Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Catalytic Enantioselective aza-Reformatsky reaction with Seven-Membered Cyclic Imines Dibenzo[*b,f*][1,4]oxazepines

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SUPPORTING INFORMATION

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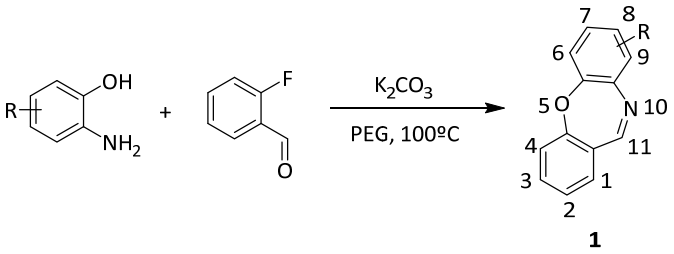
General Experimental Methods

Reactions were carried out under nitrogen in round bottom flasks oven-dried overnight at 120 ºC. Dicloromethane, 1,2-dichloroethane, toluene and diethyl ether were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. Ethyl acetate and methyl *tert*-butyl ether were dried over molecular sieves of 6Ä. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Melting points were determined in capillary tubes. NMR spectra were run at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR using residual non-deuterated solvent as internal standard ($CHCl_3$: δ 7.26 and 77.0 ppm; CD_3OD: δ 3.31 and 49.0 ppm). Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments. High resolution mass spectra (ESI) were recorded on a AB SCIEX Triple TOF^{TM} spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV(ESI). Specific optical rotations were measured using sodium light (D line 589 nm). Chiral HPLC analyses were performed in a chromatograph equipped with a UV diode-array detector using chiral stationary columns from Daicel. Most reagents were commercially available and used as purchased without further purification. 2-Aminphenol, 2-amino-4-methoxyphenol , [1,1'-binaphthalene]-2,2'-diol (**I**), Qunine (**L1**), (1R,2S)-2-(dimethylamino)-1-phenylpropan-1-ol (**L2**), (S)-diphenyl(pyrrolidin-2-yl)methanol (**L3**), (S)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (**L4**), (S)-bis(3,5-bis(trifluoromethyl)phenyl)(pyrrolidin-2-yl)methanol (**L5**), (S)-di(naphthalen-2-yl)(pyrrolidin-2-yl)methanol (**L6**) were purchased from Sigma Aldrich. 2-Fluorbenzaldehyde was purchased from fluorochem. 2-amino-5-chlorophenol, 2-amino-4-methylphenol, ethyl iodoacetate, dimethyl zinc, diethyl zinc were purchased from Acros Organics. 2-amino-4-chlorophenol, 2-amino-5-methylphenol, were purchased from Alfa Aesar.

Typical procedures and characterization data for compounds 1 and 4

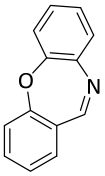
Procedures and characterization data for compounds 1 substituted in positions 7 and 8 and compound 4



1

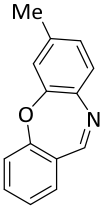
2-Aminophenol (5.5mmol, 1.1 eq.) was solved in 10mL PEG. 2-Fluorobenzaldhyd (5.0mmol, 1eq) and K_2CO_3 (5,0mmol, 1eq.) were added. The reaction mixture was heated to 100°C under reflux for 2h. The reaction process was folowed by TLC. Once terminated the reaction, the mixture was cooled to rt and 20mL water was added to quench the reaction. The mixture was extracted EtOAc (3x20 mL), washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed by evaporation and the crude product was purified by flash chromatography, obtaining product **1**.[37]

Dibenzo[*b,f*][1,4]oxazepine (1a)[1]



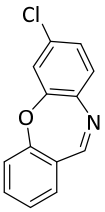
Orange solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.56 (ddd, J = 8.1, 7.4, 1.8 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.6 (CH), 160.4 (C), 152.7 (C), 140.5 (C), 133.3 (CH), 130.1 (CH), 129.2 (CH), 128.8 (CH), 127.3 (C), 125.7 (CH), 125.1 (CH), 121.4 (CH), 120.7 (CH).

8-Methyldibenzo[*b,f*][1,4]oxazepine (1b)[1]



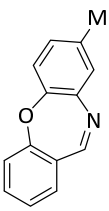
Brown solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.42 (ddd, J = 8.1, 7.4, 1.8 Hz, 1H), 7.32 (dd, J = 7.6, 1.7 Hz, 1H), 7.19 (dd, J = 7.5, 1.1 Hz, 1H), 7.15 (dt, J = 2.5, 1.0 Hz, 1H), 7.11 (dt, J = 8.1, 0.7 Hz, 1H), 7.01 – 6.98 (m, 2H), 2.30 (d, J = 0.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.6 (CH), 150.5 (C), 140.0 (C), 135.4 (C), 133.2 (CH), 130.1 (CH), 129.5 (CH), 129.3 (CH), 127.4 (C), 124.9 (CH), 120.9 (CH), 120.6 (CH), 20.6 (CH_3).

8-Chlorodibenzo[*b,f*][1,4]oxazepine (1c)[1]



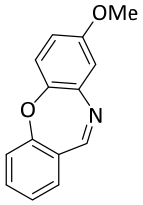
Brown solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.45 (ddd, J = 8.1, 7.3, 1.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.18 (m, 1H), 7.16 (dd, J = 8.6, 2.6 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.03 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.7 (CH), 160.3 (C), 151.3 (C), 141.4 (C), 133.6 (CH), 130.6 (C), 130.3 (CH), 128.9 (CH), 128.4 (CH), 127.1 (C), 125.3 (CH), 122.4 (CH), 120.7 (CH).

7-Methyldibenzo[*b,f*][1,4]oxazepine (1d)[1]



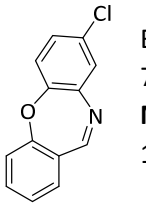
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.42 (ddd, J = 8.1, 7.3, 1.8 Hz, 1H), 7.31 (dd, J = 7.6, 1.7 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.16 (dd, J = 7.5, 1.1 Hz, 1H), 7.11 (ddd, J = 8.1, 1.0, 0.5 Hz, 1H), 7.00 – 6.90 (m, 2H), 2.31 (d, J = 0.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.3 (C), 159.8 (CH), 152.3 (C), 139.4 (C), 138.0 (C), 133.2 (CH), 130.1 (CH), 129.0 (CH), 127.4 (C), 126.4 (CH), 125.0 (CH), 121.8 (CH), 120.7 (CH), 20.8 (CH3).

8-Methoxydibenzo[*b,f*][1,4]oxazepine (1e)



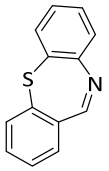
Orange oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.43 (ddd, J = 8.1, 7.4, 1.7 Hz, 1H), 7.32 (dd, J = 7.6, 1.7 Hz, 1H), 7.18 (td, J = 7.5, 1.1 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.02 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 3.1 Hz, 1H), 6.75 (dd, J = 8.8, 3.1 Hz, 1H), 3.76 (s, 3Ht), **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.1 (CH), 160.7 (C), 157.1 (C), 146.5 (C), 141.0 (C), 133.4 (CH), 130.1 (CH), 127.3 (C), 124.9 (CH), 121.7 (CH), 120.5 (CH), 114.6 (CH), 113.0 (CH), 55.7 (CH_3). **HRMS** (ESI) m/z: 226.0859 $[M + H]^+$, $C_{14}H_{12}NO_2$ requires 226.0863.

7-Chlorodibenzo[*b,f*][1,4]oxazepine (1f)[1]



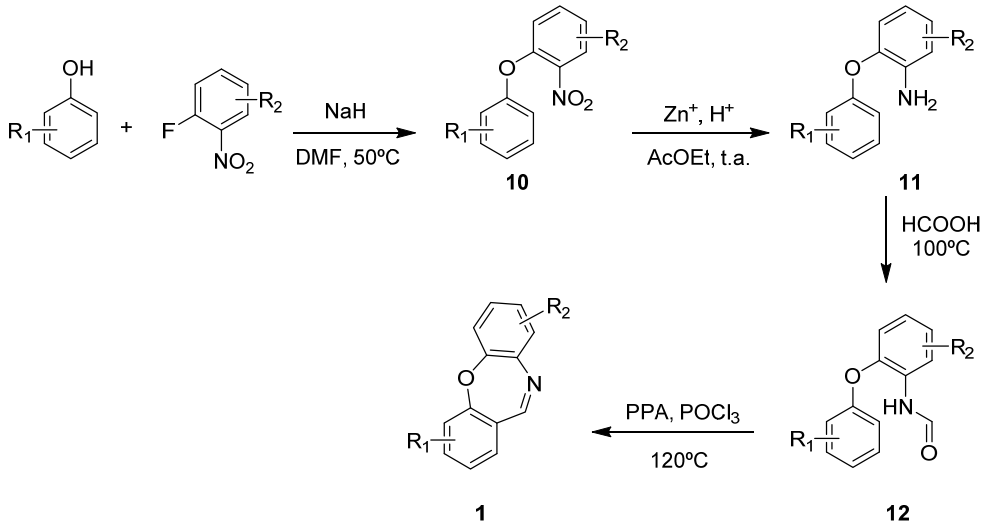
Brown solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.45 (ddd, J = 8.1, 7.3, 1.8 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.25 – 7.17 (m, 1H), 7.17 – 7.09 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.8 (CH), 159.9 (C), 152.8 (C), 139.2 (C), 133.9 (C), 133.6 (CH), 130.2 (CH), 130.0 (CH), 127.2 (C), 125.9 (CH), 125.4 (CH), 121.8 (CH), 120.7 (CH).

Dibenzo[*b,f*][1,4]thiazepine (4)[9]



Yellow solid; Mp 123-125°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.44 – 7.26 (m, 7H), 7.15 (ddd, J = 7.7, 5.6, 3.3 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.2 (CH), 148.5 (C), 139.4 (C), 137.2 (C), 132.7 (CH), 131.6 (CH), 131.4 (CH), 129.4 (CH), 129.2 (CH), 128.8 (C), 128.2 (CH), 127.2 (CH), 126.9 (CH).

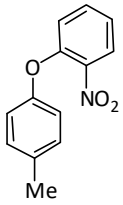
Procedures and characterization data for compounds 1 substituted in positions 1-4



Synthesis and characterization of compounds 10

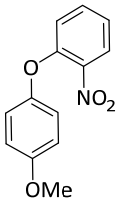
NaH (16mmol, 1.6eq.) was added to 10mL DMF. Next, a solution of phenol (15mmol, 1.5 eq.) in DMF (10mL) was added dropwise to the reaction mixture. The mixture was stirred for 30 minutes, and a solution of 1-fluoro-2-nitrobenzene (**5**) (10mmol, 1eq.) in 4 mL DMF was added drop wise. After stirring for 12 h at 50°C the mixture was cooled to room temperature 25mL saturated aqueous NH_4Cl solution was added, the mixture was extracted with 50mL EtOAc, washed with H_2O (4x 20mL) and dried over $MgSO_4$. The solvent was removed and the crude product was purified by flash chromatography, obtaining following products.

1-Nitro-2-(p-tolyloxy)benzene (10g)[2]



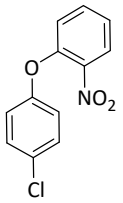
Yellow oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 1.7 Hz, 1H), 7.44 (ddd, J = 8.5, 7.4, 1.7 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.99 – 6.89 (m, 3H), 2.33 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.3 (C), 151.3 (C), 141.1 (C), 134.4 (C), 134.0 (CH), 130.5 (CH), 125.6 (CH), 122.6 (CH), 119.8 (CH), 119.4 (CH), 20.7 (CH_3).

1-(4-Methoxyphenoxy)-2-nitrobenzene (10h)[2]



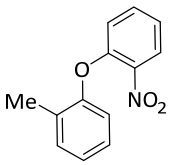
Yellow oil; ^{1}H **NMR** (300 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.1, 1.7 Hz, 1H), 7.42 (ddd, J = 8.4, 7.4, 1.7 Hz, 1H), 7.10 (ddd, J = 8.1, 7.4, 1.2 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.94 – 6.86 (m, 3H), 3.79 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.8 (C), 151.9 (C), 148.6 (C), 140.7 (C), 134.0 (CH), 125.6 (CH), 122.2 (CH), 121.1 (CH), 118.9 (CH), 115.1 (CH), 55.7 (CH_3).

1-(4-Chlorophenoxy)-2-nitrobenzene (10i)[3]



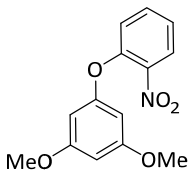
Yellow oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.1, 1.7 Hz, 1H), 7.51 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 7.33 (d, J = 2.3 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.01 (dd, J = 8.3, 1.3 Hz, 1H), 6.97 (d, J = 2.3 Hz, 1H), 6.95 (d, J = 2.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.6 (C), 150.1 (C), 142.7 (C), 134.2 (CH), 130.1 (CH), 129.7 (C), 125.8 (CH), 123.7 (CH), 120.8 (CH), 120.2 (CH).

1-Methyl-2-(2-nitrophenoxy)benzene (10j)[4]



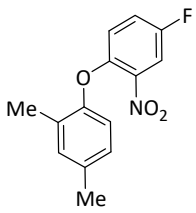
Yellow oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.2, 1.7 Hz, 1H), 7.42 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.23 – 7.16 (m, 1H), 7.16 – 7.08 (m, 2H), 6.92 (dd, J = 7.8, 1.5 Hz, 1H), 6.79 (dd, J = 8.4, 1.2 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.0 (C), 151.2 (C), 140.4 (C), 134.0 (CH), 131.8 (CH), 130.1 (C), 127.4 (CH), 125.8 (CH), 125.3 (CH), 122.1 (CH), 119.9 (CH), 118.3 (CH), 16.0 (CH_3).

1,3-Dimethoxy-5-(2-nitrophenoxy)benzene (10k)[5]



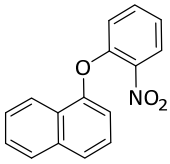
Yellow oil; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.1, 1.7 Hz, 1H), 7.49 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 7.18 (ddd, J = 8.3, 7.4, 1.3 Hz, 1H), 7.07 (dd, J = 8.3, 1.3 Hz, 1H), 6.26 (t, J = 2.2 Hz, 1H), 6.17 (d, J = 2.2 Hz, 2H), 3.74 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.7 (C), 157.6 (C), 150.2 (C), 141.3 (C), 134.1 (CH), 125.7 (CH), 123.4 (CH), 120.9 (CH), 97.6 (CH), 96.6 (CH), 55.5 (CH_3).

1-(2,4-Dimethylphenoxy)-4-fluoro-2-nitrobenzene (10l)



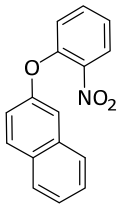
Orange oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.7, 3.1 Hz, 1H), 7.15 (ddd, J = 9.2, 7.2, 3.1 Hz, 1H), 7.06 (s, 1H), 6.98 (ddt, J = 8.0, 2.4, 0.7 Hz, 1H), 6.82 – 6.76 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (75 MHz, CDCl3) δ 156.2 (d, J = 245.8 Hz, CF), 150.9 (C), 147.9 (d, J = 3.0 Hz, C), 139.9 (d, J = 7.6 Hz, C), 135.0 (C), 132.5 (CH), 129.5 (C), 128.0 (CH), 121.2 (d, J = 23.0 Hz, CH), 119.6 (d, J = 7.7 Hz, CH), 119.4 (CH), 112.8 (d, J = 27.8 Hz, CH), 20.7 (CH_3), 15.9 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -119.1. **HRMS** (ESI) m/z: 262.0873 $[M + H]^+$, $C_{14}H_{13}FNO_3$ requires 262.0874.

1-(2-Nitrophenoxy)naphthalene (10m)[6]



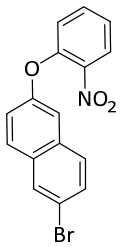
Orange oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.99 (dd, J = 8.1, 1.7 Hz, 1H), 7.88 (dd, J = 7.0, 2.4 Hz, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.45 – 7.37 (m, 2H), 7.20 – 7.13 (m, 1H), 7.03 (dd, J = 7.6, 1.0 Hz, 1H), 6.88 (dd, J = 8.4, 1.3 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$ δ 151.3 (C), 151. (C), 140.9 (C), 135.0 (C), 134.2 (CH), 127.9 (CH), 126.9 (CH), 126.6 (CH), 126.5 (C), 125.8 (CH), 125.6 (CH), 124.9 (CH), 122.9 (CH), 121.8 (CH), 119.6 (CH), 114.5 (CH).

2-(2-Nitrophenoxy)naphthalene (10n)[7]



Orange oil; ^{1}H **NMR** (300 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.2, 1.7 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.74 – 7.69 (m, 1H), 7.53 – 7.48 (m, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 1H), 7.29 – 7.18 (m, 2H), 7.05 (dd, J = 8.3, 1.3 Hz, 1H). **^{13}C NMR** (75 MHz, CDCl3) δ 153.5 (C), 150.7 (C), 141.4 (C), 134.2 (CH), 134.1 (C), 130.7 (C), 130.3 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 125.8 (CH), 125.4 (CH), 123.3 (CH), 120.8 (CH), 119.6 (CH), 115.0 (CH).

2-Bromo-6-(2-nitrophenoxy)naphthalene (10o)

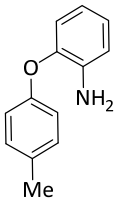


Orange solid; Mp 97-100°C; ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.76 (ddd, J = 8.2, 1.7, 0.6 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.34 – 7.20 (m, 3H), 7.07 (dd, J = 8.4, 1.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.1 (C), 150.1 (C), 147.3 (C), 134.3 (CH), 132.6 (C), 131.6 (CH), 130.2 (C), 129.9 (CH), 129.4 (CH), 128.9 (CH), 125.9 (CH), 123.8 (CH), 121.2 (CH), 120.5 (CH), 119.1 (C), 114.5 (CH). **HRMS** (ESI) m/z: 343.9918 $[M + H]^+$, $C_{16}H_{11}BrNO_3$ requires 343.9917.

Synthesis and characterization of compounds 11

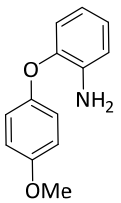
1-nitro-2-phenoxybenzene of the previous step (8mmol, 1 eq.) was dissolved in 50mL EtOAc and 62,5mL AcOH was added dropwise. The mixture was cooled to 0°C and 62,5mL conc. HCl was added drop wise. Zinc powder (240mmol, 30 eq.) was added in portions. The mixture was warmed to room temperature and stirred for 16h. The mixture was cooled to 0°C and 150mL 33% NH_3-solution was added drop wise. The crude product was extracted 4x with 100mL DCM, dried over $MgSO_4$ and the solvent was removed by evaporation, obtaining the following amines.[4]

2-(*p*-Tolyloxy)aniline (11g)[4]



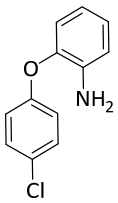
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 2H), 6.99 – 6.91 (m, 1H), 6.89 – 6.84 (m, 2H), 6.81 (td, J = 7.8, 1.5 Hz, 2H), 6.68 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 3.75 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.1 (C), 143.7 (C), 138.5 (C), 132.2 (C), 130.1 (CH), 124.5 (CH), 119.7 (CH), 118.7 (CH), 117.3 (CH), 116.3 (CH), 20.6 (CH_3).

2-(4-Methoxyphenoxy)aniline (11h)[8]



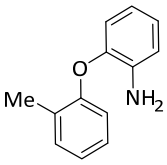
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.95 – 6.88 (m, 3H), 6.87 – 6.82 (m, 2H), 6.81 – 6.73 (m, 2H), 6.66 (ddd, J = 8.1, 7.2, 1.6 Hz, 1H), 3.77 (s, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.4 (C), 150.7 (C), 144.6 (C), 138.1 (C), 124.0 (CH), 119.0 (CH), 118.6 (CH), 118.6 (CH), 116.2 (CH), 114.8 (CH), 55.7 (CH_3).

2-(4-Chlorophenoxy)aniline (11i)[3]



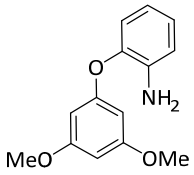
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 7.21 (d, J = 2.3 Hz, 1H), 6.97 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.87 – 6.77 (m, 3H), 6.69 (ddd, J = 8.1, 7.3, 1.7 Hz, 1H), 3.74 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.2 (C), 142.7 (C), 138.7 (C), 129.6 (CH), 127.6 (C), 125.3 (CH), 120.3 (CH), 118.9 (CH), 118.3 (CH), 116.6 (CH).

2-(*o*-Tolyloxy)aniline (11j)[4]



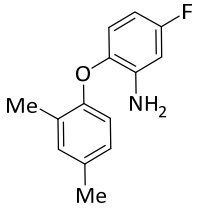
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.15 – 7.08 (m, 1H), 7.00 (td, J = 7.4, 1.3 Hz, 1H), 6.92 (ddd, J = 7.9, 5.3, 3.5 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.70 – 6.62 (m, 2H), 3.80 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.9 (C), 144.1 (C), 137.8 (C), 131.3 (CH), 128.7 (C), 127.1 (CH), 123.9 (CH), 123.2 (CH), 118.7 (CH), 118.2 (CH), 117.5 (CH), 116.2 (CH), 16.1 (CH_3).

2-(3,5-Dimethoxyphenoxy)aniline (11k)



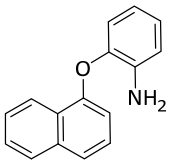
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.97 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 6.90 (dd, J = 8.0, 1.5 Hz, 1H), 6.79 (dd, J = 7.9, 1.6 Hz, 1H), 6.70 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H), 6.23 – 6.14 (m, 1H), 6.13 (d, J = 2.2 Hz, 2H), 3.74 (s, 2H), 3.77 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.6 (C), 159.5 (C), 142.5 (C), 138.8 (C), 125.1 (CH), 120.7 (CH), 118.8 (CH), 116.5 (CH), 95.6 (CH), 94.8 (CH), 55.4 (CH_3). **HRMS** (ESI) m/z: 246,1125 $[M + H]^+$, $C_{14}H_{16}NO_3$ requires 246,1125.

2-(2,4-Dimethylphenoxy)-5-fluoroaniline (11l)



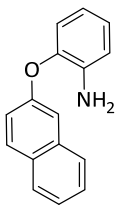
Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.03 (d, J = 1.9 Hz, 1H), 6.91 (ddt, J = 8.2, 2.3, 0.7 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 6.58 (dd, J = 8.8, 5.3 Hz, 1H), 6.50 (dd, J = 9.9, 2.9 Hz, 1H), 6.32 (ddd, J = 8.8, 8.2, 3.0 Hz, 1H), 3.91 (s, 2H), 2.28 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.3 (d, J = 239.2 Hz, CF), 152.8 (C), 140.2 (d, J = 2.4 Hz, C), 139.0 (d, J = 11.5 Hz, C), 132.7 (C), 132.0 (CH), 128.2 (C), 127.5 (CH), 118.7 (d, J = 10.1 Hz, CH), 117.0 (CH), 104.2 (d, J = 23.4 Hz, CH), 102.7 (d, J = 26.8 Hz, CH), 20.6 (CH_3), 16.0 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -120.02. **HRMS** (ESI) m/z: 232.1130 $[M + H]^+$, $C_{14}H_{15}FNO$ requires 232.1132.

2-(Naphthalen-1-yloxy)aniline (11m)[6]



Brown oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.37 – 8.29 (m, 1H), 7.91 – 7.81 (m, 1H), 7.58 – 7.47 (m, 3H), 7.32 (dd, J = 8.2, 7.6 Hz, 1H), 7.01 (ddd, J = 8.0, 7.3, 1.5 Hz, 1H), 6.87 (ddd, J = 7.9, 4.5, 1.5 Hz, 2H), 6.80 (dd, J = 7.6, 1.0 Hz, 1H), 6.72 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 3.84 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.1 (C), 143.4 (C), 138.5 (C), 134.9 (C), 127.7 (CH), 126.6 (CH), 126.0 (C), 125.8 (CH), 124.9 (CH), 122.5 (CH), 121.9 (CH), 120.2 (CH), 118.9 (CH), 116.5 (CH), 110.3 (CH).

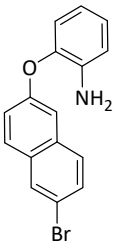
2-(Naphthalen-2-yloxy)aniline (11n)[7]



Orange solid; Mp 75-80°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.65 (d, J = 8.1 Hz, 1H), 7.46 – 7.32 (m, 2H), 7.27 (dd, J = 8.9, 2.5 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.02 (ddd, J = 7.9, 7.3, 1.4 Hz, 1H), 6.93 (dd, J = 8.0, 1.5 Hz, 1H), 6.85 (dd, J = 7.9, 1.6 Hz, 1H), 6.74 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 3.77 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.3 (C), 143.0 (C),

138.8 (C), 134.3 (C), 129.9 (C), 129.9 (CH), 127.7 (CH), 127.0 (CH), 126.5 (CH), 125.1 (CH), 124.4 (CH), 120.6 (CH), 118.9 (CH), 116.6 (CH), 111.6 (CH).

2-((6-Bromonaphthalen-2-yl)oxy)aniline (11o)



White solid; Mp 92-94°C; 1H **NMR** (300 MHz, $CDCl_3$) 7.94 (d, J = 1.7 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.47 (dd, J = 8.8, 1.8 Hz, 1H), 7.28 (dd, J = 8.9, 2.5 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.93 (dd, J = 8.1, 1.5 Hz, 1H), 6.86 (dd, J = 7.9, 1.6 Hz, 1H), 6.75 (ddd, J = 7.9, 7.3, 1.6 Hz, 1H), 3.79 (s, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.1 (C), 142.9 (C), 139.3 (C), 133.2 (C), 131.3 (C), 130.3 (CH), 130.1 (CH), 129.4 (CH), 129.1 (CH), 125.9 (CH), 121.2 (CH), 120.2 (CH), 119.3 (CH), 118.4 (C), 117.1 (CH), 111.7 (CH). **HRMS** (ESI) m/z: 314.0184 $[M + H]^+$, $C_{16}H_{13}BrNO$ requires 314.0175.

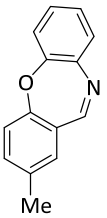
Synthesis of compounds 12

The amines of the previous step (7.5mmol, 1 eq.) was dissolved in 5mL formic acid. The mixture was heated under reflux (100 °C) for 12 h. Afterwards, the reaction mixture was cooled to room temperature and quenched with 20mL $NaHCO_3$ (sat.) solution. Followed by an extraction with dichloromethane (3x20 mL), washed with brine (20mL) and dried over $MgSO_4$. The solvent was removed and the crude product was used for the next step without purification.[9]

Synthesis and characterization of compounds 1 substituted in positions 1-4

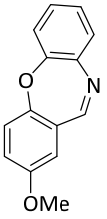
N-(2-phenoxyphenyl)formamide of the previous step (4.0 mmol, 1 eq.), polyphosphoric acid (PPA) (10.4 g) and phosphoryl chloride ($POCl_3$)(20 mmol, 5 eq.) were mixed. The mixture was stirred 3 h at 120 °C. Afterwards the mixture was cooled to room temperature, it was poured on 200mL iced water and treated with ammonia solution (33%). The mixture was extracted 3x with 100mL DCM, washed with 100mL brine and dried over $MgSO_4$. The solvent was removed by evaporation and the crude product was purified by flash chromatography, obtaining the following products.[10]

2-Methyldibenzo[*b,f*][1,4]oxazepine (1g)[9]



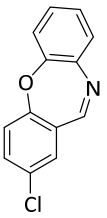
Orange solid; Mp 59-60°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.36 – 7.31 (m, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.12 (m, 1H), 7.12 – 7.07 (m, 2H), 7.01 (d, J = 8.3 Hz, 1H), 2.30 (d, J = 0.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.7 (CH), 158.3 (C), 152.8 (C), 140.5 (C), 134.7 (C), 133.9 (CH), 130.3 (CH), 129.2 (CH), 128.7 (CH), 127.0 (C), 125.5 (CH), 121.3 (CH), 120.4 (CH), 20.5 (CH_3).

2-Methoxydibenzo[*b,f*][1,4]oxazepine (1h)[9]



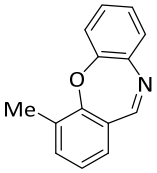
Orange solid; Mp 75-76°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.34 (dd, J = 7.2, 2.3 Hz, 1H), 7.24 – 7.12 (m, 2H), 7.11 – 7.08 (m, 1H), 7.06 (d, J = 8.9 Hz, 1H), 6.95 (dd, J = 8.8, 3.0 Hz, 1H), 6.80 (d, J = 3.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.2 (CH), 156.7 (C), 154.1 (C), 152.9 (C), 140.4 (C), 129.1 (CH), 128.8 (CH), 127.7 (C), 125.6 (CH), 121.5 (CH), 121.2 (CH), 118.9 (CH), 113.9 (CH), 55.8 (CH_3).

2-Chlorodibenzo[*b,f*][1,4]oxazepine (1i)



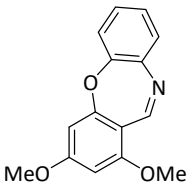
Yellow solid; Mp 98-100°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.43 – 7.30 (m, 2H), 7.29 (d, J = 2.6 Hz, 1H), 7.26 – 7.15 (m, 2H), 7.11 – 7.05 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.9 (CH), 154.4 (C), 152.4 (C), 140.2 (C), 133.0 (CH), 130.5 (C), 129.6 (CH), 129.4 (CH), 129.1 (CH), 128.4 (C), 126.0 (CH), 122.2 (CH), 121.3 (CH). **HRMS** (ESI) m/z: 230.0365 $[M + H]^+$, $C_{13}H_9ClNO$ requires 230.0367.

4-Methyldibenzo[*b,f*][1,4]oxazepine (1j)[9]



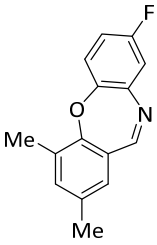
Orange oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.38 – 7.34 (m, 1H), 7.31 (ddd, J = 7.4, 1.8, 0.8 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.18 – 7.13 (m, 3H), 7.07 (t, J = 7.5 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.0 (CH), 158.3 (C), 152.6 (C), 140.8 (C), 134.6 (CH), 130.2 (C), 129.1 (CH), 128.5 (CH), 127.7 (CH), 127.3 (C), 125.6 (CH), 124.6 (CH), 121.6 (CH), 16.1 (CH_3).

1,3-Dimethoxydibenzo[*b,f*][1,4]oxazepine (1k)



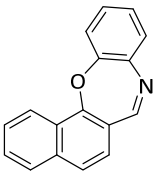
Yellow solid; Mp 102-105C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.31 – 7.26 (m, 1H), 7.18 – 7.11 (m, 2H), 7.08 – 7.01 (m, 1H), 6.27 (dd, J = 2.3, 0.6 Hz, 1H), 6.21 (d, J = 2.3 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.8 (C), 164.0 (C), 160.2 (C), 157.2 (CH), 152.6 (C), 141.6 (C), 128.5 (CH), 127.8 (CH), 125.7 (CH), 121.2 (CH), 109.8 (C), 97.3 (CH), 95.1 (CH), 55.9 (CH_3), 55.7 (CH_3). **HRMS** (ESI) m/z: 256.0972 $[M + H]^+$, $C_{15}H_{14}NO_3$ requires 256.0968.

8-Fluoro-2,4-dimethyldibenzo[*b,f*][1,4]oxazepine (1l)



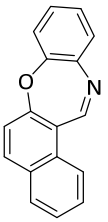
Yellow solid; Mp 73-76°C; yellow solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.13 (dt, J = 2.3, 0.7 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.96 (d, J = 2.1 Hz, 1H), 6.88 (ddd, J = 8.9, 7.6, 3.1 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.2 (C), 159.7 (d, J = 243.2 Hz, CF), 156.2 (C), 148.9 (d, J = 2.7 Hz, C), 141.8 (d, J = 10.8 Hz, C), 135.6 (CH), 134.4 (C), 129.6 (C), 128.0 (CH), 126.8 (C), 122.0 (d, J = 9.4 Hz, CH), 115.2 (d, J = 24.1 Hz, CH), 114.6 (d, J = 23.3 Hz, CH) 20.5 (CH_3), 16.0 (CH_3). **^{19}F NMR**(282 MHz, $CDCl_3$) δ -118.31. **HRMS** (ESI) m/z: 242.0971 $[M + H]^+$, $C_{15}H_{13}FNO$ requires 242.0976.

Benzo[*b*]naphtho[2,1-*f*][1,4]oxazepine (1m)



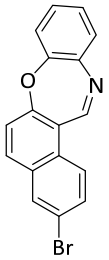
Yellow solid; Mp 90-92°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.59 – 8.54 (m, 1H), 7.85 (dd, J = 7.1, 2.4 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.46 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.18 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.3 (CH), 156.5 (C), 152.7 (C), 141.1 (C), 136.2 (C), 129.1 (CH), 129.0 (CH), 128.3 (CH), 127.8 (CH), 127.1 (CH), 126.5 (C), 125.8 (CH), 125.1 (CH), 124.8 (CH), 123.1 (CH), 122.0 (C), 121.4 (CH). **HRMS** (ESI) m/z: 246.0921 $[M + H]^+$, $C_{17}H_{12}NO$ requires 246.0913.

Benzo[*b*]naphtho[1,2-*f*][1,4]oxazepine (1n)



Orange solid; Mp 124-127°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.10 (dd, J = 8.5, 0.9 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.58 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 7.47 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.30 (d, J = 8.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.0 (C), 159.1 (CH), 153.2 (C), 141.5 (C), 134.2 (CH), 131.6 (C), 131.0 (C), 128.7 (CH), 128.4 (CH), 128.1 (CH), 125.8 (CH), 125.7 (CH), 122.7 (CH), 121.1 (CH), 120.3 (CH), 120.0 (C). **HRMS** (ESI) m/z: 246.0912 $[M + H]^+$, $C_{17}H_{12}NO$ requires 246.0913.

3-Bromobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepine (1o)



Yellow solid; Mp 170-173°C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.01 – 7.93 (m, 2H), 7.83 (d, J = 8.8 Hz, 1H), 7.65 (dd, J = 8.9, 2.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.23 – 7.10 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.1 (C), 158.3 (CH), 153.0 (C), 141.3 (C), 133.1 (CH), 132.1 (C), 131.3 (CH), 130.6 (CH), 130.1 (C), 128.6 (CH), 128.2 (CH), 126.0 (CH), 124.4 (CH), 121.6 (CH), 121.1 (CH), 120.2 (C), 119.7 (C). **HRMS** (ESI) m/z: 324.0023 [M + H]$^+$, $C_{17}H_{11}BrNO$ requires 324.0019.

Typical procedures and characterization data for compounds 3 and 5

General procedure for the enantioselective Reformatsky reaction: A two-neck 50 mL round bottom flask (one neck covered with a septum, the other neck with a drying finger, filled with $CaCl_2$), was flushed with nitrogen for 5 min. The ligand (*S*)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (0.02/0.01 mmol) was added to the flask and dissolved in 5 mL of EtOAc. Ethyl iodoacetate (0.3 mmol, 3 eq.) was added and the mixture was stirred at 0 °C. After 10 min dimethyl zinc solution (1.2 M in toluene) (0.7 mmol, 7 eq.) was added and immediately afterwards a dibenzo[*b*,*f*][1,4]oxazepine **1** (0.1 mmol, 1 eq.) solution in 1 mL EtOAc was added. The mixture was stirred for 60 min at 0°C and quenched with 10 mL saturated aqueous NH_4Cl solution. The mixture was extracted with DCM (3x20 mL), washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed; the crude product was put on silica gel and purified by flash chromatography, obtaining product **3**.

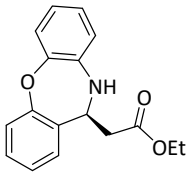
General procedure for the racemic Reformatsky reaction: A two-neck 50 mL round bottom flask (one neck covered with a septum, the other neck with a drying finger, filled with $CaCl_2$), was flushed with nitrogen for 5 min. EtOAc was added to the flask (5 mL). Ethyl iodoacetate (0.2 mmol, 2 eq.) was added. After 5 min of stirring the dimethyl zinc solution (1.2 M in toluene) (0.7 mmol, 7eq.) was added and immediately afterwards dibenzo[*b*,*f*][1,4]oxazepine **1**(0.1 mmol, 1 eq.) dissolved in 1 mL EtOAc. The mixture was stirred for 60 min at rt. After the reaction was stopped with 10 mL saturated aqueous NH_4Cl, the mixture was extracted DCM (3x20 mL), washed with brine (20 mL) and dried over $MgSO_4$.

Procedure for the enantioselective Reformatsky reaction at 0.5 mmol scale: A three-neck 100 mL round bottom flask (one neck covered with a septum, the others necks with a drying fingers, filled with $CaCl_2$), was flushed with nitrogen for 5 min. The ligand (*S*)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (0.05 mmol, 0.0155 g) was added to the flask and dissolved in 25 mL of EtOAc. Ethyl iodoacetate (1.5 mmol, 3 eq.) was added and the mixture was stirred at 0 °C. After 10 min dimethyl zinc solution (1.2 M in toluene) (3.5 mmol, 7 eq.) was added and immediately afterwards a dibenzo[*b*,*f*][1,4]oxazepine 1 (0.5 mmol, 0.0975 g, 1 eq.) solution in 5 mL EtOAc was added. The mixture was stirred for 60 min at 0°C and quenched with 10 mL saturated aqueous NH_4Cl solution. The mixture was extracted with DCM (3x50 mL), washed with brine (50 mL) and dried over $MgSO_4$. The solvent was removed; the crude product was put on silica gel and purified by flash chromatography, obtaining product **3a** (0.134 g, 95% yield, 93:7 er).

Procedure for the enantioselective Reformatsky reaction at 2 mmol scale: A three-neck 500 mL round bottom flask (one neck covered with a septum, the others necks with a drying fingers, filled with $CaCl_2$), was flushed with nitrogen for 5 min. The ligand (*S*)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (0.205 mmol, 0.0635 g) was added to the flask and dissolved in 100 mL of EtOAc. Ethyl iodoacetate (6.15 mmol, 3 eq.) was added and the mixture was stirred at 0 °C. After 10 min dimethyl zinc solution (1.2 M in toluene) (14.35 mmol, 7 eq.) was added and immediately afterwards a dibenzo[*b*,*f*][1,4]oxazepine 1 (2.05 mmol, 0.400 g, 1 eq.) solution in 20 mL EtOAc was added. The mixture was stirred for 120 min at 0°C and quenched with 100 mL saturated aqueous NH_4Cl solution. The mixture was extracted with DCM (3x150 mL), washed with brine (150 mL) and dried over $MgSO_4$.

The solvent was removed; the crude product was put on silica gel and purified by flash chromatography, obtaining product **3a** (0.5004 g, 89% yield, 85:15 er).

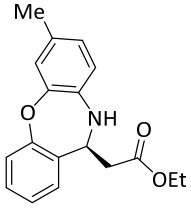
Ethyl (S)-2-(10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3a)



Enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 16.7 min, minor enantiomer t_r = 20.3 min.

Yellow oil; $[\alpha]_D^{20}$ -59.2 (c 0.5, $CHCl_3$, 86% ee); **^{1}H NMR (300 MHz, CDCl3)** δ 7.29 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 7.11 – 7.00 (m, 2H), 6.85 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 6.67 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 6.56 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.76 (dd, *J* = 10.0, 4.3 Hz, 1H), 4.47 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.32 (dd, *J* = 16.6, 10.0 Hz, 1H), 2.86 (dd, *J* = 16.6, 4.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.1 (C), 157.1 (C), 143.9 (C), 137.0 (C), 132.2 (C), 129.3 (CH), 127.8 (CH), 124.6 (CH), 124.3 (CH), 121.8 (CH), 121.2 (CH), 119.2 (CH), 118.9 (CH), 60.7 (CH_2), 54.7 (CH), 40.1 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 284,1281 $[M + H]^+$, $C_{17}H_{18}NO_3$ requires 284,1281.

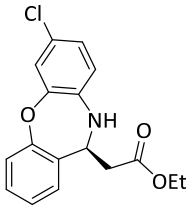
Ethyl (S)-2-(7-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3b)



Enantiomeric excess (79%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 18.9 min, minor enantiomer t_r = 21.8 min.

Yellow oil; $[\alpha]_D^{20}$ = -10.2 (c 1.0, $CHCl_3$, 79% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 1H), 7.16 – 7.10 (m, 2H), 7.07 – 7.00 (m, 1H), 6.91 (dd, J = 2.1, 0.8 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.49 (d, J = 8.0 Hz, 1H), 4.74 (dd, J = 10.0, 4.2 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.27 (dd, J = 16.6, 10.0 Hz, 1H), 2.83 (dd, J = 16.6, 4.2 Hz, 1H), 2.21 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl3) δ 172.1 (C), 157.0 (C), 144.1 (C), 134.2 (C), 132.0 (C), 129.3 (C), 129.2 (CH), 127.9 (CH), 125.1 (CH), 124.1 (CH), 122.1 (CH), 121.2 (CH), 119.2 (CH), 60.7 (CH_2), 54.9 (CH), 39.9 (CH_2), 20.2 (CH_3), 14.1 (CH_3). **HRMS** (ESI) m/z: 298.1437 $[M + H]^+$, $C_{18}H_{20}NO_3$ requires 298.1438.

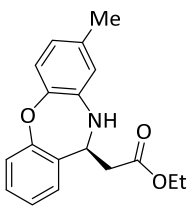
Ethyl (S)-2-(7-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3c)



Enantimeric excess (79%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 16.4 min, minor enantiomer t_r = 23.0 min.

Yellow oil; $[\alpha]_D^{20}$ = -7.6 (c 0.33, $CHCl_3$, 79% ee); **^{1}H NMR** (300 MHz, CDCl3) δ 7.32 – 7.20 (m, 1H), 7.15 (d, J = 1.1 Hz, 1H), 7.13 (d, J = 1.9 Hz, 1H), 7.13 – 7.05 (m, 1H), 7.11 – 7.03 (m, 1H), 6.81 (dd, J = 8.5, 2.4 Hz, 1H), 6.48 (d, J = 8.6 Hz, 1H), 4.74 (dd, J = 10.1, 4.1 Hz, 1H), 4.49 (s, 1H), 4.13 (q, J = 7.3 Hz, 2H), 3.30 (dd, J = 16.7, 10.1 Hz, 1H), 2.83 (dd, J = 16.6, 4.1 Hz, 1H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.0 (C), 156.7 (C), 143.9 (C), 135.8 (C), 131.9 (C), 129.5 (CH), 127.8 (CH), 124.7 (CH), 124.5 (CH), 123.0 (C), 121.8 (CH), 121.2 (CH), 119.5 (CH), 60.8 (CH_2), 54.5 (CH), 39.9 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 218.0891 $[M + H]^+$, $C_{17}H_{17}ClNO_3$ requires 218.0891.

Ethyl (S)-2-(8-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3d)

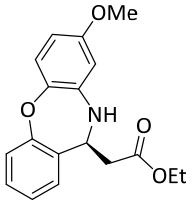


Enantiomeric excess (89%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 15.4 min, minor enantiomer t_r = 17.0 min.

