Bronsted-base-catalyzed remote cascade reactivity of 2,4-dienones – asymmetric synthesis of tetrahydrothiophenes

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Contents

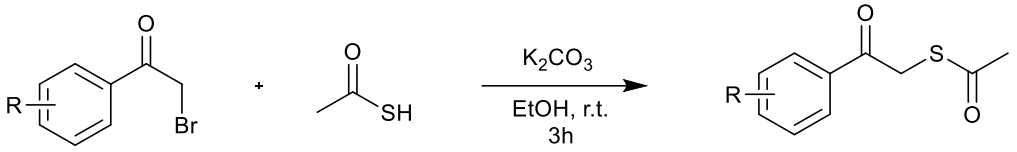
1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for 1H and 176 MHz for 13C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl3: 7.26 ppm for 1H NMR, 77.16 ppm for 13C NMR). Mass spectra were recorded on a Bruker Maxis Impact spectrometer using electrospray (ES+) ionization (referenced to the mass of the charged species). Optical rotations were measured on a Perkin-Elmer 241 polarimeter and [α]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. The enantiomeric ratio (er) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak IA and ID column). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). 2,4-Dienones **2a**-**d**, **2h**,[1] **2e**, **2f** and **2i**[2] were prepared applying Heck reaction of the suitable acrylate and vinyl bromide, according to literature precedents. Dienone **2g** was prepared following procedure described by Alexakis.[3]

1 R. Kowalczyk, P. J. Boratyński, A. J. Wierzba and J. Bąkowicz, *RSC Adv*., 2015, **5**, 66681.
2 D. Duvvuru, J.-F. Betzer, P. Retailleau, G. Frison and A. Marinetti, *Adv. Synth. Catal*., 2011, **353**, 483.
3 M. Tissot, D. Poggiali, H. Hénon, D. Müller, L. Guénée, M. Mauduit and A. Alexakis, *Chem. Eur. J.*, 2012, **18**, 8731.

2. Synthetic procedures

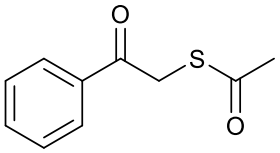
2.1 Procedure for synthesis of *S*-Acetyl-2-mercapto-1-phenylethanone



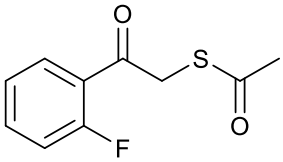
7 **8** **9**

S-Acetyl-2-mercaptoacetophenones **9** were prepared according to the literature data.[4] NMR spectra of compounds **9a** and **9e** were in accordance with the literature data.[4]

To the solution of thioacetic acid **8** (764 µL, 10 mmol, 1 equiv.) in ethanol (20 mL, 0.5 M) anhydrous potassium carbonate (1.4 g, 10 mmol, 1 equiv.) was added and the resulting mixture was stirred for 20 min. at room temperature. Subsequently, a solution of corresponding 2-bromoacetophenone **7** (10 mmol 1equiv.) in ethanol (2M) was added dropwise at room temperature and the reaction mixture was stirred at the same temperature until full substrate consumption indicated by TLC analysis (ca. 3h). Formed precipitate was filtered off, and washed with ethanol. Combined washings were concentrated *in vacuo*, dissolved in $CHCl_3$ (20 mL), washed with distilled water (2×10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford the crude product. Pure compound **9** was isolated by the flash chromatography (eluent: Hex:AcOEt 10:1).

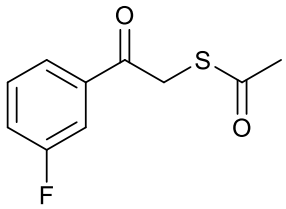


9a *S*-Acetyl-2-mercaptoacetophenone[4]
Following the general procedure **9a** was isolated as light yellow oil; yield: 90%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.60 (m, 1H), 7.48 (m, 2H), 4.40 (s, 2H), 2.41 (s, 3H).



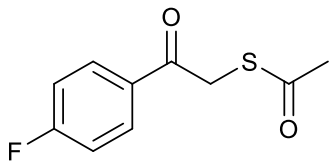
9b *S*-Acetyl-2-mercapto-2'-fluoroacetophenone
Following the general procedure **9b** was isolated as light yellow oil; yield: 85%; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.87 (td, *J* = 7.6, 1.8 Hz, 1H), 7.55 (dddd, *J* = 8.3, 7.1, 5.1, 1.9 Hz, 1H), 7.24 (ddd, *J* = 7.8, 7.3, 1.1 Hz, 1H), 7.16 (ddd, *J* = 11.1, 8.3, 1.1 Hz, 1H), 4.35 (d, *J* = 2.9 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 194.3, 191.3 (d, *J* = 4.1 Hz), 162.0 (d, *J* = 254.6 Hz), 135.3 (d, *J* = 9.0 Hz), 131.2 (d, *J* = 2.5 Hz), 124.8 (d, *J* = 3.2 Hz), 124.6 (d, *J* = 13.0 Hz), 116.8 (d, *J* = 23.6 Hz), 40.9 (d, *J* = 9.0 Hz), 30.3.

4 Y. Z. Adamczewska, J. M. Barker, P. R. Huddlestone and M. L. Wood, *Synth. Commun.* 1996, **26**, 1083.



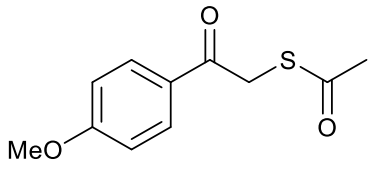
9c *S*-Acetyl-2-mercapto-3'-fluoroacetophenone

Following the general procedure **9c** was isolated as light yellow oil; yield: 97% ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (ddd, *J* = 7.8, 1.6, 1.0 Hz, 1H), 7.66 (ddd, *J* = 9.2, 2.6, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.8, 5.5 Hz, 1H), 7.29 (tdd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 4.35 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 194.0, 192.1 (d, *J* = 2.0 Hz), 162.9 (d, *J* = 248.6 Hz), 137.6 (d, *J* = 6.3 Hz), 130.5 (d, *J* = 7.7 Hz), 124.3 (d, *J* = 2.9 Hz), 120.8 (d, *J* = 21.3 Hz), 115.3 (d, *J* = 22.7 Hz), 36.6, 30.2.



9d *S*-Acetyl-2-mercapto-4'-fluoroacetophenone

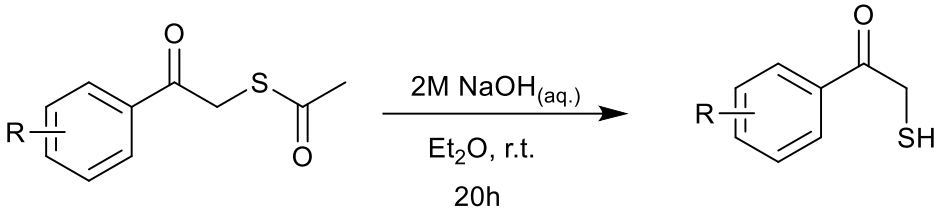
Following the general procedure **9d** was isolated as light yellow oil; yield: 96%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.14 (dd, *J* = 8.9, 8.3 Hz, 2H), 4.35 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.0 (d, *J* = 410.3 Hz), 166.8, 165.4, 132.0 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 9.5 Hz), 116.0 (d, *J* = 22.2 Hz), 36.4, 30.2.



9e *S*-Acetyl-2-mercapto-4'-methoxyacetophenone[4]

Following the general procedure **9e** was isolated as light yellow oil; yield: 51%.

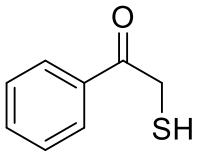
2.2 Procedure for synthesis of 2-mercapto-1-phenylethanone 3



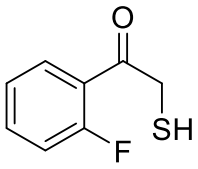
9 **3**

2-Mercaptoacetophenones **3** were prepared according to the literature procedure.[5] NMR spectra of **3a** were in accordance with literature data.[5]

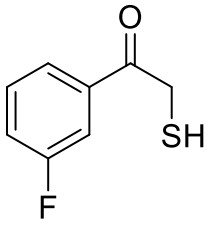
To the solution of *S*-acetyl-2-mercapto-1-phenylethanone **9** (1.75 g, 9 mmol, 1 equiv.) in Et_2O (9 mL, 1M) 2M aqueous solution of sodium hydroxide (9 mL, 2 equiv.) were added and the resulting biphasic mixture was stirred vigorously at room temperature for 20 h. Next, the aqueous phase was separated, acidified with 1M aqueous solution of HCl and extracted with $CHCl_3$ (2×15 mL). Organic phase was washed with distilled water (2×10 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford the crude product. Pure compound was isolated by the flash chromatography (eluent: Hex:AcOEt 10:1).



3a 2-Mercapto-1-phenylethanone[5]
Colorless oil; yield: 55%.

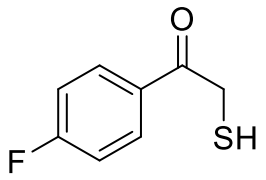


3b 2-Mercapto-1-(2'-fluorophenyl)ethanone
Following the general procedure **3b** was isolated as light yellow oil; yield: 49%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 1H), 7.55 (dddd, *J* = 8.2, 7.1, 5.1, 1.9 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.15 (ddd, *J* = 11.3, 8.3, 1.0 Hz, 1H), 3.93 (ddd, *J* = 7.7, 2.4, 0.6 Hz, 2H), 2.04 (td, *J* = 7.7, 1.0 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.0 (d, *J* = 4.3 Hz), 161.8 (d, *J* = 254.3 Hz), 135.2 (d, *J* = 9.0 Hz), 131.4 (d, *J* = 2.5 Hz), 124.8 (d, *J* = 3.5 Hz), 123.7 (d, *J* = 13.0 Hz), 116.7 (d, *J* = 23.8 Hz), 35.4 (d, *J* = 8.9 Hz).



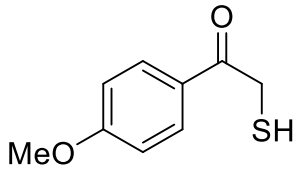
3c 2-Mercapto-1-(3'-fluorophenyl)ethanone
Following the general procedure **3c** was isolated as light yellow solid; yield: 58%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.72 (ddd, *J* = 7.8, 1.6, 1.0 Hz, 1H), 7.64 (dddd, *J* = 9.3, 2.7, 1.6, 0.4 Hz, 1H), 7.46 (dddd, *J* = 8.2, 7.8, 5.5, 0.4 Hz, 1H), 7.29 (tdd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.92 (d, *J* = 7.5 Hz, 2H), 2.11 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.6, 162.9 (d, *J* = 248.6 Hz), 137.1 (d, *J* = 6.4 Hz), 130.6 (d, *J* = 7.6 Hz), 124.3 (d, *J* = 3.1 Hz), 120.7 (d, *J* = 21.2 Hz), 115.3 (d, *J* = 22.4 Hz), 31.2.

5 C.-C. Han, R. Balakumar, *Tetrahedron Lett.* **2006**, *47*, 8255.



3d Mercapto-1-(4'-fluorophenyl)ethanone

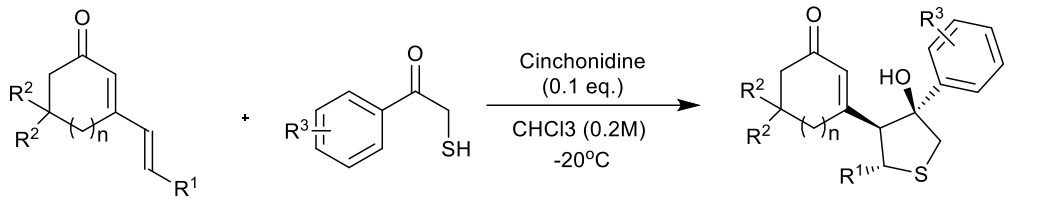
Following the general procedure **3d** was isolated as light yellow oil; yield: 52%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.15 (dd, *J* = 8.9, 8.3 Hz, 2H), 3.92 (d, *J* = 7.4 Hz, 2H), 2.11 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.29, 166.02 (d, *J* = 256.0 Hz), 131.46 (d, *J* = 3.0 Hz), 116.02 (d, *J* = 21.9 Hz), 31.02.



3e Mercapto-1-(4'-methoxyphenyl)ethanone

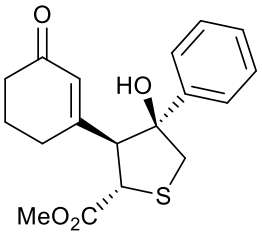
Following the general procedure **3e** was isolated as yellow solid; yield: 50%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.90 (d, *J* = 7.3 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.4, 163.9, 130.9, 128.0, 114.0, 55.6, 30.8.

2.3 Brønsted-base-catalyzed remote cascade – general procedure

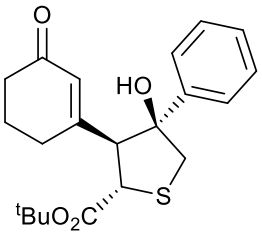


2 **3** **1** n = 0,1

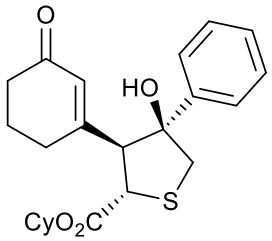
To the solution of corresponding 2-mercapto-1-phenylethanone **3** (0.15 mmol, 1.5 equiv.) in $CHCl_3$ (0.5 mL, 0.3 M) placed in a standard glass vial cinchonidine **4c** (0.01 mmol, 0.1 equiv.) was added in one portion at room temperature and the resulting mixture was stirred for 10 minutes at the same temperature. Subsequently, the reaction mixture was cooled down to -20 °C, the corresponding 2,4-dienone **2** (0.1 mmol, 1 equiv.) was added in one portion and the reaction mixture was stirred at -20 °C. Upon reaction completion (as indicated by ^{1}H NMR) the reaction mixture was directly subjected to the flash chromatography on silica (eluent: Hex:AcOEt 4:1) to afford pure **1**.



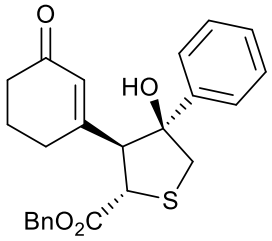
1a (2*S*,3*S*,4*S*)-Methyl 4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1a** (> 20:1 dr) was obtained in 90% yield as white foam. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.36 (td, *J* = 8.1, 7.7, 1.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 5.94 (dt, *J* = 3.6, 1.5 Hz, 1H), 4.34 (dd, *J* = 10.6, 1.7 Hz, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.74 (d, *J* = 1.6 Hz, 3H), 3.47 (dd, *J* = 10.5, 2.6 Hz, 1H), 3.14 (dt, *J* = 4.3, 1.4 Hz, 1H), 3.06 (d, *J* = 11.9 Hz, 1H), 2.26 – 2.12 (m, 3H), 1.76 – 1.68 (m, 1H), 1.67 – 1.57 (m, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.5, 172.2, 160.3, 140.5, 129.0, 128.6, 128.0, 125.0, 85.3, 62.6, 52.9, 48.7, 47.1, 37.3, 30.6, 22.5. HRMS calculated for $[C_{18}H_{20}O_4S+H]^+$: 333.1156; found: 333.1148. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 16.0 min, τ_{minor} = 36.2 min (97:3 er). $[\alpha_D^{20}]$ = - 31.3 (c 1.0, $CHCl_3$).



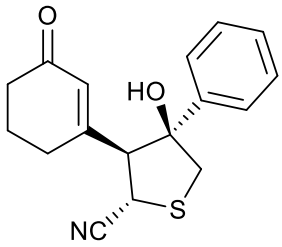
1b (2*S*,3*S*,4*S*)-*tert*-Butyl 4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1b** (> 20:1 dr) was obtained in 98% yield as a white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.93 (d, *J* = 1.9 Hz, 1H), 4.22 (d, *J* = 10.3 Hz, 1H), 3.74 (d, *J* = 11.8 Hz, 1H), 3.42 (d, *J* = 10.4 Hz, 1H), 3.03 (d, *J* = 11.9 Hz, 1H), 2.94 (s, 1H), 2.21 (dddd, *J* = 26.1, 13.0, 8.1, 5.2 Hz, 3H), 1.74 (td, *J* = 7.9, 4.9 Hz, 1H), 1.71 – 1.60 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.3, 170.7, 160.5, 140.5, 128.9, 128.6, 128.0, 125.0, 85.6, 82.5, 62.6, 50.0, 47.1, 37.3, 30.5, 28.0, 22.5. HRMS calculated for $[C_{21}H_{26}O_4S+H]^+$: 375.1625; found: 375.1636. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 8.5 min, τ_{minor} = 20.2 min (96:4 er). $[\alpha_D^{20}]$ = - 11.5 (c 0.5, $CHCl_3$).



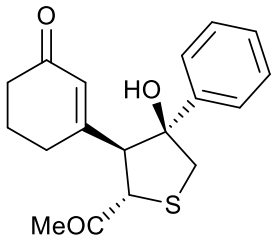
1c (2*S*,3*S*,4*S*)-Cyclohexyl 4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1c** (> 20:1 dr) was obtained in 96% yield as a white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.36 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.31 – 7.27 (m, 1H), 5.93 (d, *J* = 1.6 Hz, 1H), 4.79 (ddt, *J* = 12.9, 8.7, 3.9 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 3.76 (d, *J* = 11.8 Hz, 1H), 3.46 (d, *J* = 10.4 Hz, 1H), 3.05 (d, *J* = 11.9 Hz, 1H), 2.96 (s, 1H), 2.28 – 2.12 (m, 3H), 1.88 – 1.77 (m, 2H), 1.76 – 1.67 (m, 3H), 1.67 – 1.59 (m, 1H), 1.52 (dt, *J* = 9.8, 3.6 Hz, 1H), 1.48 – 1.41 (m, 2H), 1.39 – 1.32 (m, 2H), 1.27 (dd, *J* = 9.9, 3.4 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.3, 171.1, 160.3, 140.5, 129.0, 128.6, 128.0, 125.0, 85.5, 74.4, 62.6, 49.3, 47.1, 37.3, 31.4, 31.3, 30.6, 25.3, 23.6, 23.5, 22.5. HRMS calculated for $[C_{23}H_{28}O_4S+H]^+$: 401.1782; found: 401.1789. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 11.8 min, τ_{minor} = 29.8 min (95:5 er). $[\alpha_D^{20}]$ = - 24.4 (c 1.0, $CHCl_3$).



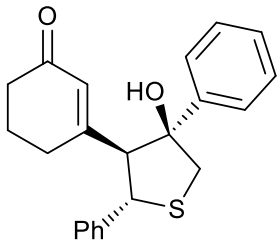
1d (2*S*,3*S*,4*S*)-Benzyl 4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1d** (> 20:1 dr) was obtained in 33% yield as a beige solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.38 – 7.32 (m, 7H), 7.32 – 7.28 (m, 1H), 5.91 (d, *J* = 1.7 Hz, 1H), 5.26 – 5.11 (m, 2H), 4.37 (d, *J* = 10.3 Hz, 1H), 3.77 (d, *J* = 11.9 Hz, 1H), 3.48 (d, *J* = 10.3 Hz, 1H), 3.05 (d, *J* = 11.9 Hz, 1H), 2.75 (s, 1H), 2.22 – 2.10 (m, 3H), 1.71 – 1.53 (m, 4H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.1, 171.5, 159.8, 140.2, 135.2, 129.1, 128.7, 128.6, 128.5, 128.2, 128.1, 125.0, 85.5, 67.6, 62.7, 48.9, 47.2, 37.3, 30.4, 22.4. HRMS calculated for $[C_{24}H_{24}O_4S+H]^+$: 409.1469; found: 409.1470. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 20.4 min, t_{minor} = 40.0 min (95:5 er). $[\alpha_D^{20}]$ = - 19.9 (c 1.0, $CHCl_3$).



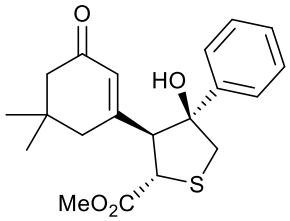
1e (2*S*,3*S*,4*S*)-4-Hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carbonitrile. Following the general procedure **1e** (> 20:1 dr) was obtained in 87% yield as a yellow oil. ^{1}H NMR (700 MHz, Acetonitrile-d_3) δ 7.53 – 7.48 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 5.73 (d, *J* = 1.7 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 3.98 (s, 1H), 3.86 (s, 1H), 3.42 (d, *J* = 11.4 Hz, 1H), 3.10 (d, *J* = 11.7 Hz, 1H), 2.27 (dddd, *J* = 18.2, 7.3, 4.5, 1.7 Hz, 1H), 2.13 (dd, *J* = 7.4, 6.0 Hz, 2H), 1.82 – 1.76 (m, 1H), 1.72 (ddd, *J* = 13.6, 6.2, 4.4 Hz, 1H), 1.69 – 1.63 (m, 1H); ^{13}C NMR (176 MHz, Acetonitrile$_{33}$) δ 199.3, 158.6, 141.7, 130.8, 129.4, 128.8, 126.4, 120.1, 118.3, 85.6, 65.2, 47.2, 37.9, 34.7, 30.0, 23.3. HRMS calculated for $[C_{17}H_{17}NO_2S+H]^+$: 300.1053; found: 300.1048. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} =12.3 min, τ_{minor} = 21.5 min (79:21 er). $[\alpha_D^{20}]$ = 4.3 (c 0.5, $CHCl_3$).



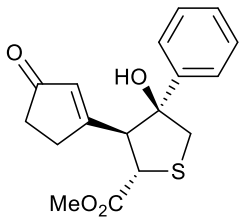
1f 3-((2*S*,3*S*,4*S*)-2-Acetyl-4-hydroxy-4-phenyltetrahydrothiophen-3-yl)cyclohex-2-enone. Following the general procedure **1f** (5:1 dr) was obtained in 84% yield as a yellow oil. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.30 (m, 1H), 6.09 (t, *J* = 1.1 Hz, 1H), 4.68 (d, *J* = 10.3 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 3.67 (d, *J* = 10.4 Hz, 1H), 3.50 (dd, *J* = 11.8, 1.2 Hz, 1H), 3.11 (d, *J* = 11.7 Hz, 1H), 2.67 (dt, *J* = 17.8, 6.0 Hz, 1H), 2.42 (ddd, *J* = 13.4, 7.4, 5.7 Hz, 2H), 2.07 (tt, *J* = 6.0, 1.8 Hz, 2H), 1.79 (s, 3H), 1.75 – 1.65 (m, 1H); ^{13}C NMR (176 MHz, Chloroform-*d*) δ 208.3, 199.1, 161.4, 141.0, 128.9, 128.2, 127.2, 124.8, 86.4, 66.5, 54.2, 47.5, 37.6, 32.7, 26.9, 23.0. HRMS calculated for $[C_{18}H_{20}O_3S+H]^+$: 317.1206; found: 317.1197. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{minor} = 32.2 min, τ_{major} = 55.4 min (29:71 er). $[\alpha_D^{20}]$ = 3.3 (c 0.5, $CHCl_3$).



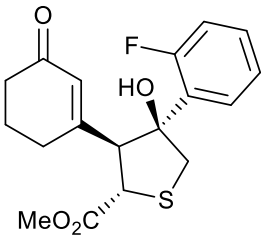
1g 3-((2*S*,3*S*,4*S*)-4-Hydroxy-2,4-diphenyltetrahydrothiophen-3-yl)cyclohex-2-enone. Following the general procedure **1g** (> 20:1 dr) was obtained in 35% yield as a colorless oli.^{1}H NMR (700 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.44 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.38 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.24 (m, 2H), 5.89 – 5.87 (m, 1H), 4.91 (d, *J* = 11.3 Hz, 1H), 3.92 (d, *J* = 12.0 Hz, 1H), 3.20 (d, *J* = 11.3 Hz, 1H), 3.16 (d, *J* = 12.0 Hz, 1H), 3.03 (d, *J* = 1.8 Hz, 1H), 2.10 (dd, *J* = 7.4, 6.0 Hz, 2H), 1.98 (dddd, *J* = 18.3, 7.7, 4.6, 1.6 Hz, 1H), 1.74 – 1.68 (m, 1H), 1.64 – 1.58 (m, 1H), 1.58 – 1.51 (m, 1H); ^{13}C NMR (176 MHz, Chloroform-*d*) δ 199.3, 160.5, 141.4, 139.2, 129.7, 128.7, 128.6, 128.0, 127.9, 127.9, 124.9, 85.7, 69.4, 53.3, 47.3, 37.2, 30.6, 22.4. HRMS calculated for $[C_{22}H_{22}O_2S+H]^+$: 351.1414; found: 351.1410. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} =10.7 min, τ_{minor} = 14.8 min (84:16 er). $[\alpha_D^{20}]$ = 24.0 (c 1.0, $CHCl_3$).



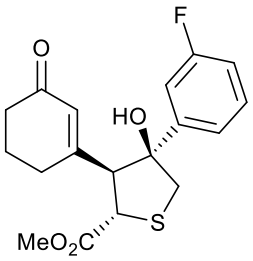
1h (2*S*,3*S*,4*S*)-Methyl 3-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)-4-hydroxy-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1h** (> 20:1 dr) was obtained in 98% yield as a yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.25 (m, 1H), 5.98 (s, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 3.74 (d, *J* = 1.0 Hz, 3H), 3.72 (d, *J* = 11.8 Hz, 1H), 3.47 (d, *J* = 10.6 Hz, 1H), 3.09 (s, 1H), 3.06 (d, *J* = 11.8 Hz, 1H), 2.21 (d, *J* = 18.4 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.64 (d, *J* = 18.3 Hz, 1H), 0.82 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.6, 172.2, 157.9, 140.3, 128.6, 128.3, 128.0, 125.2, 85.4, 62.1, 52.9, 50.8, 49.0, 47.6, 44.6, 33.3, 28.4, 27.5. HRMS calculated for $[C_{20}H_{24}O_4S+H]^+$: 361.1469; found: 361.1473. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 15.7 min, τ_{minor} = 20.1 min (96:4 er). $[\alpha_D^{20}]$ = - 18.4 (c 1.0, $CHCl_3$).



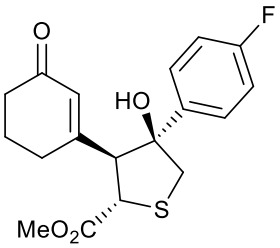
1i (2*S*,3*S*,4*S*)-Methyl 4-hydroxy-3-(3-oxocyclopent-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate. Following the general procedure **1i** (> 20:1 dr) was obtained in 90% yield as a yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.4, 1.3 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 6.00 – 5.96 (m, 1H), 4.35 (d, *J* = 10.1 Hz, 1H), 3.85 (d, *J* = 10.2 Hz, 1H), 3.77 (d, *J* = 1.2 Hz, 3H), 3.72 (d, *J* = 11.9 Hz, 1H), 3.19 (s, 1H), 3.07 (d, *J* = 11.9 Hz, 1H), 2.40 (dd, *J* = 18.9, 7.1 Hz, 1H), 2.23 – 2.07 (m, 2H), 2.06 – 1.99 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 209.3, 176.1, 172.2, 140.3, 133.0, 128.7, 128.1, 125.0, 85.5, 58.7, 53.1, 48.9, 47.6, 35.0, 31.9. HRMS calculated for $[C_{17}H_{18}O_4S+H]^+$: 319.0999; found: 319.0998. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 13.8 min, τ_{minor} = 26.9 min (92:8 er). $[\alpha_D^{20}]$ = - 14.8 (c 1.0, $CHCl_3$).



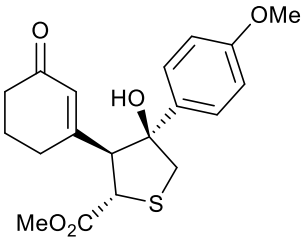
1j (2*S*,3*S*,4*S*)-Methyl 4-(2-fluorophenyl)-4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)tetrahydrothiophene-2-carboxylate. Following the general procedure **1j** (> 20:1 dr) was obtained in 95% yield as a colorless solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.63 (td, *J* = 8.0, 1.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (ddd, *J* = 12.4, 8.1, 1.2 Hz, 1H), 5.96 (d, *J* = 1.4 Hz, 1H), 4.38 (d, *J* = 10.7 Hz, 1H), 3.99 (d, *J* = 11.6 Hz, 1H), 3.85 (d, *J* = 10.7 Hz, 1H), 3.75 (s, 3H), 3.23 (s, 1H), 2.96 (dd, *J* = 11.6, 1.3 Hz, 1H), 2.35 – 2.28 (m, 1H), 2.25 – 2.11 (m, 2H), 1.75 (tddd, *J* = 9.3, 7.3, 4.4, 2.3 Hz, 2H), 1.66 – 1.58 (m, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.5, 171.8, 160.4, 158.5, 130.2 (d, *J* = 8.8 Hz), 129.0, 128.4 (d, *J* = 3.2 Hz), 127.3 (d, *J* = 10.9 Hz), 124.6 (d, *J* = 3.3 Hz), 116.2 (d, *J* = 23.5 Hz), 83.5 (d, *J* = 5.1 Hz), 59.3 (d, *J* = 5.5 Hz), 52.9, 48.3, 44.4 (d, *J* = 5.6 Hz), 37.3, 30.2, 22.5. HRMS calculated for $[C_{18}H_{19}FO_4S+H]^+$: 351.1061; found: 351.1055. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 11.3 min, t_{minor} = 14.9 min (92:8 er). $[\alpha_D^{20}]$ = - 10.5 (c 0.5, $CHCl_3$).



