

Ru-Catalyzed Asymmetric Transfer Hydrogenation of Substituted Dibenzo [*b,f*] [1,4] oxazepines in Water

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Materials and Methods. All chemicals and solvents were purchased from M/S Sigma Aldrich, S. D. Fine Chemicals, Avra synthesis and commercial suppliers. Reactions were performed using oven dried round bottom flask under an air or nitrogen atmosphere. The reaction progress was monitored by analytical thin layer chromatography (TLC) using Merck silica gel 60 F254 plates. Starting materials and products were purified by column chromatography on silica gel (60-120 mesh). The ^1H and ^{13}C NMR spectra were recorded at 400 MHz spectrometer in either CDCl_3 . The enantiomeric excess values (*ee*) of the products were determined by HPLC analysis with an Agilent 1260 Infinity-HPLC on Daicel Chiralcel OD-H and AD-H chiral columns using propan-2-ol/*n*-hexane as the eluent. The starting material **1a-1o** was prepared according to the reported procedure.⁹ The Optical rotations were measured by using a Rudolph Autopol IV Polarimeter and also compared with reported chiral HPLC graphs on Diacel Chiralcel OD-H column.⁹

General procedure for Ru-catalyzed asymmetric transfer hydrogenation (ATH) of cyclic imines: Imine **1a** (0.5 mmol) and (*R,R*)-Ru-TsDPEN (1mol%) were placed in round bottom flask under nitrogen or air atmosphere. To this mixture, 1M aqueous HCOOH-HCOONa solution (5 mL) was added. After stirring at 40 °C temperature for appropriate time, then reaction mixture was diluted with ethyl acetate (EtOAc) and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and then the resultant residue was purified by column chromatography on silica gel to give the desired cyclic amine **2a**.

(*R*)-2,11-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (**2a**).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 0.7 mL/min, 254nm; t_1 = 8.0 min (major), t_2 = 8.9 min (minor); 93% *ee*; $[\alpha]_{\text{D}}^{20}$ = +20 (Conc. 0.11 in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.07-6.99(m, 4H), 6.81 (t, J =8Hz, 1H), 6.64(t, J =7.2 Hz, 1H), 6.51(d, J =7.6Hz, 1H), 5.01(dd, J =13.6, 6.8 Hz, 1H), 3.66(br 1H), 2.30(s, 3H), 1.62 (d, J =6.8Hz,3H); ^{13}C NMR (100 MHz, CDCl_3): 155.34,

144.36, 138.12, 134.67, 133.87, 129.10, 125.76, 124.37, 121.66, 120.43, 118.85, 118.33, 49.76, 20.98, 19.88; GC-MS: (EI, 70 eV): m/z : 225, 210, 180, 167, 152, 128, 115, 91.

(R)-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2b).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 90/10, flow rate = 0.7 mL/min, 254nm; t_1 = 9.1 min (major), t_2 = 10.0 min (minor); 91% *ee*; $[\alpha]_D^{20}$ = +26.1 (Conc. 0.13 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.23-7.19 (m, 3H), 7.10 (t, J =7.6 Hz, 2H), 6.84 (t, J =7.2 Hz, 1H), 6.66 (t, J =7.2 Hz, 1H), 6.53 (d, J =6.4 Hz, 1H), 5.06 (dd, J =13.6, 6.4 Hz, 1H), 3.54 (br, 1H), 1.63 (d, J =6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.52, 144.19, 138.13, 135.12, 128.81, 125.21, 124.48, 124.41, 121.74, 120.76, 118.91, 118.33, 49.80, 19.89; GC-MS: (EI, 70 eV): m/z : 211, 196, 167, 139, 115, 98, 91.

(R)-4-chloro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2c).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min, 254nm; t_1 = 12.9 min (major), t_2 = 13.7 min (minor); 80% *ee*; $[\alpha]_D^{20}$ = -28.18 (Conc. 0.11 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.24 (m, 2H), 7.10-7.0 (m, 2H), 6.86 (t, J =7.6 Hz, 1H), 6.66 (t, J =8 Hz, 1H), 6.51 (d, J =7.6 Hz, 1H), 5.10 (dd, J =13.2, 6.8 Hz, 1H), 3.71 (br, 1H), 1.62 (d, J =6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 153.06, 143.0, 138.07, 137.23, 129.38, 126.29, 125.0, 124.98, 123.38, 122.56, 118.74, 117.95, 49.39, 19.58; GC-MS: (EI, 70 eV): m/z : 245, 230, 209, 167, 139, 115, 105, 90, 77.

(R)-2-bromo-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2d).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min, 254nm; t_1 = 14.7 min (major), t_2 = 17.8 min (minor); 85% *ee*; $[\alpha]_D^{20}$ = 29 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.30 (m, 2H), 7.04 (t, J =8 Hz, 2H), 6.84 (t, J =7.6 Hz, 1H), 6.65 (t, J =7.6 Hz, 1H), 6.52 (d, J =8 Hz, 1H), 5.01 (dd, J =13.6, 6.8 Hz, 1H), 3.65 (br, 1H), 1.60 (d, J =6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 156.46, 143.80, 137.73, 137.18, 131.61, 128.30, 124.72, 122.66, 121.64, 119.18, 118.40, 117.02, 49.48, 19.59; GC-MS: (EI, 70 eV): m/z : 289, 274, 260, 246, 209, 195, 167, 139, 117, 105, 91.

(R)-2-fluoro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2e).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min, 254nm; t_1 = 15.4 min (major), t_2 = 19.1 min (minor); 87% *ee*; $[\alpha]_D^{20}$ = +51 (Conc. 0.11 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.12-7.06 (m, 2H),

6.92- 6.82(m, 3H), 6.65(t, $J=7.2$ Hz, 1H), 6.52 (dd, $J=6.8$ Hz, 1H), 5.07(dd, $J=13.2$, 6.8 Hz, 1H), 3.67(br, 1H), 1.59(d, $J=6.8$ Hz, 3H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 159.17 (d, $J_{\text{C-F}}=241\text{Hz}$), 153.48, 144.12, 136.91, 136.84, 124.69, 122.0, 121.91, 119.0, 118.27, 114.84 (d, $J_{\text{C-F}}=23\text{Hz}$), 111.95 (d, $J_{\text{C-F}}=24\text{Hz}$), 49.06, 19.35; GC-MS: (EI, 70 eV): m/z : 229, 214, 200, 185, 170, 159, 133, 107, 92, 77.

(*R*)-4-bromo-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2f).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*- hexane/ *i*-PrOH = 99/01, flow rate = 0.8 mL/min, 254nm; t_1 = 15.4 min (major), t_2 = 17.6 min (minor); 90% *ee*; $[\alpha]_{\text{D}}^{20} = +21$ (Conc. 0.10 in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.24-7.07 (m, 4H), 6.83(t, $J=7.6\text{Hz}$, 1H), 6.64 (t, $J=8\text{Hz}$, 1H), 6.52 (dd, $J=6.4$, 1.6Hz, 1H), 5.05(dd, $J=13.7$, 6.8 Hz, 1H), 3.73(br, 1H), 1.62(d, $J=6.8\text{Hz}$, 3H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 157.52, 144.20, 138.11, 135.11, 128.79, 125.20, 124.46, 124.38, 121.72, 120.75, 118.91, 118.33, 49.82, 19.90.

(*R*)-4,11-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2g).⁹

The *ee* was determined by HPLC using a Daicel Chiralpak AD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.7 mL/min, 254nm; t_1 = 10.0 min (minor), t_2 = 10.7 min (major); 83% *ee*; $[\alpha]_{\text{D}}^{20} = +19$ (Conc. 0.10 in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.125(t, $J=7.8$ Hz, 2H), 7.05- 6.98(m, 2H), 6.83 (t, $J=7.2$ Hz, 1H), 6.64(t, $J=8\text{Hz}$, 1H), 6.51(d, $J=8\text{Hz}$, 1H), 5.09(dd, $J=13.6$, 6.8 Hz, 1H), 3.69(br, 1H), 2.41(s, 3H), 1.62(d, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.71, 143.50, 138.61, 135.29, 130.33, 130.15, 124.47, 124.12, 122.49, 122.05, 118.47, 118.13, 49.31, 19.64, 16.25; GC-MS: (EI, 70 eV): m/z : 225, 210, 180, 167, 152, 115, 105, 91, 77.

(*R*)-11-methyl-4-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2h).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*- hexane/ *i*-PrOH = 99/01, flow rate = 0.8 mL/min, 254nm; t_1 = 18.7 min (major), t_2 = 27.4 min (minor); 91% *ee*; $[\alpha]_{\text{D}}^{20} = 10$ (Conc. 0.10 in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.52 (d, $J=6.8\text{Hz}$, 2H), 7.46- 7.36(m, 3H), 7.30(d, $J=7.6\text{Hz}$, 1H), 7.24-7.14 (m, 2H), 6.77 (dd, $J=11.4$, 7.2 Hz, 1H), 6.47-6.49 (m, 3H), 5.17(dd, $J=14$, 6.8Hz, 1H), 3.75(br, 1H), 1.67(d, $J=6.8\text{Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.42, 143.79, 138.46, 137.94, 136.17, 134.77, 130.15, 129.94, 127.82, 127.19, 124.40, 124.35, 124.22, 122.0, 118.62, 117.93, 49.61, 19.66.

(R)-11-methyl-2-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2i).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 99/01, flow rate = 0.8 mL/min, 254nm; *t*₁ = 28.3 min (major), *t*₂ = 32.7 min (minor); 82% *ee*; [α]_D²⁰ = +17 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.53(t, *J*=1.2Hz, 2H), 7.45-7.38(m, 4H), 7.32(t, *J*=7.6Hz, 1H), 7.23(t, *J*=8.4Hz, 1H), 7.10(dd, *J*=6.4, 1.6 Hz, 1H), 6.87-6.83 (m, 1H), 6.69-6.65 (m, 1H), 6.56 (dd, *J*= 6.4, 1.2 Hz, 1H), 5.08 (dd, *J*=13.6, 6.8Hz, 1H), 1.68(d, *J*=6.8Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.93, 144.26, 140.79, 137.94, 137.55, 135.19, 128.72, 127.45, 127.09, 127.06, 124.50, 124.26, 121.71, 121.11, 119.10, 118.48, 50.17, 20.04.

(R)-11-ethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2j).⁹

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min, 254nm; *t*₁ = 15.4 min (major), *t*₂ = 17.4 min (minor); 80% *ee*; [α]_D²⁰ = 9 (Conc. 0.11 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.24-7.18 (m, 1H), 7.12 (t, *J*=7.6 Hz, 2H), 7.06 (t, *J*=7.6 Hz, 2H), 6.83(t, *J*=7.6 Hz, 1H), 6.65(t, *J*=7.2 Hz, 1H), 6.55(d, *J*=8 Hz, 1H), 4.31(t, *J*=7.6 Hz, 1H), 3.98(br, 1H), 2.13-1.99(m, 2H), 1.0(t, *J*=7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 157.11, 143.89, 137.62, 133.99, 128.71, 127.09, 124.34, 124.12, 121.68, 121.0, 118.73, 118.48, 58.73, 27.75, 11.43; GC-MS: (EI, 70 eV): *m/z*: 225, 196, 167, 139, 115, 98, 91.

(R)-11-ethyl-2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2k).

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min, 254nm; *t*₁ = 13.6 min (major), *t*₂ = 15.0 min (minor); 82% *ee*; [α]_D²⁰ = -40 (Conc. 0. 10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.05-6.99 (m, 3H), 6.95 (t, *J*=6.4Hz, 1H), 6.82 (t, *J*= 7.6 Hz, 1H), 6.63 (t, *J*= 6.4 Hz, 1H), 6.50 (d, *J*= 6.4 Hz, 1H), 4.26 (t, *J*= 7.6 Hz, 1H), 2.28 (s, 3H), 2.09-2.0 (m, 2H), 1.0 (t, *J*= 7.6 Hz, 3H) ; ¹³C NMR (100 MHz, CDCl₃): 154.92, 147.10, 143.88, 137.58, 133.58, 129.02, 127.62, 124.22, 121.61, 120.67, 118.69, 118.48, 58.75, 27.73, 20.83, 11.45.

(R)-2-methoxy-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2l).

The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH = 97/03, flow rate = 0.5 mL/min, 254nm; *t*₁ = 25.6 min (major), *t*₂ = 27.2 min (minor); 71% *ee*; [α]_D²⁰ = 8 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.09-7.04 (m, 2H), 6.82 (t, *J*=7.2 Hz, 1H), 6.72 (t, *J*= 7.2 Hz, 2H), 6.63 (t, *J*= 8.8 Hz, 1H), 6.50 (d, *J*= 8 Hz, 1H), 5.04 (dd, *J*= 13.6 Hz, 1H), 3.76 (s, 3H), 1.60 (d, *J*= 6.8 Hz, 3H) ; ¹³C NMR (100 MHz,

CDCl₃): 156.12, 151.39, 144.52, 138.07, 136.09, 124.42, 121.59, 121.32, 118.80, 118.24, 112.59, 111.17, 55.59, 49.50, 19.58.

(R)-2,4-dichloro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2m).

The *ee* was determined by HPLC using a Daicel Chiralcel AD-H column, *n*-hexane/ *i*-PrOH = 99/02, flow rate = 0.7 mL/min, 254nm; *t*₁ = 11.3min (major), *t*₂ = 13.9min (minor); 77 % *ee*; [α]_D²² = 27 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.32 (s, 1H), 7.31-7.21 (m, 1H), 7.07 (s, 1H), 6.87 (t, *J*=7.66 Hz, 1H), 6.67 (t, *J*= 8 Hz, 1H), 6.51 (d, *J*= 7.6 Hz, 1H), 5.09 (dd, *J*= 13.6 Hz, 1H), 3.69 (br, 1H), 1.60 (d, *J*= 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 151.74, 142.77, 138.71, 137.71, 129.53, 128.90, 127.16, 125.25, 123.74, 122.45, 118.98, 118.02, 49.17, 19.27.

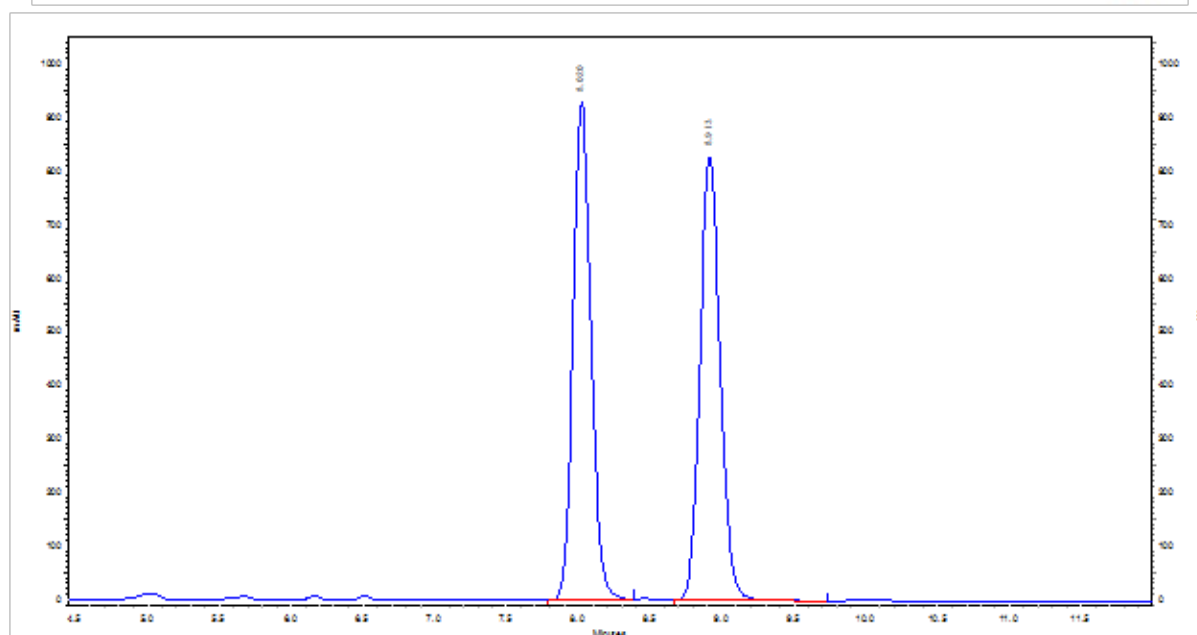
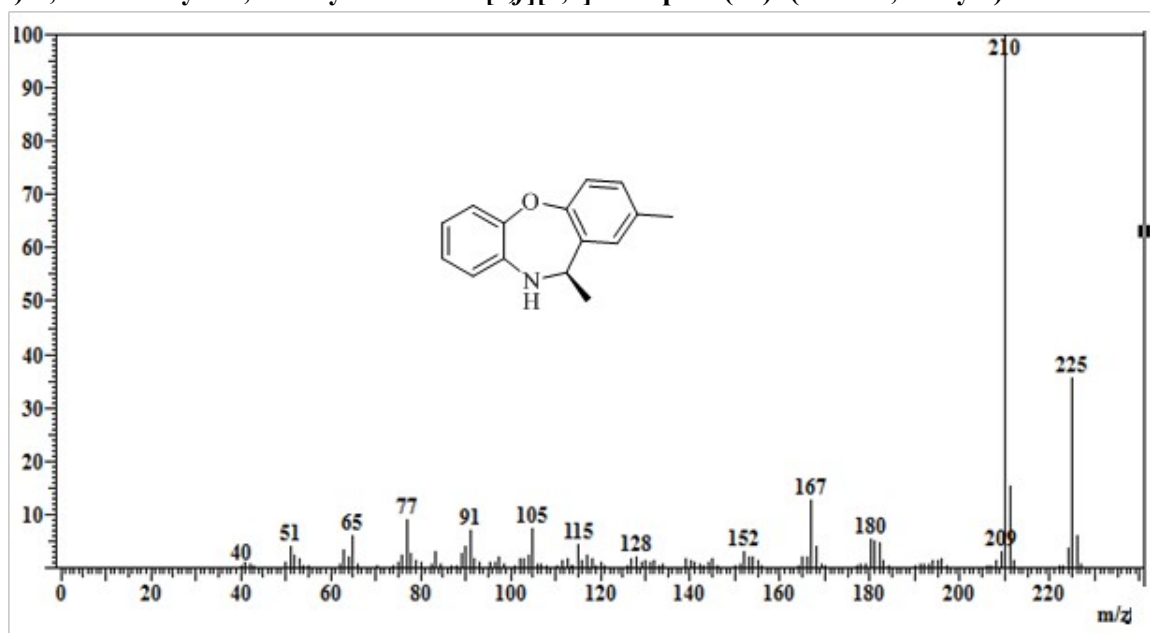
(R)-3,4,11-trimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine(2n).

The *ee* was determined by HPLC using a Daicel Chiralcel AD-H column, *n*-hexane/ *i*-PrOH = 98/02, flow rate = 0.7 mL/min, 254nm; *t*₁ = 12.7min (major), *t*₂ = 13.6min (minor); 88 % *ee*; [α]_D²² = 19 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.13 (d, *J*= 8 Hz, 1H), 6.94-6.88 (m, 2H), 6.81 (t, *J*=7.6 Hz, 1H), 6.62 (t, *J*= 8 Hz, 1H), 6.50 (d, *J*= 7.6 Hz, 1H), 5.07 (dd, *J*= 13.6 Hz, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 1.60 (d, *J*= 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 155.71, 143.58, 138.79, 137.47, 132.79, 128.68, 125.36, 124.45, 121.99, 121.47, 118.34, 118.09, 49.12, 19.98, 19.57, 12.35.

(R)-2-methyl-11-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine(2o).

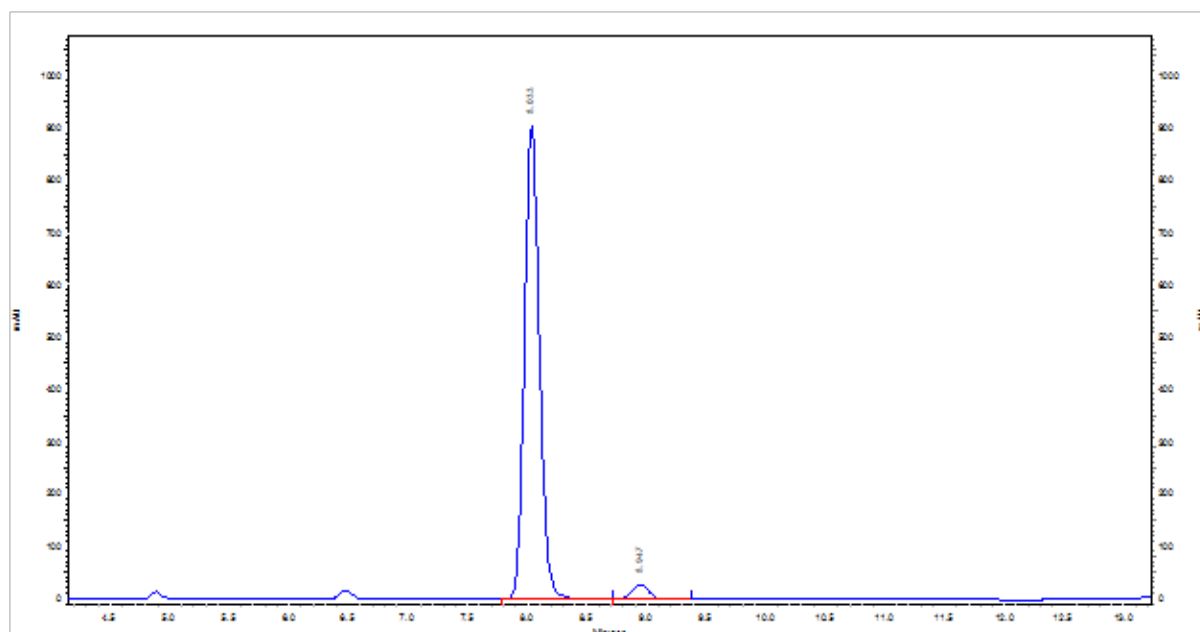
The *ee* was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ *i*-PrOH 95/05, flow rate = 0.5 mL/min, 254nm; *t*₁ = 13.8 min (major), *t*₂ = 15.7 min (minor); 80 % *ee*; [α]_D²⁰ = 11 (Conc. 0.10 in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.31 (m, 5H), 7.07-7.02 (m, 3H), 6.87 (t, *J*= 8Hz, 1H), 6.70-6.66 (m, 2H), 6.62 (d, *J*=8 Hz, 1H), 5.83 (s, 1H), 4.09 (br, 1H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 155.27, 144.84, 141.83, 138.73, 133.80, 133.73, 129.51, 128.82, 128.61, 127.58, 127.08, 124.55, 121.75, 120.82, 119.30, 118.54, 60.21, 20.87.

(*R*)-2,11-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2a): (Table 3, entry 1)



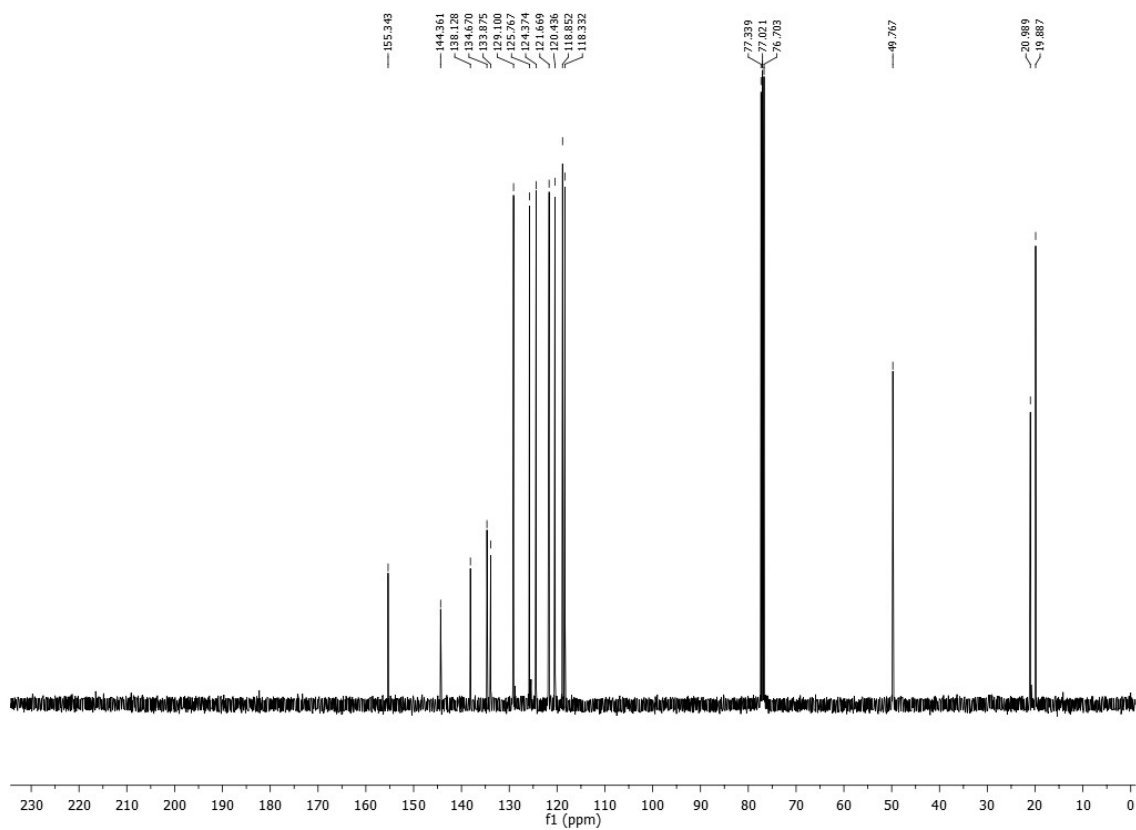
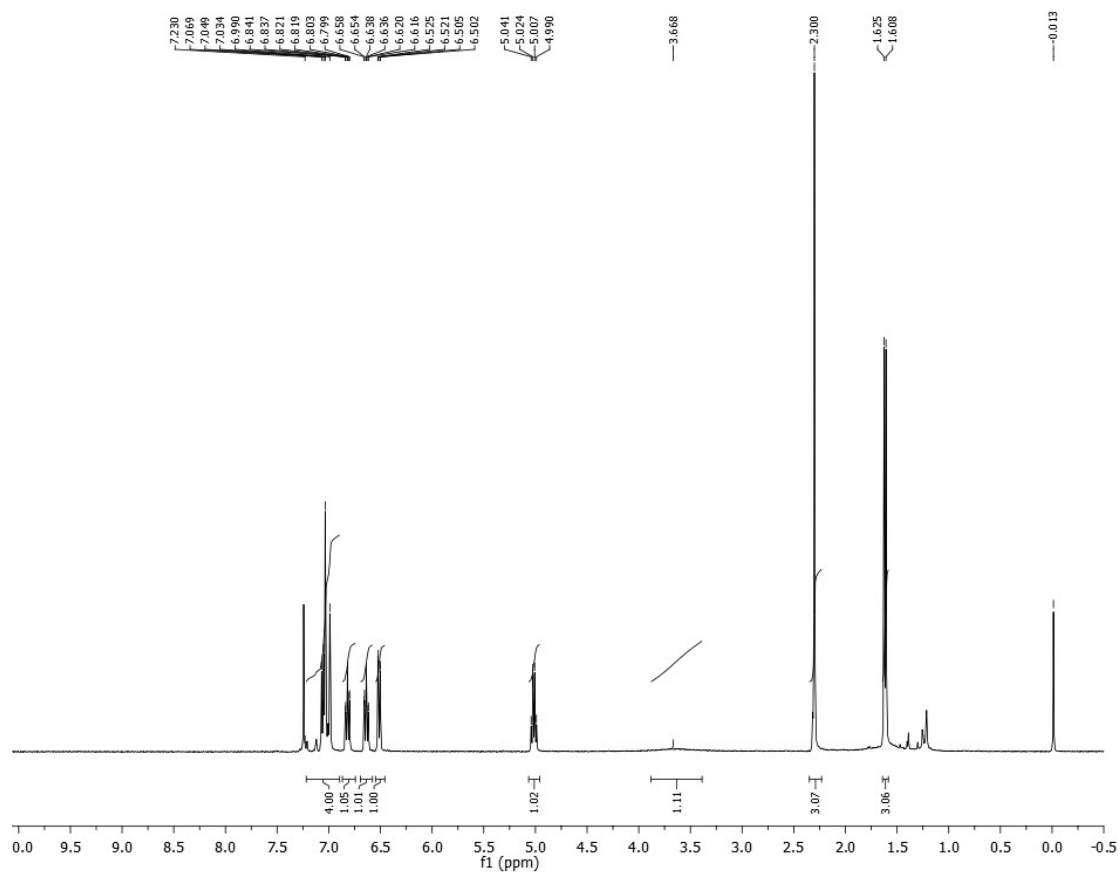
Retention Time	Area	Area %	Height	Height %
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8.913	16941770	50.15	1733213	47.09