Yellow oil; $[\alpha]_D^{20}$ = -38.3 (c 1.0, $CHCl_3$, 89% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 1H), 7.13 (dt, J = 7.5, 1.4 Hz, 2H), 7.03 (td, J = 7.4, 1.4 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.50 – 6.44 (m, 1H), 6.37 (dd, J = 2.0, 0.9 Hz, 1H), 4.74 (d, J = 9.6 Hz, 1H), 4.41 (s, 1H), 4.13

(q, J = 7.1 Hz, 2H), 3.32 (dd, J = 16.6, 10.0 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.16 (d, J = 0.7 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.1 (C), 157.3 (C), 142.0 (C), 136.6 (C), 134.2 (C), 132.2 (C), 129.3 (CH), 127.8 (CH), 124.2 (CH), 121.5 (CH), 121.2 (CH), 119.9 (CH), 119.3 (CH), 60.7 (CH_2), 54.7 (CH), 40.1 (CH_2), 20.6 (CH_3), 14.1 (CH_3). **HRMS** (ESI) m/z: 298.1436 $[M + H]^+$, $C_{18}H_{20}NO_3$ requires 298.1438.

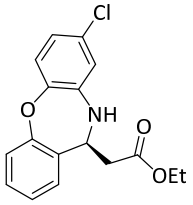
Ethyl (S)-2-(8-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3e)



Enantiomeric excess (94%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 28.5 min, minor enantiomer t_r = 34.2 min.

Yellow oil; $[\alpha]_D^{20}$ = -41.6 (c 1.0, $CHCl_3$, 94% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 1H), 7.13 (dd, J = 7.8, 1.6 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.99 (d, J = 8.7 Hz, 1H), 6.21 (dd, J = 8.7, 2.9 Hz, 1H), 6.09 (d, J = 2.9 Hz, 1H), 4.76 (dd, J = 10.0, 4.2 Hz, 1H), 4.49 (s, 1H), 4.22 – 4.07 (m, 2H), 3.68 (s, 2H), 3.35 (dd, J = 16.6, 10.0 Hz, 1H), 2.91 – 2.79 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.1 (C), 157.5 (C), 156.6 (C), 138.3 (C), 137.8 (C), 132.2 (C), 129.4 (CH), 127.8 (CH), 124.4 (CH), 122.3 (CH), 121.1 (CH), 104.3 (CH), 103.6 (CH), 60.7 (CH_2), 55.4 (CH_3), 54.5 (CH), 40.2 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 314.1379 $[M + H]^+$, $C_{18}H_{20}NO_4$ requires 314.1387.

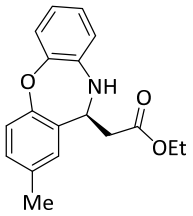
Ethyl (S)-2-(8-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3f)



Enantiomeric excess (85%) was determined by chiral HPLC (Chiralpak AD-H), hexane-^{i}PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 16.6 min, minor enantiomer t_r = 19.4 min.

Yellow oil; $[\alpha]_D^{20}$ = -44.1 (c 0.5, $CHCl_3$, 85% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.15 (t, J = 1.9 Hz, 1H), 7.13 (dd, J = 2.6, 1.6 Hz, 1H), 7.11 – 7.03 (m, 1H), 6.98 (d, J = 8.5 Hz, 1H), 6.59 (dd, J = 8.5, 2.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 4.74 (ddd, J = 9.8, 5.3, 4.1 Hz, 1H), 4.54 (d, J = 5.4 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.33 (dd, J = 16.7, 10.1 Hz, 1H), 2.84 (dd, J = 16.6, 4.2 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.9 (C), 156.9 (C), 142.3 (C), 138.2 (C), 132.0 (C), 129.6 (CH), 129.5 (C), 127.8 (CH), 124.7 (CH), 122.9 (CH), 121.2 (CH), 118.6 (CH), 117.9 (CH), 60.8 (CH_2), 54.4 (CH), 40.1 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 218.0885 $[M + H]^+$, $C_{17}H_{17}ClNO_3$ requires 218.0891.

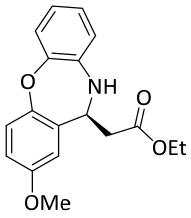
Ethyl (*S*)-2-(2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3g)



Enantiomeric excess (87%) was determined by chiral HPLC (Chiralpak IC), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 10.6 min, minor enantiomer t_r = 12.6 min.

Yellow oil; $[\alpha]_D^{20}$ = -50.7 (c 1.0, $CHCl_3$, 87% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.08 – 7.01 (m, 3H), 6.94 (s, 1H), 6.83 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 6.66 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 6.55 (dd, J = 7.9, 1.6 Hz, 1H), 4.70 (dd, J = 10.1, 4.1 Hz, 1H), 4.45 (s, 1H), 4.13 (q, J = 6.9 Hz, 2H), 3.33 (dd, J = 16.6, 10.0 Hz, 1H), 2.84 (dd, J = 16.6, 4.1 Hz, 1H), 2.27 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2 (C), 155.0 (C), 144.1 (C), 137.1 (C), 133.9 (C), 131.8 (C), 129.7 (CH), 128.3 (CH), 124.5 (CH), 121.7 (CH), 120.9 (CH), 119.1 (CH), 118.9 (CH), 60.7 (CH_2), 54.7 (CH), 40.1 (CH_2), 20.7 (CH_3), 14.1 (CH_3). **HRMS** (ESI) m/z: 298.1433 $[M + H]^+$, $C_{18}H_{20}NO_3$ requires 298.1438.

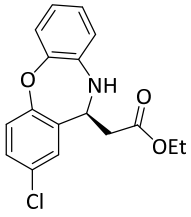
Ethyl (*S*)-2-(2-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3h)



Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak IC), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 20.7 min, minor enantiomer t_r = 26.6 min.

Beige oil, $[\alpha]_D^{20}$ = -34.7 (c 1.0, $CHCl_3$, 88% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.10 – 7.03 (m, 2H), 6.83 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 6.74 (dd, J = 8.7, 3.1 Hz, 1H), 6.70 – 6.61 (m, 2H), 6.54 (dd, J = 8.0, 1.6 Hz, 1H), 4.71 (dd, J = 10.0, 4.1 Hz, 1H), 4.45 (s, 1H), 4.13 (qd, J = 7.1, 0.7 Hz, 2H), 3.74 (s, 3H), 3.35 (dd, J = 16.6, 10.0 Hz, 1H), 2.86 (dd, J = 16.6, 4.2 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.1 (C), 156.0 (C), 151.0 (C), 144.1 (C), 137.1 (C), 133.1 (C), 124.6 (CH), 122.0 (CH), 121.6 (CH), 119.0 (CH), 118.8 (CH), 113.8 (CH), 113.1 (CH), 60.7 (CH_2), 55.7 (CH_3), 54.6 (CH), 40.0 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 314.1386 $[M + H]^+$, $C_{18}H_{20}NO_4$ requires 314.1387.

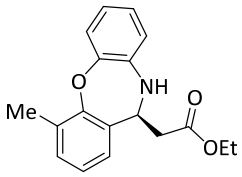
Ethyl (*S*)-2-(2-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3i)



Enantiomeric excess (84%) was determined by chiral HPLC (Chiralpak AD-H), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 14.3 min, minor enantiomer t_r = 24.7 min.

Yellow oil; $[\alpha]_D^{20}$ = -32.2 (c 1.0, $CHCl_3$, 84% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 (dd, J = 8.5, 2.6 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 7.05 (dd, J = 8.0, 1.6 Hz, 1H), 6.86 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 6.69 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 6.56 (dd, J = 7.9, 1.6 Hz, 1H), 4.72 (dd, J = 9.8, 4.3 Hz, 1H), 4.45 (s, 1H), 4.14 (qd, J = 7.1, 0.7 Hz, 2H), 3.27 (dd, J = 16.6, 9.8 Hz, 1H), 2.84 (dd, J = 16.6, 4.3 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.7 (C), 155.6 (C), 143.7 (C), 136.7 (C), 133.7 (C), 129.1 (CH), 127.7 (CH), 124.9 (CH), 122.7 (CH), 121.7 (CH), 119.6 (CH), 119.1 (CH), 60.8 (CH_2), 54.3 (CH), 39.8 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 318.0885 $[M + H]^+$, $C_{17}H_{17}ClNO_3$ requires 318.0892.

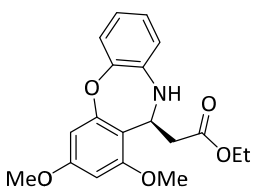
Ethyl (*S*)-2-(4-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3j)



Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak IC), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 9.9 min, minor enantiomer t_r = 8.2 min.

Yellow oil; $[\alpha]_D^{20}$= -78.2 (c 1.0, $CHCl_3$, 88% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.12 (dd, J = 2.6, 1.1 Hz, 1H), 7.11 – 7.08 (m, 1H), 7.00 – 6.96 (m, 1H), 6.97 – 6.91 (m, 1H), 6.84 (ddd, J = 8.0, 7.2, 1.5 Hz, 1H), 6.65 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.54 (dd, J = 7.9, 1.6 Hz, 1H), 4.76 (dd, J = 9.9, 4.3 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.39 (dd, J = 16.5, 9.9 Hz, 1H), 2.88 (dd, J = 16.5, 4.3 Hz, 1H), 2.40 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2 (C), 155.4 (C), 143.1 (C), 137.5 (C), 132.5 (C), 130.8 (CH), 130.6 (C), 125.2 (CH), 124.6 (CH), 124.2 (CH), 122.1 (CH), 118.7 (CH), 118.6 (CH), 60.6 (CH_2), 54.4 (CH), 40.0 (CH_2), 16.3 (CH_3), 14.1 (CH_3). **HRMS** (ESI) m/z: 298.1432 $[M + H]^+$, $C_{18}H_{20}NO_3$ requires 298.1438.

Ethyl (*S*)-2-(1,3-dimethoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3k)

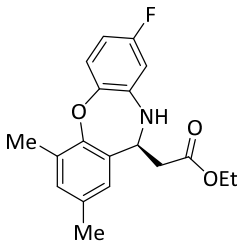


Enantiomeric excess (79%) was determined by chiral HPLC (Penomenex Lux® 5µm Amylose-1), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 42.7 min, minor enantiomer t_r = 37.8 min.

Beige oil; $[\alpha]_D^{20}$ = -26.2 (c 1.0, $CHCl_3$, 79% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.05 (dd, J = 8.0, 1.5 Hz, 1H), 6.85 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 6.68 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 6.56 (dd, J = 7.9, 1.6 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 6.20 (d, J = 2.4 Hz, 1H), 5.14 (dd, J = 10.6, 3.4 Hz, 1H), 4.53

(s, 1H), 4.12 (q, J = 7.3 Hz, 2H), 3.77 (s, 3H), 3.77 (s, 3H), 3.23 (dd, J = 16.9, 10.7 Hz, 1H), 2.66 (dd, J = 16.9, 3.4 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.6 (C), 160.3 (C), 158.3 (C), 156.7 (C), 144.3 (C), 137.5 (C), 124.7 (CH), 121.6 (CH), 119.3 (CH), 119.2 (CH), 113.0 (C), 97.8 (CH), 94.7 (CH), 60.4 (CH_2), 55.8 (CH_3), 55.4 (CH_3), 46.8 (CH), 39.8 (CH_2), 14.2 (CH_3). **HRMS** (ESI) m/z: 344.1500 $[M + H]^+$, $C_{19}H_{22}NO_5$ requires 344.1493.

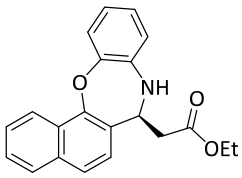
Ethyl (*S*)-2-(8-fluoro-2,4-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3l)



Enantiomeric excess (88%) was determined by chiral HPLC (Penomenex Lux® 5µm Amylose-1), hexane-*i*PrOH 80:20, 1.0 mL/min, major enantiomer t_r = 5.1 min, minor enantiomer t_r = 8.0 min.

Yellow oil; $[\alpha]_D^{20}$ = -90.8 (c 1.0, $CHCl_3$, 88% ee); **^{1}H NMR** (300 MHz, CDCl3) δ 7.01 (dd, J = 8.7, 5.6 Hz, 1H), 6.93 (dt, J = 2.3, 0.8 Hz, 1H), 6.78 (d, J = 2.1 Hz, 1H), 6.28 (ddd, J = 8.8, 7.8, 3.0 Hz, 1H), 6.21 (dd, J = 10.3, 2.9 Hz, 1H), 4.69 (dt, J = 9.4, 4.3 Hz, 1H), 4.53 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.39 (dd, J = 16.6, 10.0 Hz, 1H), 2.84 (dd, J = 16.6, 4.1 Hz, 1H), 2.34 (s, 3H), 2.23 (d, J = 0.7 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.1 (C), 159.7 (d, J = 240.1 Hz, CF), 153.3 (C), 139.3 (d, J = 2.6 Hz, C), 138.9 (d, J = 11.0 Hz, C), 133.9 (C), 131.9 (C), 131.5 (CH), 130.1 (C), 125.7 (CH), 122.8 (d, J = 10.3 Hz, CH), 104.5 (d, J = 5.6 Hz, CH), 104.2 (d, J = 9.2 Hz, CH), 60.7 (CH2), 54.1 (CH), 40.2 (CH2), 20.7 (CH3), 16.1 (CH3), 14.2 (CH3). **^{19}F NMR** (282 MHz, CDCl3) δ -119.73. **HRMS** (ESI) m/z: 330.1499 $[M + H]^+$, $C_{19}H_{20}FNO_3$ requires 330.1500.

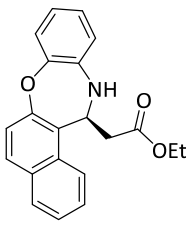
Ethyl (*S*)-2-(7,8-dihydrobenzo[*b*]naphtho[2,1-*f*][1,4]oxazepin-7-yl)acetate (3m)



Enantiomeric excess (90%) was determined by chiral HPLC (Chiralpak AD-H), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 30.5 min, minor enantiomer t_r = 36.5 min.

Orange oil; $[\alpha]_D^{20}$ = -136.1 (c 1.0, $CHCl_3$, 90% ee); **^{1}H NMR** (300 MHz, CDCl3) δ 8.50 – 8.42 (m, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.55 – 7.52 (m, 1H), 7.48 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 7.31 (dd, J = 7.9, 1.5 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 6.87 (ddd, J = 7.9, 7.3, 1.6 Hz, 1H), 6.72 (ddd, J = 7.9, 7.2, 1.6 Hz, 1H), 4.89 (dd, J = 9.9, 4.2 Hz, 1H), 4.56 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.41 (dd, J = 16.7, 10.0 Hz, 1H), 2.96 (dd, J = 16.7, 4.2 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2 (C), 152.2 (C), 144.1 (C), 137.5 (C), 134.3 (C), 127.6 (CH), 127.4 (C), 126.9 (C), 126.5 (CH), 126.4 (CH), 125.7 (CH), 124.8 (CH), 123.9 (CH), 122.1 (CH), 121.8 (CH), 119.4 (CH), 119.3 (CH), 60.7 (CH_2), 55.0 (CH), 40.3 (CH_2), 14.2 (CH_3). **HRMS** (ESI) m/z: 334.1447 $[M + H]^+$, $C_{21}H_{20}NO_3$ requires 334.1438.

Ethyl (*S*)-2-(12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3n)

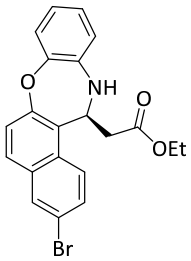


Enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak AD-H), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 18.3 min, minor enantiomer t_r = 44.2 min.

Beige oil; $[\alpha]_D^{20}$= +125.9 (c 1.0, $CHCl_3$, 91% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 1H), 7.81 (dd, J = 8.2, 1.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.53 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.41 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.14 (dd, J = 7.9, 1.5 Hz, 1H), 6.88 (ddd, J = 7.8, 7.3, 1.5 Hz, 1H), 6.72 (ddd, J = 7.9, 7.3, 1.6 Hz, 1H), 6.60 (dd, J = 7.8, 1.6 Hz, H), 5.57 (dd, J = 10.1, 3.8 Hz, 1H), 4.64 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.49 (dd, J = 17.0, 10.1 Hz, 1H), 2.89 (dd, J = 17.1, 3.9 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4 (C), 154.8 (C), 144.2 (C), 137.2 (C), 130.9 (C), 130.6 (C), 129.8 (CH), 128.8 (CH), 127.0 (CH), 124.8 (C),

124.7 (CH), 124.6 (CH), 122.2 (CH), 121.7 (CH), 121.5 (CH), 119.5 (CH), 119.0 (CH), 60.7 (CH_2), 49.2 (CH), 40.2 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 334.1439 $[M + H]^+$, $C_{21}H_{20}NO_3$ requires 334.1438.

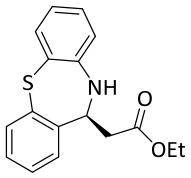
Ethyl (*S*)-2-(3-bromo-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3o)



Enantiomeric excess (92%) was determined by chiral HPLC (Penomenex Lux® 5µm Amylose-1), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 22.2 min, minor enantiomer t_r = 43.1 min.

White solid; Mp 80-82C; $[\alpha]_D^{20}$= +93.5 (c 1.0, $CHCl_3$, 92% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, J = 2.1 Hz, 1H), 7.88 (d, J = 9.5 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.58 (dd, J = 9.1, 2.1 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 7.9, 1.5 Hz, 1H), 6.89 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 6.73 (ddd, J = 7.9, 7.3, 1.7 Hz, 1H), 6.60 (dd, J = 7.9, 1.6 Hz, 1H), 5.49 (dd, J = 10.0, 4.1 Hz, 1H), 4.61 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.43 (dd, J = 17.1, 9.9 Hz, 1H), 2.88 (dd, J = 17.1, 4.0 Hz, 1H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2 (C), 154.9 (C), 144.0 (C), 137.0 (C), 132.0 (C), 130.7 (CH), 130.2 (CH), 129.2 (C), 128.8 (CH), 125.2 (C), 124.8 (CH), 124.1 (CH), 123.0 (CH), 121.5 (CH), 119.8 (CH), 119.1 (CH), 118.6 (C), 60.8 (CH_2), 49.4 (CH), 40.1 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 412.0547 $[M + H]^+$, $C_{21}H_{19}BrNO_3$ requires 412.0543.

Ethyl (*S*)-2- (10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)acetate (5)



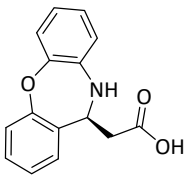
Enantiomeric excess (89%) was determined by chiral HPLC (Chiralpak AD-H), hexane-*i*PrOH 95:05, 1.0 mL/min, major enantiomer t_r = 20.6 min, minor enantiomer t_r = 19.3 min.

Clear oil; $[\alpha]_D^{20}$ = -34.8 (c=1, $CHCl_3$, 89% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.2, 1.9 Hz, 1H), 7.27 – 7.16 (m, 3H), 7.13 (dd, J = 7.0, 2.2 Hz, 1H), 6.92 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.61 (ddd, J = 7.7, 7.3, 1.4 Hz, 1H), 6.45 (dd, J = 8.1, 1.3 Hz, 1H), 5.77 (dd, J = 10.0, 4.7 Hz, 1H), 4.33 (s, 1H), 4.17 (qd, J = 7.2, 1.2 Hz, 2H), 3.21 (dd, J = 15.6, 9.9 Hz, 1H), 2.92 (dd, J = 15.6, 4.7 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.7 (C), 146.3 (C), 142.8 (C), 135.5 (C), 131.9 (CH), 131.8 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 126.2 (CH), 119.2 (CH), 118.9 (CH), 117.9 (C), 60.9 (CH_2), 54.2 (CH), 39.9 (CH_2), 14.2 (CH_3). **HRMS** (ESI) m/z: 300.1054 $[M + H]^+$, $C_{17}H_{18}NO_2S$ requires 300.1053.

<u>Typical procedures and characterization data for compounds 6-9</u>

(*S*)-2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetic acid (6)

To a solution of **3a** (0.10 mmol) in EtOH (1 mL) NaOH 1M (1 mL) is added. The dissolution was stirred at reflux temperature (73°C) for 2 hours. The reaction was quenched with HCl 2M (5 mL) and extracted with dichloromethane (3x15 mL), dried over $MgSO_4$, filtered and concentrated in vacuo, obtaining product **6**.

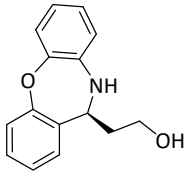


Enantiomeric excess (86%) was determined by chiral HPLC (Penomenex Lux® 5µm Amylose-1), hexane-*i*PrOH 90:10, 1mL/min, major enantiomer tr = 13.6 min, minor enantiomer tr = 20.9 min.

Brown oil; $[\alpha]_D^{20}$ = -34.1 (c 1.0, $CHCl_3$, 86% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.20 – 7.03 (m, 4H), 6.90 (td, J = 7.6, 1.4 Hz, 1H), 6.81 – 6.74 (m, 1H), 6.71 (d, J = 7.8 Hz, 1H), 4.82 (dd, J = 9.7, 3.8 Hz, 1H), 3.42 (dd, J = 17.0, 9.7 Hz, 1H), 2.96 (dd, J = 17.0, 3.8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6 (C), 157.0 (C), 144.3 (C), 136.3 (C), 131.7 (C), 129.5 (CH), 127.9 (CH), 124.8 (CH), 124.5 (CH), 121.8 (CH), 121.3 (CH), 119.9 (CH), 119.4 (CH), 54.5 (CH), 39.7 (CH2). HRMS (ESI) m/z: 256.0972 [M + H]+, $C_{15}H_{14}NO_3$ requires 256.0968.

(*S*)-2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)ethan-1-ol (7)

To a solution of **3a** (0.10 mmol) in THF (1 ml), $LiAlH_4$ (1.0 M in THF, 1.1 equivalents, 0.11 mmol) was added dropwise at 0°C over 4 min. The reaction was stirred at 0°C until completion (TLC). The mixture was diluted with EtOAc (10 ml) and acidified with aq. 2 M HCl until the aqueous layer became clear. A saturated dissolution of Rochelle salt was added (5 mL) and the mixture was stirred for 2 hours. The aqueous layer was then separated and extracted with EtOAc (2 x 15 ml). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuum. The residue was purified by flash chromatography, obtaining product **7**.



Enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak IC), hexane-*i*PrOH 90:10, 1mL/min, major enantiomer t_r = 8.2 min, minor enantiomer t_r = 19.7 min.

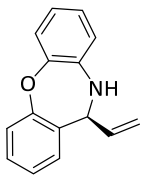
Orange oil; $[\alpha]_D^{20}$ = -6.0 (c 1.0, $CHCl_3$, 86% ee); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 1H), 7.17 (dt, *J* = 7.9, 1.6 Hz, 2H), 7.08 (ddd, *J* = 7.2, 4.0, 1.3 Hz, 2H), 6.86 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 6.68 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.68 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.90 (ddd, *J* = 11.2, 6.8, 4.5 Hz, 1H), 3.78 (ddd, *J* = 11.1, 6.8, 4.6 Hz, 1H), 2.41 (dddd, *J* = 13.8, 9.2, 7.1, 4.5 Hz, 1H), 2.24 (dddd, *J* = 13.7, 9.3, 7.0, 4.5 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.3 (C), 144.1 (C), 137.4 (C), 134,0 (C), 128.9 (CH), 127.0 (CH), 124.5 (CH), 124.4 (CH), 121.8 (CH), 121.1 (CH), 119.2 (CH), 119.0 (CH), 60.7 (CH_2), 54.8 (CH), 36.9 (CH_2). **HRMS** (ESI) m/z: 242.1174 $[M + H]^+$, $C_{15}H_{16}NO_2$ requires 242.1176.

(*S*)-11-vinyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (8)

To a solution of **3a** (0.10 mmol) in THF (1 ml), $LiAlH_4$ (1.0 M in THF, 1.1 equivalents, 0.11 mmol) was added dropwise at 0°C over 4 min. The reaction was stirred at 0°C until completion (TLC). The mixture was diluted with EtOAc (10 ml) and acidified with aq. 2 M HCl until the aqueous layer became clear. A saturated dissolution of Rochelle salt was added (5 mL) and the mixture was stirred for 2 hours. The aqueous layer was then separated and extracted with EtOAc (2 x 15 ml). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuum. The residue was purified by flash chromatography, obtaining product **7**.

To a solution of **7** in THF (1 mL), *o*-nitrophenyl selenecyanate (2.4 equivalents) and *n*-Bu_3P (2.5 equivalents) were added. The solutions was stirred 4 hours at room temperature. The solvent was removed and the crude product was used for the next step.

The crude product was dissolved in THF (1 mL) and was treated at 0ºC with 50% aqueous hydrogen peroxide (5 equivalents). The solution was, after addition of hydrogen peroxide, placed at room temperature for 2 hours. The solution was quenched with water and extracted with dichloromethane (3x15 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash chromatography, obtaining product **8**.



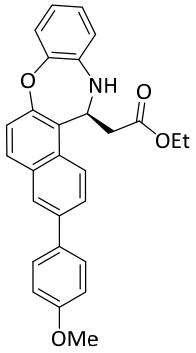
The enantiomeric excess (86%) was determined by chiral HPLC (Phenomenex Lux® 5µm Amylose 1), hexane-iPrOH 90:10, 1mL/min, major enantiomer t_r = 8.64 min, minor enantiomer t_r = 11.22 min.

Orange oil; $[\alpha]_D^{20}$ = -5.9 (c 1.0, $CHCl_3$, 86% *ee*); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.18 (ddd, *J* = 7.9, 3.2, 1.6 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.88 (ddd, *J* = 7.8, 7.4, 1.5 Hz, 1H), 6.70 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.32 (ddd, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.37 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.30 (dt, *J* = 10.3, 1.2 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 4.00 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.2 (C), 144.7 (C), 138.1 (CH), 137.6 (C), 132.8 (C), 129.1 (CH_2), 127.5

(CH), 124.5 (CH), 124.3 (CH), 121.8 (CH), 121.1 (CH), 119.5 (CH), 118.9 (CH), 116.6 (CH), 59.4 (CH). **HRMS** (ESI) m/z: 224.1063 $[M + H]^+$, $C_{15}H_{14}NO$ requires 224.1070.

Ethyl (*S*)-2-(3-(4-methoxyphenyl)-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (9)

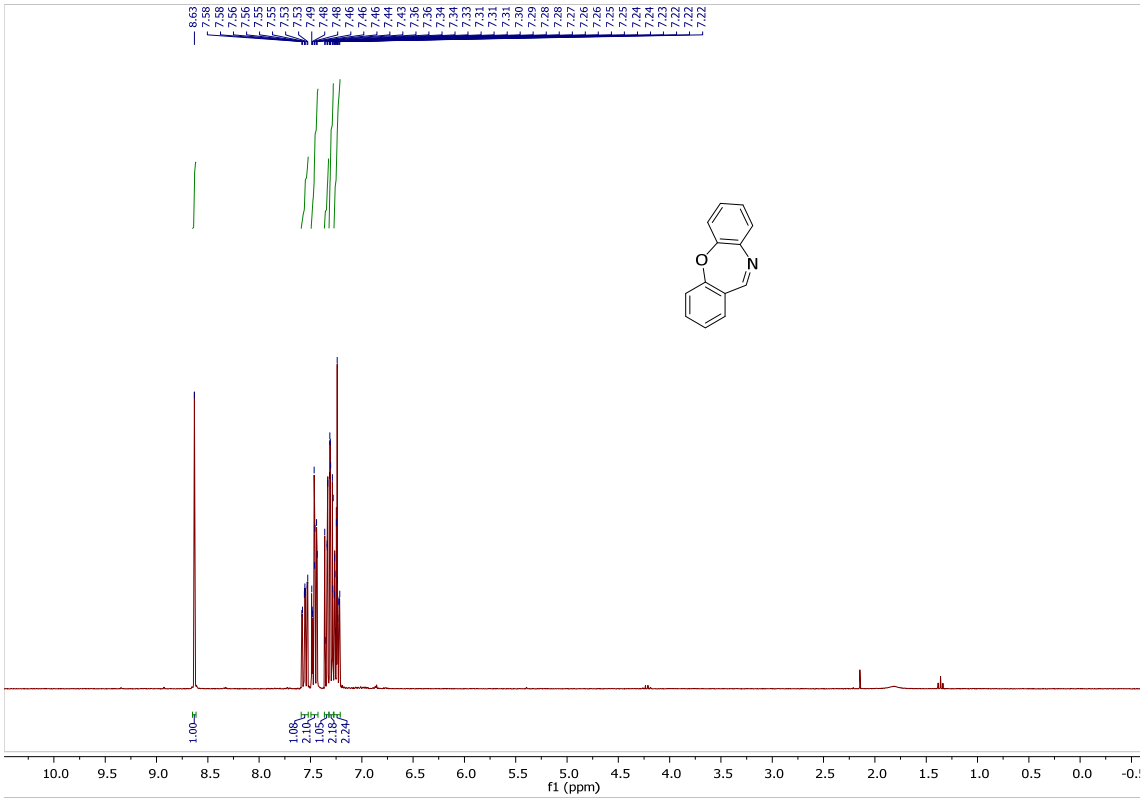
To a solution of **27a** (0.100 mmol) in DMF (2 mL), tri-potassium phosphate n-hydrate (8 equivalents) and p-methoxy-phenylboronic acid (2 equivalents) were added. This solution was bubbled with N_2 for 30 minutes and afterwards $PdCl_2(PPh)_2$ (10 mol%) was added and the reaction was placed at 100ºC for 4 hours. Afterwards, the reaction was quenched with a saturated aqueous ammonium chloride solution (10 mL) and the solution was extraced with dichloroomethane (3x15 mL). The organic phase was then washed with water (2x15 mL), dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash chromatography, obtaining product **42**.

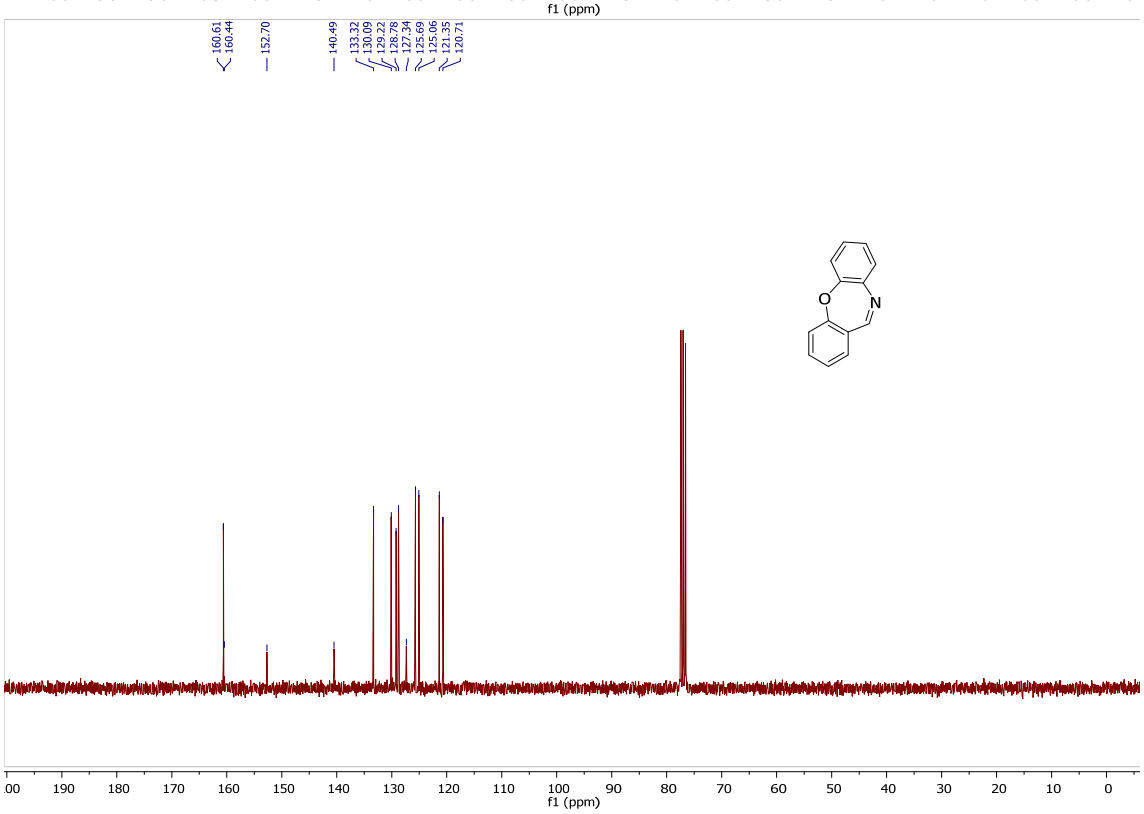


The enantiomeric excess (90%) was determined by chiral HPLC (Phenomenex Lux® 5µm Amylose 1), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 26.27 min, minor enantiomer t_r = 40.11 min.

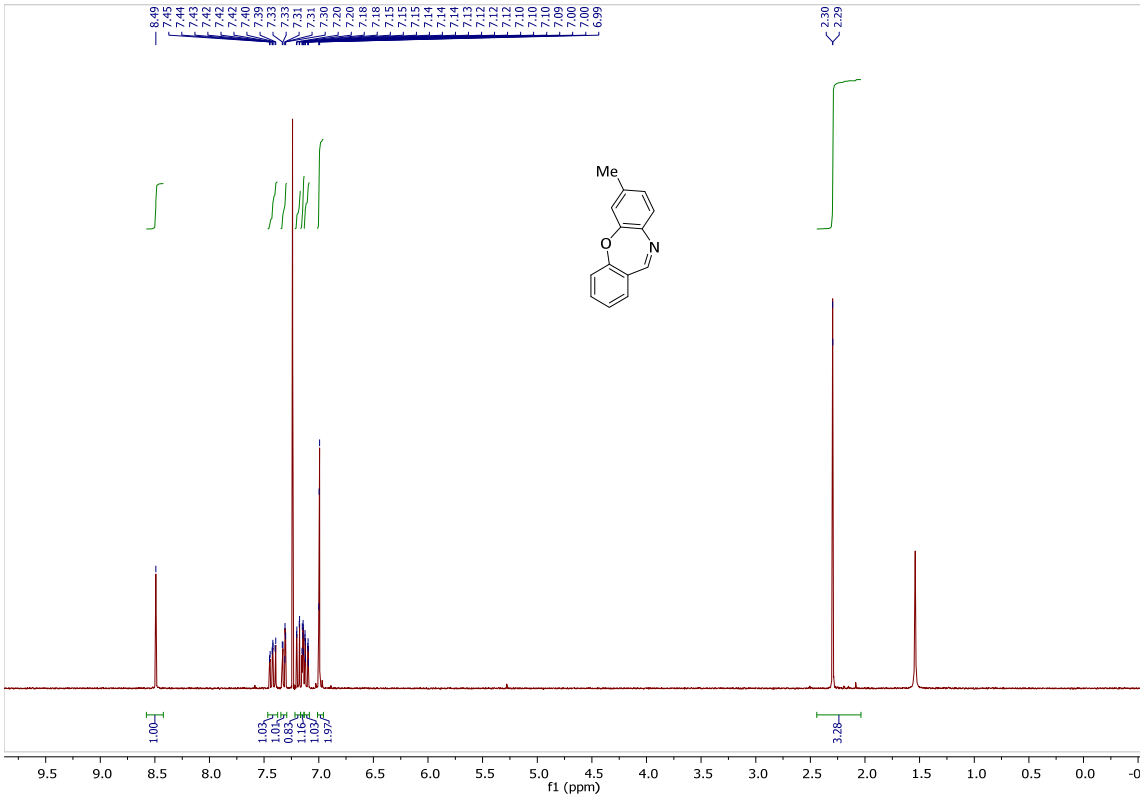
Brown oil; $[\alpha]_D^{20}$ = +57.0 (c 1.0, $CHCl_3$, 90% *ee*); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.70 – 7.62 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.91 (ddd, *J* = 7.8, 7.3, 1.5 Hz, 1H), 6.76 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.60 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.68 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.51 (dd, *J* = 17.1, 10.1 Hz, 1H), 2.94 (dd, *J* = 17.1, 3.9 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4 (C), 159.3 (C), 154.6 (C), 144.2 (C), 137.2 (C), 136.9 (C), 133.0 (C), 131.3 (C), 129.8 (CH), 129.4 (C), 128.2 (CH), 126.3 (CH), 125.8 (CH), 124.8 (C), 124.7 (CH), 122.8 (CH), 122.1 (CH), 121.5 (CH), 119.5 (CH), 119.0 (CH), 114.4 (CH), 60.7 (CH_2), 55.4 (CH), 49.4 (CH_3), 40.2 (CH_2), 14.1 (CH_3). **HRMS** (ESI) m/z: 440.1845 $[M + H]^+$, $C_{28}H_{26}NO_4$ requires 440.1856.

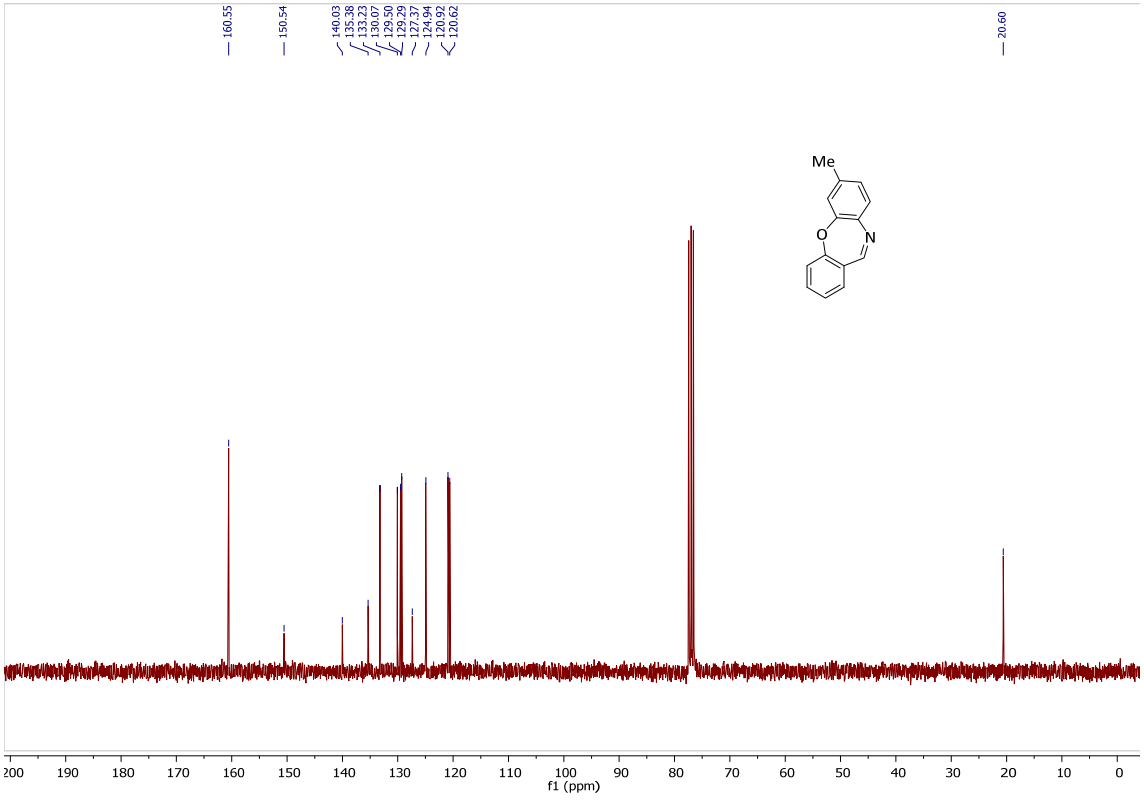
Dibenzo[*b,f*][1,4]oxazepine (1a)



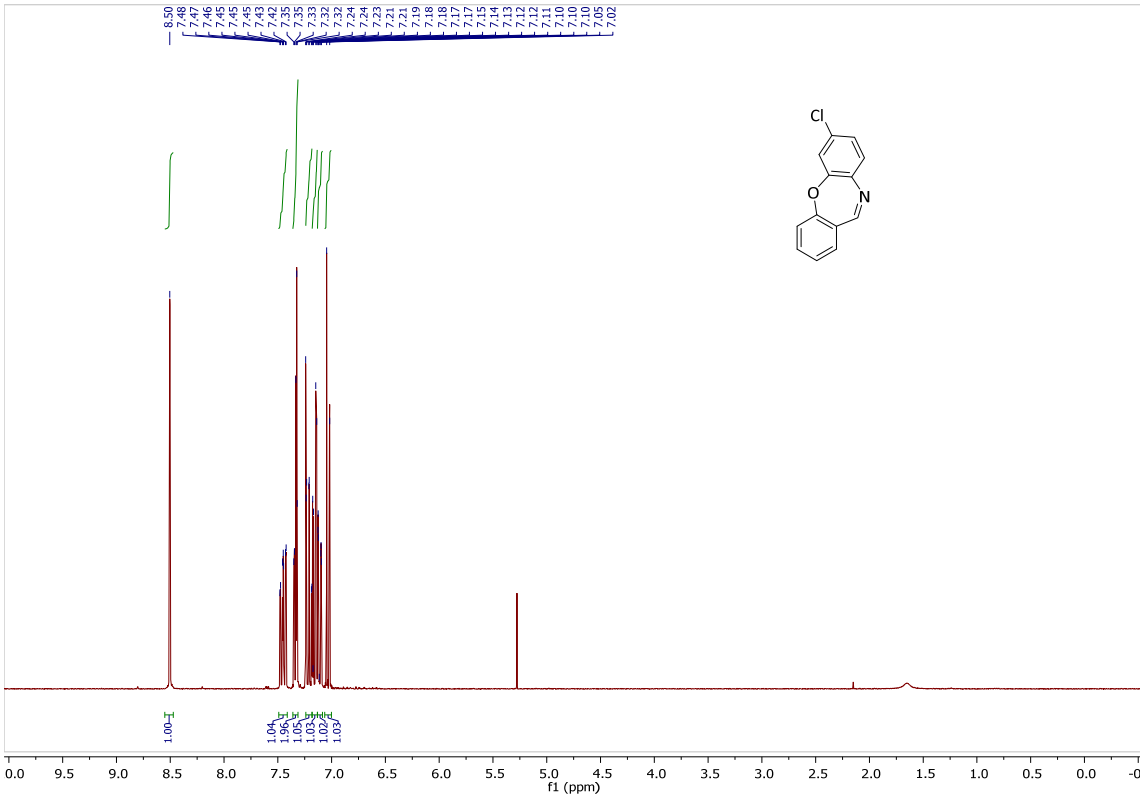


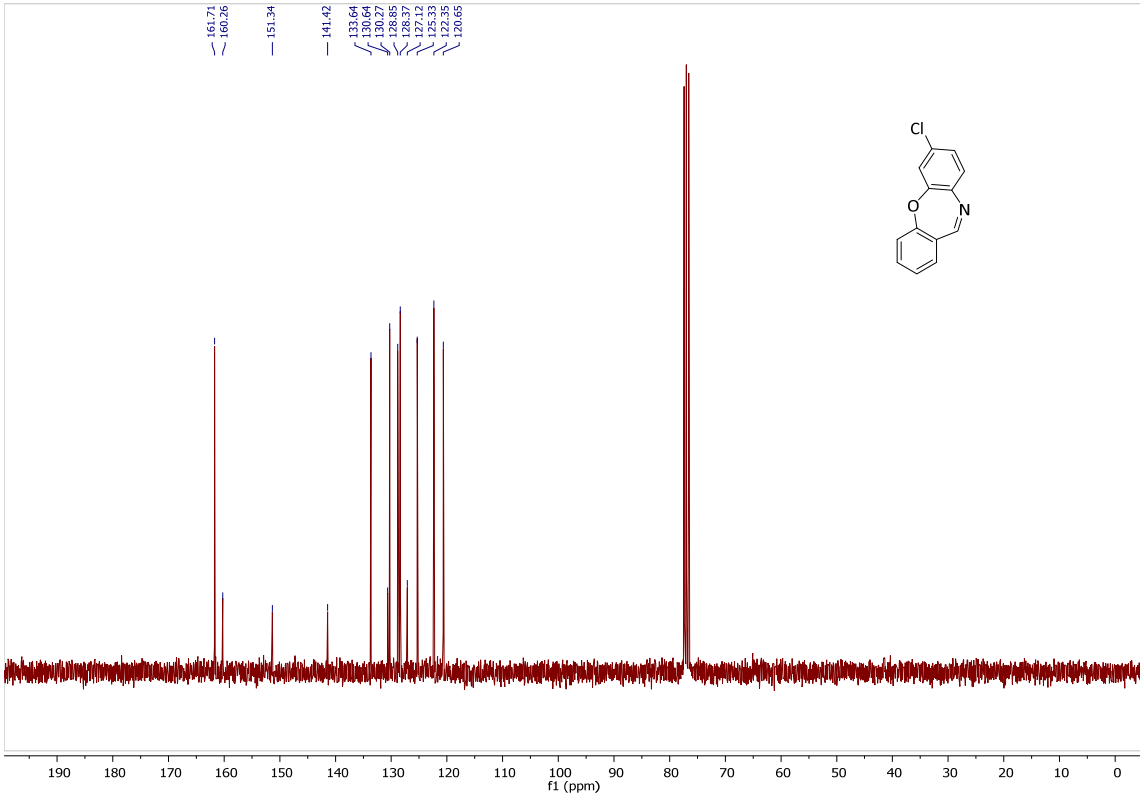
7-Methyldibenzo[*b,f*][1,4]oxazepine (1b)



