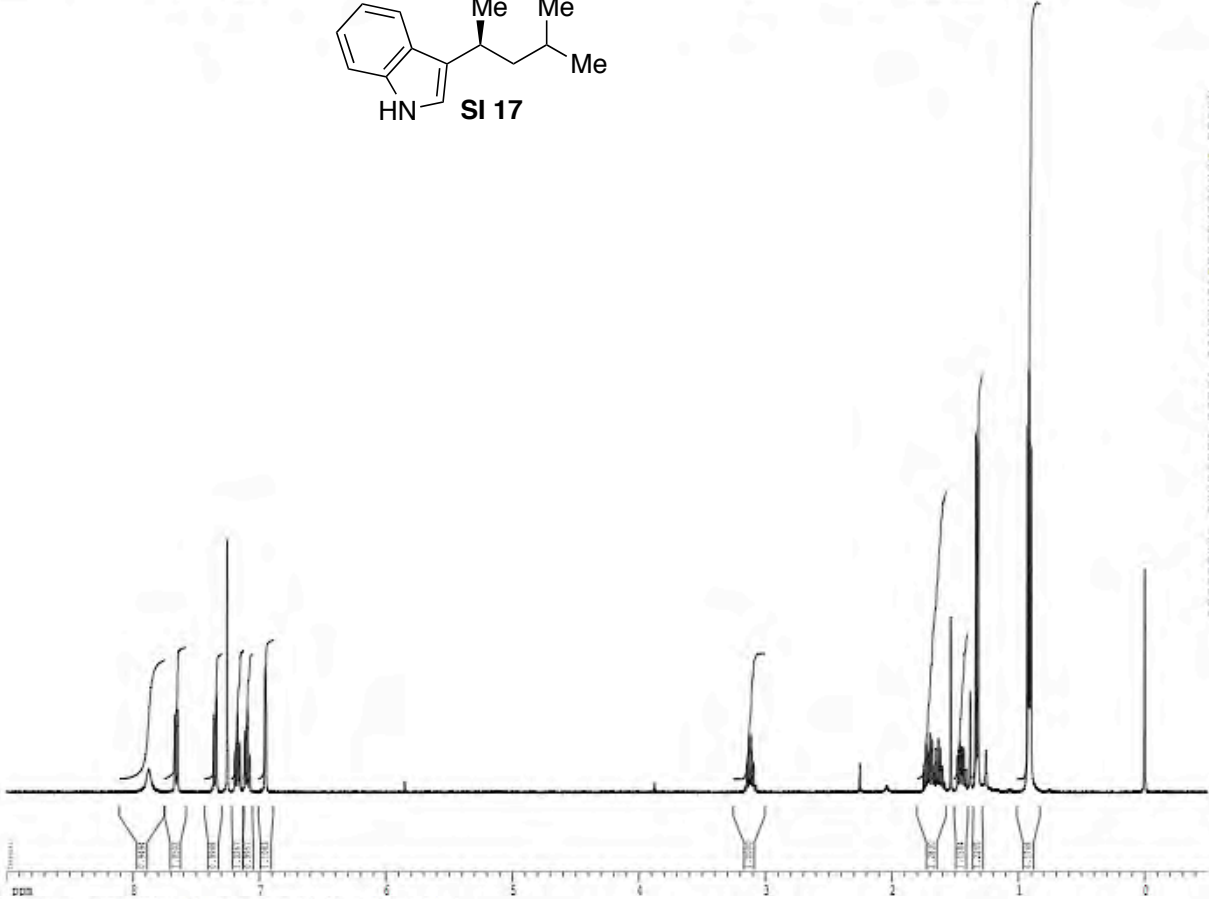
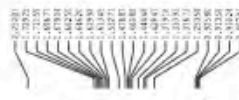
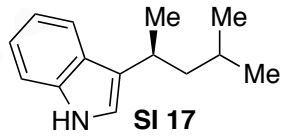
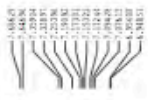
===== CHANNEL F4 =====
NUC4 1H
P4 12.00 sec
PL4 -1.00 dB
SFO4 400.1510000 MHz

===== CHANNEL F5 =====
NUC5 13C
P5 12.00 sec
PL5 -1.00 dB
SFO5 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00

===== CHANNEL F6 =====
NUC6 1H
P6 12.00 sec
PL6 -1.00 dB
SFO6 400.1510000 MHz

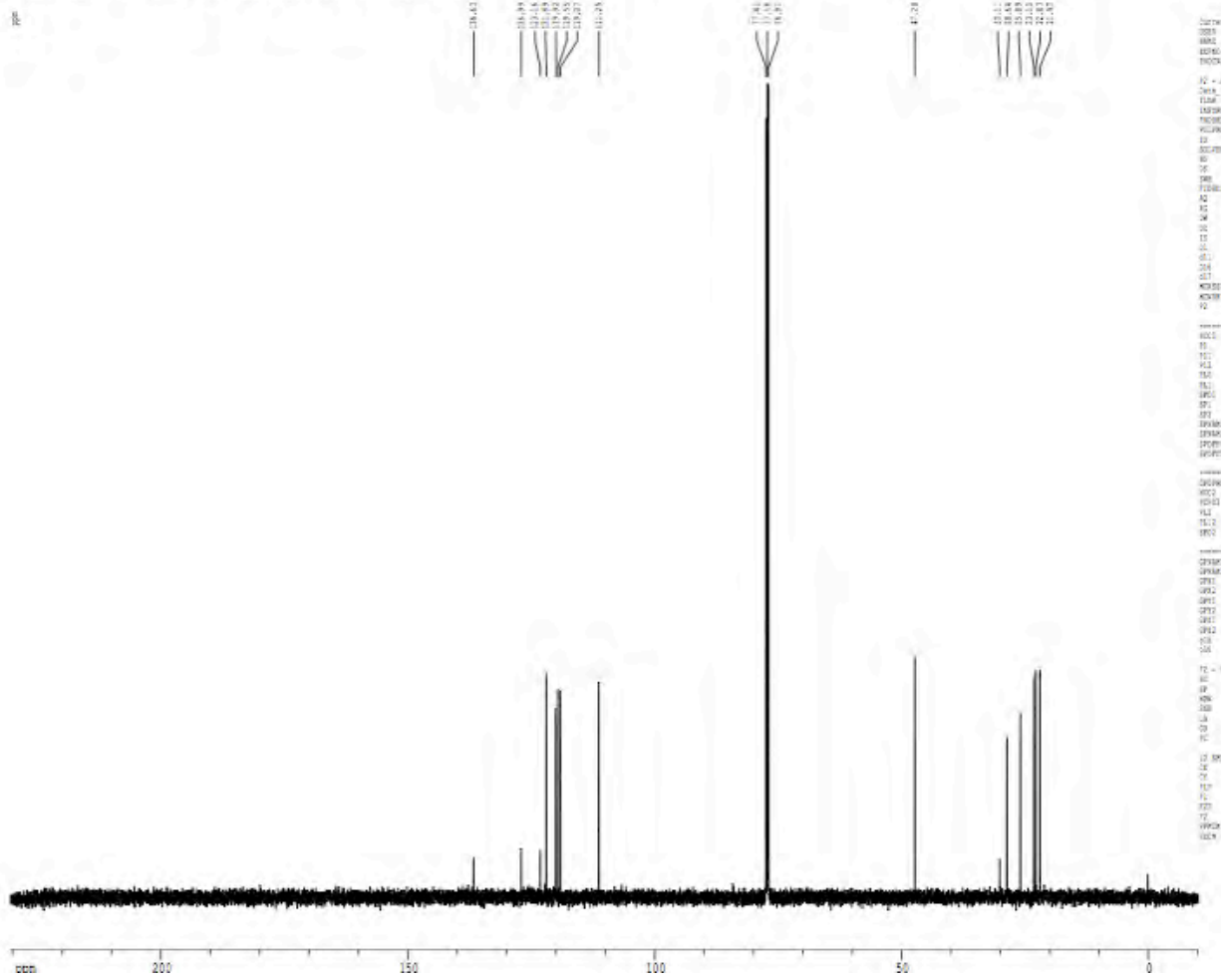
===== CHANNEL F7 =====
NUC7 13C
P7 12.00 sec
PL7 -1.00 dB
SFO7 100.6275000 MHz
WDW 50
SSB 0
GB 0.00 Hz
PC 2.00
    
```

1H spectrum



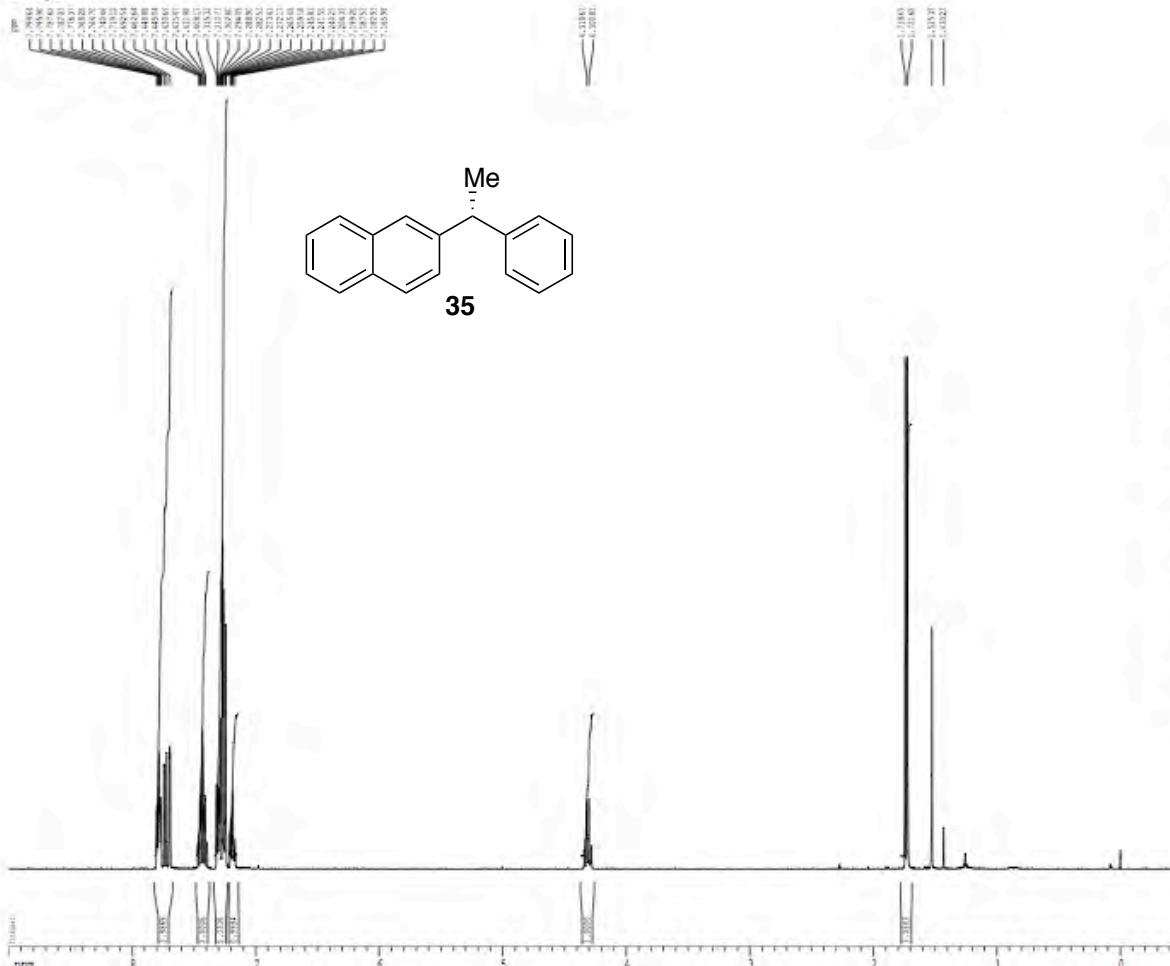
Current Data Parameters  
 Date\_ 06/15/09  
 Time 11:20:29  
 Name SI 17  
 INSTRUM spect  
 PROBR 300 MHz 1H  
 PULPROG zgpg30  
 TD 65536  
 SFO 300.1350618  
 F2 - Acquisition Parameters  
 Date\_ 06/15/09  
 Time 11:20:29  
 Name SI 17  
 INSTRUM spect  
 PROBR 300 MHz 1H  
 PULPROG zgpg30  
 TD 65536  
 SFO 300.1350618  
 F2 - Processing parameters  
 SI 17  
 F2 300.1350618 MHz  
 WVDW EM  
 GB 0  
 CB 0  
 CT 0  
 PC 3.00  
 F2 RM 1H NMR parameters  
 CH 12.00 use  
 CR 4.00 use  
 CP 4.00 ppm  
 FI 3601.37 Hz  
 FS 4.00 ppm  
 GPC 0  
 GRPC 0.41667 ppm/cycle  
 MCH 104.7266 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 Date\_ 06/15/09  
 Time 11:20:29  
 Name SI 17  
 INSTRUM spect  
 PROBR 300 MHz 1H  
 PULPROG zgpg30  
 TD 65536  
 SFO 300.1350618  
 F2 - Acquisition Parameters  
 Date\_ 06/15/09  
 Time 11:20:29  
 Name SI 17  
 INSTRUM spect  
 PROBR 300 MHz 1H  
 PULPROG zgpg30  
 TD 65536  
 SFO 300.1350618  
 F2 - Processing parameters  
 SI 17  
 F2 300.1350618 MHz  
 WVDW EM  
 GB 0  
 CB 0  
 CT 0  
 PC 3.00  
 F2 RM 13C NMR parameters  
 CH 12.00 use  
 CR 4.00 use  
 CP 4.00 ppm  
 FI 3601.37 Hz  
 FS 4.00 ppm  
 GPC 0  
 GRPC 0.41667 ppm/cycle  
 MCH 104.7266 Hz/cm

<sup>1</sup>H spectrum



```

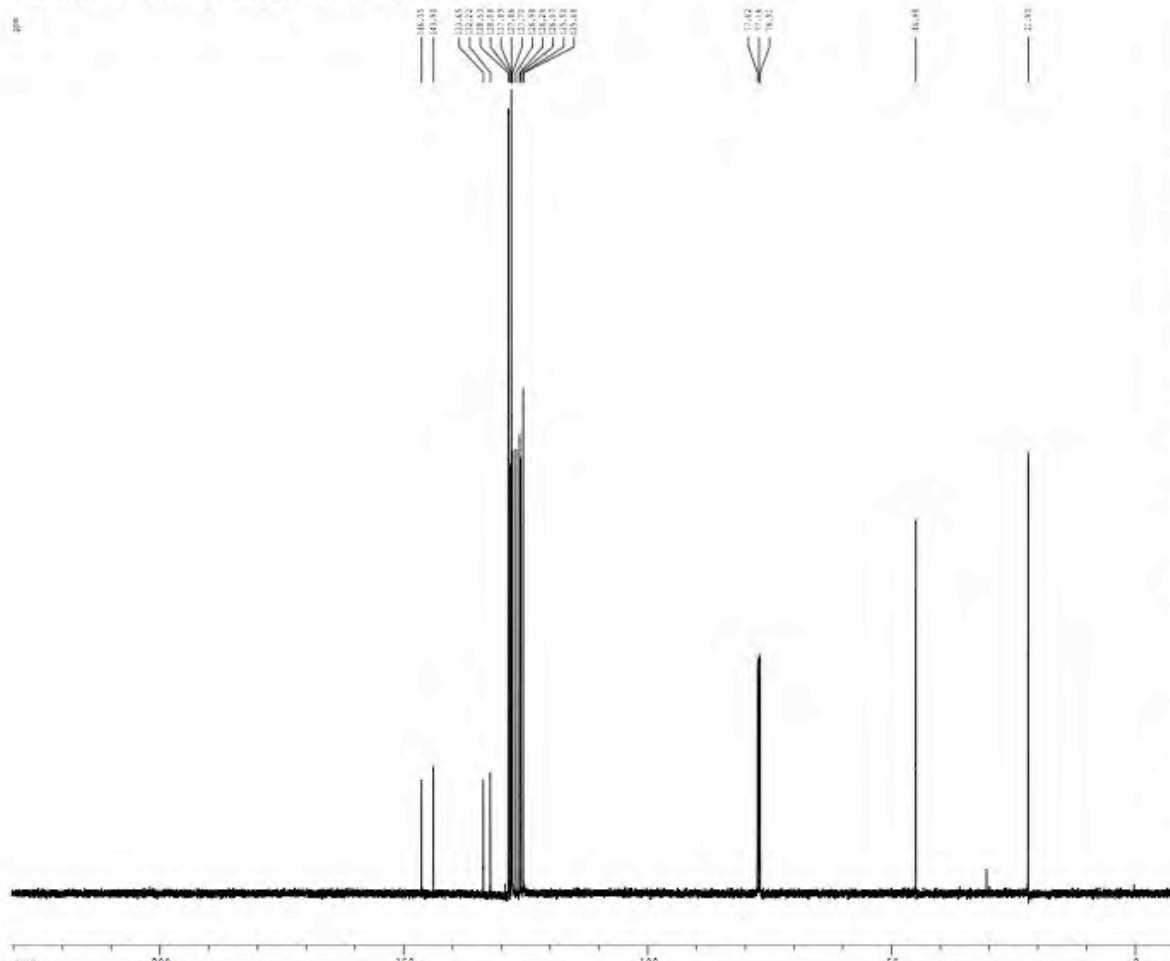
Current Data Parameters
=====
DATE      11.28.11
TIME      13.34
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PCPROG   zgpg30
TE       300.2
SOLVENT  CDCl3
NS       2
DS       4
SWH      640.2380 Hz
FIDRES   0.592313 Hz
AQ       0.111978 sec
RG       387.4
GB       0
GB2      18.000000 Hz
GB3      1.500000 Hz
GB4      236.000000 Hz
NUC1     13C
NUC2     13C
NUC3     13C
AQ3D     0.00000000 sec
AQ3D2    0.00000000 sec
AQ3D3    0.00000000 sec

===== CHANNEL F1 =====
NUC1     13C
P1       12.00 dB
PL1      -1.50 dB
SFO1     125.761444 MHz

===== CHANNEL F2 =====
NUC2     13C
P2       12.00 dB
PL2      -1.50 dB
SFO2     125.761444 MHz

===== CHANNEL F3 =====
NUC3     13C
P3       12.00 dB
PL3      -1.50 dB
SFO3     125.761444 MHz
  
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```

Current Data Parameters
=====
DATE      11.28.11
TIME      13.34
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
PCPROG   zgpg30
TE       300.2
SOLVENT  CDCl3
NS       2
DS       4
SWH      640.2380 Hz
FIDRES   0.592313 Hz
AQ       0.111978 sec
RG       387.4
GB       0
GB2      18.000000 Hz
GB3      1.500000 Hz
GB4      236.000000 Hz
NUC1     13C
NUC2     13C
NUC3     13C
AQ3D     0.00000000 sec
AQ3D2    0.00000000 sec
AQ3D3    0.00000000 sec

===== CHANNEL F1 =====
NUC1     13C
P1       12.00 dB
PL1      -1.50 dB
SFO1     125.761444 MHz

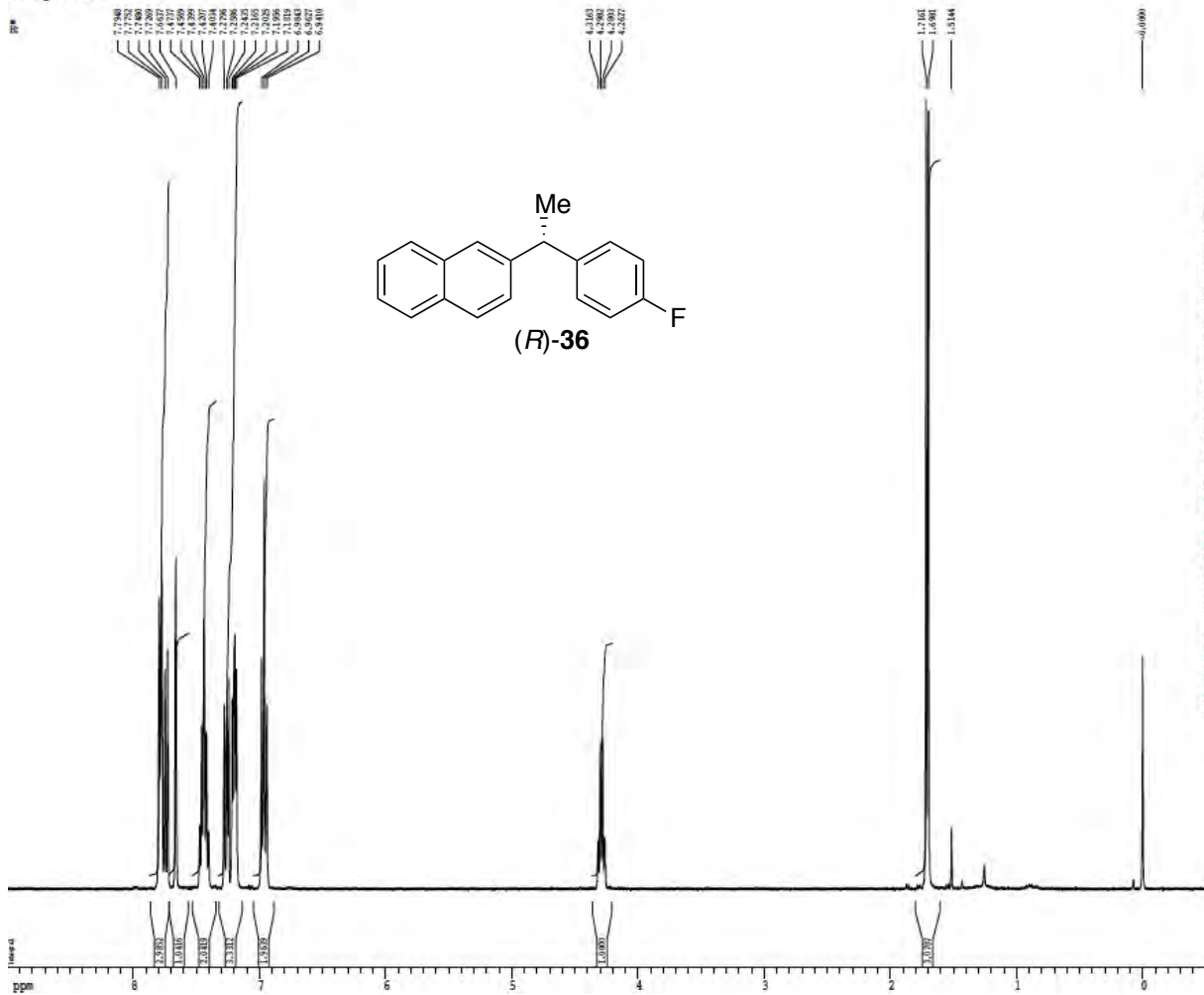
===== CHANNEL F2 =====
NUC2     13C
P2       12.00 dB
PL2      -1.50 dB
SFO2     125.761444 MHz

===== CHANNEL F3 =====
NUC3     13C
P3       12.00 dB
PL3      -1.50 dB
SFO3     125.761444 MHz

===== CHANNEL F4 =====
NUC4     13C
P4       12.00 dB
PL4      -1.50 dB
SFO4     125.761444 MHz
  
```

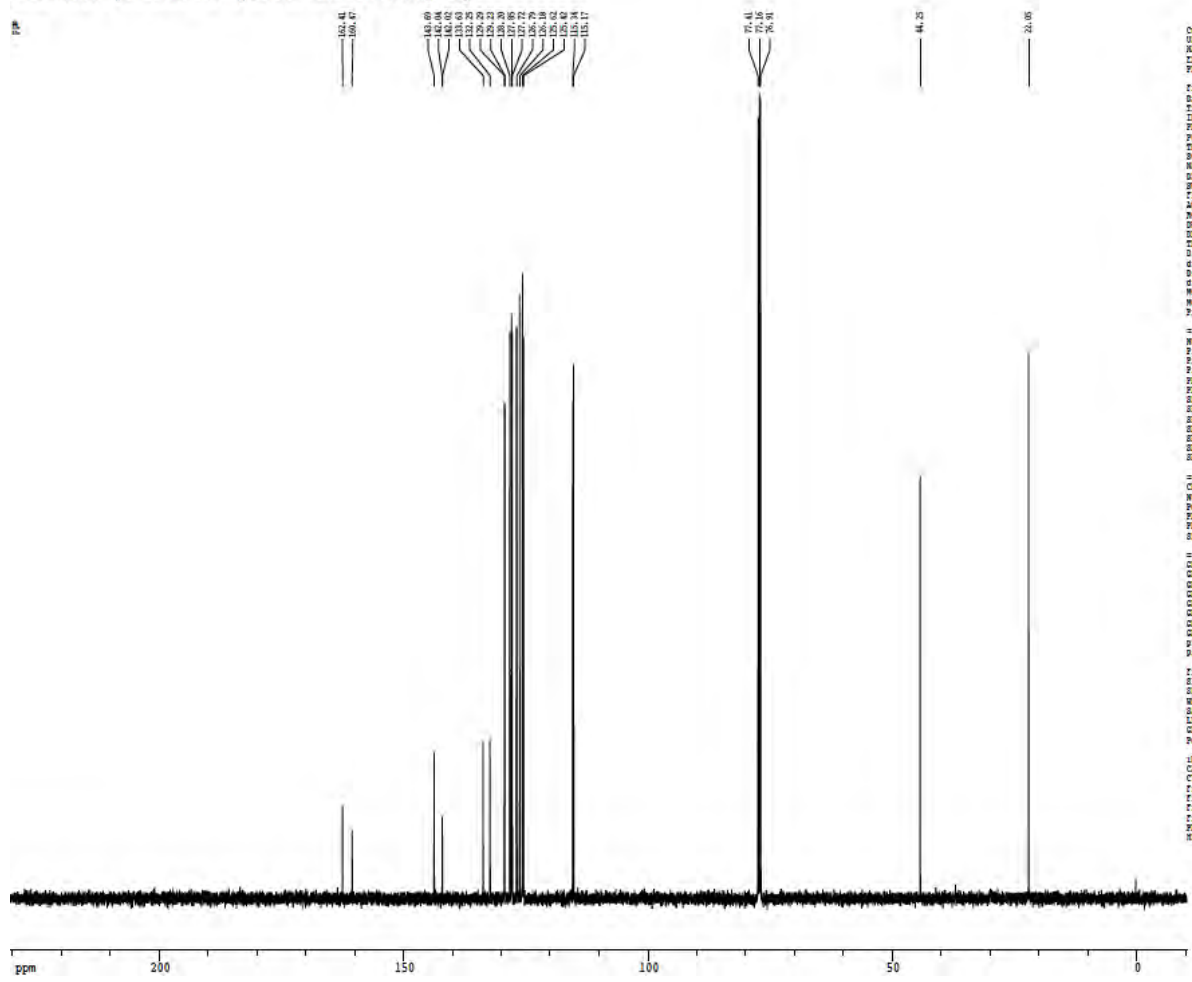


1H spectrum



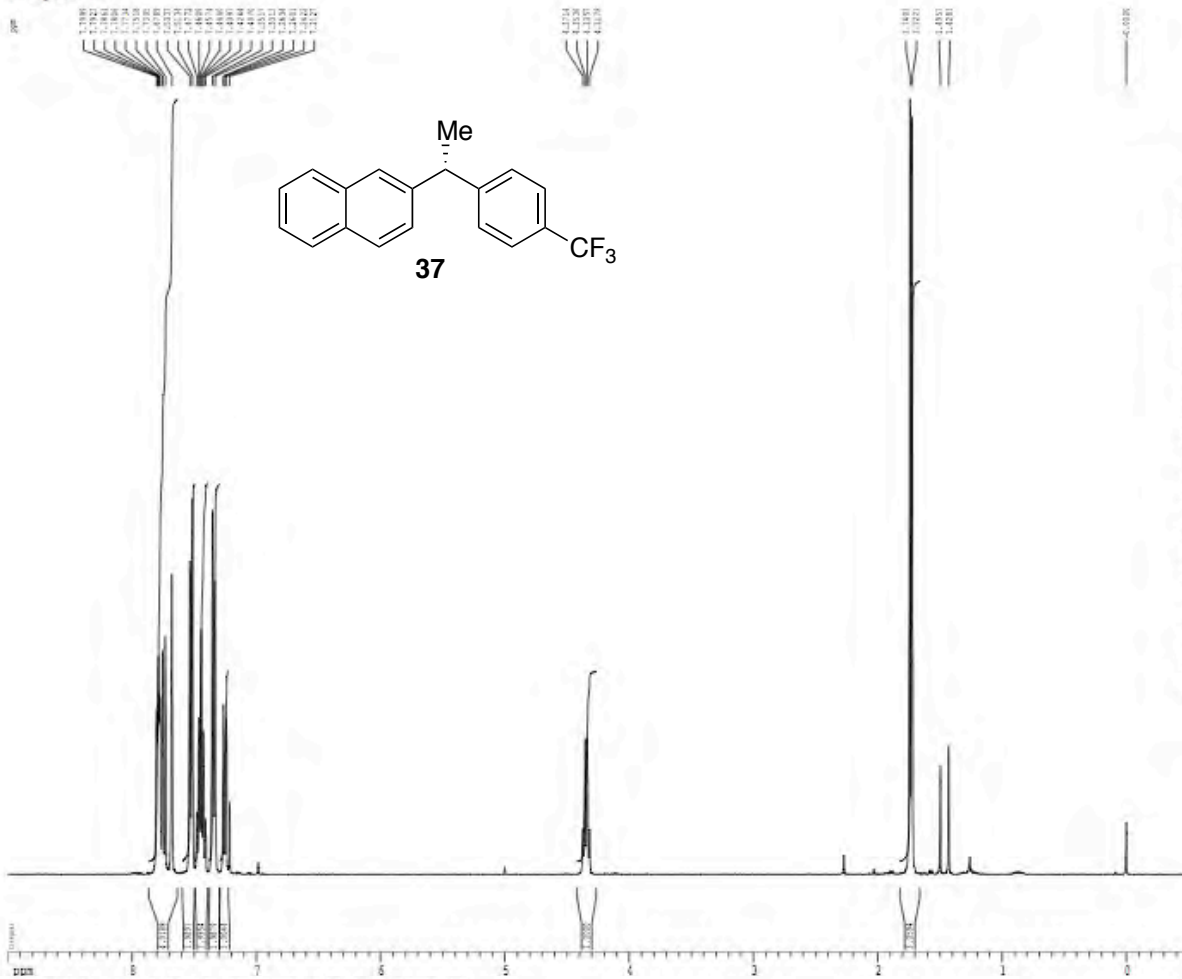
Current Data Parameters  
USER smilfz  
NAME es-4-212a-1  
EXPNO 1  
PROCNO 1  
  
F1 - Acquisition Parameters  
Date\_ 20130218  
Time 16.26  
INSTRUM cpmask  
PROBHD 5 mm QNP 1H/1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
AQ 8  
RG 3  
SFO 6416.254 Hz  
FIDRES 0.097813 Hz  
AQ 5.111870 sec  
RG 256  
SWH 78.000 Usec  
SE 4.50 Usec  
TE 298.0 K  
SFO 6.0000000 sec  
MCKEY 0.0000000 sec  
MCKEY 0.0150000 sec  
  
===== CHANNEL f1 =====  
NUC1 13  
P1 12.00 Usec  
PL1 -0.00 dB  
SFO1 400.1328009 MHz  
  
F2 - Processing parameters  
SI 65536  
SF 400.136271 MHz  
WDW no  
SSB no  
LB 0.00 Hz  
GB 0  
PC 2.00  
  
1D NMR plot parameters  
CH 22.80 cm  
CI 15.00 cm  
FID 9.000 ppm  
F2 3651.17 Hz  
F2F -0.500 ppm  
F3 -100.00 Hz  
F3CH 0.4162 ppm/cm  
NUC1 164.72084 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



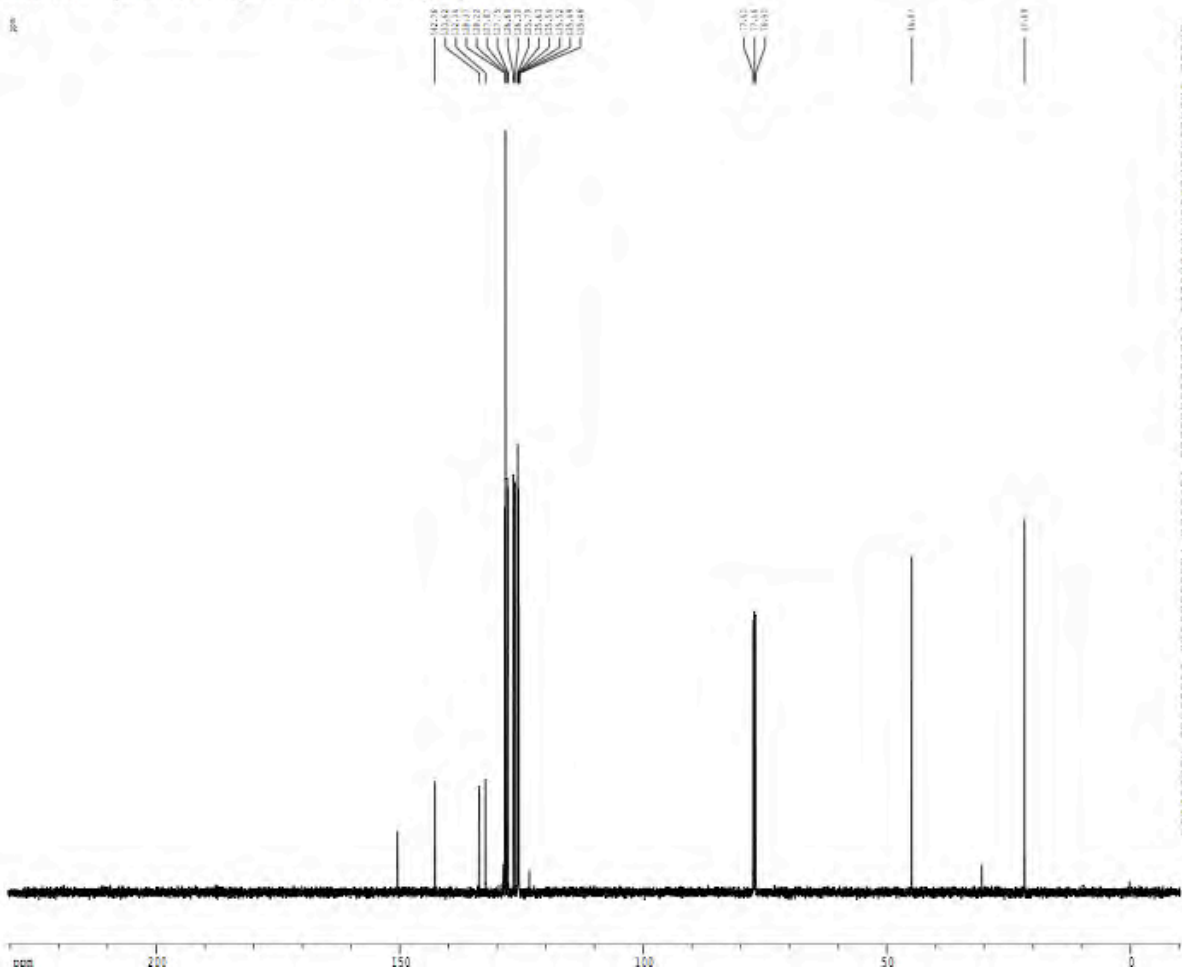
Current Data Parameters  
USER smilfz  
NAME es-4-212a-1  
EXPNO 1  
PROCNO 1  
  
F1 - Acquisition Parameters  
Date\_ 20130218  
Time 22.39  
INSTRUM cpmask  
PROBHD 5 mm QNP 1H  
PULPROG spinlock  
TD 65536  
SOLVENT CDCl3  
AQ 4.42  
RG 14  
SFO 300.0131 MHz  
FIDRES 0.462048 Hz  
AQ 1.0812848 sec  
RG 698  
SW 14.994 Usec  
SE 6.00 Usec  
TE 298.0 K  
SFO 0.2500000 sec  
SFO 0.2500000 sec  
SFO 0.0000000 sec  
SFO 0.0000000 sec  
SFO 0.0000000 sec  
MCKEY 0.0000000 sec  
MCKEY 0.0150000 sec  
MCKEY 0.0150000 sec  
F2 51.00 Usec  
  
===== CHANNEL f1 =====  
NUC1 13C  
P1 15.00 Usec  
PL1 0.00 dB  
SFO1 125.760349 MHz  
SFO2 125.7642348 MHz  
SFO3 3.20 MHz  
SFO4 1.20 MHz  
SFO5 Cmpd 6.5.20.1  
SFO6 Cmpd 6.4  
SFO7 0.00 Hz  
SFO8 0.00 Hz  
  
===== CHANNEL f2 =====  
NUC1 waltz16  
P1 15.00 Usec  
PL1 0.00 dB  
SFO1 24.49 MHz  
SFO2 90.000000 MHz  
  
===== QUANTIFY CHANNEL =====  
CPDPRG1 SINE 100  
CPDPRG2 SINE 100  
CPD1 0.00 %  
CPD2 0.00 %  
CPD3 0.00 %  
CPD4 0.00 %  
CPD5 50.00 %  
CPD6 50.00 %  
SFO 900.00 Usec  
SFO 1000.00 Usec  
  
F2 - Processing parameters  
SI 65536  
SF 125.7640348 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 2.00  
  
1D NMR plot parameters  
CH 22.80 cm  
CI 15.00 cm  
FID 9.000 ppm  
F2 36009.86 Hz  
F2F -0.500 ppm  
F3 -100.00 Hz  
F3CH 0.4162 ppm/cm  
NUC1 125.7640348 Hz/cm

1H spectrum



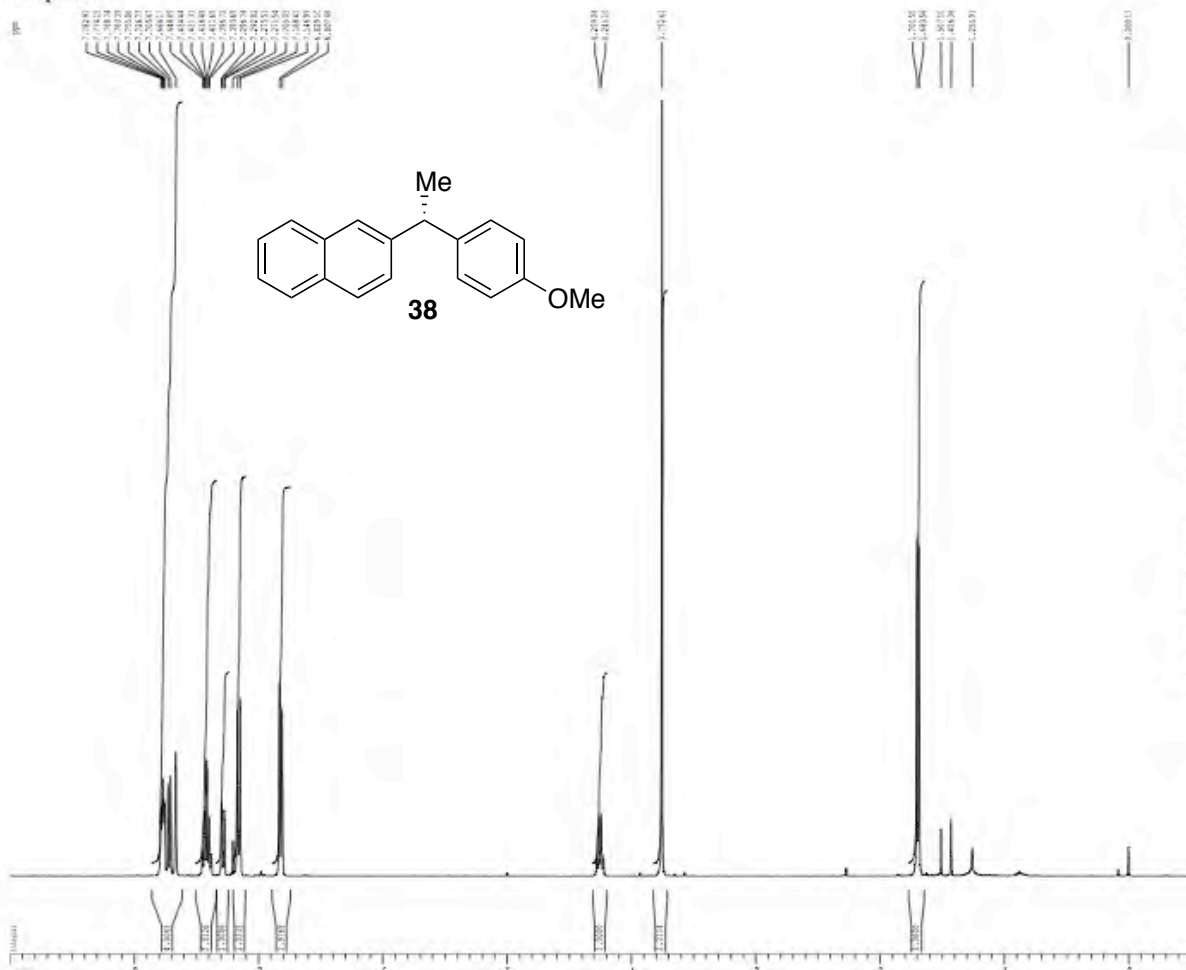
Current Data Parameters  
Date: 20120501  
Time: 14:11  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
TD: 65536  
AQ: 0.231  
RG: 3  
SD: 0  
SI: 1  
OR: 0  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - Acquisition Parameters  
Date: 20120501  
Time: 14:11  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
TD: 65536  
AQ: 0.231  
RG: 3  
SD: 0  
SI: 1  
OR: 0  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - Processing parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - NMR plot parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - NMR plot parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
Date: 20120501  
Time: 14:11  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
TD: 65536  
AQ: 0.231  
RG: 3  
SD: 0  
SI: 1  
OR: 0  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - Acquisition Parameters  
Date: 20120501  
Time: 14:11  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
TD: 65536  
AQ: 0.231  
RG: 3  
SD: 0  
SI: 1  
OR: 0  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - Processing parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - NMR plot parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00  
F2 - NMR plot parameters  
SI: 65536  
SF: 400.146400 MHz  
WDW: EM  
SSB: 0  
LB: 3.00 Hz  
GB: 0  
PC: 2.00

1H spectrum



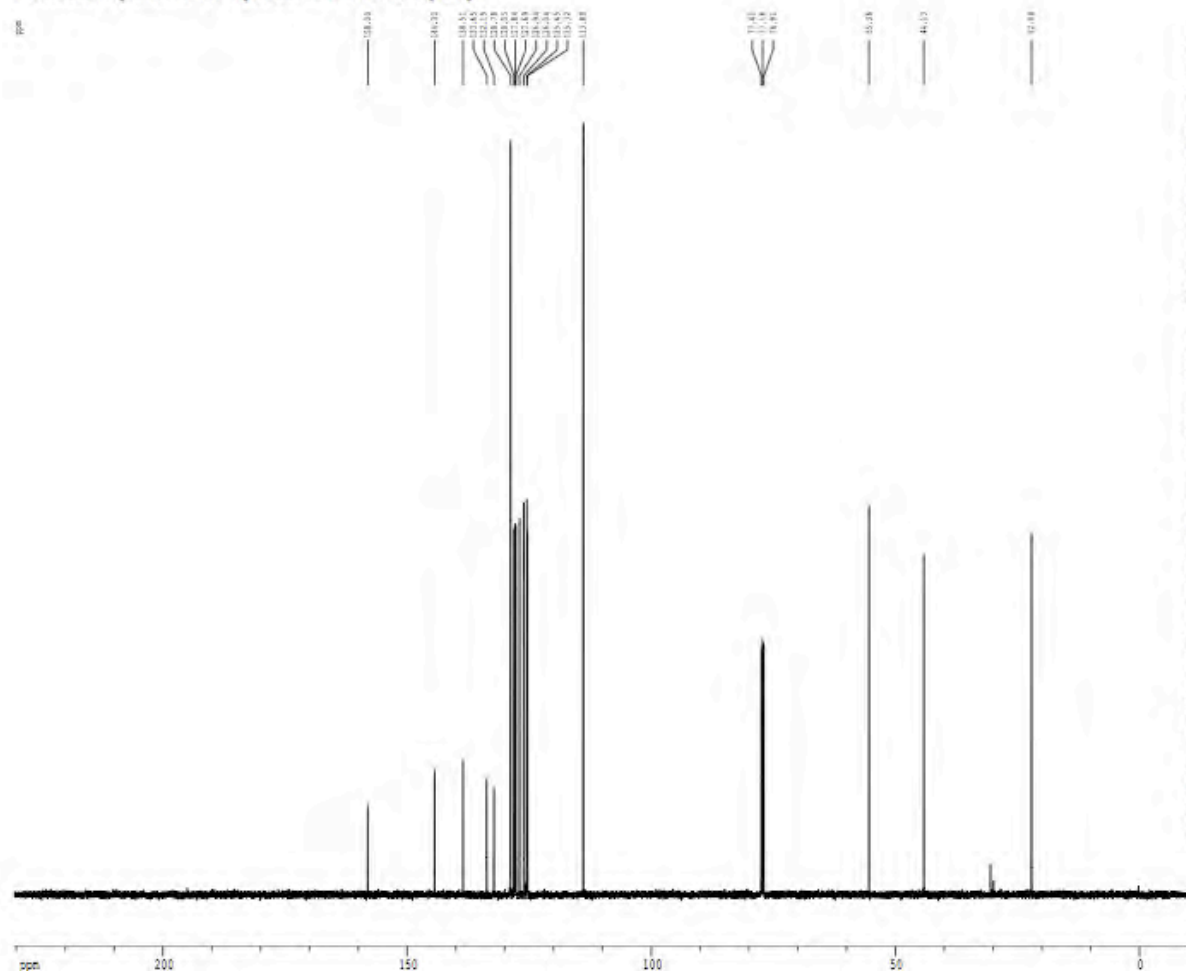
Current Data Parameters  
Date 201114  
Time 14:14  
EXPNO 1  
PROCNO 1  
PROCPS 1  
SOLVENT H<sub>2</sub>O  
NS 4  
DS 2  
SWH 9415.254 Hz  
FIDRES 0.597811 Hz  
AQ 3.113879 sec  
RG 64.3  
GB 0  
PC 19.010 sec  
TE 300.2 K  
TD 65536  
SFO 400.1460000 MHz  
WDW 0.0000000 sec  
SSB 0.0000000 sec  
LB 0.0000000 Hz

===== CHANNEL f1 =====  
NUC1 13C  
P1 15.00 usec  
PL 0.00 dB  
SFO1 101.6258000 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1460000 MHz  
WDW 0  
SSB 0  
LB 0.500 Hz  
GB 0  
PC 1.00

F3 900 MHz pilot parameters  
SI 32768  
SF 900.1460000 MHz  
WDW 0  
SSB 0  
LB 0.500 Hz  
GB 0  
PC 1.00

Z-restored spin-echo 13C spectrum with 1H decoupling



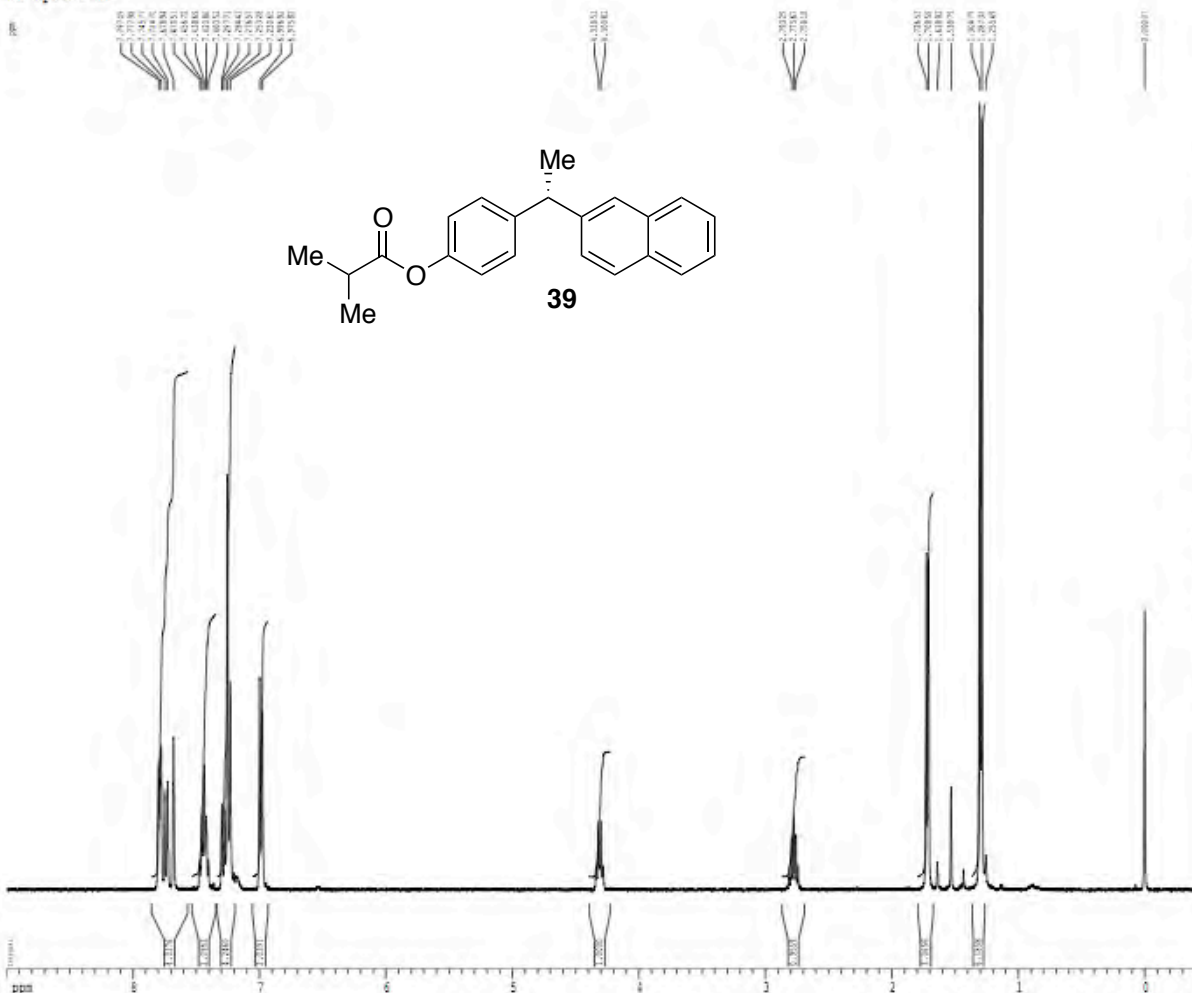
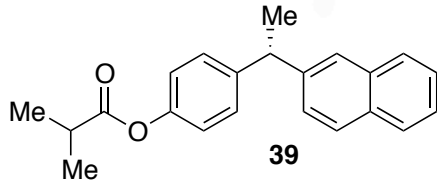
Current Data Parameters  
Date 201114  
Time 14:14  
EXPNO 1  
PROCNO 1  
PROCPS 1  
SOLVENT H<sub>2</sub>O  
NS 4  
DS 2  
SWH 9415.254 Hz  
FIDRES 0.597811 Hz  
AQ 3.113879 sec  
RG 64.3  
GB 0  
PC 19.010 sec  
TE 300.2 K  
TD 65536  
SFO 400.1460000 MHz  
WDW 0.0000000 sec  
SSB 0.0000000 sec  
LB 0.0000000 Hz

===== CHANNEL f1 =====  
NUC1 13C  
P1 15.00 usec  
PL 0.00 dB  
SFO1 101.6258000 MHz

F2 - Processing parameters  
SI 32768  
SF 400.1460000 MHz  
WDW 0  
SSB 0  
LB 0.500 Hz  
GB 0  
PC 1.00

F3 900 MHz pilot parameters  
SI 32768  
SF 900.1460000 MHz  
WDW 0  
SSB 0  
LB 0.500 Hz  
GB 0  
PC 1.00

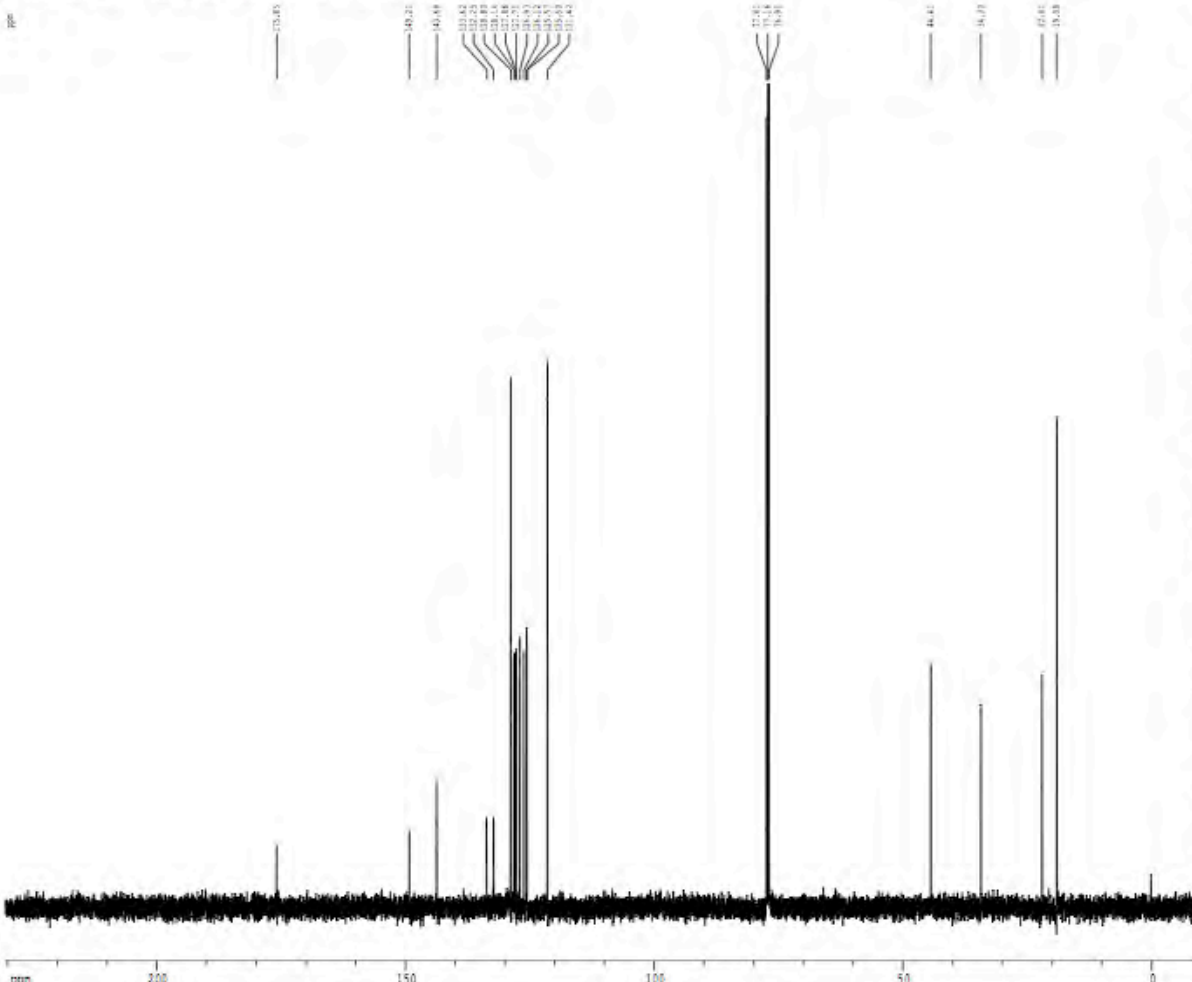
1H spectrum



```

Current Data Parameters
=====
Date_   11/11/07
Time    10:55
INSTRUM spect
PROBHD  1 mm QNP 1H/1
PULPROG zgpg30
TD       65536
SOLVENT  DMSO-d6
NS       4
DS       4
SWH      3410.254 Hz
FIDRES   0.247113 Hz
AQ       0.114879 sec
RG       142
SQ       19.800 useq
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== CHANNEL f2 =====
NUC1     13C
P1       12.00 useq
PC1      15.00 useq
SFO      101.625374 MHz
===== CHANNEL f1 =====
NUC2     1H
P2       12.00 useq
PC2      15.00 useq
SFO      400.1464078 MHz
===== Processing parameters =====
SI       65536
SF       400.1464078 MHz
AQ       0.114879 sec
RG       142
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== 13C NMR plot parameters =====
SI       65536
SF       101.625 MHz
RG       142
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== 13C NMR chemical shifts =====
129.403
148.21
149.49
112.82
118.89
117.18
117.25
116.72
116.57
116.57
117.42
17.42
16.94
44.41
16.77
45.41
15.38
    
```

Z-restored spin-echo 13C spectrum with 1H decoupling

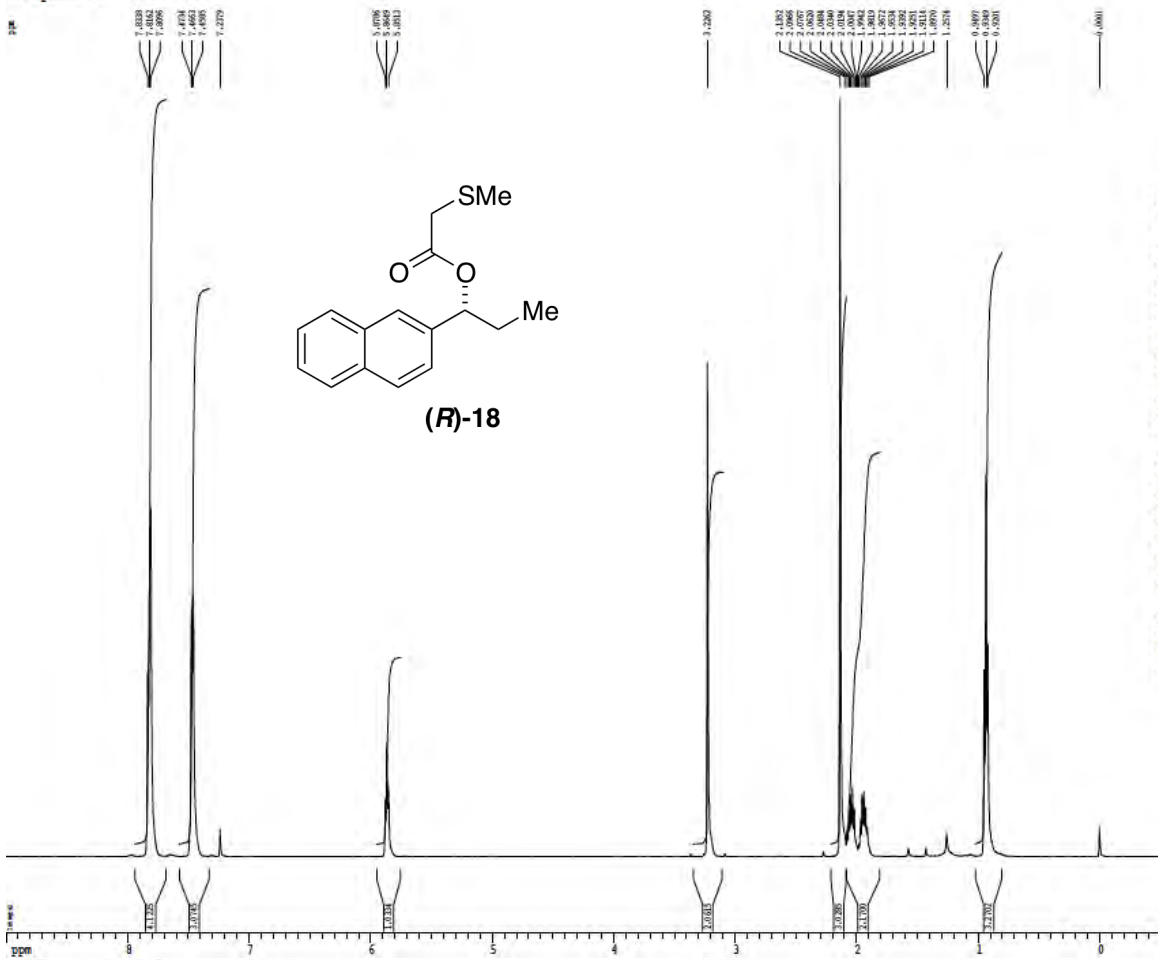


```

Current Data Parameters
=====
Date_   11/11/07
Time    10:55
INSTRUM spect
PROBHD  1 mm QNP 1H/1
PULPROG zgpg30
TD       65536
SOLVENT  DMSO-d6
NS       4
DS       4
SWH      3410.254 Hz
FIDRES   0.247113 Hz
AQ       0.114879 sec
RG       142
SQ       19.800 useq
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== CHANNEL f2 =====
NUC1     13C
P1       12.00 useq
PC1      15.00 useq
SFO      101.625374 MHz
===== CHANNEL f1 =====
NUC2     1H
P2       12.00 useq
PC2      15.00 useq
SFO      400.1464078 MHz
===== Processing parameters =====
SI       65536
SF       400.1464078 MHz
AQ       0.114879 sec
RG       142
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== 13C NMR plot parameters =====
SI       65536
SF       101.625 MHz
RG       142
WDW      EM
SSB       0.000000 sec
LB       200.1 Hz
GB       0.000000 sec
PC       0.200000 sec
===== 13C NMR chemical shifts =====
174.42
169.44
149.49
112.82
118.89
117.18
117.25
116.72
116.57
116.57
117.42
17.42
16.94
44.41
16.77
45.41
15.38
    
```



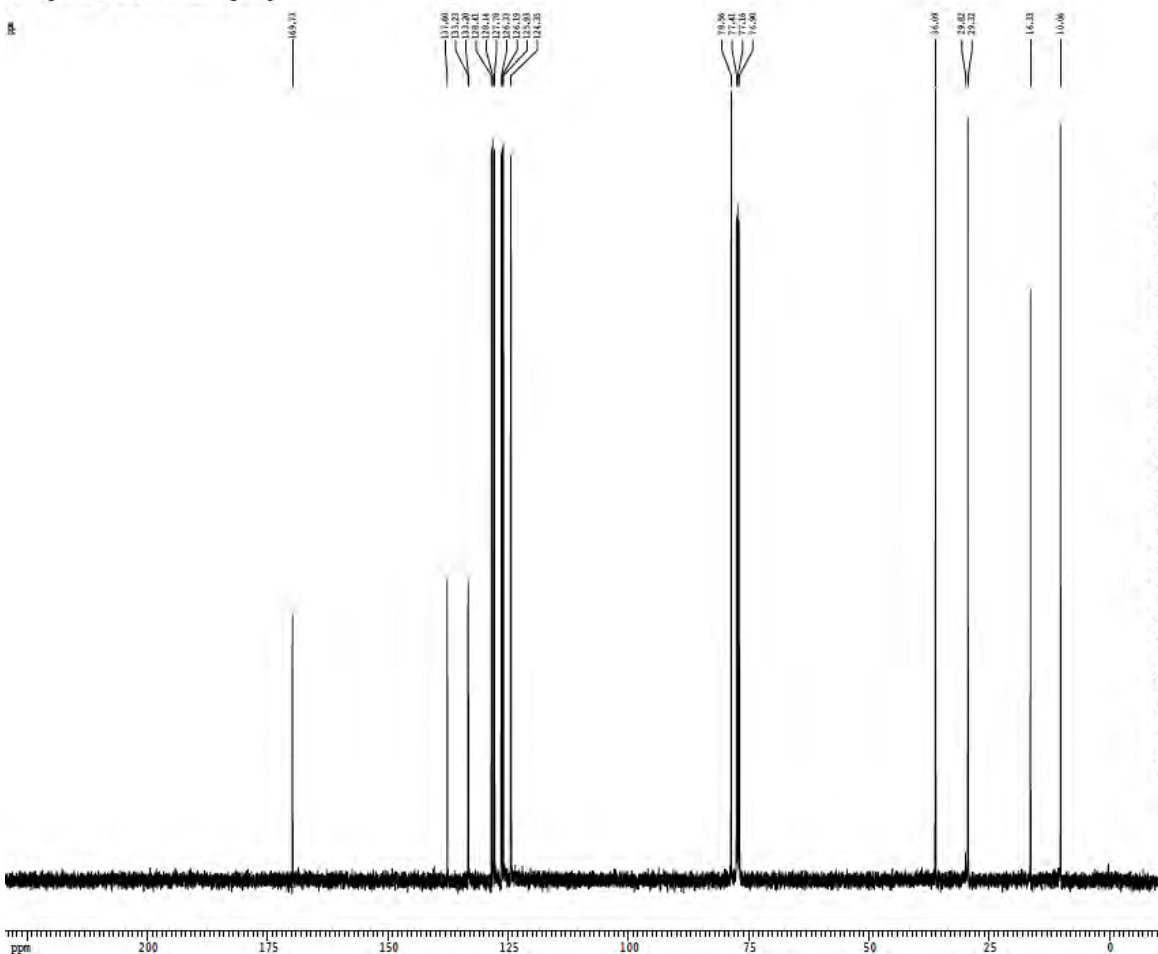
1H spectrum



```

Current Data Parameters
=====
NAME      Varose
EXPNO    1
PROCNO    1
F1 - Acquisition Parameters
Date_     201111
Time      21.29
INSTRUM   spect
PROBHD    5 mm broadband
PULPROG   zgpg30
RG         655.00
SOLVENT   CDCl3
NS         603
DS         4
SWH        8012.821 Hz
FIDRES     0.298642 Hz
AQ         5.998074 sec
RG         60.00
AQ         61.400 usec
RG         6.00 usec
RG         256.00
AQ         0.1000000 sec
RG         0.0000000 sec
RG         0.0100000 sec
===== CHANNEL f1 =====
NUC1      1H
P1         12.00 usec
PL1        -1.50 dB
SFO1      499.4024958 MHz
F1 - Processing parameters
SI         65534
SF         499.4024958 MHz
WDW        EM
SSB        0
GB         0
PC         0.10 Hz
PC         1.00
===== 1D NMR plot parameters
SI         65534
SF         499.4024958 MHz
WDW        EM
SSB        0
GB         0
PC         0.10 Hz
PC         1.00
=====
CT         22.00 cm
CT         15.00 cm
TIP        9.000 ppm
F1         4834.00 Hz
F2         -1.980 ppm
F3         -249.70 Hz
F4         4.4161 ppm/cm
F5CM       208.88326 Hz/cm
    
```

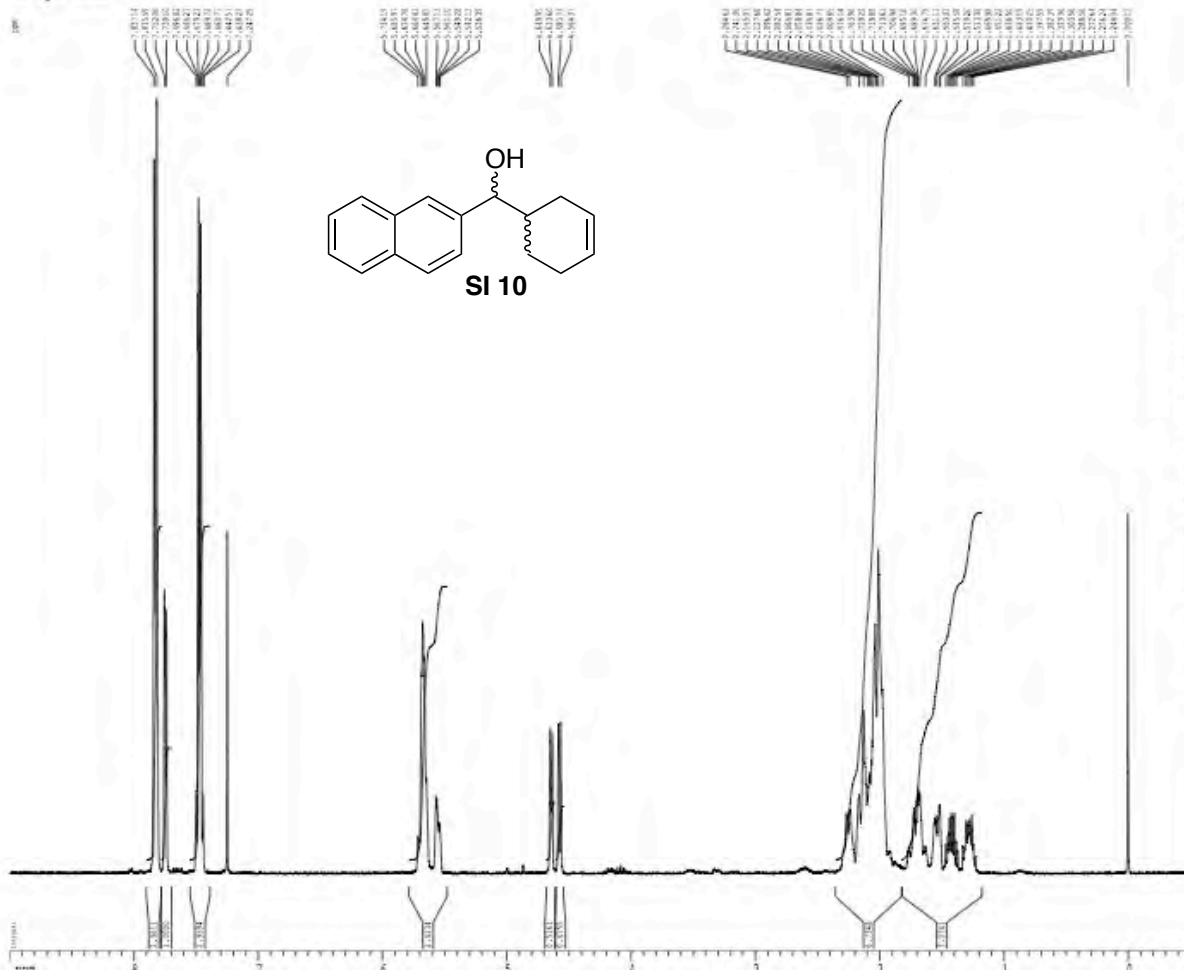
13C spectrum with 1H decoupling



```

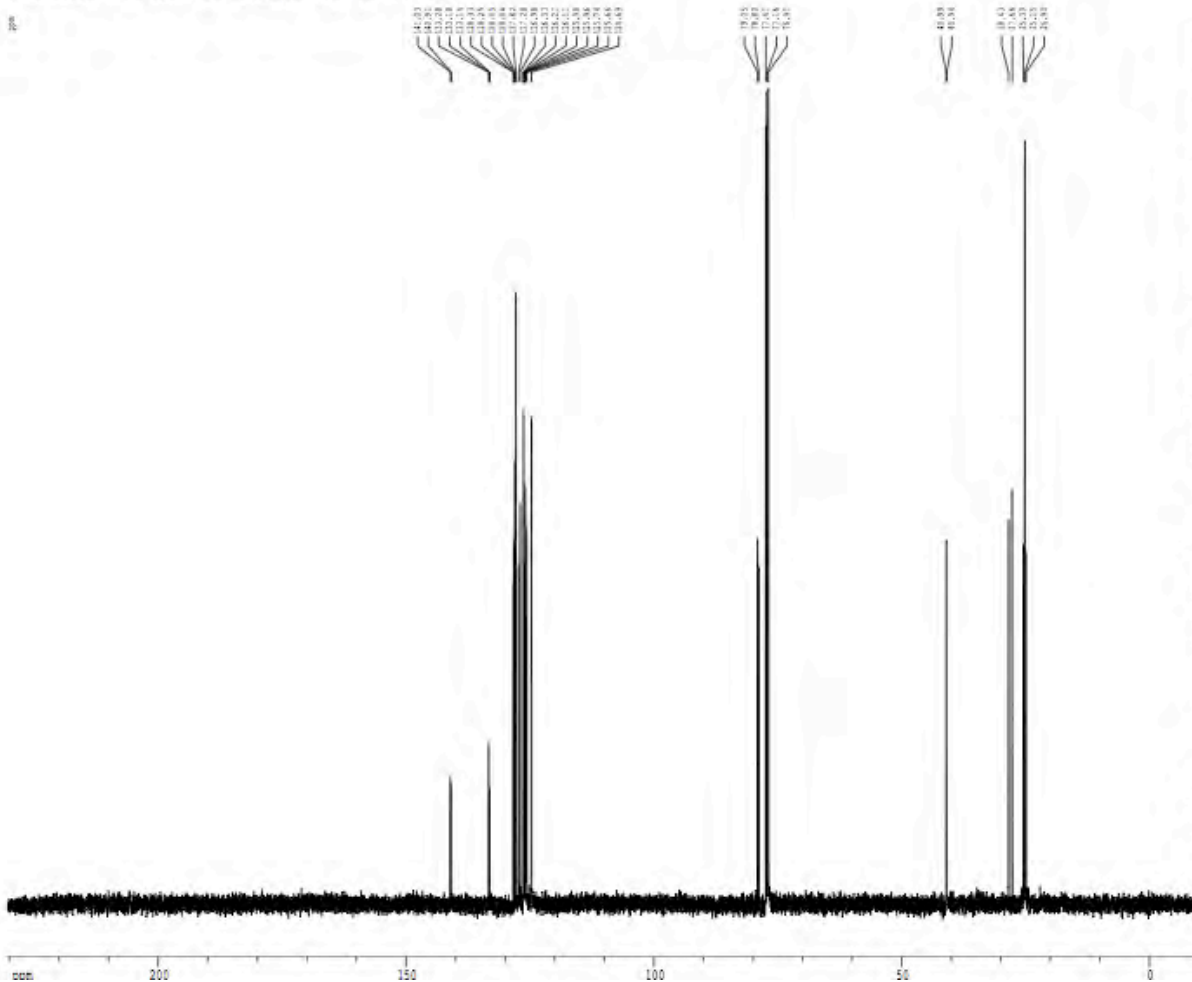
Current Data Parameters
=====
NAME      Varose
EXPNO    1
PROCNO    1
F1 - Acquisition Parameters
Date_     20110111
Time      21.33
INSTRUM   spect
PROBHD    5 mm broadband
PULPROG   zgpg30
RG         655.00
SOLVENT   CDCl3
NS         603
DS         4
SWH        30393.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813940 sec
RG         499.70
AQ         16.260 usec
RG         4.50 usec
RG         256.00
AQ         0.1000000 sec
AQ         0.0300000 sec
AQ         0.0000000 sec
AQ         0.0100000 sec
===== CHANNEL f1 =====
NUC1      13C
P1         7.70 usec
PL1        0.00 dB
SFO1      125.5880432 MHz
F1 - Processing parameters
SI         65534
SF         125.5742340 MHz
WDW        EM
SSB        0
GB         0
PC         1.00 Hz
PC         2.00
===== 1D NMR plot parameters
SI         65534
SF         125.5742340 MHz
WDW        EM
SSB        0
GB         0
PC         1.00 Hz
PC         2.00
=====
CT         22.00 cm
CT         15.00 cm
TIP        229.520 ppm
F1         28821.70 Hz
F2         -10.507 ppm
F3         -313.24 Hz
F4         11.5274 ppm/cm
F5CM       1321.97874 Hz/cm
    
```

1H spectrum



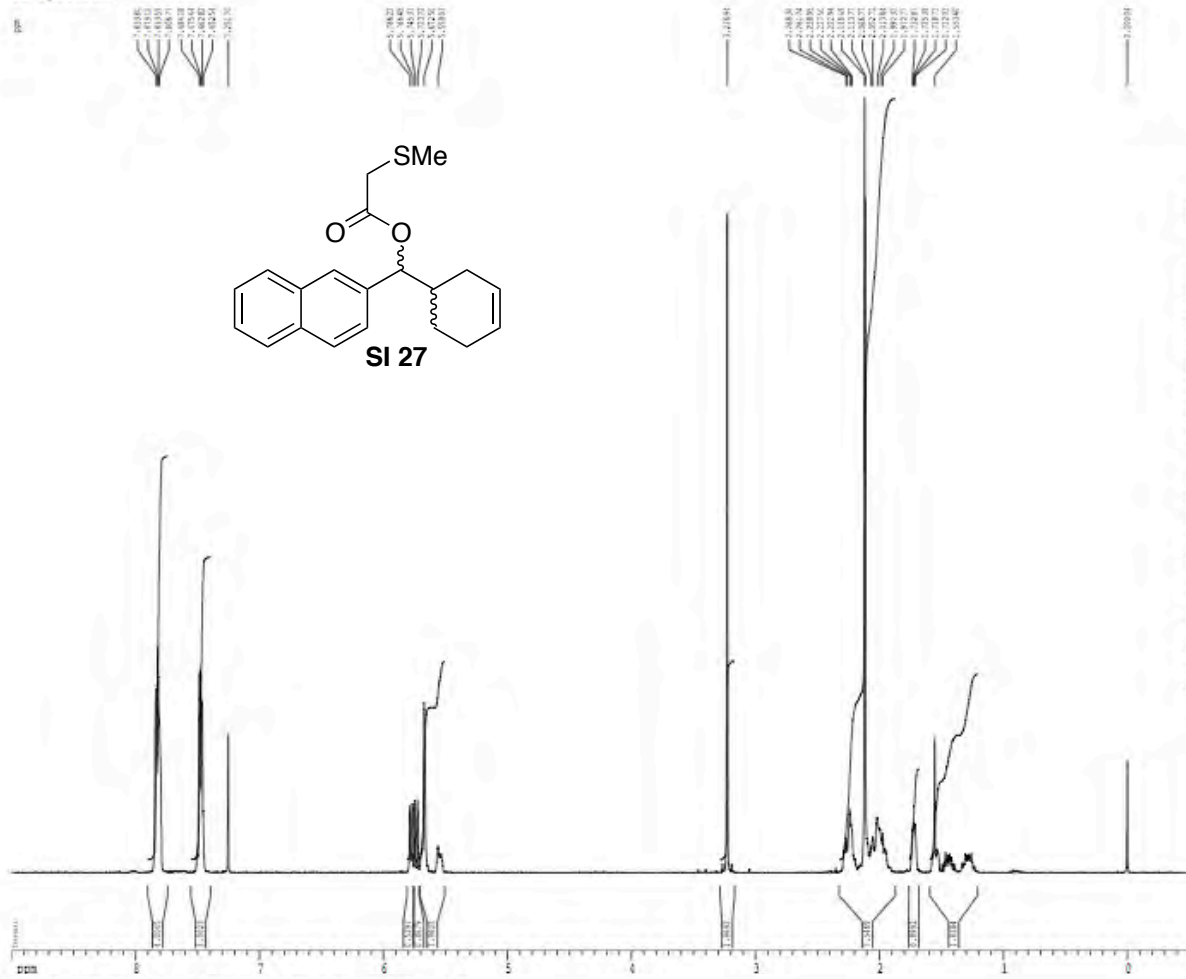
Current Data Parameters  
 DATE: 04.07.01  
 TIME: 16.28  
 INSTRUM: spect  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 CHN: 01.07.01  
 TMR: 16.28  
 FREQC: 400.141013  
 PULPROG: zgpg30  
 PCPRG2: 0  
 F2: 400.141013  
 SOLVENT: CDCl3  
 NS: 2  
 DS: 4  
 SWH: 1410.256 Hz  
 FIDRES: 0.247613 Hz  
 AQ: 0.118979 sec  
 RG: 381  
 SF: 101.626 MHz  
 TD: 65536  
 FSI: 0.1000000 sec  
 SSF: 0.0000000 sec  
 AQ2: 0.0000000 sec  
 SFO2: 101.626000 MHz  
 ===== CHANNEL f2 =====  
 NU1: 13  
 P1: 10.00 usec  
 PL1: -2.00 dB  
 SFO1: 400.141013 MHz  
 F2 - Processing parameters  
 SI: 13  
 SF: 400.141013 MHz  
 DS: 4  
 SSF: 0  
 LB: 0.50 Hz  
 GB: 0  
 PC: 2.00  
 D3 REF (ref) parameters  
 CH: 13  
 T3: 10.00 usec  
 P3: 0.00 dB  
 F1: 400.141013 MHz  
 F2: -10.00 dB  
 F3: -10.00 dB  
 SFREQ: 0.41647 ppm/Hz  
 SFO4: 101.626000 MHz

Z-restored spin-echo 13C spectrum with 1H decoupling

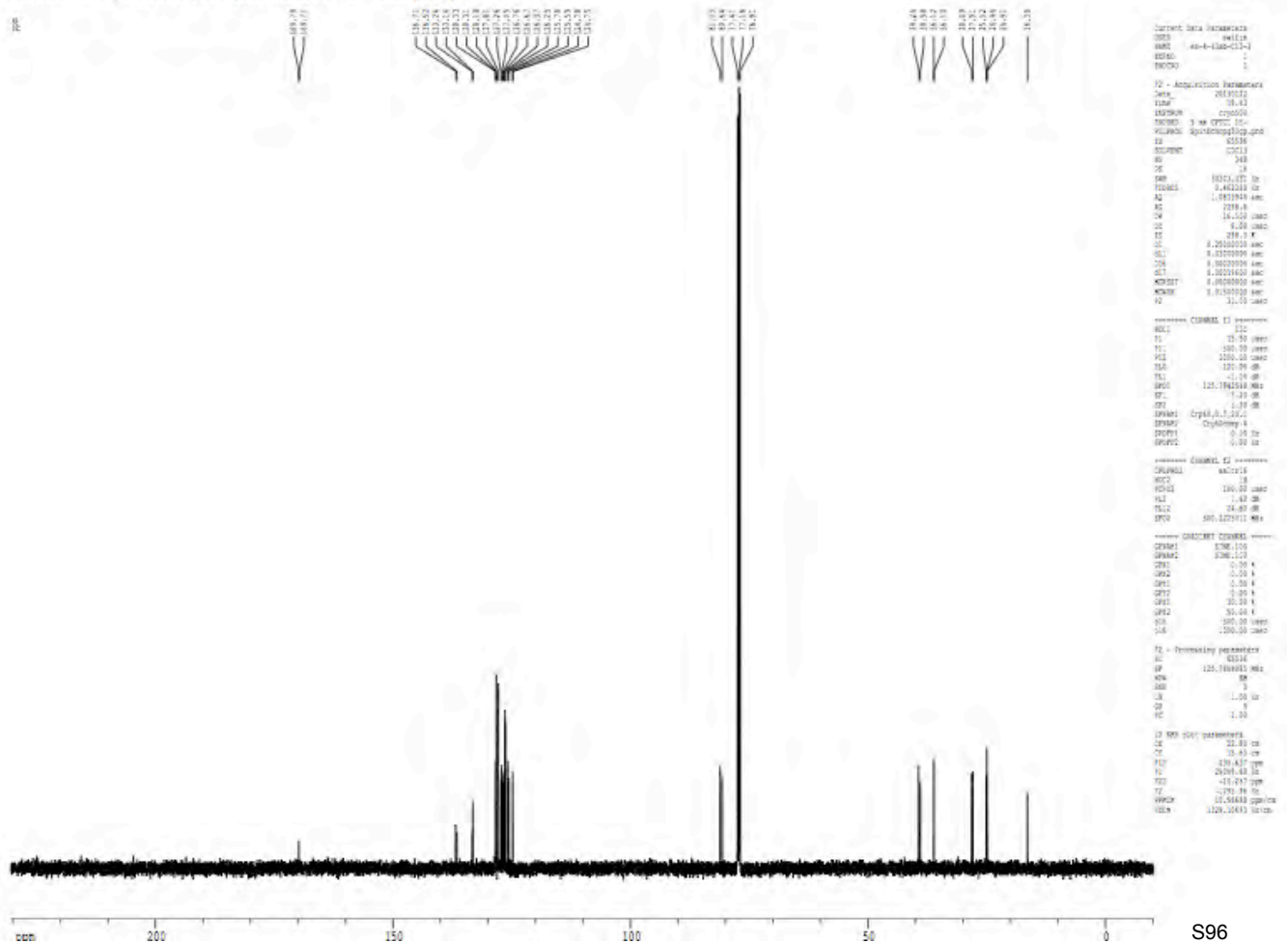


Current Data Parameters  
 DATE: 04.07.01  
 TIME: 16.28  
 INSTRUM: spect  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 CHN: 01.07.01  
 TMR: 16.28  
 FREQC: 400.141013  
 PULPROG: zgpg30  
 PCPRG2: 0  
 F2: 400.141013  
 SOLVENT: CDCl3  
 NS: 2  
 DS: 4  
 SWH: 1410.256 Hz  
 FIDRES: 0.247613 Hz  
 AQ: 0.118979 sec  
 RG: 381  
 SF: 101.626 MHz  
 TD: 65536  
 FSI: 0.1000000 sec  
 SSF: 0.0000000 sec  
 AQ2: 0.0000000 sec  
 SFO2: 101.626000 MHz  
 ===== CHANNEL f2 =====  
 NU1: 13  
 P1: 10.00 usec  
 PL1: -2.00 dB  
 SFO1: 400.141013 MHz  
 F2 - Processing parameters  
 SI: 13  
 SF: 400.141013 MHz  
 DS: 4  
 SSF: 0  
 LB: 0.50 Hz  
 GB: 0  
 PC: 2.00  
 D3 REF (ref) parameters  
 CH: 13  
 T3: 10.00 usec  
 P3: 0.00 dB  
 F1: 400.141013 MHz  
 F2: -10.00 dB  
 F3: -10.00 dB  
 SFREQ: 0.41647 ppm/Hz  
 SFO4: 101.626000 MHz

1H spectrum

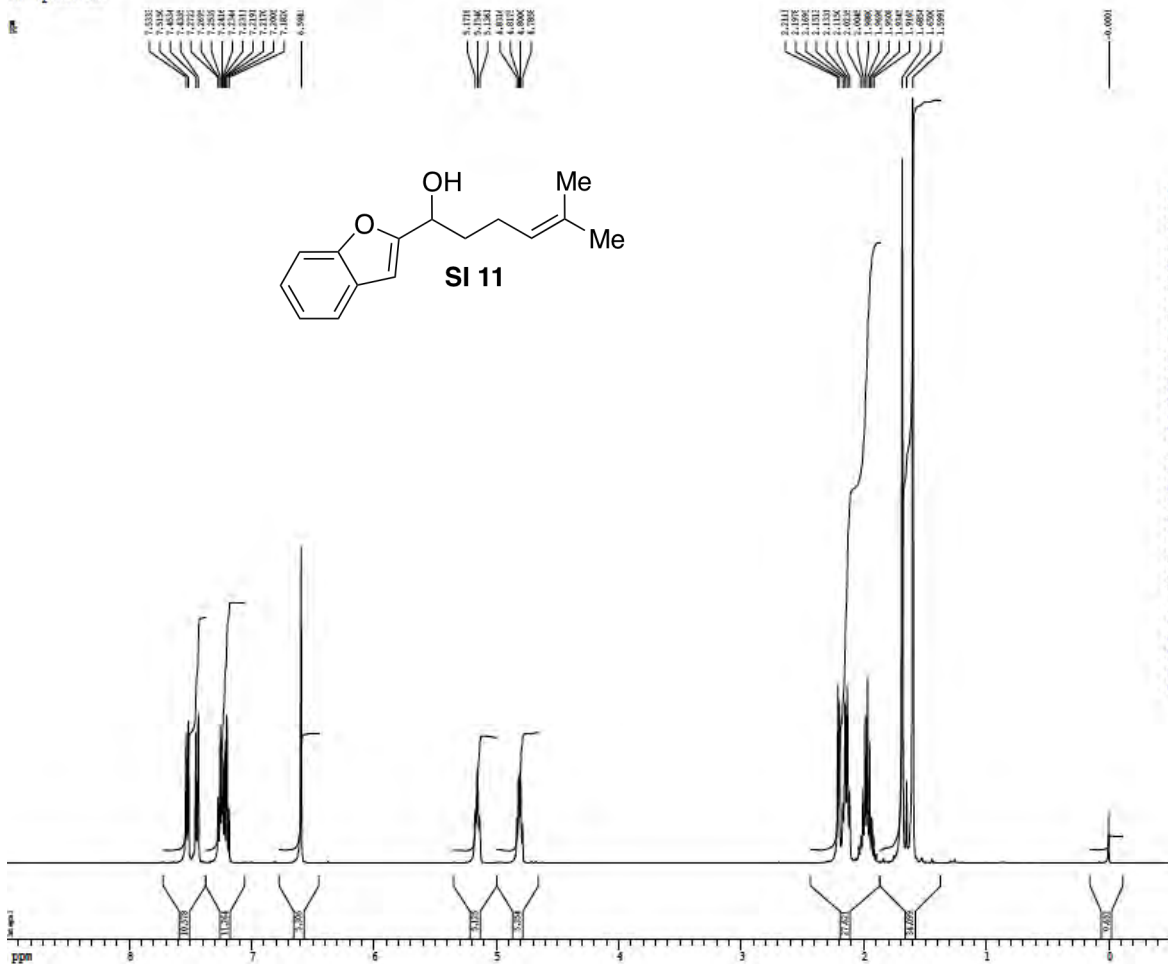


Z-restored spin-echo 13C spectrum with 1H decoupling





1H spectrum



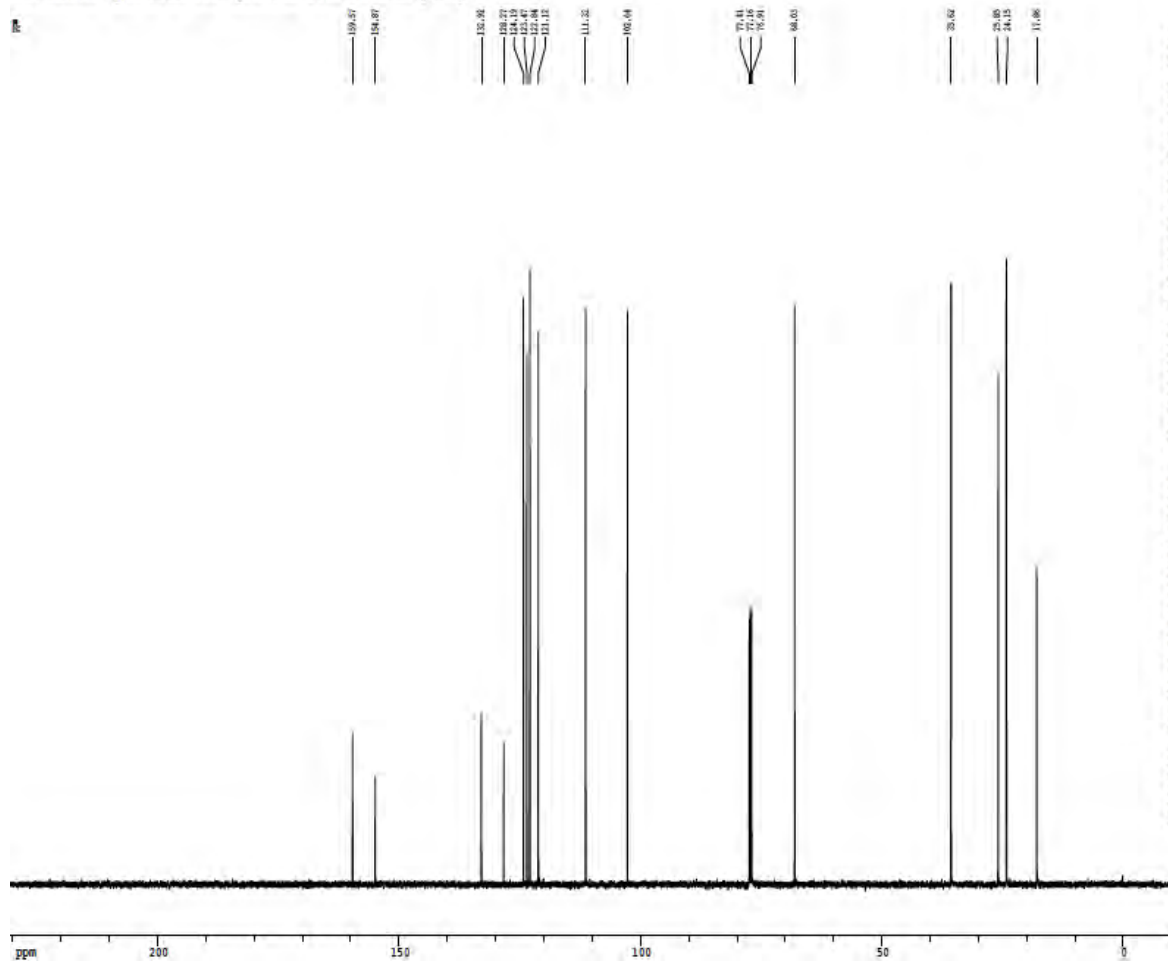
Current Data Parameters

```

NAME      SI11
EXPNO     1
PROCNO    1
Date_     20111215
Time      1.14
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
AQ         0.00000000
RG         2
SR         640.250000
FIDRES    0.00015000 Hz
AQ        1.1118770 use
RG         80.0
SF         30.00000000
DE         4.50 usec
TE         298.0 K
D1         0.10000000 usec
DELTA     0.00000000 usec
WALTZ16   0.00000000 usec
WALTZ17   0.00000000 usec
===== CHANNEL f1 =====
NUC1       1H
P1         12.00 usec
PL1        -0.60 dB
SFO1      400.1420000 MHz
===== Processing parameters =====
SI        65536
SF        400.1420000 MHz
WDW       EM
SSB        0
LB         0.30 Hz
GB         0
PC         2.00
===== ID list parameters =====
SI        22.80 cm
F1         25.00 cm
F2         0.0000 ppm
F3         5681.17 Hz
F4         -0.0000 ppm
F5         -200.06 Hz
F6         0.40000000 ppm/m
=====
===== CHANNEL f2 =====
NUC2       13C
P2         15.00 usec
PL2        0.00 dB
SFO2      100.6261250 MHz
===== Processing parameters =====
SI        65536
SF        100.6261250 MHz
WDW       EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
===== ID list parameters =====
SI        22.80 cm
F1         12.00 cm
F2         230.427 ppm
F3         15000.00 Hz
F4         -120.24 Hz
F5         0.40000000 ppm/m
=====

```

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters

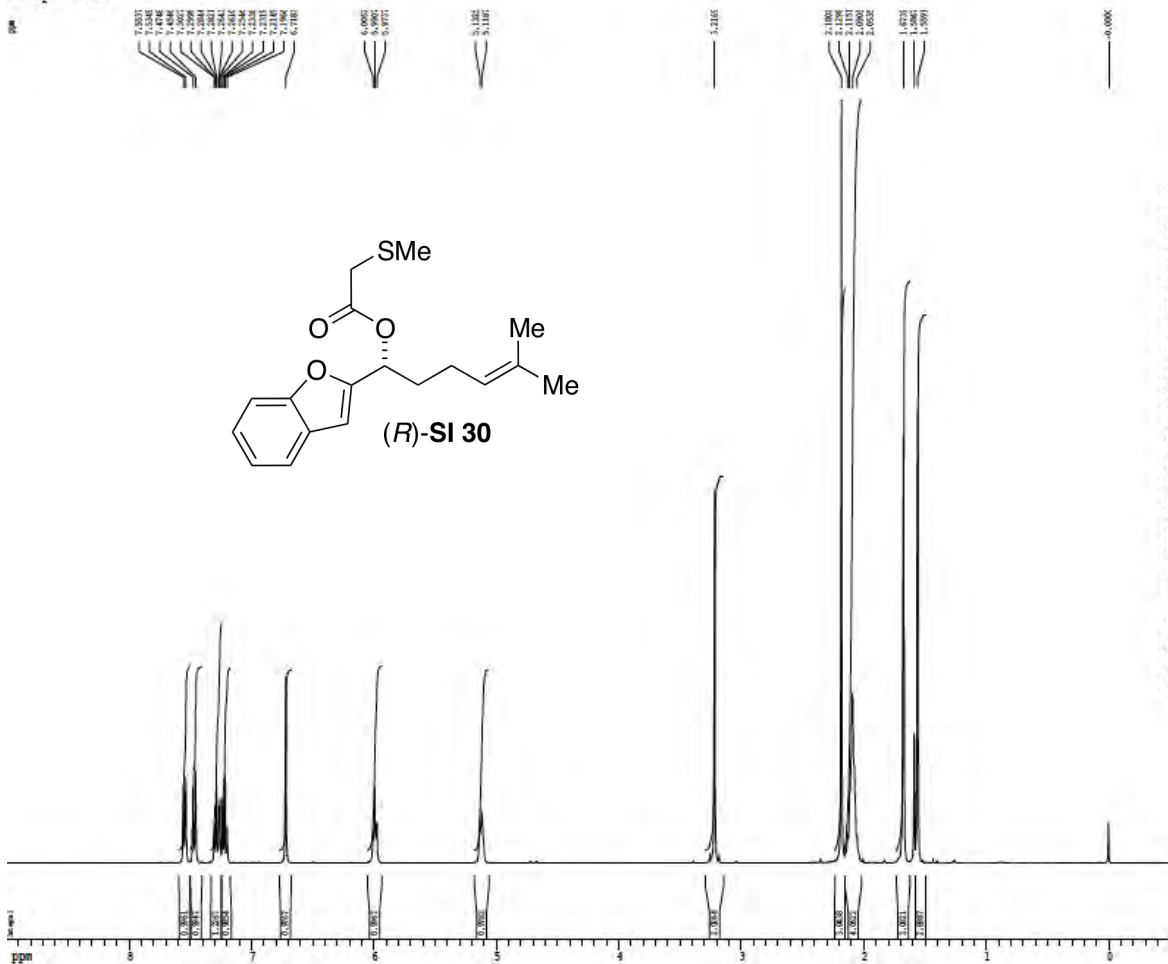
```