Totals	33785501	100.00	3680280	100.00
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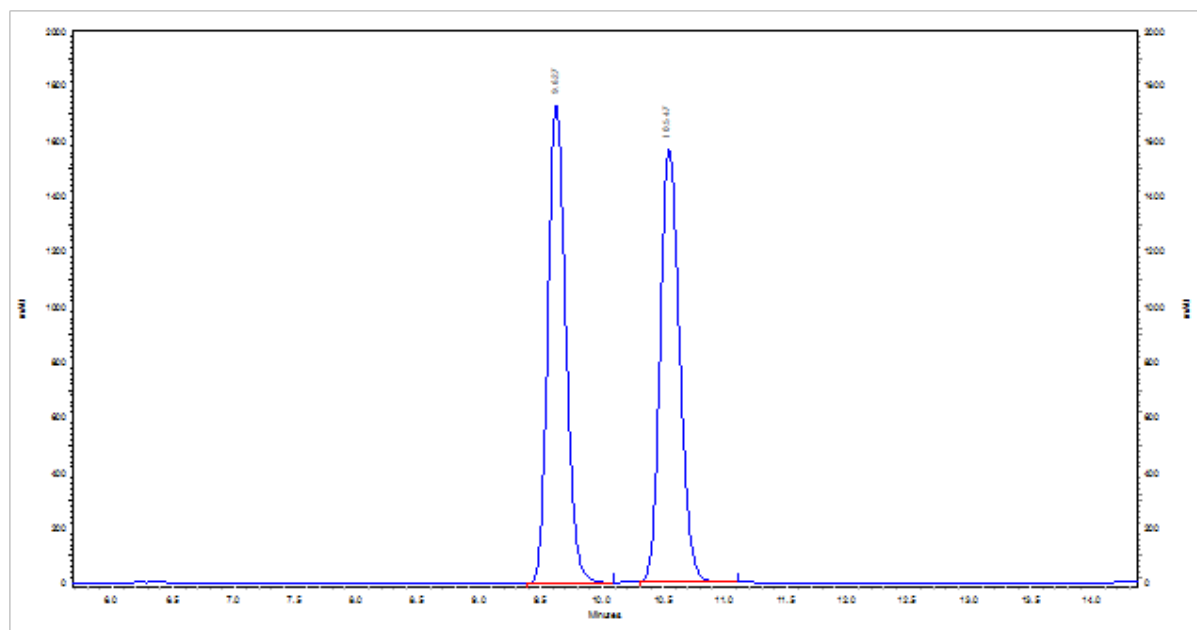
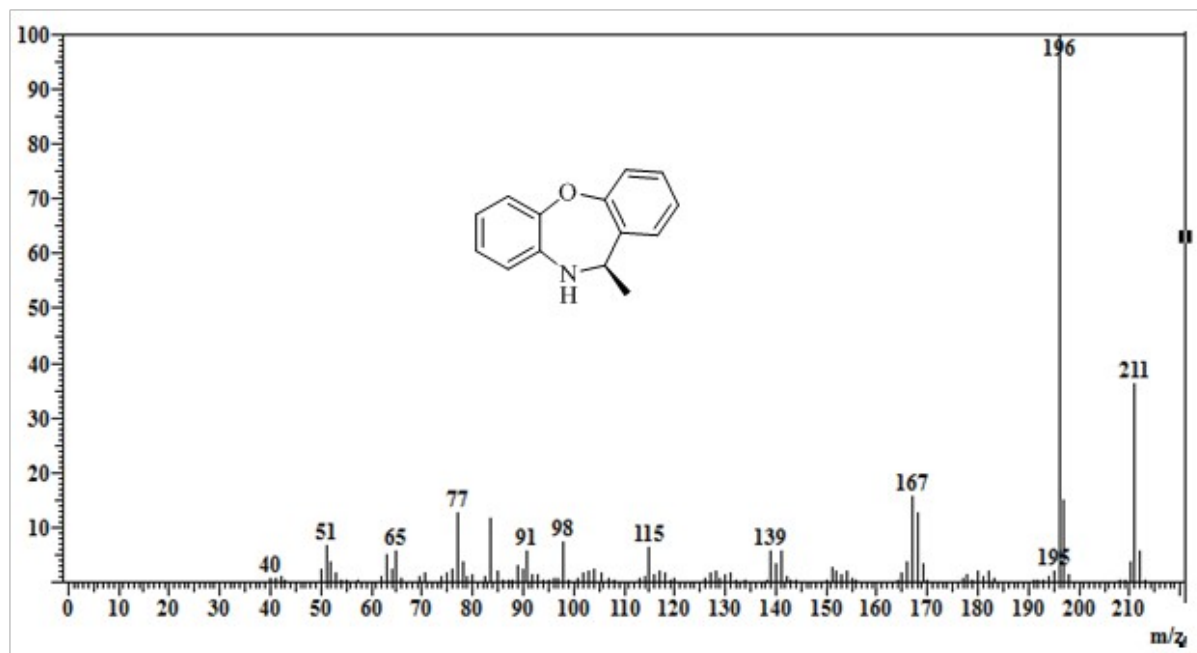


Retention Time	Area	Area %	Height	Height %
8.033	16661580	96.58	1902764	96.97
8.947	590098	3.42	59481	3.03

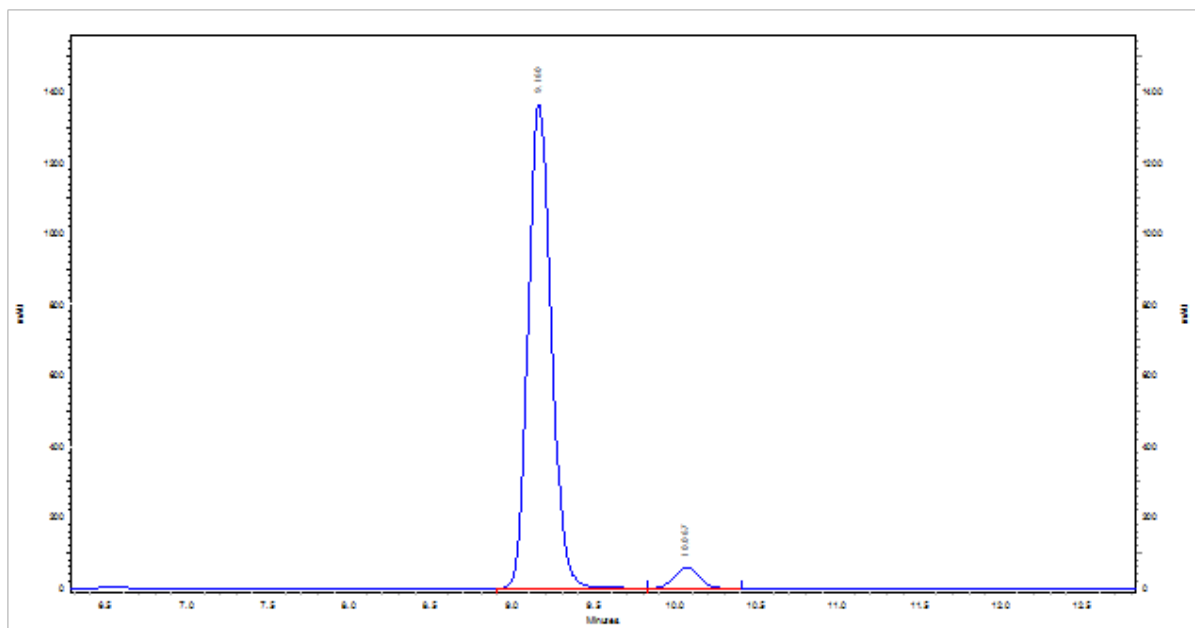
Totals	17251678	100.00	1962245	100.00
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(*R*)-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2b): (Table 3, entry 2)

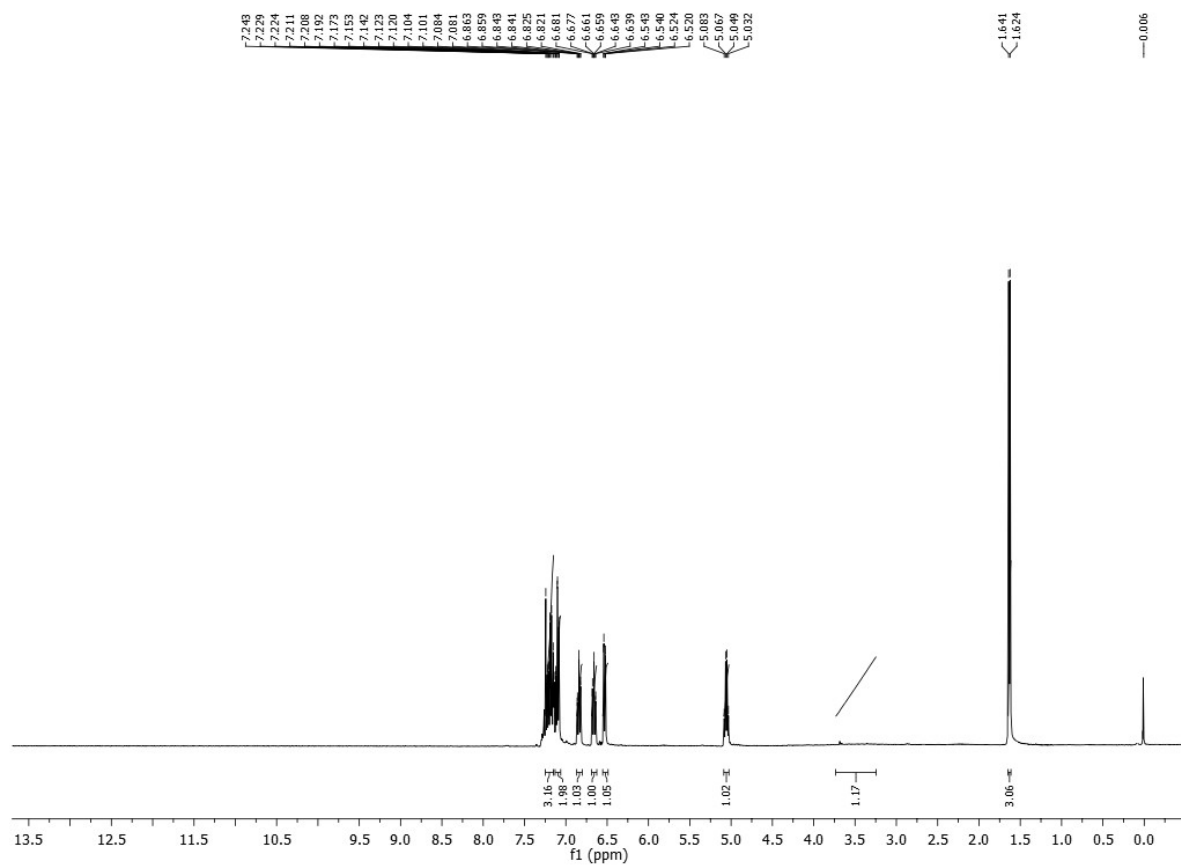


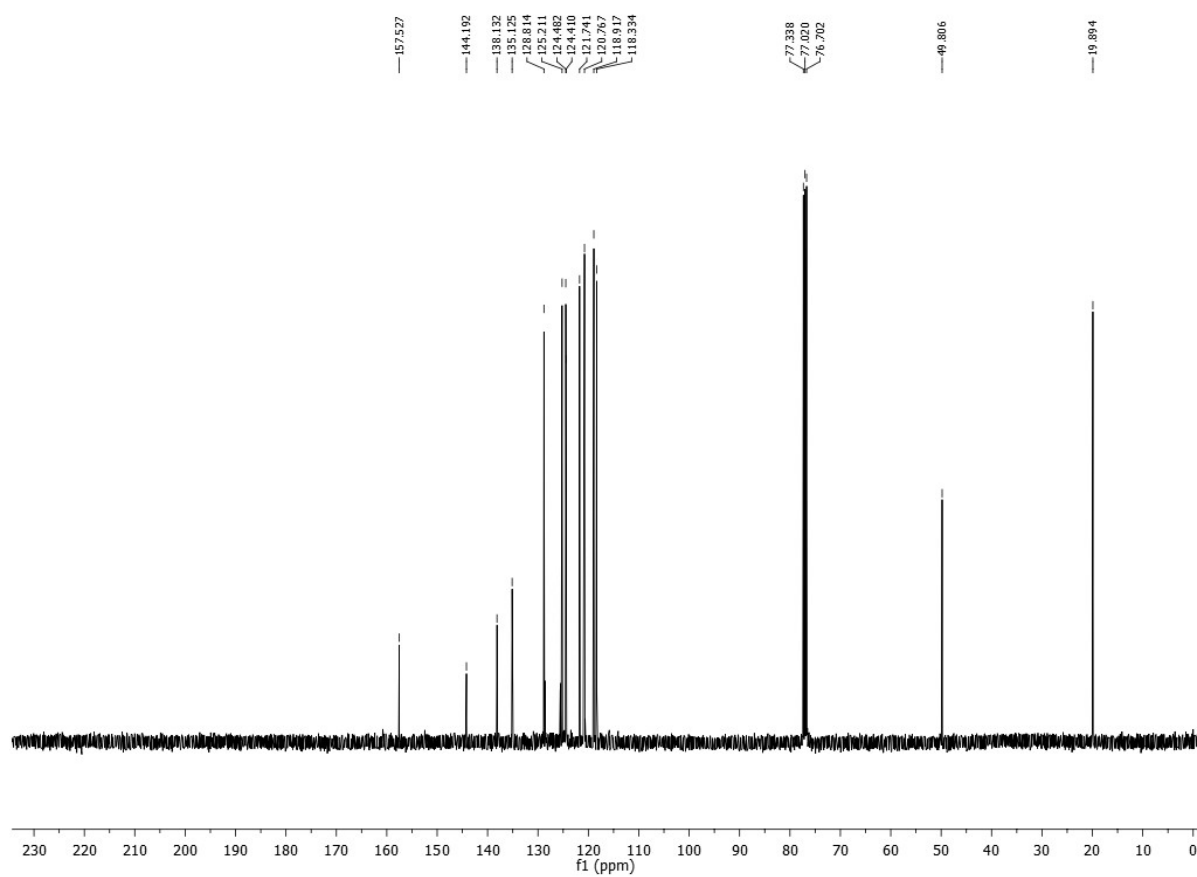
Retention Time	Area	Area %	Height	Height %
9.627	36637423	50.33	3626411	52.52
10.547	36161388	49.67	3278672	47.48
Totals	72798811	100.00	6905083	100.00



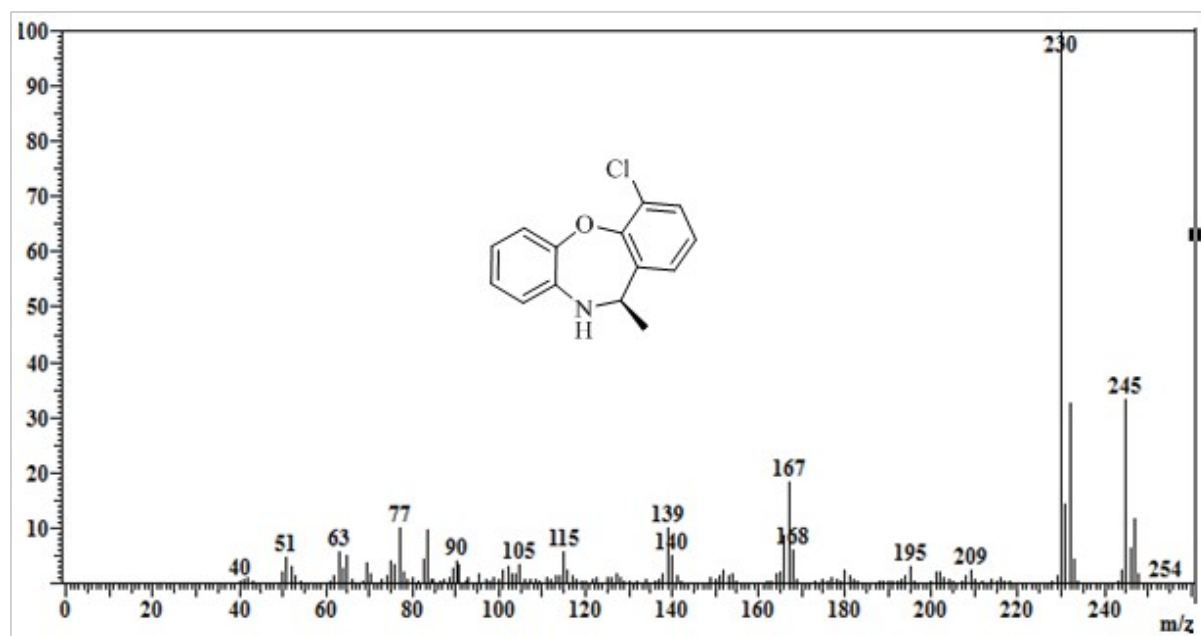
Retention Time	Area	Area %	Height	Height %
9.160	28381918	95.54	2869750	95.90
10.067	1325381	4.46	122708	4.10

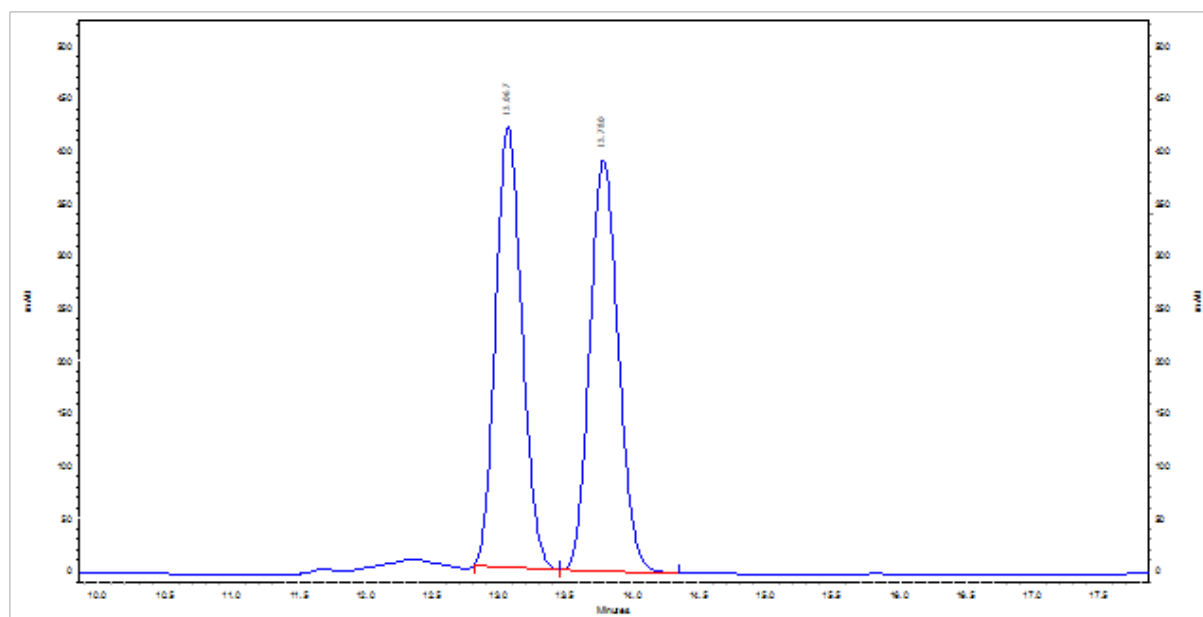
Totals	29707299	100.00	2992458	100.00
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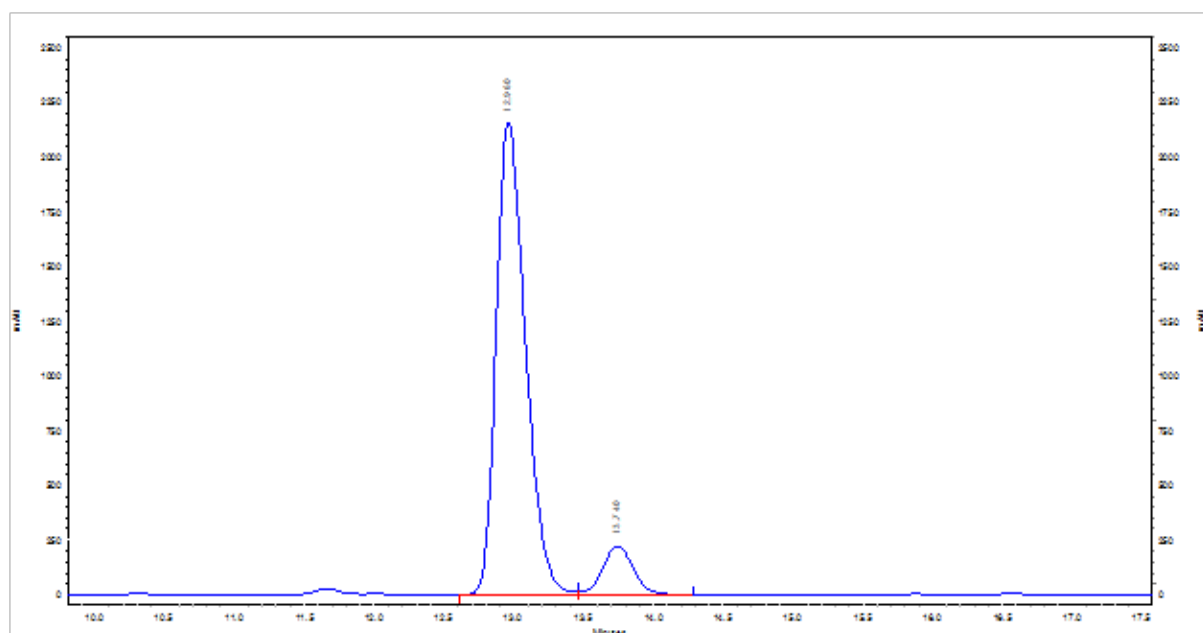
(*R*)-4-chloro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2c) : (Table 3, entry 3)





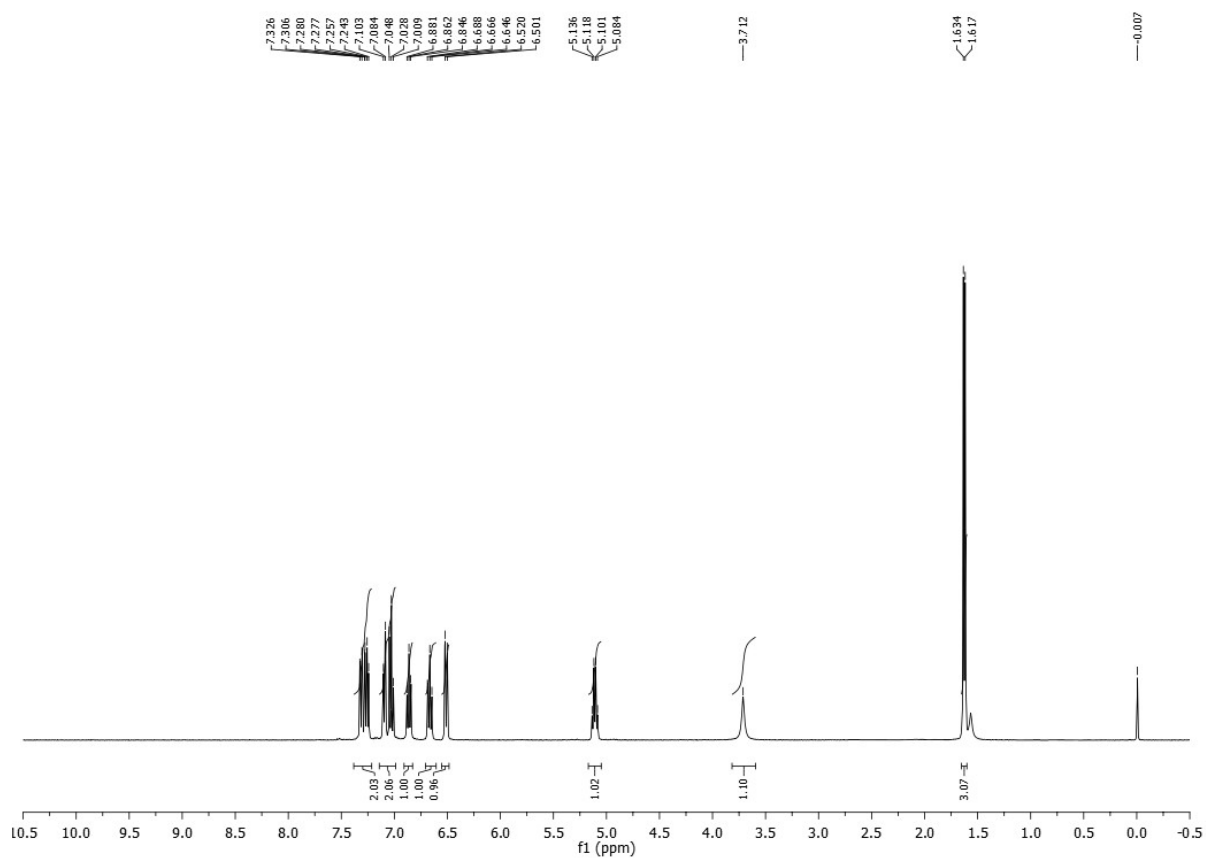
Retention Time	Area	Area %	Height	Height %
13.067	12108418	49.75	878887	51.67
13.780	12228858	50.25	822181	48.33

