# SUPPORTING INFORMATION

# Organocatalytic Asymmetric Addition of Thioglycolates to *o*-Quinone Methides: A Route to 5-substituted-5*H*-benzoxathiepine-2(3*H*)-ones

Chandan Gharui,[a] Satya Prakash,[b] Deepak Chopra[b] and Subhas Chandra Pan*[a]

[a]Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati, Assam, 781039; E-mail: span@iitg.ac.in

[b]Department of Chemistry, *Indian Institute of Science Education and Research, Bhopal, India.*
E-Mail: dchopra@iiserb.ac.in

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## 1. General information:

All needed chemicals and reagents were purchased from commercial suppliers and directly used without further purification. All solvents were redistilled using common drying agents and techniques. Progress of the reactions was monitored by using silica gel 60 F254 (0.25 mm). Every time, 60-120 mesh size silica gel was used during products purification through column chromatography. NMR spectra was recorded on Bruker 600 MHz and 400 MHz spectrometer. $CDCl_3$ had been used as the reference NMR solvent and the residual solvent peak was considered as internal reference i.e. for chloroform proton, δ: 7.260 and for chloroform carbon, δ: 77.23. Chemical shift and coupling constant values were reported in parts per million (ppm) unit and Hertz (Hz) unit respectively. Usual notations such as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), brs (broad singlet) were indicated for multiplicity description. Q-TOF electron spray ionization (ESI) mass spectrometer was used for HRMS. Enantiomeric excesses were measured in Dionex (Ultimate 3000) instrument using different stationary phase chiral columns.

**General procedure for the synthesis of 2-Sulfonylmethylphenols (1):**

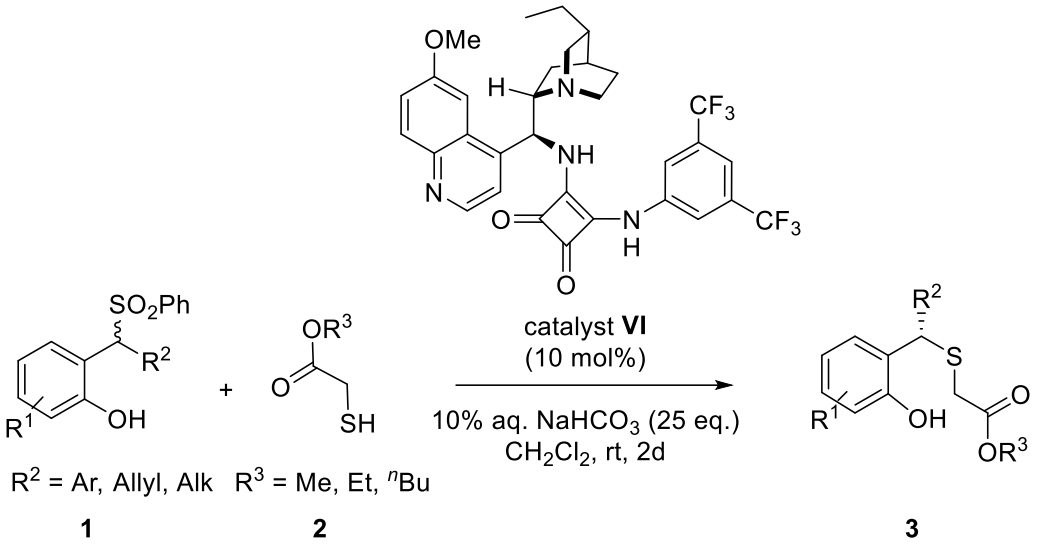
2-Sulfonylmethylphenols were prepared according to the known literature procedure.[1]

**General procedure for the synthesis of catalyst:**

The best catalyst **VI** was prepared according to earlier reported procedure.[2]

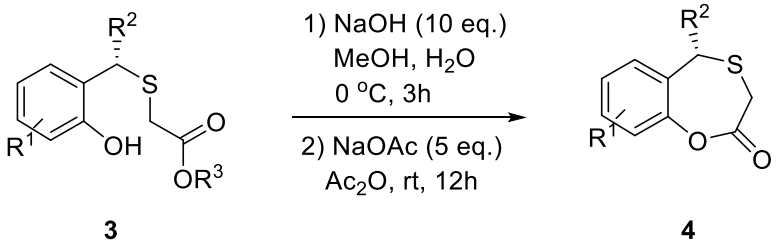
## 2. General procedure for the sulfa-Michael product (3):

In a 5 mL round bottom flask, 2-Sulfonylmethylphenols **1** (0.1 mmol), alkyl thioglycolates **2** (0.25 mmol) and the catalyst **VI** (10 mol%) were mixed in 2 mL DCM solvent. Then 10% aq. $NaHCO_3$ solution (25 equivalents) was added to the reaction mixture and continued stirring for 2 days at room temperature. After completion of the reaction, product was extracted with DCM (3 times).




Finally, the organic parts are concentrated in *vacuum* and purified by silica gel column chromatography using Hexane/EtOAc as the eluting solvent to achieve the corresponding sulfa-Michael products **3**.

## 3. General procedure for 5-substituted-5*H*-benzoxathiepine-2(3*H*)-ones (4) from sulfa-Michael product (3):




5-substituted-5*H*-benzoxathiepine-2(3*H*)-ones **4** were synthesized from sulfa-Michael product **3** in successive two steps.

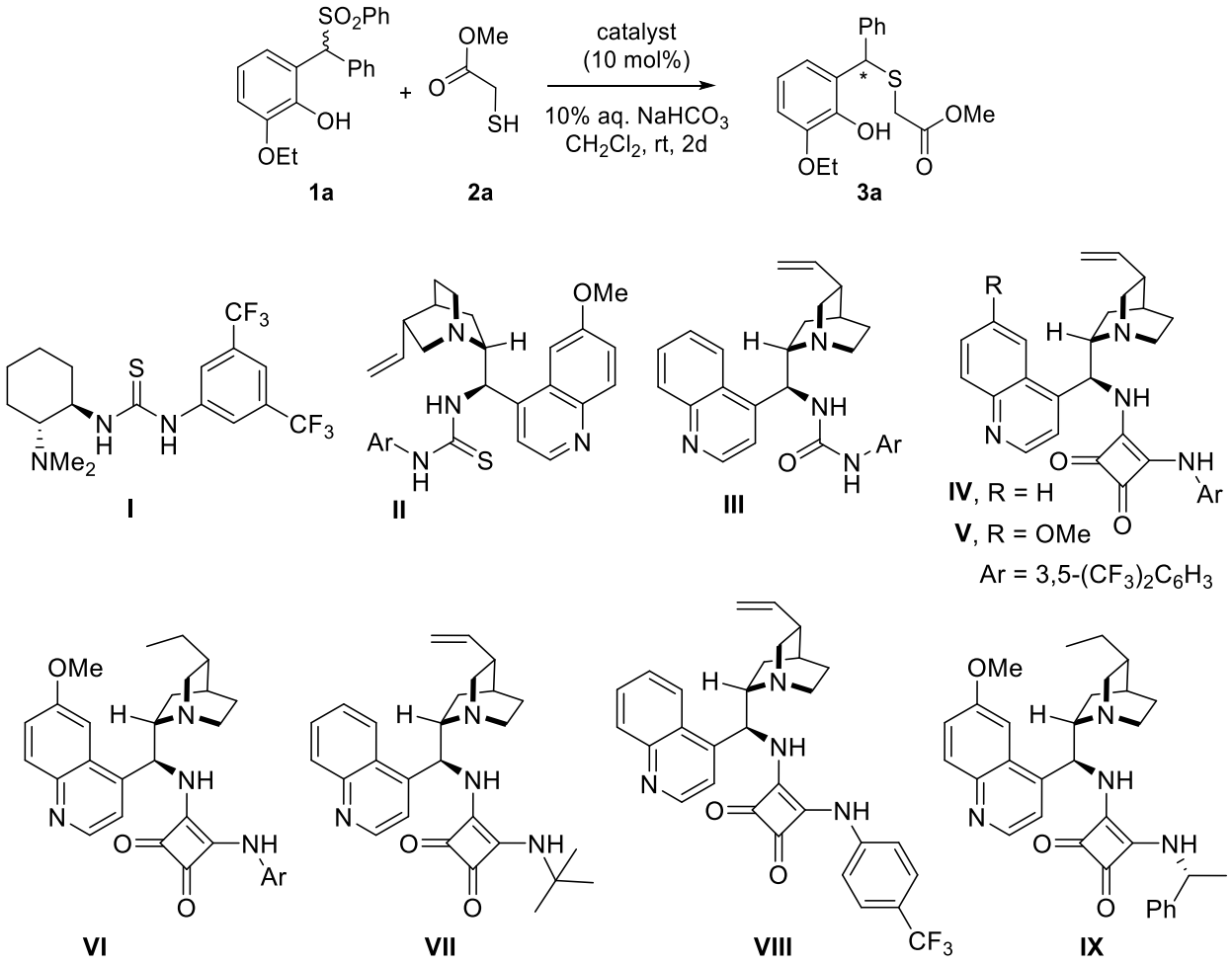
In the first step, sodium hydroxide (1 mmol) and water (60 µL) were added to a stirrer solution of products **3** (0.1 mmol) in 1 mL MeOH at 0 °C. Then the reaction mixture was allowed to stir for 3 hours for better conversion. After completion of the reaction, it was diluted with DCM and acidified with 10% aq. HCl. Thereafter, the reaction mixture was extracted with DCM (3 times)

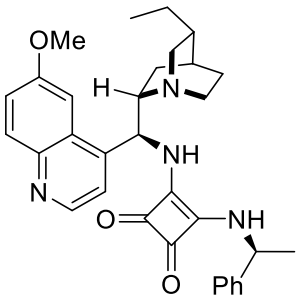
and concentrated in *vacuum*. Finally, the crude mixture was dried properly and subjected to the next step without purification.

In the second step, the crude mixture was dissolved in 0.8 mL $Ac_2O$. Then NaOAc (0.5 mmol) was added and continued stirring for 12 hours at room temperature. Finally, the reaction mixture was extracted with DCM, concentrated and purified by silica gel column chromatography to obtain the desired 5-substituted-5*H*-benzoxathiepine-2(3*H*)-ones **4**.

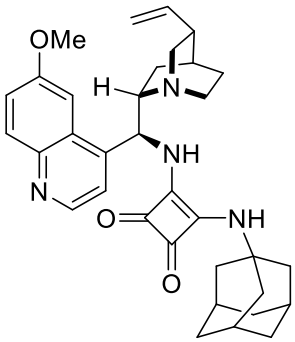
## 4. Optimization table:

**Table 1. Catalyst screening**






**X**

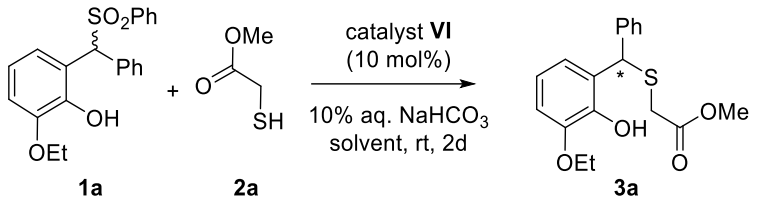



**XI**

| Entry[a] | Catalyst | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|
| 1 | **I** | 86 | 48 |
| 2 | **II** | 90 | 61 |
| 3 | **III** | 84 | 60 |
| 4 | **IV** | 95 | 93 |
| 5 | **V** | 94 | 95 |
| 6 | **VI** | **96** | **95** |
| 7 | **VII** | 90 | 74 |
| 8 | **VIII** | 95 | 91 |
| 9 | **IX** | 88 | 78 |
| 10 | **X** | 86 | 79 |
| 11 | **XI** | 82 | 79 |

[a]All reactions were carried out with 0.05 mmol of **1a** with 0.125 mmol of **2a** in 1 mL $CH_2Cl_2$ with 25 equivalents 10% $NaHCO_3$ and 10 mol% catalyst at room temperature. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC using stationary phase chiral column.

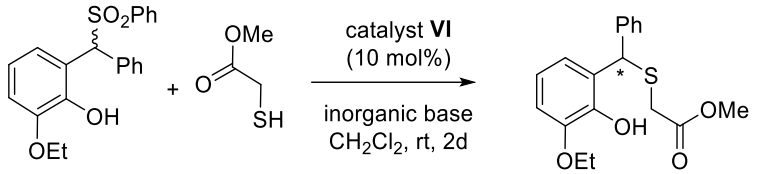
## Table 2. Solvent screening




| Entry[a] | Solvent | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | **96** | **95** |
| 2 | $CHCl_3$ | 96 | 94 |
| 3 | $(CH_2Cl)_2$ | 94 | 93 |
| 4 | toluene | 92 | 90 |
| 5 | xylene | 92 | 90 |
| 6 | $\alpha,\alpha,\alpha$-trifluoro toluene | 92 | 92 |
| 7 | diethyl ether | 85 | 92 |
| 8 | $CCl_4$ | 93 | 87 |
| 9 | EtOAc | 85 | 90 |
| 10 | $CH_3CN$ | 98 | 0 |

[a]All reactions were carried out with 0.05 mmol of **1a** with 0.125 mmol of **2a** in 1 mL solvent with 25 equivalents 10% $NaHCO_3$ and 10 mol% catalyst **VI** at room temperature. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC using stationary phase chiral column.

## Table 3. Inorganic base screening

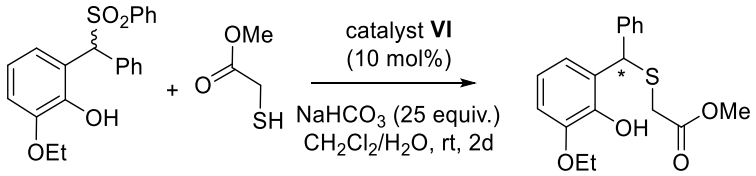



1a 2a 3a

| Entry[a] | Inorganic base (equiv.) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|
| 1 | $NaHCO_3$ (25) | 20 | 72 |
| 2 | 10% aq. $NaHCO_3$ (25) | **96** | **95** |
| 3 | 10% aq. $Na_2CO_3$ (25) | 94 | 94 |
| 4 | 10% aq. $K_2CO_3$ (25) | 96 | 94 |
| 5 | 10% aq. $NaHCO_3$ (50) | 96 | 92 |
| 6 | 10% aq. $NaHCO_3$ (10) | 94 | 94 |
| 7 | 10% aq. $NaHCO_3$ (2) | 84 | 94 |

[a]All reactions were carried out with 0.05 mmol of **1a** with 0.125 mmol of **2a** in 1 mL $CH_2Cl_2$ and 10 mol% catalyst **VI** at room temperature. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC using stationary phase chiral column.

## Table 4. Optimization of biphasic reaction conditions




1a 2a 3a

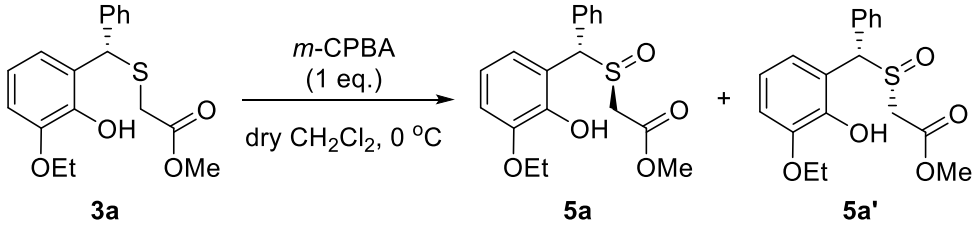
| Entry[a] | $CH_2Cl_2/H_2O$ (mL) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|

| | | | |
|---|---|---|---|
| 1 | $CH_2Cl_2/H_2O$ (1/0) | 20 | 72 |
| 2 | $CH_2Cl_2/H_2O$ (0.25/0.25) | 89 | 95 |
| 3 | $CH_2Cl_2/H_2O$ (0.5/0.25) | 88 | 95 |
| 4 | $CH_2Cl_2/H_2O$ (0.5/0.5) | 94 | 95 |
| 5 | $CH_2Cl_2/H_2O$ (1/1.05) | **96** | **95** |
| 6 | $CH_2Cl_2/H_2O$ (1/0.25) | 88 | 95 |
| 7 | $CH_2Cl_2/H_2O$ (1/0.5) | 92 | 95 |
| 8 | $CH_2Cl_2/H_2O$ (0.25/1) | 92 | 94 |

[a]All reactions were carried out with 0.05 mmol of **1a** with 0.125 mmol of **2a** under biphasic conditions using10 mol% catalyst **VI** and 25 equiv. $NaHCO_3$ at room temperature. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC using stationary phase chiral column.

## 5. Experimental procedure for the products (5) to (8):

### Procedure for the synthesis of sulfoxides (5a and 5a'):

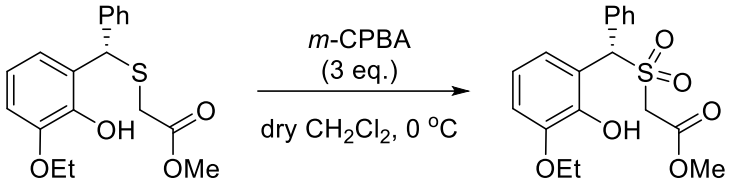



**3a** **5a** **5a'**

Products **5a** and **5a'** were synthesized under modified conditions by following the literature procedure.[3] To a stirrer solution of product **3a** (0.1 mmol) in 1 mL dry DCM at 0 °C, *m*-CPBA (0.1 mmol) was added. 1.5 Hour later, the reaction mixture was quenched with saturated $K_2CO_3$

solution. Then work up was done using DCM. Organic parts were concentrated in *vacuum* and purified by silica gel column chromatography to furnish the desired sulfoxides **5a** and **5a**.'

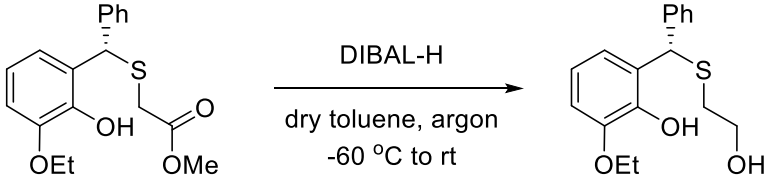
**Procedure for the synthesis of product (6):**




**3a** **6**

Similarly, product **6** was synthesized under modified conditions by following the literature procedure.[3] To a stirrer solution of product **3a** (0.1 mmol) in 1 mL dry DCM at 0 °C, *m*-CPBA (0.3 mmol) was added. Then progress of the reaction was monitored by TLC analysis. After reaction completion, the mixture was quenched with saturated $K_2CO_3$ solution and work up was performed using DCM. Organic parts were concentrated in *vacuum* and purified by silica gel column chromatography to get the desired sulfate **6**.

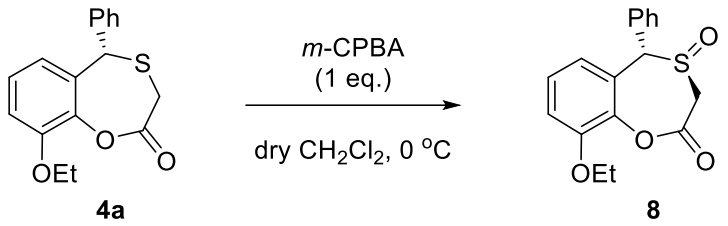
**Procedure for the synthesis of product (7):**




**3a** **7**

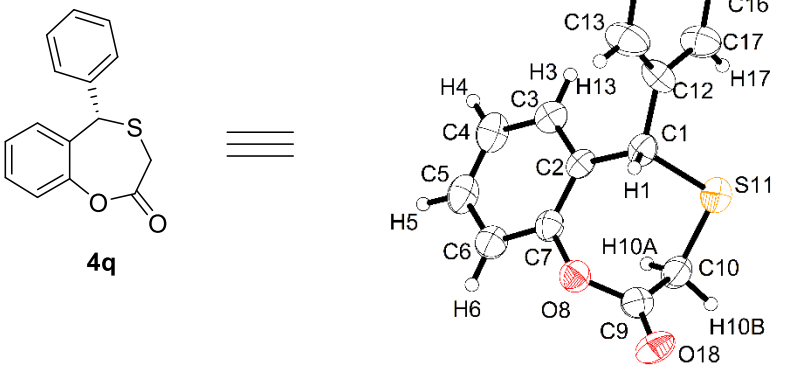
Product **7** was prepared by following the literature procedure.[4] First, the compound **3a** (0.1 mmol) was dissolved in 2.5 mL dry toluene under argon. Then the whole set up was cooled to -60 °C. After this, 0.3 mL 1 (M) DIBAL-H in cyclohexane was added dropwise to to the stirring solution of **3a**. After completion of addition, the reaction was shifted to room temperature and allowed stirring for 2.5 hours. Thereafter, it was quenched with 0.5 mL methanol and diluted with diethyl ether. Finally, product **7** was extracted with diethyl ether and purified by column chromatography.

**Procedure for the synthesis of sulfoxides (8):**




To a stirrer solution of product **4a** (0.1 mmol) in 1 mL dry DCM at 0 $^{o}$C, *m*-CPBA (0.1 mmol) was added. 1.5 Hour later, the reaction mixture was quenched with saturated $K_2CO_3$ solution. Then it was extracted using DCM (3 times). The organic parts were concentrated in *vacuum* and provided diastereomeric sulfoxides **8** as white solid in pure form. Further purification by column chromatography was not required for such case. Interestingly, when crude sulfoxides **8** was washed with cold *n*-pentane (3 mL X 2 times) diastereoselectivity of the product got significantly improved from 3:1 to 8:1.

**6. a) Crystal structure of product 4q for absolute stereochemistry determination:**




Single-crystal X-ray diffraction data were collected on a Super Nova, Single source at offset/far, Eos diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data refinement and cell reductions were carried out by CrysAlisPro[5] at 293(2) K. Structures were

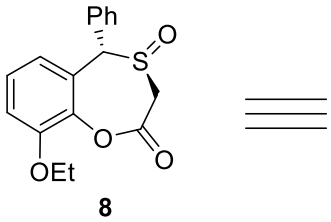
solved by direct methods using SHELXS-97 and refined by the full matrix least squares method using SHELXL-97.[6]

**Table 4. Crystal data and structure refinement for compound 4q**

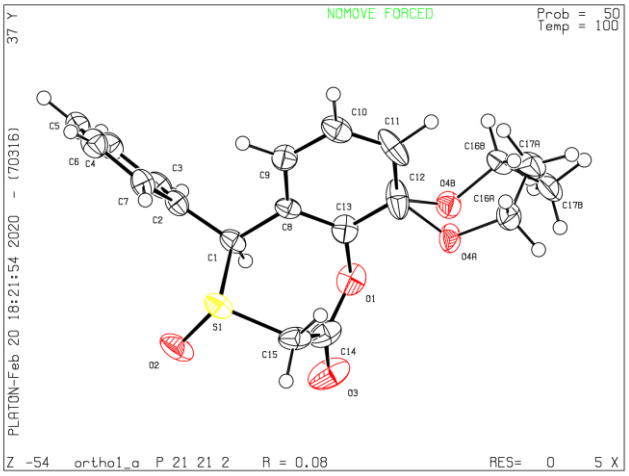
| **Parameters** | **4q** |
|---|---|
| Formula | C15 H12 O2 S |
| Fw | 256.31 |
| Crystal system | orthorhombic |
| Space group | P 21 21 21 |
| a/Å | 7.5756(8) |
| b/Å | 8.7063(6) |
| c/Å | 19.340(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| V/Å$^3$ | 1275.6(2) |
| Z | 4 |
| Dx, g cm-3 | 1.335 |
| Mu (mm-1) | 0.244 |
| F000 | 536.0 |
| T/K | 293 K |
| Theta(max) | 25.000 |

| | |
|---|---|
| Total no. of reflections | 2140 |
| Independent reflections | 1132 |
| Parameters refined | 163 |
| R (reflections) | 0.0683( 1132) |
| wR2 (reflections) | 0.1308( 2140) |
| GOF ($F^2$) | 1.006 |
| CCDC No. | 1969971 |

**b) <u>Crystal structure of product (8):</u>**




**8**




Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection was carried out at 100 K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.[7] The data were scaled and absorption correction performed using SADABS.[7] The structure was

solved by direct methods using SHELXS-18[8] and refined by full-matrix least-squares methods based on $F^2$ using SHELXL-2018.[8]

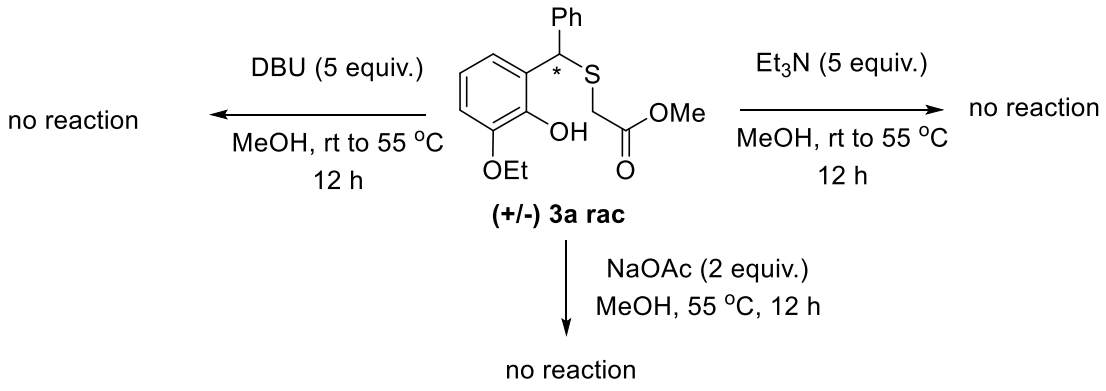
**Table 5. Crystal data and structure refinement for compound 8**

| Parameters | 8 |
|---|---|
| Formula | C17 H16 O4 S |
| Fw | 316.36 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12$ |
| a/Å | 7.969(3) |
| b/Å | 34.663(14) |
| c/Å | 5.361(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| V/Å$^3$ | 1480.9(10) |
| Z | 4 |
| Dx, g cm-3 | 1.419 |
| Mu (mm-1) | 0.234 |
| F000 | 664.0 |
| Crystal size/mm$^3$ | 0.234 × 0.204 × 0.086 |
| 2Θ range for data collection/° | 9.164 to 59.394 |

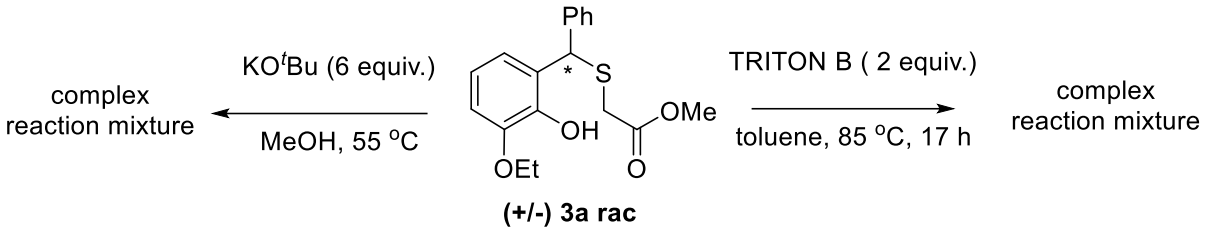
| | |
|---|---|
| Index ranges | $-11 \leq h \leq 11, -48 \leq k \leq 47, -6 \leq l \leq 7$ |
| T/K | 100 K |
| Theta(max) | 29.697 |
| Reflections collected | 12986 |
| Independent reflections | 3818 [Rint = 0.1470, Rsigma = 0.1607] |
| Parameters refined | 265 |
| R (reflections) | 0.0762( 2003) |
| wR2 (reflections) | 0.1915( 3818) |
| Largest diff. peak/hole / e Å-3 | 0.32/-0.54 |
| GOF ($F^2$) | 0.959 |
| CCDC No. | 1984977 |

## 7. Trials for 5-substituted-5*H*-benzoxathiepine-2(3*H*)-one ring synthesis:

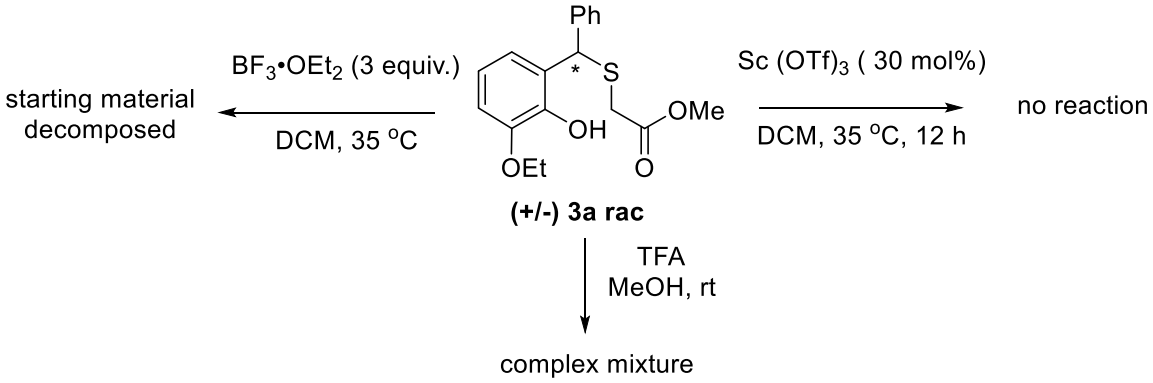
*Treatment of mild bases:*



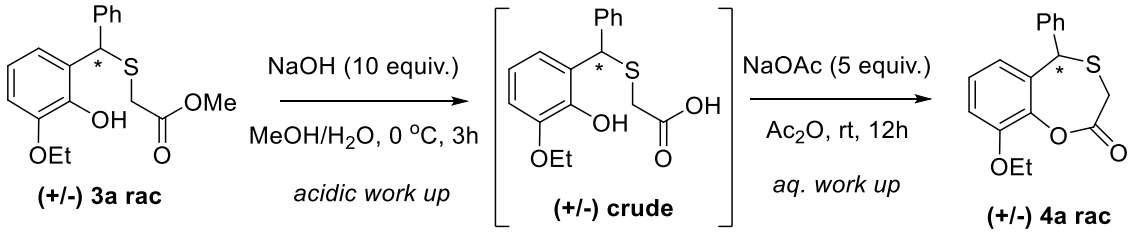
*Treatment of strong bases:*




*Treatment of mild and strong acids:*




*Treatment of hydroxide base and cyclization:*




5-substituted-5*H*-benzoxathiepine-2(3*H*)-one

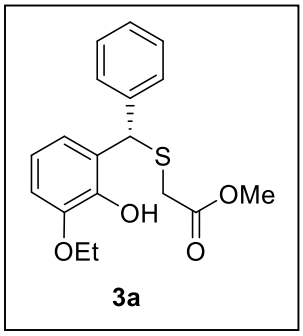
## 8. References:


1. (*a*) B. Meier, J.-N. Dumez, G. Stevanato, J. T. Hill-Cousins, S. S. Roy, P. Håkansson, S. Mamone, R. C. D. Brown, G. Pileio and M. H. Levitt, *J. Am. Chem. Soc.*, 2013, **135**, 18746; (*b*) M.-W. Chen, L.-L. Cao, Z.-S. Ye, G.-F. Jiang and Y.-G. Zhou, *Chem. Commun*., 2013, **49**, 1660.

2. For reviews, see: (*a*) J. Alemán, A. Parra, H. Jiang and K. A. Jørgensen, *Chem. Eur. J*., 2011, **17**, 6890; (*b*) P. Chauhan, S. Mahajan, U. Kaya, D. Hack and D. Enders, *Adv. Synth. Catal*., 2015, **357**, 253.
3. B. Mondal and S. C. Pan, *Synlett*, 2018, **29**, 576.
4. J. E. Rice and Z.-M. He, *J. Org. Chem.*, 1990, **55**, 5490.
5. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.40.23a (Rigaku OD, 2018).
6. G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.
7. APEX 2, SAINT, SADABS Bruker AXS Inc., Madison, WI, USA, 2012.
8. G. M. Sheldrick, 2015, Acta Cryst. C71, 3-8.

## 9. Characterization data of the products:

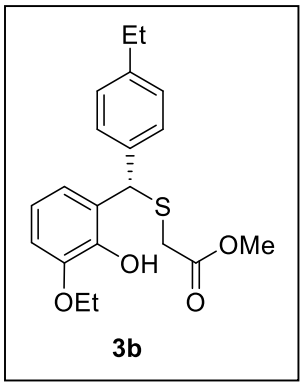
***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3a)***



**3a**

Product **3a** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (31.9 mg, 96% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.3 Hz, 1H), 5.99 (s, 1H), 5.82 (s, 1H), 4.07 (dd, *J* = 9.5, 7.1 Hz, 2H), 3.67 (s, 3H), 3.17 (q, *J* = 14.9 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.9, 145.9, 143.5, 140.4, 128.7, 128.6, 127.4, 126.3, 120.8, 119.8, 110.5, 64.7, 52.5, 47.1, 34.1, 15.1; **HRMS (+ESI):** Calc for $C_{18}H_{24}NO_4S$ $[M+NH_4]^+$ 350.1421; found: 350.1434; The ee value 95% ($t_{minor}$ = 22.9 min, $t_{major}$ = 25.2 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^o$C.

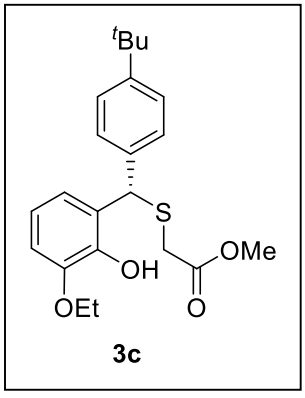
***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(4-ethylphenyl)methyl)thio)acetate (3b)***



**3b**

Product **3b** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (34.6 mg, 96% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 3H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 7.1 Hz, 1H), 5.98 (s, 1H), 5.79 (s, 1H), 4.07 (dd, *J* = 11.3, 7.0 Hz, 2H), 3.66 (s, 3H), 3.16 (q, *J* = 14.9 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.0, 145.9, 143.5, 143.4, 137.5, 128.6, 128.1, 126.5, 120.8, 119.8, 110.5, 64.7, 52.6, 46.9, 34.1, 28.7, 15.6, 15.1; **HRMS (+ESI):** Calc for $C_{20}H_{28}NO_4S$ $[M+NH_4]^+$ 378.1734; found: 378.1731; The ee value 92% ($t_{minor}$ = 12.2 min, $t_{major}$ = 20.9 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((4-(tert-butyl)phenyl)(3-ethoxy-2-hydroxyphenyl)methyl)thio)acetate (3c)***

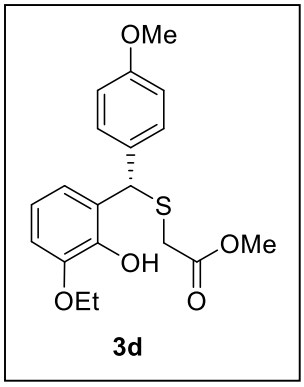


**3c**

Product **3c** was purified by silica gel column chromatography using 4-5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (37.7mg, 97% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.00 (s, 1H), 5.80 (s, 1H), 4.07 (dd, *J* = 10.7, 7.0 Hz, 2H), 3.66 (s, 3H), 3.21 – 3.13 (m, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.28 (s, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.0, 150.2, 145.9, 143.5, 137.3, 128.3, 126.5, 125.6, 120.9, 119.8, 110.5, 64.7, 52.5, 46.8, 34.6, 34.1, 31.5, 15.1; **HRMS (+ESI):** Calc for $C_{22}H_{32}NO_4S$ $[M+NH_4]^+$ 406.2047; found: 406.2045; The ee value

92% ($t_{minor}$ = 12.0 min, $t_{major}$ = 22.0 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (94:6) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

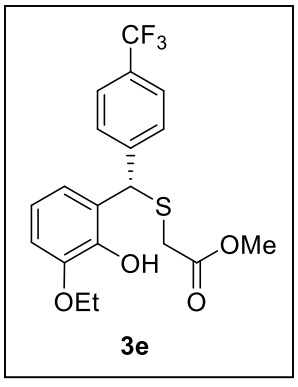
***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(4-methoxyphenyl)methyl)thio)acetate (3d)***



**3d**

Product **3d** was purified by silica gel column chromatography using 6-8% EtOAc in hexane; **Reaction time:** 2 days at room temperature; pale yellow gummy mass (34.4 mg, 95% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 1H), 5.77 (s, 1H), 4.07 (dd, *J* = 10.3, 7.0 Hz, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.15 (q, *J* = 14.9 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.0, 158.9, 146.0, 143.5, 132.4, 129.8, 126.5, 120.7, 119.8, 114.0, 110.5, 64.7, 55.4, 52.5, 46.6, 34.1, 15.1; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_5S$ $[M+NH_4]^+$ 380.1526; found: 380.1517; The ee value 94% ($t_{minor}$ = 13.2 min, $t_{major}$ = 23.8 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)thio)acetate (3e)***

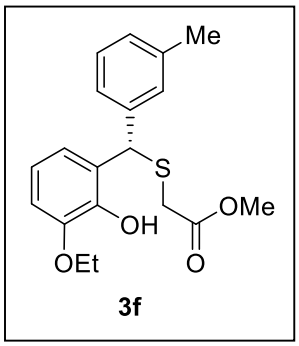


**3e**

Product **3e** was purified by silica gel column chromatography using 6-8% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless oil type (36.0 mg, 90% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 5.96 (s, 1H), 5.85 (s, 1H), 4.08 (dd, *J* = 8.1, 7.2 Hz, 2H), 3.67 (s, 3H), 3.17 (dd, *J* = 39.6, 14.9 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.7, 146.0, 144.7, 143.5, 129.0, 125.6, 125.6, 125.6, 125.5, 120.5, 120.1, 110.8, 64.8, 52.6, 46.8, 34.0, 15.1; **HRMS (+ESI):** Calc for

$C_{19}H_{23}F_3NO_4S$ $[M+NH_4]^+$ 418.1294; found: 418.1290; The ee value 92% ($t_{minor}$ = 11.0 min, $t_{major}$ = 21.2 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

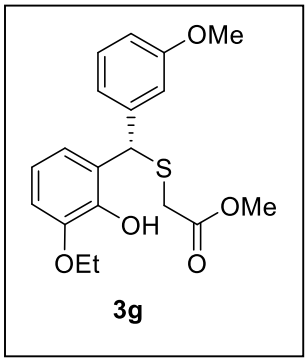
***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(m-tolyl)methyl)thio)acetate (3f)***



**3f**

Product **3f** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (32.6 mg, 94% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.29 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 1H), 5.79 (s, 1H), 4.07 (dd, *J* = 10.3, 7.0 Hz, 2H), 3.67 (s, 3H), 3.17 (q, *J* = 14.9 Hz, 2H), 2.32 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.0, 145.9, 143.5, 140.2, 138.2, 129.3, 128.5, 128.3, 126.3, 125.7, 120.8, 119.8, 110.5, 64.7, 52.5, 47.1, 34.1, 21.7, 15.1; **HRMS (+ESI):** Calc for $C_{19}H_{22}NaO_4S$ $[M+Na]^+$ 369.1131; found: 369.1157; The ee value 93% ($t_{minor}$ = 10.6 min, $t_{major}$ = 13.6 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(3-methoxyphenyl)methyl)thio)acetate (3g)***

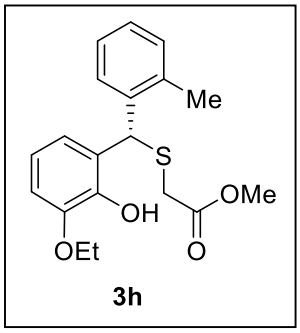


**3g**

Product **3g** was purified by silica gel column chromatography using 6-8% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (34.1 mg, 94% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.21 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 1H), 5.80 (s, 1H), 4.07 (dd, *J* = 8.7, 7.2 Hz, 2H), 3.78 (s, 3H), 3.67 (s, 3H), 3.17 (d, *J* = 6.2 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):**

δ 170.9, 159.8, 145.9, 143.5, 142.0, 129.6, 126.3, 121.1, 120.8, 119.9, 114.4, 112.8, 110.6, 64.7, 55.4, 52.5, 47.1, 34.1, 15.1; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_5S$ $[M+NH_4]^+$ 380.1526; found: 380.1522; The ee value 94% ($t_{minor}$ = 18.6 min, $t_{major}$ = 24.4 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(o-tolyl)methyl)thio)acetate (3h)***

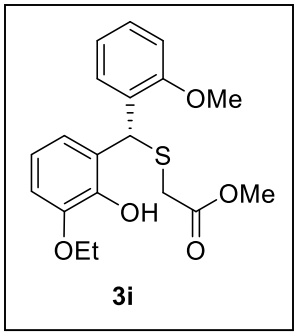


**3h**

Product **3h** was purified by silica gel column chromatography using 3-5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; pale orange gummy mass (34.0 mg, 98% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H), 4.08 (dd, *J* = 6.9, 4.9 Hz, 2H), 3.67 (s, 3H), 3.18 (q, *J* = 14.8 Hz, 2H), 2.42 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.1, 145.9, 143.7, 138.2, 137.0, 130.6, 128.2, 127.4, 126.3, 125.7, 121.3, 119.8, 110.5, 64.7, 52.5, 43.7, 34.2, 19.4, 15.1; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_4S$ $[M+NH_4]^+$ 364.1577; found: 364.1576; The ee value 90% ($t_{minor}$ = 12.8 min, $t_{major}$ = 26.8 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (94:6) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (R)-2-(((3-ethoxy-2-hydroxyphenyl)(2-methoxyphenyl)methyl)thio)acetate (3i)***

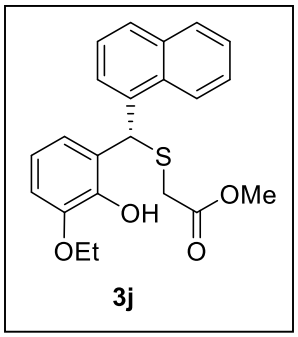
Product **3i** was purified by silica gel column chromatography using 6-8% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (35.2 mg, 97% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.79 (t, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 7.1 Hz,



**3i**

1H), 6.16 (s, 1H), 4.07 (dd, *J* = 6.9, 4.1 Hz, 2H), 3.83 (s, 3H), 3.64 (s, 3H), 3.23 (d, *J* = 2.9 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.9, 157.1, 146.0, 143.8, 129.5, 128.6, 126.3, 121.3, 120.8, 119.5, 111.2, 110.7, 64.7, 56.1, 52.4, 41.1, 34.6, 15.1; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_5S$ $[M+NH_4]^+$ 380.1526; found: 380.1519; The ee value 84% ($t_{minor}$ = 16.3 min, $t_{major}$ = 30.8 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(naphthalen-1-yl)methyl)thio)acetate (3j)***

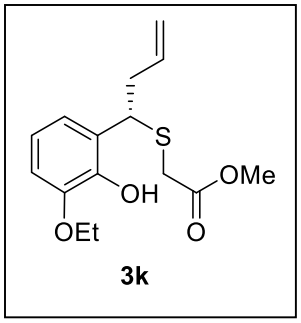


**3j**

Product **3j** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (34.0 mg, 89% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.27 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.42 (m, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.76 – 6.71 (m, 2H), 6.65 (s, 1H), 6.17 (s, 1H), 4.09 (dd, *J* = 7.0, 2.4 Hz, 2H), 3.65 (s, 3H), 3.26 (q, *J* = 15.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.0, 146.0, 143.3, 135.9, 134.2, 131.9, 128.9, 128.3, 126.6, 126.2, 126.2, 125.9, 125.5, 123.8, 121.5, 120.0, 110.7, 64.8, 52.5, 43.4, 34.5, 15.1; The ee value 90% ($t_{minor}$ = 16.5 min, $t_{major}$ = 27.2 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-((1-(3-ethoxy-2-hydroxyphenyl)but-3-en-1-yl)thio)acetate (3k)***

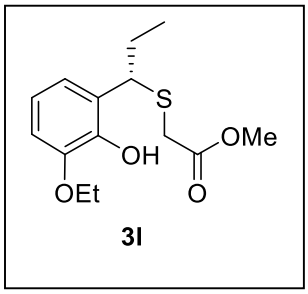
Product **3k** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless oil type (23.1 mg, 78% yield); **$^1$H NMR**



3k

**(600 MHz, $CDCl_3$):** δ 6.95 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 5.77 - 5.71 (m, 1H), 5.06 (dd, *J* = 17.1, 1.4 Hz, 1H), 4.99 (dd, *J* = 10.2, 0.7 Hz, 1H), 4.54 (t, *J* = 7.6 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.65 (s, 3H), 3.12 (d, *J* = 3.7 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.1, 145.9, 143.9, 135.4, 126.5, 120.5, 119.9, 117.2, 110.3, 64.7, 52.5, 42.8, 39.3, 33.1, 15.1; **HRMS (+ESI):** Calc for $C_{15}H_{24}NO_4S$ $[M+NH_4]^+$ 314.1421; found: 314.1430; The ee value 85% ($t_{minor}$ = 9.9 min, $t_{major}$ = 8.3 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

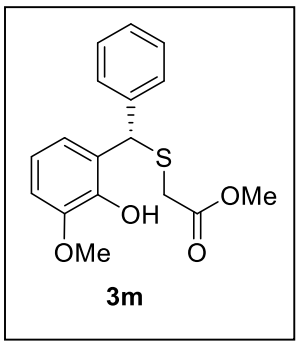
***Methyl (S)-2-((1-(3-ethoxy-2-hydroxyphenyl)propyl)thio)acetate (3l)***



3l

Product **3l** was purified by silica gel column chromatography using 4% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless oil type (25.3 mg, 89% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 6.94 (d, *J* = 7.9 Hz, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 1H), 4.39 (dd, *J* = 8.6, 6.6 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.65 (s, 3H), 3.11 (d, *J* = 2.0 Hz, 2H), 1.98 - 1.86 (m, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.3, 145.8, 144.1, 127.0, 120.4, 119.9, 110.1, 64.7, 52.5, 44.8, 33.1, 28.3, 15.1, 12.4; **HRMS (+ESI):** Calc for $C_{14}H_{24}NO_4S$ $[M+NH_4]^+$ 302.1421; found: 302.1437; The ee value 84% ($t_{minor}$ = 8.3 min, $t_{major}$ = 7.4 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

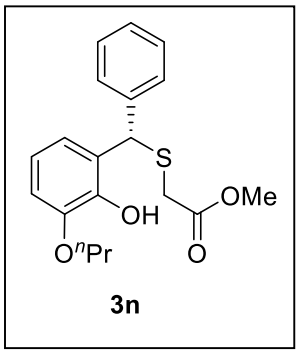
***Methyl (S)-2-(((2-hydroxy-3-methoxyphenyl)(phenyl)methyl)thio)acetate (3m)***



**3m**

Product **3m** was purified by silica gel column chromatography using 3% EtOAc in hexane; **Reaction time:** 2 days at room temperature; pale yellow gummy mass (29.9 mg, 94% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 1H), 5.81 (s, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 3.17 (q, *J* = 14.9 Hz, 2H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.9, 146.8, 143.5, 140.4, 128.7, 128.6, 127.5, 126.4, 121.0, 119.9, 109.8, 56.3, 52.5, 47.2, 34.1; **HRMS (+ESI):** Calc for $C_{17}H_{22}NO_4S$ $[M+NH_4]^+$ 336.1264; found: 336.1258; The ee value 96% ($t_{minor}$ = 15.3 min, $t_{major}$ = 26.2 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (88:12) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((2-hydroxy-3-propoxyphenyl)(phenyl)methyl)thio)acetate (3n)***

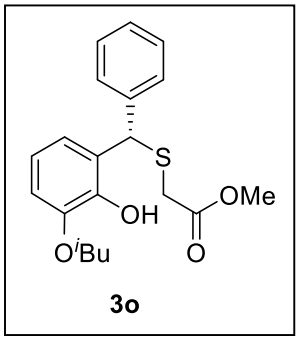


**3n**

Product **3n** was purified by silica gel column chromatography using 5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (28.8 mg, 83% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.1 Hz, 1H), 5.97 (s, 1H), 5.83 (s, 1H), 4.01 – 3.92 (m, 2H), 3.67 (s, 3H), 3.17 (q, *J* = 14.9 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.9, 146.0, 143.5, 140.4, 128.7, 128.6, 127.4, 126.3, 120.7, 119.8, 110.5, 70.6, 52.5, 47.1, 34.1, 22.8, 10.7; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_4S$ $[M+NH_4]^+$ 364.1577; found: 364.1578; The ee value

94% ($t_{minor}$ = 8.9 min, $t_{major}$ = 13.1 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (85:15) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((2-hydroxy-3-isobutoxyphenyl)(phenyl)methyl)thio)acetate (3o)***

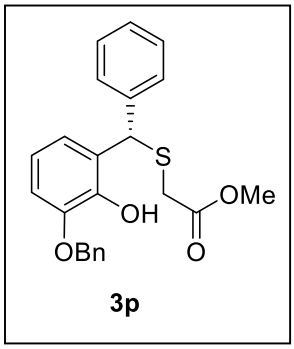


**3o**

Product **3o** was purified by silica gel column chromatography using 5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (31.0 mg, 86% yield); **$^1$H NMR (600 MHz, CDCl$_3$):** δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 5.94 (s, 1H), 5.83 (s, 1H), 3.77 (dd, *J* = 11.3, 6.6 Hz, 2H), 3.67 (s, 3H), 3.17 (q, *J* = 14.9 Hz, 2H), 2.14 – 2.07 (m, 1H), 1.03 (d, *J* = 2.5 Hz, 3H), 1.02 (d, *J* = 2.4 Hz, 3H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 170.9, 146.1, 143.5, 140.4, 128.7, 128.6, 127.4, 126.3, 120.7, 119.9, 110.5, 75.4, 52.5, 47.1, 34.1, 28.4, 19.4; **HRMS (+ESI):** Calc for $C_{20}H_{28}NO_4S$ $[M+NH_4]^+$ 378.1734; found: 378.1733; The ee value 90% ($t_{minor}$ = 7.3 min, $t_{major}$ = 8.5 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (85:15) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-(benzyloxy)-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3p)***

Product **3p** was purified by silica gel column chromatography using 5% EtOAc in hexane;

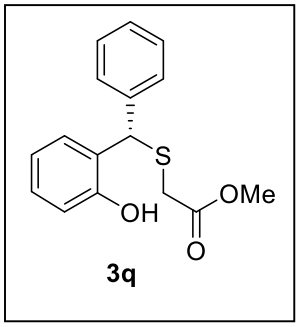


**3p**

**Reaction time:** 2 days at room temperature; colorless gummy mass (32.0 mg, 81% yield); **$^1$H NMR (600 MHz, CDCl$_3$):** δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.83 (d, *J* = 4.4 Hz, 2H), 6.01 (s, 1H), 5.83 (s, 1H), 5.08 (d, *J* = 5.1 Hz, 2H), 3.66 (s, 3H), 3.18 (q, *J* = 14.9 Hz, 2H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 170.9, 145.9, 143.6, 140.3, 136.4, 128.9, 128.7, 128.6, 128.6, 128.0, 127.5, 126.6, 121.3, 119.9, 111.2, 71.4, 52.5, 47.1, 34.1; **HRMS (+ESI):** Calc for $C_{23}H_{26}NO_4S$ $[M+NH_4]^+$

412.1577; found: 412.1576; The ee value 90% ($t_{minor}$ = 20.5 min, $t_{major}$ = 17.8 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (85:15) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^{o}$C.

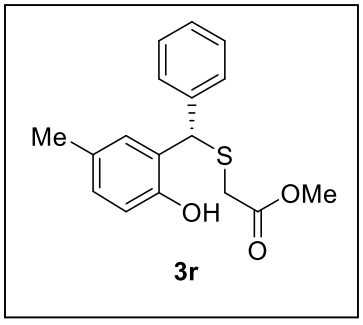
***Methyl (S)-2-(((2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3q)***



**3q**

Product **3q** was purified by silica gel column chromatography using 5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; pale yellow gummy mass (27.4 mg, 95% yield); **$^{1}$H NMR (600 MHz, CDCl$_3$):** δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.81 (t, *J* = 7.5 Hz, 1H), 5.53 (s, 1H), 3.76 (s, 3H), 3.21 (d, *J* = 1.8 Hz, 2H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 171.8, 155.0, 139.5, 138.3, 129.5, 129.5, 129.2, 128.9, 128.0, 125.6, 120.8, 117.6, 114.3, 53.2, 49.8, 33.6; **HRMS (+ESI):** Calc for $C_{16}H_{16}NaO_3S$ $[M+Na]^+$ 311.0712; found: 311.0713; The ee value 88% ($t_{minor}$ = 22.2 min, $t_{major}$ = 24.1 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (94:6) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^{o}$C.

***Methyl (S)-2-(((2-hydroxy-5-methylphenyl)(phenyl)methyl)thio)acetate (3r)***

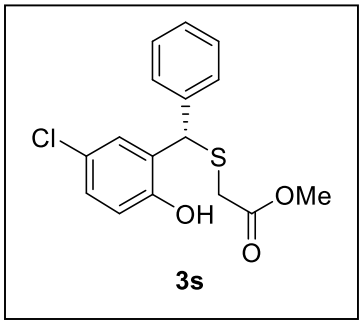


**3r**

Product **3r** was purified by silica gel column chromatography using 3-5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (26.9 mg, 89% yield); **$^{1}$H NMR (600 MHz, CDCl$_3$):** δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.75 (s, 1H), 5.53 (s, 1H), 3.75 (s, 3H), 3.19 (d, *J* = 2.1 Hz, 2H), 2.18 (s, 3H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 171.6, 152.6, 138.6, 130.0, 130.0, 130.0, 129.2, 128.9, 127.9, 125.3, 117.5, 53.0,

49.9, 33.7, 20.8; **HRMS (+ESI):** Calc for $C_{17}H_{18}NaO_3S$ $[M+Na]^+$ 325.0869; found: 325.0881; The ee value 90% ($t_{minor}$ = 10.9 min, $t_{major}$ = 12.2 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (94:6) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

***Methyl (S)-2-(((5-chloro-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3s)***

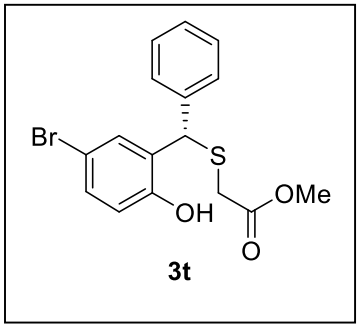


**3s**

Product **3s** was purified by silica gel column chromatography using 8-10% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (31.6 mg, 98% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (s, 1H), 7.47 (s, 1H), 7.39 (t, *J* = 7.4 Hz, 3H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.89 (dd, *J* = 7.5, 5.6 Hz, 2H), 5.47 (s, 1H), 3.77 (s, 3H), 3.21 (d, *J* = 3.9 Hz, 2H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.9, 153.6, 137.6, 129.3, 129.2, 129.1, 129.0, 128.3, 127.6, 125.5, 118.9, 53.3, 49.2, 33.6; **HRMS (+ESI):** Calc for $C_{16}H_{15}ClNaO_3S$ $[M+Na]^+$ 345.0323; found: 345.0297; The ee value 84% ($t_{minor}$ = 12.8 min, $t_{major}$ = 15.5 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

***Methyl (S)-2-(((5-bromo-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3t)***

Product **3t** was purified by silica gel column chromatography using 8-10% EtOAc in hexane;

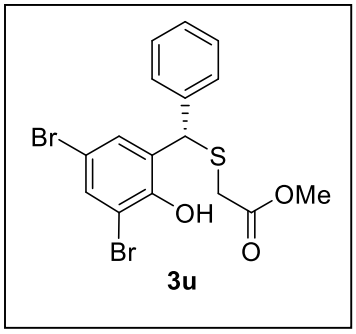


**3t**

**Reaction time:** 2 days at room temperature; colorless gummy mass (36.0 mg, 98% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.44 (s, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 2.2 Hz, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 5.47 (s, 1H), 3.77 (s, 3H), 3.21 (d, *J* = 4.1 Hz, 2H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.9, 154.1, 137.6, 132.2, 131.9, 129.1, 129.1, 128.3, 128.1, 119.4, 112.7, 53.3, 49.2, 33.6; **HRMS (+ESI):** Calc for $C_{16}H_{15}BrNaO_3S$ $[M+Na]^+$ 388.9817;

found: 388.9821; The ee value 82% ($t_{minor}$ = 13.0 min, $t_{major}$ = 16.5 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^{o}$C.