NAME      SI11
EXPNO     2
PROCNO    1
Date_     20111215
Time      20.33
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   spincbpggpgp
TD         65536
SOLVENT   CDCl3
AQ         0.00000000
RG         2
SR         250.130100
FIDRES    0.00012000 Hz
AQ        1.0012040 usec
RG         720.0
SF         100.62612500
DE         4.50 usec
TE         298.0 K
D1         0.10000000 usec
DELTA     0.00000000 usec
WALTZ16   0.00000000 usec
WALTZ17   0.00000000 usec
===== CHANNEL f1 =====
NUC1       13C
P1         15.00 usec
PL1        0.00 dB
SFO1      100.6261250 MHz
===== Processing parameters =====
SI        65536
SF        100.6261250 MHz
WDW       EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
===== ID list parameters =====
SI        22.80 cm
F1         12.00 cm
F2         230.427 ppm
F3         15000.00 Hz
F4         -120.24 Hz
F5         0.40000000 ppm/m
=====
===== CHANNEL f2 =====
NUC2       1H
P2         1.00 usec
PL2        0.00 dB
SFO2      400.1420000 MHz
===== Processing parameters =====
SI        65536
SF        400.1420000 MHz
WDW       EM
SSB        0
LB         0.30 Hz
GB         0
PC         2.00
===== ID list parameters =====
SI        22.80 cm
F1         12.00 cm
F2         230.427 ppm
F3         15000.00 Hz
F4         -120.24 Hz
F5         0.40000000 ppm/m
=====

```



1H spectrum



Current Data Parameters  
 UEXP 1 Name  
 NAME 096.07.10042  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20111207  
 Time 15.35  
 INSTRUM spect  
 PULPROG zgpg30  
 F2 - Processing parameters  
 AC 400.1300212 MHz  
 RF 400.1300212 MHz  
 KW 32  
 SFO 400.1300212 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.00 usec  
 PL1 -0.40 dB  
 SFO1 400.1250000 MHz

F1 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

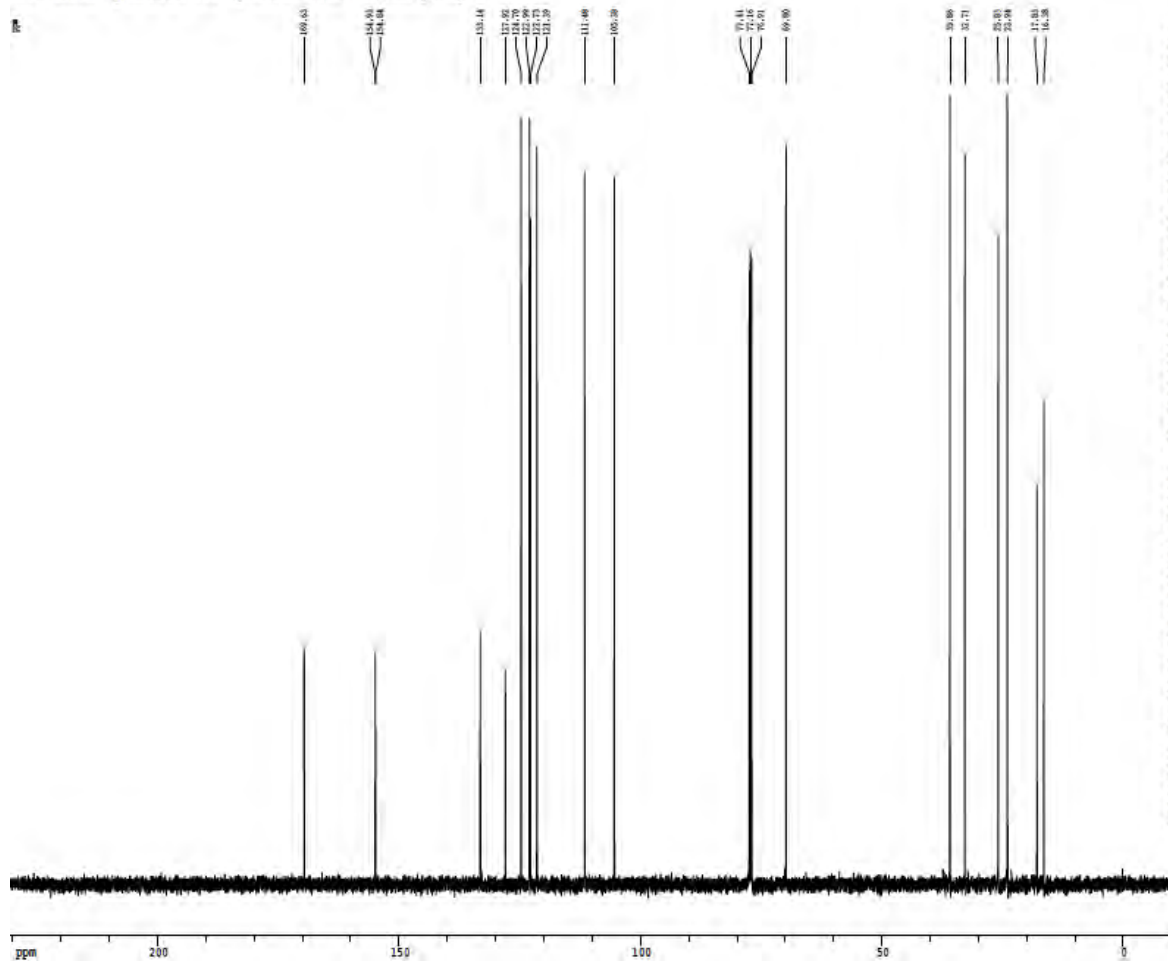
===== CHANNEL f2 =====  
 NUC2 1H  
 P2 12.00 usec  
 PL2 -0.40 dB  
 SFO2 400.1250000 MHz

F2 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

===== CHANNEL f3 =====  
 NUC3 13C  
 P3 12.00 usec  
 PL3 -0.40 dB  
 SFO3 400.1250000 MHz

F3 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 UEXP 1 Name  
 NAME 096.07.10042  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20111207  
 Time 15.35  
 INSTRUM spect  
 PULPROG zgpg30  
 F2 - Processing parameters  
 AC 400.1300212 MHz  
 RF 400.1300212 MHz  
 KW 32  
 SFO 400.1300212 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 12.00 usec  
 PL1 -0.40 dB  
 SFO1 400.1250000 MHz

F1 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

===== CHANNEL f2 =====  
 NUC2 1H  
 P2 12.00 usec  
 PL2 -0.40 dB  
 SFO2 400.1250000 MHz

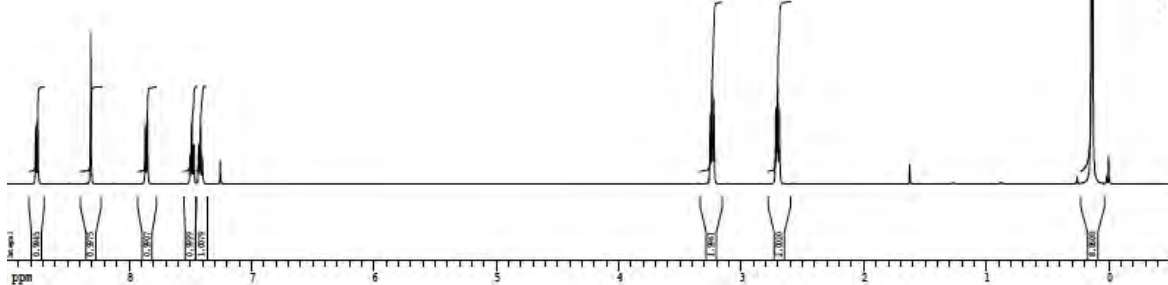
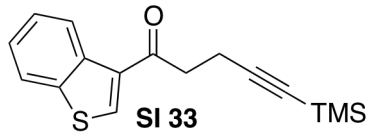
F2 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

===== CHANNEL f3 =====  
 NUC3 13C  
 P3 12.00 usec  
 PL3 -0.40 dB  
 SFO3 400.1250000 MHz

F3 - Processing parameters  
 AC 65536  
 SF 400.1250000 MHz  
 KW 32  
 SFO 400.1250000 MHz  
 DS 2  
 AS 120  
 SW 30.000 MHz  
 ZF 4.50 MHz  
 DE 230.1 F  
 FI 0.10000000 sec  
 DI 0.00000000 sec  
 MEZFI 0.00000000 sec  
 WDMZ 0.00000000 sec

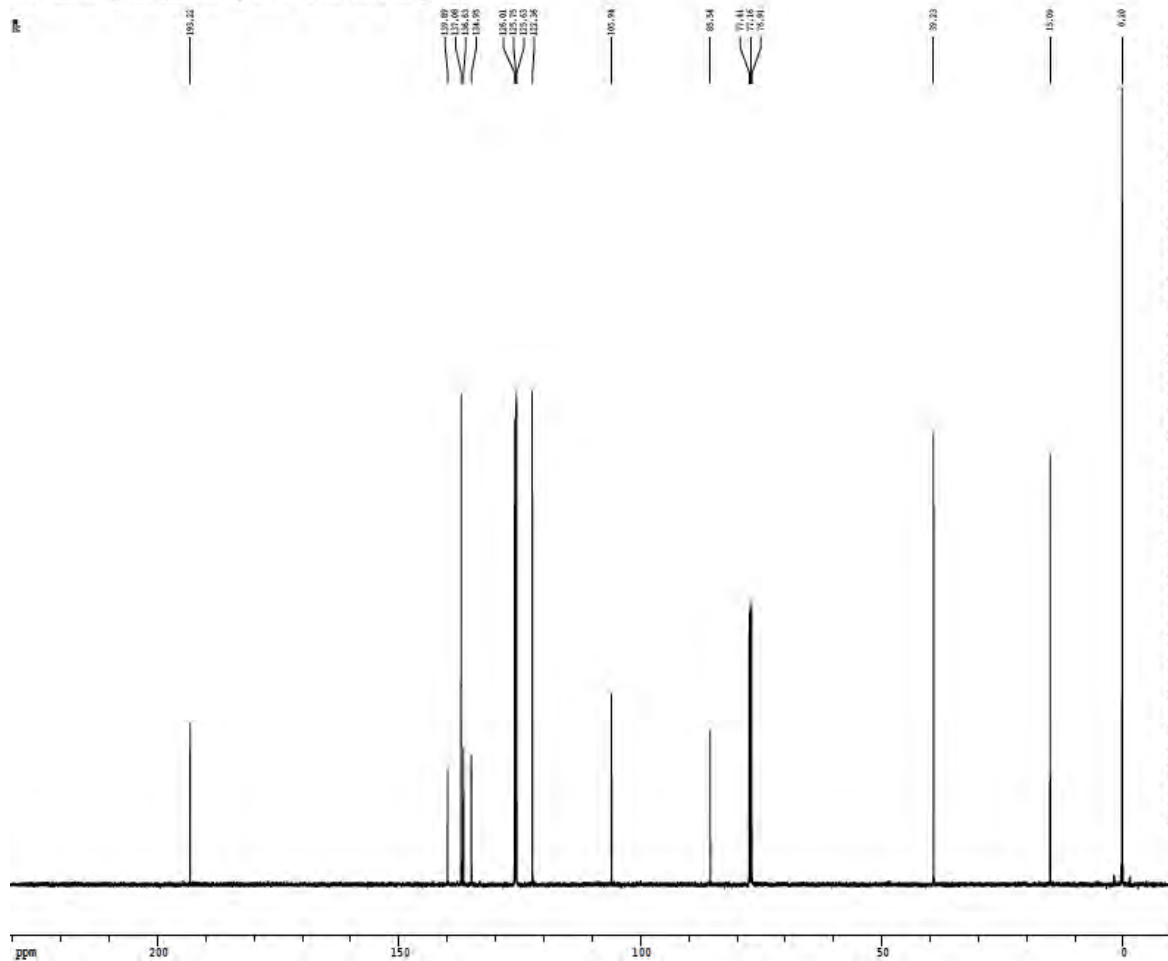


1H spectrum



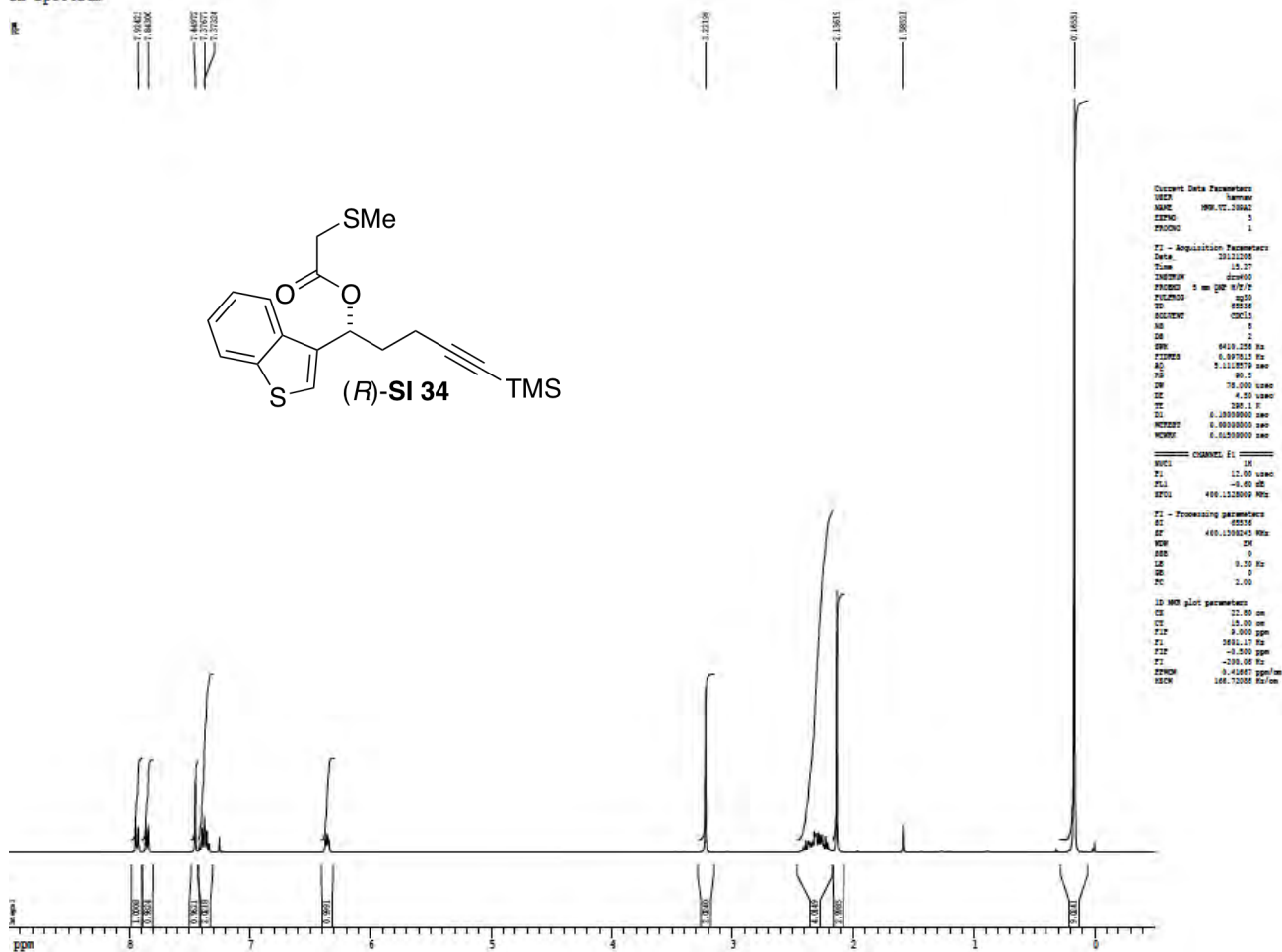
Current Data Parameters  
 Date: 20120311  
 Time: 13.17  
 Name: SI 33  
 P1: 1.00  
 P2: 1.00  
 P3: 1.00  
 P4: 1.00  
 P5: 1.00  
 P6: 1.00  
 P7: 1.00  
 P8: 1.00  
 P9: 1.00  
 P10: 1.00  
 P11: 1.00  
 P12: 1.00  
 P13: 1.00  
 P14: 1.00  
 P15: 1.00  
 P16: 1.00  
 P17: 1.00  
 P18: 1.00  
 P19: 1.00  
 P20: 1.00

Z-restored spin-echo 13C spectrum with 1H decoupling

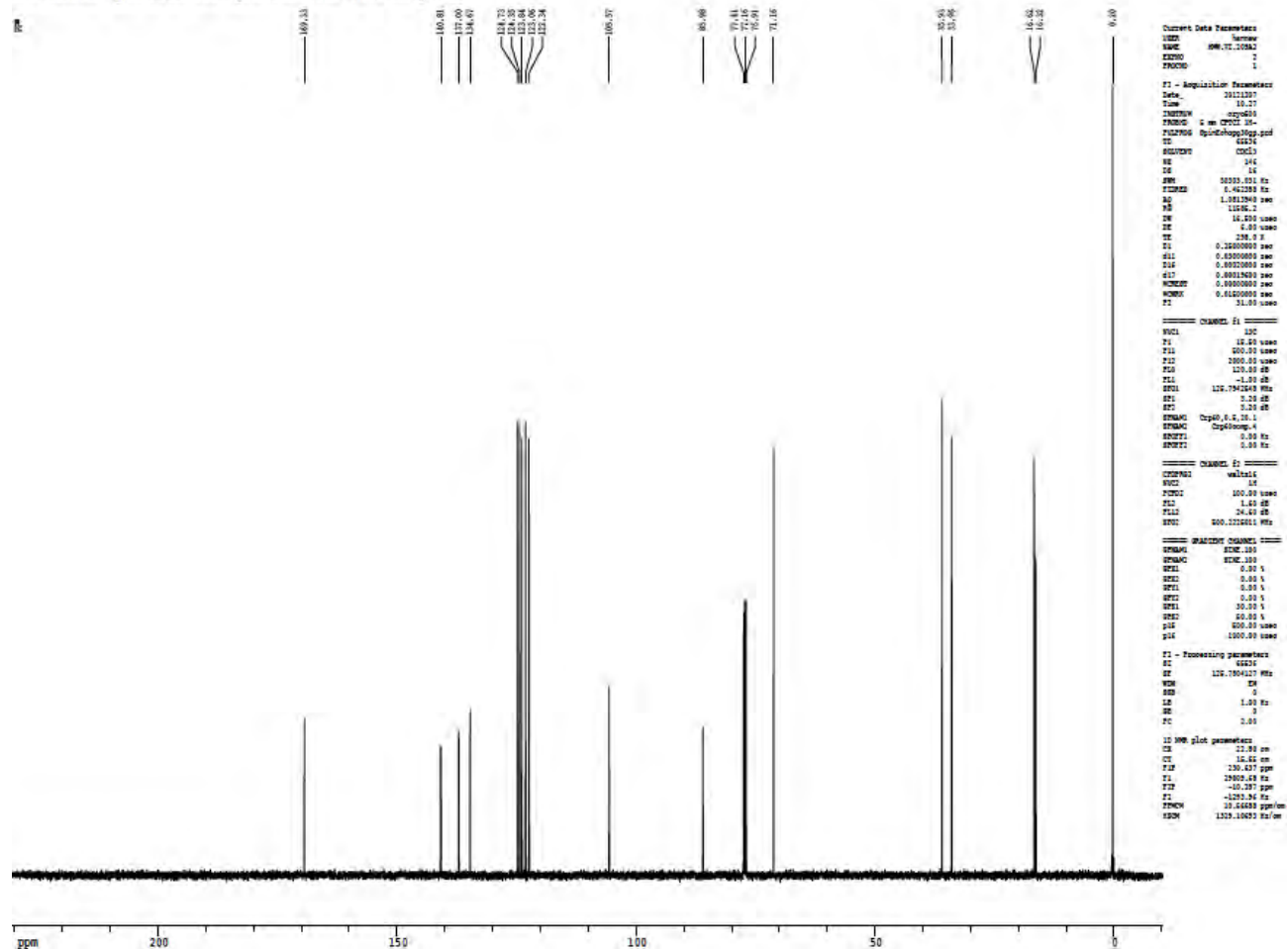


Current Data Parameters  
 Date: 20120311  
 Time: 13.20  
 Name: SI 33  
 P1: 1.00  
 P2: 1.00  
 P3: 1.00  
 P4: 1.00  
 P5: 1.00  
 P6: 1.00  
 P7: 1.00  
 P8: 1.00  
 P9: 1.00  
 P10: 1.00  
 P11: 1.00  
 P12: 1.00  
 P13: 1.00  
 P14: 1.00  
 P15: 1.00  
 P16: 1.00  
 P17: 1.00  
 P18: 1.00  
 P19: 1.00  
 P20: 1.00

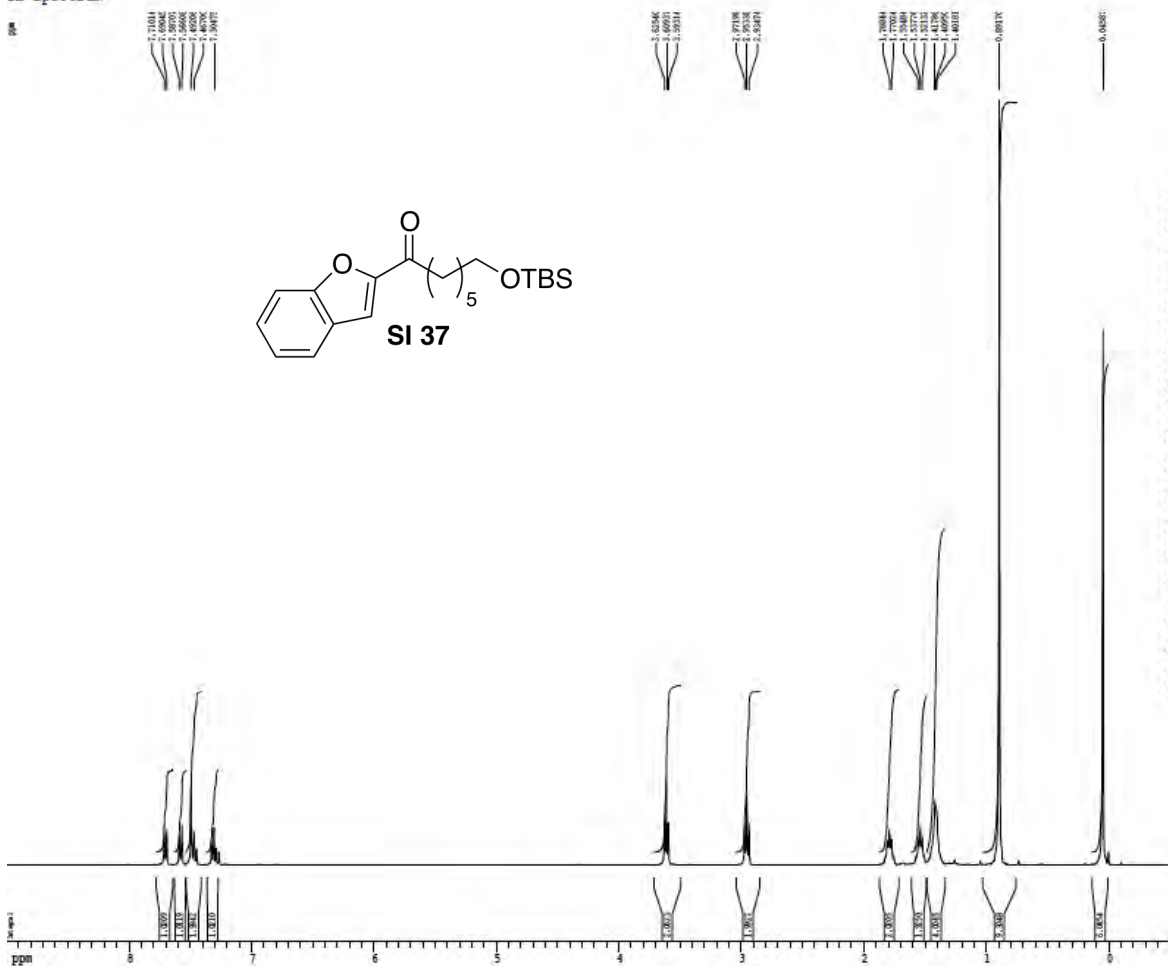
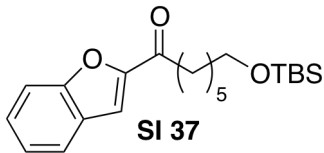
1H spectrum



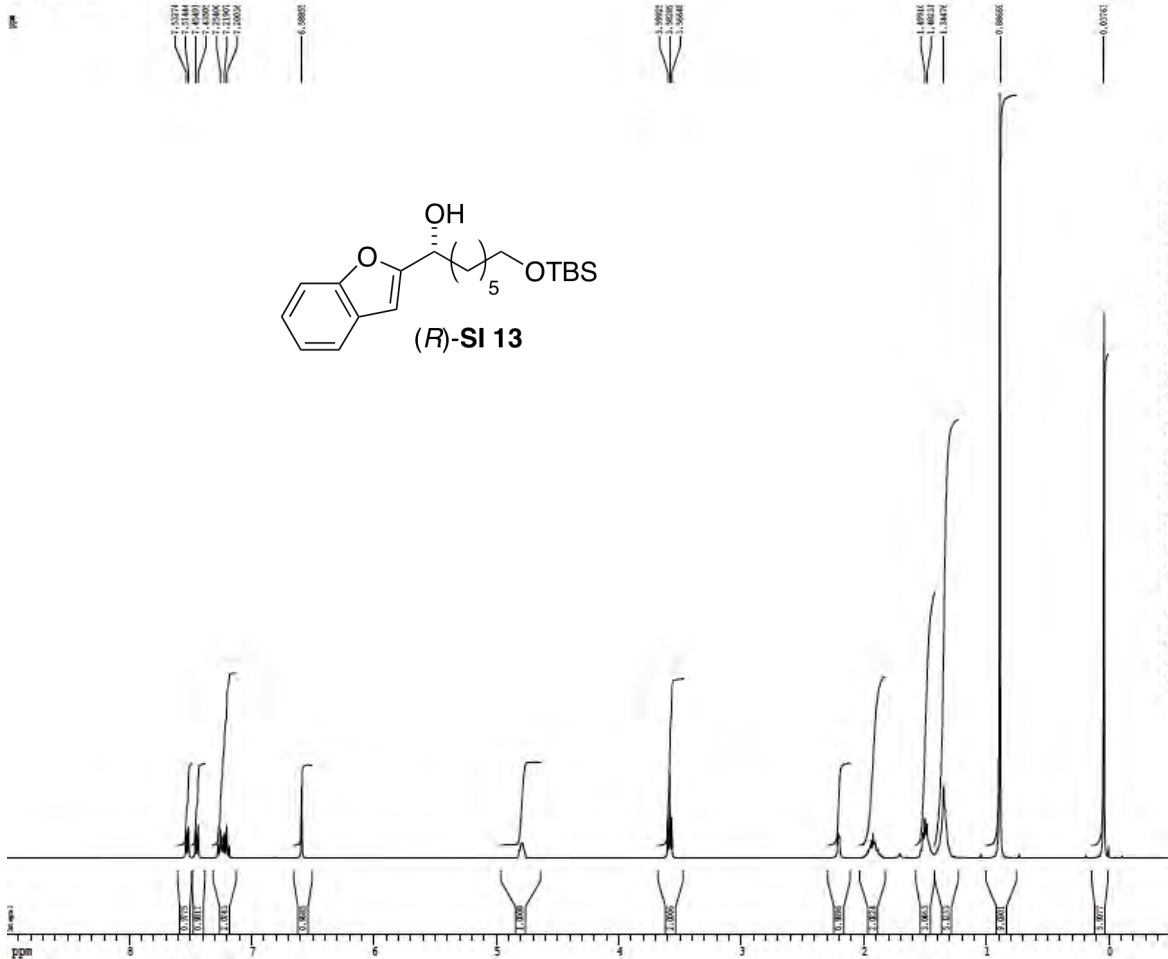
Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum

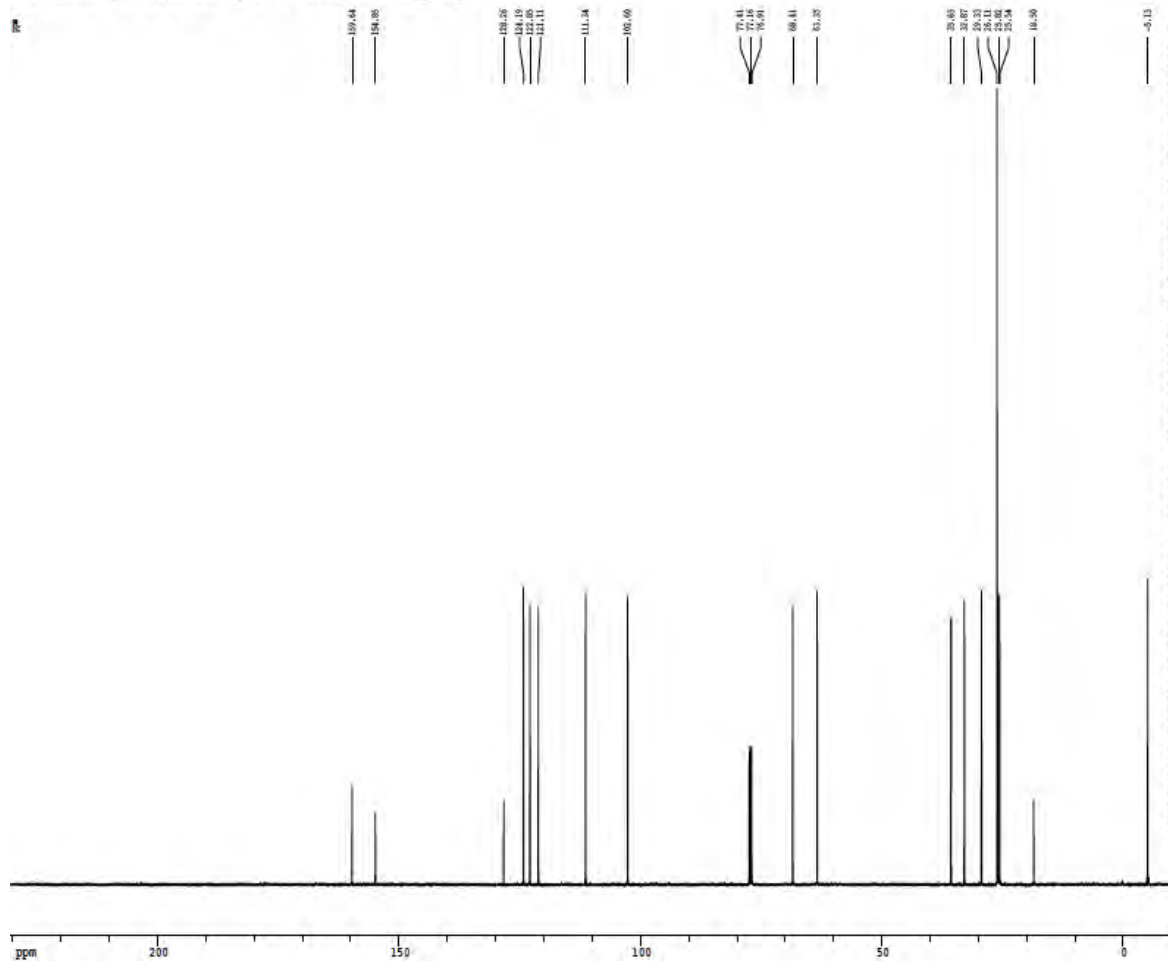


1H spectrum



Current Data Parameters  
 UEXP: 500  
 NAME: 500-01-10642  
 EXPNO: 1  
 PROCNO: 1  
 FI - Acquisition Parameters  
 Date\_: 20121001  
 Time: 15.12  
 INSTRUM: spect  
 PULPROG: zgpg30  
 SOLVENT: dms  
 ACQUIS: 40019  
 NS: 2  
 DS: 4  
 SWH: 6419.250 Hz  
 FIDRES: 0.00761 Hz  
 AQ: 0.1218719 sec  
 RG: 40.5  
 SF: 30.000 MHz  
 DE: 4.50 usec  
 TE: 300.2 K  
 D1: 0.1000000 sec  
 MCH2F2: 0.0000000 sec  
 MCH2F1: 0.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 12.00 usec  
 PL1: -0.60 dB  
 SFO1: 400.1500000 MHz  
 FI - Processing parameters  
 SC: 65216  
 SF: 400.1500000 MHz  
 WHW: 30  
 SSB: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 2.00  
 ID: 500 plot parameters  
 CH: 22.80 cm  
 CT: 25.00 cm  
 FT: 0.000 ppm  
 FI: 300.000 Hz  
 FID: -0.200 ppm  
 F2: -200.00 Hz  
 F3: -200.00 Hz  
 FWHM: 0.4000000 ppm/m  
 SFO: 400.1500000 MHz

Z-restored spin-echo 13C spectrum with 1H decoupling

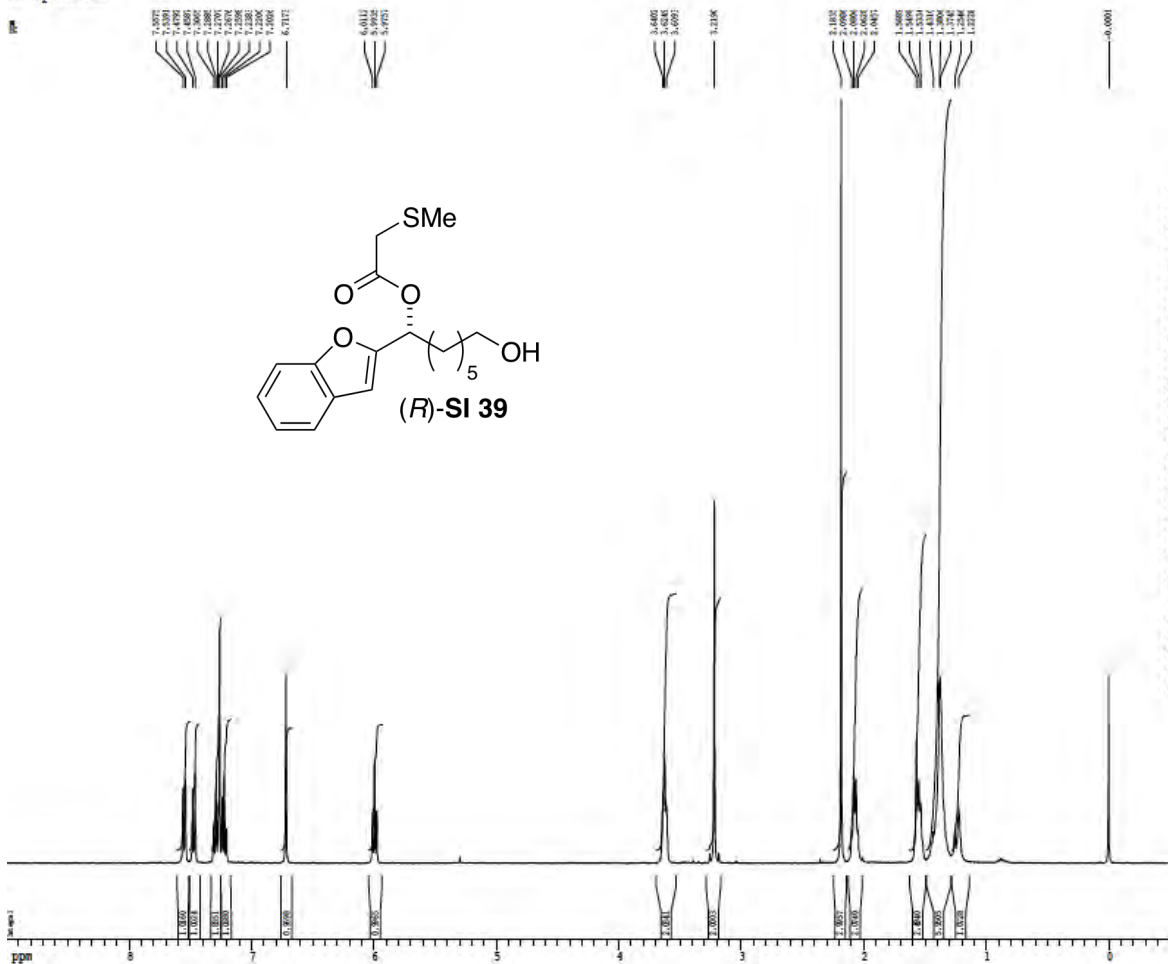


Current Data Parameters  
 UEXP: 500  
 NAME: 500-01-10642  
 EXPNO: 1  
 PROCNO: 1  
 FI - Acquisition Parameters  
 Date\_: 20121001  
 Time: 14.23  
 INSTRUM: spect  
 PULPROG: zgpg30  
 SOLVENT: dms  
 ACQUIS: 40019  
 NS: 2  
 DS: 4  
 SWH: 6419.250 Hz  
 FIDRES: 0.00761 Hz  
 AQ: 0.1218719 sec  
 RG: 40.5  
 SF: 30.000 MHz  
 DE: 4.50 usec  
 TE: 300.2 K  
 D1: 0.1000000 sec  
 MCH2F2: 0.0000000 sec  
 MCH2F1: 0.0000000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 15.00 usec  
 PL1: 0.00 usec  
 SFO1: 101.62530 MHz  
 FI - Processing parameters  
 SC: 65216  
 SF: 101.62530 MHz  
 WHW: 30  
 SSB: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 2.00  
 ID: 500 plot parameters  
 CH: 22.80 cm  
 CT: 25.00 cm  
 FT: 0.000 ppm  
 FI: 300.000 Hz  
 FID: -0.200 ppm  
 F2: -200.00 Hz  
 F3: -200.00 Hz  
 FWHM: 0.4000000 ppm/m  
 SFO: 400.1500000 MHz



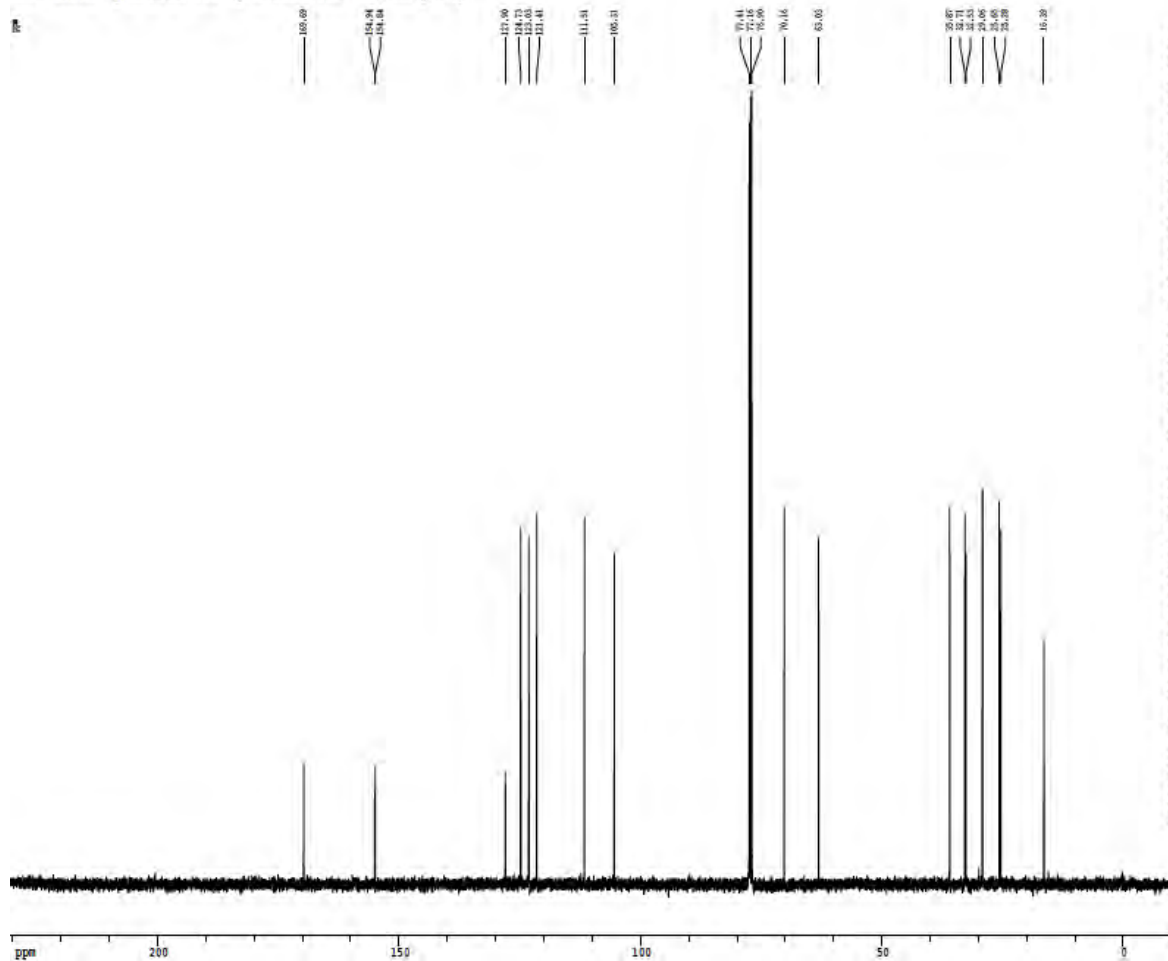


1H spectrum



Current Data Parameters  
 Date: 20100203  
 Time: 14.31  
 Name: 096.17.2133A  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20100203  
 Time: 14.31  
 Name: 096.17.2133A  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Processing parameters  
 AC: 400.1100115 MHz  
 DE: 2.00  
 SF: 400.1100115 MHz  
 AS: 0  
 DS: 0  
 EQ: 0  
 F2: 400.1100115 MHz  
 PC: 2.00  
 ID 100 plot parameters  
 CE: 22.00 cm  
 CF: 25.00 cm  
 FID: 0.000 ppm  
 FI: 3681.17 Hz  
 FID: -0.200 ppm  
 FI: -230.06 Hz  
 F2PC: 0.41667 ppm/cm  
 F2CM: 167.70000 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



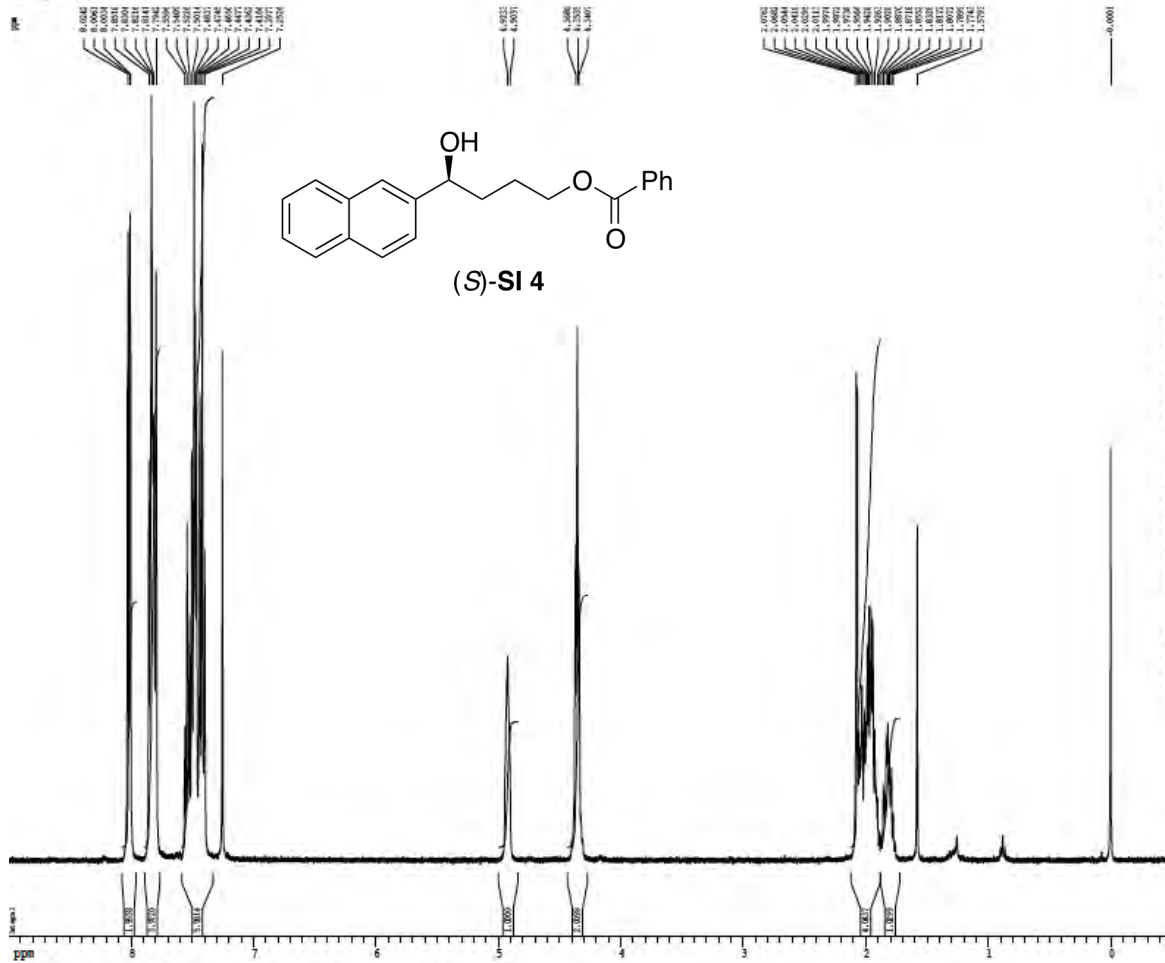
Current Data Parameters  
 Date: 20100203  
 Time: 14.31  
 Name: 096.17.2133A  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20100203  
 Time: 14.31  
 Name: 096.17.2133A  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Processing parameters  
 AC: 125.7604284 MHz  
 DE: 0  
 SF: 125.7604284 MHz  
 AS: 0  
 DS: 0  
 EQ: 0  
 F2: 125.7604284 MHz  
 PC: 2.00  
 ID 100 plot parameters  
 CE: 22.00 cm  
 CF: 16.00 cm  
 FID: 230.427 ppm  
 FI: 29029.43 Hz  
 FID: -10.207 ppm  
 FI: -1292.84 Hz  
 F2PC: 10.64488 ppm/cm  
 F2CM: 1239.10623 Hz/cm







1H spectrum



(S)-SI 4

Current Data Parameters  
 UEXP 1  
 NAME 199.07.1038A  
 EXPNO 1  
 PROCNO 1

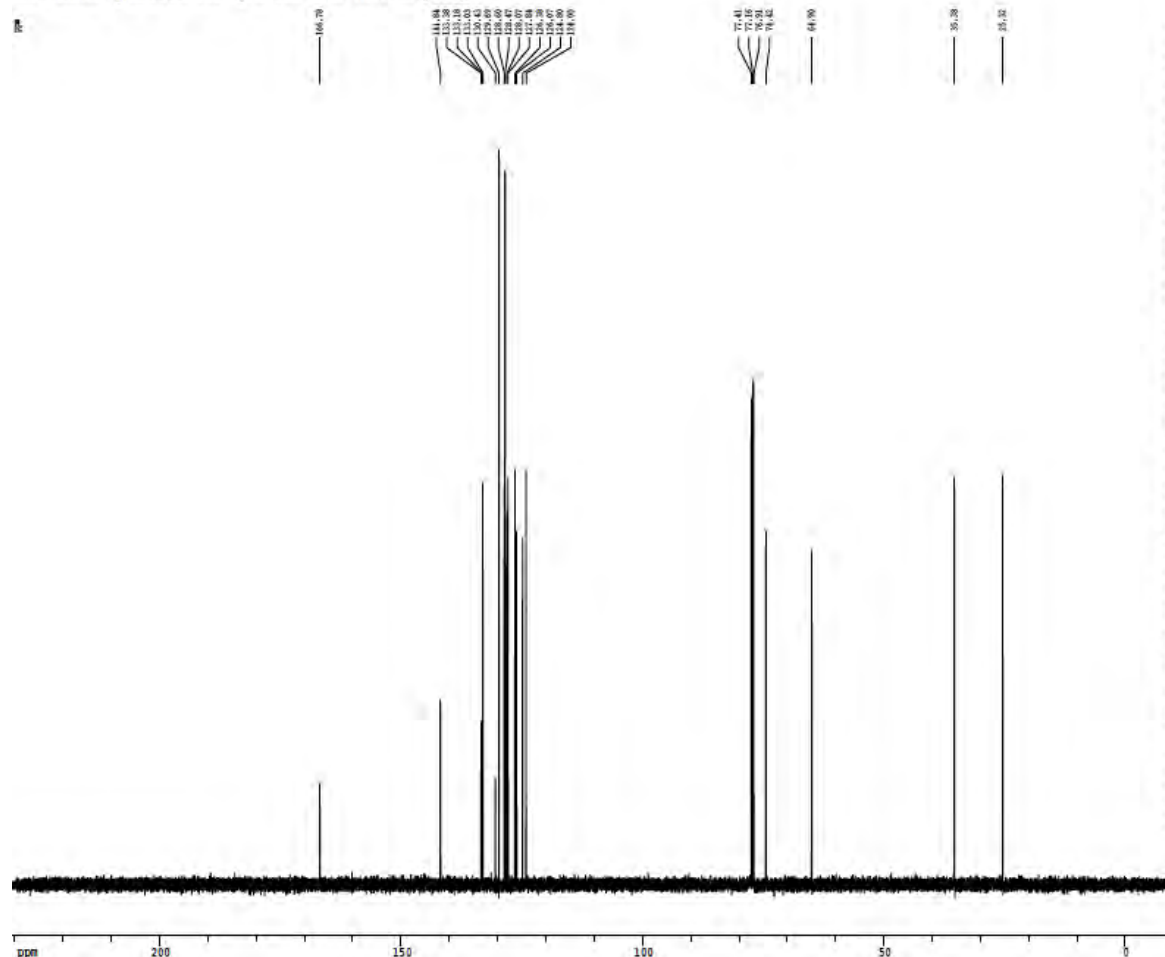
F1 - Acquisition Parameters  
 Date\_ 20130313  
 Time 14:25  
 INSTRUM spect  
 FREQC 300.135100  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 2  
 DS 2  
 SWH 6433.258 Hz  
 FIDRES 0.001619 Hz  
 AC 1.1110070 sec  
 FB 287.4  
 SR 30.000 usec  
 DE 4.20 usec  
 TE 298.0 K  
 D1 0.1000000 sec  
 DELT 0.0000000 sec  
 ACQFSZ 0.0000000 sec  
 WDELT 0.0000000 sec

===== CHANNEL f1 =====  
 NUCL 13C  
 P1 12.00 usec  
 PL1 -0.40 dB  
 SFO1 400.125000 MHz

F2 - Processing parameters  
 SI 65536  
 SF 400.125000 MHz  
 DS 4  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00

1D 90D plot parameters  
 CR 22.00 um  
 CT 25.00 um  
 CPT 0.000 ppm  
 FI 5681.17 Hz  
 FID -0.200 ppm  
 F2 -200.06 Hz  
 F3  
 FWHM 0.41087 ppm/m  
 SCAW 187.70000 Hz/m

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 UEXP 1  
 NAME 199.07.1038A  
 EXPNO 4  
 PROCNO 1

F1 - Acquisition Parameters  
 Date\_ 20130313  
 Time 14:43  
 INSTRUM spect  
 FREQC 300.135100  
 PULPROG specthoppzpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 4  
 DS 4  
 SWH 5050.501 Hz  
 FIDRES 0.0012080 Hz  
 AC 1.0012040 sec  
 FB 470.4  
 SR 30.000 usec  
 DE 4.20 usec  
 TE 298.0 K  
 D1 0.1000000 sec  
 DELT 0.0000000 sec  
 FID 0.0000000 sec  
 F2 0.0000000 sec  
 WDELT 0.0000000 sec  
 WOHNS 0.0000000 sec  
 WOHNS 0.0000000 sec  
 WT 31.00 usec

===== CHANNEL f1 =====  
 NUCL 13C  
 P1 15.00 usec  
 PL1 0.00 usec  
 PL2 2800.00 usec  
 PLO 120.00 dB  
 TICL -1.20 dB  
 SFO1 125.7641418 MHz  
 SFO2 75.27 MHz  
 SFO3 25.32 MHz  
 SFO4 25.32 MHz  
 SFO5 25.32 MHz  
 SFO6 25.32 MHz  
 SFO7 25.32 MHz  
 SFO8 25.32 MHz  
 SFO9 25.32 MHz  
 SFO10 25.32 MHz  
 SFO11 25.32 MHz  
 SFO12 25.32 MHz  
 SFO13 25.32 MHz  
 SFO14 25.32 MHz  
 SFO15 25.32 MHz  
 SFO16 25.32 MHz  
 SFO17 25.32 MHz  
 SFO18 25.32 MHz  
 SFO19 25.32 MHz  
 SFO20 25.32 MHz  
 SFO21 25.32 MHz  
 SFO22 25.32 MHz  
 SFO23 25.32 MHz  
 SFO24 25.32 MHz  
 SFO25 25.32 MHz  
 SFO26 25.32 MHz  
 SFO27 25.32 MHz  
 SFO28 25.32 MHz  
 SFO29 25.32 MHz  
 SFO30 25.32 MHz

===== CHANNEL f2 =====  
 NUCL 13C  
 P1 1.00 usec  
 PL1 0.00 usec  
 PL2 24.40 dB  
 SFO1 200.125000 MHz

===== CHANNEL f3 =====  
 NUCL 13C  
 P1 1.00 usec  
 PL1 0.00 usec  
 PL2 24.40 dB  
 SFO1 200.125000 MHz

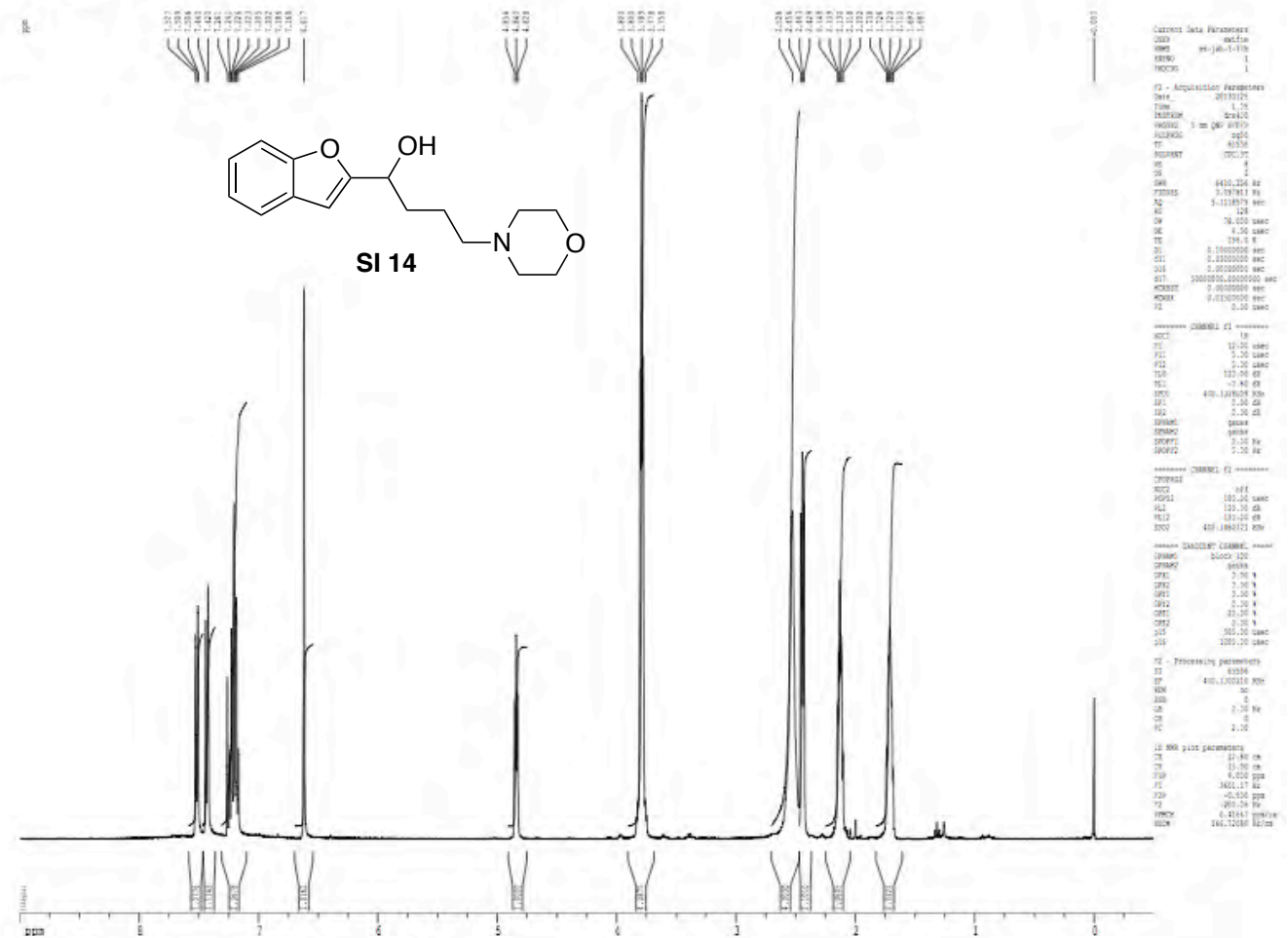
===== CHANNEL f4 =====  
 NUCL 13C  
 P1 1.00 usec  
 PL1 0.00 usec  
 PL2 24.40 dB  
 SFO1 200.125000 MHz

F1 - Processing parameters  
 SI 65536  
 SF 125.7641418 MHz  
 DS 4  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00

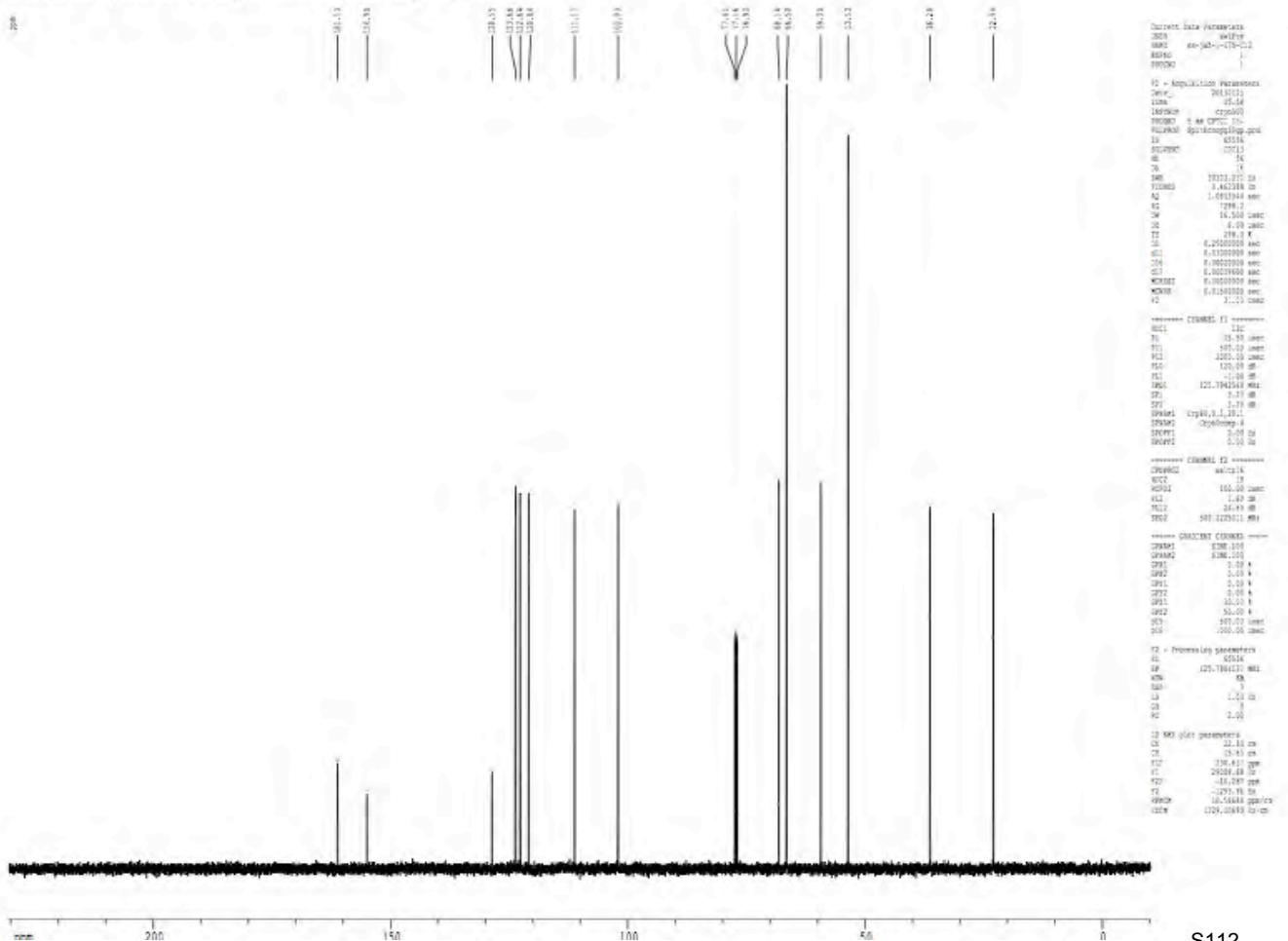
1D 90D plot parameters  
 CR 22.00 um  
 CT 16.00 um  
 CPT 230.420 ppm  
 FI 24628.43 Hz  
 FID -0.200 ppm  
 F2 -120.26 Hz  
 F3  
 FWHM 0.40483 ppm/m  
 SCAW 123.10000 Hz/m



**<sup>1</sup>H Spectrum**



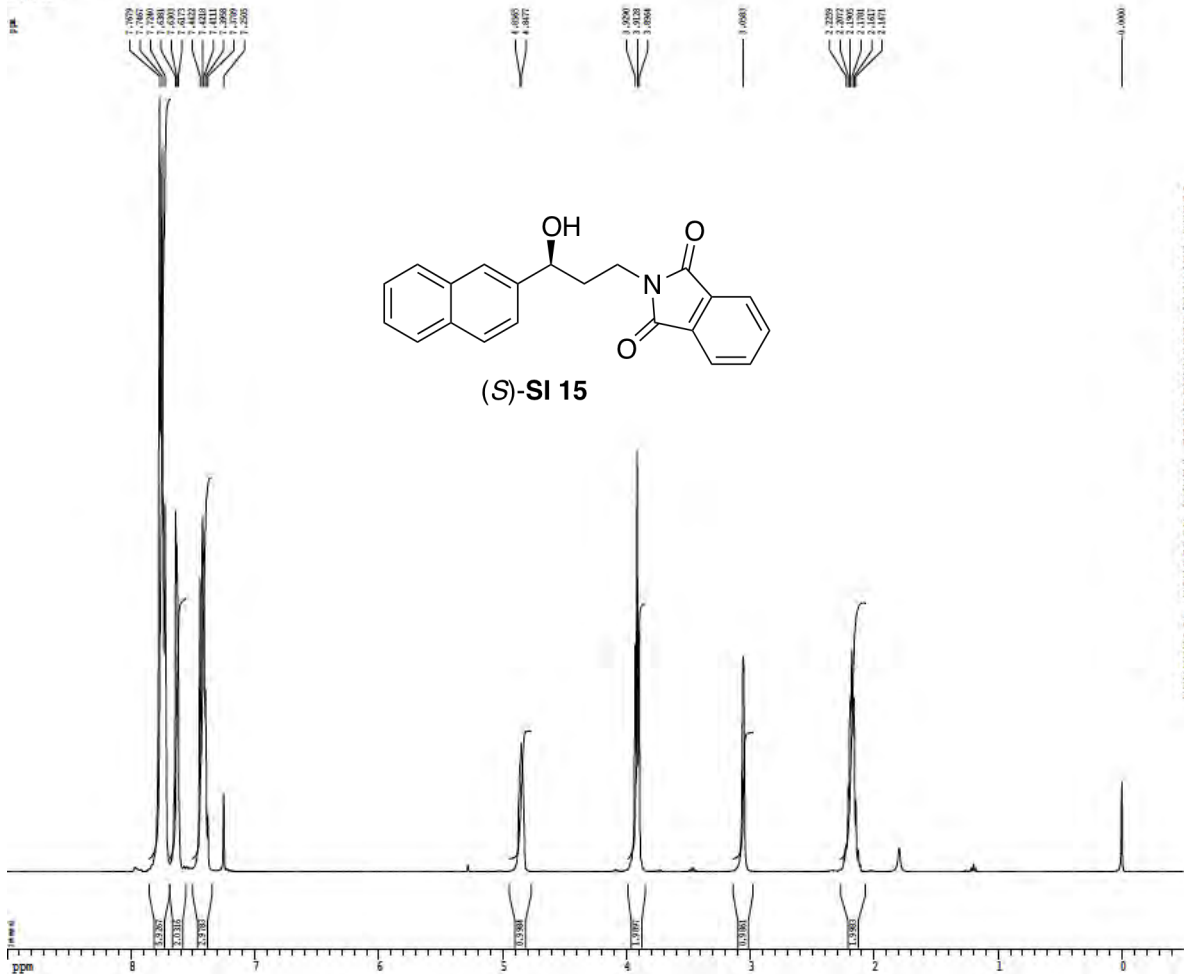
**Z-restored spin-echo 13C spectrum with <sup>1</sup>H decoupling**







096\_VI\_15283 in CDCl3  
post 2nd recrystallization  
October 31, 2011  
1H spectrum



Current Data Parameters  
NAME: 096\_VI\_15283  
EXPNO: 1  
PROCNO: 1

F2 - Acquisition Parameters  
DATE\_: 20111031  
TIME: 12.24  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
SOLVENT: CDCl3  
NS: 8  
DS: 2  
SWH: 6400.156 Hz  
FIDRES: 0.097013 Hz  
AQ: 5.118579 sec  
RG: 128  
AQ: 78.000 usec  
SFO: 400.146400 MHz  
TE: 298.0 K  
D1: 0.11000000 sec  
MCHSET: 0.00000000 sec  
MCHW: 0.01500000 sec

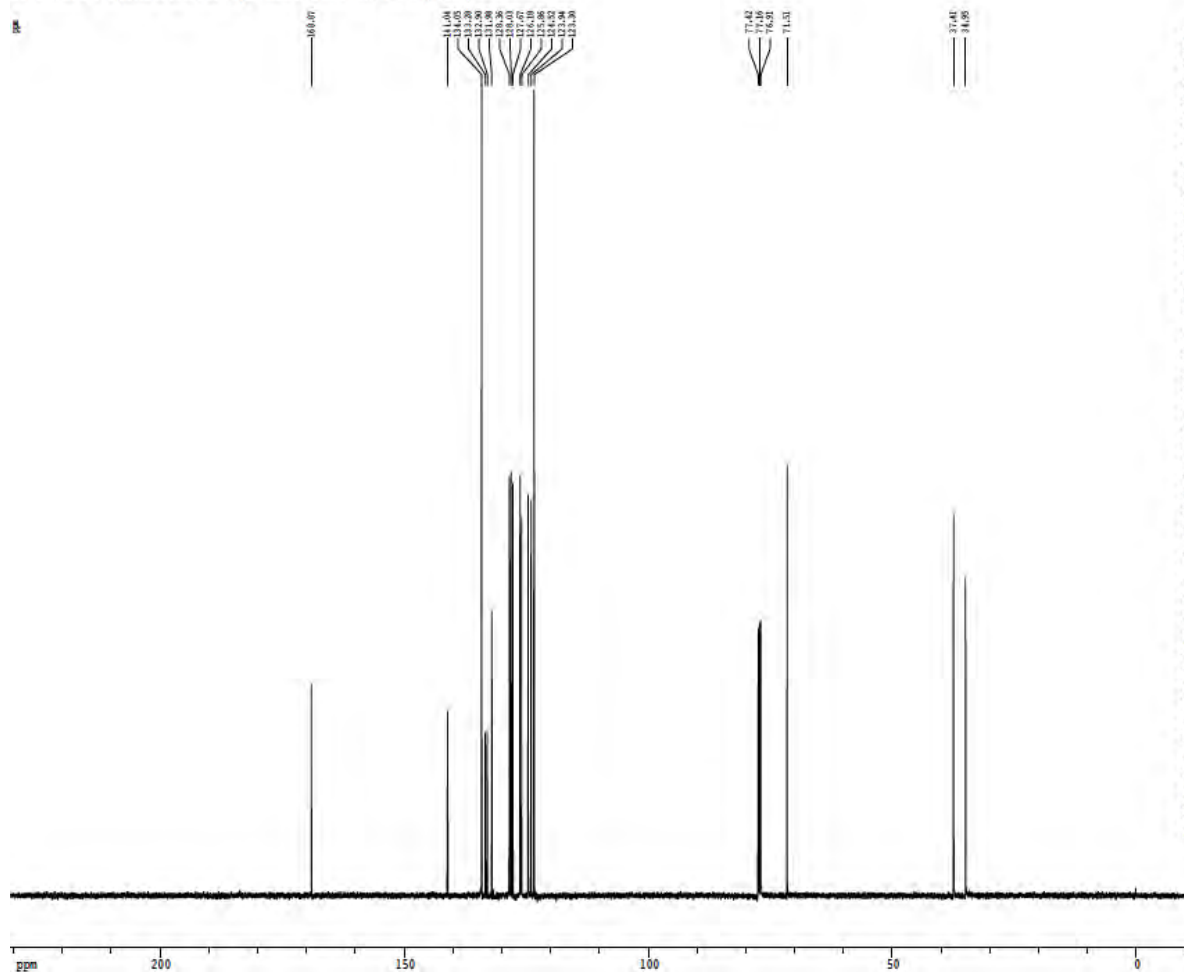
===== CHANNEL f1 =====  
NUC1: 13C  
P1: 12.00 usec  
PL1: -0.40 dB  
SFO1: 400.146400 MHz

F2 - Processing parameters  
SI: 65536  
SF: 400.1464047 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f2 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f3 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0  
PC: 2.00

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
NAME: 096\_VI\_15283  
EXPNO: 3  
PROCNO: 1

F2 - Acquisition Parameters  
DATE\_: 20111031  
TIME: 15.08  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H-  
PULPROG: zgpg30  
SOLVENT: CDCl3  
NS: 128  
DS: 2  
SWH: 20000.031 Hz  
FIDRES: 0.462388 Hz  
AQ: 1.0812940 sec  
RG: 368.1  
AQ: 18.500 usec  
SFO: 125.7603500 MHz  
TE: 298.0 K  
D1: 0.25000000 sec  
MCHSET: 0.00000000 sec  
MCHW: 0.00000000 sec  
MCHW: 0.00016000 sec  
MCHW: 0.00000000 sec  
MCHW: 0.01500000 sec  
PC: 51.00 usec

===== CHANNEL f1 13C =====  
NUC1: 13C  
P1: 15.00 usec  
PL1: 0.00 dB  
SFO1: 125.7603500 MHz

===== CHANNEL f2 1H =====  
NUC2: 1H  
P2: 1.00 usec  
PL2: 0.00 dB  
SFO2: 400.1464000 MHz

===== CHANNEL f3 1H =====  
NUC3: 1H  
P3: 1.00 usec  
PL3: 0.00 dB  
SFO3: 400.1464000 MHz

F2 - Processing parameters  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f4 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

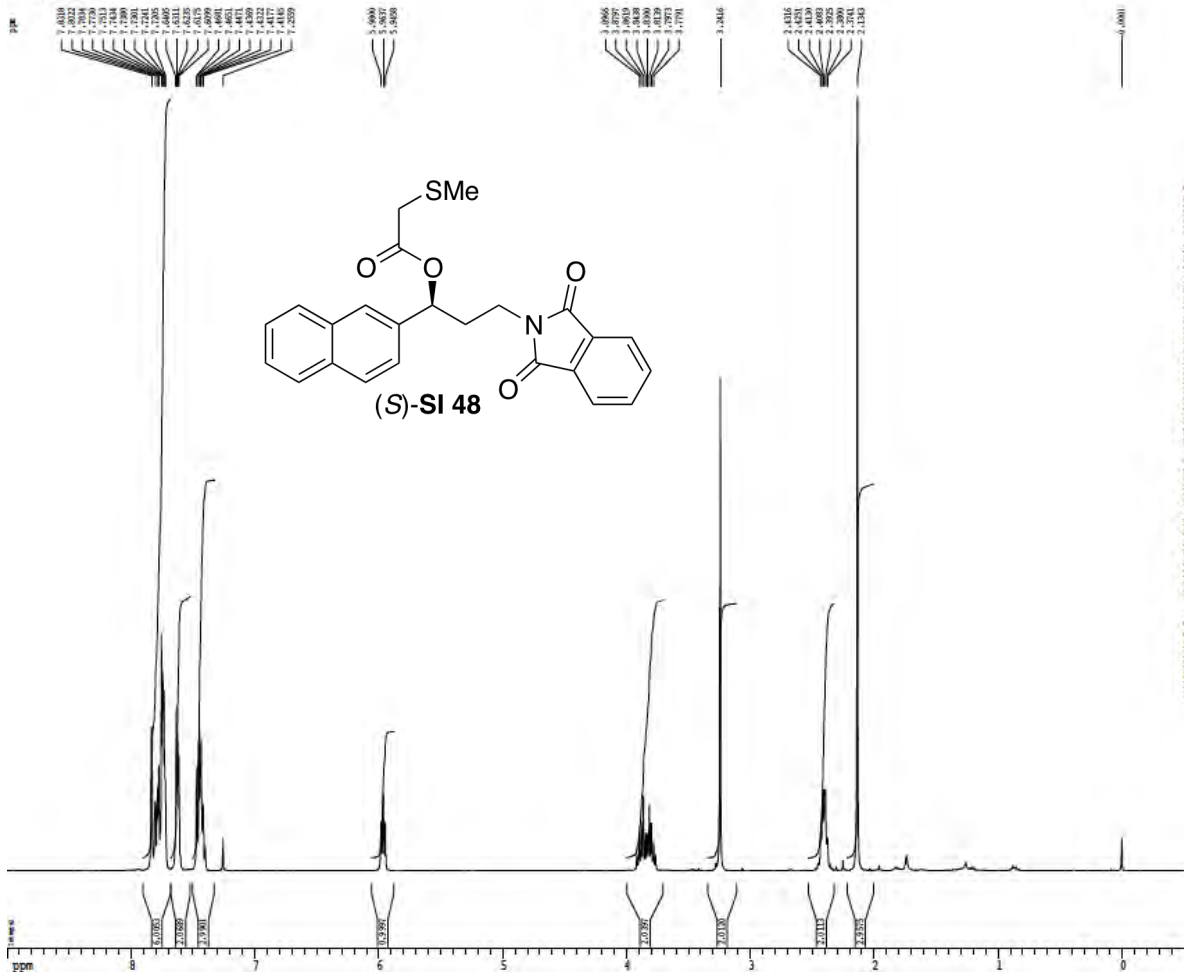
===== CHANNEL f5 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f6 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f7 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

===== CHANNEL f8 =====  
SI: 65536  
SF: 125.7603500 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 2.00

1H spectrum



Current Data Parameters  
 NAME: NMR1  
 EXPNO: 3  
 PROCNO: 1

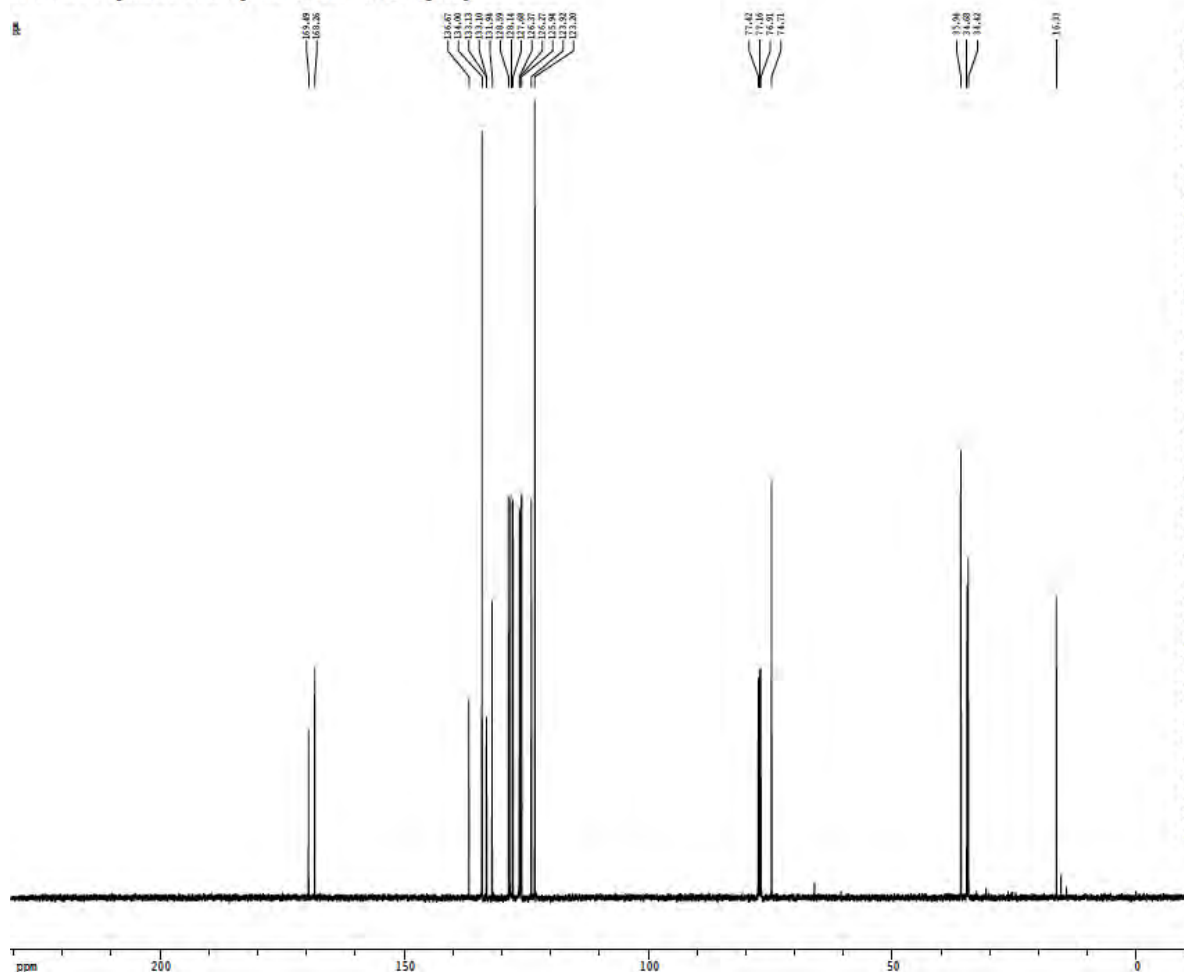
F2 - Acquisition Parameters  
 Date\_: 20121201  
 TIME: 15.01  
 INSTRUM: spect  
 PROCNO: 5  
 PULPROG: zgpg30  
 DS: 4096  
 SWH: 6410.256 Hz  
 FWHZ: 0.897813 Hz  
 AQ: 5.118579 sec  
 RG: 65.6  
 SW: 78.000 uspc  
 SF: 400.146000 MHz  
 F2: 398.111  
 SI: 0.1000000 sec  
 WDELTA: 0.0000000 sec  
 WDETA: 0.0100000 sec

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 12.00 uspc  
 PL1: -0.60 dB  
 SFO1: 400.126000 MHz

F1 - Processing parameters  
 SI: 4096  
 SF: 400.126000 MHz  
 DS: 4  
 SW: 78.000 Hz  
 W: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 2.00

1D NMR plot parameters  
 SI: 22.80 cm  
 CF: 15.00 cm  
 FID: 9.000 ppm  
 F1: 398.111 Hz  
 F2: -1.500 ppm  
 F3: -200.00 Hz  
 FWHZ: 0.41662 ppm/cm  
 XCHN: 166.72088 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 NAME: NMR1  
 EXPNO: 2  
 PROCNO: 1

F1 - Acquisition Parameters  
 Date\_: 201212  
 TIME: 8.37  
 INSTRUM: spect  
 PROCNO: 5  
 PULPROG: zgpg30  
 DS: 4096  
 SWH: 6410.256 Hz  
 FWHZ: 0.897813 Hz  
 AQ: 5.118579 sec  
 RG: 65.6  
 SW: 78.000 uspc  
 SF: 400.146000 MHz  
 F1: 398.111  
 SI: 0.1000000 sec  
 WDELTA: 0.0000000 sec  
 WDETA: 0.0100000 sec

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 15.00 uspc  
 PL1: 0.00 dB  
 SFO1: 125.7642548 MHz

===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 100.00 uspc  
 PL2: 1.00 dB  
 SFO2: 500.1364514 MHz

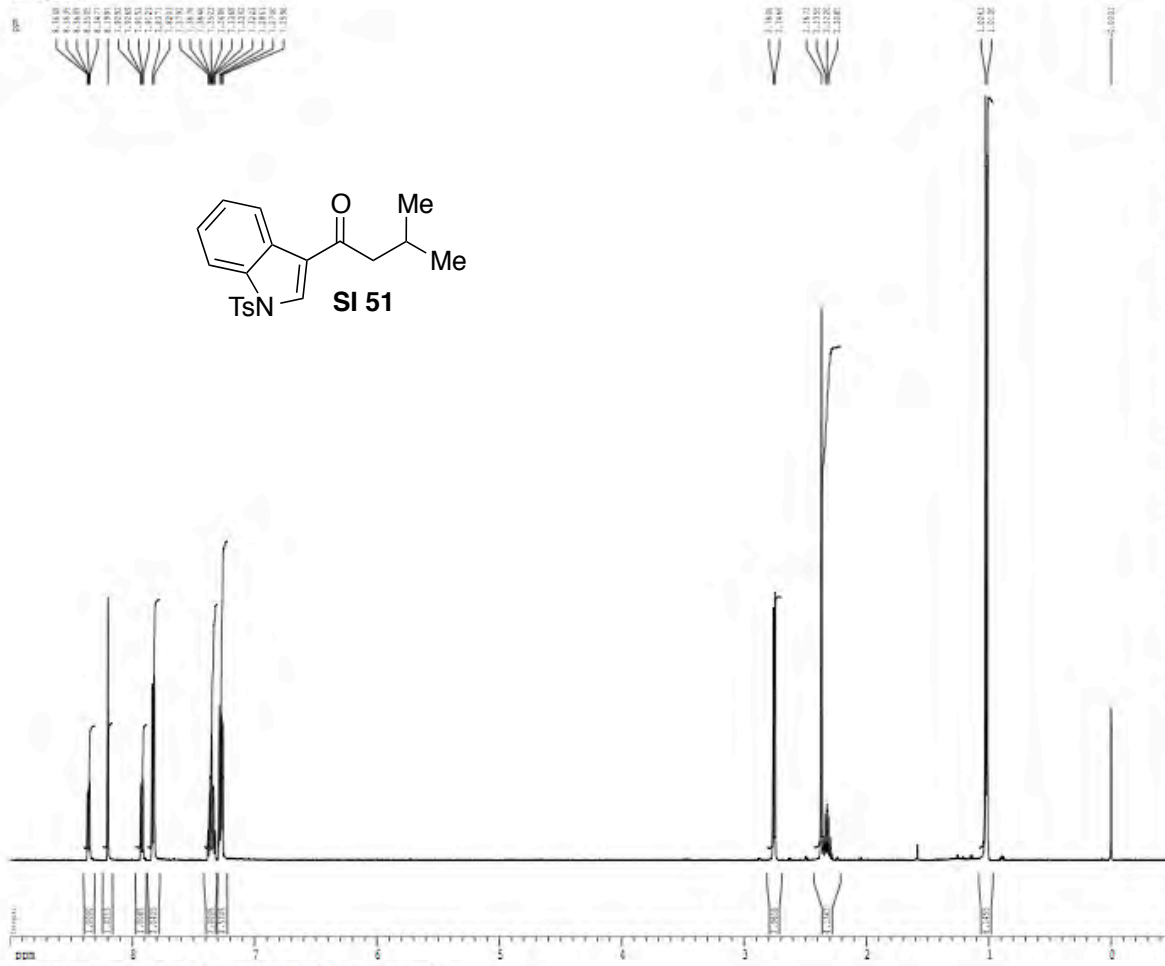
===== CHANNEL f3 =====  
 NUC3: 13C  
 P3: 0.00 %  
 PL3: 0.00 %  
 SFO3: 0.00 MHz  
 SFO4: 50.00 MHz  
 SFO5: 50.00 MHz  
 SFO6: 500.00 MHz  
 SFO7: 1000.00 MHz

F1 - Processing parameters  
 SI: 4096  
 SF: 125.7642548 MHz  
 DS: 4  
 SW: 100.000 Hz  
 W: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 2.00

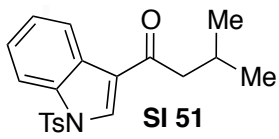
1D NMR plot parameters  
 SI: 22.80 cm  
 CF: 15.00 cm  
 FID: 330.457 ppm  
 F1: 398.111 Hz  
 F2: -1.500 ppm  
 F3: -1200.00 Hz  
 FWHZ: 10.56888 ppm/cm  
 XCHN: 1370.10706 Hz/cm



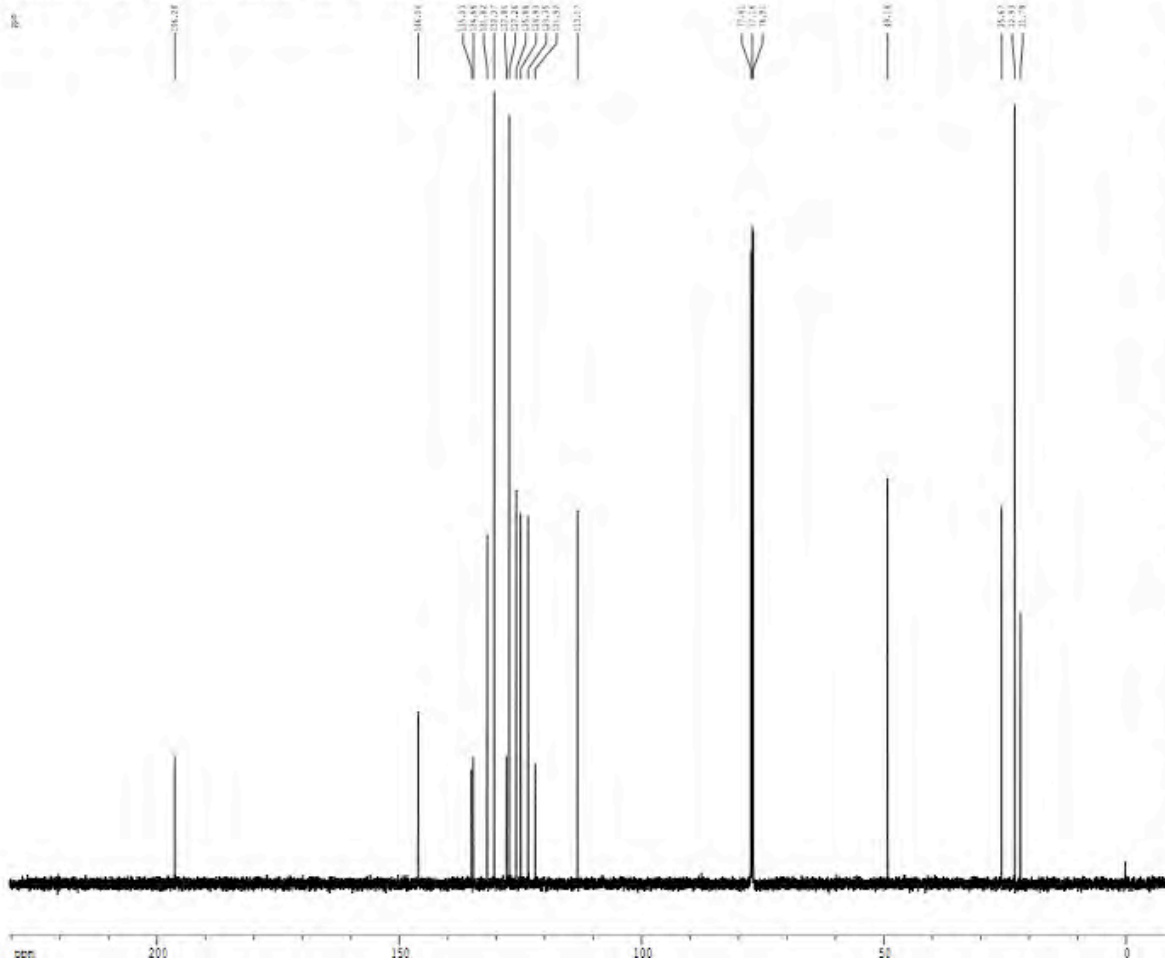
**<sup>1</sup>H spectrum**



Current Data Parameters  
 Date 201214  
 Time 20:00  
 INSTRUM spect  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date 201214  
 Time 20:00  
 INSTRUM spect  
 PROCNO 1  
 F2 - Processing parameters  
 SI 4309  
 SF 501.215013 MHz  
 SI 4309  
 SF 501.215013 MHz  
 SI 4309  
 SF 501.215013 MHz  
 SI 4309  
 SF 501.215013 MHz  
 SI 4309  
 SF 501.215013 MHz  
 SI 4309  
 SF 501.215013 MHz

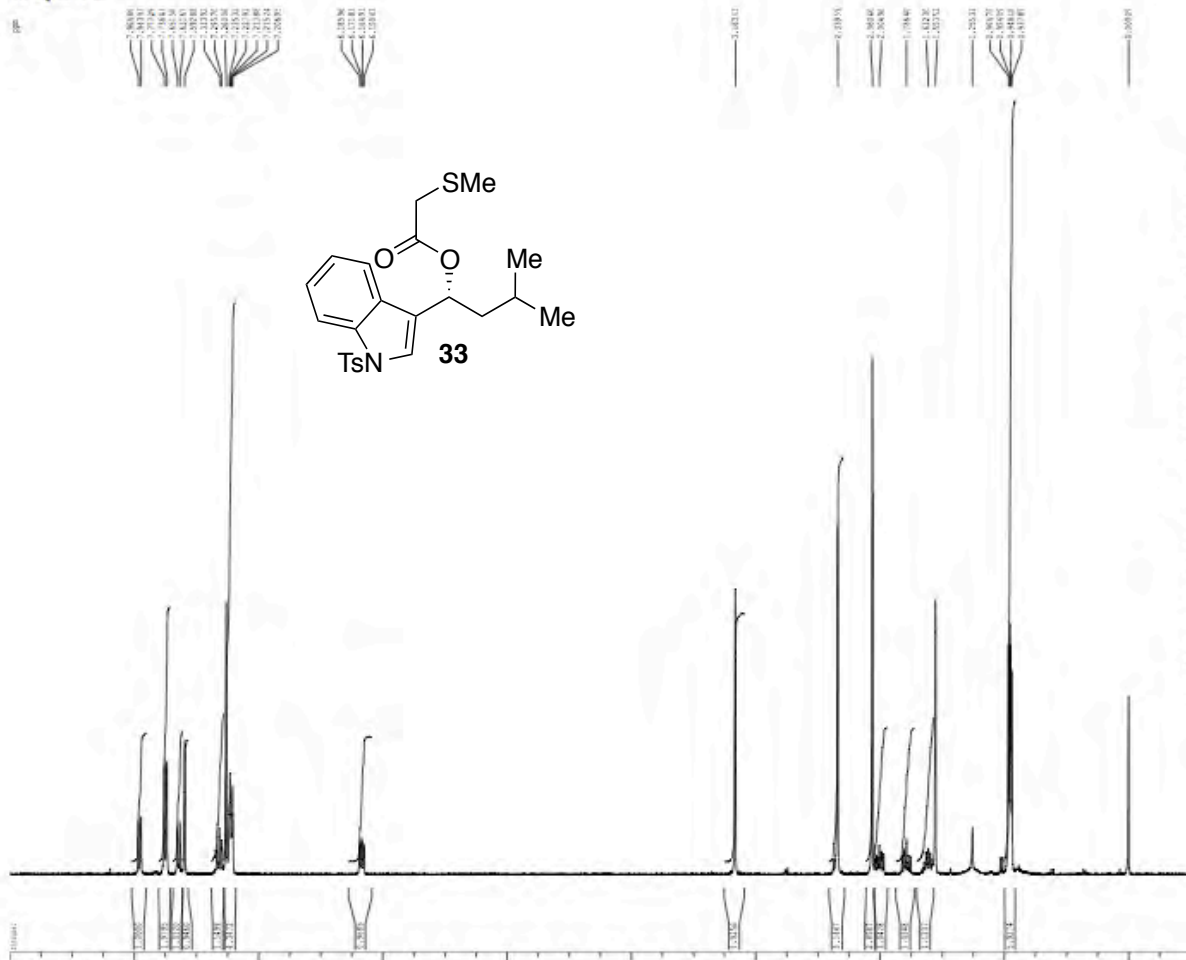


**Z-restored spin-echo 13C spectrum with 1H decoupling**



Current Data Parameters  
 Date 201214  
 Time 20:00  
 INSTRUM spect  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date 201214  
 Time 20:00  
 INSTRUM spect  
 PROCNO 1  
 F2 - Processing parameters  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz  
 SI 4309  
 SF 125.761415 MHz

1H spectrum

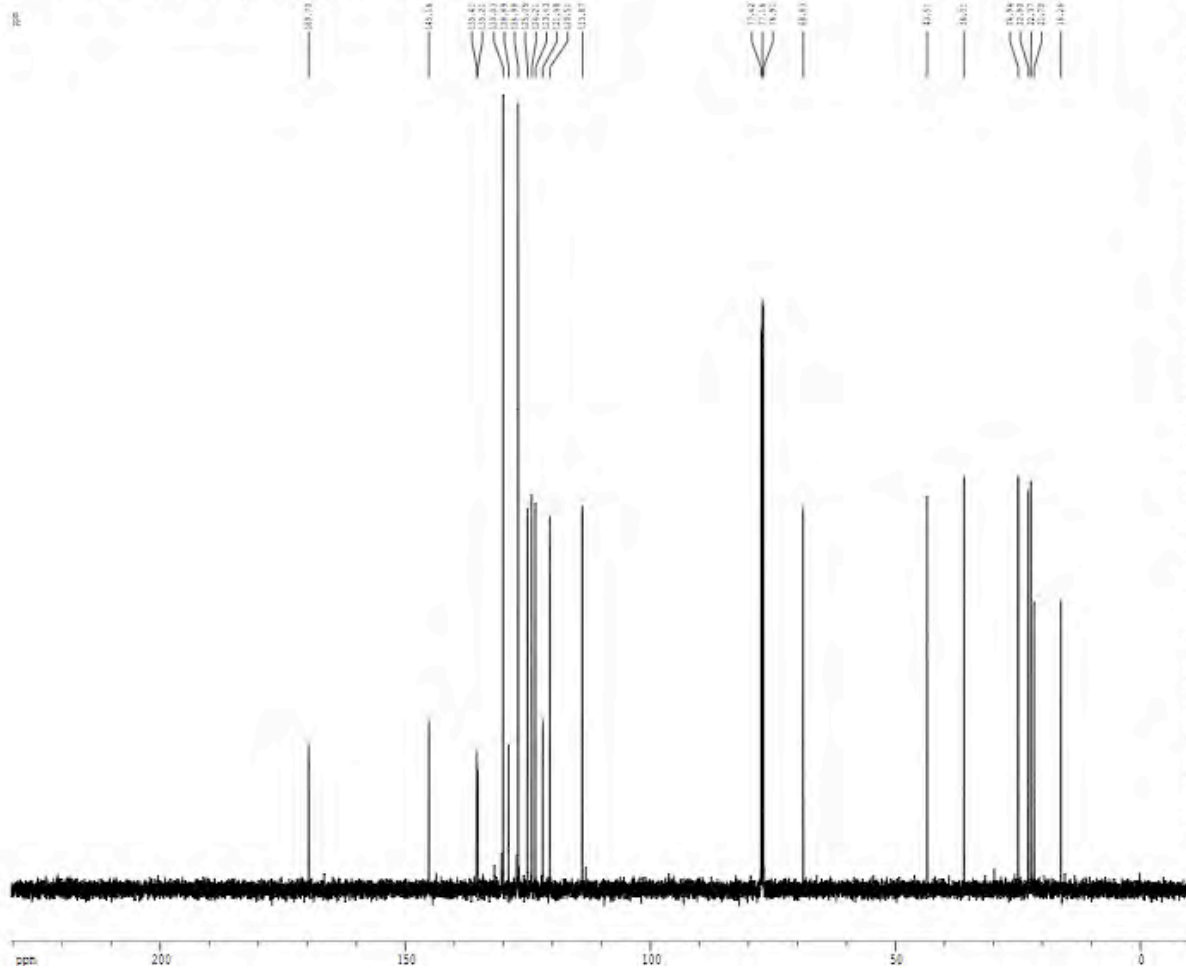


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Current Data Parameters
NAME          44424
EXPNO        04-4-134a-1
PROCNO       1
F2 - Acquisition Parameters
Date_         201207
Time          22.20
INSTRUM      spect
PROBHD       5 mm ZPP 1H/1
PULPROG      zgpg30
PCPDPRG2     cpdprg2
SI           65536
AQ           0.187500 sec
RG           409.6
WDW           EM
SS           2
LB           3.00 Hz
GB           0
PC           1.50 sec
TE           300.2 K
NUC1         13C
NUC2         1H
ACQRES      0.0002000 sec
AQRES      0.0002000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Processing parameters
SI          65536
SF          400.1426010 MHz
AQ          0.187500 sec
RG          409.6
WDW          EM
SS          2
LB          3.00 Hz
GB          0
PC          1.50
===== CHANNEL f2 =====
NUC1        1H
P1          12.00 usec
PL1         -0.40 dB
SFO         400.1426010 MHz
F2 - Acquisition Parameters
Date_         201207
Time          22.20
INSTRUM      spect
PROBHD       5 mm ZPP 1H/1
PULPROG      zgpg30
PCPDPRG2     cpdprg2
SI           65536
AQ           0.187500 sec
RG           409.6
WDW           EM
SS           2
LB           3.00 Hz
GB           0
PC           1.50
TE           300.2 K
NUC1         13C
NUC2         1H
ACQRES      0.0002000 sec
AQRES      0.0002000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Processing parameters
SI          65536
SF          125.7618150 MHz
AQ          0.187500 sec
RG          409.6
WDW          EM
SS          2
LB          3.00 Hz
GB          0
PC          1.50
===== CHANNEL f2 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Acquisition Parameters
Date_         201207
Time          22.20
INSTRUM      spect
PROBHD       5 mm ZPP 1H/1
PULPROG      zgpg30
PCPDPRG2     cpdprg2
SI           65536
AQ           0.187500 sec
RG           409.6
WDW           EM
SS           2
LB           3.00 Hz
GB           0
PC           1.50
TE           300.2 K
NUC1         13C
NUC2         1H
ACQRES      0.0002000 sec
AQRES      0.0002000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Processing parameters
SI          65536
SF          125.7618150 MHz
AQ          0.187500 sec
RG          409.6
WDW          EM
SS          2
LB          3.00 Hz
GB          0
PC          1.50
===== CHANNEL f2 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz