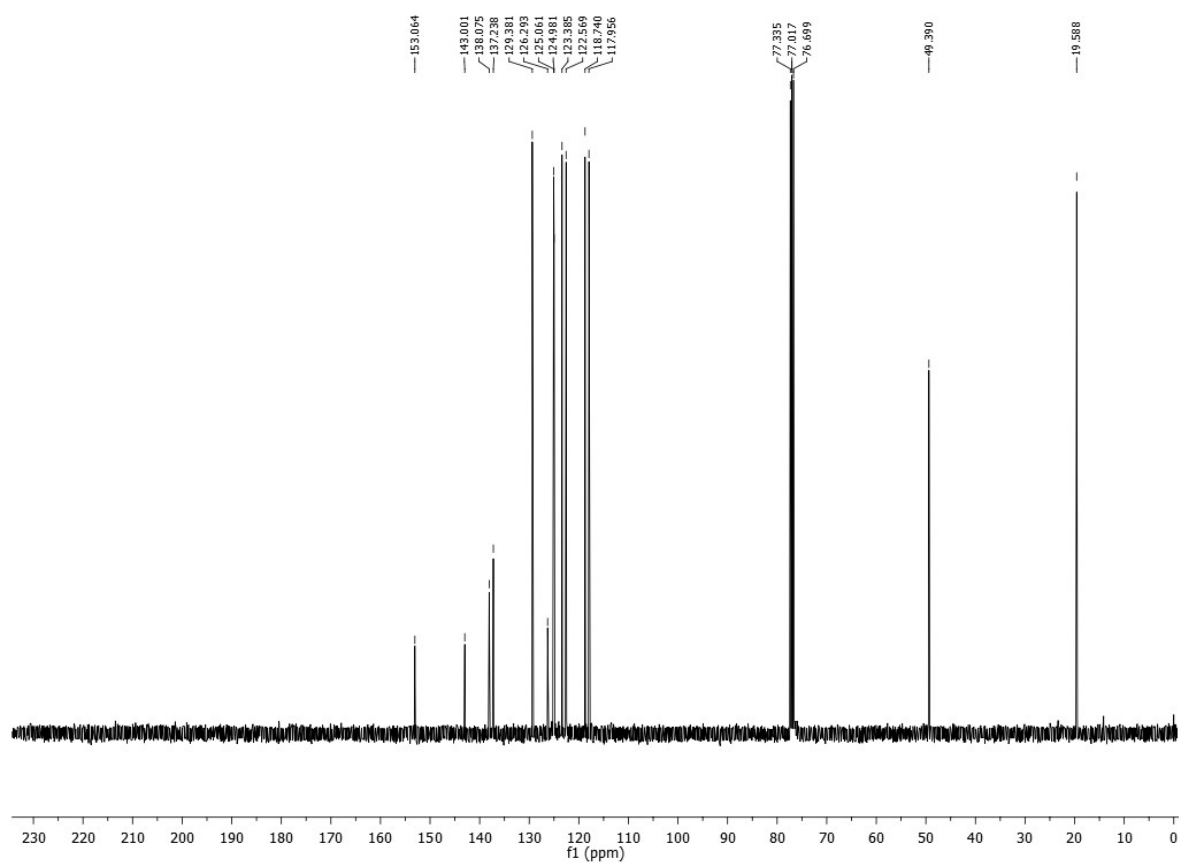
Totals	24337276	100.00	1701068	100.00
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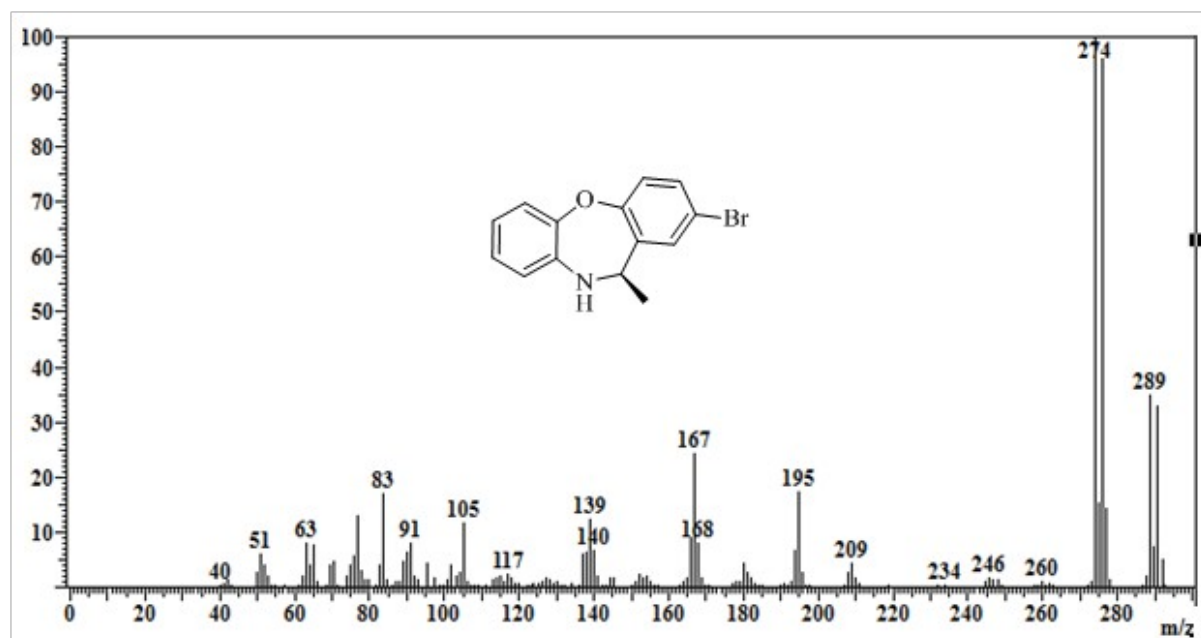
Retention Time	Area	Area %	Height	Height %
12.960	65991475	90.19	4525563	90.58
13.740	7181559	9.81	470896	9.42

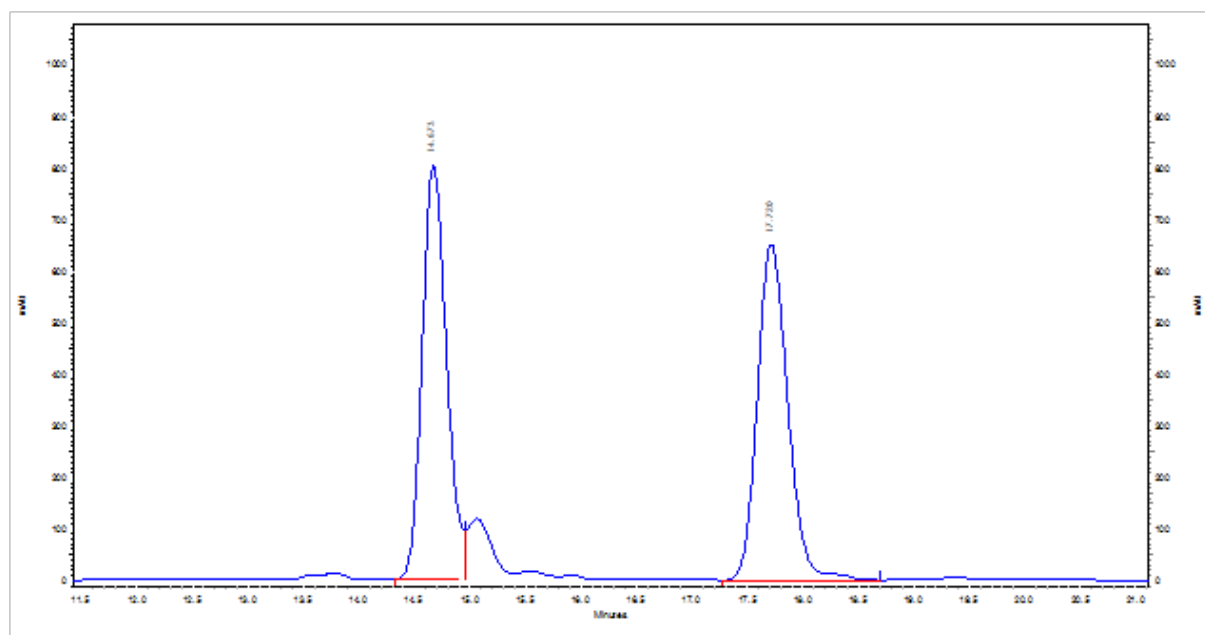
Totals	73173034	100.00	4996459	100.00
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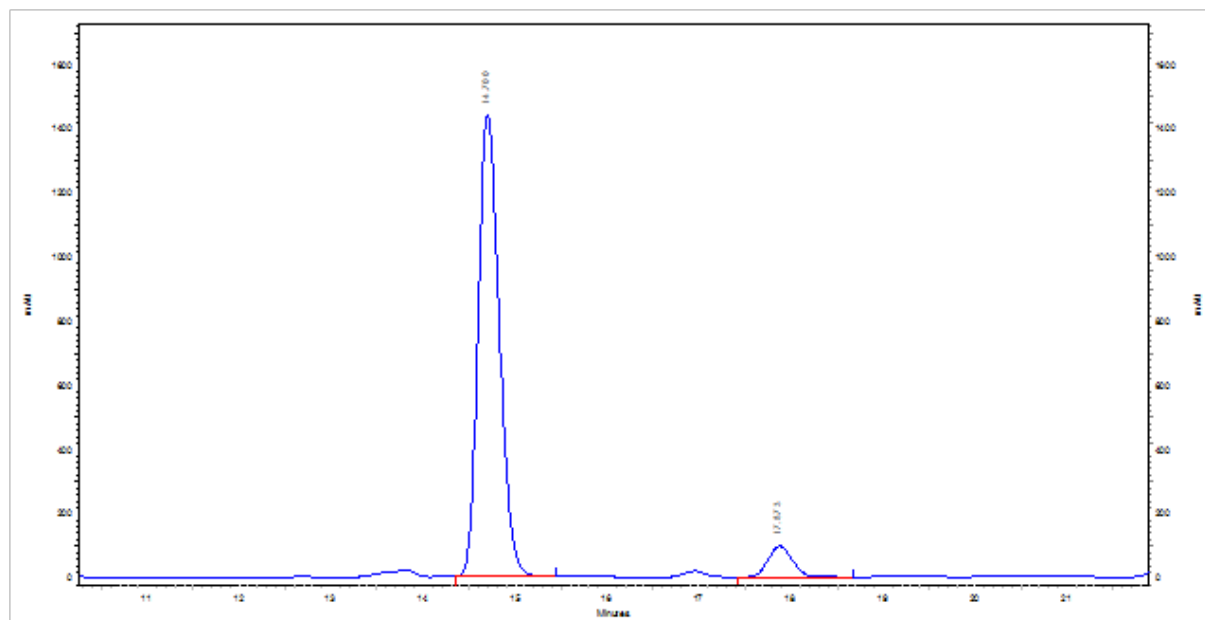
(R)-2-bromo-11-methyl-10,11-dihydrodibenzo[b,f][1,4]oxazepine (2d): (Table 3, entry 4)





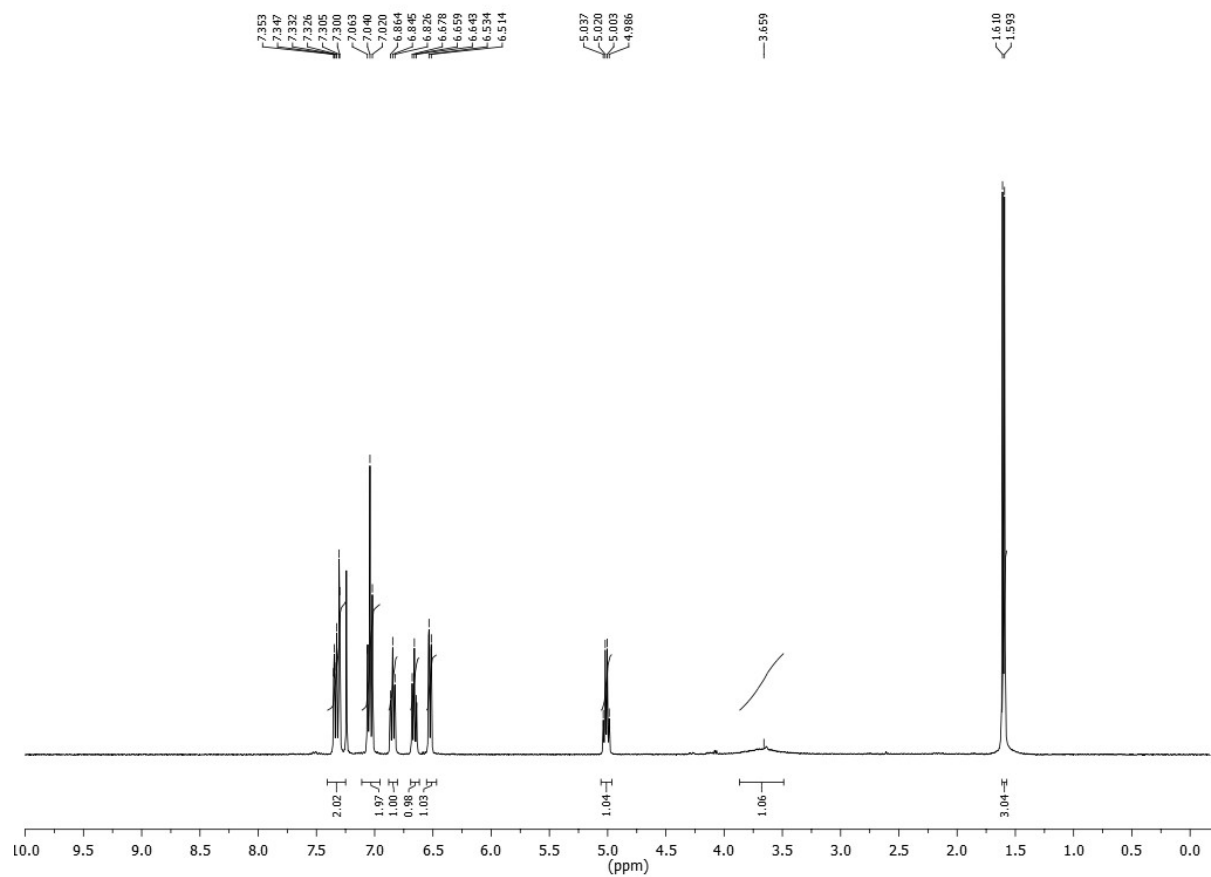
Retention Time	Area	Area %	Height	Height %
14.673	25700939	49.75	1684866	55.24
17.720	25955046	50.25	1365449	44.76

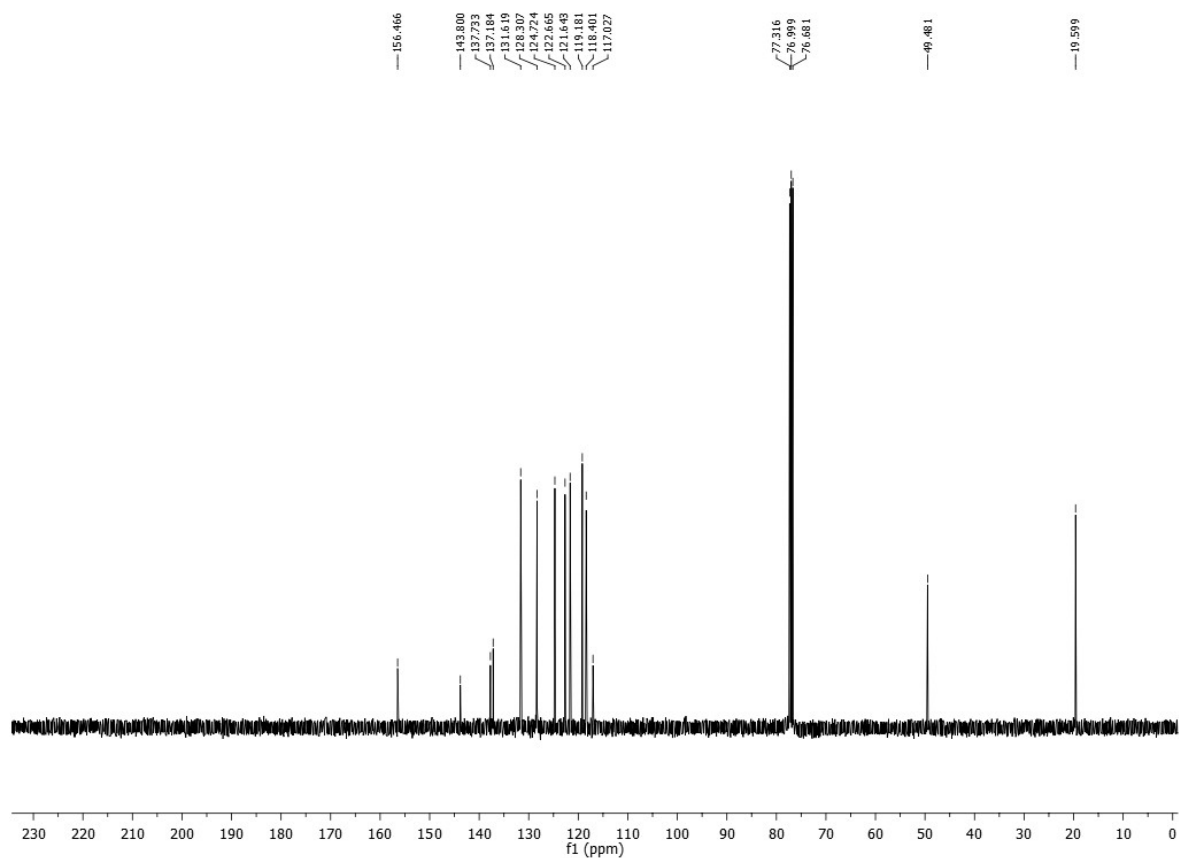
Totals	51655985	100.00	3050315	100.00
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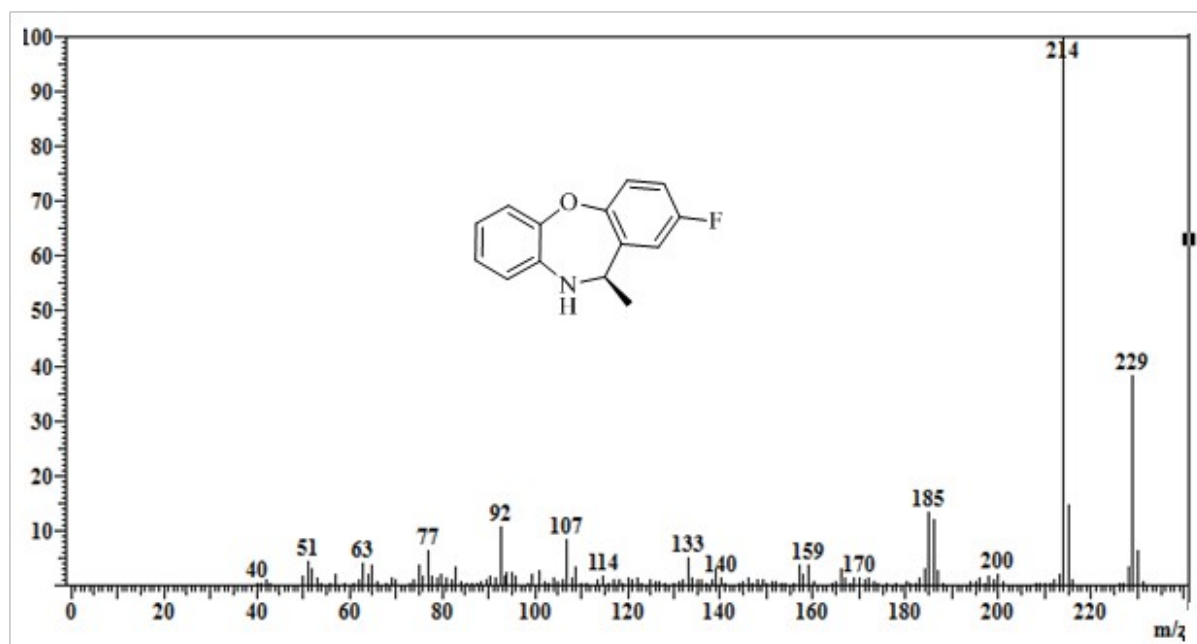
Retention Time	Area	Area %	Height	Height %
14.700	47975095	92.48	3019732	93.61
17.873	3899169	7.52	206045	6.39

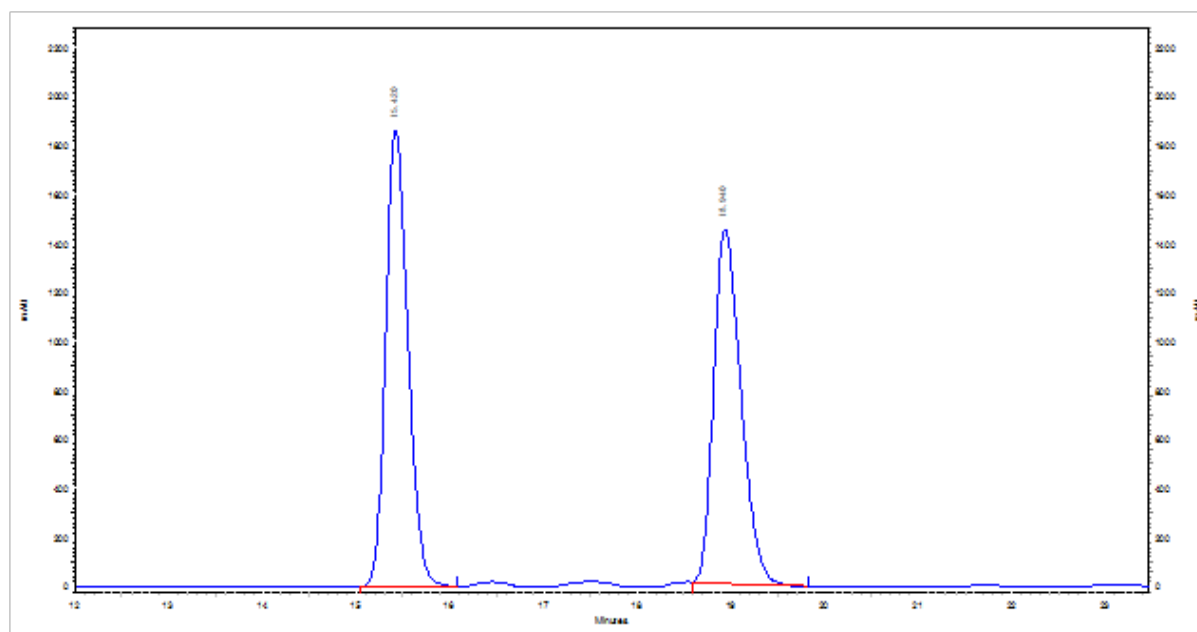
Totals	51874264	100.00	3225777	100.00
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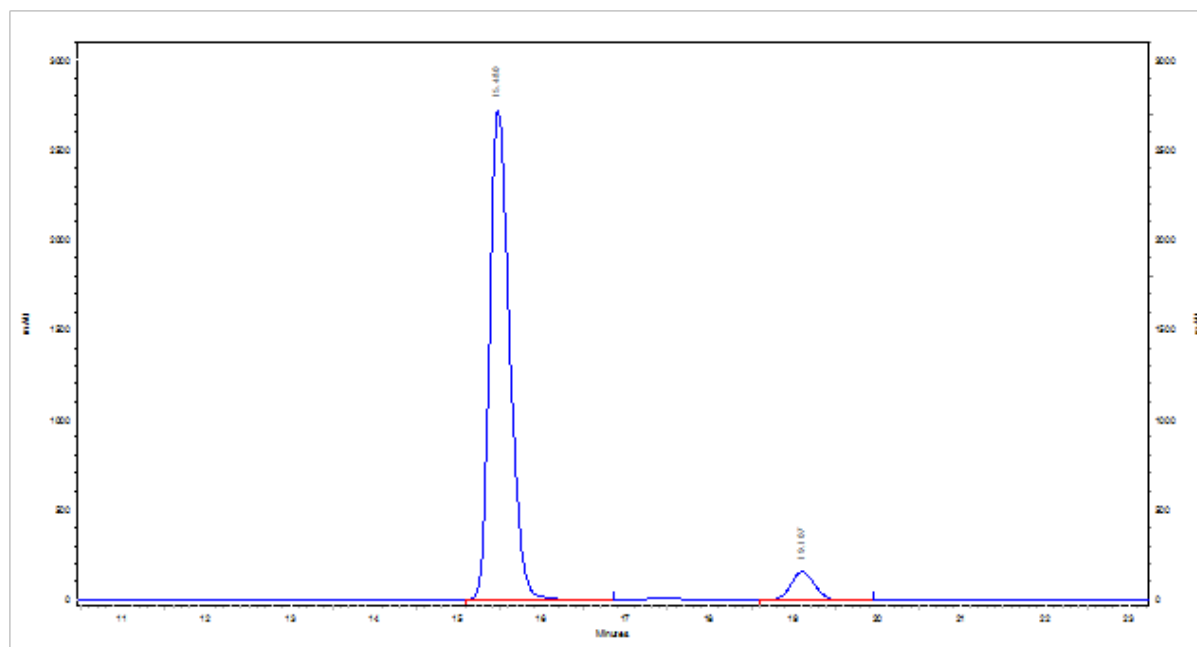
(*R*)-2-fluoro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2e): (Table 3, entry 5)





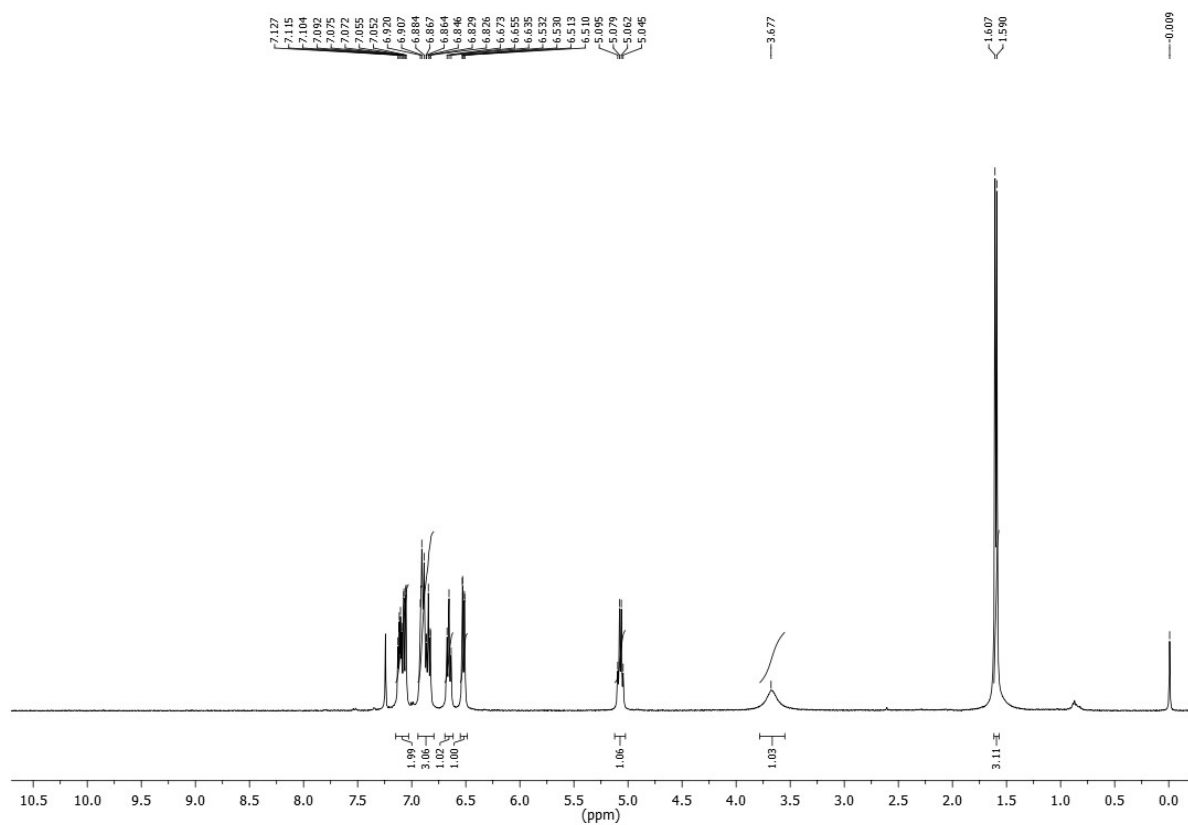
Retention Time	Area	Area %	Height	Height %
15.420	10684601	49.48	3909279	56.32
18.940	10911116	50.52	3031679	43.68

