

Organocatalytic asymmetric [4 + 4]-annulation reaction between ynones and benzylidene thiazolones: Synthesis of eight-membered ether containing 4,5-fused thiazoles

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1. General information:

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. All dry solvents were dried using activated 4Å molecular sieves and stored under argon. Flash chromatography was performed using Merck silica gel60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. ¹H NMR spectra were recorded on 400 MHz, 500 MHz and 600 MHz spectrometer, respectively (CDCl₃ as solvent). ¹³C NMR spectra were recorded on 100 MHz, 125 MHz and 150 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.260), carbon (chloroform δ 77.23). Multiplicity was indicated as follows: s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet, bs = broad singlet. The number of protons (n) for a given resonance is indicated by nH. Coupling constants were reported as a J value in Hertz (Hz). Using ESI positive mode HRMS spectra were recorded. Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using Daicel Chiral PAK IA and ID Columns. For visualizing the products UV light was used. Silica gel. Reactions were monitored by TLC on silica gel 60 with fluorescence indicator F254 (0.25 mm).

2. Preparation of starting materials:

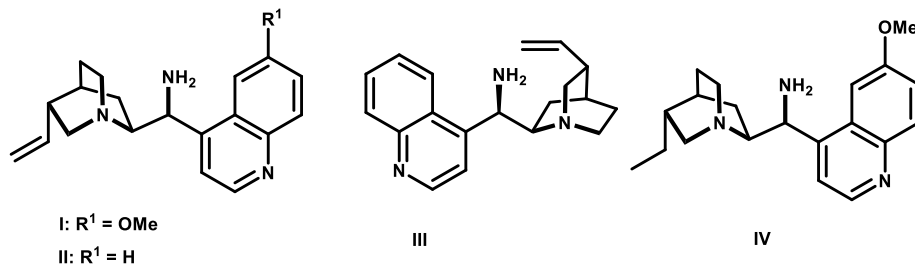
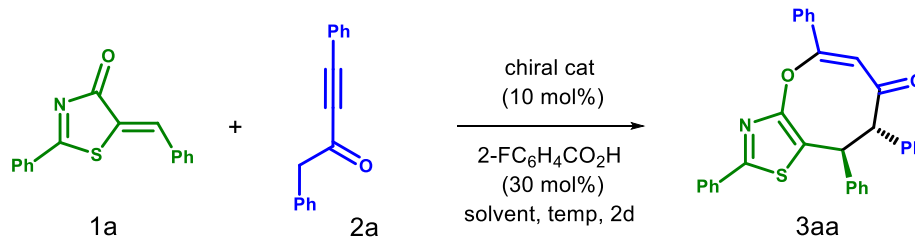
2.1 Methods for the preparation of 5-alkenyl thiazolone 1

All 5-alkenyl thiazolone derivatives were prepared using the reported procedure from the previous literature.^[1] The spectra are in accordance with literature.

2.2 Methods for the preparation of ynones 2

All ynones were prepared using the reported procedure from the corresponding phenyl acetylenes and phenyl acetic acids.^[2,3]

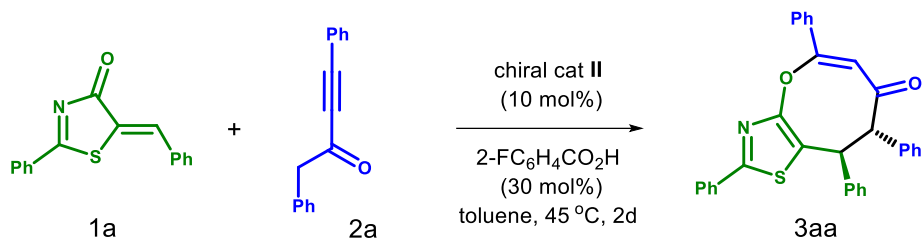
3. Catalyst & solvent optimization:



entry ^a	Catalyst (10 mol%)	Solvent	<i>T</i> (°C)	Yield (%) ^b	ee (%) ^c
1	I	toluene	45	55	86
2	II	toluene	45	65	90
3	III	toluene	45	58	57
4	IV	toluene	45	50	88
5	II	EtOAc	45	68	84
6	II	CH ₃ CN	45	80	81
7	II	(CHCl) ₂	45	85	56
8 ^d	II	toluene	60	78	82
9 ^d	II	toluene	80	58	75
10 ^e	II	toluene	45	60	93
11 ^f	II	toluene	-	68	72

^aUnless specified, 0.075 mmol of **1a** and 0.05 mmol of **2a** were stirred in 0.5 mL toluene with 10 mol% chiral amine catalyst, 30 mol% 2-FC₆H₄COOH at 45 °C for 2 days. ^bIsolated yield after silica gel column chromatography for the single diastereomer. ^cDetermined by HPLC. ^dReaction time 12h. ^eReaction was run in 1 mL toluene. ^fReaction was performed at rt for 12 days.

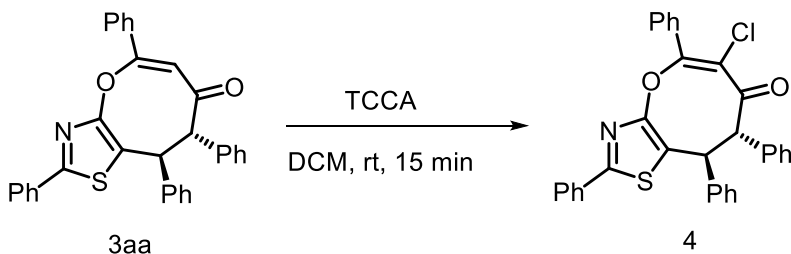
4. General procedure for the enantioselective [4+4]-annulation reaction



Under an argon atmosphere, an oven dried round bottom flask was charged with cat II (3.39 mg, 10 mol %), 2-FC₆H₄COOH (3.66 mg, 30 mol %). After the flask was evacuated and backfilled with argon, dry toluene (2.0 mL) was added, then stirred at rt for 30 minutes. Then 5-alkenyl thiazolones 1a (0.15 mmol, 1.5 equiv) and ynones 2a (0.1 mmol, 1 equiv) were added sequentially. The reaction mixture was stirred at 45 °C for 2 days. After the completion of reaction, mixture was directly purified by flash column chromatography on silica gel with hexane/ethyl acetate (3%) to afford desired product 3aa.

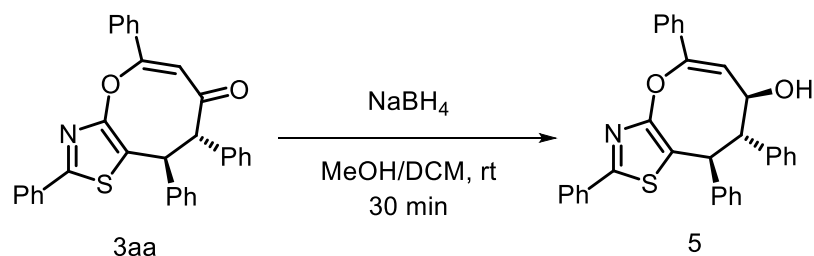
5. Synthetic transformations

➤ 5.1 General procedure for the synthesis of compound 4^[4]



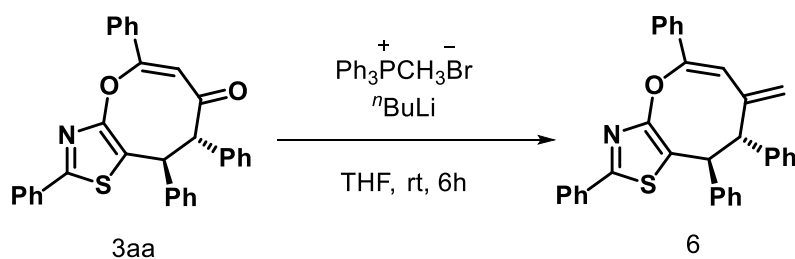
In an oven dried 5 mL vial, 2a (48.5 mg, 0.1 mmol, 1eq) was taken in 0.5 ml DCM. In that resulting solution, trichloroisocyanuric acid (TCCA) (0.1mmol, 1.0 equiv) was added and stirred at room temperature until 2a fully consumed. At the end of the reaction, the solvent was removed in vacuum. The residue was purified by flash column chromatography with (gradient eluent of EtOAc/petroleum ether: 95/5) to afford product 4 as white solid (38.5 mg, 74% yield, >20:1 dr, 88% ee).

➤ 5.2 General procedure for the synthesis of compound **5** ^[3]



To 0.5 mL of methanol and 0.5 mL of DCM was added compound **3aa** (48.5 mg, 0.1 mmol), followed by sodium borohydride (0.5 mmol, 5 equiv) in portion wise at 0 °C, and the reaction mixture was stirred for 30 min at rt. The TLC was checked, and the reaction showed full conversion. After complete consumption of **3aa**, H₂O (5 mL) was added dropwise. The resulting mixture was diluted with 5 mL of DCM. The organic layer was separated, and the aqueous layer was extracted with DCM (3 × 5 mL). Combined organic layer was washed with brine (3 × 5 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate = 90:10) to give product **5** as white solid (42.9 mg, 88% yield, >20:1 dr, 82% ee).

➤ 5.3 General procedure for the synthesis of compound **6** ^[2]



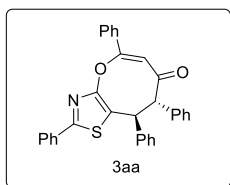
To a solution of methyltriphenylphosphoniumbromide (71.4 mg, 0.2 mmol, 2.0 equiv.) in THF (5 mL) under Ar atmosphere, n-butyllithium (0.2 mL, 1.6M, 0.2 mmol, 2.0 equiv.) was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at room temperature. Then **3aa** (48.5 mg, 0.1 mmol, 1.0 equiv.) was added and the reaction was stirred for 6 h at room temperature and quenched with saturated NH₄Cl aqueous solution. The solvent was removed in vacuo and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the solvent followed by purification by flash chromatography on silica gel (Hexane/ethyl acetate = 100:1) gave the pure compound **6** (34.9 mg, 72% yield, >20:1 dr, 94% ee).

6. References

1. A. Manna, S. Rohilla, V. K. Singh, *Org. Lett.* **2024**, *26*, *1*, 280-285.
2. D. Barman, S. C. Pan, *Org. Lett.* **2025**, *27*, *21*, 5338-5342.
3. R. Khuntia, S. K. Mahapatra, S. C. Pan, *Chem. Sci.* **2023**, *14*, 10768-10776.
4. G. Jaiswal, S. C. Pan, *Org. Biomol. Chem.* **2024**, *22*, 3602-3605.

7. Characterization of products

(8S,9S, Z)-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3aa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3aa** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 208-210 °C. **Yield** = 60% (29.1 mg), **d.r.** = 20:1, **ee** = 93%.

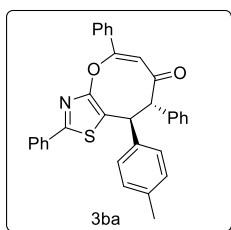
¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.25 (m, 2H), 7.92 – 7.87 (m, 2H), 7.67 – 7.62 (m, 3H), 7.53 – 7.48 (m, 2H), 7.45 (p, *J* = 2.8 Hz, 3H), 7.32 – 7.26 (m, 3H), 7.26 – 7.21 (m, 3H), 7.20 – 7.16 (m, 1H), 6.33 (s, 1H), 5.64 (d, *J* = 12.1 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.8, 167.9, 163.0, 159.2, 141.6, 137.0, 133.6, 132.9, 131.7, 130.7, 129.8, 129.0, 128.7, 128.3, 128.2, 127.9, 127.6, 127.4, 126.0, 124.9, 114.1, 60.4, 47.8.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₄NO₂S: 486.1523, found 486.1527.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 19.77 min, *t*_{minor} = 16.1 min).

(8S,9S, Z)-2,5,8-triphenyl-9-(*p*-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ba)



Prepared according to the general procedure using 5-alkenyl thiazolone **1b** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ba** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 196-198 °C. **Yield** = 75% (37.5 mg), **d.r.** = 20:1, **ee** = 86%.

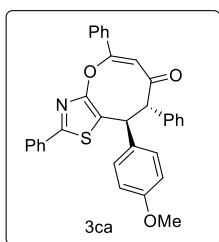
¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 6.3 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.50 (m, 3H), 7.46 – 7.33 (m, 5H), 7.20 (td, *J* = 14.9, 7.1 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.22 (s, 1H), 5.53 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 2.18 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 201.9, 167.8, 162.9, 159.1, 138.6, 137.2, 137.0, 133.7, 133.0, 131.6, 130.6, 129.9, 129.4, 129.0, 128.3, 128.2, 127.7, 127.5, 126.0, 125.2, 114.0, 60.4, 47.3, 21.2.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1693.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 18.0 min, *t*_{minor} = 13.1 min).

(8S,9S, Z)-9-(4-methoxyphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ca)



Prepared according to the general procedure using 5-alkenyl thiazolone **1c** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ca** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 190-192 °C. **Yield** = 77% (39.7 mg), **d.r.** = 20:1, **ee** = 86%.

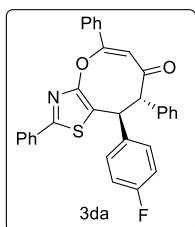
¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.03 (m, 2H), 7.77 – 7.67 (m, 2H), 7.52 – 7.45 (m, 3H), 7.37 – 7.25 (m, 5H), 7.18 – 7.07 (m, 3H), 7.04 – 6.97 (m, 2H), 6.63 – 6.53 (m, 2H), 6.15 (s, 1H), 5.43 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 3.59 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.9, 167.8, 162.9, 159.1, 158.7, 137.2, 133.7, 133.6, 133.0, 131.6, 130.6, 129.9, 129.0, 128.9, 128.3, 128.1, 127.5, 126.0, 125.3, 114.0, 114.0, 60.6, 55.2, 47.0.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₃S: 516.1628, found 516.1644.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 20.69 min, *t*_{minor} = 25.48 min).

(8S,9S, Z)-9-(4-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3da)



Prepared according to the general procedure using 5-alkenyl thiazolone **1d** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3da** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 204-206 °C.

Yield = 72% (36.2 mg), **d.r.** = 20:1, **ee** = 82%.

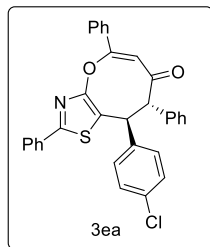
¹H NMR (500 MHz, CDCl₃) δ 8.09 – 8.02 (m, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.26 (d, *J* = 17.1 Hz, 6H), 7.09 (td, *J* = 12.8, 12.1, 6.4 Hz, 4H), 6.98 (t, *J* = 7.0 Hz, 2H), 6.69 (t, *J* = 8.5 Hz, 2H), 6.11 (s, 1H), 5.35 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.6, 167.9, 163.3, 163.0, 161.0, 159.3, 137.4, 137.4, 136.9, 133.5, 132.9, 131.8, 130.8, 129.9, 129.5, 129.4, 129.1, 129.1, 128.4, 128.2, 127.7, 126.1, 124.6, 115.7, 115.5, 114.2, 60.6, 47.2.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃FNO₂S: 504.1429, found 504.1454.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 26.93 min, *t*_{minor} = 21.3 min).

(8S,9S, Z)-9-(4-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ea)



Prepared according to the general procedure using 5-alkenyl thiazolone **1e** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ea** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 188-190 °C.

Yield = 62% (32.2 mg), **d.r.** = 20:1, **ee** = 82%.

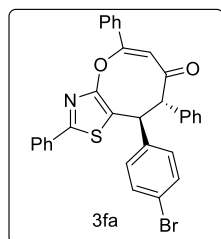
¹H NMR (500 MHz, CDCl₃) δ 8.19 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.41 (d, *J* = 7.2 Hz, 5H), 7.24 (td, *J* = 13.1, 11.8, 4.9 Hz, 4H), 7.11 (q, *J* = 4.8, 3.2 Hz, 4H), 6.25 (s, 1H), 5.49 (d, *J* = 12.1 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.5, 168.0, 163.3, 159.4, 140.2, 136.8, 133.5, 133.2, 132.9, 131.8, 130.8, 129.8, 129.3, 129.1, 129.1, 128.9, 128.5, 128.2, 127.8, 126.1, 124.2, 114.2, 60.3, 47.3.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃ClNO₂S: 520.1133, found 520.1134.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 27.56 min, *t*_{minor} = 18.73 min).

(8S,9S,Z)-9-(4-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3fa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1f** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ba** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 195-197 °C.

Yield = 60% (33.8 mg), **d.r.** = 20:1, **ee** = 96%.

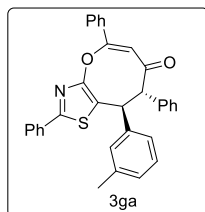
¹H NMR (500 MHz, CDCl₃) δ 8.05 (dq, *J* = 7.6, 4.1, 3.2 Hz, 2H), 7.68 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.26 (d, *J* = 12.8 Hz, 6H), 7.14 – 7.06 (m, 6H), 6.91 – 6.86 (m, 2H), 6.12 – 6.08 (m, 1H), 5.37 – 5.32 (m, 1H), 4.55 – 4.50 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.5, 168.0, 163.4, 159.4, 140.7, 136.8, 133.5, 132.9, 131.9, 131.8, 130.9, 129.9, 129.6, 129.1, 129.1, 128.5, 128.2, 127.8, 126.1, 124.2, 121.4, 114.2, 60.3, 47.4.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃BrNO₂S: 564.0628, found 564.0634.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 21.8 min, *t*_{minor} = 9.68 min).

(8S,9S,Z)-2,5,8-triphenyl-9-(*m*-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ga)



Prepared according to the general procedure using 5-alkenyl thiazolone **1g** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ga** was obtained after column

chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 196-198 °C. **Yield** = 75% (37.5 mg), **d.r.** = 20:1, **ee** = 84%.

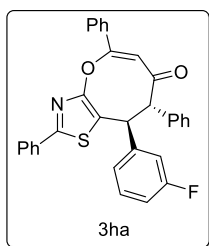
¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.07 (m, 2H), 7.77 – 7.69 (m, 2H), 7.53 – 7.43 (m, 3H), 7.36 – 7.32 (m, 2H), 7.29 (dd, *J* = 5.1, 2.1 Hz, 3H), 7.17 – 7.08 (m, 3H), 6.96 – 6.84 (m, 3H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.15 (s, 1H), 5.46 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.9, 167.8, 162.9, 159.2, 141.5, 138.4, 137.1, 133.0, 131.7, 130.7, 129.9, 129.1, 128.5, 128.5, 128.2, 128.2, 128.2, 127.5, 126.0, 125.1, 125.1, 114.1, 60.3, 47.7, 21.6.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆BrNO₂S: 500.1679, found 500.1667.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 15.32 min, *t*_{minor} = 9.3 min).

(8*S*,9*S*,*Z*)-9-(3-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ha)



Prepared according to the general procedure using 5-alkenyl thiazolone **1h** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ha** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 228-230 °C.

Yield = 68% (34.2 mg), **d.r.** = 20:1, **ee** = 80%.

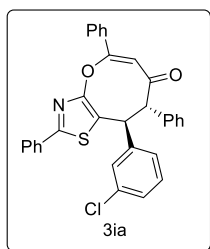
¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.17 (m, 2H), 7.82 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.46 – 7.41 (m, 2H), 7.38 (d, *J* = 7.0 Hz, 3H), 7.24 (dt, *J* = 10.1, 6.6 Hz, 4H), 7.10 (td, *J* = 8.1, 5.8 Hz, 1H), 6.93 (ddd, *J* = 7.8, 4.1, 1.7 Hz, 2H), 6.80 (td, *J* = 8.3, 2.8 Hz, 1H), 6.27 (s, 1H), 5.54 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.4, 168.0, 164.1, 163.3, 161.7, 159.3, 144.1, 144.0, 136.7, 133.5, 132.9, 131.8, 130.8, 130.2, 130.1, 129.8, 129.1, 128.4, 128.2, 127.8, 126.0, 124.1, 123.7, 123.7, 114.9, 114.7, 114.6, 114.4, 114.2, 60.1, 47.5, 47.5.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃FNO₂S: 504.1429, found 504.1457.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 26.3 min, *t*_{minor} = 13.96 min).

(8*S*,9*S*,*Z*)-9-(3-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ia)



Prepared according to the general procedure using 5-alkenyl thiazolone **1i** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ia** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 221-223 °C.

Yield = 70% (36.4 mg), **d.r.** = 20:1, **ee** = 82%.

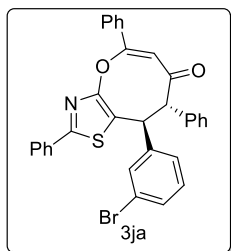
¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 5.5 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 3H), 7.47 (q, *J* = 8.0 Hz, 5H), 7.34 – 7.23 (m, 5H), 7.10 (dd, *J* = 22.1, 8.9 Hz, 3H), 6.31 (d, *J* = 2.5 Hz, 1H), 5.61 – 5.52 (m, 1H), 4.78 – 4.70 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.4, 168.0, 163.4, 159.4, 143.6, 136.7, 134.6, 133.5, 132.9, 131.8, 130.8, 129.9, 129.9, 129.1, 128.5, 128.2, 128.0, 127.8, 127.7, 126.3, 126.1, 123.9, 114.2, 60.2, 47.5.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃ClNO₂S: 520.1133, found 520.1147.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 23.07 min, *t*_{minor} = 11.68 min).

(8*S*,9*S*, *Z*)-9-(3-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-*d*]thiazol-7-one (3ja)



Prepared according to the general procedure using 5-alkenyl thiazolone **1j** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ja** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 220-222 °C.

Yield = 63% (35.28 mg), **d.r.** = 20:1, **ee** = 82%.

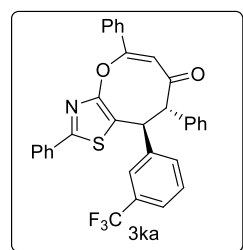
¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.79 – 7.66 (m, 2H), 7.53 – 7.41 (m, 3H), 7.29 (q, *J* = 6.6 Hz, 5H), 7.20 (s, 1H), 7.12 (dt, *J* = 10.3, 6.0 Hz, 4H), 6.98 – 6.82 (m, 2H), 6.14 (s, 1H), 5.39 (d, *J* = 12.3 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.4, 168.0, 163.4, 159.4, 143.8, 136.6, 133.5, 132.9, 131.8, 130.8, 130.6, 130.2, 129.8, 129.1, 129.1, 128.4, 128.2, 127.8, 126.7, 126.1, 123.9, 122.7, 114.2, 60.1, 47.5.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃BrNO₂S: 564.0628, found 564.0626.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 22.8 min, *t*_{minor} = 11.52 min).

(8*S*,9*S*, *Z*)-2,5,8-triphenyl-9-(3-(trifluoromethyl)phenyl)-8,9-dihydro-7H-oxocino[2,3-*d*]thiazol-7-one (3ka)



Prepared according to the general procedure using 5-alkenyl thiazolone **1k** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ka** was obtained after column chromatography (hexane/EtOAc =33:1) as a brown solid. **m.p.** 211-213 °C. **Yield** = 67% (37.11 mg), **d.r.** = 20:1, **ee** = 76%.

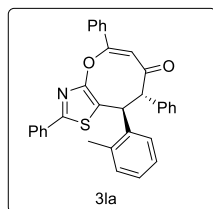
¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 5.5 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.30 – 7.21 (m, 7H), 7.19 (s, 1H), 7.15 – 7.05 (m, 4H), 6.14 (d, *J* = 3.8 Hz, 1H), 5.37 (dd, *J* = 12.2, 3.8 Hz, 1H), 4.64 (dd, *J* = 12.2, 4.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.3, 168.0, 163.6, 159.6, 142.5, 136.6, 133.5, 132.9, 131.8, 131.2, 130.9, 129.8, 129.2, 129.1, 129.1, 128.5, 128.2, 127.9, 126.1, 124.8, 124.8, 124.8, 124.8, 124.4, 124.3, 124.3, 124.3, 123.5, 114.3, 60.3, 47.8.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₃F₃NO₂S: 554.1397, found 554.1387.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 18.74 min, t_{minor} = 8.7 min).

(8S,9S,Z)-2,5,8-triphenyl-9-(o-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3la)



Prepared according to the general procedure using 5-alkenyl thiazolone **1l** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3la** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 208-210 °C.

Yield = 65% (32.5 mg), **d.r.** = 20:1, **ee** = 82%.

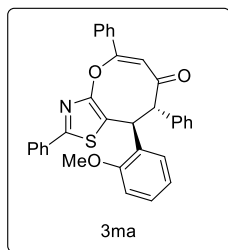
¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, J = 4.1 Hz, 2H), 7.75 – 7.63 (m, 2H), 7.48 – 7.41 (m, 4H), 7.32 (d, J = 7.9 Hz, 2H), 7.25 (s, 3H), 7.14 (s, 1H), 7.03 (dq, J = 16.0, 7.9 Hz, 4H), 6.84 (dd, J = 27.5, 7.8 Hz, 2H), 6.10 (s, 1H), 5.54 (d, J = 12.2 Hz, 1H), 4.98 – 4.87 (m, 1H), 2.13 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 202.1, 167.3, 162.6, 158.8, 140.1, 136.8, 135.1, 133.7, 133.0, 131.6, 130.7, 130.7, 129.7, 129.1, 128.9, 128.2, 128.2, 127.6, 127.6, 127.2, 126.9, 126.0, 125.6, 113.6, 60.1, 45.1, 20.2, 20.0.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1670.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 7.25 min, t_{minor} = 8.82 min).

(Z)-9-(2-methoxyphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ma)



Prepared according to the general procedure using 5-alkenyl thiazolone **1m** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ma** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 175-177 °C.

Yield = 68% (35 mg), **d.r.** = 20:1, **ee** = 84%.

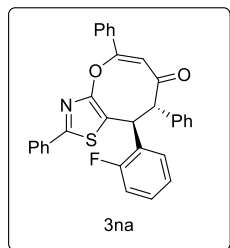
¹H NMR (400 MHz, CDCl₃) δ 8.18 – 8.00 (m, 2H), 7.76 – 7.63 (m, 2H), 7.53 – 7.38 (m, 3H), 7.37 – 7.21 (m, 6H), 7.06 (dt, J = 14.4, 7.2 Hz, 3H), 6.95 (t, J = 7.9 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 8.3 Hz, 1H), 6.14 (s, 1H), 5.68 (d, J = 12.6 Hz, 1H), 5.28 (d, J = 13.0 Hz, 1H), 3.63 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.2, 167.9, 162.4, 159.3, 156.4, 137.1, 133.8, 133.2, 131.6, 130.5, 130.0, 129.7, 129.0, 128.4, 128.2, 127.9, 127.3, 126.0, 125.0, 121.1, 114.0, 111.0, 58.5, 55.6.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{25}\text{NO}_3\text{S}$: 516.1628, found 516.1642.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{\text{major}} = 10.36$ min, $t_{\text{minor}} = 11.27$ min).

(8S,9S,Z)-9-(2-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3na)



Prepared according to the general procedure using 5-alkenyl thiazolone **1n** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3na** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 223-225 °C.

Yield = 60% (30.24 mg), **d.r.** = 20:1, **ee** = 82%.

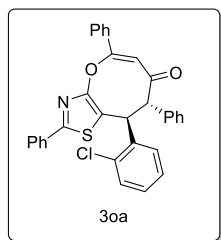
^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 6.8, 3.0$ Hz, 2H), 7.82 (dd, $J = 6.7, 3.1$ Hz, 2H), 7.61 – 7.53 (m, 3H), 7.45 (t, $J = 6.1$ Hz, 3H), 7.42 – 7.35 (m, 4H), 7.20 (dt, $J = 12.0, 6.8$ Hz, 3H), 7.11 – 7.04 (m, 1H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.85 (t, $J = 9.1$ Hz, 1H), 6.26 (s, 1H), 5.74 (d, $J = 12.5$ Hz, 1H), 5.17 (d, $J = 12.5$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.5, 168.1, 163.1, 161.2, 159.4, 158.7, 136.6, 133.6, 133.0, 131.8, 130.8, 129.7, 129.3, 129.2, 129.2, 129.1, 129.1, 129.1, 128.3, 128.3, 127.7, 126.1, 124.8, 124.7, 123.8, 115.9, 115.7, 114.1, 58.5, 39.8.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{32}\text{H}_{23}\text{FNO}_2\text{S}$: 504.1429, found 504.1453.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{\text{major}} = 12.5$ min, $t_{\text{minor}} = 11.58$ min).

(8S,9S,Z)-9-(2-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3oa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1o** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3oa** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 202-204 °C.

Yield = 62% (32.2 mg), **d.r.** = 20:1, **ee** = 84%.

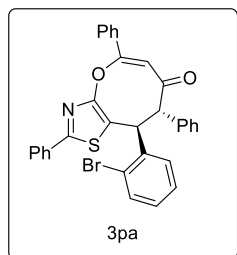
^1H NMR (500 MHz, CDCl_3) δ 8.35 – 8.23 (m, 2H), 7.97 – 7.82 (m, 2H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.68 – 7.62 (m, 3H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.46 (d, $J = 6.2$ Hz, 3H), 7.32 – 7.21 (m, 5H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.36 (s, 1H), 5.90 (d, $J = 12.6$ Hz, 1H), 5.57 (d, $J = 11.0$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 201.2, 168.0, 163.1, 159.1, 139.2, 136.3, 133.6, 133.1, 132.9, 131.8, 130.7, 129.9, 129.7, 129.1, 129.1, 128.6, 128.2, 128.2, 127.7, 127.7, 126.0, 124.1, 114.0, 58.8.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{32}\text{H}_{23}\text{ClNO}_2\text{S}$: 520.1133, found 520.1140.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{\text{major}} = 8.5$ min, $t_{\text{minor}} = 9.8$ min).

(8S,9S, Z)-9-(2-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3pa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1p** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3pa** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 224-226 °C. **Yield** = 67% (37.7 mg), **d.r.** = 20:1, **ee** = 92%.

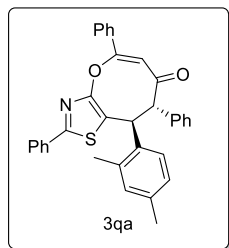
^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 4.4, 2.8$ Hz, 2H), 7.88 – 7.80 (m, 2H), 7.65 (d, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 3.0$ Hz, 3H), 7.52 – 7.45 (m, 2H), 7.43 – 7.33 (m, 4H), 7.20 (ddd, $J = 14.4, 7.8, 6.2$ Hz, 4H), 6.95 (td, $J = 7.5, 1.6$ Hz, 1H), 6.27 (s, 1H), 5.81 (d, $J = 12.0$ Hz, 1H), 5.49 (d, $J = 12.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.1, 167.9, 163.1, 159.0, 141.0, 136.2, 133.6, 133.2, 132.9, 131.8, 130.7, 129.8, 129.1, 129.1, 128.9, 128.3, 128.2, 128.2, 127.7, 126.1, 124.1, 124.0, 114.0, 59.1, 44.5.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{32}\text{H}_{23}\text{BrNO}_2\text{S}$: 564.0628, found 564.0614.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{\text{major}} = 9.0$ min, $t_{\text{minor}} = 10.76$ min).

(8S,9S, Z)-9-(2,4-dimethylphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3qa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1q** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3qa** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 200-202 °C.

Yield = 82% (42.1 mg), **d.r.** = 20:1, **ee** = 74%.

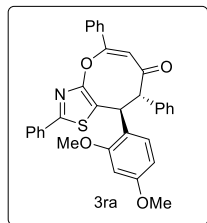
^1H NMR (400 MHz, CDCl_3) δ 8.22 – 8.16 (m, 2H), 7.85 – 7.79 (m, 2H), 7.60 – 7.53 (m, 3H), 7.50 – 7.44 (m, 3H), 7.38 (dd, $J = 5.1, 1.9$ Hz, 3H), 7.24 – 7.16 (m, 3H), 6.93 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.77 (d, $J = 2.0$ Hz, 1H), 6.23 (s, 1H), 5.66 (d, $J = 12.1$ Hz, 1H), 5.03 (d, $J = 12.1$ Hz, 1H), 2.24 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.2, 167.1, 162.5, 158.6, 137.1, 136.9, 136.7, 134.8, 133.7, 133.0, 131.6, 131.5, 130.6, 129.7, 129.0, 128.1, 128.1, 127.6, 127.6, 126.0, 113.5, 60.1, 21.1, 19.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{34}H_{28}NO_2S$: 514.1836, found 514.1857.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{major} = 6.58$ min, $t_{minor} = 7.5$ min).

(8S,9S,Z)-9-(2,4-dimethoxyphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ra)



Prepared according to the general procedure using 5-alkenyl thiazolone **1r** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ra** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 182-184 °C.

Yield = 78% (42.5 mg), **d.r.** = 20:1, **ee** = 82%.

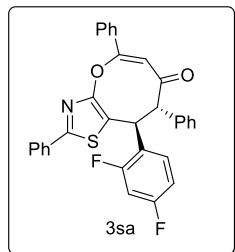
¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, $J = 6.8, 3.1$ Hz, 2H), 7.88 (dd, $J = 6.8, 3.0$ Hz, 2H), 7.67 – 7.58 (m, 3H), 7.51 (d, $J = 7.0$ Hz, 2H), 7.47 – 7.41 (m, 3H), 7.32 (s, 1H), 7.24 (dt, $J = 14.5, 6.9$ Hz, 3H), 7.04 (d, $J = 2.9$ Hz, 1H), 6.72 – 6.62 (m, 2H), 6.31 (s, 1H), 5.82 (d, $J = 12.5$ Hz, 1H), 5.43 (d, $J = 12.5$ Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 202.0, 168.0, 162.5, 159.3, 153.8, 150.7, 137.0, 133.7, 133.1, 131.6, 131.1, 130.5, 129.7, 129.0, 128.2, 128.0, 127.4, 126.0, 124.9, 114.6, 113.9, 112.6, 112.1, 58.5, 56.2, 55.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{34}H_{28}NO_4S$: 546.1734, found 546.1711.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{major} = 13.8$ min, $t_{minor} = 15.6$ min).

(8S,9S,Z)-9-(2,4-difluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3sa)



Prepared according to the general procedure using 5-alkenyl thiazolone **1s** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3sa** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 164-166 °C.

Yield = 67% (34.97 mg), **d.r.** = 20:1, **ee** = 88%.

¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, $J = 6.6, 3.2$ Hz, 2H), 7.89 (d, $J = 7.1$ Hz, 2H), 7.63 (q, $J = 2.8$ Hz, 3H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.45 (d, $J = 7.1$ Hz, 4H), 7.29 (dt, $J = 14.9, 8.4$ Hz, 3H), 6.81 (t, $J = 8.4$ Hz, 1H), 6.66 (t, $J = 9.5$ Hz, 1H), 6.33 (d, $J = 2.5$ Hz, 1H), 5.76 (dd, $J = 12.5, 2.0$ Hz, 1H), 5.18 (dd, $J = 12.4, 2.2$ Hz, 1H).

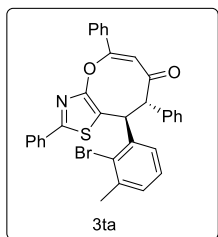
¹³C NMR (126 MHz, CDCl₃) δ 201.1, 168.1, 163.3, 163.1, 163.0, 161.1, 161.0, 161.0, 159.5, 159.1, 159.0, 136.5, 133.5, 132.9, 131.8, 130.9, 130.2, 130.2, 130.2, 130.1, 129.7, 129.1, 129.1, 128.4, 128.3,

127.9, 126.1, 124.8, 124.8, 124.7, 124.7, 123.5, 114.1, 112.2, 112.2, 112.1, 112.0, 104.3, 104.1, 103.9, 58.6, 39.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{32}H_{22}F_2NO_2S$: 522.1334, found 522.1346.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{major} = 13.0$ min, $t_{minor} = 11.0$ min).

(8S,9S,Z)-9-(2-bromo-3-methylphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ta)



Prepared according to the general procedure using 5-alkenyl thiazolone **1t** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ta** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 158-160 °C.

Yield = 78% (45 mg), **d.r.** = 20:1, **ee** = 90%.

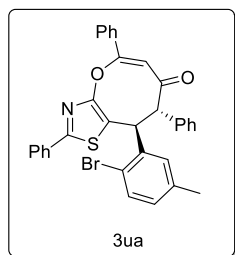
¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.93 (m, 2H), 7.63 – 7.57 (m, 2H), 7.38 – 7.31 (m, 3H), 7.30 – 7.23 (m, 3H), 7.15 (dd, $J = 5.1, 2.1$ Hz, 3H), 6.99 (dd, $J = 8.3, 6.4$ Hz, 2H), 6.96 – 6.91 (m, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.74 (dd, $J = 7.6, 1.8$ Hz, 1H), 6.03 (s, 1H), 5.57 (d, $J = 12.5$ Hz, 1H), 5.42 (d, $J = 12.5$ Hz, 1H), 2.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.2, 167.8, 162.8, 158.9, 141.3, 139.1, 136.4, 133.6, 133.0, 131.7, 130.7, 129.9, 129.7, 129.1, 129.0, 127.7, 126.1, 113.8, 59.4, 44.7, 24.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{33}H_{25}BrNO_2S$: 578.0784, found 578.0779.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{major} = 7.66$ min, $t_{minor} = 9.94$ min).

(8S,9S,Z)-9-(2-bromo-5-methylphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ua)



Prepared according to the general procedure using 5-alkenyl thiazolone **1u** (0.15mmol, 1.5 equiv), ynone **2a** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ua** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 182-184 °C.

Yield = 75% (43.3 mg), **d.r.** = 20:1, **ee** = 84%.

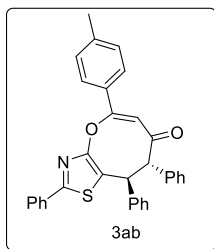
¹H NMR (400 MHz, CDCl₃) δ 8.11 (dd, $J = 6.8, 3.1$ Hz, 2H), 7.73 (dd, $J = 6.4, 3.3$ Hz, 2H), 7.55 – 7.43 (m, 3H), 7.42 – 7.34 (m, 2H), 7.28 (dt, $J = 4.8, 2.9$ Hz, 4H), 7.12 (dd, $J = 13.3, 8.0$ Hz, 3H), 7.07 (d, $J = 7.1$ Hz, 1H), 6.64 (dd, $J = 8.3, 2.4$ Hz, 1H), 6.16 (s, 1H), 5.69 (d, $J = 12.1$ Hz, 1H), 5.35 (d, $J = 12.6$ Hz, 1H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.2, 168.0, 163.0, 159.0, 140.6, 138.3, 136.3, 133.6, 133.0, 132.8, 131.8, 130.7, 130.0, 129.8, 129.3, 129.1, 129.1, 128.3, 128.2, 127.7, 126.1, 124.4, 120.6, 114.1, 59.0, 44.3, 21.2.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{25}\text{BrNO}_2\text{S}$: 578.0784, found 578.0797.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 10.05 min, t_{minor} = 11.04 min).

(8S,9S,Z)-2,8,9-triphenyl-5-(p-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ab)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2b** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3ab** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 242-244 °C.

Yield = 63% (31.5 mg), **d.r.** = 20:1, **ee** = 96%.

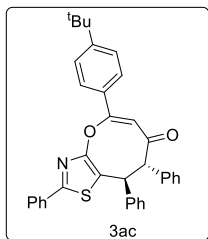
^1H NMR (500 MHz, CDCl_3) δ 8.27 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.58 (q, J = 10.9, 9.3 Hz, 7H), 7.34 (tdd, J = 24.6, 16.0, 7.4 Hz, 9H), 6.39 (s, 1H), 5.74 (d, J = 12.2 Hz, 1H), 4.89 (d, J = 12.2 Hz, 1H), 2.66 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 201.8, 168.2, 162.9, 159.3, 142.3, 141.7, 137.2, 133.0, 130.8, 130.6, 129.9, 129.8, 129.0, 128.7, 128.2, 128.2, 127.9, 127.5, 127.4, 126.0, 124.9, 113.4, 60.3, 47.9, 21.8.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{NO}_2\text{S}$: 500.1679, found 500.1697.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 17.0 min, t_{minor} = 18.74 min).

(8S,9S, Z)-5-(4-(tert-butyl)phenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ac)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2c** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2- $\text{FC}_6\text{H}_4\text{COOH}$ (30 mol%) and dry toluene (2 mL). The product **3ac** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 226-228 °C.

Yield = 70% (37.9 mg), **d.r.** = 20:1, **ee** = 89%.

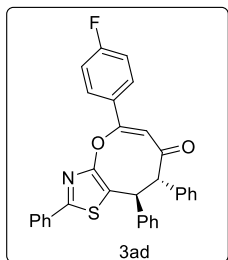
^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.02 (m, 2H), 7.78 – 7.70 (m, 2H), 7.56 – 7.48 (m, 2H), 7.37 – 7.25 (m, 5H), 7.18 – 6.97 (m, 8H), 6.16 (s, 1H), 5.48 (d, J = 12.1 Hz, 1H), 4.64 (d, J = 12.1 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.8, 168.1, 162.9, 159.3, 155.4, 141.7, 137.2, 133.0, 130.7, 130.6, 129.9, 129.0, 128.7, 128.2, 128.1, 127.9, 127.5, 127.4, 126.1, 126.0, 124.9, 113.4, 60.4, 47.8, 35.2, 31.4.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{32}\text{NO}_2\text{S}$: 542.2149, found 542.2155.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 10.88 min, t_{minor} = 7.79 min).

(8S,9S, Z)-5-(4-fluorophenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ad)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2d** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ad** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 208-210 °C.

Yield = 60% (30.2 mg), **d.r.** = 20:1, **ee** = 94%.

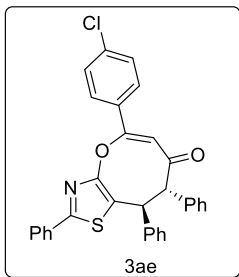
¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.15 (m, 2H), 7.83 – 7.75 (m, 2H), 7.44 – 7.32 (m, 5H), 7.26 – 7.06 (m, 10H), 6.17 (s, 1H), 5.53 (d, J = 12.1 Hz, 1H), 4.70 (d, J = 12.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.6, 167.0, 166.3, 163.8, 163.1, 159.1, 141.5, 137.0, 132.9, 130.7, 130.5, 130.4, 129.9, 129.1, 128.7, 128.3, 127.9, 127.6, 127.4, 126.0, 124.9, 116.3, 116.1, 114.0, 114.0, 60.4, 47.9.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃FNO₂S: 504.1429, found 504.1433.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 18.79 min, t_{minor} = 17.49 min).

(8S,9S, Z)-5-(4-chlorophenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ae)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2e** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ae** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 232-234 °C.

Yield = 61% (31.7 mg), **d.r.** = 20:1, **ee** = 92%.

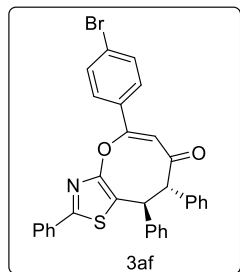
¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.09 (m, 2H), 7.86 – 7.77 (m, 2H), 7.58 – 7.50 (m, 2H), 7.40 (ddt, J = 7.4, 5.4, 2.3 Hz, 5H), 7.25 – 7.19 (m, 3H), 7.18 – 7.13 (m, 4H), 7.13 – 7.09 (m, 1H), 6.22 (s, 1H), 5.54 (d, J = 12.1 Hz, 1H), 4.71 (d, J = 12.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.6, 166.7, 163.2, 159.1, 141.5, 137.9, 136.9, 132.9, 132.2, 130.8, 129.9, 129.4, 129.4, 129.1, 128.7, 128.3, 127.9, 127.6, 127.5, 126.0, 124.9, 114.5, 60.4, 47.9.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃ClNO₂S: 520.1133, found 520.1129.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ID Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 11.7 min, t_{minor} = 9.95 min).

(8S,9S, Z)-5-(4-bromophenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3af)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2f** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3af** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 209-211 °C.

Yield = 60% (33.8 mg), **d.r.** = 20:1, **ee** = 82%.

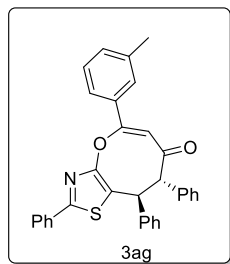
¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 6.8, 3.1 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.81 (ddd, *J* = 7.6, 5.6, 2.4 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.40 (td, *J* = 5.4, 2.5 Hz, 6H), 7.24 – 7.18 (m, 3H), 7.15 (ddt, *J* = 8.0, 5.3, 2.7 Hz, 4H), 7.12 – 7.08 (m, 1H), 6.26 – 6.19 (m, 1H), 5.53 (dd, *J* = 12.1, 9.3 Hz, 1H), 4.70 (dd, *J* = 12.2, 4.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.8, 201.6, 167.8, 166.7, 163.2, 159.0, 147.3, 141.6, 141.4, 137.0, 136.9, 133.6, 133.0, 132.9, 132.6, 132.3, 131.6, 130.7, 130.7, 130.6, 129.9, 129.8, 129.8, 129.5, 129.2, 129.1, 129.0, 129.0, 128.7, 128.7, 128.7, 128.3, 128.2, 128.2, 128.2, 127.9, 127.8, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 126.3, 126.0, 126.0, 124.9, 124.8, 114.5, 114.1, 113.3, 60.4, 60.4, 60.3, 47.9, 47.8.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃BrNO₂S: 564.0628, found 564.0614.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ID Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 10.26 min, *t*_{minor} = 12.56 min).

(8*S*,9*S*, *Z*)-2,8,9-triphenyl-5-(*m*-tolyl)-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ag**)**



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2g** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ag** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 212-214 °C.

Yield = 67% (33.5 mg), **d.r.** = 20:1, **ee** = 90%.

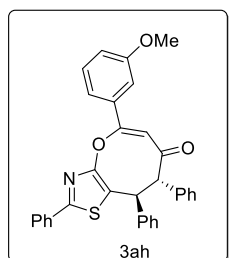
¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 9.2 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 3H), 7.29 (d, *J* = 10.3 Hz, 4H), 7.14 (dd, *J* = 16.6, 8.9 Hz, 5H), 7.07 (q, *J* = 7.6, 5.3 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.18 (d, *J* = 4.1 Hz, 1H), 5.50 (dd, *J* = 12.2, 4.1 Hz, 1H), 4.67 (dd, *J* = 12.2, 4.3 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 201.7, 168.0, 162.9, 159.2, 141.6, 138.6, 137.0, 133.5, 132.9, 132.5, 130.6, 129.8, 129.0, 128.9, 128.7, 128.6, 128.2, 127.8, 127.5, 127.3, 125.9, 125.4, 124.9, 113.9, 60.4, 47.7, 21.7.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1683.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 17.8 min, *t*_{minor} = 12.48 min).

(8S,9S,Z)-5-(3-methoxyphenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ah)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2h** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ah** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 170-172 °C.

Yield = 71% (36.6 mg), **d.r.** = 20:1, **ee** = 90%.

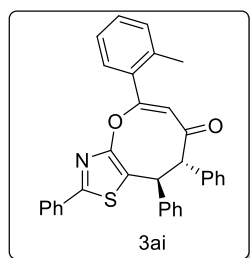
¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.65 (m, 3H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.22 (m, 6H), 7.04 (ddd, *J* = 24.8, 12.9, 7.2 Hz, 10H), 6.11 (s, 1H), 5.43 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 3.84 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.8, 167.7, 163.0, 160.1, 159.2, 141.6, 137.0, 135.0, 133.0, 130.7, 130.0, 129.9, 129.0, 128.7, 128.3, 127.9, 127.6, 127.4, 125.9, 124.9, 120.6, 118.1, 114.4, 112.9, 60.3, 55.7, 47.9.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₃S: 516.1628, found 516.1622.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 35.0 min, *t*_{minor} = 18.0 min).

