Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Highly Enantioselective Hydroamination of Six-Membered Rings by Heterobimetallic Catalysts

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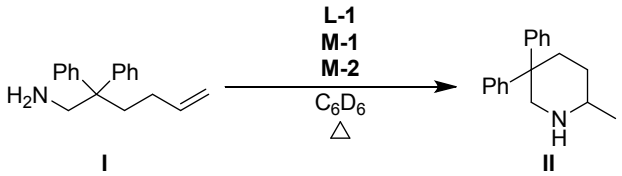
Table S1: Screening of different metal combinations for hydroamination reactions.



I II

entry	metal source		temp	time	conversion	*ee*
	M-1	**M-2**	**(°C)**	**(h)**	**(%)**	**(%)**
1	$ZnMe_2$	$ZnMe_2$	120	24	0	-
2	$ZnMe_2$	$Zr(NMe_2)_4$	80	24	100	96
3	$ZnMe_2$	BEt_3*THF	120	36	0	-
4	$ZnMe_2$	$Ti(NMe_2)_4$	80	72	100	2
5[a]	**Zn-1**	$Zr(NMe_2)_4$	80	5 d	88	96
6	$Cu(OAc)_2$	$Zr(NMe_2)_4$	80	24	96	77
7[b]	**Cu-1a**	$Zr(NMe_2)_4$	80	24	99	96
8[c]	**Cu-1a**	$Zr(NMe_2)_4$	80	28	97	96
9	-	$Zr(NMe_2)_4$	80	18	99	77
10[d]	-	$Zr(NMe_2)_4$	80	24	-	-

0.25 mmol of **I**, 15 mol% of **L-1**, 15 mol% M-1, 15 mol% M-2, 0.5 ml toluene-d_8, sealed NMR-tube, conversion has been determined by ^{1}H-NMR; [a] **Zn-1** was used directly, [b] **Cu-1a** was used directly, [c] 5 mol% of **Cu-1a** and 5 mol% of $Zr(NMe_2)_4$ were used ,[d] Jacobsen-ligand was used instead of **L-1**.

Table S2: Enantioselectivity of the different metalloligands.

entry	metalloligand	conversion [%]	*ee* [%]
1	**Cu-1a**	**97**	**96**
2	**Cu-1b**	96	95
3	**Cu-1c**	97	-96
4	**Cu-1d**	95	-94

5 mol% of **Cu-1a-d**, 5 mol% of $Zr(NMe_2)_4$, 0.43 mmol of **I**, 0.7 ml C_6D_6, 80 °C, 28 h, sealed NMR-tube, conversions were determined by ^{1}H-NMR, *ee* were determined by HPLC.

Table S3: Comparison of different catalytic systems based on the bromine-free ligand **L-2**.

entry	ligand	temp [°C]	time [h]	conversion [%]	*ee* [%]
1	**Cu-2**	80	24	96	93
2	**Zn-2**	80	5 d	90	96
3	**L-2**/ $ZnMe_2$	**80**	**18**	**99**	**97**

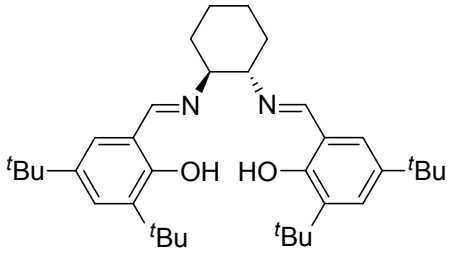
0.25 mmol of **I**, 15 mol% of **Cu-2**, **Zn-2** or **L-2**/$ZnMe_2$, 15 mol% of $Zr(NMe_2)_4$, 0.5 ml toluene-d_8, sealed NMR-tube, conversions were determined by ^{1}H-NMR, *ee* were determined by HPLC.

Table S4: Determining the optimal ligand-metal-metal-ratio.

entry	L-2 [mol%]	$ZnMe_2$ [mol%]	$Zr(NMe_2)_4$ [mol%]	time [h]	conversion [%]	*ee* [%]
1	10	0	15	18	99	77
2	10	0	9	36	99	93
3	10	10	9.5	84	81	98
4	10	15	15	18	99	97
5	5	7.5	7.5	24	99	89

0.25 mmol of **I**, 0.5 ml toluene-d_8, 80 °C, sealed NMR-tube, conversions were determined by ^{1}H-NMR, *ee* were determined by HPLC.

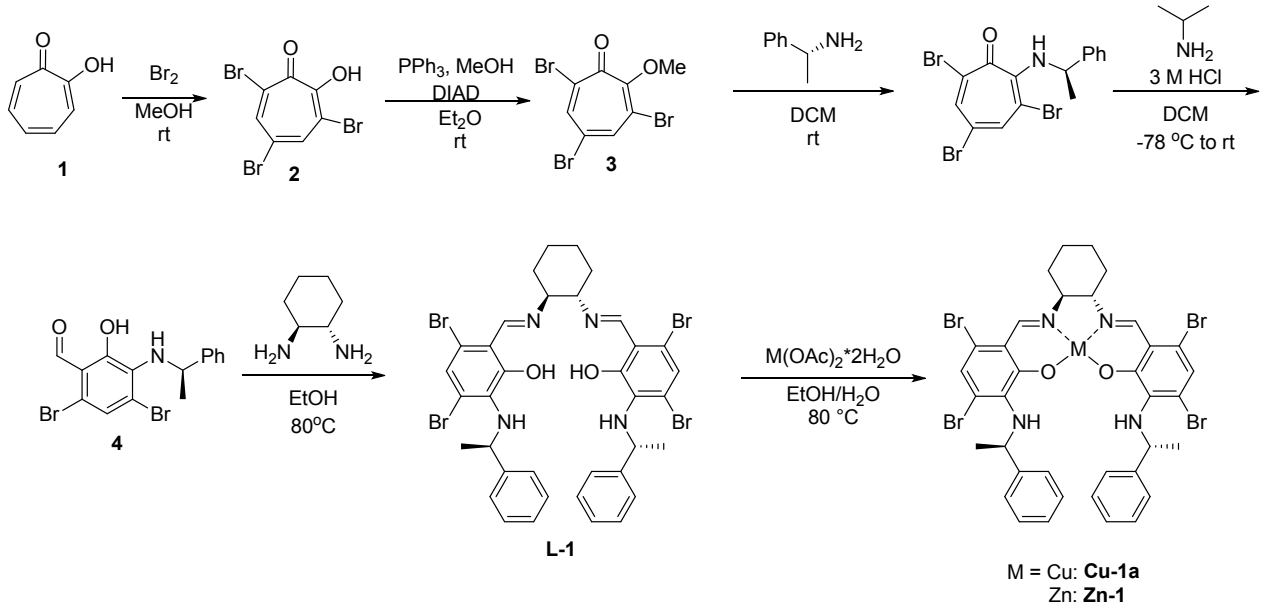
Scheme S1: Jacobson type ligand



Experimental Section

General Procedures: All reactions were performed in oven- or flame-dried glassware under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox unless otherwise indicated. Dry, oxygen-free benzene-*d6* was purified by distillation from CaH_2 under nitrogen atmosphere and stored in a glovebox over sodium. MeOH was dried over Mg. Et_2O, THF and toluene were dried over Na. DCM and DMF were dried over CaH_2. All solvents were redistilled prior to use. ^{1}H and ^{13}C spectra were recorded on a Bruker AM 400 at 25 °C. Chemical shifts are reported in ppm using tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer infrared-spectrometer 881 or a Bruker Equinox 55 FT-IR-spectrometer. MS and HR-MS spectra were recorded on a Finnigan MAT 95 SQ or a Varian MAT 711. HPLC analysis was carried out on an Agilent 1100 series instrument with auto sampler, multiple wavelength detectors and mass detector. 2,2-Diphenylhex-5-en-1-amine **I**,[6] 2,2-diphenylpent-4-en-1-amine **V**,[7] (1-(but-3-en-1-yl)cyclohexyl)methanamine **XI**[7] and potassium cyanoacetat[5] were prepared according to published procedures. All aminoalkenes were stored in a glovebox prior to use. All commercially available chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, TCI Europe, Acros Organics or abcr and used directly without further purification if not noted. (*S*)-(-)-1-Phenylethylamine and (*R*)-(+)-1-phenylethylamine were sublimated prior to use. The chemical names were determined according to ChemDraw Ultra 12.0.

Ligand and metal complex synthesis



3,5,7-Tribromo-2-hydroxycyclohepta-2,4,6-trienone (2)

2 was synthesized following a literature procedure. The NMR spectroscopic data is in agreement with the data reported in the literature.[1]

3,5,7-Tribromo-2-methoxycyclohepta-2,4,6-trienone (3)

3 was synthesized following a literature procedure.[2]

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.25 (s, *J* = 1.9 Hz, 1H), 7.92 (s, *J* = 1.9 Hz, 1H), 3.99 (s, 3H).

(*R*)-3,5,7-Tribromo-2-((1-phenylethyl)amino)cyclohepta-2,4,6-trienone

To a solution of **3** (2.1 g, 5.6 mmol) in 25 ml abs. CH_2Cl_2 was added (*R*)-1-phenylethylamine (800 mg, 6.60 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/MTBE 30:1) to afford (*R*)-3,5,7-tribromo-2-((1-phenylethyl)amino)cyclohepta-2,4,6-trienone as red, highly viscous oil. Yield: 2.4 g (92%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.12 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.31-7.16 (m, 5H), 5.60 (quin, *J* = 13.3, 6.6 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 3H).

(*R*)-4,6-Dibromo-2-hydroxy-3-((1-phenylethyl)amino)benzaldehyde (4)

Isopropyl amine (17 ml, 200 mmol) was added slowly to a solution of (*R*)-3,5,7-tribromo-2-((1-phenylethyl)amino)cyclohepta-2,4,6-trienone (5.4 g, 11.7 mmol) in 100 ml abs. CH_2Cl_2 at -78 °C. After the addition, the mixture was allowed to reach room temperature and stirred for 12 h. The solvent was removed by reduced pressure, the oil was solved in 55 ml THF, 11 ml 3M HCl were added and the mixture was stirred overnight at room temperature. 20 ml distilled water were added and the mixture was extracted with 6 x 50 ml CH_2Cl_2. The combined CH_2Cl_2 layers were dried over Mg_2SO_4, filtered, and the solvent was removed by reduced pressure. Purification of the crude product by flash chromatography on silica gel (cyclohexane/MTBE 80:1) would afford **4** as red, highly viscous oil. Yield: 1.5 g (32 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.16 (s, 1H), 7.31-7.24 (m, 5H), 7.21-7.17 (m, 1H), 5.21 (q, *J* = 9.4 Hz, 1H), 1.52 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 197.9, 155.5, 144.4, 135.4, 128.4, 127.4, 127.1, 126.1, 121.3, 116.1, 55.1, 23.8.

(*R*)-6,6'-((1*E*,1'*E*)-((1*S*,2*S*)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3,5-dibromo-2-(((*R*)-1-phenylethyl)amino)phenol) (L-1)

4 (600 mg, 1.50 mmol) and (1*S*,2*S*)-1,2-diaminocyclohexane (100 mg, 0.88 mmol) were dissolved in 40 ml toluene and *p*-toluenesulfonic acid (3 mg, 0.017 mmol) was added. The mixture was stirred for 12 h at 130 °C in a Dean-Stark apparatus. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc 85:15). The pure product was obtained as orange foam. Yield: 596 mg (90 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.44 (s, 2H), 7.31-7.10 (m, 10H), 6.93 (s, 2H), 5.23 (q, *J* = 6.6 Hz, 2H), 3.46-3.40 (m, 2H), 2.18-2.10 (m, 2H), 1.98-1.91 (m, 2H), 1.78-1.70 (m, 2H), 1.54-1.49 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.1, 161.5, 145.4, 137.0, 128.3, 126.8, 126.1, 124.5, 116.4, 114.5, 112.6, 69.2, 54.5, 32.4, 24.0, 23.7; HR-MS ($C_{36}H_{37}Br_4N_4O_2^+$, $[M-H]^+$): calc. 876.9604; found. 876.9604; ($C_{36}H_{36}Br_4N_4NaO_2^+$, $[M-Na]^+$): calc. 898.9424; found. 898.9421.

(1*S*,2*S*)-Cyclohexanediamino-*N,N´*-bis[3-{(1*R*)-phenylethylamino}-4,6-dibromsalicylidene]-copper (Cu-1a)

L-1 (50.0 mg, 0.057 mmol) was suspended in 4.4 ml EtOH/H_2O (10:1) and copper(II) acetate monohydrate (11.4 mg, 0.057 mmol) was added. The resulting mixture was stirred for 5 h at 80 °C. 4 ml H_2O were added, the solid was filtered, washed with H_2O and Et_2O and dried under high vacuum overnight. **Cu-1a** was obtained as brown powder. Yield: 50.1 mg (93 %). MS (ESI, rt): m/z (%) = 937 (11), 613 (14), 569 (30), 525 (54), 481 (80), 437 (98), 393 (100), 349 (68), 305 (30), 282 (10); HR-MS

($C_{36}H_{35}Br_4CuN_4O_2^+$, $[M-H]^+$): calc. 937.8744; found. 937.8746; IR (ATR) υ (cm^{-1}) = 3360, 3319, 3093, 3081, 3059, 3024, 2969, 2954, 2928, 2861, 1720, 1636, 1619, 1575, 1567, 1522, 1492, 1478, 1468, 1454, 1447, 1436, 1401, 1370, 1342, 1332, 1308, 1295, 1287, 1276, 1231, 1226, 1191, 1157, 1121, 1092, 1072, 1041, 1031, 1006, 998, 967, 960, 938, 931, 916, 907, 863, 838, 824, 797, 770, 755, 740, 700, 674.

(1*S*,2*S*)-Cyclohexanediamino-*N,N´*-bis[3-{(1*R*)-phenylethylamino}-4,6-dibromsalicylidene]zinc (Zn-1)

L-1 (50.0 mg, 0.057 mmol) was suspended in 4.4 ml EtOH/H_2O (10:1) and zinc (II) acetate dihydrate (12.5 mg, 0.057 mmol) was added. The resulting mixture was stirred for 5 h at 80 °C. 4 ml H_2O were added, the solid was filtered, washed with H_2O and Et_2O and dried under high vacuum overnight. **Zn-1** was obtained as orange powder. Yield: 47.1 mg (88 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.71 (s, 2H), 7.30-7.28 (m, 4H), 7.19-7.11 (m, 4H), 7.10-7.07 (m, 2H), 6.75 (s, 2H), 5.61-5.58 (m, 2H), 5.33-5.28 (m, 2H), 3.35 (br s, 2H), 2.36 (br s, 2H), 1.91 (br s, 2H), 1.41-1.38 (m, 4H), 1.29 (d, *J* = 6.7 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.2, 163.1, 145.8, 140.0, 128.3, 126.6, 125.8, 120.7, 116.4, 112.8, 112.0, 65.2, 53.8, 27.9, 25.1, 23.8; MS-EI ($C_{36}H_{34}Br_4N_4O_2Zn$, [M]): calc. 933.8707; found. 933.8707; IR (ATR) υ (cm^{-1}) = 3305, 3084, 3060, 3026, 2969, 2930, 2859, 1701, 1624, 1568, 1518, 1492, 1436, 1401, 1348, 1327, 1287, 1259, 1223, 1185, 1122, 1090, 1072, 1029, 1006, 995, 975, 930, 915, 901, 860, 825, 806, 758, 739, 699.

Cu-1b, **Cu-1c** and **Cu-1d** were synthesized according to the above shown procedure, using the appropriate 1-phenylethylamine and 1,2-diaminocyclohexane.

(*S*)-3,5,7-Tribromo-2-((1-phenylethyl)amino)cyclohepta-2,4,6-trienone

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.12 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.31-7.16 (m, 5H), 5.60 (quin, *J* = 13.3, 6.6 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 3H).

(*S*)-4,6-Dibromo-2-hydroxy-3-((1-phenylethyl)amino)benzaldehyde

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.15 (s, 1H), 7.31-7.24 (m, 5H), 7.21-7.16 (m, 1H), 5.21 (q, *J* = 9.5 Hz, 1H), 1.52 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 197.9, 155.5, 144.4, 135.4, 128.4, 127.5, 127.2, 126.1, 121.3, 116.1, 55.1, 23.8.

(*S*)-6,6'-((1*E*,1'*E*)-((1*S*,2*S*)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3,5-dibromo-2-(((*R*)-1-phenylethyl)amino)phenol)

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.43 (s, 2H), 7.31-7.10 (m, 10H), 6.93 (s, 2H), 5.24 (q, *J* = 6.6 Hz, 2H), 3.48-3.42 (m, 2H), 2.19-2.11 (m, 2H), 1.98-1.91 (m, 2H), 1.81-1.67 (m, 2H), 1.62-1.44 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.1, 161.3, 145.0, 136.7, 128.3, 126.8, 126.1, 124.5, 116.4, 114.5, 112.6, 69.2, 54.5, 32.4, 24.0, 23.8.

(*R*)-6,6'-((1*E*,1'*E*)-((1*R*,2*R*)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3,5-dibromo-2-(((*R*)-1-phenylethyl)amino)phenol)

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.43 (s, 2H), 7.30-7.10 (m, 10H), 6.92 (s, 2H), 5.23 (q, *J* = 6.6 Hz, 2H), 3.47-3.41 (m, 2H), 2.19-2.10 (m, 2H), 1.97-1.91 (m, 2H), 1.81-1.69 (m, 2H), 1.54-1.45 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.2, 128.3, 127.0, 126.2, 124.4, 112.6, 69.1, 54.8, 32.4, 24.0, 23.6.

(*S*)-6,6'-((1*E*,1'*E*)-((1*R*,2*R*)-Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3,5-dibromo-2-(((*R*)-1-phenylethyl)amino)phenol)

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.44 (s, 2H), 7.30-7.12 (m, 10H), 6.93 (s, 2H), 5.23 (q, *J* = 6.6 Hz, 2H), 3.45-3.40 (m, 2H), 2.18-2.10 (m, 2H), 1.98-1.90 (m, 2H), 1.78-1.71 (m, 2H), 1.50-1.44 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.1, 161.2, 145.0, 137.7, 128.3, 126.8, 126.1, 124.5, 114.5, 112.6, 69.2, 54.5, 32.4, 24.0, 23.7.

(1*S*,2*S*)-Cyclohexanediamino-*N,N´*-bis[3-{(1*S*)-phenylethylamino}-4,6-dibromsalicylidene]-copper (Cu-1b)

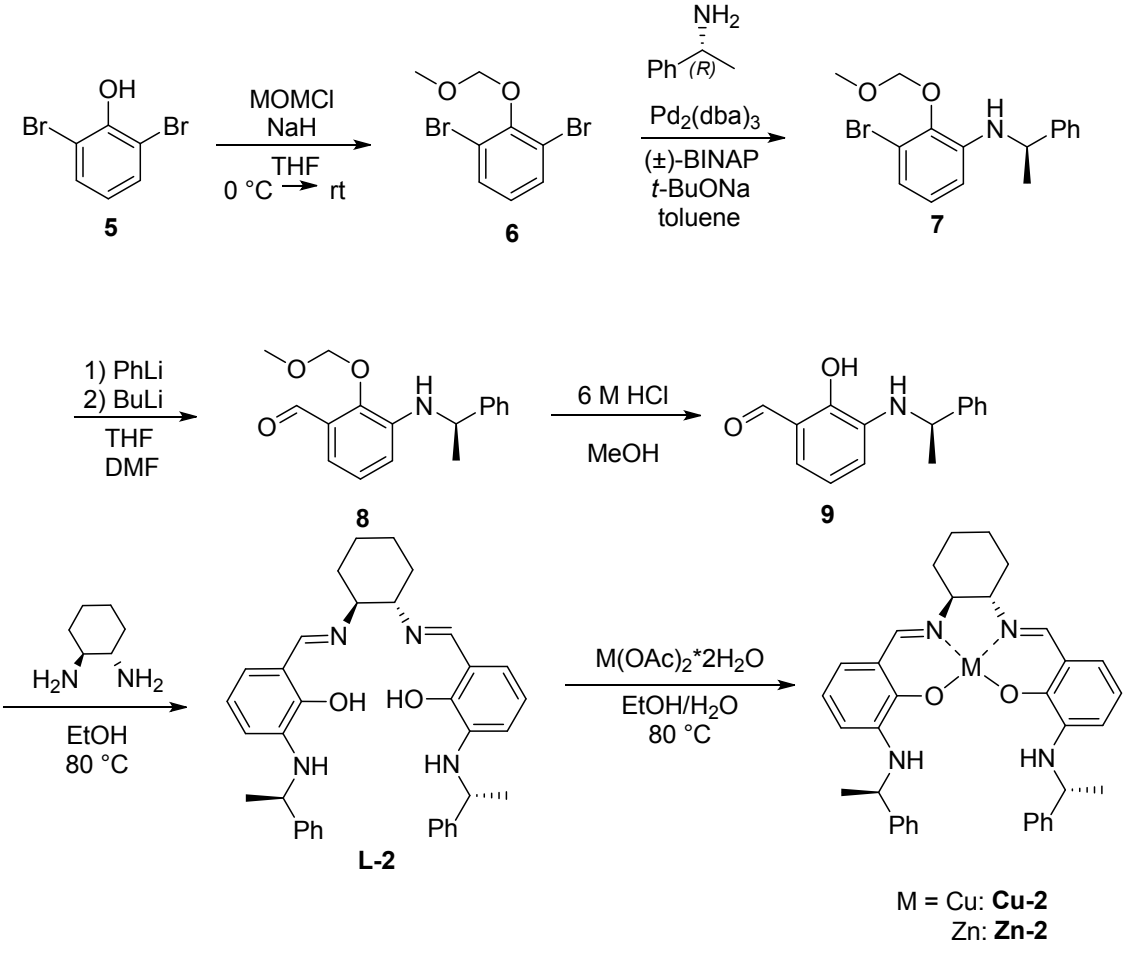
HR-MS ($C_{36}H_{35}Br_4CuN_4O_2^+$, $[M-H]^+$): calc. 937.8744; found. 937.8740; IR (ATR) υ (cm^{-1}) = 3730, 3627, 3319, 3083, 3058, 3021, 2971, 2938, 2864, 1620, 1569, 1521, 1492, 1438, 1400, 1332, 1307, 1294, 1273, 1229, 1191, 1156, 1122, 1093, 1072, 1055, 1035, 1010, 1003, 964, 934, 907, 862, 823, 769, 751, 737, 699, 674, 638, 623, 605, 573, 544, 521, 472, 418.

(1*R*,2*R*)-Cyclohexanediamino-*N*,*N*´-bis[3-{(1*R*)-phenylethylamino}-4,6-dibromsalicylidene]-copper (Cu-1c)

HR-MS ($C_{36}H_{35}Br_4CuN_4O_2^+$, $[M-H]^+$): calc. 937.8744; found. 937.8744; IR (ATR) υ (cm^{-1}) = 3361, 3319, 2971, 2938, 2864, 1978, 1620, 1569, 1521, 1492, 1438, 1400, 1332, 1309, 1294, 1273, 1228, 1189, 1154, 1122, 1095, 1072, 1055, 1033, 1006, 963, 934, 909, 860, 823, 793, 768, 753, 736, 699, 674, 638, 606, 573, 546, 519, 480, 472.

(1*R*,2*R*)-Cyclohexanediamino-*N*,*N*´-bis[3-{(1*S*)-phenylethylamino}-4,6-dibromsalicylidene]-copper (Cu-1d)

HR-MS ($C_{36}H_{35}Br_4CuN_4O_2^+$, $[M-H]^+$): calc. 937.8744; found. 937.8737; IR (ATR) υ (cm^{-1}) = 3361, 3319, 3101, 3081, 3059, 3024, 2972, 2939, 2864, 1712, 1637, 1620, 1575, 1567, 1523, 1493, 1468, 1447, 1436, 1401, 1370, 1342, 1332, 1308, 1295, 1288, 1277, 1231, 1226, 1203, 1191, 1156, 1121, 1093, 1072, 1055, 1041, 1030, 1006, 998, 967, 960, 940, 931, 916, 907, 863, 838, 824, 819, 797, 770, 755, 740, 700, 674.



1,3-Dibromo-2-(methoxymethoxy)benzene (6)

6 was synthesized following a literature procedure. The NMR spectroscopic data is in agreement with the data reported in the literature.[4]

(*R*)-3-Bromo-2-(methoxymethoxy)-*N*-(1-phenylethyl)aniline (7)

6 (300 mg, 1.00 mmol), (*R*)-1-phenylethylamine (0.13 ml, 1.00 mmol), sodium-*tert*-butoxide (130 mg, 1.35 mmol), BINAP (24 mg, 0.04 mmol) and $Pd_2(dba)_3$ (18 mg, 0.02 mmol) were solved in 20 ml abs. toluene and heated for 5 h at 70 °C. Subsequently, 2 ml Et_2O was added at room temperature, the solid was filtered and washed with Et_2O. The solvent of the filtrate was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/ toluene 1:1). The product was obtained as yellow oil. Yield: 235 mg (70 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.37-7.29 (m, 4H), 7.25-7.20 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 8.2 Hz, 1H), 5.14 (q, *J* = 7.7 Hz, 2H), 4.45 (q, *J* = 10.1 Hz, 1H), 3.67 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 144.7, 142.5, 141.9, 128.7, 127.0, 126.2, 125.8, 120.3, 116.7, 111.5, 100.0, 57.9, 53.4, 25.0.

(*R*)-2-(Methoxymethoxy)-3-((1-phenylethyl)amino)benzaldehyde (8)

7 (0.20 g, 0.60 mmol) was dissolved in 5 ml THF, PhLi (0.50 ml, 1.58 M in THF, 0.78 mmol) was added at -78 °C and the mixture stirred for 20 min at this temperature. *n*BuLi (0.45 ml, 1.75 M in THF, 0.78 mmol) was added at -78 °C, the solution was stirred for 1 h at this temperature and freshly distilled DMF (0.46 ml, 6.02 mmol) was added. After stirring for 30 min at – 78 °C, the mixture was warmed to 0 °C and the reaction was quenched with 2 ml sat. NH_4Cl-solution. The phases were separated and the aqueous layer was extracted with 3 x 3 ml Et_2O. The combined organic layers were washed with 2 x 5 ml brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/MTBE 4:1). The product was obtained as yellow oil. Yield: 0.12 g (70 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.25 (s, 1H), 7.36-7.30 (m, 4H), 7.25-7.21 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.15 (q, *J* = 8.7 Hz, 2H), 5.04 (br s, 1H), 4.48 (q, *J* = 9.9 Hz, 1H), 3.65 (s, 3H), 1.57 (d, *J* = 6.7 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 190.8, 147.2, 144.4, 141.2, 129.0, 128.8, 127.2, 125.8, 125.3, 117.9, 116.8, 101.2, 57.9, 53.5, 25.0.

(*R*)-2-Hydroxy-3-((1-phenylethyl)amino)benzaldehyde (9)

8 (140 mg, 0.50 mmol) was dissolved in 2 ml MeOH and 1 ml 6 M HCl were added slowly. The solution was stirred at room temperature for 4 h and $NaHCO_3$-solution was added to adjust pH 7. The mixture was extracted with 3 x 7 ml DCM, the combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/MTBE 97:3). The product was obtained as yellow crystals. Yield: 116 mg (95 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 11.38 (s, 1H), 9.83 (s, 1H), 7.37-7.25 (m, 4H), 7.25-7.20 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 4.73 (br s, 1H), 4.50 (q, *J* = 10.0 Hz, 1H), 1.58 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 197.2, 149.1, 144.4, 136.2, 128.7, 127.1, 125.8, 120.1, 120.1, 119.1, 117.5, 53.6, 24.9.

(1*S*,2*S*)-Cyclohexanediamino-*N,N´*-bis[3-{(1*R*)-phenylethylamino}salicylidene] (L-2)

9 (100.0 mg, 0.414 mmol) and (1*S*,2*S*)-1,2-diaminocyclohexane (25.0 mg, 0.219 mmol) were dissolved in 15 ml toluene and *p*-toluenesulfonic acid (0.7 mg, 0.004 mmol) was added. The mixture was stirred for 3 h at 130 °C in a Dean-Stark apparatus. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc 85:15). The pure product was obtained as orange foam. Yield: 103 mg (89 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 13.95 (br s, 2H), 8.19 (s, 2H), 7.37-7.15 (m, 10H), 6.55-6.48 (m, 4H), 6.27 (dd, *J* = 6.9 Hz, *J* = 4.6 Hz, 2H), 4.68 (br s, 2H), 4.45 (q, *J* = 10.0 Hz, 2H), 3.38-3.31 (m, 2H), 2.01-1.93 (m, 2H), 1.91-1.86 (m, 2H), 1.77-1.65 (m, 2H), 1.57-1.53 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.2, 150.4, 145.2, 136.8, 128.6, 126.8, 125.8, 118.7, 118.3, 116.1, 112.8, 71.8, 53.4, 33.2, 25.2, 24.2; HR-MS ($C_{36}H_{41}N_4O_2^+$, $[M-H]^+$): calc. 561.3225; found. 561.3213.

(1*S*,2*S*)-Cyclohexanediamone-*N,N‘*-bis[3-{(1*R*)-phenylethylamino}salicylidene]copper (Cu-2)

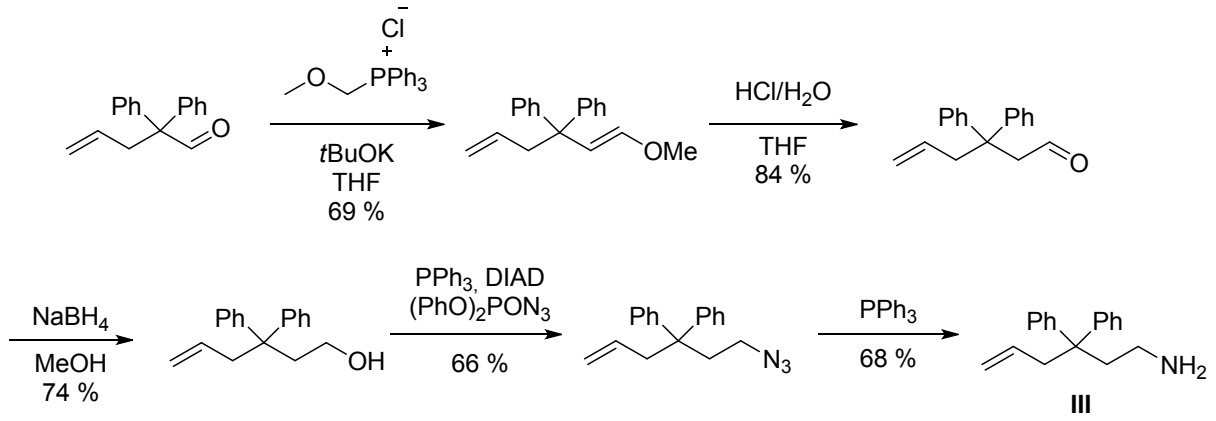
L-2 (450 mg, 0.8 mmol) was suspended in 22 ml EtOH/H_2O (10:1) and copper(II) acetate monohydrate (160 mg, 0.8 mmol) was added. The mixture was stirred for 4 h at 80 °C and 20 ml H_2O were added. The formed solid was filtered, washed with H_2O and Et_2O and dried under vacuum overnight. The product was obtained as a brown powder. Yield: 330 mg (66 %). HR-MS ($C_{36}H_{39}CuN_4O_2^+$, $[M-H]^+$): calc. 622.2364; found. 622.2346; ($C_{36}H_{38}CuN_4NaO_2^+$, $[M+Na]^+$): calc. 644.2183; found. 644.2160; IR (ATR) υ (cm^{-1}) = 3391, 3082, 3055, 3027, 2999, 2962, 2929, 2857, 1945, 1870, 1711, 1621, 1601, 1555, 1491, 1470, 1450, 1434, 1394, 1370, 1348, 1311, 1290, 1277,

1258, 1224, 1203, 1174, 1155, 1146, 1133, 1099, 1084, 1071, 1048, 1028, 1006, 998, 967, 923, 865, 855, 807, 780, 761, 728, 700.

(1*S*,2*S*)-Cyclohexanediamone-*N*,*N*'-bis[3-{(1*R*)-phenylethylamino}salicylidene]zinc (Zn-2)

L-2 (450 mg, 0.8 mmol) was suspended in 22 ml EtOH/H_2O (10:1) and zinc(II) acetate dihydrate (175 mg, 0.8 mmol) was added. The mixture was stirred for 4 h at 80 °C and 20 ml H_2O were added. The formed solid was filtered, washed with H_2O and Et_2O and dried under vacuum overnight. The product was obtained as a yellow powder. Yield: 378 mg (76 %). ^{1}H-NMR (400 MHz, C_6D_6): δ (ppm) = 8.17 (s, 2H), 7.44-7.36 (m, 4H), 7.15-7.07 (m, 8H), 7.04-6.99 (m, 2H), 6.96 (s, 2H), 5.59-5.49 (m, 2H), 5.00-4.90 (m, 2H), 2.34-2.22 (m, 2H), 1.45 (d, *J* = 3.4 Hz, 6H), 1.38-1.33 (m, 2H), 1.32-1.26 (m, 2H), 1.05-0.96 (m, 2H), 0.84-0.75 (m, 2H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) = 165.3, 159.3, 146.5, 140.9, 128.9, 127.0, 126.1, 122.0, 116.0, 112.9, 110.6, 65.1, 52.7, 28.2, 25.3, 24.4; HR-MS ($C_{36}H_{39}N_4O_2Zn^+$, [M-H]$^+$): calc. 623.2359; found.623.2355; ($C_{36}H_{38}N_4NaO_2Zn^+$, [M-Na]$^+$): calc. 645.2179; found. 645.2170.

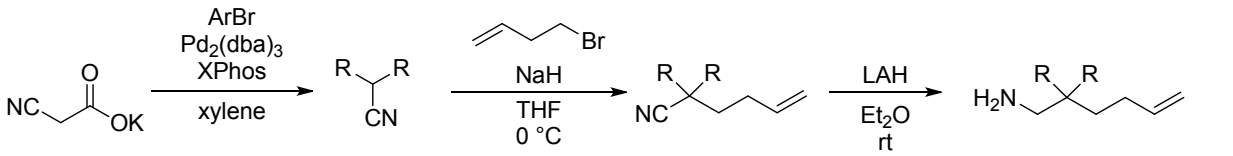
Substrate synthesis



To an ice cold suspension of phosphoric acid salt (3.94 g, 11.5 mmol) in 30 ml THF a solution of KO*t*Bu (1.29 g, 11.5 mmol) in 20 ml THF was added dropwise and then this mixture was stirred for 1 h at 0 °C. A solution of 2,2-diphenylpent-4-enal (907 mg, 3.84 mmol) in 5 ml THF was added at 0 °C and the mixture was stirred for 14 h at room temperature. 30 ml H_2O were added and the solution was extracted with 3 x 100 ml MTBE. The combined organic layers were dried over $NaSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash

chromatography on silica gel (cyclohexane/MTBE 95:5) to obtain (*E*)-(1-methoxyhexa-1,5-diene-3,3-diyl)dibenzene in 69 % yield. Hydrolysis of the ether with 5 ml 3 M HCl in 20 ml THF of 12 h at room temperature gave the alcohol which isomerizes to the corresponding aldehyde 3,3-diphenylhex-5-enal in 84% isolated yield. Sodium borohydrid (205 mg, 5.40 mmol) was stirred in 10 ml MeOH until it dissolved and 3,3-diphenylhex-5-enal (671 mg, 2.68 mmol) was added dropwise to the solution at 0 °C over 45 min. The reaction mixture was allowed to stand at room temperature for 15 minutes under occasional stirring. 30 ml H_2O were added, the solution was extracted with 3 x 20 ml Et_2O and the combined organic layers were washed with the equal volume of distilled H_2O. The organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc 9:1) to obtain alcohol 3,3-diphenylhex-5-en-1-ol in 74 % yield. The synthesised alcohol (815 mg, 3.23 mmol) was dissolved in 30 ml THF and treated with PPh_3 (1.02 g, 3.88 mmol), DIAD (762 µl, 3.88 mmol) and diphenyl phosphoryl azide (834 µl, 3.88 mmol) at 0 °C to give (1-azidohex-5-ene-3,3-diyl)dibenzene in 66 % yield. In the final step of the synthesis, the obtained azide (710 mg, 2.56 mmol) was diluted in 15 ml THF and PPh_3 (739 mg, 2.82 mmol) was added. After stirring for 1 h at room temperature 10 ml H_2O were added and the mixture was stirred an additional 24 h at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (DCM/MeOH 95:5 → 4:1) to obtain amine **III** in 68 % yield as colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32-7.26 (m, 4H), 7.23-7.15 (m, 6H), 5.82-5.71 (m, 1H), 4.99-4.88 (m, 2H), 3.34 (s, 2H), 2.23-2.16 (m, 2H), 1.79-1.71 (m, 2H), 1.49-1.33 (m, 2H); HR-MS ($C_{18}H_{22}N^+$, $[M-H]^+$): calc. 252.1747; found. 252.1742.

