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Inverting the reactivity of troponoid system in the higher-order cycloaddition

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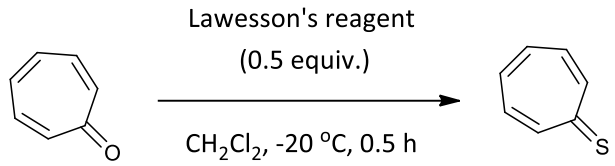
Contents

1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). Mass spectra were recorded on a Bruker Maxis Impact spectrometer using electrospray (ES+) ionization (referenced to the mass of the charged species, due to the oxidative conditions of the analysis in the mass spectra of the products **3** only the molecular peaks of the corresponding **9** were observed and therefore are reported). Optical rotations were measured on a Perkin-Elmer 241 polarimeter and $[\alpha]_D$ values are given in deg•cm•g^{-1}•dm^{-1}; concentration *c* is listed in g•(100 mL)$^{-1}$. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or Hanessian's stain. The enantiomeric ratio (er) of the products was determined by chiral stationary phase UPC^2 (Daicel Chiralpak IA and IC column). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (60, 35-70 µm, Merck KGaA). Aromatic unsaturated aldehydes were obtained using literature procedure.[1]

1 N. Daubresse, C. Francesch and C. Rolando, *Tetrahedron*, 1998, **54**, 10761.

2. Synthesis of tropothione 1

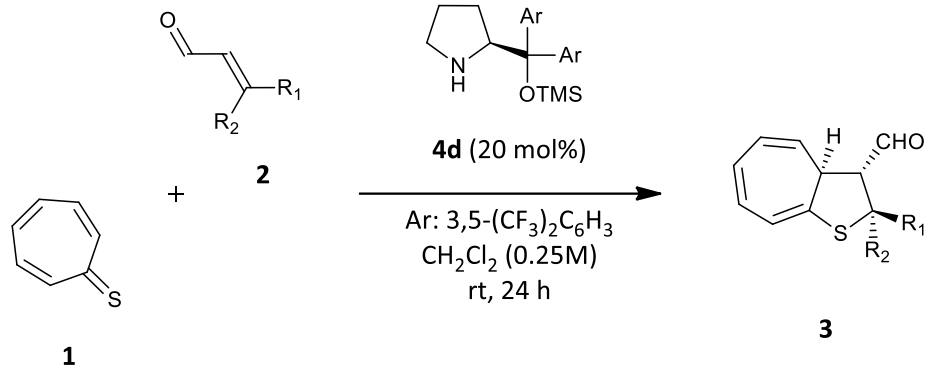


1

Tropone (212 mg, 195 µL, 2 mmol) was placed in a flame-dried round bottom flask and dry CH_2Cl_2 (2 mL) was added. After cooling to -20 °C Lawesson's reagent (202 mg, 1 mmol, 0.5 equiv.) was added in one portion. After stirring for 0.5 h at -20 °C, the reaction mixture was subjected to flash chromatography on silica gel (eluent: CH_2Cl_2). Fraction containing pure product **1** was evaporated under reduced pressure with ice-cold bath cooling. Pure product **1** was obtained as a red solid (146 mg, 60% yield) and stored as 1.0 M solution in dry CH_2Cl_2 at -20 °C. Spectroscopic data were in accordance with those reported in literature[2].

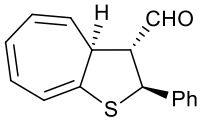
2 T. Machiguchi, *Tetrahedron* 1995, **51**, 1133.

3. Organocatalytic higher-order cycloaddition in the synthesis of 3



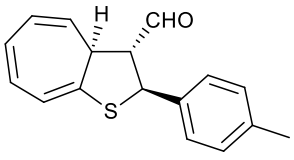
In an ordinary 4 mL glass vial, equipped with a teflon-coated magnetic stirring bar and a screw cap corresponding α,β-unsaturated aldehyde **2** (1.0 equiv., 0.1 mmol), catalyst **4d** (0.2 equiv., 0.02 mmol, 12 mg) were dissolved in CH_2Cl_2 (0.25 mL) and 1.0 M solution of tropothione **1** in CH_2Cl_2 (0.15 mL, 0.15 mmol) was added. After stirring for 24 h at ambient temperature pure products **3** were isolated by flash chromatography on silica gel (eluent: hexanes: CH_2Cl_2 from 80:20 to 70:30).

(2*S*,3*R*,3a*S*)-2-Phenyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3a



Following the general procedure, **3a** was isolated by FC on silica gel in 80% yield (20.3 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.70 (d, *J* = 1.9 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.37 – 7.35 (m, 2H), 7.33 – 7.29 (m, 1H), 6.48 (dd, *J* = 11.2, 6.4 Hz, 1H), 6.43 (dd, *J* = 11.2, 5.8 Hz, 1H), 6.24 (dd, *J* = 6.6, 1.7 Hz, 1H), 6.17 (ddd, *J* = 9.4, 5.8, 1.7 Hz, 1H), 5.16 (d, *J* = 9.4 Hz, 1H), 5.02 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.56 (ddd, *J* = 9.7, 8.0, 1.9 Hz, 1H), 3.19 – 3.10 (m, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.2, 137.4, 137.0, 130.5, 129.1 (2C), 128.6, 128.2, 128.1 (2C), 127.4, 124.7, 116.1, 69.6, 54.6, 48.6. HRMS calculated for [$C_{16}H_{12}OS+H^+$]: 253.0682; found: 253.0685. $[\alpha]_D^{22}$ = 34.5° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 260 nm; τ_{major} = 2.95 min, τ_{minor} = 2.82 min, (>99:1 er).

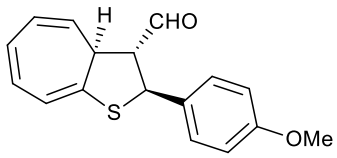
(2*S*,3*R*,3a*S*)-2-(*p*-Tolyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3b



Following the general procedure, **3b** was isolated by FC on silica gel in 60% yield (16.1 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 2.0 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.17 – 7.16 (m, 2H), 6.47 (dd, *J* = 11.2, 6.5 Hz, 1H), 6.42 (dd, *J* = 11.1, 5.7 Hz, 1H), 6.23 (dd, *J* = 6.5, 1.7 Hz, 1H), 6.16 (ddd, *J* = 9.5, 5.7, 1.7 Hz, 1H), 5.12 (d, *J* = 9.6 Hz, 1H), 5.02 (dd, *J* = 9.4, 4.2 Hz, 1H), 3.54 (ddd, *J* = 9.9, 8.1, 2.0 Hz, 1H), 3.14 (ddt, *J* = 8.0, 3.9, 1.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.4, 138.4, 137.6, 133.8, 130.4, 129.8 (2C), 128.2, 127.9 (2C), 127.4, 124.8, 116.0, 69.6, 54.5, 48.6, 21.3. HRMS calculated for [$C_{17}H_{14}OS+H^+$]: 267.0838; found: 267.0840. $[\alpha]_D^{23}$ = 26.4° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to

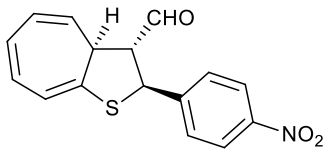
40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 334 nm; τ_{major} = 3.14 min, τ_{minor} = 2.92 min, (>99:1 er).

(2*S*,3*R*,3a*S*)-2-(4-Methoxyphenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3c



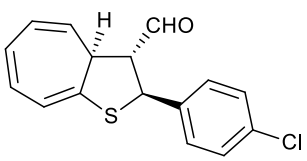
Following the general procedure, **3c** was isolated by FC on silica gel in 88% yield (25.0 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 2.0 Hz, 1H), 7.41 – 7.36 (m, 2H), 6.90 – 6.87 (m, 2H), 6.46 (dd, *J* = 11.1, 6.4 Hz, 1H), 6.42 (dd, *J* = 11.1, 5.7 Hz, 1H), 6.23 (dd, *J* = 6.5, 1.7 Hz, 1H), 6.18 – 6.14 (m, 1H), 5.11 (d, *J* = 9.7 Hz, 1H), 5.02 (dd, *J* = 9.4, 4.2 Hz, 1H), 3.80 (s, 3H), 3.52 (ddd, *J* = 10.0, 8.0, 2.1 Hz, 1H), 3.14 (ddt, *J* = 8.0, 3.9, 1.8 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.4, 159.8, 137.6, 130.4, 129.2 (2C), 128.6, 128.2, 127.4, 124.8, 116.1, 114.5 (2C), 69.7, 55.5, 54.2, 48.5. HRMS calculated for [$C_{17}H_{14}O_2S$+H^+]: 283.0787; found: 283.0789. $[\alpha]_D^{22}$ = 57.3° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 325 nm; τ_{major} = 3.53 min, τ_{minor} = 3.36 min, (>99:1 er).

(2*S*,3*R*,3a*S*)-2-(4-Nitrophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3d



Following the general procedure, **3d** was isolated by FC on silica gel in 72% yield (21.5 mg) as yellow crystal solid (tt.= 123-124°C) (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.73 (d, *J* = 1.4 Hz, 1H), 8.23-8.20 (m, 2H), 7.68-7.65 (m, 2H), 6.54 – 6.50 (m, 1H), 6.46 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.26 (dd, *J* = 6.6, 1.6 Hz, 1H), 6.19 (ddd, *J* = 9.3, 5.8, 1.7 Hz, 1H), 5.27 (d, *J* = 8.5 Hz, 1H), 5.01 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.53 (ddd, *J* = 8.6, 7.4, 1.4 Hz, 1H), 3.14 (ddt, *J* = 7.6, 4.4, 1.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 198.3, 147.9, 145.0, 135.9, 130.8, 129.2 (2C), 128.6, 127.8, 124.3 (2C), 124.2, 116.5, 69.4, 53.2, 48.6. HRMS calculated for [$C_{16}H_{11}O_3S$+H^+]: 297.0460; found: 297.0462. $[\alpha]_D^{22}$ = 176.0° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 290 nm; τ_{major} = 4.06 min, τ_{minor} = 3.69 min, (>99:1 er).

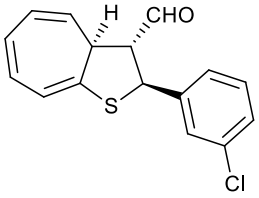
(2*S*,3*R*,3a*S*)-2-(4-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3e



Following the general procedure, **3e** was isolated by FC on silica gel in 70% yield (20.2 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.70 (d, *J* = 1.8 Hz, 1H), 7.42 – 7.40 (m, 2H), 7.34 – 7.31 (m, 2H), 6.48 (dd, *J* = 11.1, 6.4 Hz, 1H), 6.43 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.25 – 6.22 (m, 1H), 6.17 (ddd, *J* = 9.4, 5.8, 1.7 Hz, 1H), 5.13 (d, *J* = 9.1 Hz, 1H), 5.01

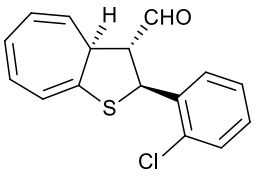
(dd, *J* = 9.4, 4.3 Hz, 1H), 3.49 (ddd, *J* = 9.4, 7.8, 1.8 Hz, 1H), 3.12 (ddt, *J* = 7.9, 3.9, 1.8 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 198.9, 136.8, 135.7, 134.3, 130.6, 129.5 (2C), 129.3 (2C), 128.4, 127.5, 124.5, 116.2, 69.6, 53.7, 48.6. HRMS calculated for [$C_{16}H_{11}ClOS+H^+$]: 287.0292; found: 287.0289. $[\alpha]_D^{22}$ = 23.6° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 343 nm; τ_{major} = 3.31 min, τ_{minor} = 3.02 min, (>99:1 er).

(2*S*,3*R*,3a*S*)-2-(3-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3f



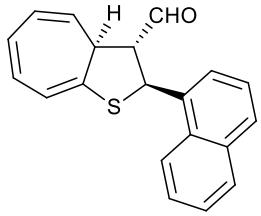
Following the general procedure, **3f** was isolated by FC on silica gel in 63% yield (18.1 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.71 (d, *J* = 1.8 Hz, 1H), 7.48-7.47 (m, 1H), 7.37-7.34 (m, 1H), 7.29 – 7.28 (m, 2H), 6.51 – 6.47 (m, 1H), 6.44 (dd, *J* = 11.1, 5.7 Hz, 1H), 6.24 (dd, *J* = 6.5, 1.6 Hz, 1H), 6.18 (ddd, *J* = 9.4, 5.7, 1.7 Hz, 1H), 5.12 (d, *J* = 9.3 Hz, 1H), 5.02 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.52 (ddd, *J* = 9.4, 7.8, 1.8 Hz, 1H), 3.12 (ddt, *J* = 7.8, 4.4, 1.8 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 198.8, 139.3, 136.7, 135.0, 130.6, 130.3, 128.8, 128.4, 128.2, 127.5, 126.4, 124.5, 116.3, 69.5, 53.8, 48.6. HRMS calculated for [$C_{16}H_{11}ClOS+H^+$]: 287.0292; found: 287.0295. $[\alpha]_D^{22}$ = 59.9° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 326 nm; τ_{major} = 2.66 min, τ_{minor} = 2.81 min, (98:2 er)

(2*S*,3*R*,3a*S*)-2-(2-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3g



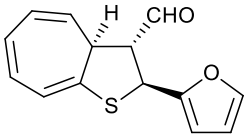
Following the general procedure, **3g** was isolated by FC on silica gel in 67% yield (19.3 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.73 (d, *J* = 1.7 Hz, 1H), 7.70 – 7.69 (m, 1H), 7.42 – 7.40 (m, 1H), 7.29 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 6.53 (ddd, *J* = 11.1, 6.4, 0.8 Hz, 1H), 6.42 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.25 (dd, *J* = 6.4, 1.6 Hz, 1H), 6.10 (ddd, *J* = 9.4, 5.8, 1.7 Hz, 1H), 5.67 (d, *J* = 6.5 Hz, 1H), 4.79 (dd, *J* = 9.3, 4.6 Hz, 1H), 3.48 (ddd, *J* = 6.8, 5.4, 1.7 Hz, 1H), 3.19 (ddt, *J* = 5.0, 3.4, 1.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 198.5, 137.3, 135.1, 133.8, 131.1, 130.1, 129.6, 129.5, 128.1, 127.5, 127.1, 124.5, 116.0, 68.1, 50.6, 47.6. HRMS calculated for [$C_{16}H_{11}ClOS+H^+$]: 287.0292; found: 287.0295. $[\alpha]_D^{22}$ = 41.8° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 341 nm; τ_{major} = 2.81 min, τ_{minor} = 2.92 min, (98:2 er)

(2*S*,3*R*,3a*S*)-2-(Naphthalen-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3h



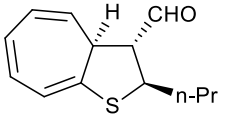
Following the general procedure, **3h** was isolated by FC on silica gel in 65% yield (19.8 mg) as dark red viscous oil (>20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.75 (d, *J* = 1.7 Hz, 1H), 8.22 – 8.20 (m, 1H), 7.93 – 7.88 (m, 1H), 7.85 – 7.80 (m, 2H), 7.61 – 7.59 (m, 1H), 7.55 – 7.53 (m, 1H), 7.47 – 7.45 (m, 1H), 6.56 (ddd, *J* = 11.1, 6.5, 0.8 Hz, 1H), 6.44 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.30 (dd, *J* = 6.5, 1.7 Hz, 1H), 6.12 (ddd, *J* = 9.4, 5.8, 1.7 Hz, 1H), 6.01 (d, *J* = 7.0 Hz, 1H), 4.84 (dd, *J* = 9.3, 4.6 Hz, 1H), 3.77 (ddd, *J* = 7.2, 5.8, 1.7 Hz, 1H), 3.23 (ddt, *J* = 6.1, 4.5, 1.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.7, 137.6, 134.2, 132.5, 131.3, 131.0, 129.3, 129.1, 128.0, 127.0, 126.9, 126.1, 125.6, 125.5, 124.7, 122.9, 115.9, 67.3, 50.3, 48.3. HRMS calculated for [$C_{20}H_{14}OS+H^+$]: 303.0838; found: 303.0840. $[\alpha]_D^{22}$ = 65.3° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 350 nm; τ_{major} = 3.69 min, τ_{minor} = 3.59 min, (>99:1 er).

(2*S*,3*R*,3a*S*)-2-(Furan-2-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3i



Following the general procedure, **3i** was isolated by FC on silica gel in 64% yield (15.6 mg)as dark red viscous oil (>20:1 dr).^{1}H NMR (700 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.5 Hz, 1H), 7.40 – 7.39 (m, 1H), 6.49 (ddd, *J* = 11.1, 6.5, 0.8 Hz, 1H), 6.42 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.36 (dt, *J* = 3.3, 0.8 Hz, 1H), 6.33 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.19 (dd, *J* = 6.3, 1.6 Hz, 1H), 6.14 (ddd, *J* = 9.4, 5.9, 1.7 Hz, 1H), 5.26 (dd, *J* = 7.6, 0.8 Hz, 1H), 4.99 (dd, *J* = 9.3, 4.6 Hz, 1H), 3.73 (ddd, *J* = 7.7, 6.4, 1.5 Hz, 1H), 3.11 (ddt, *J* = 6.3, 4.6, 1.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 198.8, 150.6, 143.0, 136.3, 130.8, 128.2, 127.1, 124.3, 116.0, 110.9, 108.4, 65.5, 47.9, 46.9. HRMS calculated for [$C_{14}H_{10}O_2S+H^+$]: 243.0474; found: 243.0480. $[\alpha]_D^{23}$ = 168.8° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 265 nm; τ_{major} = 2.74 min, τ_{minor} = 2.53 min, (98:2 er).

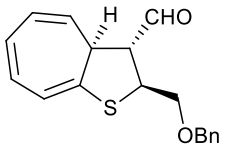
(2*R*,3*R*,3a*S*)-2-Propyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3j



Following the general procedure, **3j** was isolated by FC on silica gel in 65% yield (14.3 mg) as dark red viscous oil (12:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 1.9 Hz, 1H), 6.46 (dd, *J* = 11.1, 6.5 Hz, 1H), 6.38 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.17 – 6.13 (m, 2H), 5.06 (dd, *J* = 9.4, 3.8 Hz, 1H), 4.05 – 4.02 (m, 1H), 3.09 – 3.06 (m, 2H), 1.87 (dddd, *J* = 14.1, 10.3, 6.2, 4.4 Hz, 1H), 1.70 (dtd, *J* = 13.5, 9.9, 5.0 Hz, 1H), 1.49 – 1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.2, 137.6, 131.1, 127.7, 127.3, 124.3, 115.9, 67.2, 51.6, 48.5, 36.6, 22.5, 13.9. HRMS calculated for [$C_{13}H_{14}OS+H^+$]: 219.0838; found: 219.0841. $[\alpha]_D^{22}$ = 76.7° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-

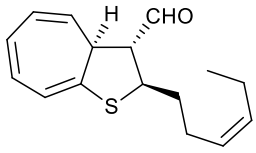
PrOH, 2.5 mL/min; detection wavelength = 350 nm; τ_{major} = 2.87 min, τ_{minor} = 2.08 min, (98.5:1.5 er).

(2*R*,3*R*,3a*S*)-2-Hexyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3k



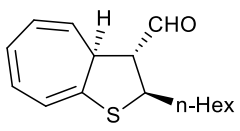
Following the general procedure, **3k** was isolated by FC on silica gel in 63% yield (16.5 mg) as dark red viscous oil (17:1:1 dr) ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 1.9 Hz, 1H), 6.46 (dd, *J* = 11.1, 6.5 Hz, 1H), 6.38 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.17 – 6.13 (m, 2H), 5.05 (dd, *J* = 9.4, 3.7 Hz, 1H), 4.02 (ddd, *J* = 10.0, 6.7, 4.5 Hz, 1H), 3.10 – 3.06 (m, 2H), 1.92 – 1.85 (m, 1H), 1.73 – 1.67 (m, 1H), 1.41 – 1.25 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.2, 137.6, 131.1, 127.7, 127.3, 124.3, 115.9, 67.2, 51.9, 48.5, 34.5, 31.7, 29.2, 29.1, 22.7, 14.2. HRMS calculated for [$C_{16}H_{20}OS+H^+$]: 261.1308; found: 261.1310. $[\alpha]_D^{22}$ = 66.2° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 352 nm; τ_{major} = 3.12 min, τ_{minor} =2.36 min, (98:2 er).

(2*S*,3*R*,3a*S*)-2-((Benzyloxy)methyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3l



Following the general procedure, **3l** was isolated by FC on silica gel in 65% yield (19.4 mg) as dark red viscous oil (13:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.67 (d, *J* = 1.3 Hz, 1H), 7.39 – 7.30 (m, 5H), 6.50 – 6.46 (m, 1H), 6.38 (dd, *J* = 11.1, 5.8 Hz, 1H), 6.14 – 6.12 (m, 1H), 6.10 (ddd, *J* = 9.4, 5.8, 1.7 Hz, 1H), 4.96 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.28 (ddd, *J* = 8.8, 6.3, 4.8 Hz, 1H), 3.68 (dd, *J* = 9.7, 6.3 Hz, 1H), 3.63 (dd, *J* = 9.7, 8.8 Hz, 1H), 3.41 (td, *J* = 4.6, 1.3 Hz, 1H), 3.15 (tt, *J* = 4.6, 1.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.7, 137.6, 137.0, 131.5, 128.7 (2C), 128.2, 128.1 (2C), 127.7, 127.2, 124.1, 115.9, 73.4, 70.6, 62.6, 49.6, 47.2. HRMS calculated for [$C_{18}H_{16}O_2S+H^+$]: 296.0944; found: 297.0947. $[\alpha]_D^{23}$ = 72.8° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 344 nm; τ_{major} = 3.39 min, τ_{minor} = 3.08 min, (98.5:1.5er)

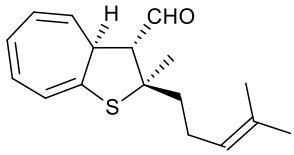
(2*R*,3*R*,3a*S*)-2-((*Z*)-Hex-3-en-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3m



Following the general procedure, **3m** was isolated by FC on silica gel in 67% yield (17.4 mg) as dark red viscous oil (20:1 dr). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 1.7 Hz, 1H), 6.49 – 6.45 (m, 1H), 6.40 – 6.37 (m, 1H), 6.18 – 6.13 (m, 2H), 5.46 – 5.42 (m, 1H), 5.31 – 5.27 (m, 1H), 5.08 – 5.05 (m, 1H), 4.06 – 4.02 (m, 1H), 3.10 – 3.07 (m, 2H), 2.18 – 2.13 (m, 2H), 2.07 – 2.03 (m, 2H), 1.96 – 1.91 (m, 1H), 1.82 – 1.77 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.1, 137.4,

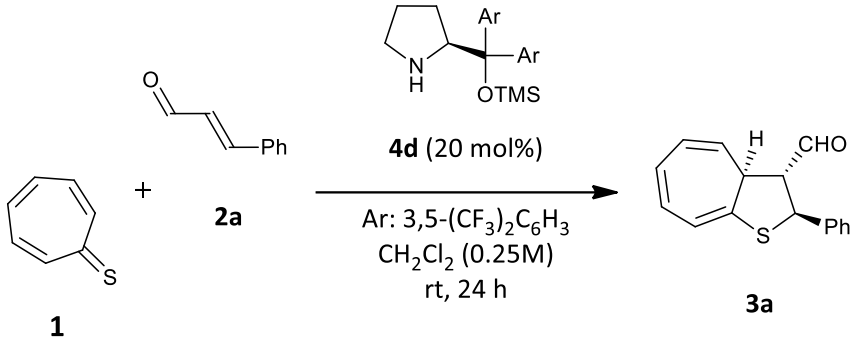
133.6, 131.2, 127.6, 127.3, 127.0, 124.3, 115.8, 66.9, 51.1, 48.3, 34.5, 26.6, 20.8, 14.4. HRMS calculated for [$C_{16}H_{18}OS+H^+$]: 259.1151; found: 259.1158. $[\alpha]_D^{22}$ = 71.1° (*c* = 1.0, $CHCl_3$). The er was determined by UPC[2] using a chiral Chiralpack IG column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 299 nm; τ_{major} = 3.13 min, τ_{minor} = 2.27 min, (98.5:1.5 er).