```

Z-restored spin-echo 13C spectrum with 1H decoupling

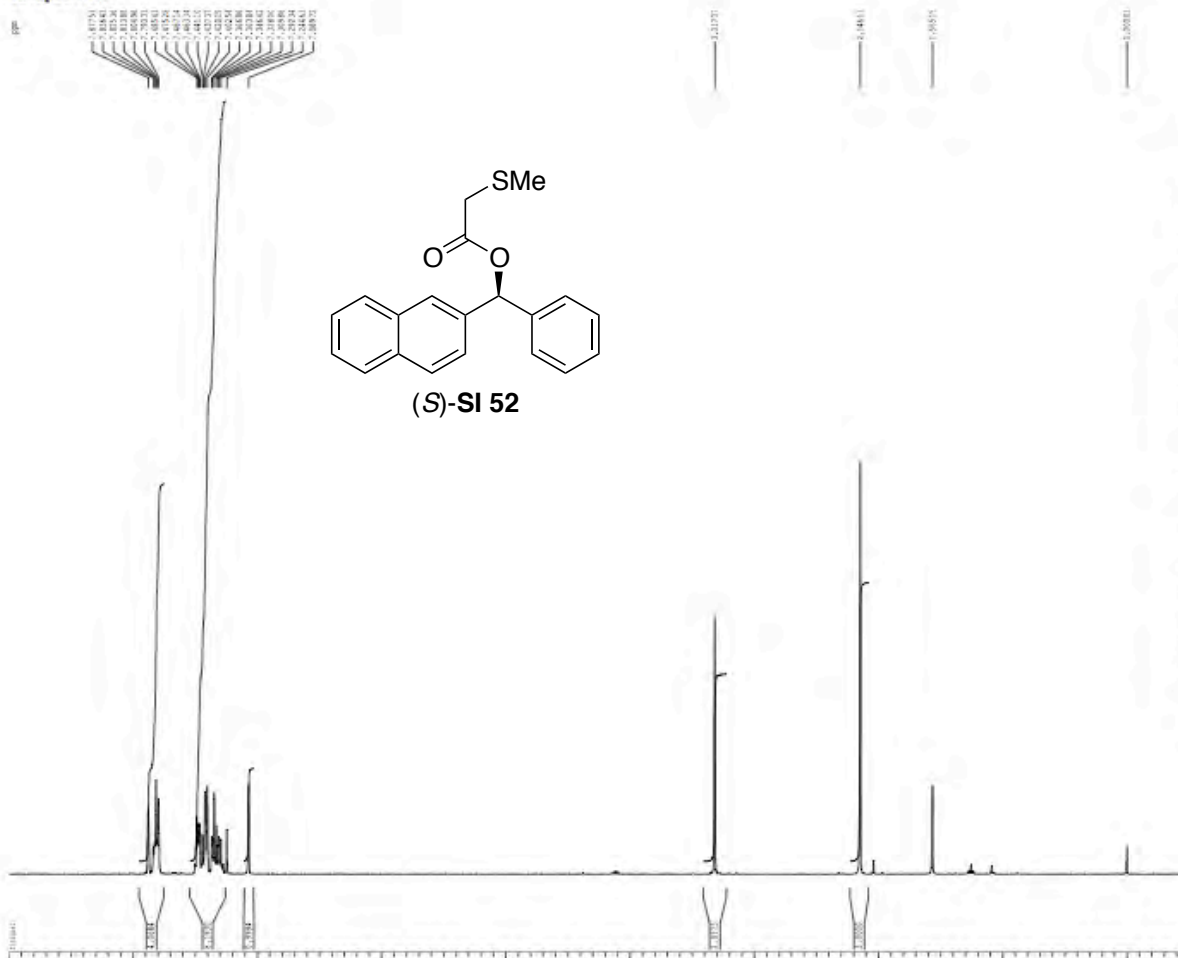


```

Current Data Parameters
NAME          44424
EXPNO        04-4-134a-1
PROCNO       1
F2 - Acquisition Parameters
Date_         201207
Time          22.20
INSTRUM      spect
PROBHD       5 mm ZPP 1H/1
PULPROG      zgpg30
PCPDPRG2     cpdprg2
SI           65536
AQ           0.187500 sec
RG           409.6
WDW           EM
SS           2
LB           3.00 Hz
GB           0
PC           1.50
TE           300.2 K
NUC1         13C
NUC2         1H
ACQRES      0.0002000 sec
AQRES      0.0002000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Processing parameters
SI          65536
SF          125.7618150 MHz
AQ          0.187500 sec
RG          409.6
WDW          EM
SS          2
LB          3.00 Hz
GB          0
PC          1.50
===== CHANNEL f2 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Acquisition Parameters
Date_         201207
Time          22.20
INSTRUM      spect
PROBHD       5 mm ZPP 1H/1
PULPROG      zgpg30
PCPDPRG2     cpdprg2
SI           65536
AQ           0.187500 sec
RG           409.6
WDW           EM
SS           2
LB           3.00 Hz
GB           0
PC           1.50
TE           300.2 K
NUC1         13C
NUC2         1H
ACQRES      0.0002000 sec
AQRES      0.0002000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz
F2 - Processing parameters
SI          65536
SF          125.7618150 MHz
AQ          0.187500 sec
RG          409.6
WDW          EM
SS          2
LB          3.00 Hz
GB          0
PC          1.50
===== CHANNEL f2 =====
NUC1        13C
P1          12.00 usec
PL1         -0.40 dB
SFO         101.254999 MHz

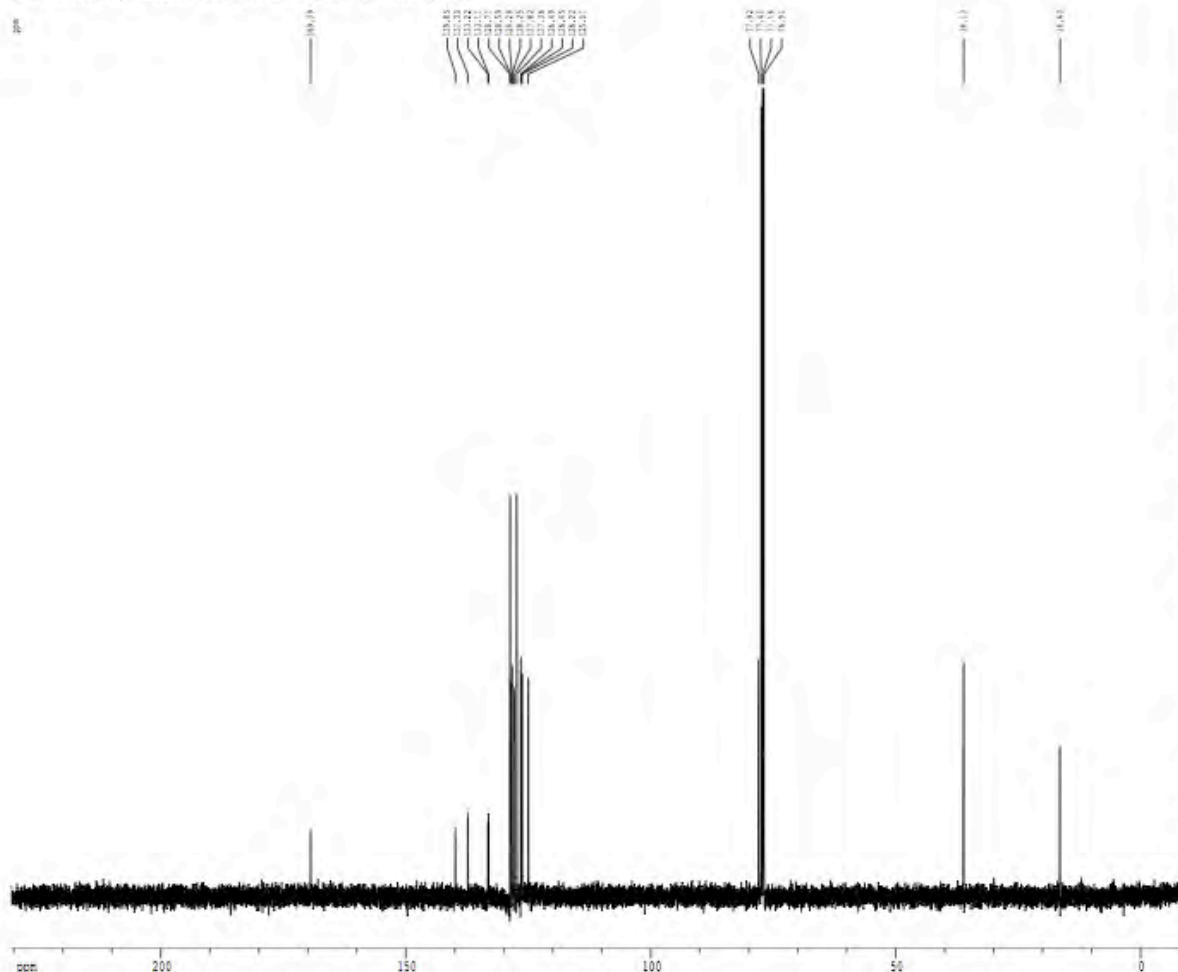
```

1H spectrum



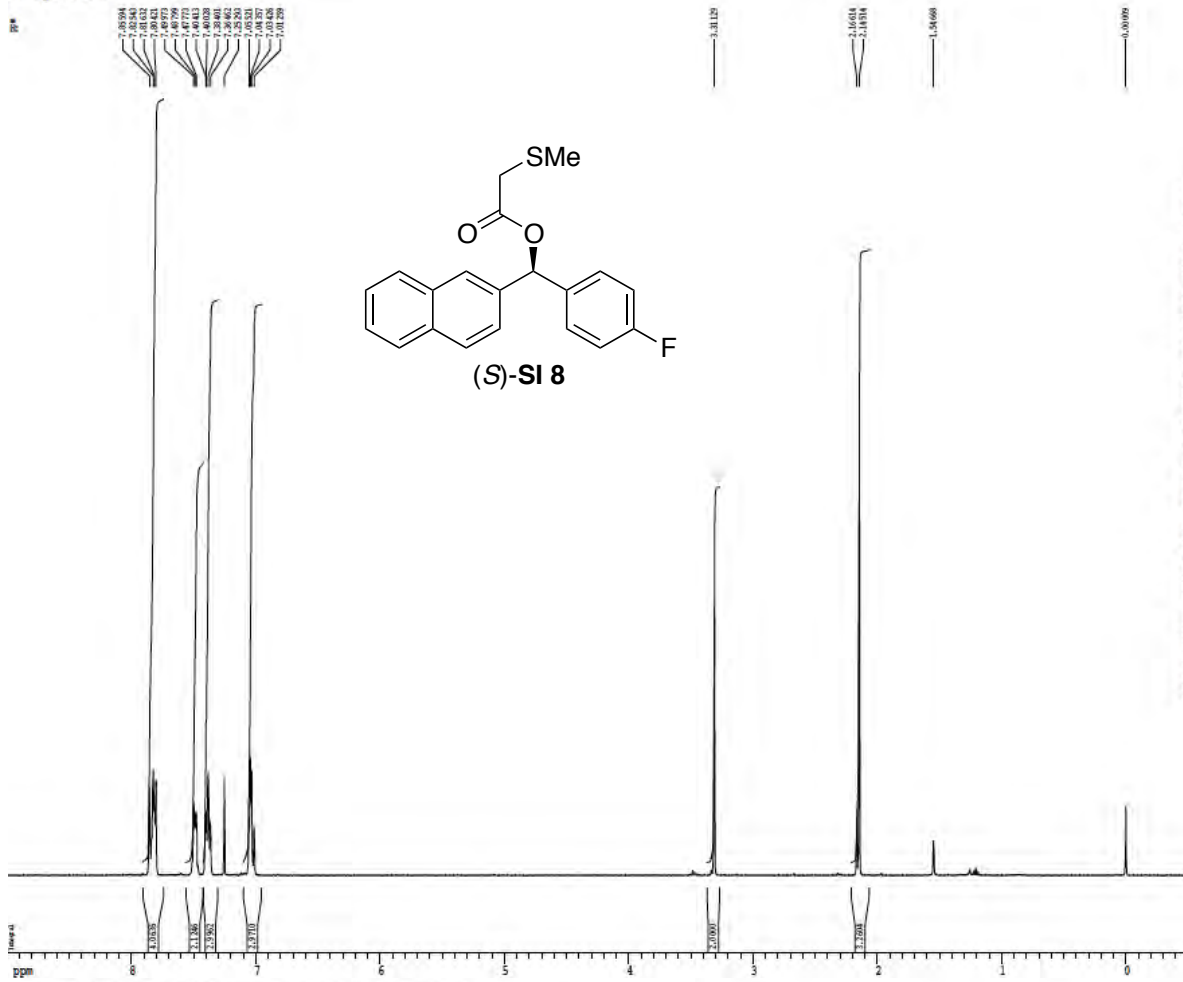
Current Data Parameters  
 Date: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Acquisition Parameters  
 Date\_: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Processing Parameters  
 SI: 6218  
 SF: 400.150072 MHz  
 AS: 0  
 DS: 4  
 SS: 2.00 Hz  
 SC: 2.00  
 IC: 2.00  
 LC: 2.00  
 PC: 2.00  
 F2 - Acquisition Parameters  
 Date\_: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Processing Parameters  
 SI: 6218  
 SF: 400.150072 MHz  
 AS: 0  
 DS: 4  
 SS: 2.00 Hz  
 SC: 2.00  
 IC: 2.00  
 LC: 2.00  
 PC: 2.00  
 F2 - Acquisition Parameters  
 Date\_: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Processing Parameters  
 SI: 6218  
 SF: 400.150072 MHz  
 AS: 0  
 DS: 4  
 SS: 2.00 Hz  
 SC: 2.00  
 IC: 2.00  
 LC: 2.00  
 PC: 2.00

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 Date: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Acquisition Parameters  
 Date\_: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Processing Parameters  
 SI: 6218  
 SF: 400.150072 MHz  
 AS: 0  
 DS: 4  
 SS: 2.00 Hz  
 SC: 2.00  
 IC: 2.00  
 LC: 2.00  
 PC: 2.00  
 F2 - Acquisition Parameters  
 Date\_: 11/20/04  
 Time: 11:11  
 INSTRUM: spect  
 PROCNO: 5  
 F2 - Processing Parameters  
 SI: 6218  
 SF: 400.150072 MHz  
 AS: 0  
 DS: 4  
 SS: 2.00 Hz  
 SC: 2.00  
 IC: 2.00  
 LC: 2.00  
 PC: 2.00

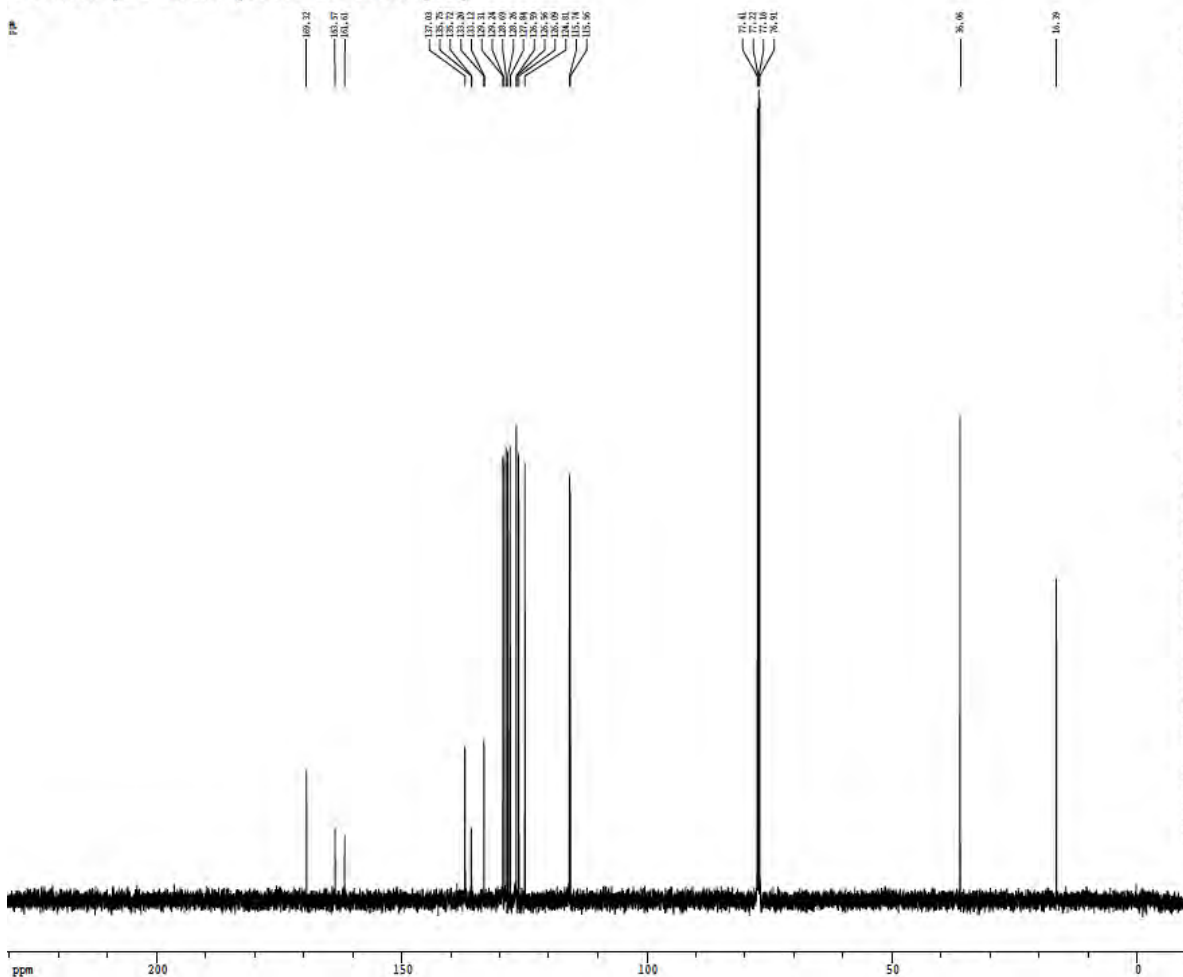
1H spectrum



Current Data Parameters  
 USER smf6a  
 NAME ns-4-2118-1  
 EXPNO 1  
 PROCNO 1

F1 - Acquisition Parameters  
 Date\_ 20110520  
 Time 18.22  
 INSTRUM spect  
 PULPROG zgpg30  
 PROCNO 5 mm QNP 31P/CP  
 F2 - Acquisition Parameters  
 Date\_ 20110520  
 Time 18.22  
 INSTRUM spect  
 PULPROG zgpg30  
 PROCNO 5 mm QNP 31P/CP  
 F2 - Acquisition Parameters  
 Date\_ 20110520  
 Time 18.22  
 INSTRUM spect  
 PULPROG zgpg30  
 PROCNO 5 mm QNP 31P/CP

Z-restored spin-echo 13C spectrum with 1H decoupling

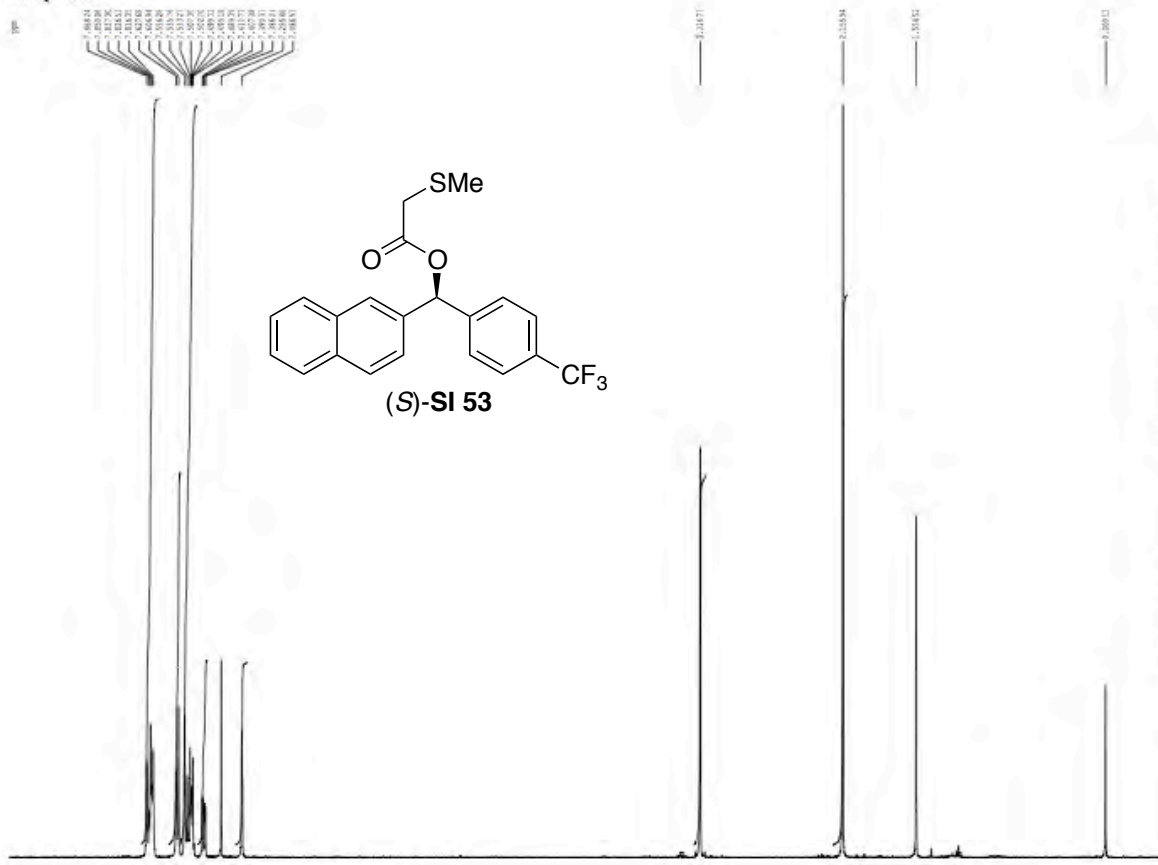


Current Data Parameters  
 USER smf6a  
 NAME ns-4-2118-1  
 EXPNO 4  
 PROCNO 1

F1 - Acquisition Parameters  
 Date\_ 20110520  
 Time 18.43  
 INSTRUM spect  
 PULPROG zgpg30  
 PROCNO 5 mm QNP 13C  
 F2 - Acquisition Parameters  
 Date\_ 20110520  
 Time 18.43  
 INSTRUM spect  
 PULPROG zgpg30  
 PROCNO 5 mm QNP 13C



1H spectrum



```

===== CHANNEL F1 =====
NUC1 13C
P1 120.00 usec
PL1 0.00 dB
SFO1 400.125874 MHz

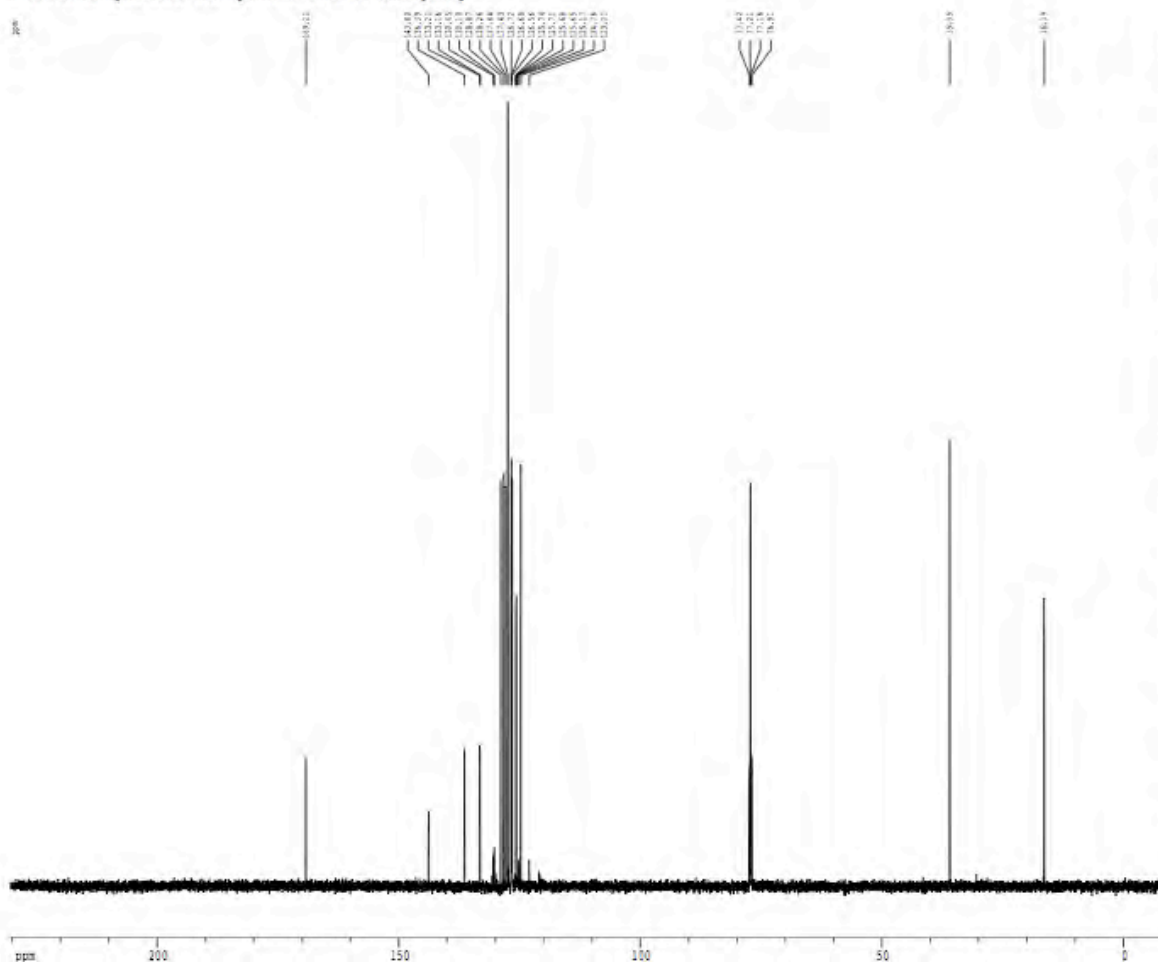
F2 - Acquisition Parameters
Date_ 20121111
Time 10.11
INSTRUM spect
PROBHD 1 mm QNP 1H/13
PULPROG zgpg30
PC 45.00
TD 65536
SOLVENT dms-d6
NS 2
DS 4
SWH 9415.296 Hz
F2RES 0.59743 Hz
AQ 3.1118970 sec
RG 320.0
WDW EM
SS 78.000 usec
LB 0.000000 usec
GB 0.000000 usec
PC 2.000000 usec
DC 0.000000 usec
===== CHANNEL F2 =====
NUC2 13C
P2 120.00 usec
PL2 0.00 dB
SFO2 400.125874 MHz

F3 - Processing parameters
SI 32768
SF 400.125874 MHz
WDW EM
SS 78.000 usec
GB 0.000000 usec
PC 2.000000 usec
===== CHANNEL F3 =====
NUC3 1H
P3 120.00 usec
PL3 0.00 dB
SFO3 400.125874 MHz

F4 - Acquisition Parameters
Date_ 20121111
Time 10.11
INSTRUM spect
PROBHD 1 mm QNP 1H/13
PULPROG zgpg30
PC 45.00
TD 65536
SOLVENT dms-d6
NS 2
DS 4
SWH 9415.296 Hz
F4RES 0.59743 Hz
AQ 3.1118970 sec
RG 320.0
WDW EM
SS 78.000 usec
LB 0.000000 usec
GB 0.000000 usec
PC 2.000000 usec
DC 0.000000 usec
===== CHANNEL F5 =====
NUC5 13C
P5 120.00 usec
PL5 0.00 dB
SFO5 400.125874 MHz

F6 - Processing parameters
SI 32768
SF 400.125874 MHz
WDW EM
SS 78.000 usec
GB 0.000000 usec
PC 2.000000 usec
===== CHANNEL F6 =====
NUC6 1H
P6 120.00 usec
PL6 0.00 dB
SFO6 400.125874 MHz
  
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```

===== CHANNEL F1 =====
NUC1 13C
P1 120.00 usec
PL1 0.00 dB
SFO1 400.125874 MHz

F2 - Acquisition Parameters
Date_ 20121111
Time 10.11
INSTRUM spect
PROBHD 1 mm QNP 1H/13
PULPROG zgpg30
PC 45.00
TD 65536
SOLVENT dms-d6
NS 2
DS 4
SWH 9415.296 Hz
F2RES 0.59743 Hz
AQ 3.1118970 sec
RG 320.0
WDW EM
SS 78.000 usec
LB 0.000000 usec
GB 0.000000 usec
PC 2.000000 usec
DC 0.000000 usec
===== CHANNEL F2 =====
NUC2 13C
P2 120.00 usec
PL2 0.00 dB
SFO2 400.125874 MHz

F3 - Processing parameters
SI 32768
SF 400.125874 MHz
WDW EM
SS 78.000 usec
GB 0.000000 usec
PC 2.000000 usec
===== CHANNEL F3 =====
NUC3 1H
P3 120.00 usec
PL3 0.00 dB
SFO3 400.125874 MHz

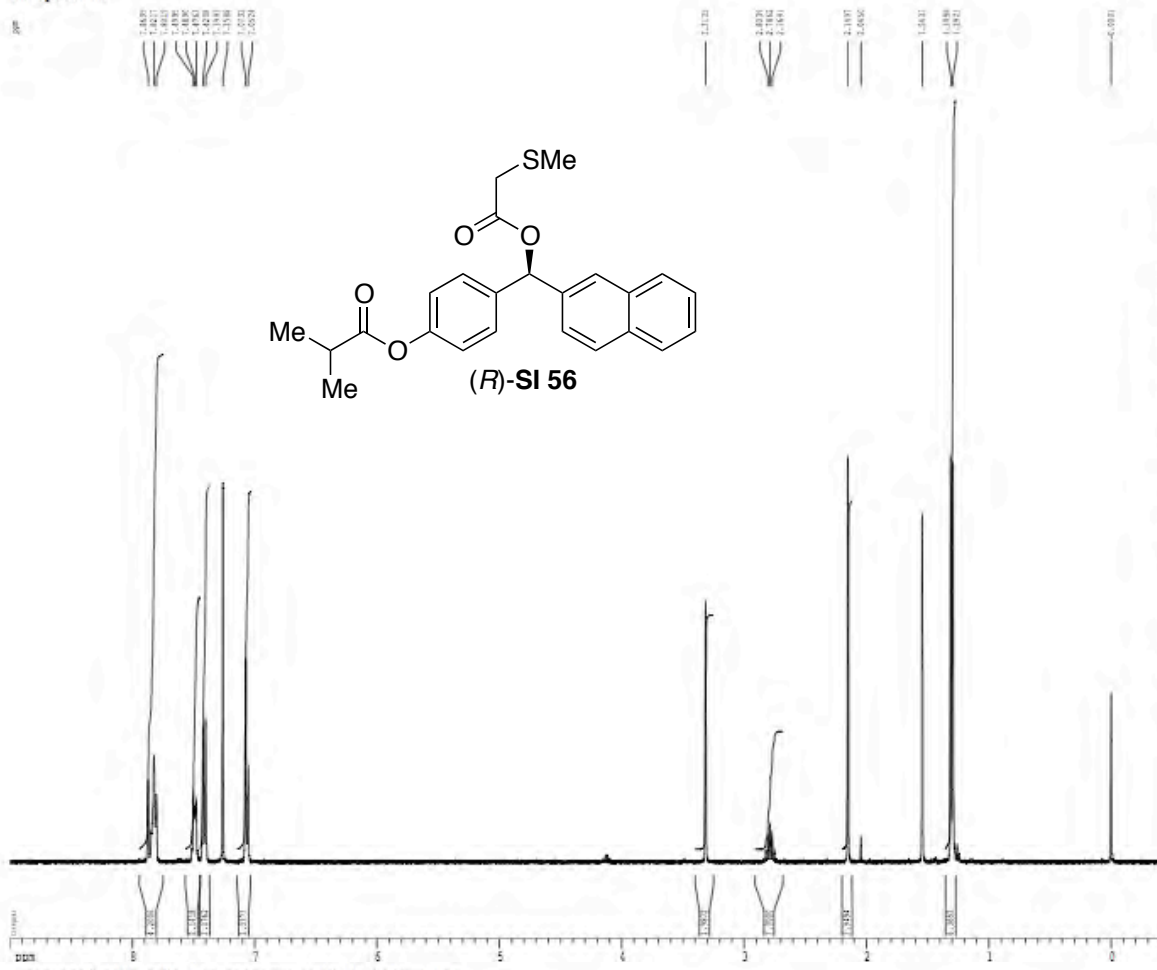
F4 - Acquisition Parameters
Date_ 20121111
Time 10.11
INSTRUM spect
PROBHD 1 mm QNP 1H/13
PULPROG zgpg30
PC 45.00
TD 65536
SOLVENT dms-d6
NS 2
DS 4
SWH 9415.296 Hz
F4RES 0.59743 Hz
AQ 3.1118970 sec
RG 320.0
WDW EM
SS 78.000 usec
LB 0.000000 usec
GB 0.000000 usec
PC 2.000000 usec
DC 0.000000 usec
===== CHANNEL F5 =====
NUC5 13C
P5 120.00 usec
PL5 0.00 dB
SFO5 400.125874 MHz

F6 - Processing parameters
SI 32768
SF 400.125874 MHz
WDW EM
SS 78.000 usec
GB 0.000000 usec
PC 2.000000 usec
===== CHANNEL F6 =====
NUC6 1H
P6 120.00 usec
PL6 0.00 dB
SFO6 400.125874 MHz
  
```



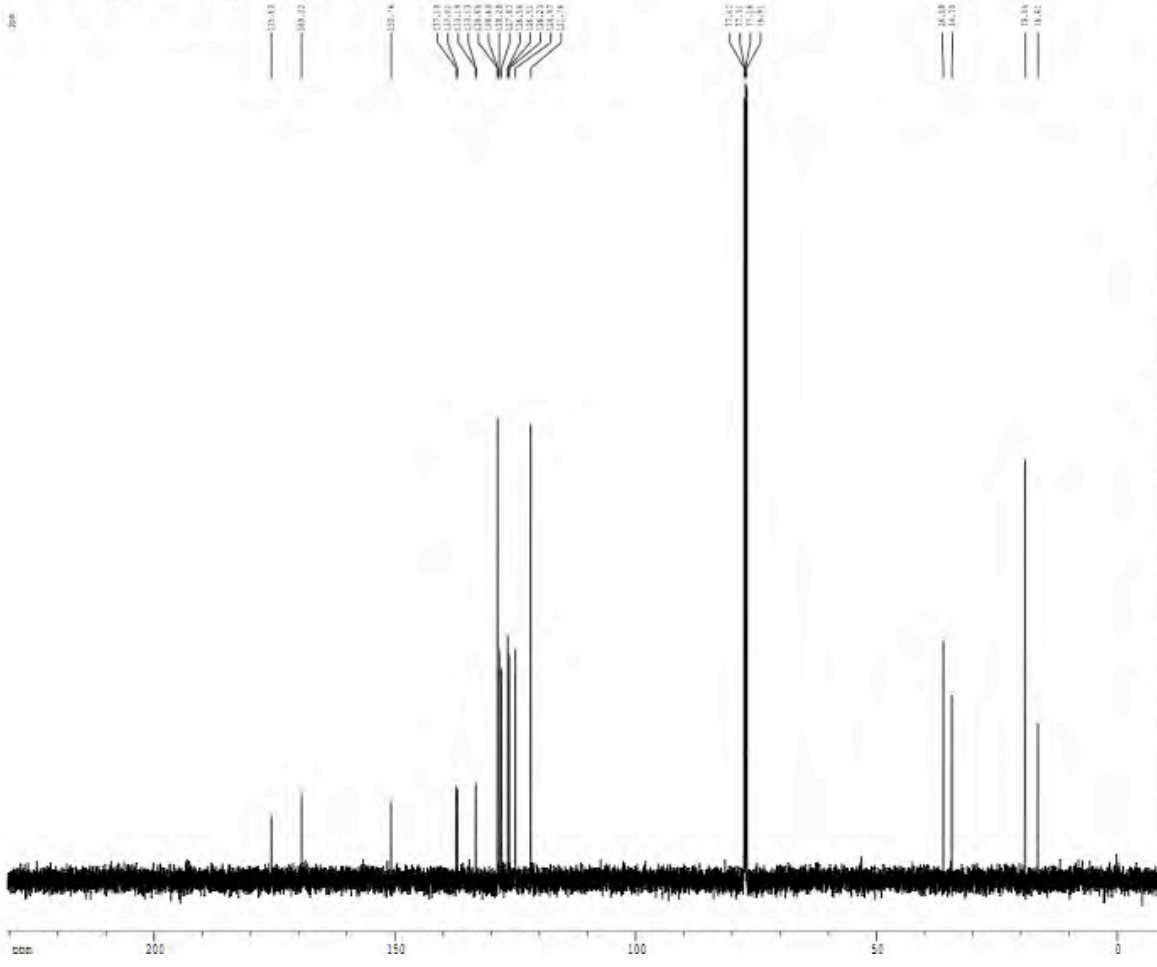


**1H spectrum**



Current Data Parameters  
 QM 1  
 NAME 05-4-15a-5  
 LSNM 1  
 PROCNO 1  
 \* Acquisition Parameters  
 Date: 18/11/10  
 Time: 15:29  
 INSTRUM spect  
 FREQ02 500.136  
 PCPROG 3.00.019  
 \* Processing parameters  
 SI 18114  
 SI 0.5000000 sec  
 SI 0.0500000 sec  
 SI 0.0500000 sec  
 SI 0.0500000 sec  
 SI 0.0500000 sec  
 SI 0.0500000 sec  
 ===== CHANNEL f2 =====  
 CH1 18  
 PU 12.00 usec  
 PL 0.00 usec  
 SFO 400.1500117 MHz  
 \* Processing parameters  
 SI 18114  
 SI 400.1500117 MHz  
 SI 30  
 SI 5.00 Hz  
 SI 9  
 SI 2.00  
 \* 13C NMR parameters  
 CH 18  
 PU 8.00 usec  
 PL 0.00 usec  
 SFO 100.6270000 MHz  
 SI 18114  
 SI 100.6270000 MHz  
 SI 1.0000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec

**Z-restored spin-echo 13C spectrum with 1H decoupling**

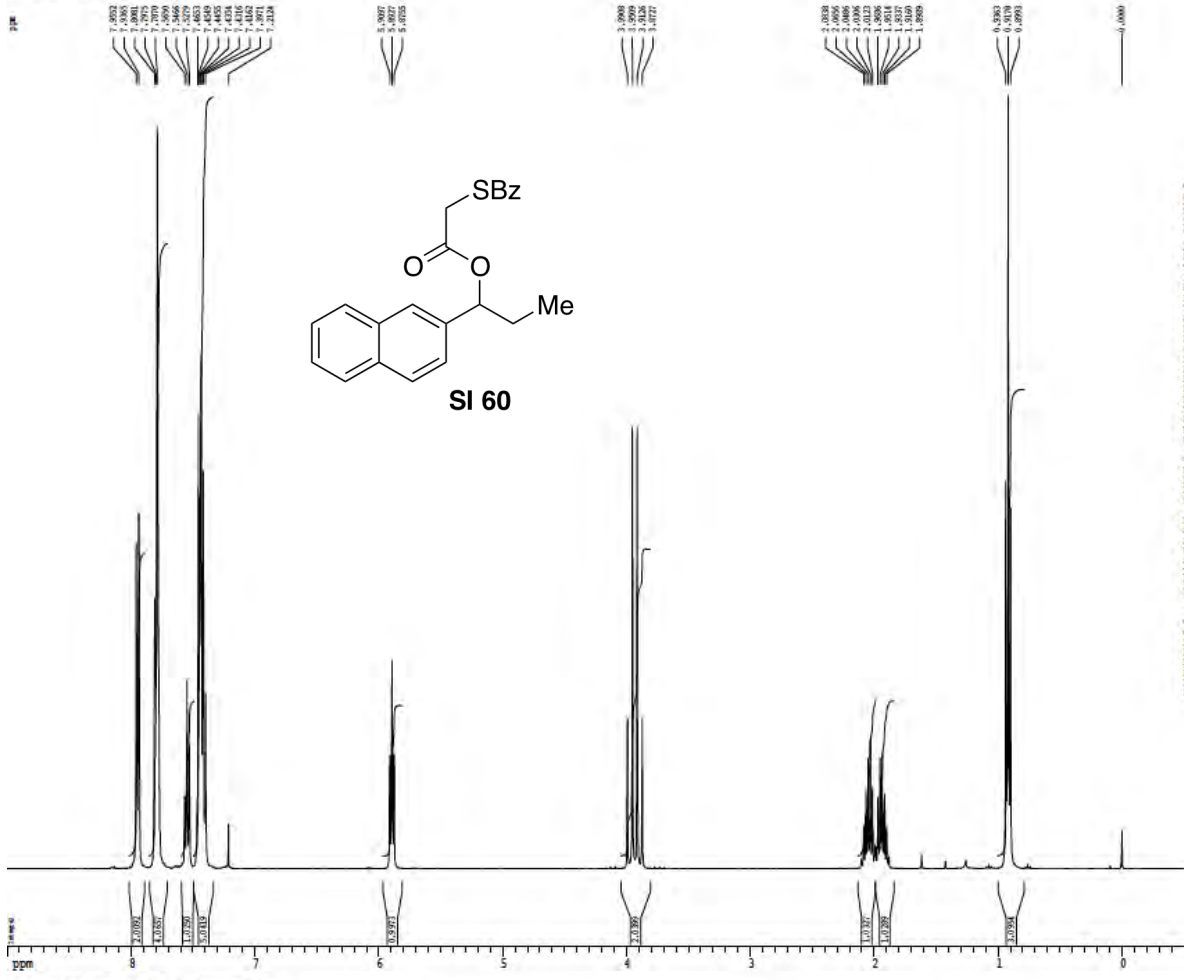


Current Data Parameters  
 QM 1  
 NAME 05-4-15a-12  
 LSNM 1  
 PROCNO 1  
 \* Acquisition Parameters  
 Date: 18/11/10  
 Time: 15:29  
 INSTRUM spect  
 FREQ02 100.627  
 PCPROG 3.00.019  
 \* Processing parameters  
 SI 18114  
 SI 400.1500117 MHz  
 SI 30  
 SI 5.00 Hz  
 SI 9  
 SI 2.00  
 \* 13C NMR parameters  
 CH 18  
 PU 8.00 usec  
 PL 0.00 usec  
 SFO 100.6270000 MHz  
 SI 18114  
 SI 100.6270000 MHz  
 SI 1.0000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 ===== CHANNEL f2 =====  
 CH1 18  
 PU 12.00 usec  
 PL 0.00 usec  
 SFO 400.1500117 MHz  
 \* Processing parameters  
 SI 18114  
 SI 400.1500117 MHz  
 SI 30  
 SI 5.00 Hz  
 SI 9  
 SI 2.00  
 \* 13C NMR parameters  
 CH 18  
 PU 8.00 usec  
 PL 0.00 usec  
 SFO 100.6270000 MHz  
 SI 18114  
 SI 100.6270000 MHz  
 SI 1.0000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec  
 SI 0.5000000 sec





1H spectrum



```

Current Data Parameters
NAME      harrow
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_     20120115
Time      21.54
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
SOLVENT   CDCl3
NS         64
DS         4
SWH        640.254 Hz
FIDRES     0.497813 Hz
AQ         5.118579 sec
RG         64
SQ         78.000 usec
RG         4.50 usec
SI         256.0 F
SF         0.18000000 sec
RG         0.08000000 sec
RG2       0.01500000 sec

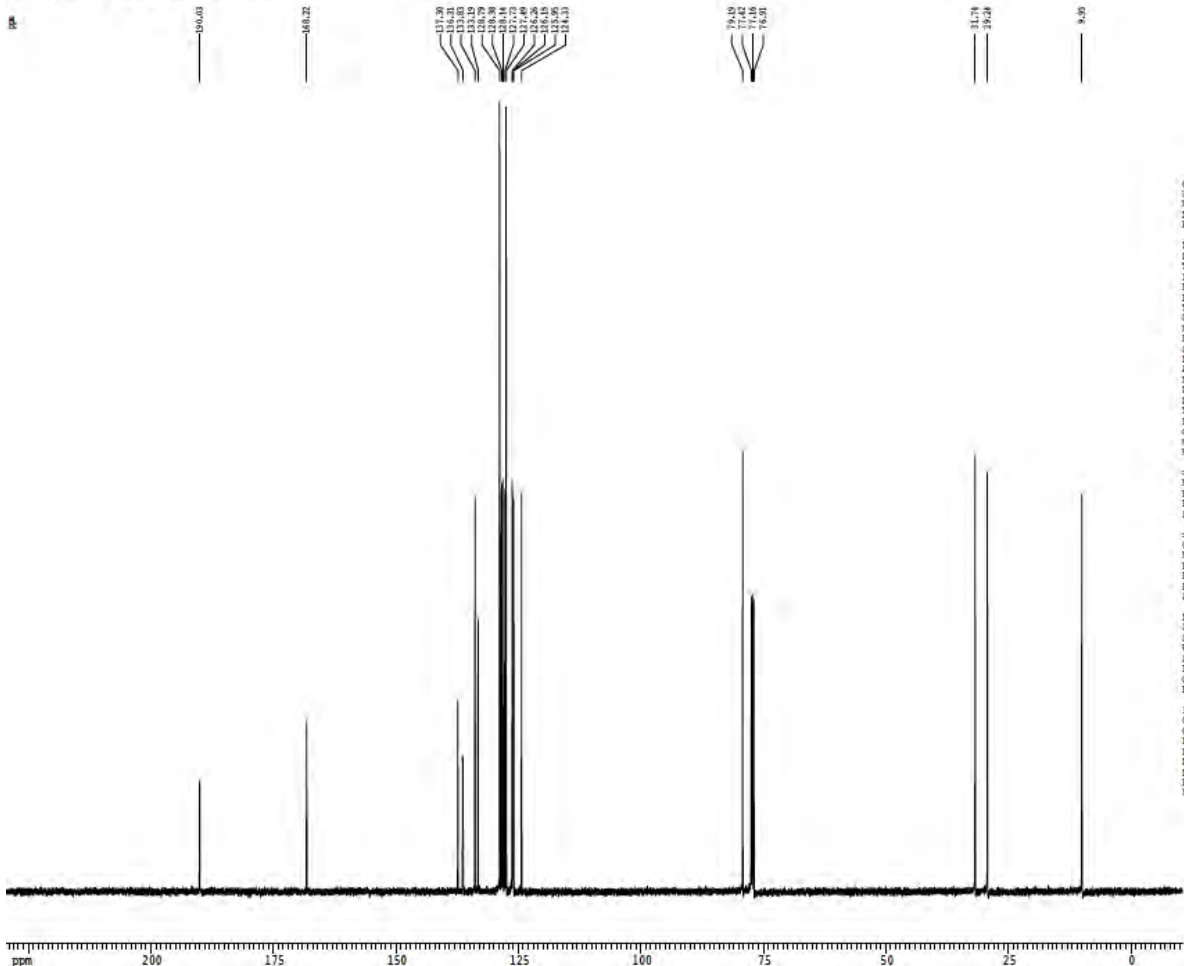
===== CHANNEL f1 =====
NUC1       1H
P1         12.00 usec
PL1        -0.60 dB
SFO1       400.1264500 MHz

F2 - Processing parameters
SI         6536
SF         400.1264500 MHz
WDW        EM
SSB         0
GB          0.30 Hz
PC         0
PC2        0
PC3        0.00

===== CHANNEL f2 =====
NUC2       13C
P2         16.00 usec
PL2        0.00 dB
SFO2       125.7613500 MHz

===== CHANNEL f3 =====
NUC3       13C
P3         16.00 usec
PL3        0.00 dB
SFO3       125.7613500 MHz
  
```

13C spectrum with 1H decoupling



```

Current Data Parameters
NAME      harrow
EXPNO    4
PROCNO   1

F2 - Acquisition Parameters
Date_     20120115
Time      21.18
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
SOLVENT   CDCl3
NS         414
DS         4
SWH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.8612940 sec
RG         4634
SQ         16.500 usec
RG         4.50 usec
SI         256.0 F
SF         0.25000000 sec
RG         0.01000000 sec
RG2       0.08000000 sec
RG3       0.01500000 sec

===== CHANNEL f1 =====
NUC1       13C
P1         17.00 usec
PL1        0.00 dB
SFO1       125.7613500 MHz

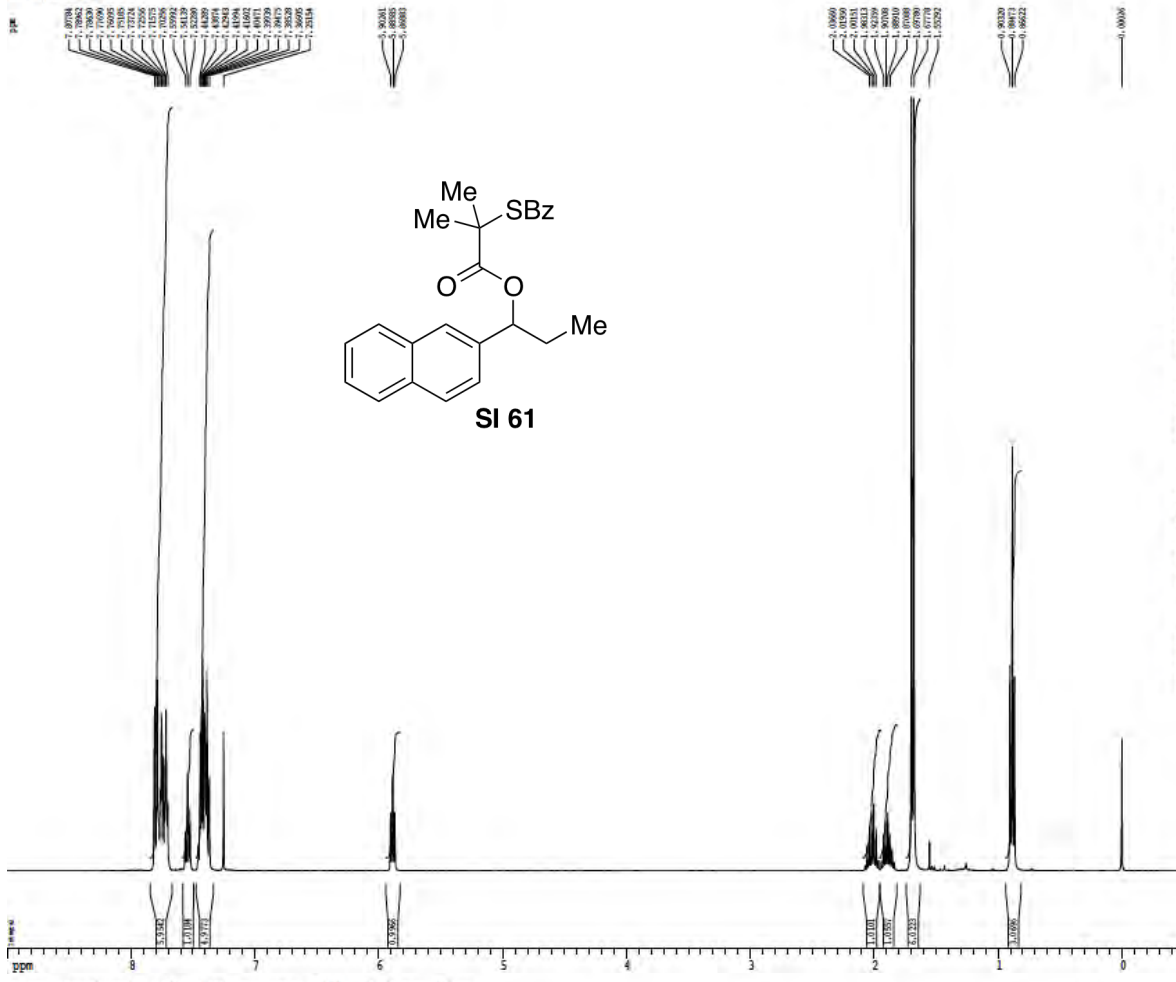
===== CHANNEL f2 =====
NUC2       13C
P2         16.00 usec
PL2        -0.00 dB
SFO2       125.7613500 MHz

===== CHANNEL f3 =====
NUC3       13C
P3         16.00 usec
PL3        -0.00 dB
SFO3       125.7613500 MHz

===== CHANNEL f4 =====
NUC4       13C
P4         16.00 usec
PL4        -0.00 dB
SFO4       125.7613500 MHz

===== CHANNEL f5 =====
NUC5       13C
P5         16.00 usec
PL5        -0.00 dB
SFO5       125.7613500 MHz
  
```

1H spectrum

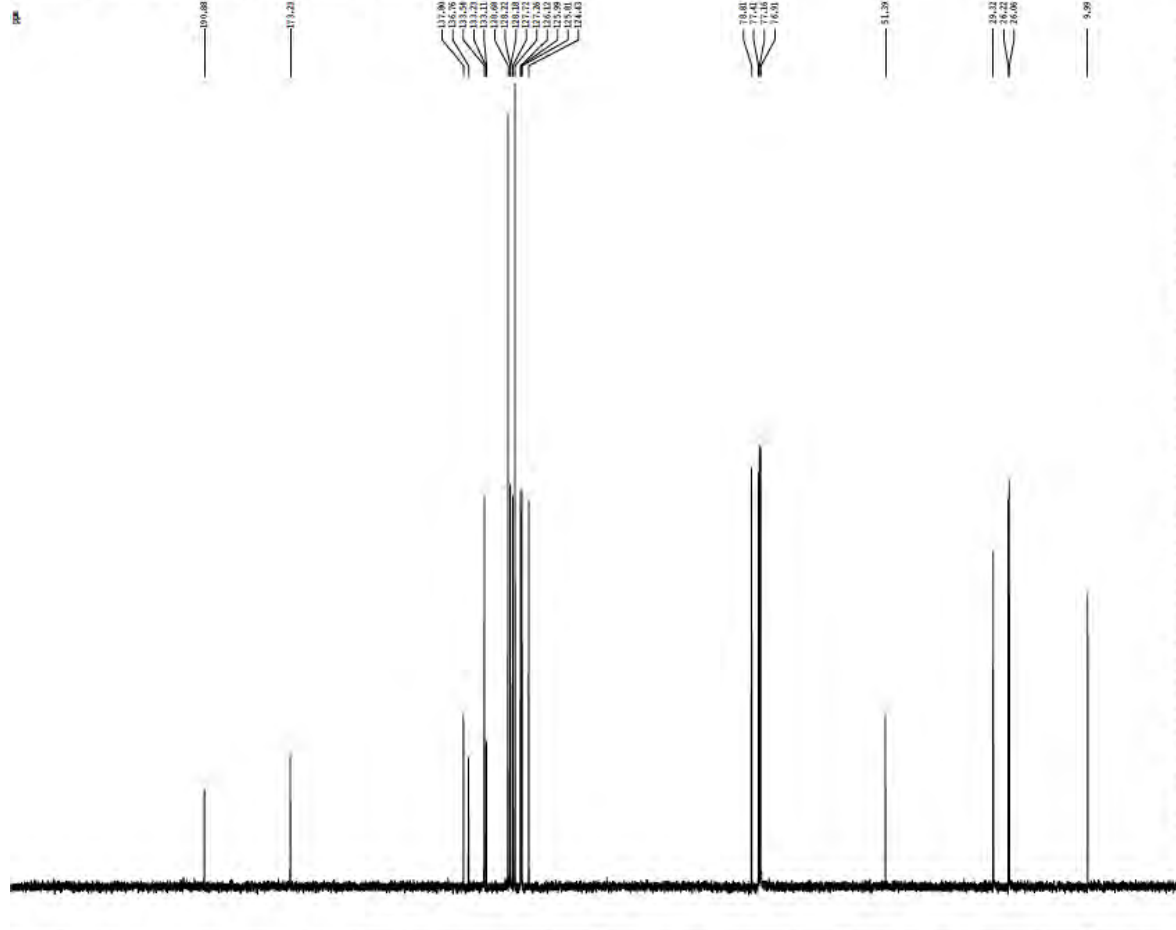


```

Current Data Parameters
NAME      bartaw
EXPNO    2
PROCNO   1
F2 - Acquisition Parameters
Date_    20121112
TIME     12.55
INSTRUM  spect
PROBHD  5 mm QNP 1H/1
PULPROG  zgpg30
SS       90
SOLVENT  DMS-d6
NS       640
DS       4
SWH      6410.254 Hz
FIDRES   0.497813 Hz
AQ       5.118579 sec
RG        328.1
SQ       78.000 ussq
RG2      4.50 ussq
SI       198.0 K
CT1      0.12000000 sec
WALTZ17 0.00000000 sec
WALTZ9  0.01500000 sec
=====
===== CHANNEL f1 =====
NUC1     13C
P1       15.00 ussq
PL1      0.00000000 dB
RF1      125.760416 MHz
SFO1     125.760416 MHz
=====
F2 - Processing parameters
SI       65536
SF       400.146047 MHz
WDW      EM
SS       0
DS       0
LB       0.30 Hz
GB       0
PC       2.00
=====
===== 1D NMR plot parameters =====
SI       22.50 cm
CT1      15.00 cm
FIDRES   9.000 ppm
F2       3913.11 Hz
F3       -1.500 ppm
RF1       125.760416 MHz
PULPROG  zgpg30
PCPROG  168.72088 Hz/cm
=====

```

Z-restored spin-echo 13C spectrum with 1H decoupling



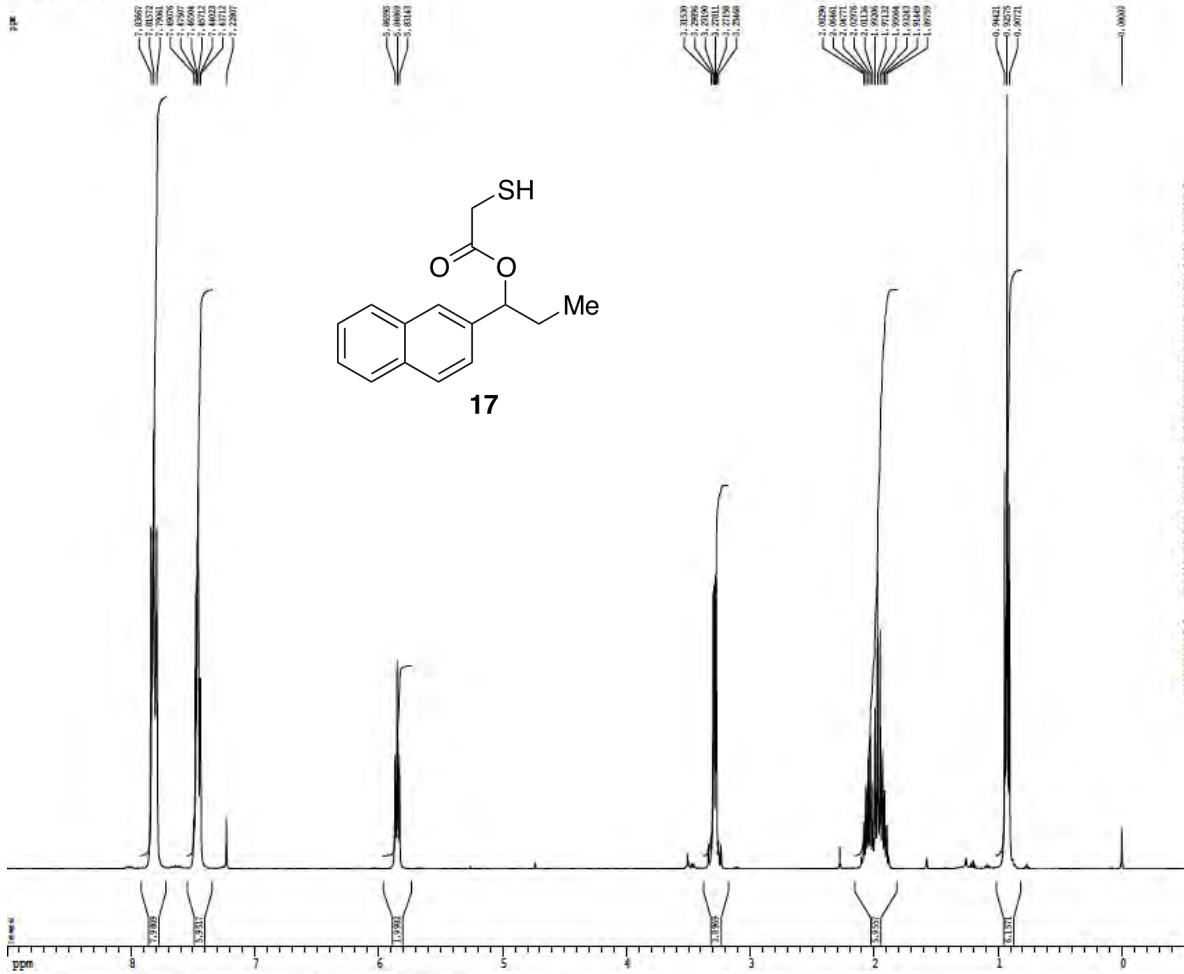
```

Current Data Parameters
NAME      bartaw
EXPNO    4
PROCNO   1
F2 - Acquisition Parameters
Date_    20121112
TIME     12.05
INSTRUM  spect
PROBHD  5 mm QNP 13
PULPROG  zgpg30
SS       90
SOLVENT  DMS-d6
NS       65536
DS       128
SWH      50003.031 Hz
FIDRES   0.462346 Hz
AQ       1.0812640 sec
RG        328.1
SQ       1292.8
RG2      18.700 ussq
SI       65536
CT1      0.25000000 sec
WALTZ17 0.00000000 sec
WALTZ9  0.00000000 sec
SI       0.00016000 sec
WALTZ1  0.00000000 sec
WALTZ9  0.01500000 sec
=====
===== CHANNEL f1 =====
NUC1     13C
P1       15.00 ussq
PL1      0.00000000 dB
RF1      125.760416 MHz
SFO1     125.760416 MHz
=====
===== CHANNEL f2 =====
CPDPRG2  zgpg30
P2       150.00 ussq
PL2      0.00000000 dB
RF2      100.628156 MHz
SFO2     100.628156 MHz
=====
===== 1D NMR plot parameters =====
SI       22.50 cm
CT1      15.00 cm
FIDRES   9.000 ppm
F2       3913.11 Hz
F3       -1.500 ppm
RF1       125.760416 MHz
PULPROG  zgpg30
PCPROG  168.72088 Hz/cm
=====
===== 1D NMR plot parameters =====
SI       22.50 cm
CT1      15.00 cm
FIDRES   9.000 ppm
F2       3913.11 Hz
F3       -1.500 ppm
RF1       125.760416 MHz
PULPROG  zgpg30
PCPROG  168.72088 Hz/cm
=====

```

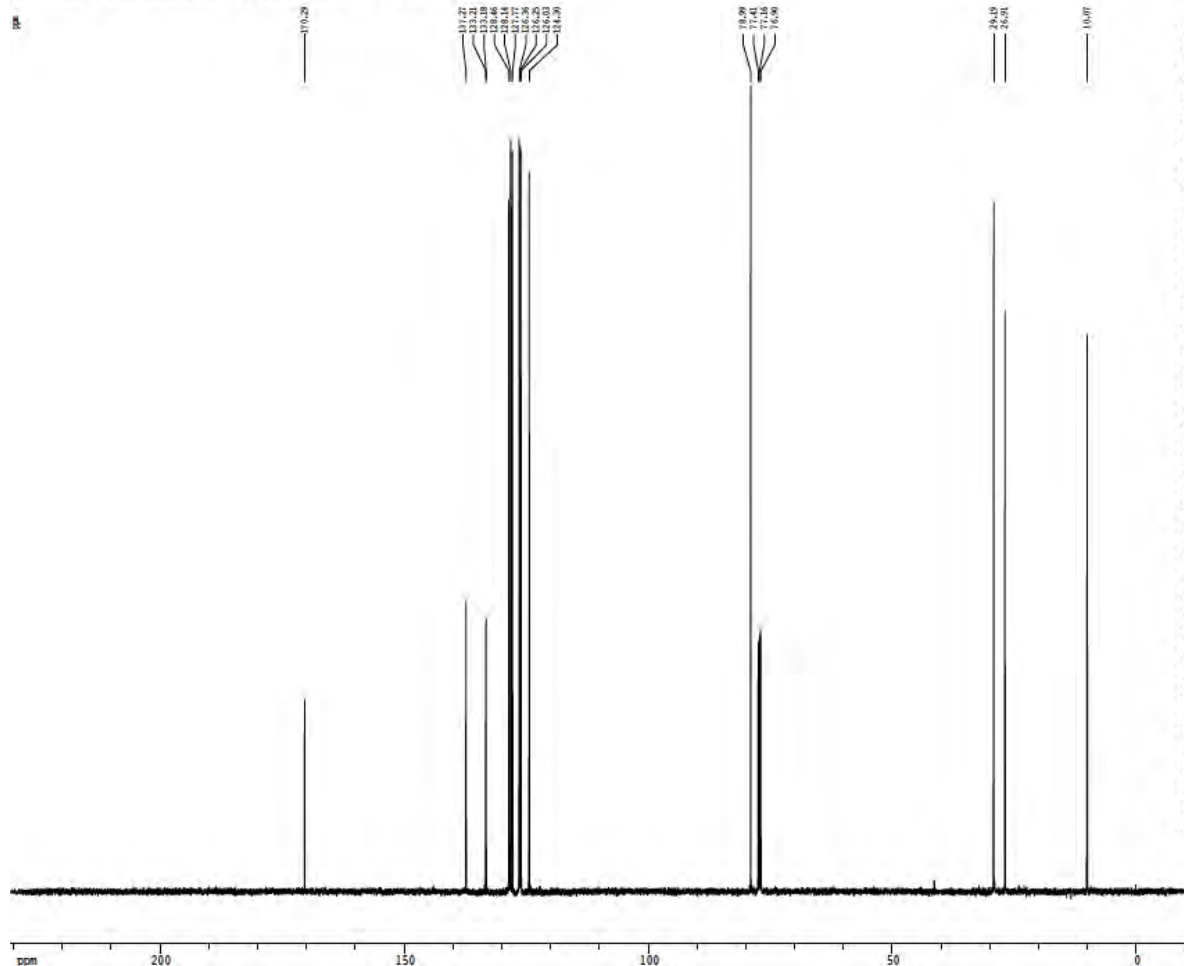


1H spectrum



Current Data Parameters  
 NAME: harraw  
 EXPNO: 1  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20121212  
 Time: 11.54  
 INSTRUM: gcp400  
 PRGNO: 5 nm gpc 8.719  
 PULPROG: zgpg  
 SOLVENT: DMSI-D  
 NS: 8  
 DS: 4  
 SWH: 640.254 Hz  
 FWHM: 0.89783 Hz  
 AQ: 5.118579 sec  
 RG: 65.6  
 SW: 78.000 uspc  
 SF: 400.146000 MHz  
 SI: 198.0 K  
 SL: 0.1000000 sec  
 SFL: 0.0000000 sec  
 WDELTA: 0.0100000 sec  
 =====  
 CHANNEL f1  
 NU1: 13  
 F1: 125.00 uspc  
 P1: -0.60 dB  
 SFO1: 400.146000 MHz  
 =====  
 F2 - Processing parameters  
 SI: 6536  
 SF: 400.146000 MHz  
 SWH: 640.254  
 DS: 4  
 SW: 0.30 Hz  
 CH: 0  
 FC: 2.00  
 =====  
 F2 MW plot parameters  
 CI: 22.80 cm  
 CF: 15.00 cm  
 F1F: 9.000 ppm  
 F1: 381.1 Hz  
 F2F: -1.500 ppm  
 F2: -204.96 Hz  
 FWHM: 0.4162 ppm/cm  
 SFO: 164.72088 Hz/cm

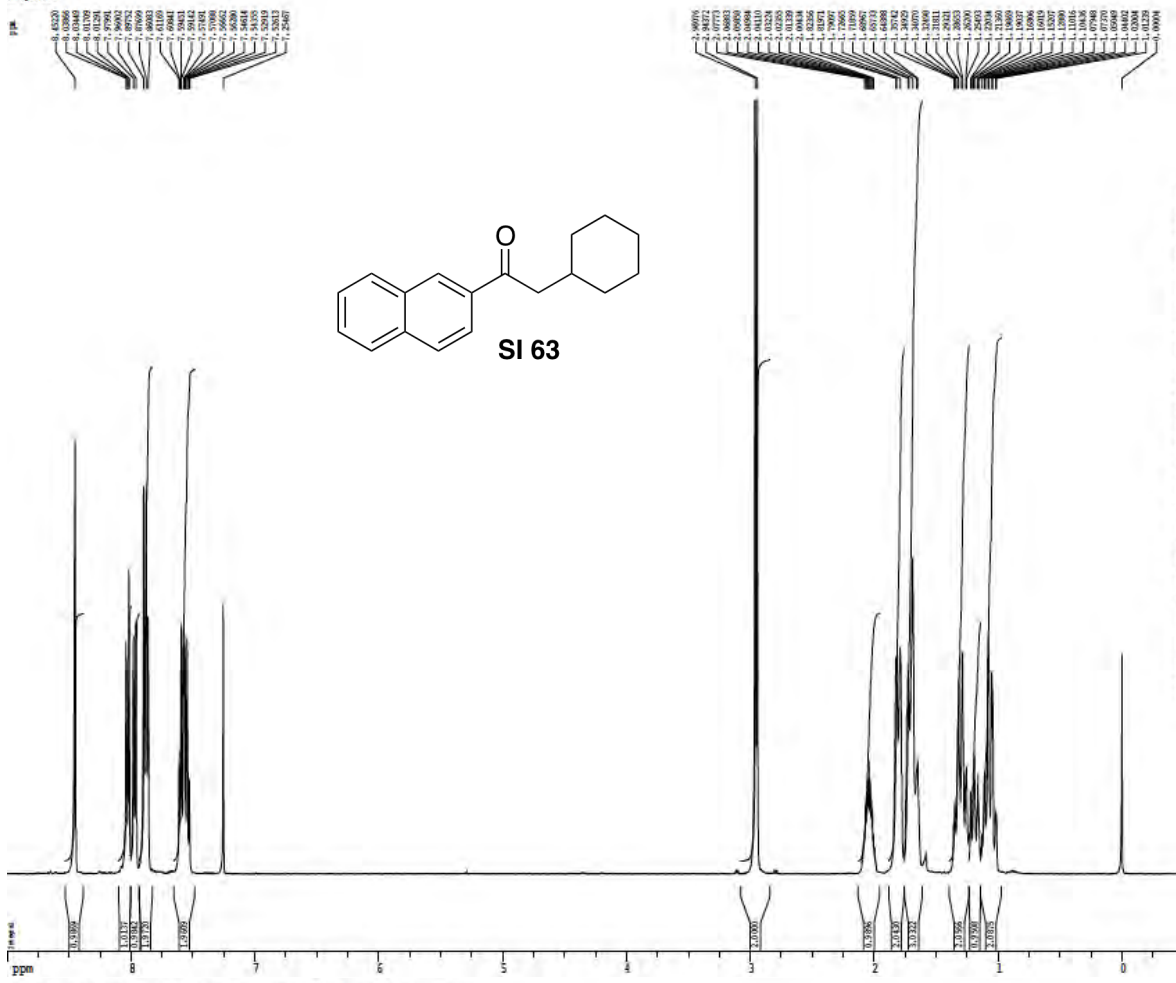
Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
 NAME: harraw  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20121212  
 Time: 16.12  
 INSTRUM: gcp400  
 PRGNO: 5 nm gpc 14-  
 PULPROG: zgpg30  
 SOLVENT: DMSI-D  
 NS: 8  
 DS: 4  
 SWH: 50003.031 Hz  
 FWHM: 0.862368 Hz  
 AQ: 1.0812940 sec  
 RG: 128.0  
 SW: 14.500 uspc  
 SF: 125.000 MHz  
 SI: 198.0 K  
 SL: 0.2000000 sec  
 SFL: 0.0000000 sec  
 S17: 0.0001000 sec  
 WDELTA: 0.0000000 sec  
 WDELTA: 0.0100000 sec  
 F2: 51.00 uspc  
 =====  
 CHANNEL f1  
 NU1: 13  
 F1: 15.50 uspc  
 P1: 500.00 uspc  
 P12: 5000.00 uspc  
 P13: 132.00 dB  
 SFO1: 125.7642348 MHz  
 SFO2: 50.00 MHz  
 SFO3: 50.00 MHz  
 SFO4: 500.00 uspc  
 SFO5: 1000.00 uspc  
 =====  
 CHANNEL f2  
 NU2: 13  
 P2: 100.00 uspc  
 P22: 24.80 dB  
 SFO2: 500.1325011 MHz  
 =====  
 F2 - Processing parameters  
 SI: 6536  
 SF: 125.7642348 MHz  
 SWH: 50003.031  
 DS: 4  
 SW: 1.00 Hz  
 CH: 0  
 FC: 2.00  
 =====  
 F2 MW plot parameters  
 CI: 22.80 cm  
 CF: 15.45 cm  
 F1F: 130.457 ppm  
 F1: 30002.88 Hz  
 F2F: -13.287 ppm  
 F2: -1393.96 Hz  
 FWHM: 10.54688 ppm/cm  
 SFO: 1325.10706 Hz/cm



900.053A in CDCl3  
post recrystallization  
January 5, 2012  
1H spectrum



Current Data Parameters  
NAME: 900.053A  
PROC: 900.053A  
EXPNO: 1  
PROCNO: 1

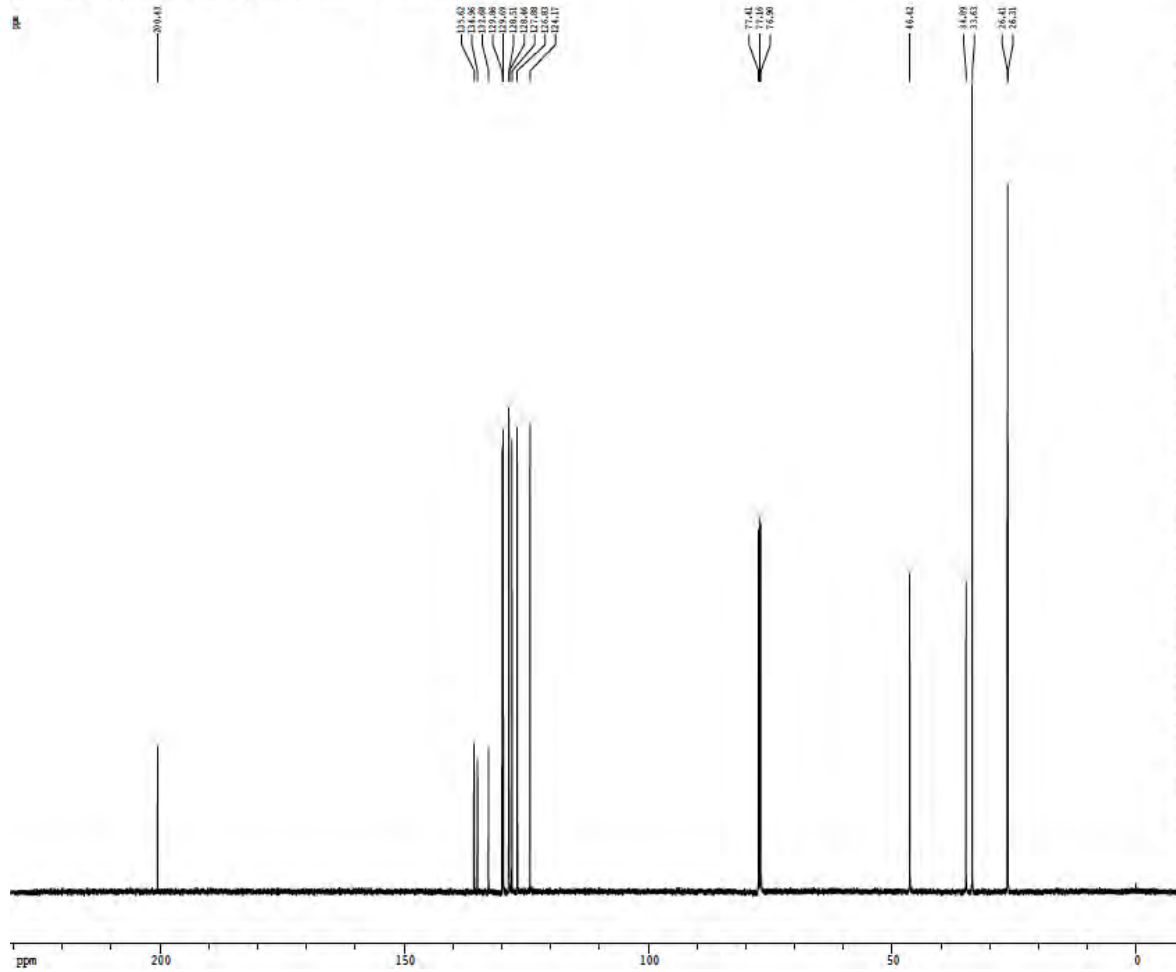
F2 - Acquisition Parameters  
DATE\_: 20120105  
TIME: 16.06  
INSTRUM: spect  
PROBHD: 5 mm CPD 1H/13  
PULPROG: zgpg30  
SOLVENT: CDCl3  
NS: 8  
DS: 8  
SWH: 6400.156 Hz  
FIDRES: 0.097613 Hz  
AQ: 5.118879 sec  
RG: 443.7  
SQ: 78.000 uspc  
CV: 4.50 uspc  
RG2: 258.0 F  
F2: 0.11800000 sec  
PCYCLE: 0.00000000 sec  
PCYCLE2: 0.01000000 sec

===== CHANNEL f1 =====  
NUC1: 13C  
P1: 12.00 uspc  
PL1: -0.40 dB  
SFO1: 400.126237 MHz

F2 - Processing parameters  
SI: 6124  
SF: 400.126237 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0.00  
PC: 2.00

===== SMOI plot parameters =====  
SI: 22.80 cm  
CF: 15.00 cm  
FID: 3.500 ppm  
F1: 3691.17 Hz  
F2: -3.500 ppm  
F3: -248.16 Hz  
SFMCN: 0.41687 ppm/cm  
SFCN: 164.72688 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
NAME: 900.053A  
PROC: 900.053A  
EXPNO: 1  
PROCNO: 1

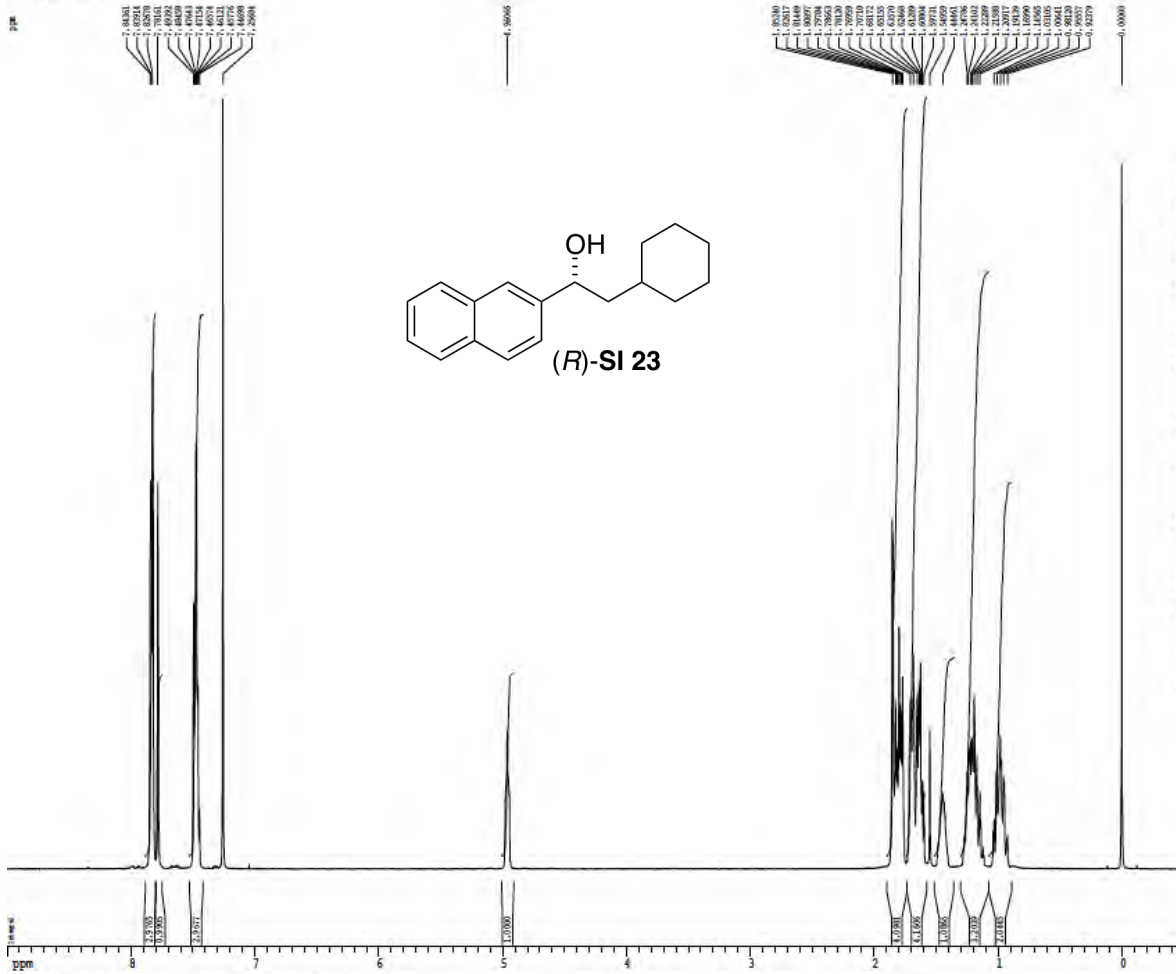
F2 - Acquisition Parameters  
DATE\_: 20120105  
TIME: 17.09  
INSTRUM: spect  
PROBHD: 5 mm CPD 1H-13  
PULPROG: zgpg30  
SOLVENT: CDCl3  
NS: 42  
DS: 16  
SWH: 20203.031 Hz  
FIDRES: 0.462388 Hz  
AQ: 1.0812940 sec  
RG: 518.0  
SQ: 18.500 uspc  
CV: 8.00 uspc  
F2: 258.0 F  
SI: 0.25000000 sec  
SIL: 0.03000000 sec  
SIS: 0.00000000 sec  
SIT: 0.00016000 sec  
PCYCLE: 0.00000000 sec  
PCYCLE2: 0.01000000 sec

===== CHANNEL f1 13C =====  
NUC1: 13C  
P1: 15.00 uspc  
PL1: 500.00 uspc  
PL2: 2000.00 uspc  
PL3: 130.00 dB  
PL4: -1.00 dB  
SFO1: 125.7642548 MHz  
SFO2: 3.20 MHz  
SFO3: 1.20 MHz  
SFO4: 0.5, 20.1  
SFO5: 0.5, 20.1  
SFO6: 0.00 MHz  
SFO7: 0.00 MHz

===== CHANNEL f2 =====  
NAME: 900.053A  
P1: 1.00 uspc  
PL1: 24.80 dB  
SFO1: 500.1262371 MHz

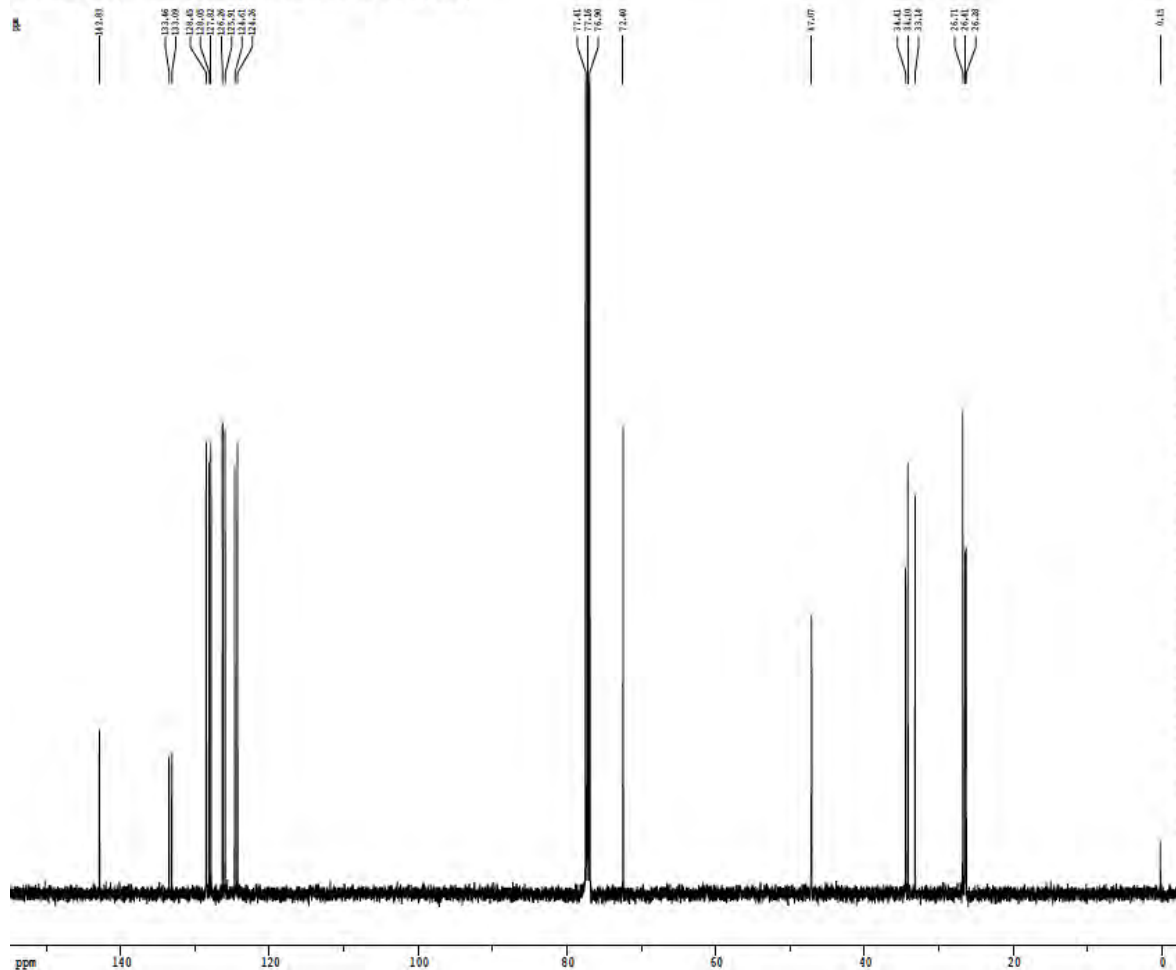
===== SMOI plot parameters =====  
SI: 22.80 cm  
CF: 15.00 cm  
FID: 3.500 ppm  
F1: 3691.17 Hz  
F2: -3.500 ppm  
F3: -248.16 Hz  
SFMCN: 0.41687 ppm/cm  
SFCN: 164.72688 Hz/cm

1H spectrum



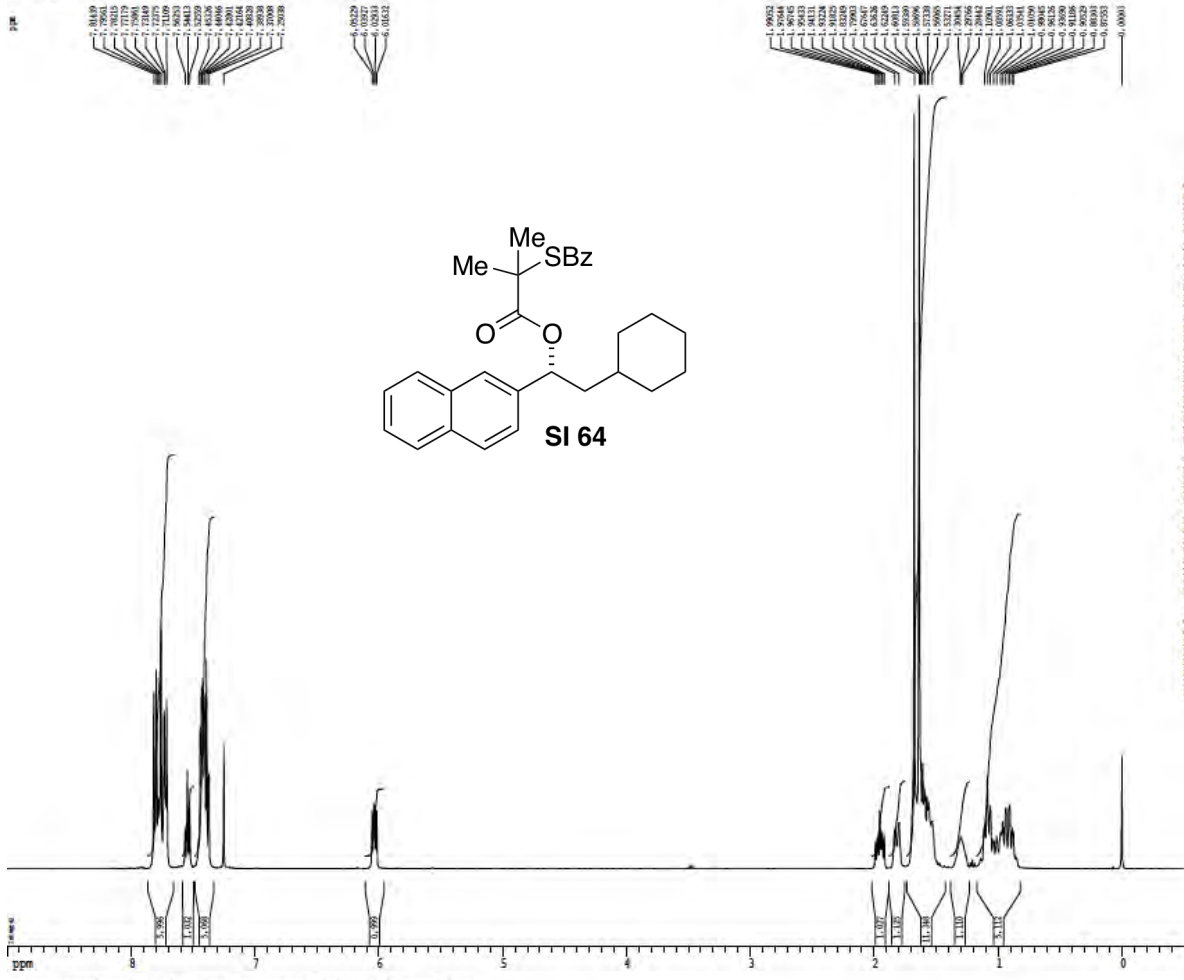
Output Data Parameters  
 NAME: ACI\_1\_Exp\_07\_01  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 DATE\_: 20120602  
 TIME: 22.56  
 INSTRUM: cryo600  
 PROBRG: 5 mm CPDPR 1H-  
 PULPROG: zgpg  
 SI: 81238  
 SOLVENT: CDCl3  
 NS: 8  
 DS: 4  
 SWH: 8812.820 Hz  
 FIDRES: 0.398043 Hz  
 AQ: 5.599776 sec  
 RG: 5.7  
 SW: 63.400 USPC  
 SF: 600.135000 MHz  
 TD: 65536  
 TE: 298.0 K  
 D1: 0.10000000 sec  
 DECFMT: 0.00000000 sec  
 WDELTA: 0.01500000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 15.00 USPC  
 PL1: 1.80 dB  
 SFO1: 500.125015 MHz  
 F2 - Processing parameters  
 SI: 81238  
 SF: 500.125015 MHz  
 WDW: EM  
 SSB: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 4.00  
 IS MR plot parameters  
 OI1: 22.80 cm  
 CI: 15.00 cm  
 FID: 9.500 ppm  
 FI: 4591.98 Hz  
 FID: -1.500 ppm  
 F2: -25.11 Hz  
 FWHM: 0.41667 ppm/cm  
 SCA: 201.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Output Data Parameters  
 NAME: ACI\_1\_Exp\_07\_01  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 DATE\_: 20120602  
 TIME: 23.01  
 INSTRUM: cryo600  
 PROBRG: 5 mm CPDPR 1H-  
 PULPROG: zgpg30  
 SI: 89538  
 SOLVENT: CDCl3  
 NS: 10  
 DS: 4  
 SWH: 50202.031 Hz  
 FIDRES: 0.462388 Hz  
 AQ: 1.0812940 sec  
 RG: 364.1  
 SW: 14.500 USPC  
 SF: 600.135000 MHz  
 TD: 65536  
 TE: 298.0 K  
 D1: 0.25000000 sec  
 D11: 0.25000000 sec  
 D12: 0.00000000 sec  
 D17: 0.00010000 sec  
 DECFMT: 0.00000000 sec  
 WDELTA: 0.01500000 sec  
 F2: 51.00 USPC  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 15.00 USPC  
 PL1: 500.00 USPC  
 PL2: 2000.00 USPC  
 PL3: 132.00 dB  
 SFO1: 125.7642548 MHz  
 SFO2: 3.20 MHz  
 SFO3: 3.20 MHz  
 SFO4: 0.5, 20.1  
 SFO5: cryo600, 4  
 SFO6: 0.00 MHz  
 SFO7: 0.00 MHz  
 ===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 1.00 dB  
 PL2: 24.80 dB  
 SFO2: 500.125015 MHz  
 ===== CHANNEL f3 =====  
 NUC3: 13C  
 P3: 15.00 USPC  
 PL3: 500.00 USPC  
 PL4: 2000.00 USPC  
 PL5: 132.00 dB  
 SFO5: 125.7642548 MHz  
 SFO6: 3.20 MHz  
 SFO7: 3.20 MHz  
 SFO8: 0.5, 20.1  
 SFO9: cryo600, 4  
 SFO10: 0.00 MHz  
 SFO11: 0.00 MHz  
 ===== CHANNEL f4 =====  
 NUC4: 1H  
 P4: 1.00 dB  
 PL4: 24.80 dB  
 SFO4: 500.125015 MHz  
 ===== CHANNEL f5 =====  
 NUC5: 13C  
 P5: 15.00 USPC  
 PL5: 500.00 USPC  
 PL6: 2000.00 USPC  
 PL7: 132.00 dB  
 SFO7: 125.7642548 MHz  
 SFO8: 3.20 MHz  
 SFO9: 3.20 MHz  
 SFO10: 0.5, 20.1  
 SFO11: cryo600, 4  
 SFO12: 0.00 MHz  
 SFO13: 0.00 MHz  
 ===== CHANNEL f6 =====  
 NUC6: 1H  
 P6: 1.00 dB  
 PL6: 24.80 dB  
 SFO6: 500.125015 MHz

1H spectrum



Output Data Parameters  
 NAME: harpaw  
 EXPNO: 2  
 PROCNO: 1

F1 - Acquisition Parameters  
 Date\_: 20121115  
 Time: 10.47  
 INSTRUM: spect  
 FREQID: 500 MHz 1H  
 PULPROG: zgpg30  
 SOLVENT: DMSO-d6  
 NS: 6  
 DS: 4  
 SWH: 6401.254 Hz  
 FWHM: 0.897813 Hz  
 AQ: 5.118579 sec  
 RG: 381  
 SW: 78.000 uspc  
 SF: 4.50 uspc  
 SI: 256.0 K  
 SFO: 0.10000000 sec  
 WDELTA: 0.00000000 sec  
 WDEXT: 0.01000000 sec

===== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 12.00 uspc  
 PL1: -0.60 dB  
 SFO1: 400.1260000 MHz

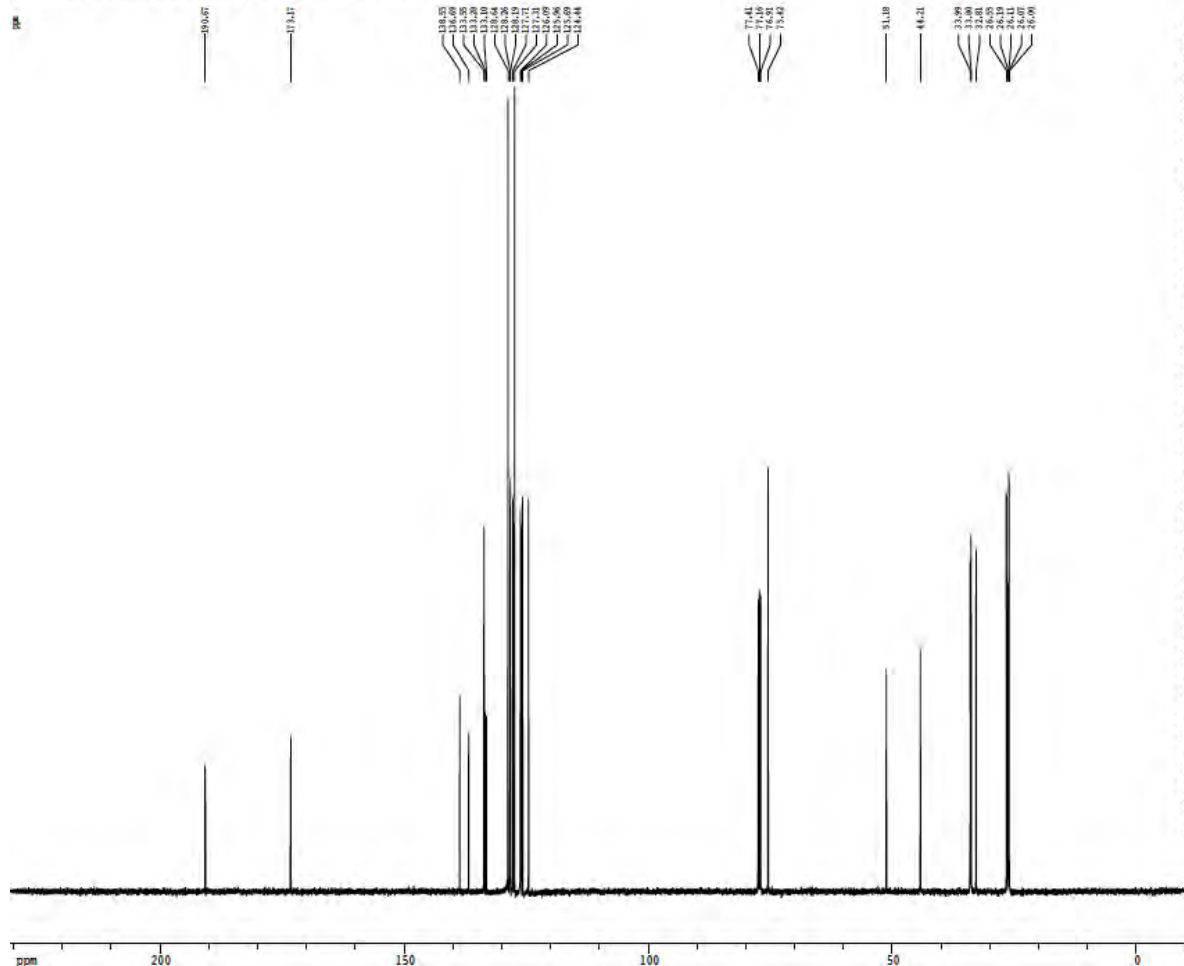
F2 - Processing parameters  
 SI: 65536  
 SF: 400.1260000 MHz  
 DS: 4  
 SWH: 6401.254 Hz  
 FWHM: 0.897813 Hz  
 AQ: 5.118579 sec  
 RG: 381  
 SW: 78.000 uspc  
 SF: 4.50 uspc  
 SI: 256.0 K  
 SFO: 0.10000000 sec  
 WDELTA: 0.00000000 sec  
 WDEXT: 0.01000000 sec

===== CHANNEL f2 =====  
 NUC2: 13C  
 P2: 15.00 uspc  
 PL2: 0.00 dB  
 SFO2: 100.6281500 MHz

===== CHANNEL f3 =====  
 NUC3: 13C  
 P3: 15.00 uspc  
 PL3: 0.00 dB  
 SFO3: 100.6281500 MHz

===== CHANNEL f4 =====  
 NUC4: 13C  
 P4: 15.00 uspc  
 PL4: 0.00 dB  
 SFO4: 100.6281500 MHz

Z-restored spin-echo 13C spectrum with 1H decoupling



Output Data Parameters  
 NAME: harpaw  
 EXPNO: 4  
 PROCNO: 1

F1 - Acquisition Parameters  
 Date\_: 20121115  
 Time: 12.18  
 INSTRUM: spect  
 FREQID: 500 MHz 13C  
 PULPROG: zgpg30  
 SOLVENT: DMSO-d6  
 NS: 6  
 DS: 4  
 SWH: 50000.031 Hz  
 FWHM: 0.862388 Hz  
 AQ: 1.0812040 sec  
 RG: 3762.0  
 SW: 14.500 uspc  
 SF: 8.00 uspc  
 SI: 256.0 K  
 SFO: 0.10000000 sec  
 WDELTA: 0.00000000 sec  
 WDEXT: 0.00000000 sec  
 WDEXT2: 0.01000000 sec  
 WDEXT3: 0.01000000 sec  
 F2: 51.00 uspc

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 15.00 uspc  
 PL1: 0.00 dB  
 SFO1: 100.6281500 MHz

===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 15.00 uspc  
 PL2: 0.00 dB  
 SFO2: 400.1260000 MHz

===== CHANNEL f3 =====  
 NUC3: 13C  
 P3: 15.00 uspc  
 PL3: 0.00 dB  
 SFO3: 100.6281500 MHz

===== CHANNEL f4 =====  
 NUC4: 13C  
 P4: 15.00 uspc  
 PL4: 0.00 dB  
 SFO4: 100.6281500 MHz

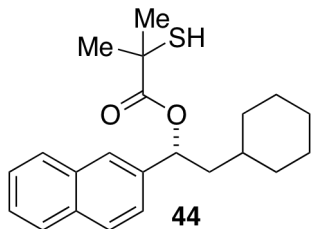
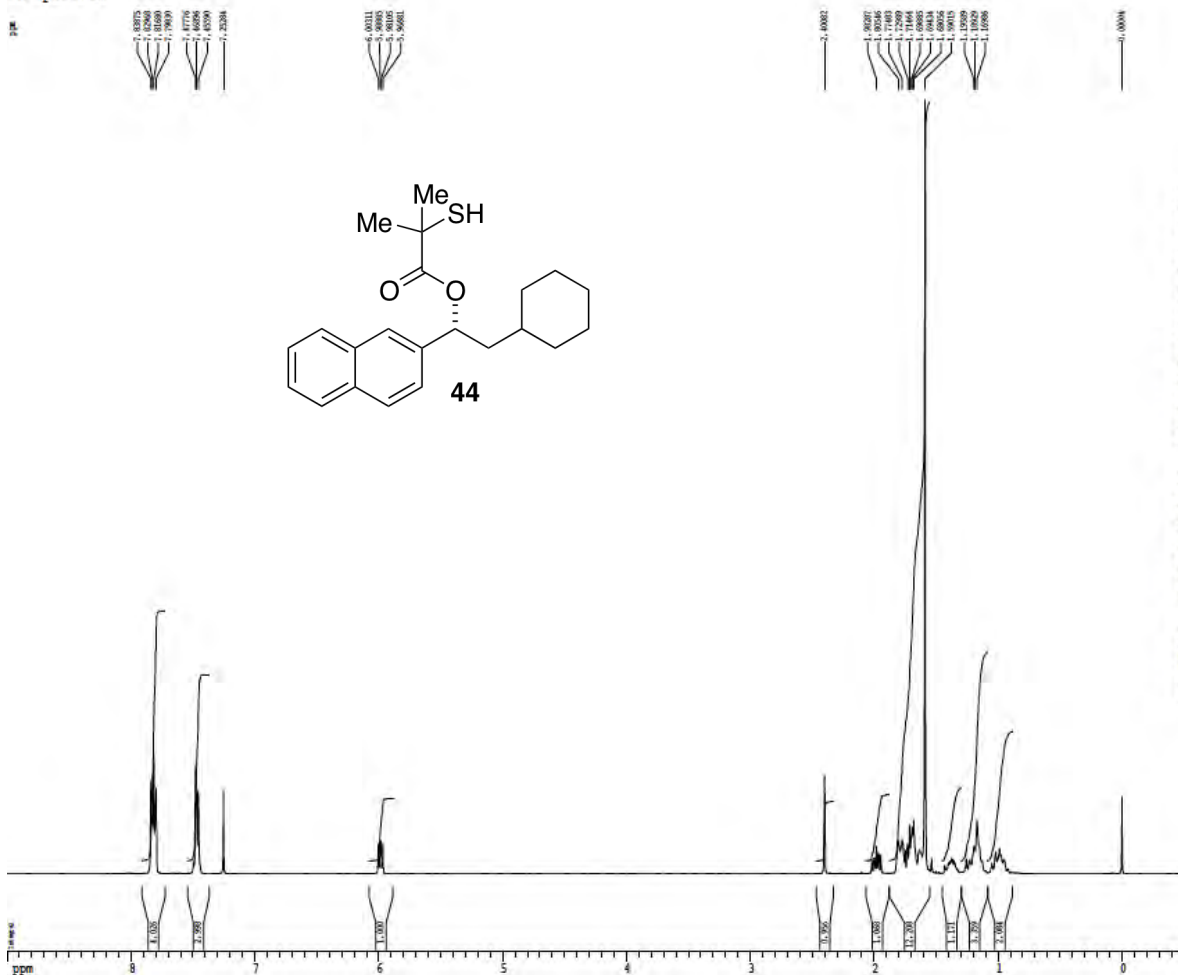
===== CHANNEL f5 =====  
 NUC5: 13C  
 P5: 15.00 uspc  
 PL5: 0.00 dB  
 SFO5: 100.6281500 MHz