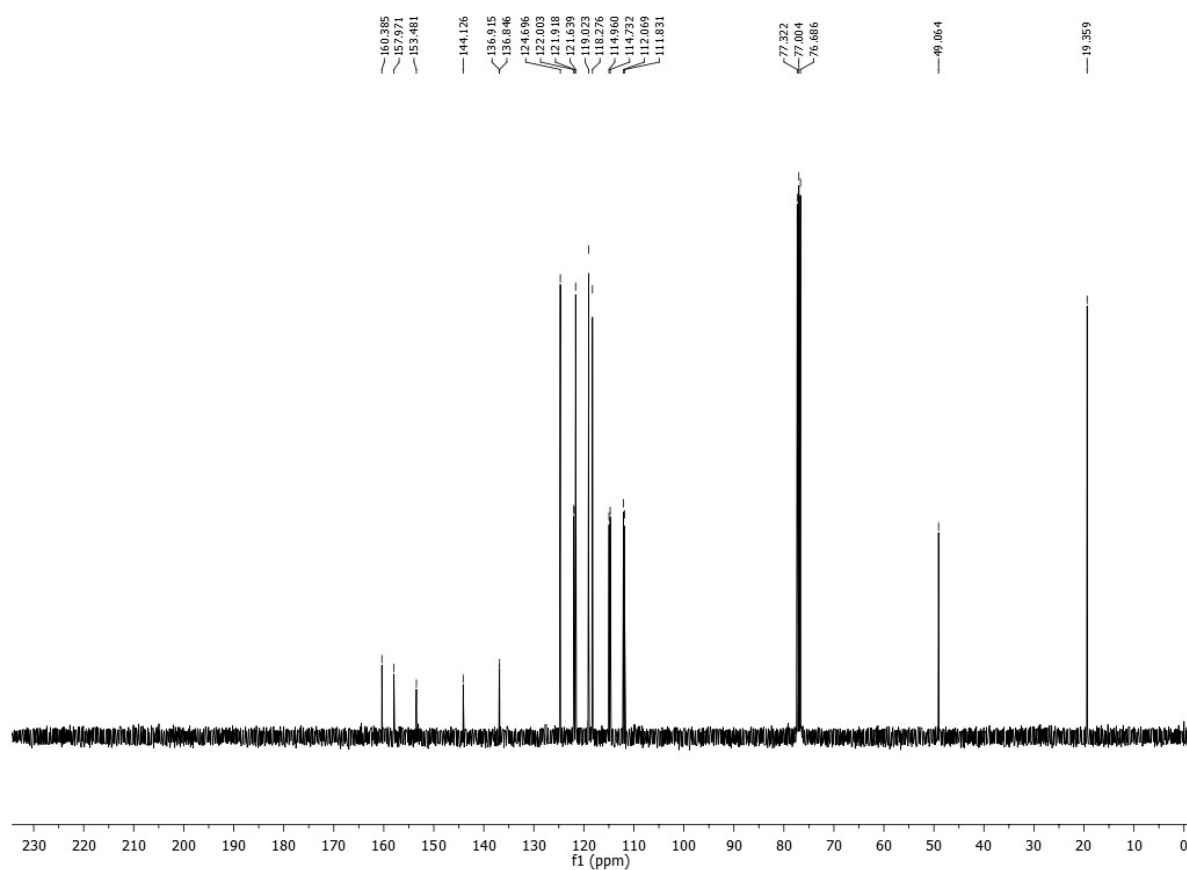
Totals	125676991	100.00	6940958	100.00
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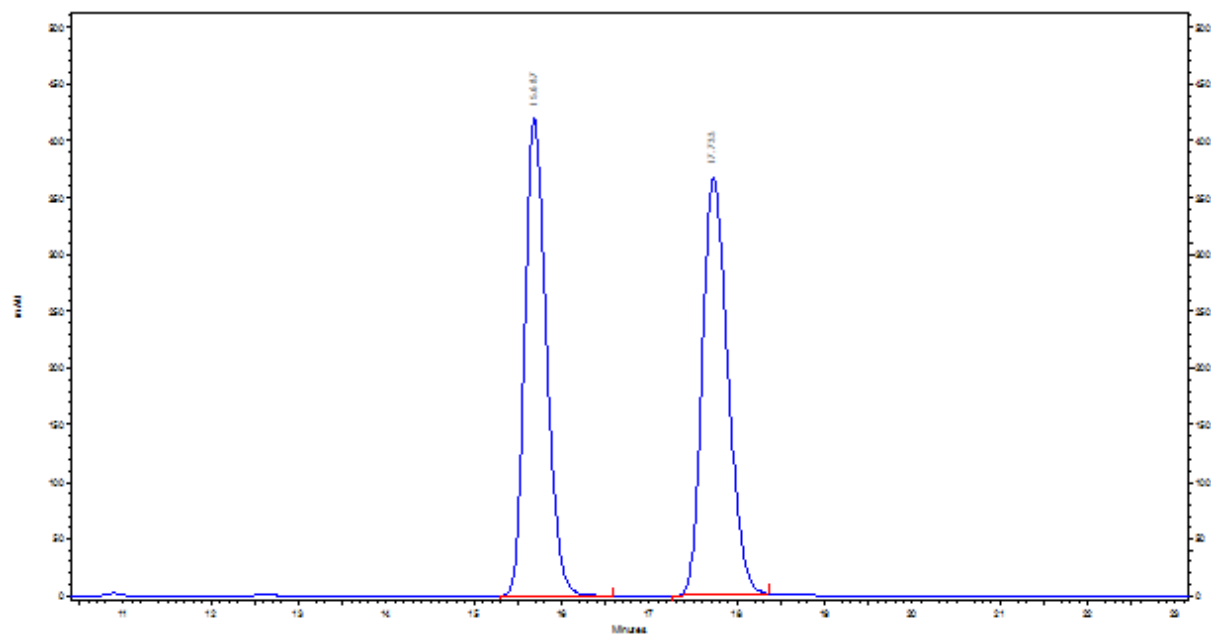
Retention Time	Area	Area %	Height	Height %
15.480	94309605	93.61	5705705	94.55
19.107	6433004	6.39	329187	5.45

Totals	100742609	100.00	6034892	100.00
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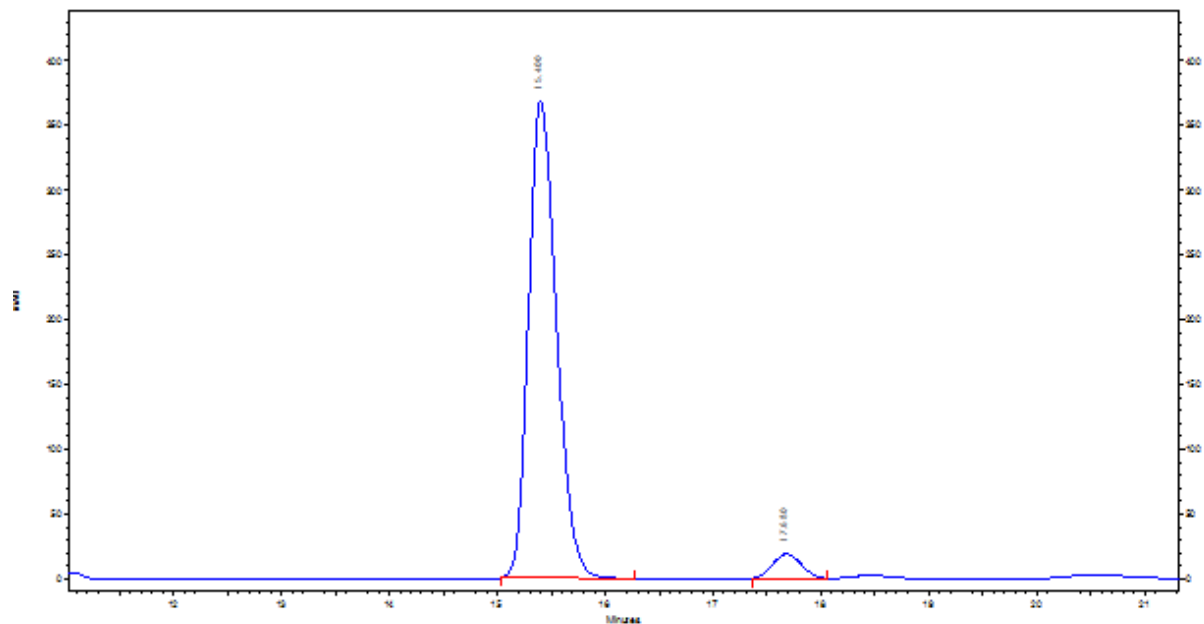


(*R*)-4-bromo-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2f) : (Table 3, entry 6)



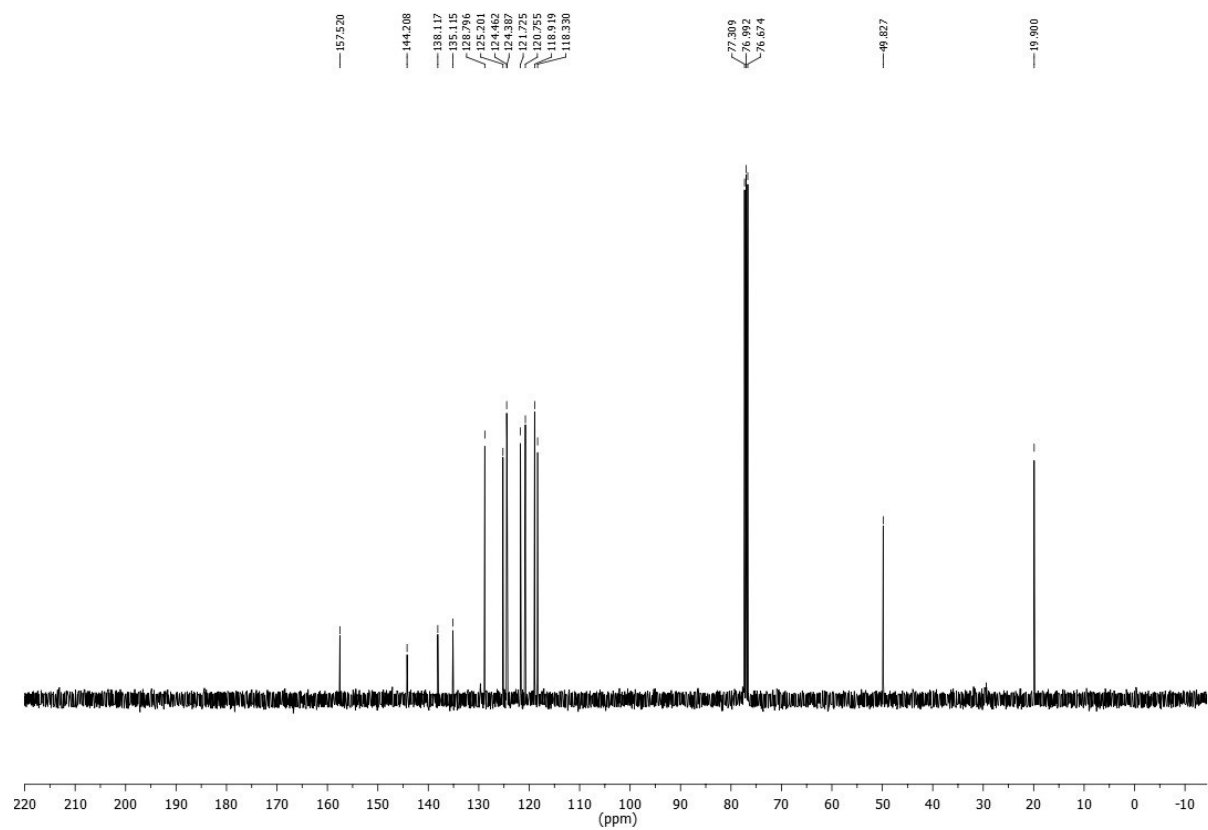
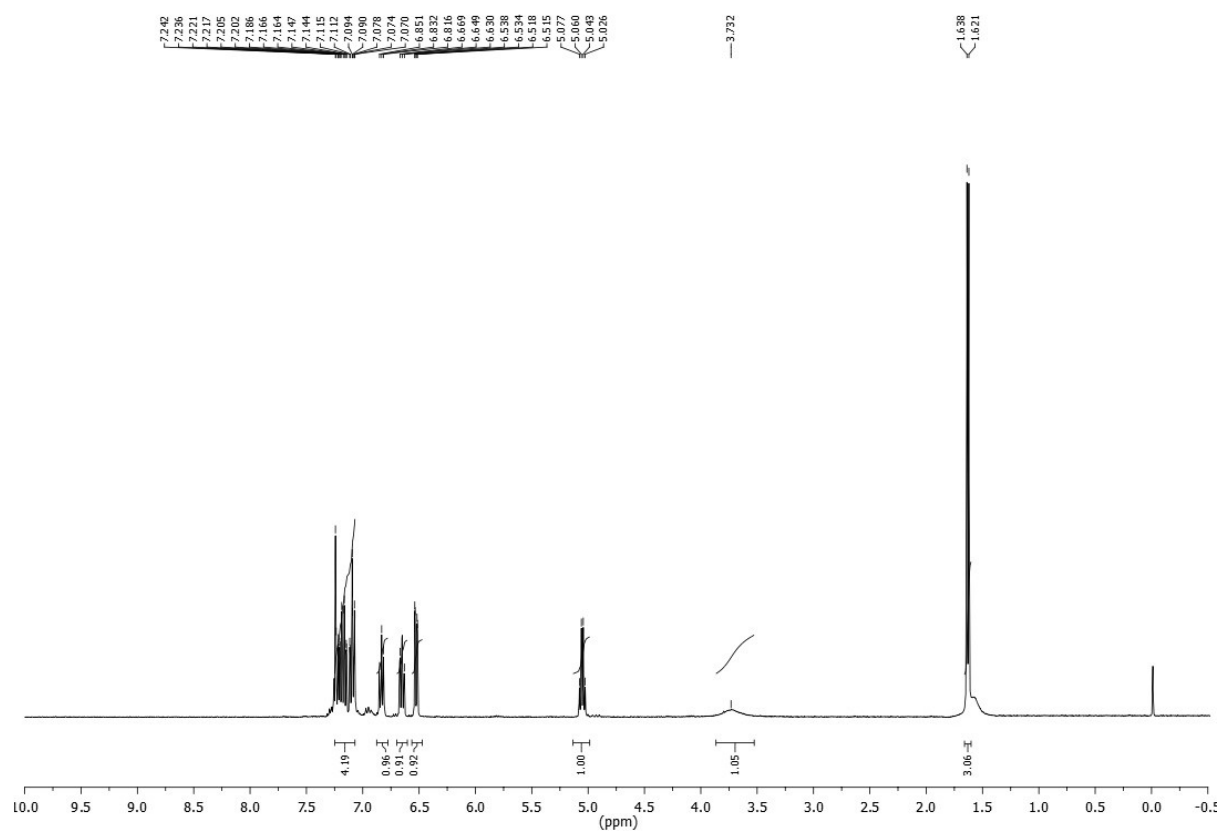
Retention Time	Area	Area %	Height	Height %
15.687	15158342	49.33	880978	53.35
17.733	15569438	50.67	770362	46.65

Totals	30727780	100.00	1651340	100.00
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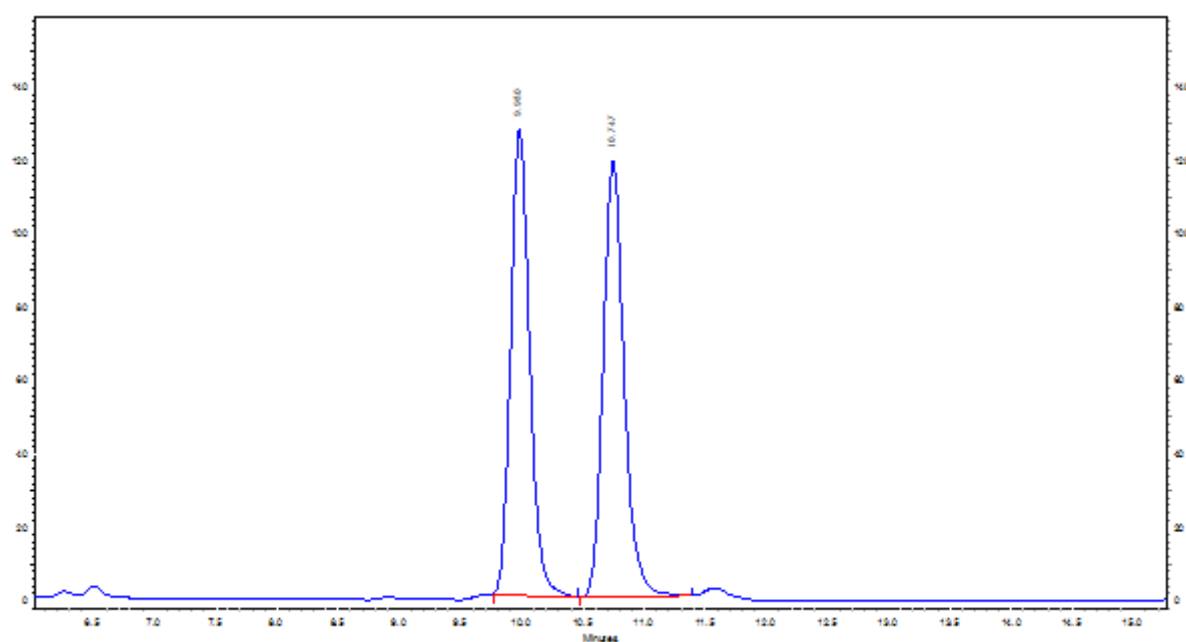
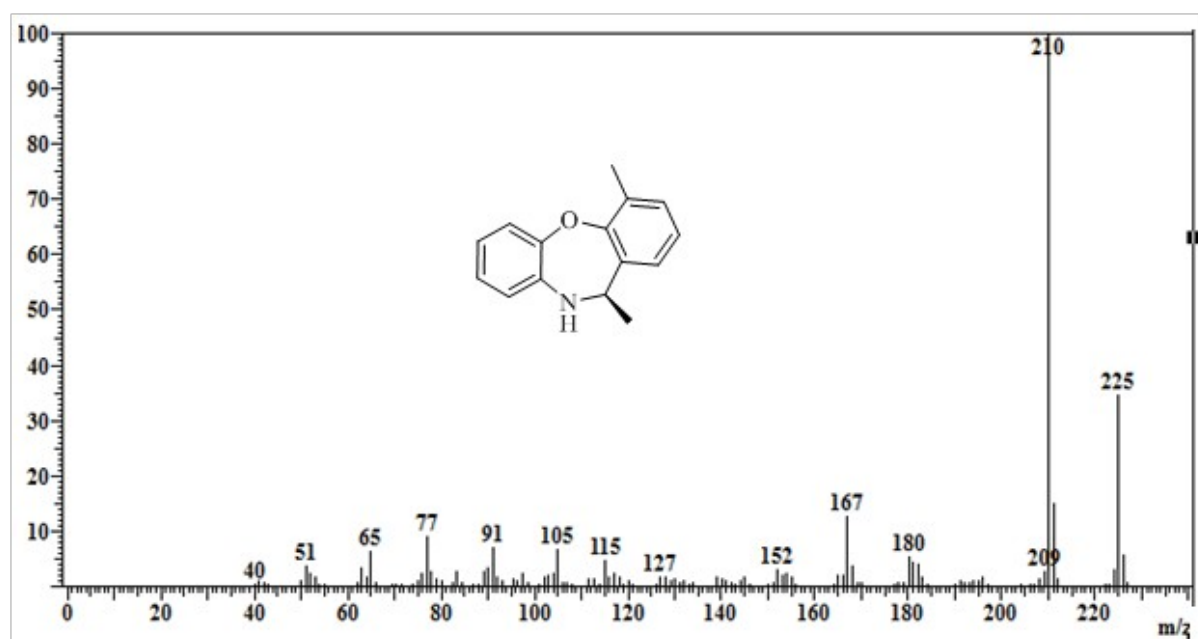


Retention Time	Area	Area %	Height	Height %
15.400	13857689	94.84	770081	95.02
17.680	754663	5.16	40357	4.98

Totals	14612352	100.00	810438	100.00
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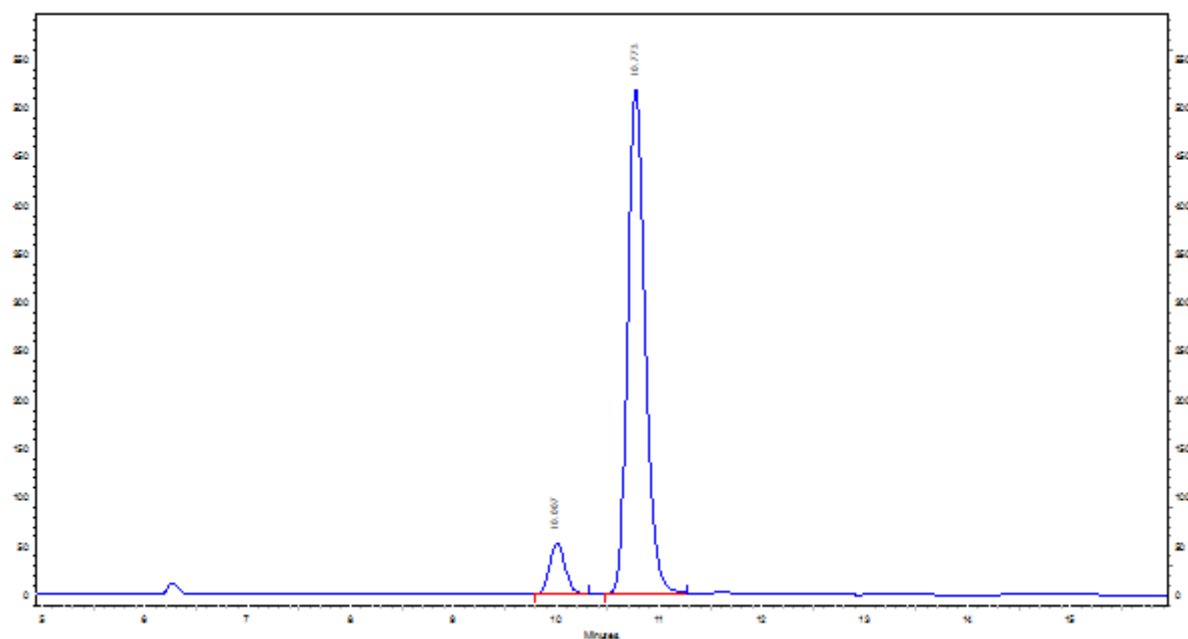


(*R*)-4,11-dimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine(2g): (Table 3, entry 7)



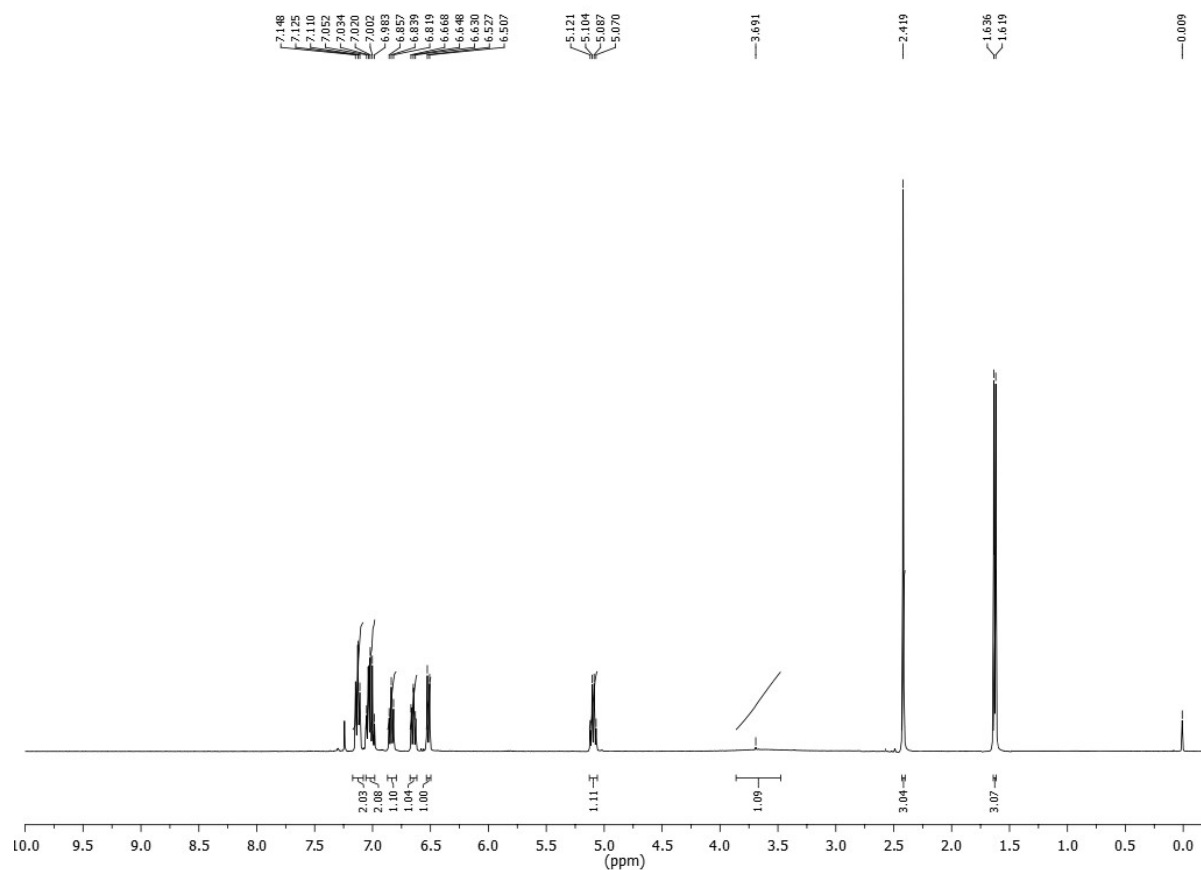
Retention Time	Area	Area %	Height	Height %
9.980	2882370	49.27	266931	51.68
10.747	2967439	50.73	249585	48.32