(2*R*,3*R*,3a*S*)-2-Methyl-2-(5-methylhex-4-en-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3n



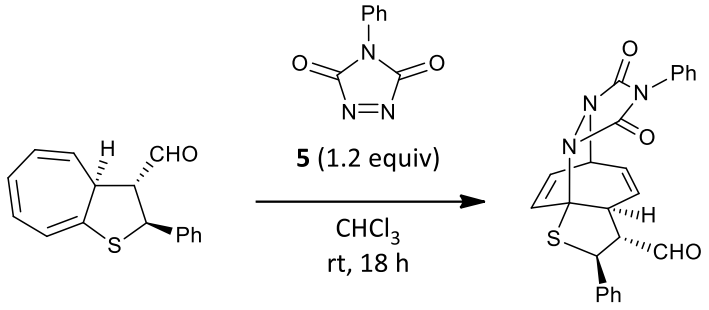
Following the general procedure, **3n** was isolated by FC on silica gel in 67% yield (18.4 mg) as dark red viscous oil (3.5:1 dr). Major diastereoisomer: ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 2.4 Hz, 1H), 6.47 – 6.36 (m, 2H), 6.24 (dd, *J* = 6.6, 1.8 Hz, 1H), 6.15 (ddd, *J* = 9.7, 5.8, 1.9 Hz, 1H), 5.12 (dddd, *J* = 7.1, 5.7, 3.0, 1.5 Hz, 1H), 4.92 (dd, *J* = 9.5, 4.0 Hz, 1H), 3.28 (ddt, *J* = 9.5, 3.8, 1.8 Hz, 1H), 3.20 (dd, *J* = 9.4, 2.4 Hz, 1H), 2.28 – 2.21 (m, 1H), 2.08 (ddd, *J* = 19.3, 12.5, 6.2 Hz, 1H), 2.02 (ddd, *J* = 13.8, 11.0, 4.8 Hz, 1H), 1.95 (ddd, *J* = 13.8, 11.2, 5.4 Hz, 1H), 1.70 (s, 3H), 1.63(s, 3H), 1.53 (s, 3H). ^{13}C NMR (176 MHz, CDCl3) δ 200.6, 137.1, 132.9, 130.1, 127.9, 127.2, 124.2, 123.2, 117.6, 70.9, 61.9, 47.3, 40.7, 25.8, 25.2, 24.9, 17.9. Minor diastereoisomer: ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.88 (d, *J* = 2.2 Hz, 1H), 6.46 – 6.37 (m, 2H, overlapping with major diastereoisomer), 6.22 (dd, *J* = 6.4, 1.7 Hz, 1H), 6.15 (ddt, *J* = 9.0, 5.0, 2.3 Hz, 1H, overlapping with major diastereoisomer), 5.09 (ddq, *J* = 8.6, 5.7, 1.5 Hz, 1H), 4.91 (ddd, *J* = 9.9, 5.9, 4.1 Hz, 1H, overlapping with major diastereoisomer), 3.26 (dd, *J* = 3.9, 1.9 Hz, 1H), 3.20 (dd, *J* = 9.4, 2.4 Hz, 1H, overlapping with major diastereoisomer), 2.28 – 2.21 (m, 1H, overlapping with major diastereoisomer), 2.08 (ddd, *J* = 19.3, 12.5, 6.2 Hz, 1H, overlapping with major diastereoisomer), 2.02 (ddd, *J* = 13.8, 11.0, 4.8 Hz, 1H, overlapping with major diastereoisomer), 1.95 (ddd, *J* = 13.8, 11.2, 5.4 Hz, 1H, overlapping with major diastereoisomer), 1.67 (s, 3H), 1.66 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.3, 137.2, 132.7, 130.1 (overlapping with major diastereoisomer), 127.9, 127.1, 124.7, 123.4, 117.2, 77.2, 73.0, 62.0, 47.6, 38.5, 29.9, 25.8, 25.8, 24.7, 24.3, 17.8. HRMS calculated for [$C_{17}H_{20}OS+H^+$]: 273.1308; found: 273.1313. $[\alpha]_D^{22}$ = 73.5° (*c* = 1.0, $CHCl_3$). The er was determined by UPC[2] using a chiral Chiralpack IA column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 354 nm; τ_{major} = 2.36 min, τ_{minor} = 1.94 min, (98:2 er).

4. Enantioselective synthesis of (2*S*,3*R*,3a*S*)-2-phenyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3a on a 1 g scale



In a round-bottom flask equipped with a magnetic stirring bar, aldehyde **2a** (1 equiv., 7.58 mmol, 1.00 g), catalyst **4d** (0.2 equiv., 1.52 mmol, 0.905 g) were dissolved in CH_2Cl_2 (19 mL). Subsequently, 1.0 M solution of tropothione **1** in CH_2Cl_2 (11.4 mL, 11.4 mmol) was added and the reaction mixture was stirred for 24 h at ambient temperature. Crude product **3a** was purified by the flash chromatography on silica gel (eluent: hexanes: CH_2Cl_2 from 80:20 to 70:30) to afford **3a** in 78% yield (1.500 g, >20:1 dr) as a dark red viscous oil. NMR and HPLC data were in accordance with previously obtained results.

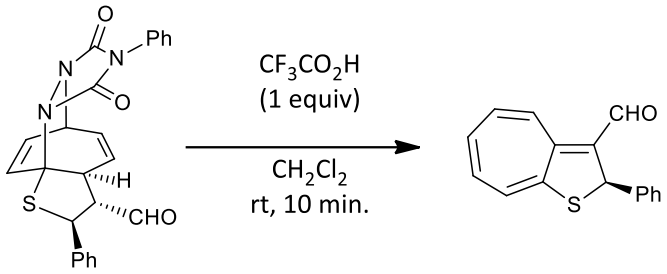
5. Hetero-Diels-Alder reaction of 3a with electron-poor N=N double bond



3a **6**

In an ordinary 4 mL glass vial, equipped with a Teflon-coated magnetic stirring bar and a screw cap **3a** (25.4 mg, 0.1 mmol, 1.0 equiv.) was dissolved in $CHCl_3$ (1 mL) and 4-phenyl-1,2,4-triazoline-3,5-dione **5** (21.0 mg, 0.12 mmol, 1.2 equiv.) was added in one portion. After stirring at ambient temperature for 18 h crude reaction mixture was directly subjected to flash chromatography (eluent: Et_2O : hexanes 8:2). Product **6** was obtained as white crystals in 90% yield (38.7 mg). **(2*S*,3*R*,3a*S*,6*S*,11a*R*)-8,10-Dioxo-2,9-diphenyl-3,3a,6,8,9,10-hexahydro-2*H*-6,11a-ethenothieno[2,3-*c*][1,2,4]triazolo[1,2-*a*][1,2]diazepine-3-carbaldehyde 6** ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.61 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.55 – 7.53 (m, 2H), 7.48 – 7.50 (m, 2H), 7.42 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 6.65 (dd, *J* = 8.9, 7.1 Hz, 1H), 6.56 (dd, *J* = 8.9, 1.0 Hz, 1H), 6.01 (ddd, *J* = 11.2, 7.3, 2.9 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.15 – 5.07 (m, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.13 (ddd, *J* = 12.8, 11.2, 1.8 Hz, 1H), 3.54 (dt, *J* = 12.6, 2.5 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.4, 150.8, 150.7, 135.9, 134.3, 131.5, 131.1, 130.8, 129.3 (2C), 129.2 (2C), 129.1 (2C), 128.8, 128.5, 126.3 (2C), 123.3, 75.2, 62.4, 58.8, 54.7, 49.6. HRMS calculated for [$C_{24}H_{19}N_3O_3S$+H^+]: 430.1220; found: 430.1229. $[\alpha]_D^{24}$ = -81.8° (*c* = 1.0, $CHCl_3$).

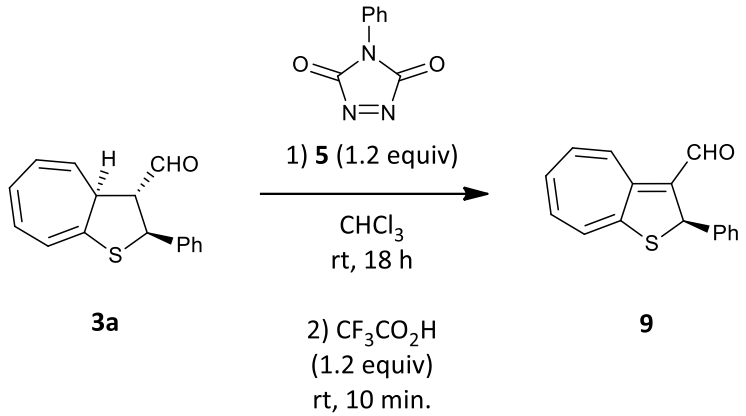
6. Synthesis of (*R*)-2-phenyl-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 9



6 **9**

In an ordinary 4 mL glass vial, equipped with a Teflon-coated magnetic stirring bar and a screw cap **6** (42.9 mg; 0.1 mmol; 1.0 equiv.) was dissolved in CH_2Cl_2 (1mL) and trifluoroacetic acid (11.4 mg; 0.1 mmol; 1.0 equiv.) was added in one portion. After stirring in ambient temperature for 10 minutes crude reaction mixture was directly subjected to flash column chromatography (eluent: CH_2Cl_2). Product was obtained as a red amorphous solid in 75% yield (18.9 mg). **(*R*)-2-Phenyl-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde** ^{1}H NMR (700 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 7.38 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 (d, *J* = 11.9 Hz, 1H), 7.24 – 7.21 (m, 1H), 6.43 (dt, *J* = 8.7, 1.0 Hz, 1H), 6.42 (s, 1H), 6.24 (ddt, *J* = 10.8, 8.7, 0.9 Hz, 1H), 6.20 – 6.16 (m, 1H), 6.03 (s, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 185.0, 160.6, 153.8, 143.8, 135.2, 133.9, 130.4, 129.6, 128.8 (2C), 127.7, 127.5 (2C), 124.2, 123.9, 56.6. HRMS calculated for [$C_{16}H_{12}OS$+H^+]: 253.0682; found: 253.0685. $[\alpha]_D^{23}$ = -790.0° (*c* = 1.0, $CHCl_3$). The er was determined by UPC^2 using a chiral Chiralpack IA column gradient from 100% CO_2 up to 40%; *i*-PrOH, 2.5 mL/min; detection wavelength = 336 nm; τ_{major} = 4.52 min, τ_{minor} = 4.69 min, (98:2 er).

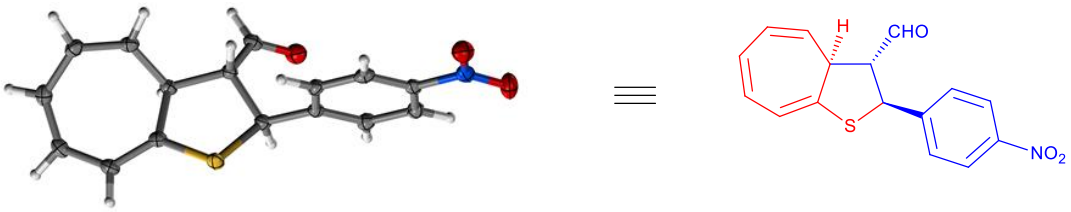
7. One-pot synthesis of (*R*)-2-phenyl-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 9



3a **9**

In an ordinary 4 mL glass vial, equipped with a Teflon-coated magnetic stirring bar and a screw cap **3a** (25.4 mg; 0.1 mmol; 1.0 equiv) was dissolved in $CHCl_3$ (1mL) and 4-phenyl-1,2,4-triazoline-3,5-dione (21.0 mg; 0.12 mmol; 1.2 equiv) was added in one portion. After stirring in ambient temperature for 18 h trifluoroacetic acid (13.7 mg; 0.12 mmol; 1.2 equiv) was added in one portion. After stirring in room temperature for 30 minutes crude reaction mixture was directly subjected to flash column chromatography (eluent: CH_2Cl_2). Product was obtained as a red amorphous solid in 52% yield (13.1 mg). NMR and HPLC data were in accordance with previously obtained results.

8. Crystal and X-ray data for (2*S*,3*R*,3a*S*)-2-(4-nitrophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3d



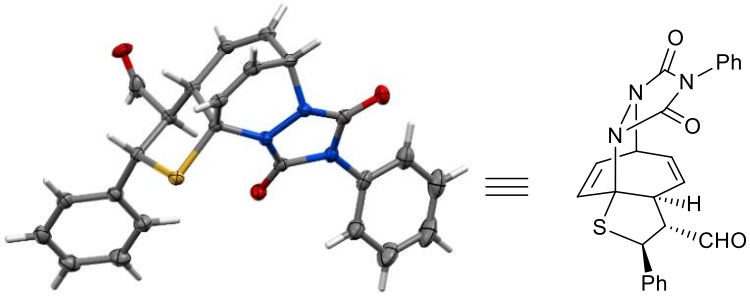
Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer[3] with PhotonJet micro-focus X-ray Source Cu-Kα (λ = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software.[3] The crystal structure was solved by using direct methods with the SHELXT 2018/2 program.[4] Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic thermal parameters by using the SHELXL 2018/3 program.[5] All hydrogen atoms were placed in calculated positions (C–H = 0.95–1.00 Å) and included as riding contributions with isotropic displacement parameters set to 1.2 times the U_{eq} of the parent atom.

3d: Formula $C_{16}H_{13}NO_3S$, orthorhombic, space group $P2_12_12_1$, Z = 4, unit cell constants a = 6.9092(1), b = 10.1436(1), c = 19.7001(1) Å, V = 1380.67(3) Å^3. The integration of the data yielded a total of 40039 reflections with θ angles in the range of 4.49 to 66.53°, of which all 2435 unique (R_{int} = 2.04%) were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 191 parameters converged at R_1 = 1.92% and wR_2 = 4.83% for all data. The largest peak in the final difference electron density synthesis was 0.152 e Å^{-3} and the largest hole was -0.150 e Å^{-3}. The goodness-of-fit was 1.100. The absolute configuration was unambiguously determined from anomalous scattering, by calculating the x Flack parameter[6] of -0.007(3) using 995 quotients.

CCDC 1906777 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

9. Crystal and X-ray data for (2*S**,3*R**,3a*S**,6*S**,11a*R**)-8,10-dioxo-2,9-diphenyl-3,3a,6,8,9,10-hexahydro-2*H*-6,11a-ethenothieno[2,3-*c*][1,2,4]triazolo[1,2-*a*][1,2]diazepine-3-carbaldehyde *rac*-6

The relative configuration of **6** was assigned based on the single crystal X-ray analysis of crystals obtained via recrystallization of racemic sample of *rac*-**6**. The absolute configuration of **6** was established given the result of this expaeriment and the assignment of the absolute configuration of **3** (for details see paragraph above). The single crystal X-ray diffraction study at 100 K revealed that compound *rac*-**6** ($C_{24}H_{19}N_3O_3S$) crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (Z = 8) and the crystal structure consists of two crystallographically independent formula units in the unit cell. The independent molecules have an inverted configuration and a similar conformation. One of these molecules has a disordered formyl group.



Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer[3] with PhotonJet micro-focus X-ray Source Cu-Kα (*λ* = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software.[3] The crystal structure was solved by using direct methods with the SHELXT 2018/2 program.[4] Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic thermal parameters by using the SHELXL 2018/3 program.[5] All hydrogen atoms were placed in calculated positions (C–H = 0.95–1.00 Å) and included as riding contributions with isotropic displacement parameters set to 1.2 times the U_{eq} of the parent atom.

rac-**6:** Formula $C_{24}H_{19}N_3O_3S$, monoclinic, space group $P2_1/c$, Z = 8, unit cell constants a = 10.2822(1), b = 14.2079(1), c = 27.6670(1) Å, b = 100.257(1)°, V = 3977.24(5) Å^3. The integration of the data yielded a total of 134496 reflections with θ angles in the range of 3.25 to 66.60 of which 7009 were independent (R_{int} = 2.72%), and 6889 were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 568 parameters converged to R_1 = 3.32% for observed data and wR_2 = 8.36% for all data. The goodness-of-fit was 1.074.

The largest peak in the final difference electron density synthesis was 0.357 e Å^{-3} and the largest hole was -0.263 e Å^{-3}. CCDC 1920168 contain the supplementary crystallographic data

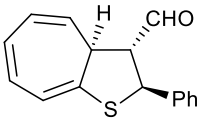
for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

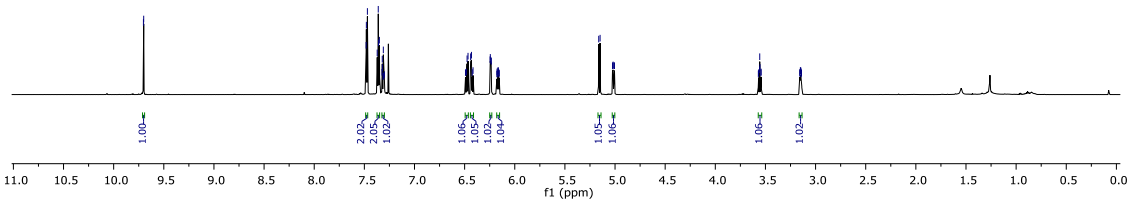
3 Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England, 2019.
4 G. M. Sheldrick *Acta Cryst.* 2015, **A71**, 3.
5 G. M. Sheldrick *Acta Cryst.* 2015, **C71**, 3.
6 S. Parsons, H. D. Flac and T. Wagner *Acta Cryst.* 2013, **B69**, 249.

10. NMR data

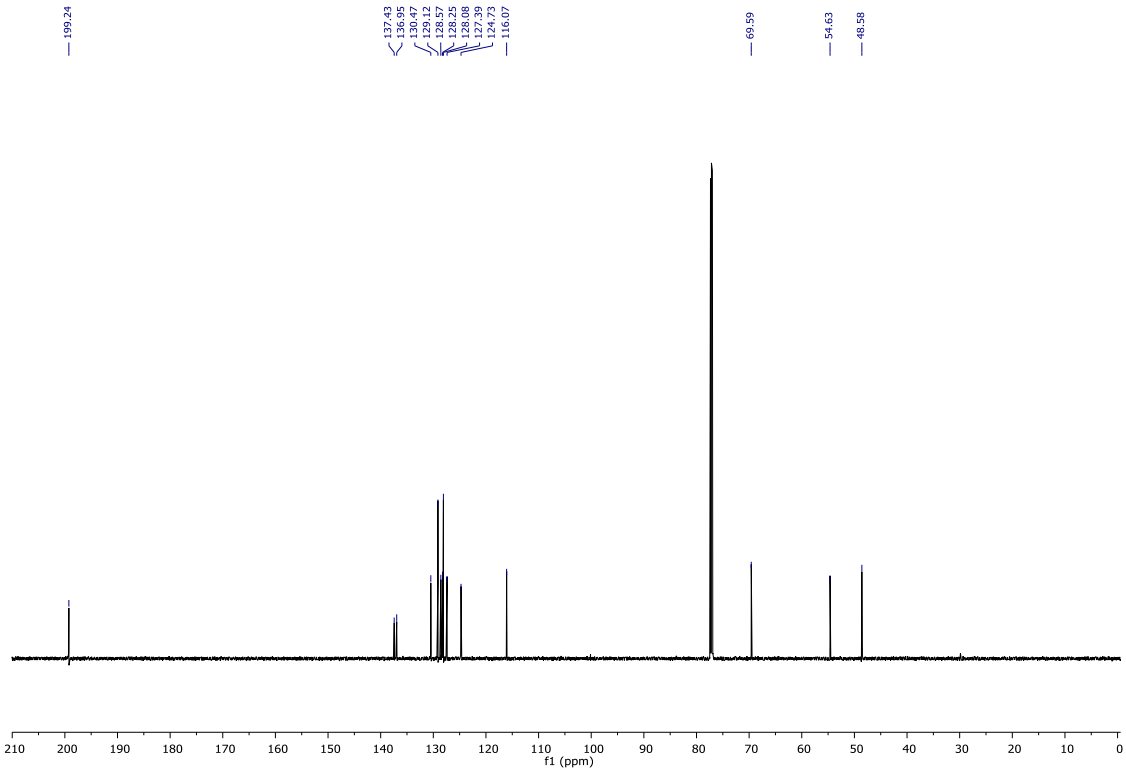
(2*S*,3*R*,3a*S*)-2-Phenyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3a