(8S,9S,Z)-2,8,9-triphenyl-5-(*o*-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ai)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2i** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ai** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 170-172 °C. **Yield** = 65% (32.5 mg), **d.r.** = 20:1, **ee** = 94%.

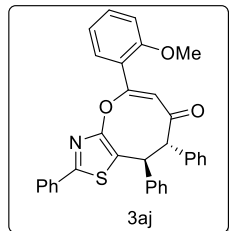
¹H NMR (500 MHz, CDCl₃) δ 8.40 (d, *J* = 7.4 Hz, 1H), 7.81 (dd, *J* = 7.0, 2.8 Hz, 2H), 7.44 – 7.35 (m, 7H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 3H), 7.12 (dp, *J* = 22.2, 7.2 Hz, 6H), 5.78 (s, 1H), 5.42 (d, *J* = 12.1 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 2.57 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 201.6, 166.0, 163.1, 158.9, 141.2, 137.6, 137.0, 133.7, 133.1, 131.5, 131.0, 130.8, 130.7, 129.6, 129.1, 128.8, 128.5, 127.9, 127.7, 127.5, 126.5, 126.1, 125.3, 117.4, 61.4, 46.9, 21.9.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1687.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 22.85 min, *t*_{minor} = 17.69 min).

(8S,9S,Z)-5-(2-methoxyphenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3aj)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2j** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3aj** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 216-218 °C.

Yield = 60% (31 mg), **d.r.** = 20:1, **ee** = 80%.

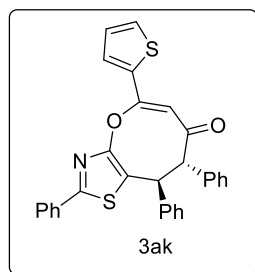
¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 3H), 7.20 – 7.07 (m, 6H), 7.04 (t, *J* = 7.5 Hz, 2H), 7.02 – 6.97 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 1H), 5.53 (dd, *J* = 12.1, 2.0 Hz, 1H), 4.63 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.77 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 203.2, 162.8, 162.8, 159.4, 158.7, 141.7, 137.4, 133.1, 132.5, 131.7, 130.5, 129.9, 129.0, 128.6, 128.2, 127.9, 127.4, 127.3, 126.0, 124.9, 121.8, 121.0, 119.6, 111.3, 60.4, 55.6, 48.0.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₃S: 516.1628, found 516.1632.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 57.67 min, *t*_{minor} = 61.4 min).

(8R,9S,Z)-2,5,9-triphenyl-8-(thiophen-2-yl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ak)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2k** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ak** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 196-198 °C. **Yield** = 72% (35.4 mg), **d.r.** = 20:1, **ee** = 80%.

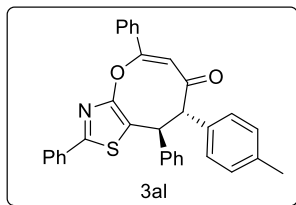
¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.90 (m, 1H), 7.87 – 7.75 (m, 2H), 7.65 – 7.57 (m, 1H), 7.38 (td, *J* = 6.6, 5.4, 2.0 Hz, 5H), 7.25 – 7.12 (m, 8H), 7.12 – 7.06 (m, 1H), 6.13 (s, 1H), 5.54 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 200.9, 163.1, 162.6, 158.7, 141.7, 138.0, 137.0, 133.0, 131.1, 130.7, 130.5, 130.0, 129.1, 128.8, 128.7, 128.2, 127.9, 127.5, 127.4, 126.0, 124.9, 112.5, 60.2, 48.0.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₀H₂₂NO₂S₂: 492.1087, found 492.1083.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 22.52 min, *t*_{minor} = 18.1 min).

(8S,9S,Z)-2,5,9-triphenyl-8-(p-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3al)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2l** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3al** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 208-210 °C. **Yield** = 67% (33.5 mg), **d.r.** = 20:1, **ee** = 92%.

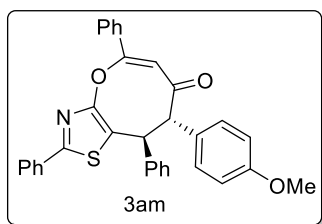
¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.13 (m, 2H), 8.00 – 7.89 (m, 1H), 7.86 – 7.77 (m, 2H), 7.57 (dd, *J* = 6.1, 2.8 Hz, 3H), 7.38 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.29 – 7.20 (m, 3H), 7.17 – 7.04 (m, 4H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.26 (s, 1H), 6.04 (d, *J* = 12.3 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.6, 167.8, 163.1, 159.2, 141.5, 136.7, 135.3, 133.7, 133.0, 131.7, 130.7, 130.1, 129.4, 129.1, 128.7, 128.2, 127.9, 127.5, 127.2, 126.2, 126.1, 125.1, 114.4, 54.4, 47.2, 20.4.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1699.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 22.1 min, *t*_{minor} = 12.5 min).

(8S,9S,Z)-8-(4-methoxyphenyl)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3am)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2m** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3am** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 217-219 °C.

Yield = 62% (32 mg), **d.r.** = 20:1, **ee** = 90%.

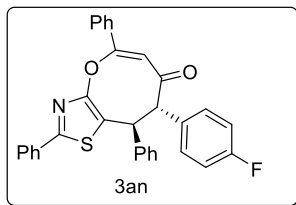
¹H NMR (400 MHz, CDCl₃) δ 8.25 – 8.16 (m, 2H), 7.86 – 7.78 (m, 2H), 7.56 (h, *J* = 2.3 Hz, 3H), 7.42 – 7.30 (m, 5H), 7.21 – 7.09 (m, 5H), 6.80 – 6.74 (m, 2H), 6.24 (s, 1H), 5.50 (d, *J* = 12.1 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 3.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 202.3, 167.7, 163.0, 159.2, 159.0, 141.7, 133.6, 133.0, 131.6, 130.8, 130.6, 129.2, 129.0, 128.7, 128.2, 127.9, 127.4, 126.0, 124.9, 114.1, 113.7, 59.6, 55.3, 47.9.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₃S: 516.1628, found 516.1664.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 26.38 min, *t*_{minor} = 19.0 min).

(8S,9S,Z)-8-(4-fluorophenyl)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3an)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2n** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3an** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 185-187 °C. **Yield** = 61% (30.7 mg), **d.r.** = 20:1, **ee** = 92%.

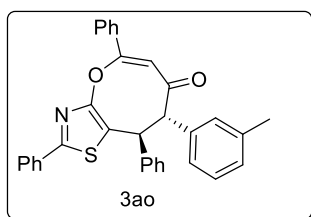
¹H NMR (400 MHz, CDCl₃) δ 8.31 (dt, *J* = 6.6, 3.4 Hz, 2H), 7.97 – 7.86 (m, 2H), 7.73 – 7.61 (m, 3H), 7.49 (q, *J* = 6.6, 6.1 Hz, 5H), 7.26 (d, *J* = 9.1 Hz, 5H), 7.01 (td, *J* = 8.8, 2.9 Hz, 2H), 6.43 – 6.29 (m, 1H), 5.66 (dt, *J* = 12.1, 3.8 Hz, 1H), 4.74 (dt, *J* = 12.3, 4.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.7, 168.2, 163.6, 163.1, 161.1, 159.3, 141.5, 141.5, 133.5, 132.9, 132.9, 131.8, 131.4, 131.3, 130.7, 129.1, 128.8, 128.2, 127.8, 127.5, 126.0, 124.6, 115.2, 115.0, 114.1, 114.1, 59.5, 48.2.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃FNO₂S: 504.1429, found 504.1404.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 14.29 min, *t*_{minor} = 10.4 min).

(8S,9S,Z)-2,5,9-triphenyl-8-(*m*-tolyl)-8,9-dihydro-7H-oxocino[2,3-*d*]thiazol-7-one (3ao**)**



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2o** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ao** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 186-188 °C. **Yield** = 59% (29.5 mg), **d.r.** = 20:1, **ee** = 90%.

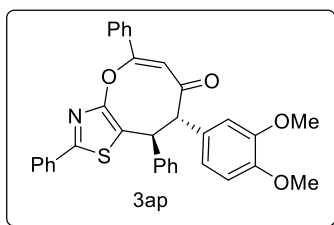
¹H NMR (500 MHz, CDCl₃) δ 8.29 – 8.21 (m, 2H), 7.87 (dd, *J* = 7.3, 2.4 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.43 (dt, *J* = 5.4, 2.6 Hz, 3H), 7.31 – 7.23 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.15 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 2.0 Hz, 1H), 5.59 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.79 (dd, *J* = 12.2, 2.5 Hz, 1H), 2.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 201.9, 167.7, 163.0, 159.2, 141.7, 137.8, 136.9, 133.7, 133.0, 131.6, 130.7, 130.5, 129.0, 129.0, 128.7, 128.3, 128.2, 128.1, 127.9, 127.4, 126.9, 126.0, 125.1, 114.0, 60.4, 47.5, 21.6.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₃H₂₆NO₂S: 500.1679, found 500.1692.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 17.47 min, *t*_{minor} = 11.38 min).

(8S,9S,Z)-2,5,9-triphenyl-8-(*o*-tolyl)-8,9-dihydro-7H-oxocino[2,3-*d*]thiazol-7-one (3ap**)**



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2p** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ap** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 242-244 °C.

Yield = 71% (38.7 mg), **d.r.** = 20:1, **ee** = 80%.

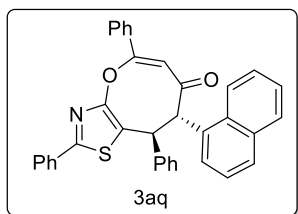
¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.15 (m, 2H), 7.85 – 7.80 (m, 2H), 7.59 – 7.52 (m, 3H), 7.38 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.15 (d, *J* = 4.6 Hz, 4H), 7.13 – 7.08 (m, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.89 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.25 (s, 1H), 5.45 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 3.83 (d, *J* = 14.5 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 202.3, 167.8, 163.1, 159.3, 148.7, 148.5, 141.6, 133.6, 133.0, 131.7, 130.7, 129.6, 129.1, 129.1, 128.7, 128.2, 127.9, 127.4, 126.0, 124.8, 122.3, 114.1, 112.9, 110.8, 59.9, 56.2, 55.9, 48.2.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₄H₂₈NO₄S: 546.1734, found 546.1754.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 32.78 min, *t*_{minor} = 26.2 min).

(8S,9S,Z)-8-(naphthalen-1-yl)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3aq)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2q** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3aq** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid.

m.p. 230-232 °C. **Yield** = 78% (41.8 mg), **d.r.** = 20:1, **ee** = 89%.

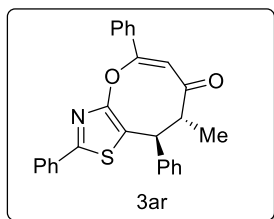
¹H NMR (500 MHz, CDCl₃) δ 8.24 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 3H), 7.77 (dd, *J* = 9.3, 5.9 Hz, 3H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.46 – 7.36 (m, 5H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.30 (s, 1H), 5.79 (d, *J* = 12.2 Hz, 1H), 4.91 (d, *J* = 12.1 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.8, 168.0, 163.1, 159.2, 141.5, 134.6, 133.6, 133.3, 133.0, 132.9, 131.7, 130.7, 129.1, 129.0, 128.8, 128.2, 128.1, 127.9, 127.7, 127.5, 127.5, 126.0, 126.0, 126.0, 125.0, 114.1, 60.5, 47.6.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₆H₂₅NO₂S: 536.1679, found 536.1699.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 24.5 min, *t*_{minor} = 17.8 min).

(8R,9S,Z)-8-methyl-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ar)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2r** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3ar** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 186-

188 °C. **Yield** = 73% (31 mg), **d.r.** = 20:1, **ee** = 94%.

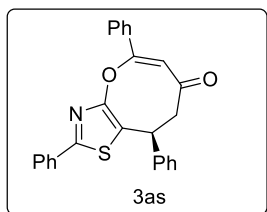
¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.17 (m, 2H), 7.82 – 7.75 (m, 2H), 7.58 – 7.52 (m, 3H), 7.42 – 7.31 (m, 7H), 7.31 – 7.24 (m, 1H), 6.28 (s, 1H), 4.40 (dq, *J* = 11.4, 6.5 Hz, 1H), 4.00 (d, *J* = 11.6 Hz, 1H), 1.07 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 204.7, 168.6, 162.7, 159.2, 142.6, 133.7, 133.0, 131.7, 130.6, 129.1, 129.0, 128.2, 128.0, 127.7, 126.0, 125.4, 114.3, 48.0, 48.0, 16.1.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₂₇H₂₁NO₂S: 424.1366, found 424.1392.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 8.07 min, *t*_{minor} = 12.2 min).

(S, Z)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3as)



Prepared according to the general procedure using 5-alkenyl thiazolone **1a** (0.15mmol, 1.5 equiv), ynone **2s** (0.1 mmol, 1 equiv), catalyst **II** (10 mol%), 2-FC₆H₄COOH (30 mol%) and dry toluene (2 mL). The product **3as** was obtained after column chromatography (hexane/EtOAc =33:1) as a white solid. **m.p.** 154-

156 °C. **Yield** = 78% (32 mg), **d.r.** = 20:1, **ee** = 84%.

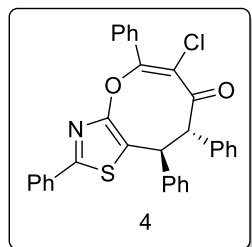
¹H NMR (500 MHz, CDCl₃) δ 8.27 – 8.21 (m, 2H), 7.85 – 7.77 (m, 2H), 7.59 – 7.51 (m, 3H), 7.42 – 7.32 (m, 7H), 7.28 (s, 1H), 6.35 (s, 1H), 4.53 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.18 (t, *J* = 11.9 Hz, 1H), 2.95 (dd, *J* = 11.5, 5.1 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 199.9, 169.3, 163.0, 159.9, 143.7, 133.6, 133.1, 131.9, 130.7, 129.3, 129.1, 129.0, 128.4, 127.7, 127.4, 126.0, 124.0, 115.0, 48.2, 41.8.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₂₆H₂₀NO₂S: 410.1210, found 410.1227.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 9.8 min, *t*_{minor} = 13.35 min).

(8S,9S,E)-6-chloro-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (4)



White solid, **m.p.** 246-248 °C. **Yield** = 74% (38.5 mg), >20:1 dr, **ee** = 88%

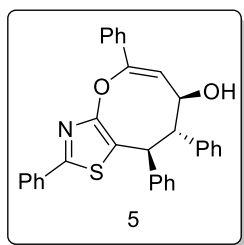
¹H NMR (500 MHz, CDCl₃) δ 8.50 – 8.45 (m, 2H), 7.89 – 7.83 (m, 2H), 7.63 – 7.57 (m, 3H), 7.43 (td, *J* = 6.1, 4.9, 2.0 Hz, 5H), 7.23 (d, *J* = 7.2 Hz, 3H), 7.11 (s, 4H), 5.60 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 197.8, 165.1, 163.5, 159.6, 140.8, 136.7, 132.9, 132.7, 131.9, 131.5, 130.9, 129.9, 129.2, 128.7, 128.5, 128.5, 127.9, 127.6, 126.1, 124.8, 121.7, 60.2, 48.3.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₃ClNO₂S: 520.1133, found 520.1134.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK IA Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 9.63 min, *t*_{minor} = 17.03 min).

(7S,8S,9S,Z)-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-ol (5)



White solid, **m.p.** 148-150 °C. **Yield** = 88% (42.9 mg), >20:1 dr, **ee** = 82%

¹H NMR (400 MHz, CDCl₃) δ 7.86 (td, *J* = 7.3, 6.8, 2.0 Hz, 4H), 7.50 – 7.38 (m, 6H), 7.35 – 7.30 (m, 2H), 7.26 (td, *J* = 9.3, 7.9, 4.5 Hz, 7H), 7.22 – 7.16 (m, 2H), 5.36 (d, *J* = 8.3 Hz, 1H), 5.19 (d, *J* = 8.6 Hz, 1H), 5.00 (d, *J* = 11.8 Hz, 1H), 3.72

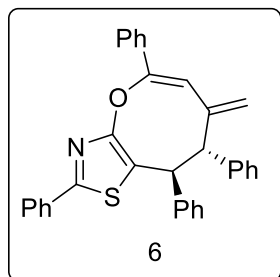
(dd, *J* = 11.8, 5.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6, 155.7, 148.9, 140.8, 137.6, 135.2, 133.2, 130.3, 129.9, 129.1, 129.0, 128.9, 128.8, 128.7, 127.6, 127.6, 126.0, 125.9, 117.2, 107.3, 68.7, 49.3, 44.8.

HRMS (ESI-TOF) m/z: [M+H]⁺calculated for C₃₂H₂₆NO₂S: 488.1679, found 488.1679.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n-Hexane/i-PrOH* = 90/10, flow rate 1.0 mL/min, λ = 220 nm (*t*_{major} = 22.28 min, *t*_{minor} = 57.57 min).

(8R,9S,Z)-7-methylene-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazole (6)



White solid, **m.p.** 188-190 °C. **Yield** = 72% (34.9 mg), >20:1 dr, **ee** = 94%

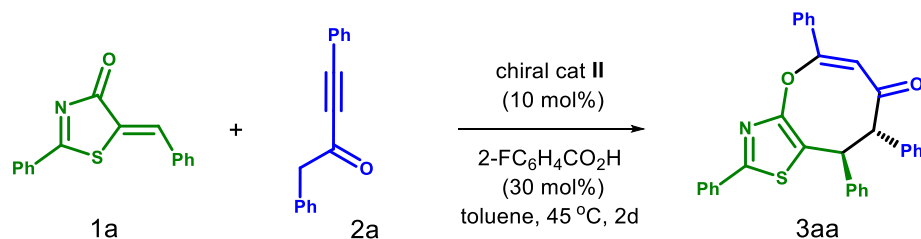
¹H NMR (400 MHz, DMSO) δ 8.12 – 8.04 (m, 2H), 7.82 – 7.75 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (td, *J* = 10.5, 10.1, 4.4 Hz, 8H), 7.20 (td, *J* = 7.6, 6.0 Hz, 4H), 7.13 – 7.04 (m, 2H), 6.61 (s, 1H), 5.27 (s, 1H), 5.17 (d, *J* = 4.0 Hz, 3H).

¹³C NMR (101 MHz, DMSO) δ 161.3, 156.7, 152.9, 146.6, 143.6, 141.9, 135.1, 132.5, 130.7, 129.4, 129.2, 128.8, 128.6, 128.3, 127.7, 126.9, 126.5, 126.3, 126.2, 125.4, 120.6, 115.1, 52.0, 46.4.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{33}H_{26}NO_2S$: 484.1730, found 484.1732.

HPLC Analysis: The enantiomeric excess was determined using ChiralPAK ADH Column, *n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 220$ nm ($t_{major} = 5.29$ min, $t_{minor} = 13.64$ min).

8. Scale-up reaction for compound **3aa**



Under an argon atmosphere, an oven dried round bottom flask was charged with cat. **II** (67.8 mg, 10 mol %), 2-FC₆H₄COOH (84 mg, 30 mol %). After the flask was evacuated and backfilled with argon, dry toluene (2.0 mL) was added, then stirred at rt for 30 minutes. Then 5-alkenyl thiazolones **1a** (660 mg, 3 mmol, 1.5 equiv) and ynones **2a** (530mg, 2 mmol, 1 equiv) were added sequentially. The reaction mixture was stirred at 45 °C for 2 days. After the completion of reaction, mixture was directly purified by flash column chromatography on silica gel with hexane/ethyl acetate (33:1) to afford desired product **3aa**.

Yield = 58% (562.2 mg), **ee** = 91%

9. Single crystal X-ray diffraction analysis:

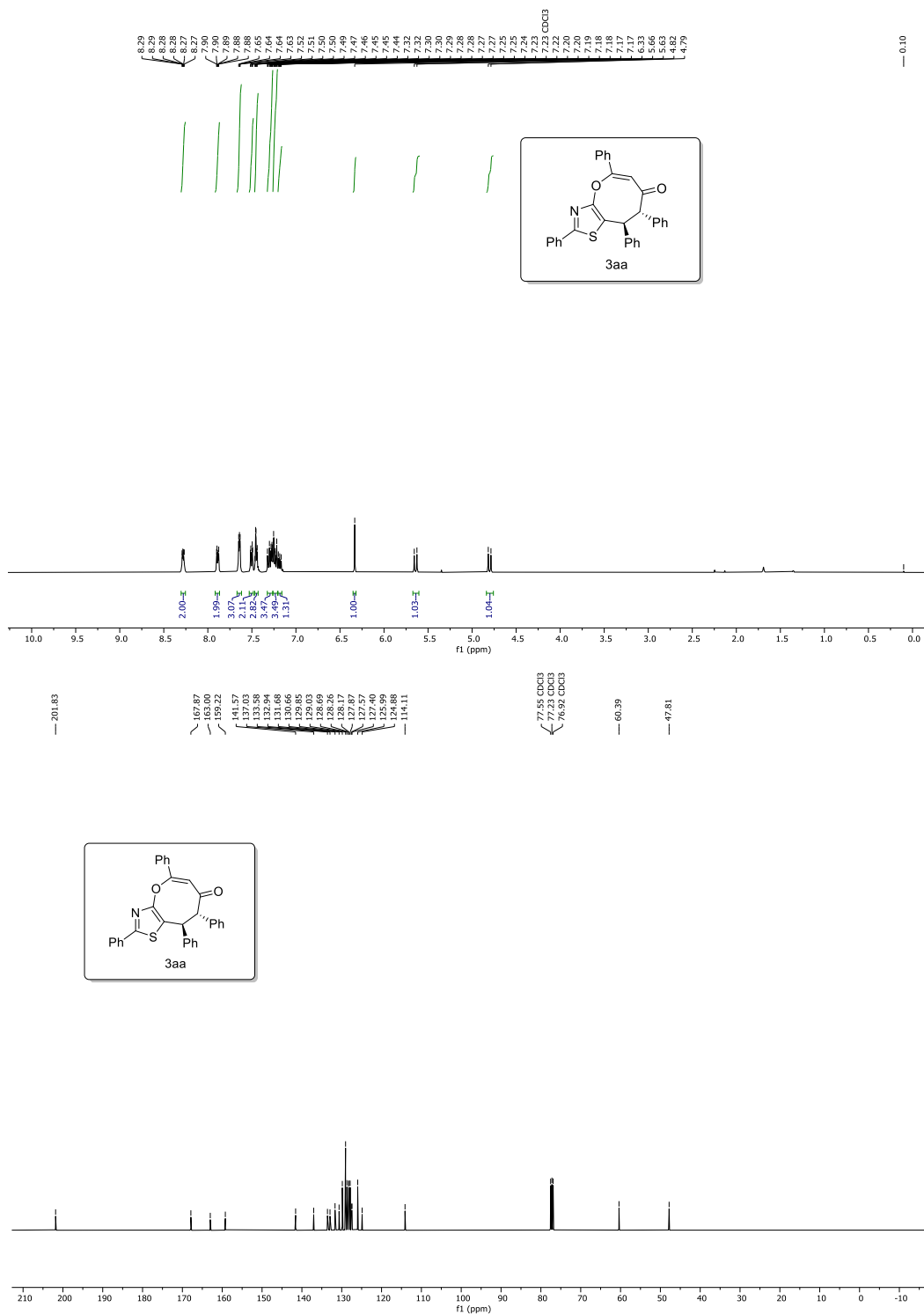
Method for crystal growth:

In a round bottom flask, compound **3pa** dissolved in minimum amount of hexane/DCM (3:1) and it kept in dark place at room temperature for slow evaporation to get colourless crystal of compound **3pa**. X-ray crystallographic data were collected using Bruker D8 QUEST diffractometer. Data refinement and cell reduction were carried out by APEX4. Structures were solved by direct methods using Olex2 v1.5 and refined by a full-matrix least-squares method using Olex2 v1.5. The ORTEP diagram was obtained with ORTEP3 software with 30% thermal ellipsoid. The crystallographic parameters and refinement data are:

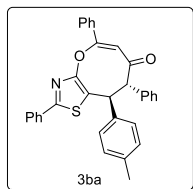
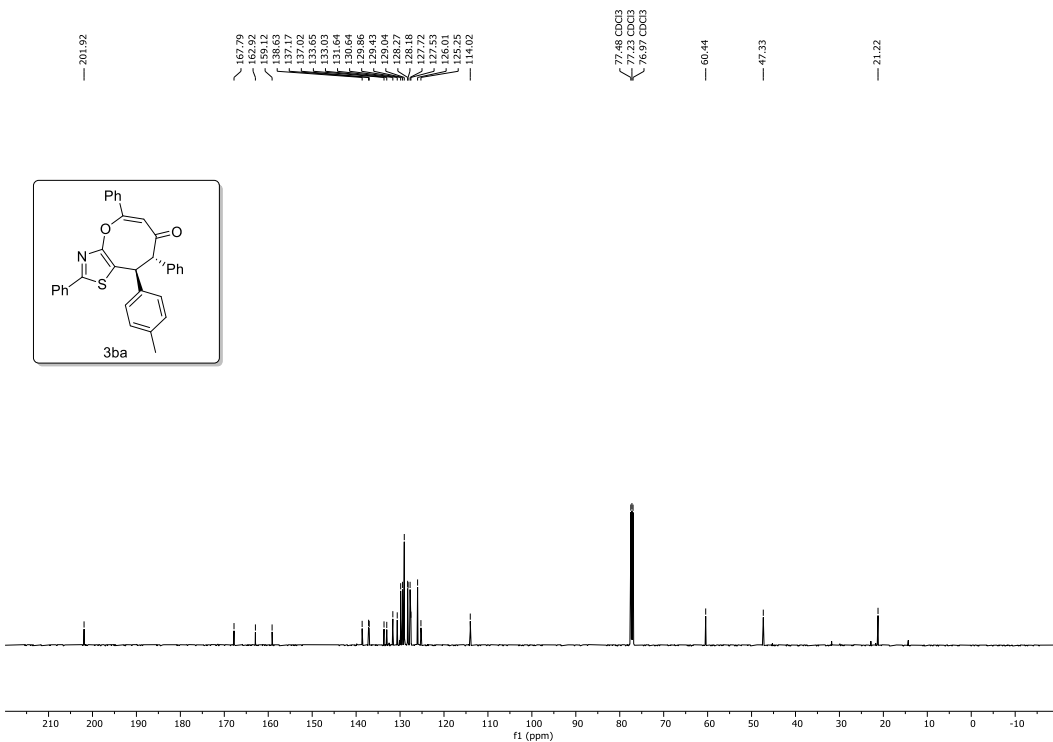
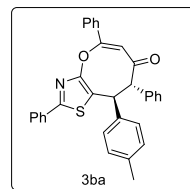
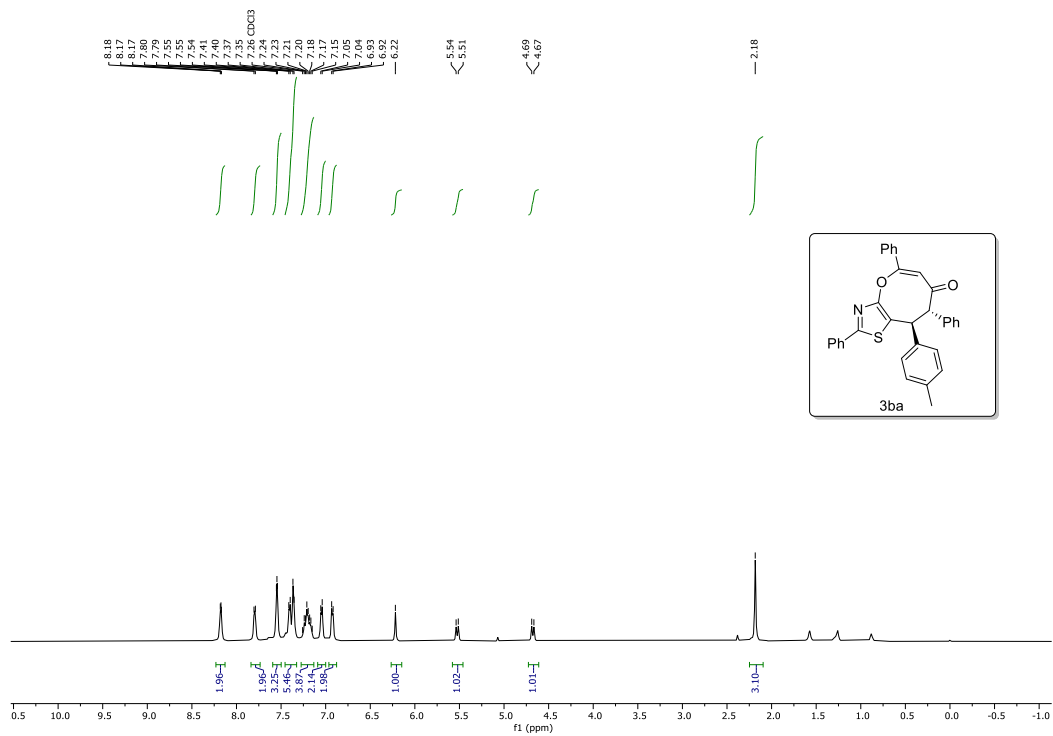
CCDC No.	2516428
Empirical formula	C ₃₂ H ₂₂ BrNO ₂ S
Formula weight	564.4970
Crystal habit, colour	Needle, clear colourless
Temperature, (T)	297 K
Bond precision	C-C = 0.0115 Å
Wavelength (λ)	0.71073 Å

10. ¹H NMR and ¹³C NMR spectra:

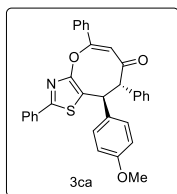
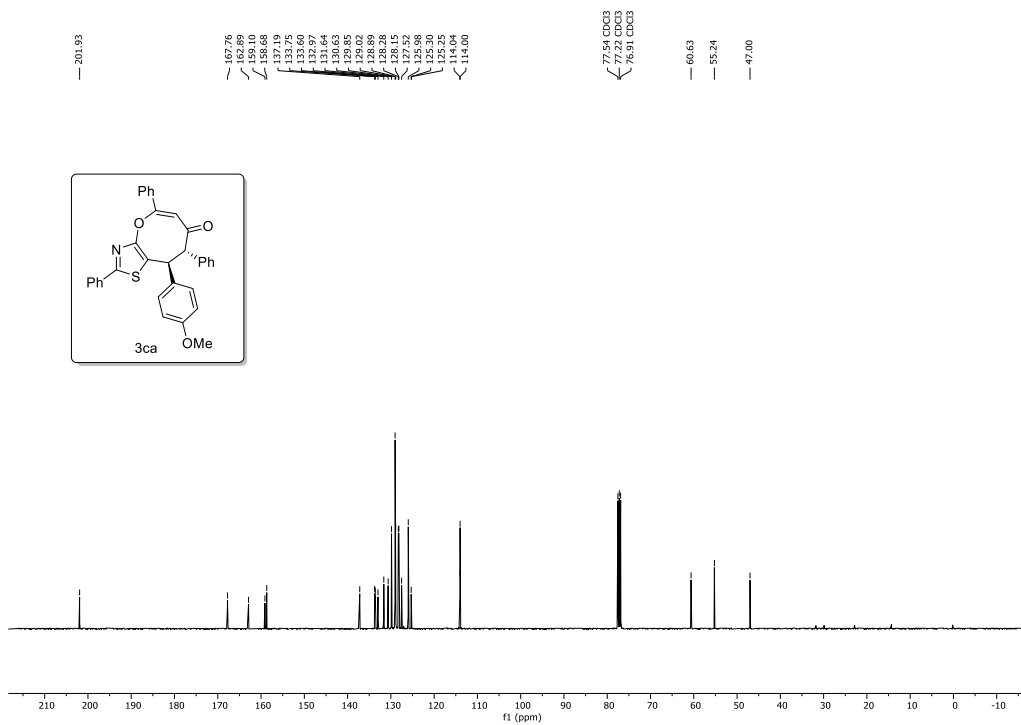
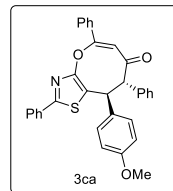
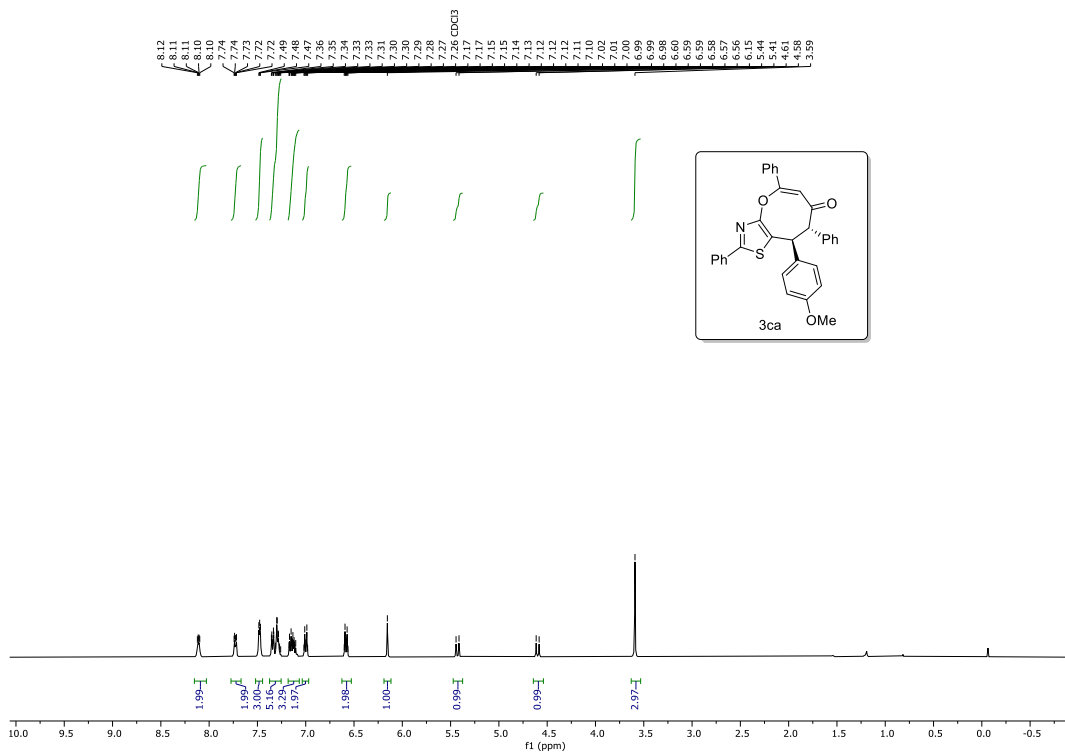
(Z)-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3aa)



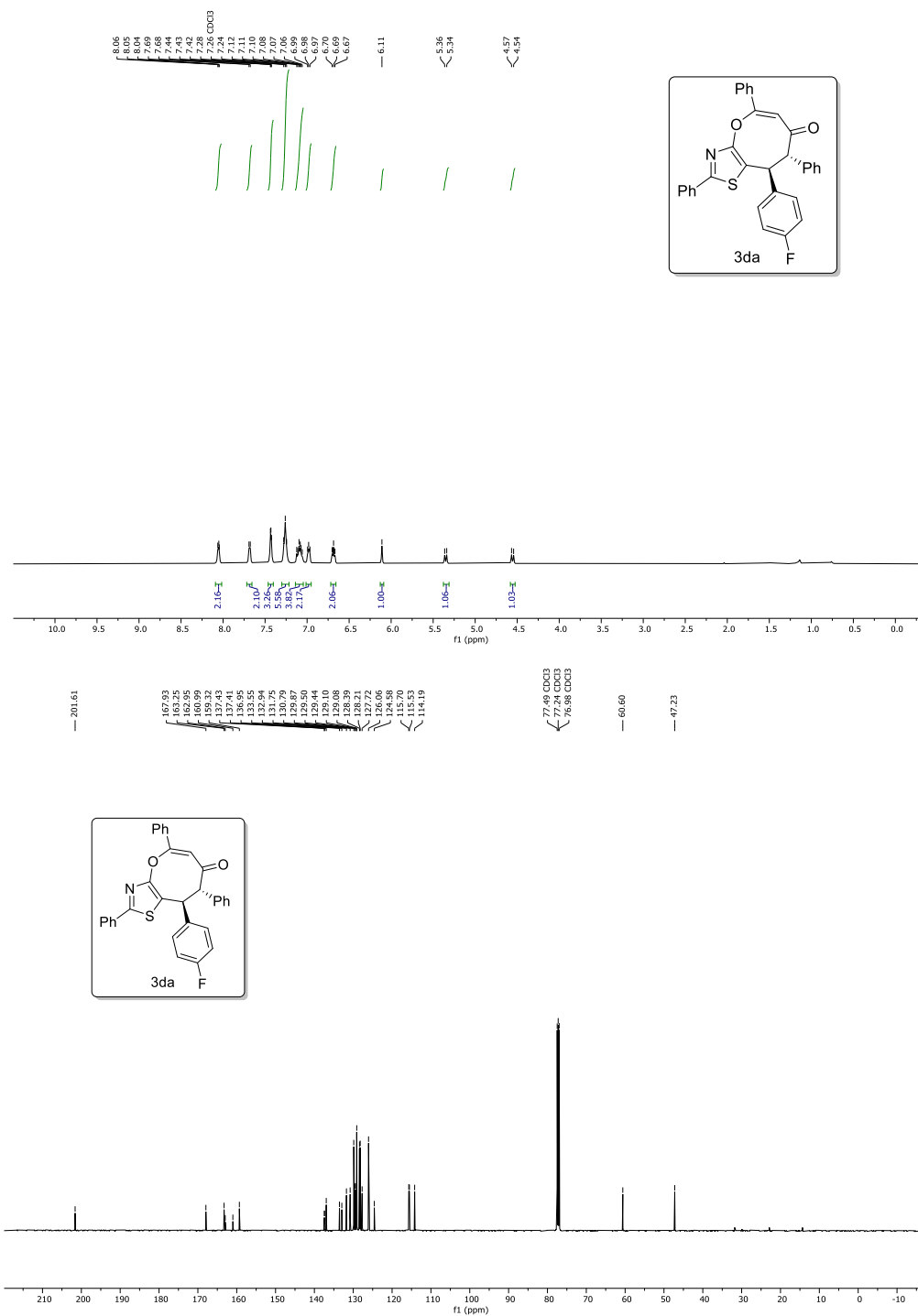
(Z)-2,5,8-triphenyl-9-(p-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ba)



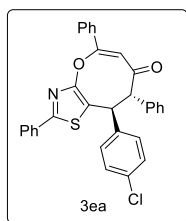
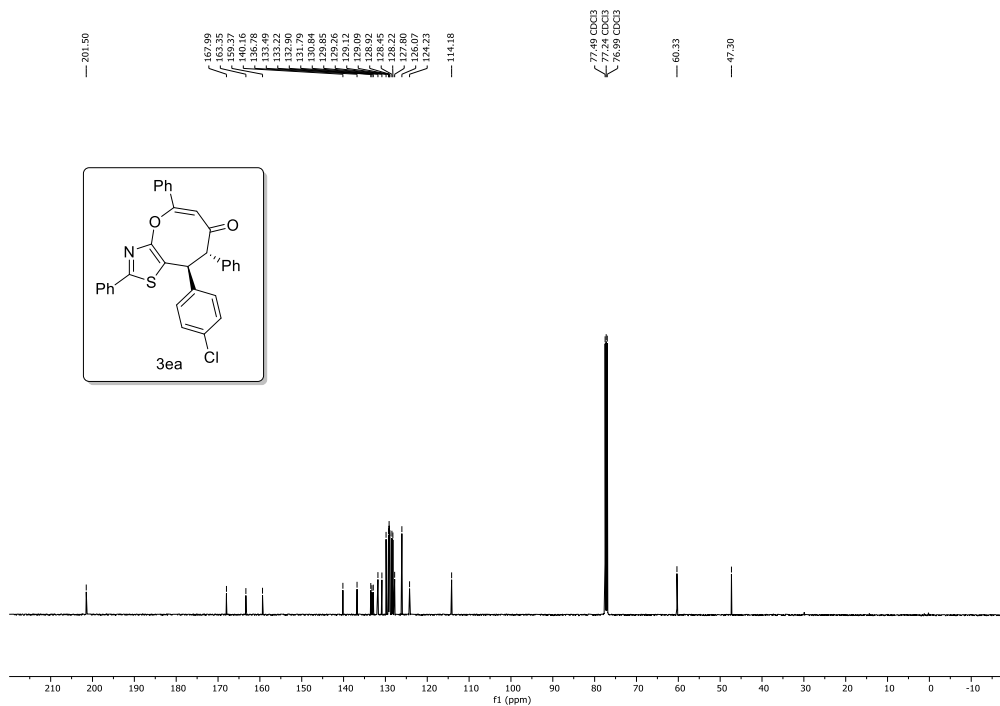
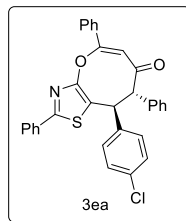
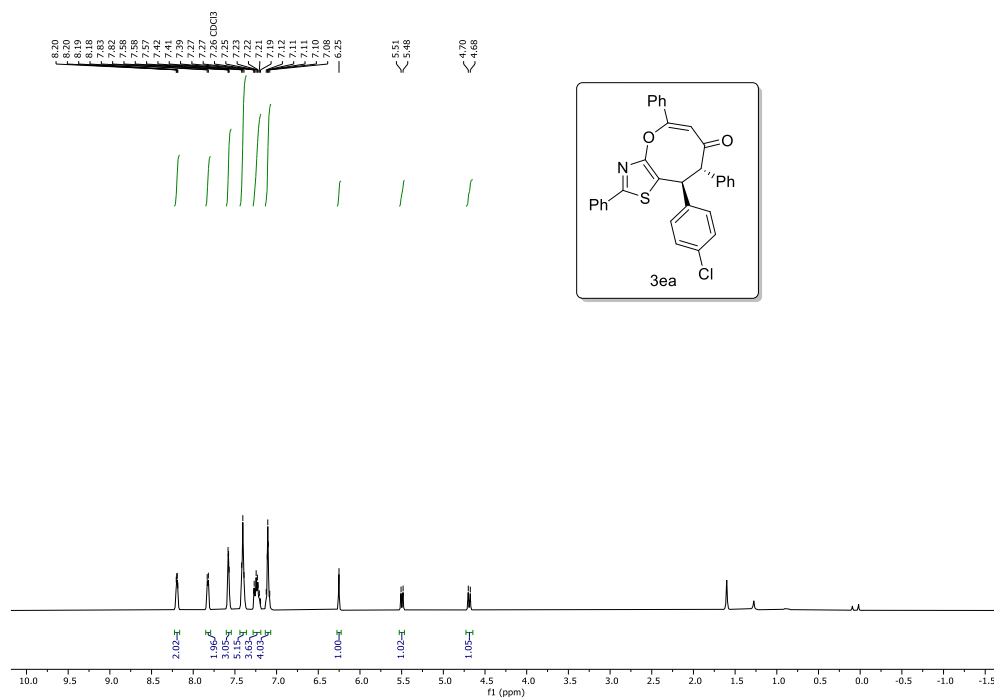
(Z)-9-(4-methoxyphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ca)



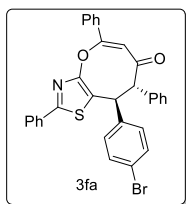
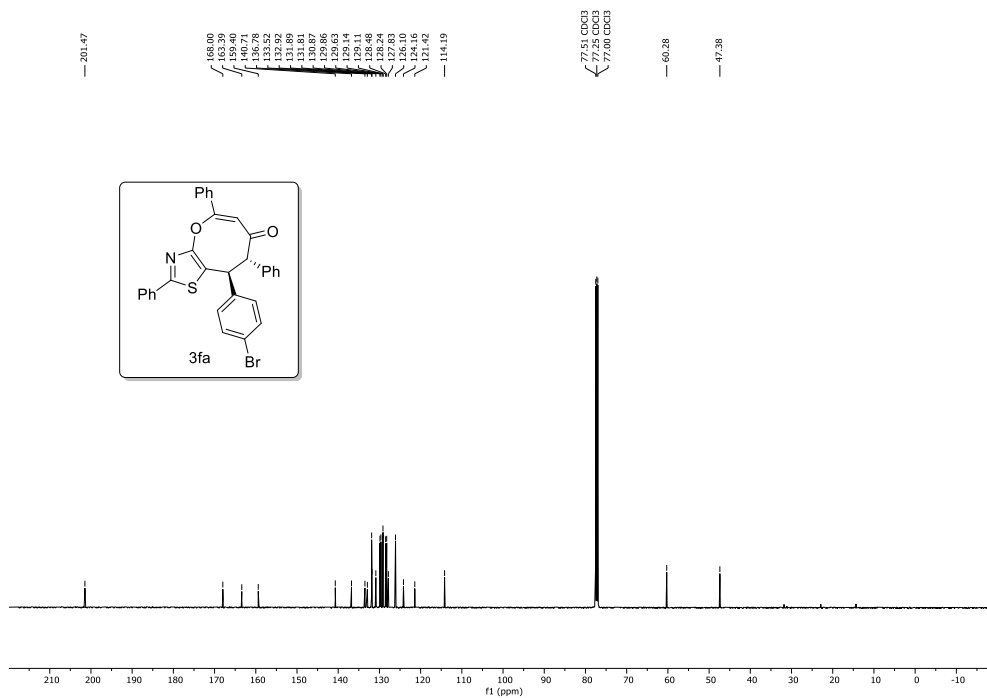
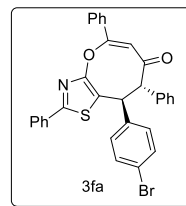
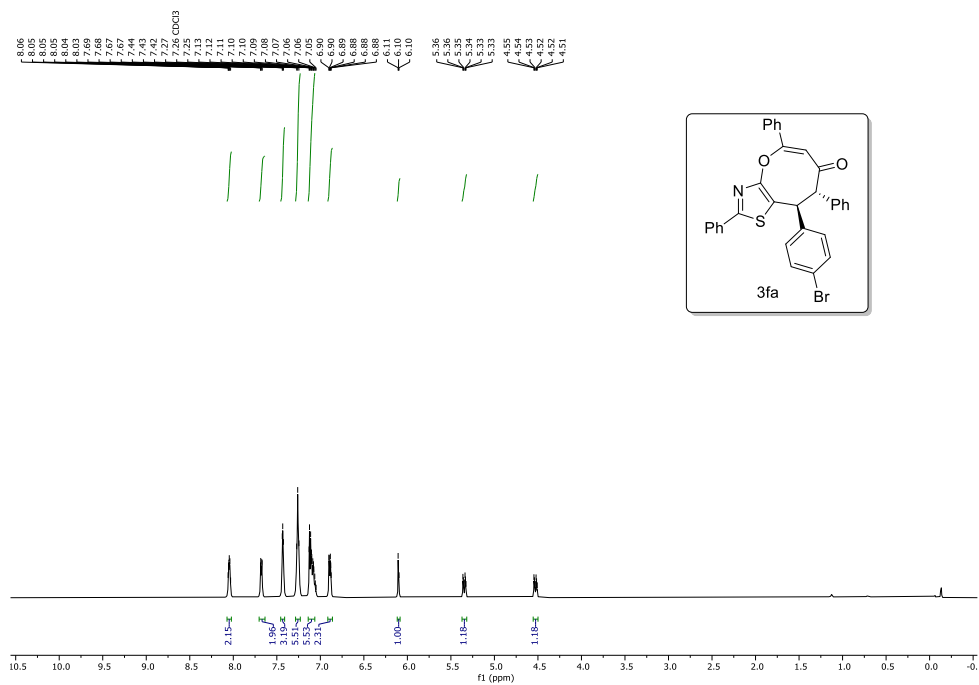
(Z)-9-(4-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3da)