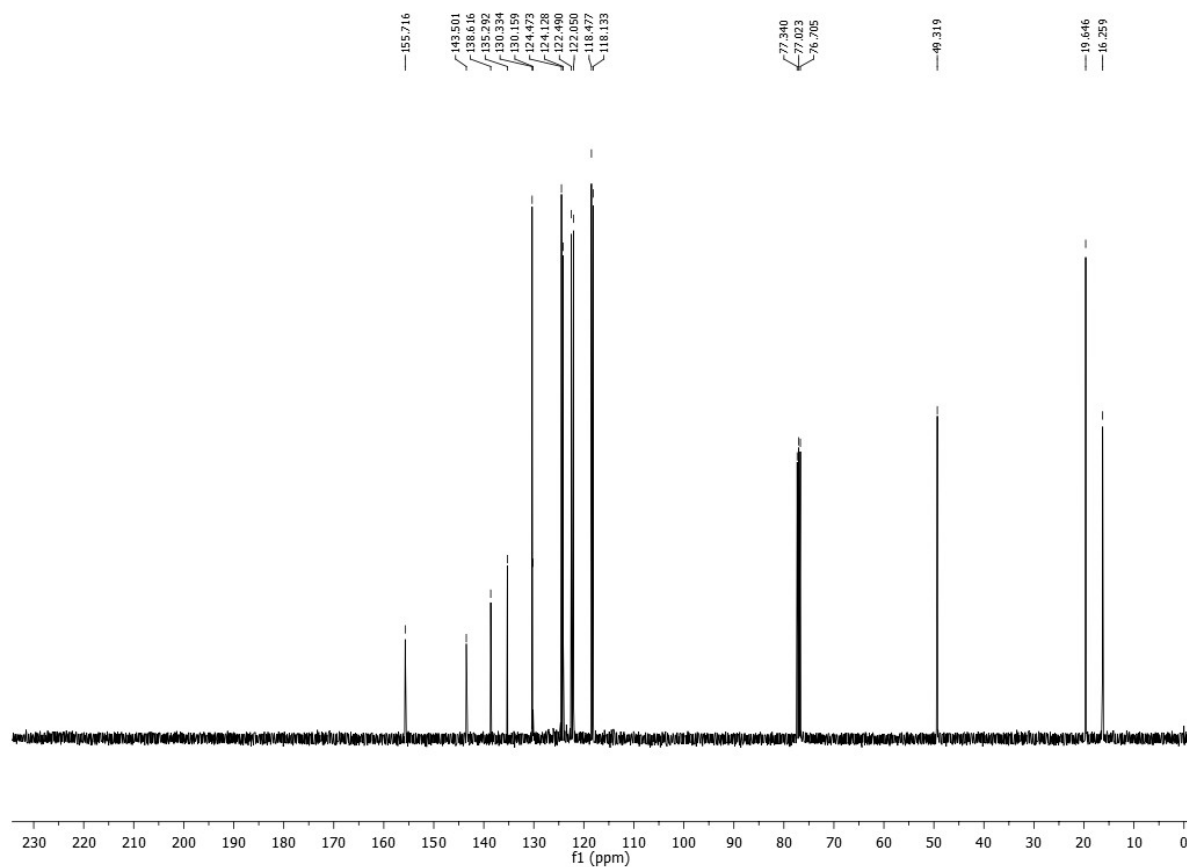
Totals	5849809	100.00	516516	100.00
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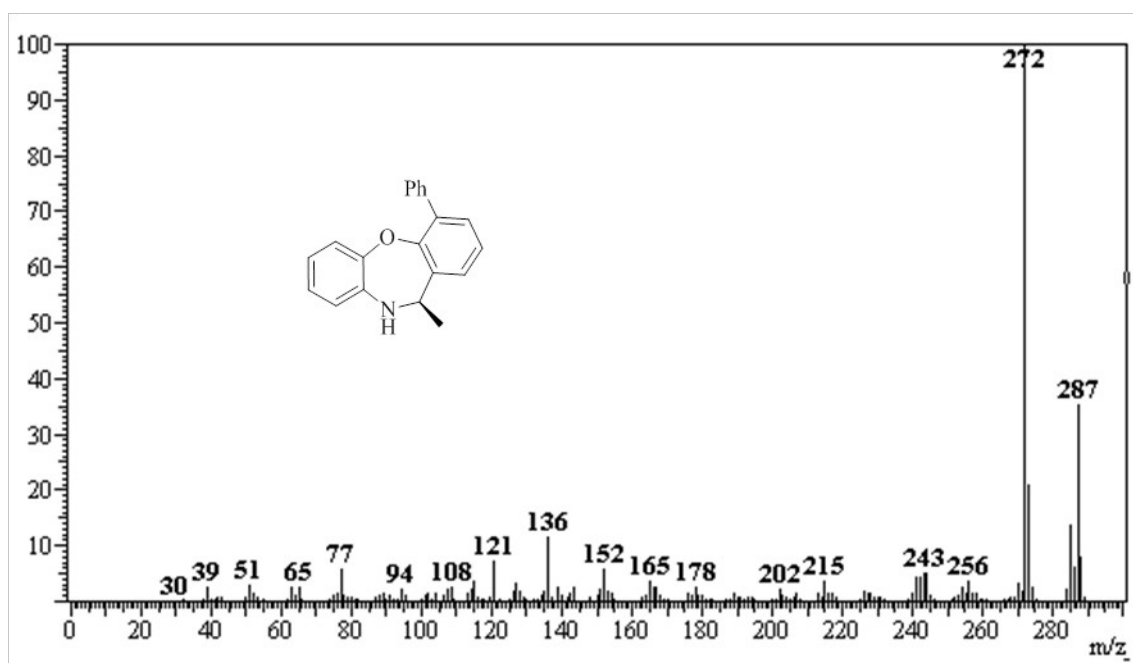
Retention Time	Area	Area %	Height	Height %
10.007	1182398	8.44	111439	9.30
10.773	12821885	91.56	1087474	90.70

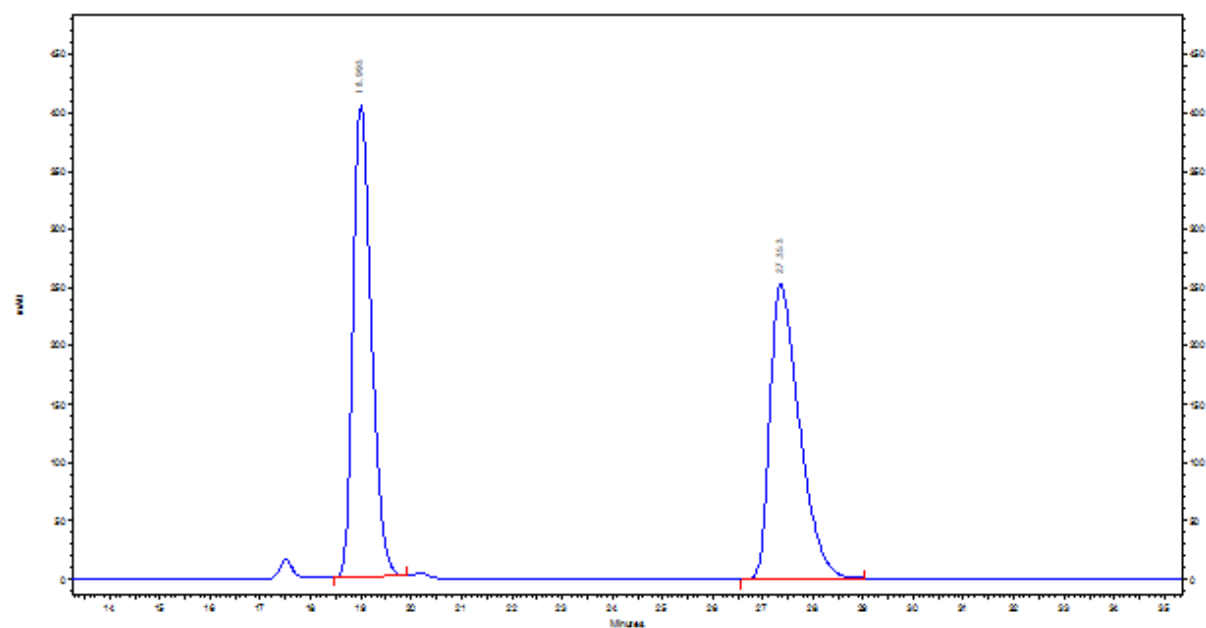
Totals	Area	Area %	Height	Height %
	14004283	100.00	1198913	100.00





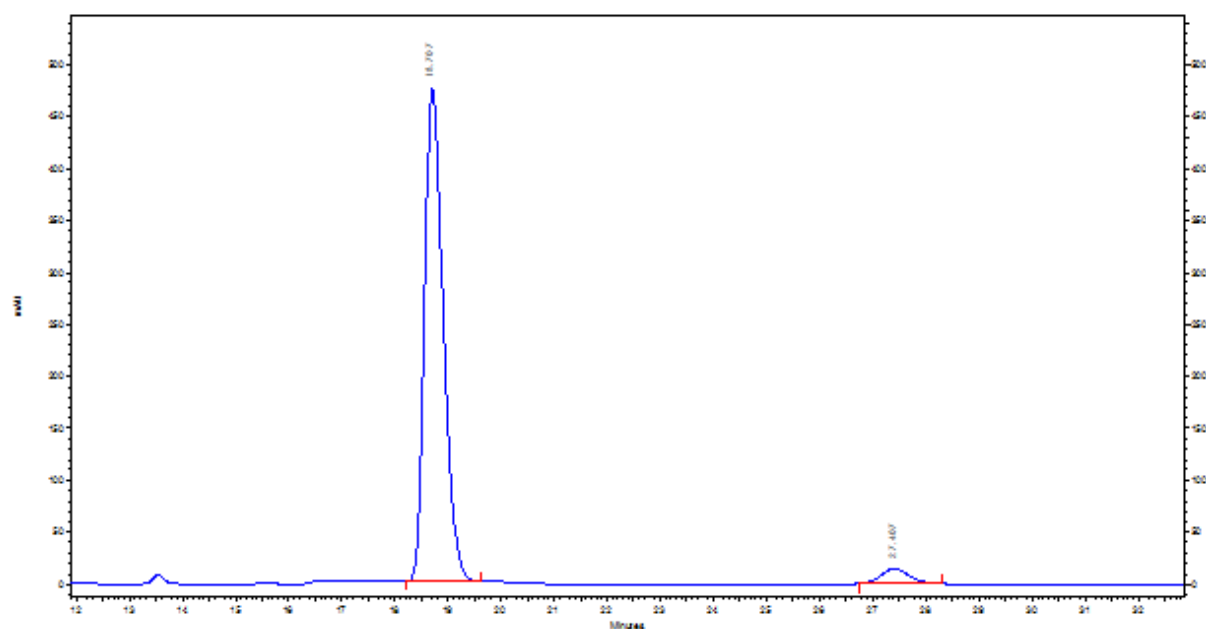
(*R*)-11-methyl-4-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2h): (Table 3 entry 8)



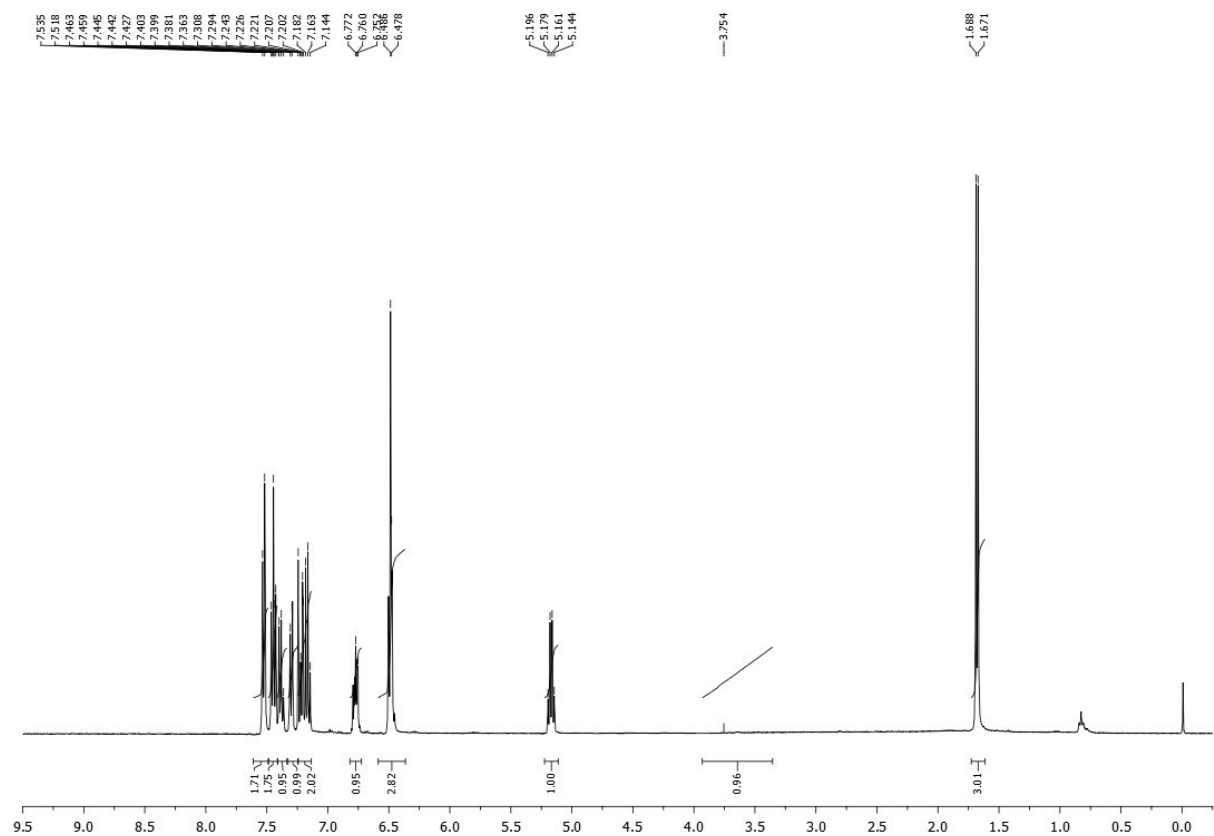


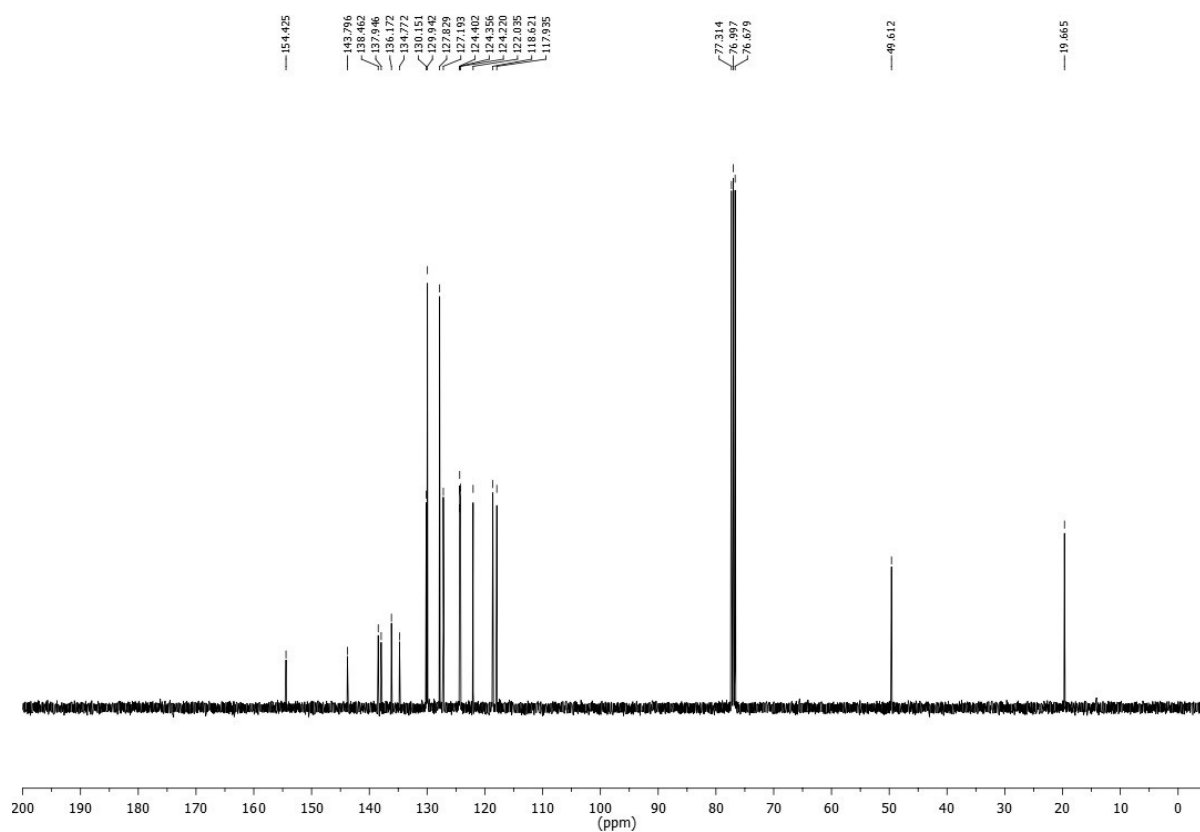
Retention Time	Area	Area %	Height	Height %
18.993	21596445	50.01	849447	61.60
27.353	21585542	49.99	529504	38.40

Totals	43181987	100.00	1378951	100.00
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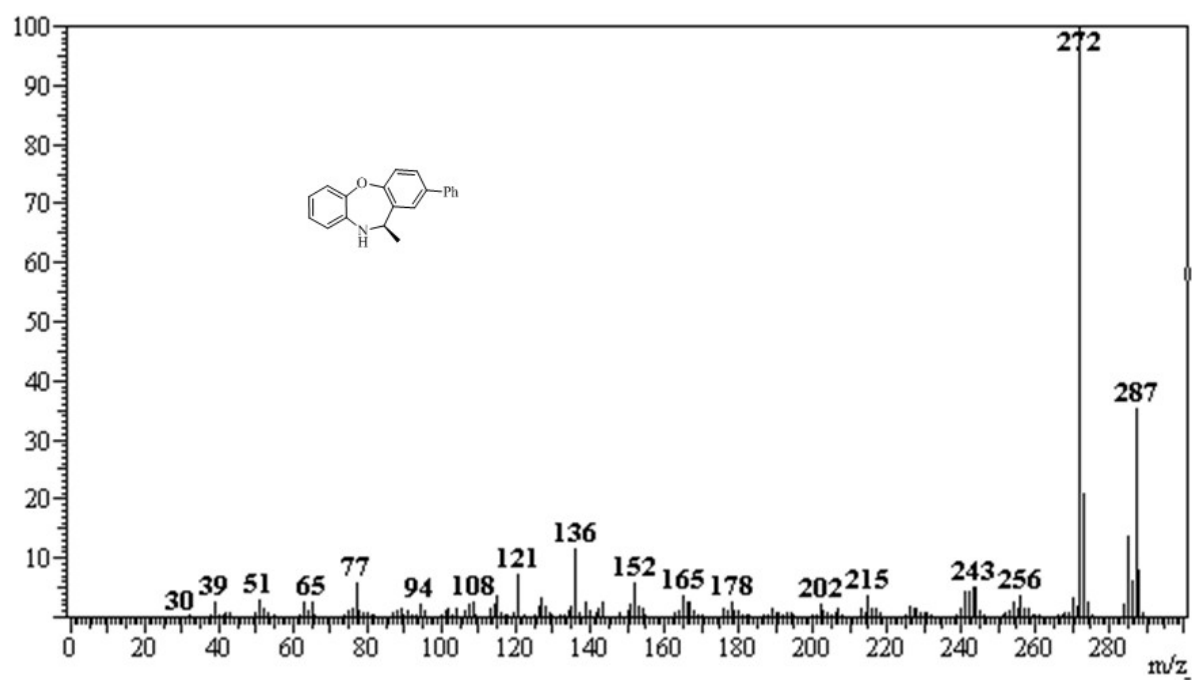


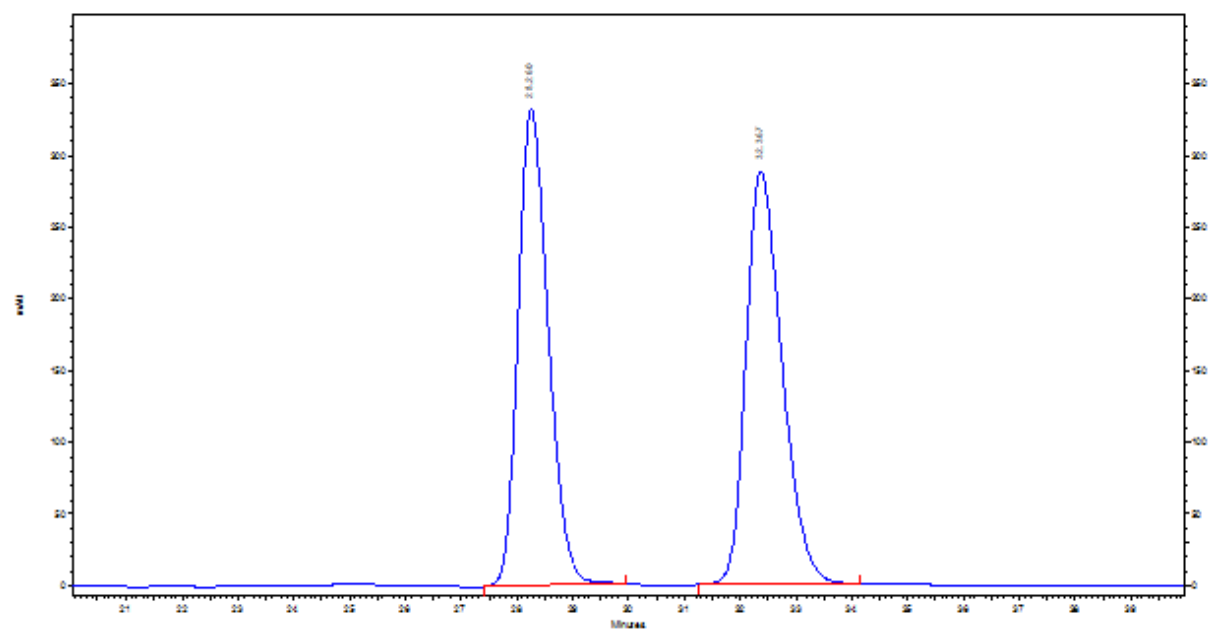
Retention Time	Area	Area %	Height	Height %
18.707	24430620	95.45	994758	97.05
27.407	1163642	4.55	30225	2.95
Totals	25594262	100.00	1024983	100.00





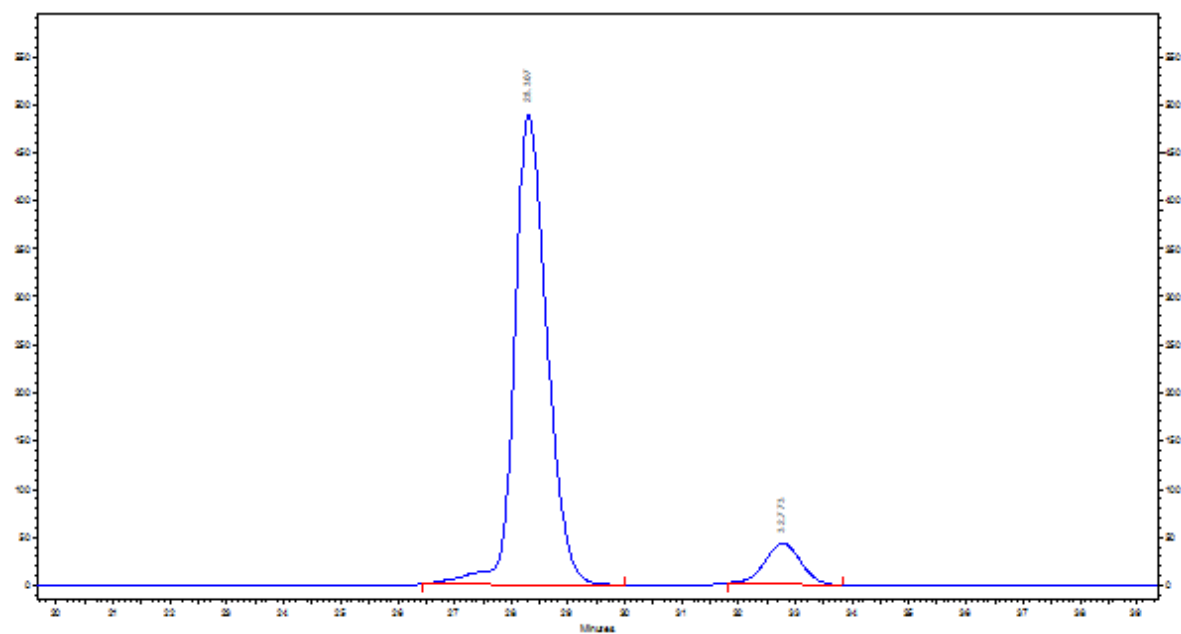
(R)-11-methyl-2-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2i): (Table 3, entry 9)





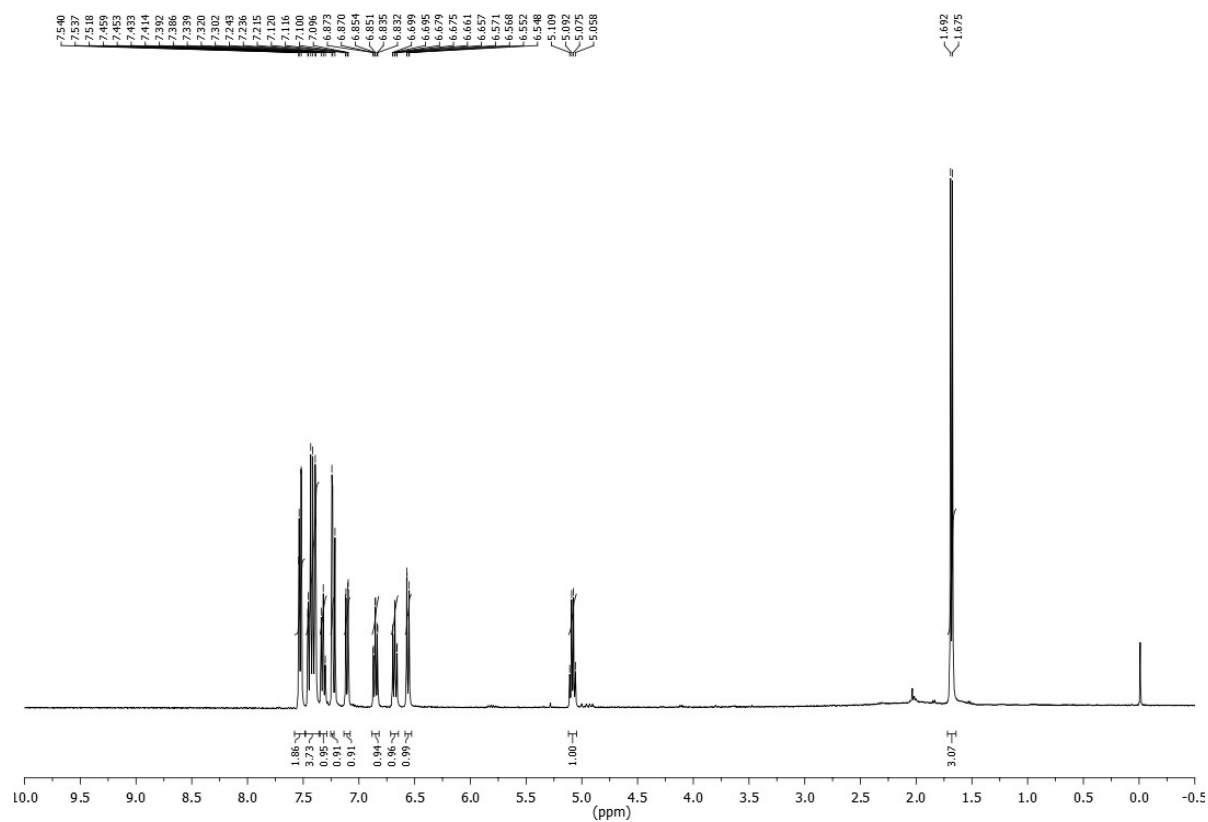
Retention Time	Area	Area %	Height	Height %
28.260	26151169	49.07	696114	53.57
32.367	27146063	50.93	603306	46.43