^{1}H NMR



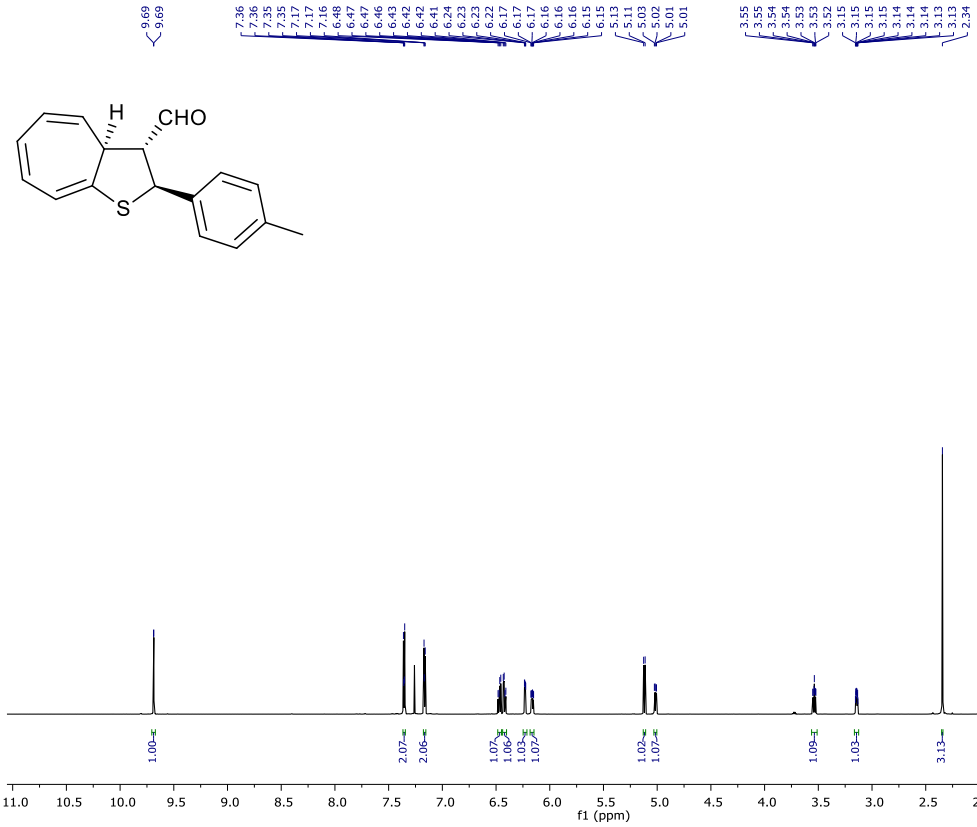


^{13}C NMR

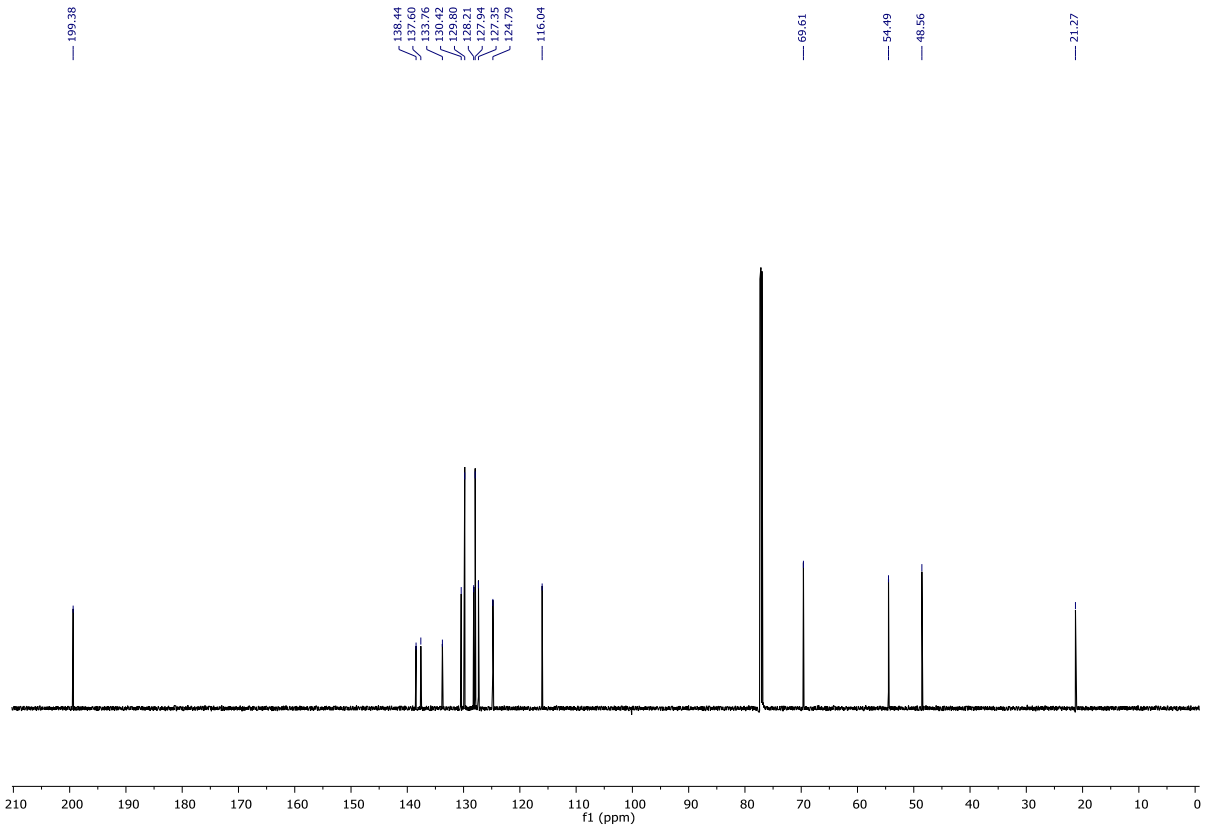


(2*S*,3*R*,3a*S*)-2-(*p*-Tolyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3b

^{1}H NMR

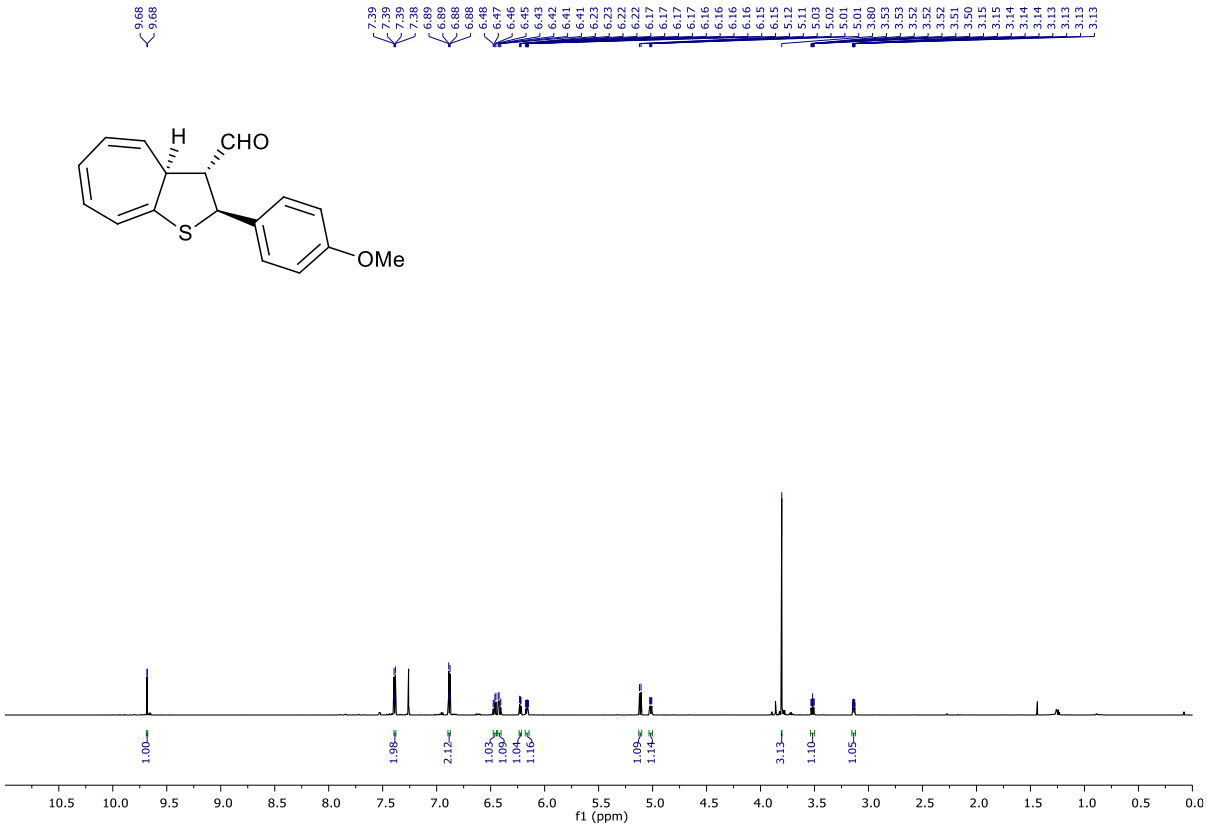


^{13}C NMR

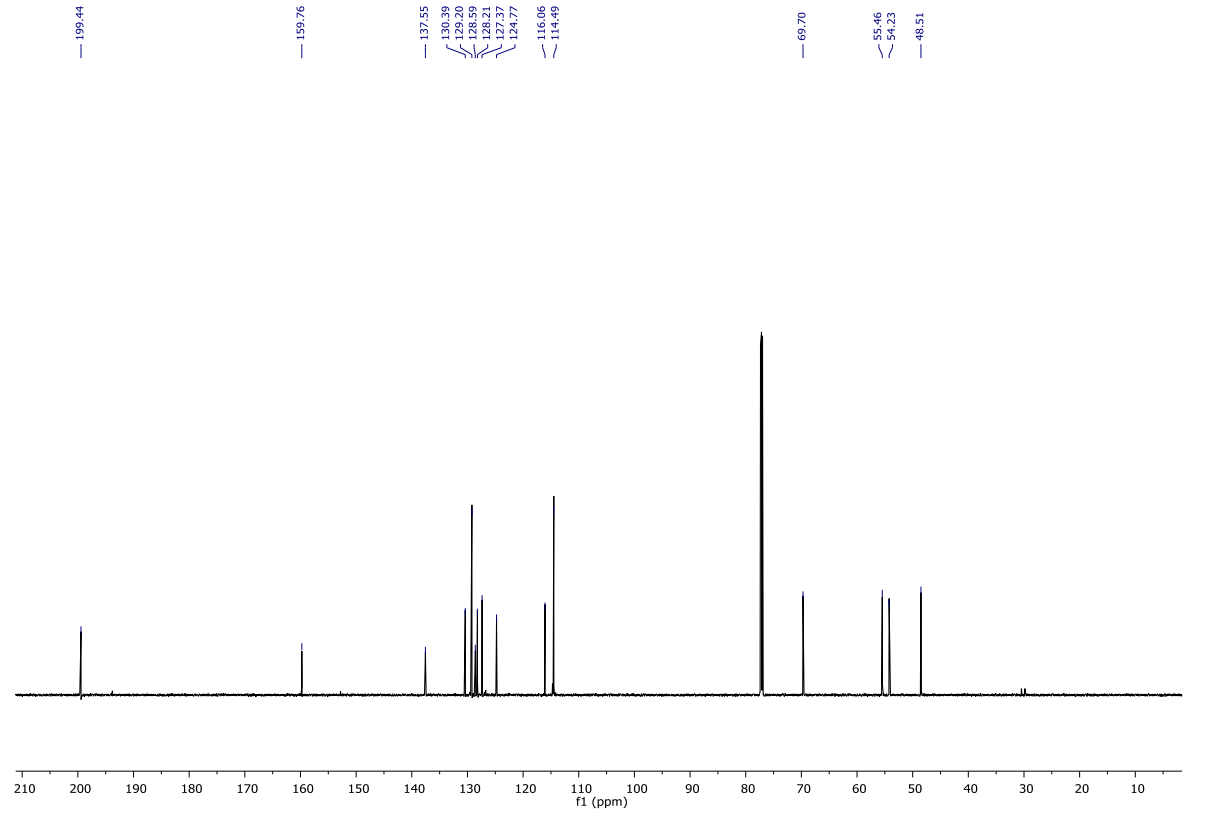


(2*S*,3*R*,3a*S*)-2-(4-Methoxyphenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3c

^{1}H NMR

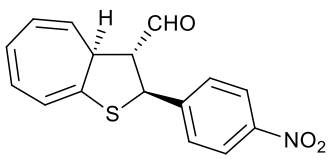


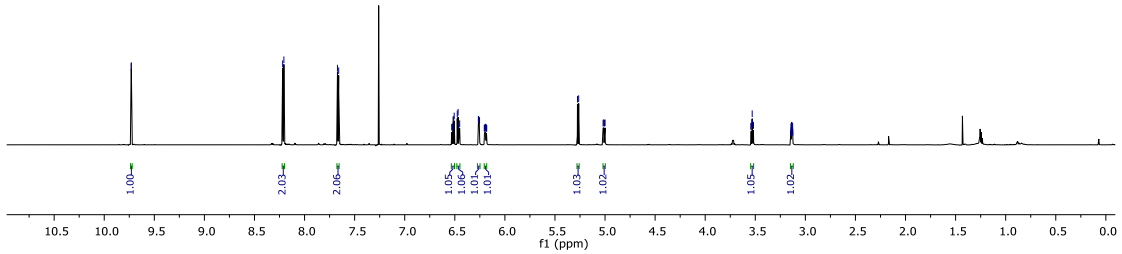
^{13}C NMR



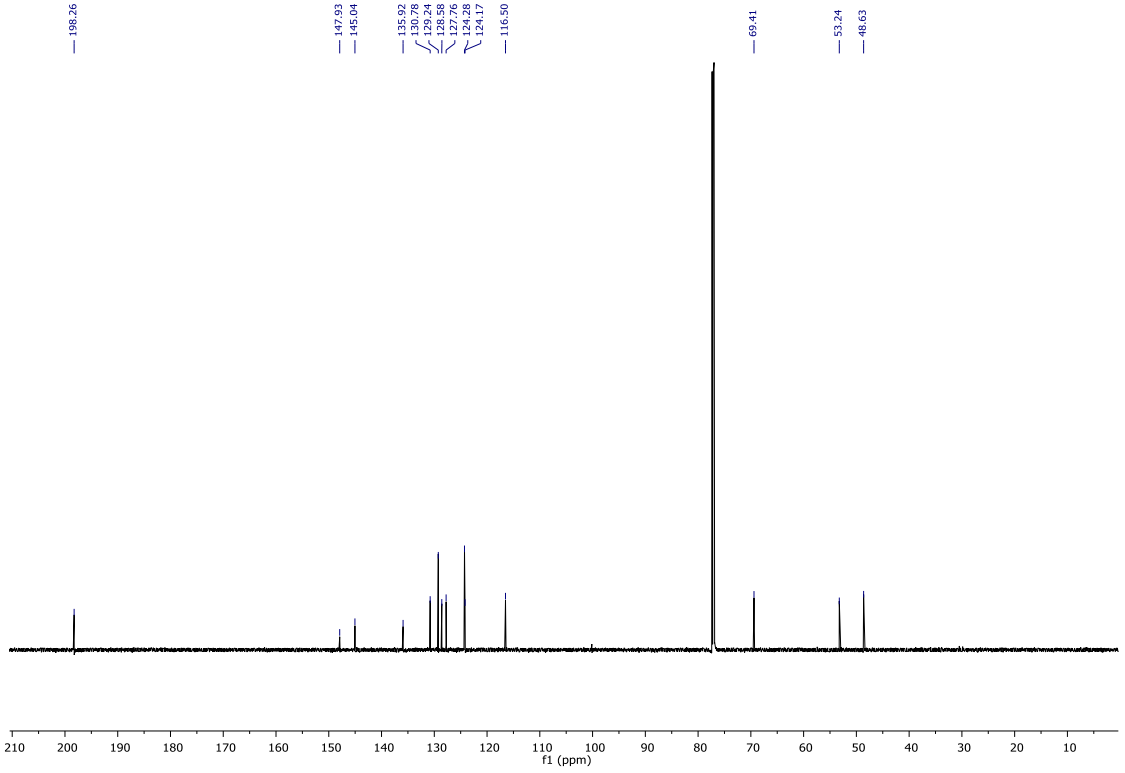
(2*S*,3*R*,3a*S*)-2-(4-Nitrophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3d

^{1}H NMR



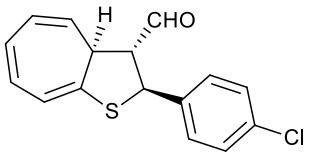


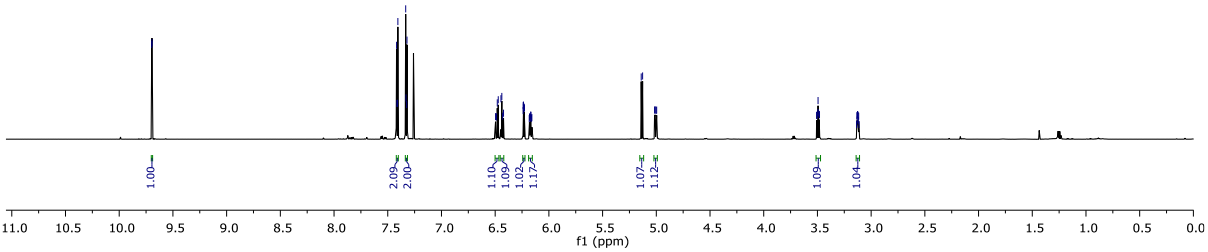
^{13}C NMR



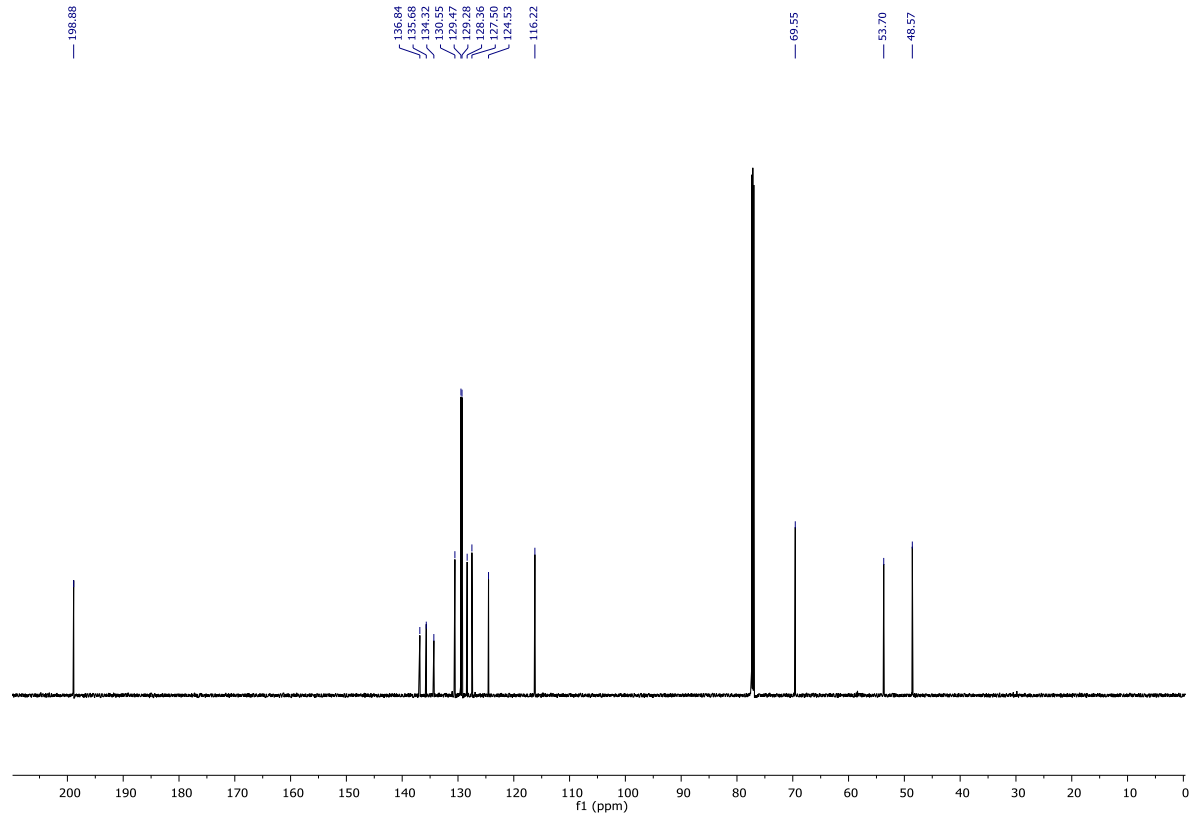
(2*S*,3*R*,3a*S*)-2-(4-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde
3e

^{1}H NMR



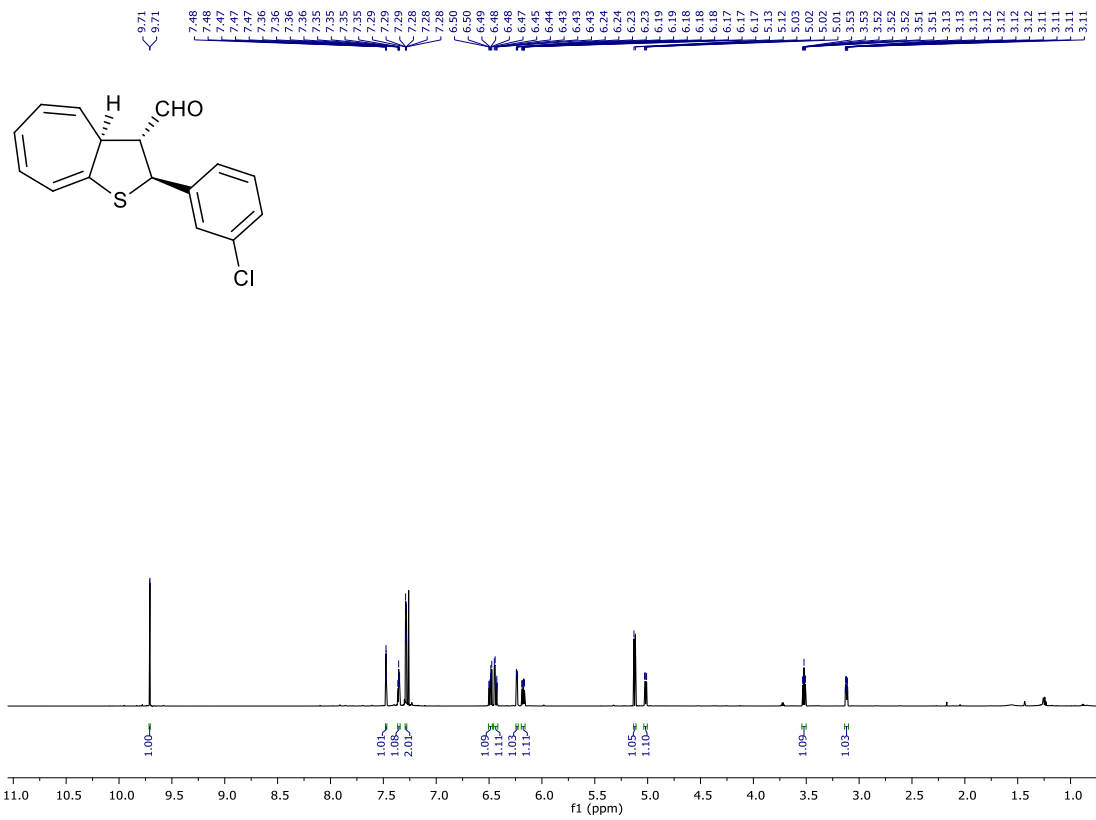


^{13}C NMR

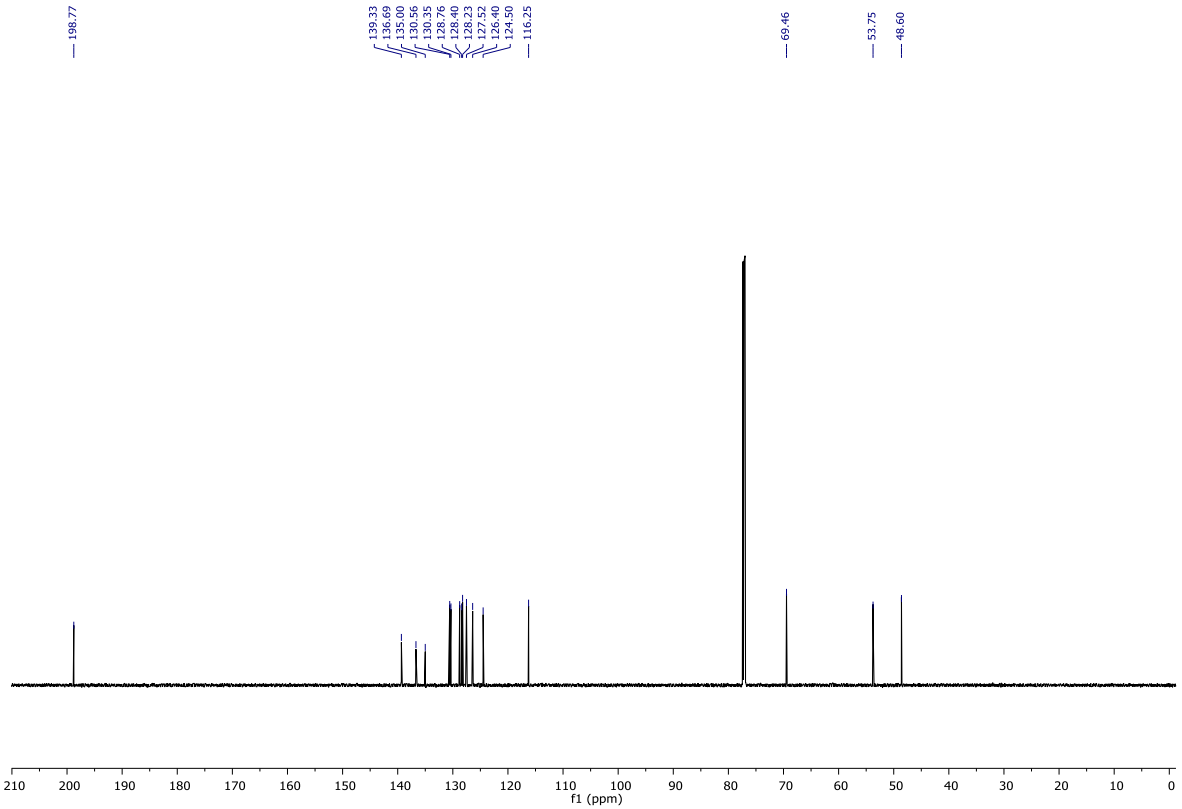


(2*S*,3*R*,3a*S*)-2-(3-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde
3f