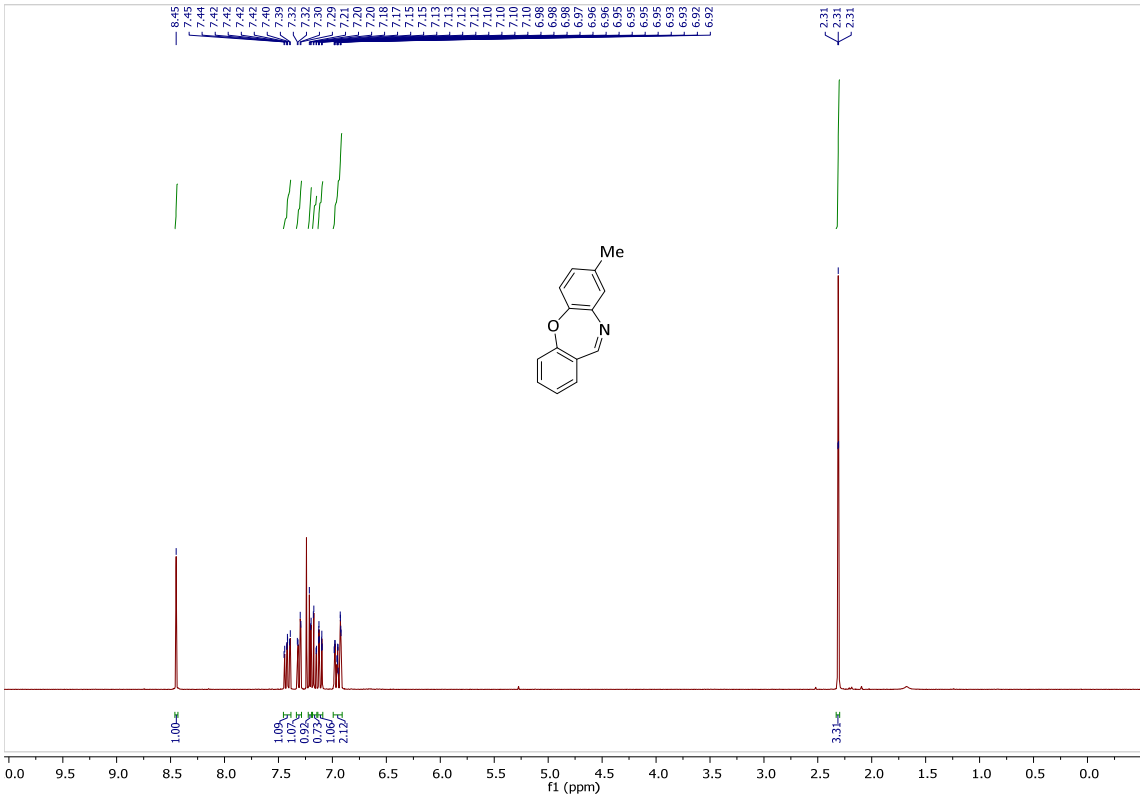


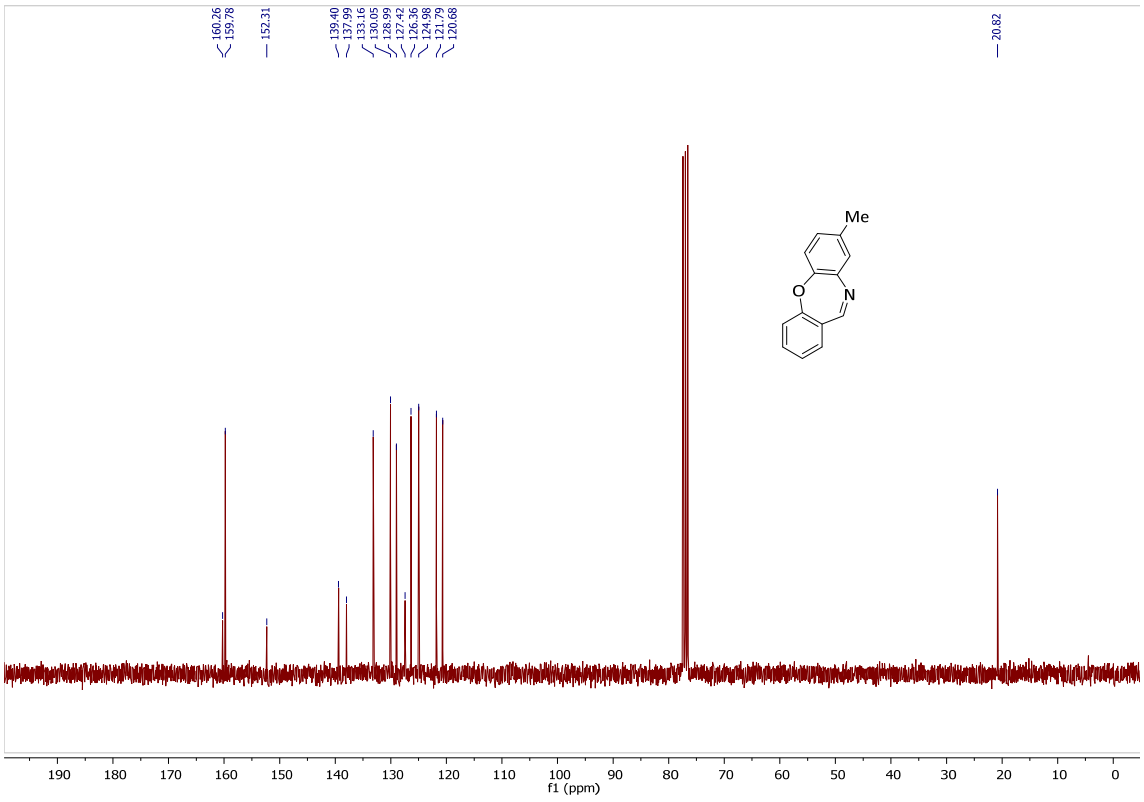
7-Chlorodibenzo[*b,f*][1,4]oxazepine (1c)



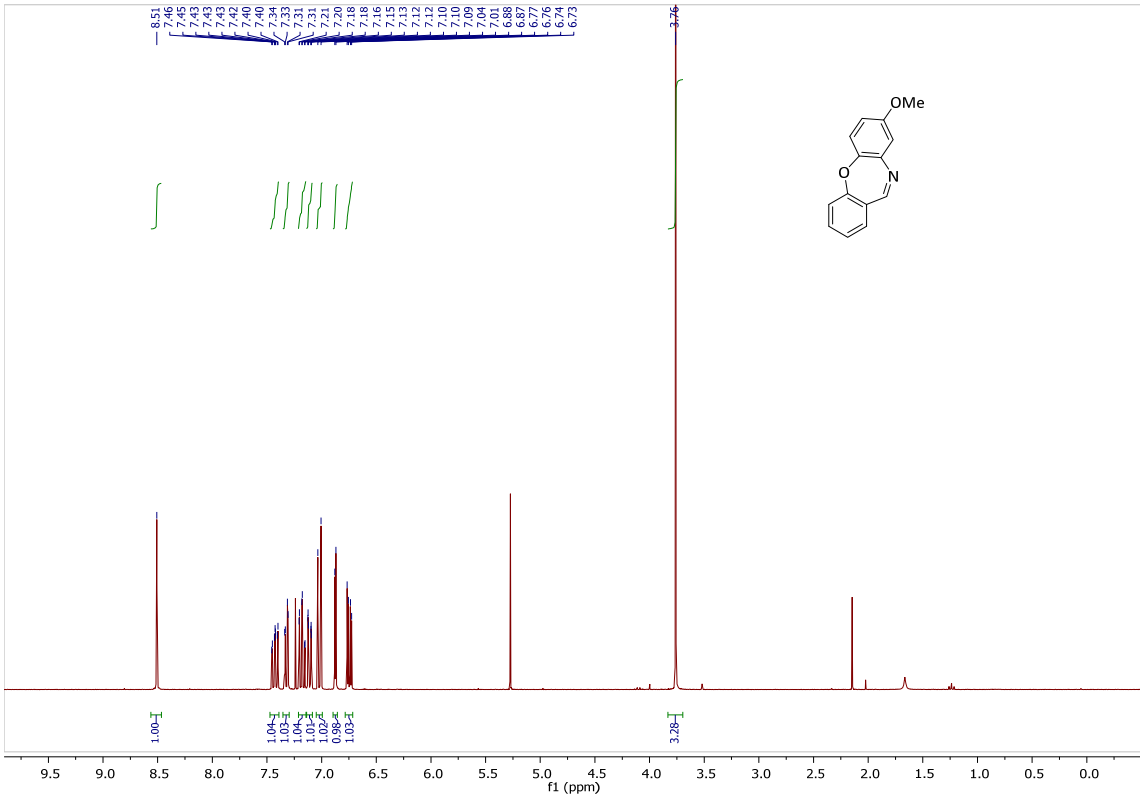


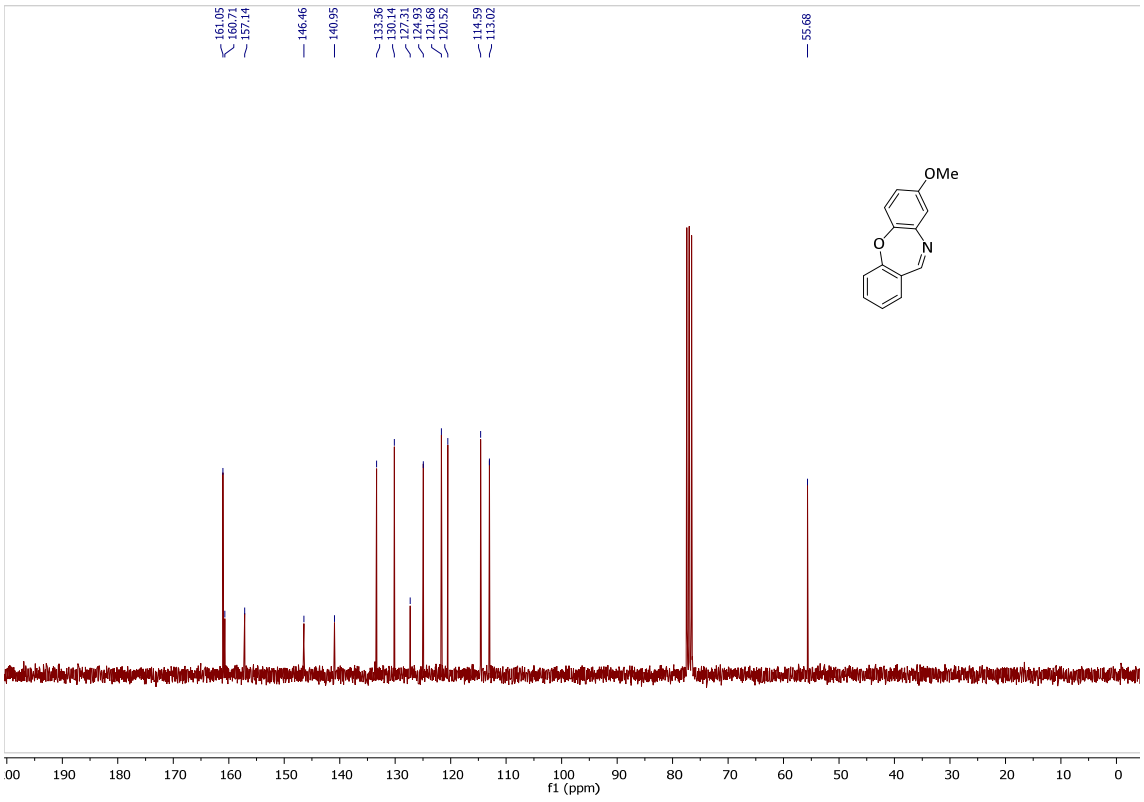
8-Methyldibenzo[*b,f*][1,4]oxazepine (1d)



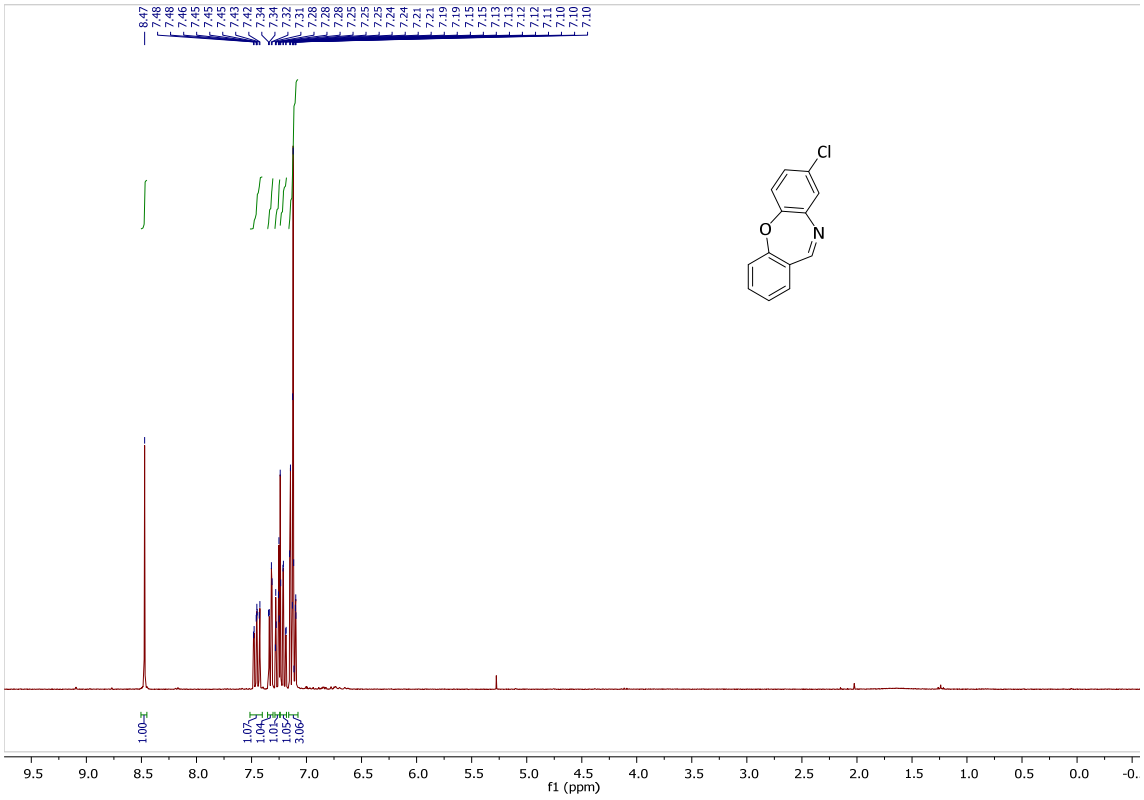


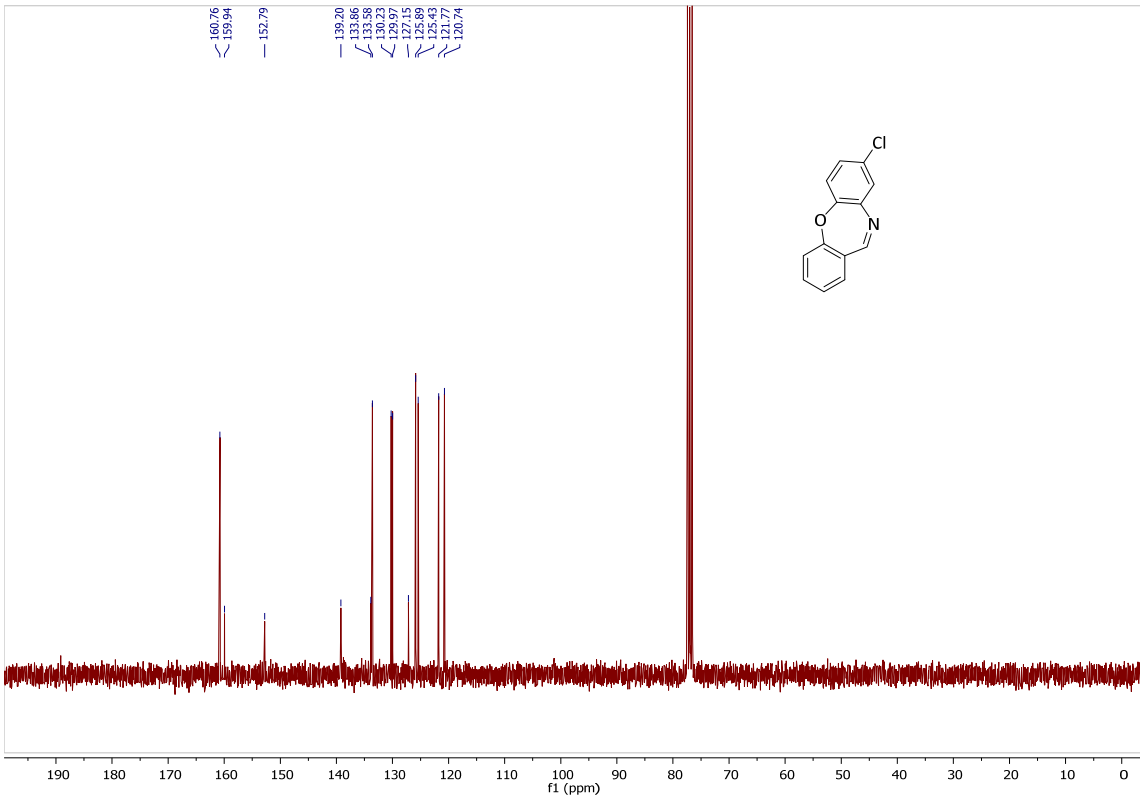
8-Methoxydibenzo[*b,f*][1,4]oxazepine (1e)



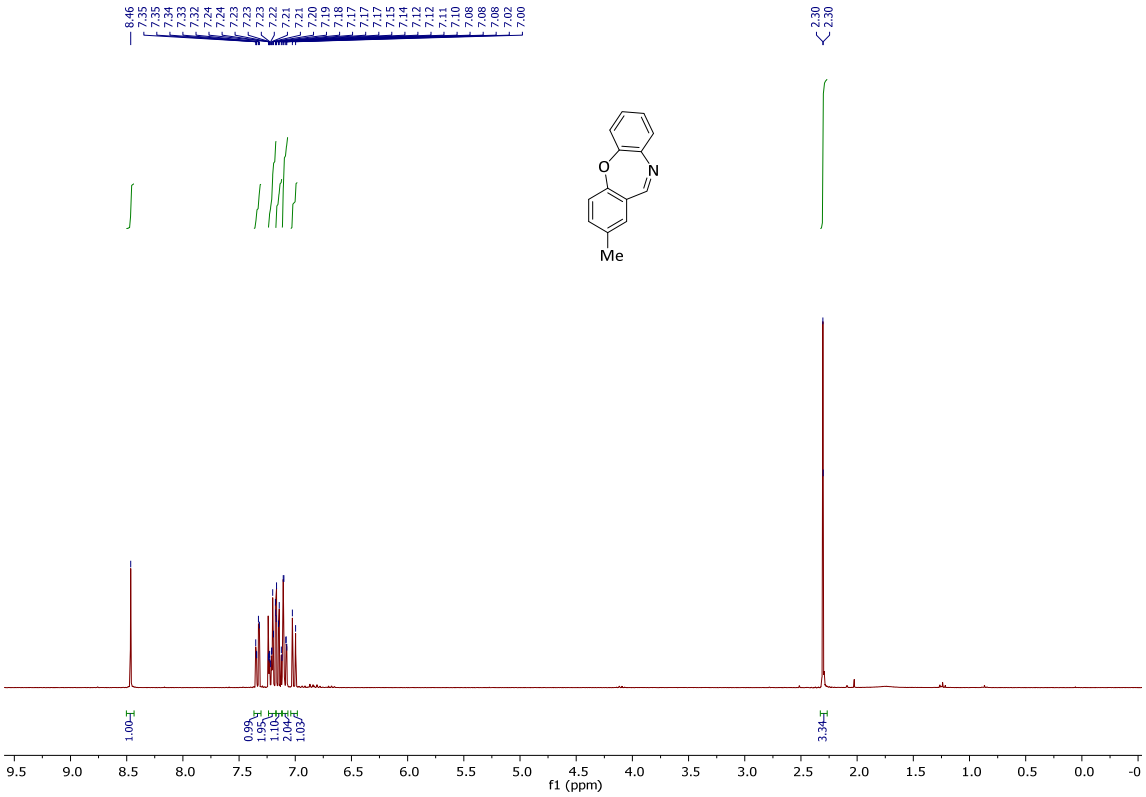


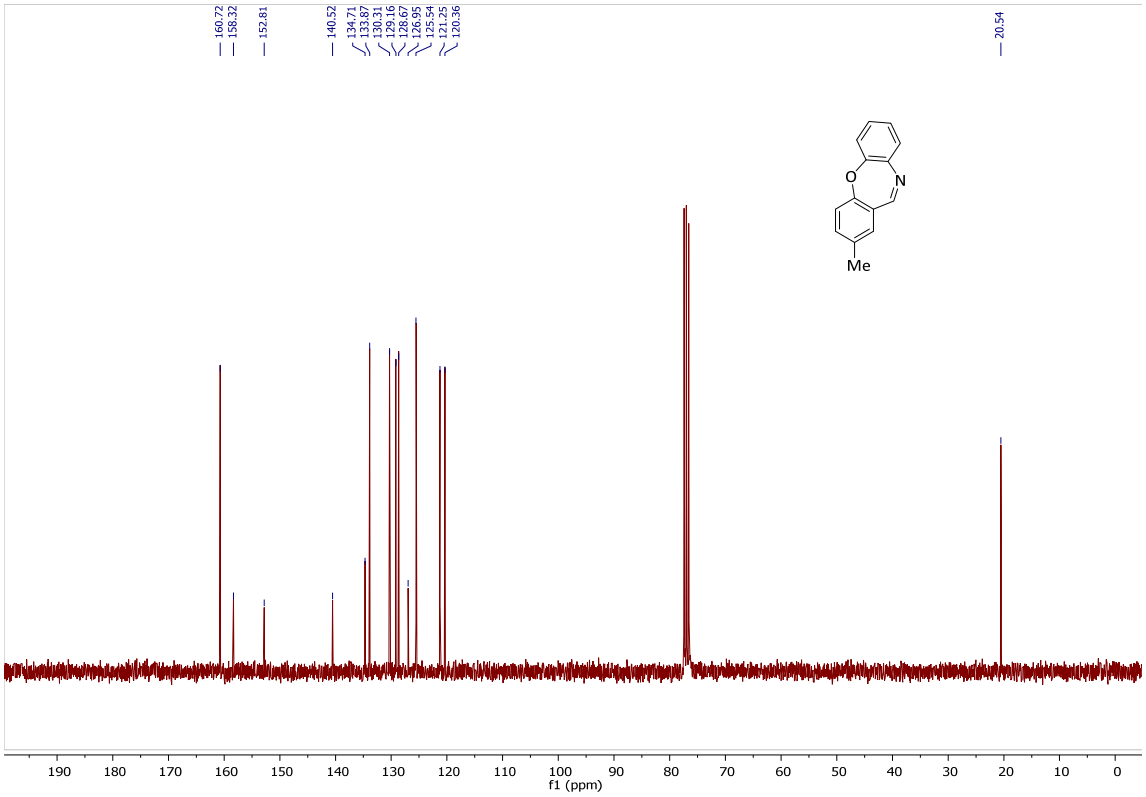
8-Chlorodibenzo[*b,f*][1,4]oxazepine (1f)



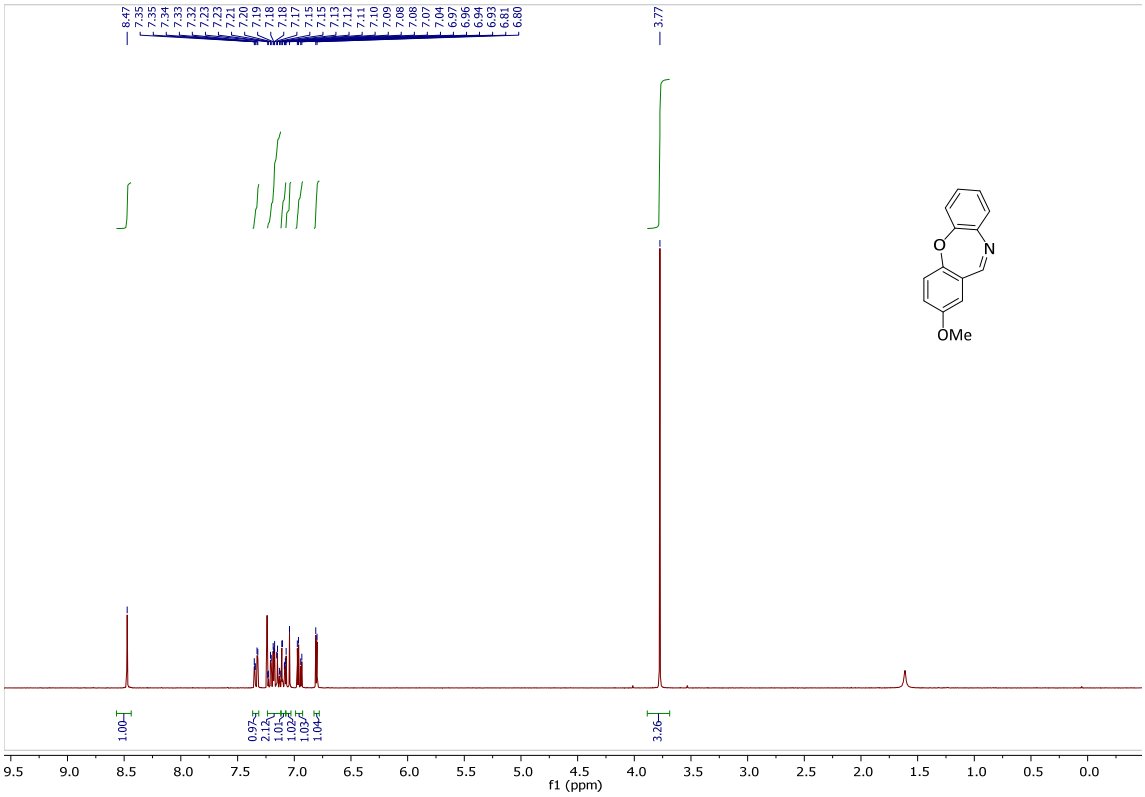


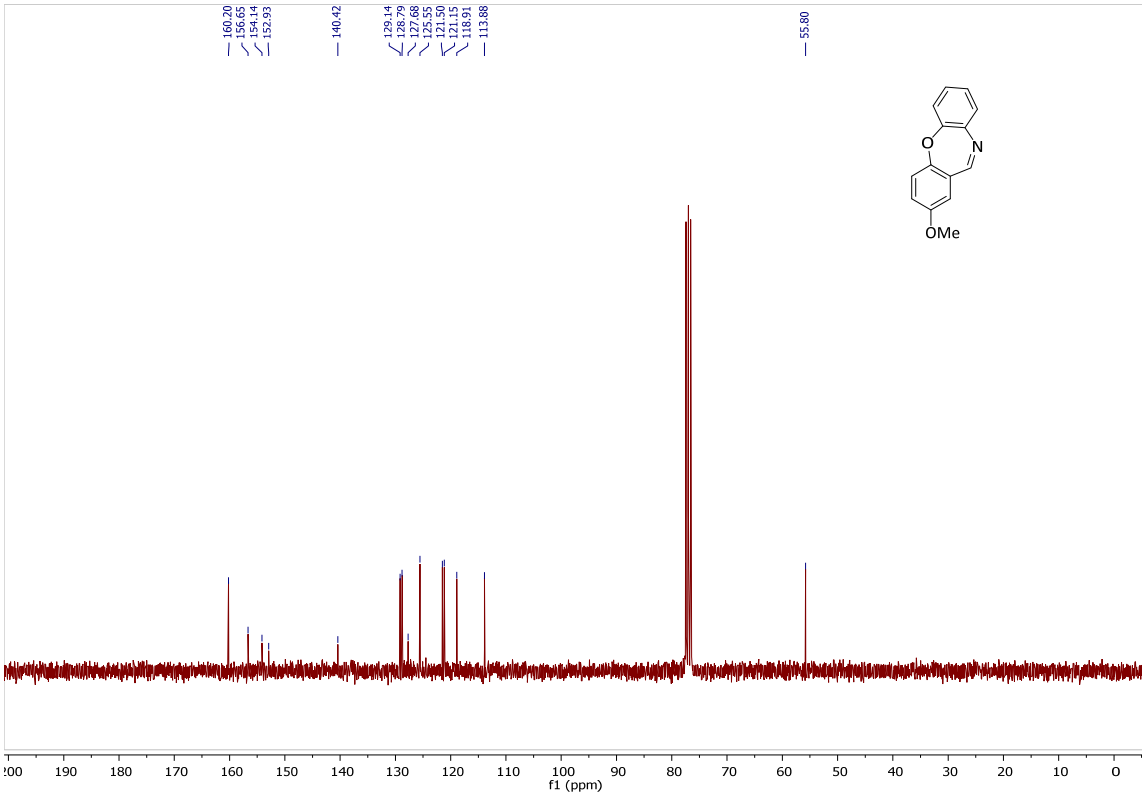
2-Methyldibenzo[*b,f*][1,4]oxazepine (1g)



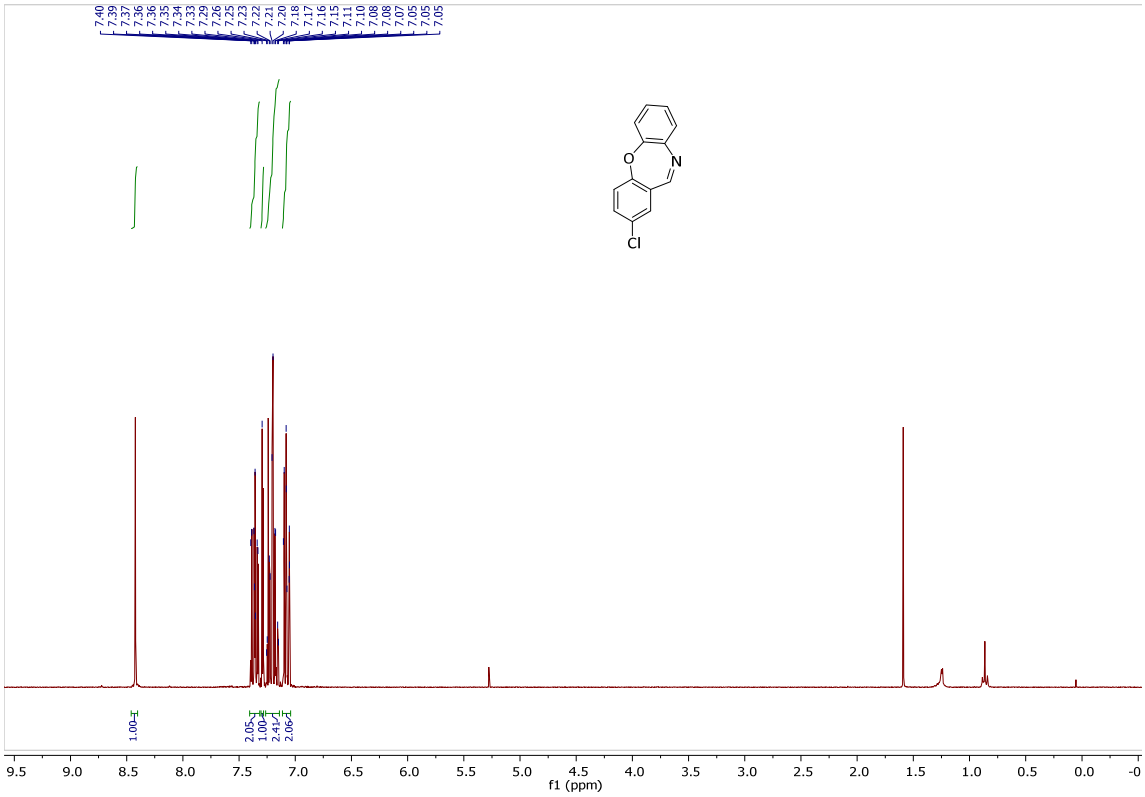


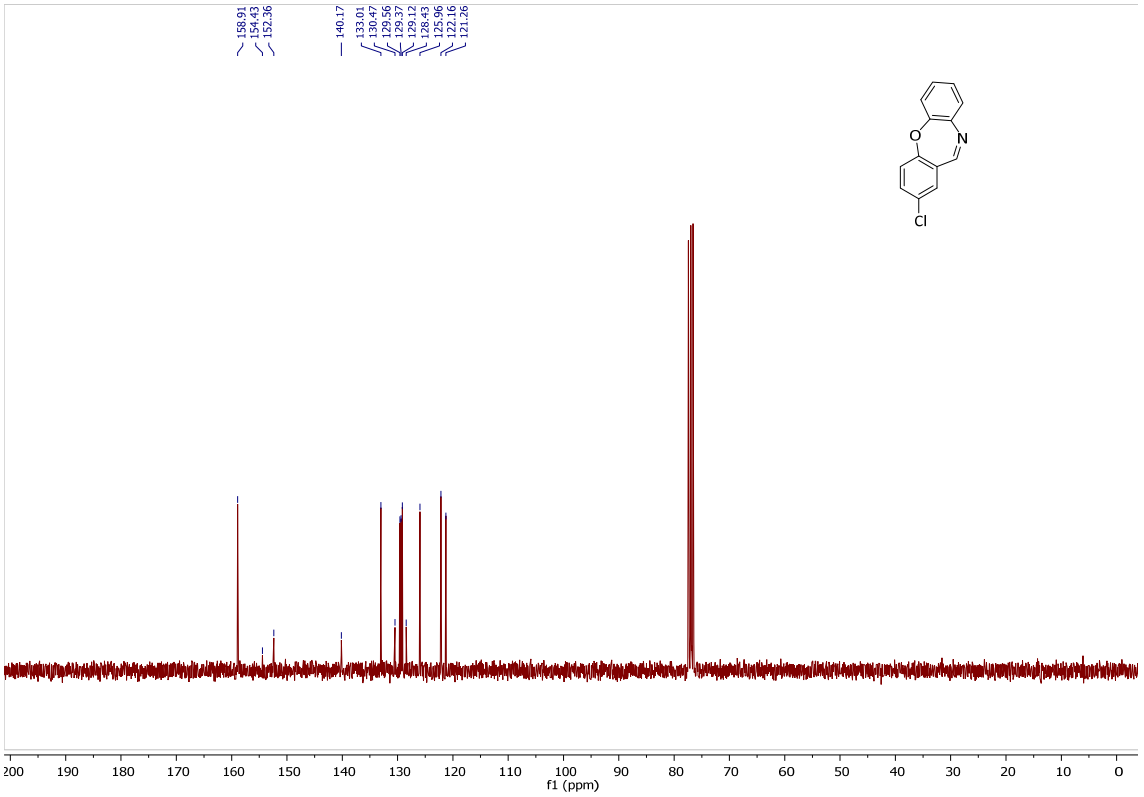
2-Methoxydibenzo[*b,f*][1,4]oxazepine (1h)



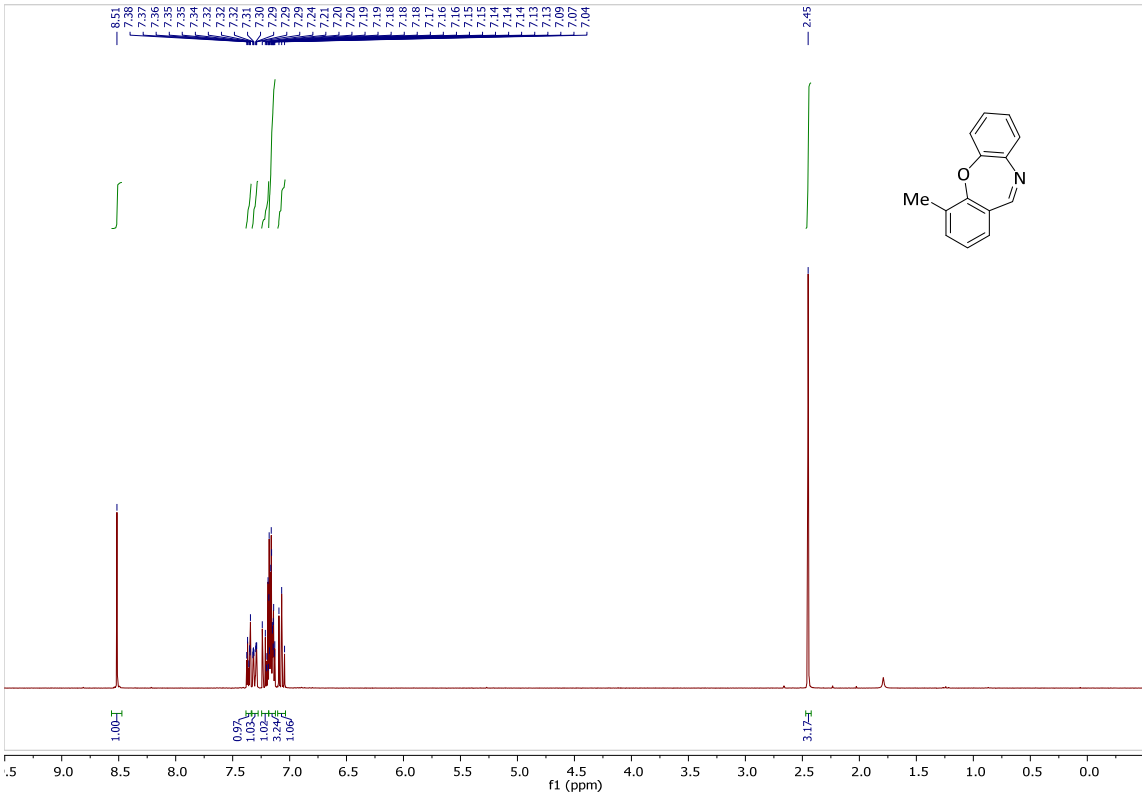


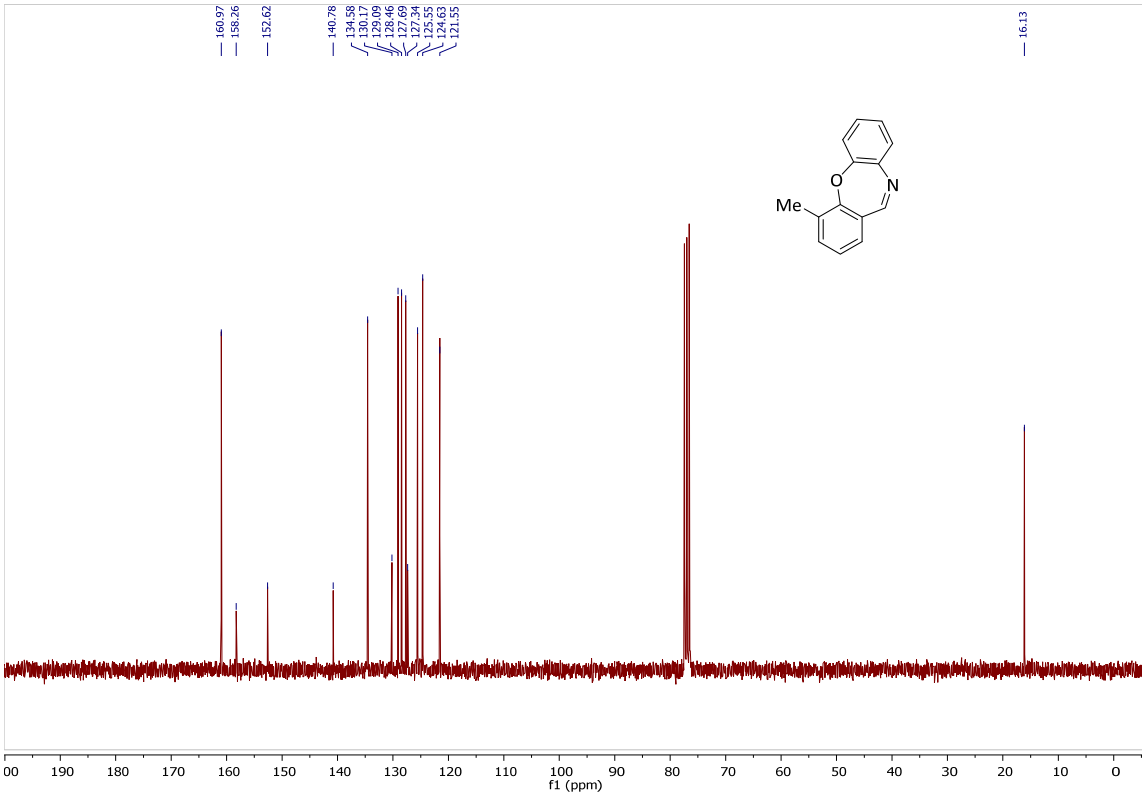
2-Chlorodibenzo[*b,f*][1,4]oxazepine (1i)