===== CHANNEL f6 =====  
 NUC6: 13C  
 P6: 15.00 uspc  
 PL6: 0.00 dB  
 SFO6: 100.6281500 MHz

===== CHANNEL f7 =====  
 NUC7: 13C  
 P7: 15.00 uspc  
 PL7: 0.00 dB  
 SFO7: 100.6281500 MHz

===== CHANNEL f8 =====  
 NUC8: 13C  
 P8: 15.00 uspc  
 PL8: 0.00 dB  
 SFO8: 100.6281500 MHz

1H spectrum



Current Data Parameters  
NAME: harraw  
EXPNO: 2  
PROCNO: 1

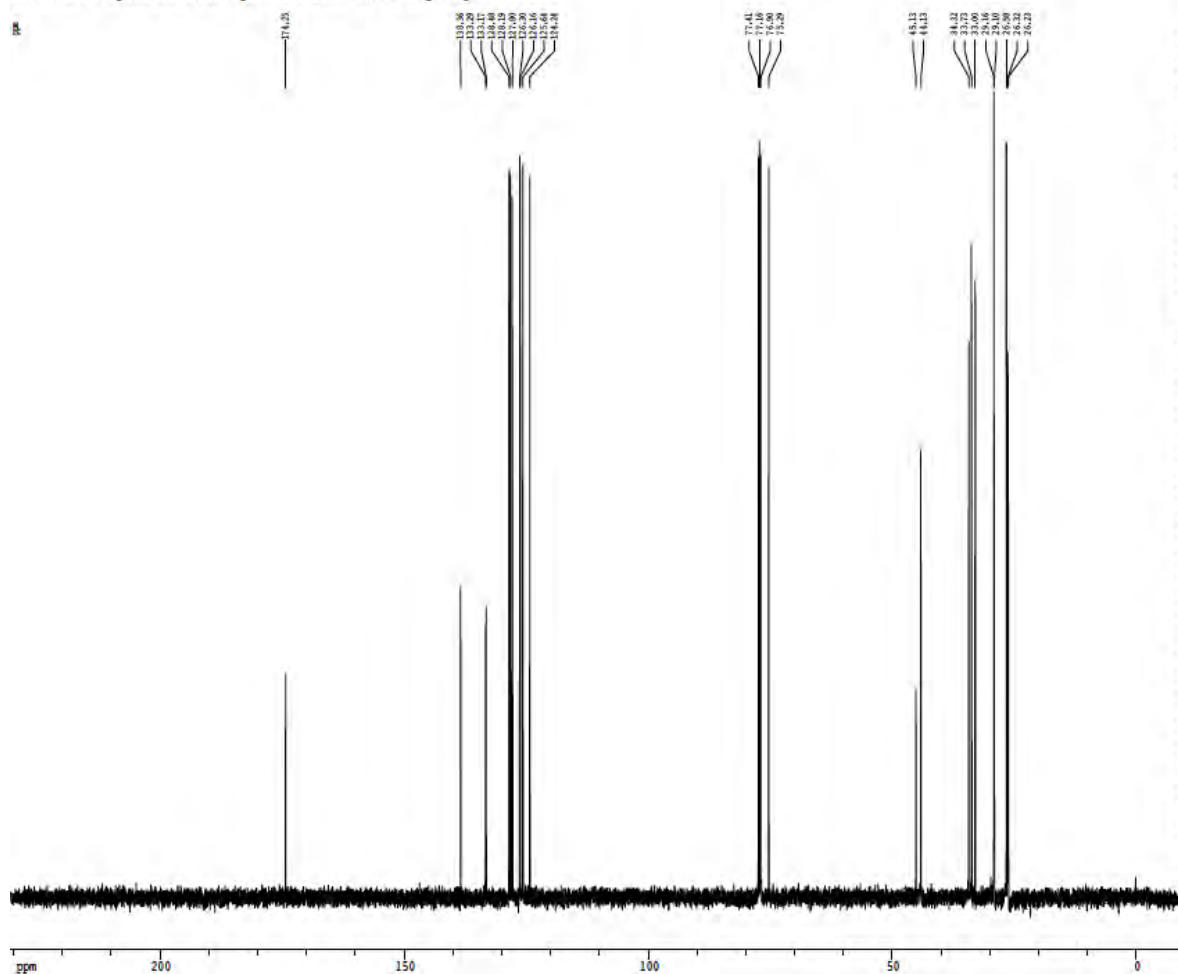
F1 - Acquisition Parameters  
Date\_: 20121115  
Time: 15.50  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H/1  
PULPROG: zgpg30  
SI: 65536  
SOLVENT: DMS  
NS: 8  
DS: 4  
SWH: 6410.256 Hz  
FIDRES: 0.897033 Hz  
AQ: 5.110579 sec  
RG: 256.0  
SW: 78.000 uspc  
TE: 4.50 uspc  
SI: 256.0 K  
SFO: 0.100000000 sec  
WDWHT: 0.000000000 sec  
MCHW: 0.010000000 sec

===== CHANNEL f1 =====  
NUC1: 1H  
P1: 12.00 uspc  
PL1: -0.60 dB  
SFO1: 400.1464000 MHz

F2 - Processing parameters  
SI: 65536  
SF: 400.1464000 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0  
PC: 2.00

F3 - NMR plot parameters  
SI: 256.00 cm  
CF: 15.00 cm  
FID: 9.000 ppm  
PL: 381.1 Hz  
PL2: -1.500 ppm  
F2: -200.96 Hz  
SFREQ: 0.41667 ppm/cm  
SCN: 166.72088 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters  
NAME: harraw  
EXPNO: 4  
PROCNO: 1

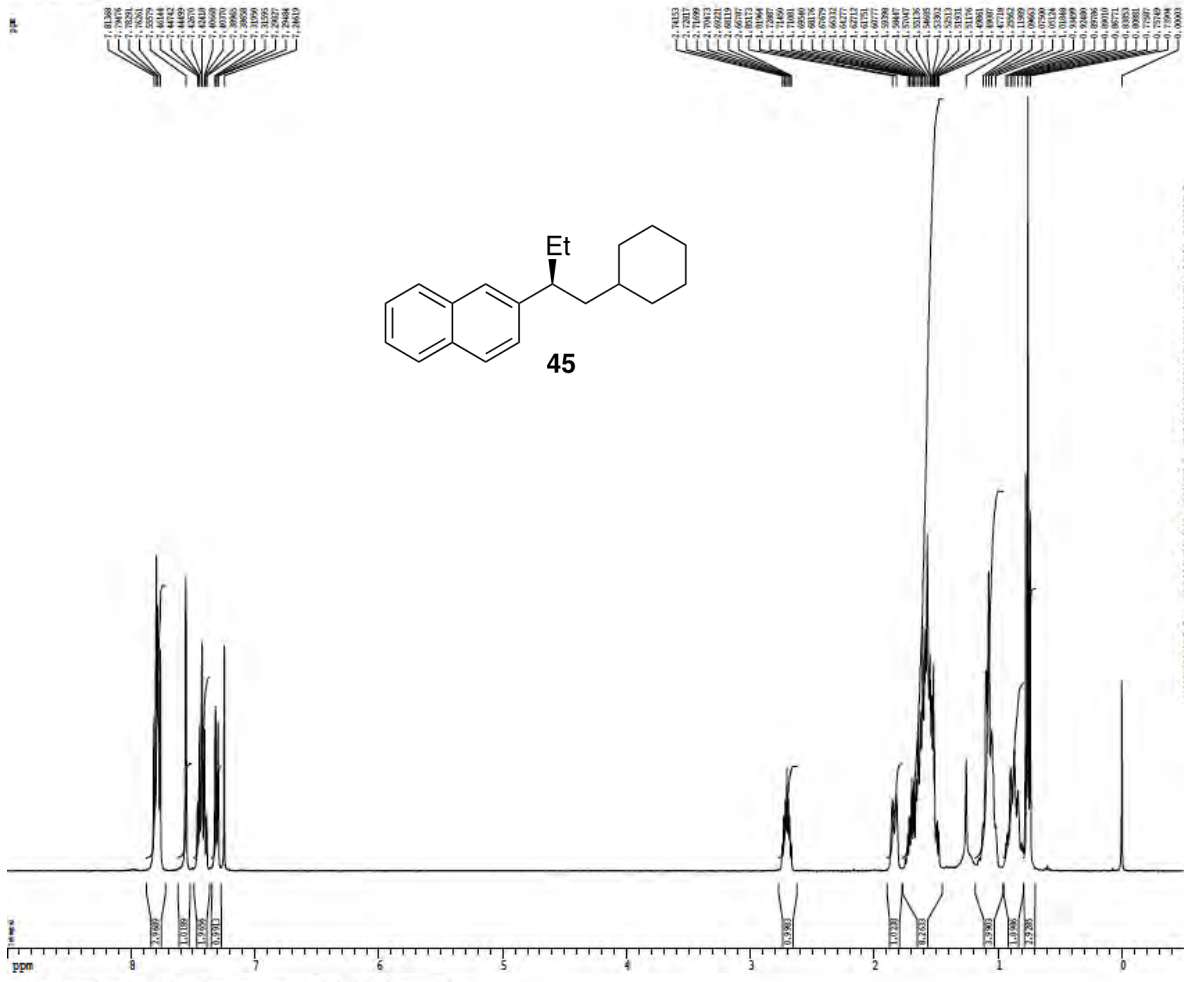
F1 - Acquisition Parameters  
Date\_: 20121116  
Time: 12.77  
INSTRUM: spect  
PROBHD: 5 mm QNP 1H-  
PULPROG: zgpg30p1  
SI: 65536  
SOLVENT: DMS  
NS: 16  
DS: 4  
SWH: 50000.031 Hz  
FIDRES: 0.862368 Hz  
AQ: 1.0812640 sec  
RG: 256.0  
SW: 14.700 uspc  
TE: 8.00 uspc  
SI: 256.0  
SFO: 0.250000000 sec  
WDWHT: 0.000000000 sec  
MCHW: 0.000000000 sec  
SFT: 0.000140000 sec  
WDWHT: 0.000000000 sec  
MCHW: 0.010000000 sec  
F2: 51.00 uspc

===== CHANNEL f1 =====  
NUC1: 13C  
P1: 15.00 uspc  
PL1: 500.00 uspc  
PL2: 2000.00 uspc  
PL3: 130.00 dB  
PL4: -1.00 dB  
SFO1: 125.7642348 MHz  
SFO2: 51.00 MHz  
SFO3: 51.00 MHz  
SFO4: 51.00 MHz  
SFO5: 51.00 MHz  
SFO6: 51.00 MHz  
SFO7: 51.00 MHz  
SFO8: 51.00 MHz  
SFO9: 51.00 MHz  
SFO10: 51.00 MHz  
SFO11: 51.00 MHz  
SFO12: 51.00 MHz  
SFO13: 51.00 MHz  
SFO14: 51.00 MHz  
SFO15: 51.00 MHz  
SFO16: 51.00 MHz  
SFO17: 51.00 MHz  
SFO18: 51.00 MHz  
SFO19: 51.00 MHz  
SFO20: 51.00 MHz

===== CHANNEL f2 =====  
NUC2: 13C  
P2: 15.00 uspc  
PL2: 500.00 uspc  
PL3: 2000.00 uspc  
PL4: 130.00 dB  
PL5: -1.00 dB  
SFO2: 125.7642348 MHz  
SFO3: 51.00 MHz  
SFO4: 51.00 MHz  
SFO5: 51.00 MHz  
SFO6: 51.00 MHz  
SFO7: 51.00 MHz  
SFO8: 51.00 MHz  
SFO9: 51.00 MHz  
SFO10: 51.00 MHz  
SFO11: 51.00 MHz  
SFO12: 51.00 MHz  
SFO13: 51.00 MHz  
SFO14: 51.00 MHz  
SFO15: 51.00 MHz  
SFO16: 51.00 MHz  
SFO17: 51.00 MHz  
SFO18: 51.00 MHz  
SFO19: 51.00 MHz  
SFO20: 51.00 MHz

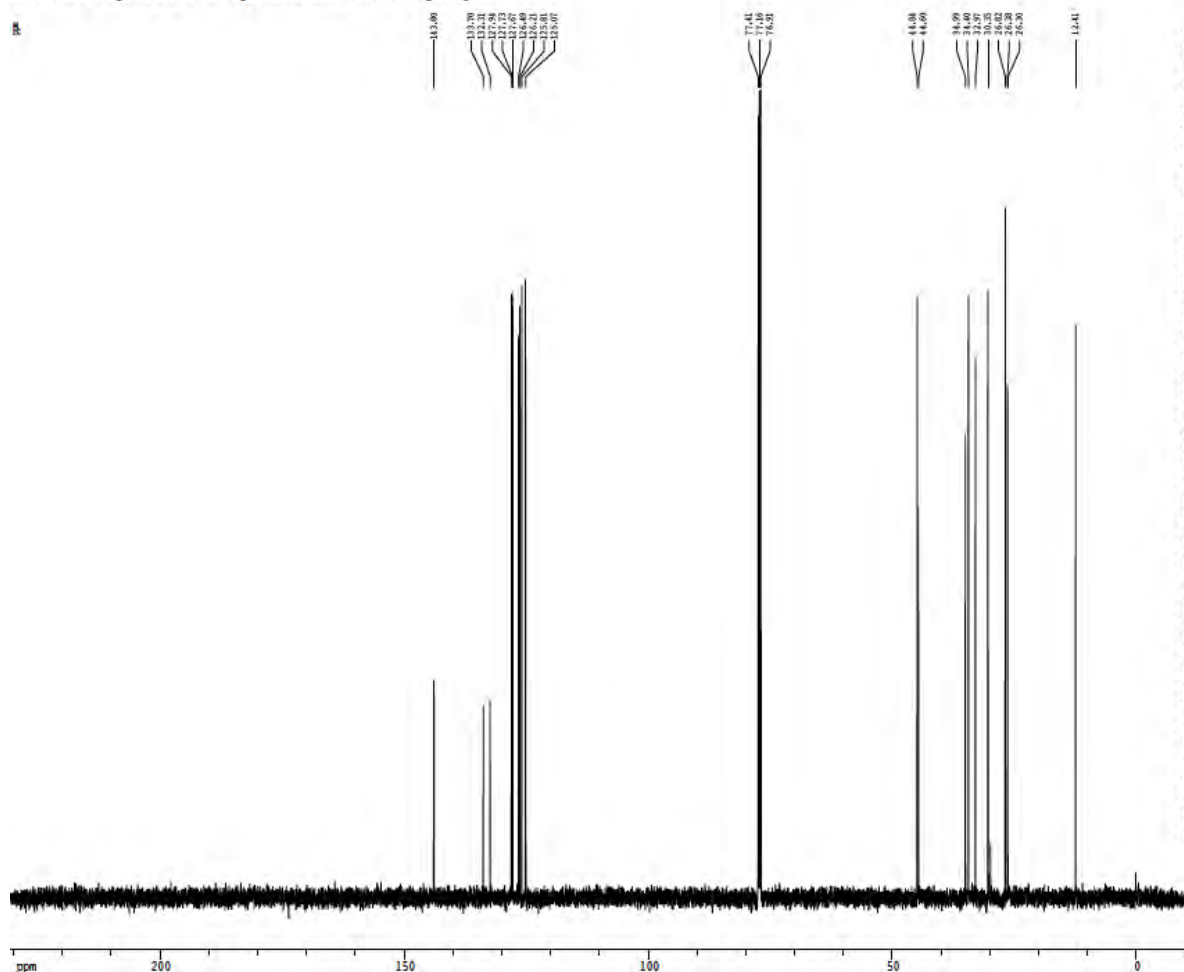
===== CHANNEL f3 =====  
NUC3: 13C  
P3: 15.00 uspc  
PL3: 500.00 uspc  
PL4: 2000.00 uspc  
PL5: 130.00 dB  
PL6: -1.00 dB  
SFO3: 125.7642348 MHz  
SFO4: 51.00 MHz  
SFO5: 51.00 MHz  
SFO6: 51.00 MHz  
SFO7: 51.00 MHz  
SFO8: 51.00 MHz  
SFO9: 51.00 MHz  
SFO10: 51.00 MHz  
SFO11: 51.00 MHz  
SFO12: 51.00 MHz  
SFO13: 51.00 MHz  
SFO14: 51.00 MHz  
SFO15: 51.00 MHz  
SFO16: 51.00 MHz  
SFO17: 51.00 MHz  
SFO18: 51.00 MHz  
SFO19: 51.00 MHz  
SFO20: 51.00 MHz

1H spectrum



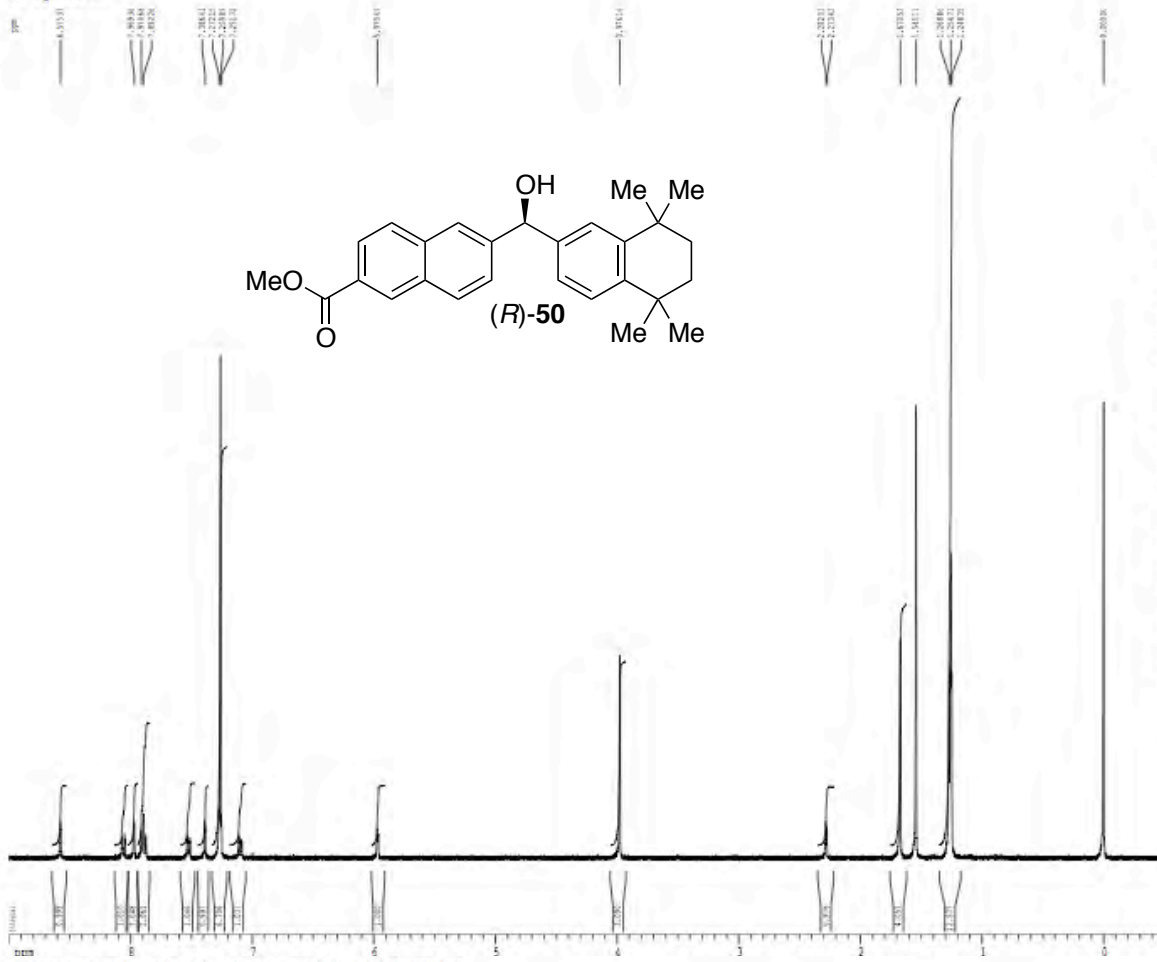
Output Data Parameters  
 NAME: narraw  
 PROCNO: 1  
 F1 - Acquisition Parameters  
 Date\_: 20120114  
 TIME: 0.51  
 INSTRUM: spect  
 FREQID: 500 MHz  
 PULPROG: zgpg30  
 SOLVENT: CDCl3  
 NS: 8  
 DS: 2  
 SWH: 6410.254 Hz  
 FWHM: 0.897813 Hz  
 AQ: 5.118579 sec  
 RG: 381  
 SW: 78.000 uspc  
 SF: 4.50 uspc  
 SI: 198.0 K  
 SL: 0.1000000 sec  
 WDELT: 0.0000000 sec  
 WCNV: 0.0100000 sec  
 =====  
 CHANNEL f1  
 NUCL: 13  
 P1: 12.00 uspc  
 PL1: -0.60 dB  
 SFO1: 400.126000 MHz  
 F2 - Processing parameters  
 SI: 400.126000 MHz  
 SF: 0  
 SW: 0  
 LB: 0.30 Hz  
 GB: 0  
 PC: 2.00  
 IS - 90 plot parameters  
 CI: 22.80 cm  
 CJ: 15.00 cm  
 FID: 9.000 ppm  
 F1: 381.1 Hz  
 F2: -1.500 ppm  
 F3: -200.00 Hz  
 FWHM: 0.4162 ppm/cm  
 XCH: 164.72088 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



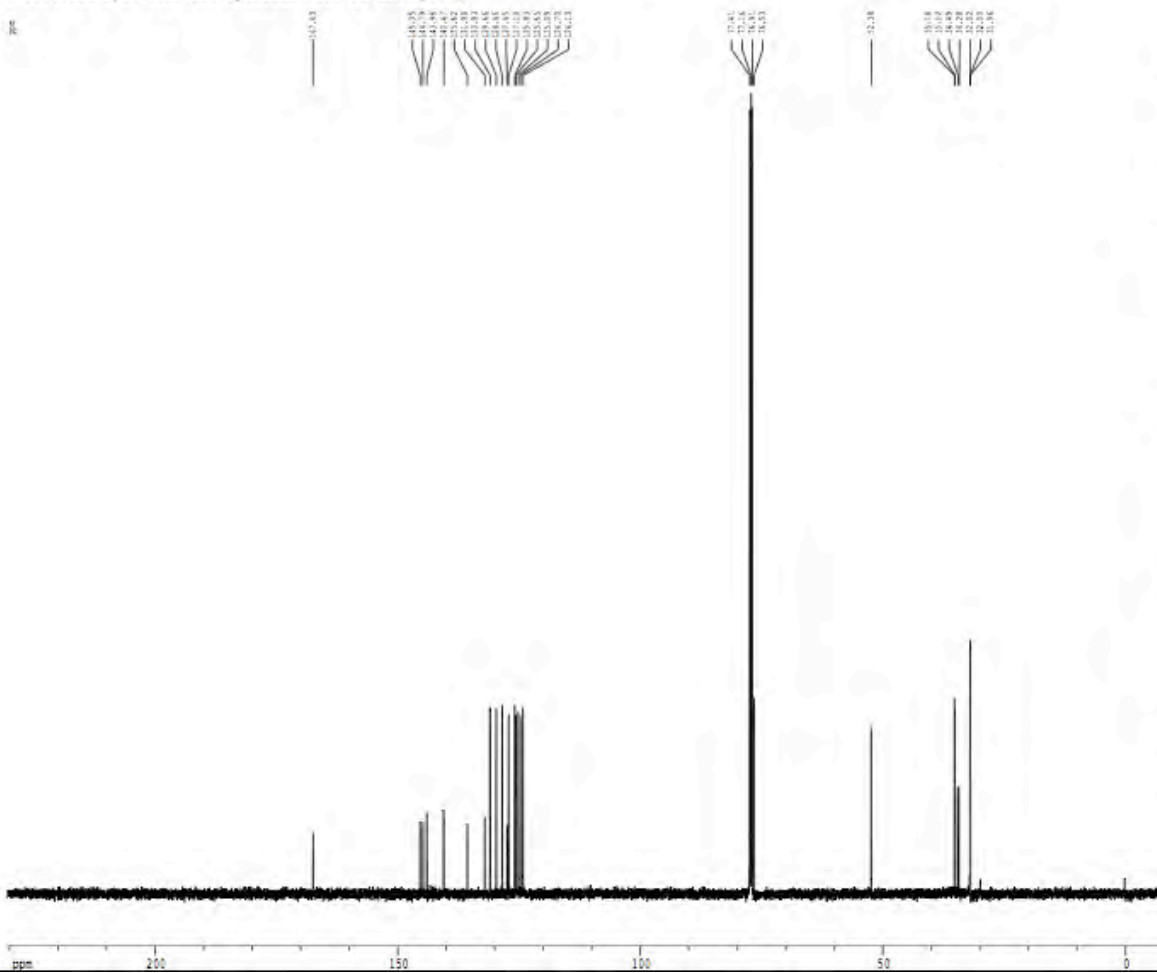
Output Data Parameters  
 NAME: narraw  
 PROCNO: 1  
 F1 - Acquisition Parameters  
 Date\_: 20120114  
 TIME: 15.08  
 INSTRUM: spect  
 FREQID: 5 mm spect 13  
 PULPROG: zgpg30p0p0p0p0p0p0  
 SOLVENT: CDCl3  
 NS: 240  
 DS: 15  
 SWH: 50000.031 Hz  
 FWHM: 0.462388 Hz  
 AQ: 1.0812940 sec  
 RG: 800  
 SW: 14.500 uspc  
 SF: 8.00 uspc  
 SI: 198.0 K  
 SL: 0.2000000 sec  
 SLL: 0.2000000 sec  
 SLP: 0.0000000 sec  
 SFT: 0.00018000 sec  
 WDELT: 0.0000000 sec  
 WCNV: 0.0100000 sec  
 F2  
 F1: 51.00 uspc  
 =====  
 CHANNEL f1  
 NUCL: 13C  
 P1: 15.00 uspc  
 PL1: 500.00 uspc  
 PL2: 3000.00 uspc  
 PL3: 132.00 dB  
 SFO1: 125.7642348 MHz  
 SFO2: 3.20 MHz  
 SFO3: 3.20 MHz  
 SFO4: 0.5, 20.1  
 SFO5: 0.5000000 Hz  
 SFO6: 0.00 Hz  
 SFO7: 0.00 Hz  
 =====  
 CHANNEL f2  
 NAME: waltz16  
 P1: 100.00 uspc  
 PL1: 24.80 dB  
 SFO1: 500.1259111 MHz  
 =====  
 CHANNEL CHANNELS  
 CHANNEL: SINE, 100  
 CHANNEL: SINE, 100  
 SFO1: 0.00 %  
 SFO2: 0.00 %  
 SFO3: 0.00 %  
 SFO4: 0.00 %  
 SFO5: 50.00 %  
 SFO6: 50.00 %  
 SFO7: 500.00 uspc  
 SFO8: 1000.00 uspc  
 F2 - Processing parameters  
 SI: 400.126000 MHz  
 SF: 125.7642348 MHz  
 SW: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 2.00  
 IS - 90 plot parameters  
 CI: 22.80 cm  
 CJ: 15.00 cm  
 FID: 330.457 ppm  
 F1: 3000.00 Hz  
 F2: -10.00 Hz  
 F3: -1203.00 Hz  
 FWHM: 10.54088 ppm/cm  
 XCH: 1370.10889 Hz/cm

<sup>1</sup>H spectrum



```
Current Data Parameters:
===== CHANNEL F1 =====
NAME_1 20130214
TIME 03:59
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
PC 92.00
DC 0.50
SFO 400.1464000 MHz
FIDRES 0.0000000 sec
AQ 0.2160000 sec
RG 327.5
DA 19.000000
DE 1.90
TE 300.2 K
D1 0.1000000 sec
dCHIRP 0.0000000 sec
ADWX 0.0100000 sec
===== CHANNEL F2 =====
NAME_2
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
===== CHANNEL F3 =====
NAME_3
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
===== CHANNEL F4 =====
NAME_4
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
```

Z-restored spin-echo <sup>13</sup>C spectrum with <sup>1</sup>H decoupling



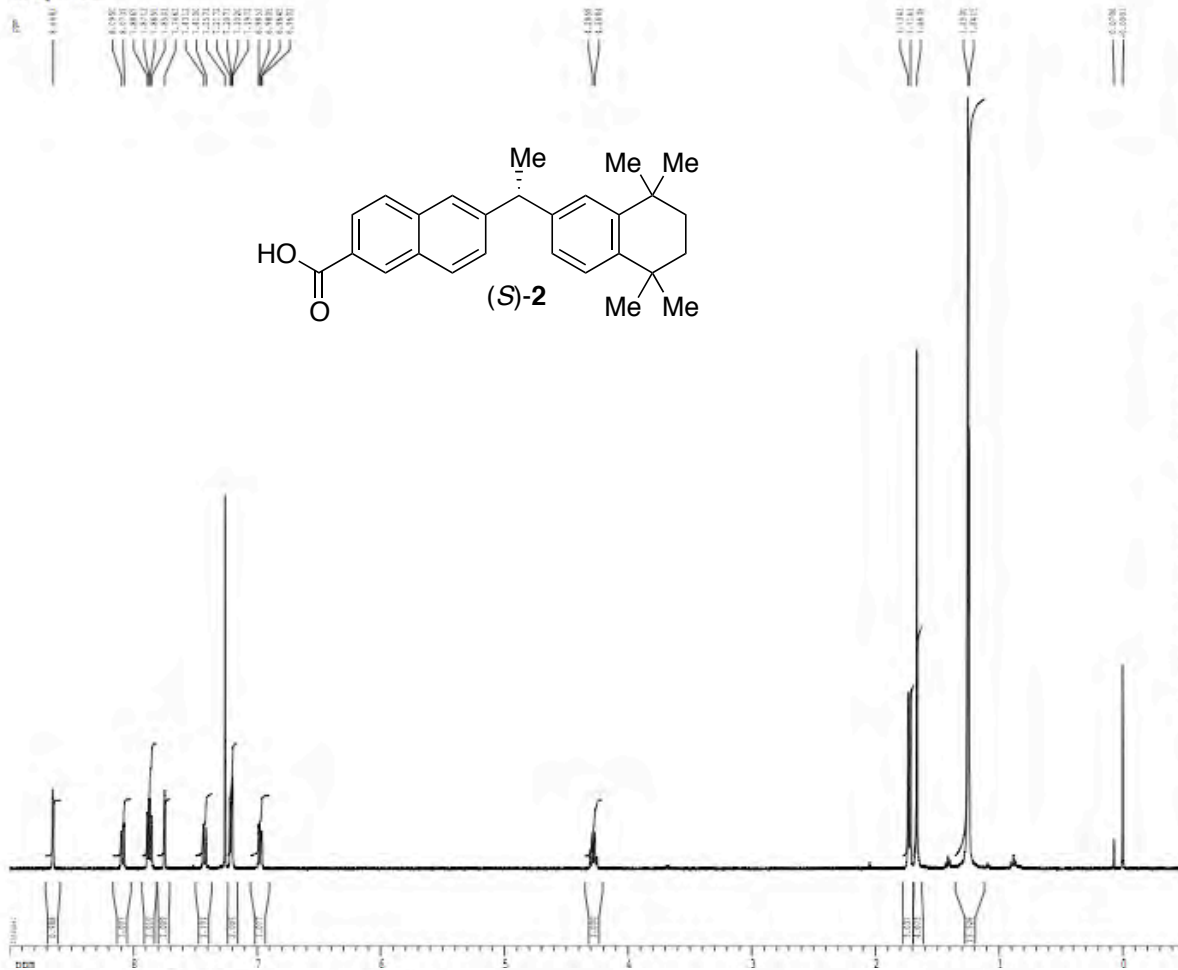
```
Current Data Parameters:
===== CHANNEL F1 =====
NAME_1 20130214
TIME 03:59
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
PC 92.00
DC 0.50
SFO 400.1464000 MHz
FIDRES 0.0000000 sec
AQ 0.2160000 sec
RG 327.5
DA 19.000000
DE 1.90
TE 300.2 K
D1 0.1000000 sec
dCHIRP 0.0000000 sec
ADWX 0.0100000 sec
===== CHANNEL F2 =====
NAME_2
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
===== CHANNEL F3 =====
NAME_3
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
===== CHANNEL F4 =====
NAME_4
TIME
INSTRUM
PROBHD
PULPROG
PC
DC
SFO
FIDRES
AQ
RG
DA
DE
TE
D1
dCHIRP
ADWX
```



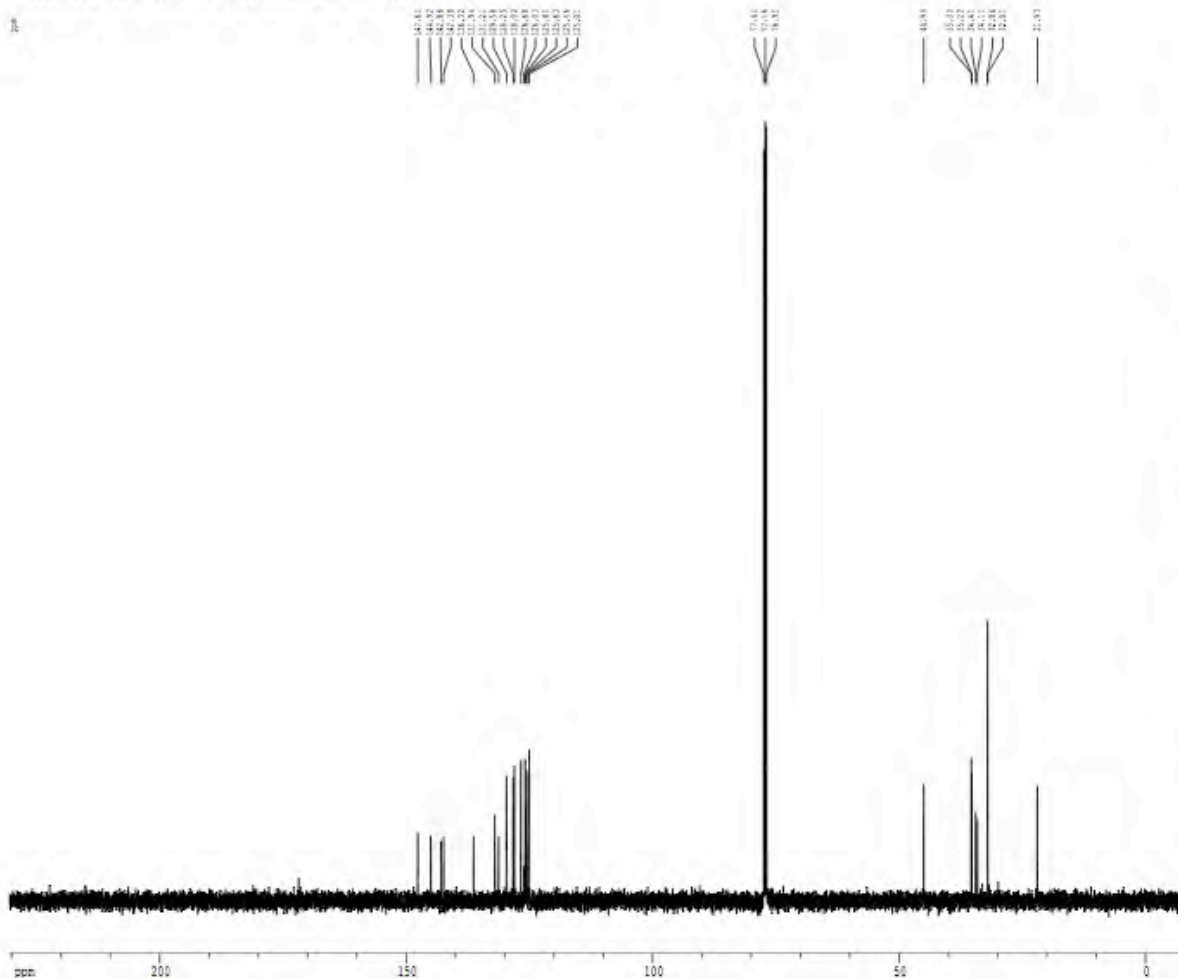




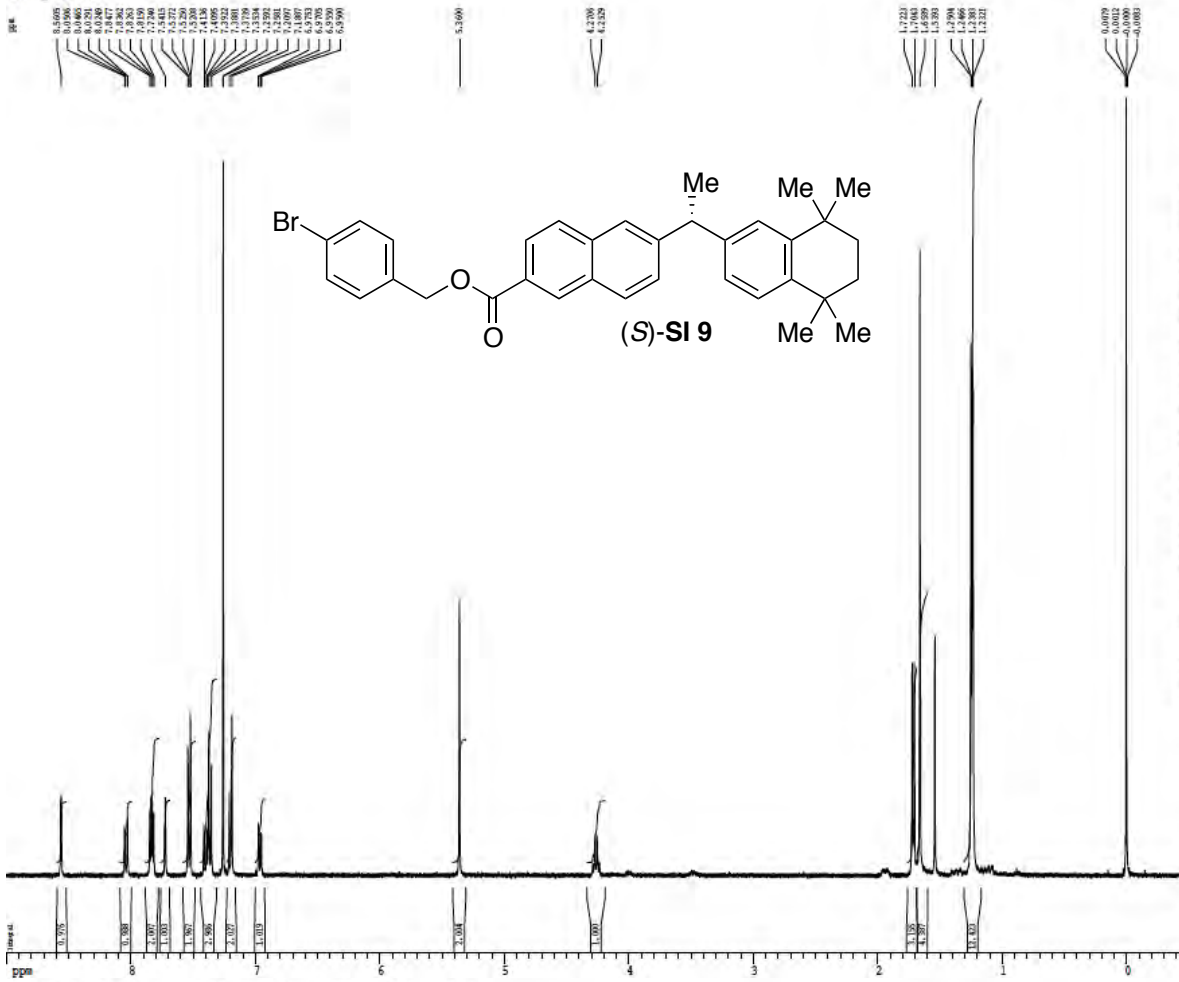
1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



```

Current Data Parameters
USER          mcPhe
NAME          ps-4-121a-1
EXPNO        1
PROCNO       1

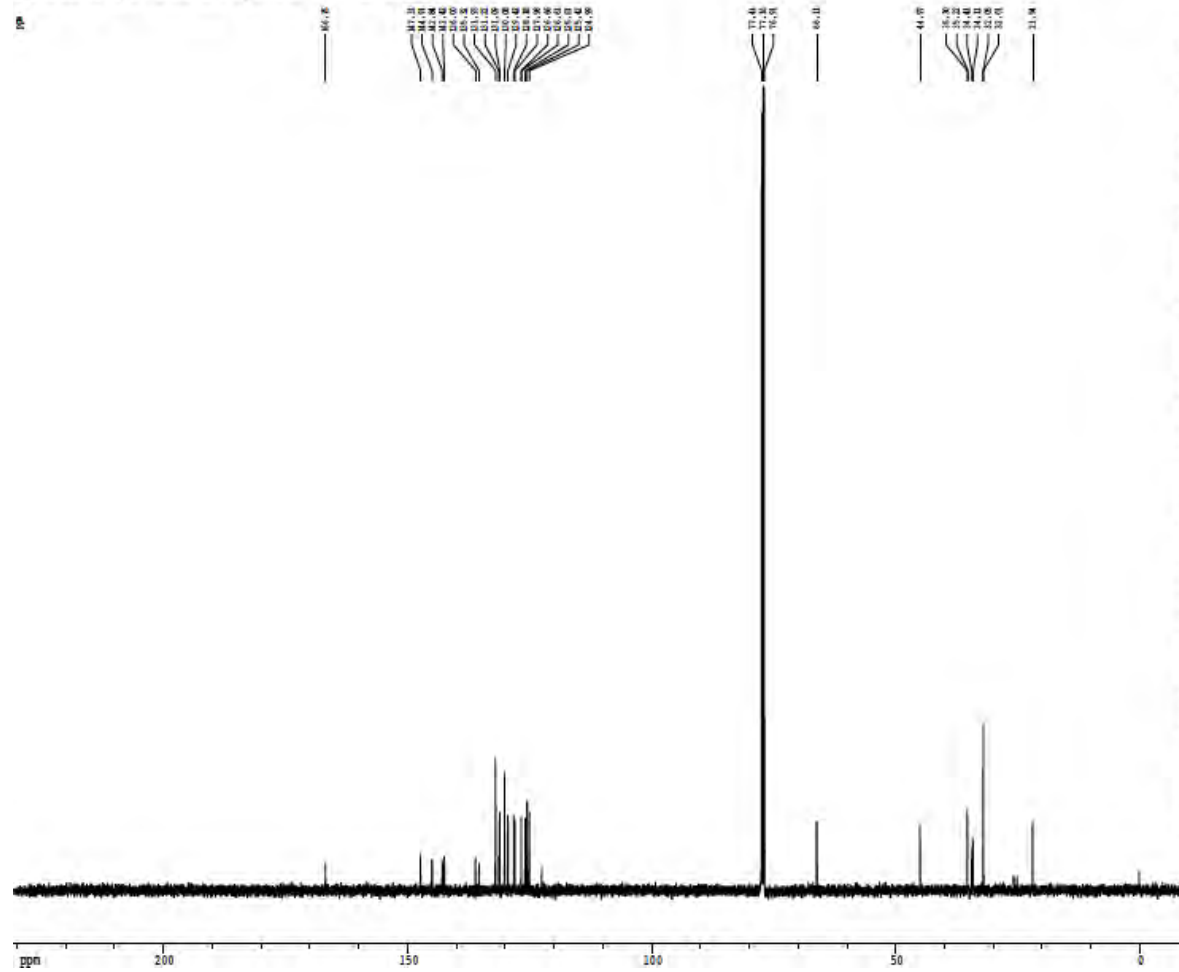
F1 - Acquisition Parameters
Date_        20190520
Time         21.56
INSTRUM      cryo400
PROBHD       5 mm QNP 1H/1
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           2
DS           4
SWH           6416.206 Hz
FIDRES       0.497813 Hz
AQ           5.111879 sec
RG           512
DQ           18.000 usec
DE           4.50 usec
TE           298.2 K
OL           0.10000000 sec
RGHGT        0.00000000 sec
RGDM         0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            12.00 usec
PL1          -0.50 dB
SFO1         400.132009 MHz

F1 - Processing parameters
SI            65536
SF            400.1304233 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            2.00

ID NMR plot parameters
CX           12.00 cm
CY           15.00 cm
FID         3.000 ppm
FT          3041.17 Hz
F2F         -4.500 ppm
F3          -300.04 Hz
SFCH2       0.41647 ppm/cm
RG          166.72084 Hz/cm
    
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```

Current Data Parameters
USER          mcPhe
NAME          ps-4-121a-011
EXPNO        1
PROCNO       1

F2 - Acquisition Parameters
Date_        20190520
Time         21.56
INSTRUM      cryo400
PROBHD       5 mm QNP 1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           2
DS           4
SWH           50201.011 Hz
FIDRES       9.462200 Hz
AQ           1.1812043 sec
RG           12004
DQ           14.000 usec
DE           1.00 usec
TE           299.2 K
OL           0.10000000 sec
RGHGT        0.02000000 sec
RGDM         0.00000000 sec
SI            65536
SF            125.760370 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            2.00

===== CHANNEL f1 =====
NUC1          13C
P1            12.00 usec
PL1          -0.00 usec
SFO1         125.760370 MHz

===== CHANNEL f2 =====
NUC2          1H
P2            100.00 usec
PL2          1.00 dB
SFO2         400.132009 MHz

===== CHANNEL f3 =====
NUC3          13C
P3            100.00 usec
PL3          1.00 dB
SFO3         125.760370 MHz

===== CHANNEL f4 =====
NUC4          1H
P4            100.00 usec
PL4          1.00 dB
SFO4         400.132009 MHz

===== CHANNEL f5 =====
NUC5          13C
P5            100.00 usec
PL5          1.00 dB
SFO5         125.760370 MHz

F2 - Processing parameters
SI            65536
SF            125.7604076 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            2.00

ID NMR plot parameters
CX           12.00 cm
CY           15.00 cm
FID         250.427 ppm
FT          25000.00 Hz
F2F         -15.787 ppm
F3          -279.16 Hz
SFCH2       19.56428 ppm/cm
RG          125.18465 Hz/cm
    
```

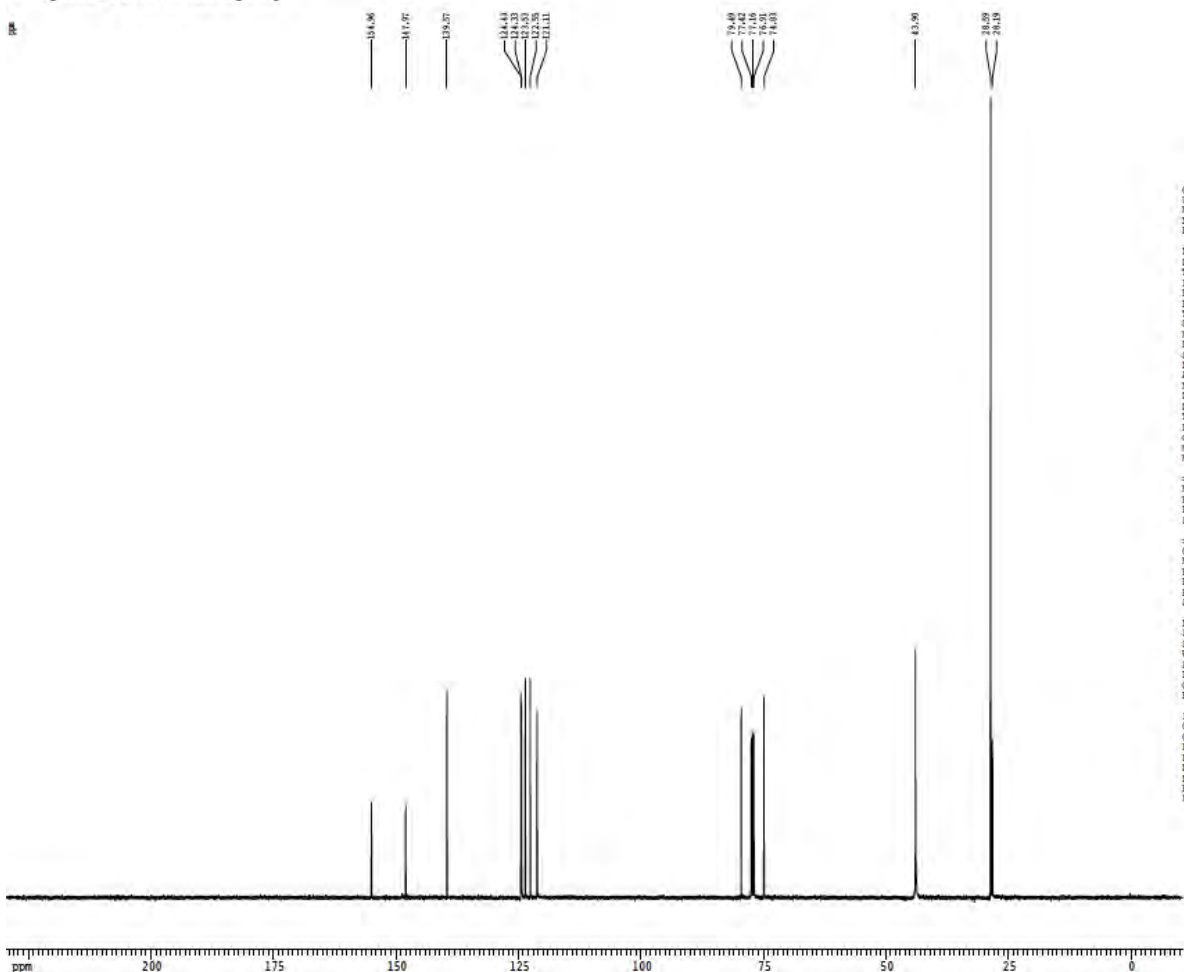


1H spectrum



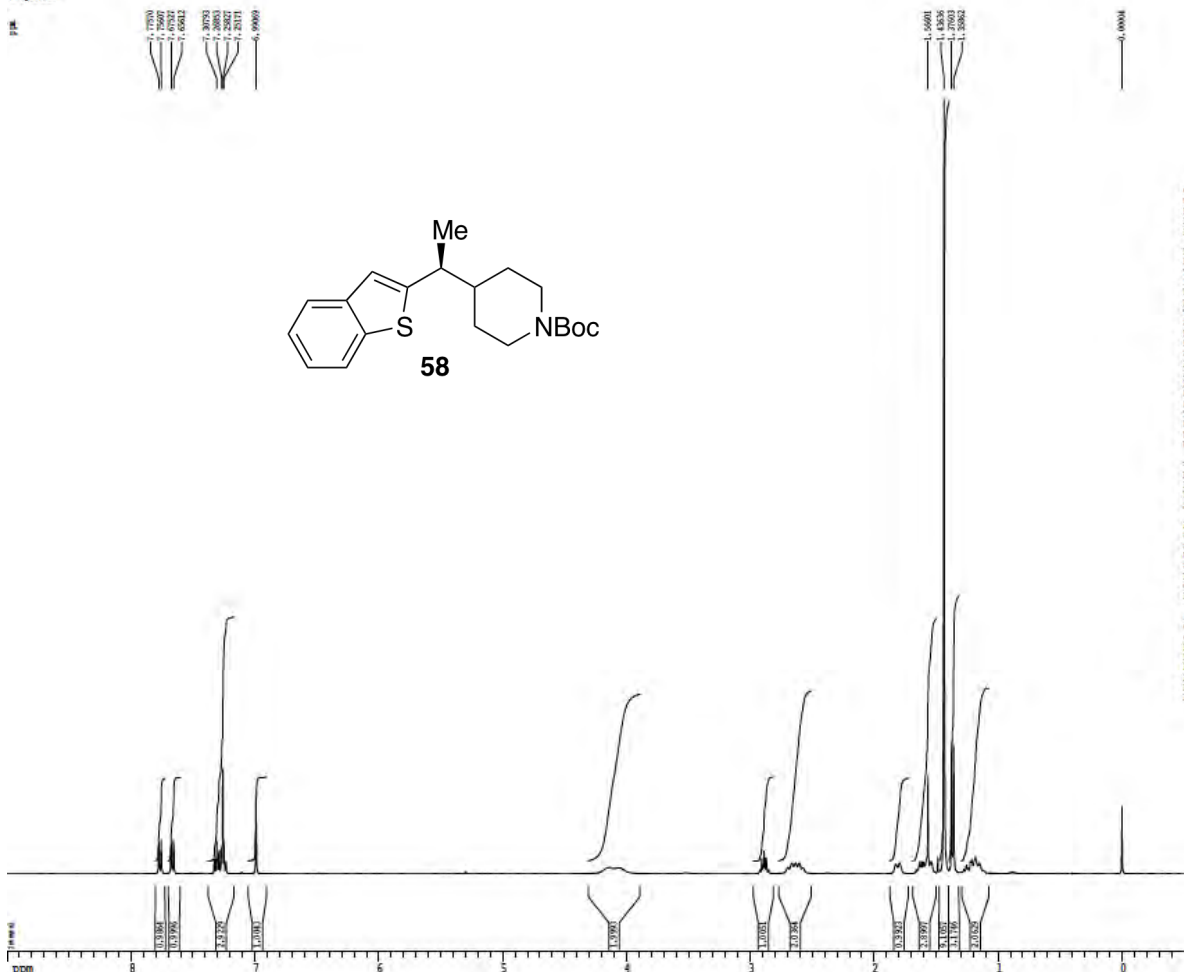
Current Data Parameters  
 NAME: 56  
 EXPNO: 1  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20120117  
 Time: 15.13  
 INSTRUM: spect  
 PROBHD: 5 mm broadbanc  
 PULPROG: zgpg30  
 DS: 4  
 SFO1: 499.812478 MHz  
 NS: 64  
 DSF: 4  
 SFO2: 303.031 MHz  
 FIDRES: 0.462388 Hz  
 AQ: 1.862394 sec  
 TE: 463K  
 DW: 16.500 usec  
 DE: 4.50 usec  
 HX: 323.0 F  
 DI: 1.0000000 sec  
 D11: 0.0100000 sec  
 MCH2: 0.0000000 sec  
 MCH3: 0.0100000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 1.70 usec  
 PL1: 0.00 dB  
 SFO1: 125.588431 MHz  
 ===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 80.00 usec  
 PL2: -1.00 dB  
 PL12: 19.20 dB  
 SFO2: 499.812478 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 125.5742189 MHz  
 DSF: 0  
 SSB: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 1.00  
 IS MRB plot parameters  
 CH: 22.00 cm  
 CI: 15.00 cm  
 F1: 9.000 ppm  
 F2: 4494.50 Hz  
 F3: -1.500 ppm  
 F4: -245.70 Hz  
 FWHM: 4.4167 ppm/cm  
 XCH: 208.98336 Hz/cm

13C spectrum with 1H decoupling



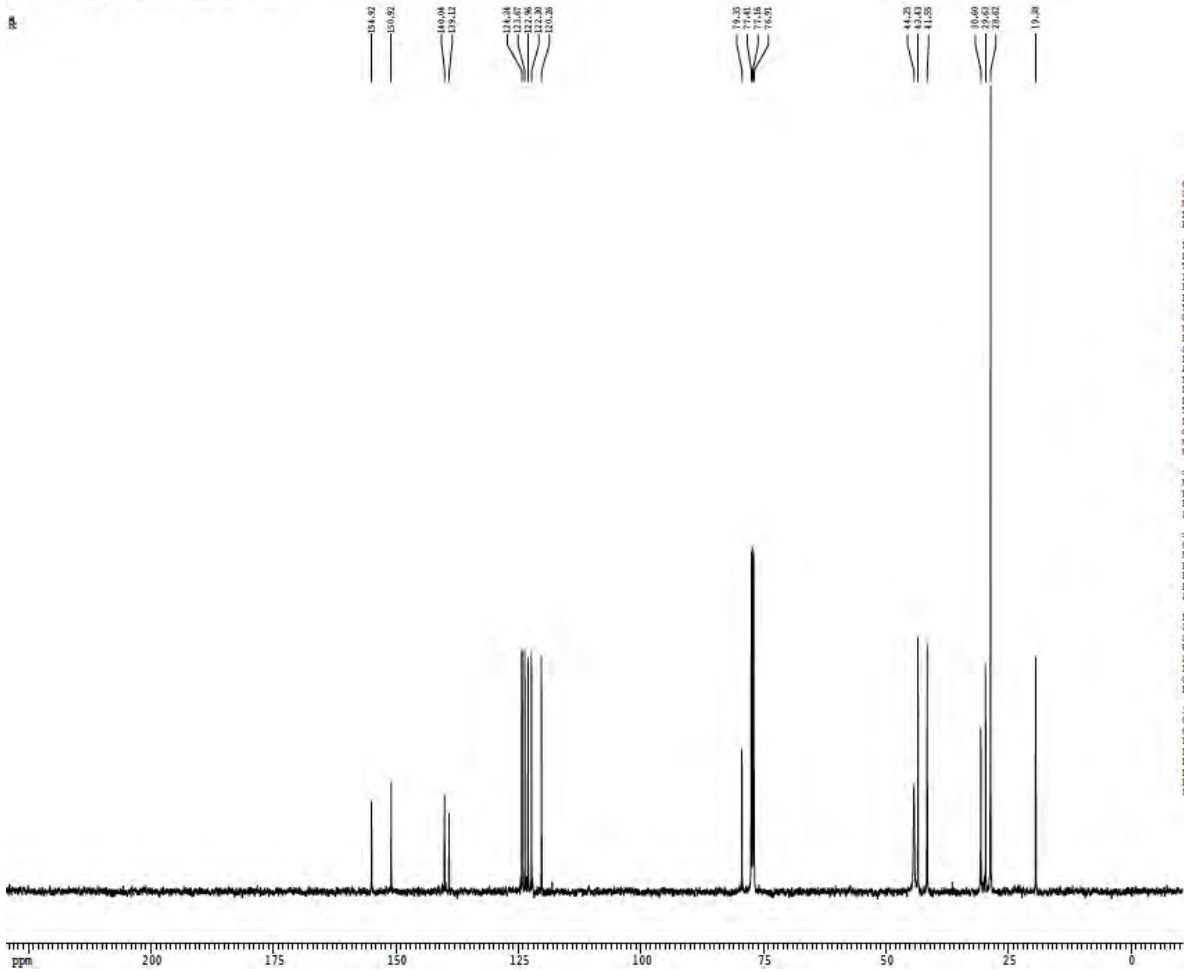
Current Data Parameters  
 NAME: 56  
 EXPNO: 2  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20120117  
 Time: 15.13  
 INSTRUM: spect  
 PROBHD: 5 mm broadbanc  
 PULPROG: zgpg30  
 DS: 4  
 SFO1: 499.812478 MHz  
 NS: 64  
 DSF: 4  
 SFO2: 303.031 MHz  
 FIDRES: 0.462388 Hz  
 AQ: 1.862394 sec  
 TE: 463K  
 DW: 16.500 usec  
 DE: 4.50 usec  
 HX: 323.0 F  
 DI: 1.0000000 sec  
 D11: 0.0100000 sec  
 MCH2: 0.0000000 sec  
 MCH3: 0.0100000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 1.70 usec  
 PL1: 0.00 dB  
 SFO1: 125.588431 MHz  
 ===== CHANNEL f2 =====  
 NUC2: 1H  
 P2: 80.00 usec  
 PL2: -1.00 dB  
 PL12: 19.20 dB  
 SFO2: 499.812478 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 125.5742189 MHz  
 DSF: 0  
 SSB: 0  
 LB: 1.00 Hz  
 GB: 0  
 PC: 1.00  
 IS MRB plot parameters  
 CH: 22.00 cm  
 CI: 15.00 cm  
 F1: 229.520 ppm  
 F2: 23821.76 Hz  
 F3: -16.507 ppm  
 F4: -1319.36 Hz  
 FWHM: 15.52747 ppm/cm  
 XCH: 1321.97864 Hz/cm





**Current Data Parameters**  
 NAME XMG-VI.233A470  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20130207  
 Time 11:31  
 INSTRUM spect  
 PROCD 5 mm QNP 1H/2  
 PULPROG zgpg30  
 DS 4  
 SOLVENT CDCl3  
 NS 252  
 DS 4  
 SWH 640.256 Hz  
 FIDRES 0.397013 Hz  
 AQ 5.118579 sec  
 RG 362  
 CW 78.000 usec  
 INEPT 4.50 usec  
 F1 298.1 K  
 T2 0.10000000 sec  
 MCHYZ 0.00000000 sec  
 MCHYZ 0.01500000 sec  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 12.00 usec  
 PL1 -0.40 dB  
 SFO1 400.126009 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 400.1260211 MHz  
 DS 4  
 SWH 4.00 Hz  
 FIDRES 0.30 Hz  
 AQ 2.00  
 RG 362  
 ===== CHANNEL f2 =====  
 NUC2 13C  
 P2 15.00 usec  
 PL2 -1.00 dB  
 SFO2 101.253750 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 101.253750 MHz  
 DS 4  
 SWH 4.00 Hz  
 FIDRES 0.30 Hz  
 AQ 2.00  
 RG 362

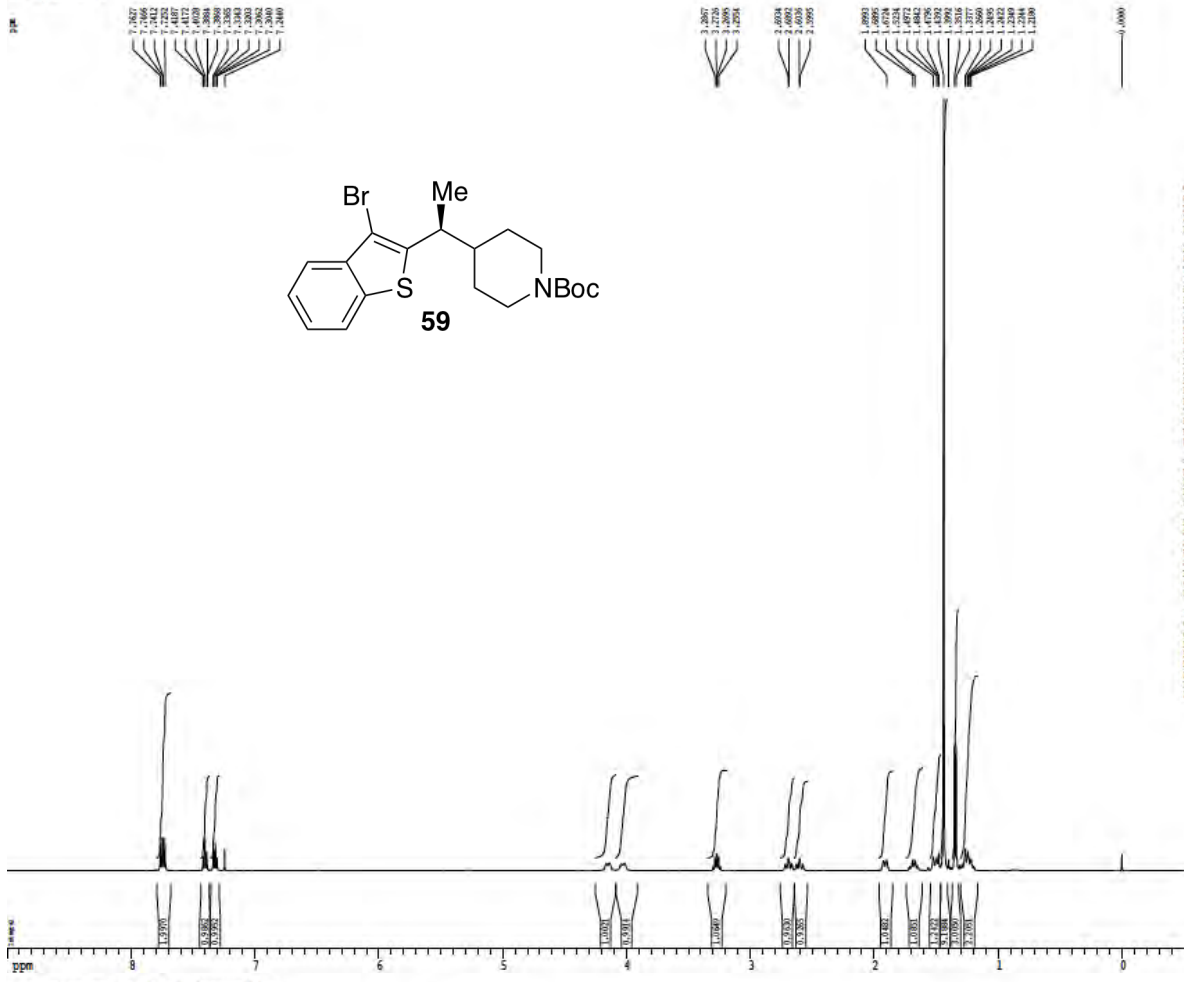
13C spectrum with 1H decoupling



**Current Data Parameters**  
 NAME XMG-VI.237A  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20130207  
 Time 10:27  
 INSTRUM spect  
 PROCD 5 mm QNP 1H/13  
 PULPROG zgpg30  
 DS 4  
 SOLVENT CDCl3  
 NS 252  
 DS 4  
 SWH 30393.031 Hz  
 FIDRES 0.461388 Hz  
 AQ 1.8612940 sec  
 RG 3170.5  
 CW 16.500 usec  
 INEPT 4.50 usec  
 F1 298.1 K  
 T2 0.10000000 sec  
 MCHYZ 0.00000000 sec  
 MCHYZ 0.01500000 sec  
 ===== CHANNEL f1 =====  
 NUC1 13C  
 P1 7.70 usec  
 PL1 0.00 dB  
 SFO1 125.5886432 MHz  
 ===== CHANNEL f2 =====  
 NUC2 1H  
 P2 80.00 usec  
 PL2 -1.00 dB  
 SFO2 499.4024970 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 125.5742158 MHz  
 DS 4  
 SWH 4.00 Hz  
 FIDRES 0.30 Hz  
 AQ 2.00  
 RG 362  
 ===== CHANNEL f3 =====  
 NUC3 13C  
 P3 15.00 usec  
 PL3 -1.00 dB  
 SFO3 101.253750 MHz  
 F3 - Processing parameters  
 SI 65536  
 SF 101.253750 MHz  
 DS 4  
 SWH 4.00 Hz  
 FIDRES 0.30 Hz  
 AQ 2.00  
 RG 362



1H spectrum



Current Data Parameters  
 NAME: harraw  
 PROCNO: 3  
 F2 - Acquisition Parameters  
 Date\_: 20121211  
 Time: 12.02  
 INSTRUM: gpc500  
 FREQID: 5 mm broadband  
 PULPROG: zgpg30  
 DS: 8170  
 SOLVENT: CDCl3  
 NS: 8  
 DSF: 4  
 SWH: 8012.810 Hz  
 FIDRES: 0.090043 Hz  
 AQ: 5.8990774 sec  
 PC: 314  
 SFO: 62.400 uspc  
 ST: 8.00 uspc  
 SC: 323.0 F  
 SI: 0.10000000 sec  
 WDELT: 0.00000000 sec  
 MCHN: 0.01000000 sec

---

===== CHANNEL f1 =====  
 NUC1: 1H  
 F1: 500.136261 MHz  
 P1: -0.00 dB  
 SFO1: 499.4024958 MHz

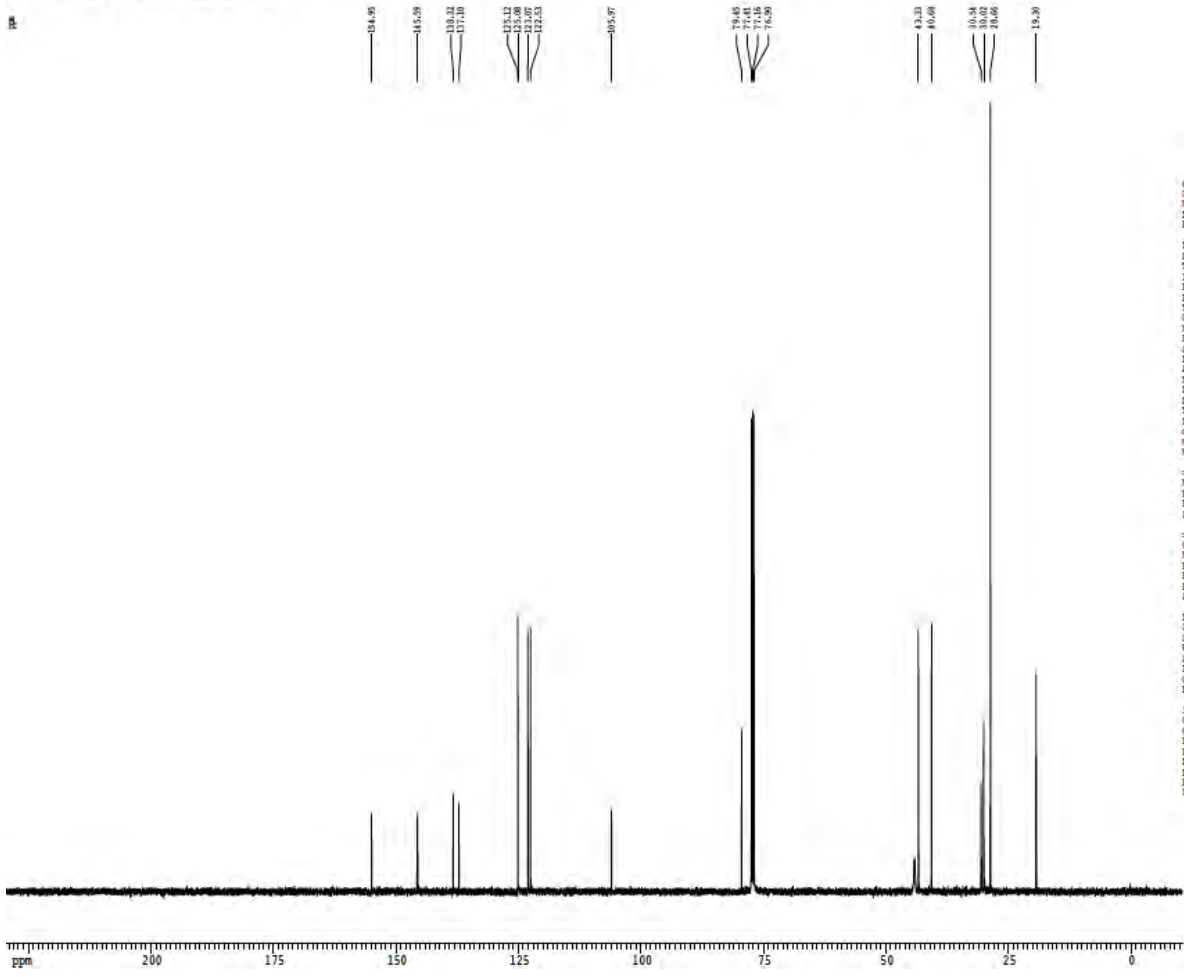
---

F2 - Processing parameters  
 SI: 65536  
 SF: 499.4024958 MHz  
 DSF: 4  
 SWH: 8012.810 Hz  
 SFO: 62.400 Hz  
 PC: 1.00

---

1D NMR plot parameters  
 CH: 22.00 cm  
 CL: 15.00 cm  
 FID: 9.000 ppm  
 F1: 4844.00 Hz  
 F2: -1.500 ppm  
 F3: -245.70 Hz  
 FWHM: 0.41667 ppm/cm  
 SFO: 208.00334 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters  
 NAME: harraw  
 PROCNO: 4  
 F2 - Acquisition Parameters  
 Date\_: 20121211  
 Time: 12.18  
 INSTRUM: gpc500  
 FREQID: 5 mm broadband  
 PULPROG: zgpg30  
 DS: 65536  
 SOLVENT: CDCl3  
 NS: 1024  
 DSF: 4  
 SWH: 30303.031 Hz  
 FIDRES: 0.462388 Hz  
 AQ: 1.9823940 sec  
 PC: 23170.5  
 SFO: 16.500 uspc  
 ST: 4.50 uspc  
 SC: 323.0 F  
 SI: 1.00000000 sec  
 WDELT: 0.00000000 sec  
 MCHN: 0.00000000 sec  
 MCHN: 0.01000000 sec

---

===== CHANNEL f1 =====  
 NUC1: 13C  
 F1: 77.74 uspc  
 P1: 0.00 dB  
 SFO1: 125.5886431 MHz

---

===== CHANNEL f2 =====  
 NUC2: 1H  
 F2: 500.136261 MHz  
 P2: -0.00 dB  
 SFO2: 499.4024970 MHz

---

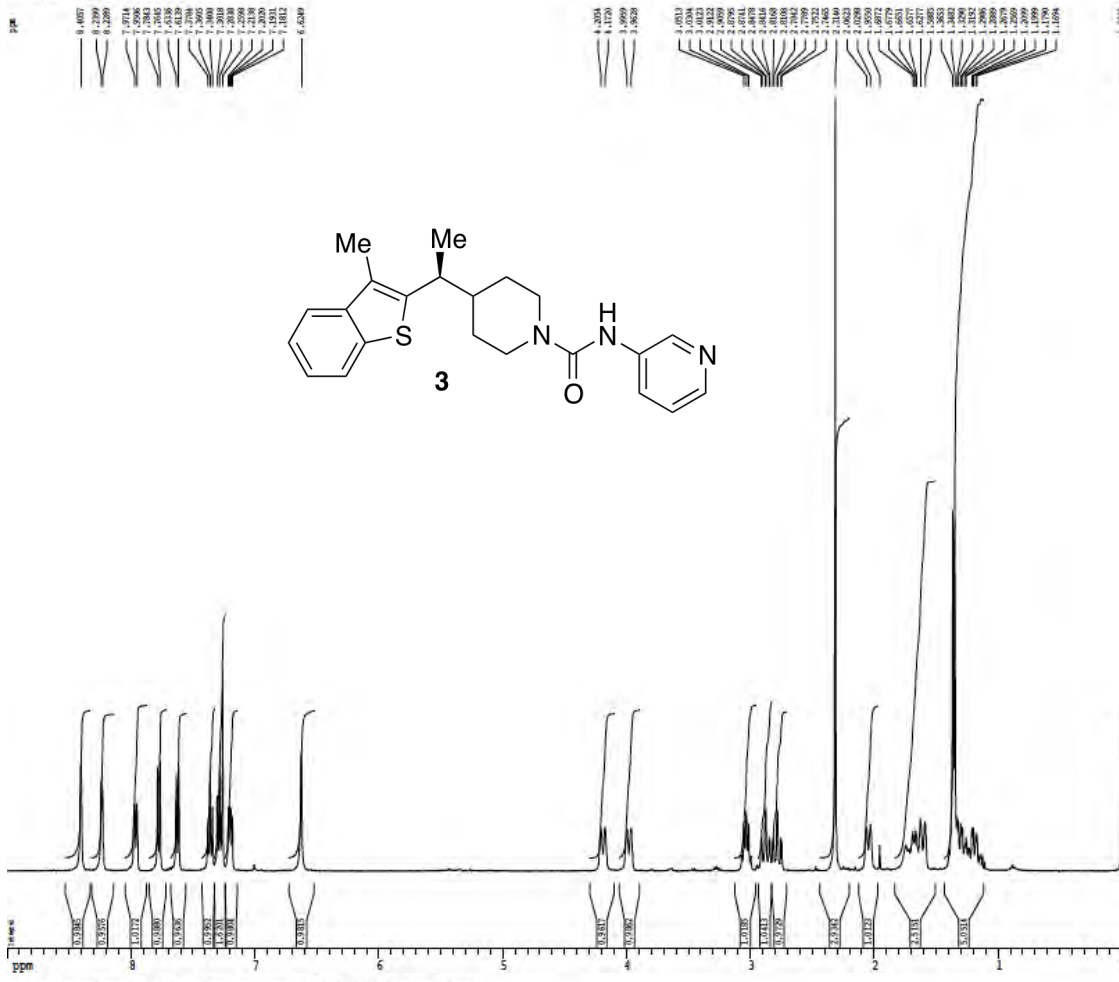
F2 - Processing parameters  
 SI: 65536  
 SF: 125.5742006 MHz  
 DSF: 4  
 SWH: 30303.031 Hz  
 SFO: 16.500 Hz  
 PC: 1.00

---

1D NMR plot parameters  
 CH: 22.00 cm  
 CL: 15.00 cm  
 FID: 229.520 ppm  
 F1: 23821.75 Hz  
 F2: -18.507 ppm  
 F3: -1319.36 Hz  
 FWHM: 15.52747 ppm/cm  
 SFO: 1321.97882 Hz/cm

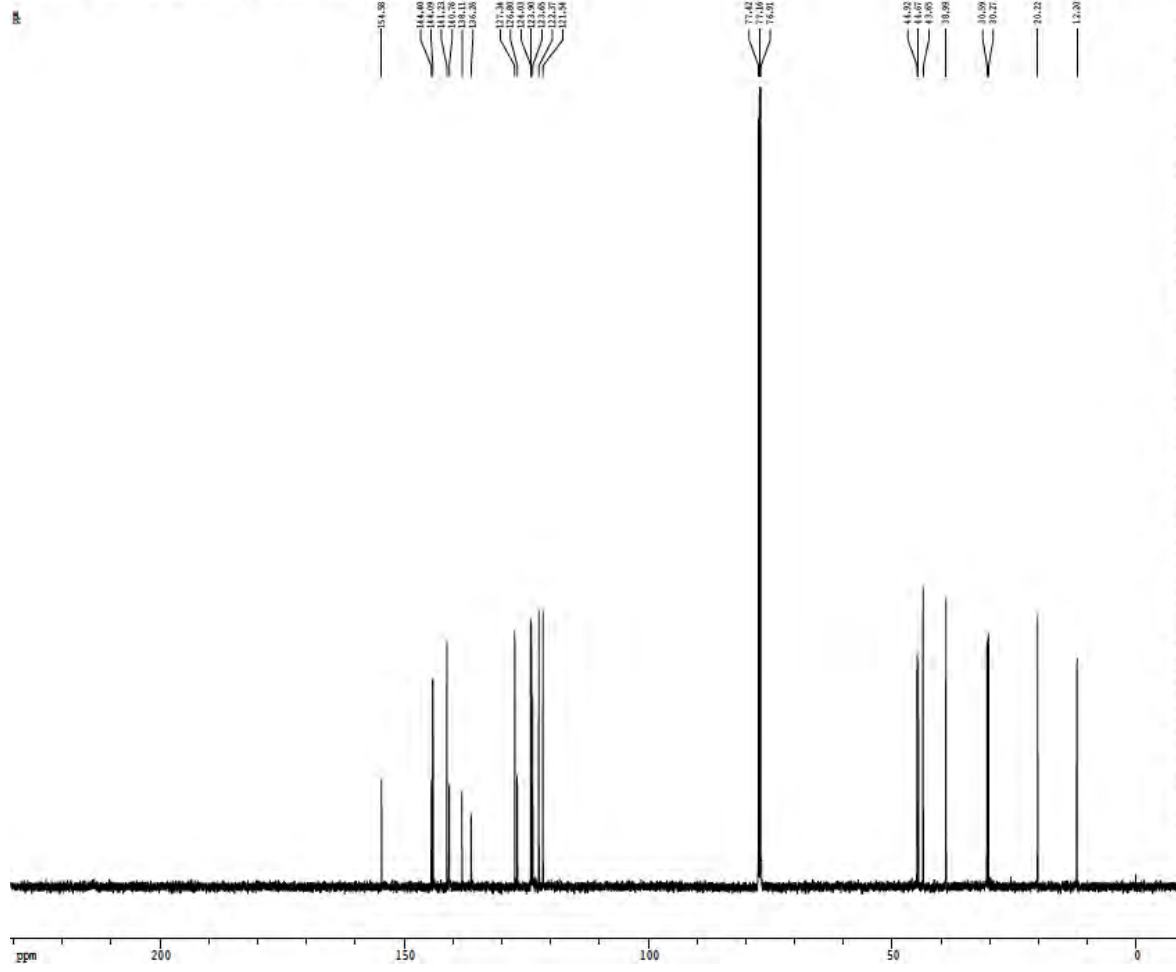


1H spectrum

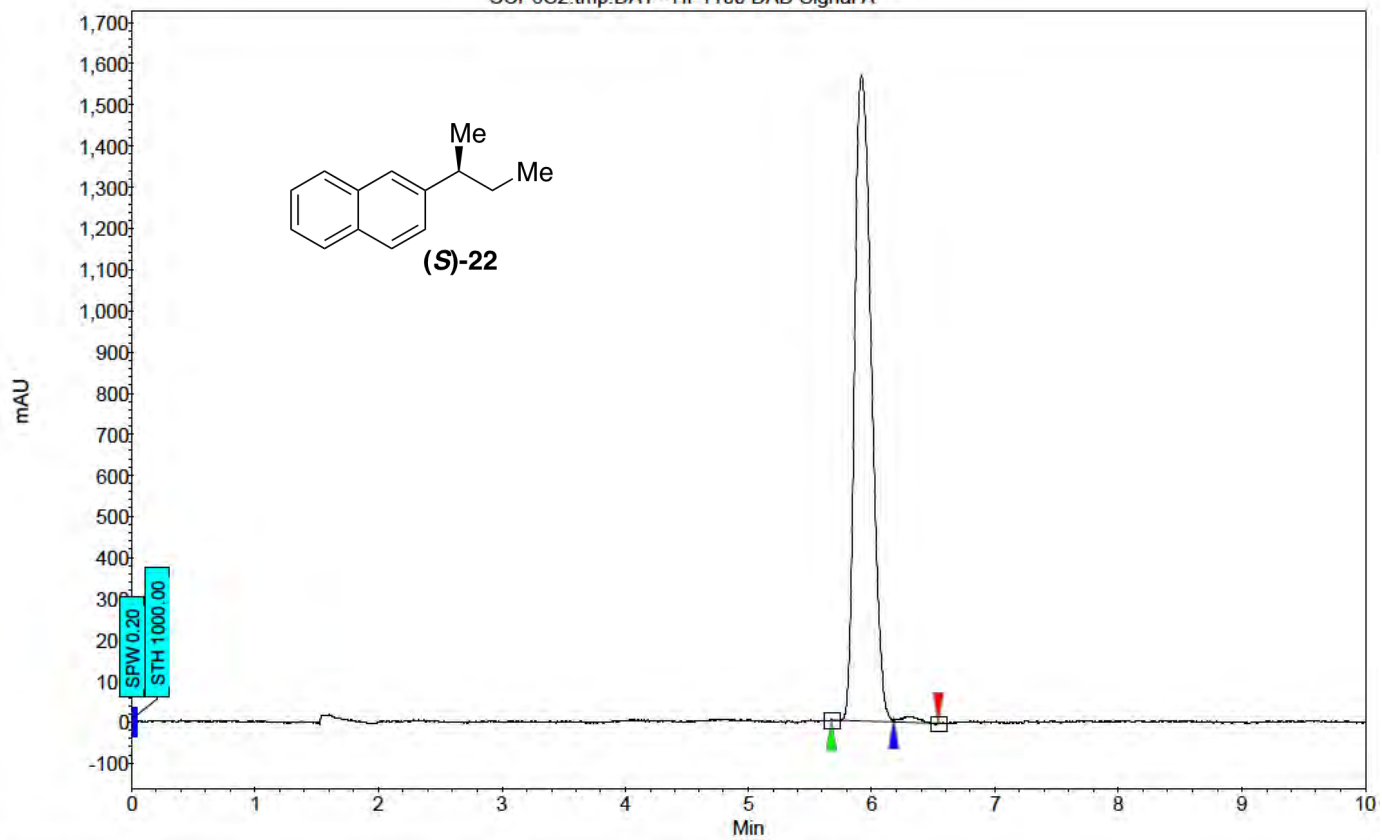
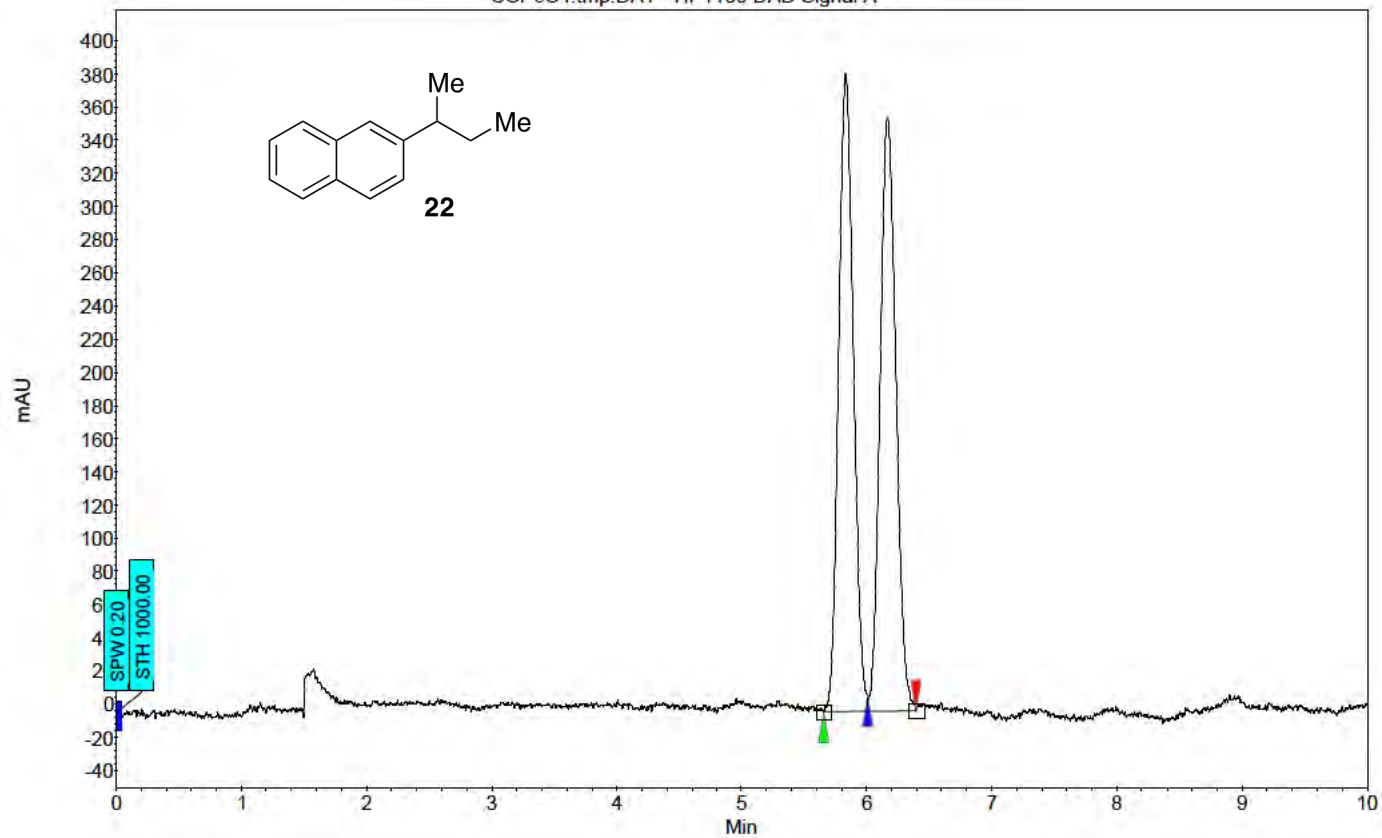


Output Data Parameters  
 NAME harrow  
 EXPNO 1  
 PROCNO 1  
 F1 - Acquisition Parameters  
 Date\_ 20120111  
 Time 15:31  
 INSTRUM spect  
 PRGNO 5  
 PULPROG zgpg30  
 DS 65516  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 6410.264 Hz  
 FWHZ 0.897813 Hz  
 AQ 5.112579 sec  
 RG 257.4  
 SW 78.000 uspc  
 TE 4.50 uspc  
 SI 256.0 K  
 SC 0.12000000 sec  
 WDELT 0.00000000 sec  
 WCNV 0.01200000 sec  
 =====  
 CHANNEL f1  
 NUC1 13  
 P1 12.00 uspc  
 PL 0.00 dB  
 SFO1 400.126000 MHz  
 F2 - Processing parameters  
 SI 65516  
 SF 400.126000 MHz  
 DS 2  
 SW 0  
 LB 0.30 Hz  
 GB 0  
 PC 2.00  
 IS - MSI plot parameters  
 CI 22.80 cm  
 CT 15.00 cm  
 F1F 9.000 ppm  
 F2F 381.17 Hz  
 F3F -1.500 ppm  
 F4F -202.06 Hz  
 F5F 6.4161 ppm/cm  
 SFOH 166.72088 Hz/cm

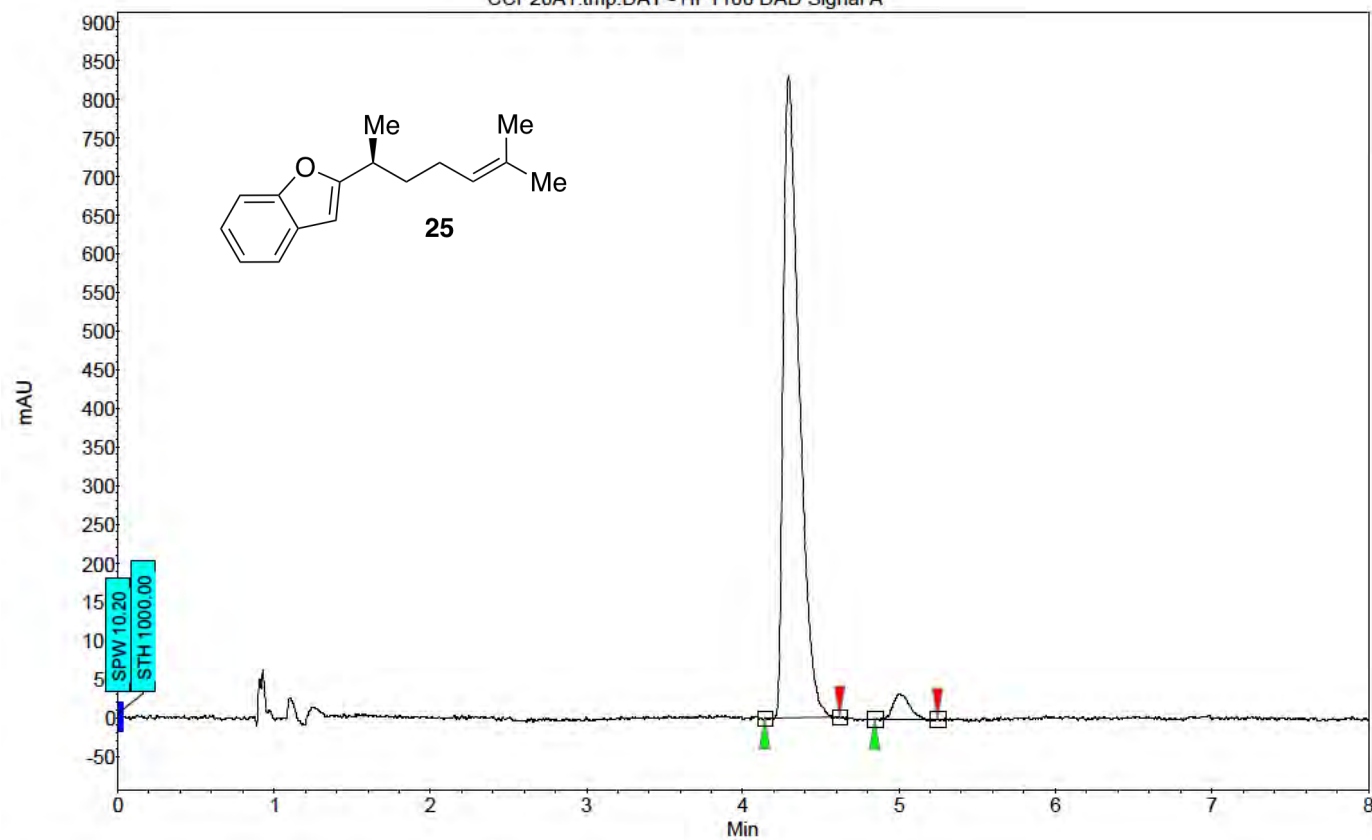
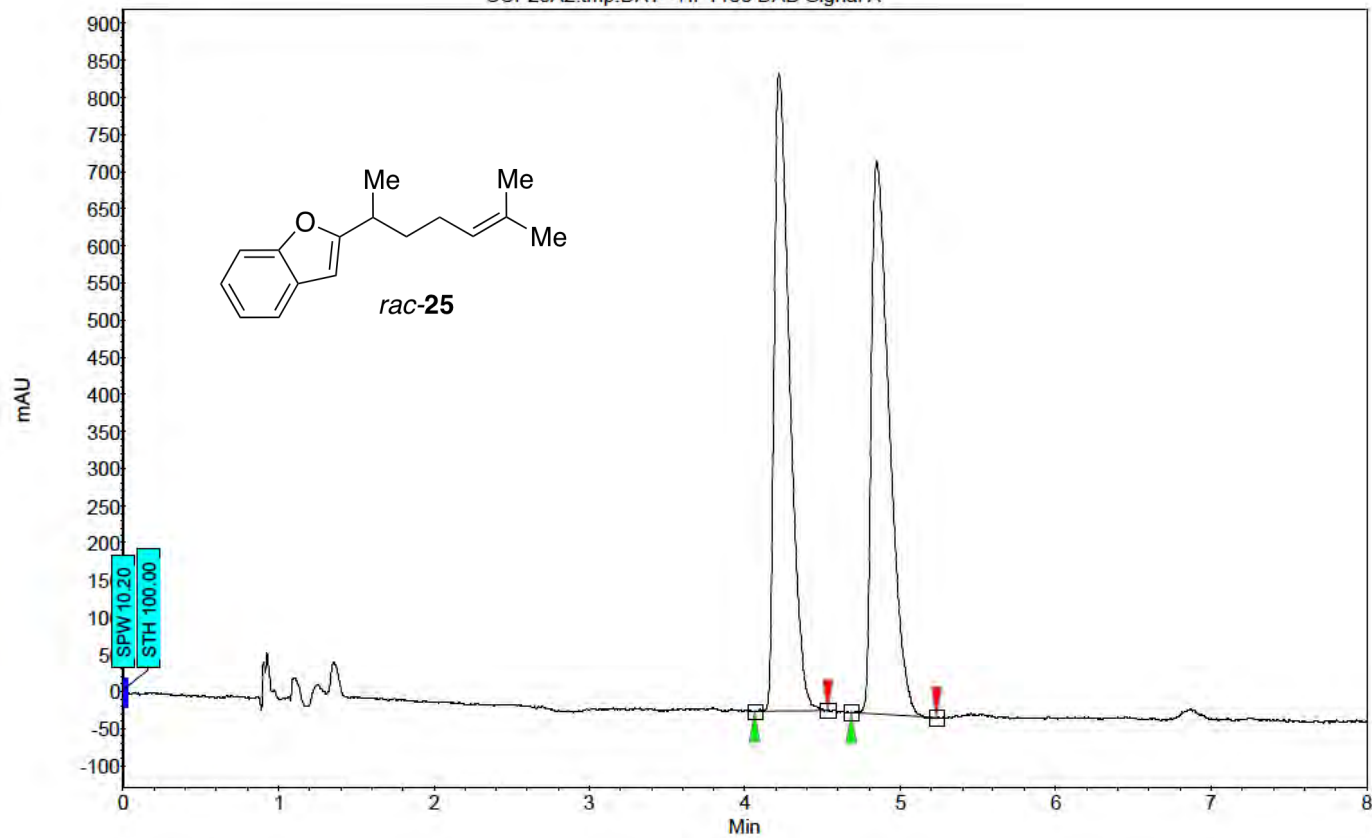
Z-restored spin-echo 13C spectrum with 1H decoupling