^{1}H NMR

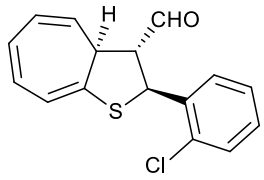


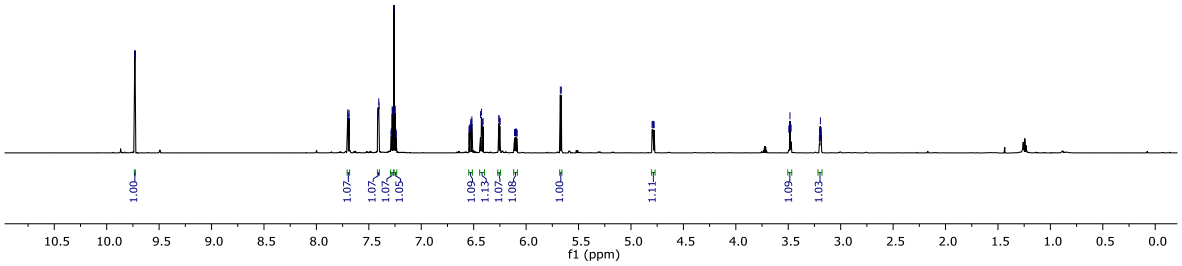
^{13}C NMR



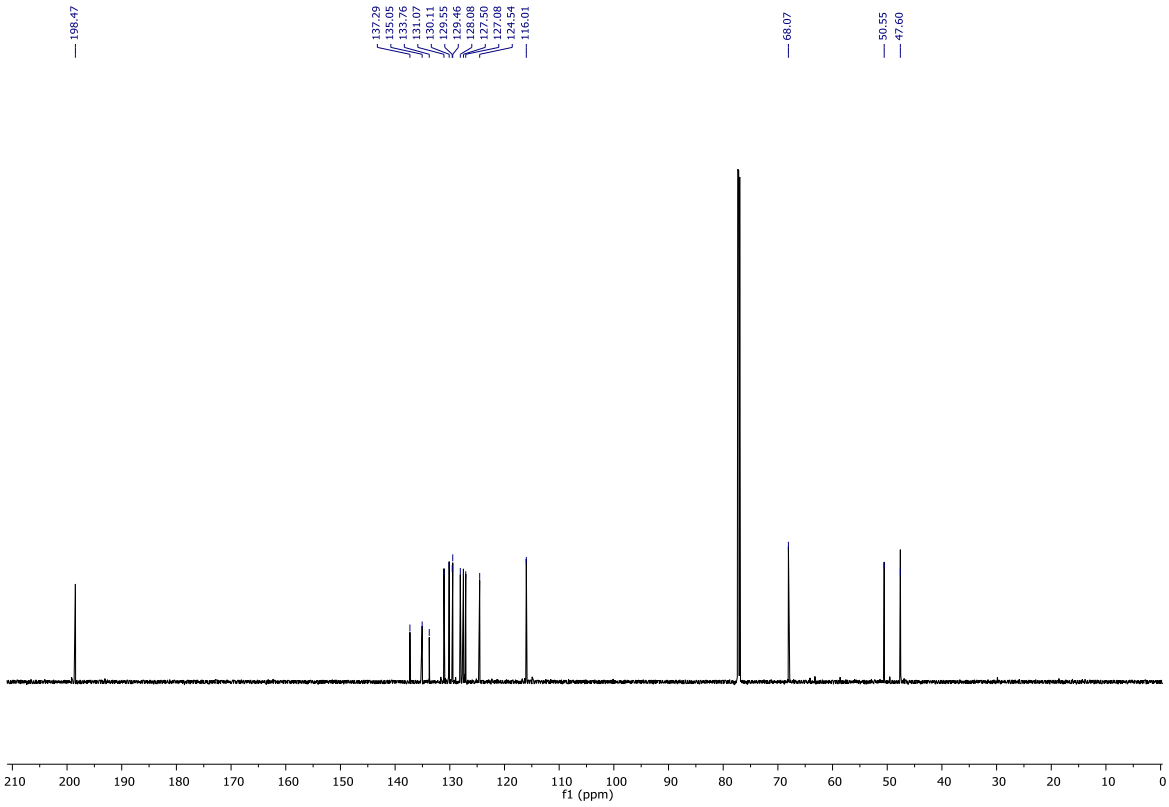
(2*S*,3*R*,3a*S*)-2-(2-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3g

^{1}H NMR



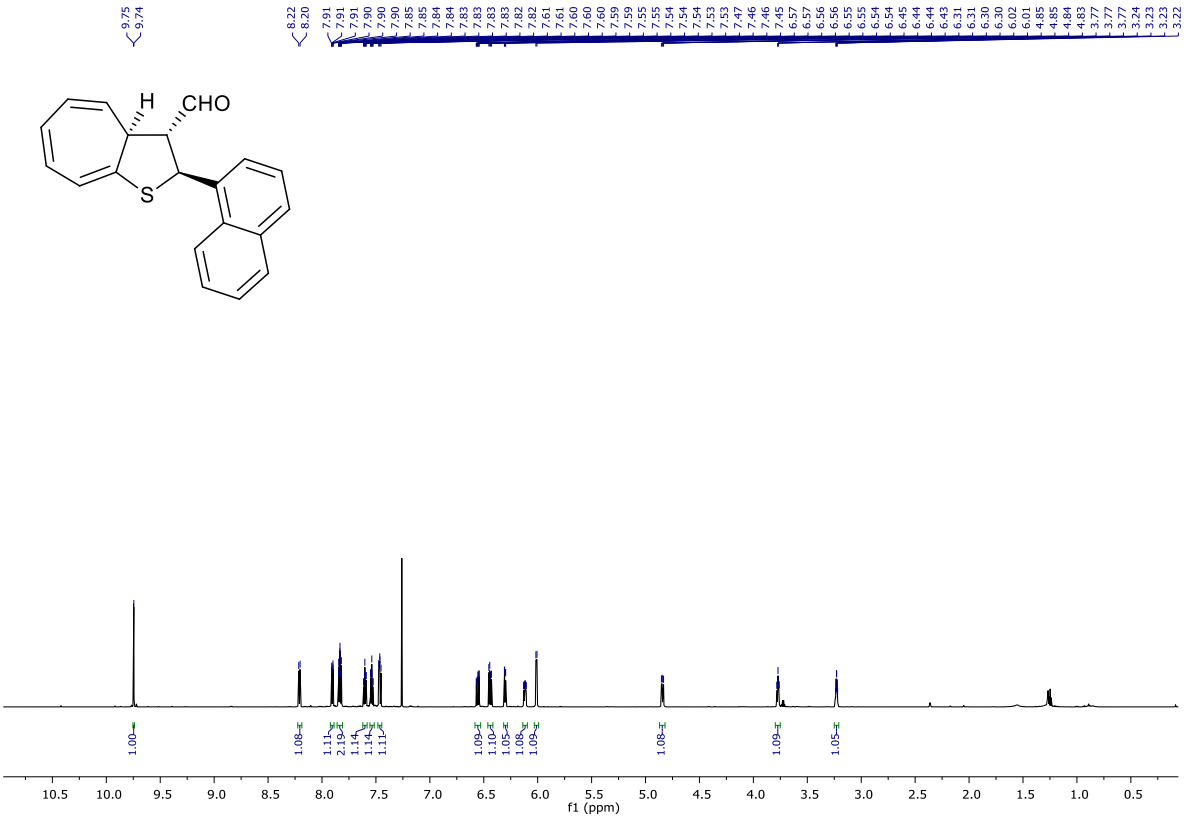


^{13}C NMR

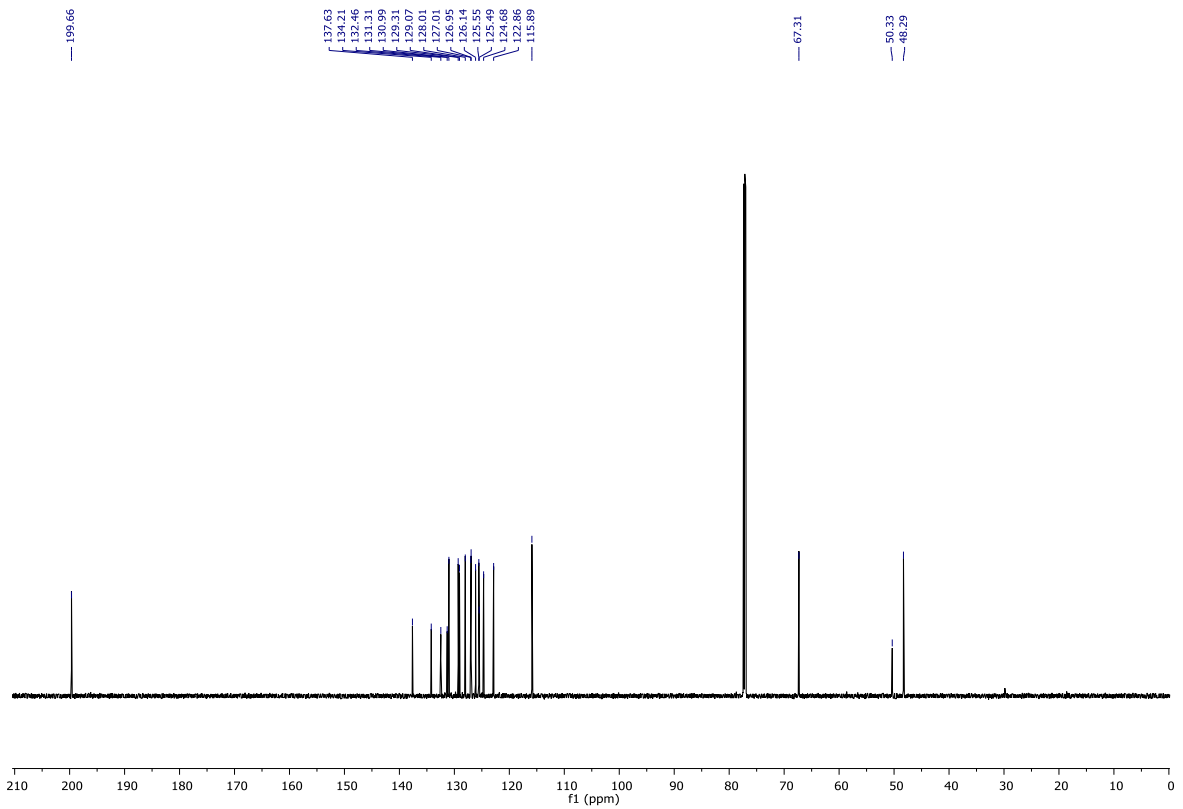


(2*S*,3*R*,3a*S*)-2-(Naphthalen-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3h

^{1}H NMR

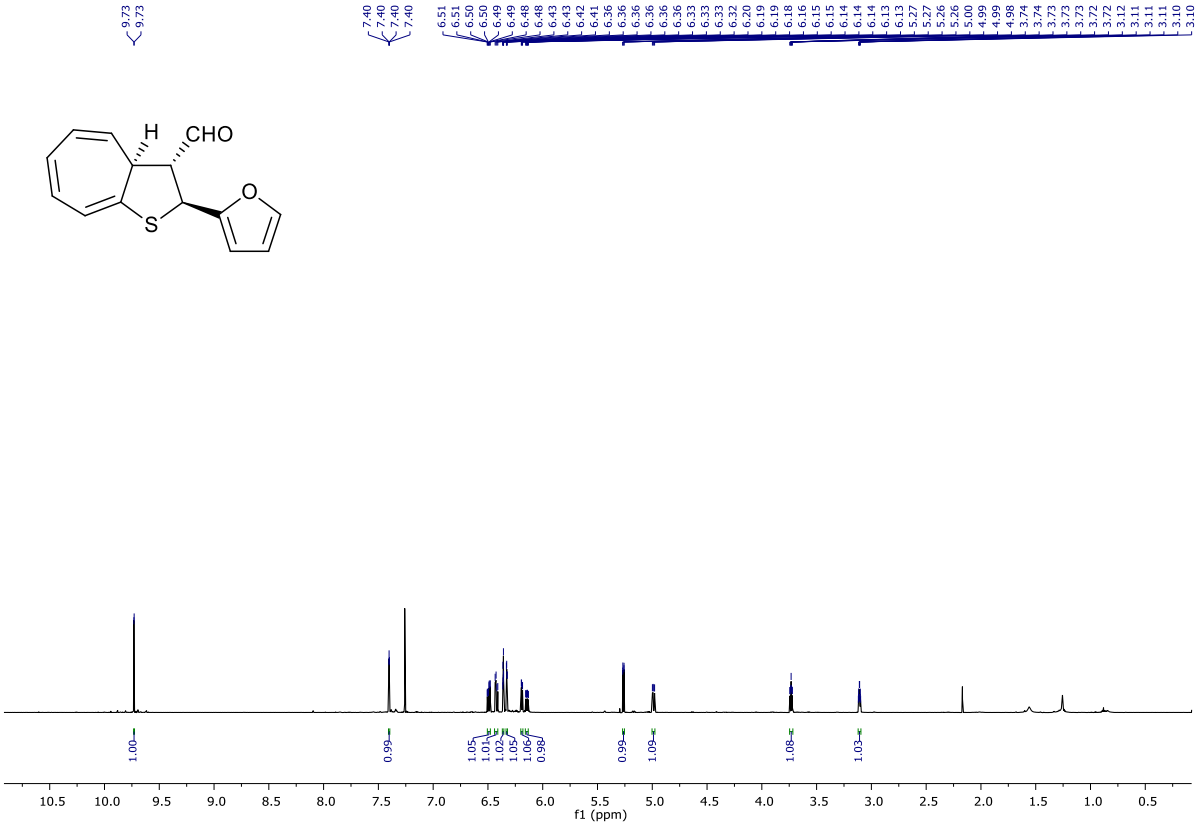


^{13}C NMR

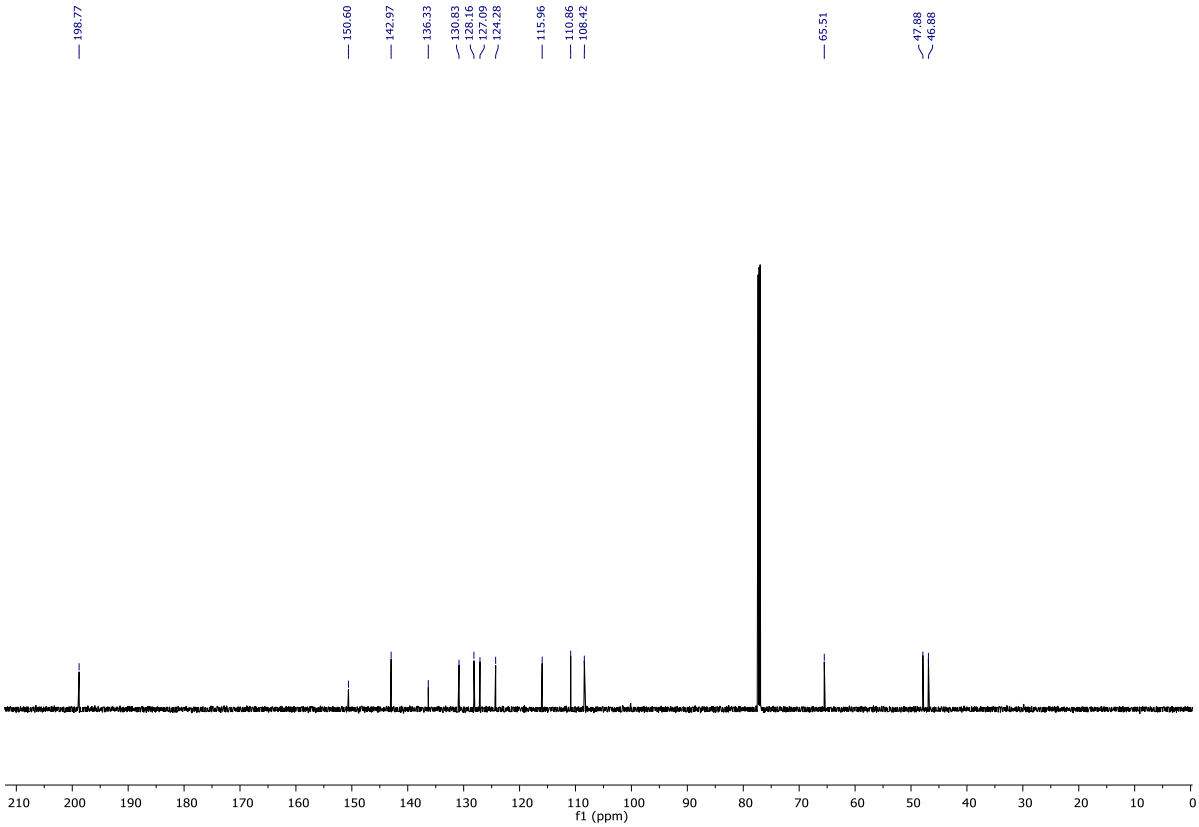


(2*S*,3*R*,3a*S*)-2-(Furan-2-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3i

^{1}H NMR

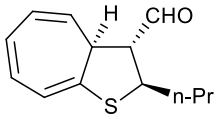


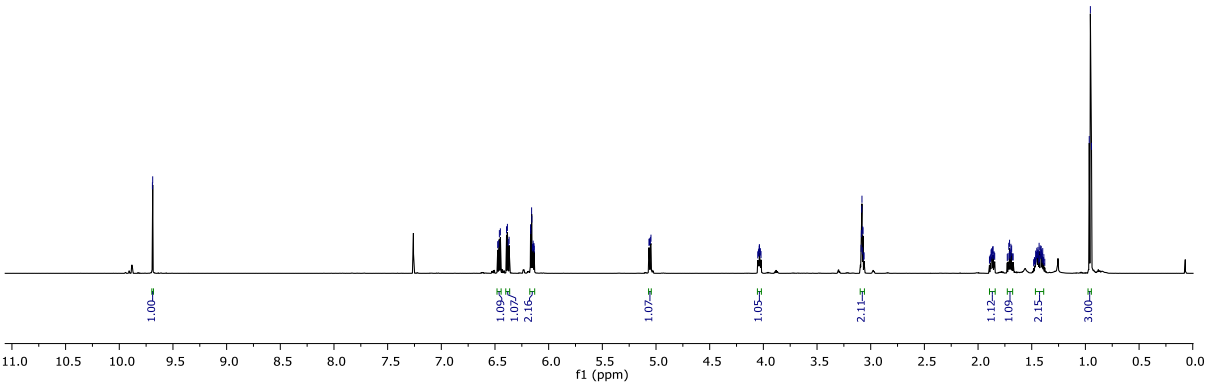
^{13}C NMR



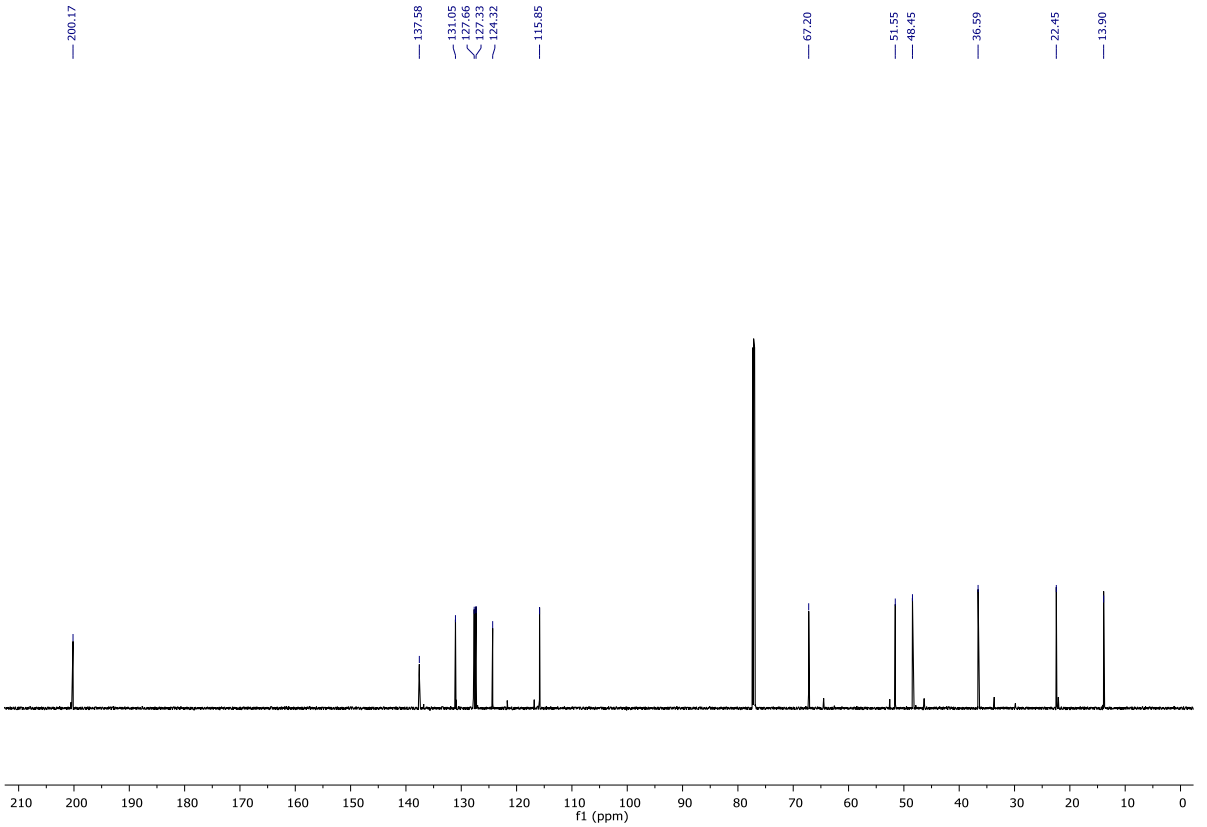
(2*R*,3*R*,3a*S*)-2-Propyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3j