1k (2*S*,3*S*,4*S*)-Methyl 4-(3-fluorophenyl)-4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)tetrahydrothiophene-2-carboxylate. Following the general procedure **1k** (> 20:1 dr) was obtained in 98% yield as a light yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 (td, *J* = 8.2, 5.9 Hz, 1H), 7.26 (ddt, *J* = 5.4, 4.6, 1.9 Hz, 2H), 7.00 (tdd, *J* = 8.3, 2.5, 1.1 Hz, 1H), 5.94 (d, *J* = 1.7 Hz, 1H), 4.31 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.72 (d, *J* = 11.9 Hz, 1H), 3.47 (d, *J* = 10.2 Hz, 1H), 3.12 (s, 1H), 3.06 (d, *J* = 11.9 Hz, 1H), 2.30 – 2.18 (m, 3H), 1.83 – 1.62 (m, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.3, 172.0, 162.3, 159.6, 143.3 (d, *J* = 7.0 Hz), 130.2 (d, *J* = 8.0 Hz), 129.2, 120.6 (d, *J* = 3.0 Hz), 115.0 (d, *J* = 21.0 Hz), 112.7 (d, *J* = 23.3 Hz), 85.0, 62.5, 53.0, 48.6, 47.1, 37.3, 30.4, 22.5. HRMS calculated for $[C_{18}H_{19}FO_4S+H]^+$: 351.1061; found: 351.1051. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 11.9 min, t_{minor} = 21.4 min (89:11 er). $[\alpha_D^{20}]$ = - 12.7 (c 0.5, $CHCl_3$).

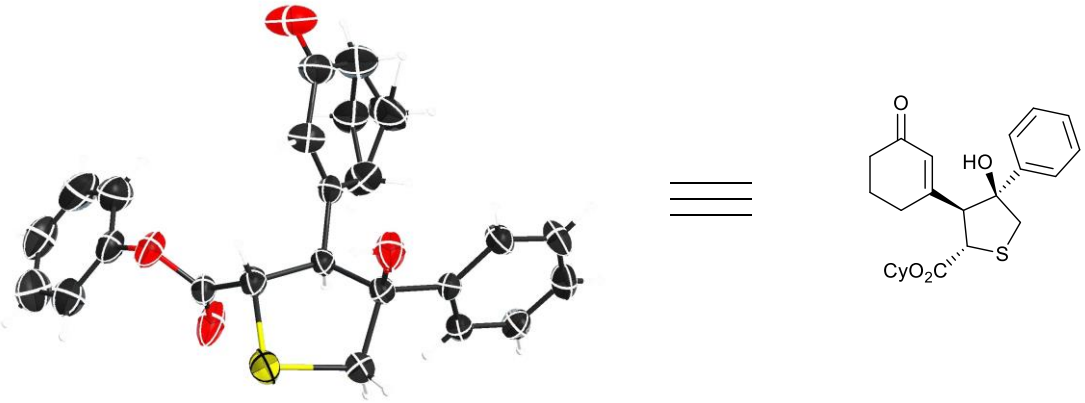


1l (2*S*,3*S*,4*S*)-Methyl 4-(4-fluorophenyl)-4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)tetrahydrothiophene-2-carboxylate. Following the general procedure **1l** (> 20:1 dr) was obtained in 87% yield as a light yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.09 – 7.03 (m, 2H), 5.93 (q, *J* = 2.8, 2.2 Hz, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.73 (d, *J* = 11.9 Hz, 1H), 3.46 (d, *J* = 10.2 Hz, 1H), 3.04 (d, *J* = 11.9 Hz, 1H), 3.00 – 2.96 (m, 1H), 2.27 – 2.18 (m, 3H), 1.82 – 1.62 (m, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.20, 172.08, 163.04, 161.63, 159.70, 136.11 (d, *J* = 3.2 Hz), 129.19, 126.93 (d, *J* = 8.1 Hz), 115.52 (d, *J* = 21.3 Hz), 85.10, 62.40, 53.45, 52.99, 48.48, 47.22, 37.26, 30.55, 22.49. HRMS calculated for $[C_{18}H_{19}FO_4S+H]^+$: 351.1061; found: 351.1060. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 12.5 min, τ_{minor} = 28.1 min (90:10 er). $[\alpha_D^{20}]$ = - 8.6 (c 0.5, $CHCl_3$).



1m (2*S*,3*S*,4*S*)-Methyl 4-hydroxy-4-(4-methoxyphenyl)-3-(3-oxocyclohex-1-en-1-yl)tetrahydrothiophene-2-carboxylate. Following the general procedure **1m** (> 20:1 dr) was obtained in 85% yield as a colorless solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.94 (d, *J* = 1.6 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 3H), 3.75 (d, *J* = 0.6 Hz, 3H), 3.73 (d, *J* = 11.8 Hz, 1H), 3.45 (d, *J* = 10.4 Hz, 1H), 3.02 (d, *J* = 11.9 Hz, 1H), 2.82 (d, *J* = 5.2 Hz, 1H), 2.26 – 2.18 (m, 3H), 1.80 – 1.73 (m, 1H), 1.72 – 1.63 (m, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 199.3, 172.2, 160.2, 159.2, 132.3, 129.0, 126.2, 113.9, 85.2, 62.3, 55.3, 52.9, 48.5, 47.1, 37.3, 30.6, 22.5. HRMS calculated for $[C_{19}H_{22}O_5S+H]^+$: 363.1261; found: 363.1259. The er was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH (80:20)]; flow rate 1mL×min^{-1} τ_{major} = 23.6 min, τ_{minor} = 37.1 min (72:28 er). $[\alpha_D^{20}]$ = -4.9 (c 1.0, $CHCl_3$).

3. Crystal and X-ray data for (2*S*,3*S*,4*S*)-cyclohexyl 4-hydroxy-3-(3-oxocyclohex-1-en-1-yl)-4-phenyltetrahydrothiophene-2-carboxylate

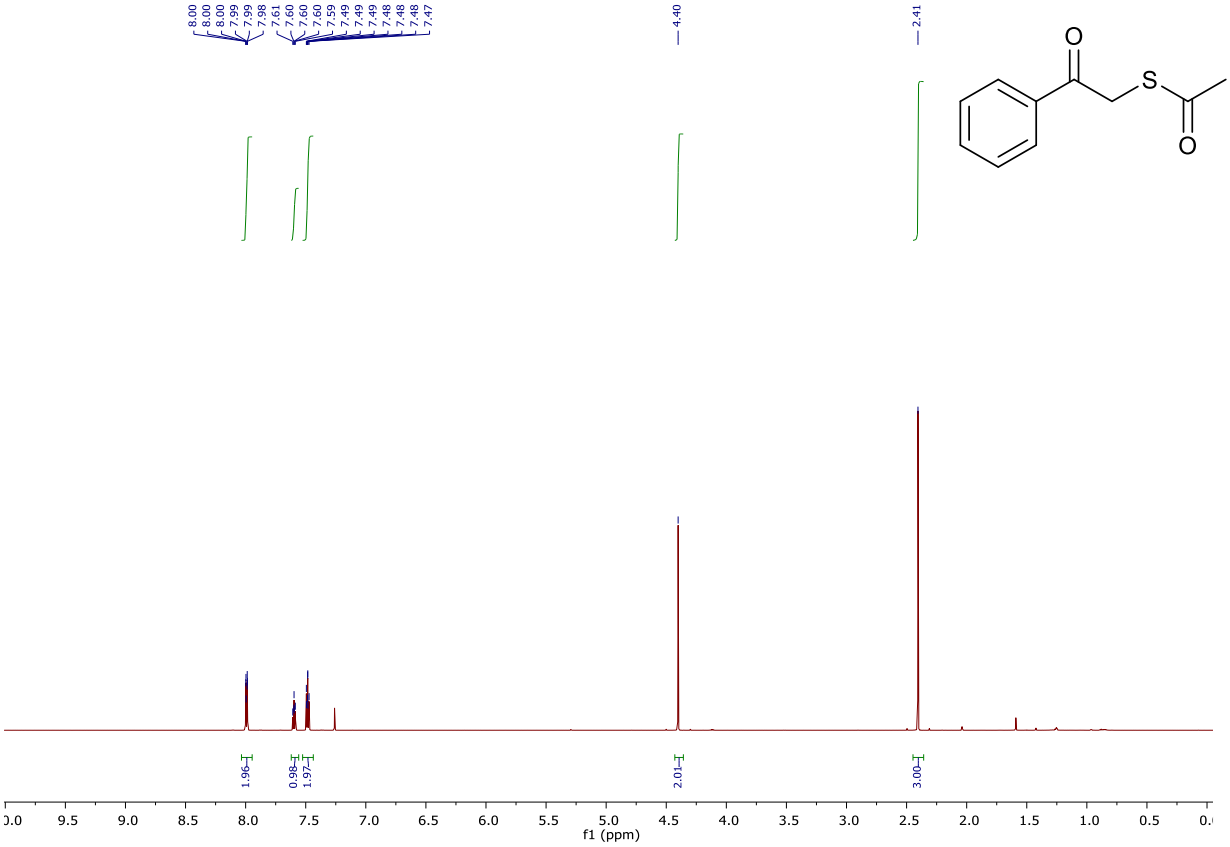


Formula $C_{23}H_{22}O_4S_1$, triclimic, space group P1, Z = 1, cell constants a = 5.6715(2) Å, b = 8.7531(2) Å, c = 10.1807(2) Å, α = 84.0710(10)°, β = 82.0360(10)°, γ = 83.6930(10)°, V = 495.503(17) $Å^3$. The data was collected on a Bruker Smart Apex2 diffractometer at 100 K using Incoatec IμS Cu-Kα (λ =1.54178 Å) as a source of radiation. The integration of the data yielded a total of 5975 reflections to a θ angle of 84.6°, of which 3276 were independent (Rint =1. 5%,) and 3241 were greater than $2\sigma(F^2)$. The final anisotropic full-matrix least-squares refinement on F^2 with 265 variables converged at R_1 = 3.64%, for the observed data and wR_2 = 9.17% for all data. The hydrogen atoms were placed in calculated positions and refined isotropically by using a riding model. The goodness-of-fit was 1.119.

The absolute configuration of X was determined from anomalous scattering, by calculating the Flack parameter: -0.004(9) from 1299 selected quotients (Parsons' method).

CCDC 1548930 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/data_request/cif.

4. NMR data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7.49
7.49
7.48
7.48
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S
O
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1.97
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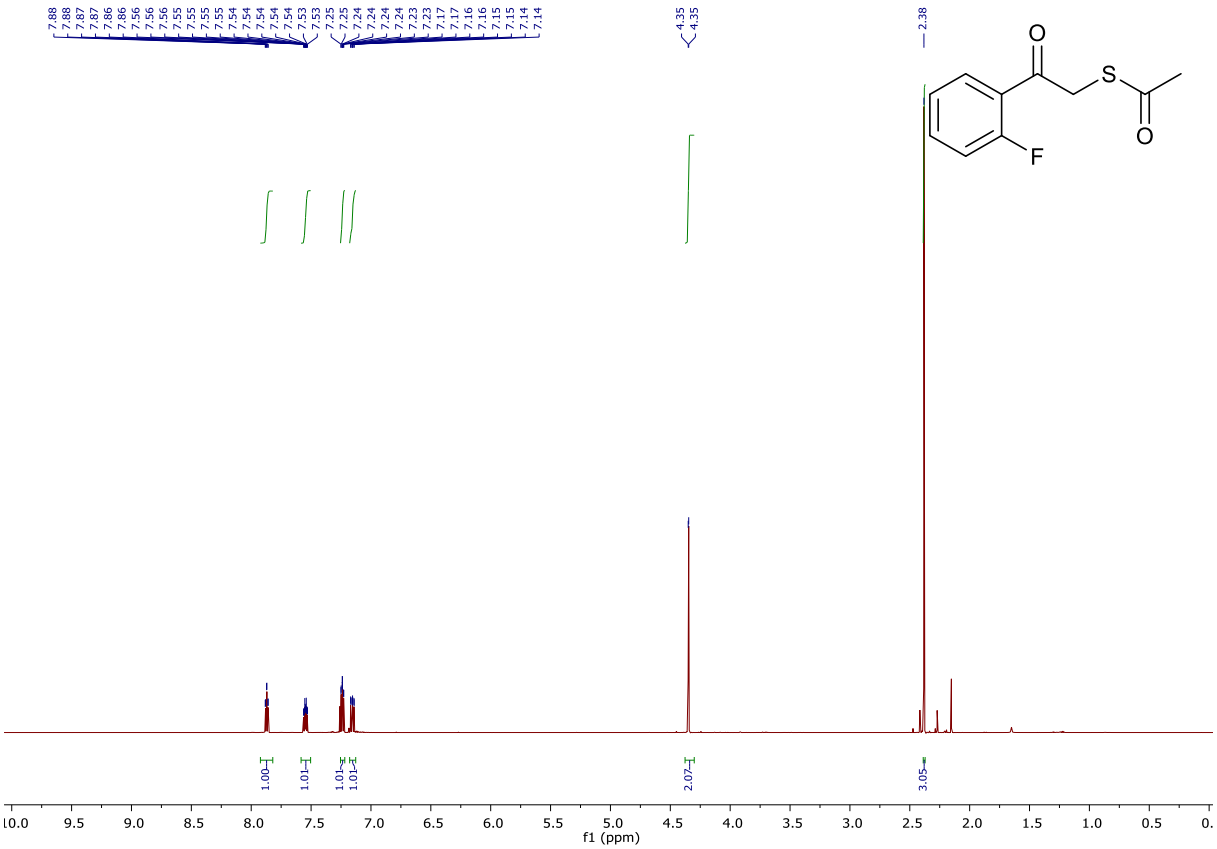
3.00
f1 (ppm)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O
S
O
F
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1.01
1.01
1.01
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3.05
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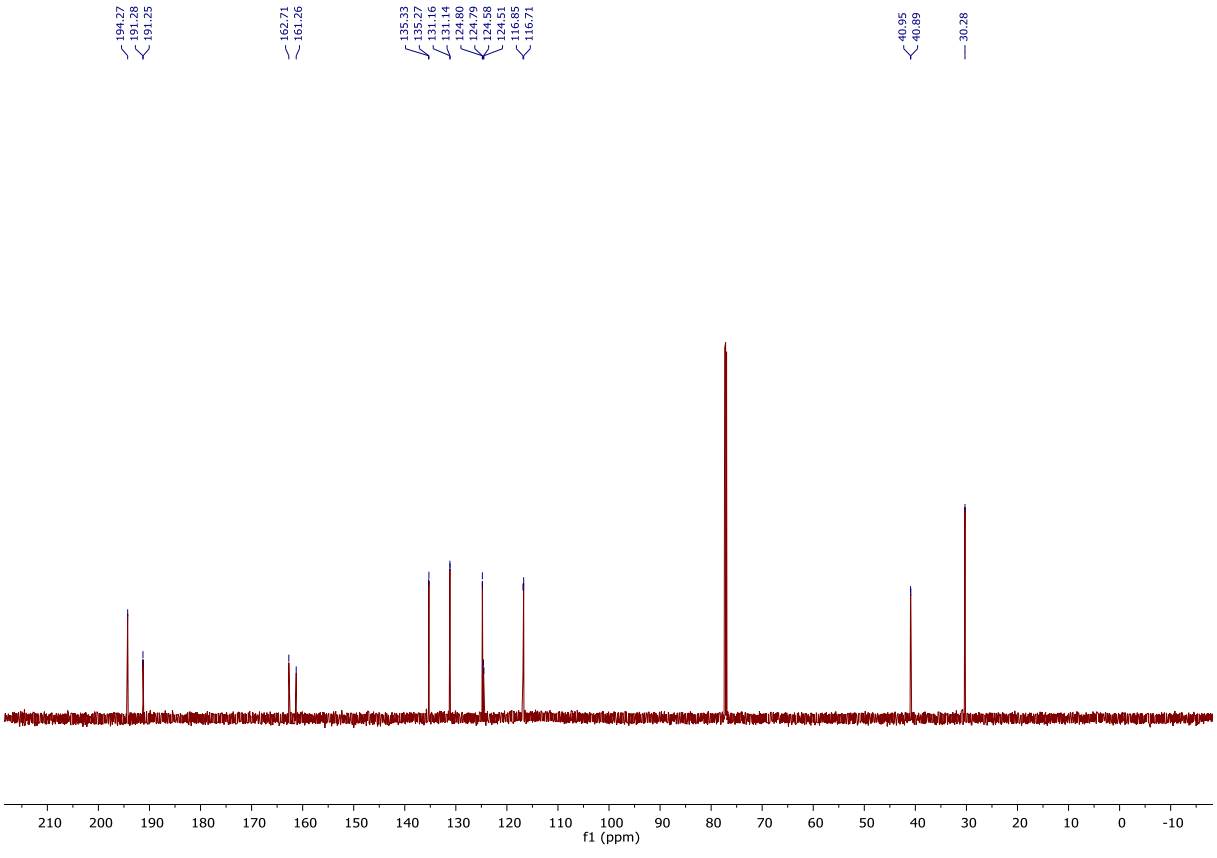
f1 (ppm)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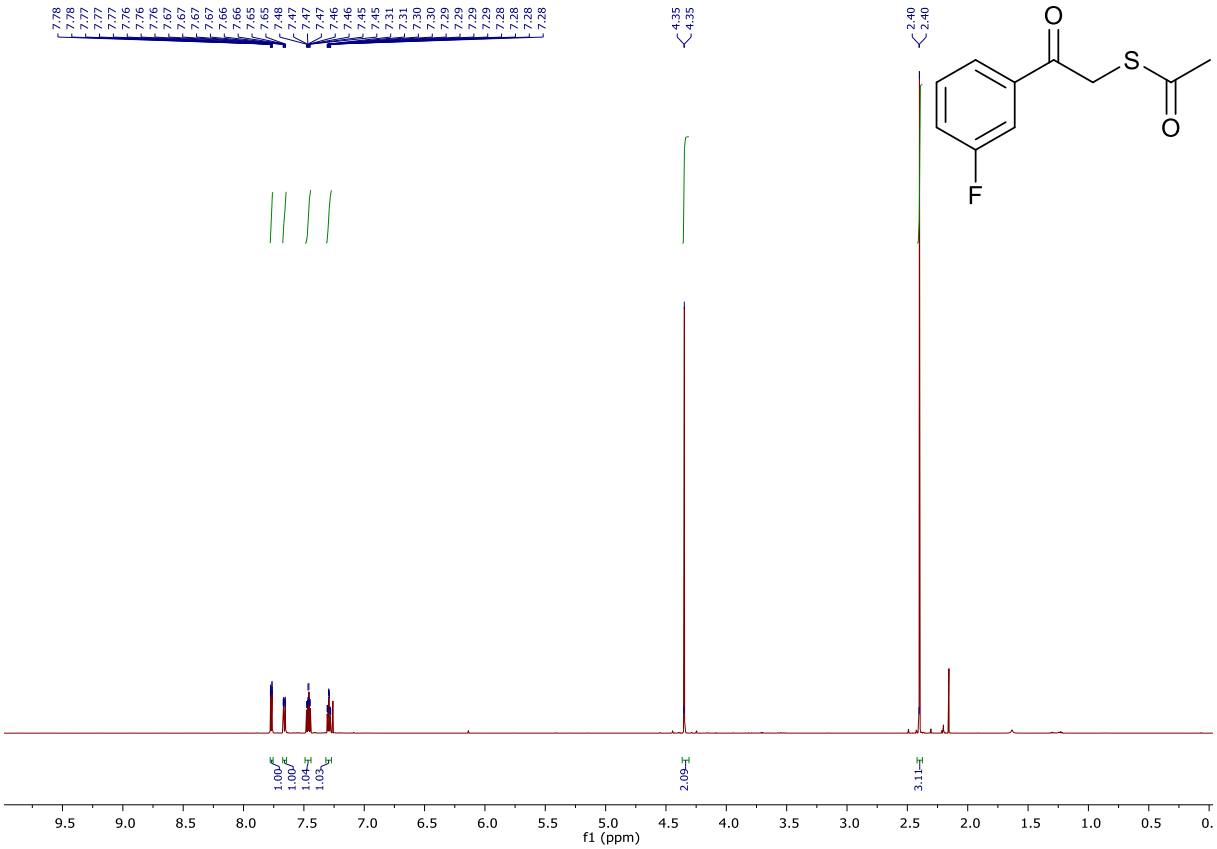
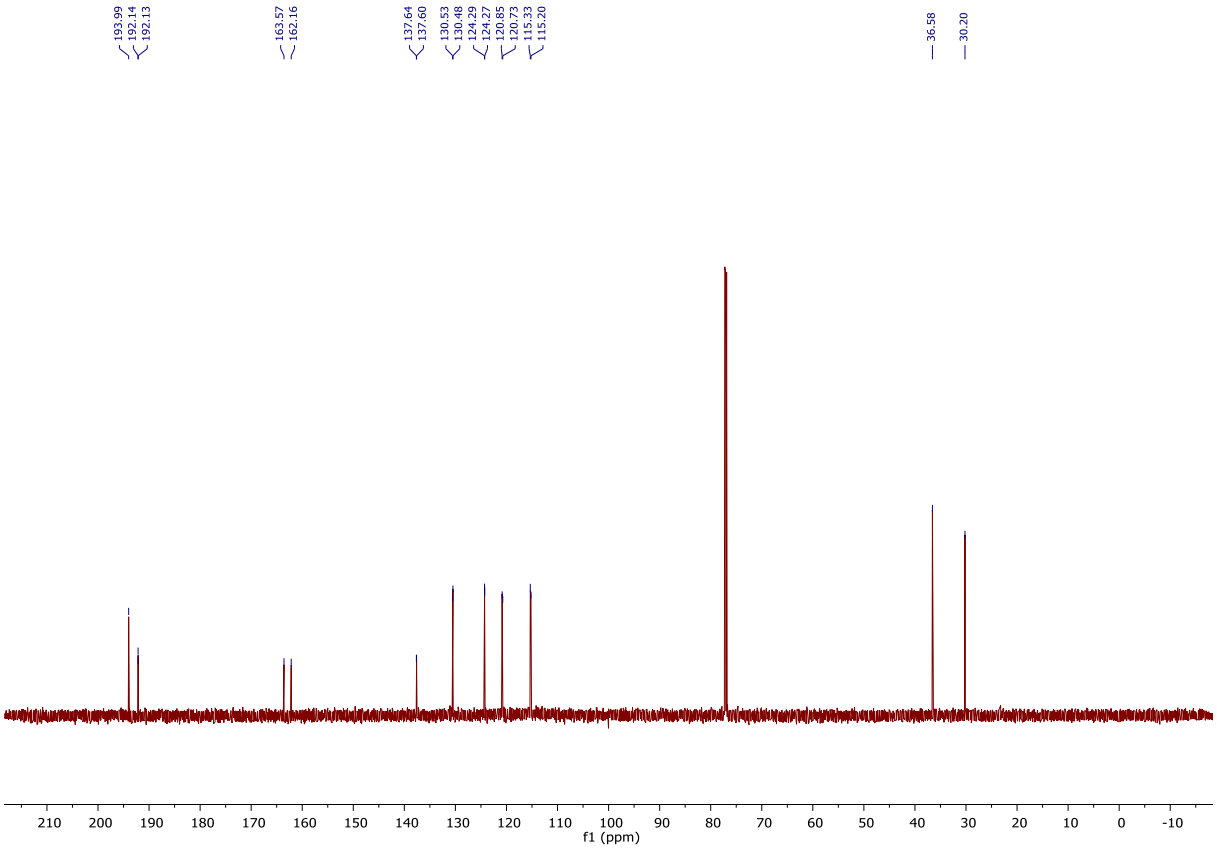
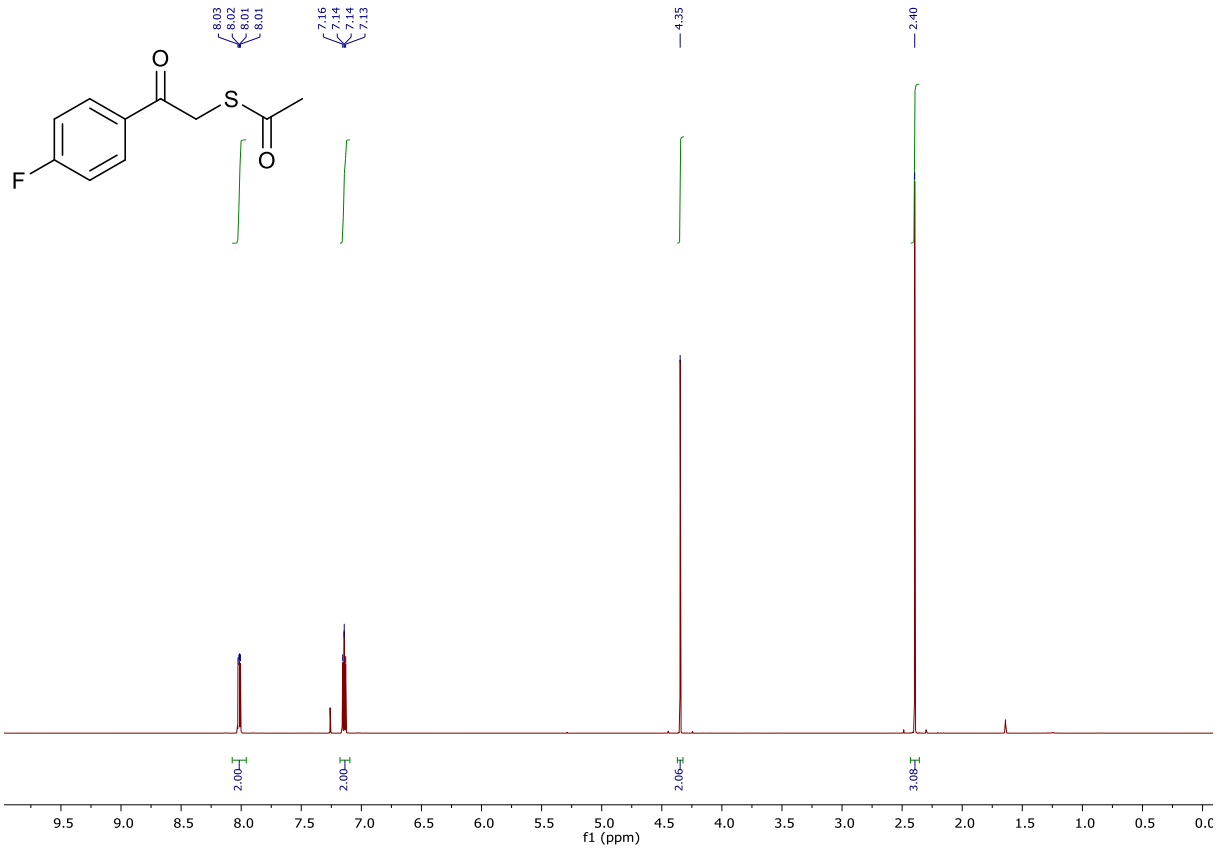
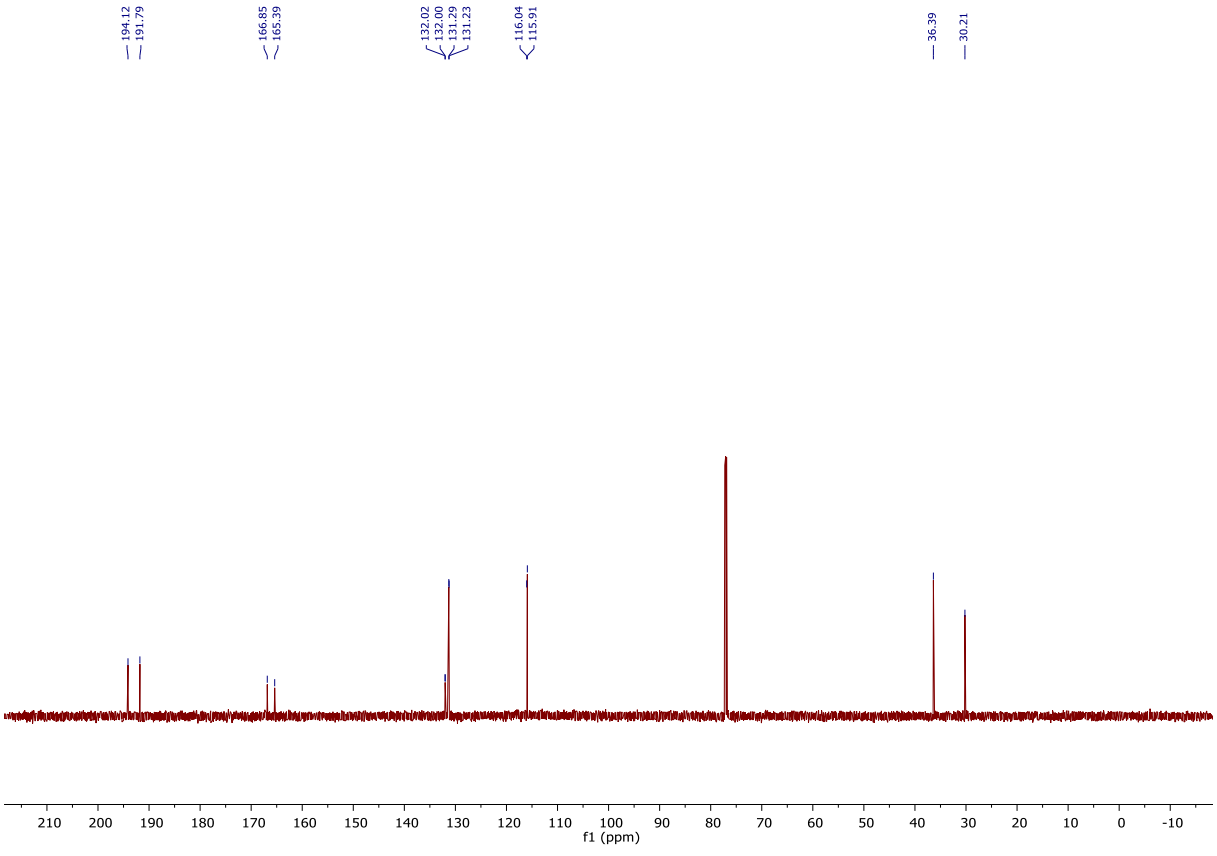
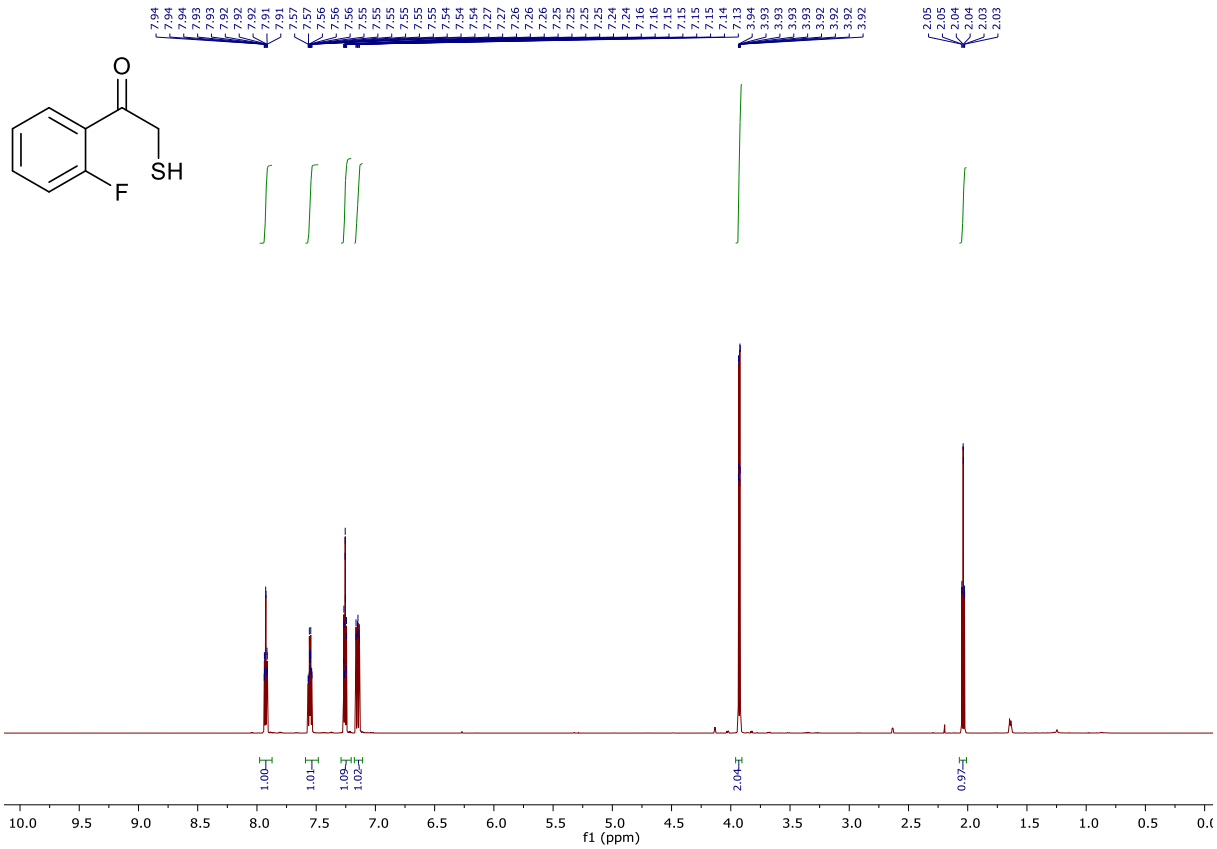
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