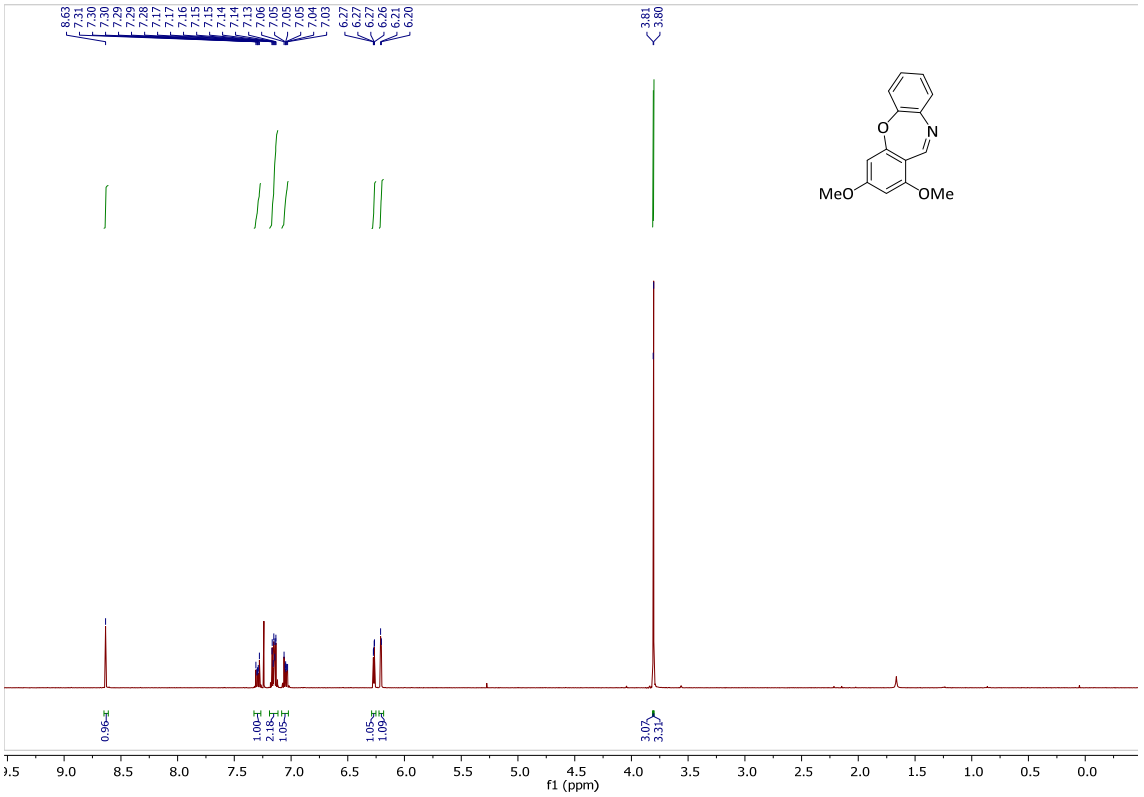


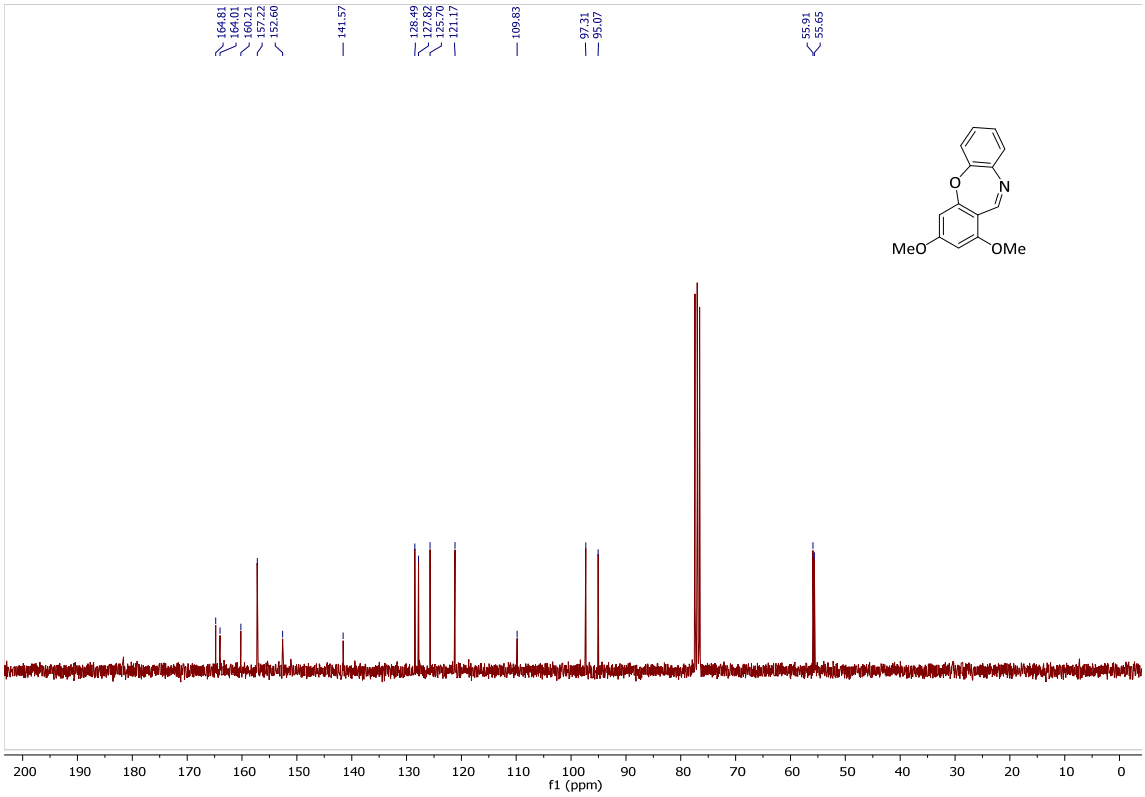
4-Methyldibenzo[*b,f*][1,4]oxazepine (1j)



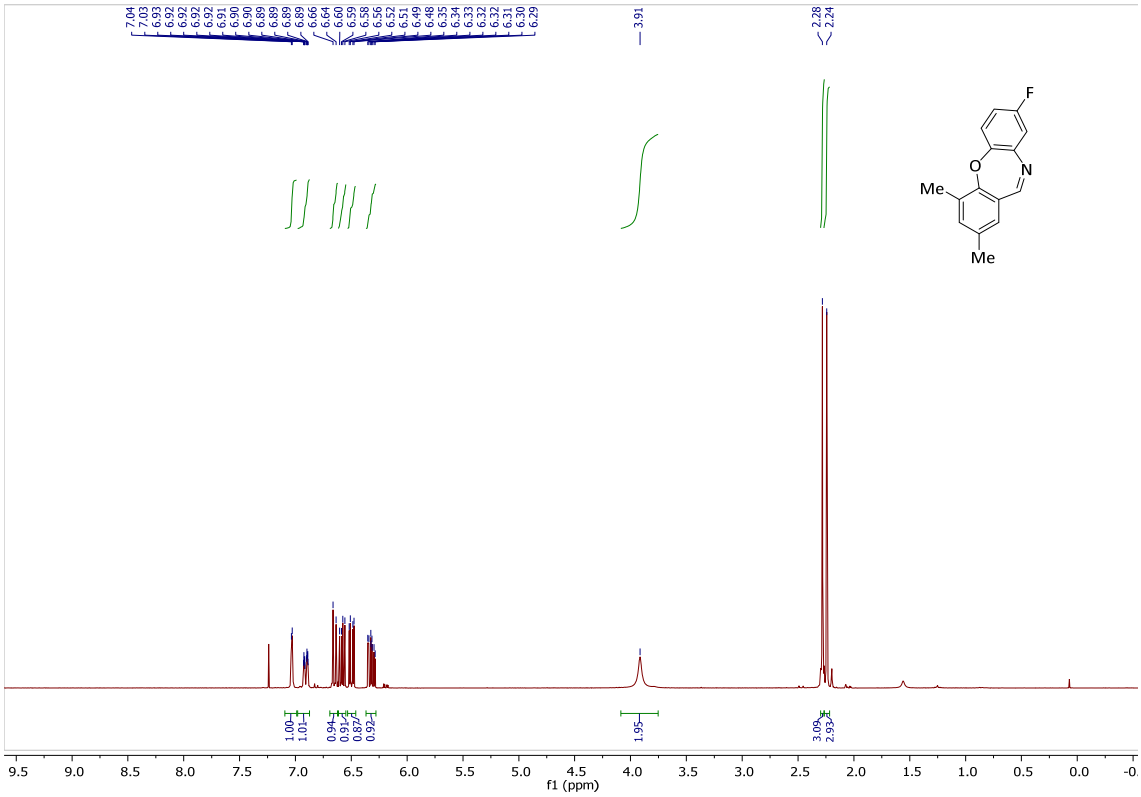


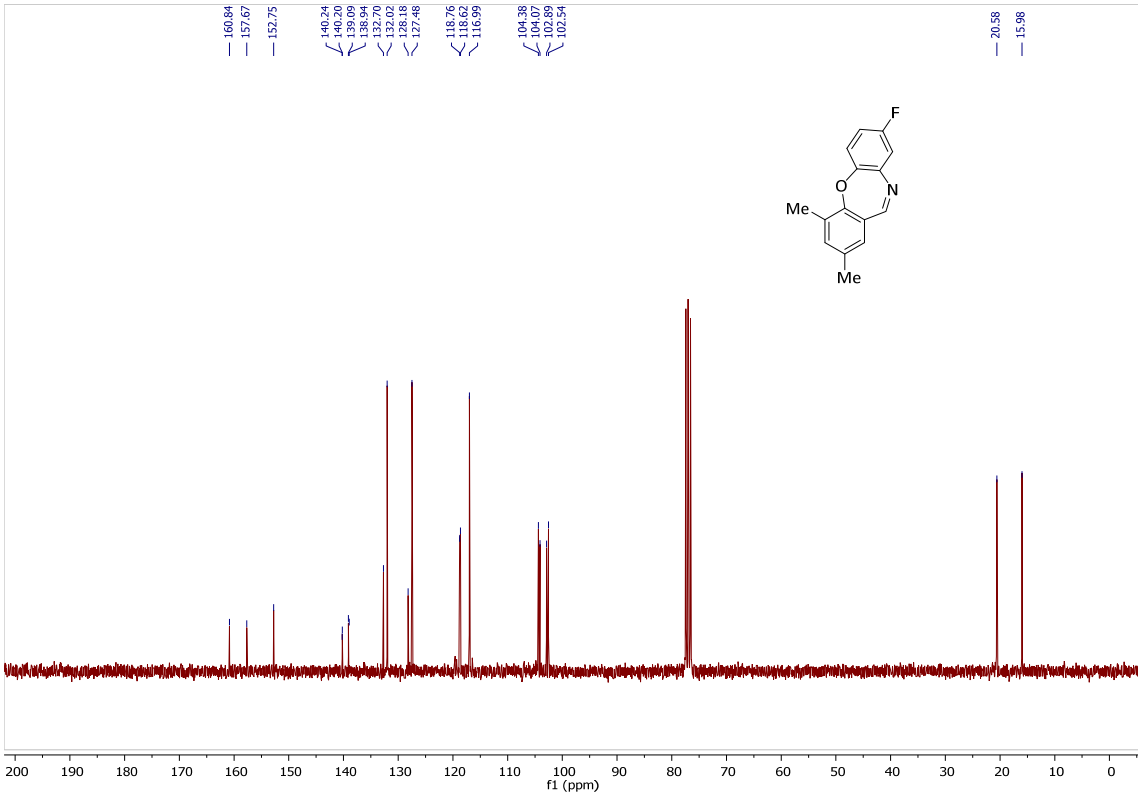
1,3-Dimethoxydibenzo[*b,f*][1,4]oxazepine (1k)



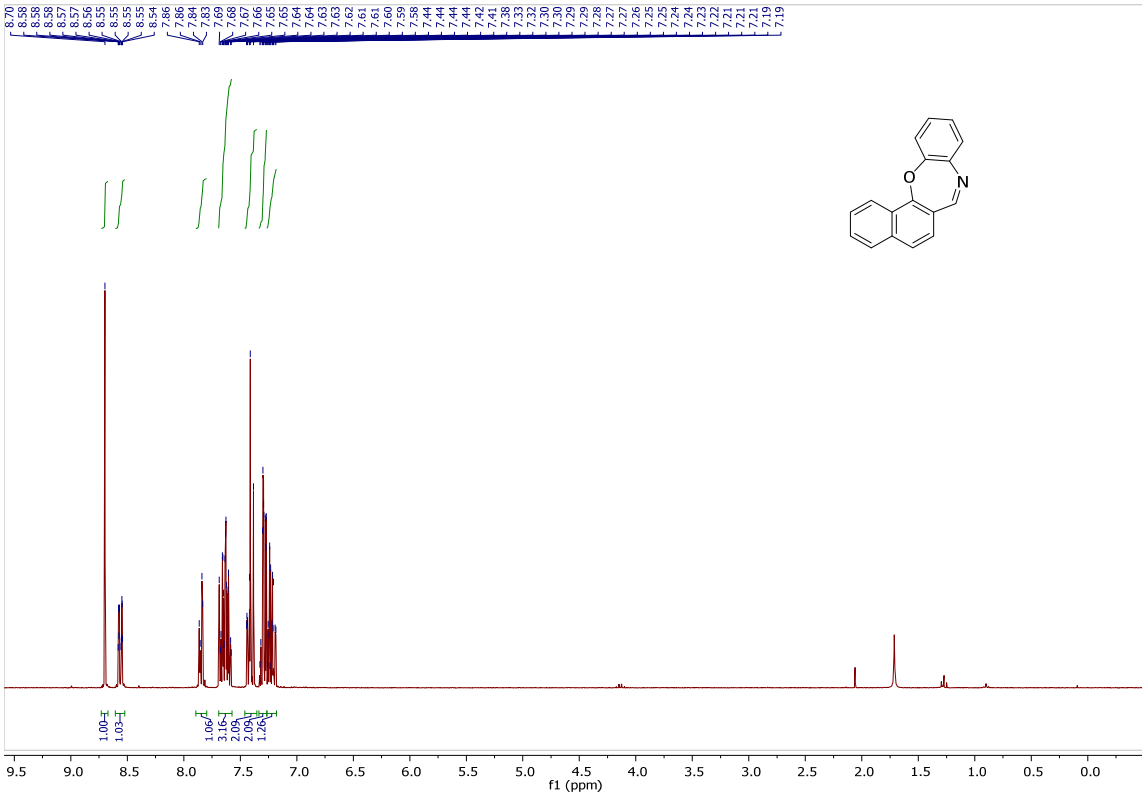


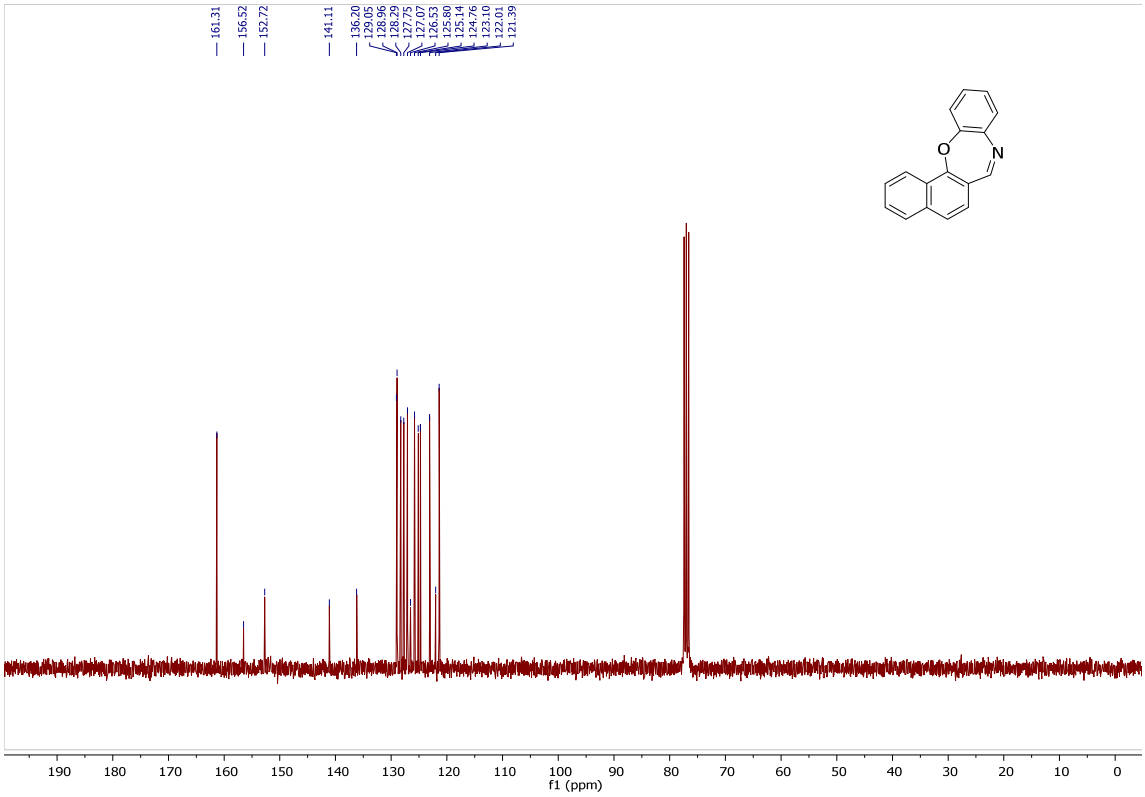
8-Fluoro-2,4-dimethyldibenzo[*b,f*][1,4]oxazepine (1l)



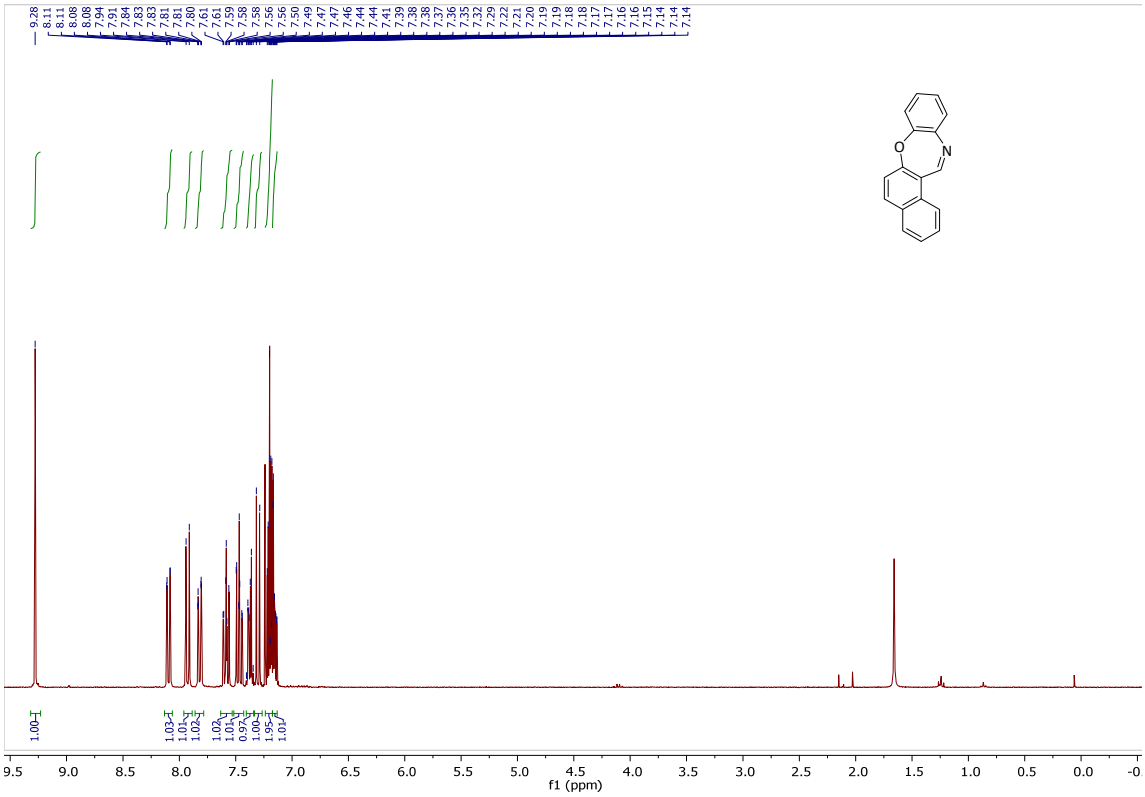


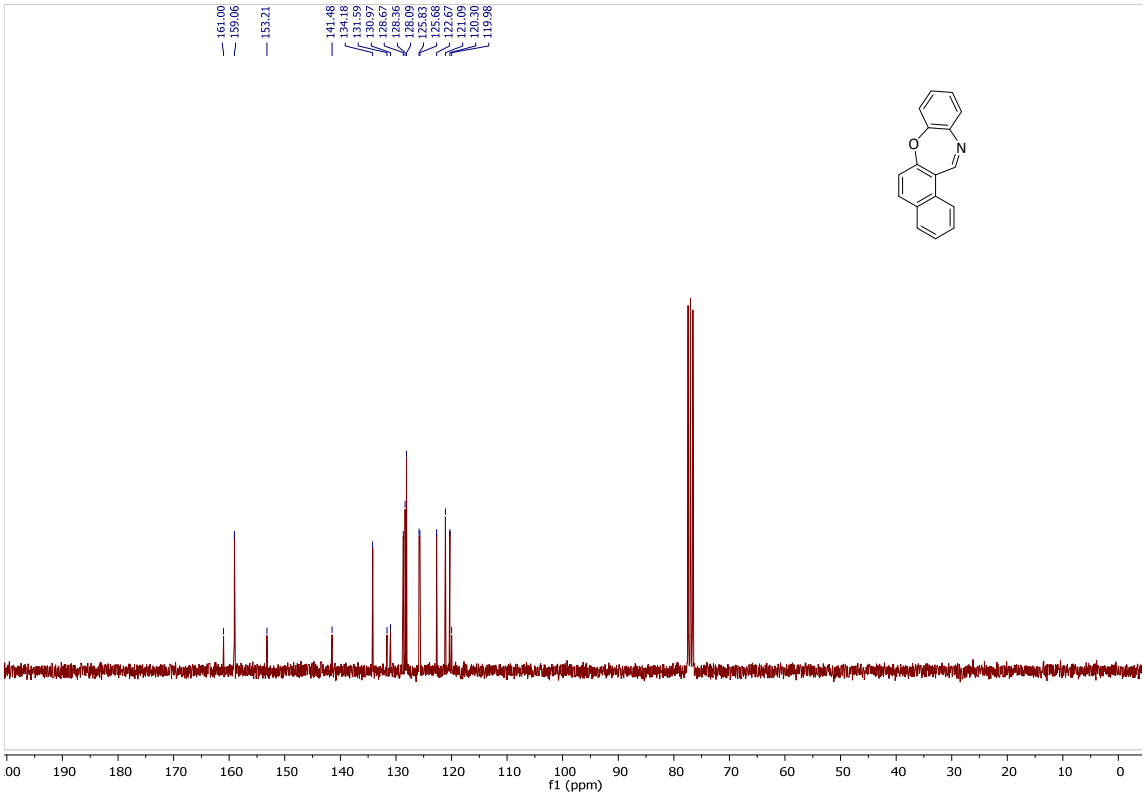
Benzo[*b*]naphtho[2,1-*f*][1,4]oxazepine (1m)



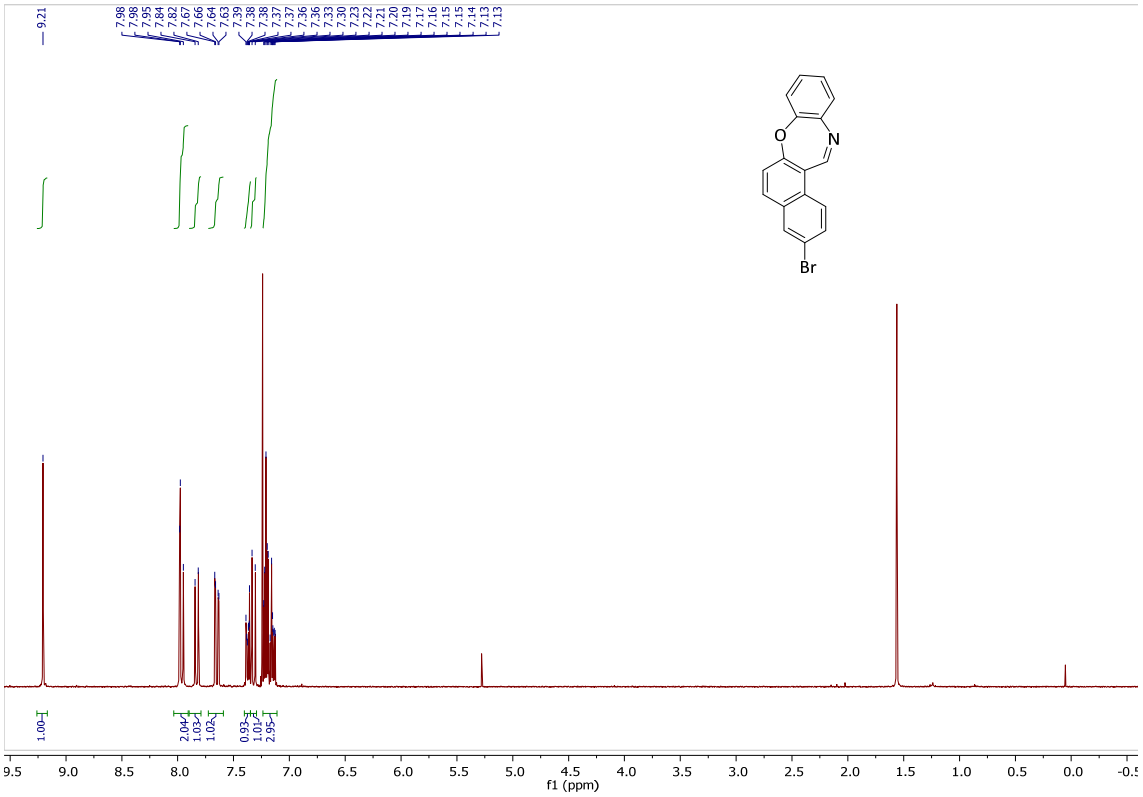


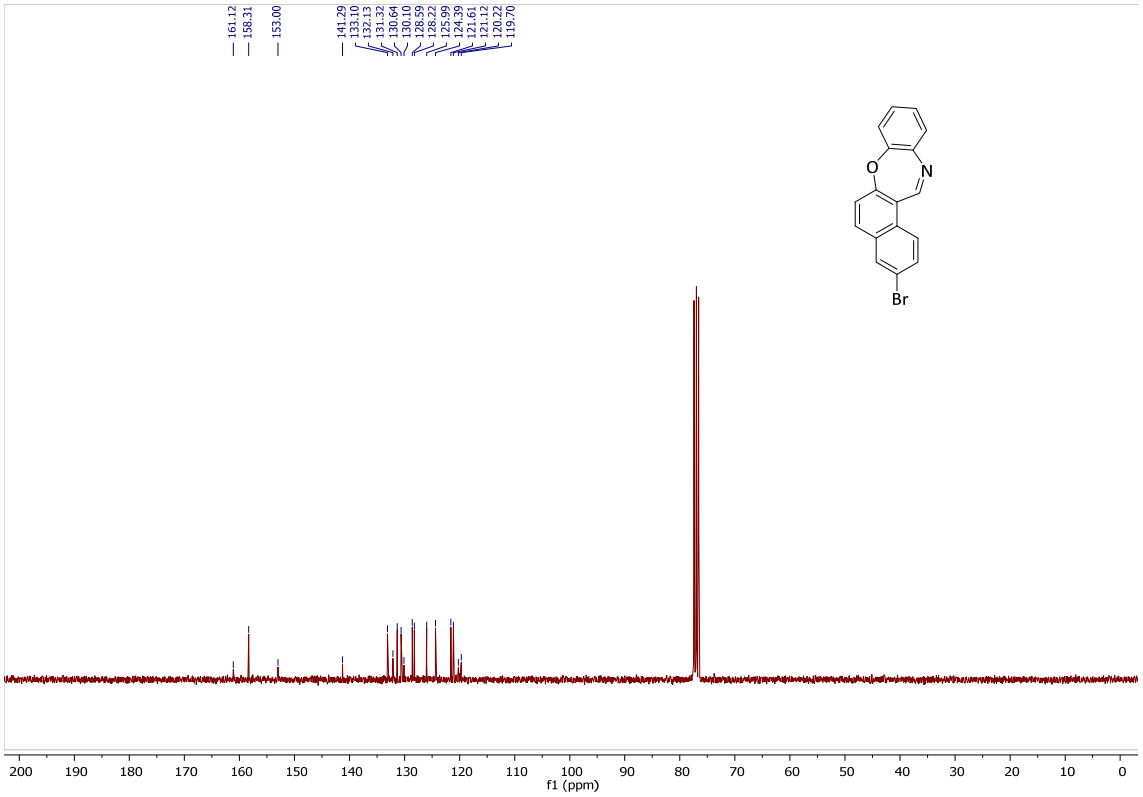
Benzo[*b*]naphtho[1,2-*f*][1,4]oxazepine (1n)



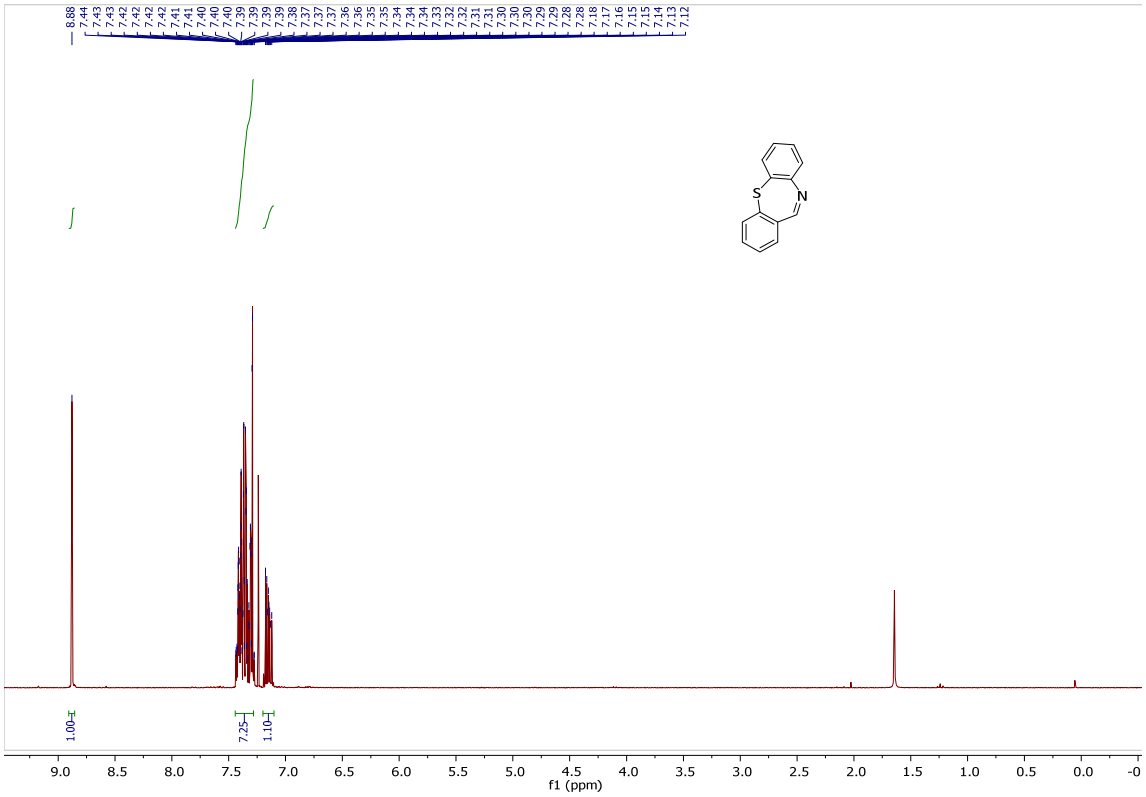


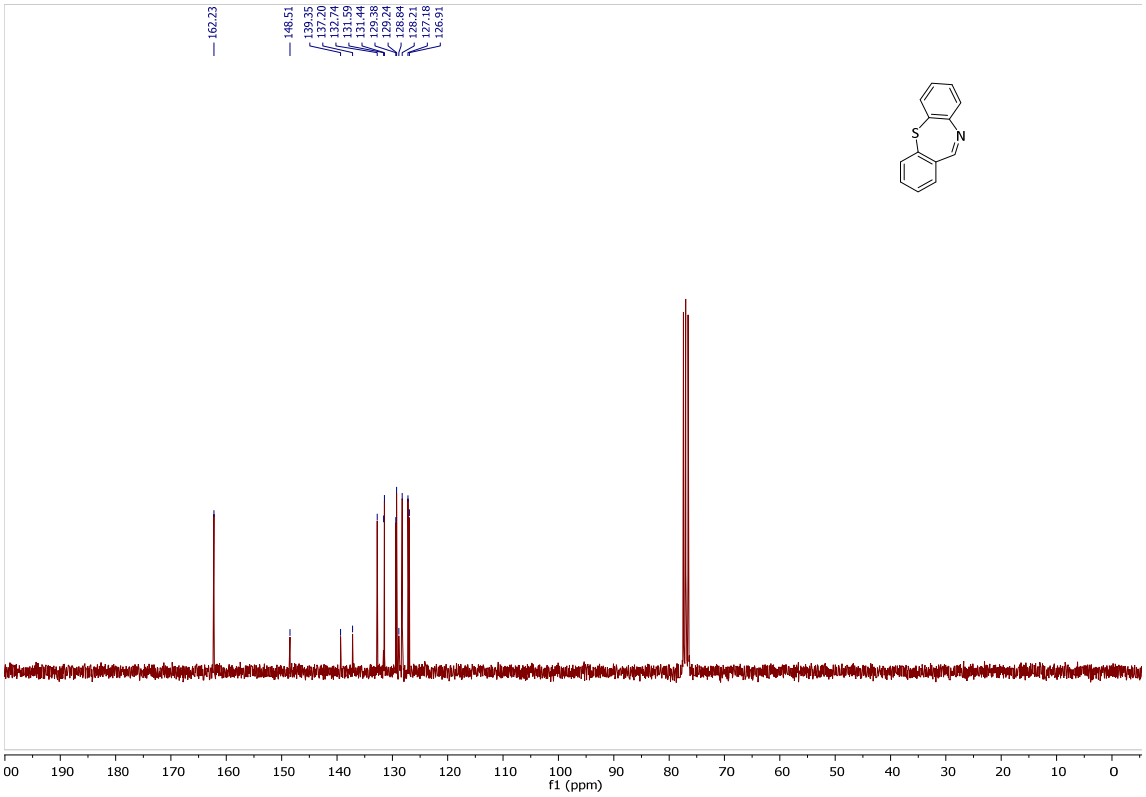
3-Bromobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepine (1o)



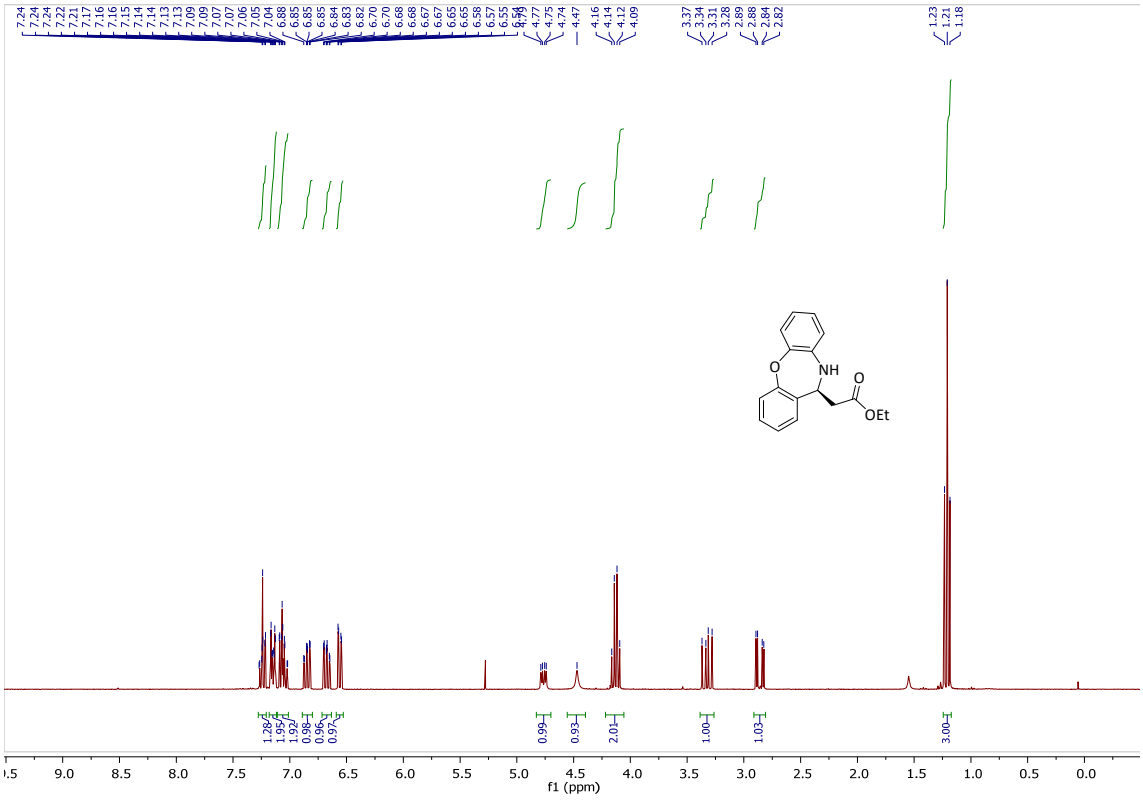


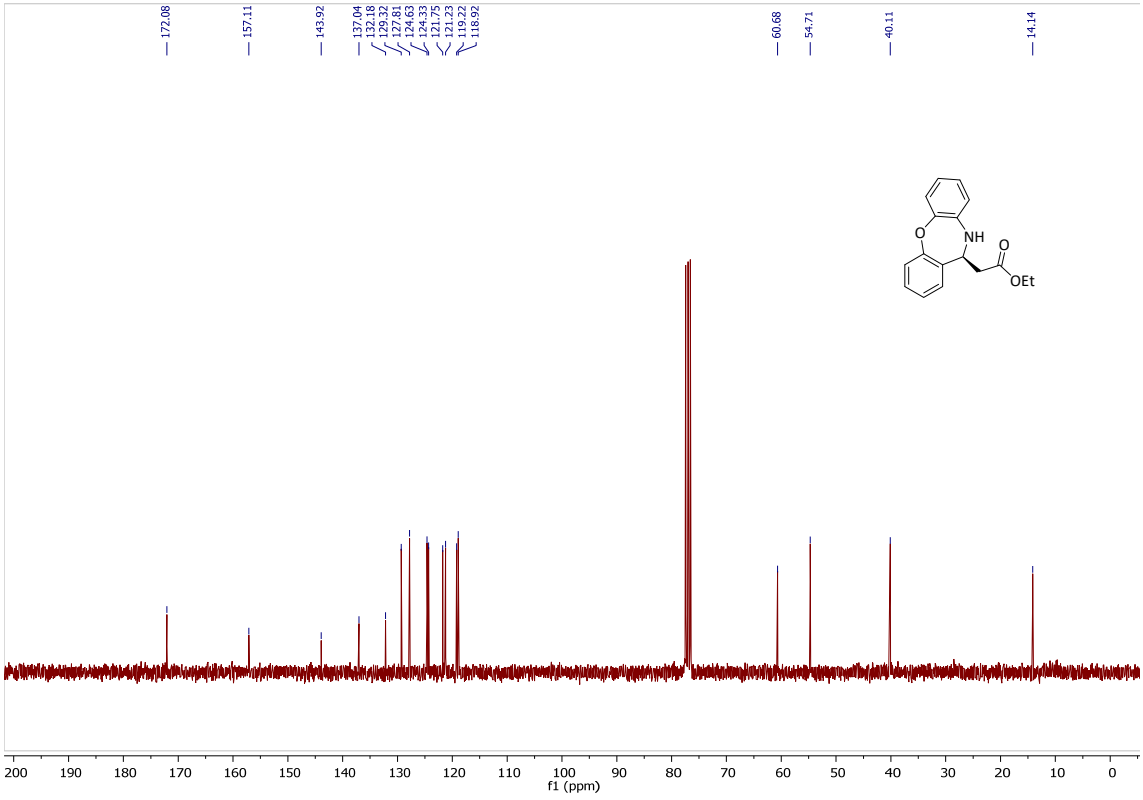
Dibenzo[*b,f*][1,4]thiazepine (4)



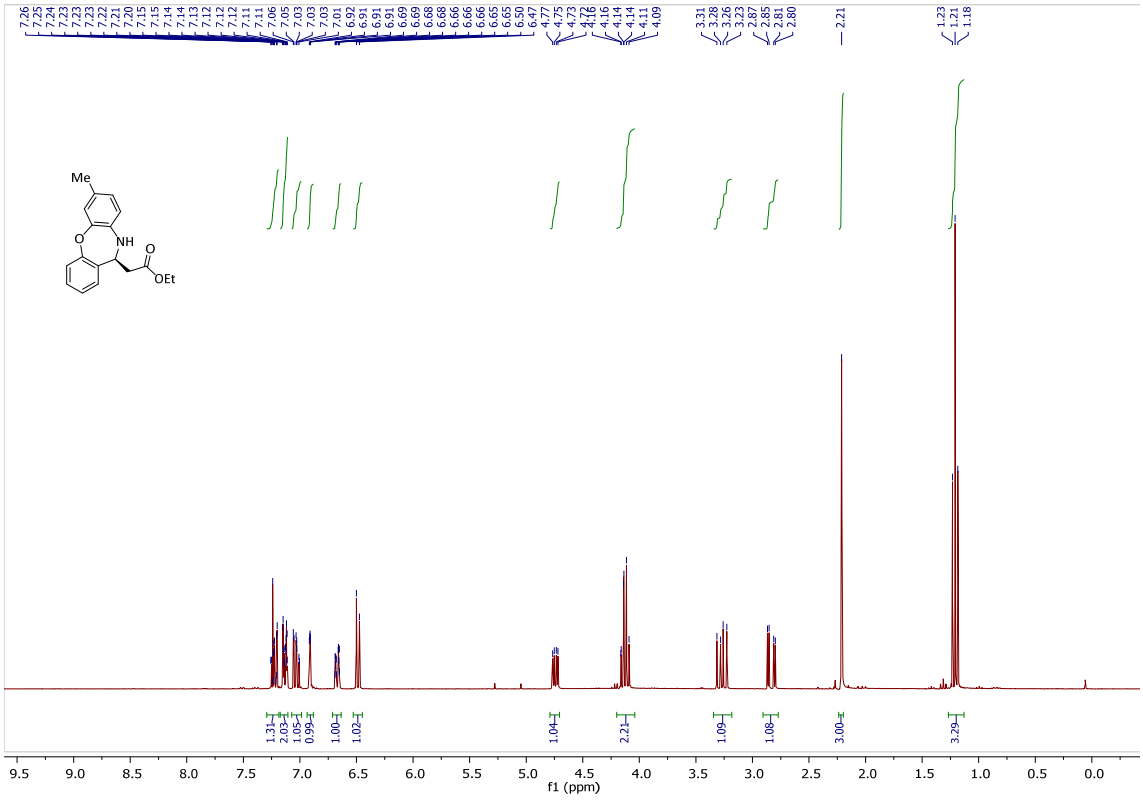


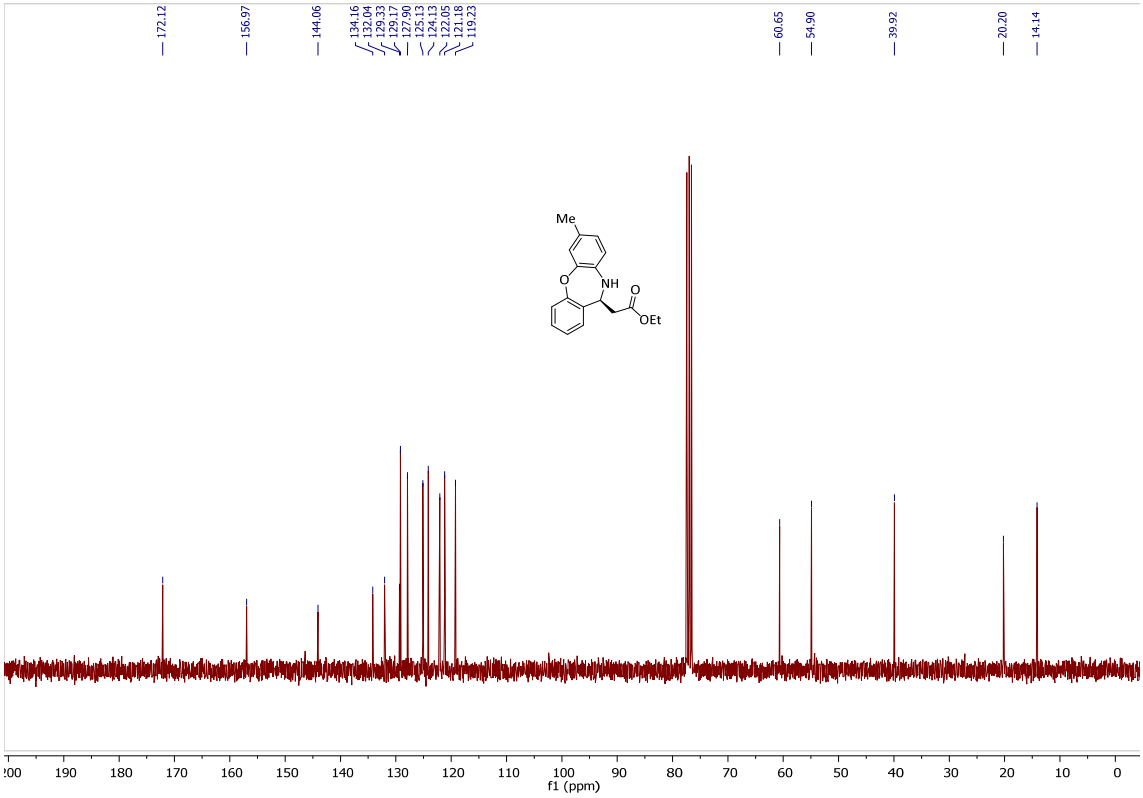
Ethyl (S)-2-(10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3a)