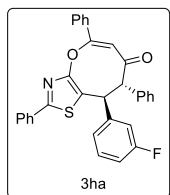
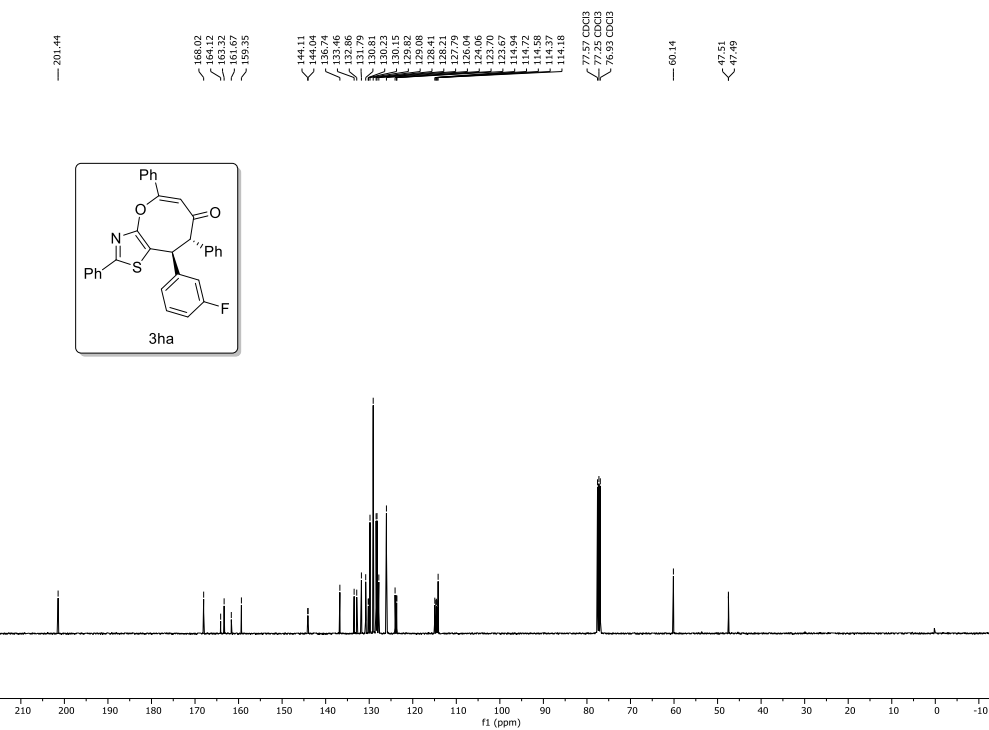
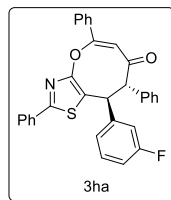
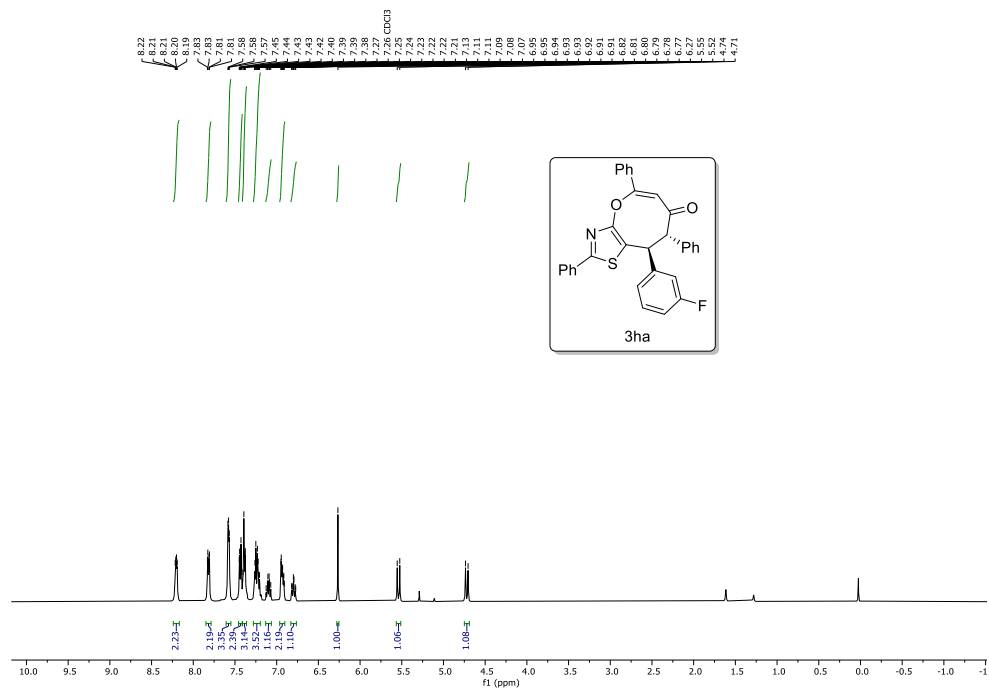
(Z)-9-(4-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ea)



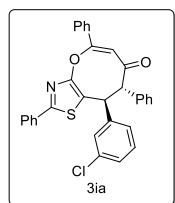
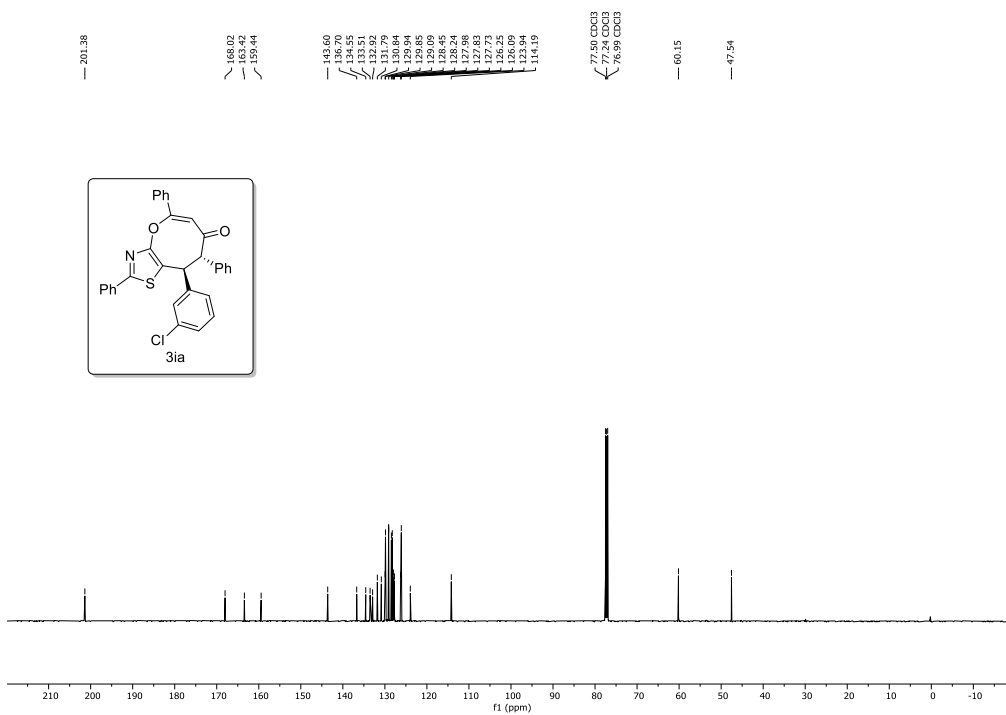
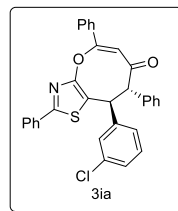
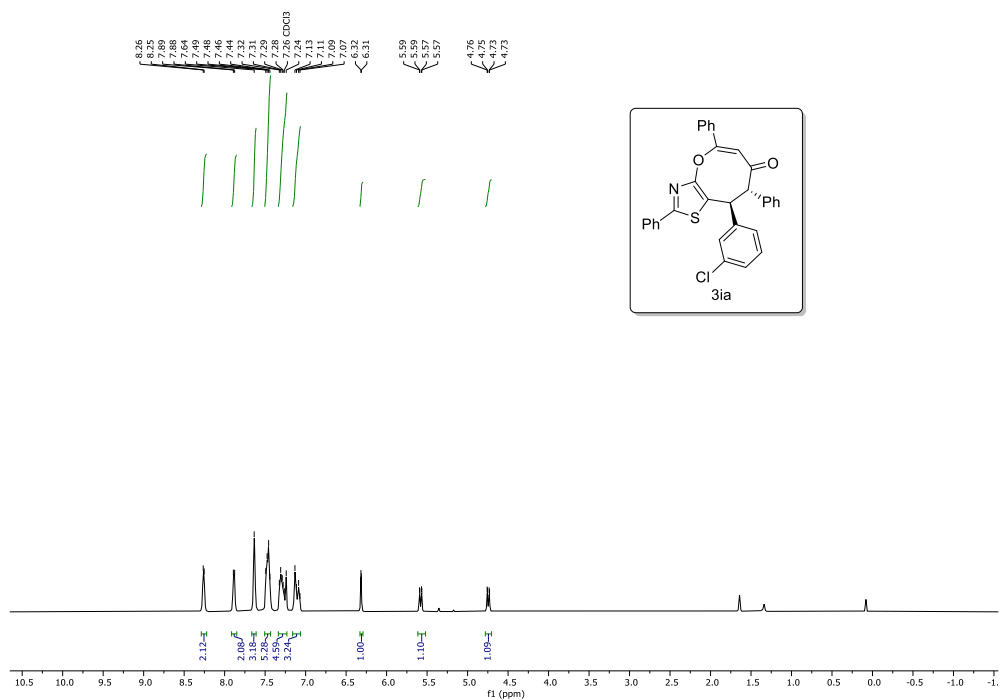
(Z)-9-(4-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3fa)



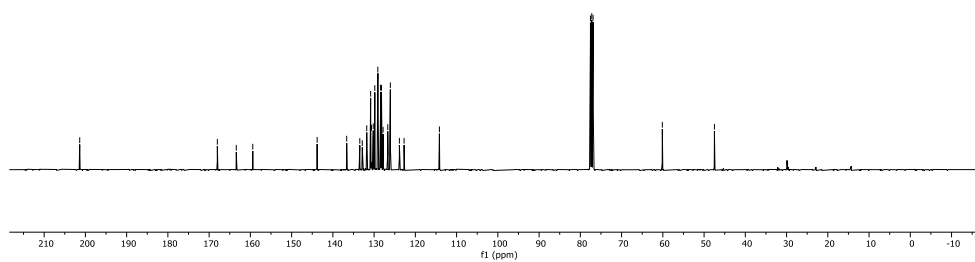
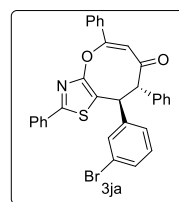
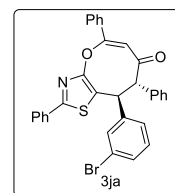
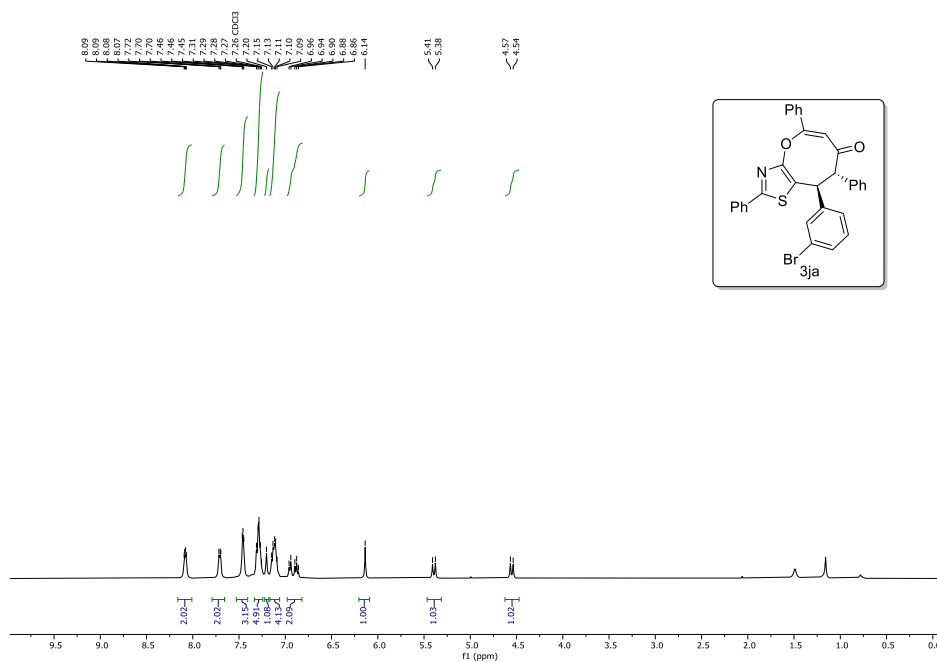
(Z)-9-(3-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ha)



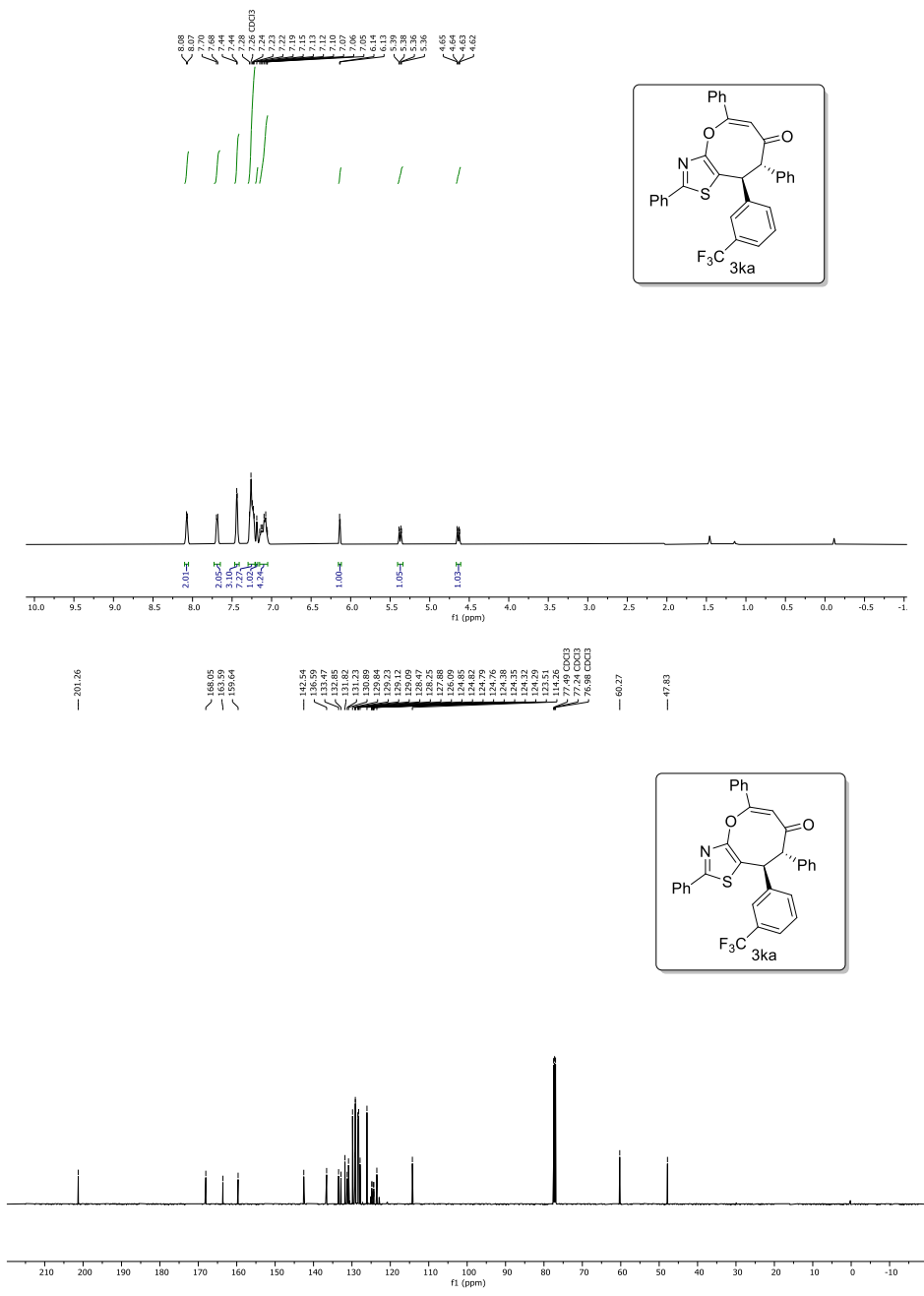
(Z)-9-(3-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ia)



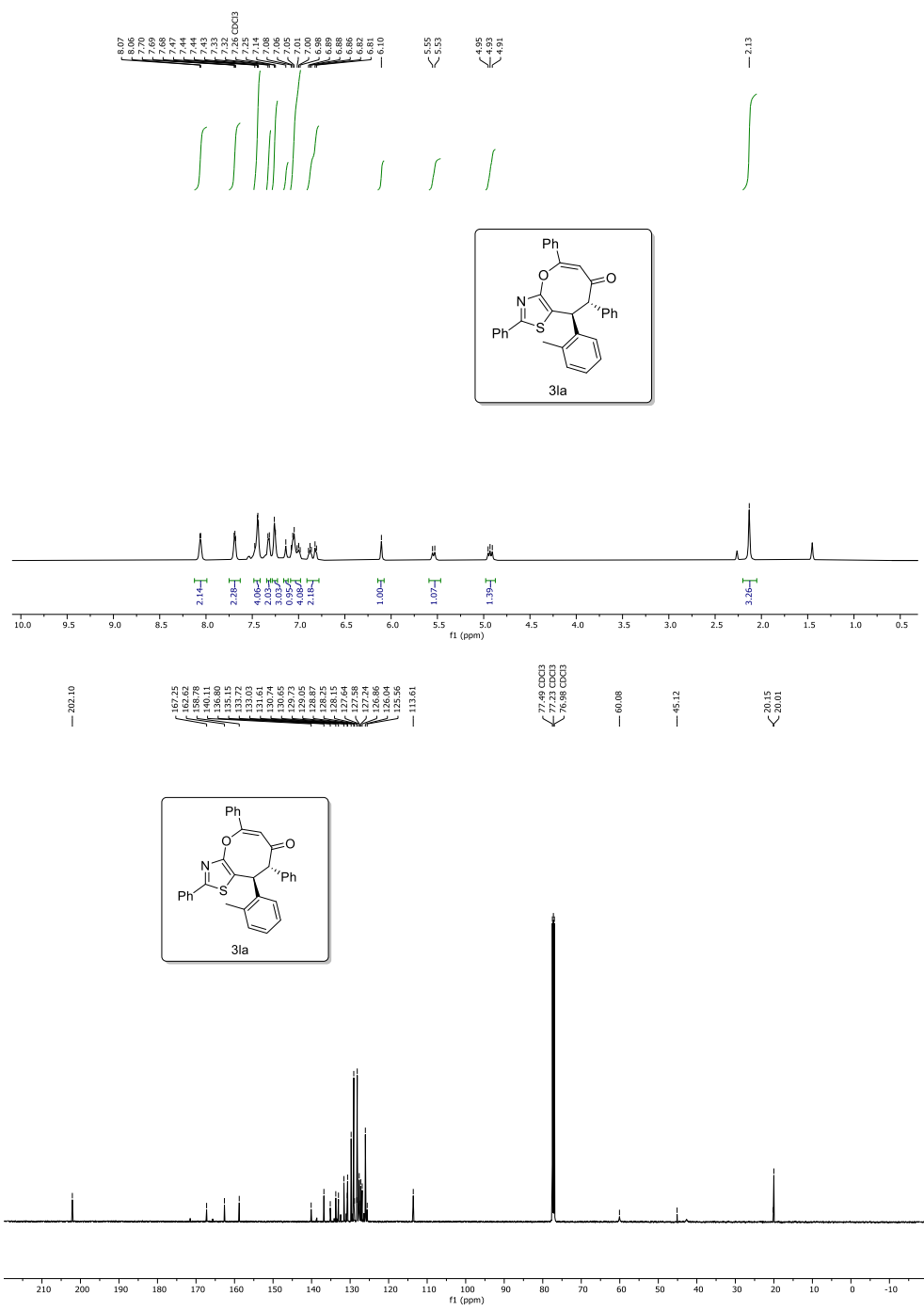
(8*S*,9*S*,*Z*)-9-(3-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ja)



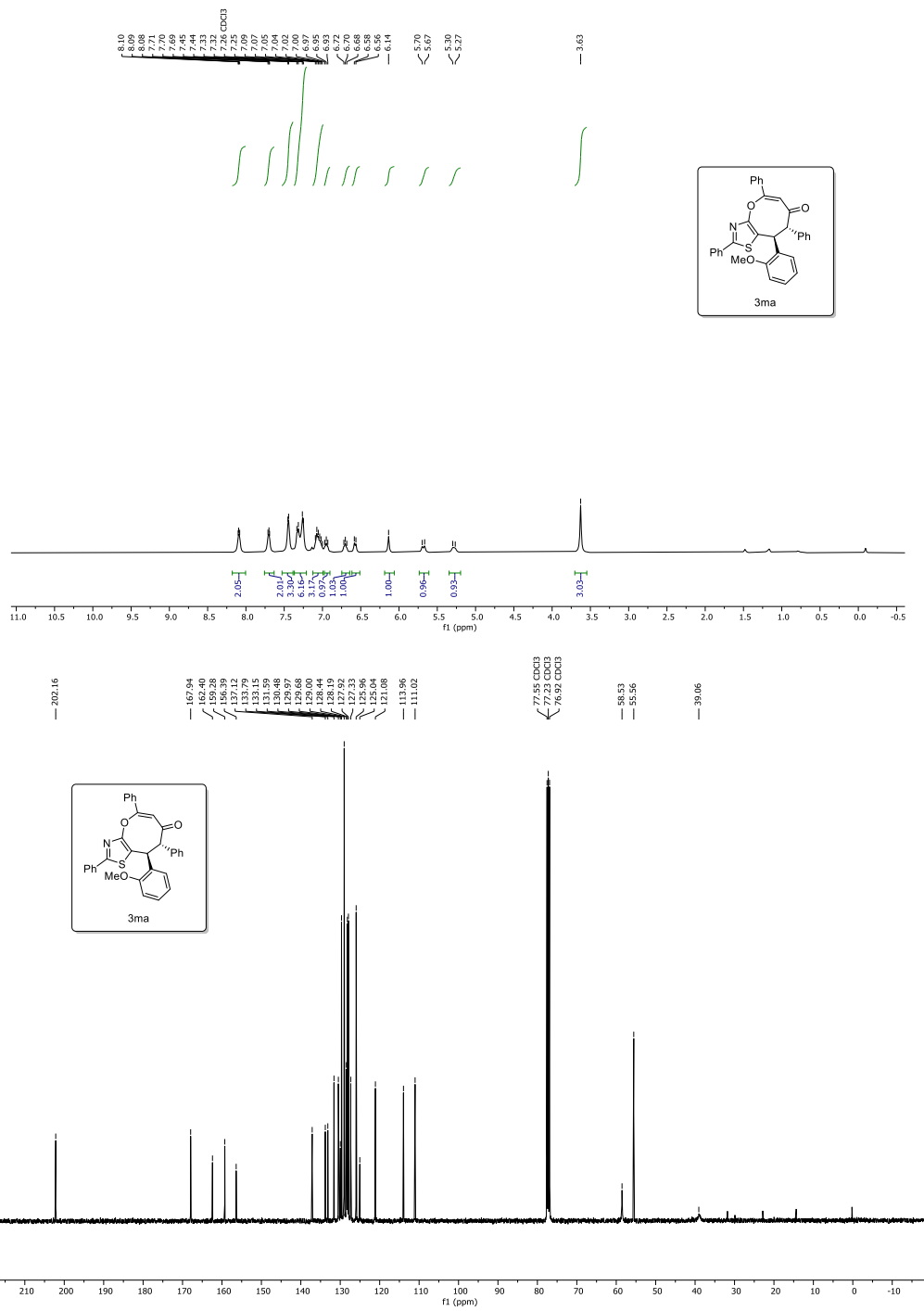
(8*S*,9*S*,*Z*)-2,5,8-triphenyl-9-(3-(trifluoromethyl)phenyl)-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ka)



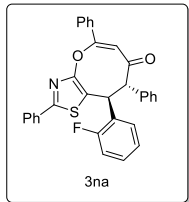
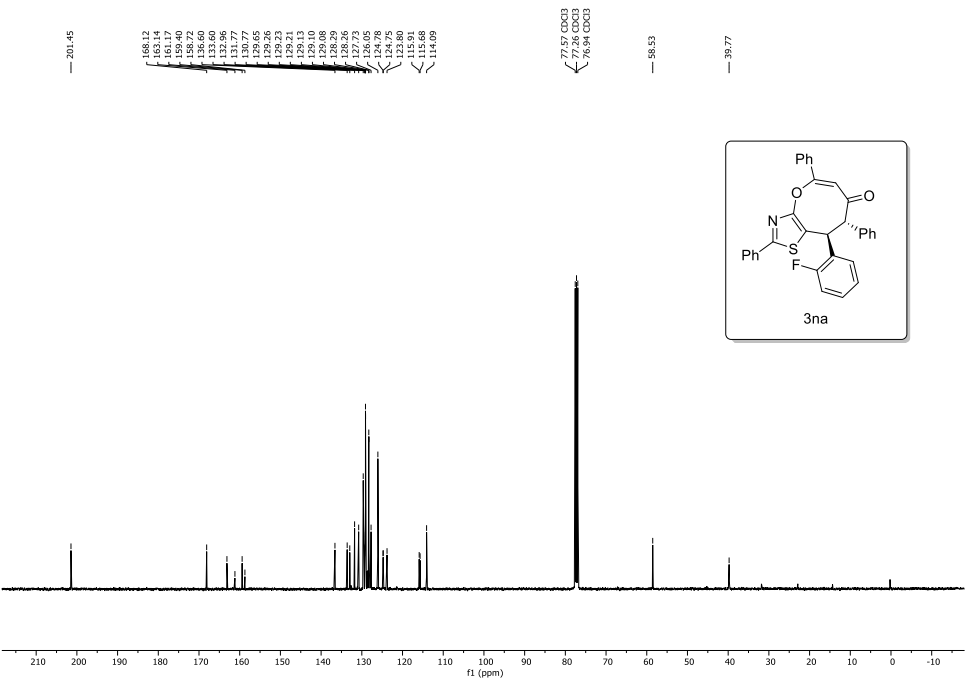
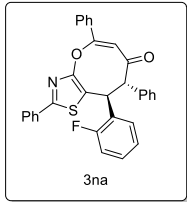
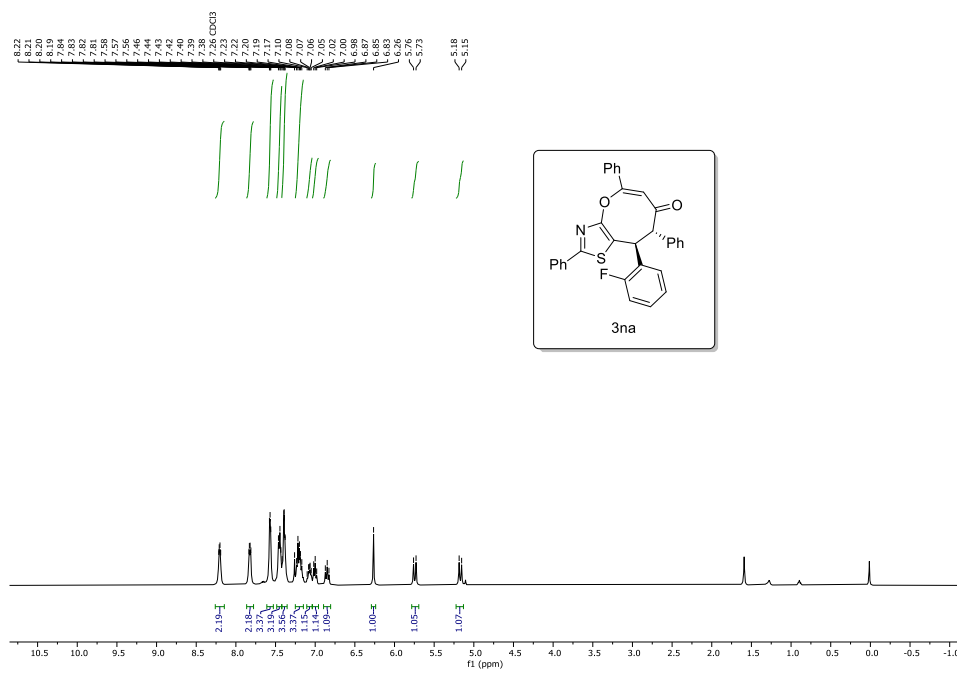
(8S,9S,Z)-2,5,8-triphenyl-9-(o-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3la)



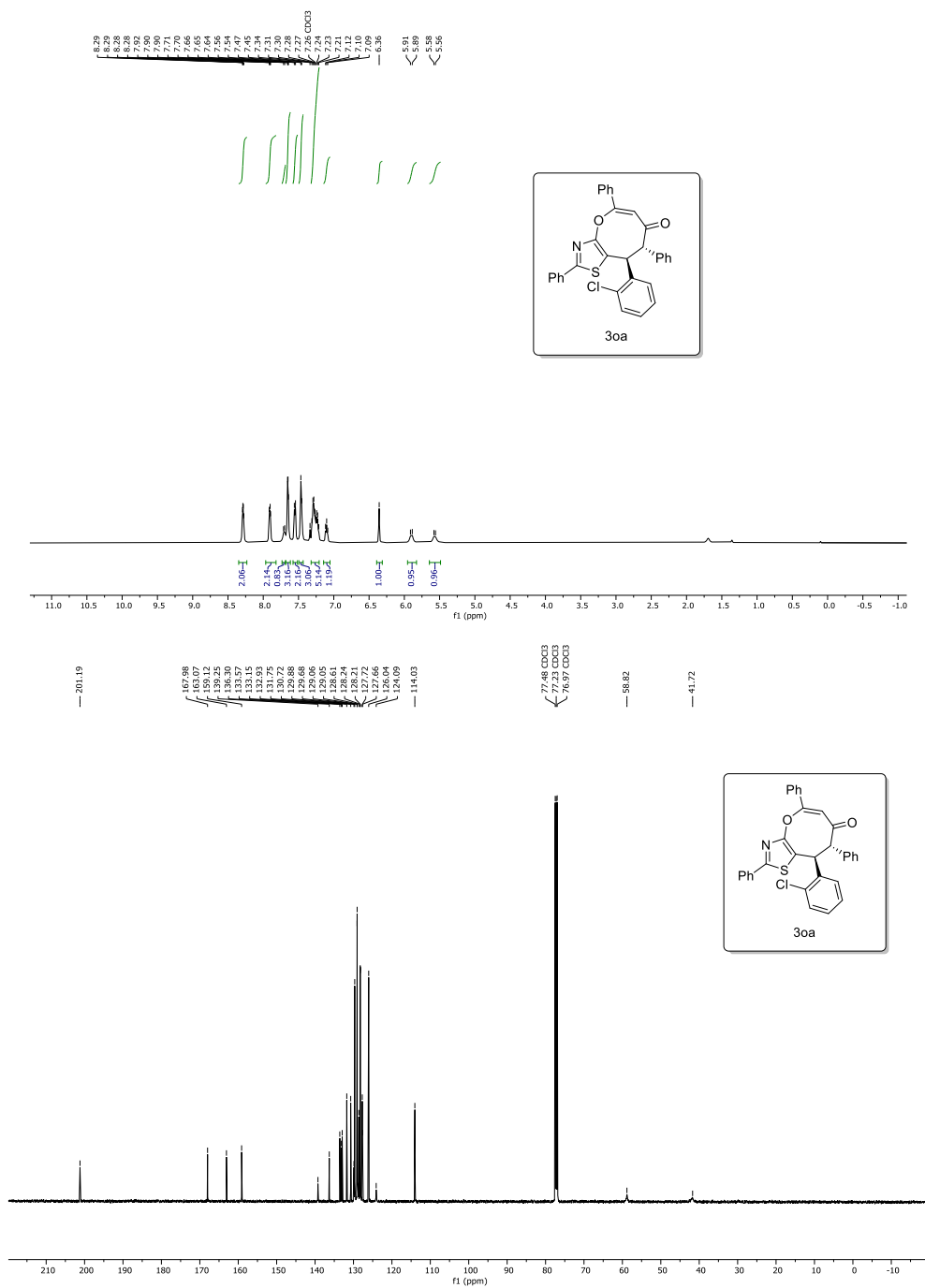
(Z)-9-(2-methoxyphenyl)-2,5,8-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ma)



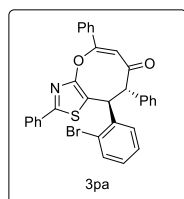
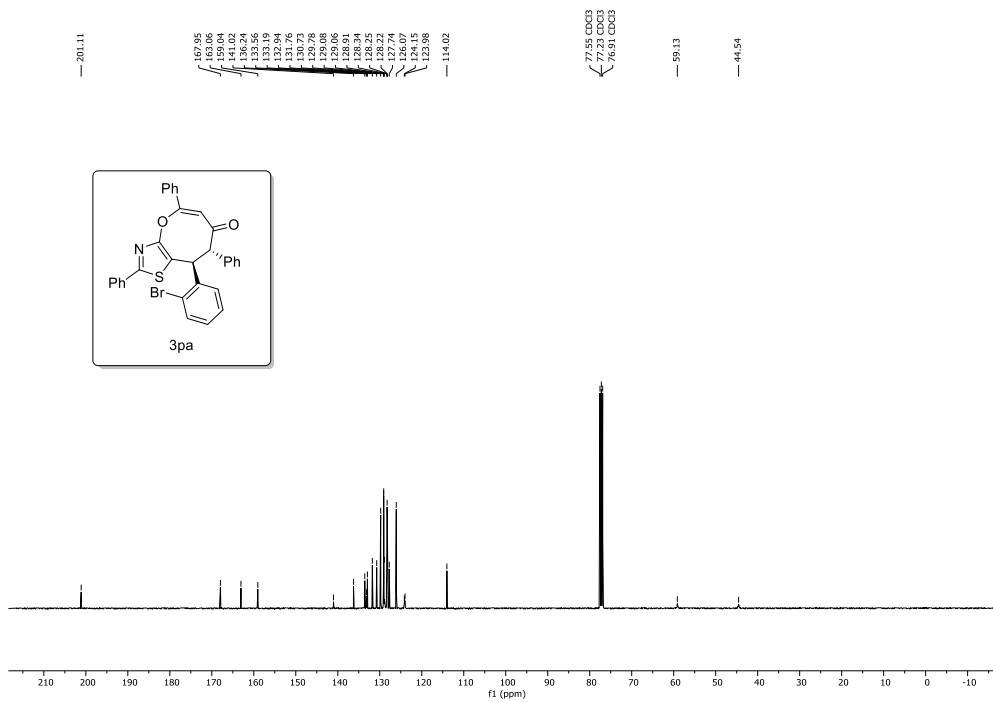
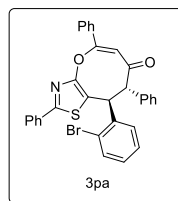
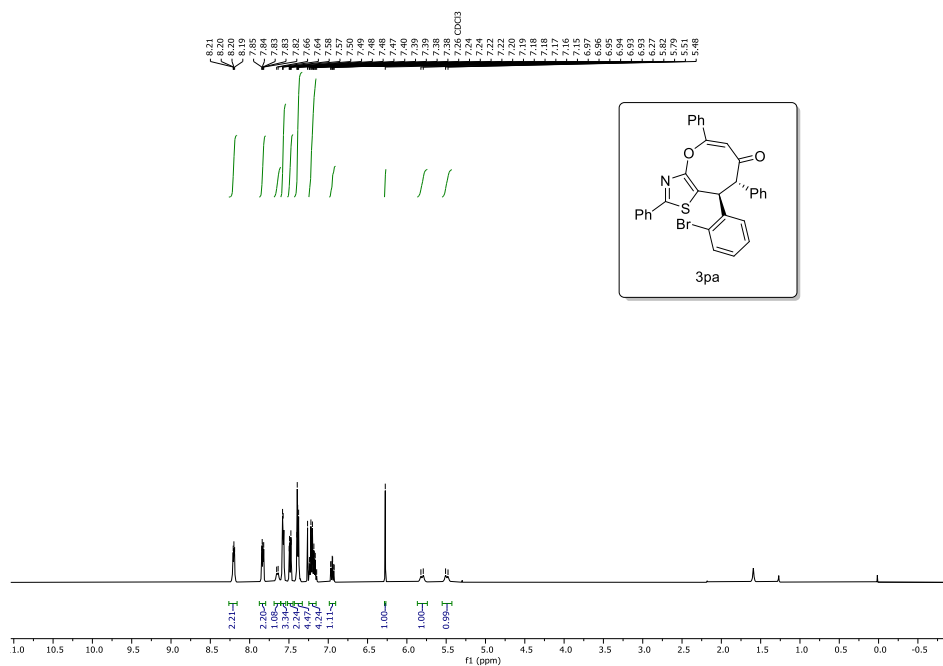
(8*S*,9*S*,*Z*)-9-(2-fluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3na)



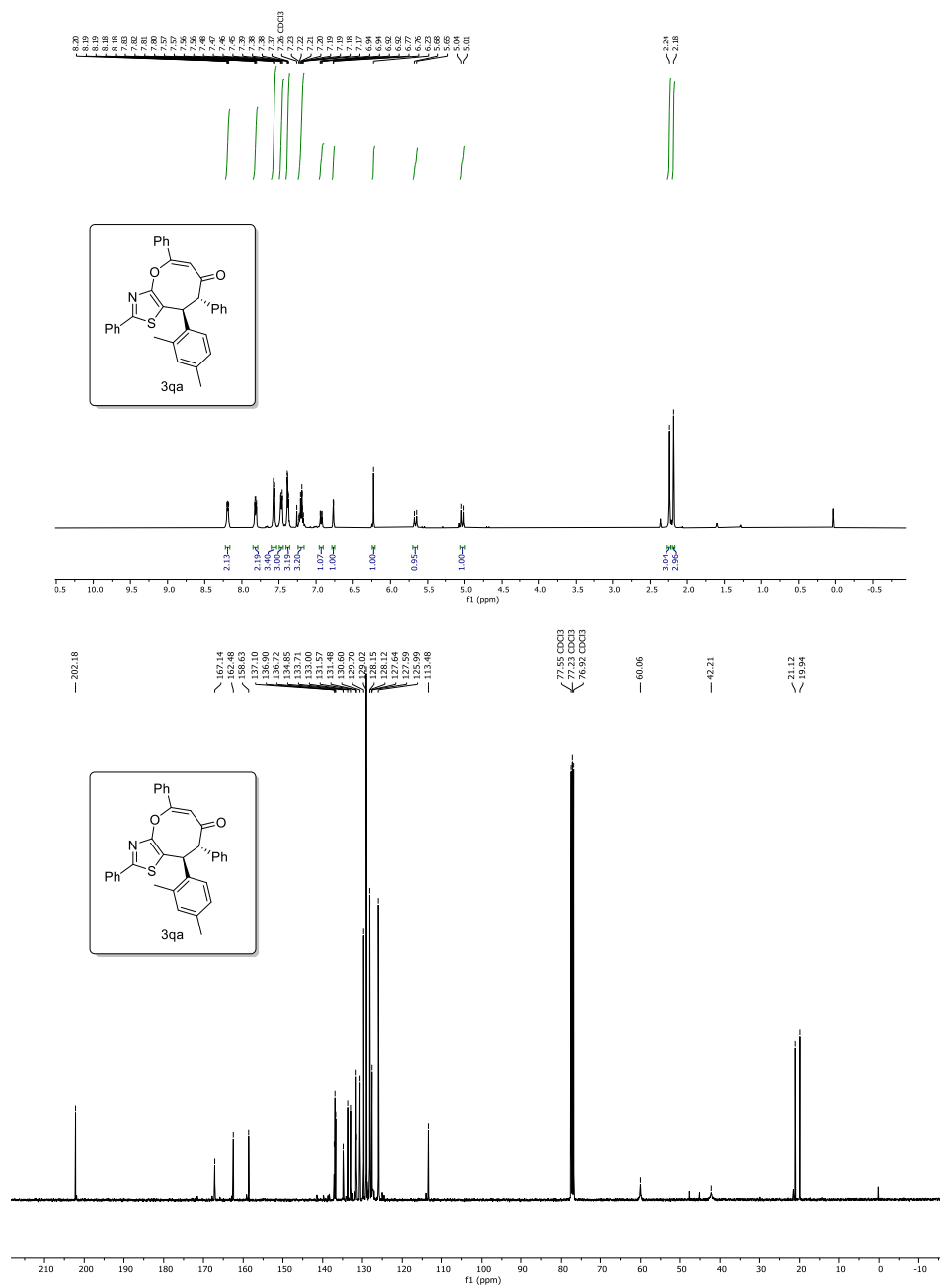
(8*S*,9*S*,*Z*)-9-(2-chlorophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3*oa*)



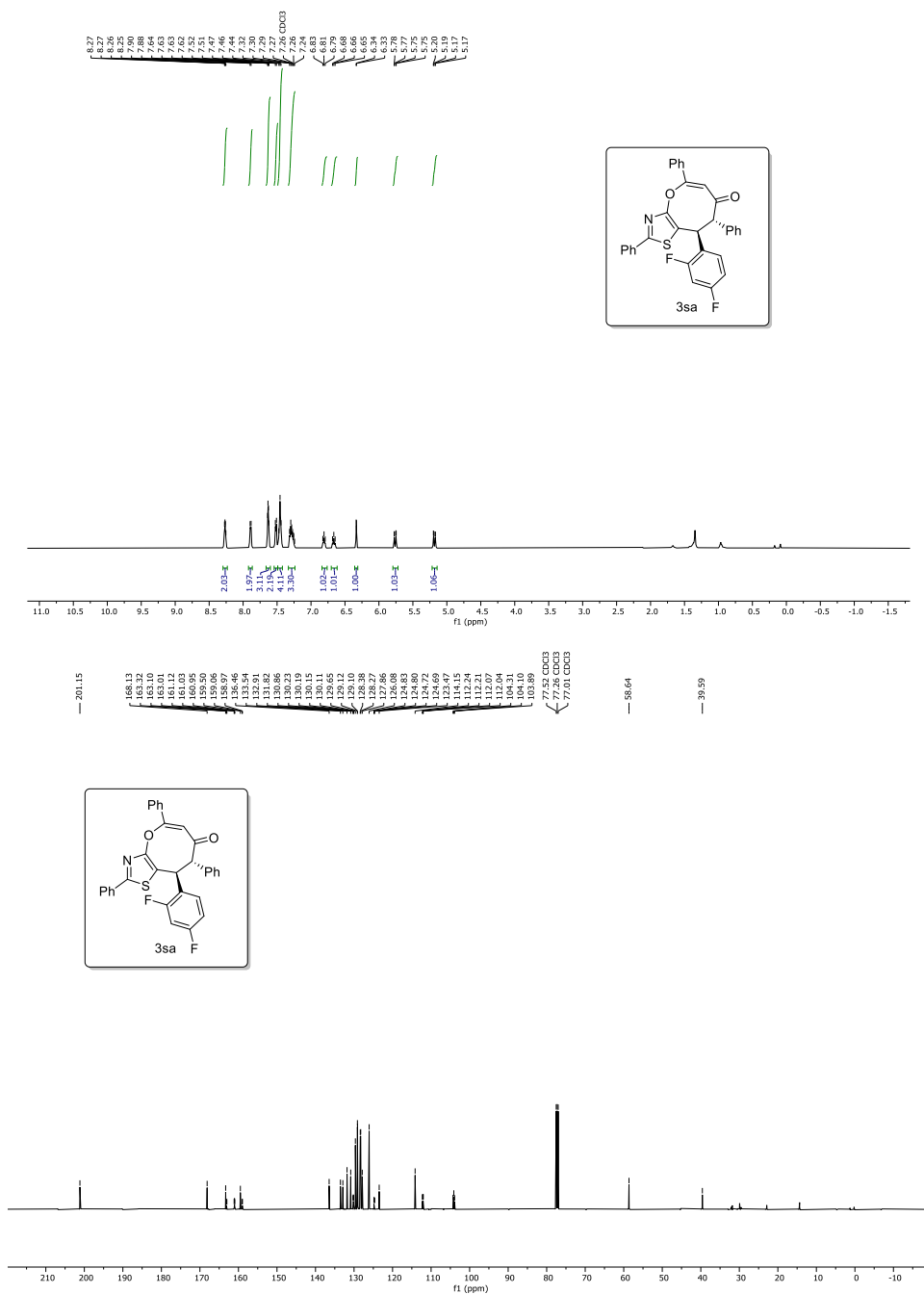
(8*S*,9*S*,*Z*)-9-(2-bromophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3pa)



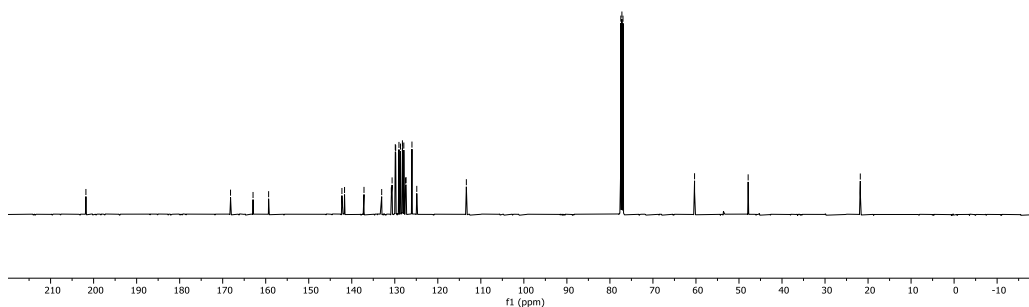
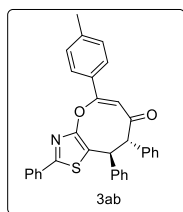
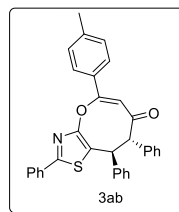
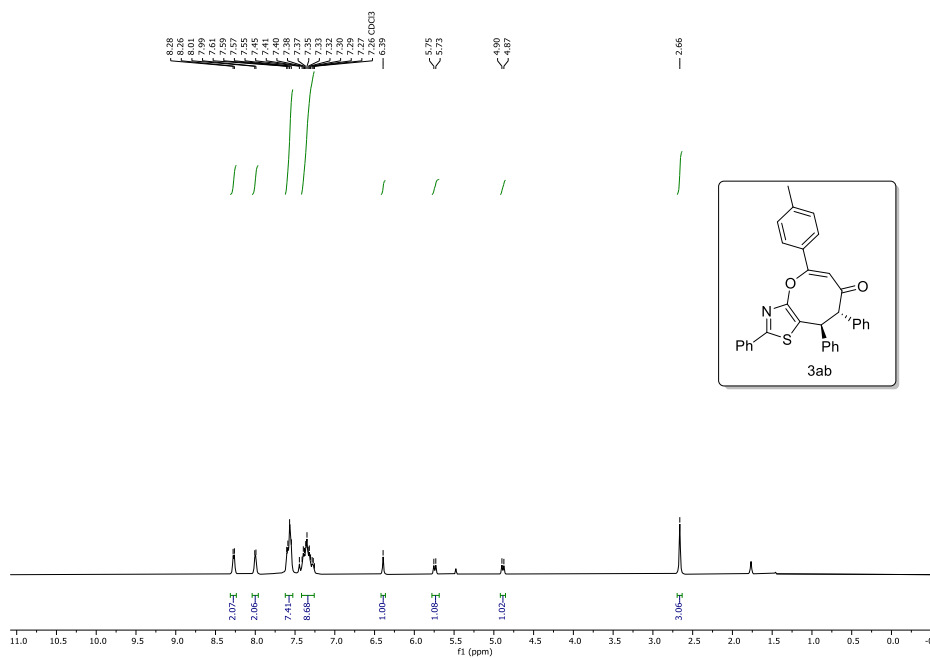
(8*S*,9*S*,*Z*)-9-(2,4-dimethylphenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3qa)