^{1}H NMR



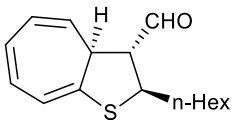


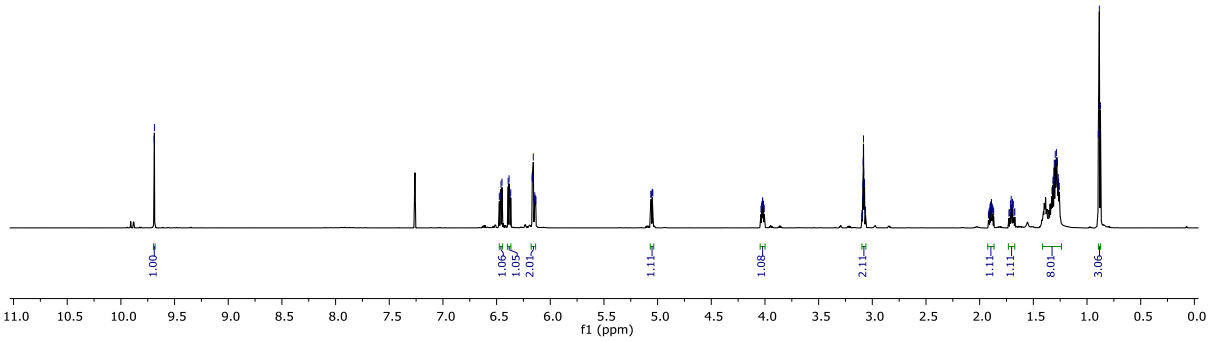
^{13}C NMR



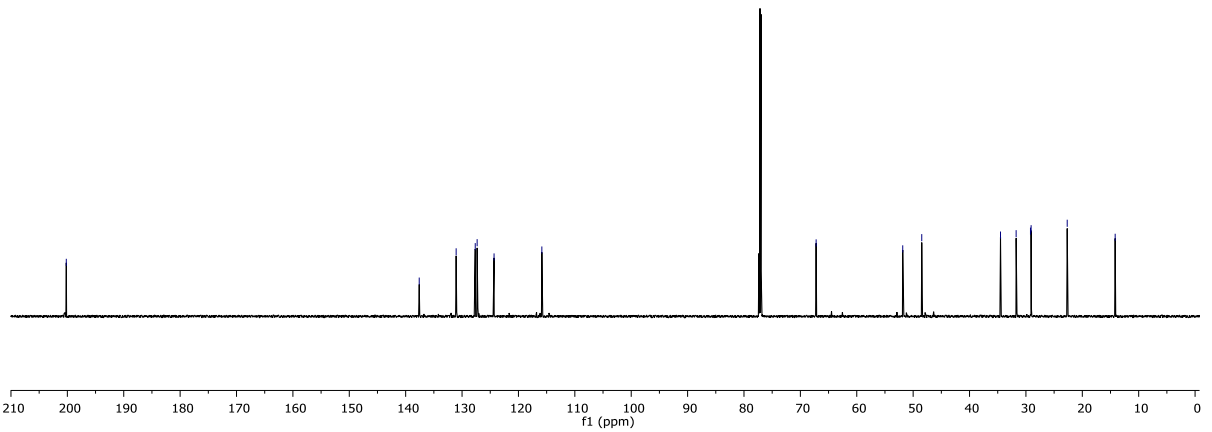
(2*R*,3*R*,3a*S*)-2-Hexyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3k

^{1}H NMR



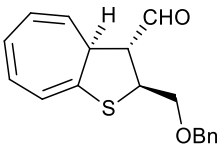


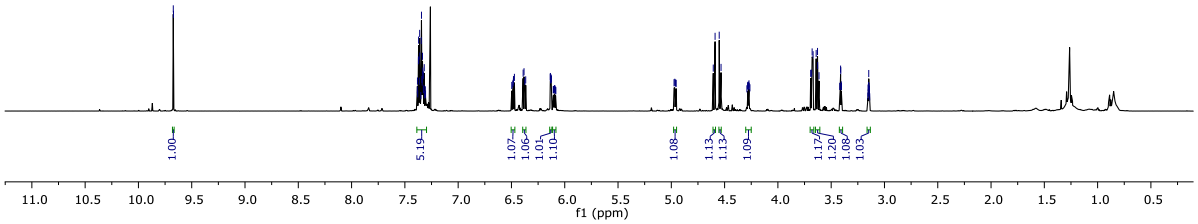
^{13}C NMR



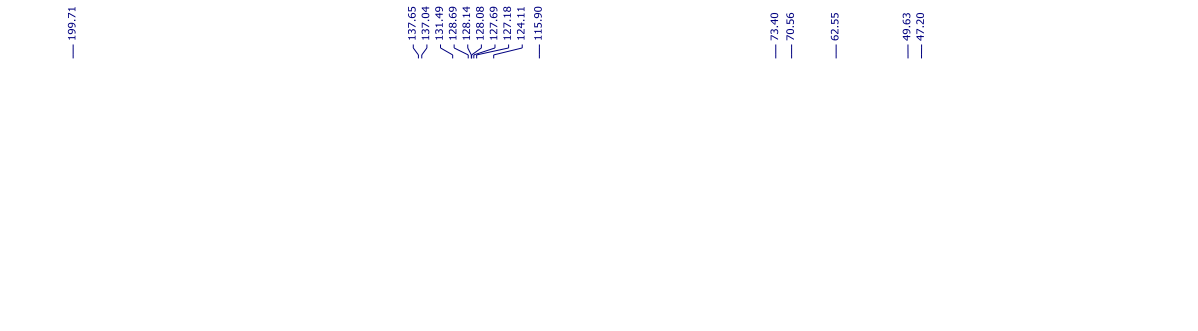
(2*S*,3*R*,3a*S*)-2-((Benzyloxy)methyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3l

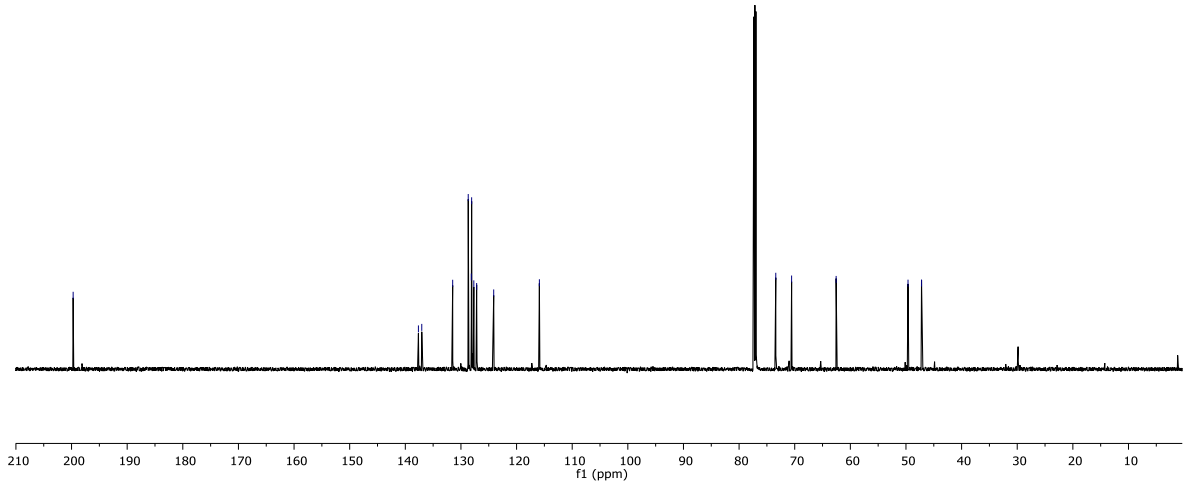
^{1}H NMR





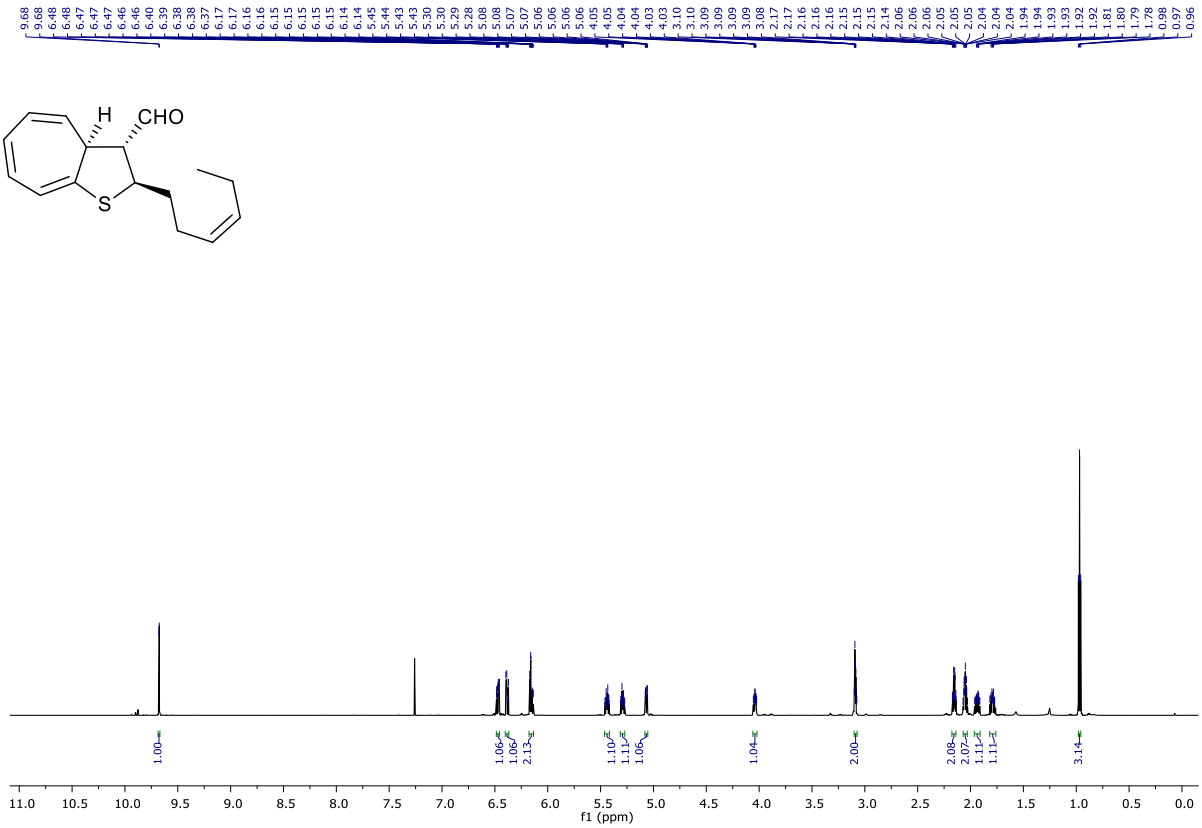
^{13}C NMR



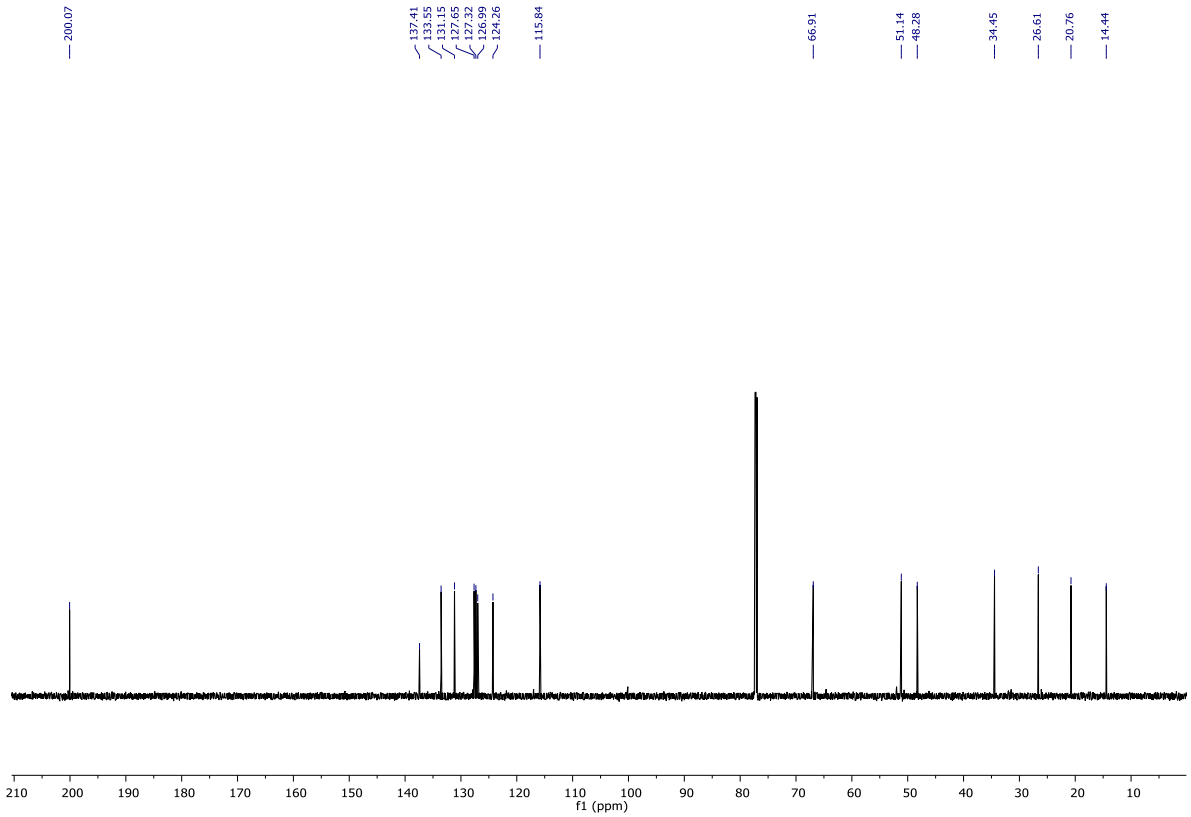


(2*R*,3*R*,3a*S*)-2-((*Z*)-Hex-3-en-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3m

^{1}H NMR

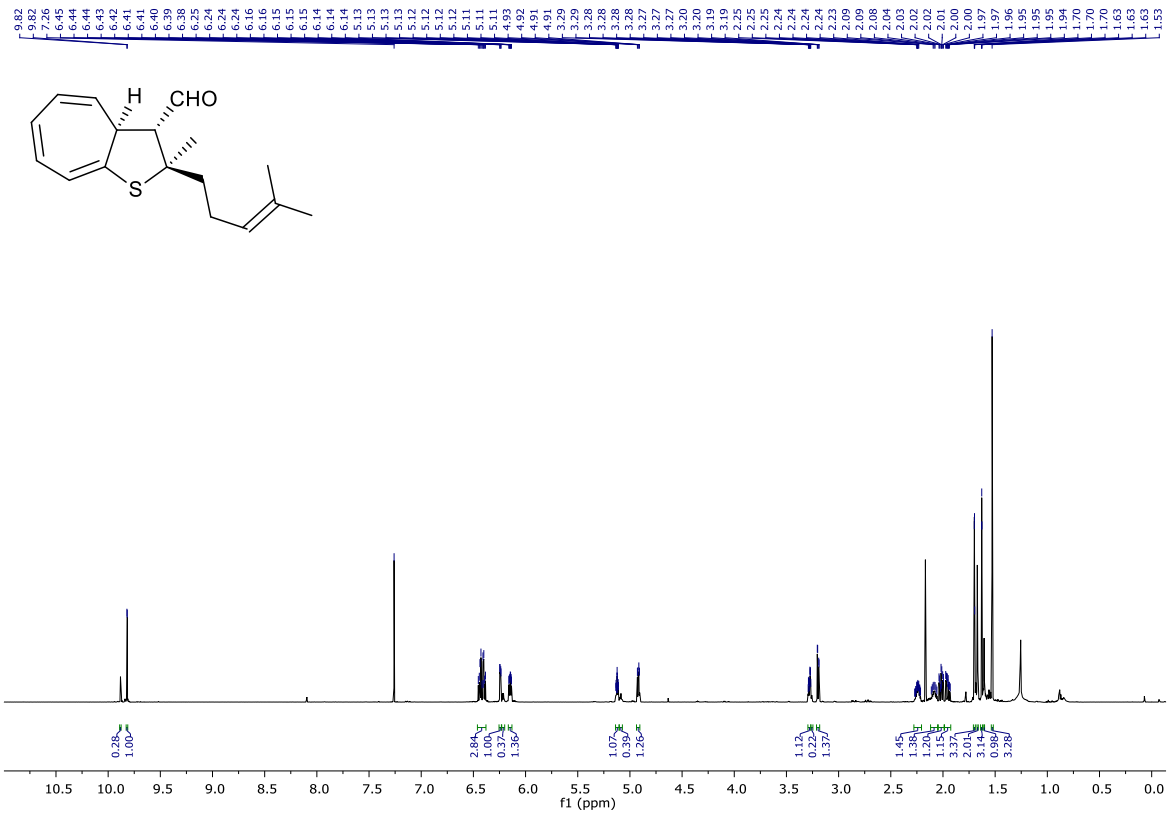


^{13}C NMR

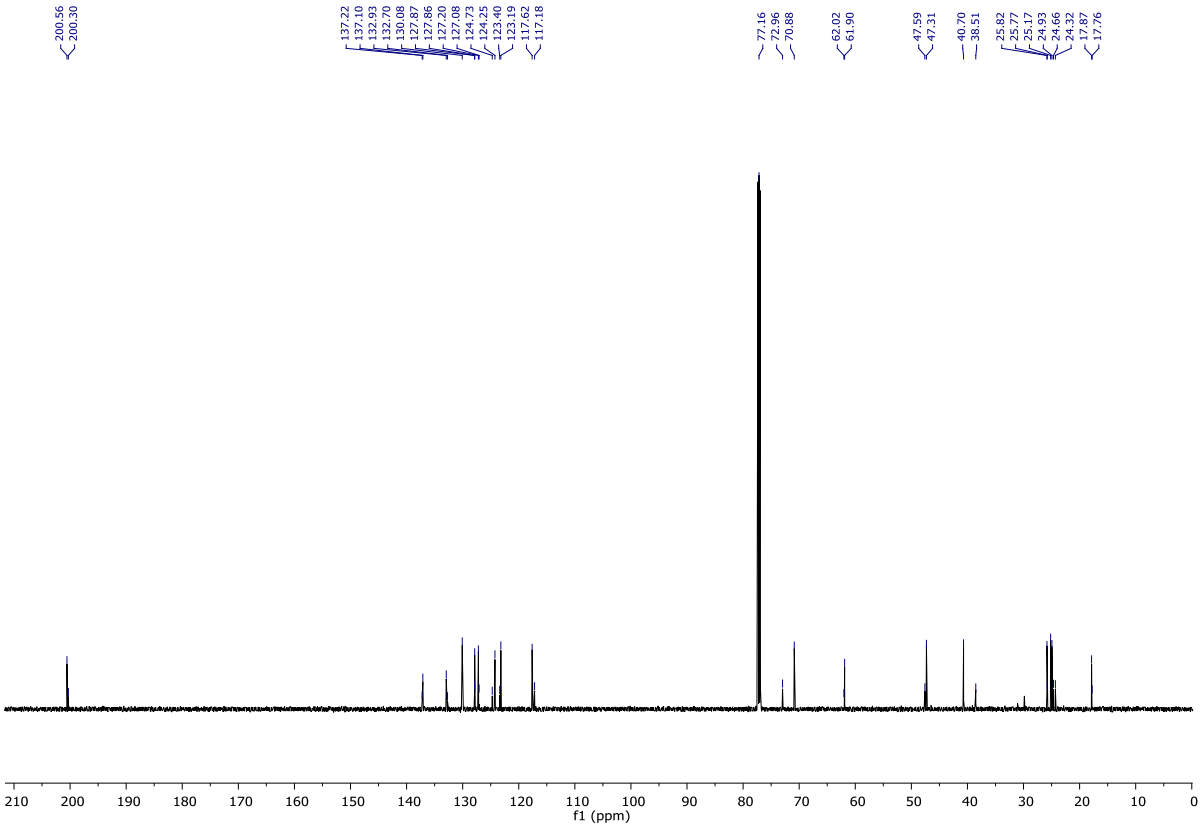


(2*R*,3*R*,3a*S*)-2-Methyl-2-(5-methylhex-4-en-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3n