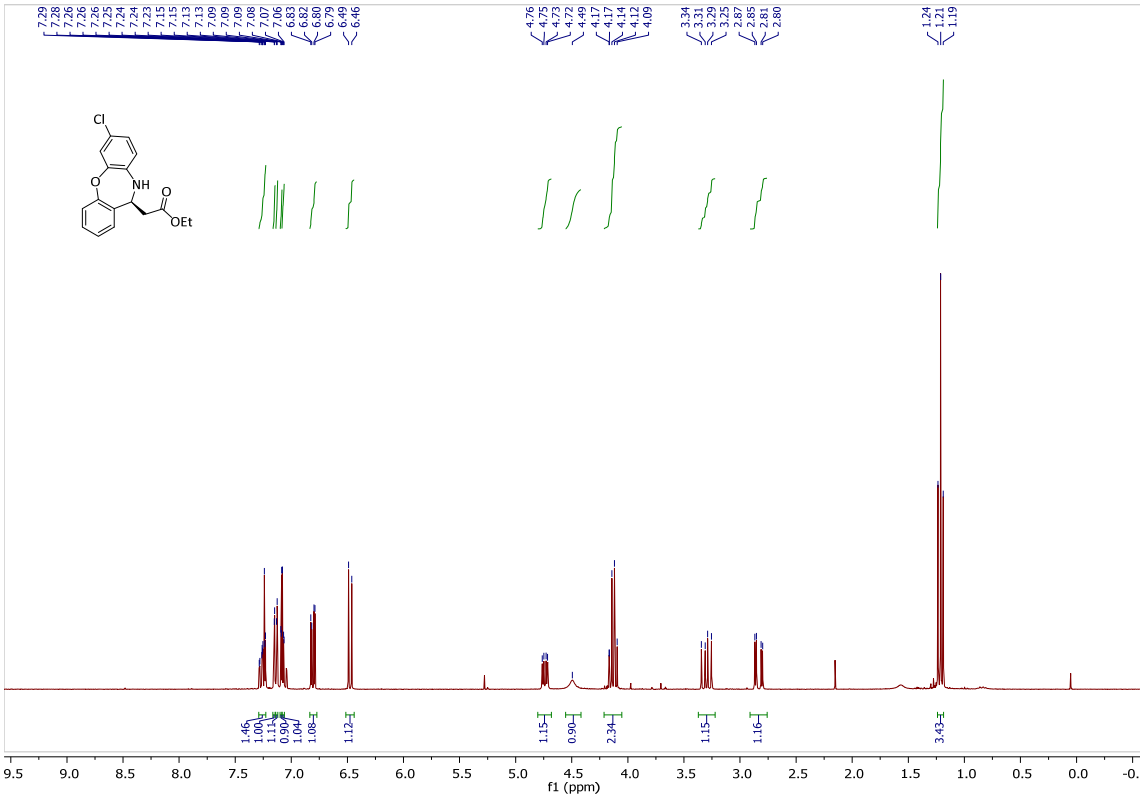


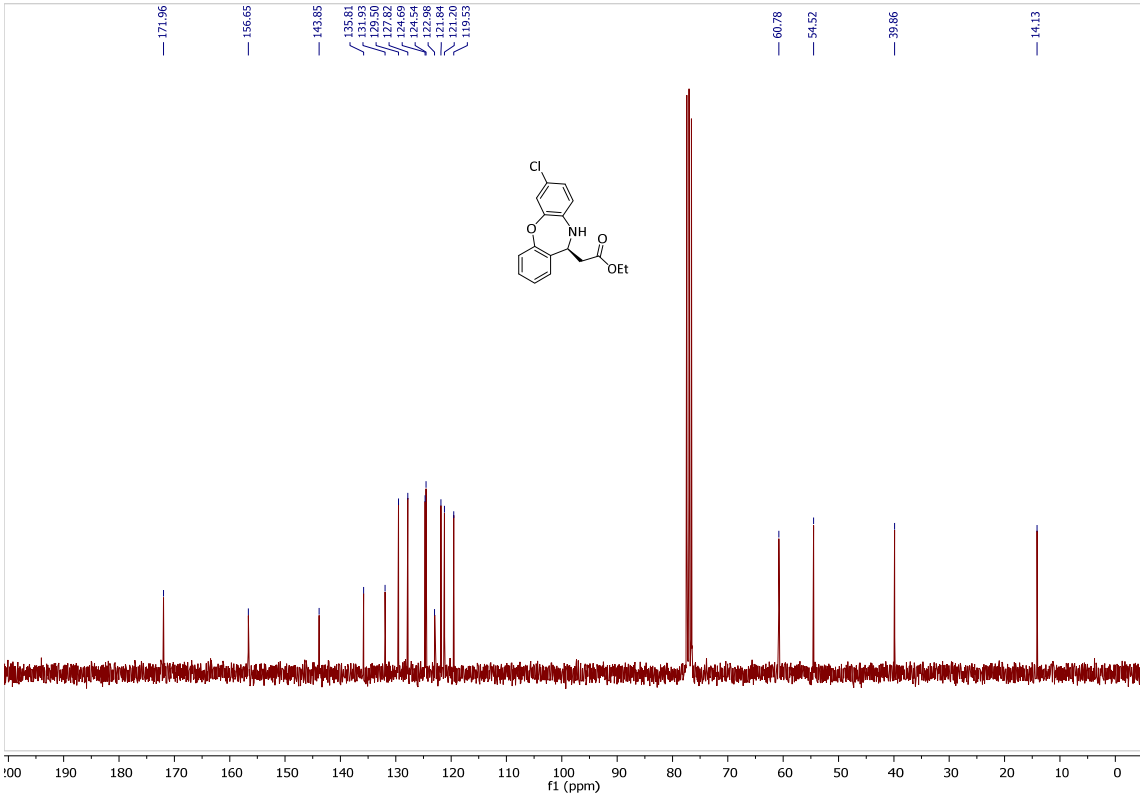
Ethyl (S)-2-(7-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3b)



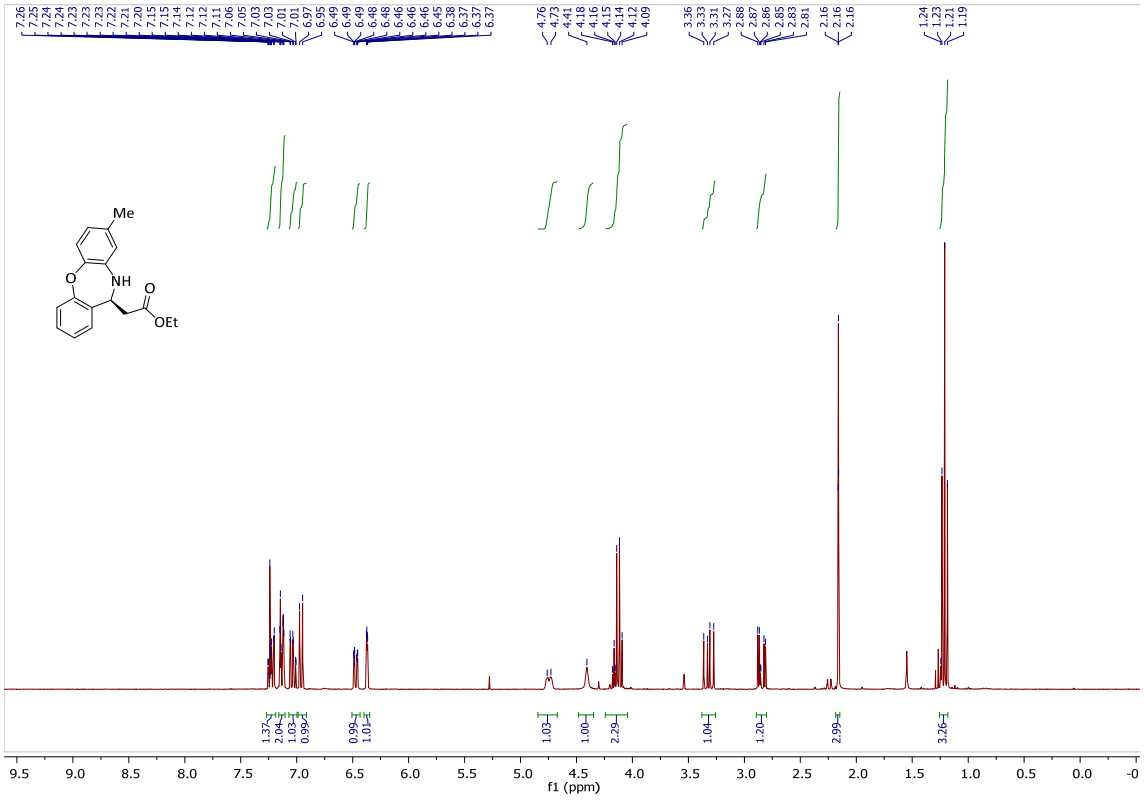


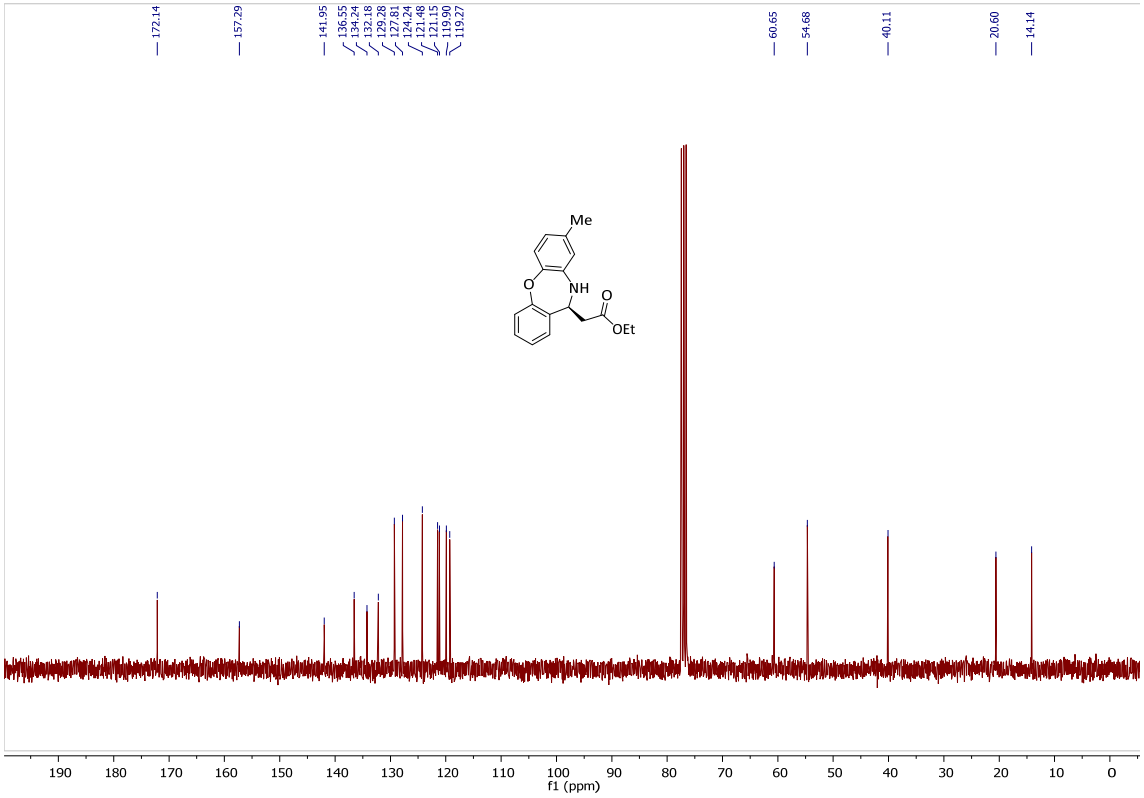
Ethyl (S)-2-(7-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3c)



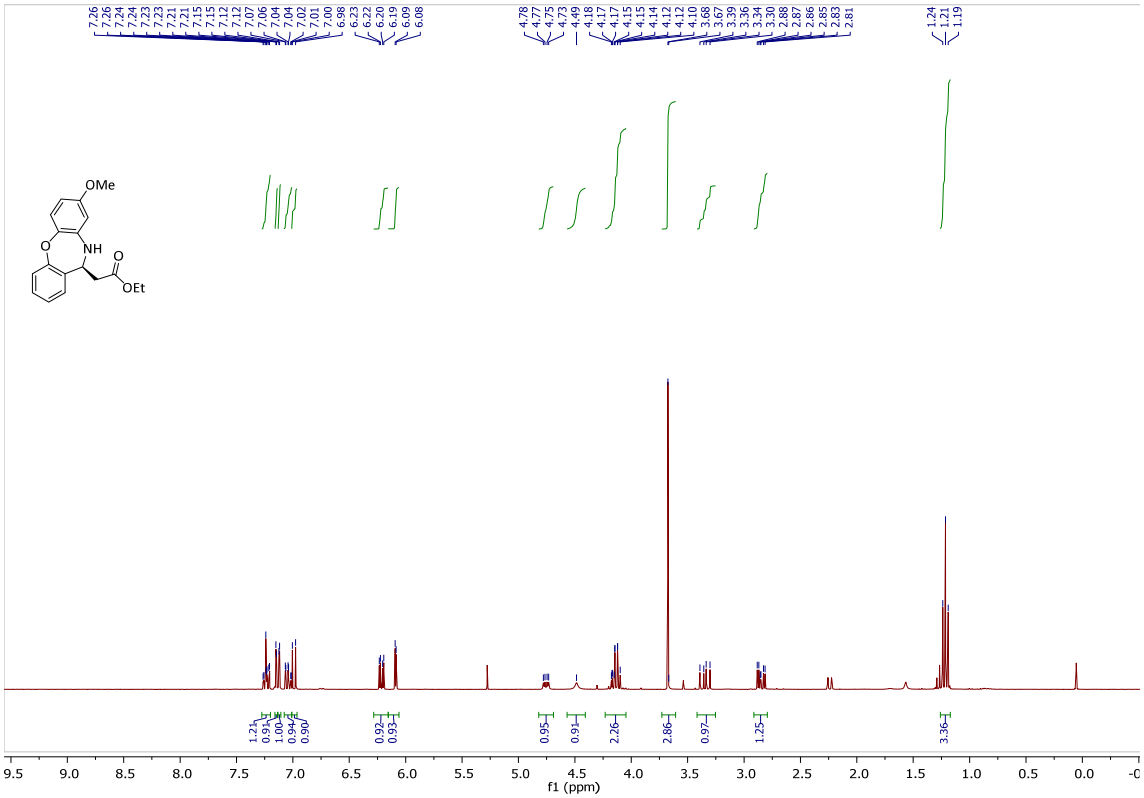


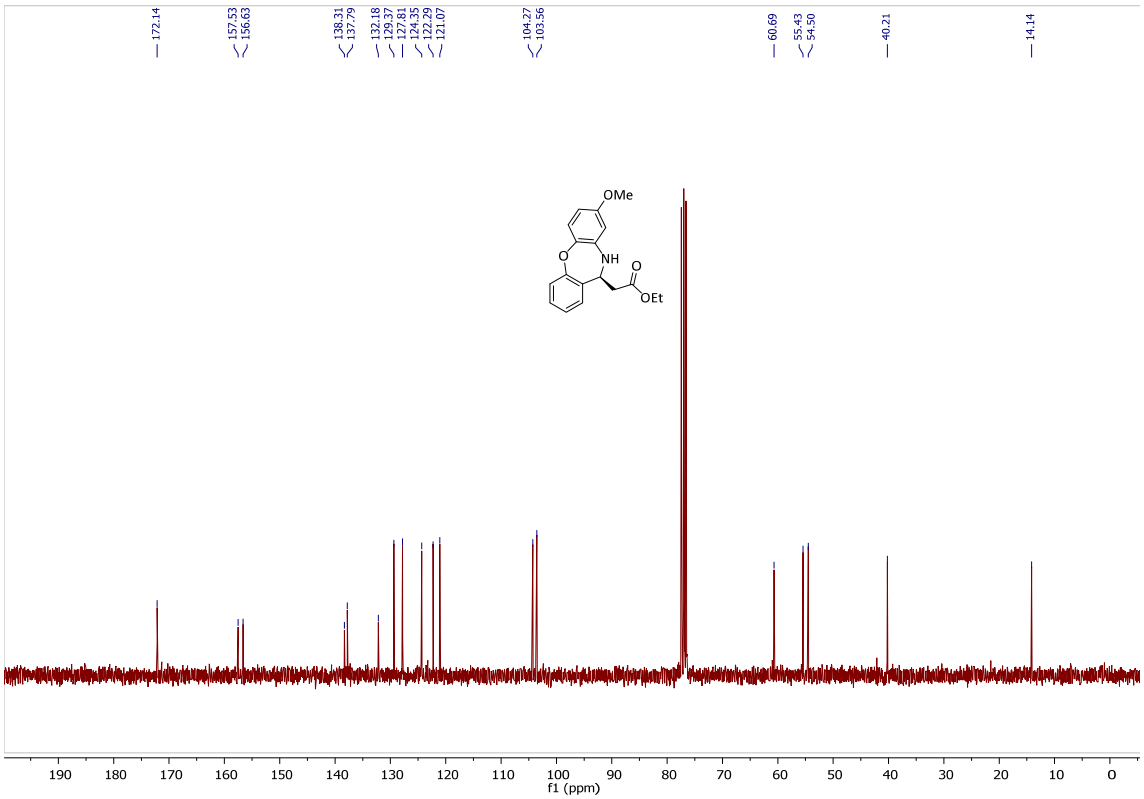
Ethyl (S)-2-(8-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3d)



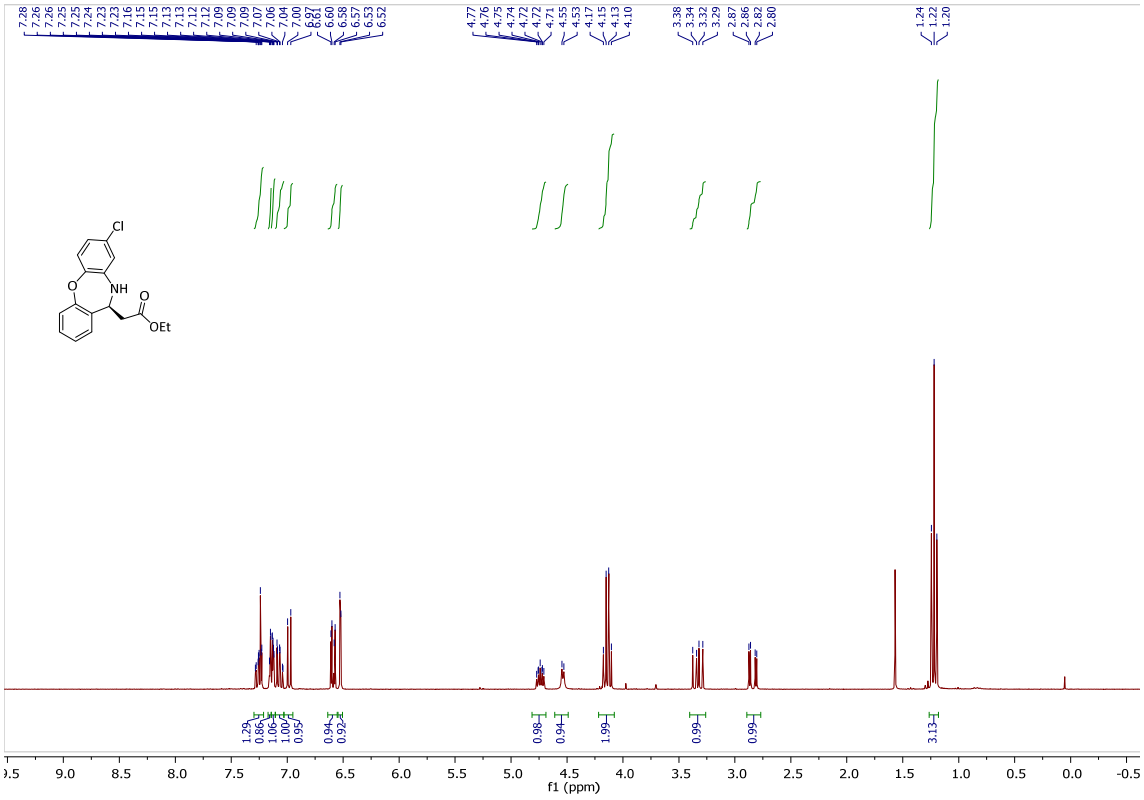


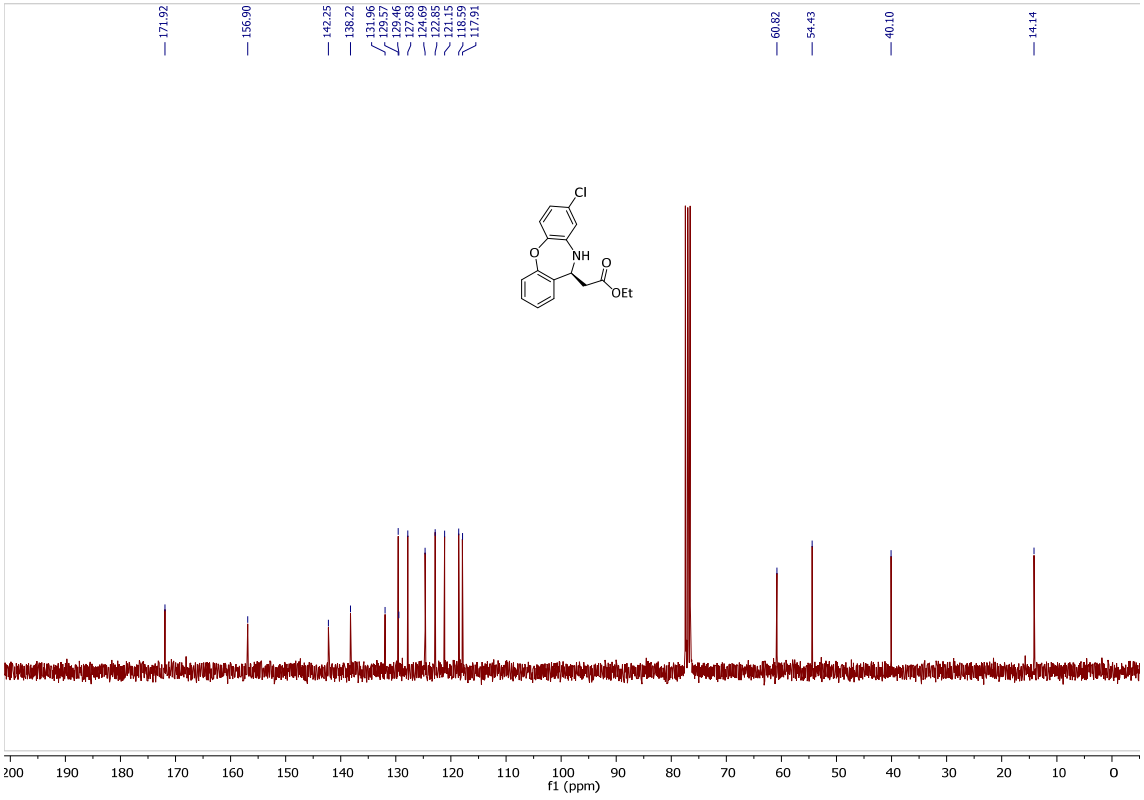
Ethyl (S)-2-(8-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3e)



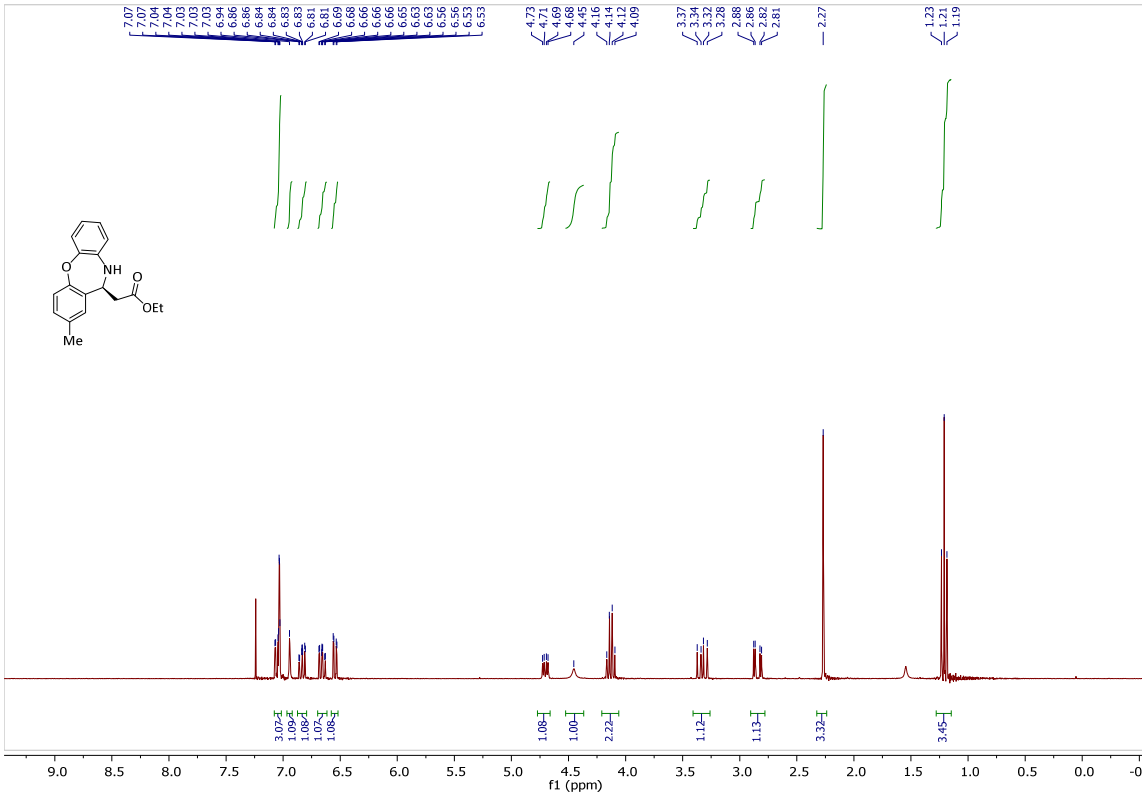


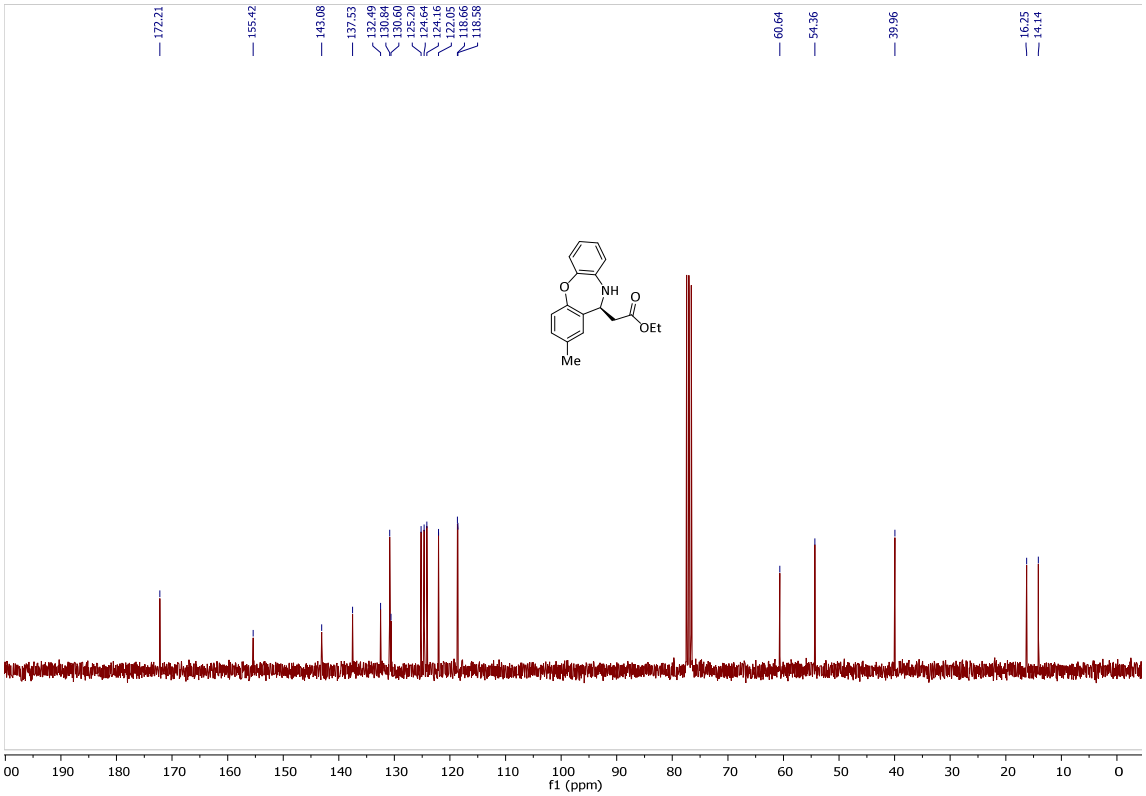
Ethyl (S)-2-(8-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3f)



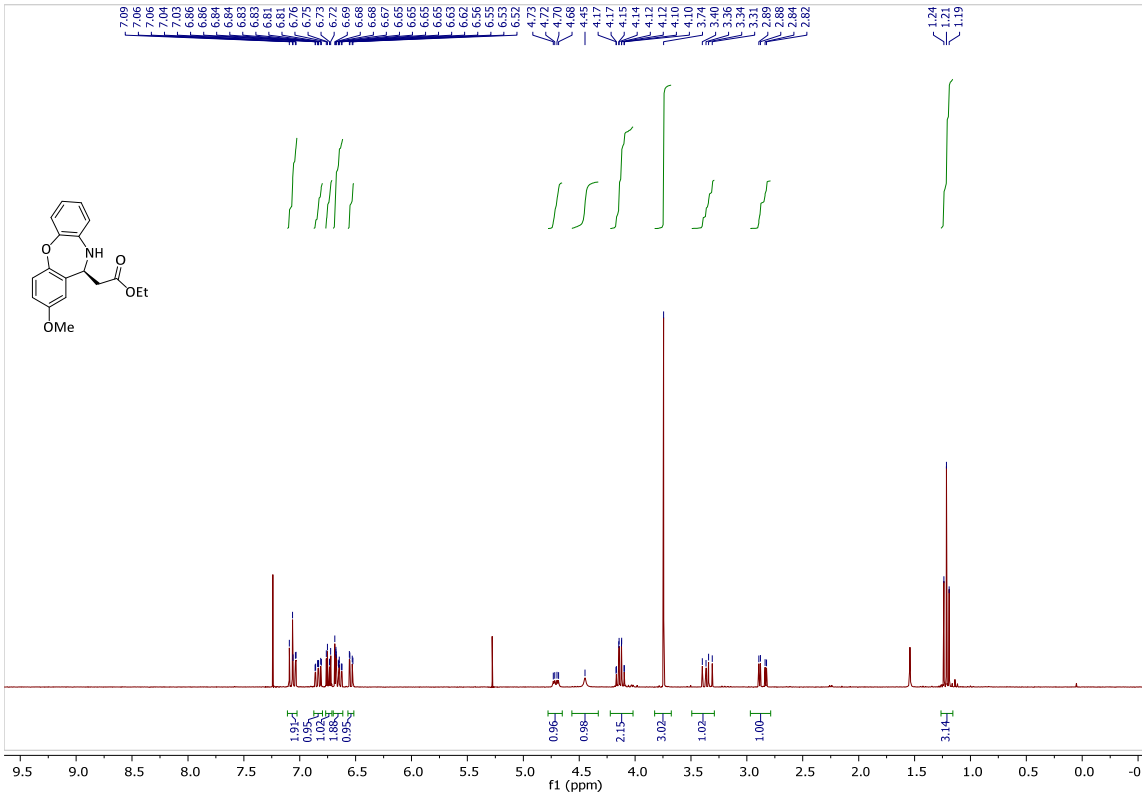


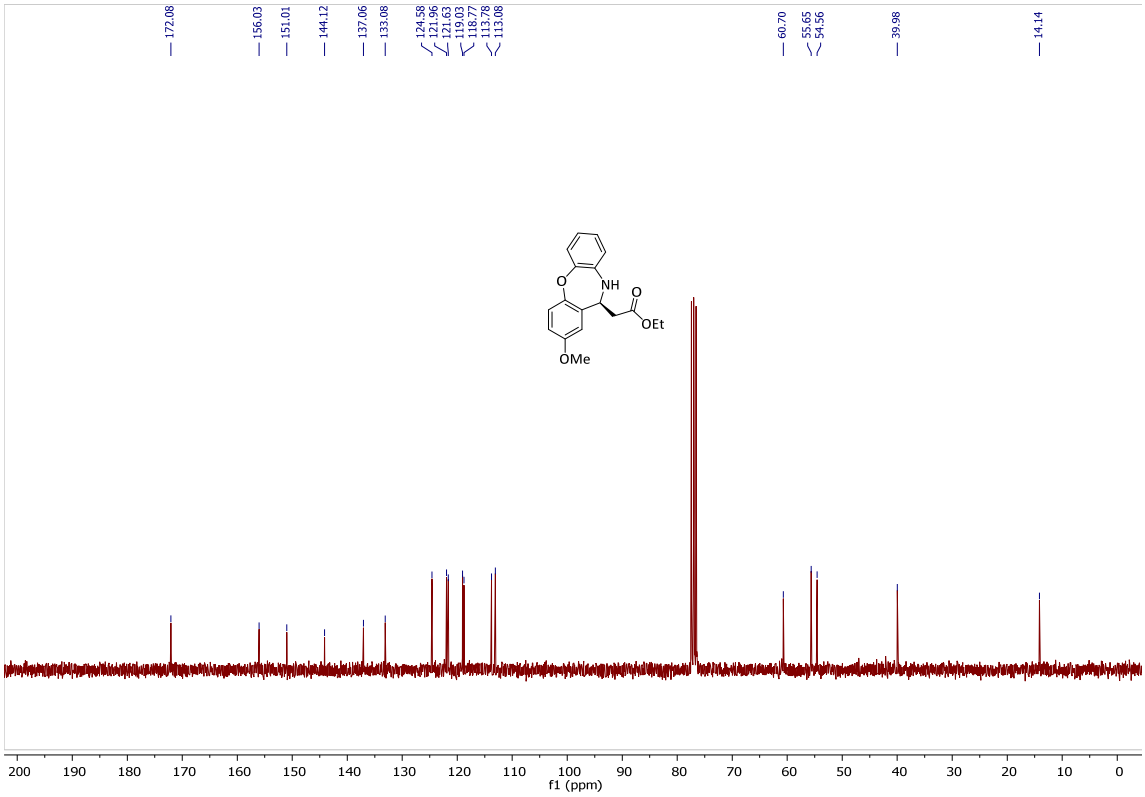
Ethyl (*S*)-2-(2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3g)



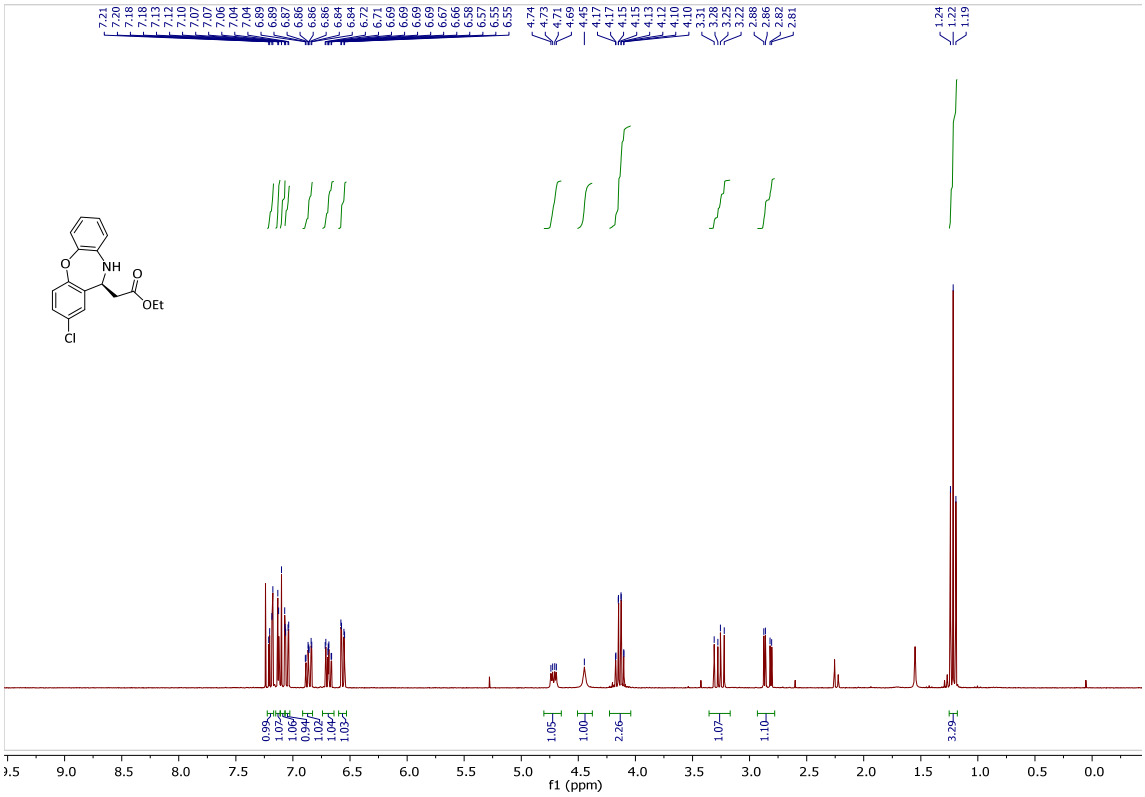


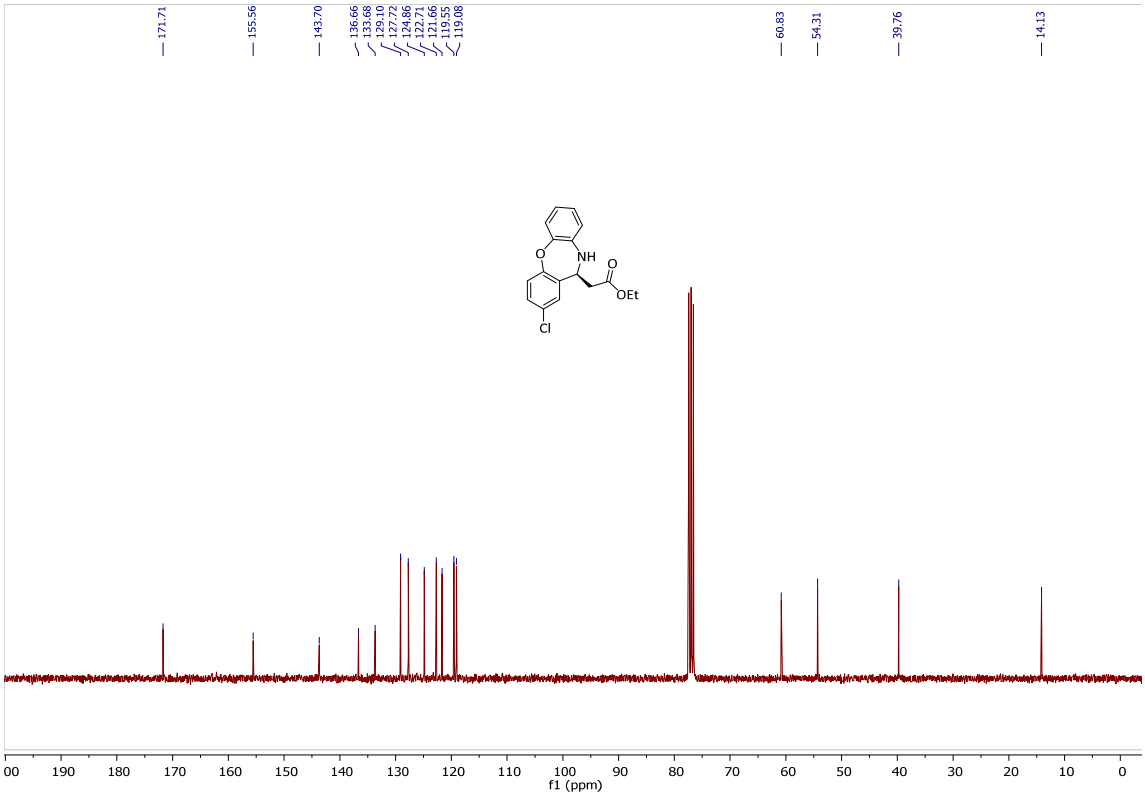
Ethyl (*S*)-2-(2-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3h)