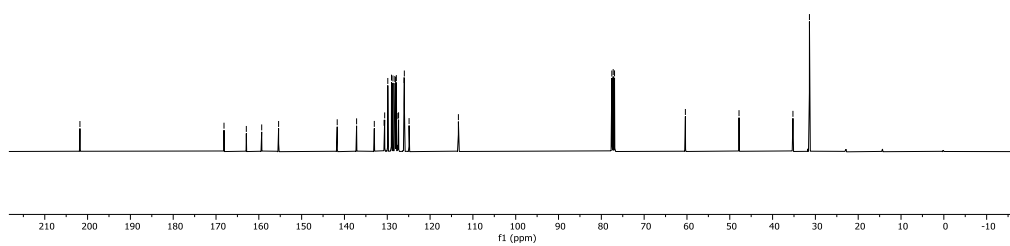
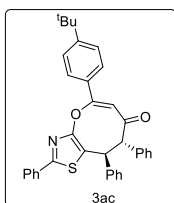
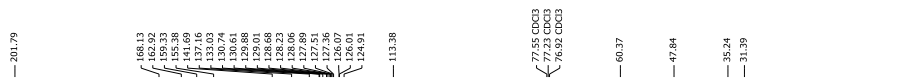
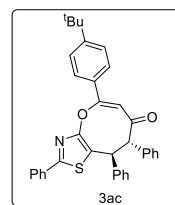
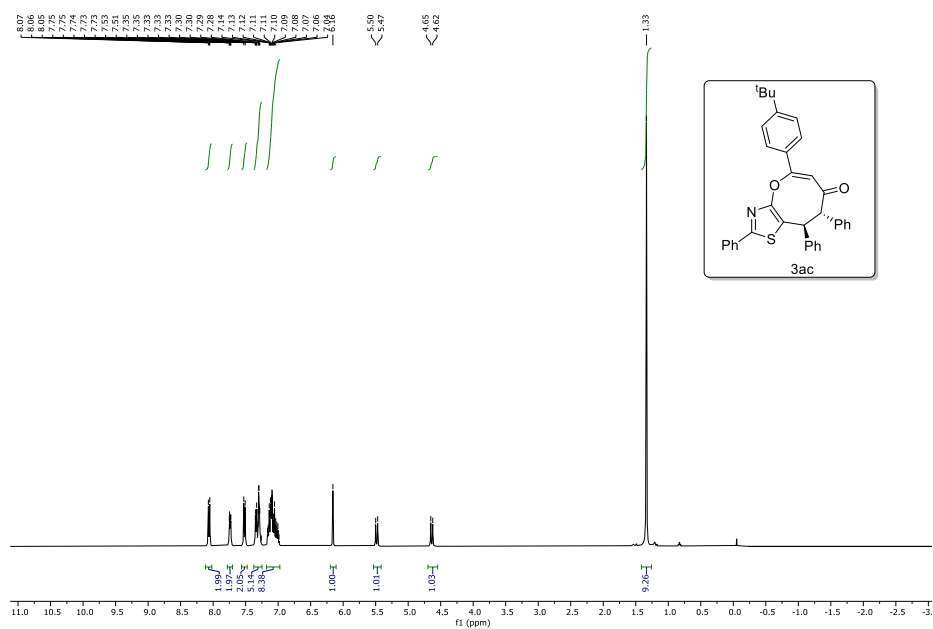
(8*S*,9*S*, *Z*)-9-(2,4-difluorophenyl)-2,5,8-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3*sa*)



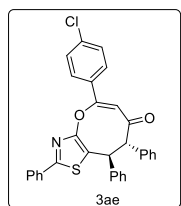
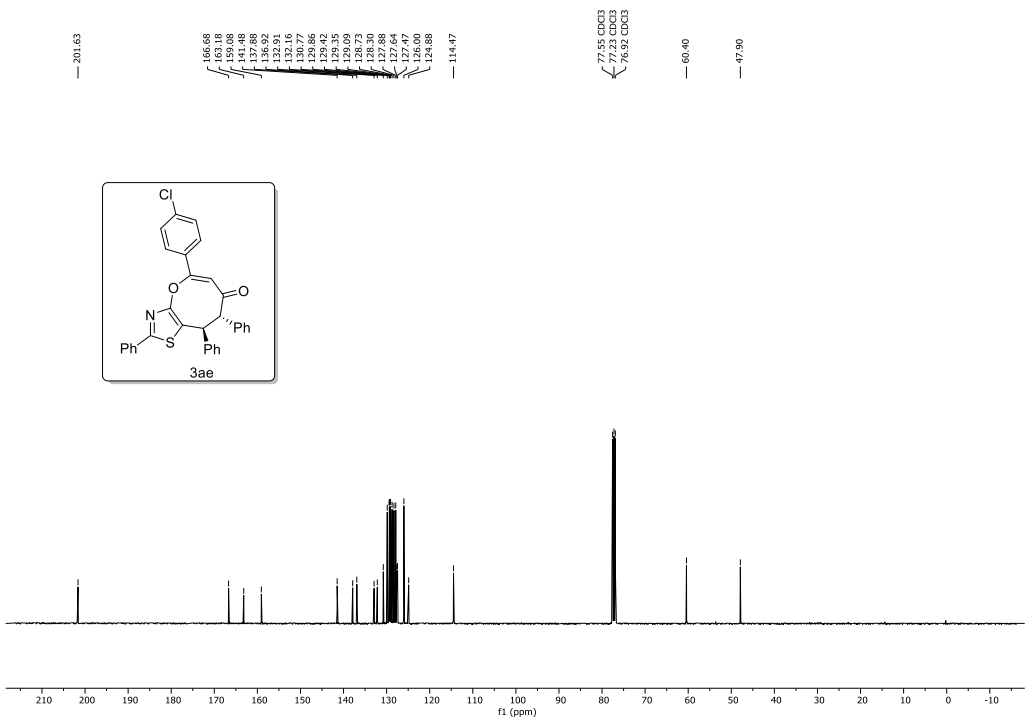
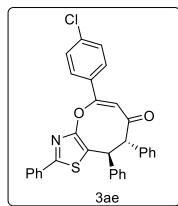
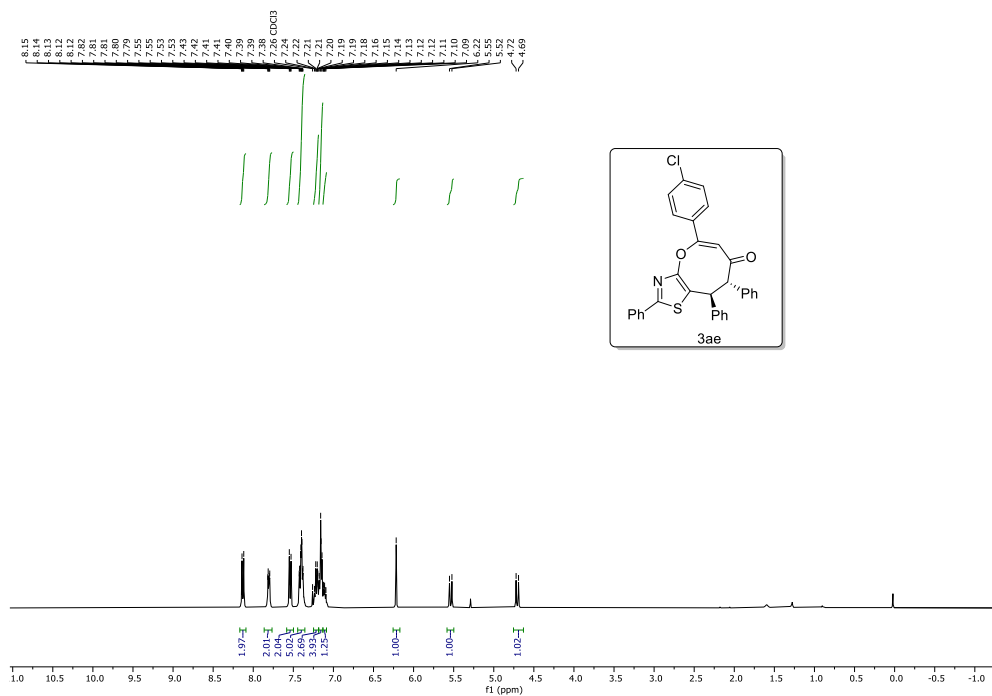
(8S,9S, Z)-2,8,9-triphenyl-5-(p-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ab)



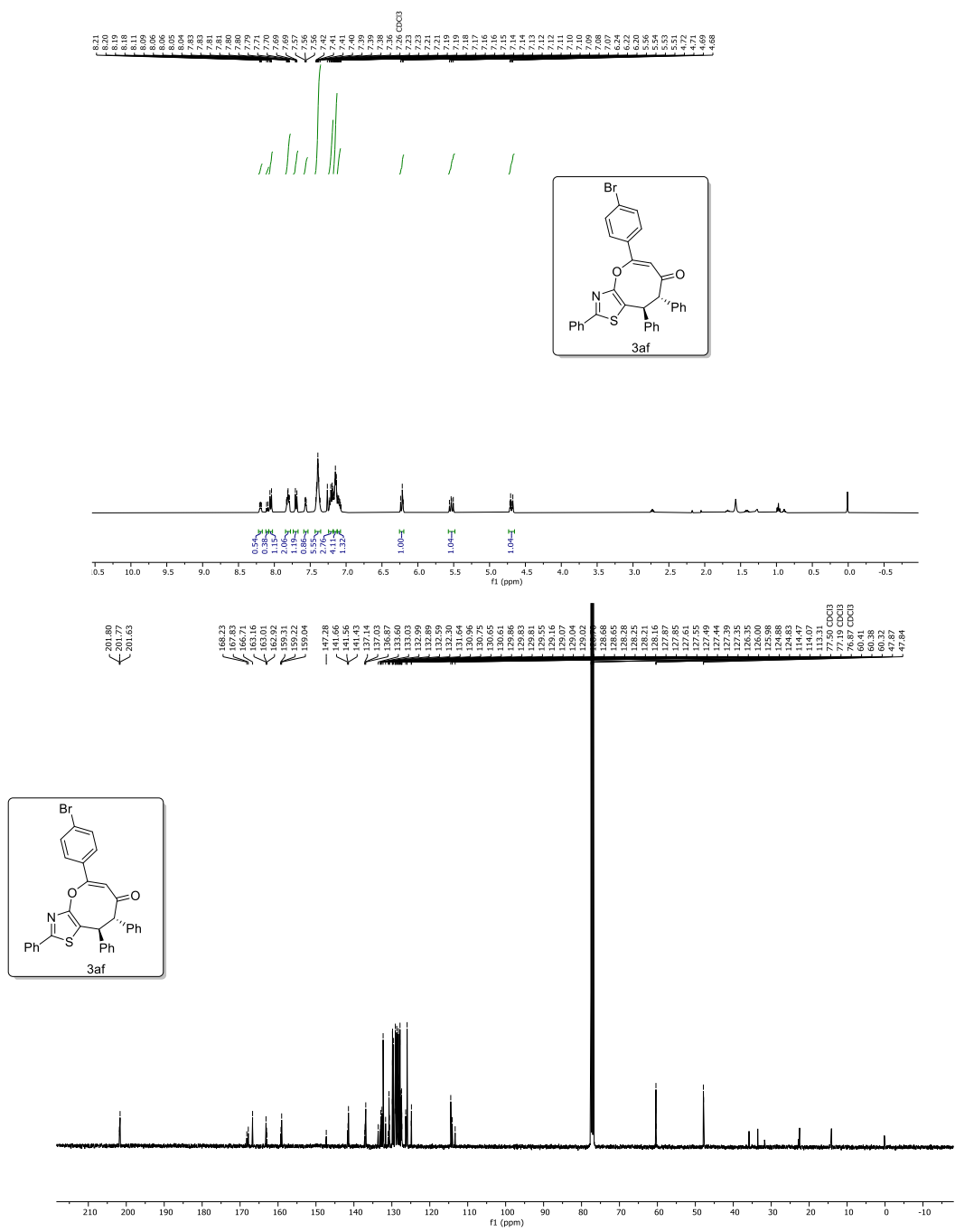
(8*S*,9*S*, *Z*)-5-(4-(*tert*-butyl)phenyl)-2,8,9-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ac)



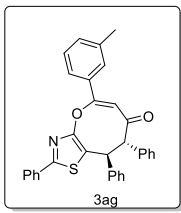
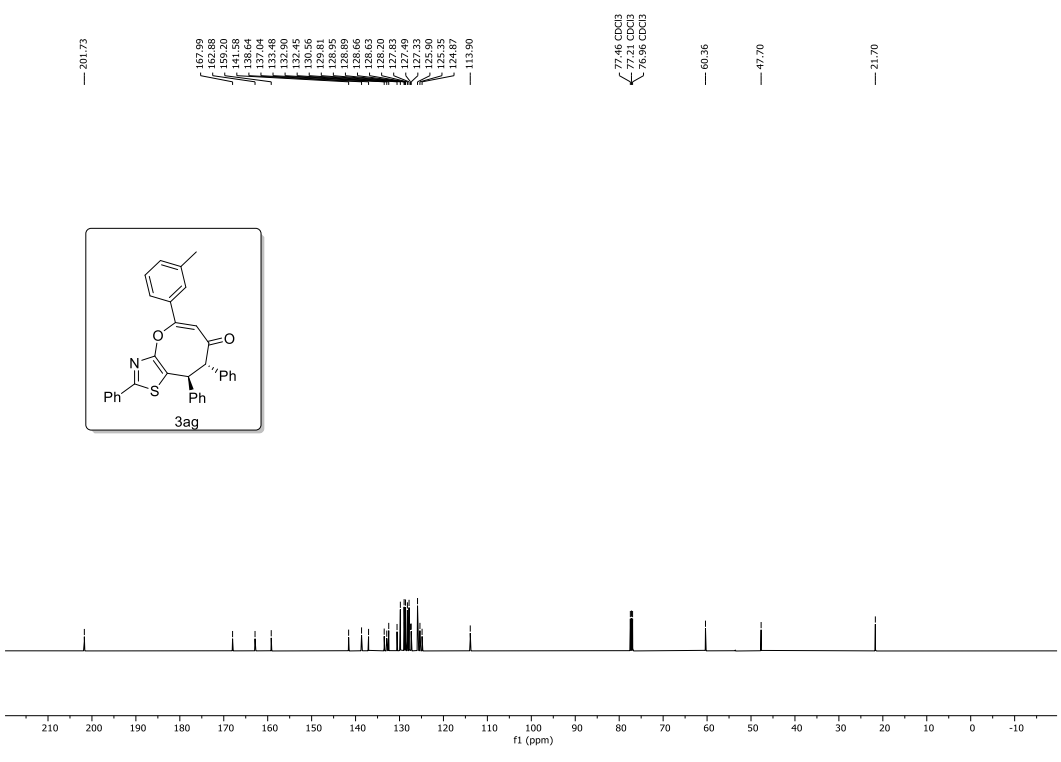
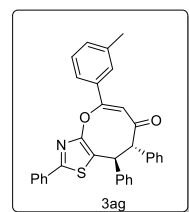
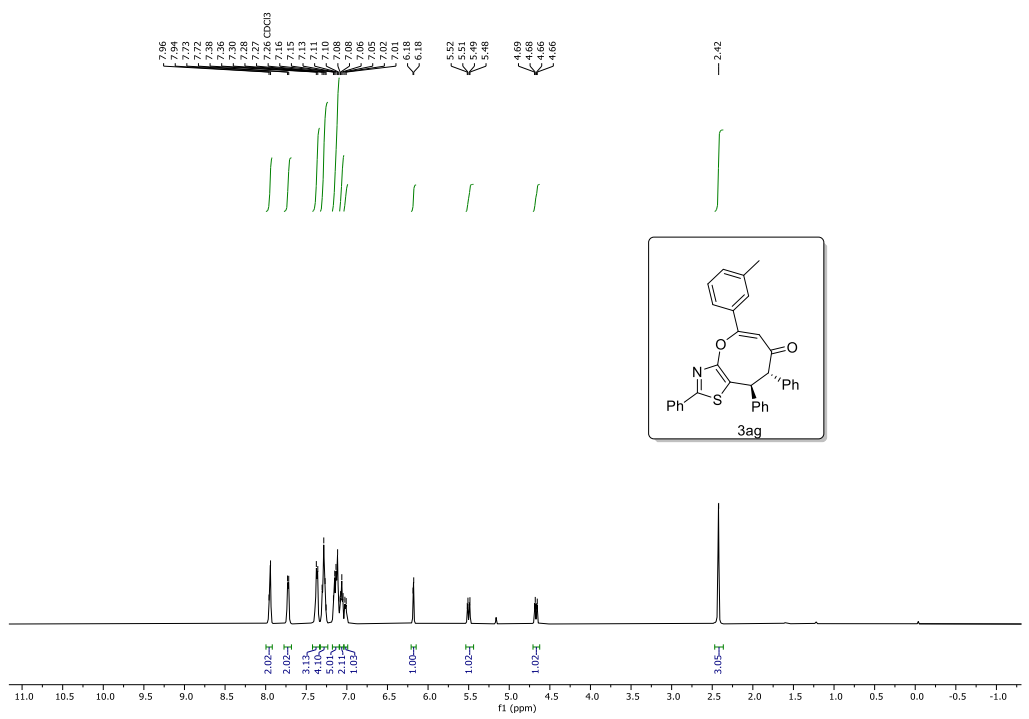
(8S,9S, Z)-5-(4-chlorophenyl)-2,8,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ae)



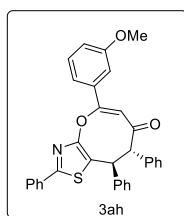
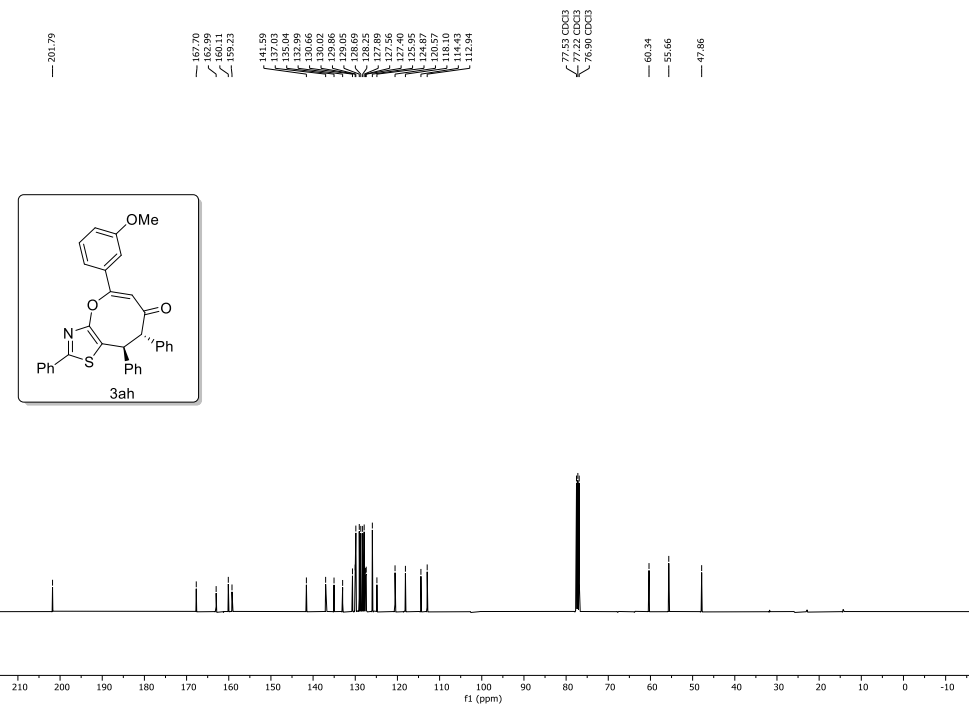
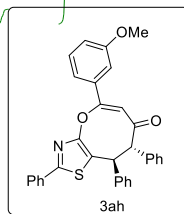
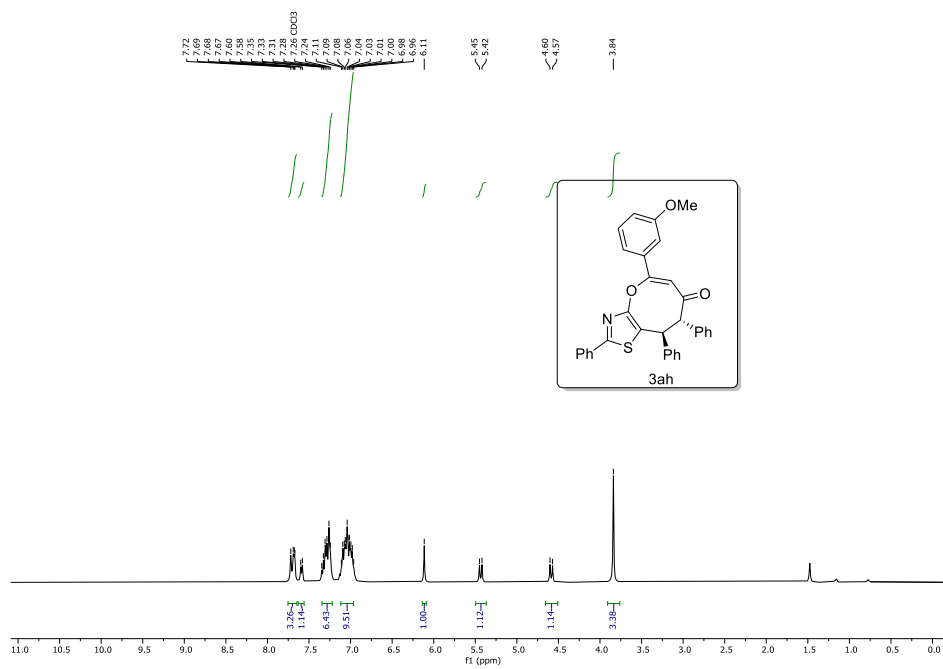
(8*S*,9*S*,*Z*)-5-(4-bromophenyl)-2,8,9-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3af)



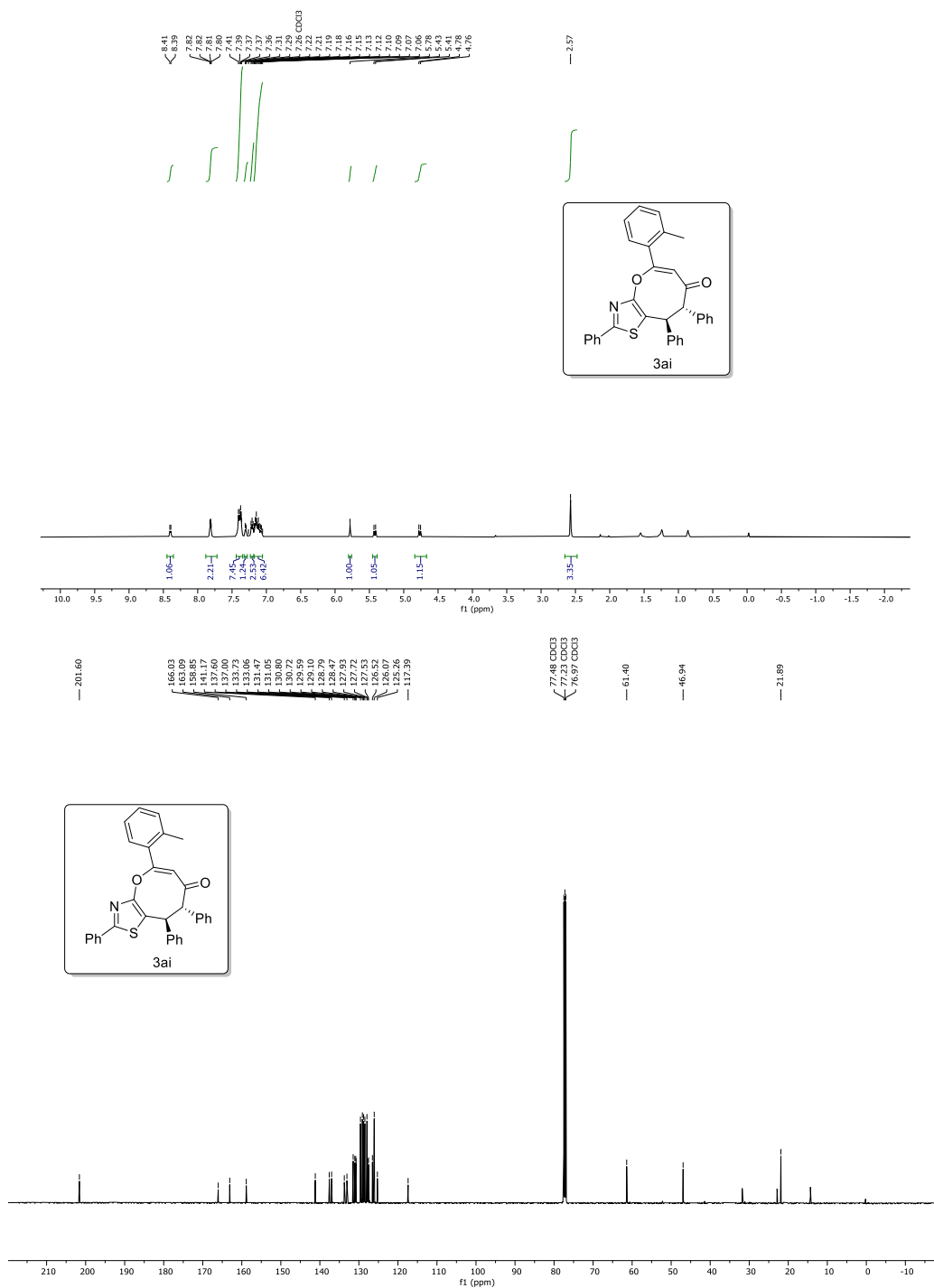
(8*S*,9*S*,*Z*)-2,8,9-triphenyl-5-(*m*-tolyl)-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ag)



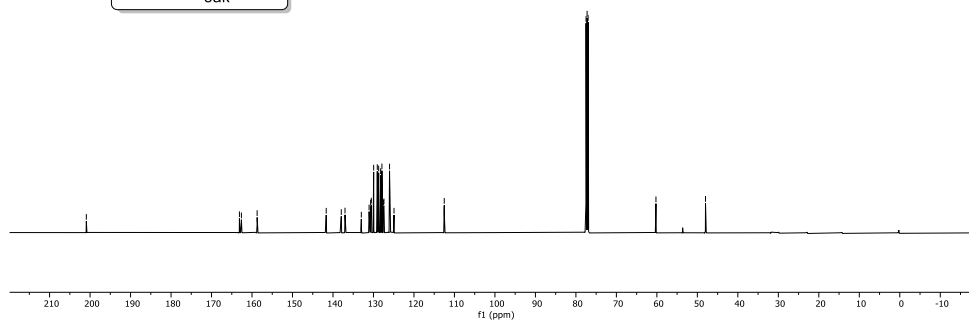
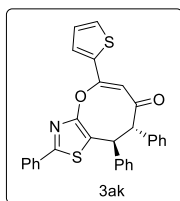
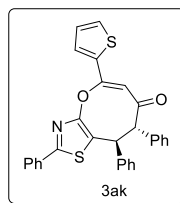
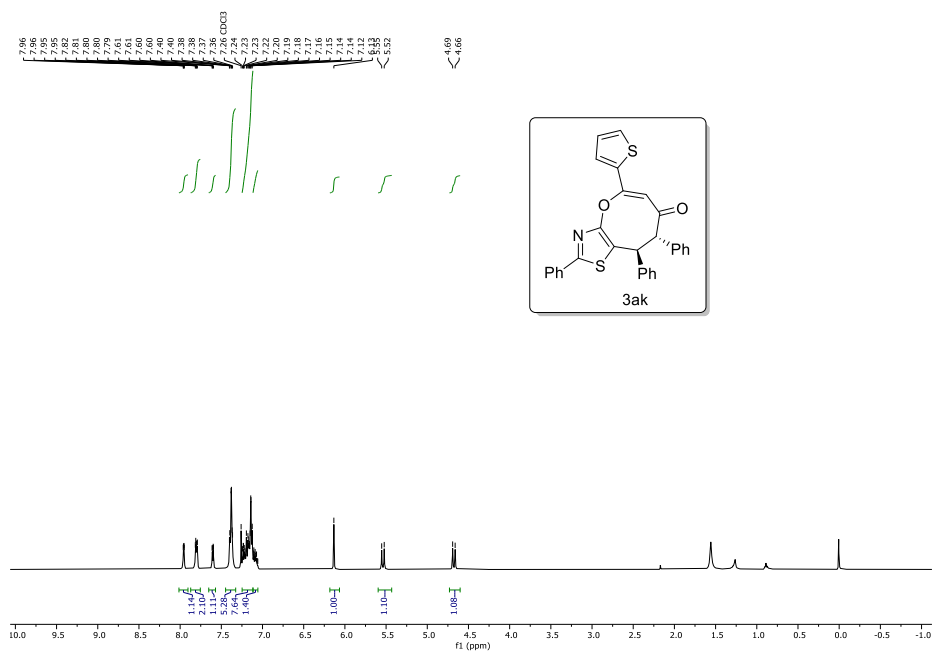
(8*S*,9*S*,*Z*)-5-(3-methoxyphenyl)-2,8,9-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ah)



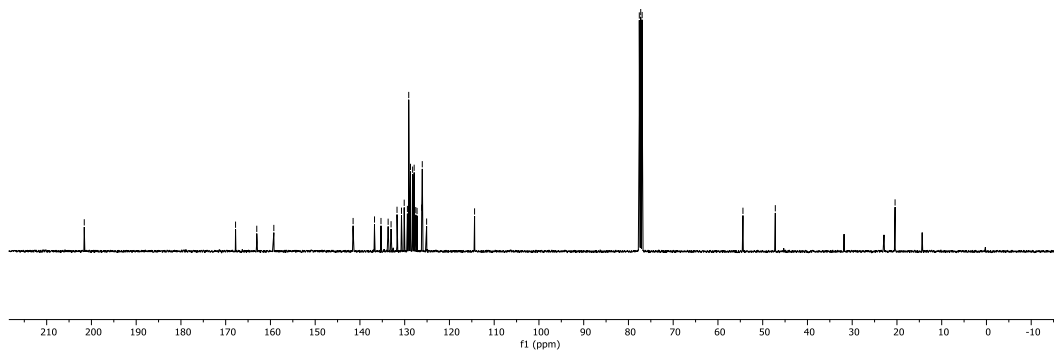
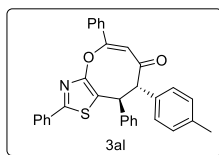
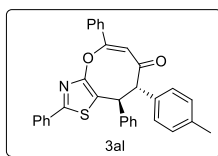
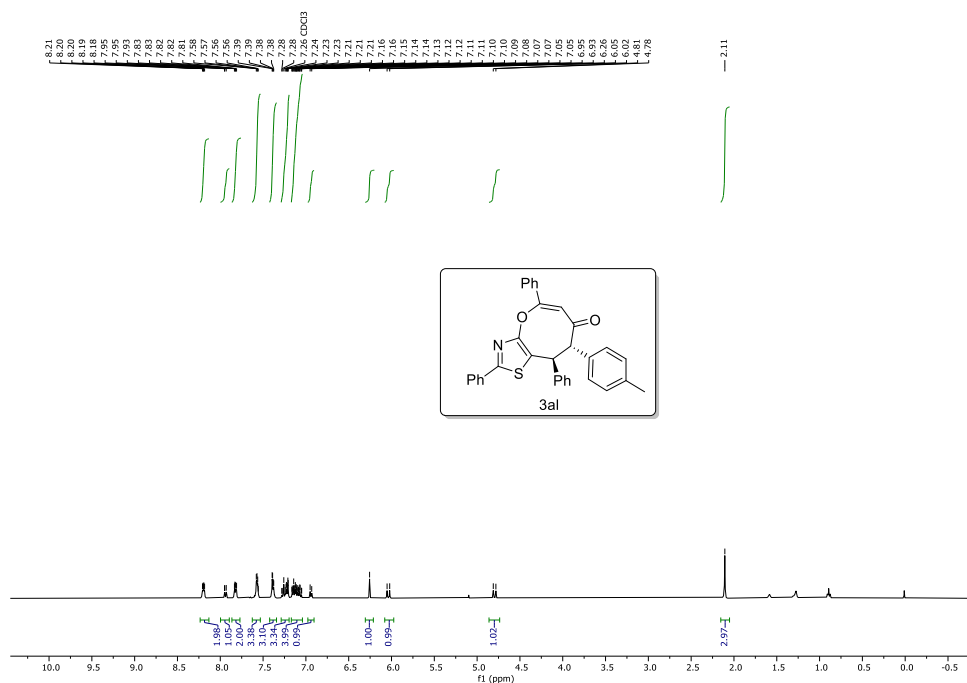
(8S,9S,Z)-2,8,9-triphenyl-5-(o-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ai)



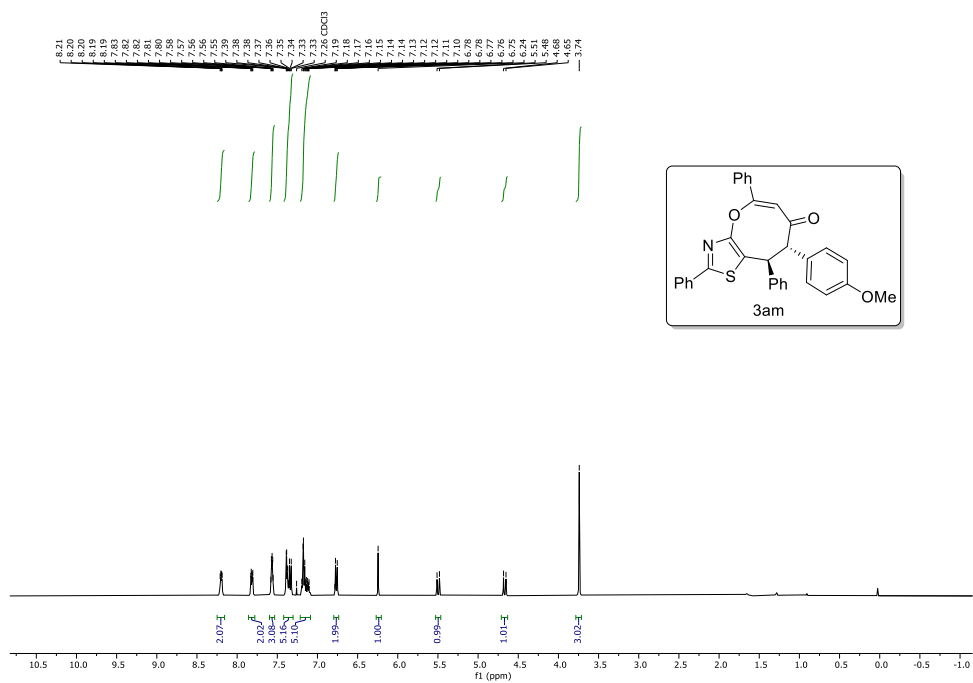
(8R,9S,Z)-2,5,9-triphenyl-8-(thiophen-2-yl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ak)



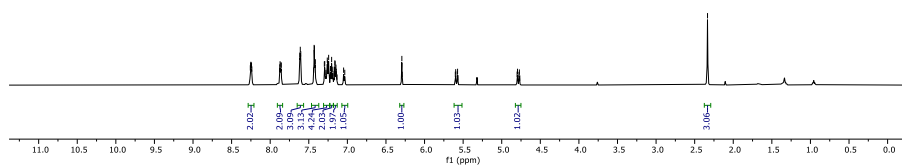
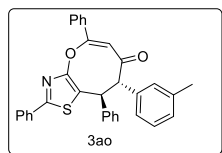
(8*S*,9*S*,*Z*)-2,5,9-triphenyl-8-(*p*-tolyl)-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3al)



(8*S*,9*S*,*Z*)-8-(4-methoxyphenyl)-2,5,9-triphenyl-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3am)



(8S,9S,Z)-2,5,9-triphenyl-8-(m-tolyl)-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ao)



201.95

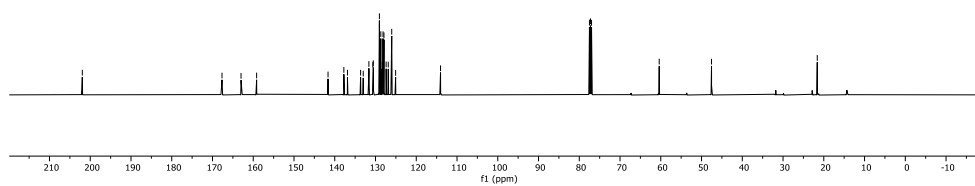
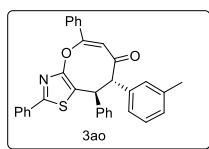
167.67
163.00
159.17
158.66
137.77
136.88
136.86
133.02
131.63
130.86
128.04
128.03
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126.02
125.07
114.04

77.24 CDCl₃
76.99 CDCl₃

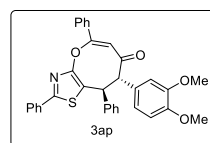
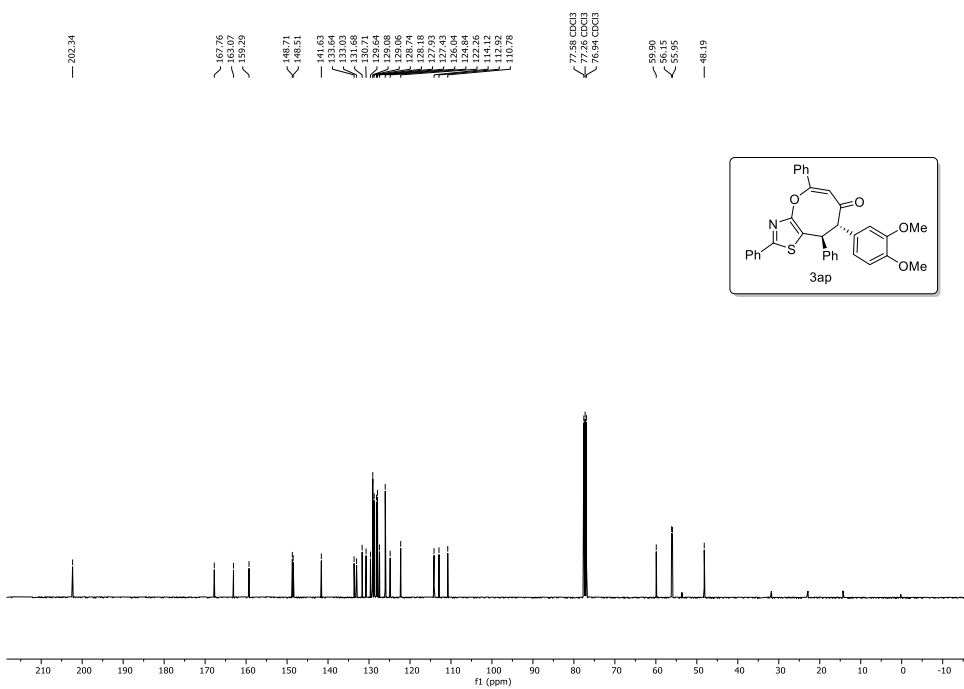
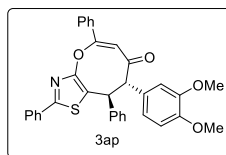
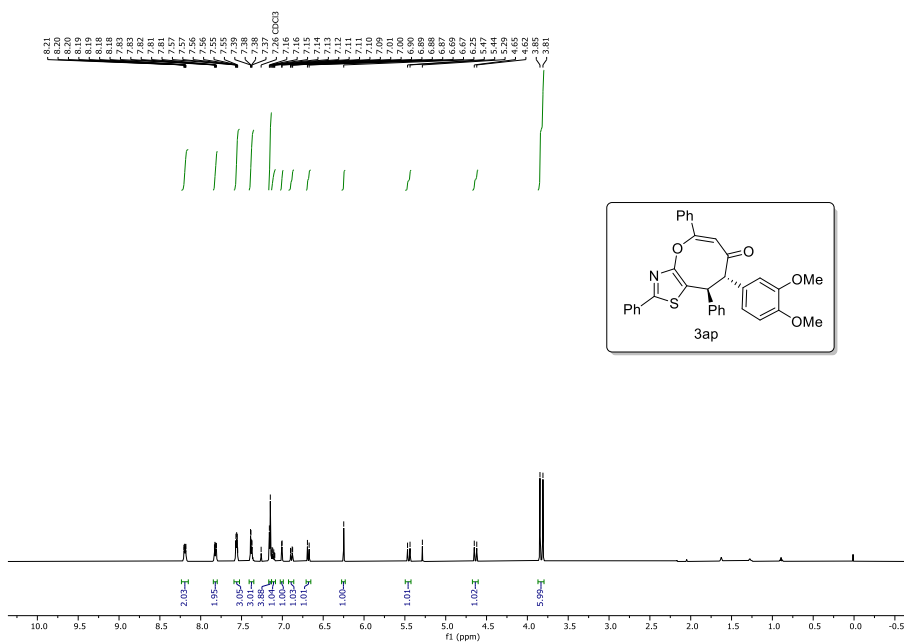
60.38

47.55

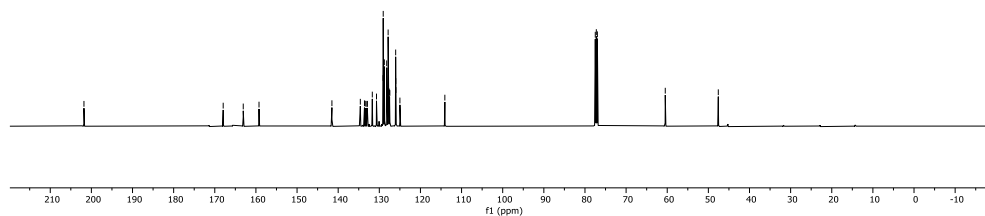
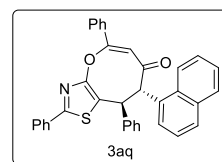
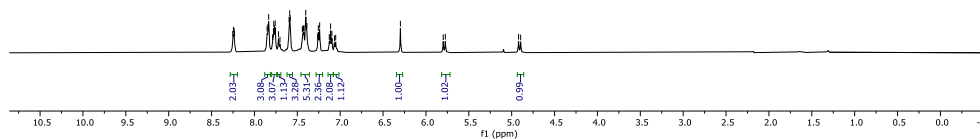
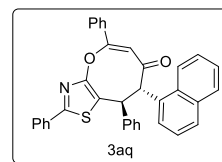
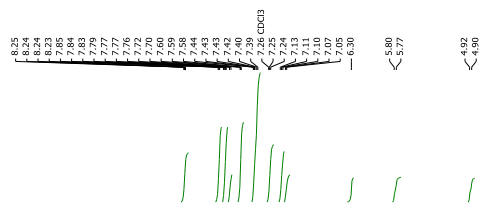
21.60



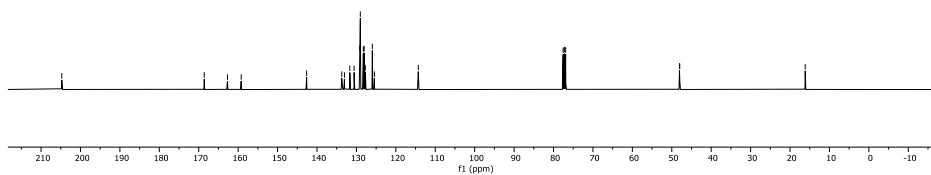
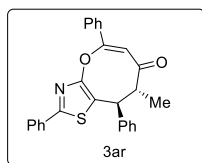
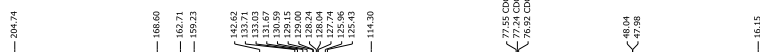
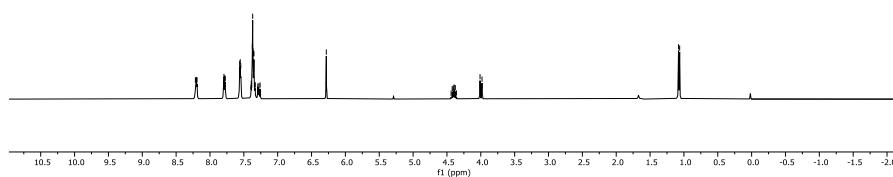
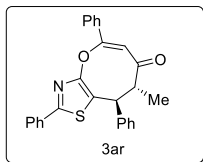
(8*S*,9*S*,*Z*)-2,5,9-triphenyl-8-(*o*-tolyl)-8,9-dihydro-7*H*-oxocino[2,3-*d*]thiazol-7-one (3ap)



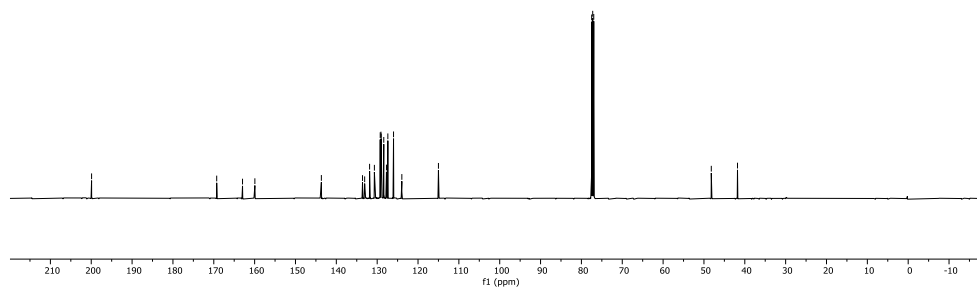
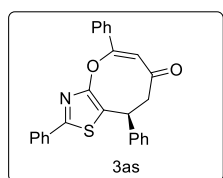
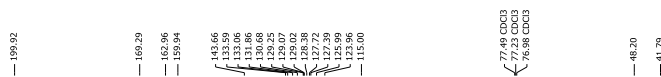
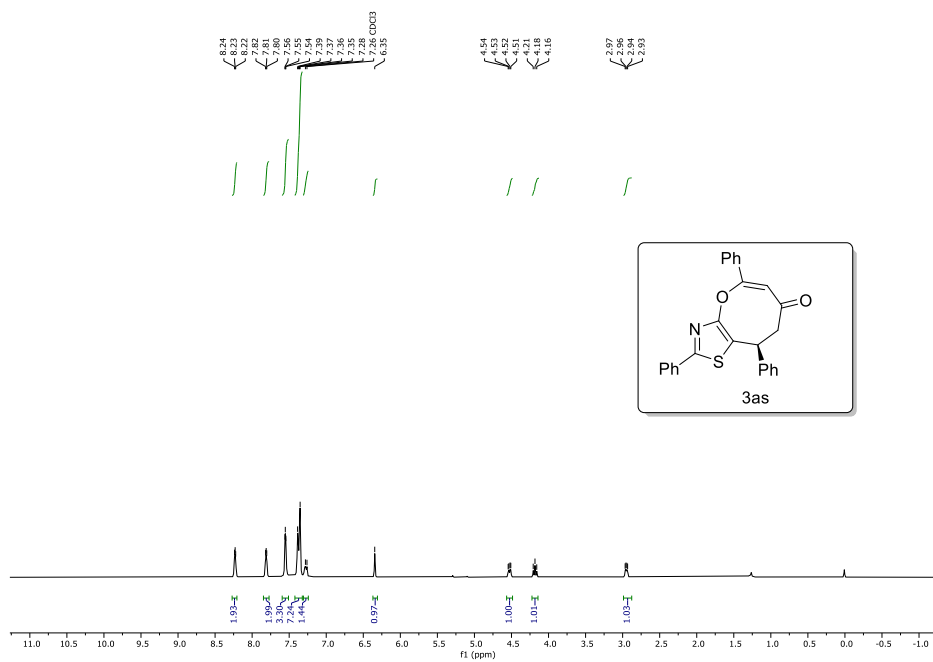
(8S,9S,Z)-8-(naphthalen-1-yl)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3aq)