^{1}H NMR

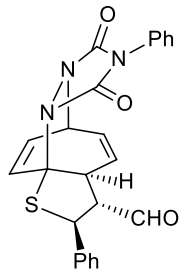


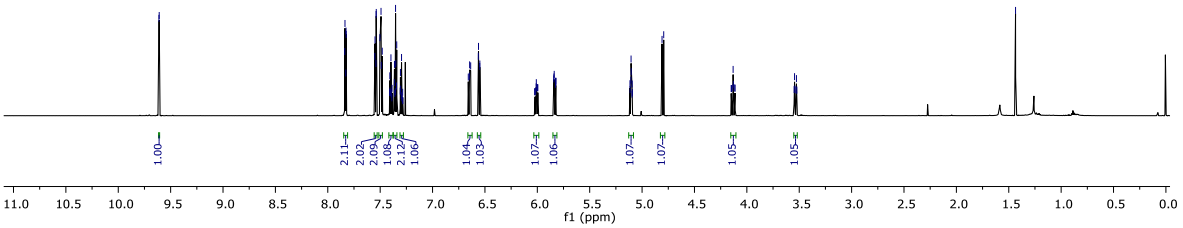
^{13}C NMR



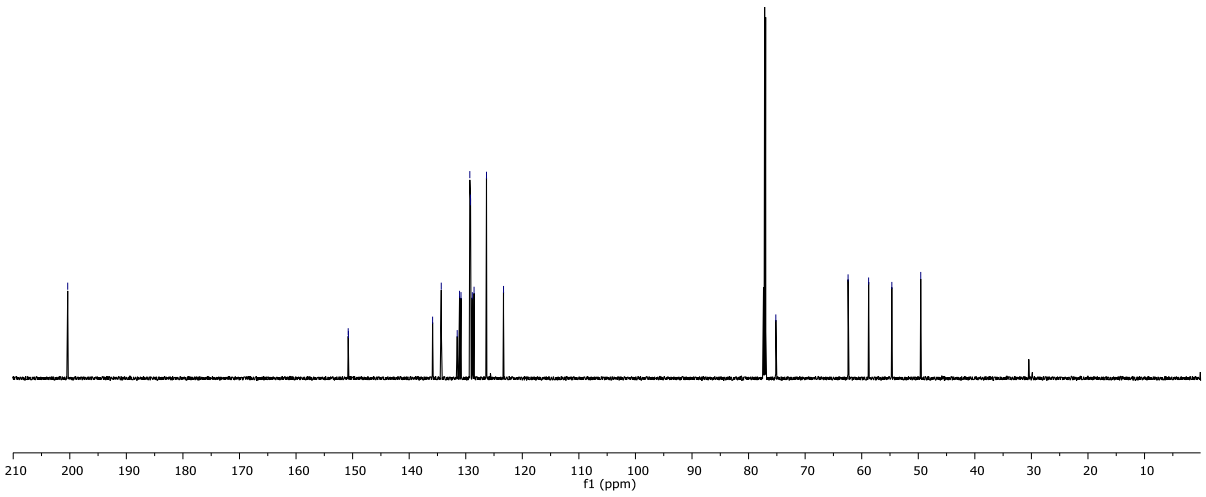
(2*S*,3*R*,3a*S*,6*S*,11a*R*)-8,10-Dioxo-2,9-diphenyl-3,3a,6,8,9,10-hexahydro-2*H*-6,11a-ethenothieno[2,3-*c*][1,2,4]triazolo[1,2-*a*][1,2]diazepine-3-carbaldehyde 6

^{1}H NMR



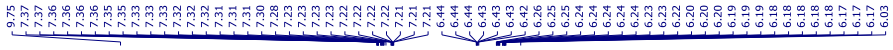


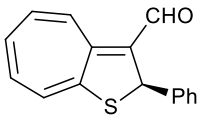
^{13}C NMR

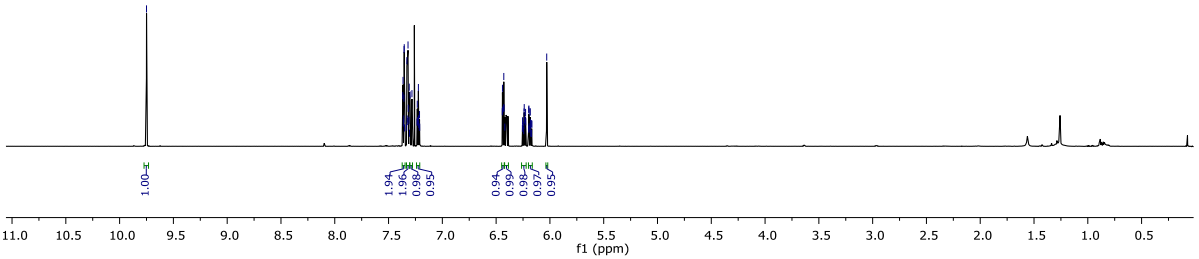


(*R*)-2-Phenyl-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 9

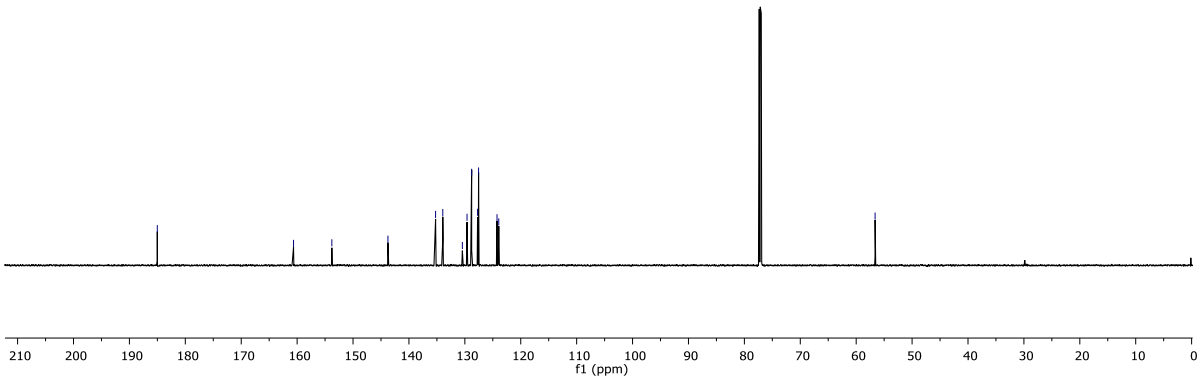
^{1}H NMR





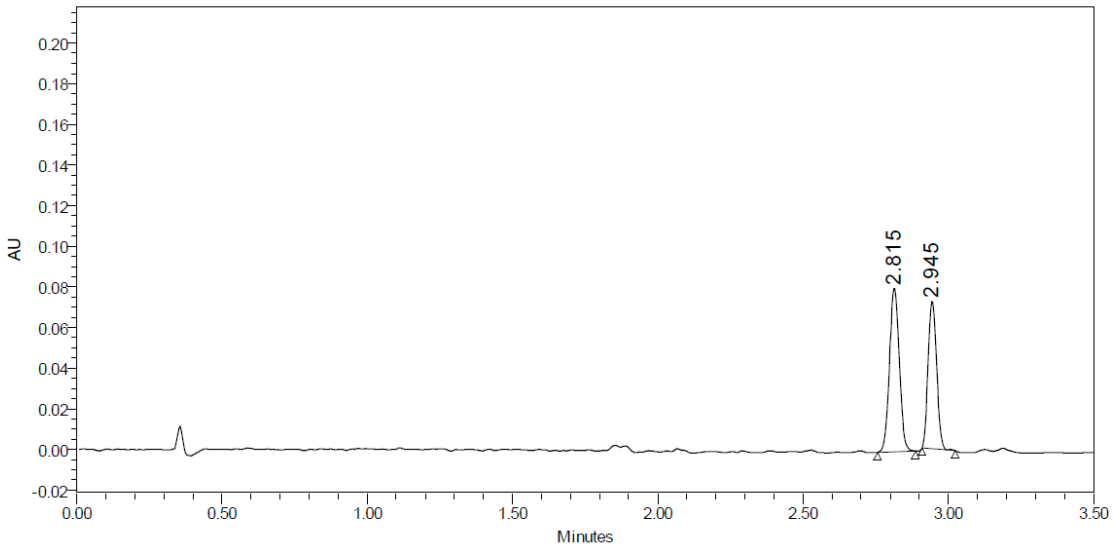


^{13}C NMR

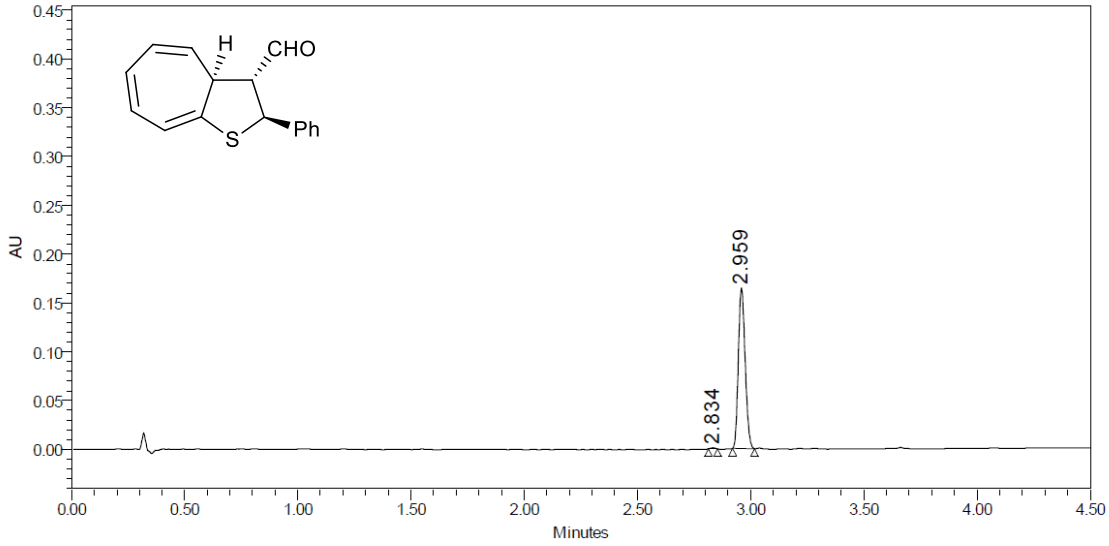


11. UPC^2 traces

(2*S*,3*R*,3a*S*)-2-Phenyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3a

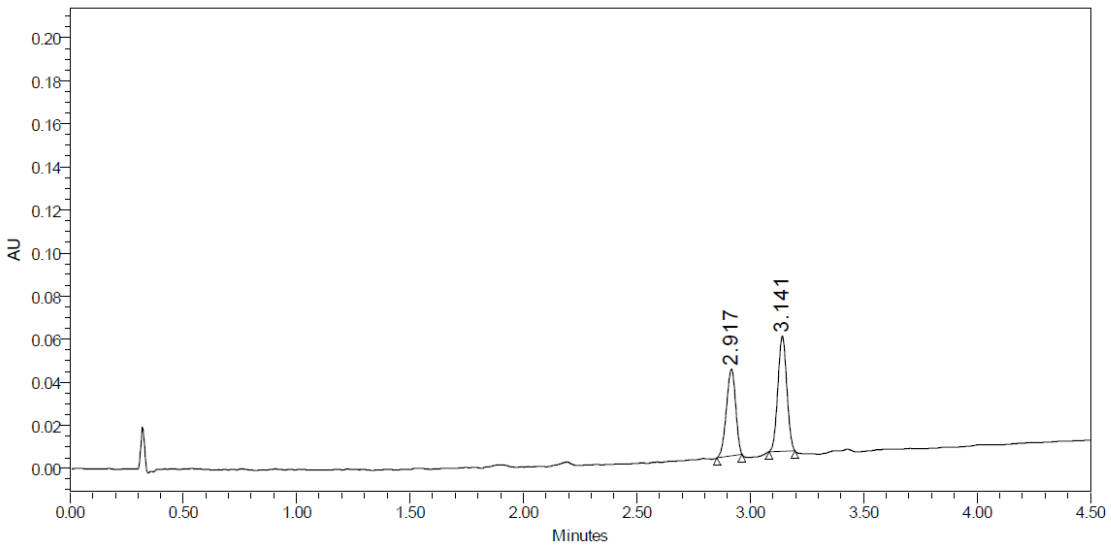


	RT	Area	% Area	Height
1	2.815	187820	56.08	80507
2	2.945	147075	43.92	72573

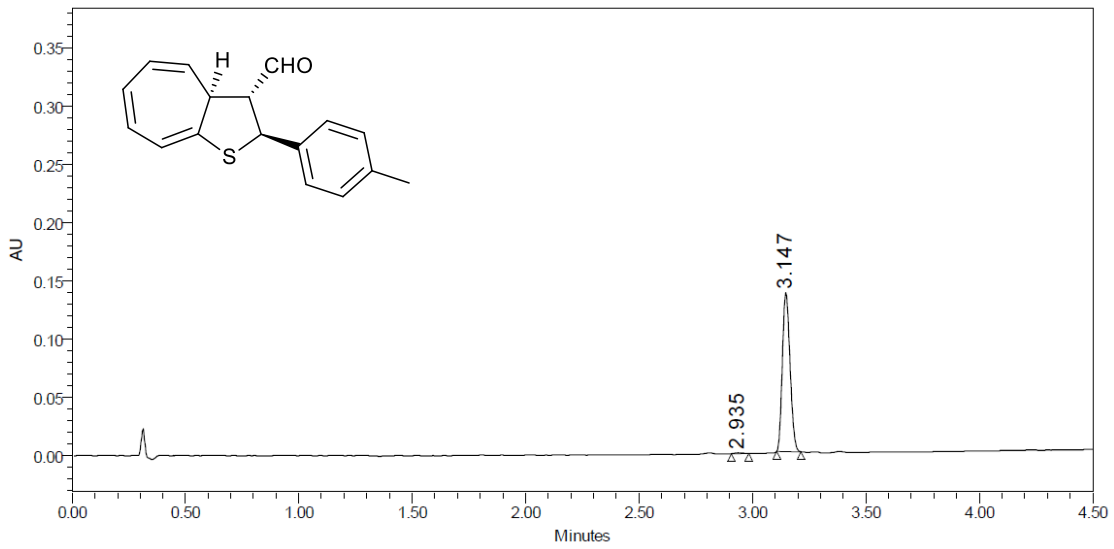


	RT	Area	% Area	Height
1	2.834	1660	0.48	1145
2	2.959	343710	99.52	164630

(2*S*,3*R*,3a*S*)-2-(*p*-Tolyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3b

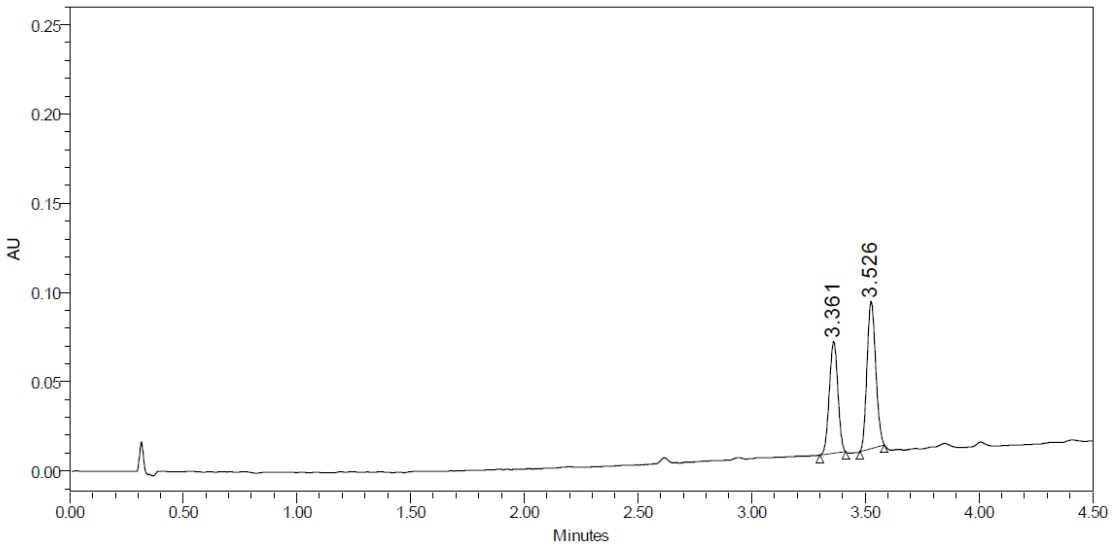


	RT	Area	% Area	Height
1	2.917	113546	43.67	40139
2	3.141	146442	56.33	53585

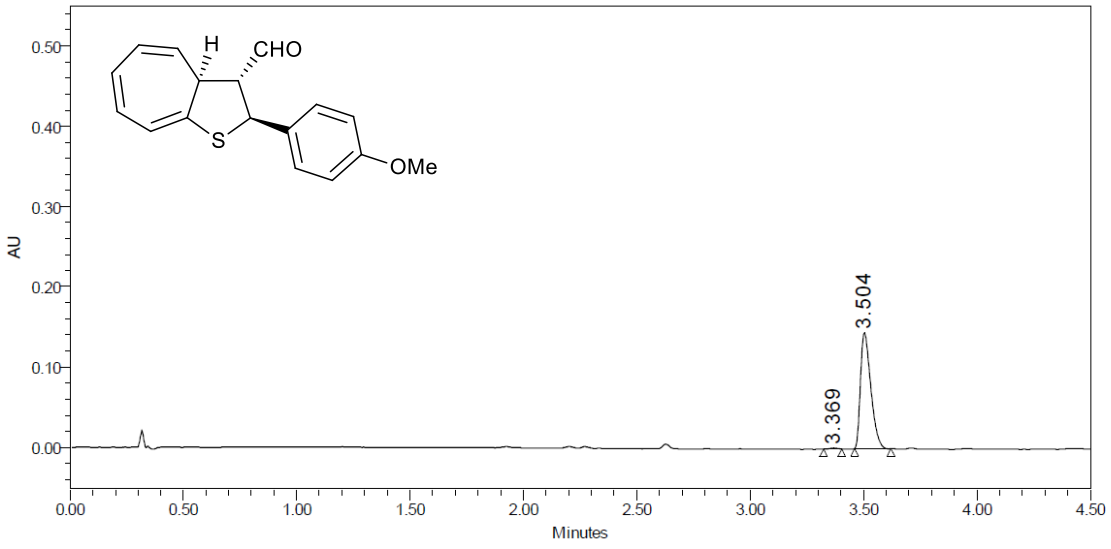


	RT	Area	% Area	Height
1	2.935	1811	0.56	772
2	3.147	320220	99.44	136273

(2*S*,3*R*,3a*S*)-2-(4-Methoxyphenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3c

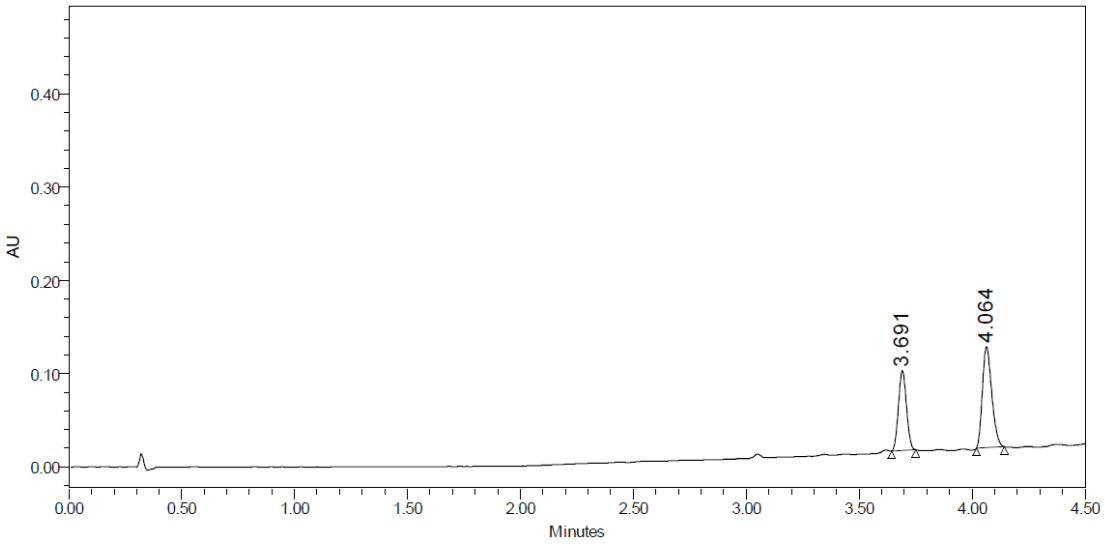


	RT	Area	% Area	Height
1	3.361	163383	42.66	62558
2	3.526	219644	57.34	82435

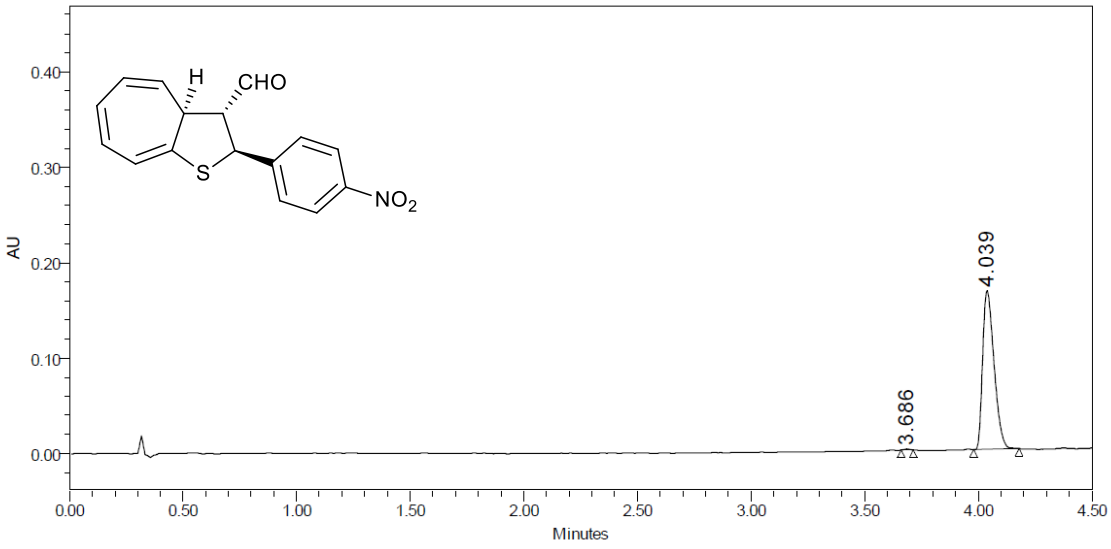


	RT	Area	% Area	Height
1	3.369	3304	0.72	1495
2	3.504	455912	99.28	144578

(2*S*,3*R*,3a*S*)-2-(4-Nitrophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3d