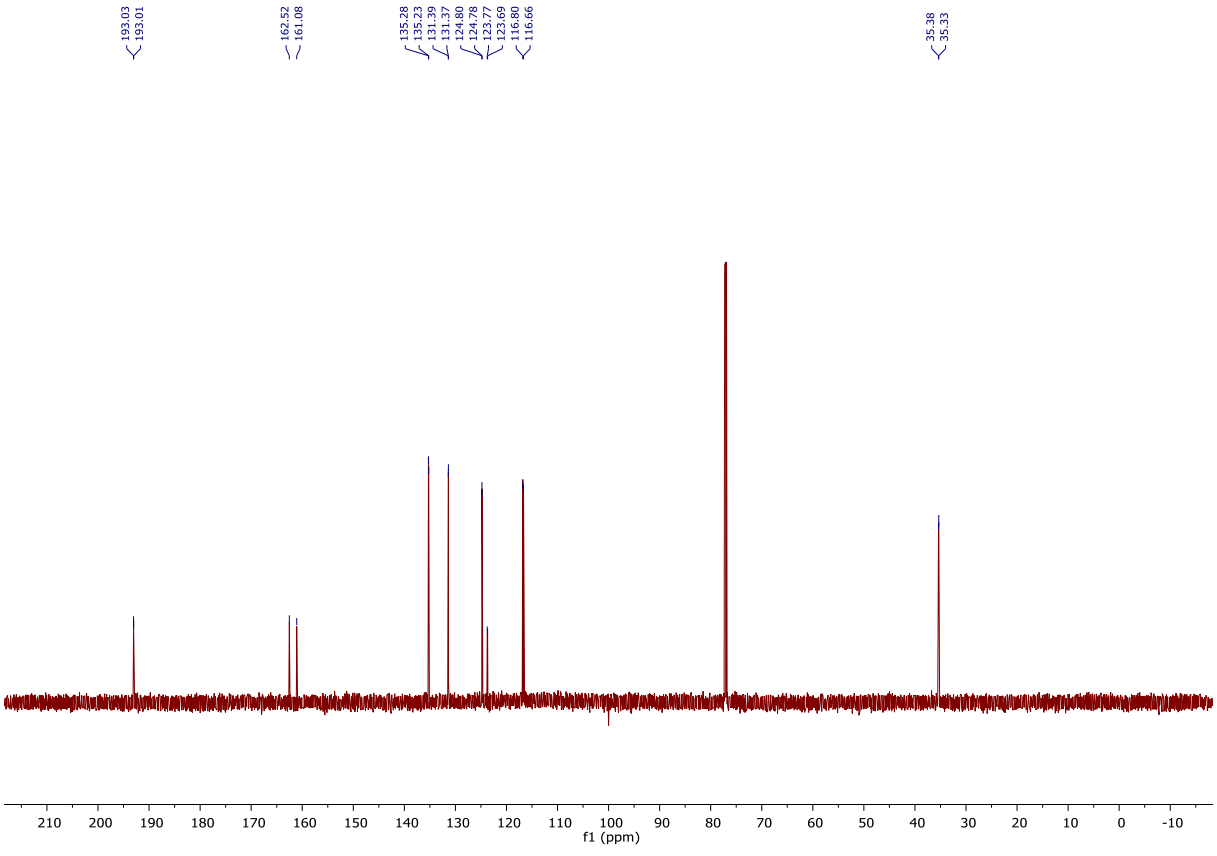

7.78
7.78
7.77
7.77
7.77
7.76
7.76
7.76
7.67
7.67
7.67
7.67
7.66
7.66
7.65
7.65
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
4.35
4.35
2.40
2.40
O
S
O
F
1.00
1.00
1.04
1.03
2.09
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

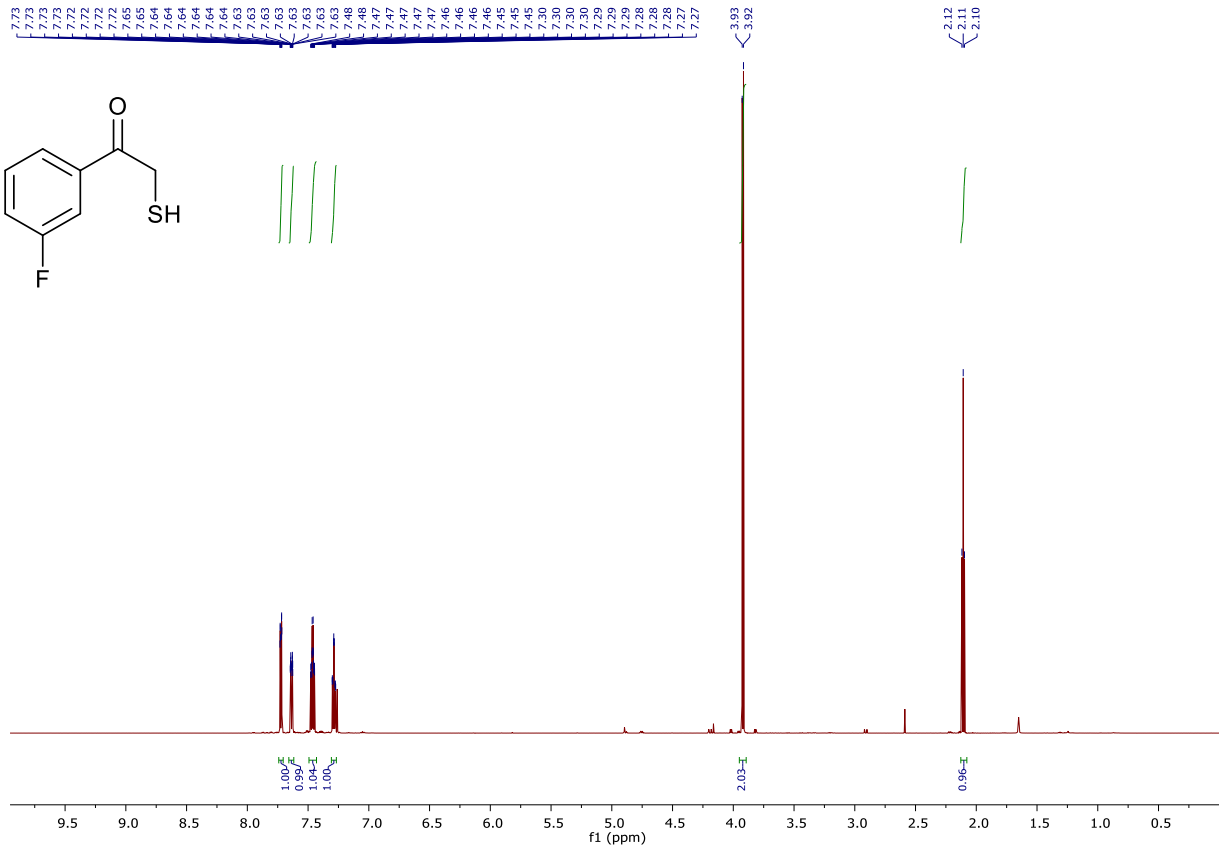

193.99
192.14
192.13
163.57
162.16
137.64
137.60
130.53
130.48
124.29
124.27
120.85
120.73
115.33
115.20
36.58
30.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

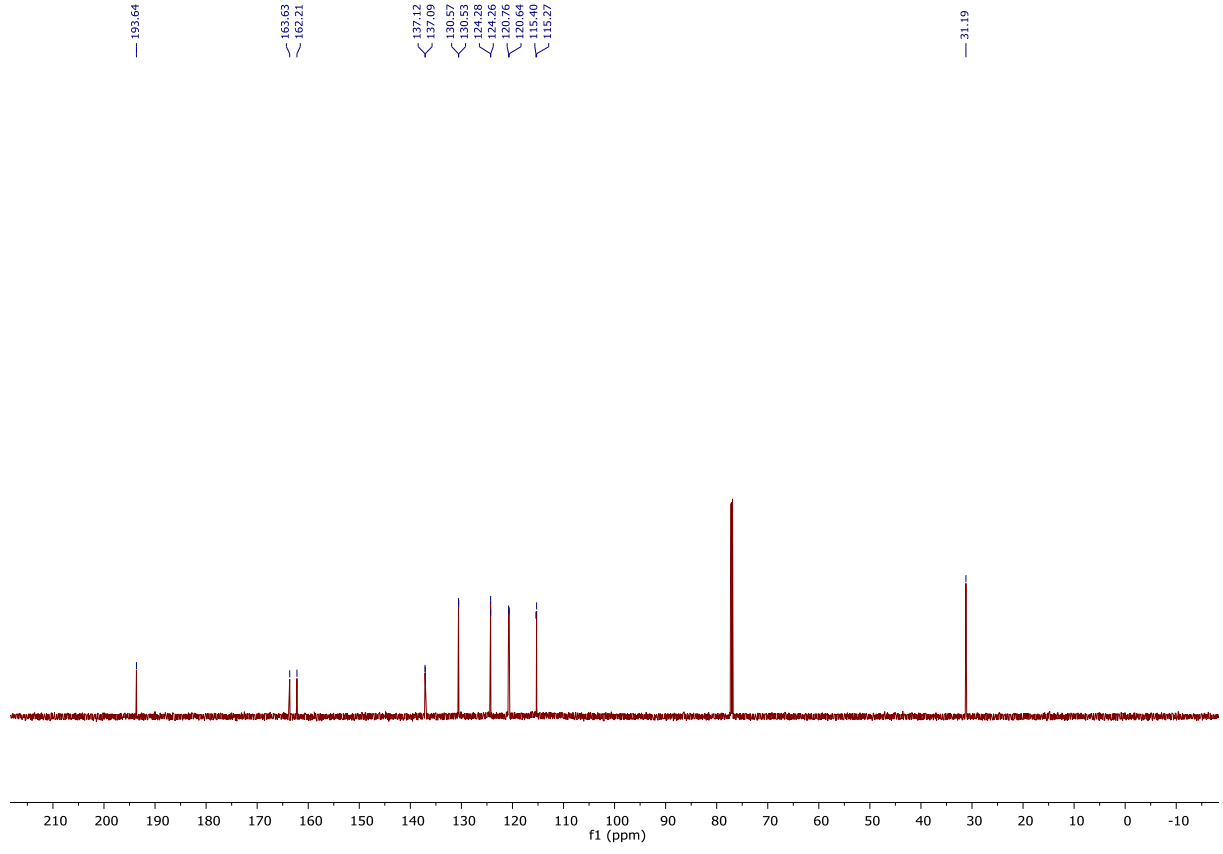

8.03
8.02
8.01
8.01
7.16
7.14
7.14
7.13
4.35
2.40
O
S
O
F
2.00
2.00
2.06
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

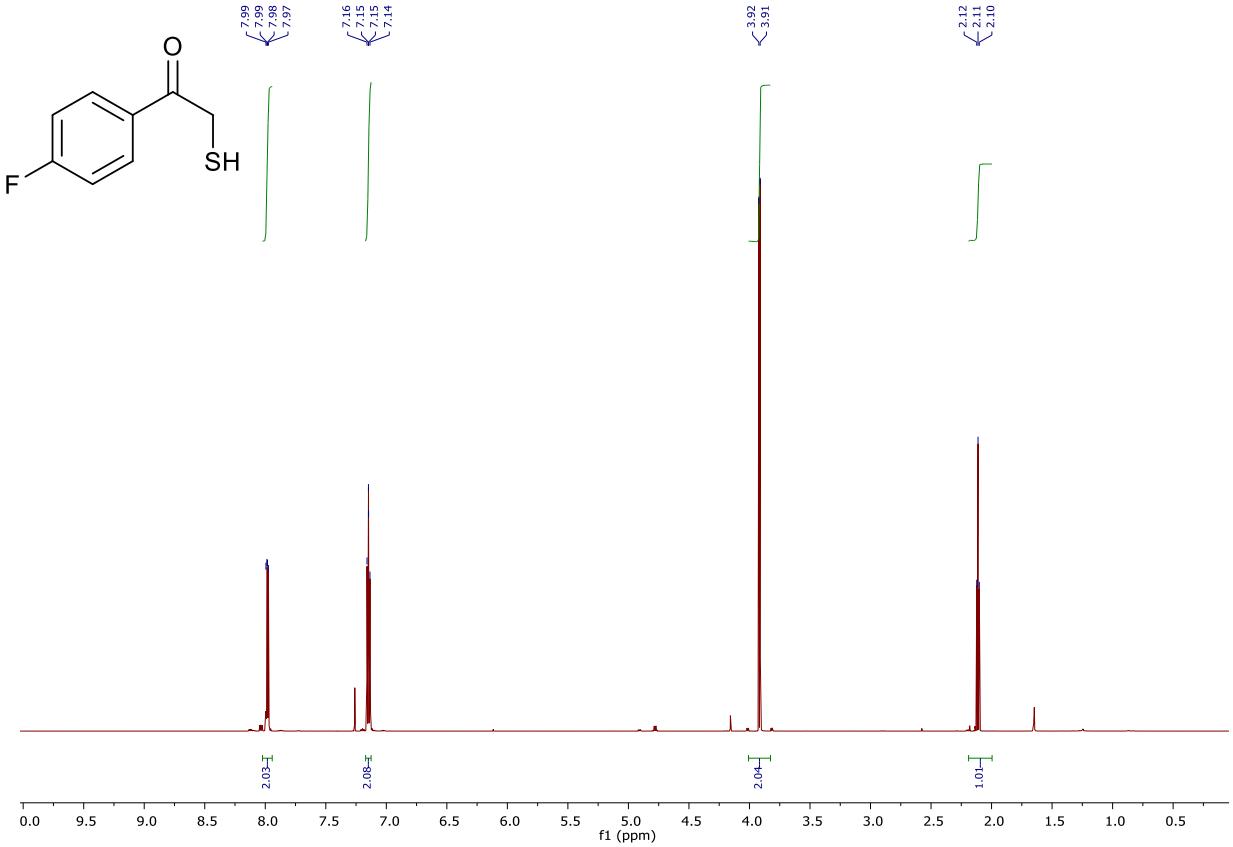

194.12
191.79
166.85
165.39
132.02
132.00
131.29
131.23
116.04
115.91
36.39
30.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

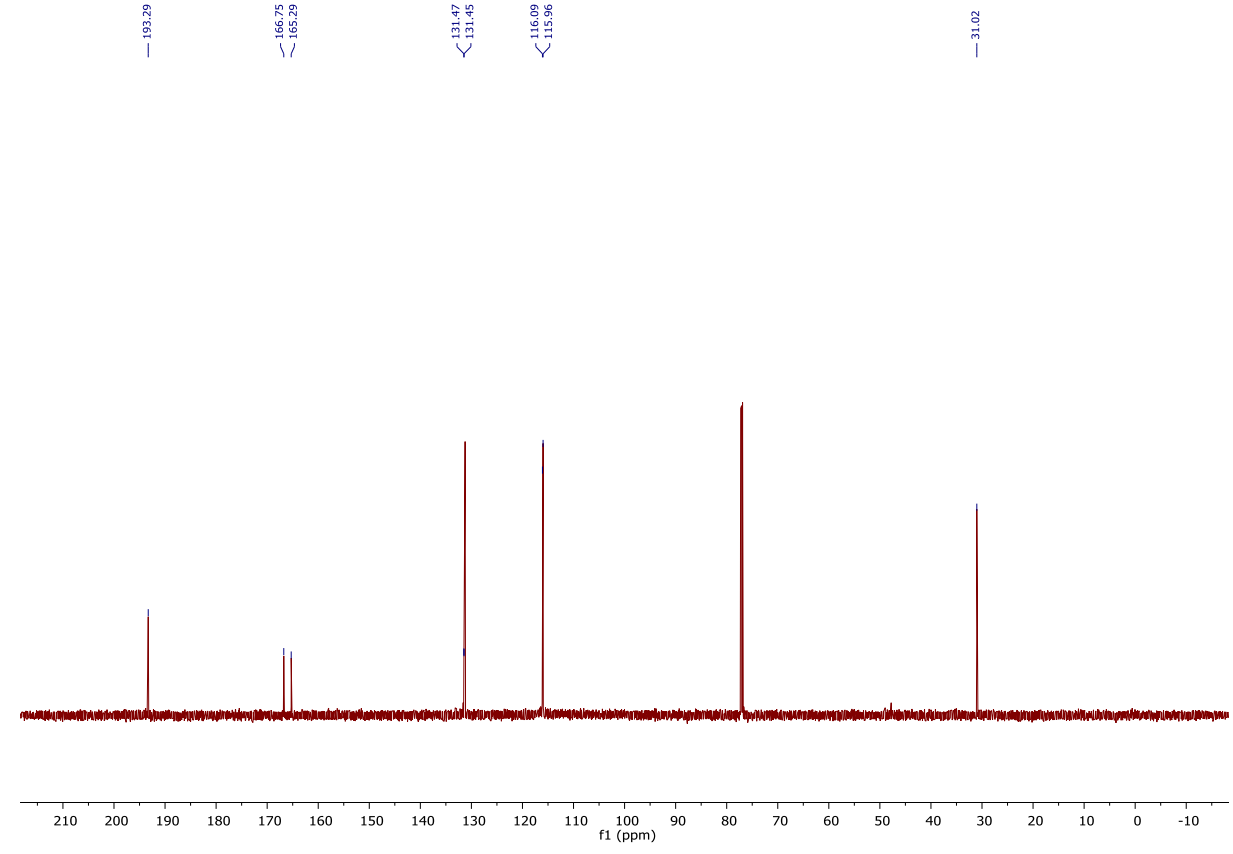

O
SH
F
f1 (ppm)

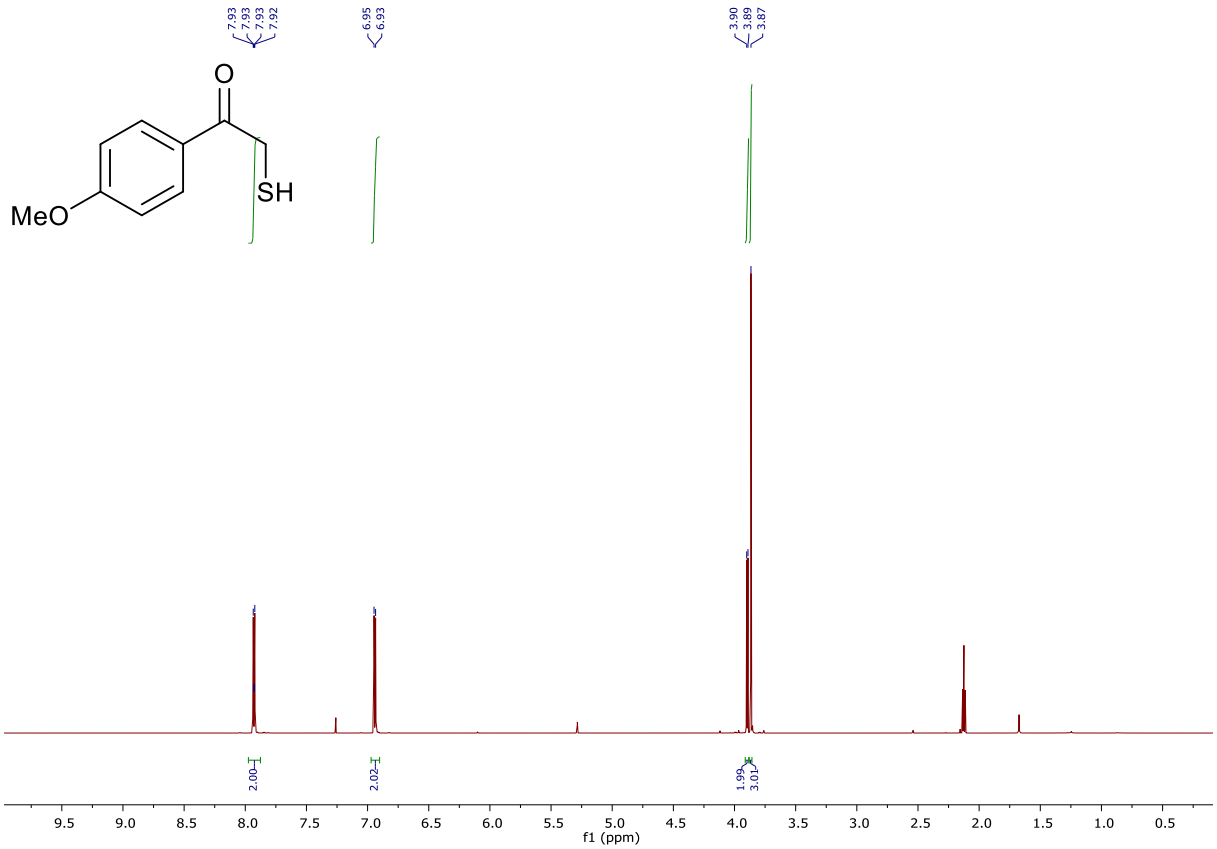

f1 (ppm)

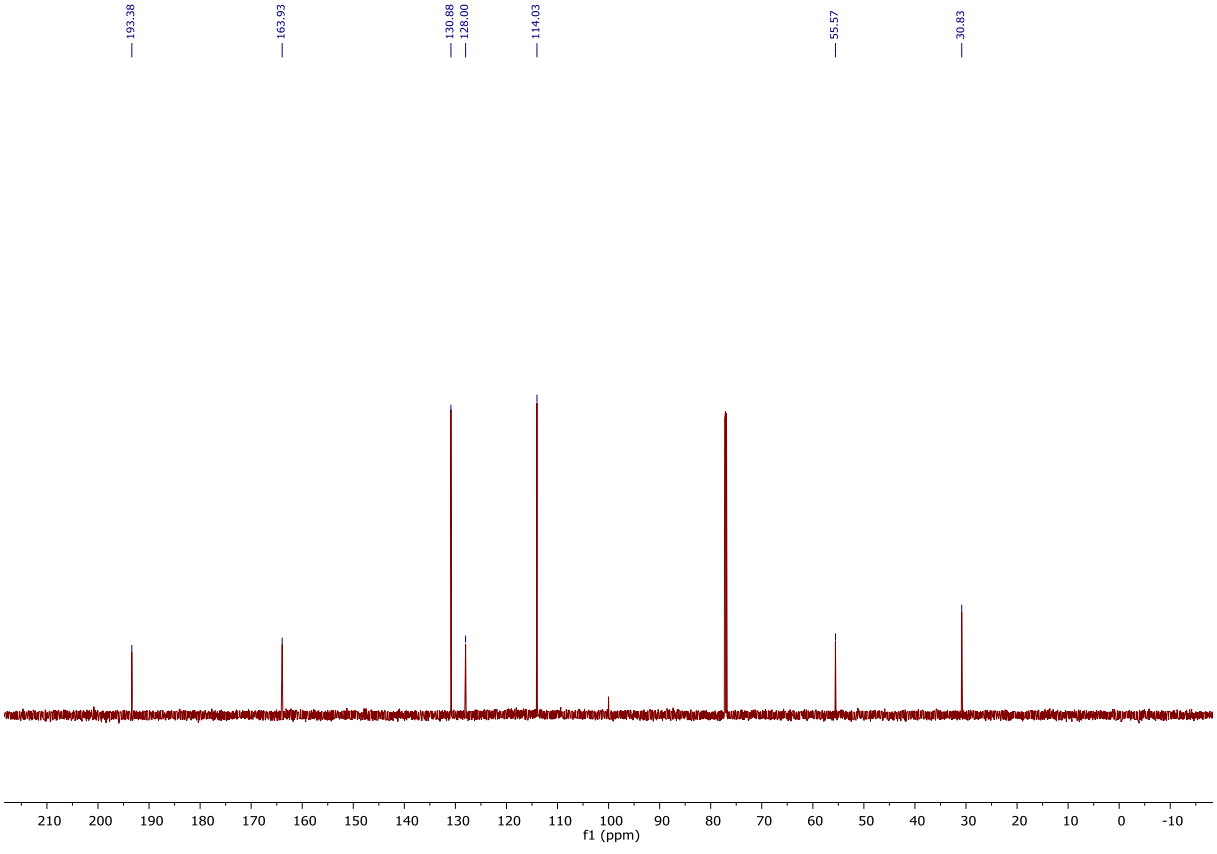

O
SH
F
f1 (ppm)