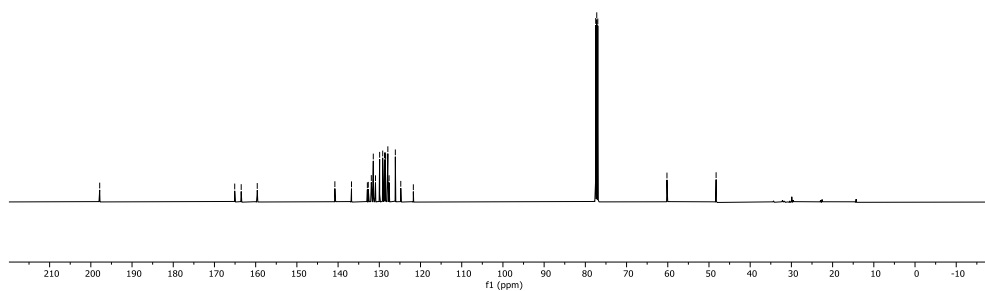
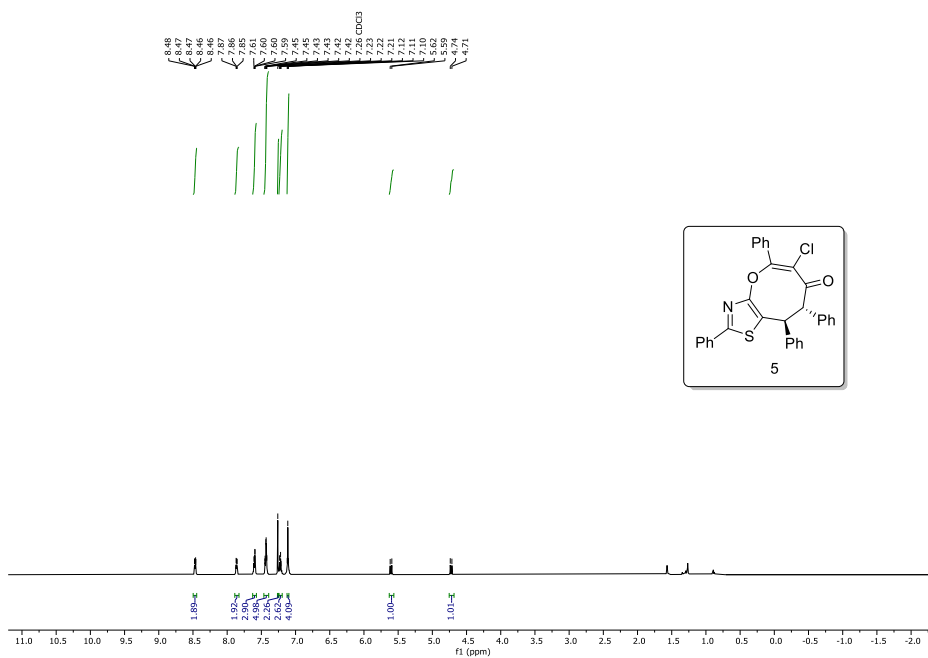
(8R,9S,Z)-8-methyl-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3ar)



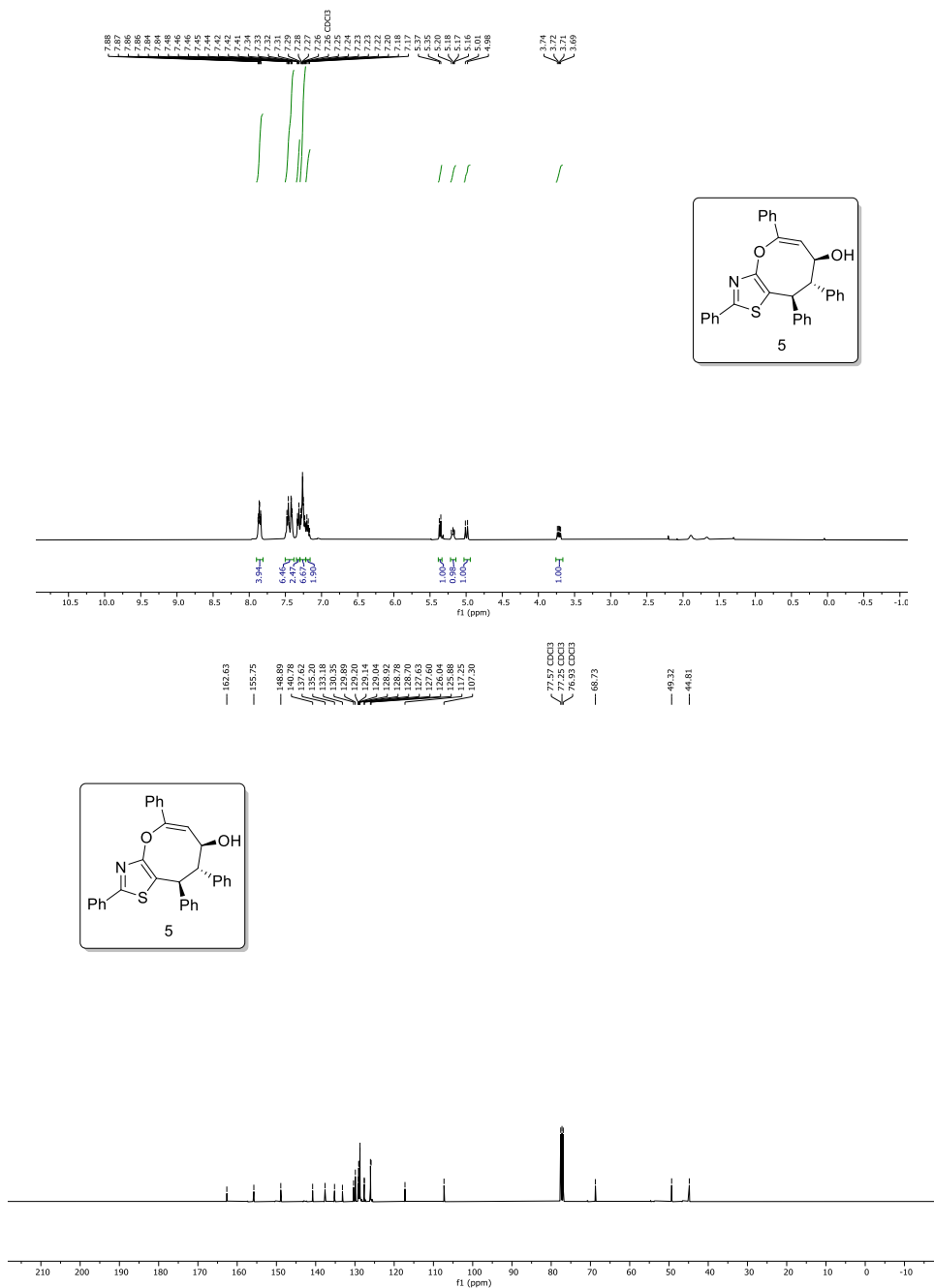
(S,Z)-2,5,9-triphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (3as)



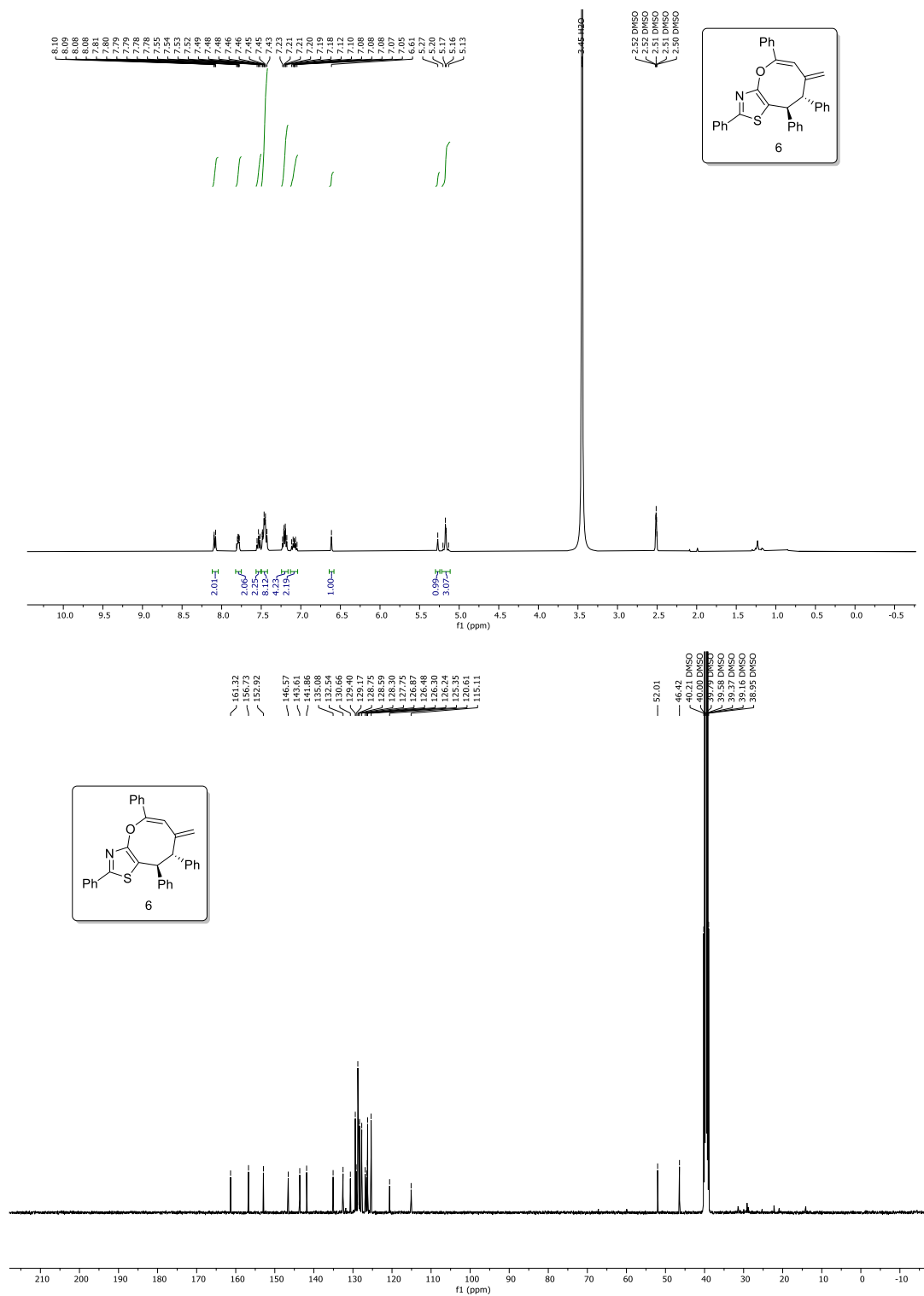
(8S,9S,E)-6-chloro-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-one (4)



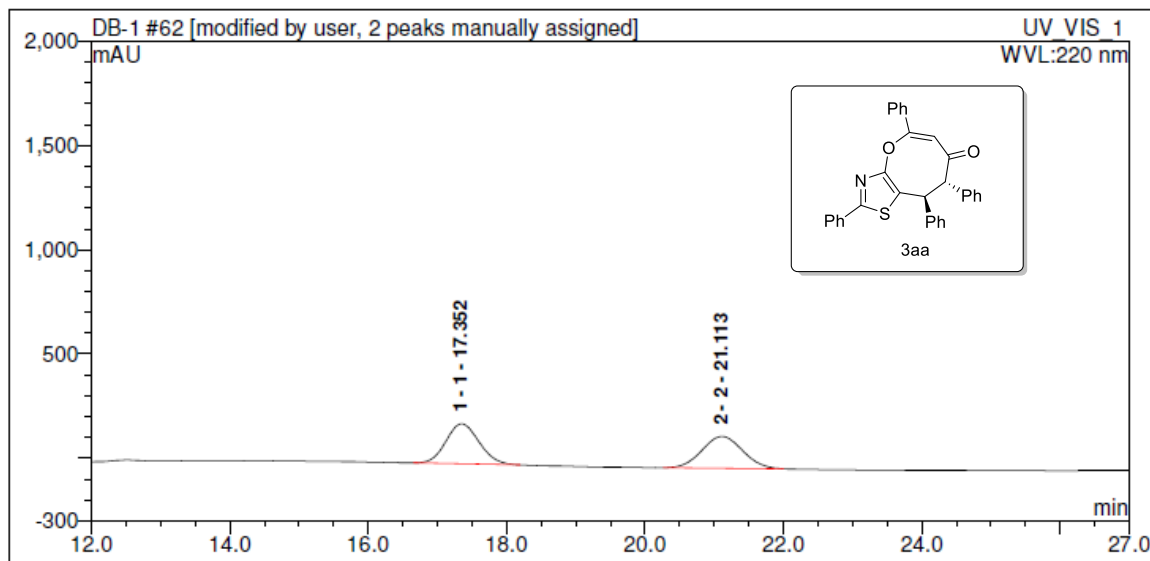
(7S,8S,9S,Z)-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazol-7-ol (5)



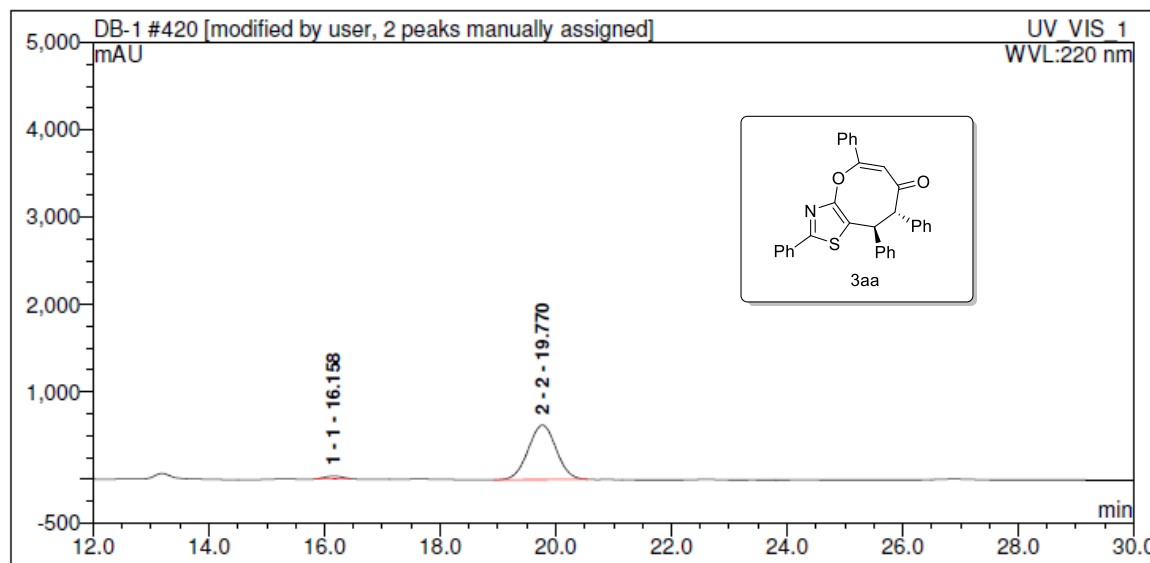
(8R,9S,Z)-7-methylene-2,5,8,9-tetraphenyl-8,9-dihydro-7H-oxocino[2,3-d]thiazole (6)



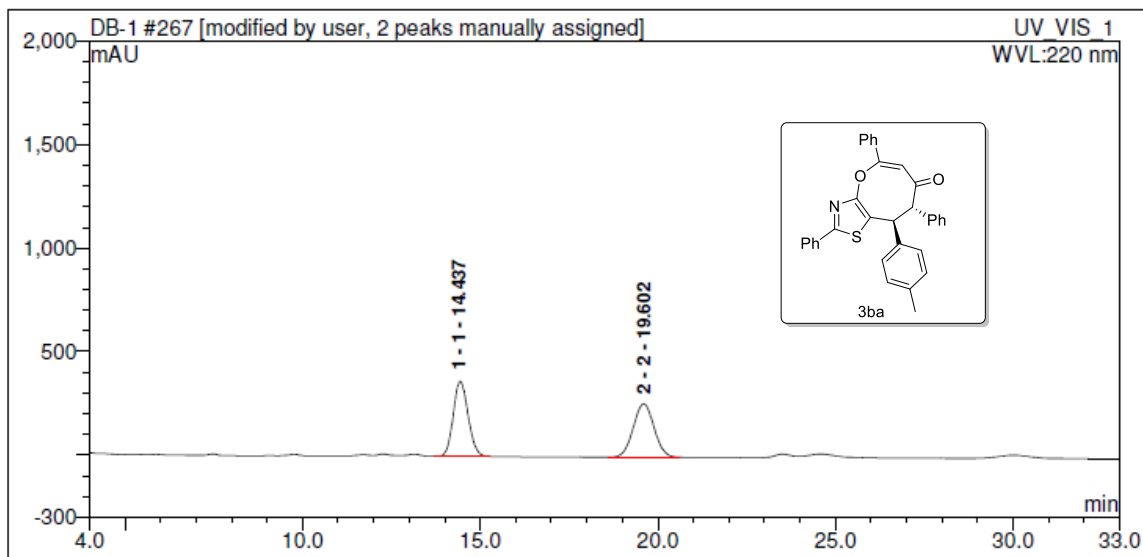
11. HPLC chromatogram:



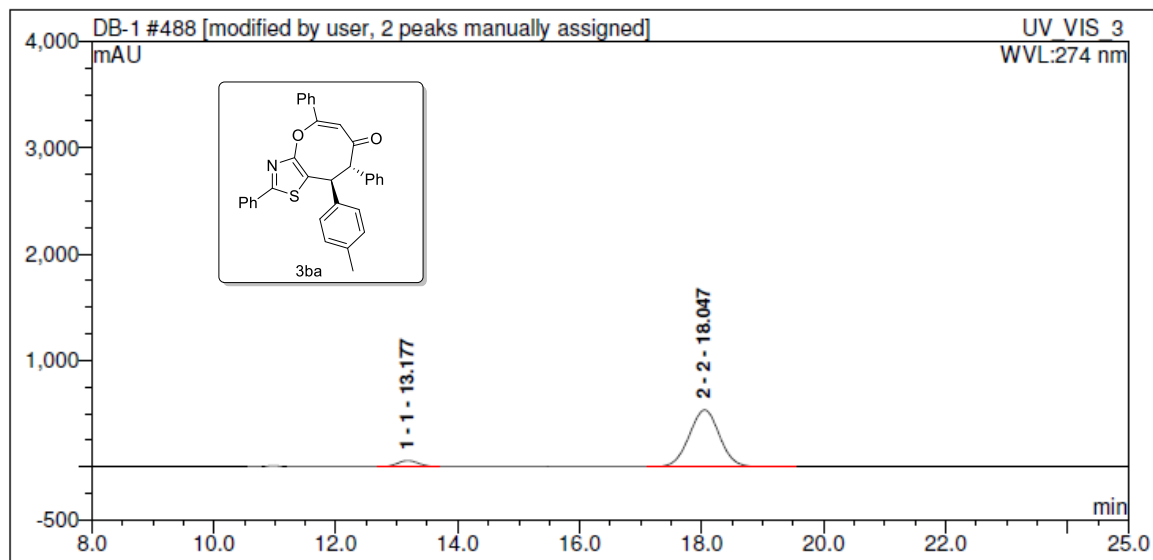
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.35166667	106.4364	50.60708692	191.7717	n.a.
2	2	21.11333333	103.8828	49.39291308	152.5382	n.a.



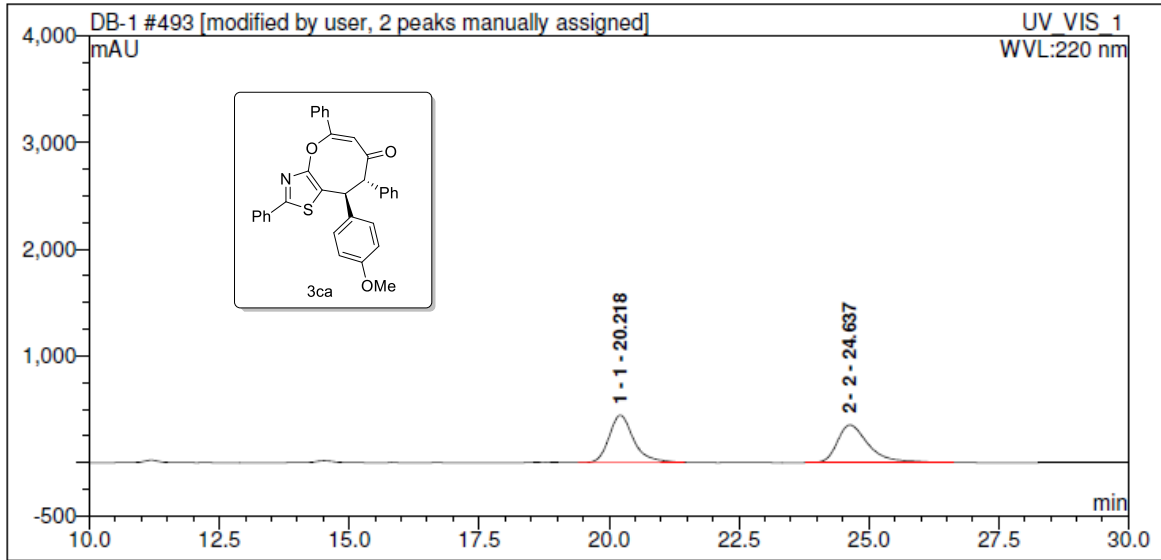
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.15833333	10.11327	2.817583151	30.42845	n.a.
2	2	19.77	348.8209	97.18241685	622.4742	n.a.



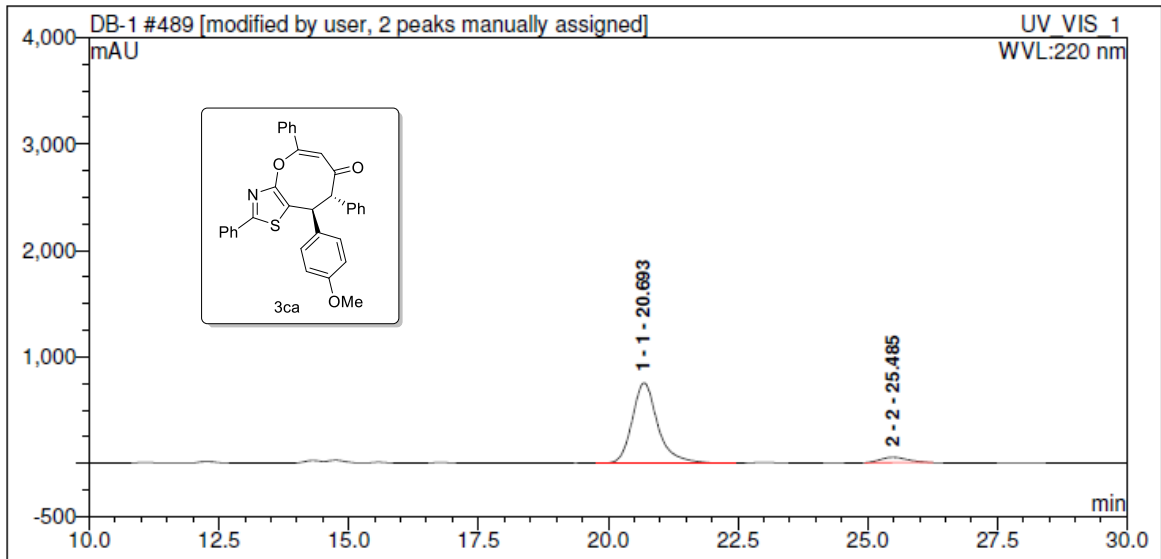
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.4366667	176.1525	50.20674305	362.8765	n.a.
2	2	19.6016667	174.7017	49.79325695	257.8816	n.a.



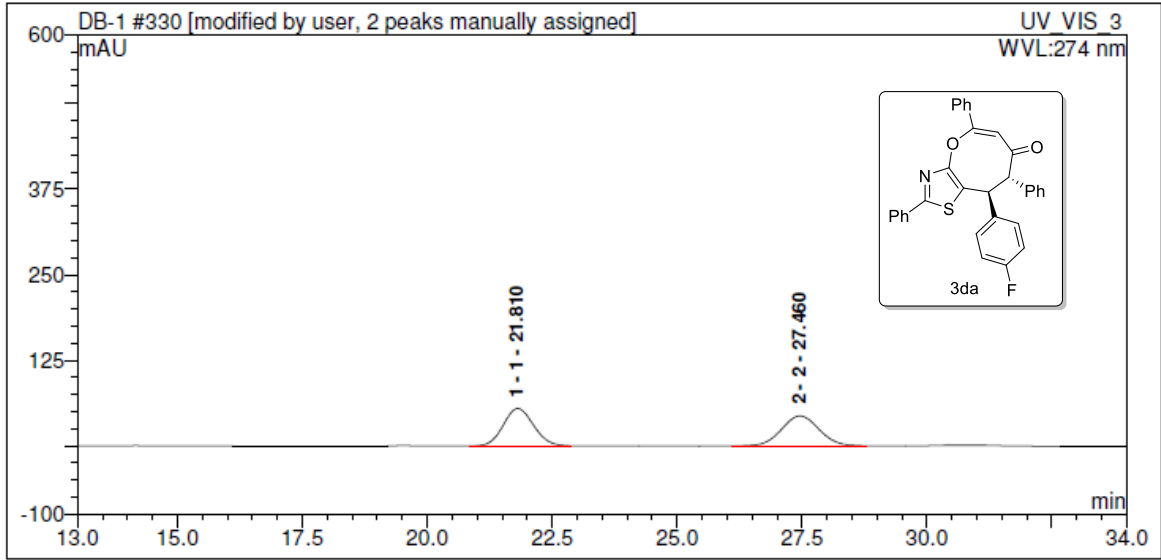
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.1766667	22.78326	6.913494427	57.57419	n.a.
2	2	18.0466667	306.7644	93.08650557	532.7118	n.a.



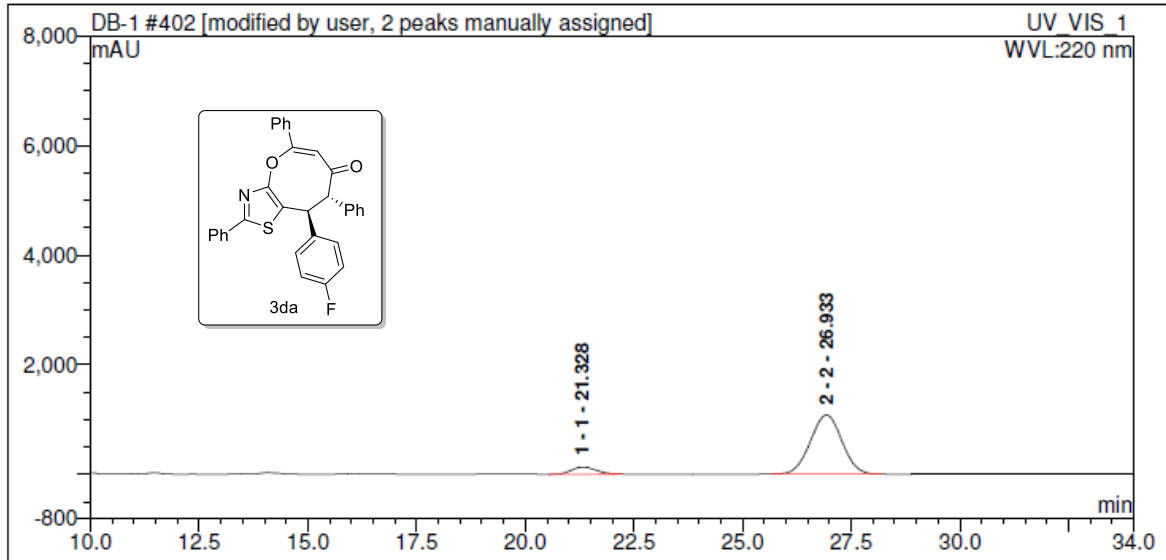
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.21833333	242.6664	49.63613199	443.0755	n.a.
2	2	24.63666667	246.2242	50.36386801	351.6315	n.a.



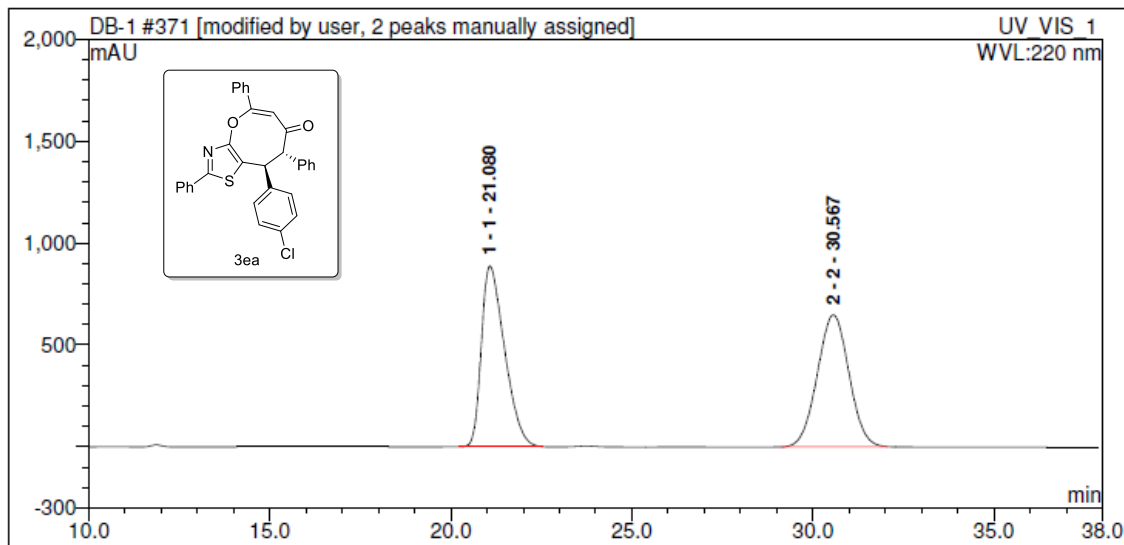
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.69333333	429.1134	93.44591037	752.491	n.a.
2	2	25.485	30.09707	6.554089627	49.77677	n.a.



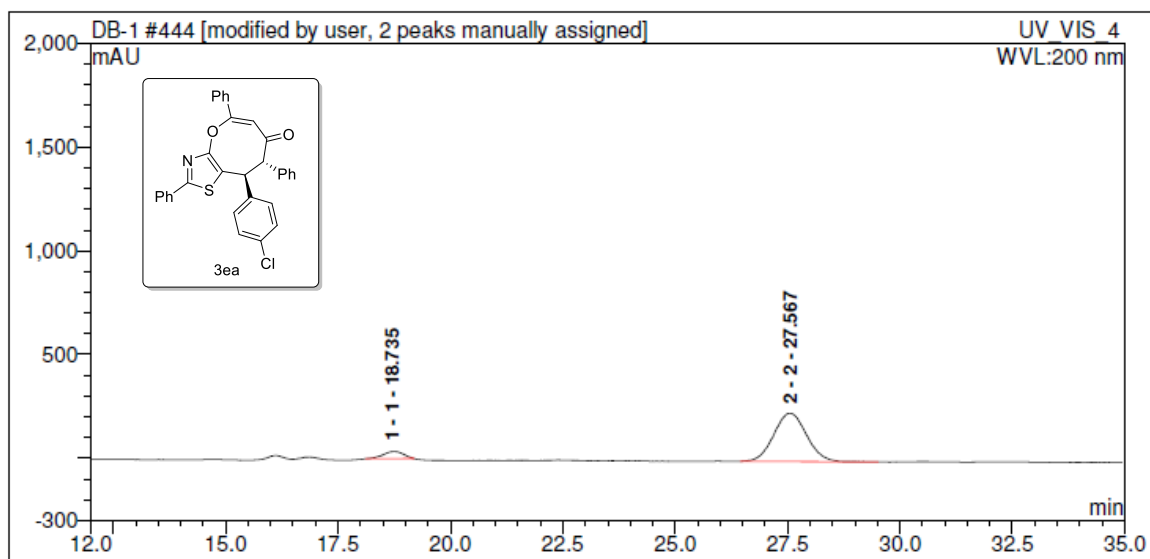
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.81	38.18904	50.19442157	54.48512	n.a.
2	2	27.46	37.8932	49.80557843	43.59817	n.a.



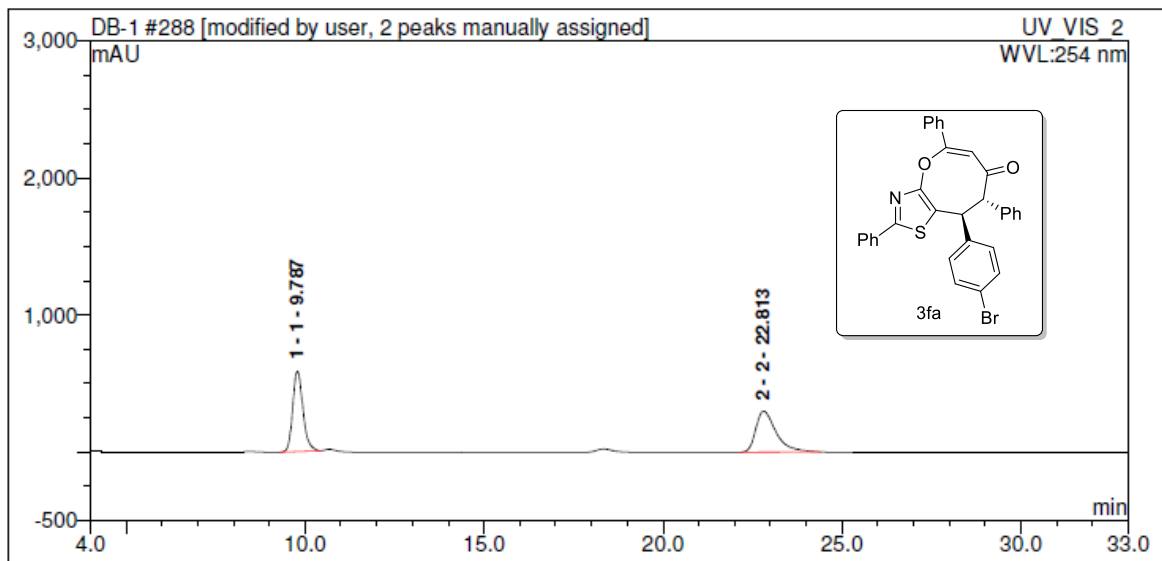
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.32833333	89.53858	8.962394854	133.1819	n.a.
2	2	26.93333333	909.5089	91.03760515	1078.929	n.a.



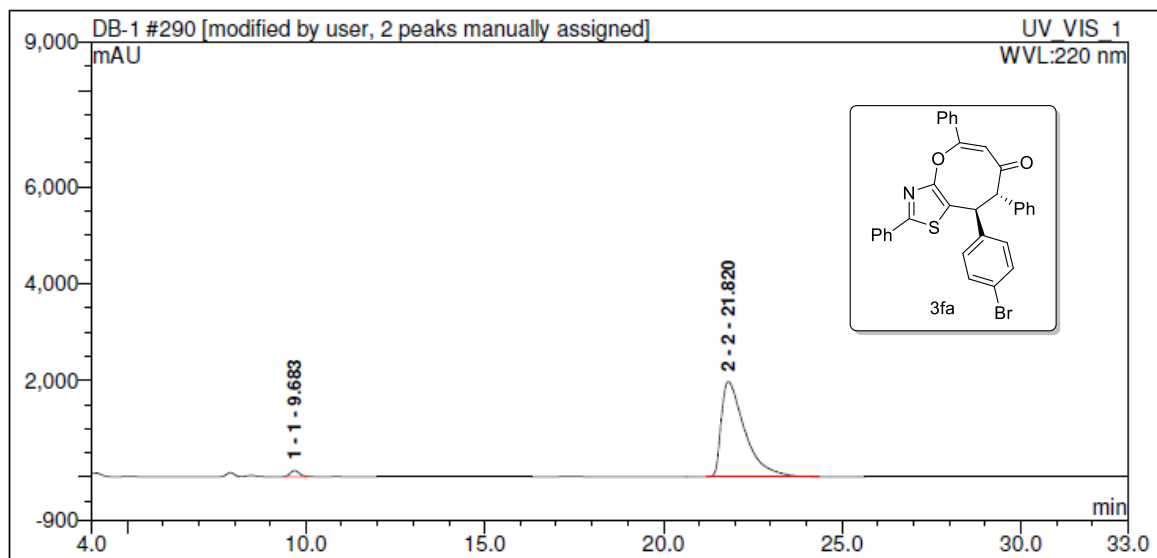
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.08	657.4999	50.07525316	887.3239	n.a.
2	2	30.56666667	655.5237	49.92474684	646.6083	n.a.



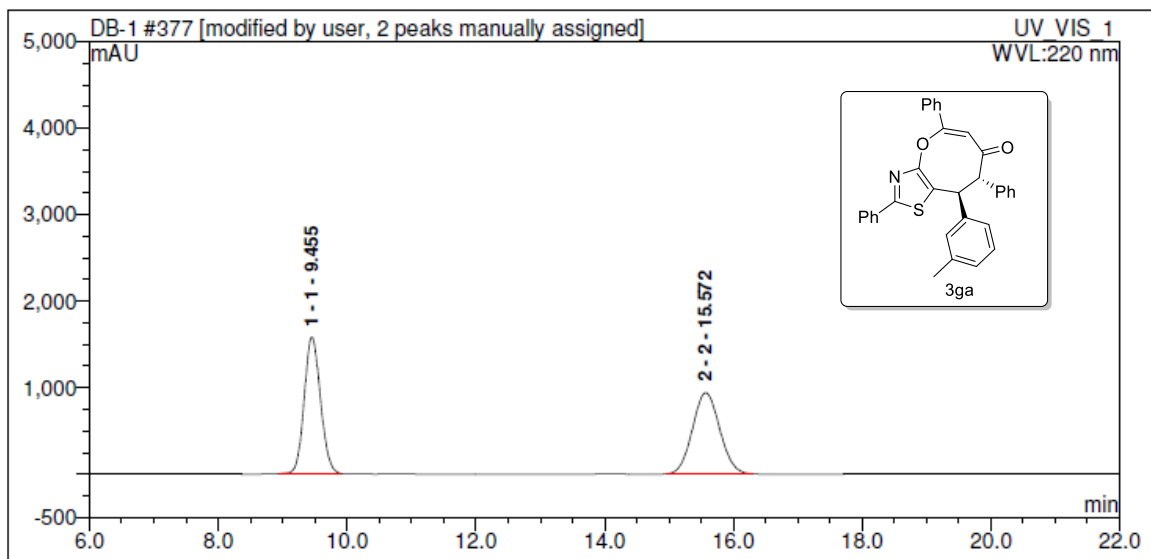
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.735	17.78109	8.334395584	34.40759	n.a.
2	2	27.56666667	195.5648	91.66560442	231.9828	n.a.



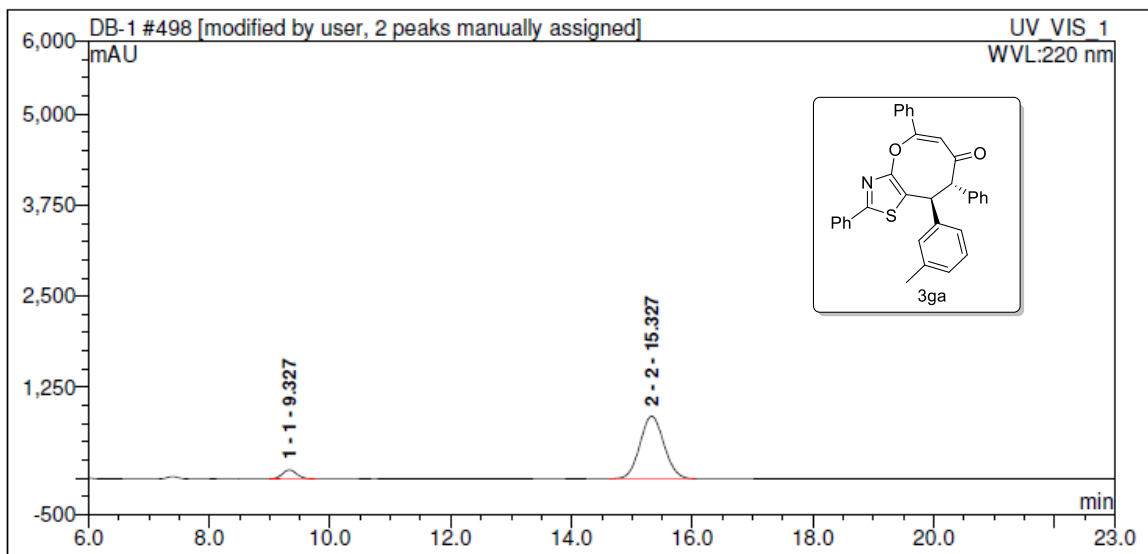
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.78666667	194.5341	49.74078791	585.5839	n.a.
2	2	22.81333333	196.5616	50.25921209	298.5214	n.a.



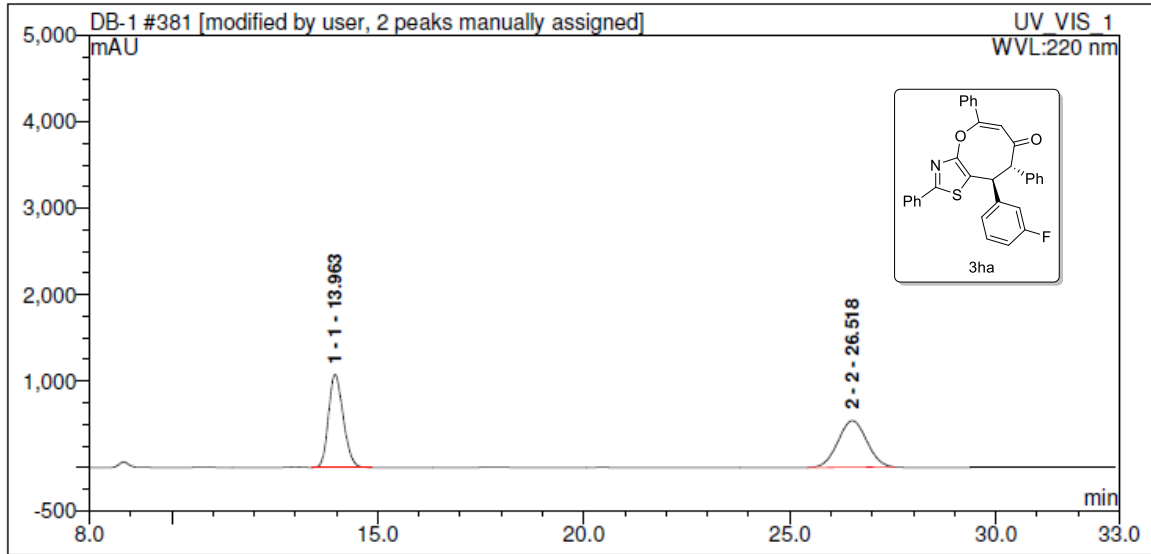
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.683333333	37.22869	2.399329963	125.3346	n.a.
2	2	21.82	1514.4	97.60067004	1972.957	n.a.



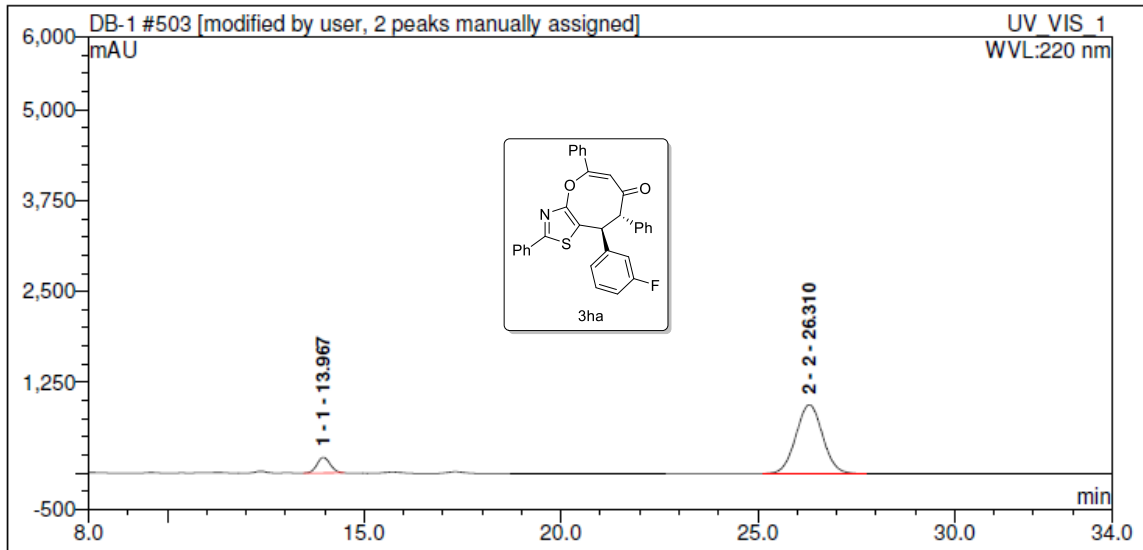
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.455	460.1083	49.95426097	1574.255	n.a.
2	2	15.57166667	460.9509	50.04573903	937.5053	n.a.