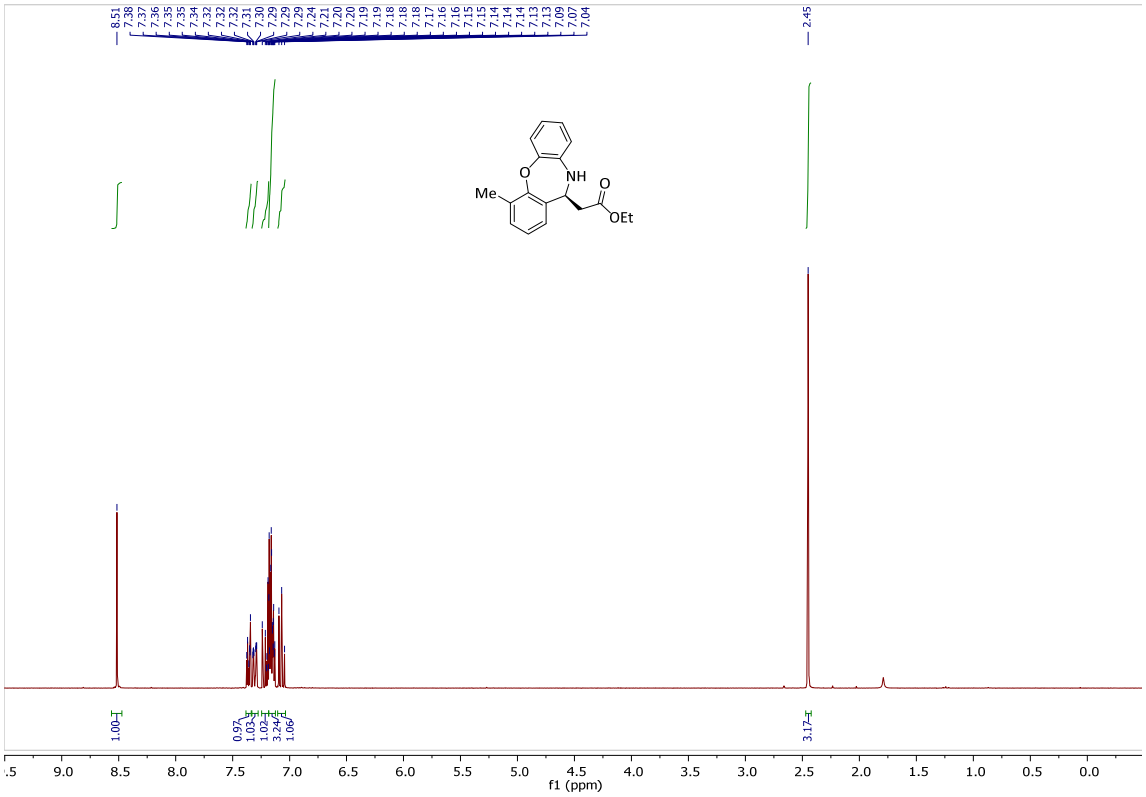


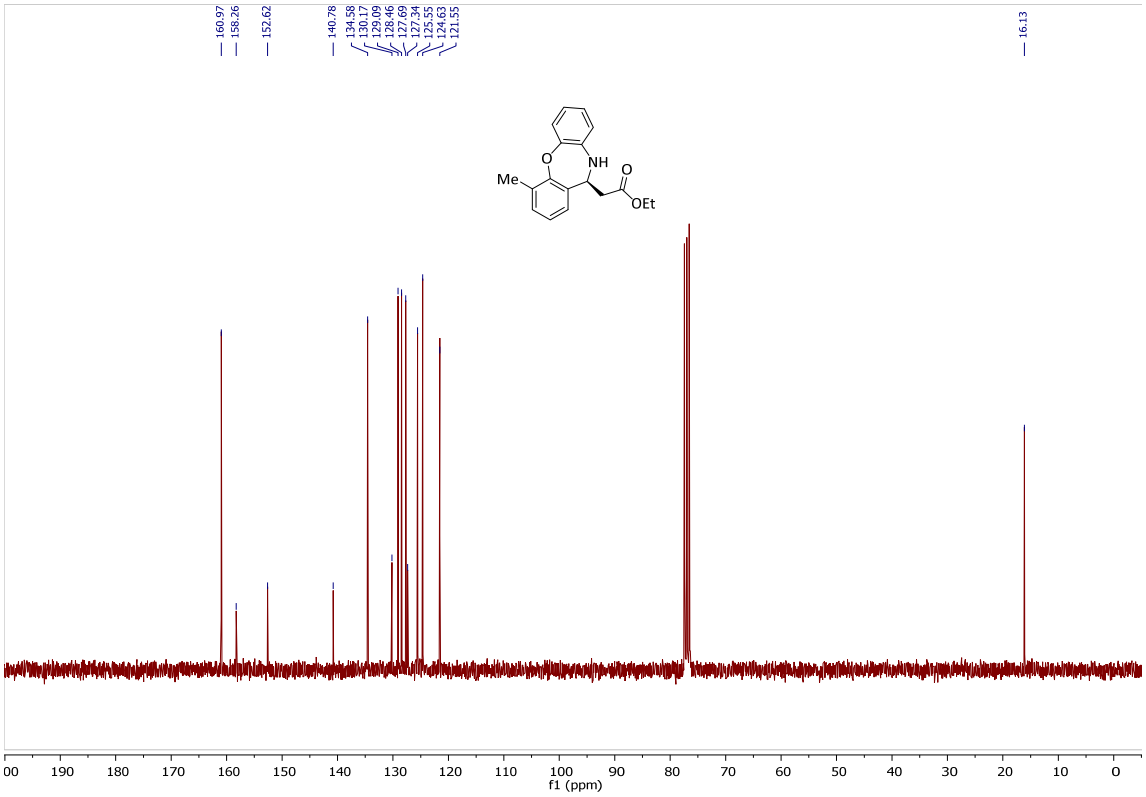
Ethyl (*S*)-2-(2-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3i)



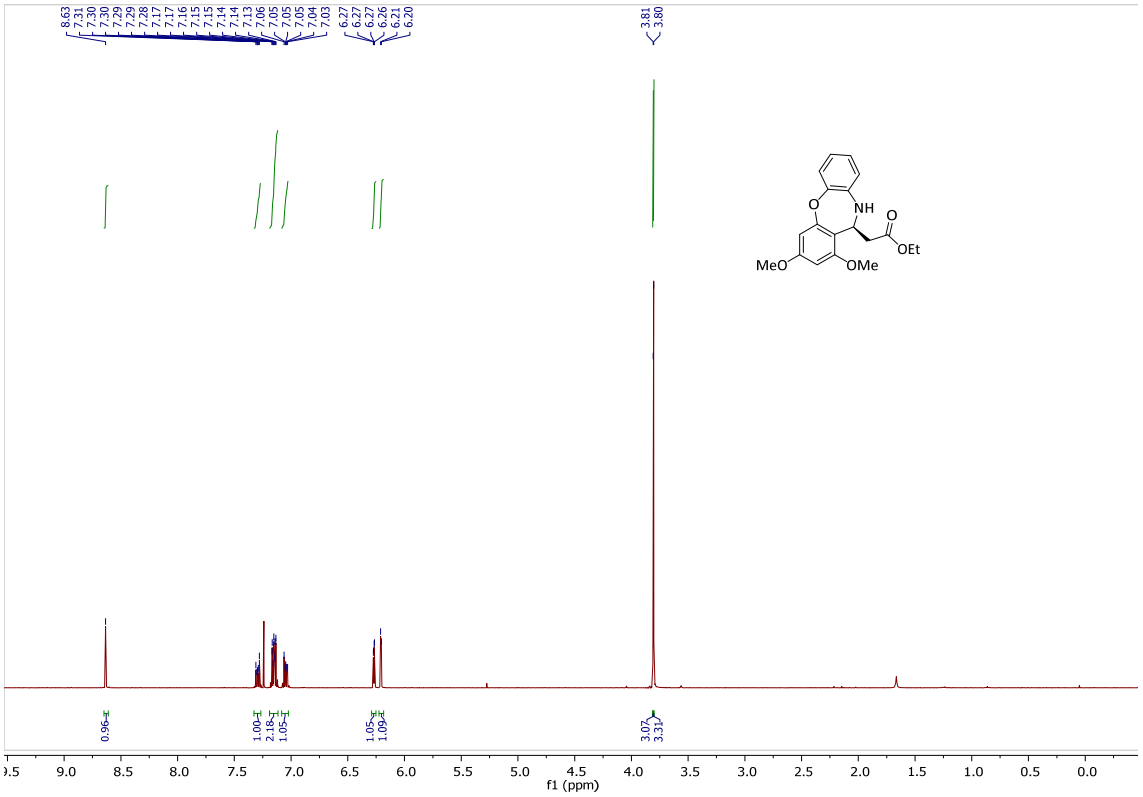


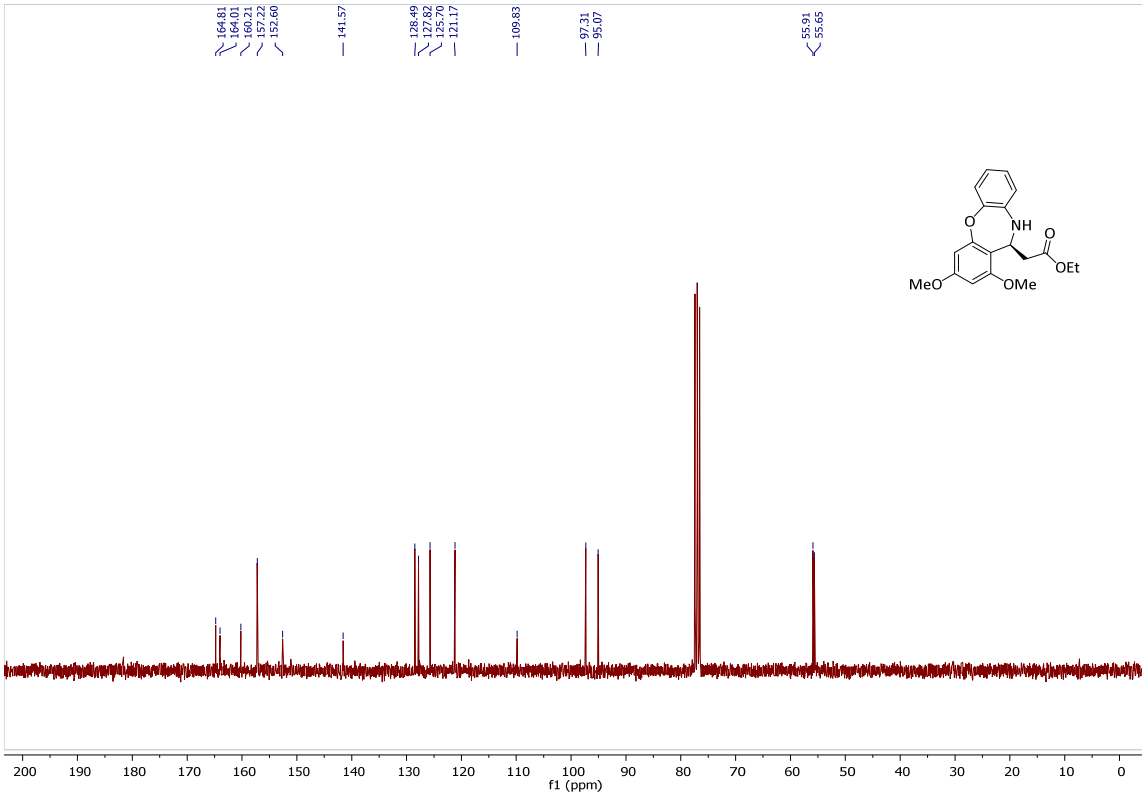
Ethyl (*S*)-2-(4-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3j)



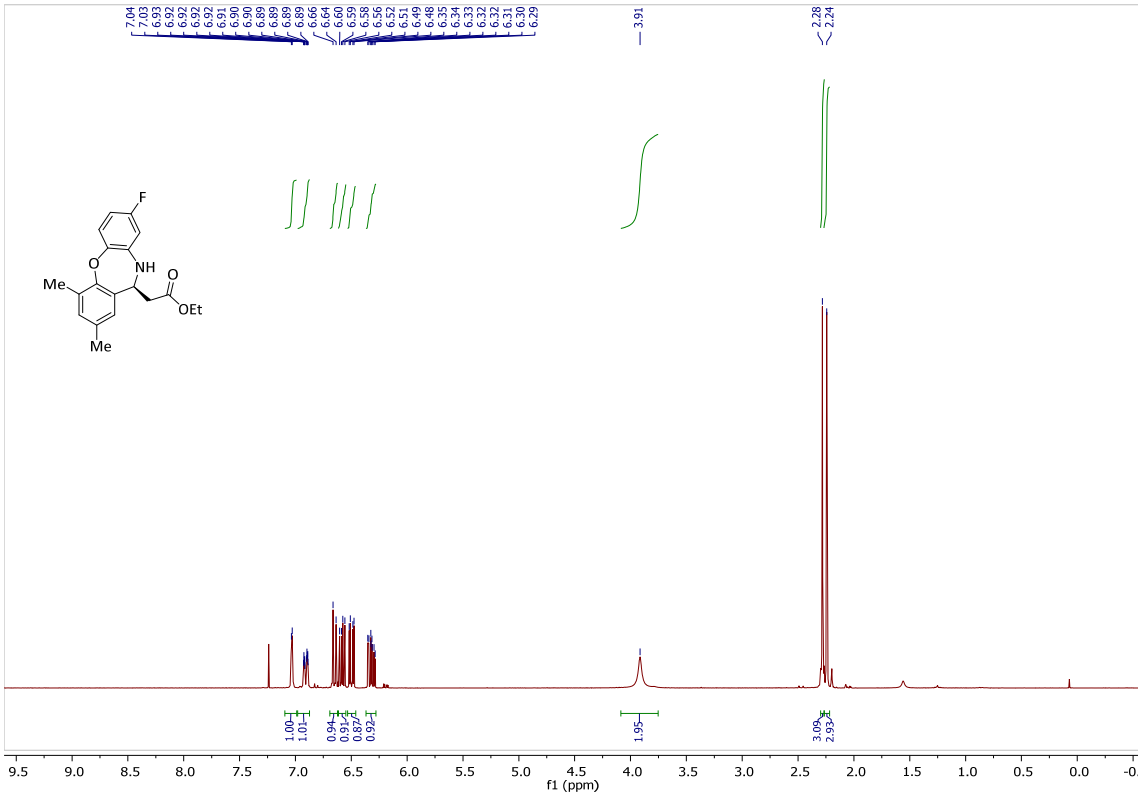


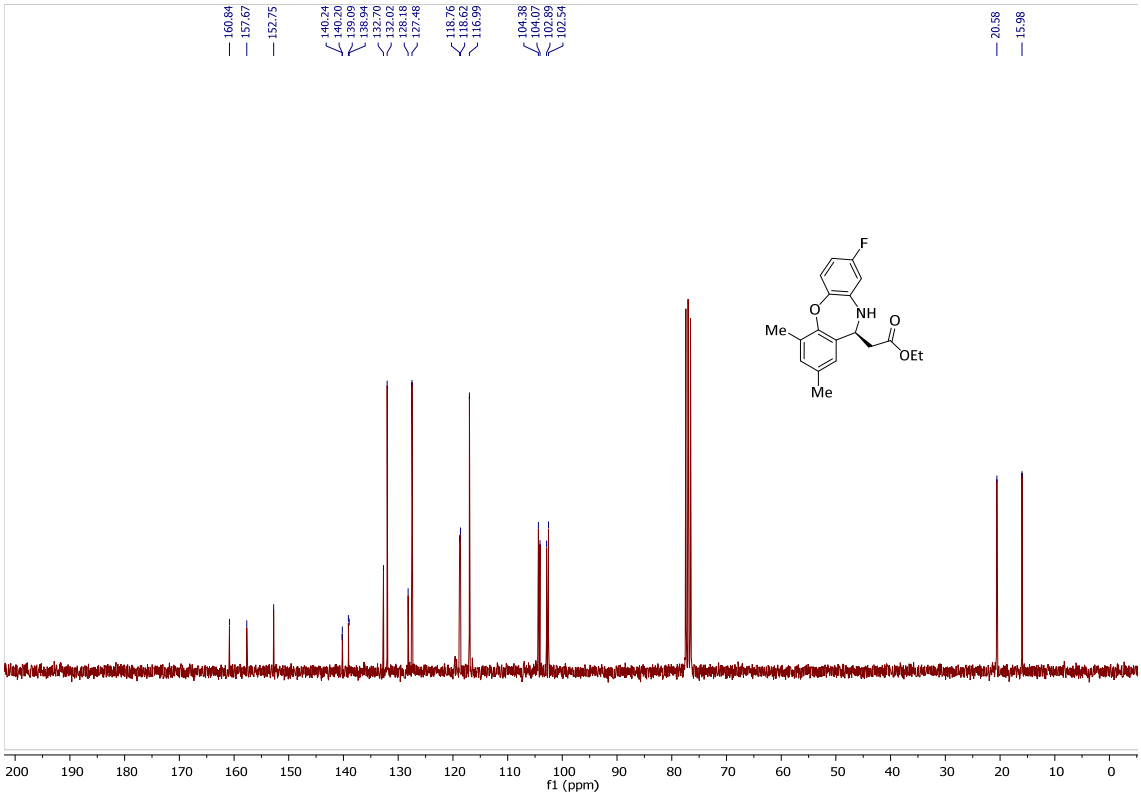
Ethyl (*S*)-2-(1,3-dimethoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3k)



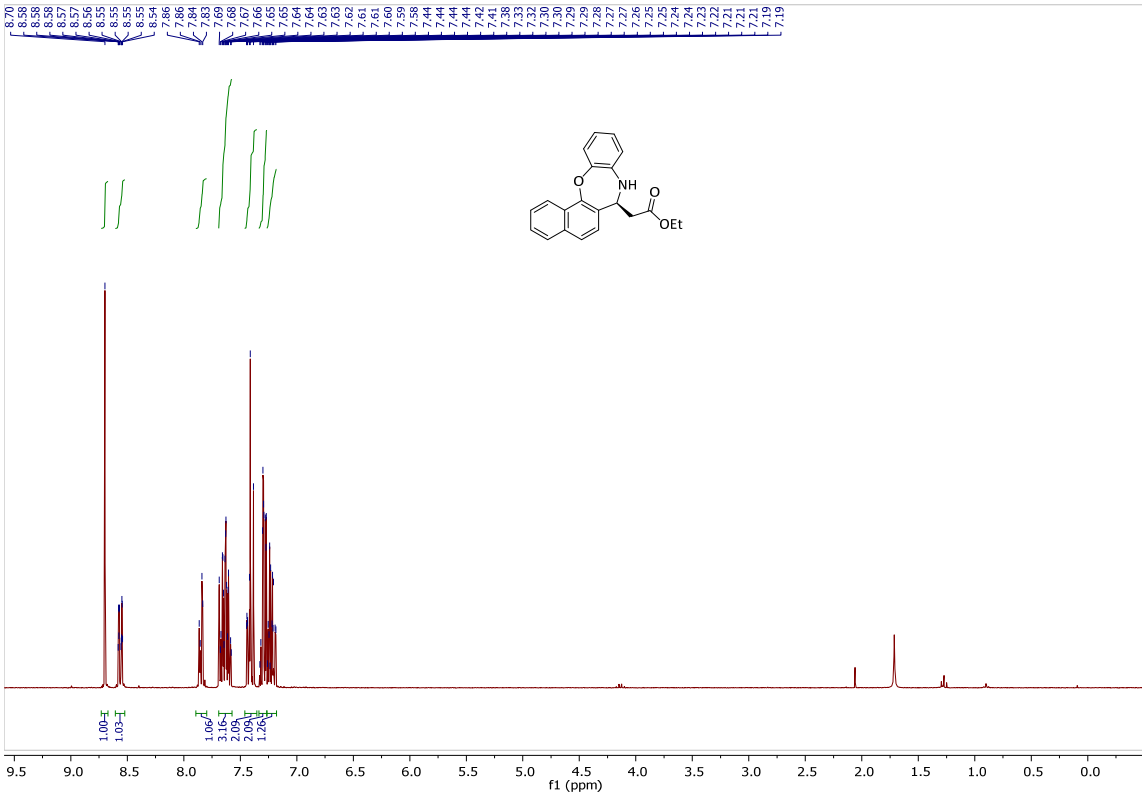


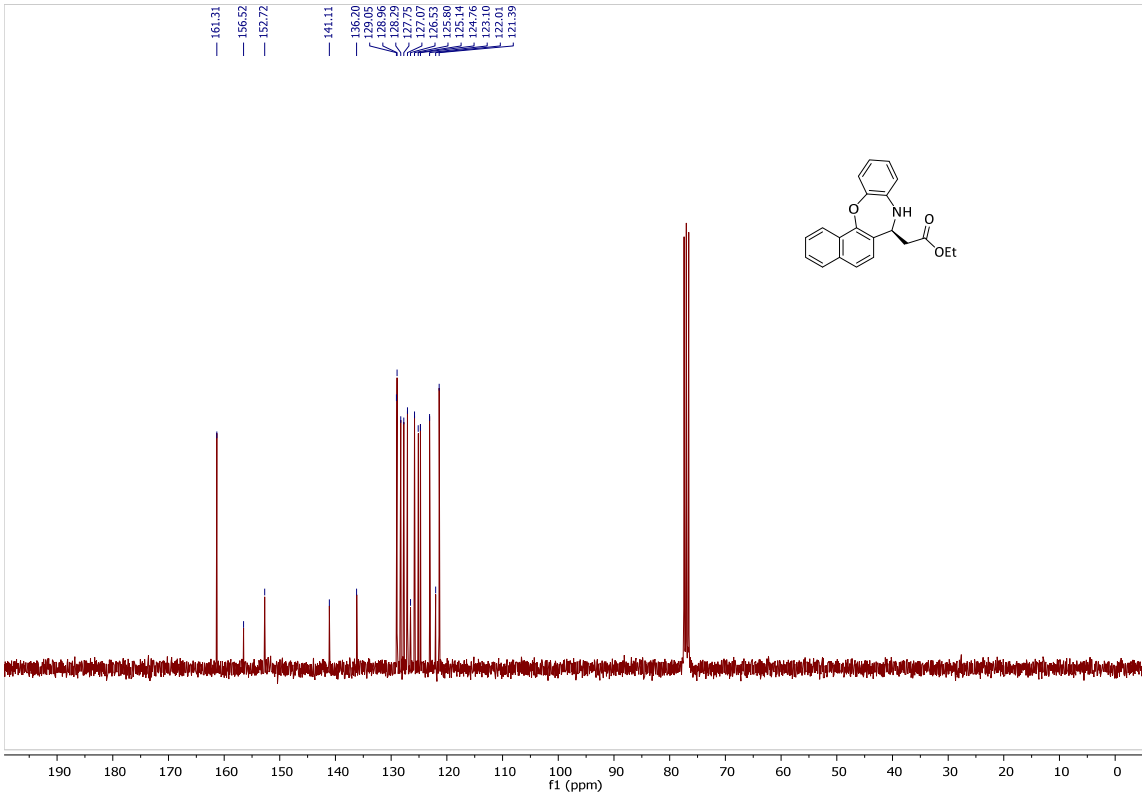
Ethyl (*S*)-2-(8-fluoro-2,4-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3l)



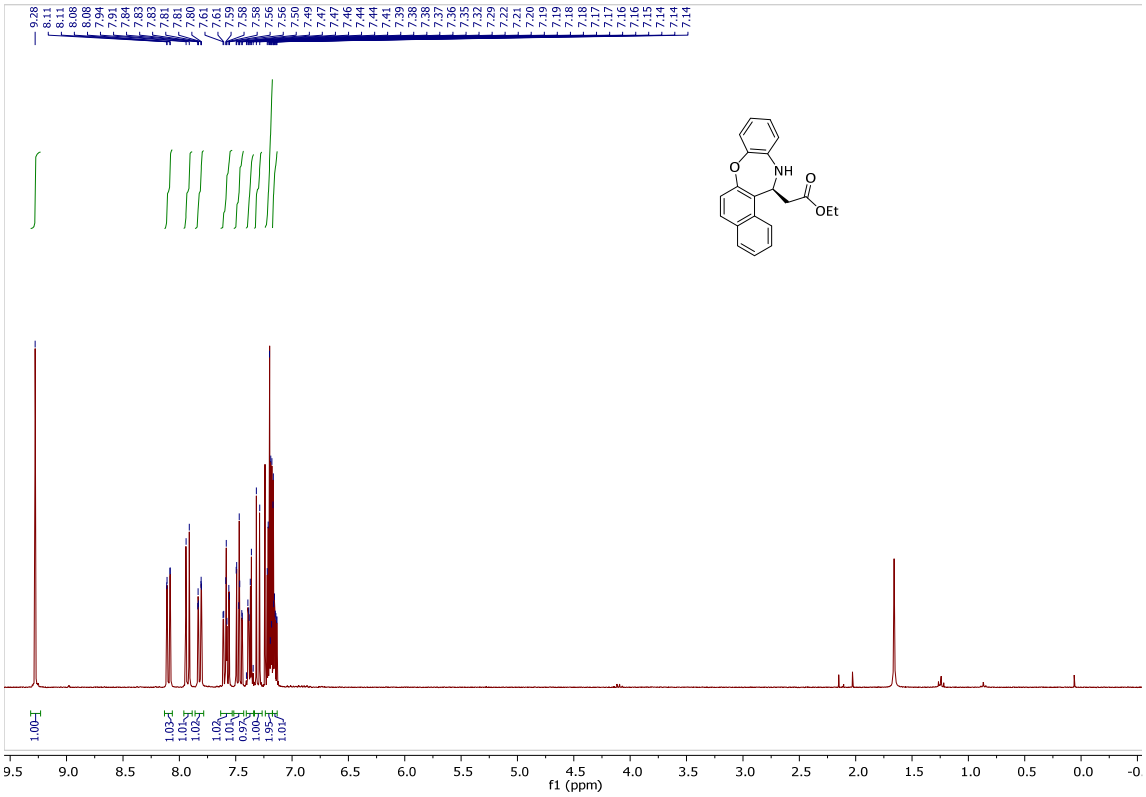


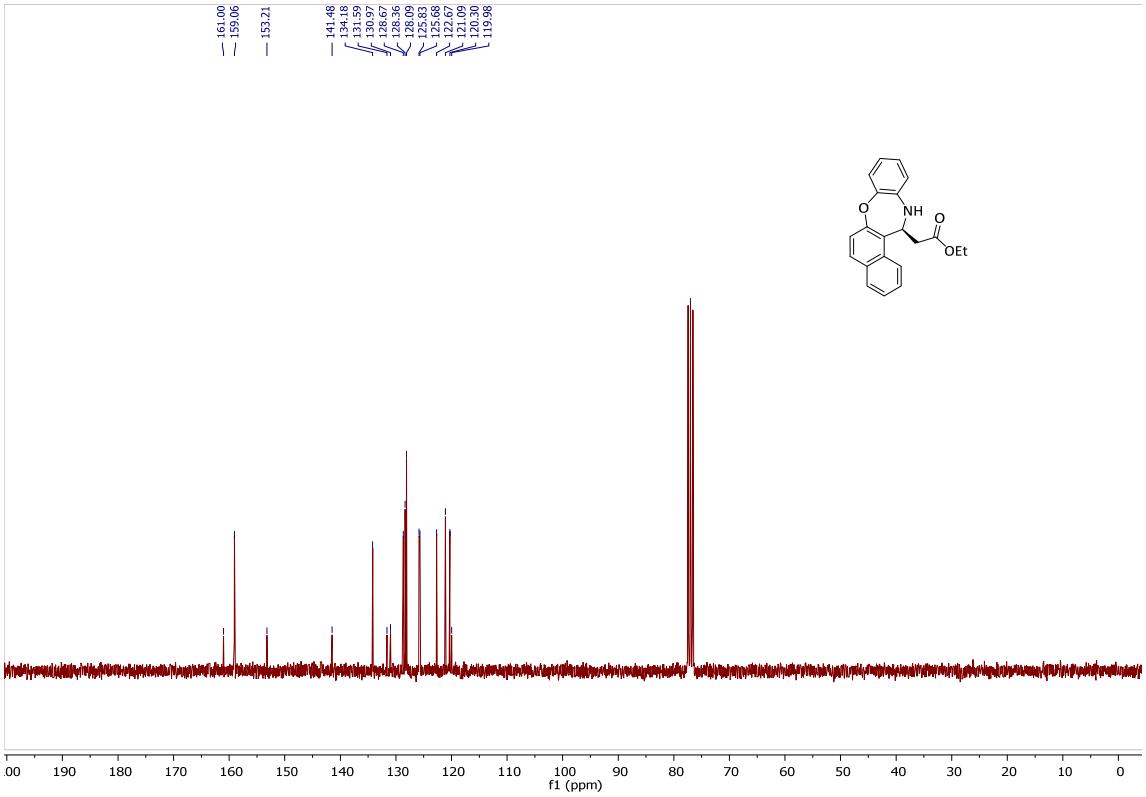
Ethyl (*S*)-2-(7,8-dihydrobenzo[*b*]naphtho[2,1-*f*][1,4]oxazepin-7-yl)acetate (3m)



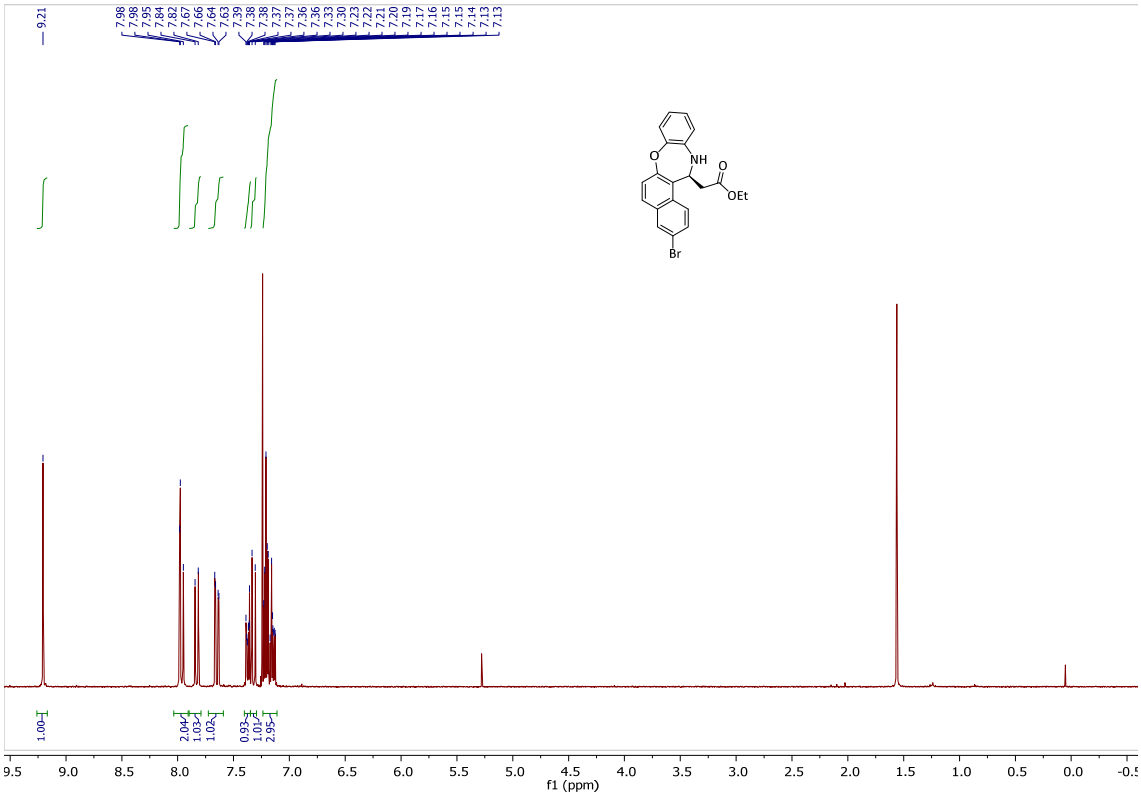


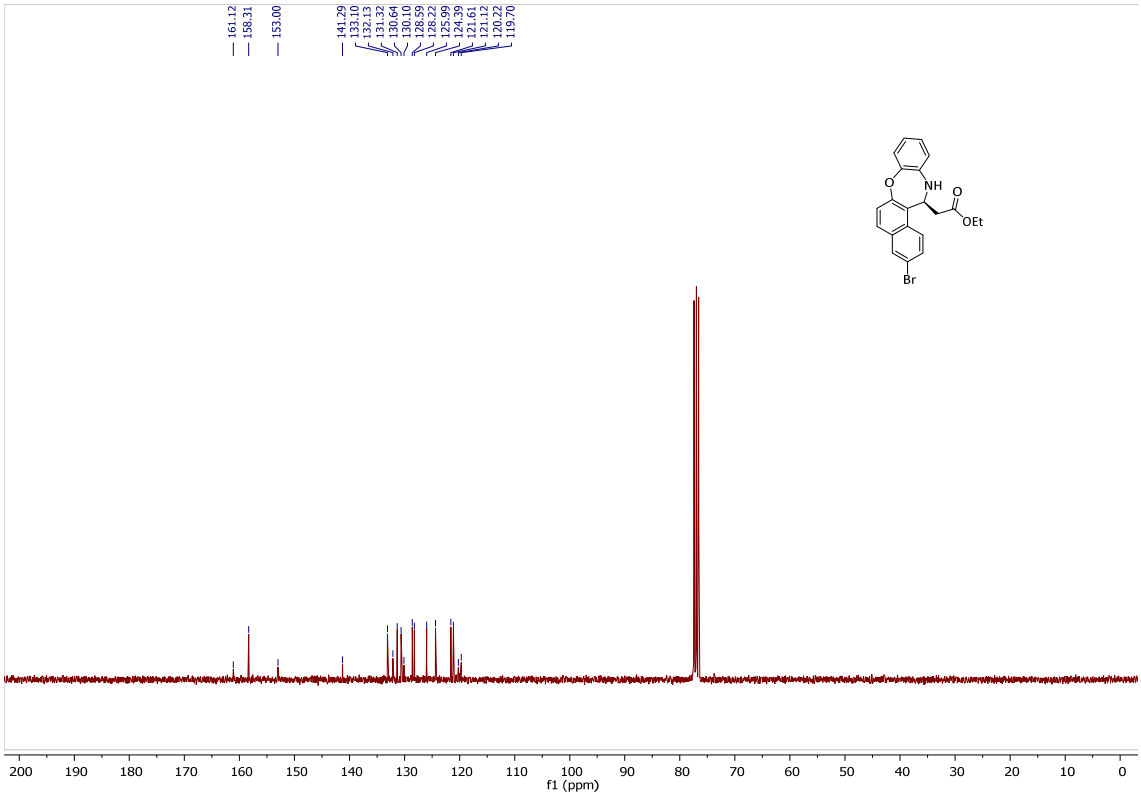
Ethyl (*S*)-2-(12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3n)



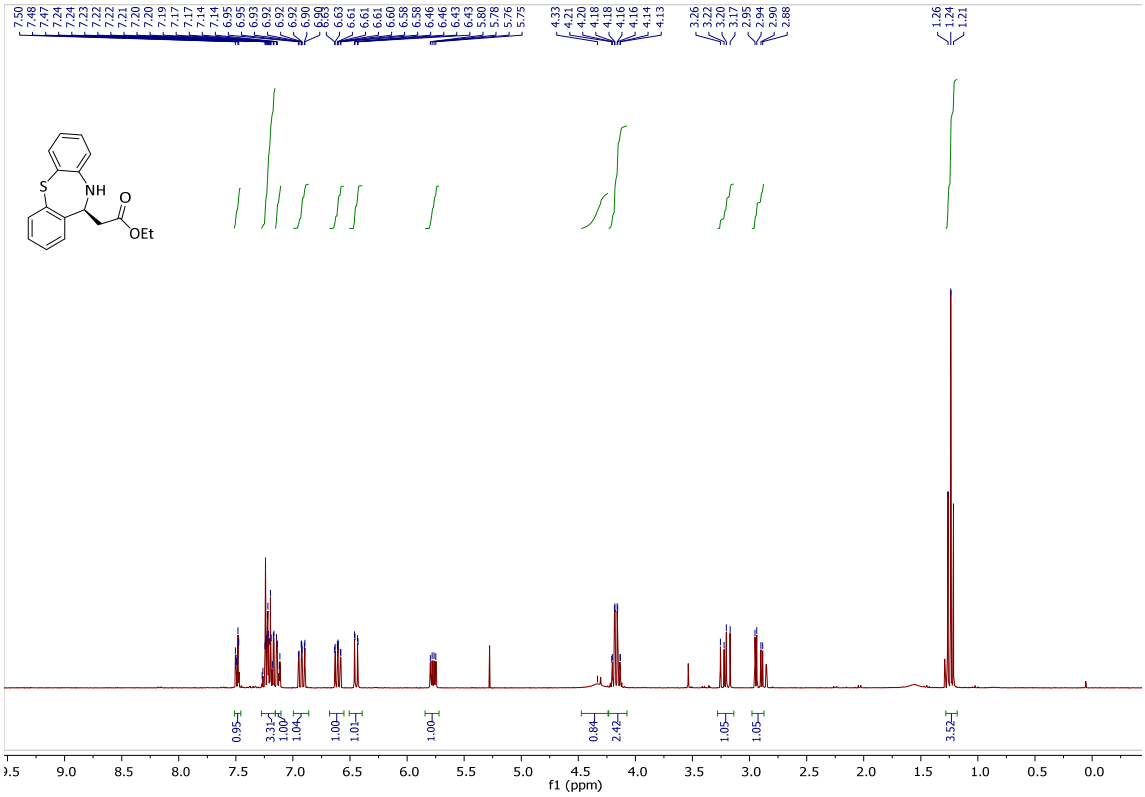


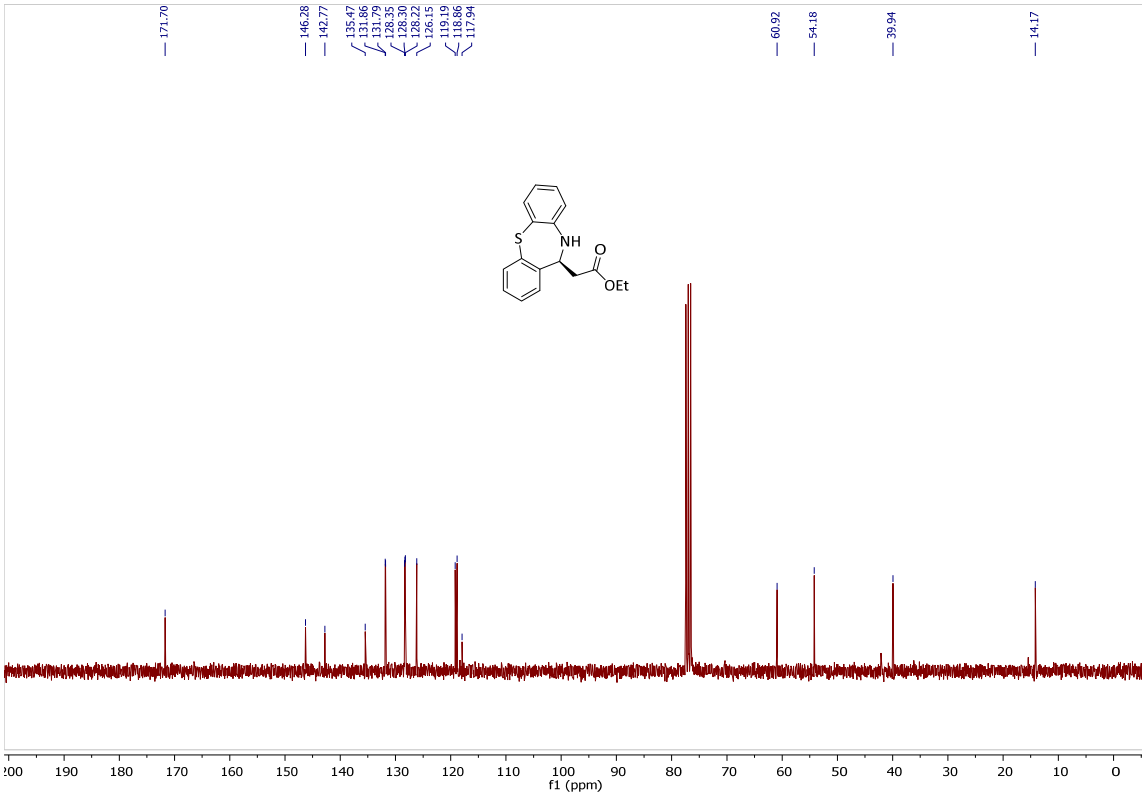
Ethyl (*S*)-2-(3-bromo-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3o)



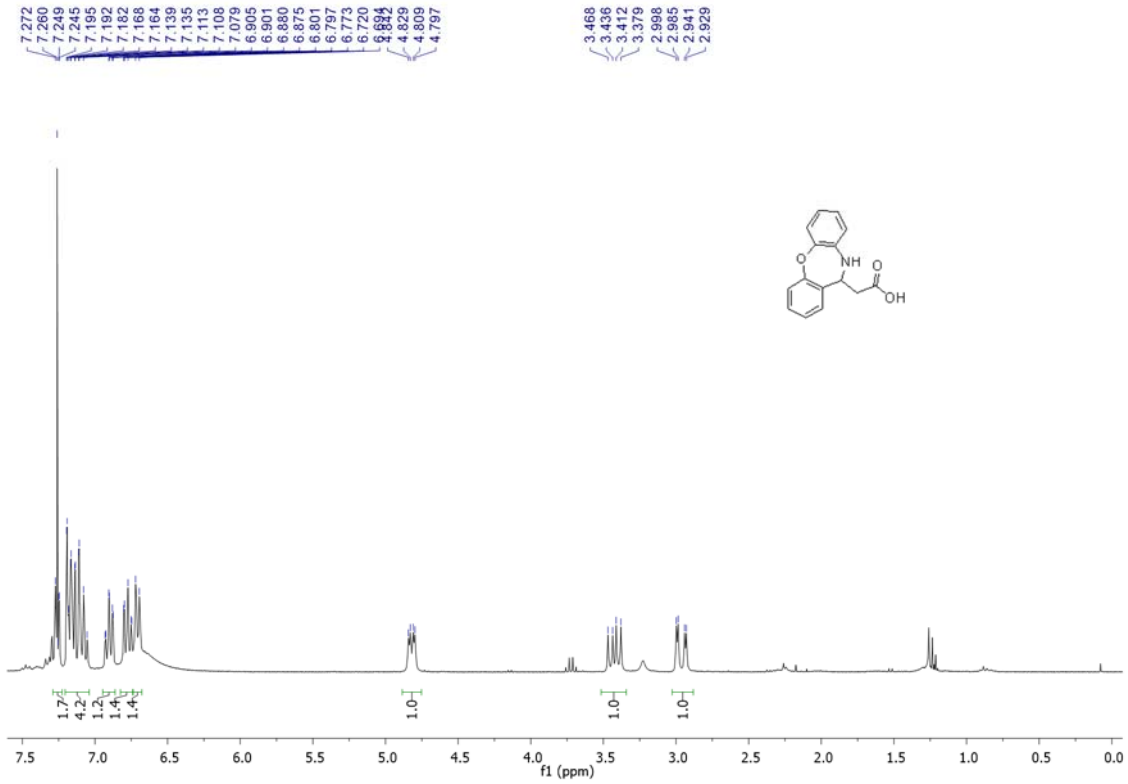


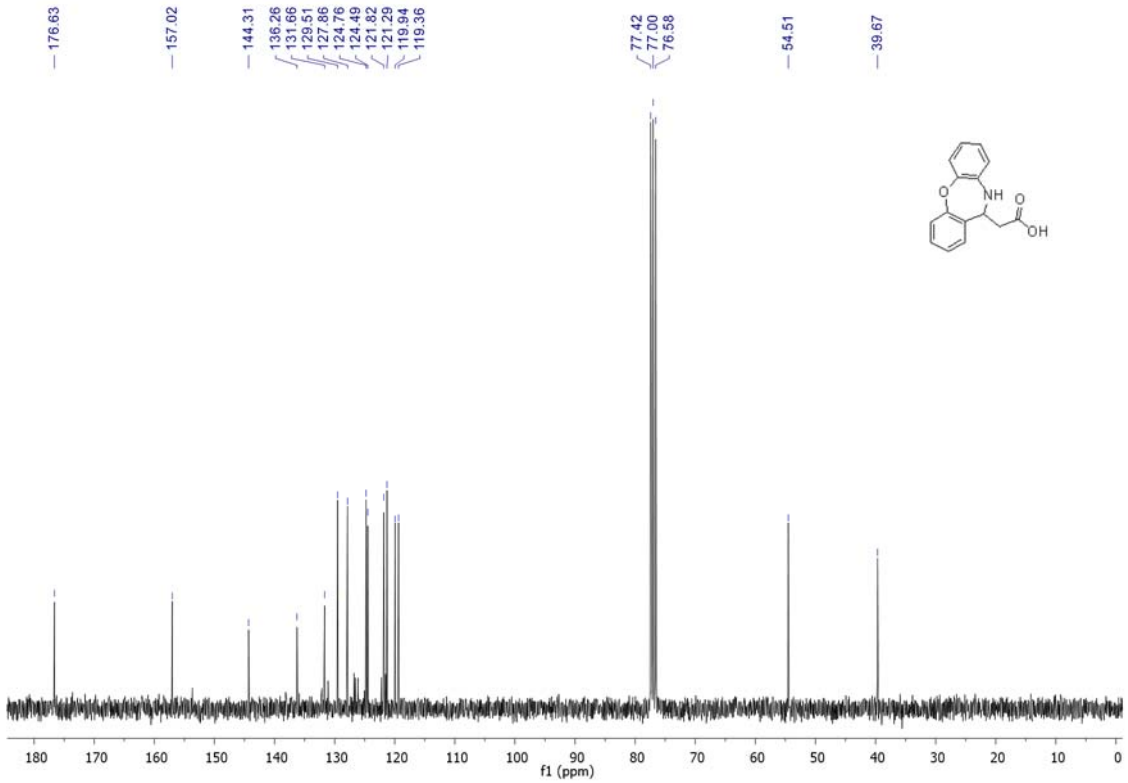
Ethyl (*S*)-2- (10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)acetate (5)