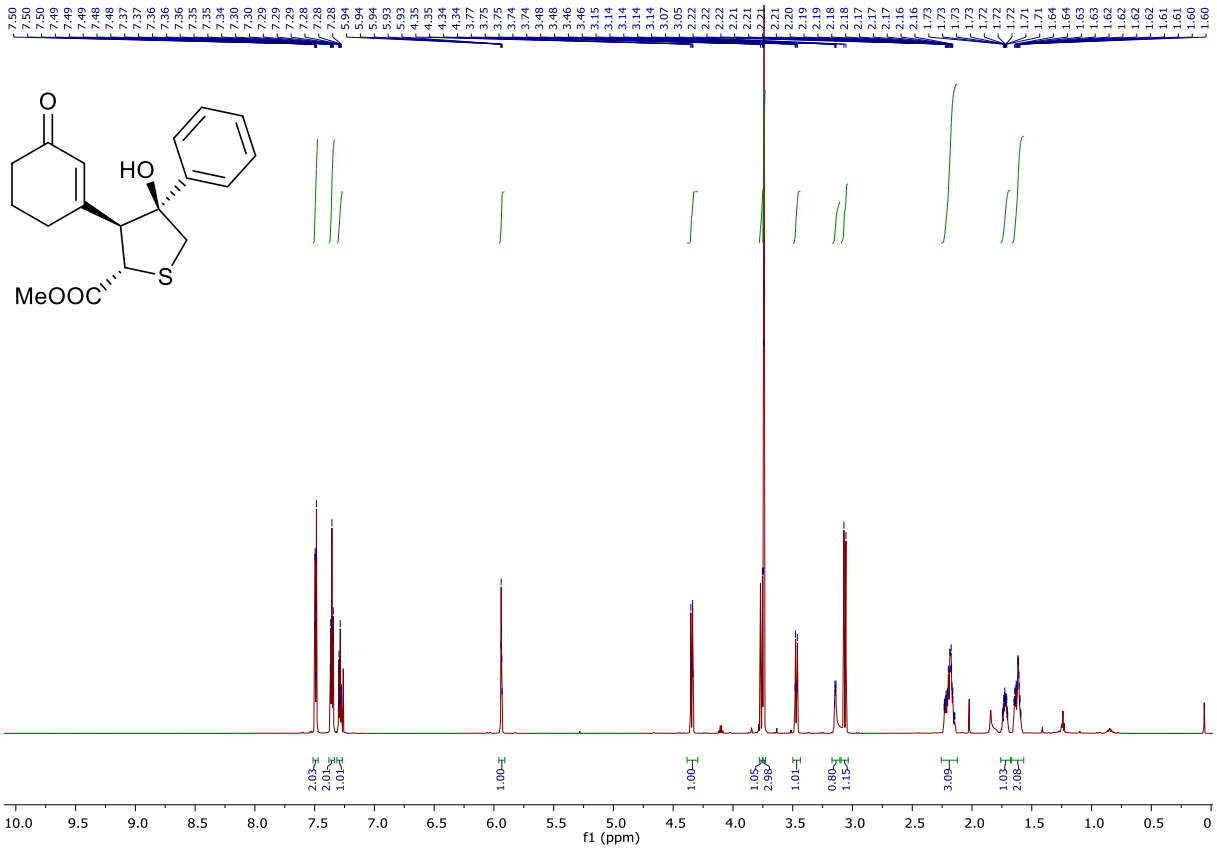

f1 (ppm)

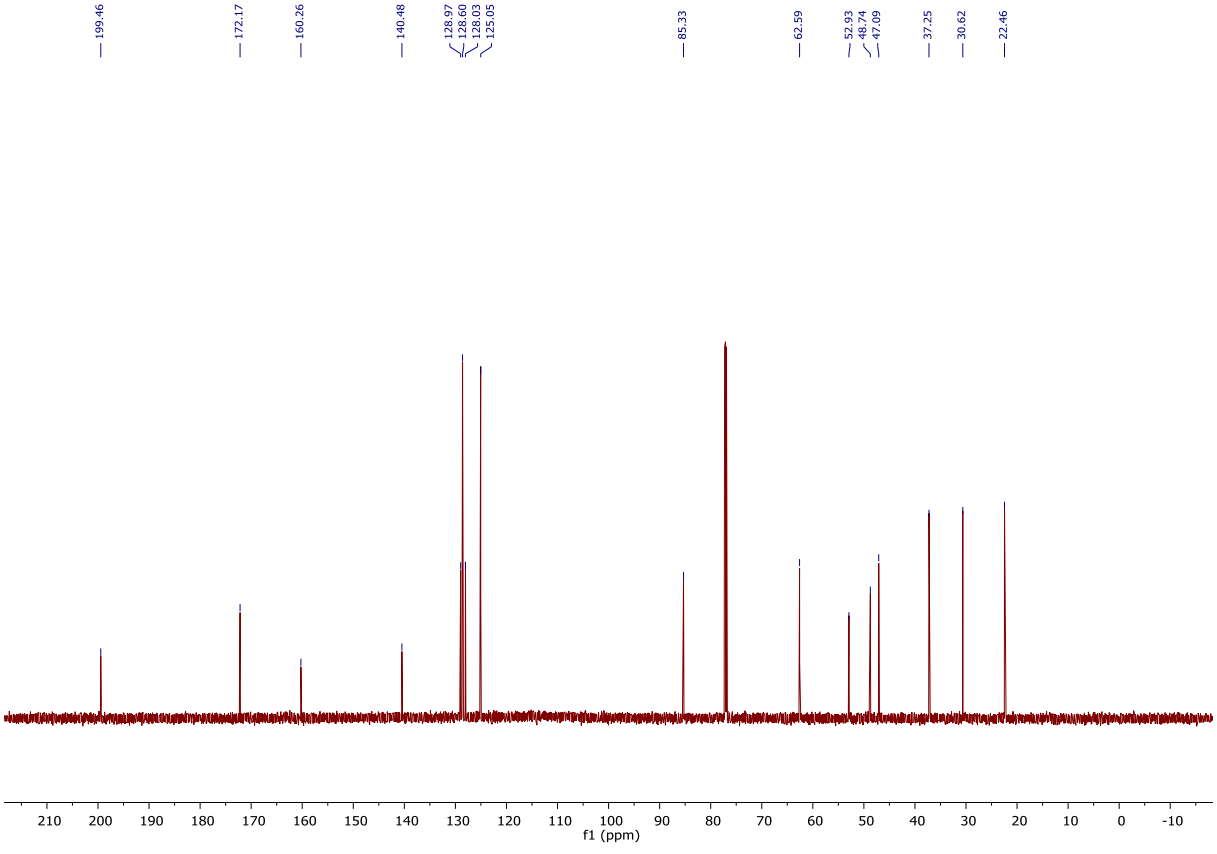

O
SH
F
7.99
7.99
7.98
7.97
7.16
7.15
7.15
7.14
3.92
3.91
2.12
2.11
2.10
2.03
2.08
2.04
1.01
f1 (ppm)

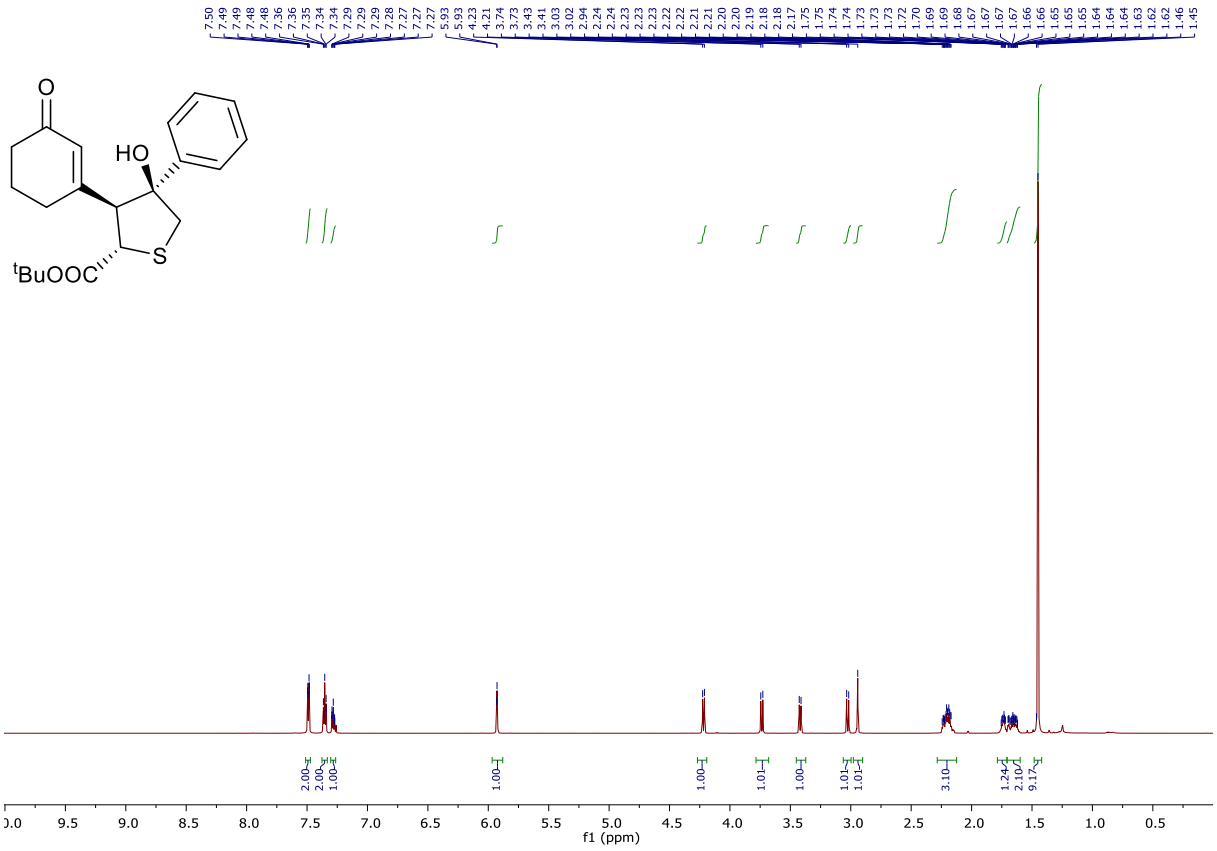

193.29
166.75
165.29
131.47
131.45
116.09
115.96
31.02
f1 (ppm)

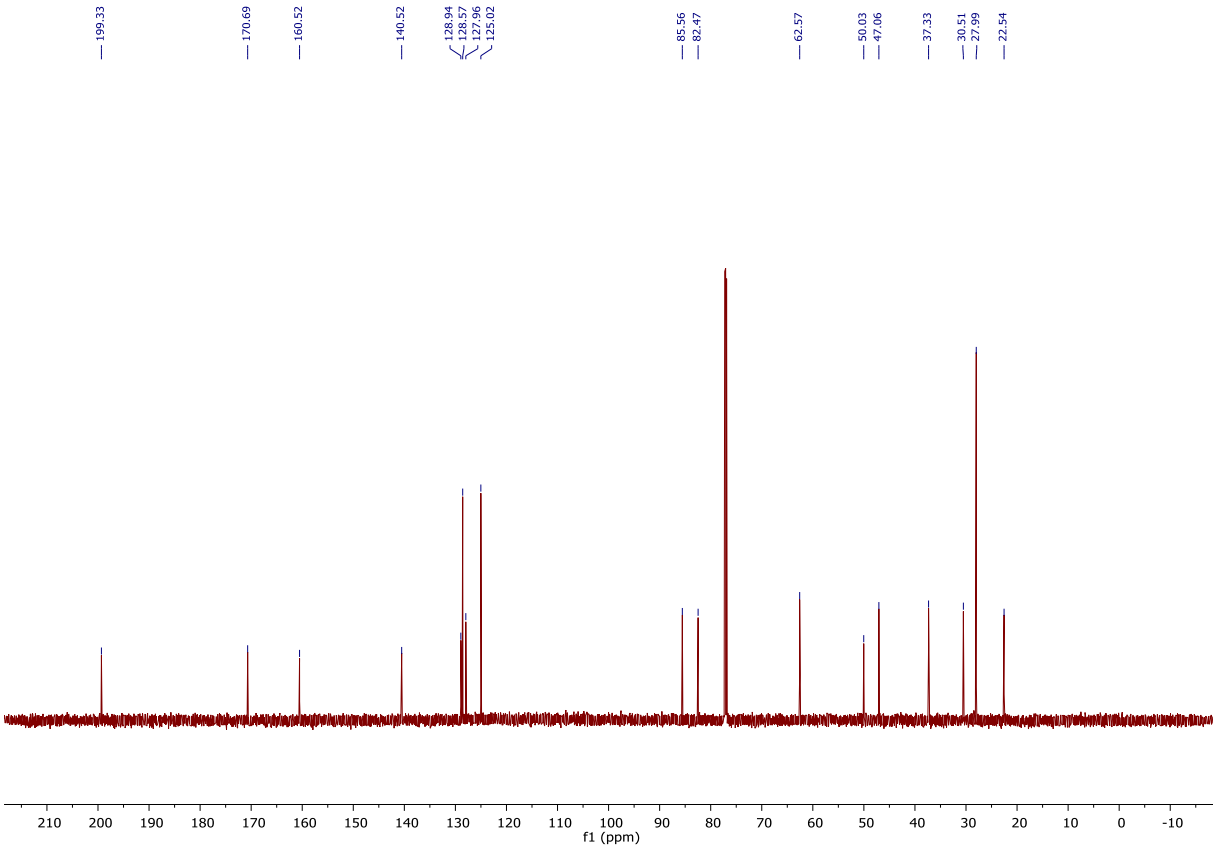

7.93
7.93
7.93
7.92
6.95
6.93
3.90
3.89
3.87
O
SH
MeO
2.00
2.02
1.99
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

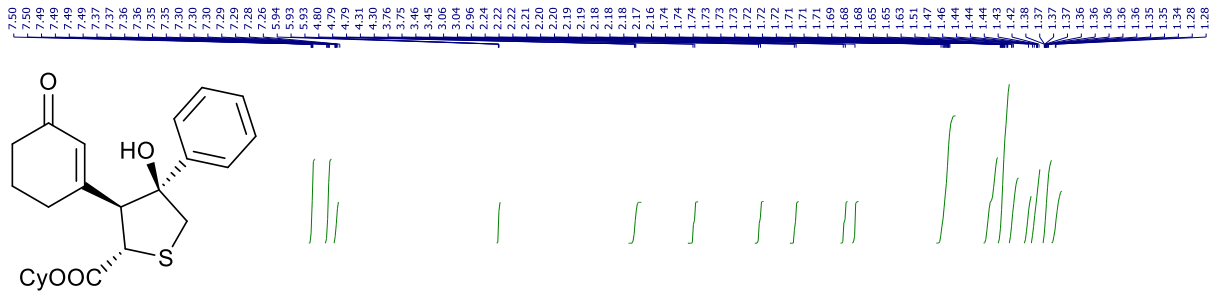

193.38
163.93
130.88
128.00
114.03
55.57
30.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

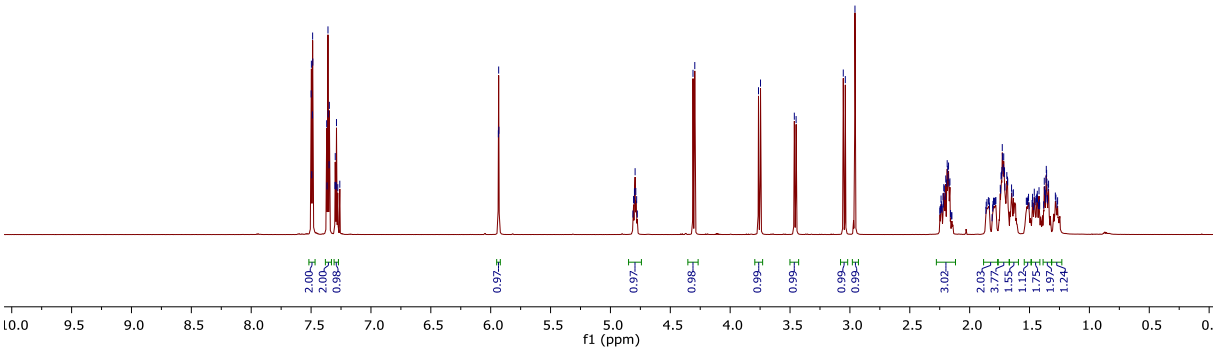

O
HO
S
MeOOC
f1 (ppm)

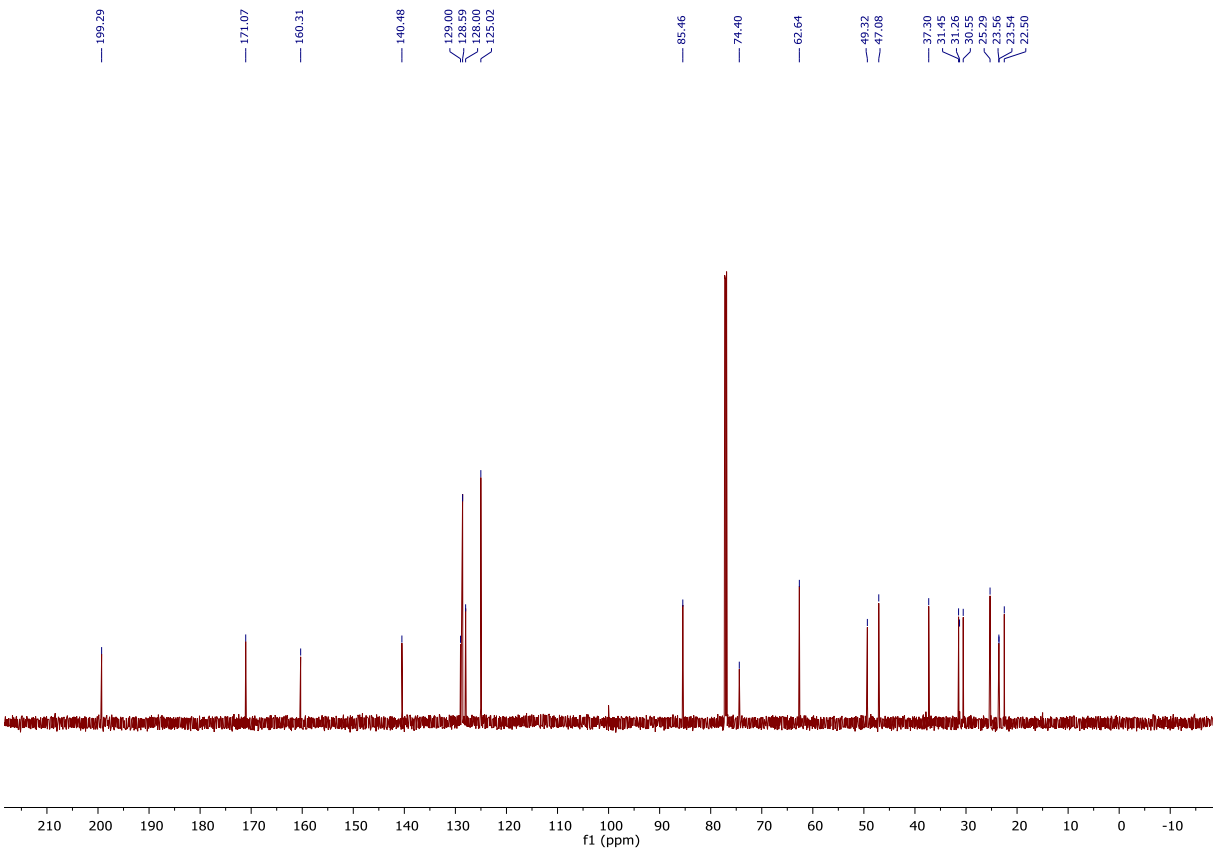

199.46
172.17
160.26
140.48
128.97
128.60
128.03
125.05
85.33
62.59
52.93
48.74
47.09
37.25
30.62
22.46
f1 (ppm)

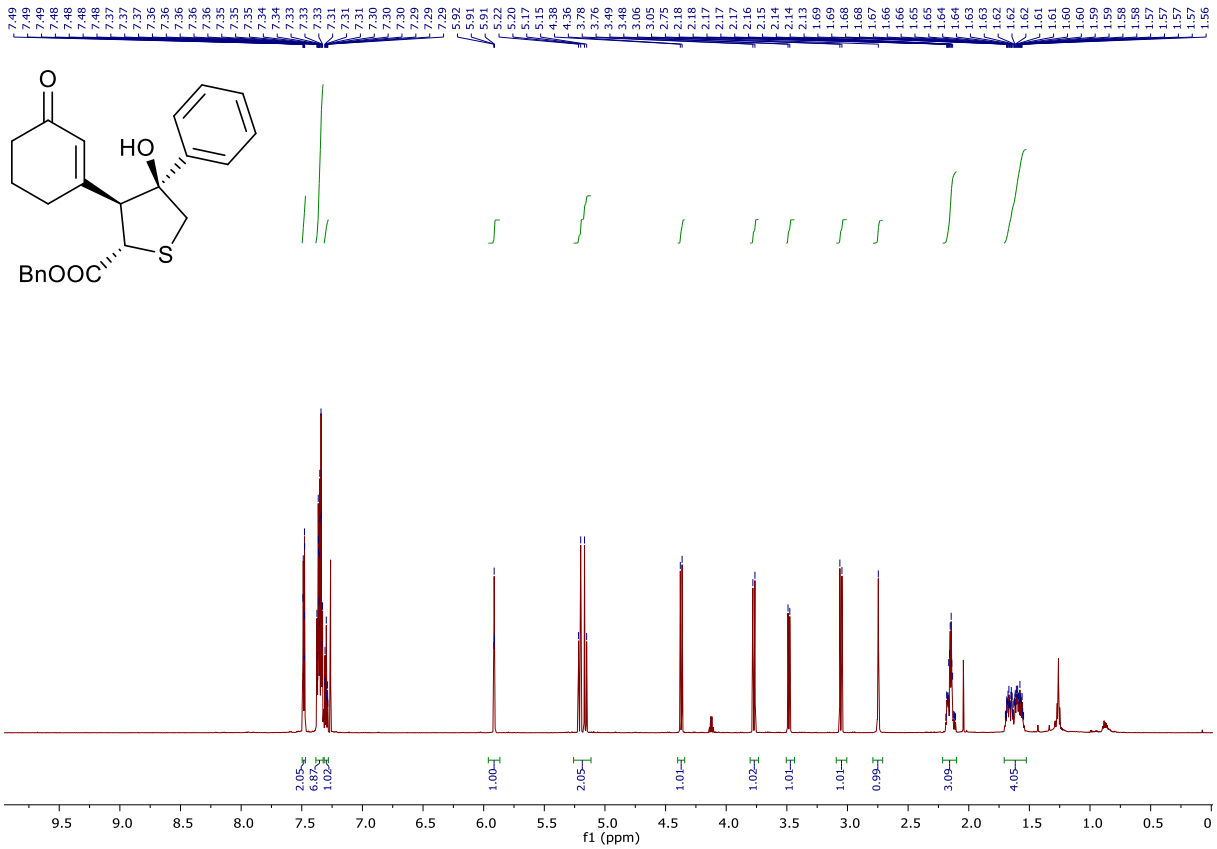

O
HO
S
tBuOOC
f1 (ppm)

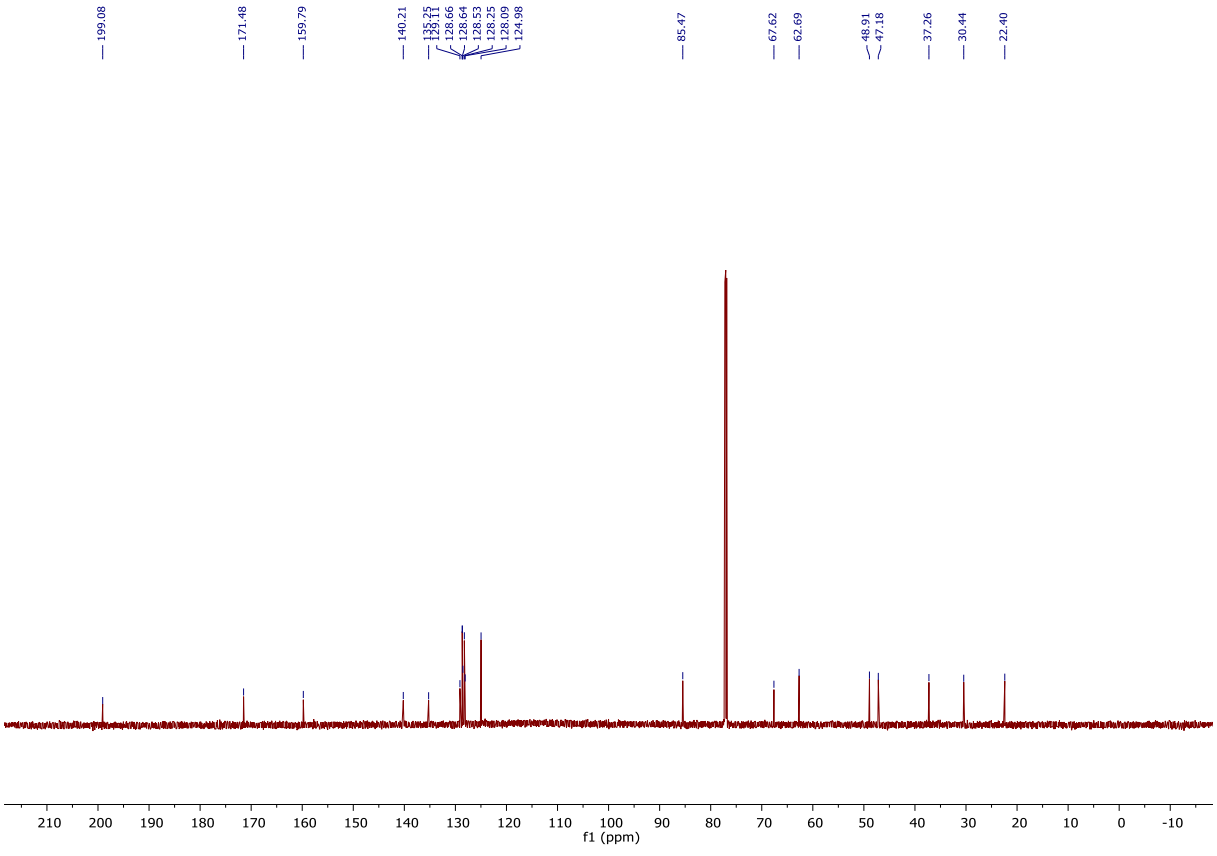

f1 (ppm)

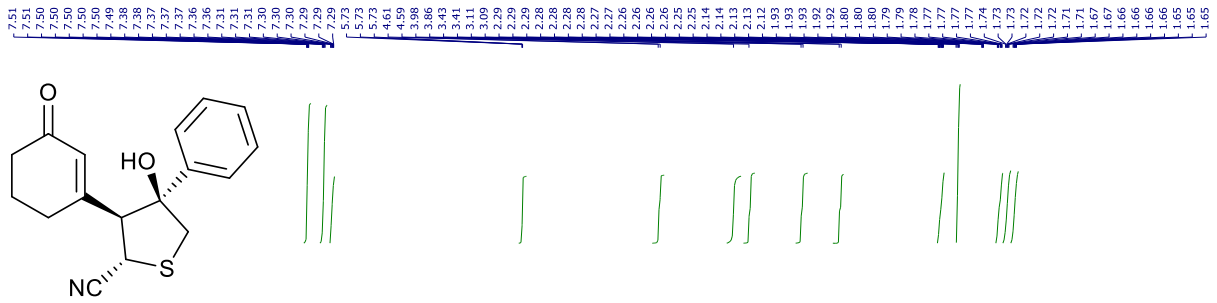

O
HO
S
CyOOC

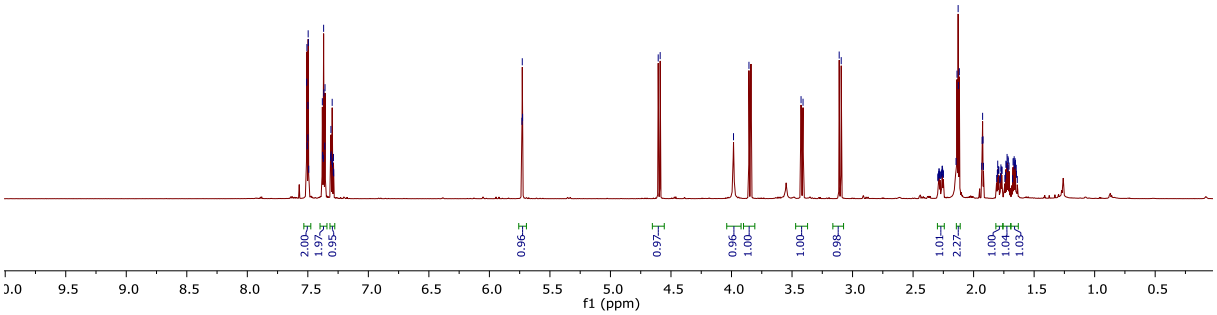

f1 (ppm)