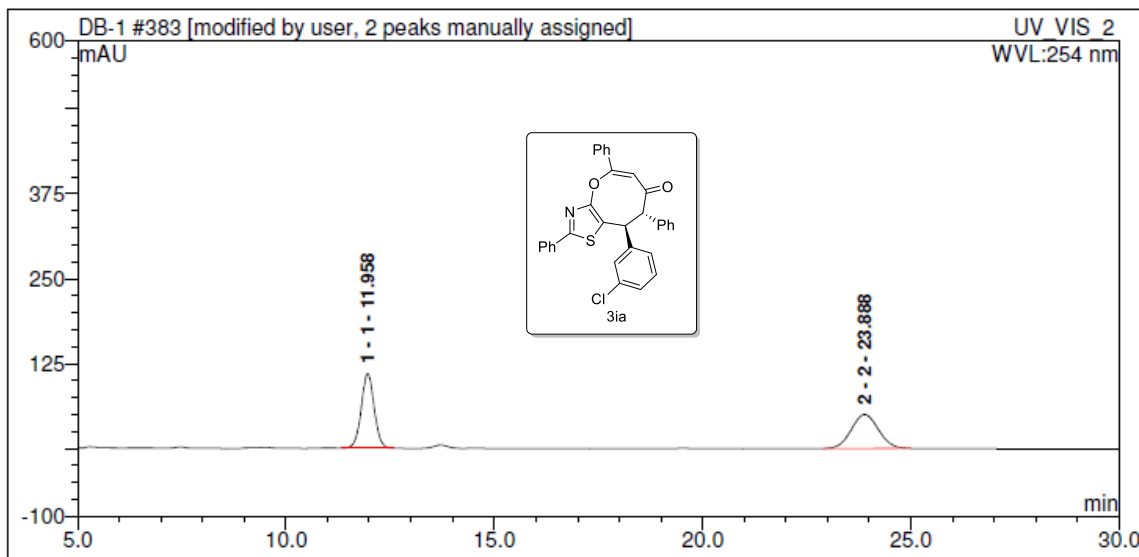
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.326666667	34.66019	8.076279643	122.6311	n.a.
2	2	15.32666667	394.5002	91.92372036	856.9588	n.a.



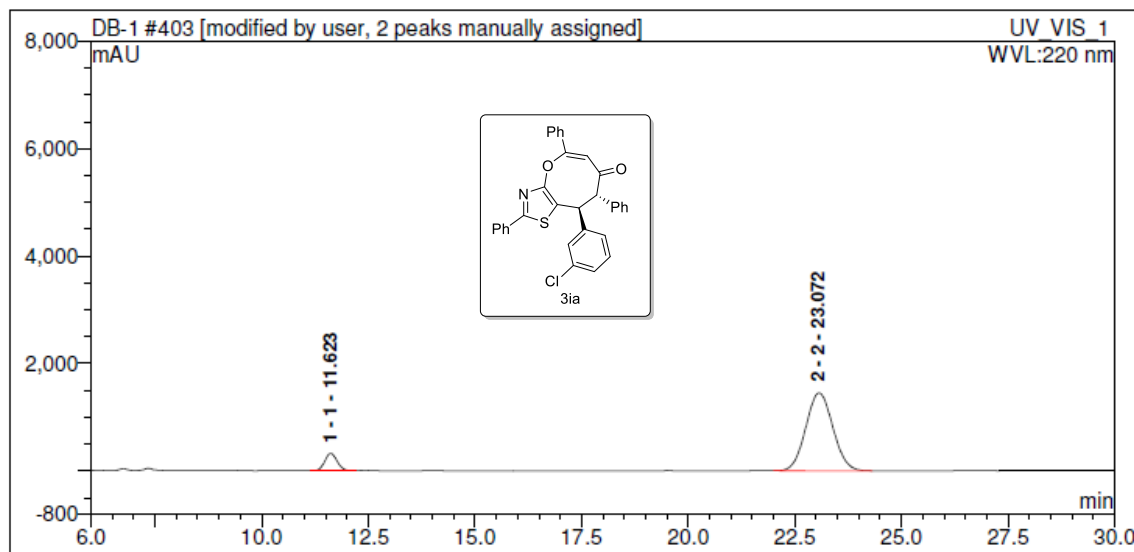
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.96333333	447.5866	50.690891	1075.339	n.a.
2	2	26.51833333	435.3858	49.309109	537.2867	n.a.



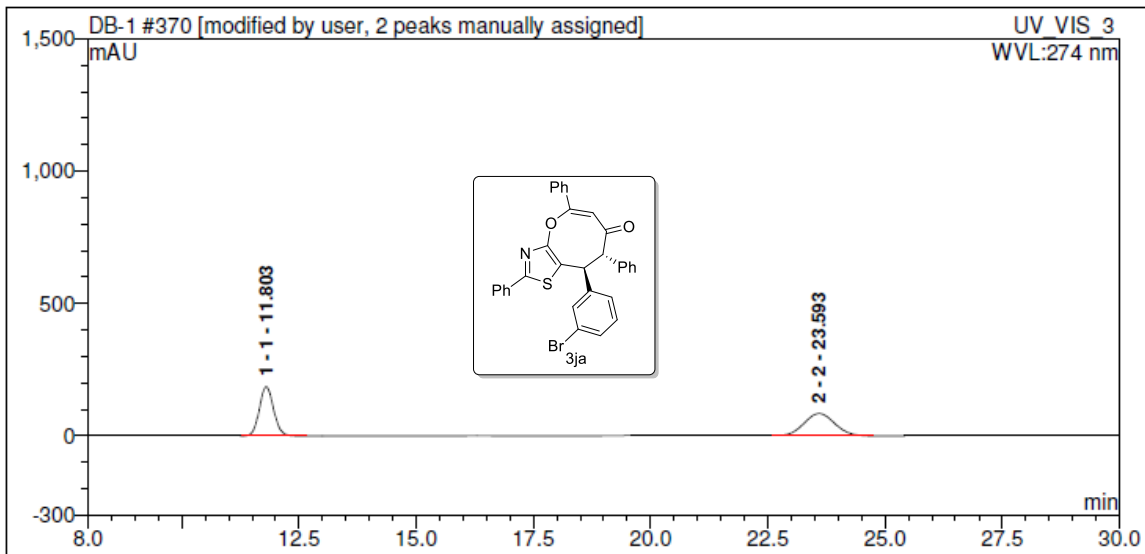
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.96666667	83.17734	10.08022375	215.4835	n.a.
2	2	26.31	741.9763	89.91977625	944.018	n.a.



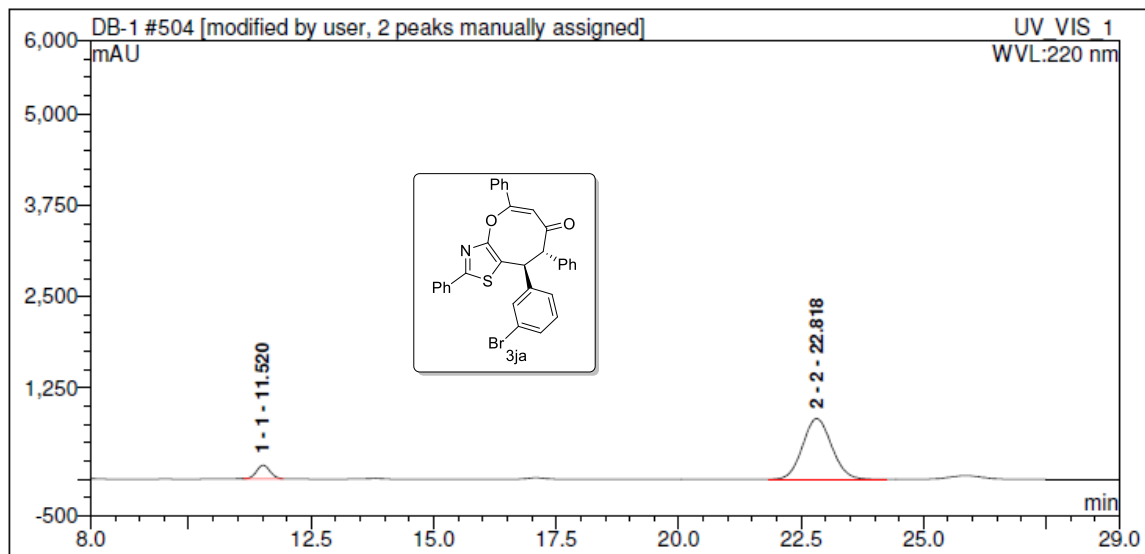
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.95833333	39.80825	51.36584493	109.9952	n.a.
2	2	23.88833333	37.69121	48.63415507	49.8674	n.a.



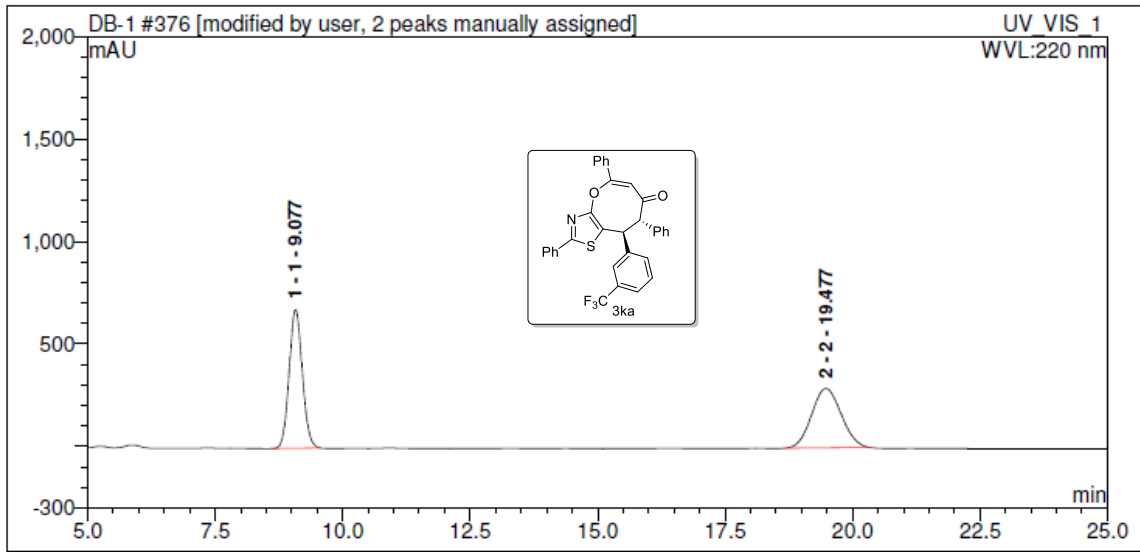
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.62333333	109.4862	9.28024163	323.5075	n.a.
2	2	23.07166667	1070.291	90.71975837	1449.031	n.a.



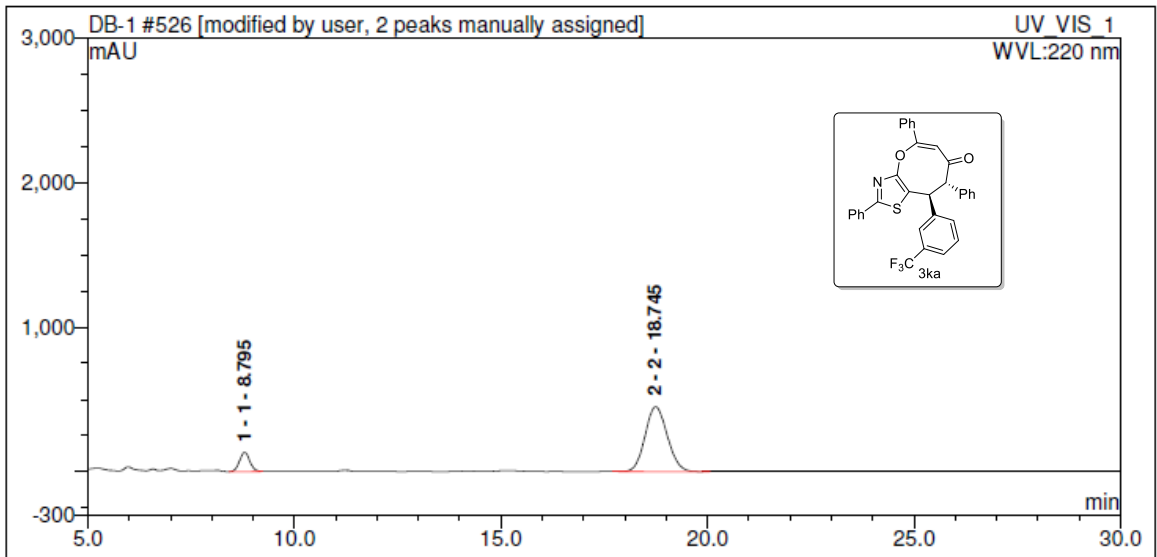
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.80333333	65.26951	50.23993413	185.8989	n.a.
2	2	23.59333333	64.64608	49.76006587	84.54416	n.a.



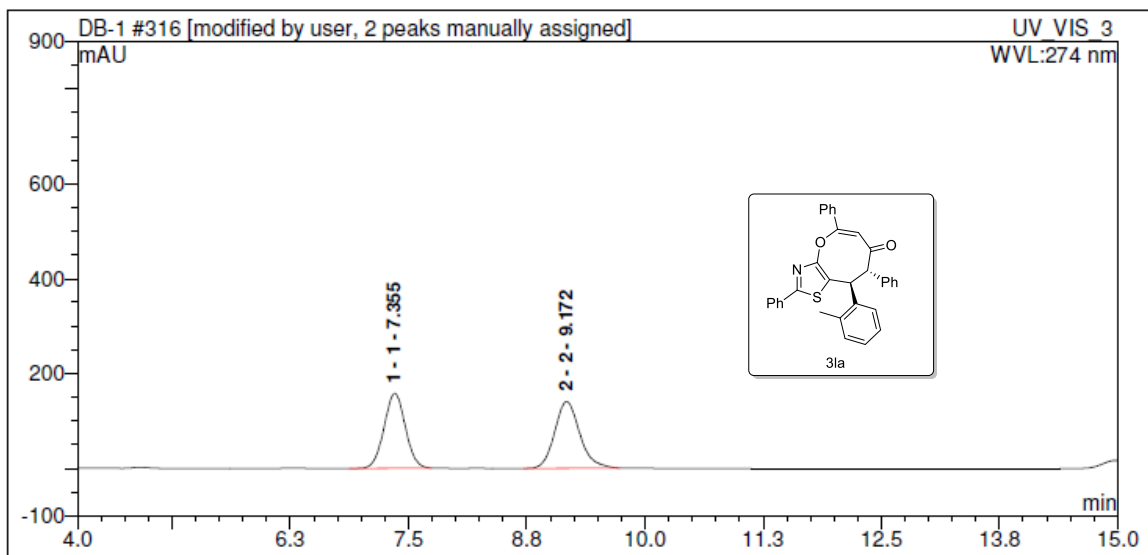
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.52	59.01651	9.38543263	185.2792	n.a.
2	2	22.81833333	569.7932	90.61456737	828.2034	n.a.



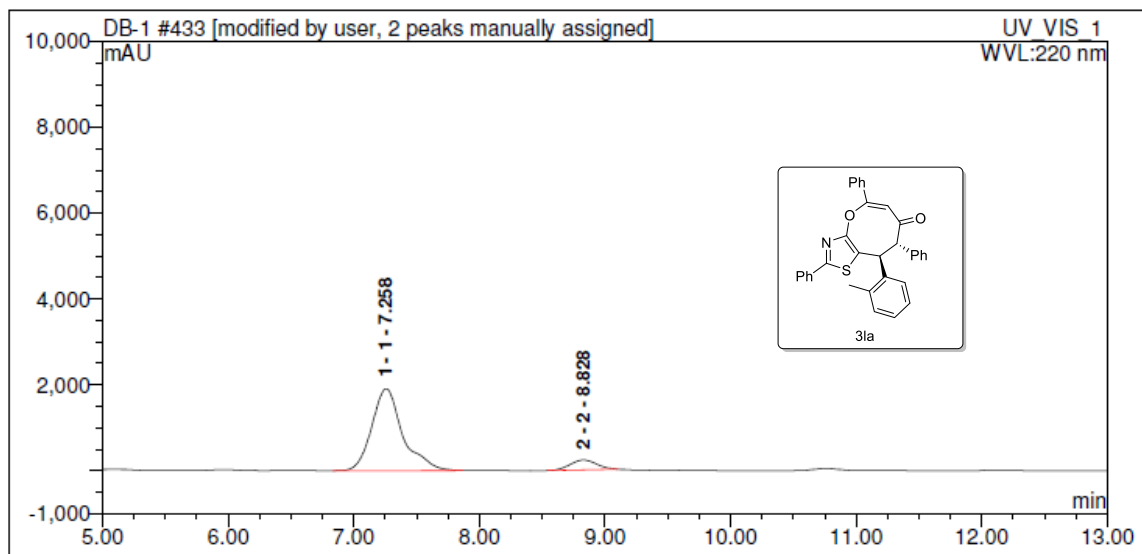
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.07666667	203.3841	50.99014078	675.6496	n.a.
2	2	19.47666667	195.4854	49.00985922	290.251	n.a.



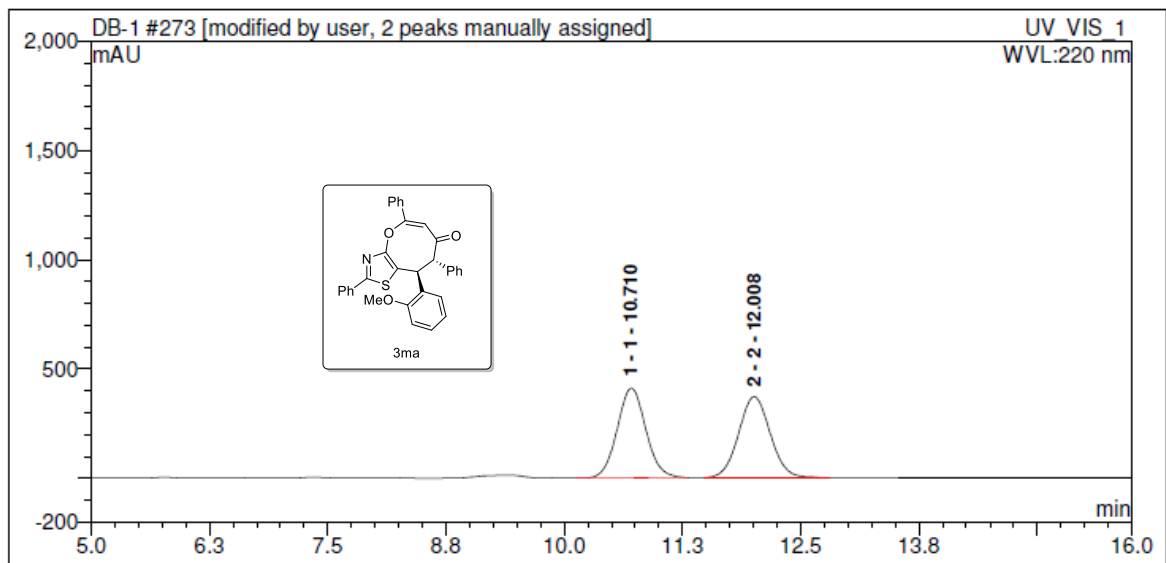
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	8.795	38.12632	11.94718206	132.962	n.a.
2	2	18.745	280.9976	88.05281794	448.5583	n.a.



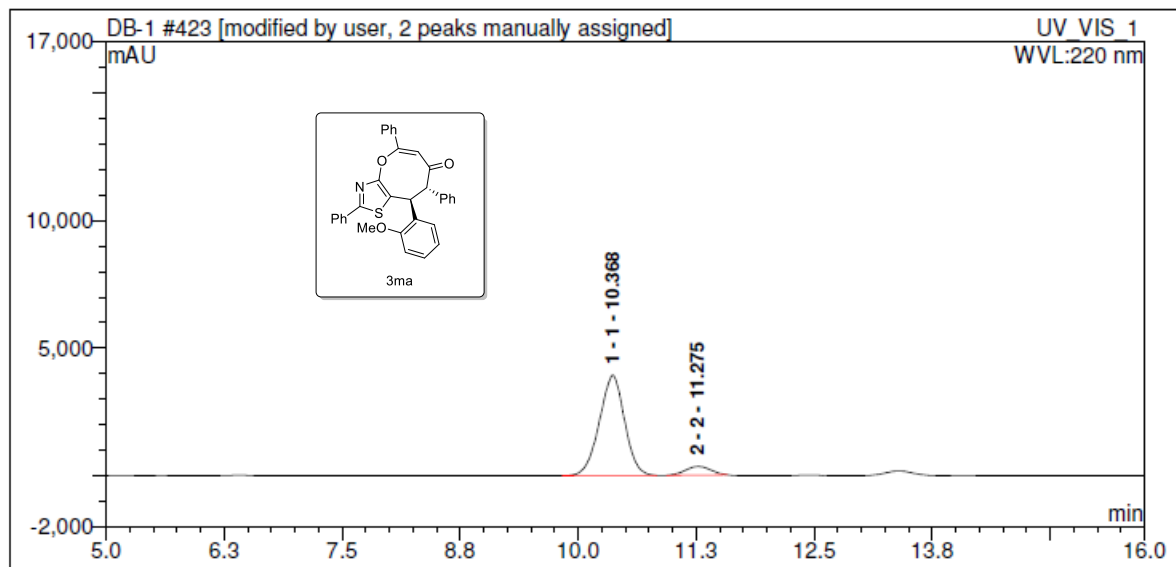
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.355	41.21251	48.78314016	157.7822	n.a.
2	2	9.171666667	43.26854	51.21685984	140.5686	n.a.



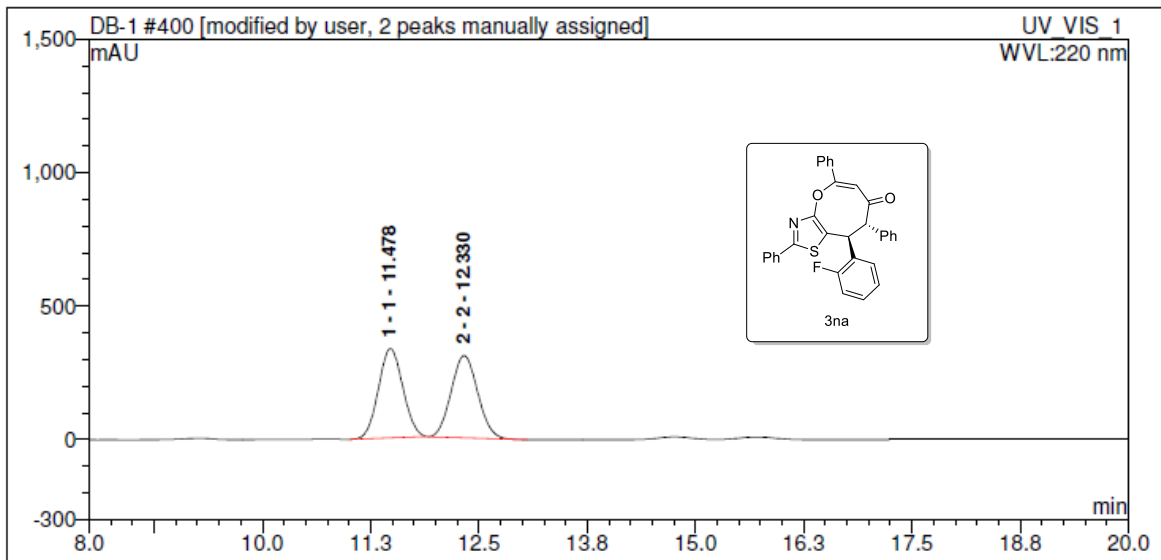
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.258333333	543.8524	90.60856719	1906.372	n.a.
2	2	8.828333333	56.36943	9.391432811	229.3882	n.a.



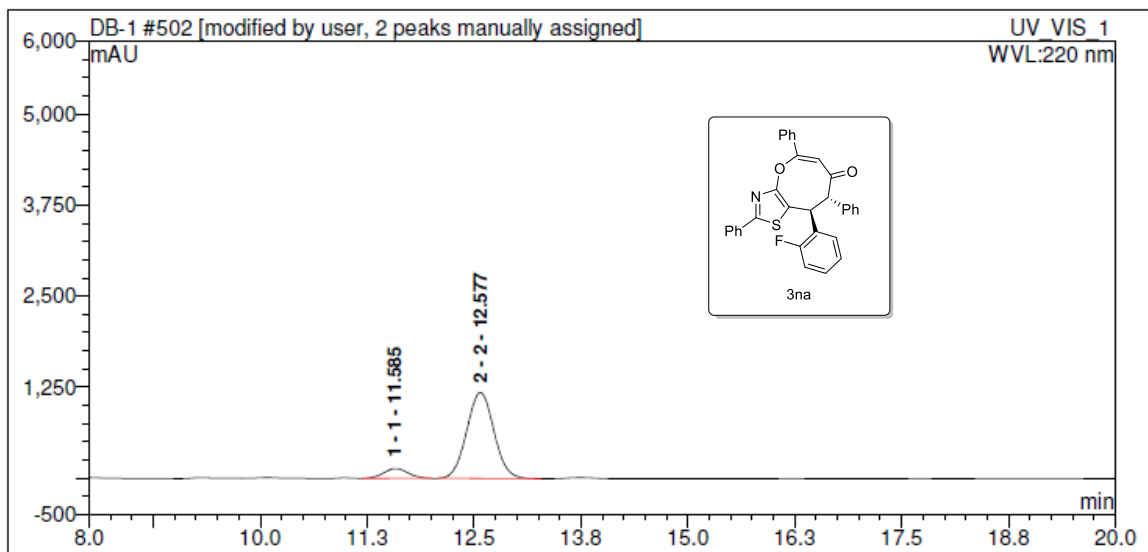
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.71	144.1027	49.89665394	410.405	n.a.
2	2	12.00833333	144.6996	50.10334606	371.3042	n.a.



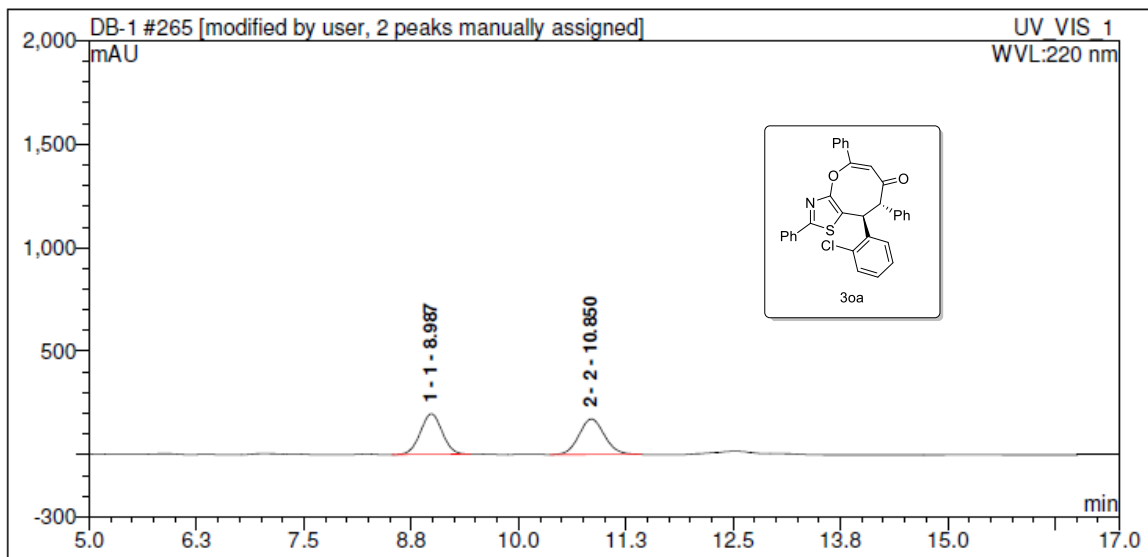
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.36833333	1214.701	92.14588503	3930.017	n.a.
2	2	11.275	103.5358	7.854114967	336.8867	n.a.



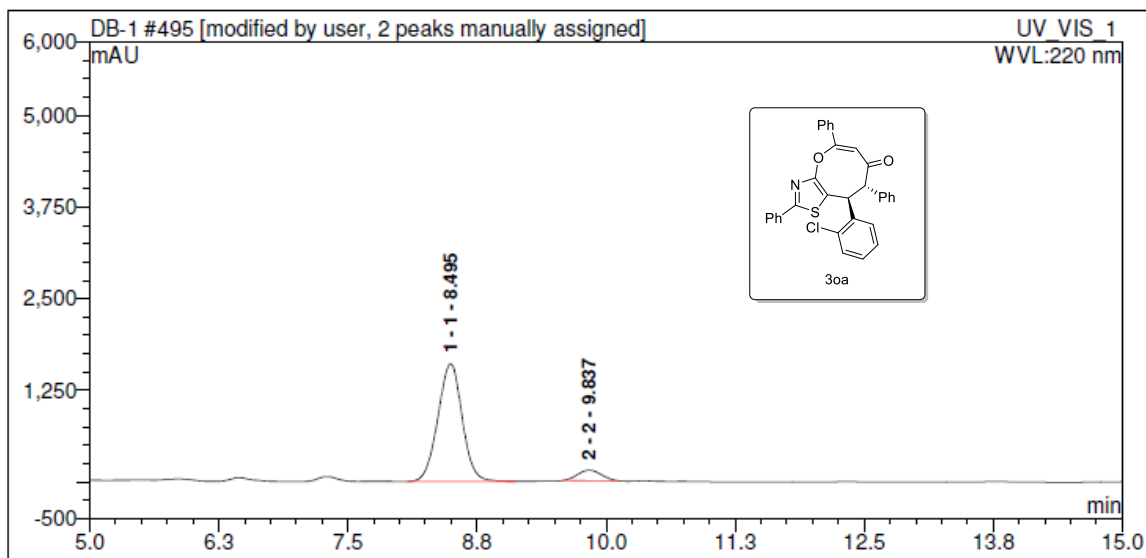
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.47833333	108.9214	49.93533316	333.7097	n.a.
2	2	12.33	109.2035	50.06466684	307.5974	n.a.



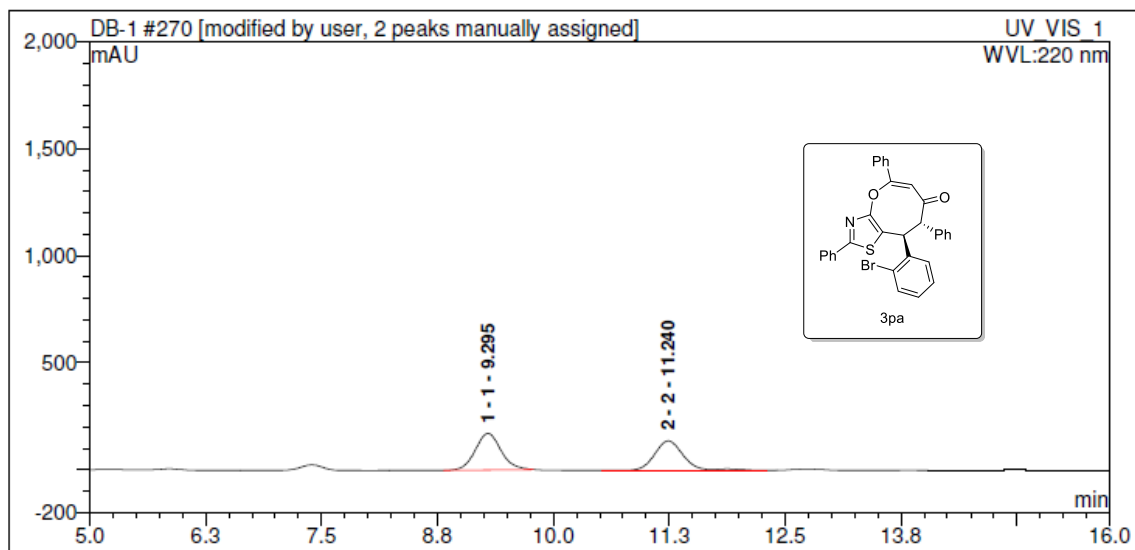
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.585	43.80093	9.146149762	133.5295	n.a.
2	2	12.57666667	435.0993	90.85385024	1178.078	n.a.



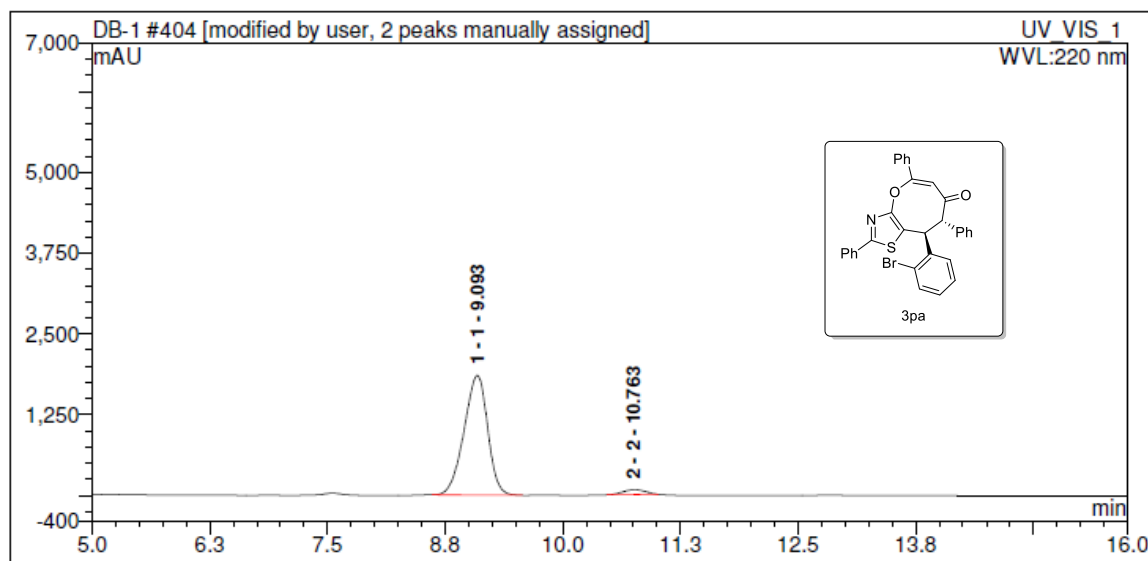
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	8.98666667	57.95822	49.67666275	195.7758	n.a.
2	2	10.85	58.7127	50.32333725	171.0845	n.a.



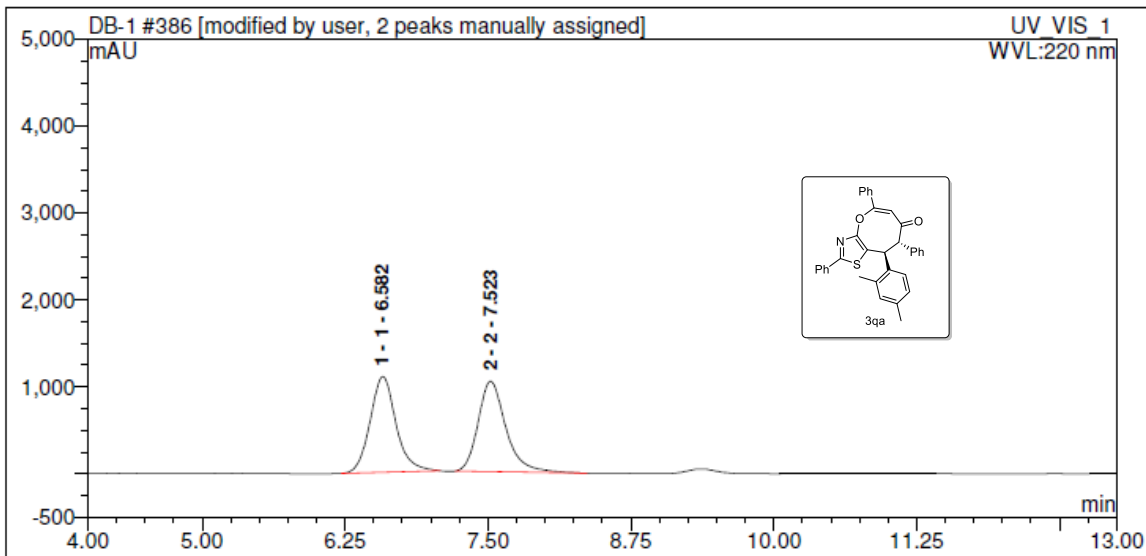
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	8.495	438.4296	92.05377775	1603.897	n.a.
2	2	9.83666667	37.84591	7.946222253	142.5984	n.a.



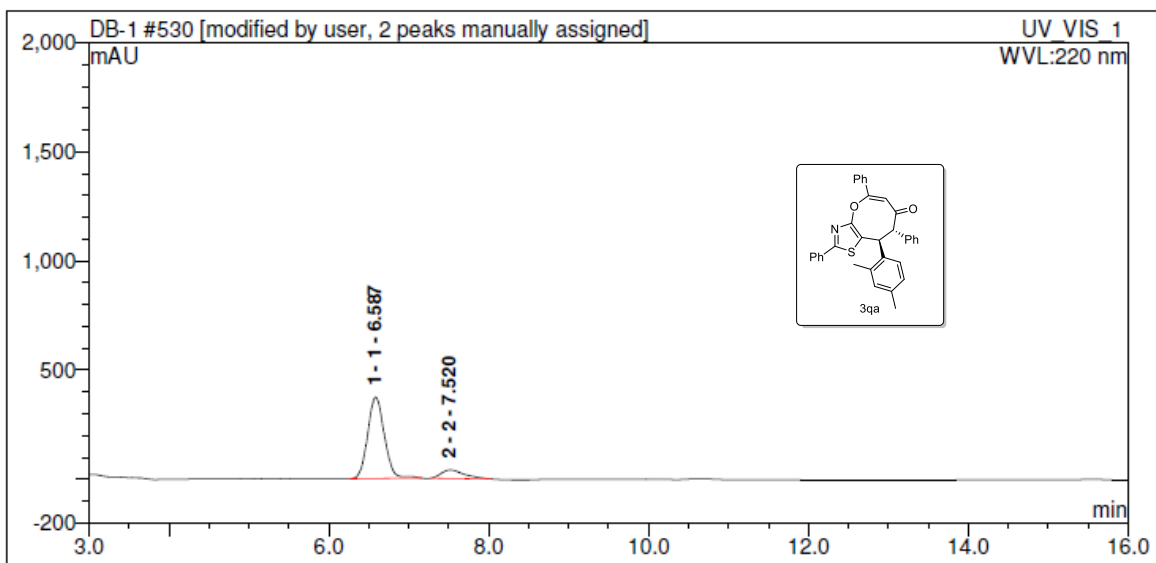
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1 1		9.295	54.95431	52.20086934	170.5168	n.a.
2 2		11.24	50.32039	47.79913066	137.6529	n.a.



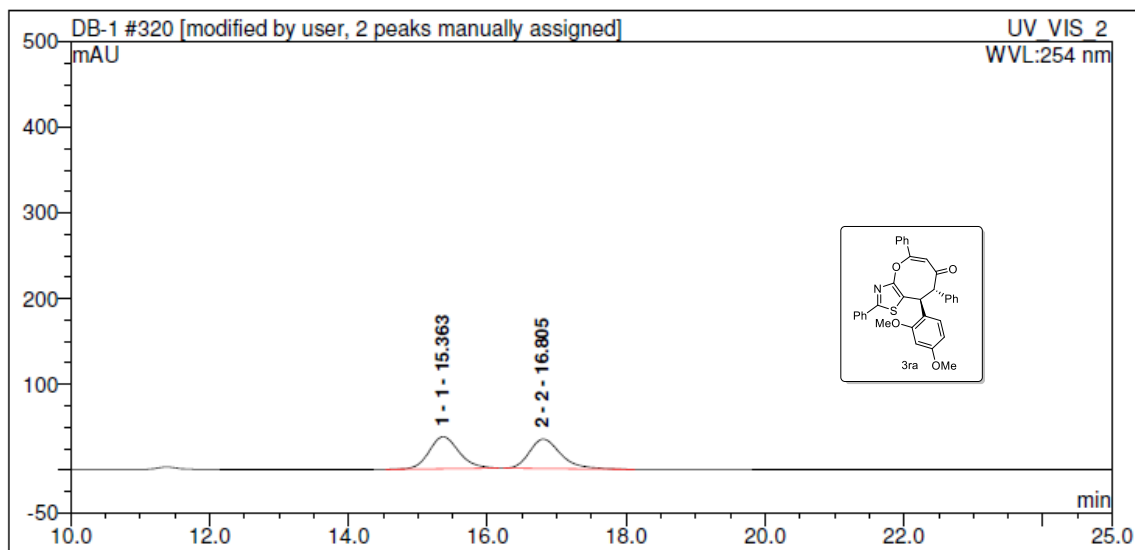
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1 1		9.093333333	539.5996	96.24931303	1850.598	n.a.
2 2		10.76333333	21.02736	3.750686972	76.32585	n.a.



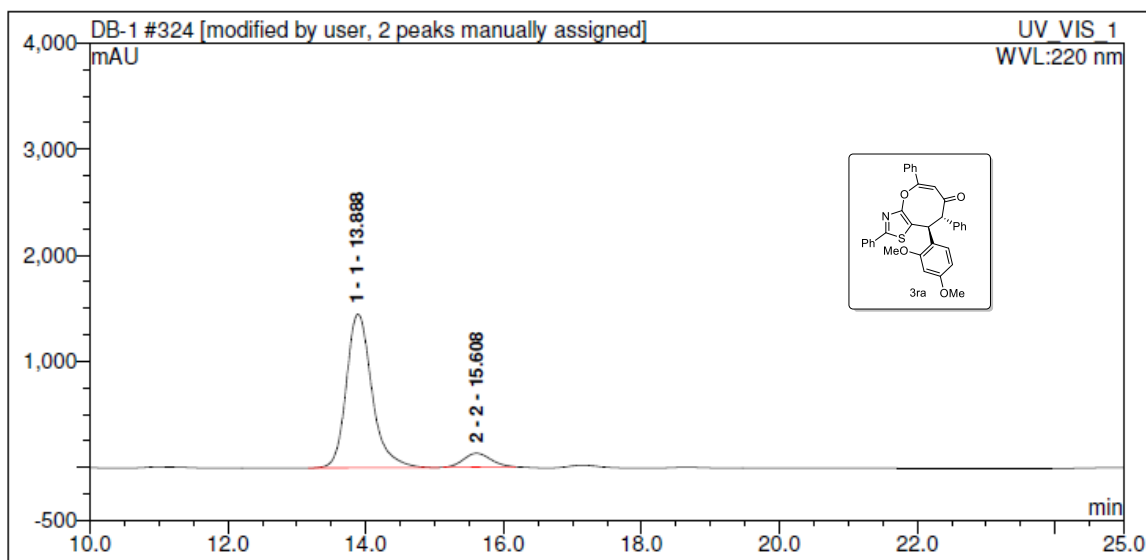
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	6.581666667	289.8843	49.75066794	1101.691	n.a.
2	2	7.523333333	292.7899	50.24933206	1038.528	n.a.



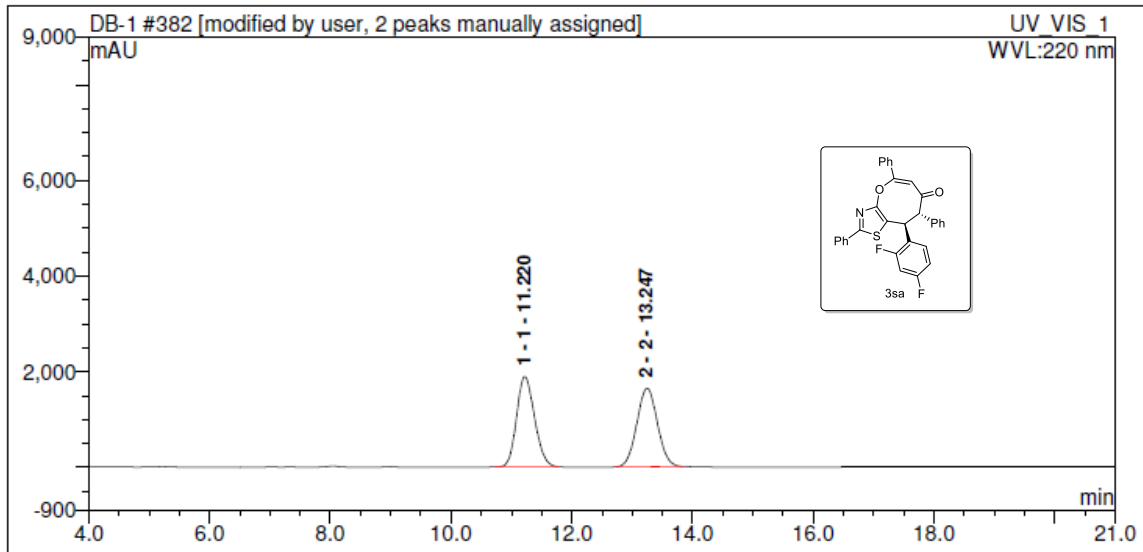
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	6.586666667	90.25217	87.21274014	372.3257	n.a.
2	2	7.52	13.23291	12.78725986	39.42076	n.a.



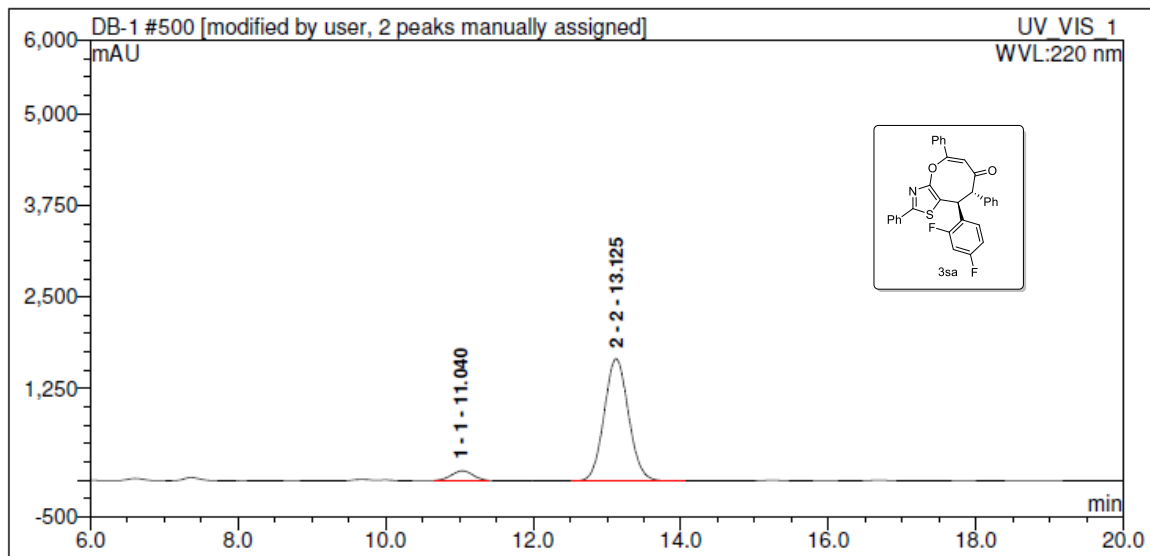
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.36333333	18.53596	50.83570655	37.20559	n.a.
2	2	16.805	17.92652	49.16429345	34.27266	n.a.