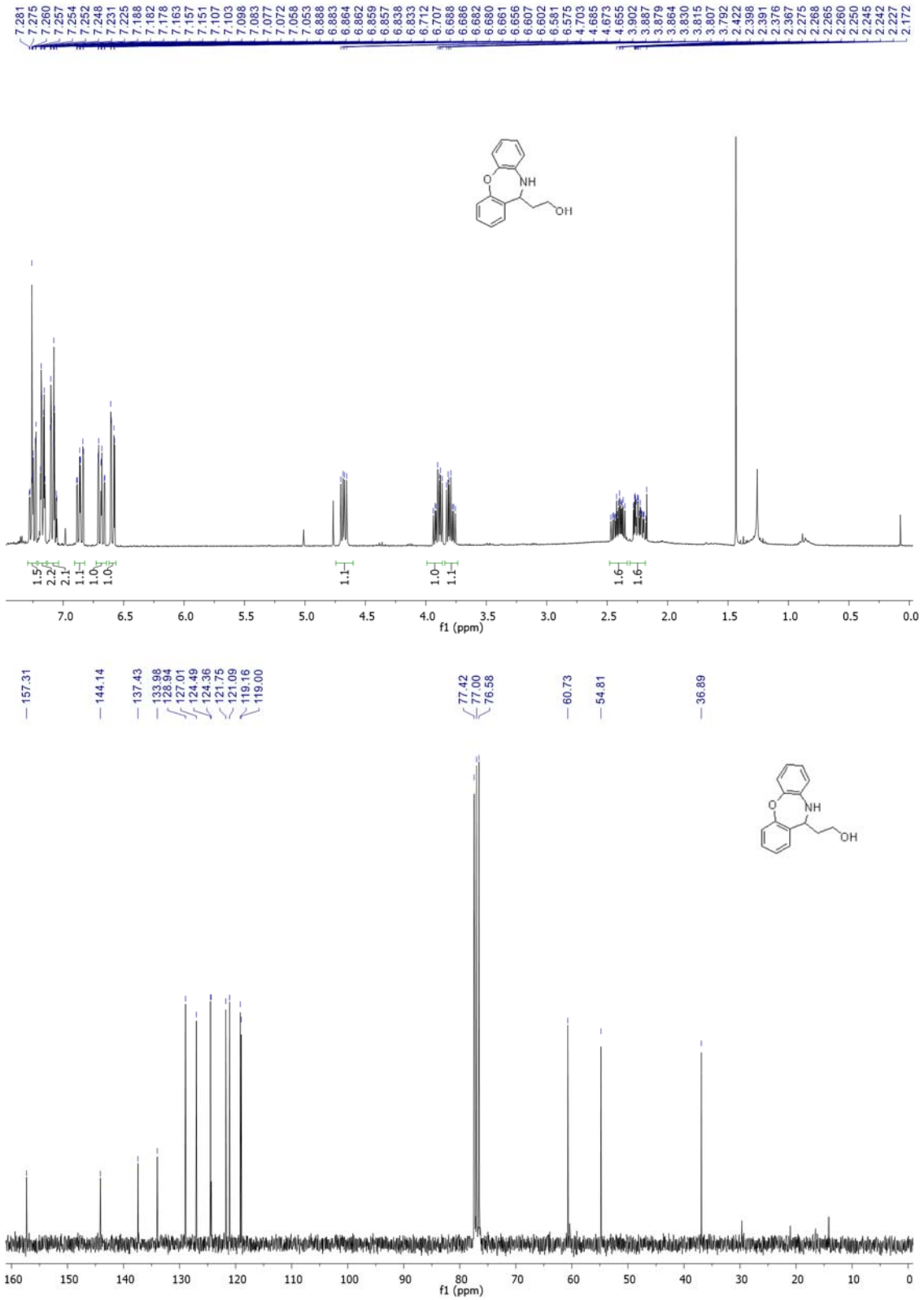


2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetic acid (6)

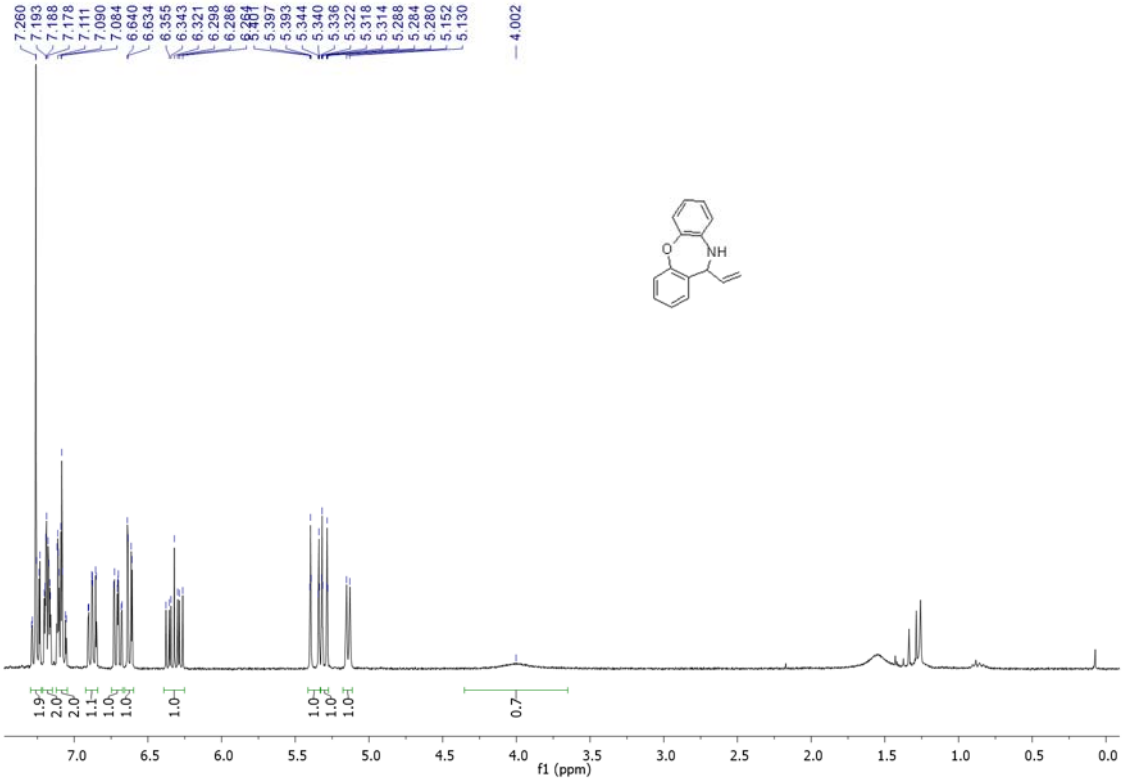


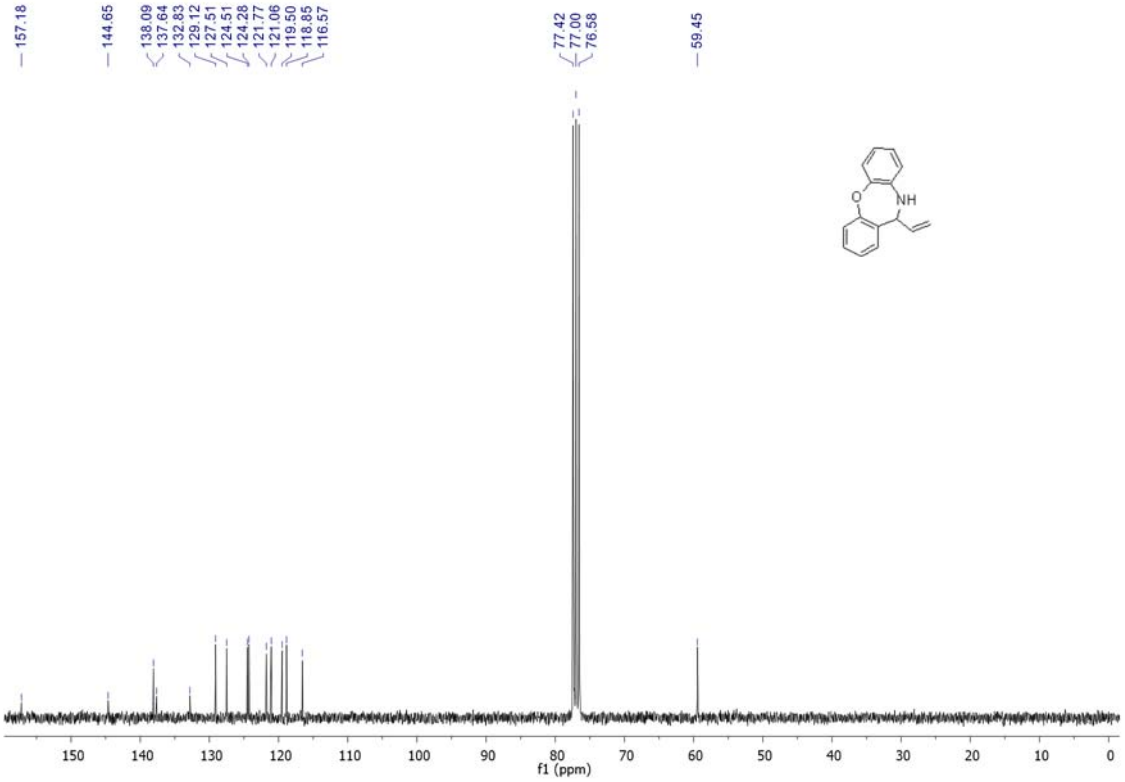


2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)ethan-1-ol (7)

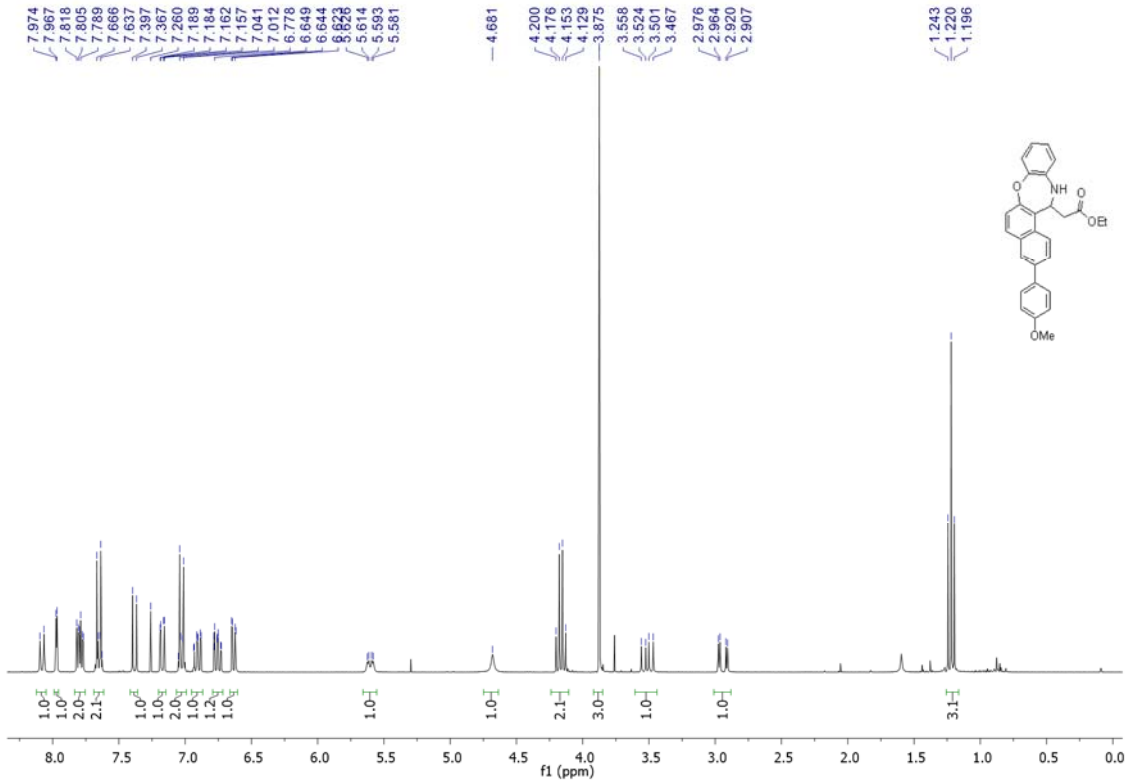


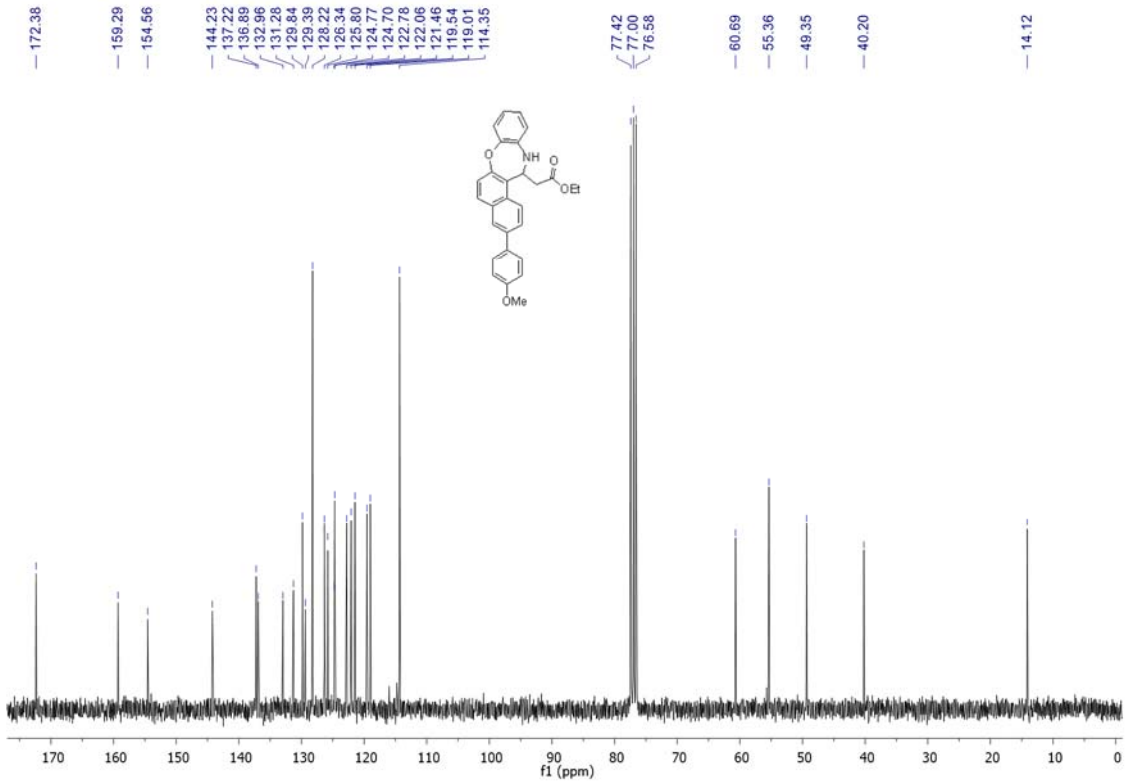
11-vinyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (8)



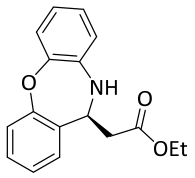


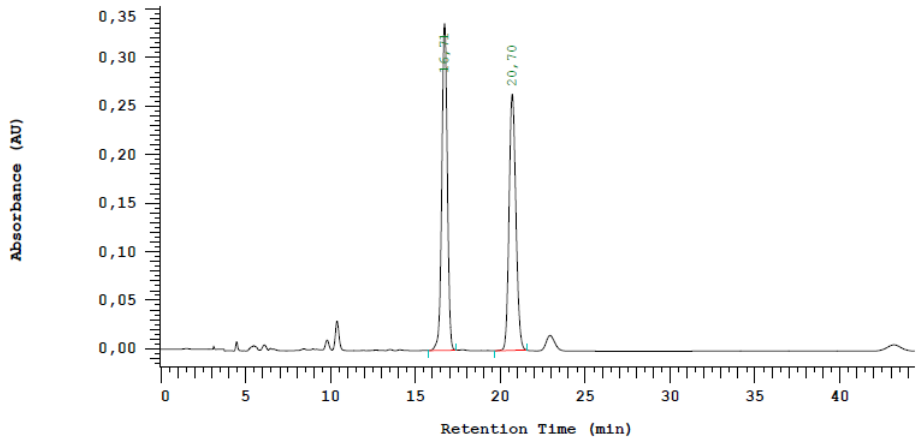
Ethyl 2-(3-(4-methoxyphenyl)-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (9)





Ethyl (S)-2-(10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3a)





No.	RT	Area	Area %	Name
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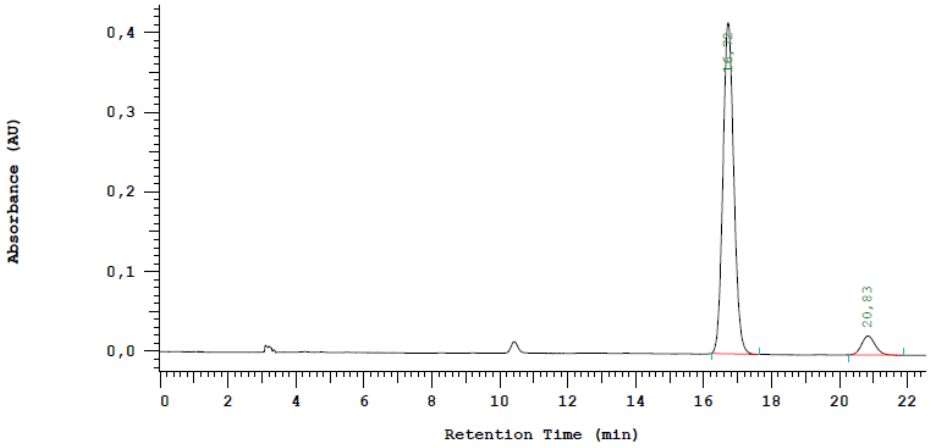
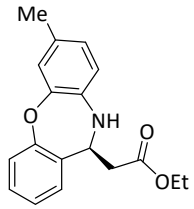
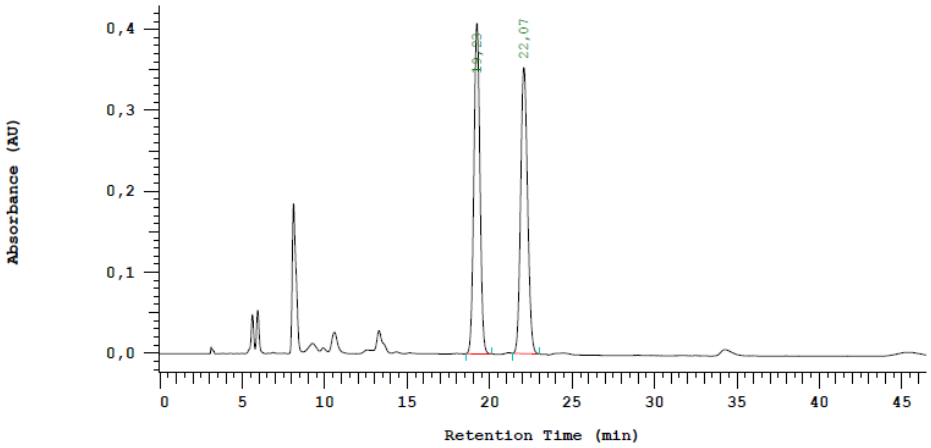
2	20,70	3621490	49,367	
		7335880	100,000	



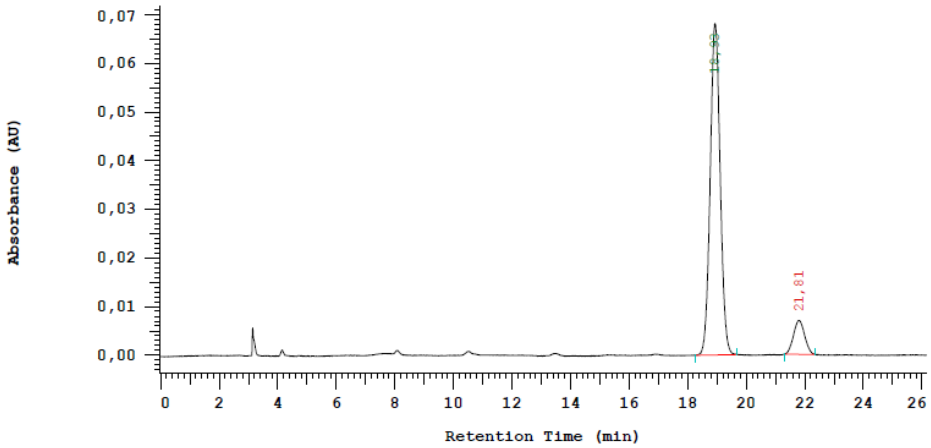
No.	RT	Area	Area %	Name
1	16,72	4600130	93,289	
2	20,83	330925	6,711	
		4931055	100,000	

Ethyl (S)-2-(7-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3b)



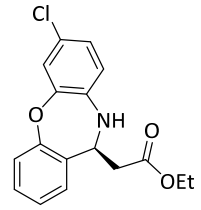


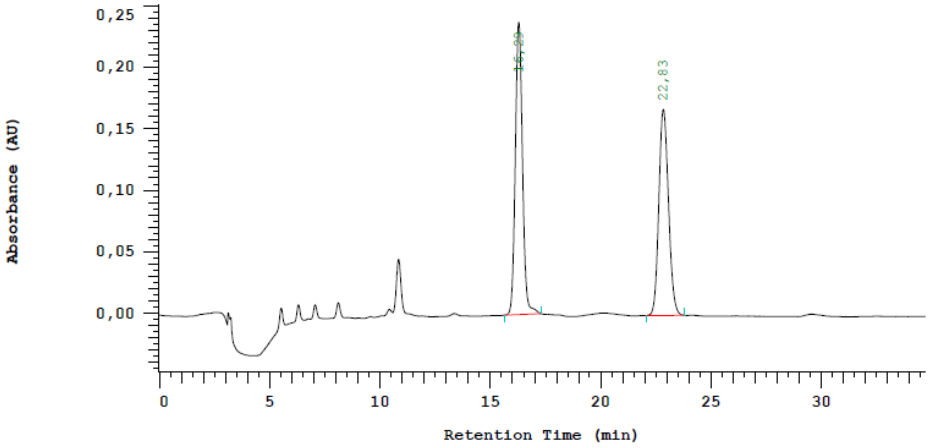
No.	RT	Area	Area %	Name
1	19,23	5084480	50,107	
2	22,07	5062755	49,893	enant. (+)
		10147235	100,000	



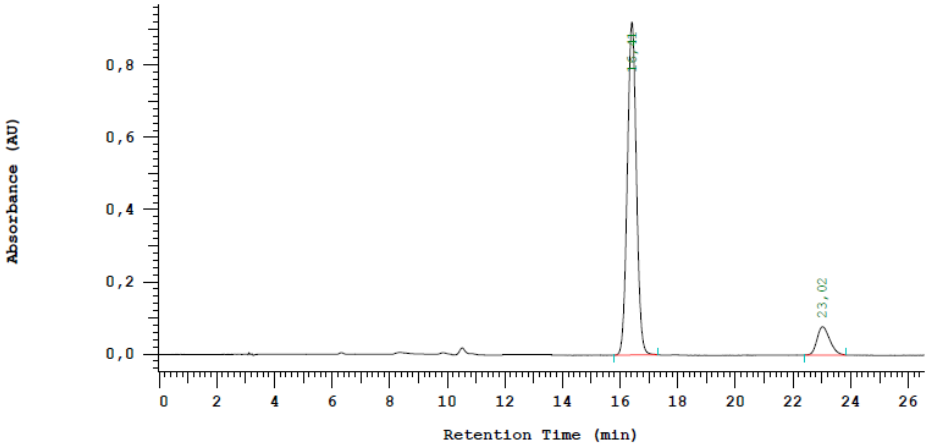
No.	RT	Area	Area %	Name
1	18,93	808160	89,676	
2	21,81	93040	10,324	enant. (+)
		901200	100,000	

Ethyl (S)-2-(7-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3c)



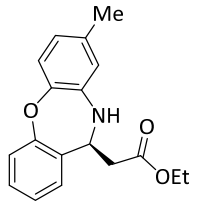


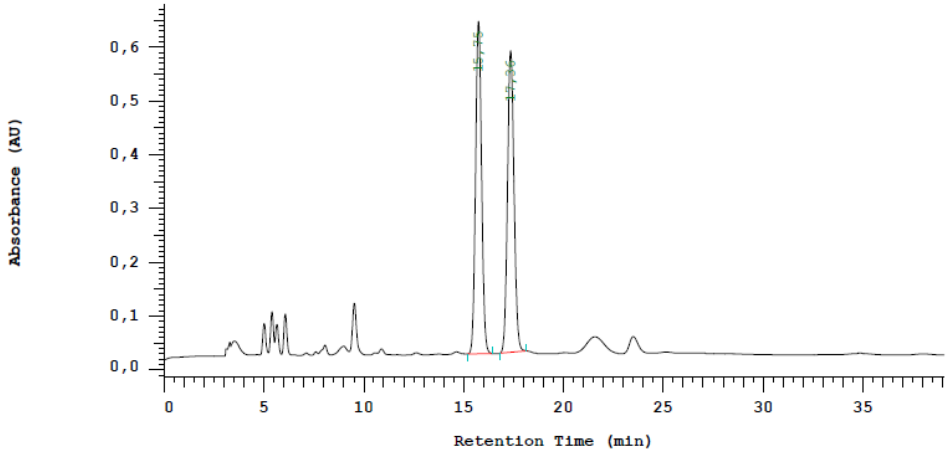
No.	RT	Area	Area %	Name
1	16,29	2642160	51,103	
2	22,83	2528140	48,897	enant. (+)
		5170300	100,000	



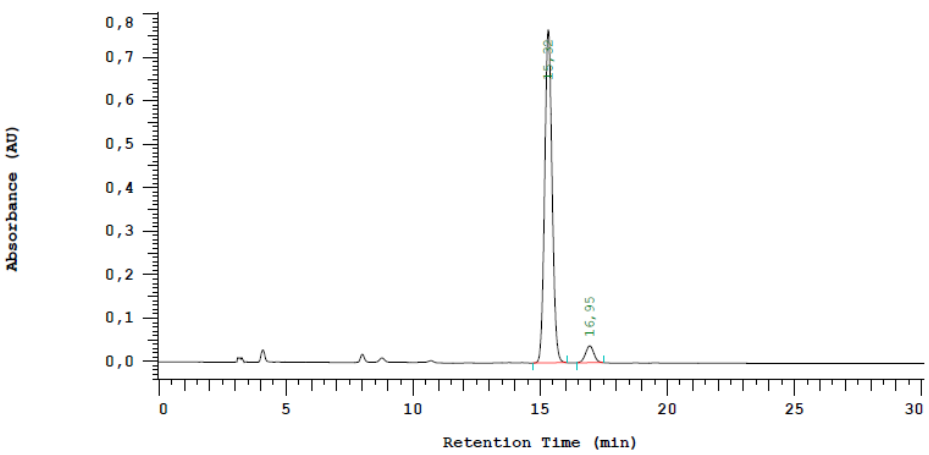
No.	RT	Area	Area %	Name
1	16,41	10036075	89,432	
2	23,02	1185890	10,568	enant. (+)
		11221965	100,000	

Ethyl (S)-2-(8-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3d)



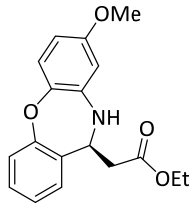


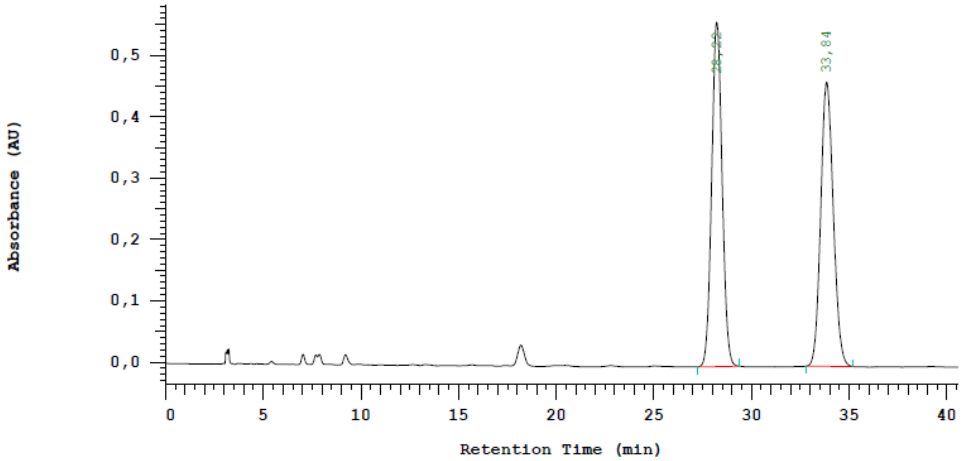
No.	RT	Area	Area %	Name
1	15,75	6367775	50,142	
2	17,36	6331740	49,858	
		12699515	100,000	



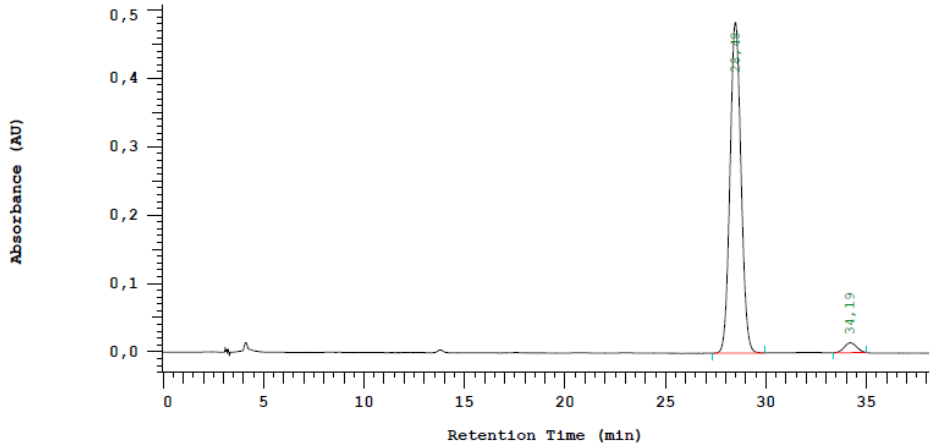
No.	RT	Area	Area %	Name
1	15,32	7685840	94,637	
2	16,95	435590	5,363	
		8121430	100,000	

Ethyl (S)-2-(8-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3e)



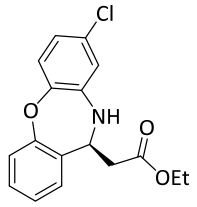


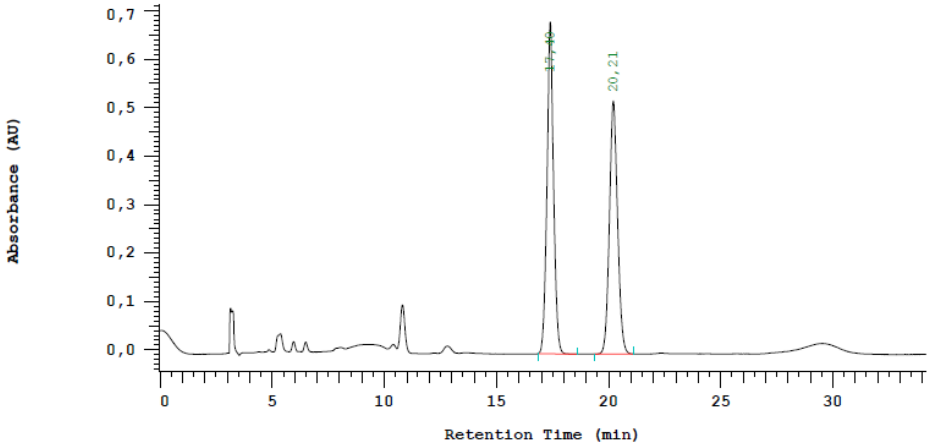
No.	RT	Area	Area %	Name
1	28,22	10291460	49,877	enanti (-)
2	33,84	10342380	50,123	
		20633840	100,000	



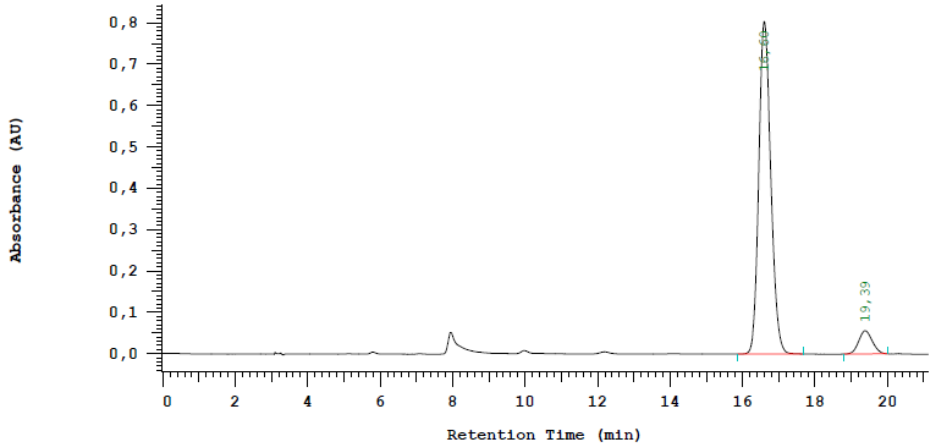
No.	RT	Area	Area %	Name
1	28,48	9120240	96,746	enanti (-)
2	34,19	306790	3,254	
		9427030	100,000	

Ethyl (S)-2-(8-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3f)



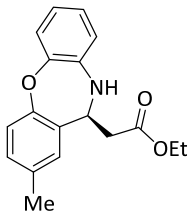


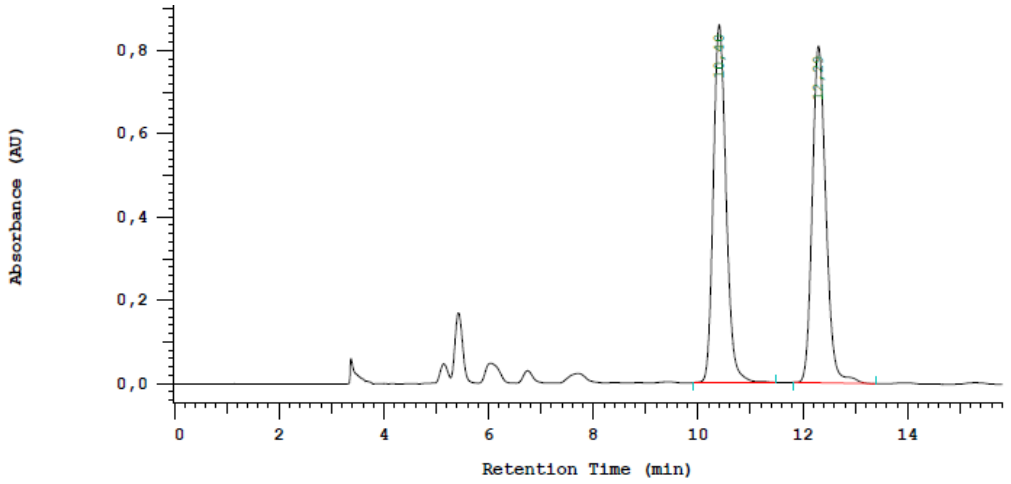
No.	RT	Area	Area %	Name
1	17,40	6837904	51,261	
2	20,21	6501524	48,739	
		13339428	100,000	



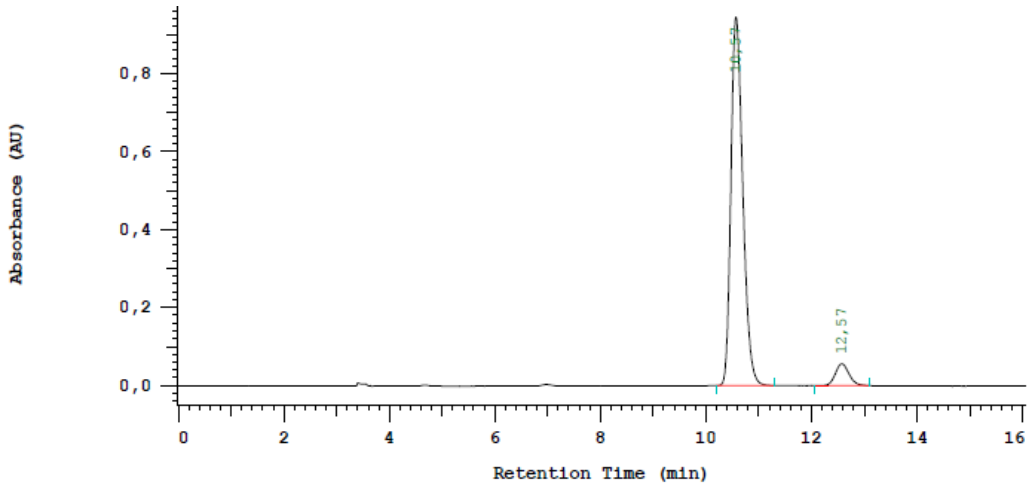
No.	RT	Area	Area %	Name
1	16,60	9261500	92,644	
2	19,39	735330	7,356	
		9996830	100,000	

Ethyl (*S*)-2-(2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3g)



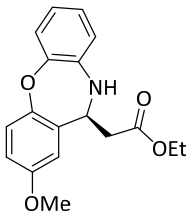


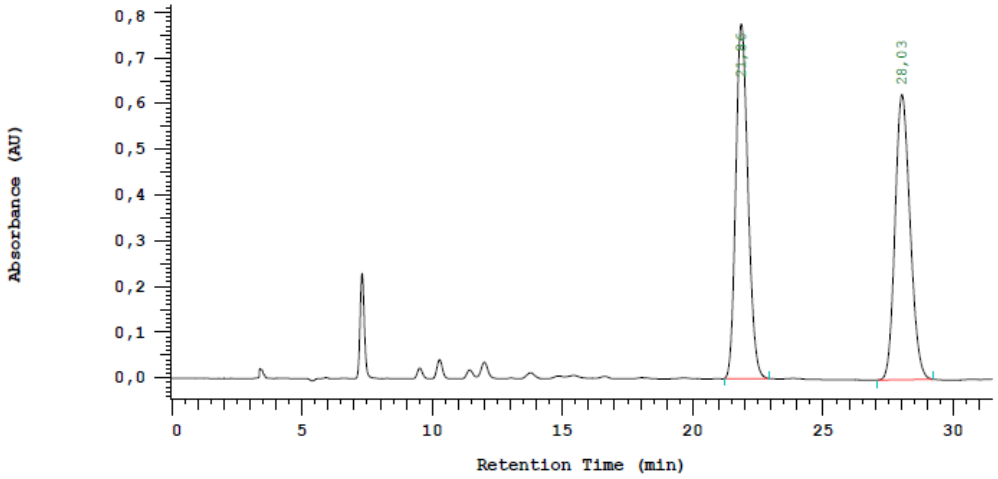
No.	RT	Area	Area %	Name
1	10,40	7325590	49,799	
2	12,29	7384630	50,201	
		14710220	100,000	



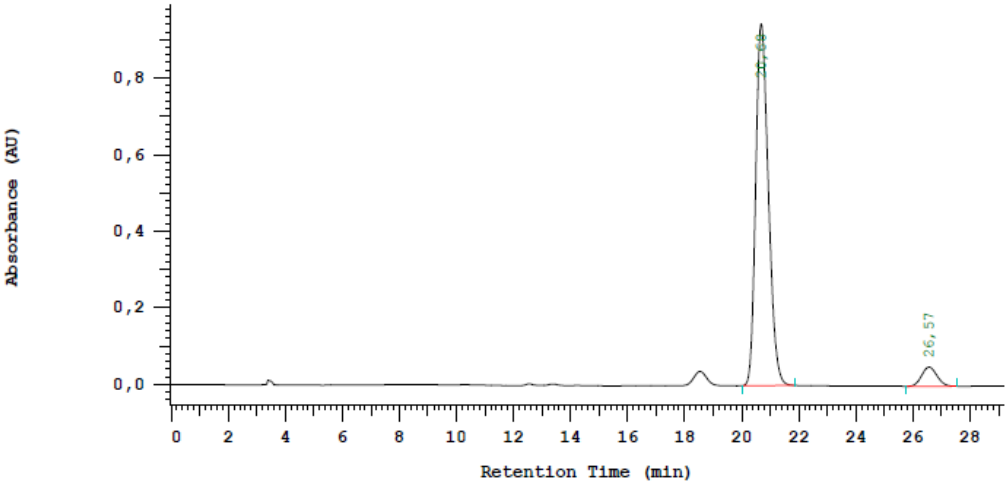
No.	RT	Area	Area %	Name
1	10,57	7399630	93,609	
2	12,57	505220	6,391	
		7904850	100,000	

Ethyl (*S*)-2-(2-methoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3h)



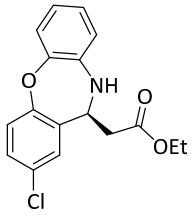


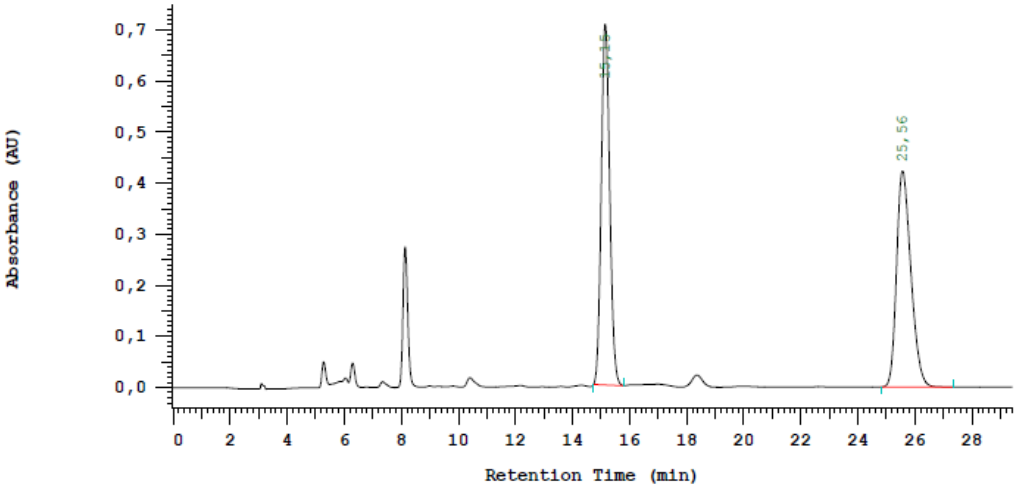
No.	RT	Area	Area %	Name
1	21,86	12482475	49,975	enant. (+)
2	28,03	12494870	50,025	enanti (-)
		24977345	100,000	