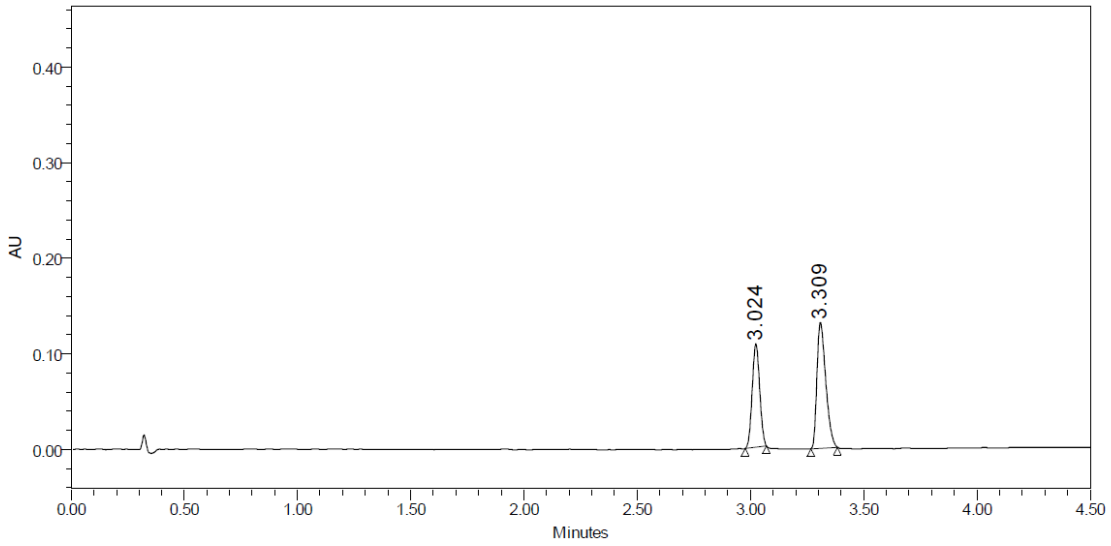


	RT	Area	% Area	Height
1	3.691	211605	40.46	85663
2	4.064	311372	59.54	108205

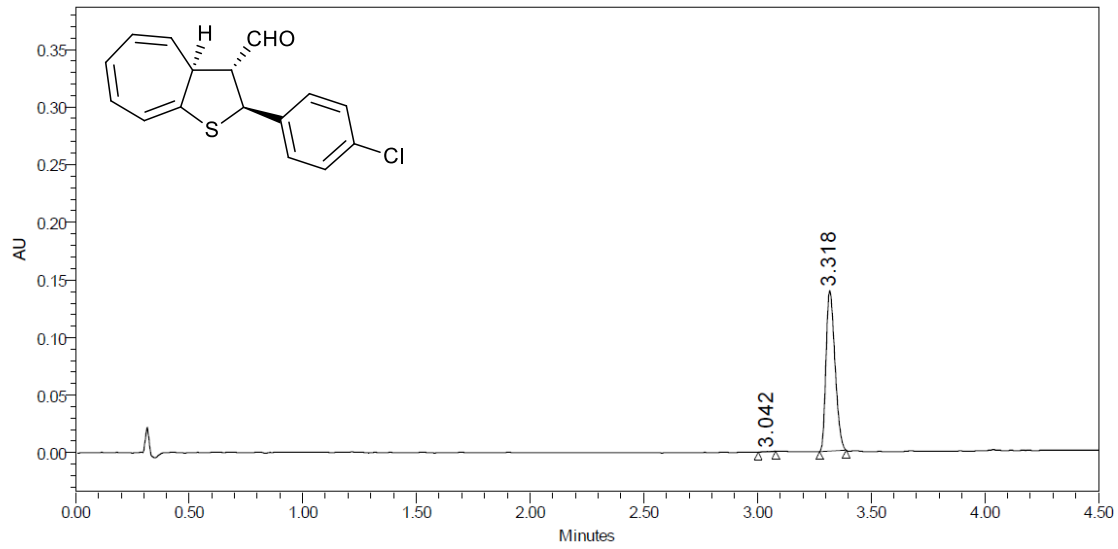


	RT	Area	% Area	Height
1	3.686	2134	0.37	1105
2	4.039	578614	99.63	166339

(2*S*,3*R*,3a*S*)-2-(4-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde
3e

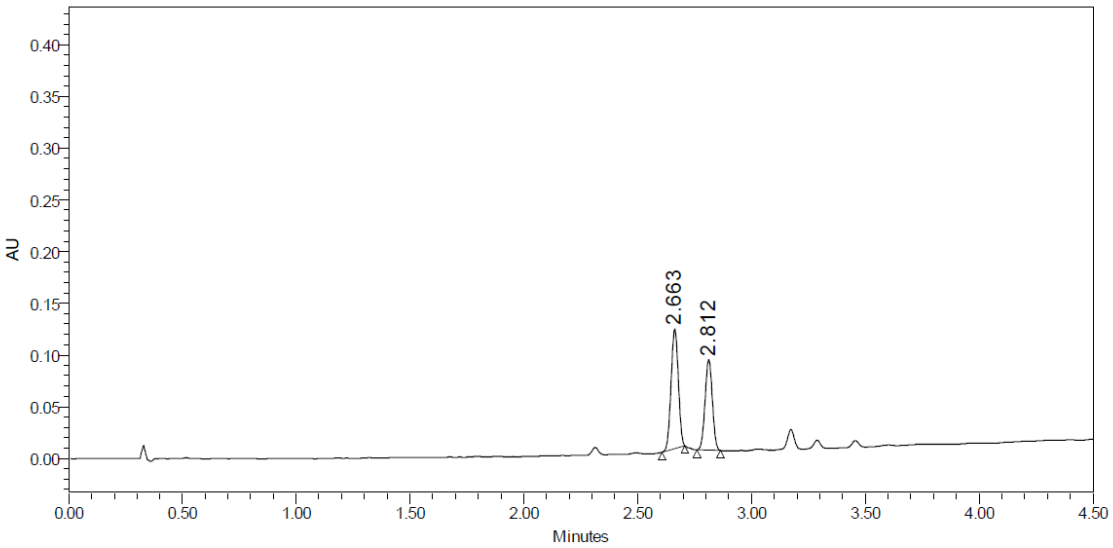


	RT	Area	% Area	Height
1	3.024	246716	40.95	107902
2	3.309	355697	59.05	131648

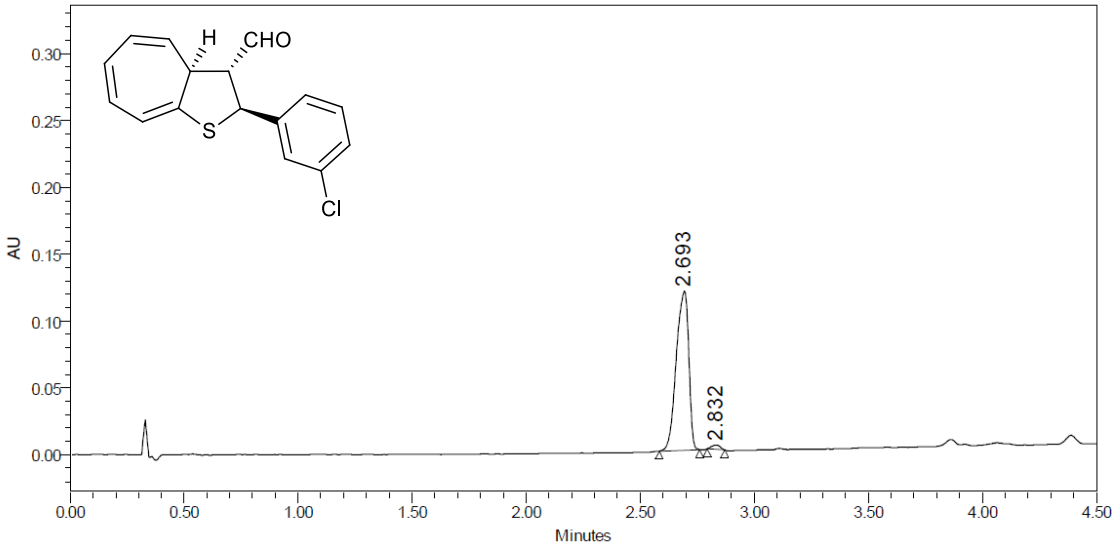


	RT	Area	% Area	Height
1	3.042	488	0.13	265
2	3.318	381457	99.87	139616

(2*S*,3*R*,3a*S*)-2-(3-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde
3f

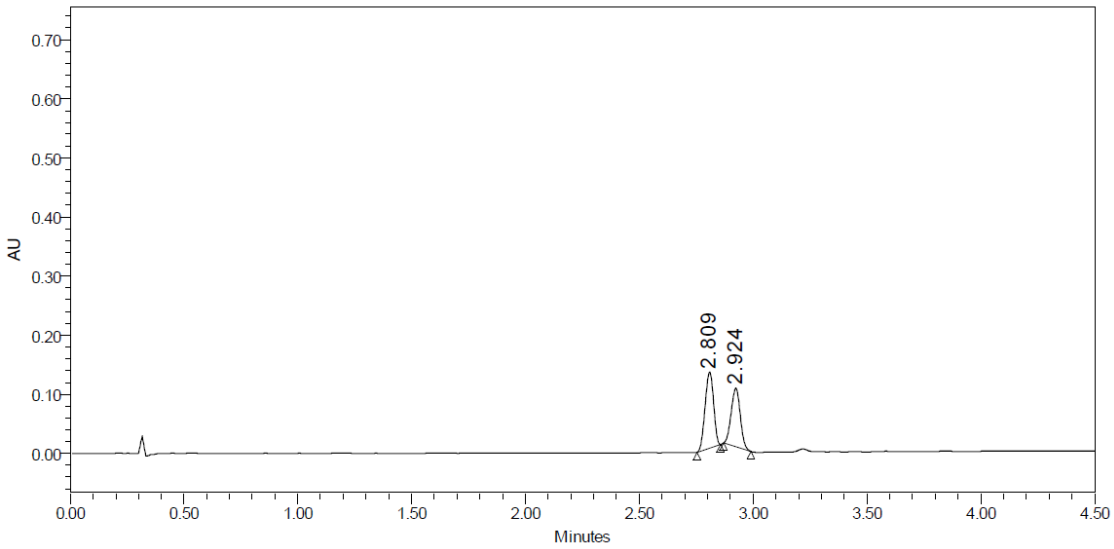


	RT	Area	% Area	Height
1	2.663	255991	56.74	115585
2	2.812	195188	43.26	87838

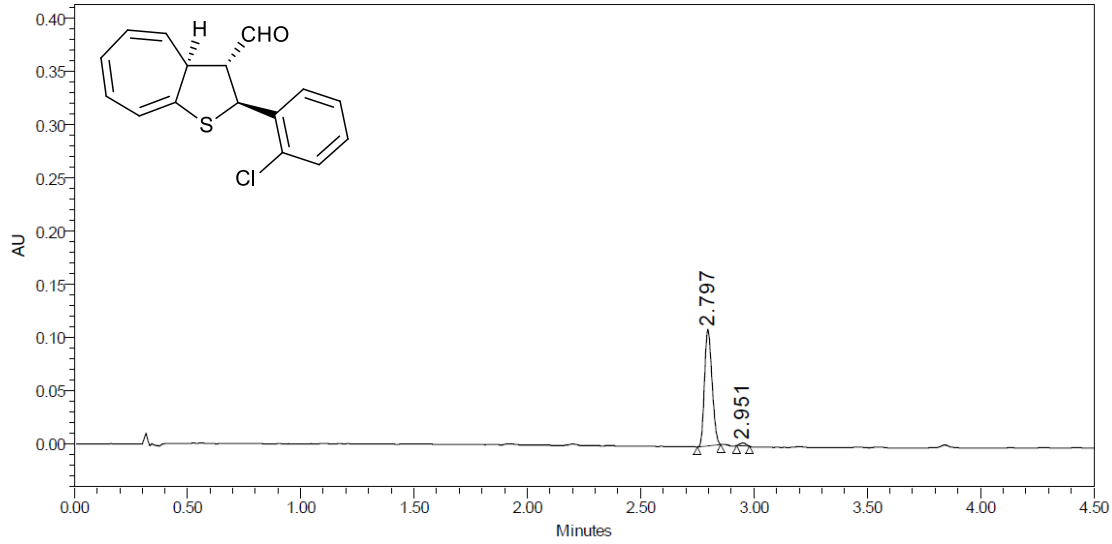


	RT	Area	% Area	Height
1	2.693	450933	98.14	119026
2	2.832	8528	1.86	3326

(2*S*,3*R*,3a*S*)-2-(2-Chlorophenyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3g

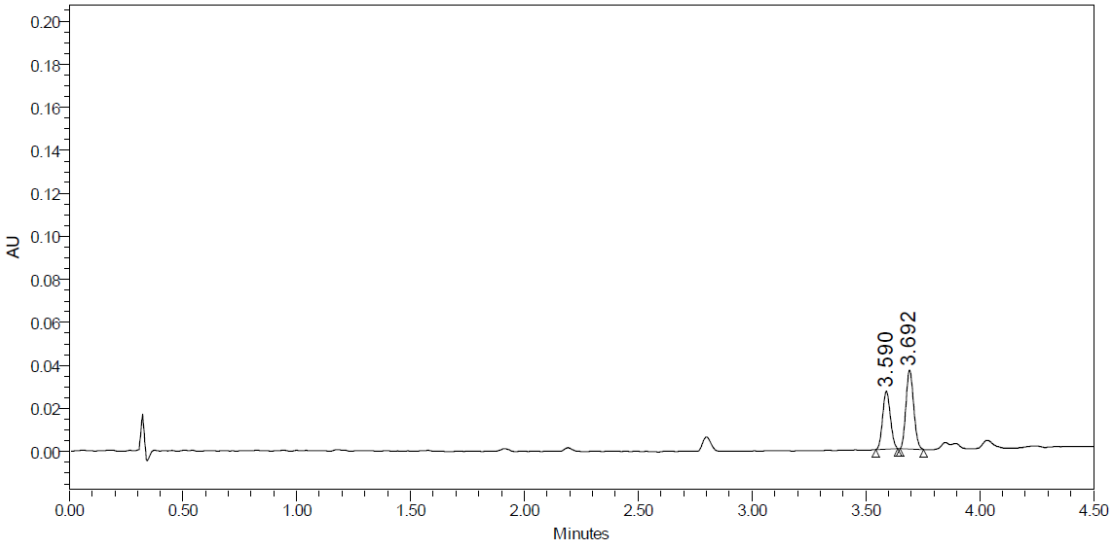


	RT	Area	% Area	Height
1	2.809	333019	54.72	128942
2	2.924	275519	45.28	99036

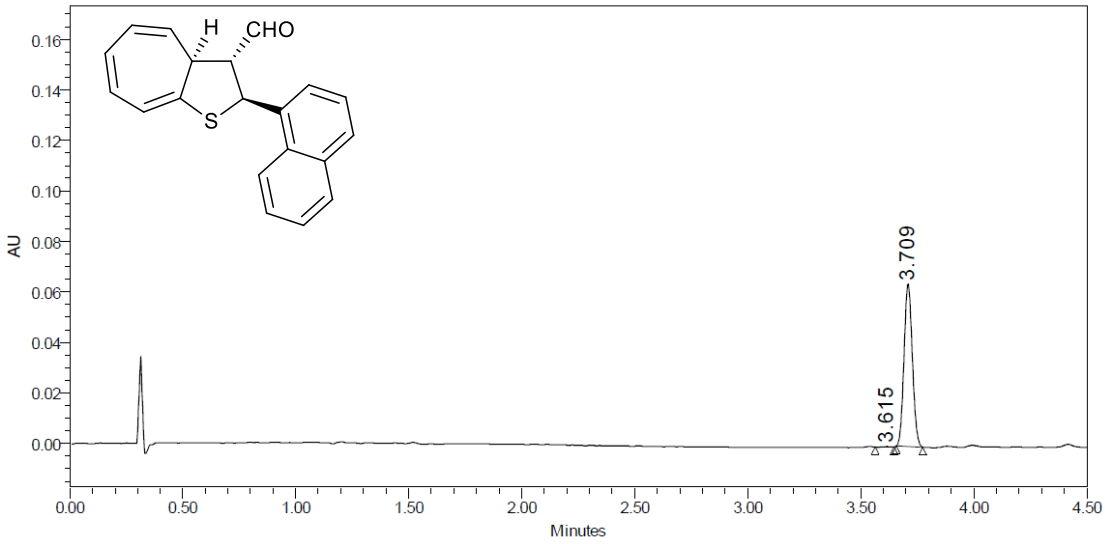


	RT	Area	% Area	Height
1	2.797	251435	97.96	109038
2	2.951	5238	2.04	2833

(2*S*,3*R*,3a*S*)-2-(Naphthalen-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3h

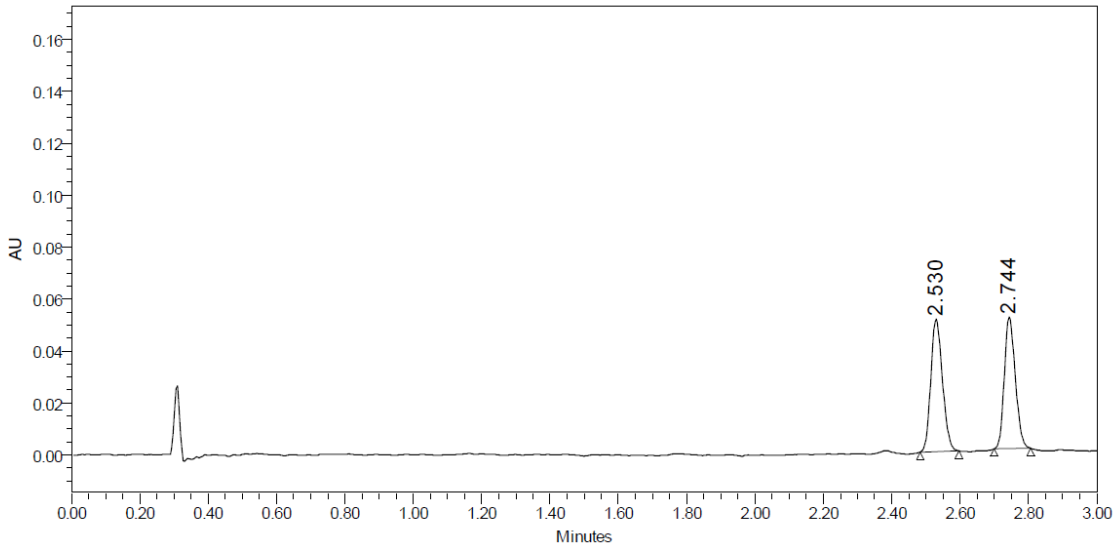


	RT	Area	% Area	Height
1	3.590	63008	42.24	26858
2	3.692	86141	57.76	36676

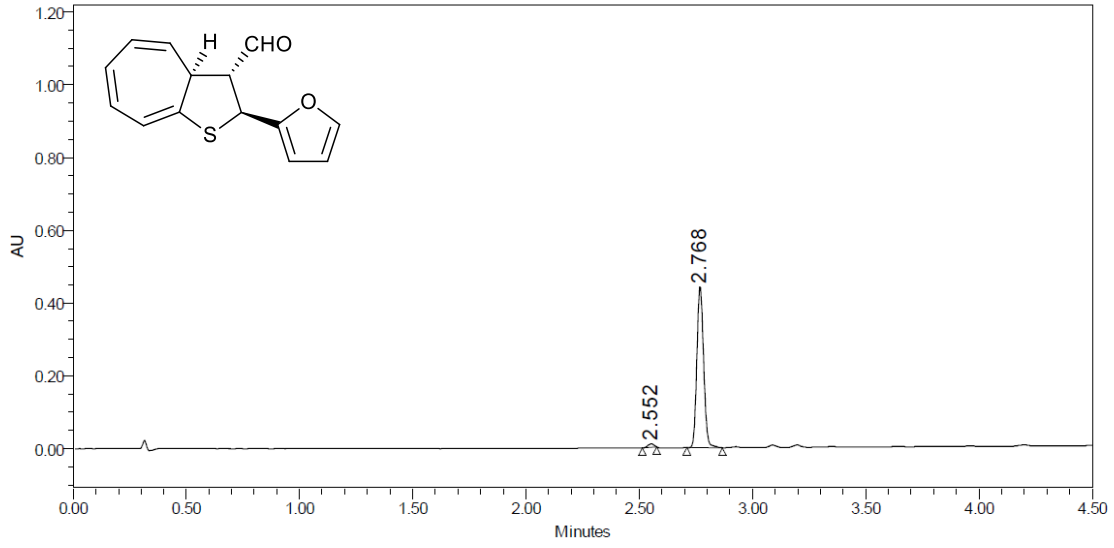


	RT	Area	% Area	Height
1	3.615	283	0.17	120
2	3.709	164685	99.83	64424

(2*S*,3*R*,3a*S*)-2-(Furan-2-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3i