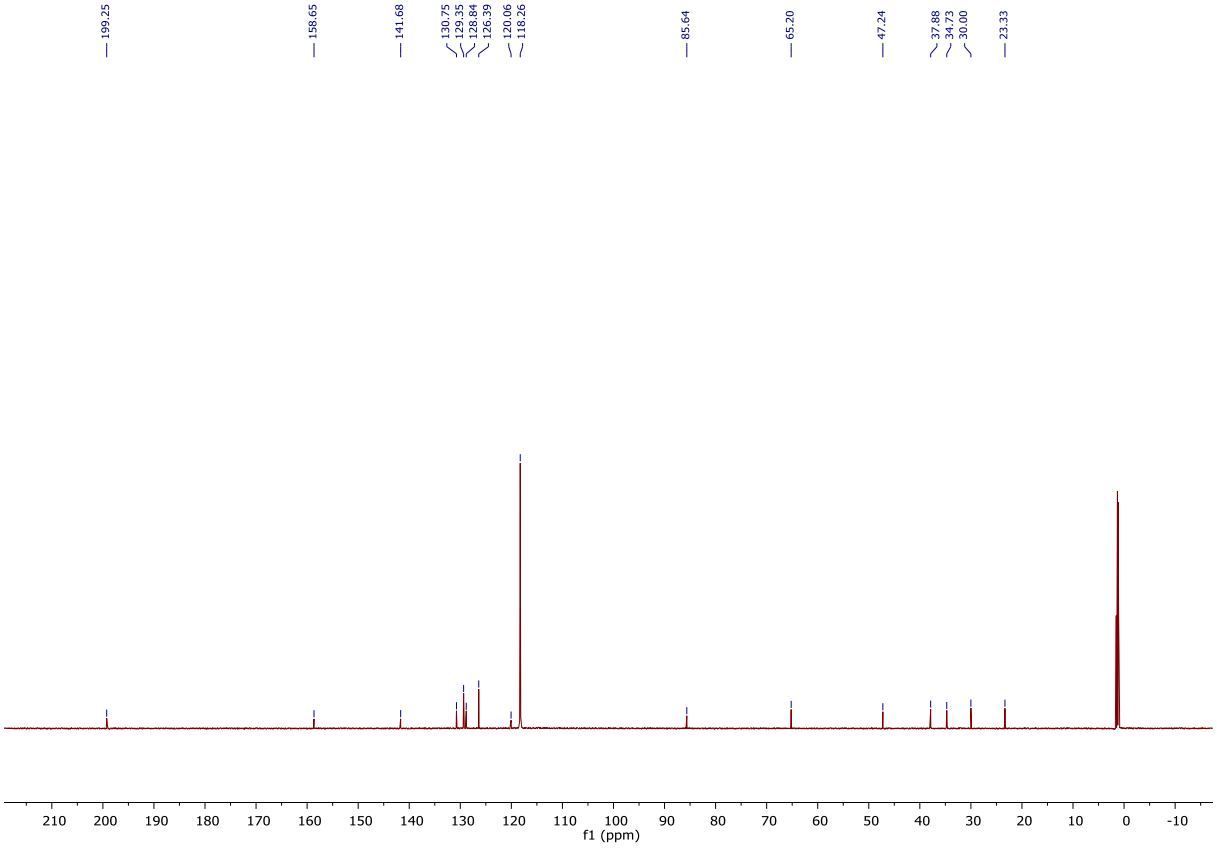

f1 (ppm)

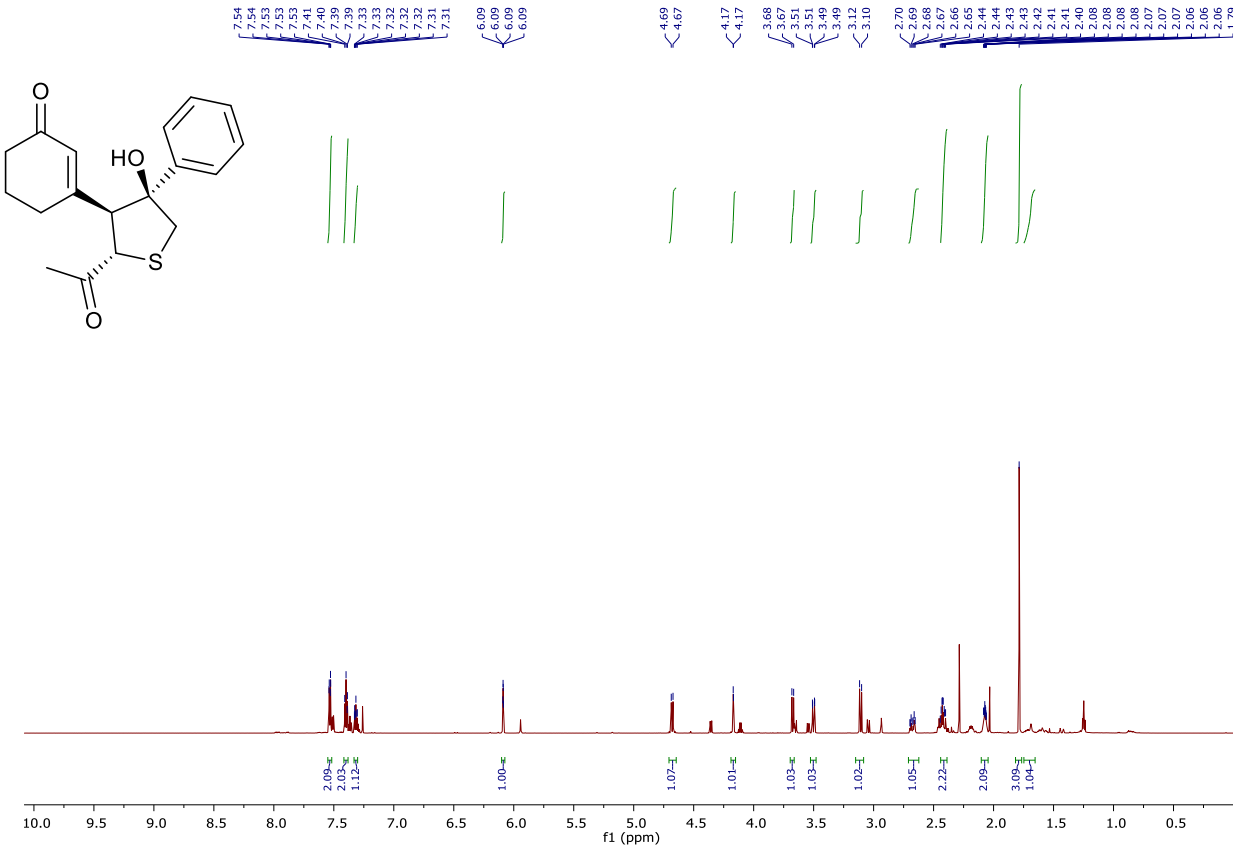

O
HO
S
BnOOC
f1 (ppm)

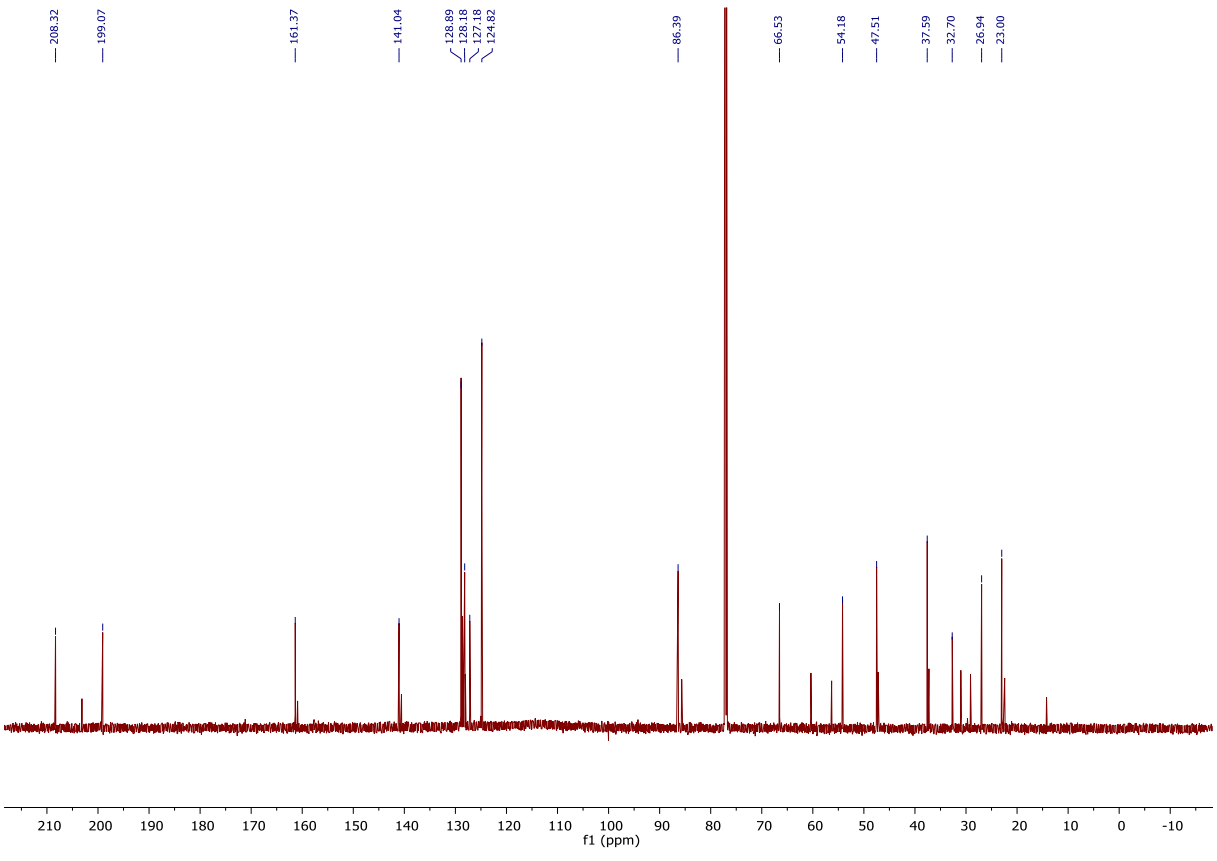

f1 (ppm)

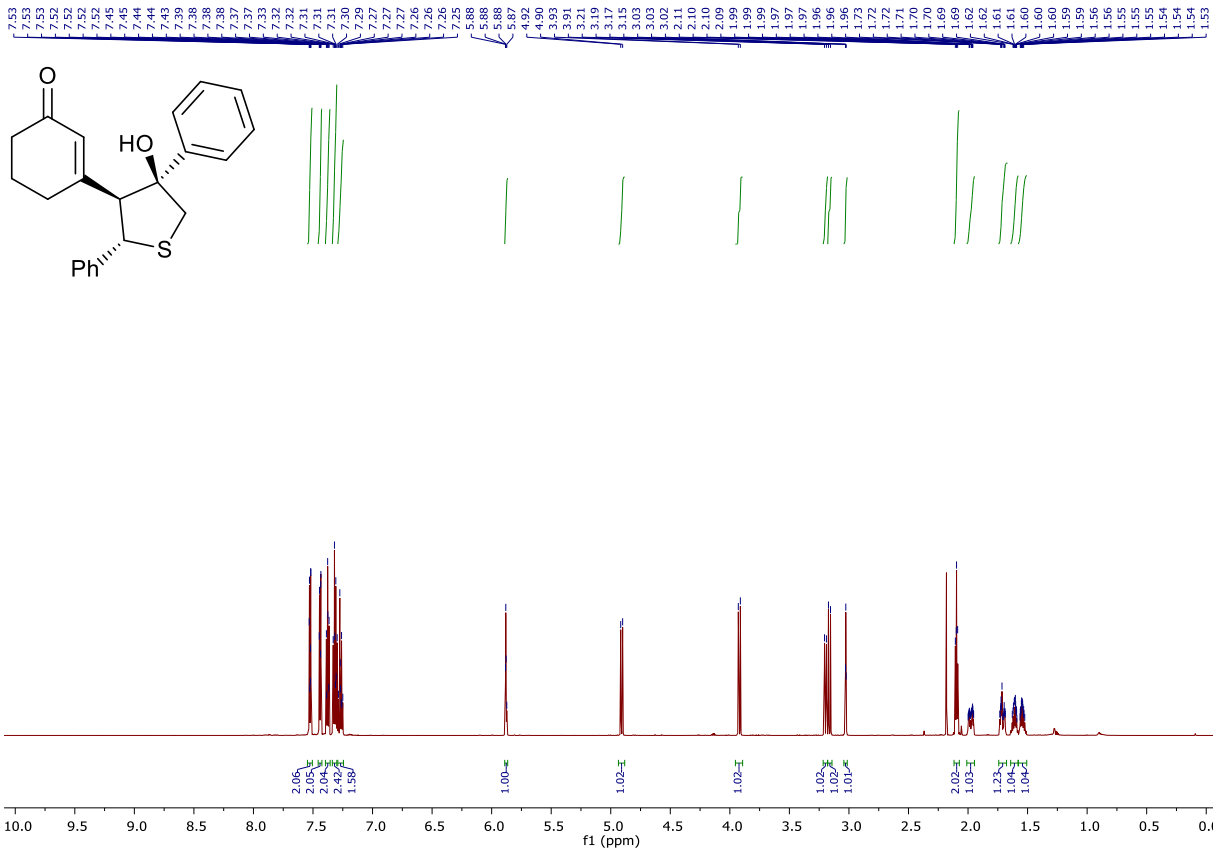

O
HO
S
NC

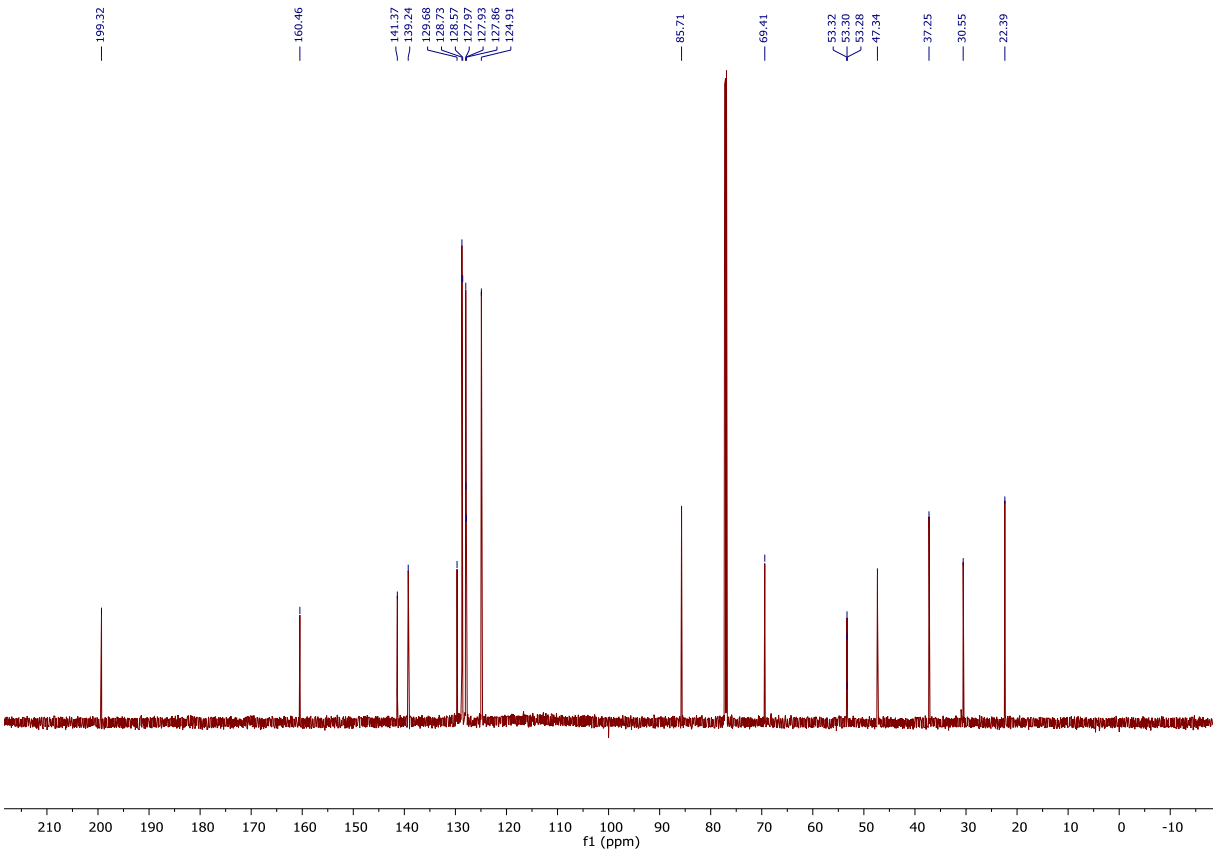

2.00
1.92
0.95
0.96
0.97
0.96
1.00
1.00
0.98
1.01
2.27
1.00
1.04
1.03
f1 (ppm)


199.25
158.65
141.68
130.75
129.35
128.84
126.39
120.06
118.26
85.64
65.20
47.24
37.88
34.73
30.00
23.33
f1 (ppm)


O
HO
S
O
7.54 7.54 7.53 7.53 7.53 7.41 7.40 7.39 7.39 7.33 7.33 7.32 7.32 7.32 7.31 7.31
6.09 6.09 6.09 6.09
4.69 4.67
4.17 4.17
3.68 3.67 3.51 3.51 3.49 3.49
3.12 3.10
2.70 2.69 2.68 2.67 2.66 2.65 2.44 2.44 2.43 2.43 2.42 2.41 2.41 2.40 2.08 2.08 2.08 2.08 2.07 2.07 2.06 2.06 2.06
2.09 2.03 1.12 1.00 1.07 1.01 1.03 1.03 1.02 1.05 2.22 2.09 3.09 1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


208.32
199.07
161.37
141.04
128.89
128.18
127.18
124.82
86.39
66.53
54.18
47.51
37.59
32.70
26.94
23.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
HO
S
Ph
f1 (ppm)


199.32
160.46
141.37
139.24
129.68
128.73
128.57
127.97
127.93
127.86
124.91
85.71
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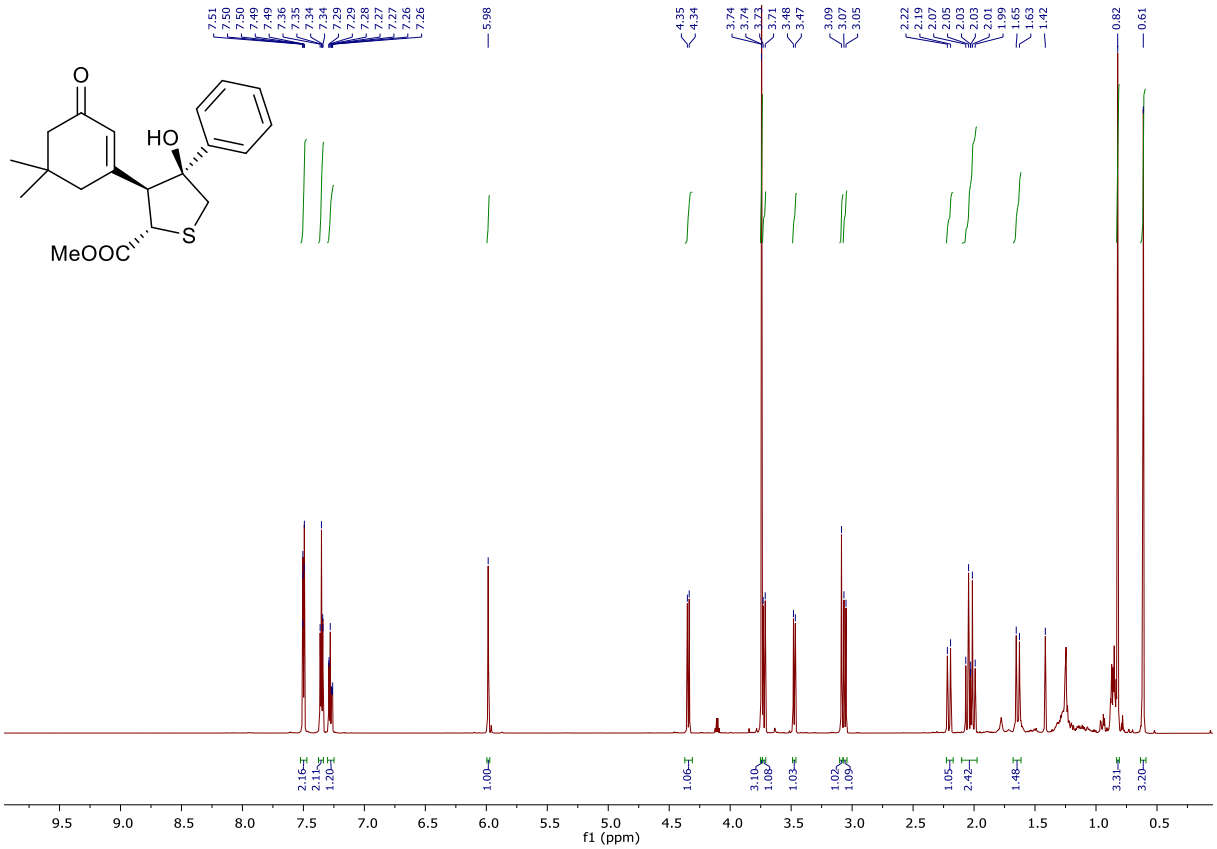
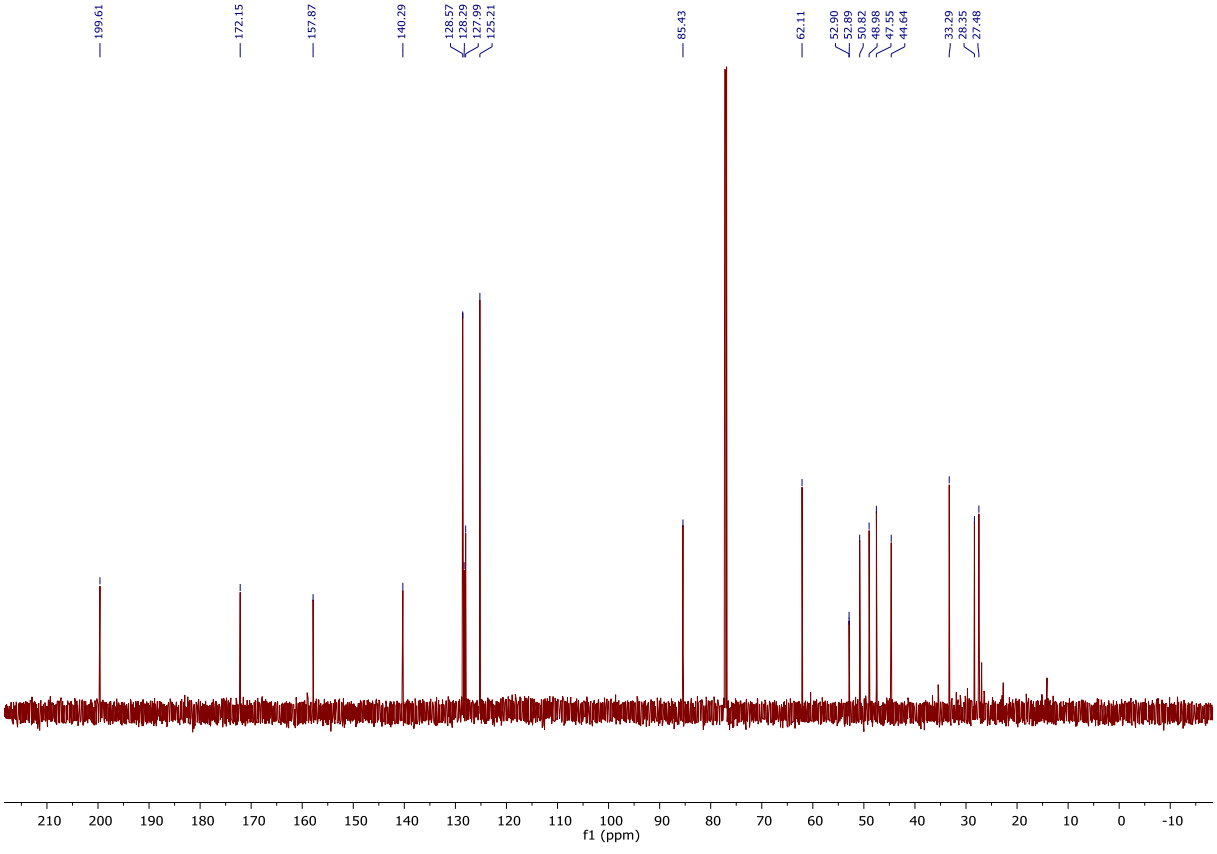
47.34
37.25
30.55
22.39
f1 (ppm)