***Methyl (S)-2-(((3,5-dibromo-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3u)***

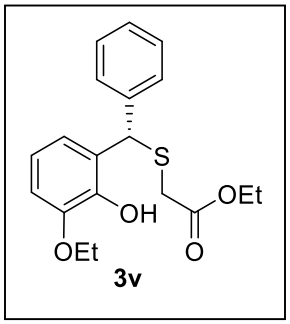


**3u**

Product **3u** was purified by silica gel column chromatography using 6-8% EtOAc in hexane; **Reaction time:** 2 days at room temperature; colorless gummy mass (44.2 mg, 99% yield); **$^{1}$H NMR (600 MHz, CDCl$_3$):** δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.45 (s, 1H), 7.43 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.76 (s, 1H), 5.63 (s, 1H), 3.73 (s, 3H), 3.18 (d, *J* = 6.9 Hz, 2H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 171.2, 150.0, 138.3, 133.9, 131.4, 129.8, 129.0, 128.9, 128.2, 112.8, 112.0, 53.0, 48.4, 33.8; **HRMS (+ESI):** Calc for $C_{16}H_{18}Br_2NO_3S$ $[M+NH_4]^+$ 461.9369; found: 461.9381; The ee value 62% ($t_{minor}$ = 13.8 min, $t_{major}$ = 17.9 min) was determined by HPLC analysis using Daicel Chiralpak IB with *n*-hexane/*i*-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^{o}$C.

***Ethyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3v)***

Product **3v** was purified by silica gel column chromatography using 3-5% EtOAc in hexane;

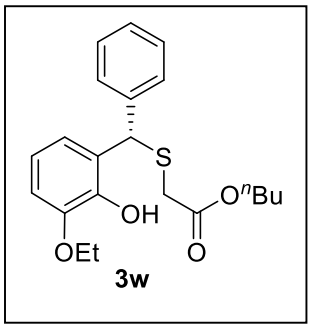


**3v**

**Reaction time:** 2 days at room temperature; pale yellow gummy mass (31.9 mg, 92% yield); **$^{1}$H NMR (600 MHz, CDCl$_3$):** δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.3 Hz, 1H), 5.99 (s, 1H), 5.85 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.11 – 4.04 (m, 2H), 3.14 (q, *J* = 14.8 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 170.5, 146.0, 143.6, 140.5, 128.7, 128.6, 127.4, 126.4, 120.9, 119.8, 110.6, 64.8, 61.5, 47.1, 34.3,

15.1, 14.3; **HRMS (+ESI):** Calc for $C_{19}H_{26}NO_4S$ $[M+NH_4]^+$ 364.1577; found: 364.1572; The ee value 92% ($t_{minor}$ = 7.8 min, $t_{major}$ = 11.9 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

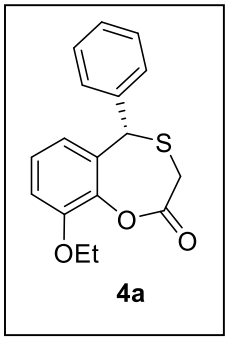
***Butyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)thio)acetate (3w)***



**3w**

Product **3w** was purified by silica gel column chromatography using 3-5% EtOAc in hexane; **Reaction time:** 2 days at room temperature; yellow oil type (36.7 mg, 98% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 5.85 (s, 1H), 4.08 (dd, *J* = 11.8, 5.2 Hz, 4H), 3.15 (q, *J* = 14.9 Hz, 2H), 1.62 (dd, *J* = 14.7, 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.38 (t, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 170.6, 146.0, 143.6, 140.5, 128.7, 128.6, 127.4, 126.4, 120.9, 119.8, 110.6, 65.4, 64.8, 47.1, 34.3, 30.8, 19.3, 15.1, 13.9; **HRMS (+ESI):** Calc for $C_{21}H_{30}NO_4S$ $[M+NH_4]^+$ 392.1890; found: 392.1883; The ee value 92% ($t_{minor}$ = 7.1 min, $t_{major}$ = 12.5 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***(S)-9-ethoxy-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4a)***

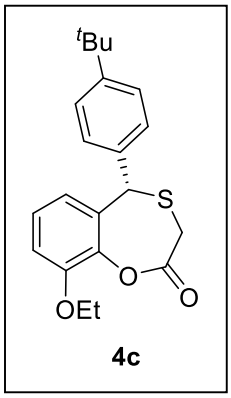


**4a**

Product **4a** was purified by silica gel column chromatography using 2-3% EtOAc in hexane; white solid (15.6 mg, 52% yield); **M.P.** = 93-94 °C; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.49 (s, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.73 (s, 1H), 4.09 (dd, *J* = 7.0, 2.4 Hz, 2H), 3.36 (d, *J* = 12.0 Hz, 1H), 3.14 (d, *J* = 12.0 Hz, 1H), 1.43 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.4, 149.8, 139.4,

136.0, 131.1, 129.6, 129.0, 128.7, 127.5, 119.3, 113.7, 65.2, 46.6, 30.4, 15.0; **HRMS (+ESI):** Calc for $C_{17}H_{20}NO_3S$ $[M+NH_4]^+$ 318.1158; found: 318.1175; The ee value 94% ($t_{minor}$ = 14.2 min, $t_{major}$ = 13.3 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

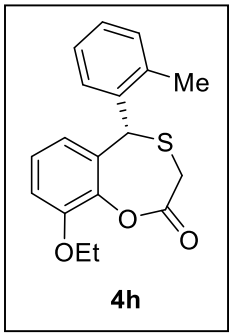
***(S)-5-(4-(tert-butyl)phenyl)-9-ethoxy-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4c)***



**4c**

Product **4c** was purified by silica gel column chromatography using 2% EtOAc in hexane; white solid (22.8 mg, 64% yield); **M.P.** = 204-205 °C; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 5.1 Hz, 4H), 7.11 (t, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.71 (s, 1H), 4.09 (dd, *J* = 7.0, 2.4 Hz, 2H), 3.35 (d, *J* = 12.0 Hz, 1H), 3.12 (d, *J* = 12.0 Hz, 1H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 9H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.5, 151.7, 149.7, 139.3, 132.8, 131.2, 129.3, 127.5, 125.9, 119.3, 113.5, 65.1, 46.2, 34.9, 31.5, 30.5, 15.0; **HRMS (+ESI):** Calc for $C_{21}H_{28}NO_3S$ $[M+NH_4]^+$ 374.1784; found: 374.1789; The ee value 81% ($t_{minor}$ = 22.7 min, $t_{major}$ = 16.3 min) was determined by HPLC analysis using Daicel Chiralpak IE with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***(S)-9-ethoxy-5-(o-tolyl)-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4h)***

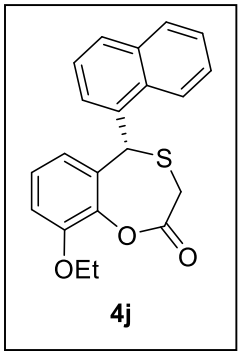


**4h**

Product **4h** was purified by silica gel column chromatography using 1-2% EtOAc in hexane; white solid (23.0 mg, 73% yield); **M.P.** = 156-157 °C; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 5.94 (s, 1H), 4.10 (dd, *J* = 6.9, 5.3 Hz, 2H), 3.36 (d, *J* = 12.0 Hz, 1H), 3.16 (d, *J* = 12.0 Hz, 1H), 2.13 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.6, 149.5, 139.5, 137.0, 134.2, 131.2, 130.5, 129.2,

128.5, 127.6, 126.4, 118.7, 113.5, 65.0, 42.7, 30.4, 19.6, 15.0; **HRMS (+ESI):** Calc for $C_{18}H_{22}NO_3S$ $[M+NH_4]^+$ 332.1315; found: 332.1302; The ee value 68% ($t_{minor}$ = 22.0 min, $t_{major}$ = 15.1 min) was determined by HPLC analysis using Daicel Chiralpak IE with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

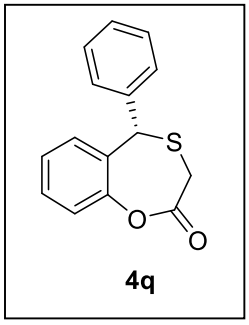
***(S)-9-ethoxy-5-(naphthalen-1-yl)-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4j)***



**4j**

Product **4j** was purified by silica gel column chromatography using 3% EtOAc in hexane; white solid (25.2 mg, 72% yield); **M.P.** = 207-208 $^oC$; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 17.0, 7.4 Hz, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 6.21 (d, *J* = 7.6 Hz, 1H), 4.11 (dd, *J* = 6.9, 4.4 Hz, 2H), 3.43 (d, *J* = 11.9 Hz, 1H), 3.25 (d, *J* = 11.9 Hz, 1H), 1.47 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.6, 149.5, 139.1, 134.1, 131.7, 131.3, 131.0, 129.3, 129.1, 127.8, 127.3, 126.9, 126.2, 125.3, 123.5, 118.9, 113.4, 65.0, 42.4, 30.5, 15.0; **HRMS (+ESI):** Calc for $C_{21}H_{22}NO_3S$ $[M+NH_4]^+$ 368.1315; found: 368.1311; The ee value 70% ($t_{minor}$ = 20.3 min, $t_{major}$ = 18.6 min) was determined by HPLC analysis using Daicel Chiralpak IE with *n*-hexane/*i*-PrOH (85:15) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

***(S)-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4q)***

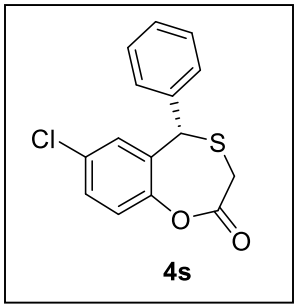


**4q**

Product **4q** was purified by silica gel column chromatography using 2-3% EtOAc in hexane; colorless solid (14.1 mg, 55% yield); **M.P.** = 157-158 $^oC$; **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 6.8 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.75 (s, 1H), 3.34 (d, *J* = 12.1 Hz, 1H), 3.15 (d,

*J* = 12.1 Hz, 1H); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.3, 150.3, 135.9, 129.9, 129.6, 129.1, 128.8, 128.4, 127.5, 120.3, 46.4, 30.3; **HRMS (+ESI):** Calc for $C_{15}H_{16}NO_2S$ $[M+NH_4]^+$ 274.0896; found: 274.0899; The ee value 84% ($t_{minor}$ = 15.0 min, $t_{major}$ = 7.7 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

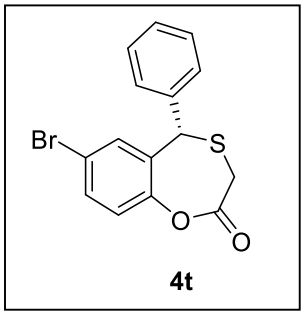
***(S)-7-chloro-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4s)***



**4s**

Product **4s** was purified by silica gel column chromatography using 1-2% EtOAc in hexane; colorless gummy mass (19.5 mg, 67% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.50 – 7.40 (m, 5H), 7.29 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 5.70 (s, 1H), 3.36 (d, *J* = 12.1 Hz, 1H), 3.17 (d, *J* = 12.2 Hz, 1H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.7, 148.7, 135.0, 132.9, 131.6, 129.6, 129.5, 129.3, 129.2, 128.3, 121.7, 46.1, 30.3; **HRMS (+ESI):** Calc for $C_{15}H_{15}ClNO_2S$ $[M+NH_4]^+$ 308.0507; found: 308.0524; The ee value 81% ($t_{minor}$ = 16.3 min, $t_{major}$ = 10.2 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 $^oC$.

***(S)-7-bromo-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4t)***

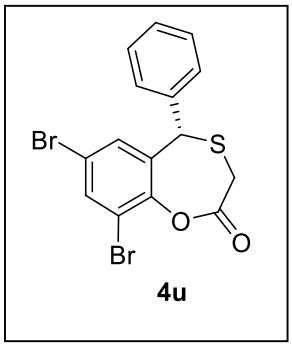


**4t**

Product **4t** was purified by silica gel column chromatography using 1-2% EtOAc in hexane; colorless gummy mass (21.1 mg, 63% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.47 (t, *J* = 6.5 Hz, 3H), 7.44 (d, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 2.2 Hz, 1H), 5.69 (s, 1H), 3.35 (d, *J* = 12.2 Hz, 1H), 3.17 (d, *J* = 12.2 Hz, 1H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 149.3, 135.0, 132.6, 132.0, 131.3, 129.5, 129.3, 129.2, 122.1, 120.5, 46.1, 30.3; **HRMS (+ESI):** Calc for $C_{15}H_{15}BrNO_2S$ $[M+NH_4]^+$ 352.0001;

found: 352.0016; The ee value 78% ($t_{minor}$ = 15.6 min, $t_{major}$ = 10.9 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (95:5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

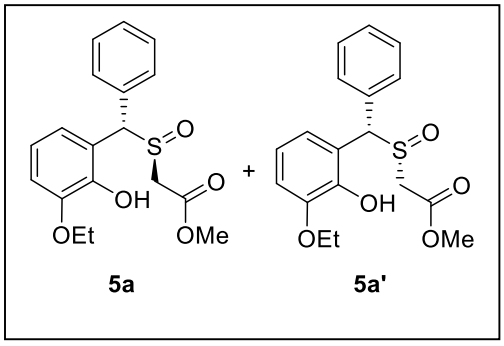
***(S)-7,9-dibromo-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one (4u)***



**4u**

Product **4u** was purified by silica gel column chromatography using 2-3% EtOAc in hexane; colorless gummy mass (30.6 mg, 74% yield); **$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.41 (m, 5H), 6.96 (d, *J* = 2.1 Hz, 1H), 5.70 (s, 1H), 3.30 (d, *J* = 12.3 Hz, 1H), 3.20 (d, *J* = 12.3 Hz, 1H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 165.3, 146.5, 135.5, 134.5, 133.3, 130.3, 129.5, 129.4, 120.6, 116.1, 46.4, 30.3; **HRMS (+ESI):** Calc for $C_{15}H_{14}Br_2NO_2S$ $[M+NH_4]^+$ 429.9107; found: 429.9109; The ee value 72% ($t_{minor}$ = 9.6 min, $t_{major}$ = 7.8 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (93:7) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl 2-((S)-((S)-(3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)sulfinyl)acetate (5a) & methyl 2-((R)-((S)-(3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)sulfinyl)acetate (5a')***

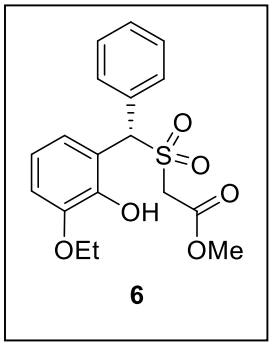


**5a** **5a'**

Products **5a and 5a'** were inseparable in silica gel column chromatography, purified by using 40% EtOAc in hexane; **Reaction time:** 1.5 h at 0 °C; pale orange gummy mass (27.2 mg, 78% yield); **Diastereomeric ratio:** 1:1; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.69 (s, 1H), 5.64 (s, 1H), 4.09 (dd, *J* = 14.4, 7.3 Hz, 4H), 3.74 (s, 3H), 3.72 (s,

3H), 3.64 (d, *J* = 14.5 Hz, 1H), 3.60 (s, 2H), 3.48 (d, *J* = 14.5 Hz, 1H), 1.45 – 1.42 (m, 6H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.3, 166.3, 146.7, 146.3, 144.6, 143.5, 135.7, 134.4, 129.9, 129.3, 129.1, 128.9, 128.5, 128.5, 122.1, 121.6, 120.9, 120.4, 120.3, 120.3, 111.9, 111.5, 65.5, 65.0, 64.8, 64.8, 55.2, 54.6, 53.0, 52.95, 15.04, 15.0; **HRMS (+ESI):** Calc for $C_{18}H_{20}NaO_5S$ $[M+Na]^+$ 371.0924; found: 371.0927; The ee value of one diastereomer 94% ($t_{minor}$ = 67.7 min, $t_{major}$ = 38.5 min) and ee value of other diastereomer 93% ($t_{minor}$ = 148.7 min, $t_{major}$ = 42.5 min) were determined by HPLC analysis using Lux® 5 μm Amylose-2 with *n*-hexane/EtOH (85:15) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***Methyl (S)-2-(((3-ethoxy-2-hydroxyphenyl)(phenyl)methyl)sulfonyl)acetate (6)***

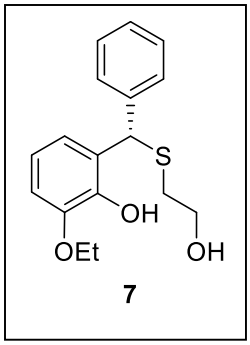


**6**

Product **6** was purified by silica gel column chromatography using 25-30% EtOAc in hexane; **Reaction time:** 1.5 h at 0 °C; pale orange gummy mass (21.1 mg, 58% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.34 (m, 3H), 6.91 (t, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 6.08 (s, 1H), 4.09 (dd, *J* = 10.6, 7.0 Hz, 2H), 3.92 (s, 2H), 3.80 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 163.6, 146.1, 144.4, 132.1, 130.6, 129.2, 129.1, 121.2, 120.3, 118.6, 111.9, 65.1, 64.8, 55.8, 53.4, 15.0; **HRMS (+ESI):** Calc for $C_{18}H_{24}NO_6S$ $[M+NH_4]^+$ 382.1319; found: 382.1325; The ee value 92% ($t_{minor}$ = 25.7 min, $t_{major}$ = 31.5 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***(S)-2-ethoxy-6-(((2-hydroxyethyl)thio)(phenyl)methyl)phenol (7)***

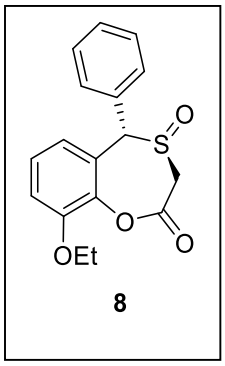
Product **7** was purified by silica gel column chromatography using 15-20% EtOAc in hexane; **Reaction time:** 2.5 h at -60°C to room temperature; pale orange gummy mass (27.1 mg, 89% yield); **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t,



**7**

*J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 1H), 5.69 (s, 1H), 4.11 – 4.05 (m, 2H), 3.76 – 3.69 (m, 2H), 2.66 (t, *J* = 4.7 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 145.8, 143.1, 141.0, 128.7, 128.6, 127.3, 127.2, 120.9, 120.0, 110.3, 64.7, 60.4, 45.8, 35.6, 15.1; **HRMS (+ESI):** Calc for $C_{17}H_{20}NaO_3S$ $[M+Na]^+$ 327.1025; found: 327.1028; The ee value 92% ($t_{minor}$ = 8.9 min, $t_{major}$ = 9.4 min) was determined by HPLC analysis using Lux® 5 μm Amylose-1 with *n*-hexane/*i*-PrOH (80:20) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

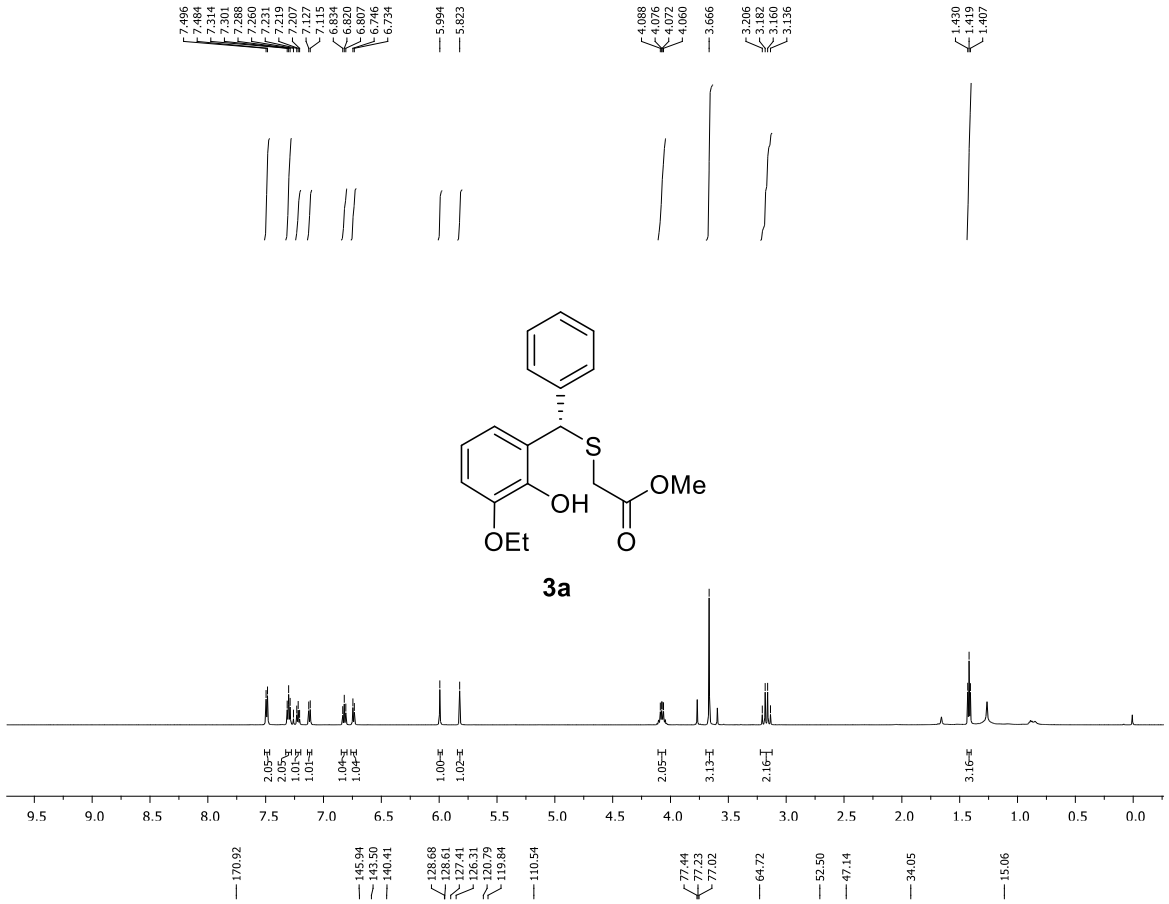
***(4S,5S)-9-ethoxy-5-phenyl-5H-benzo[f][1,4]oxathiepin-2(3H)-one 4-oxide (8)***

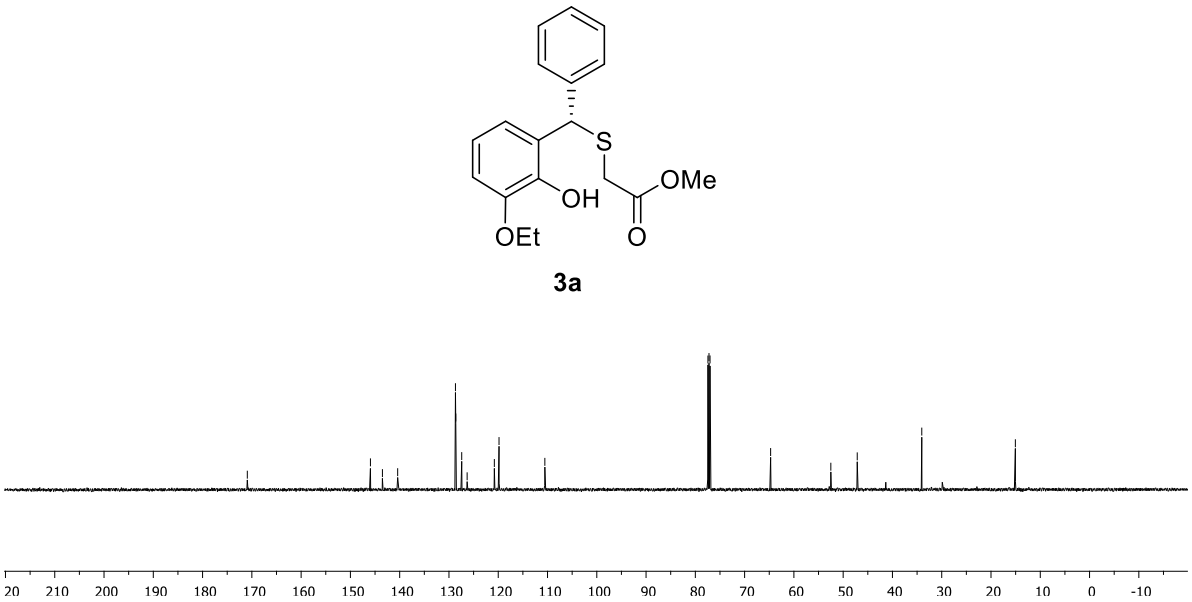


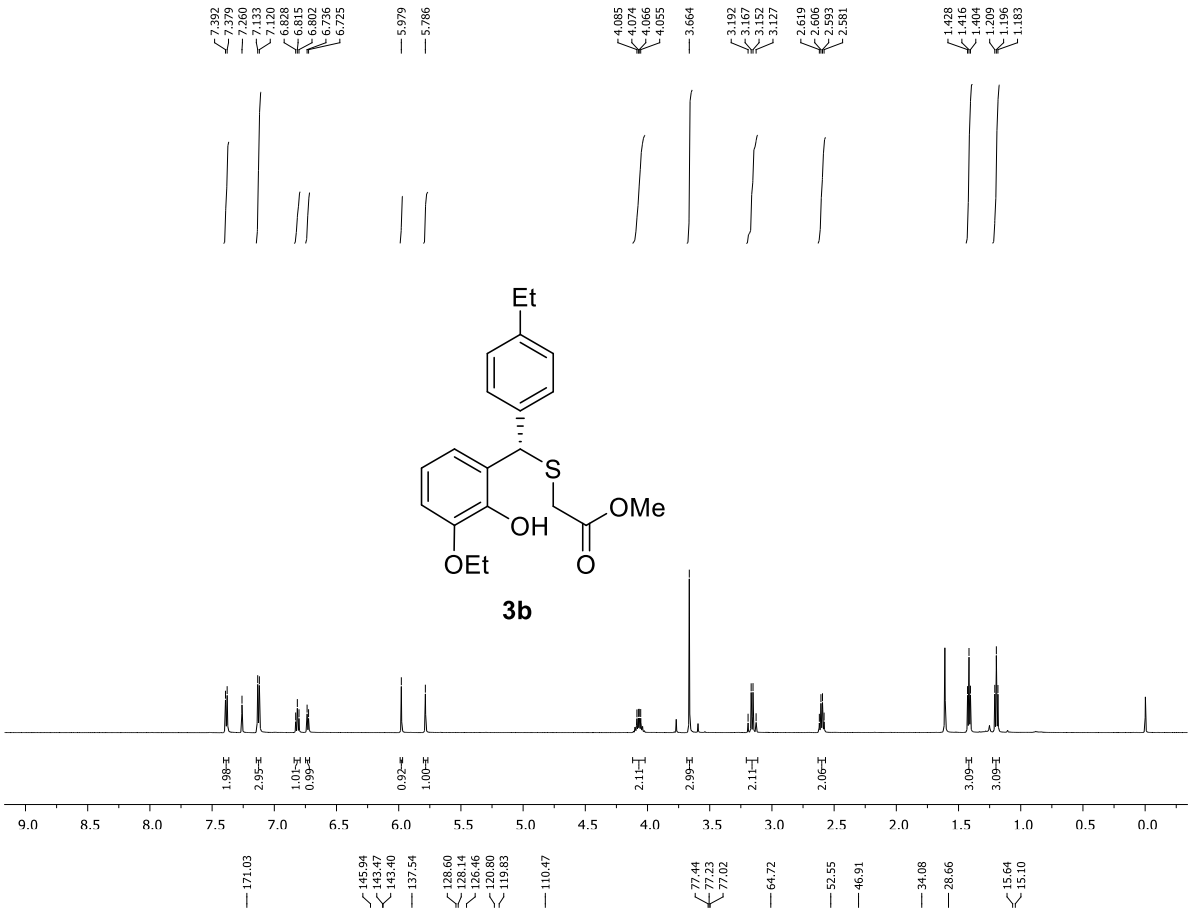
**8**

**Reaction time:** 1.5 h at 0 °C; white solid (22.2 mg, 70% yield); **M.P.** = 161-162 °C; **Diastereomeric ratio:** 8:1; **$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.52 – 7.42 (m, 5H), 7.10 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.48 (s, 1H), 4.10 (dd, *J* = 6.9, 1.4 Hz, 2H), 3.84 (d, *J* = 12.9 Hz, 1H), 3.68 (d, *J* = 12.9 Hz, 1H), 1.45 (t, *J* = 7.0 Hz, 3H); **$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 161.5, 150.2, 140.1, 131.8, 130.5, 130.1, 129.7, 129.4, 127.0, 121.0, 115.1, 70.5, 65.2, 51.6, 14.9; **HRMS (+ESI):** Calc for $C_{17}H_{17}O_4S$ $[M+H]^+$ 317.0842; found: 317.0844; The ee value of major diastereomer 90% ($t_{minor}$ = 67.0 min, $t_{major}$ = 36.4 min) was determined by HPLC analysis using Daicel Chiralpak ID with *n*-hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

## 10. Copies of NMR spectra of the products:

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4.066
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3.664
3.192
3.167
3.152
3.127
2.619
2.606
2.593
2.581
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1.416
1.404
1.209
1.196
1.183
Et
S
OMe
OH
OEt
O
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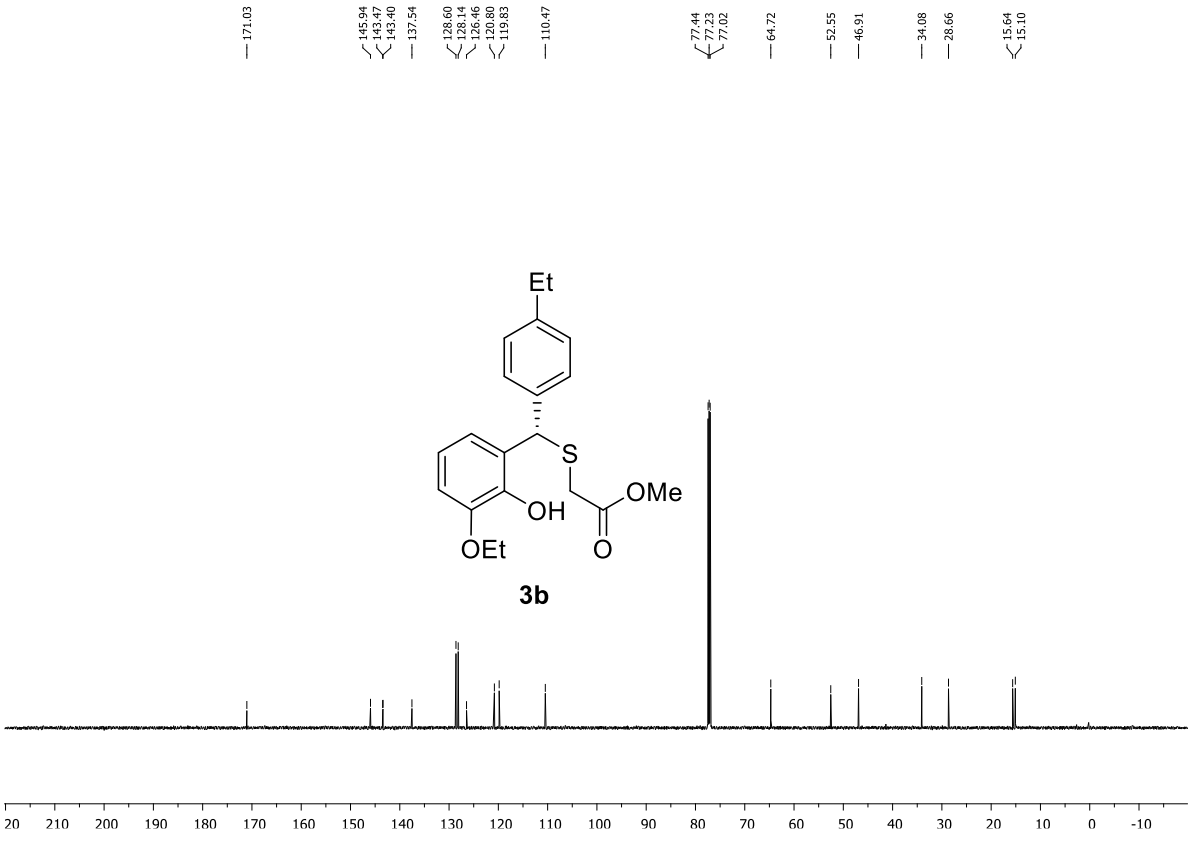
2.95
1.01
0.99
0.92
1.00
2.11
2.99
2.11
2.06
3.09
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

**3b**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119.83
110.47
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77.02
64.72
52.55
46.91
34.08
28.66
15.64
15.10
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S
OMe
OH
OEt
O
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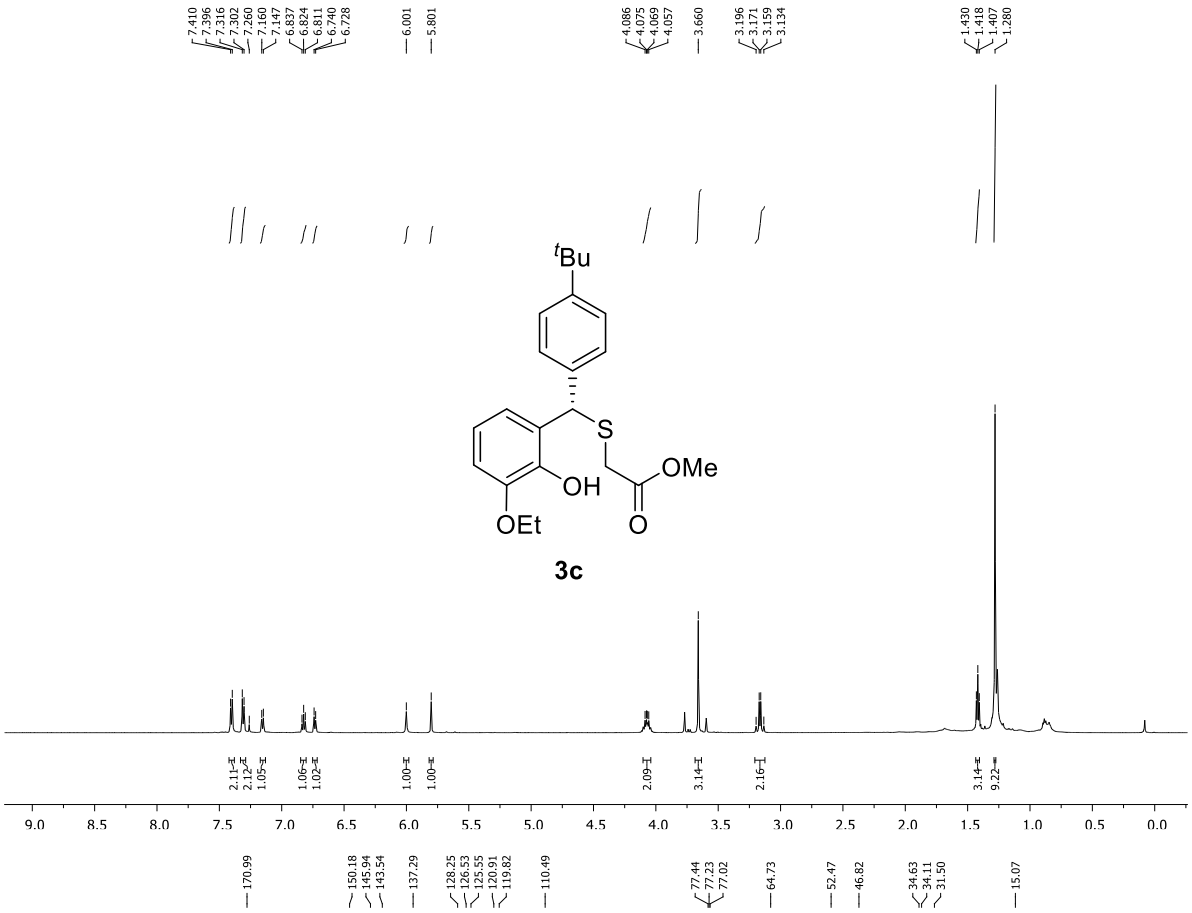
**3b**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4.057
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3.159
3.134
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2.12
1.05
1.06
1.02
1.00
1.00
2.09
3.14
2.16
3.14
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9.0
8.5
8.0
7.5
7.0
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6.0
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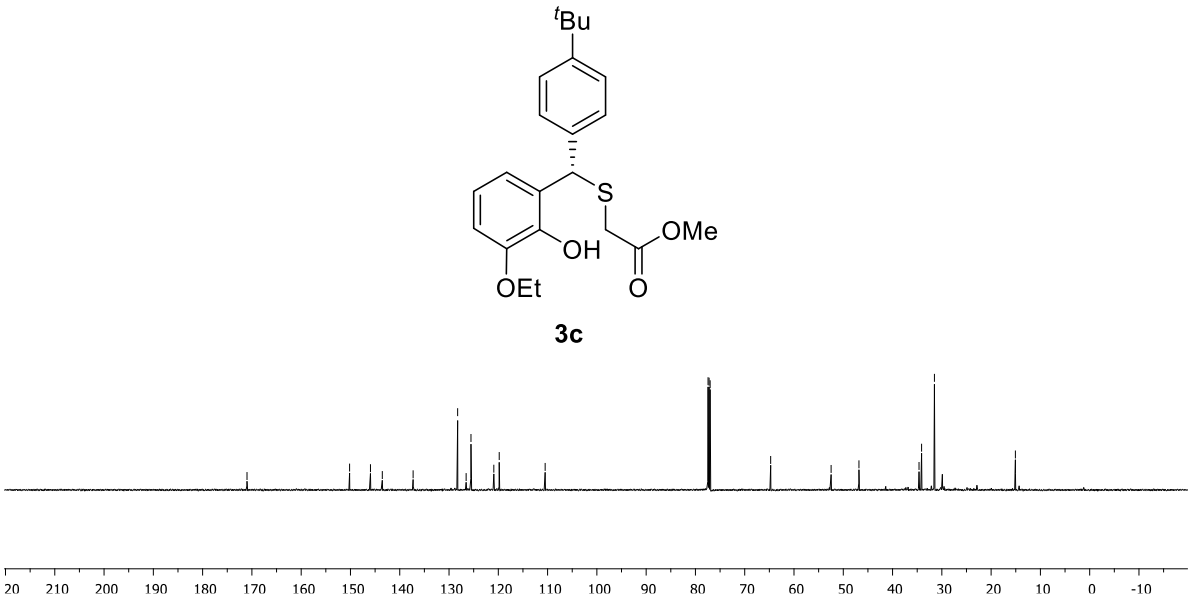
0.0

**3c**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126.53
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110.49
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77.23
77.02
64.73
52.47
46.82
34.63
34.11
31.50
15.07
tBu
S
OMe
OH
OEt
O
220
210
200
190
180
170
160
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80
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60
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40
30
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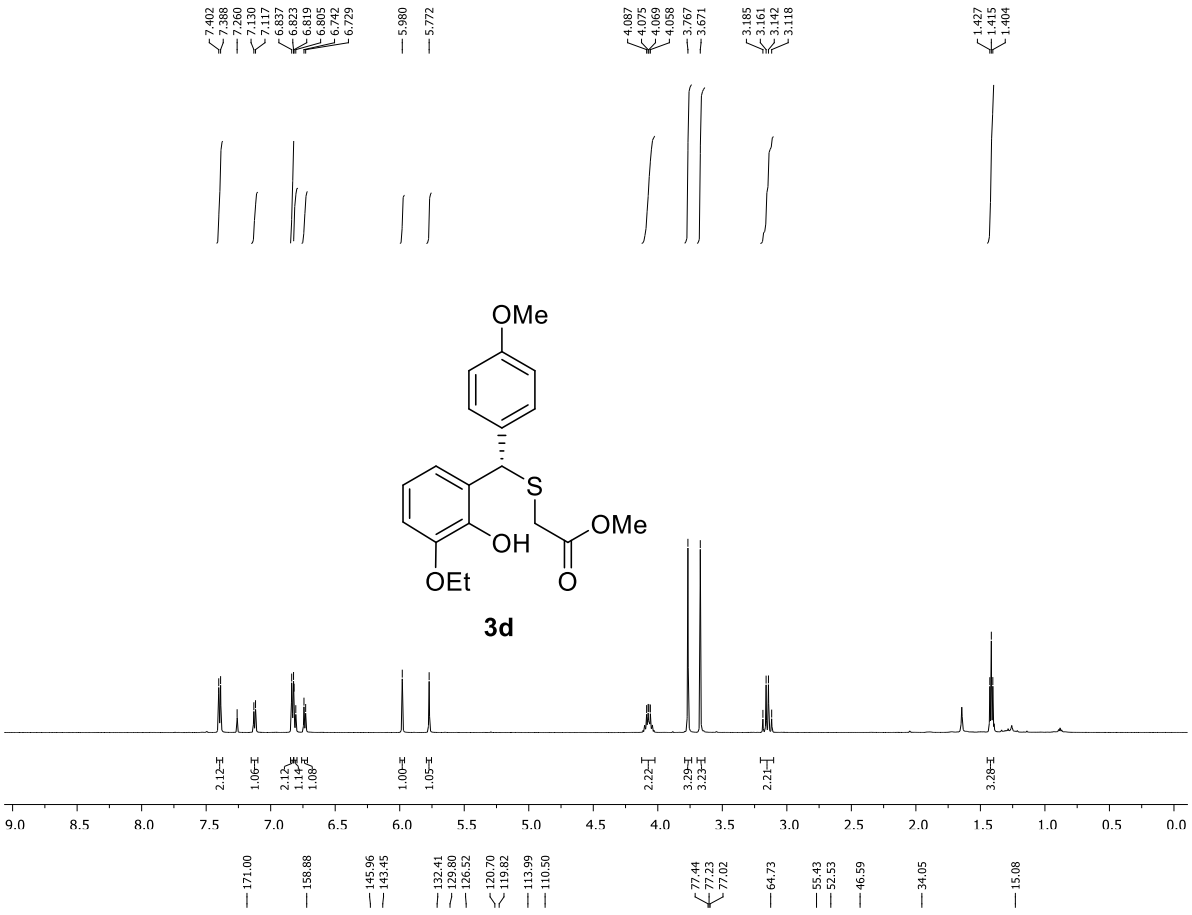
10
0
-10

**3c**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4.087
4.075
4.069
4.058
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3.671
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1.415
1.404
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S
OMe
OH
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O
3d
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2.12
1.14
1.08
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1.05
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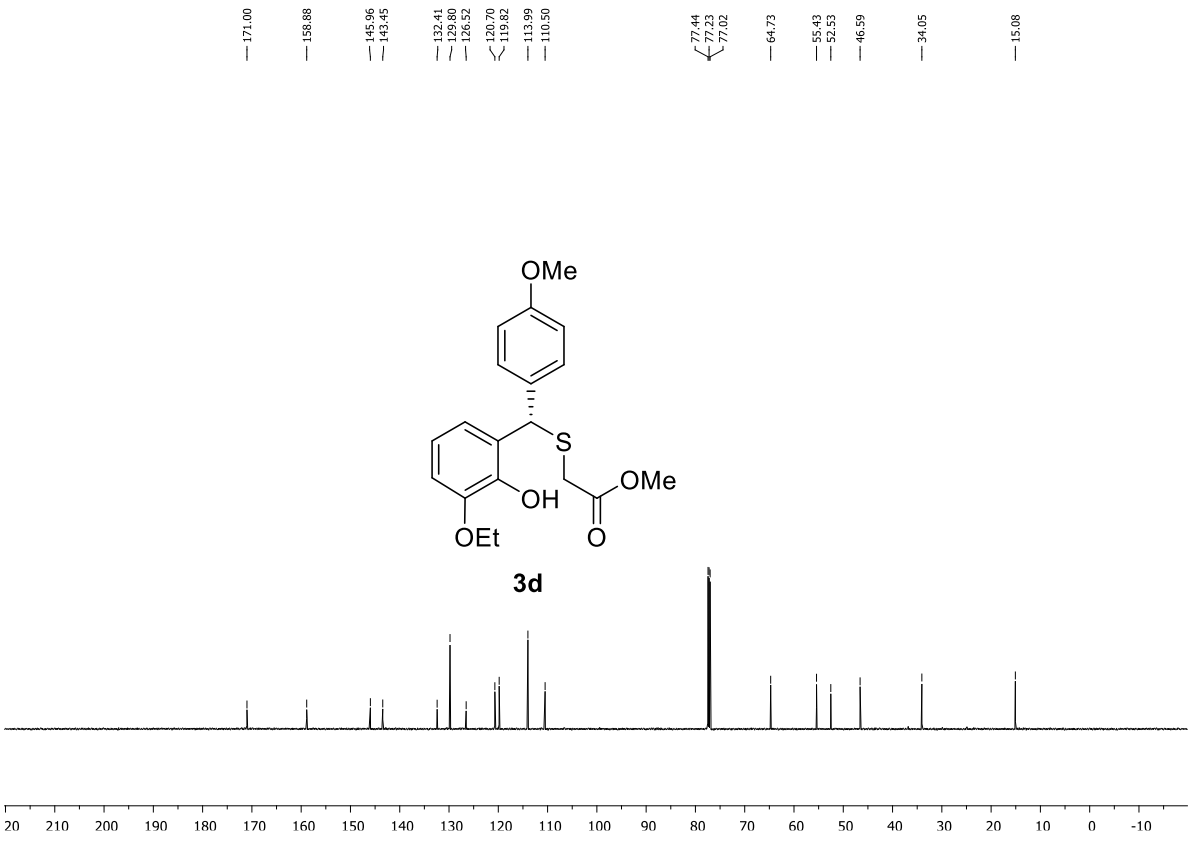
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52.53
46.59
34.05
15.08
OMe
S
OMe
OH
OEt
O
3d
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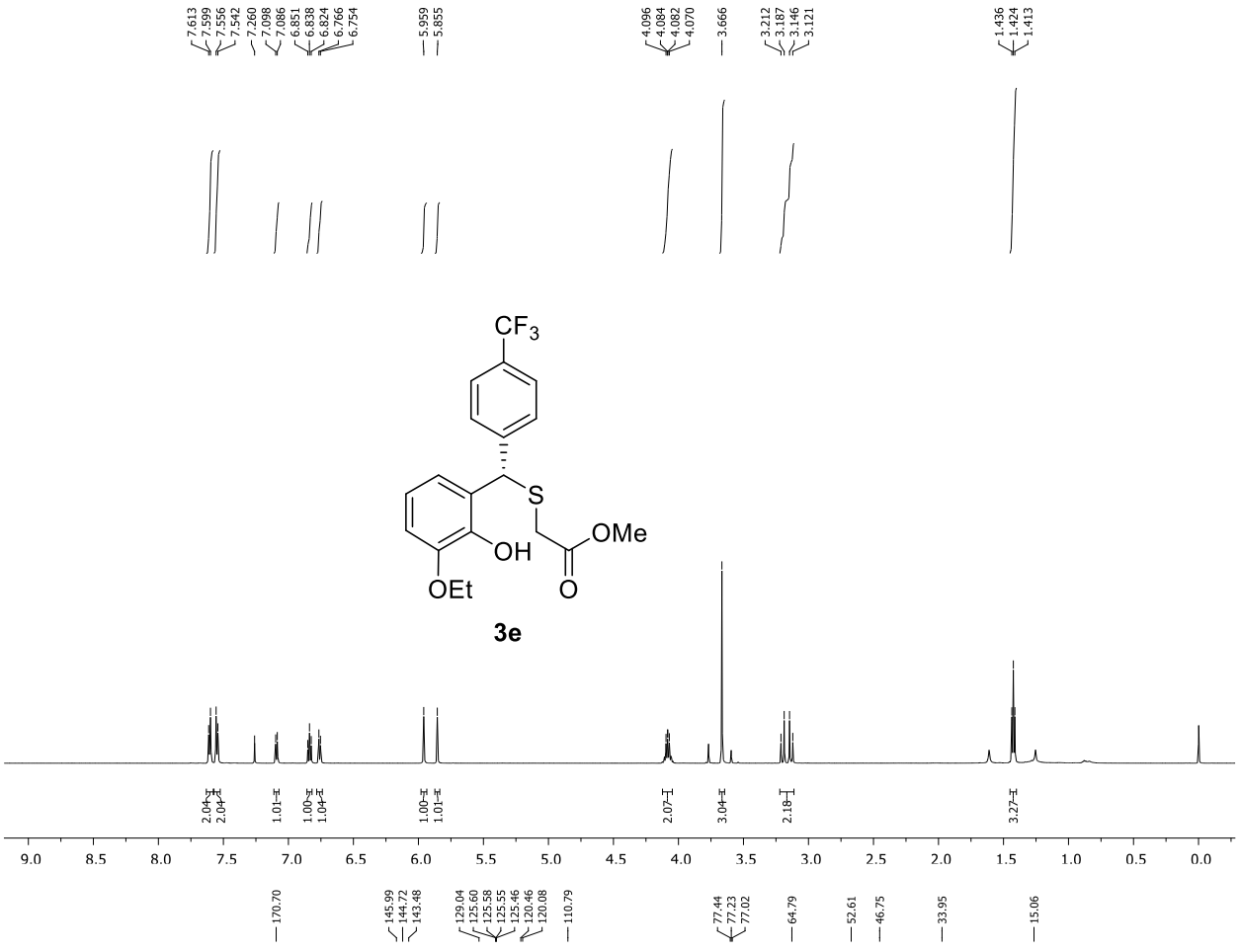
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4.070
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3.187
3.146
3.121
1.436
1.424
1.413
CF3
S
OH
OMe
OEt
O
3e
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2.04
1.01
1.00
1.04
1.00
1.01
2.07
3.04
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8.0
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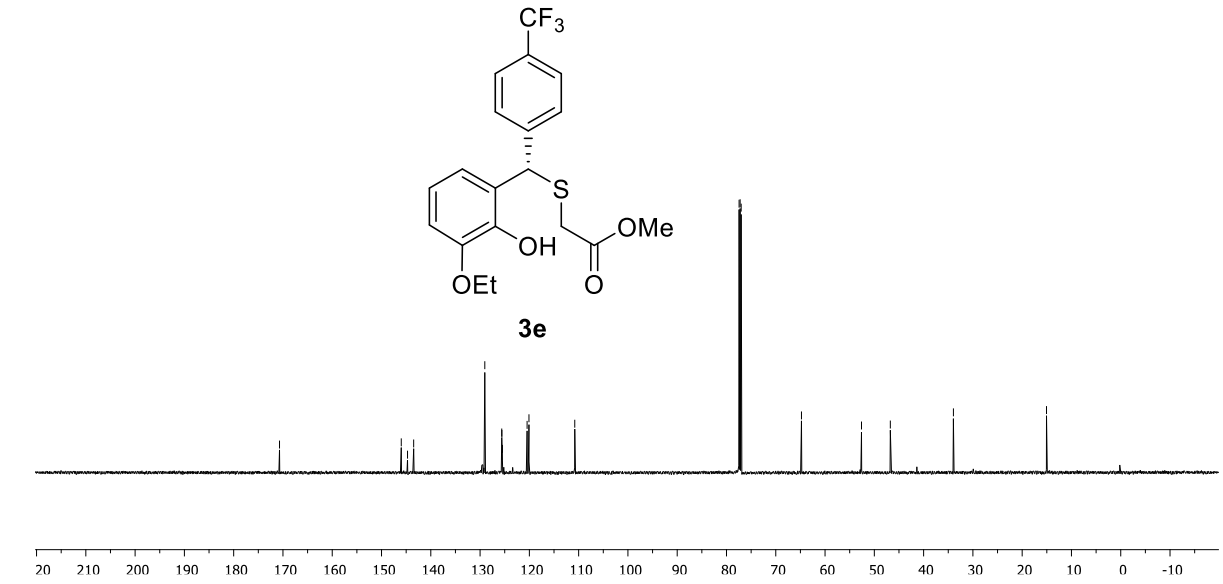
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46.75
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15.06
CF3
S
OH
OMe
OEt
O
3e
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200
190
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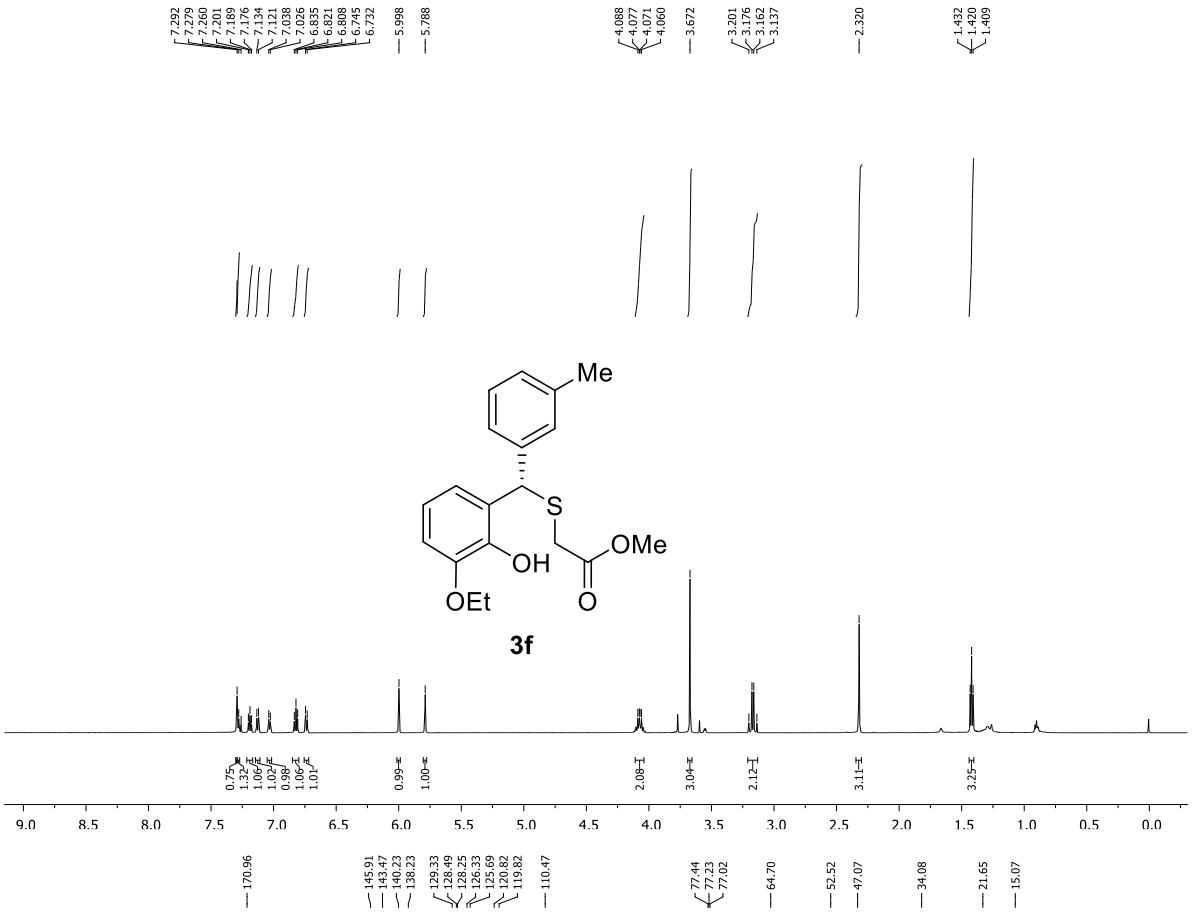
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7.121
7.038
7.026
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6.821
6.808
6.745
6.732
5.998
5.788
4.088
4.077
4.071
4.060
3.672
3.201
3.176
3.162
3.137
2.320
1.432
1.420
1.409
Me
S
OH
OMe
OEt
O
3f
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1.32
1.06
1.02
0.98
1.06
1.01
0.99
1.00
2.08
3.04
2.12
3.11
3.25
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6.0
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5.0
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4.0
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3.0
2.5
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1.5
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0.0