Synthesis of 2-diaryl amines



R = 4-methylbenzene: **VII**
R = 3-methoxybenene: **IX**

$Pd_2(dba)_3$ (69 mg, 0.075 mmol), XPhos (286 mg, 0.6 mmol), and potassium cyanoacetate (615 mg, 5.0 mmol) were added into a Schlenk tube and 4-bromotoluene or 3-methoxybromobenzene (5.0 mmol) and 10.0 ml xylene were then added. The mixture was stirred overnight at 140 °C. The reaction was quenched by cooling to ambient temperature and 50 ml EtOAc and 50 ml H_2O were added. The organic supernatant was analyzed by GC. The organic layer was isolated and the remained water was

further extracted with 3 x 50 ml EtOAc. The combined organic phases were concentrated. To a solution of crude nitrile in 10 ml THF was added NaH (60 w/w% in mineral oil, 200 mg, 5 mmol) at 0 °C. The mixture was stirred for 20 min at room temperature and homoallylbromide (0.5 ml, 5 mmol) were added at 0 °C. After finishing the addition the reaction mixture was warmed to room temperature and stirred for 3 h. 5 ml 10% NH_4Cl aqueous solution were added and the solution was extracted with 2 x 5 ml Et_2O. The combined organic layers were dried over MgSO4, the solvent was removed under reduced pressure and the crude product disolved in Et_2O (50 ml). This solution was added dropwise to the suspension of $LiAlH_4$ (2 eq) in Et_2O (10 ml) at 0 °C. The suspension was stirred at room temperature overnight and then treated with ice water and 15% NaOH aqueous solution. The suspension was filtered, the solid was washed with Et_2O and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc).

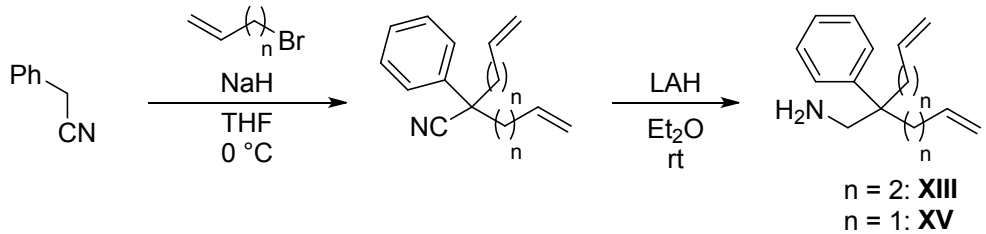
2,2-Di-*p*-tolylhex-5-en-1-amine (VII)

Yield: 73 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.11-7.04 (m, 8H), 5.83-5.69 (m, 1H), 5.01-4.85 (m, 2H), 3.28 (s, 2H), 2.33 (s, 6H), 2.18-2.10 (m, 2H), 1.75 (ddd, *J* = 11.9, 8.5, 5.8 Hz, 2H), 1.08-0.92 (s, 2H); HR-MS ($C_{20}H_{26}N^+$, $[M-H]^+$): calc. 280.2060; found. 280.2056.

2,2-Bis(3-methoxyphenyl)hex-5-en-1-amine (IX)

Yield: 71 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.23-7.18 (m, 2H), 6.78-6.71 (m, 6H), 5.82-5.71 (m, 1H), 4.99-4.88 (m, 2H), 3.76 (s, 6H), 3.30 (br s, 2H), 2.19-2.13 (m, 2H), 1.80-1.72 (m, 2H), 1.00 (br s, 2H); HR-MS ($C_{20}H_{26}NO_2^+$, $[M-H]^+$): calc. 312.1959; found. 312.1954; IR (ATR) υ (cm^{-1}) = 3388, 3309, 3075, 3027, 2997, 2937, 2912, 2869, 2856, 2834, 2093, 1925, 1834, 1729, 1666, 1640, 1605, 1598, 1581, 1489, 1464, 1449, 1432, 1367, 1315, 1291, 1248, 1170, 1110, 1090, 1049, 996, 910, 876, 819, 777, 745, 721, 701.

Synthesis of diallylated and dihomoallylated amines



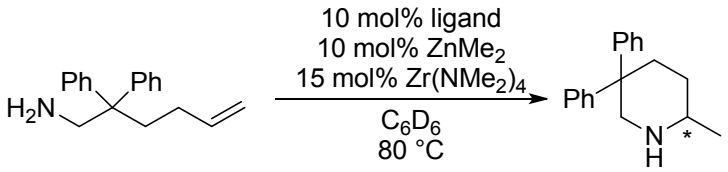
To a solution of phenylacetonitrile (11.5 ml, 100 mmol) in 200 ml THF was added NaH (60 w/w% in mineral oil, 4 g, 100 mmol) at 0 °C. The mixture was stirred for 20 min at room temperature and allylbromid or homoallylbromide (100 mmol) was added at 0 °C. After finishing the addition the reaction mixture was warmed to room temperature and stirred for 3 h. 50 ml 10% NH_4Cl aqueous solution were added and the solution was extracted with 2 x 50 ml Et_2O. The combined organic layers were dried over MgSO4, the solvent was removed under reduced pressure and the crude product disolved in Et_2O (50 ml). This solution was added dropwise to the suspension of $LiAlH_4$ (2 eq) in Et_2O (100 ml) at 0 °C. The suspension was stirred at room temperature overnight and then treated with ice water and 15% NaOH aqueous solution. The suspension was filtered, the solid was washed with Et_2O and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc).

2-(But-3-en-1-yl)-2-phenylhex-5-en-1-amine (XIII)

Yield: 75 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 4H), 7.24-7.17 (m, 1H), 5.89-5.74 (m, 2H), 5.06-4.90 (m, 4H), 2.92 (s, 2H), 1.99-1.74 (m, 8H), 0.87 (br s, 2H); HR-MS ($C_{16}H_{24}N^+$, $[M-H]^+$): calc. 230.1904; found. 230.1896.

2-Allyl-2-phenylpent-4-en-1-amine (XV)

Yield: 72 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H), 7.24-7.18 (m, 1H), 5.67-5.54 (m, 2H), 5.11-4.99 (m, 4H), 2.91 (s, 2H), 2.50-2.44 (m, 4H), 1.22 (br s, 2H); HR-MS ($C_{14}H_{20}N^+$, $[M-H]^+$): calc. 202.1591; found. 202.1586.



Inside a glovebox ligand (10 mol%) was dissolved in 0.7 ml C_6D_6 and Me_2Zn solution (10 mol%, 1.2 M in toluene) was added. $Zr(NMe_2)_4$ (15 mol%) and amine (0.43 mmol) were added and the resulting reaction mixture was transferred into a NMR tube, which was sealed. The reaction was heated outside the glovebox.

Procedure for determination of enantiomeric excess

After finishing the reaction the solvent was evaporated under reduced pressure and the product was diluted in DCM (conc. = 0.05 M). Triethylamine (1.50 eq.) was added to the solution of the amine (1.00 eq.) followed by 1-naphthoylchlorid (1.05 eq.) and the resulting mixture was stirred at room temperature until TLC showed full conversion (usually 2-3 h). The solvent and volatile materials were removed under reduced pressure, the crude product was dissolved in pentane and the mixture was washed with 1M HCl. The organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (cyclohexane/MTBE 9:1 → 1:1). The enantiomeric excess of chiral amines were determined by HPLC analysis (mobile phase = hexane/isopropanol 75:25, flow rate = 0.75 ml/min, back pressure = 50 bar, wavelength = 254 nm) using (*R*,*R*)-ß-Gem column (25 cm x 4.6 mm) from *Regis Technologies Inc.*.

2-Methyl-5,5-diphenylpiperidine (II)

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50-7.41 (m, 2H), 7.41-7.33 (m, 2H), 7.29-7.21 (m, 3H), 7.21-7.10 (m, 3H), 3.95 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.15 (d, *J* = 13.7 Hz, 1H), 2.90-2.77 (m, 1H), 2.73 (dq, *J* = 13.6, 3.4 Hz, 1H), 2.33-2.16 (m, 1H), 2.01 (s, 1H), 1.75-1.58 (m, 1H), 1.30-1.11 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H). The NMR data is in agreement with the literature.[8]

2-Methyl-4,4-diphenylpiperidine (IV)

^{1}H-NMR (400 MHz, C_6D_6) δ (ppm) = 7.27-7.10 (m, 8H), 7.10-6.98 (m, 2H), 2.78 (dd, *J* = 10.9, 2.5 Hz, 3H), 2.55-2.40 (m, 2H), 1.97 (ddd, *J* = 13.5, 11.5, 5.2 Hz, 1H), 1.64 (dd, *J* = 13.3, 11.2 Hz, 1H), 0.98 (d, *J* = 6.2 Hz, 3H), 0.63 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.7, 145.9, 128.6, 128.4, 126.4, 125.7, 48.1, 46.1, 45.5, 43.6, 37.3, 23.3; HR-MS ($C_{18}H_{22}N^+$, $[M\text{-}H]^+$): calc. 252.1747; found. 252.1747.

2-Methyl-4,4-diphenylpyrrolidine (VI)

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.01 (m, 10H), 4.94-4.78 (br s, 1H), 3.74-3.68 (d, *J* = 11.2 Hz, 1H), 3.46-3.40 (d, *J* =11.2 Hz, 1H), 3.26-3.16 (m, 1H), 2.37-2.30 (dd, *J* = 9.1, 6.3 Hz, 1H), 1.95-1.87 (dd, *J* = 11.2, 10.0 Hz, 1H), 1.13-1.08 (d, *J* = 6.3 Hz, 3H). The NMR data is in agreement with the literature.[8]

2-Methyl-5,5-di-*p*-tolylpiperidine (**VIII**).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31-7.26 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 4H), 3.91 (dd, *J* = 13.7, 3.0 Hz, 1H), 3.12 (d, *J* = 13.7 Hz, 1H), 2.84 (dqd, *J* = 12.8, 6.4, 3.1 Hz, 1H), 2.75 (s,

1H), 2.68 (ddd, *J* = 13.7, 6.7, 3.3 Hz, 1H), 2.35-2.29 (s, 3H), 2.26 (s, 3H), 2.18 (td, *J* = 13.4, 3.6 Hz, 1H), 1.66 (dq, *J* = 13.4, 3.5 Hz, 1H), 1.27-1.14 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 145.7, 141.2, 135.4, 129.5, 128.9, 127.8, 126.2, 55.3, 52.4, 44.5, 35.2, 31.0, 22.1, 20.9; HR-MS ($C_{20}H_{26}N^+$, $[M-H]^+$): calc. 280.2060; found. 280.2056.

5,5-Bis(3-methoxyphenyl)-2-methylpiperidine (X).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.29-7.23 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.02-6.96 (m, 2H), 6.79-6.71 (m, 3H), 6.66 (ddd, *J* = 8.1, 2.5, 0.7 Hz, 1H), 3.88 (dd, *J* = 13.7, 3.1 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.09 (d, *J* = 13.8 Hz, 1H), 2.81-2.71 (m, 1H), 2.67 (ddd, *J* = 13.6, 6.7, 3.3 Hz, 1H), 2.17 (td, *J* = 13.4, 3.6 Hz, 1H), 1.64 (ddd, *J* = 13.3, 6.7, 3.5 Hz, 1H), 1.47 (d, *J* = 32.4 Hz, 1H), 1.24-1.10 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.8, 159.4, 150.3, 146.2, 129.6, 129.1, 128.7, 120.5, 118.9, 114.9, 113.2, 110.3, 110.2, 55.7, 55.1, 55.1, 52.3, 45.2, 35.4, 31.4, 22.4; HR-MS ($C_{20}H_{26}NO_2^+$, $[M-H]^+$): calc. 312.1959; found. 312.1956.

3-Methyl-2-azaspiro[5.5]undecane (**XII**).

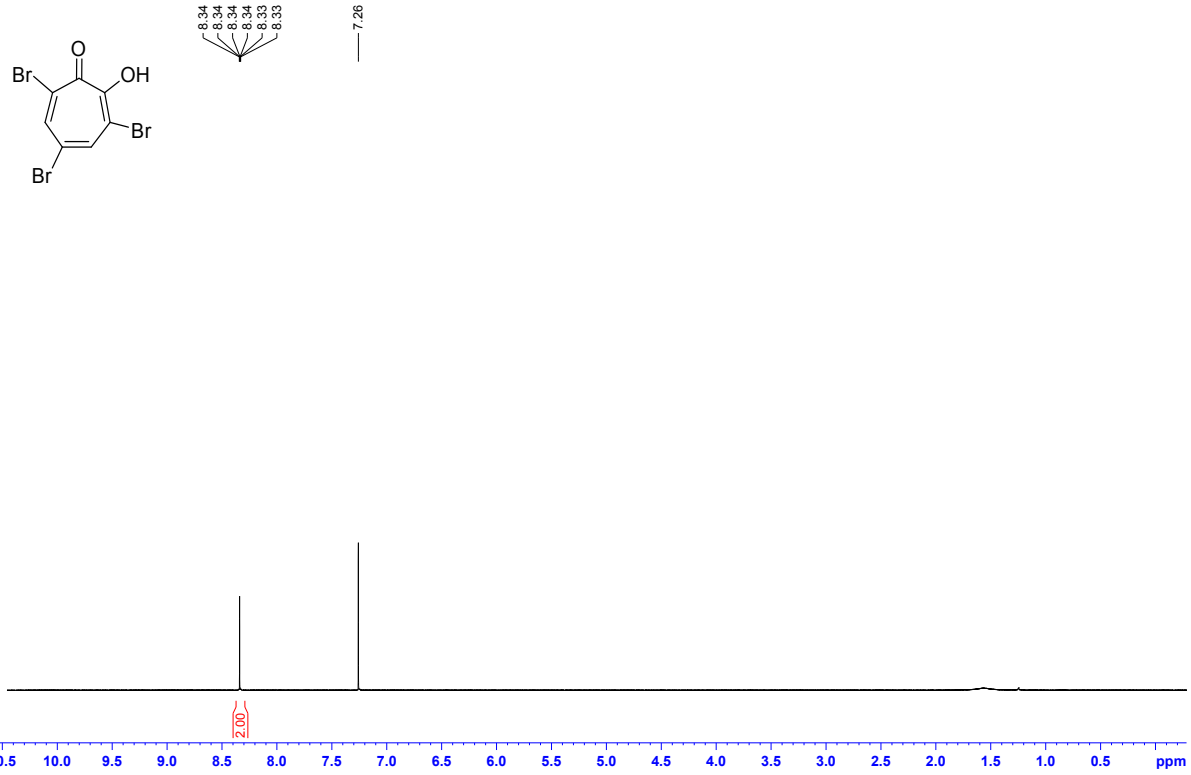
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.87 (dd, *J* = 12.3, 2.5 Hz, 1H), 2.60-2.46 (m, 1H), 2.33 (d, *J* = 12.3 Hz, 1H), 1.66 (ddd, *J* = 14.1, 8.5, 5.5 Hz, 1H), 1.48 (d, *J* = 13.0 Hz, 1H), 1.46-1.35 (m, 8H), 1.26-1.07 (m, 5H), 1.04 (d, *J* = 6.3 Hz, 3H). The NMR data is in agreement with the literature.[9]

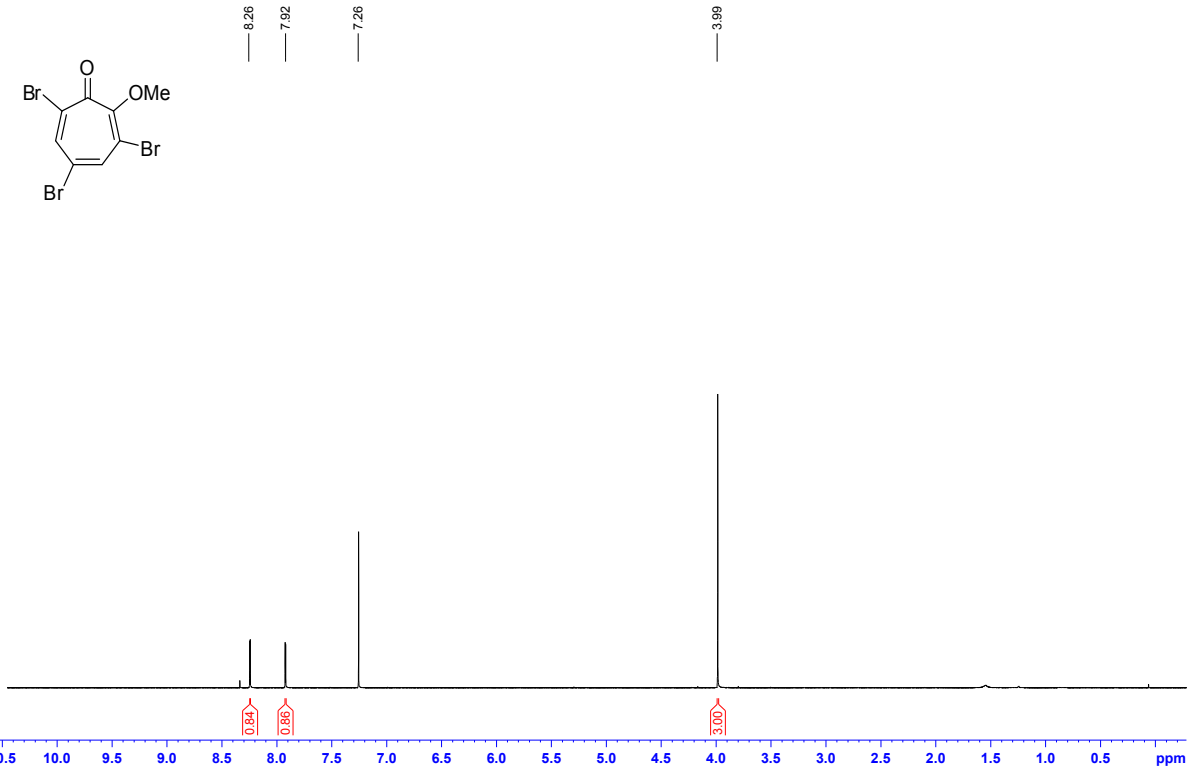
5-(But-3-enyl)-2-methyl-5-phenylpiperidine (**XIV**).

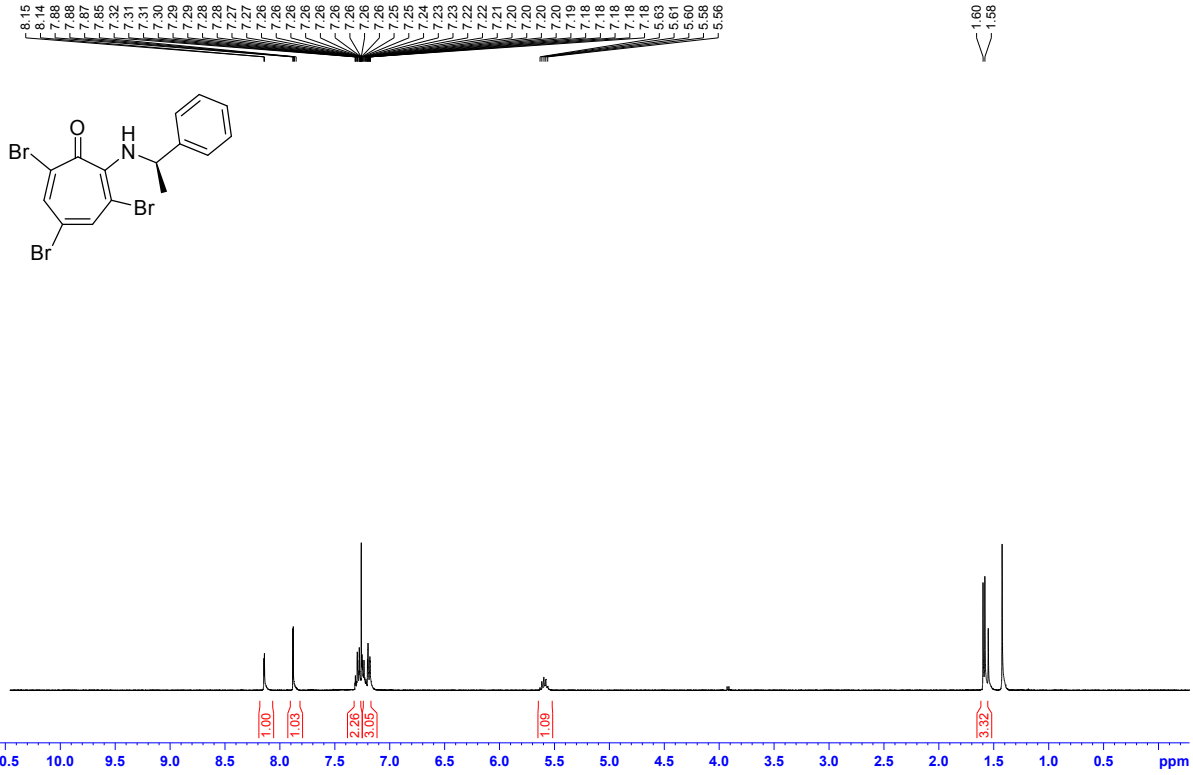
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 3H), 7.33-7.24 (m, 1H), 7.24-7.15 (m, 1H), 5.67 (dddt, *J* = 32.2, 16.8, 10.2, 6.5 Hz, 1H), 4.94-4.76 (m, 2H), 3.65 (dd, *J* = 13.6, 3.1 Hz) and 3.26 (dd, *J* = 12.3, 2.7 Hz, 1H), 2.80 (dd, *J* = 12.3, 6.9 Hz) and 2.75-2.56 (m, 2H), 2.50-2.41 (m) and 2.18-2.09 (m, 1H), 2.09-1.94 (m) and 1.84 (dtd, *J* = 18.1, 11.9, 6.0 Hz, 1H), 1.77-1.57 (m, 3H), 1.56-1.37 (m, 3H), 1.32 (s, 1H), 1.13 (d, *J* = 6.3 Hz) and 0.94 (d, *J* = 6.4 Hz, 3H), 1.11-0.98 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 147.6, 143.9, 139.1, 128.6, 127.5, 125.7, 114.1, 55.8, 53.0, 43.6, 40.6, 35.0, 31.1, 27.8, 22.5; HR-MS ($C_{16}H_{24}N^+$, $[M-H]^+$): calc. 230.1904; found. 230.1895.

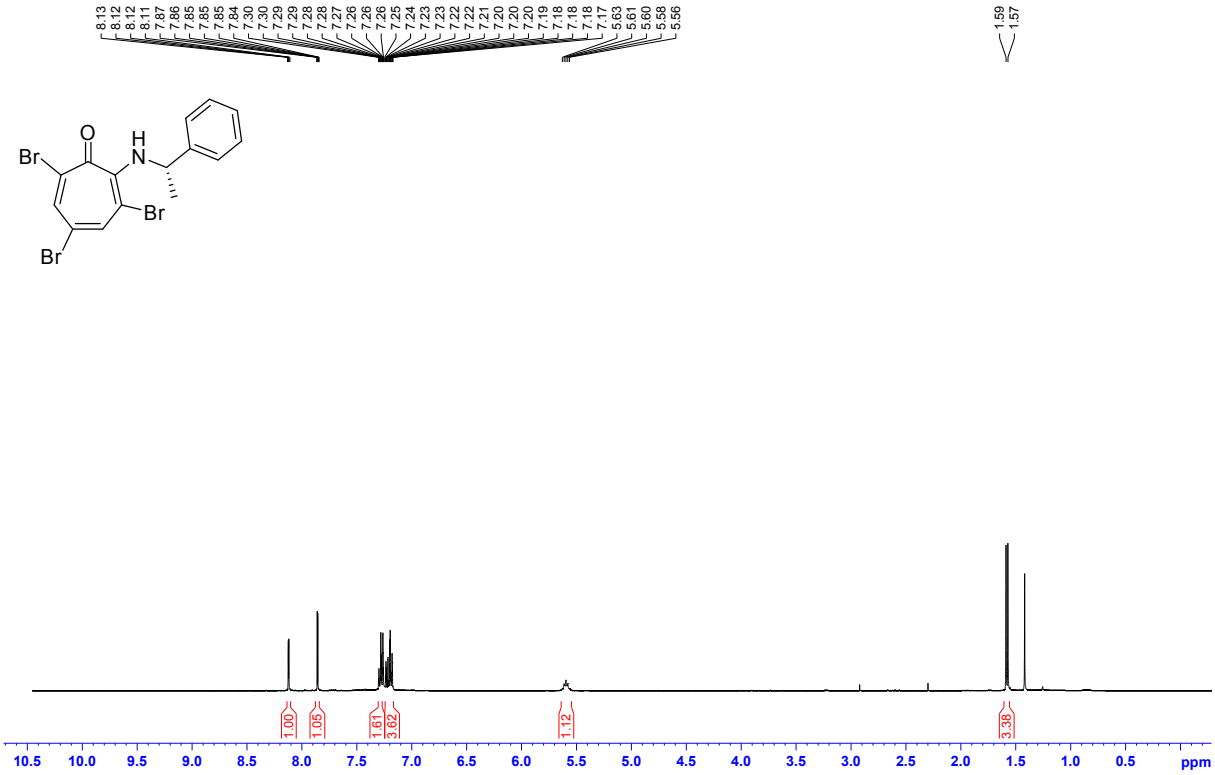
4-Allyl-2-methyl-4-phenylpyrrolidine (XVI)

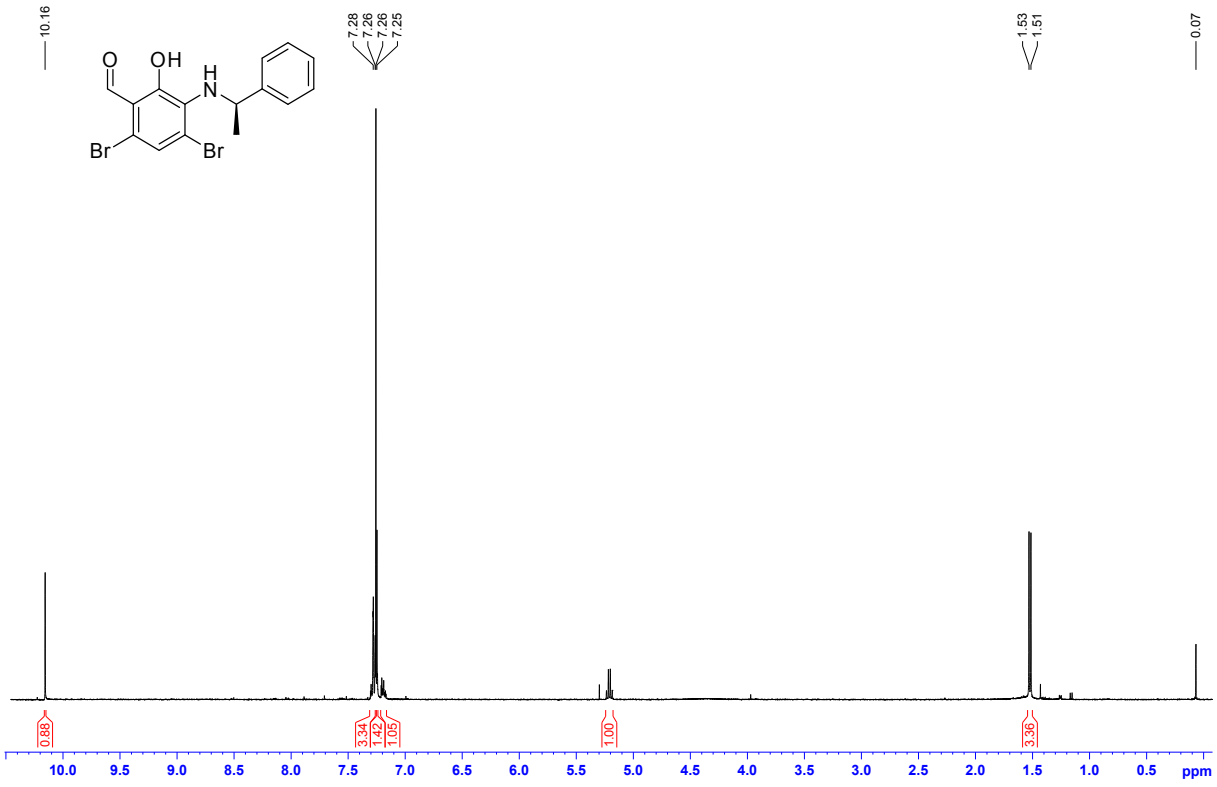
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.25-7.14 (m, 3H), 5.52-5.39 (m, 1H), 4.99-4.89 (m, 2H), 3.55-3.46 (m, 0.5H), 3.30-3.16 (m, 2.5H), 2.92-2.72 (br s, 1H), 2.52-2.27 (m, 3H), 1.68-1.52 (m, 1H), 1.27-1.16 (m, 3H). The NMR data is in agreement with the literature.[9]

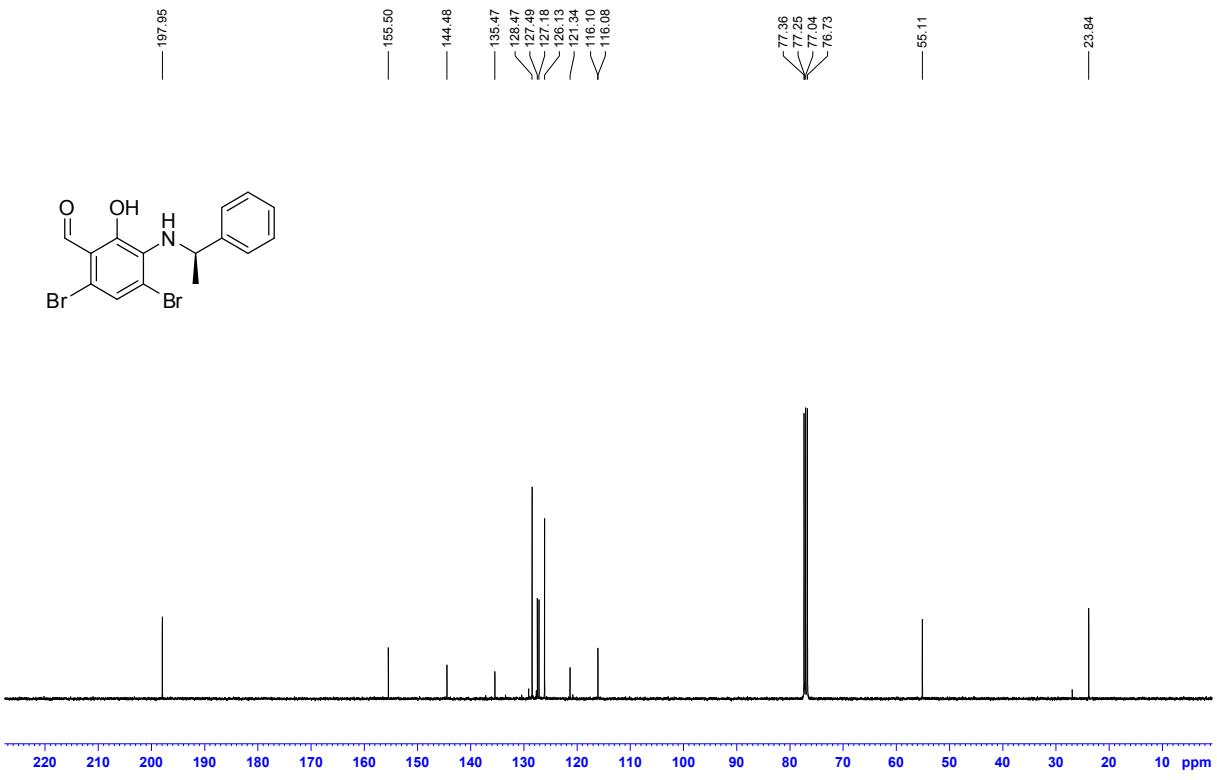

8.34
8.34
8.34
8.34
8.33
8.33
7.26
O
Br
OH
Br
Br
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

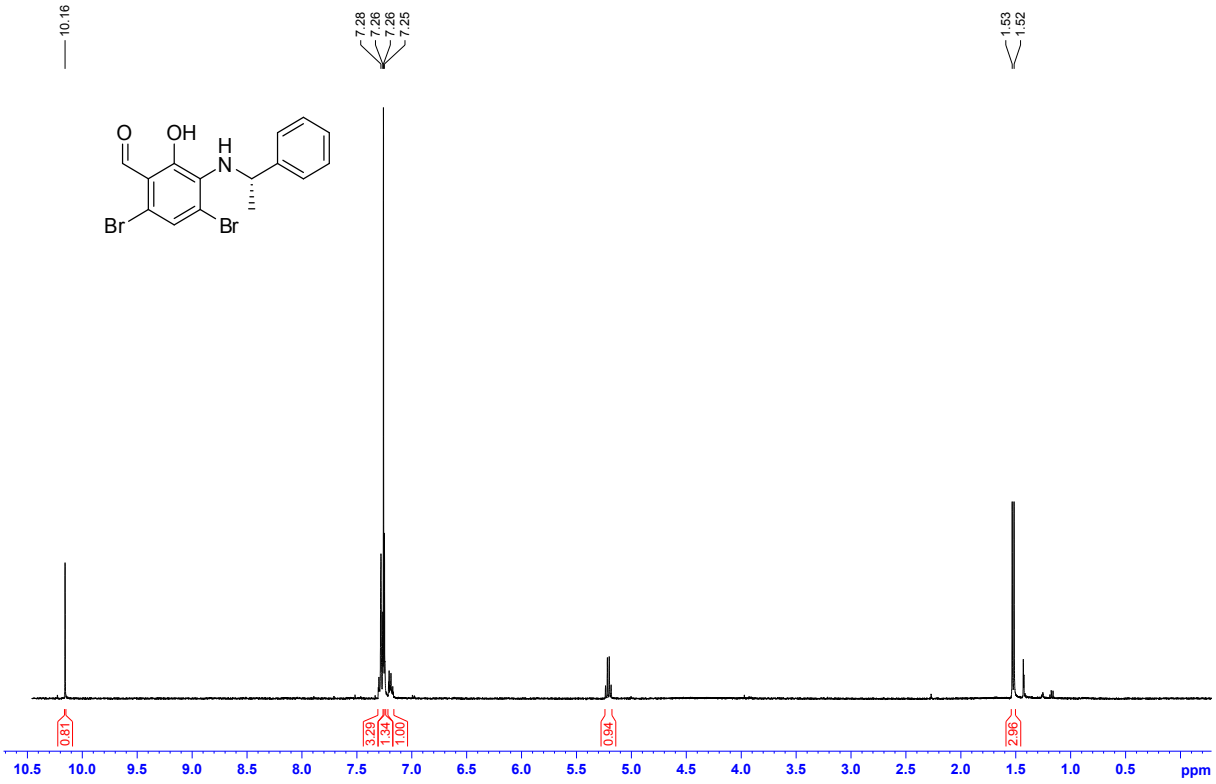

8.26
7.92
7.26
3.99
O
Br
OMe
Br
Br
0.84
0.86
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