O
HO
S
MeOOC
7.51
7.50
7.50
7.49
7.49
7.36
7.35
7.34
7.34
7.29
7.29
7.28
7.27
7.27
7.26
7.26
5.98
4.35
4.34
3.74
3.74
3.73
3.71
3.48
3.47
3.09
3.07
3.05
2.22
2.19
2.07
2.05
2.03
2.03
2.01
1.99
1.65
1.63
1.42
0.82
0.61
2.16
2.11
1.20
1.00
1.06
3.10
1.08
1.03
1.02
1.09
1.05
2.42
1.48
3.31
3.20
f1 (ppm)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128.57
128.29
127.99
125.21
85.43
62.11
52.90
52.89
50.82
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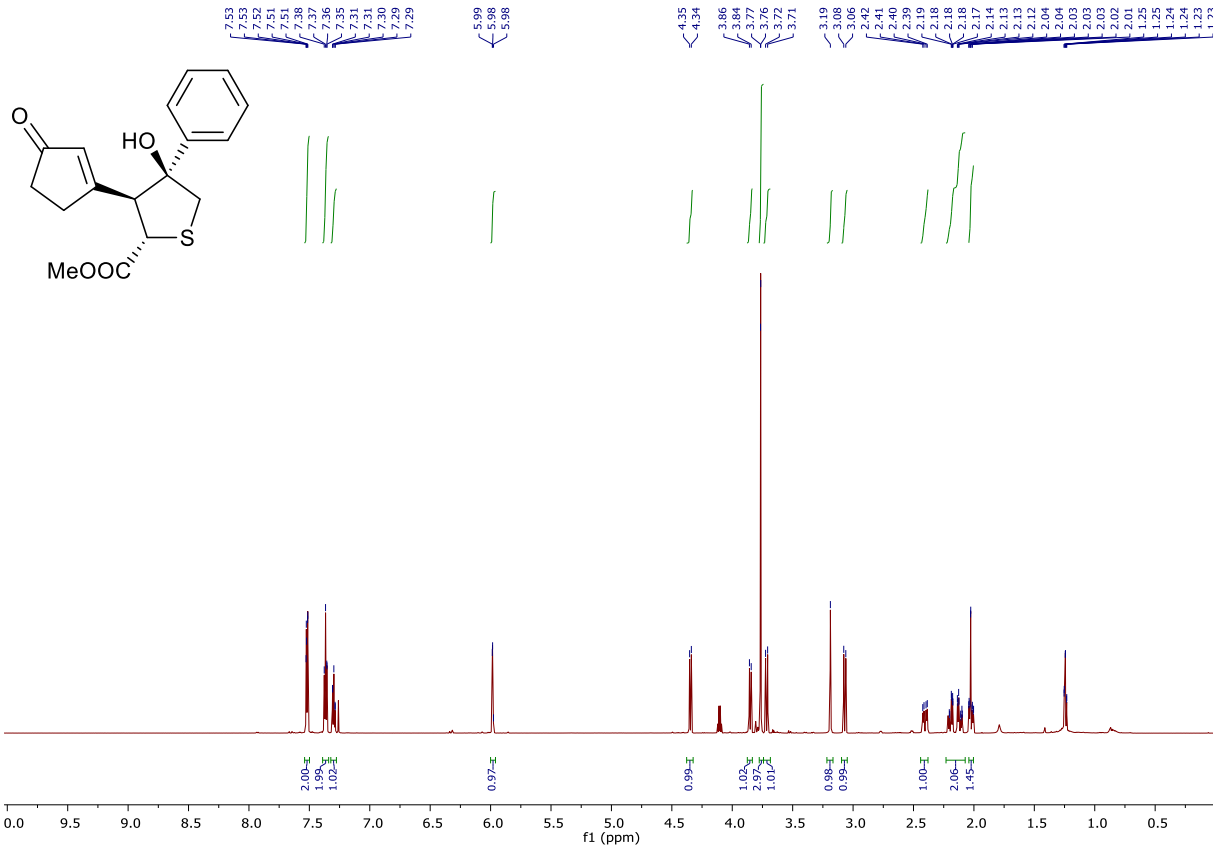
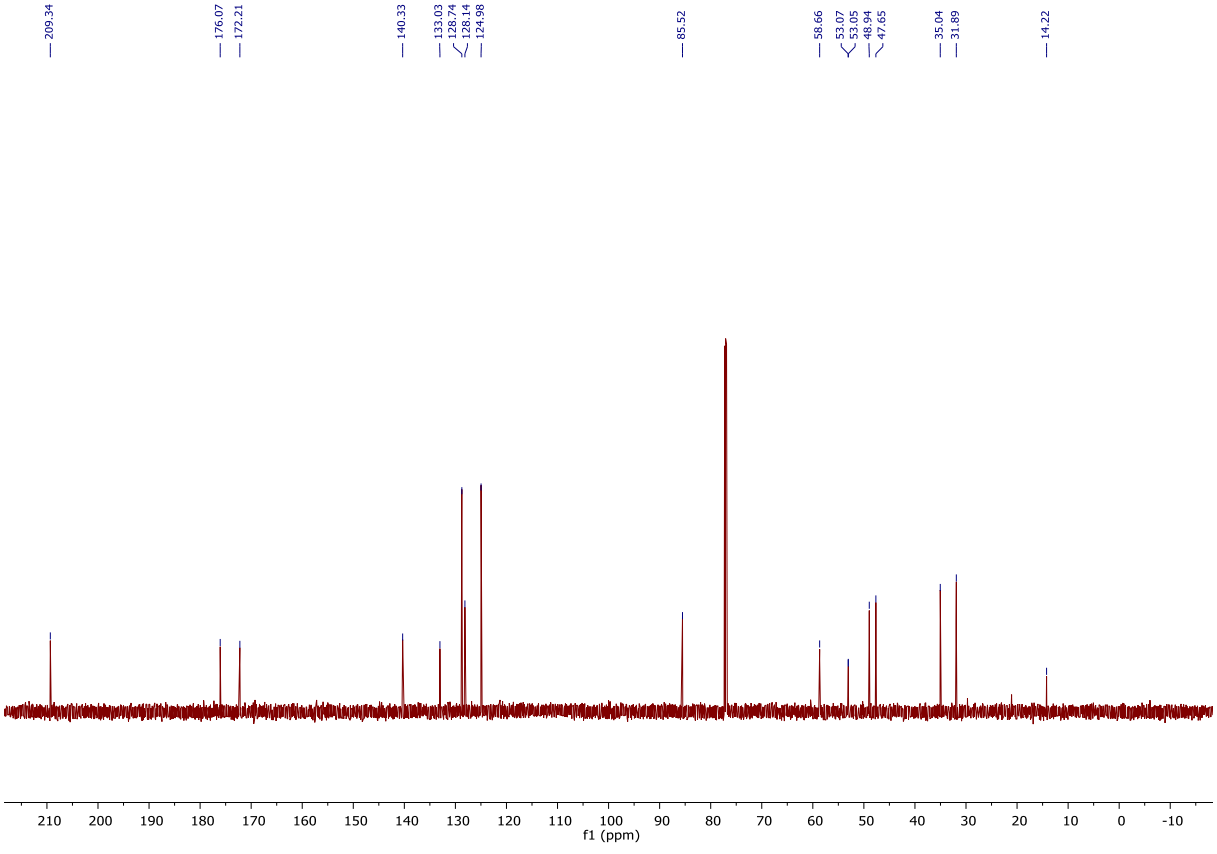
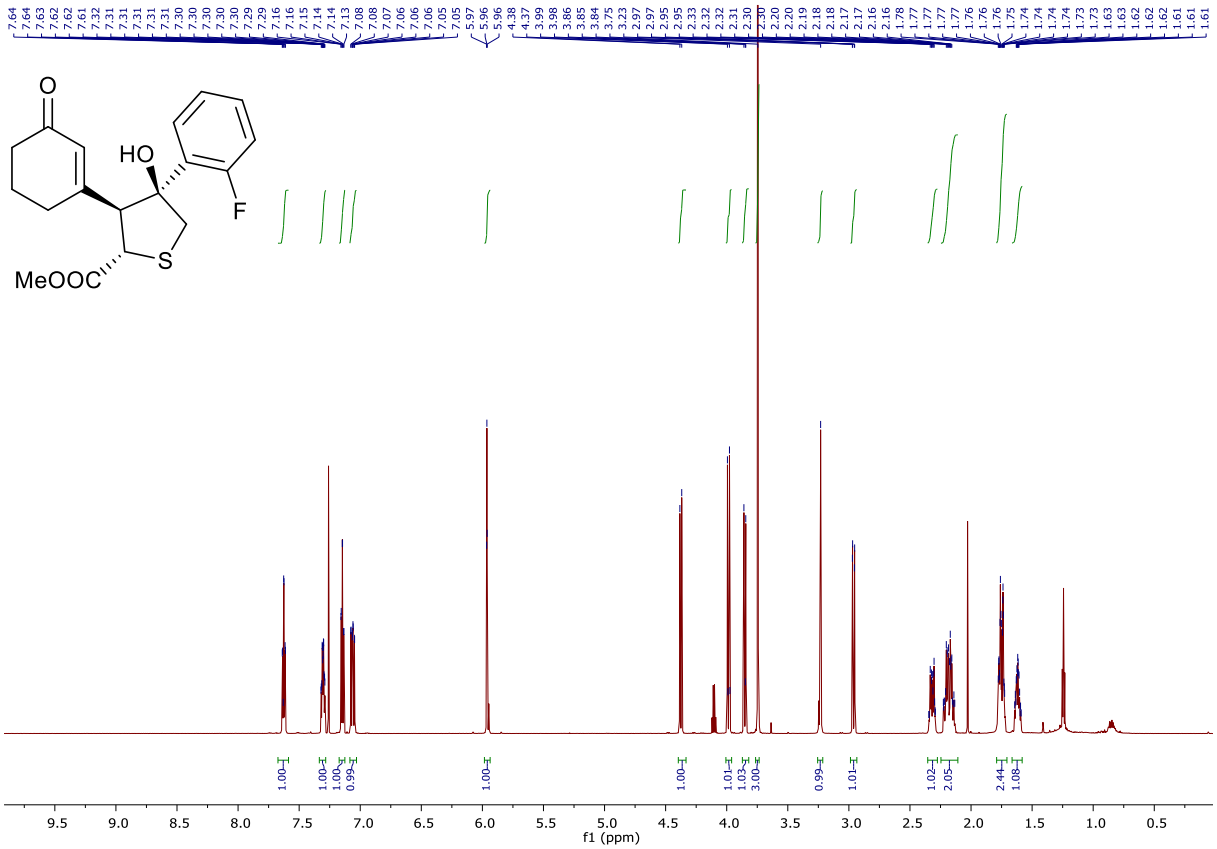
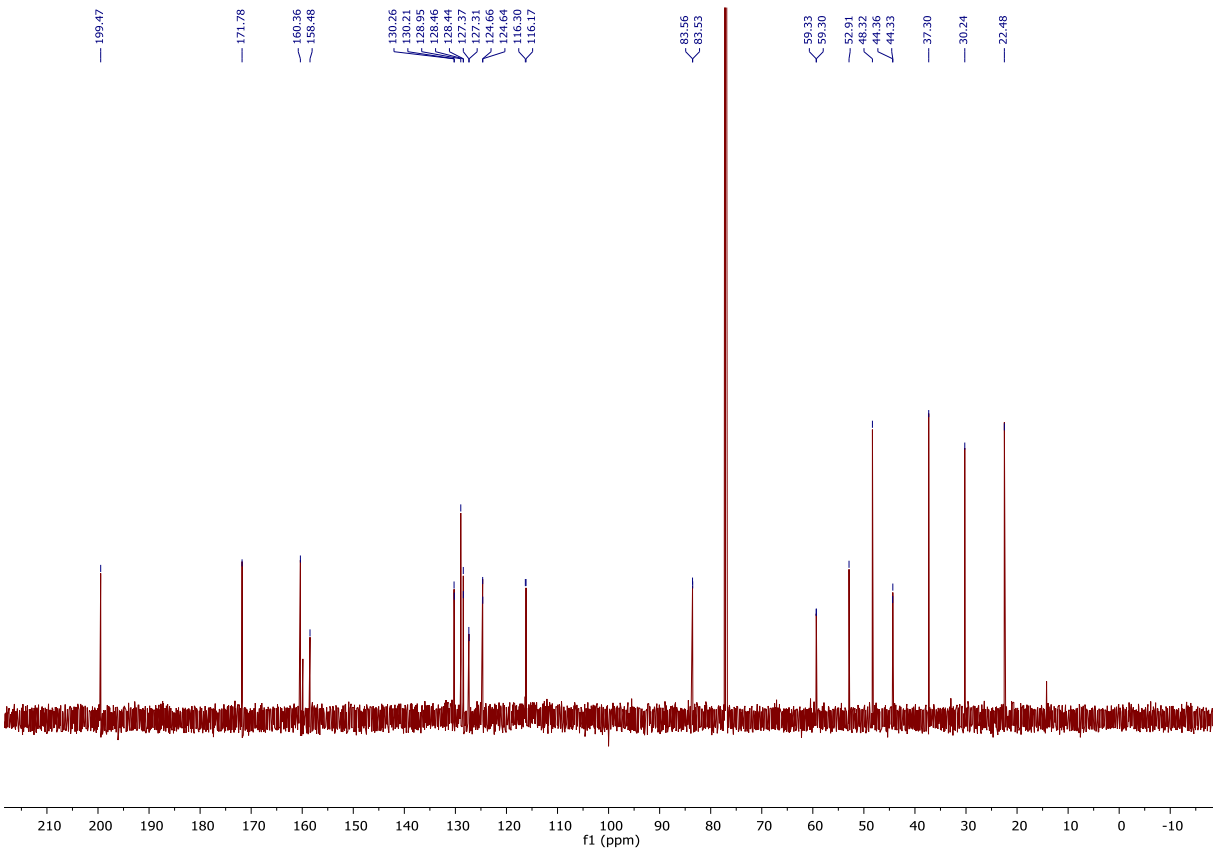
44.64
33.29
29.35
27.48
f1 (ppm)


O
HO
S
MeOOC
f1 (ppm)


f1 (ppm)


O
HO
F
S
MeOOC
f1 (ppm)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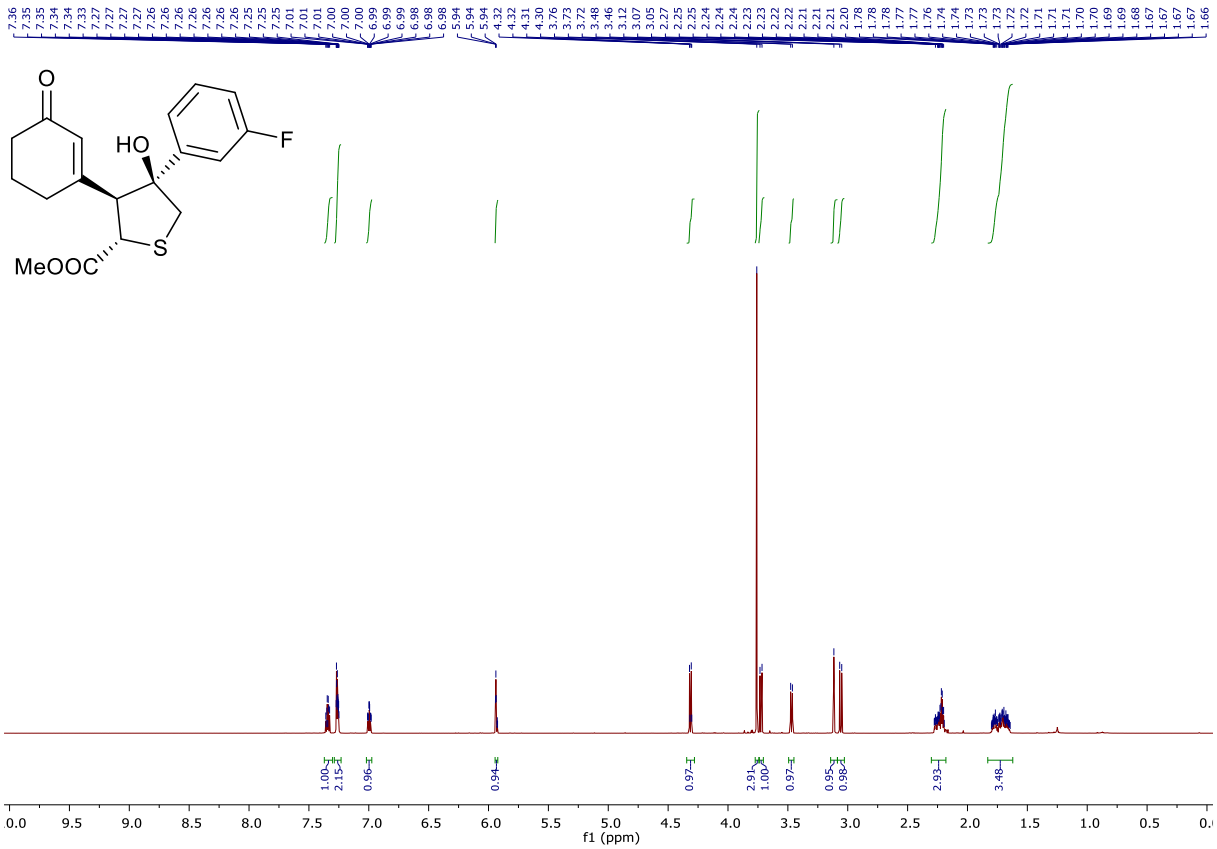
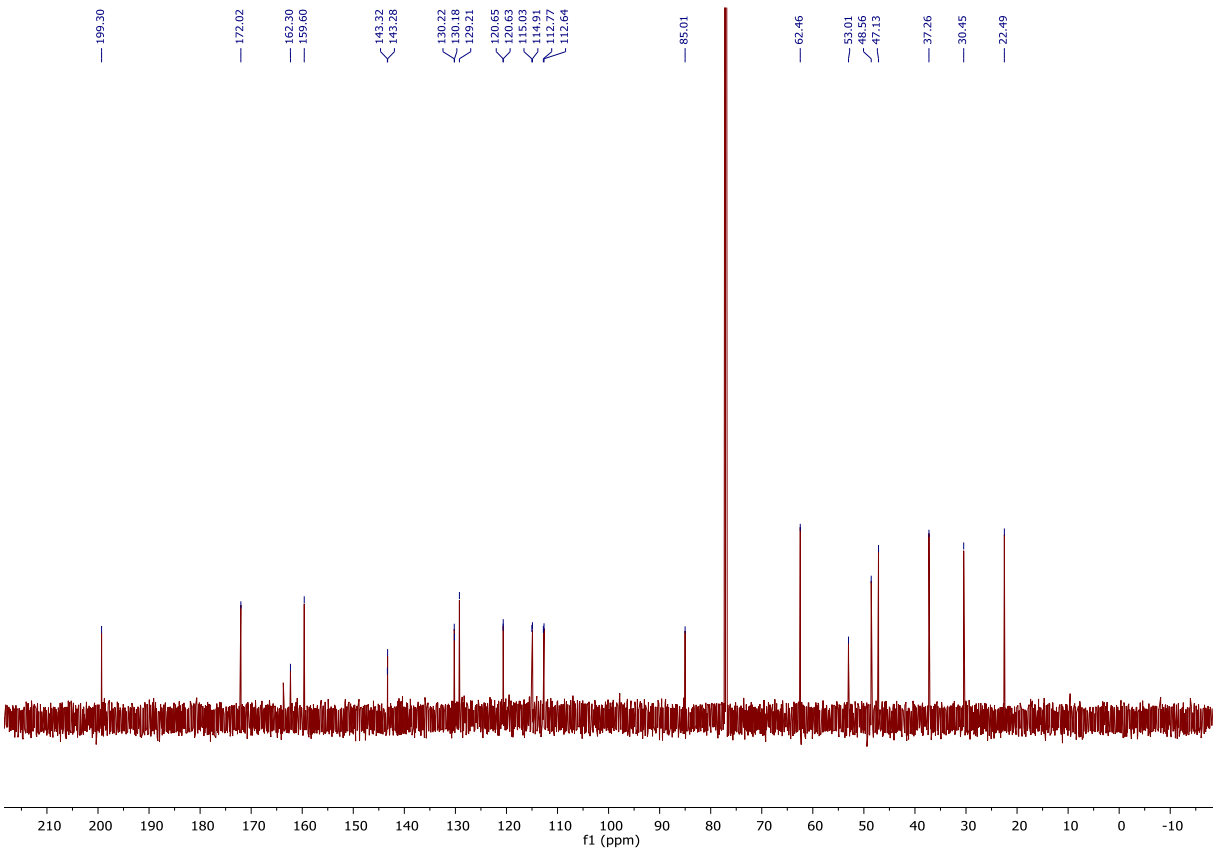
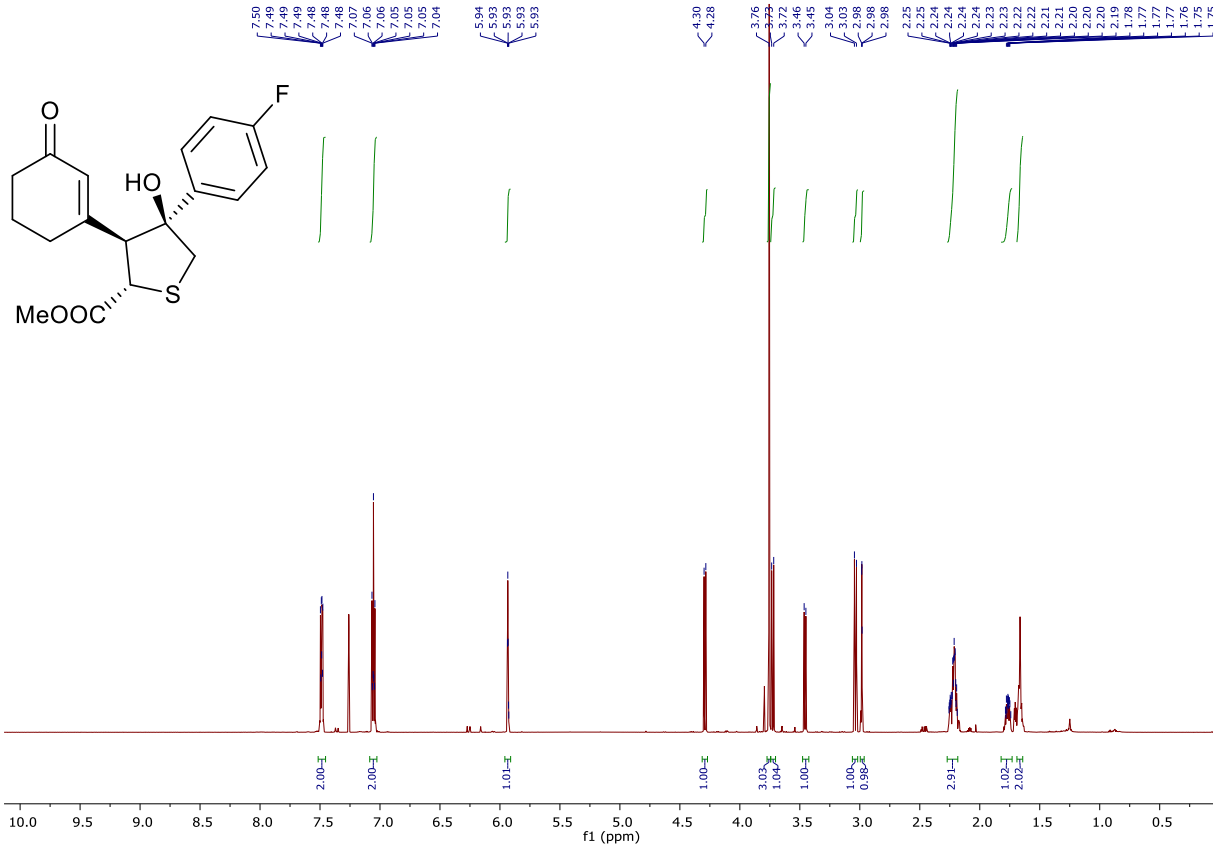
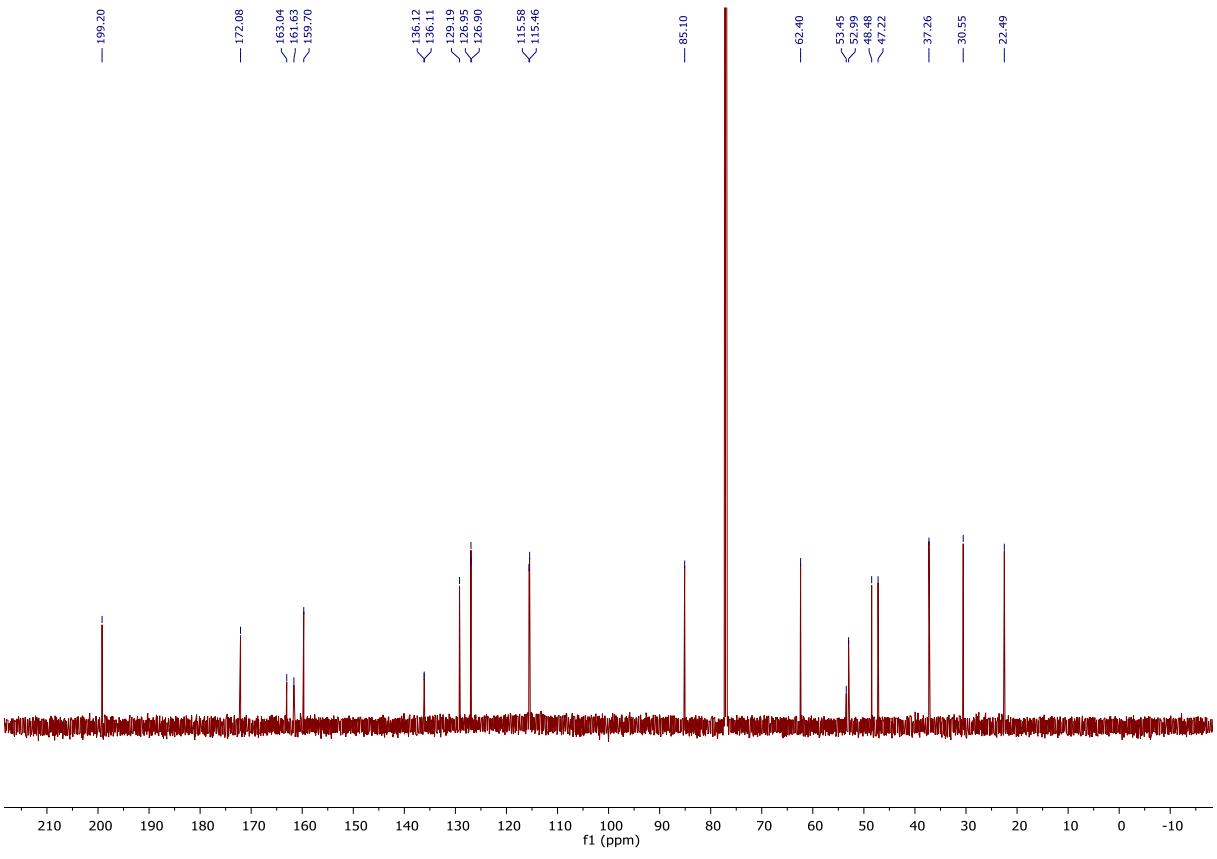
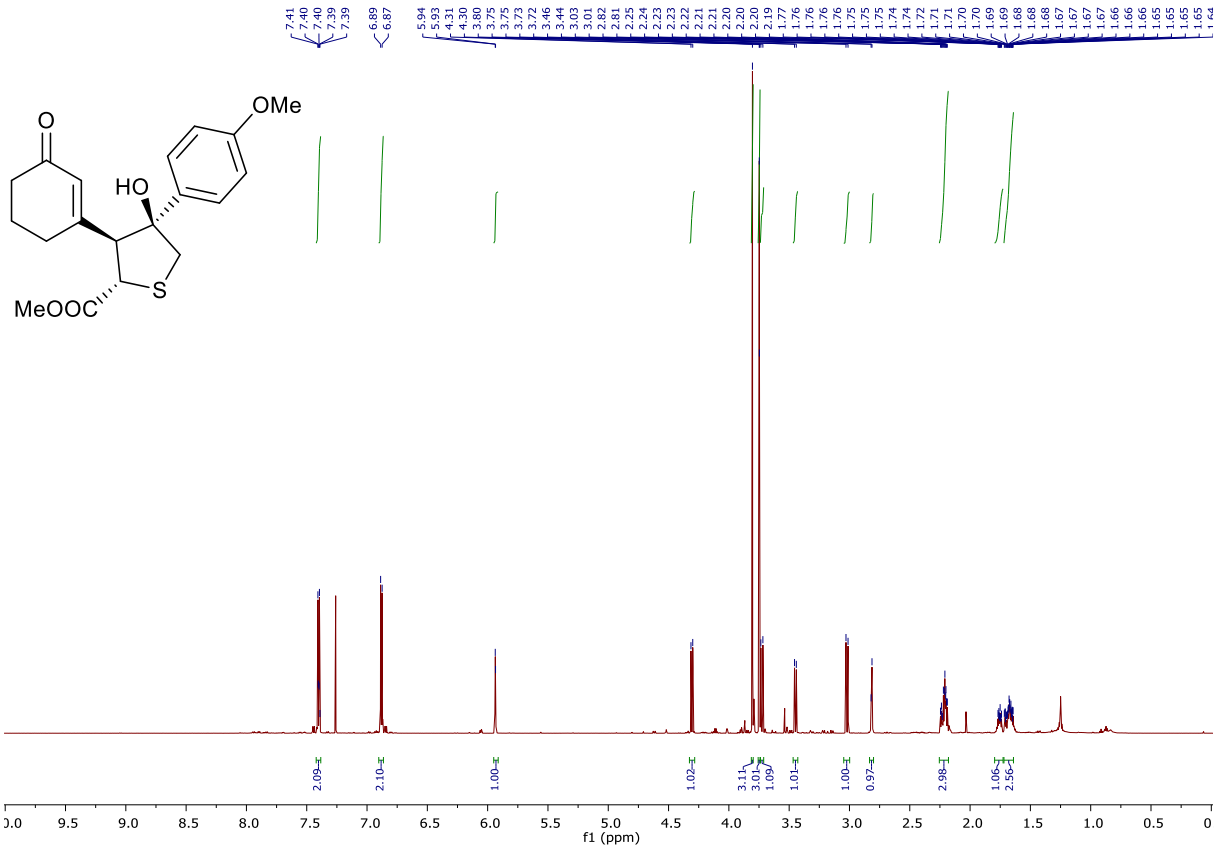
158.48
130.26
130.21
128.95
128.46
128.44
127.37
127.31
124.66
124.64
116.30
116.17
83.56
83.53
59.33
59.30
52.91
48.32
44.36
44.33
37.30
30.24
22.48
f1 (ppm)

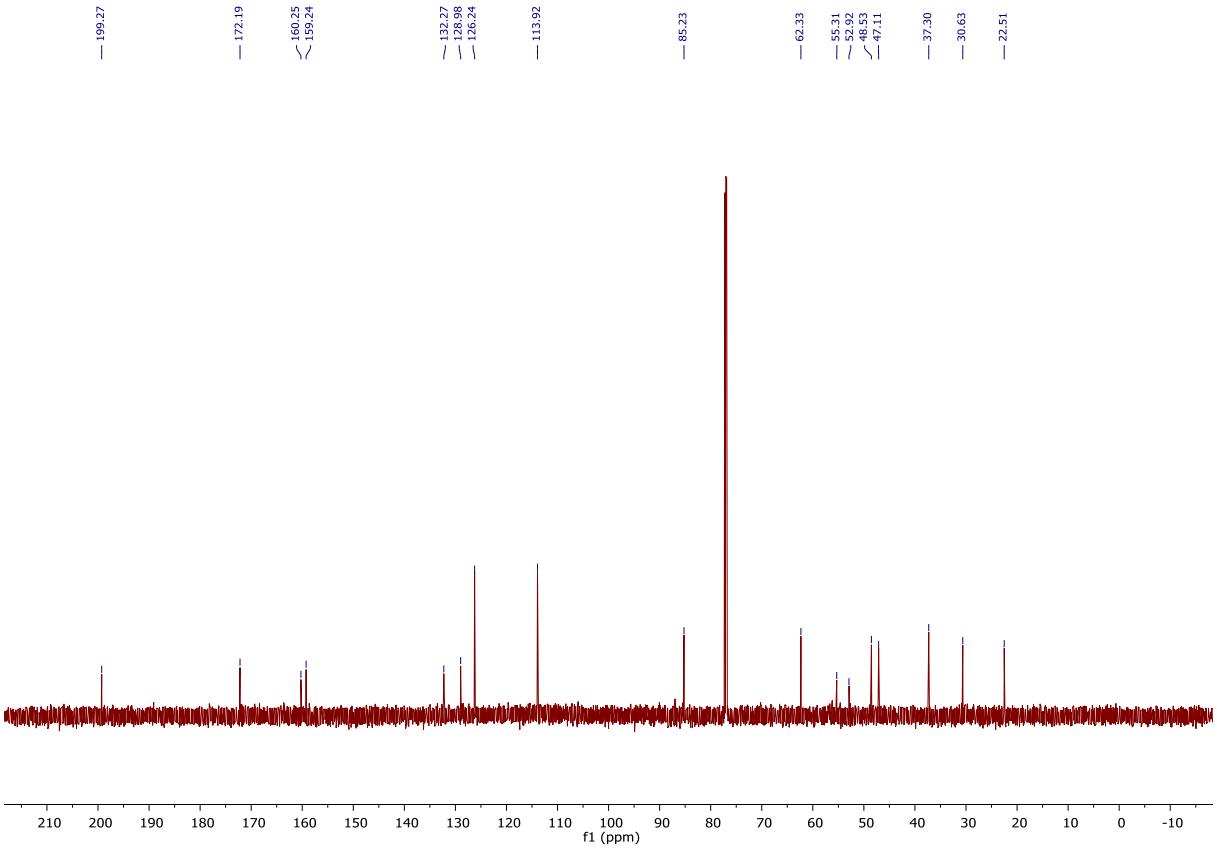

O
HO
F
S
MeOOC
f1 (ppm)


f1 (ppm)

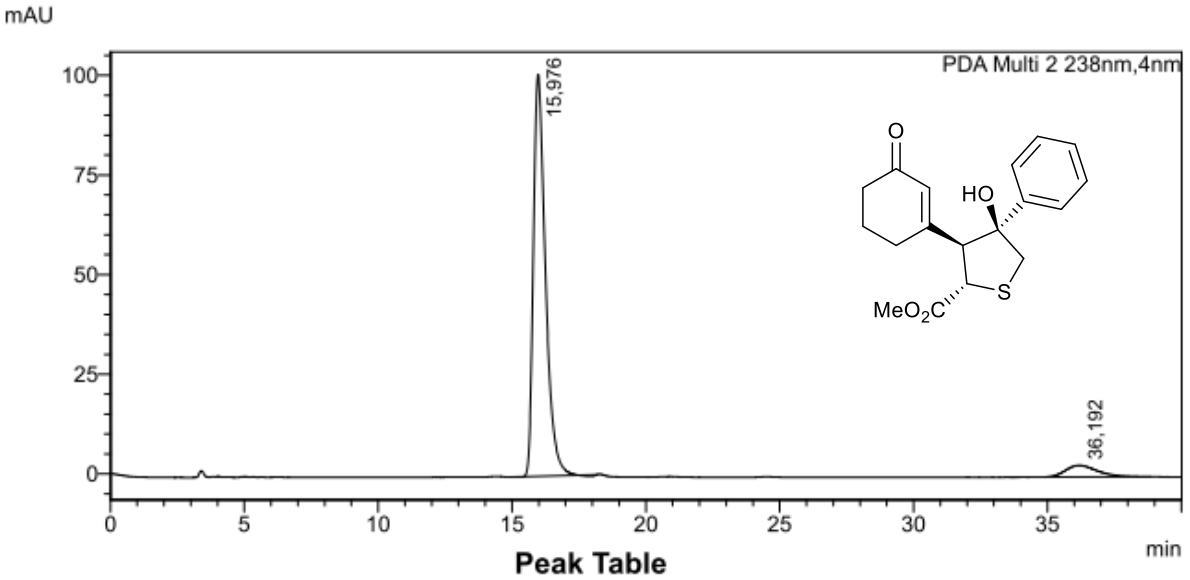

O
F
HO
S
MeOOC
f1 (ppm)


f1 (ppm)