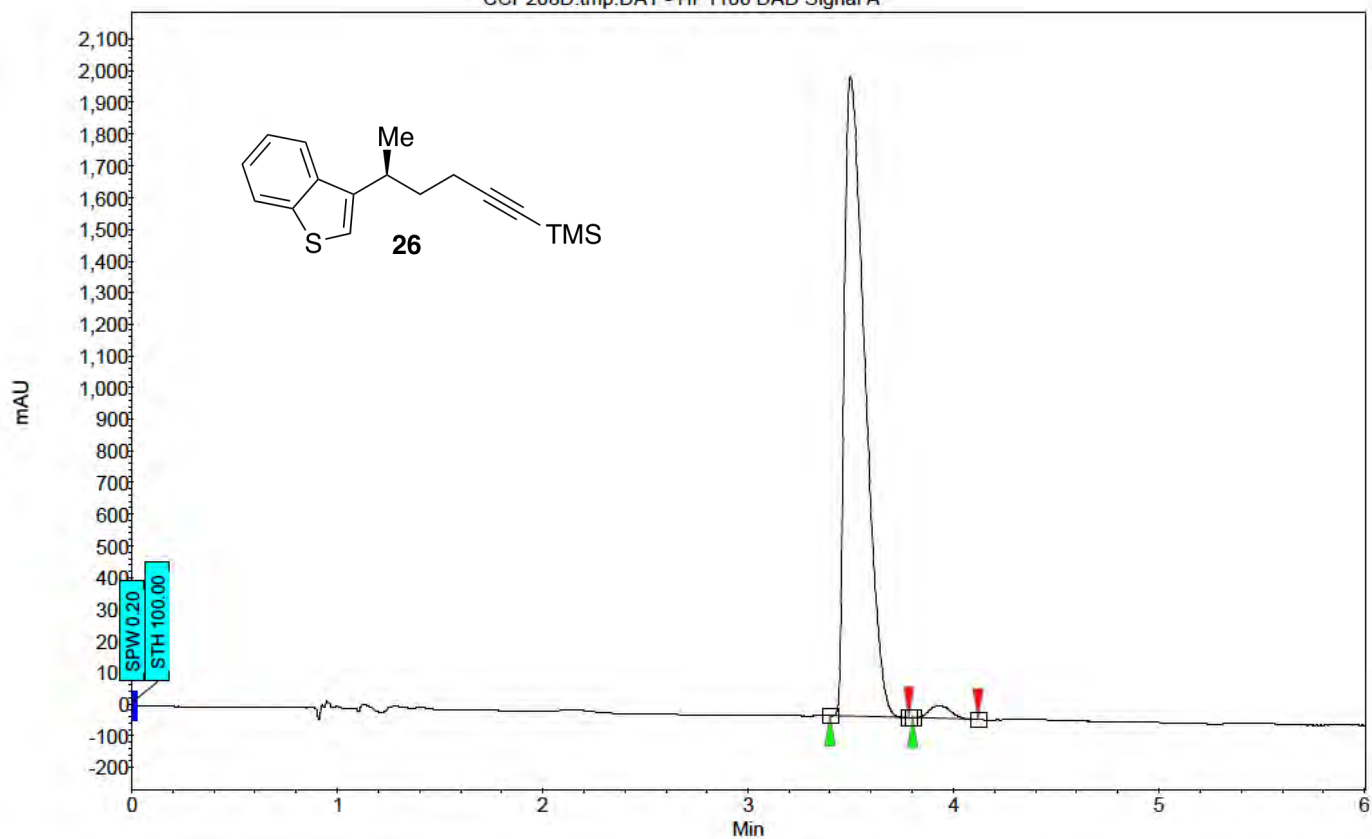
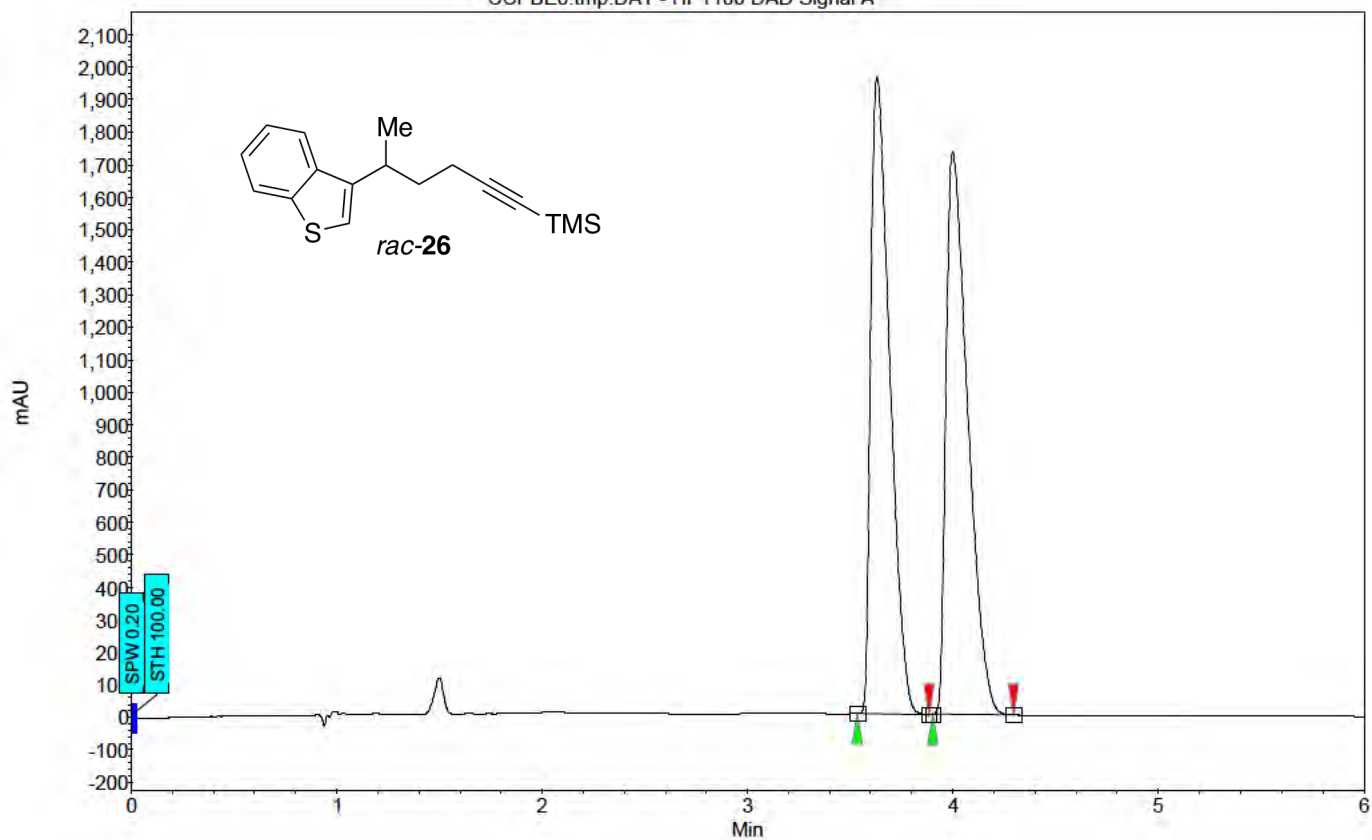
Output Data Parameters  
 NAME harrow  
 EXPNO 1  
 PROCNO 1  
 F1 - Acquisition Parameters  
 Date\_ 20120111  
 Time 20:28  
 INSTRUM spect  
 PRGNO 5  
 PULPROG zgpg30  
 DS 65516  
 SOLVENT CDCl3  
 NS 124  
 DS 16  
 SWH 50003.031 Hz  
 FWHZ 0.862368 Hz  
 AQ 1.081244 sec  
 RG 249  
 SW 14.500 uspc  
 TE 8.00 uspc  
 SI 256.0 K  
 SC 0.12000000 sec  
 WDELT 0.00000000 sec  
 WCNV 0.00000000 sec  
 F2 - Processing parameters  
 SI 65516  
 SF 125.760400 MHz  
 DS 2  
 SW 0  
 LB 1.00 Hz  
 GB 0  
 PC 2.00  
 IS - MSI plot parameters  
 CI 22.80 cm  
 CT 15.00 cm  
 F1F 3000.08 Hz  
 F2F -1.000 ppm  
 F3F 10.5808 Hz  
 F4F -1293.96 Hz  
 SFOH 1270.10585 Hz/cm



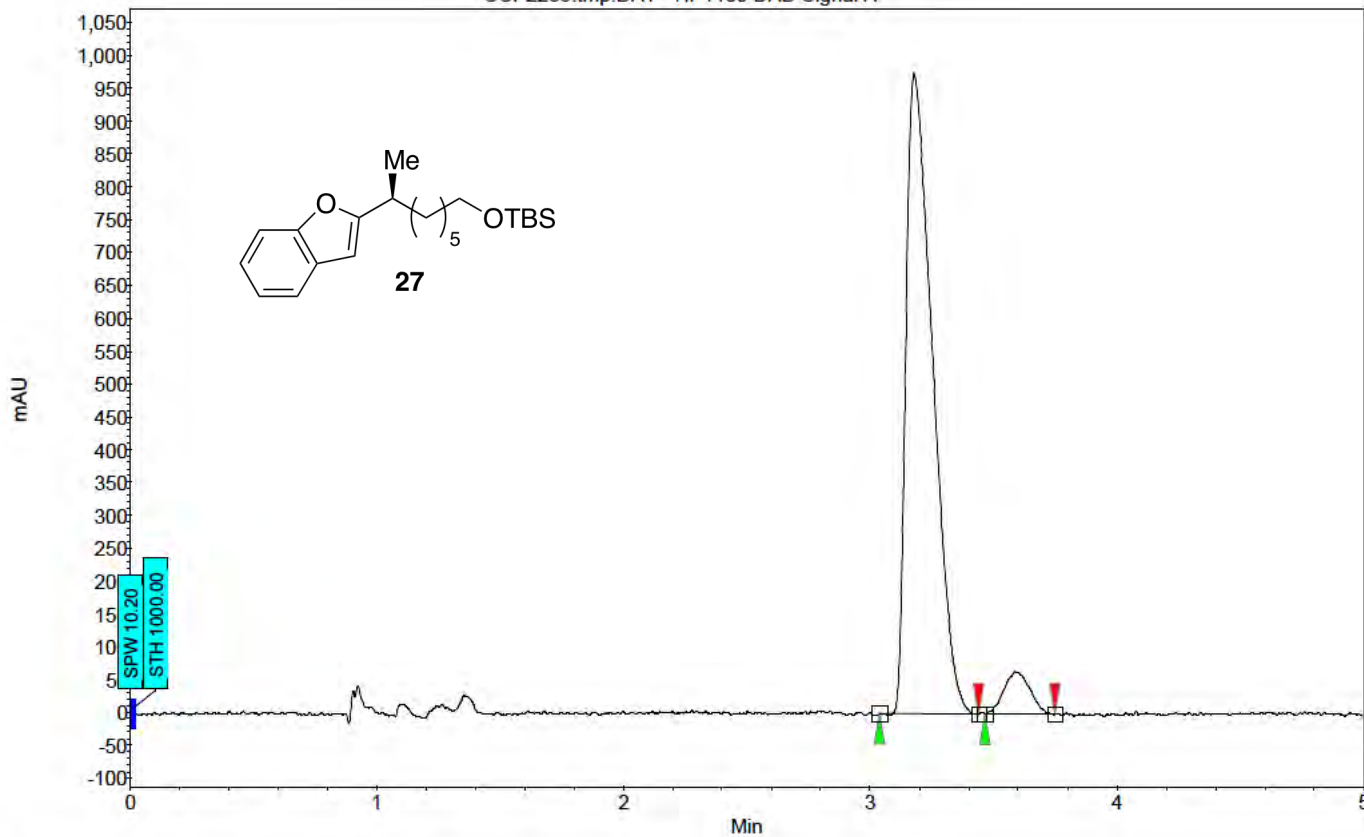
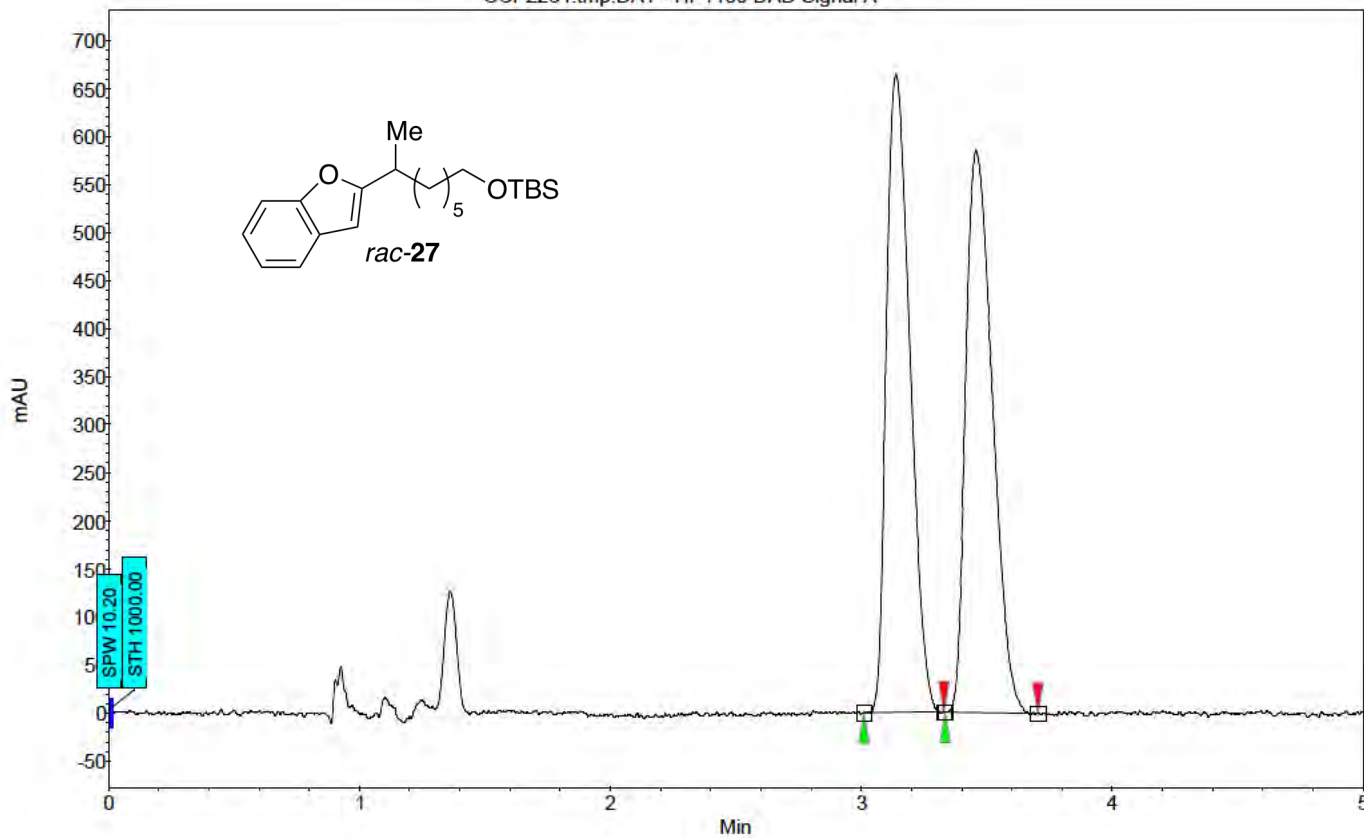
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	5.68	5.92	6.18	0.00	98.96	1568.2	246.5	98.964
2	UNKNOWN	6.18	6.29	6.54	0.00	1.04	15.7	2.6	1.036
Total						100.00	1583.9	249.1	100.000



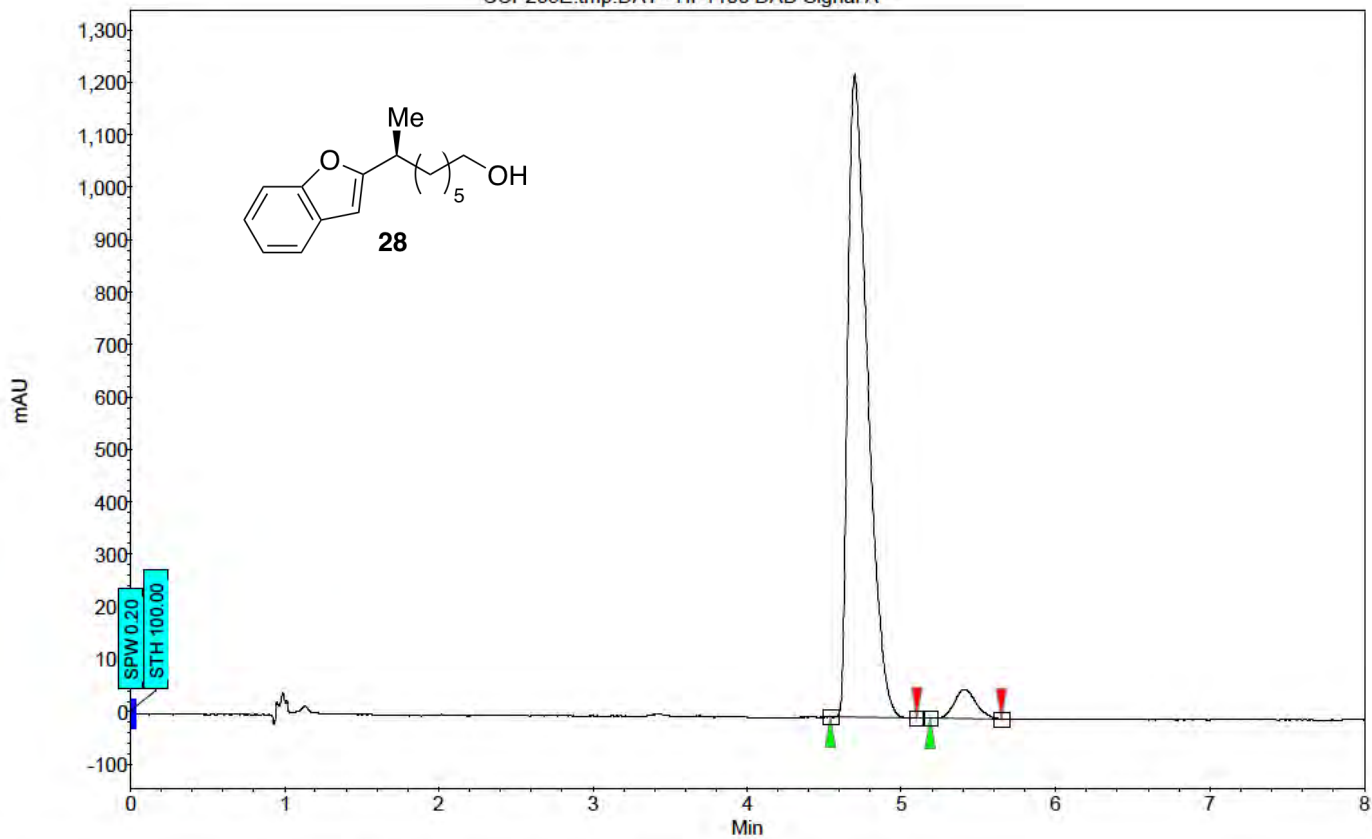
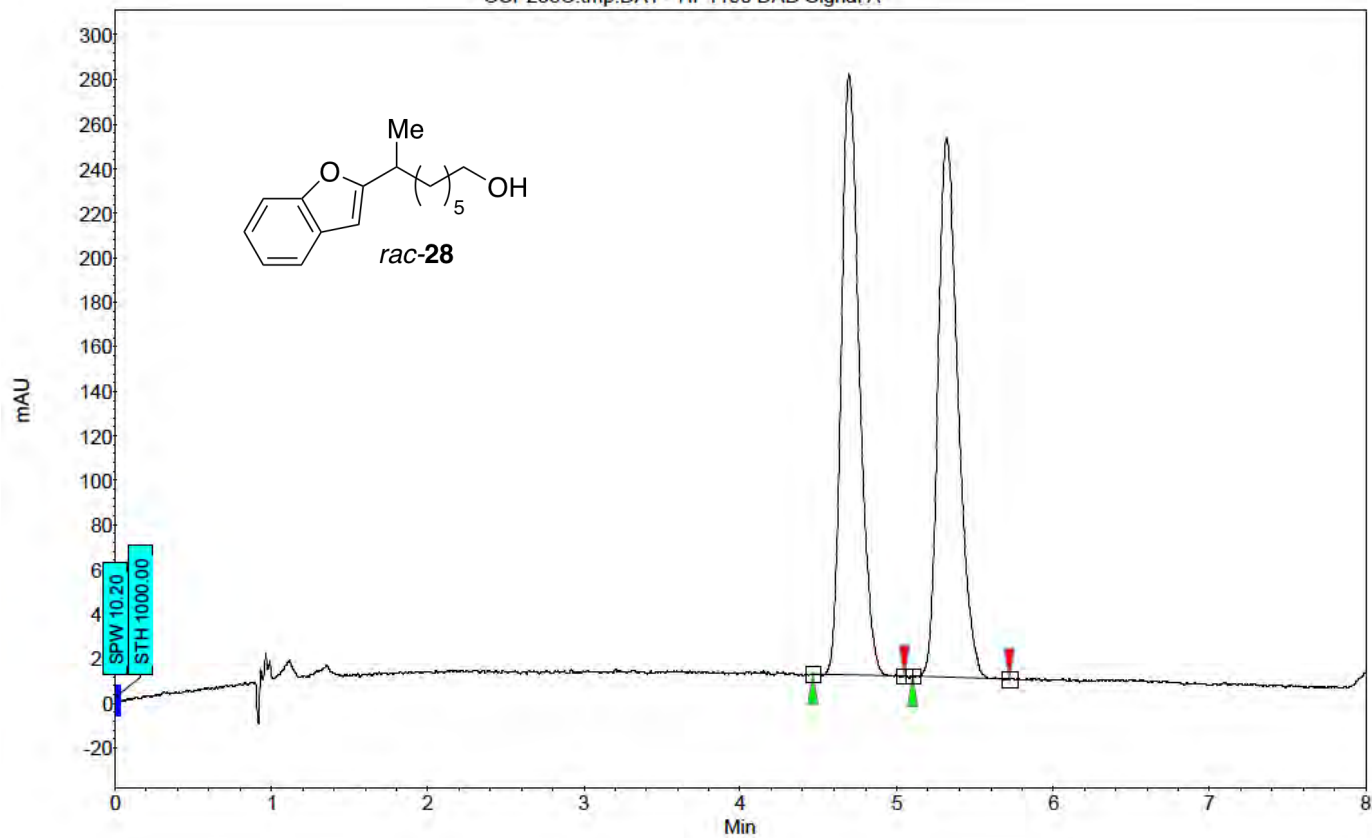
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	4.14	4.29	4.62	0.00	96.37	828.7	97.5	96.371
2	UNKNOWN	4.84	5.00	5.25	0.00	3.63	31.8	3.7	3.629
Total						100.00	860.5	101.2	100.000



Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	3.40	3.50	3.78	0.00	97.95	2017.3	232.3	97.946
2	UNKNOWN	3.80	3.93	4.12	0.00	2.05	41.7	4.9	2.054
Total						100.00	2059.1	237.2	100.000

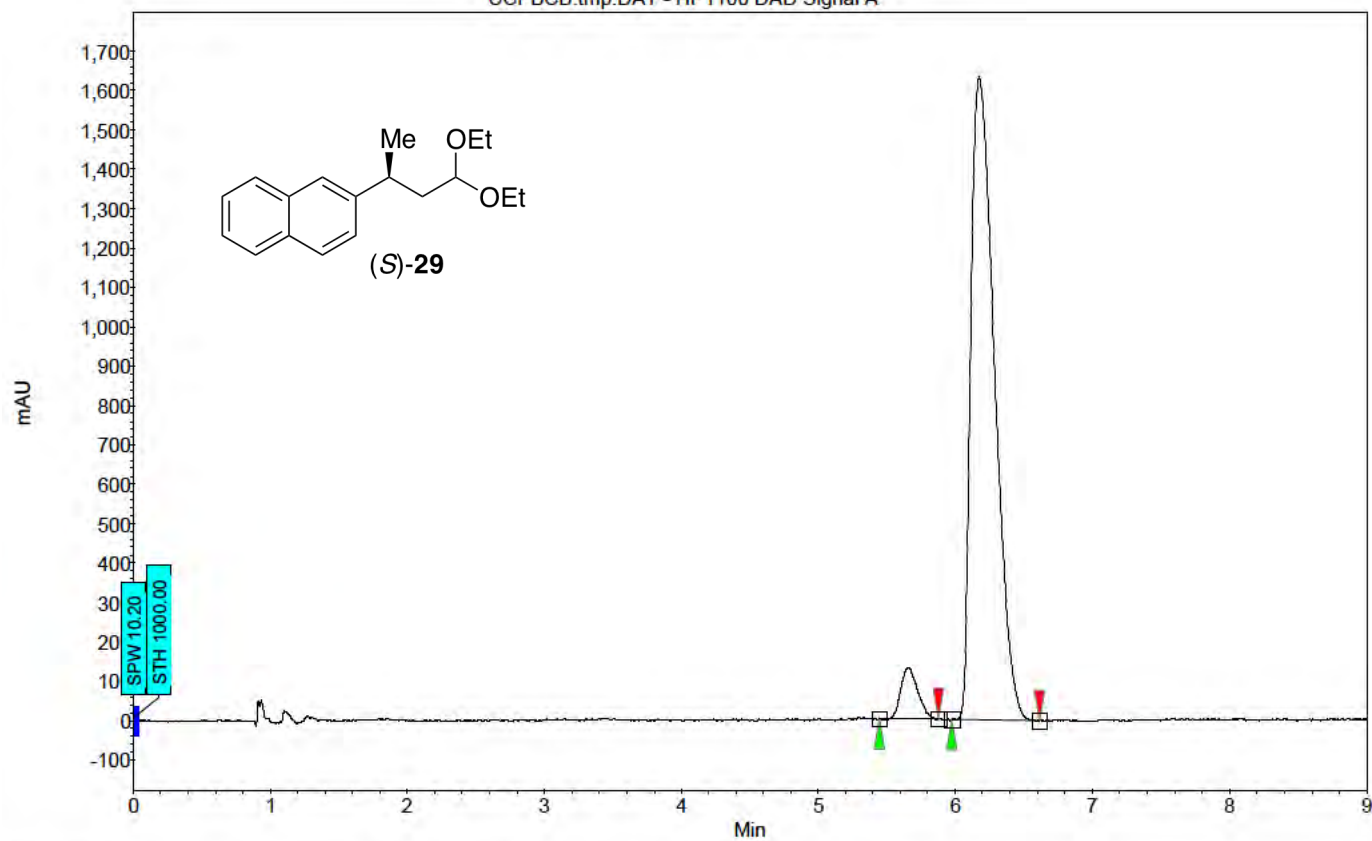
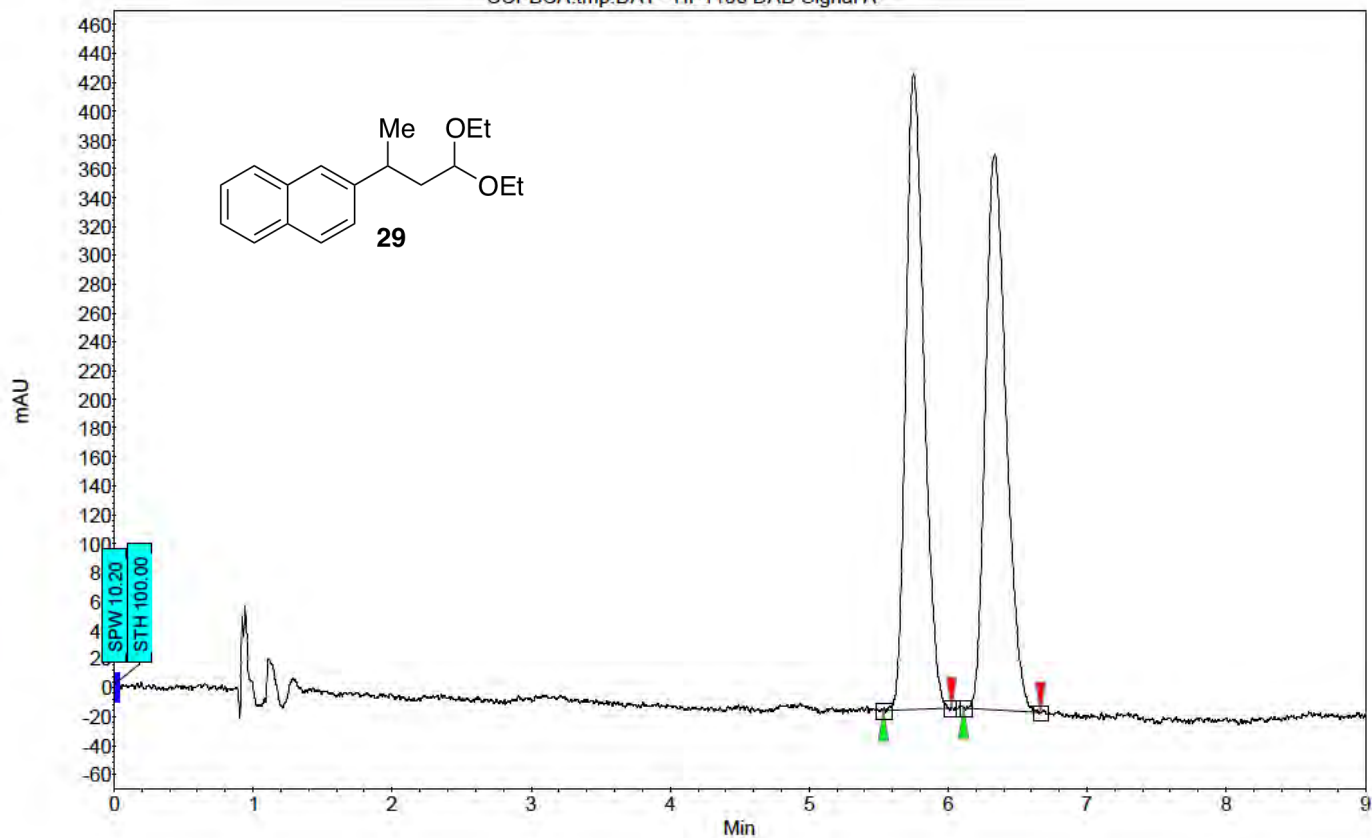


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV_Min]
1	UNKNOWN	3.04	3.18	3.44	0.00	93.91	973.9	121.5 93.911
2	UNKNOWN	3.47	3.59	3.75	0.00	6.09	64.4	7.9 6.089
Total						100.00	1038.3	129.3 100.000

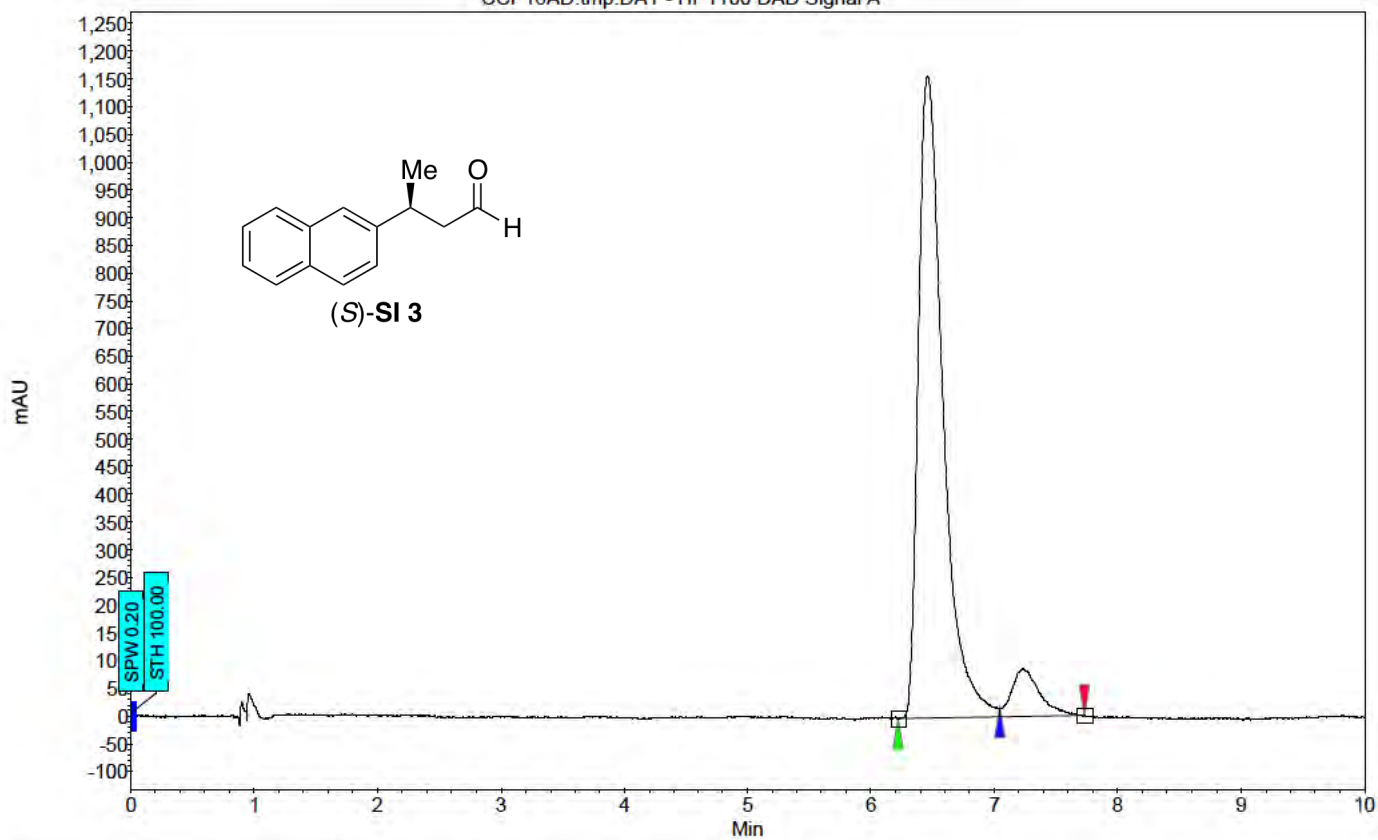
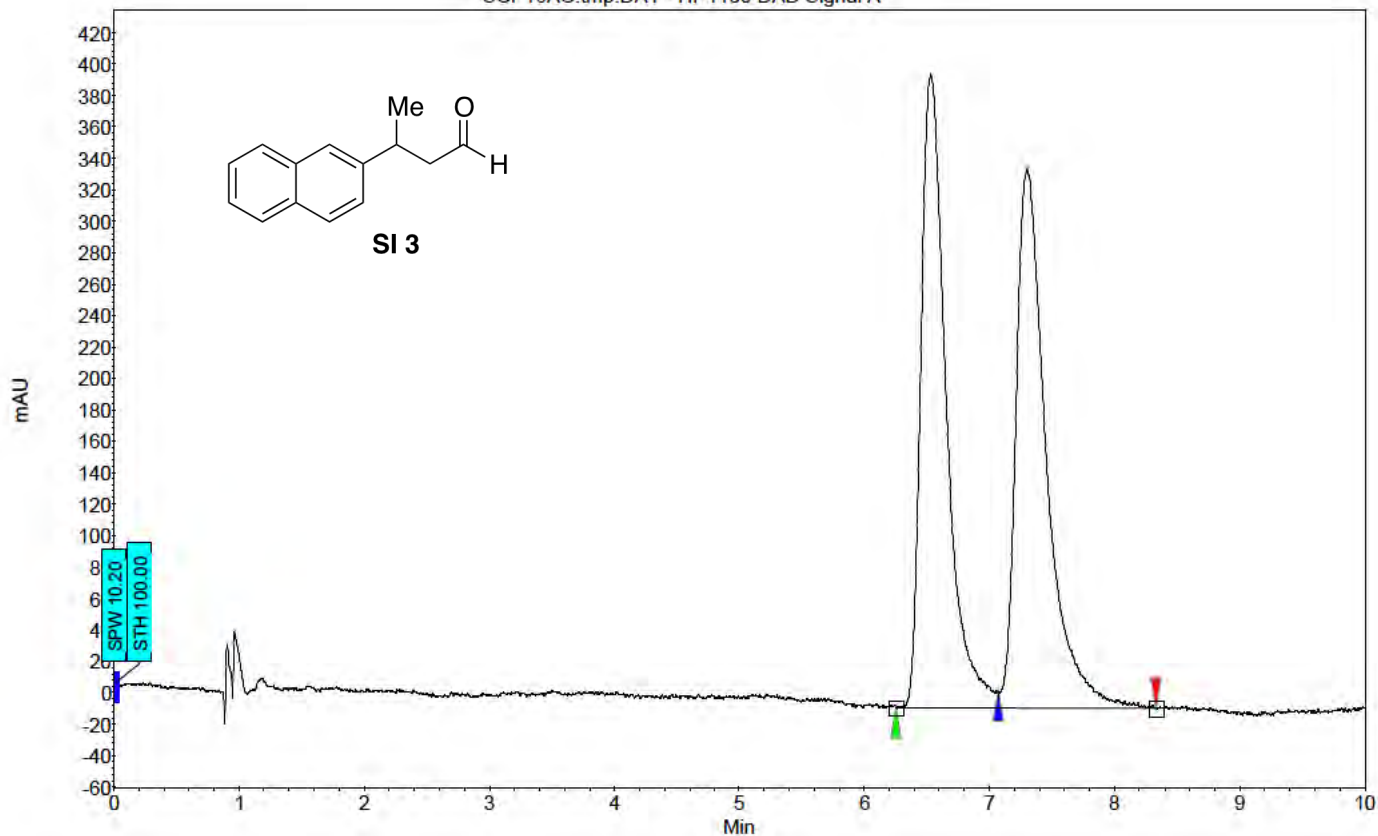


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	4.54	4.70	5.10	0.00	95.24	1224.0	181.6	95.242
2	UNKNOWN	5.19	5.41	5.65	0.00	4.76	56.0	9.1	4.758
Total						100.00	1280.0	190.7	100.000

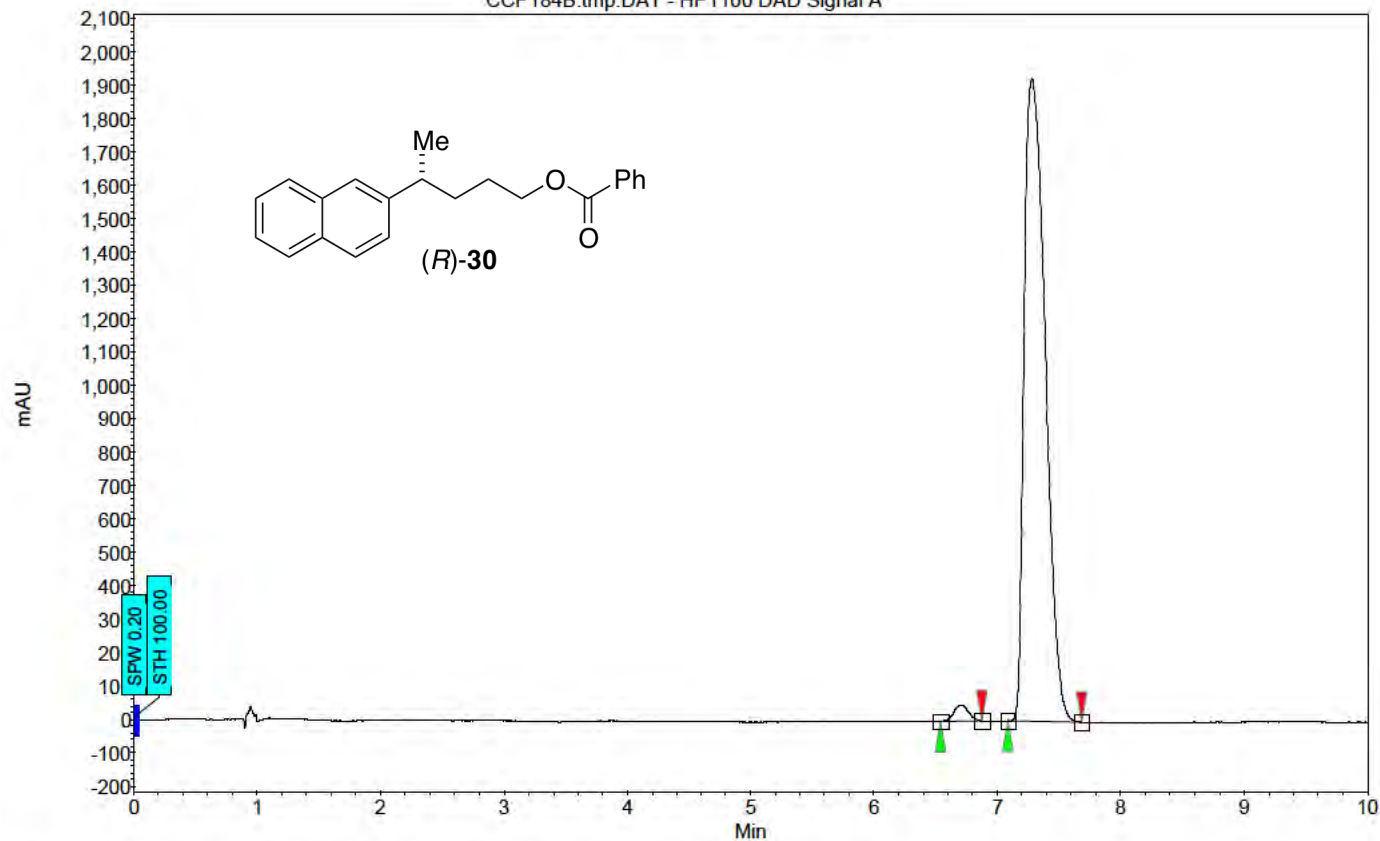
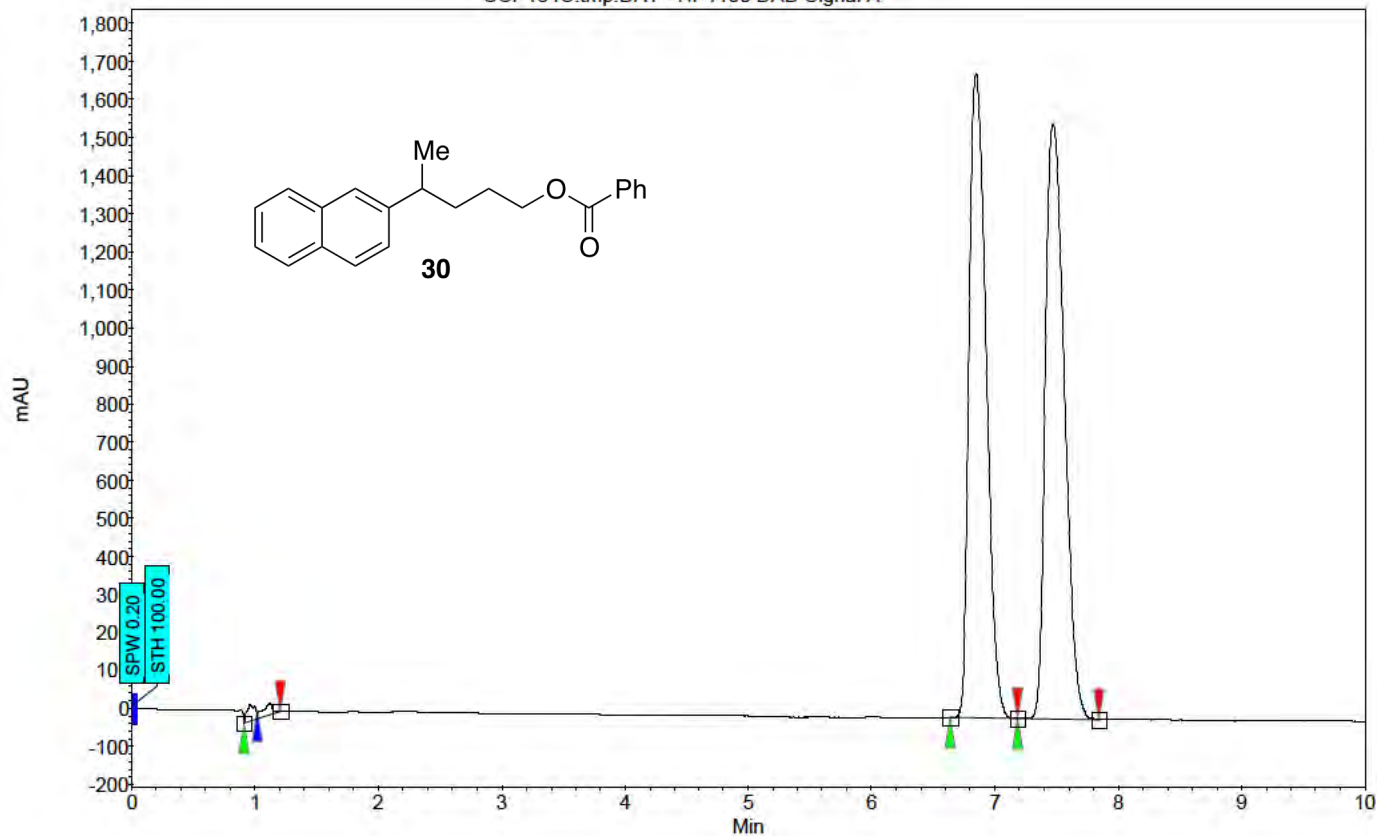




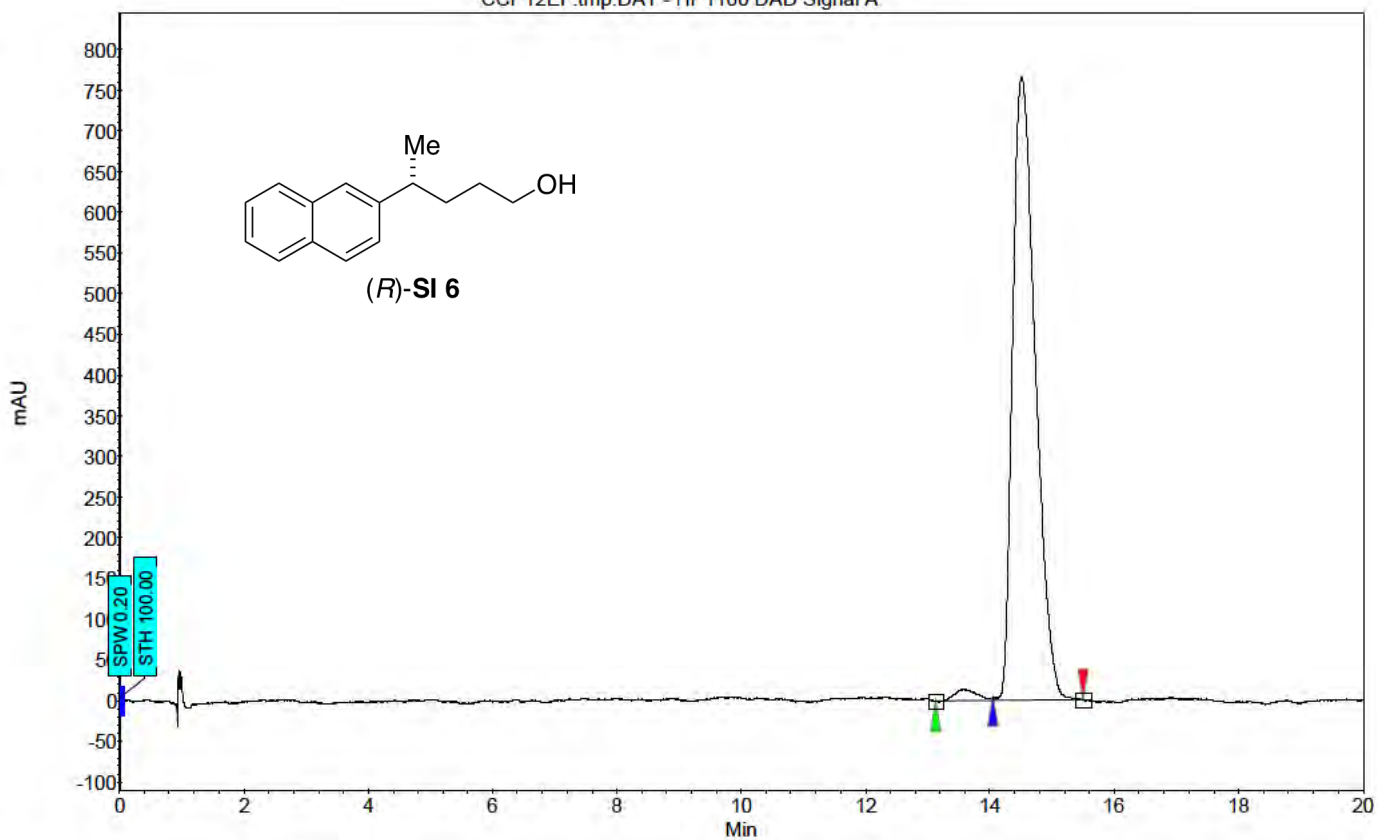
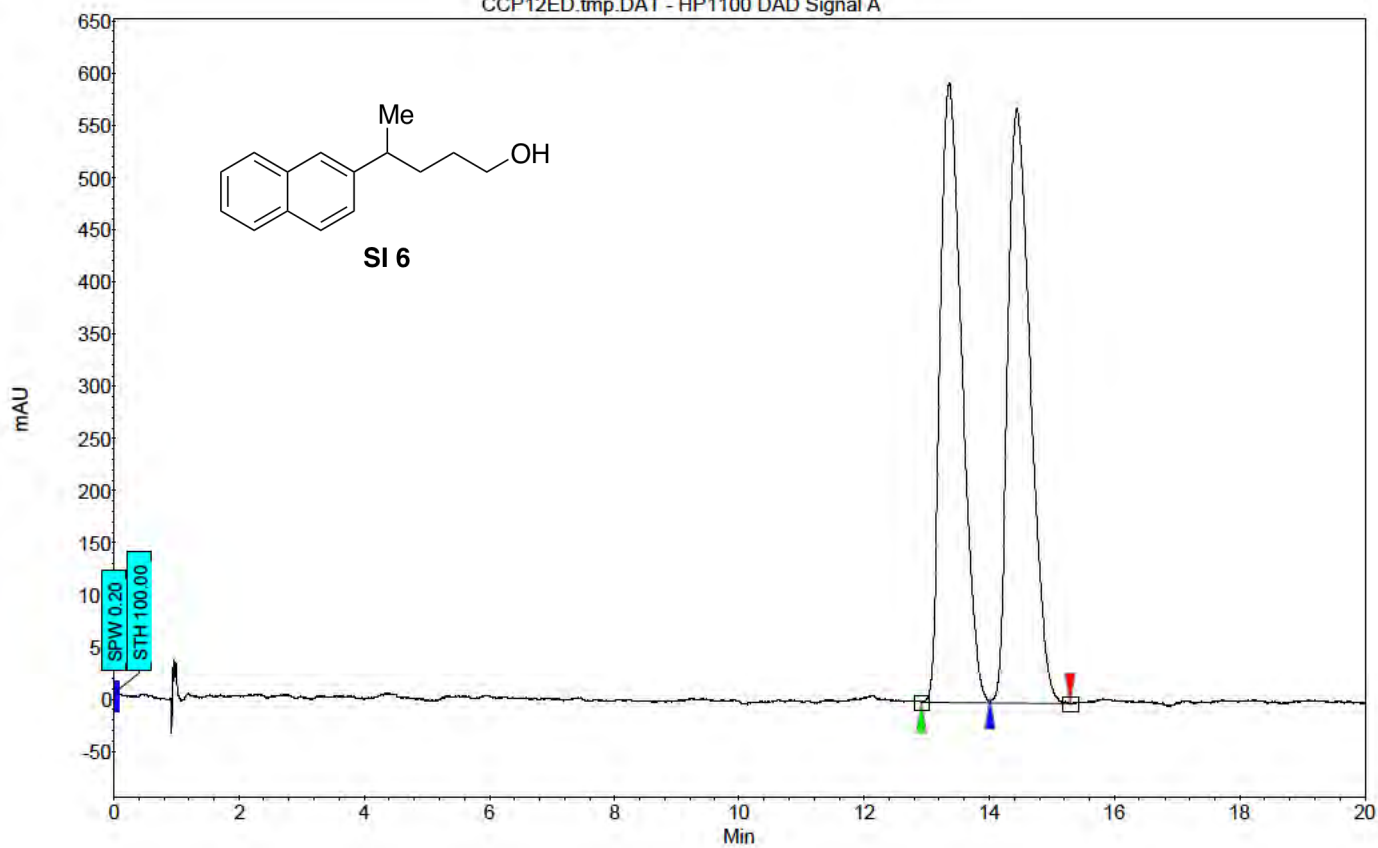
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	5.45	5.66	5.88	0.00	5.34	128.7	18.3	5.342
2	UNKNOWN	5.98	6.17	6.62	0.00	94.66	1630.9	324.9	94.658
Total						100.00	1759.7	343.3	100.000



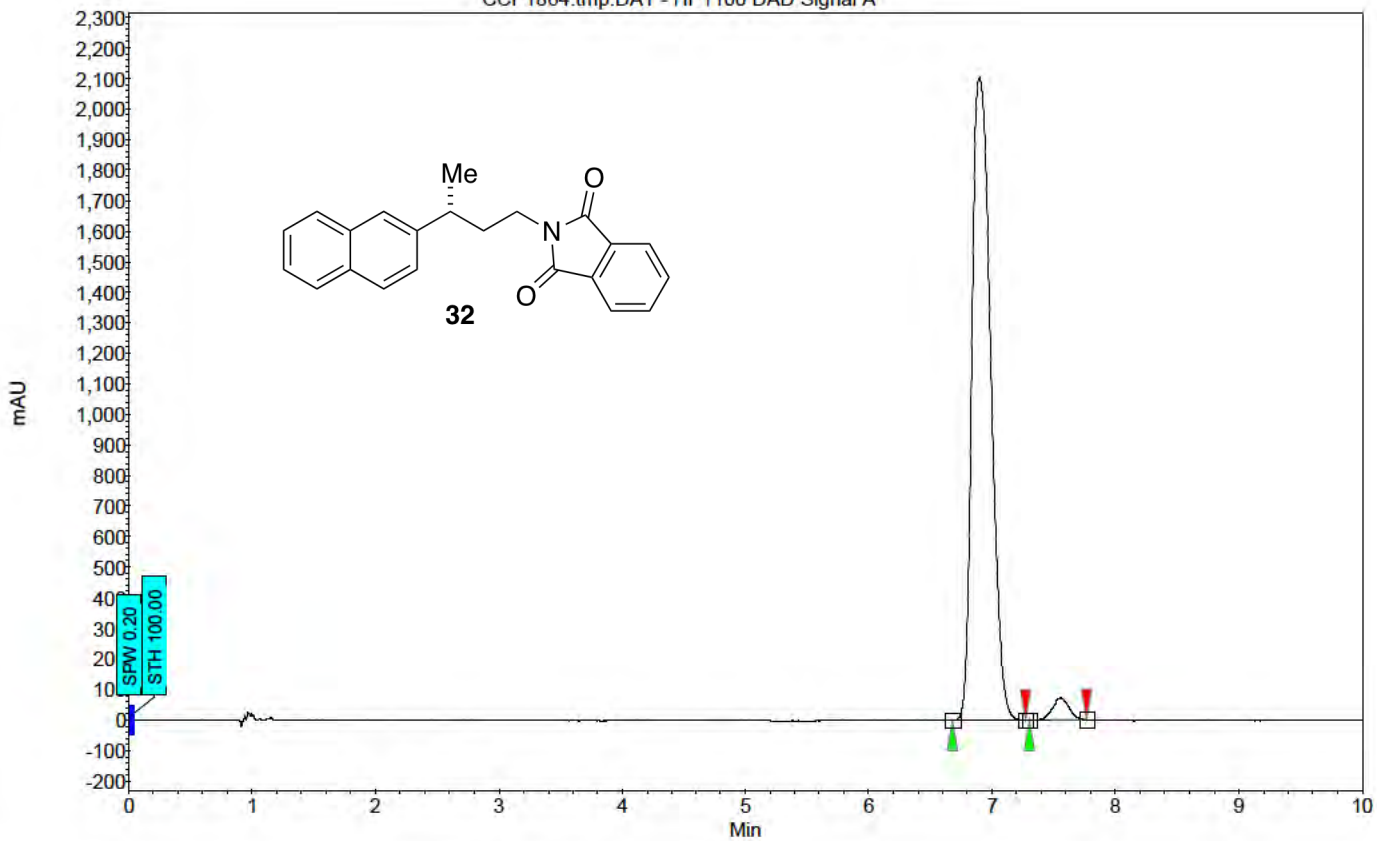
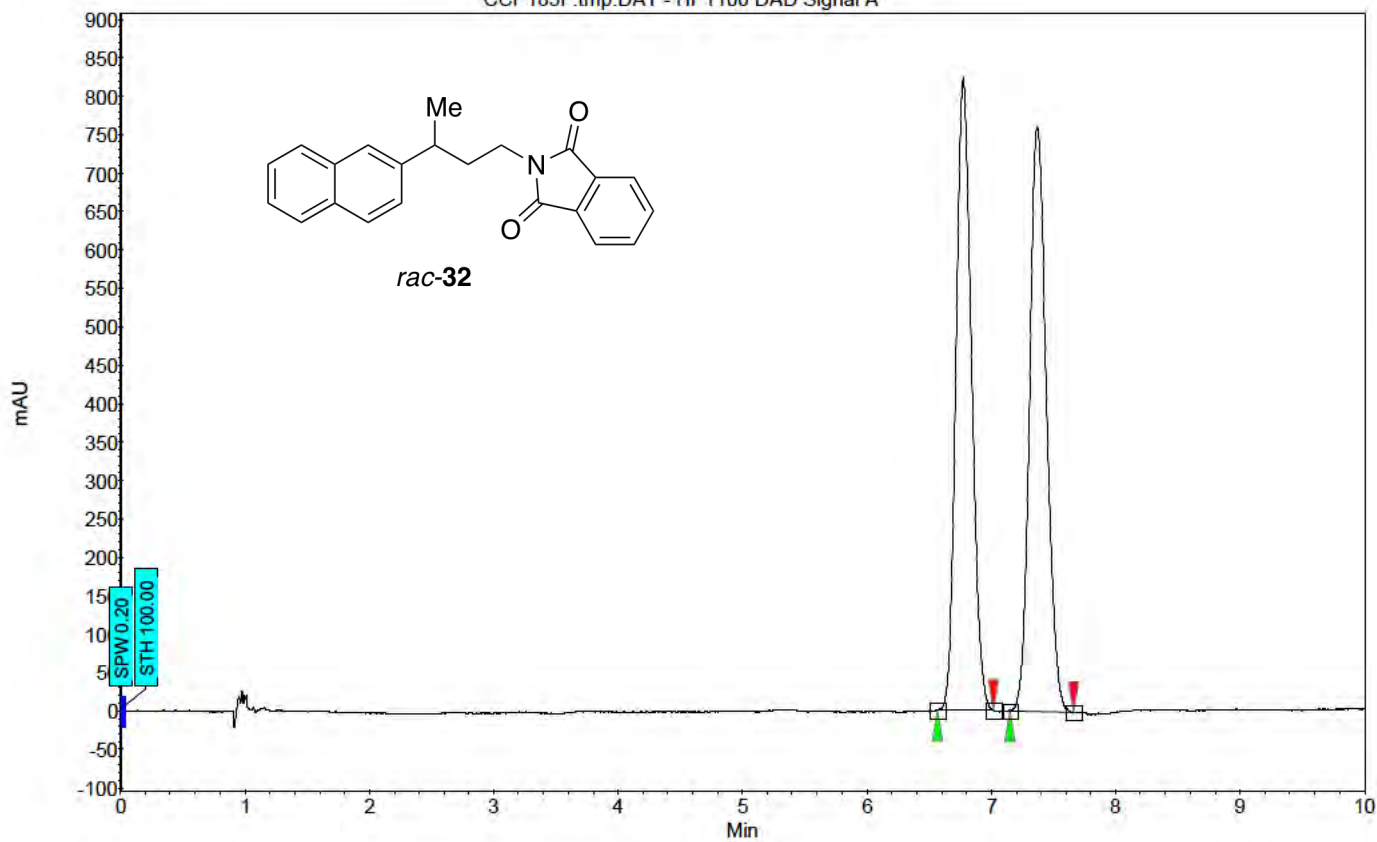
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	6.22	6.46	7.04	0.00	92.20	1157.6	267.9	
2	UNKNOWN	7.04	7.23	7.73	0.00	7.80	86.2	22.7	
Total						100.00	1243.7	290.5	100.000



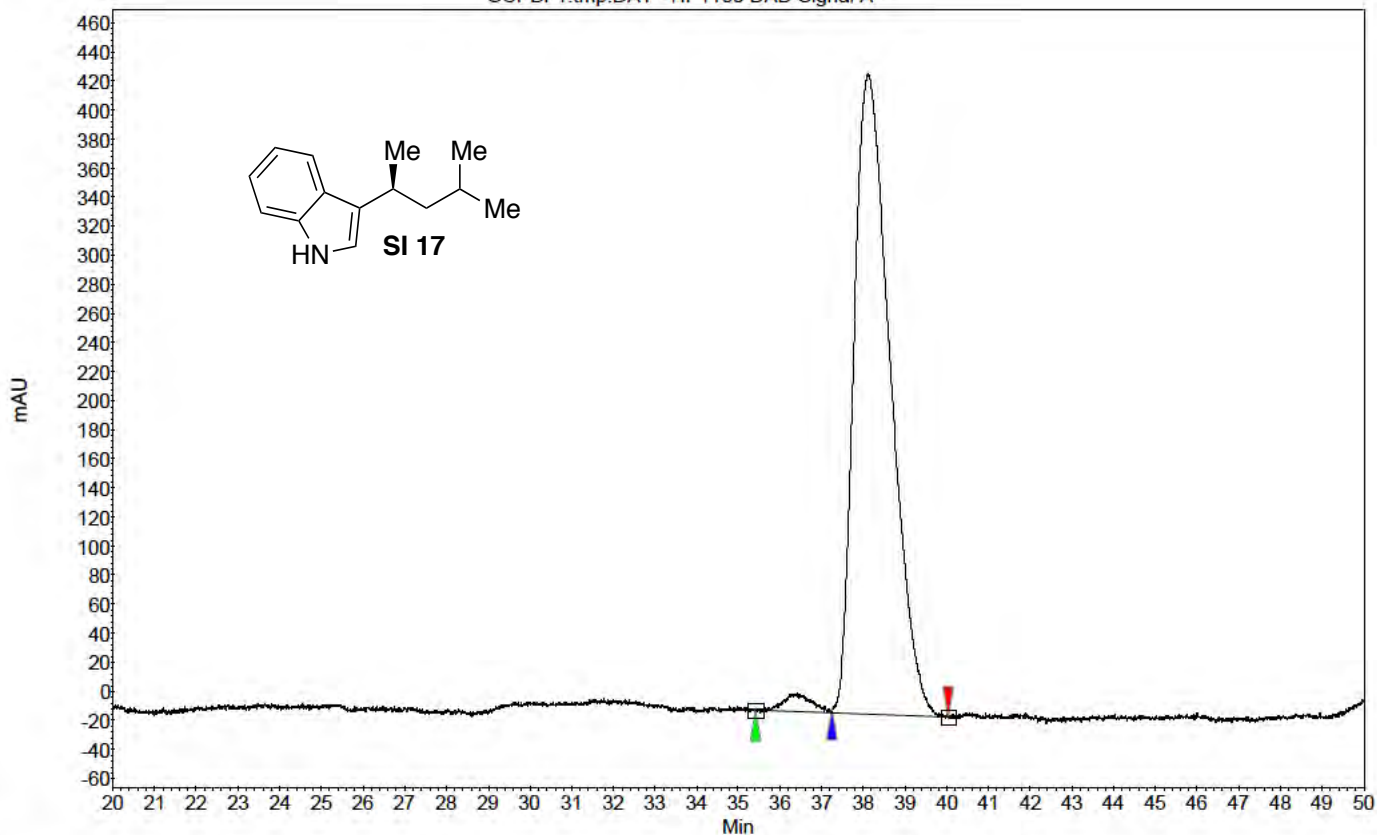
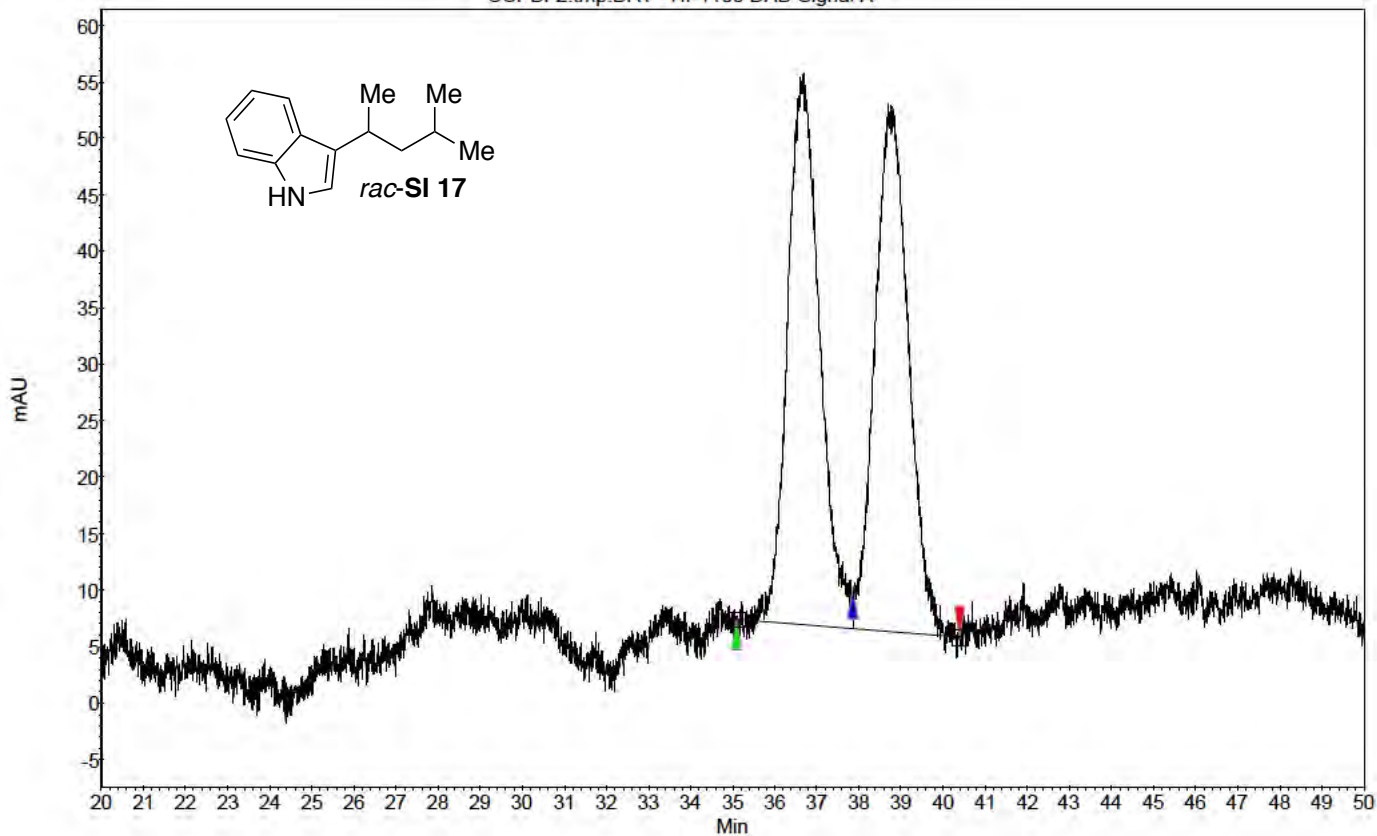
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	6.54	6.71	6.88	1.67	48.6	6.5	1.671
1	UNKNOWN	7.09	7.28	7.69	98.33	1924.0	380.3	98.329
Total					100.00	1972.6	386.7	100.000



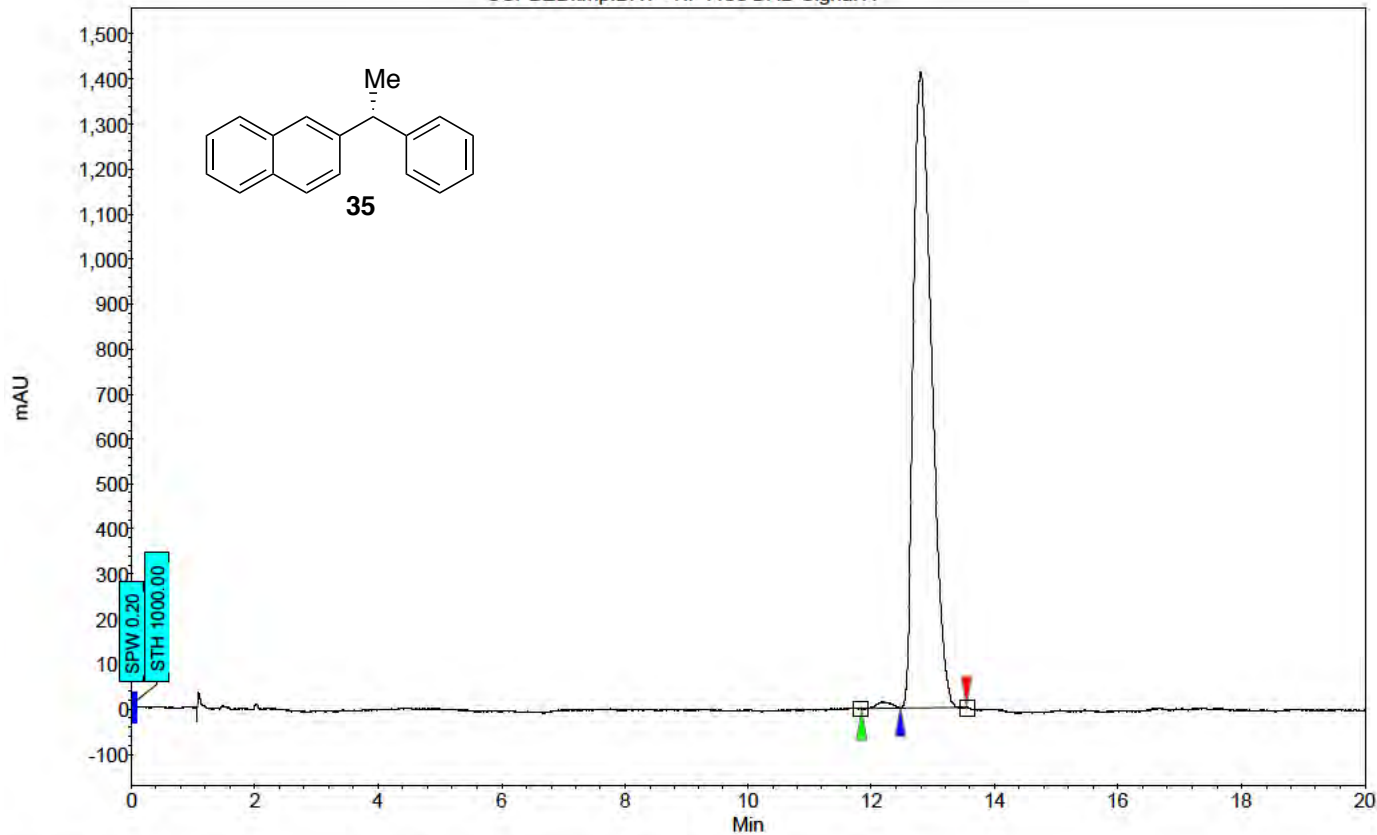
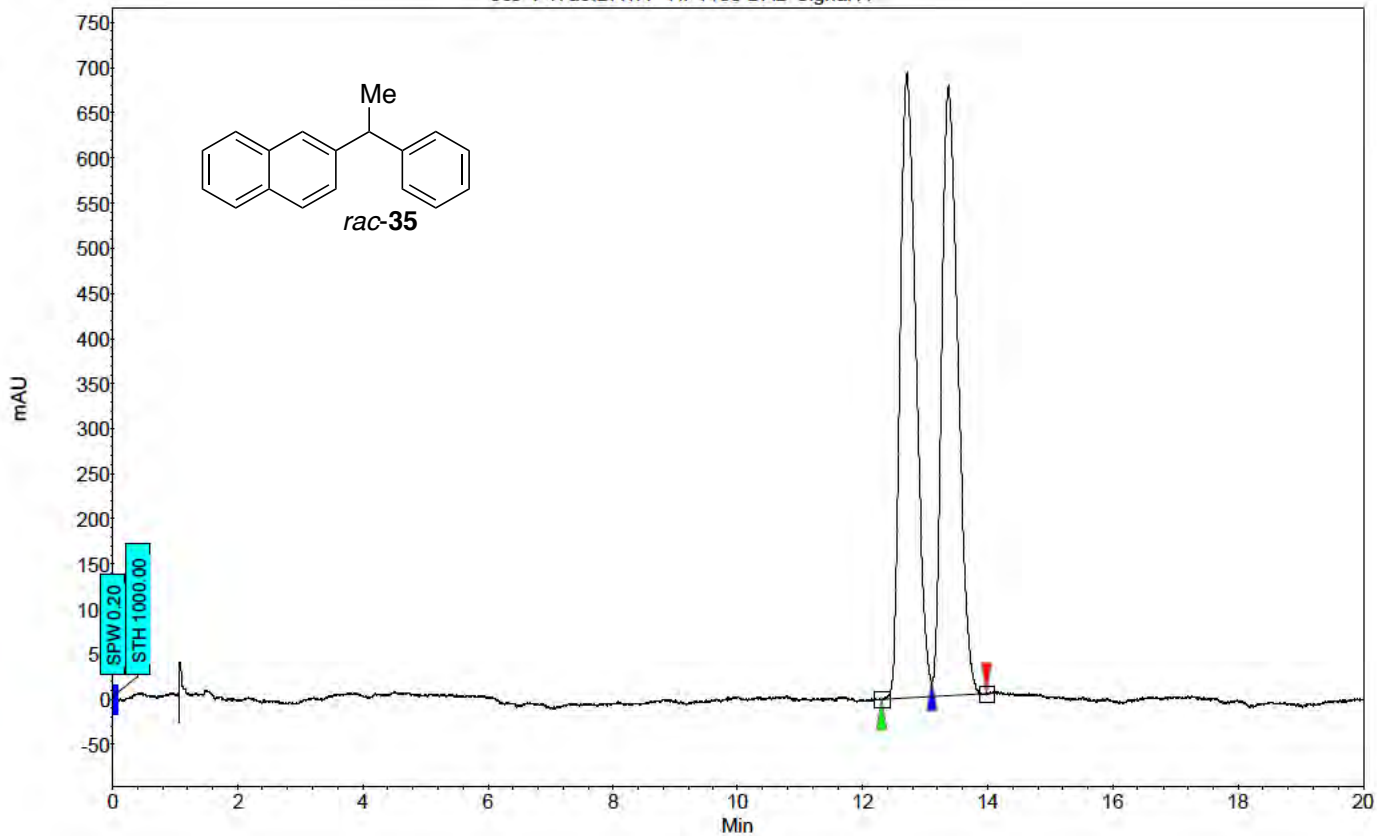
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	13.13	13.58	14.04	0.00	1.79	14.7	5.9	1.789
2	UNKNOWN	14.04	14.51	15.49	0.00	98.21	764.3	323.8	98.211
Total						100.00	778.9	329.7	100.000



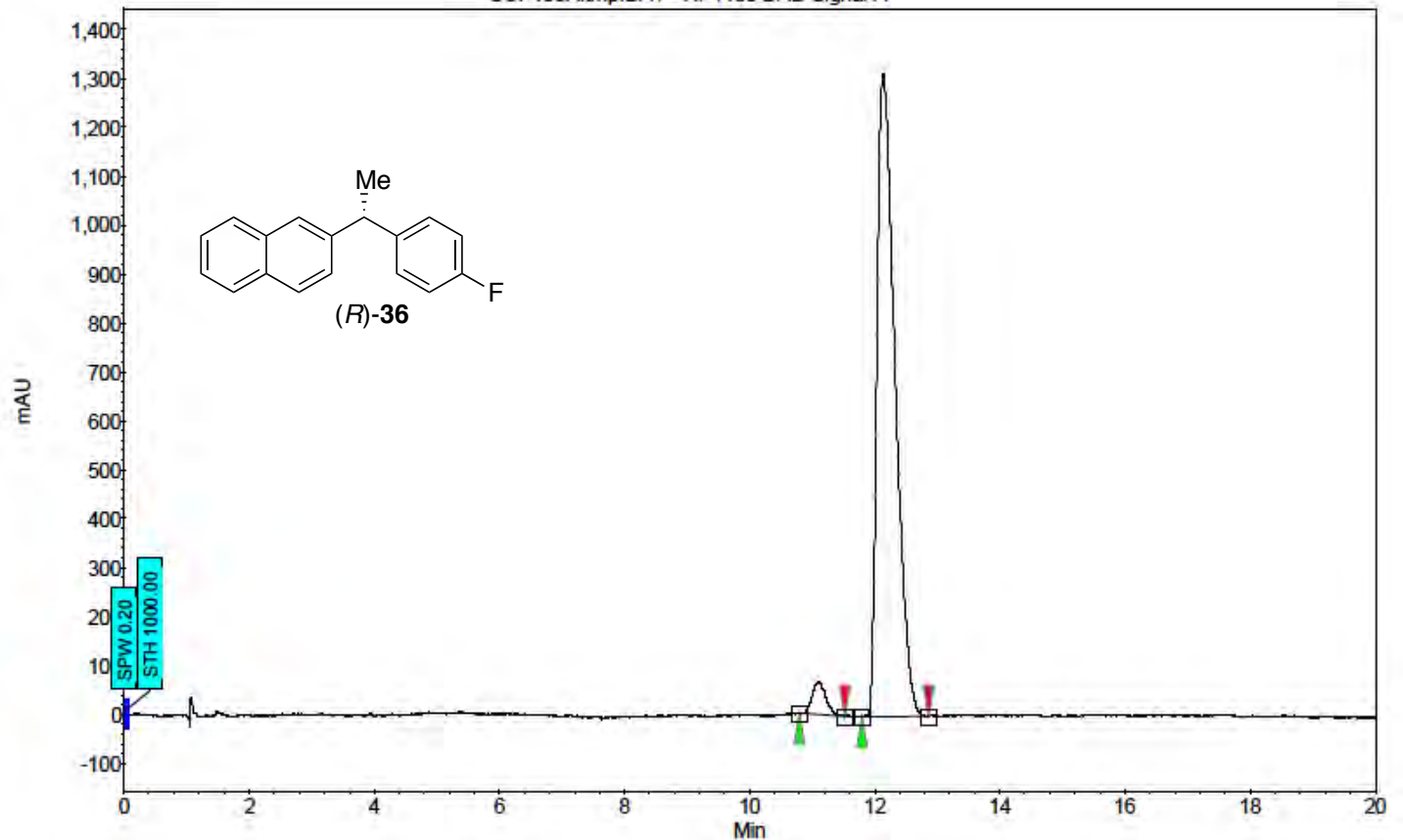
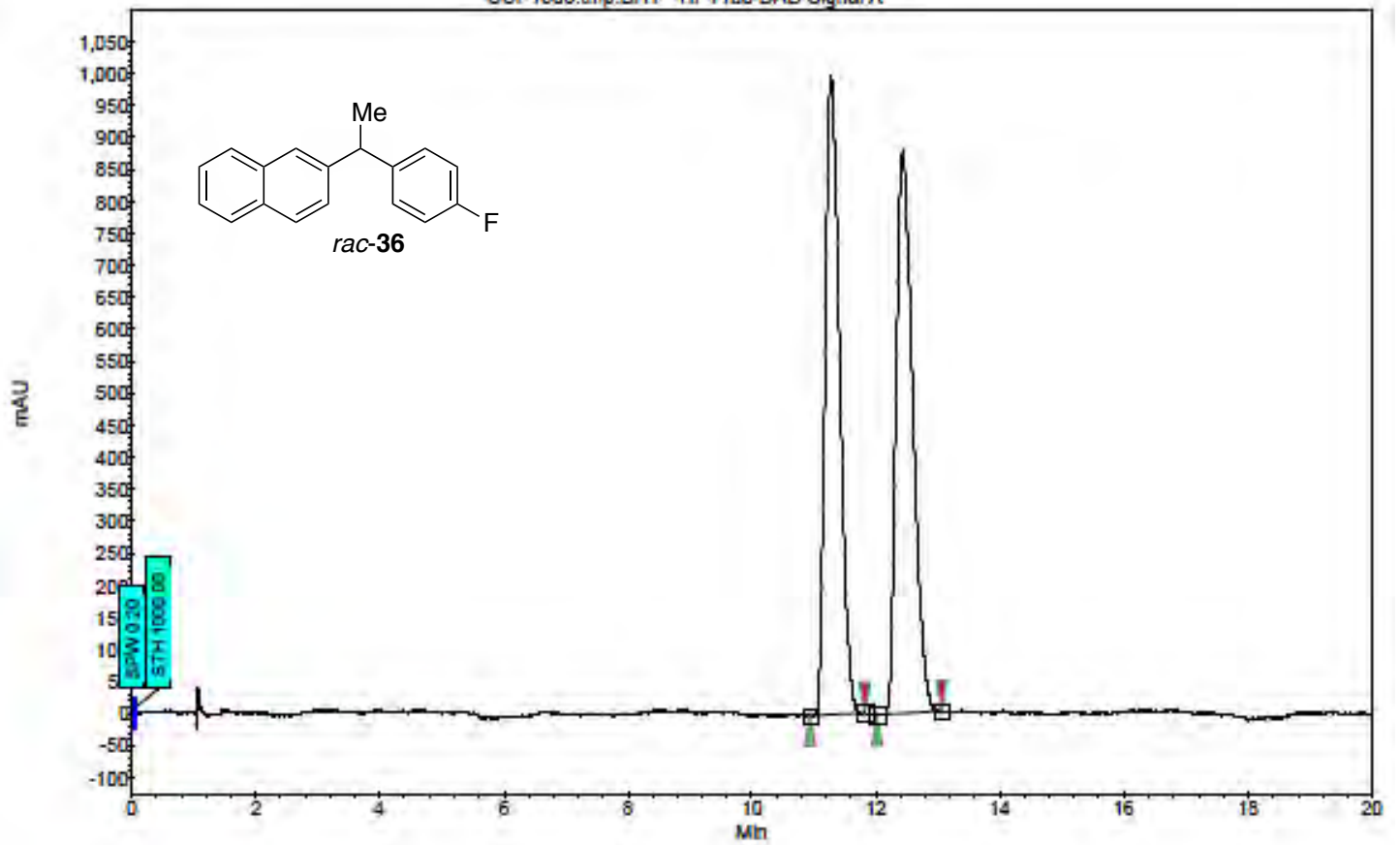
Index	Name	Start Time			End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]						
1	UNKNOWN	6.68	6.90	7.27	0.00	97.13	2101.8	371.3	97.129	
2	UNKNOWN	7.30	7.56	7.77	0.00	2.87	70.3	11.0	2.871	
Total						100.00	2172.1	382.3	100.000	



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	35.43	36.34	37.24	0.00	2.03	12.0	9.2	2.032
2	UNKNOWN	37.24	38.10	40.03	0.00	97.97	440.0	443.4	97.968
Total						100.00	452.0	452.5	100.000

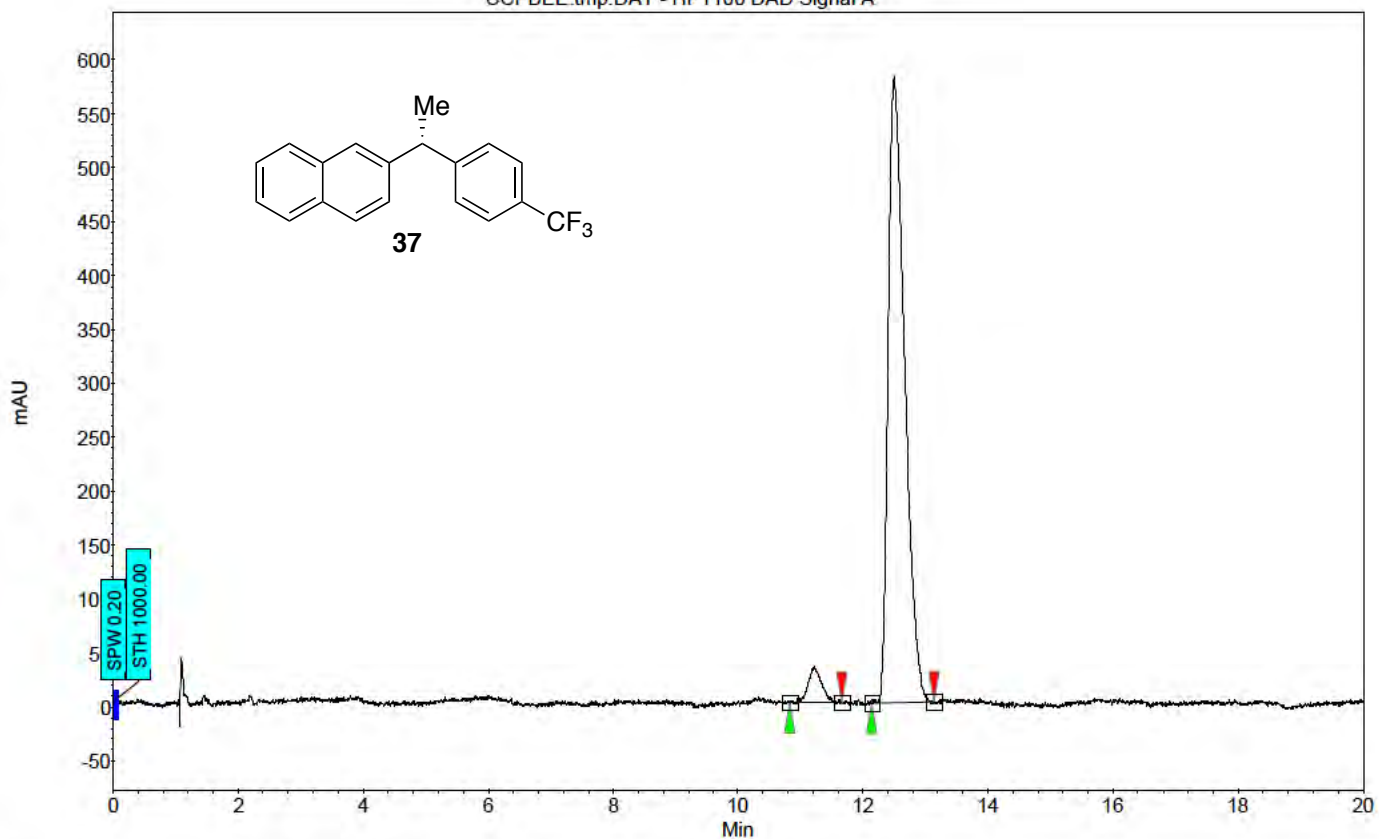
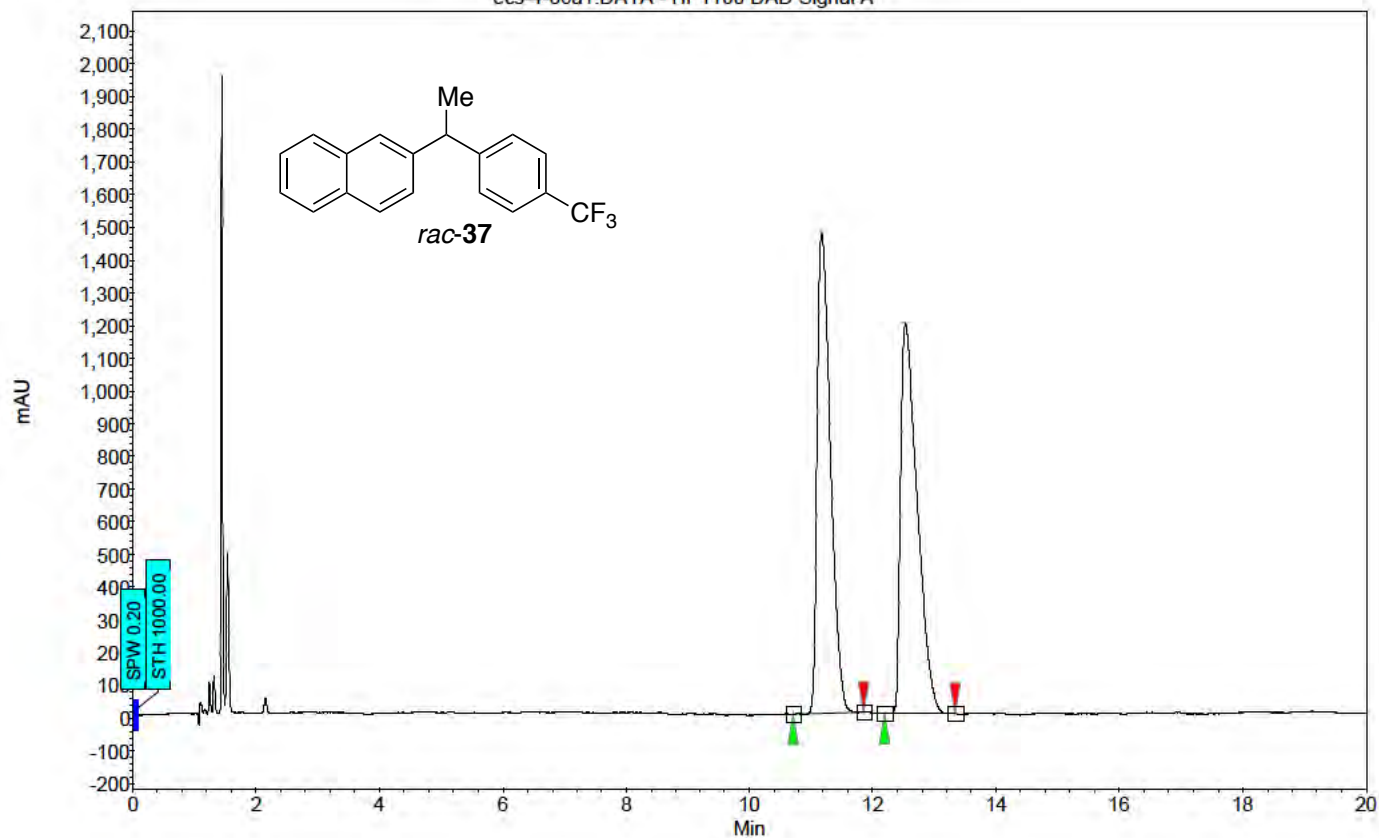


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	11.84	12.20	12.47	0.00	0.82	15.6	4.0	0.824
1	UNKNOWN	12.47	12.80	13.55	0.00	99.18	1411.1	481.4	99.176
Total						100.00	1426.7	485.4	100.000

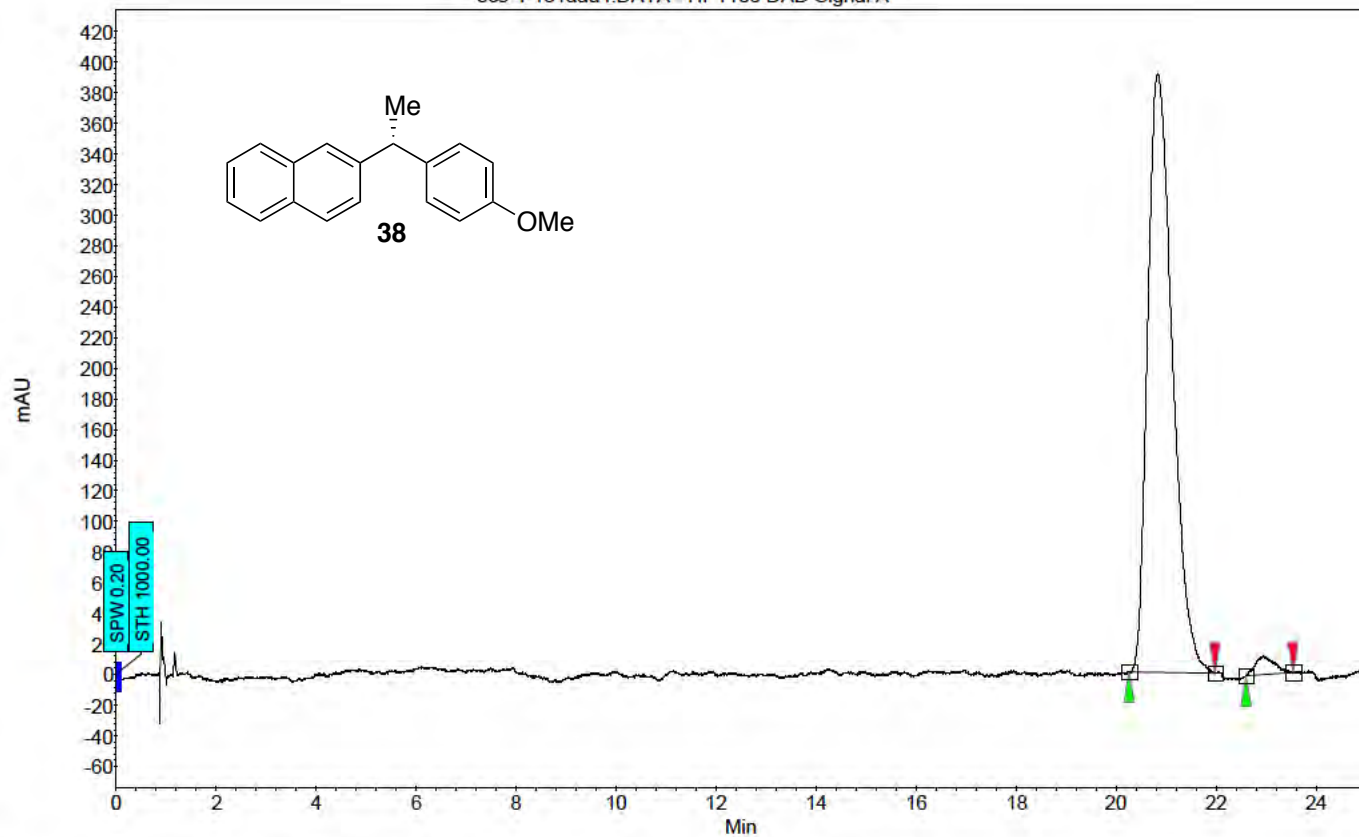
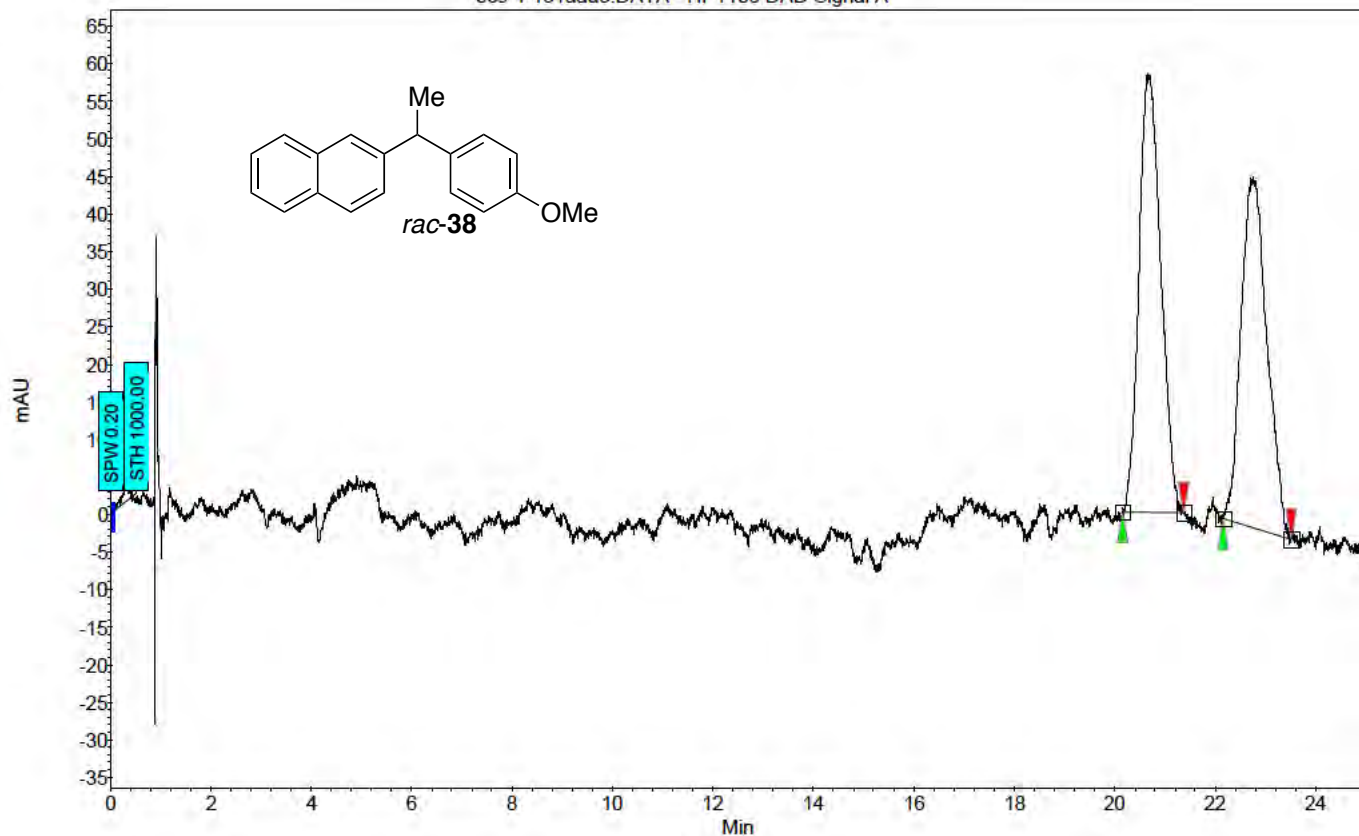


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	10.80	11.11	11.52	0.00	3.69	67.1	16.7	3.687
2	UNKNOWN	11.80	12.14	12.86	0.00	96.31	1313.8	436.0	96.313
Total						100.00	1380.8	452.7	100.000

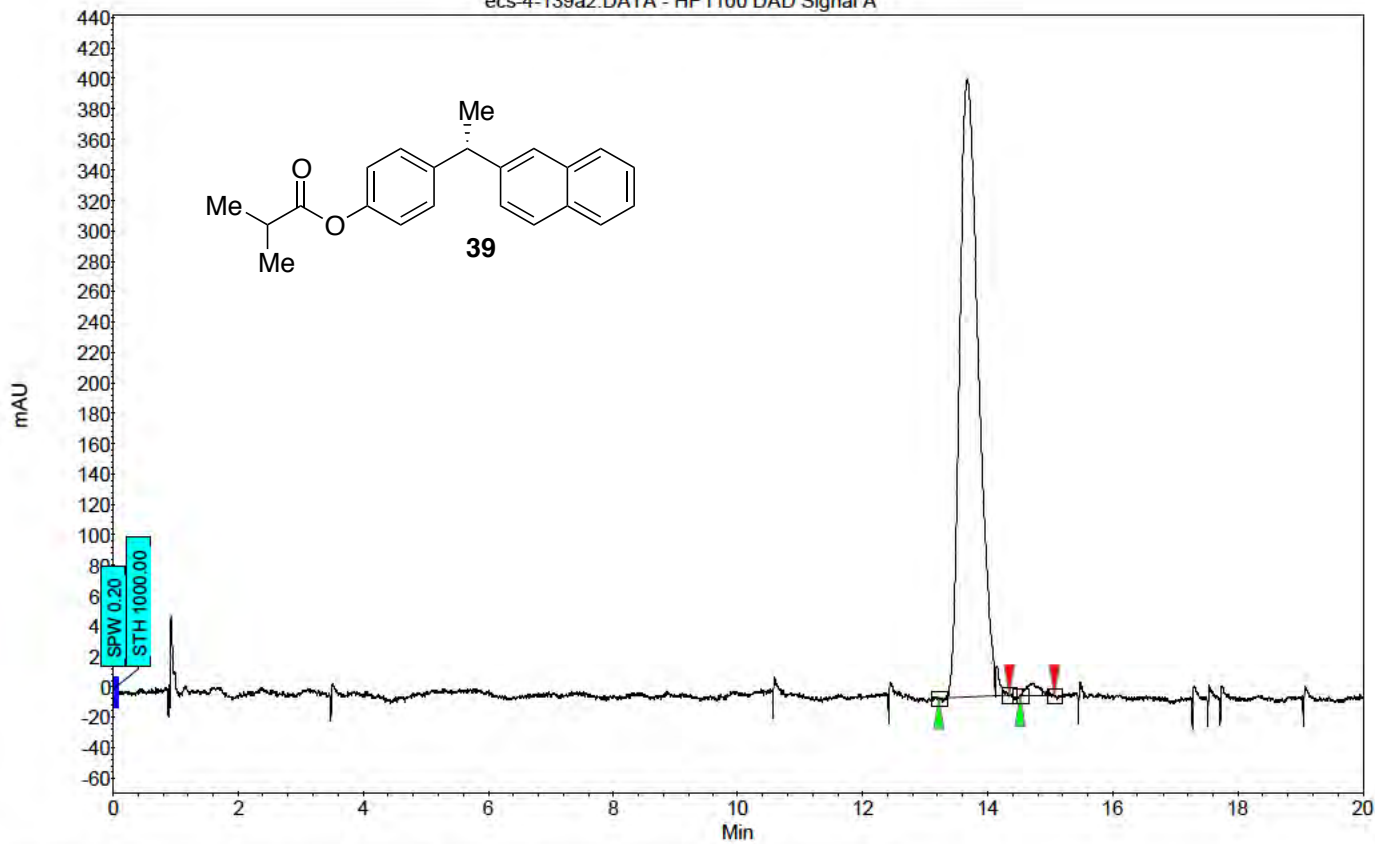
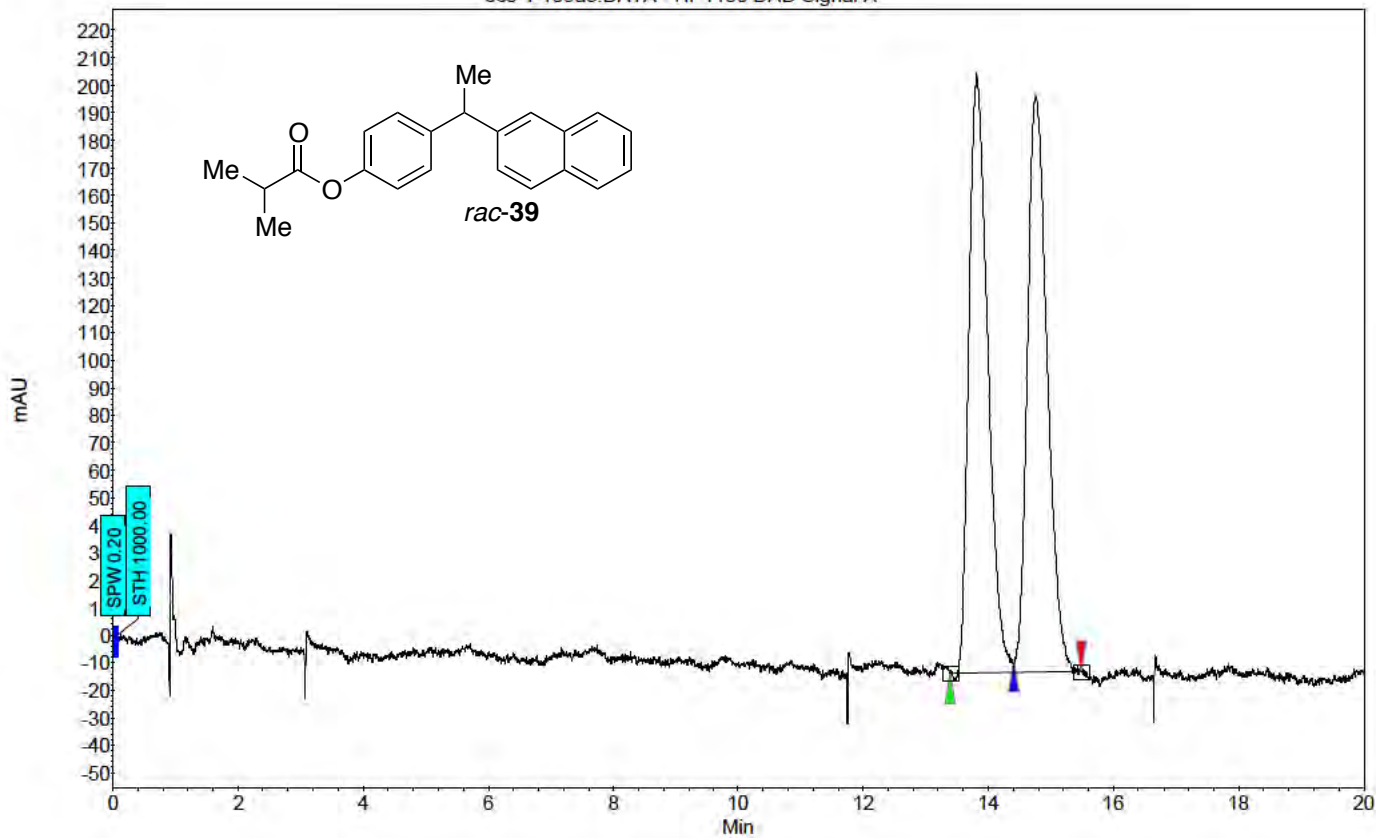