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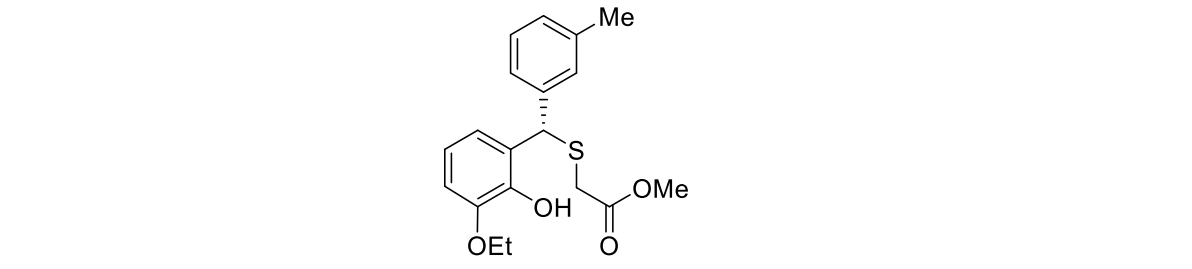
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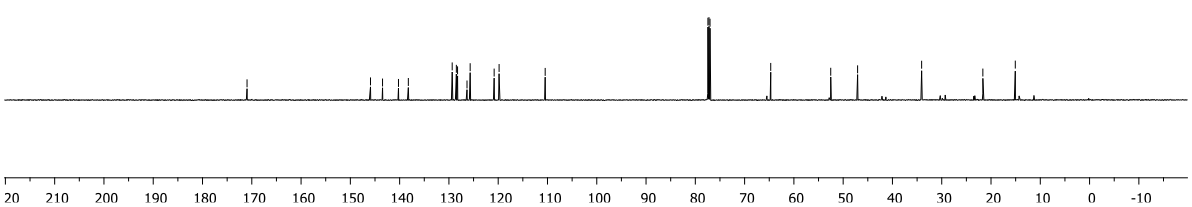
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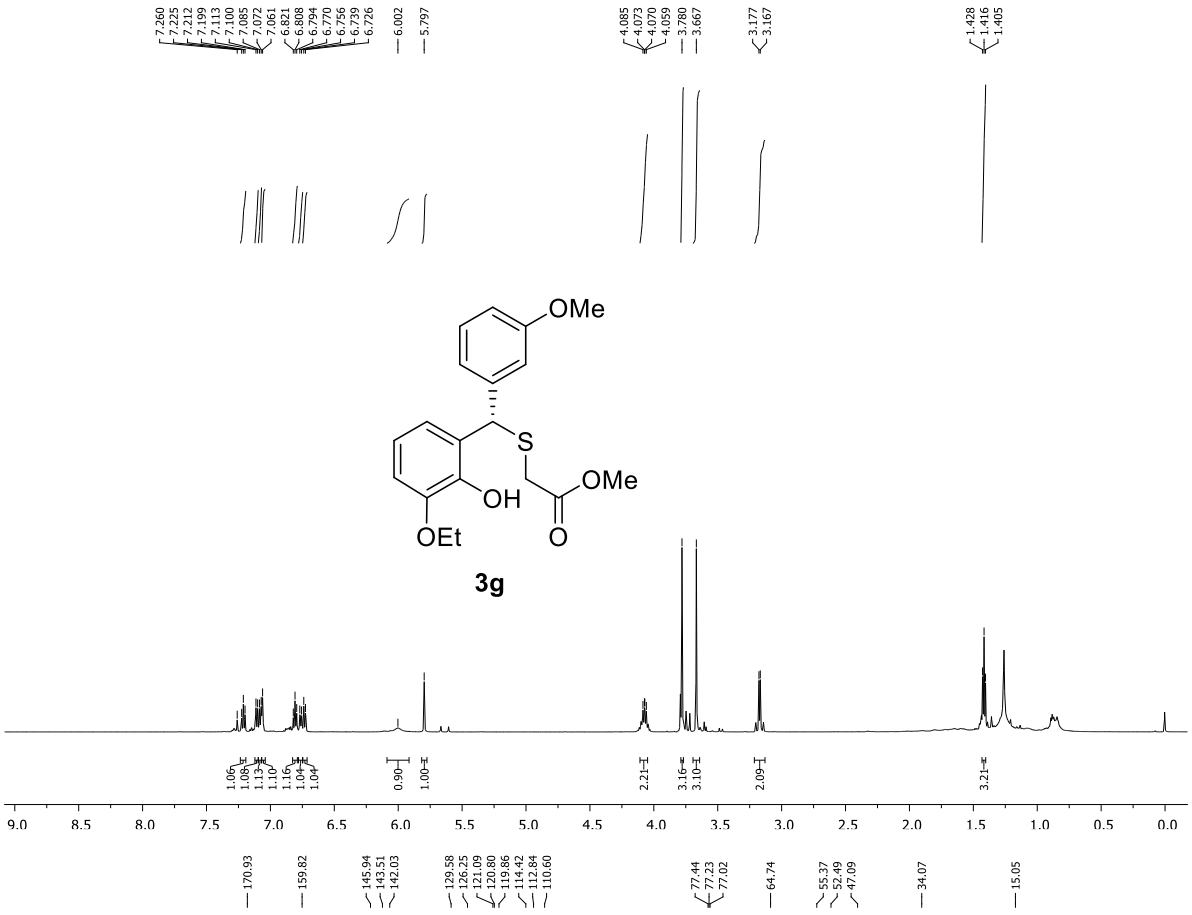
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7.072
7.061
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6.808
6.794
6.770
6.756
6.739
6.726
6.002
5.797
4.085
4.073
4.070
4.059
3.780
3.667
3.177
3.167
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1.416
1.405
OMe
S
OH
OMe
OEt
O
3g
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1.08
1.13
1.10
1.16
1.04
1.04
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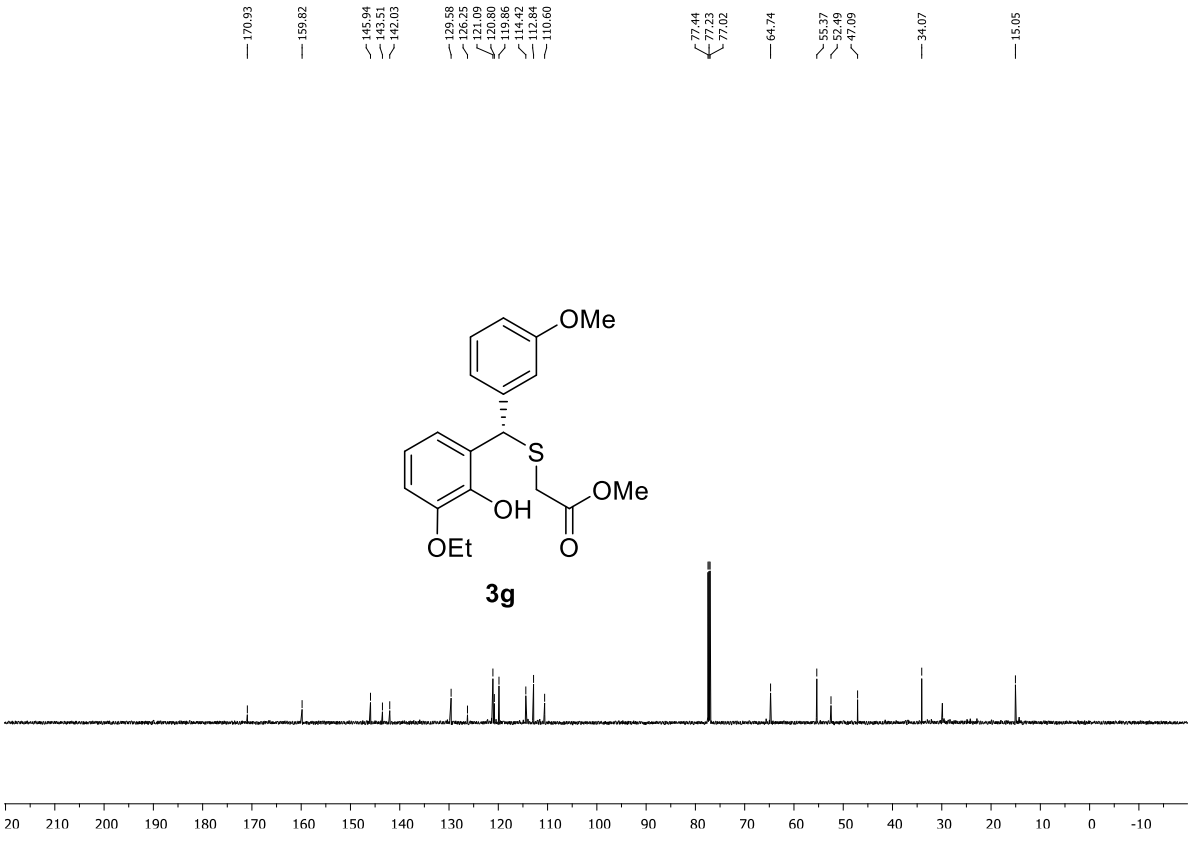
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77.23
77.02
64.74
55.37
52.49
47.09
34.07
15.05
OMe
S
OH
OMe
OEt
O
3g
220
210
200
190
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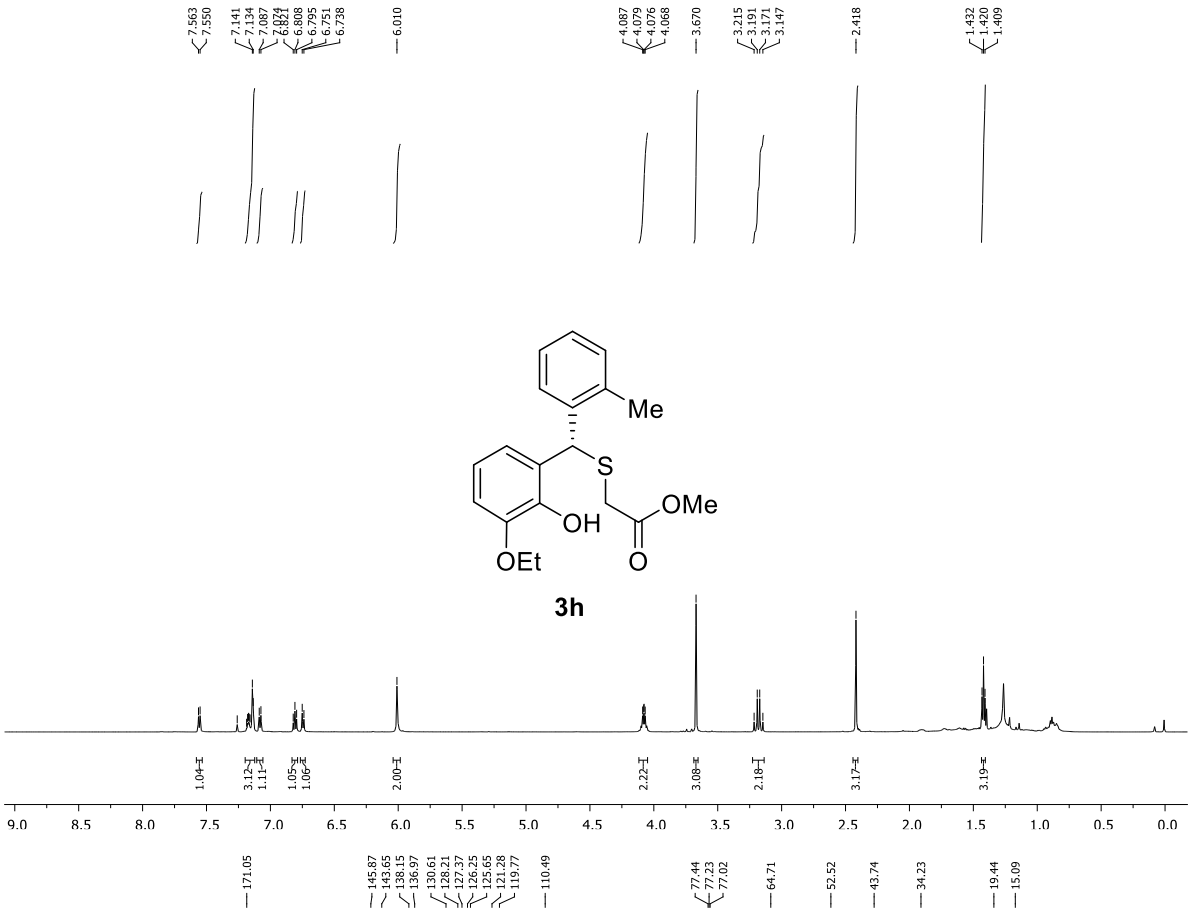
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6.738
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4.079
4.076
4.068
3.670
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3.191
3.171
3.147
2.418
1.432
1.420
1.409
Me
S
OMe
OH
OEt
O
1.04
3.12
1.11
1.05
1.06
2.00
2.22
3.08
2.18
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8.0
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1.0
0.5
0.0

**3h**


171.05
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127.37
126.25
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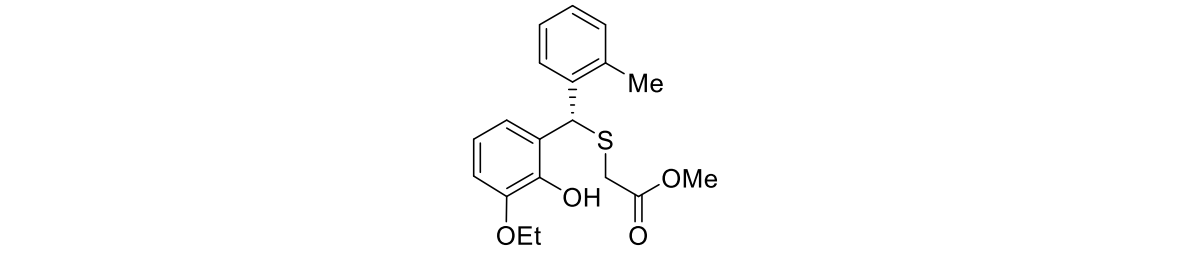
15.09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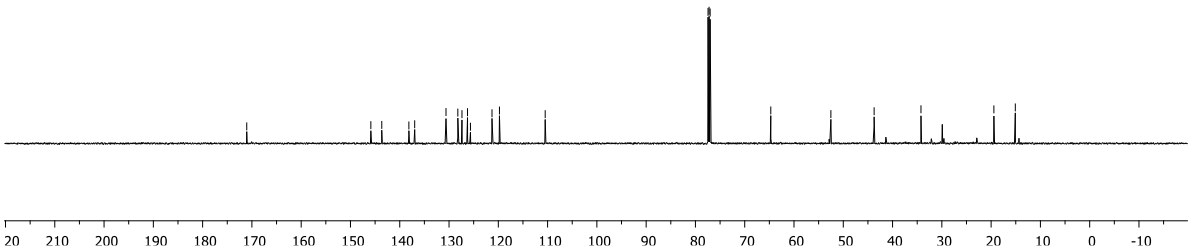
S
OMe
OH
OEt
O

**3h**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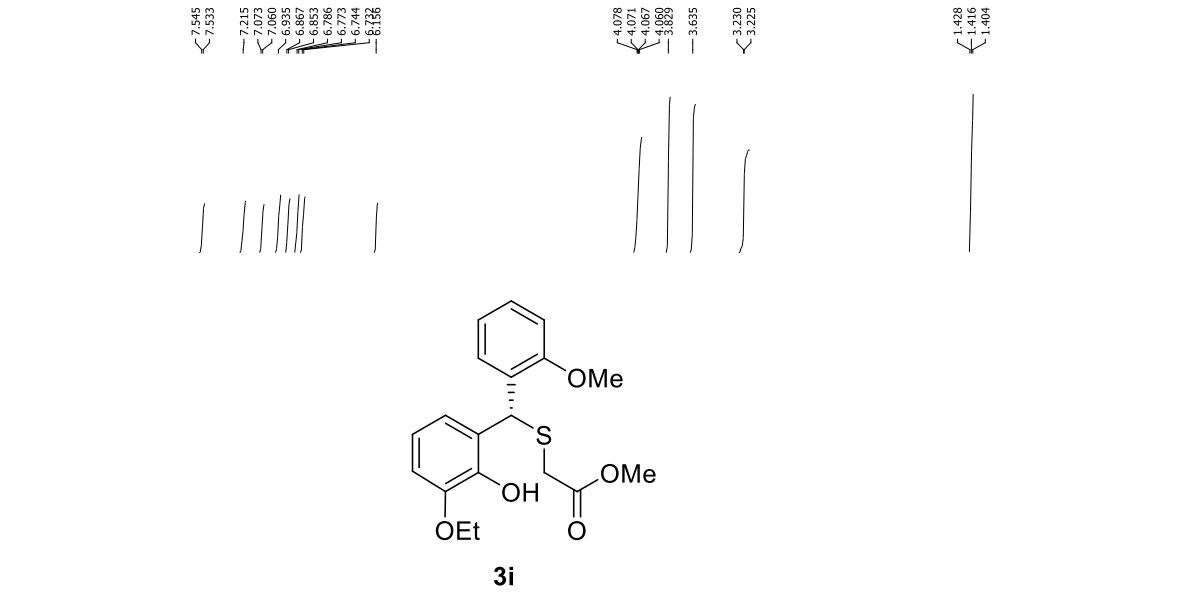
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6.786
6.773
6.744
6.732
6.156
4.078
4.071
4.067
4.060
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3.635
3.230
3.225
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1.416
1.404
OMe
S
OMe
OH
OEt
O
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1.04
0.97
1.16
1.09
1.17
1.12
1.00
2.32
3.12
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2.06
3.18
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8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**3i**


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146.04
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129.49
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126.34
121.32
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111.19
110.66
77.44
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77.02
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56.11
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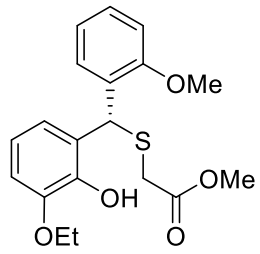
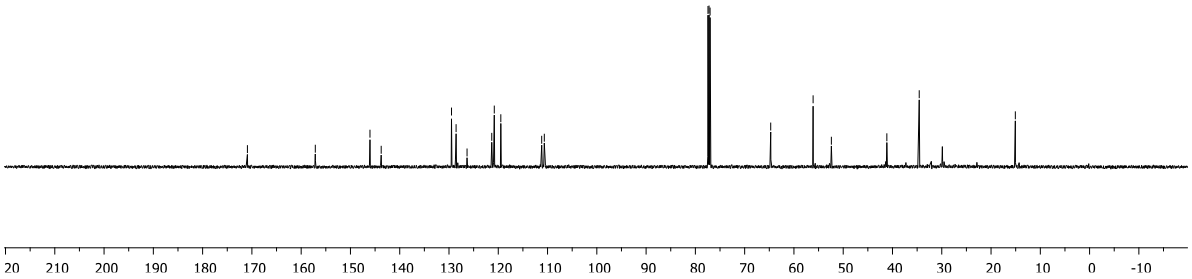
34.57
15.07


OMe
S
OMe
OH
OEt
O

**3i**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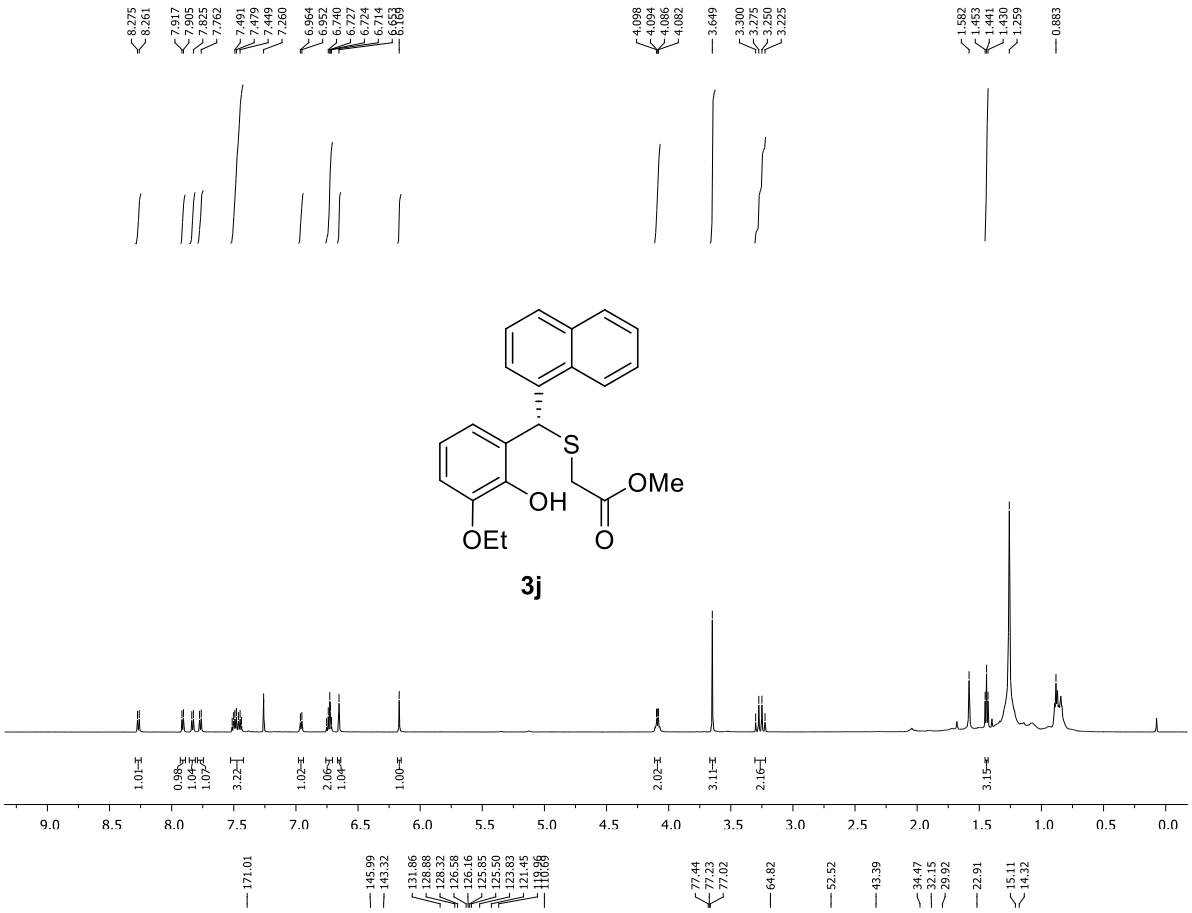
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6.169
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S
OH
OMe
OEt
O
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1.07
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1.04
1.00
2.02
3.11
2.16
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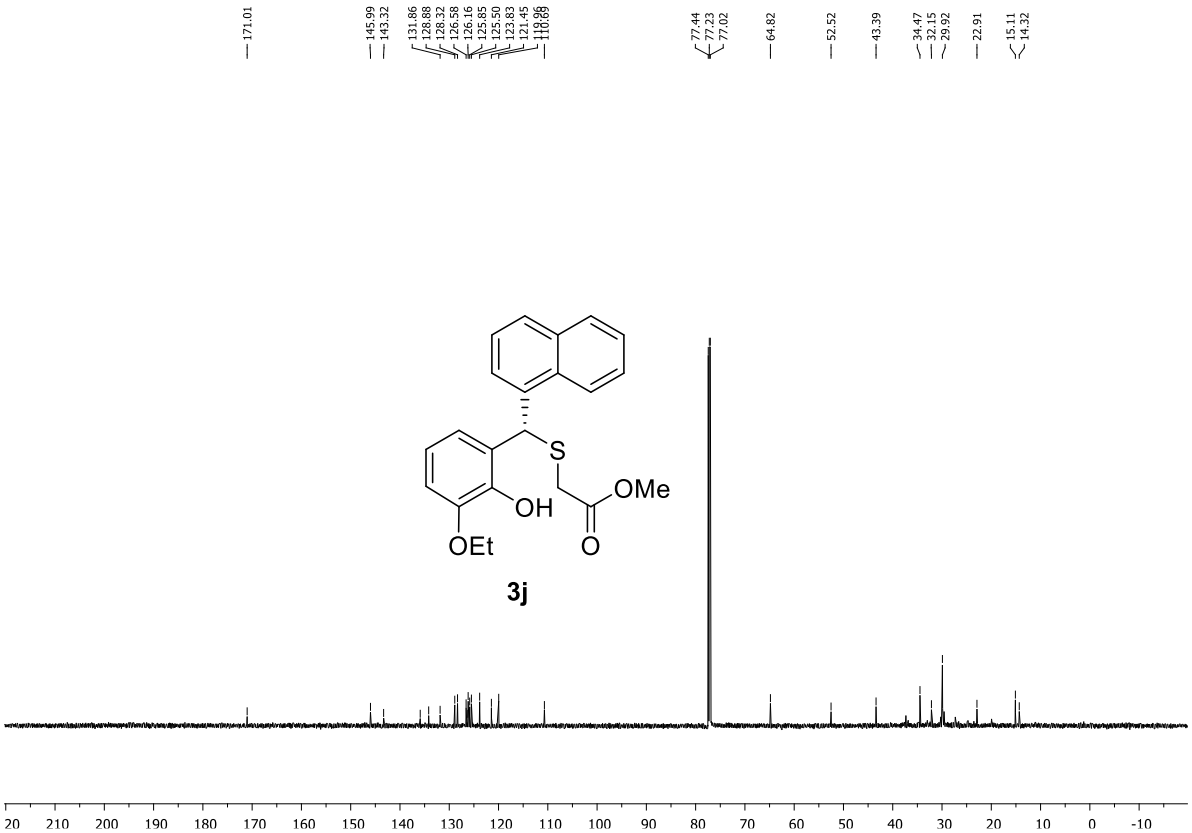
**3j**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77.23
77.02
64.82
52.52
43.39
34.47
32.15
29.92
22.91
15.11
14.32
S
OH
OMe
OEt
O
20
210
200
190
180
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80
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0
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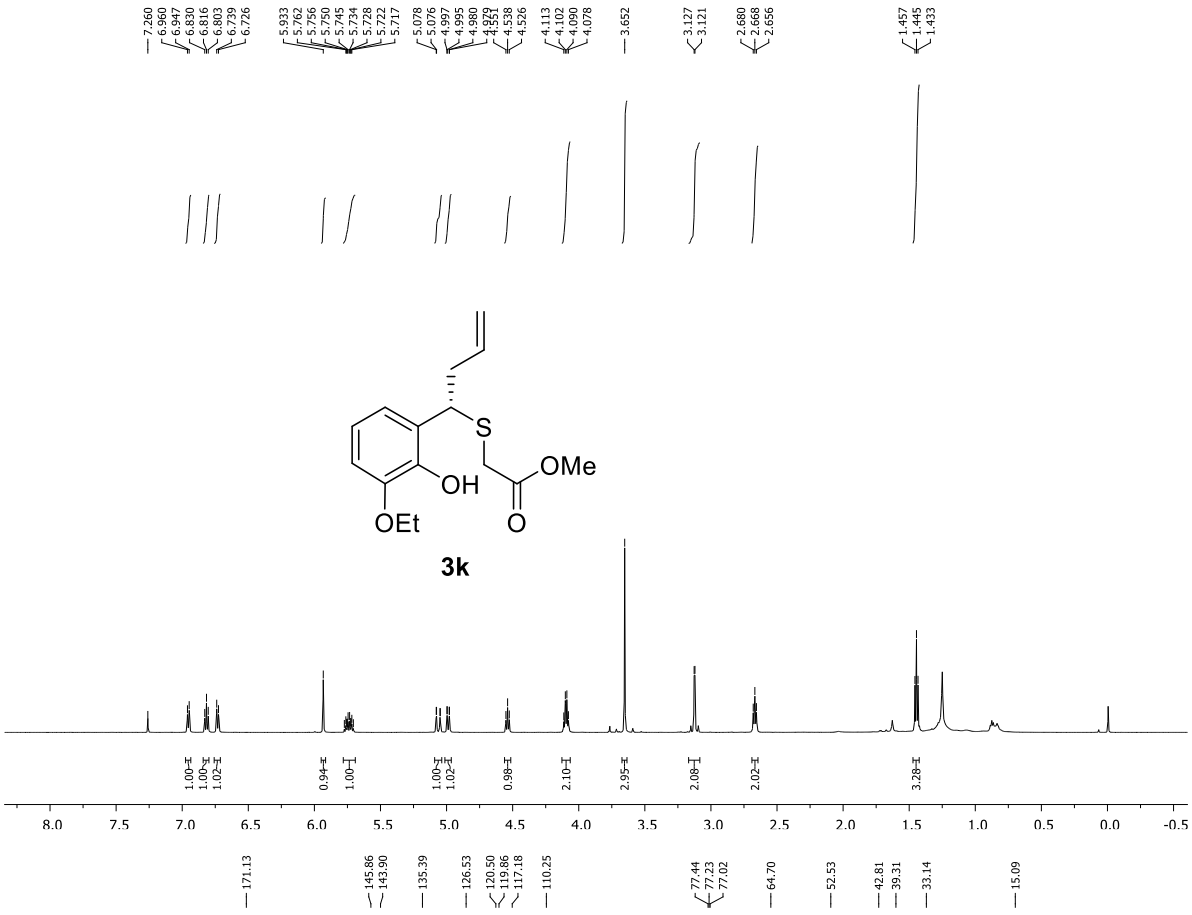
**3j**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5.717
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5.076
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4.995
4.980
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4.538
4.526
4.113
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4.090
4.078
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3.121
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2.656
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1.445
1.433
S
OMe
OH
OEt
O
3k
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1.00
1.02
0.94
1.00
1.00
1.02
0.98
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2.95
2.08
2.02
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7.5
7.0
6.5
6.0
5.5
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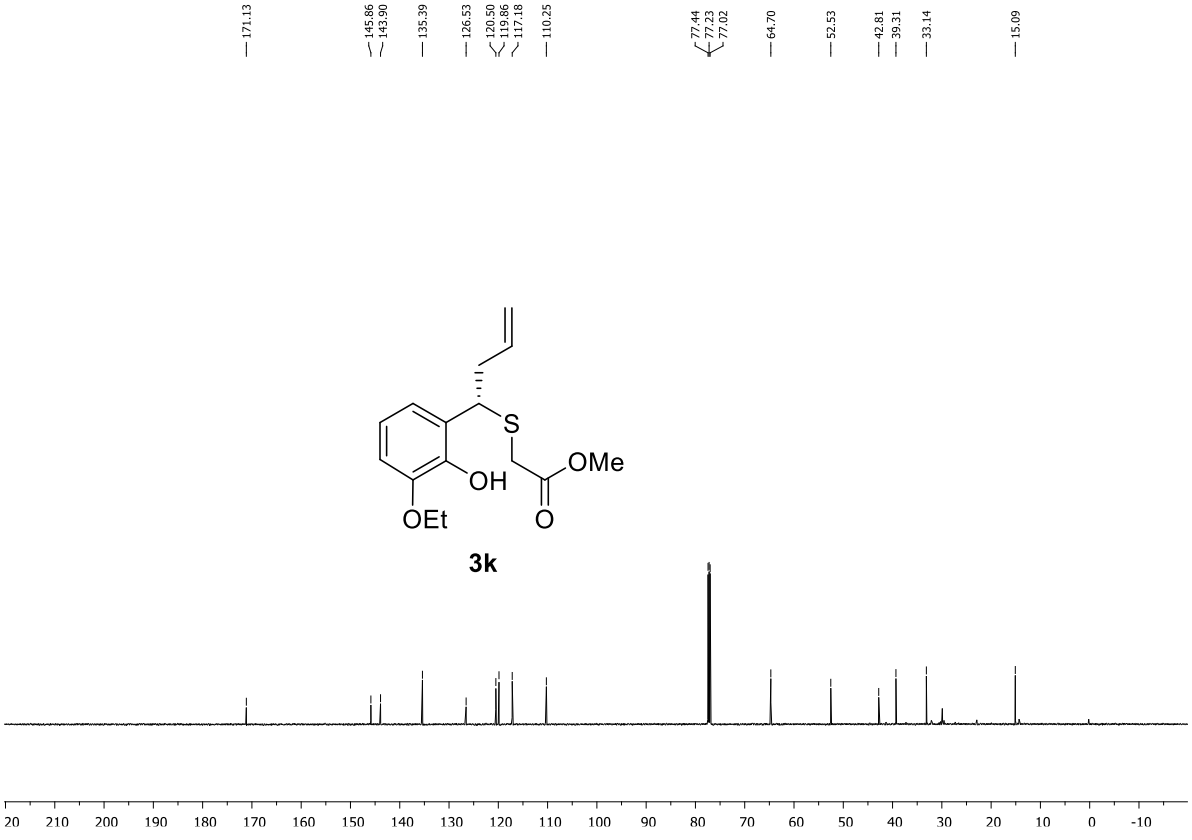
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117.18
110.25
77.44
77.23
77.02
64.70
52.53
42.81
39.31
33.14
15.09
S
OMe
OH
OEt
O
3k
220
210
200
190
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140
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120
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100
90
80
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60
50
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0
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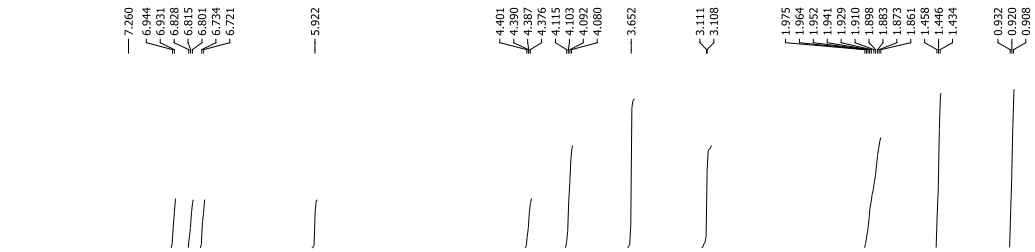
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4.387
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4.103
4.092
4.080
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3.111
3.108
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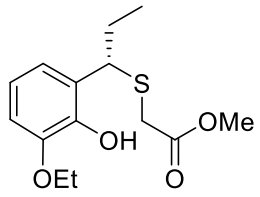
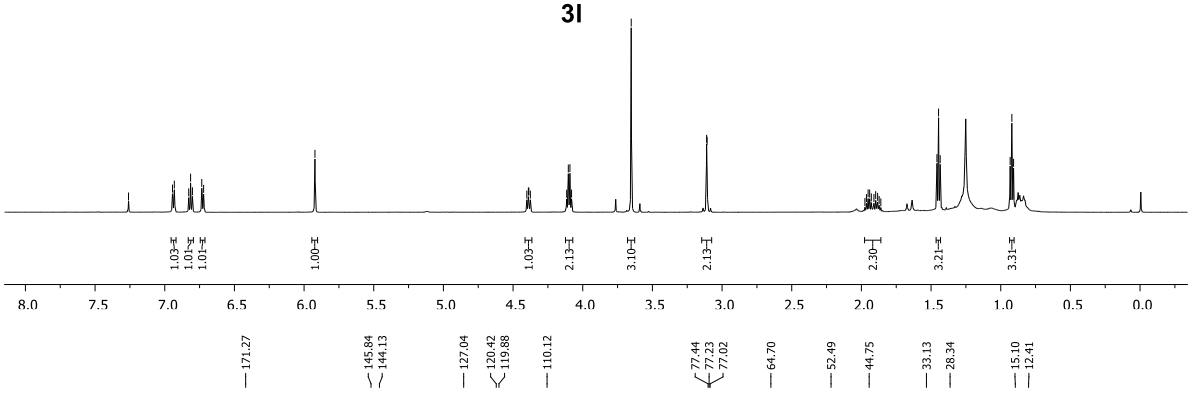
0.908


S
OMe
OH
OEt
O

**3l**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7.0
6.5
6.0
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4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.27
145.84
144.13
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77.02
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52.49
44.75
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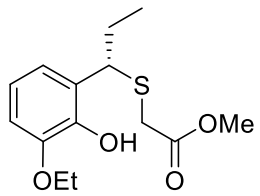
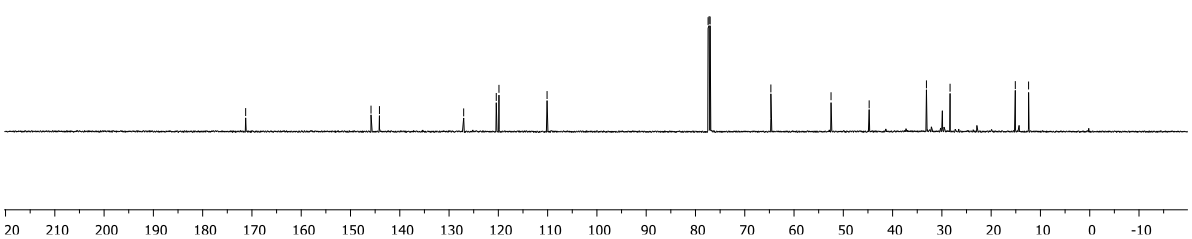
28.34
15.10
12.41


S
OMe
OH
OEt
O

**3l**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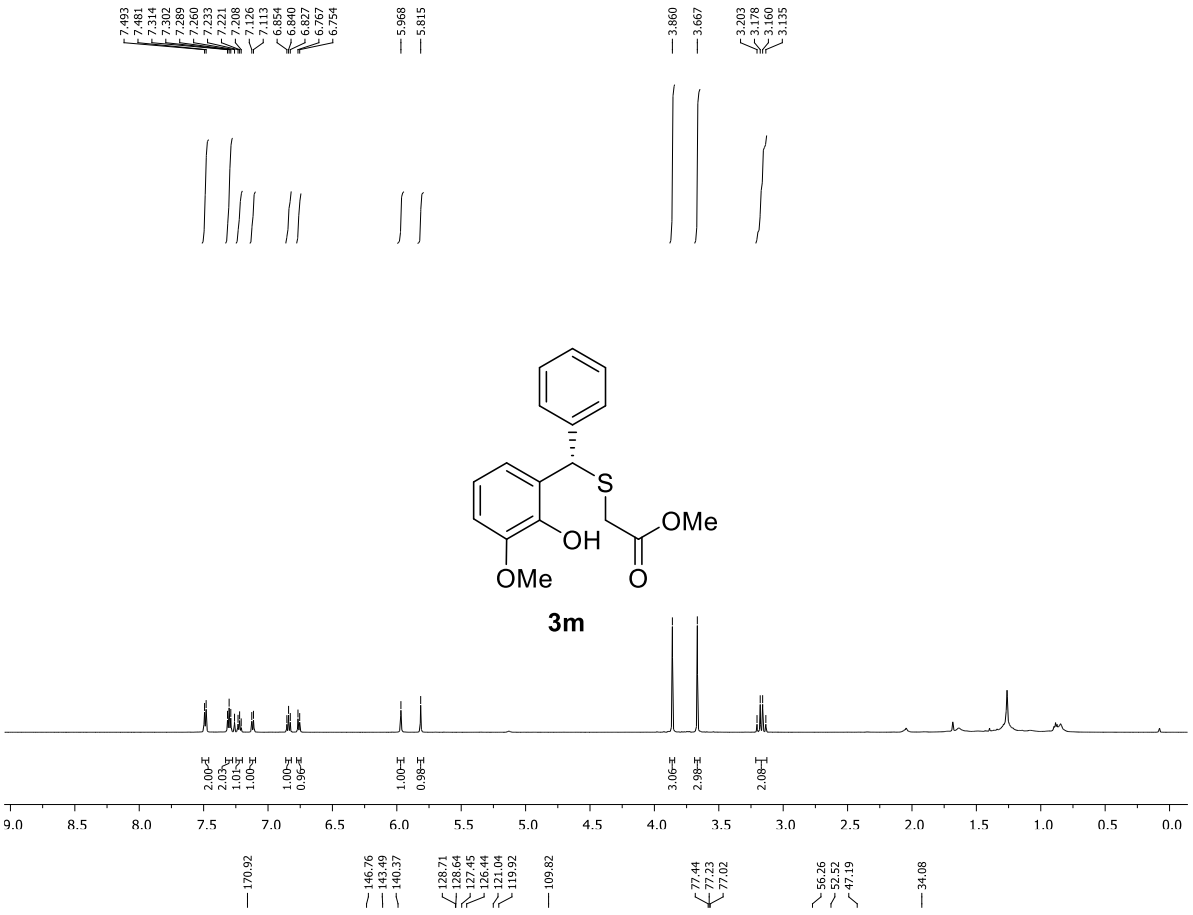
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3.178
3.160
3.135
S
OH
OMe
OMe
O
3m
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1.00
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0.98
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2.98
2.08
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170.92
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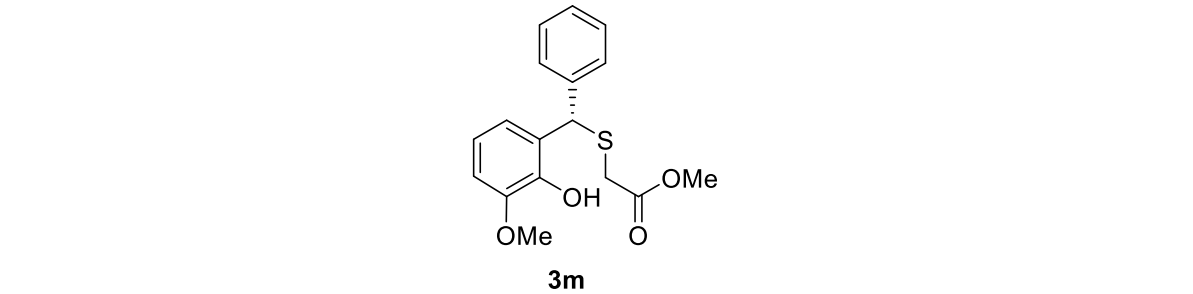
34.08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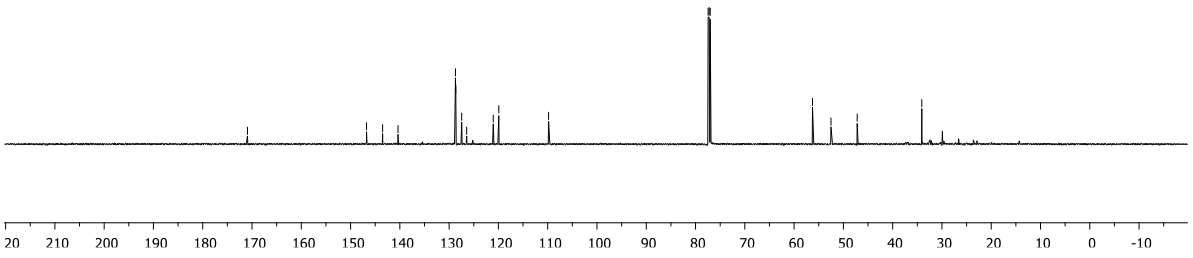
OH
OMe
OMe
O
3m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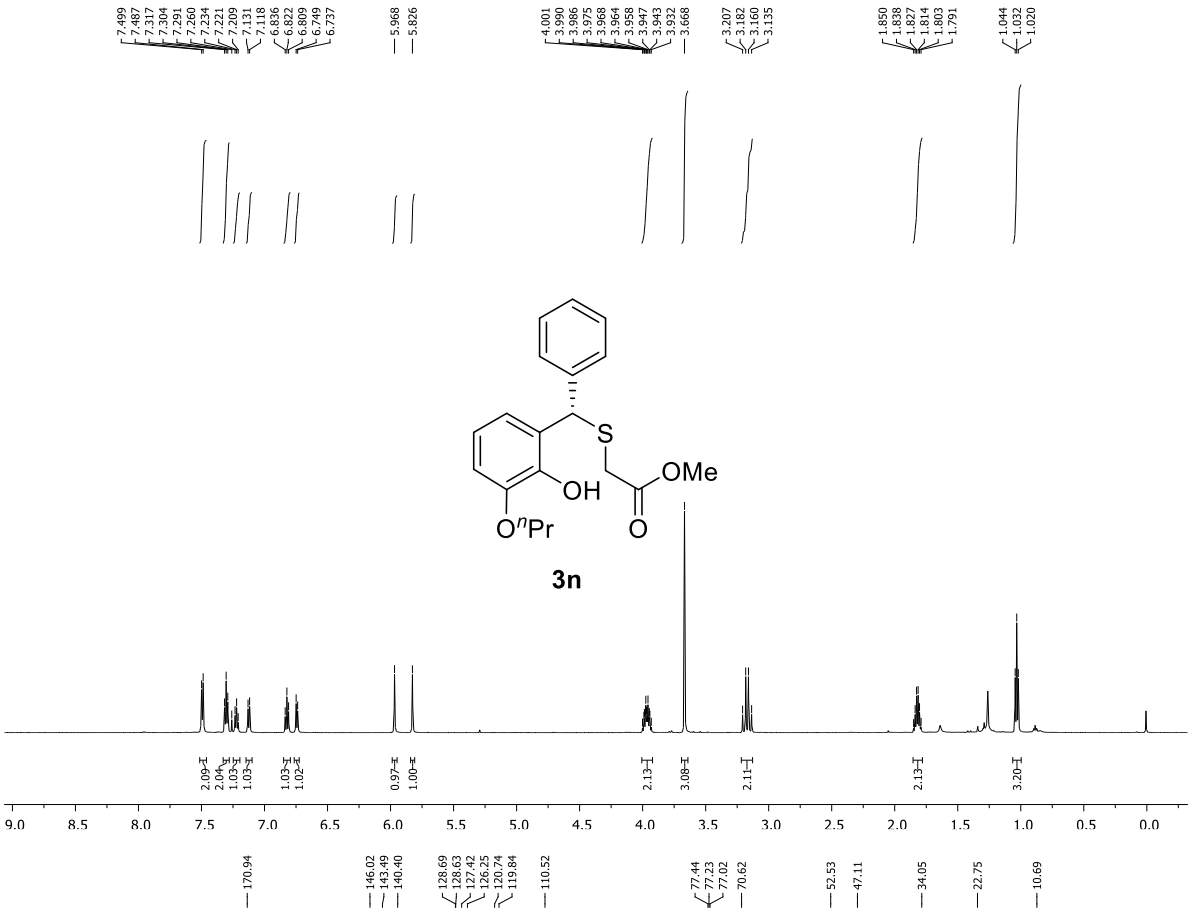
0
-10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7.221
7.209
7.131
7.118
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6.822
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6.749
6.737
5.968
5.826
4.001
3.990
3.986
3.975
3.968
3.964
3.958
3.947
3.943
3.932
3.668
3.207
3.182
3.160
3.135
1.850
1.838
1.827
1.814
1.803
1.791
1.044
1.032
1.020
S
OMe
OH
O
O^nPr
3n
2.09
2.04
1.03
1.03
1.03
1.02
0.97
1.00
2.13
3.08
2.11
2.13
3.20
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8.5
8.0
7.5
7.0
6.5
6.0
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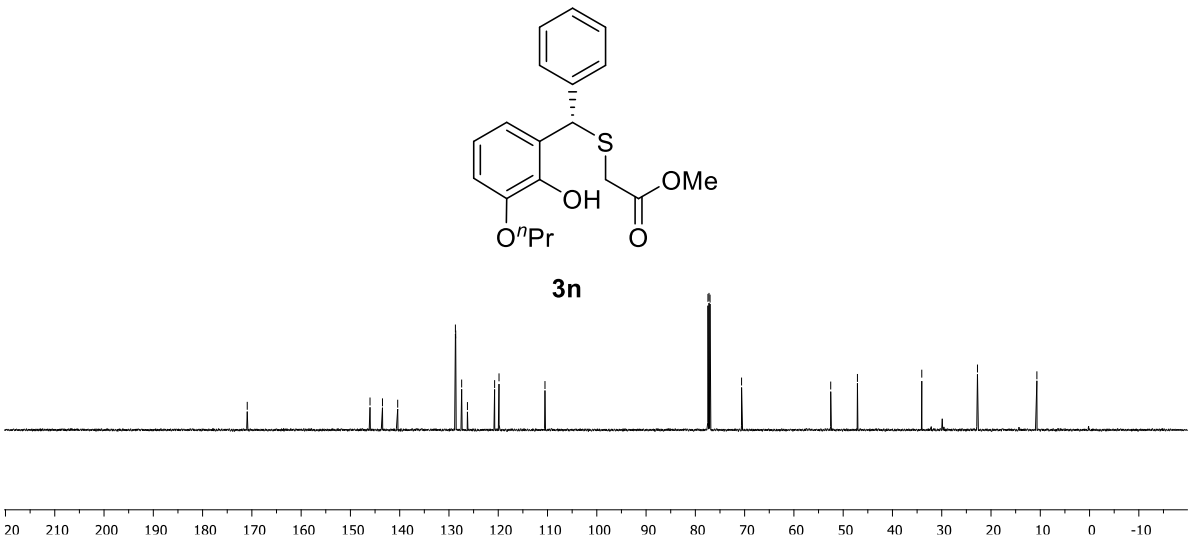
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128.63
127.42
126.25
120.74
119.84
110.52
77.44
77.23
77.02
70.62
52.53
47.11
34.05
22.75
10.69
S
OMe
OH
O
O^nPr
3n
220
210
200
190
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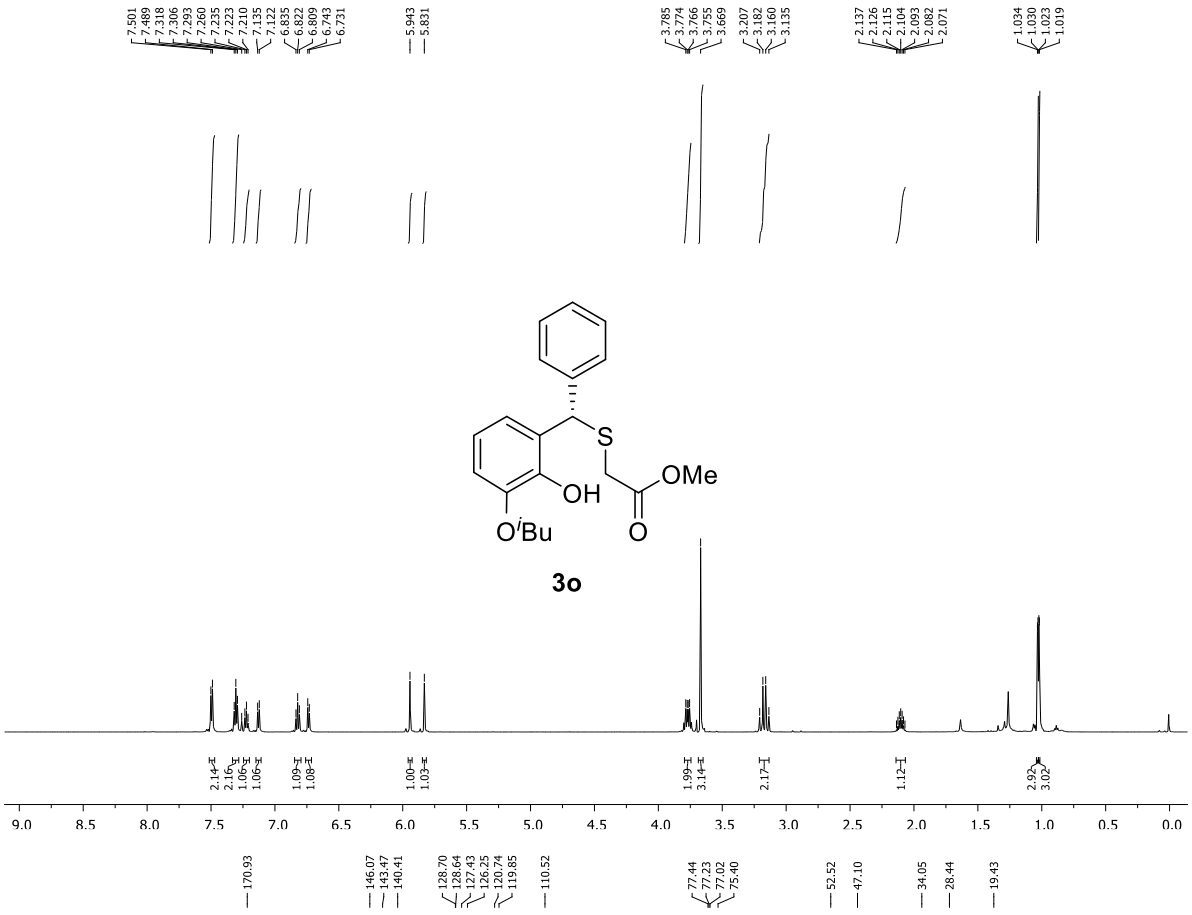
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7.223
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7.135
7.122
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6.822
6.809
6.743
6.731
5.943
5.831
3.785
3.774
3.766
3.755
3.669
3.207
3.182
3.160
3.135
2.137
2.126
2.115
2.104
2.093
2.082
2.071
1.034
1.030
1.023
1.019
S
OMe
OH
O
O'Bu
2.14
2.16
1.06
1.06
1.09
1.08
1.00
1.03
1.99
3.14
2.17
1.12
2.92
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**3o**


170.93
146.07
143.47
140.41
128.70
128.64
127.43
126.25
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77.44
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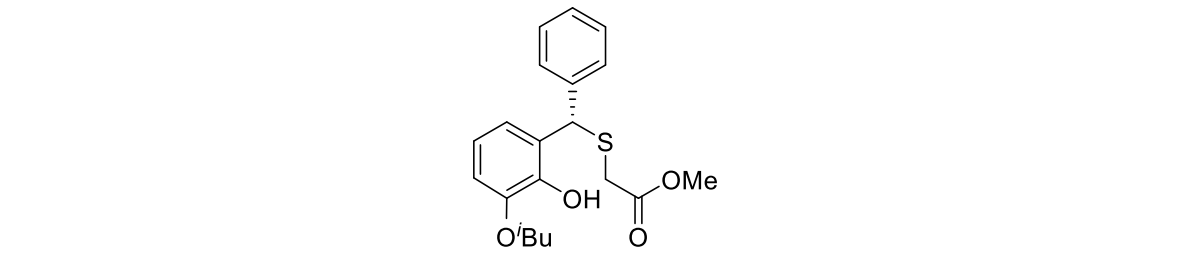
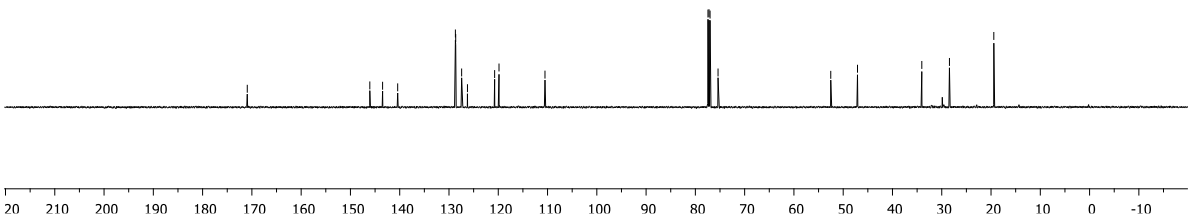
19.43