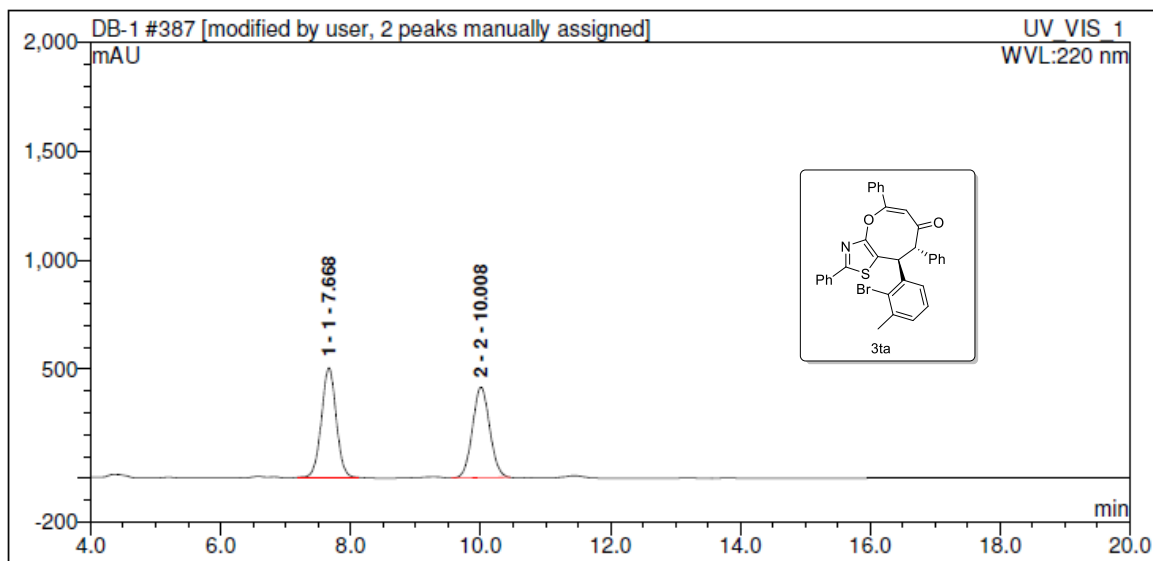
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.88833333	625.0956	91.41585545	1446.785	n.a.
2	2	15.60833333	58.69781	8.584144551	129.5889	n.a.



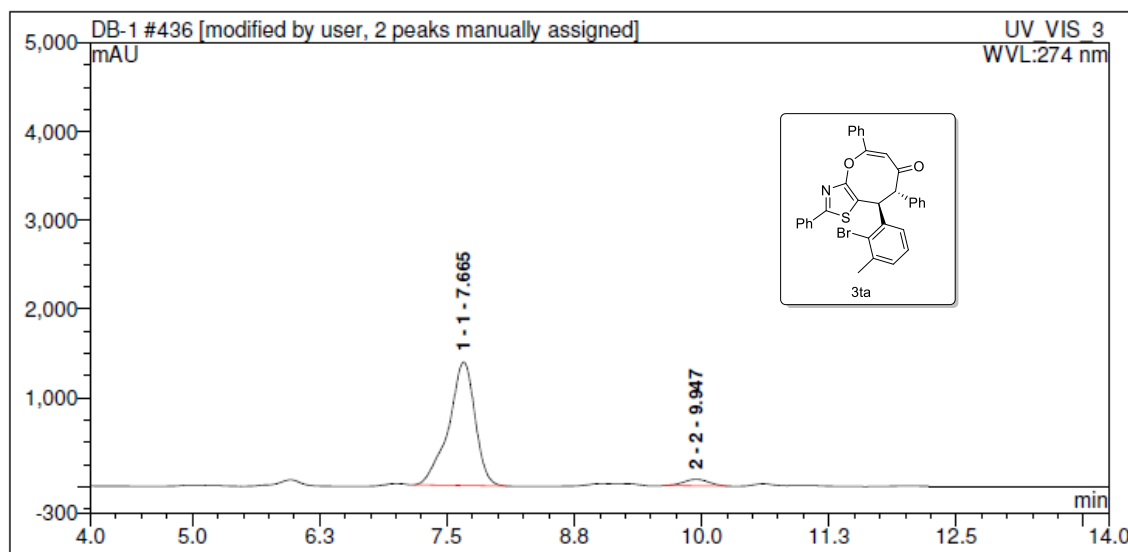
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.22	652.81	50.18759172	1889.689	n.a.
2	2	13.24666667	647.9298	49.81240828	1640.508	n.a.



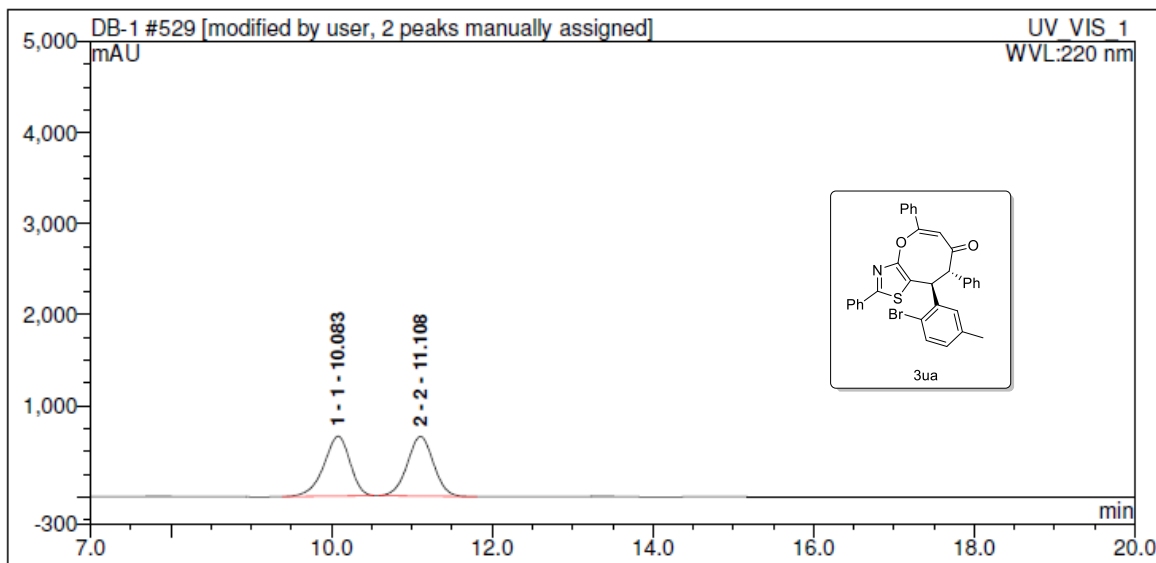
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.04	43.14039	6.350632938	130.152	n.a.
2	2	13.125	636.1681	93.64936706	1663.131	n.a.



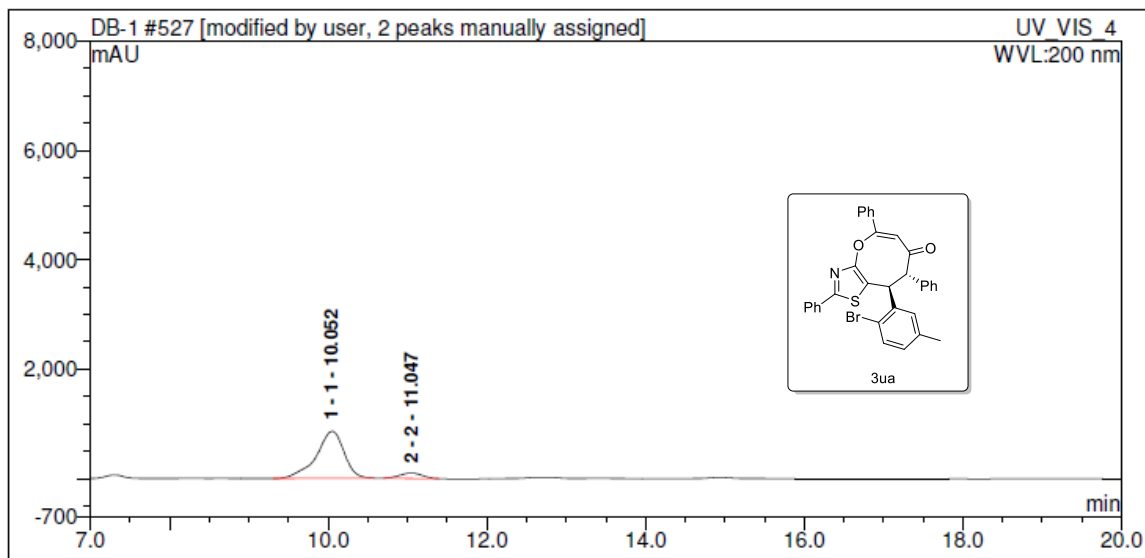
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.66833333	132.1241	50.86034908	501.8468	n.a.
2	2	10.00833333	127.6541	49.13965092	414.4039	n.a.



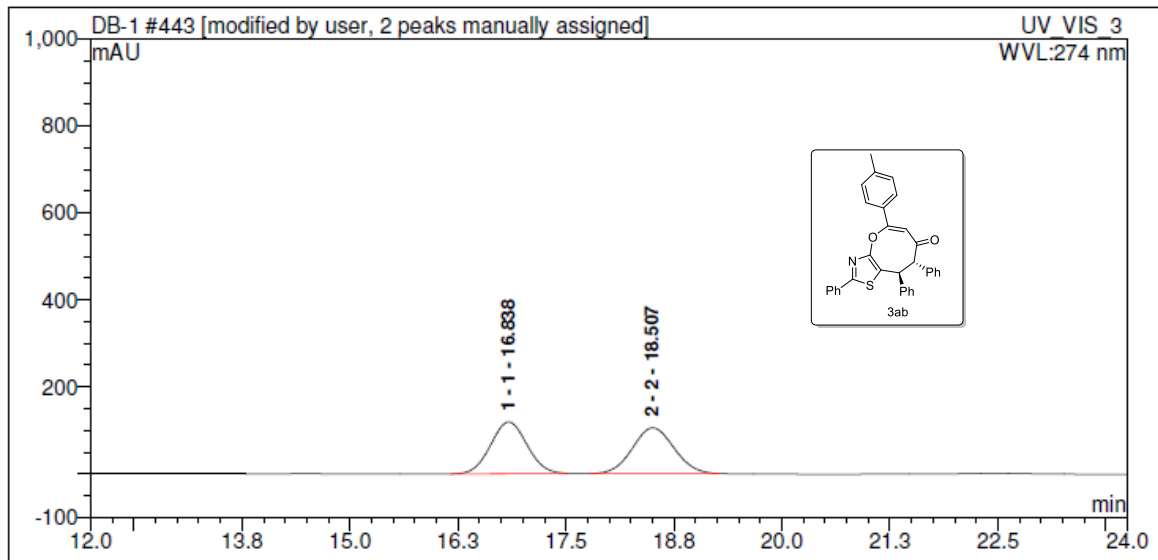
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.665	418.0618	95.30136427	1389.595	n.a.
2	2	9.94666667	20.61167	4.698635732	72.74986	n.a.



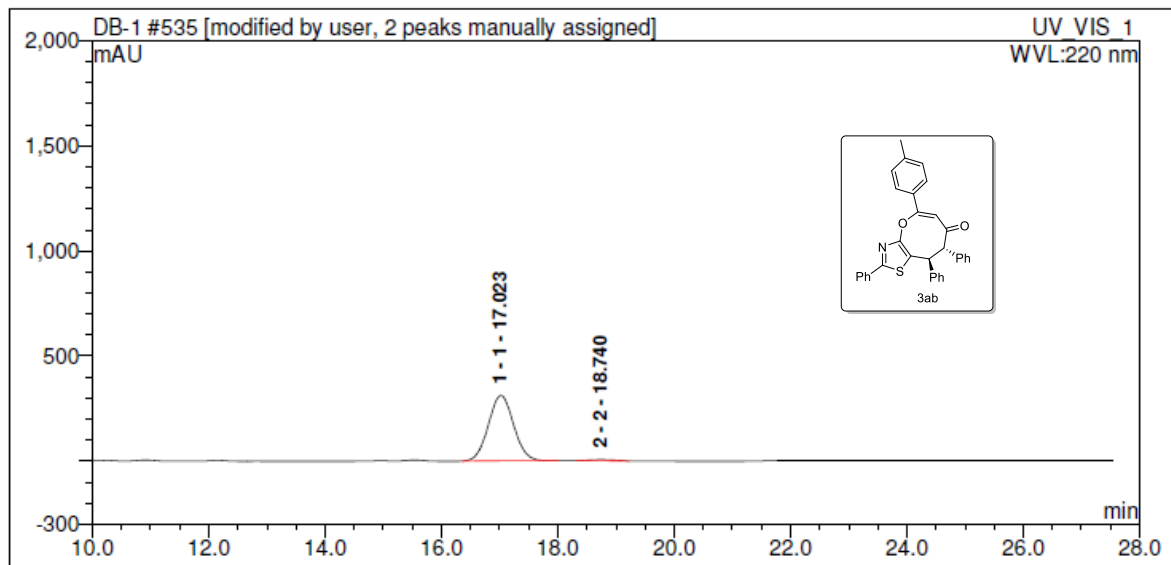
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.08333333	248.6284	50.06300598	655.6447	n.a.
2	2	11.10833333	248.0026	49.93699402	654.5556	n.a.



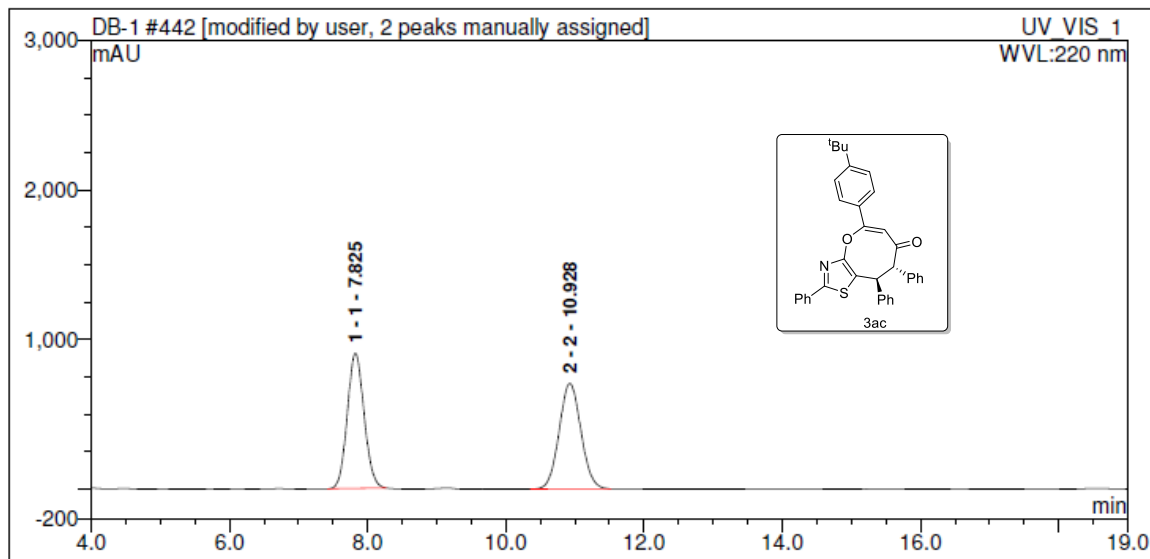
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.05166667	349.9044	91.60412048	858.6424	n.a.
2	2	11.04666667	32.07012	8.39587952	97.93444	n.a.



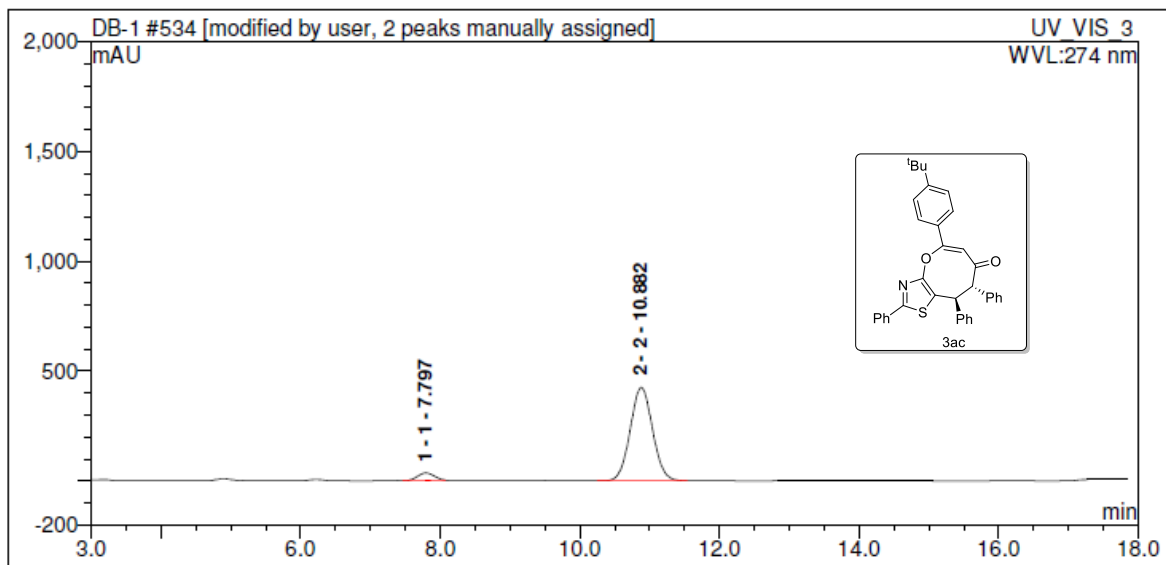
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.83833333	58.10809	49.70212465	118.7087	n.a.
2	2	18.50666667	58.8046	50.29787535	105.1063	n.a.



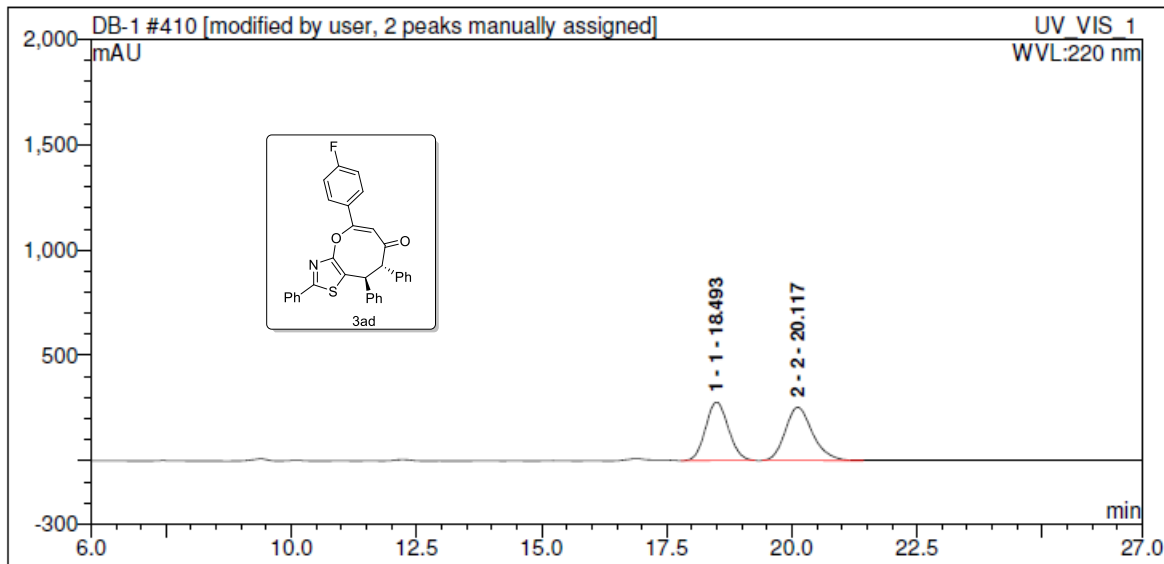
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.02333333	156.4495	98.28512739	310.9712	n.a.
2	2	18.74	2.729721	1.714872612	5.78364	n.a.



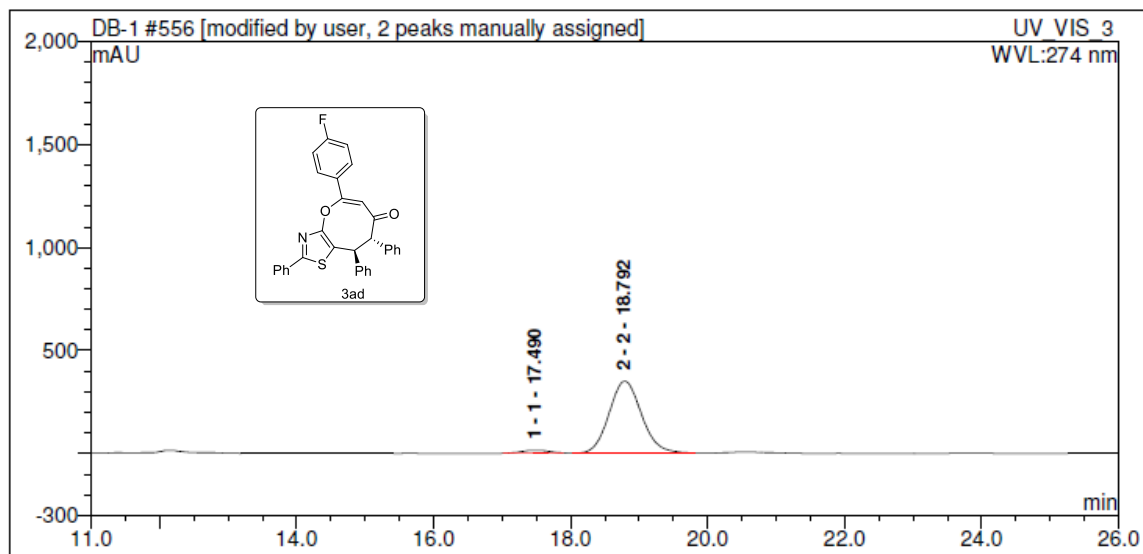
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.825	254.7838	49.74344084	901.7608	n.a.
2	2	10.92833333	257.4119	50.25655916	705.1667	n.a.



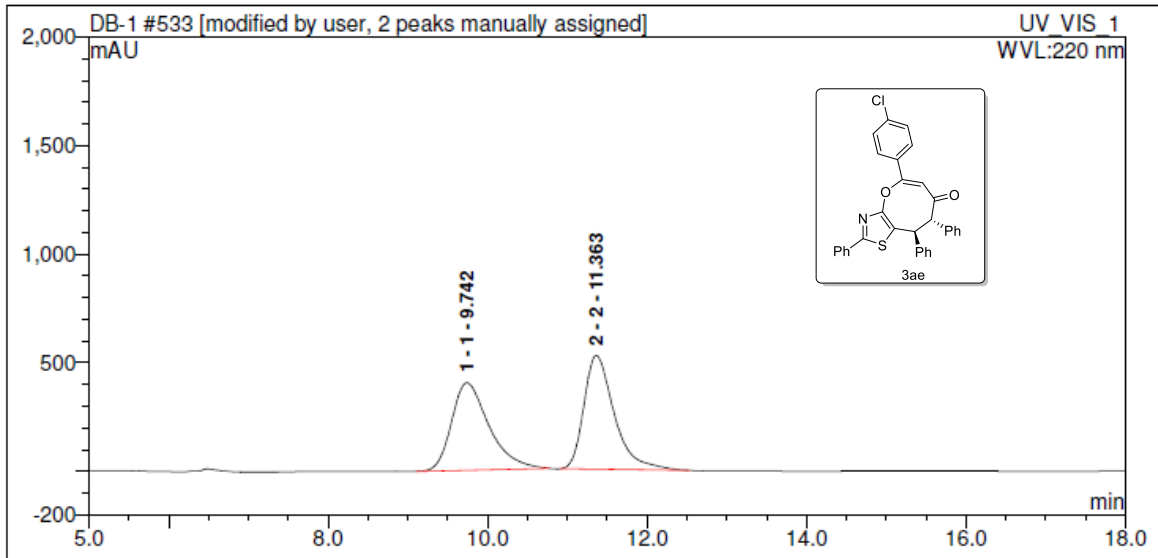
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.796666667	9.342922	5.612635197	33.80197	n.a.
2	2	10.88166667	157.1194	94.3873648	424.1762	n.a.



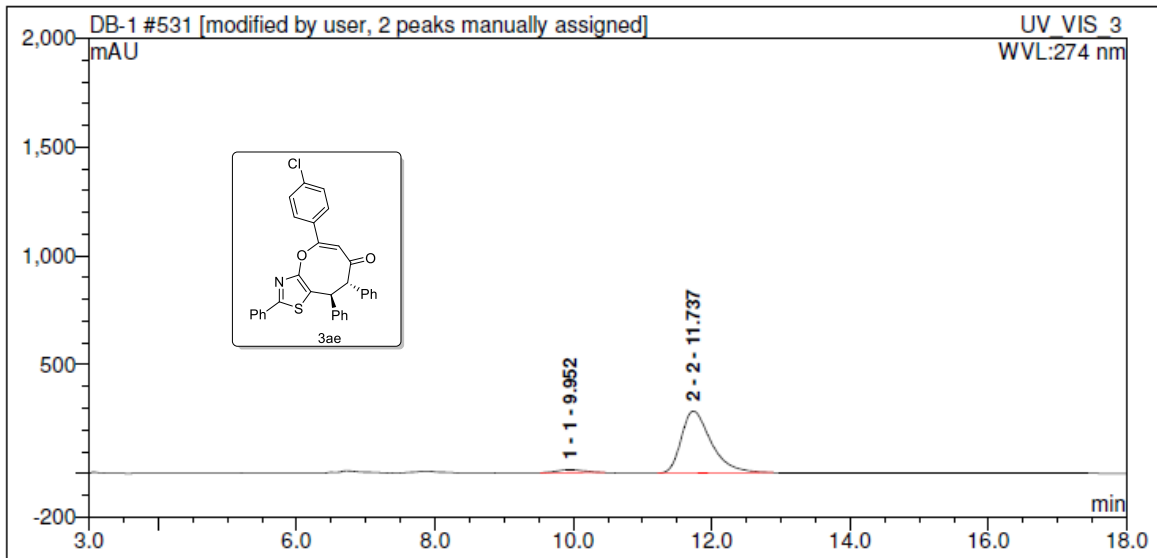
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.49333333	145.827	47.68727675	276.607	n.a.
2	2	20.11666667	159.9716	52.31272325	252.3927	n.a.



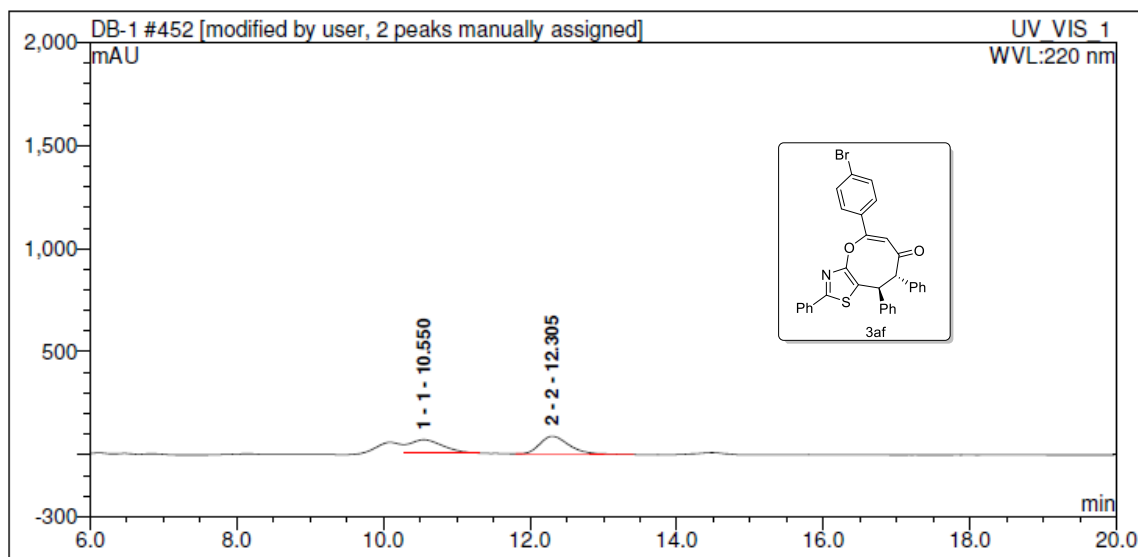
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.49	6.195135	3.12790199	14.11	n.a.
2	2	18.79166667	191.8653	96.87209801	349.4529	n.a.



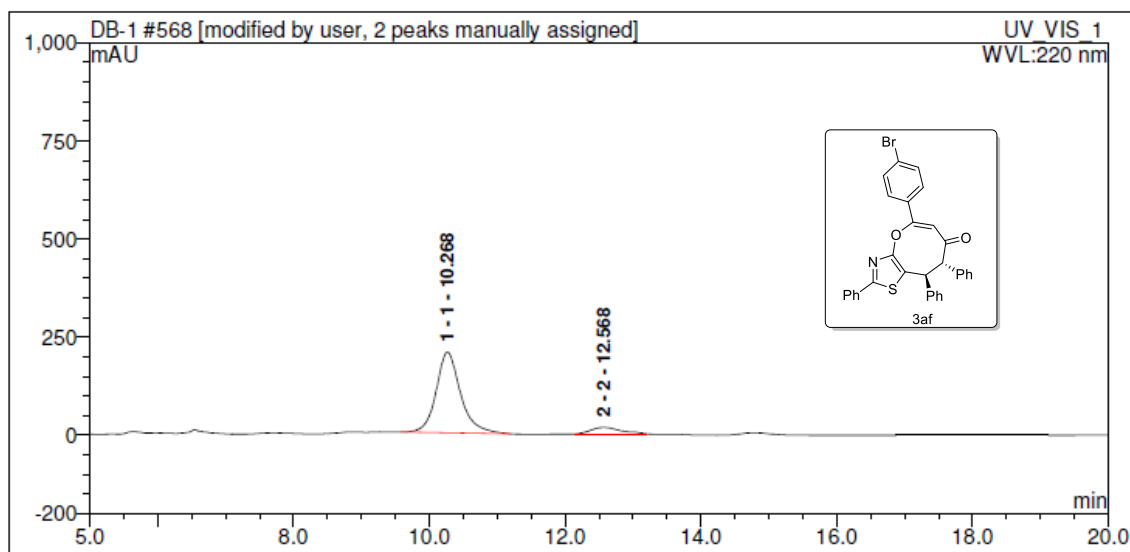
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.74166667	218.9211	48.60611899	402.2252	n.a.
2	2	11.36333333	231.4771	51.39388101	522.6293	n.a.



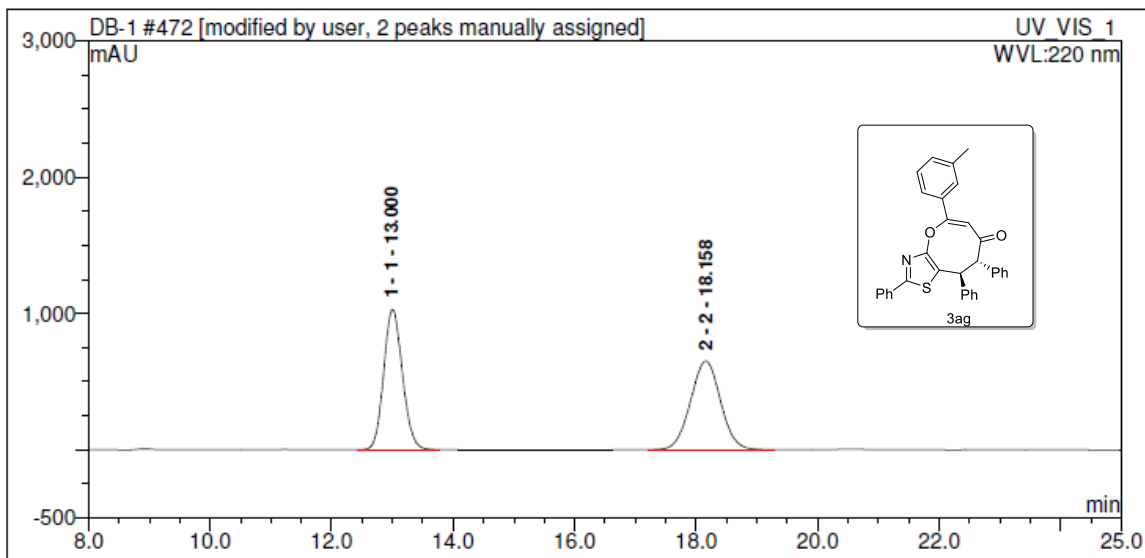
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.95166667	6.045262	4.074817467	12.84688	n.a.
2	2	11.73666667	142.3114	95.92518253	284.4824	n.a.



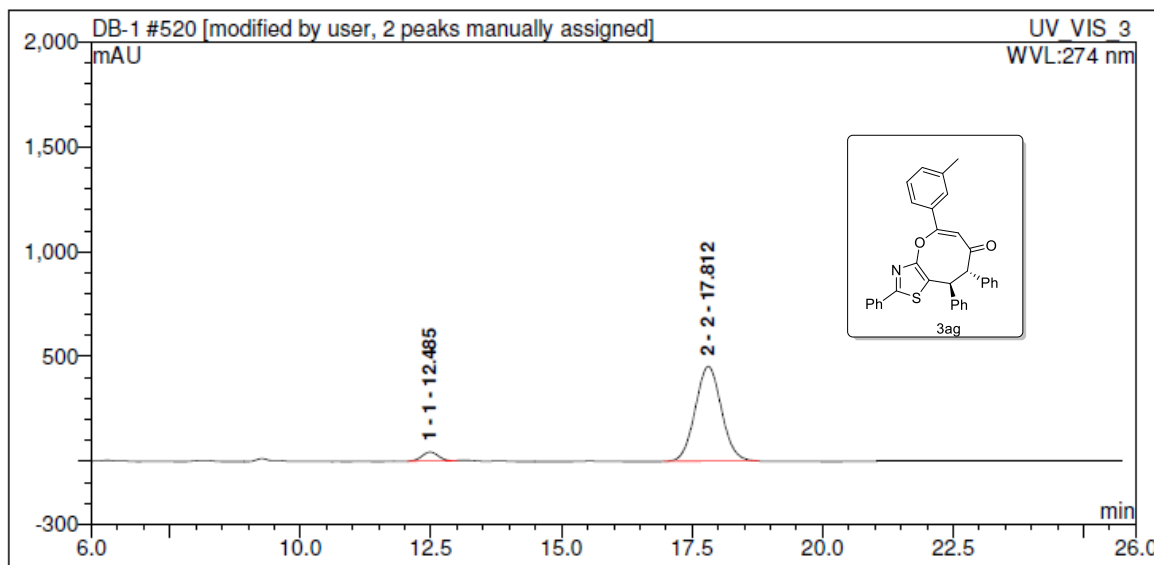
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.55	34.22569	46.14467915	64.69031	n.a.
2	2	12.305	39.9447	53.85532085	86.42644	n.a.



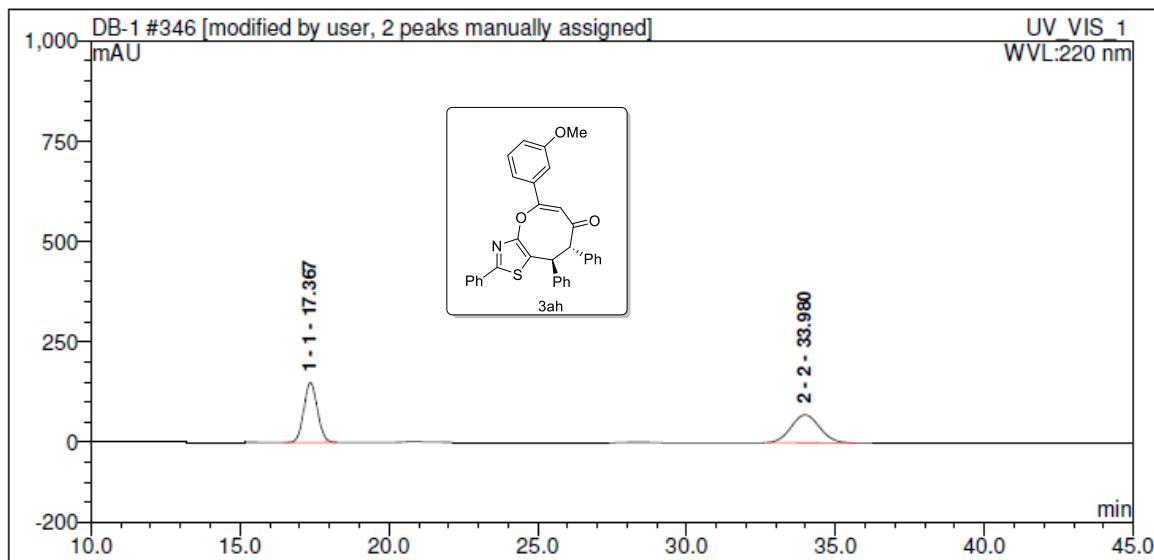
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.26833333	85.53092	91.09965484	204.9526	n.a.
2	2	12.56833333	8.356285	8.900345157	16.59323	n.a.



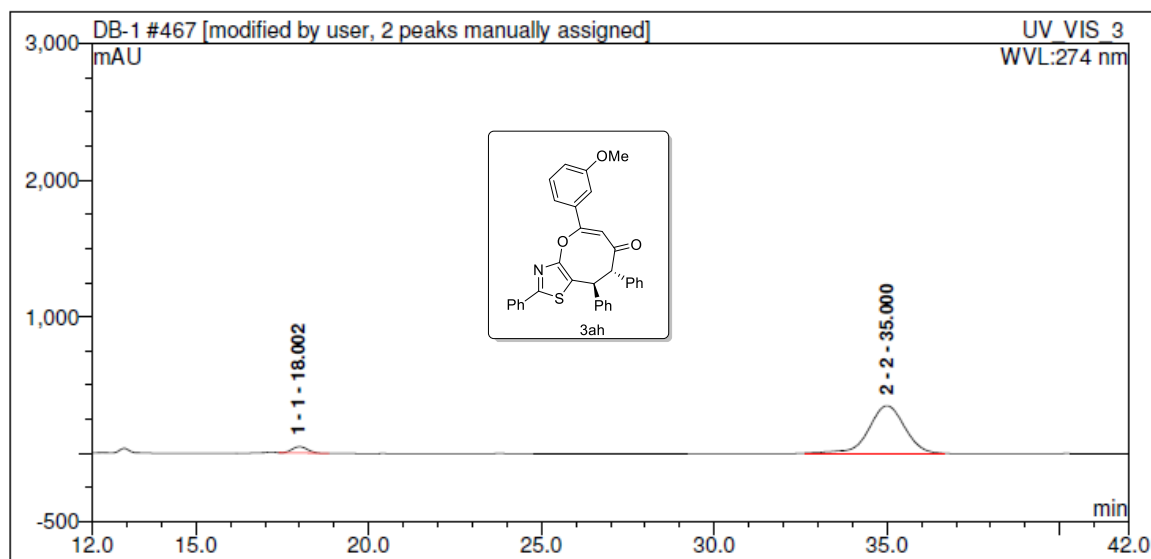
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13	366.0605	49.66701547	1027.336	n.a.
2	2	18.15833333	370.9689	50.33298453	648.5408	n.a.



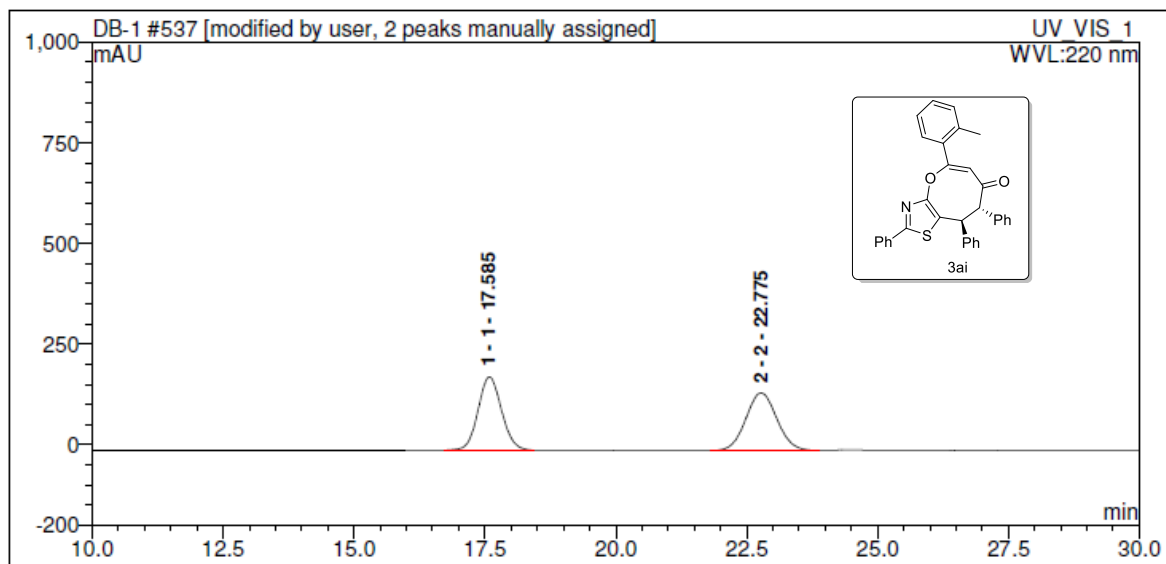
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	12.485	14.7045	5.300614165	41.96989	n.a.
2	2	17.81166667	262.7068	94.69938584	451.1646	n.a.



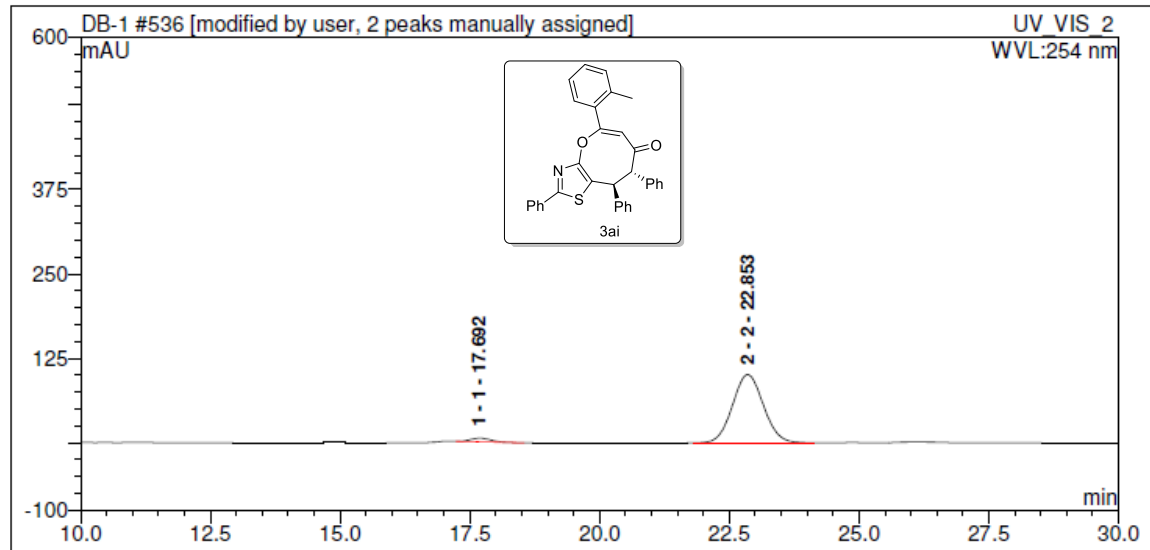
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.3666667	79.19154	50.75289151	148.8118	n.a.
2	2	33.98	76.84201	49.24710849	69.38648	n.a.



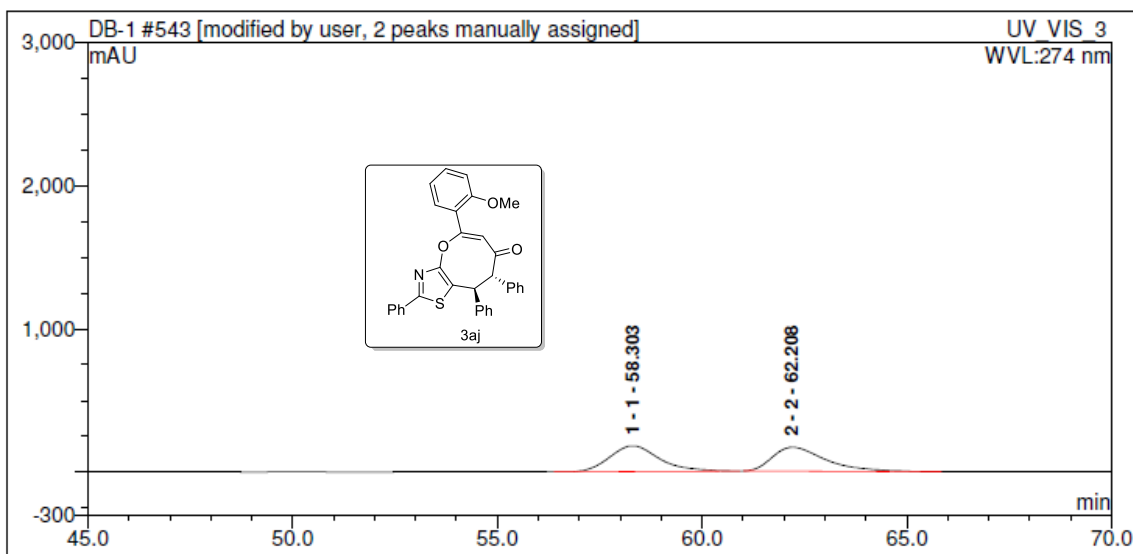
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.00166667	23.94242	5.448494874	46.3381	n.a.
2	2	35	415.4894	94.55150513	347.3595	n.a.



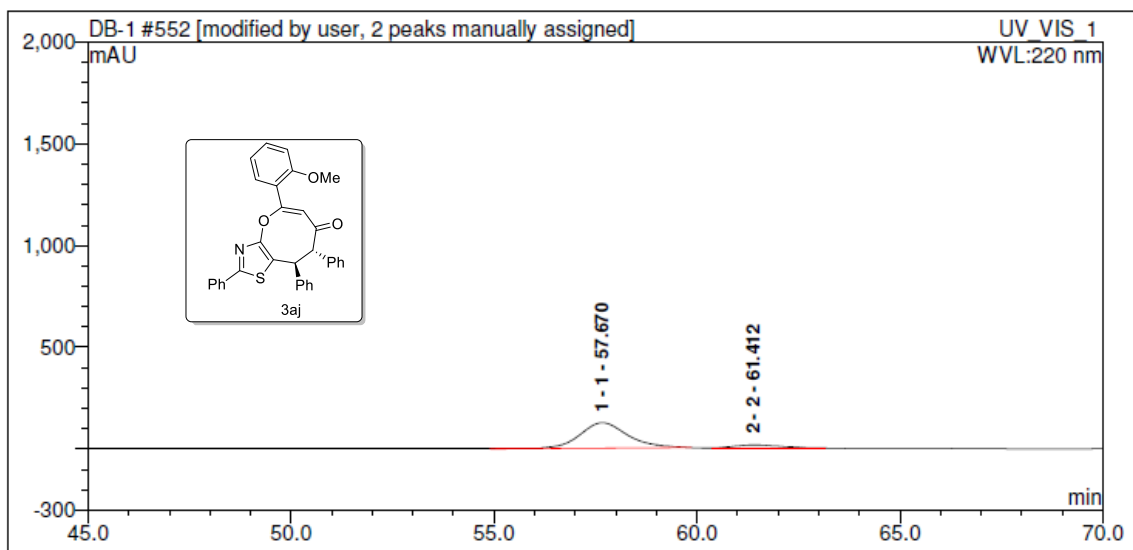
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.585	94.0614	49.13273371	181.6197	n.a.
2	2	22.775	97.38205	50.86726629	142.7095	n.a.