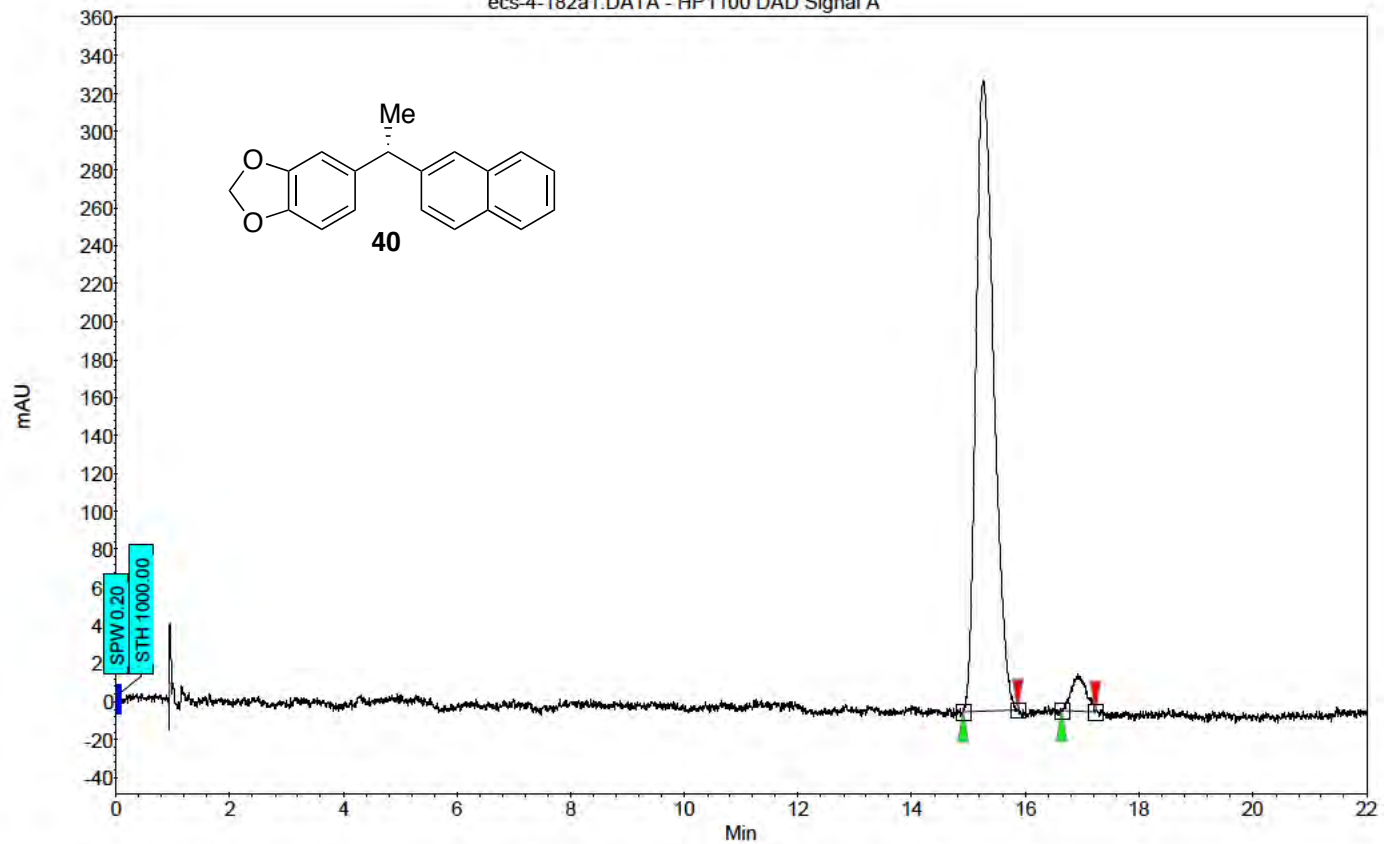
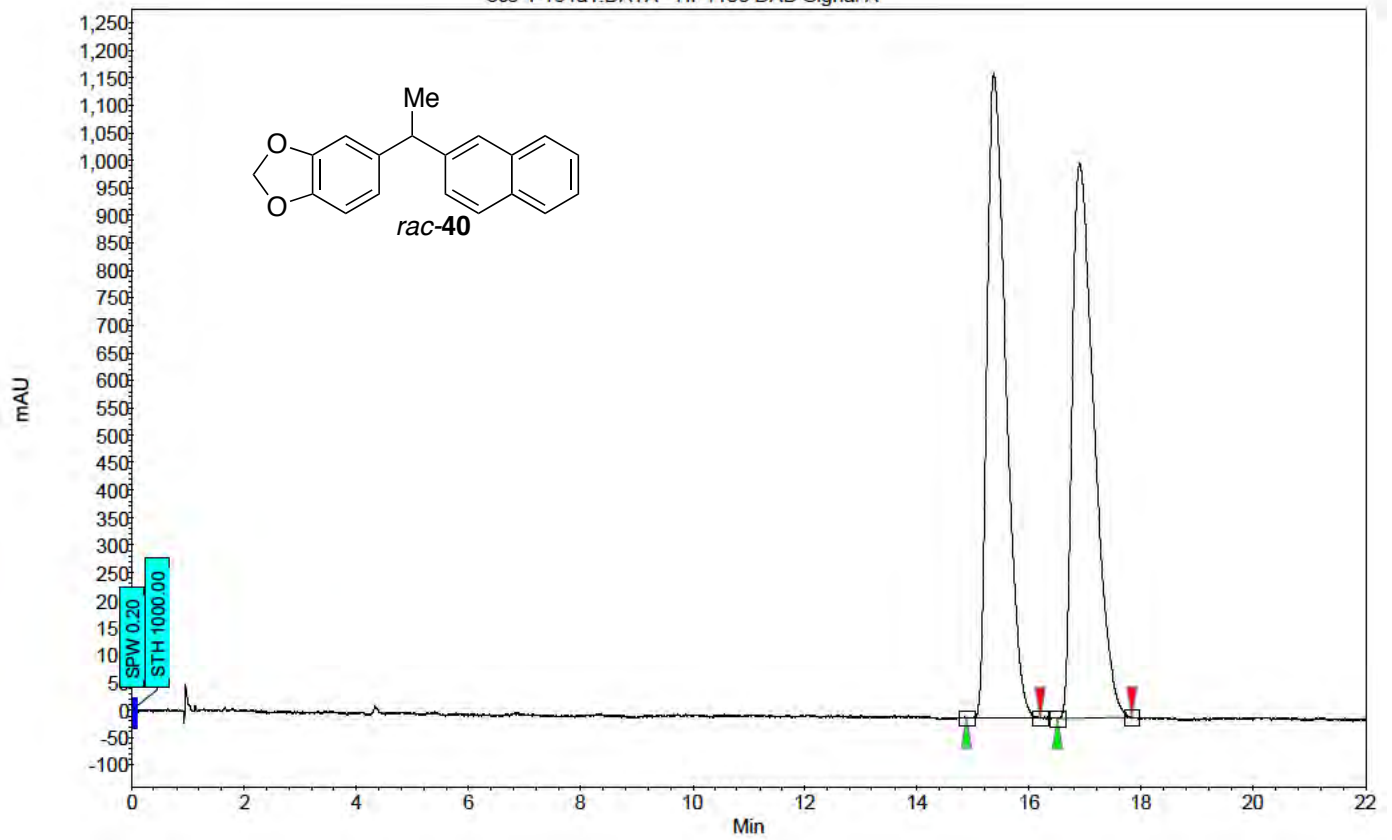
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	10.82	11.23	11.66	0.00	4.51	33.2	8.4	4.510
1	UNKNOWN	12.13	12.50	13.14	0.00	95.49	580.5	176.9	95.490
Total						100.00	613.7	185.3	100.000



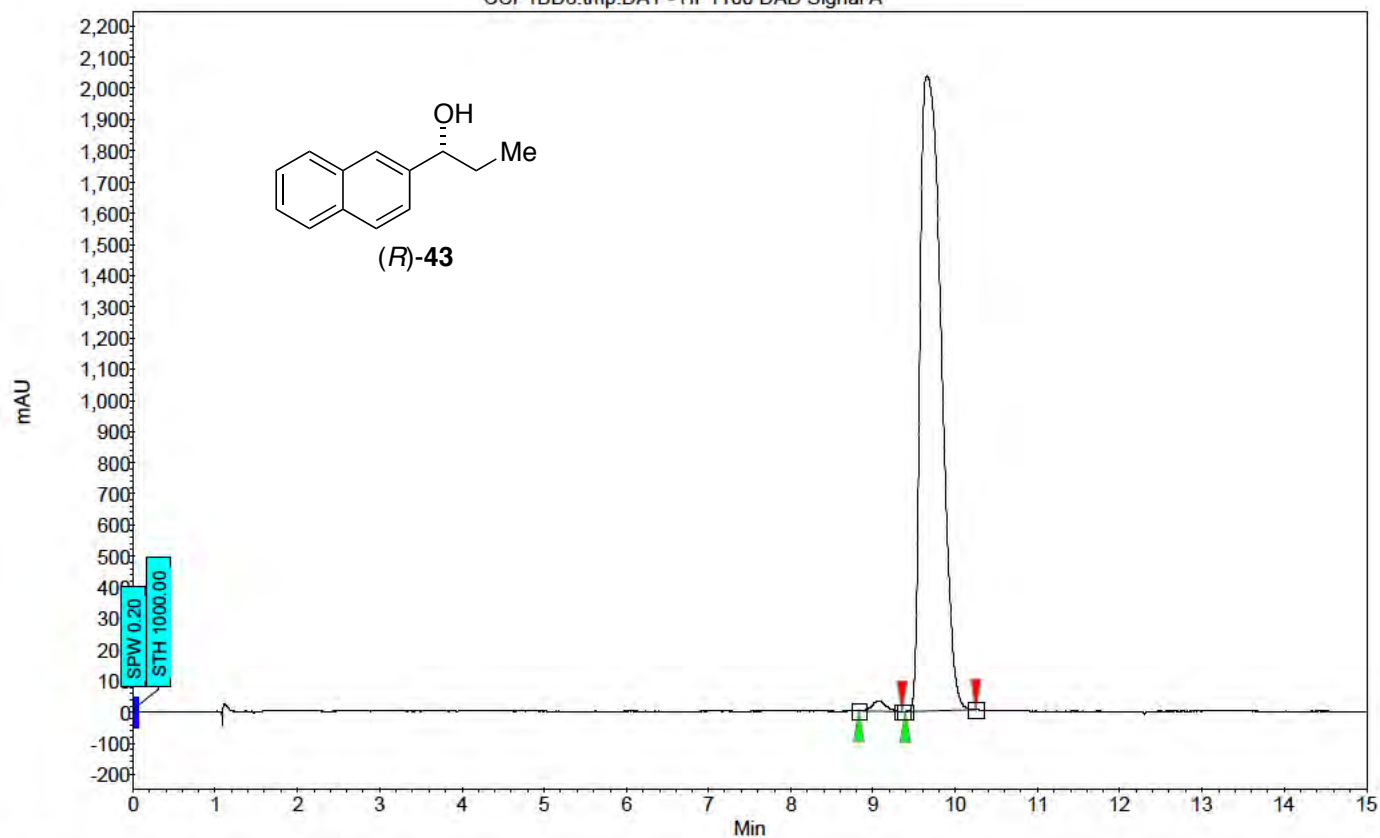
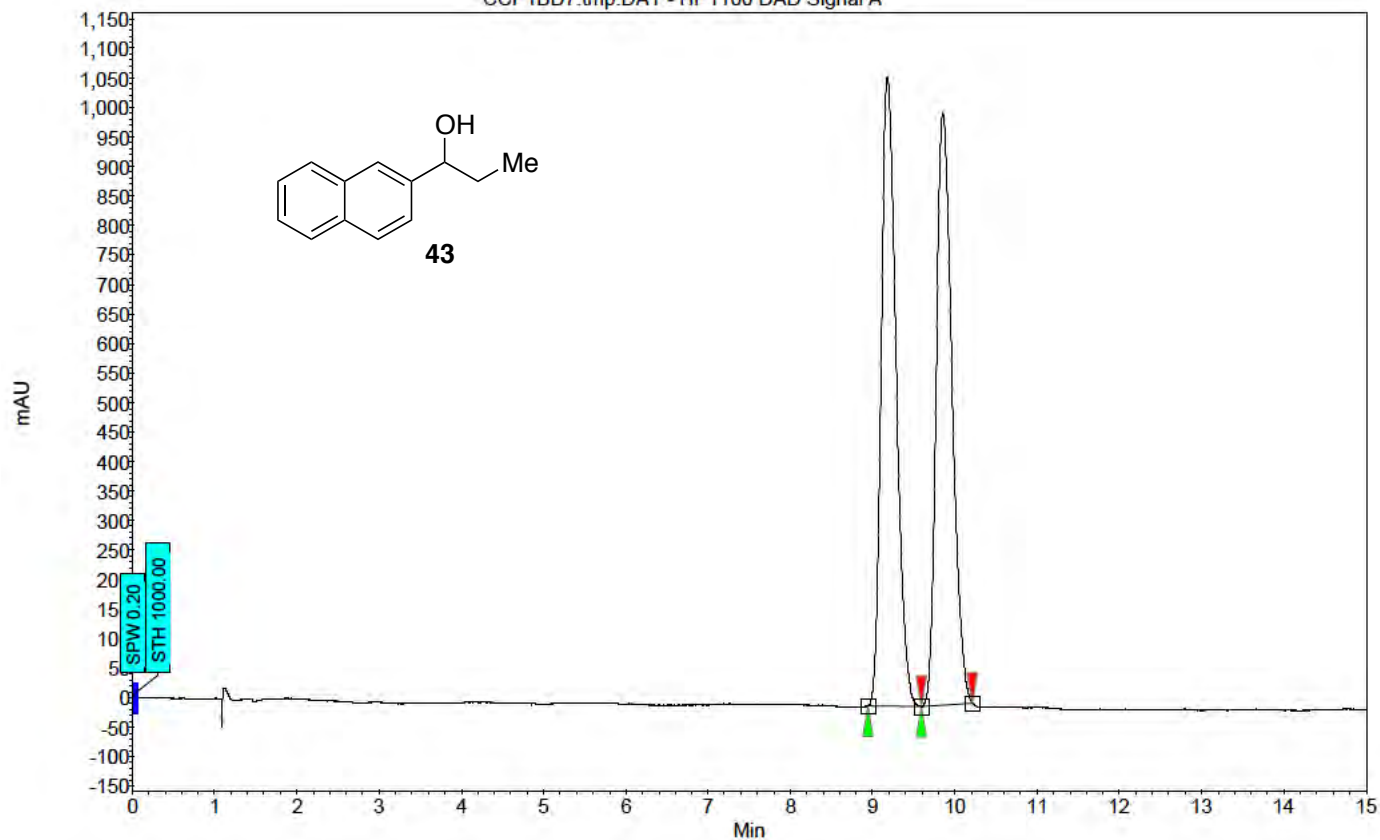
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	20.25	20.82	21.97	0.00	97.67	390.5	223.6	97.672
2	UNKNOWN	22.59	22.95	23.53	0.00	2.33	12.5	5.3	2.328
Total						100.00	403.0	228.9	100.000



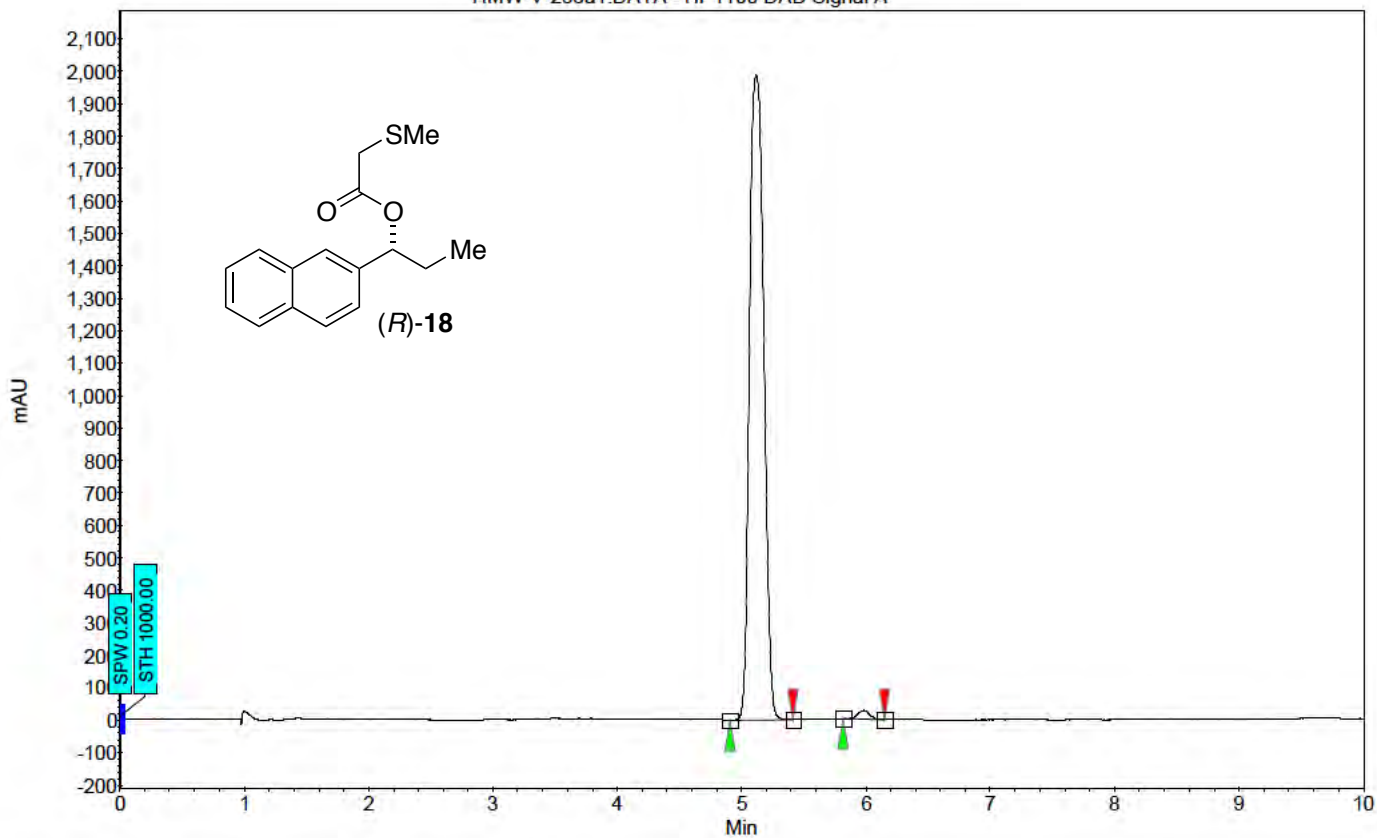
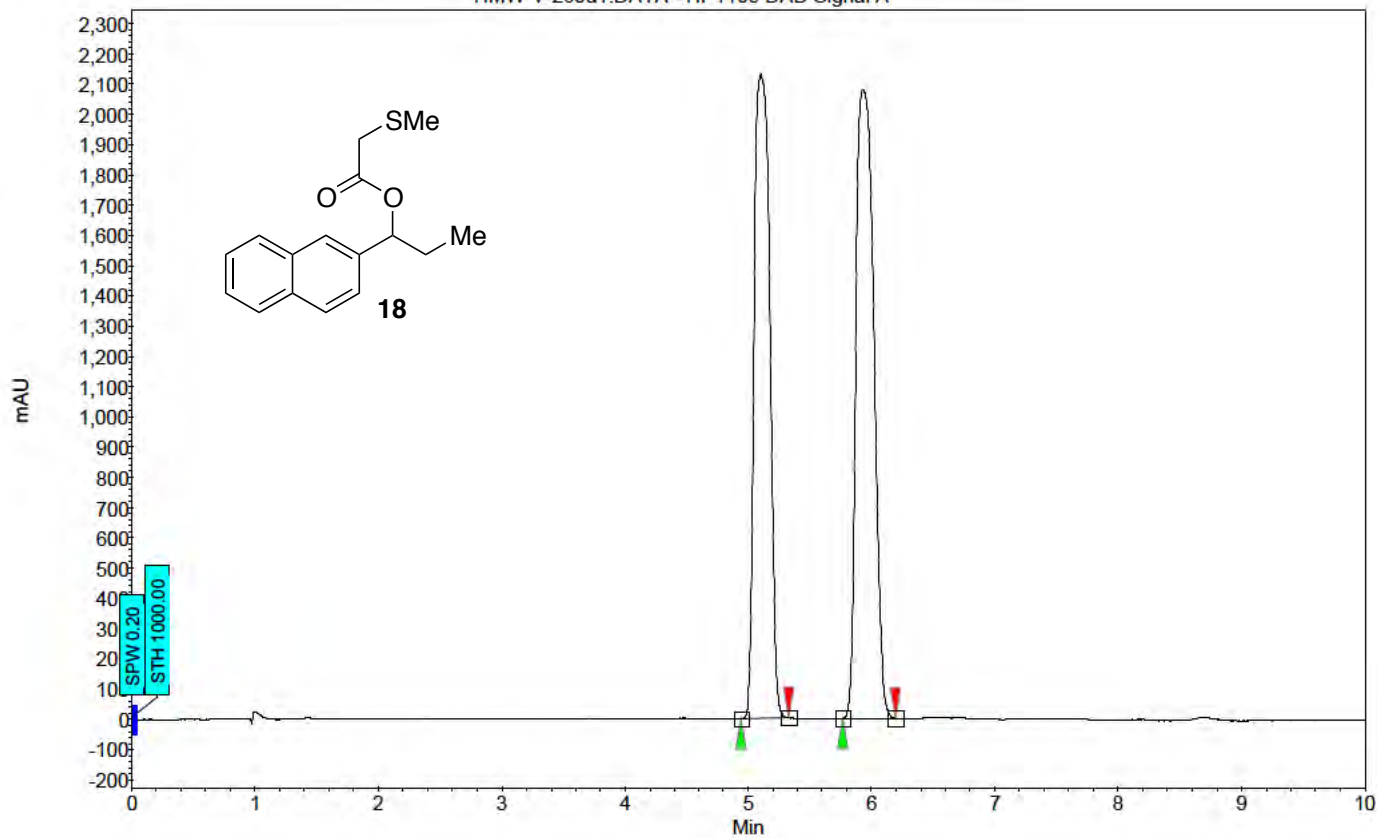
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]		[Min]		[% Area]	[μV.Min]
1	UNKNOWN	13.22	13.67	14.34	0.00	98.50	405.8	142.5	98.498
2	UNKNOWN	14.52	14.71	15.06	0.00	1.50	8.1	2.2	1.502
Total						100.00	414.0	144.7	100.000



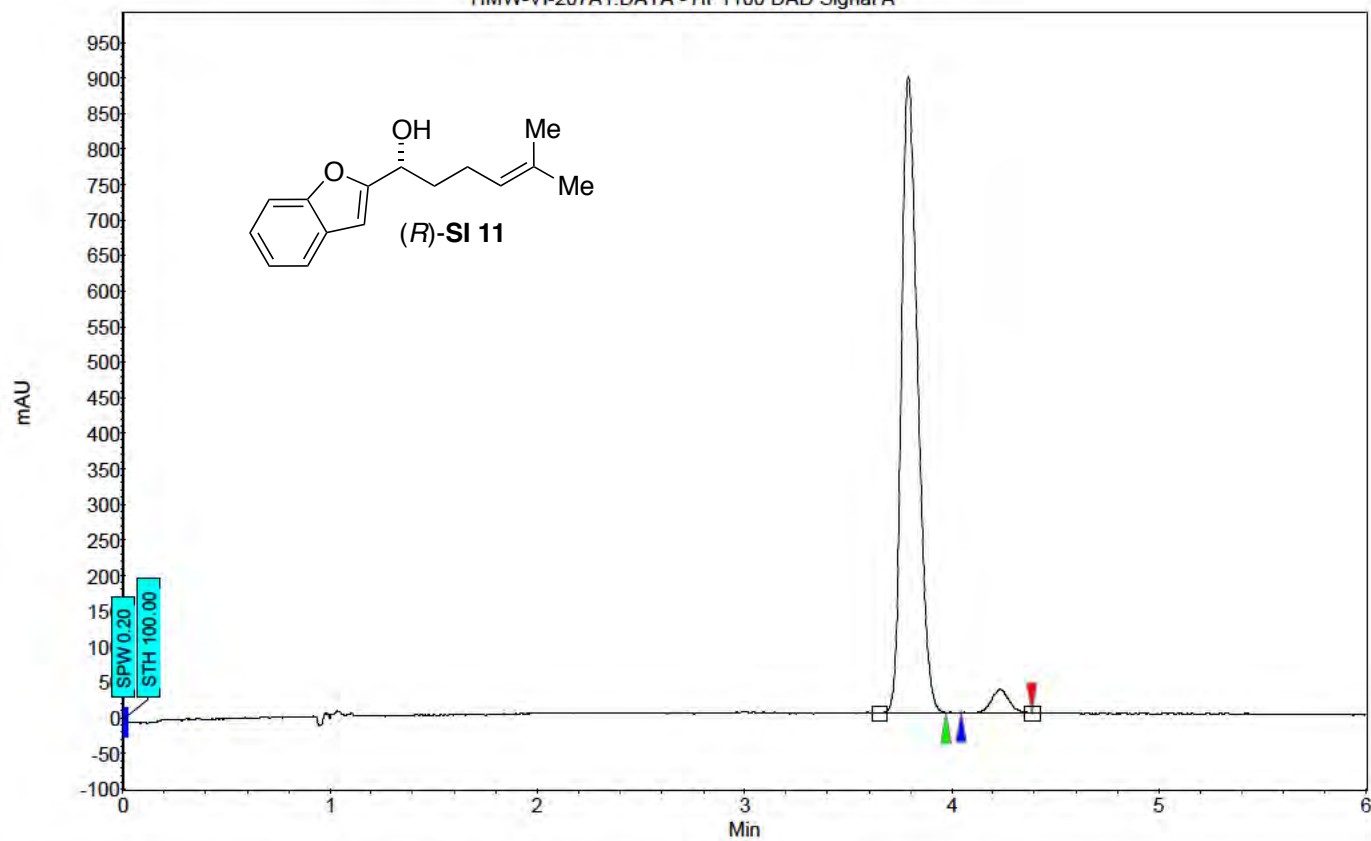
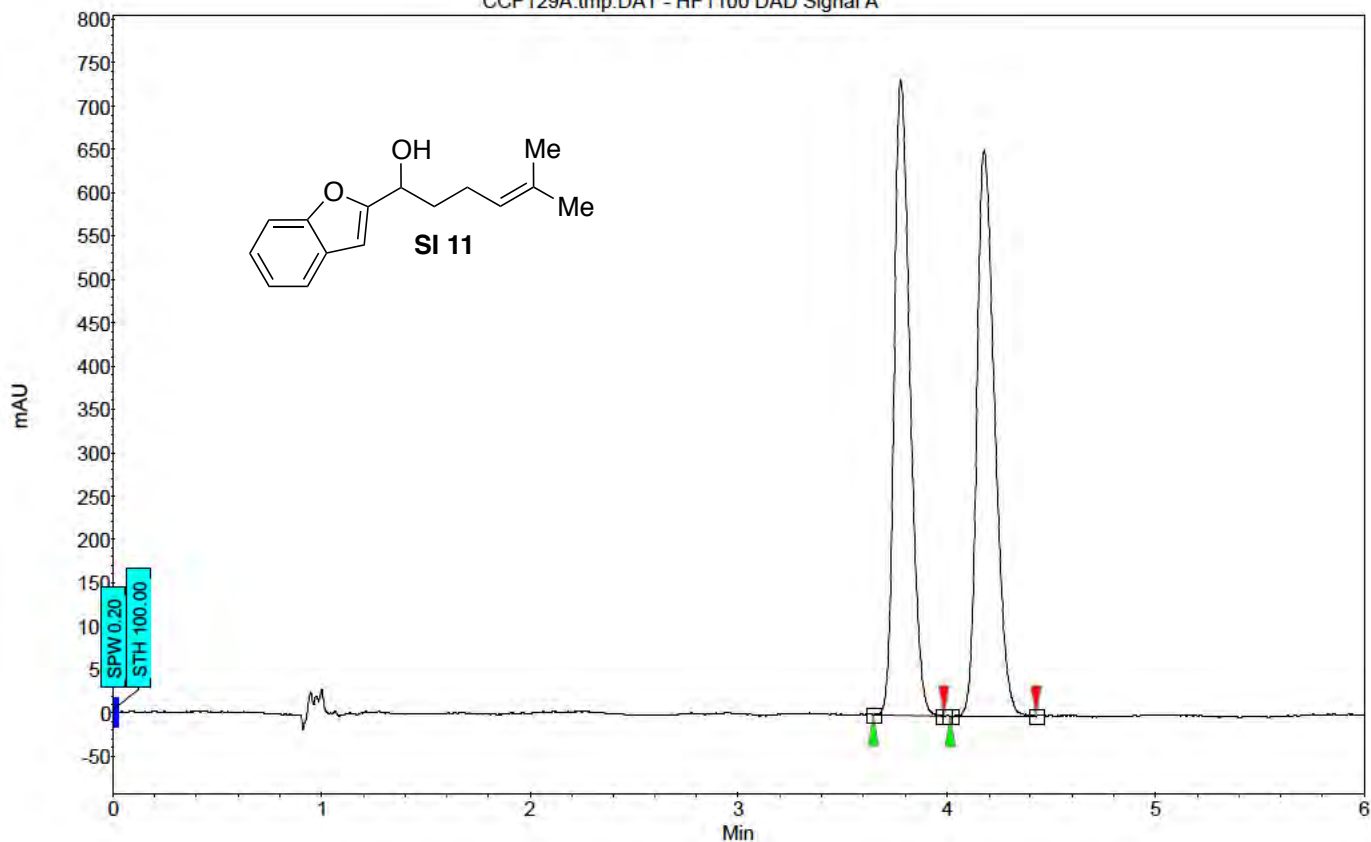
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	14.90	15.26	15.86	0.00	95.54	331.5	120.8	95.543
2	UNKNOWN	16.64	16.93	17.23	0.00	4.46	19.3	5.6	4.457
Total						100.00	350.9	126.4	100.000



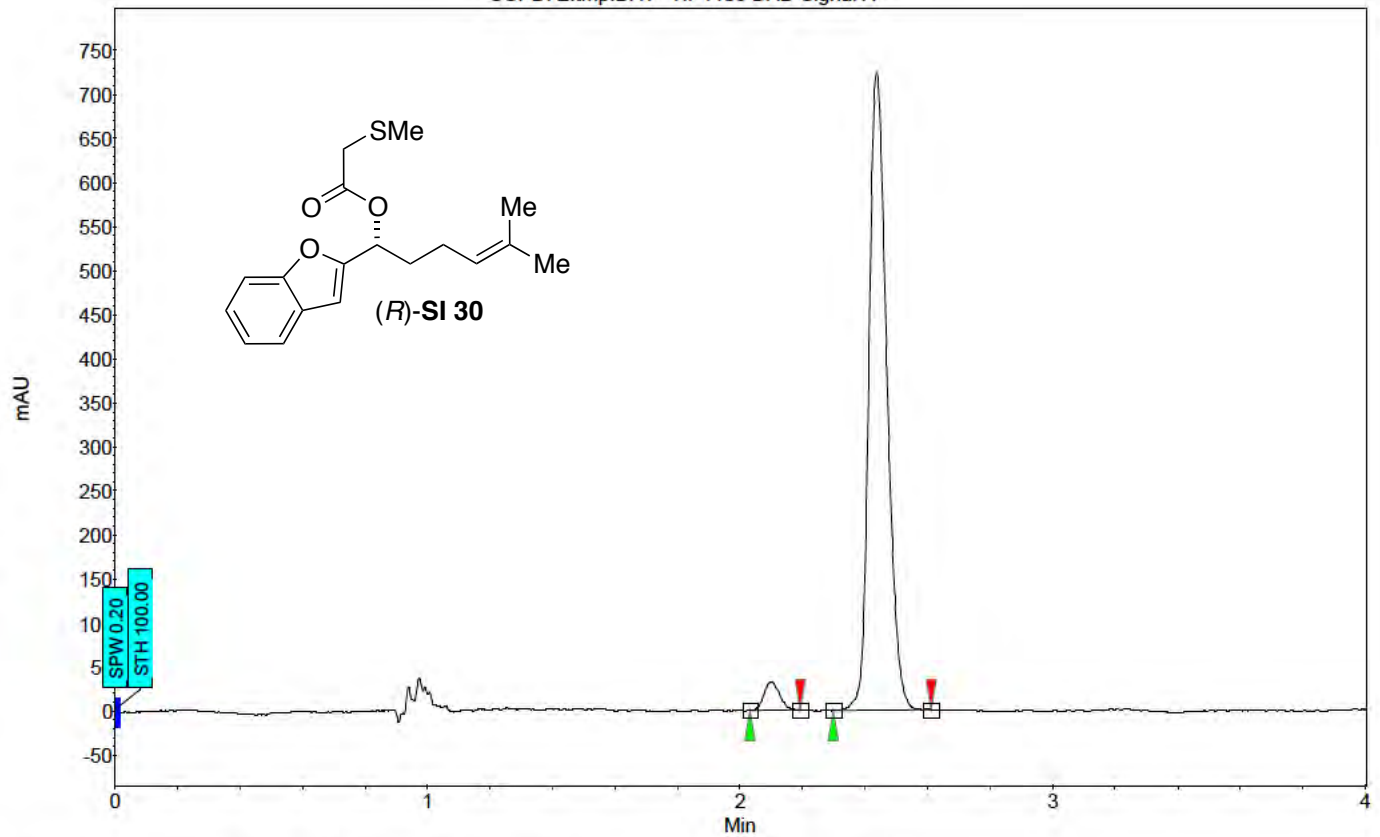
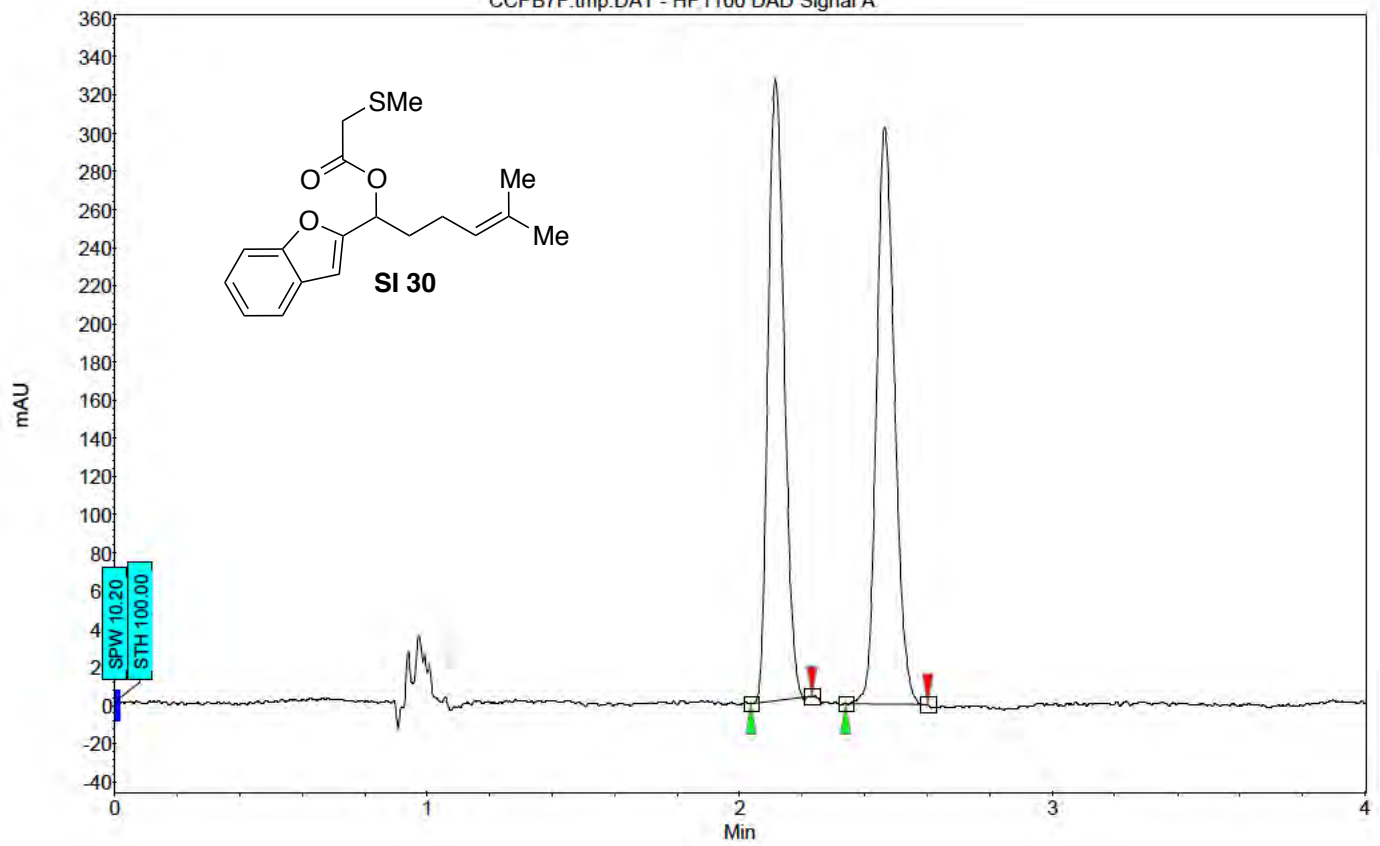
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	8.83	9.07	9.35	0.00	1.05	33.5	6.4	1.048
2	UNKNOWN	9.39	9.66	10.25	0.00	98.95	2034.5	600.3	98.952
Total						100.00	2067.9	606.6	100.000



Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	4.91	5.12	5.41	0.00	98.84	1986.9	264.7	
2	UNKNOWN	5.82	5.98	6.15	0.00	1.16	26.8	3.1	
Total						100.00	2013.7	267.8	100.000

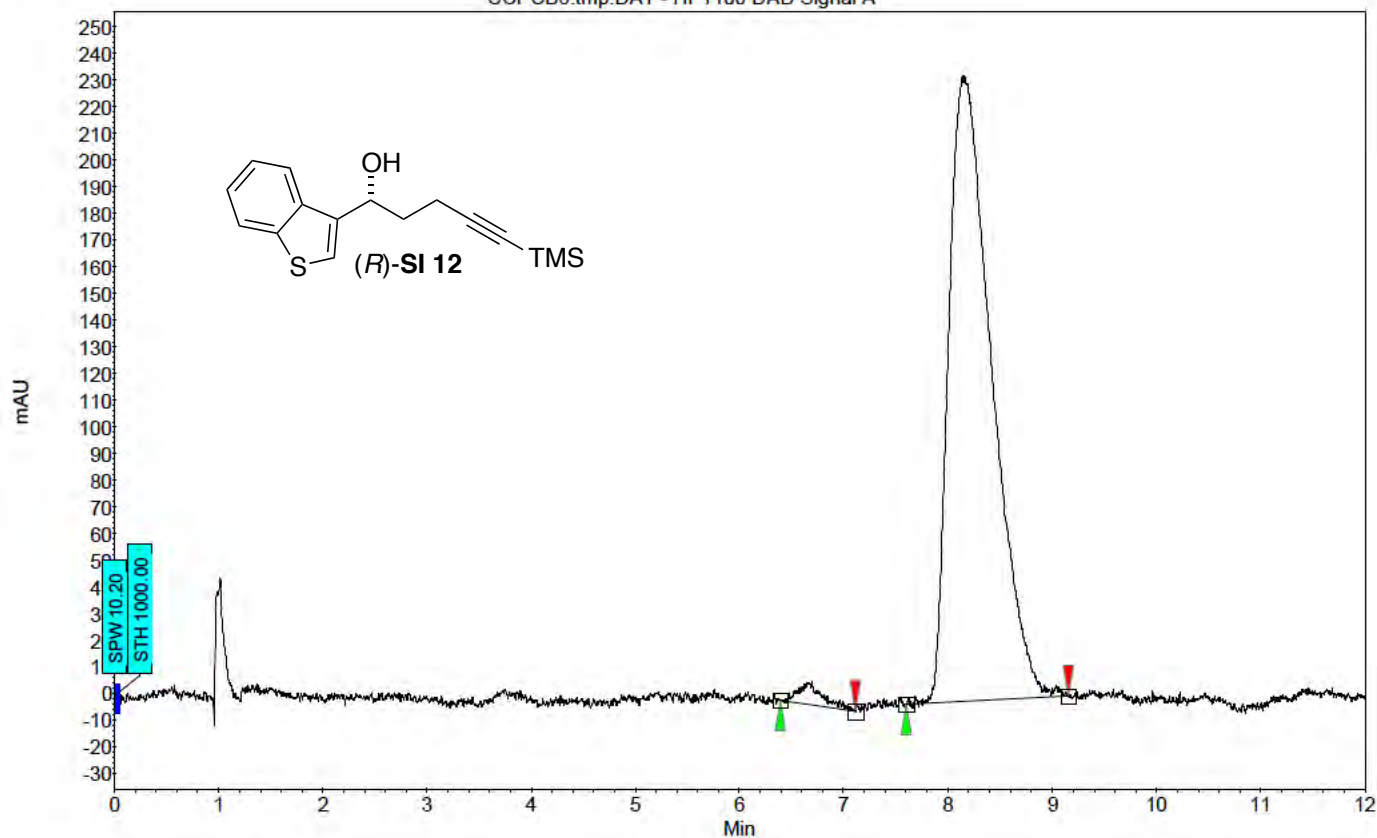
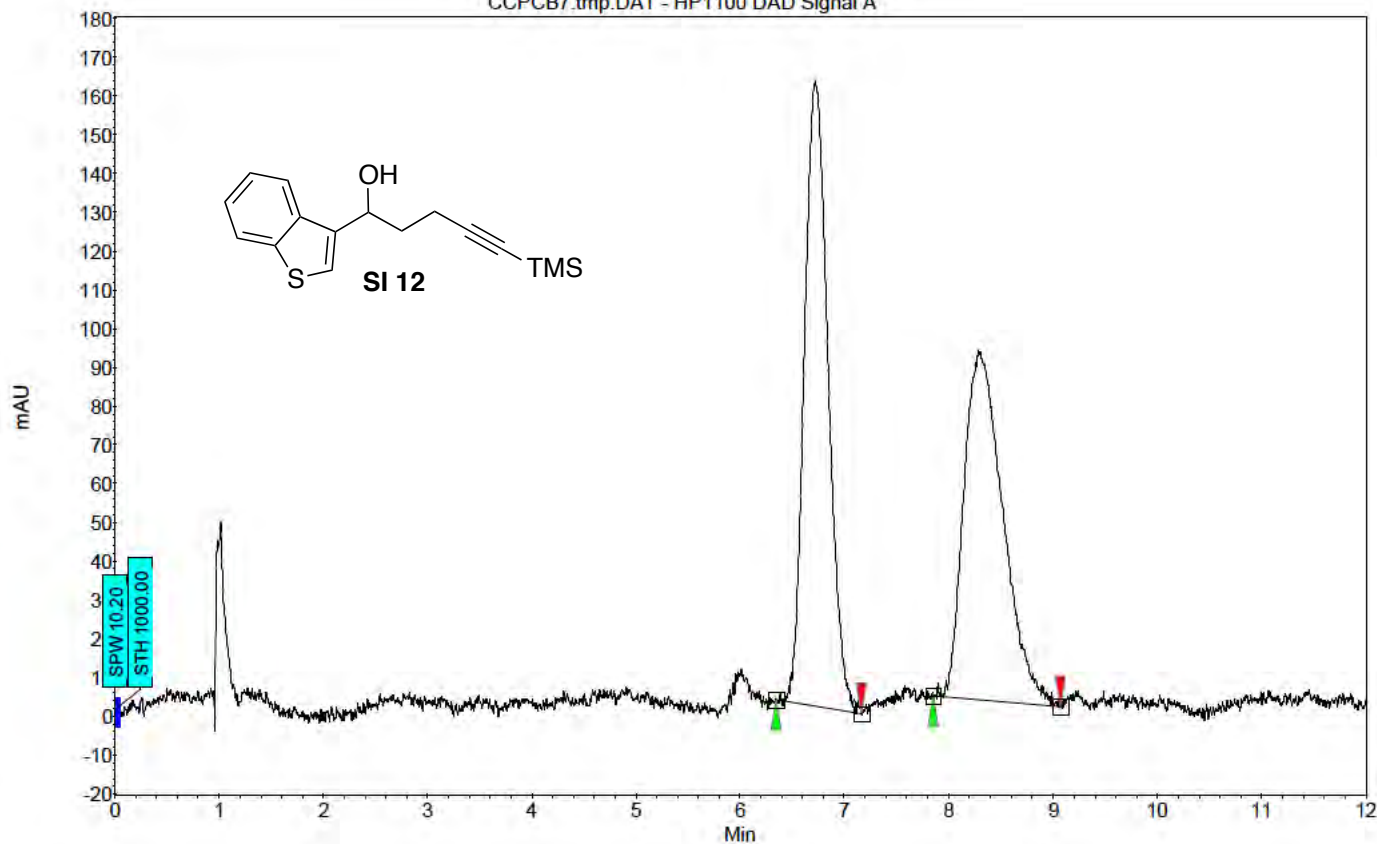


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]
1	UNKNOWN	3.97	3.99	4.04	0.00	1.68	1.4	0.1
2	UNKNOWN	4.04	4.23	4.39	0.00	98.32	34.2	3.5
Total						100.00	35.7	3.6

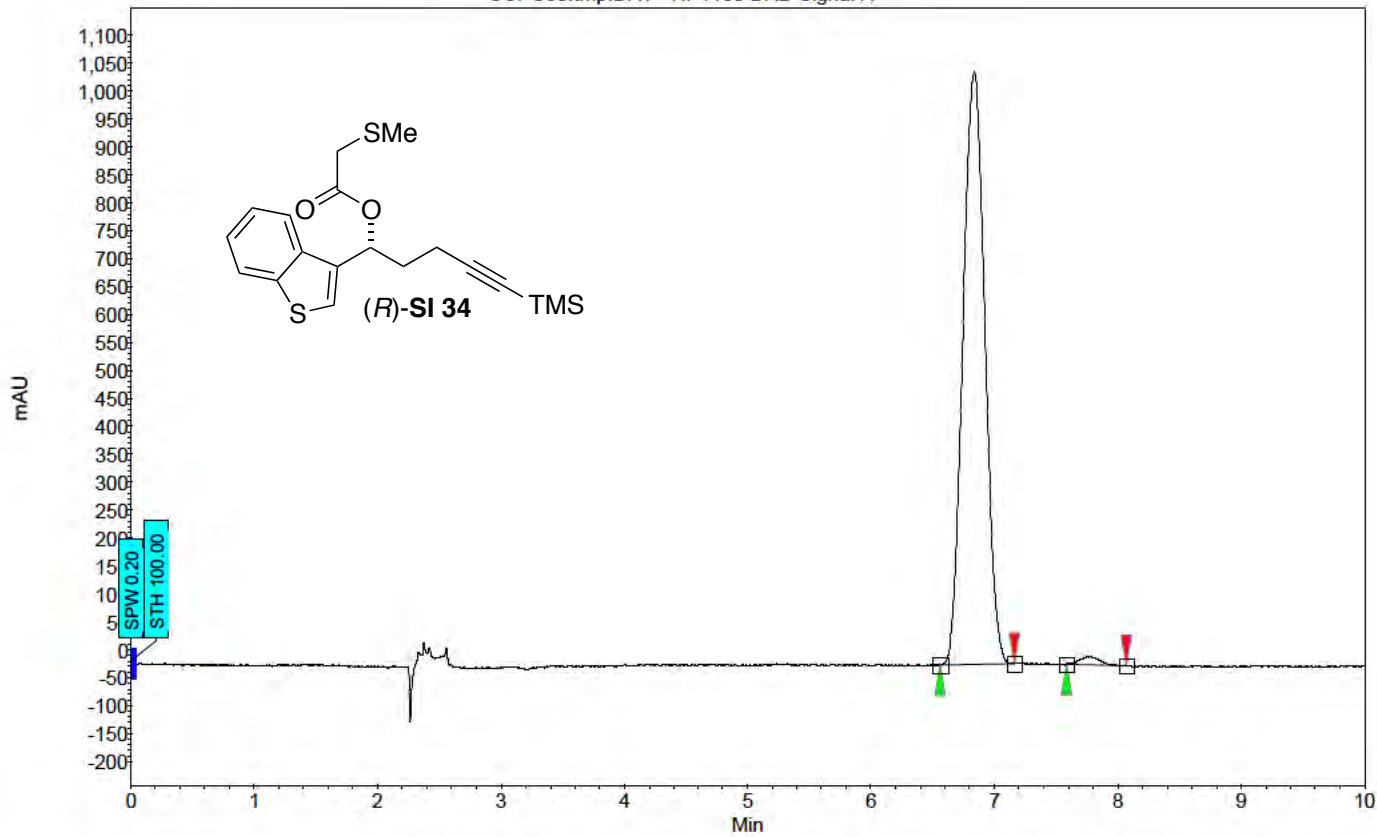
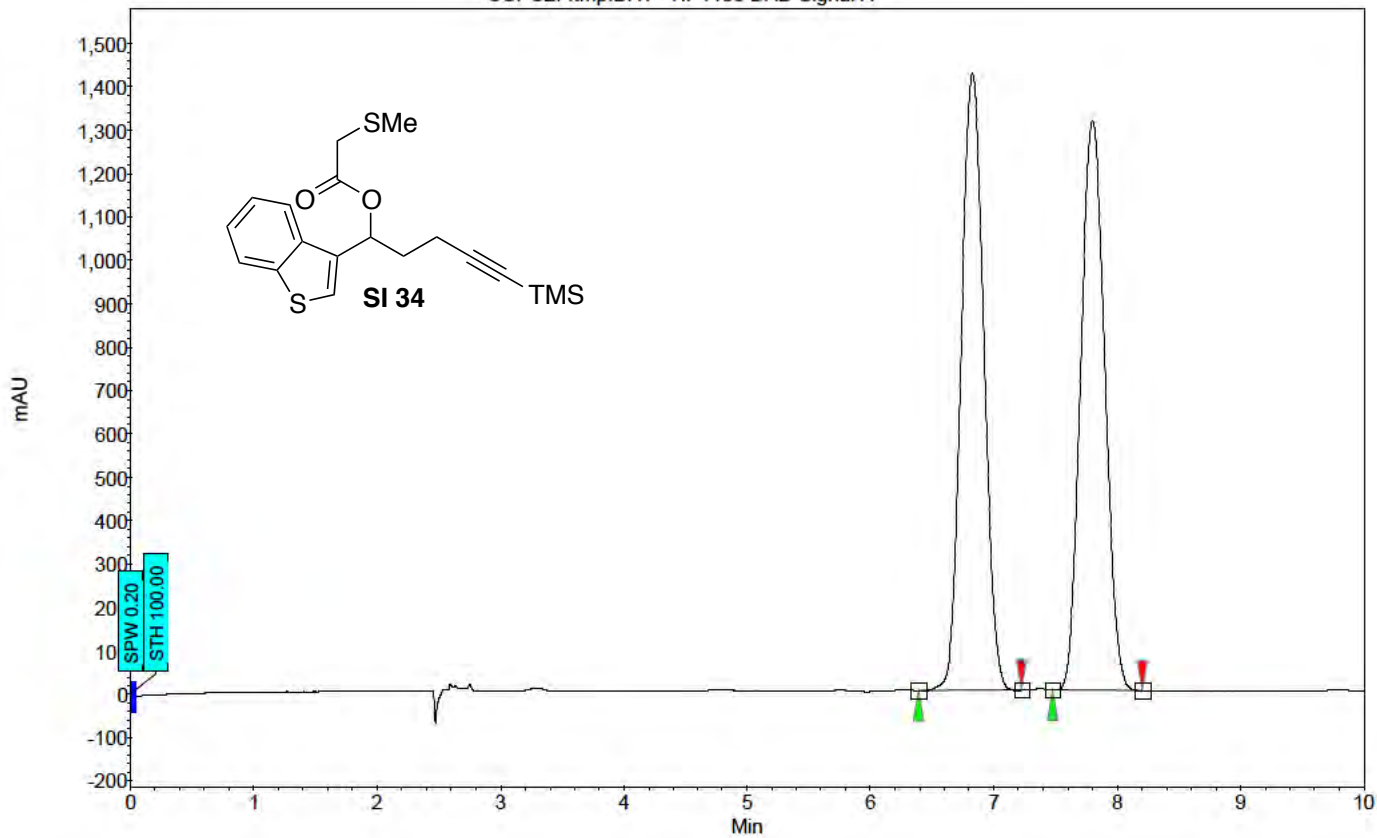


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	2.03	2.10	2.19	0.00	3.73	32.4	1.9	3.732
2	UNKNOWN	2.30	2.44	2.61	0.00	96.27	722.7	47.8	96.268
Total						100.00	755.1	49.7	100.000

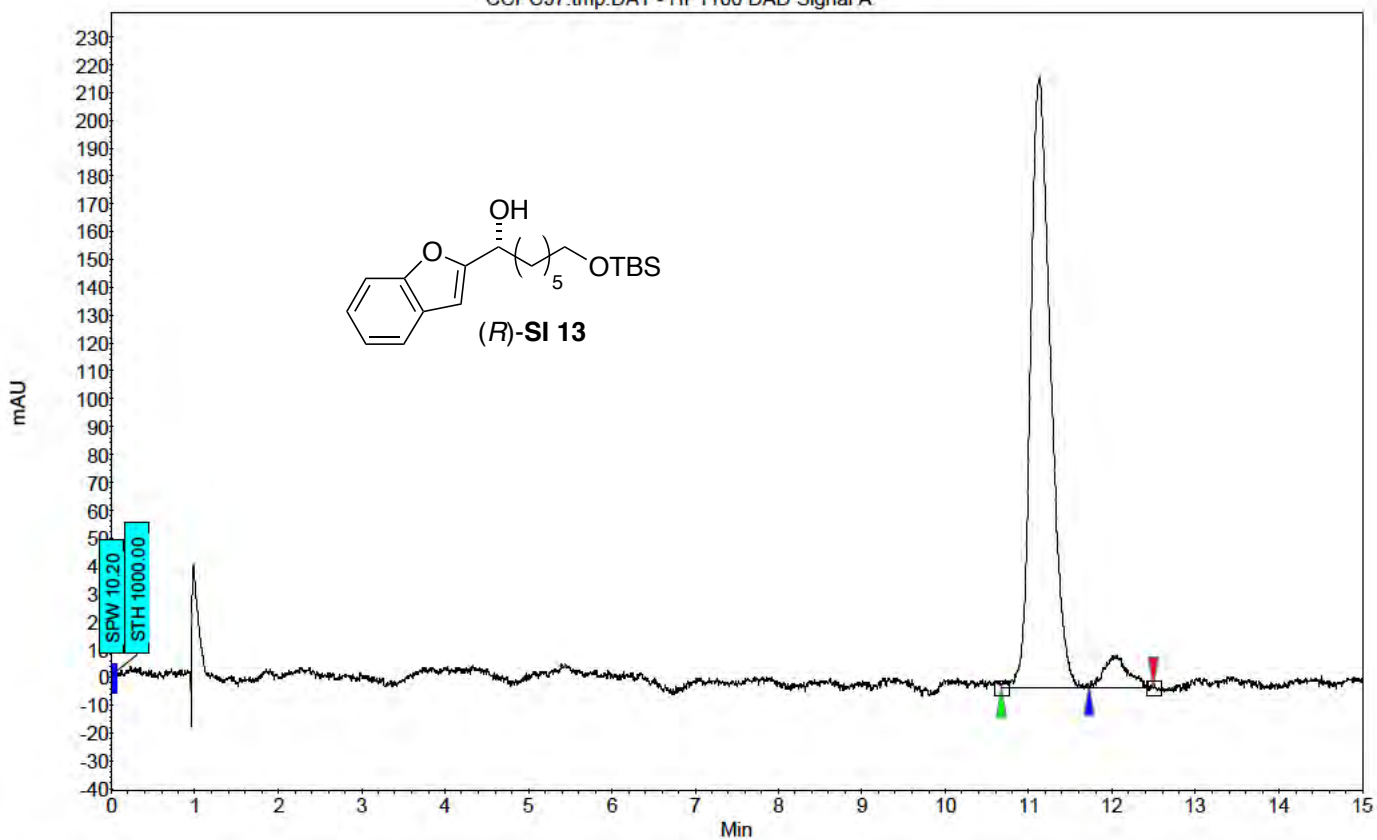
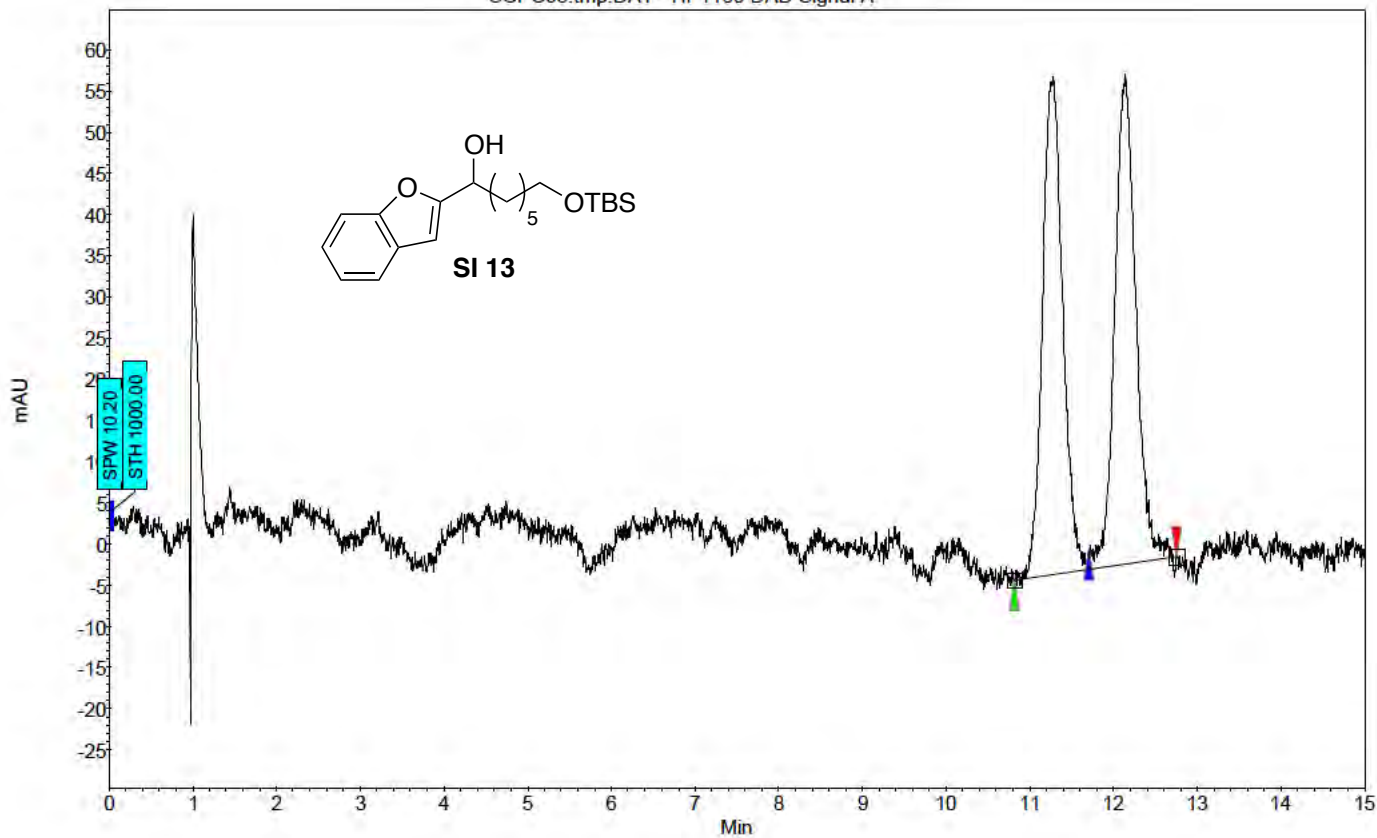




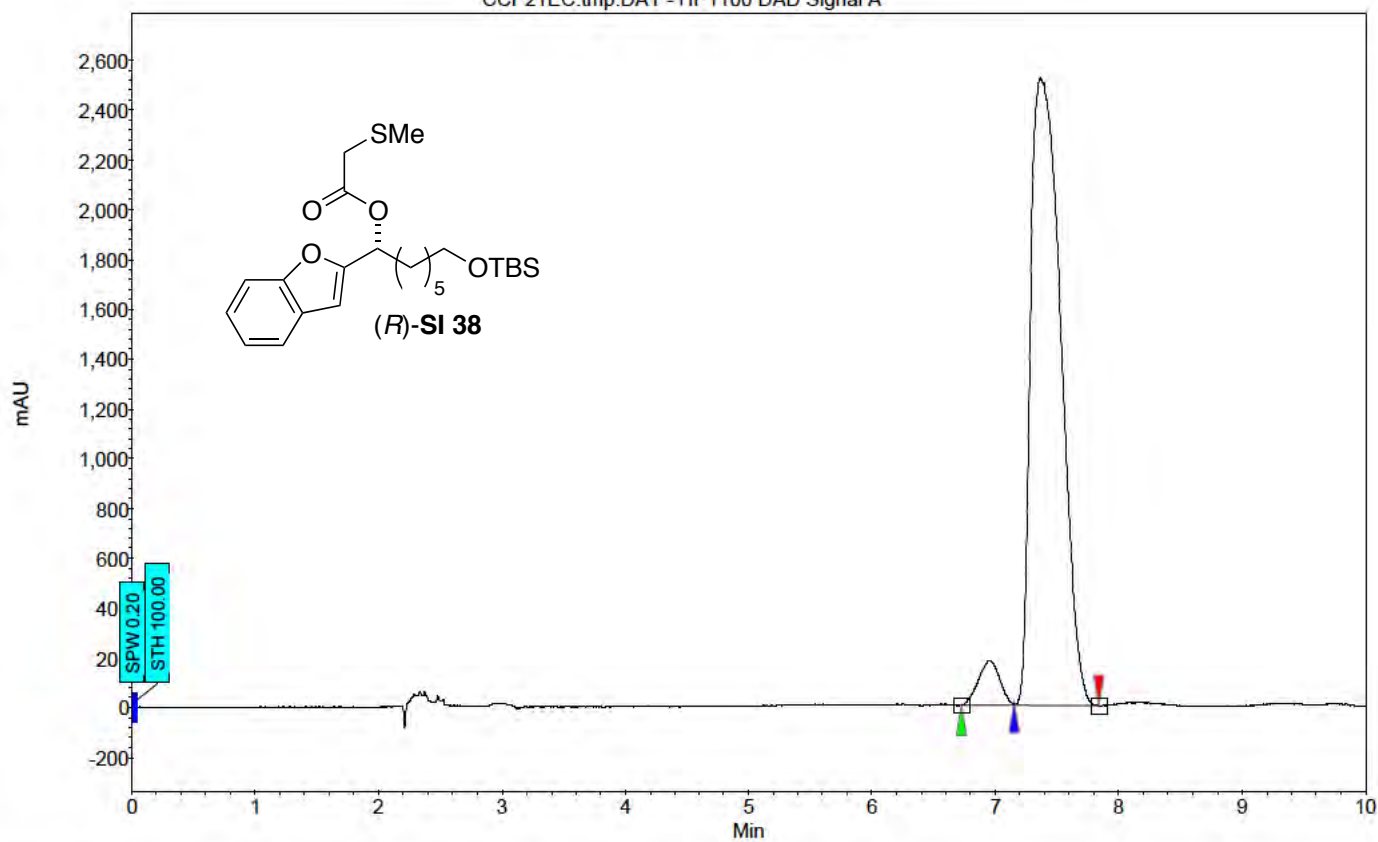
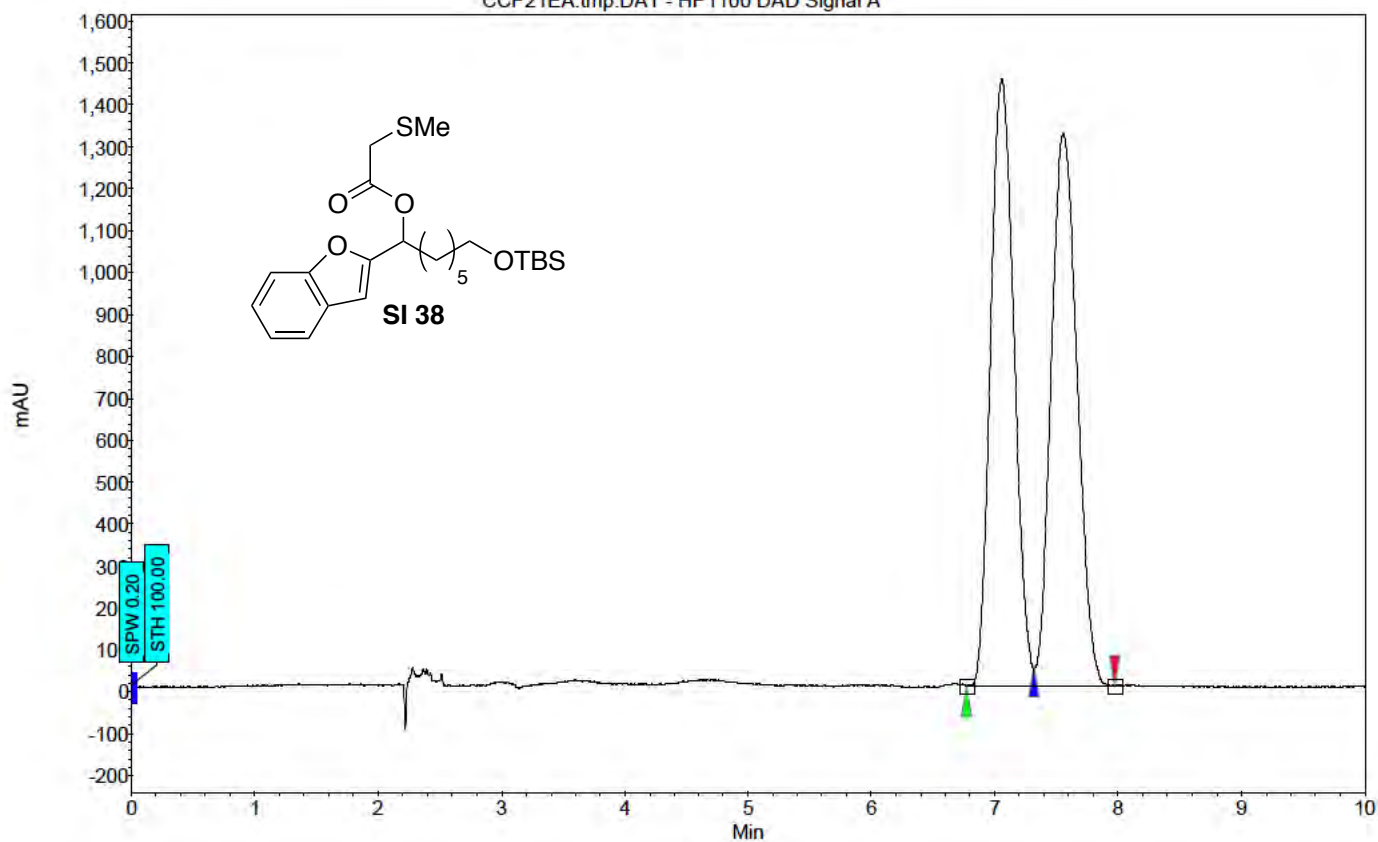
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	6.39	6.69	7.11	0.00	1.93	8.5	2.2	1.925
2	UNKNOWN	7.60	8.14	9.16	0.00	98.07	234.3	111.6	98.075
Total						100.00	242.9	113.8	100.000



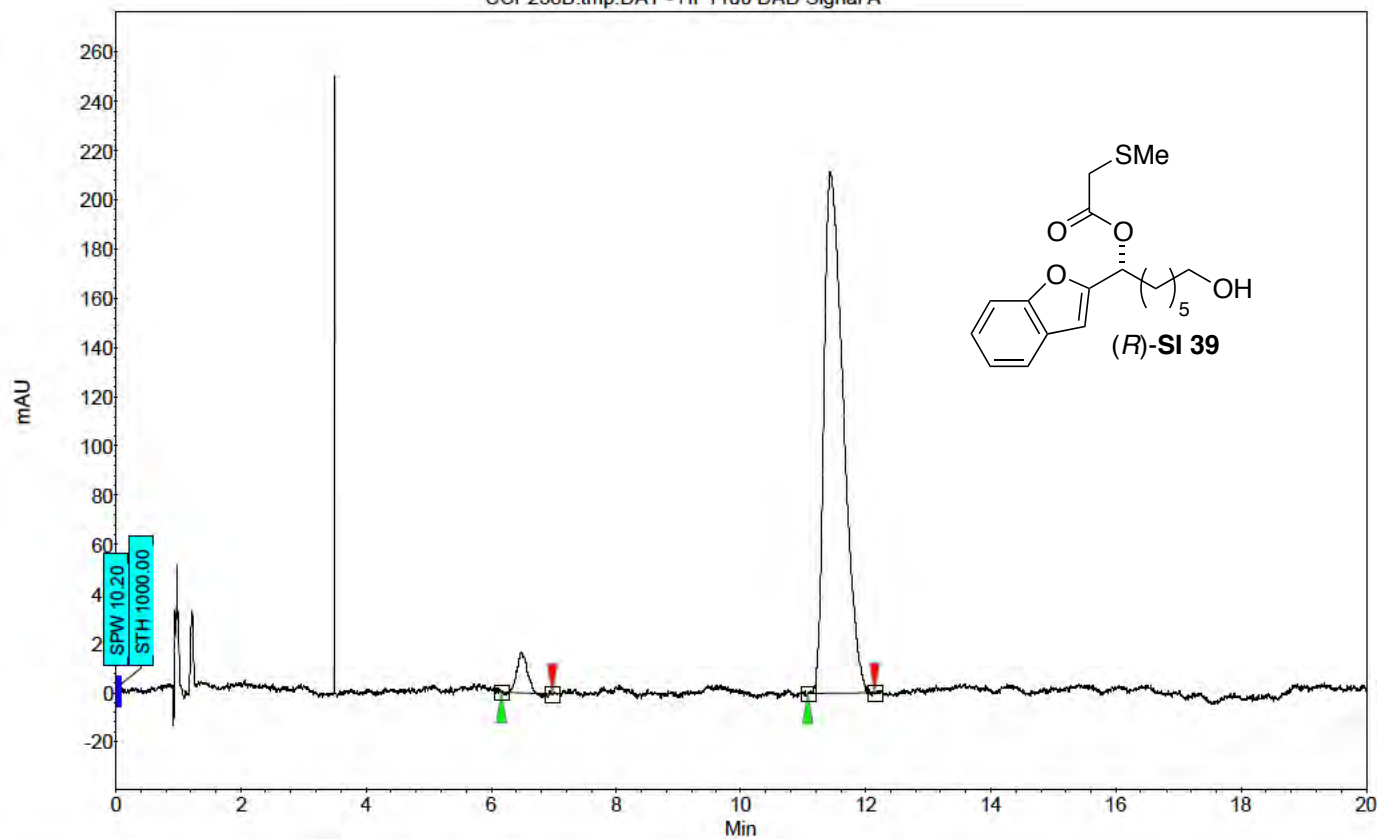
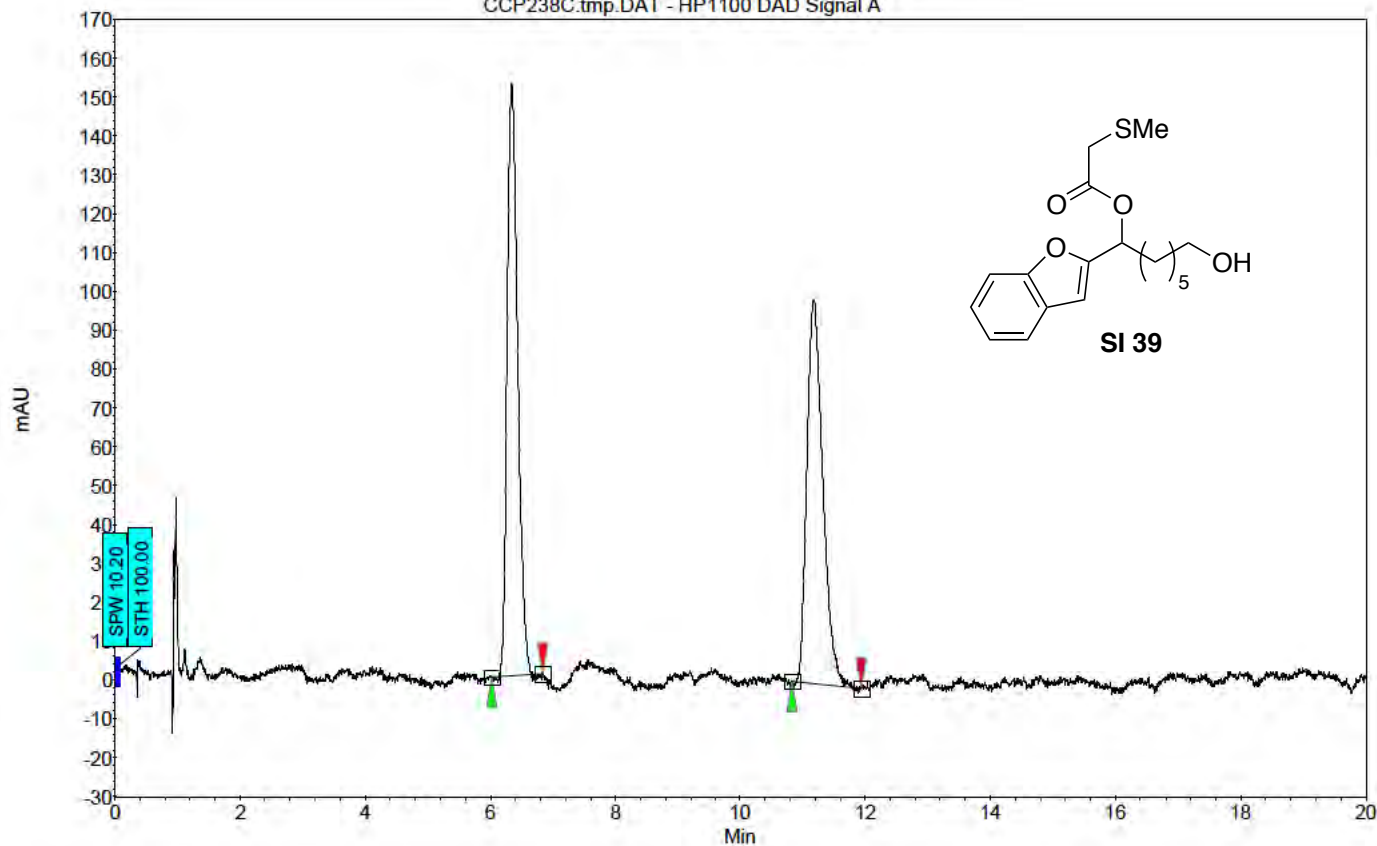
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	6.56	6.84	7.16	0.00	98.76	1058.4	217.6	
2	UNKNOWN	7.58	7.79	8.07	0.00	1.24	15.2	2.7	
Total						100.00	1073.6	220.4	100.000



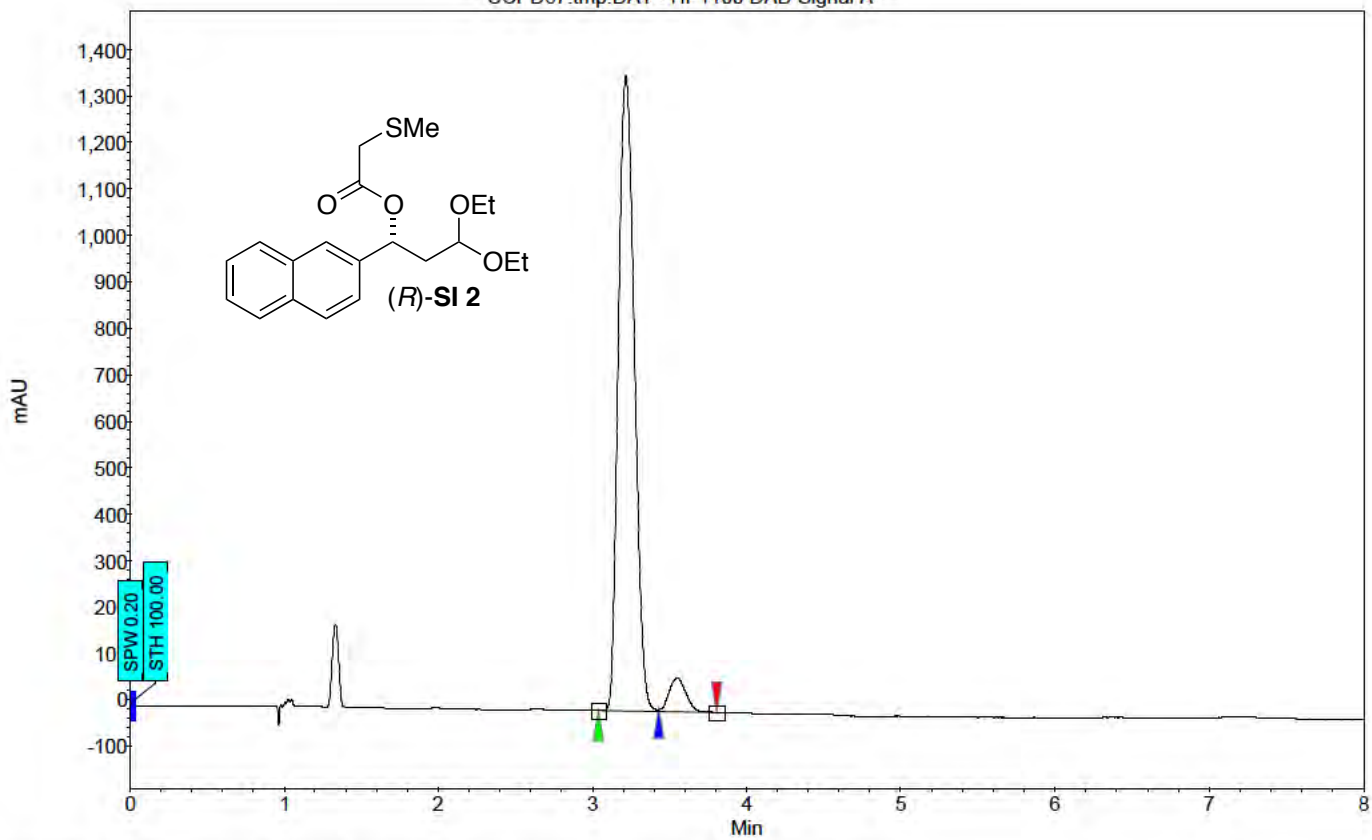
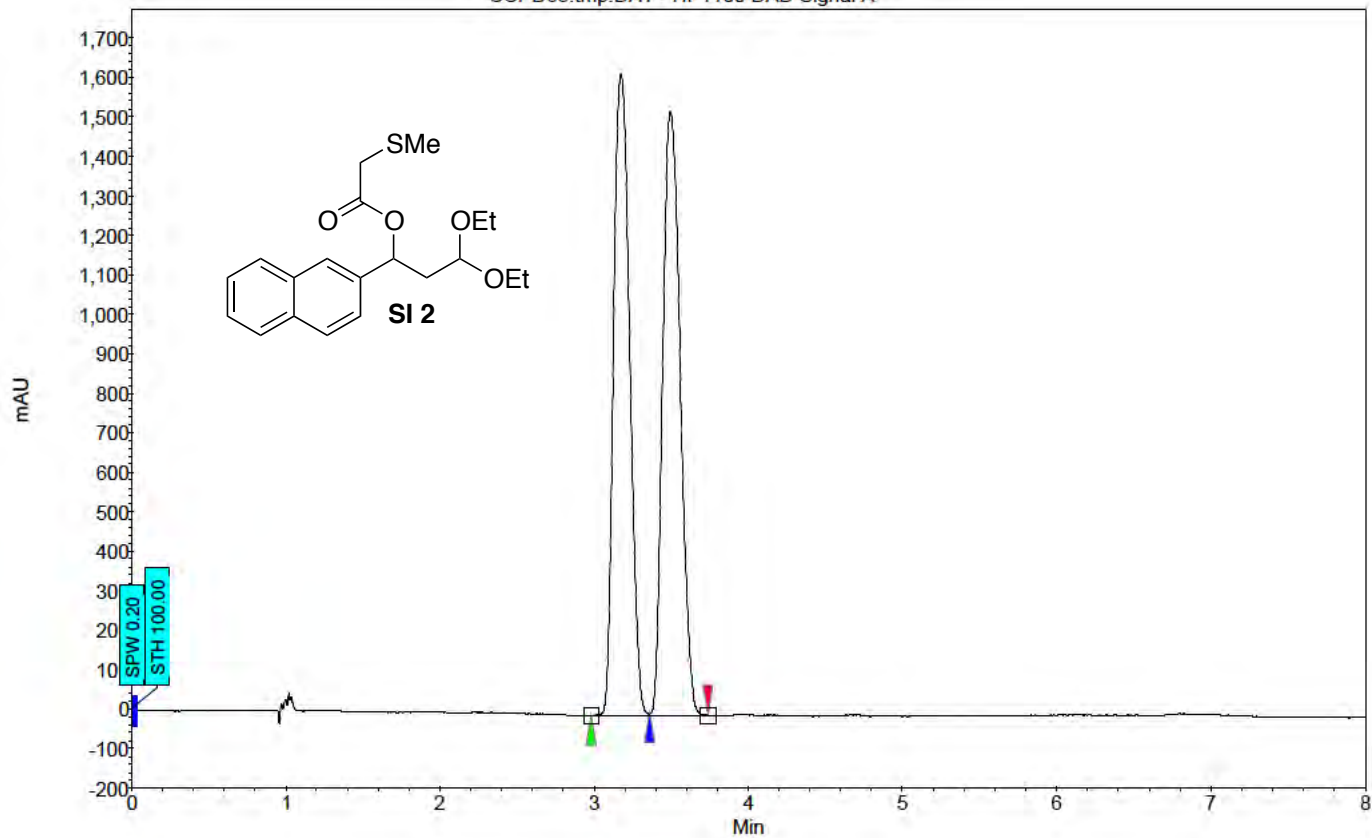
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	10.68	11.13	11.73	0.00	94.13	219.0	60.5	94.127
2	UNKNOWN	11.73	12.06	12.50	0.00	5.87	11.7	3.8	5.873
Total						100.00	230.7	64.3	100.000



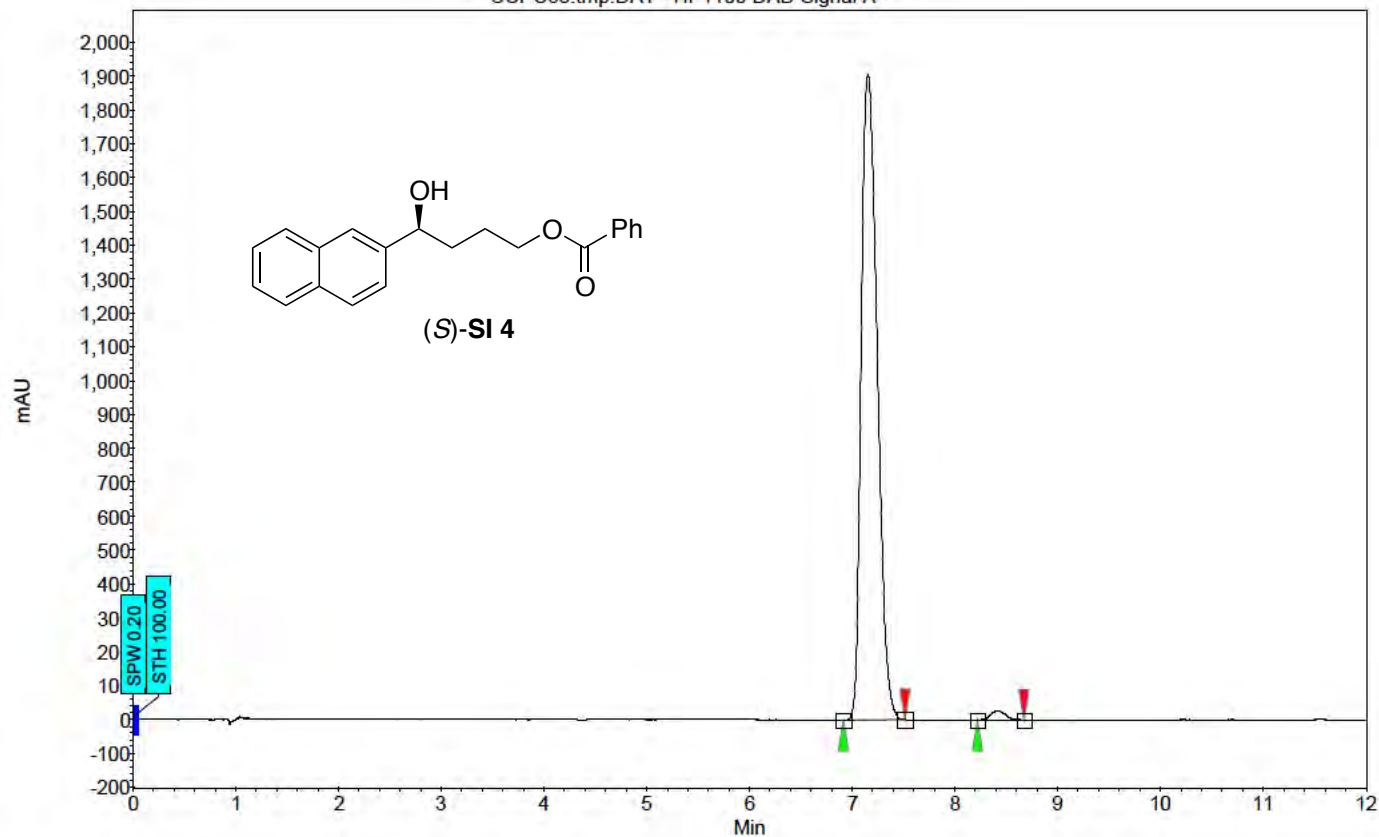
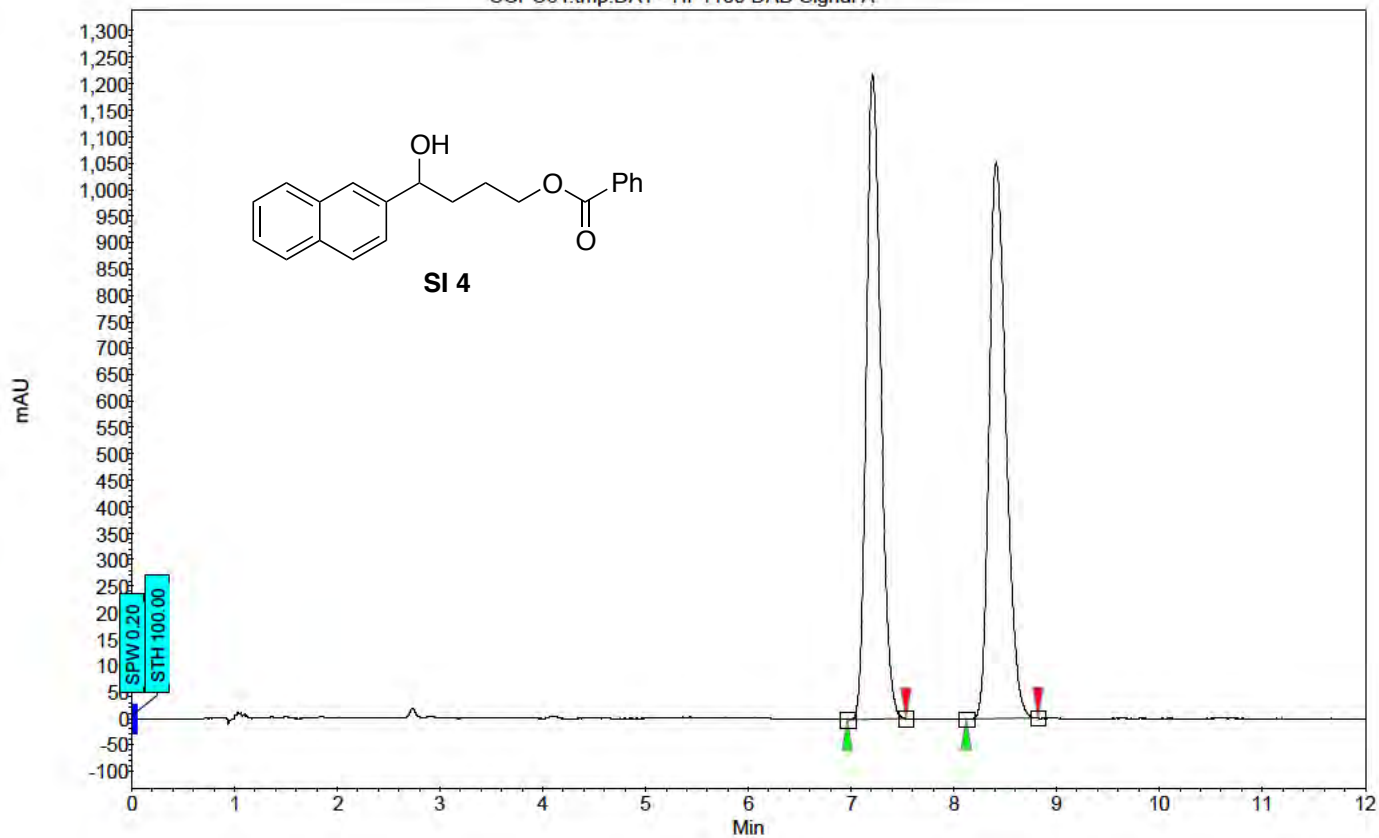
Index	Name	Start Time			End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]						
1	UNKNOWN	6.72	6.97	7.16	0.00	4.79	178.1	35.9	4.790	
2	UNKNOWN	7.16	7.36	7.84	0.00	95.21	2518.9	714.2	95.210	
Total							100.00	2697.0	750.1	100.000



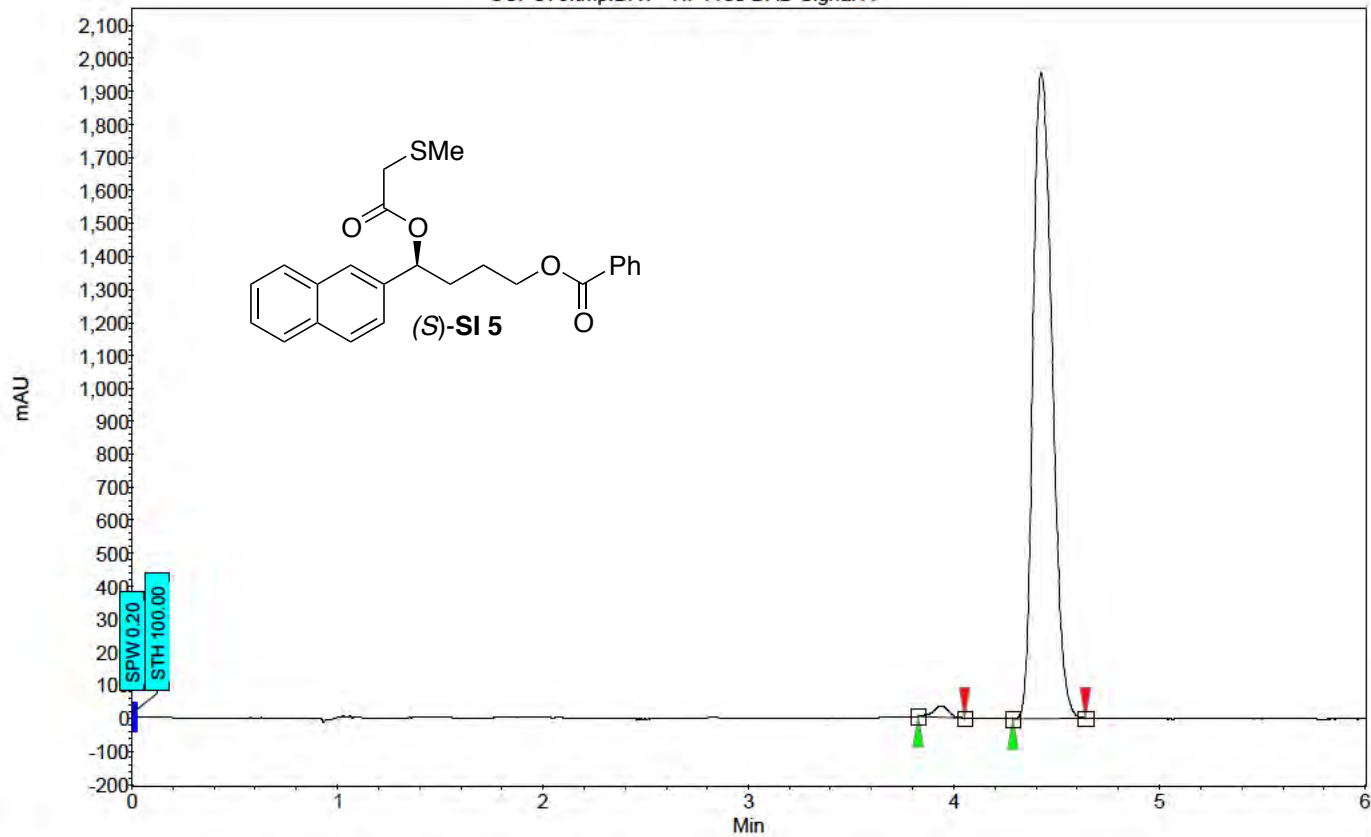
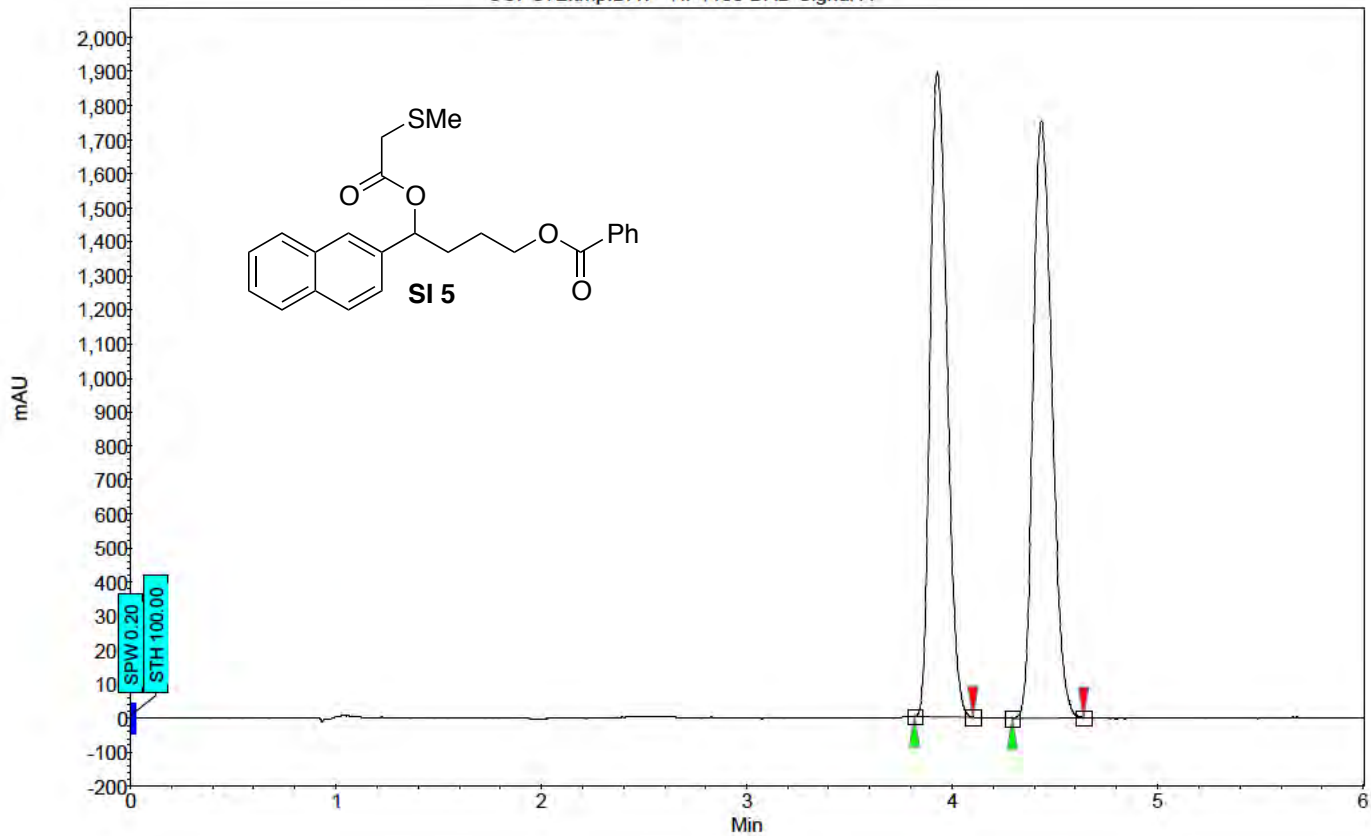
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	6.17	6.48	6.97	0.00	3.79	16.1	3.0	3.789
2	UNKNOWN	11.07	11.44	12.13	0.00	96.21	211.6	75.4	96.211
Total						100.00	227.7	78.3	100.000



Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	3.04	3.22	3.43	0.00	94.75	1367.1	164.9	94.747
2	UNKNOWN	3.43	3.55	3.81	0.00	5.25	73.6	9.1	5.253
Total						100.00	1440.7	174.0	100.000