S
OMe
OH
O
O'Bu

**3o**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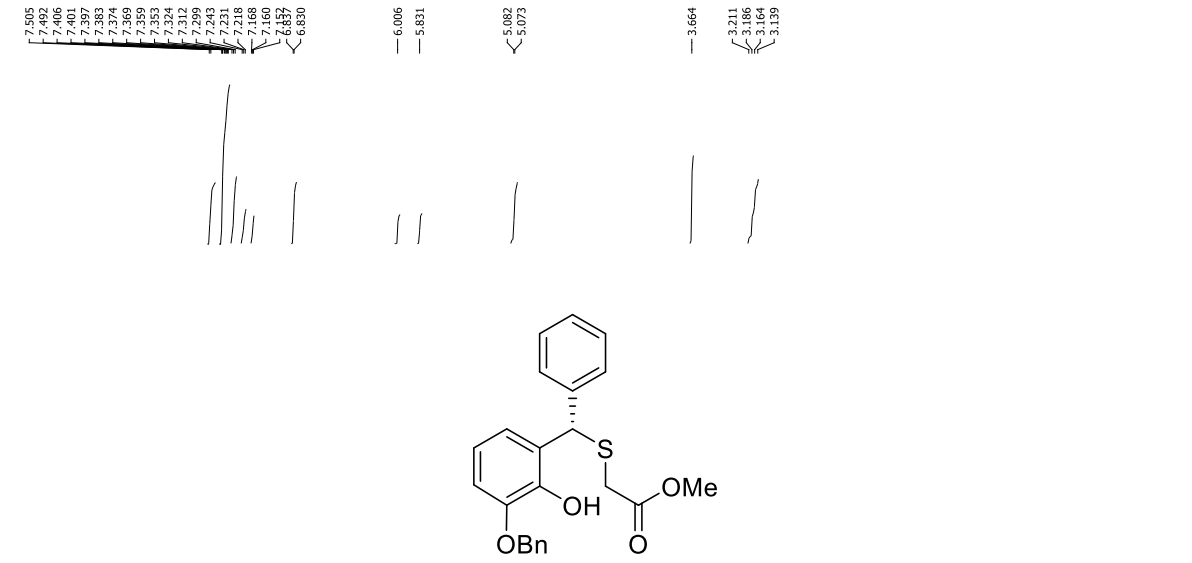
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7.406
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7.374
7.369
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7.353
7.324
7.312
7.299
7.243
7.231
7.218
7.168
7.160
7.152
6.837
6.830
6.006
5.831
5.082
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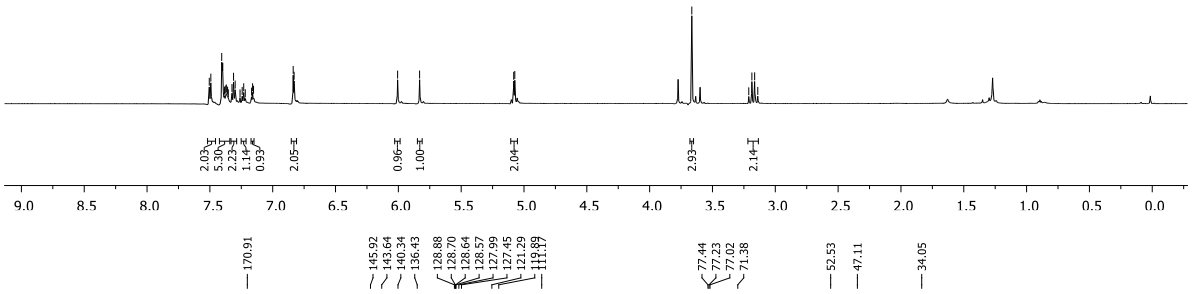
3.664
3.211
3.186
3.164
3.139
S
OH
OMe
OBn
O

**3p**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2.23
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2.05
0.96
1.00
2.04
2.93
2.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


170.91
145.92
143.64
140.34
136.43
128.88
128.70
128.64
128.57
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127.45
121.29
111.87
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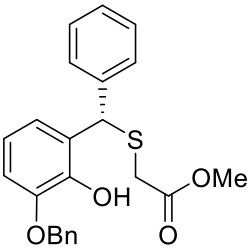
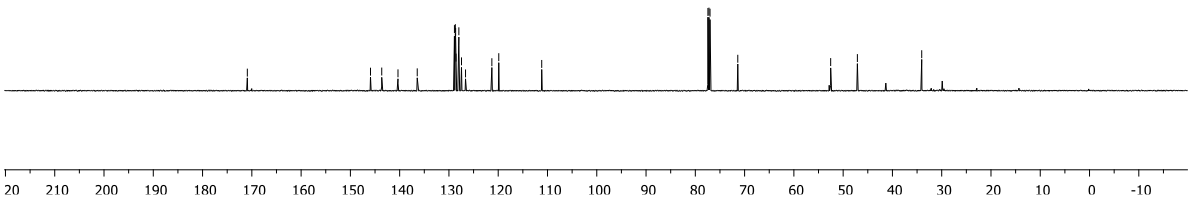
77.23
77.02
71.38
52.53
47.11
34.05


S
OH
OMe
OBn
O

**3p**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210
200
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100
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60
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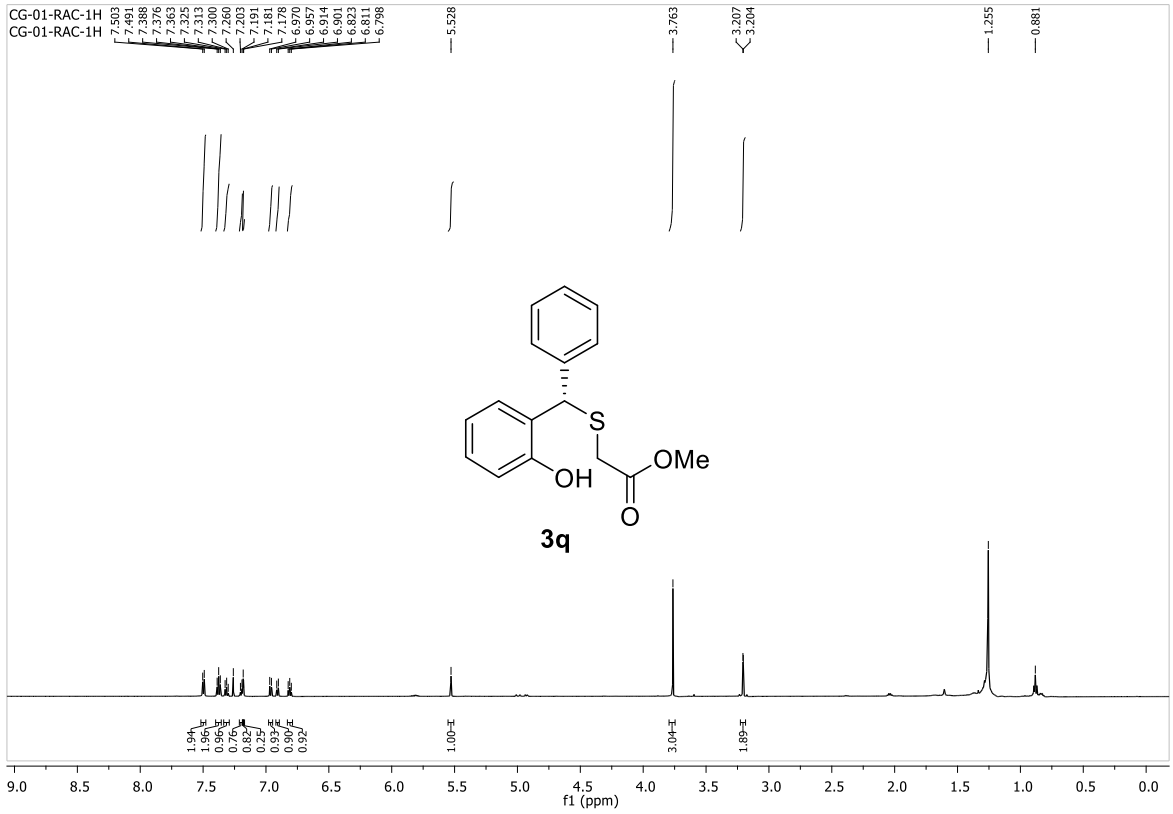
-10


CG-01-RAC-1H
CG-01-RAC-1H
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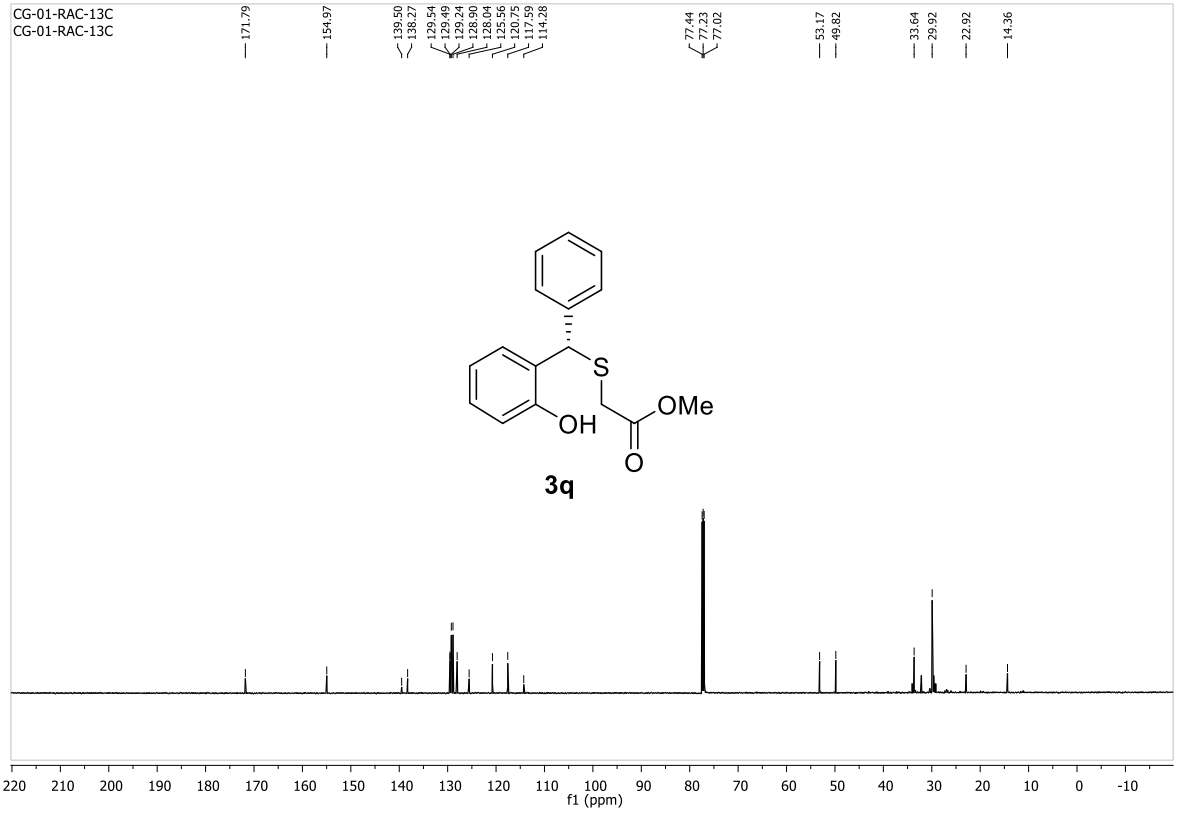
7.376
7.363
7.325
7.313
7.300
7.260
7.203
7.191
7.181
7.178
6.970
6.957
6.914
6.901
6.823
6.811
6.798
5.528
3.763
3.207
3.204
1.255
0.881
S
OMe
OH
O
3q
1.94
1.96
0.96
0.76
0.82
0.25
0.93
0.90
0.92
1.00
3.04
1.89
f1 (ppm)


CG-01-RAC-13C
CG-01-RAC-13C
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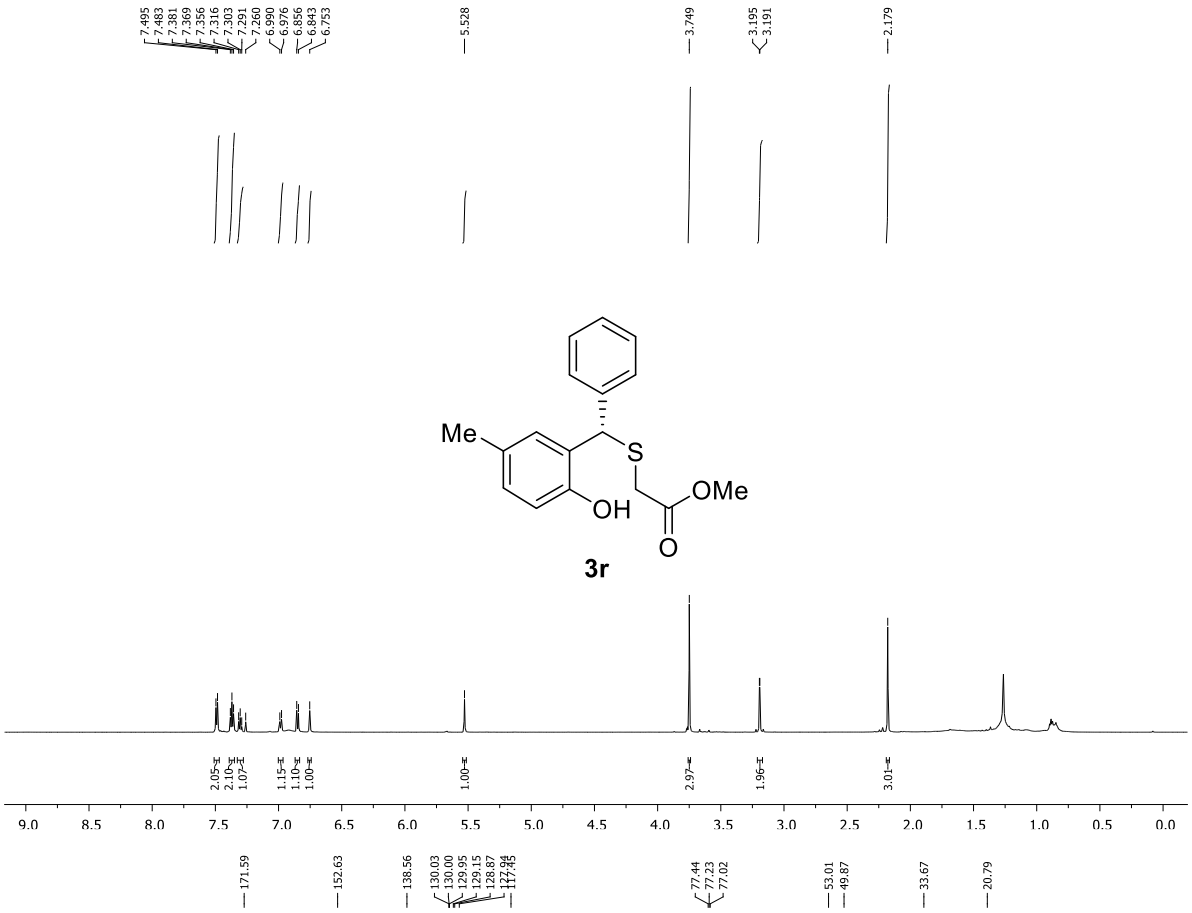
154.97
139.50
138.27
129.54
129.49
129.24
128.90
128.04
125.56
120.75
117.59
114.28
77.44
77.23
77.02
53.17
49.82
33.64
29.92
22.92
14.36
S
OMe
OH
O
3q
f1 (ppm)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7.291
7.260
6.990
6.976
6.856
6.843
6.753
5.528
3.749
3.195
3.191
2.179
Me
S
OMe
OH
O
3r
2.05
2.10
1.07
1.15
1.10
1.00
1.00
2.97
1.96
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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1.0
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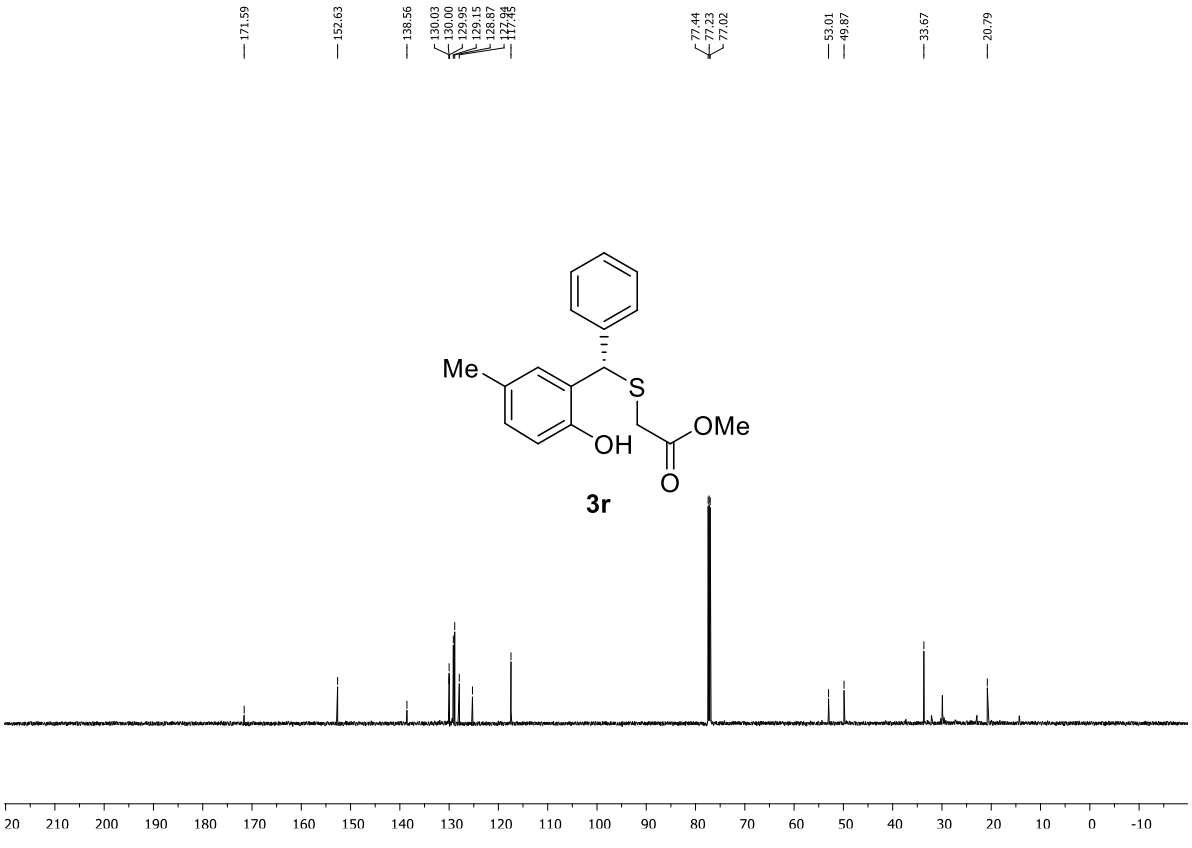
0.0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138.56
130.03
130.00
129.95
129.15
128.87
127.94
117.45
77.44
77.23
77.02
53.01
49.87
33.67
20.79
Me
S
OMe
OH
O
3r
220
210
200
190
180
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160
150
140
130
120
110
100
90
80
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60
50
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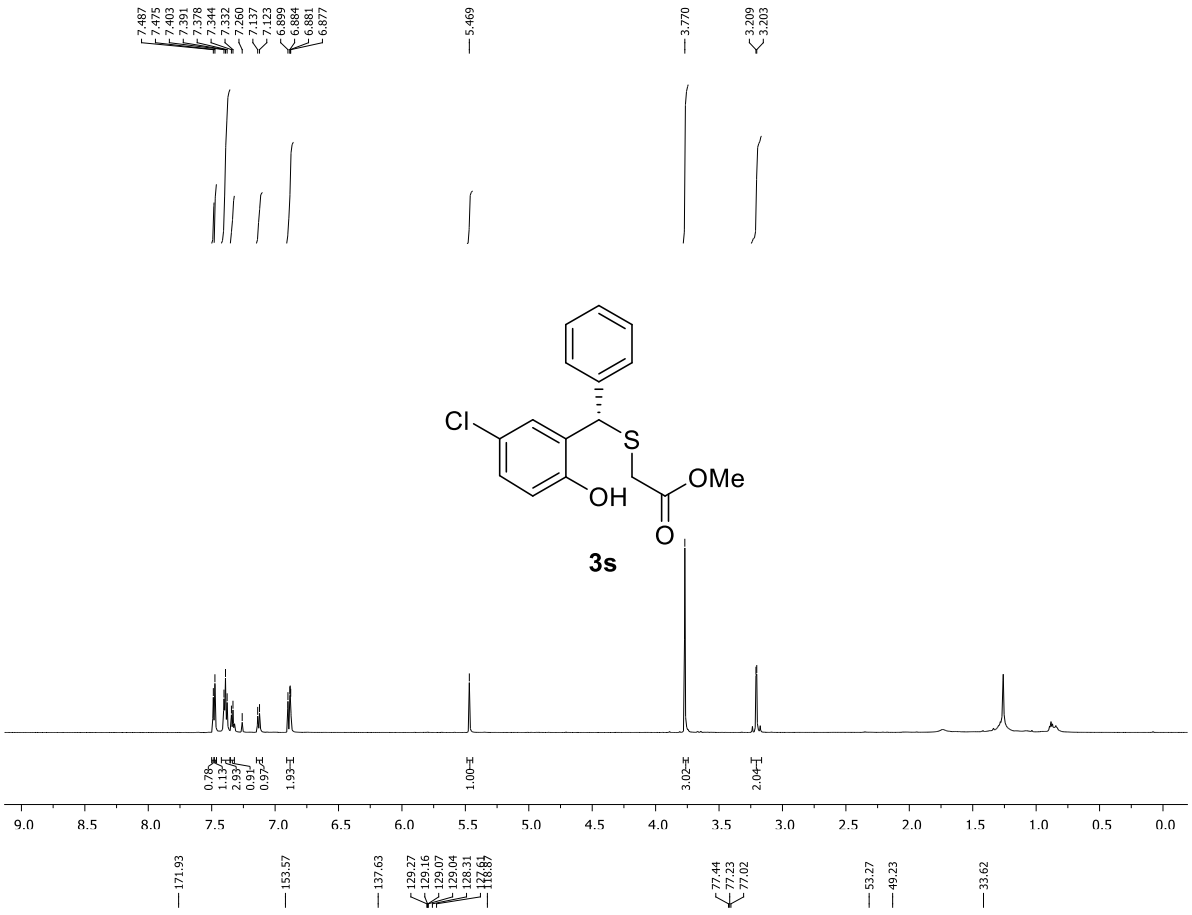
0
-10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7.137
7.123
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6.881
6.877
5.469
3.770
3.209
3.203
Cl
S
OMe
OH
O
3s
0.78
1.13
2.93
0.91
0.97
1.93
1.00
3.02
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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2.0
1.5
1.0
0.5
0.0


171.93
153.57
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77.23
77.02
53.27
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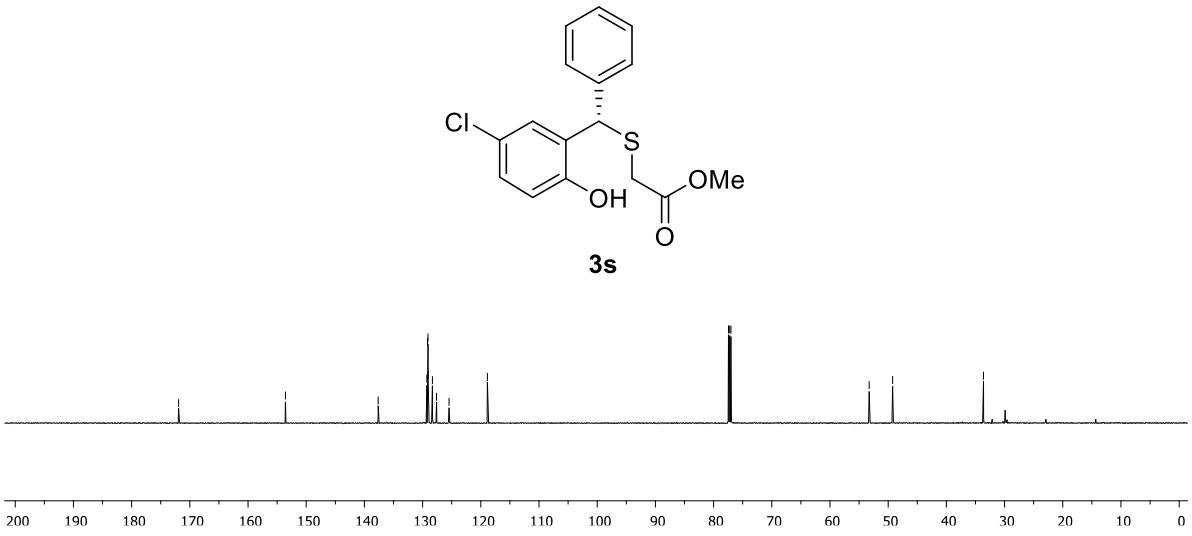
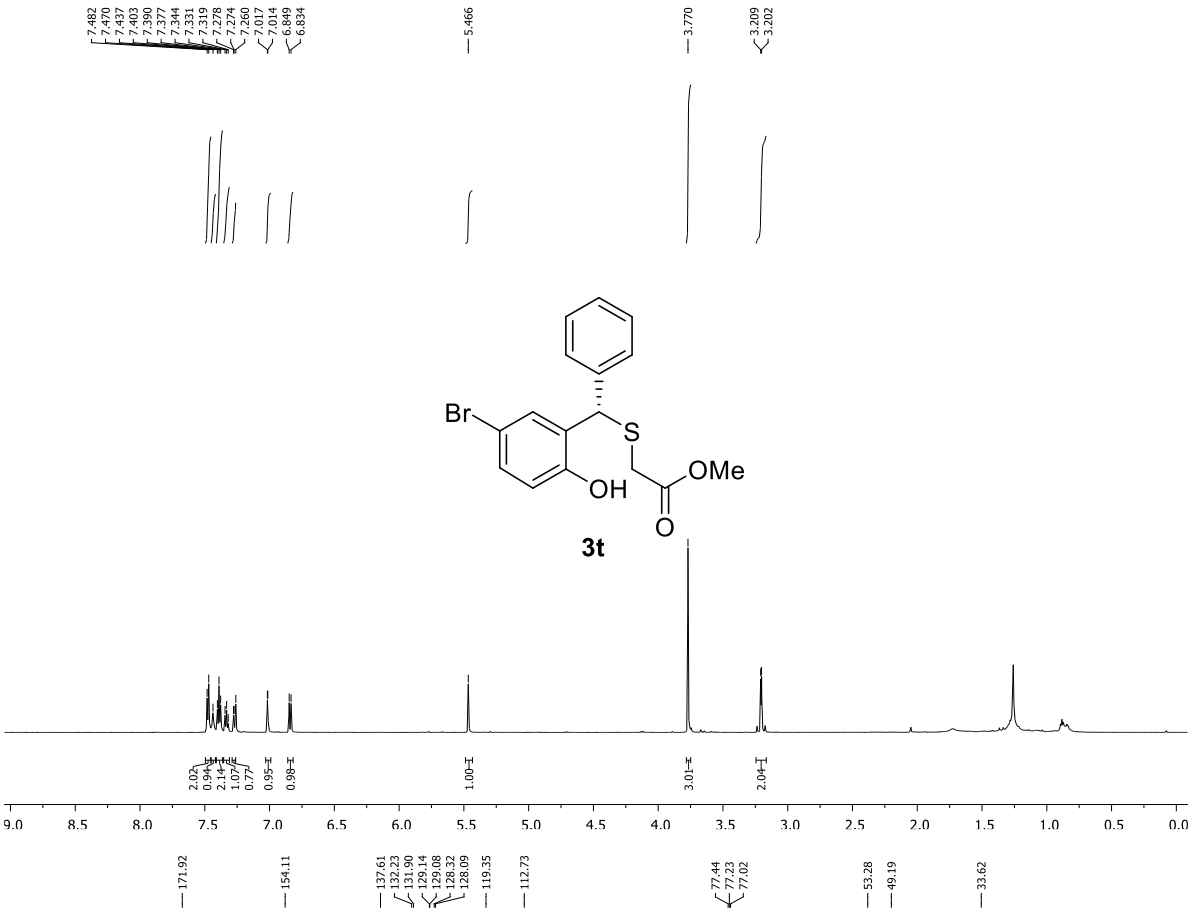
33.62


Cl
S
OMe
OH
O
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.377
7.344
7.331
7.319
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7.274
7.260
7.017
7.014
6.849
6.834
5.466
3.770
3.209
3.202
Br
S
OMe
OH
O
3t
2.02
0.94
2.14
1.07
0.77
0.95
0.98
1.00
3.01
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.92
154.11
137.61
132.23
131.90
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128.09
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112.73
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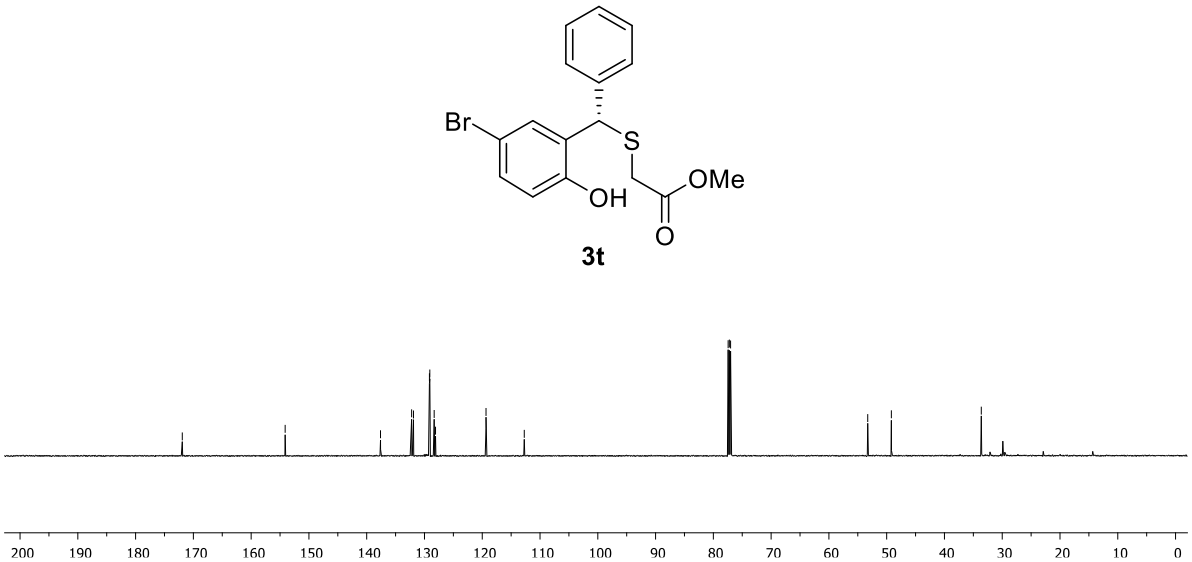
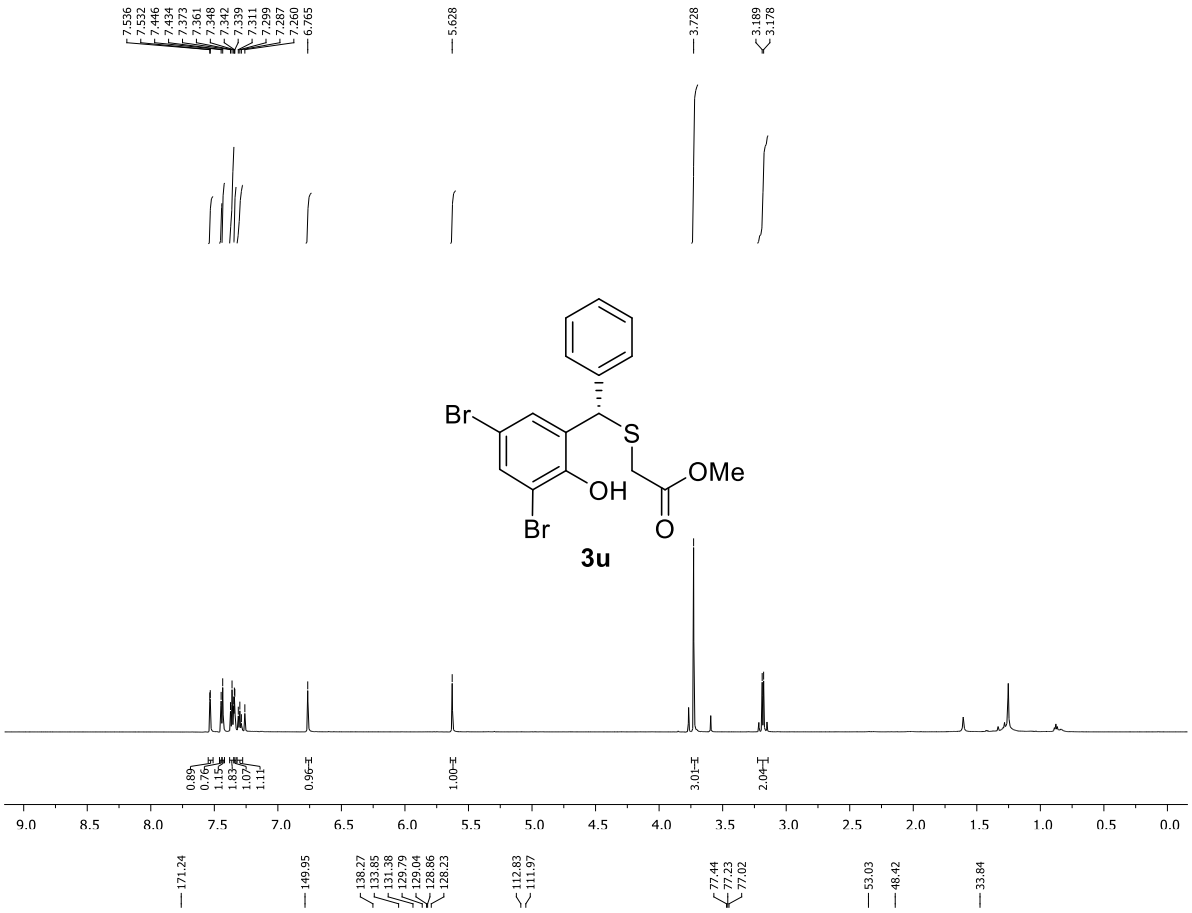
77.23
77.02
53.28
49.19
33.62


Br
S
OMe
OH
O
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.260
6.765
5.628
3.728
3.189
3.178
Br
S
OMe
OH
Br
O
3u
0.89
0.76
1.15
1.83
1.07
1.11
0.96
1.00
3.01
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


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133.85
131.38
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111.97
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77.23
77.02
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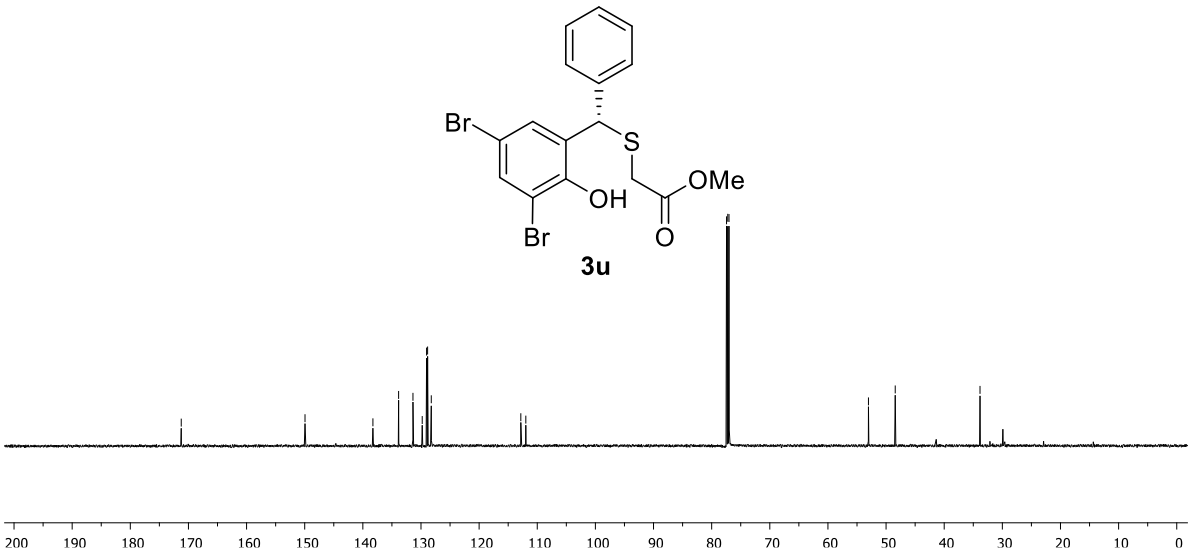
48.42
33.84


Br
S
OMe
OH
Br
O
3u
200
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180
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150
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120
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100
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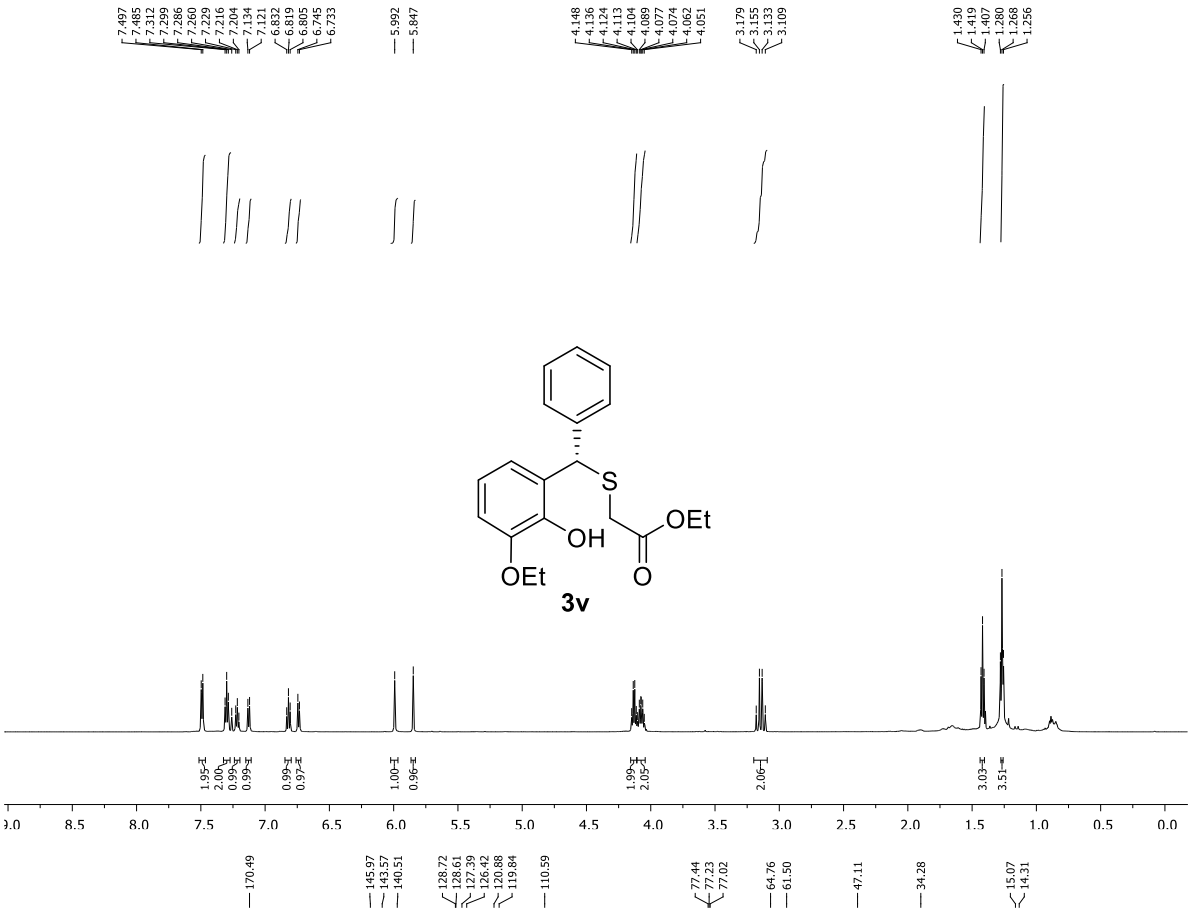
10
0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6.805
6.745
6.733
5.992
5.847
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4.136
4.124
4.113
4.104
4.089
4.077
4.074
4.062
4.051
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3.155
3.133
3.109
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1.419
1.407
1.280
1.268
1.256
S
OH
OEt
OEt
O
3v
1.95
2.00
0.99
0.99
0.99
0.97
1.00
0.96
1.99
2.05
2.06
3.03
3.51
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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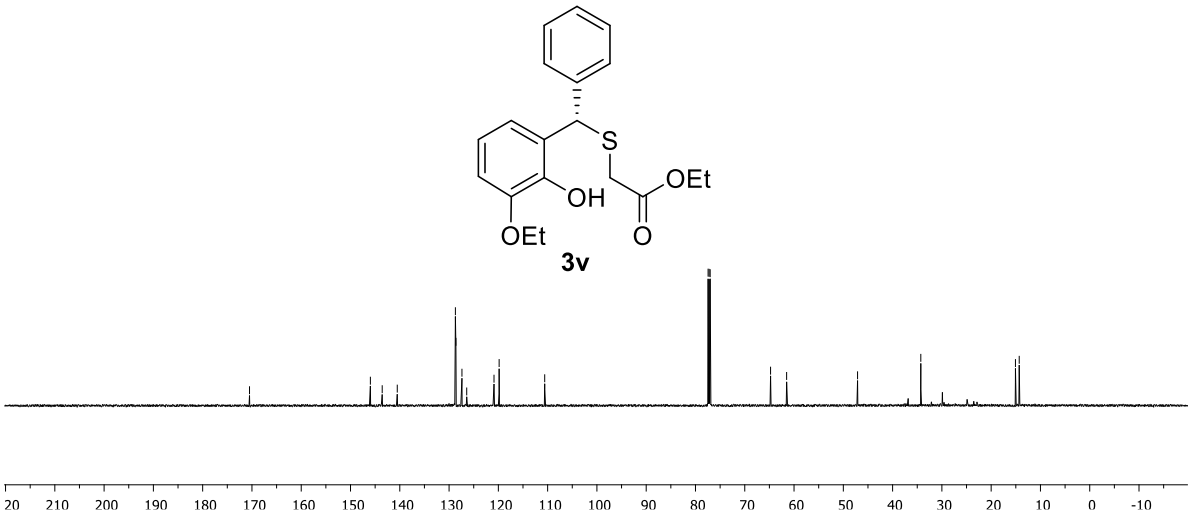
0.0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110.59
77.44
77.23
77.02
64.76
61.50
47.11
34.28
15.07
14.31
S
OH
OEt
OEt
O
3v
220
210
200
190
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120
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100
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80
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50
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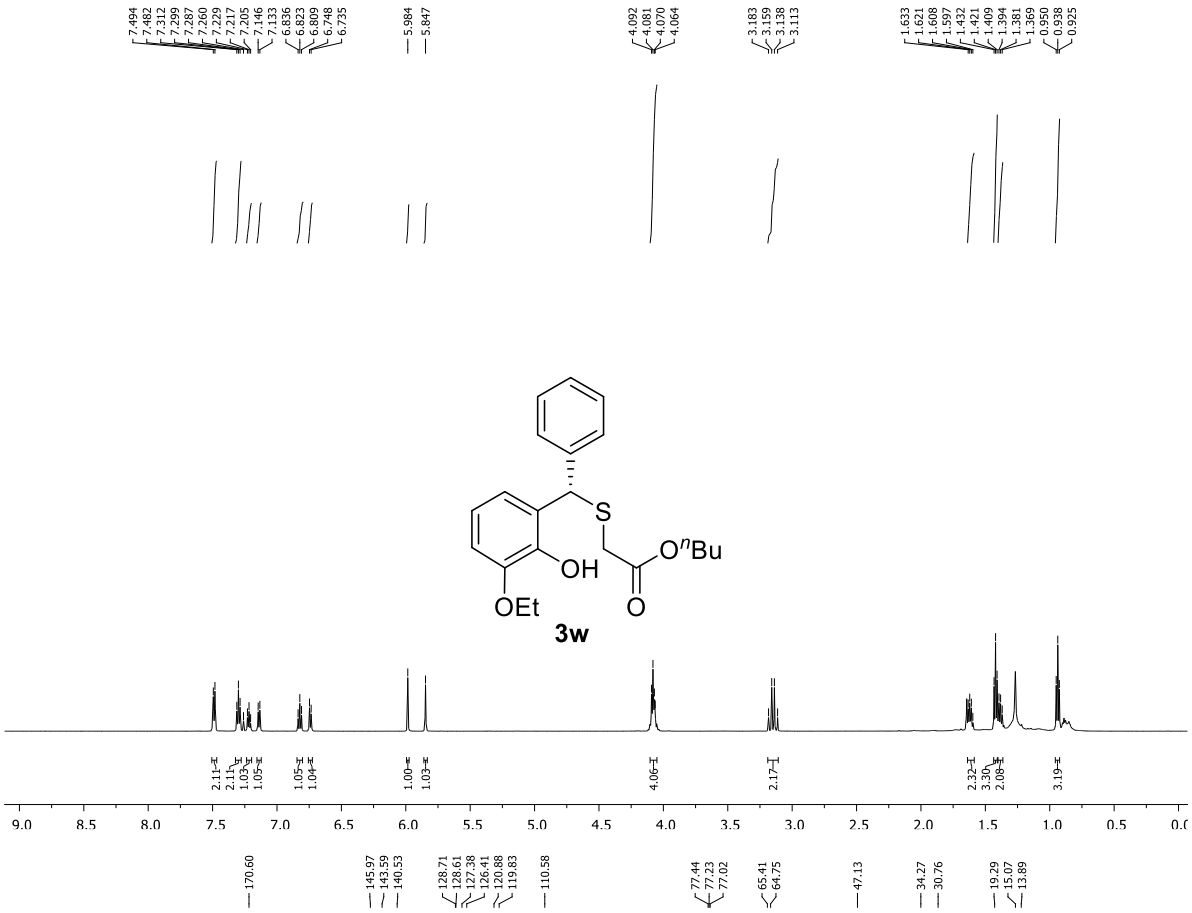
-10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6.823
6.809
6.748
6.735
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5.847
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4.070
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3.159
3.138
3.113
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0.938
0.925
S
OH
OEt
O
O$^{n}$Bu
3w
2.11
2.11
1.05
1.05
1.05
1.04
1.00
1.03
4.06
2.17
2.32
3.30
2.08
3.19
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6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


170.60
145.97
143.59
140.53
128.71
128.61
127.38
126.41
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119.83
110.58
77.44
77.23
77.02
65.41
64.75
47.13
34.27
30.76
19.29
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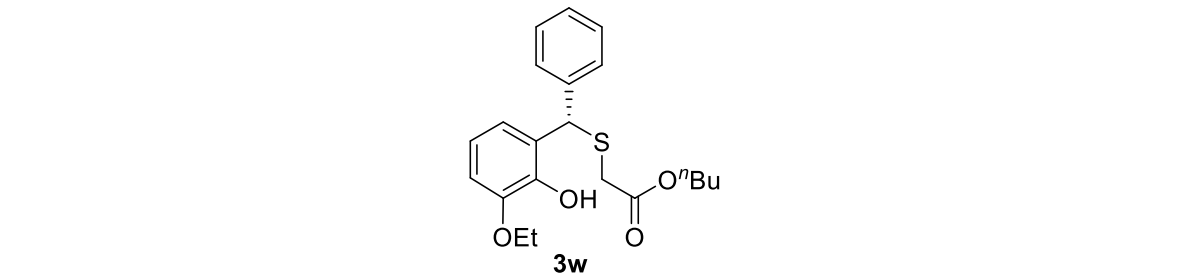
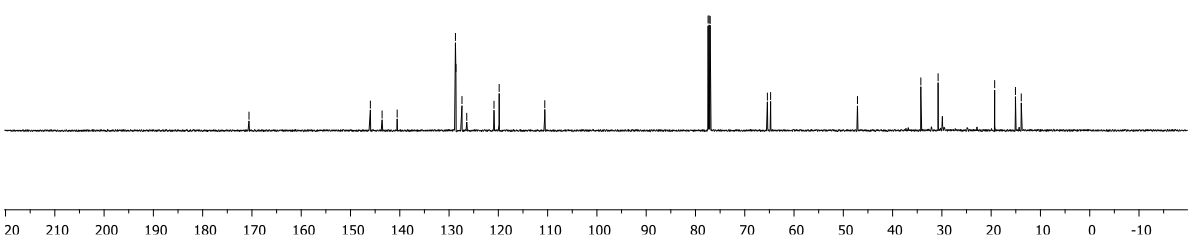
13.89


S
OH
OEt
O
O$^{n}$Bu
3w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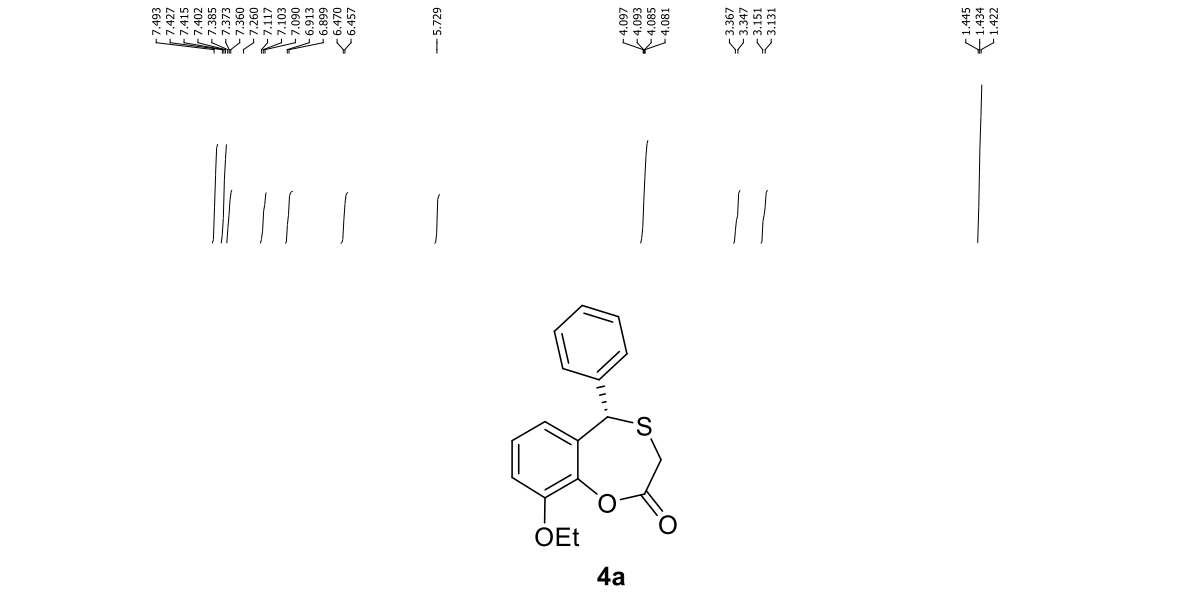
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7.360
7.260
7.117
7.103
7.090
6.913
6.899
6.470
6.457
5.729
4.097
4.093
4.085
4.081
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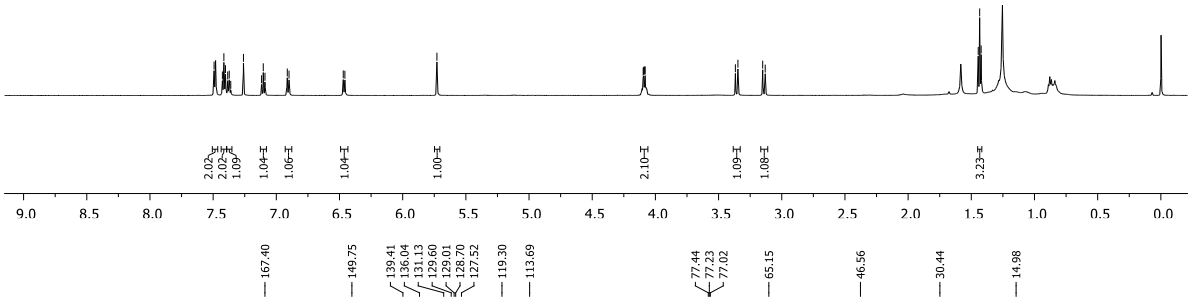
3.347
3.151
3.131
1.445
1.434
1.422
S
O
O
OEt

**4a**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1.04
1.06
1.04
1.00
2.10
1.09
1.08
3.23
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8.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.40
149.75
139.41
136.04
131.13
129.60
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127.52
119.30
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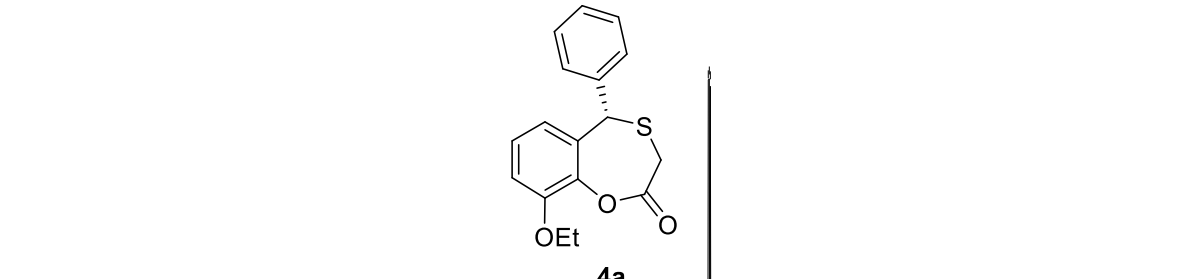
77.44
77.23
77.02
65.15
46.56
30.44
14.98