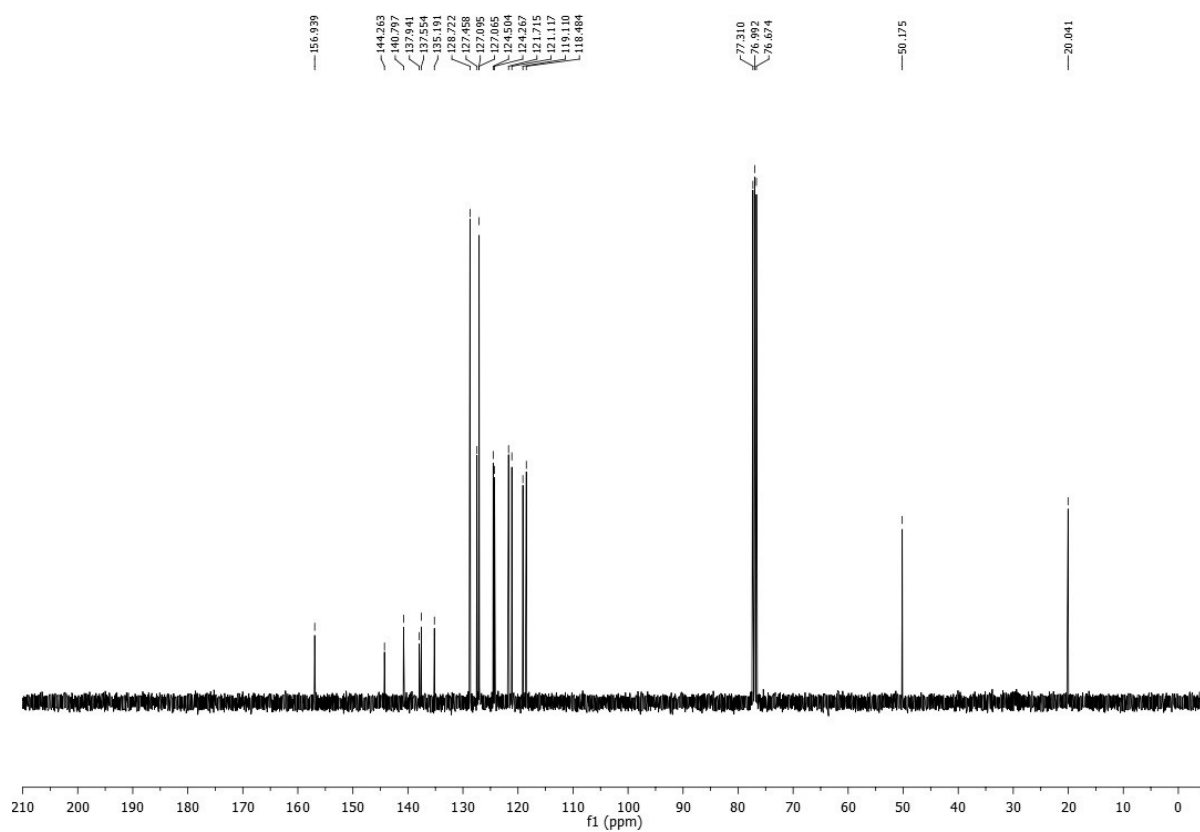
Totals	53297232	100.00	1299420	100.00
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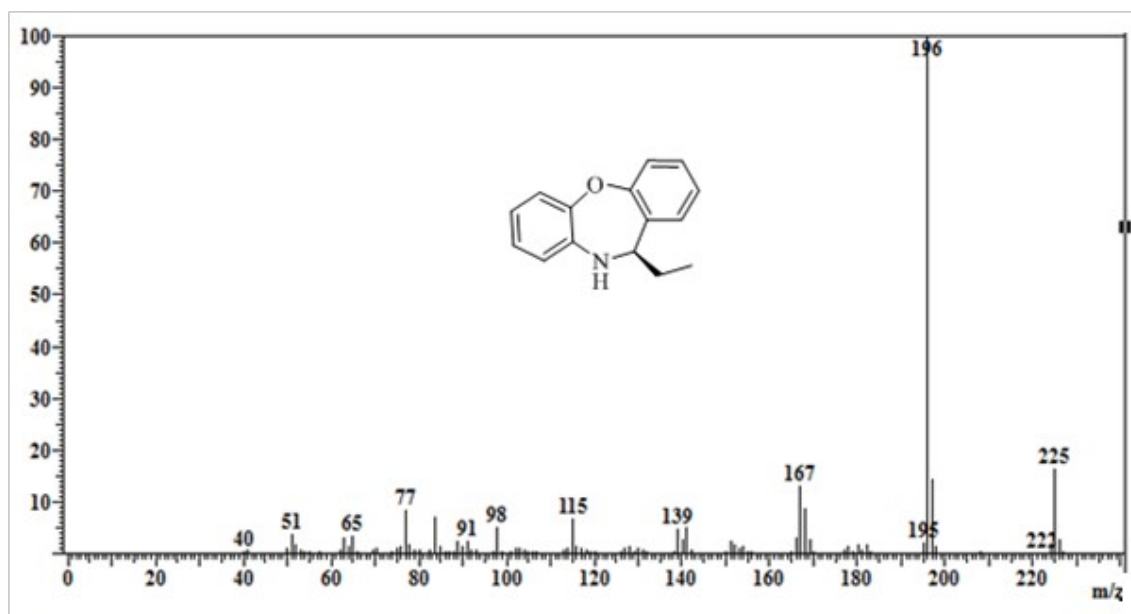
Retention Time	Area	Area %	Height	Height %
28.307	40820272	91.20	1027707	92.00
32.773	3941198	8.80	89343	8.00

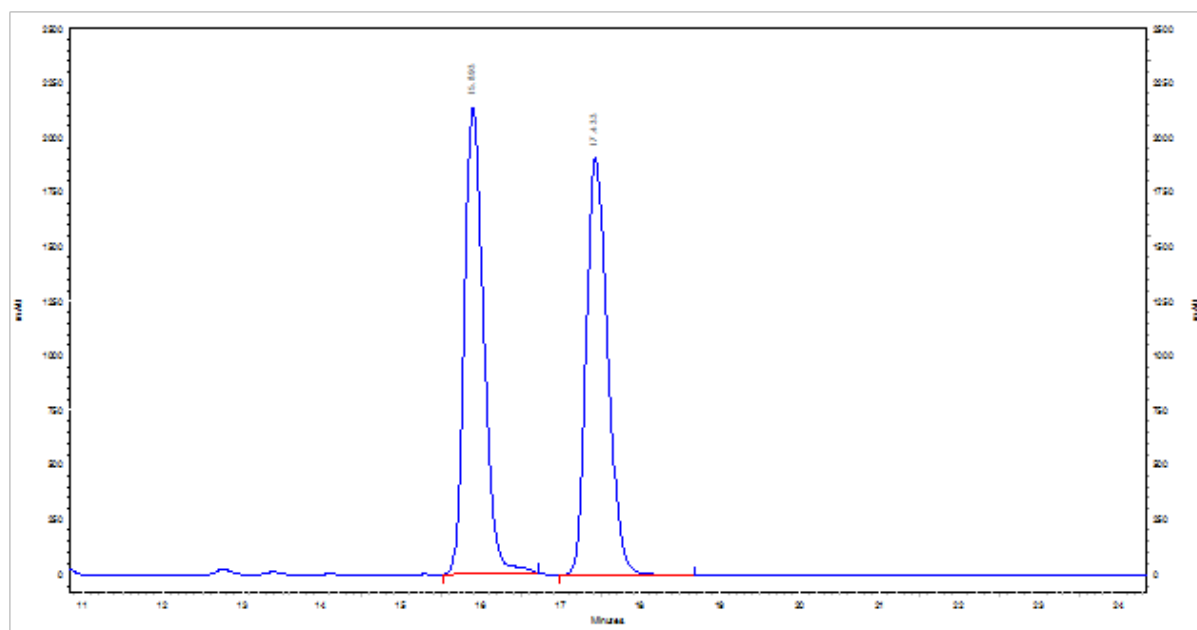
Totals	44761470	100.00	1117050	100.00
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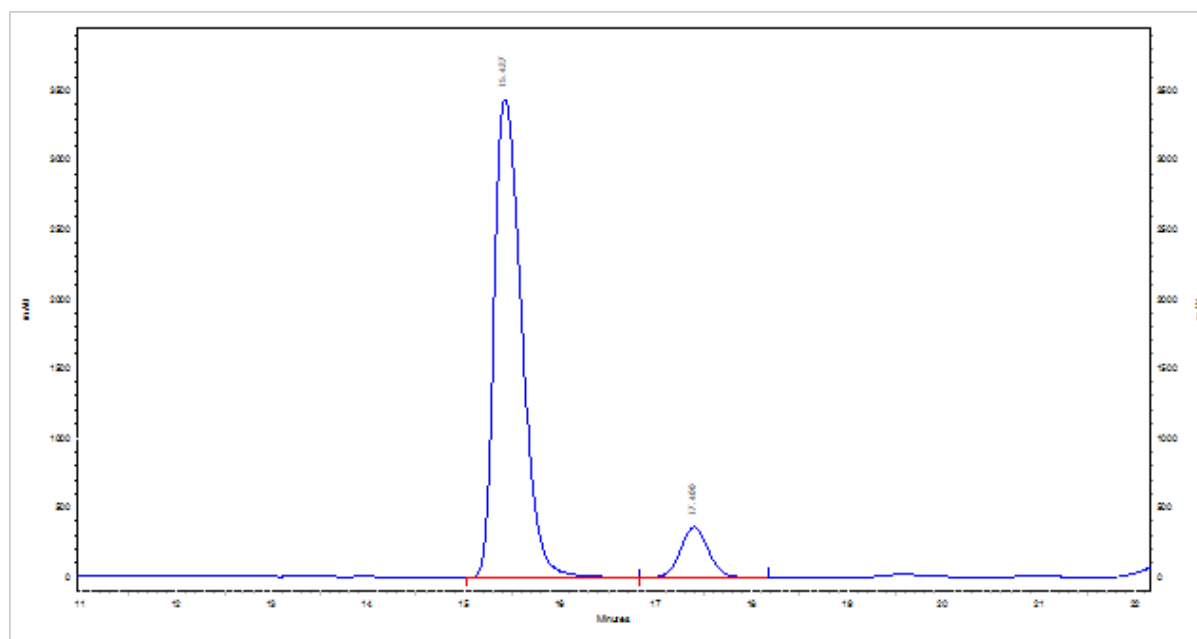
(R)-11-ethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine(2j): (Table 3, entry 10)





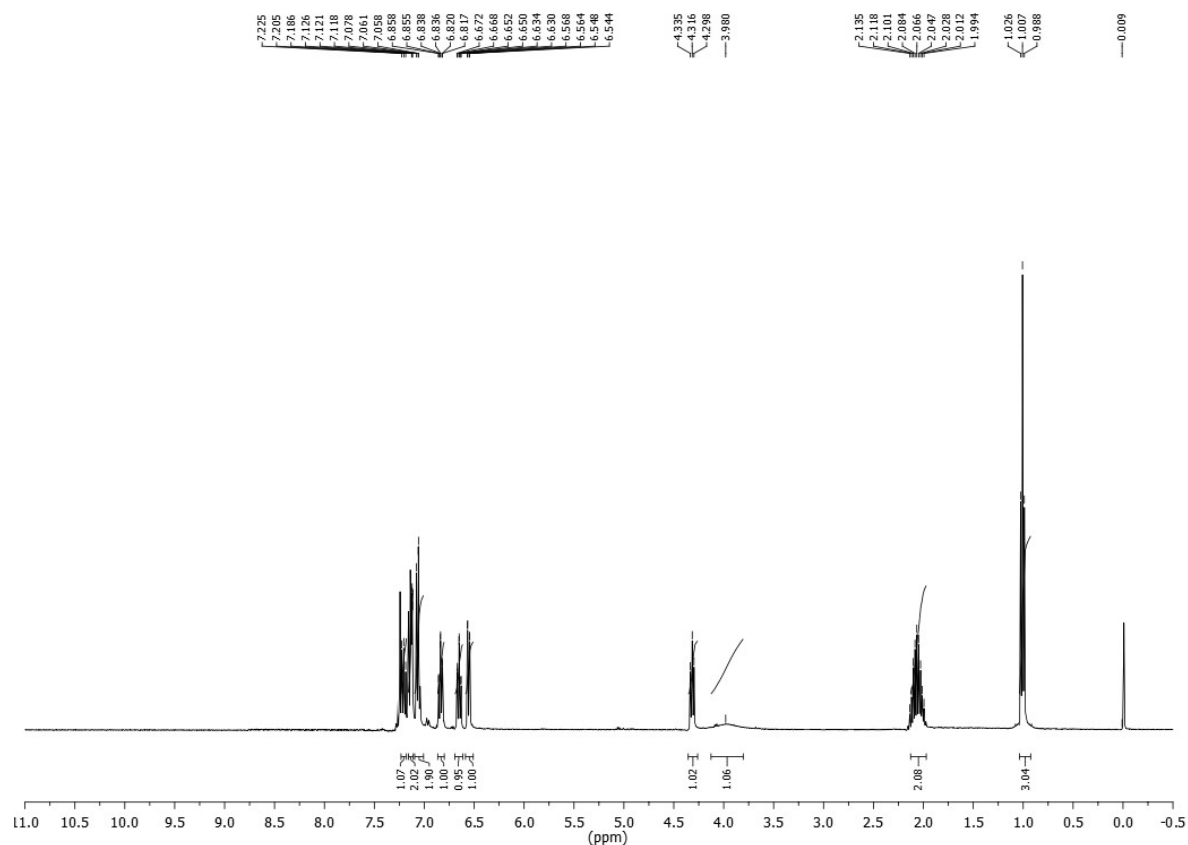
Retention Time	Area	Area %	Height	Height %
15.893	75078740	50.19	4477971	52.80
17.433	74520696	49.81	4002624	47.20

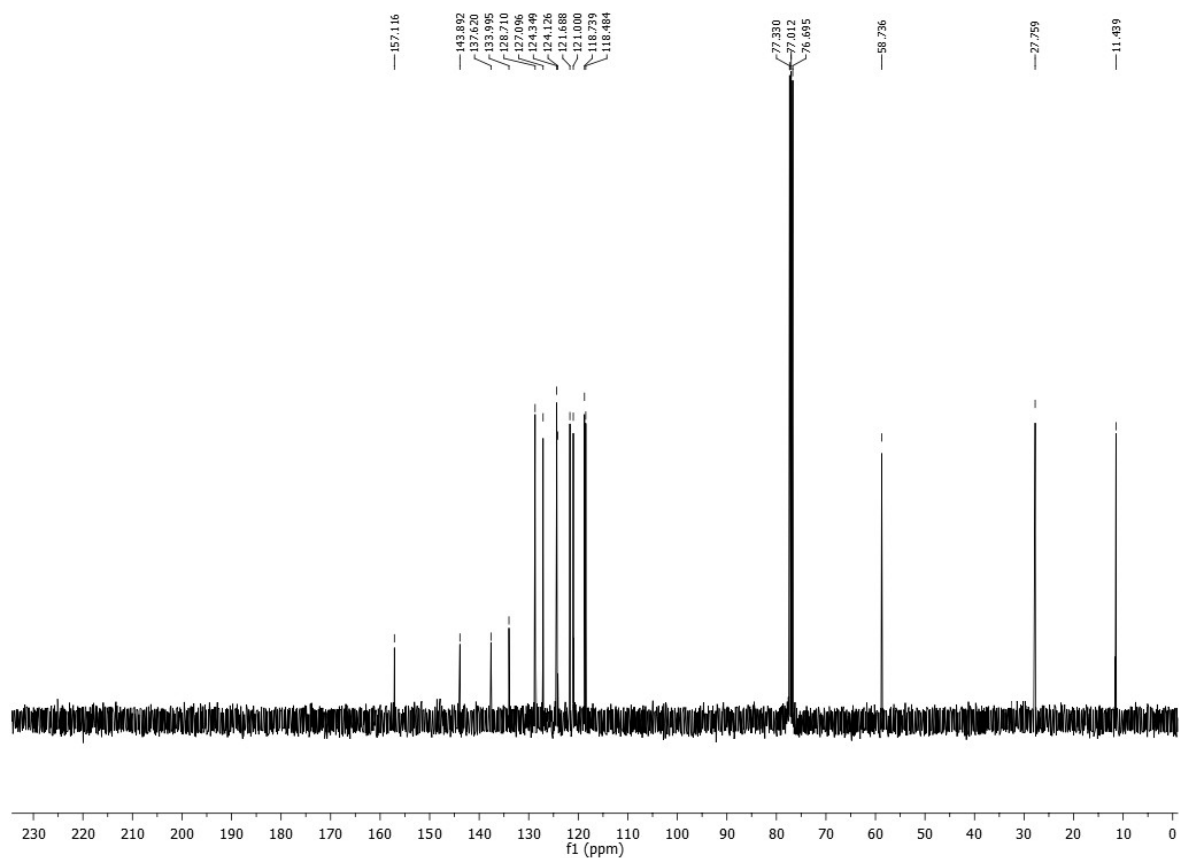
Totals	149599436	100.00	8480595	100.00
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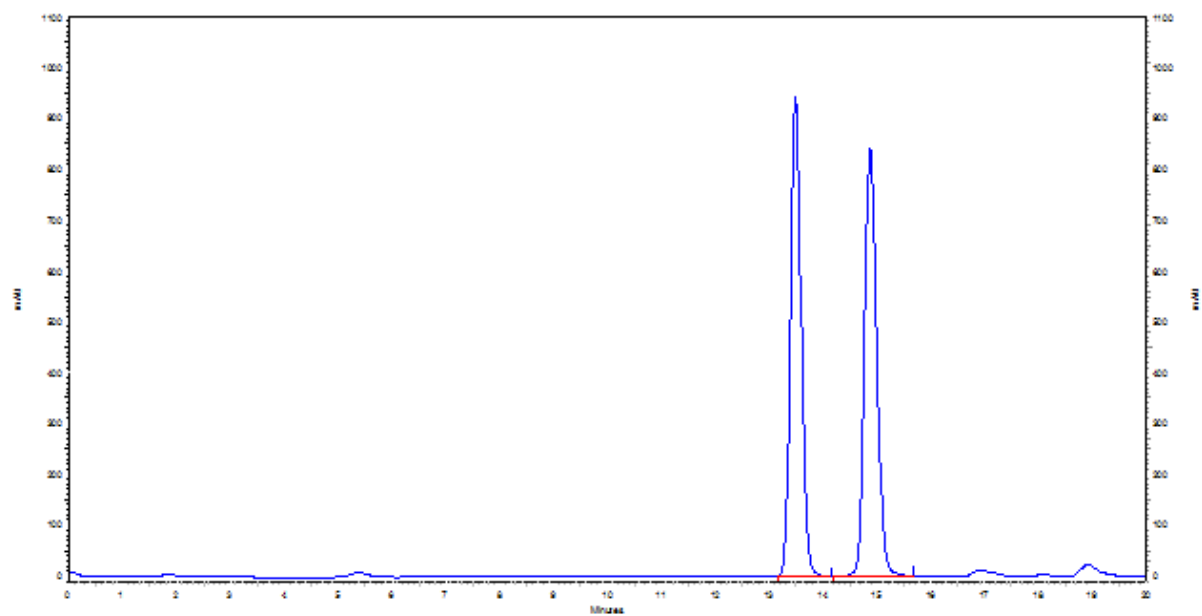
Retention Time	Area	Area %	Height	Height %
15.427	143632564	90.21	7219367	90.44
17.400	15584264	9.79	762686	9.56

Totals	159216828	100.00	7982053	100.00
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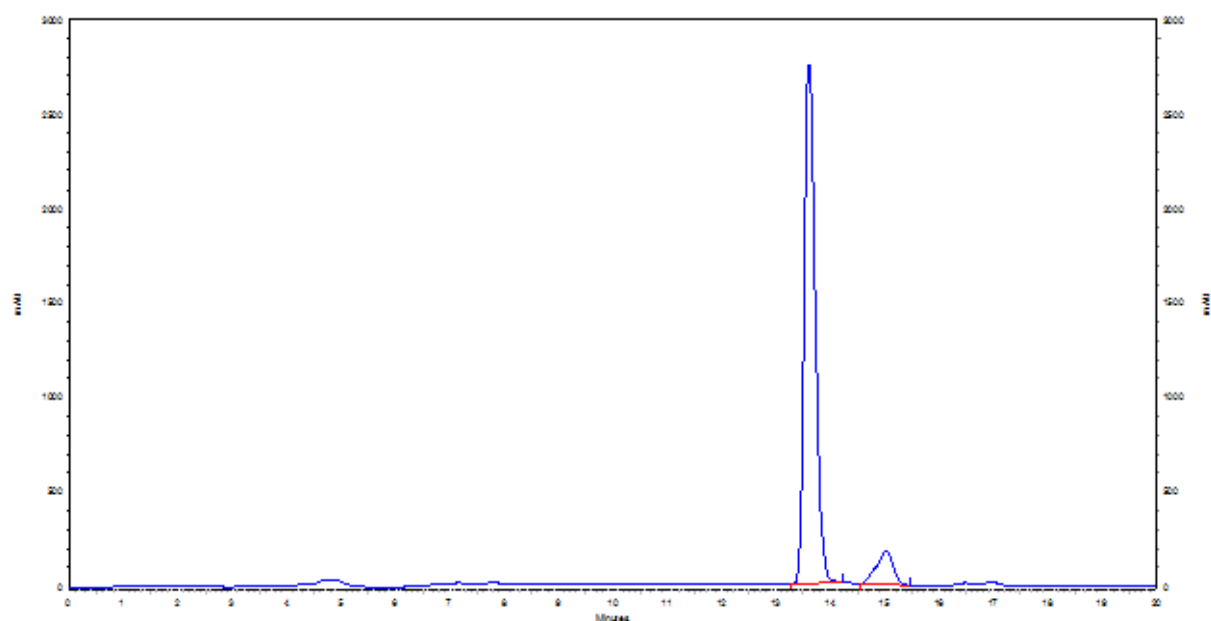


(*R*)-11-ethyl-2-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2k): (Table 3, entry 11)



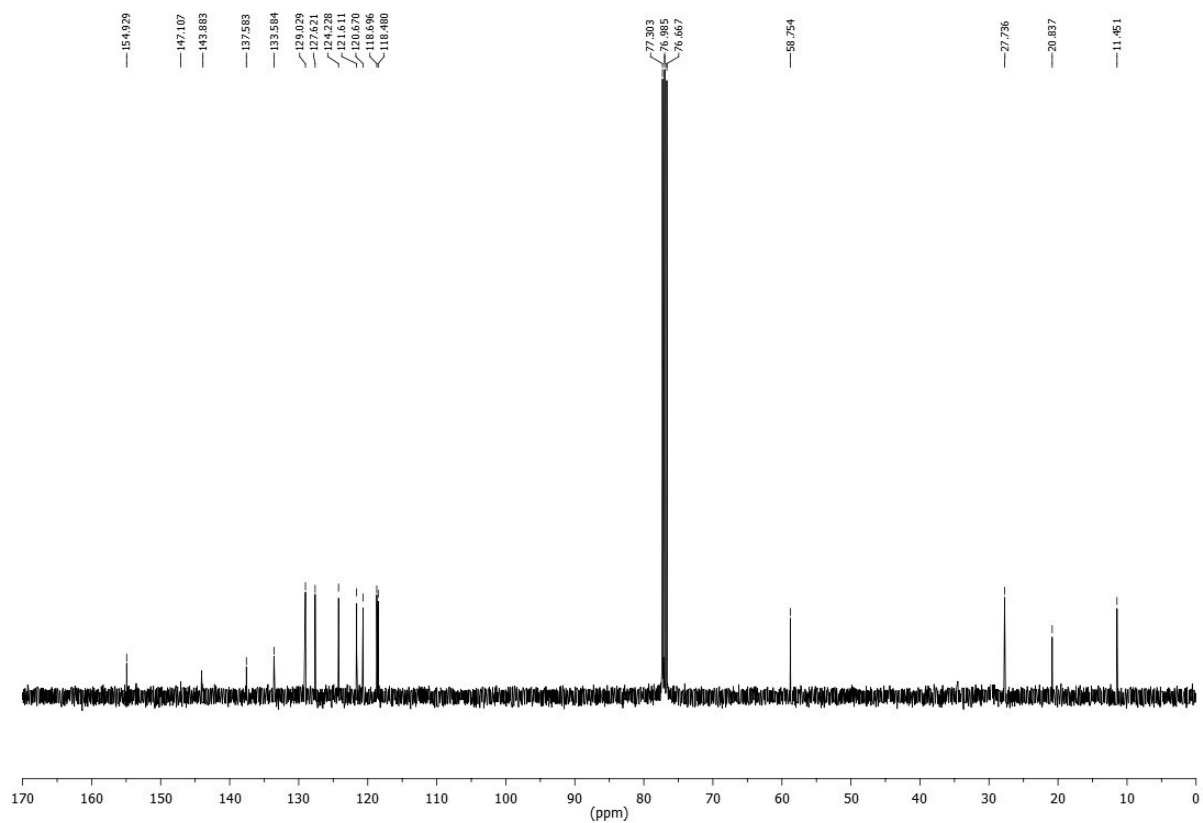
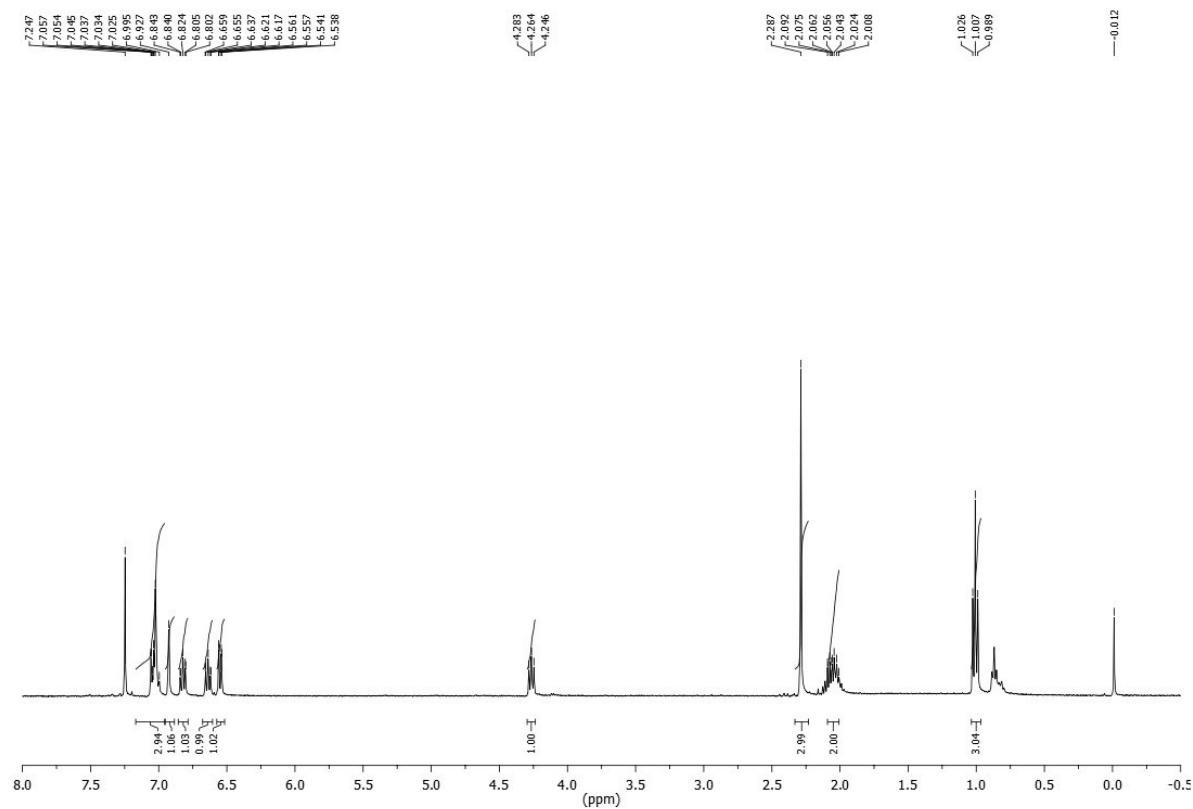
Retention Time	Area	Area %	Height	Height %
13.487	27524116	49.77	1976483	52.86
14.873	27772971	50.23	1762371	47.14