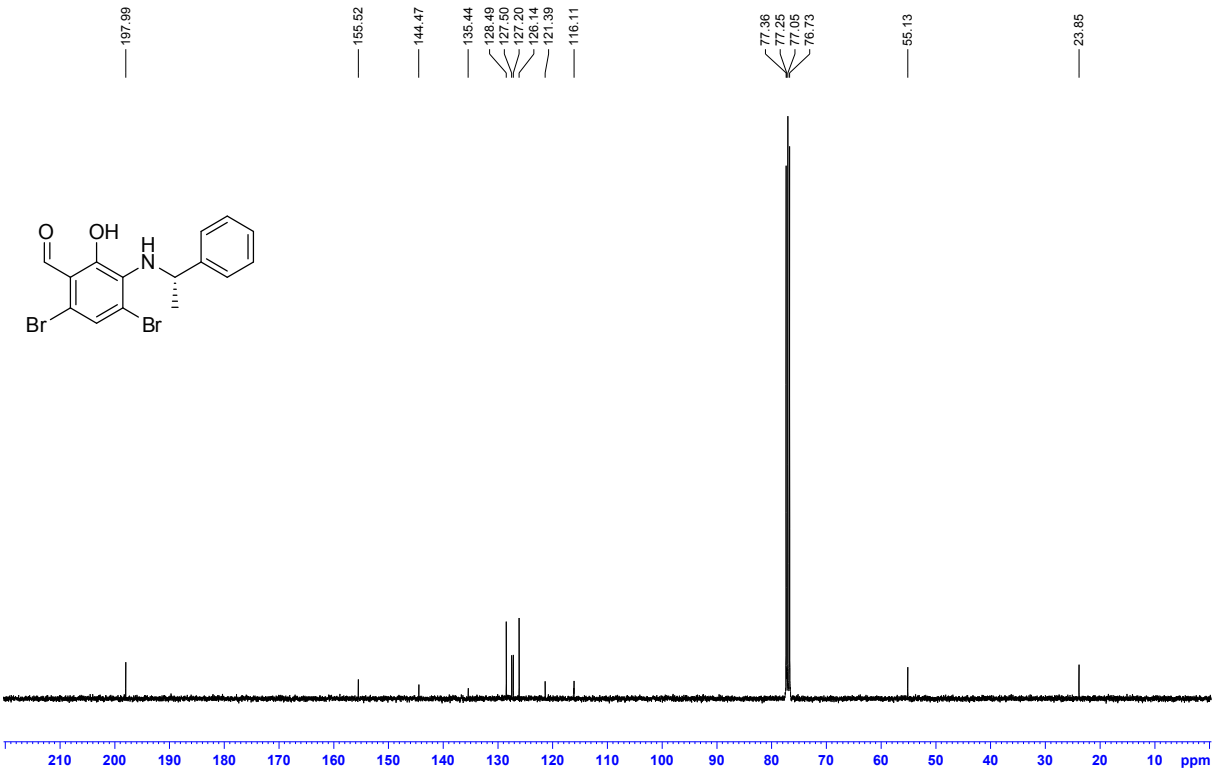

8.15 8.14 7.88 7.88 7.87 7.85 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.26 7.26 7.26 7.26 7.26 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.18 7.18 5.63 5.61 5.60 5.58 5.56
1.60 1.58
O
H
N
Br
Br
Br
1.00 1.03 2.26 3.05 1.09 3.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

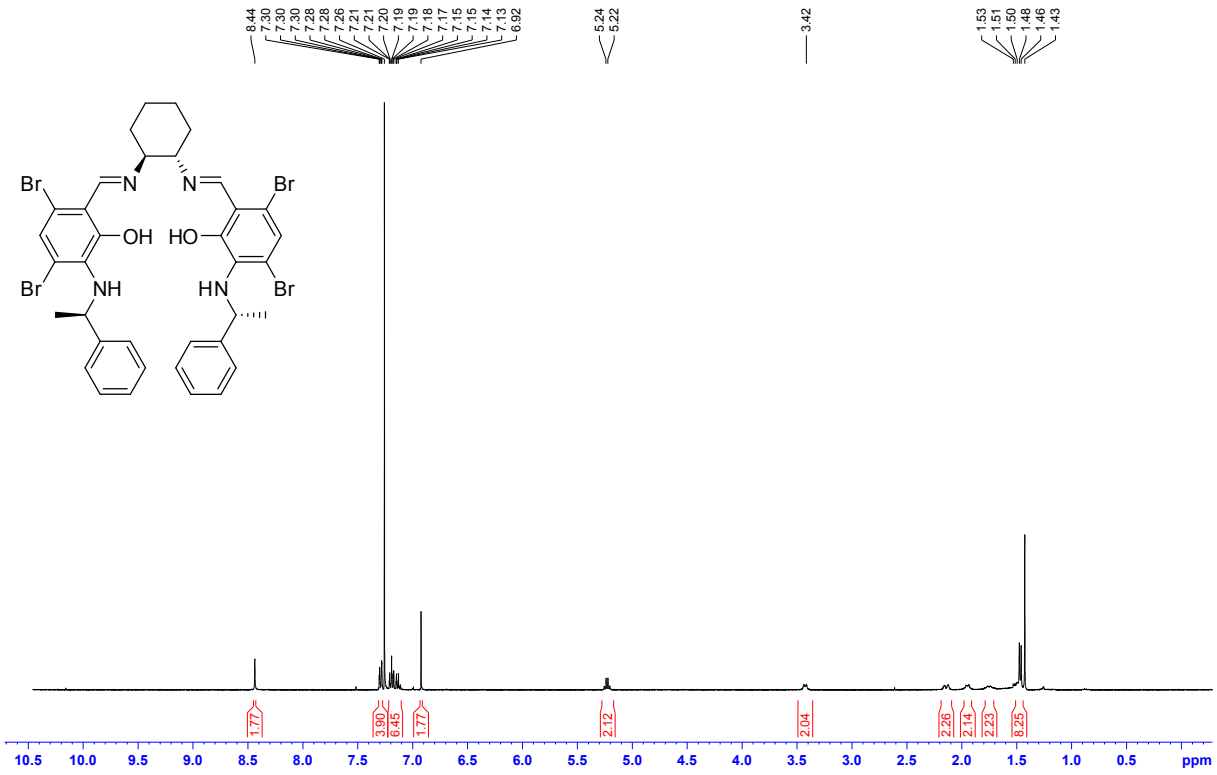

8.13 8.12 8.12 8.11 7.87 7.86 7.85 7.85 7.85 7.84 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.17 5.63 5.61 5.60 5.58 5.56
1.59 1.57
O
H
N
Br
Br
Br
1.00 1.05 1.61 3.62 1.12 3.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

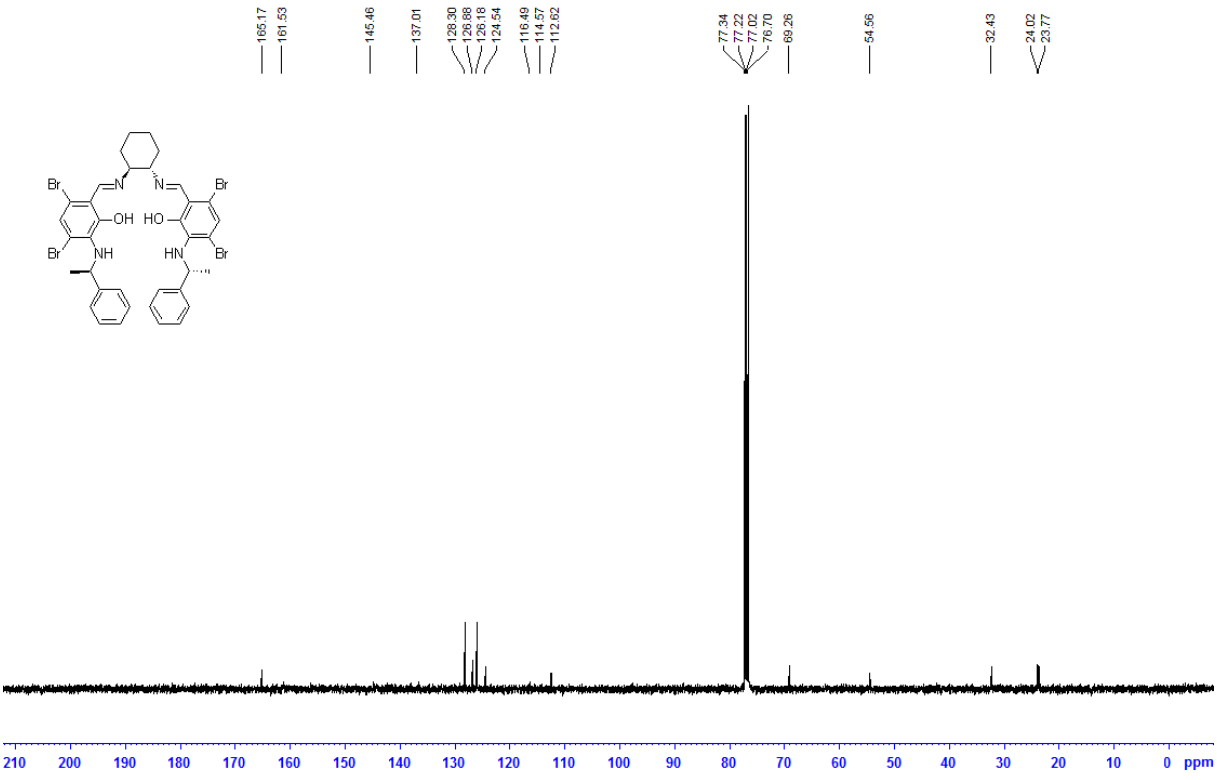

10.16
7.28
7.26
7.26
7.25
1.53
1.51
0.07
O
OH
H
N
Br
Br
0.88
3.34
1.42
1.05
1.00
3.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

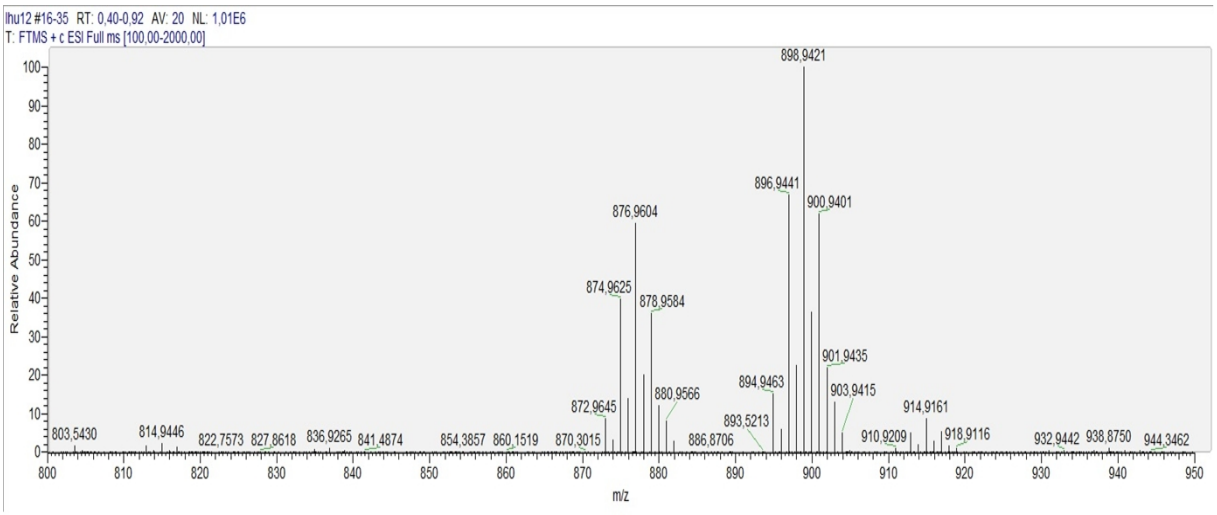

197.95
155.50
144.48
135.47
128.47
127.49
127.18
126.13
121.34
116.10
116.08
77.36
77.25
77.04
76.73
55.11
23.84
O
OH
H
N
Br
Br
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

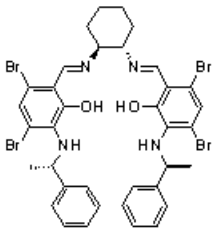

10.16
7.28
7.26
7.26
7.25
1.53
1.52
O
OH
H
N
Br
Br
0.81
3.29
1.34
1.00
0.94
2.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

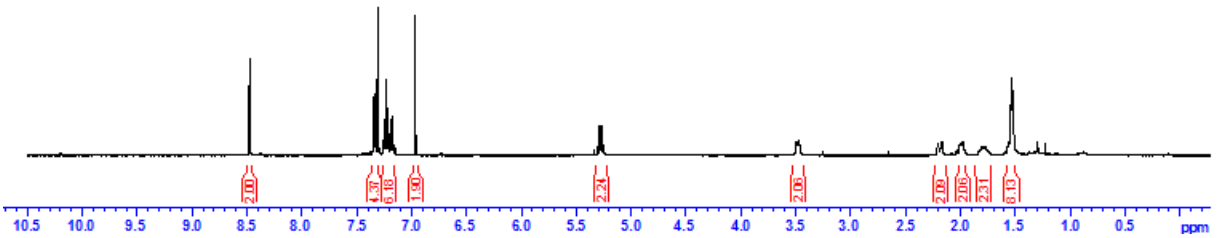

197.99
155.52
144.47
135.44
128.49
127.50
127.20
126.14
121.39
116.11
77.36
77.25
77.05
76.73
55.13
23.85
O
OH
H
N
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

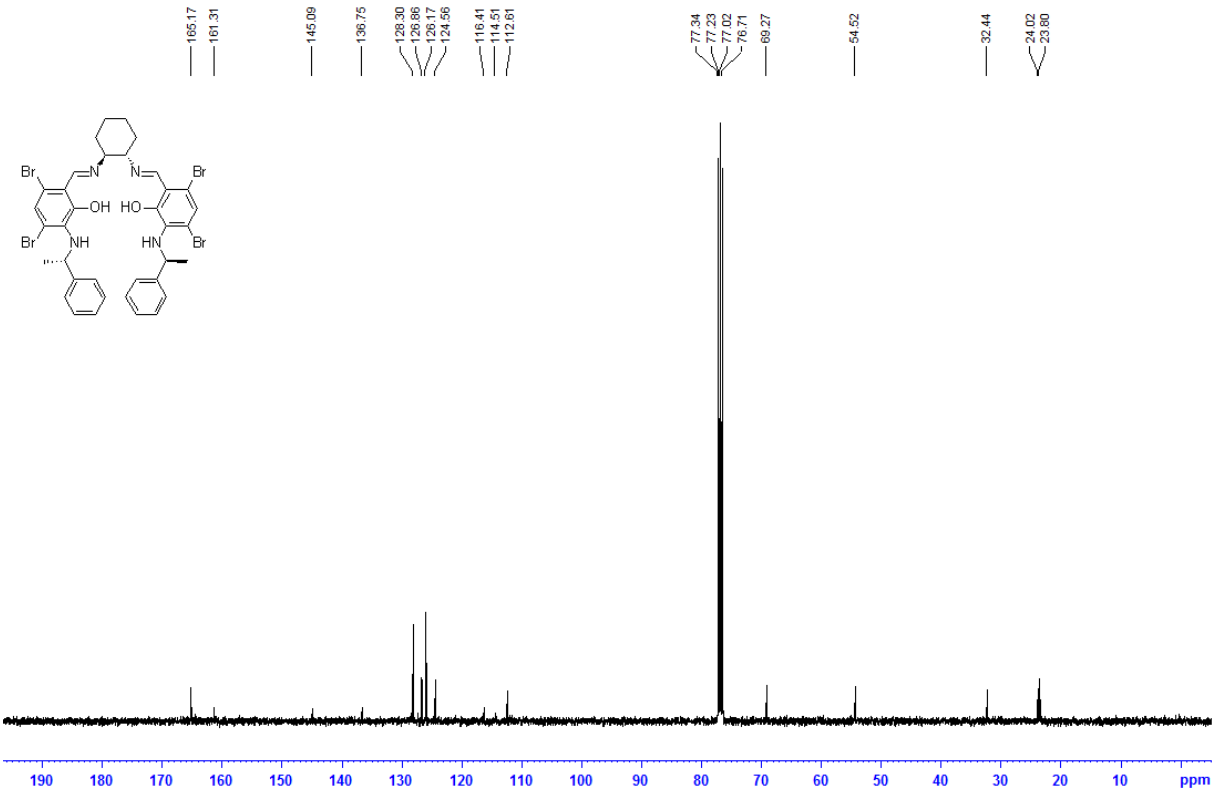

8.44
7.30
7.30
7.30
7.28
7.28
7.26
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.15
7.15
7.14
7.13
6.92
5.24
5.22
3.42
1.53
1.51
1.50
1.48
1.46
1.43
Br
N
N
Br
OH
HO
Br
NH
HN
Br
1.77
3.90
6.45
1.77
2.12
2.04
2.26
2.14
2.23
8.25
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

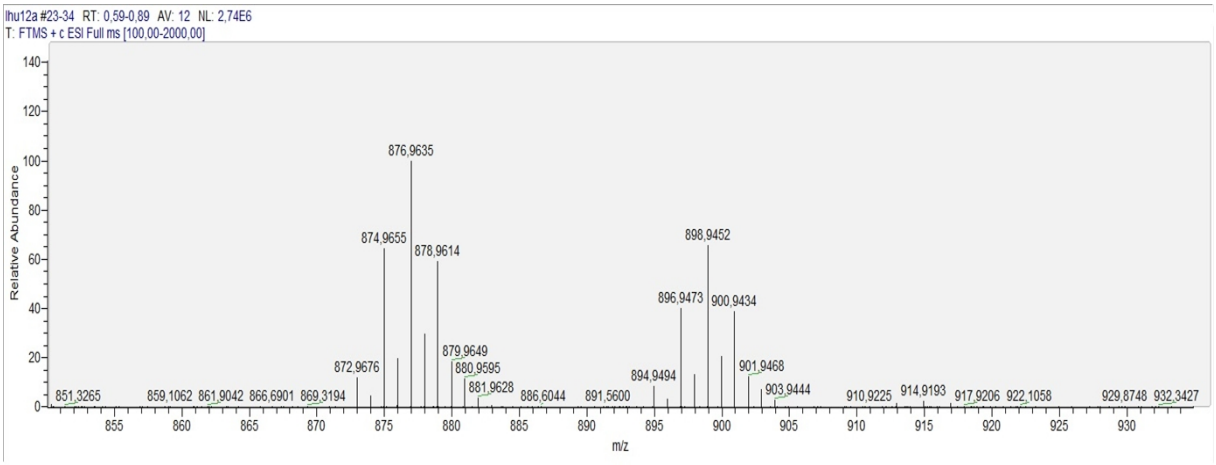

165.17
161.53
145.46
137.01
128.30
126.88
126.18
124.54
116.49
114.57
112.62
77.34
77.22
77.02
76.70
69.26
54.56
32.43
24.02
23.77
Br
N
N
Br
OH
HO
Br
NH
HN
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

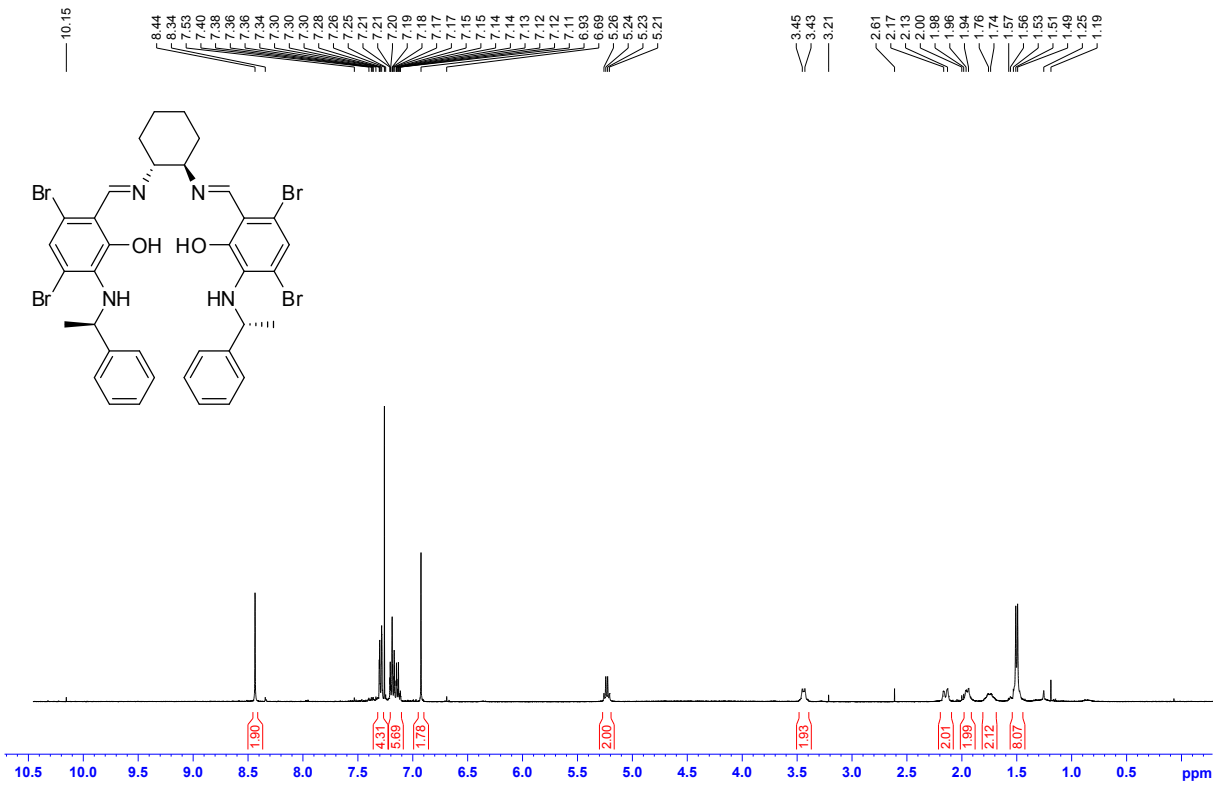

lhu12 #16-35 RT: 0.40-0.92 AV: 20 NL: 1.01E6
T: FTMS + c ESI Full ms [100.00-2000.00]
Relative Abundance
m/z
898.9421
896.9441
900.9401
876.9604
874.9625
878.9584
901.9435
894.9463
903.9415
880.9566
872.9645
914.9161
893.5213
803.5430
814.9446
822.7573
827.8618
836.9265
841.4874
854.3857
860.1519
870.3015
886.8706
910.9209
918.9116
932.9442
938.8750
944.3462

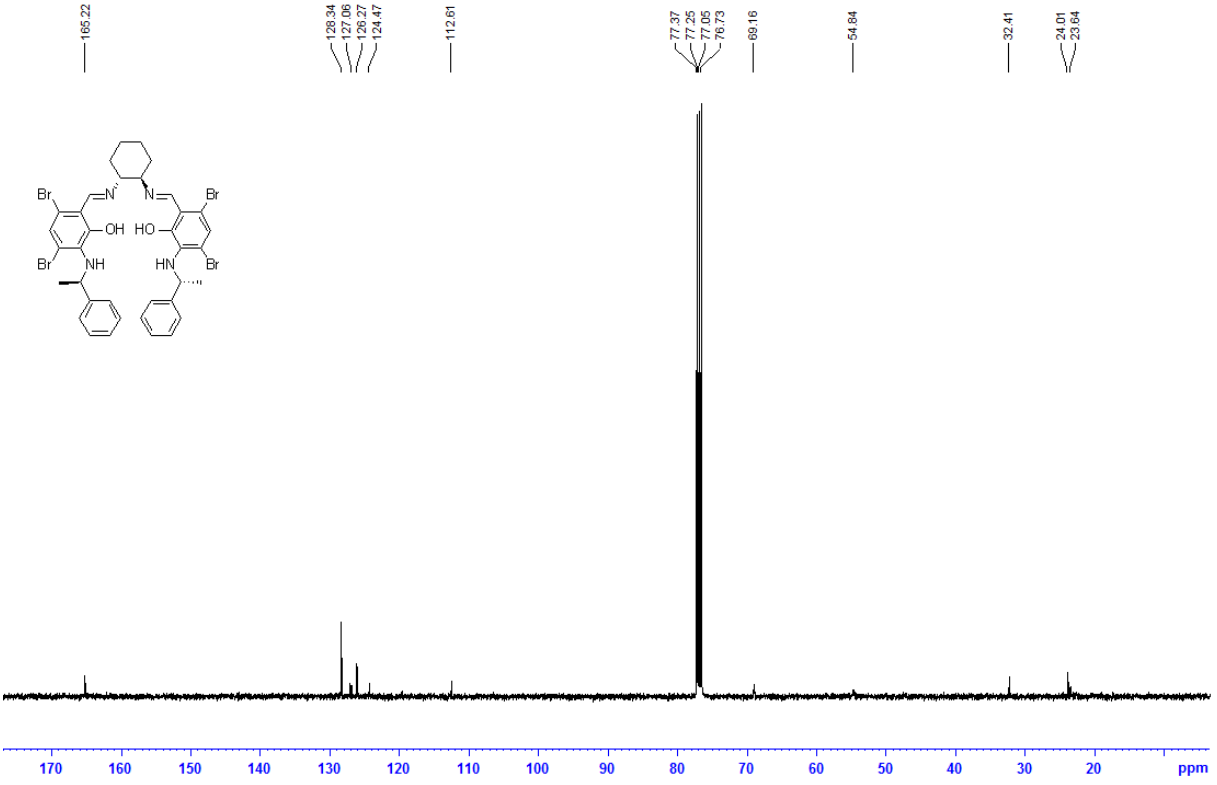

Br
N
N
Br
OH
HO
Br
NH
HN
Br

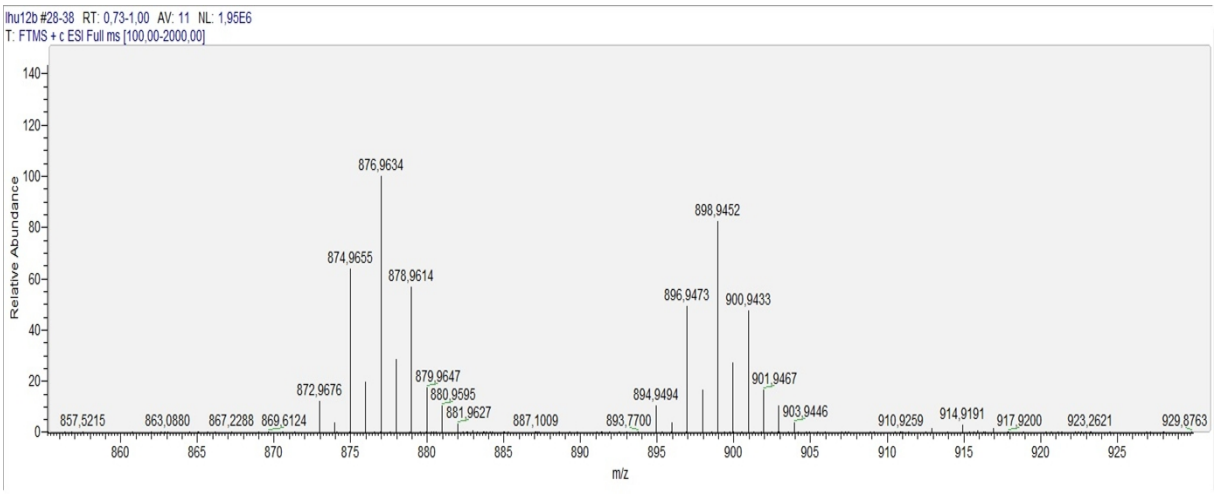

2.00
4.37
6.18
1.00
2.24
2.06
2.09
2.05
2.31
8.13
ppm

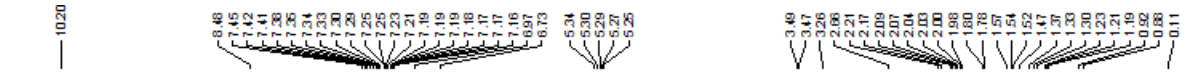

165.17
161.31
145.09
136.75
128.30
126.86
126.17
124.56
116.41
114.51
112.61
77.34
77.23
77.02
76.71
69.27
54.52
32.44
24.02
23.80
Br
N
N
Br
OH
HO
Br
NH
HN
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

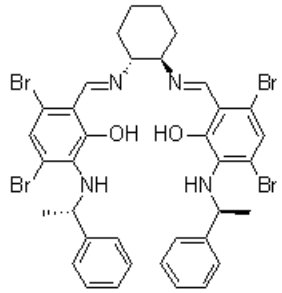

lhu12a #23-34 RT: 0,59-0,89 AV: 12 NL: 2,74E6
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
876,9635
874,9655
878,9614
898,9452
896,9473
900,9434
879,9649
880,9595
881,9628
872,9676
894,9494
901,9468
903,9444
851,3265
859,1062
861,9042
866,6901
869,3194
886,6044
891,5600
910,9225
914,9193
917,9206
922,1058
929,8748
932,3427

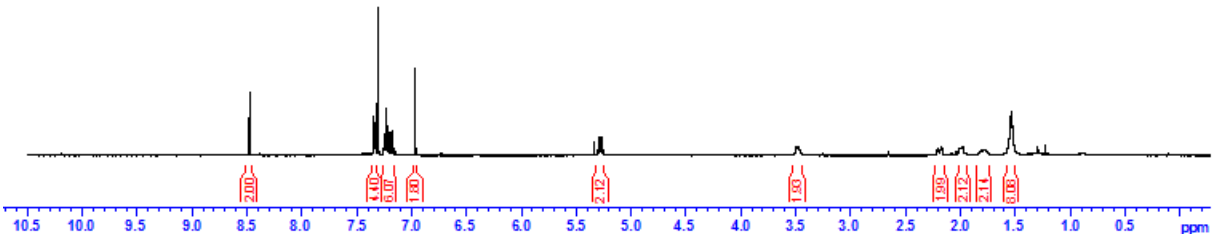

10.15
8.44
8.34
7.53
7.40
7.38
7.36
7.36
7.34
7.30
7.30
7.28
7.26
7.25
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.15
7.15
7.14
7.14
7.13
7.12
7.12
7.11
6.93
6.69
5.26
5.24
5.23
5.21
3.45
3.43
3.21
2.61
2.17
2.13
2.00
1.98
1.96
1.94
1.76
1.74
1.57
1.56
1.53
1.51
1.49
1.25
1.19
Br
N
N
Br
OH
HO
Br
NH
HN
Br
1.90
4.31
5.69
1.78
2.00
1.93
2.01
1.99
2.12
8.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

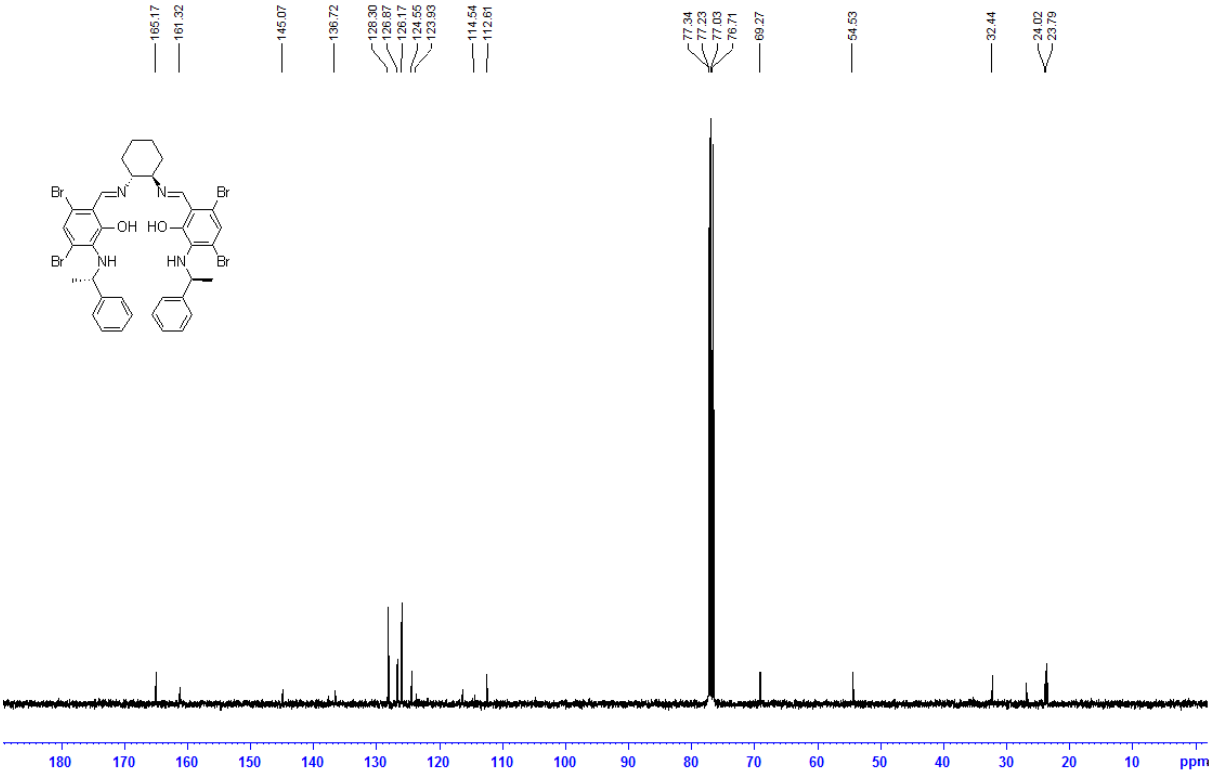

165.22
128.34
127.06
126.27
124.47
112.61
77.37
77.25
77.05
76.73
69.16
54.84
32.41
24.01
23.64
Br
N
N
Br
OH
HO
Br
NH
HN
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

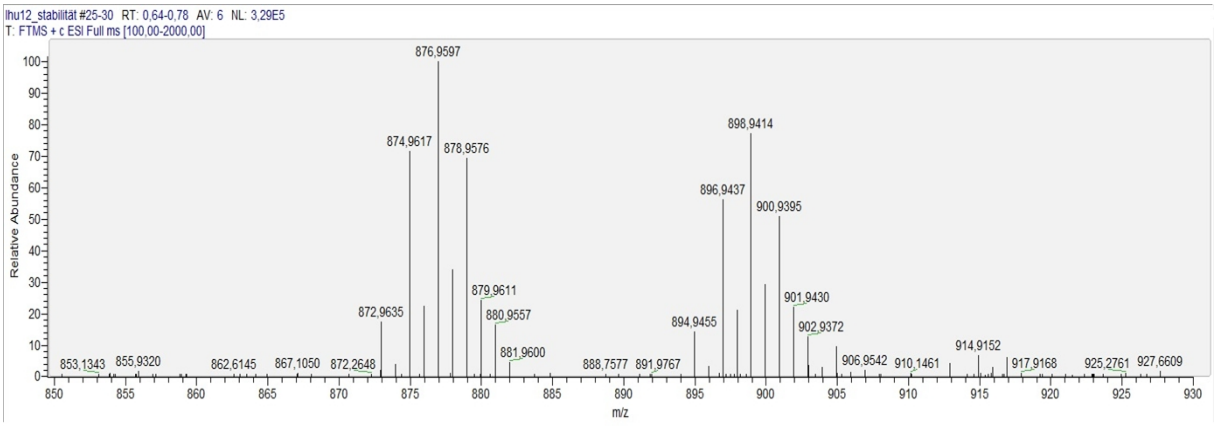

lhu12b #28-38 RT: 0,73-1,00 AV: 11 NL: 1,95E6
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
876,9634
898,9452
874,9655
878,9614
896,9473
900,9433
872,9676
879,9647
901,9467
880,9595
894,9494
881,9627
903,9446
857,5215
863,0880
867,2288
869,6124
887,1009
893,7700
910,9259
914,9191
917,9200
923,2621
929,8763