S
O
O
OEt

**4a**


220
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20
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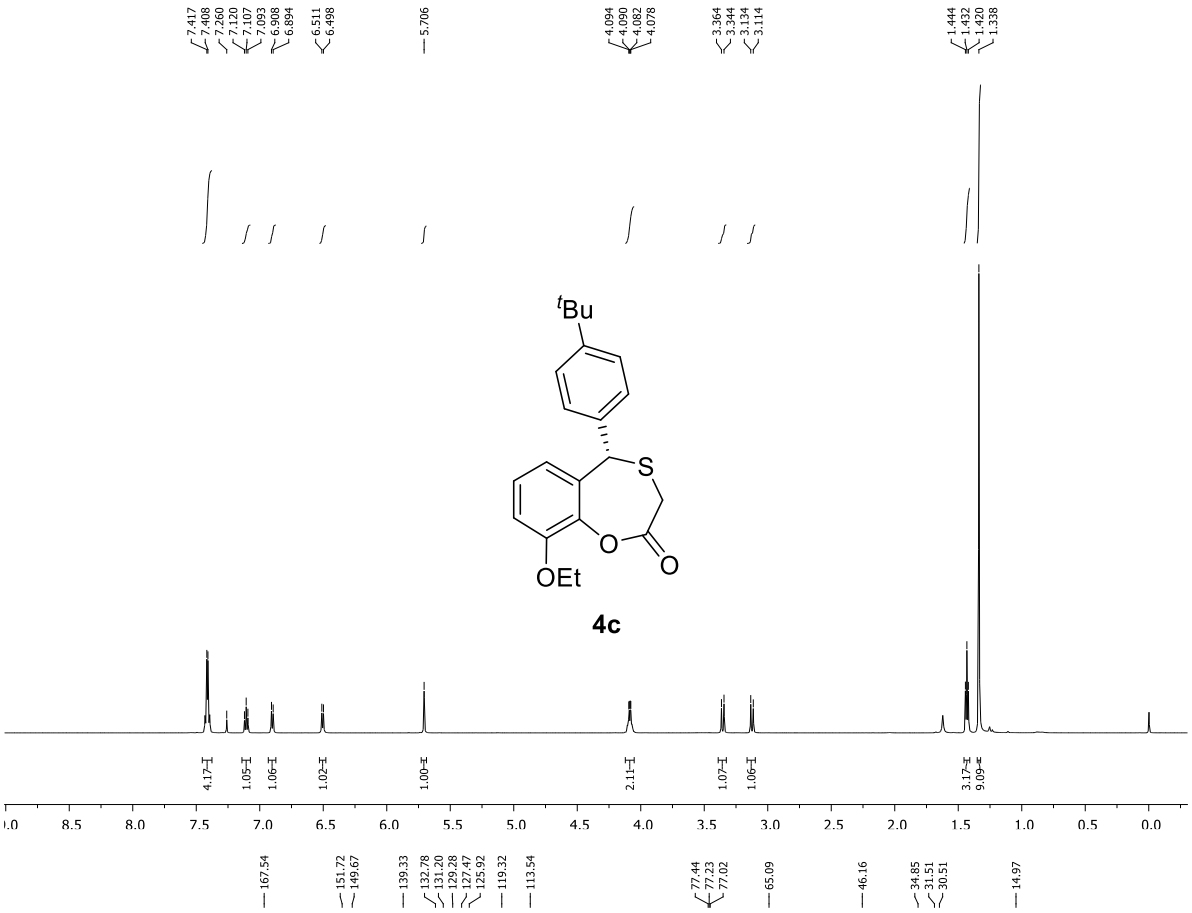
-10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6.498
5.706
4.094
4.090
4.082
4.078
3.364
3.344
3.134
3.114
1.444
1.432
1.420
1.338
tBu
S
O
O
OEt
4c
4.17
1.05
1.06
1.02
1.00
2.11
1.07
1.06
3.17
9.09
167.54
151.72
149.67
139.33
132.78
131.20
129.28
127.47
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77.23
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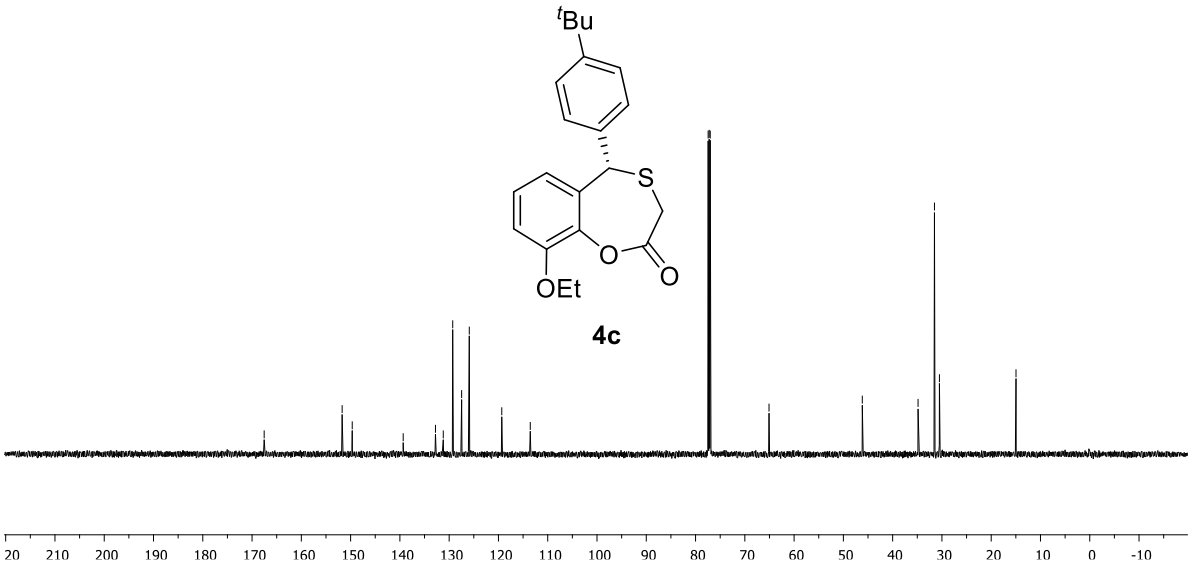
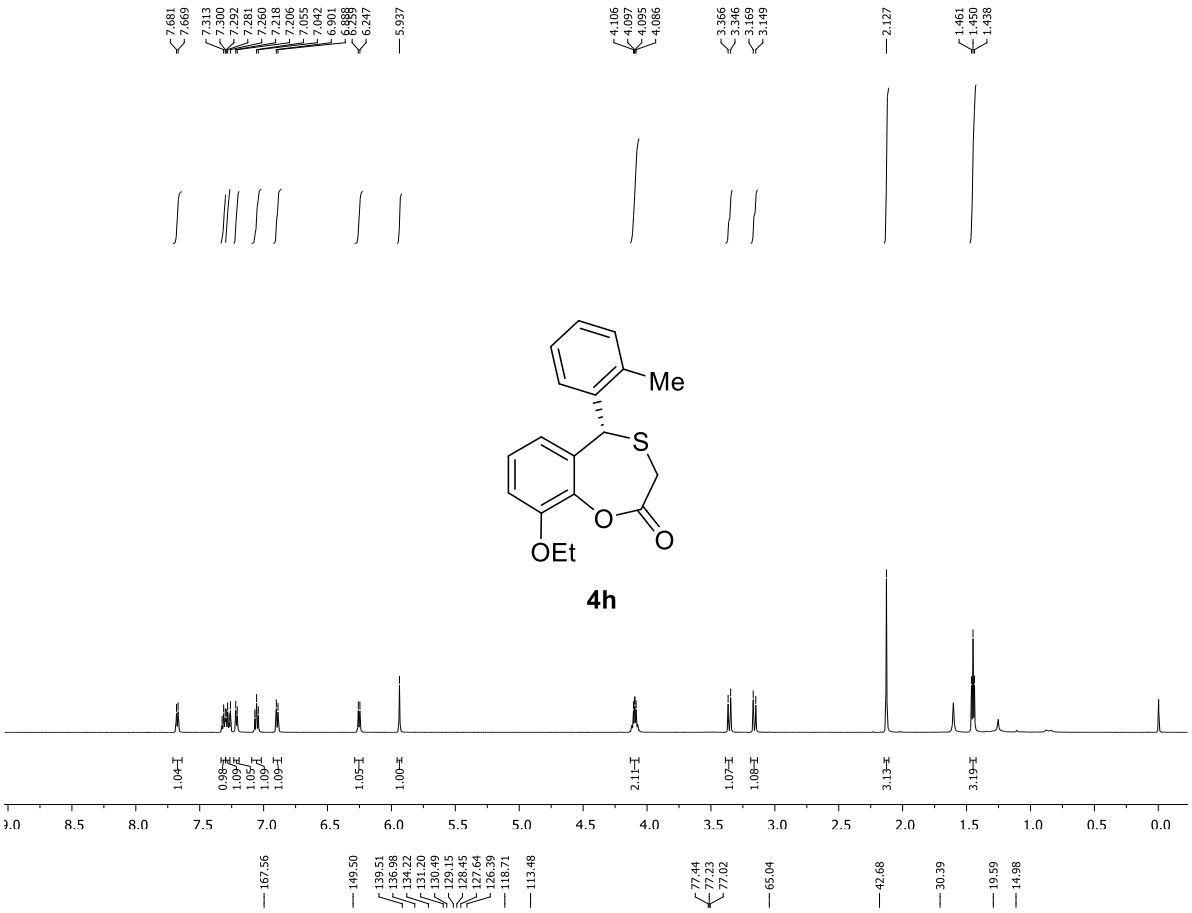
14.97


tBu
S
O
O
OEt
4c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6.247
5.937
4.106
4.097
4.095
4.086
3.366
3.346
3.169
3.149
2.127
1.461
1.450
1.438
Me
S
O
O
OEt
4h
1.04
0.98
1.09
1.05
1.09
1.05
1.00
2.11
1.07
1.08
3.13
3.19
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8.5
8.0
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6.5
6.0
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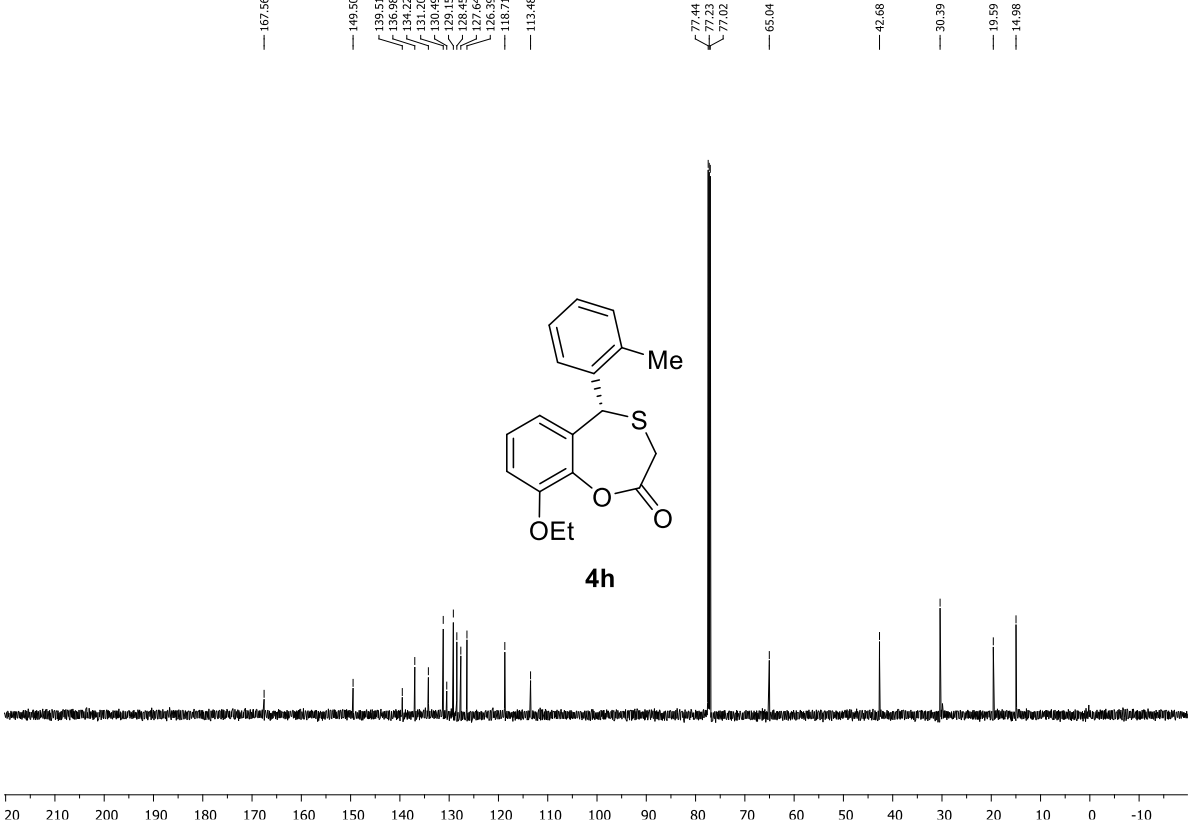
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129.15
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127.64
126.39
118.71
113.48
77.44
77.23
77.02
65.04
42.68
30.39
19.59
14.98
Me
S
O
O
OEt
4h
220
210
200
190
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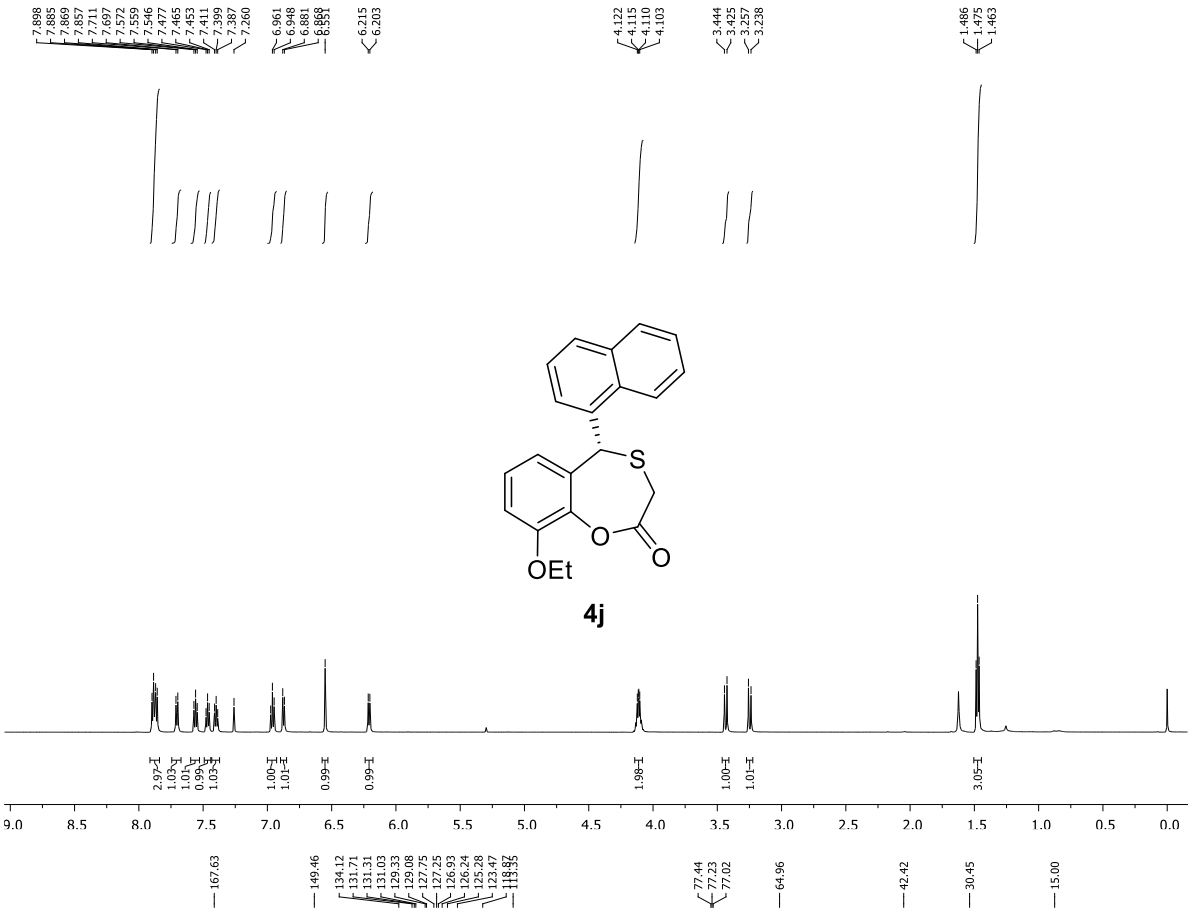
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7.559
7.546
7.477
7.465
7.453
7.411
7.399
7.387
7.260
6.961
6.948
6.881
6.868
6.851
6.215
6.203
4.122
4.115
4.110
4.103
3.444
3.425
3.257
3.238
1.486
1.475
1.463
S
O
O
OEt
4j
2.97
1.03
1.07
0.99
1.03
1.00
1.01
0.99
0.99
1.98
1.00
1.01
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.63
149.46
134.12
131.71
131.31
131.03
129.33
129.08
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77.02
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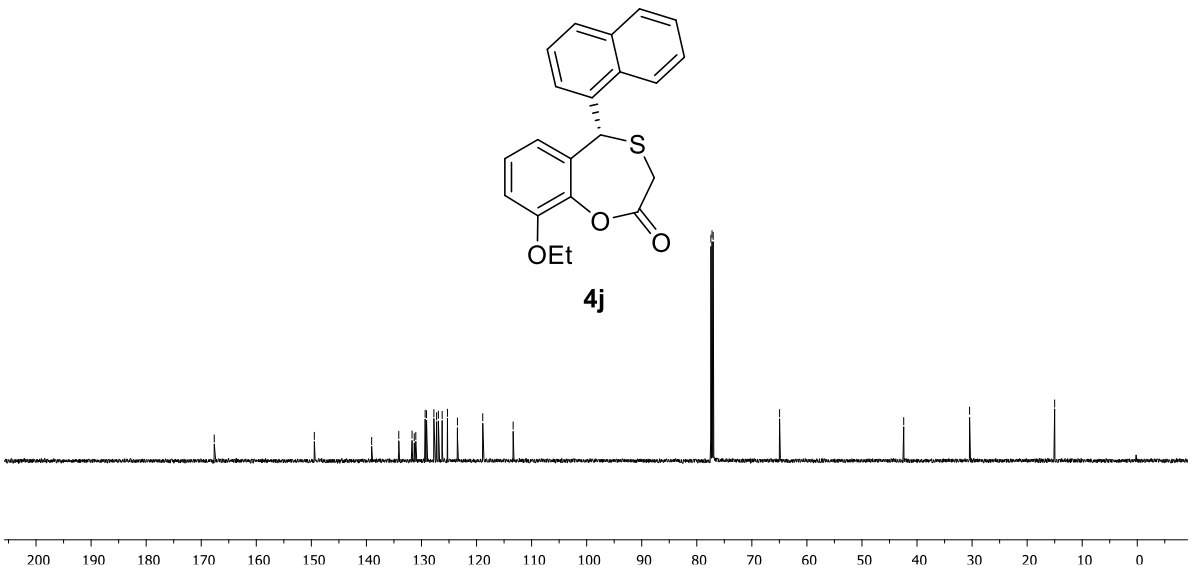
30.45
15.00


S
O
O
OEt
4j
200
190
180
170
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150
140
130
120
110
100
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80
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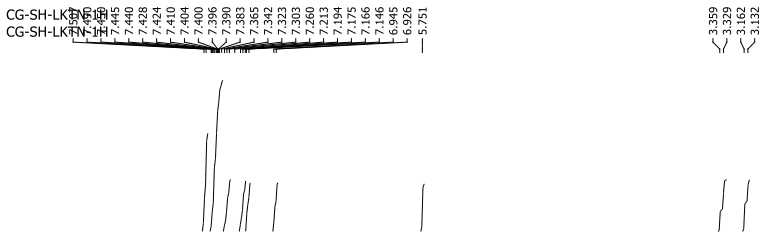
30
20
10
0


CG-SH-LKTN-1H
CG-SH-LKTN-1H
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7.410
7.404
7.400
7.396
7.390
7.383
7.365
7.342
7.323
7.303
7.260
7.213
7.194
7.175
7.166
7.146
6.945
6.926
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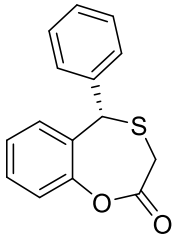
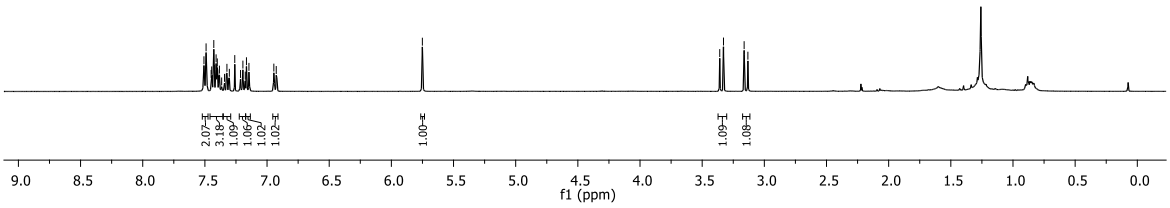
3.329
3.162
3.132


S
O
O

**4q**


2.07
3.18
1.09
1.06
1.02
1.02
1.00
1.09
1.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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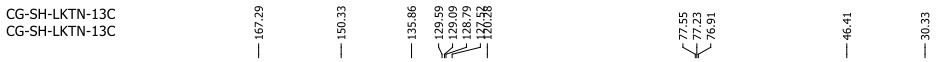
0.0
f1 (ppm)


CG-SH-LKTN-13C
CG-SH-LKTN-13C
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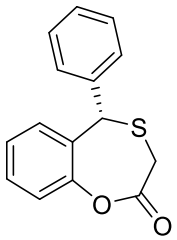
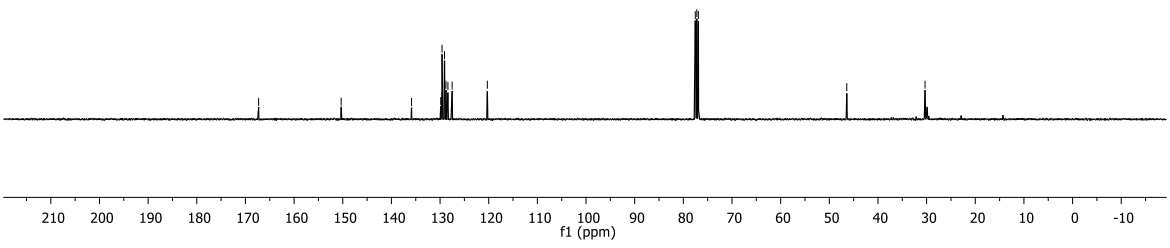
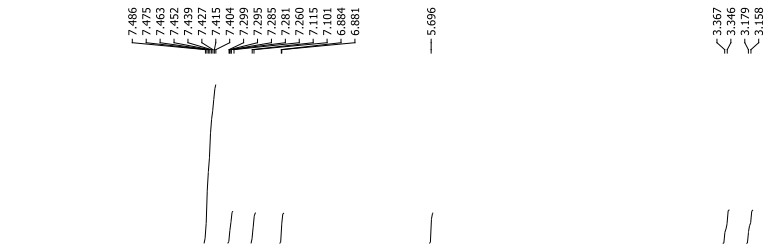
129.09
128.79
127.52
120.28
77.55
77.23
76.91
46.41
30.33


S
O
O

**4q**


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.295
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5.696
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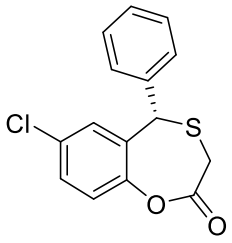
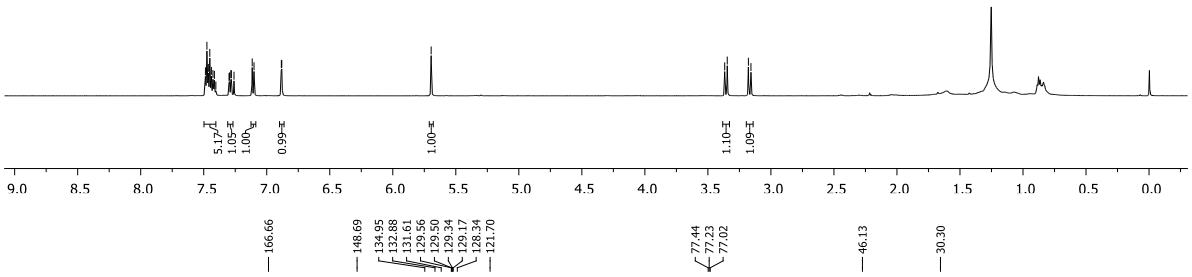
3.346
3.179
3.158


Cl
S
O
O

**4s**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1.10
1.09
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


166.66
148.69
134.95
132.88
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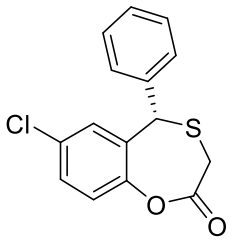
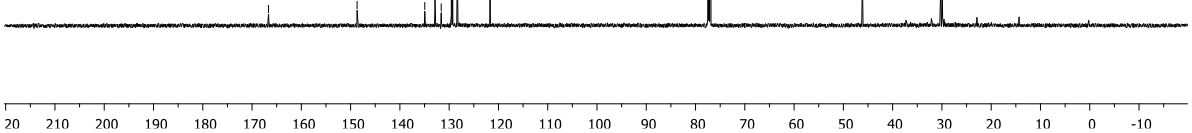
129.34
129.17
128.34
121.70
77.44
77.23
77.02
46.13
30.30


Cl
S
O
O

**4s**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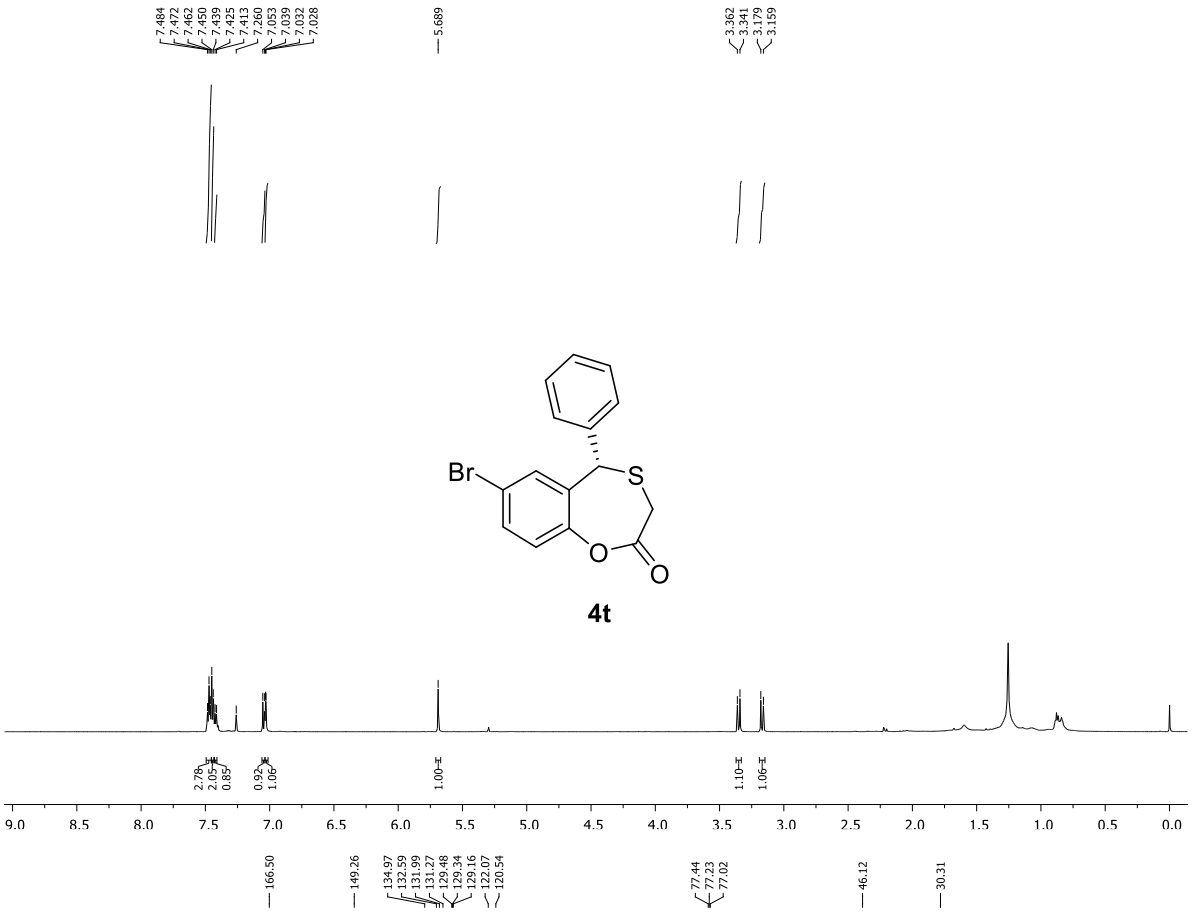
-10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7.053
7.039
7.032
7.028
5.689
3.362
3.341
3.175
3.159
Br
S
O
O
4t
2.78
2.05
0.85
0.92
1.06
1.00
1.10
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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149.26
134.97
132.59
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122.07
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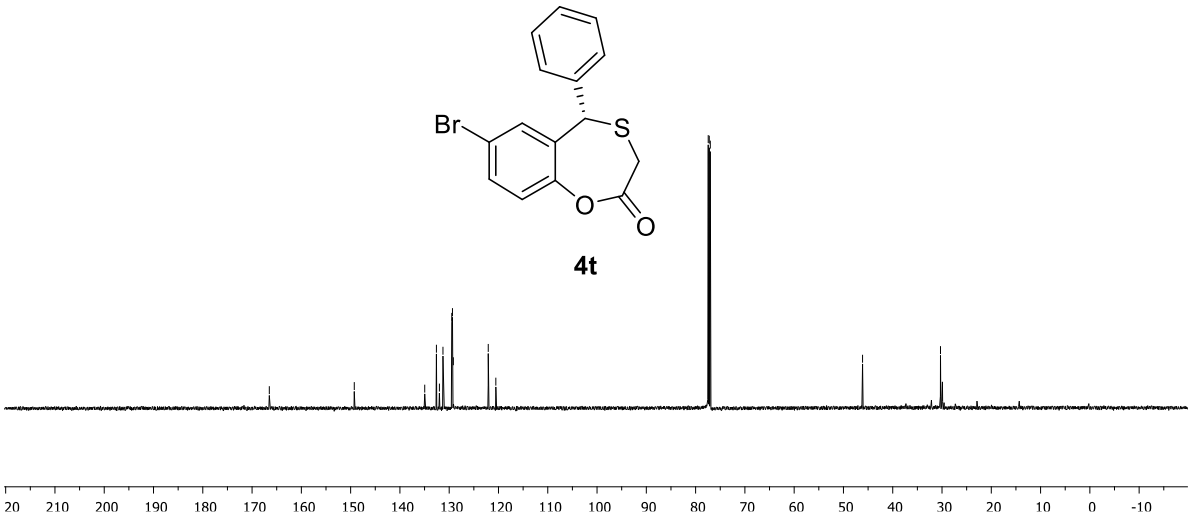
77.23
77.02
46.12
30.31


Br
S
O
O
4t
20
210
200
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60
50
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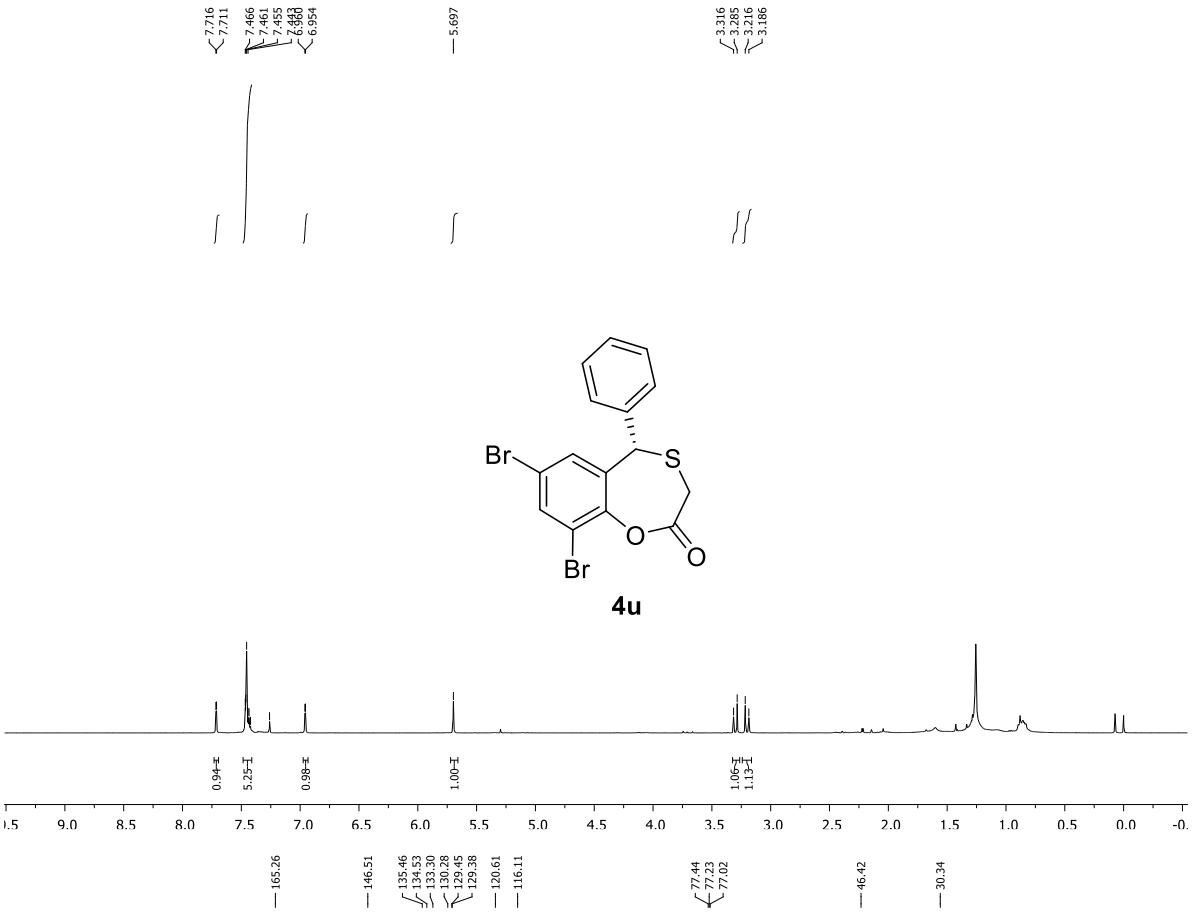
20
10
0
-10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3.285
3.216
3.186
Br
S
O
O
Br
4u
0.94
5.25
0.98
1.00
1.06
1.13
9.0
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8.0
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7.0
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2.0
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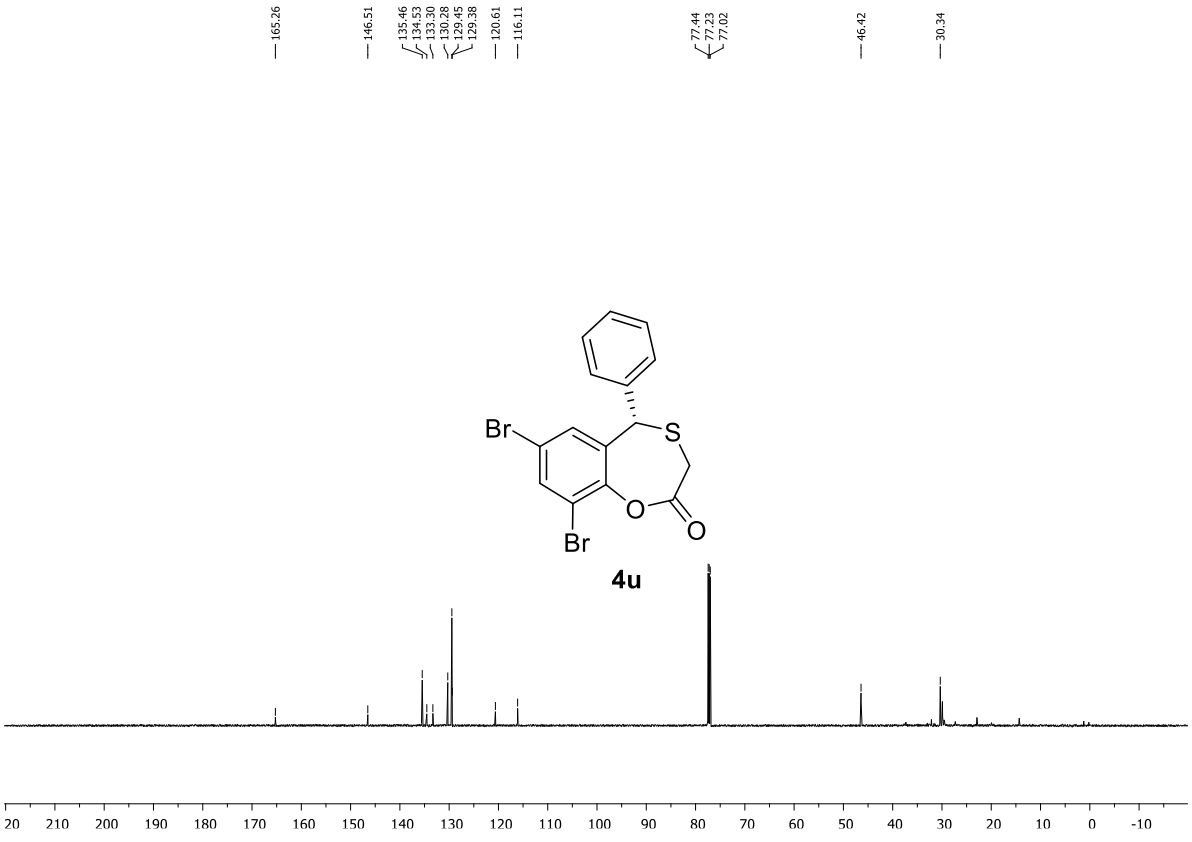
0.0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116.11
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77.23
77.02
46.42
30.34
Br
S
O
O
Br
4u
210
200
190
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120
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100
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80
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50
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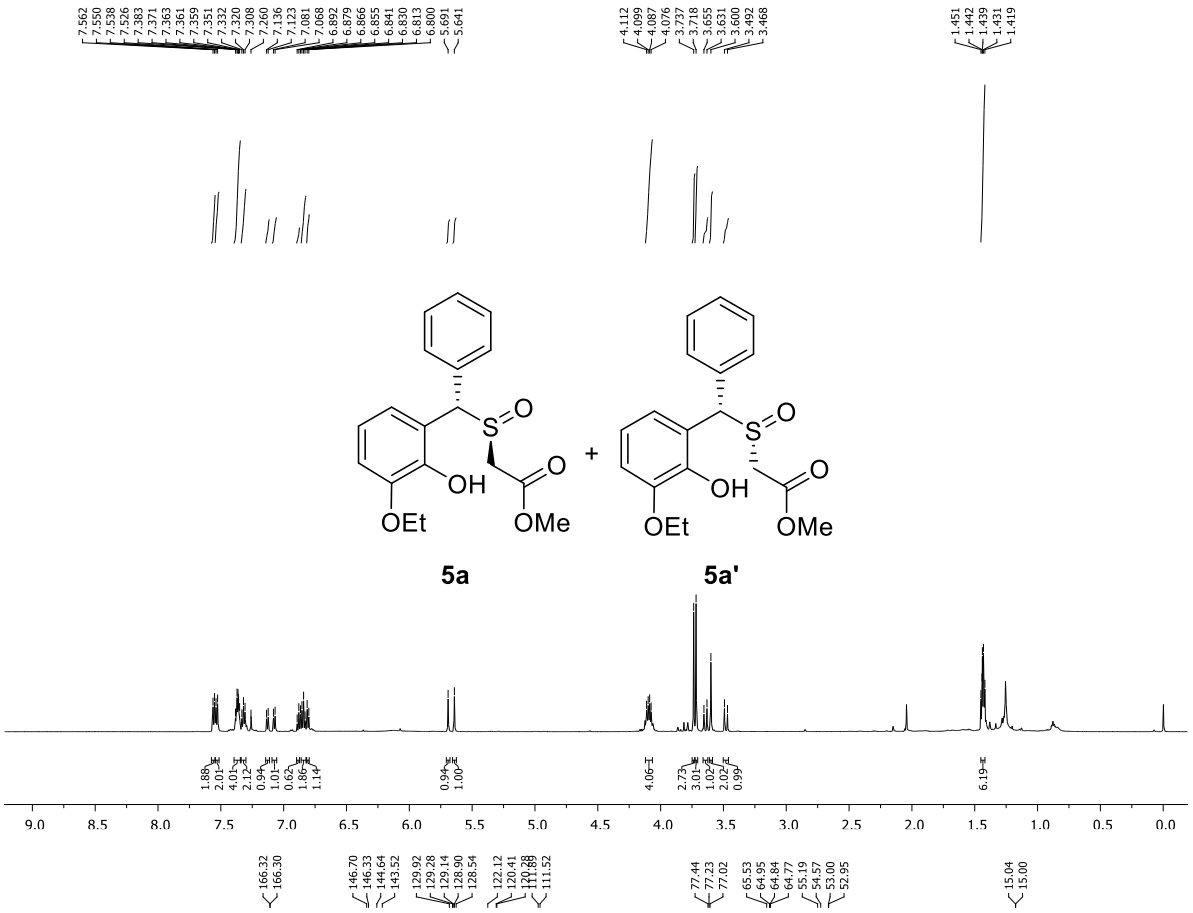
0
-10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4.099
4.087
4.076
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3.655
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1.442
1.439
1.431
1.419
S
O
OH
OEt
OMe
+
5a
5a'
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2.01
4.01
2.12
0.94
1.01
0.62
1.86
1.14
0.94
1.00
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1.02
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6.0
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3.5
3.0
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2.0
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1.0
0.5
0.0
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129.14
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77.23
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54.57
53.00
52.95
15.04
15.00
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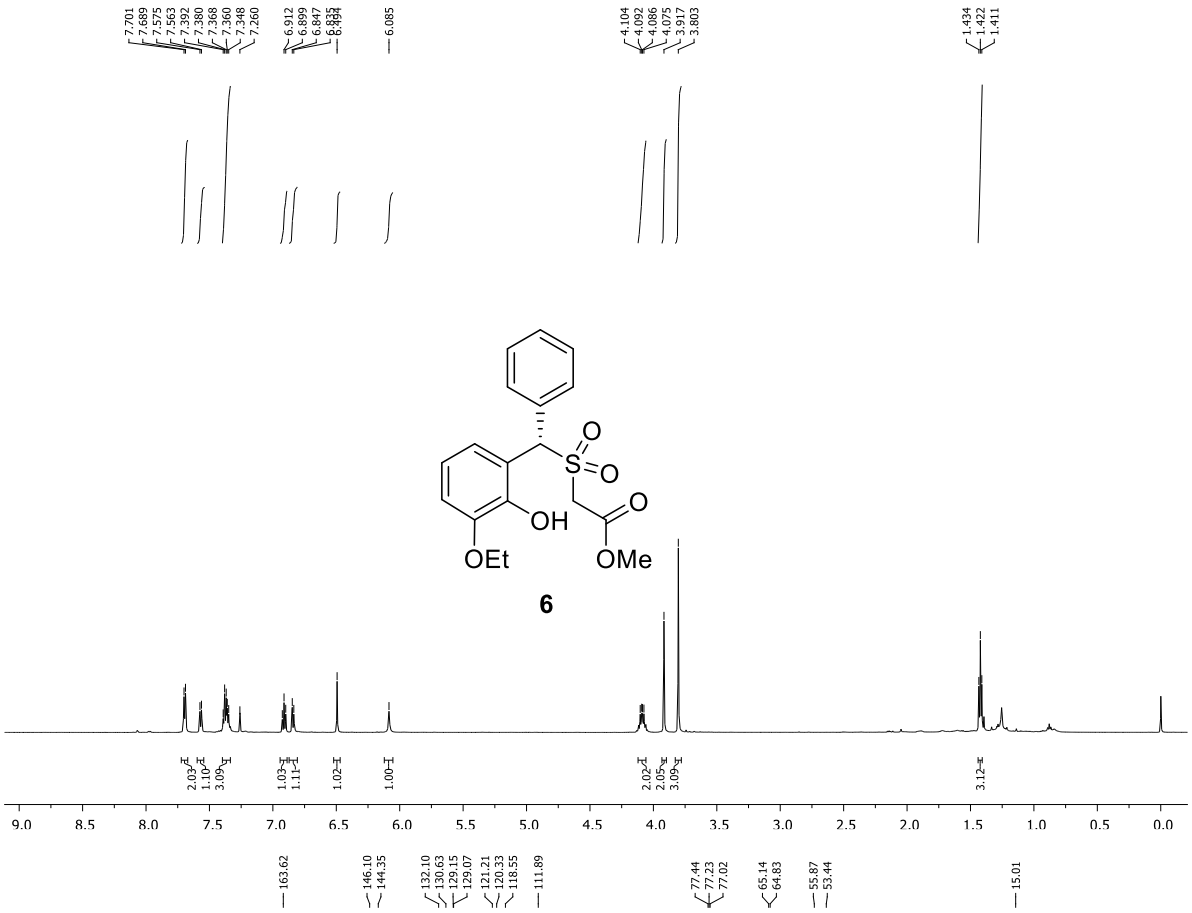
0
-10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6.847
6.085
4.104
4.092
4.086
4.075
3.917
3.803
1.434
1.422
1.411
O
S
O
O
OH
OEt
OMe
6
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1.10
3.09
1.03
1.11
1.02
1.00
2.02
2.05
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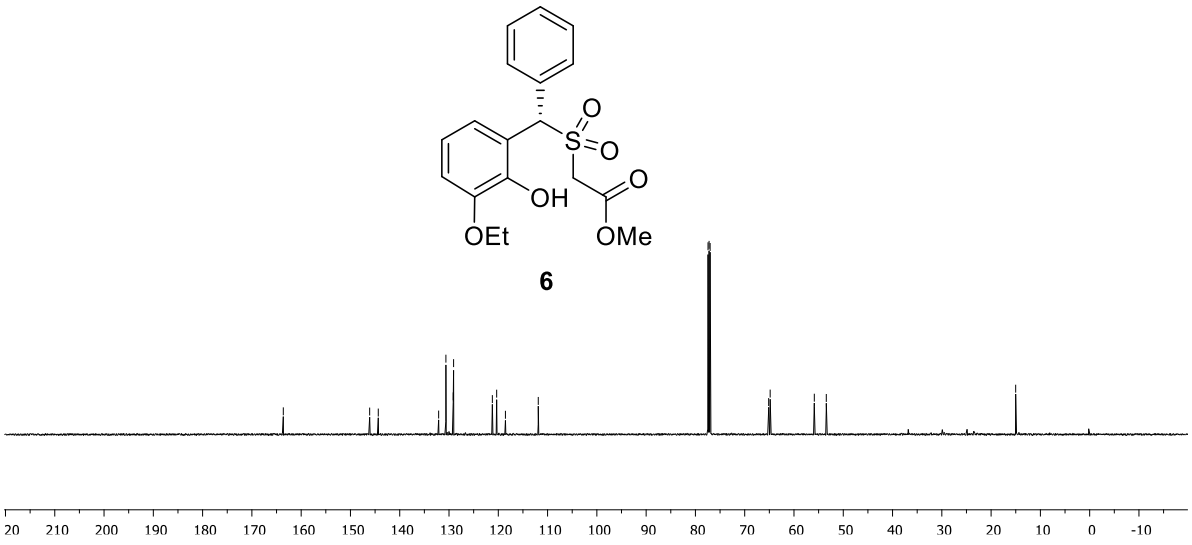
0.0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118.55
111.89
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77.23
77.02
65.14
64.83
55.87
53.44
15.01
O
S
O
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OH
OEt
OMe
6
220
210
200
190
180
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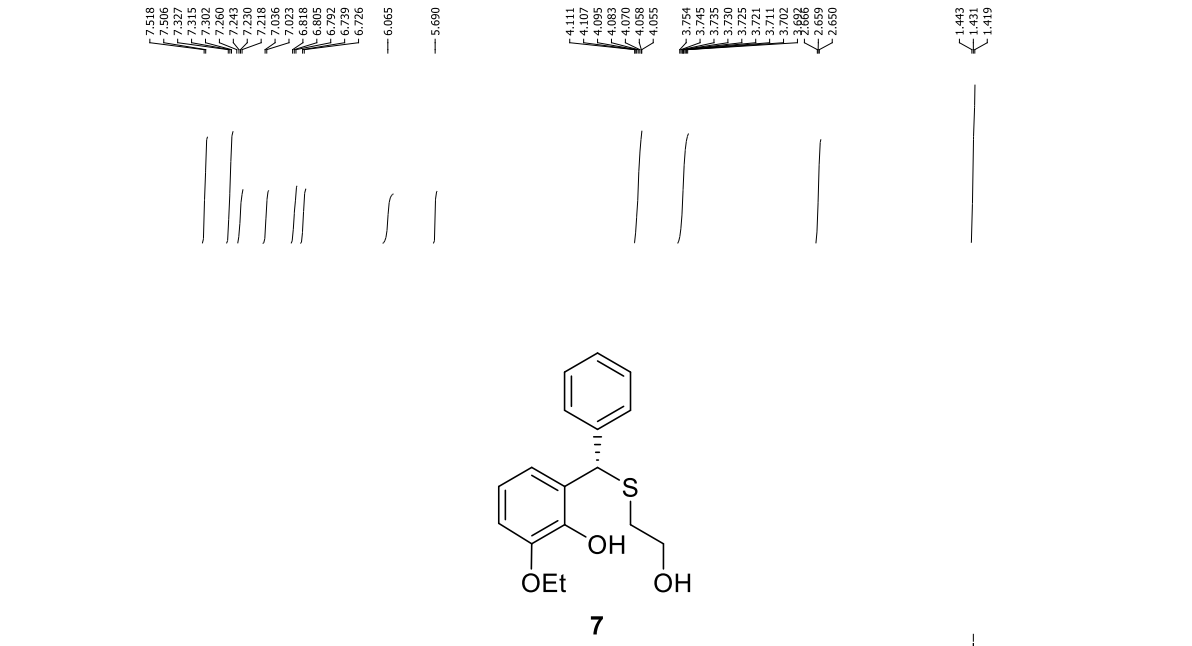
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S
OH
OEt
OH
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1.99
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77.44
77.23
77.02
64.73
60.43
45.82
35.64
15.09


S
OH
OEt
OH
7
220
210
200
190
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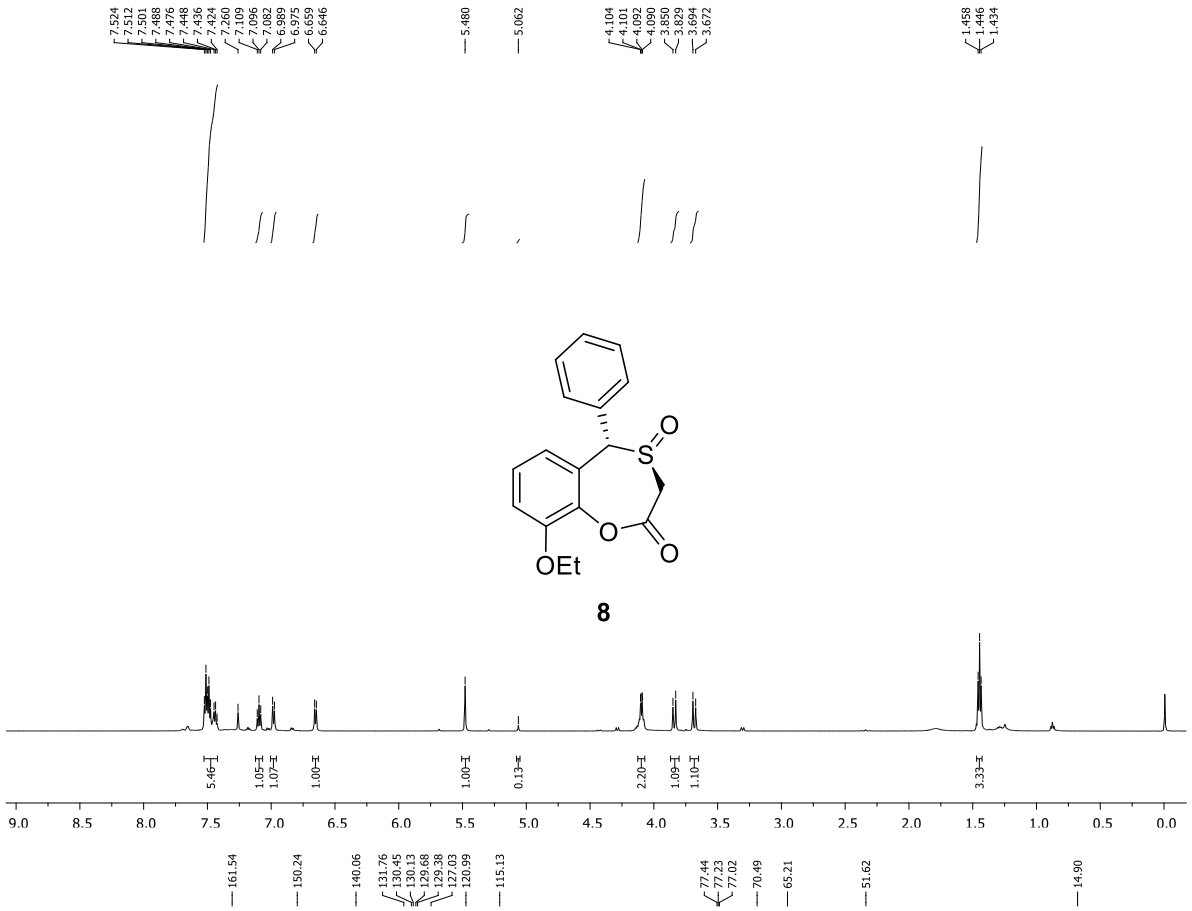
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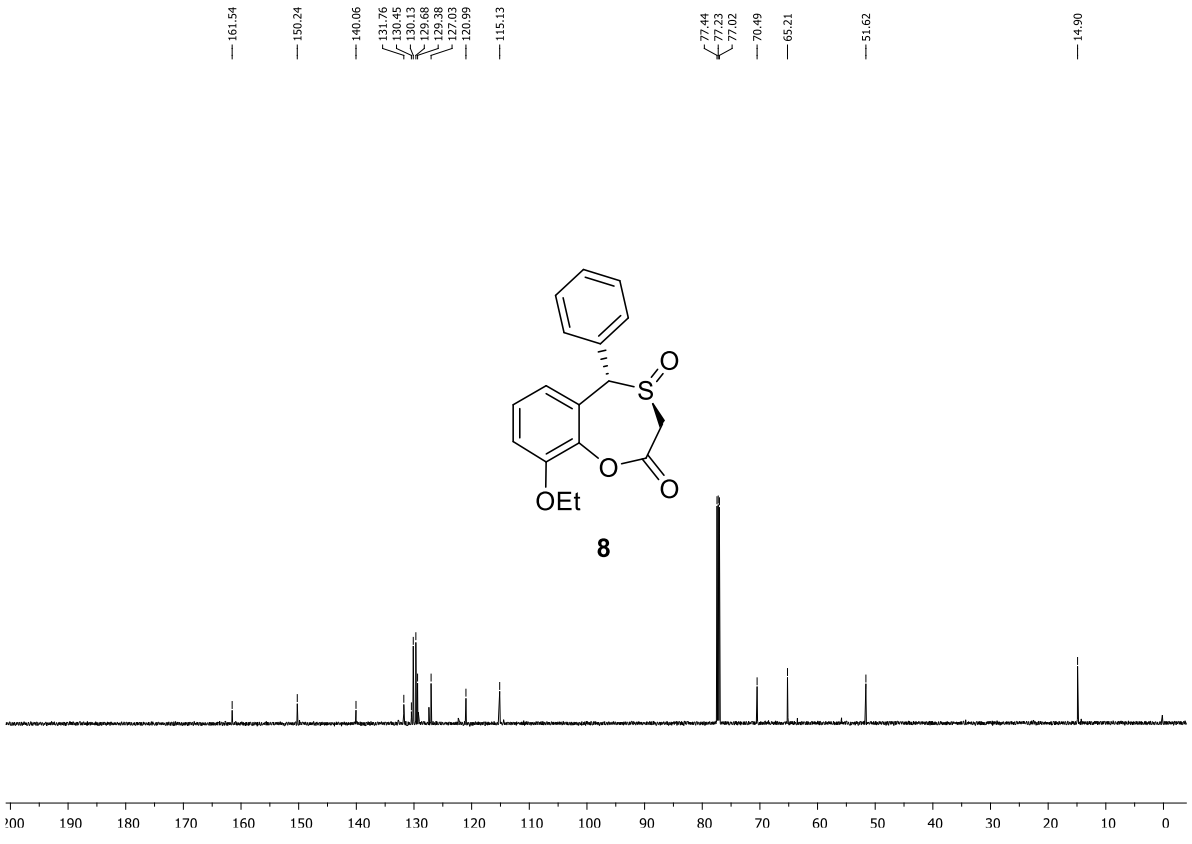
**8**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70.49
65.21
51.62
14.90
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S
O
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OEt
200
190
180
170
160
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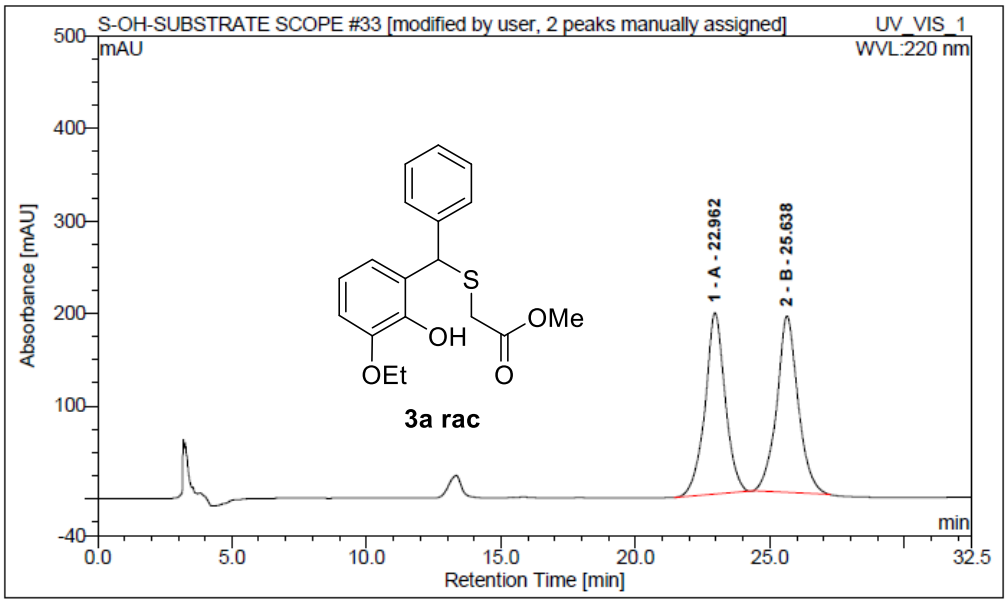
**8**