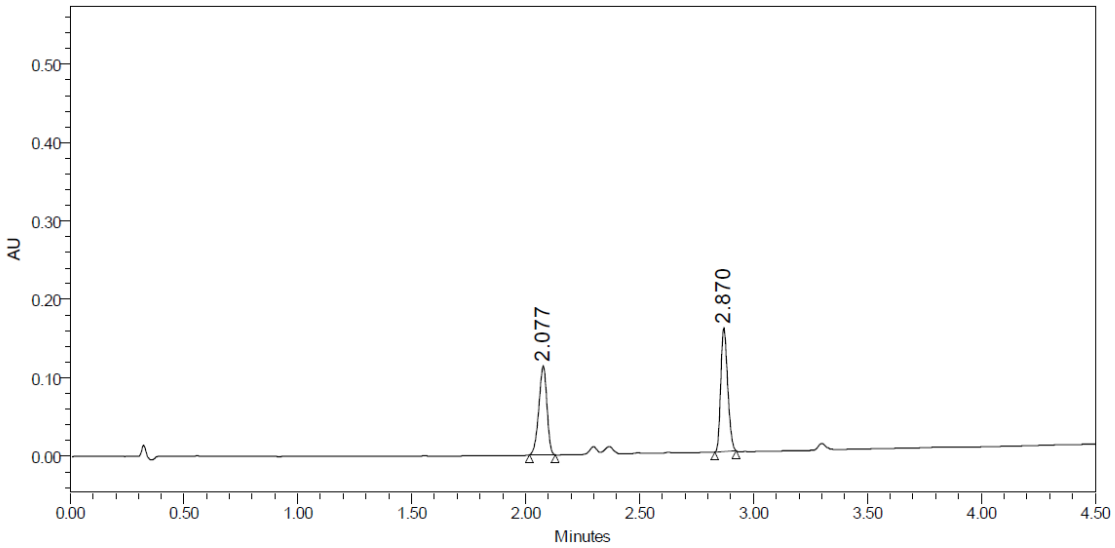


	RT	Area	% Area	Height
1	2.530	120475	51.68	51066
2	2.744	112626	48.32	50701

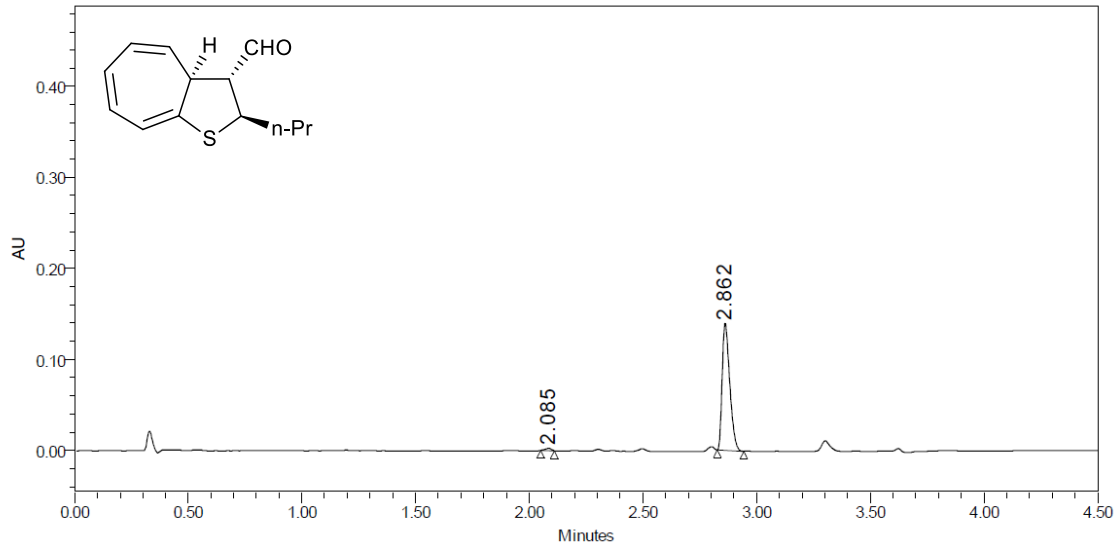


	RT	Area	% Area	Height
1	2.552	17816	1.90	9715
2	2.768	917792	98.10	443659

(2*R*,3*R*,3a*S*)-2-Propyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3j

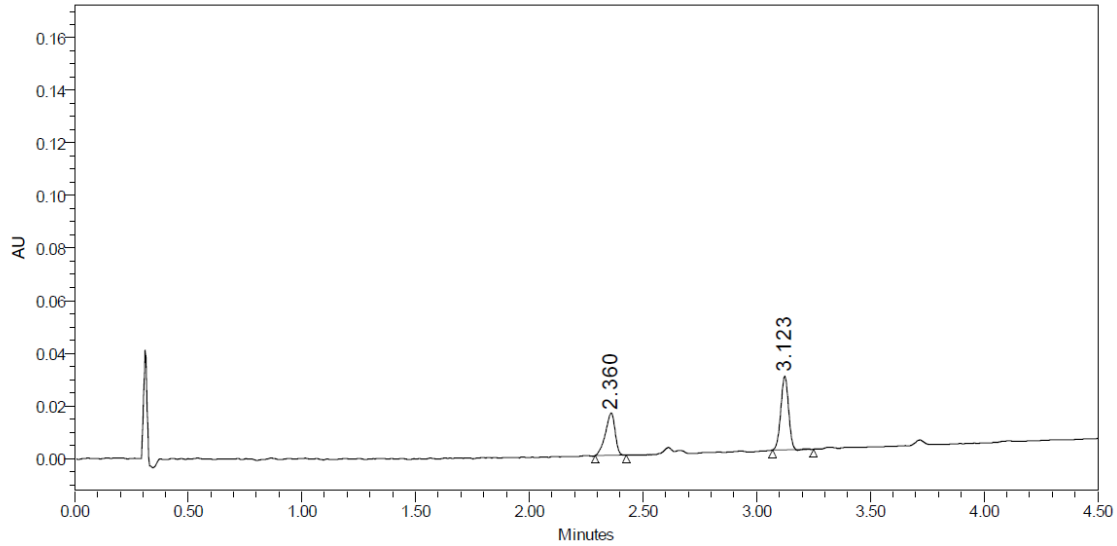


	RT	Area	% Area	Height
1	2.077	279743	45.85	113451
2	2.870	330345	54.15	157890

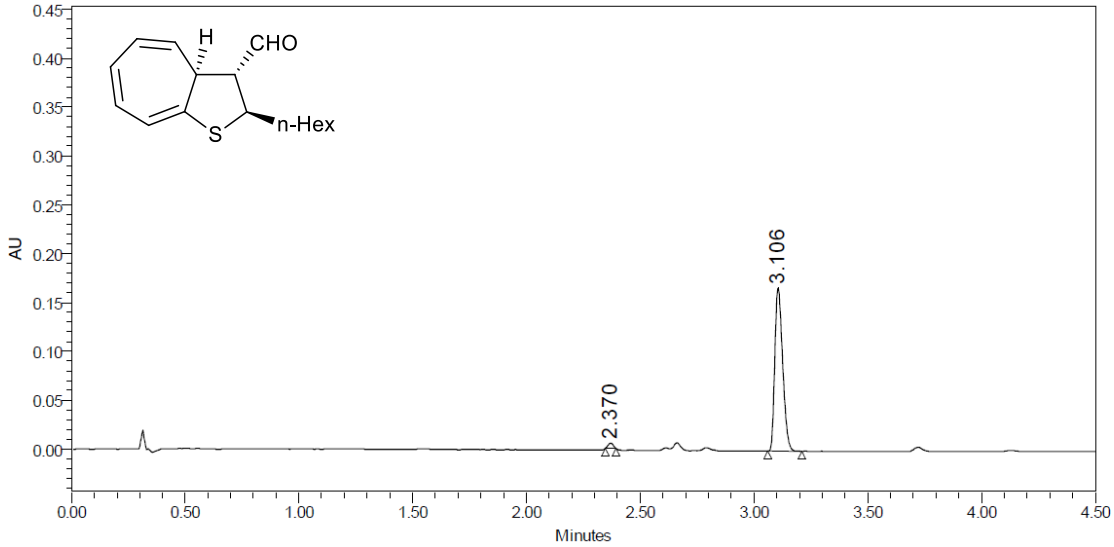


	RT	Area	% Area	Height
1	2.085	4685	1.43	2399
2	2.862	322670	98.57	140151

(2*R*,3*R*,3a*S*)-2-Hexyl-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3k

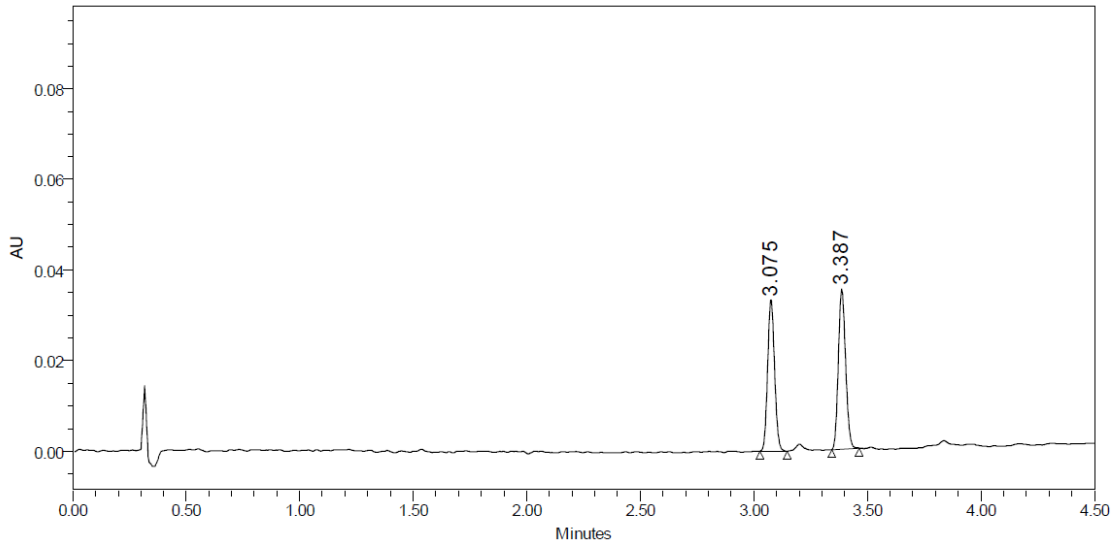


	RT	Area	% Area	Height
1	2.360	47526	41.62	16087
2	3.123	66672	58.38	28099

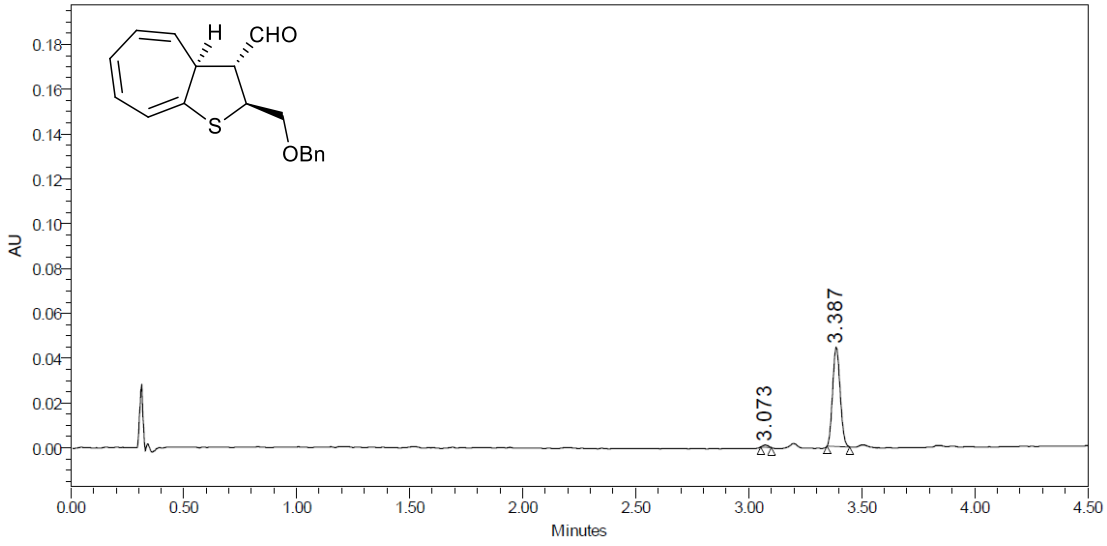


	RT	Area	% Area	Height
1	2.370	8342	2.04	5266
2	3.106	399834	97.96	167040

(2*S*,3*R*,3a*S*)-2-((Benzyloxy)methyl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3l

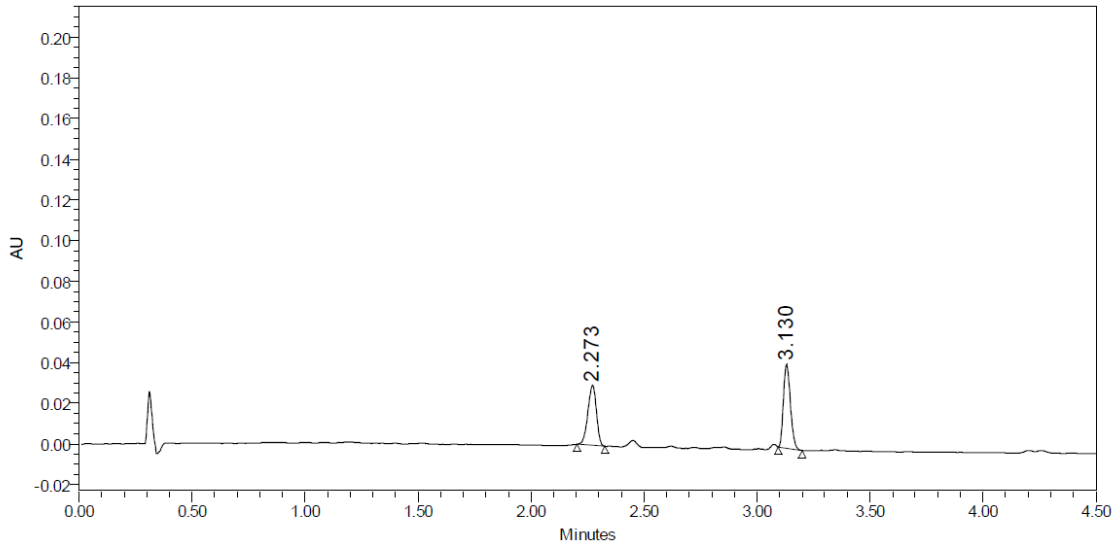


	RT	Area	% Area	Height
1	3.075	71023	47.55	33469
2	3.387	78328	52.45	35253

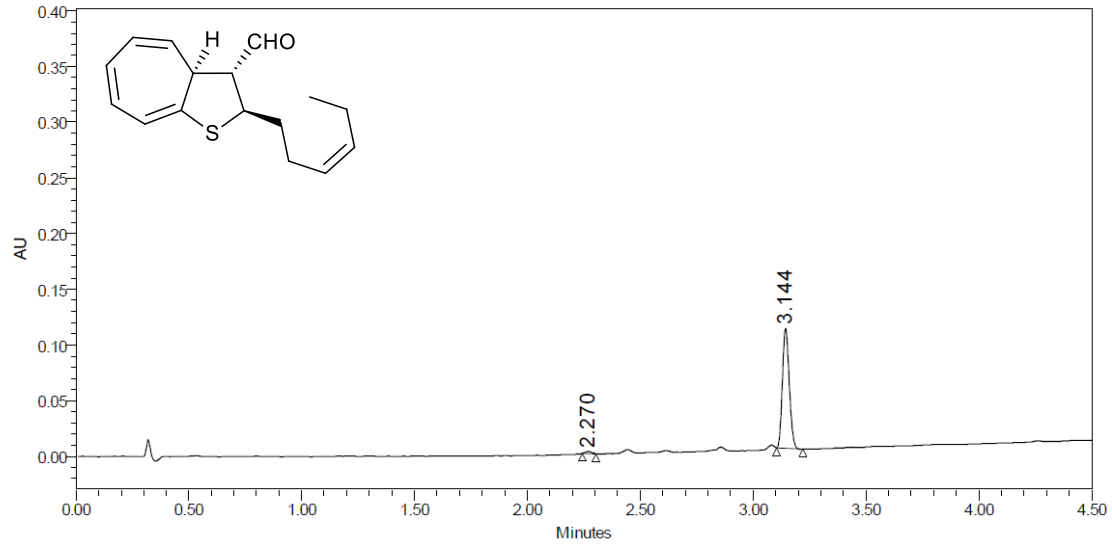


	RT	Area	% Area	Height
1	3.073	1510	1.46	948
2	3.387	102126	98.54	44272

(2*R*,3*R*,3a*S*)-2-((*Z*)-Hex-3-en-1-yl)-3,3a-dihydro-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 3m

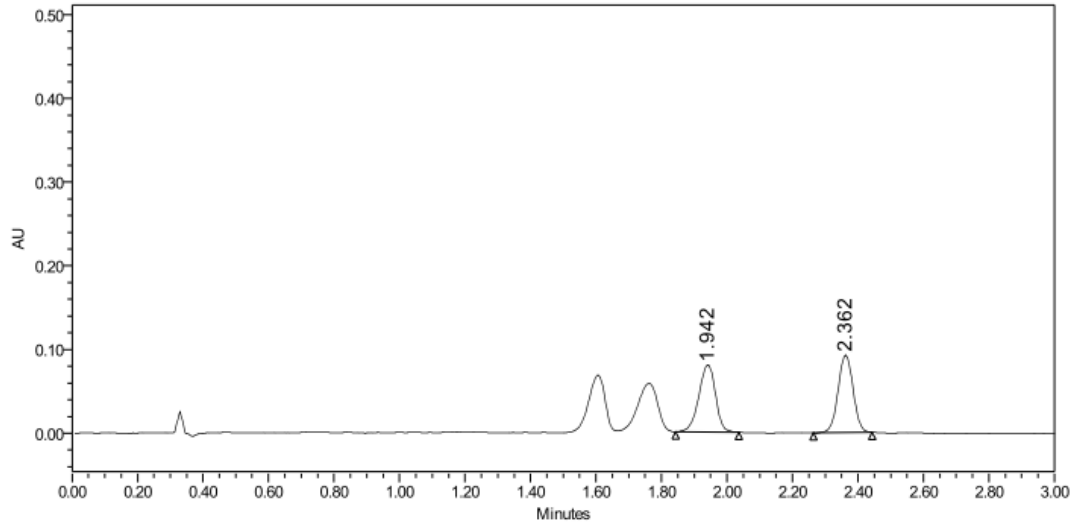


	RT	Area	% Area	Height
1	2.273	77891	46.66	29615
2	3.130	89055	53.34	41056

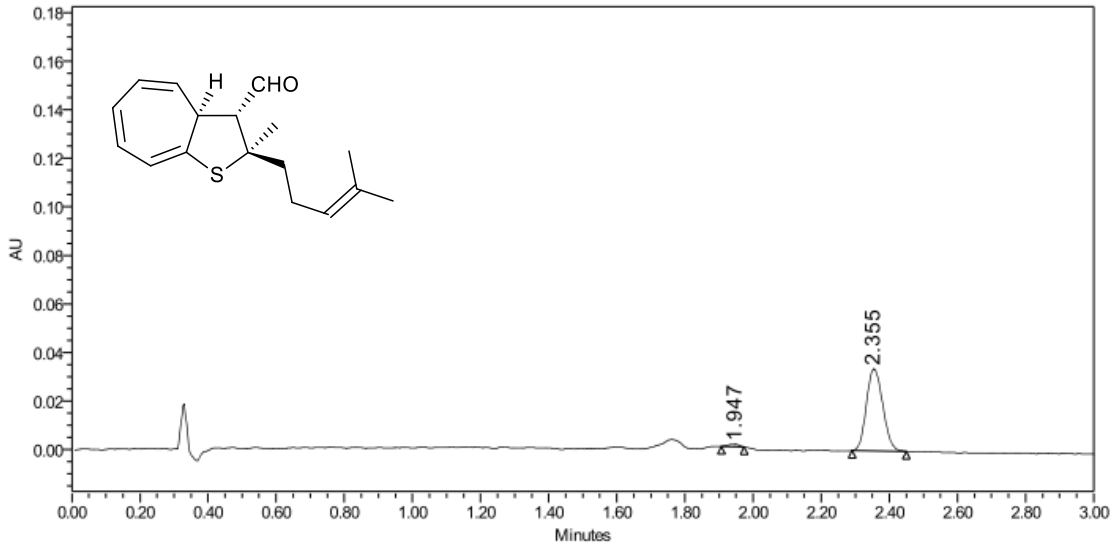


	RT	Area	% Area	Height
1	2.270	3375	1.46	1743
2	3.144	227274	98.54	107749

(2R,3R,3aS)-2-Methyl-2-(5-methylhex-4-en-1-yl)-3,3a-dihydro-2H-cyclohepta[b]thiophene-3-carbaldehyde 3n

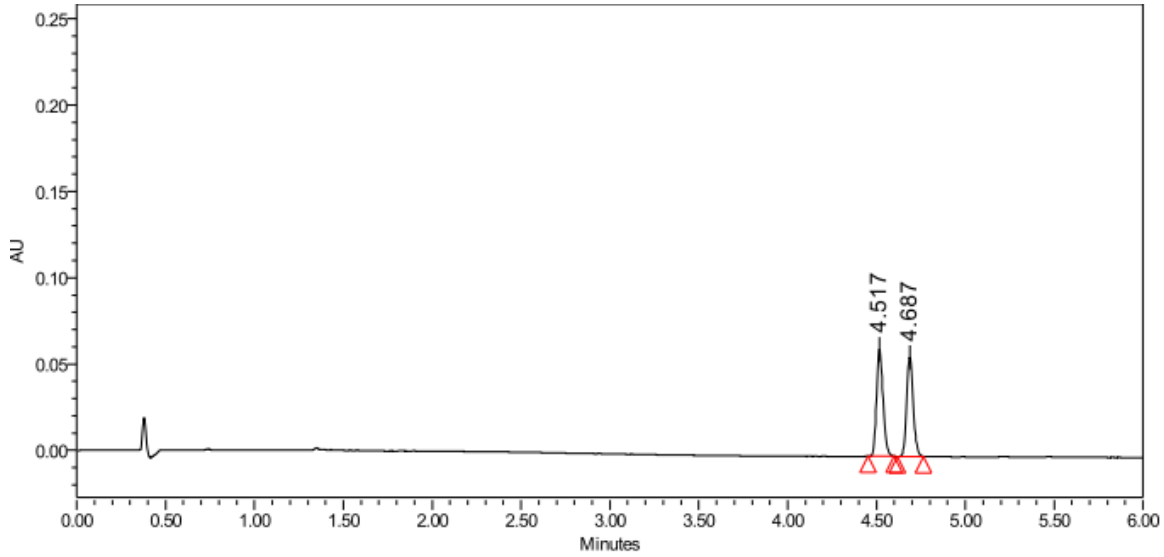


	RT	Area	% Area	Height
1	1.942	284434	49.09	80059
2	2.362	294956	50.91	92322



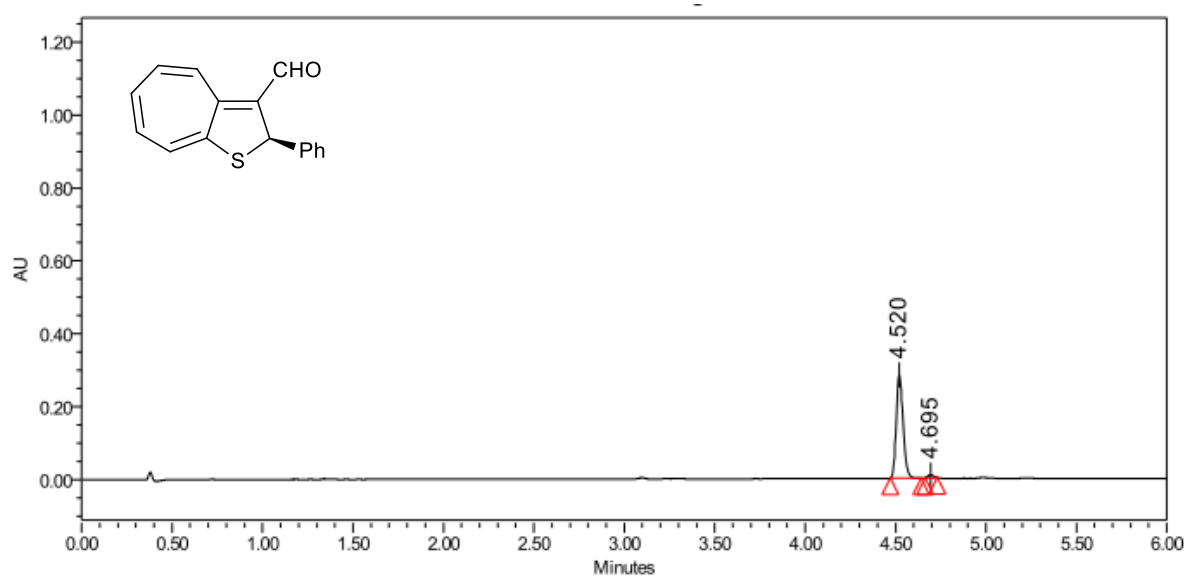
	RT	Area	% Area	Height
1	1.947	2341	2.03	981
2	2.355	112889	97.97	33783

(*R*)-2-Phenyl-2*H*-cyclohepta[*b*]thiophene-3-carbaldehyde 9



Peak Results

	RT	% Area
1	4.517	51.67
2	4.687	48.33



Peak Results

	RT	% Area
1	4.520	97.97
2	4.695	2.03