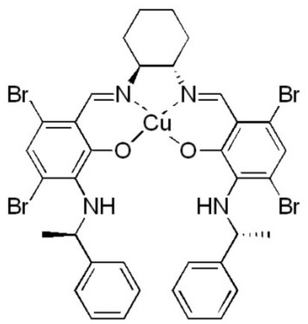


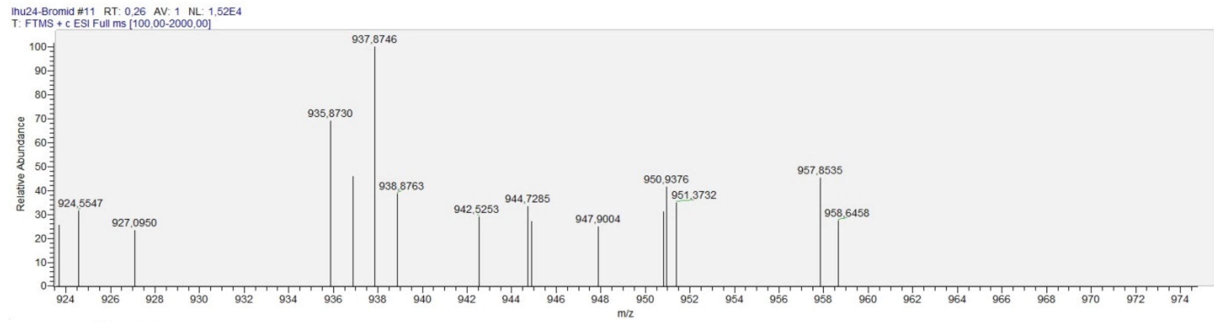

Br
N
N
Br
OH
HO
Br
NH
HN
Br

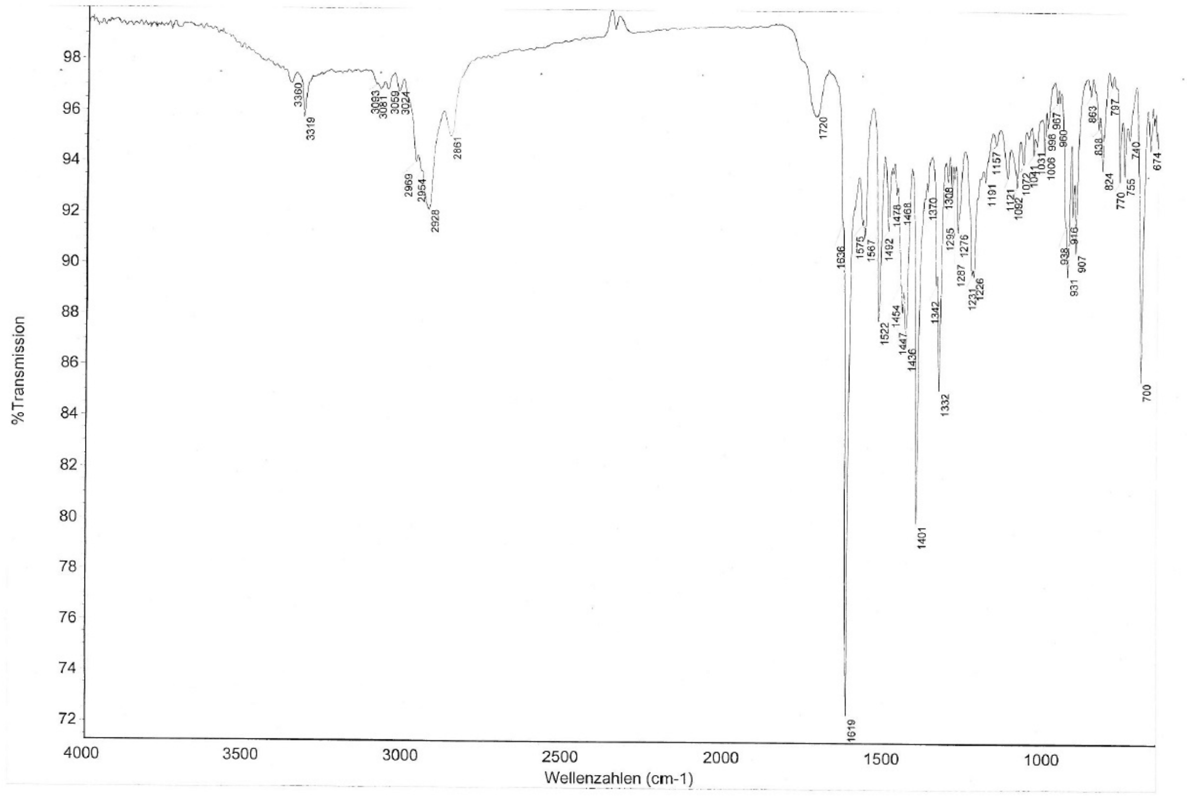

2.00
4.15
3.00
1.88
2.12
1.90
1.99
2.12
2.14
6.08
ppm

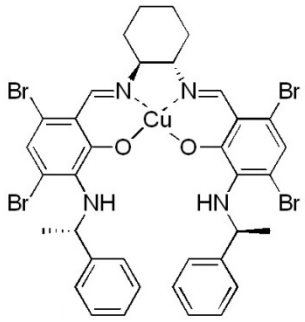

165.17
161.32
145.07
136.72
128.30
126.87
126.17
124.55
123.93
114.54
112.61
77.34
77.23
77.03
76.71
69.27
54.53
32.44
24.02
23.79
Br
N
N
Br
OH
HO
Br
NH
HN
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

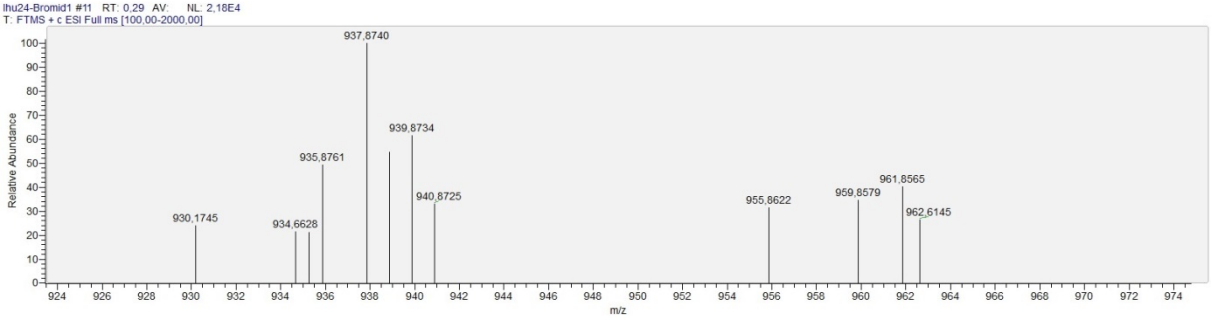

lhu12_stabilität #25-30 RT: 0,64-0,78 AV: 6 NL: 3,29E5
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
876,9597
874,9617
878,9576
898,9414
896,9437
900,9395
879,9611
880,9557
872,9635
901,9430
902,9372
894,9455
881,9600
914,9152
853,1343
855,9320
862,6145
867,1050
872,2648
888,7577
891,9767
906,9542
910,1461
917,9168
925,2761
927,6609

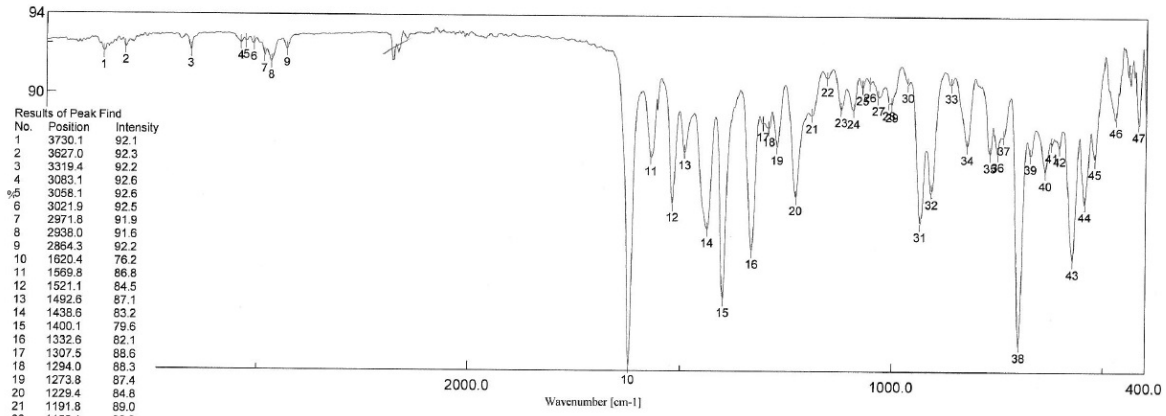

Br
N
Cu
N
Br
O
O
Br
NH
HN
Br


lhu24-Bromid #11 RT: 0,26 AV: 1 NL: 1,52E4
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
937,8746
935,8730
938,8763
942,5253
944,7285
947,9004
950,9376
951,3732
957,8535
958,6458
924,5547
927,0950
m/z


%Transmission
Wellenzahlen (cm-1)
3360
3319
3093
3081
3059
3024
2969
2954
2928
2861
1720
1636
1619
1576
1567
1522
1492
1478
1468
1454
1447
1436
1401
1370
1342
1332
1306
1295
1287
1276
1231
1226
1191
1157
1121
1092
1072
1041
1031
1006
998
967
960
938
931
916
907
863
838
824
797
770
755
740
700
674

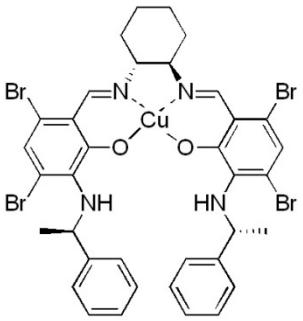


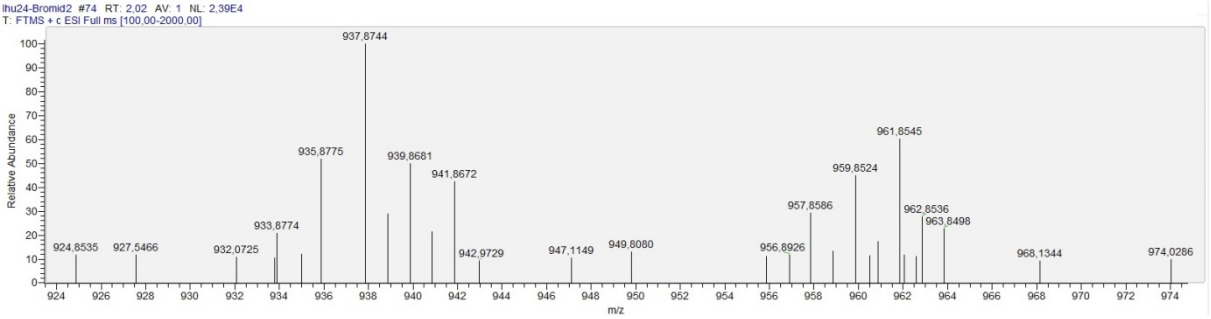


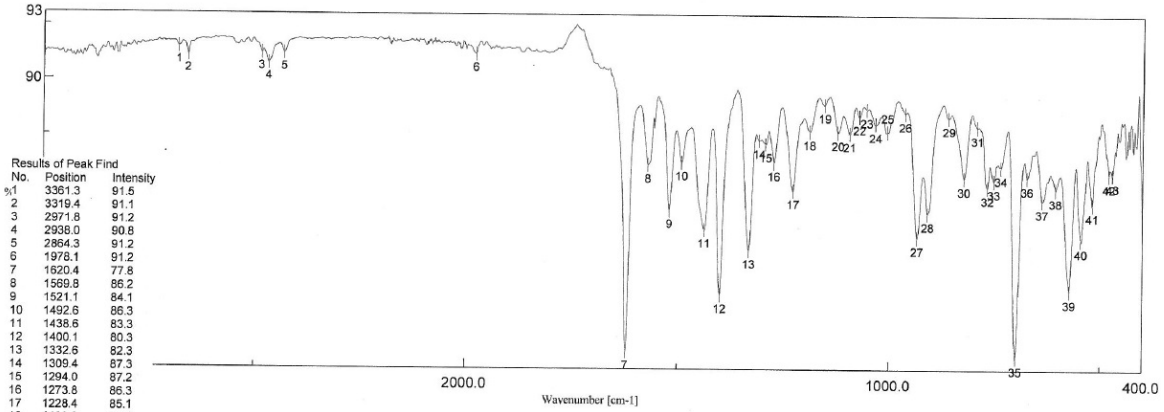


Results of Peak Find

No.	Position	Intensity
1	3730.1	92.1
2	3627.0	92.3
3	3319.4	92.2
4	3083.1	92.6
5	3058.1	92.6
6	3021.9	92.5
7	2971.8	91.9
8	2938.0	91.6
9	2864.3	92.2
10	1620.4	76.2
11	1569.8	86.8
12	1521.1	84.5
13	1492.6	87.1
14	1438.6	83.2
15	1400.1	79.6
16	1332.6	82.1
17	1307.5	88.6
18	1294.0	88.3
19	1273.8	87.4
20	1229.4	84.8
21	1191.8	89.0
22	1156.1	90.9
23	1122.8	89.3
24	1093.9	89.2
25	1072.2	90.4
26	1055.4	90.6
27	1035.1	89.9
28	1010.0	89.7
29	1003.3	89.6
30	964.7	90.6
31	934.3	83.5
32	907.3	85.2
33	862.0	90.6
34	823.9	87.4
35	769.9	87.0
36	751.1	87.1
37	737.6	87.9
38	699.1	77.4
39	674.0	87.0
40	638.8	86.1
41	623.4	87.6
42	605.1	87.4
43	573.2	81.6
44	544.3	84.6
45	521.2	86.7
46	472.5	88.9
47	418.5	88.6

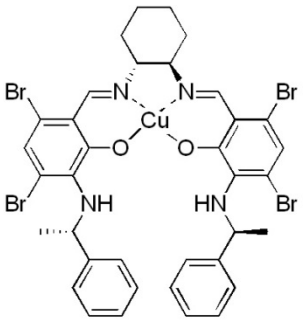


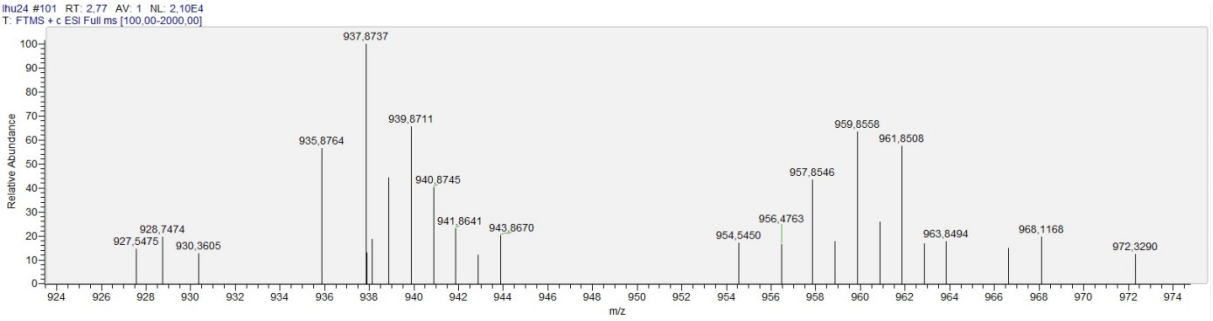


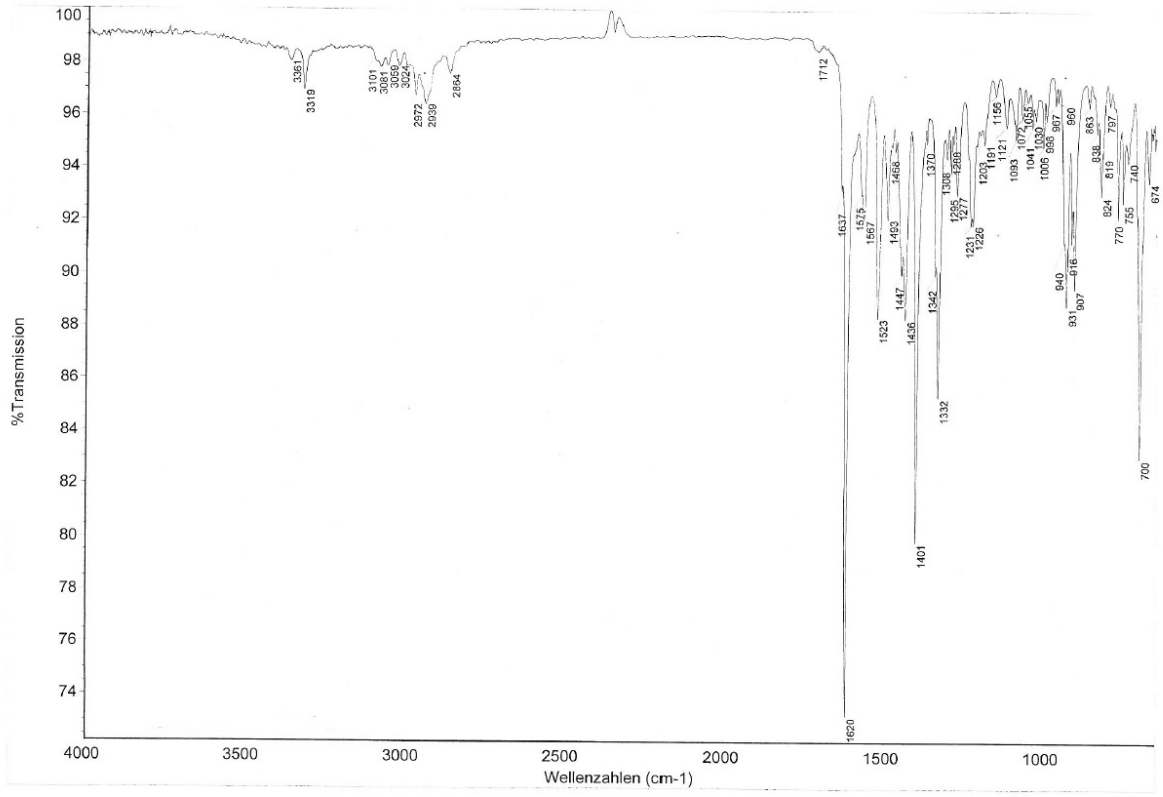


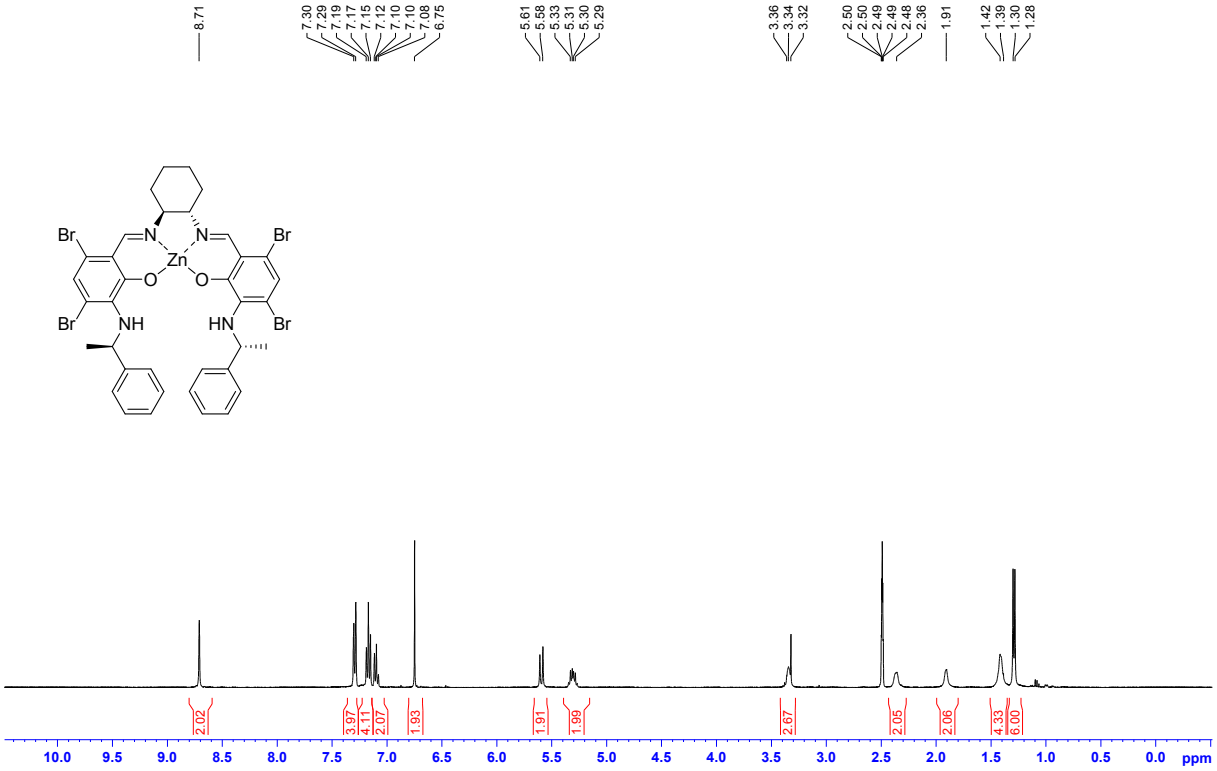
Results of Peak Find

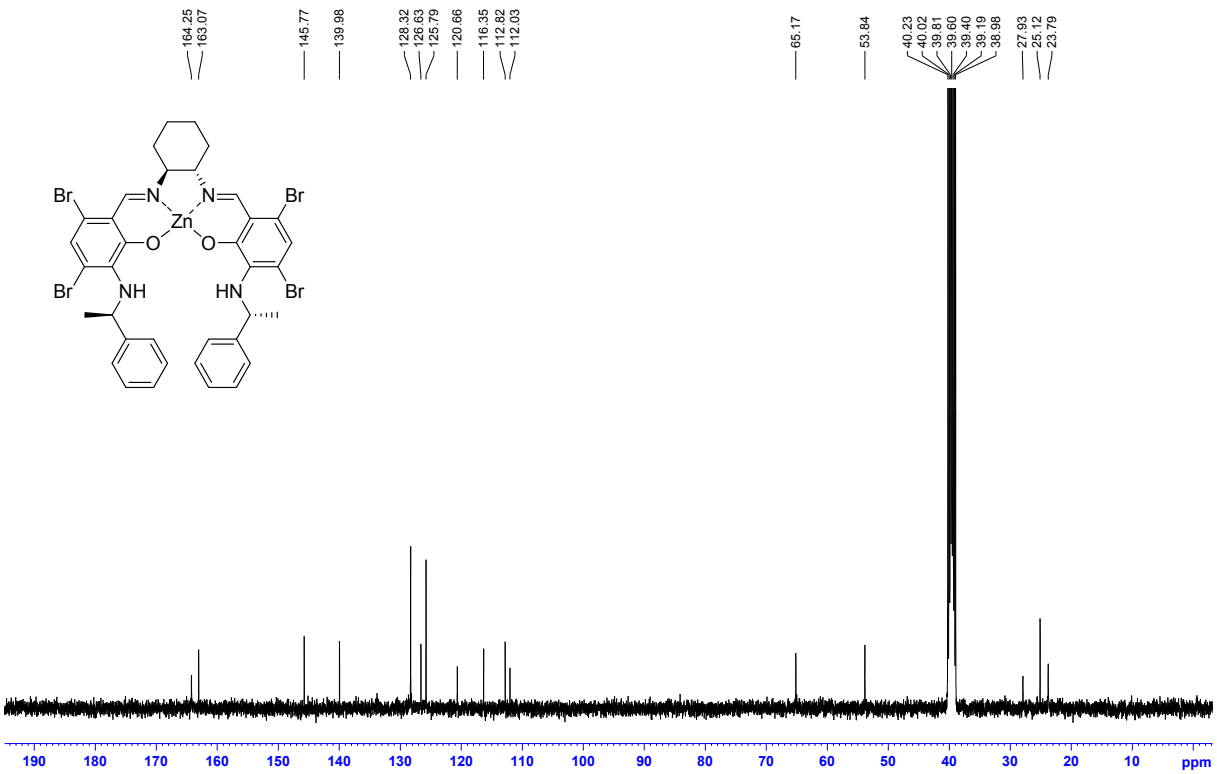
No.	Position	Intensity
%1	3361.3	91.5
2	3319.4	91.1
3	2971.8	91.2
4	2938.0	90.8
5	2864.3	91.2
6	1978.1	91.2
7	1620.4	77.8
8	1569.8	86.2
9	1521.1	84.1
10	1492.6	86.3
11	1438.6	83.3
12	1400.1	80.3
13	1332.6	82.3
14	1309.4	87.3
15	1294.0	87.2
16	1273.8	86.3
17	1228.4	85.1
18	1189.9	87.7
19	1154.7	88.9
20	1122.8	87.7
21	1095.9	87.7
22	1072.2	88.4
23	1055.4	88.7
24	1033.7	88.1
25	1006.7	87.7
26	963.3	88.6
27	934.3	82.9
28	909.3	84.0
29	860.6	88.4
30	823.5	85.7
31	793.1	87.9
32	768.0	85.2
33	753.1	85.5
34	736.2	86.2
35	699.1	77.6
36	674.0	85.7
37	638.8	84.6
38	606.5	85.1
39	573.2	80.6
40	546.2	82.9
41	519.2	84.5
42	480.7	85.8
43	472.5	85.8

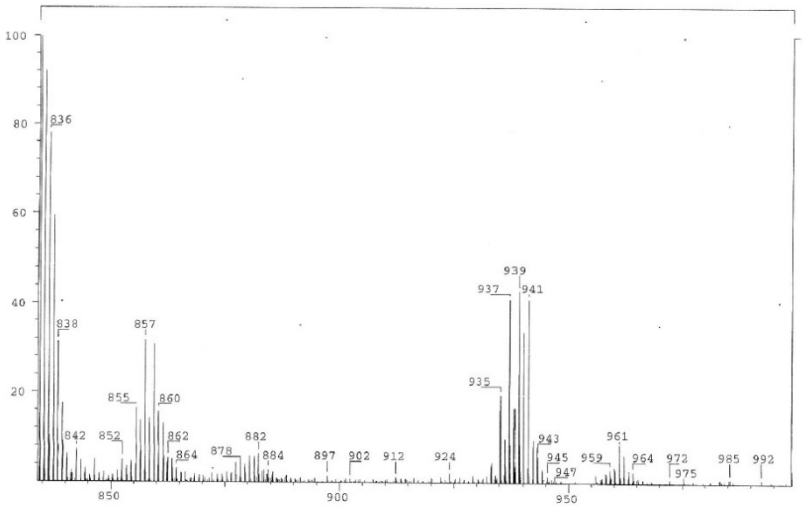

Br
N
N
Br
Cu
O
O
Br
NH
HN
Br

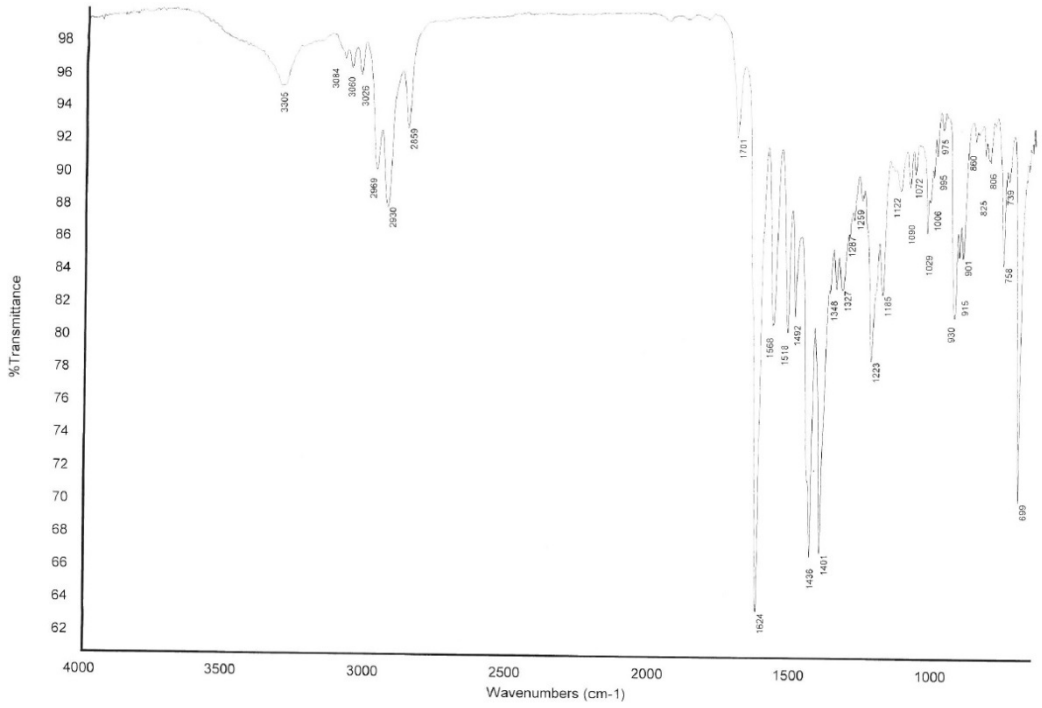

lhu24 #101 RT: 2,77 AV: 1 NL: 2,10E4
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
937,8737
939,8711
935,8764
940,8745
941,8641
943,8670
928,7474
927,5475
930,3605
959,8558
961,8508
957,8546
956,4763
954,5450
963,8494
968,1168
972,3290

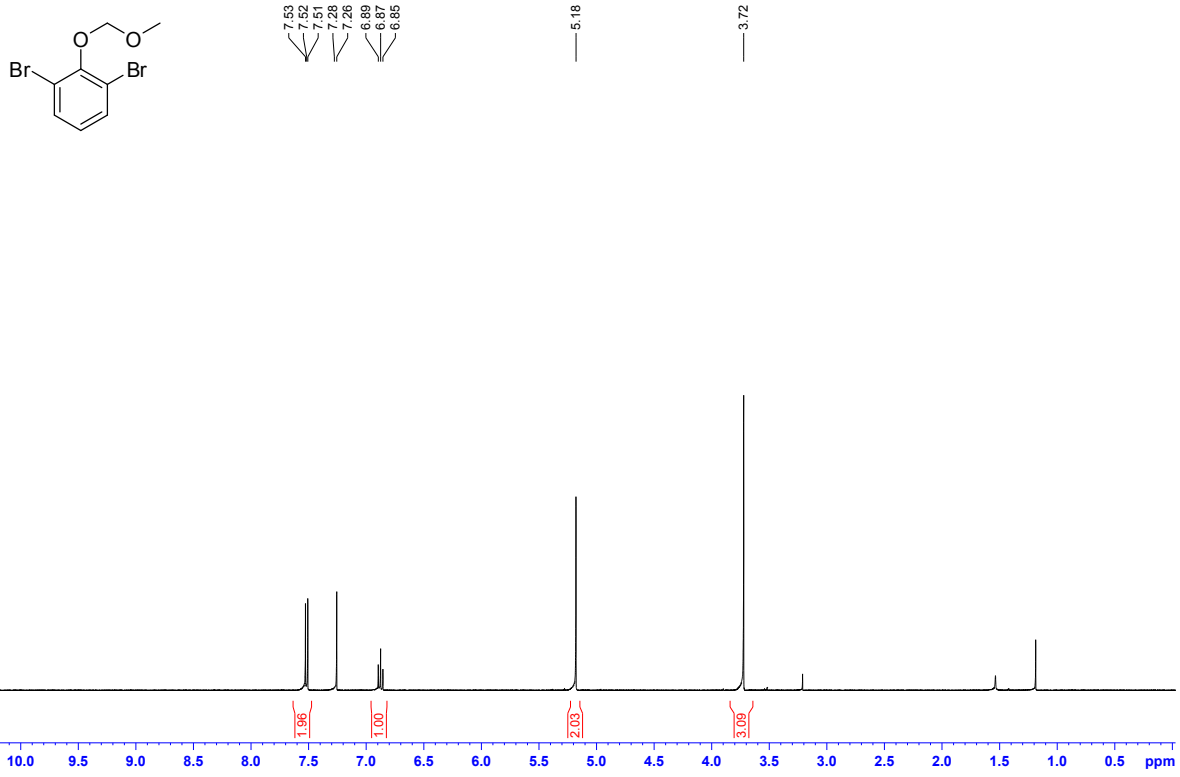

%Transmission
Wellenzahlen (cm-1)
3361
3319
3101
3081
3059
3024
2872
2939
2864
1712
1637
1620
1575
1567
1523
1493
1468
1447
1436
1401
1370
1342
1332
1308
1285
1277
1266
1231
1226
1201
1191
1156
1121
1093
1072
1055
1041
1030
1006
988
967
960
940
931
916
907
883
863
838
824
797
770
755
740
700
674
619

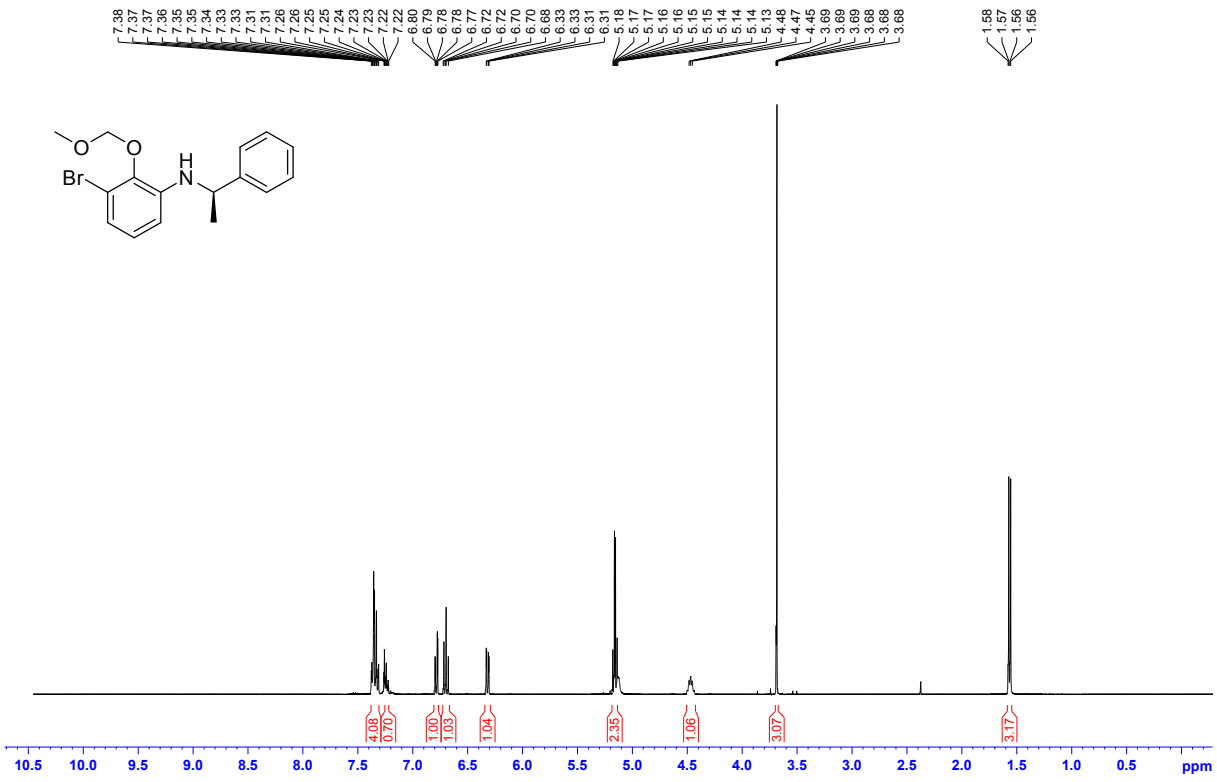

8.71
7.30
7.29
7.19
7.17
7.15
7.12
7.10
7.10
7.08
6.75
5.61
5.58
5.33
5.31
5.30
5.29
3.36
3.34
3.32
2.50
2.50
2.49
2.49
2.48
2.36
1.91
1.42
1.39
1.30
1.28
Br
N
N
Br
Zn
O
O
Br
NH
HN
Br
2.02
3.97
4.11
2.07
1.93
1.91
1.99
2.67
2.05
2.06
4.33
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