Totals	55297087	100.00	3738854	100.00
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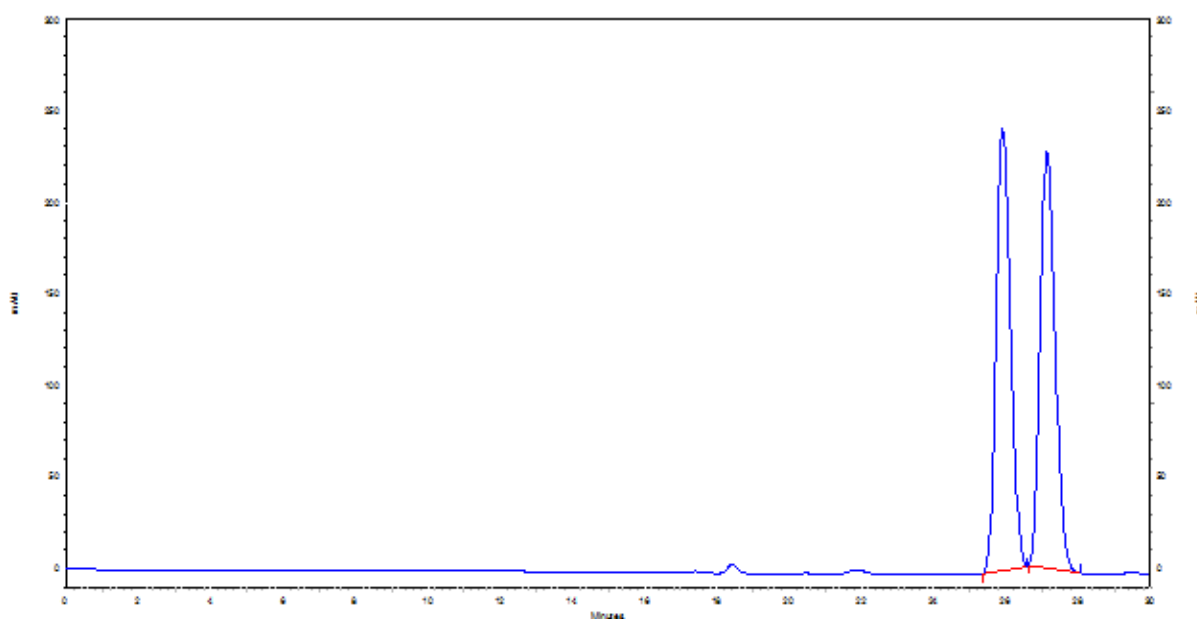
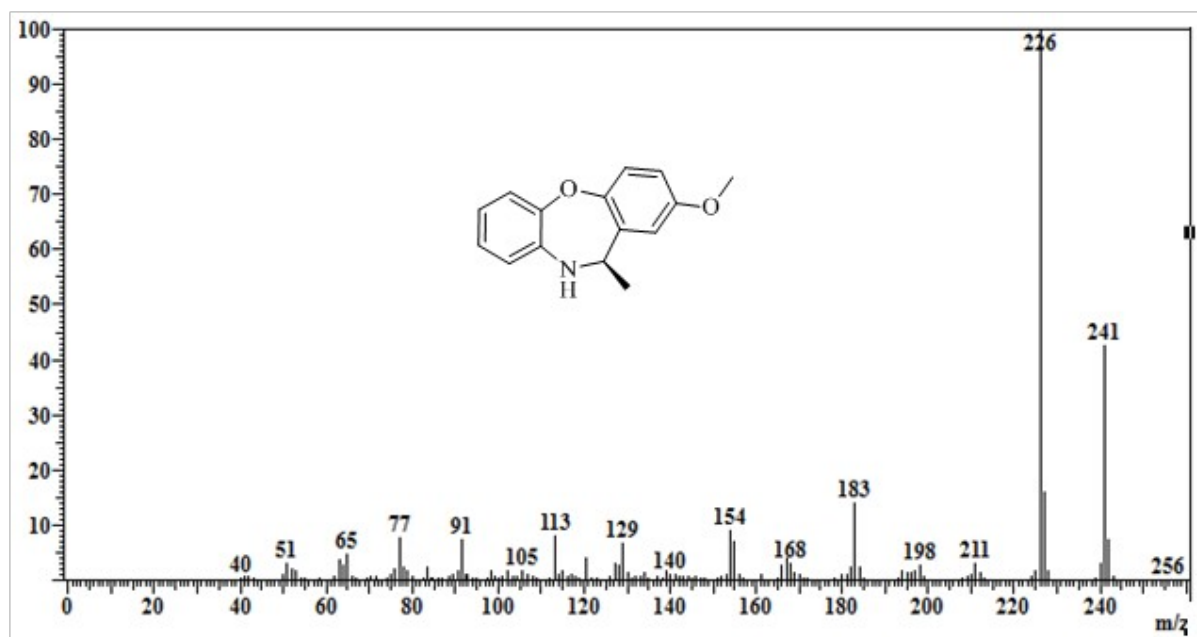


Retention Time	Area	Area %	Height	Height %
13.607	80985709	91.17	5758231	94.01
15.020	7843605	8.83	366724	5.99

Totals	88829314	100.00	6124955	100.00
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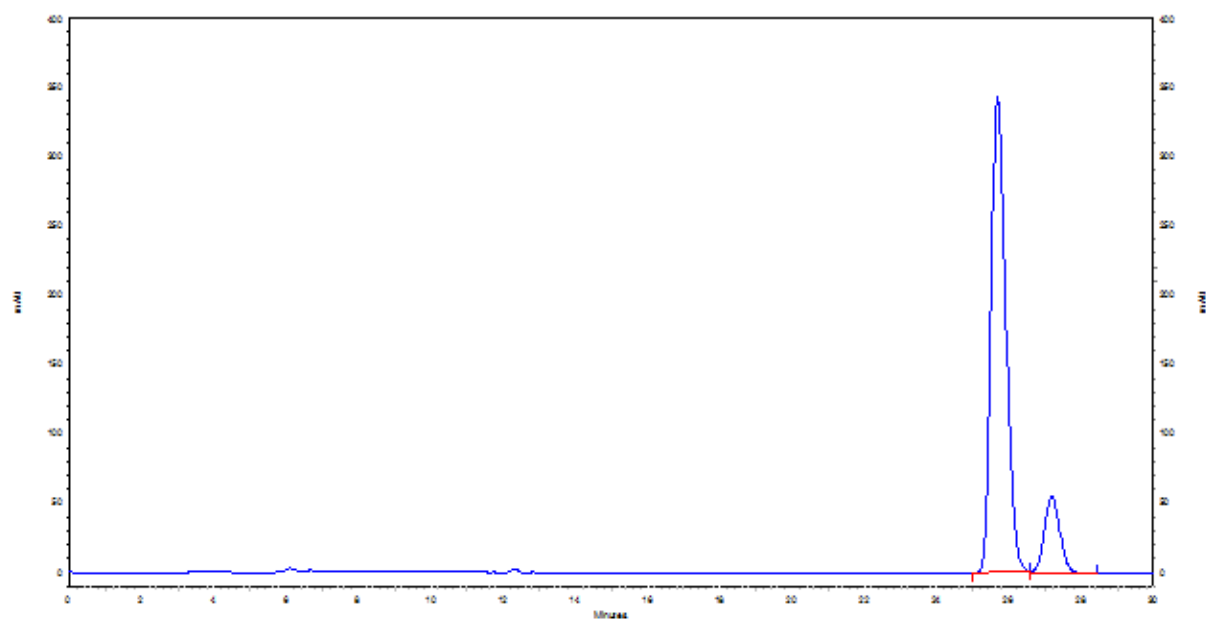


(R)-2-methoxy-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2m): (Table 3, entry 12)



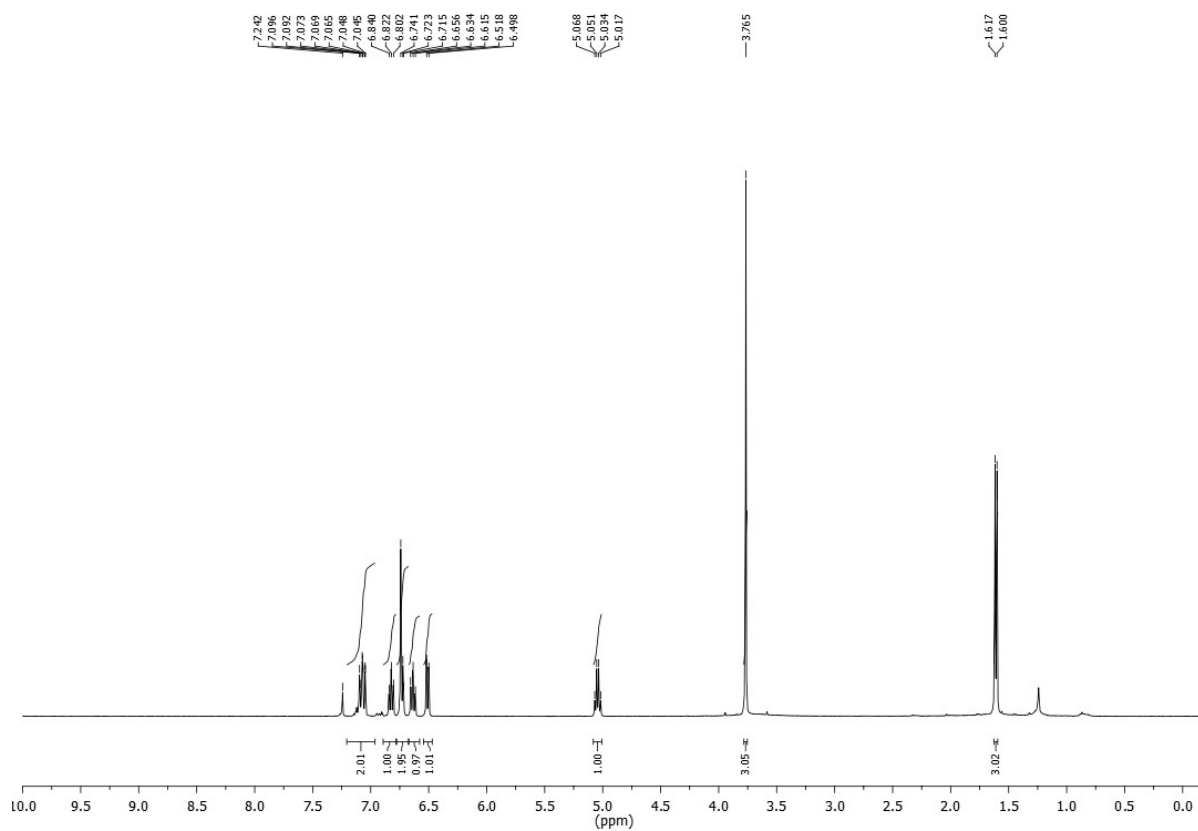
Retention Time	Area	Area %	Height	Height %
25.920	13968563	50.12	505555	51.48
27.147	13903508	49.88	476530	48.52

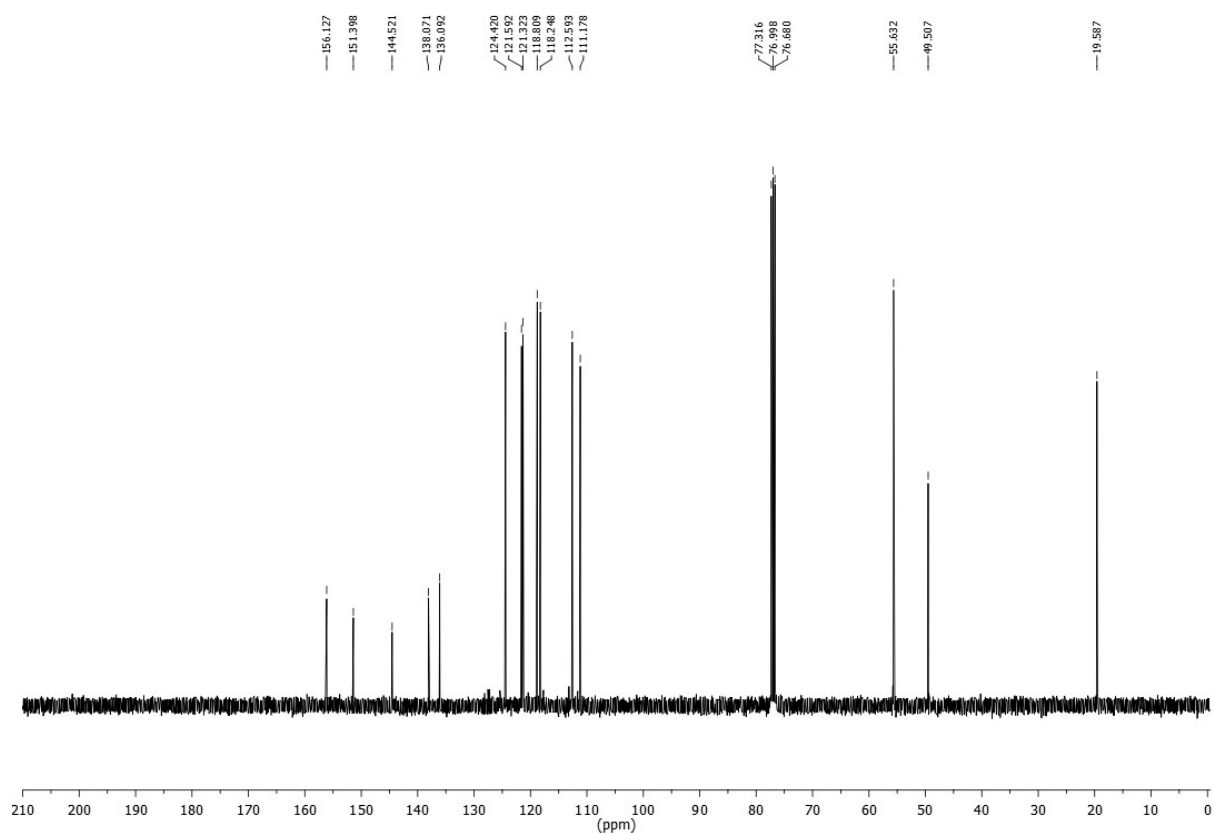
Totals	27872071	100.00	982085	100.00
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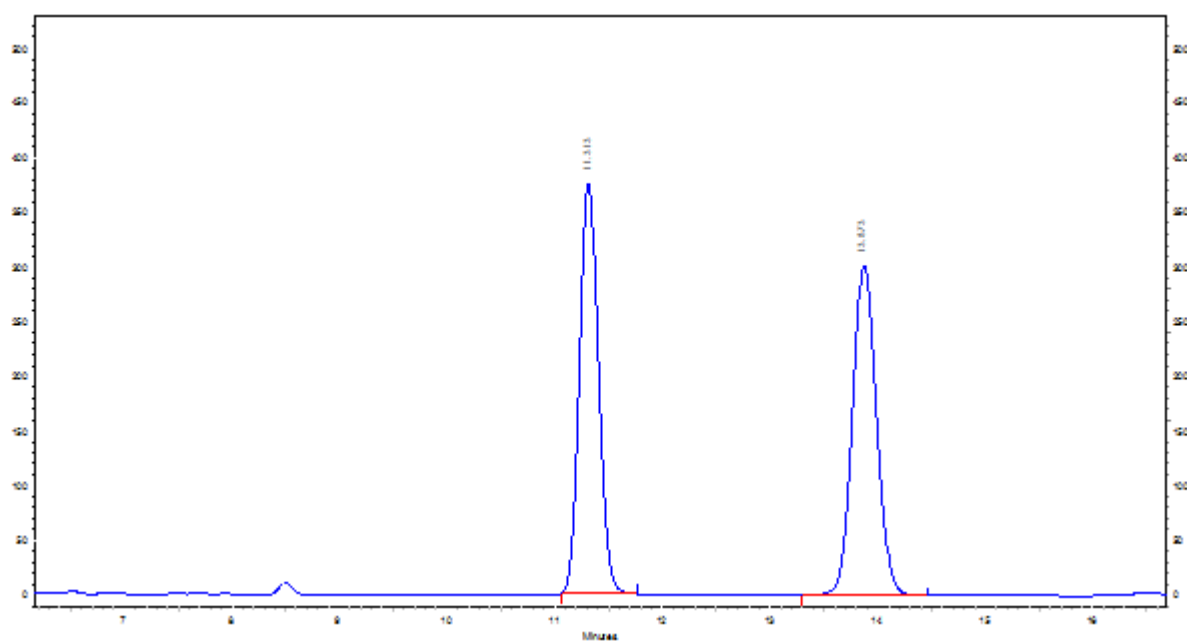
Retention Time	Area	Area %	Height	Height %
25.693	20427486	85.30	718776	85.96
27.200	3521668	14.70	117361	14.04

Totals	23949154	100.00	836137	100.00
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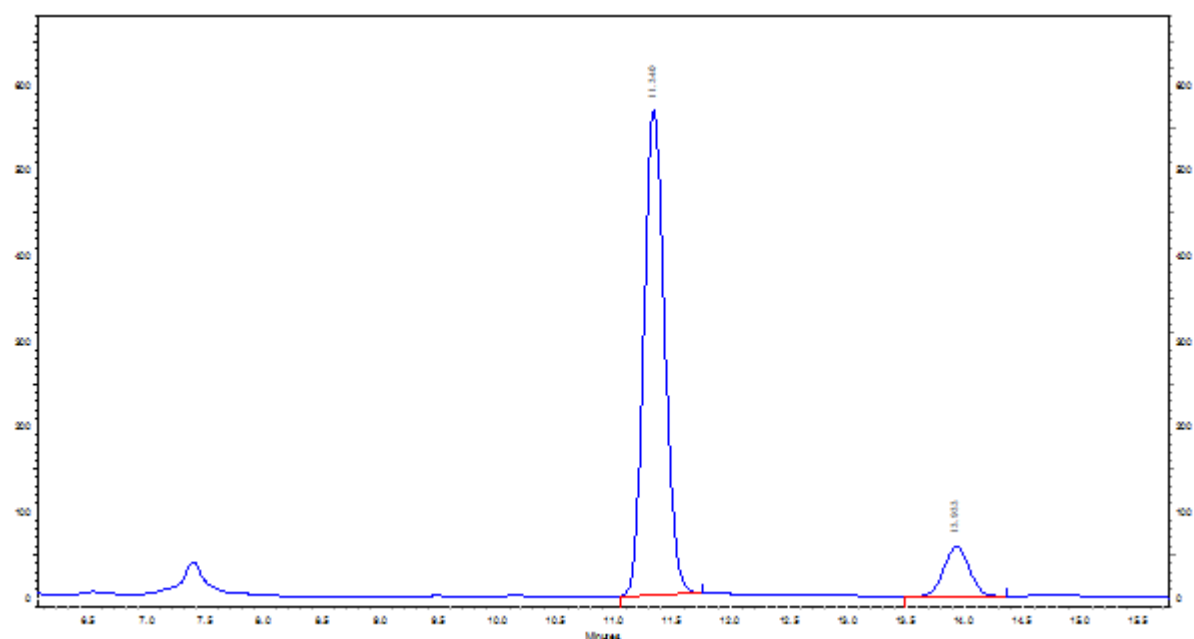


(*R*)-2,4-dichloro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2m): (Table 3, entry 13)



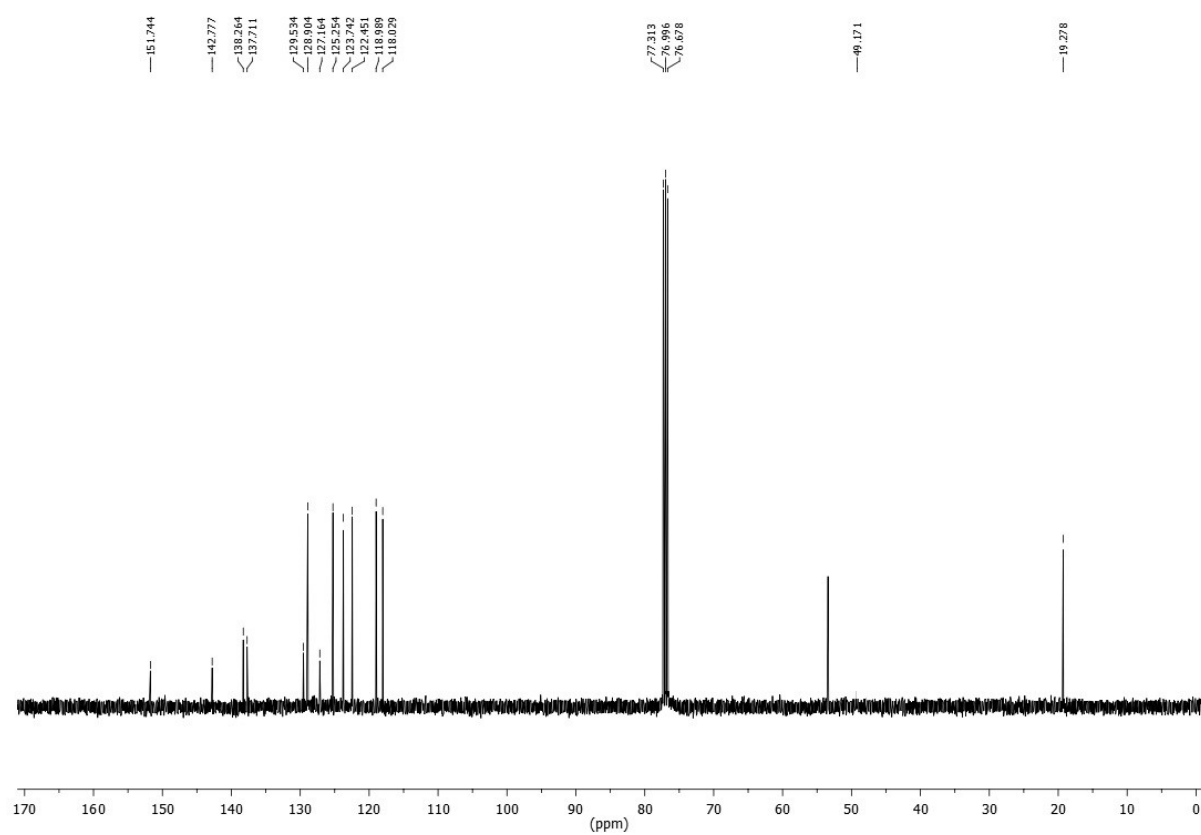
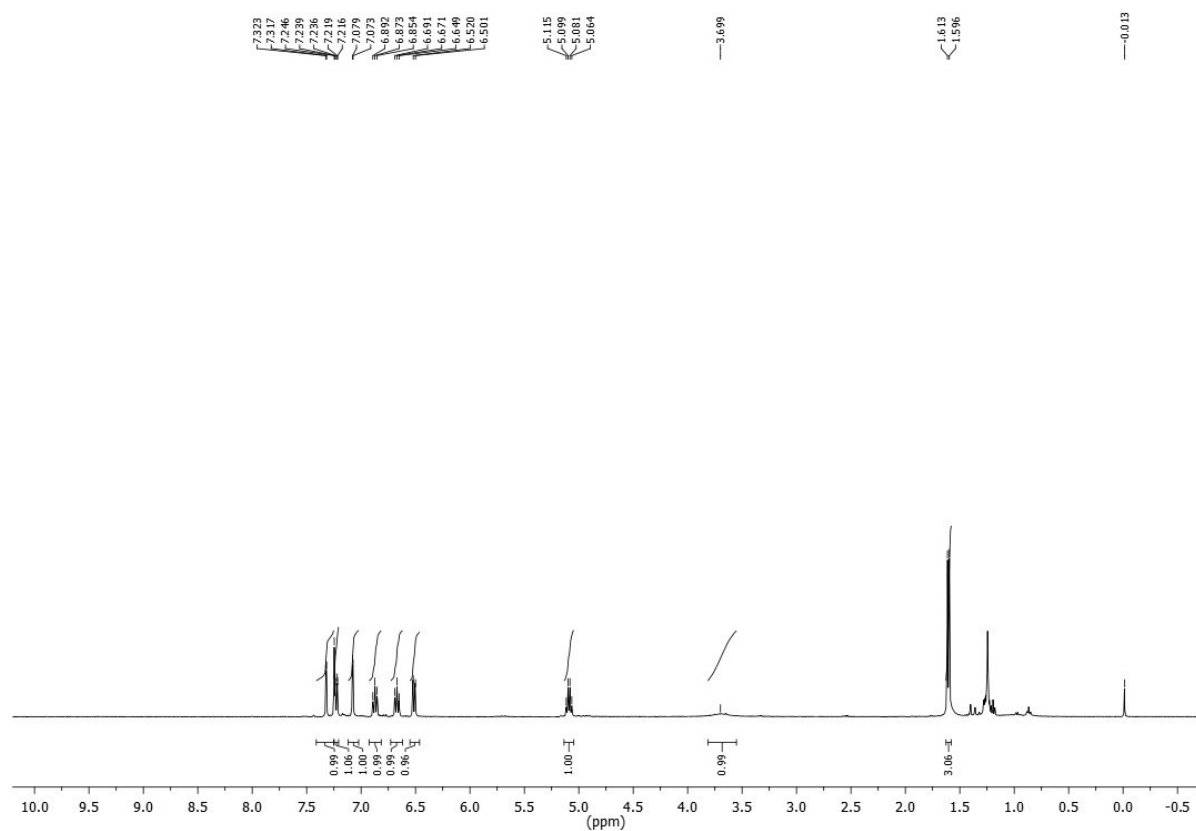
Retention Time	Area	Area %	Height	Height %
11.313	9663487	49.41	787585	55.41
13.873	9896141	50.59	633782	44.59

Totals	19559628	100.00	1421367	100.00
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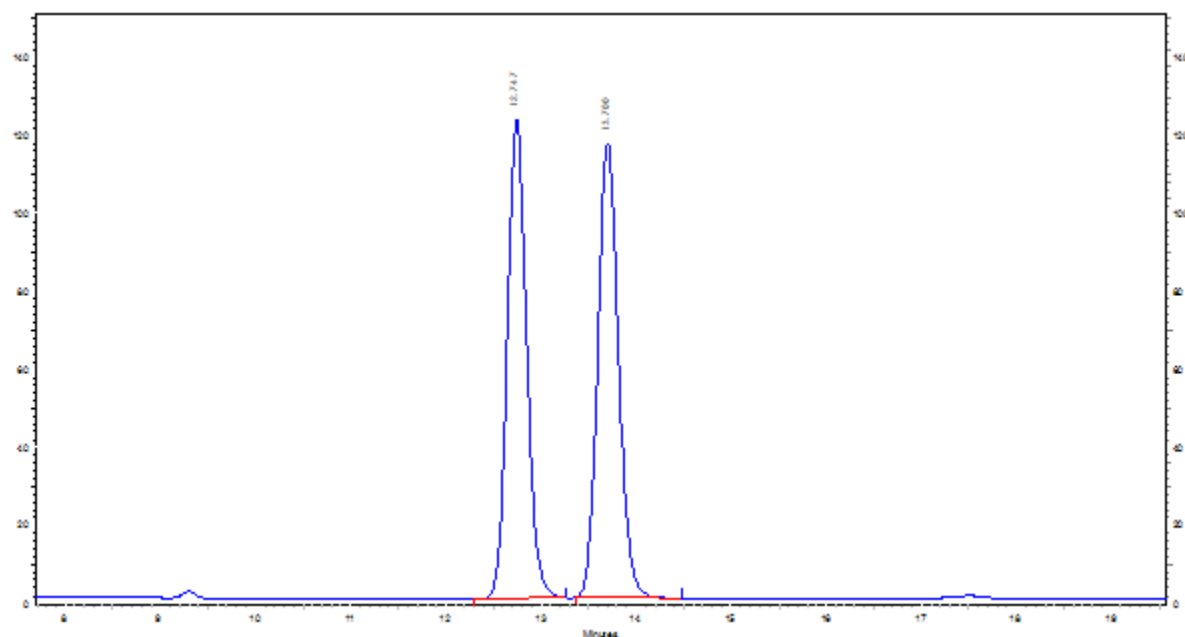