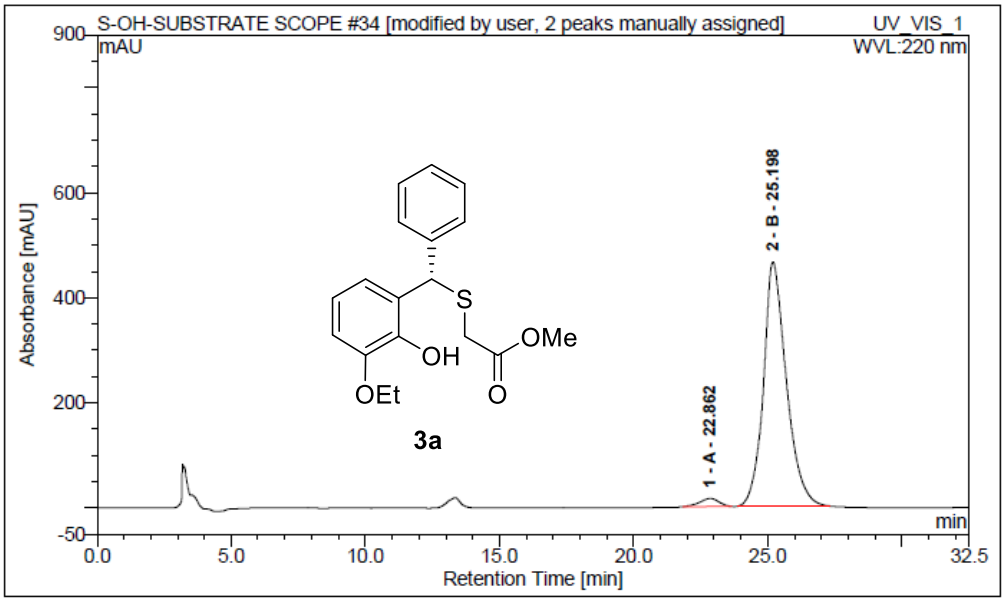
## 11. HPLC chromatogram of the products:

3-OEt-SALI-S-OH-IB-R



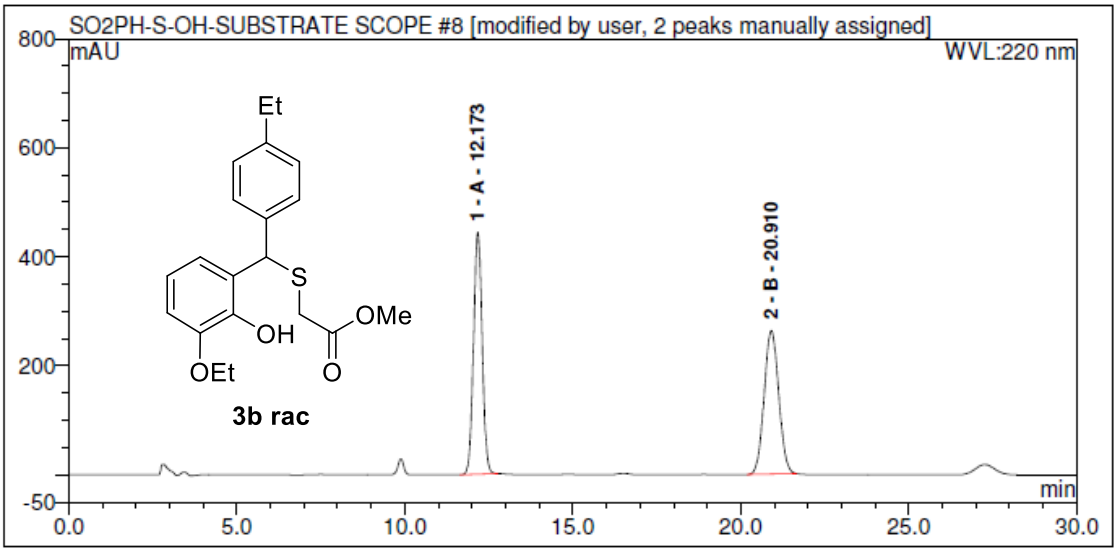

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 22.96 | 169.7495 | 49.09824003 | 195.8707 | n.a. |
| 2 | B | 25.64 | 175.985 | 50.90175997 | 190.556 | n.a. |

3-OEt-SALI-S-OH-IB-CHI



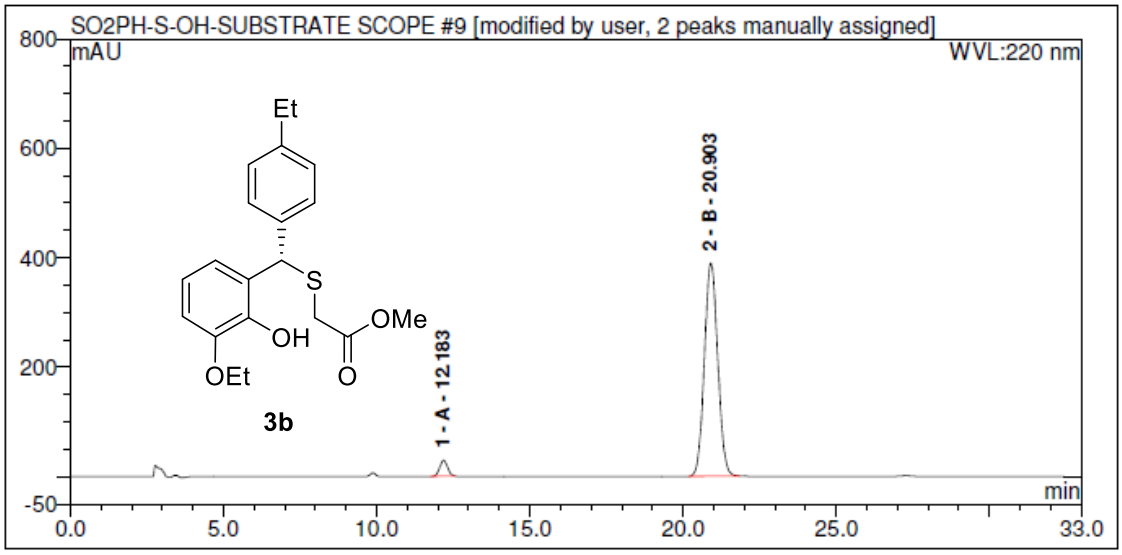

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 22.86 | 12.62895 | 2.670508594 | 15.43966 | n.a. |
| 2 | B | 25.20 | 460.276 | 97.32949141 | 464.828 | n.a. |

3-OEt-SAL-4-Et-GR-Me-GLYCO-AMYLOSE-1-RAC



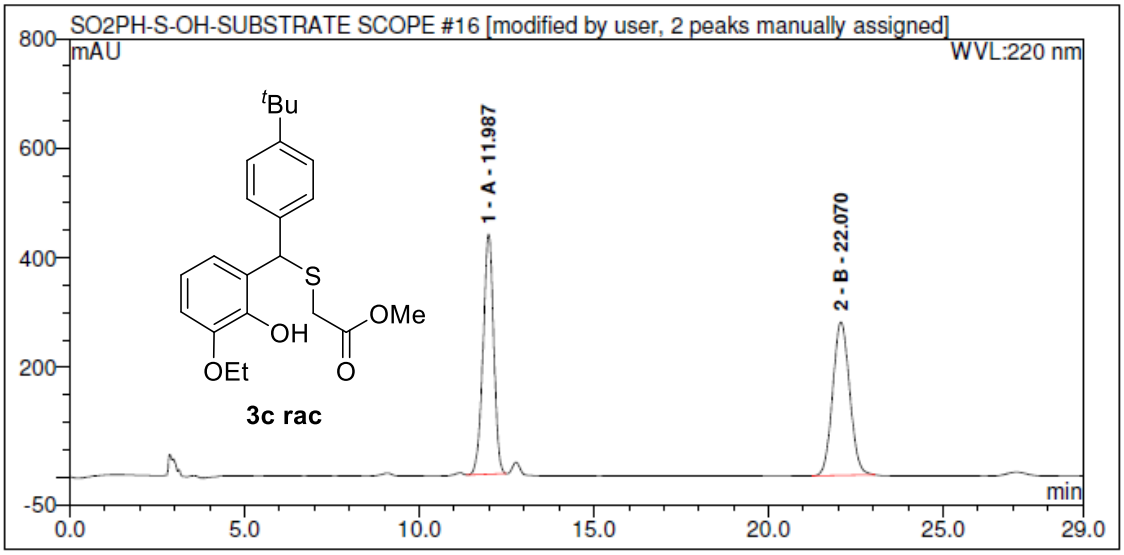

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.17 | 132.7042 | 50.06246102 | 443.697 | n.a. |
| 2 | B | 20.91 | 132.373 | 49.93753898 | 263.394 | n.a. |

3-OEt-SAL-4-Et-GR-Me-GLYCO-AMYLOSE-1-CHI



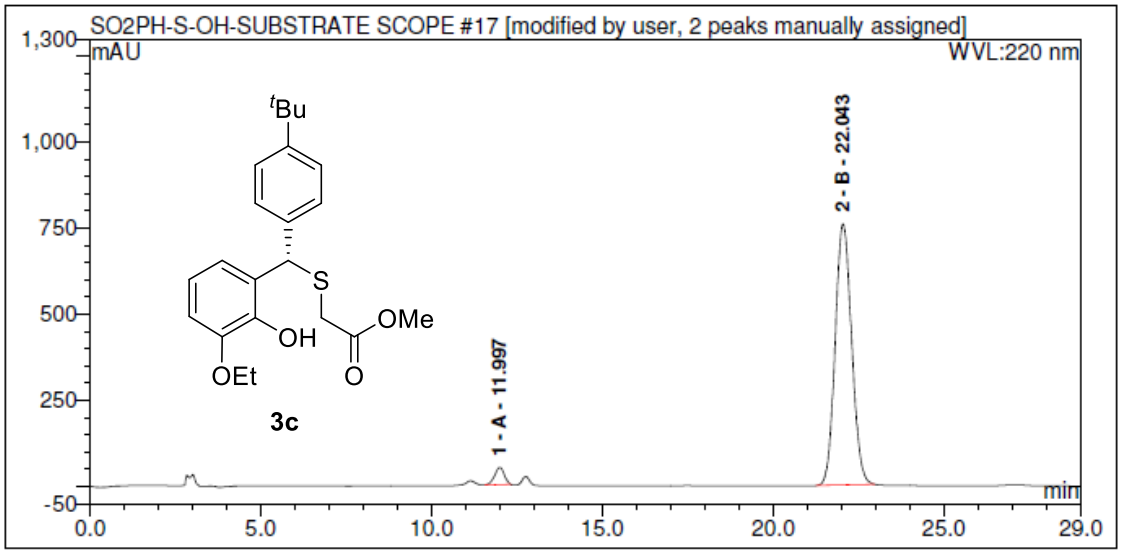

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.18 | 8.563323 | 4.169327476 | 29.09466 | n.a. |
| 2 | B | 20.90 | 196.825 | 95.83067252 | 389.696 | n.a. |

3-OEt-SAL-4-t-BUTYL-GR-Me-GLYCO-S-OH-AMYLOSE-1-RAC



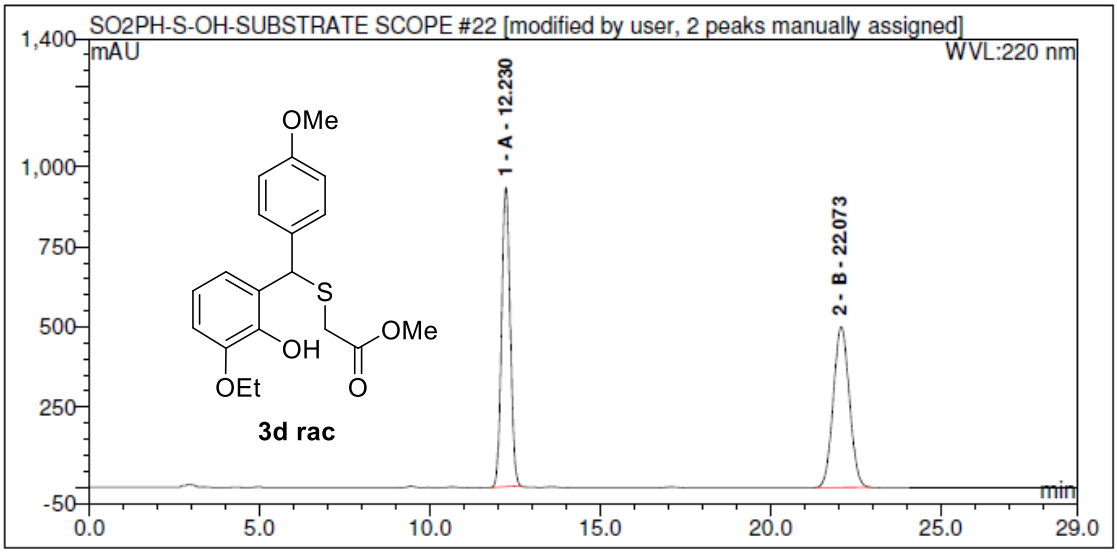

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 11.99 | 154.7821 | 49.58915451 | 437.525 | n.a. |
| 2 | B | 22.07 | 157.347 | 50.41084549 | 279.657 | n.a. |

3-OEt-SAL-4-t-BUTYL-GR-Me-GLYCO-S-OH-AMYLOSE-1-CHI



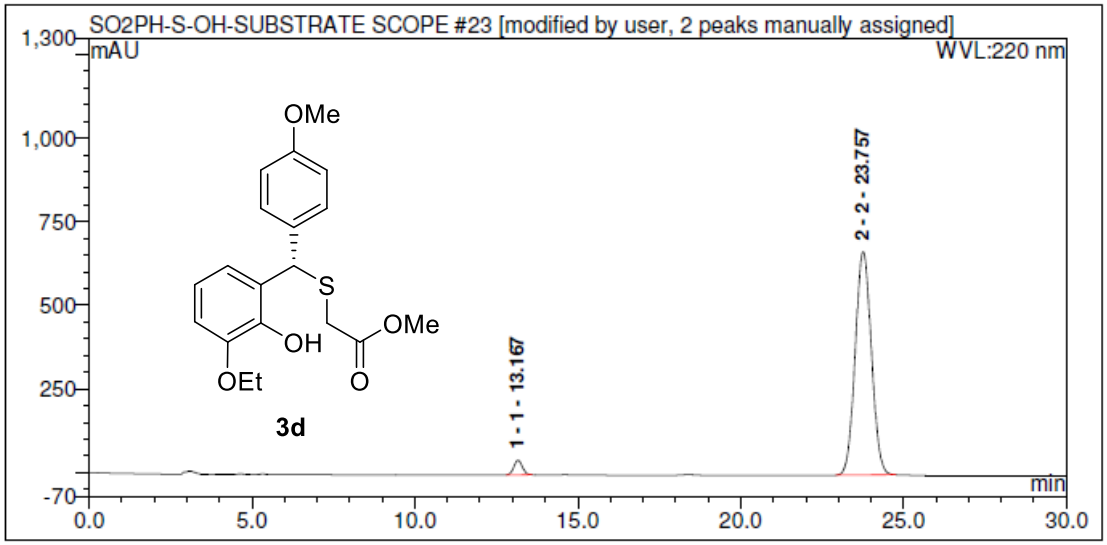

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.00 | 16.21589 | 3.689030304 | 49.71687 | n.a. |
| 2 | B | 22.04 | 423.355 | 96.3109697 | 758.802 | n.a. |

3-OEt-SAL-4-OMe-GR-Me-GLYCO-S-OH-AMYLOSE-1-RAC



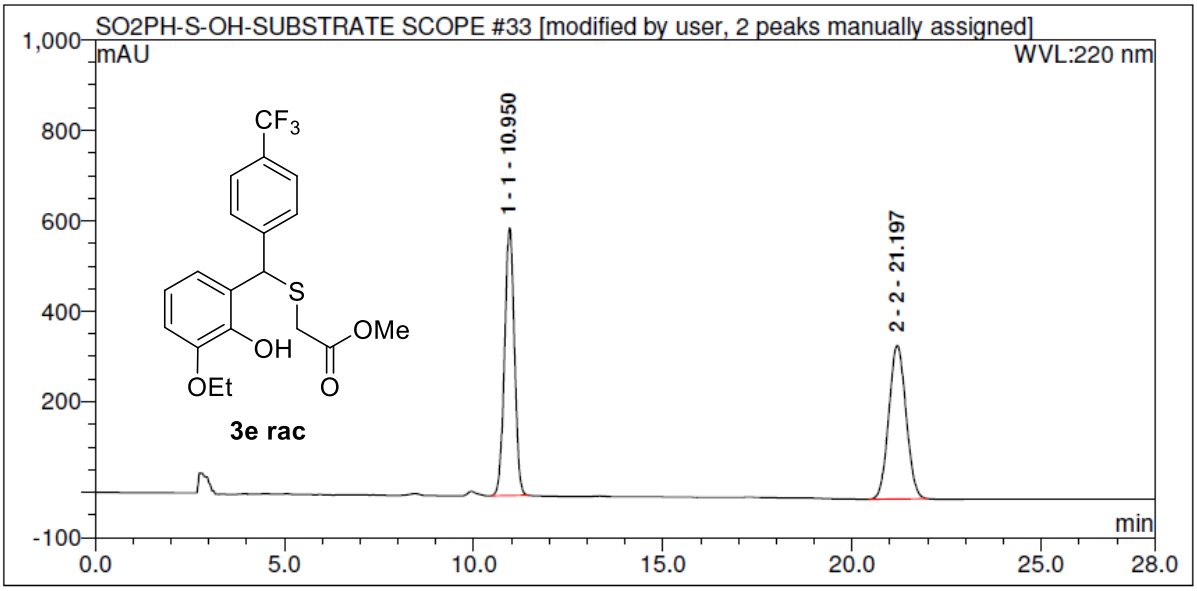

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.23 | 272.8344 | 49.83097519 | 934.1645 | n.a. |
| 2 | B | 22.07 | 274.685 | 50.16902481 | 501.285 | n.a. |

3-OET-SL-4-OMe-GR-S-OH-MYLOSE-1-CHI



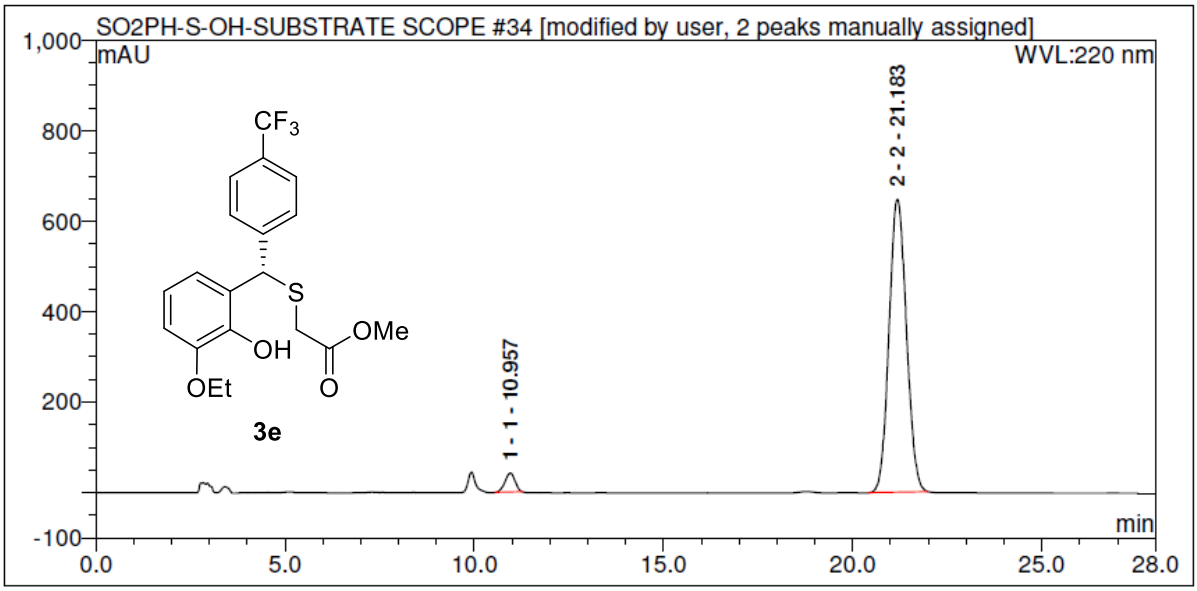

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 13.17 | 13.21433 | 3.318544183 | 43.4131 | n.a. |
| 2 | 2 | 23.76 | 384.982 | 96.68145582 | 667.265 | n.a. |

4-CF3-GR-S-OH-RC-AMYLOSE-1



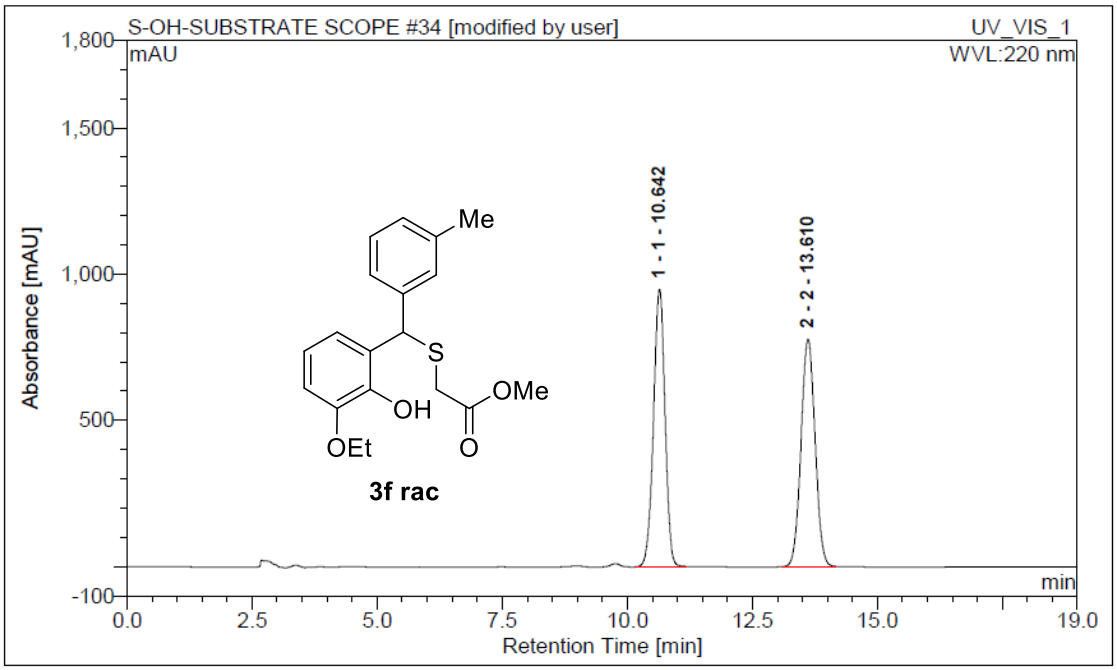

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.95 | 178.8645 | 49.96955185 | 591.3372 | n.a. |
| 2 | 2 | 21.20 | 179.082 | 50.03044815 | 339.234 | n.a. |

4-CF3-GR-S-OH-CHI-AMYLOSE-1



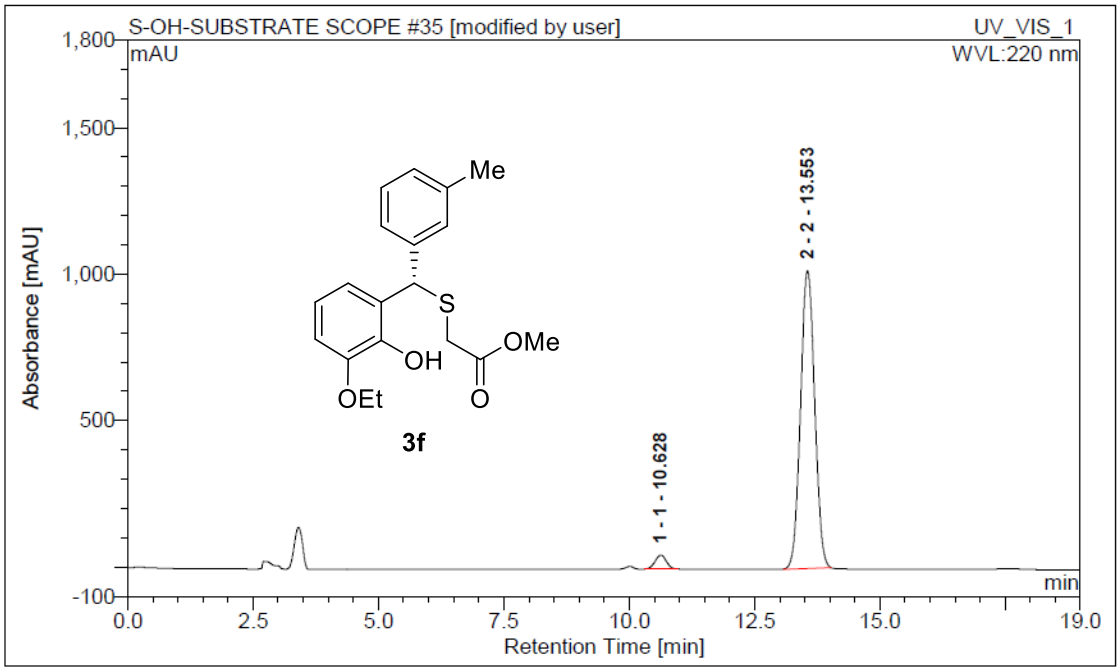

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.96 | 12.9249 | 3.616737222 | 41.83543 | n.a. |
| 2 | 2 | 21.18 | 344.439 | 96.38326278 | 648.035 | n.a. |

3-Me-GR-S-OH-AMYLOSE-1-RAC



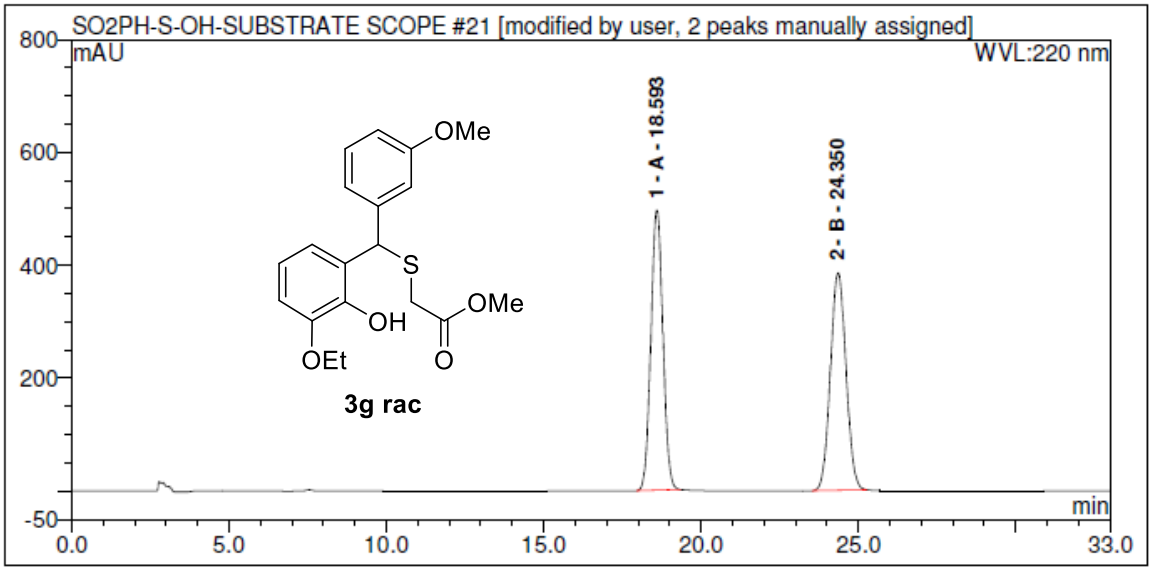

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.64 | 252.3193 | 49.941883 | 947.5228 | n.a. |
| 2 | 2 | 13.61 | 252.907 | 50.058117 | 776.325 | n.a. |

3-Me-GR-S-OH-AMYLOSE-1-CHI



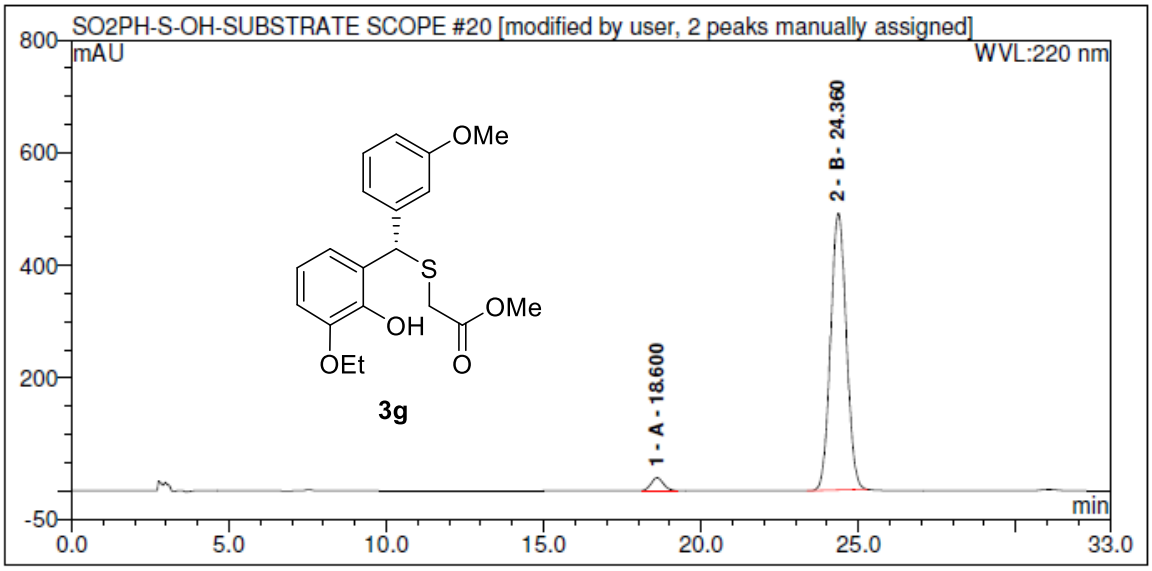

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 10.63 | 12.34905 | 3.59206992 | 47.52796 | n.a. |
| 2 | 2 | 13.55 | 331.437 | 96.40793008 | 1015.803 | n.a. |

3-OEt-SAL-3-OMe-GR-Me-GLYCO-S-OH-AMYLOSE-1-RAC



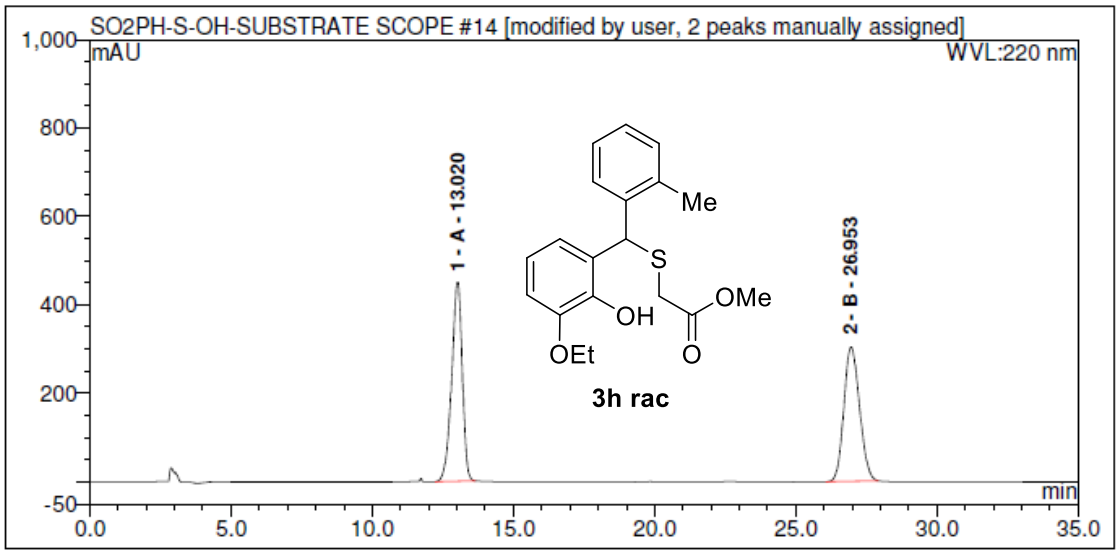

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 18.59 | 219.9315 | 49.81809985 | 496.1228 | n.a. |
| 2 | B | 24.35 | 221.538 | 50.18190015 | 385.307 | n.a. |

3-OEt-SAL-3-OMe-GR-Me-GLYCO-S-OH-AMYLOSE-1-CHI



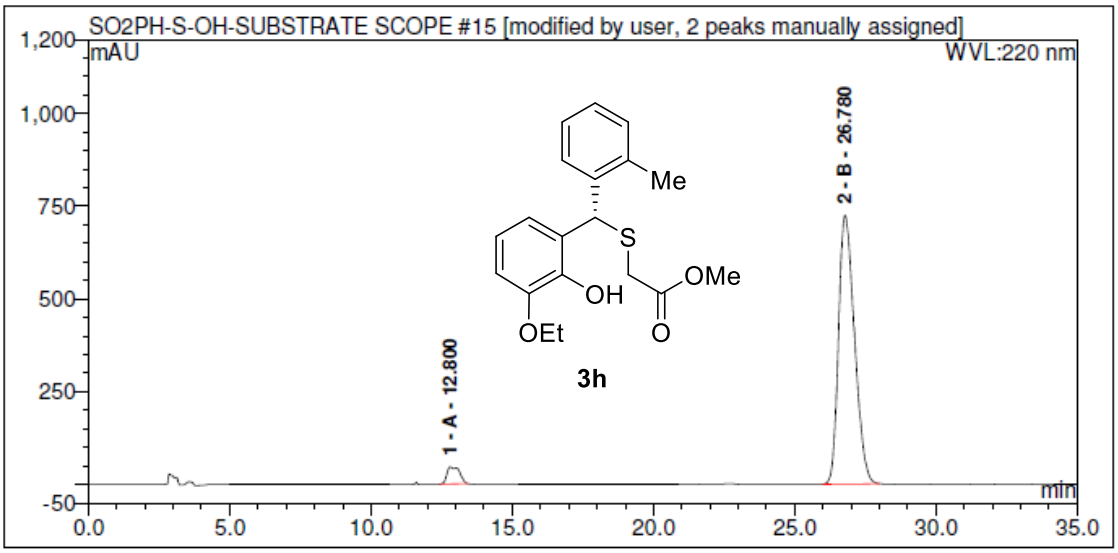

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 18.60 | 9.999141 | 3.394993211 | 22.48116 | n.a. |
| 2 | B | 24.36 | 284.527 | 96.60500679 | 491.322 | n.a. |

3-OEt-SAL-2-Me-GR-Me-GLYCO-S-OH-AMYLOSE-1-RAC



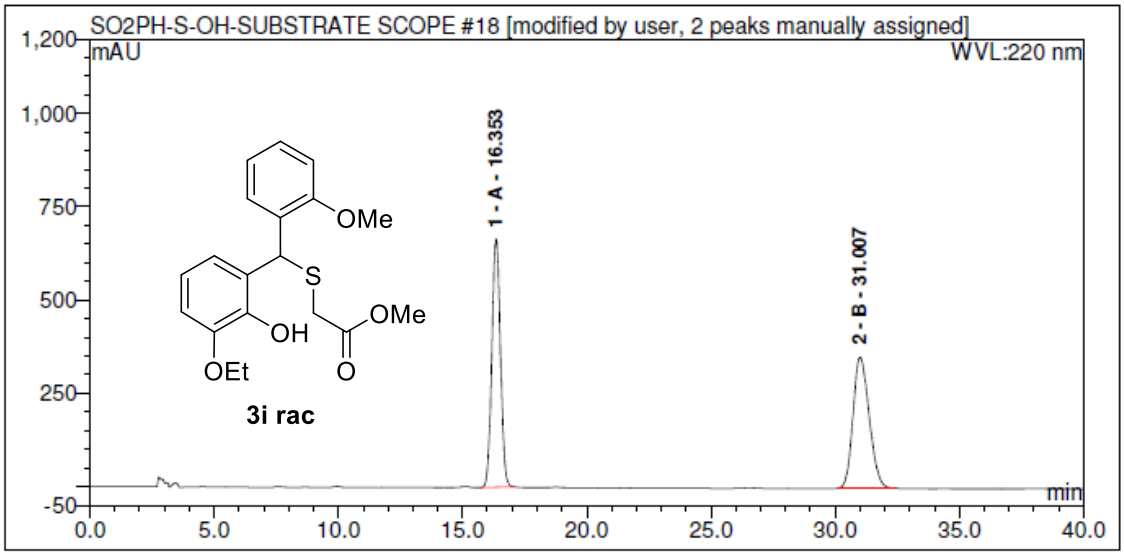

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.02 | 196.225 | 50.13108183 | 450.6364 | n.a. |
| 2 | B | 26.95 | 195.199 | 49.86891817 | 303.775 | n.a. |

3-OEt-SAL-2-Me-GR-Me-GLYCO-S-OH-AMYLOSE-1-CHI



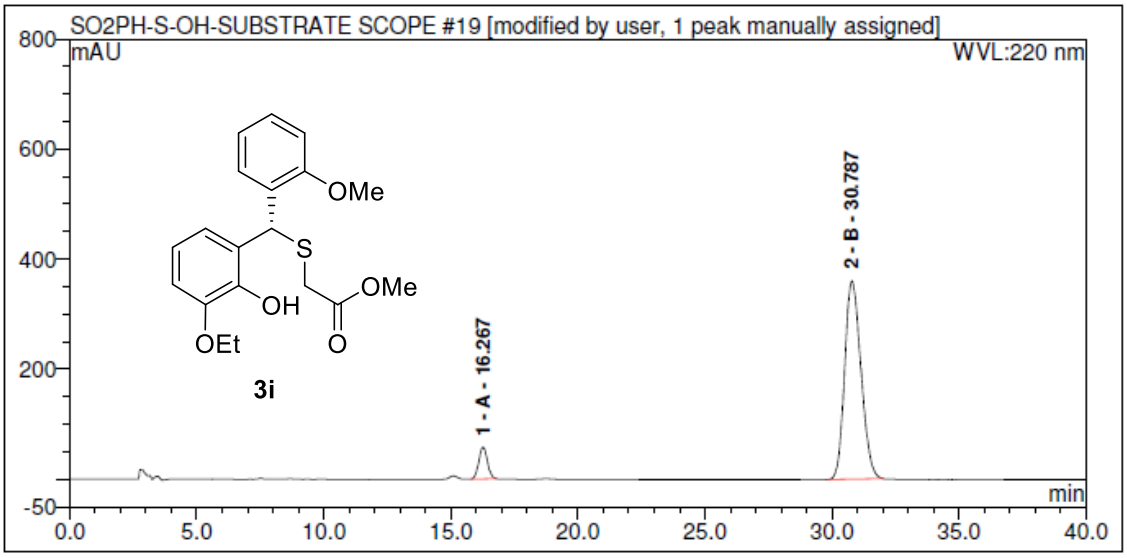

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.80 | 23.53185 | 4.729713913 | 45.85937 | n.a. |
| 2 | B | 26.78 | 474.000 | 95.27028609 | 724.267 | n.a. |

3-OEt-SAL-2-OMe-GR-Me-GLYCO-S-OH-AMYLOSE-1-RAC



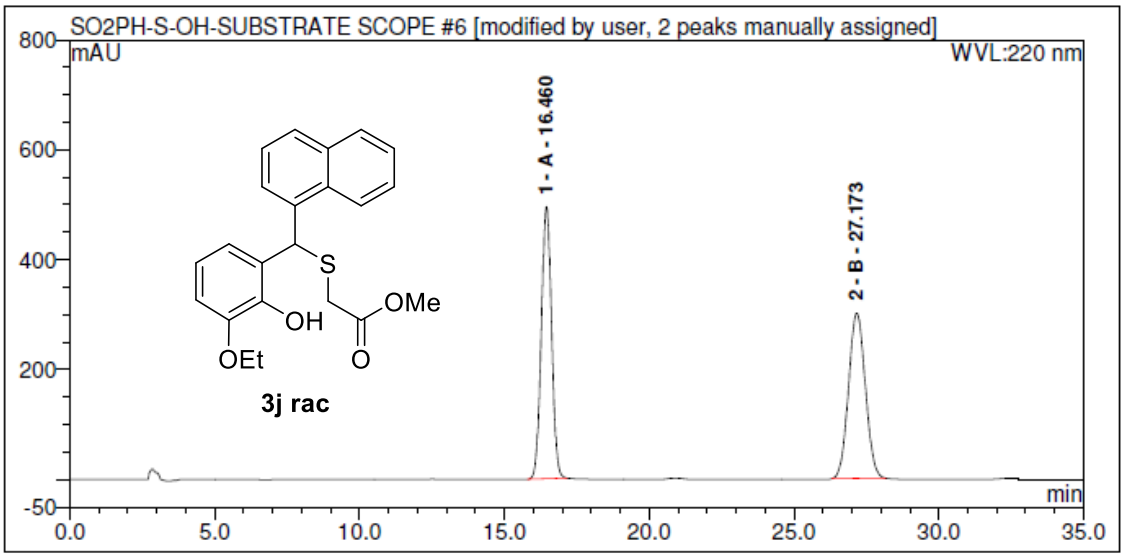

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.35 | 266.5907 | 50.04991288 | 665.7317 | n.a. |
| 2 | B | 31.01 | 266.059 | 49.95008712 | 351.394 | n.a. |

3-OEt-SAL-2-OMe-GR-Me-GLYCO-S-OH-AMYLOSE-1-CHI



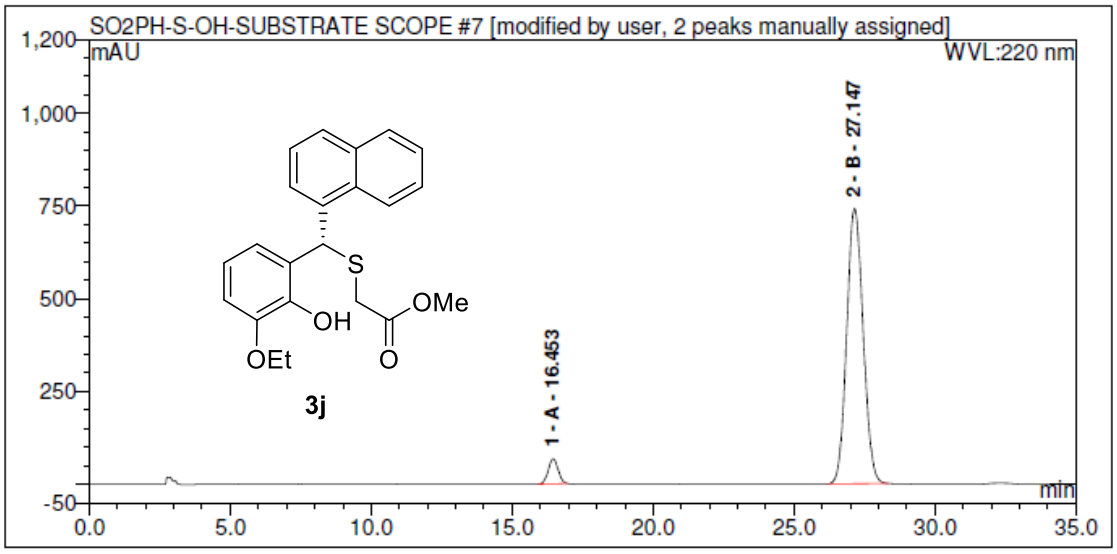

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.27 | 22.6662 | 7.78980643 | 57.62648 | n.a. |
| 2 | B | 30.79 | 268.306 | 92.21019357 | 360.345 | n.a. |

3-OEt-SAL-1-NAPHTHYL-GR-Me-GLY-S-OH-AMYLOSE-1-RAC



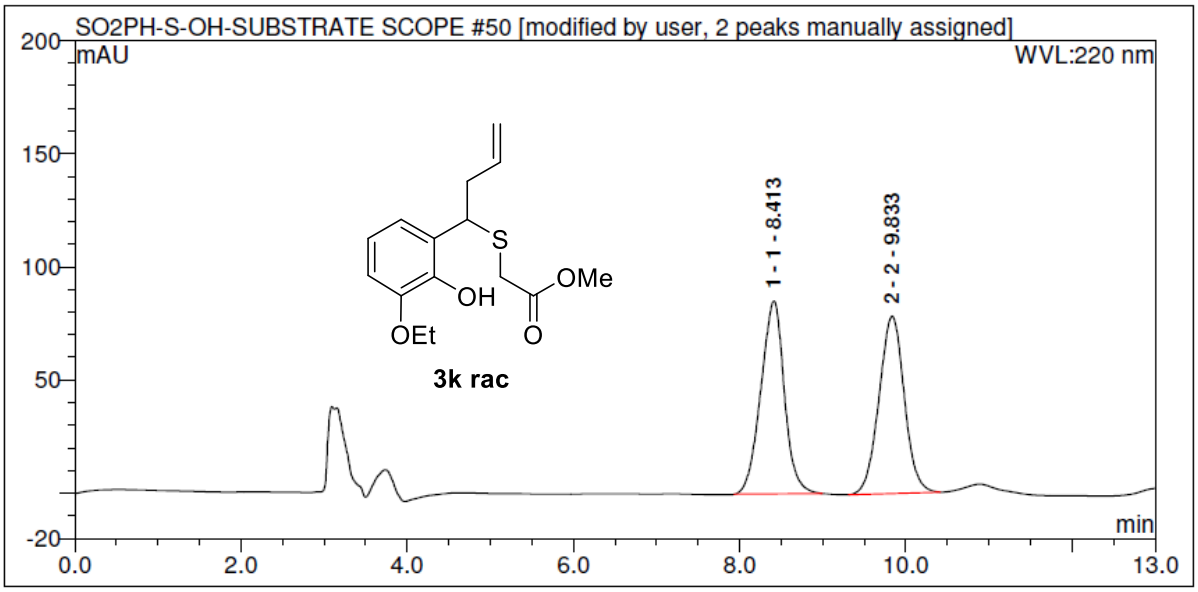

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.46 | 203.8112 | 50.21558521 | 495.3661 | n.a. |
| 2 | B | 27.17 | 202.061 | 49.78441479 | 300.987 | n.a. |

3-OEt-SAL-1-NAPHTHYL-GR-Me-GLY-S-OH-AMYLOSE-1-CHI



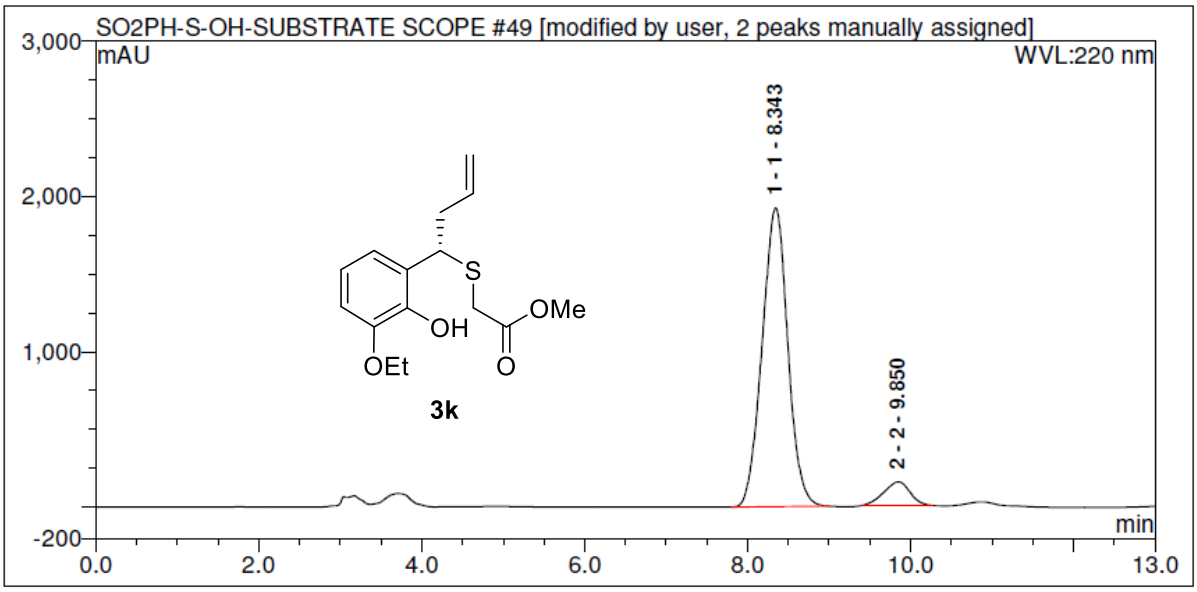

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.45 | 26.96877 | 5.10855474 | 66.73637 | n.a. |
| 2 | B | 27.15 | 500.945 | 94.89144526 | 742.038 | n.a. |

Allyl-GR-S-OH-RC-UP-IB



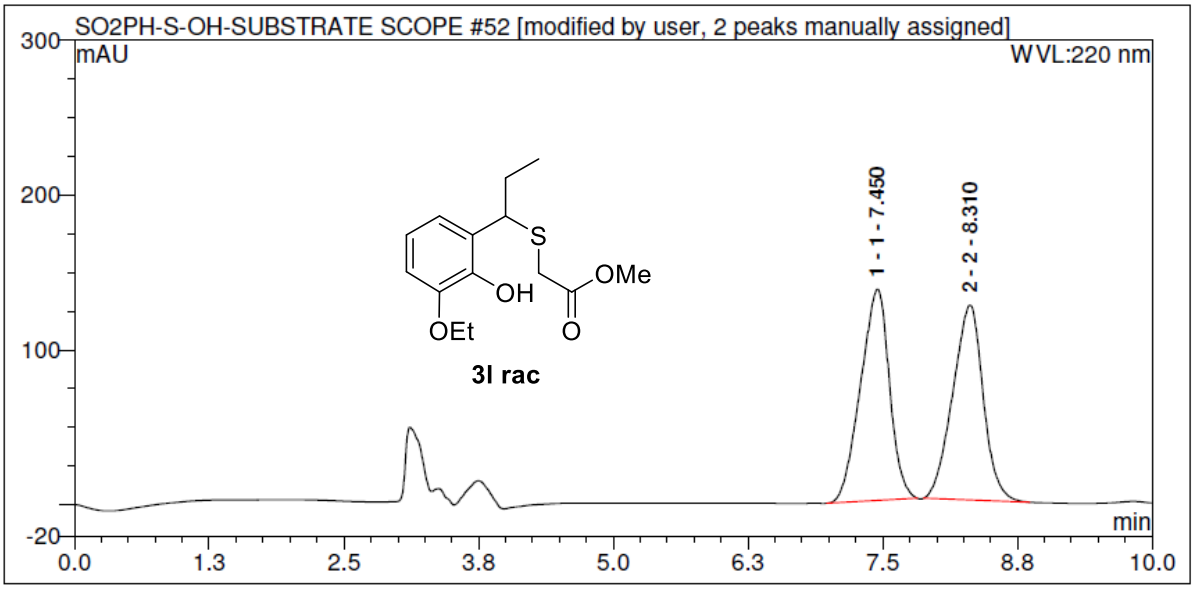

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.41 | 27.97618 | 50.28335625 | 85.19685 | n.a. |
| 2 | 2 | 9.83 | 27.661 | 49.71664375 | 78.322 | n.a. |

Allyl-GR-S-OH-CHI-UP-IB



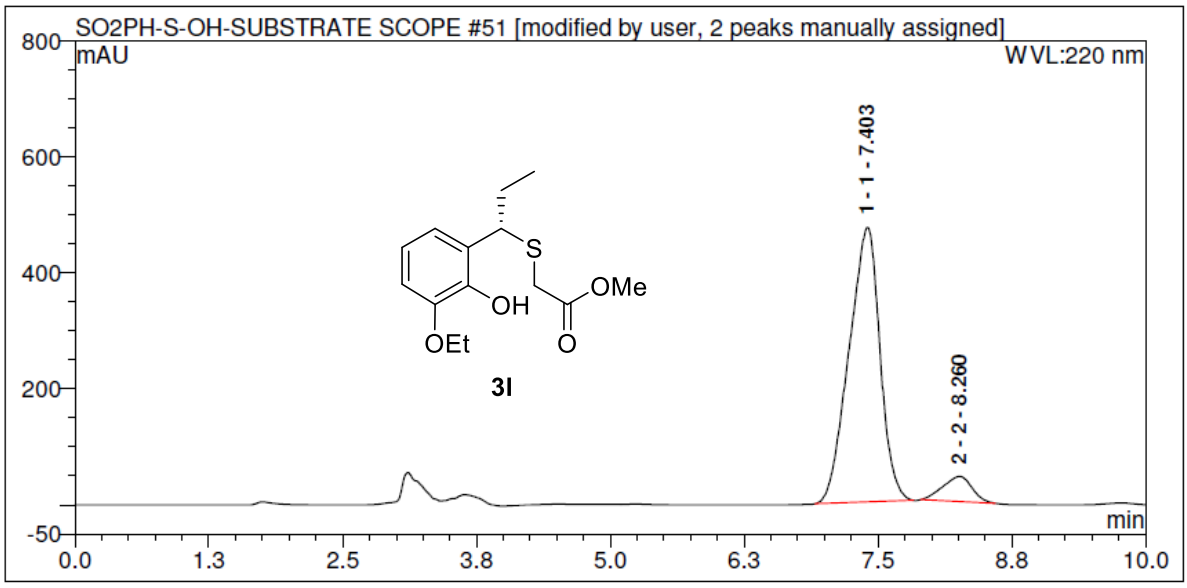

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.34 | 702.7781 | 92.46764656 | 1922.606 | n.a. |
| 2 | 2 | 9.85 | 57.248 | 7.532353441 | 152.960 | n.a. |

ETHYL-GR-S-OH-RC-UP-IB



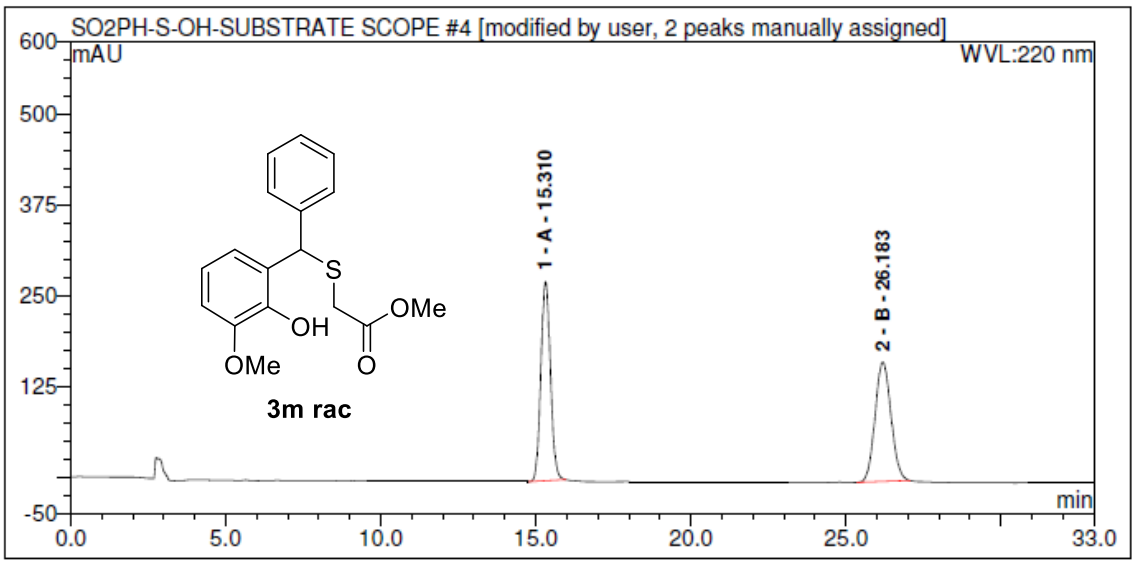

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.45 | 42.39874 | 50.70592004 | 136.3044 | n.a. |
| 2 | 2 | 8.31 | 41.218 | 49.29407996 | 125.715 | n.a. |