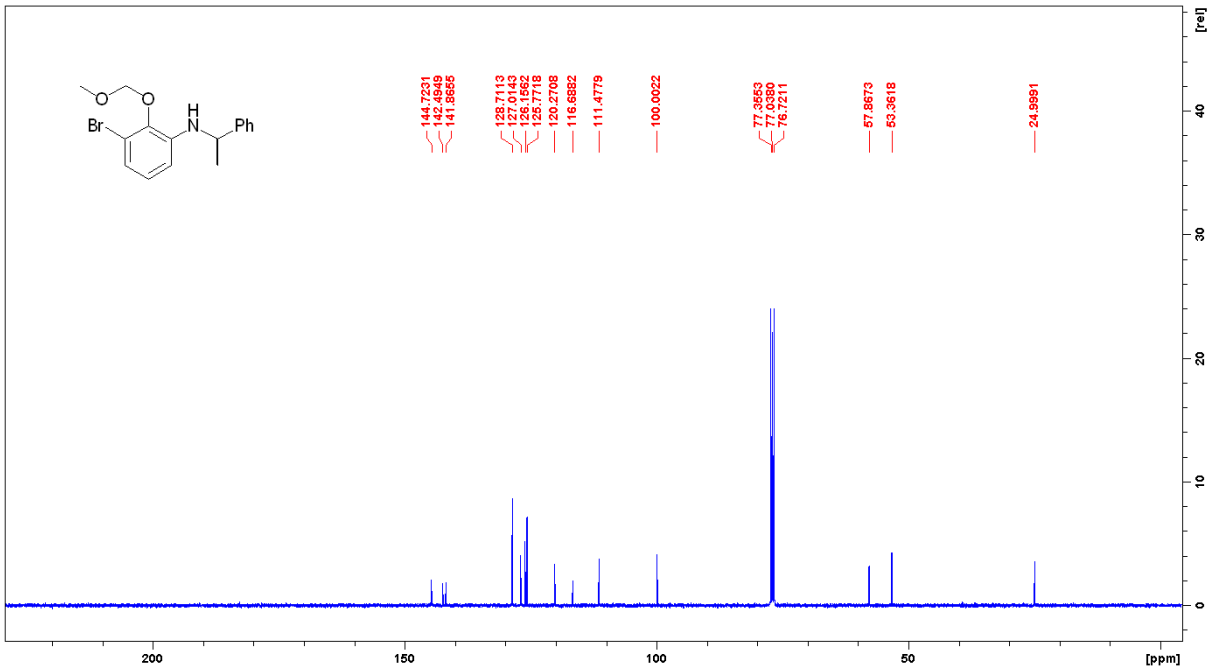

164.25
163.07
145.77
139.98
128.32
126.63
125.79
120.66
116.35
112.82
112.03
65.17
53.84
40.23
40.02
39.81
39.60
39.40
39.19
38.98
27.93
25.12
23.79
Br
N
N
Br
Zn
O
O
Br
NH
HN
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

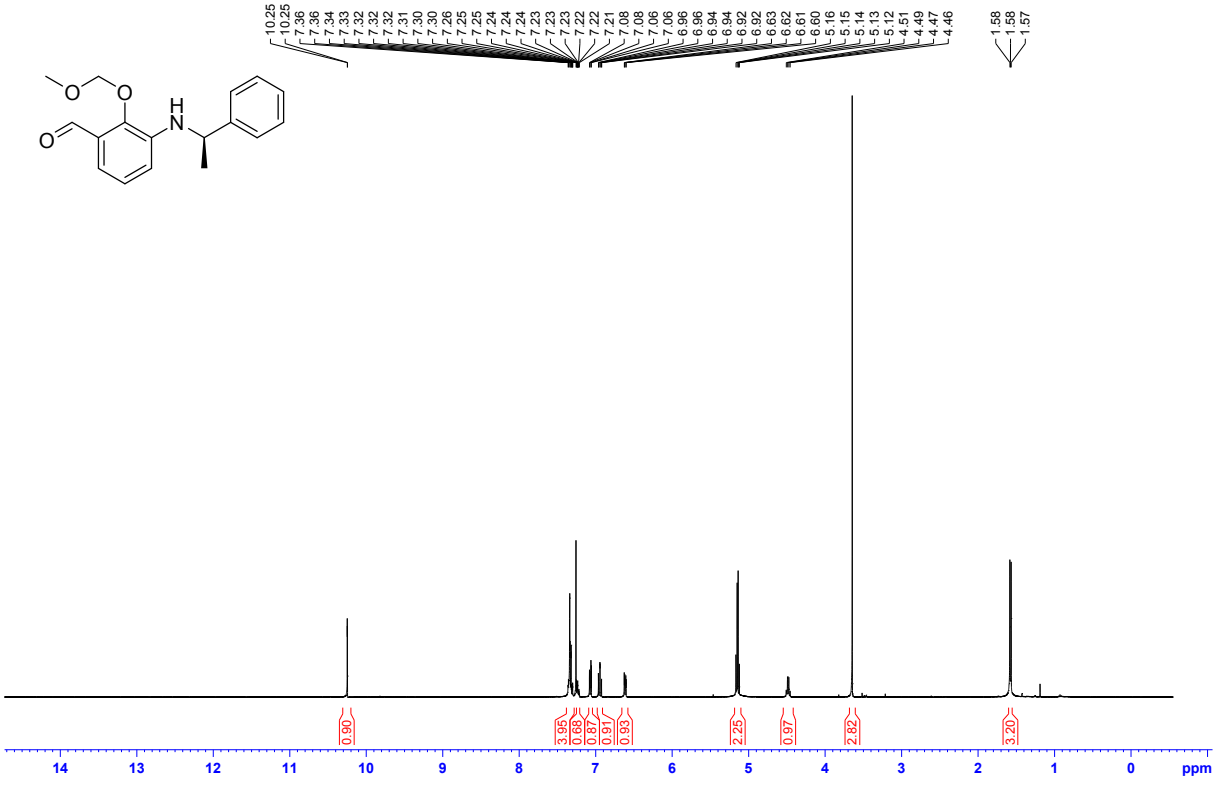

E+05
2.70
Limt: (0)
: (1301) C100 H100
Peak: 1000.00 mmu R+D: -1.0 > 24.5
Mass of (C36.H34.N4.O2.Br4.Zn) = 933.870713621
Abs Abun. .0209487043
gefunden: %
No. exact mass abun. %
1 933.870714 10.673693
2 934.873668 4.532495
3 935.868678 48.640572
4 936.871454 21.283001
5 937.866747 93.351486
6 938.869255 41.843937
7 939.864948 100.000000
8 940.867153 44.979527
9 941.863358 66.724205
10 942.865318 28.834349
11 943.862113 28.205305
12 944.863863 10.992109
13 945.861582 6.625851
14 946.863127 2.152517
15 947.864220 0.546646
16 948.865405 0.110829
17 969.867381 0.017509
18 950.869622 0.002191
19 951.872300 0.000224
20 952.874658 0.000019

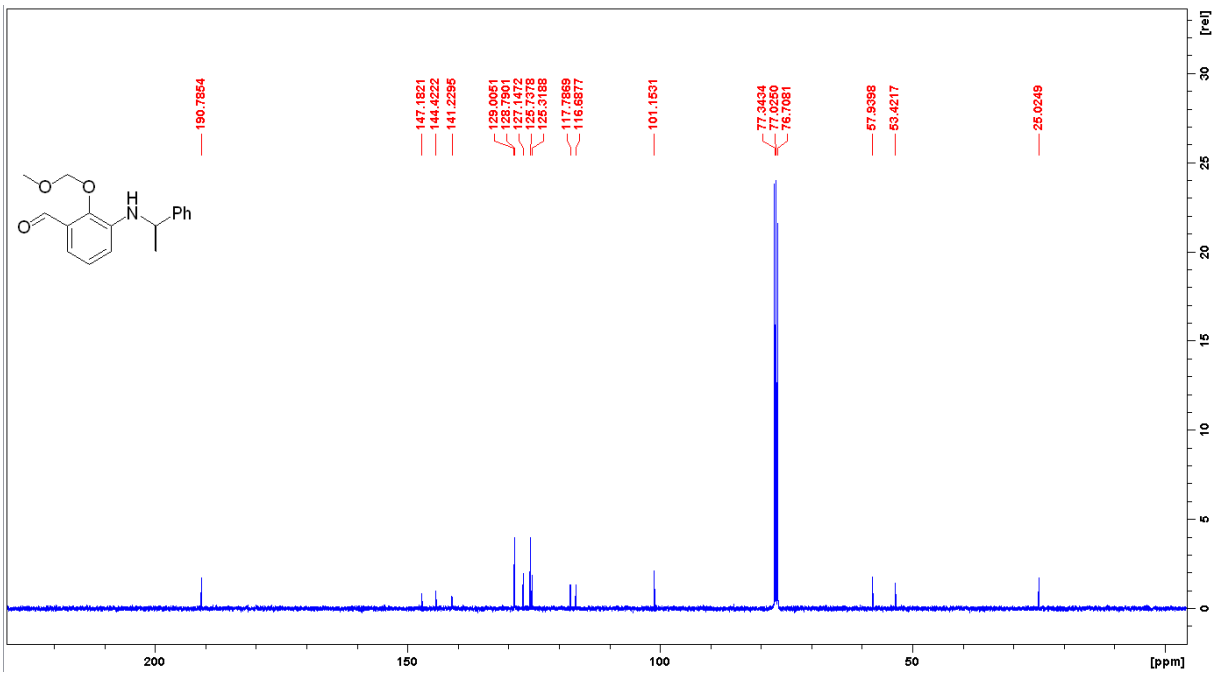

%Transmittance
Wavenumbers (cm-1)

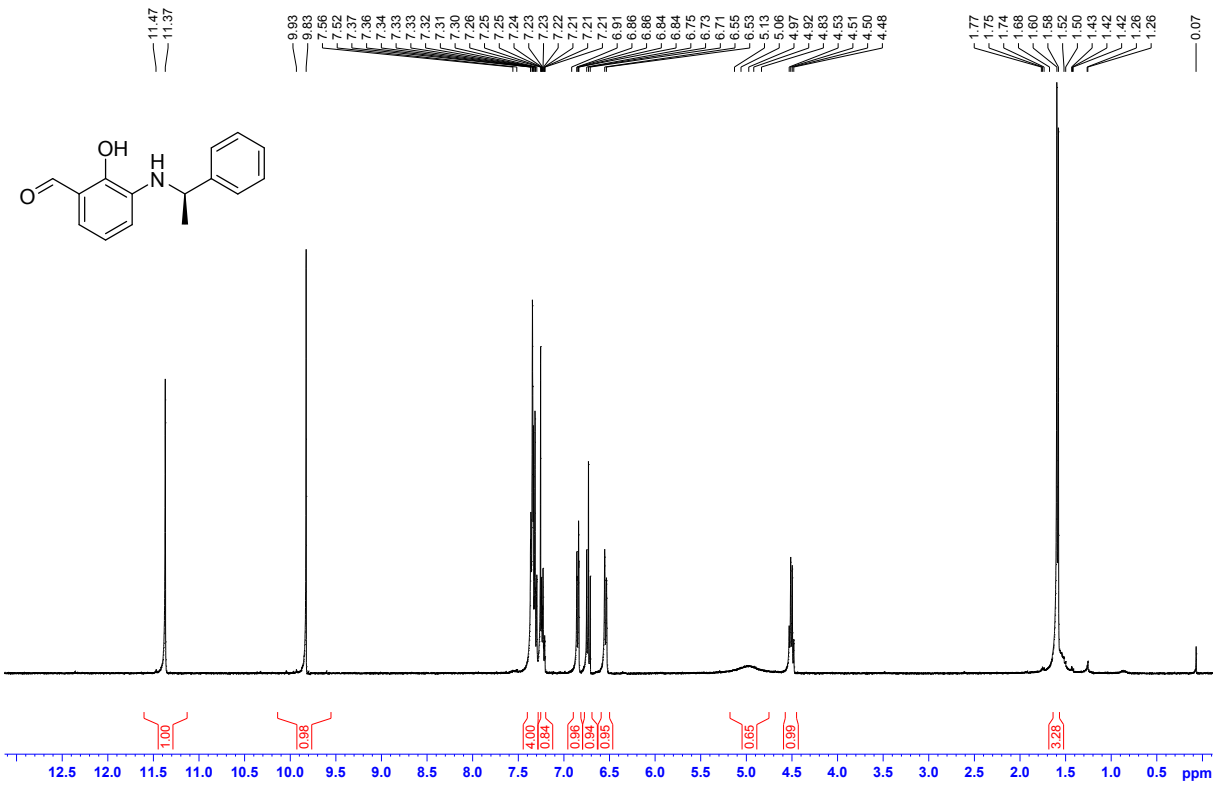

Br
O
O
Br
7.53
7.52
7.51
7.28
7.26
6.89
6.87
6.85
5.18
3.72
1.96
1.00
2.03
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

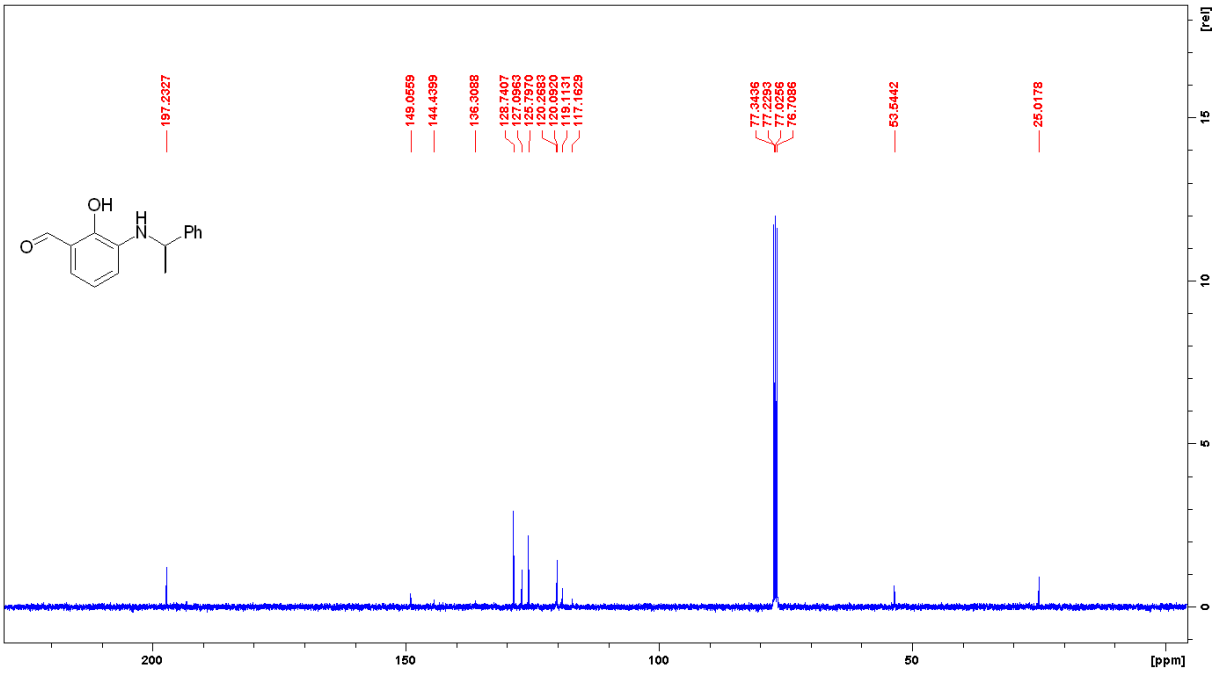

7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
6.80
6.79
6.78
6.78
6.77
6.72
6.72
6.70
6.70
6.68
6.33
6.33
6.31
6.31
5.18
5.17
5.17
5.16
5.16
5.15
5.15
5.14
5.14
5.13
4.48
4.47
4.45
3.69
3.69
3.69
3.68
3.68
3.68
1.58
1.57
1.56
1.56
O
O
H
N
Br
4.08
0.70
1.00
1.03
1.04
2.35
1.06
3.07
3.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

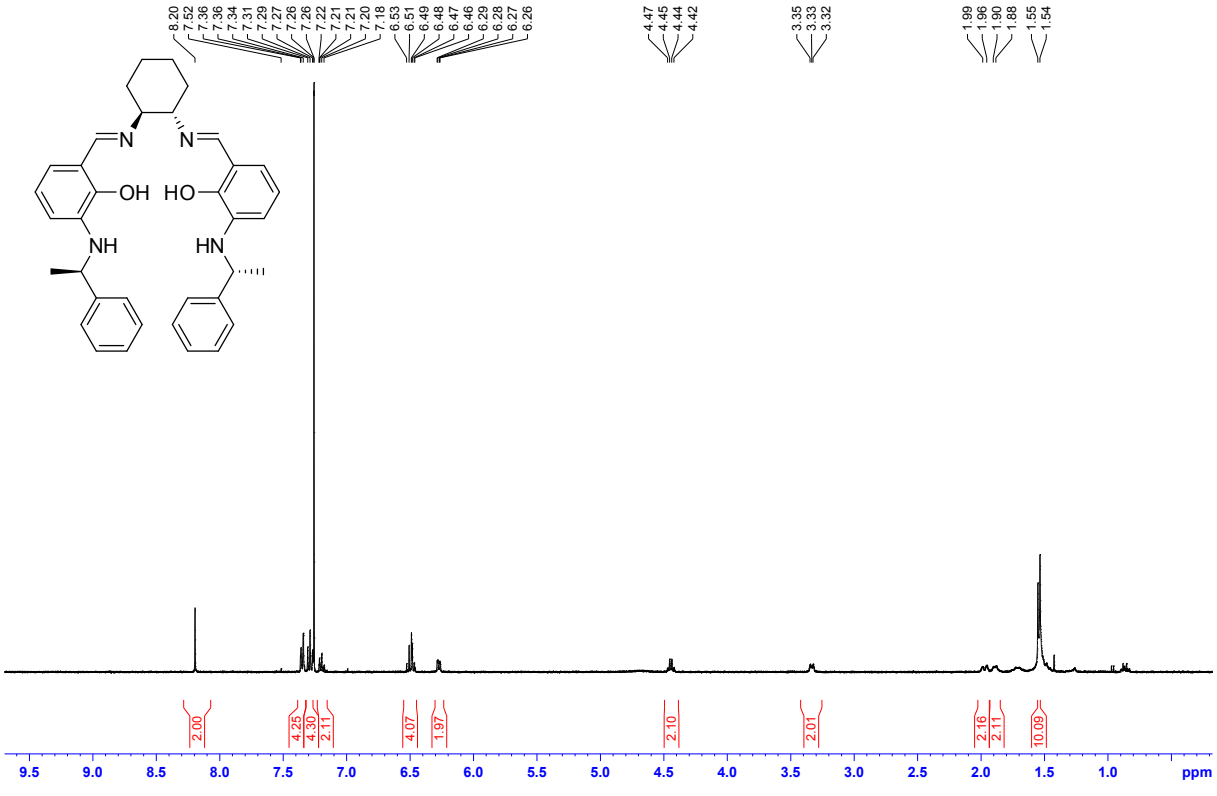

Br
O
O
H
N
Ph
144.7231
142.4949
141.8655
128.7113
127.0143
126.1562
125.7718
120.2708
116.6882
111.4779
100.0022
77.3553
77.0380
76.7211
57.8673
53.3618
24.9991
[rel]
200
150
100
50
[ppm]

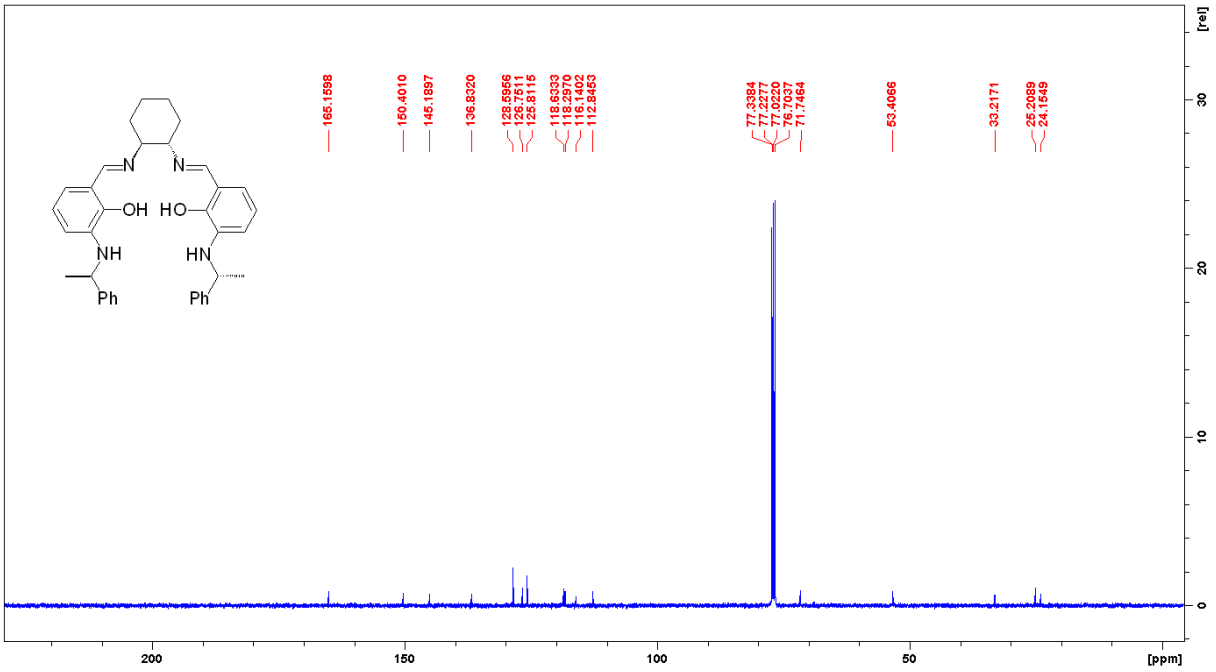

O
O
H
N
O
10.25
10.25
7.36
7.36
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.08
7.08
7.06
7.06
6.96
6.96
6.94
6.94
6.92
6.92
6.63
6.62
6.61
6.60
5.16
5.15
5.14
5.13
5.12
4.51
4.49
4.47
4.46
1.58
1.58
1.57
0.90
3.95
0.68
0.87
0.91
0.93
2.25
0.97
2.82
3.20
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

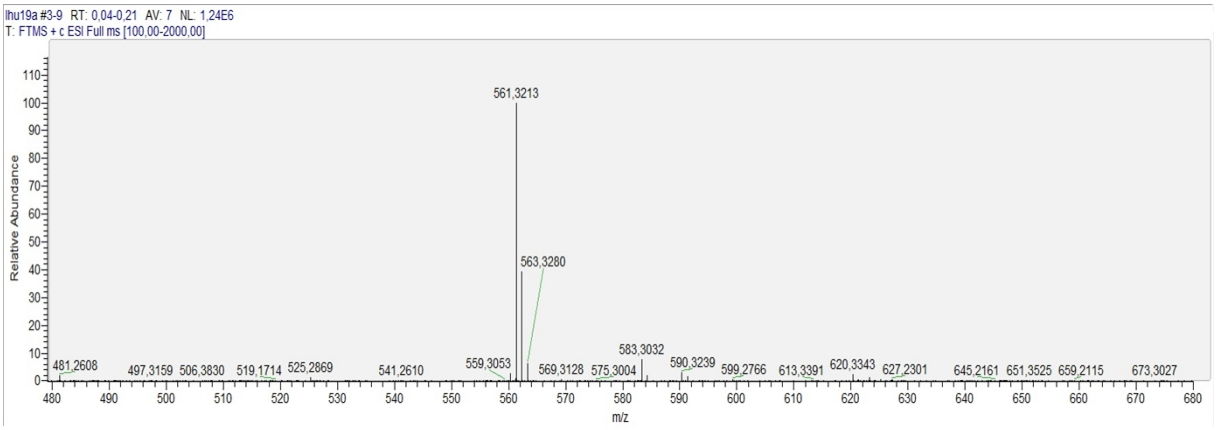

190.7854
147.1821
144.4222
141.2295
129.0051
128.7901
127.1472
125.7378
125.3188
117.7869
116.6877
101.1531
77.3434
77.0250
76.7081
57.5398
53.4217
25.0249
[rel]
[ppm]

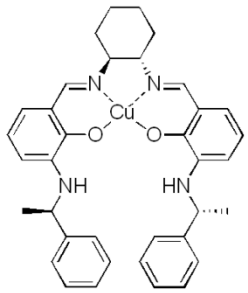

11.47
11.37
9.93
9.83
7.56
7.52
7.37
7.36
7.34
7.33
7.33
7.32
7.31
7.30
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.21
6.91
6.86
6.86
6.84
6.84
6.75
6.73
6.71
6.55
6.53
5.13
5.06
4.97
4.92
4.83
4.53
4.51
4.50
4.48
1.77
1.75
1.74
1.68
1.60
1.58
1.52
1.50
1.43
1.42
1.42
1.26
1.26
0.07
1.00
0.98
4.00
0.84
0.96
0.94
0.95
0.65
0.99
3.28
ppm

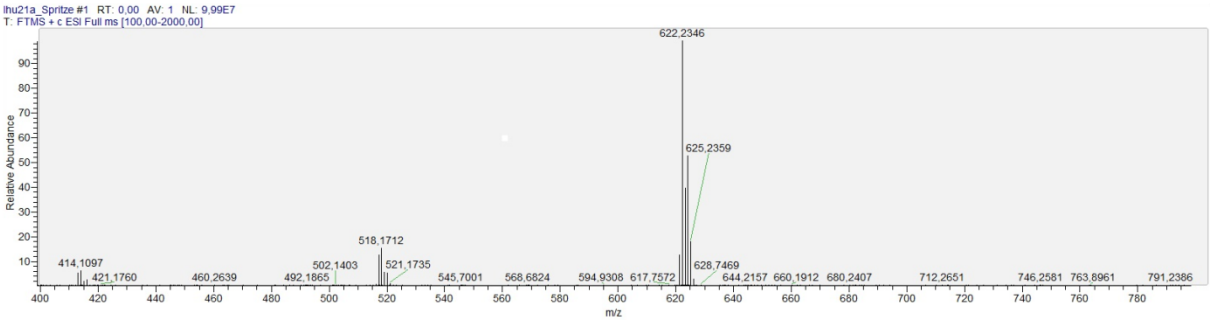

197.2327
149.0559
144.4399
136.3088
128.7407
127.0963
125.7970
120.6853
120.0500
119.1131
117.1629
77.3436
77.2293
77.0256
76.7088
53.5442
25.0178
OH
H
N
Ph
O
[rel]
200
150
100
50
[ppm]

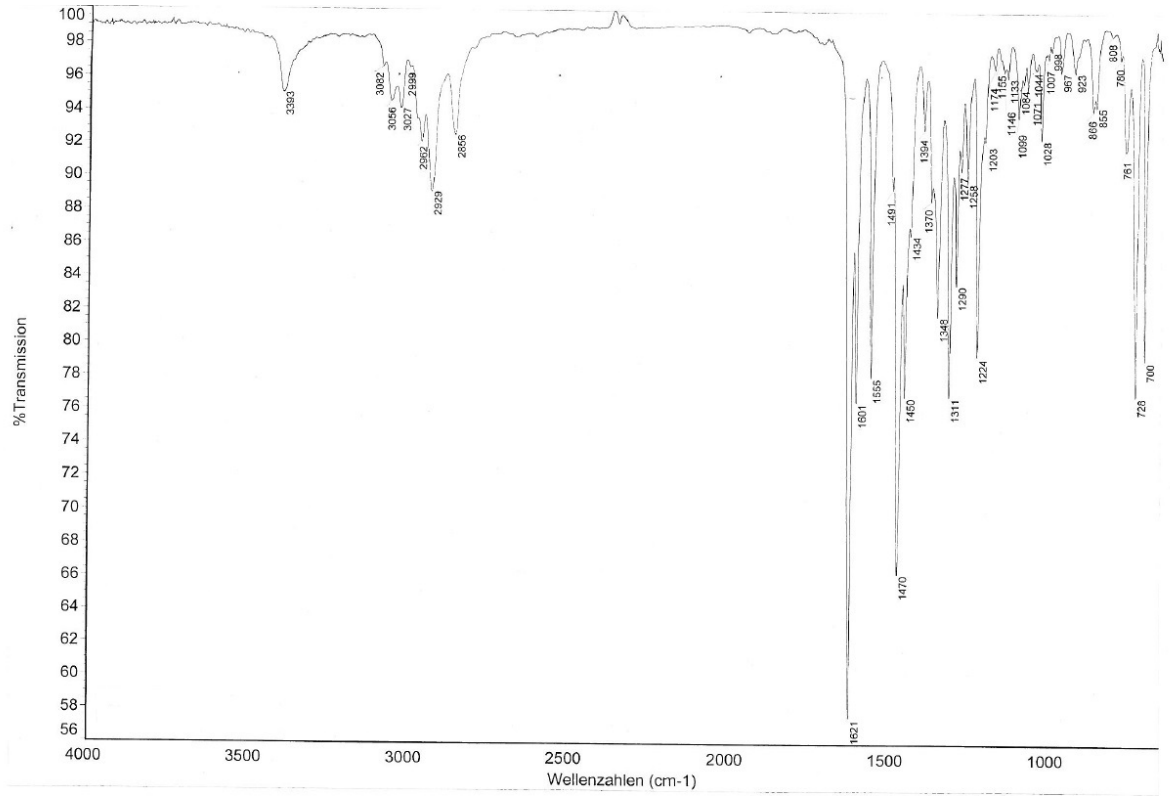

8.20
7.52
7.36
7.34
7.31
7.29
7.27
7.26
7.22
7.21
7.20
7.18
6.53
6.51
6.49
6.48
6.47
6.46
6.29
6.28
6.27
6.26
4.47
4.45
4.44
4.42
3.35
3.33
3.32
1.99
1.96
1.90
1.88
1.55
1.54
N
N
OH
HO
NH
HN
2.00
4.25
4.30
2.11
4.07
1.97
2.10
2.01
2.16
2.11
10.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

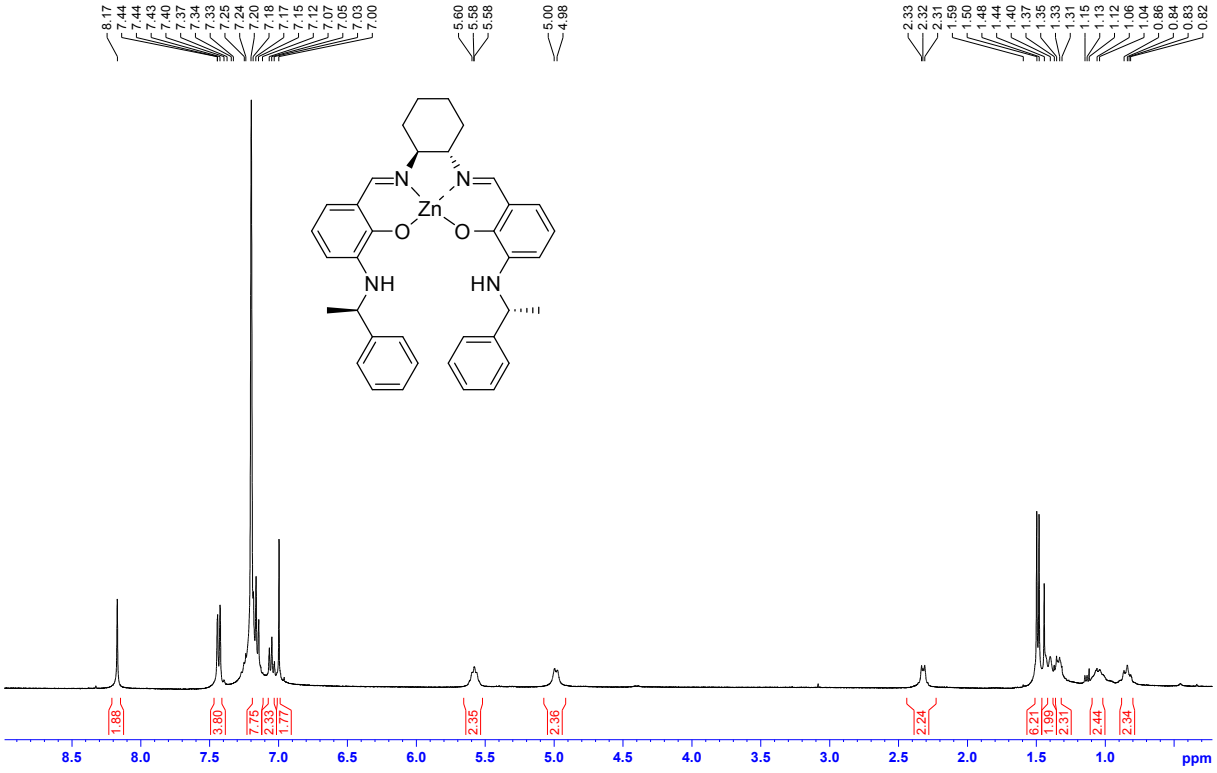

165.1598
150.4010
145.1897
136.8320
128.5966
126.7511
125.8115
118.6333
118.2970
116.1402
112.8453
77.3384
77.2277
77.0220
76.7037
71.7464
53.4066
33.2171
25.2089
24.1549
OH
HO
NH
HN
Ph
Ph
200
150
100
50
[ppm]

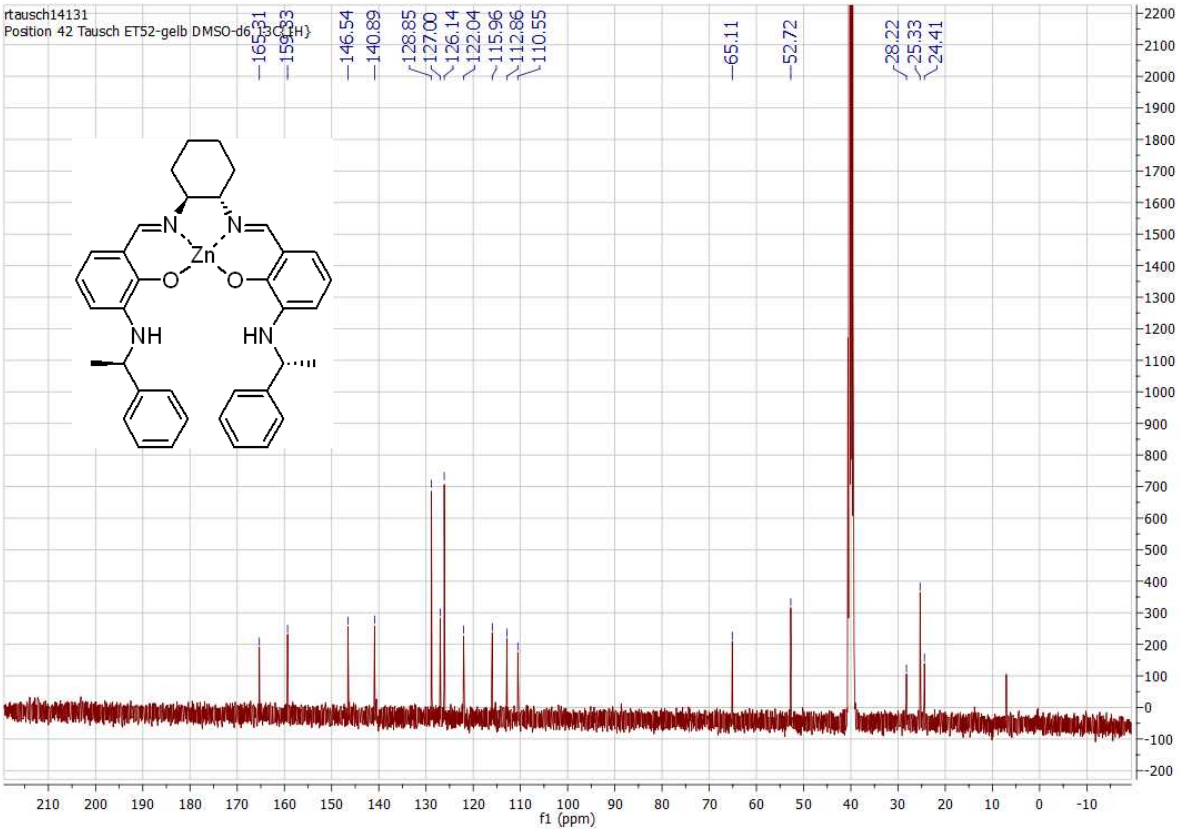

lhu19a #3-9 RT: 0,04-0,21 AV: 7 NL: 1,24E6
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
561,3213
563,3280
481,2608
497,3159
506,3830
519,1714
525,2869
541,2610
559,3053
569,3128
575,3004
583,3032
590,3239
599,2766
613,3391
620,3343
627,2301
645,2161
651,3525
659,2115
673,3027