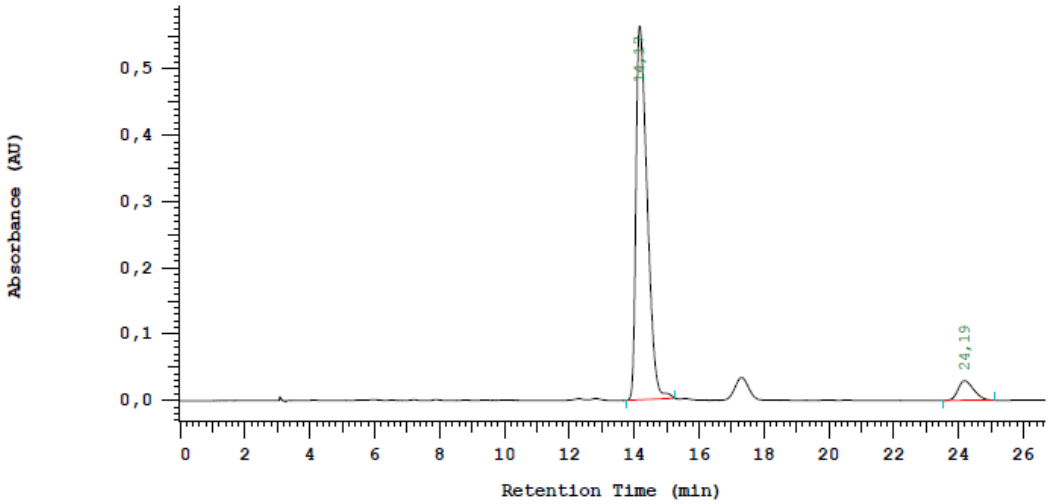
No.	RT	Area	Area %	Name
1	20,68	14478140	93,898	
2	26,57	940870	6,102	enanti (-)
		15419010	100,000	

Ethyl (*S*)-2-(2-chloro-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3i)



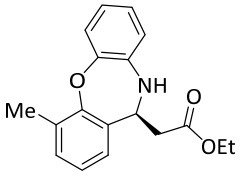


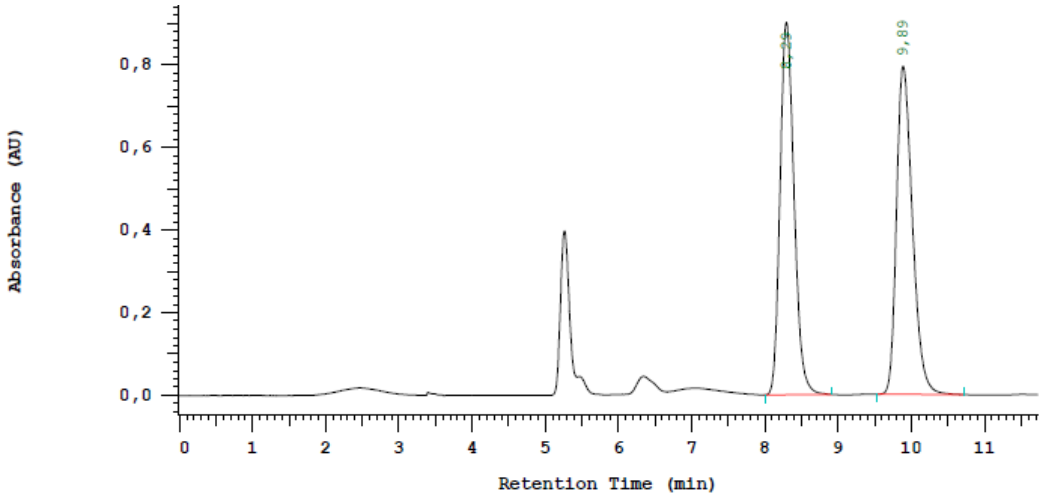
No.	RT	Area	Area %	Name
1	15,15	7203249	49,556	
2	25,56	7332464	50,444	enant. (+)
		14535713	100,000	



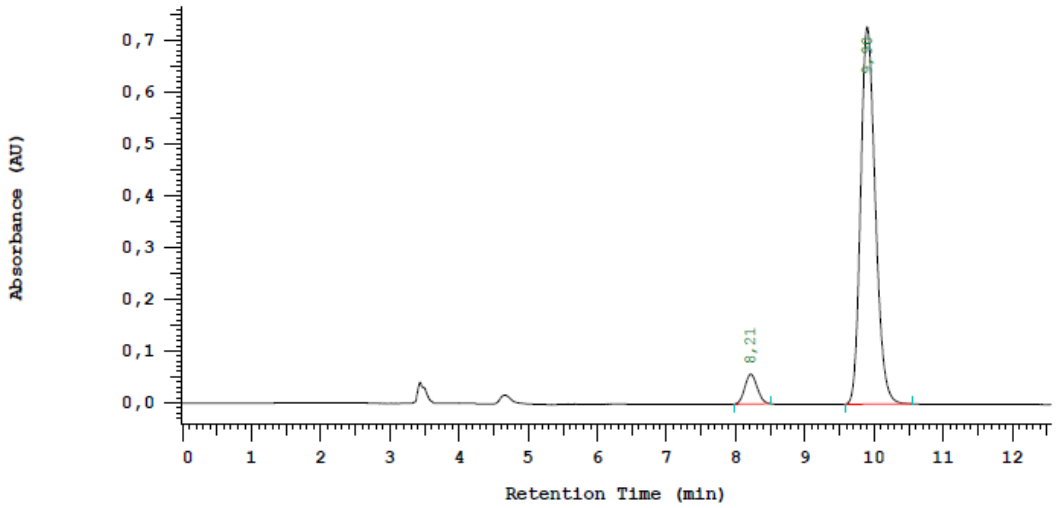
No.	RT	Area	Area %	Name
1	14,17	6697370	93,151	
2	24,19	492460	6,849	enant. (+)
		7189830	100,000	

Ethyl (*S*)-2-(4-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3j)



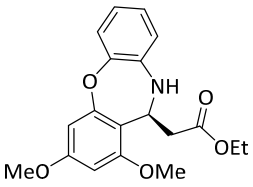


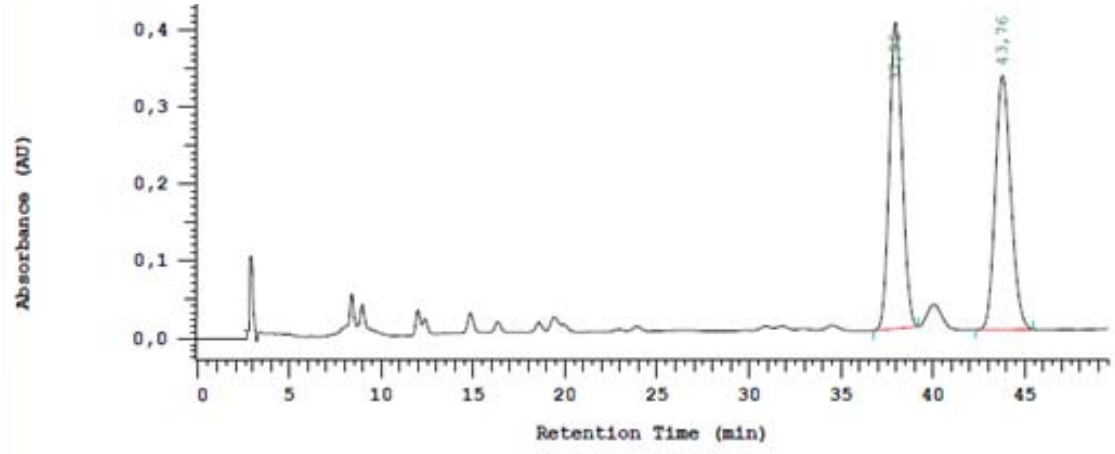
No.	RT	Area	Area %	Name
1	8,29	6004440	49,931	
2	9,89	6021030	50,069	
		12025470	100,000	



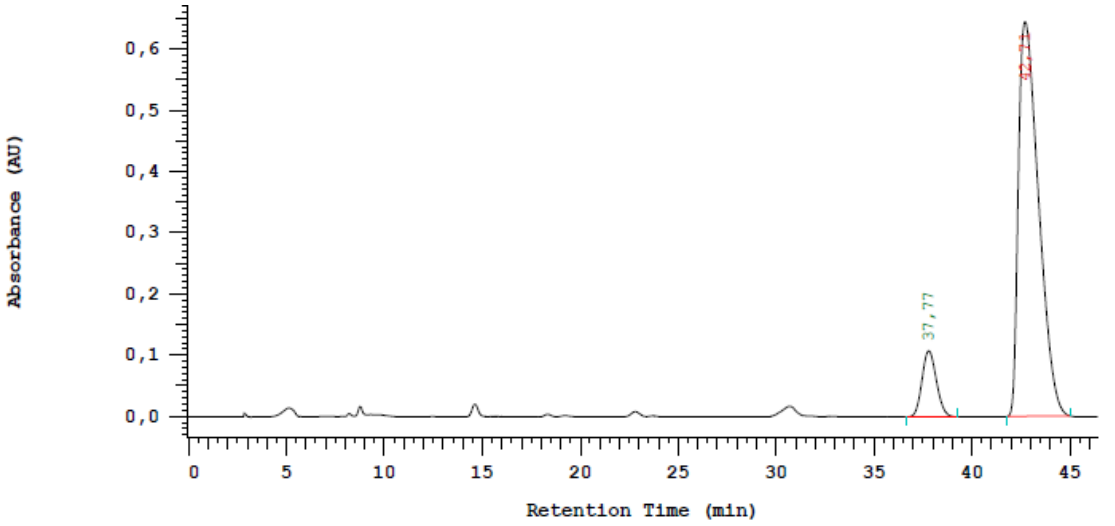
No.	RT	Area	Area %	Name
1	8,21	356210	6,200	
2	9,90	5388870	93,800	
		5745080	100,000	

Ethyl (*S*)-2-(1,3-dimethoxy-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3k)



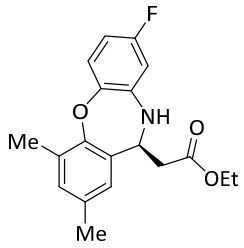


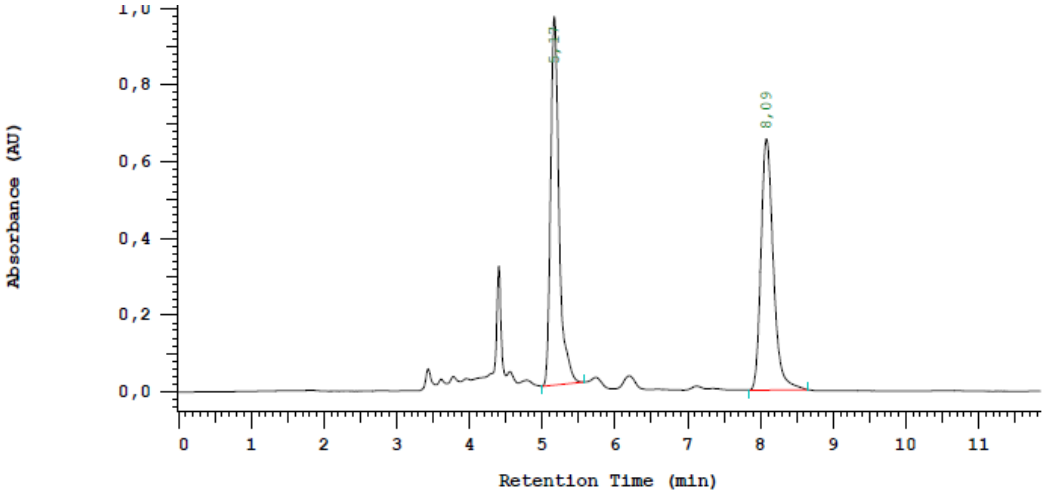
No.	RT	Area	Area %	Name
1	37,95	9697089	49,829	
2	43,76	9763660	50,171	
		19460749	100,000	



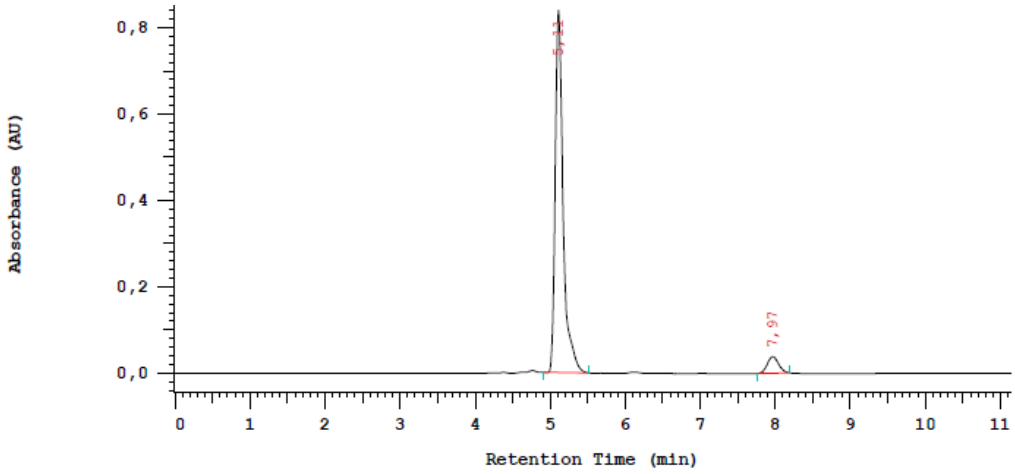
No.	RT	Area	Area %	Name
1	37,77	2727000	10,676	
2	42,71	22815390	89,324	
		25542390	100,000	

Ethyl (*S*)-2-(8-fluoro-2,4-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetate (3l)



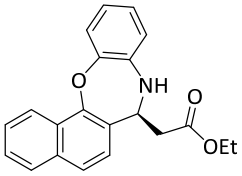


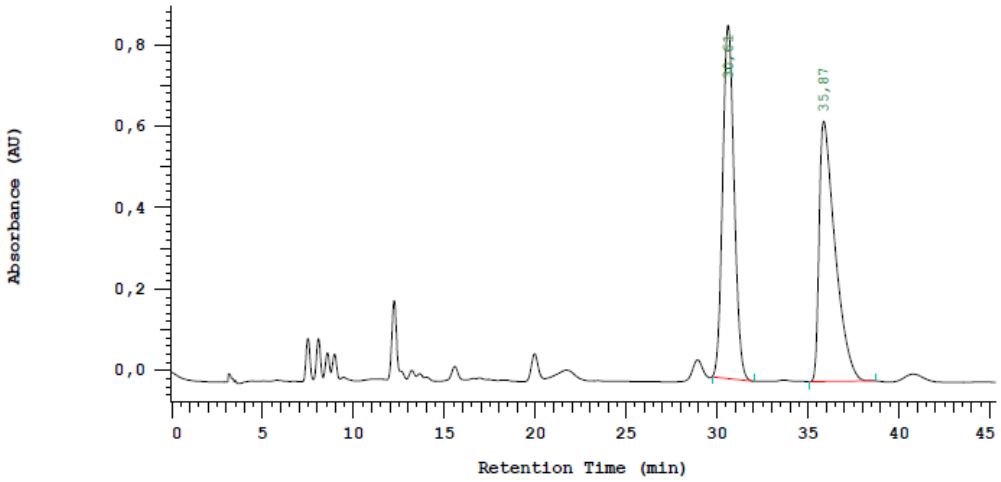
No.	RT	Area	Area %	Name
1	5,17	3881890	50,295	
2	8,09	3836300	49,705	
		7718190	100,000	



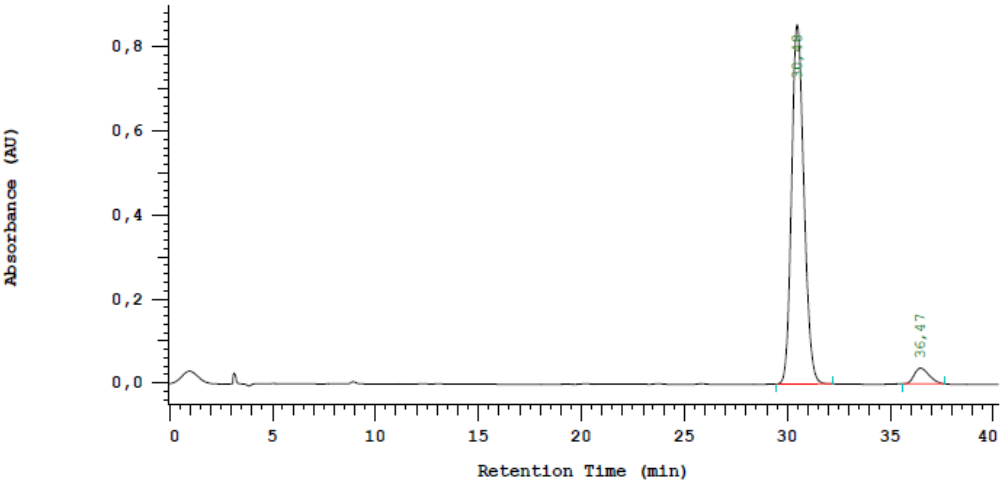
No.	RT	Area	Area %	Name
1	5,11	3052960	93,812	
2	7,97	201370	6,188	
		3254330	100,000	

Ethyl (*S*)-2-(7,8-dihydrobenzo[*b*]naphtho[2,1-*f*][1,4]oxazepin-7-yl)acetate (3m)



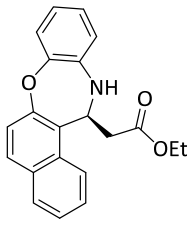


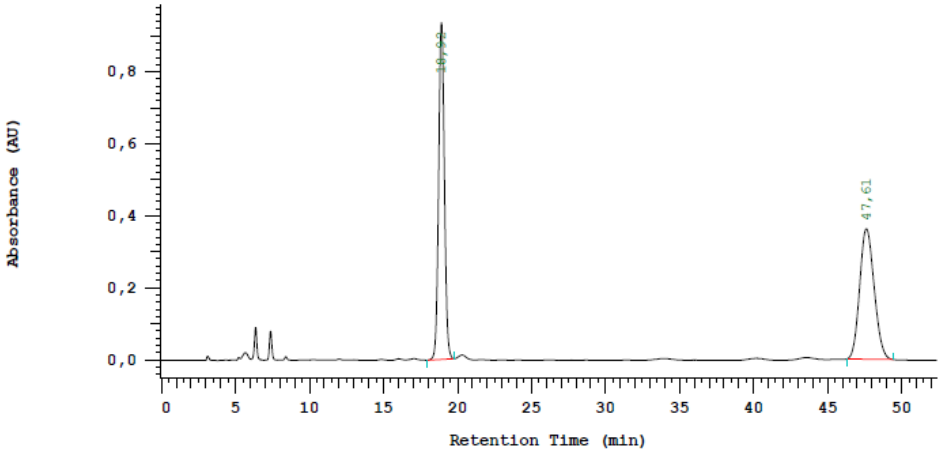
No.	RT	Area	Area %	Name
1	30,61	18810060	49,402	enanti (-)
2	35,87	19265120	50,598	
		38075180	100,000	



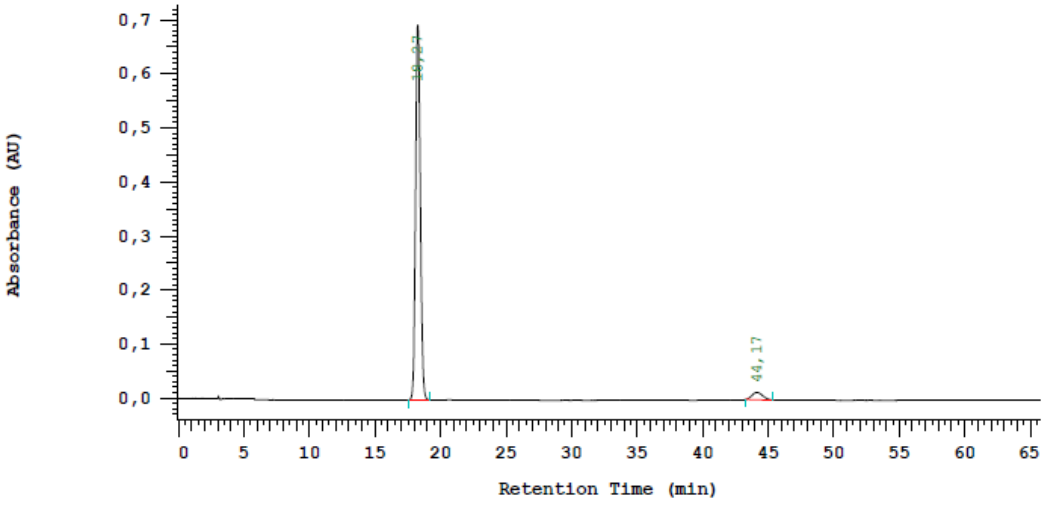
No.	RT	Area	Area %	Name
1	30,48	17606080	94,971	enanti (-)
2	36,47	932360	5,029	
		18538440	100,000	

Ethyl (*S*)-2-(12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3n)



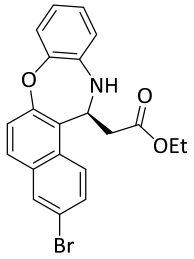


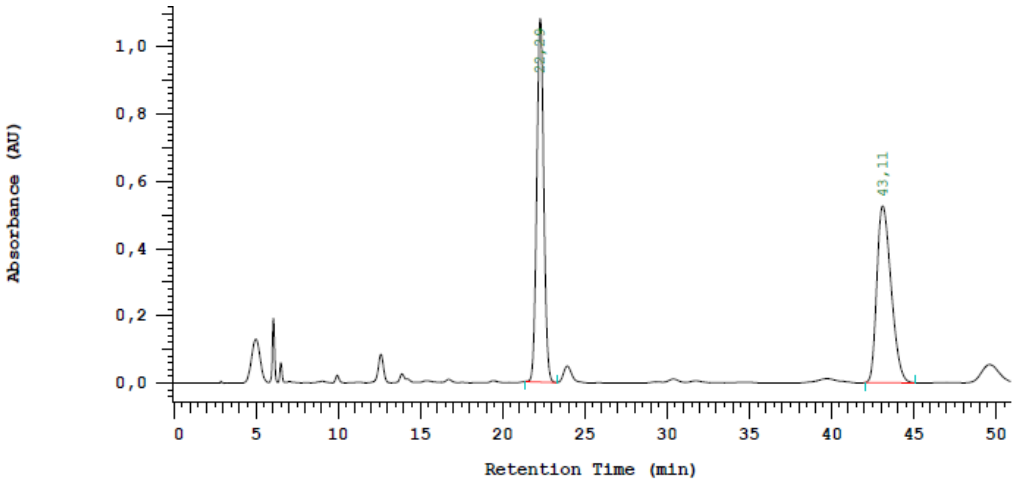
No.	RT	Area	Area %	Name
1	18,92	12366400	50,375	
2	47,61	12182190	49,625	
		24548590	100,000	



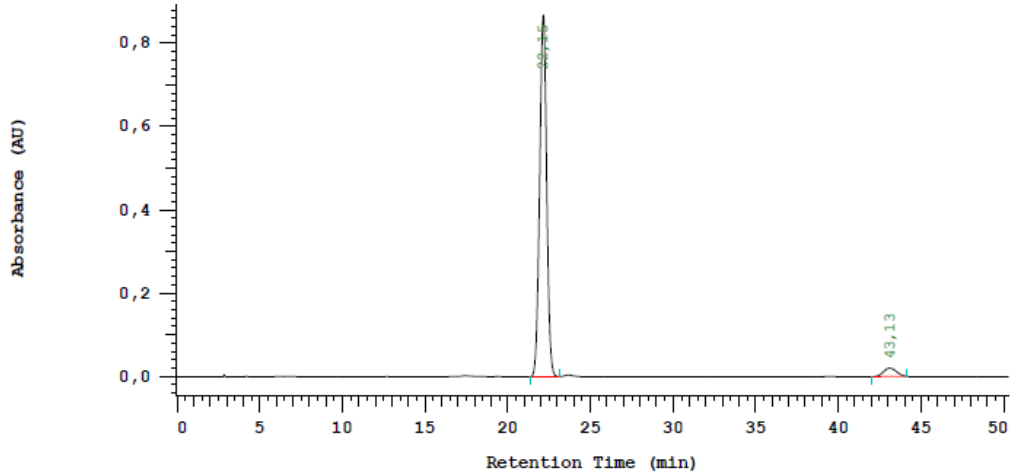
No.	RT	Area	Area %	Name
1	18,27	8521840	95,644	
2	44,17	388110	4,356	
		8909950	100,000	

Ethyl (*S*)-2-(3-bromo-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (3o)



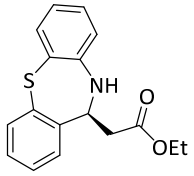


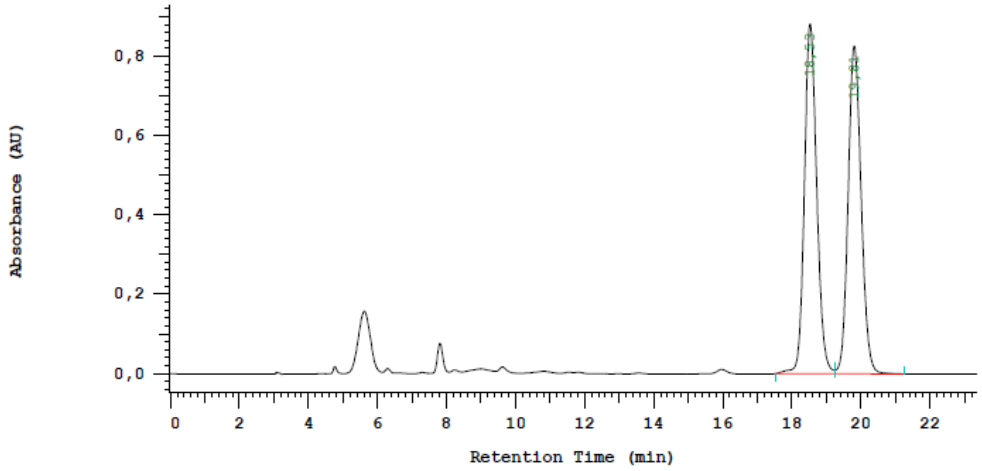
No.	RT	Area	Area %	Name
1	22,29	15846140	50,226	enant. (+)
2	43,11	15703680	49,774	
		31549820	100,000	



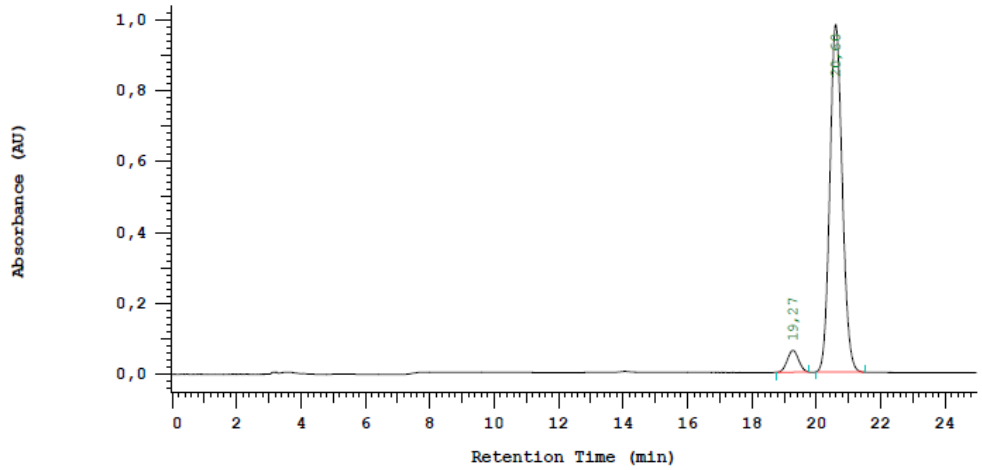
No.	RT	Area	Area %	Name
1	22,15	12725390	95,881	enant. (+)
2	43,13	546740	4,119	
		13272130	100,000	

Ethyl (*S*)-2- (10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)acetate (5)



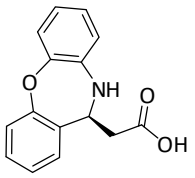


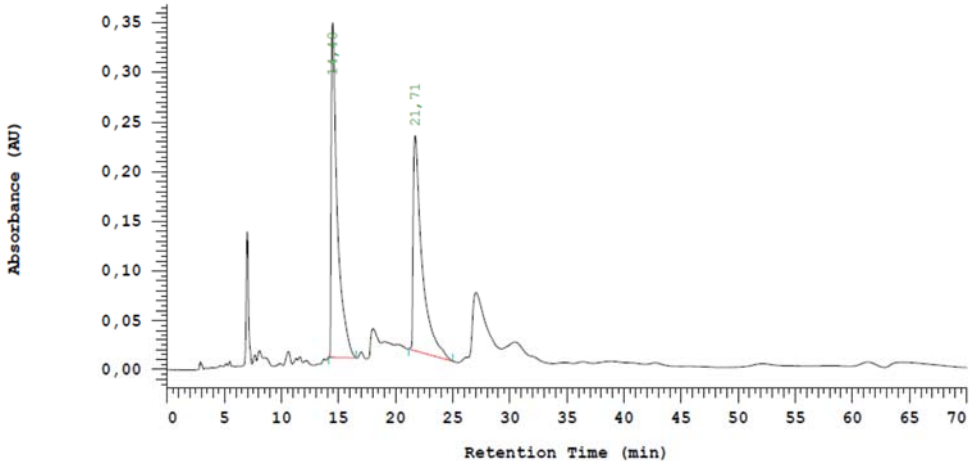
No.	RT	Area	Area %	Name
1	18,53	10909053	50,253	
2	19,81	10799316	49,747	
		21708369	100,000	



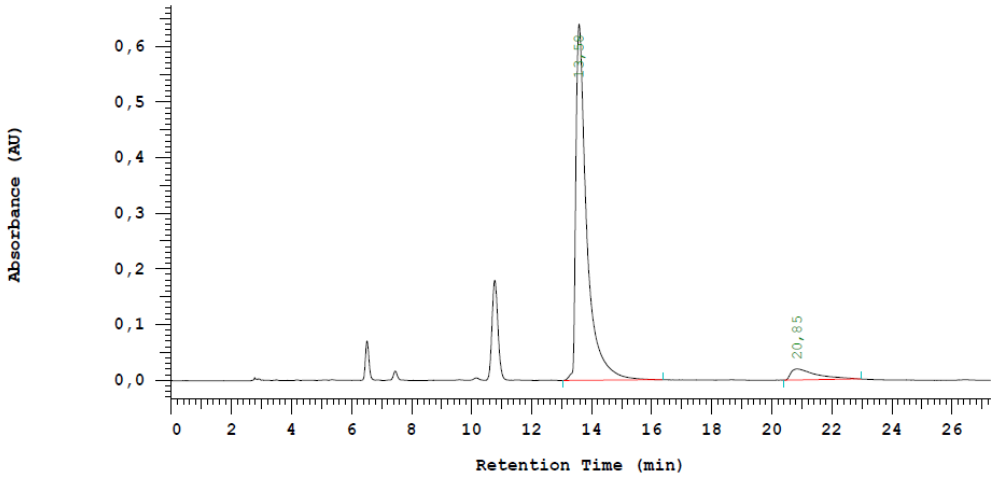
No.	RT	Area	Area %	Name
1	19,27	757840	5,441	
2	20,60	13170860	94,559	
		13928700	100,000	

(*S*)-2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)acetic acid (6)



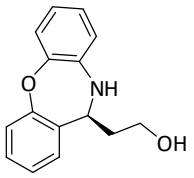


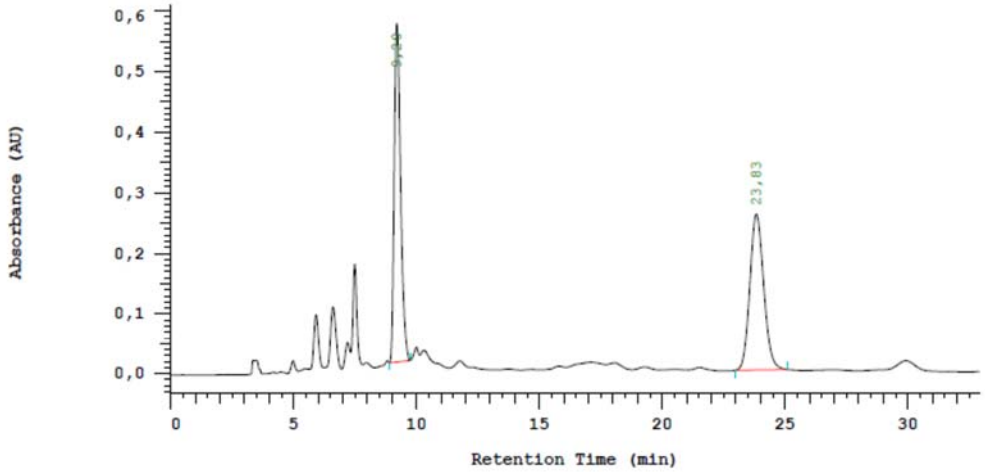
No.	RT	Area	Area %	Name
1	14,48	6159130	51,712	
2	21,71	5751340	48,288	enant. (+)
		11910470	100,000	



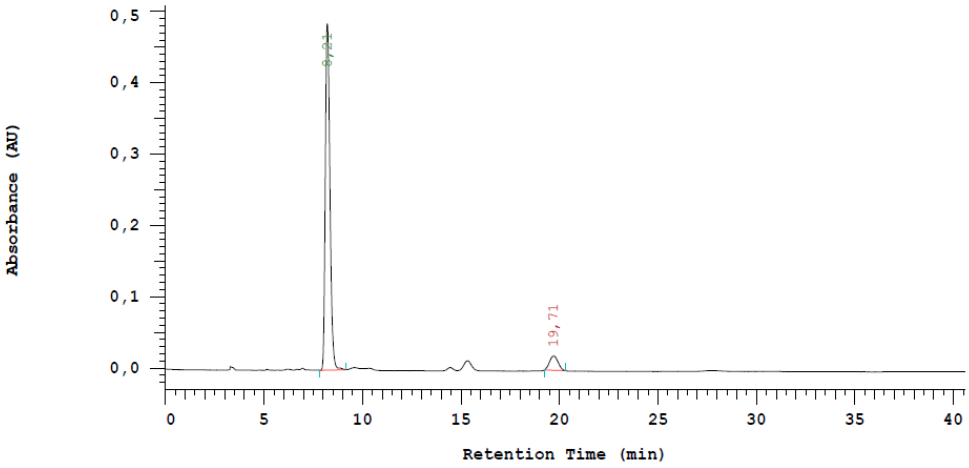
No.	RT	Area	Area %	Name
1	13,58	8132409	93,322	
2	20,85	581920	6,678	
		8714329	100,000	

(*S*)-2-(10,11-Dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)ethan-1-ol (7)



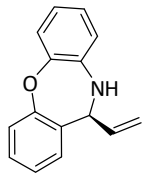


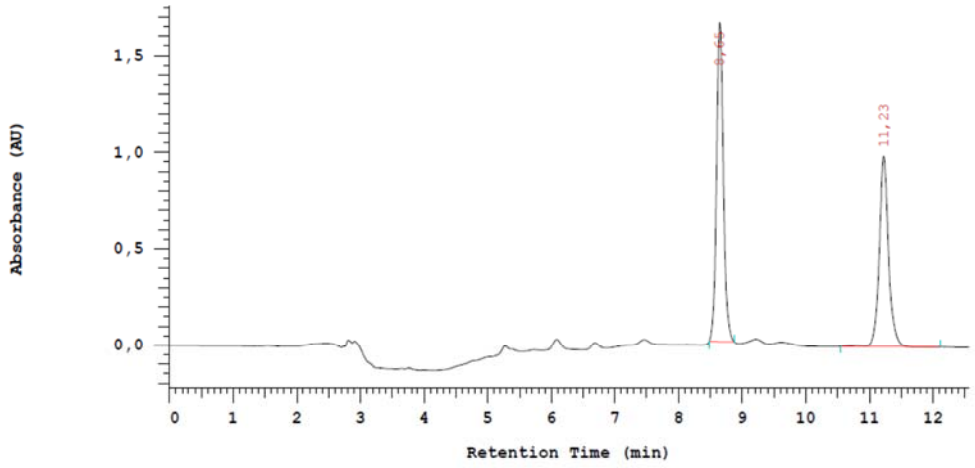
No.	RT	Area	Area %	Name
1	9,20	5002690	49,641	
2	23,83	5075130	50,359	enant. (+)
		10077820	100,000	



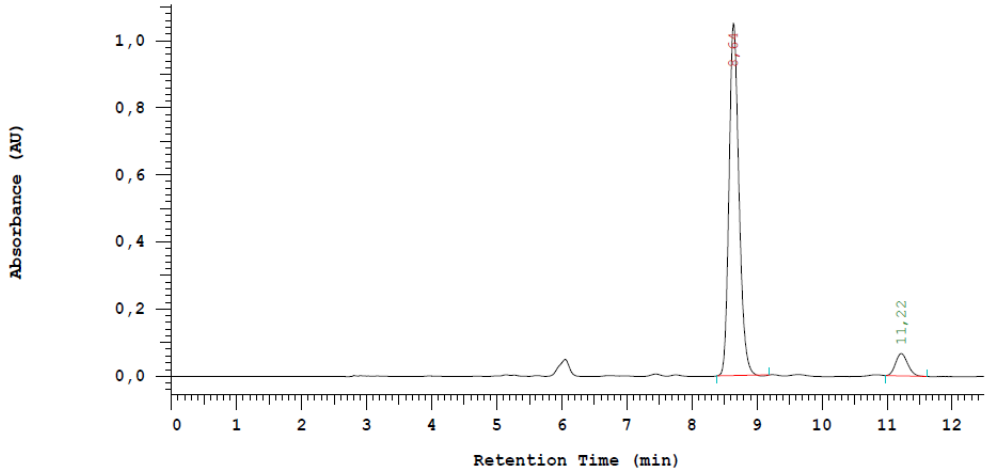
No.	RT	Area	Area %	Name
1	8,21	3875410	92,954	
2	19,71	293760	7,046	
		4169170	100,000	

(*S*)-11-Vinyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (8)



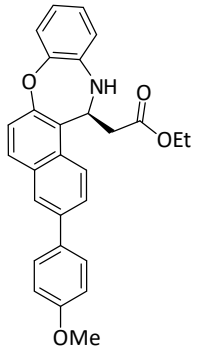


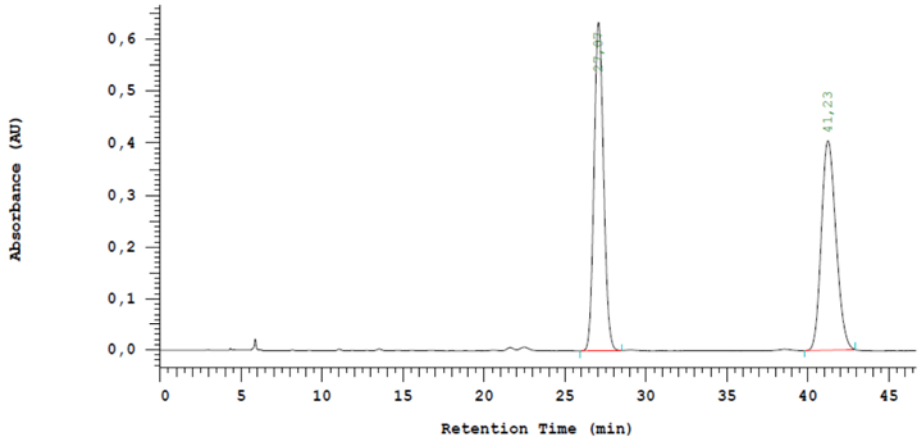
No.	RT	Area	Area %	Name
1	8,65	6163770	55,156	
2	11,23	5011464	44,844	
		11175234	100,000	



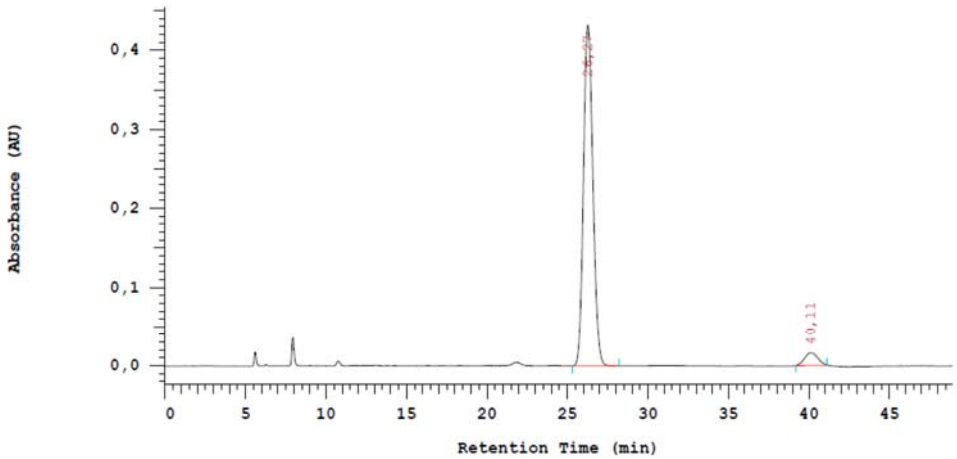
No.	RT	Area	Area %	Name
1	8,64	5535855	92,779	
2	11,22	430830	7,221	
		5966685	100,000	

Ethyl (*S*)-2-(3-(4-methoxyphenyl)-12,13-dihydrobenzo[*b*]naphtho[1,2-*f*][1,4]oxazepin-13-yl)acetate (9)



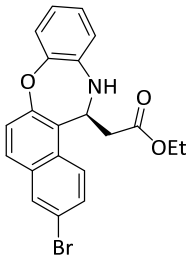


No.	RT	Area	Area %	Name
1	27,07	12835129	50,212	enanti (-)
2	41,23	12726675	49,788	
		25561804	100,000	

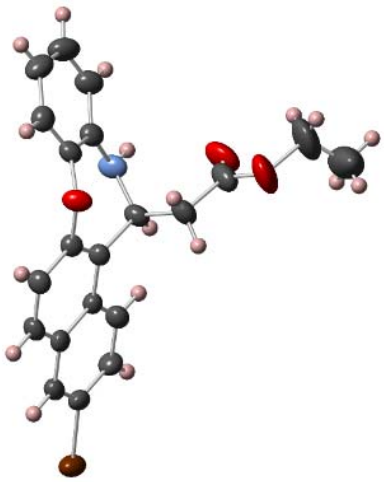


No.	RT	Area	Area %	Name
1	26,27	8641675	95,016	enant. (+)
2	40,11	453255	4,984	
		9094930	100,000	

X-ray data for compound 3o



X-ray data for compound **3o**: crystallized from DCM/n-hexane; $C_{21}H_{18}BrNO_3$; Mr=412.27; monoclinic; space group=$P2_1$; a=10.4368(4), b=6.0294(2); c=15.7294(5) Å; □ = 107.537(4), V=943.81(6) Å^3; Z=2; ρ_{calcd}=1.451 Mg m^{-3}; μ=2.197 mm^{-1}; F(000)=420. A colorless crystal of 0.10x0.18x0.18 mm^3 was used; 4081 [R(int)=0.0301] independent reflections were collected on a SuperNova, single source at offset, Sapphire3 equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å). The structures were solved by using direct methods with SHELXS-2014 and refined by using full matrix least squares on F^2 with SHELXL-2014. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined by using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Final R(ωR) values were R=0.0362 and ωR=0.0782. CCDC 1530500 contains 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.



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