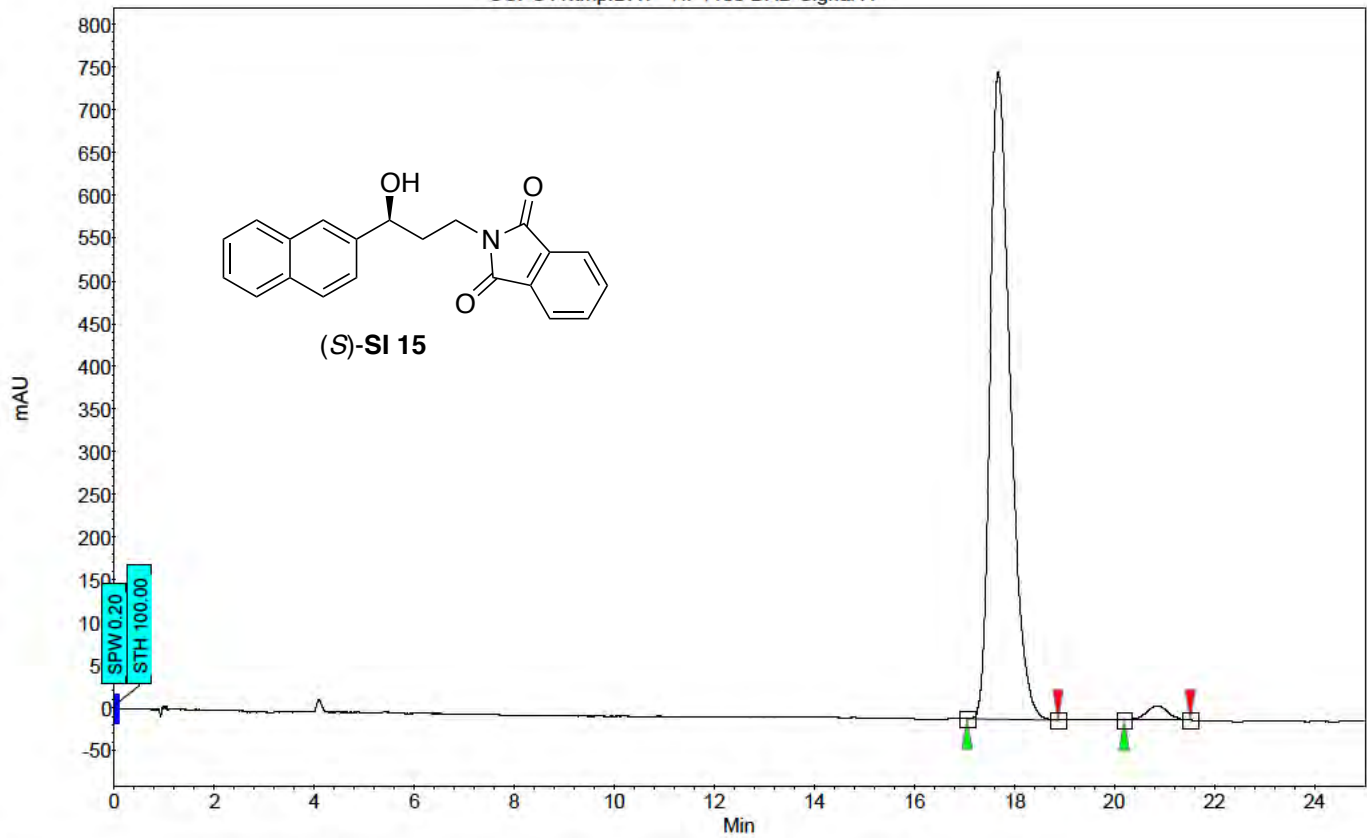
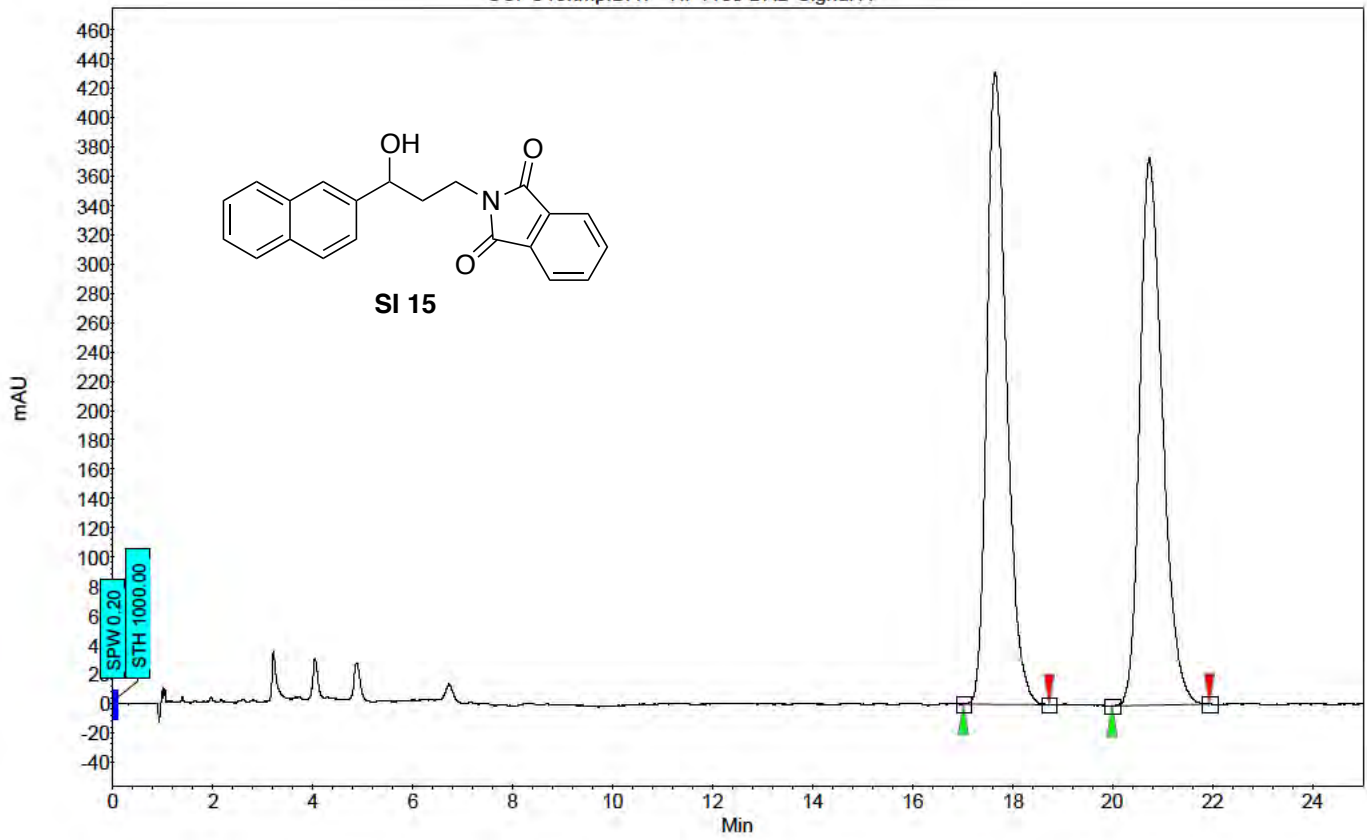


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	6.91	7.15	7.52	0.00	98.61	1904.2	344.0	98.608
2	UNKNOWN	8.22	8.42	8.67	0.00	1.39	27.4	4.9	1.392
Total						100.00	1931.7	348.9	100.000

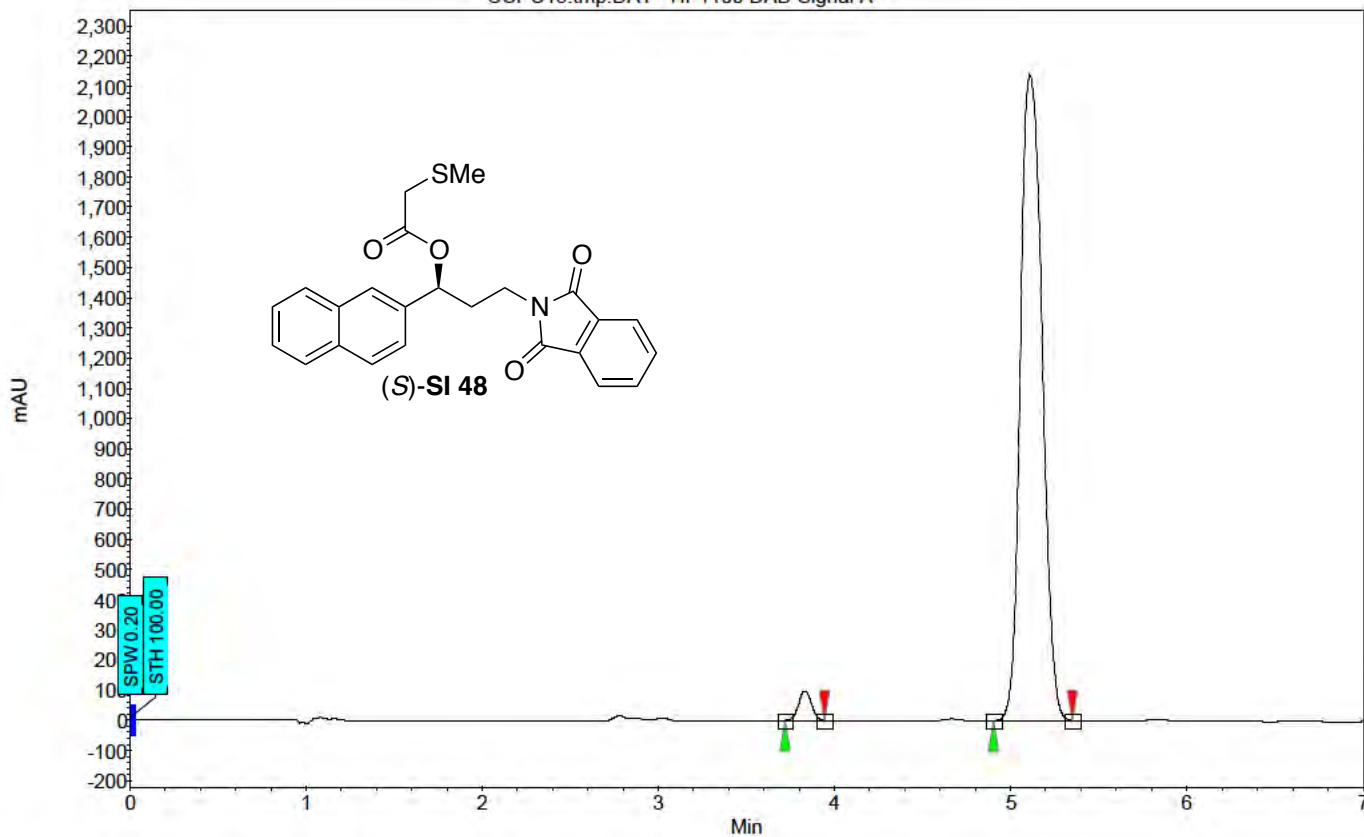
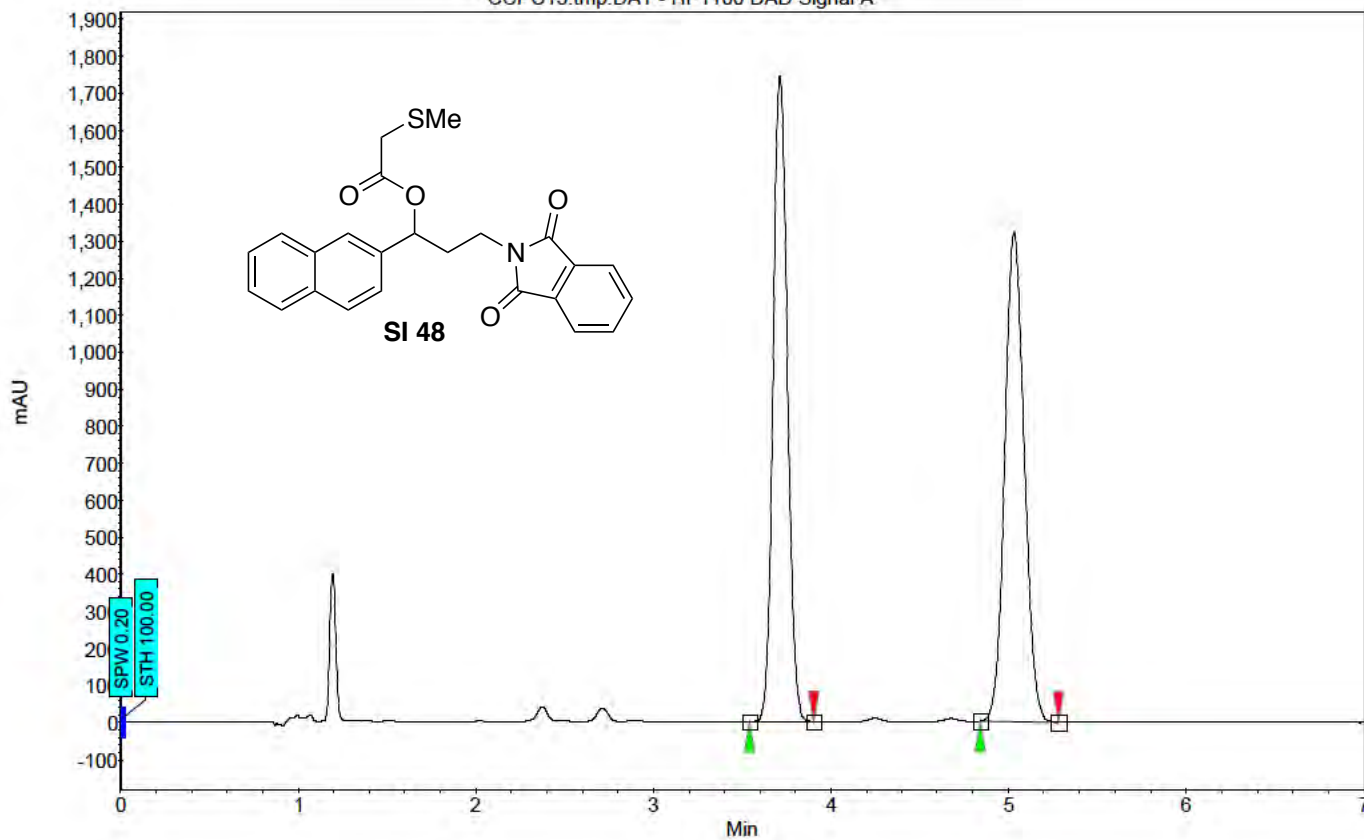


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
2	UNKNOWN	3.83	3.94	4.05	0.00	1.36	33.6	2.9	1.356
1	UNKNOWN	4.29	4.42	4.64	0.00	98.64	1956.1	210.4	98.644
Total						100.00	1989.7	213.3	100.000

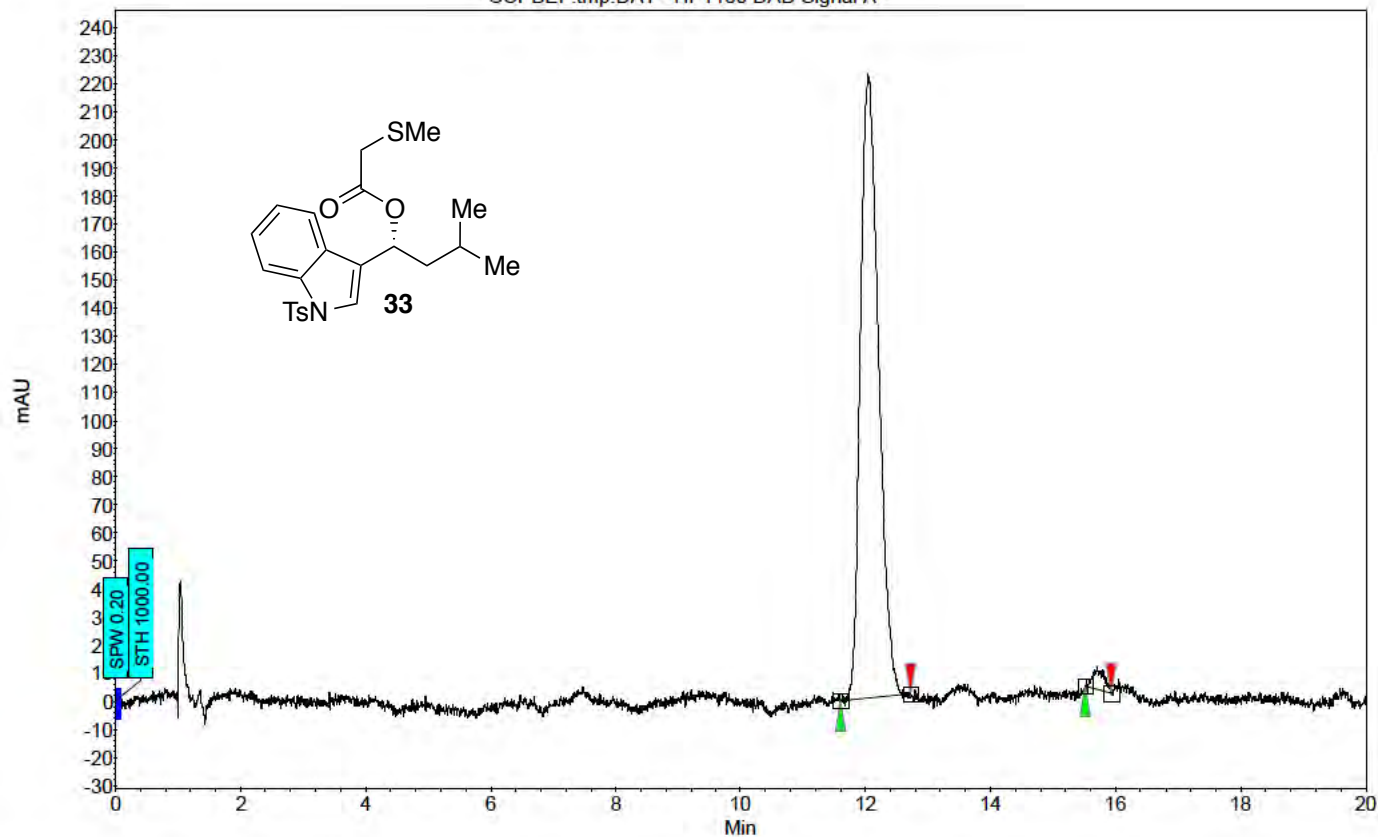
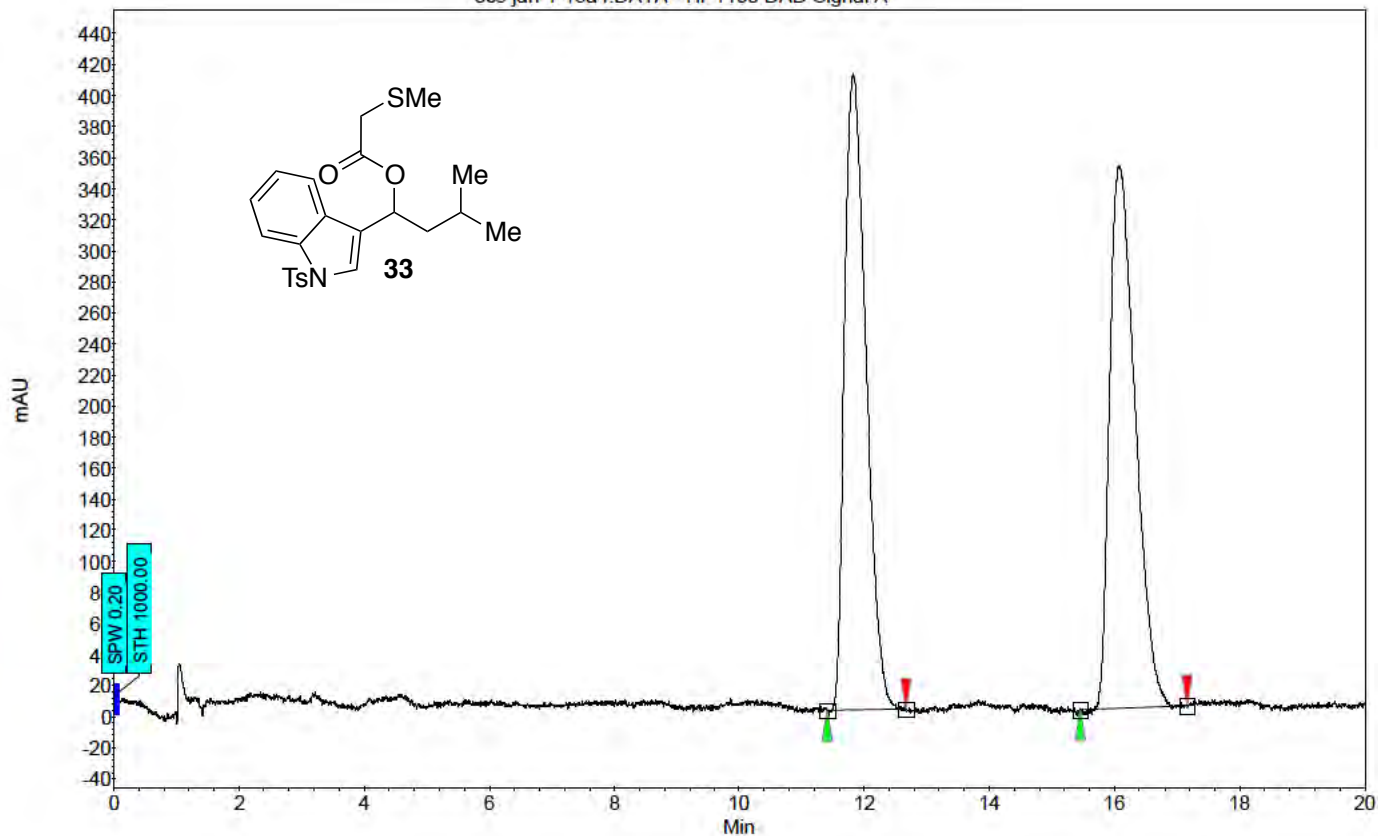




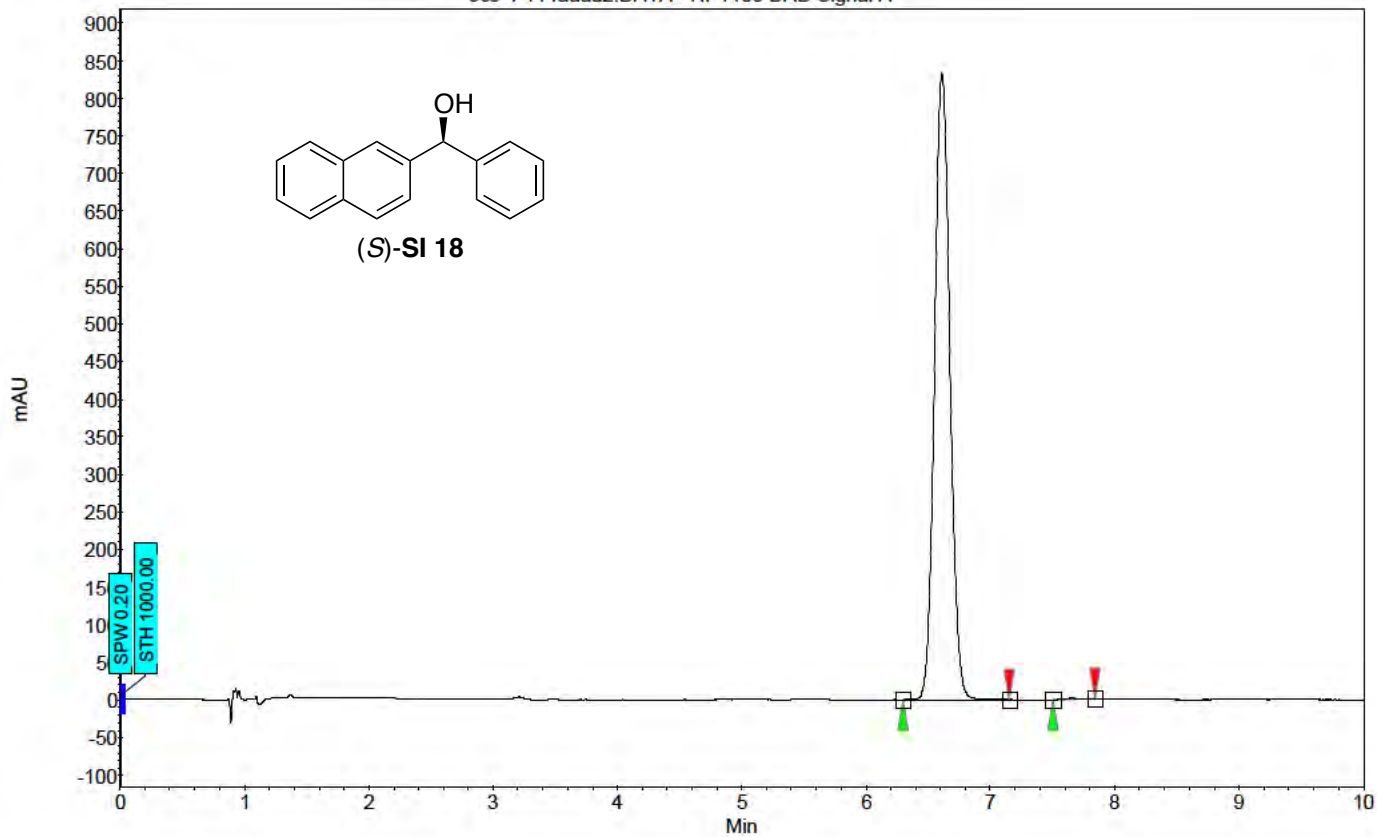
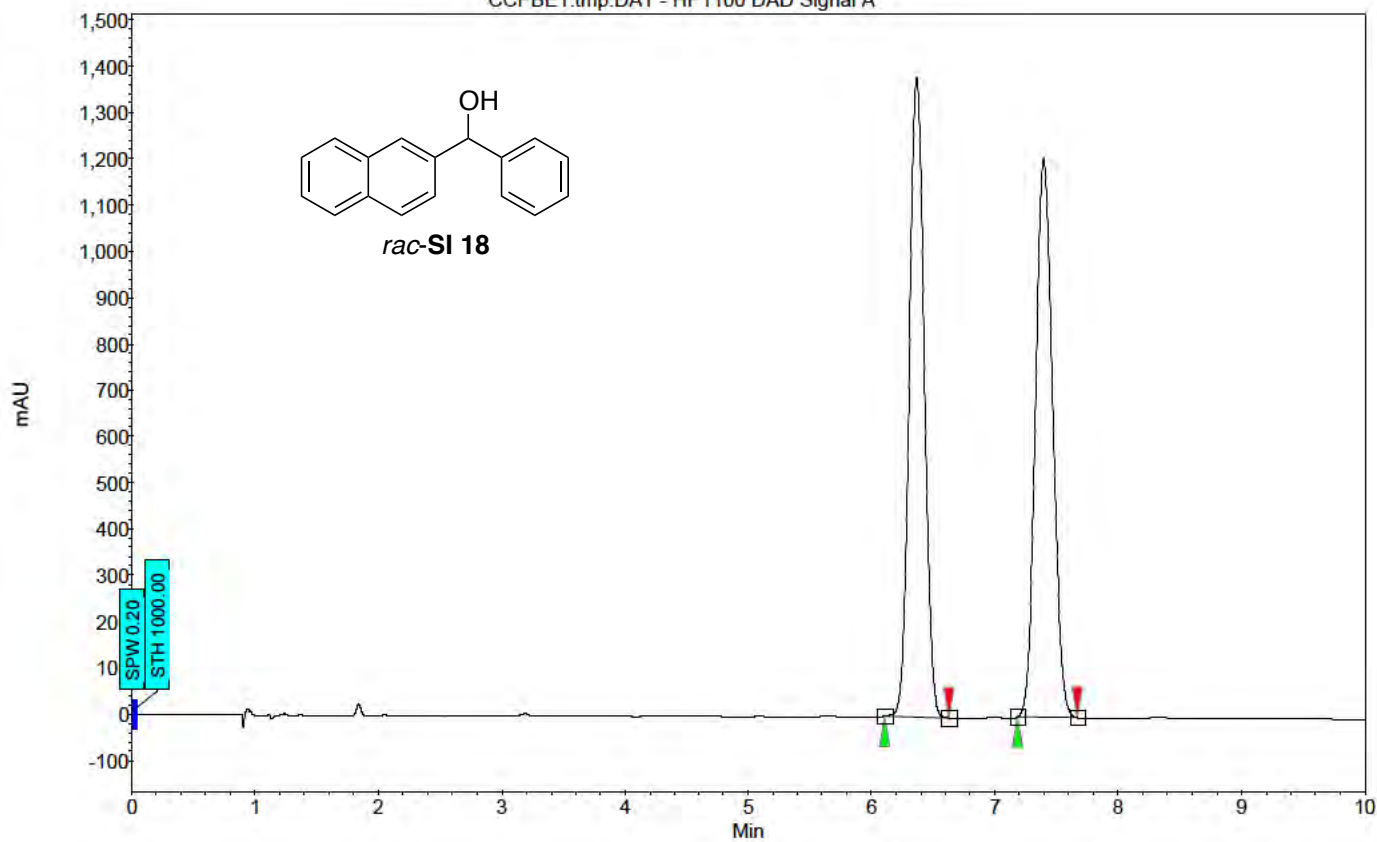
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	17.05	17.67	18.86	0.00	97.63	756.9	352.6	97.629
2	UNKNOWN	20.19	20.86	21.51	0.00	2.37	16.6	8.6	2.371
Total						100.00	773.5	361.2	100.000



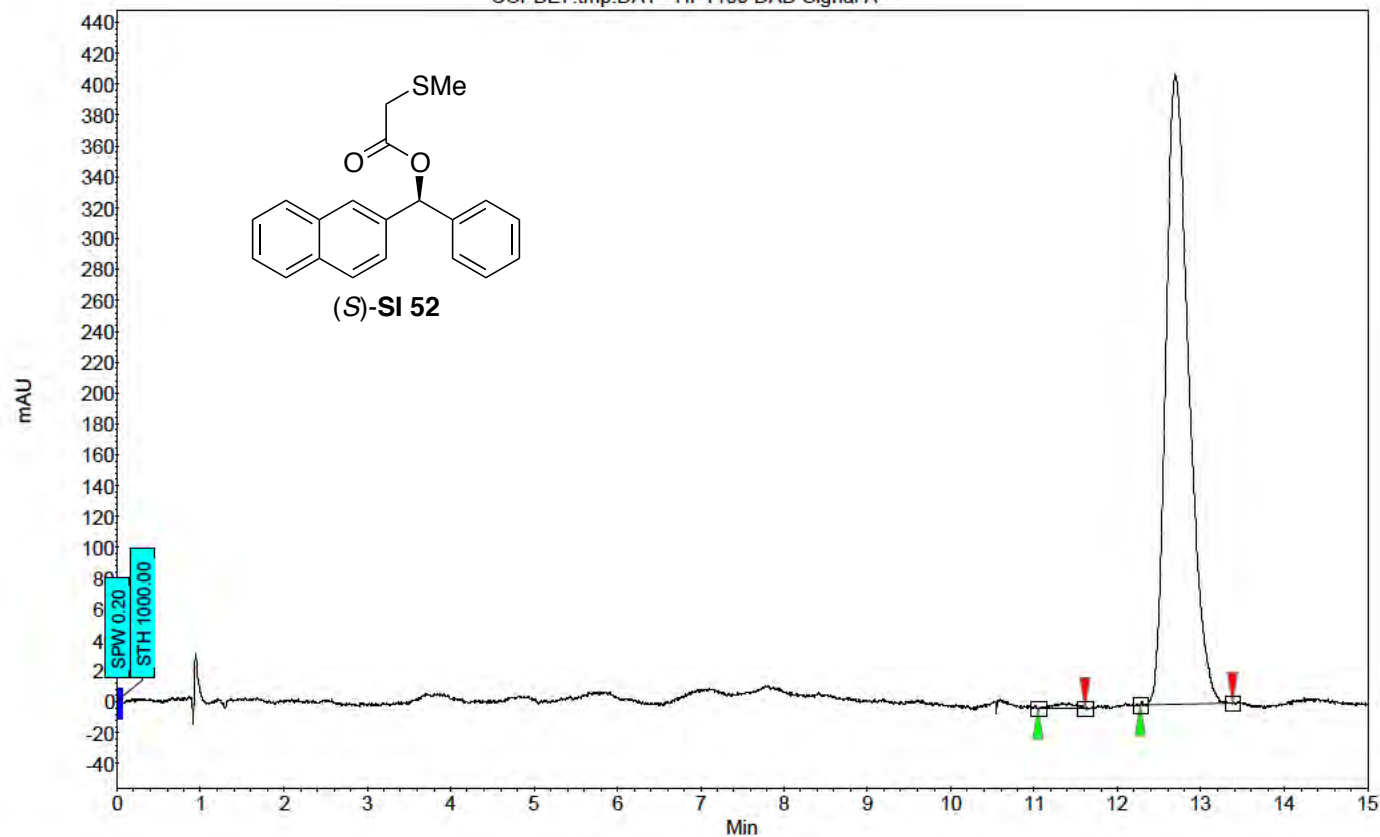
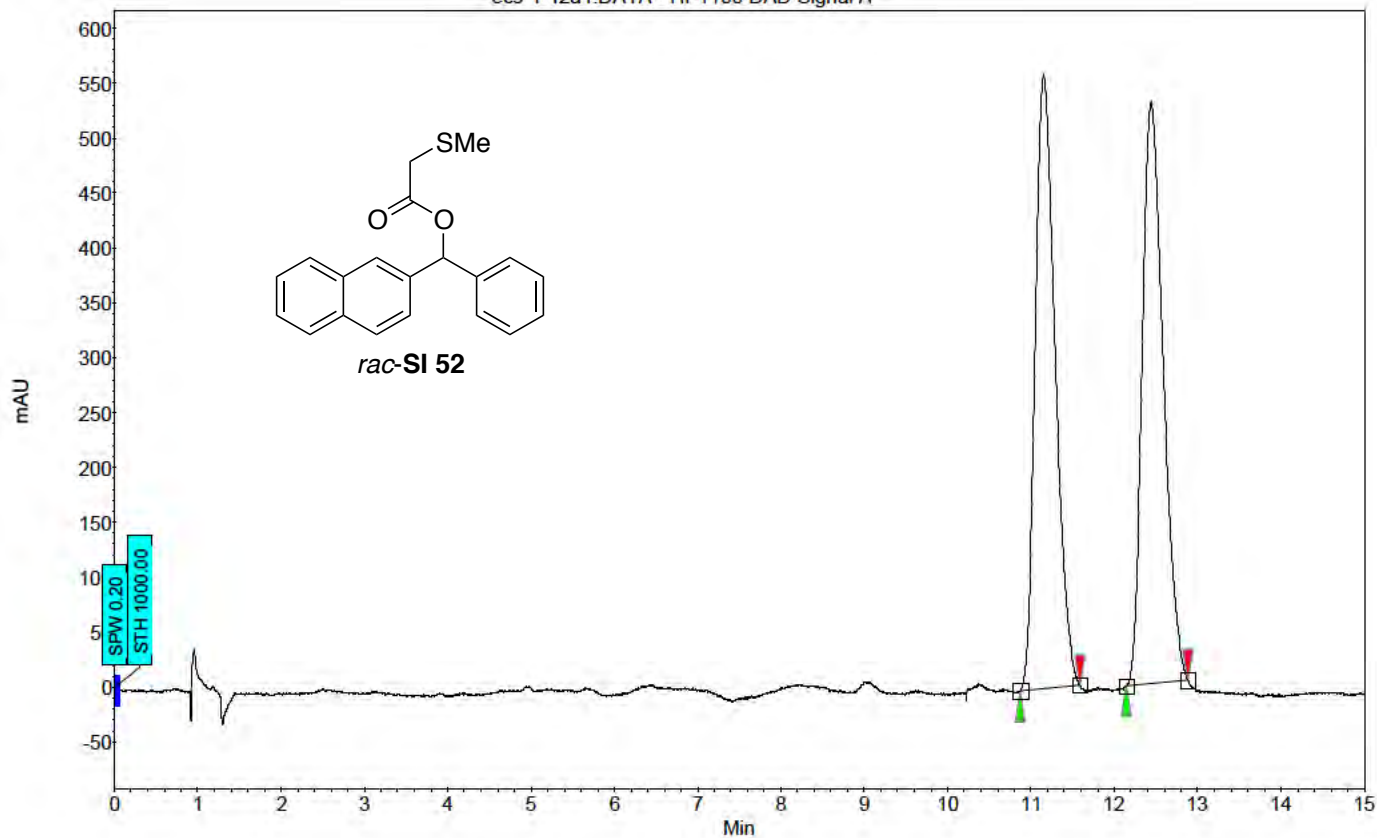
Index	Name	Start Time			End	RT Offset	Quantity	Height	Area	
		[Min]	[Min]	[Min]					[% Area]	[ $\mu$ V.Min]
1	UNKNOWN	3.72	3.83	3.95	0.00	2.70	99.2	8.5	2.695	
2	UNKNOWN	4.90	5.11	5.35	0.00	97.30	2139.2	306.8	97.305	
Total						100.00	2238.4	315.3	100.000	



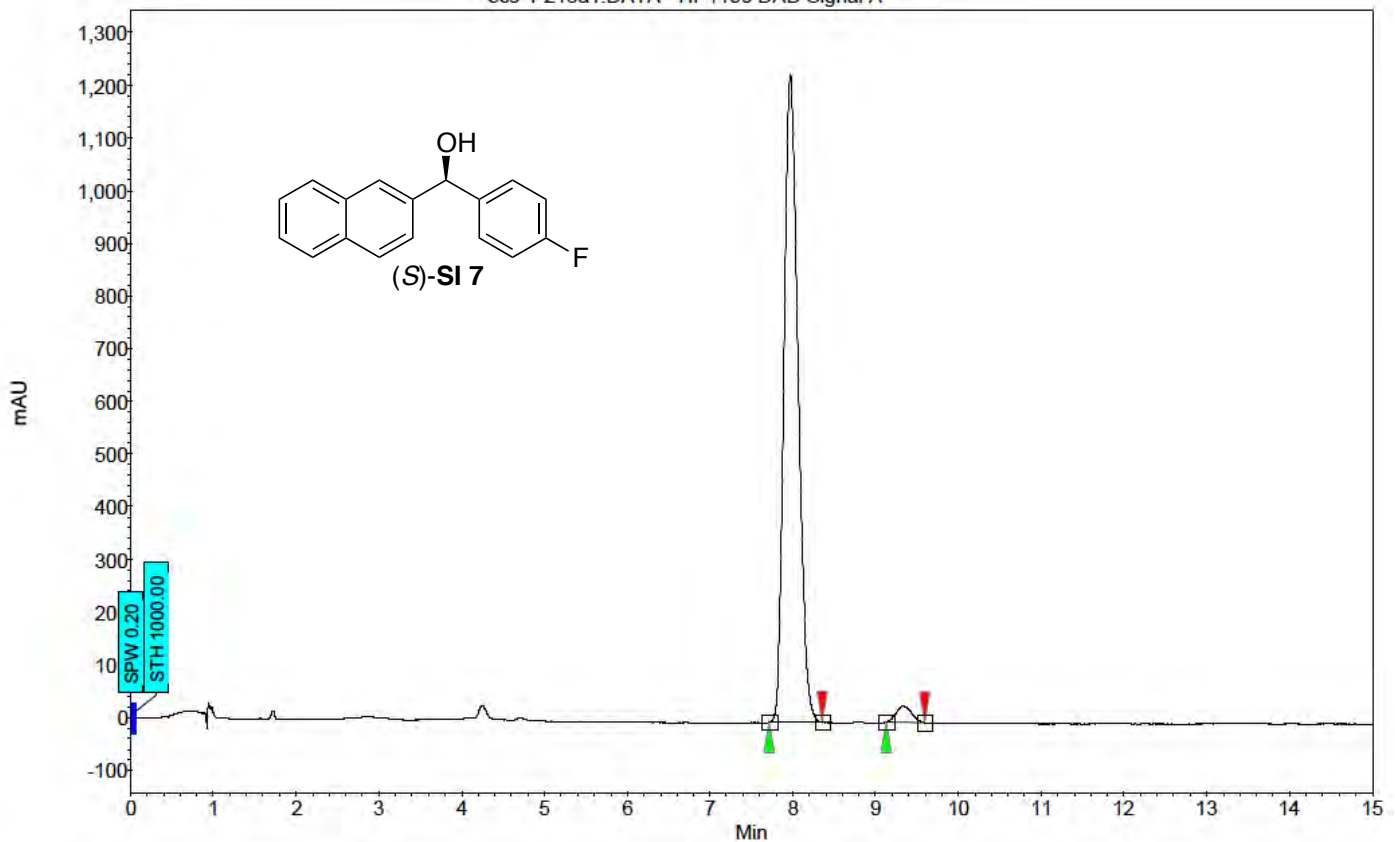
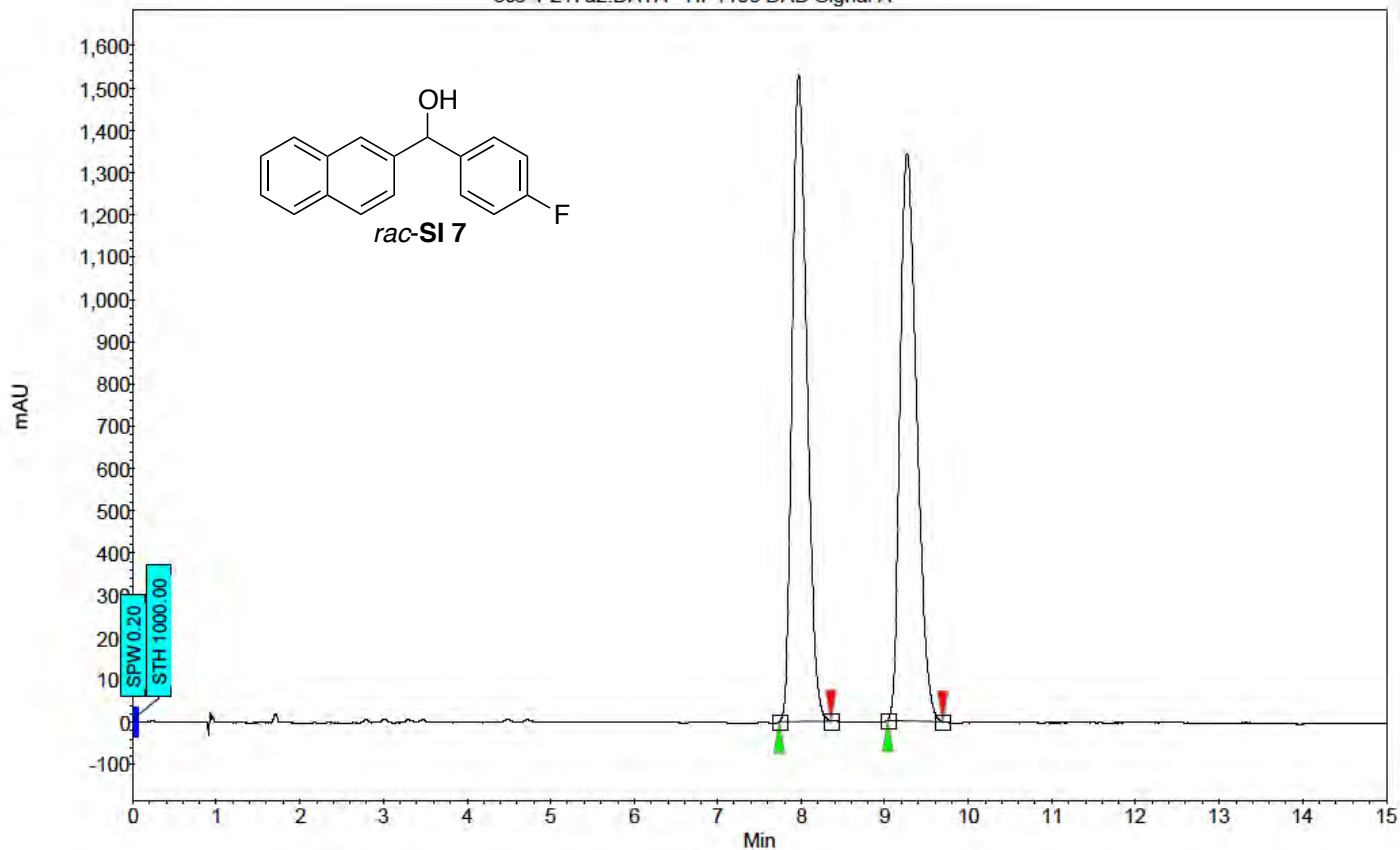
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	11.60	12.04	12.72	0.00	97.94	221.7	74.6	97.936
2	UNKNOWN	15.51	15.70	15.93	0.00	2.06	8.2	1.6	2.064
Total						100.00	229.9	76.2	100.000



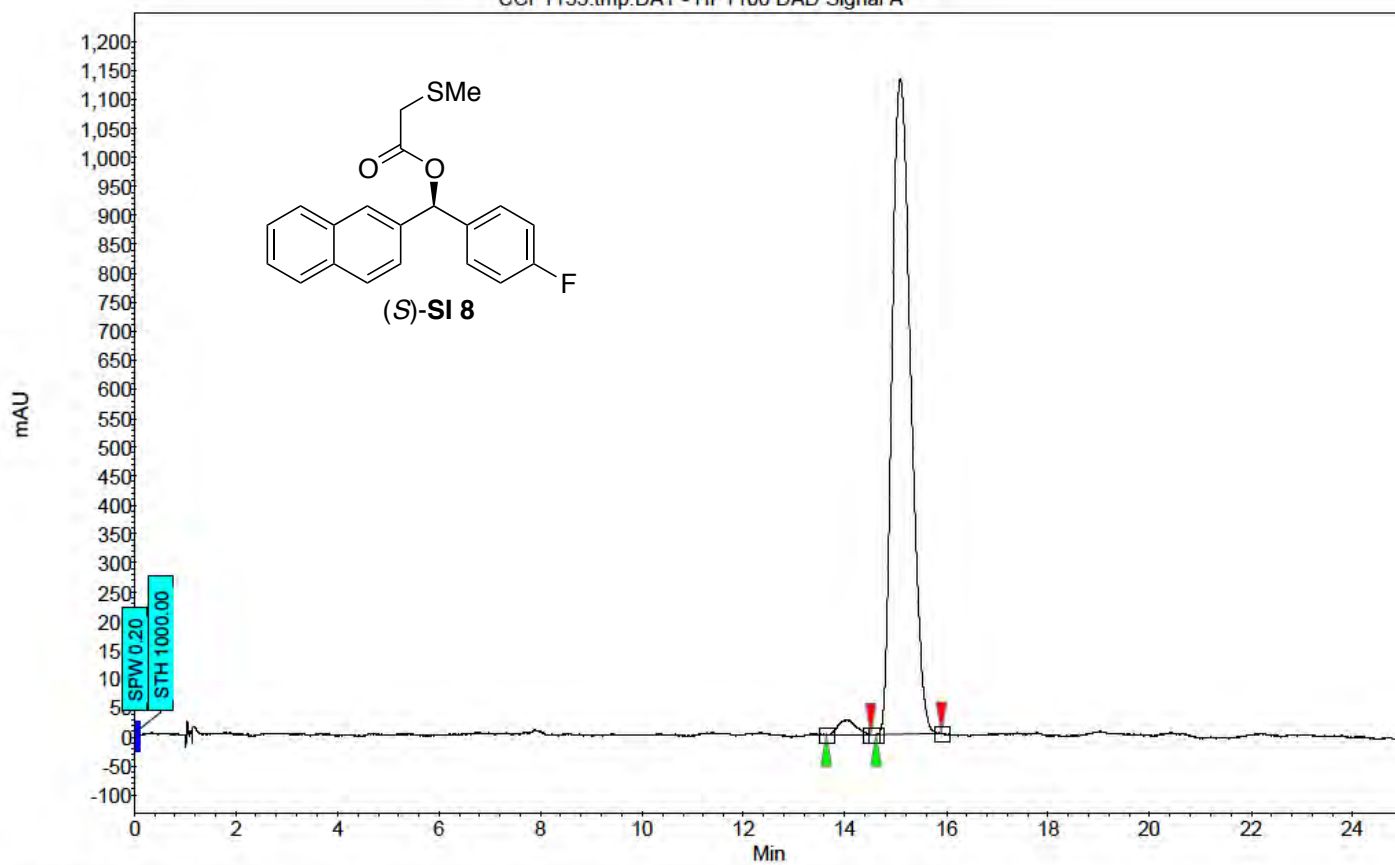
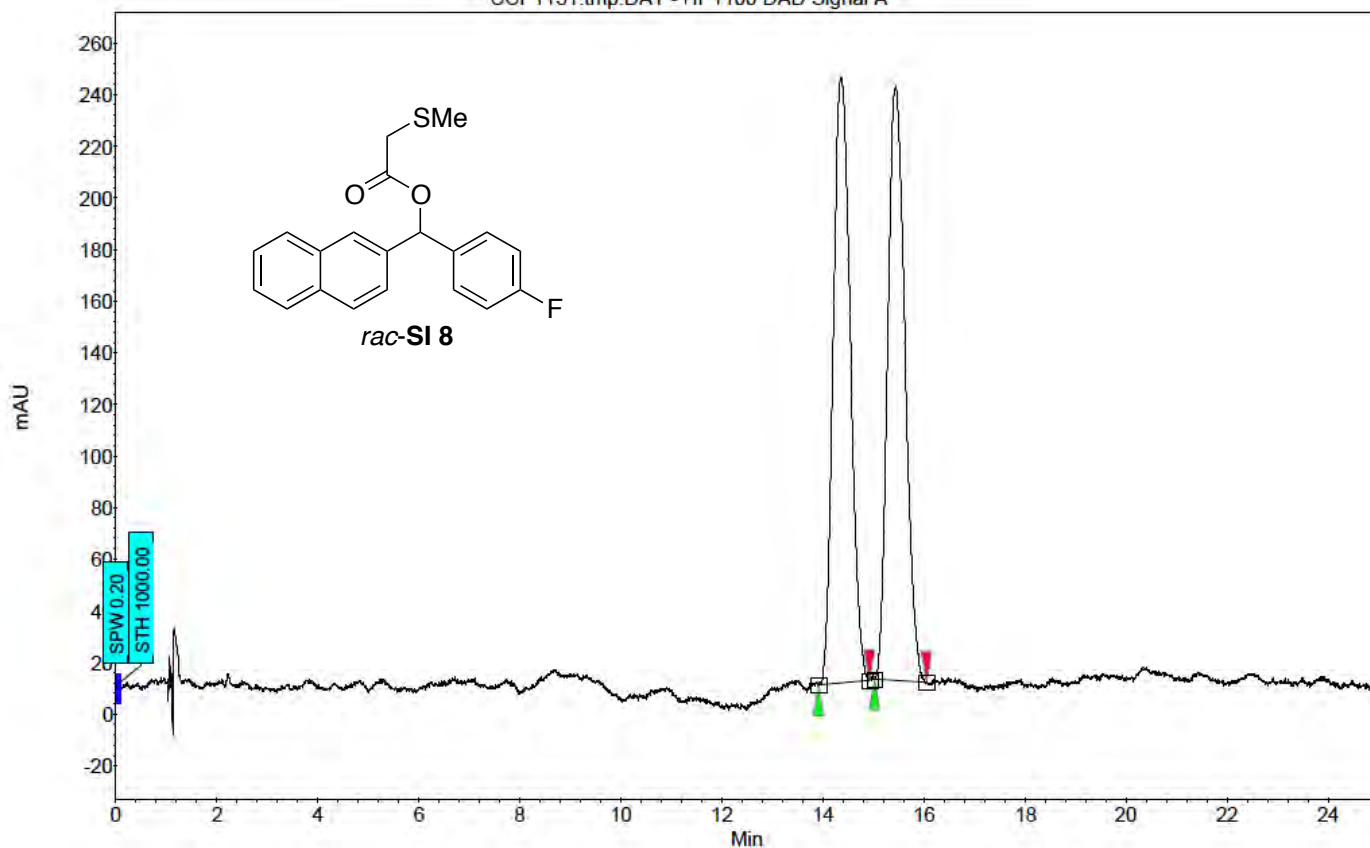
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]	
1	UNKNOWN	6.30	6.61	7.15	0.00	99.80	832.1	118.7	99.800
2	UNKNOWN	7.50	7.65	7.84	0.00	0.20	1.6	0.2	0.200
Total						100.00	833.8	119.0	100.000



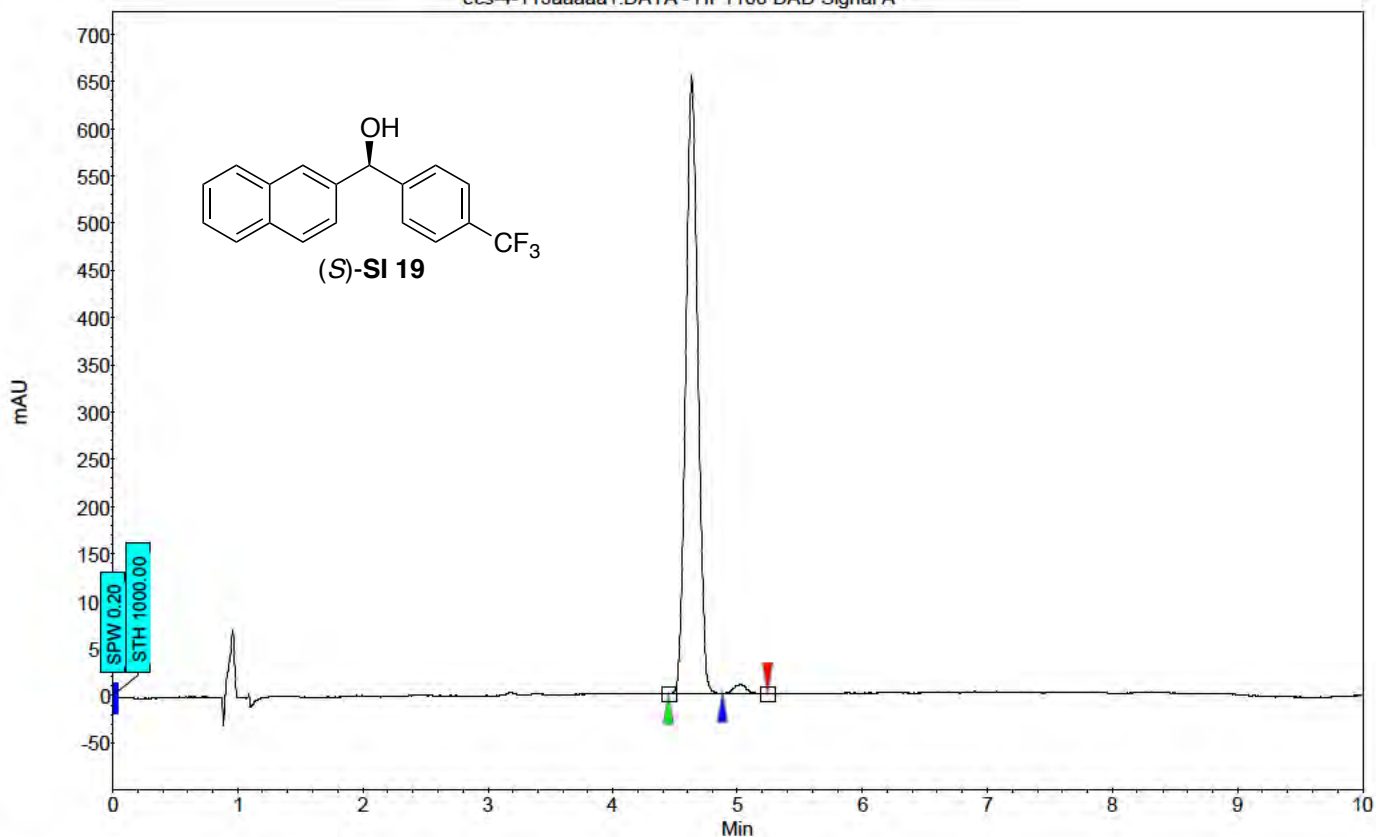
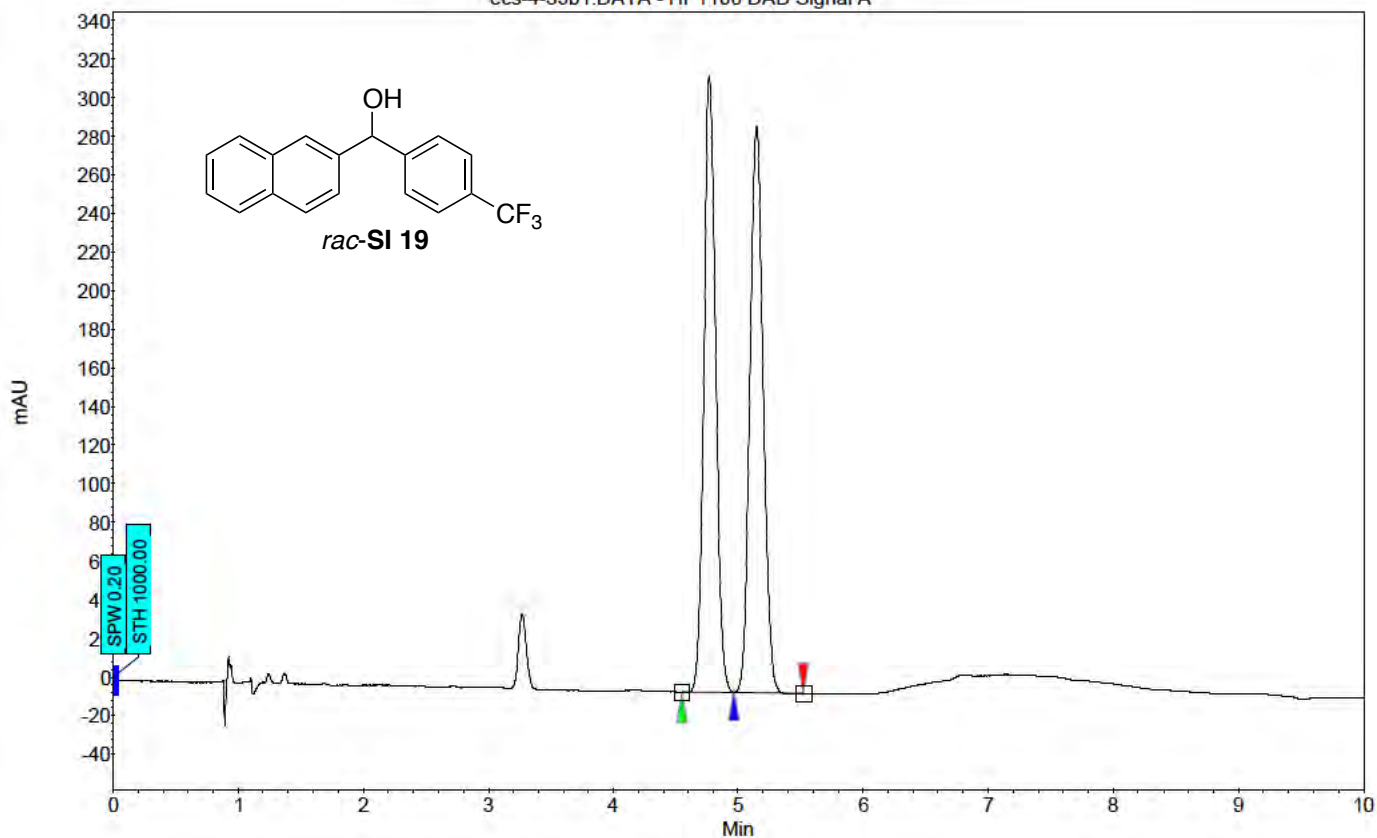
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	11.05	11.42	11.61	0.00	0.65	3.8	0.9	0.651
1	UNKNOWN	12.27	12.70	13.38	0.00	99.35	407.2	129.8	99.349
Total						100.00	411.0	130.6	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	7.72	7.97	8.36	0.00	97.39	1227.3	241.3	97.394
2	UNKNOWN	9.13	9.34	9.59	0.00	2.61	30.4	6.5	2.606
Total						100.00	1257.7	247.8	100.000

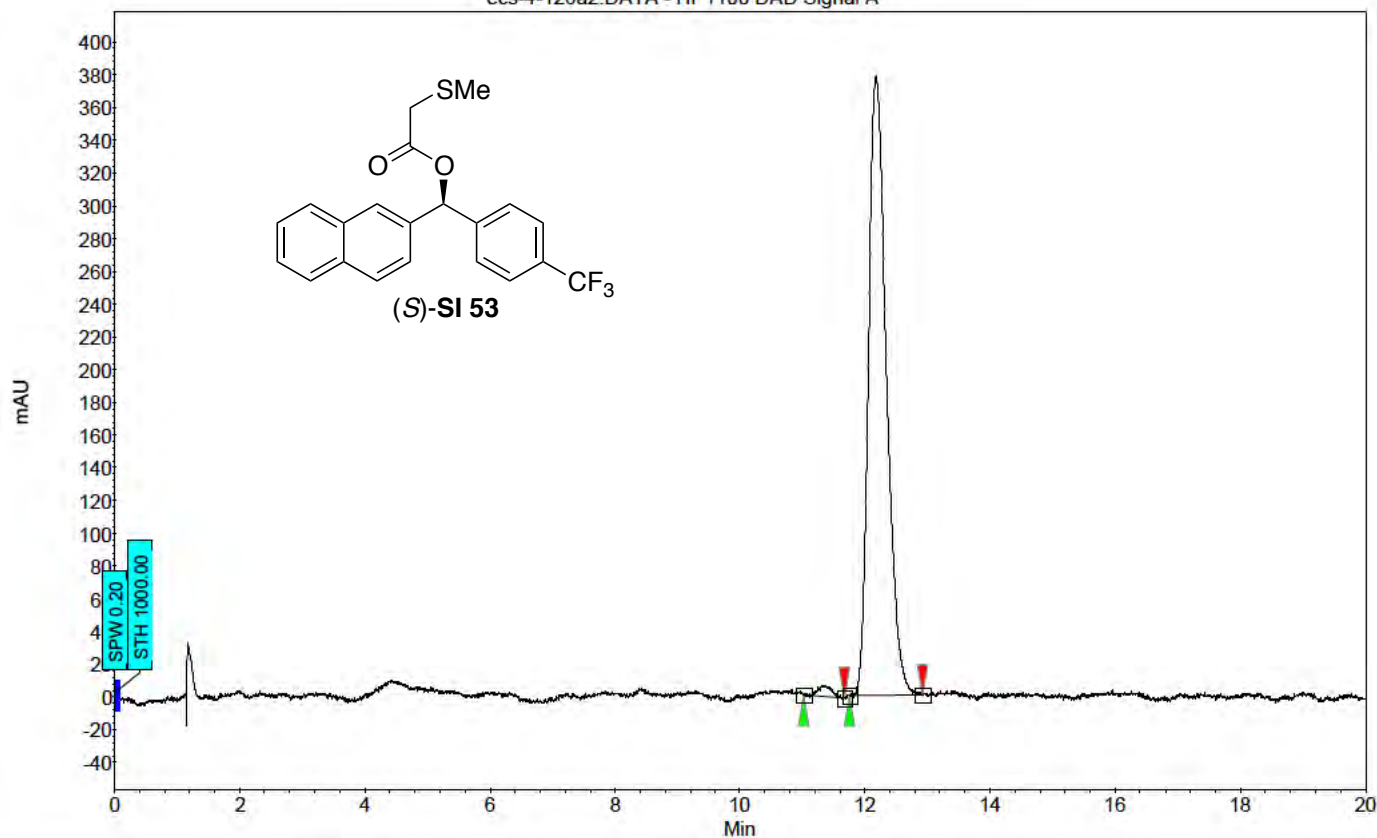
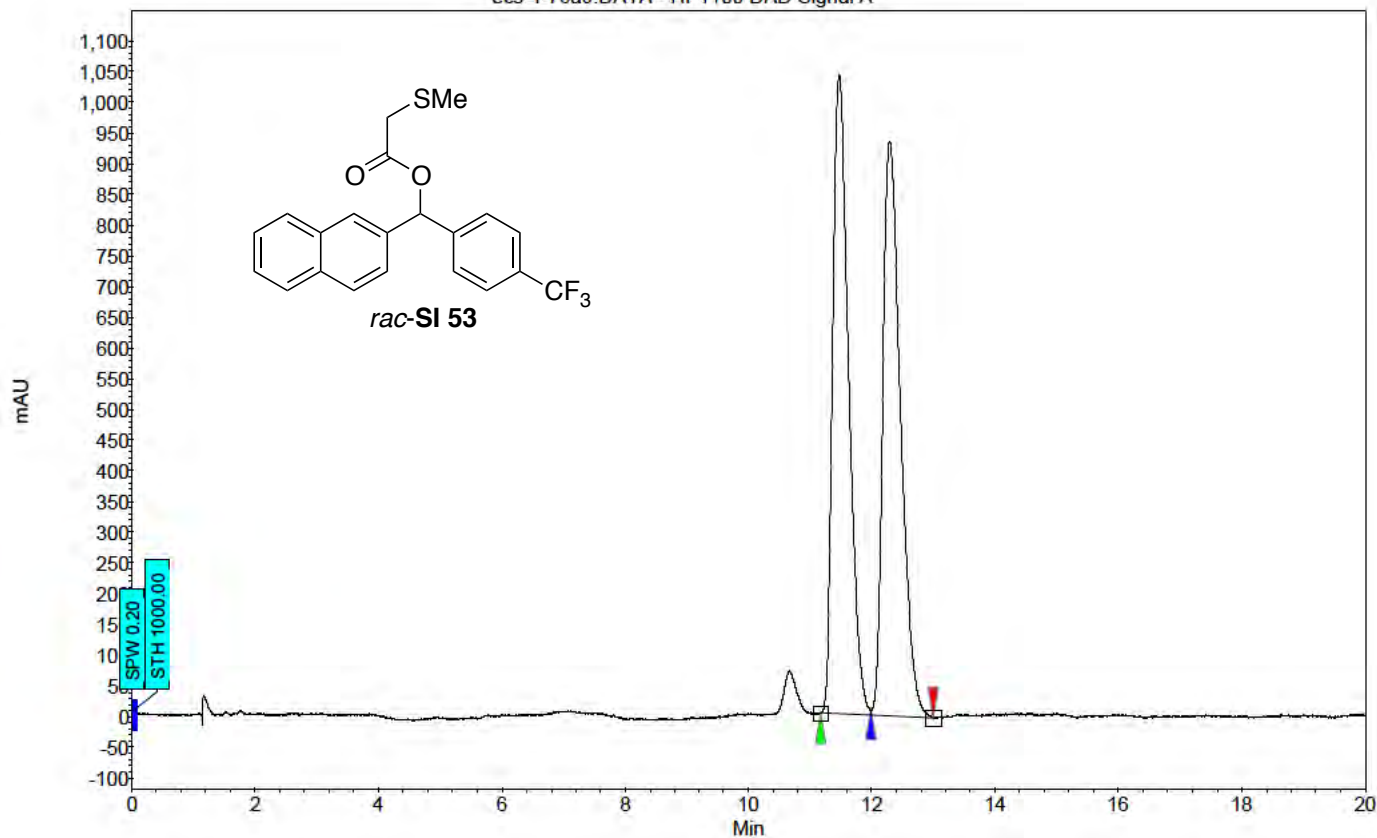


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[μV]	[μV.Min]	[%]	
1	UNKNOWN	13.63	14.02	14.51	0.00	2.02	26.1	10.0	
2	UNKNOWN	14.61	15.09	15.90	0.00	97.98	1129.2	483.6	
Total						100.00	1155.3	493.5	100.000

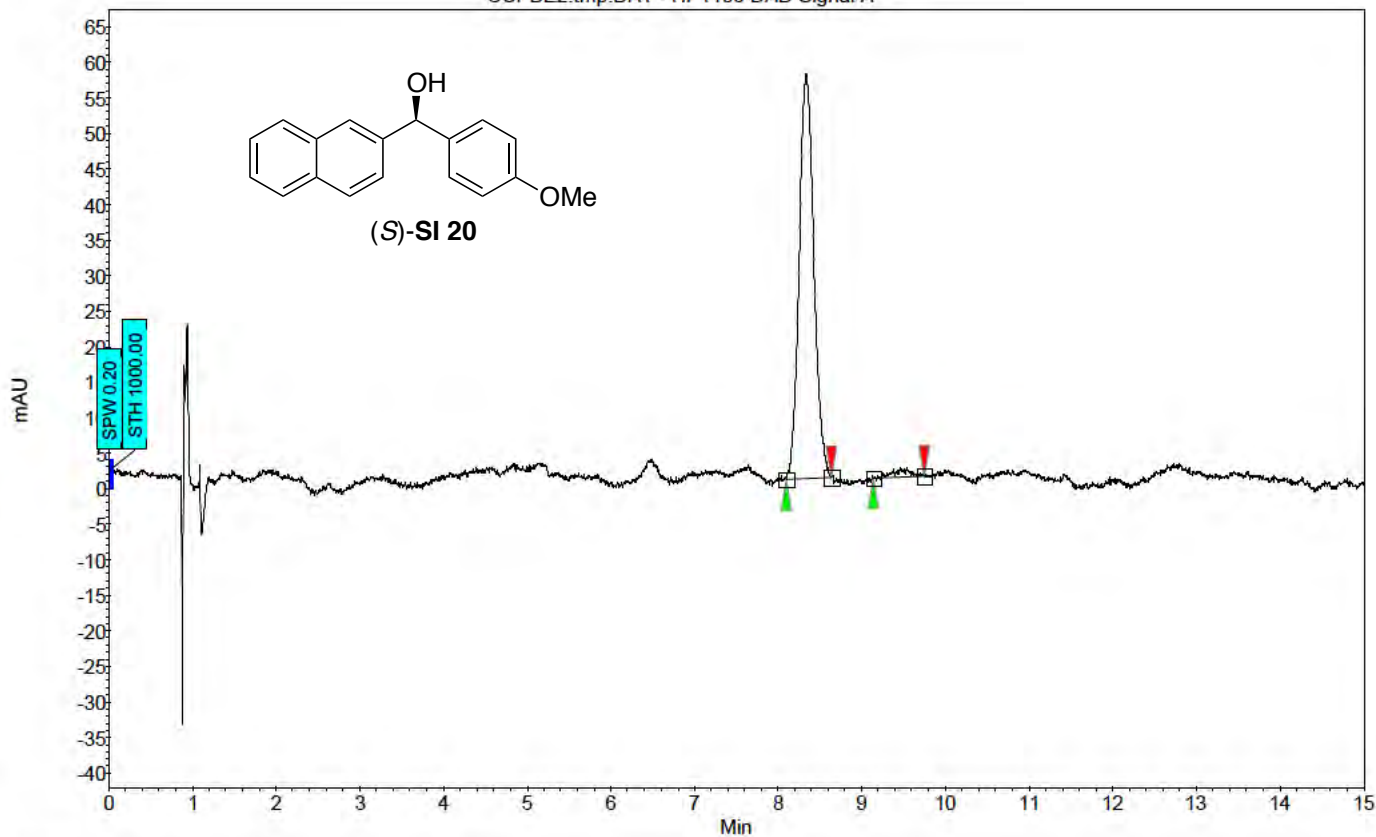
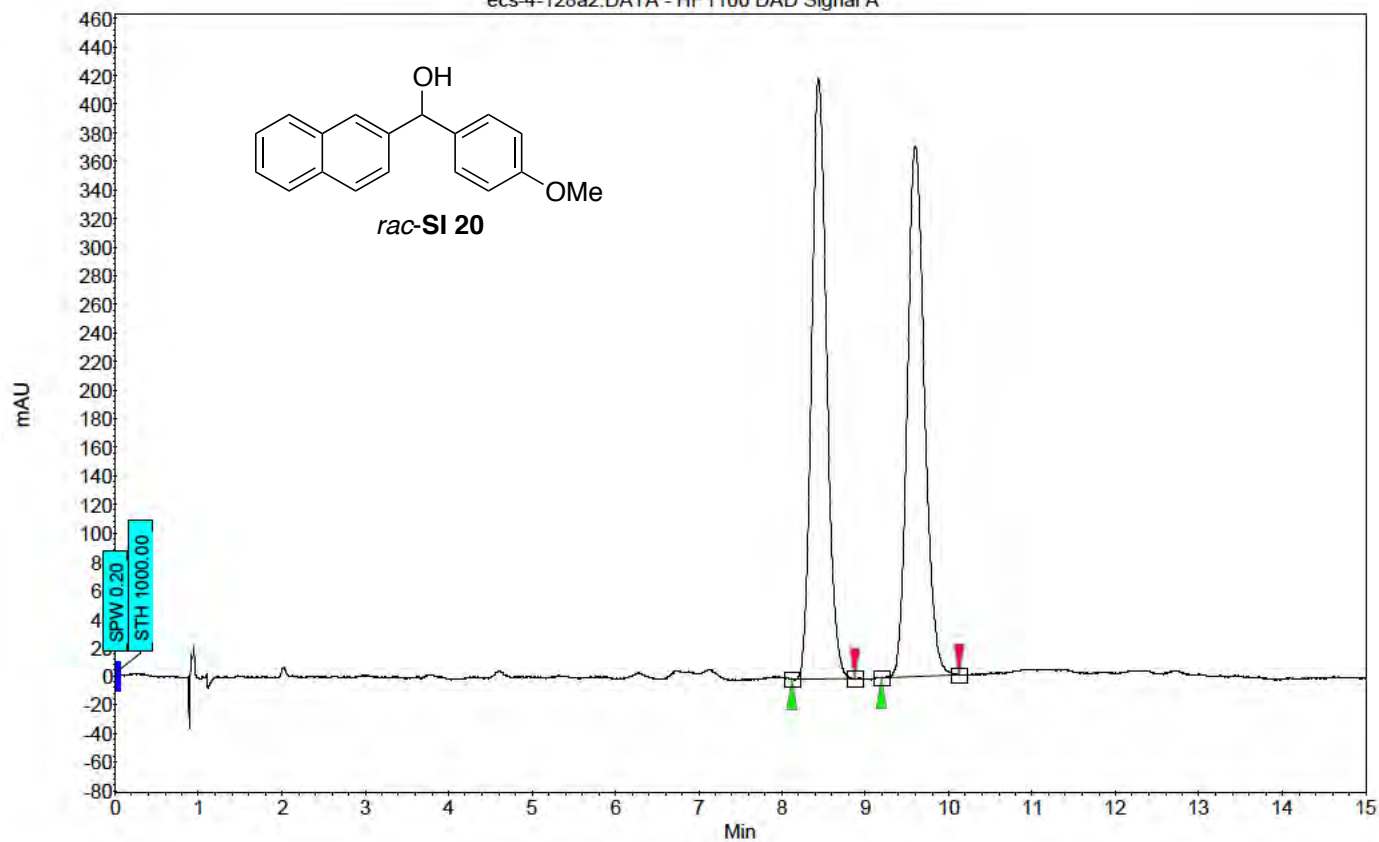


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	4.44	4.63	4.88	0.00	98.24	653.3	73.3	98.243
2	UNKNOWN	4.88	5.02	5.24	0.00	1.76	9.8	1.3	1.757
Total						100.00	663.1	74.6	100.000

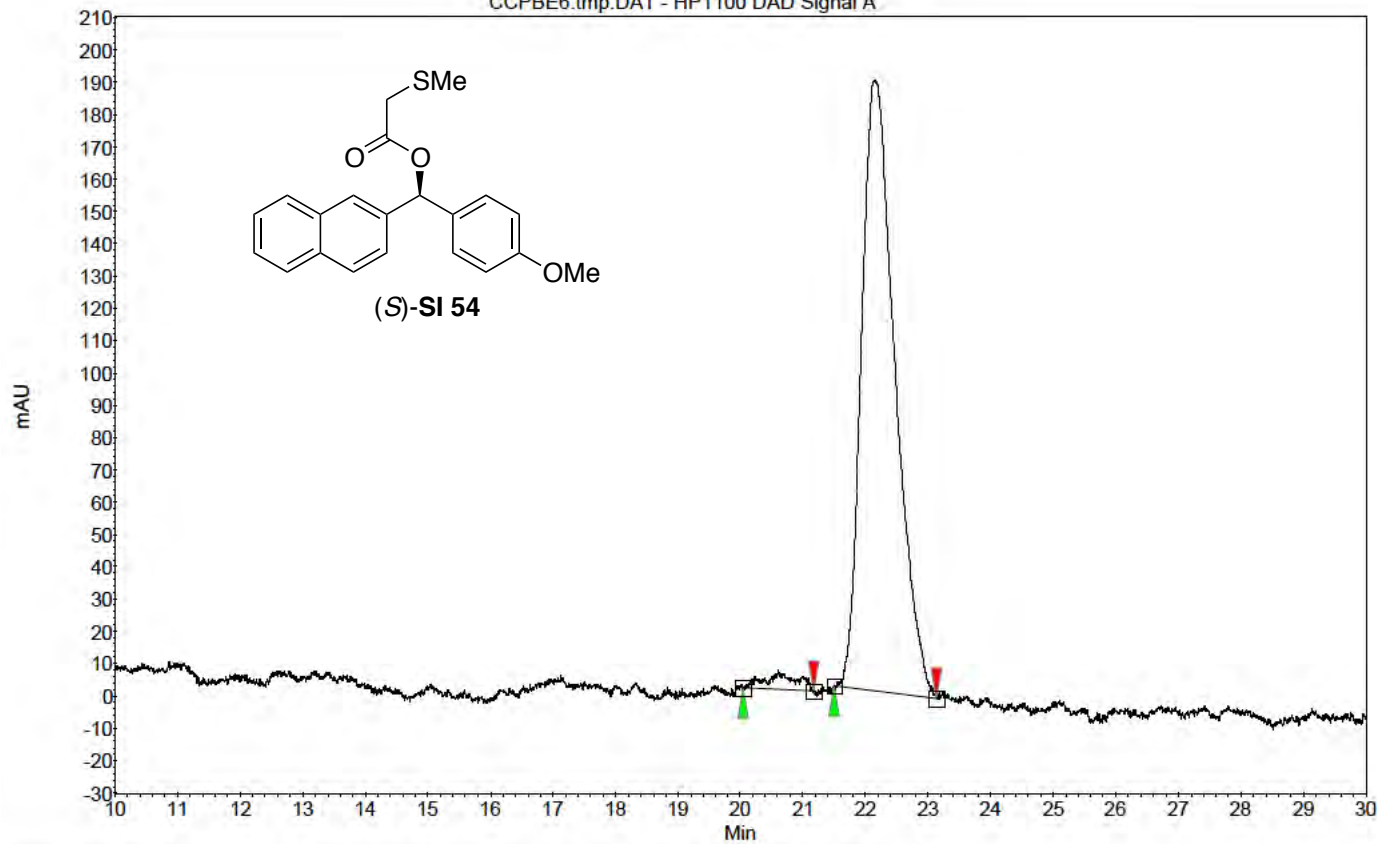
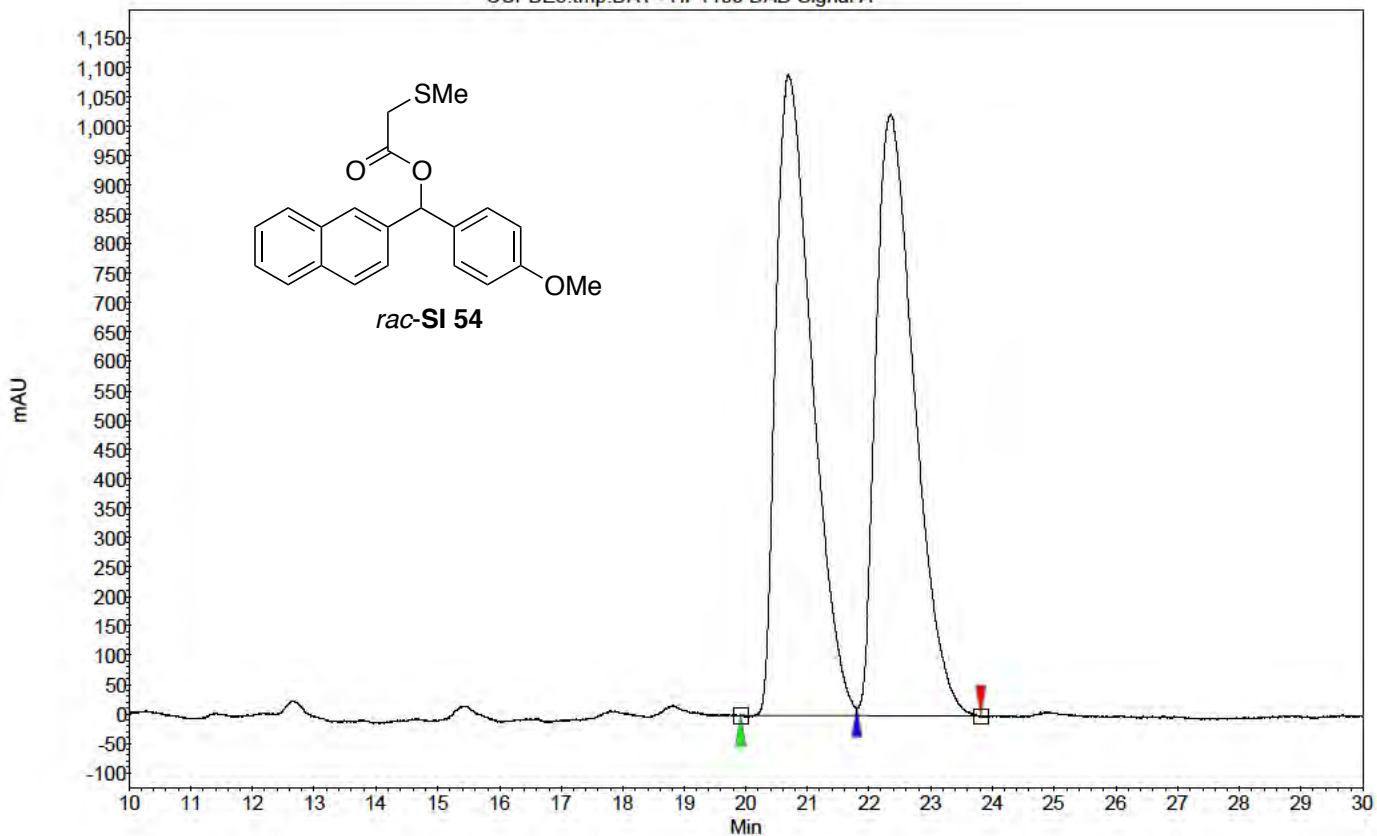




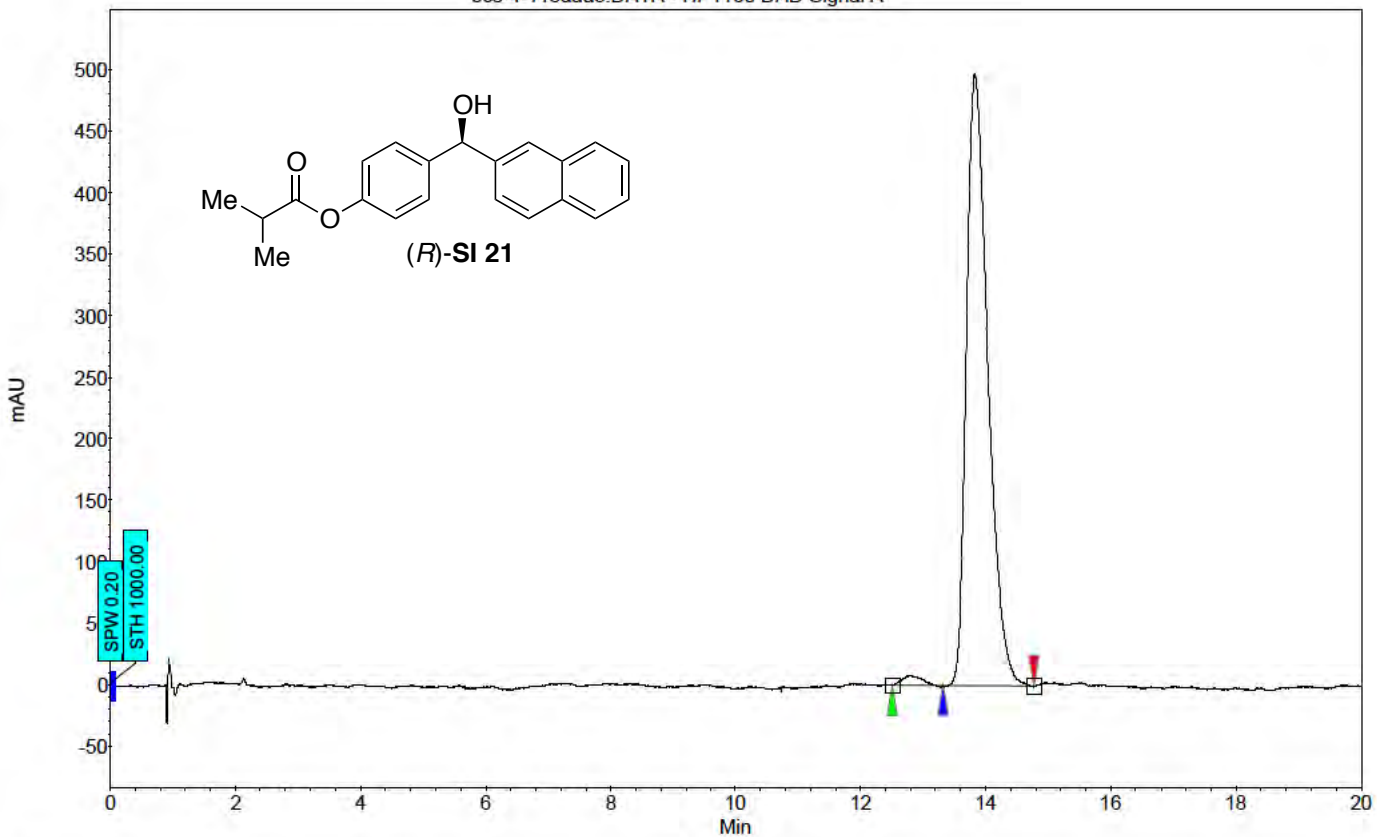
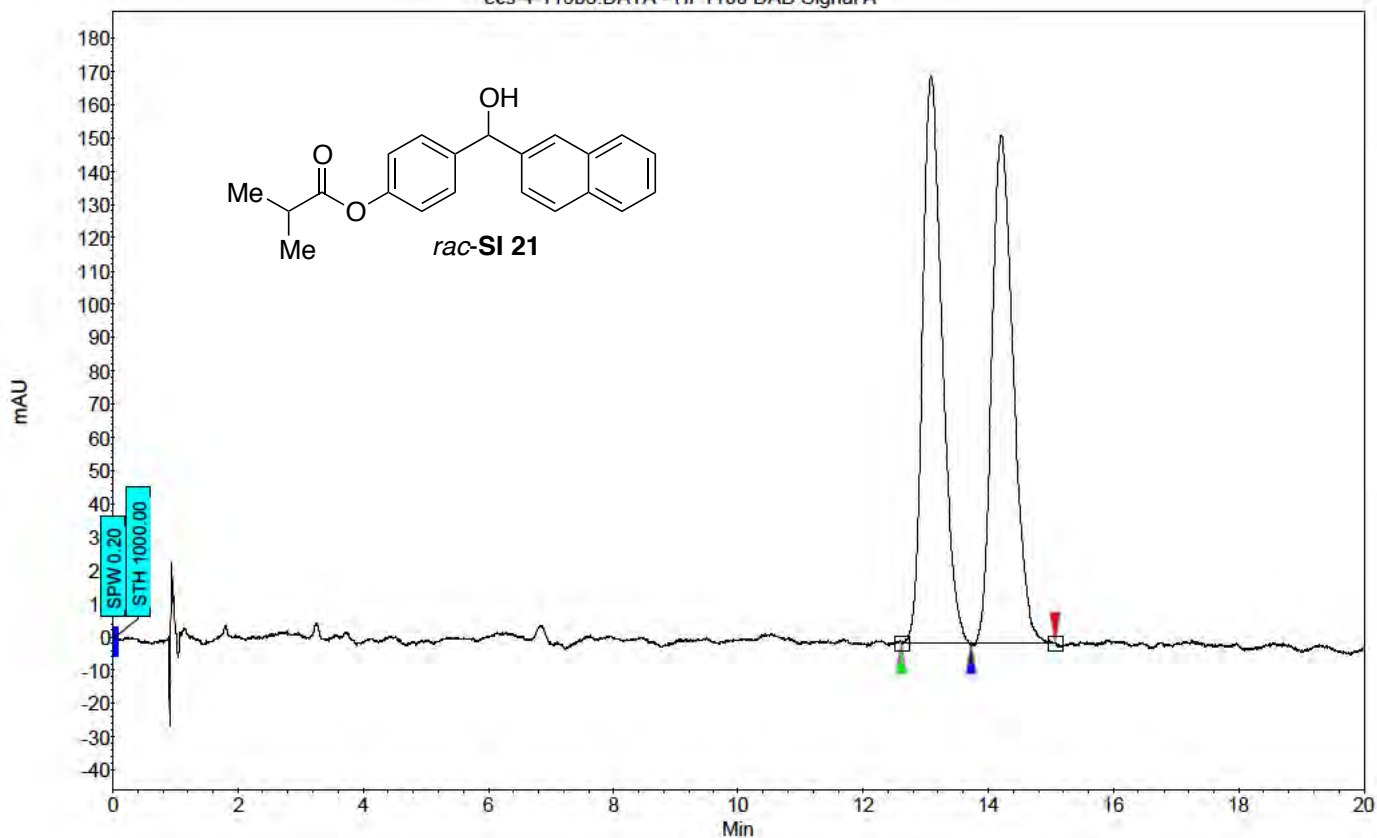
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	11.02	11.38	11.67	0.00	1.28	6.8	1.6	1.283
2	UNKNOWN	11.75	12.18	12.92	0.00	98.72	377.9	125.0	98.717
Total						100.00	384.7	126.6	100.000



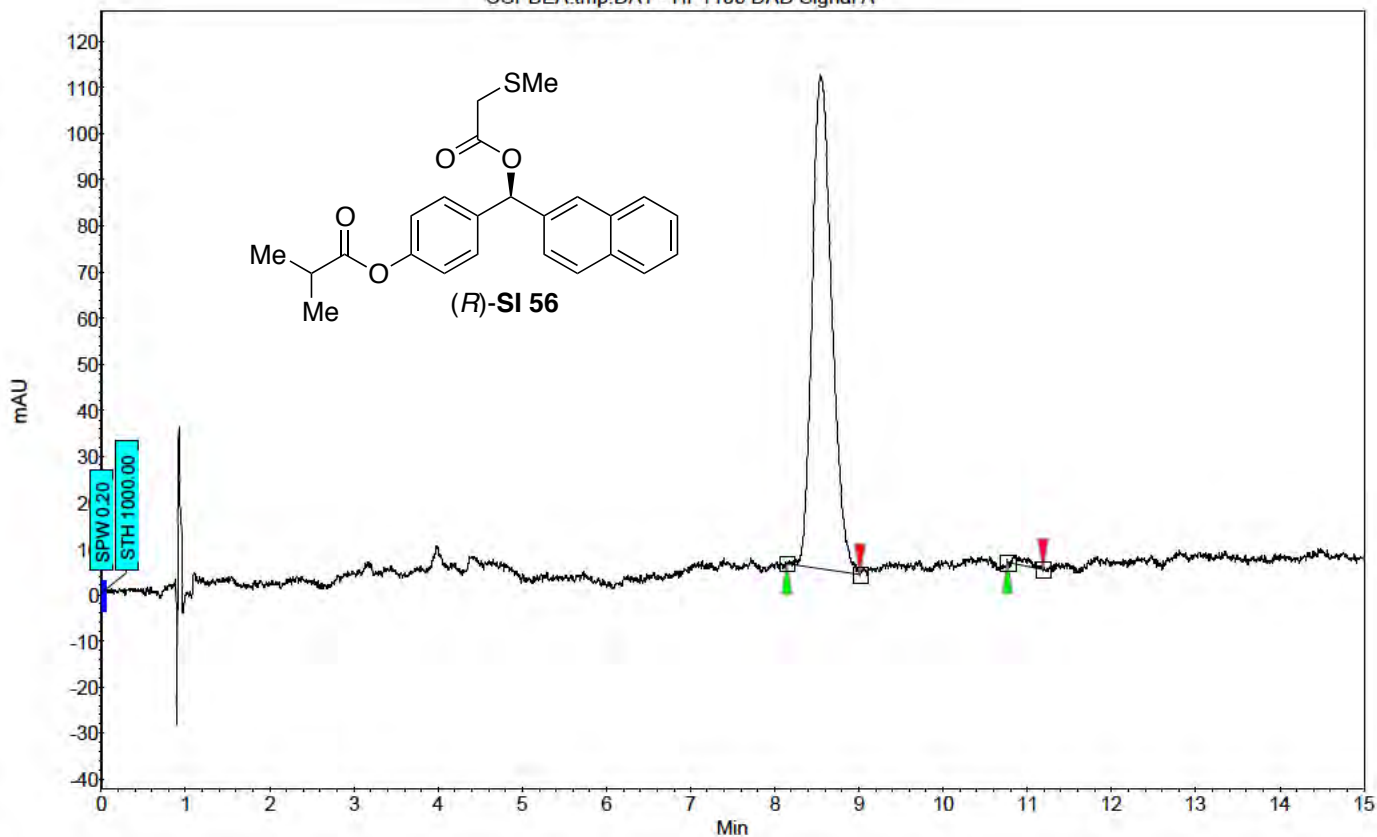
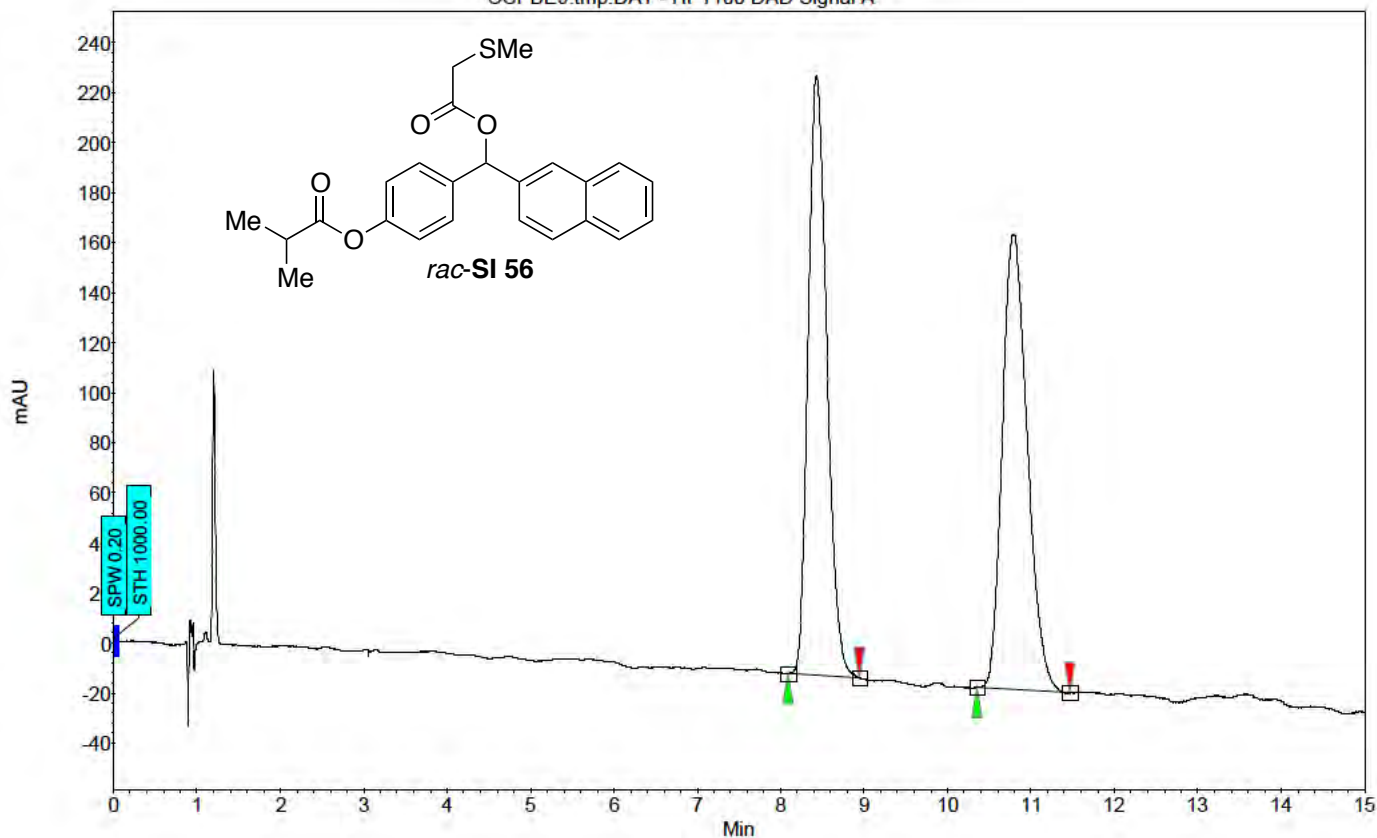
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	8.10	8.34	8.64	0.00	97.59	56.9	11.6	97.586
2	UNKNOWN	9.14	9.54	9.75	0.00	2.41	1.3	0.3	2.414
Total						100.00	58.2	11.9	100.000



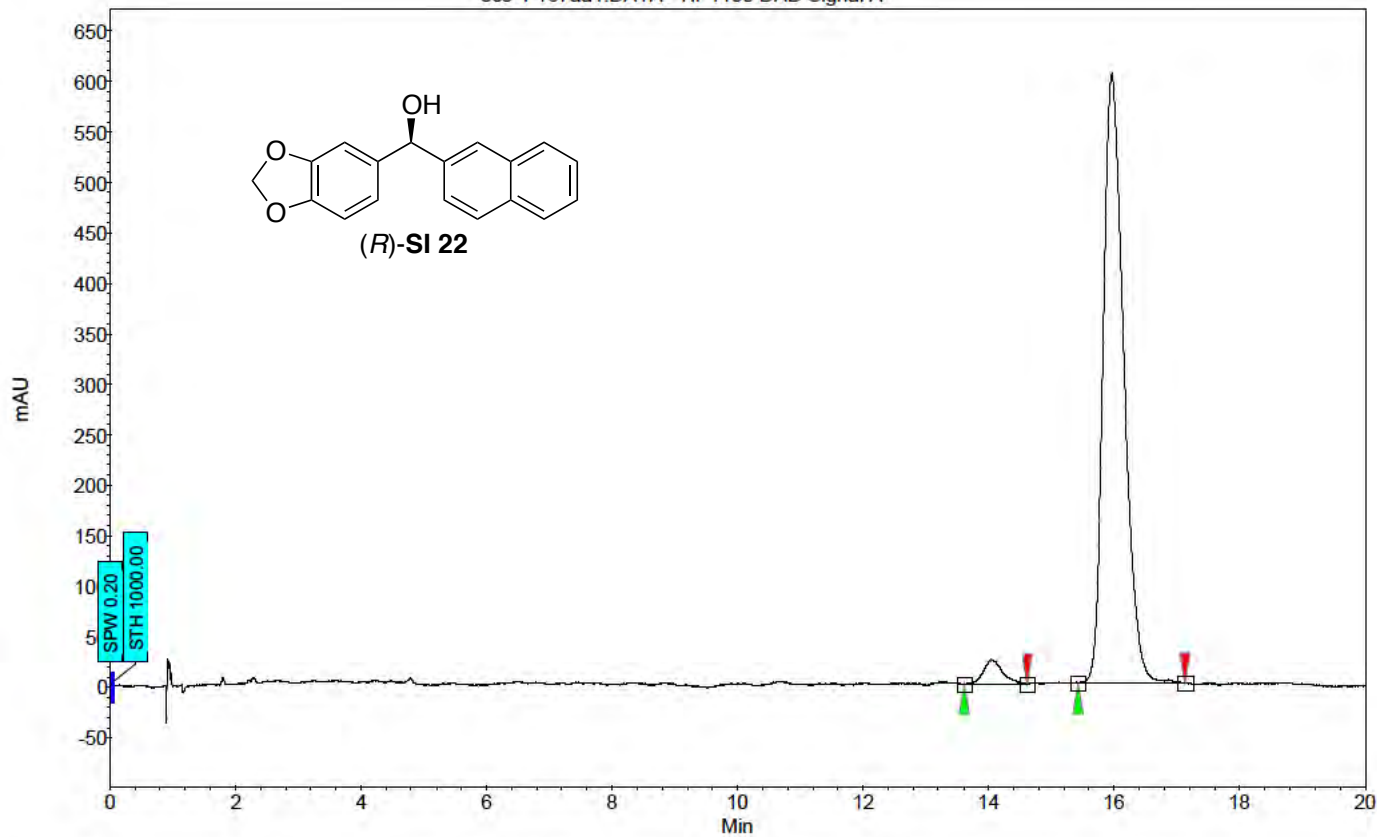
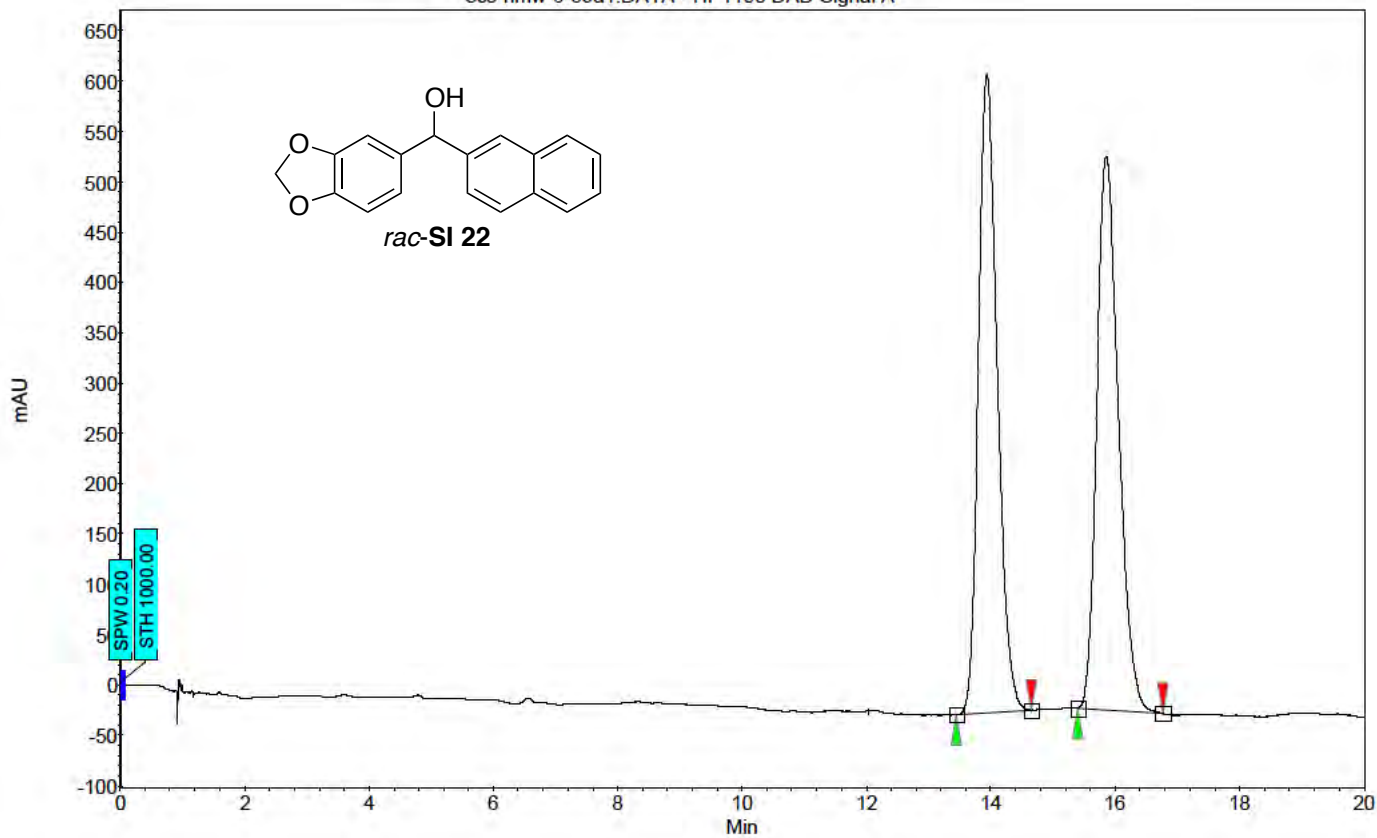
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	20.04	20.61	21.17	0.00	2.55	6.2	3.1	2.555
1	UNKNOWN	21.50	22.16	23.13	0.00	97.45	188.8	117.3	97.445
Total						100.00	195.0	120.4	100.000