ETHYL-GR-S-OH-CHI-UP-IB



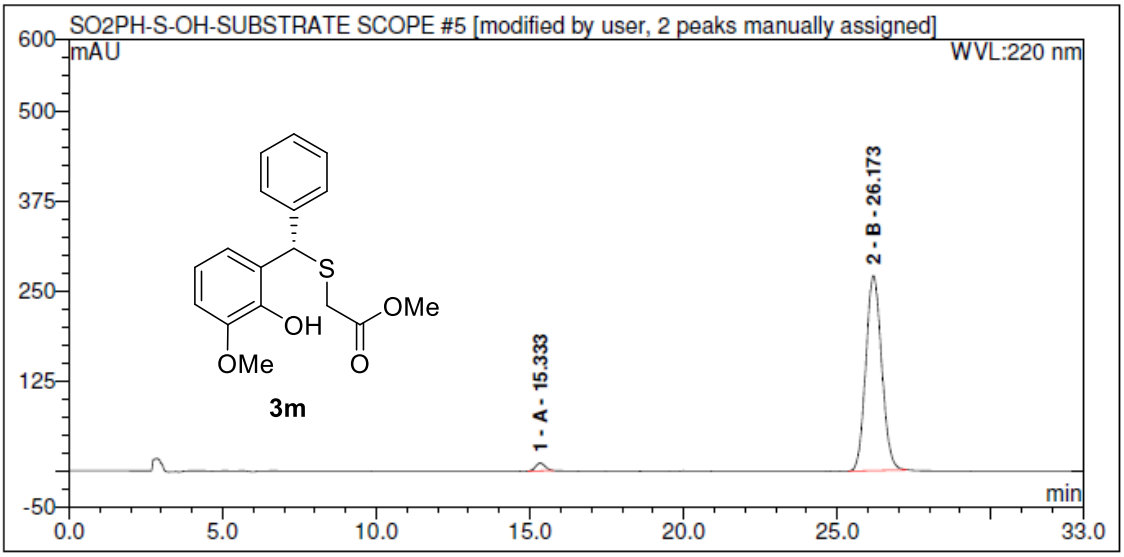

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.40 | 158.5737 | 92.08486549 | 473.3916 | n.a. |
| 2 | 2 | 8.26 | 13.630 | 7.915134506 | 43.161 | n.a. |

3-OMe-SAL-Me-GLY-S-OH-AMYLOSE-1-RAC



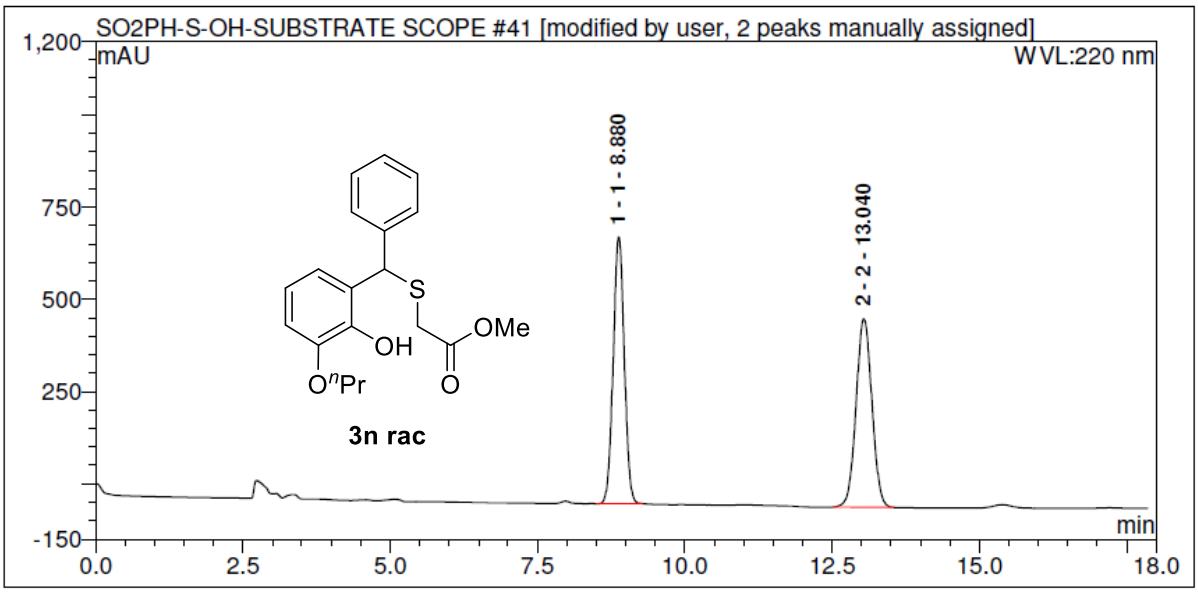

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 15.31 | 97.87236 | 49.95400375 | 274.1918 | n.a. |
| 2 | B | 26.18 | 98.053 | 50.04599625 | 164.511 | n.a. |

3-OMe-SAL-Me-GLY-S-OH-AMYLOSE-1-CHI



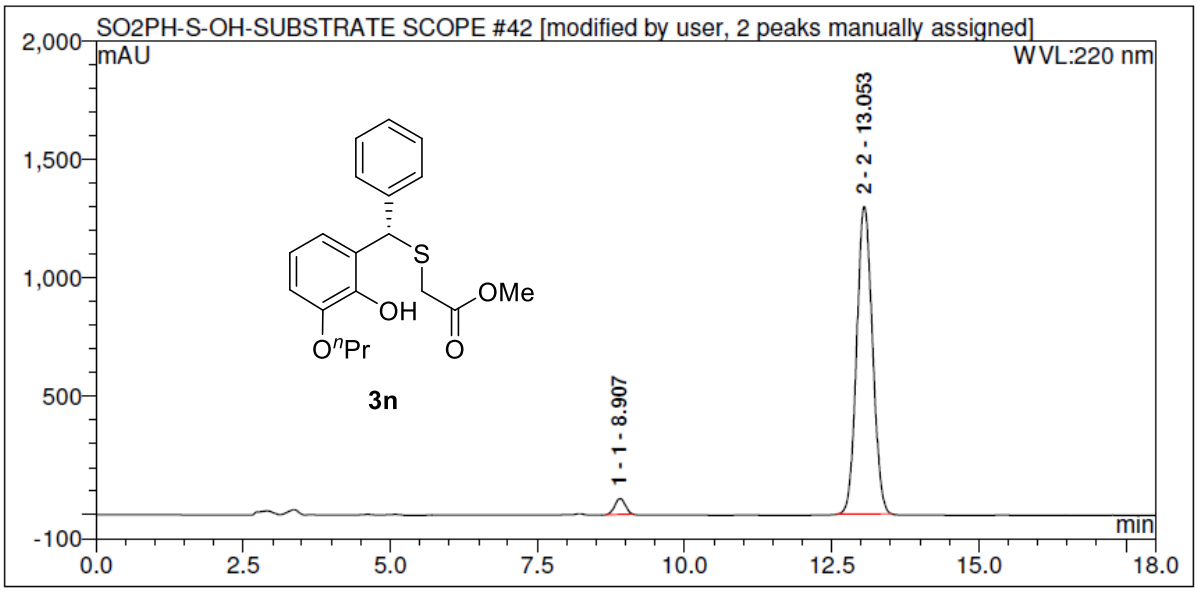

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 15.33 | 3.860885 | 2.322804475 | 10.82849 | n.a. |
| 2 | B | 26.17 | 162.356 | 97.67719553 | 270.977 | n.a. |

3-O-PROPYL-S-OH-RC-AMYLOSE-1



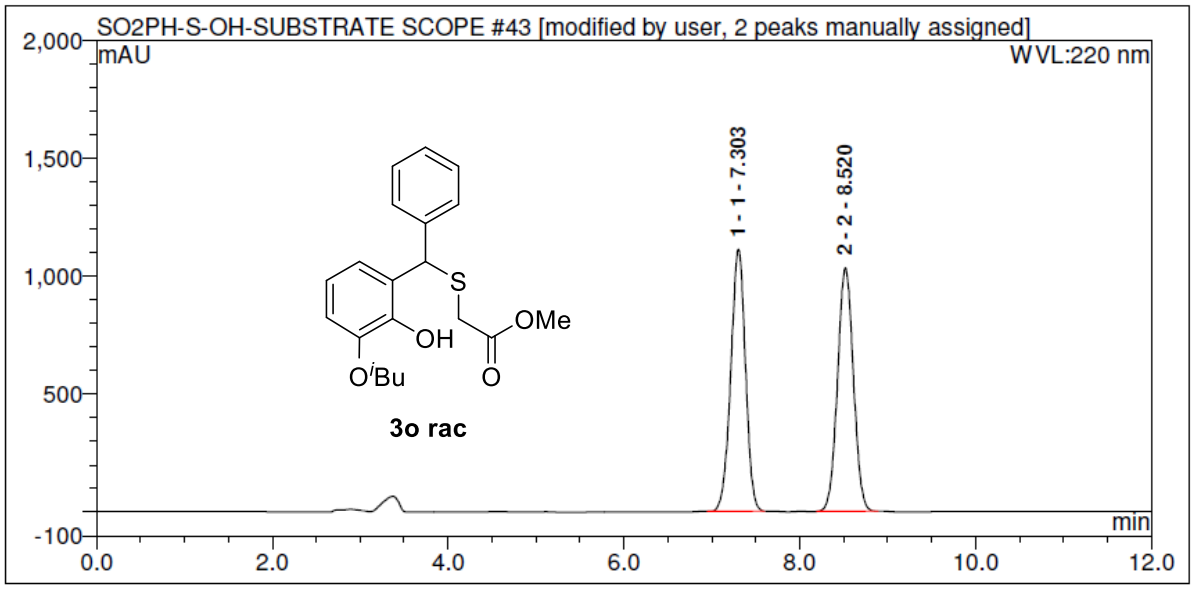

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.88 | 158.0848 | 49.77175189 | 723.449 | n.a. |
| 2 | 2 | 13.04 | 159.535 | 50.22824811 | 511.318 | n.a. |

3-O-PROPYL-S-OH-CHI-AMYLOSE-1



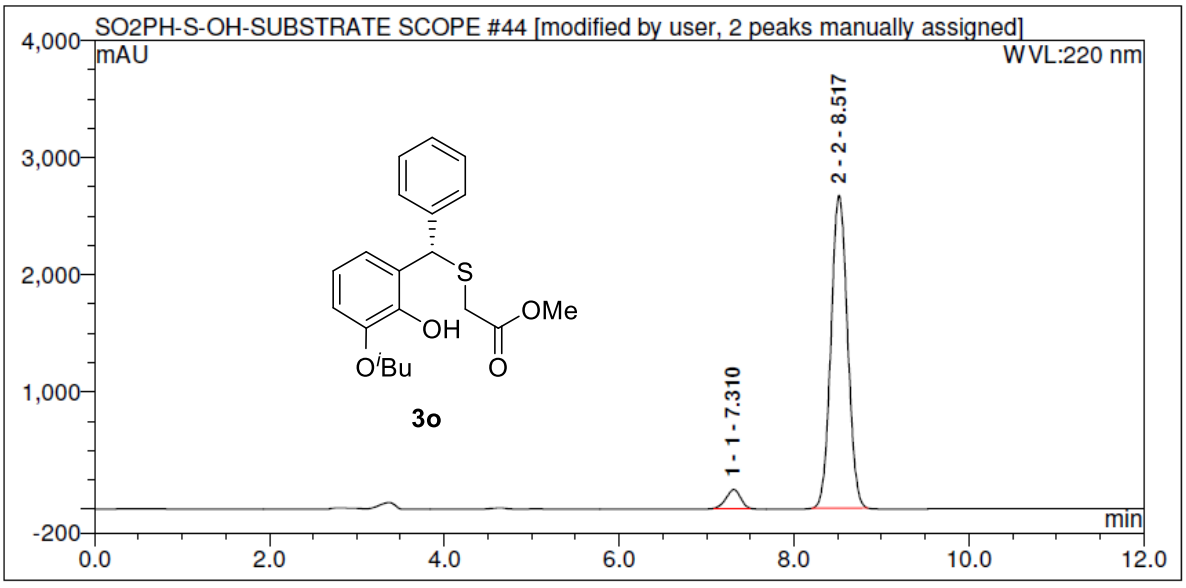

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.91 | 13.69761 | 3.27966639 | 66.92807 | n.a. |
| 2 | 2 | 13.05 | 403.955 | 96.72033361 | 1297.949 | n.a. |

3-O-CH2-IPR-S-OH-RC-AMYLOSE-1



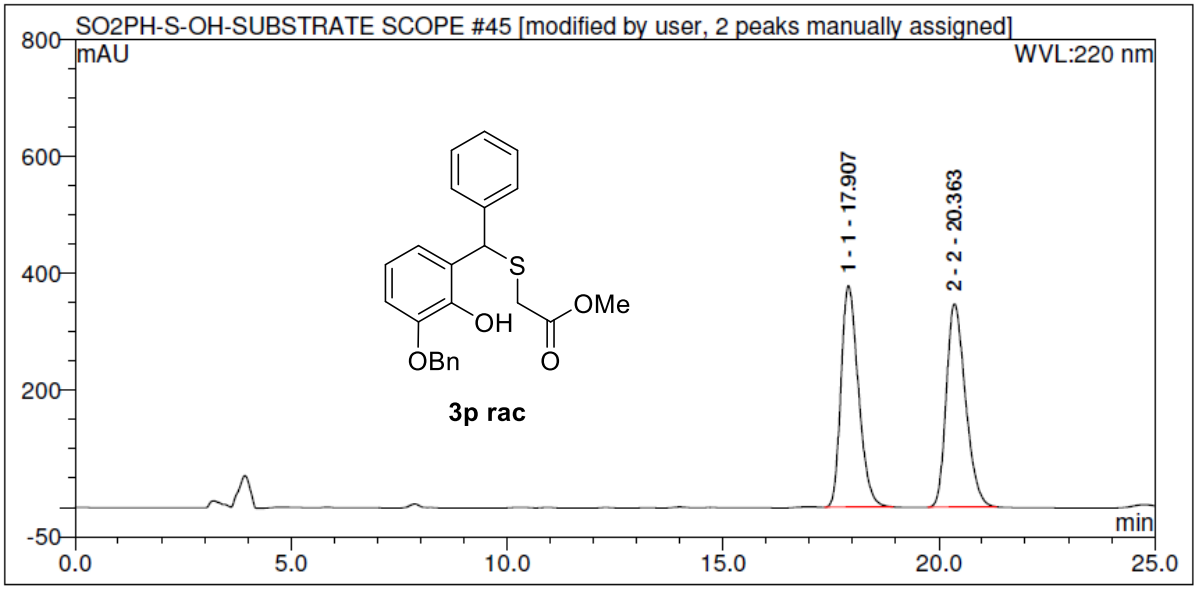

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.30 | 215.0975 | 49.90786559 | 1110.592 | n.a. |
| 2 | 2 | 8.52 | 215.892 | 50.09213441 | 1032.243 | n.a. |

3-O-CH2-IPR-S-OH-CHI-AMYLOSE-1



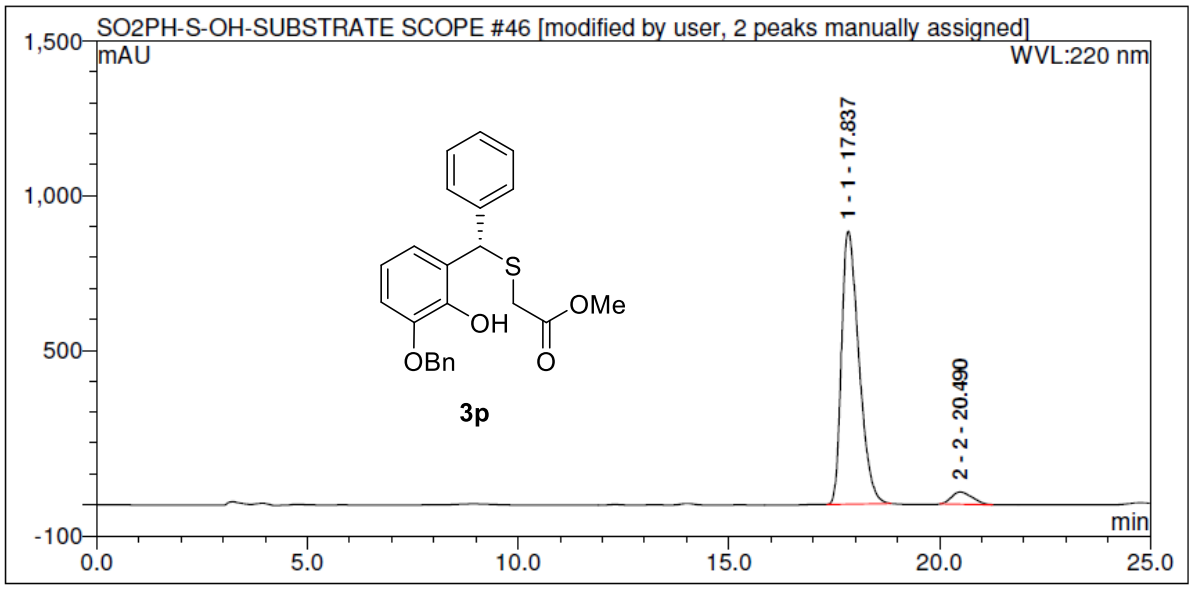

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.31 | 29.5418 | 4.813729039 | 158.068 | n.a. |
| 2 | 2 | 8.52 | 584.157 | 95.18627096 | 2668.221 | n.a. |

3-O-CH2-Ph-S-OH-RC-ID



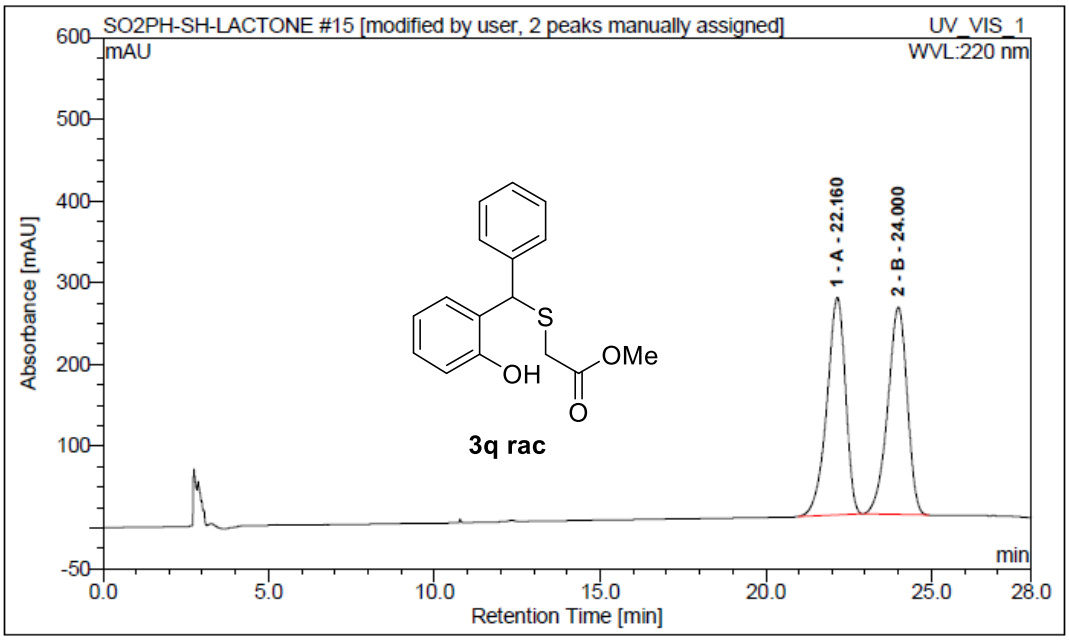

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 17.91 | 176.6549 | 49.66936898 | 378.5583 | n.a. |
| 2 | 2 | 20.36 | 179.007 | 50.33063102 | 347.183 | n.a. |

3-O-CH2-Ph-S-OH-CHI-ID



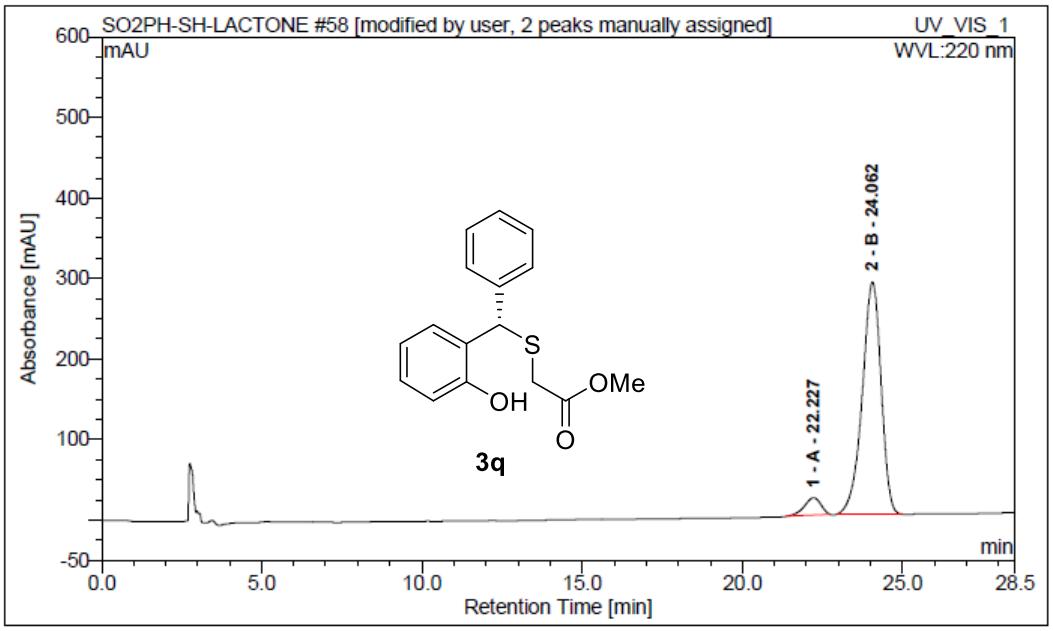

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 17.84 | 421.8475 | 94.92546716 | 882.3687 | n.a. |
| 2 | 2 | 20.49 | 22.551 | 5.074532841 | 39.801 | n.a. |

SALI-S-OH-AMYLOSE-1-RAC



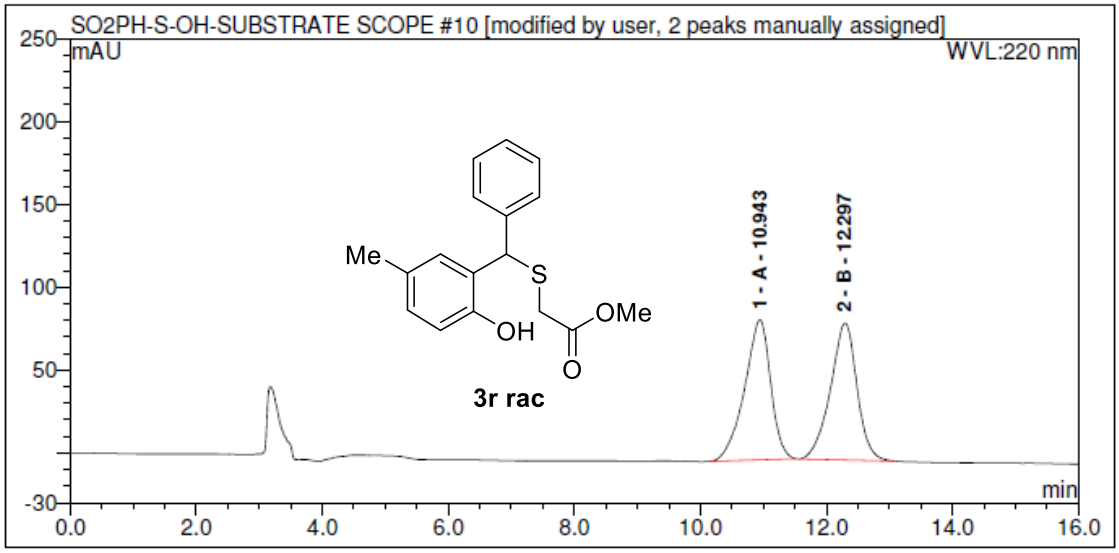

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 22.16 | 173.1295 | 50.05807857 | 265.8718 | n.a. |
| 2 | B | 24.00 | 172.728 | 49.94192143 | 253.646 | n.a. |

SALI-S-OH-AMYLOSE-1-CHI



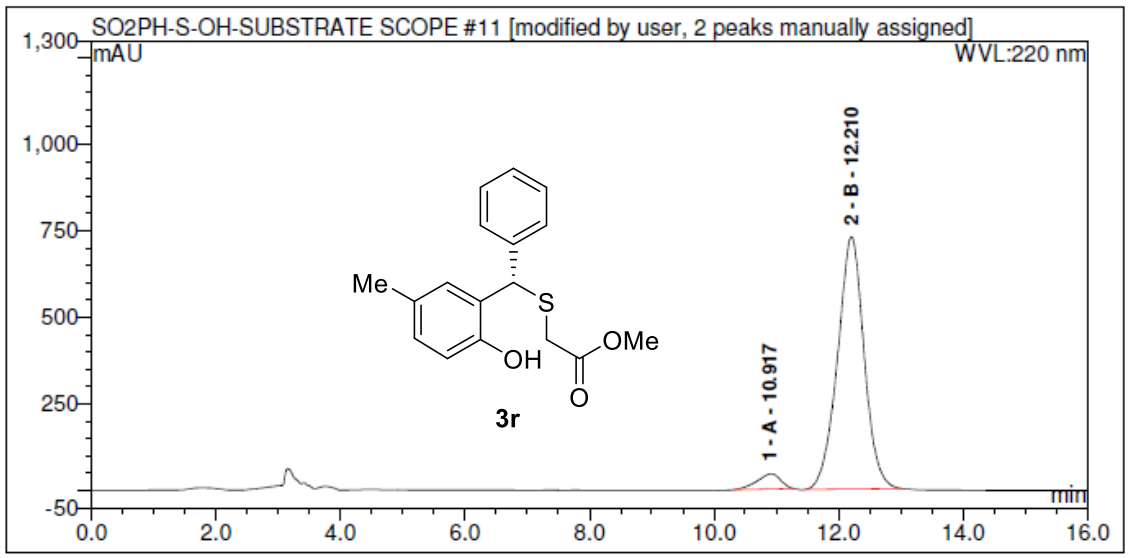

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 22.23 | 12.66275 | 6.058391405 | 21.40209 | n.a. |
| 2 | B | 24.06 | 196.349 | 93.9416086 | 288.375 | n.a. |

5-Me-SAL-Me-GLYCO-IB-RAC



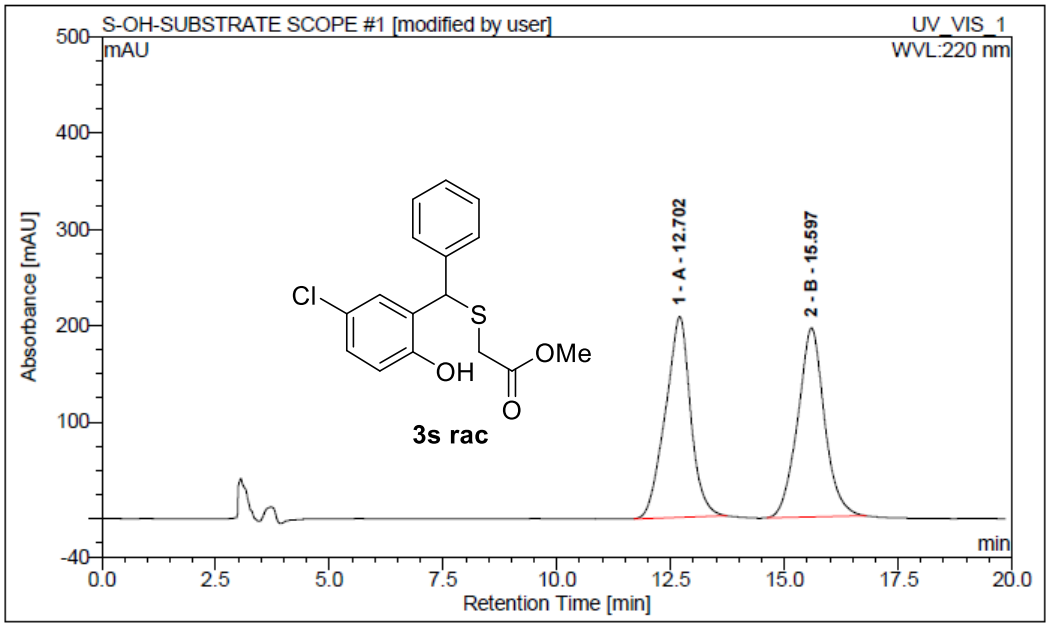

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.94 | 40.41234 | 50.0936799 | 84.25539 | n.a. |
| 2 | B | 12.30 | 40.261 | 49.9063201 | 82.455 | n.a. |

5-Me-SAL-Me-GLYCO-S-OH-IB-CHI



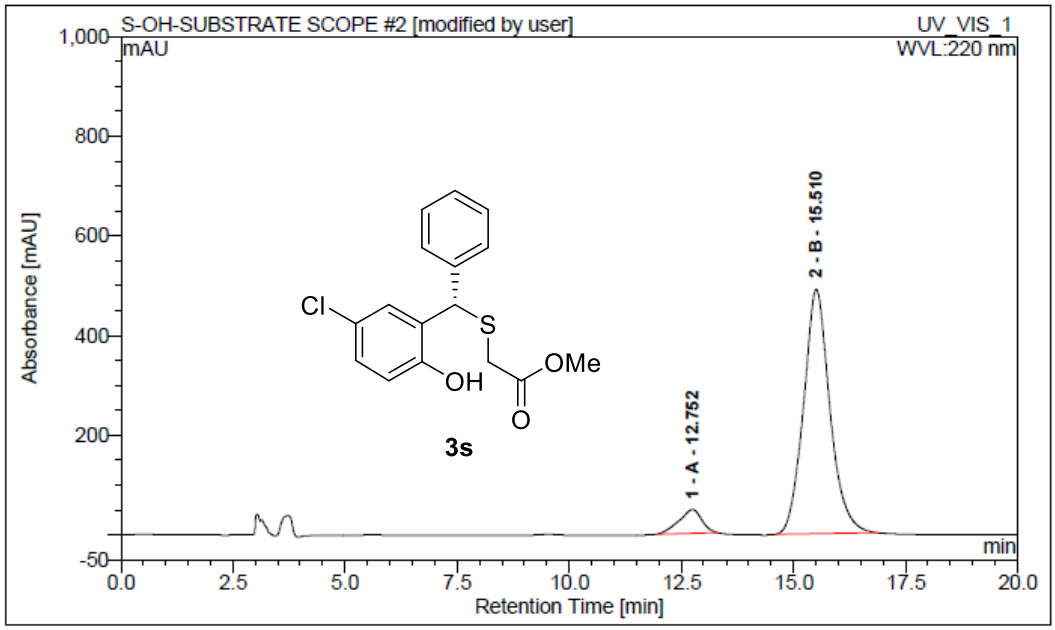

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.92 | 19.22375 | 5.054447075 | 44.00718 | n.a. |
| 2 | B | 12.21 | 361.110 | 94.94555292 | 729.407 | n.a. |

5-Cl-SALI-S-OH-IB-RAC



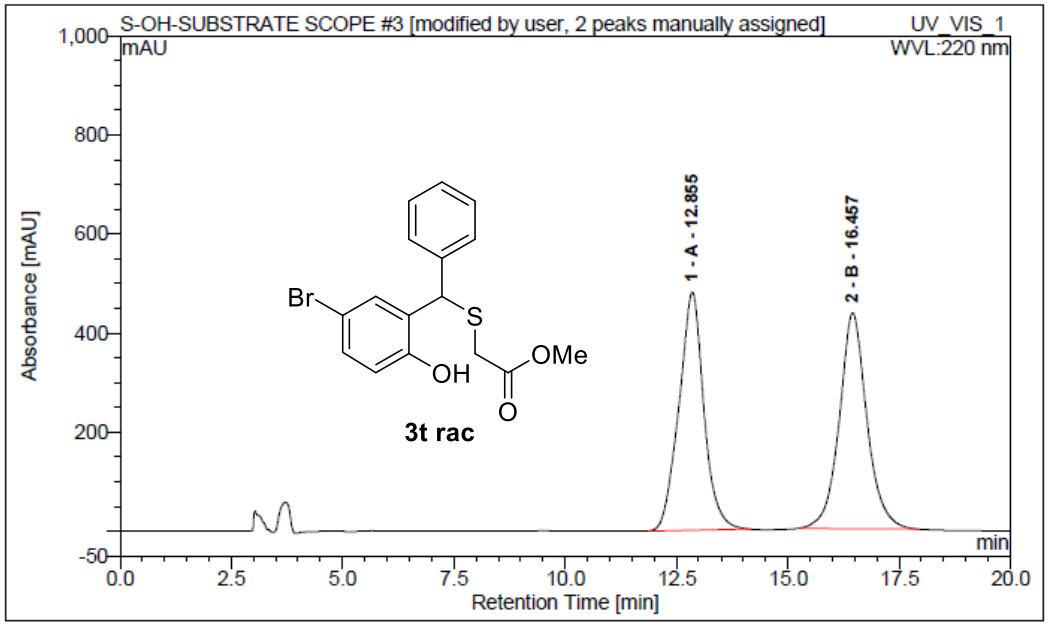

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.70 | 133.8221 | 49.98703917 | 208.0829 | n.a. |
| 2 | B | 15.60 | 133.891 | 50.01296083 | 195.896 | n.a. |

5-Cl-SALI-S-OH-IB-CHI



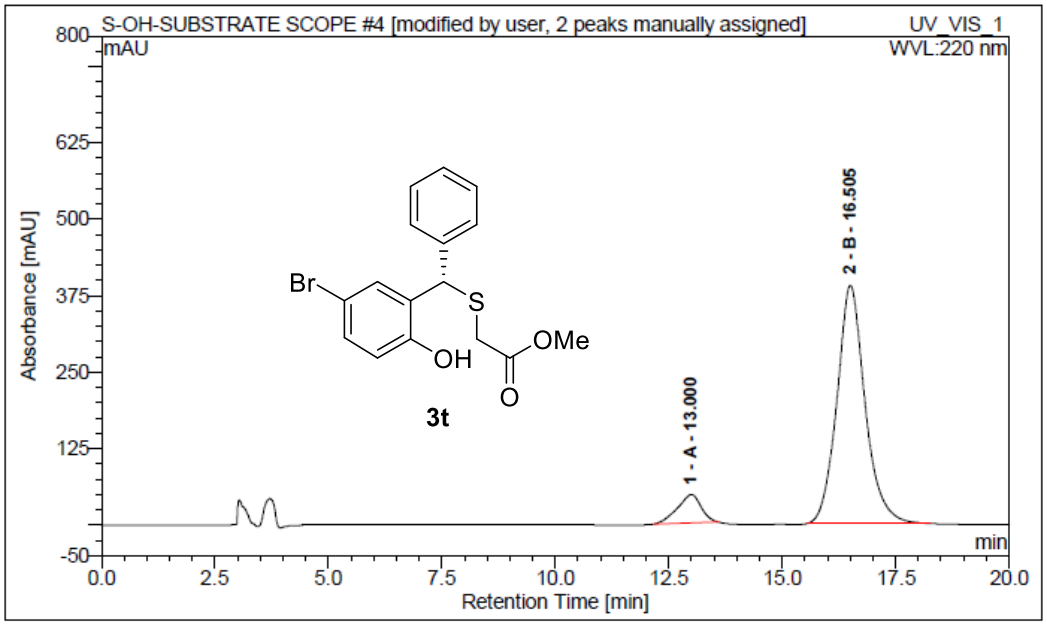

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.75 | 28.50038 | 7.835741816 | 47.9243 | n.a. |
| 2 | B | 15.51 | 335.222 | 92.16425818 | 490.599 | n.a. |

5-Br-SALI-S-OH-IB-RAC



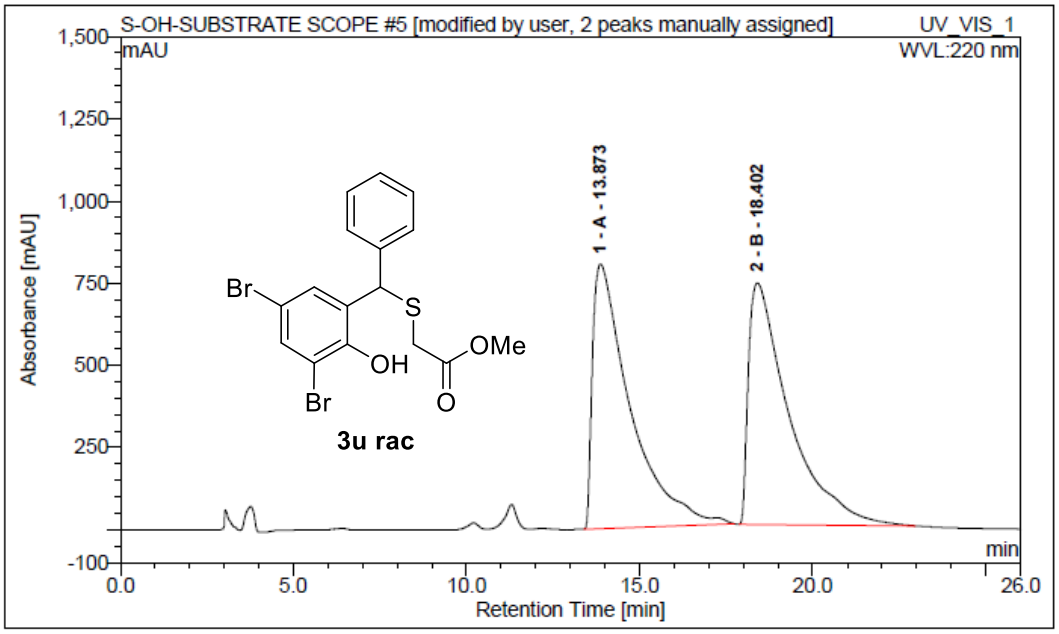

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 12.86 | 311.9618 | 49.87846252 | 480.8071 | n.a. |
| 2 | B | 16.46 | 313.482 | 50.12153748 | 435.396 | n.a. |

5-Br-SALI-S-OH-IB-CHI



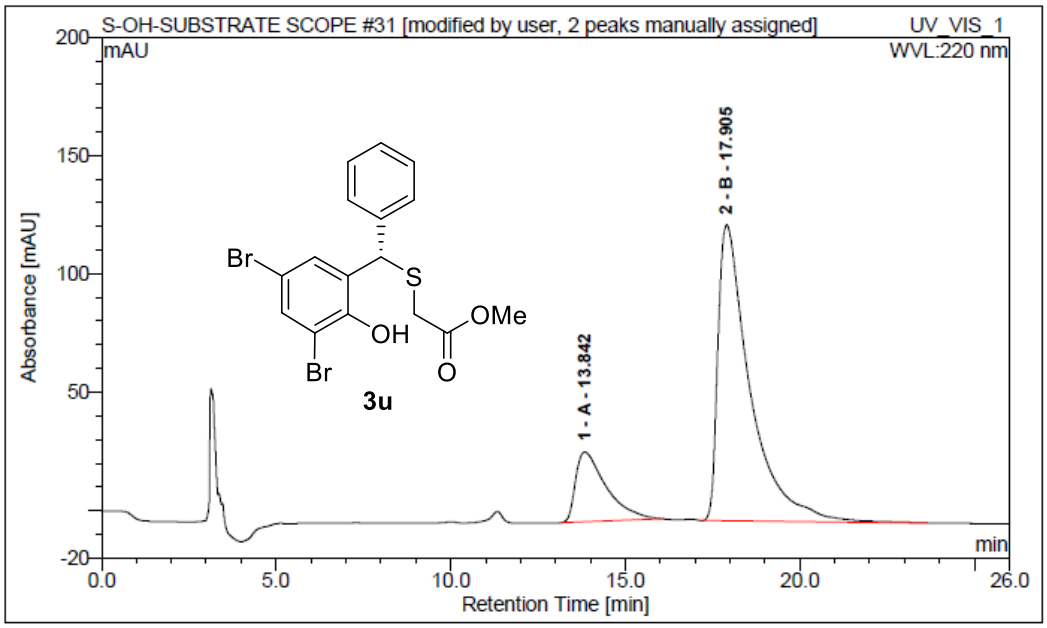

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.00 | 28.16094 | 9.122412134 | 46.51139 | n.a. |
| 2 | B | 16.51 | 280.540 | 90.87758787 | 390.084 | n.a. |

3,5-diBr-SALI-S-OH-IB-RAC



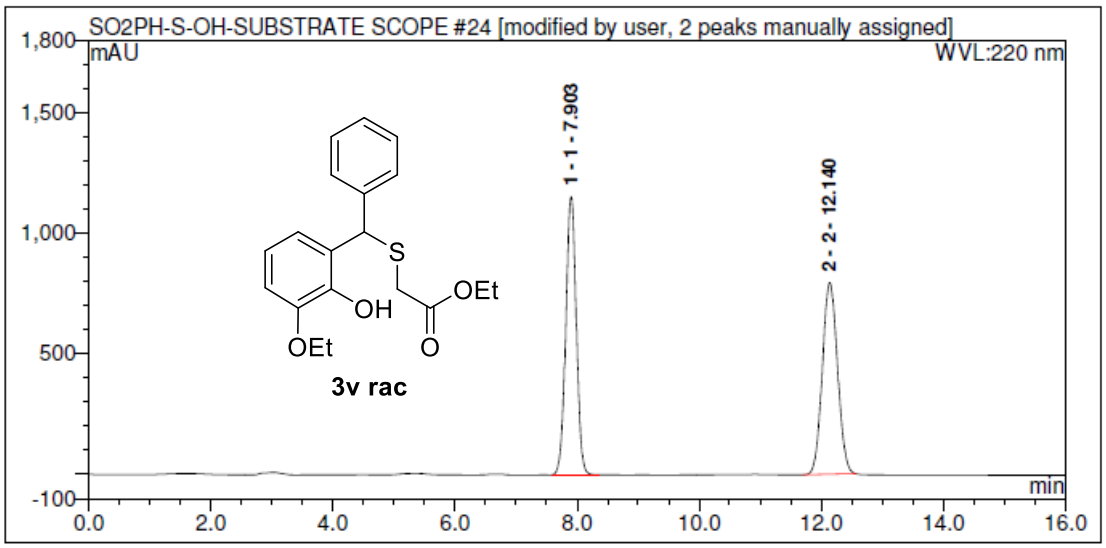

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.87 | 1010.179 | 50.38816628 | 804.4486 | n.a. |
| 2 | B | 18.40 | 994.615 | 49.61183372 | 734.882 | n.a. |

3,5-DIBr-SAL-Me-GLYCO-S-OH-IB-CHI



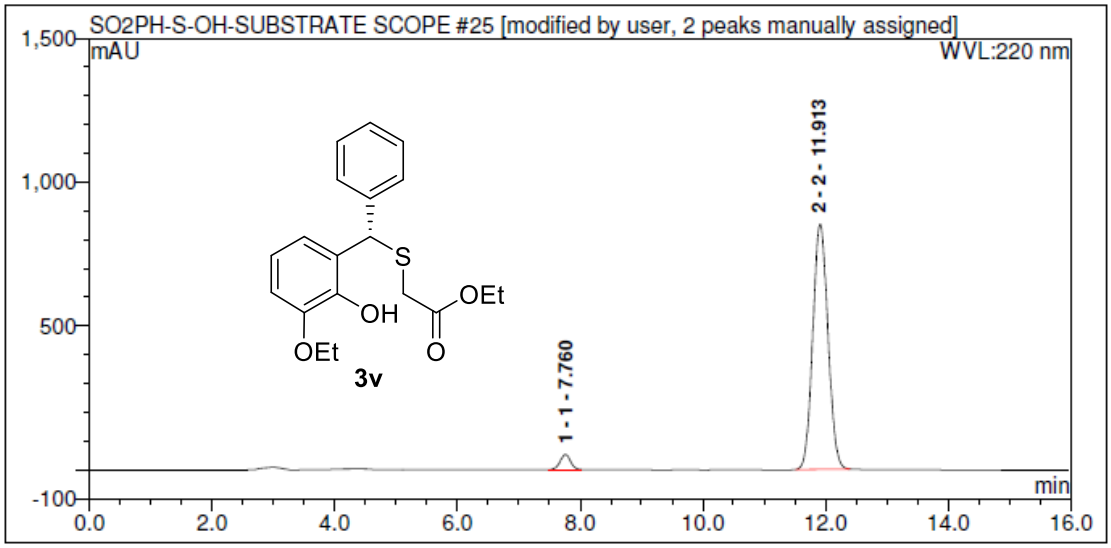

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.84 | 29.87954 | 18.33902083 | 29.39485 | n.a. |
| 2 | B | 17.91 | 133.049 | 81.66097917 | 125.000 | n.a. |

3-OEt-SL-ET-GLYCO-S-OH-MYLOSE-1-R



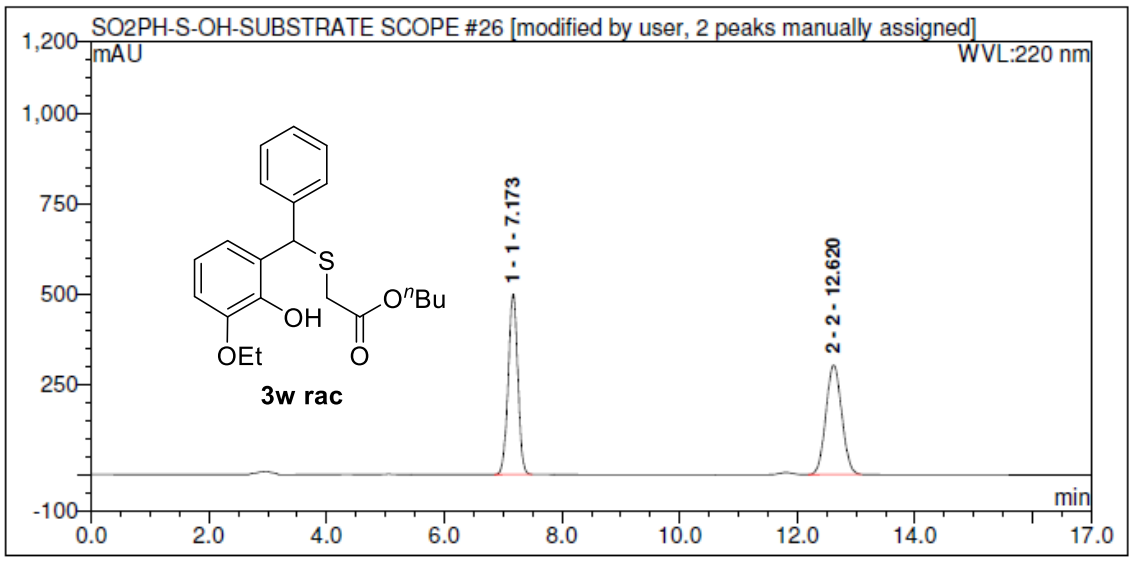

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.90 | 229.4531 | 50.04607919 | 1151.424 | n.a. |
| 2 | 2 | 12.14 | 229.031 | 49.95392081 | 794.253 | n.a. |

3-OEt-SL-ET-GLYCO-S-OH-MYLOSE-1-CHI



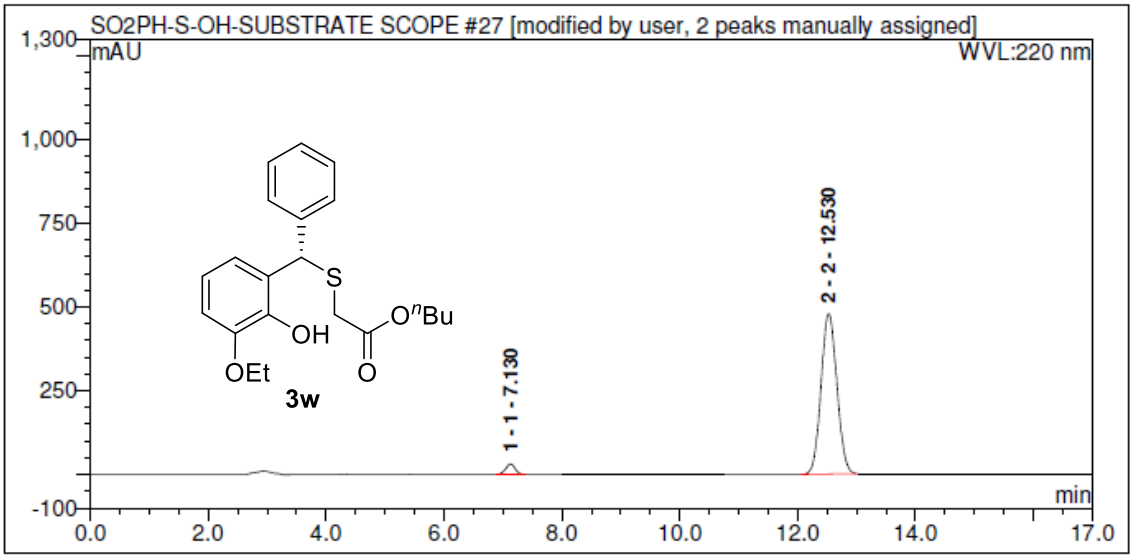

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.76 | 10.19997 | 4.005831924 | 52.11564 | n.a. |
| 2 | 2 | 11.91 | 244.428 | 95.99416808 | 852.510 | n.a. |

3-OEt-SL-BUTYL-GLYCO-S-OH-MYLOSE-1-R



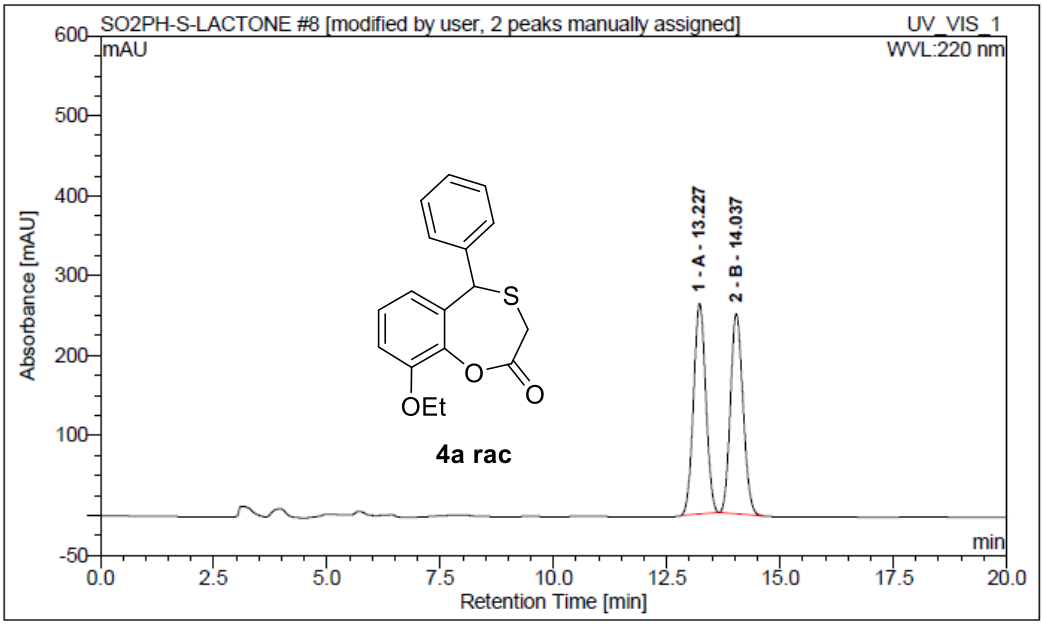

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.17 | 94.66739 | 50.03060657 | 499.5026 | n.a. |
| 2 | 2 | 12.62 | 94.552 | 49.96939343 | 302.795 | n.a. |

3-OEt-SL-BUTYL-GLYCO-S-OH-MYLOSE-1-CHI



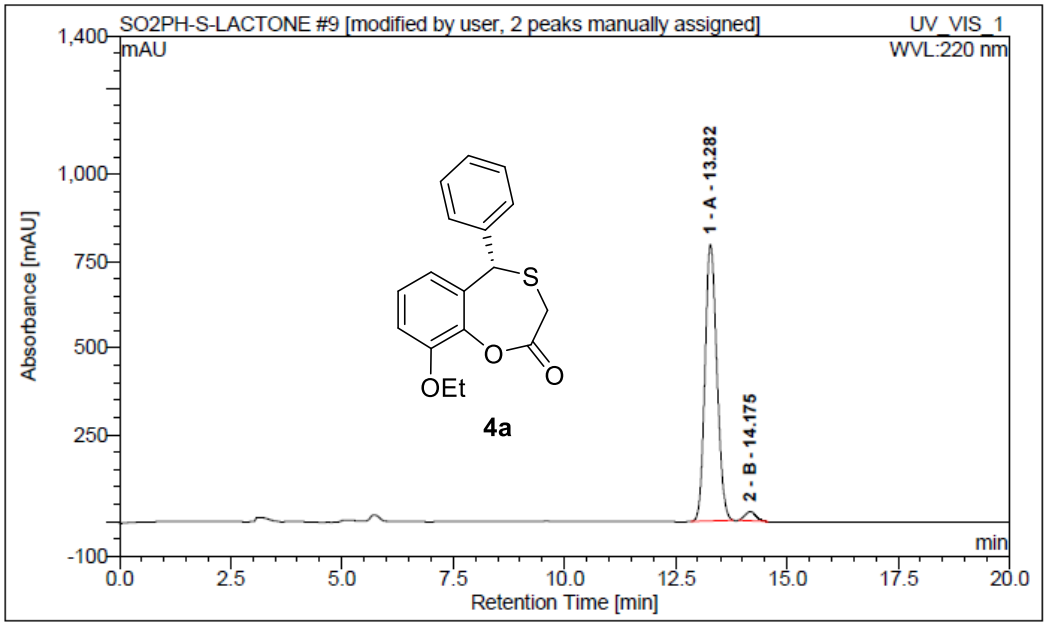

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.13 | 5.676005 | 3.678678033 | 30.80612 | n.a. |
| 2 | 2 | 12.53 | 148.619 | 96.32132197 | 478.011 | n.a. |

3-OEt-SALI-Me-GLYCO-ID-RAC



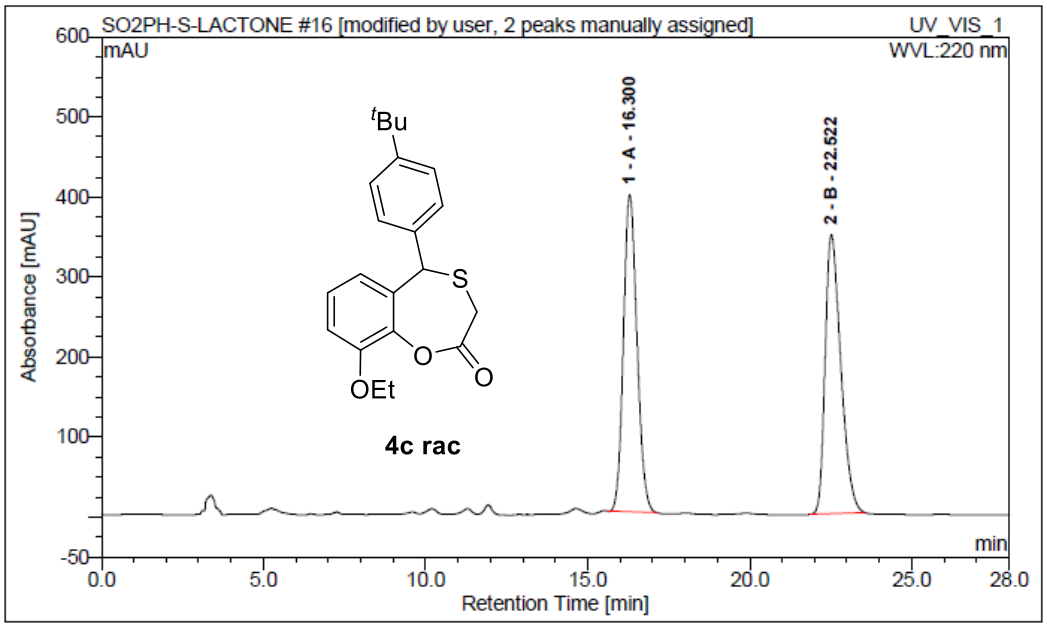

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.23 | 82.48868 | 50.55503914 | 263.279 | n.a. |
| 2 | B | 14.04 | 80.677 | 49.44496086 | 250.268 | n.a. |