Retention Time	Area	Area %	Height	Height %
11.340	14728351	88.66	1189634	90.65
13.933	1884336	11.34	122638	9.35

Totals	16612687	100.00	1312272	100.00
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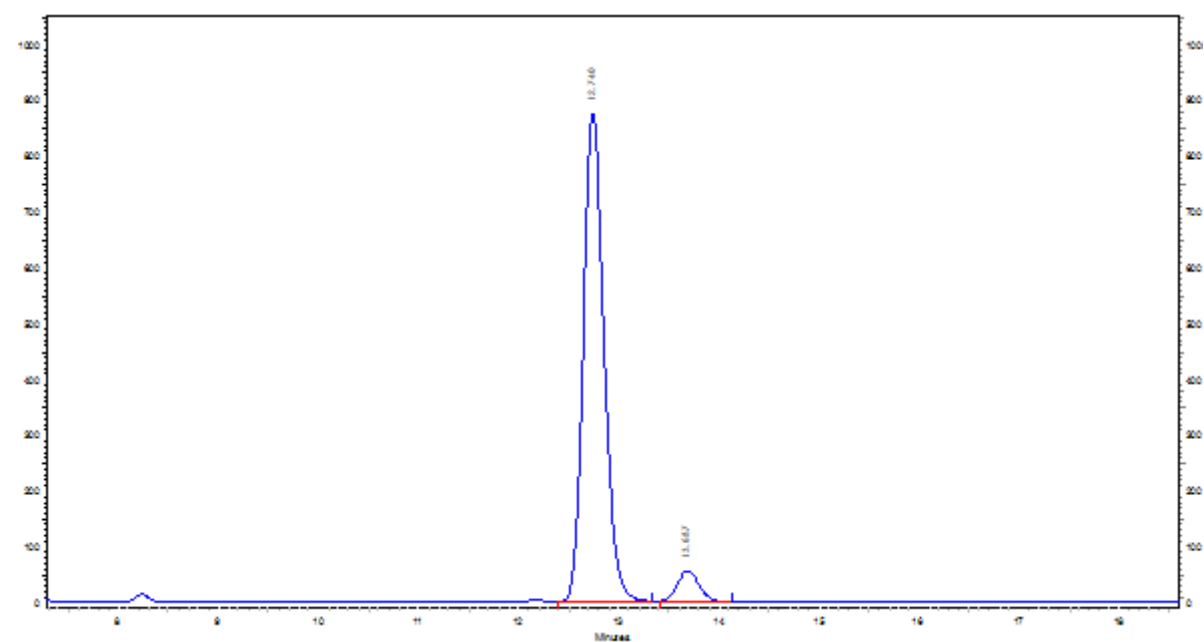


(R)-3,4,11-trimethyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2n): (Table 3, entry 14)



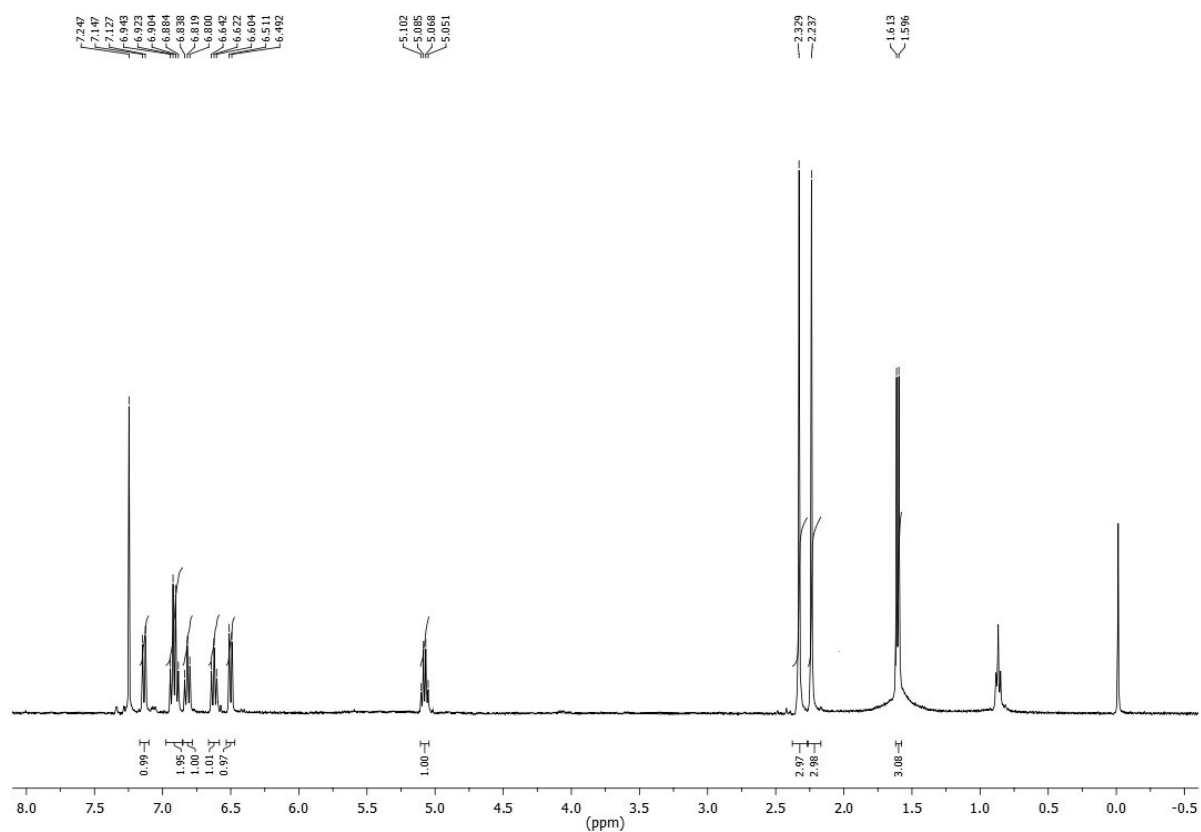
Retention Time	Area	Area %	Height	Height %
12.747	3618181	49.34	257863	51.33
13.700	3714254	50.66	244452	48.67

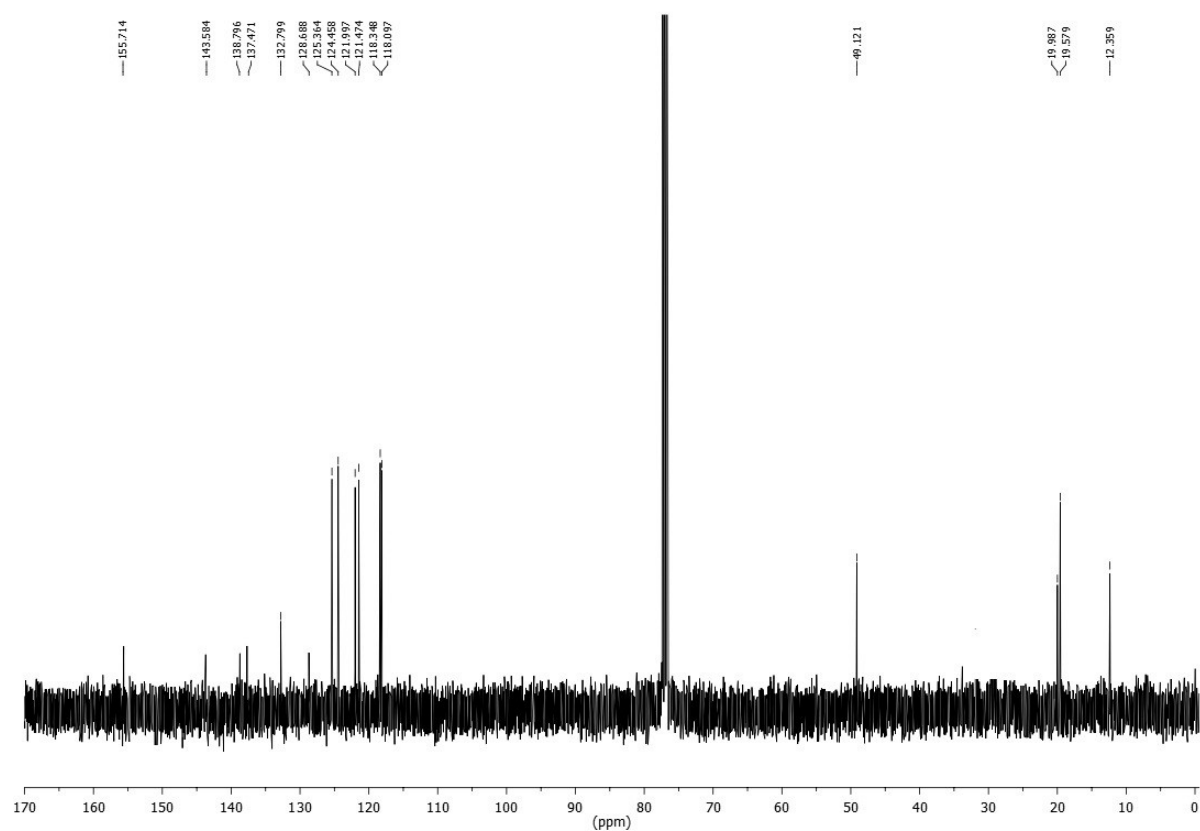
Totals	7332435	100.00	502315	100.00
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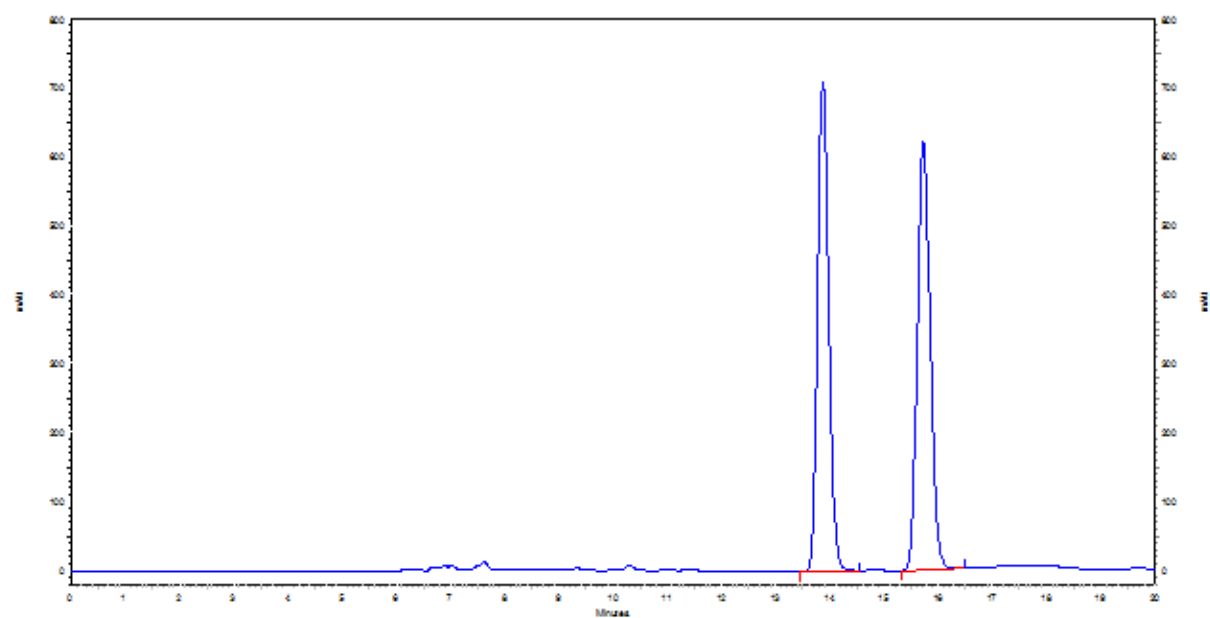
Retention Time	Area	Area %	Height	Height %
12.740	26162441	93.91	1834060	94.07
13.687	1696058	6.09	115585	5.93

Totals	27858499	100.00	1949645	100.00
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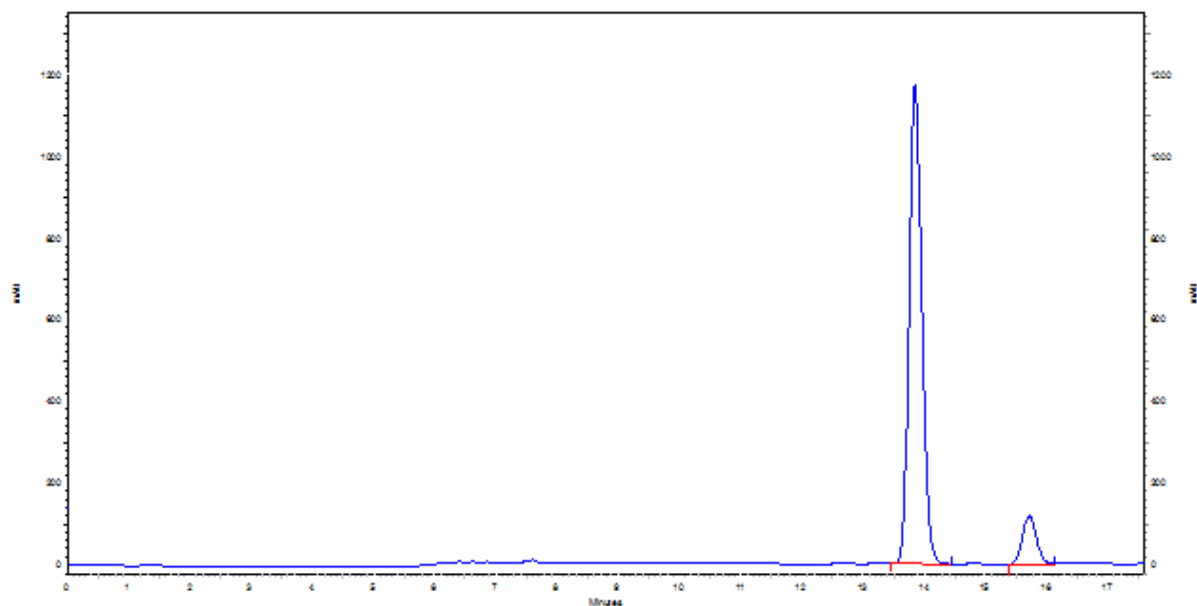


(*R*)-2-methyl-11-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2o): (Table 3, entry 15)



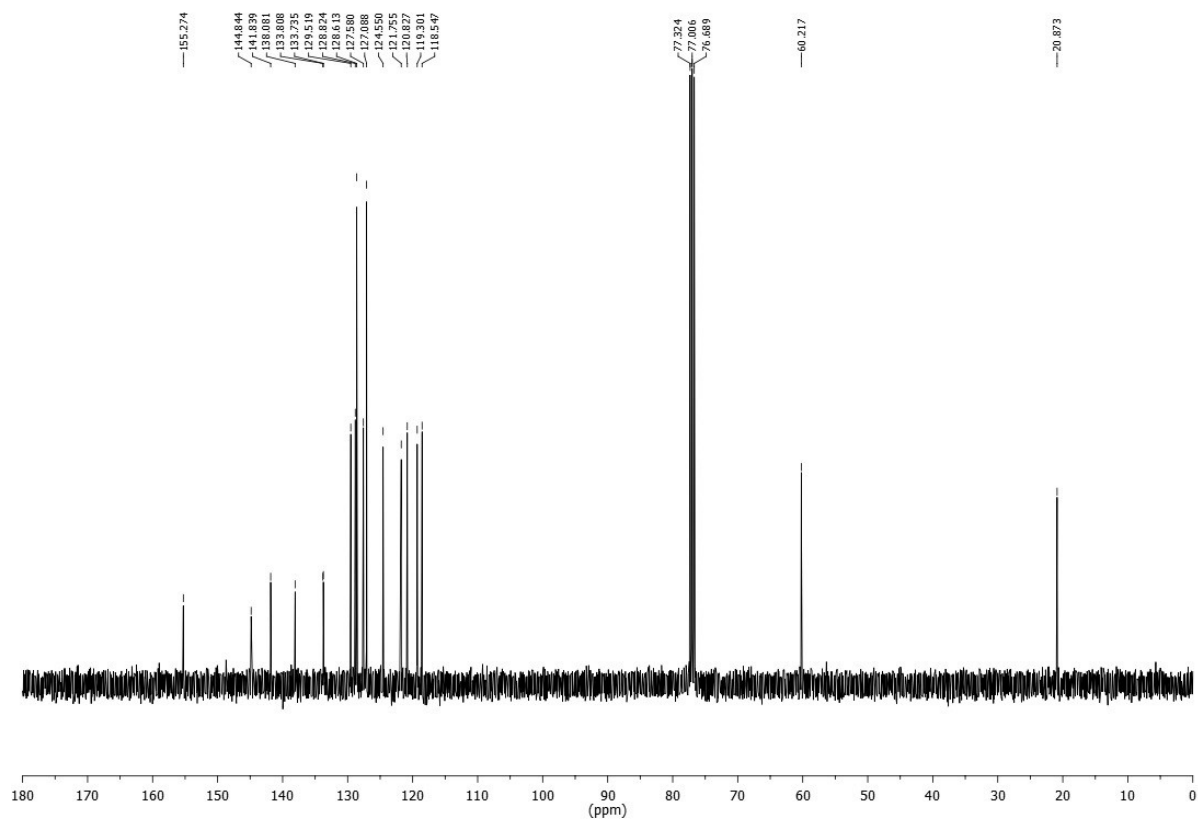
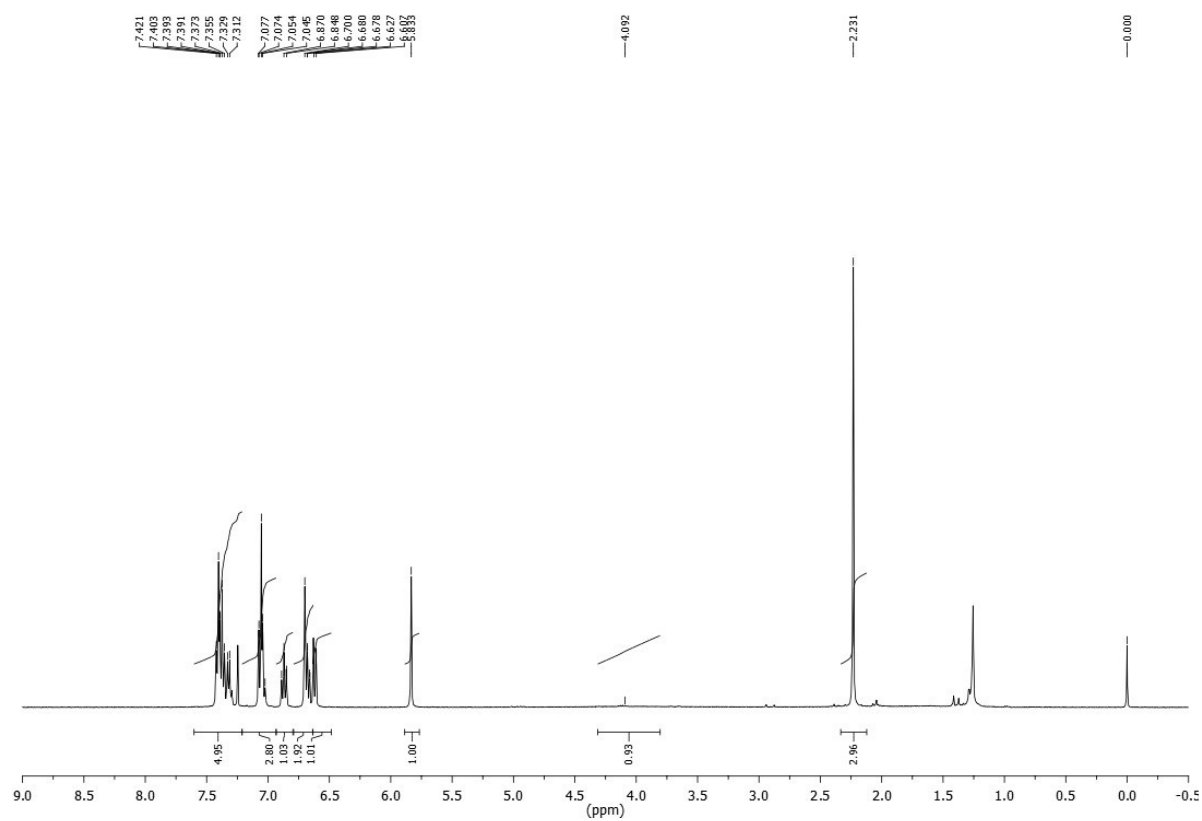
Retention Time	Area	Area %	Height	Height %
13.873	21311847	49.71	1489691	53.36
15.727	21561470	50.29	1302071	46.64

Totals	42873317	100.00	2791762	100.00
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Retention Time	Area	Area %	Height	Height %
13.847	35368658	89.96	2451395	90.79
15.720	3946944	10.04	248732	9.21

Totals	39315602	100.00	2700127	100.00
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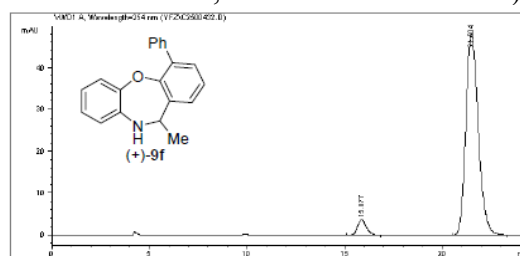
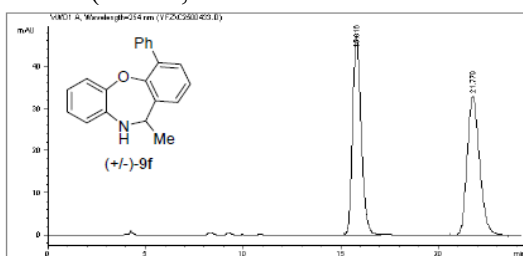


Comparison of chiral HPLC graphs by OD-H column for configuration.

Reported HPLC graphs:

(+)-(S)-11-methyl-4-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine: This compound was reported in *Chem. Commun.*, **2011**, 47, 7845-7847 (see supporting information compound **9f**)

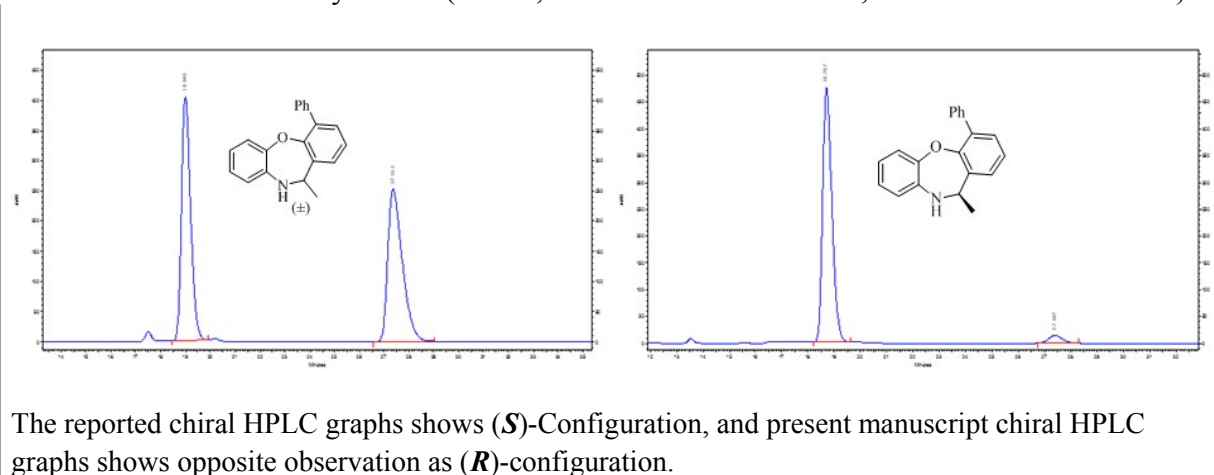
HPLC (OD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.8 mL/min).



Present Manuscript HPLC graphs:

(*R*)-11-methyl-4-phenyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (**2h**):

The *ee* was determined by HPLC (OD-H, hexane/ *i*-PrOH = 99/01, flow rate = 0.8 mL/min)

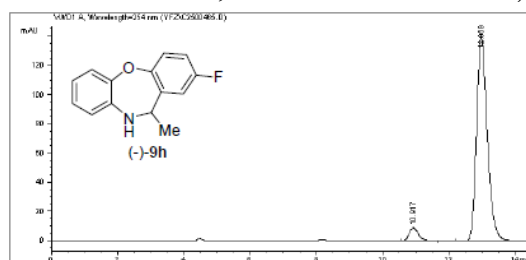
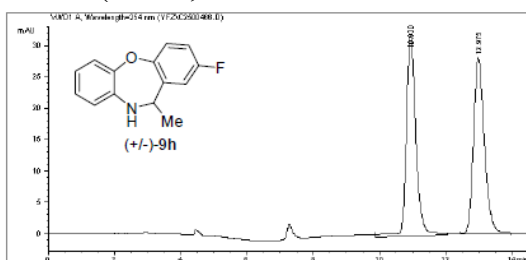


The reported chiral HPLC graphs shows (*S*)-Configuration, and present manuscript chiral HPLC graphs shows opposite observation as (*R*)-configuration.

Reported HPLC graphs:

(-)-(S)-2-fluoro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine: This compound was reported in *Chem. Commun.*, **2011**, 47, 7845-7847 (see supporting information compound **9h**)

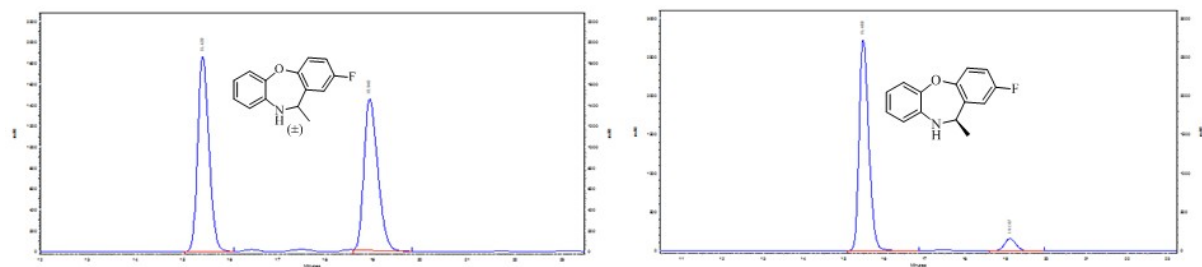
HPLC (OD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.7 mL/min)



Present Manuscript HPLC graphs:

(R)-2-fluoro-11-methyl-10,11-dihydrodibenzo[*b,f*][1,4]oxazepine (2e).

The *ee* was determined by HPLC (OD-H, *n*-hexane/ *i*-PrOH = 95/05, flow rate = 0.5 mL/min)



The reported chiral HPLC graphs shows (*S*)-Configuration, and present manuscript chiral HPLC graphs shows opposite observation as (*R*)-configuration.