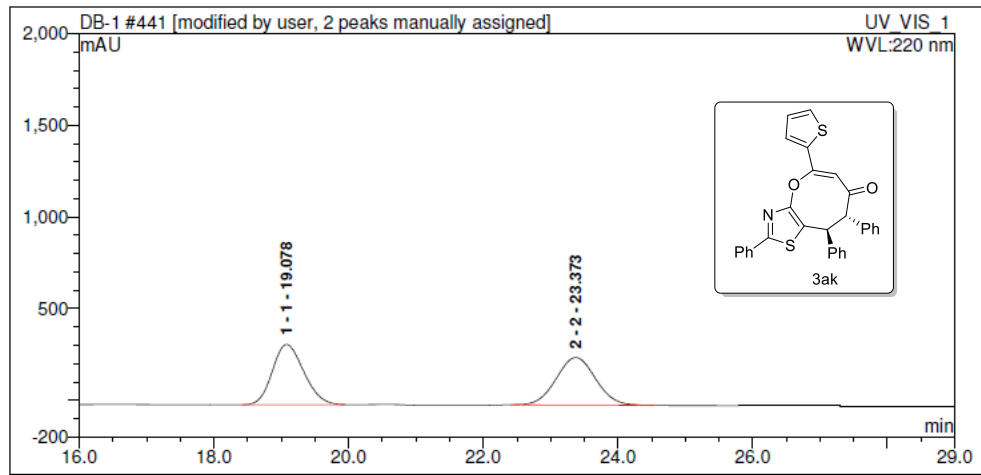
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.69166667	2.323331	3.231409307	5.31393	n.a.
2	2	22.85333333	69.57504	96.76859069	100.7969	n.a.



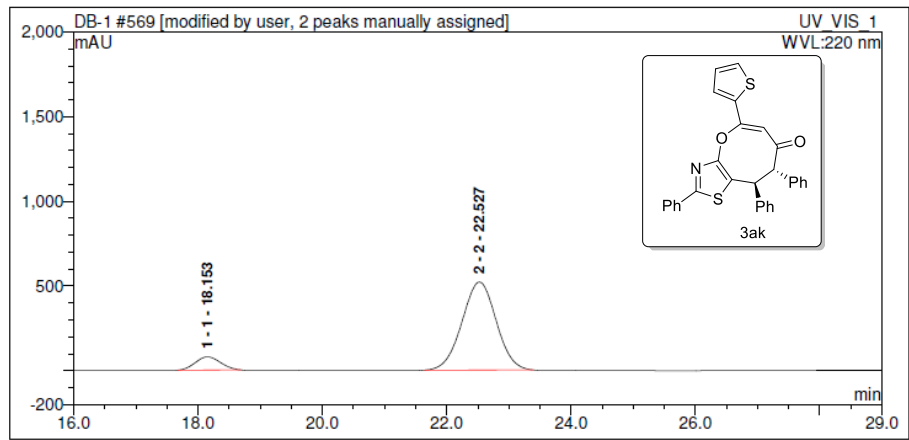
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	58.30333333	255.4095	50.26147586	180.2512	n.a.
2	2	62.20833333	252.7521	49.73852414	166.7045	n.a.



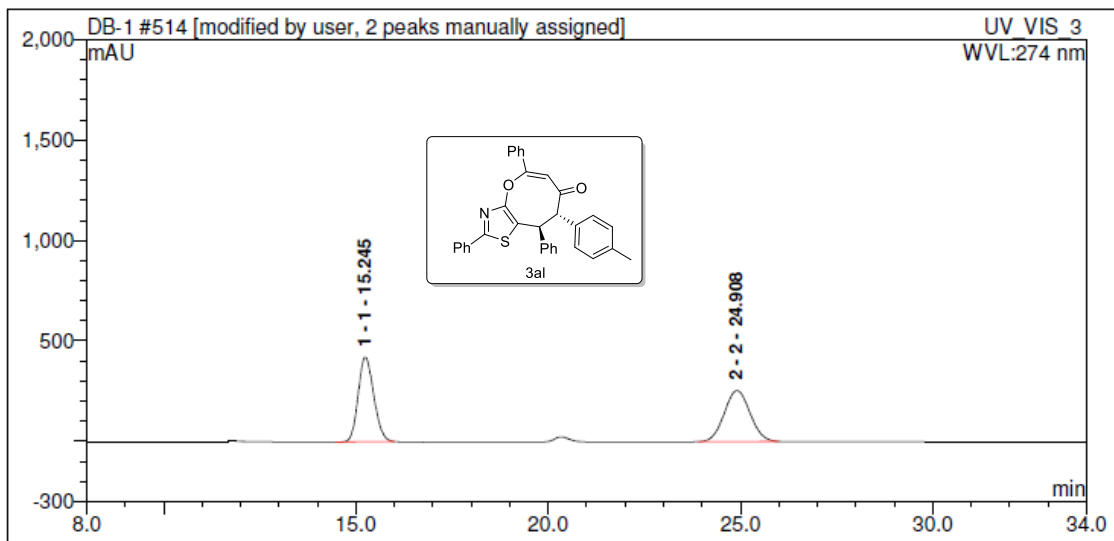
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	57.67	170.2319	89.579087	124.745	n.a.
2	2	61.41166667	19.80341	10.420913	14.9738	n.a.



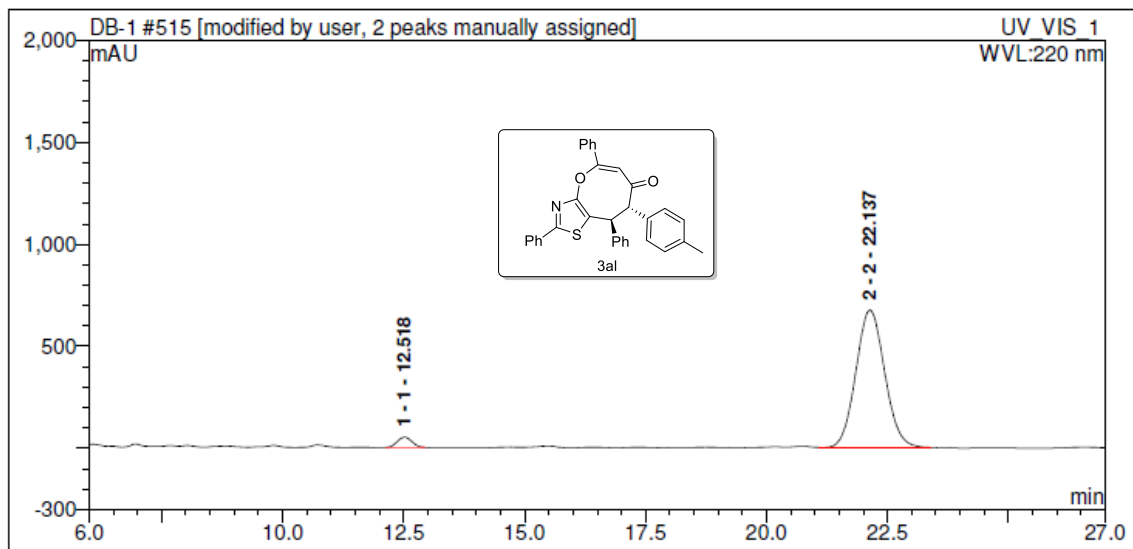
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.07833333	177.5868	50.32462912	328.2913	n.a.
2	2	23.37333333	175.2957	49.67537088	258.7539	n.a.



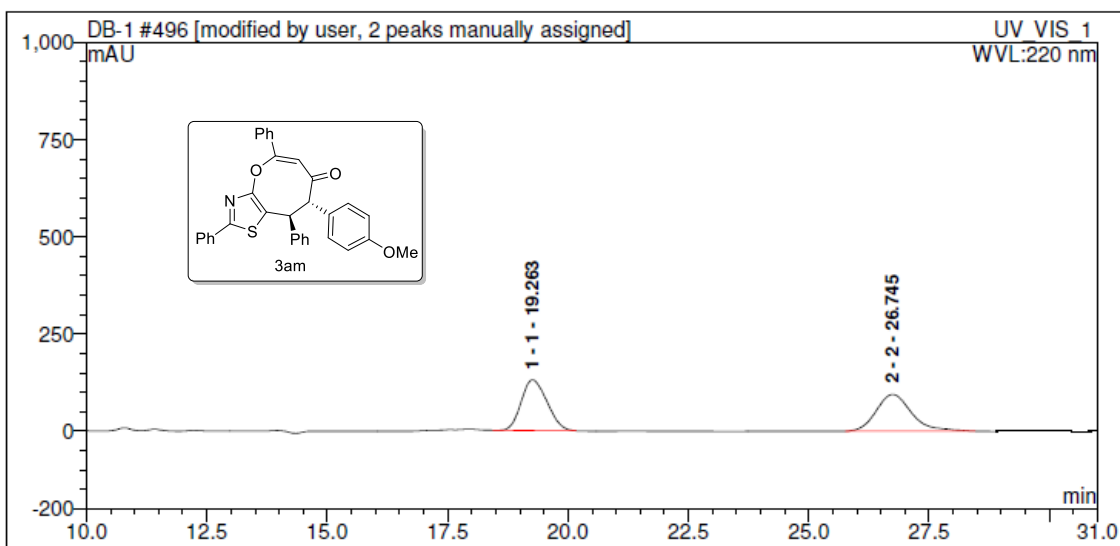
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.15333333	36.40806	9.895067117	77.71987	n.a.
2	2	22.52666667	331.5334	90.10493288	518.5578	n.a.



No.	Peak Name	Ret. Time (detected) min	Area mAU*min	Rel. Area(ident.) %	Height mAU	Amount
1	1	15.245	197.5824	50.07210711	420.5449	n.a.
2	2	24.90833333	197.0133	49.92789289	253.9416	n.a.



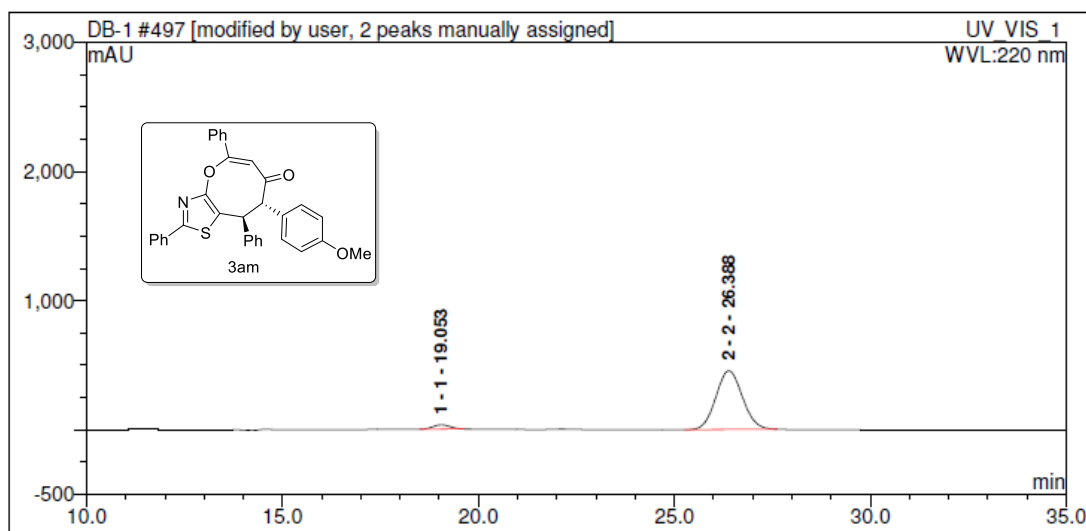
No.	Peak Name	Ret. Time (detected) min	Area mAU*min	Rel. Area(ident.) %	Height mAU	Amount
1	1	12.51833333	17.71098	3.663365958	50.47764	n.a.
2	2	22.13666667	465.7509	96.33663404	673.5787	n.a.



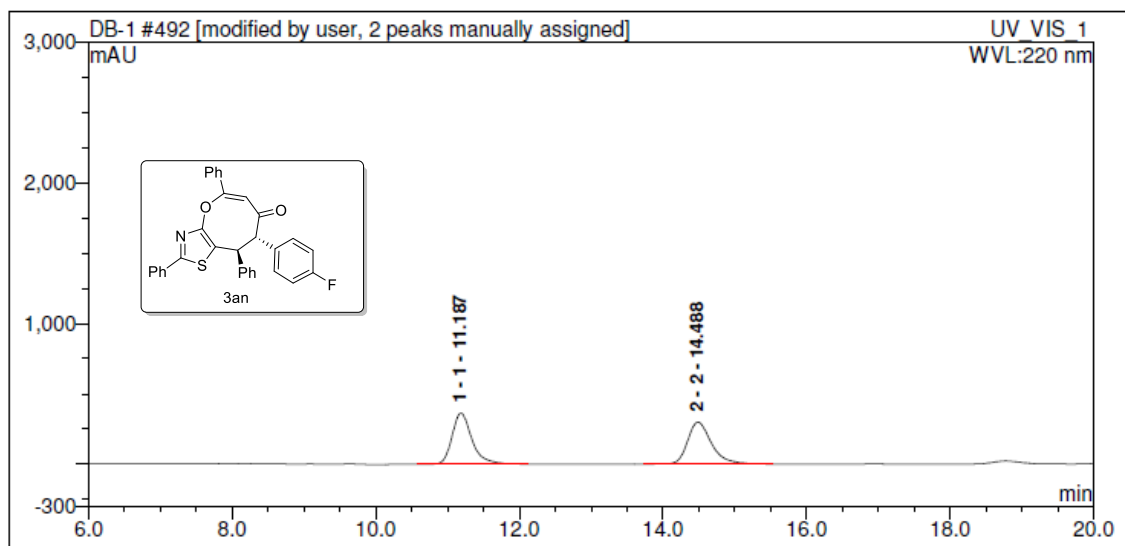
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.26333333	80.97766	50.2618981	130.4308	n.a.
2	2	26.745	80.13377	49.7381019	94.32082	n.a.

Operator:user Timebase:SCP_HPLC-2 Sequence:DB-1

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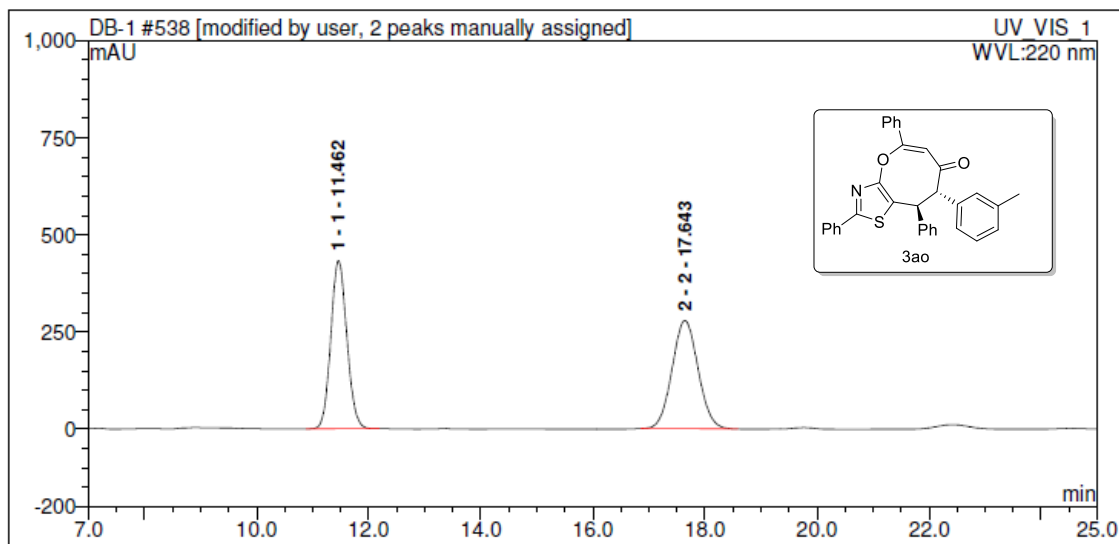
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.05333333	17.15618	4.581007963	33.08403	n.a.
2	2	26.38833333	357.3504	95.41899204	454.459	n.a.



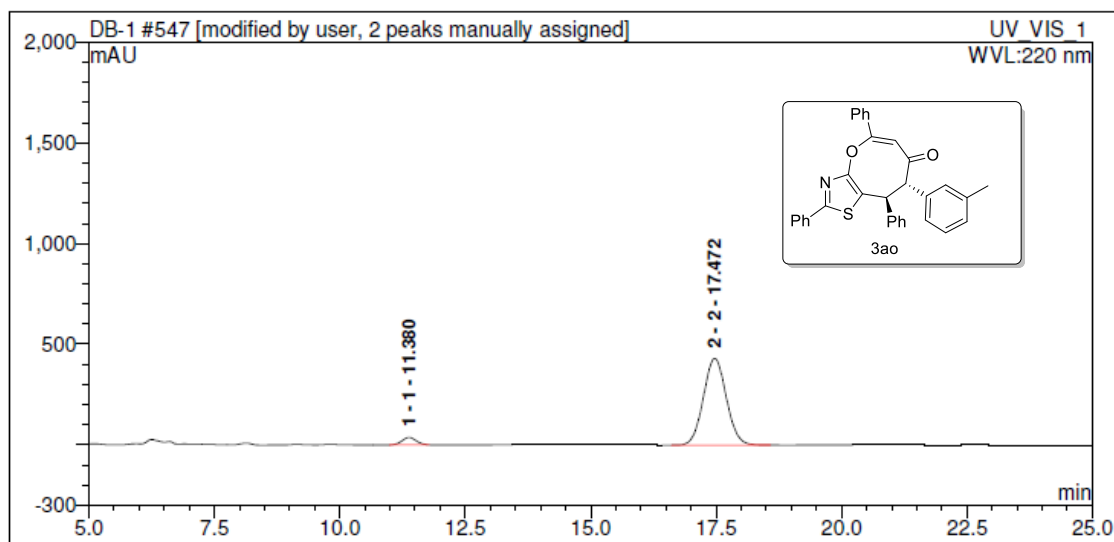
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.1866667	116.8537	50.05083296	363.2125	n.a.
2	2	14.4883333	116.6163	49.94916704	299.2496	n.a.



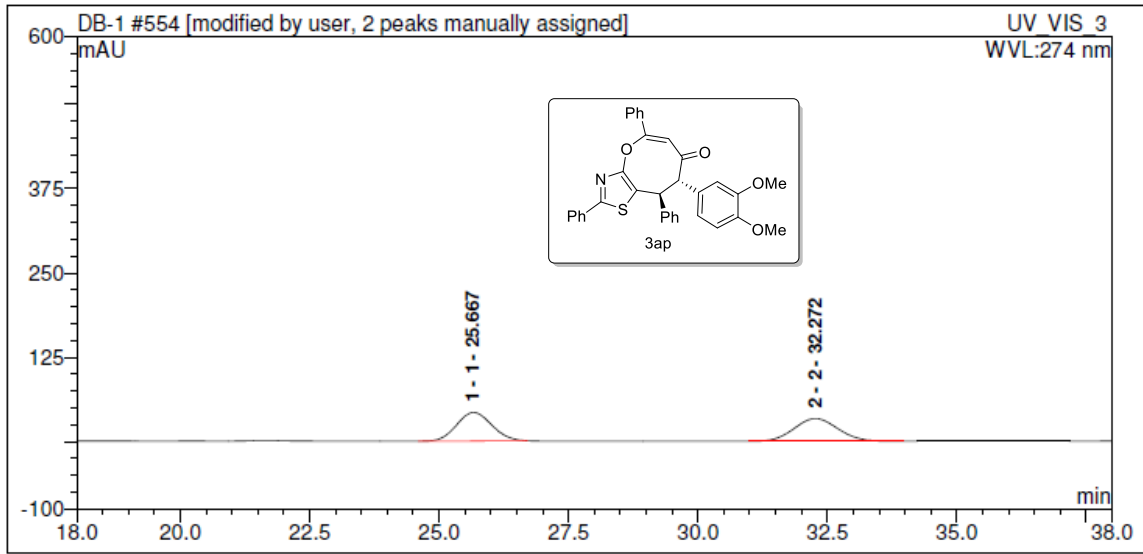
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.4166667	1.270806	4.061606843	5.10939	n.a.
2	2	14.2983333	30.01745	95.93839316	76.16825	n.a.



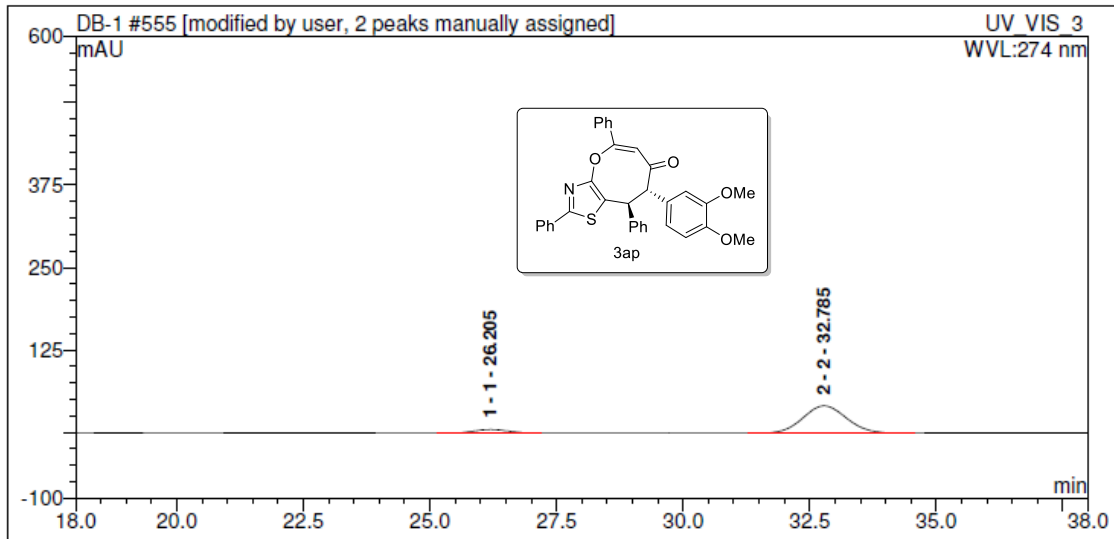
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.46166667	143.5963	48.91117499	433.3686	n.a.
2	2	17.64333333	149.9896	51.08882501	278.5612	n.a.



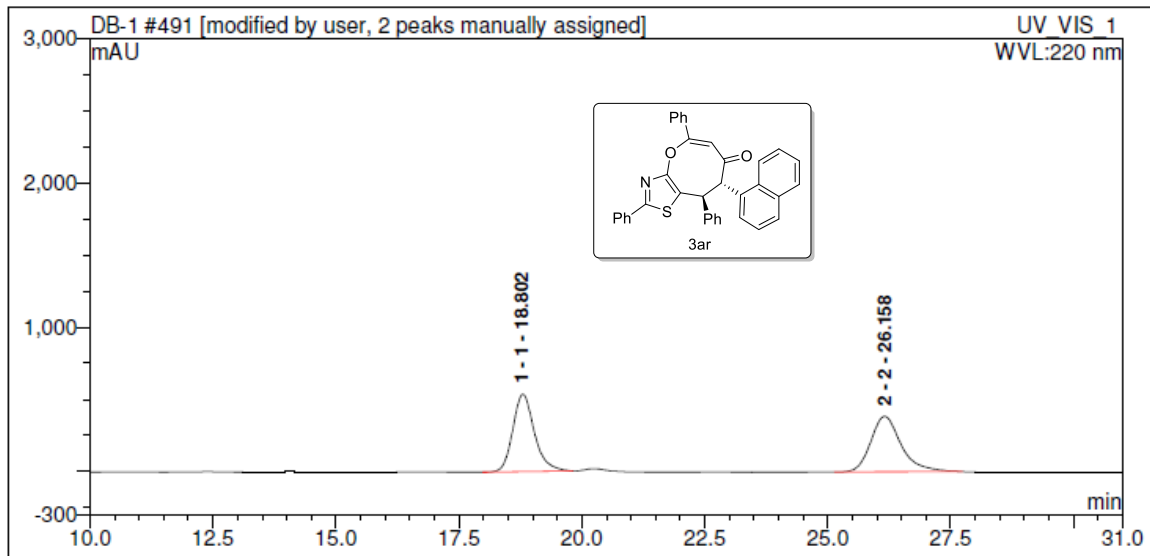
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.38	11.77564	4.910684766	36.77394	n.a.
2	2	17.47166667	228.0207	95.08931523	430.3469	n.a.



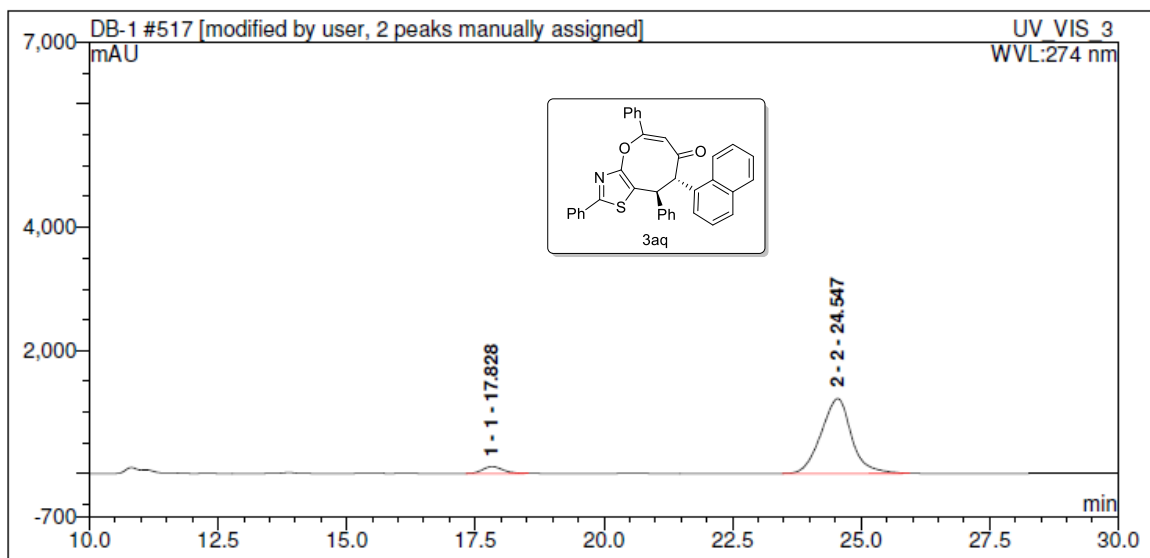
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	25.6666667	33.31768	49.88624566	42.2464	n.a.
2	2	32.2716667	33.46963	50.11375434	33.73113	n.a.



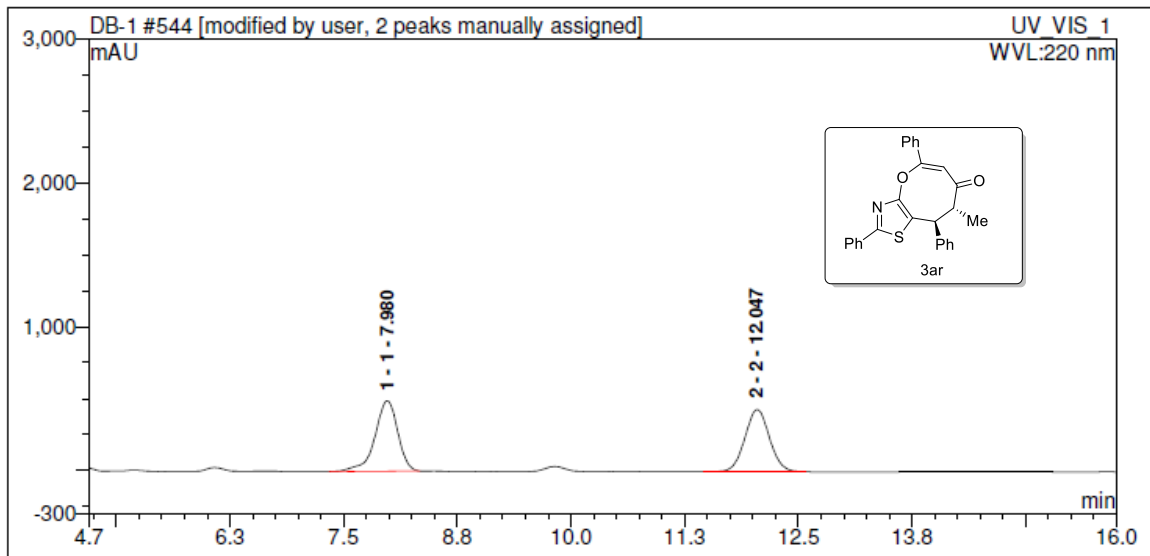
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	26.205	4.491429	9.70325739	5.70419	n.a.
2	2	32.785	41.79641	90.29674261	41.43716	n.a.



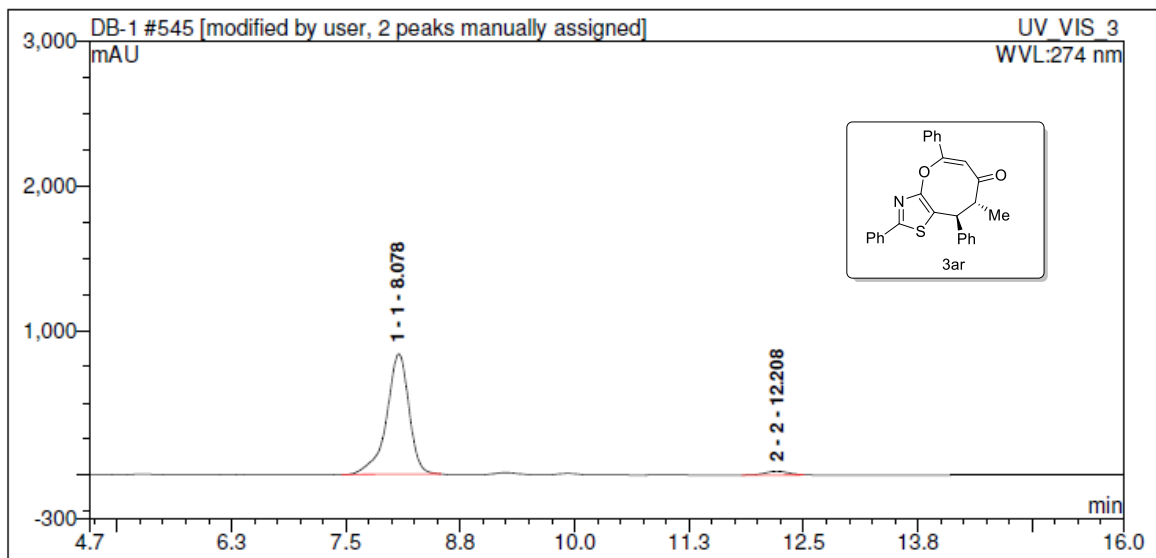
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.80166667	272.3092	49.71366864	535.04	n.a.
2	2	26.15833333	275.446	50.28633136	383.999	n.a.



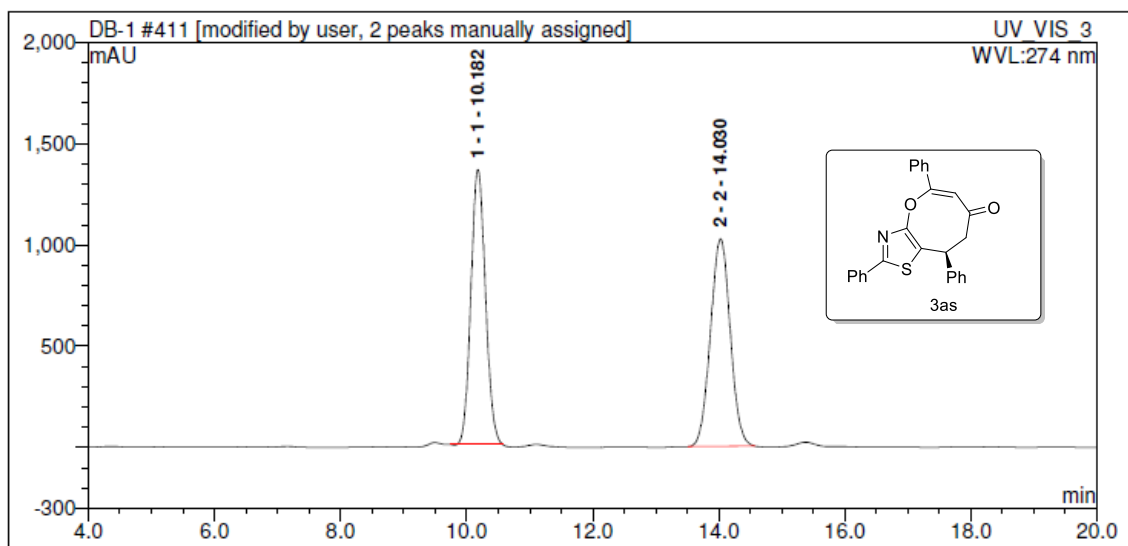
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.82833333	51.49857	5.817053922	112.5725	n.a.
2	2	24.54666667	833.8047	94.18294608	1214.137	n.a.



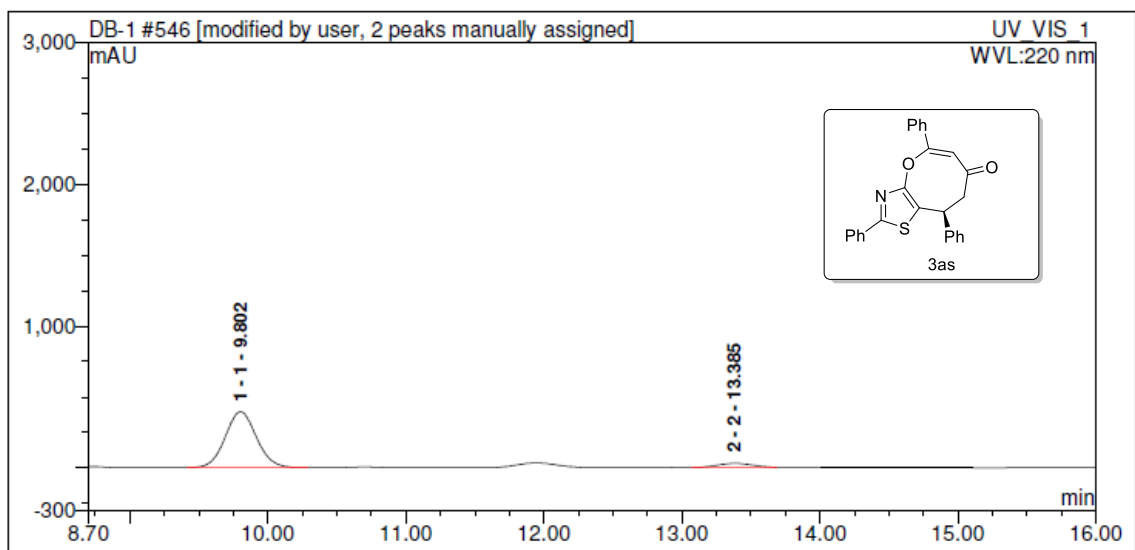
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1 1		7.98	142.8601	51.17346573	489.6427	n.a.
2 2		12.04666667	136.3082	48.82653427	432.7163	n.a.



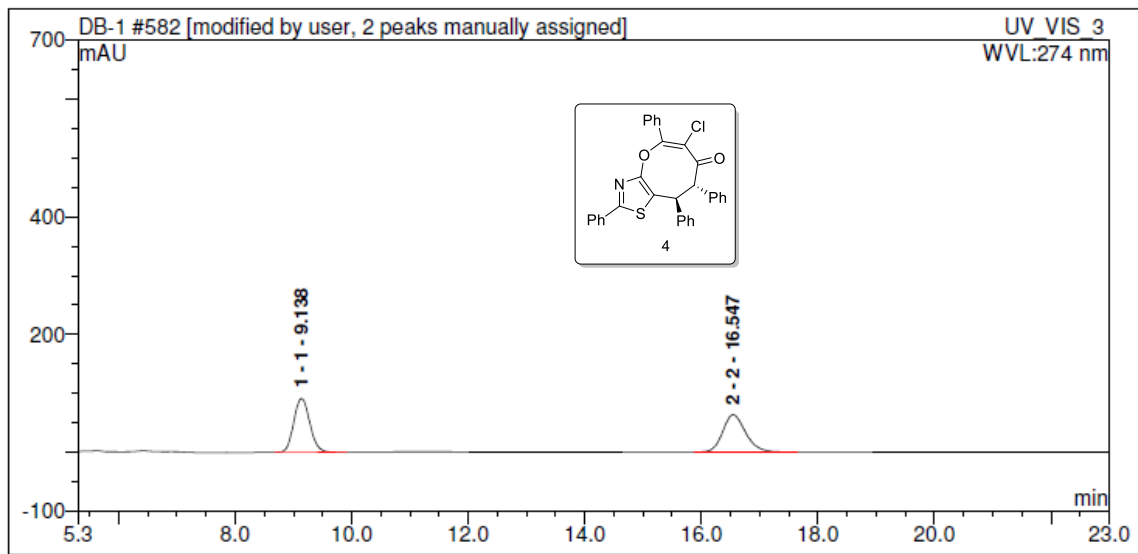
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1 1		8.078333333	236.6847	96.94813326	830.6967	n.a.
2 2		12.20833333	7.450686	3.051866742	25.21936	n.a.



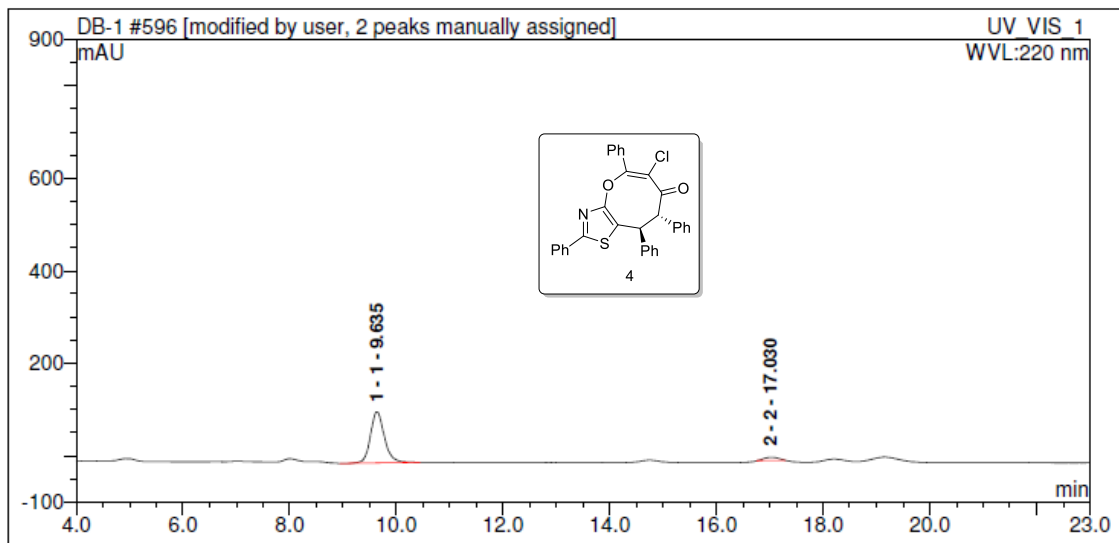
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.18166667	363.7767	49.3555388	1357.722	n.a.
2	2	14.03	373.2765	50.64444612	1025.884	n.a.



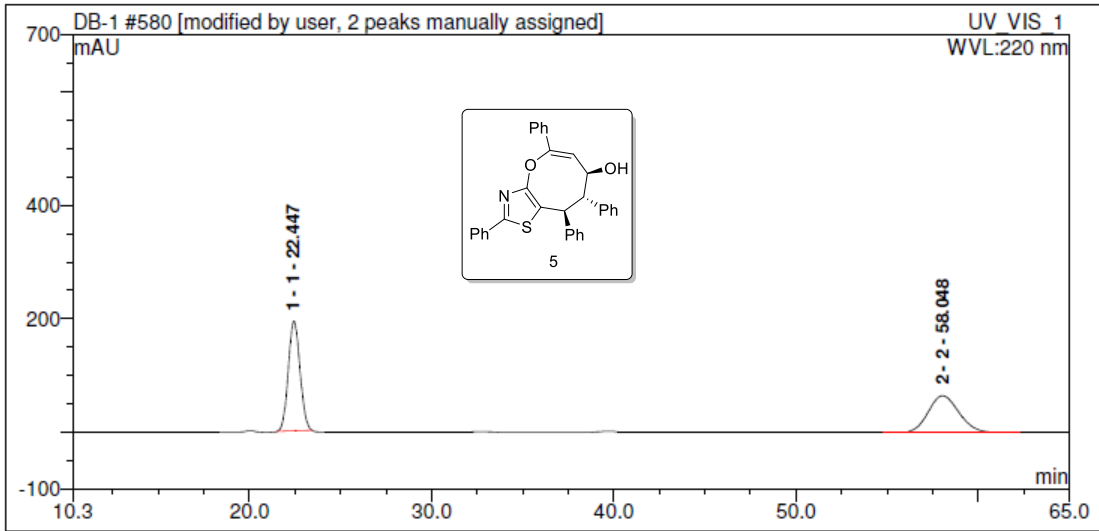
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.801666667	103.2075	92.32162371	393.2049	n.a.
2	2	13.385	8.583752	7.67837629	28.62494	n.a.



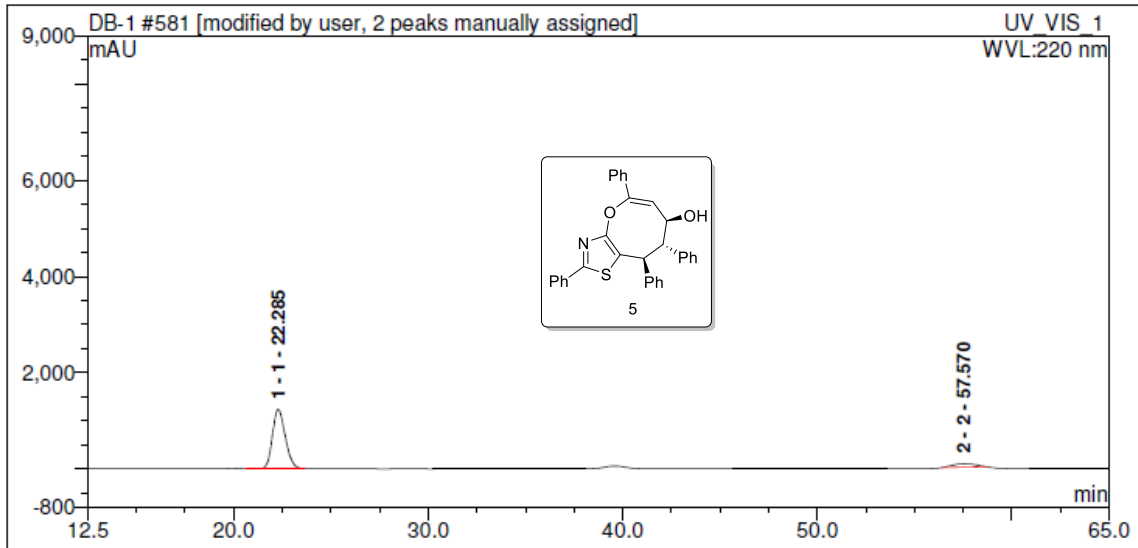
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.138333333	28.92474	49.62130837	91.10418	n.a.
2	2	16.54666667	29.36623	50.37869163	63.6697	n.a.



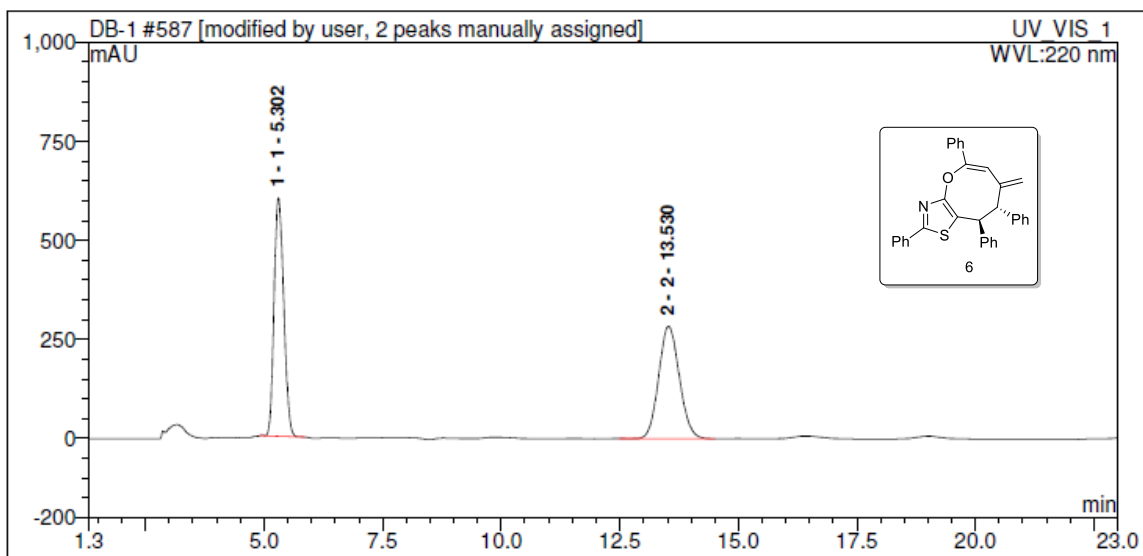
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	9.635	33.41325	93.60184996	110.3137	n.a.
2	2	17.03	2.283961	6.398150035	7.20052	n.a.



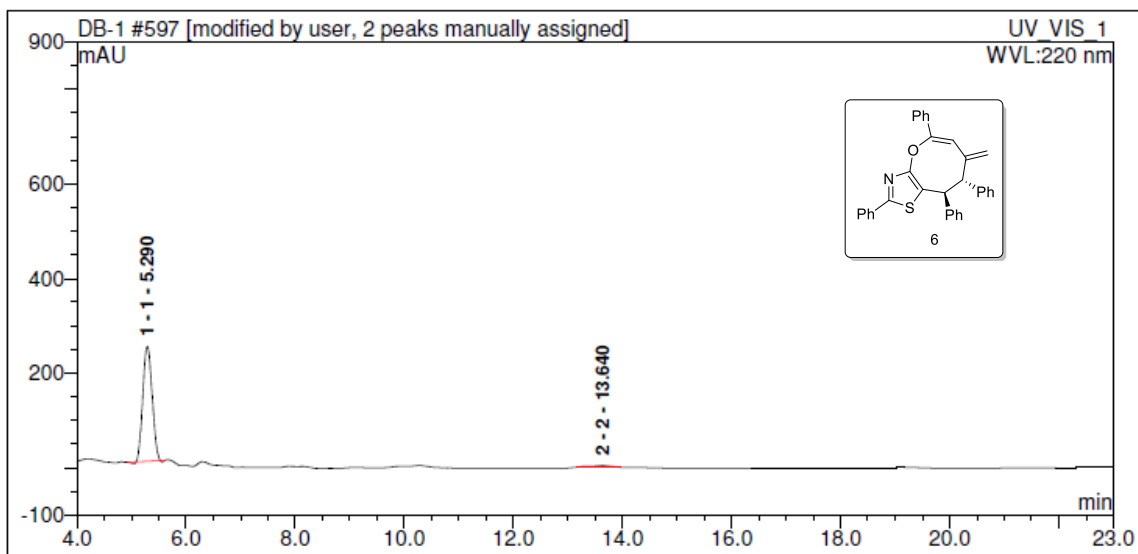
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.4466667	144.1098	53.28329814	193.2535	n.a.
2	2	58.0483333	126.3498	46.71670186	64.58702	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.285	943.8172	90.63131974	1231.649	n.a.
2	2	57.57	97.56365	9.368680261	71.79842	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	5.30166667	142.1706	49.75200346	602.4125	n.a.
2	2	13.53	143.5879	50.24799654	283.7144	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	5.29	47.93964	96.93104678	242.1977	n.a.
2	2	13.64	1.517827	3.068953224	3.11702	n.a.