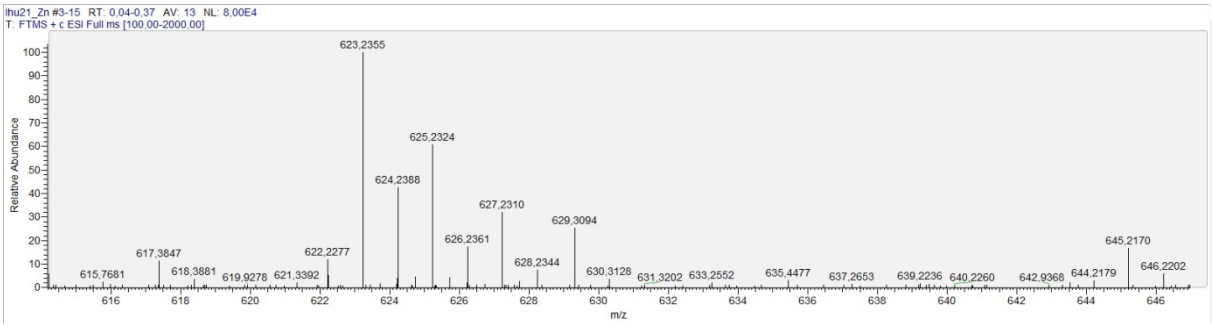

N
N
Cu
O
O
NH
HN

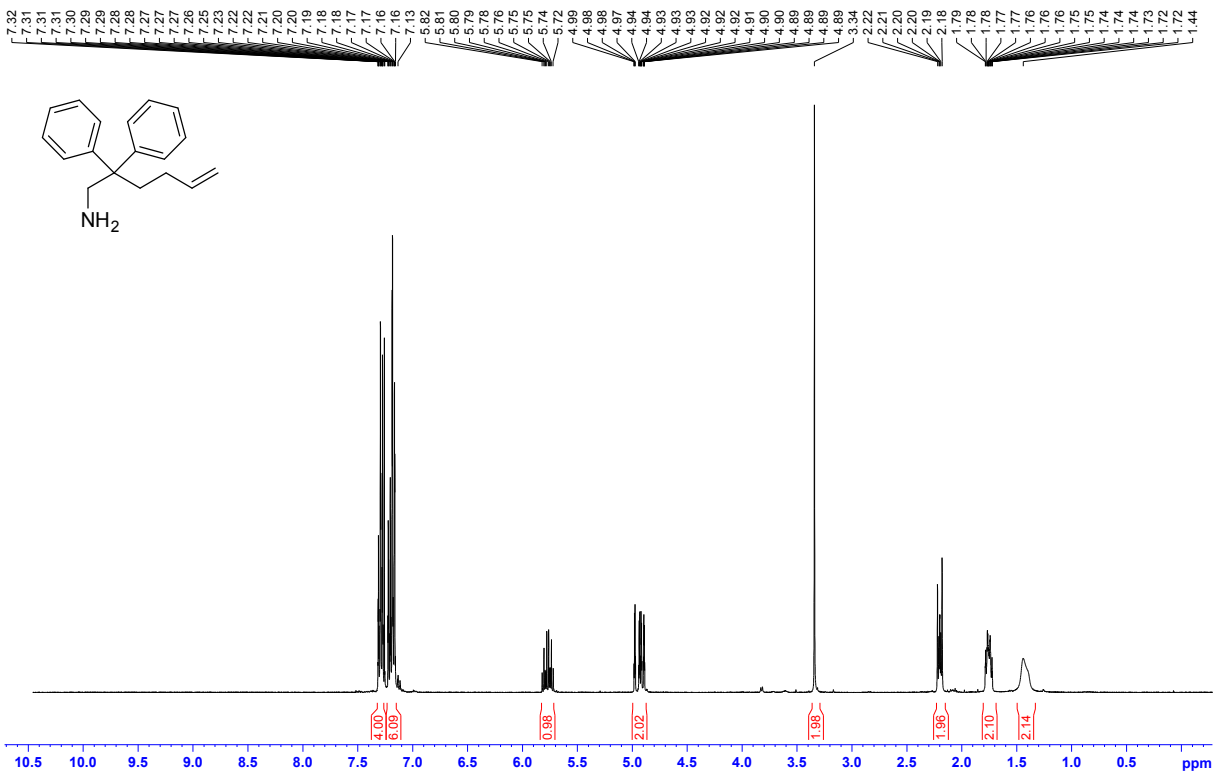

lhu21a_Spritze #1 RT: 0,00 AV: 1 NL: 9,99E7
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
622,2346
625,2359
518,1712
414,1097
421,1760
460,2639
492,1865
502,1403
521,1735
545,7001
568,6824
594,9308
617,7572
628,7469
644,2157
660,1912
680,2407
712,2651
746,2581
763,8961
791,2386

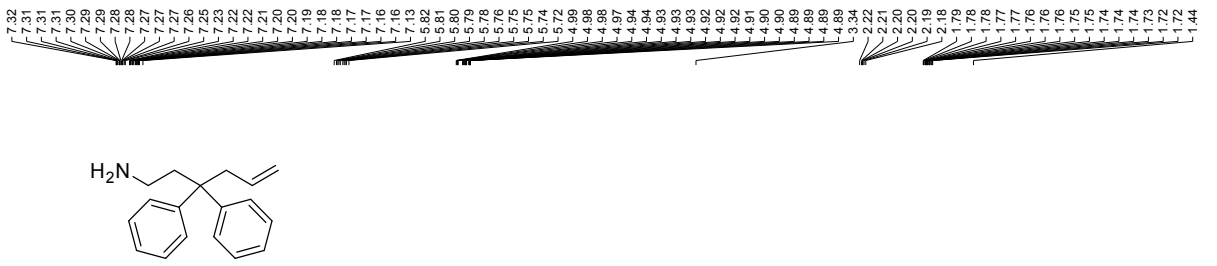

%Transmission
Wellenzahlen (cm-1)
3393
3082
3056
3027
2999
2962
2929
2855
1621
1601
1555
1491
1470
1450
1434
1394
1370
1348
1311
1290
1272
1252
1224
1203
1174
1155
1146
1133
1084
1071
1044
1028
1007
998
967
923
855
808
780
761
728
700

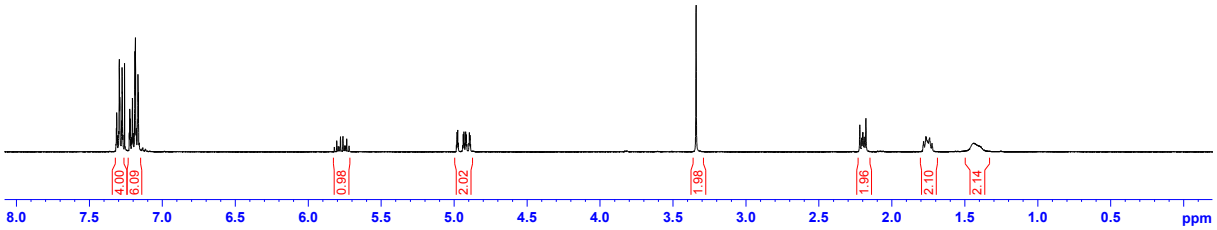

8.17
7.44
7.44
7.43
7.40
7.37
7.34
7.33
7.25
7.24
7.20
7.18
7.17
7.15
7.12
7.07
7.05
7.03
7.00
5.60
5.58
5.58
5.00
4.98
2.33
2.32
2.31
1.59
1.50
1.48
1.44
1.40
1.37
1.35
1.33
1.31
1.15
1.13
1.12
1.06
1.04
0.86
0.84
0.83
0.82
N
N
Zn
O
O
NH
HN
1.88
3.80
7.75
2.33
1.77
2.35
2.36
2.24
6.21
1.99
2.31
2.44
2.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

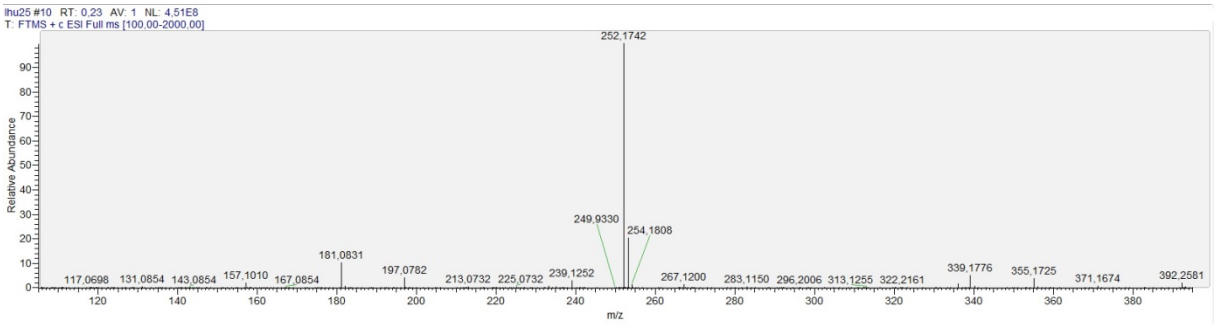

rtausch14131
Position 42 Tausch ET52-gelb DMSO-d6 {13C{1H}
165.31
159.33
146.54
140.89
128.85
127.00
126.14
122.04
115.96
112.86
110.55
65.11
52.72
28.22
25.33
24.41
N
N
Zn
O
O
NH
HN
f1 (ppm)

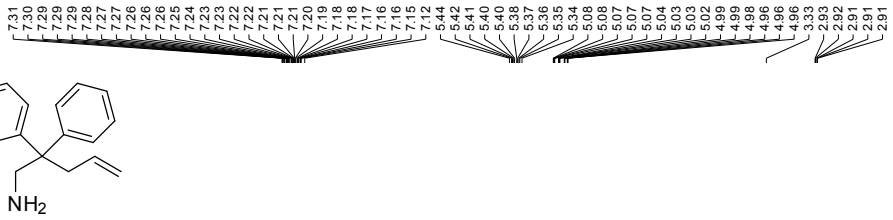

lhu21_Zn #3-15 RT: 0,04-0,37 AV: 13 NL: 8,00E4
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
623,2355
625,2324
624,2388
627,2310
629,3094
626,2361
628,2344
617,3847
622,2277
615,7681
618,3881
619,9278
621,3392
630,3128
631,3202
633,2552
635,4477
637,2653
639,2236
640,2260
642,9368
644,2179
645,2170
646,2202


NH2
4.00
6.09
0.98
2.02
1.98
1.96
2.10
2.14
ppm

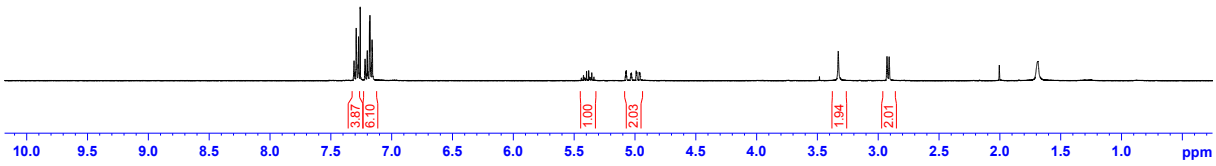

H2N

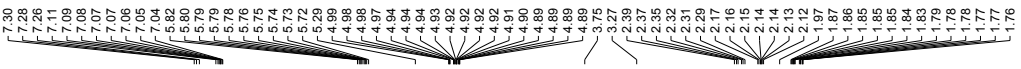

4.00
6.09
0.98
2.02
1.98
1.96
2.10
2.14
ppm

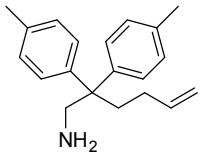

lhu25 #10 RT: 0,23 AV: 1 NL: 4,51E8
T: FTMS + c ESI Full ms [100,00-2000,00]
Relative Abundance
m/z
252,1742
249,9330
254,1808
181,0831
117,0698
131,0854
143,0854
157,1010
167,0854
197,0782
213,0732
225,0732
239,1252
267,1200
283,1150
296,2006
313,1255
322,2161
339,1776
355,1725
371,1674
392,2581

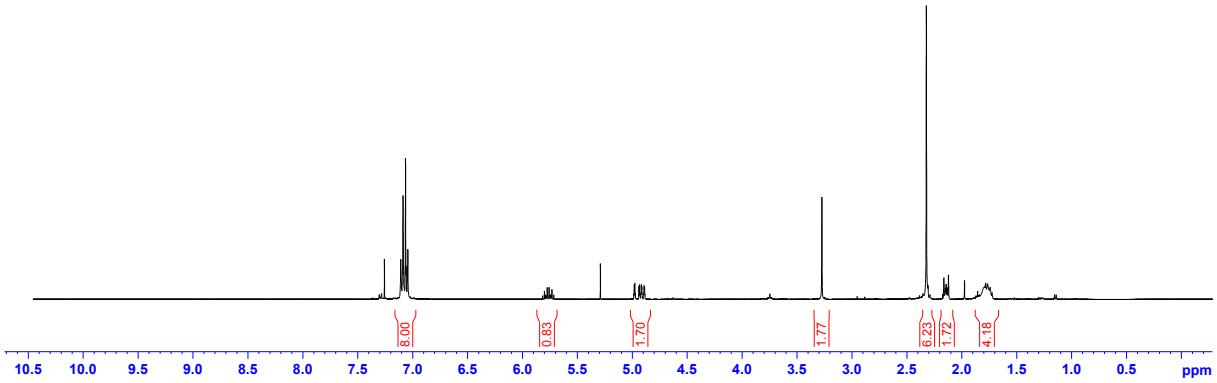

7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.21 7.20 7.19 7.18 7.18 7.17 7.16 7.16 7.15 7.12
5.44 5.42 5.41 5.40 5.40 5.38 5.37 5.36 5.35 5.34 5.08 5.08 5.07 5.07 5.07 5.04 5.03 5.03 5.02 4.99 4.99 4.98 4.96 4.96 4.96
3.33 2.93 2.92 2.91 2.91 2.91

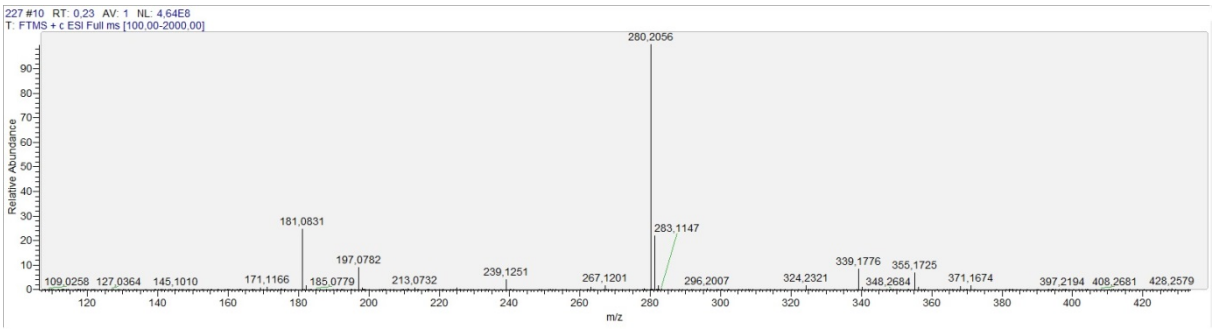
NH2

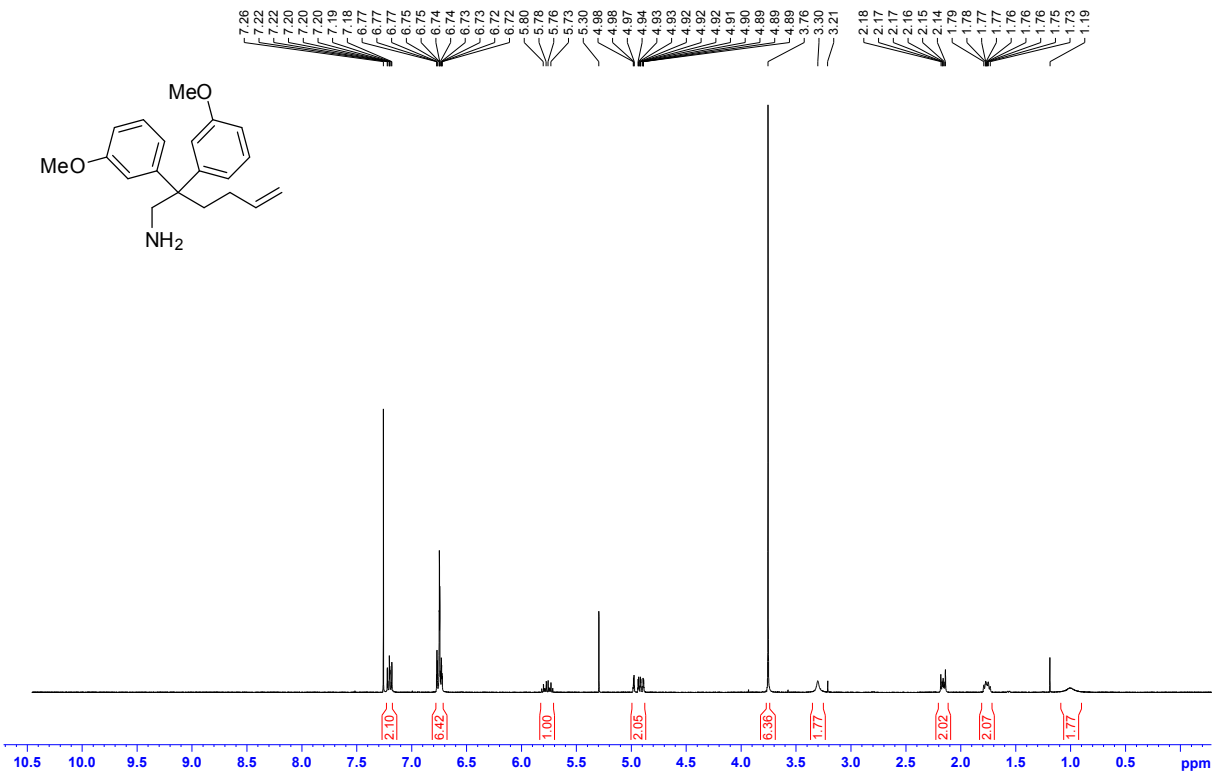

3.87
6.10
1.00
2.03
1.94
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

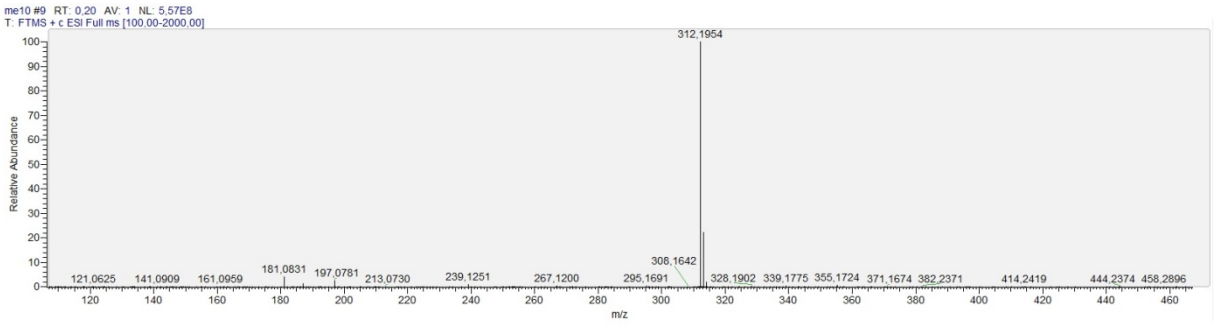

7.30
7.28
7.26
7.11
7.09
7.08
7.07
7.07
7.06
7.05
7.04
5.82
5.80
5.79
5.79
5.78
5.76
5.75
5.74
5.73
5.72
5.29
4.99
4.98
4.98
4.97
4.94
4.94
4.94
4.93
4.92
4.92
4.92
4.91
4.90
4.89
4.89
4.89
4.89
3.75
3.27
2.39
2.37
2.35
2.32
2.31
2.29
2.17
2.16
2.15
2.14
2.14
2.13
2.12
1.97
1.87
1.86
1.85
1.85
1.85
1.84
1.83
1.79
1.78
1.78
1.77
1.77
1.76

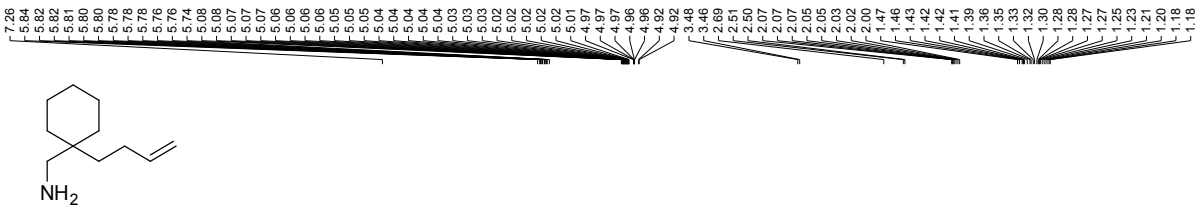

NH2


8.00
0.83
1.70
1.77
6.23
1.72
4.18
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

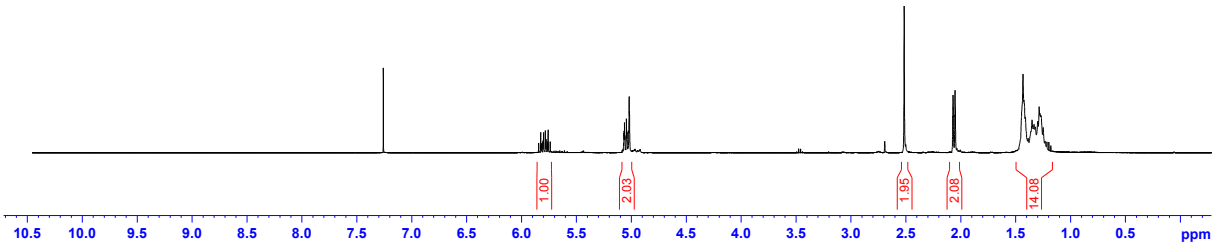

227 #10 RT: 0.23 AV: 1 NL: 4.64E8
T: FTMS + c ESI Full ms [100.00-2000.00]
Relative Abundance
m/z
280.2056
283.1147
181.0831
197.0782
109.0258
127.0364
145.1010
171.1166
185.0779
213.0732
239.1251
267.1201
296.2007
324.2321
339.1776
348.2684
355.1725
371.1674
397.2194
408.2681
428.2579

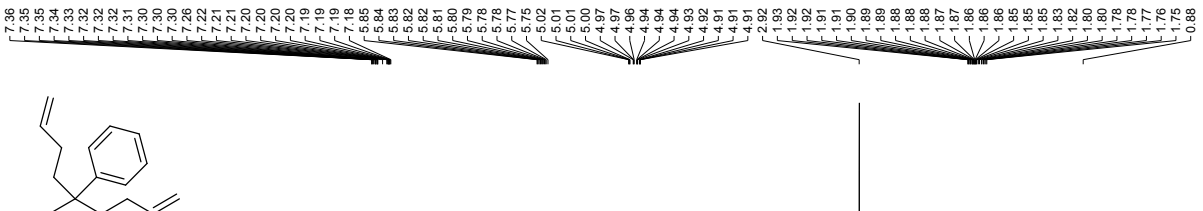

7.26 7.22 7.22 7.20 7.20 7.20 7.19 7.18 6.77 6.77 6.77 6.75 6.75 6.74 6.74 6.73 6.73 6.72 6.72 5.80 5.78 5.76 5.73 5.30 4.98 4.98 4.97 4.94 4.93 4.93 4.92 4.92 4.92 4.91 4.90 4.89 4.89 4.89 3.76 3.30 3.21 2.18 2.17 2.17 2.16 2.15 2.14 1.79 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.73 1.19
MeO
MeO
NH2
2.10 6.42 1.00 2.05 6.36 1.77 2.02 2.07 1.77
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


me10 #9 RT: 0.20 AV: 1 NL: 5.57E8
T: FTMS + c ESI Full ms [100.00-2000.00]
Relative Abundance
m/z
312.1954
308.1642
121.0625 141.0909 161.0959 181.0831 197.0781 213.0730 239.1251 267.1200 295.1691 328.1902 339.1775 355.1724 371.1674 382.2371 414.2419 444.2374 458.2896



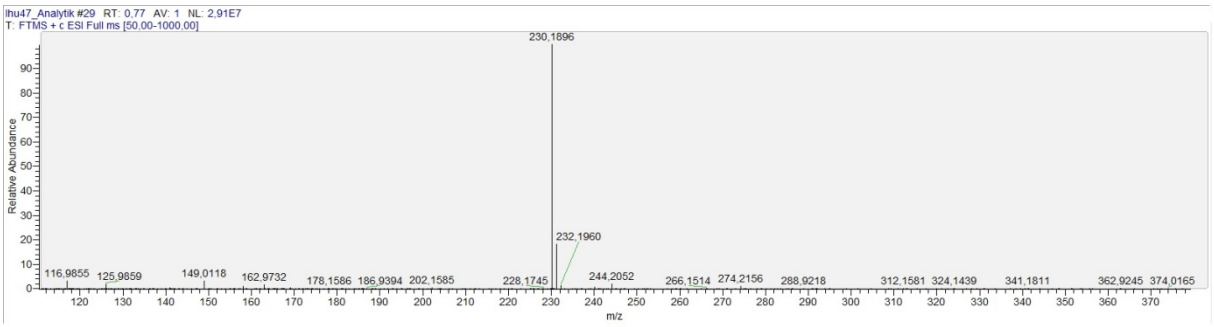
NH2

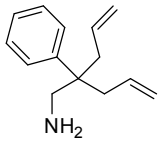

1.00
2.03
1.95
2.08
14.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

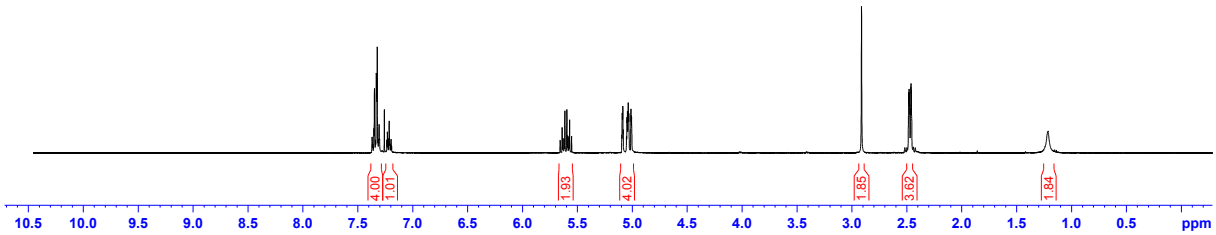


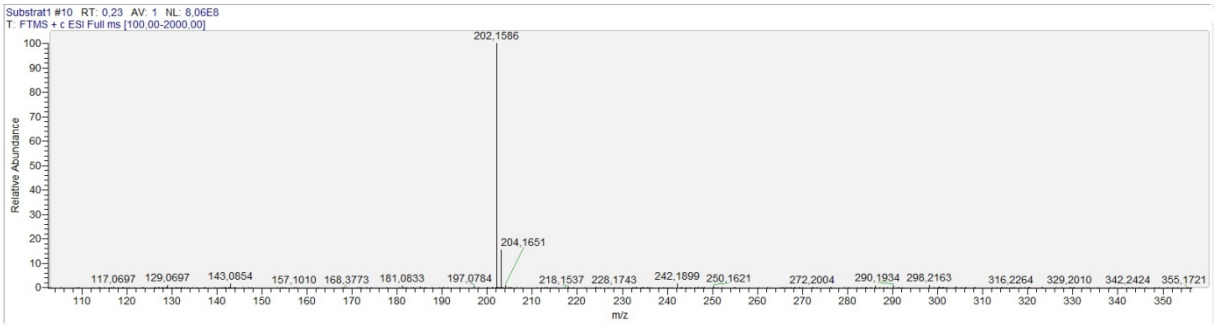
NH2

4.37
1.00
2.00
4.12
2.10
8.72
2.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

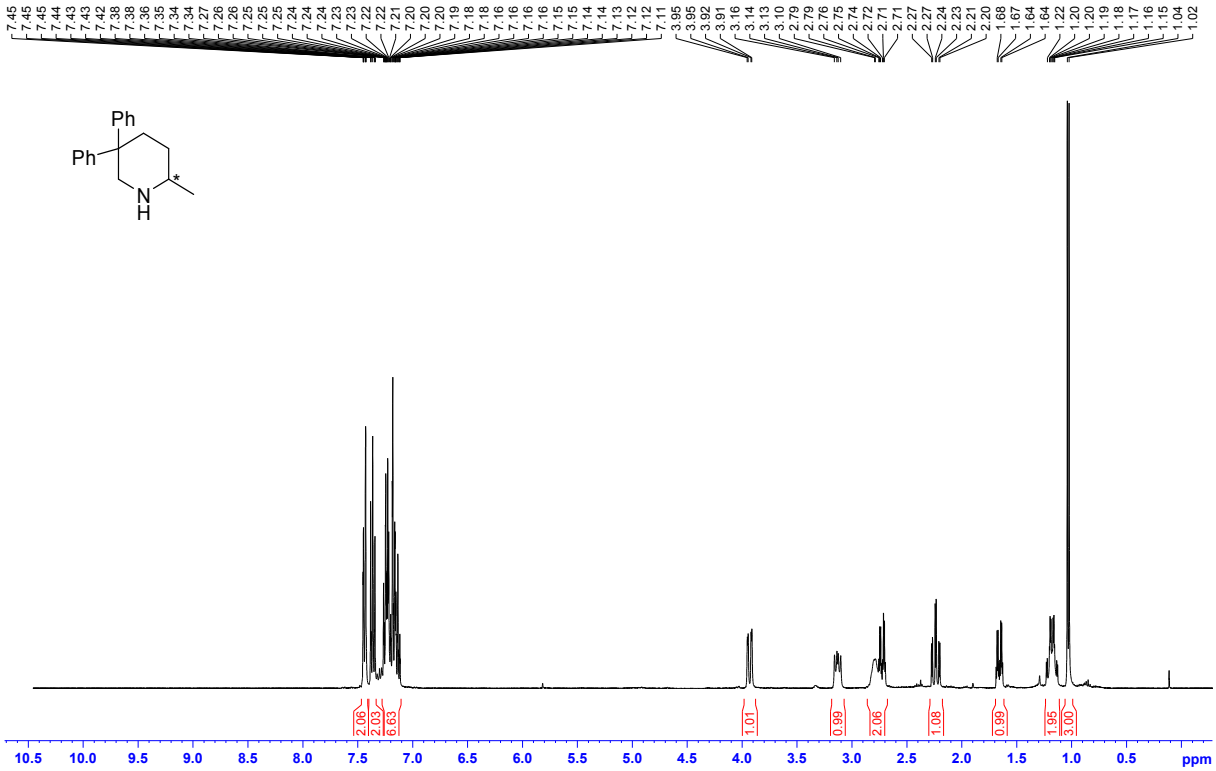

lhu47_Analytik #29 RT: 0,77 AV: 1 NL: 2,91E7
T: FTMS + c ESI Full ms [50,00-1000,00]
230,1896
232,1960
Relative Abundance
m/z

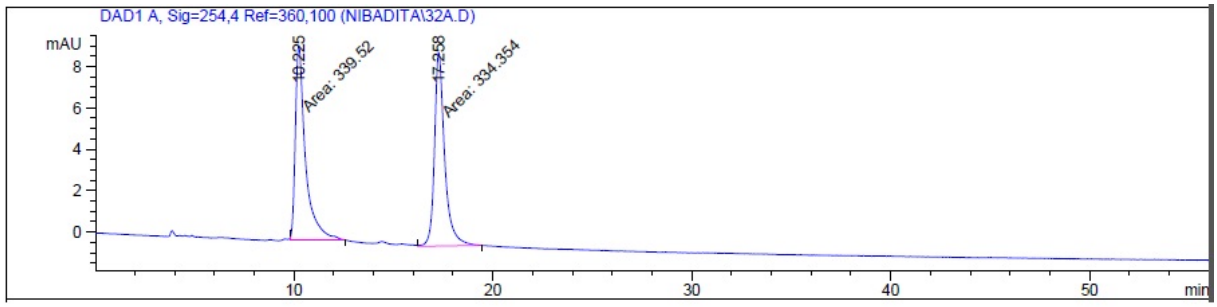

NH2


4.00
1.01
1.93
4.02
1.85
3.62
1.84
ppm


Substrat1 #10 RT: 0,23 AV: 1 NL: 8,06E8
T: FTMS + c ESI Full ms [100,00-2000,00]
202,1586
204,1651
Relative Abundance
m/z

Products

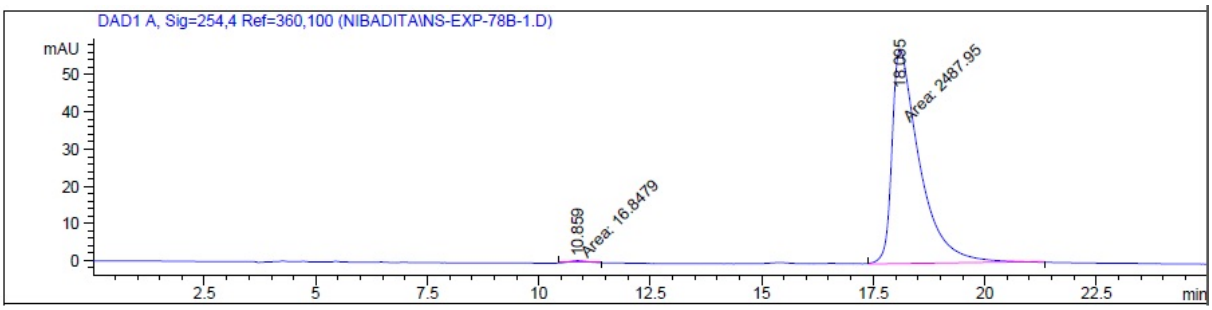




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.225	MM	0.6010	339.52017	9.41541	50.3833
2	17.258	MM	0.5969	334.35437	9.33530	49.6167
Totals :				673.87454	18.75071	

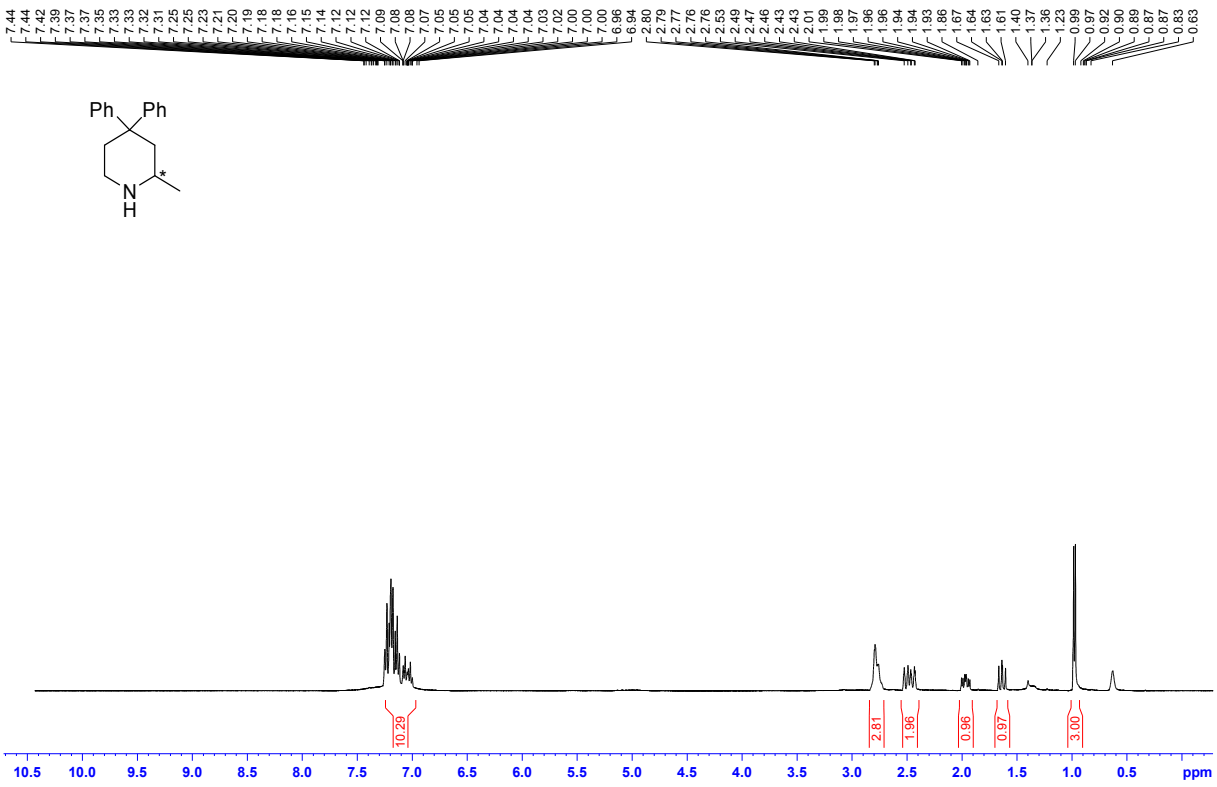
Figure S1: Racemic sample.