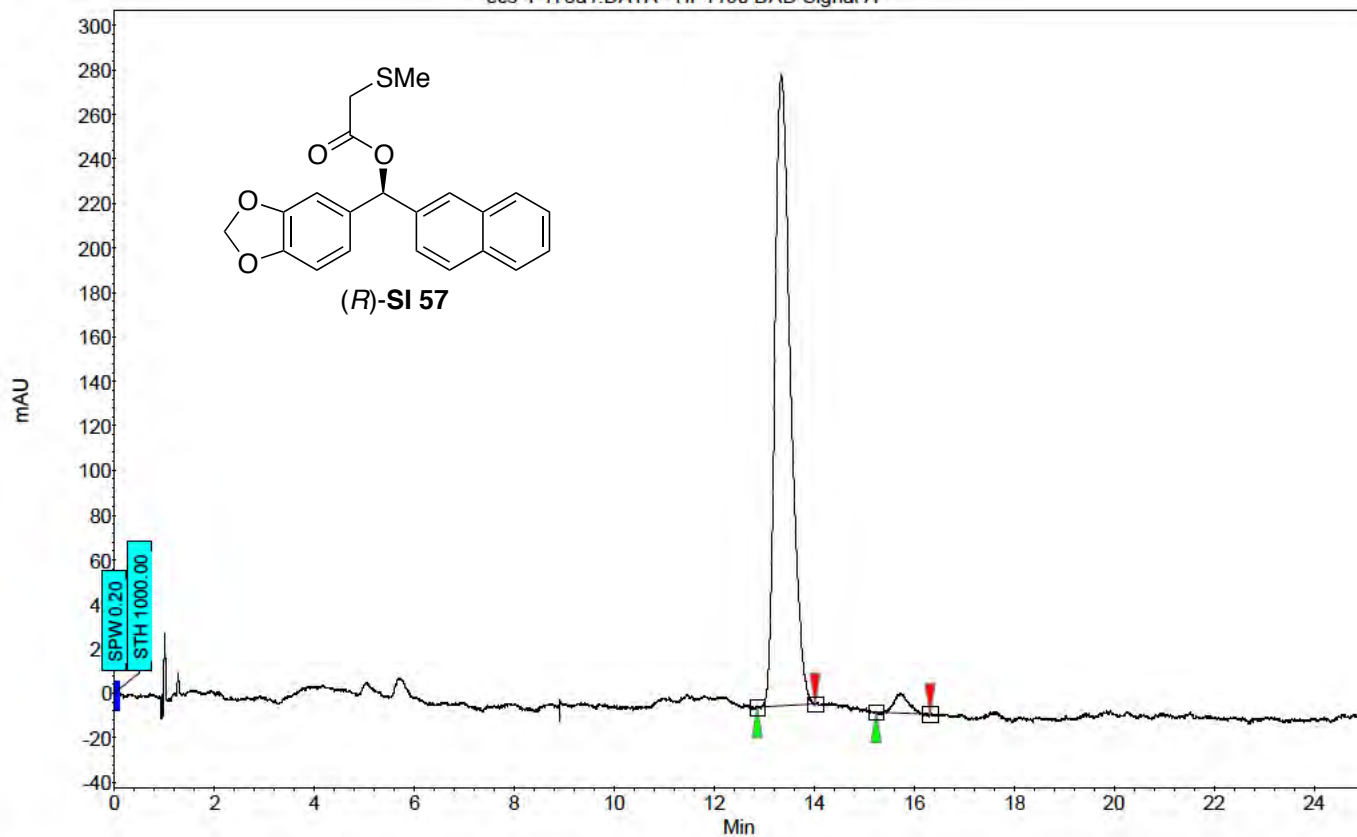
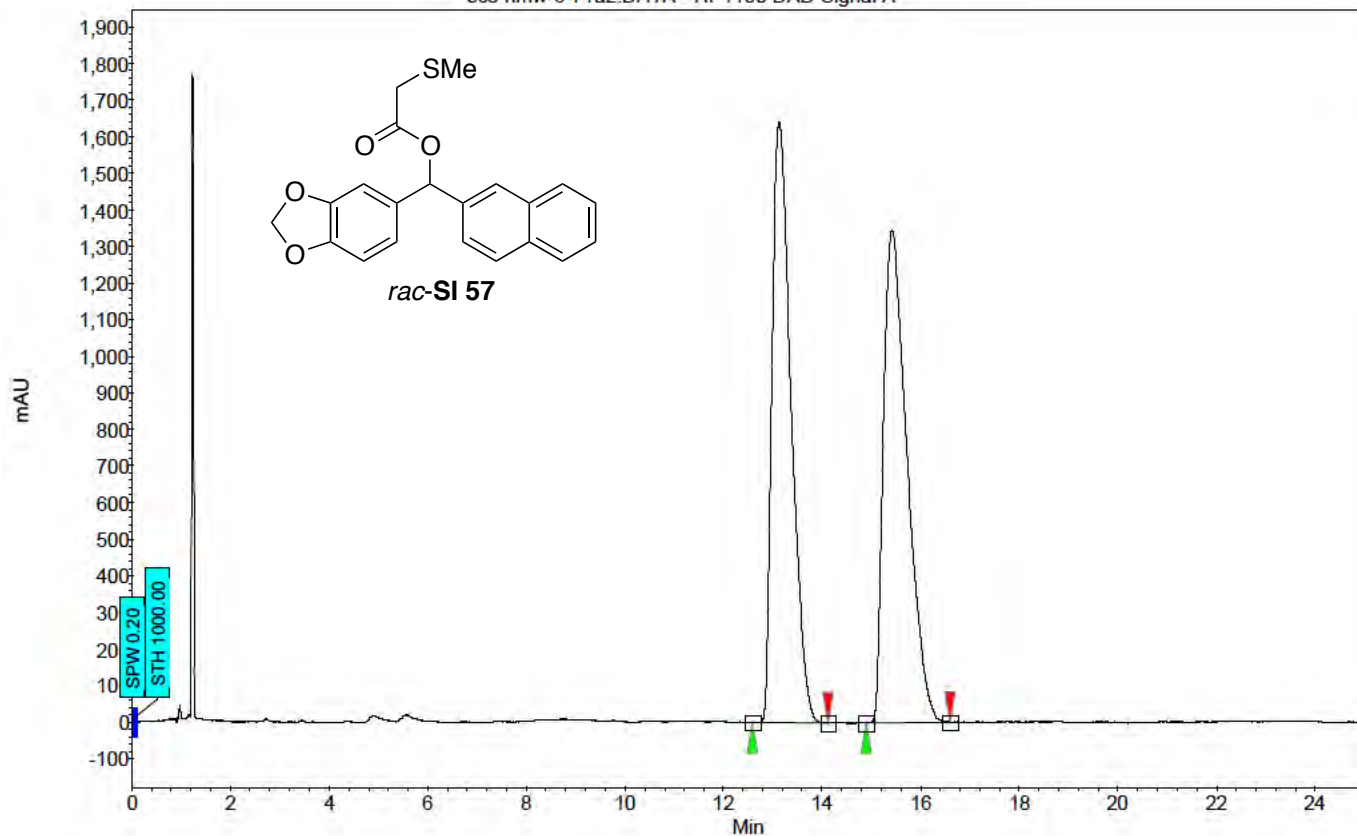
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	12.50	12.81	13.32	0.00	1.46	8.5	2.9	1.459
2	UNKNOWN	13.32	13.83	14.77	0.00	98.54	496.8	197.4	98.541
Total						100.00	505.3	200.3	100.000



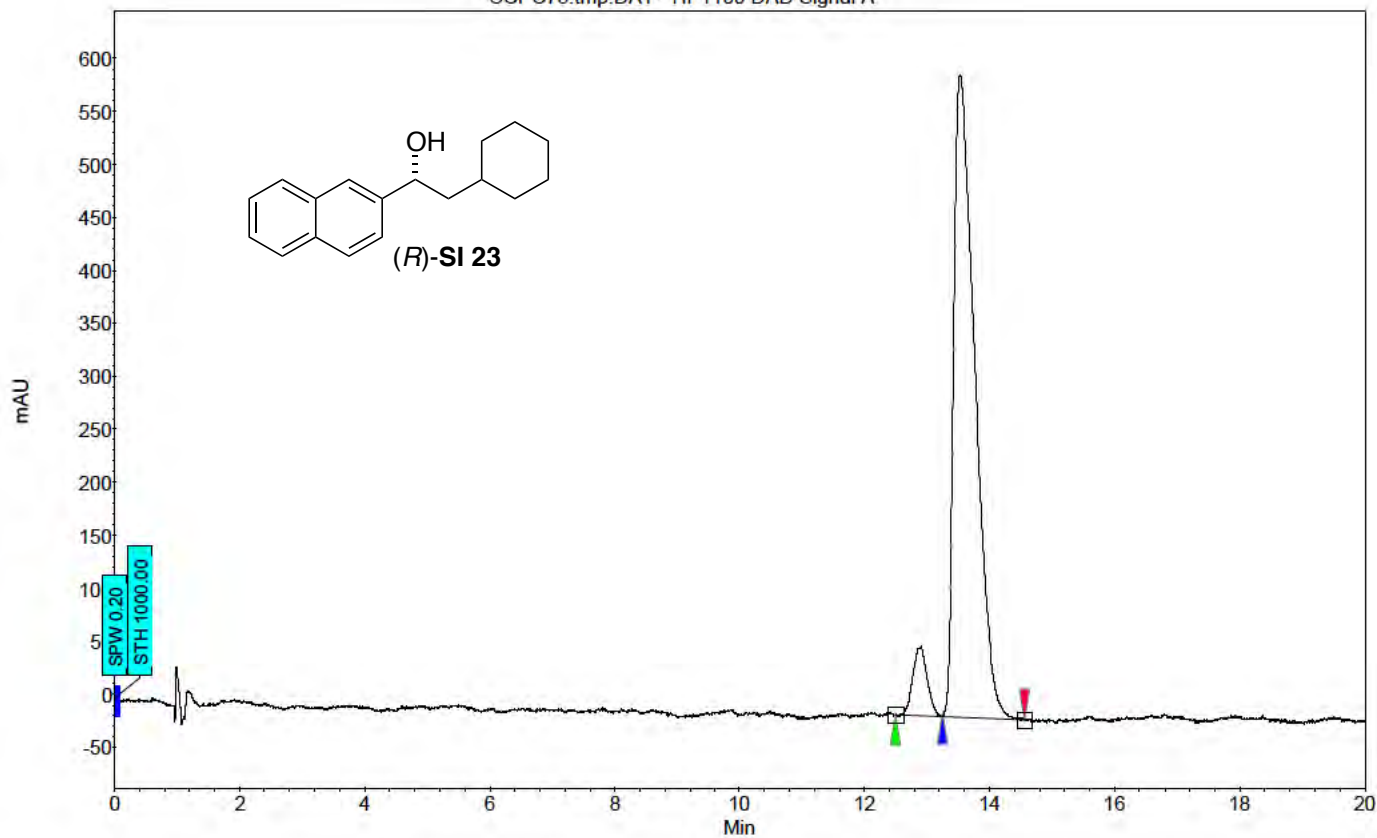
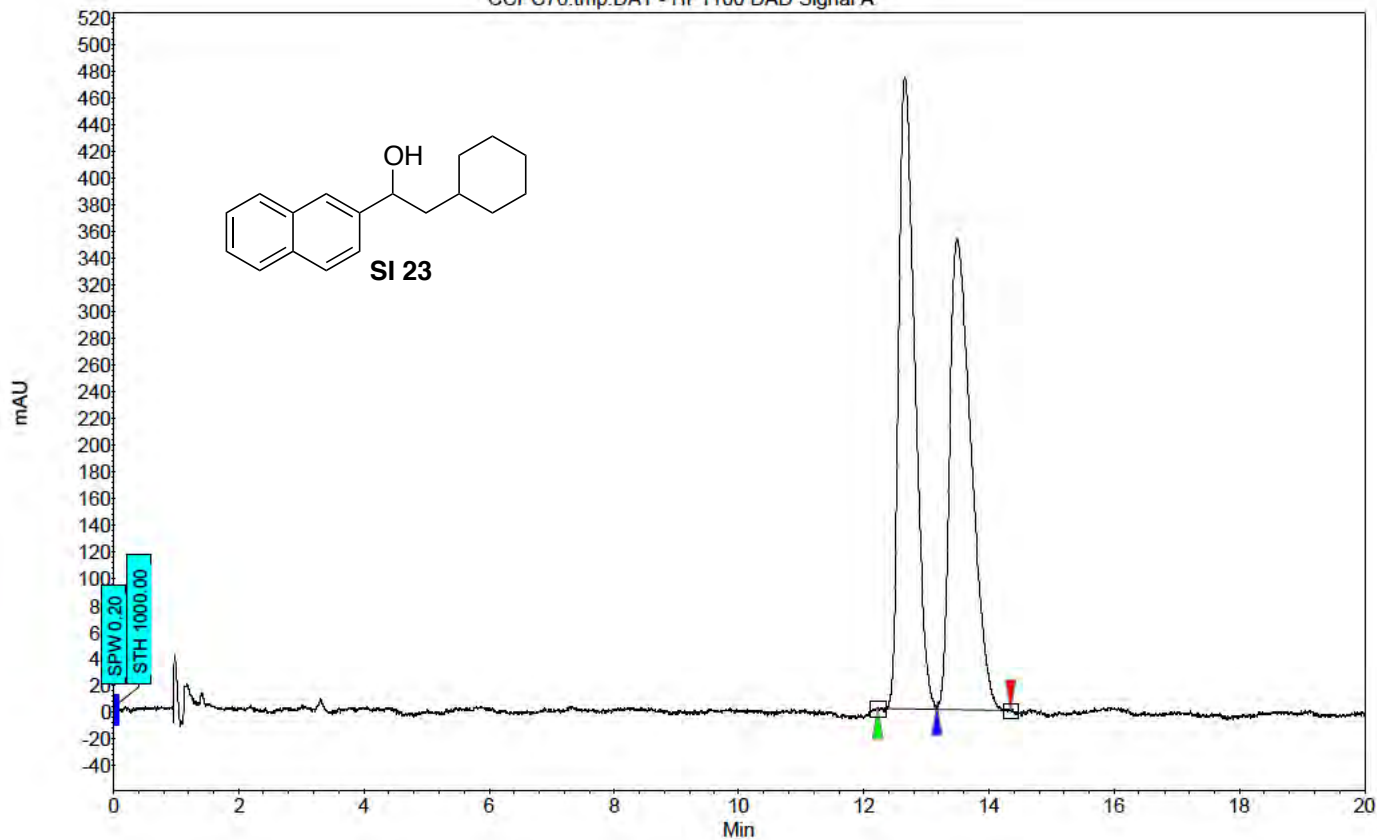
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	8.15	8.55	9.01	0.00	98.85	106.9	28.9	98.854
2	UNKNOWN	10.77	11.01	11.19	0.00	1.15	1.8	0.3	1.146
Total						100.00	108.7	29.3	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	13.61	14.05	14.62	0.00	3.52	24.4	8.4	3.524
2	UNKNOWN	15.43	15.97	17.13	0.00	96.48	603.3	228.9	96.476
Total						100.00	627.8	237.2	100.000

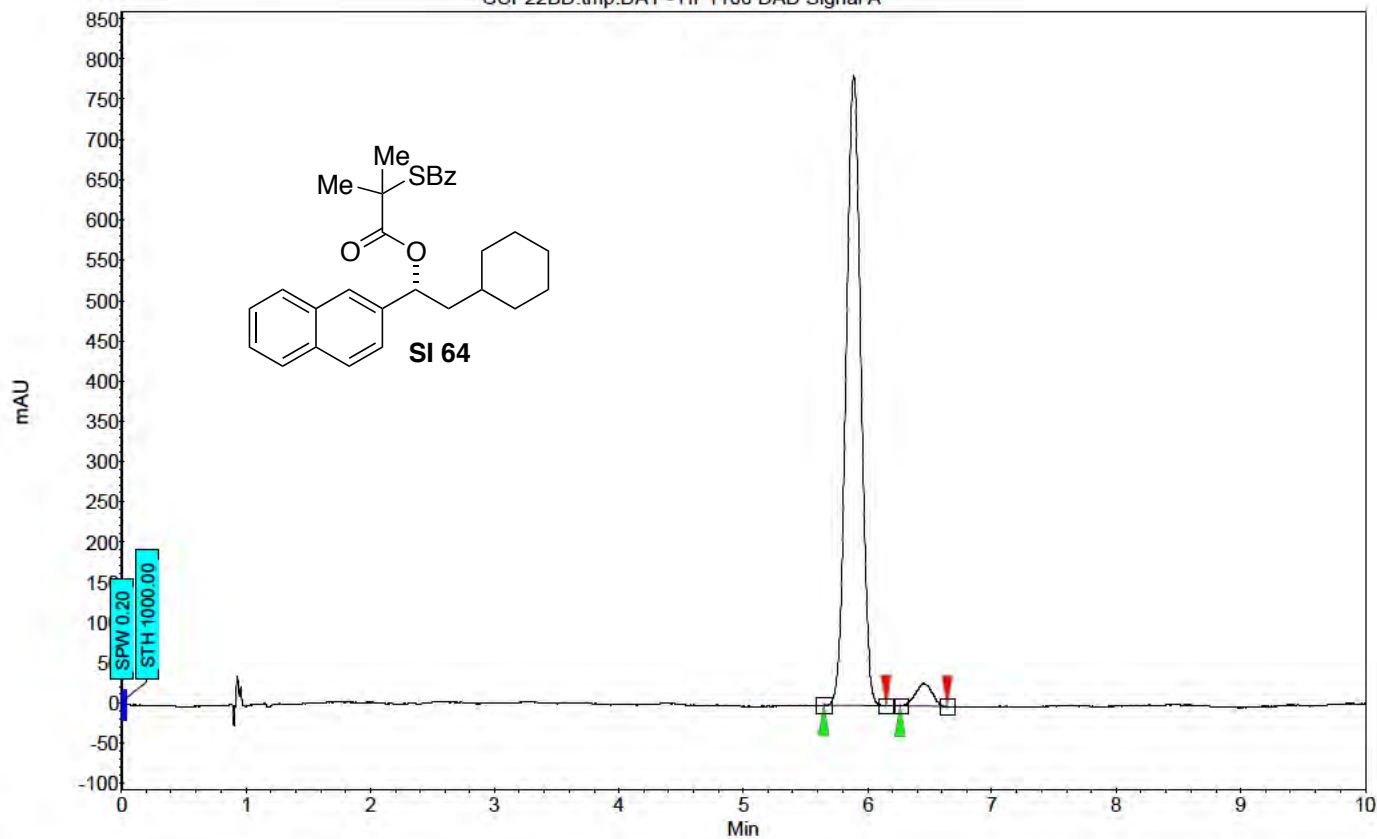
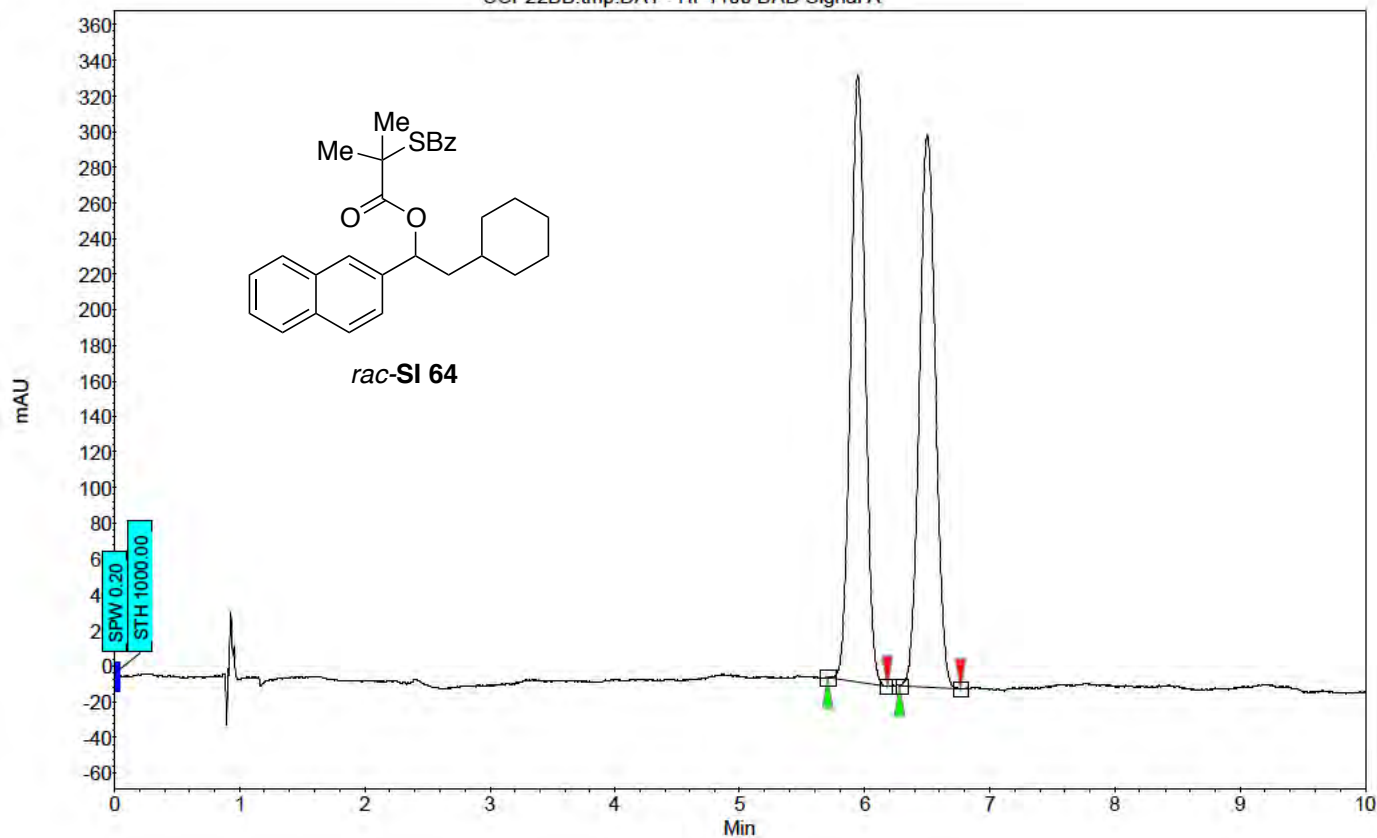


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]
1	UNKNOWN	12.87	13.34	14.02	0.00	97.33	283.3	102.5
2	UNKNOWN	15.24	15.73	16.32	0.00	2.67	9.0	2.8
Total						100.00	292.2	105.3
								100.000

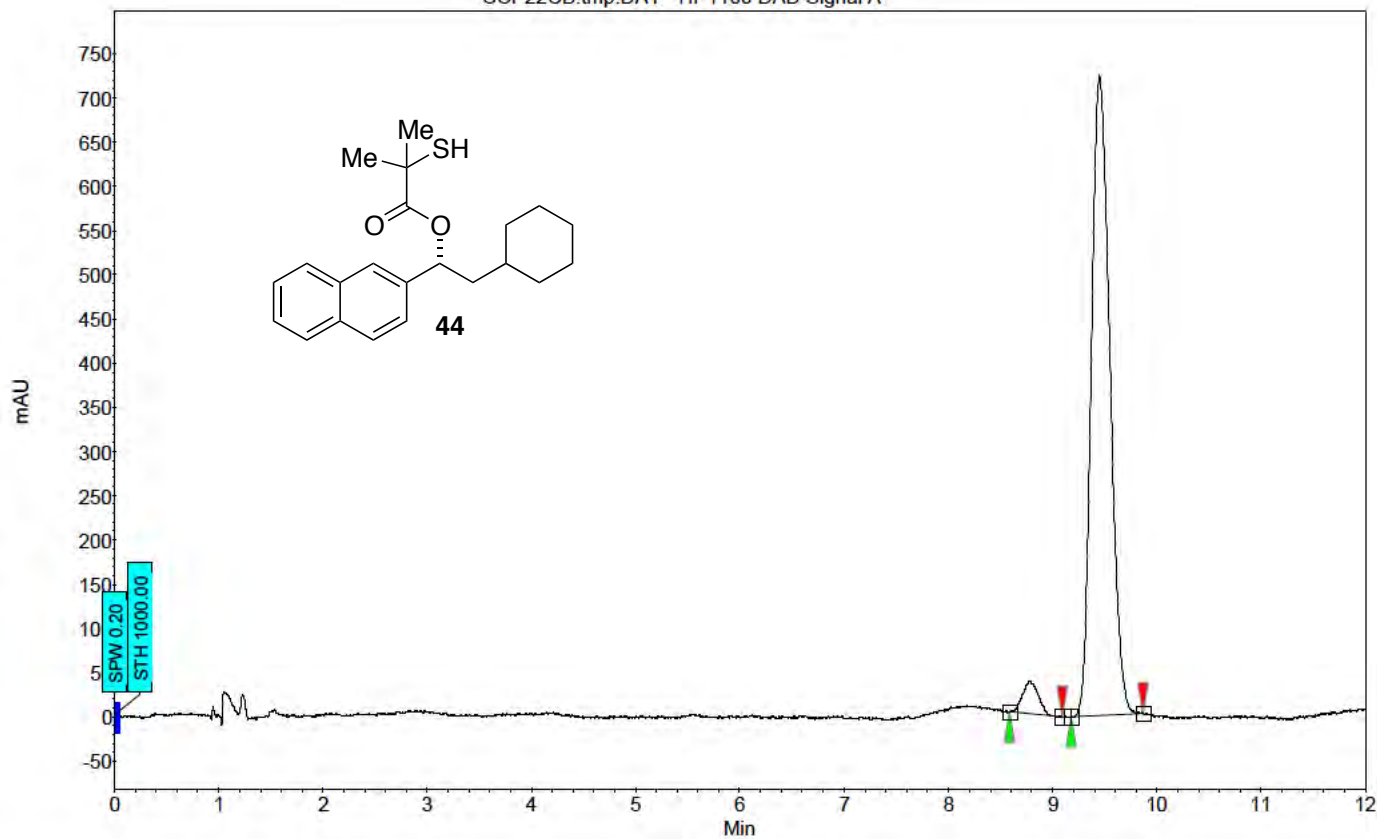
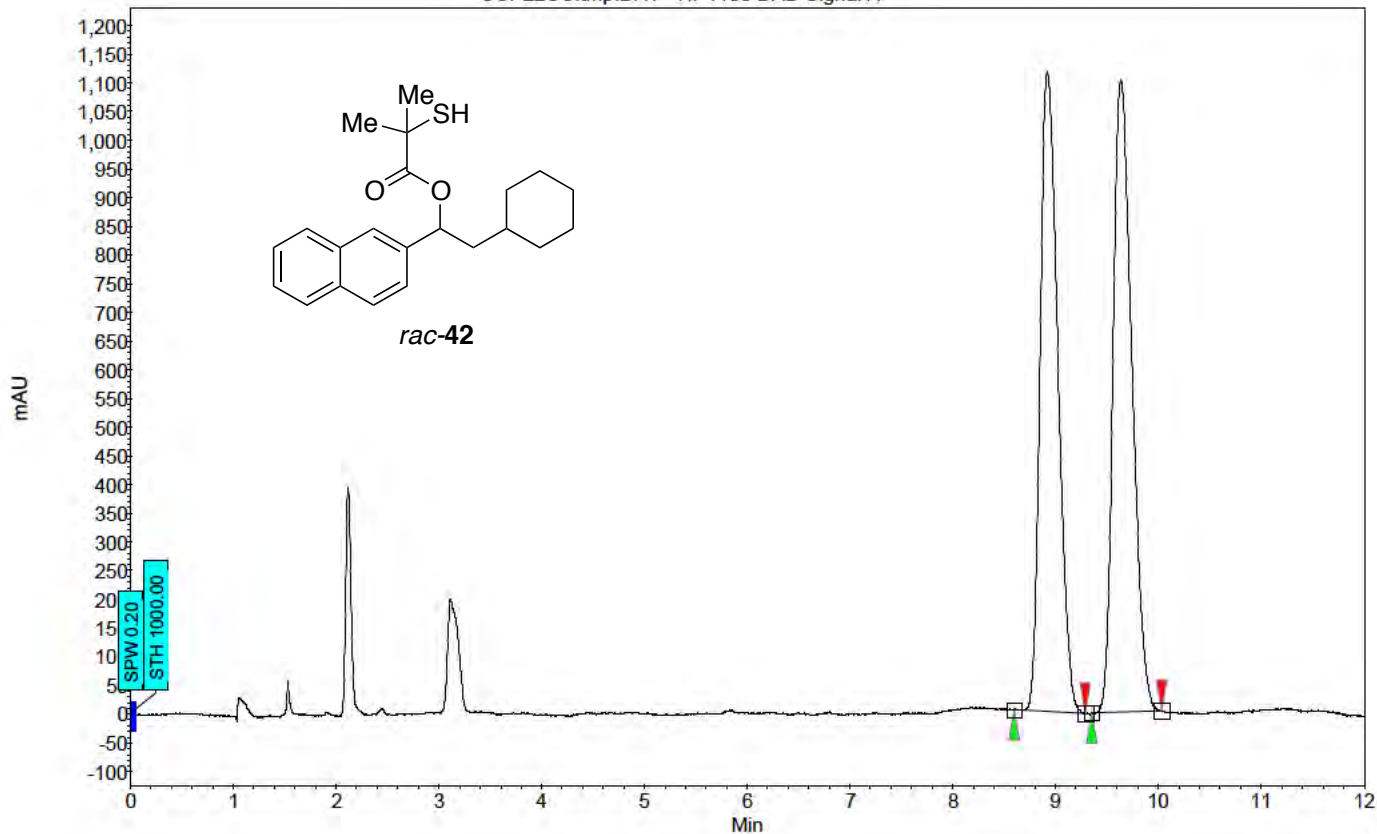


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	12.50	12.90	13.25	0.00	6.85	65.5	17.4	6.852
2	UNKNOWN	13.25	13.53	14.56	0.00	93.15	605.4	236.4	93.148
Total						100.00	670.9	253.7	100.000

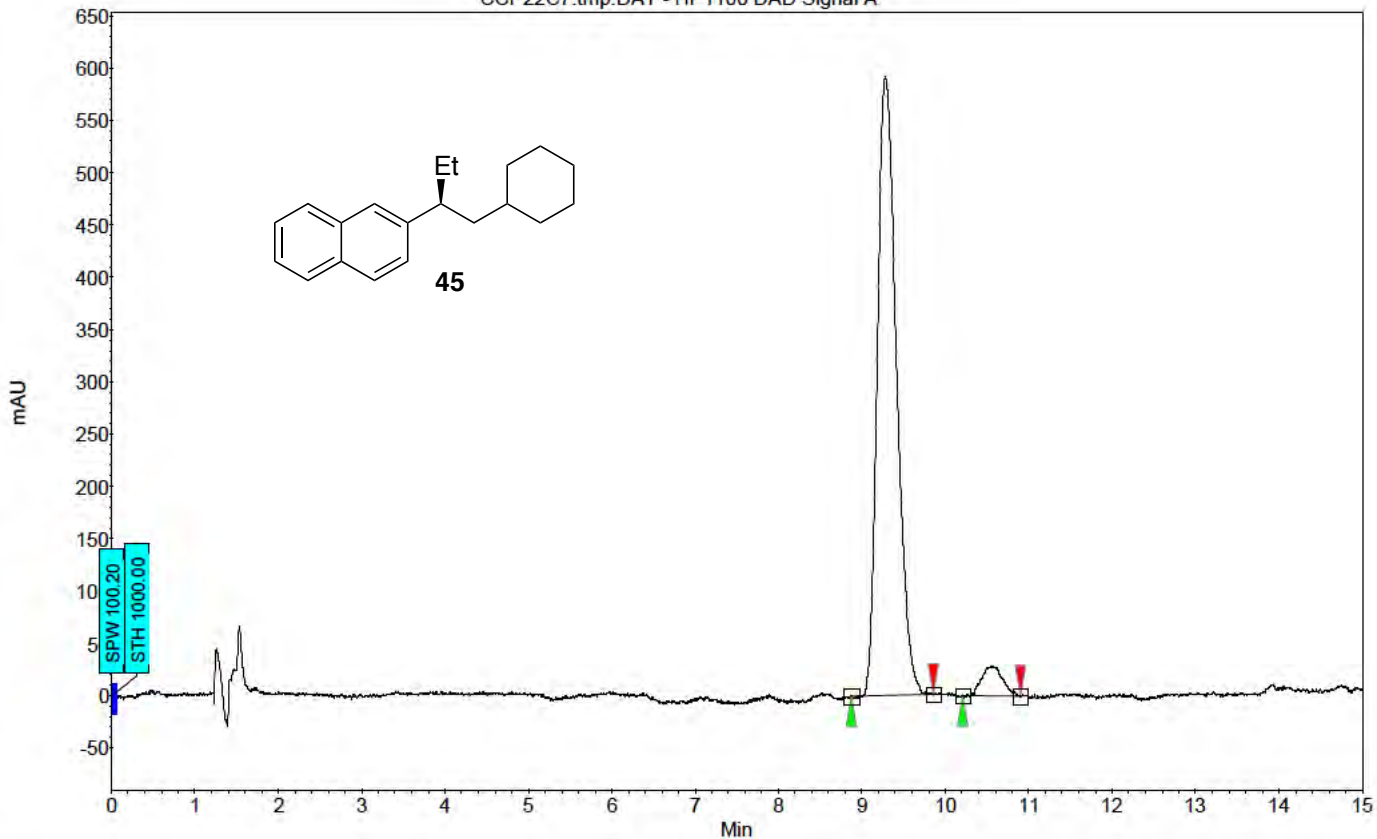
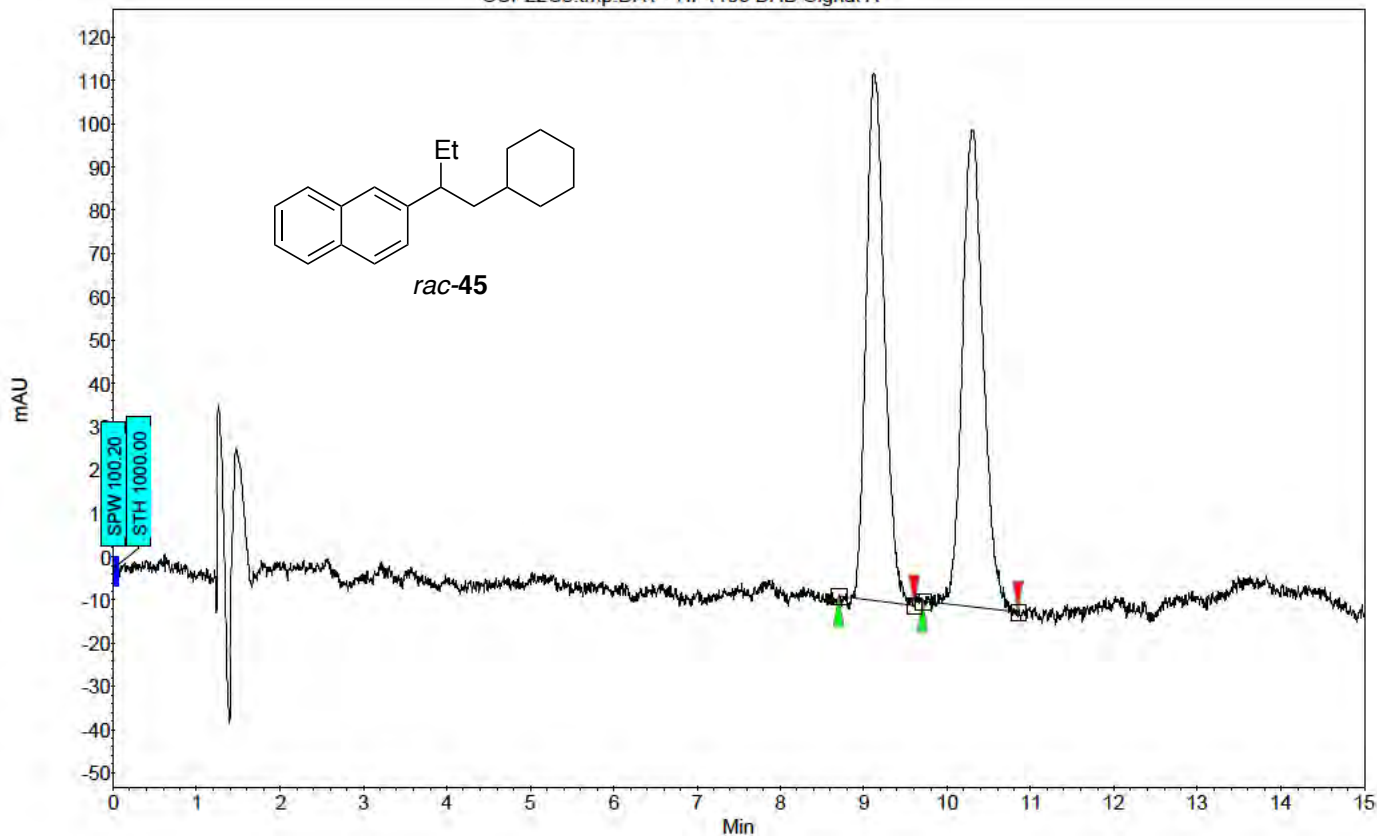




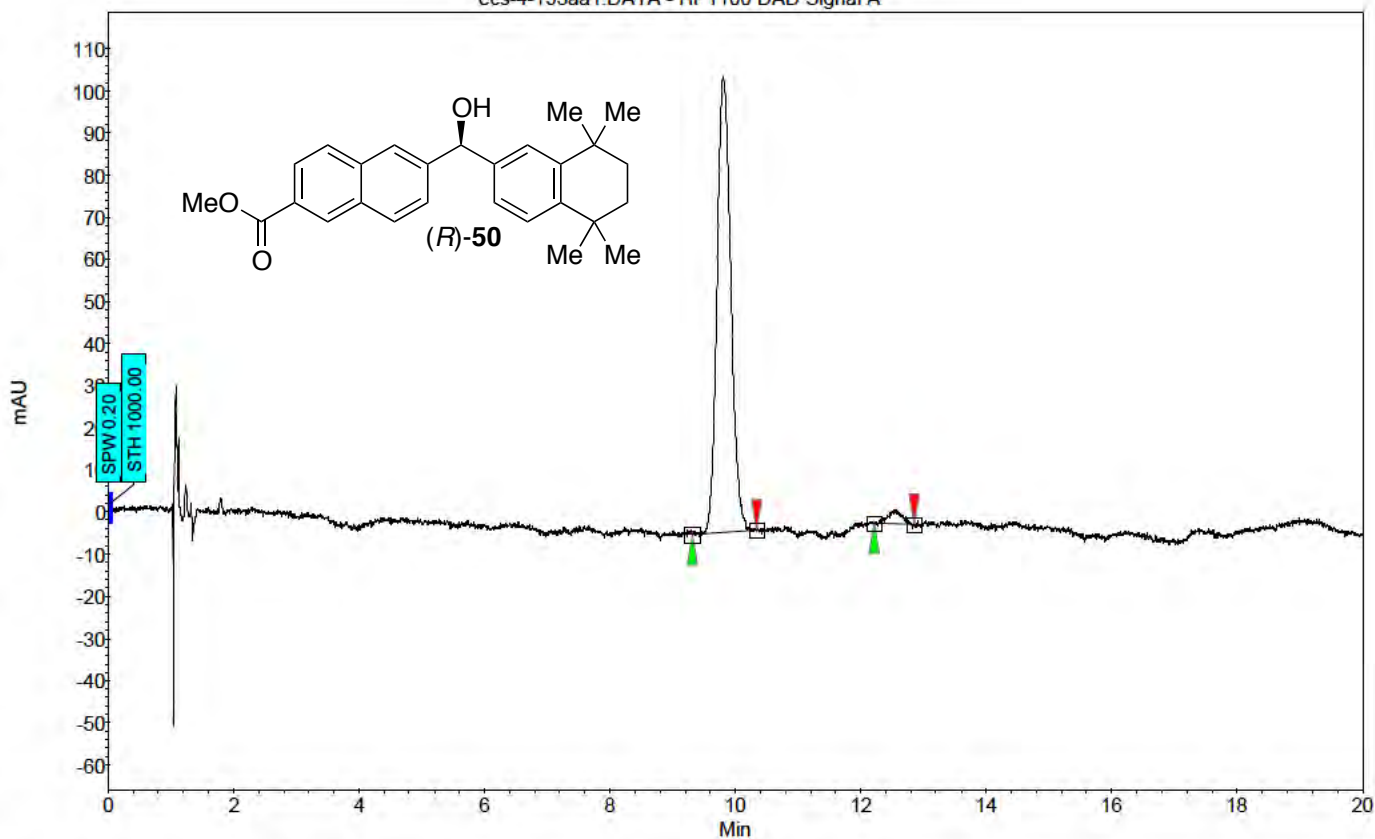
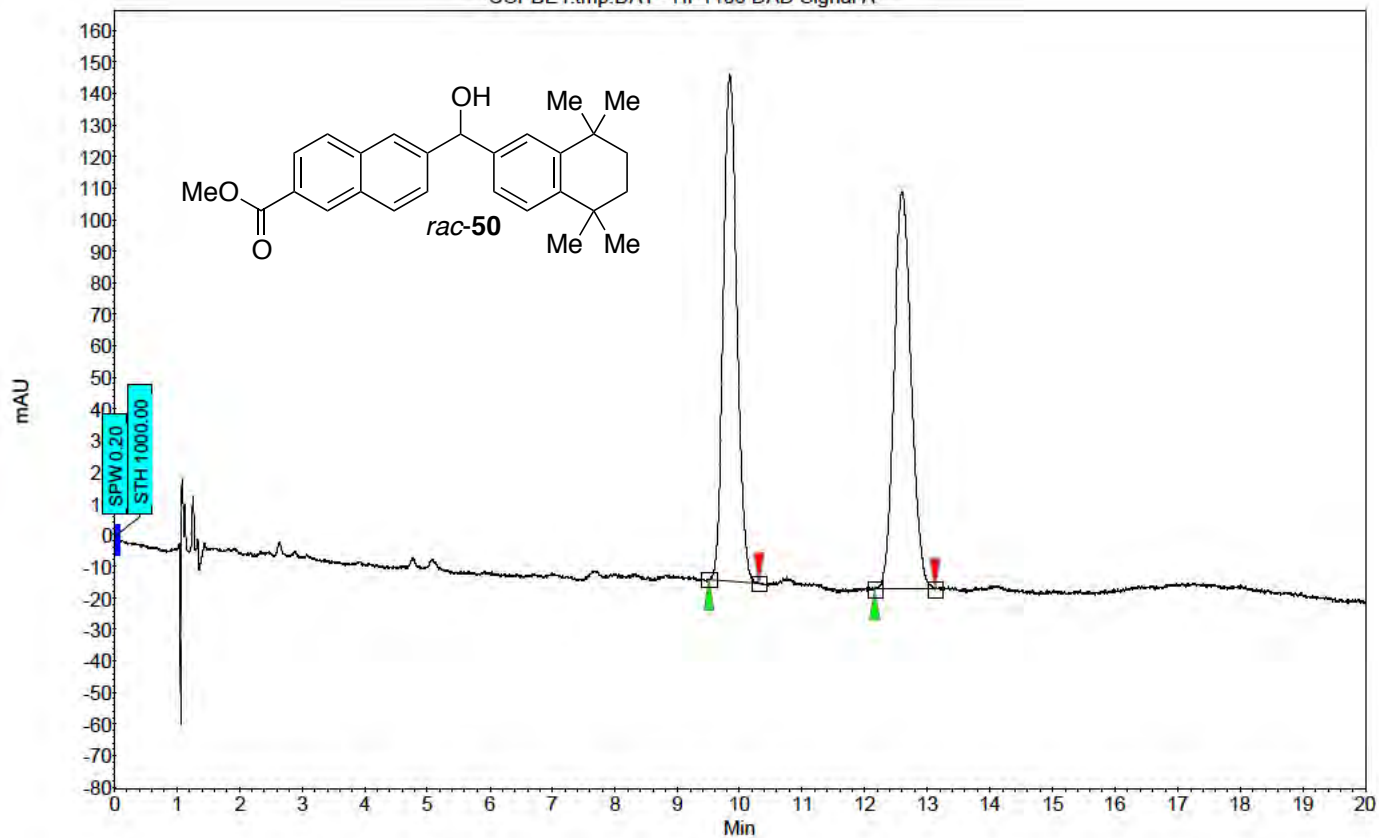
Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	5.65	5.89	6.15	0.00	96.13	781.2	107.2	96.132
2	UNKNOWN	6.26	6.45	6.64	0.00	3.87	27.7	4.3	3.868
Total						100.00	808.9	111.5	100.000



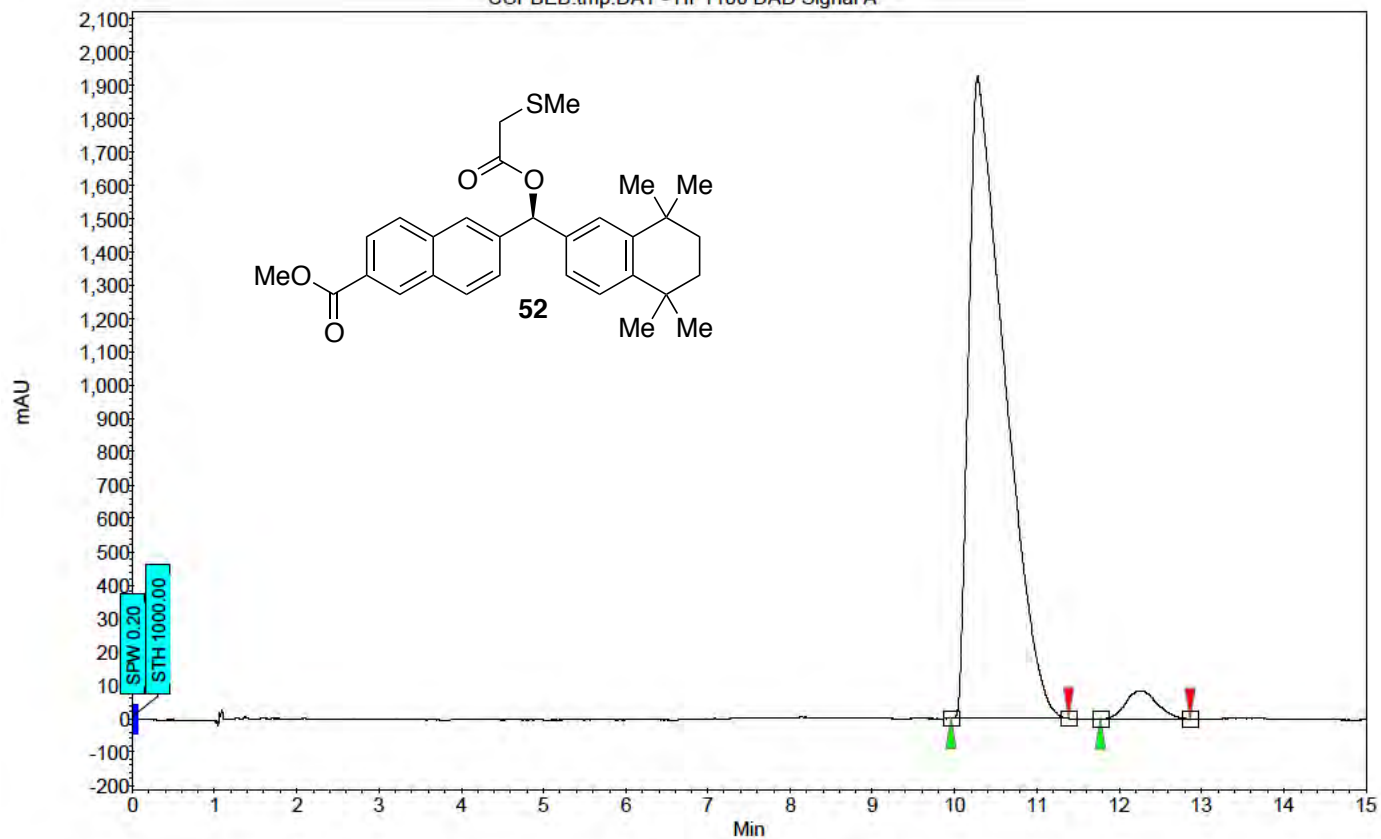
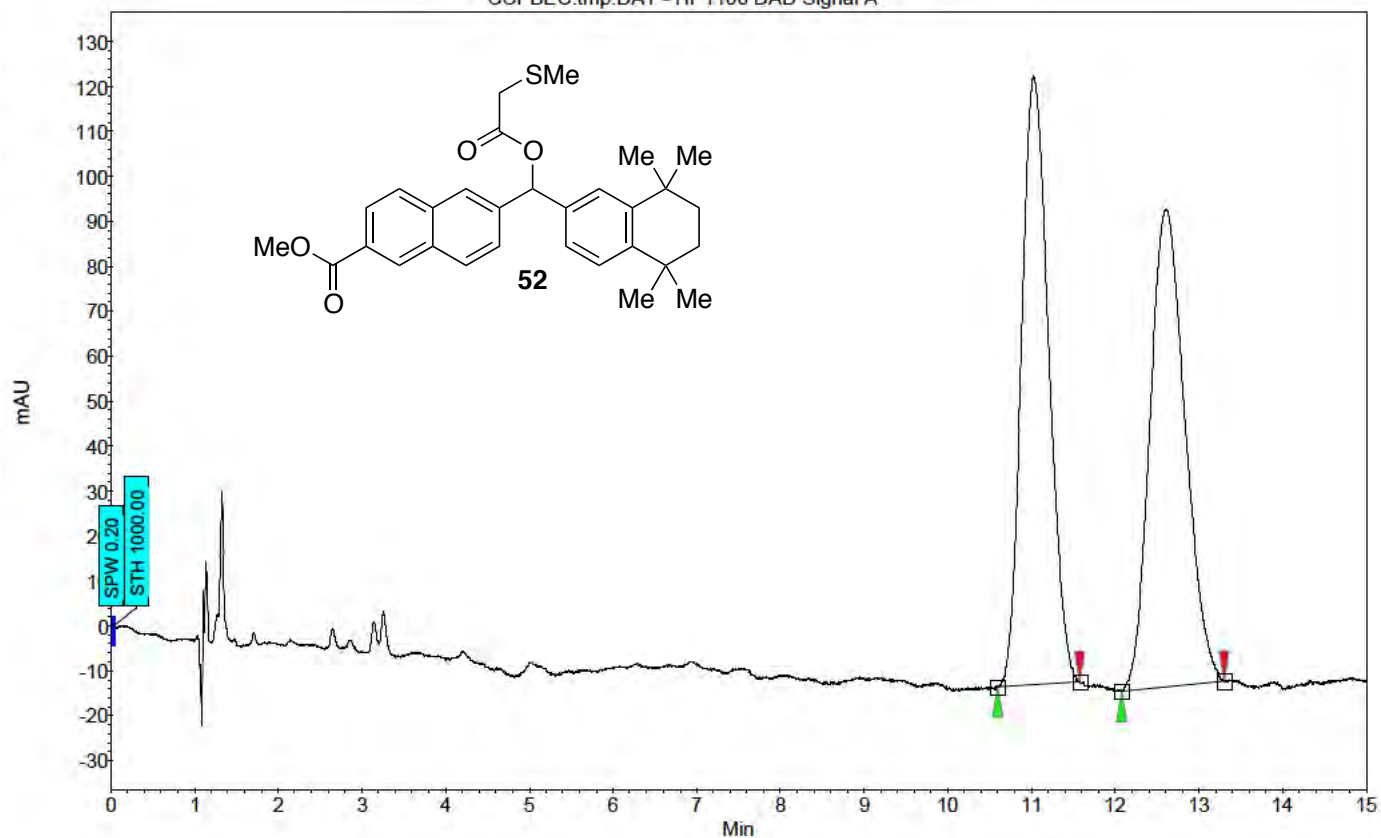
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	8.59	8.78	9.09	0.00	4.16	37.1	6.5	4.161
2	UNKNOWN	9.18	9.45	9.87	0.00	95.84	723.5	148.6	95.839
Total						100.00	760.6	155.0	100.000



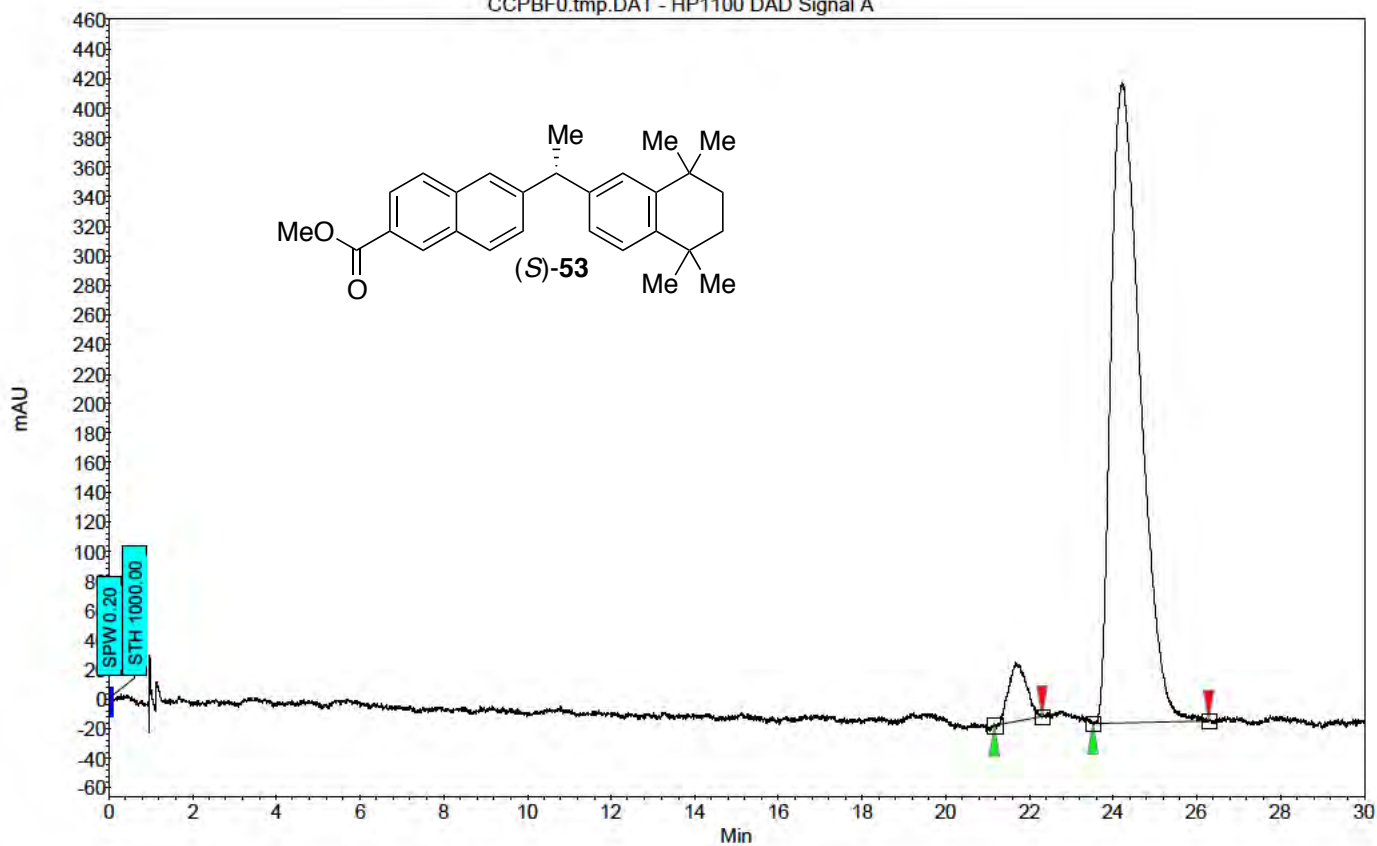
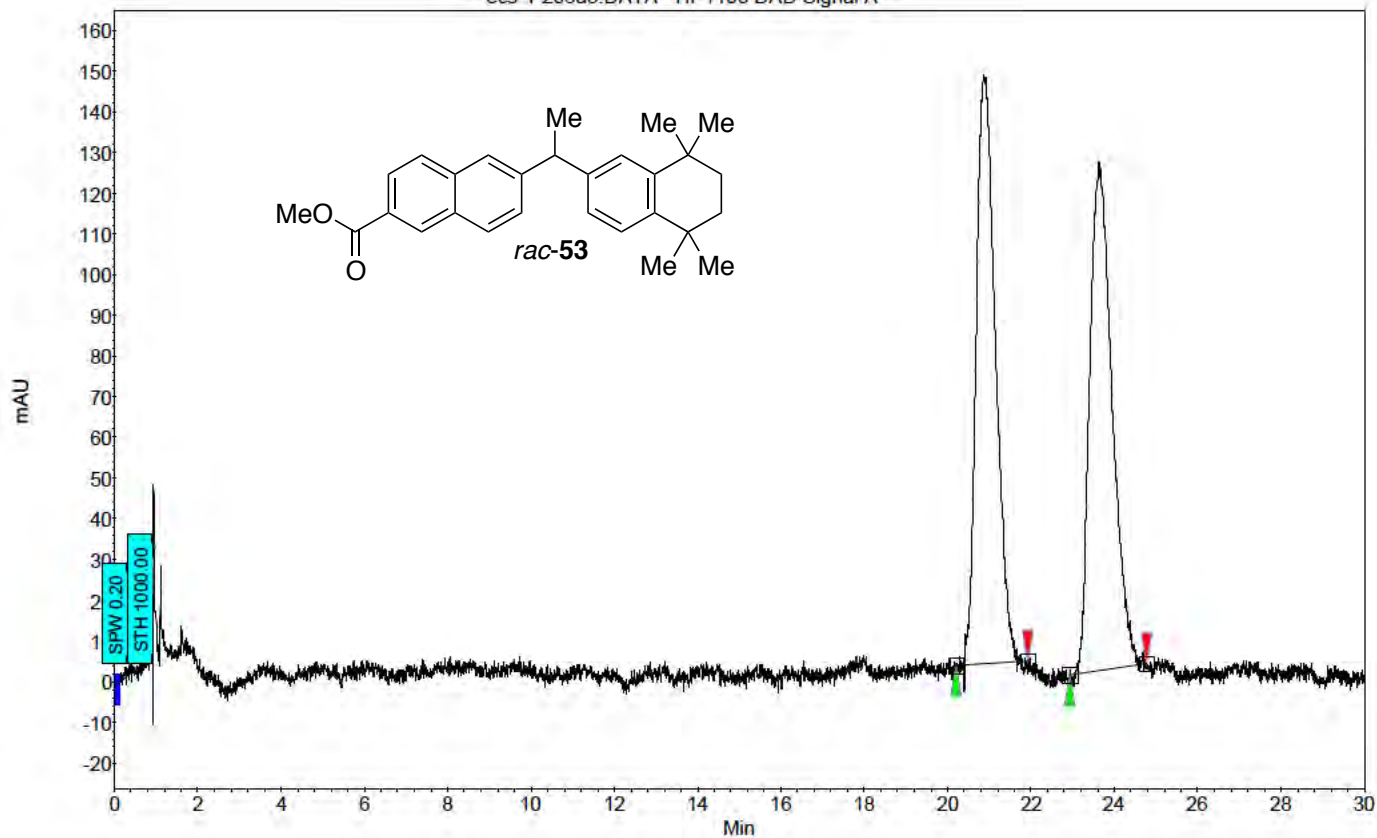
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	8.87	9.29	9.85	0.00	95.01	591.2	156.5	95.007
2	UNKNOWN	10.21	10.56	10.90	0.00	4.99	28.8	8.2	4.993
Total						100.00	619.9	164.8	100.000



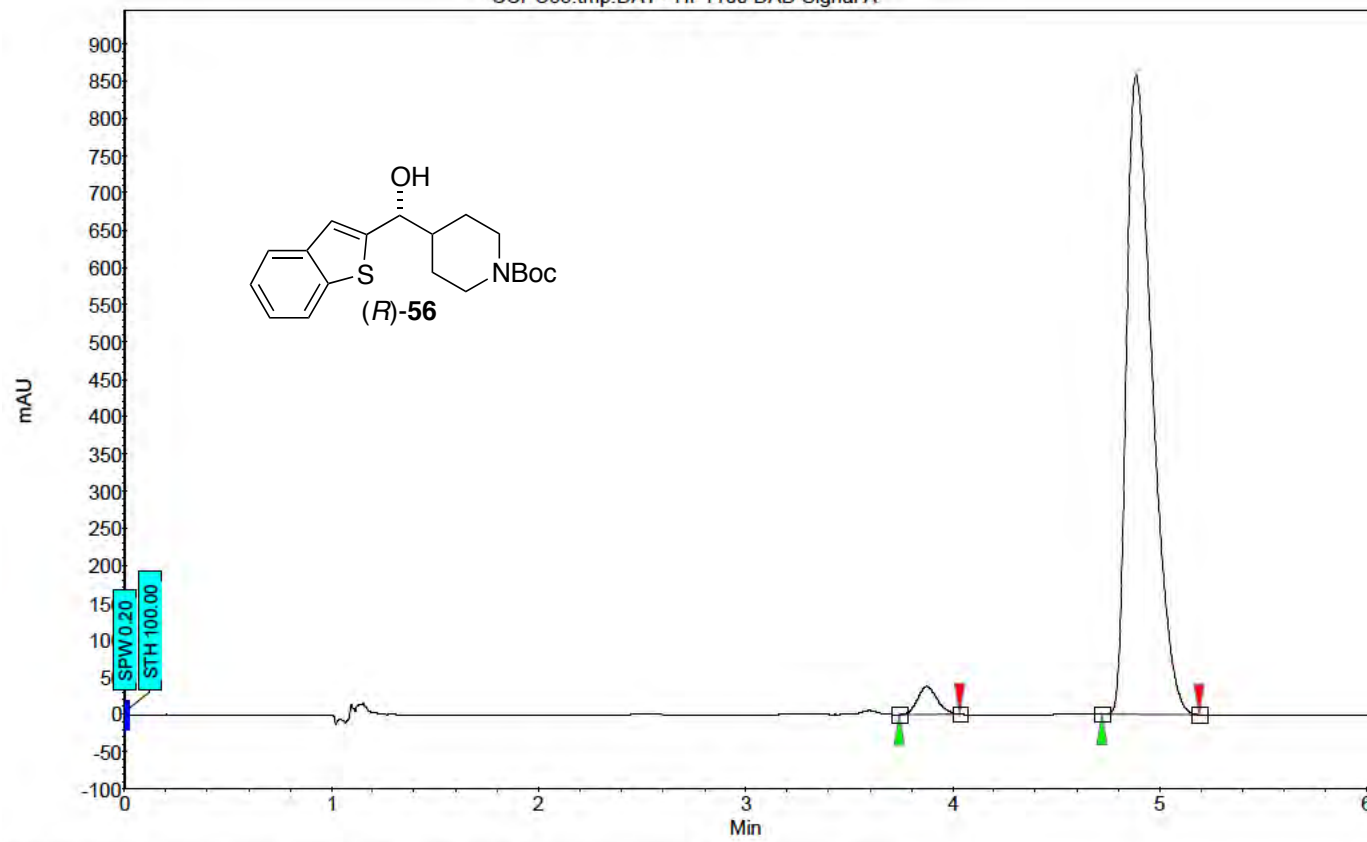
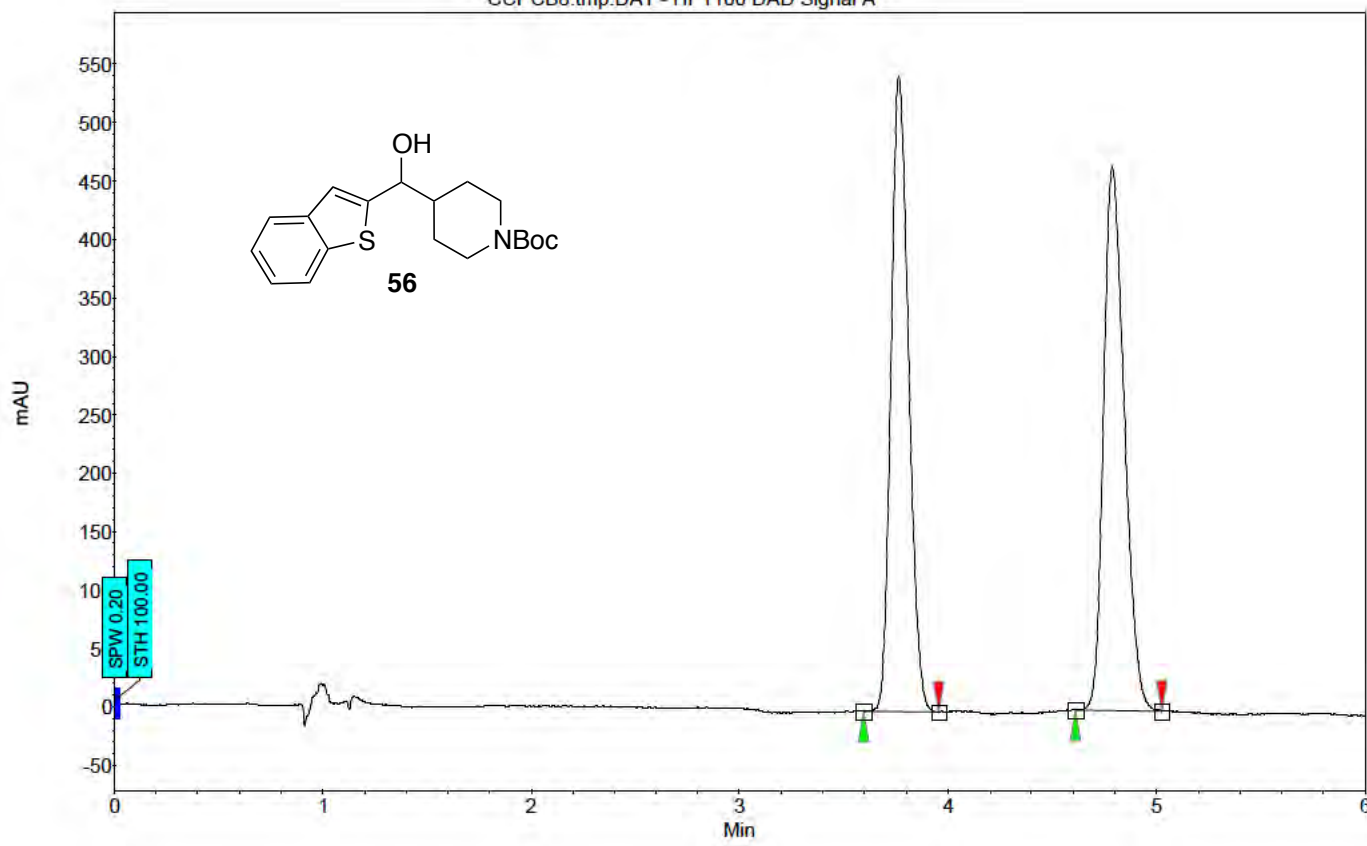
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	9.32	9.82	10.35	0.00	97.11	108.1	27.5	97.114
2	UNKNOWN	12.22	12.55	12.86	0.00	2.89	3.2	0.8	2.886
Total						100.00	111.4	28.3	100.000



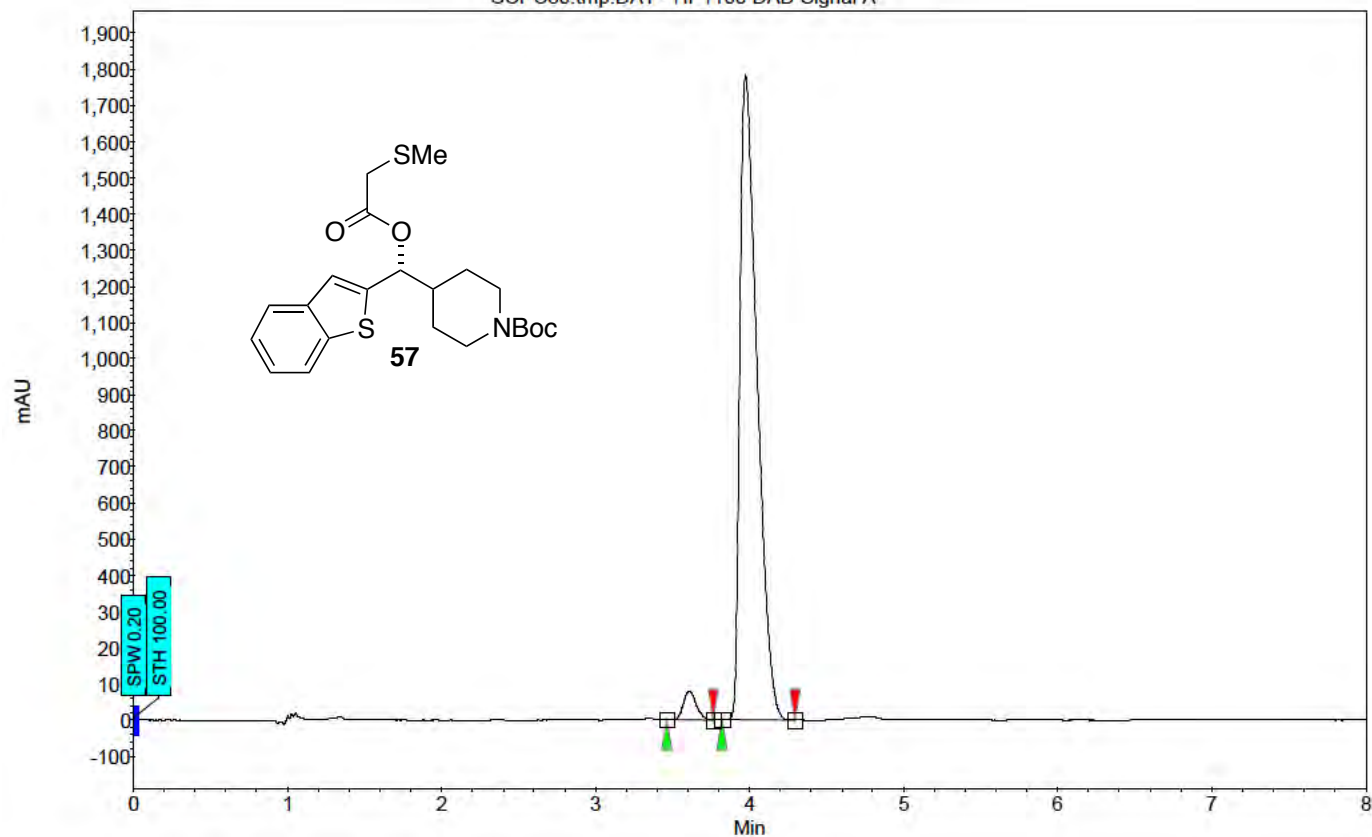
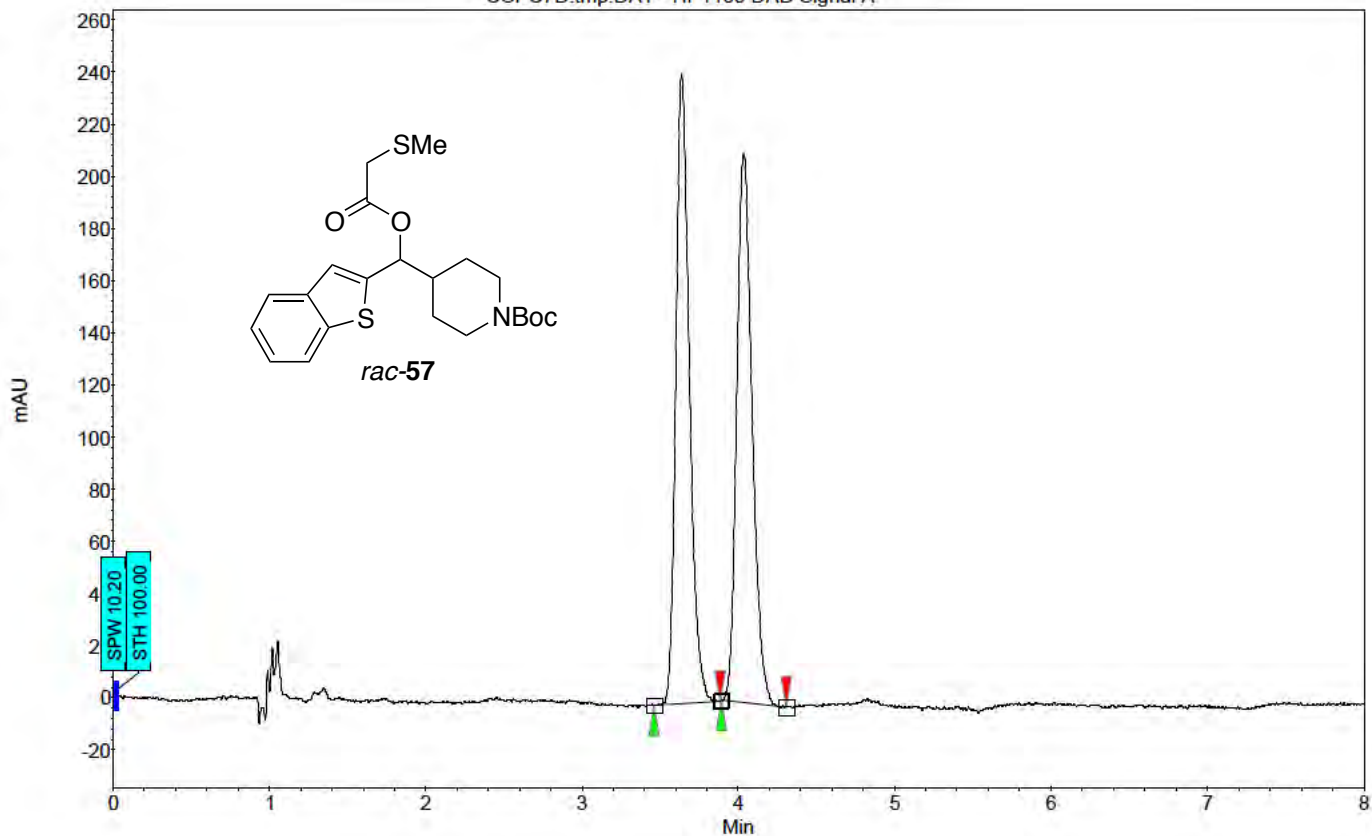
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	9.96	10.28	11.38	0.00	96.39	1926.3	975.5	96.386
2	UNKNOWN	11.77	12.26	12.86	0.00	3.61	84.5	36.6	3.614
Total						100.00	2010.7	1012.1	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
2	UNKNOWN	21.17	21.66	22.30	0.00	5.24	39.9	19.4	5.236
1	UNKNOWN	23.52	24.20	26.28	0.00	94.76	432.6	351.6	94.764
Total						100.00	472.5	371.0	100.000

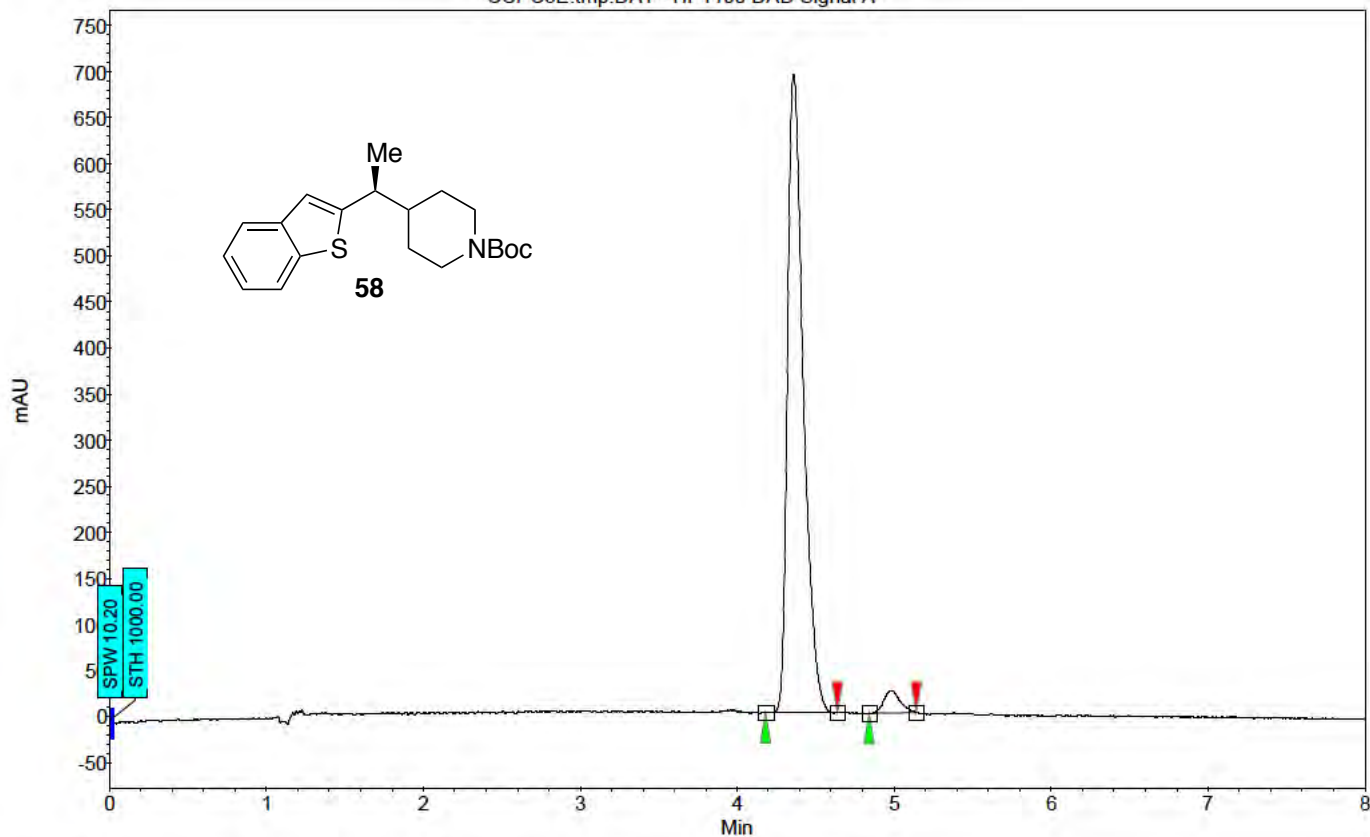
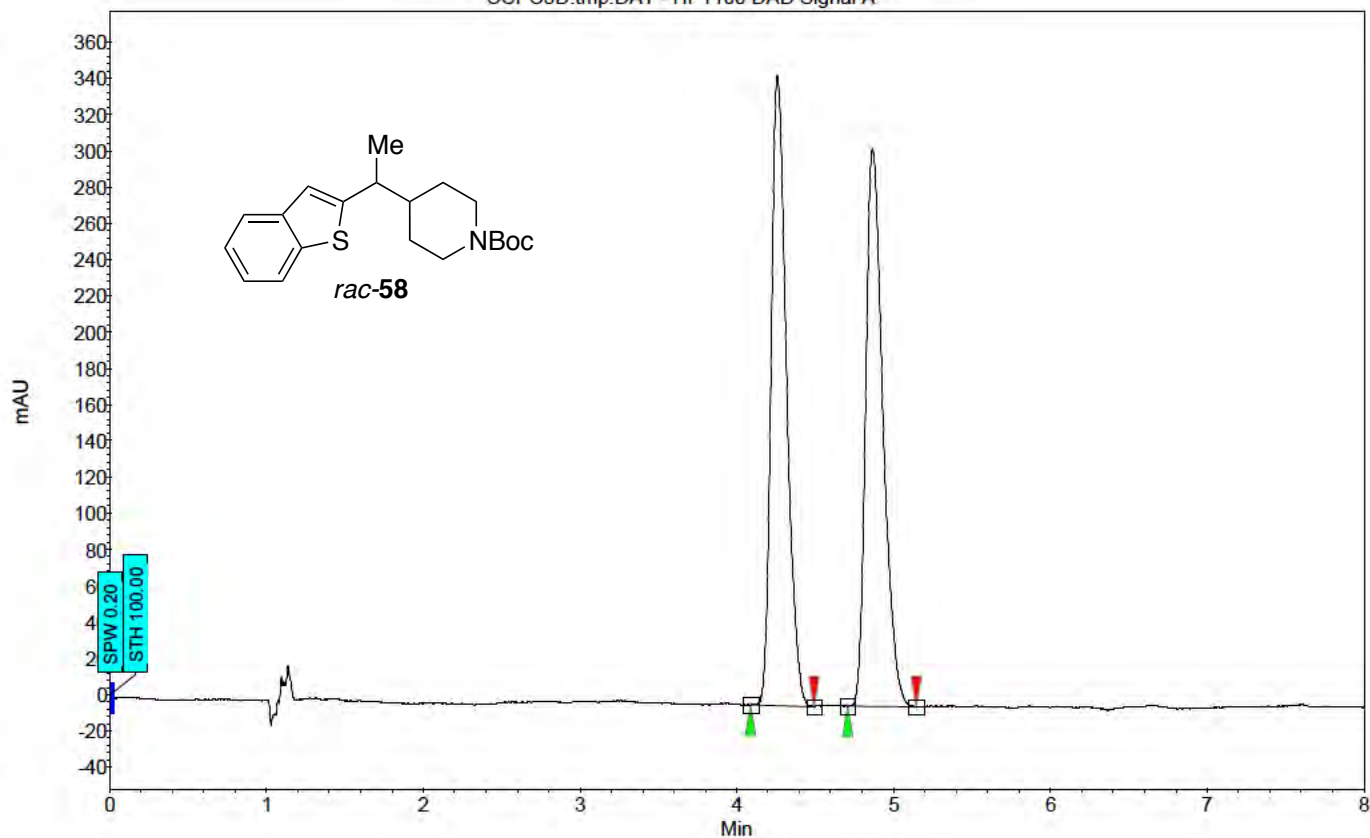


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	3.74	3.88	4.03	0.00	3.25	37.6	4.1	
2	UNKNOWN	4.72	4.89	5.19	0.00	96.75	857.8	122.8	
Total						100.00	895.5	126.9	100.000

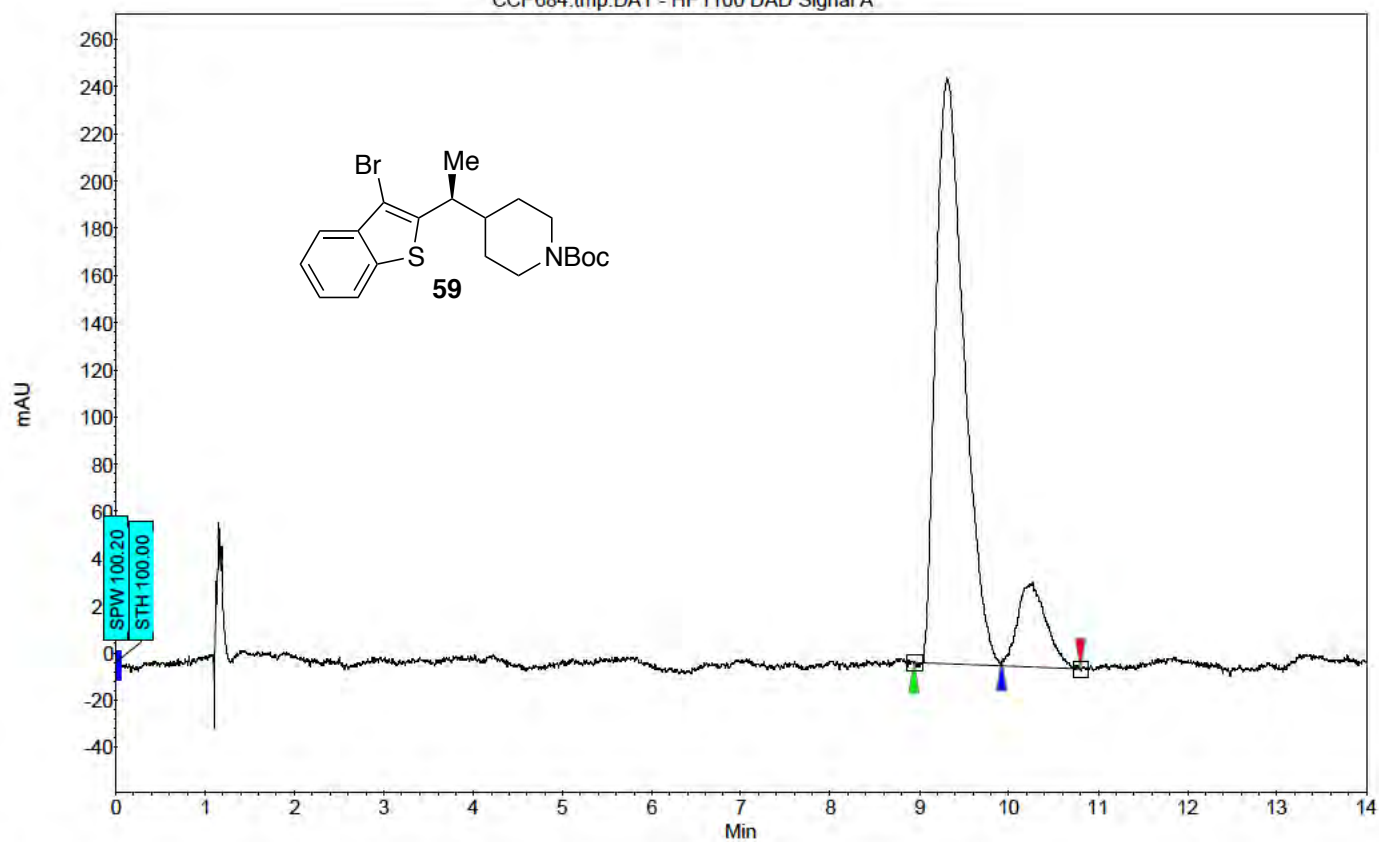
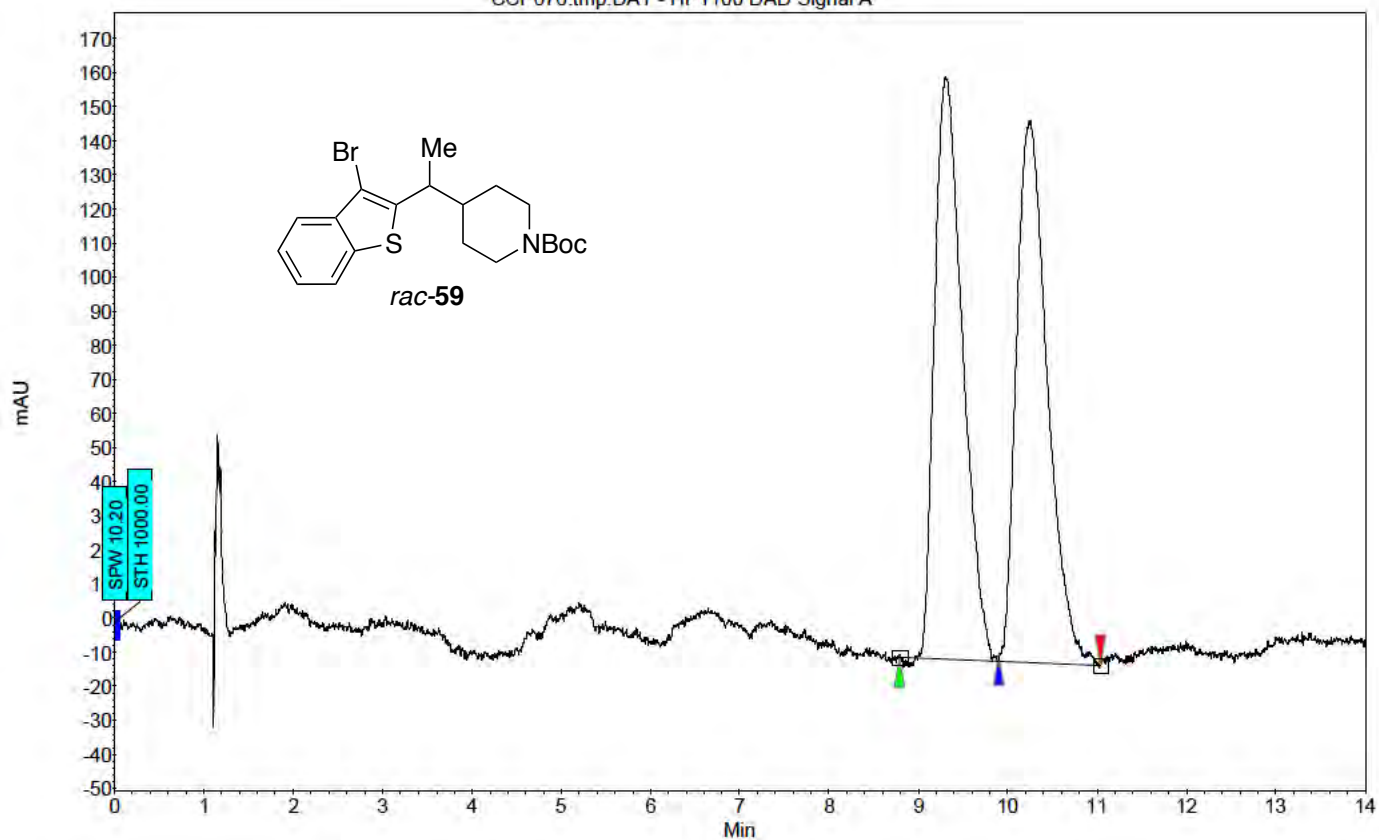


Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	
1	UNKNOWN	3.46	3.61	3.77	0.00	3.22	80.0	7.7	3.224
2	UNKNOWN	3.82	3.98	4.30	0.00	96.78	1781.1	230.5	96.776
Total						100.00	1861.1	238.2	100.000

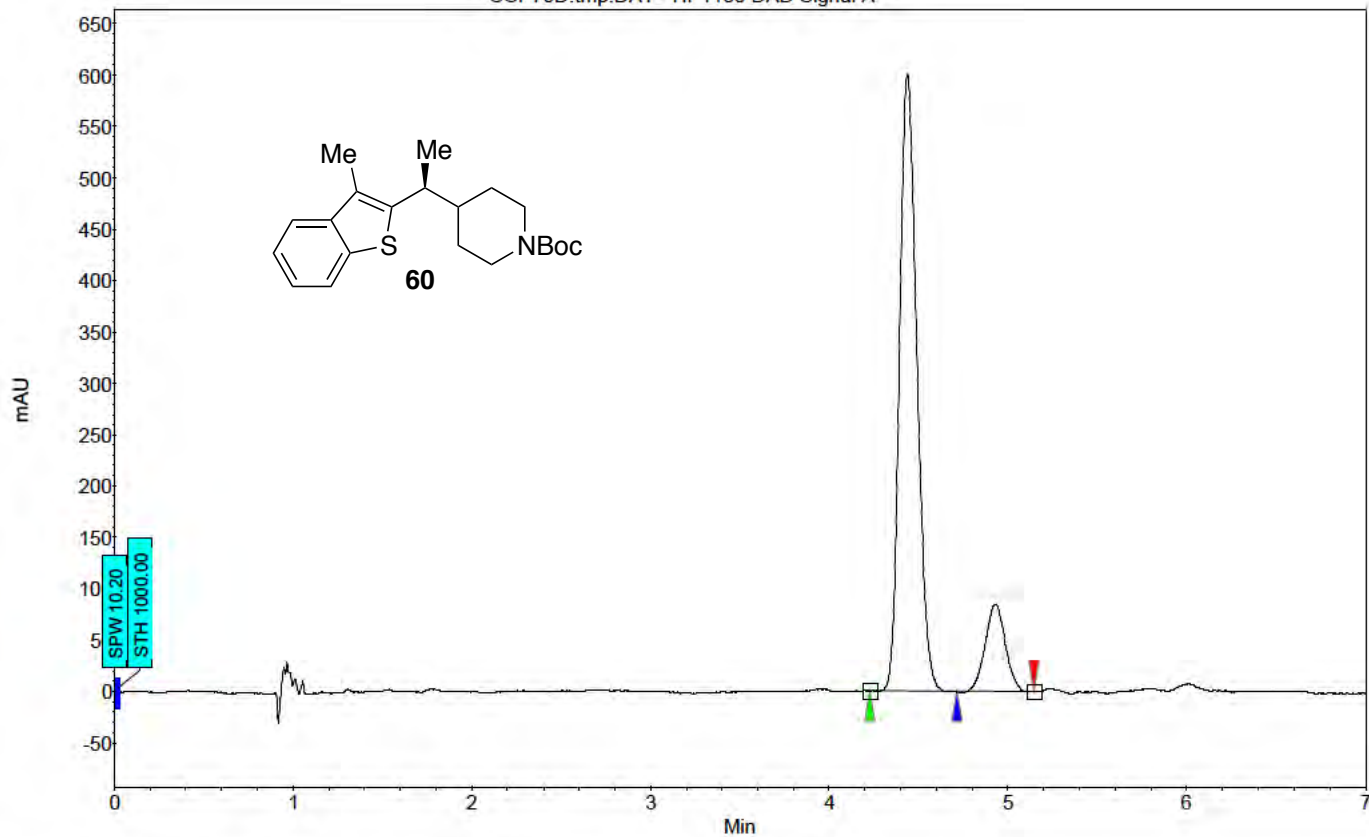
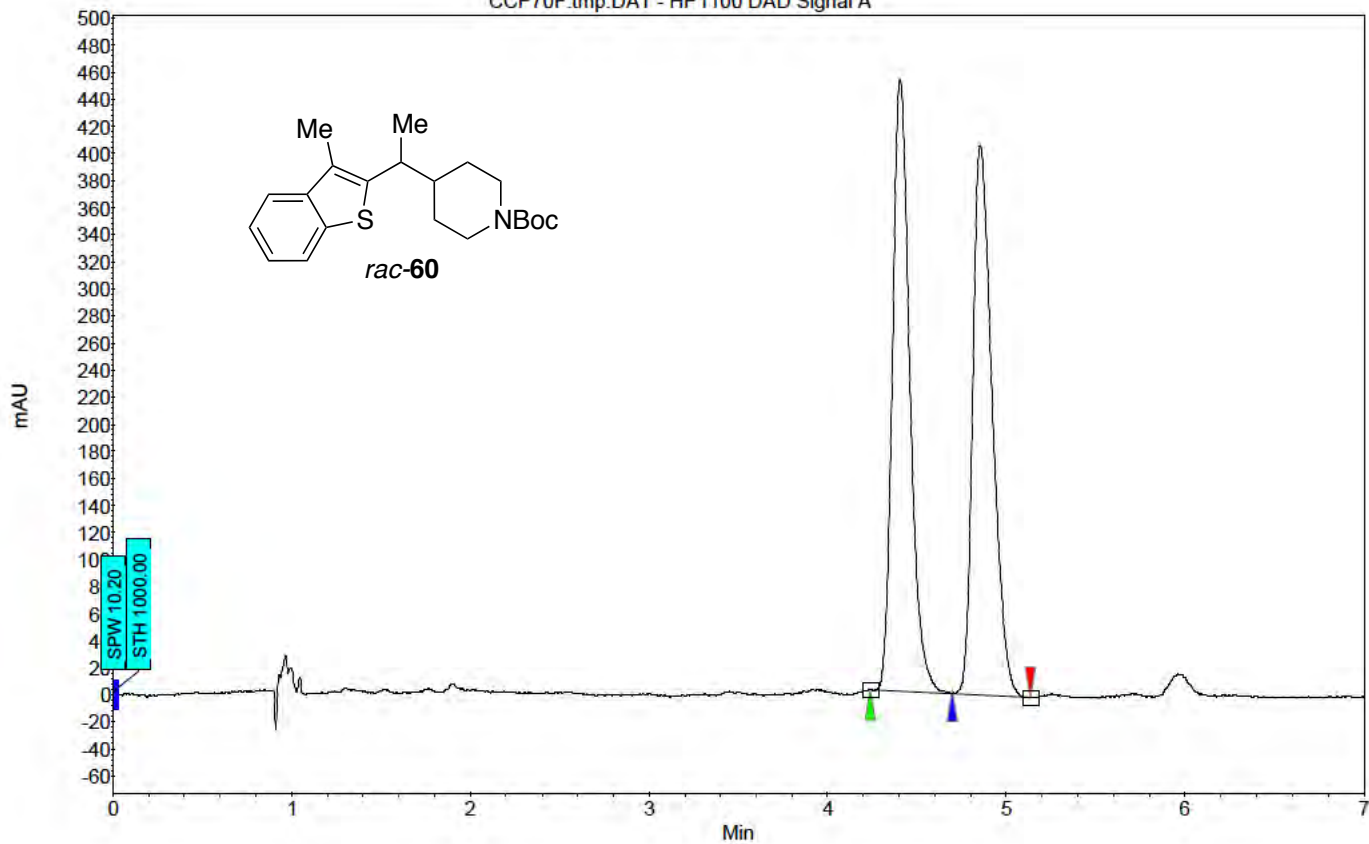




Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	4.18	4.36	4.64	0.00	96.44	692.0	80.8	96.437
2	UNKNOWN	4.84	4.98	5.14	0.00	3.56	24.5	3.0	3.563
Total						100.00	716.5	83.8	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	8.94	9.32	9.92	0.00	87.30	247.9	90.4	87.299
2	UNKNOWN	9.92	10.27	10.80	0.00	12.70	35.5	13.2	12.701
Total						100.00	283.3	103.6	100.000



Index	Name	Start Time	End	RT Offset	Quantity	Height	Area	Area	
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	
1	UNKNOWN	4.23	4.44	4.72	0.00	85.91	600.3	67.3	85.908
2	UNKNOWN	4.72	4.93	5.15	0.00	14.09	85.0	11.0	14.092
Total						100.00	685.3	78.3	100.000