O
OMe
HO
S
MeOOC
f1 (ppm)


f1 (ppm)

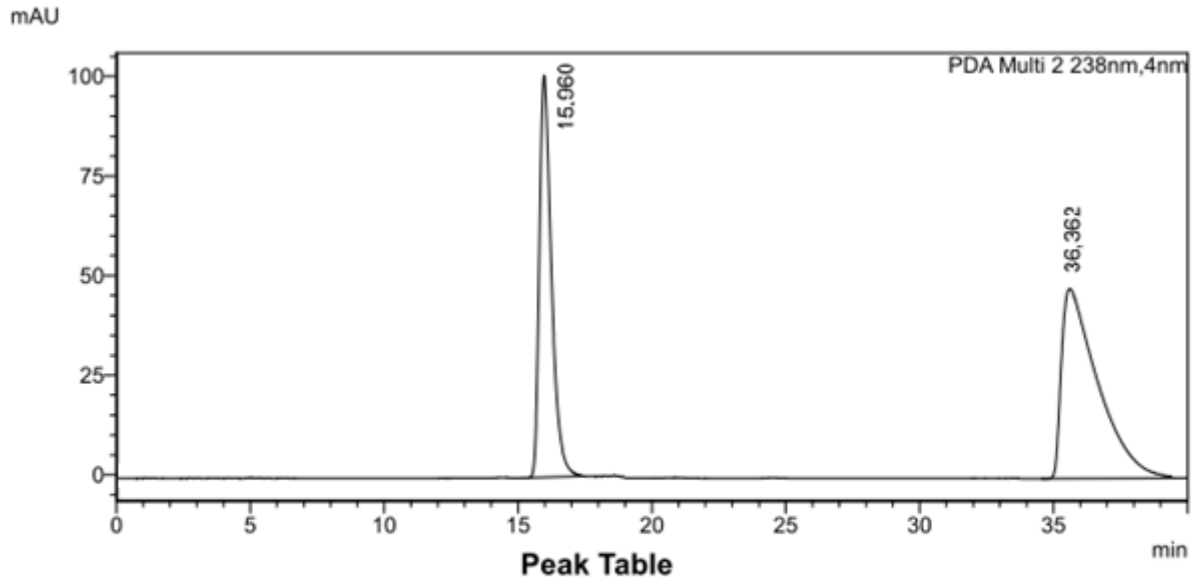
5. HPLC traces



Peak Table

PDA Ch2 238nm

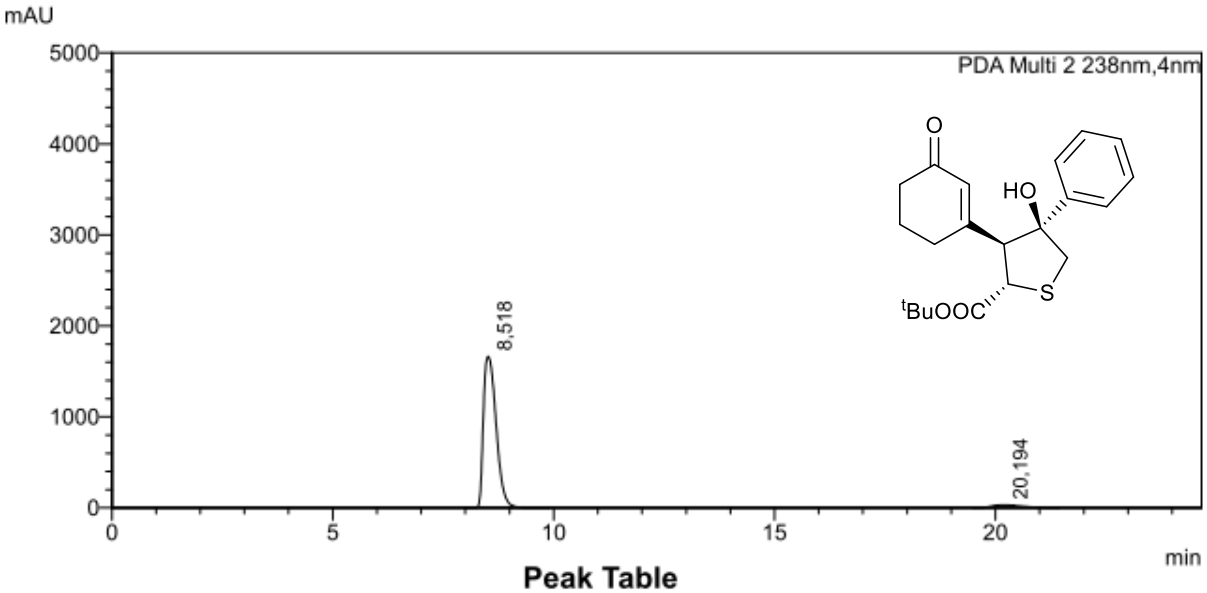
Peak#	Ret. Time	Area%
1	15,976	92,860
2	36,192	7,140
Total		100,000



Peak Table

PDA Ch2 238nm

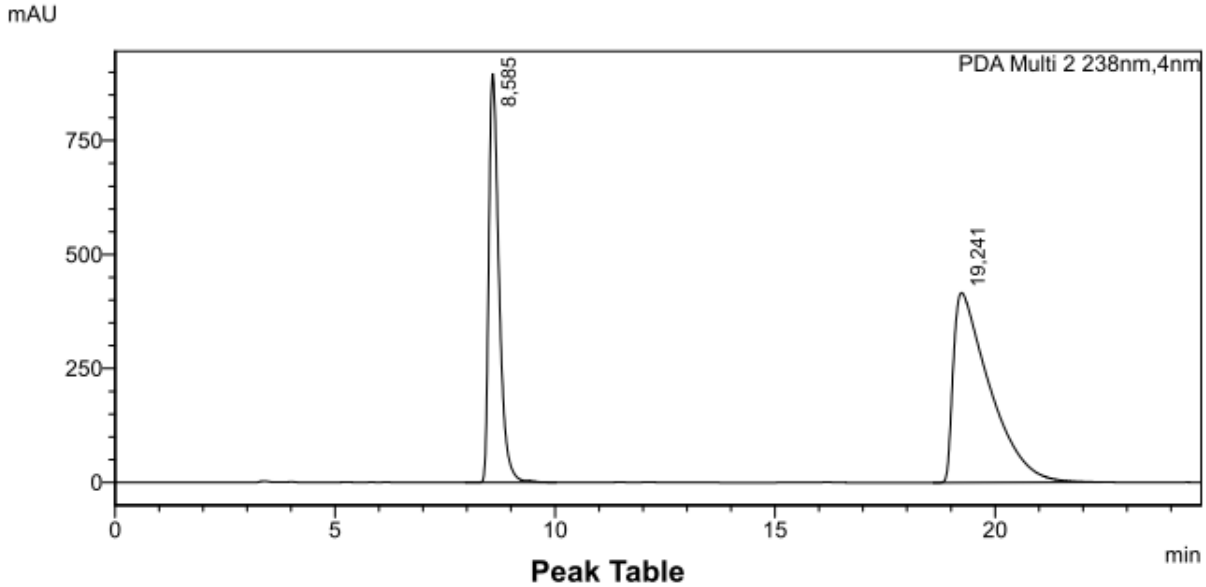
Peak#	Ret. Time	Area%
1	15,960	51,192
2	36,362	48.808
Total		100,000



Peak Table

PDA Ch2 238nm

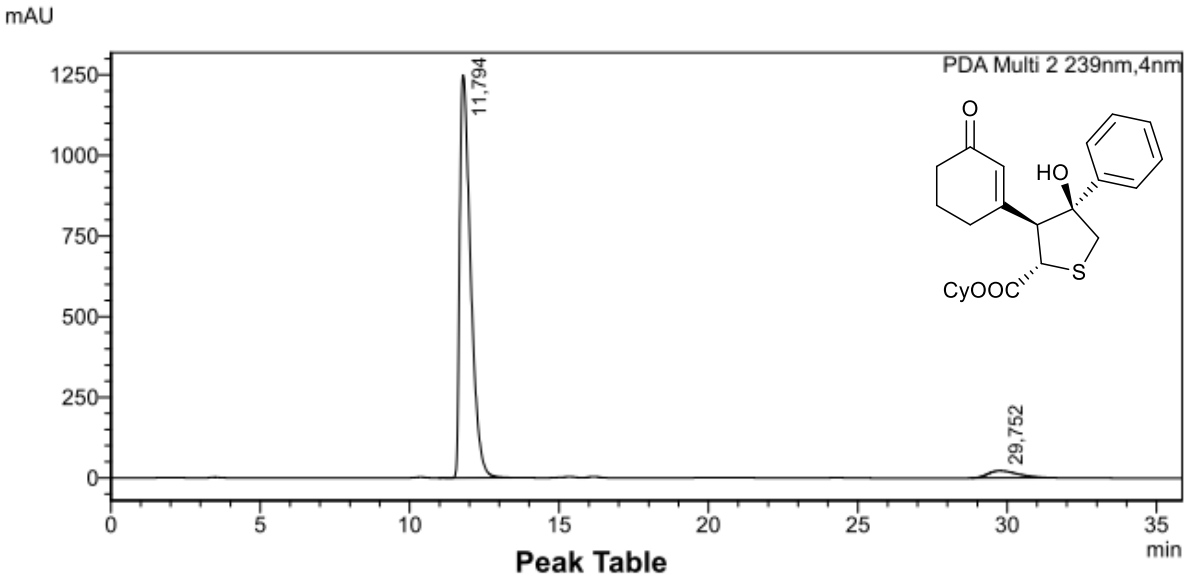
Peak#	Ret. Time	Area%
1	8,518	95,678
2	20,194	4,322
Total		100,000



Peak Table

PDA Ch2 238nm

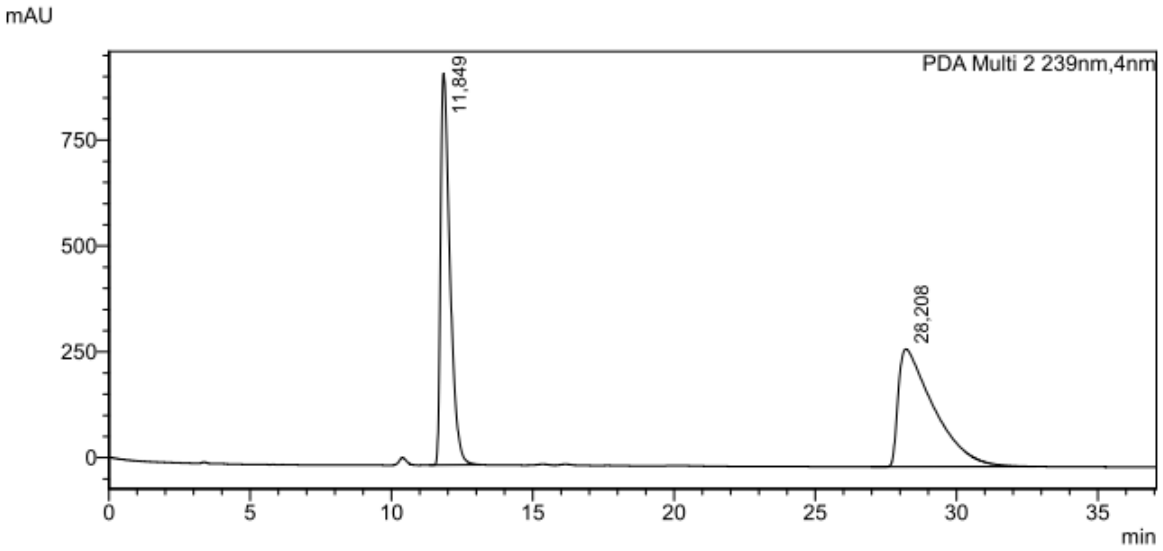
Peak#	Ret. Time	Area%
1	8,585	37,608
2	19,241	62,392
Total		100,000



Peak Table

PDA Ch2 239nm

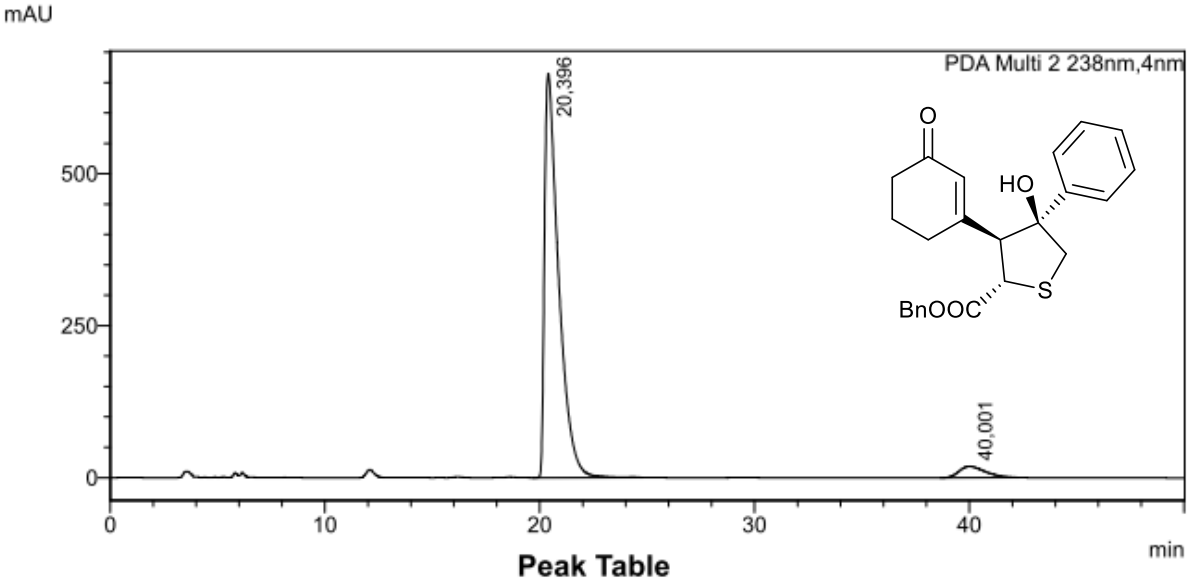
Peak#	Ret. Time	Area%
1	11,794	95,318
2	29,752	4,682
Total		100,000



Peak Table

PDA Ch2 239nm

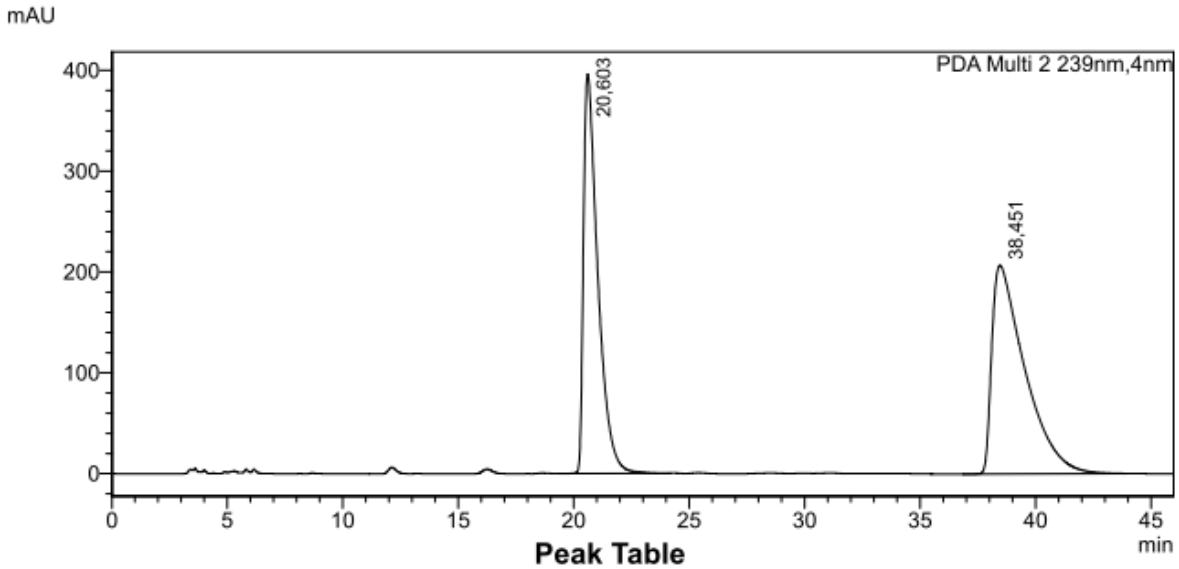
Peak#	Ret. Time	Area%
1	11,849	46,808
2	28,208	53,192
Total		100,000



Peak Table

PDA Ch2 238nm

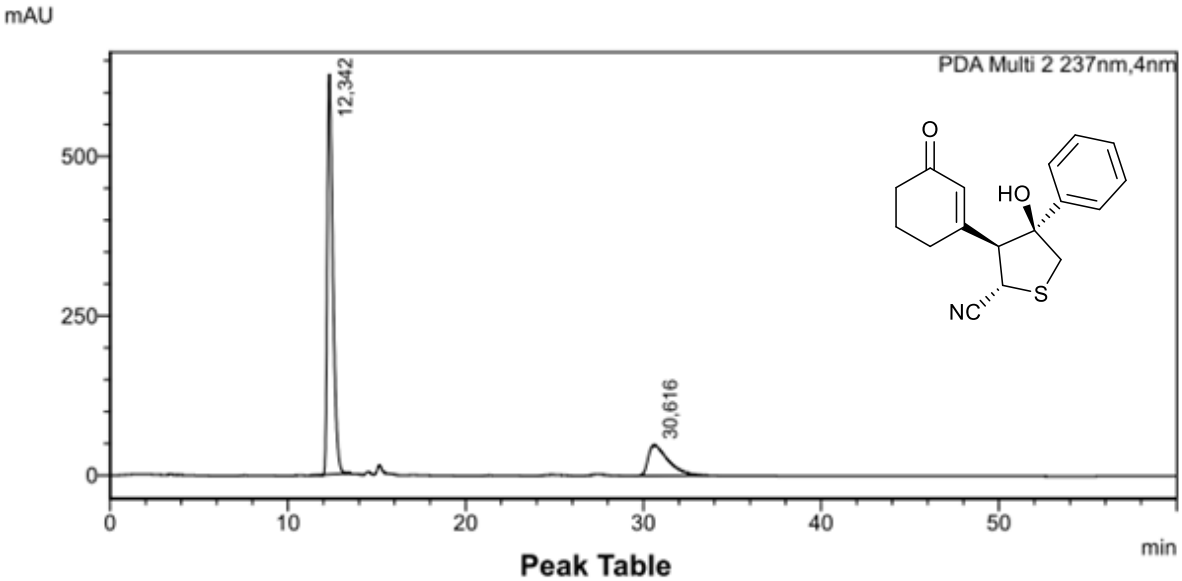
Peak#	Ret. Time	Area%
1	20,396	95,073
2	40,001	4,927
Total		100,000



Peak Table

PDA Ch2 239nm

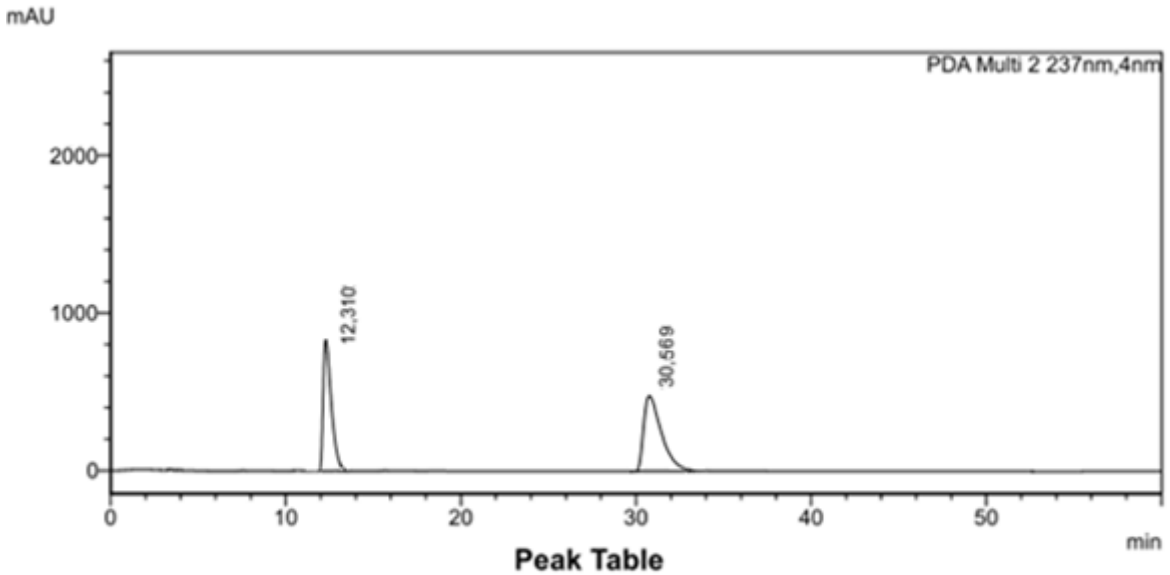
Peak#	Ret. Time	Area%
1	20,603	45,440
2	38,451	54,560
Total		100,000



Peak Table

PDA Ch2 237nm

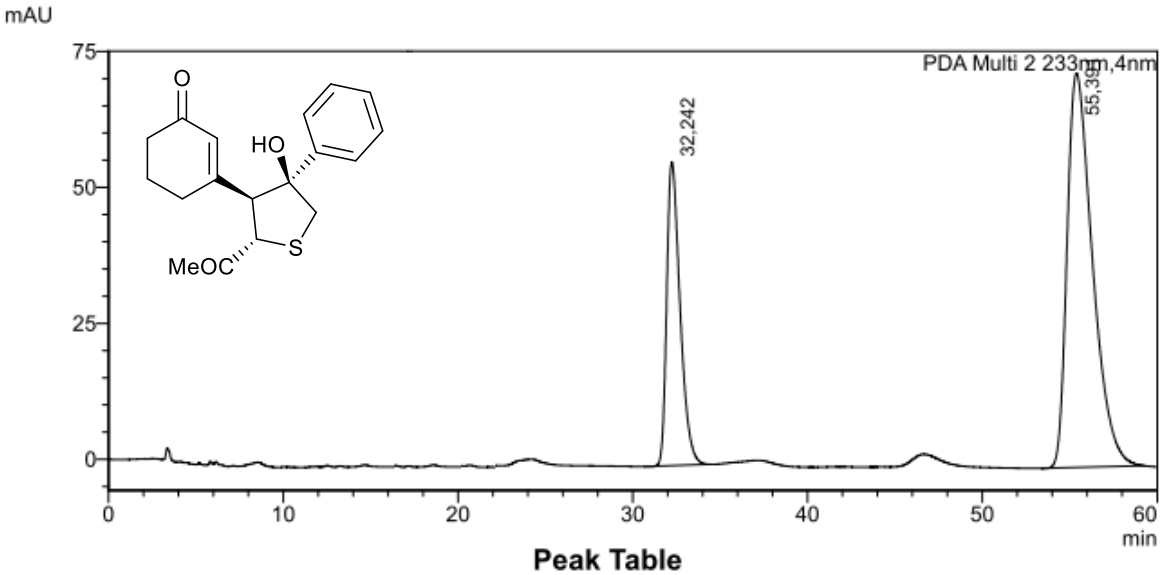
Peak#	Ret. Time	Area%
1	12,342	78,461
2	30,616	21,539
Total		100,000



Peak Table

PDA Ch2 237nm

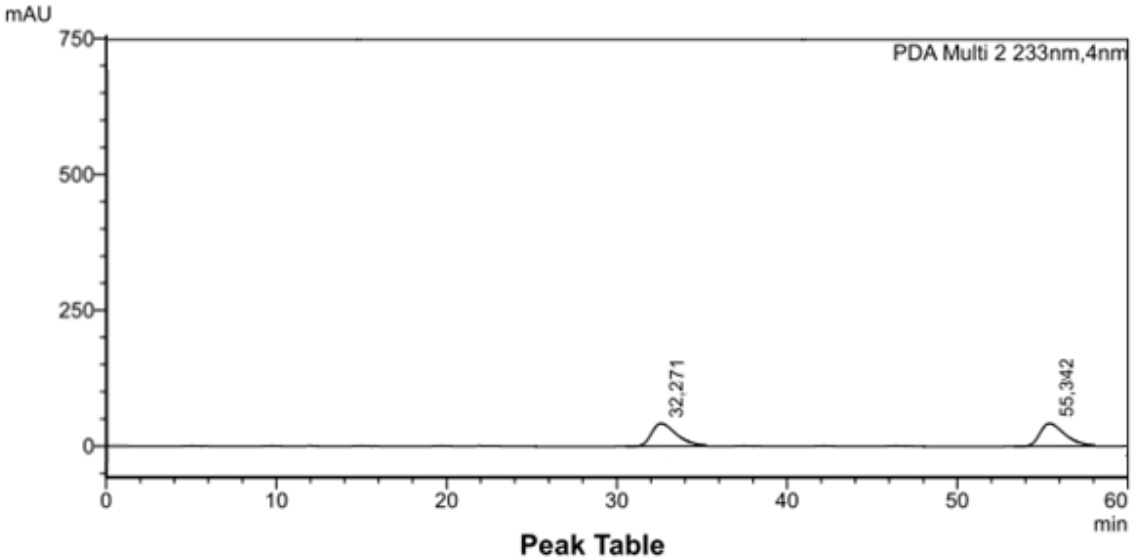
Peak#	Ret. Time	Area%
1	12,310	49,593
2	30,569	50,407
Total		100,000



Peak Table

PDA Ch2 233nm

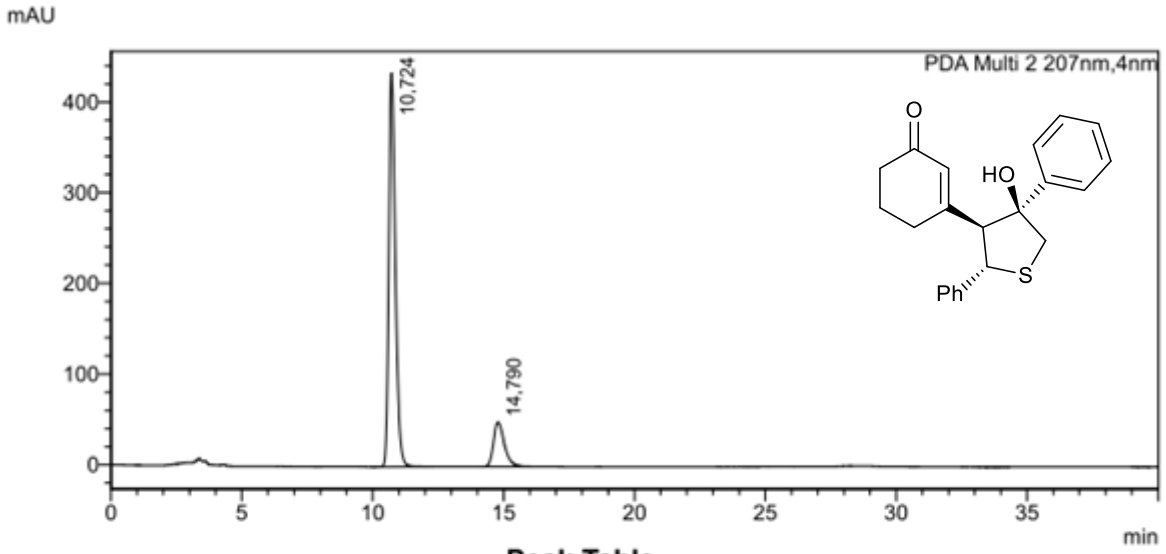
Peak#	Ret. Time	Area%
1	32,242	28,785
2	55,391	71,215
Total		100,000