3-OEt-SALI-Me-GLYCO-LACTONE-ID-CHI



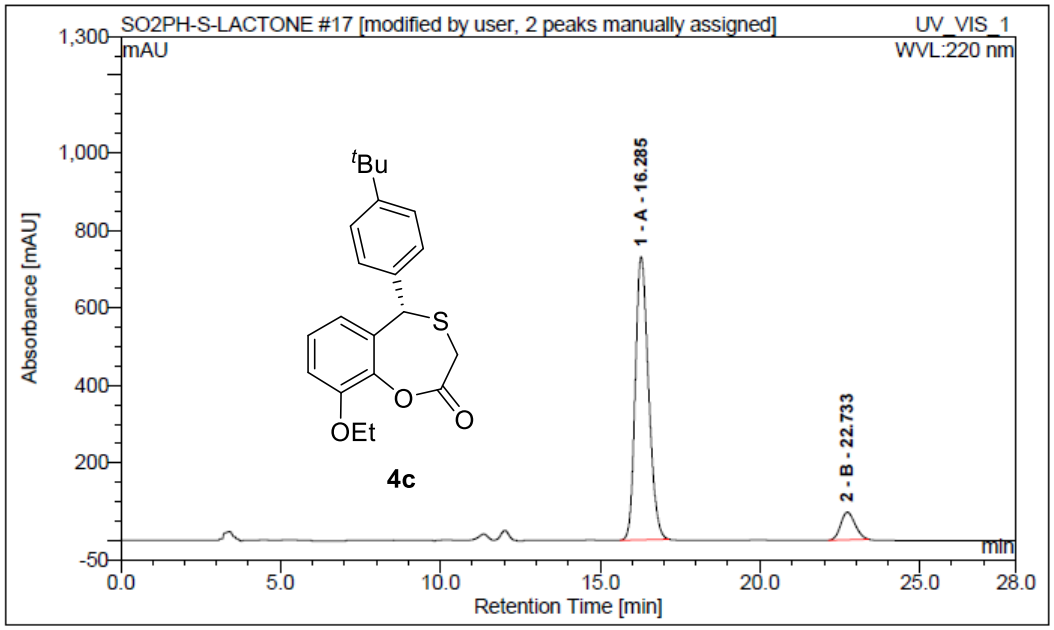

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 13.28 | 247.9938 | 97.04532561 | 797.3713 | n.a. |
| 2 | B | 14.18 | 7.551 | 2.954674385 | 26.158 | n.a. |

3-OEt-SAL-4-t-BUTYL-GR-Me-GLYCO-IE-RAC



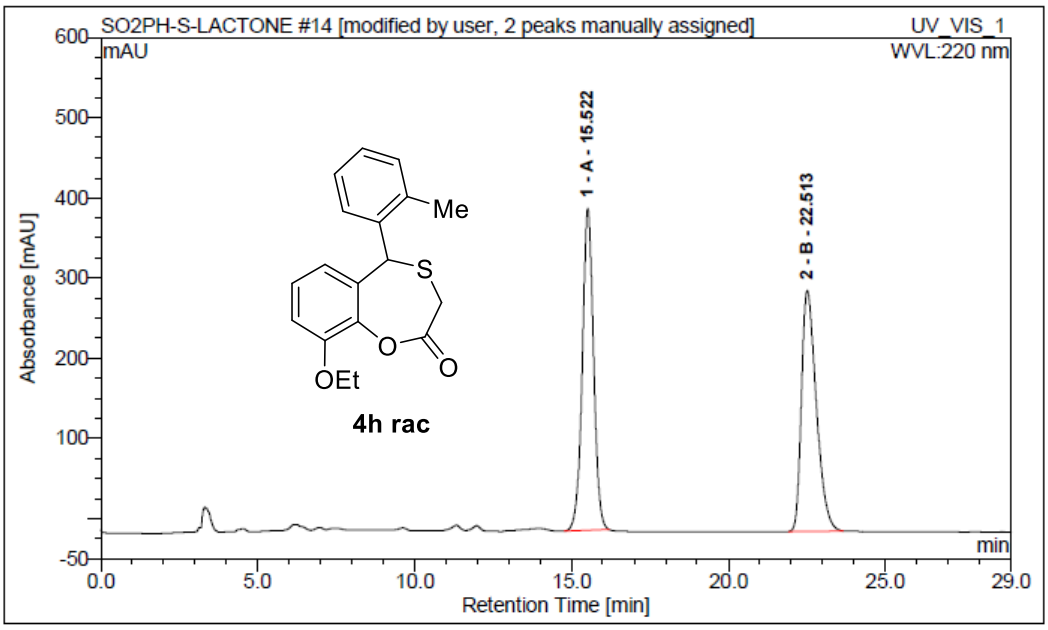

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.30 | 191.7828 | 49.61884133 | 396.0476 | n.a. |
| 2 | B | 22.52 | 194.729 | 50.38115867 | 348.475 | n.a. |

3-OEt-SAL-4-t-BUTYL-GR-Me-GLYCO-IE-CHI



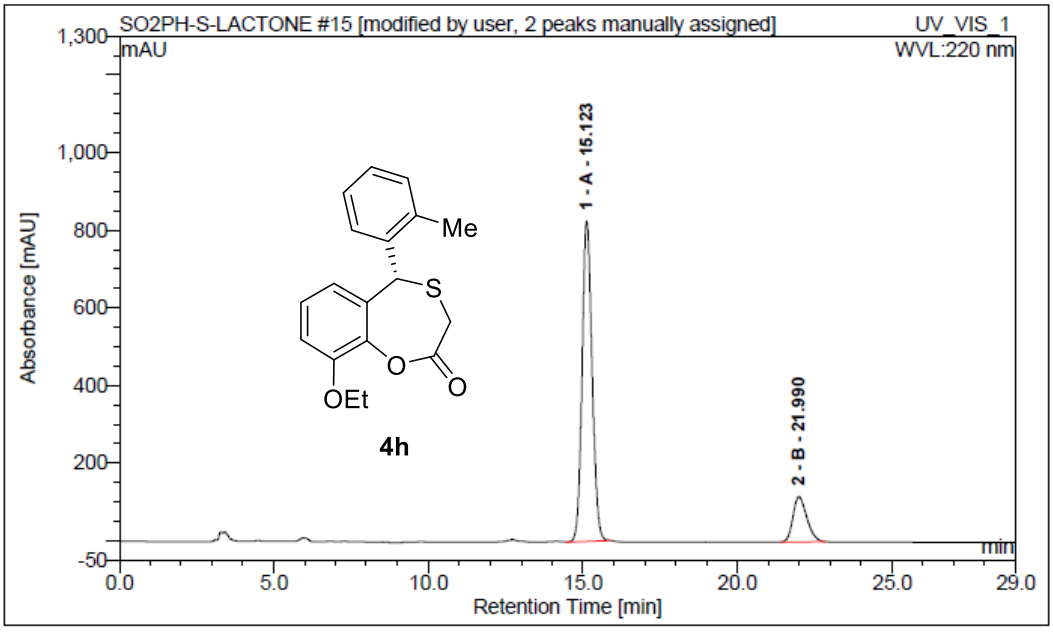

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 16.29 | 349.9004 | 90.48526908 | 729.346 | n.a. |
| 2 | B | 22.73 | 36.793 | 9.514730915 | 70.696 | n.a. |

3-OEt-SAL-2-Me-GR-Me-GLYCO-IE-RAC



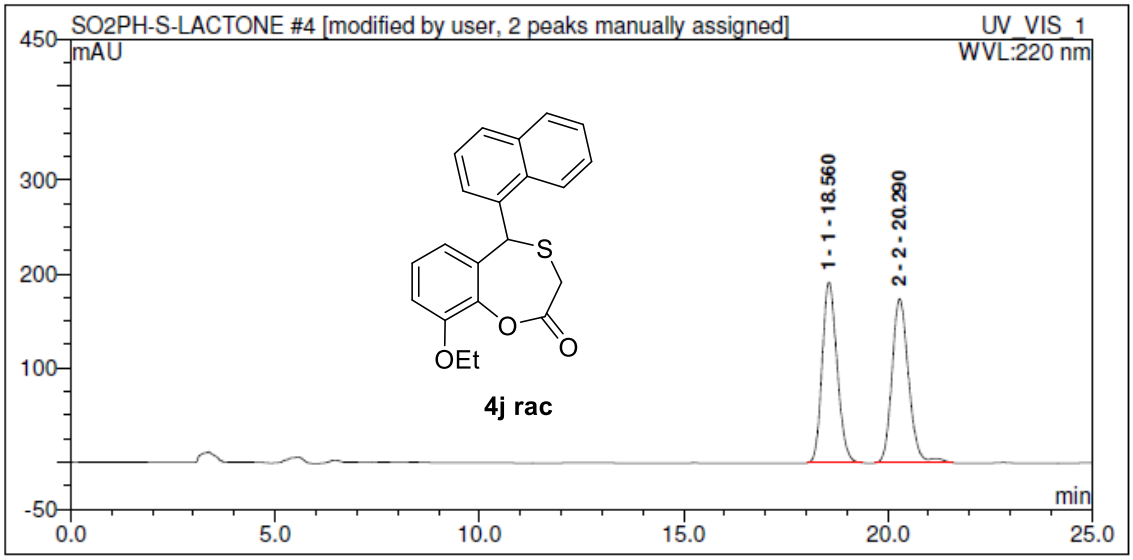

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 15.52 | 166.6832 | 50.37168611 | 401.544 | n.a. |
| 2 | B | 22.51 | 164.223 | 49.62831389 | 300.432 | n.a. |

3-OEt-SAL-2-Me-GR-Me-GLYCO-IE-CHI



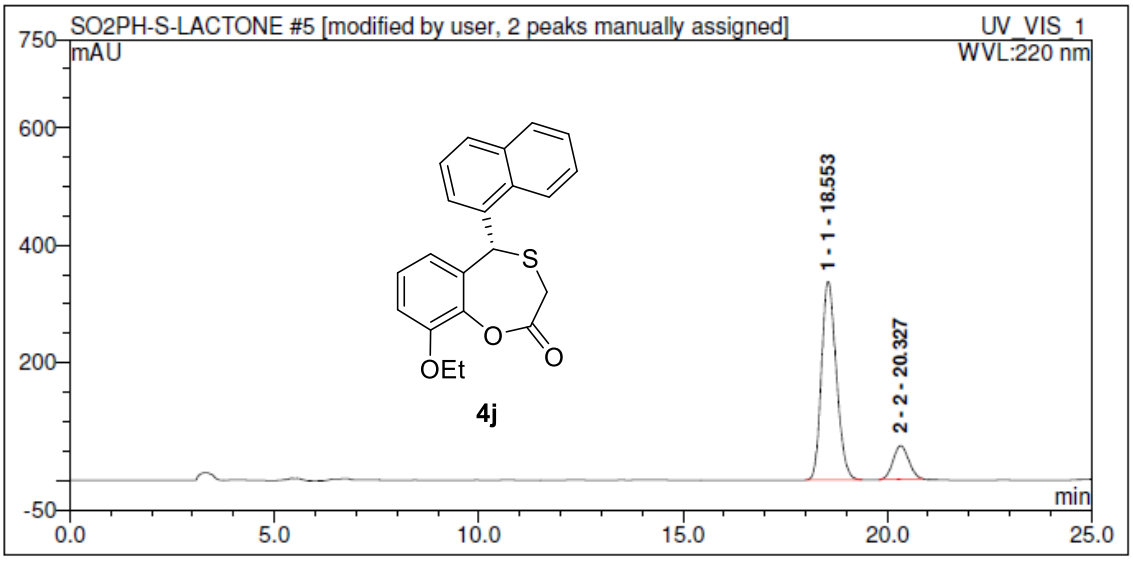

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 15.12 | 308.118 | 83.61051949 | 825.0164 | n.a. |
| 2 | B | 21.99 | 60.398 | 16.38948051 | 116.537 | n.a. |

3-OEt-SL-1-NPHTHYL-GR-Me-GLYCO-LCTONE-IE-R



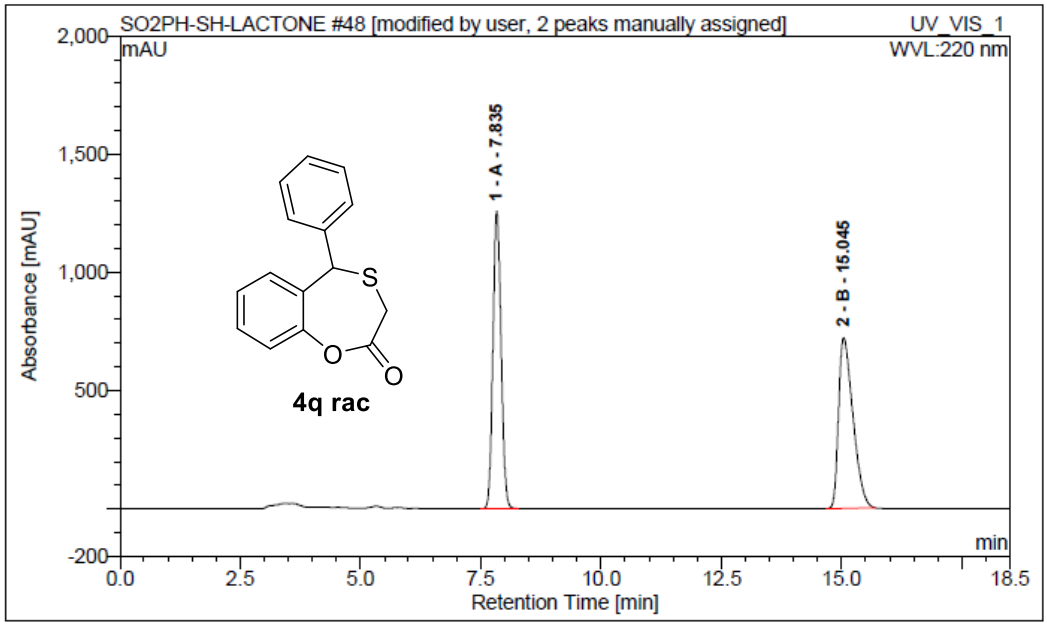

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 18.56 | 81.09577 | 49.61352833 | 191.7269 | n.a. |
| 2 | 2 | 20.29 | 82.359 | 50.38647167 | 174.368 | n.a. |

3-OEt-SL-1-NPHTHYL-GR-Me-GLYCO-LCTONE-IE-CHI



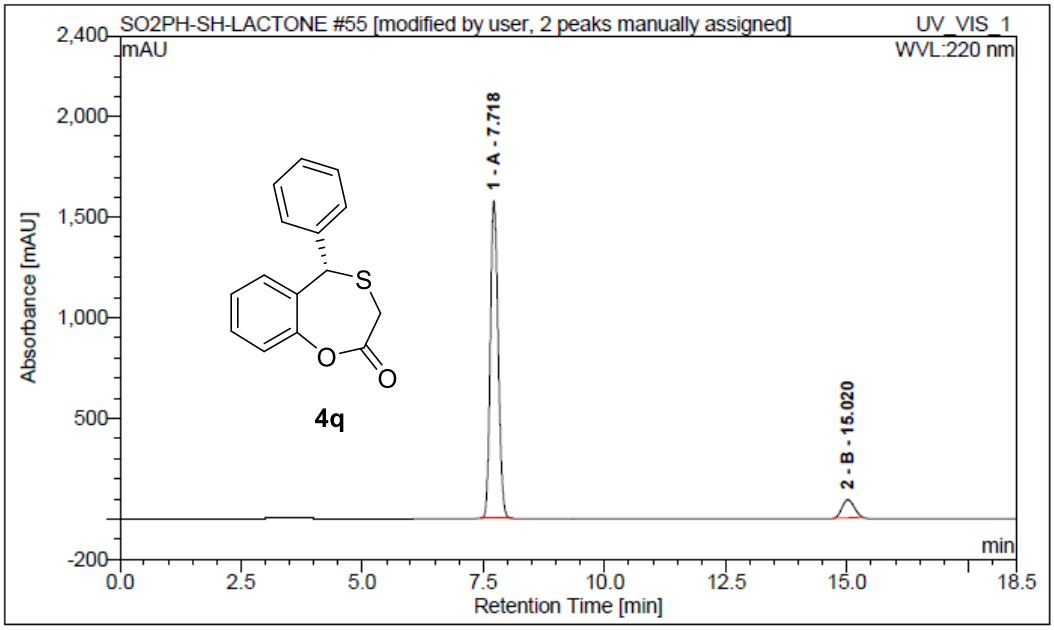

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 18.55 | 142.3723 | 84.94148702 | 337.4417 | n.a. |
| 2 | 2 | 20.33 | 25.240 | 15.05851298 | 57.075 | n.a. |

SO2Ph-Me-GLYCO-R-ID



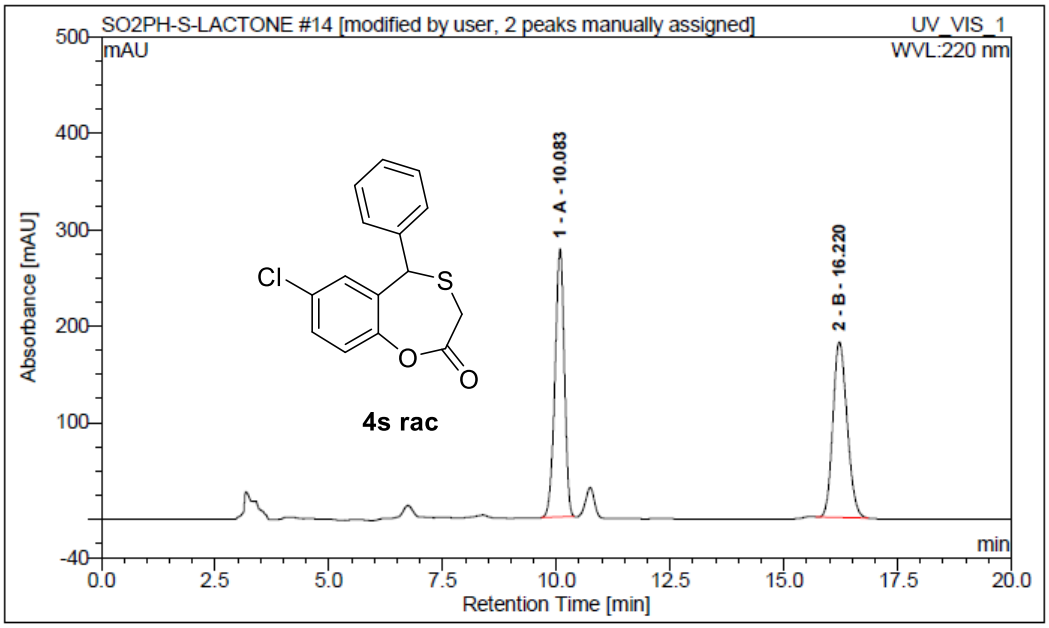

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 7.84 | 247.193 | 49.79692194 | 1258.19 | n.a. |
| 2 | B | 15.05 | 249.209 | 50.20307806 | 721.235 | n.a. |

SO2Ph-Me-GLYCO-CHI-ID



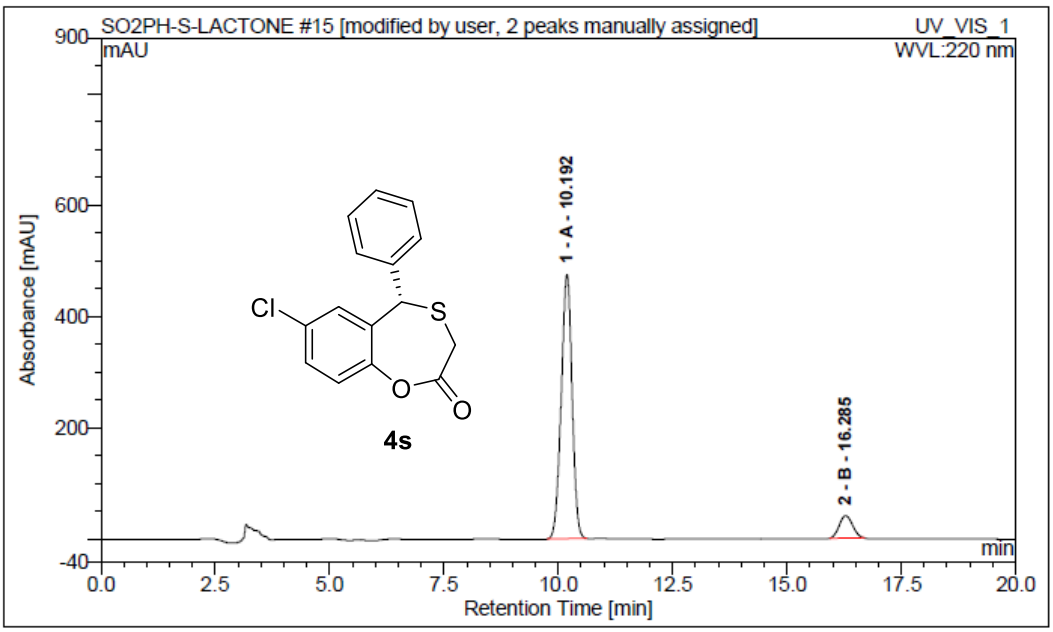

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 7.72 | 296.46 | 91.92211341 | 1578.641 | n.a. |
| 2 | B | 15.02 | 26.052 | 8.077886595 | 89.694 | n.a. |

5-Cl-SALI-LAC-ID-RAC



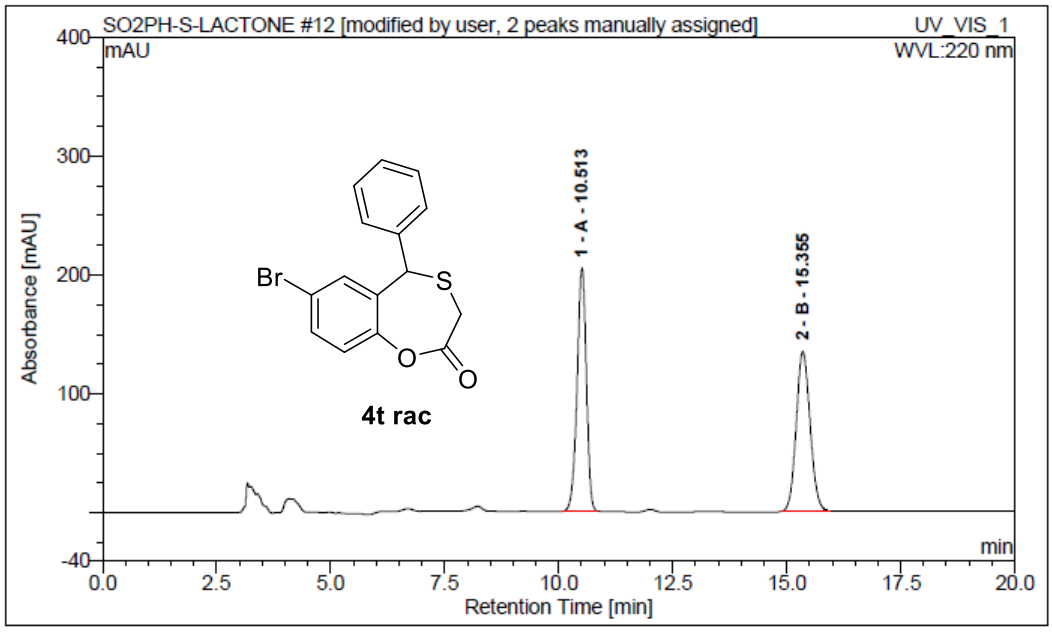

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.08 | 66.51805 | 50.22120754 | 277.6056 | n.a. |
| 2 | B | 16.22 | 65.932 | 49.77879246 | 181.847 | n.a. |

5-Cl-SALI-LAC-ID-CHI



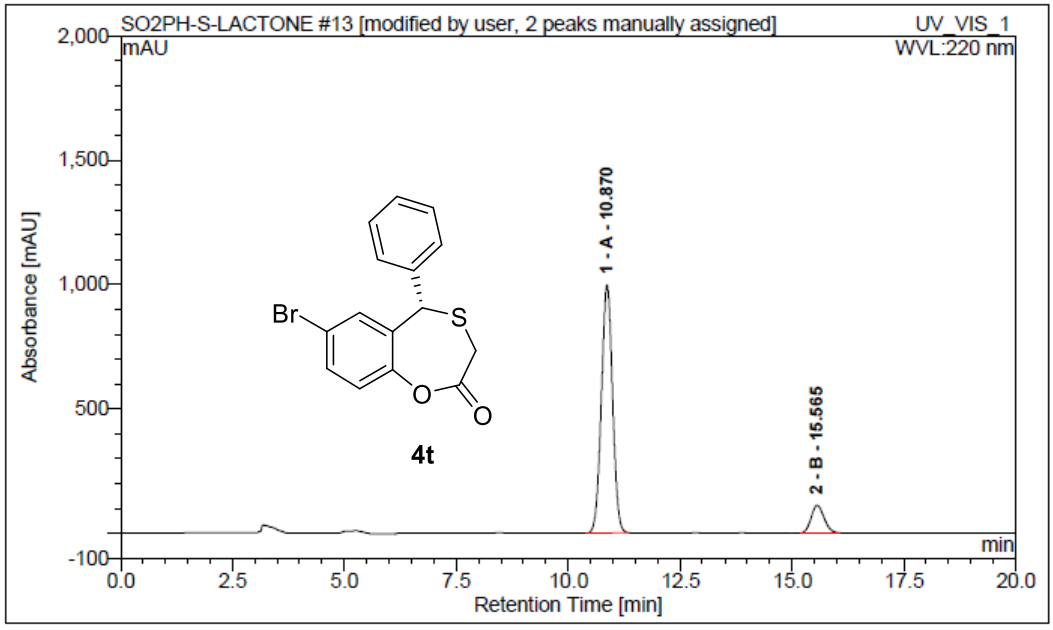

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.19 | 130.9911 | 90.52710977 | 474.0293 | n.a. |
| 2 | B | 16.29 | 13.707 | 9.472890234 | 40.714 | n.a. |

5-Br-SALI-LAC-ID-RAC



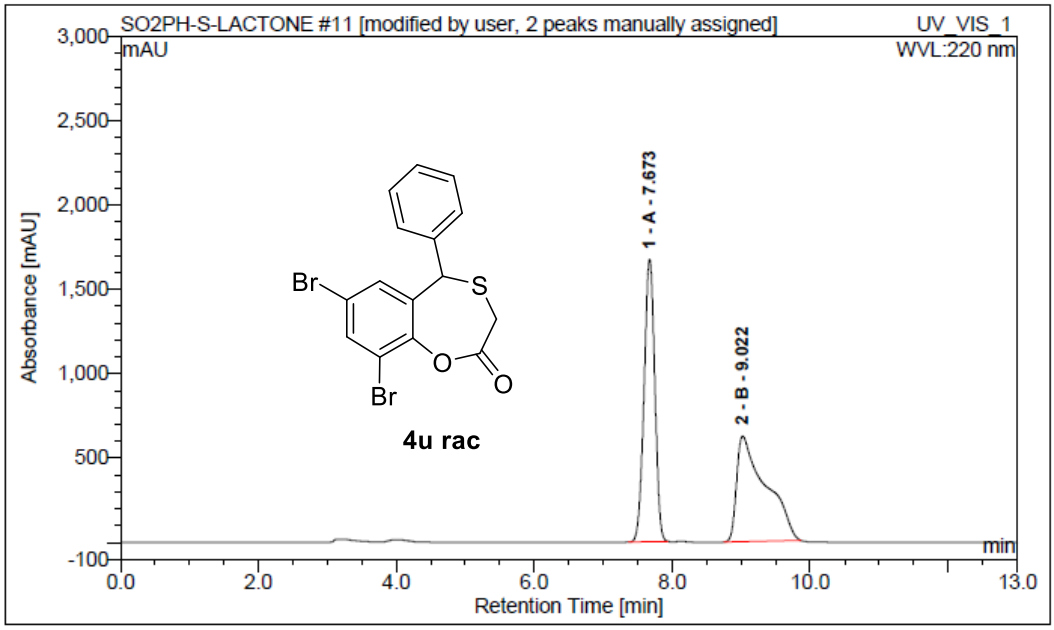

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.51 | 47.96755 | 50.43887932 | 204.5209 | n.a. |
| 2 | B | 15.36 | 47.133 | 49.56112068 | 134.029 | n.a. |

5-Br-SALI-LAC-ID-CHI



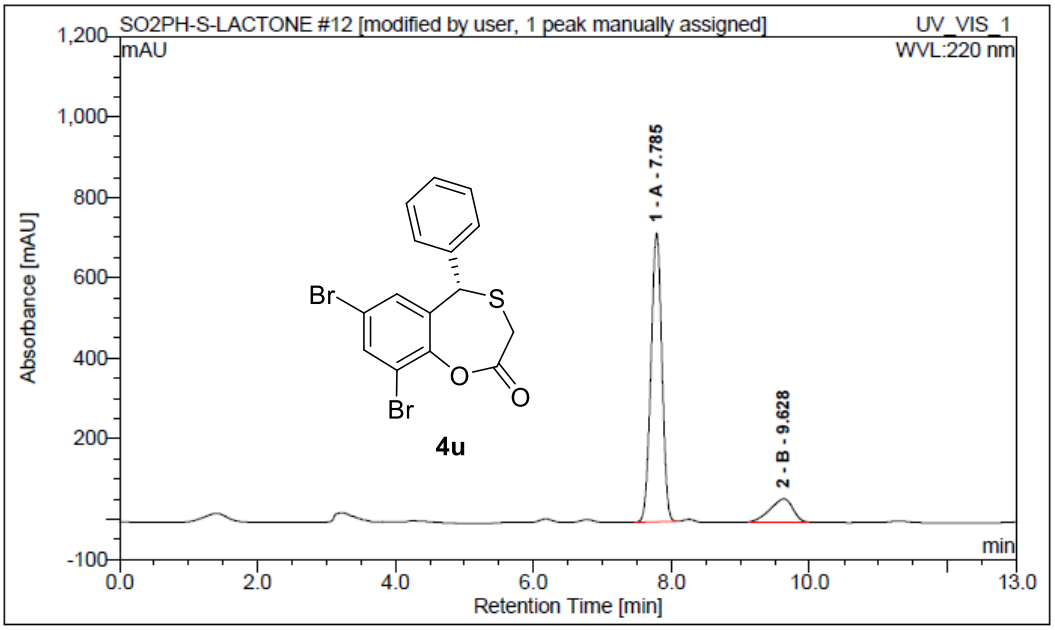

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 10.87 | 288.2596 | 88.8037635 | 997.3096 | n.a. |
| 2 | B | 15.57 | 36.343 | 11.1962365 | 110.245 | n.a. |

3,5-diBr-SALI-LAC-ID-RAC



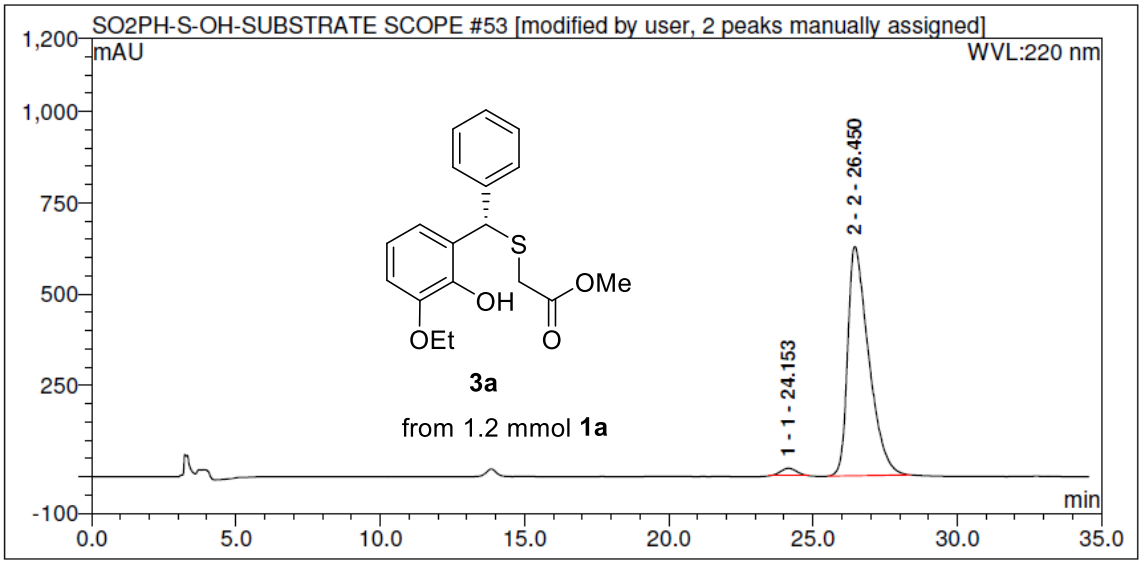

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 7.67 | 301.2838 | 49.58592391 | 1673.453 | n.a. |
| 2 | B | 9.02 | 306.316 | 50.41407609 | 626.184 | n.a. |

3,5-diBr-SALI-LAC-ID-CHI



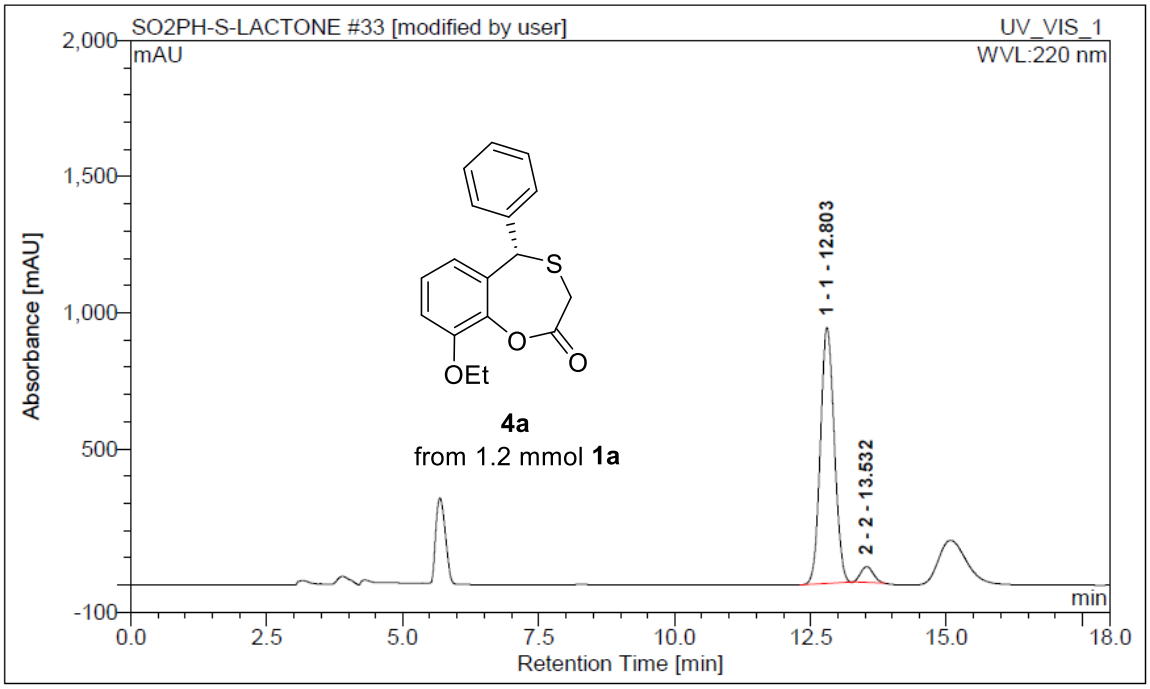

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | A | 7.79 | 131.9244 | 85.94120829 | 717.3446 | n.a. |
| 2 | B | 9.63 | 21.581 | 14.05879171 | 57.420 | n.a. |

SCALE UP-S-OH-CHI-IB



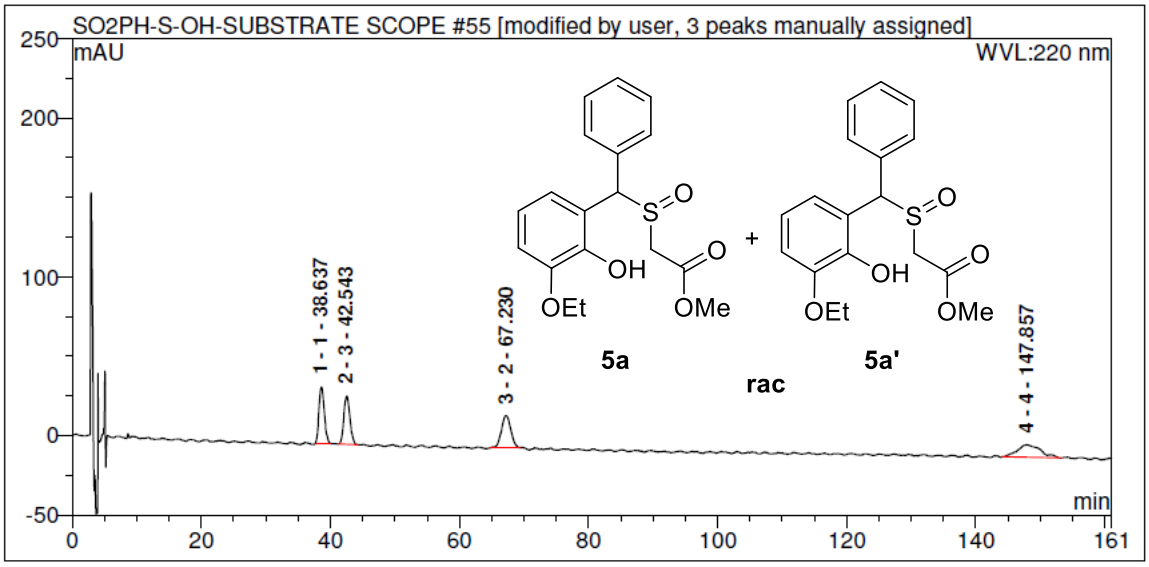

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 24.15 | 13.53533 | 2.495015061 | 20.59907 | n.a. |
| 2 | 2 | 26.45 | 528.960 | 97.50498494 | 627.117 | n.a. |

SCALE UP-3-OEt-S-LAC-ID



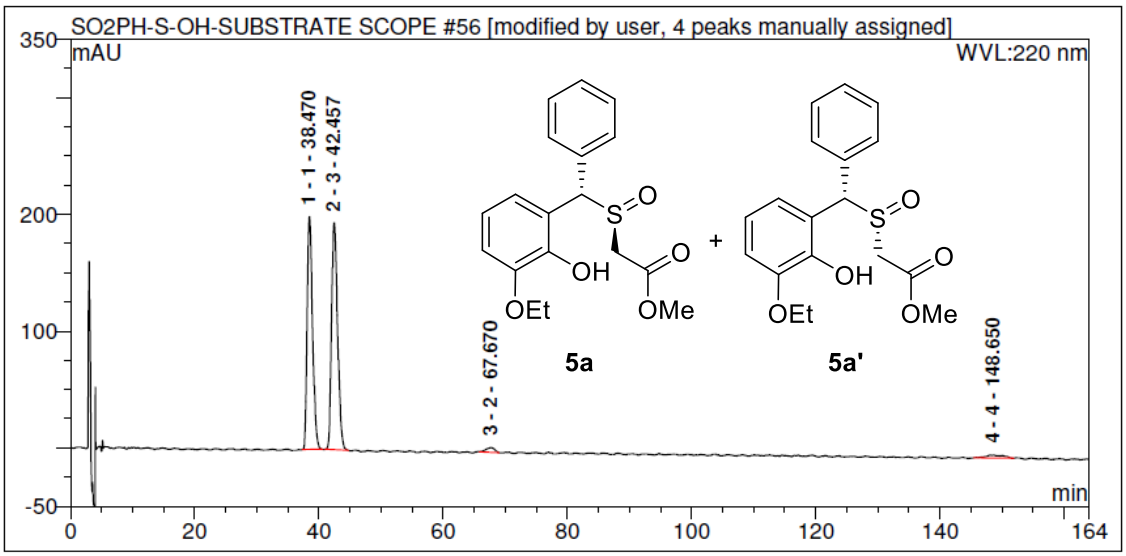

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 12.80 | 277.9895 | 94.76300638 | 939.4422 | n.a. |
| 2 | 2 | 13.53 | 15.363 | 5.236993621 | 57.558 | n.a. |

1eq-MCPBA-S-OH-RC-AMYLOSE-2



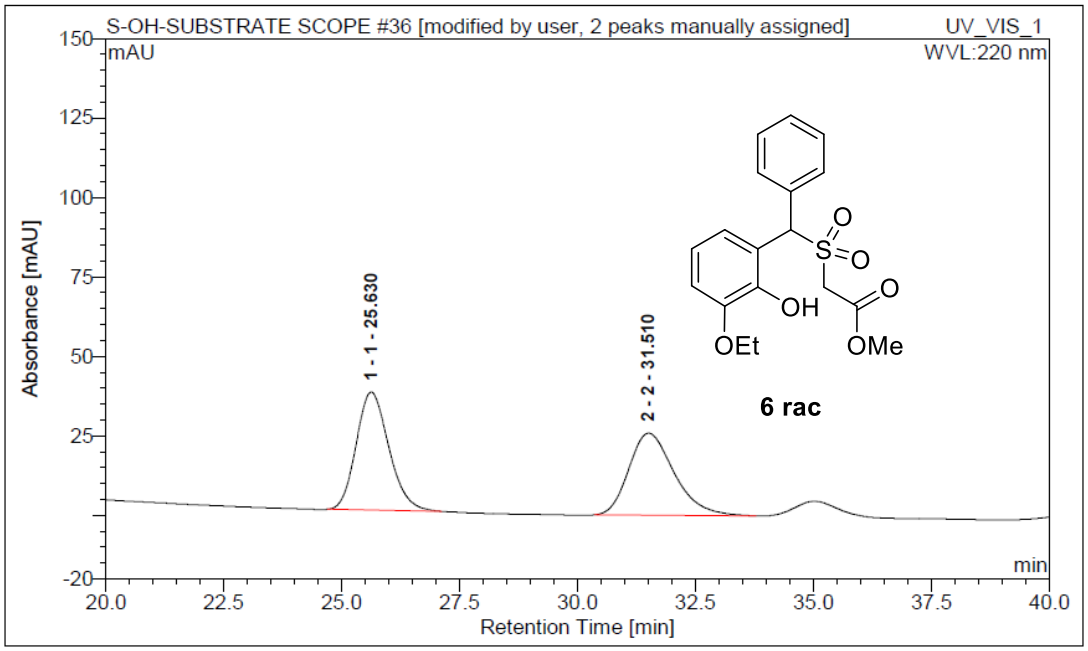

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 38.64 | 34.18475 | 25.37008557 | 35.51991 | n.a. |
| 2 | 3 | 42.54 | 33.16501 | 24.6132947 | 30.35997 | n.a. |
| 3 | 2 | 67.23 | 34.35309 | 25.49502512 | 20.26102 | n.a. |
| 4 | 4 | 147.86 | 33.041 | 24.5215946 | 7.937 | n.a. |

1eq-MCPBA-S-OH-CHI-AMYLOSE-2



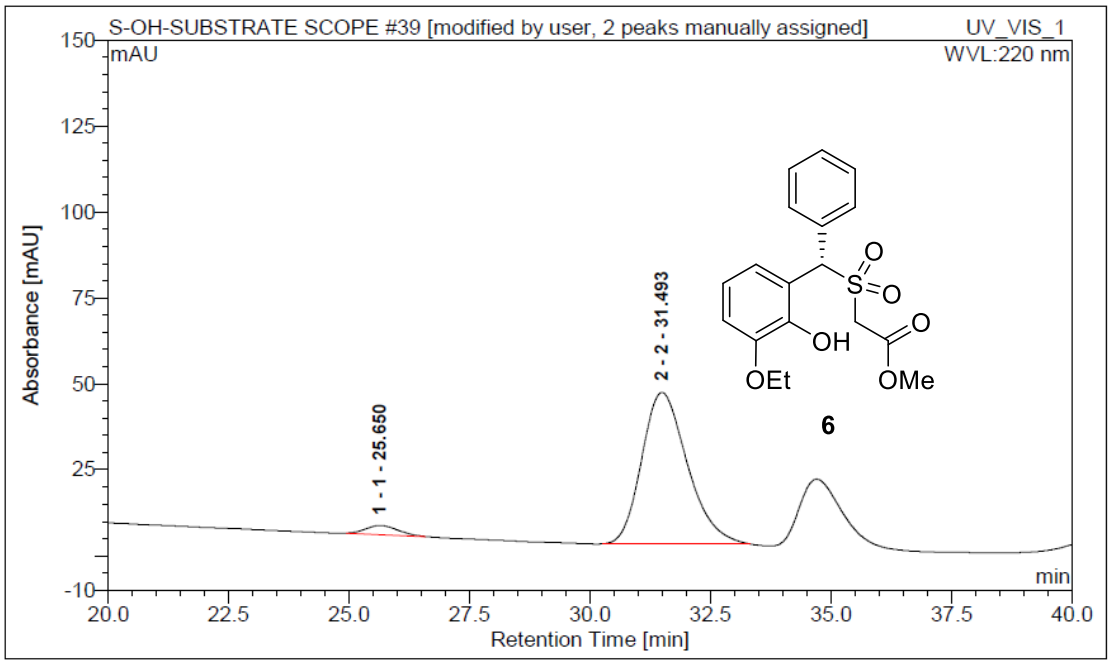

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 38.47 | 200.6097 | 46.27754155 | 199.549 | n.a. |
| 2 | 3 | 42.46 | 218.5642 | 50.41936268 | 194.3258 | n.a. |
| 3 | 2 | 67.67 | 6.329706 | 1.460164505 | 3.94943 | n.a. |
| 4 | 4 | 148.65 | 7.989 | 1.842931271 | 2.424 | n.a. |

3-EQ-MCPBA-SO2-OH-RAC-ID



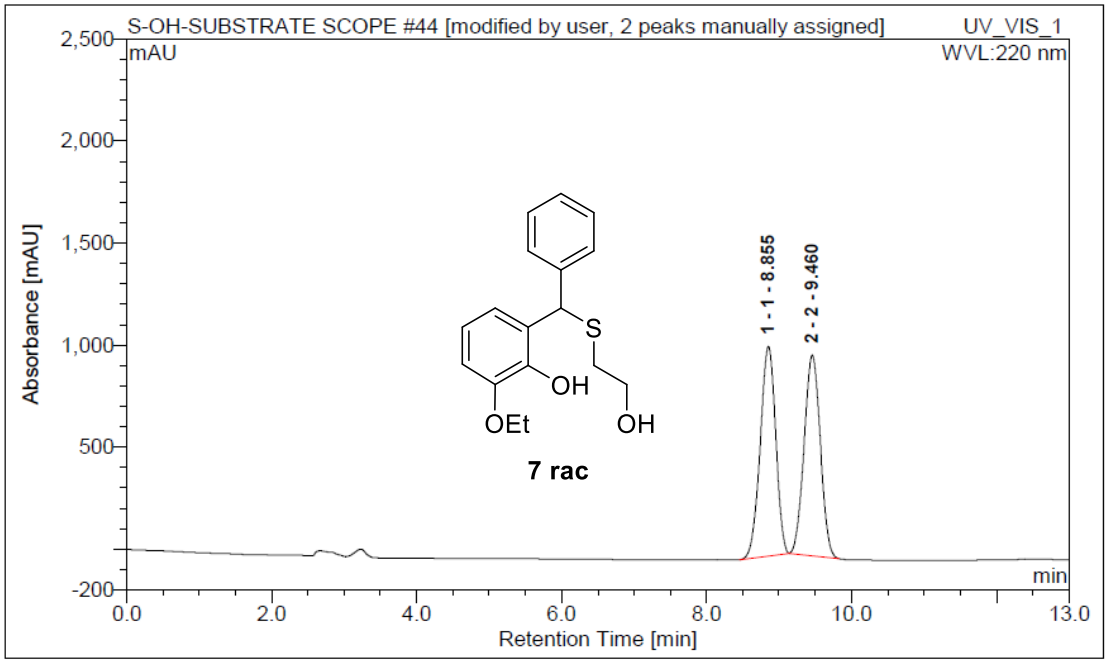

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 25.63 | 29.8455 | 50.83162131 | 37.14589 | n.a. |
| 2 | 2 | 31.51 | 28.869 | 49.16837869 | 25.836 | n.a. |

3-EQ-MCPBA-SO2-OH-CHI-ID-0oC



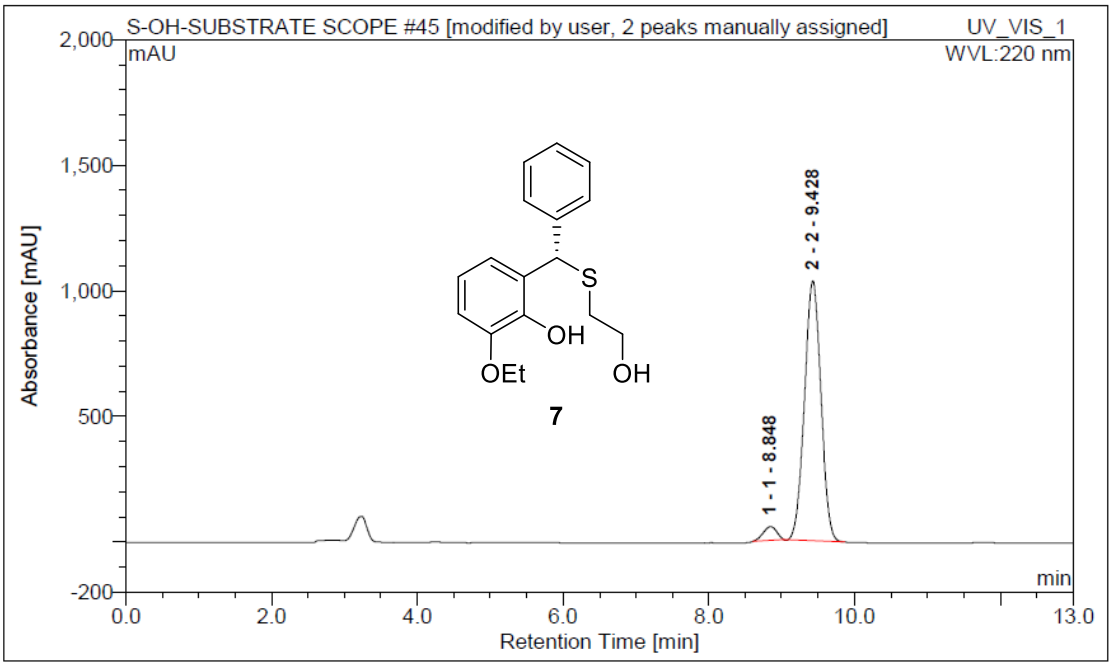

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 25.65 | 2.031334 | 4.027698549 | 2.64921 | n.a. |
| 2 | 2 | 31.49 | 48.403 | 95.97230145 | 44.046 | n.a. |

3-EQ-DIBALH-S-OH-OH-RAC-AMYLOSE-1



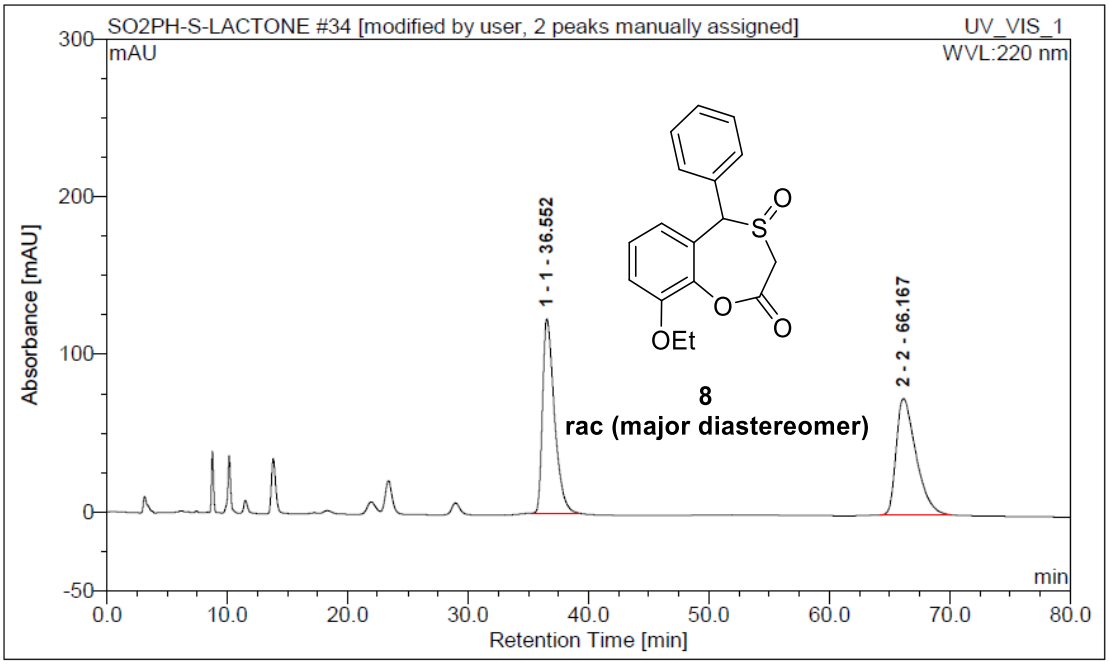

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.86 | 254.2293 | 49.95951217 | 1027.939 | n.a. |
| 2 | 2 | 9.46 | 254.641 | 50.04048783 | 983.925 | n.a. |

3-EQ-DIBALH-S-OH-OH-CHI-AMYLOSE-1



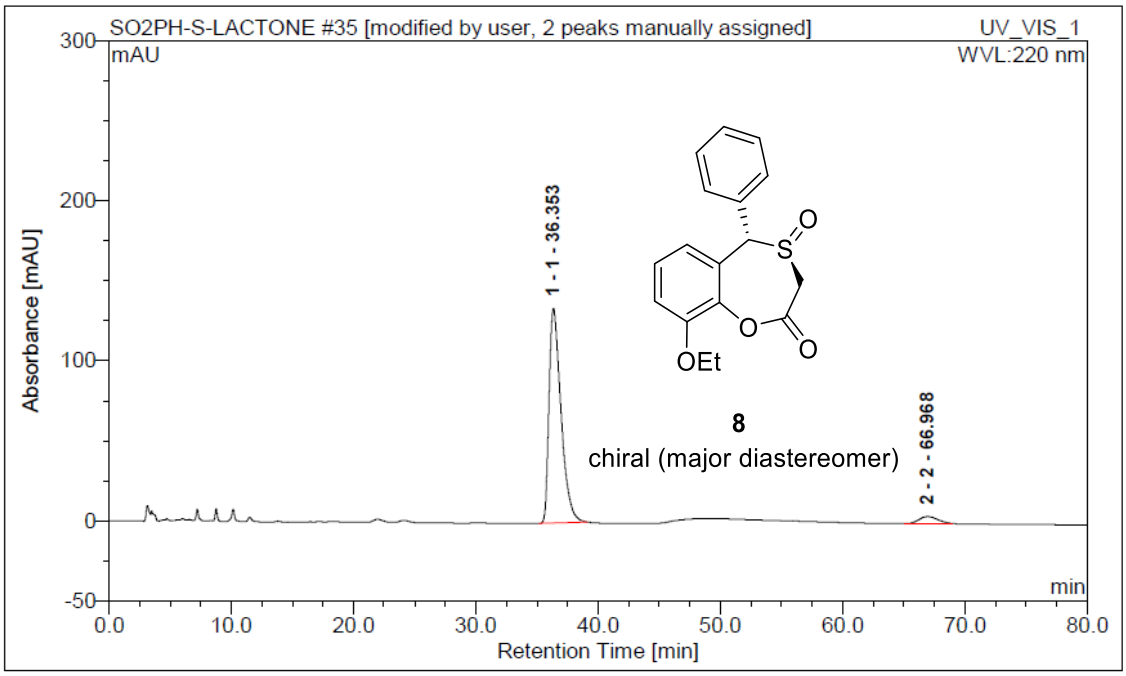

| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 8.85 | 11.54384 | 4.084998356 | 54.0741 | n.a. |
| 2 | 2 | 9.43 | 271.047 | 95.91500164 | 1034.756 | n.a. |

1-eq-MCPBA-SO2-lac-ID-rac




| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 36.55 | 140.4331 | 49.97981856 | 123.2565 | n.a. |
| 2 | 2 | 66.17 | 140.547 | 50.02018144 | 73.775 | n.a. |

1-eq-MCPBA-SO2-lac-ID-chi




| No. | Peak Name | Ret.Time (detected) min | Area mAU*min | Rel.Area(ident.) % | Height mAU | Amount |
|---|---|---|---|---|---|---|
| 1 | 1 | 36.35 | 152.1167 | 95.25926947 | 134.3095 | n.a. |
| 2 | 2 | 66.97 | 7.570 | 4.740730526 | 4.376 | n.a. |