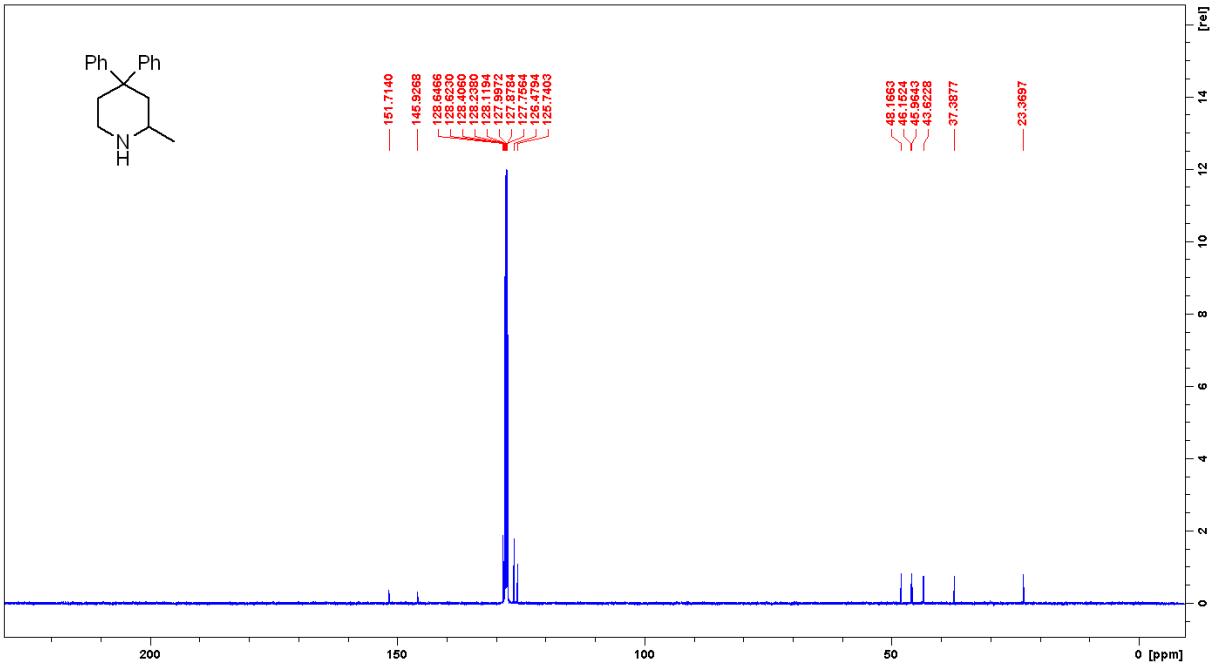


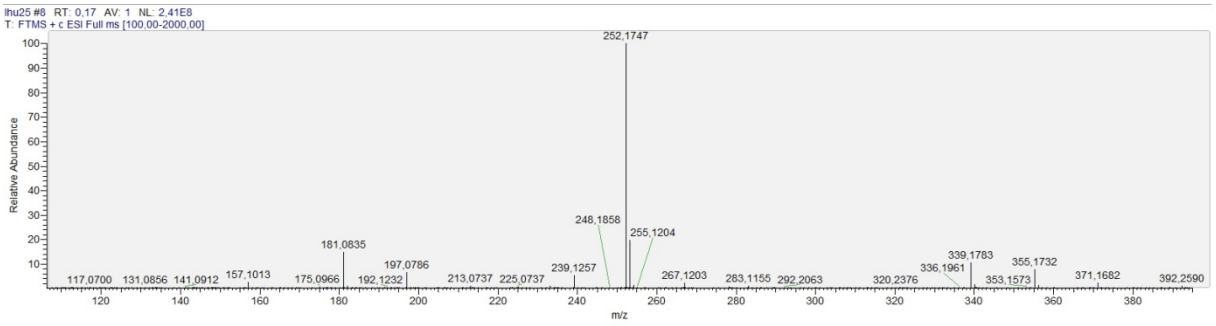
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

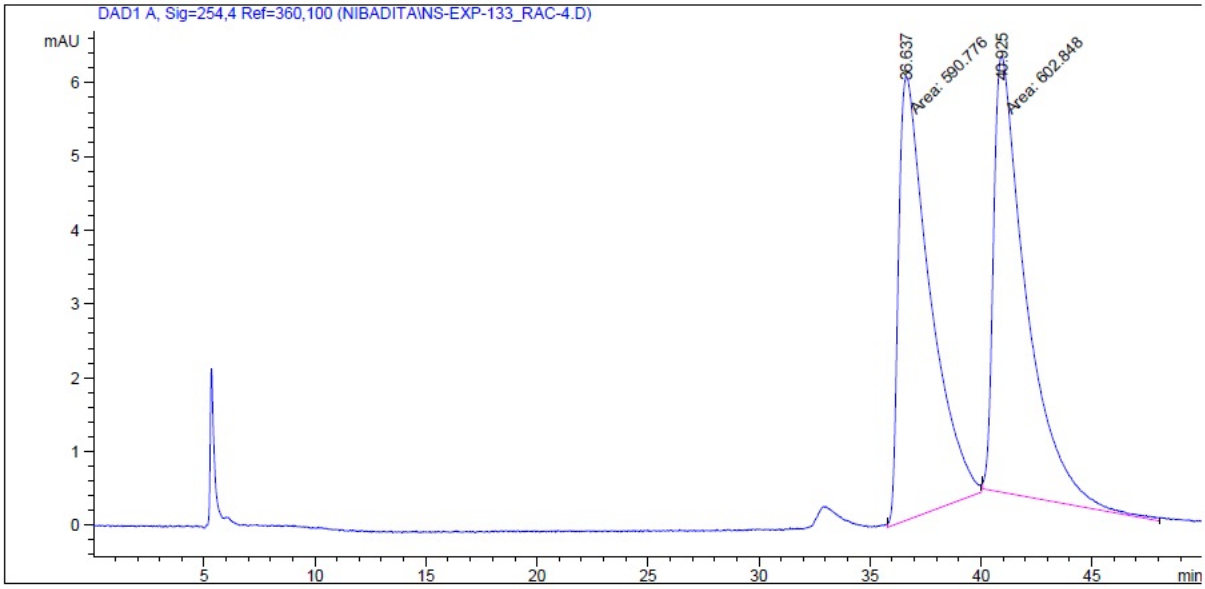
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.859	MM	0.4677	16.84792	6.00319e-1	0.6726
2	18.095	MM	0.7206	2487.95312	57.54667	99.3274
Totals :				2504.80104	58.14698	

Figure S2: Enantiomerically enriched sample.




Ph
Ph
N
H
151.7140
145.9268
128.6466
128.6230
128.4060
128.2380
128.1194
127.9972
127.8784
127.7564
126.4794
125.7403
48.1663
46.1524
45.9643
43.6228
37.3877
23.3697
[rel]
200
150
100
50
0 [ppm]

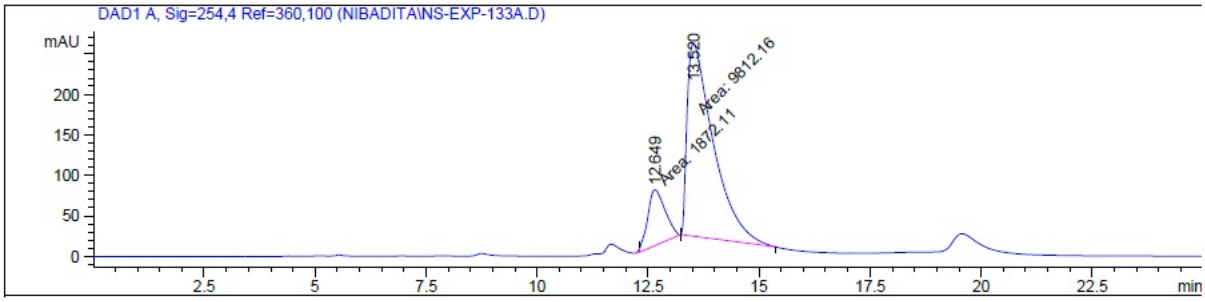

lhu25 #8 RT: 0.17 AV: 1 NL: 2.41E8
T: FTMS + c ESI Full ms [100.00-2000.00]
Relative Abundance
m/z
252.1747
248.1858
255.1204
181.0835
197.0786
239.1257
339.1783
336.1961
355.1732
117.0700
131.0856
141.0912
157.1013
175.0966
192.1232
213.0737
225.0737
267.1203
283.1155
292.2063
320.2376
353.1573
371.1682
392.2590



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.637	MM	1.6351	590.77600	6.02179	49.4943
2	40.925	MM	1.6980	602.84839	5.91730	50.5057
Totals :				1193.62439	11.93909	

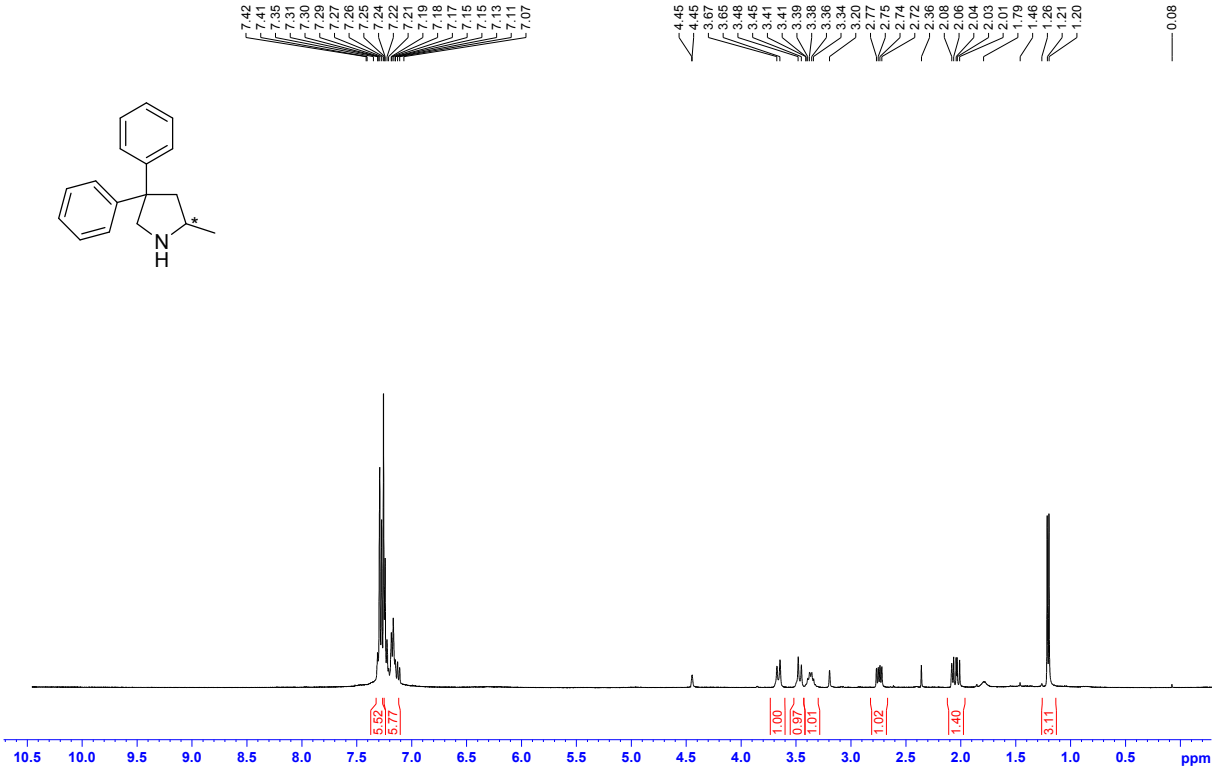
Figure S3:Racemic sample.

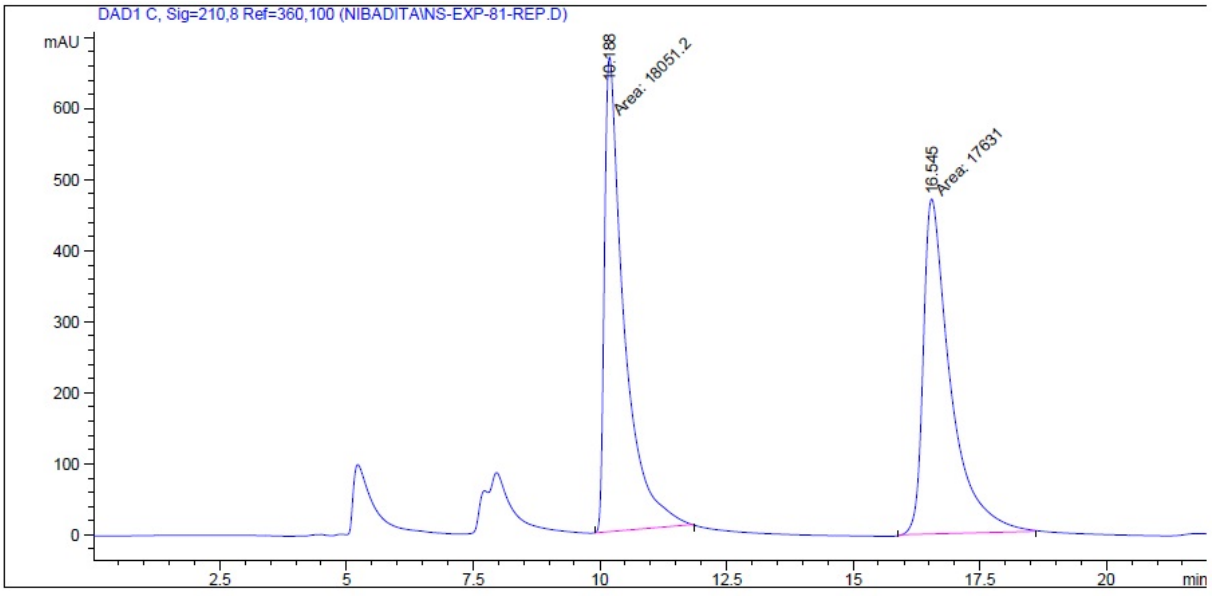


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.649	MM	0.4519	1872.10547	69.04920	16.0225
2	13.520	MM	0.6868	9812.15918	238.09744	83.9775
Totals :				1.16843e4	307.14664	

Figure S4: Enantiomerically enriched sample.

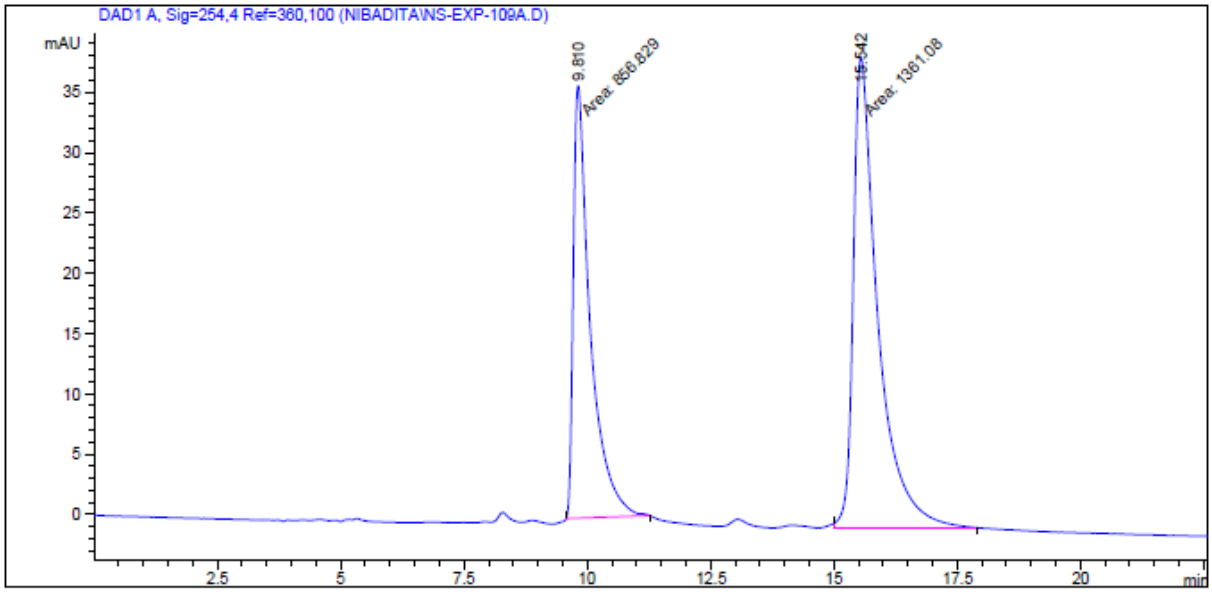




Signal 1: DAD1 C, Sig=210,8 Ref=360,100

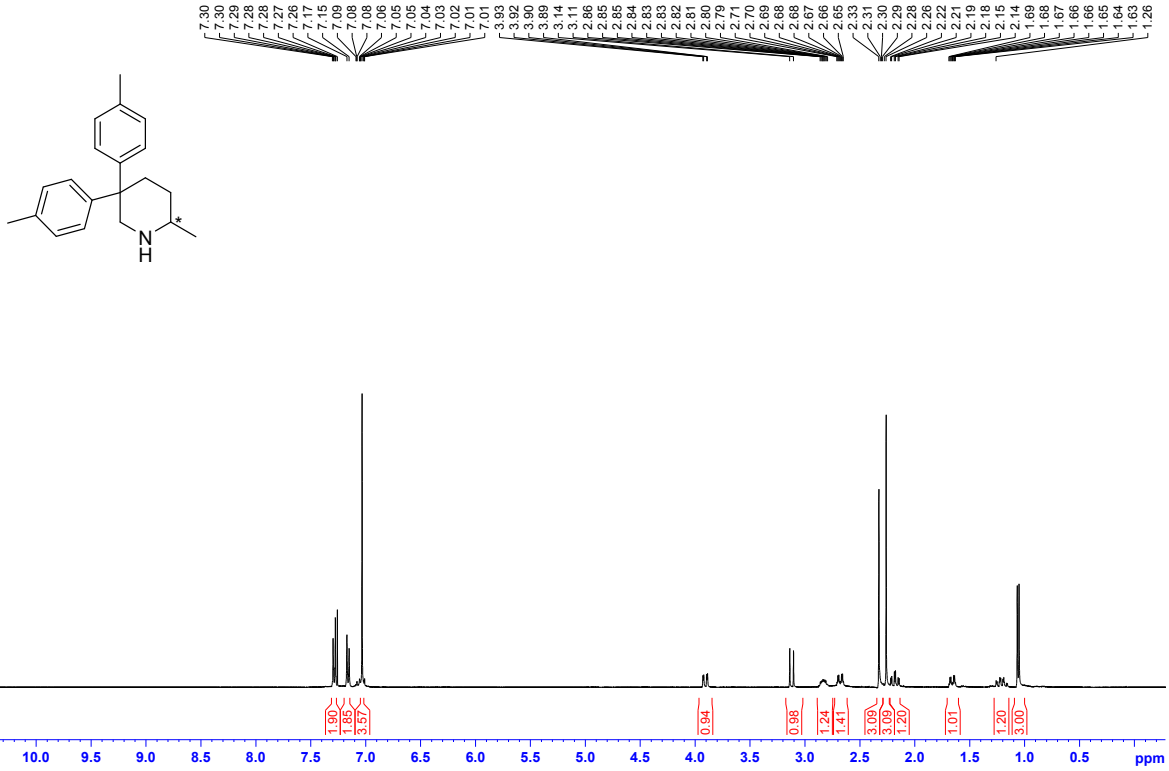
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.188	MM	0.4499	1.80512e4	668.67944	50.5887
2	16.545	MM	0.6230	1.76310e4	471.68631	49.4113
Totals :				3.56822e4	1140.36575	

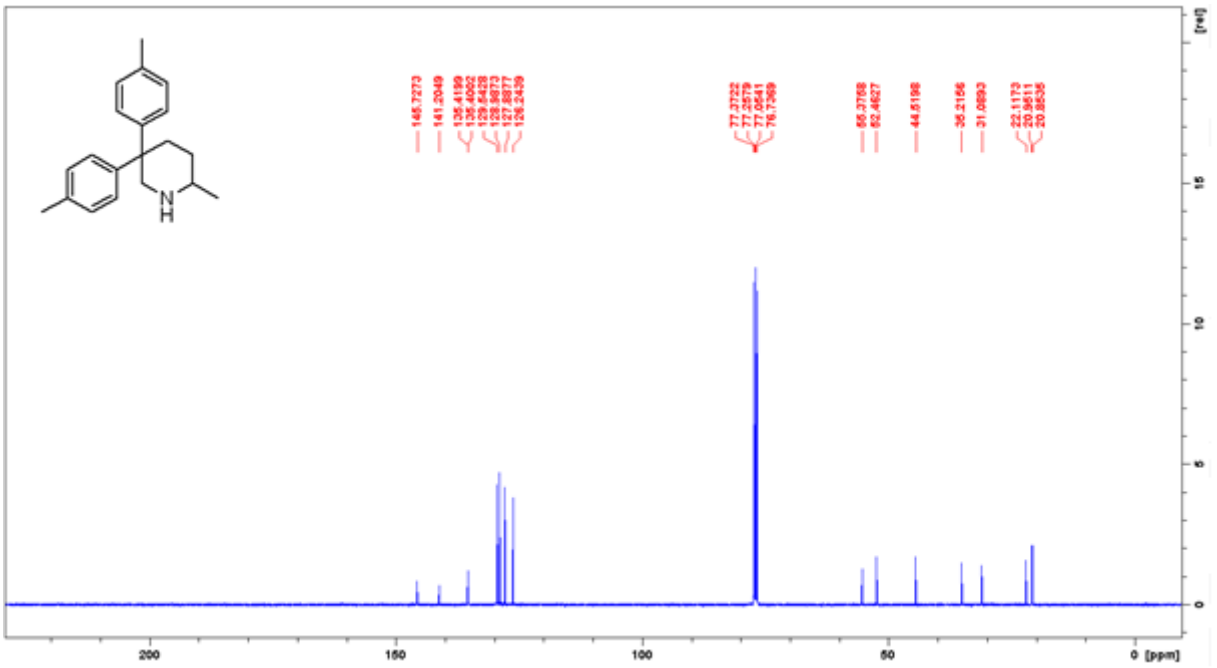
Figure S5: Racemic sample.

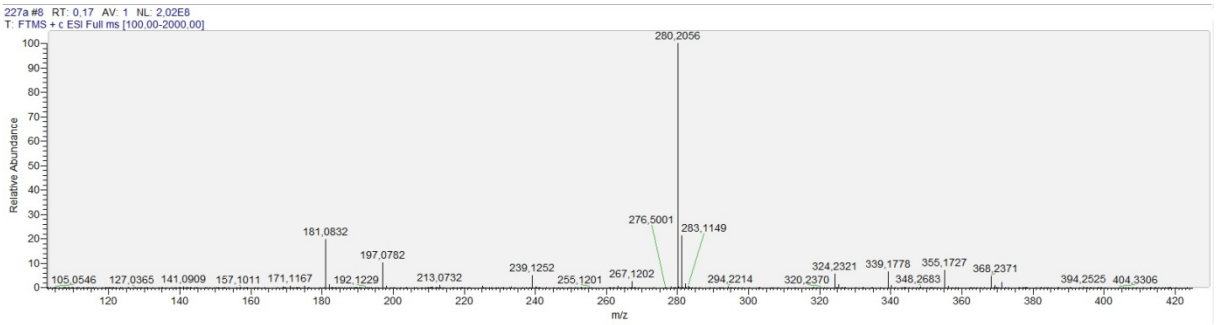


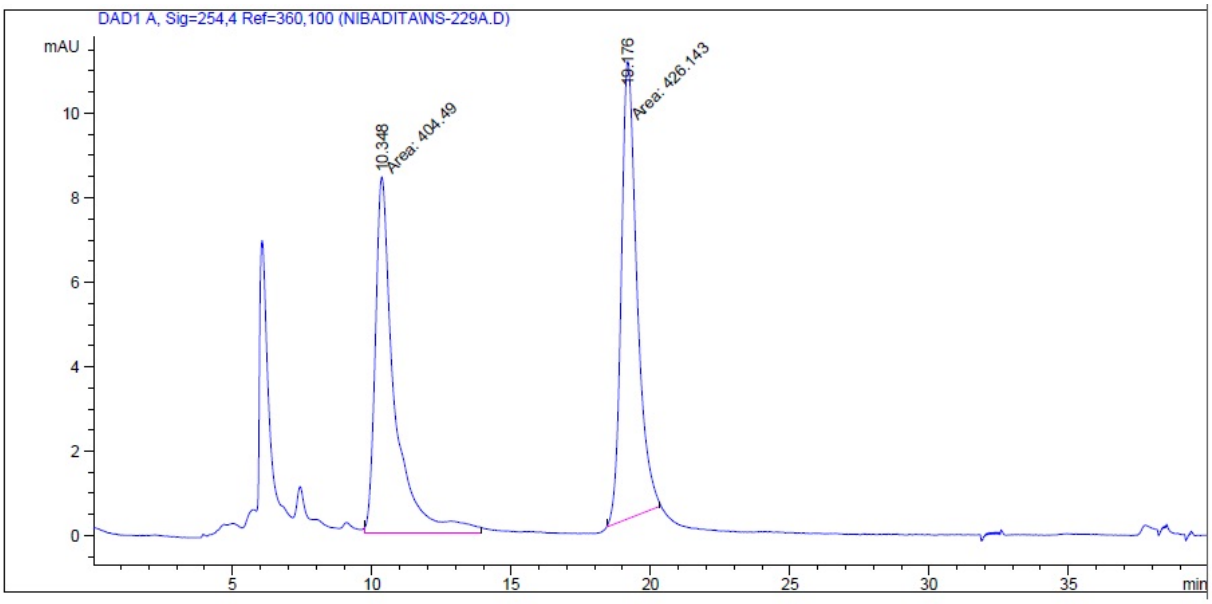
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.810	MM	0.3980	856.82855	35.87663	38.6322
2	15.542	MM	0.5814	1361.08411	39.01543	61.3678
Totals :				2217.91266	74.89206	

Figure S6: Enantiomerically enriched sample.





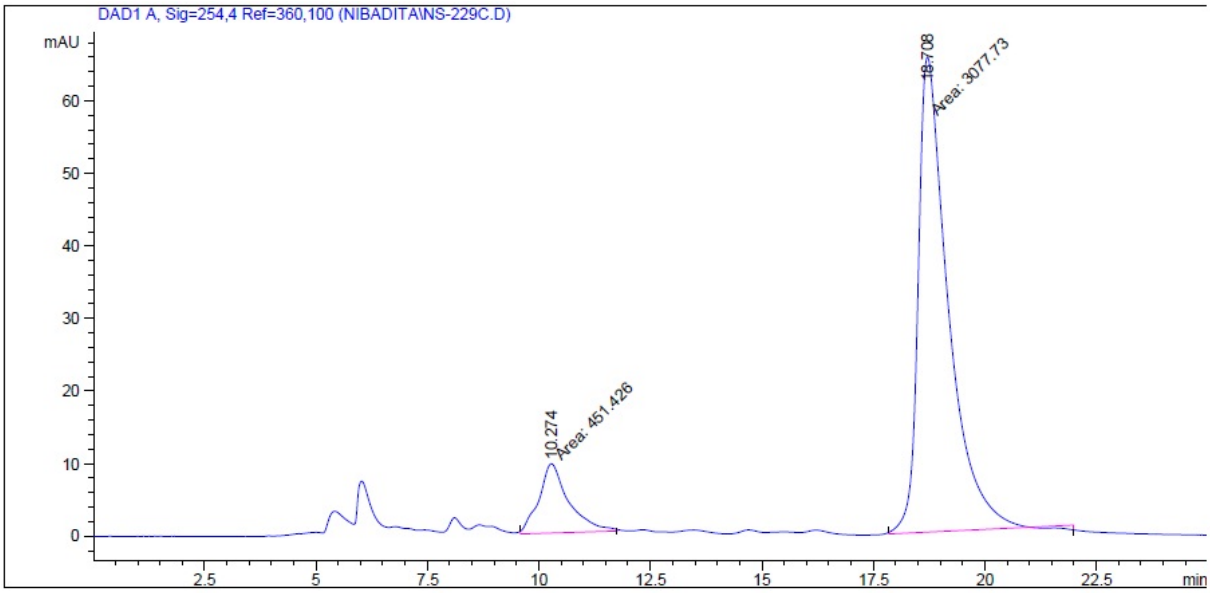




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.348	MM	0.8003	404.49033	8.42321	48.6966
2	19.176	MM	0.6556	426.14276	10.83357	51.3034
Totals :				830.63309	19.25677	

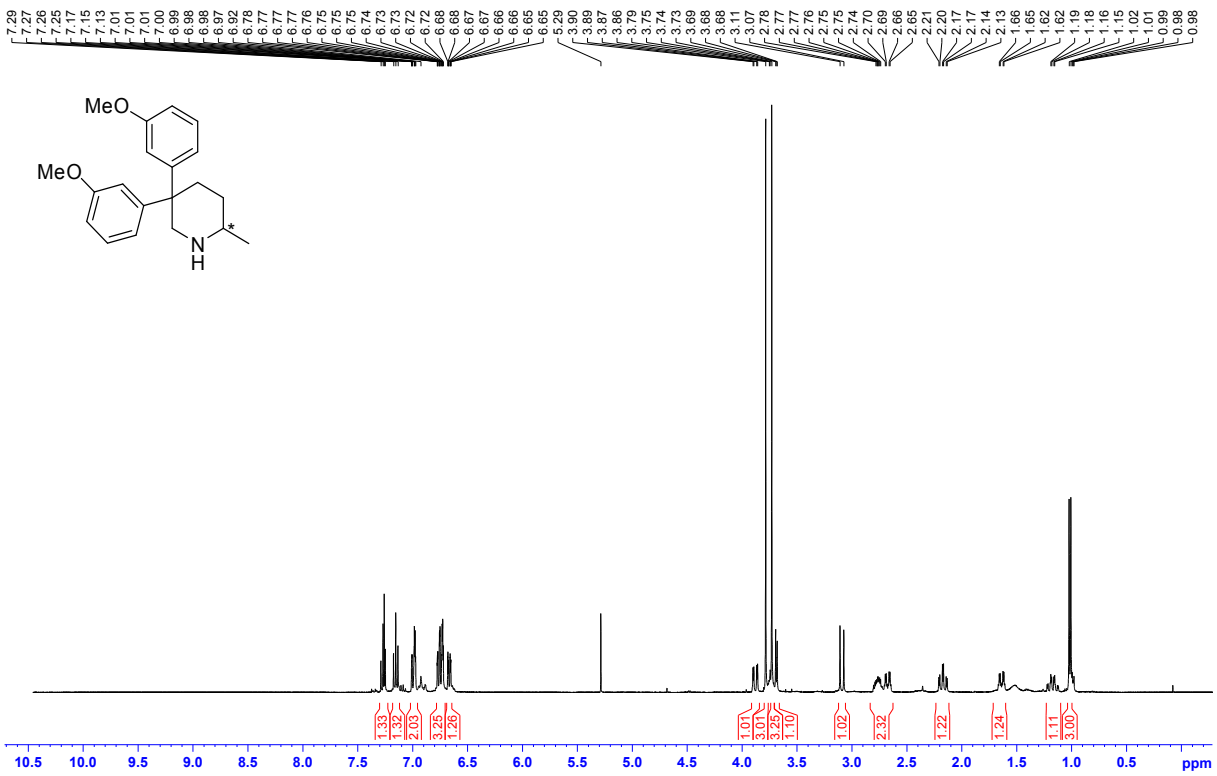
Figure S7: Racemic sample.