Peak Table

PDA Ch2 233nm

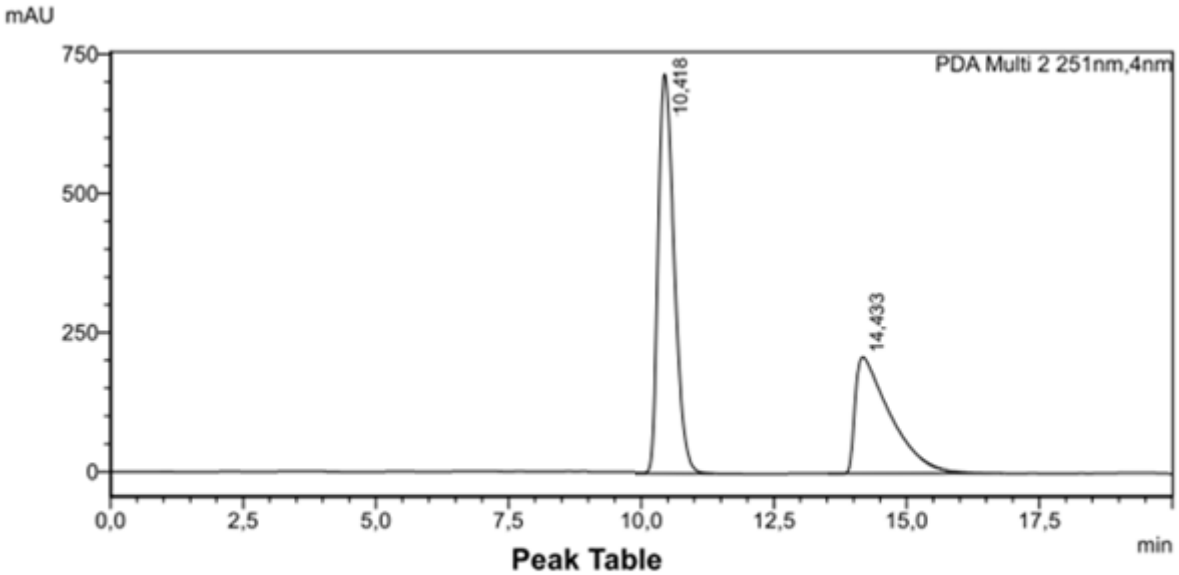
Peak#	Ret. Time	Area%
1	32,271	41,808
2	55,342	59,192
Total		100,000



Peak Table

PDA Ch2 207nm

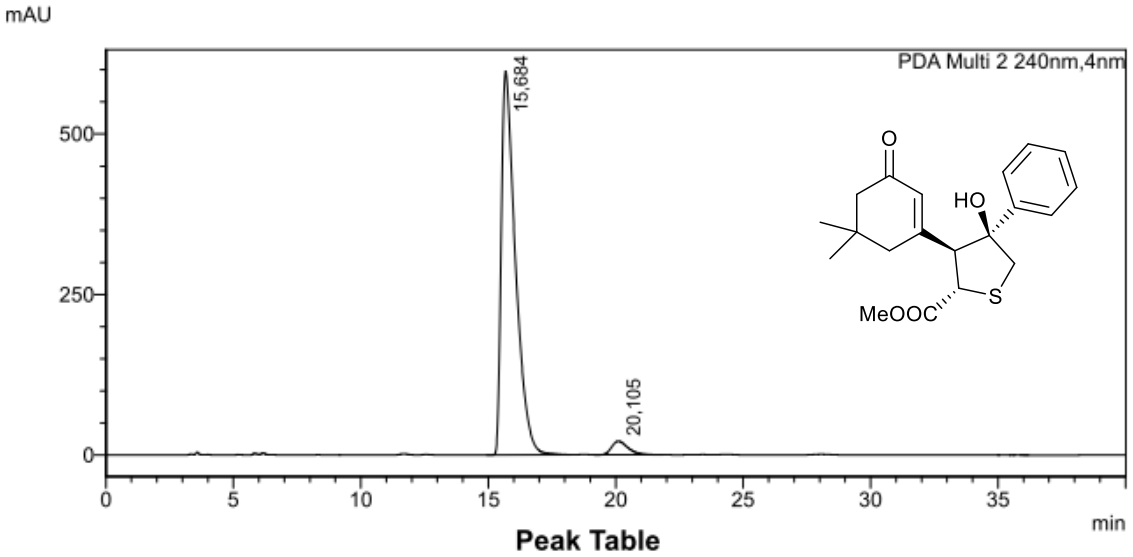
Peak#	Ret. Time	Area%
1	10,724	84,177
2	14,790	15,823
Total		100,000



Peak Table

PDA Ch2 251nm

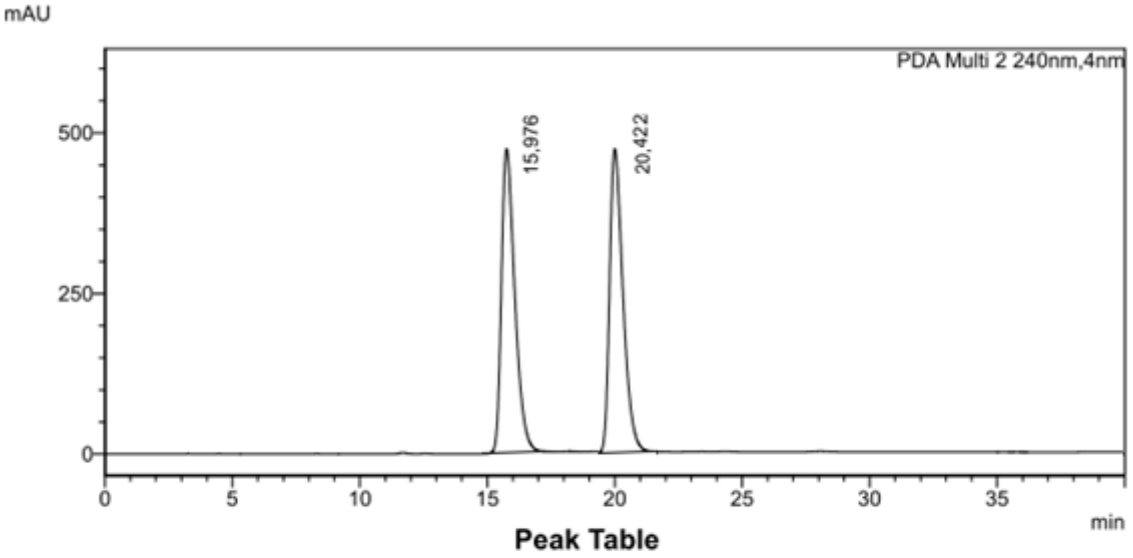
Peak#	Ret. Time	Area%
1	10,418	56,808
2	10,433	43,192
Total		100,000



Peak Table

PDA Ch2 240nm

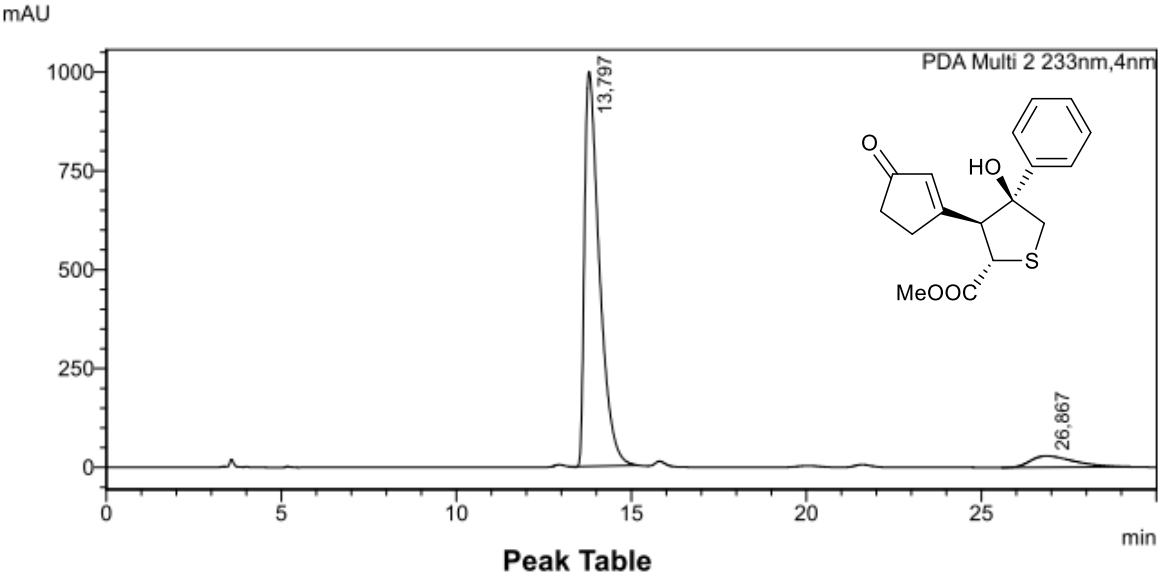
Peak#	Ret. Time	Area%
1	15,684	96,025
2	20,105	3,975
Total		100,000



Peak Table

PDA Ch2 240nm

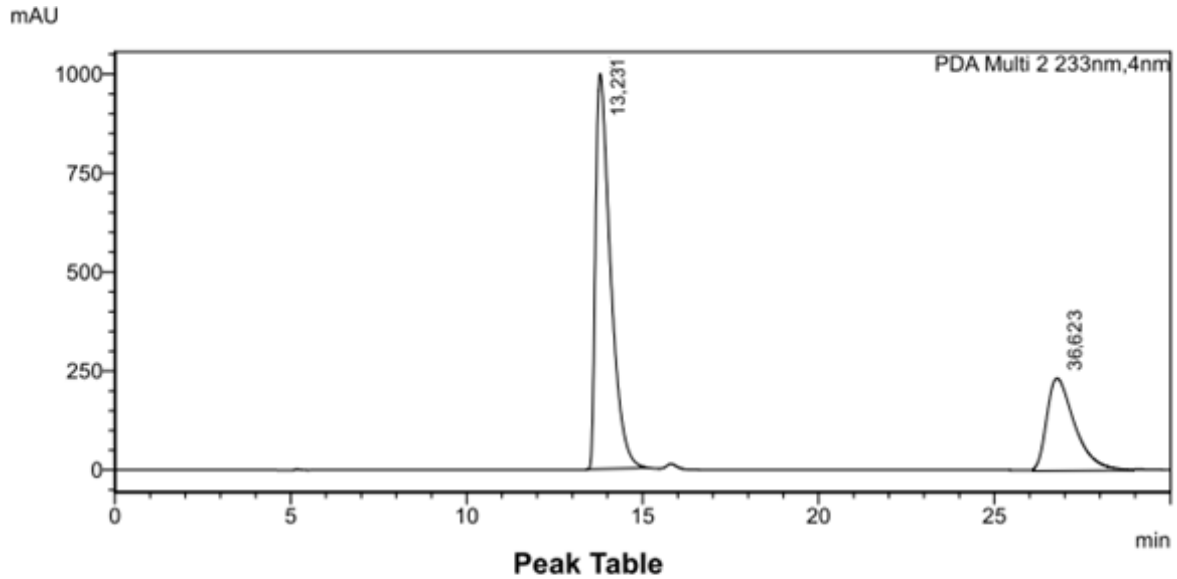
Peak#	Ret. Time	Area%
1	15,976	50,401
2	20,422	49,599
Total		100,000



Peak Table

PDA Ch2 233nm

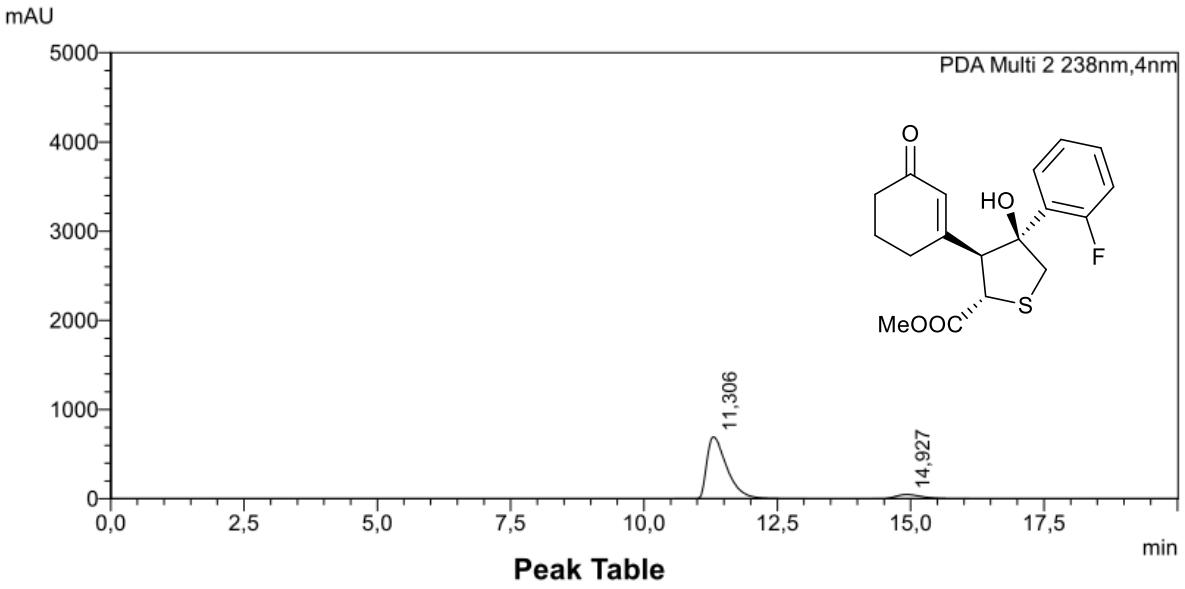
Peak#	Ret. Time	Area%
1	13,797	92,315
2	26,867	7,685
Total		100,000



Peak Table

PDA Ch2 233nm

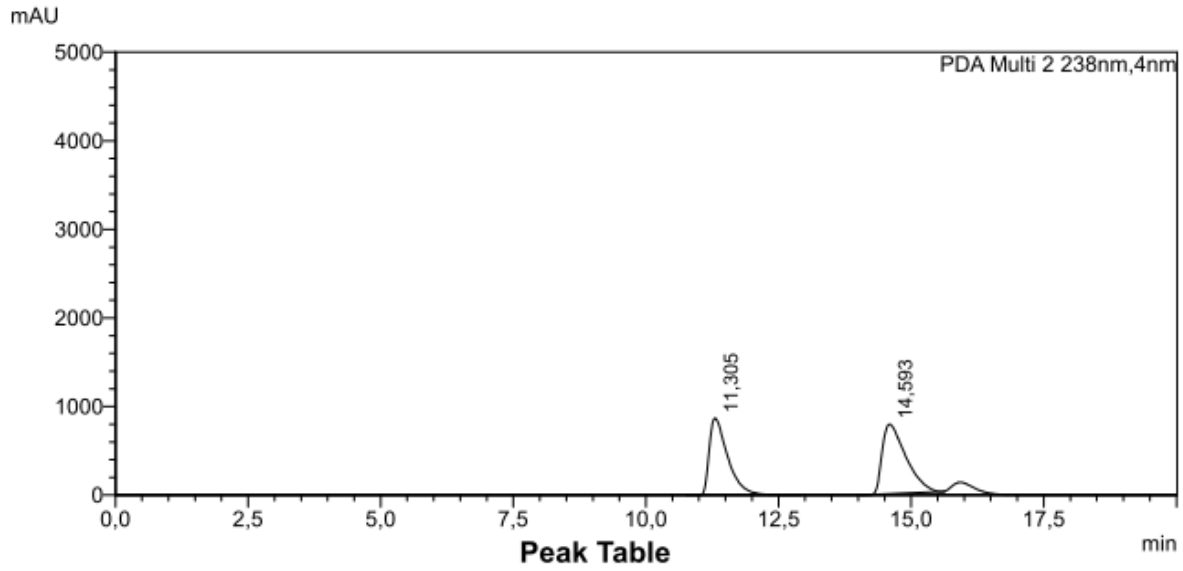
Peak#	Ret. Time	Area%
1	13,231	48,928
2	36,623	51,072
Total		100,000



Peak Table

PDA Ch2 238nm

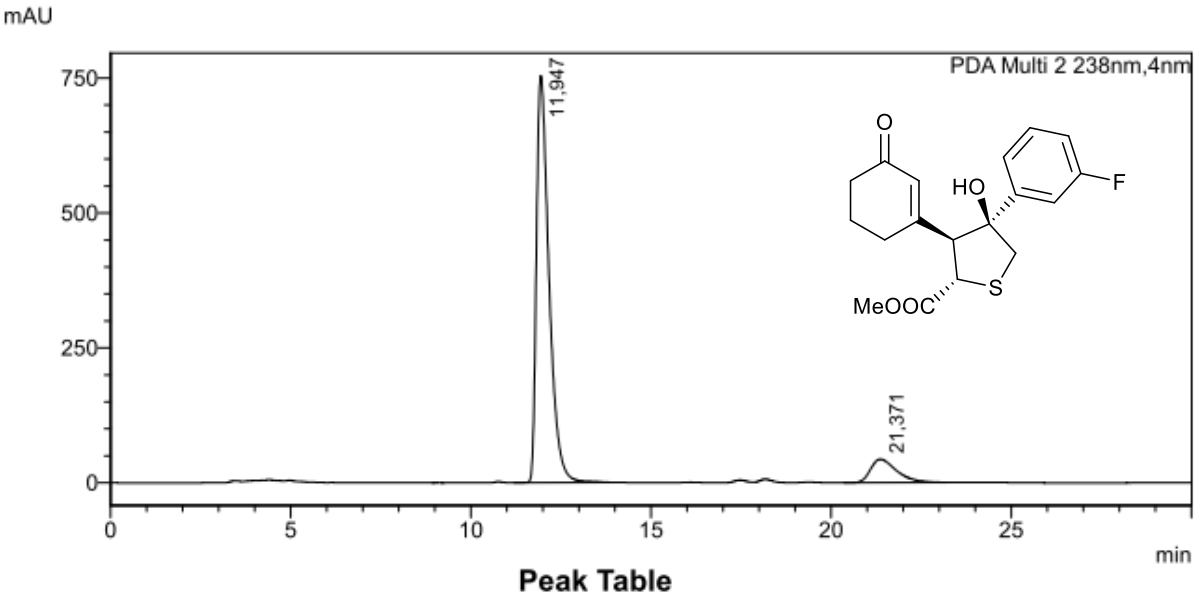
Peak#	Ret. Time	Area%
1	11,306	91,732
2	14,927	8,268
Total		100,000



Peak Table

PDA Ch2 238nm

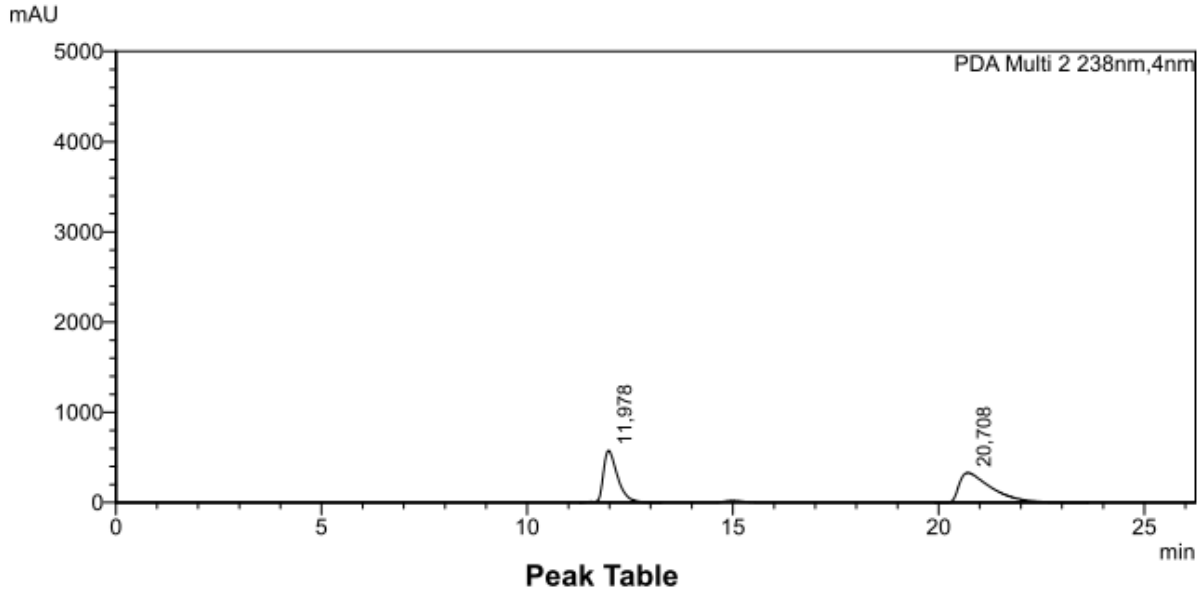
Peak#	Ret. Time	Area%
1	11,305	46,482
2	14,593	53,518
Total		100,000



Peak Table

PDA Ch2 238nm

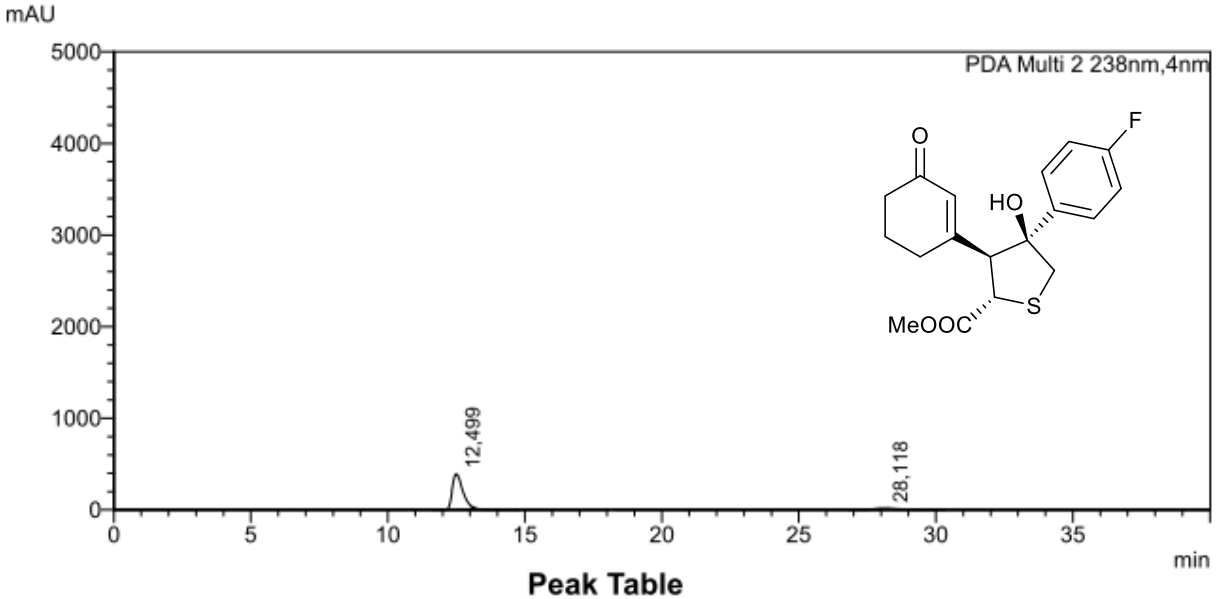
Peak#	Ret. Time	Area%
1	11,947	89,399
2	21,371	10,601
Total		100,000



Peak Table

PDA Ch2 238nm

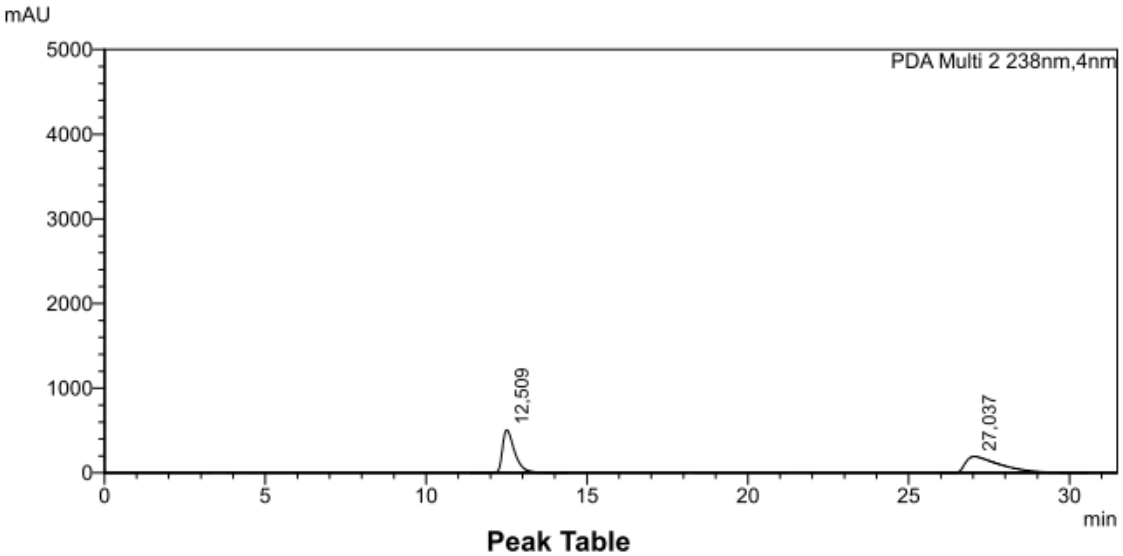
Peak#	Ret. Time	Area%
1	11,978	43,484
2	20,708	56,516
Total		100,000



Peak Table

PDA Ch2 238nm

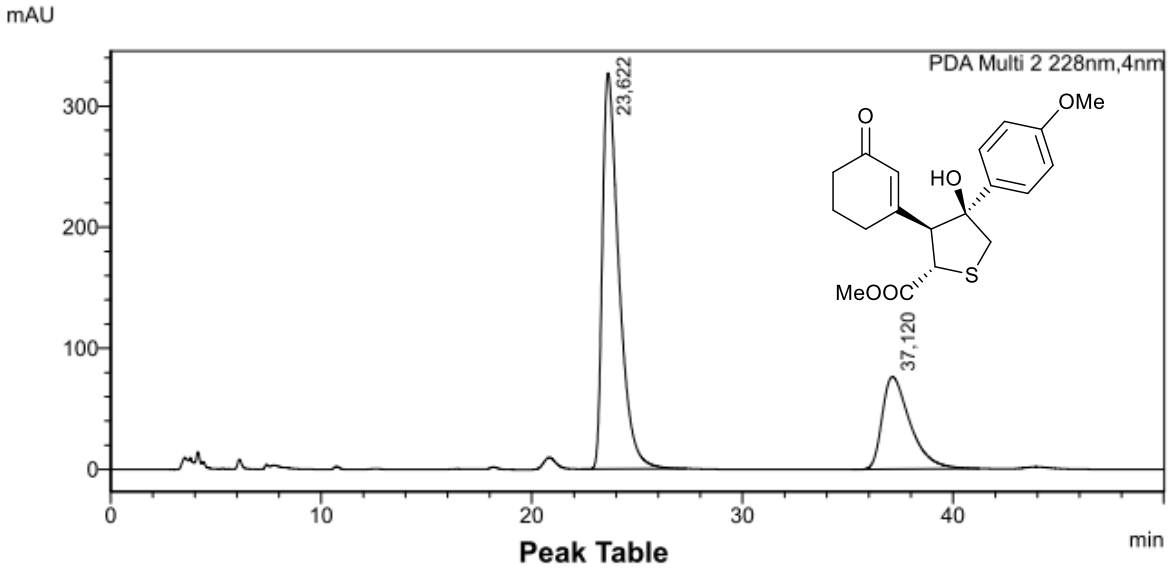
Peak#	Ret. Time	Area%
1	12,499	89,879
2	28,118	10,121
Total		100,000



Peak Table

PDA Ch2 238nm

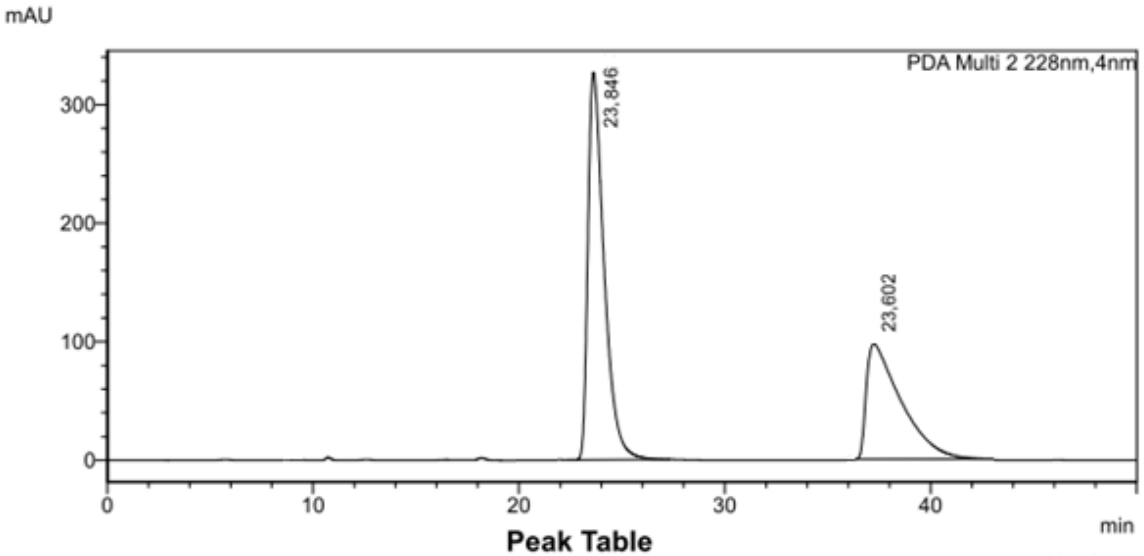
Peak#	Ret. Time	Area%
1	12,509	48,099
2	27,037	51,901
Total		100,000



Peak Table

PDA Ch2 228nm

Peak#	Ret. Time	Area%
1	23,622	71,663
2	37,120	28,337
Total		100,000



Peak Table

PDA Ch2 228nm

Peak#	Ret. Time	Area%
1	23,846	56,192
2	37,602	43,808
Total		100,000