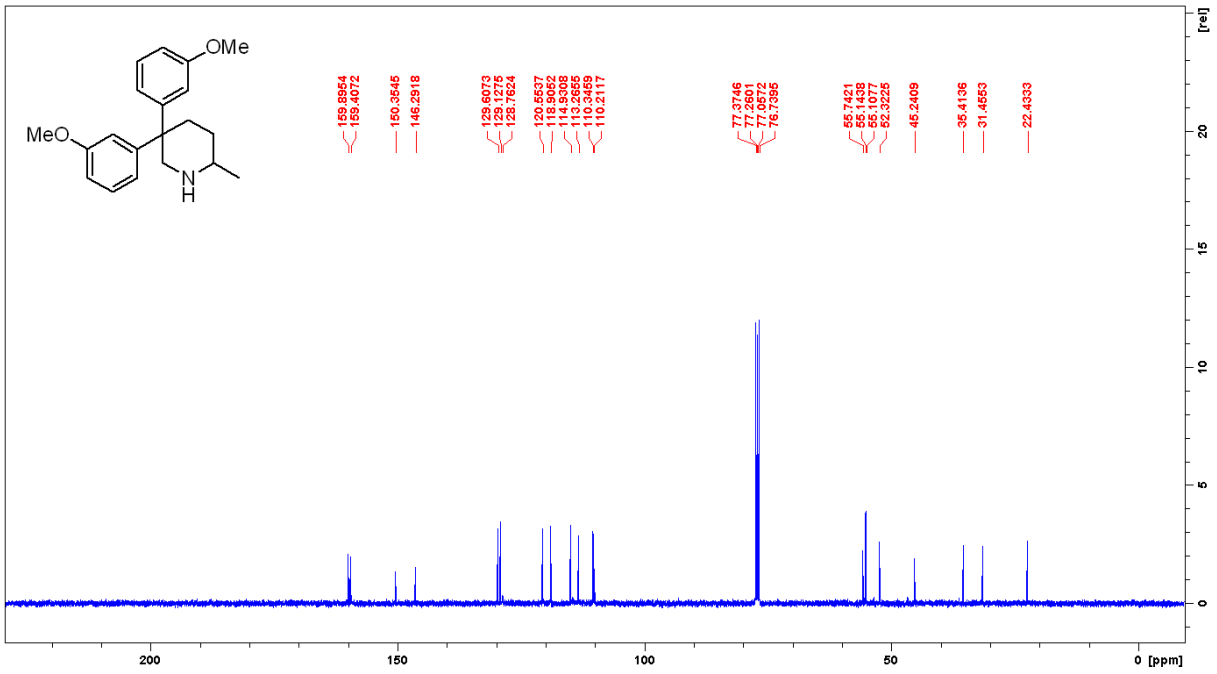


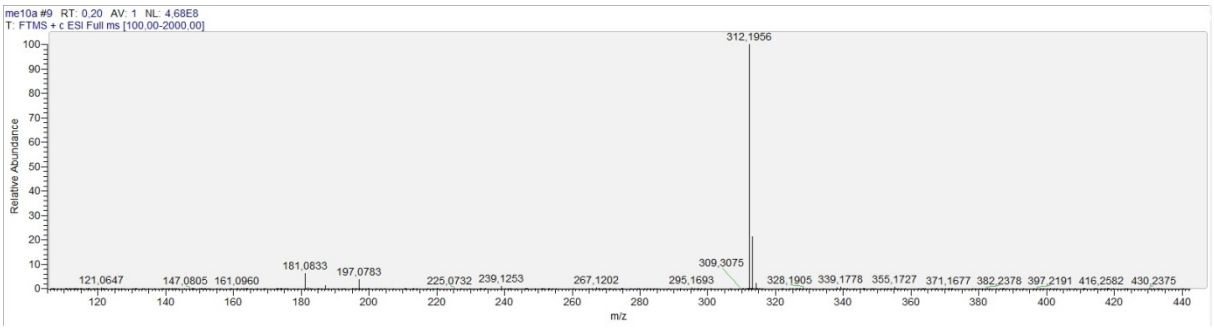
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

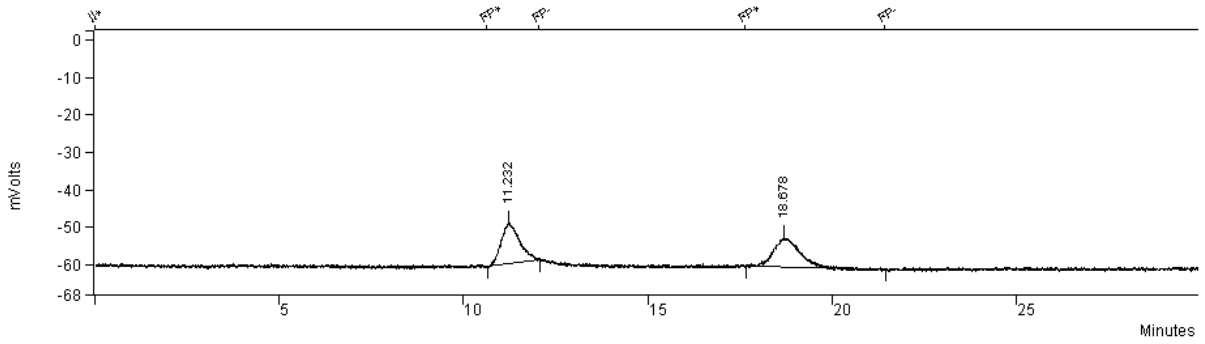
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.274	MM	0.7843	451.42596	9.59259	12.7913
2	18.708	MM	0.7827	3077.73315	65.54030	87.2087
Totals :				3529.15912	75.13289	

Figure S8: Enantiomerically enriched sample.


MeO
MeO
N
H
*
ppm


OMe
MeO
N
H
[rel]
[ppm]

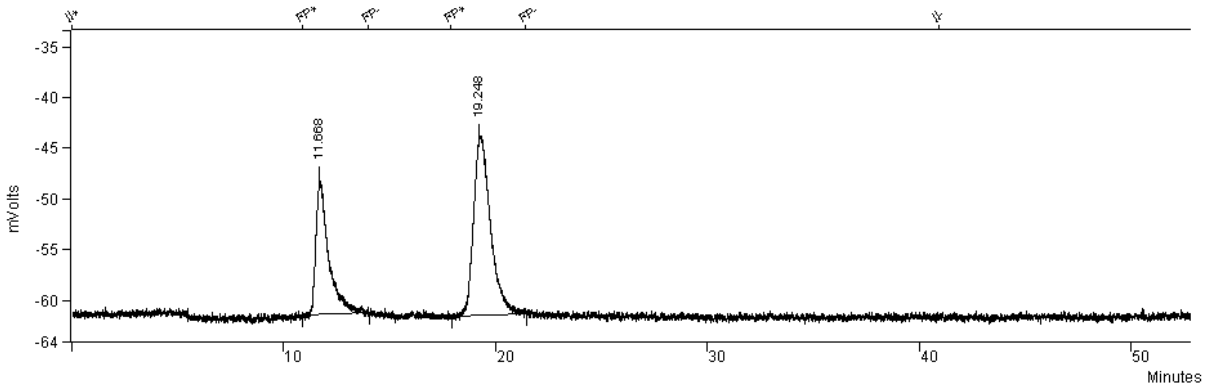




Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		51.2286	11.232	0.000	378831	BB	33.5	
2		48.7714	18.678	0.000	360661	BB	40.6	
	Totals:	100.0000		0.000	739492			

Total Unidentified Counts : 739492 counts

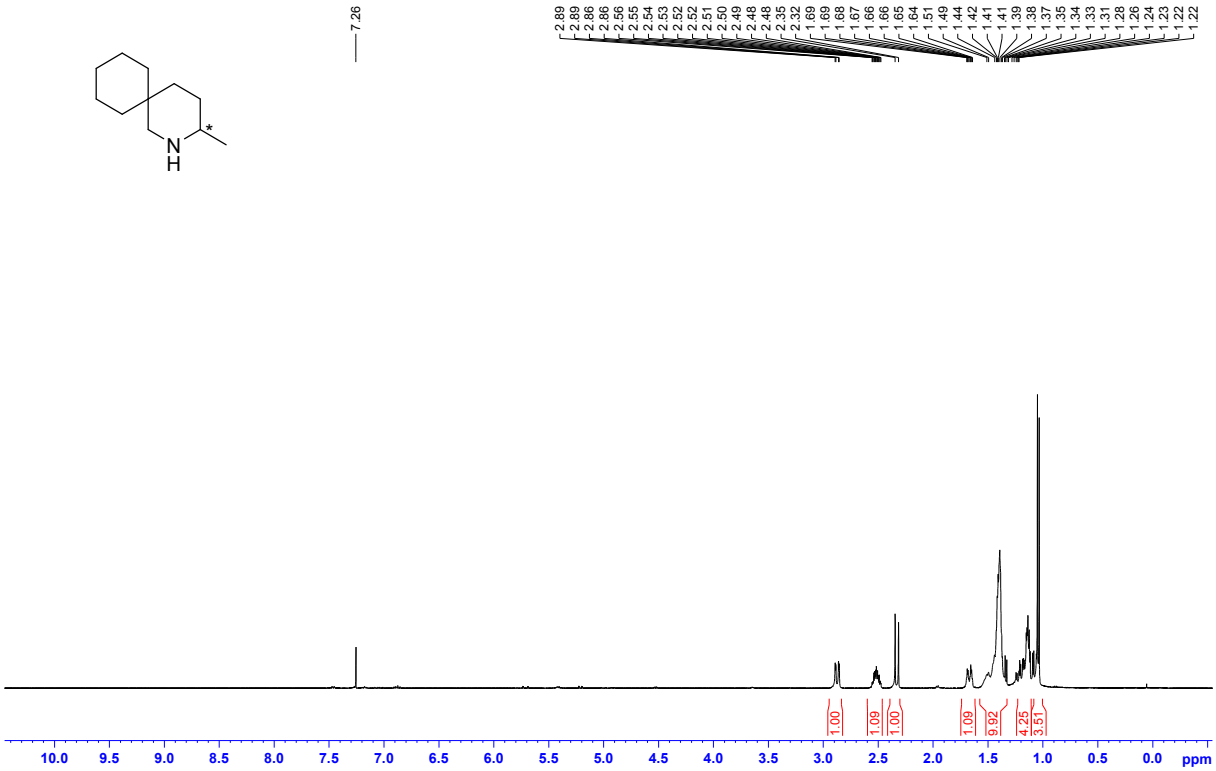
Figure S9: Racemic sample.

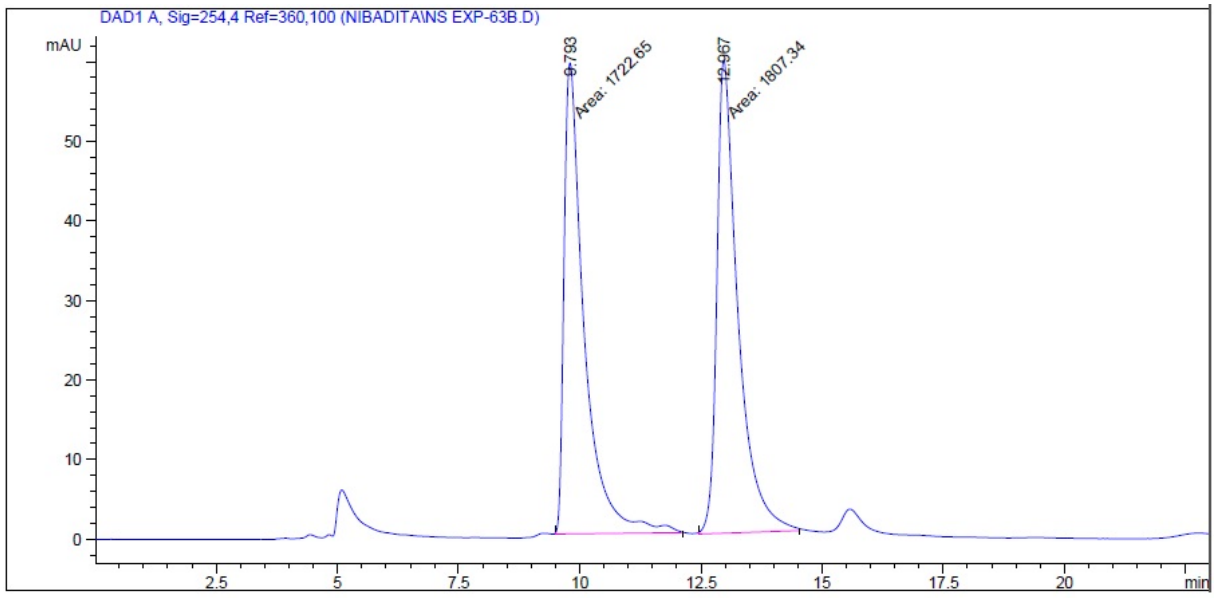


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		35.2781	11.668	0.000	539870	BB	33.1	
2		64.7219	19.248	0.000	990457	BB	49.3	
	Totals:	100.0000		0.000	1530327			

Total Unidentified Counts : 1530327 counts

Figure S10: Enantiomerically enriched sample.



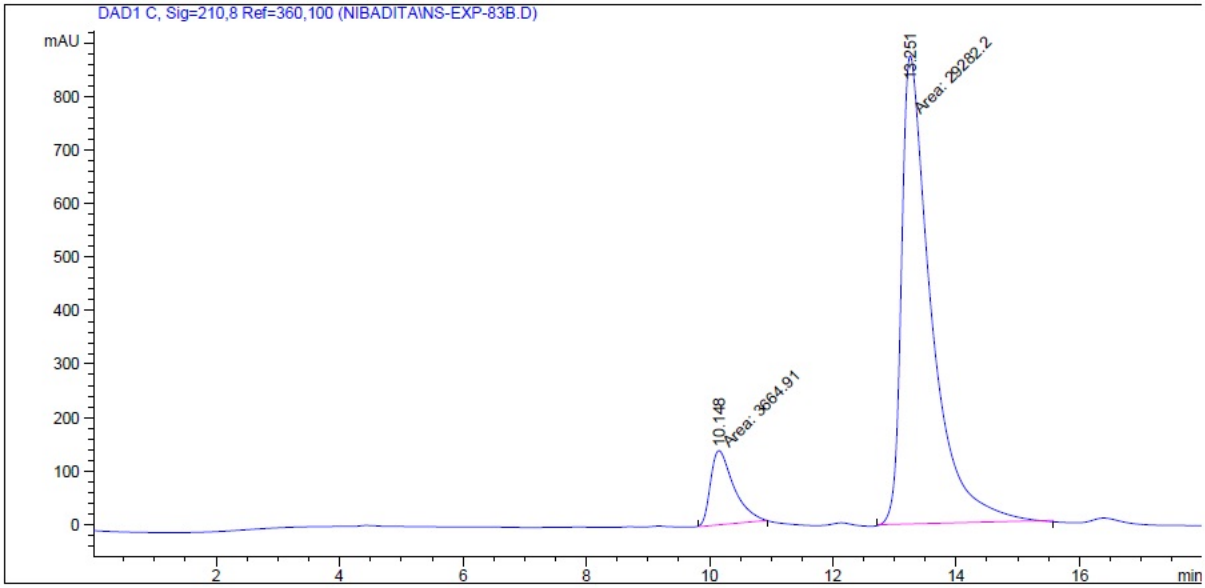



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.793 MM    0.4848 1722.65479   59.22229  48.8004
   2  12.967 MM    0.5063 1807.34448   59.49329  51.1996

Totals :                  3529.99927  118.71558
```

Figure S11: Racemic sample.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.148	MM	0.4394	3664.91260	139.01511	11.1236
2	13.251	MM	0.5576	2.92822e4	875.20648	88.8764
Totals :				3.29471e4	1014.22159	

Figure S12: Enantiomerically enriched sample.


7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.28
7.28
7.26
7.22
7.21
7.20
7.20
7.19
5.67
5.64
5.62
5.60
4.92
4.91
4.88
4.87
4.87
4.86
4.86
4.84
4.83
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4.81
4.81
4.81
3.67
3.67
3.64
3.63
3.25
2.82
2.79
2.73
2.70
2.45
1.88
1.86
1.85
1.73
1.73
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1.63
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1.52
1.51
1.51
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1.46
1.44
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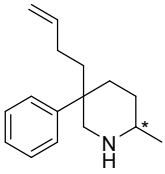
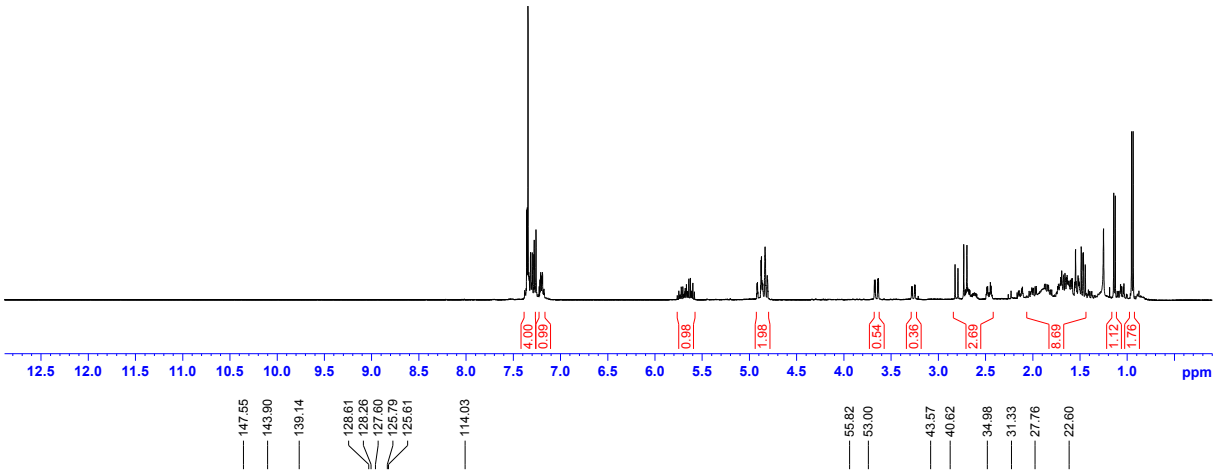
1.14
1.13
1.07
1.04
0.95
0.94


N
H
*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1.98
0.54
0.36
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8.69
1.12
1.76
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

147.55
143.90
139.14
128.61
128.26
127.60
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125.61
114.03
55.82
53.00
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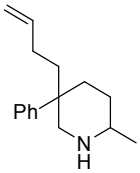
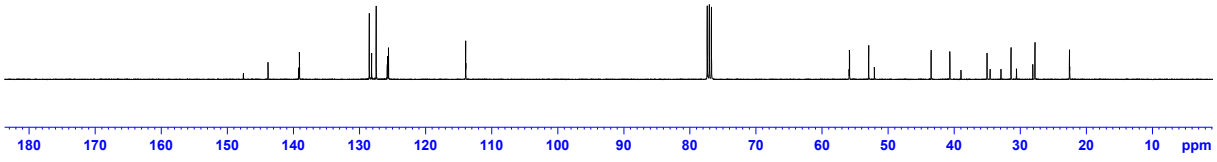
40.62
34.98
31.33
27.76
22.60


Ph
N
H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170
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150
140
130
120
110
100
90
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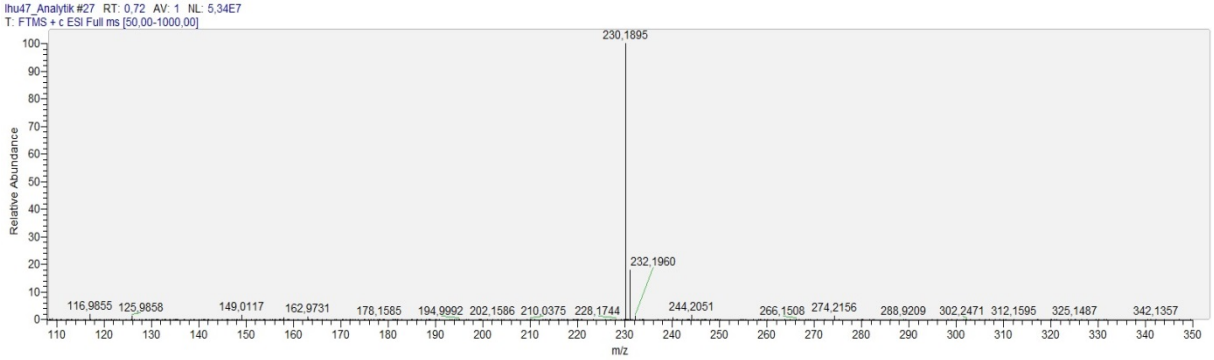
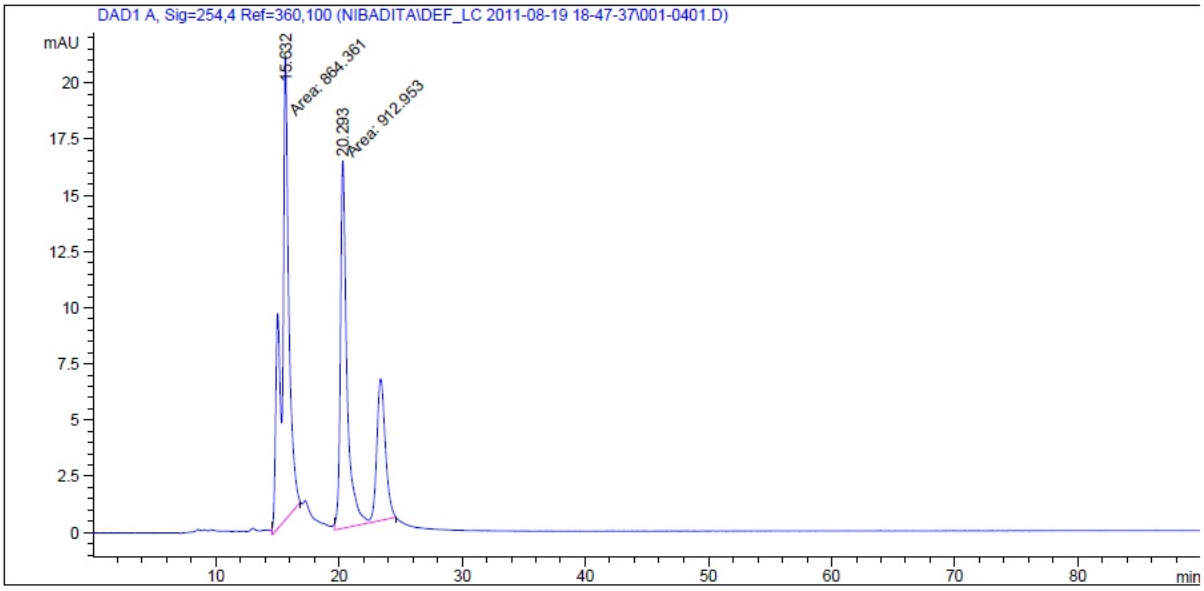
70
60
50
40
30
20
10
ppm

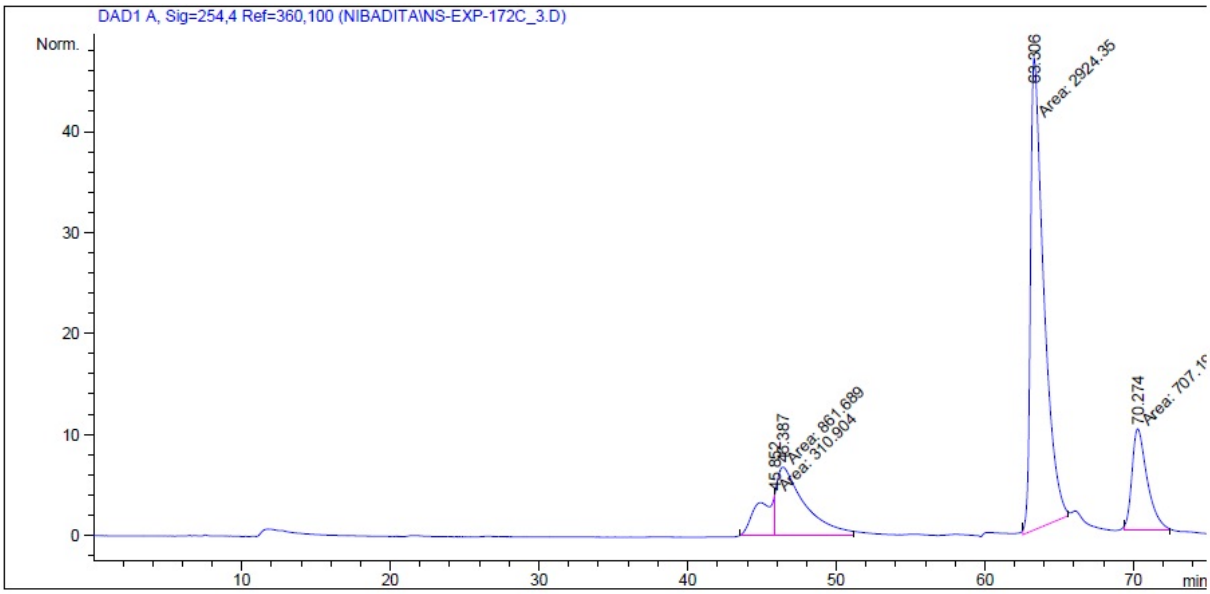




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.632	MM	0.6992	864.36139	20.60295	48.6330
2	20.293	MM	0.9304	912.95306	16.35408	51.3670
Totals :				1777.31445	36.95702	

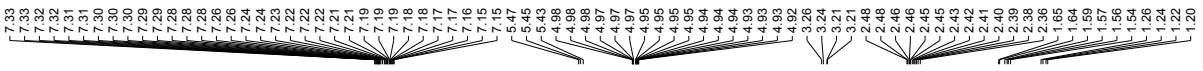
Figure S13: Racemic sample.

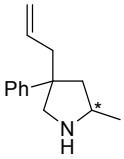


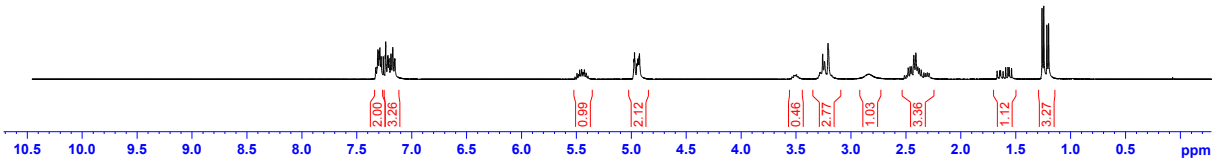
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.852	MF	1.3017	310.90433	3.98063	6.4716
2	46.387	FM	2.1459	861.68933	6.69249	17.9364
3	63.306	MM	1.0426	2924.35425	46.74686	60.8715
4	70.274	MM	1.1818	707.19336	9.97373	14.7205
Totals :				4804.14127	67.39372	

Figure S14: Enantiomerically and diastereomerically enriched sample.


7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.26 7.26 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.15 7.15
5.47 5.45 5.43 4.98 4.98 4.97 4.97 4.95 4.95 4.95 4.94 4.94 4.94 4.93 4.93 4.92
3.26 3.24 3.21 3.21
2.48 2.46 2.46 2.45 2.45 2.43 2.42 2.41 2.40 2.39 2.38 2.36
1.65 1.64 1.59 1.57 1.56 1.54 1.26 1.24 1.22 1.20


Ph
N
H
*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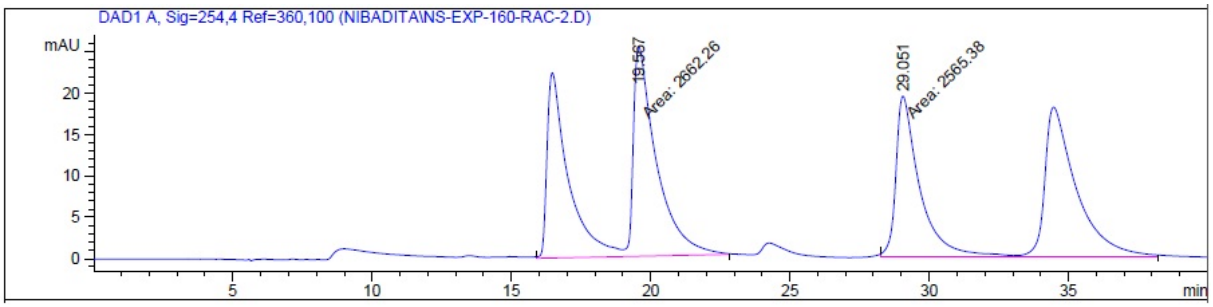
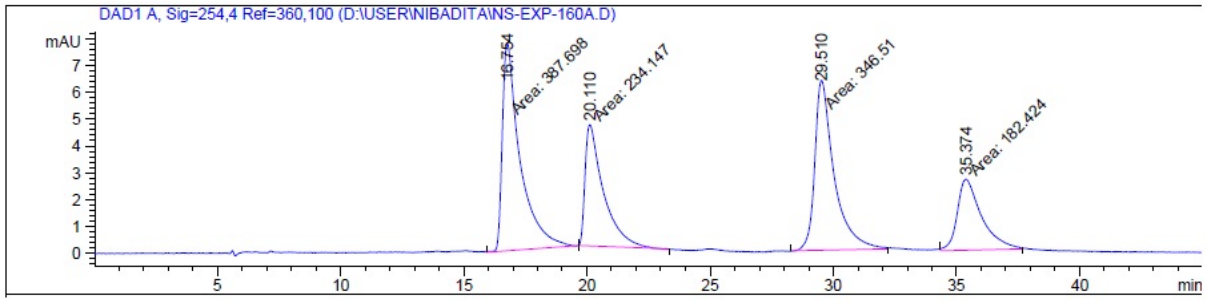
2.12
0.46
2.77
1.03
3.36
1.12
3.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.567	MM	1.7507	2662.25952	25.34521	50.9266
2	29.051	MM	2.2048	2565.38257	19.39227	49.0734
Totals :				5227.64209	44.73748	

Figure S15: Racemic sample.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.754	MM	0.8353	387.69839	7.73563	33.6901
2	20.110	MM	0.8636	234.14702	4.51861	20.3468
3	29.510	MM	0.9115	346.51019	6.33595	30.1109
4	35.374	MM	1.1480	182.42436	2.64850	15.8522
Totals :				1150.77997	21.23869	

Figure S16: Enantiomerically and diastereomerically enriched sample.

X-ray Crystallographic Studies of Zn-1, Cu-2 and Zn2

X-ray crystallographic studies were conducted by placing single crystals in perfluorinated oil on a glass capillary tube in a cold nitrogen flow. An Agilent Technologies SuperNova (single source) device was used (temperature N_2: 150 K; wavelength: 1.5418 Å; type: Cu Ka)

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 965327 (**Zn-1**), 965328 (**Cu-2**), and 965329 (**Zn-2**). Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [FAX +44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Table S5. Crystal data and structure refinement for **Zn-1**.

Empirical formula	$C_{38}H_{40}Br_4N_4O_3SZn$	
Formula weight	1017.81	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 12.0384(4) Å	α= 111.550(4)°.
	b = 13.2068(6) Å	β= 102.220(3)°.
	c = 14.0473(6) Å	γ = 102.211(4)°.
Volume	1924.64(14) $Å^3$	
Z	2	
Density (calculated)	1.756 mg/m^3	
Absorption coefficient	4.887 mm^{-1}	
F(000)	1012	
Crystal size	0.32 x 0.17 x 0.16 mm^3	
Theta range for data collection	3.16 to 25.00°.	
Index ranges	-13<=h<=14, -15<=k<=14, -16<=l<=16	
Reflections collected	15395	
Independent reflections	9933 [R(int) = 0.0279]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5085 and 0.3038	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9933 / 21 / 927	
Goodness-of-fit on F^2	0.902	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0471	
R indices (all data)	R1 = 0.0417, wR2 = 0.0485	
Absolute structure parameter	0.016(6)	
Largest diff. peak and hole	0.432 and -0.499 $e.Å^{-3}$	

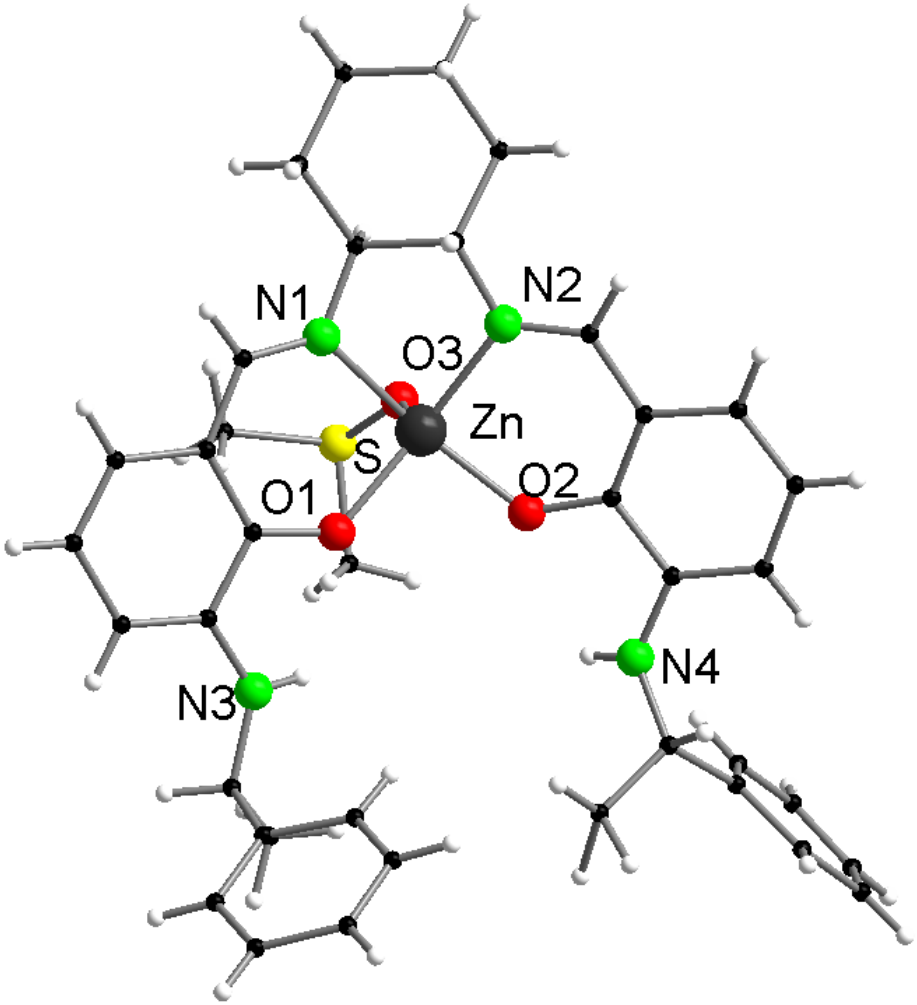
Table S6. Crystal data and structure refinement for **Cu-2**.

Empirical formula	$C_{37}H_{40}Cl_2CuN_4O_2$	
Formula weight	707.17	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 30.212(2) Å	α= 90°.
	b = 7.0191(6) Å	β= 90.159(8)°.
	c = 16.0347(15) Å	γ = 90°.
Volume	3400.3(5) $Å^3$	
Z	4	
Density (calculated)	1.381 mg/m^3	
Absorption coefficient	0.839 mm^{-1}	
F(000)	1476	
Crystal size	0.59 x 0.14 x 0.07 mm^3	
Theta range for data collection	3.24 to 25.00°.	
Index ranges	-28<=h<=35, -8<=k<=8, -19<=l<=16	
Reflections collected	10978	
Independent reflections	5886 [R(int) = 0.0570]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9436 and 0.6374	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5886 / 1 / 418	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1054	
R indices (all data)	R1 = 0.0766, wR2 = 0.1114	
Absolute structure parameter	0.02(2)	
Largest diff. peak and hole	0.713 and -0.516 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for **Zn-2**.

Empirical formula	$C_{38}H_{44}N_4O_3SZn$	
Formula weight	702.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.1989(6) Å	α= 90°.
	b = 11.6090(7) Å	β= 90°.°.
	c = 36.4888(22) Å	γ = 90°.
Volume	3473.1(4) $Å^3$	
Z	4	
Density (calculated)	1.343 mg/m^3	
Absorption coefficient	0.810 mm^{-1}	
F(000)	1480	
Crystal size	0.134 x 0.103 x 0.101 mm^3	
Theta range for data collection	1.116 to 25.250 °.	
Index ranges	-9<=h<=9, -12<=k<=13, -43<=l<=27	
Reflections collected	22651	
Independent reflections	6272 [R(int) = 0.1743]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	none	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6272 / 6 / 436	
Goodness-of-fit on F^2	0.806	
Final R indices [I>2sigma(I)]	R1 = 0.0657, wR2 = 0.1230	
R indices (all data)	R1 = 0.1339, wR2 = 0.1418	
Absolute structure parameter	0.03(3)	
Largest diff. peak and hole	0.875 and -0.703 $e.Å^{-3}$	

Figure S17: Solid state structure of **Zn-2**



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